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Cross-dimerization of fluorenones for synthesis of dibenzo[*g,p*]chrysenes

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ABSTRACT

Cross-dimerization reactions that employ nonequivalent 9-fluorenones have been accomplished. This *cross*-dimerization doesn't employ any additives such as metals and salts, that was unthinkable heretofore. Because the *cross*-couplings were achieved by phosphite solvent alone, they were not only operationally simple but also productively efficient owing to suppression of *homo*-dimerization. Significantly, the resulting single spiroketones were transformed into a hexacycle core of dibenzo[*g,p*]chrysene having twofold *tert*-butyl groups and twofold halogen atoms. The synthesis of solution-processable and multi-tunable hexacycle, coupled with the mechanistic aspects, enables general access to non-planar polyarenes from the viewpoint of diversity-oriented synthesis.

1. Introduction

Controlling selectivity in organic reactions is an ongoing quest in chemistry. When the reaction system brings two different reactants together to result in a dimerization event, there is a selectivity problem with *homo*- and *cross*-adducts. *Cross*-dimerization is addressed by transition metal catalysis and organocatalysis that have been well developed over the past decades, which enables diversity-oriented synthesis and increases molecular diversity [1,2]. Nowadays the catalytic *cross*--coupling protocols are indispensable for modern synthetic organic chemistry, whereas it still awaits full accomplishment from the viewpoint of green chemistry [3,4]. For game-changing production of *cross*-adduct materials, alternative methodology is strongly desirable: for example, metal-free yet efficient *cross*-coupling system between two nonequivalent molecules is expected [5–7].

Non-planar polyarene is one of the functional organic materials those would be applicable to ongoing research and future technology, in which the effect of non-planarity appears in opto-electrical characteristics [8-10]. Among such a type of polyarenes, one of the most attractive fused-rings is a dibenzo[*g,p*]chrysene (DBC) that features helically distortion, four-quadrant symmetry, and compact hydrocarbon. For example, we give a description of two DBCs that clearly exhibit the significant non-planar pi-conjugation (Fig. 1): Thus, twisted structures are evident in a side view from a *cove* or *bay* area [11]. Chemists have tried to synthetically functionalize the DBC core to set up molecular diversity for tuning properties. However, most of the reported methods generally involve multiple metal-mediated coupling reactions that tend to face step-by-step procedures and relay on expensive starting compounds [12,13]. DBCs in particular those that lack symmetry take significant effort to prepare.

Here we report metal-free cross-dimerization between two different carbonyl compounds that afford a hexa-arene DBC core (Scheme 1). When fluorenones **1** and **2** are heated in triisopropyl phosphite (P(O*i*Pr)$_3$), the *cross*-coupling which gave spiroketone **3** as a single isomer with significant suppression of *homo*-adducts **4** and **5** was achieved. The following two-step conventional transformation (reduction, then rearrangement) yielded DBC having two *tert*-butyl groups and two bromine atoms. Of note is that the materials at each stage retain significant solubility in organic solvents owing to the two *tert*-butyl groups.

2. Results and discussion

2.1. Cross-dimerization between fluorenones 1 and 2

This result came from an exploration of a good fluorenones combination under P(O*i*Pr)$_3$ solvent condition. We previously reported that *homo*-dimerization of two fluorenones in heating P(O*i*Pr)$_3$ produced the corresponding spiroketone [14]. In this work, our preliminary results after several tests reached an initial starting point for study. Entry 1 in Table 1: 2,7-di-*tert*-butyl-9-fluorenone **1** and 2,7-dibromo-9-fluorenone

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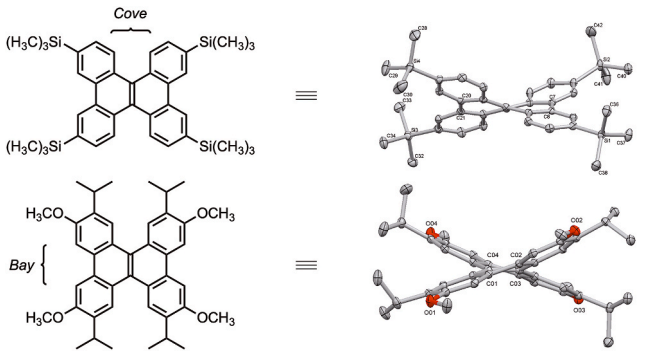
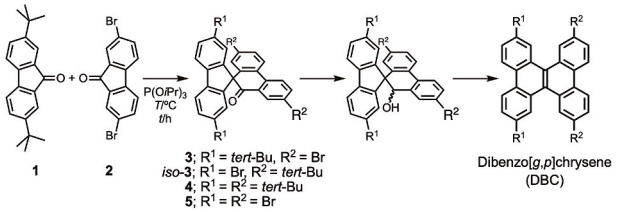


Fig. 1. Non-planar pi-conjugation of DBC cores: For example, conjugated pi-systems in two molecules that we previously reported are distinctly twisted in a side view from a *cove* or a *bay* area (red for oxygen atoms). [11]



Scheme 1. *Cross*-dimerization between 2,7-di-*tert*-butyl-9-fluorenone **1** and 2,7-di-bromo-9-fluorenone **2** to produce spiroketones of *cross*-auct **3**, and *homo*-aucts **4** and **5**. The following two-step access, including a reduction and a rearrangement, to dibenzo[*g*,*p*]chrysene (DBC) derivatives.

Table 1
Evaluation of reaction conditions conducted *via* Scheme 1. [a].

Entry	*T*/°C	*t*/h	Yield/%				
			1 [b] [d]	2 [b] [d]	3 [c] [d]	4 [b] [e]	5 [b] [e]
1	95	24	7	0	48	5	1
2	110	3	35	0	58	1	7
3	140	1	29	0	50	4	11

[a] Conditions: **1** (439 mg, 1.5 mmol), **2** (507 mg, 1.5 mmol), $P(OiPr)_3$ (10 mL). Reactions were stopped when **2** disappeared in TLC monitoring.
[b] Determined by ^1H NMR analysis of mixtures those consisted of just **1**, **3**, **4**, and **5**. The mixtures were obtained by silica-gel short-plugged column chromatography of crude samples.
[c] Isolated yields after silica-gel column chromatography.
[d] Numbers of %Yield are the proportion to 1.5 mmol (100%).
[e] Numbers of %Yield are the proportion to 0.75 mmol (100%).

2 were coupled at 95 °C to yield *cross*-adduct **3** in 48% with *homo*-adduct **4** in 5% and **5** in 1%. Increase of the temperature to 110 °C and 140 °C shortened reaction times, and made yields of **3**, **4** and **5** largely unchanged, in which **1** remained while **2** disappeared (entries 2 and 3). Of important is to note that *cross*-adduct **3** appeared singly without production of *iso*-**3**. The molecular structure of **3** was determined with crystallographic analysis (Fig. 2) [15]. The ketone moiety was preferentially tethered to an aromatic ring having a bromine atom.

Encouraged by this selective transformation, we pursued increasing production of **3** and studied the effect of 2,7-dihalogenated fluorenones according to Scheme 2. For entry 1 of Table 2, high-yielding and multigram transformation was achieved with 70% yield (7.7 g) of **3**. On larger scale, using employment of 1.2 equiv of **2** reduced the unreacted-**1** to less than 5% and byproduct-**4** to less than 5%. Further, this enabled us to greatly simplify purification by simple washing of crude materials with methanol to give only **3** and **5** (**1** and **4** being soluble in the filtrate). For entries 2 and 3, diiodo- and dichloro-substrates yielded spiroketones **6** and **7** in 80% and 76% yield, respectively. The corresponding isomers

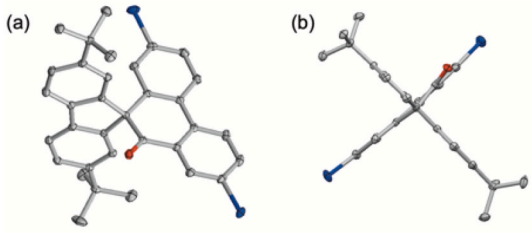
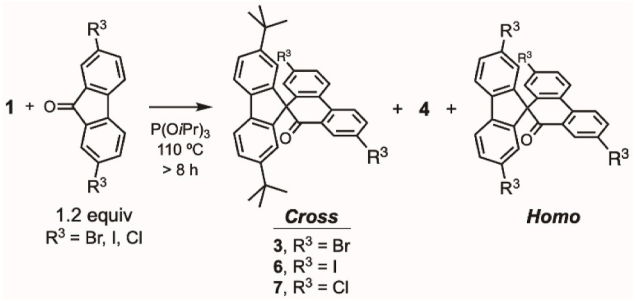


Fig. 2. Molecular structures with ORTEP drawing of **3** with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity), and red of oxygen and blue of bromine; (a) side view; (b) top view.



Scheme 2. Effect of 2,7-disubstituted fluorenones (R^3=Br, I, Cl) on the *cross*-dimerization with **1**. *Cross*-aucts **6** and **7** were singly formed in high yields, and *homo*-aucts resulted in low yield. The stereochemistry of **6** and **7** was inferred from evidence of ORTEP drawing in Fig. 2.

Table 2
Evaluation of substituents (R^3) conducted *via* Scheme 2.

Entry	R^3	Yield/% [c]		
		Cross [d] [e]	4 [f]	*Homo* [f]
1 [a]	Br	**3**, 70 (7.7 g)	<5	**5**, <5
2 [b]	I	**6**, 80	3	0
3 [b]	Cl	**7**, 76	5	0

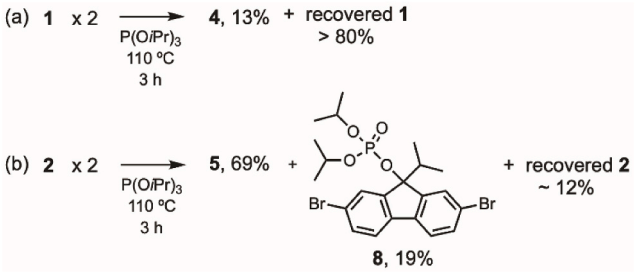
[a] Conditions: **1** (5.3 g, 18 mmol), **2** (7.3 g, 22 mmol), $P(OiPr)_3$ (9.8 mL, 43 mmol).
[b] Conditions: **1** (440 mg, 1.5 mmol), counter-fluorenone (1.8 mmol), $P(OiPr)_3$ (4.0 mL, 18 mmol).
[c] Isolated yields after silica-gel column chromatography.
[d] Yields are the proportion to 18 mmol for entry 1 and 1.5 mmol for entries 2–3.
[e] The stereochemistry of **6** and **7** was inferred from evidence of ORTEP drawing in Fig. 2.
[f] Yields are the proportion to 9 mmol for entry 1 and 0.75 mmol for entries 2–3.

were not observed at all, and the only *homo*-adduct **4** was found in 3–5% yield. Thus, halogen atoms of R^3 drove the dimerization to occur in *cross*-coupling mode.

2.2. Development of understanding the cross-dimerization

To understand the reaction system, control experiments of *homo*-dimerization of **1** and **2** were performed at 110 °C for 3 h, respectively (Scheme 3): Although unreacted **1** remained in 87% yield (part (a)), most of the starting **2** was consumed and dimer **5** was observed in 69% yield (part (b)). In part (b), we interestingly found a noticeable side-product **8** in 19% yield: Its structure was identified as illustrated. Formation of **8** was caused presumably due to phosphation process which was reported by Shah and co-workers [16–18]. Obviously, **2** is more reactive than **1** in this reaction system.

Do the two halogen atoms of **2** serve as essential groups? We tested a

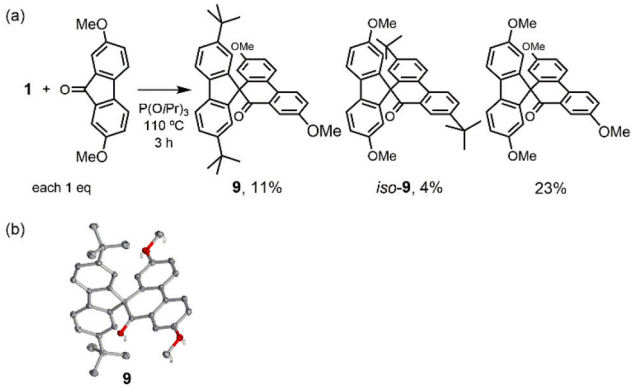


Scheme 3. Control experiments of *homo*-dimerization of (a) 2,7-di-*tert*-butyl-9-fluorenone **1** and, (b) 2,7-di-bromo-9-fluorenone **2**. Side-product of **8** was observed.

