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Article

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A One-pot Synthesis of Spirocyclopenta[*a*]indene Derivatives *via* a Cascade Ring Expansion and Intramolecular Friedel-Crafts-type Cyclization

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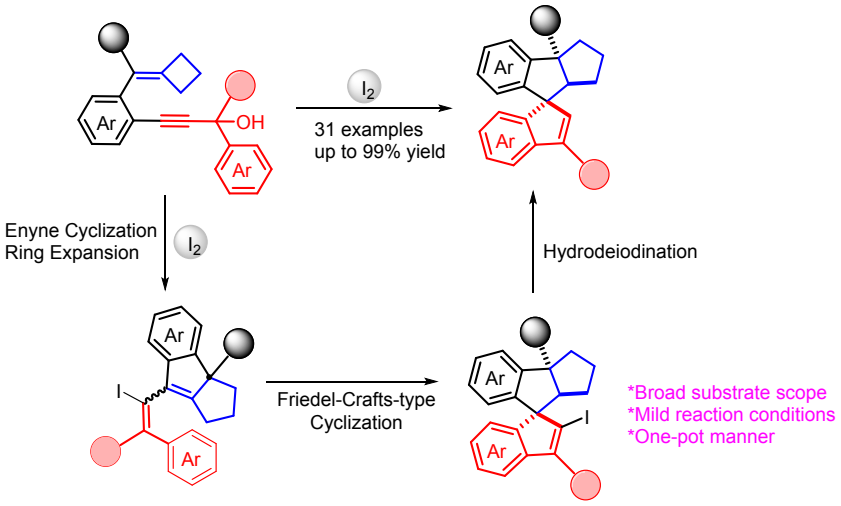


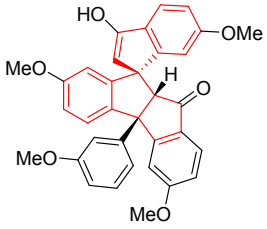
Abstract: A one-pot efficient synthetic approach for the rapid construction of spirocyclopenta[*a*]indene derivatives has been developed via an iodine-initiated cascade ring expansion and intramolecular Friedel-Crafts-type cyclization from propargyl alcohol-tethered alkylidenecyclobutanes under mild conditions with broad substrate scope. This cascade process can be elegantly conducted in a gram-scale. A plausible reaction mechanism has been proposed on the basis of a series of deuterium labeling and control experiments.

INTRODUCTION

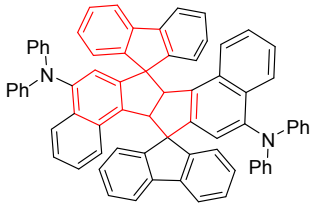
The all-carbon polycyclic scaffolds are the significant structural frameworks in a series of natural products[1] and functional materials.[2] Recently, tricyclic [6,5,5]-fused systems,[3] as a unique framework, are attracting the attention of researchers because of the applications in the synthesis of natural products and functional molecules.[4] Among these different types of tricyclic [6,5,5]-fused systems, spirocyclopenta[*a*]indene derivatives constitute core scaffolds, that widely distributed in numerous compounds such as dendrimer core[5] and organic electroluminescence device materials (Scheme 1).[6] Thus, it is a highly desirable work using a strategic cascade reaction to rapidly construct tricyclic [6,5,5]-fused system and spiroindene motif since they can introduce molecular complexity through a simple chemical operation. In the past several years, tandem or cascade reactions

to afford polycyclic scaffolds have been extensively explored.[7] However, simultaneously affording tricyclic [6,5,5]-fused systems and spiroindene scaffolds in a one-pot manner was less exploited and could be a challenging task at the present stage.[8]

Scheme 1 Representative examples containing spirocyclopenta[*a*]indene skeleton.



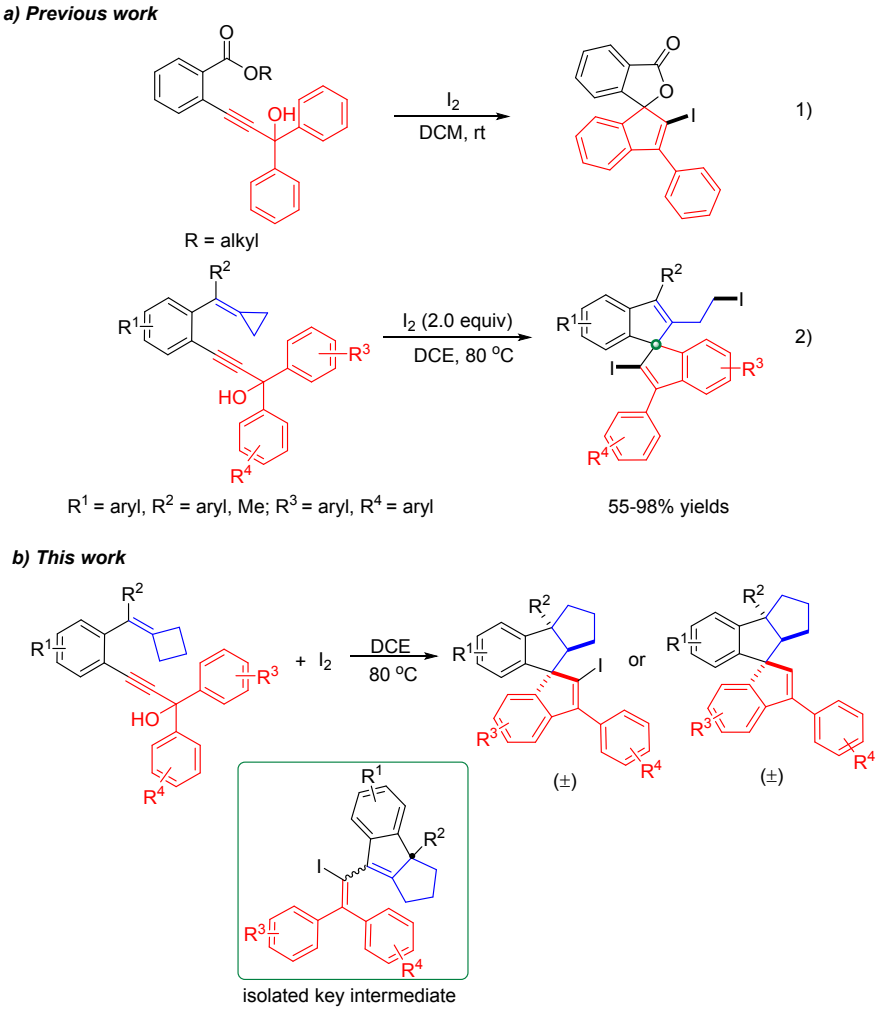
Dendrimer Core



Organic Electroluminescence Device Materials

In 2012, Liang[9] and co-workers reported an efficient cascade cyclization approach for the synthesis of substituted spiro[indene-1,10-isobenzofuran] derivatives in good yields under mild reaction conditions from simple propargylic alcohols in the presence of I_2 (Scheme 2, eq 1). Moreover, our group recently developed a novel protocol for the synthesis of all-carbon spirobi(indene) scaffold from a class of propargyl alcohol-tethered alkylidenecyclopropanes in good to excellent yields upon treating with I_2 also under mild reaction conditions (Scheme 2, eq 2).[10] On the other hand, it has been reported that methylenecyclobutanes (MCBs), as another class of strained small rings bearing an exo-methylene moiety, could be also used as a precursor for the production of 2-phenylcyclopentan-1-one and (1-phenylcyclobutyl)methanone derivatives due to its high reactivity.[11] As part of our continuous efforts to develop new cascade reactions based on strained small rings with easily available reactants, we attempted to use propargyl alcohol-tethered alkylidenecyclobutanes as substrates for the rapid construction of ring expanded spiroindene frameworks in one step in the presence of I_2 (Scheme 1, *this work*). In this paper, we wish to disclose our findings along with the isolation of the key intermediate.

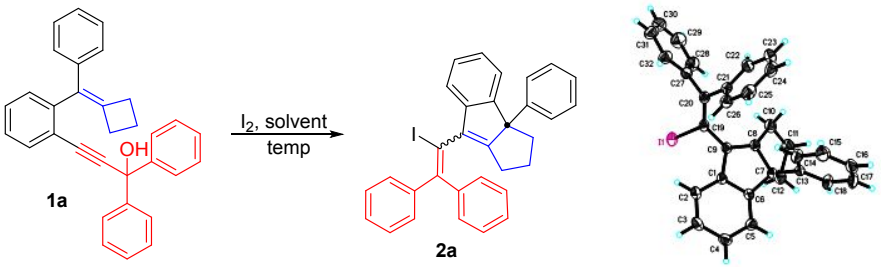
Scheme 2 Previous work[9,10] and this work.



RESULTS AND DISCUSSION

Initially, propargyl alcohol-tethered alkylidenecyclobutane **1a** (0.2 mmol) was used as a model substrate in the reaction with iodine (2.0 equiv) to seek out the optimal reaction conditions. As shown in Table 1, the desired cyclized product **2a** was obtained in 48% yield as an atropisomeric mixture (dr = 2.2:1) at room temperature in 1,2-dichloroethane (DCE) (Table 1, entry 1). The examination of reaction temperature revealed that carrying out this cascade cyclization at 60 °C gave the best result, affording **2a** in 86% yield (dr = 3:1) and this reaction was not sensitive to visible light irradiation (Table 1, entries 2-7). Decreasing or increasing the loading amount of I_2, no improvement could be realized, giving **2a** in 40% (dr = 2.2:1), 77% (dr = 2.1:1), and 31% (dr = 1.8:1) yields, respectively (Table 1, entries 8-10). The investigation on solvent effects suggested that DCE was the solvent of choice (Table 1, entries 11-15). Using fluorobenzene and (trifluoromethyl)benzene as solvents, the reactions became sluggish, affording **2a** in trace (Table 1, entries 14 and 15). The major atropisomer's configuration of **2a** has been determined by X-ray diffraction. The ORTEP drawing is shown in Table 1 and the CIF data are presented in the Supporting Information.

Table 1 Optimization of the reaction conditions for the synthesis of **2a**.



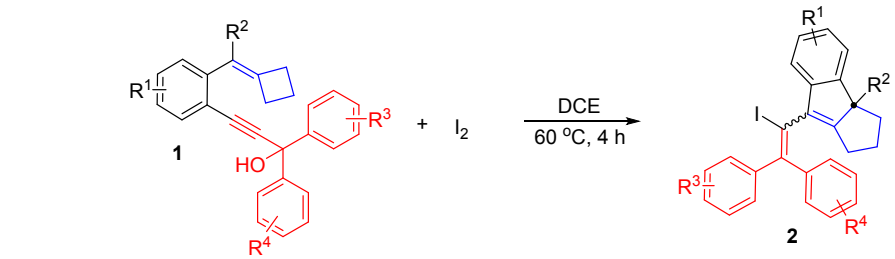
entry[a]	solvent	temp (°C)	I_2 (equiv)	yield (%)[c]
1	DCE	rt	2	48 (2.2:1)
2	DCE	40	2	55 (2.4:1)
3	DCE	50	2	60 (2.4:1)
4	DCE	60	2	86 (3:1)[d]
5[b]	DCE	60	2	86 (3:1)
6	DCE	70	2	63 (2.8:1)
7	DCE	80	2	40 (2.9:1)
8	DCE	60	1	40 (2.2:1)
9	DCE	60	3	77 (2.1:1)
10	DCE	60	5	31 (1.8:1)
11	DCM	60	2	72 (2.4:1)
12	THF	60	2	70 (2.3:1)
13	toluene	60	2	33 (2.2:1)
14	PhF	60	2	trace
15	$PhCF_3$	60	2	trace

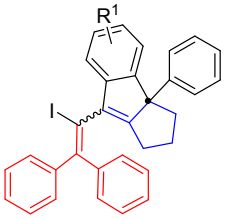
[a] Reaction was run under the following conditions: a solution of **1a** (0.2 mmol) in dry solvent (2.0 mL) for 4 h. [b] Reaction was run under the following conditions: a solution of **1a** (0.2 mmol) in DCE (2.0 mL) under dark condition. [c] NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [d] Isolated yield.

With the optimized reaction conditions in hand, we next turned our attention towards the substrate scope, and the results are shown in Scheme 3. Substrates **1b**-**1n**, bearing a variety of substituted aromatic rings, were tolerated, giving the desired products **2b**-**2n** in good to high yields ranging from 60%-95% regardless of whether they are electron-rich or -poor ones. For substrate **1j** bearing a trifluoromethyl group, the corresponding product **2j** was given in 79% yield after 24 hours. In the cases of substrates **1k** and **1l**, in which the propargyl alcohol moiety containing two different aromatic rings, the corresponding products **2k** and **2l** were obtained in 93% and 77% yields, respectively as a pair of regioisomers combined with their corresponding atropisomers. For substrate **1o**, in which the propargyl alcohol moiety had an aliphatic methyl group, the reaction also proceeded smoothly, delivering the corresponding product **2o** in 84% yield (dr = 4.0:1). For substrates **1p** and **1q** containing a 9*H*-fluoren-9-ol unit, the reactions were also compatible, affording the desired products **2p** and **2q** in 74% yield and 69% yield. The use of **1s** as substrate, in which R^2 = Me, products **2s** and **3s** were both obtained, and product **3s** was derived from the further reaction of **2s** under the reaction conditions (see Table 2). In the case of substrate **1r** (R^1 = CF_3, R^2 = Me) and **1t** (R^1 = Ph, R^2 = Me), the corresponding products **2r** and **2t** were obtained in 65% and 80% yields as a pair of diastereoisomers. However, the corresponding products **3r** and **3t** could not be formed perhaps due to the strongly electron-withdrawing property of CF_3 group and steric hindrance of phenyl group, which could impair the Friedel-Crafts-type cyclization for the

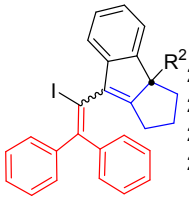
formation of **3r** and **3t**, respectively. Unfortunately, using **1u** as substrate did not give the desired product after examining several reaction conditions, presumably due to the electronic effect.

Scheme 3 Substrate scope for the synthesis of **2**.[a,b]

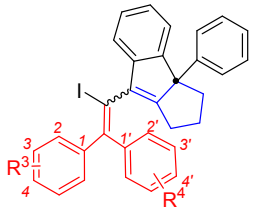




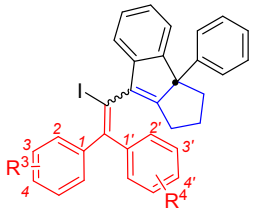
2b: R^1 = 4-Cl, 95% (dr = 3.0:1)
2c: R^1 = 4-CF_3, 70% (dr = 2.8:1)
2d: R^1 = 5-Cl, 60% (dr = 2.7:1)
2e: R^1 = 5-Br, 85% (dr = 2.4:1)
2f: R^1 = 5-Me, 95% (dr = 3.2:1)



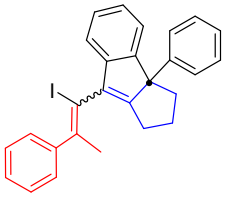
2g: R^2 = 3-ClC_6H_4, 76% (dr = 2.9:1)
2h: R^2 = 4-ClC_6H_4, 90% (dr = 2.9:1)
2i: R^2 = 4-BrC_6H_4, 75% (dr = 3.1:1)
2j[c]: R^2 = 4-$CF_3C_6H_4$, 79% (dr = 3.6:1)



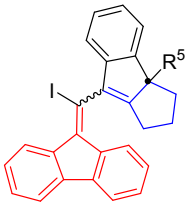
2k: R^3 = 4-Me R^4 = H or R^3 = H, R^4 = 4-Me (1:1), 93% (dr = 3.8:1) (dr = 3.8:1)
2l: R^3 = 4-OMe, R^4 = H or R^3 = H, R^4 = 4-OMe (1:0.9), 77% (dr = 2.5:1) (dr = 2.5:1)



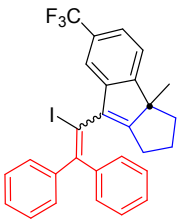
2m: R^3 = 4-Cl, R^4 = 4'-Cl, 88% (dr = 4.0:1)
2n: R^3 = 4-Me, R^4 = 4'-Me, 89% (dr = 4.4:1)



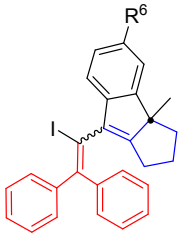
2o: 84% (dr = 4.0:1)



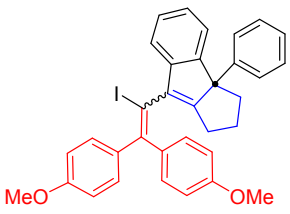
2p: R^5 = Me, 74% (dr = 2.9:1)
2q: R^5 = Ph, 69% (dr = 12.5:1)



2r[d]: 65% (dr = 1.5:1)



2s[e]: R^6 = Br, 45% (dr = 1.3:1)
2t: R^6 = Ph, 80% (dr = 1.5:1)



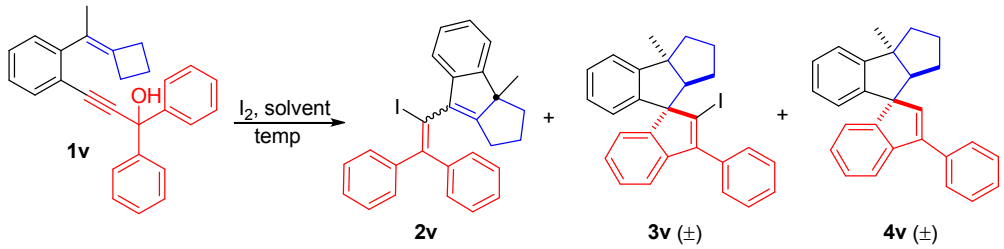
2u: complex

[a] Reaction was run under the following conditions: a solution of **1** (0.2 mmol), I_2 (0.4 mmol) in DCE (2.0 mL) at 60 °C for 4 h. [b] Isolated yield. [c] A solution of **1j** (0.2 mmol), I_2 (0.4 mmol) in DCE (2.0 mL) at 60 °C for 24 h. [d] A solution of **1r** (0.2 mmol), I_2 (0.4 mmol) in DCE (2.0 mL) at 80 °C for 4 h. [e] **3s** was also obtained in 41% yield.

