JOC The Journal of Organic Chemistry

pubs.acs.org/joc Article

One-Pot Synthesis of 2,3-Disubstituted Indanone Derivatives in Water under Exogenous Ligand-Free and Mild Conditions

Anqiao Zhu, Yu Sun, Jingru Lai, Ziyan Chen, Xiaoli Bu, Yan-Ni Yue,* Mengtao Ma,* and Fei Xue*

Cite This: J. Org. Chem. 2022, 87, 7884−7894 Read Online

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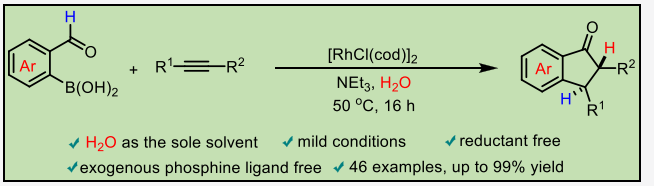
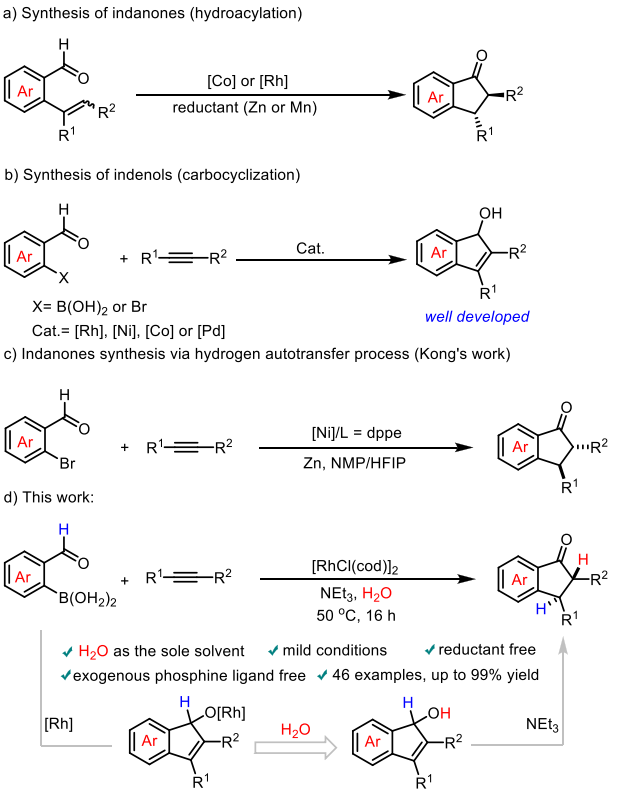
ABSTRACT: Diverse 2,3-substituted indanones are accessed in an efficient and robust protocol by a rhodium-catalyzed tandem carborhodium/cyclization and intramolecular proton shift pathway. The reaction is compatible with a broad range of functional internal acetylenes, especially for natural and functionalized alkynes derivatives, affording the desired indanones in good to excellent yields. Remarkably, this reaction features very mild and sustainable conditions using water as the sole solvent and without exogenous ligands. Control studies support that indanone is formed through the intramolecular proton transfer process from the key intermediate indenol.



INTRODUCTION

Indanone derivatives are widely found in many biological natural products and pharmaceuticals and often employed as versatile transformation platforms in organic synthesis.[1] In particular, 2,3-disubstituted indanones display the unique bioactivities. For example, Pauciflorol F[2] has a potent anticancer property and Pterosin B[3] exhibits an anti-inflammatory activity. Therefore, much effort has been devoted to the expedient preparation of indanone frameworks.[4] Among these, intramolecular hydroacylation is an efficient approach that enables the direct construction of carbocycles (Scheme 1a).[5] As such, seminal discoveries for the synthesis of indanones have emerged from this process involving Rh[6] or Co[7] as catalyst. Besides, two successful strategies of metal-free methods for intramolecular hydroacylation were recently developed.[8,9] However, the hydroacylation reaction requires tedious preparation of precursors for further cyclization and also exhibits a limited substrate scope with regard to disubstituted alkenes. To our knowledge, only two examples of hydroacylation reactions could be tolerated with trisubstituted alkenes to give 2,3-disubstituted indanones. Alternatively, since the pioneer work of Yamamoto,[10] transition-metal-catalyzed intermolecular carbocyclization reactions have been well developed for the construction of 2,3-disubstituted indenols (Scheme 1b), where the utility of these indenol derivatives need further subsequent transformations to access relative 2,3-substituted indanone frameworks.[10−13] Until recently, Kong's group clearly demonstrated a nickel-catalyzed domino reductive cyclization of alkynes and *o*-bromoaryl aldehydes to afford indanones through a hydrogen auto transfer process (Scheme 1c).[14a] More recently, direct C−H bond functionalization to access indanones through the photoredox/hydrogen atom transfer process has also been developed.[14c] Notwithstanding the advancement in this field, we reasoned that the establishment of an environmentally

Scheme 1. Methods for the Synthesis of Indanones



Received: March 9, 2022
Published: May 25, 2022

https://doi.org/10.1021/acs.joc.2c00544
J. Org. Chem. 2022, 87, 7884−7894

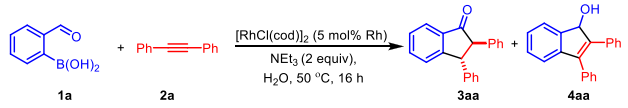
benign scenario to access 2,3-disubstituted indanones is of high appeal under mild conditions, especially for those that consider the demand of environmental friendliness and sustainability.

Inspired by the role of the amine base which allows the stereospecific [1,3]-allylic rearrangements,[15] we envisioned that a domino reaction of 2-formylarylboronic acids and alkynes may directly allow access to indanones (Scheme 1d). This one-pot reaction proceeds via the in situ generated indenols through Rh-catalyzed arylation of alkynes, carbocyclization, and subsequent 1,3-H intramolecular transfer process using amine as a base. Herein, we reported a rhodium-catalyzed one-pot synthesis of 2,3-disubstituted indanone frameworks from 2-formylarylboronic acids and alkynes using water as the sole solvent.[16] The significant features of this approach include: (i) one pot synthesis of 2,3-disubstituted indanones with excellent regio- and diastereo-selectivity; (ii) water as the sole solvent of inherent "green chemistry" features; (iii) no need of exogenous ligands and reductants; and (iv) applicability to the late-stage complex compound.

RESULTS AND DISCUSSION

We started our investigation by evaluating the reaction of 2-formylbenzene boronic acid with commercially available diphenylacetylene as the model substrates. Gratifyingly, when the reaction was conducted in water at 50 °C for 16 h employing 1.5 equiv of 2-formylbenzene boronic acid (**1a**) and 1.0 equiv of diphenylacetylene (**2a**) in the presence of $[RhCl(cod)]_2$ (5.0 mol % [Rh]) as catalyst and triethylamine (2.0 equiv) as a base, 97% isolated yield of **3aa** could be obtained with excellent diastereoselectivity (Table 1, entry 1). Replacing Rh with other transition-metal catalysts (Ni, Co, Pd, or Ir) resulted in invalid results, no indanone products were detected (Table 1, entries 2−5). Further screening of other rhodium catalysts such as $RhCl_3{\cdot}XH_2O$ or $[Cp^*Cl_2Rh]$ showed that no reaction occurred due to no implicit conversion of diphenylacetylene (Table 1, entry 6). The use of DABCO afforded the product in 64% yield, while the other two organic bases were inferior or even invalid (Table 1, entries 7−9). Decreasing the amount of NEt_3 to 0.2 equiv led to the mixture of indanone **3aa** and indenol **4aa** in 10% and 75% yields, respectively, which may well suggest that the reaction proceeds through a key intermediate indenol (vide infra). The use of a stronger inorganic base gave the exclusive indenol product **4aa** in 97% yield, probably because the reaction is terminated in the protonation step.[13,17] In addition, the reaction in ethanol dioxane, or toluene all gave a similar efficiency, while using MTBE as the solvent gave a lower yield. Furthermore, instead of 2-formylbenzene boronic acid, potassium 2-formylphenyl trifluoroborate was also found to be well compatible with this reaction system. In contrast, 2-formylbenzene boroxine resulted in less low efficiency. These results suggest that the good solubility of substrates in water could be beneficial for this reaction.

Table 1. Optimization of Reaction Conditions[a]



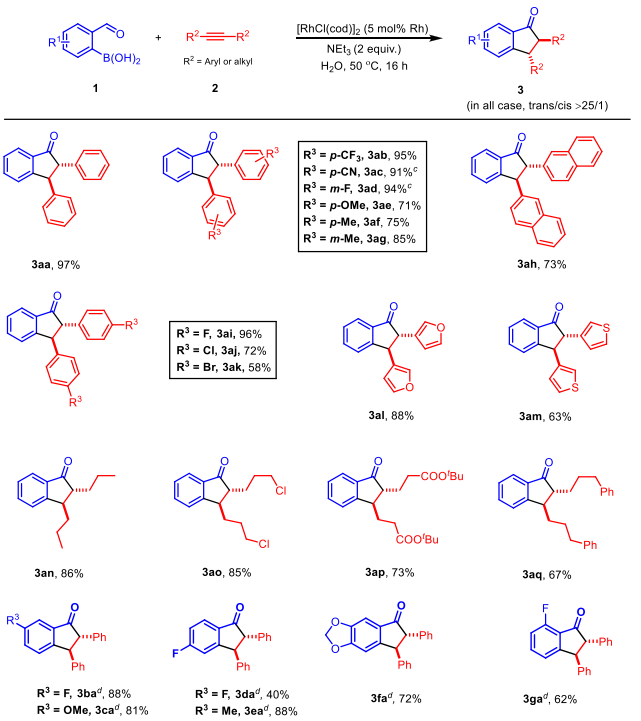
1a 2a 3aa 4aa

entry	variation	yield of **3aa** (%)[b]	yield of **4aa** (%)b
1	no	98(97[c])	0
2	$Ni(OAc)_2$	N.D.	N.D.
3	$Co(OAc)_2$, $Co(acac)_2$, or $[Cp^*_2Co]PF_6$	N.D.	N.D.
4	$Pd(OAc)_2$	N.D.	N.D.
5	$[IrCl(cod)]_2$	N.D.	N.D.
6	$RhCl_3{\cdot}XH_2O$ or $[Cp^*Cl_2Rh]_2$	N.D	N.D
7	DIPEA	20	64
8	DBU	23	22
9	DABCO	64	0
10	20 mol % NEt_3	10	75
11	20 mol % KOH	0	97
12	EtOH	96	0
13	dioxane	95	0
14	toluene	96	0
15	MTBE	80	0
16	Bpin	76	0
17	BF_3K	97(95[c])	0

[a]Standard condition: **1a** (0.225 mmol), **2a** (0.15 mmol), catalyst (5.0 mol %), base (2.0 equiv) was dissolved in solvent (0.5 mL), and the mixture was stirred at 50 °C for 16 h. [b]^1H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield. N.D. = not detected.