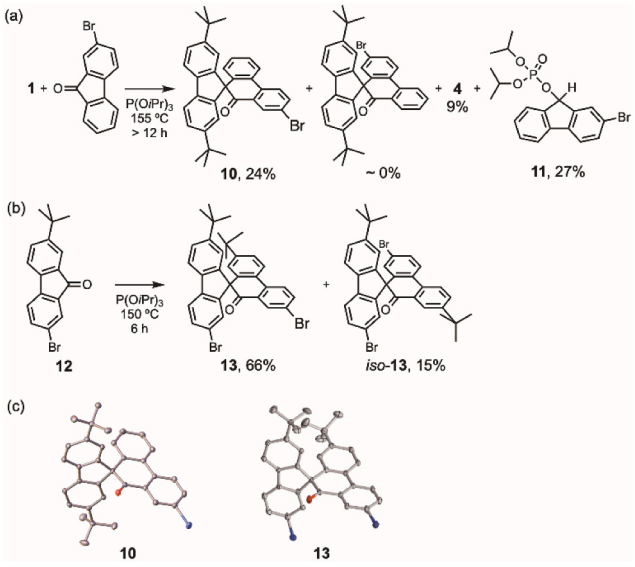
fluorenone having two methoxy moieties, instead of the halogens in **2**, on the *cross*-dimerization with **1** (Scheme 4). The reaction conducted at 110 °C for 3 h, which yielded *cross*-aucts **9** in 11% and *iso*-**9** in 4% along with 23% of the *homo*-auct having fourfold methoxy groups (part (a)). The structure of **9** was determined by crystallographic analysis (part (b)) [19]. The methoxy moieties lead lower productivity, compared with **2**. Thus, two halogens of **2** can be regarded as crucial substituents.

Continuing on, we pursued to consider that the *cross*-dimerization between **1** and **2** prefers **3** to *iso*-**3**. We conducted two experiments: One is a *cross*-dimerization utilizing 2-bromo-fluoren-9-one that lacks one bromine atom in comparison with **2** (Scheme 5(a)), and the other is a *homo*-dimerization of **12** that has a *tert*-butyl group and a bromine (Scheme 5(b)) [(11b)]. For part (a), the reaction required harsh condition of 155 °C for dimerization progress, wherein only one of the three possible *cross*-adducts was formed in 24% yield of **10** and the only one *homo*-adduct **4** was observed in 9% yield. Interestingly, a considerable amount of phosphate **11** was observed. For part (b), the *homo*-dimerization preferred yielding **13** in 66% to producing *iso*-**13** in 15%. The molecular structures of **13** as well as **10** were unequivocally determined by crystallographic analysis (Scheme 5(c)), which revealed that both **10** and **13** are structured around the *meta*-positioned keto-bromoarene [20,21]. This substructure was also recognized in **3** as shown in Fig. 2. Thus, the *meta*-keto-bromoarene formation is a commonly favorable in a series of *cross*-couplings.

The reaction mechanism resulting in high stereochemical control to produce predominantly *cross*-adducts is not yet fully known: On the other hand, based on the aforementioned experimental results, we have begun to grasp the mechanism, albeit in a vague manner. We prepared an illustration of Fig. 3 that is grounded in previous reports of *homo*-dimerization of 9-fluorenones [14] [16-18]. For upper scheme of part (a), as di-bromide **2** is more reactive to P(O*i*Pr)$_3$ than di-*tert*-butyl **1**, the



Scheme 4. (a) *Cross*-dimerization of **1** with 2,7-di-methoxy-9-fluorenone to give **9** and *iso*-**9**; (b) ORTEP drawing of **9** with thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity. Gray, carbon. Red, oxygen.).



Scheme 5. (a) *Cross*-dimerization between **1** and 2-bromo-fluoren-9-one; (b) homo-dimerization of **12**, and (c) ORTEP drawing of **10** and **13** with thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity. Red of oxygen, and blue of bromine).

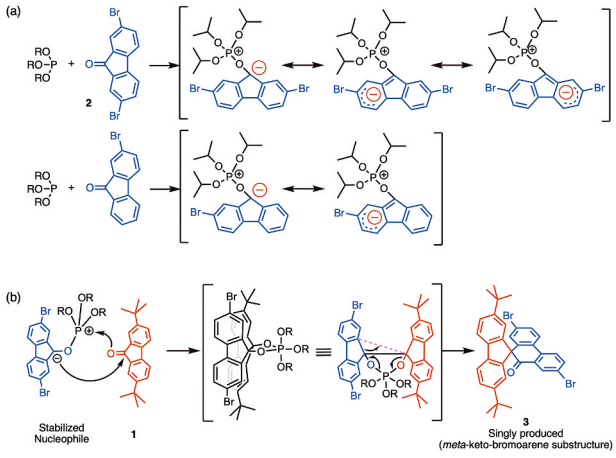


Fig. 3. (a) Upper scheme shows three resonance forms of oxy-phosphonium betaines generated from **2**, and lower scheme displays two resonance form of the betaines generated from 2-bromo-9-fluorenone; (b) plausible path to the single production of **3** *via* phosphorane intermediate that is caused by the reaction between **1** and the stabilized nucleophilic carbanion of the betaine.

oxy-phosphonium betaine was predominantly derived from **2** along with three possible resonance forms. On the other hand, for lower scheme, the carbanion of the betaine would be stabilized between only two resonance forms owing to the single bromine atom. This delocalization effect is the reason why two bromine atoms of **2** are indispensable for clean productive *cross*-dimerization. The betaine stability would make difference in the side-product structures between **8** and **11**, wherein the benzylic carbon of **8** doesn't have a proton but that of **11** has one proton. For part (b), the above-mentioned stabilized betaine attacks the carbonyl carbon of inert **1** to cause the *cross*-dimerized event, which would build a penta-oxy-phosphorane conformer. In the phosphorane, pinacol type-rearrangement of aromatic ring relevant to the product **3** occurs exclusively. Considering that the *meta*-keto-bromoarene substructures were formed predominantly, we aren't entirely convinced, but speculate the bromoarene moiety may positively migrate.

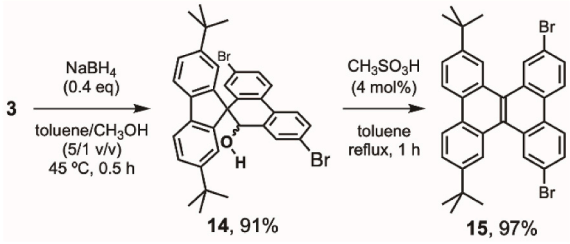
2.3. Construction of DBCs 15–27

With a new, multigram scale synthesis of spiroketone **3**, we applied it to the synthesis of a new DBC **15** (Scheme 6). **3** was subjected to reduction by $NaBH_4$, giving the alcohol **14** in 91% yield. **14** undertook Wagner-Meerwein rearrangement in the presence of catalytic methanesulfonic acid, forming **15** in 97% yield. **15** is an intriguing DBC that acquires solubility by two *tert*-butyl groups and reactivity by two bromine atoms.

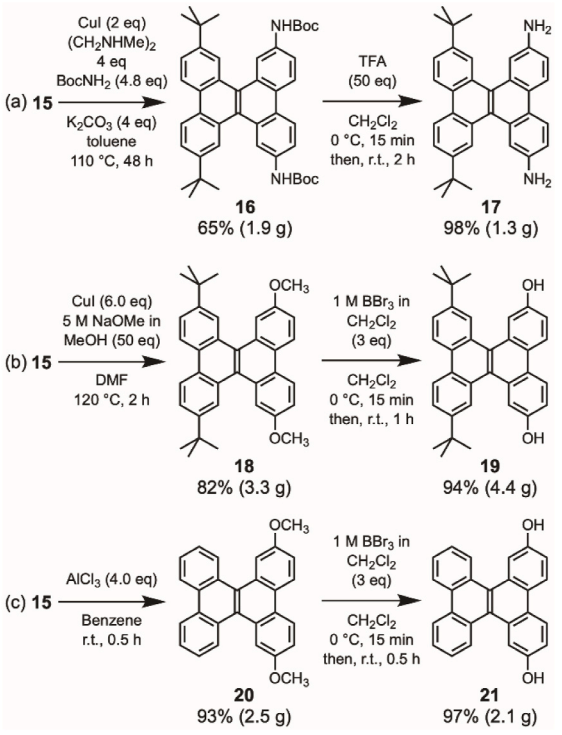
Substitution reactions at the two bromines for amine and hydroxy groups were carried out (Scheme 7). Firstly, in part (a), copper-mediated amidation of **15** afforded **16** in 65% yield, and the following removal of Boc-protection by TFA (trifluoroacetic acid) gave diamine **17** in 98% yield [22]. Secondly, in part (b), copper-mediated etherification of **15** yielded **18** in 82% yield, which was followed by demethylation using BBr_3 to lead diol **19** in 94% yield [23]. Thirdly, in part (c), successful dealkylation of **15** by $AlCl_3$ was achieved in 93% yield of **20**, and the following demethylation by BBr_3 was also successful in 97% yield of **21**. Each derivative in the sequence was readily soluble and could be elaborated on multi-gram scale.

We further investigated peripheral reactivity of our solution-processable DBC core (Scheme 8). Using **18**, the catalytic alkylation to **22** in 83% yield was followed by demethylation to **23** in 80% and bromination to **24** in 67% and methylation to **25** in 70%. The activation of two bromine atoms of **25** was carried out through the lithiation: Dimethyl disulfide reacted to afford **26** in 89% yield, although diphenyl disulfide and di-*tert*-butyl disulfide were not substituted presumably due to the steric hindrance. Finally, **26** undertook oxidation to form sterically demanding bis-sulfone **27** in 79% yield. The molecular structure of **27** was elucidated by crystallographic analysis, exhibiting its torsion angle of 39.84 (17)° (Fig. 4) [24]. Thus, **18** was amenable to the solution-phase transformations with regio-selective manner even in its overcrowded *cove* regions, which provides an opportunity of creating a group of polyarene molecules previously unattainable.

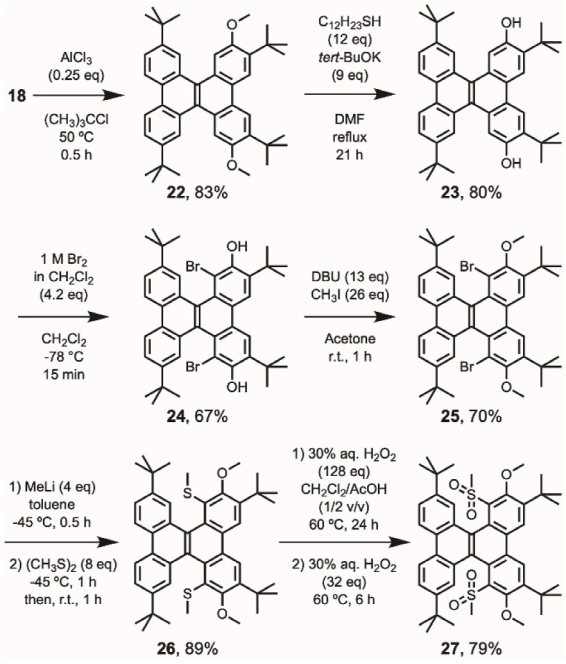
Such a congested architecture drove us to check if **27** has a chiral motif or not: the twisted geometry may increase the energetic barrier for the interconversion between the two enantiomeric forms. Actually, the enantiomers of **27** were partially separated using DAICEL CHIRALPAK ID3; however, the chromatograms of **27** revealed that racemization of the both enantiomers occurred during HPLC analysis at 25 °C [25,26]. Namely, a plateau peak was present between the two enantiomers' peaks in the chromatograms; the ratio of the peak areas was dependent on the temperature, and as increasing temperature, the plateau peak increased. We changed the flow rate (0.2–1.0 mL) to extend the retention (racemization) time and performed the analysis at 27 °C, 31 °C and 41 °C (Figs. S1–S3). We roughly integrated the areas of three peaks, assigning the plateau and the two peaks to the racemized and the non-racemized species, respectively. Racemization time is defined as the average value of retention time of both enantiomers. The plots of the ratios of the non-racemized species provided a first-order curve (Fig. 5): We obtained the rate constants k 0.000429 and 0.000674 at 27 °C and 31 °C, from the slope of the straight line of the plot of ln [(peak area of enantiomers)/(all area)] with respect to time; we calculated the activation free energy of racemization process ($\Delta G^{\ddagger}$) of 92.8 and 93.0 kJ/mol (~22.2 kcal/mol) at 27 °C and 31 °C, respectively. This value is comparable to the $\Delta G^{\ddagger}$ of 24.1 kcal/mol in [5]helicene at the ambient temperature [27], which means the inversion barrier of **27** is so small that its enantiomers are configurationally unstable.