Since different reaction outcome was observed in the case of substrate **1s**, we used substrate **1v** (0.2 mmol), in which R^2 = Me, to further optimize the reaction conditions and the results are outlined in Table 2. Upon examination of the solvent effect at 60 °C, we found that product **2v**

could be formed in 59% yield in DCE (2.0 mL) (Table 2, entries 1-5). Using THF as the solvent, the reaction was sluggish for substrate **1v** (Table 1, entry 12 *vs* Table 2, entry 4). However, a product mixture of spirocyclopenta[*a*]indene derivatives **3v** and **4v** was given in 70% and 7% yields, respectively if the reaction was carried out at 80 °C in DCE (2.0 mL) (Table 2, entry 6). Lowering the reaction temperature to 40 °C or room temperature, **2v** was obtained as the single product in 48% and 45% yields, respectively (Table 2, entries 7 and 8), suggesting that **3v** and **4v** were derived from the further transformation of **2v** at higher reaction temperature. Decreasing the loading amount of I_2 to 1.0 or 1.5 equiv and carrying out the reaction at 80 °C afforded **2v** in 34% yield or 48% yield under otherwise identical conditions (Table 2, entries 9 and 10). Increasing the loading amount of I_2 to 5 equiv gave **3v** in 70% yield along with **4v** in 6% yield (Table 2, entry 11). Prolonging the reaction time to 24 hours, the hydrodeiodinated product **4v** was obtained in 67% yield even in the presence of 2.0 equiv of I_2, indicating that **4v** might be derived from **3v** (Table 2, entry 12). When the reaction was performed in 4.0 mL of DCE, **2v** was afforded as the sole product in 64% yield in the diluted reaction solution (Table 2, entry 13).

Table 2 Optimization of the reaction conditions for the synthesis of **3v** and **4v**.



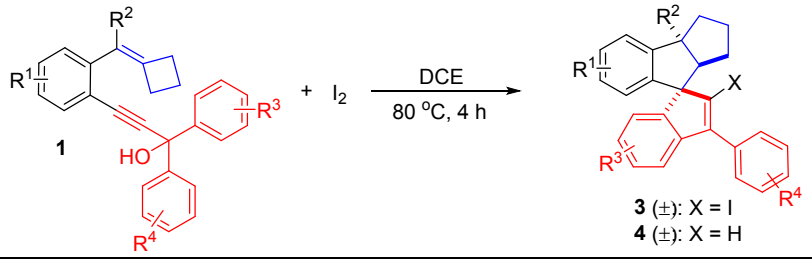
entry[a]	solvent	temp (°C)	I_2 (equiv)	time (h)	yield (%)[c] 2v	3v	4v
1	DCE	60	2	4	59	-	-
2	toluene	60	2	4	11	-	-
3	MeCN	60	2	4	-	-	-
4	THF	60	2	4	19	-	-
5	CH_3NO_2	60	2	4	-	-	-
6	DCE	80	2	4	-	70	7
7	DCE	40	2	4	48	-	-
8	DCE	rt	2	4	45	-	-
9	DCE	80	1	4	34	-	-
10	DCE	80	1.5	4	48	-	-
11	DCE	80	5	4	-	70	6
12	DCE	80	2	24	-	-	67
13[b]	DCE	80	2	4	64	-	-

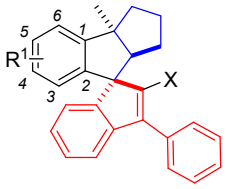
[a] Reaction was run under the following conditions: a solution of **1v** (0.2 mmol) in dry solvent (2.0 mL). [b] Reaction was run under the following conditions: a solution of **1v** (0.2 mmol) in dry solvent (4.0 mL). [c] NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

With these optimal reaction conditions in hand, we next explored the scope of this iodine-initiated cascade ring expansion and cyclization reaction. As shown in Scheme 4, in the cases of substrates **1w** and **1x** bearing a methoxy or a chloro substituent on the benzene ring, the corresponding products **3w** and **3x** were produced in 74% and 58% yields, respectively along with

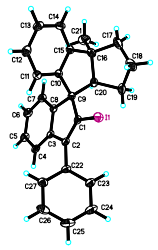
trace of deiodinated products **4w** and **4x**. For substrates **1y-1aa**, in which R^2 = ethyl, n-hexyl, or phenylpropyl group, the reactions proceeded smoothly, delivering the corresponding products **3y-3aa** in 32% to 83% yields along with deiodinated products **4y-4aa** in 16% to 28% yields. Interestingly, in the case of substrate **1aa**, another polycyclic iodinated product **5aa** derived from the further cyclization of **3aa** was also obtained in 41% yield and its structure was confirmed by X-ray diffraction (Scheme 4). As for substrate **1ab** having an isopentyl group, product **4ab** was obtained in 42% yield along with other complex. For substrate **1ac**, in which the propargyl alcohol moiety had two different aromatic rings, the corresponding products **3ac** and **3ac'** were obtained as a pair of regioisomers both in 43% yields. For substrates **1ad** and **1ae**, in which the propargyl alcohol moiety had electron-rich aromatic rings (4-MeC_6H_4) and electron-deficient aromatic rings (4-ClC_6H_4), the desired products **3ad** and **3ae** were given in 6% and 46% yields, respectively along with **4ad** in 89% yield and **4ae** in trace, indicating that hydrodeiodination process may more easily occur in electron-rich one. The use of **1af** as substrate, in which the propargyl alcohol moiety had a methyl group, the desired product **3af** was obtained in 69% yield. We failed to get the desired product **3ag** from substrate **1ag** similar as that of **1u** due to the electronic effect. Using substrates **1y**, **1ae** and **1af**, the corresponding products **4y**, **4ae** and **4af** could be obtained in 66%, 63%, and 59% yields, respectively after prolonging the reaction time to 24 hours under the optimized conditions.

Scheme 4 Substrate scope for the synthesis of **3** and **4**.[a,b]

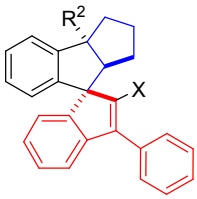




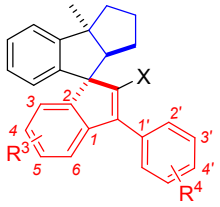
3v: R^1 = H, 70% (X = I); **4v**: 7% (X = H)
3w: R^1 = 4-OMe, 74% (X = I); **4w**: trace (X = H)
3x: R^1 = 5-Cl, 58% (X = I); **4x**: trace (X = H)



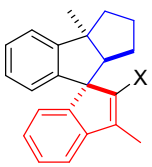
x-ray crystal structure of **3v**



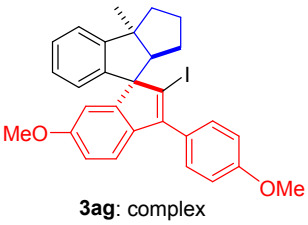
3y: R^2 = Et, 63% (X = I); **4y**: 28% (X = H)
After 24 h, **4y** was obtained in 66% yield[c]
3z: R^2 = n-hexyl, 83% (X = I); **4z**: 16% (X = H)
3aa: R^2 = phenylpropyl, 32% (X = I); **4aa**: 16% (X = H)
3ab: R^2 = isopentyl, trace; R^2 = **4ab**: 42% (X = H)



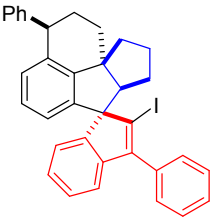
3ac: R^3 = 4-OMe, R^4 = H, 43% (X = I); **3ac'**: R^3 = H, R^4 = 4-OMe, 43% (X = I)
3ad: R^3 = 4-Me, R^4 = 4-Me, 6% (X = I); **4ad**: 89% (X = H)
3ae: R^3 = 4-Cl, R^4 = 4-Cl, 46% (X = I); **4ae**: trace (X = H)
After 24 h, **4ae** was obtained in 63% yield[c]



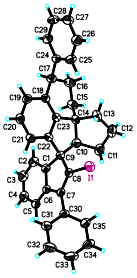
3af: 69% (X = I)
4af: trace (X = H)
After 24 h, **4af** was obtained in 59% yield[c]



3ag: complex



5aa: 41%



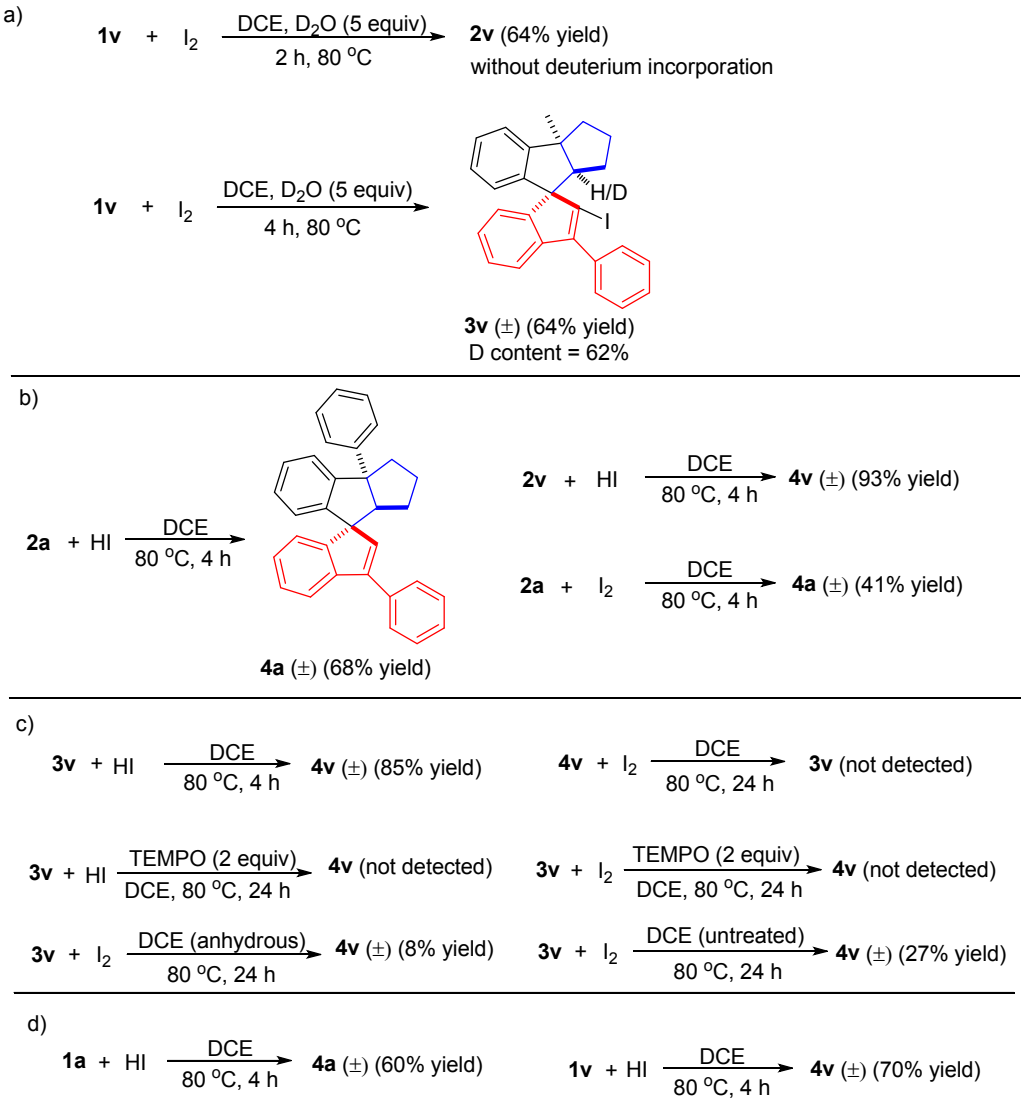
x-ray crystal structure of **5aa**

[a] Reaction was run under the following conditions: a solution of **1** (0.2 mmol), I_2 (0.4 mmol) in DCE (2.0 mL) at 80 °C for 4 h. [b] Isolated yield. [c] Reaction was run under the following conditions: a solution of **1** (0.2 mmol), I_2 (0.4 mmol) in DCE (2.0 mL) at 80 °C for 24 h.

To investigate the reaction mechanism on the formation of spirocyclopenta[*a*]indene framework, several deuterium labeling and control experiments were conducted and the results are summarized in Scheme 5. Upon treatment of **1v** with I_2 (2.0 equiv) at 80 °C in DCE containing D_2O (5.0 equiv) for 2 h, the deuterium incorporation was not observed in product **2v** at all. However, prolonging the reaction time to 4 h, **1v** was completely consumed and 62% deuterium incorporation was identified in product **3v**, suggesting a protonation by exogenous proton source (Scheme 5, eq a). Moreover, treating **2a** or **2v** with HI (2.0 equiv) at 80 °C successfully afforded the corresponding product **4a** or **4v** in 68% and 93% yields, respectively and **2a** could be also converted to **4a** in 41% yield in the presence of I_2 (Scheme 5, eq b). In addition, when **3v** was

treated with HI (2.0 equiv) at 80 °C in DCE, **4v** was afforded in 85% yield, which was intact upon further treatment with I_2 (2.0 equiv), indicating that the transformation of **3v** to **4v** was irreversible (Scheme 5, eq c). For the formation of **4v**, several control experiments were performed. A well-known radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (2.0 equiv), was added into reaction solution upon treating **3v** with HI (2.0 equiv) or with I_2 (2.0 equiv) for 24 hours and we found that no reactions occurred, suggesting that the deiodination process might go through a radical pathway (Scheme 5, eq c). Furthermore, carrying out the reaction of **3v** with I_2 in anhydrous DCE and untreated DCE for 24 hours, **4v** was afforded in 8% and 27% yields, indicating that H_2O as a proton source was indeed required in this transformation (Scheme 5, eq c). Furthermore, substrates **1a** and **1v** could be directly transformed into products **4a** and **4v** in 60% and 70% yields respectively as a single diastereomer in the presence of HI (2.0 equiv) (Scheme 5, eq d). All these results suggested that both **2a** or **2v** and **3v** could be the intermediates in this reaction.

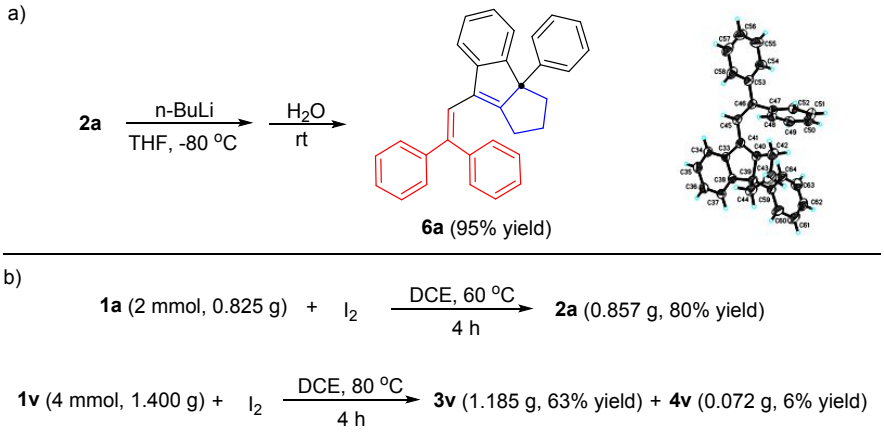
Scheme 5 Deuterium labeling and control experiments.



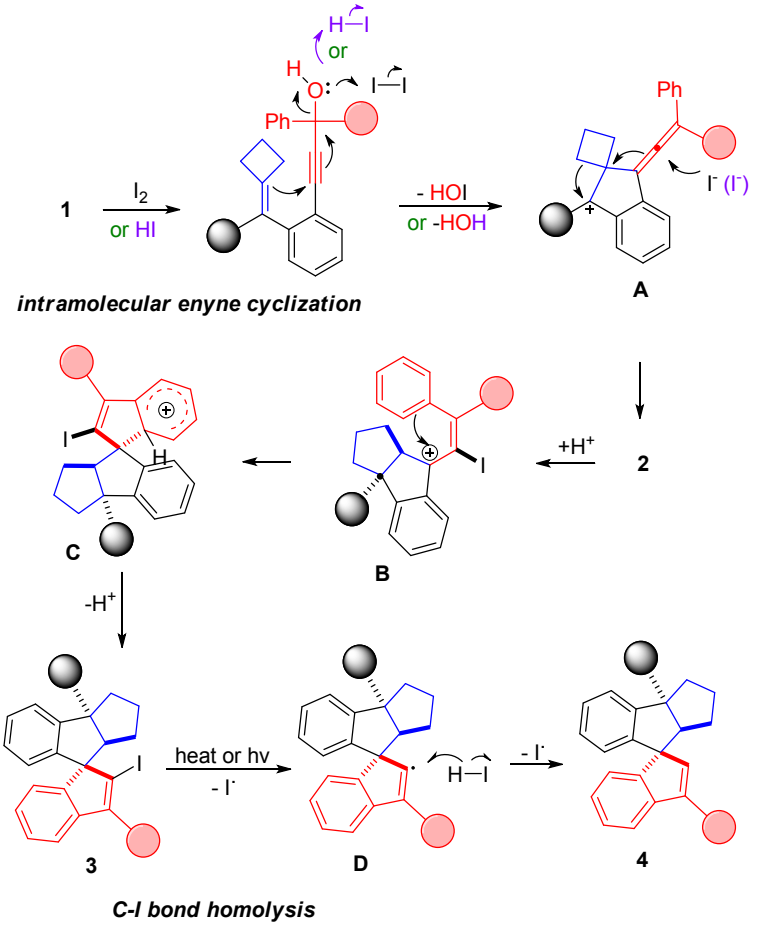
To verify the atropisomeric character of **2a**, we treated **2a** with n-BuLi in THF at -80 °C and

quenched the reaction with H_2O sequentially, affording **6a** in 95% yield as a sole product because of losing the axial chirality (Scheme 6, eq a). Its structure has been also determined by X-ray diffraction. The gram-scale synthesis of **2a** (0.857 g) in 80% yield as well as **3v** (1.185 g) in 63% yield and **4v** (0.072 g) in 6% yield were simply achieved to demonstrate the practical utility of this cascade ring expansion and cyclization reaction (Scheme 6, eq b).

