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PAPER

Facile assembly of indeno[1,2-*c*]chromenes *via* a palladium-catalyzed reaction of 2-alkynylhalobenzene†

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2-Alkynylhalobenzene reacts with 2-alkynylphenol in the presence of a palladium catalyst, leading to indeno[1,2-*c*]chromenes in good to excellent yields. Furthermore, the scaffold of indeno[1,2-*c*]chromene could be constructed *via* a palladium-catalyzed reaction of 2-alkynylbromobenzene with water, in which four bonds are formed with high efficiency.

1. Introduction

It is well recognized that heterocyclic compounds with a core of natural products have attracted considerable attention for the study of chemical genetics.[1] Efficient and novel approaches have appeared for the construction of heterocyclic compounds using the strategy of diversity-oriented synthesis. As a part of our continuing efforts for accessing natural product-like compounds,[2] we are interested in the development of methods of tandem reactions[3] for the facile assembly of such small molecules. Gnetuhainin S from *Gnetum macrostachyum* lianas, displays antioxidant activity as a radical scavenging against DPPH (Fig. 1).[4] The lack of efficient ways to access this [6-5-6-6] tetracyclic skeleton[5] narrows their broader and further applications in medicinal chemistry. Therefore, it is highly desirable to develop efficient synthetic protocols for the construction of the [6-5-6-6] tetracyclic core, among which, the tandem reaction is highlighted to us due to its well-known advantages.[6,7]

Recently, we reported a highly selective pathway for the preparation of 5*H*-cyclopenta[*c*]quinolines starting from 2-alkynylhalobenzene with an amine in the presence of a palladium catalyst (Scheme 1, eqn (1)).[8] The preliminary biological evaluation discovered that several hits showed anti-HBV activity. To look for more active compounds, we need to generate a small library of 5*H*-cyclopenta[*c*]quinolines with related compounds. The mechanism study of the synthetic route revealed that the reaction proceeded through a double insertion of triple bonds[9] and 2-alkynylaniline was identified as the intermediate. Encouraged by the results, we envisioned that 2-alkynylphenol could be employed in the reaction of 2-alkynylhalobenzene as well due to the structural similarity of 2-alkynylphenol with 2-alkynylaniline (Scheme 1, eqn (2)). The indeno[1,2-*c*]chromene **3** with [6-5-6-6] tetracyclic skeleton would be generated if the

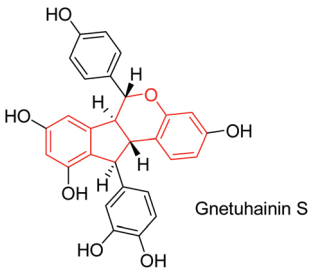
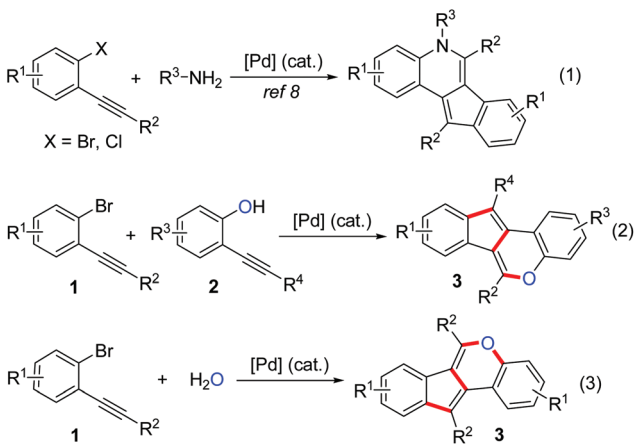


Fig. 1 Structures of Gnetuhainin S.



Scheme 1 The proposed synthetic route for the formation of indeno-[1,2-*c*]chromene **3**.

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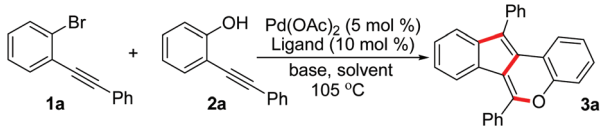
reaction proceeded as expected. Additionally, we anticipated that these compounds could be formed in the meantime from the reaction of 2-alkynylhalobenzene with water (Scheme 1, eqn (3)). We reasoned that 2-alkynylphenol would be produced during the reaction process,[10] which would then undergo the subsequent transformation to afford indeno[1,2-*c*]chromene **3**.