As shown in Scheme 2, the scope with a series of symmetric acetylenes was first investigated. Diarylacetylenes containing electron-deficient groups in the para- or meta-positions led to the desired products in excellent reactivity and high selectivity for the trans/cis of diastereoisomer (>60/1) (Scheme 2, **2b**−**2d**). In contrast, replacing the substituents by electron-donating groups afforded the corresponding products (**3ae**−

Scheme 2. Scope of Symmetric Diarylacetylenes and Dialkyacetlyenes[a,b]



[a]Reaction conditions: **1a** (0.225 mmol), **2a** (0.15 mmol), catalyst (5.0 mol %), NEt_3 (2.0 equiv) was dissolved in H_2O (0.5 mL), and the mixture was stirred at 50 °C for 16 h. [b]Isolated yield. [c]NEt_3 (5.0 equiv). [d]NEt_3 (5.0 equiv), 80 °C.

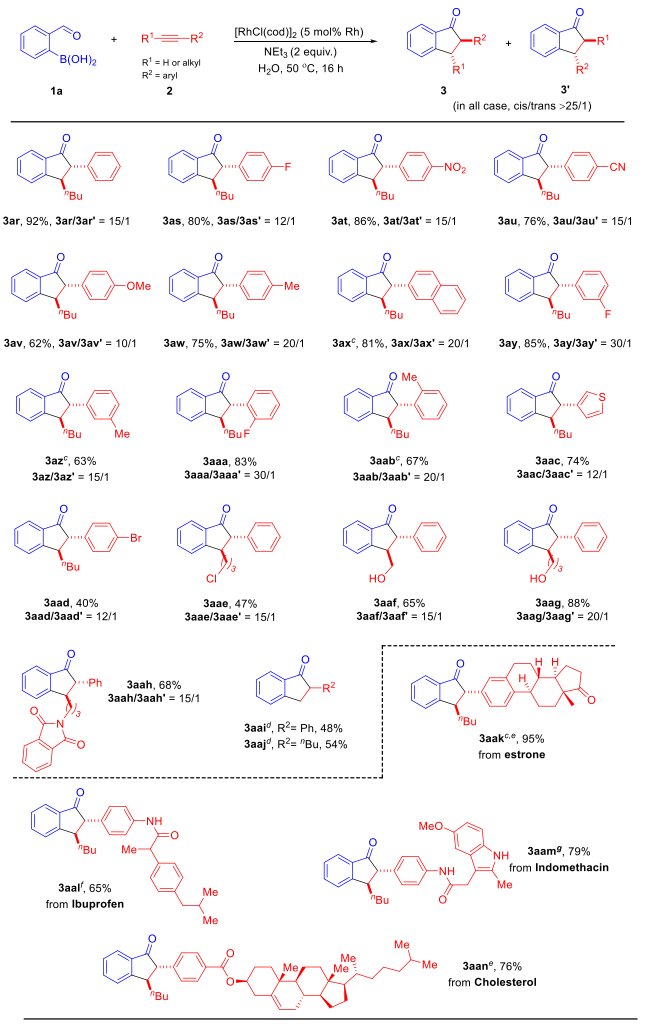
https://doi.org/10.1021/acs.joc.2c00544
J. Org. Chem. 2022, 87, 7884−7894

3ag) in 71%−85% yields. In addition, the naphthyl-containing acetylene 2 h could proceed smoothly for the target product **3ah** in 73% yield. It is noteworthy that synthetically useful halogens (F, Cl, and Br) on the phenyl ring were allowed to react with 2-formylbenzene boronic acid (**1a**), producing the corresponding products **3ai**−**3ak** in moderate to excellent yields. To our delight, symmetric heteroaryl-containing acetylenes, such as, furan and thiophene, were amenable for this transformation, affording the indanones **3al** and **3am** in 88% and 63% yields, respectively. Of note, 4-octyne and those possessing tailed, tethered substituents, such as Cl, ester, and Ph, worked well in this protocol, giving the corresponding indanones **3an**−**3aq** in good yields. Furthermore, a range of 2-formylaryl boronic acid, electron-rich and electron-deficient, such as F, Me, and OMe, underwent this reaction with diphenylacetylene to provide the products **3ba**−**3fa** in moderate to high yields. In addition, sterically hindered boronic acid **2g** was also transformed into the desired **3ga** in 62% yield. Finally, the steric symmetric alkynes, such as bis(1-naphthyl)acetylene and 1,2-bis(2-methoxyphenyl)acetylene are not suitable for this strategy.

Next, for unsymmetrical alkyl(aryl)acetylenes, the excellent regioselectivity is in contrast to our alkyne carbocylization reaction[18] and others,[19] where the steric aryl group of arylrhodium intermediate installs to the less hindered end of the unsymmetric alkyne (Scheme 3). It was found that aryl butyl acetylenes with different electronic properties at the para-positions of the phenyl ring, such as F, NO_2, CN, OMe, and Me, reacted well with 2-formylbenzene boronic acid (**1a**) to generate corresponding products (**3ar**−**3aw**), in 62−92% yields. Also, the F and Me group at meta-positions of the phenyl ring release similar efficiency. Notaby, sterically hindered alkyl(aryl)acetylenes (**2aa** and **2ab**) were also suit for this protocol that provided indanones in 83% and 67% yields, respectively. Additionally, when aryl butyl acetylene employing a weak electron-deficient Br group, the relative lower yield was observed. Thiophen-3-yl butyl acetylene could be successfully applied in this reaction system, albeit furnishing the desired product **3aac** in 74% yield. For broader synthetic interests, functional tethered alkyl phenyl acetylenes, such as Cl (**2ae**), free hydroxyl groups (**2af** and **2ag**), and amide (**2ai**) proved to be amenable to the domino transformation. Also, terminal alkynes, such as 1-hexyne and phenylacetylene, were both tolerated in this transformation, giving the desired products **3aai** and **3aaj** with moderated yields with exclusive regioselectivity. Remarkably, we applied this reaction to late-stage functionalization of pharmaceutical compound. It was pleasing to find that estrone and cholesterol-derived aryl butyl acetylenes successfully participated in the domino process and resulted in the correspondingly indanones **3aak** and **3aan** in high yields. Also, the anti-inflammatory drug ibuprofen scaffold was proven to be compatible for furnishing the corresponding indanones (**3aal**). The hydrolysis of the substrate-containing indomethacin unit will occur under standard conditions, delivering **3aam** in 79% yield.

To further illustrate the practicality and utility of this protocol (Scheme 4), a large-scale reaction was conducted with diphenylacetylene (10.0 mmol) and 2-formylbenzene boronic acid (15.0 mmol) under standard conditions. Pleasingly, the corresponding product **3aa** was obtained with 92% yield and maintenance of excellent diastereoselectivity. To our delight, when reducing the catalyst loading to 1 mol %, the reaction still worked well with a marginally lower yield.

Scheme 3. Scope of Unsymmetric Alkyl(aryl)acetylenes[a,b]



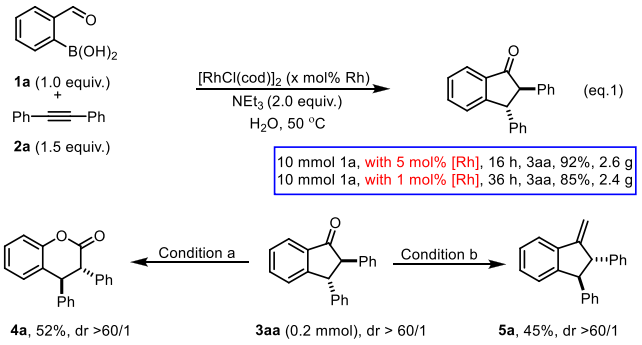
[a]Reaction Condition: **1a** (0.225 mmol), **2a** (0.15 mmol), catalyst (5.0 mol %), NEt_3 (2.0 equiv) was dissolved in H_2O (0.5 mL), and the mixture was stirred at 50 °C for 16 h, 80 °C. [b]Isolated yield. [c]NEt_3 (5.0 equiv), 80 °C. [d]EtOH instead of H_2O, 80 °C, single regioisomer. [e]Obtained as a 1:1 mixture of the two possible *trans* indanone products. [f]Obtained as a 1:1:1:1 mixture of the four possible *trans* indanone products. [g]Generated by in situ hydrolysis of *N*-(4-(1-butyl-3-oxo-2,3-dihydro-1H-inden-2-yl)phenyl)-2-(1-(4-chloroben zoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetamide.

Furthermore, subsequent transformations of the 2,3-diphenyl indanone derivative **3aa** have been performed. For instance, compound **3aa** could be converted into lactone **4a** by a Baeyer−Villiger oxidation reaction[20] or olefin **5a** through the Wittig reaction,[21] respectively.