Scheme 6 Deiodination and large-scale synthesis.



Scheme 7 A plausible reaction mechanism.



On the basis of the above control experiments, a plausible reaction mechanism for this ring

expansion and cyclization process for the formation of spirocyclopenta[*a*]indene derivatives was proposed in Scheme 7. The I_2 or HI activates the hydroxyl group[12] in **1** to afford intermediate **A** through an intramolecular enyne cyclization, which undergoes a nucleophilic attack of I^- to the allene moiety, followed by a ring expansion of cyclobutane, affording the corresponding product **2**. Product **2** can be continuously converted to intermediate **B** upon protonation. Then, an intramolecular Friedel-Crafts-type cyclization can take place to afford intermediate **C**, which releases a proton to deliver the desired product **3**. Moreover, the homolysis of C-I bond can take place with the help of heat or light to give the radical intermediate **D**, which abstract a hydrogen atom from HI or the solvent to afford the final product **4**.[13]

CONCLUSION

In summary, we have developed a novel protocol for the rapid construction of spirocyclopenta[*a*]indene scaffolds through the iodination of a class of well designed propargyl alcohol-tethered alkylidenecyclobutanes under mild conditions with a broad substrate scope. The reaction proceeded through a cascade iodine-initiated enyne cyclization, ring expansion, and an intramolecular Friedel-Crafts-type cyclization to give the spiropolycyclic products in moderate to good yields. A plausible reaction mechanism has been proposed on the basis of deuterium labeling and control experiments. The further explorations on the synthesis of useful spirocyclopenta[*a*]indene compounds are underway.

EXPERIMENT SECTION

General information. ^{1}H NMR spectra were recorded on a Varian Mercury-400 and 600 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-400 and 600 spectrophotometers (100 or 150 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass and HRMS spectra were recorded by EI, DART or ESI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. The reactions were carried out in an oil bath. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

Compounds **S2-S5** were prepared according to the previous literature.[14]

General procedure for the preparation of compound 1b: To a stirred solution of commercially available **2-amino-4-chlorobenzoic acid S_{1b}** (25 g, 1.0 equiv) in anhydrous THF (150 mL, 0.975 mol/L) was added 1,1′-carbonyldiimidazole (23.7 g, 1.0 equiv) at 0 °C under argon atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 2 h, then a suspension of N,O-dimethylhydroxylamine hydrochloride (14.2 g, 1.0 equiv) and Et_3N (15.6 g, 1.0 equiv) in THF (100 mL, 0.975 mol/L) was added, and the reaction mixture was stirred overnight. The residue was poured into H_2O (200 mL). The mixture was extracted with ethyl

acetate (3 × 50 mL). The combined organic layers were washed with brine (1 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 50:50) to yield **2-amino-4-chloro-N-methoxybenzamide S_{2b}** as a colorless solid in 82% yield (24.9 g). To a solution of **2-amino-4-chloro-N-methoxybenzamide S_{2b}** (18.1 g, 1.0 equiv.) in 200 mL of freshly distilled anhydrous THF (0.58 mol/L) was added **bromobenzene S_3** (18.1 g, 1.0 equiv.) and n-butyllithium (232 mmol, 2.0 equiv.) by dropwise at -78℃. The reaction mixture was capped under argon atmosphere. The mixture was poured into 5% HCl in ethanol at -0 ℃ and the mixture was partitioned between brine and a 1:1 mixture of ether and methylene chloride. The organic extract was dried with Na_2SO_4 and evaporated in vacuo. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 30 / 1) to afford **(2-amino-4-chlorophenyl)(phenyl)methanone S_{4b}** as yellow solid in 34% yield (9.154 g). To a 500 mL flask charged with **(2-amino-4-chlorophenyl)(phenyl)methanone S_{4b}** (9.154 g, 1.0 equiv) and TsOH (22.7 g, 3.0 equiv) in MeCN (200 mL, 0.198 mol/mL) was added $NaNO_2$ (5.469 g, 2.0 equiv) and KI (16.4g, 2.5 equiv) dissolved in H_2O (100 mL) dropwise at room temperature and the resulting solution was stirred at room temperature for another 2 h. Upon completion, saturated aqueous sodium sulfite was added to the solution to quench the reaction until the reaction mixture turned to be yellow. After removal of the most of MeCN solvent under reduced pressure, the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 50 / 1) to afford **(4-chloro-2-iodophenyl)(phenyl)methanone S_{5b}** as colorless oil in 61% yield (8.310g). A solution of (4-bromobutyl)triphenylphosphonium bromide (13.937 g, 1.2 equiv) and t-BuOK (6.72g, 2.5 equiv) in THF (60 mL) was stirred at 40 °C in oil bath under Ar for 10 min. Afterwards compound **(4-chloro-2-iodophenyl)(phenyl)methanone S_{5b}** (8.310 g, 1.0 equiv) in THF (50 mL, 0.4 mol/L) was added and the reaction solution was stirred at 40 °C in oil bath for another 10 min. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether) to afford **4-chloro-1-(cyclobutylidene(phenyl)methyl)-2-iodobenzene S_{6b}** as colorless oil in 19% (1.751 g). To a stirred solution of iodine-tethered **4-chloro-1-(cyclobutylidene(phenyl)methyl)-2-iodobenzene S_{6b}** (1.751 g, 1.1 equiv) and **1,1-diphenylprop-2-yn-1-ol S_7** (0.958 g, 1.0 equiv) in i-Pr_2NH (50 mL, 0.092 mol/L) was added $PdCl_2(PPh_3)_2$ (65 mg, 2 mol%) and CuI (17 mg, 2 mol%) in Ar atmosphere. The resulted mixture was stirred at 80 °C in oil bath for 8 h. After the separation of solid by filtration and the removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the corresponding compound **3-(5-chloro-2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol 1b** as a white solid in 98% yield (2.354 g).

General procedure for the preparation of compound 1y: To a solution of **2-aminobenzonitrile S_{8y}** (4.72g, 1.0 equiv) in 50 mL of freshly distilled anhydrous THF (0.4 mol/L) was added EtMgBr (3.0 equiv.) dropwise at 0 °C. The reaction mixture was capped under argon atmosphere and warmed up to room temperature. After the reaction completion monitored by TLC analysis, the mixture was poured into 5% NH_4Cl in water at room tempeture., and the mixture was partitioned

between brine and a 1:1 mixture of ether and methylene chloride. The organic extract was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 30 / 1) to afford compound **1-(2-aminophenyl)propan-1-one S_{9y}** as yellow solid in 64 % yield (3.813g). To a 250 mL flask charged with **1-(2-aminophenyl)propan-1-one S_{9y}** (3.813 g, 1.0 equiv) and TsOH (14.663 g, 3.0 equiv) in MeCN (100 mL, 0.256 mol/mL) was added $NaNO_2$ (3.588 g, 2.0 equiv) and KI (10.79g, 2.5 equiv) dissolved in H_2O (50 mL) dropwise at room temperature and the resulting solution was stirred at room temperature for another 2 h. Upon completion, saturated aqueous sodium sulfite was added to the solution to quench the reaction until the reaction mixture turned to be yellow. After removal of the most of MeCN solvent under reduced pressure, the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 50 / 1) to afford **1-(2-iodophenyl)propan-1-one S_{10y}** as a white solid in 81% yield (5.385g). A solution of (4-bromobutyl)triphenylphosphonium bromide (12.046 g, 1.2 equiv) and t-BuOK (5.645 g, 2.4 equiv) in THF (50 mL) was stirred at 40 °C in oil bath under Ar for 10 min. Afterwards compound **1-(2-iodophenyl)propan-1-one S_{10y}** (5.385 g, 1.0 equiv) in THF (50 mL, 0.42 mol/L) was added and the reaction solution was stirred at 40 ° C in oil bath for another 2 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether) to afford **1-(1-cyclobutylidenepropyl)-2-iodobenzene S_{11}** as colorless oil in 34% (2.013 g). To a stirred solution of iodine-tethered **1-(1-cyclobutylidenepropyl)-2-iodobenzene S_{11y}** (2.013 g, 1.1 equiv) and **1,1-diphenylprop-2-yn-1-ol S_7** (1.456 g, 1.0 equiv) in i-Pr_2NH (50 mL, 0.14 mol/L) was added $PdCl_2(PPh_3)_2$ (98 mg, 2 mol%) and CuI (27 mg, 2 mol%) in Ar atmosphere. The resulted mixture was stirred at 80 °C in oil bath for 8 h. After the separation of solid by filtration and the removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the corresponding compound **3-(2-(1-cyclobutylidenepropyl)phenyl)-1,1-diphenylprop-2-yn-1-ol 1y** as a white solid in 94% yield (2.495 g).

3-(2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1a**). Yield: 57%, 630 mg; A light yellow solid; Mp: 102-104 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.96 (m, 2H), 2.60-2.64 (m, 3H), 3.04 (t, *J* = 7.2 Hz, 2H), 7.07-7.10 (m, 2H), 7.10-7.16 (m, 1H), 7.16-7.25 (m, 10H), 7.28-7.34 (m, 1H), 7.42-7.47 (m, 4H), 7.51 (d, *J* = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.7, 32.8, 74.7, 86.6, 93.8, 122.5, 125.87, 125.93, 126.7, 127.4, 128.0, 128.7, 130.2, 131.6, 132.3, 139.7, 142.7, 143.0, 145.0; IR (neat): ν 3551, 3057, 2988, 2955, 1652, 1592, 1447, 1158, 1045, 772, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{27}O$ $[M+H]^+$: 427.2056, found: 427.2056.

3-(5-chloro-2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1b**). Yield: 98%, 2354 mg; A light yellow solid; Mp: 133-135 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.88-1.98 (m, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.63 (s, 1H), 3.00 (t, *J* = 7.2 Hz, 2H), 7.05-7.12 (m, 4H), 7.14-7.22 (m, 8H), 7.24-7.28 (m, 1H), 7.39-7.43 (m, 4H), 7.48-7.50 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.2, 31.6, 32.8, 74.6, 85.2, 95.0, 124.2, 125.8, 126.0, 127.3, 127.4, 128.02, 128.04, 128.9, 130.5, 131.5, 132.0, 132.3, 139.2, 141.4, 143.2, 144.6; IR (neat): ν 3552, 3089, 3023, 2853, 2900, 1587, 1491, 1472, 1164, 982, 766, 693

cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{24}Cl$ [M-OH]$^+$: 443.1561, found: 443.1558.

3-(2-(cyclobutylidene(phenyl)methyl)-5-(trifluoromethyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1c**). Yield: 75%, 446 mg; White needles; Mp: 149-151 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.92-2.02 (m, 2H), 2.57-2.63 (m, 2H), 2.65 (s, 1H), 3.00-3.07 (m, 2H), 7.02-7.09 (m, 2H), 7.11-7.27 (m, 9H), 7.31–7.36 (m, 1H), 7.38-7.48 (m, 4H), 7.52–7.57 (m, 1H), 7.80 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.6, 32.8, 74.7, 85.1, 95.4, 123.5, 123.8 (q, *J* = 272.2 Hz), 125.2 (q, *J* = 3.4 Hz), 125.9, 126.2, 127.3, 127.5, 128.1, 128.2, 129.2 (q, *J* = 32.3 Hz), 129.3 (q, *J* = 3.7 Hz), 130.7, 130.9, 138.9, 143.7, 144.6, 146.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.44; IR (neat): ν 3552, 3047, 2989, 2961, 2908, 1190, 1451, 1328, 1167, 1114, 1070, 982, 767, 693 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{33}H_{24}F_3$ [M-OH]$^+$: 477.1825, found: 477.1829.

3-(4-chloro-2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1d**). Yield: 73%, 543 mg; A light yellow solid; Mp: 119-121 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.93-2.03 (m, 2H), 2.56 (s, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.15-7.27 (m, 11H), 7.40–7.46 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.6, 32.8, 74.7, 85.5, 94.7, 121.2, 125.9, 126.1, 127.0, 127.3, 127.5, 128.09, 128.13, 130.3, 130.6, 133.5, 134.5, 139.1, 143.6, 144.7, 144.8; IR (neat): ν 3576, 3086, 3029, 2906, 2225, 1596, 1488, 1449, 1162, 1042, 979, 759 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{24}Cl$ [M-OH]$^+$: 443.1561, found: 443.1557.

3-(4-bromo-2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1e**). Yield: 84%, 1691 mg; A white solid; Mp: 128-130 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.92-2.02 (m, 2H), 2.58 (s, 1H), 2.63 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.14-7.27 (m, 9H), 7.36–7.45 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.6, 32.8, 74.7, 85.6, 94.9, 121.6, 122.7, 125.9, 126.1, 127.3, 127.5, 128.06, 128.11, 129.9, 130.6, 133.2, 133.6, 139.1, 143.6, 144.7, 144.9; IR (neat): ν 3560, 3097, 3057, 3021, 2947, 1600, 1576, 1494, 1171, 982, 822, 745, 690 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{24}OBr$ [M-H]$^+$: 503.1005, found: 503.1001.

3-(2-(cyclobutylidene(phenyl)methyl)-4-methylphenyl)-1,1-diphenylprop-2-yn-1-ol (**1f**). Yield: 87%, 653 mg; A white solid; Mp: 112-114 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.91-2.01 (m, 2H), 2.35 (s, 3H), 2.54 (s, 1H), 2.61 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H), 7.02-7.12 (m, 4H), 7.16-7.26 (m, 9H), 7.40-7.48 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 21.4, 31.7, 32.8, 74.7, 86.8, 93.0, 119.5, 125.8, 126.0, 127.3, 127.4, 127.5, 127.99, 128.02, 130.9, 131.6, 132.2, 138.8, 139.8, 142.5, 143.0, 145.1; IR (neat): ν 3539, 3086, 3068, 2981, 2947, 2230, 1597, 1489, 1448, 1339, 1181, 1003, 825, 781, 691 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{27}$ [M-OH]$^+$: 423.2107, found: 423.2104.

3-(2-((3-chlorophenyl)(cyclobutylidene)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1g**). Yield: 85%, 1759 mg; A white solid; Mp: 105-107 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.89-1.98 (m, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.70 (s, 1H), 2.99 (t, *J* = 7.2 Hz, 2H), 6.93–6.98 (m, 1H), 7.08-7.11 (m, 3H), 7.15-7.24 (m, 8H), 7.27-7.33 (m, 1H), 7.42-7.47 (m, 4H), 7.51 (d, *J* = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.2, 31.7, 32.7, 74.7, 86.3, 94.0, 122.5, 125.4, 125.9, 126.9, 127.1, 127.4, 128.0, 128.8, 129.2, 130.1, 130.5, 132.4, 133.9, 141.4, 142.2, 144.5, 144.8; IR (neat): ν 3548, 3060, 2958, 2913, 1641, 1587, 1476, 1446, 1158, 1046, 1030, 872, 771, 712 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{24}OCl$ [M-H]$^+$: 459.1510, found: 459.1509.

3-(2-((4-chlorophenyl)(cyclobutylidene)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1h**).

Yield: 72%, 2091 mg; A white solid; Mp: 107-109 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.91-2.01 (m, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.68 (s, 1H), 2.99 (t, *J* = 7.2 Hz, 2H), 6.97-7.25 (m, 12H), 7.29-7.34 (m, 1H), 7.40-7.44 (m, 4H), 7.51 (d, *J* = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.7, 32.8, 74.7, 86.3, 94.0, 122.5, 125.9, 126.9, 127.5, 128.0, 128.1, 128.5, 128.8, 130.1, 130.6, 131.5, 132.4, 138.0, 143.4, 144.8; IR (neat): ν 3524, 3057, 2987, 2908, 2220, 1654, 1600, 1488, 1449, 1162, 1046, 1009, 752, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{24}OCl$ $[M-H]^+$: 459.1510, found: 459.1513.