2-Alkynylphenols could be easily converted to benzo[*b*]furans in the presence of a palladium catalyst.[11] Usually, R-Pd^{II}X would activate the triple bond of 2-alkynylphenol, which would promote the subsequent nucleophilic addition of the phenolic oxide to the triple bond. Additionally, the direct coupling of aryl halide with 2-alkynylphenol[12] seems inevitable. Although theoretically the above two possible competitive pathways would hamper the efficiency of the proposed synthetic route (Scheme 1), we believed that the hypothesis would be feasible due to the highly selective process of double insertion of triple bonds. Therefore, we started to explore the possibility of this transformation and a part of this work has been communicated.[9c]

2. Results and discussion

For the model reaction, 1-bromo-2-(phenylethynyl)benzene **1a** and 2-(2-phenylethynyl)phenol **2a** were adopted, and the preliminary screening for the reaction was performed in the presence of $Pd(OAc)_2$ (5 mol%) at 105 °C (Table 1). Different ligands were examined first (Fig. 2), but with only a trace amount of product, including **L1–L4**, $^tBu_3P$ and BINAP (Table 1, entries 1–6). The reaction became complex when DPPF was employed as a replacement for the above ligands (Table 1, entry 7). To our delight, the desired product **3a** was furnished in 59% yield in the presence of tricyclohexyphosphine

Table 1 Initial studies of the palladium-catalyzed reaction of 1-bromo-2-(phenylethynyl)benzene **1a** with 2-(2-phenylethynyl)phenol **2a**



Entry	Ligand	Base	Solvent	Yield[a] (%)
1	**L1**	K_3PO_4	Toluene	Trace
2	**L2**	K_3PO_4	Toluene	Trace
3	**L3**	K_3PO_4	Toluene	Trace
4	**L4**	K_3PO_4	Toluene	Trace
5	$^tBu_3P{\cdot}HBF_4$	K_3PO_4	Toluene	Trace
6	BINAP	K_3PO_4	Toluene	Trace
7	DPPF	K_3PO_4	Toluene	Complex
8	PCy_3	K_3PO_4	Toluene	59
9	PCy_3	NaO^{t}Bu	Toluene	87
10	PCy_3	K_2CO_3	Toluene	79
11	PCy_3	KO^{t}Bu	Toluene	67
12	PCy_3	LiO^{t}Bu	Toluene	81
13	PCy_3	KOH	Toluene	55
14	PCy_3	$NaOCH_3$	Toluene	95
15	PCy_3	Cs_2CO_3	Toluene	72
16	PCy_3	$NaOCH_3$	1,4-Dioxane	96
17	PCy_3	$NaOCH_3$	DMF	Trace
18	PCy_3	$NaOCH_3$	DMSO	nr

[a] Isolated yield based on 1-bromo-2-(phenylethynyl)benzene **1a**.

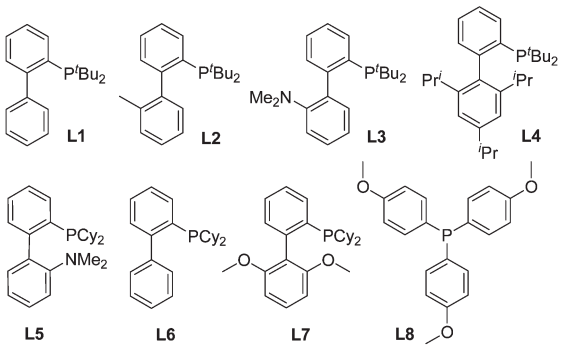


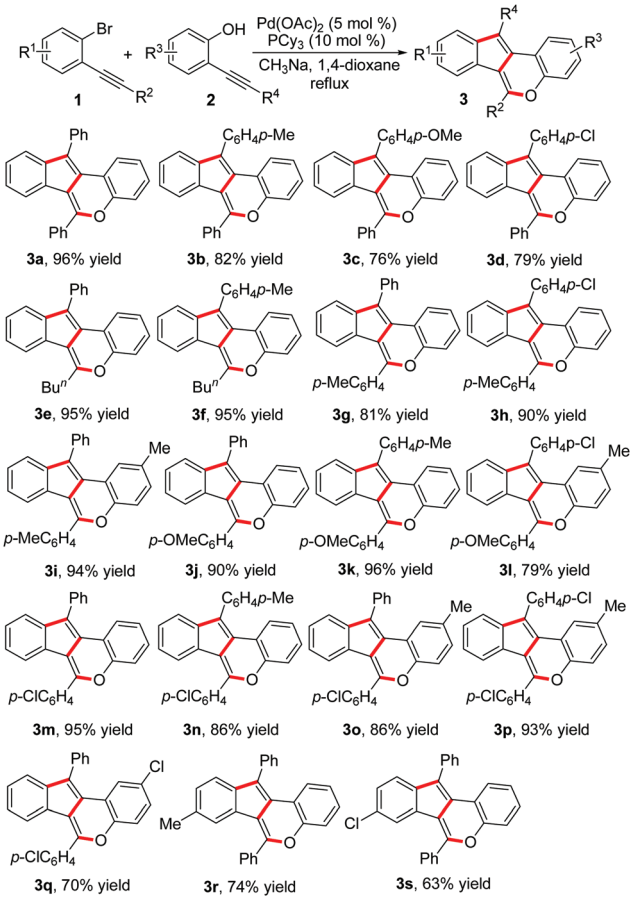
Fig. 2 Phosphine ligands.