To gain more insights into the reaction mechanism of this transformation, several control experiments were implemented (Scheme 5). Initially, when the reaction was conducted for a shorter duration time (15 min) with the mixture solvent (toluene/water), a mixture of **3aa** and **4aa** was obtained in 11% and 51% yields, respectively, with 65% conversion of diphenylacetylene (eq 1). The result revealed that the reaction likely generated the indenols first and subsequently transferred to corresponding indanones. Next, to demonstrate the proton shift process, the deuterium experiment of diphenylacetylenes with 2-formylbenzene boronic acids in D_2O delivered the products with the 92% deuterium incorporation of the 2-

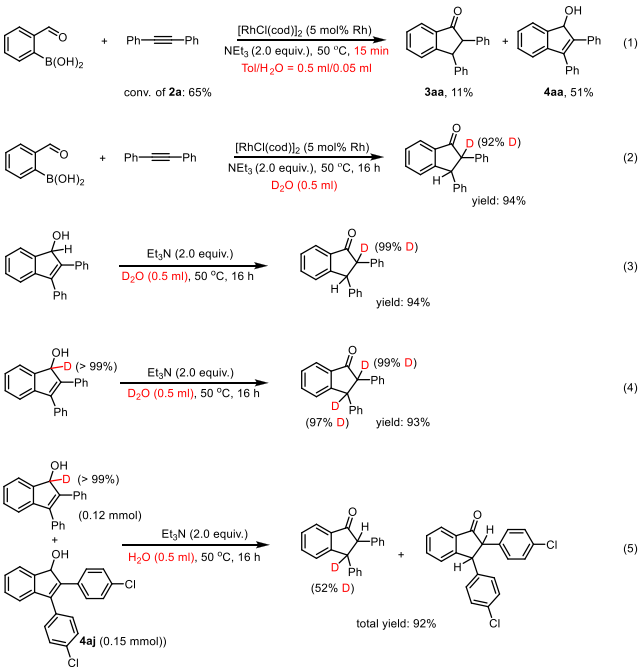
https://doi.org/10.1021/acs.joc.2c00544
J. Org. Chem. 2022, 87, 7884−7894

Scheme 4. Gram-Scale Reaction and Transformations[a]



[a]Conditions: (a) **3aa** (0.2 mmol, 1.0 equiv), m-CPBA (4.0 equiv), and p-TsOH·H_2O (0.2 equiv) in DCM, reflux for 24 h; (b) **3aa** (0.2 mmol, 1.0 equiv), CH_3PPh_3Br (2.5 equiv), and *n*-BuLi (2.5 equiv) in THF, at 0 °C for 1 h, and then stirred at room temperature for another 4 h. m-CPBA = *m*-chloroperbenzoic acid; p-TsOH = p-toluenesulfonic acid.

Scheme 5. Control Experiments



postion of indanone, whereas no deuterium incorporation was observed at C3 of indanone (eq 2). Further, compound **4aa** and deuterium-labeled indenole **4aa**-D were subjected to triethylamine and D_2O for 16 h at 50 °C. Equation (3) shows the deuterium incorporation into the 2-position of indanone with 99% D, consistent with eq (2), while eq (4) exhibited high deuterium incorporation into both C2 and C3 of the related indanone. These results clearly indicated that high deuterium transfer to the 2-position of indanone was from D_2O, and indanone deuterated at the C3 position was derived from the deuterium at the α-position of indenol. A crossover experiment employing a mixture of indenol **4aa**-D and **4aj** was performed, and no deuterium incorporation of **3aj** was observed, thus indicating an intramolecular proton shift process which following Paton's work[15b] (eq 5).

CONCLUSION

In conclusion, we have developed a practical and sustainable strategy for the synthesis of 2,3-disubstituted indanones with high regioselectivity and excellent diastereoselectivity via a rhodium-mediated domino reaction of internal acetylenes and 2-formylaryl boronic acids under mild, robust, and sustainable conditions. Moreover, this strategy could tolerate diverse functional groups and produce corresponding indanones in good to excellent yields. In addition, we could extend this protocol to access late-stage modification of the pharmaceutical substrate. Control experiments confirmed that intramolecular proton shift is the key step for the successful one-pot preparation of indanone with amine as the base.

EXPERIMENTAL SECTION

General Information. All anaerobic manipulations were carried out with standard Schlenk techniques under nitrogen gas. Analytical thin-layer chromatography (TLC) was performed on silica gel, irradiation with UV light. For column chromatography, 200−300 mesh silica gel was used. The NMR spectra were recorded using a BRUKER 600 MHz (or 400 Hz) Fourier-transform and a JEOL 400 MHz Fourier-transform NMR spectrometer. Chemical shifts (δ) for protons are reported in ppm and are referenced to residual $CHCl_3$ (7.26 ppm). Chemical shifts (δ) for carbon are reported in ppm and are referenced to the deuterated solvent $CDCl_3$ (77.0 ppm). The following abbreviations were used to explain the multiplicities: s (singlet), bs (broad singlet), d (doublet), t (triplet), heptet (hept), sextet (sext), quintet (quint), m (multiplet); coupling constants (J) are in Hertz (Hz). HRMS spectra were recorded on a Xevo G2-XS QTof (Waters Corporation) using electrospray ionization. Unless otherwise noted, all the solvents and commercially available reagents were used as received for the reactions without further purification. All commercially available reagents were purchased and used without further purification unless otherwise noted. Preparation of all these starting materials, such as aryl(alkyl)acetylenes, aryl(aryl)acetylenes **2a−2m**,[22] **2o−2q**,[23] **2r−2ag**,[24] **2ah**,[25] **2ak**,[26] 2-(2′-formylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,[27] and potassium (2-formylphenyl)trifluoroborate[28] were synthesized according to the reported references, and they were assigned by comparison of their NMR spectra with the reported data.

General Procedure for the Synthesis of 2al and 2am. To a Schlenk tube (50 mL) under an atmosphere of nitrogen was added ibuprofen or indomethacin (3.8 mmol, 1.0 equiv), 4-(hex-1-yn-1-yl)aniline (657 mg, 3.8 mmol, 1.0 equiv). The mixture was closed by a septum, purged by nitrogen gas several times, and then the freshly degassed DCM (15 mL) and 4-dimethylaminopyridine (470 mg, 3.8 mmol, 1.0 equiv) and dicyclohexylcarbodiimide (790 mg, 3.8 mmol, 1.0 equiv) were added into the reaction mixture and kept stirring at room temperature for 24 h. The resulting mixture was diluted with water (30 mL), the aqueous layer was extracted with EA (3 × 10 mL), and the combined organic layers were washed with brine (2 × 20 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford the indicated compounds.

N-(4-(Hex-1-yn-1-yl)phenyl)-2-(4-isobutylphenyl)-propan-amide (***2al***). Using (PE/EA = 10/1) as an eluent gave a white solid (1.17 g, 85% yield); mp 65.6−66.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−7.36 (m, 2H), 7.29−7.28 (m, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 3.68 (q, J = 7.1 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 2.38 (t, J = 7.1 Hz, 2H), 1.87 (hept, J = 6.7 Hz, 1H), 1.62−1.51 (m, 5H, overlap 1.56 (d, J = 7.2 Hz, 3H)), 1.47 (sext, J = 7.6 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 172.7, 141.1, 137.9, 137.3, 132.1, 129.9, 127.4, 119.7, 119.3, 89.9, 80.2, 47.7, 45.0, 30.9, 30.2, 22.4, 22.0, 19.1, 18.5, 13.7. HRMS (ESI): $[M + H]^+$ calcd for $C_{25}H_{32}NO$, 362.2478; found, 362.2479.

2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-N-(4-(hex-1-yn-1-yl)phenyl)acetamide (***2am***). Using (PE/EA = 10/1)

https://doi.org/10.1021/acs.joc.2c00544
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as an eluent gave a yellow oil (1.58 g, 81% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.36 (s, 1H), 7.32 (q, J = 8.7 Hz, 4H), 6.93 (d, J = 2.5 Hz, 1H), 6.87 (d, J = 9.0 Hz, 1H), 6.71 (dd, J = 9.1, 2.5 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 2H), 2.43 (s, 3H), 2.38 (t, J = 7.1 Hz, 2H), 1.57 (quint, J = 7.2 Hz, 2H), 1.46 (sext, J = 7.6 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 168.3, 168.1, 156.4, 139.7, 137.8, 136.7, 136.67, 133.5, 132.2, 131.2, 131.0, 130.1, 129.3, 120.2, 119.7, 115.2, 112.5, 112.2, 100.8, 90.2, 80.1, 55.8, 33.4, 30.8, 22.0, 19.1, 13.7, 13.4. HRMS (ESI): [M + H]$^+$ calcd for $C_{31}H_{30}ClN_2O_3$, 513.1939; found, 513.1938.

General Procedure for Synthesis of 2an. To a Schlenk tube (50 mL) under an atmosphere of nitrogen was added cholesterol (1.483 g, 3.8 mmol, 1.0 equiv) and 4-(hex-1-yn-1-yl)benzoic acid (775 mg, 3.8 mmol, 1.0 equiv). The mixture was closed by a septum, purged by nitrogen gas several times, then the freshly degassed DCM (15 mL) and 4-dimethylaminopyridine (470 mg, 3.8 mmol, 1.0 equiv) and dicyclohexylcarbodiimide (790 mg, 3.8 mmol, 1.0 equiv) was then added into the reaction mixture and kept stirring at room temperature for 24 h. The resulting mixture was diluted with water (30 mL), the aqueous layer was extracted with EA (3 × 10 mL), and the combined organic layers were washed with brine (2 × 20 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford the indicated compound.

*(3S, 8S, 9S, 10R, 13R, 14S, 17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15, 16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(Hex-1-yn-1-yl)-benzoate (**2an**).* Using (PE/EA = 10/1) as an eluent to give a white solid (1.95 g, 90% yield); mp 144.5−145.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 5.41 (d, J = 5.0 Hz, 1H), 4.88−4.80 (m, 1H), 2.49−2.39 (m, 4H), 2.00−1.97 (m, 3H), 1.90 (dt, J = 13.6, 3.6 Hz, 1H), 1.85−1.81 (m, 1H), 1.72 (qd, J = 11.6, 3.4 Hz, 1H), 1.62−1.44 (m, 10H), 1.38−1.34 (m, 3H), 1.27−1.08 (m, 8H), 1.06 (s, 3H), 1.03−0.97 (m, 3H), 0.95 (t, J = 7.3 Hz, 3H), 0.92 (d, J = 6.4 Hz, 3H), 0.87 (dd, J = 6.7, 2.7 Hz, 6H), 0.69 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 165.5, 139.6, 131.4, 129.5, 129.4, 128.7, 122.8, 93.7, 80.2, 74.7, 56.7, 56.2, 50.1, 42.3, 39.8, 39.6, 38.2, 37.1, 36.6, 36.2, 35.8, 32.0, 31.9, 30.7, 28.3, 28.0, 27.9, 24.3, 23.9, 22.8, 22.6, 22.1, 21.1, 19.4, 19.2, 18.7, 13.7, 11.9. HRMS (ESI): [M + H]$^+$ calcd for $C_{40}H_{59}O_2$, 571.4510; found, 571.4508.

