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Palladium-Catalyzed Domino Reaction for Stereoselective Synthesis of Multisubstituted Olefins: Building up Blue Luminogens

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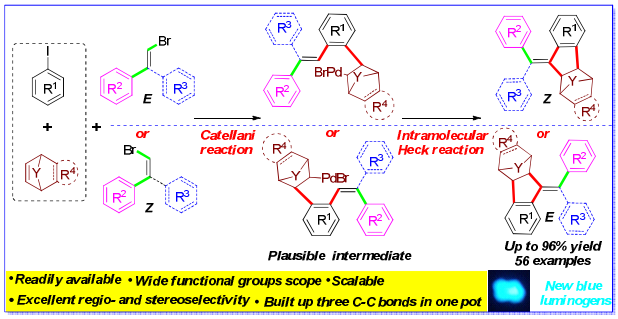


Abstract: The first Pd-catalyzed multicomponent reaction of aryl iodides, alkenyl bromides, and strained alkenes have been developed, which allowed us to synthesize a variety of multisubsituted olefins in yields of 45%-96% with excellent stereoselectivity. The configuration of the product was controlled by the configuration of the alkenyl bromides. Moreover, this practical methodology employing readily available substrates was found to be tolerant with wide range of functional groups. 56 examples of high stereoselective tri- or tetrasubstituted olefins have been successfully synthesized via this methodology. Most of the synthesized tetrasubstituted olefins are good aggregation-induced emission (AIE) luminogens.

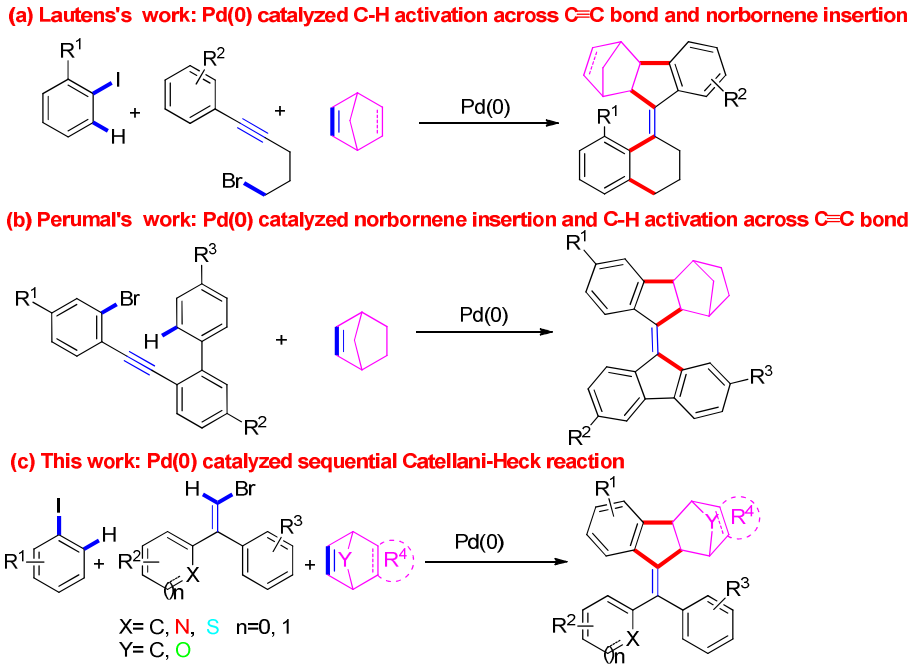
Introduction

Multisubstituted olefins are one of the major classes of chemical building blocks for organic synthesis,[1] the significance of multisubstituted olefins is reflected in pharmaceuticals and bioactive natural products,[2-4] as well as the photoresponsive organomaterials, molecular devices, and bio-imaging.[5] However, the efficient regio- and stereoselective synthesis of tri-and tetrasubstituted olefins has presented a formidable challenge for synthetic organic chemists for years.[6] Great efforts have been made to develop the methodology for synthesis of multisubstituted olefins. The most frequently utilized strategies include direct carbometalation of alkynes,[7] transition-metal-catalyzed carbon-heteroatom bond cleaving and cross-coupling reactions,[8] carbonylolefination,[6a] olefin metathesis,[6a] or using directing groups strategy.[9] The majority of these methods, however, suffer from the one or more of the following limitations such as limited availability of starting materials, tedious reaction procedure, poor regio- and /or stereoselectivity. Therefore, the development of more practical and efficient way for synthesis of multisubstituted olefins with high stereoselectivity is still highly desirable.

Heck reaction has been considered as a useful method for preparation of substituted olefins, [10] which usually features cost-effectivity and high stereoselectivity. However, the Pd(0)-catalyzed intermolecular Heck reaction has seldom been employed for synthesis of tetrasubstituted olefins because of the low reactivity, possibly due to the steric hindrance exerted by the trisubstitued olefin during the carbopalladation process.[10c] The Catellani-Heck reaction provides a powerful way for the formation of multiple carbon-carbon bonds in a tandem process by using norbornene as a transient mediator. Yet, in most cases, the norbornene is extruded from the target molecules at the end of the reaction. A literature survey

revealed the incorporation of norbornene as an alkyl chain into an extensive π-conjugated structure could improve its solubility, [11] which made it the potential of being applicable to solution processing and easy fabrication of large-area optoelectronic devices. To our surprise, the norbornene incorporation reactions are scarce in the literature and always confronted with the limited functional groups. Besides, the scope in terms of the other alkenes has not been well explored. Although Lautens[12a] and Perumal groups[12b] successively realized the synthesis of norbornene-incorporated tetrasubsituted olefins by Pd-catalyzed reactions of aryl halide, internal alkyne and norbornene, which involve a sequential insertion of norbornene and internal alkyne into the aryl-palladium bond (Scheme1 a, b), these methods were only limited to synthesize the tetrasubstituted olefins and usually required the tedious multistep synthesis of the internal alkyne. So far, only one example for synthesis of trisubstituted olefin containing a norbornyl group was reported by Catellani in 2001, wherein a stoichiometric amount of dimeric arylnorbornylpalladium chloride complex was used to react with a large excess of alkenyl bromide (10.0 equiv).[13] However, the relatively high cost of arylnorbornylpalladium complex and poor stereoselectivity greatly precluded the practicability of this method. We herein developed the first Pd-catalyzed domino reaction of aryl iodides, alkenyl bromides and norbornene to synthesize various tri- and tetrasubstituted olefins with more structural diversity. In addition, the catalytic system could be extended to other strain alkenes. The reaction features a wide substrate scope, high functional group tolerance, and high stereoselectivity due to an intramolecular Heck reaction is involved (Scheme1 c). This methodology could enable us to synthesize a new kind skeleton for blue AIE luminogens.[14]

Scheme 1. Representative examples for synthesis of norbornyl-containing multisubstituted olefins via Catellani reaction.

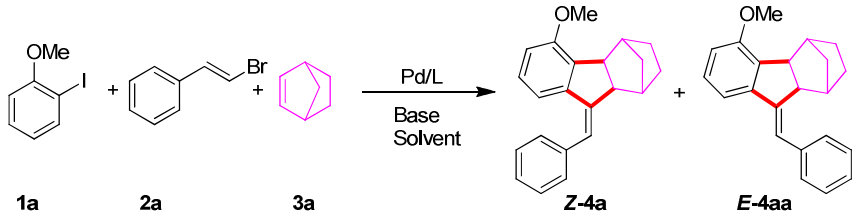


Results and Discussion

We initiated our studies by reacting 1-iodo-2-methoxy-benzene (**1a**, 0.20 mmol) and norbornene (**3a**, 0.6 mmol) directly with (*E*)-2-bromovinyl benzene (**2a**, 0.30 mmol) using a catalytic amounts of $Pd(OAc)_2$ (10 mol%) in the presence of methyl isonicotine (50 mol%)[13] as ligand and K_2CO_3 (2.0 equiv.) as base in DMAc at 80 °C for 12 h, only trace amount of the desired product was detected (Table 1, entry 1). To our delight, the replacement of methyl isonicotine with triphenylphosphine successfully afforded the coupling product trisubstituted olefin *Z*-**4a** in 25% yield along with 5.6% of *E* isomer **4aa** (Table 1, entry 2). The configurations of *Z*-**4a** and *E*-**4aa** were confirmed by ^{1}H NMR analysis (see ESI†).[13] By carefully screening the conditions (see ESI†, Tables S1-S2) we found that the phosphine ligand was crucial for the reaction, and no desired product was obtained in the absence of phosphine ligand (Table 1, entry 4). The tri-(2-furyl) phosphine (TFP) proved to be the most efficient ligand. CH_3CN and $Pd(OAc)_2$ were the best solvent and palladium source,

respectively. The amount of K_2CO_3 also significantly influenced the outcome of the reaction. When 5.0 equiv of K_2CO_3 was used, the stereoselectivity of the product towards the *Z*-isomer was improved remarkably to 92% (Table 1, entry 6). Raising the temperature to 120 °C further increased the yield and the stereoselectivity to 82% and 93%, respectively (Table 1, entry 8).

Table 1. Optimization of the reaction conditions [a]



Entry	L+ Solvent	T(℃)	Yield (%) 4a	4aa	Selectivity of 4a (%)
1	Methyl isonicotine + DMAc	80	trace	trace	-
2	PPh_3 + DMAc	80	25	5.6	81
3	PPh_3 + CH_3CN	80	46	11	80
4	-	80	-	-	-
5	TFP + CH_3CN	80	55	12	82
6[b]	TFP + CH_3CN	80	62	5	92
7[b]	TFP + CH_3CN	100	73	6	92
8[b]	**TFP + CH_3CN**	**120**	**82**	**6**	**93**

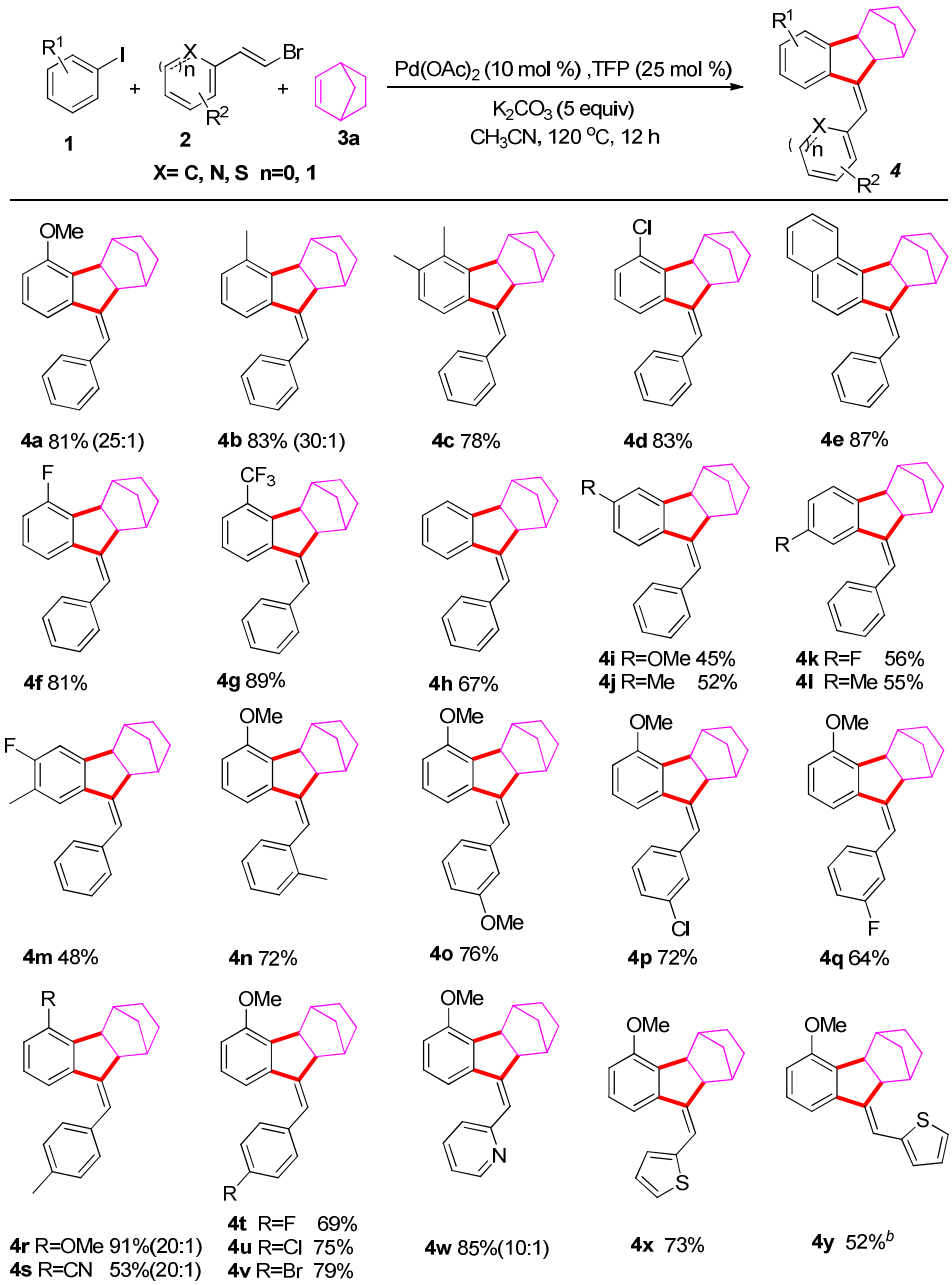
[a]All reactions were run using 0.2 mmol of **1a**, 1.5 equiv. of **2a**, 3.0 equiv. of **3a**, 2.0 equiv. of K_2CO_3, and 10 mol% of $Pd(OAc)_2$, 25 mol% of L in 1.5 mL of solvent for 12h; GC yield, using mesitylene as an internal standard. [b] Reaction run at 5.0 equiv. of K_2CO_3.