3-(2-((4-bromophenyl)(cyclobutylidene)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1i**). Yield: 71%, 2119 mg; A white solid; Mp: 130-132 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.91-2.00 (m, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.68 (s, 1H), 2.98 (t, *J* = 7.2 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 7.15-7.25 (m, 8H), 7.28-7.33 (m, 3H), 7.39-7.44 (m, 4H), 7.51 (d, *J* = 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.7, 32.8, 74.7, 86.3, 94.0, 119.7, 122.5, 125.9, 126.9, 127.5, 128.0, 128.8, 128.9, 130.1, 130.7, 131.0, 132.4, 138.4, 142.4, 143.6, 144.8; IR (neat): ν 3516, 3015, 2992, 2932, 2215, 1654, 1486, 1449, 1393, 1161, 1046, 1001, 823, 752, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{24}Br$ $[M-OH]^+$: 487.1056, found: 487.1059.

3-(2-(cyclobutylidene(4-(trifluoromethyl)phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1j**). Yield: 69%, 1860 mg; A white solid; Mp: 105-107 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.95-2.05 (m, 2H), 2.60-2.67 (m, 3H), 3.03 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.18-7.31 (m, 8H), 7.34-7.47 (m, 7H), 7.56 (d, *J* = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.8, 32.9, 74.7, 86.3, 94.1, 122.6, 124.9 (q, *J* = 3.7 Hz), 125.7, 127.0 (q, *J* = 270.1 Hz), 127.1, 127.4, 127.59, 127.64 (q, *J* = 32.2 Hz), 128.1, 128.9, 130.1, 130.8, 132.5, 142.2, 143.0, 144.8, 145.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.21; IR (neat): ν 3518, 3060, 3000, 2900, 1609, 1488, 1451, 1321, 1116, 1046, 762, 751, 703 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{24}F_3$ $[M-OH]^+$: 477.1825, found: 477.1829.

3-(2-(cyclobutylidene(phenyl)methyl)phenyl)-1-phenyl-1-(p-tolyl)prop-2-yn-1-ol (**1k**). Yield: 75%, 2150 mg; A white solid; Mp: 99-101 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.90-2.00 (m, 2H), 2.26 (s, 3H), 2.55 (s, 1H), 2.62 (t, *J* = 8.8 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.08-7.13 (m, 3H), 7.14-7.23 (m, 7H), 7.27-7.35 (m, 3H), 7.41-7.52 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 21.0, 31.7, 32.8, 74.5, 86.4, 94.0, 122.6, 125.8, 125.87, 125.89, 126.6, 127.3, 127.4, 128.0, 128.6, 128.7, 130.2, 131.6, 132.3, 137.0, 139.7, 142.2, 142.6, 143.0, 145.1; IR (neat): ν 3563, 3057, 3023, 2940, 2908, 1649, 1592, 1445, 1163, 1031, 796, 717, 691 cm^{-1}; HRMS (EI-TOF) Calcd. for $C_{33}H_{28}O$ $[M]^+$: 440.2140, found: 440.2143.

3-(2-(cyclobutylidene(phenyl)methyl)phenyl)-1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol (**1l**). Yield: 93%, 1691 mg; A white solid; Mp: 135-137 °C; Eluent: PE/EA = 8/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.90-2.00 (m, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.68 (s, 1H), 3.04 (t, *J* = 7.6 Hz, 2H), 3.69 (s, 3H), 6.69 (d, *J* = 8.0 Hz, 2H), 7.07-7.22 (m, 10H), 7.23-7.36 (m, 3H), 7.42-7.45 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.6, 32.8, 55.1, 74.3, 86.7, 94.0, 113.2, 122.6, 125.82, 125.84, 126.6, 127.2, 127.27, 127.34, 127.9, 128.0, 128.6, 130.2, 131.6, 132.3, 137.3, 139.7, 142.6, 143.0, 145.2, 158.7; IR (neat): ν 3456, 3052, 2963, 2929, 2905, 1605, 1506, 1494, 1242, 1027, 990, 789, 701, 690 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{33}H_{27}O$ $[M-OH]^+$: 439.2056, found: 439.2058.

1,1-bis(4-chlorophenyl)-3-(2-(cyclobutylidene(phenyl)methyl)phenyl)prop-2-yn-1-ol (**1m**). Yield: 86%, 2131 mg; A light yellow solid; Mp: 148-150 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.94-2.03 (m, 2H), 2.58 (s, 1H), 2.61 (t, *J* = 7.2 Hz, 2H), 3.06 (t, *J* =

6.4 Hz, 2H), 7.06-7.10 (m, 2H), 7.13-7.19 (m, 5H), 7.20-7.28 (m, 4H), 7.29-7.37 (m, 5H), 7.50 (d, J = 8.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 17.4, 31.7, 33.0, 73.8, 87.3, 92.8, 122.0, 126.0, 126.8, 127.28, 127.33, 128.1, 128.2, 129.0, 130.4, 131.6, 132.3, 133.5, 139.6, 142.8, 143.0, 143.2; IR (neat): ν 3535, 3084, 3060, 2987, 2903, 2228, 1592, 1486, 1439, 1170, 1085, 1034, 841, 769, 713 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{25}OCl_2$ $[M+H]^+$: 495.1277, found: 495.1276.

3-(2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-di-p-tolylprop-2-yn-1-ol (**1n**). Yield: 73%, 1659 mg; A white solid; Mp: 99-101 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.94-2.03 (m, 2H), 2.28 (s, 6H), 2.47 (s, 1H), 2.63 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.2 Hz, 2H), 7.01 (d, J = 8.0 Hz, 4H), 7.08-7.18 (m, 3H), 7.20-7.36 (m, 9H), 7.51 (d, J = 7.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 17.3, 21.0, 31.7, 32.8, 74.5, 86.3, 94.2, 122.7, 125.9, 126.6, 127.4, 128.0, 128.6, 128.7, 130.2, 131.7, 132.4, 137.0, 139.8, 142.4, 142.6, 143.1; IR (neat): ν 3521, 3063, 3021, 2961, 1654, 1594, 1507, 1439, 1177, 1020, 779, 758, 693 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{34}H_{29}$ $[M-OH]^+$: 437.2264, found: 437.2266.

4-(2-(cyclobutylidene(phenyl)methyl)phenyl)-2-phenylbut-3-yn-2-ol (**1o**). Yield: 64%, 698 mg; A white solid; Mp: 82-84 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.64 (s, 3H), 1.95-2.05 (m, 2H), 2.13 (s, 1H), 2.67 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 8.0 Hz, 2H), 7.08-7.16 (m, 3H), 7.20-7.27 (m, 7H), 7.30-7.35 (m, 1H), 7.47-7.52 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 17.3, 31.6, 32.8, 33.0, 70.2, 84.4, 94.8, 122.6, 125.0, 125.8, 126.7, 127.4, 127.5, 127.9, 128.1, 128.5, 130.3, 131.7, 132.3, 139.9, 142.5, 143.0, 145.6; IR (neat): ν 3285, 3055, 2979, 2947, 1597, 1493, 1443, 1088, 943, 761, 691 cm^{-1}; HRMS (EI-TOF) Calcd. for $C_{27}H_{24}O$ $[M]^+$: 364.1827, found: 364.1819.

9-((2-(1-cyclobutylideneethyl)phenyl)ethynyl)-9H-fluoren-9-ol (**1p**). Yield: 61%, 1101 mg; A yellow liquid; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.64-1.74 (m, 5H), 2.32 (t, J = 7.2 Hz, 2H), 2.55 (t, J = 7.6 Hz, 2H), 2.73 (s, 1H), 7.03-7.10 (m, 2H), 7.16-7.22 (m, 1H), 7.29-7.42 (m, 5H), 7.59 (d, J = 6.8 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 15.9, 17.9, 29.7, 30.1, 75.2, 82.9, 90.8, 120.1, 120.6, 124.3, 125.81, 125.85, 128.2, 128.3, 128.4, 129.5, 132.6, 138.3, 138.9, 145.4, 147.3; IR (neat): ν 3390, 3060, 2945, 2995, 1605, 1449, 1188, 1098, 767, 746, 730 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{23}O$ $[M+H]^+$: 363.1743, found: 363.1742.

9-((2-(cyclobutylidene(phenyl)methyl)phenyl)ethynyl)-9H-fluoren-9-ol (**1q**). Yield: 82%, 1034 mg; A yellow liquid; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.73-1.82 (m, 2H), 2.44-2.50 (m, 3H), 2.83 (t, J = 7.2 Hz, 2H), 7.01 (d, J = 7.2 Hz, 2H), 7.07-7.27 (m, 8H), 7.31 (t, J = 7.6 Hz, 2H), 7.40-7.45 (m, 3H), 7.54 (d, J = 7.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 17.1, 31.4, 32.5, 74.8, 82.6, 91.2, 119.9, 122.3, 124.2, 125.7, 126.5, 127.4, 127.8, 128.3, 128.5, 129.3, 130.0, 131.2, 132.3, 138.9, 139.7, 142.6, 143.3, 147.0; IR (neat): ν 3394, 3057, 3015, 2903, 2220, 1493, 1449, 1343, 1187, 1048, 765, 747, 695 cm^{-1}; HRMS (EI-TOF) Calcd. for $C_{32}H_{24}O$ $[M]^+$: 424.1827, found: 424.1833.

3-(2-(1-cyclobutylideneethyl)-5-(trifluoromethyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1r**). Yield: 69%, 1139mg; A yellow liquid; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.75-1.95 (m, 5H), 2.30-2.60 (m, 2H), 2.68-2.72 (m, 2H), 3.02 (s, 1H), 7.20-7.27 (m, 3H), 7.29-7.35 (m, 4H), 7.48 (d, J = 8.0 Hz, 1H), 7.61-7.67 (m, 4H), 7.74 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 16.1, 18.0, 29.8, 30.1, 74.9, 85.6, 94.8, 121.7, 123.8 (q, J = 270.7 Hz), 125.0 (q, J = 3.6 Hz), 125.4, 126.1, 127.7, 128.2, 128.6, (q, J = 32.3 Hz), 129.0, 129.4 (q, J = 3.7

Hz), 139.8, 144.8, 148.7; IR (neat): ν 3432, 3060, 3021, 2911, 1578, 1468, 1448, 1164, 1041, 1002, 748, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{28}H_{22}F_3$ $[M\text{-}OH]^+$: 415.1668, found: 415.1671.

3-(4-bromo-2-(1-cyclobutylideneethyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1s**). Yield: 71%, 1095mg; A yellow liquid; Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.89 (m, 5H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.87 (s, 1H), 7.23-7.36 (m, 9H), 7.64 (d, *J* = 7.6 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.1, 18.1, 29.8, 30.2, 74.9, 86.1, 94.3, 119.9, 122.5, 125.3, 126.1, 127.7, 128.2, 129.3, 131.4, 133.8, 139.5, 144.9, 147.0; IR (neat): ν 3432, 3060, 3021, 2911, 1578, 1468, 1448, 1164, 1041, 1002, 748, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{24}OBr$ $[M+H]^+$: 443.1005, found: 443.1001.

3-(3-(1-cyclobutylideneethyl)-[1,1'-biphenyl]-4-yl)-1,1-diphenylprop-2-yn-1-ol (**1t**). Yield: 69%, 2120 mg; A yellow liquid; Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.82-1.92 (m, 5H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.87 (s, 1H), 7.24-7.30 (m, 2H), 7.31-7.37 (m, 5H), 7.38-7.45 (m, 4H), 7.52-7.60 (m, 3H), 7.67-7.71 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.2, 18.4, 29.8, 30.3, 75.0, 87.1, 93.9, 119.8, 124.8, 126.1, 126.4, 127.0, 127.1, 127.56, 127.63, 128.2, 128.8, 133.0, 138.5, 140.4, 141.2, 145.2, 145.6; IR (neat): ν 3403, 3055, 3023, 2906, 2220, 1597, 1468, 1448, 1176, 1039, 762, 723, 695 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{29}O$ $[M+H]^+$: 441.2213, found: 441.2209.

3-(2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (**1u**). Yield: 83%, 2019 mg; A White solid; Mp: 137-139 °C; Eluent: PE/EA = 6/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.92-2.01 (m, 2H), 2.56 (s, 1H), 2.62 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 6.8 Hz, 2H), 3.73 (s, 6H), 6.69-6.73 (m, 4H), 7.08-7.16 (m, 3H), 7.19-7.25 (m, 4H), 7.29-7.36 (m, 5H), 7.49-7.52 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 17.3, 31.7, 32.9, 55.2, 74.0, 86.2, 94.2, 113.3, 122.7, 125.8, 126.6, 127.3, 127.4, 128.0, 128.6, 130.2, 131.6, 132.3, 137.6, 139.7, 142.7, 143.0, 158.7; IR (neat): ν 3459, 2983, 2946, 2890, 1607, 1506, 1236, 1171, 1056, 767, 693 cm^{-1}; HRMS (EI-TOF) Calcd. for $C_{34}H_{30}O_3$ $[M]^+$: 486.2195, found: 486.2191.

3-(2-(1-cyclobutylideneethyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1v**). Yield: 48%, 412 mg; A light yellow solid; Mp: 66-68 °C; Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.88 (m, 5H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.87 (s, 1H), 7.11-7.17 (m, 2H), 7.22-7.28 (m, 3H), 7.30-7.36 (m, 4H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.1, 18.3, 29.8, 30.2, 74.9, 87.2, 93.3, 120.9, 126.08, 126.12, 126.4, 127.6, 128.2, 128.4, 128.5, 132.5, 138.2, 145.1, 145.2; IR (neat): ν 3517, 3060, 3018, 2908, 2843, 2233, 1597, 1449, 1168, 1026, 990, 746, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{23}$ $[M\text{-}OH]^+$: 347.1794, found: 347.1792.

3-(2-(1-cyclobutylideneethyl)-5-methoxyphenyl)-1,1-diphenylprop-2-yn-1-ol (**1w**). Yield: 85%, 1607 mg; A yellow liquid; Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.60-1.75 (m, 5H), 2.30-2.38 (m, 2H), 2.52-2.61 (m, 2H), 3.15 (s, 1H), 3.47 (s, 3H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.82-6.90 (m, 2H), 7.03-7.18 (m, 6H), 7.50-7.57 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.0, 18.4, 29.7, 30.1, 55.1, 74.7, 86.9, 93.1, 115.3, 116.5, 121.5, 125.9, 126.0, 127.5, 128.0, 129.3, 137.7, 137.9, 145.1, 157.3; IR (neat): ν 3451, 3059, 2940, 2830, 2225, 1599, 1489, 1286, 1209, 1024, 853, 770, 697 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{28}H_{25}O_2$ $[M\text{-}H]^+$: 393.1849, found: 393.1844.

3-(4-chloro-2-(1-cyclobutylideneethyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1x**). Yield: 66%, 917 mg; A yellow liquid; Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.79-1.88

(m, 5H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.92 (s, 1H), 7.08-7.13 (m, 2H), 7.22-7.38 (m, 7H), 7.61-7.66 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 16.1, 18.1, 29.7, 30.1, 74.9, 86.0, 94.2, 119.5, 125.3, 126.1, 126.3, 127.6, 128.2, 128.5, 133.6, 134.2, 139.4, 144.9, 146.8; IR (neat): ν 3557, 2979, 2911, 2851, 2222, 1584, 1488, 1448, 1161, 1031, 749 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{24}OCl$ $[M+H]^+$: 399.1510, found: 399.1505.

3-(2-(1-cyclobutylidenepropyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1y**). Yield: 94%, 2495 mg; A White solid; Mp: 85-87 ºC; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.85 (t, *J* = 7.6 Hz, 3H), 1.78-1.87 (m, 2H), 2.28 (q, *J* = 7.6 Hz, 2H), 2.45 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.98 (s, 1H), 7.07-7.16 (m, 3H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 4H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 12.7, 16.3, 25.7, 29.5, 30.1, 74.8, 87.3, 93.0, 121.6, 126.0, 126.1, 127.5, 128.1, 128.2, 128.9, 132.4, 132.6, 137.5, 143.6, 145.2; IR (neat): ν 3550, 3086, 3057, 2932, 1594, 1449, 1156, 1000, 769, 703, 693 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{28}H_{27}O$ $[M+H]^+$: 379.2056, found: 379.2056.

3-(2-(1-cyclobutylideneheptyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1z**). Yield: 85%, 2590 mg; A light yellow liquid; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.79-0.85 (m, 3H), 1.12-1.26 (m, 8H), 1.78-1.88 (m, 2H), 2.22-2.28 (m, 2H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.73 (s, 1H), 7.07-7.16 (m, 2H), 7.21-7.28 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 4H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 14.1, 16.3, 22.6, 28.0, 29.2, 29.7, 30.2, 31.7, 32.5, 74.9, 87.4, 93.1, 121.4, 126.0, 126.1, 127.6, 128.1, 128.2, 128.9, 131.3, 132.5, 138.2, 143.9, 145.2; IR (neat): ν 3453, 3055, 2958, 2853, 2228, 1600, 1448, 1030, 754, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{35}O$ $[M+H]^+$: 435.2682, found: 435.2683.

3-(2-(1-cyclobutylidene-4-phenylbutyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1aa**). Yield: 89%, 2991 mg; A light yellow liquid; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.50-1.60 (m, 2H), 1.76-1.87 (m, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 2.42-2.54 (m, 4H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.80 (s, 1H), 7.02 (d, *J* = 7.2 Hz, 2H), 7.07-7.30 (m, 12H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 16.3, 29.67, 29.75, 30.3, 32.1, 35.6, 74.8, 87.3, 93.2, 121.5, 125.5, 126.1, 127.5, 128.1, 128.28, 128.32, 128.8, 130.7, 132.7, 138.9, 142.5, 143.6, 145.1; IR (neat): ν 3565, 3060, 2981, 2929, 1597, 1489, 1449, 1159, 1030, 748 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{35}H_{33}O$ $[M+H]^+$: 469.2526, found: 469.2520.