General Procedure for the Synthesis of 3. To a Schlenk tube (10 mL) under an atmosphere of nitrogen was added acetylene (**2**, 0.15 mmol, 1.0 equiv), $[RhCl(cod)]_2$ (1.8 mg, 5 mol %[Rh]), 2-formylbenzene boronic acid (**1a**, 33.8 mg, 0.225 mmol, 1.5 equiv). The mixture was closed by a septum, purged by nitrogen gas three times, and then the freshly degassed H_2O (0.5 mL) and NEt_3 (30.4 mg, 0.3 mmol, 2.0 equiv) was added. The resulting mixture was stirred at 50 °C (oil bath temperature) for 16 h and then passed through a short pad of silica gel with ethyl acetate (5.0 mL) as the eluent. The dr value of the target product was determined to be more than >60/1 by 1H NMR. Further, the crude product was purified by preparative TLC on silica gel to give the target compound **3**.

*2,3-Diphenyl-2,3-dihydro-1H-inden-1-one (**3aa**).* Purification by preparative TLC on silica gel (eluents: PE/EA = 10/1) to afford **3aa** (42.1 mg, 97% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.7 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.31 (m, 7H), 7.12 (t, J = 7.0 Hz, 4H), 4.60 (d, J = 4.8 Hz, 1H), 3.83 (d, J = 4.8 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 205.3, 156.1, 142.4, 138.5, 136.1, 135.4, 128.9, 128.8, 128.32, 128.26, 127.9, 127.16, 127.15 126.7, 124.0, 64.6, 54.8. HRMS (ESI): [M + H]$^+$ calcd for $C_{21}H_{17}O$, 285.1274; found, 285.1272.

*2,3-Bis(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-inden-1-one (**3ab**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford **3ab** (60.1 mg, 95% yield) as a white solid, mp 116−117 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, J = 7.7 Hz, 1H), 7.70 (td, J = 7.5, 1.3 Hz, 1H), 7.60 (dd, J = 8.4, 2.5 Hz, 4H), 7.55 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.23 (dd, J = 8.3, 2.9 Hz, 4H), 4.64 (d, J = 5.2 Hz, 1H), 3.85 (d, J = 5.2 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$): δ −62.56 (s), −62.60 (s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 203.7, 154.9, 146.0, 141.9, 136.1, 136.0, 130.1 (q, J = 32.8 Hz) 129.1, 129.0, 128.4, 126.7, 126.2 (q, J = 3.8 Hz), 125.5 (q, J = 5.3 Hz), 124.5, 124.3 (q, J = 273.2 Hz), 64.3, 54.5. HRMS (ESI): [M + H]$^+$ calcd for $C_{23}H_{15}F_6O$, 421.1022; found, 421.1014.

*4,4′-(3-Oxo-2,3-dihydro-1H-indene-1,2-diyl)dibenzonitrile (**3ac**).* Purification by preparative TLC on silica gel (PE/EA = 2/1) to afford the product **3ac** (46.2 mg, 91% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.64 (dd, J = 8.2, 3.5 Hz, 4H), 7.56 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H), 7.21 (dd, J = 8.1, 4.8 Hz, 4H), 4.61 (d, J = 5.2 Hz, 1H), 3.81 (d, J = 5.2 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 202.5, 154.1, 147.0, 142.9, 136.2, 135.8, 133.0, 132.8, 129.3, 128.7, 126.5, 124.6, 118.5, 118.4, 111.8, 111.7, 64.2, 54.4, 29.7. HRMS (ESI): [M + H]$^+$ calcd for $C_{23}H_{15}N_2O$, 335.1179; found, 335.1190.

*2,3-Bis(3-fluorophenyl)-2,3-dihydro-1H-inden-1-one (**3ad**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (45.2 mg, 94% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.32−7.26 (m, 3H), 6.99 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 7.4 Hz, 2H), 6.84−6.78 (m, 2H), 4.56 (d, J = 5.0 Hz, 1H), 3.78 (d, J = 5.0 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$): δ −111.99, −112.34. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 204.1, 163.2 (d, J = 248.5 Hz), 163.1 (d, J = 248.5 Hz), 155.2, 144.7 (d, J = 6.8 Hz), 140.5 (d, J = 7.2 Hz), 136.0, 135.9, 130.7 (d, J = 8.5 Hz), 130.6 (d, J = 8.0 Hz), 128.8, 126.7, 124.4, 124.3 (d, J = 2.0 Hz), 123.7 (d, J = 3.0 Hz), 115.4 (d, J = 22.0 Hz), 114.8 (d, J = 21.4 Hz), 114.5 (d, J = 20.9 Hz), 64.1, 54.4. HRMS (ESI) [M + H]$^+$ calcd for $C_{21}H_{15}F_2O$, 321.1085; found, 321.1095.

*2,3-Bis(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-one (**3ae**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (36.6 mg, 71% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 7.7 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.02 (m, 4H), 6.85 (dd, J = 8.8, 2.6 Hz, 4H), 4.48 (d, J = 5.0 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.72 (d, J = 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 205.7, 158.74 158.71, 156.3, 136.1, 135.3, 134.6, 130.6, 129.4, 128.9, 128.2, 126.6, 123.9, 114.30, 114.27, 64.2, 55.3, 54.3. HRMS (ESI) [M + H]$^+$ calcd for $C_{23}H_{21}O_3$, 345.1485; found, 345.1485.

*2,3-Bis(4-methylphenyl)-2,3-dihydro-1H-inden-1-one (**3af**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (35.1 mg, 75% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.7 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 7.7 Hz, 1H), 7.13 (dd, J = 8.1, 2.3 Hz, 4H), 7.01 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 4.53 (d, J = 4.8 Hz, 1H), 3.77 (d, J = 4.8 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 205.6, 156.4, 139.6, 136.8, 136.2, 135.6, 135.3, 129.58, 129.55, 128.3, 128.2, 127.8, 126.7, 124.0, 64.4, 54.6, 21.12, 21.09. HRMS (ESI) [M + H]$^+$ calcd for $C_{23}H_{21}O$, 313.1587; found, 313.1584.

*2,3-Bis(3-methylphenyl)-2,3-dihydro-1H-inden-1-one (**3ag**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (40.2 mg, 85% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, J = 7.7 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.32 (dd, J = 7.8, 1.0 Hz, 1H), 7.21 (td, J = 7.6, 2.3 Hz, 2H), 7.09 (d, J = 7.6 Hz, 2H), 6.94−6.89 (m, 4H), 4.53 (d, J = 4.6 Hz, 1H), 3.77 (d, J = 4.6 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 205.7, 156.5, 142.6, 138.7, 138.6, 138.5, 136.2, 135.4, 129.1, 128.8, 128.7, 128.6, 128.2, 128.0, 127.9, 126.8, 125.4, 125.1, 124.0, 64.5, 54.9, 21.46, 21.45. HRMS (ESI): [M + H]$^+$ calcd for $C_{23}H_{21}O$, 313.1587; found, 313.1583.

*2,3-Di(naphthalen-2-yl)-2,3-dihydro-1H-inden-1-one (**3ah**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (42.1 mg, 73% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.7 Hz, 1H), 7.86−7.82 (m, 4H), 7.78−7.71 (m, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.62 (s, 2H), 7.57 (d, J = 7.5 Hz, 1H), 7.47 (m, 4H), 7.36 (d, J = 7.7 Hz, 1H), 7.23 (dd, J = 8.5, 1.8 Hz,1H), 7.19 (dd, J = 8.5, 1.8 Hz, 1H), 4.86 (d, J = 4.9 Hz, 1H), 4.10 (d, J = 4.9 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 205.3,

https://doi.org/10.1021/acs.joc.2c00544
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156.2, 139.7, 136.4, 135.9, 135.6, 133.6, 133.5, 132.7, 129.1, 128.8, 128.5, 127.83, 127.75, 127.7, 127.0, 126.9, 126.4, 126.2, 126.1, 126.0, 125.9, 125.7, 124.2, 64.8, 55.3. HRMS (ESI): $[M + H]^+$ calcd for $C_{29}H_{21}O$, 385.1587; found, 385.1584.

*2,3-Bis(4-fluorophenyl)-2,3-dihydro-1H-inden-1-one (**3ai**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (46.3 mg, 96% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.7 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 7.7 Hz, 1H), 7.19−6.91 (m, 8H), 4.50 (d, J = 5.2 Hz, 1H), 3.73 (d, J = 5.2 Hz, 1H). ^{19}F NMR (565 MHz, CDCl3): δ −110.79, −112.87 (s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 204.9, 162.2 (d, J = 247.4 Hz), 162.1 (d, J = 247.1 Hz), 155.6, 137.9 (d, J = 3.5 Hz), 136.0, 135.8, 133.9 (d, J = 3.5 Hz), 130.1 (d, J = 8.2 Hz), 129.5 (d, J = 8.3 Hz), 128.7, 126.6, 124.2, 115.99 (d, J = 21.7 Hz), 115.98 (d, J = 21.6 Hz), 64.2, 54.4. HRMS (ESI): $[M + H]^+$ calcd for $C_{21}H_{15}F_2O$, 321.1085; found, 321.1064.

*2,3-Bis(4-chlorophenyl)-2,3-dihydro-1H-inden-1-one (**3aj**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (38.4 mg, 72% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, J = 7.7 Hz, 1H), 7.66 (td, J = 7.5, 1.2 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.39−7.24 (m, 5H), 7.02 (dd, J = 8.5, 2.2 Hz, 4H), 4.49 (d, J = 5.2 Hz, 1H), 3.72 (d, J = 5.2 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 204.1, 155.2, 140.6, 136.5, 136.0, 135.7, 133.3, 133.28, 129.8, 129.3, 129.2, 129.1, 128.7, 126.5, 124.2, 64.1, 54.2. HRMS (ESI): $[M + H]^+$ calcd for $C_{21}H_{15}{}^{35}Cl_2O$, 353.0494; found, 353.0488. $[M + Na]^+$ calcd for $C_{21}H_{14}{}^{37}Cl_2ONa$, 377.0284; found, 377.0300.