Having the optimal conditions in hand, the scope of the reaction was investigated. As shown in Scheme 2, various trisubstituted olefins could be synthesized by this straightforward and efficient methodology. Both electron-rich and deficient aryl iodides were well tolerated,

leading to expected products in very good yields with excellent *Z*-selectivity (> 92%) (**4a-4h**). Notably, the position of substituents influences the reaction greatly. In comparison with *ortho*-substituted iodobenzene, the *meta*- or *para*- substituted counterparts decreased the yields dramatically to 45-56% (**4i-4m**), accompanied by complicated by-products, which were frequently associated with Catellani reaction.[15] Whereas the use of ethyl 2-iodobenzoate gave no desired product, might be ascribed to the coordination of carbonyl oxygen to the palladium center.[16] And then, the scope of *E*-2-arylvinyl bromides was investigated. Here, no significant effect was observed when the substituents were located on the *ortho-, meta-* or *para*-position of *E*-2-arylvinyl bromides, and generally the reactions gave the corresponding products in good yields with a high *Z* stereoselectivity (**4n-4v**). When (*E*)-1-bromo-4-(2-bromovinyl)benzene that has two different bromine atom was investigated, only **4v** the desired product was obtained, without any Catellani arylation product. We also carried out the reaction using bromophenyl instead of (*E*)-1-bromo-4-(2-bromovinyl)benzene under the otherwise identical conditions, the Catallani arylation product was neither detected. This clearly showed that the present optimized condition is not suitable for the Catellani arylation. It is noteworthy that the heteroaryl rings, such as pyridine and thiophene were all tolerated and afforded the desired products in moderate to good yields (**4w**-**4y**). Interestingly, when using *Z*-type alkenyl bromides instead of its ***E*** isomer, the trisubstituted olefins was generated exclusively in *E*-configuration (**4y**), which indicated that the configuration of the product could be controlled by the configuration of the alkenyl bromides. It is noteworthy, that at this point a relatively low reactivity was observed with *Z*-alkenyl bromide, and only 52% yield of product was produced (**4y** versus **4x**). The low reactivity of *Z*-alkenyl bromides

possibly resulted from other side reactions. A literature survey revealed that the *Z*-alkenyl bromides may react with the strained alkenes in many different ways.[17] Actually, the reaction products of *Z*-alkenyl bromides turns out to be very complicated under our standard condition.

Scheme 2. Synthesis of trisubstituted olefins [a]

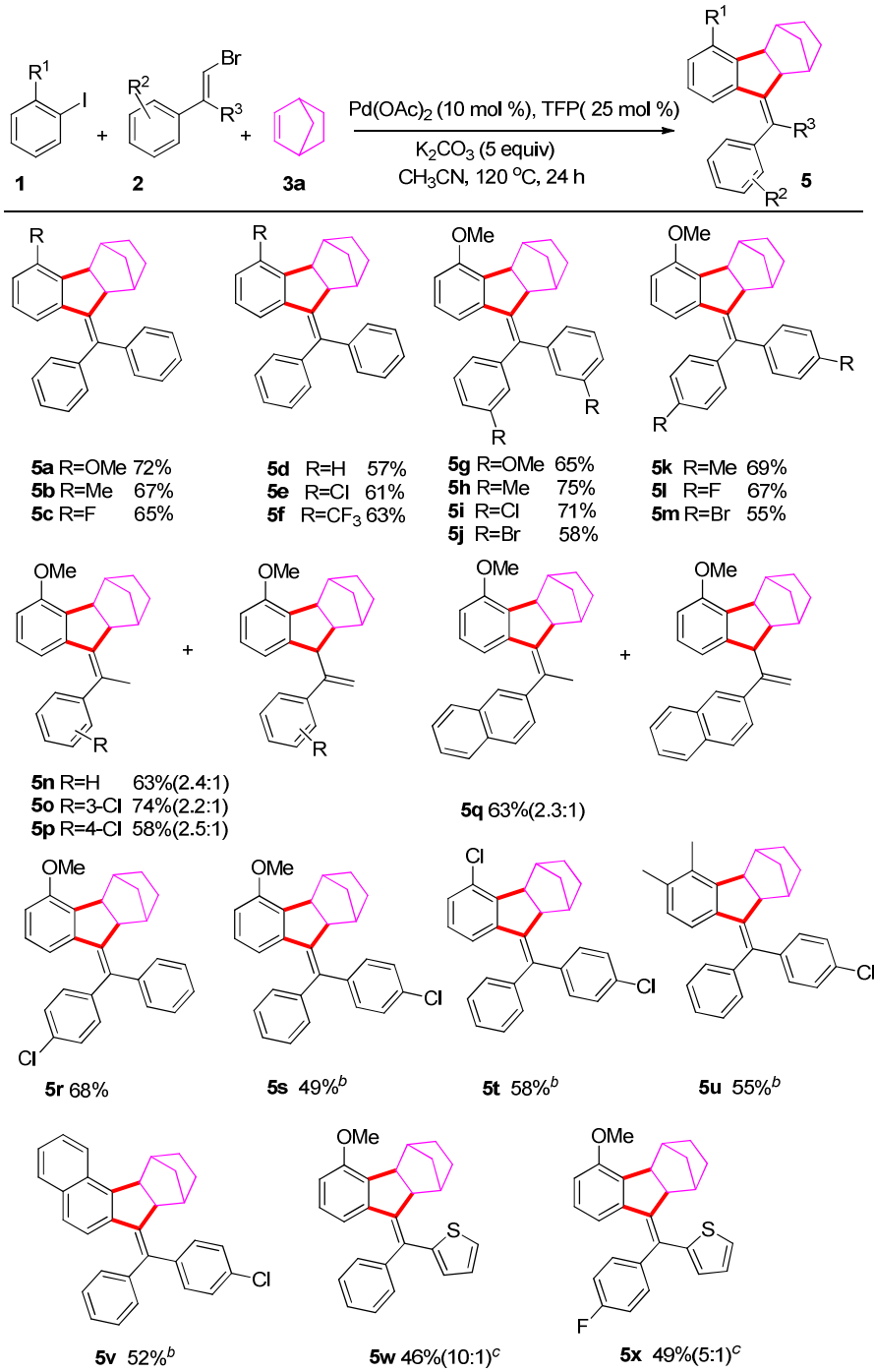


[a]All reactions were run using 0.5 mmol of **1**, 0.75 mmol of **2**, 1.5 mmol of 3a, 2.5 mmol of K_2CO_3, and 10 mol% of $Pd(OAc)_2$, 25 mol% of TFP in 3.0 mL of CH_3CN for 12h; isolated yield. [b] (*Z*)-2-(2-bromovinyl)thiophene was used.

Encouraged by the attained satisfactory results in synthesis of trisubstituted olefins, we subsequently tried this procedure to synthesize the tetrasubstituted olefins. When 2, 2-diphenyl-1-bromoethene was coupled with 1-iodo-2-methoxybenzene and norbornene under the established conditions, the tetrasubstituted olefin **5a**, confirmed by X-ray single crystal analysis (Figure 1, d), was obtained with the yield of 35% yield, and the majority of the starting materials were recovered. The low yield was presumably due to the large steric hindrance exerted by two phenyl groups in vinyl bromide.[18] We were pleased to find that the yield could be improved to 72% simply by prolonging the reaction time to 24 h (Scheme 3, **5a**). By prolonging the reaction time, various tetrasubstituted olefins could be easily accessible in moderate to good yields (Scheme 3). In case of unsymmetrically (*E* or *Z*)-2, 2-diaryl-1-bromoethenes, the reaction could provide the *Z*- or *E*-tetrasubstituted olefins stereospecifically, depending on the configuration of 2, 2-diaryl-1-bromoethenes. Particularly, it even could discriminate such a small difference between the two aryl groups in 2-phenyl-2-(4-chlorophenyl)-1-bromo- ethene (Scheme 3, **5r**-**5v**). The structure of compounds **5v** was confirmed by X-ray analysis (see ESI†, Table S5). In addition, it should be noted that a significant amount of geminally disubstituted olefin was observed when using 2-aryl-1-bromopropene as the coupling reagent (Scheme 3, **5n**-**5q**), the structure of **5n** was confirmed by the X-ray single crystal diffraction (see ESI†, Table S4), which resulted from the β-H elimination of the alkylpalladium complex, a catalytic active species. This result

revealed that the process involved a 5-exo-Heck cyclization reaction.[13] When the mixture of 1:1 *E*/*Z* ratio of 2, 2-disubstituted-1-bromoethenes was submitted to the reaction conditions, the product was obtained as an inseparable *E*/*Z* mixture (Scheme 3, **5w** and **5x**), the *E*/*Z* ratio of *ca.* 10:1 for **5w** and of *ca.* 5:1 for **5x.** By analyzing the outcome of the reaction of the 2-(2-bromo-1-phenylvinyl)thiophene (*E*:*Z*=1:1), we found the *E*/*Z* ratios of the olefin were turn into 8:1 in the recovered starting materials.

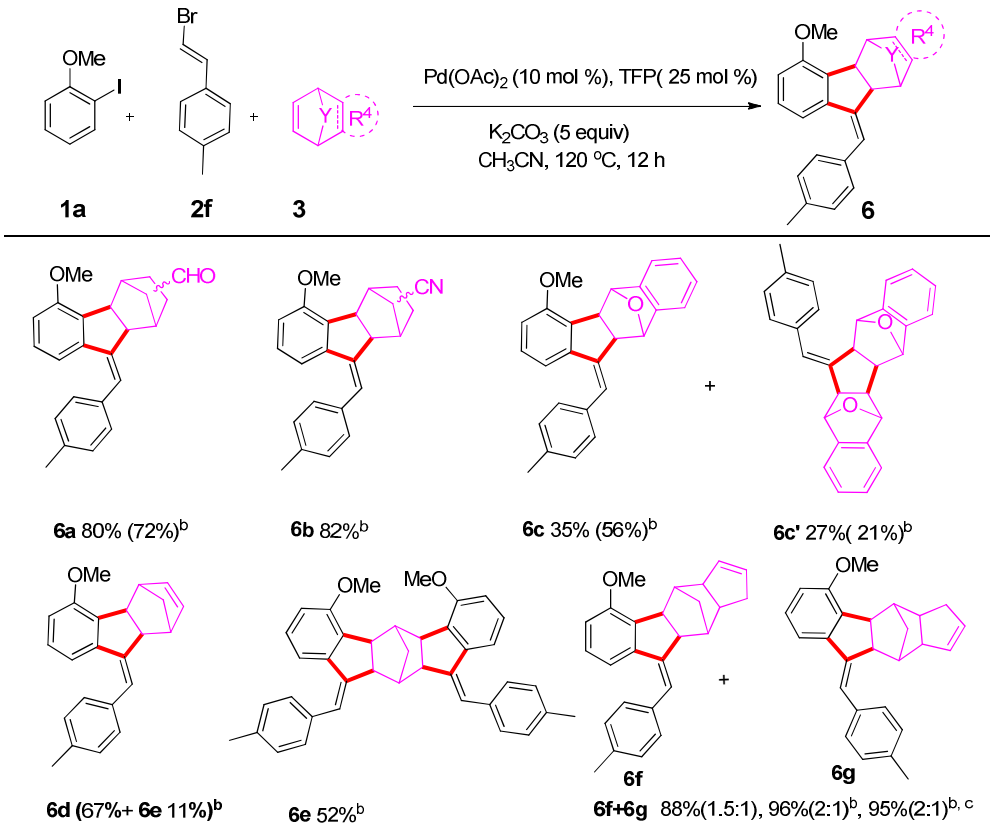
Scheme 3. Synthesis of tetrasubstituted olefins [a]



[a]All reactions were run using 0.5 mmol of **1**, 0.75 mmol of **2** (*E*-type configuration), 1.5 mmol of **3a**, 2.5 mmol of K_2CO_3, and 10 mol% of $Pd(OAc)_2$, 25 mol% of TFP in 3.0 mL of CH_3CN for 24h; isolated yield. [b]Z-type alkenyl bromide was used; [c]the mixture of 2, 2-disubstituted-1-bromoethenes (*E*:*Z*=1:1) was used.

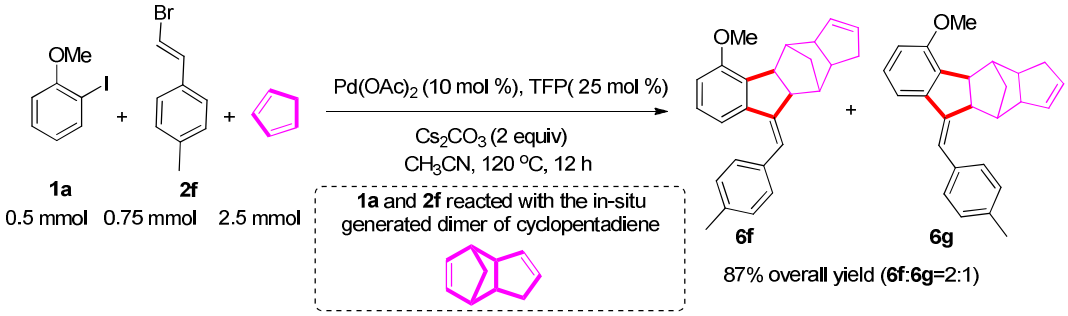
We next investigated the efficacy of this reaction process for other norbornene-type alkenes by reacting with **1a** and **2f** under the standard conditions. As shown in Scheme 4, the norbornene with relatively sensitive functional groups, such as -CHO and -CN reacted smoothly to generate the corresponding annulated products **6a** and **6b** in an inseparable mixture of regioisomers in good to excellent yields. The reaction of 1,4-dihydro-1,4-epoxynaphthalene only yielded the desired product **6c** with only 35% of isolated yield, probably due to the competing side reaction, which led to a significant amount of byproduct **6c′**， but the yield of **6c** was remarkably improved to 56% when using Cs_2CO_3 as the base. It was important to note that norbornadiene, a less efficient mediator of the Catellani process, could also undergo the reaction, just upon switching the base from K_2CO_3 to Cs_2CO_3, providing 67% yield of **6d** together with 11% yield of **6e**. The survived double bond in product **6d** could serve as a valuable synthetic handle for further transformations, such as epoxidation, dihydroxylation,[12a] Catellani type reaction, etc. For example, when **6d** was subjected to our established conditions a secondary Catellani reaction occurred to give **6e** in 52% yield. In case of dicyclopentadiene bearing two different double bonds, the reaction proceeded exclusively at the more strained double bond, affording a high yield of mixture of **6f** and **6g** with the ratio of 2:1. In addition, the reaction was scalable and a comparable yield was achieved when the reaction was conducted with **1a** in 10 mmol scale, demonstrating the practical utility of the developed methodology. When using cyclopentadiene instead of dicyclopentadiene in this reaction we also gained the desired product in comparable yield with that using dicyclopentadiene, which was attributed to rapid dimerization of cyclopentadiene under the standard conditions (Scheme 5).

Scheme 4. The scope of other strained alkenes[a]



[a]All reactions were run using 0.5 mmol of **1a**, 0.75 mmol of **2f**, 1.5 mmol of **3**, 2.5 mmol of K_2CO_3, and 10 mol % of $Pd(OAc)_2$, 25 mol % of TFP in 3.0 mL of CH_3CN for 12 h; isolated yield. [b] 1.0 mmol of Cs_2CO_3 was used instead of K_2CO_3. [c]10 mmol scale reaction.