3-(2-(1-cyclobutylidene-4-methylpentyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (**1ab**). Yield: 94%, 788 mg; A light yellow liquid; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.78 (d, *J* = 6.8 Hz, 6H), 1.09-1.17 (m, 2H), 1.44-1.51 (m, 1H), 1.76-1.86 (m, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.94 (s, 1H), 7.07-7.14 (m, 2H), 7.20-7.26 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 4H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 16.3, 22.5, 27.6, 29.7, 30.2, 30.4, 37.0, 74.9, 87.4, 93.1, 121.5, 126.0, 126.1, 127.5, 128.1, 128.2, 128.8, 131.3, 132.5, 138.1, 143.8, 145.2; IR (neat): ν 3549, 3021, 2951, 2927, 2220, 1597, 1466, 1414, 1161, 1030, 754, 697 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{31}H_{33}O$ $[M+H]^+$: 421.2526, found: 421.2521.

3-(2-(1-cyclobutylideneethyl)phenyl)-1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol (**1ac**). Yield: 77%, 1213 mg; A light yellow liquid; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.89 (m, 5H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.92 (s, 1H), 3.77 (s, 3H), 6.83-6.87 (m, 2H), 7.11-7.17 (m, 2H), 7.21-7.28 (m, 2H), 7.30-7.35 (m, 2H), 7.44-7.48 (m, 1H), 7.55-7.59 (m, 2H), 7.63-7.68 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 16.1, 18.3,

29.8, 30.2, 55.2, 74.6, 86.9, 93.5, 113.4, 120.9, 126.1, 126.4, 127.5, 128.1, 128.36, 128.41, 132.5, 137.5, 138.2, 145.1, 145.4, 159.0; IR (neat): ν 3447, 3052, 2909, 2840, 1607, 1507, 1246, 1031, 794, 732, 697 cm^{-1}; HRMS (EI-TOF) Calcd. for $C_{28}H_{26}O_2$ $[M]^+$: 394.1933, found: 394.1940.

3-(2-(1-cyclobutylideneethyl)phenyl)-1,1-di-p-tolylprop-2-yn-1-ol (**1ad**). Yield: 92%, 1302 mg; A light yellow liquid; Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.81-1.90 (m, 5H), 2.31 (s, 6H), 2.48 (t, *J* = 8.4 Hz, 2H), 2.73 (t, *J* = 8.4 Hz, 2H), 2.82 (s, 1H), 7.10-7.15 (m, 6H), 7.21-7.27 (m, 1H), 7.43-7.47 (m, 1H), 7.52-7.56 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.1, 18.3, 21.0, 29.8, 30.2, 74.7, 86.8, 93.6, 121.0, 126.0, 126.5, 128.32, 128.34, 128.8, 132.5, 137.1, 138.2, 142.5, 145.1; IR (neat): ν 3447, 3052, 2976, 2953, 2917, 2217, 1607, 1508, 1319, 1178, 1056, 1041, 817, 781, 757 cm^{-1}; HRMS (EI-TOF) Calcd. for $C_{29}H_{28}O$ $[M]^+$: 392.2140, found: 392.2139.

1,1-bis(4-chlorophenyl)-3-(2-(1-cyclobutylideneethyl)phenyl)prop-2-yn-1-ol (**1ae**). Yield: 95%, 1649 mg; A light yellow liquid; Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.90 (m, 5H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 3.01 (s, 1H), 7.12-7.18 (m, 2H), 7.27-7.31 (m, 5H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.1, 18.3, 29.8, 30.1, 55.2, 74.2, 86.6, 93.8, 113.4, 121.0, 126.0, 126.4, 127.4, 128.3, 132.4, 137.7, 138.1, 145.0, 158.9; IR (neat): ν 3398, 2972, 2910, 2225, 1589, 1486, 1400, 1090, 1014, 814, 757, 723 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{27}H_{21}Cl_2$ $[M\text{-}OH]^+$: 415.1015, found: 415.1007.

4-(2-(1-cyclobutylideneethyl)phenyl)-2-phenylbut-3-yn-2-ol (**1af**). Yield: 97%, 1091 mg; A white solid; Mp: 79-81 °C; Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$) δ 1.84-1.87 (m, 4H), 1.87-1.92 (m, 3H), 2.52 (t, *J* = 6.8 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 7.10-7.15 (m, 2H), 7.21-7.30 (m, 2H), 7.32-7.38 (m, 2H), 7.42-7.46 (m, 1H), 7.71-7.75 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.1, 18.1, 29.8, 30.2, 33.2, 70.4, 84.8, 94.2, 120.9, 125.0, 126.0, 126.4, 127.6, 128.18, 128.24, 128.3, 132.4, 138.1, 145.0, 145.8; IR (neat): ν 3385, 3055, 2978, 2910, 1600, 1445, 1141, 1070, 938, 756, 697 cm^{-1}; HRMS (EI-TOF) Calcd. for $C_{22}H_{22}O$ $[M]^+$: 302.1671, found: 302.1663.

3-(2-(1-cyclobutylideneethyl)phenyl)-1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (**1ag**). Yield: 84%, 1424; A light yellow liquid; Eluent: PE/EA = 6/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.89 (m, 5H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 3.02 (s, 1H), 3.75 (s, 6H), 6.82-6.86 (m, 4H), 7.09-7.15 (m, 2H), 7.21-7.26 (m, 1H), 7.42-7.46 (m, 1H), 7.53-7.58 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.1, 18.3, 29.8, 30.1, 55.2, 74.2, 86.6, 93.8, 113.4, 121.0, 126.0, 126.4, 127.4, 128.3, 132.4, 137.7, 138.1, 145.0, 158.9; IR (neat): ν 3450, 3057, 2947, 2908, 2835, 1607, 1507, 1247, 1171, 1033, 829, 759 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{29}H_{27}O_2$ $[M\text{-}OH]^+$: 407.2006, found: 407.2009.

General procedure for the synthesis of compound 2b: To a stirred solution of compound **3-(5-chloro-2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol 1b** (92 mg, 1.0 equiv) in DCE (2 mL) was added I_2 (101 mg, 2.0 equiv). The resulted mixture was stirred at 60 °C for 4 h. After quenching the remaining I_2 by Na_2SO_3 solution and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 200 / 1) to afford the corresponding product **6-chloro-8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene 2b** in 95% yield (108 mg).

8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2a**) (major). Yield: 65%, 69 mg, 3.0:1 dr (determined by ^{1}H NMR); A white solid; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.32-1.42 (m, 1H), 1.74-2.00 (m, 2H), 2.07-2.21 (m, 1H), 2.34-2.47 (m, 2H), 6.61-6.65 (m, 2H), 7.00-7.09 (m, 4H), 7.15-7.28 (m, 7H), 7.32-7.44 (m, 5H), 7.48-7.54 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 22.7, 28.6, 32.5, 66.0, 94.0, 121.6, 123.5, 124.9, 126.0, 126.4, 126.7, 127.0, 127.6, 127.9, 128.2, 128.3, 128.4, 128.7, 129.6, 138.2, 141.9, 142.2, 144.1, 145.3, 150.6, 153.5, 160.4; IR (neat): 3060, 3015, 2959, 2921, 2835, 1600, 1579, 1458, 1441, 1124, 761, 694 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{26}I$ $[M+H]^+$: 537.1074, found: 537.1072.

8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2a**) (minor). Yield: 21%, 23 mg, 3.0:1 dr (determined by ^{1}H NMR); A white solid; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.79-0.88 (m, 1H), 1.32-1.42 (m, 1H), 1.74-2.00 (m, 2H), 2.07-2.21 (m, 1H), 2.34-2.47 (m, 1H), 7.00-7.09 (m, 6H), 7.15-7.28 (m, 7H), 7.32-7.44 (m, 5H), 7.48-7.54 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.3, 28.5, 30.6, 65.4, 93.7, 120.7, 123.6, 125.8, 126.6, 126.9, 127.5, 127.8, 128.7, 129.7, 138.0, 140.5, 142.0, 145.5, 145.7, 10.6, 157.8.

6-chloro-8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2b**) (major). Yield: 71%, 81 mg, 3.0:1 dr (determined by ^{1}H NMR); A white solid; Mp; 179-181 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.30-1.42 (m, 1H), 1.75-2.02 (m, 2H), 2.07-2.23 (m, 1H), 2.34-2.48 (m, 2H), 6.59 (d, J = 7.2 Hz, 2H), 6.97-7.15 (m, 5H), 7.16-7.28 (m, 5H), 7.33-7.49 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 22.8, 28.5, 32.4, 65.6, 92.7, 121.6, 124.5, 124.7, 125.8, 126.6, 127.1, 128.2, 128.4, 128.5, 128.6, 129.5, 132.7, 137.5, 141.6, 141.7, 145.1, 145.9, 148.8, 154.2, 162.3. IR (neat): ν 2995, 2970, 2942, 2900, 1596, 1451, 1072, 792, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{25}ClI$ $[M+H]^+$: 571.0684, found: 571.0687.

6-chloro-8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2b**) (minor). Yield: 24%, 27 mg, 3.0:1 dr (determined by ^{1}H NMR); A white solid; Mp; 179-181 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.75-0.90 (m, 1H), 1.30-1.42 (m, 1H), 1.75-2.02 (m, 2H), 2.07-2.23 (m, 1H), 2.34-2.48 (m, 1H), 6.97-7.15 (m, 6H), 7.16-7.28 (m, 6H), 7.33-7.49 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 28.5, 30.6, 65.0, 91.9, 120.8, 125.6, 126.6, 127.7, 128.0, 128.7, 128.8, 129.6, 132.8, 137.3, 140.4, 141.3, 145.2, 147.4, 148.9, 151.2, 159.9.

8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-6-(trifluoromethyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2c**) (major). Yield: 51%, 62 mg, 2.8:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 1.30-1.44 (m, 1H), 1.75-1.98 (m, 2H), 2.05-2.25 (m, 1H), 2.37-2.50 (m, 2H), 6.61 (d, J = 7.2 Hz, 2H), 6.95-7.15 (m, 3H), 7.19-7.46 (m, 12H), 7.74 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 22.8, 28.5, 32.4, 66.0, 92.4, 118.2 (q, J = 4.2 Hz), 122.0 (q, J = 3.9 Hz), 124.6 (q, J = 270 Hz), 125.9, 126.8, 127.2, 127.7, 128.0, 128.3, 128.5, 128.60, 128.62, 128.9, 129.2 (q, J = 31.7 Hz), 129.5, 137.6, 141.1, 141.8, 144.7, 145.0, 153.9, 154.4, 162.2.; IR (neat): ν 3060, 2961, 2919, 2848, 1492, 1445, 1259, 1112, 1090, 1017, 795, 740, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{25}F_3I$ $[M+H]^+$: 605.0948, found: 605.0942.

8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-6-(trifluoromethyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2c**) (minor). Yield: 19%, 22 mg, 2.8:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.82-0.94 (m, 1H), 1.30-1.44

(m, 1H), 1.75-1.98 (m, 2H), 2.05-2.25 (m, 1H), 2.37-2.50 (m, 1H), 6.95-7.15 (m, 5H), 7.19-7.46 (m, 12H), 7.64 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 28.4, 30.6, 65.5, 91.3, 117.3 (q, J = 4.2 Hz), 125.7, 127.0, 127.8, 128.7, 129.6, 137.6, 140.4, 140.9, 145.2, 145.9, 151.5, 160.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.67.

5-chloro-8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2d**) (major). Yield: 44%, 50 mg, 2.7:1 dr (determined by ^{1}H NMR); A white solid; Mp＞200°C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.34-1.43 (m, 1H), 1.73-1.97 (m, 2H), 2.07-2.12 (m, 1H), 2.33-2.46 (m, 2H), 6.60 (d, J = 7.2 Hz, 2H), 7.03-7.14 (m, 4H), 7.19-7.28 (m, 5H), 7.34-7.45 (m, 7H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 22.7, 28.4, 32.4, 65.9, 93.0, 122.3, 124.2, 125.9, 126.7, 126.9, 127.1, 128.0, 128.2, 128.4, 128.6, 129.5, 130.8, 137.6, 141.4, 141.8, 142.5, 145.1, 152.1, 154.0, 160.8; IR (neat): ν 3050, 2979, 2916, 2851, 1594, 1490, 1443, 1123, 1092, 817, 693 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{25}ClI$ $[M+H]^+$: 571.0684, found: 571.0677.

5-chloro-8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2d**) (minor). Yield: 16%, 18 mg, 2.7:1 dr (determined by ^{1}H NMR); A white solid; Mp＞200°C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.79-0.88 (m, 1H), 1.34-1.43 (m, 1H), 1.73-1.97 (m, 2H), 2.07-2.12 (m, 1H), 2.33-2.46 (m, 1H), 6.95-6.99 (m, 2H), 7.03-7.14 (m, 4H), 7.19-7.28 (m, 6H), 7.34-7.45 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 28.4, 30.6, 65.3, 92.2, 121.5, 125.7, 127.7, 127.9, 128.7, 128.8, 129.6, 130.7, 137.4, 140.4, 141.2, 144.1, 145.3, 151.0, 152.1, 158.3.

5-bromo-8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2e**) (major). Yield: 60%, 74 mg, 2.4:1 dr (determined by ^{1}H NMR); White needles; Mp＞200°C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.30-1.42 (m, 1H), 1.70-2.01 (m, 2H), 2.05-2.23 (m, 1H), 2.33-2.45 (m, 2H), 6.60 (d, J = 7.2 Hz, 2H), 6.95-7.15 (m, 3H), 7.16-7.28 (m, 6H), 7.32-7.43 (m, 7H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 22.7, 28.5, 32.4, 66.0, 92.9, 118.9, 122.7, 125.9, 126.7, 127.0, 127.1, 128.0, 128.2, 128.4, 128.6, 129.5, 129.8, 137.7, 141.3, 141.8, 143.0, 145.0, 152.4, 154.0, 160.8; IR (neat): ν 2987, 2953, 2898, 1600, 1445, 1066, 751, 694 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{25}BrI$ $[M+H]^+$: 615.0179, found: 615.0175.

5-bromo-8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2e**) (minor). Yield: 25%, 31 mg, 2.4:1 dr (determined by ^{1}H NMR); White needles; Mp＞200°C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.78-0.91 (m, 1H), 1.30-1.42 (m, 1H), 1.70-2.01 (m, 2H), 2.05-2.23 (m, 1H), 2.33-2.45 (m, 1H), 6.95-7.15 (m, 6H), 7.16-7.28 (m, 6H), 7.32-7.43 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 28.4, 30.5, 65.4, 92.2, 118.9, 121.9, 125.7, 126.7, 127.7, 127.9, 128.6, 128.8, 129.6, 130.0, 137.5, 140.4, 141.0, 144.6, 145.3, 151.1, 152.4, 158.3.

8-(1-iodo-2,2-diphenylvinyl)-5-methyl-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2f**) (major). Yield: 73%, 79 mg, 3.2:1 dr (determined by ^{1}H NMR); Light yellow needles; Mp; 159-161 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.30-1.41 (m, 1H), 1.71-1.94 (m, 2H), 2.02-2.20 (m, 1H), 2.28 (s, 3H), 2.32-2.45 (m, 2H), 6.64 (d, J = 7.2 Hz, 2H), 7.01-7.09 (m, 5H), 7.17-7.27 (m, 5H), 7.32-7.43 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 22.6, 28.5, 32.6, 65.8, 94.3, 121.2, 124.6, 126.0, 126.3, 126.9, 127.4, 127.8, 128.2, 128.3, 128.4, 128.7, 129.6, 134.5, 138.1, 141.4, 141.9, 142.4, 145.3, 150.7, 153.3, 159.4; IR (neat): ν 3055, 3023, 2960, 2919, 2858, 1594, 1589, 1442, 1028, 754, 695 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{28}I$ $[M+H]^+$: 551.1230, found: 551.1231.

8-(1-iodo-2,2-diphenylvinyl)-5-methyl-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2f**) (minor). Yield: 22%, 25 mg, 3.2:1 dr (determined by ^{1}H NMR); Light yellow needles; Mp; 159-161 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.77-0.90 (m, 1H), 1.30-1.41 (m, 1H), 1.71-1.94 (m, 2H), 2.02-2.20 (m, 1H), 2.28 (s, 3H), 2.32-2.45 (m, 1H), 6.99 (s, 1H), 7.01-7.09 (m, 5H), 7.17-7.27 (m, 6H), 7.32-7.43 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.2, 28.5, 30.6, 65.1, 93.7, 120.3, 125.8, 126.5, 127.46, 127.55, 127.60, 127.8, 128.6, 128.7, 129.7, 134.5, 137.7, 140.5, 142.2, 143.0, 145.6, 150.2, 150.8, 156.5.

3a-(3-chlorophenyl)-8-(1-iodo-2,2-diphenylvinyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2g**) (major). Yield: 56%, 64 mg, 2.9:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.31-1.45 (m, 1H), 1.70-2.04 (m, 2H), 2.05-2.26 (m, 1H), 2.28-2.46 (m, 2H), 6.47 (d, J = 7.6 Hz, 1H), 6.83-6.86 (m, 1H) 6.92-7.17 (m, 5H), 7.18-7.47 (m, 10H), 7.49-7.56 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 22.6, 28.6, 32.6, 65.7, 93.6, 121.8, 123.6, 124.3, 125.0, 126.0, 126.8, 127.0, 127.6, 127.9, 128.2, 128.4, 128.6, 129.56, 129.58, 134.3, 138.8, 141.5, 144.0, 144.3, 145.4, 149.9, 153.7, 159.2; IR (neat): ν 2995, 2919, 2864, 1590, 1489, 1456, 1072, 740, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{25}ClI$ $[M+H]^+$: 571.0684, found: 571.0685.