(PCy_3) (Table 1, entry 8). Other bases were then screened and the reaction worked efficiently when sodium methanolate ($NaOCH_3$) was utilized as the base (95% yield, Table 1, entry 14). Reactions in various solvents were explored as well and 1,4-dioxane was demonstrated as the best (96% yield, Table 1, entry 16). Yet a lower temperature did not provide a satisfactory result (data not shown in Table 1).

The protocol generality was then investigated under the optimized conditions, as highlighted in Table 1 (entry 16). A range of desired indeno[1,2-*c*]chromenes was obtained in good to excellent yields through the palladium-catalyzed tandem reactions of 2-alkynylbromobenzenes with 2-alkynylphenols (Scheme 2). The starting materials with substituents, whether on the aromatic ring of the substrates or attached on the triple bond, reacted well to afford the desired products. Additionally, under the standard conditions the reaction of 1-chloro-2-(2-phenylethynyl)-benzene with 2-(2-phenylethynyl)phenol **2a** was examined, which gave rise to the corresponding product **3a** in 78% yield. This result indicated that the substrate scope of this transformation could be expanded to 2-alkynylchlorobenzenes.

As mentioned above, 2-alkynylphenols could be obtained from the reaction of 2-alkynylbromobenzenes with water.[10] Therefore, it would provide a concise route to indeno[1,2-*c*]chromenes from 2-alkynylbromobenzenes if 2-alkynylphenols could be formed *in situ*. Since both processes would be fulfilled in the presence of a palladium catalyst, we envisioned that the direct formation of indeno[1,2-*c*]chromenes *via* a palladium-catalyzed reaction of 2-alkynylbromobenzene with water would be possible under suitable conditions. If the conversion proceeded as expected, four bonds would be formed in a tandem procedure. Considering the high efficiency and the easy availability of starting materials, we started to explore the possibility of this transformation.

The initial studies were performed for the reaction of 1-bromo-2-((4-methoxyphenyl)ethynyl)benzene with water by using 5 mol% of $Pd(OAc)_2$, 10 mol% phosphine ligand and 5.0 equiv. of water in the presence of a suitable base (Table 2). Initially, only a trace amount of product was detected when the reaction occurred in 1,4-dioxane at 105 °C in the presence of X-Phos and potassium carbonate (Table 2, entry 1). No reaction took place when *t*-BuOK was employed as the base (Table 2, entry 2). The reaction failed as well when NaOMe was used as a replacement (Table 2, entry 3). Interestingly, the desired product **3t** was obtained when the base was changed to *t*-BuONa

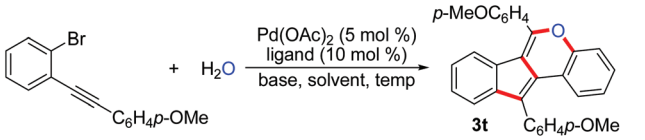


Scheme 2 The synthesis of indeno[1,2-*c*]chromenes *via* a palladium-catalyzed reaction of 2-alkynylbromobenzene with 2-alkynylphenol.

(32% yield, Table 2, entry 4). A slightly lower yield was afforded when the reaction was performed at 75 °C (Table 2, entry 5). To our delight, a good result was obtained when the reaction occurred at 90 °C (Table 2, entry 6). The yield could not be improved when the amount of water was reduced or increased. Further exploration revealed that KOH was the best choice for this transformation (Table 2, entry 7). Other phosphine ligands were then screened. However, no better results were observed (Table 2, entries 10–15). No reaction occurred without the addition of a phosphine ligand in a control experiment (data not shown in Table 2). Other palladium sources were investigated in the meantime, which furnished the inferior yields. No improvement was found when the reaction was performed in other solvents (Table 2, entries 16 and 17). Reducing the catalytic amount of palladium acetate to 2.5 mol% resulted in a lower yield.