*2,3-Bis(4-bromophenyl)-2,3-dihydro-1H-inden-1-one (**3ak**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (38.3 mg, 58% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, J = 7.7 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 8.2 Hz, 4H), 7.28 (d, J = 7.8 Hz, 1H), 6.96 (dd, J = 8.4, 2.0 Hz, 4H), 4.47 (d, J = 5.2 Hz, 1H), 3.70 (d, J = 5.2 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 204.0, 155.1, 141.0, 137.0, 136.0, 135.7, 132.2, 132.1, 130.1, 129.6, 128.7, 126.5, 124.2, 121.5, 121.4, 64.1, 54.3. HRMS (ESI): $[M + H]^+$ calcd for $C_{21}H_{15}{}^{79}Br_2O$, 440.9484; found, 440.9471. Calcd for $C_{21}H_{15}{}^{81}Br_2O$, 442.9464; found, 442.9478.

*2,3-Di(furan-3-yl)-2,3-dihydro-1H-inden-1-one (**3al**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (35.0 mg, 88% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, J = 7.7, 1H), 7.65 (td, J = 7.5, 1.3 Hz, 1H), 7.47 (tt, J = 7.5, 1.9 Hz, 1H), 7.46−7.45 (m, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.41−7.40 (m, 2H), 6.36 (d, J = 1.9, Hz, 1H), 6.21 (dd, J = 1.9, 0.9 Hz, 1H), 4.42 (d, J = 5.5 Hz, 1H), 3.72 (d, J = 5.6 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 203.5, 154.5, 144.1, 143.4, 140.1, 139.8, 135.5, 135.4, 128.4, 126.1, 125.6, 124.1, 121.0, 109.7, 109.2, 53.7, 43.6. HRMS (ESI): $[M + H]^+$ calcd for $C_{17}H_{13}O_3$, 265.0859; found, 265.0864.

*2,3-Di(thiophen-3-yl)-2,3-dihydro-1H-inden-1-one (**3am**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (28.3 mg, 63% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, J = 7.6 Hz, 1H), 7.65 (td, J = 7.5, 1.3 Hz, 1H), 7.48 (tt, J = 7.5, 1.0 Hz, 1H), 7.38 (dd, J = 7.7, 1.0 Hz, 1H), 7.33 (td, J = 5.1, 2.9 Hz, 2H), 7.16 (m, 1H), 7.08 (dd, J = 3.1, 1.3 Hz, 1H), 6.98 (dd, J = 5.0, 1.3 Hz, 1H), 6.86 (dd, J = 5.0, 1.4 Hz, 1H), 4.70 (d, J = 5.0 Hz, 1H), 3.95 (d, J = 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 203.9, 155.1, 142.6, 137.6, 135.5, 135.4, 128.4, 126.92, 126.87, 126.6, 126.5, 126.3, 124.2, 122.3, 121.9, 58.6, 49.0. HRMS (ESI): $[M + H]^+$ calcd for $C_{17}H_{13}OS_2$, 297.0402; found, 297.0402.

*2,3-Dipropyl-2,3-dihydro-1H-inden-1-one (**3an**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (28.0 mg, 86% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, J = 7.6 Hz, 1H), 7.58 (td, J = 7.5, 1.2 Hz, 1H), 7.47 (dd, J = 7.6, 1.0 Hz, 1H), 7.39−7.31 (m, 1H), 3.06 (ddd, J = 8.1, 4.8, 2.7 Hz, 1H), 2.36 (ddd, J = 8.1, 5.3, 2.8 Hz, 1H), 1.88−1.68 (m, 2H), 1.68−1.51 (m, 2H), 1.48−1.33 (m, 4H), 0.94 (t, J = 17.3 Hz, 3H), 0.93 (t, J = 17.3 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 209.2, 158.0, 136.3, 134.6, 127.4, 125.7, 123.7, 53.6, 44.7, 38.6, 34.4, 20.5, 20.4, 14.34, 14.27. HRMS (ESI): $[M + H]^+$ calcd for $C_{15}H_{21}O$, 217.1587; found, 217.1585.

*2,3-Bis(3-chloropropyl)-2,3-dihydro-1H-inden-1-one (**3ao**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (36.2 mg, 85% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, J = 7.6 Hz, 1H), 7.63 (td, J = 7.5, 1.2 Hz, 1H), 7.50 (dd, J = 7.8, 1.0 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 3.60−3.54 (m, 4H), 3.11 (dt, J = 7.5, 3.8 Hz, 1H), 2.38 (ddd, J = 6.9, 5.9, 3.1 Hz, 1H), 2.04−1.78 (m, 8H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 207.7, 156.6, 136.1, 135.1, 127.9, 125.6, 123.9, 52.4, 44.9, 44.8, 44.2, 32.9, 30.0, 29.9, 29.2. HRMS (ESI): $[M^+H]^+$ calcd for $C_{15}H_{19}{}^{35}Cl_2O$, 285.0807; found, 285.0805. Calcd for $C_{15}H_{19}{}^{37}Cl_2O$, 287.0778; found, 287.0773.

*Di-tert-butyl-3,3′-(3-oxo-2,3-dihydro-1H-indene-1,2-diyl)-dipropionate (**3ap**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (42.7 mg, 73% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.5, 1.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 3.07 (dt, J = 8.0, 3.9 Hz, 1H), 2.40 (t, J = 7.6 Hz, 2H), 2.35 (td, J = 7.0, 3.1 Hz, 1H), 2.29 (td, J = 8.8, 6.4 Hz, 2H), 2.20−2.13 (m, 1H), 2.03−1.96 (m, 1H), 1.96−1.83 (m, 2H), 1.43 (s, 9H), 1.41 (s, 9H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 207.6, 172.3, 156.5, 136.1, 135.0, 127.9, 125.8, 123.9, 80.6, 80.4, 52.1, 43.8, 32.9, 32.7, 30.7, 28.1, 27.0. HRMS (ESI): $[M + H]^+$ calcd for $C_{23}H_{33}O_5$, 389.2323; found, 389.2306.

*2,3-Bis(3-phenylpropyl)-2,3-dihydro-1H-inden-1-one (**3aq**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (37.0 mg, 67% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.31−7.22 (m, 4H), 7.20−7.14 (m, 6H), 3.07−3.05 (m, 1H), 2.63 (t, J = 7.6 Hz, 3H), 2.37 (ddd, J = 7.9, 5.2, 2.8 Hz, 1H), 1.93−1.61 (m, 9H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 208.7, 157.6, 142.1, 141.9, 136.3, 134.8, 128.4, 128.39, 128.38, 128.33, 127.6, 125.9, 125.8, 125.7, 123.8, 53.4, 44.5, 36.1, 36.0, 35.5, 31.8, 28.93, 28.90. HRMS (ESI): $[M^+H]^+$ calcd for $C_{27}H_{29}O$, 369.2213; found, 369.2210.

*6-Fluoro-2,3-diphenyl-2,3-dihydro-1H-inden-1-one (**3ba**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (40.1 mg, 88% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (dd, J = 7.4, 2.5 Hz, 1H), 7.42−7.24 (m, 8H), 7.10 (t, J = 7.3 Hz, 4H), 4.55 (d, J = 4.8 Hz, 1H), 3.86 (d, J = 4.8 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$): δ −113.05. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 204.3 (d, J = 2.8 Hz), 162.9 (d, J = 249.4 Hz), 151.7, 142.2, 138.1, 138.0 (d, J = 7.5 Hz), 129.1 (d, J = 9.7 Hz), 128.4, 128.4, 128.36, 127.9, 127.5, 123.3 (d, J = 23.6 Hz), 109.8 (d, J = 22.1 Hz), 65.4, 54.4. HRMS (ESI): $[M + H]^+$ calcd for $C_{21}H_{16}FO$, 303.1180; found, 303.1180.

*6-Methoxy-2,3-diphenyl-2,3-dihydro-1H-inden-1-one (**3ca**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (38.4 mg, 81% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36−7.26 (m, 8H), 7.23−7.21 (m, 1H), 7.14−7.05 (m, 4H), 4.52 (d, J = 4.4 Hz, 1H), 3.89 (s, 3H), 3.82 (d, J = 4.5 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 205.3, 160.1, 149.1, 142.8, 138.7, 137.5, 128.91, 128.88, 128.4, 127.8, 127.5, 127.22, 127.16, 124.9, 105.0, 65.4, 55.7, 54.3. HRMS (ESI): $[M + H]^+$ calcd for $C_{22}H_{19}O_2$, 315.1380; found, 315.1379.

*5-Fluoro-2,3-diphenyl-2,3-dihydro-1H-inden-1-one (**3da**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (18.5 mg, 40% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (dd, J = 8.5, 5.3 Hz, 1H), 7.40−7.27 (m, 6H), 7.19 (td, J = 8.5, 2.3 Hz, 1H), 7.14−7.02 (m, 4H), 6.96 (dd, J = 8.8, 2.3 Hz, 1H), 4.54 (d, J = 4.9 Hz, 1H), 3.84 (d, J = 4.9 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$): δ −110.15. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 203.5, 167.6 (d, J = 248.5 Hz), 159.2 (d, J = 9.1 Hz), 141.8, 138.3, 132.6 (d, J = 1.9 Hz), 129.2, 129.0, 128.4, 127.9, 127.6, 127.4, 126.5 (d, J = 10.3 Hz), 116.8 (d, J = 24.1 Hz), 113.4 (d, J = 22.6 Hz), 64.8, 54.8. HRMS (ESI): $[M + H]^+$ calcd for $C_{21}H_{16}FO$, 303.1180; found, 303.1179.

*5-Methyl-2,3-diphenyl-2,3-dihydro-1H-inden-1-one (**3ea**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the

https://doi.org/10.1021/acs.joc.2c00544
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product (35.3 mg, 78% yield) as a white solid, mp 112−113 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, J = 7.9 Hz, 1H), 7.41−7.26 (m, 7H), 7.15−7.00 (m, 5H), 4.53 (d, J = 4.7 Hz, 1H), 3.81 (d, J = 4.7 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 204.8, 156.7, 146.8, 142.7, 138.9, 134.0, 129.6, 128.9, 128.85, 128.3, 128.0, 127.2, 126.9, 123.9, 64.8, 54.9, 22.2. HRMS (ESI): $[M + H]^+$ calcd for $C_{22}H_{19}O$, 299.1430; found, 299.1430.