Scheme 6. Synthetic development of alcohol **14** and DBC **15**.



Scheme 7. Synthetic development of molecular scaffold **15**. Synthesis of (a) diamide **16** and diamine **17**, and (b) diether **18** and diol **19**, and (c) dealkylated **20**, and demethylated **21**. TFA, trifluoroacetic acid. Boc, *tert*-butoxycarbonyl.



Scheme 8. Latent reactivity of **18**: regio-selective substitution reactions proceeded, providing new DBC derivatives 22–27.

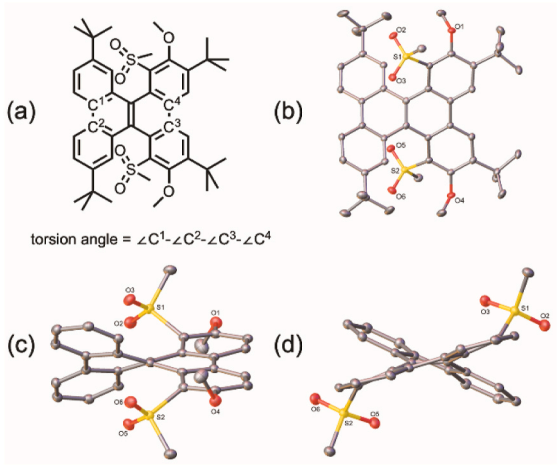


Fig. 4. Molecular structures with ORTEP drawing of **27** with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity), and red of oxygen and yellow of sulfur; (a) torsion angle determined by the four carbon atoms of C^1, C^2, C^3, and C^4; (b) top view; (c) side view from a *cove* region with torsion angle 39.84 (17)° (*tert*-butyl groups are removed for ease of viewing); (d) side view from a *bay* region (*tert*-butyl groups and methoxy moieties are removed for ease of viewing).

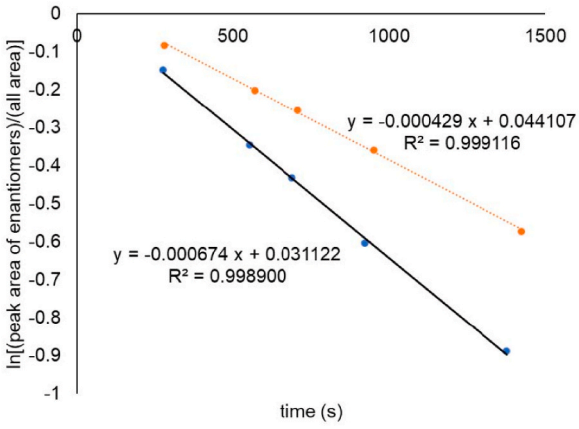


Fig. 5. First-order plots for racemization reaction of **27** under HPLC conditions at 27 °C and 31 °C. We calculated the activation free energy of racemization process ($\Delta G^{\ddagger}$) from the plot and the next equation. $\Delta G^{\ddagger} = -RT \times \ln(k \times h/k_B \times T)$, k: rate constant, k_B: Boltzmann constant, h: Planck constant.

3. Conclusion

In conclusion, the P(O*i*Pr)$_3$ solvent-driven *cross*-coupling stands alone in the area of polycyclic aromatic hydrocarbon syntheses. Two different fluorenones in which one has two *tert*-butyl groups and the other possesses two halogen atoms, provide a new opportunity of selective *cross*-couplings. Moreover, the resultant *cross*-adduct was formed as a single isomer. The results suggest three salient features: One, a difference in reactivity toward P(O*i*Pr)$_3$ between two fluorenones conducts the selective and productive reactions. Two, crystallographic analyses clarified that the *cross*-coupled spiroketones preferentially form into keto-haloarene substructures. Three, the resultant spiroketone was transformed into a skeletal dibenzo[*g,p*]chrysene, and the hexacycle was so solution-compatible that we demonstrated its synthetic versatility and approached an enantiomeric question connected with inversion barrier. Development of other possible synthetic and material advantages will be reported in due course.

Deposition Numbers 2093667 (for **3**), 2079414 (for **9**), 2242974 (for **10**), 2129618 (for **13**), and 2260286 (for **27**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Center and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

4. Experimental section

4.1. General

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. All reactions were carried out under an argon or a nitrogen atmosphere in dried glassware using standard vacuum-line technique, unless otherwise noted. When reactions required heating, oil bath apparatuses were employed. All work-up operation and purification procedures were carried out with reagent-grade solvent in air, and analytical thin layer chromatography was carried out on Merck silica 60F_{254} pre-coated plates. The developed chromatogram was analyzed by UV lamp (254 nm or 354 nm). Flash column chromatography was carried out with silica gel 60 $_N$ (Kanto Chemical Co.). All melting points were recorded on the melting point apparatus of "Stanford Research Systems OptiMelt" and are not corrected. IR spectra were reported with a JASCO FT/IR-6000 infrared spectrometer and the data are expressed in cm^{-1}. High-resolution mass spectra (HRMS) were determined on the basis of TOF (time of flight)-MS (LCMS-IT-TOF), and DART (Direct Analysis in Real Time)-MS. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECZ400S (^{1}H 400 MHz and ^{13}C 100 MHz and ^{31}P 162 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CHCl_3$ (7.26), CH_2Cl_2 (5.32), DMSO (2.50). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (77.0), CD_2Cl_2 (53.8), [D6]-DMSO (39.5). Data are reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constants (Hz), and integration.

4.2. Synthesis of 2,7-di-tert-butyl-9H-fluoren-9-one (1) [28], for Scheme 1

2,7-di-*tert*-butyl-9H-fluorene (8.4 g, 30 mmol) was added to the solution of $FeCl_3{\cdot}6H_2O$ (1.6 g, 6.0 mmol) in pyridine (60 mL), and *tert*-butyl hydroperoxide (TBHP, 70% in H_2O, 12 mL, 90 mmol) was added over 5 min. After the mixture was heated at 80 °C for 1 h, aitional TBHP (4.2 mL, 30 mmol) was poured over 5 min, and the reaction was conducted for further 12 h. Then, the mixture was allowed to cool to room temperature and filtered through a pad of Celite and silica-gel (CH_2Cl_2), and the filtrate was evaporated off. The resultant residue was diluted with CH_2Cl_2, which was transferred into a 100 mL separatory funnel, and washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give crude products. Purification by short-plugged silica-gel column chromatography (Hexane/CH_2Cl_2, 2:1) yielded 7.9 g of **1** in 90% (CAS# 58,775-13-6) as yellow solid materials. Rf value 0.28 (Hexane/EtOAc, 19:1); M. p. 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.69 (d, $J = 1.4$ Hz, 2H, H-1), 7.48 (dd, $J = 7.8$, 1.4 Hz, 2H, H-3), 7.39 (d, $J = 7.8$ Hz, 2H, H-4), 1.34 (s, 18H, CH_3) ppm.

4.3. Representative procedure for the cross-dimerization between 1 and 2, for Table 2, entry 1

1 (5.3 g, 18 mmol) and **2** (7.3 g, 22 mmol) were suspended in P(O*i*Pr)$_3$ (9.8 mL, 43 mmol), and the mixture was stirred for 5 min at room temperature. The mixture was heated to 110 °C. After stirred for 14 h, the reaction mixture was cooled to 60 °C, and water (10 mL) was added over 5 min, and re-heated to 80 °C for hydrolyzing the residual P(O*i*Pr)$_3$. After stirred for aitional 2 h, the reaction mixture was cooled to room temperature, and the mixture was filtered, and the precipitates were washed with cold CH_3OH (70 mL). The resultant sample was dried in *vacuo* (150 °C, 2 h), giving whitish red solid. Purification by silica-gel

column chromatography (Hexane/EtOAc, 19:1) yielded whitish yellow solid materials of **3** in 70% (7.7 g).

4.3.1. 2′,7′-Dibromo-2,7-di-tert-butyl-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (3)

70% yield (7.7 g); *Rf* value 0.44 (Hexane/EtOAc, 9:1); M. p. 259–260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.07 (d, J = 2.2 Hz, 1H, H-1′), 8.02 (d, J = 8.6 Hz, 1H, H-4′), 7.90 (d, J = 8.5 Hz, 1H, H-5′), 7.89 (dd, J = 8.6, 2.2 Hz, 1H, H-3′), 7.67 (d, J = 8.0 Hz, 2H, H-4), 7.50 (dd, J = 8.5, 2.0 Hz, 1H, H-6′), 7.43 (dd, J = 8.0, 1.6 Hz, 2H, H-3), 6.99 (d, J = 1.6 Hz, 2H, H-1), 6.78 (d, J = 2.0 Hz, 1H, H-8′), 1.20 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 195.8 (C═O), 151.4 (C-2), 145.8 (C-9a), 142.2 (C-8a′), 139.2 (C-4a), 137.9 (C-10a′), 136.6 (C-4a′), 131.8 (C-4b′), 131.6 (two peaks are overlapped, C-1′ and C-8′), 131.4 (C-4), 129.3 (C-3′), 126.2 (C-1), 125.9 (C-5′), 125.2 (C-3), 124.0 (C-6′), 123.1 (C-4′), 121.8 (C-7′), 120.4 (C-2’), 69.1 (C-9), 35.2 (C(CH$_3$)$_3$), 31.7 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 615 $[MH]^+$; IR (neat) 2956, 1686 (C═O), 1458, 1399, 1249, 1225, 810, 742 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{31}Br(79)_2O$: 615.0721 $[MH]^+$, found: 615.0707; Anal. Calcd for $C_{34}H_{30}Br(79)_2O$; C, 66.46; H, 4.92. Found: C, 66.31; H, 4.87.

4.3.2. 2,7-Di-tert-butyl-2′,7′-diiodo-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (6)

80% yield (850 mg), yellowish white solid materials; *Rf* value 0.50 (Hexane/EtOAc, 9:1); M. p. 294–296 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.24 (d, J = 1.9 Hz, 1H, H-1′), 8.09 (dd, J = 8.6, 1.9 Hz, 1H, H-3′), 7.87 (d, J = 8.6 Hz, 1H, H-4′), 7.75 (d, J = 8.5 Hz, 1H, H-5′), 7.70 (dd, J = 8.5, 1.6 Hz, 1H, H-6′), 7.66 (d, J = 7.9 Hz, 2H, H-4), 7.42 (dd, J = 7.9, 1.6 Hz, 2H, H-3), 6.98 (d, J = 1.6 Hz, 2H, H-1), 6.96 (d, J = 1.6 Hz, 1H, H-8′), 1.20 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 195.4 (C═O, C-10′), 151.2 (C-1), 145.5 (C-8a′), 143.5 (C-9a), 141.9 (C-3′), 139.0 (C-4a), 137.44 (C-8′), 137.36 (C-10a′), 137.2 (C-1′), 137.0 (C-4a′), 131.6 (C-6′), 129.9 (C-4b′), 126.0 (C-4), 125.7 (C-5′), 124.9 (C-4′), 121.7 (C-1), 120.1 (C-3), 95.7 (C-2′), 94.0 (C-7’), 68.7 (C-9), 35.0 (C(CH$_3$)$_3$), 31.5 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 709 $[MH]^+$; IR (neat): 2961, 1672 (C═O), 1457, 1251, 1226, 999, 810, 736, 589 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{31}I_2O$: 709.0464 $[MH]^+$, found: 709.0476.