3a-(3-chlorophenyl)-8-(1-iodo-2,2-diphenylvinyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2g**) (minor). Yield: 20%, 22 mg, 2.9:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.78-0.91 (m, 1H), 1.31-1.45 (m, 1H), 1.70-2.04 (m, 2H), 2.05-2.26 (m, 1H), 2.28-2.46 (m, 1H), 6.92-7.17 (m, 5H), 7.18-7.47 (m, 12H), 7.49-7.56 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 28.5, 30.6, 65.1, 92.7, 120.9, 124.1, 125.0, 126.0, 126.9, 127.2, 128.7, 129.7, 130.0, 134.4, 138.5, 140.5, 144.3, 145.4, 145.6, 149.9, 150.7, 156.9.

3a-(4-chlorophenyl)-8-(1-iodo-2,2-diphenylvinyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2h**) (major). Yield: 67%, 76 mg, 2.9:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.32-1.43 (m, 1H), 1.70-1.92 (m, 2H), 2.05-2.24 (m, 1H), 2.28-2.45 (m, 2H), 6.54 (d, J = 8.4 Hz, 2H), 6.95-7.14 (m, 4H), 7.15-7.31 (m, 6H), 7.32-7.46 (m, 5H), 7.48-7.55 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 22.5, 28.5, 32.4, 65.4, 93.5, 121.7, 123.4, 125.0, 126.9, 127.0, 127.4, 127.9, 128.2, 128.4, 128.5, 128.6, 129.5, 132.1, 138.5, 140.8, 142.0, 144.0, 145.1, 150.1, 153.7, 159.8; IR (neat): ν 3076, 3052, 2963, 2861, 1597, 1488, 1442, 1179, 1047, 789, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{25}ClI$ $[M+H]^+$: 571.0684, found: 571.0687.

3a-(4-chlorophenyl)-8-(1-iodo-2,2-diphenylvinyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2h**) (minor). Yield: 23%, 26 mg, 2.9:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.77-0.90 (m, 1H), 1.32-1.43 (m, 1H), 1.70-1.92 (m, 2H), 2.05-2.24 (m, 1H), 2.28-2.45 (m, 1H), 6.95-7.14 (m, 6H), 7.15-7.31 (m, 7H), 7.32-7.46 (m, 4H), 7.48-7.55 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.2, 28.5, 30.5, 64.8, 92.8, 120.8, 123.5, 127.1, 127.2, 127.58, 127.64, 127.9, 128.7, 128.8, 129.7, 132.3, 138.2, 140.4, 140.5, 145.4, 145.6, 150.2, 150.7, 157.2.

3a-(4-bromophenyl)-8-(1-iodo-2,2-diphenylvinyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2i**) (major). Yield: 57%, 70 mg, 3.1:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.31-1.44 (m, 1H), 1.70-2.01 (m, 2H), 2.05-2.24 (m, 1H), 2.28-2.45 (m, 2H), 6.48 (d, J = 8.0 Hz, 2H), 6.96-7.17 (m, 5H), 7.17-7.31 (m, 5H), 7.32-7.44 (m, 5H), 7.46-7.55 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 22.5,

28.5, 32.3, 65.5, 93.5, 120.3, 121.7, 123.4, 125.0, 126.9, 127.0, 127.8, 127.9, 128.2, 128.4, 128.6, 129.5, 131.5, 138.6, 141.4, 142.0, 144.0, 145.1, 150.0, 153.7, 159.7; IR (neat): ν 3073, 3047, 2955, 2911, 2868, 1594, 1484, 1441, 1186, 1105, 738, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{23}BrI$ $[M+H]^+$: 613.0022, found: 613.0026.

3a-(4-bromophenyl)-8-(1-iodo-2,2-diphenylvinyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2i**) (minor). Yield: 18%, 22 mg, 3.1:1 dr (determined by ^1H NMR); White needles; Mp＞200°C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 0.77-0.90 (m, 1H), 1.31-1.44 (m, 1H), 1.70-2.01 (m, 2H), 2.05-2.24 (m, 1H), 2.28-2.45 (m, 1H), 6.96-7.17 (m, 4H), 7.17-7.31 (m, 8H), 7.32-7.44 (m, 5H), 7.46-7.55 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 21.2, 28.5, 30.5, 64.9, 92.8, 120.5, 120.8, 123.5, 127.1, 127.58, 127.64, 127.9, 128.7, 129.7, 131.8, 138.3, 140.5, 141.1, 145.4, 145.6, 150.1, 150.7, 157.2.

8-(1-iodo-2,2-diphenylvinyl)-3a-(4-(trifluoromethyl)phenyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2j**) (major). Yield: 62%, 74 mg, 3.6:1 dr (determined by ^1H NMR); White needles; Mp ＞ 200°C; Eluent: PE/EA = 100/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.37-1.49 (m, 1H) 1.72-1.88 (m, 2H), 1.98-2.24 (m, 1H), 2.41-2.47 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 7.00-7.14 (m, 3H), 7.20-7.31 (m, 7H), 7.34-7.42 (m, 5H), 7.49-7.56 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 22.6, 28.6, 32.4, 65.8, 93.2, 121.8, 123.5, 124.2 (q, *J* = 270. 5 Hz), 125.1, 125.4 (q, *J* = 3.5 Hz), 126.3, 127.09, 127.10, 128.0, 128.2, 128.4, 128.6, 128.7, (q, *J* = 32.2 Hz), 129.5, 138.9, 142.0, 144.1, 145.1, 146.6, 149.7, 153.8, 159.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43; IR (neat): ν 3060, 3021, 2989, 2953, 1613, 1442, 1411, 1324, 1119, 1016, 735, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{24}F_3$ $[M-I]^+$: 477.1825, found: 477.1825.

8-(1-iodo-2,2-diphenylvinyl)-3a-(4-(trifluoromethyl)phenyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2j**) (minor). Yield: 17%, 21 mg, 3.6:1 dr (determined by ^1H NMR); White needles; Mp ＞ 200°C; Eluent: PE/EA = 100/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 0.85-0.92 (m, 1H), 1.37-1.49 (m, 1H) 1.72-1.88 (m, 1H), 1.98-2.24 (m, 2H), 2.41-2.47 (m, 1H), 7.00-7.14 (m, 3H), 7.20-7.31 (m, 7H), 7.34-7.42 (m, 6H), 7.49-7.56 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 21.2, 28.5, 30.5, 65.2, 92.5, 120.9, 123.6, 125.7 (q, *J* = 3.7 Hz), 126.2, 127.3, 127.7, 127.9, 128.7, 129.6, 138.6, 140.4, 145.3, 145.7, 146.4, 149.8, 150.9, 156.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43.

8-(1-iodo-2-phenyl-2-(p-tolyl)vinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2k** and **2k'**). Yield: 93%, 102 mg (1:1), 3.8:1 dr (determined by ^1H NMR); Yellow needles; Mp; 141-143 °C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 0.8-0.99 (m, 0.34H), 1.32-1.39 (m, 1.40H), 1.76-1.89 (m, 2.75H), 2.13-2.18 (m, 1.55H), 2.30-2.34 (m, 1.37H), 2.36-2.46 (m, 4.43H), 6.62 (d, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 7.2 Hz, 1H), 6.82-6.93 (m, 0.51H), 7.00-7.12 (m, 7.43H), 7.15-7.43 (m, 14.08H), 7.48-7.53 (m, 1.35H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 21.1, 21.2, 21.3, 21.4, 22.7, 28.5, 28.6, 30.6, 30.7, 32.50, 32.54, 65.3, 65.9, 92.6, 92.7, 93.4, 93.5, 120.7, 121.6, 123.5, 124.8, 125.8, 125.9, 126.1, 126.35, 126.40, 126.6, 126.7, 126.8, 126.9, 127.4, 127.5, 127.7, 127.8, 128.1, 128.2, 128.28, 128.36, 128.58, 128.62, 128.66, 128.72, 128.9, 129.0, 129.49, 129.55, 129.59, 129.67, 136.8, 137.4, 137.59, 137.64, 138.05, 138.08, 138.3, 139.1, 140.7, 142.1, 142.22, 142.24, 142.4, 142.6, 144.08, 144.13, 145.4, 150.46, 150.52, 150.6, 153.4, 153.5, 157.7, 160.1, 160.3; IR (neat): ν 2980, 2958, 2924, 2900, 1597, 1489, 1442, 1259, 1080, 743, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{26}I$ $[M+H]^+$: 549.1074, found: 549.1074.

8-(1-iodo-2-(4-methoxyphenyl)-2-phenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]i

ndene (**2l** and **2l'**). 77%, 87 mg (1:0.91), 2.5:1 dr (determined by ^{1}H NMR); White needles; Mp: 189-191 ^{o}C; Eluent: PE/EA = 80/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.80-0.98 (m, 0.83H), 1.34-1.39 (m, 3.03H), 1.74-2.15 (m, 7.52H), 2.38-2.43 (m, 4.39H), 3.62 (s, 0.68H), 3.71 (s, 2.74H), 3.79 (s, 3.00H), 6.53-6.62 (m, 2.36H), 6.70-6.74 (m, 3.75H), 6.90-6.93 (m, 2.93H), 6.99-7.25 (m, 23.54H), 7.31-7.53 (m, 10.75H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.3, 22.6, 28.5, 30.6, 30.8, 32.50, 32.55, 55.0, 55.1, 65.7, 65.9, 91.9, 92.8, 93.2, 112.9, 113.4, 113.6, 120.6, 121.4, 121.5, 123.5, 124.8, 125.7, 125.9, 126.1, 126.3, 126.46, 126.53, 126.7, 126.8, 127.5, 127.7, 128.1, 128.2, 128.3, 128.6, 128.7, 129.6, 129.7, 129.9, 130.0, 131.0, 134.3, 137.5, 137.7, 138.1, 138.4, 140.8, 141.9, 142.20, 142.22, 144.0, 144.1, 145.4, 145.7, 150.0, 150.5, 152.9, 153.6, 157.6, 158.8, 159.0, 159.1, 159.9, 160.2; IR (neat): ν 2986, 2969, 2900, 1602, 1505, 1455, 1242, 1065, 1027, 832, 740, 694 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{28}OI$ $[M+H]^+$: 567.1179, found: 567.1179.

8-(2,2-bis(4-chlorophenyl)-1-iodovinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2m**) (major). Yield: 70%, 85 mg, 4.0:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.32-1.43 (m, 1H), 1.73-2.00 (m, 2H), 2.10-2.24 (m, 1H), 2.29-2.50 (m, 2H), 6.62-6.67 (m, 2H), 7.01-7.14 (m, 5H), 7.17-7.29 (m, 5H), 7.30-7.42 (m, 4H), 7.43-7.51 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 22.7, 28.6, 32.6, 66.1, 95.1, 121.5, 123.7, 125.1, 125.9, 126.7, 126.8, 128.5, 128.6, 128.7, 130.0, 131.1, 133.4, 134.1, 138.0, 140.1, 141.9, 142.9, 143.7, 150.5, 151.0, 160.7; IR (neat): ν 3068, 2981, 2924, 2864, 1587, 1487, 1104, 757, 700 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{24}Cl_2I$ $[M+H]^+$: 605.0294, found: 605.0289.

8-(2,2-bis(4-chlorophenyl)-1-iodovinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2m**) (minor). Yield: 18%, 21 mg, 4.0:1 dr (determined by ^{1}H NMR); White needles; Mp＞200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.82-0.92 (m, 1H), 1.32-1.43 (m, 1H), 1.73-2.00 (m, 2H), 2.10-2.24 (m, 1H), 2.29-2.50 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H), 7.01-7.14 (m, 7H), 7.17-7.29 (m, 4H), 7.30-7.42 (m, 4H), 7.43-7.51 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 28.5, 30.8, 65.5, 94.4, 120.5, 123.8, 125.7, 127.0, 127.9, 128.7, 131.2, 133.7, 134.0, 137.6, 138.6, 141.8, 143.3, 145.2, 148.1, 150.6, 158.3.

8-(1-iodo-2,2-di-p-tolylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2n**) (major). Yield: 72%, 81 mg, 4.4:1 dr (determined by ^{1}H NMR); White needles; Mp ＞ 200 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.32-1.42 (m, 1H), 1.73-2.00 (m, 2H), 2.02-2.16 (m, 1H), 2.31 (s, 3H), 2.37 (s, 3H), 2.38-2.46 (m, 2H), 6.68 (d, J = 7.6 Hz, 2H), 6.97-7.11 (m, 7H), 7.13-7.33 (m, 7H), 7.48-7.54 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.2, 21.4, 22.6, 28.5, 32.6, 65.9, 92.9, 121.6, 123.5, 124.8, 126.1, 126.4, 126.6, 128.2, 128.6, 128.8, 128.9, 129.5, 136.7, 137.6, 138.4, 139.3, 142.2, 142.5, 144.2, 150.5, 153.4, 160.1; IR (neat): ν 2962, 2913, 1738, 1594, 1455, 1047, 1023, 743, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{34}H_{30}I$ $[M+H]^+$: 565.1387, found: 565.1382.

8-(1-iodo-2,2-di-p-tolylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2n**) (minor). Yield: 17%, 19 mg, 4.4:1 dr (determined by ^{1}H NMR); White needles; Mp ＞ 200 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.83-0.93 (m, 1H), 1.32-1.42 (m, 1H), 1.73-2.00 (m, 2H), 2.02-2.16 (m, 1H), 2.18 (s, 3H), 2.39 (s, 3H), 2.38-2.46 (m, 1H), 6.80-6.90 (m, 4H), 6.97-7.11 (m, 6H), 7.13-7.33 (m, 6H), 7.48-7.54 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) δ 21.1, 21.3, 28.5, 30.7, 65.3, 92.2, 120.7, 125.8, 126.4, 126.8, 128.2, 128.7, 128.8, 129.6, 137.3, 137.5, 137.9, 138.1, 142.0, 142.8, 145.7, 150.4, 150.6, 157.6.

8-(1-iodo-2-phenylprop-1-en-1-yl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (2o)

(major). Yield: 67%, 64 mg, 4.0:1 dr (determined by ^{1}H NMR); Light yellow needles; Mp; 149-151 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.25-1.32 (m, 1H), 1.64-1.85 (m, 2H), 1.99-2.14 (m, 1H), 2.15-2.41 (m, 2H), 2.49 (s, 3H), 6.53-6.58 (m, 2H), 6.96-7.06 (m, 4H), 7.09-7.12 (m, 1H), 7.14-7.23 (m, 6H), 7.38-7.42 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 22.5, 28.6, 30.8, 32.3, 65.8, 92.8, 121.2, 123.3, 124.7, 125.9, 126.3, 126.6, 126.7, 127.2, 128.3, 128.4, 138.0, 142.1, 142.3, 144.4, 147.9, 150.4, 159.8.; IR (neat): ν 3167, 3049, 3015, 2958, 2864, 1594, 1487, 1456, 1440, 1133, 990, 761, 698 cm^{-1}; HRMS (EI-TOF) Calcd. for $C_{27}H_{23}I$ $[M]^+$: 474.0845, found: 474.0851.

8-(1-iodo-2-phenylprop-1-en-1-yl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (2o) (minor). Yield: 17%, 16 mg, 4.0:1 dr (determined by ^{1}H NMR); Light yellow needles; Mp; 149-151 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.64-0.75 (m, 1H), 1.25-1.32 (m, 1H), 1.64-1.85 (m, 2H), 1.99-2.14 (m, 1H), 2.15-2.41 (m, 1H), 2.50 (s, 3H), 6.53-6.58 (m, 1H), 6.96-7.06 (m, 6H), 7.09-7.12 (m, 1H), 7.14-7.23 (m, 5H), 7.38-7.42 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 21.2, 30.4, 30.7, 65.1, 92.8, 120.4, 123.4, 125.7, 126.5, 126.8, 127.1, 127.6, 128.6, 138.0, 140.9, 142.0, 144.7, 146.0, 150.5, 157.5.

9-(iodo(3a-methyl-1,2,3,3a-tetrahydrocyclopenta[a]inden-8-yl)methylene)-9H-fluorene (2p) (major). Yield: 55%, 51 mg, 2.9:1 dr (determined by ^{1}H NMR); Yellow needles; Mp; 113-115 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24-1.31 (m, 1H), 1.46 (s, 3H), 1.79-1.87 (m, 1H), 2.08-2.18 (m, 1H), 2.22-2.33 (m, 1H), 2.35-2.51 (m, 2H), 6.91-6.98 (m, 1H), 7.16-7.26 (m, 4H), 7.36-7.49 (m, 3H), 7.58-7.76 (m, 3H), 9.06-9.14 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 20.6, 22.0, 28.5, 31.9, 58.5, 93.9, 118.9, 119.5, 121.0, 122.6, 124.9, 125.3, 126.3, 127.0, 127.1, 128.2, 129.4, 137.2, 138.0, 138.6, 139.2, 141.66, 141.69, 142.7, 151.6, 161.6; IR (neat): ν 3063, 3039, 2958, 2919, 2856, 1605, 1463, 1444, 1046, 752, 727 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{22}I$ $[M+H]^+$: 473.0761, found: 473.0753.