*6,7-Diphenyl-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-one (**3fa**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (35.4 mg, 72% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32−7.27 (m, 6H), 7.22 (s, 1H), 7.10−7.08 (m, 4H), 6.64 (s, 1H), 6.08 (d, J = 1.3 Hz, 2H), 4.42 (d, J = 4.1 Hz, 1H), 3.78 (d, J = 4.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 203.2, 154.8, 153.9, 149.0, 142.5, 131.0, 129.0, 128.9, 128.2, 127.8, 127.2, 127.1, 105.8, 102.4, 102.3 64.8, 54.8 2. HRMS (ESI): $[M + H]^+$ calcd for $C_{22}H_{17}O_3$, 329.1173; found, 329.1194.

*7-Fluoro-2,3-diphenyl-2,3-dihydro-1H-inden-1-one (**3ga**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (28.1 mg, 62% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (td, J = 7.9, 5.0 Hz, 1H), 7.34−7.28 (m, 6H), 7.11−7.06 (m, 6H), 4.57 (d, J = 5.0 Hz, 1H), 3.85 (d, J = 5.0 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$): δ −113.93. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 201.2, 158.7 (d, J = 265.1 Hz), 158.0, 141.8, 137.8, 137.2 (d, J = 8.1 Hz), 128.9, 128.8, 128.3, 127.8, 127.3, 124.0, 124.5 (d, J = 12.9 Hz), 122.4 (d, J = 3.9 Hz), 115.0 (d, J = 19.1 Hz), 64.8, 54.8. HRMS (ESI): $[M + H]^+$ calcd for $C_{21}H_{16}FO$, 303.1180; found, 303.1200.

*3-Butyl-2-phenyl-2,3-dihydro-1H-inden-1-one (**3ar**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (40.2 mg, 92% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 7.7 Hz, 1H), 7.69 (td, J = 7.5, 1.3 Hz, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.35−7.32 (m, 2H), 7.28−7.26 (m, 1H),7.18−7.17 (m, 2H), 7.24−7.11 (m, 2H), 3.56 (d, J = 3.7 Hz, 1H), 3.51 (dt, J = 8.5, 4.2 Hz, 1H), 2.05−2.02 (m, 1H), 1.78−1.73 (m, 1H), 1.55−1.24 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 205.8, 157.8, 140.0, 135.9, 135.1, 128.8, 128.1, 127.9, 127.0, 125.5, 124.3, 60.7, 48.0, 35.5, 29.4, 22.8, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{19}H_{21}O$, 265.1587; found, 265.1587.

*3-Butyl-2-(4-fluorophenyl)-2,3-dihydro-1H-inden-1-one (**3as**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (32.3 mg, 80% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.7 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.11 (dd, J = 8.5, 5.4 Hz, 2H), 7.00 (t, J = 8.6 Hz, 2H), 3.50 (d, J = 5.7 Hz, 1H), 3.51 (dt, J = 8.7, 4.2 Hz, 1H), 2.04−1.96 (m, 1H), 1.77−1.67 (m, 1H), 1.43−1.17 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H). ^{19}F NMR (565 MHz, CDCl3): δ −115.90 $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 205.8, 161.9 (d, J = 245.1 Hz), 157.6, 135.8, 135.7 (d, J = 3.6 Hz), 135.3, 129.7 (d, J = 7.7 Hz), 128.1, 125.5, 124.4, 115.8 (d, J = 21.6 Hz), 59.9, 48.1, 35.4, 29.5, 22.9, 13.8. HRMS (ESI): $[M + H]^+$ calcd for $C_{19}H_{20}FO$, 283.1493; found, 283.1493.

*3-Butyl-2-(4-nitrophenyl)-2,3-dihydro-1H-inden-1-one (**3at**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (38.1 mg, 86% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 7.7 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.5 Hz, 2H), 3.64 (d, J = 3.9 Hz, 1H), 3.51 (dt, J = 9.0, 4.3 Hz, 1H), 2.08−1.98 (m, 1H), 1.76−1.71 (m, 1H), 1.37−1.30 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 204.0, 157.2, 147.4, 147.0, 135.6, 135.3, 129.1, 128.3, 125.5, 124.6, 124.1, 60.4, 47.8, 35.4, 29.6, 22.7, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{19}H_{19}NO_3Na$, 332.1257; found, 332.1259.

*4-(1-Butyl-3-oxo-2,3-dihydro-1H-inden-2-yl)benzonitrile (**3au**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (32.5 mg, 76% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, J = 7.7 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 7.7 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 3.57 (d, J = 3.9 Hz, 1H), 3.47 (dt, J = 8.7, 4.3 Hz, 1H), 2.06−1.97 (m, 1H), 1.74−1.68 (m, 1H), 1.35−1.29 (m, 4H), 0.86 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 204.2, 157.3, 145.3, 135.5, 132.6, 129.0, 128.3, 125.5, 124.5, 118.8, 110.9, 60.6, 47.7, 35.4, 29.5, 22.7, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{20}H_{20}NO$, 290.1539; found, 290.1537.

*3-Butyl-2-(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-one (**3av**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (26.2 mg, 62% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 7.6 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 3.47 (d, J = 3.9 Hz, 1H), 3.43 (dt, J = 8.6, 4.2 Hz, 1H), 2.05−1.92 (m, 1H), 1.76−1.67 (m, 1H), 1.44−1.25 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 206.2, 158.6, 157.7, 135.9, 135.0, 132.0, 129.1, 127.8, 125.4, 124.3, 114.3, 59.9, 55.3, 48.0, 35.4, 29.4, 22.8, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{20}H_{23}O_2$, 295.1693; found, 295.1693.

*3-Butyl-2-(4-methylphenyl)-2,3-dihydro-1H-inden-1-one (**3aw**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (31.3 mg, 75% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 7.6 Hz, 1H), 7.66 (td, J = 7.5, 1.3 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.12 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 3.50 (d, J = 3.8 Hz, 1H), 3.46 (dt, J = 8.6, 4.2 Hz, 1H), 2.32 (s, 3H), 2.02−1.99 (m, 1H), 1.77−1.67 (m, 1H), 1.44−1.24 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 206.0, 157.8, 136.9, 136.5, 136.0, 135.0, 129.5, 128.0, 127.8, 125.4, 124.3, 60.3, 48.0, 35.5, 29.4, 22.8, 21.1, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{20}H_{23}O$, 279.1743; found, 279.1741.

*3-Butyl-2-(naphthalen-2-yl)-2,3-dihydro-1H-inden-1-one (**3ax**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (38.1 mg, 81% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 7.6 Hz, 1H), 7.80−7.78 (m, 3H), 7.69 (td, J = 7.7, 1.5 Hz, 2H), 7.67 (s, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.48−7.43 (m, 3H), 7.22 (dd, J = 8.5, 1.8 Hz, 1H), 3.71 (d, J = 3.7 Hz, 1H), 3.60 (dt, J = 8.5, 4.2 Hz, 1H), 2.08−2.02 (m, 1H), 1.81−1.75 (m, 1H), 1.42 (qd, J = 8.4, 7.7, 5.9 Hz, 2H), 1.38−1.26 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 205.8, 157.8, 137.4, 136.0, 135.2, 133.6, 132.5, 128.7, 127.9, 127.7, 127.65, 127.2, 126.2, 125.9, 125.7, 125.5, 124.4, 60.8, 48.0, 35.5, 29.5, 22.8, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{23}H_{23}O$, 315.1743; found, 315.1741.

*3-Butyl-2-(3-fluorophenyl)-2,3-dihydro-1H-inden-1-one (**3ay**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (36.5 mg, 85% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 7.6 Hz, 1H), 7.68 (td, J = 7.5, 1.2 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.35−7.19 (m, 1H), 7.03−6.89 (m, 2H), 6.85 (dt, J = 9.9, 2.1 Hz, 1H), 3.52 (d, J = 3.8 Hz, 1H), 3.46 (dt, J = 8.6, 4.1 Hz, 1H), 2.02−1.97 (m, 1H), 1.73−1.70 (m, 1H), 1.39−1.30 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H). ^{19}F NMR (565 MHz, CDCl3): δ −112.77. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 205.2, 163.0 (d, J = 245.9 Hz), 157.6, 142.3 (d, J = 7.6 Hz), 135.7, 135.4, 130.4 (d, J = 8.3 Hz), 128.1, 125.6, 124.5, 124.0, 115.1 (d, J = 21.4 Hz), 114.0 (d, J = 21.1 Hz), 60.3, 48.0, 35.5, 29.5, 22.8, 14.0. HRMS (ESI): $[M + H]^+$ calcd for $C_{19}H_{20}FO$, 283.1493; found, 283.1493.

*3-Butyl-2-(3-methylphenyl)-2,3-dihydro-1H-inden-1-one (**3az**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (26.1 mg, 63% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, J = 7.6 Hz, 1H), 7.67 (td, J = 7.5, 1.3 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 9.0 Hz, 2H), 3.49−3.46, (m, 2H) 2.31 (s, 3H), 2.03−1.94 (m, 1H), 1.77−1.68 (m, 1H), 1.45−1.25 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 206.0, 157.9, 139.9, 138.4, 136.0, 135.0, 128.8, 128.7, 127.8, 127.76, 125.5, 125.1, 124.3, 60.6, 48.1, 35.5, 29.4, 22.8, 21.5, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{20}H_{23}O$, 279.1743; found, 279.1743.