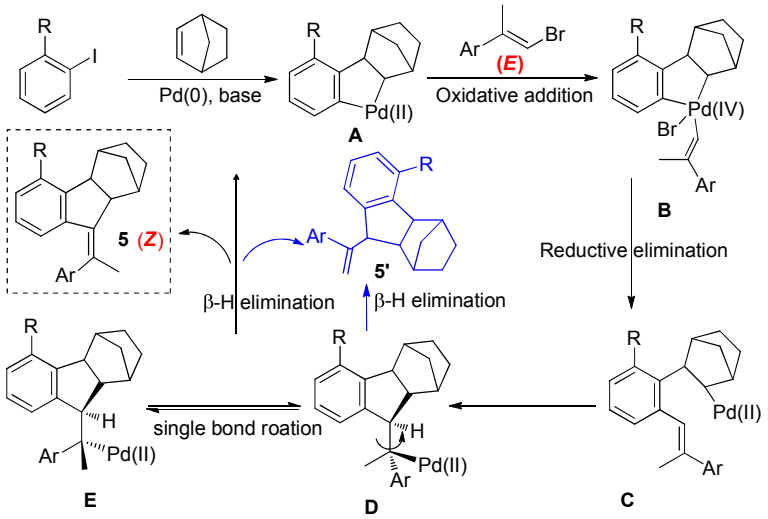
Scheme 5. Synthesis of **6f** and **6g** from cyclopentadiene



According to the literature[13, 15] and the above observed results, a plausible mechanism is proposed in Scheme 6. First, the reaction of aryl iodide with norbornene in the presence of

Pd(0) and base, produces an five-membered palladacycle A, which coordinates with (*E*)-vinyl bromide and followed by oxidative addition to generate an arylpalladium species **B**. The complexes **B** then undergoes reductive elimination to afford **C**, in which the *E*-configuration of double bond is maintained. [19] A subsequent *cis*-insertion of the double bond into Pd-C bond takes place to form a new palladium species **D**, which undergoes a C-C single bond rotation followed by a *cis*-coplanar *β*-H elimination, thus giving the final product **5** with *Z* double bond configuration opposite to that in the alkenyl bromides. Alternatively, the *β*-H elimination can also occur on the methyl group of **D** and **E** to deliver the geminally disubstituted olefin **5′.** The mechanism discussed above well reveals the origin of the high stereoselectivity of this reaction.

Scheme 6. Plausible reaction mechanism.



Aggregation-induced emission (AIE) is a phenomenon that a luminogens exhibits weak luminescence in solution but much enhanced emission in the aggregated state. It is reported that the restriction of intramolecular rotation (RIR) is the main cause of the AIE effect.[14]

Realizing that the presence of the norbornyl group in the molecule would restrict the free intramolecular rotation, we subsequently measured the photoluminescence (PL) behavior of these tetrasubstituted olefins to evaluate the effect of the norbonyl group on the molecular photoluminescence properties. Initially, we measured PL spectra of the compound **5d**, as well as the 1,1,2-triphenylbut-1-ene (**3E**) for comparison. As expected, the compound **5d** exhibited an evident PL signinal than **3E** in the thin film (Figure 1, c). Actually, the RIR effect introduced by the incorporated norbornyl group (Figure 1, e) imparted these multisubstituted olefin an obvious AIE properties (see ESI†, Figure S7). Take the compound **5a** for example, it emitted faintly in dilute THF (10 μm), but brightly in the THF/H_2O mixture with 99% water content, with a 250 fold increment in the PL intensity (Figure 1, a, b). The PL enhancement was possible due to the low solubility of **5a** in water and the aggregation with the water content increase. In addition, **5a** also displays a pronounced deep-blue fluorescence in solid state with the maximum of emission at 451 nm, comparing with tetraphenylethene (**TPE**) at 445nm, a well-known splendid blue luminogen.[20] The quantum yield of **5a** was 52.5% in solid state, slightly higher than that of TPE (49.2%).[20b] These phenomena clearly showed that the **5a** is well AIE-active. Furthermore, the good solubility of these tetrasubstituted olefins in organic solvents such as CH_2Cl_2, CH_3CN, THF and toluene, due to incorporate alkyl chains to the conjugated skeleton, made it the potential of being applicable to solution processing and easy fabrication of large-area optoelectronic devices.[11]

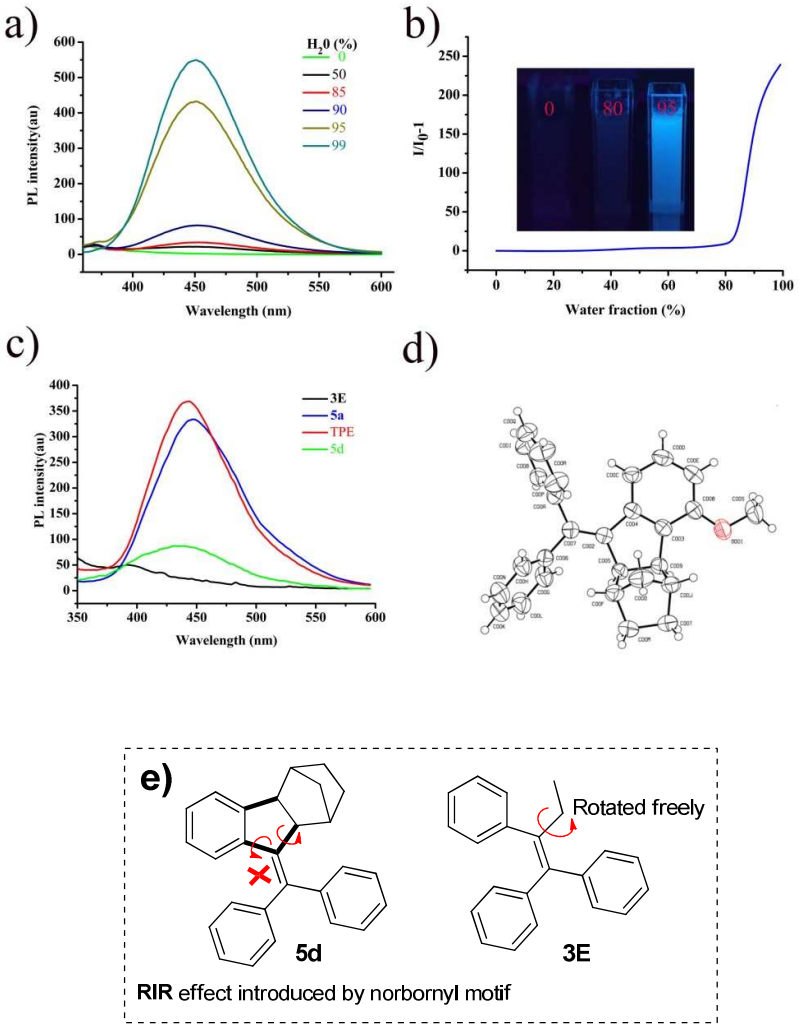


Figure 1. a) PL spectra of **5a** in THF and THF/H_2O mixtures. Concentration: 10^{-5} M; excitation wavelength: 330 nm. b) Plot of (I/I_0–1) values versus the compositions of the THF/H_2O mixtures. Inset: Photos of **5a** in THF/H_2O mixtures (f_w = 0, 80, and 95%) taken under UV luminescence. c) PL spectra of **3E**, **5a**, **5d** and **TPE** in the film state. d) ORTEP of **5a.** e) Comparison of **5d** versus **3E** in term of RIR (restriction of intramolecular rotation) effect.

Conclusions

In conclusion, we have developed a palladium catalyzed multicomponent reaction of aryl iodide, substituted alkenyl bromide and strained alkenes, which assembles the three substrates in great ordered sequence, and forms three new carbon-carbon bonds in one pot. The involved 5-exo-intramolecular Heck reaction enabled us to synthesize a variety of multisubstituted olefins with excellent stereoselectivity. Most remarkably, most of the synthesized tetrasubstituted olefins are AIE-active. Further studies on the application of the new AIE materials are currently in progress in our laboratory.

Experimental section

General Information. All solvents, reagents and deuterated solvents were purchased from Aldrich, Adamas and TCI. Column chromatography was performed with silica gel (Merck, 300-400 mesh). ^{1}H NMR spectra were recorded on Bruker Avance 400 MHz or 600 MHz spectrometers. Chemical shifts were reported in ppm referenced to 7.26 ppm of chloroform-*d* (2.50 ppm of DMSO-d_6). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker Avance 100 MHz or 150 MHz spectrometers, and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of chloroform-*d* (39.52 ppm of DMSO-d_6). HRMS was recorded on a commercial apparatus (ESI Source, TOF). Melting points were obtained by XT4A micro Melting-point Measurement Instruments. Solution state UV-Visible spectra were measured by Shimadzu UV-3600 spectrophotometer, fluorescence spectra were measured using a Edison RF-5301PC spectrofluoremeter. Starting

materials **2i**,[25] **2j**,[26] **2k**,[27] **2z**,[27] **2za**[27] were synthesized following literature protocols.

The synthesis of substituted styryl bromide (2b-2h, 2l-2y). Adapted from a previously reported procedure with some modification.[21] α，β-Unsaturated carboxylic acid (2.0 mmol) was added to a solution of LiOAc (0.4 mmol) in 10 mL of CH_3CN-H_2O (97:3 v/v). After the mixture was stirred for 5 min at room temperature, *N*-halosuccinimide (2.2 mmol) was added as a solid. The progress of the reaction was monitored by TLC (silica gel, n-hexane-ethyl acetate 3:2). Usual workup by flash chromatography (silica gel, petroleum ether) afforded the haloalkene.

Typical procedure for the synthesis 4a-4x, 6a-6g: A dried 25 mL Schlenk tube equipped with magnetic stirring bar was charged with **1** (0.5 mmol), **2** (0.75 mmol), **3** (1.5 mmol) and $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), TFP (29.5 mg, 0.125 mmol), K_2CO_3 (332.5 mg, 2.5 mmol), CH_3CN (3.0 mL). The tube was sealed well, then the solution was stirred at 120 °C for 12 h. The reaction mixture was cooled down to room temperature, washed with CH_2Cl_2 (10 mL), filtered and then the solvent was evaporated in vacuum. The crude product was finally purified by chromatography using petroleum ether/ethyl acetate (50:1) as the eluent to afford the desired products.

Typical procedure for the synthesis 5a-5x: A dried 25 mL Schlenk tube equipped with magnetic stirring bar was charged with **1** (0.5 mmol), **2** (0.75 mmol), **3** (1.5 mmol) and $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), TFP (29.5 mg, 0.125 mmol), K_2CO_3 (332.5 mg, 2.5 mmol), CH_3CN (3.0 mL). The tube was sealed well, then the solution was stirred at 120 °C for 24 h. The reaction mixture was cooled down to room temperature, washed with CH_2Cl_2 (10 mL), filtered and then the solvent was evaporated in vacuum. The crude product was finally

purified by chromatography using petroleum ether/ethyl acetate (50:1) as the eluent to afford the desired products.

(*E*)-1-(2-bromovinyl)-2-methylbenzene (2b).[22] pale-yellow liquid (yield: 215.5 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 7.25 – 7.12 (m, 3H), 6.66(d, J = 13.8 Hz, 1H), 2.36 (s, 3H).

(*E*)-1-(2-bromovinyl)-3-methoxybenzene (2c).[23] colorless liquid (yield: 284.2 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.04 (d, J = 14.0 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.61 (d, J = 14.0 Hz, 1H), 3.81 (s, 3H).

(*E*)-1-(2-bromovinyl)-3-chlorobenzene (2d).[24] pale-yellow liquid (yield: 99.5 mg, 23%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.27 – 7.25 (m, 2H), 7.17 (dd, J = 5.0, 1.1 Hz, 1H), 7.05 (d, J = 14.0 Hz, 1H), 6.81 (d, J = 14.0 Hz, 1H).

(*E*)-1-(2-bromovinyl)-4-methylbenzene (2e).[23] white solid (yield: 321.5 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 14.0 Hz, 1H), 6.71 (d, J = 14.0 Hz, 1H), 2.33 (s, 3H).

(*E*)-1-(2-bromovinyl)-4-fluorobenzene (2f).[23] colorless liquid (yield: 199.7 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J = 8.5, 5.3 Hz, 2H), 6.97 (d, J = 14.0 Hz, 1H), 6.93 (dd, J = 8.4, 8.4 Hz, 2H), 6.60 (d, J = 14.0 Hz, 1H).

(*E*)-1-(2-bromovinyl)-4-chlorobenzene (2g).[23] colorless liquid (yield: 198.6 mg, 46%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 (m, 2H), 7.05 (d, J = 14.0 Hz, 1H), 6.76 (d, J = 14.0 Hz, 1H).

(*E*)-1-bromo-4-(2-bromovinyl)benzene (2h).[23] white solid (yield: 311.5 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.16 (m, 2H), 7.04 (d, J = 14.0 Hz, 1H), 6.78

(d, *J* = 14.0 Hz, 1H).

(*E*)-2-(2-bromovinyl)pyridine (2i).[25] Prepared according to a procedure reported by Gelson Perin and coworkers; yellow liquid (yield: 164.7 mg, 45%); ^{1}H NMR (400 MHz, CDCl3) δ 8.54 (d, *J* = 4.7 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 (d, *J* = 13.7 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.14 (d, *J* = 13.7 Hz, 1H).

(*E*)-2-(2-bromovinyl)thiophene (2j).[26] Prepared according to a procedure reported by Jianbo Wang and coworkers; yellow liquid (yield: 255.5 mg, 68%); ^{1}H NMR (400 MHz, CDCl3) δ 7.22 – 7.17 (m, 1H), 7.19 (d, *J* = 14.0 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.62 (d, *J* = 14.0 Hz, 1H).

(*Z*)-2-(2-bromovinyl)thiophene (2k).[27] Prepared according to a procedure reported by Anthony Hayford and coworkers; yellow liquid (yield: 139.2 mg, 37%); ^{1}H NMR (400 MHz, CDCl3) δ 7.40 (d, *J* = 5.2 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.07 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 1H).

(2-bromoethene-1,1-diyl)dibenzene (2l).[28] colorless liquid (yield: 464.4 mg, 90%); ^{1}H NMR (400 MHz, DMSO) δ 7.43 (m, 3H), 7.36 – 7.28 (m, 3H), 7.27 – 7.17 (m, 5H).

3,3'-(2-bromoethene-1,1-diyl)bis(methylbenzene) (2m).[29] colorless liquid (yield: 400.5 mg, 70%); ^{1}H NMR (400 MHz, DMSO) δ 7.31 (dd, *J* = 9.7, 5.9 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 7.06 (s, 1H), 7.04 – 6.96 (m, 3H), 2.31 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 146.4, 139.9, 139.0, 137.7, 137.6, 129.5, 128.9, 128.6, 128.4, 128.3, 127.8, 126.3, 124.6, 106.2, 21.02 , 21.01.

3,3'-(2-bromoethene-1,1-diyl)bis(methoxybenzene) (2n).[29] colorless liquid (yield: 413.4 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31(m, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.96 –

6.81 (m, 5H), 6.79 (s, 1H), 6.78 – 6.74 (m, 1H), 3.82 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 159.2, 146.4, 141.7, 140.0, 129.2, 129.1, 121.8, 119.9, 114.9, 113.4, 113.3, 113.2, 105.3, 55.1.