9-(iodo(3a-methyl-1,2,3,3a-tetrahydrocyclopenta[a]inden-8-yl)methylene)-9H-fluorene (2p) (minor). Yield: 19%, 19 mg, 2.9:1 dr (determined by ^{1}H NMR); Yellow needles; Mp; 113-115 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24-1.31 (m, 1H), 1.37 (s, 3H), 1.95-2.02 (m, 1H), 2.08-2.18 (m, 1H), 2.22-2.33 (m, 1H), 2.35-2.51 (m, 2H), 6.82-6.88 (m, 1H), 7.07-7.12 (m, 1H), 7.16-7.26 (m, 1H), 7.36-7.49 (m, 4H), 7.58-7.76 (m, 3H), 7.80-7.91 (m, 1H), 9.06-9.14 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 21.0, 22.0, 28.0, 31.3, 93.3, 119.5, 120.4, 122.8, 124.5, 124.86, 124.91, 126.4, 127.0, 127.1, 138.0, 139.1, 140.5, 141.6, 144.1, 151.0, 160.1.

9-(iodo(3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]inden-8-yl)methylene)-9H-fluorene (2q) (major). Yield: 64%, 69 mg, 12.5:1 dr (determined by ^{1}H NMR); Yellow needles; Mp > 200^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.69-1.80 (m, 1H), 2.04-2.20 (m, 2H), 2.25-2.41 (m, 2H), 2.75-2.83 (m, 1H), 6.88 (m, 1H), 7.05-7.17 (m, 2H), 7.18-7.24 (m, 4H), 7.27-7.35 (m, 3H), 7.40-7.52 (m, 4H), 7.64-7.67 (m, 1H), 7.70-7.85 (m, 1H), 9.08-9.19 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 21.5, 28.7, 31.1, 66.1, 92.1, 119.0, 119.6, 120.4, 124.1, 124.6, 124.9, 125.3, 125.6, 126.5, 126.8, 127.1, 127.2, 128.4, 128.8, 129.5, 138.0, 139.2, 140.8, 141.1, 141.7, 142.8, 143.9, 150.5, 158.6; IR (neat): ν 3057, 2992, 2950, 2900, 1734, 1455, 1443, 1075, 776, 745, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{24}I$ $[M+H]^+$: 535.0917, found: 535.0920.

9-(iodo(3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]inden-8-yl)methylene)-9H-fluorene (2q) (minor). Yield: 5%, 5 mg, 12.5:1 dr (determined by ^{1}H NMR); Yellow needles; Mp > 200^{o}C;

Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.80-0.90 (m, 1H), 1.69-1.80 (m, 1H), 2.04-2.20 (m, 2H), 2.25-2.41 (m, 2H), 6.88 (m, 1H), 7.05-7.17 (m, 1H), 7.18-7.24 (m, 4H), 7.27-7.35 (m, 4H), 7.40-7.52 (m, 4H), 7.64-7.67 (m, 1H), 7.70-7.85 (m, 1H), 9.08-9.19 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 22.9, 29.2, 33.6, 66.8, 121.0, 124.0, 125.5, 125.8, 126.4, 127.0, 127.3, 128.5, 128.8, 129.6, 138.0, 140.6, 142.7, 142.9, 150.7, 159.2.

8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-6-(trifluoromethyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2r**) (major). Yield: 39%, 42 mg, 1.5:1 dr (determined by ^{1}H NMR); Light yellow needles; Mp; 165-167 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 0.95 (s, 3H), 1.59-1.80 (m, 2H), 1.94-2.15 (m, 1H), 2.16-2.37 (m, 3H), 6.87-7.03 (m, 2H), 7.02-7.12 (m, 3H), 7.27-7.45 (m, 7H), 7.77 (s, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, TMS) *δ* 20.7, 22.2, 27.9, 31.3, 58.1, 93.1, 118.1 (q, *J* = 4.1 Hz), 121.4 (q, *J* = 3.2 Hz), 122.4, 124.7 (q, *J* = 270.3 Hz), 127.2, 127.7, 128.0, 128.2, 128.9, 129.1 (q, *J* = 31.8 Hz), 129.7, 133.6, 141.1, 145.3, 145.5, 153.5, 154.8, 164.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.66; IR (neat): ν 3060, 3023, 2961, 2924, 2861, 1445, 1330, 1165, 1122, 1056, 1006, 830, 760, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{28}H_{22}F_3$ $[M-I]^+$: 415.1668, found: 415.1671.

8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-6-(trifluoromethyl)-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2r**) (minor). Yield: 26%, 28 mg, 1.5:1 dr (determined by ^{1}H NMR); Light yellow needles; Mp; 165-167 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 0.64-0.76 (m, 1H), 1.25 (s, 3H), 1.59-1.80 (m, 2H), 1.94-2.15 (m, 1H), 2.16-2.37 (m, 2H), 6.87-7.03 (m, 1H), 7.02-7.12 (m, 3H), 7.27-7.45 (m, 8H), 7.66 (s, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, TMS) *δ* 20.8, 21.2, 27.8, 31.2, 57.6, 92.3, 117.2 (q, *J* = 4.4 Hz), 121.5 (q, *J* = 3.9 Hz), 124.7 (q, *J* = 270.8 Hz), 127.58, 127.62, 127.9, 128.2, 128.7, 129.6, 134.6, 140.5, 145.4, 146.2, 151.2, 154.4, 161.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.66.

5-bromo-8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2s**) (major). Yield: 26%, 29 mg, 1.3:1 dr (determined by ^{1}H NMR); Light yellow needles; Mp; 161-163 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.93 (s, 3H), 1.50-1.72 (m, 2H), 1.84-2.08 (m, 1H), 2.13-2.30 (m, 3H), 6.89-6.93 (m, 1H), 6.96-7.12 (m, 4H), 7.32-7.45 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 20.8, 22.1, 27.8, 31.4, 58.1, 93.6, 118.5, 122.7, 125.9, 127.2, 127.6, 127.8, 128.2, 128.8, 129.65, 129.70, 133.7, 141.1, 143.6, 145.5, 153.1, 153.3, 162.8; IR (neat): ν 2989, 2950, 2919, 2866, 1644, 1473, 1258, 1072, 880, 775, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{23}BrI$ $[M+H]^+$: 553.0022, found: 553.0018.

5-bromo-8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2s**) (minor). Yield: 19%, 21 mg, 1.3:1 dr (determined by ^{1}H NMR); Light yellow needles; Mp; 161-163 ^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.58-0.70 (m, 1H), 1.21 (s, 3H), 1.21-1.23 (m, 1H), 1.50-1.72 (m, 2H), 1.84-2.08 (m, 1H), 2.13-2.30 (m, 1H), 6.96-7.12 (m, 4H), 7.20-7.24 (m, 1H), 7.32-7.45 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 20.7, 21.0, 27.7, 31.2, 57.6, 93.1, 118.6, 121.8, 126.0, 127.5, 128.2, 128.6, 129.6, 129.8, 134.3, 134.5, 140.5, 144.8, 145.5, 150.8, 153.0, 159.9.

8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-5-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2t**) (major). Yield: 48%, 53 mg, 1.5:1 dr (determined by ^{1}H NMR); White needles; Mp; 140-142^{o}C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.98 (s, 3H), 1.55-1.76 (m, 2H), 1.84-2.35 (m, 4H), 6.94-6.99 (m, 2H), 7.02-7.12 (m, 3H), 7.26-7.49 (m, 9H), 7.52-7.66 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 21.0, 22.2, 27.9, 31.6, 58.0, 94.6, 121.3, 121.7, 125.6, 126.8, 127.1, 127.5, 127.6, 128.1, 128.6, 129.0, 129.8, 134.0, 137.4, 141.2, 141.7, 144.0,

145.8, 152.0, 152.7, 162.9; IR (neat): ν 3055, 3029, 2957, 2858, 1598, 1464, 1439, 1118, 1075, 946, 730, 694 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{33}H_{28}I$ $[M+H]^+$: 551.1230, found: 551.1221.

8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-5-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2t**) (minor). Yield: 32%, 35 mg, 1.5:1 dr (determined by ^1H NMR); White needles; Mp; 140-142°C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 0.65-0.77 (m, 1H), 1.27 (s, 3H), 1.55-1.76 (m, 2H), 1.84-2.35 (m, 3H), 6.94-6.99 (m, 1H), 7.02-7.12 (m, 4H), 7.26-7.49 (m, 9H), 7.52-7.66 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 21.0, 27.8, 31.4, 57.5, 94.1, 120.7, 121.4, 125.9, 127.0, 127.1, 127.4, 127.7, 128.66, 128.73, 129.7, 134.7, 137.5, 140.5, 141.7, 145.2, 145.6, 150.3, 151.6, 159.7.

General procedure for the synthesis of 2v; To a stirred solution of **3-(2-(1-cyclobutylideneethyl)phenyl)-1,1-diphenylprop-2-yn-1-ol 1v** (73 mg, 1.0 equiv) in DCE (2 mL) was added I_2 (101mg, 2 equiv). The resulted mixture was stirred at 60 °C for 2 h. After quenching the remaining I_2 by Na_2SO_3 solution and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 200 / 1) to afford the corresponding product **8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-1,2,3,3a-tetrahydrocyclopenta[a]indene 2v** in 73% yield (69 mg).

8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2v**) (major). Yield: 44%, 42 mg, 1.5:1 dr (determined by ^1H NMR); White needles; Mp; 160-162 °C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 0.94 (s, 3.00H), 1.24-1.30 (m, 1.00H), 1.45-1.74 (m, 2H), 1.86-2.09 (m, 1H) 2.10-2.35 (m, 2H), 6.92-6.98 (m, 2H), 7.02-7.18 (m, 4H), 7.20-7.40 (m, 7H), 7.57 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 20.9, 22.1, 27.9, 31.5, 57.9, 94.8, 121.5, 122.3, 124.3, 126.5, 127.0, 127.47, 127.52, 128.1, 128.9, 129.7, 134.2, 141.2, 144.7, 145.8, 151.3, 152.6, 162.3; IR (neat): ν 3057, 2958, 2919, 2853, 1626, 1594, 1462, 1257, 1018, 791, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{24}I$ $[M+H]^+$: 475.0917, found: 475.0921.

8-(1-iodo-2,2-diphenylvinyl)-3a-methyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**2v**) (minor). Yield: 29%, 27 mg, 1.5:1 dr (determined by ^1H NMR); White needles; Mp; 160-162 °C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 0.59-0.67 (m, 1H), 1.15-1.22 (m, 1H), 1.23 (s, 3H), 1.45-1.74 (m, 2H), 1.86-2.09 (m, 1H) 2.10-2.35 (m, 1H), 6.92-6.98 (m, 1H), 7.02-7.18 (m, 5H), 7.20-7.40 (m, 7H), 7.52 (d, J = 7.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ 20.9, 27.9, 31.3, 57.4, 94.2, 120.5, 122.3, 124.4, 126.8, 127.3, 127.7, 128.7, 129.7, 134.9, 140.6, 145.7, 145.9, 150.2, 150.9, 159.2; IR (neat): ν 3057, 2958, 2919, 2853, 1626, 1594, 1462, 1257, 1018, 791, 696 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{24}I$ $[M+H]^+$: 475.0917, found: 475.0921.

General procedure for the synthesis of compounds 3y and 4y; To a stirred solution of compounds **3-(2-(1-cyclobutylidenepropyl)phenyl)-1,1-diphenylprop-2-yn-1-ol 1y** (76 mg, 1.0 equiv) in DCE (2 mL) was added I_2 (101 mg, 2 equiv). The resulted mixture was stirred at 80 °C for 4 h. After quenching the remaining I_2 by Na_2SO_3 solution and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 200 / 1) to afford the corresponding product mixtures **3y** in 63% yield (62 mg) and **4y** in 28% yield (20 mg).

(3aS,8S,8aR)-5-bromo-2'-iodo-3a-methyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3s**). Yield: 41%, 45 mg; Light yellow needles; Mp: 137-139 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.62 (s, 3H), 1.80-2.00 (m, 4H), 2.20-2.35 (m, 2H), 3.07-3.12 (m, 1H), 6.38 (d, *J* = 8.4, 1H), 7.08-7.24 (m, 5H), 7.42-7.52 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 28.4, 29.8, 29.9, 42.1, 57.4, 62.1, 70.6, 110.5, 120.0, 122.0, 123.0, 126.1, 126.2, 126.7, 127.0, 128.3, 128.5, 129.3, 130.4, 135.9, 141.6, 143.0, 150.9, 155.2, 156.8; IR (neat): ν 3345, 1683, 1137, 1104, 756, 710 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{23}BrI$ $[M+H]^+$: 553.0022, found: 553.0018.

(3aS,8S,8aR)-2'-iodo-3a-methyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3v**). Yield: 70%, 66 mg; White needles; Mp: 128-130 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.63 (s, 3H), 1.75–1.92 (m, 3H), 1.93-2.05 (m, 1H), 2.18-2.40 (m, 2H), 3.08-3.14 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 7.06-7.15 (m, 5H), 7.20-7.31 (m, 2H), 7.36-7.54 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 28.5, 29.97, 30.0, 42.1, 57.3, 61.8, 71.1, 111.6, 119.9, 123.1, 123.6, 124.4, 126.0, 126.4, 127.1, 128.16, 128.20, 128.43, 129.3, 136.1, 141.6, 143.8, 150.5, 153.0, 157.2; IR (neat): ν 3162, 3063, 3023, 2944, 2918, 2845, 1645, 1441, 1259, 1021, 747, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{24}I$ $[M+H]^+$: 475.0917, found: 475.0921.

(3aS,8R,8aR)-3a-methyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**4v**). Yield: 73%, 51 mg; White needles; Mp: 148-150 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.66 (s, 3H), 1.67-1.90 (m, 5H), 1.96-2.05 (m, 1H), 2.93-2.98 (m, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 7.09-7.18 (m, 2H), 7.20-7.28 (m, 3H), 7.34-7.40 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 27.0, 29.6, 32.5, 43.0, 56.7, 60.5, 66.7, 120.3, 123.2, 123.4, 123.6, 126.0, 126.4, 126.9, 127.65, 127.73, 128.6, 135.8, 139.2, 141.9, 143.2, 144.2, 152.8, 156.8; IR (neat): ν 3060, 2943, 2922, 2852, 1482, 1442, 1263, 1072, 869, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{25}$ $[M+H]^+$: 349.1951, found: 349.1948.

(3aS,8S,8aR)-2'-iodo-6-methoxy-3a-methyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3w**). Yield: 74%, 74 mg; Light yellow needles; Mp: 148-150 °C; Eluent: PE/EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.61 (s, 3H), 1.75-1.83 (m, 3H), 1.84-1.89 (m, 1H), 2.15-2.21 (m, 1H), 2.30-2.38 (m, 1H), 3.06-3.12 (m, 1H), 3.65 (s, 3H), 6.01-6.03 (m, 1H), 6.85-6.89 (m, 1H), 7.09-7.13 (m, 4H), 7.14-7.20 (m, 1H), 7.42-7.45 (m, 1H), 7.47-7.54 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 28.5, 30.1, 30.2, 42.3, 55.3, 56.6, 62.4, 71.1, 108.9, 111.3, 114.8, 119.9, 123.1, 124.1, 126.0, 126.4, 127.7, 128.2, 128.4, 128.5, 129.4, 136.1, 141.5, 145.1, 145.4, 150.6, 157.1, 159.2; IR (neat): ν 3345, 1683 1137 1104, 756, 710 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{28}H_{26}IO$ $[M+H]^+$: 505.1023, found: 505.1014.

(3aS,8S,8aR)-5-chloro-2'-iodo-3a-methyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3x**). Yield: 58%, 59 mg; White needles; Mp: 137-139 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.62 (s, 3H), 1.75-2.05 (m, 4H), 2.17-2.45 (m, 2H), 3.08-3.14 (m, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 7.04-7.16 (m, 5H), 7.25-7.27 (m, 1H), 7.40-7.52 (m, 5H), 7.50 (d, *J* = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 28.4, 29.8, 29.9, 42.1, 57.3, 62.1, 70.5, 110.7, 120.0, 123.0, 123.9, 125.7, 126.2, 126.7, 127.6, 128.3, 128.5, 129.3, 133.8, 135.9, 141.6, 142.4, 150.9, 154.8, 156.8; IR (neat): ν 3063, 2940, 2921, 2857, 1593, 1451, 1072, 749, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{23}ClI$ $[M+H]^+$: 509.0527, found: 509.0524.

(3aS,8S,8aR)-3a-ethyl-2'-iodo-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3y**). Yield: 63%, 62 mg; A colorless liquid; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.00-1.10 (m, 3H), 1.59-2.02 (m, 6H), 2.20-2.34 (m, 2H), 3.22-3.30 (m, 1H), 6.52 (d, *J* = 7.2 Hz, 1H), 7.06-7.28 (m, 7H), 7.30-7.54 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 10.1, 28.5, 30.0, 33.8, 40.0, 58.0, 61.8, 71.3, 112.2, 119.9, 123.1, 123.9, 124.5, 126.0, 126.5, 127.1, 127.7, 128.4, 129.3, 136.1, 140.2, 141.9, 144.3, 151.8, 157.2; IR (neat): ν 3152, 3063, 2972, 2872, 1478, 1450, 1376, 1089, 1046, 879, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{28}H_{26}I$ $[M+H]^+$: 489.1074, found: 489.1070.

(3aS,8R,8aR)-3a-ethyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**4y**). Yield: 28%, 20 mg; White needles; Mp: 146-148 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (t, *J* = 7.2 Hz, 3H), 1.60-1.78 (m, 3H), 1.80-2.06 (m, 5H), 1.80-2.01 (m, 5H), 3.09-3.15 (m, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.58 (s, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 7.04-7.28 (m, 5H), 7.34-7.40 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 10.3, 26.8, 32.7, 34.0, 40.1, 56.7, 61.2, 66.7, 120.3, 123.2, 123.5, 124.0, 126.0, 126.4, 126.8, 127.4, 127.7, 128.5, 135.7, 140.20, 140.24, 142.1, 142.9, 144.7, 151.8, 156.9; IR (neat): ν 3065, 3021, 2954, 2858, 1479, 1448, 1332, 1260, 1090, 1026, 772, 746, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{28}H_{26}$ $[M]^+$: 362.2035, found: 362.2022.