*3-Butyl-2-(2-fluorophenyl)-2,3-dihydro-1H-inden-1-one (**3aaa**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (35.1 mg, 83% yield) as a colorless oil. ^{1}H NMR

https://doi.org/10.1021/acs.joc.2c00544
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(600 MHz, $CDCl_3$): δ 7.82 (d, J = 7.7 Hz, 1H), 7.66 (td, J = 7.5, 1.3 Hz, 1H), 7.55 (dd, J = 7.7, 1.1 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.32−7.19 (m, 1H), 7.18−7.00 (m, 3H), 3.71 (d, J = 4.6 Hz, 1H), 3.47 (tt, J = 9.0, 5.0 Hz, 1H), 2.09−2.00 (m, 1H), 1.77 (m, 1H), 1.43−1.17 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H). ^{19}F NMR (565 MHz, CDCl3): δ −116.26. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 205.2, 161.0 (d, J = 246.4 Hz), 157.2, 135.9, 135.1, 130.7 (d, J = 4.5 Hz), 128.9 (d, J = 8.5 Hz), 127.9, 127.4 (d, J = 15.2 Hz), 125.3, 124.5 (d, J = 3.4 Hz), 124.2, 115.8 (d, J = 22.0 Hz), 55.3, 47.4, 34.7, 29.1, 22.8, 14.0. HRMS (ESI): $[M + H]^+$ calcd for $C_{19}H_{20}FO$, 283.1493; found, 283.1493.

*3-Butyl-2-(2-methylphenyl)-2,3-dihydro-1H-inden-1-one (**3aab**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (28.2 mg, 67% yield) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 3.77 (d, J = 4.0 Hz, 1H), 3.50 (dt, J = 8.5, 4.4 Hz, 1H), 2.35 (s, 3H), 2.03−1.97 (m, 1H), 1.81−1.75 (m, 1H), 1.38−1.31 (m, 4H), 0.87 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 206.1, 157.4, 138.4, 136.5, 136.2, 134.9, 130.8, 128.2, 127.8, 127.0, 126.3, 125.4, 124.2, 58.1, 47.7, 35.1, 29.2, 22.8, 20.3, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{20}H_{23}O$, 279.1743; found, 279.1743.

*3-Butyl-2-(thiophen-3-yl)-2,3-dihydro-1H-inden-1-one (**3aac**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (30.2 mg, 74% yield) as a yellow oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.78 (d J = 7.7 Hz, 1H), 7.65 (td, J = 7.5, 1.3 Hz, 1H), 7.54 (dd, J = 7.8, 0.9 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.29 (dd, J = 5.0, 2.9 Hz, 1H), 7.11 (dt, J = 2.9, 1.0 Hz, 1H), 6.94 (dd, J = 5.0, 1.3 Hz, 1H), 3.67 (d, J = 3.7 Hz, 1H), 3.49 (dt, J = 8.5, 4.2 Hz, 1H), 2.01−1.97 (m, 1H), 1.74−1.71 (m, 1H), 1.49−1.29 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 205.0, 157.3, 139.1, 135.6, 135.1, 127.8, 126.9, 126.1, 125.5, 124.3, 121.6, 55.6, 47.1, 35.4, 29.4, 22.8, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{17}H_{19}OS$, 271.1151; found, 271.1155.

*2-(4-Bromophenyl)-3-butyl-2,3-dihydro-1H-inden-1-one (**3aad**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (20.7 mg, 40% yield) as a yellow oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, J = 7.7 Hz, 1H), 7.67 (td, J = 7.5, 1.2 Hz, 1H), 7.56 (dd, J = 7.8, 1.0 Hz, 1H), 7.44−7.42 (m, 3H), 7.03 (d, J = 8.4 Hz, 2H), 3.48 (d, J = 3.9 Hz, 1H), 3.43 (dt, J = 8.6, 4.2 Hz, 1H), 2.02−1.97 (m, 1H), 1.74−1.67 (m, 1H), 1.37−1.30 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 205.1, 157.5, 138.9, 135.6, 135.3, 131.9, 129.9, 128.0, 125.4, 124.4, 120.9, 60.1, 47.8, 35.4, 29.5, 22.8, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{19}H_{20}{}^{79}BrO$, 343.0692; found, 343.0682. Calcd for $C_{19}H_{20}{}^{81}BrO$, 345.0672; found, 345.0682.

*3-(3-Chloropropyl)-2-phenyl-2,3-dihydro-1H-inden-1-one (**3aae**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (20.3 mg, 47% yield) as a yellow oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 7.7 Hz, 1H), 7.71 (td, J = 7.5, 1.2 Hz, 1H), 7.61 (dd, J = 7.8, 1.0 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.39−7.32 (m, 2H), 7.28 (dt, J = 14.7, 1.3 Hz, 1H), 7.20−7.14 (m, 2H), 3.57−3.49 (m, 4H), 2.27−2.23 (m, 1H), 1.95−1.85 (m, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$): δ 205.2, 156.8, 139.5, 135.9, 135.2, 129.0, 128.2, 128.1, 127.2, 125.3, 124.5, 60.6, 47.3, 44.8, 32.7, 30.1. HRMS (ESI): $[M + H]^+$ calcd for $C_{18}H_{18}{}^{35}ClO$, 285.1041; found, 285.1039. Calcd for $C_{18}H_{18}{}^{37}ClO$, 287.1011; found, 287.1022.

*3-(Hydroxymethyl)-2-phenyl-2,3-dihydro-1H-inden-1-one (**3aaf**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (23.2 mg, 65% yield) as a yellow oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 7.6 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.3 Hz, 2H), 7.28−7.23 (m, 1H), 7.17 (dd, J = 7.1, 1.7 Hz, 2H), 4.09 (dd, J = 10.9, 5.2 Hz, 1H), 4.00 (dd, J = 10.9, 5.2 Hz, 1H), 3.78 (d, J = 4.1 Hz, 1H), 3.61 (q, J = 4.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 205.2, 153.8, 139.1, 136.9, 135.2, 128.9, 128.5, 128.3, 127.2, 125.6, 124.6, 64.4, 57.1, 50.6. HRMS (ESI): $[M^+H]^+$ calcd for $C_{16}H_{15}O_2$, 239.1067; found, 239.1064.

*3-(3-Hydroxypropyl)-2-phenyl-2,3-dihydro-1H-inden-1-one (**3aag**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (35.2 mg, 88% yield) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 7.7 Hz, 1H), 7.67 (td, J = 7.5, 1.0 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.26−7.22 (m, 1H), 7.15−7.13 (m, 2H), 3.63 (t, J = 6.4 Hz, 2H), 3.54−3.51 (m, 2H), 2.15−2.09 (m, 1H), 1.82−1.77 (m, 1H), 1.67−1.63 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 205.7, 157.3, 139.7, 135.9, 135.2, 128.9, 128.1, 128.0, 127.1, 125.5, 124.4, 62.6, 60.7, 47.7, 31.9, 30.3. HRMS (ESI): $[M + H]^+$ calcd for $C_{18}H_{19}O_2$, 267.1380; found, 267.1378.

*2-(3-(3-Oxo-2-phenyl-2,3-dihydro-1H-inden-1-yl)propyl)-isoindoline-1,3-dione (**3aah**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (40.3 mg, 68% yield) as a colorless solid, mp 103−104 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.83 (dd, J = 5.4, 3.0 Hz, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.71 (dd, J = 5.5, 3.0 Hz, 2H), 7.66 (td, J = 7.5, 1.1 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.22 (tt, J = 7.3, 1.2 Hz, 1H), 7.13−7.12 (m, 2H), 3.71−3.68 (m, 2H), 3.56−3.53 (m, 1H), 3.49 (d, J = 3.7 Hz, 1H), 2.07−2.02 (m, 1H), 1.83−1.76 (m, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 205.3, 168.4, 156.9, 139.5, 135.8, 135.2, 134.0, 132.0, 128.9, 128.1, 127.1, 125.5, 124.4, 123.3, 60.6, 47.4, 37.8, 33.0, 26.5. HRMS (ESI): $[M + H]^+$ calcd for $C_{26}H_{22}NO_3$, 396.1594; found, 396.1583.

*2-Phenyl-2,3-dihydro-1H-inden-1-one (**3aai**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (15.2 mg, 48% yield) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.82 (d, J = 7.7 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.26−7.24 (m, 1H), 7.19 (d, J = 7.4 Hz, 2H), 3.90 (dd, J = 8.3, 4.1 Hz, 1H), 3.70 (dd, J = 17.4, 8.3 Hz, 1H), 3.28 (dd, J = 17.4, 4.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 206.0, 153.7, 139.7, 136.3, 135.0, 128.9, 127.9, 127.8, 127.0, 126.4, 124.6, 53.4, 35.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{15}H_{13}O$, 209.0961; found, 209.0950.

*2-Butyl-2,3-dihydro-1H-inden-1-one (**3aaj**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (15.2 mg, 54% yield) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 3.32 (dd, J = 17.1, 7.8 Hz, 1H), 2.82 (dd, J = 17.1, 3.9 Hz, 1H), 2.67−2.63 (m, 1H), 1.98−1.93 (m, 1H), 1.48−1.44 (m, 1H), 1.43−1.33 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 209.2, 153.8, 136.9, 134.6, 127.3, 126.5, 123.9, 47.5, 32.9, 31.2, 29.6, 22.7, 14.0. HRMS (ESI): $[M + H]^+$ calcd for $C_{13}H_{17}O$, 189.1274; found, 189.1268.

*(8S,9R,13R,14R)-3-(1-Butyl-3-oxo-2,3-dihydro-1H-inden-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]-phenanthren-17-one (**3aak**).* Purification by preparative TLC on silica gel (PE/EA = 10/1) to afford the product (63.1 mg, 95% yield) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 7.7 Hz, 1H), 7.66 (td, J = 7.5, 1.2 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 6.91 (ddd, J = 8.0, 5.8, 2.0 Hz, 1H), 6.87 (dd, J = 5.4, 1.9 Hz, 1H), 3.47 (d, J = 1.6 Hz, 2H), 2.94−2.79 (m, 2H), 2.49 (dd, J = 19.1, 8.7 Hz, 1H), 2.43−2.34 (m, 1H), 2.28 (td, J = 11.0, 4.1 Hz, 1H), 2.13 (dt, J = 19.0, 9.0 Hz, 1H), 2.08−1.89 (m, 4H), 1.76−1.68 (m, 1H), 1.67−1.57 (m, 2H), 1.56−1.42 (m, 4H), 1.40−1.29 (m, 4H), 0.90 (s, 3H), 0.88 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 221.0, 206.2, 206.1, 157.9, 138.4, 137.32, 137.31, 136.9, 136.0, 135.0, 128.7, 128.6, 127.8, 125.83, 125.81, 125.5, 125.4, 124.3, 60.2, 50.5, 48.00, 47.98, 44.34, 44.32, 38.1, 35.9, 35.4, 31.6, 29.4, 29.3, 26.5, 25.6, 22.9, 21.6, 13.94, 13.86. HRMS (ESI): $[M + H]^+$ calcd for $C_{31}H_{37}O_2$, 441.2788; found, 441.2780.