3,3'-(2-bromoethene-1,1-diyl)bis(chlorobenzene) (2o). pale-yellow liquid (yield: 378.2 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.36 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 7.13 – 7.09 (m, 1H), 6.87 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 141.9, 140.2, 134.7, 134.5, 130.0, 129.9, 129.7, 128.6, 128.0, 127.7, 125.9, 107.6; HRMS (ESI) m/z: Calcd for $C_{14}H_9BrCl_2$ $[M+H]^+$: 326.9337; found: 326.9332.

3,3'-(2-bromoethene-1,1-diyl)bis(bromobenzene) (2p). white solid (yield: 601.5 mg, 72%); mp 58 – 60 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.47 (m, 3H), 7.47 – 7.27 (m, 4H), 7.20 (d, J = 7.8 Hz, 1H), 6.92 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.2, 140.4, 132.5, 131.5, 130.5, 130.2, 130.1, 128.4, 126.3, 122.8, 122.6; HRMS (ESI) m/z: calcd for $C_{14}H_9Br_3$ $[M+H]^+$: 416.8312; found: 416.8305.

4,4'-(2-bromoethene-1,1-diyl)bis(methylbenzene) (2q).[30] white solid. (yield: 469.5 mg, 82%); mp 47 – 49 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.20 (m, 4H), 7.13 – 7.10 (m, 4H), 6.70 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 138.3, 138.2, 137.9, 136.4, 129.7, 129.2, 129.0, 127.7, 104.1, 21.5, 21.3.

4,4'-(2-bromoethene-1,1-diyl)bis(fluorobenzene) (2r).[31] colorless liquid (yield: 400.6 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 8.8, 5.4 Hz, 2H), 7.17 (dd, J = 8.9, 5.3 Hz, 2H), 7.10 (t, J = 8.8 Hz, 2H), 6.99 (t, J = 8.7 Hz, 2H), 6.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, J = 248.5 Hz), 162.5 (d, J = 247.9 Hz), 145.0, 136.9 (d, J = 3.3 Hz), 134.9 (d, J = 3.4 Hz), 131.7, 131.6, 129.5, 129.4, 115.6 (d, J = 21.6 Hz), 115.5(d, J = 21.6 Hz),

105.3.

4,4'-(2-bromoethene-1,1-diyl)bis(bromobenzene) (2s).[32] white solid (yield: 580.2 mg, 70%); mp 108 – 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.46 – 7.38 (m, 2H), 7.22 – 7.14 (m, 2H), 7.09 – 7.02 (m, 2H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 139.3, 137.5, 131.9, 131.8, 131.5, 129.3, 122.7, 122.6, 106.3.

(*E*)-(1-bromoprop-1-en-2-yl)benzene (2t).[21] colorless liquid (yield: 294.3 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 5H), 6.48 (dd, *J* = 2.3, 1.2 Hz, 1H), 2.27 (dd, *J* = 2.5, 1.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 141.5, 129.1, 128.4, 126.5, 105.9, 20.2.

(*E*)-1-(1-bromoprop-1-en-2-yl)-3-chlorobenzene (2u). colorless liquid (yield: 262.5 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 1H), 7.19 – 7.10 (m, 3H), 6.39 (dd, *J* = 2.5, 1.2 Hz, 1H), 2.11 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 140.5, 134.6, 129.9, 127.9, 126.3, 124.3, 106.8, 19.7; HRMS (ESI) m/z: calcd for C_9H_8BrCl $[M+H]^+$: 230.9571; found: 230.9567.

(*E*)-1-(1-bromoprop-1-en-2-yl)-4-chlorobenzene (2v).[33] colorless liquid (yield: 276.5 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (m, 4H), 6.37 (d, *J* = 1.3 Hz, 1H), 2.12 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 140.5, 139.4, 133.8, 129.2, 128.8, 128.5, 127.3, 106.1, 19.7.

(*E*)-2-(1-bromoprop-1-en-2-yl)naphthalene (2w).[33] white solid (yield: 393.6 mg, 80%); mp 50 – 53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 4H), 7.52 – 7.46 (m, 3H), 6.61 (dd, *J* = 2.4, 1.2 Hz, 1H), 2.34 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 141.5, 138.3, 133.5, 133.0, 128.3, 127.7, 126.6, 126.4, 125.0, 124.2, 106.1, 19.8.

(*E*)-1-(2-bromo-1-phenylvinyl)-4-chlorobenzene (2x).[34] colorless liquid (yield: 263.2 mg, 45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 3H), 7.21 – 7.16 (m, 4H), 7.12 – 7.03 (m, 2H), 6.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 138.3, 137.8, 133.3, 130.3, 128.7, 128.0, 127.8, 127.7, 127.5, 127.4, 126.8, 104.8.

(*Z*)-1-(2-bromo-1-phenylvinyl)-4-chlorobenzene (2y).[34] white solid (yield: 438.7 mg, 75%); mp 78 – 80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.20 – 7.17 (m, 2H), 7.11 (dd, *J* = 6.6, 3.2 Hz, 2H), 6.70 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 140.9, 138.0, 134.5, 131.7, 129.1, 128.9, 128.2, 106.2.

2-(2-bromo-1-phenylvinyl)thiophene (2z). Prepared according to a procedure reported by Jianbo Wang[27] and coworkers, the mixture of (*E*:*Z*=1:1); yellow liquid (yield: 337.9 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 4H), 7.38 – 7.33 (m, 7H), 7.24 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.13 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.87 (s, 1H), 6.73 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.49 (s, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 143.9, 141.4, 140.8, 140.4, 140.2, 138.6, 130.4, 129.4, 128.7, 128.5, 128.5, 128.4 ,128.3, 128.1, 128.5, 127.5, 127.2, 126.6, 126.5, 125.6, 104.3; HRMS (ESI) m/z: calcd for $C_{12}H_{10}BrS$ $[M+H]^+$: 264.9681; found: 264.9685.

2-(2-bromo-1-(4-fluorophenyl)vinyl)thiophene (2za). Prepared according to a procedure reported by Jianbo Wang[27] and coworkers, the mixture of (*E*:*Z*=1:1); yellow liquid (yield: 338.2 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.36 – 7.29 (m, 4H), 7.25 (d, *J* = 1.2 Hz, 1H), 7.15 – 7.11 (m, 3H), 7.08 – 7.03 (m, 3H), 6.95 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.87 (s, 1H), 6.74 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.46 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 248.1 Hz), 162.7 (d, *J* = 247.8 Hz), 143.8, 140.3, 139.9, 139.2, 137.5,

137.4 (d, *J* = 3.3 Hz), 134.4, 134.3 (d, *J* = 3.5 Hz), 131.4, 131.3, 130.5, 130.4, 127.6, 127.4, 126.6, 125.9, 115.5 (d, *J* = 21.6 Hz), 115.5 (d, *J* = 21.6 Hz), 104.6, 104.2; HRMS (ESI) m/z: calcd for $C_{12}H_9BrFS$ $[M+H]^+$: 282.9587; found: 282.9583.

(4aR, 9aS, *Z*)-9-benzylidene-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4a). white solid (yield:123.2 mg, 81%); mp 108 –110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 6.91 (t, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.63 (s, 1H), 3.85 (s, 3H), 3.12 (d, *J* = 7.1 Hz, 1H), 2.93 (d, *J* = 7.0 Hz, 1H), 2.55 (s, 1H), 2.34 (s, 1H), 1.70 – 1.59 (m, 2H), 1.48 – 1.41 (m, 2H), 1.21 (d, *J* = 10.0 Hz, 1H), 1.03 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 144.8, 144.6, 144.2, 143.7, 138.0, 136.8, 129.1, 128.3, 127.4, 127.0, 126.6, 117.0, 109.0, 55.2, 51.8, 49.5, 41.8, 40.5, 32.6, 29.3, 28.6; HRMS (ESI) m/z: calcd for $C_{22}H_{22}O$ $[M+H]^+$: 303.1743; found: 303.1748.

(4aR, 9aS, *Z*)-9-benzylidene-5-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4b).[13] yellow oil (yield:118.6 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 6.8, 3.1 Hz, 4H), 7.30 – 7.26 (m, 1H), 6.98 (dd, *J* = 12.7, 7.6 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 1.9 Hz, 1H), 3.03 (d, *J* = 7.2 Hz, 1H), 2.95 (d, *J* = 7.1 Hz, 1H), 2.42 – 2.39 (m, 1H), 2.37 (d, *J* = 3.9 Hz, 1H), 2.34 (s, 3H), 1.66 (dd, *J* = 3.2, 1.9 Hz, 1H), 1.49 – 1.44 (m, 1H), 1.27 (s, 2H), 1.05 – 1.01 (m, 1H), 0.87 (dd, *J* = 7.2, 3.9 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 149.0, 147.8, 141.3, 138.9, 134.6, 129.6, 128.7, 128.5, 126.7, 126.3, 122.8, 121.3, 53.7, 50.9, 45.4, 40.5, 32.5, 29.9, 28.4, 18.9; HRMS (ESI) m/z: calcd for $C_{22}H_{22}$ $[M+H]^+$: 287.1794; found: 287.1788.

(4aR, 9aS, *E*)-9-benzylidene-5-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4bb).[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.41– 7.36 (m, 3H),

7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 3.38 (d, *J* = 6.8 Hz, 1H), 3.21 (d, *J* = 6.8 Hz, 1H), 2.46 (d, *J* = 4.0 Hz, 2H), 2.38 (s, 3H), 1.65 – 1.60 (m, 1H), 1.48 (dd, *J* = 8.0, 1.9 Hz, 2H), 1.27 (s, 1H), 1.06 (d, *J* = 10.2 Hz, 1H), 0.94 – 0.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.6, 144.4, 137.8, 134.7, 129.7, 128.8, 128.6 , 127.3, 126.3, 119.2, 117.1, 52.8, 51.1, 40.9, 40.3, 32.9, 29.2, 28.9, 18.8.

(4aR, 9aS, *Z*)-9-benzylidene-5,6-dimethyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4c). yellow oil (yield: 117.1 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.55 (s, 1H), 3.06 (d, *J* = 7.2 Hz, 1H), 2.96 (d, *J* = 7.1 Hz, 1H), 2.39 (s, 2H), 2.26 (s, 3H), 2.24 (s, 3H) 1.68 (dd, *J* = 13.6, 7.0 Hz, 2H), 1.46 (dd, *J* = 24.5, 6.0 Hz, 2H), 1.27 (d, *J* = 10.1 Hz, 1H), 1.04 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 147.9, 139.1, 137.2, 132.9, 128.8, 128.5, 128.2, 126.6, 121.8, 120.9, 53.9, 51.2, 45.4, 41.0, 32.4, 29.9, 28.4, 19.9, 15.9; HRMS (ESI) m/z: calcd for $C_{23}H_{24}$ $[M+H]^+$: 301.1951; found: 301.1949.

(4aR, 9aS, *Z*)-9-benzylidene-5-chloro-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4d). white solid (yield: 126.9 mg, 83%); mp 61– 63 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 –7.28 (m, 5H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.84 (dd, *J* =7.8, 1.6 Hz, 1H), 6.66 (s, 1H), 3.13 (d, *J* = 7.0 Hz, 1H), 2.96 (d, *J* = 7.1 Hz, 1H), 2.67 (s, 1H), 2.37 (s, 1H), 1.73 – 1.60 (m, 2H), 1.53 – 1.37 (m, 2H), 1.21 (d, *J* = 10.1 Hz, 1H), 1.06 (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 147.6, 147.2, 143.6, 138.4, 131.6, 128.7, 128.6, 128.5, 127.7, 127.1, 124.4, 122.0, 53.3, 51.4, 45.7, 40.1, 32.5, 29.7, 28.4; HRMS (ESI) m/z: calcd for $C_{21}H_{19}Cl$ $[M+H]^+$: 307.1248; found: 307.1250.

(7aS, 11aR, *Z*)-7-benzylidene-7a,8,9,10,11,11a-hexahydro-7H-8,11-methanobenzo[c]fluo-

rene (4e). white solid (yield: 140.3 mg ,87%); mp 75 – 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.48 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.44 – 7.35 (m, 6H), 7.31 – 7.22 (m, 2H), 6.66 (d, *J* = 1.2 Hz, 1H), 3.47 (d, *J* = 7.0 Hz, 1H), 3.09 (d, *J* = 6.9 Hz, 1H), 2.63 (d, *J* = 3.5 Hz, 1H), 2.40 (d, *J* = 1.8 Hz, 1H), 1.78 – 1.59 (m, 3H), 1.50 – 1.43 (m, 1H), 1.27 – 1.22 (m, 1H), 1.13 – 0.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 146.9, 138.9, 138.8, 133.9, 130.6, 128.9, 128.6, 128.5, 126.9, 126.8, 126.1, 125.9, 125.0, 122.3, 122.1, 54.2, 50.8, 45.1, 41.3, 32.7, 30.1, 28.5; HRMS (ESI) m/z: calcd for $C_{25}H_{22}$ $[M+H]^+$: 323.1794; found: 323.1789.

(4aR, 9aS, *Z*)-9-benzylidene-5-fluoro-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4f). yellow oil (yield:117.8 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 6.89 – 6.78 (m, 3H), 6.65 (s, 1H), 3.19 (d, *J* = 7.2 Hz, 1H), 2.96 (d, *J* = 7.2 Hz, 1H), 2.49 (s, 1H), 2.34 (d, *J* = 2.8 Hz, 1H), 1.65 (t, *J* = 2.9 Hz, 1H), 1.47 (d, *J* = 9.3 Hz, 1H), 1.39 (s, 1H), 1.26 (s, 1H), 1.21 – 1.17 (m, 1H), 1.09 – 1.05 (m, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 159.9 (d, *J* = 245.9 Hz), 146.9 (d, *J* = 2.2 Hz), 144.6 (d, *J* = 6.0 Hz), 138.4, 136.4 (d, *J* = 17.8 Hz), 128.7，128.6, 128.0 (d, *J* = 7.1 Hz), 127.0, 124.2, 119.5 (d, *J* = 3.5 Hz), 114.6 (d, *J* = 20.3 Hz), 53.9, 48.5, 45.6, 40.7, 32.6, 29.6, 28.5; HRMS (ESI) m/z: calcd for $C_{21}H_{19}F$ $[M+H]^+$: 291.1544; found: 291.1542.

(4aR, 9aS, *Z*)-9-benzylidene-5-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4g). yellow oil (yield:151.5 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 7H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.70 (s, 1H), 3.33 (d, *J* = 7.1 Hz, 1H), 3.00 (d, *J* = 7.3 Hz, 1H), 2.52 (s, 1H), 2.38 (s, 1H), 1.71 – 1.59 (m, 2H), 1.53 – 1.35 (m, 2H), 1.27 – 1.22 (m, 1H), 1.11 – 1.01 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.1, 143.5, 138.4, 128.8,

128.5, 127.4 (q, J = 31.5 Hz), 127.2, 126.9, 126.5, 126.0 (q, J = 5.1 Hz), 124.8 (q, J = 273.6 Hz), 124.4, 53.8, 50.9, 45.7, 42.6, 32.4, 30.2, 28.2; HRMS (ESI) m/z: calcd for $C_{22}H_{19}F_3$ $[M+H]^+$: 341.1512; found: 341.1517.