(3aS,8S,8aR)-3a-hexyl-2'-iodo-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3z**). Yield: 83%, 90 mg; A yellow liquid; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.85-0.95 (m, 3H), 1.28-1.42 (m, 7H), 1.53-1.71 (m, 1H), 1.75-2.05 (m, 6H), 2.22-2.34 (m, 2H), 3.25-3.31 (m, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 7.05-7.25 (m, 6H), 7.30-7.55 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 14.1, 22.7, 25.6, 28.5, 30.10, 30.13, 31.8, 40.3, 41.7, 58.5, 61.4, 71.4, 112.2, 119.9, 123.0, 123.9, 124.5, 126.0, 126.5, 127.1, 128.0, 128.1, 128.4, 129.3, 136.1, 141.8, 144.2, 150.3, 152.1, 157.2; IR (neat): ν 3060, 2963, 2925, 2872, 1488, 1450, 1406, 1250, 1073, 748, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{34}I$ $[M+H]^+$: 545.1700, found: 545.1696.

(3aS,8R,8aR)-3a-hexyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**4z**). Yield: 16%, 13 mg; A yellow liquid; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.85-0.95 (m, 5H), 1.28-1.42 (m, 7H), 1.53-1.71 (m, 2H), 1.75-2.05 (m, 5H), 3.10-3.15 (m, 1H), 6.56-6.58 (m, 1H), 6.94-7.00 (m, 1H), 7.05-7.25 (m, 7H), 7.30-7.55 (m, 2H), 7.62-7.67 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 25.7, 26.7, 32.7, 40.6, 41.9, 57.2, 60.7, 66.7, 120.2, 123.2, 123.4, 124.0, 126.0, 126.4, 126.8, 127.4, 127.7, 128.5, 135.7, 140.2, 142.0, 142.9, 144.5, 152.0, 156.8.

(3aR,8S,8aR)-2'-iodo-3'-phenyl-3a-(3-phenylpropyl)-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3aa**). Yield: 32%, 37 mg; White needles; Mp: 170-172 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.60-2.07 (m, 8H), 2.00-2.32 (m, 2H), 2.60-2.78 (m, 2H), 3.20-3.27 (m, 1H), 6.48-6.53 (m, 1H), 6.95-7.15 (m, 4H), 7.17-7.32 (m, 8H), 7.35-7.52 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 27.4, 28.5, 30.3, 36.5, 41.2, 58.6, 61.3, 71.4, 112.0, 119.9, 123.0, 124.0, 124.5, 125.8, 126.1, 126.4, 127.2, 127.7, 128.3, 128.4, 129.4, 136.2, 140.1, 141.8, 142.3, 144.2, 150.5, 152.0, 157.1; IR (neat): ν 3070, 3018, 2950, 2868, 1600, 1450, 1073, 1028, 843, 754, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{35}H_{32}I$ $[M+H]^+$: 579.1543, found: 579.1539.

(3aR,8R,8aR)-3'-phenyl-3a-(3-phenylpropyl)-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]i

ndene-8,1'-indene] (**4aa**). Yield: 16%, 14 mg; White needles; Mp: 170-172 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.60-2.07 (m, 10H), 2.60-2.78 (m, 2H), 3.05-3.10 (m, 1H), 6.55 (s, 1H), 6.95-7.15 (m, 5H), 7.17-7.32 (m, 6H), 7.35-7.52 (m, 4H), 7.62-7.66 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 26.8, 27.5, 32.8, 40.1, 40.4, 57.3, 60.6, 66.7, 120.3, 123.2, 123.5, 124.0, 125.7, 126.0, 126.4 126.9, 127.5, 128.0, 128.2, 128.6, 135.7, 142.0, 142.3, 143.0, 144.5, 151.9, 156.7.

(3aR,4S,8R,10aR)-2'-iodo-3',8-diphenyl-1,2,3,3a,9,10-hexahydro-8H-spiro[cyclopenta[b]acenaphthylene-4,1'-indene] (**5aa**). Yield: 41%, 47 mg, Yellow needles; Mp: 170-172 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.78-2.33 (m, 8H), 2.40-2.59 (m, 2H), 3.31-3.55 (m, 1H), 4.10-4.14 (m, 1H), 6.38 (d, *J* = 7.6 Hz, 1H), 6.78-7.00 (m, 3H), 7.01-7.13 (m, 3H), 7.21-7.35 (m, 5H), 7.43-7.56 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 27.1, 27.9, 32.5, 34.9, 39.3, 44.5, 56.5, 64.1, 72.4, 110.5, 119.7, 122.0, 123.3, 126.08, 126.10, 126.4, 127.7, 128.0, 128.2, 128.4, 128.47, 128.52, 129.4, 136.3, 137.3, 141.7, 142.6, 147.7, 148.9, 150.9, 158.4; IR (neat): ν 3070, 3018, 2950, 2868, 1600, 1450, 1073, 754, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{35}H_{30}I$ [M+H]+: 577.1387, found: 577.1382.

(3aR,8R,8aR)-3a-isopentyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**4ab**). Yield: 32%, 34 mg; White needles; Mp: 119-121 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.93-0.98 (m, 6H), 1.25-1.30 (m, 1H), 1.43-1.76 (m, 5H), 1.80-2.01 (m, 5H), 3.08-3.15 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.57 (s, 1H), 6.97-7.02 (m, 1H), 7.15-7.19 (m, 2H), 7.22-7.27 (m, 2H), 7.34-7.39 (m, 1H), 7.41-7.47 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.63-7.67 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 22.7, 22.8, 26.7, 28.8, 32.7, 34.9, 39.4, 40.5, 57.1, 60.6, 66.8, 120.3, 123.2, 123.5, 124.0, 126.0, 126.4, 126.8, 127.5, 127.7, 128.6, 135.8, 140.2, 142.1, 142.9, 144.5, 152.2, 156.9; IR (neat): ν 3068, 3018, 2951, 2924, 2848, 1592, 1466, 1449, 1369, 1152, 755, 698 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{31}H_{31}$ [M-H]$^+$: 403.2420, found: 403.2414.

(3aS,8R,8aR)-2'-iodo-6'-methoxy-3a-methyl-3'-phenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3ac** and **3 ac'**). Yield (**3ac**): 43%, 43 mg, Yield (**3ac'**): 43%, 43 mg; White needles; Mp: 148-150 °C; Eluent: PE/EA = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.65 (s, 6H), 1.66-1.88 (m, 10H), 1.94-2.04 (m, 2H), 2.88-2.96 (m, 2H), 3.72 (s, 3H), 3.83 (s, 3H), 6.45-6.48 (m, 1H), 6.49-6.57 (m, 3H), 6.68-6.72 (m, 1H), 6.74-6.79 (m, 1H), 6.95-7.02 (m, 4H), 7.07-7.24 (m, 5H), 7.31-7.38 (m, 1H), 7.39-7.46 (m, 3H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.56-7.67 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 27.0, 29.6, 32.2, 32.5, 42.9, 43.0, 55.3, 55.4, 56.6, 60.4, 61.0, 66.6, 110.3, 111.0, 114.0, 120.2, 120.7, 123.2, 123.4, 123.48, 123.51, 123.53, 125.9, 126.3, 126.8, 126.9, 127.6, 127.7, 128.3, 128.5, 128.9, 134.8, 136.0, 137.8, 138.7, 142.1, 142.6, 142.7, 144.4, 144.5, 152.6, 152.7, 156.9, 158.7, 159.3; IR (neat): ν 3026, 2945,2916, 2859, 1507, 1478, 1447, 1110, 817, 747 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{28}H_{24}OI$ [M+H]$^+$: 503.0866, found: 503.0863.

(3aS,8R,8aR)-2'-iodo-3a,6'-dimethyl-3'-(p-tolyl)-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3ad**). Yield: 6%, 6 mg; White needles; Mp: 110-112 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.65 (s, 3H), 1.66-1.90 (m, 5H), 1.95-2.03 (m, 1H), 2.29 (s, 3H), 2.39 (s, 3H), 2.91-2.97 (m, 1H), 6.48 (s, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.91-6.93 (m, 1H), 6.96-7.01 (m, 1H), 7.02-7.07 (m, 1H), 7.17-7.22 (m, 1H), 7.23-7.25 (m, 1H), 7.25-7.30 (m, 1H), 7.38-7.42 (m, 1H), 7.53-7.57 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 21.3, 21.5, 27.0, 29.6, 32.2, 42.9, 56.6, 60.7, 66.5, 120.0, 123.50, 123.54, 124.1, 126.8, 127.0, 127.5, 129.2,

133.0, 135.6, 137.4, 138.4, 139.4, 142.8, 144.7, 152.7, 157.1; IR (neat): ν 3065, 2943, 2858, 1442, 1258, 1028, 760, 699 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{29}H_{28}I$ $[M+H]^+$: 503.1230, found: 503.1227.

(3aS,8S,8aR)-3a,6'-dimethyl-3'-(p-tolyl)-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**4ad**). Yield: 89%, 67 mg; White needles; Mp: 110-112 °C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.63 (s, 3H), 1.66-1.90 (m, 4H), 1.95-2.03 (m, 2H), 2.26 (s, 3H), 2.40 (s, 3H), 3.06-3.12 (m, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.91-6.93 (m, 1H), 6.96-7.01 (m, 1H), 7.02-7.07 (m, 2H), 7.17-7.22 (m, 1H), 7.23-7.25 (m, 1H), 7.25-7.30 (m, 1H), 7.38-7.42 (m, 2H), 7.53-7.57 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 14.1, 22.7, 28.5, 29.8, 30.0, 42.1, 57.3, 62.0, 70.9, 109.9, 119.6, 124.0, 124.6, 127.1, 128.1, 129.1, 133.3, 135.9, 137.9, 139.3, 144.2, 150.3, 153.0, 157.5.

(3aS,8R,8aR)-6'-chloro-3'-(4-chlorophenyl)-2'-iodo-3a-methyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3ae**). Yield: 46%, 50 mg; Light yellow needles; Mp: 135-137 °C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.63 (s, 3H), 1.75-2.02 (m, 4H), 2.18-2.33 (m, 2H), 3.03-3.10 (m, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.98-7.03 (m, 1H), 7.05-7.16 (m, 3H), 7.30-7.34 (m, 2H), 7.41-7.50 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 28.4, 29.9, 30.1, 42.1, 57.5, 61.9, 71.3, 112.4, 120.5, 123.78, 123.81, 124.4, 126.8, 127.3, 128.6, 128.9, 130.7, 132.4, 134.1, 134.3, 139.8, 142.8, 148.6, 153.0, 158.5; IR (neat): ν 2987, 2924, 2898, 1597, 1481, 1456, 1398, 1088, 1057, 817, 703 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{22}Cl_2I$ $[M+H]^+$: 543.0138, found: 543.0137.

(3aS,8S,8aR)-2'-iodo-3a,3'-dimethyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**3af**). Yield: 69%, 57 mg; White needles; Mp: 95-97 °C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.60 (s, 3H), 1.72-1.83 (m, 3H), 1.88-1.97 (m, 1H), 2.14-2.23 (m, 2H), 2.25 (s, 3H), 2.98-3.05 (m, 1H), 6.37 (d, *J* = 7.6 Hz, 1H), 7.00-7.10 (m, 3H), 7.16-7.23 (m, 1H), 7.24-7.29 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 16.3, 28.4, 29.9, 42.3, 57.1, 61.2, 70.4, 110.6, 118.5, 122.7, 123.5, 124.3, 125.8, 126.4, 127.0, 128.0, 141.7, 144.2, 145.4, 152.8, 157.1; IR (neat): ν 3070, 3023, 2949, 2859, 1479, 1445, 1291, 999, 760, 730 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{22}H_{22}I$ $[M+H]^+$: 413.0761, found: 413.0759.

General procedure for the synthesis of 4a. To a stirred solution of **3-(2-(cyclobutylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol 1a** (1.0 equiv) in DCE (2 mL) was added HI (5.0 equiv). The resulted mixture was stirred at 80 °C for 4 h. After quenching the remaining I_2 by Na_2SO_3 solution and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 200 / 1) to afford the corresponding product **4a** in 68% yield (56 mg).

(3aS,8R,8aR)-3a,3'-diphenyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**4a**). Yield: 77%, 63 mg; White needles; Mp: 135-137 °C; Eluent: PE/EA = 200/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.75-1.85 (m, 1H), 1.91-2.09 (m, 3H), 2.34-2.52 (m, 2H), 3.31-3.36 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.62 (s, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 7.06-7.15 (m, 2H), 7.20-7.26 (m, 1H), 7.27-7.48 (m, 10H), 7.66 (d, *J* = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) *δ* 27.9, 33.6, 44.7, 64.0, 65.4, 66.7, 120.2, 123.5, 123.7, 125.86, 125.91, 126.3, 126.6, 127.0, 127.3, 127.5, 127.7, 127.8, 128.2, 128.6, 135.7, 139.2, 141.4, 143.9, 145.4, 149.5, 149.9, 155.7; IR (neat): ν 3055, 3026, 2947, 2859, 1599, 1464, 1440, 1073, 757, 695 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{27}$ $[M+H]^+$: 411.2107, found: 411.2104.

General procedure for the synthesis of 4y. To a stirred solution of **3-(2-(1-cyclobutylidenepropyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (**1y**) (1.0 equiv) in DCE (2 mL) was added I_2 (2.0 equiv). The resulted mixture was stirred at 80 °C for 24 h. After quenching the remaining I_2 by Na_2SO_3 solution and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 200 / 1) to afford the corresponding product **4y** in 66% yield (48 mg).

(3aS,8S,8aR)-6'-chloro-3'-(4-chlorophenyl)-3a-methyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**4ae**). Yield: 59%, 49 mg; White needles; Mp: 145-147 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.65 (s, 3H), 1.66-1.85 (m, 5H), 1.95-2.06 (m, 1H), 2.90-2.95 (m, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.55 (s, 1H), 6.99-7.06 (m, 2H), 7.20-7.30 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 27.0, 29.6, 32.3, 42.8, 56.8, 60.5, 66.8, 121.0, 123.3, 123.8, 123.9, 126.7, 127.0, 128.1, 128.87, 128.91, 132.1, 133.7, 133.8, 140.0, 140.4, 141.4, 143.0, 152.8, 158.3; IR (neat): ν 3065, 3018, 2940, 2922, 2857, 1486, 1455, 1401, 1251, 1088, 1016, 926, 830, 821, 759, 703 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{27}H_{23}Cl_2$ $[M+H]^+$: 417.1171, found: 417.1169.

(3aS,8R,8aR)-3a,3'-dimethyl-2,3,3a,8a-tetrahydro-1H-spiro[cyclopenta[a]indene-8,1'-indene] (**4af**). Yield: 63%, 36 mg; Colorless liquid; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.62 (s, 3H), 1.63-1.80 (m, 5H), 1.91-2.00 (m, 1H), 2.18 (s, 3H), 2.80-2.83 (m, 1H), 6.18 (s, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 7.06-7.12 (m, 1H), 7.13-7.25 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 13.0, 26.9, 29.6, 32.5, 43.0, 56.5, 59.9, 66.5, 118.7, 122.5, 123.3, 123.4, 125.6, 126.3, 126.7, 127.4, 137.8, 138.2, 144.2, 144.8, 152.6, 156.4; IR (neat): ν 3065, 3013, 2946, 2861, 1478, 1464, 1382, 1105, 820, 755, 742 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{22}H_{22}$ $[M]^+$: 286.1722, found: 286.1714.

General procedure for the synthesis of 6a. To a stirred solution of **8-(1-iodo-2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene 2a** (1.0 equiv) in THF (2 mL, 0.1 mol/L) was added n-BuLi (1.5 equiv) dropwise for 30 min at -80 °C. The resulted mixture was warmed up to r.t. for 4 h. After quenching the mixture with H_2O and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 200 / 1) to afford the corresponding product **2-bromo-2'-(2-bromoethyl)-3,3'-diphenyl-1,1'-spirobi[indene] 6a** in 95% yield (78 mg).

8-(2,2-diphenylvinyl)-3a-phenyl-1,2,3,3a-tetrahydrocyclopenta[a]indene (**6a**). Yield: 95%, 78 mg, White needles; Mp: 155-157 °C; Eluent: PE/EA = 200/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.22-1.34 (m, 2H), 1.68-1.82 (m, 1H), 1.89-2.10 (m, 2H), 2.43-2.50 (m, 1H), 6.85 (s, 1H), 6.96-7.03 (m, 1H), 7.08-7.14 (m, 3H), 7.14-7.26 (m, 6H), 7.27-7.40 (m, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, TMS) *δ* 23.7, 28.9, 33.7, 66.7, 119.2, 120.9, 123.3, 124.5, 126.3, 126.4, 126.77, 126.85, 127.7, 128.0, 128.2, 128.3, 130.6, 132.3, 141.3, 142.8, 143.2, 146.2, 146.7, 150.6, 160.5; IR (neat): ν 3057, 3026, 2861, 2861, 1596, 1441, 1317, 745, 697 cm^{-1}; HRMS (DART-FTICR) Calcd. for $C_{32}H_{27}$ $[M+H]^+$: 411.2107, found: 411.2106.

Supporting Information Available: Reaction optimization, NMR spectra, absorption spectra,

and CIF files for compounds for **2a**, **3v**, **5aa** and **6a** are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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