*N-(4-(1-Butyl-3-oxo-2,3-dihydro-1H-inden-2-yl)phenyl)-2-(4-isobutylphenyl)propanamide (**3aal**).* Purification by preparative TLC on silica gel (PE/EA = 2/1) to afford the product (45.6 mg, 65% yield) as a yellow oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.33−7.22 (m, 4H), 7.12 (t, J = 7.0 Hz, 2H), 6.91 (dd, J = 22.2, 8.3 Hz, 2H), 3.69−3.62 (m, 1H), 3.40−3.38 (m, 2H), 2.45 (dd, J = 7.2, 4.4 Hz, 2H), 1.99−1.95 (m, 1H), 1.87−1.82 (m,

https://doi.org/10.1021/acs.joc.2c00544
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1H), 1.69−1.65 (m, 1H), 1.55−1.53 (m, 3H), 1.31−1.27 (m, 4H), 0.91−0.89 (m, 6H), 0.86 (d, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 206.4, 206.3, 172.6, 172.6, 157.84, 157.78, 140.9, 138.44, 138.36, 137.0, 135.8, 135.2, 129.7, 128.5, 128.45, 127.9, 127.4, 127.36, 125.5, 124.2, 120.2, 120.17, 60.3, 48.0, 47.5, 45.0, 35.3, 30.2, 29.5, 22.8, 22.4, 18.7, 18.67, 13.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{32}H_{38}NO_2$, 468.2897; found, 468.2891.

*N-(4-(1-Butyl-3-oxo-2,3-dihydro-1H-inden-2-yl)phenyl)-2-(5-methoxy-1H-indol-3-yl)acetamide (**3aam**).* Purification by preparative TLC on silica gel (PE/EA = 2/1) to afford the product (55.6 mg, 79% yield) as a yellow oil. ^1H NMR (600 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.65 (td, J = 7.5, 1.3 Hz, 1H), 7.58−7.51 (m, 1H), 7.48 (s, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 2.4 Hz, 1H), 6.80 (dd, J = 8.7, 2.4 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 2H), 3.42 (d, J = 3.9 Hz, 1H), 3.39 (dt, J = 8.6, 4.2 Hz, 1H), 2.35 (s, 3H), 2.01−1.89 (m, 1H), 1.67 (ddt, J = 15.8, 8.6, 6.7 Hz, 1H), 1.36−1.24 (m, 4H), 0.85 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 205.9, 169.9, 157.6, 154.5, 136.4, 135.7, 135.6, 135.1, 134.4, 130.4, 128.5, 127.8, 125.4, 124.2, 120.4, 111.6, 111.4, 103.9, 99.5, 60.1, 55.8, 47.8, 35.3, 33.3, 29.4, 22.7, 13.9, 11.7. HRMS (ESI): $[M + H]^+$ calcd for $C_{31}H_{33}N_2O_3$, 481.2486; found, 481.2491.

*(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(1-Butyl-3-oxo-2,3-dihydro-1H-inden-2-yl)benzoate (**3aan**).* Purification by preparative TLC on silica gel (PE/EA = 5/1) to afford the product (77.1 mg, 76% yield) as a white solid, mp 121−122 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 7.7 Hz, 1H), 7.68 (td, J = 7.5, 1.3 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H), 5.43−5.39 (m, 1H), 4.85 (dtd, J = 12.2, 8.3, 4.5 Hz, 1H), 3.58 (d, J = 3.9 Hz, 1H), 3.49 (dt, J = 8.7, 4.2 Hz, 1H), 2.45 (d, J = 8.2 Hz, 2H), 2.06−1.94 (m, 4H), 1.91 (dt, J = 13.4, 3.6 Hz, 1H), 1.84 (dtd, J = 13.4, 9.5, 5.9 Hz, 1H), 1.77−1.67 (m, 2H), 1.63−1.43 (m, 6H), 1.41−1.28 (m, 7H), 1.24−1.08 (m, 8H), 1.06 (s, 3H), 1.05−0.96 (m, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (dd, J = 6.7, 2.6 Hz, 9H), 0.69 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 204.8, 165.8, 157.5, 145.0, 139.7, 135.7, 135.3, 130.1, 129.6, 128.1, 128.0, 125.5, 124.4, 122.8, 74.5, 60.7, 56.7, 56.2, 50.1, 47.9, 42.3, 39.8, 39.5, 38.2, 37.1, 36.7, 36.2, 35.8, 35.5, 32.0, 31.9, 29.5, 28.3, 28.0, 27.9, 24.3, 23.9, 22.8, 22.7, 22.6, 21.1, 19.4, 18.7, 13.9, 11.9. HRMS (ESI): $[M + H]^+$ calcd for $C_{47}H_{65}O$, 677.4928; found, 677.4932.

General Procedure for the Synthesis of Gram-Scale Experimental. To a Schlenk tube (150 mL) under an atmosphere of nitrogen was added diphenylacetylene (1.8 g, 10 mmol, 1.0 equiv), $[RhCl(cod)]_2$ (0.18 g, 5 mol %), and 2-formylbenzeneboronic acid (2.25g, 15 mmol, 1.5 equiv). The mixture was closed by a septum, purged by nitrogen gas for several times, and then the freshly degassed H_2O (15 mL) and NEt_3 (3.0 g, 30 mmol, 3.0 equiv) were added into the reaction mixture and kept stirring at 50 °C for 16 h. The resulting mixture directly passed through a short pad of Celite with ethyl acetate as eluent and concentrated under reduced pressure. The crude product was purified by flash chromatography using PE/EA (10/1) as an eluent to give the compound **3aa** (2.6 g, 92% yield.)

*Procedure for the Synthesis of **4a**.* To a Schlenk tube (25 mL) under an atmosphere of nitrogen were added **3aa** (57.3 mg, 0.2 mmol, 1.0 equiv), m-CPBA (138.0 mg, 4.0 equiv), p-TsOH·H_2O (7.7 mg, 20 mol %). The mixture was closed by a septum, purged by nitrogen gas for several times, and then the freshly degassed DCM (4 mL) was added into the reaction mixture and kept stirring at 60 °C (oil bath temperature), refluxing for 24 h. The mixture was washed with $NaHCO_3$ and $Na_2S_2O_3$, the organic layer was extracted with EA for 3 times, and then dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography using 10:1 PE/EA as an eluent to give colorless oil **4a** (31.2 mg, 52% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 8.24 (dd, J = 7.8, 1.5 Hz, 1H), 7.50 (td, J = 7.6, 1.5 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.26−7.23 (m, 3H), 7.21 (dd, J = 5.2, 2.0 Hz, 3H), 7.17 (dd, J = 6.6, 2.9 Hz, 2H), 7.06−6.98 (m, 2H), 6.92 (d, J = 7.7 Hz, 1H), 5.64 (d, J = 10.2 Hz, 1H), 4.50 (d, J = 10.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 165.0, 142.5, 137.8, 137.3, 134.1, 130.3, 129.6, 129.0, 128.8, 128.5, 128.2, 128.0, 127.9, 127.7, 127.1, 125.1, 85.3, 51.0. HRMS (ESI): $[M + H]^+$ calcd for $C_{21}H_{17}O_2$, 301.1223; found, 301.1223.

*Procedure for the Synthesis of **5a**.* To a Schlenk tube (10 mL) under an atmosphere of nitrogen was added methyltriphenylphosphonium bromide (178.6 mg, 0.5 mmol, 2.5 equiv) in dry THF (1.0 mL), and then *n*-BuLi (313 μL, 0.5 mmol, 1.6 M in hexane, 2.5 equiv) was added slowly at 0 °C. After the mixture was stirred for 1 h, the compound **3aa** (56.8 mg, 0.2 mmol, 1.0 equiv) was added and kept stirring at room temperature until full conversion. The solution was extracted with EA and washed with brine, and then dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography using 40:1 PE/EA as the eluent to give the compound **5a** (25.4 mg, 45% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 7.63−7.59 (m, 1H), 7.33−7.26 (m, 5H), 7.26−7.21 (m, 3H), 7.16 (dd, J = 8.2, 1.4 Hz, 2H), 7.09−7.05 (m, 2H), 7.04 (dd, J = 7.5, 1.0 Hz, 1H), 5.63 (d, J = 2.8 Hz, 1H), 4.79 (d, J = 2.4 Hz, 1H), 4.42 (d, J = 6.6 Hz, 1H), 4.04 (dt, J = 6.7, 2.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 147.1, 129.1, 128.54, 128.51, 128.4, 128.1, 127.5, 126.6, 126.5, 125.7, 120.6, 105.2, 61.5, 59.4. HRMS (ESI): $[M + H]^+$ calcd for $C_{22}H_{19}$, 283.1481; found, 283.1475.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c00544.

Detailed experimental procedures, ^1H NMR, ^{19}F NMR, and $^{13}C\{^1H\}$ NMR reprints (PDF)

FAIR data, including the primary NMR FID files, for compounds **2al-2an**, **3aa-3az**, **3aaa-3aan**, **3ba-3ga**, **4a**, and **5a** (ZIP)

■ AUTHOR INFORMATION

Corresponding Authors

Yan-Ni Yue − *Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, P. R. China;* orcid.org/0000-0002-3266-0981; Email: ias_ynyue@njtech.edu.cn

Mengtao Ma − *Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China;* orcid.org/0000-0001-9629-6464; Email: mengtao@njfu.edu.cn

Fei Xue − *Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China;* orcid.org/0000-0002-9257-5076; Email: xuefei@njfu.edu.cn

Authors

Anqiao Zhu − *Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China*

Yu Sun − *Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China*

Jingru Lai − *Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China*

Ziyan Chen − *Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, P. R. China*

Xiaoli Bu − *Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.2c00544

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge financial support by the Natural Science Foundation of Jiangsu Province, China (BK20201383), the National Natural Science Foundation of China (21772093), the National Key research and Development Program of China (2016YFC0502605), and the Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX21_0875).

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