4.3.3. 2,7-Di-tert-butyl-2′,7′-dichloro-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (7)

76% yield (600 mg), yellowish white solid materials; *Rf* value 0.46 (Hexane/EtOAc, 9:1); M. p. 258–260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.09 (d, J = 8.6 Hz, 1H, H-4′), 7.97 (d, J = 8.5 Hz, 1H, H-5′), 7.92 (d, J = 2.3 Hz, 1H, H-1′), 7.74 (dd, J = 8.6, 2.3 Hz, 1H, H-3′), 7.67 (d, J = 8.0 Hz, 2H, H-4), 7.43 (dd, J = 8.0, 1.5 Hz, 2H, H-3), 7.34 (dd, J = 8.5, 2.2 Hz, 1H, H-6′), 6.99 (d, J = 1.5 Hz, 2H, H-1), 6.63 (d, J = 2.2 Hz, 1H, H-8′), 1.19 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 196.0 (C═O), 151.4 (C-2), 145.9 (C-9a), 142.0 (C-8a′), 139.2 (C-4a), 136.1 (C-10a′), 135.6 (C-4a′), 135.1 (C-3′), 135.0 (C-7′), 131.6 (C-2′), 128.8 (C-4b′), 128.7 (C-5′), 128.6 (C-1′), 128.5 (C-8′), 126.2 (C-4), 125.8 (C-6′), 125.1 (C-4’), 121.8 (C-1), 120.3 (C-3), 69.1 (C-9), 35.2 (C(CH$_3$)$_3$), 31.7 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 525 $[MH]^+$; IR (neat): 2963, 1676 (C═O), 1594, 1464, 1406, 1248, 1229, 1101, 813, 751 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{31}Cl_2O$: 525.1752 $[MH]^+$, found: 525.1719.

4.4. Representative procedure for the homo-dimerization of 1 and 2, for Scheme 3

Under an argon atmosphere, **1** (440 mg, 1.5 mmol) was suspended in P(O*i*Pr)$_3$ (1.0 mL, 4.5 mmol), and the mixture was stirred at 150 °C (oil bath temp.) for 93 h. The mixture was cooled to 60 °C, and consecutively water (1.0 mL) was added over 3 min, and the whole was re-heated to 80 °C for hydrolyzing the residual P(O*i*Pr)$_3$. After stirred for more than 2 h, the reaction mixture was allowed to cool to ambient temperature. The aqueous layer was extracted with toluene (5.0 mL × 3) and the combined organic phases were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give yellow oil. Purification by short-plugged silica-gel column chromatography (Hexane/$CHCl_3$, 1:1) afforded **4** of 270 mg (64%) as white solid materials.

4.4.1. 2,2′,7,7′-Tetra-tert-butyl-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (4)

64% yield (270 mg), white solid materials; *Rf* value 0.35 (Hexane/$CHCl_3$, 2:1); M. p. 210–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.05 (d, J = 8.3 Hz, 1H, H-4′), 7.95 (d, J = 8.4 Hz, 1H, H-5′), 7.86 (d, J = 2.1 Hz, 1H, H-1′), 7.80 (dd, J = 8.4, 2.1 Hz, 1H, H-6′), 7.65 (d, J = 8.0 Hz, 2H, H-4), 7.39 (dd, J = 8.3, 2.1 Hz, 1H, H-3′), 7.37 (dd, J = 8.0, 1.7 Hz, 2H, H-3), 7.06 (d, J = 1.7 Hz, 2H, H-1), 6.71 (d, J = 2.1 Hz, 1H, H-8′), 1.33 (s, 9H, CH_3), 1.17 (s, 18H, CH_3), 1.10 (s, 9H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 199.3 (C═O, C-10′), 151.8 (C-2′), 151.3 (C-7′), 150.6 (C-2), 146.3 (C-9a), 139.3 (C-4a), 139.1 (C-4a′), 136.3 (C-8a′), 132.0 (C-10a′), 130.7 (C-5′), 129.0 (C-4′), 125.34 (C-4), 125.30 (C-4b′), 125.2 (C-8′), 125.1 (C-1′), 124.2 (C-3′), 123.1 (C-6’), 122.6 (C-1), 119.9 (C-3), 70.3 (C-9), 35.1 (two peaks are overlapped, C(CH$_3$)$_3$), 34.9 (C(CH$_3$)$_3$), 31.7 (CH_3), 31.4 (CH_3), 31.3 (CH_3) ppm; MS (DART-TOF) *m/z*: 569 $[MH]^+$; IR (neat) 2956, 1690 (C═O), 1606, 1479, 1232, 818, 750 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{49}O$: 569.3783 $[MH]^+$, found: 569.3773.

4.4.2. 2,2′,7,7′-Tetrabromo-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (5) [29]

65% yield (260 mg), orange solid materials; *Rf* value 0.43 (Hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.11 (d, J = 2.2 Hz, 1H, H-1′), 8.03 (d, J = 8.6 Hz, 1H, H-4′), 7.92 (d, J = 8.6 Hz, 1H, H-5′), 7.92 (dd, J = 8.6, 2.2 Hz, 1H, H-3′), 7.65 (d, J = 8.1 Hz, 2H, H-4), 7.56 (dd, J = 8.1, 1.8 Hz, 2H, H-3), 7.55 (dd, J = 8.6, 2.1 Hz, 1H, H-6′), 7.09 (d, J = 1.8 Hz, 2H, H-1), 6.67 (d, J = 2.1 Hz, 1H, H-8’) ppm; MS (DART-TOF) *m/z*: 661 $[MH]^+$; IR (neat) 3064, 1683 (C═O), 1588, 1451, 1224, 1059, 804, 734 cm^{-1}; HRMS (DART-TOF) calcd for $C_{26}H_{13}Br_4O$: 660.7659 $[MH]^+$, found: 660.7652.

4.4.3. 2,7-Dibromo-9-isopropyl-9H-fluoren-9-yl diisopropyl phosphate (8)

19% yield (155 mg), white solid materials; *Rf* value 0.43 (Toluene/EtOAc, 4:1); M.p. 129-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.69 (d, J = 1.7 Hz, 2H, H-1), 7.51 (dd, J = 8.1, 1.7 Hz, 2H, H-3), 7.44 (d, J = 8.1 Hz, 2H, H-4), 4.35 (sept, J = 6.3 Hz, 1H, phosphate CH), 4.33 (sept, J = 6.2 Hz, 1H, phosphate CH), 2.59 (sept, J = 6.8 Hz, 1H, CH), 1.13 (d, J = 6.2 Hz, 6H, phosphate CH_3), 1.08 (d, J = 6.3 Hz, 6H, phosphate CH_3), 0.81 (d, J = 6.8 Hz, 6H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 146.6 (C-8a), 139.3 (C-4b), 133.0 (C-8), 129.2 (C-5), 122.1 (C-6), 121.7 (C-7), 91.8 ($^2J_{CP}$ = 8.6 Hz, C-7), 72.7 ($^2J_{CP}$ = 5.7 Hz, two peaks are overlapped, CH(CH$_3$)$_2$), 38.5 ($^3J_{CP}$ = 9.3 Hz, CH), 24.1 ($^3J_{CP}$ = 4.8 Hz, CH_3), 24.0 ($^3J_{CP}$ = 4.8 Hz, CH_3), 17.4 (CH_3) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) -7.59 ppm; MS (DART-TOF) m/z: 546 $[MH]^+$; IR (neat) 2977, 2933, 1256 (P=O), 989 (P-O-C), 961, 822 cm^{-1}; HRMS (DART-TOF) calcd for $C_{22}H_{27}Br_2O_4P$: 545.9993 $[M]^+$, found; 546.0003; Anal. Calcd for $C_{22}H_{27}Br_2O_4P$; C, 48.38; H, 4.98. Found: C, 48.50; H, 5.02.

4.5. Synthesis of 9 and iso-9, for Scheme 4

Under an argon atmosphere, **1** (150 mg, 0.50 mmol) and 2,7-dimethoxy-9H-fluoren-9-one (120 mg, 0.50 mmol) were suspended in P(O*i*Pr)$_3$ (1.0 mL, 4.5 mmol), and the mixture was stirred at 110 °C for 3 h. The reaction mixture was cooled to 60 °C, and consecutively water (1.0 mL) was added over 1 min, and the whole was re-hearted to 80 °C for hydrolyzing the residual P(O*i*Pr)$_3$. After stirred for more than 2 h, the reaction mixture was allowed to cool to ambient temperature. The aqueous layer was extracted with toluene (10 mL × 3) and the combined organic phases were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give crude products. Purification by short-plugged silica-gel column chromatography (Toluene/EtOAc, 19:1) afforded products as orange solid materials. Purification by short-

plugged silica-gel column chromatography (Toluene) afforded **9** of 28 mg (11%) as yellow solid materials and iso-**9** of 10 mg (4%) as yellow solid materials.

*4.5.1. 2,7-Di-tert-butyl-2′,7′-dimethoxy-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (**9**)*

11% yield (28 mg), yellow solid materials; *Rf* value 0.56 (Toluene/CH_2Cl_2, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.01 (d, J = 8.8 Hz, 1H, H-4'), 7.92 (d, J = 8.7 Hz, 1H, H-5'), 7.64 (d, J = 7.9 Hz, 2H, H-4), 7.41 (d, J = 2.6 Hz, 1H, H-1'), 7.38 (dd, J = 7.9, 1.6 Hz, 2H, H-3), 7.31 (dd, J = 8.8, 2.6 Hz, 1H, H-3'), 7.07 (d, J = 1.6 Hz, 2H, H-1), 6.88 (dd, J = 8.7, 2.6 Hz, 1H, H-6'), 6.15 (d, J = 2.6 Hz, 1H, H-1'), 3.84 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 1.91 (s, 18 H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 197.8 (C=O, C-10'), 159.3 (C-7'), 158.9 (C-2'), 150.7 (C-2), 146.6 (C-8a'), 140.8 (C-9a), 139.0 (C-4a), 131.9 (C-10a'), 130.8 (C-4), 125.3 (C-5'), 125.0 (C-4a'), 124.2 (C-4'), 124.0 (C-1), 122.9 (C-3), 121.8 (C-4b'), 119.7 (C-3'), 113.8 (C-1'), 112.9 (C-8'), 110.4 (C-6'), 69.5 (C-9), 55.6 (OCH_3), 55.0 (OCH_3), 34.9 ($\underline{C}(CH_3)_3$), 31.4 (CH_3) ppm; MS (DART-TOF) m/z: 517 $[MH]^+$; IR (neat) 2960, 1670, 1602 (C=O), 1479, 1280, 1252, 1049, 830, 794 cm^{-1}; HRMS (DART-TOF) calcd for $C_{36}H_{37}O_3$: 517.2743 $[MH]^+$, found: 517.2739.

*4.5.2. 2′,7′-Di-tert-butyl-2,7-dimethoxy-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (iso-**9**)*

4% (10 mg), yellow solid materials; *Rf* value 0.44 (Toluene/CH_2Cl_2, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.06 (d, J = 8.5 Hz, 1H, H-4′), 7.98 (d, J = 2.2 Hz, 1H, H-8′), 7.97 (d, J = 8.2 Hz, 1H, H-5′), 7.78 (dd, J = 8.2, 2.2 Hz, 1H, H-6′), 7.59 (d, J = 8.3 Hz, 2H, H-4), 7.37 (dd, J = 8.5, 2.0 Hz, 1H, H-3′), 6.89 (d, J = 8.3, 2.3 Hz, 2H, H-3), 6.63 (d, J = 2.0 Hz, 1H, H-1′), 6.55 (d, J = 2.3 Hz, 2H, H-1), 3.65 (s, 6H, OCH_3), 1.35 (s, 9H, CH_3), 1.09 (s, 9H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 198.1 (C=O, C-10′), 159.3 (C-4), 152.2 (C-2′), 151.4 (C-7′), 149.0 (C-2), 139.2 (C-8a′), 136.0 (C-4a′), 134.9 (C-5′), 132.6 (C-10a′), 129.7 (C-4a), 128.3 (C-9a), 125.45 (C-3′), 125.35 (C-4b′), 125.3 (C-8′), 123.9 (C-1′), 123.2 (C-6′), 120.6 (C-4'), 114.3 (C-1), 110.9 (C-3), 69.4 (C-9), 55.7 (OCH_3), 35.1 ($\underline{C}(CH_3)_3$), 34.9 ($\underline{C}(CH_3)_3$), 31.4 (CH_3), 31.3 (CH_3) ppm; MS (DART-TOF) *m/z*: 517 $[MH]^+$; IR (neat) 2956, 1682 (C=O), 1606, 1463, 1267, 1228, 1041, 806 cm^{-1}; HRMS (DART-TOF) calcd. For $C_{36}H_{37}O_3$: 517.2743 $[MH]^+$, found: 517.2736.