(4aR, 9aS, *Z*)-9-benzylidene-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4h). yellow liquid (yield: 92.2 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.23 (dd, J = 7.2, 0.8 Hz, 1H), 7.17 – 7.14 (m, 2H), 6.93 – 6.86 (m, 1H), 6.62 (d, J = 1.8 Hz, 1H), 3.07 (d, J = 7.2 Hz, 1H), 2.93 (d, J = 7.1 Hz, 1H), 2.33 (d, J = 3.3 Hz, 1H), 2.30 (d, J = 3.3 Hz, 1H), 1.67 – 1.63 (m, 1H), 1.48 – 1.39 (m, 2H), 1.26 (s, 2H), 1.16 (dd, J = 5.9, 4.2 Hz, 1H), 1.04 – 1.00 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 147.5, 141.4, 138.8, 128.7, 128.6, 126.8, 126.1, 125.3, 123.7, 123.0, 53.6, 51.8, 45.6, 42.9, 32.4, 29.6, 28.7; HRMS (ESI) m/z: calcd for $C_{21}H_{20}$ $[M+H]^+$: 273.1638; found: 273.1633.

(4aR, 9aS, *Z*)-9-benzylidene-6-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4i). white solid (yield: 67.7 mg, 45%); mp 135 – 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 8.3 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.20 (d, J = 7.4 Hz, 1H), 6.83 – 6.72 (m, 3H), 3.84 (s, 3H), 3.35 (d, J = 6.7 Hz, 1H), 3.19 (d, J = 6.8 Hz, 1H), 2.44 (d, J = 3.7 Hz, 1H), 2.36 (d, J = 3.9 Hz, 1H), 1.58 (d, J = 7.1 Hz, 1H), 1.47 (dd, J = 8.2, 1.6 Hz, 2H), 1.27 (s, 1H), 1.04 (d, J = 10.2 Hz, 1H), 0.93 (d, J = 10.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 150.1, 146.8, 138.0, 137.3, 128.6, 128.5, 125.9, 120.5, 117.3, 114.0, 109.2, 55.5, 53.5, 51.4, 43.0, 40.4, 32.8, 29.1, 28.9; HRMS (ESI) m/z: calcd for $C_{22}H_{22}O$ $[M+H]^+$: 303.1743; found: 303.1736.

(4aR, 9aS, *Z*)-9-benzylidene-6-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4j). white solid (yield: 73.8 mg, 52%); mp 105 – 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.56 (d, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.87 (d, *J* = 2.1 Hz, 1H), 3.35 (d, *J* = 6.7 Hz, 1H), 3.19 (d, *J* = 6.8 Hz, 1H), 2.45 (d, *J* = 3.7 Hz, 1H), 2.38 (s, 3H), 2.35 (d, *J* = 4.0 Hz, 1H), 1.67 – 1.61 (m, 2H), 1.51 – 1.44 (m, 2H), 1.03 (d, *J* = 10.2 Hz, 1H), 0.97 – 0.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.2, 141.8, 138.5, 137.9, 128.7, 128.6, 128.1, 126.2, 125.6, 119.4, 118.4, 53.3, 51.2, 43.1, 40.4, 32.8, 29.1, 28.9, 21.7; HRMS (ESI) m/z: calcd for $C_{22}H_{22}$ $[M+H]^+$: 287.1794; found: 287.1786.

(4aR, 9aS, *Z*)-9-benzylidene-7-fluoro-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4k). white solid (yield: 81.2 mg, 56%); mp 77 – 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 7.15 (dd, *J* = 8.3, 5.5 Hz, 1H), 6.85 (d, *J* = 8.5, 1H), 6.77 (dd, *J* = 10.5, 2.4 Hz, 1H), 6.66 (s, 1H), 3.03 (d, *J* = 7.1 Hz, 1H), 2.96 (d, *J* = 7.2 Hz, 1H), 2.33 (d, *J* = 3.1 Hz, 1H), 2.26 (d, *J* = 3.3 Hz, 1H), 1.65 (s, 2H), 1.48 – 1.36 (m, 2H), 1.18 – 1.15 (m, 1H), 1.06 – 1.00 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 241.8 Hz), 146.7 (d, *J* = 3.3 Hz), 146.3 (d, *J* = 2.1 Hz), 143.1 (d, *J* = 8.6 Hz), 138.1, 128.7, 128.6, 127.2, 125.9 (d, *J* = 9.0 Hz), 124.3, 115.7 (d, *J* = 23.3 Hz), 110.1 (d, *J* = 23.4 Hz), 54.1, 51.1, 45.6, 42.8, 32.3, 29.4, 28.7; HRMS (ESI) m/z: calcd for $C_{21}H_{19}F$ $[M+H]^+$: 291.1544; found: 291.1542.

(4aR, 9aS, *Z*)-9-benzylidene-7-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4l). yellow oil (yield: 78.7 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 4H), 7.34 – 7.28 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 5.5 Hz, 2H), 6.63 (d, *J* = 1.5 Hz, 1H), 3.05 (d, *J* = 7.1 Hz, 1H), 2.95 (d, *J* = 7.1 Hz, 1H), 2.35 (d, *J* = 3.3 Hz, 1H), 2.30 (d, *J* = 3.1 Hz, 1H), 2.13 (s, 3H), 1.71 – 1.60 (m, 2H), 1.50 – 1.37 (m, 2H), 1.23 – 1.18 (m, 1H), 1.05 – 0.99 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.5, 141.5, 138.8, 135.4, 129.7,

128.8, 128.4, 126.8, 124.9, 124.2, 122.8, 53.9, 51.4, 45.5, 42.8, 32.3, 29.5, 28.7, 21.5; HRMS (ESI) m/z: calcd for $C_{22}H_{22}$ $[M+H]^+$: 287.1794; found: 287.1785.

(4aR, 9aS, *Z*)-9-benzylidene-6-fluoro-7-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4m). yellow oil (yield: 73.3 mg, 48%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 9.6 Hz, 1H), 6.55 (d, *J* = 1.4 Hz, 1H), 3.01 (d, *J* = 7.1 Hz, 1H), 2.94 (s, 1H), 2.32 (d, *J* = 3.1 Hz, 1H), 2.25 (d, *J* = 3.3 Hz, 1H), 2.01 (d, *J* = 2.0 Hz, 3H), 1.67 – 1.56 (m, 2H), 1.45 – 1.34 (m, 2H), 1.19 – 1.14 (m, 1H), 1.05 – 1.00 (m, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 161.8 (d, *J* = 247.2 Hz), 150.7 (d, *J* = 7.6 Hz), 146.5 (d, *J* = 1.0 Hz), 138.7, 137.1 (d, *J* = 2.9 Hz), 128.7, 128.5, 126.8, 126.1 (d, *J* = 5.5 Hz), 122.6 (d, *J* = 18.4 Hz), 121.9 (d, *J* = 2.5 Hz), 111.2 (d, *J* = 22.2 Hz), 54.1, 51.5 (d, *J* = 1.9 Hz), 45.5, 42.7, 32.3, 29.4, 28.6, 14.9 (d, *J* = 3.7 Hz); HRMS (ESI) m/z: calcd for $C_{22}H_{21}F$ $[M+H]^+$: 305.1700; found: 305.1691.

(4aR, 9aS, *Z*)-5-methoxy-9-(2-methylbenzylidene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4n). white solid (yield: 113.4 mg, 72%); mp 80 – 82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 4H), 6.86 (t, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.55 (s, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 3H), 3.12 (d, *J* = 7.1 Hz, 1H), 2.96 (d, *J* = 7.1 Hz, 1H), 2.54 (s, 1H), 2.36 (s, 1H), 2.26 (s, 3H), 1.67 – 1.57 (m, 2H), 1.51 – 1.37 (m, 2H), 1.20 (d, *J* = 10.0 Hz, 1H), 1.06 – 1.00 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 147.8, 143.5, 138.1, 137.9, 136.4, 130.0, 129.1, 127.8, 127.0, 125.9, 122.2, 116.1, 109.5, 55.2, 53.3, 49.5, 45.6, 40.0, 32.6, 29.8, 28.6, 20.0; HRMS (ESI) m/z: calcd for $C_{23}H_{24}O$ $[M+H]^+$: 317.1900; found: 317.1891.

(4aR, 9aS, *Z*)-5-methoxy-9-(3-methoxybenzylidene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-me-

thanofluorene (4o). white solid (yield: 126.2 mg, 76%); mp 159 – 161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.8 Hz, 1H), 7.13 – 6.44 (m, 6H), 6.43 (d, *J* = 1.6 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.11 (d, *J* = 7.0 Hz, 1H), 2.96 (d, *J* = 7.0 Hz, 1H), 2.53 (s, 1H), 2.39 (s, 1H), 1.67 – 1.58 (m, 2H), 1.46 –1.45 (m, 2H), 1.19 (s, 1H), 1.02 (dd, *J* = 6.3, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 156.6, 148.8, 142.7, 139.7, 138.5, 133.3, 127.8, 122.1, 116.3, 115.7, 115.1, 114.6, 109.8, 55.6, 55.3, 53.4, 49.5, 45.3, 39.9, 32.7, 29.7, 28.5; HRMS (ESI) m/z: calcd for $C_{23}H_{24}O_2$ $[M+H]^+$: 333.1849; found: 333.1841.

(4aR, 9aS, *Z*)-9-(3-chlorobenzylidene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1, 4-methanofluorene (4p). white solid (yield:121.4 mg, 72%); mp 144 – 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 –7.25 (m, 4H), 6.92 (t, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 13.6, 7.9 Hz, 2H), 6.51 (d, *J* = 0.8 Hz, 1H), 3.83 (s, 3H), 3.09 (d, *J* = 7.1 Hz, 1H), 2.89 (d, *J* = 7.0 Hz, 1H), 2.52 (d, *J* = 2.6 Hz, 1H), 2.29 (d, *J* = 2.8 Hz, 1H), 1.67 – 1.56 (m, 2H), 1.50 – 1.33 (m, 2H), 1.15 (d, *J* = 10.1 Hz, 1H), 1.04 – 0.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 149.1, 142.6, 140.7, 138.6, 134.2, 129.7, 128.9, 127.7, 127.1, 126.8, 121.4, 116.2, 109.9, 55.3, 53.7, 49.4, 45.5, 39.9, 32.5, 29.7, 28.5; HRMS (ESI) m/z: calcd for $C_{22}H_{21}ClO$ $[M+H]^+$: 337.1354; found: 337.1349.

(4aR, 9aS, *Z*)-9-(3-fluorobenzylidene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1, 4-methanofluorene (4q). white solid (yield:102.5 mg, 64%); mp 111 – 114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 6.1 Hz, 1H), 7.03 – 6.95 (m, 4H), 6.73 – 6.68 (m, 2H), 6.54 (s, 1H), 3.84 (s, 3H), 3.09 (d, *J* = 7.1 Hz, 1H), 2.90 (d, *J* = 7.1 Hz, 1H), 2.52 (d, *J* = 2.6 Hz, 1H), 2.30 (d, *J* = 2.9 Hz, 1H), 1.63 (d, *J* = 2.5 Hz, 2H), 1.45 – 1.41 (m, 2H), 1.20 – 1.12 (m, 1H), 1.01 (dd, *J* = 6.4, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 245.6 Hz), 156.6,

148.9, 142.6, 141.1 (d, J = 7.8 Hz), 138.6, 129.9 (d, J = 8.5 Hz), 127.7, 124.6 (d, J = 2.8 Hz), 121.6 (d, J = 2.1 Hz), 116.3, 115.6 (d, J = 20.9 Hz), 113.6 (d, J = 21.1 Hz), 109.9, 55.3, 53.7, 49.4, 45.5, 39.9, 32.5, 29.7, 28.5; HRMS (ESI) m/z: calcd for $C_{22}H_{21}FO$ $[M+H]^+$: 321.1649; found: 321.1645.

(4aR, 9aS, *Z*)-5-methoxy-9-(4-methylbenzylidene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4r). white solid (yield: 144.2 mg, 91%); mp 134 – 136 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 6.80 (d, J = 7.9 Hz, 1H), 6.72 (d, J = 7.8 Hz, 1H), 6.55 (d, J = 7.9 Hz, 1H), 6.48 (s, 1H), 3.74 (s, 3H), 2.99 (d, J = 7.1 Hz, 1H), 2.81 (d, J = 7.1 Hz, 1H), 2.43 (d, J = 2.6 Hz, 1H), 2.29 (s, 3H), 2.22 (d, J = 2.8 Hz, 1H), 1.57 – 1.47 (m, 2H), 1.40 – 1.23 (m, 2H), 1.10 (d, J = 10.0 Hz, 1H), 0.95 – 0.86 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 147.5, 143.2, 138.2, 136.3, 135.7, 129.1, 128.7, 127.5, 123.2, 116.3, 109.5, 55.2, 53.7, 49.4, 45.6, 39.9, 32.5, 29.8, 28.6, 21.4; HRMS (ESI) m/z: calcd for $C_{23}H_{24}O$ $[M+H]^+$: 317.1900; found: 317.1891.

(4aS, 9aR, *Z*)-9-(4-methylbenzylidene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene-5-carbonitrile (4s). white solid (yield: 82.5 mg, 53%); mp 146 – 149 ^oC; ^1H NMR (400 MHz, CDCl3) δ 7.39 (d, J = 7.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.22 – 7.17 (m, 4H), 6.97 (t, J = 7.8 Hz, 1H), 6.70 (s, 1H), 3.25 (d, J = 7.3 Hz, 1H), 3.00 (d, J = 7.2 Hz, 1H), 2.66 (d, J = 3.4 Hz, 1H), 2.39 (s, 3H), 2.37 (d, J = 3.5 Hz, 1H), 1.76 – 1.61 (m, 2H), 1.58 – 1.53 (m, 1H), 1.45 – 1.35 (m, 1H), 1.11 (q, J = 10.3 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 153.8, 145.3, 143.0, 137.1, 134.9, 131.8, 129.5, 128.3, 127.7, 126.9, 125.7, 117.9, 109.5, 53.3, 51.4, 45.7, 41.5, 32.6, 29.7, 28.4, 21.4. HRMS (ESI) m/z: calcd for $C_{23}H_{21}N$ $[M+H]^+$: 312.1747; found: 312.1753.