*4.6. Synthesis of **10** via the cross-dimerization, for Scheme 5(a)*

To a 50 mL flask charged with 2,7-di-*tert*-butyl-9H-fluoren-9-one (1.30 g, 4.50 mmol) and 2-bromo-9H-fluoren-9-one (1.40 g, 5.40 mmol) was added $P(OiPr)_3$ (12.0 mL, 54.0 mmol). After the mixture was stirred for 14 h at 155 °C, the reaction mixture was cooled to 60 °C. To the mixture was slowly added water (12.0 mL) over 5 min, and the reaction system was re-heated to 80 °C for hydrolyzing the residual $P(OiPr)_3$. After stirred for more than 2 h, the reaction mixture was allowed to cool to ambient temperature. The aqueous layer was extracted with toluene (10 mL × 3) and the combined organic phases were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give orangish yellow oil. Purification by short-plugged silica-gel column chromatography (Toluene only) afforded 2.71 g of products as orange solid materials. Purification by silica-gel column chromatography (Hexane/$CHCl_3$, 2:1) afforded **10** of 566 mg (24%) as whitish yellow solid materials.

*4.6.1. 2′-Bromo-2,7-di-tert-butyl-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (**10**)*

24% yield (566 mg), yellow solid materials; *Rf* value 0.60 (Hexane/Toluene, 1:9); M.p. 235-237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.08 (d, J = 8.5 Hz, 1H, H-4'), 8.07 (d, J = 2.3 Hz, 1H, H-1'), 8.05 (dd, J = 8.2, 1.2 Hz, 1H, H-5'), 7.89 (dd, J = 8.5, 2.2 Hz, 1H, H-3'), 7.66 (d, J = 8.1 Hz, 2H, H-4), 7.40 (dd, J = 8.1, 1.6 Hz, 2H, H-3), 7.37 (ddd, J = 8.2, 7.8, 1.2 Hz, 1H, H-6'), 7.11 (ddd, J = 7.9, 7.8, 1.2 Hz, 1H, H-7'), 7.01 (d, J = 1.6 Hz, 2H, H-1), 6.64 (dd J = 7.9, 1.2 Hz, 1H, H-8'), 1.18 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 196.7 (C=O), 151.1 (C-2), 146.6 (C-9a), 140.1 (C-8a'), 139.2 (C-4a), 137.7 (C-10a'), 137.5 (C-3'), 132.0 (C-4a'), 131.4 (C-1'), 130.1 (C-4b'), 129.9 (C-8'), 128.6 (C-7'), 128.3 (C-6'), 125.9 (C-4), 125.3 (C-5'), 124.4 (C-4'), 122.6 (C-2'), 121.9 (C-1), 120.1 (C-3), 69.3 (C-9), 35.2 ($\underline{C}(CH_3)_3$), 31.7 (CH_3) ppm; MS (DART-TOFMS) m/z: 534 $[MH]^+$; IR (neat): 2961, 1673 (C=O), 1587, 1473, 1394, 1283, 1248, 907, 818, 752 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{31}Br(79)O$: 535.1637 $[MH]^+$, found: 535.1644.

*4.6.2. 2-Bromo-9H-fluoren-9-yl diisopropyl phosphate (**11**)*

27% yield (564 mg), white solid materials; *Rf* value 0.48 (hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.90 (d, J = 1.6 Hz, 1H, H-1), 7.73 (d, J = 7.1 Hz, 1H, H-4), 7.61 (d, J = 7.4 Hz, 1H, H-8), 7.54 (dd, J = 7.1, 1.6 Hz, 1H, H-3), 7.50 (d, J = 8.0 Hz, 1H, H-5), 7.41 (ddd, J = 7.5, 7.4, 1.1 Hz, 2H, H-7), 7.34 (ddd, J = 8.0, 7.5, 1.1 Hz, 1H, H-6), 6.19 (d, J_{PH} = 9.3 Hz, 1H, CH), 4.80-4.71 (m, 2H, $C\underline{H}(CH_3)_2$), 1.40-1.36 (m, 12H, CH_3) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) 144.7 (d, $^3J_{CP}$ = 4.3 Hz, C-9a), 142.4 (d, $^3J_{CP}$ = 5.0 Hz, C-8a), 139.9 (C-4b), 139.8 (C-4a), 133.0 (C-1), 130.2 (C-4), 129.8 (C-3), 128.7 (C-7), 126.4 (C-6), 121.8 (C-5), 121.7 (C-2), 120.5 (C-8), 77.6 (d, $^2J_{CP}$ = 5.5 Hz, C-9), 73.43 (d, $^2J_{CP}$ = 6.2 Hz, CH), 73.40 (d, $^2J_{CP}$ = 6.0 Hz, CH), 23.90 (d, $^3J_{CP}$ = 5.2 Hz, CH_3), 23.87 (d, $^3J_{CP}$ = 5.5 Hz, CH_3), 23.85 (d, $^3J_{CP}$ = 5.3 Hz, CH_3), 23.8 (d, $^3J_{CP}$ = 5.0 Hz, CH_3) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) -1.88 ppm; MS (DART-TOFMS) m/z: 424 $[MH]^+$; IR (neat): 2979, 1449, 1258 (P=O), 991 (P-O-C), 772, 742 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{19}H_{22}Br(79)O_4P$: 425.0517 $[MH]^+$, found: 425.0496.

*4.7. Homo-dimerization of **12**, for Scheme 5(b)*

*4.7.1. Synthesis of 2-bromo-7-(tert-butyl)-9H-fluoren-9-one (**12**)*

To a solution of 2-bromo-9-fluorene (16 g, 65 mmol) in CH_2Cl_2 (80 mL) was added $FeCl_3$ (1.1 g, 6.5 mmol) and 2-chloro-2-methylpropane (7.9 mL, 72 mmol), and the mixture was stirred at 0 °C for 10 min. After the complete consumption of the starting bromide was confirmed in TLC monitoring, the reaction mixture was filtered through a pad of Celite and silica-gel (Toluene), and the filtrate was thoroughly dried. The resultant crude products were provided in the next oxidation step without further purification. To the crude products were added pyridine (96 mL) and $FeCl_3{\cdot}6H_2O$ (3.5 g, 13 mmol), then *tert*-butyl hydroperoxide (TBHP, 70% in H_2O, 27 mL, 200 mmol) was slowly added over 7 min. After the mixture was stirred at 80 °C for 1 h, the extra amounts of TBHP (9.0 mL, 65 mmol) were added. The reaction was conducted at 80 °C for 1 h, and the mixture was allowed to cool to room temperature, and filtered through a pad of Celite and silica-gel (CH_2Cl_2), and the filtrate was dried. The resultant residue was diluted with CH_2Cl_2, which was transferred into a 500 mL separatory funnel, and washed with brine (150 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give crude products. Purification by silica-gel column chromatography (Hexane/Toluene, 4:1) gave **12** of 17 g (81%) as yellow solid. *Rf* value 0.50 (Hexane/CH_2Cl_2, 4:1); M. p. 194–195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.74 (d, J = 1.8 Hz, 1H, H-1), 7.71 (d, J = 1.7 Hz, 1H, H-8), 7.58 (dd, J = 7.9, 1.8 Hz, 1H, H-3), 7.53 (dd, J = 7.8, 1.7 Hz, 1H, H-6), 7.42 (d, J = 7.8 Hz, 1H, H-5), 7.36 (d, J = 7.9 Hz, 1H, H-4), 1.34 (s, 9H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 193.2 (C=O), 153.6 (C-7), 143.4 (C-4a), 141.3 (C-9a), 137.3 (C-4b), 136.5 (C-8a), 134.1 (C-3), 132.2 (C-1), 127.8 (C-6), 122.7 (C-8), 122.2 (C-2), 121.8 (C-4), 120.5 (C-5), 35.4 ($\underline{C}(CH_3)_3$), 31.5 (CH_3) ppm; MS (DART-TOF) *m/z*: 314 $[M]^+$; IR (neat) 2955, 1712 (C=O), 1599, 1407, 1362, 1246, 1183, 1154, 823, 778, 694 cm^{-1}; HRMS (DART-TOF) calcd. For $C_{17}H_{15}BrO$: 314.0306 $[M]^+$, found: 314.0287; Anal. Calcd. For $C_{17}H_{15}BrO$; C, 64.78; H, 4.80. Found: C, 64.96; H, 4.82.

4.7.2. Synthesis of (S)-2,2′-dibromo-7,7′-di-tert-butyl-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (**13**)*

12 (5.7 g, 18 mmol) was suspended in $P(OiPr)_3$ (12 mL, 54 mmol),

and the mixture was stirred at 150 °C for 22 h. The mixture was cooled to 60 °C, and consecutively water (12 mL) was added over 10 min, and the whole was re-heated to 80 °C for hydrolyzing the residual $P(OiPr)_3$. After stirred for more than 2 h, the reaction mixture was cooled to room temperature, and the collected precipitates were washed with CH_3OH (chilled at 0 °C, 50 mL). The resultant crude samples were dried *in vacuo* (150 °C, 2 h), which gave 11 g of white solid as crude products. Purification by silica-gel column chromatography (Hexane/Toluene, 2:1) afforded **13** of 3.6 g (66%) and iso-**13** of 820 mg (15%) as white solid materials. *Rf* value 0.50 (Hexane/Toluene, 1:1); M. p. 277–280 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.04 (d, J = 2.2 Hz, 1H, H-1′), 8.03 (d, J = 8.7 Hz, 1H, H-5′), 7.96 (d, J = 8.5 Hz, 1H, H-4′), 7.87 (dd, J = 8.7, 2.0 Hz, 1H, H-6′), 7.70 (d, J = 8.0 Hz, 1H, H-4), 7.60 (d, J = 8.2 Hz, 1H, H-5), 7.48 (dd, J = 8.0, 1.6 Hz, 1H, H-3), 7.46 (dd, J = 8.2, 1.8 Hz, 1H, H-6), 7.42 (dd, J = 8.5, 2.2 Hz, 1H, H-3′), 7.10 (d, J = 1.6 Hz, 1H, H-1), 7.05 (d, J = 1.8 Hz, 1H, H-8), 6.59 (d, J = 2.0 Hz, 1H, H-8′), 1.23 (s, 9H, CH_3), 1.08 (s, 9H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 196.2 (C═O), 153.2 (C-7′), 152.4 (C-2), 148.6 (C-8a′), 146.8 (C-9a), 140.6 (C-8a), 138.6 (C-4a), 138.5 (C-4b), 138.1 (C-10a′), 137.4 (C-4a′), 131.8 (C-4b′), 131.5 (C-4), 131.3 (C-8), 127.7 (C-8′), 127.5 (C-6′), 126.1 (C-5), 125.9 (C-6), 125.6 (C-3), 125.3 (C-1), 124.4 (C-4′), 122.7 (C-1′), 122.4 (C-3′), 122.2 (C-5′), 120.9 (C-7), 120.4 (C-7'), 69.4 (C-9), 35.4 (C$(CH_3)_3$), 35.0 (C$(CH_3)_3$), 31.7 (CH_3), 31.2 (CH_3) ppm; MS (DART-TOF) *m/z*: 613 $[MH]^+$; IR (neat) 2960, 1686 (C═O), 1455, 1248, 814, 746, 456 cm^{-1}; HRMS (DART-TOF) calcd. For $C_{34}H_{31}Br(79)_2O$: 613.0742 $[MH]^+$, found: 613.0714; Anal. Calcd. For $C_{34}H_{30}Br_2O$; C, 66.46; H, 4.92. Found: C, 66.40; H, 4.98.