(4aR, 9aS, *Z*)-9-(4-fluorobenzylidene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4t). white solid (yield: 111.4 mg, 69%); mp 121 – 123 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.04 (t, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.66 (dd, *J* = 7.9, 2.2 Hz, 2H), 6.54 (s, 1H), 3.83 (s, 3H), 3.09 (d, *J* = 7.1 Hz, 1H), 2.89 (d, *J* = 7.1 Hz, 1H), 2.52 (d, *J* = 2.5 Hz, 1H), 2.30 (s, 1H), 1.63 (d, *J* = 2.5 Hz, 2H), 1.47 (s, 2H), 1.15 (s, 1H), 1.05– 0.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.3 Hz), 156.6, 148.4, 142.9, 138.4, 134.7 (d, *J* = 3.4 Hz), 130.4 (d, *J* = 7.8 Hz), 127.6, 121.9, 116.1, 115.4 (d, *J* = 21.2 Hz), 109.7, 55.3, 53.6, 49.4, 45.5, 39.9, 32.5, 29.7, 28.6; HRMS (ESI) m/z: calcd for $C_{22}H_{21}FO$ $[M+H]^+$: 321.1649; found: 321.1642.

(4aR, 9aS, Z)-9-(4-chlorobenzylidene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4u). white solid (yield: 126 mg, 75%); mp 150 – 152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 6.91 (t, *J* = 7.9 Hz, 1H), 6.70 – 6.67(m, 2H), 6.51 (d, *J* = 1.5 Hz, 1H), 3.83 (s, 3H), 3.08 (d, *J* = 7.1 Hz, 1H), 2.89 (d, *J* = 7.1 Hz, 1H), 2.51 (d, *J* = 2.6 Hz, 1H), 2.29 (s, 1H), 1.66 – 1.58 (m, 2H), 1.46 (s, 1H), 1.38 (dd, *J* = 7.1, 1.6 Hz, 1H), 1.15 (d, *J* = 10.1 Hz, 1H), 1.03 – 0.98 (m, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 156.6, 148.8, 142.8, 138.5, 137.2, 132.4, 130.3, 128.6, 127.7, 121.7, 116.2, 109.8, 55.3, 53.7, 49.4, 45.5, 39.9, 32.5, 29.7, 28.6; HRMS (ESI) m/z: calcd for $C_{22}H_{21}ClO$ $[M+H]^+$: 337.1354; found: 337.1355.

(4aR, 9aS, Z)-9-(4-bromobenzylidene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (4v). white solid (yield:150.0 mg, 79%); mp 147 – 149 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.72 – 6.69 (m, 2H), 6.49 (s, 1H), 3.84 (s, 3H), 3.09 (d, *J* = 7.1 Hz, 1H), 2.89 (d, *J* = 7.1 Hz, 1H), 2.52 (d,

J = 2.8 Hz, 1H), 2.30 (d, *J* = 2.8 Hz, 1H), 1.69 – 1.56 (m, 2H), 1.51 – 1.35 (m, 2H), 1.16 (d, *J* = 10.1 Hz, 1H), 1.04 – 0.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 148.7, 142.7, 138.5, 137.7, 131.6, 130.6, 127.7, 121.6, 120.5, 116.2, 109.8, 55.3, 53.7, 49.4, 45.5, 39.9, 32.5, 29.7, 28.5; HRMS (ESI) m/z: calcd for $C_{22}H_{21}BrO$ $[M+H]^+$: 381.0849; found: 381.0843.

2-((Z)-((4aR, 9aS)-5-methoxy-2,3,4,4a-tetrahydro-1H-1,4-methanofluoren-9(9aH)-ylidene)methyl)pyridine (4w). pale-yellow solid (yield:128.8 mg, 85%); mp 109 – 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.3 Hz, 1H), 7.65 (dd, *J* = 8.6, 6.8 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.19 – 7.09 (m, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.60 (s, 1H), 3.83 (s, 3H), 3.10 (d, *J* = 6.9 Hz, 1H), 2.95 (d, *J* = 6.9 Hz, 1H), 2.52 (s, 1H), 2.36 (s, 1H), 1.64 – 1.58 (m, 2H), 1.47 – 1.36 (m, 2H), 1.15 (d, *J* = 10.1 Hz, 1H), 0.97 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 156.5, 151.4, 149.3, 142.4, 139.2, 136.2, 127.7, 124.4, 122.3, 121.4, 117.2, 110.4, 55.3, 54.4, 49.4, 45.4, 39.8, 32.6, 29.7, 28.6; HRMS (ESI) m/z: calcd for $C_{21}H_{22}NO$ $[M+H]^+$: 304.1696; found: 304.1696.

2-((Z)-((4aR, 9aS)-5-methoxy-2,3,4,4a-tetrahydro-1H-1,4-methanofluoren-9(9aH)-ylidene)methyl)thiophene (4x). Pale green solid (yield: 112.5 mg, 73%); mp 62 – 65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.08 – 7.01 (m, 3H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 6.50 (d, *J* = 1.7 Hz, 1H), 3.84 (s, 3H), 3.09 (d, *J* = 7.0 Hz, 1H), 2.89 (d, *J* = 7.0 Hz, 1H), 2.52 (s, 1H), 2.31 (s, 1H), 1.66 – 1.56 (m, 2H), 1.46 (dd, *J* = 12.8, 6.2 Hz, 1H), 1.41 – 1.33 (m, 1H), 1.18 – 1.11 (m, 1H), 1.02 – 0.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 150.8, 142.7, 140.8, 138.6, 127.8, 127.3, 126.1, 124.9, 116.4, 114.6, 110.0, 55.3, 53.9, 49.4, 45.3, 39.8, 32.6, 29.7, 28.6; HRMS (ESI) m/z: calcd for

$C_{20}H_{21}OS$ $[M+H]^+$: 309.1308; found: 309.1313.

2-((E)-((4aR, 9aS)-5-methoxy-2,3,4,4a-tetrahydro-1H-1,4-methanofluoren-9(9aH)-ylidene)methyl)thiophene (4y). Pale green oil (yield: 80.1mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 5.0 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.16 – 7.10 (m, 3H), 7.07 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 3.87 (s, 3H), 3.31 (d, *J* = 6.7 Hz, 1H), 3.21 (d, *J* = 6.6 Hz, 1H), 2.64 – 2.60 (m, 2H), 1.73 – 1.62 (m, 2H), 1.59 – 1.50 (m, 2H), 1.10 – 1.05 (m, 1H), 0.98 – 0.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 145.9, 145.5, 141.7, 138.5, 139.2, 136.0, 132.2, 125.1, 113.1, 111.8, 109.5, 55.3, 51.5, 51.0, 40.7, 40.1, 32.9, 29.2, 28.7; HRMS (ESI) m/z: calcd for $C_{20}H_{21}OS$ $[M+H]^+$: 309.1308; found: 309.1310.

(4aR, 9aS)-9-(diphenylmethylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-meth-ano-fluorene (5a). white solid (yield: 136.1 mg, 72%); mp 173 – 175 °C; ^{1}H NMR (400 MHz, CDCl3) δ 7.47 – 7.13 (m, 10H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.97 (d, *J* = 7.9 Hz, 1H), 3.83 (s, 3H), 3.31 (d, *J* = 7.3 Hz, 1H), 3.08 (d, *J* = 7.2 Hz, 1H), 2.52 (d, *J* = 3.5 Hz, 1H), 1.21 – 1.97 (m, 1H), 1.56 – 1.49 (m, 1H), 1.37 – 1.21 (m, 3H), 0.99 – 0.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 144.8, 144.6, 144.3, 143.7, 138.0, 136.8, 129.2, 128.3, 127.4, 127.1, 126.6, 117.0, 109.0, 55.3, 51.9, 49.6, 41.8, 40.6, 32.6, 29.4, 28.6; HRMS (ESI) m/z: calcd for $C_{28}H_{26}O$ $[M+H]^+$: 379.2056; found: 379.2056.

(4aR, 9aS)-9-(diphenylmethylene)-5-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methano-fluorene (5b). white solid (yield: 121.5 mg, 67%); mp 161 – 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.09 (m, 10H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.74 (t, *J* = 7.7 Hz, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 3.36 (d, *J* = 7.4 Hz, 1H), 3.01 (d, *J* = 7.4 Hz, 1H), 2.40 (d, *J* = 3.8 Hz, 1H), 2.33 (s, 3H), 2.01 (d, *J* = 4.0 Hz, 1H), 1.58 – 1.54 (m, 1H), 1.33 – 1.27 (m, 3H), 0.99 – 0.89 (m,

2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 145.0, 144.7, 144.2, 143.2, 136.8, 134.7, 129.5, 129.4，128.6, 127.4, 126.9, 126.7, 122.4, 52.3, 51.5, 41.9, 41.4, 32.9, 29.9, 28.8, 19.2; HRMS (ESI) m/z: calcd for $C_{28}H_{26}$ $[M+H]^+$: 363.2107; found: 363.2104.

(4aR, 9aS)-9-(diphenylmethylene)-5-fluoro-2,3,4,4a,9,9a-hexahydro-1H-1,4-methano-fluorene (5c). white solid (yield: 119.3 mg, 65%); mp 117 – 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 10H), 6.81 – 6.72 (m, 2H), 6.10 (dd, *J* = 6.1, 2.6 Hz, 1H), 3.34 (d, *J* = 7.4 Hz, 1H), 3.17 (d, *J* = 7.4 Hz, 1H), 2.48 (d, *J* = 3.7 Hz, 1H), 2.01 (d, *J* = 3.9 Hz, 1H), 1.56 – 1.53 (m, 1H), 1.35 – 1.22 (m, 3H), 1.00 – 0.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 245.4 Hz), 146.1 (d, *J* = 5.8 Hz), 143.9 (d, *J* = 2.2 Hz), 143.8, 143.4, 137.9, 136.1 (d, *J* = 17.9 Hz), 130.4, 129.0, 128.4, 128.2 (d, *J* = 7.8 Hz), 127.8 (d, *J* = 7.1 Hz)，127.3，126.8, 120.3 (d, *J* = 3.4 Hz), 114.0 (d, *J* = 20.2 Hz), 52.0, 48.6, 41.9, 41.3, 32.6, 29.2, 28.5; HRMS (ESI) m/z: calcd for $C_{27}H_{23}F$ $[M+H]^+$: 367.1857; found: 367.1858.

(4aR, 9aS)-9-(diphenylmethylene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluoren (5d). white solid (yield: 99.3 mg, 57%); mp 157 – 159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 –7.26 (m, 5H), 7.21 – 6.99 (m, 5H), 6.97 (dd, *J* = 5.7, 3.2 Hz, 1H), 6.92 (dd, *J* = 10.2, 4.5 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.56 (t, *J* = 7.6 Hz, 1H), 3.25 (d, *J* = 9.7 Hz, 1H), 3.08 (d, *J* = 9.7 Hz, 1H), 2.37 (s, 1H), 2.22 (s, 1H), 1.72 – 1.53 (m, 4H), 1.46 (d, *J* = 11.1 Hz, 1H), 1.05 – 0.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 141.6, 140.4, 139.8, 132.7, 131.9, 131.3, 130.8, 130.5, 129.8, 127.8, 127.7, 127.5, 125.6, 50.8, 50.1, 47.9, 47.6, 34.1, 31.8, 30.7; HRMS (ESI) m/z: calcd for $C_{27}H_{24}$ $[M+H]^+$: 349.1951; found: 349.1946.

(4aR, 9aS)-5-chloro-9-(diphenylmethylene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-me-thano-fluorene (5e). white solid (yield: 116.5 mg, 61%); mp 116 – 118 °C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.43 – 7.22 (m, 10H), 7.09 – 7.06 (m, 1H), 6.75 (t, *J* = 7.9 Hz, 1H), 6.25 (d, *J* = 7.9 Hz, 1H), 3.37 (d, *J* = 7.4 Hz, 1H), 3.12 (d, *J* = 7.4 Hz, 1H), 2.67 (d, *J* = 3.9 Hz, 1H), 2.03 (d, *J* = 3.9 Hz, 1H), 1.60 – 1.53 (m, 1H), 1.40 – 1.24 (m, 3H), 1.07 – 0.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 145.2, 144.0, 143.9, 143.3, 138.1, 129.8, 129.0, 128.4, 128.0, 127.6, 127.4, 126.9, 122.8, 51.6, 41.9, 40.8, 32.7, 29.3, 28.4; HRMS (ESI) m/z: calcd for $C_{27}H_{23}Cl$ $[M+H]^+$: 383.1561; found: 383.1556.

(4aR, 9aS)-9-(diphenylmethylene)-5-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5f). white solid (yield: 131.6 mg, 63%); mp 109 – 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 6.97 (m, 11H), 6.89 (t, *J* = 7.9 Hz,1H), 6.54 (d, *J* = 8.1 Hz, 1H), 3.40 (d, *J* = 7.5 Hz, 1H), 3.30 (d, *J* = 7.3 Hz, 1H), 2.51 (s, 1H), 2.01 (s, 1H), 1.62 – 1.50 (m, 2H), 1.41 – 1.24 (m, 3H), 1.04 – 0.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.1, 143.8, 143.4, 143.1, 138.1, 129.1, 128.5, 127.8, 127.5, 127.1 (q, *J* = 31.3 Hz), 127.0, 126.4, 125.4(q, *J* = 5.0 Hz), 124.8(q, *J* = 273.6 Hz), 52.4, 51.0, 43.2, 41.8, 32.5, 29.8, 28.2; HRMS (ESI) m/z: calcd for $C_{28}H_{23}F_3$ $[M+H]^+$: 417.1825; found: 417.1820.

(4aR, 9aS)-9-(bis(3-methoxyphenyl)methylene)-5-methoxy-2,3,4,4a,9,9a-hexahy-dro-1H-1,4-methanofluorene (5g). white solid (yield: 142.5 mg, 65%); mp 141 – 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 6.61 (m, 9H), 6.53 (d, *J* = 8.0 Hz, 1H), 5.94 (d, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 6H) 3.22 (d, *J* = 7.1 Hz, 1H), 2.99 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 1H), 1.94 (s, 1H), 1.50 – 1.42 (m, 1H), 1.31 – 1.28 (m, 2H), 1.12 (d, *J* = 9.9 Hz, 1H), 0.95 – 0.91 (m, 1H), 0.81 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 157.2, 146.2, 145.7, 145.6, 145.2, 138.8, 137.1, 130.0, 128.2, 122.5, 117.9, 115.6, 112.6, 109.8, 56.1, 56.0, 52.6, 50.3, 42.6, 41.3, 33.4, 30.1, 29.5. HRMS (ESI) m/z: calcd for $C_{30}H_{30}O_3$ $[M+H]^+$: 439.2268;

found: 439.2263.

(4aR, 9aS)-9-(di-m-tolylmethylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5h). white solid (yield: 152.3 mg, 75%); mp 140 – 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 6.93 (m, 8H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 5.99 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 3.33 (d, *J* = 7.3 Hz, 1H), 3.11 (d, *J* = 7.3 Hz, 1H), 2.55 (d, *J* = 3.6 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 2.03 (s, 1H), 1.59 – 1.53 (m, 1H), 1.40 – 1.25 (m, 3H), 1.03 – 0.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 144.8, 144.4, 144.2, 143.7, 137.9, 137.7, 137.2, 129.7, 128.1, 127.8, 127.4, 127.3, 126.2, 117.1, 108.9, 55.2, 51.8, 49.5, 41.8, 40.6, 32.6, 29.4, 28.7, 21.7, 21.6; HRMS (ESI) m/z: calcd for $C_{30}H_{30}O$ $[M+H]^+$: 407.2369; found: 407.2377.