4.7.3. (R*)-2,7′-Dibromo-2′,7-di-tert-butyl-10′H-spiro [fluorene-9,9′-phenanthren]-10′-one (iso-13)

15% yield (820 mg), white solid materials; *Rf* value 0.45 (Hexane/Toluene, 1:1); M. p. 247–248 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.07 (d, J = 8.2 Hz, 1H, H-5′), 7.98 (d, J = 1.7 Hz, 1H, H-1′), 7.94 (d, J = 8.1 Hz, 1H, H-4′), 7.84 (dd, J = 8.2, 2.2 Hz, 1H, H-6′), 7.67 (d, J = 8.3 Hz, 1H, H-5), 7.63 (d, J = 8.4 Hz, 1H, H-4), 7.52 (dd, J = 8.3, 1.7 Hz, 1H, H-6), 7.50 (dd, J = 8.4, 1.6 Hz, 1H, H-3), 7.43 (dd, J = 8.1, 1.7 Hz, 1H, H-3′), 7.15 (d, J = 1.7 Hz, 1H, H-8), 6.93 (d, J = 1.6 Hz, 1H, H-1), 6.71 (d, J = 2.2 Hz, 1H, H-8′), 1.36 (s, 9H, CH_3), 1.15 (s, 9H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 196.8 (C═O), 152.9 (C-7′), 152.7 (C-2), 149.1 (C-8a′), 147.1 (C-8a), 141.5 (C-9a), 141.2 (C-4b), 138.4 (C-4a), 135.2 (C-10a′), 133.3 (C-4a′), 132.4 (C-4b′), 132.1 (C-4), 131.4 (C-8), 130.4 (C-3′), 130.0 (C-1′), 128.6 (C-5), 126.6 (C-6), 126.2 (C-3), 125.9 (C-1), 123.8 (C-4′), 123.5 (C-6′), 122.4 (C-8′), 122.1 (C-7), 121.7 (C-2′), 120.9 (C-5'), 69.0 (C-9), 35.6 (two peaks are overlapped, C$(CH_3)_3$, C$(CH_3)_3$), 31.9 (CH_3), 31.6 (CH_3) ppm; MS (DART-TOF) *m/z*: 613 $[MH]^+$; IR (neat) 2956, 1683 (C═O), 1455, 1228, 814, 742 cm^{-1}; HRMS (DART-TOF) calcd. For $C_{34}H_{31}Br(79)_2O$: 613.0742 $[MH]^+$, found: 613.0720; Anal. Calcd. For $C_{34}H_{30}Br_2O$; C, 66.46; H, 4.92. Found: C, 66.31; H, 4.87.

4.8. Synthesis of 14 and 15, for Scheme 6

4.8.1. 2′,7′-Dibromo-2,7-di-tert-butyl-10′H-spiro [fluorene-9,9′-phenanthren]-10′-ol (14)

To a 50 mL flask charged with **3** (2.8 g, 4.6 mmol) was added toluene (14 mL) and methanol (2.8 mL), and then flask was heated at 45 °C. To the mixture, $NaBH_4$ (70 mg, 1.8 mmol) was added at 5 min intervals (7 times in all). After the mixture was stirred for 30 min, the reaction was quenched with acetone (18 mL) and treated for additional 15 min. The organic layer was washed with water (20 mL × 4), and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give 2.8 g of crude products. Purification by silica-gel column chromatography (Hexane/EtOAc, 9:1) afforded **14** of 2.6 g (91%) as whitish orange solid materials. *Rf* value 0.56 (Hexane/CH_2Cl_2, 1:1); M. p. 136–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.77 (d, J = 8.0 Hz, 1H, H-4), 7.74 (d, J = 8.0 Hz, 1H, H-5), 7.68 (d, J = 8.0 Hz, 1H, H-5′), 7.66–7.63 (m, 2H, H-3′, H-8′), 7.62 (d, J = 8.0 Hz, 1H, H-4′), 7.48 (, J = 8.0, 2.0 Hz, 1H, H-6), 7.47 (, J = 8.0, 1.8 Hz, 1H, H-3), 7.34 (, J = 8.0, 1.8 Hz, 1H, H-6′), 7.23 (br s, 1H, H-8), 6.85 (d, J = 2.0 Hz, 1H, H-1′), 6.69 (br s, 1H, H-1), 5.26 (d, J = 6.2 Hz, 1H, OH), 1.58 (d, J = 6.2 Hz, 1H, CH), 1.30 (s, 9H, CH_3), 1.08 (s, 9H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 151.5 (C-2), 150.5 (C-7), 146.4 (C-8a′), 144.3 (C-8′), 141.7 (C-4a), 139.9 (C-10a′), 139.7 (C-4b), 138.5 (C-9a), 132.63 (C-1′), 132.57 (C-3′), 131.9 (C-5′), 131.6 (C-4′), 131.0 (C-6′), 130.1 (C-4a′), 126.1 (C-8a), 126.0 (C-4), 125.9 (C-5), 125.4 (C-1), 123.0 (C-8), 122.9 (C-3), 122.8 (C-4b′), 121.8 (C-6), 119.9 (C-7′), 119.8 (C-2′), 74.6 (C-10'), 61.2 (C-9), 35.4 (C$(CH_3)_3$), 35.0 (C$(CH_3)_3$), 31.8 (CH_3), 31.5 (CH_3) ppm; MS (DART-TOF) *m/z*: 616 $[MH]^+$; IR (neat) 3528 (OH), 2956, 1593, 1462, 1362, 1254, 1085, 1004, 809, 747, 731 cm^{-1}; HRMS (DART-TOF) calcd. For $C_{34}H_{32}Br_2O$: 616.0799 $[M]^+$, found: 616.0810.

4.8.2. 3,14-Dibromo-6,11-di-tert-butyldibenzo[g,p]chrysene (15)

To a solution of **14** (2.6 g, 4.2 mmol) in toluene (50 mL) was added methanesulfonic acid (MsOH, 0.01 mL, 0.15 mmol) at 120 °C. After the mixture was stirred for 1 h, the reaction was allowed to cool to ambient temperature. The organic layer was washed with brine (30 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give 2.5 g of crude products. Purification by short-plugged silica-gel column chromatography (CH_2Cl_2) afforded **15** of 2.4 g (97%) as whitish yellow materials. *Rf* value 0.67 (Hexane/CH_2Cl_2, 2:1); M. p. 303–305 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.89 (d, J = 1.8 Hz, 2H, H-5), 8.63 (d, J = 1.9 Hz, 2H, H-4), 8.61 (d, J = 8.9 Hz, 2H, H-1), 8.51 (d, J = 8.8 Hz, 2H, H-8), 7.77 (d, J = 8.9, 1.9 Hz, 2H, H-2), 7.76 (d, J = 8.8, 1.8 Hz, 2H, H-7), 1.48 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.7 (C-6), 131.8 (C-2), 131.2 (C-4a), 129.8 (C-4), 129.13 (C-8), 129.09 (C-1), 128.4 (C-16 b), 127.9 (C-4b), 125.44 (C-8a), 125.39 (C-4c), 125.3 (C-7), 123.6 (C-3), 121.2 (C-5), 35.4 (C$(CH_3)_3$), 31.7 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 598 $[M]^+$; IR (neat) 2963, 1588, 1469, 1358, 1089, 910, 883, 808, 792 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{30}Br(79)_2$: 598.0694 $[M]^+$, found: 598.0679; Anal. Calcd for $C_{34}H_{30}Br(79)_2$; C, 68.24; H, 5.05. Found: C, 68.15; H, 5.00.

4.9. Synthesis of 16 and 17, for Scheme 7(a)

4.9.1. Di-tert-butyl (6,11-di-tert-butyldibenzo[g,p]chrysene-3,14-diyl) dicarbamate (16)

Under an argon atmosphere, to a 200 mL flask charged with **15** (2.5 g, 4.2 mmol) and CuI (1.6 g, 8.4 mmol) and tert-butylcarbamate (2.4 g, 20 mmol) and K_2CO_3 (2.3 g, 17 mmol) were added toluene (63 mL) and *N,N′*-dimethylethylenediamine (1.8 mL, 17 mmol). After stirred at 110 °C for 48 h, the reaction mixture was allowed to cool to ambient temperature. The mixture was filtered through a pad of Celite, then the filtrate was washed with brine (50 mL × 3), and dried over Na_2SO_4, and concentrated *in vacuo* to give products as brownish yellow solid materials. Purification by short-plugged silica-gel column chromatography (Hexane/EtOAc, 4:1) gave **16** of 1.9 g (65%) as yellowish white solid materials. *Rf* value 0.24 (Hexane/EtOAc, 9:1); M. p. 215 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 8.91 (s, 2H, NH), 8.75 (d, J = 1.8 Hz, 2H, H-4), 8.58 (d, J = 8.6 Hz, 2H, H-1), 8.51 (d, J = 8.7 Hz, 2H, H-8), 7.73 (d, J = 8.6, 1.8 Hz, 2H, H-2), 7.49 (d, J = 8.7, 2.0 Hz, 2H, H-7), 6.61 (d, J = 2.0 Hz, 2H, H-5), 1.53 (s, 18H, CH_3), 1.48 (s, 18H, Boc CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 152.6 (C(O)OC$(CH_3)_3$), 148.9 (C-6), 136.4 (C-3), 129.8 (C-8), 128.8 (C-1), 128.6 (C-4c), 128.5 (C-8a), 126.5 (C-16 b), 124.9 (C-4a), 124.7 (C-2), 123.9 (C-7), 123.0 (C-5), 117.9 (C-4b), 117.5 (C-4), 80.5 (COOC$(CH_3)_3$), 35.1 (CH_3), 31.4 (CH_3), 28.3 (CH_3) ppm; MS (DART-TOF) *m/z*: 669 $[M - H]^-$; IR (neat) 3414 (-NHBoc), 2956, 1722 (C═O), 1510, 1363, 1217, 1148, 1053, 877 cm^{-1}; HRMS (DART-TOF) calcd. For $C_{44}H_{49}N_2O_4$: 669.3692 $[M - H]^-$, found: 669.3705; Anal. Calcd for $C_{44}H_{50}N_2O_4$; C, 78.77; H, 7.55; N, 4.22. Found: C, 78.49; H, 7.51; N, 4.18.

4.9.2. 6,11-Di-tert-butyldibenzo[g,p]chrysene-3,14-diamine (17)

To a solution of **16** (1.9 g, 2.9 mmol) in CH_2Cl_2 (48 mL) was slowly

added trifluoroacetic acid (11 mL, 140 mmol) over 3 min at 0 °C. The reaction mixture was allowed to warm to ambient temperature, and then stirred for further 2 h. The mixture was quenched with saturated aq. $NaHCO_3$ (100 mL). The organic phase was washed with $NaHCO_3$ (50 mL × 3), brine (50 mL × 3), dried over Na_2SO_4, and concentrated *in vacuo* to give crude products as brownish yellow solid materials. Purification by short-plugged silica-gel column chromatography (Hexane/EtOAc, 2:1) gave **17** of 1.3 g (98%) as yellow solid materials. *Rf* value 0.19 (Hexane/EtOAc, 2:1); M. p. 197 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 8.76 (d, J = 1.7 Hz, 2H, H-4), 8.57 (d, J = 8.5 Hz, 2H, H-1), 8.38 (d, J = 8.6 Hz, 2H, H-8), 7.93 (d, J = 2.2 Hz, 2H, H-5), 7.71 (d, J = 8.5, 1.7 Hz, 2H, H-2), 7.05 (d, J = 8.6, 2.2 Hz, 2H, H-7), 3.79 (br s, 4H, NH_2), 1.46 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 148.4 (C-6), 143.8 (C-3), 129.6 (C-8), 129.1 (C-1), 128.4 (C-4c), 128.2 (C-8a), 124.9 (C-16 b), 124.1 (two peaks are overlapped, C-4a, C-4b), 124.06 (C-7), 123.0 (C-2), 116.1 (C-5), 113.0 (C-4), 35.0 ($\underline{C}(CH_3)_3$), 31.5 (CH_3) ppm; MS (DART-TOF) *m/z*: 471 $[MH]^+$; IR (neat) 3446, 3355, 3208, 2952, 1610, 1483, 1189, 1137, 806 cm^{-1}; HRMS (DART-TOF) calcd for $C_{34}H_{35}N_2$: 471.2795 $[MH]^+$, found: 471.2788; Anal. Calcd for $C_{34}H_{34}N_2$; C, 86.77; H, 7.28; N, 5.95. Found: C, 86.76; H, 7.06; N, 5.90.