(4aR, 9aS)-9-(bis(3-chlorophenyl)methylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5i). white solid (yield: 159.0 mg, 71%); mp 167 – 169 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.40 – 6.95 (m, 8H), 6.84 (s, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.97 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.24 (d, *J* = 7.2 Hz, 1H), 3.07 (d, *J* = 7.2 Hz, 1H), 2.51 (d, *J* = 3.8 Hz, 1H), 1.94 (d, *J* = 3.7 Hz, 1H), 1.59 – 1.49 (m, 1H), 1.36 – 1.26 (m, 2H), 1.16 (d, *J* = 10.0 Hz, 1H), 1.03 – 0.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 146.8, 145.4, 144.8, 143.7, 138.5, 134.3, 133.6, 129.8, 129.2, 127.7, 127.6, 127.4, 127.0, 116.9, 109.6, 55.3, 51.9, 49.6, 41.9, 40.4, 32.6, 29.3, 28.6; HRMS (ESI) m/z: calcd for $C_{28}H_{24}Cl_2O[M+H]^+$: 447.1277; found: 447.1282.

(4aR, 9aS)-9-(bis(3-bromophenyl)methylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro -1H-1,4-methanofluorene (5j). white solid (yield: 155.3 mg, 58%); mp 163 – 165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.00 (m, 8H), 6.85 (t, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H),

5.97 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.24 (d, *J* = 7.2 Hz, 1H), 3.08 (d, *J* = 7.2 Hz, 1H), 2.52 (d, *J* = 3.8 Hz, 1H), 1.94 (d, *J* = 3.3 Hz, 1H), 1.61 – 1.52 (m, 1H), 1.38 – 1.27 (m, 2H), 1.16 (d, *J* = 10.6 Hz, 1H), 1.01 – 0.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 146.9, 145.7, 145.0, 143.6, 138.5, 133.4, 132.1, 130.5, 130.0, 129.9, 127.9, 127.7, 122.6, 116.9, 109.7, 55.3, 51.9, 49.6, 41.9, 40.4, 32.6, 29.3, 28.6; HRMS (ESI) m/z: calcd for $C_{28}H_{24}Br_2O$ $[M+H]^+$: 535.0267; found: 535.0274.

(4aR, 9aS)-9-(di-p-tolylmethylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5k). white solid (yield: 140.4 mg, 69%); mp 146 – 148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 6.91 (m, 8H), 6.72 (7, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 5.94 (d, *J* = 7.9 Hz, 1H), 3.73 (s, 3H), 3.23 (d, *J* = 7.4 Hz, 1H), 2.97 (d, *J* = 7.4 Hz, 1H), 2.42 (d, *J* = 3.8 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H), 1.91 (d, *J* = 3.8 Hz, 1H), 1.47 – 1.41 (m, 1H), 1.26 – 1.14 (m, 3H), 0.94 – 0.86 (m, 1H), 0.80 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 144.9, 144.3, 141.6, 141.0, 137.9, 136.8, 136.6, 136.0, 129.0, 128.9, 127.3, 117.1, 108.8, 55.2, 51.9, 49.6, 41.8, 40.7, 32.6, 29.4, 28.7, 21.5, 21.4; HRMS (ESI) m/z: calcd for $C_{30}H_{30}O$ $[M+H]^+$: 407.2369; found: 407.2361.

(4aR, 9aS)-9-(bis(4-fluorophenyl)methylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5l). white solid (yield:138.8 mg, 67%); mp 146 – 148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 3H), 7.17 – 6.90 (m, 5H), 6.85 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.00 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.26 (d, *J* = 7.3 Hz, 1H), 3.09 (d, *J* = 7.3 Hz, 1H), 2.54 (d, *J* = 3.8 Hz, 1H), 1.96 (d, *J* = 3.9 Hz, 1H), 1.63 – 1.51 (m, 1H), 1.42 – 1.27 (m, 2H), 1.21 (d, *J* = 10.0 Hz, 1H), 1.03 – 0.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.1 Hz), 161.6 (d, *J* = 245.9 Hz), 156.5, 145.7, 144.2, 140.1 (d, *J* = 3.3 Hz),

139.5 (d, *J* = 3.4 Hz), 138.2, 134.4, 130.8 (d, *J* = 7.9 Hz), 127.5, 116.8, 115.3 (d, *J* = 21.2 Hz), 109.3, 55.3, 51.9, 49.6, 41.7, 40.6, 32.6, 29.3, 28.6; HRMS (ESI) m/z: calcd for $C_{28}H_{23}F_2O$ $[M+H]^+$: 415.1868; found: 415.1873.

(4aR, 9aS)-9-(bis(4-bromophenyl)methylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro -1H-1, 4-methanofluorene (5m). white solid (yield: 149.1 mg, 55%); mp 163 – 165 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 6.93 (m, 8H), 6.85 (t, *J* = 8.0 Hz ,1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.04 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.24 (d, *J* = 7.2 Hz, 1H), 3.07 (d, *J* = 7.3 Hz, 1H), 2.51 (d, *J* = 3.8 Hz, 1H), 1.94 (d, *J* = 3.9 Hz, 1H), 1.60 – 1.48 (m, 1H), 1.43 – 1.27(m, 2H), 1.17 (d, *J* = 10.1 Hz, 1H), 1.03 – 0.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 146.2, 143.9, 142.8, 142.2, 138.4, 133.9, 131.6, 131.0, 127.7, 121.4, 120.8, 116.9, 109.5, 55.3, 52.0, 49.6, 41.8, 40.5, 32.6, 29.4, 28.7; HRMS (ESI) m/z: calcd for $C_{28}H_{24}Br_2O[M+H]^+$: 535.0267; found: 535.0275.

(4aR, 9aS, *Z*)-5-methoxy-9-(1-phenylethylidene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-meth-anofluorene (5n). white solid (yield: 99.5 mg, 63%); mp 178 – 180 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.17 (m, 5H), 6.73 (t, *J* = 8.0, Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.77 (d, *J* = 7.9 Hz, 1H), 3.81 (s, 3H), 3.17 (d, *J* = 7.2 Hz, 1H), 2.97 (d, *J* = 7.2 Hz, 1H), 2.56 (d, *J* = 3.5 Hz, 1H), 2.46 (d, *J* = 3.2 Hz, 1H), 2.18 (s, 3H), 1.67 – 1.55 (m, 2H), 1.51 – 1.39 (m, 2H), 1.17 – 1.11 (m, 1H), 1.03 – 0.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 145.5, 144.8, 142.0, 137.5, 131.9, 129.4, 127.8, 127.2, 116.7, 108.8, 55.6, 52.0, 49.9, 42.7, 40.6, 33.1, 29.5, 29.4, 25.2. HRMS (ESI) m/z: calcd for $C_{23}H_{24}O$ $[M+H]^+$: 317.1900; found: 317.1892.

(4aR, 9aS, *Z*)-9-(1-(3-chlorophenyl)ethylidene)-5-methoxy-2,3,4,4a,9,9a-hexahy-dro-1H-1,4-methanofluorene (5o). white solid (yield:130.2 mg, 74%); mp 121 – 123 ^oC; ^1H NMR

(400 MHz, $CDCl_3$) δ 7.34 – 7.07 (m, 4H), 6.78 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 5.82 (d, *J* = 7.9 Hz, 1H), 3.81 (s, 3H), 3.16 (d, *J* = 7.1 Hz, 1H), 2.95 (d, *J* = 7.1 Hz, 1H), 2.56 (s, 1H), 2.43 (s, 1H), 2.16 (s, 3H), 1.68 – 1.56 (m, 2H), 1.52 – 1.37 (m, 2H), 1.11 (d, *J* = 10.1 Hz, 1H), 0.98 (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 147.3, 144.2, 142.9, 137.7, 130.2, 127.9, 127.4, 116.6, 109.1, 55.7, 52.0, 49.9, 42.6, 40.5, 33.1, 29.5, 29.4, 24.9; HRMS (ESI) m/z: calcd for $C_{23}H_{23}ClO$ $[M+H]^+$: 351.1510; found: 351.1512.

(4aR, 9aS, *Z*)-9-(1-(4-chlorophenyl)ethylidene)-5-methoxy-2,3,4,4a,9,9a-hexahy-dro-1H-1,4-methanofluorene (5p). white solid (yield: 101.5 mg, 58%); mp 161 – 163 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.05 (m, 2H), 6.78 (t, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.84 (d, *J* = 7.9 Hz, 1H), 3.81 (s, 3H), 3.16 (d, *J* = 7.2 Hz, 1H), 2.94 (d, *J* = 7.1 Hz, 1H), 2.56 (d, *J* = 3.3 Hz, 1H), 2.43 (d, *J* = 2.9 Hz, 1H), 2.15 (s, 3H), 1.67 – 1.56 (m, 2H), 1.51 – 1.38 (m, 2H), 1.10 (d, *J* = 10.1 Hz, 1H), 1.00 – 0.93 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 144.1, 143.5, 142.4, 137.4, 132.6, 130.0, 129.4, 127.6, 116.3, 108.7, 55.3, 51.7, 49.6, 42.3, 40.2, 32.8, 29.2, 29.1, 24.7; HRMS (ESI) m/z: calcd for $C_{23}H_{23}ClO$ $[M+H]^+$: 351.1510; found: 351.1514.

(4aR, 9aS, *Z*)-5-methoxy-9-(1-(naphthalen-2-yl)ethylidene)-2,3,4,4a,9,9a-hexahy-dro-1H-1,4-methanofluorene (5q). white solid (yield: 115.5 mg, 63%); mp 177 – 179 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.29 (m, 7H), 6.64 (t, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 5.82 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 3.20 (d, *J* = 7.2 Hz, 1H), 3.04 (s, 1H), 2.59 (d, *J* = 2.6 Hz, 1H), 2.52 (s, 1H), 2.26 (s, 3H), 1.75 – 1.58 (m, 1H), 1.56 – 1.40 (m, 1H), 1.20 (d, *J* = 9.7 Hz, 1H), 1.03 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 144.3, 142.6, 142.2, 137.2, 134.2, 132.6, 131.3, 128.8, 128.2, 128.0, 127.6, 127.1, 126.9, 126.1, 125.8,

116.5, 108.5, 55.3, 51.9, 49.7, 42.4, 40.3, 32.9, 29.2, 29.1, 24.8; HRMS (ESI) m/z: calcd for $C_{27}H_{26}O$ $[M+H]^+$: 367.2056; found: 367.2049.

(4aR, 9aS)-5-methoxy-9-(1-(naphthalen-2-yl)vinyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5qq). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 4H), 7.49 – 7.46 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.42 (d, *J* = 1.3 Hz, 1H), 5.01 (s, 1H), 4.11 (d, *J* = 3.8 Hz, 1H), 3.90 (s, 3H), 3.24 (d, *J* = 7.7 Hz, 1H), 2.60 (d, *J* = 3.9 Hz, 1H), 2.26 – 2.17 (m, 1H), 1.62 – 1.53 (m, 1H), 1.52 – 1.41 (m, 1H), 1.40 – 1.29 (m, 1H), 1.22 (d, *J* = 10.0 Hz, 1H), 1.16 – 1.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 153.9, 149.3, 139.9, 135.0, 134.2, 133.6, 129.1, 128.9, 128.5, 128.4, 126.9, 126.6, 126.3, 118.2, 114.9, 109.1, 59.3, 55.9, 54.7, 53.7, 44.4, 41.2, 34.1, 29.9, 29.6; HRMS (ESI) m/z: calcd for $C_{27}H_{26}O$ $[M+H]^+$: 367.2056; found: 367.2050.

(4aR, 9aS, *Z*)-9-((4-chlorophenyl)(phenyl)methylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5r). white solid (yield: 140.1 mg, 68%); mp 221 – 223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 7H), 7.24 (d, *J* = 6.6 Hz, 2H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.07 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.29 (d, *J* = 7.2 Hz, 1H), 3.08 (d, *J* = 7.2 Hz, 1H), 2.52 (s, 1H), 1.97 (s, 1H), 1.59 – 1.51 (m, 1H), 1.40 – 1.27 (m, 2H), 1.21 (d, *J* = 9.9 Hz, 1H), 1.00 – 0.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 145.6, 144.2, 143.9, 142.2, 138.3, 135.3, 132.9, 129.2, 128.4, 127.6, 126.8, 116.9, 109.3, 55.3, 52.0, 49.6, 41.8, 40.5, 32.6, 29.4, 28.6; HRMS (ESI) m/z: calcd for $C_{28}H_{25}ClO$ $[M+H]^+$: 413.1667; found: 413.1661.

(4aR, 9aS, *E*)-9-((4-chlorophenyl)(phenyl)methylene)-5-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5s). white solid (yield: 101 mg, 49%); mp 146 – 148 °C; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 8H), 7.14 – 6.96 (m, 1H), 6.79 (t, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 5.93 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.26 (d, *J* = 7.3 Hz, 1H), 3.07 (d, *J* = 7.3 Hz, 1H), 2.51 (d, *J* = 3.9 Hz, 1H), 1.96 (d, *J* = 4.0 Hz, 1H), 1.62 – 1.45 (m, 1H), 1.40 – 1.25 (m, 2H), 1.20 (d, *J* = 10.1 Hz, 1H), 1.03 – 0.95 (m, 1H), 0.90 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 145.9, 144.8, 143.8, 143.2, 138.6, 135.8, 132.7, 131.0, 129.7, 129.0, 127.9, 127.7, 117.5, 109.7, 55.7, 52.3, 50.1, 42.3, 41.0, 33.1, 29.8, 29.1; HRMS (ESI) m/z: calcd for $C_{28}H_{25}ClO$ $[M+H]^+$: 413.1667; found: 413.1659.

(4aR, 9aS, *E*)-5-chloro-9-((4-chlorophenyl)(phenyl)methylene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5t). white solid (yield: 120.6 mg, 58%); mp 131 – 134 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.32 – 7.25 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.75 (t, *J* = 8.1 Hz, 1H), 6.23 (d, *J* = 7.9 Hz, 1H), 3.34 (d, *J* = 7.4 Hz, 1H), 3.13 (d, *J* = 7.4 Hz, 1H), 2.68 (d, *J* = 3.8 Hz, 1H), 2.02 (d, *J* = 3.9 Hz, 1H), 1.62 – 1.56 (m, 1H), 1.41 – 1.33 (m, 2H), 1.26 – 1.22 (m, 1H), 1.06 – 0.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 145.4, 145.1, 143.4, 142.8, 137.1, 133.0, 131.9, 130.9, 129.1, 128.6, 128.1, 128.0, 123.3, 52.1, 52.0, 42.3, 41.2, 33.1, 30.3, 28.9; HRMS (ESI) m/z: calcd for $C_{27}H_{22}Cl_2$ $[M+H]^+$: 417.1171; found: 417.1165.