4.10. Synthesis of **18** and **19**, for Scheme 7(b)

4.10.1. 3,14-Di-tert-butyl-6,11-dimethoxydibenzo[g,p]chrysene (**18**)

Under an argon atmosphere, to a suspension of **15** (9.6 g, 16 mmol) in *N*,*N*-dimethylformamide (160 mL) was added CuI (18 g, 96 mmol) and 28% $NaOCH_3$ in CH_3OH (160 mL, 800 mmol). The mixture was stirred for 2 h at 120 °C, and the reaction was filtered through a pad of Celite and silica-gel (Toluene). The organic layer was washed with brine (50 mL × 3), dried over Na_2SO_4, and concentrated *in vacuo* to give 7.9 g of crude products. Purification by short-plugged silica-gel column chromatography (Hexane/Toluene, 2:1) afforded **18** of 6.6 g (82%) as whitish yellow solid materials. *Rf* value 0.40 (Hexane/CH_2Cl_2, 2:1); M. p. 239–240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.77 (d, J = 1.8 Hz, 2H, H-4), 8.60 (d, J = 8.6 Hz, 2H, H-1), 8.52 (d, J = 9.0 Hz, 2H, H-8), 8.14 (d, J = 2.5 Hz, 2H, H-5), 7.74 (d, J = 8.6, 1.8 Hz, 2H, H-2), 7.29 (d, J = 9.0, 2.5 Hz, 2H, H-7), 3.93 (s, 6H, OCH_3), 1.46 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.9 (C-9), 149.2 (C-3), 130.1 (C-8), 129.3 (C-4a), 128.84 (C-16 b), 128.83 (C-8a), 125.5 (C-4b), 125.02 (C-1), 124.99 (C-4c), 124.8 (C-2), 123.6 (C-4), 116.9 (C-7), 110.3 (C-5), 55.7 (OCH_3), 35.4 ($\underline{C}(CH_3)_3$), 31.9 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 501 $[MH]^+$; IR (neat) 2952, 1610, 1483, 1459, 1272, 1228, 1049, 806, 786 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{36}H_{37}O_2$: 501.2794 $[MH]^+$, found: 501.2781; Anal. Calcd for $C_{36}H_{36}O_2$; C, 86.36; H, 7.25. Found: C, 86.36; H, 7.24.

4.10.2. 6,11-Di-tert-butyldibenzo[g,p]chrysene-3,14-diol (**19**)

Under an argon atmosphere, to a solution of **18** (5.0 g, 10 mmol) in dry CH_2Cl_2 (40 mL) at 0 °C was added BBr_3 (30 mL, 30 mmol, 1 M CH_2Cl_2) dropwise over 5 min. After stirred at 0 °C for 15 min, the reaction mixture was allowed to cool to ambient temperature for 1.5 h, and then the mixture was quenched with H_2O (50 mL). The aqueous layer was extracted with EtOAc (30 mL × 3), and the combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 5.0 g of crude products as yellowish white solid materials. Purification by short-plugged silica-gel column chromatography (Toluene/EtOAc, 4/1) afforded **19** of 4.4 g (94%) as yellowish white solid materials. *Rf* value 0.33 (Hexane/EtOAc, 2:1); M. p. 301–318 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.71 (d, J = 2.0 Hz, 2H, H-5), 8.59 (d, J = 8.6 Hz, 2H, H-8), 8.49 (d, J = 8.8 Hz, 2H, H-1), 8.09 (d, J = 2.6 Hz, 2H, H-4), 7.73 (d, J = 8.6, 2.0 Hz, 2H, H-7), 7.20 (, J = 8.8, 2.6 Hz, 2H, H-2), 4.87 (s, 2H, OH), 1.46 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 155.5 (C-3), 148.5 (C-6), 129.0 (C-4a), 128.2 (C-8a), 127.7 (C-4c), 127.4 (C-4b), 124.82 (C-16 b), 124.78 (C-8), 123.8 (C-1), 123.7 (C-7), 123.3 (C-5), 116.8 (C-2), 112.1 (C-4), 34.7 ($\underline{C}(CH_3)_3$), 31.1 (CH_3) ppm; MS (DART-TOF) *m/z*: 473 $[MH]^+$; IR (neat) 3339 (OH), 2955, 1612, 1578, 1482, 1215, 1176, 958, 792, 479 cm^{-1}; HRMS (DART-TOF) calcd for $C_{34}H_{33}O_2$: 473.2481 $[MH]^+$, found: 473.2468.

4.11. Synthesis of **20** and **21**, for Scheme 7(c)

4.11.1. 3,14-Dimethoxydibenzo[g,p]chrysene (**20**)

Under an argon atmosphere, to a solution of **18** (3.5 g, 7.0 mmol) in benzene (50 mL) was added $AlCl_3$ (3.7 g, 28 mmol). After stirred at room temperature for 0.5 h, the reaction was quenched at 0 °C with slow aition (8 min) of water (50 mL). The aqueous phase was extracted with toluene (25 mL × 3) and the combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 3.5 g of crude products. Purification by short-plugged column chromatography (Hexane/Toluene, 1:1) afforded **20** of 2.5 g (93%) as whitish yellow solid materials. *Rf* value 0.56 (Hexane/CH_2Cl_2, 1:1); M.p. 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.79 (dd, J = 8.0, 1.2 Hz, 2H, H-5), 8.70 (dd, J = 8.2, 1.4 Hz, 2H, H-8), 8.52 (d, J = 9.0 Hz, 2H, H-1), 8.15 (d, J = 2.6 Hz, 2H, H-4), 7.68 (ddd, J = 8.0, 7.5, 1.4 Hz, 2H, H-6), 7.62 (ddd, J = 8.2, 7.5, 1.2 Hz, 2H, H-7), 7.29 (dd, J = 9.0, 2.6 Hz, 2H, H-2), 3.94 (s, 6H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.9 (C-3), 131.1 (C-4a), 129.9 (C-8a), 129.8 (C-4c), 128.5 (C-8), 128.3 (C-4b), 126.9 (C-6), 126.8 (C-7), 125.5 (C-16b), 124.9 (C-1), 124.0 (C-5), 116.0 (C-2), 111.4 (C-4), 55.9 (OCH_3) ppm; MS (DART-TOF) m/z: 389 $[MH]^+$; IR (neat) 3062, 2932, 2831, 1610, 1480, 1265, 1229, 1170, 1042, 801, 754, 526 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{28}H_{21}O_2$: 389.1542 $[MH]^+$, found; 389.1534.

4.11.2. Dibenzo[g,p]chrysene-3,14-diol (**21**)

Under an argon atmosphere, to a solution of **20** (2.3 g, 6.0 mmol) in dry CH_2Cl_2 (40 mL) at 0 °C was added BBr_3 (18 mL, 1.0 M CH_2Cl_2 solution) dropwise over 5 min. After stirred for 15 min, the reaction mixture was allowed to warm to room temperature and conducted for 0.5 h. The reaction was quenched with H_2O (60 mL) at 0 °C. The aqueous layer was extracted with EtOAc (30 mL × 3) and the combined organic layers were washed with brine (100 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give 2.1 g of crude products. Purification by short-plugged column chromatography (Toluene/EtOAc, 9:1) afforded **21** of 2.1 g (97%) as greenish white solid materials. *Rf* value 0.44 (Hexane/EtOAc, 1:1); M.p. 320-323 °C; ^{1}H NMR (400 MHz, CD_3CN) 8.764 (dd, J = 8.0, 1.5 Hz, 2H, H-5), 8.757 (dd, J = 8.0, 1.5 Hz, 2H, H-8), 8.51 (d, J = 8.9 Hz, 2H, H-1), 8.06 (d, J = 2.5 Hz, 2H, H-4), 7.72 (ddd, J = 8.0, 7.0, 1.5 Hz, 2H, H-6), 7.67 (ddd, J = 8.0, 7.0, 1.5 Hz, 2H, H-7), 7.25 (br s, 2H, OH), 7.21 (dd, J = 8.9, 2.5 Hz, 2H, H-2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 155.4 (C-3), 130.0 (C-8), 128.7 (C-6), 128.6 (C-7), 127.9 (C-4a), 127.0 (C-1), 126.91 (C-8a), 126.87 (C-4c), 124.8 (C-16b), 123.9 (C-4b), 123.7 (C-5), 116.9 (C-2), 112.4 (C-4) ppm; MS (DART-TOF) m/z: 361 $[MH]^+$; IR (neat) 3646, 3062 (br, OH), 1613, 1578, 1429, 1234, 1182, 890, 800, 750, 716, 524 cm^{-1}; HRMS (DART-TOF) calcd. for $C_{26}H_{17}O_2$: 361.1229 $[MH]^+$, found; 361.1230.

4.12. Synthesis of 2,6,11,15-tetra-tert-butyl-3,14-dimethoxydibenzo[g,p]chrysene (**22**), for Scheme 8

Under an argon atmosphere, to a suspension of **18** (3.6 g, 7.2 mmol) in *tert*-butyl chloride (35 mL, 340 mmol) was added $AlCl_3$ (240 mg, 1.8 mmol). After stirred for 30 min at 50 °C, the reaction mixture was allowed to cool to ambient temperature. The reaction was quenched at 0 °C with 1 M HCl (10 mL). The aqueous layer was extracted with toluene (10 mL × 3). The combined organic phases were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 10 g of crude products. Purification by silica-gel column chromatography (Hexane/CH_2Cl_2, 4:1) afforded **22** of 3.7 g (83%) as whitish yellow solid materials. *Rf* value 0.49 (Hexane/CH_2Cl_2, 4:1); M. p. 208 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) 8.77 (d, J = 1.9 Hz, 2H, H-5), 8.60 (d, J = 8.6 Hz, 2H, H-8), 8.52 (s, 2H, H-1), 8.09 (s, 2H, H-4), 7.71 (, J = 8.6, 1.9 Hz, 2H, H-7), 3.95 (s, 6H, OCH_3), 1.58 (s, 18H, CH_3), 1.46 (s, 18H,

CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.3 (C-3), 149.1 (C-6), 138.7 (C-2), 129.6 (C-4a), 128.7 (C-8a), 128.3 (C-4c), 128.1 (C-4b), 125.0 (C-16 b), 124.8 (C-8), 124.4 (C-7), 123.6 (C-1), 121.6 (C-5), 110.0 (C-4), 55.4 (OCH_3), 35.7 ($\underline{C}(CH_3)_3$), 35.4 ($\underline{C}(CH_3)_3$), 32.0 (CH_3), 30.2 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 613 $[MH]^+$; IR (neat) 2947, 1616, 1486, 1463, 1399, 1361, 1222, 1178, 1055, 816 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{44}H_{53}O_2$: 613.4046 $[MH]^+$, found: 613.4046.

4.13. Synthesis of 2,6,11,15-tetra-tert-butyldibenzo[g,p]chrysene-3,14-diol (**23**), for Scheme 8

Under an argon atmosphere, to a solution of 1-decanethiol (15 mL, 72 mmol) in anhydrous *N*,*N*-dimethylformamide (120 mL) at 0 °C was added potassium tert-butoxide (6.1 g, 54 mmol). The mixture was stirred for 15 min at 0 °C, and allowed to warm to ambient temperature, then **22** (3.7 g, 6.0 mmol) was added. After the mixture was refluxed for 21 h, the reaction was quenched with 3 M HCl (42 mL) at 0 °C. The aqueous layer was extracted with EtOAc (20 mL × 3), and combined organic phases were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give crude products as greenish brown viscous materials. Purification by short-plugged silica-gel column chromatography (Hexane/EtOAc, 19:1) afforded **23** of 2.7 g (80%) as gray solid materials. *Rf* value 0.53 (Hexane/EtOAc, 4:1); M. p. 163 °C (dec.); ^1H NMR (400 MHz, $CDCl_3$) 8.69 (d, $J = 2.0$ Hz, 2H, H-5), 8.58 (d, $J = 8.6$ Hz, 2H, H-8), 8.51 (s, 2H, H-1), 7.92 (s, 2H, H-4), 7.70 (, $J = 8.6$, 2.0 Hz, 2H, H-7), 4.91 (s, 2H, OH), 1.62 (s, 18H, CH_3), 1.46 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 153.0 (C-3), 149.0 (C-6), 136.9 (C-2), 129.3 (C-4a), 128.7 (C-8a), 128.4 (C-4c), 127.6 (C-4b), 125.5 (C-16 b), 124.9 (C-8), 124.5 (C-7), 123.5 (C-1), 122.1 (C-5), 114.6 (C-4), 35.5 ($\underline{C}(CH_3)_3$), 35.3 ($\underline{C}(CH_3)_3$), 31.9 (CH_3), 30.1 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 585 $[MH]^+$; IR (neat) 3606 (OH), 3551 (OH), 2953, 1620, 1418, 1404, 1389, 1361, 1164, 813 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{42}H_{49}O_2$: 585.3733 $[MH]^+$, found: 585.3729.

4.14. Synthesis of 4,13-dibromo-2,6,11,15-tetra-tert-butyldibenzo[g,p]chrysene-3,14-diol (**24**), for Scheme 8

Under an argon atmosphere, to a solution of **23** (1.8 g, 3.1 mmol) in anhydrous CH_2Cl_2 (31 mL) at −78 °C was added Br_2 (13 mL, 1 M CH_2Cl_2 solution) dropwise over 15 min. After the mixture was stirred for 15 min, the reaction was quenched with 3 M aq. $Na_2S_2O_3$ (9 mL) at −78 °C, and followed by the aition of 1 M HCl (54 mL) at 0 °C. The aqueous layer was extracted with EtOAc (20 mL × 3). The combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give 2.5 g of crude products. Purification by silica-gel column chromatography (Hexane/Toluene, 9:1) afforded **24** of 1.5 g (67%) as yellow solid materials. *Rf* value 0.40 (Hexane/Toluene, 9:1); M. p. 166–176 °C; ^1H NMR (400 MHz, $CDCl_3$) 8.70 (s, 2H, H-1), 8.45 (d, $J = 8.5$ Hz, 2H, H-5), 7.82 (d, $J = 2.0$ Hz, 2H, H-8), 7.66 (, $J = 8.5$, 2.0 Hz, 2H, H-7), 6.60 (s, 2H, OH), 1.64 (s, 18H, CH_3), 1.40 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 151.5 (C-3), 147.3 (C-6), 137.2 (C-2), 131.3 (C-4a), 129.6 (C-8a), 127.5 (C-8), 127.2 (C-16 b), 126.3 (C-4b), 126.0 (C-4c), 124.5 (C-7), 122.9 (C-3), 121.8 (C-5), 110.4 (C-4), 36.4 ($\underline{C}(CH_3)_3$), 35.2 ($\underline{C}(CH_3)_3$), 31.7 (CH_3), 29.9 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 743 $[MH]^+$; IR (neat) 3463 (OH), 2953, 1596, 1464, 1400, 1386, 1362, 1185, 813, 740, 626, 421 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{42}H_{47}Br_2O_2$: 743.1922 $[MH]^+$, found: 743.1928.

4.15. Synthesis of 4,13-dibromo-2,6,11,15-tetra-tert-butyl-3,14-dimethoxydibenzo[g,p]chrysene (**25**), for Scheme 8

Under an argon atmosphere, to a solution of **24** (3.5 g, 4.7 mmol) in acetone (40 mL) was added CH_3I (7.6 mL, 120 mmol), and then 1,8-diazabicyclo [5,4,0]undec-7-ene (9.1 mL, 61 mmol) was added dropwise over 5 min. After stirred at room temperature for 1 h, the mixture was quenched with 3 M HCl (40 mL), and treated for aitional 15 min at 0 °C. The aqueous layer was extracted with toluene (20 mL × 3). The combined organic phases were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in *vacuo* to give 3.6 g of crude products. Purification by silica-gel column chromatography (Hexane/CH_2Cl_2, 9:1) afforded **25** of 2.5 g (70%) as yellow solid materials. *Rf* value 0.28 (Hexane/CH_2Cl_2, 4:1); M. p. 280 °C (dec.); ^1H NMR (400 MHz, $CDCl_3$) 8.72 (s, 2H, H-1), 8.47 (d, $J = 8.5$ Hz, 2H, H-8), 7.93 (d, $J = 1.9$ Hz, H-5), 7.68 (, $J = 8.5$, 1.9 Hz, 2H, H-7), 4.21 (s, 6H, OCH_3), 1.62 (s, 18H, CH_3), 1.41 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 159.6 (C-3), 147.4 (C-6), 142.9 (C-2), 131.6 (C-4a), 130.0 (C-8a), 128.9 (C-4b), 128.4 (C-16 b), 127.2 (C-8), 127.1 (C-4c), 124.5 (C-7), 122.9 (C-1), 122.4 (C-5), 117.0 (C-4), 62.6 (OCH_3), 36.3 ($\underline{C}(CH_3)_3$), 35.2 ($\underline{C}(CH_3)_3$), 31.7 (CH_3), 31.1 (CH_3) ppm; MS (DART-TOFMS) *m/z*: 771 $[MH]^+$; IR (neat) 2955, 1610, 1463, 1360, 1258, 1228, 1059, 991, 812, 795, 740 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{44}H_{51}Br(79)_2O_2$: 771.2235 $[MH]^+$, found: 771.2245; Anal. Calcd for $C_{44}H_{50}Br(79)_2O_2$; C, 68.57; H, 6.54. Found: C, 68.56; H, 6.53.

4.16. Synthesis of (2,6,15-tri-tert-butyl-11-isopropyl-3,14-dimethoxydibenzo[g,p]chrysene-4,13-diyl)bis (methylsulfane) (**26**), for Scheme 8

Under an argon atmosphere, to a solution of **25** (1.5 g, 1.9 mmol) in dry toluene (19 mL) at 0 °C was added methyl lithium (6.3 mL, 1.2 M in Et_2O) dropwise over 5 min. The mixture was stirred at −45 °C for 30 min, and dimethyl disulfide (1.4 mL, 15 mmol) was added over 5 min, and the resultant mixture was conducted for 1 h. After stirred for aitional 1 h at room temperature, the mixture was quenched with water (20 mL) at 0 °C and diluted with toluene. The aqueous phase was extracted with toluene (10 mL × 3), and combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in *vacuo* to give crude products. Purification by silica-gel column chromatography (Hexane/Toluene, 9:1) gave **26** of 1.2 g (89%) as yellow solid materials. Rf value 0.36 (Hexane/Toluene, 4:1); M. p. 308–318 °C; ^1H NMR (400 MHz, $CDCl_3$) 8.61 (s, 2H, H-1), 8.54 (d, $J = 8.6$ Hz, 2H, H-8), 7.94 (d, $J = 2.0$ Hz, 2H, H-5), 7.69 (, $J = 8.6$, 2.0 Hz, 2H, H-7), 4.31 (s, 6H, OCH_3), 1.81 (s, 6H, SCH 3, 1.60 (s, 18H, CH_3), 1.42 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 160.9 (C-3), 148.1 (C-6), 142.4 (C-8a), 132.3 (C-2), 131.1 (C-4b), 130.3 (C-8), 127.0 (C-16 b), 126.6 (C-7), 124.4 (two peaks are overlapped, C-4a, C-4c), 124.3 (C-1), 123.2 (C-5), 121.2 (C-4), 60.4 (OCH_3), 36.2 ($\underline{C}(CH_3)_3$), 35.3 ($\underline{C}(CH_3)_3$), 31.7 (CH_3), 30.9 (CH_3), 20.3 (SCH 3 ppm; MS (DART-TOF) *m/z*: 705 $[MH]^+$; IR (neat): 2954, 1357, 1227, 1061, 994, 812, 758, 629 cm^{-1}; HRMS (DART-TOF) calcd. For $C_{46}H_{57}O_2S_2$: 705.3794 $[MH]^+$, found: 705.3787.

4.17. Synthesis of 2,6,11,15-tetra-tert-butyl-3,14-dimethoxy-4,13-bis (methylsulfonyl)dibenzo[g,p]chrysene (**27**), for Scheme 8

The starting **26** (1.5 g, 2.2 mmol) and hydrogen peroxide (30% aq. H_2O_2, 3.0 mL) were dissolved in the mixed solvent of CH_2Cl_2 (12 mL) and acetic acid (24 mL). After the reaction was conducted at 60 °C for 24 h, the extra amounts of hydrogen peroxide (30% aq. H_2O_2, 3.0 mL) were slowly added over 3 min. The reaction was further treated at 60 °C for 6 h, and then quenched with saturated aq. $NaHCO_3$ (50 mL) at 0 °C, and the whole was diluted with toluene. The aqueous phase was extracted with toluene (20 mL × 3), and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude products. Purification by silica-gel column chromatography ($CHCl_3$) gave **27** of 1.3 g (79%) as yellow solid materials. *Rf* value 0.36 (Hexane/Toluene, 4:1); M. p. 300 °C (dec.); ^1H NMR (400 MHz, $CDCl_3$) 8.89 (s, 2H, H-1), 8.48 (d, $J = 8.6$ Hz, 2H, H-8), 8.43 (d, $J = 1.7$ Hz, 2H, H-5), 7.69 (, $J = 8.6$, 1.7 Hz, 2H, H-7), 4.49 (s, 6H, OCH_3), 2.78 (s, 6H, SCH_3), 1.64 (s, 18H, CH_3), 1.42 (s, 18H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 161.7 (C-3), 148.1 (C-6), 142.4 (C-2), 134.3 (16 b), 134.0 (C-8a), 129.7 (C-4b), 127.0 (C-8), 126.9 (two peaks are overlapped, C-4a, C-4c), 126.2 (C-4), 125.8 (C-1), 123.0 (C-7), 122.0 (C-5), 67.9 (SCH_3), 46.2

(OCH_3), 35.9 ($\underline{C}(CH_3)_3$), 35.1 ($\underline{C}(CH_3)_3$), 31.2 (CH_3), 30.7 (CH_3) ppm; MS (DART-TOF) *m/z*: 786 $[M + NH_4]^+$; IR (neat): 2952, 1427, 1361, 1304, 1228, 1138, 1127, 752 cm^{-1}; HRMS (DART-TOF) calcd. For $C_{46}H_{60}NO_6S_2$: 786.3857 $[M + NH_4]^+$, found: 786.3851; Anal. Calcd. For $C_{46}H_{56}O_6S_2$; C, 71.84; H, 7.34. Found: C, 71.59; H, 7.22.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2023.133549.

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[20]. The single crystal of **10** was prepared by slow evaporation of EtOH (1 mL) solution of the sample (5 mg); CCDC-2242974. Monoclinic, space group P 1 21/n 1, colorless, a = 12.0779(2) Å, b =10.5711(3) Å, c = 20.7241(4) Å, α = 90°, β = 90.701(2)°, γ = 90°, V = 2645.79(10) $Å^3$, Z = 4, T = 93 K, $D_{calcd.}$ = 1.344 g cm^{-3}, μ(Mo-Kα) = 2.295 mm^{-1}, R_1= 0.0320, wR_2= 0.0891, GOF = 1.056.
[21]. The single crystal of **12** was prepared by slow evaporation of CH_3CN (2 mL) solution of the sample (5 mg); CCDC-2129618. Monoclinic, space group C 1 C 1, colorless, a = 16.7649(2) Å, b =17.0928(3) Å, c = 9.7733(2) Å, α = 90°, β = 98.315(2)°, γ = 90°, V = 2771.19 (8) $Å^3$, Z = 12, T = 93 K, $D_{calcd.}$ = 1.473 g cm^{-3}, μ(Mo-Kα) = 3.894 mm^{-1}, R_1= 0.0318, wR_2= 0.0999, GOF = 1.186.
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