(4aR, 9aS, *E*)-9-((4-chlorophenyl)(phenyl)methylene)-5,6-dimethyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (5u). white solid (yield: 113.3 mg, 55%); mp 141 – 143 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.01 (m, 9H), 6.56 (d, *J* = 8.1 Hz, 1H), 6.01 (d, *J* = 8.1 Hz, 1H), 3.24 (d, *J* = 7.3 Hz, 1H), 2.94 (d, *J* = 7.3 Hz, 1H), 2.29 (d, *J* = 3.2 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 1.91 (s, 1H), 1.53 – 1.43 (m, 1H), 1.33 – 1.23 (m, 2H), 1.19 (d, *J* = 8.3 Hz, 1H), 0.97 – 0.89 (m, 1H), 0.87 – 0.76 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 145.9,

144.0, 143.4, 140.9, 137.3, 134.4, 133.2, 132.5, 131.1, 129.7, 129.0, 128.7, 127.6, 122.2, 52.7, 51.9, 42.1, 42.0, 33.0, 30.1, 28.9, 20.3, 16.2; HRMS (ESI) m/z: calcd for $C_{29}H_{27}Cl$ $[M+H]^+$: 411.1874; found: 411.1873.

(7aS, 11aR, *E*)-7-((4-chlorophenyl)(phenyl)methylene)-7a,8,9,10,11,11a-hexa-hydro-7H-8,11-methanobenzo[c]fluorene (5v). white solid (yield: 112.5 mg, 52%); mp 218 – 220 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.34 (m, 6H), 7.29 (d, *J* = 8.1 Hz, 5H), 7.21 – 7.01 (m, 1H), 6.49 (d, *J* = 8.8 Hz, 1H), 3.48 (dd, *J* = 16.1, 7.1 Hz, 2H), 2.66 (d, *J* = 3.8 Hz, 1H), 2.06 (d, *J* = 4.2 Hz, 1H), 1.70 – 1.60 (m, 1H), 1.58 – 1.48 (m, 1H), 1.47 – 1.38 (m, 1H), 1.32 (d, *J* = 10.1 Hz, 1H), 1.16 – 1.06 (m, 1H), 0.97 (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 146.5, 143.8, 143.4, 140.7, 135.2, 134.0, 132.8, 131.2, 130.9, 129.0, 128.9, 127.9, 127.2, 126.6, 126.5, 125.2, 123.1, 53.3, 51.5, 42.6, 41.8, 33.3, 30.2, 29.1; HRMS (ESI) m/z: calcd for $C_{31}H_{25}Cl$ $[M+H]^+$: 433.1718; found: 433.1712.

2-((*E*)-((4aR, 9aS)-5-methoxy-2,3,4,4a-tetrahydro-1H-1,4-methanofluoren-9(9aH) –ylid-ene)(phenyl)methyl)thiophene (5w). Pale green solid (yield: 88.5 mg, 46%); mp 158 –160 ^oC; ^1H NMR (400 MHz, CDCl3) δ 7.49 – 7.40 (m, 3H), 7.38 – 7.33 (m, 1H), 7.30 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.96 (dd, *J* = 5.1, 3.8 Hz, 1H), 6.75 (t, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.49 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.54 (d, *J* = 7.0 Hz, 1H), 3.26 (d, *J* = 7.0 Hz, 1H), 2.60 (d, *J* = 3.6 Hz, 1H), 2.53 (d, *J* = 2.8 Hz, 1H), 1.71 – 1.64 (m, 1H), 1.63 –1.50 (m, 3H), 1.16 (d, *J* = 10.1 Hz, 1H), 0.98 (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 156.2, 146.5, 144.9, 144.3, 143.0, 137.9, 130.4, 129.8, 129.6, 129.4, 129.1, 127.9, 127.6, 127.5, 126.6, 125.4, 117.4, 109.1, 55.2, 52.1, 50.4, 42.0, 40.6, 32.9, 29.1, 29.0; HRMS

(ESI) m/z: calcd for $C_{26}H_{25}OS$ $[M+H]^+$: 385.1621; found: 385.1618.

2-((*E*)-(4-fluorophenyl) ((4aR, 9aS)-5-methoxy-2,3,4,4a-tetrahydro-1H-1,4- methano-fluoren-9(9aH)-ylidene)methyl)thiophene (5x). Pale green solid (yield: 98.4 mg, 49%); mp 176 – 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.17 –7.14 (m, 3H), 6.97 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.74 (dd, *J* = 3.7, 1.0 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 5.54 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.52 (d, *J* = 7.0 Hz, 1H), 3.25 (d, *J* = 7.0 Hz, 1H), 2.60 (d, *J* = 4.0 Hz, 1H), 2.51 (d, *J* = 3.5 Hz, 1H), 1.66 – 1.54 (m, 3H), 1.14 (d, *J* = 10.1 Hz, 1H), 0.98 (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.2 Hz), 156.3, 146.4, 144.9, 144.6, 138.9 (d, *J* = 3.5 Hz), 138.1, 132.1, 131.6, 128.4, 127.9, 127.6, 126.6, 125.5, 117.2, 116.1 (d, *J* = 21.5 Hz), 109.2, 55.3, 52.2, 50.4, 41.9, 40.6, 32.9, 29.1, 29.0; HRMS (ESI) m/z: calcd for $C_{26}H_{24}FOS$ $[M+H]^+$: 403.1526; found: 403.1521.

(*Z*)-5-methoxy-9-(4-methylbenzylidene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluore-ne-3-carbaldehyde (6a). yellow oil (yield: 137.7 mg, 80%); A major isomer. ^{1}H NMR (400 MHz, CDCl3) δ 9.75 (d, *J* = 1.4 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.92 (t, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 2H), 3.84 (s, 3H), 3.20 (d, *J* = 7.2 Hz, 1H), 3.05 (d, *J* = 7.0 Hz, 1H), 2.68 (s, 1H), 2.64 (d, *J* = 3.7 Hz, 1H), 2.59 – 2.53 (m, 1H), 2.40 (s, 3H), 2.15 – 2.01 (m, 1H), 1.72 – 1.60 (m, 1H), 1.20 (d, *J* = 11.5 Hz, 1H), 1.00 (d, *J* = 10.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 156.4, 146.1, 142.9, 137.1, 136.6, 135.2, 129.2, 128.6, 127.9, 124.0, 116.3, 109.7, 55.2, 53.7, 53.2, 49.2, 46.6, 39.8, 30.5, 30.3, 21.4; HRMS (ESI) m/z: calcd for $C_{24}H_{24}O_2$ $[M+H]^+$: 345.1849; found: 345.1841.

(*Z*)-5-methoxy-9-(4-methylbenzylidene)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene-3-carbonitrile(6b). white solid (yield: 139.9 mg, 82%); A major isomer. ^{1}H NMR (400 MHz, CDCl3) δ 7.26 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.95 (t, *J* = 7.9 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.71 – 6.59 (m, 2H), 3.84 (s, 3H), 3.52 (d, *J* = 7.0 Hz, 1H), 3.27 (d, *J* = 7.1 Hz, 1H), 2.93 (d, *J* = 6.0 Hz, 1H), 2.89 – 2.79 (m, 2H), 2.41 (s ,3 H) 2.12 – 2.01 (m, 1H), 1.82 – 1.74 (m, 1H), 1.11 (d, *J* = 10.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 144.5, 141.7, 135.5, 135.4, 133.9, 128.0, 127.4, 127.0, 126.9, 123.2, 115.2, 108.6, 54.1, 47.7, 47.5, 47.0, 38.8, 34.3, 31.9, 28.1, 20.3; HRMS (ESI) m/z: calcd for $C_{24}H_{23}NO$ $[M+H]^+$: 342.1852; found: 342.1845.

(*Z*)-4-methoxy-11-(4-methylbenzylidene)-5,10,10a,11-tetrahydro-4bH-5,10-epoxybenzo[b]fluorine (6c). white solid (yield: 102.5 mg, 56%); mp 213 – 215 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.18 (m, 4H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.87 – 6.84 (m, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.45 (s, 1H), 5.40 (s, 1H), 3.92 (s, 3H), 3.48 (d, *J* = 6.8 Hz, 1H), 3.23 (dd, *J* = 6.8, 1.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 146.4, 145.6, 143.7, 143.6, 136.8, 135.0, 134.4, 129.2, 128.7, 128.6, 126.9, 126.8, 124.7, 119.8, 119.4, 116.8, 109.8, 87.2, 81.9, 55.4, 53.0, 48.9, 21.4; HRMS (ESI) m/z: calcd for $C_{26}H_{22}O_2$ $[M+H]^+$: 367.1693; found: 367.1697.

12-(4-methylbenzylidene)-5a,5b,6,11,11a,12,12a,13-octahydro-5H-5,13:6,11-diepoxydibenzo[b,h]fluorine (6c'). white solid (yield: 42.4 mg, 21%); mp 275 – 277 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.27 – 7.22 (m, 3H), 7.18 (dd, *J* = 4.9, 3.4 Hz, 4H), 6.64 (s, 1H), 5.29 (s, 2H), 5.25 (s, 1H), 5.15 (s, 1H), 3.65 (d, *J* = 7.5 Hz, 1H), 3.27 (d, *J* = 7.5 Hz, 1H), 2.58 (dd, *J* = 7.5, 2.9 Hz, 1H), 2.44 (dd, *J* = 7.5, 2.9 Hz, 1H),

2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 145.8, 145.6, 145.5, 145.4, 136.6, 134.8, 129.4, 128.6, 127.0, 126.9, 126.8, 126.7, 124.6, 119.6, 119.4, 118.8, 88.2, 86.2, 86.1, 84.2, 59.9, 55.3, 53.7, 51.3, 21.4; HRMS (ESI) m/z: calcd for $C_{29}H_{24}O_2$ $[M+H]^+$: 405.1849; found: 405.1856.

(*Z*)-5-methoxy-9-(4-methylbenzylidene)-4,4a,9,9a-tetrahydro-1H-1,4-methanofluorene (6d). white solid (yield: 105.2 mg, 67%); mp 106 – 108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 2H), 6.35 (dd, *J* = 5.5, 2.9 Hz, 1H), 6.24 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.85 (s, 3H), 3.19 (d, *J* = 7.0 Hz, 1H), 3.08 (s, 1H), 3.01 (d, *J* = 6.9 Hz, 1H), 2.87 (s, 1H), 2.39 (s, 3H), 1.33 – 1.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 147.9, 144.2, 138.8, 137.4, 136.4, 134.8, 134.5, 129.4, 128.8, 128.6, 119.9, 112.4, 109.3, 55.3, 49.5, 49.2, 45.8, 45.5, 42.9, 21.4; HRMS (ESI) m/z: calcd for $C_{23}H_{22}O$ $[M+H]^+$: 315.1743; found: 315.1751.

(10*Z*,12*Z*)-4,6-dimethoxy-10,12-bis(4-methylbenzylidene)-4b,5,5a,10,10a,11,11a,12-octahydro-5,11-methanoindeno[2,1-b]fluorine (6e). white solid (yield: 139.4 mg, 52%); mp 220 – 223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.9 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 7.7 Hz, 2H), 6.74 (s, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 3.91 (s, 6H), 3.45 (d, *J* = 7.1 Hz, 2H), 3.16 (d, *J* = 7.1 Hz, 2H), 2.91 (s, 1H), 2.46 (s, 1H), 2.42 (s, 6H), 1.02 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 155.4, 145.7, 145.5, 145.6, 144.7, 142.1, 136.7, 136.5, 135.3, 134.4, 134.1, 133.5, 128.2, 128.0, 127.7, 127.5, 127.4, 126.6, 126.5, 122.5, 122.3, 118.6, 115.2, 110.8, 108.6, 108.3, 54.3, 51.9, 51.5, 50.4, 49.1, 48.6, 48.1, 47.4, 42.5, 26.0, 20.2; HRMS (ESI) m/z: calcd for $C_{39}H_{36}O_2$ $[M+H]^+$: 537.2788; found: 537.2779.

(*Z*)-5-methoxy-9-(4-methylbenzylidene)-1,3a,4,4a,9,9a,10,10a-octahydro-4,10-methanocyclopenta[b]fluorine (6f). white solid (yield: 113.3 mg, 64%); mp 150 – 151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.10 (m, 4H), 6.88 (s, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 5.82 (d, *J* = 9.8, 2H), 3.85 (s, 3H), 3.38 (d, *J* = 6.2 Hz, 1H), 3.32 (d, *J* = 6.4 Hz, 1H), 3.26 – 3.19 (m, 1H), 2.72 (d, *J* = 4.5 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.48 – 2.45 (m, 1H), 2.39 (s, 3H), 2.29 (d, *J* = 3.6 Hz, 1H), 1.20 – 1.08 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 147.6, 146.7, 136.2 136.1, 134.8, 132.8, 131.0, 129.2, 128.7, 128.1, 119.1, 111.9, 109.3, 55.3, 53.4, 46.6, 44.8, 43.3, 42.3, 36.1, 32.3, 21.4; HRMS (ESI) m/z: calcd for $C_{26}H_{26}O$ $[M+H]^+$: 355.2056; found: 355.2051.

(*Z*)-5-methoxy-9-(4-methylbenzylidene)-3,3a,4,4a,9,9a,10,10a-octahydro-4,10-methanocyclopenta[b]fluorine (6g). white solid (yield: 56.6 mg, 32%); mp 138 – 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.13 (m, 4H), 6.84 (s, 1H), 6.69 (d, *J* = 7.4, 1H), 5.82 (d, *J* = 9.2, 2H), 3.84 (s, 3H), 3.43 (d, *J* = 6.8 Hz, 1H), 3.33 (d, *J* = 6.8 Hz, 1H), 3.16 – 3.10 (m, 1H), 2.72 – 2.64 (m, 1H), 2.58 – 2.47 (m, 3H), 2.43 – 2.38 (m, 1H), 2.37 (s, 3H), 1.21–1.06 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 146.5, 145.6, 135.0, 134.8, 133.7, 131.0, 130.6, 128.0, 127.5, 126.9, 117.7, 110.8, 108.1, 54.1, 52.1, 45.2, 43.8, 42.6, 41.7, 41.1, 34.9, 31.2, 20.2; HRMS (ESI) m/z: calcd for $C_{26}H_{26}O$ $[M+H]^+$: 355.2056; found: 355.2059.

ASSOCIATED CONTENT

Supporting Information.

supplementary experimental data. Copies of ^{1}H and ^{13}C NMR spectra for all products and X-ray structural information for **5a**, **5n**, **5v**, **5w**, **6f**, **6g** (PDF).

CIF data for **5a**, **5n**, **5v**, **5w**, **6f, 6g** (CIF).

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