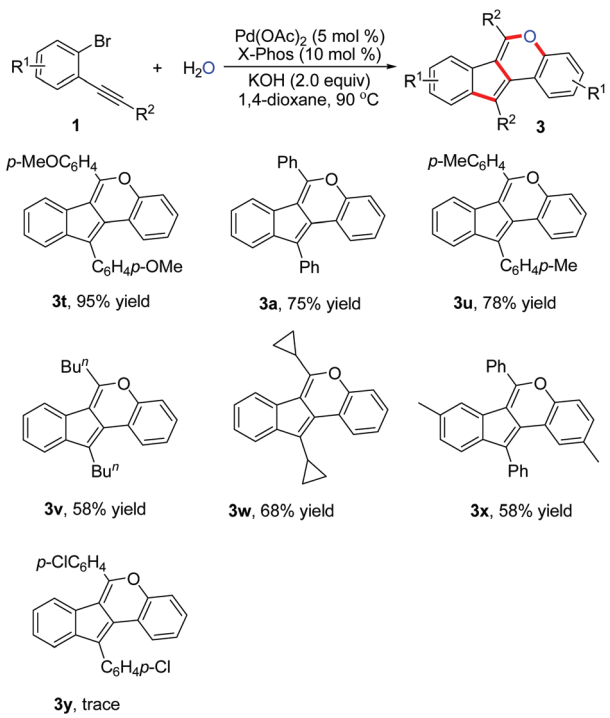
The reaction scope was then examined under the optimized conditions (5 mol% of $Pd(OAc)_2$, 10 mol% of X-Phos, 2.0 equiv. of KOH, 1,4-dioxane, 90 °C). The results are summarized in Scheme 3. For the R^2 group attached on the triple bond of 2-alkynylbromobenzene **1**, it seems that alkyl groups, as well as electron-donating aryl groups, are all tolerated under the conditions. For instance, the *n*-butyl or cyclopropyl-substituted indeno[1,2-*c*]chromenes **3v/3w** were afforded in 58% and 68% yields, respectively. However, when a *p*-chlorophenyl group was

Table 2 The initial studies for the palladium-catalyzed reaction of 2-alkynylbromobenzenes with water[a]

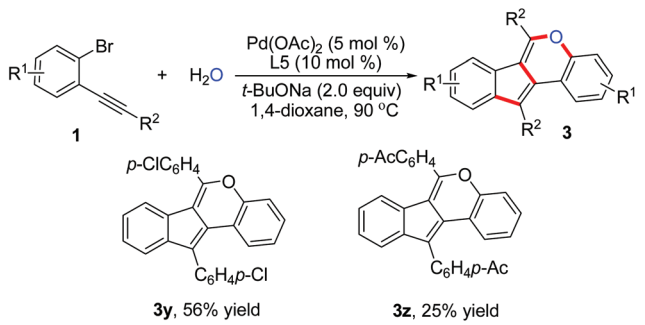


Entry	Ligand	Base	Solvent	Temp (°C)	Yield[b] (%)
1	X-Phos	K_2CO_3	1,4-Dioxane	105	Trace
2	X-Phos	*t*-BuOK	1,4-Dioxane	105	nr
3	X-Phos	NaOMe	1,4-Dioxane	105	Trace
4	X-Phos	*t*-BuONa	1,4-Dioxane	105	32
5	X-Phos	*t*-BuONa	1,4-Dioxane	75	26
6	X-Phos	*t*-BuONa	1,4-Dioxane	90	70
7	X-Phos	KOH	1,4-Dioxane	90	95
8	X-Phos	K_2CO_3	1,4-Dioxane	90	71
9	X-Phos	K_3PO_4	1,4-Dioxane	90	80
10	**L5**	KOH	1,4-Dioxane	90	36
11	**L6**	KOH	1,4-Dioxane	90	50
12	**L7**	KOH	1,4-Dioxane	90	24
13	**L8**	KOH	1,4-Dioxane	90	nr
14	DPPE	KOH	1,4-Dioxane	90	25
15	PCy_3	KOH	1,4-Dioxane	90	30
16	X-Phos	KOH	Toluene	90	61
17	X-Phos	KOH	DMF	90	Trace

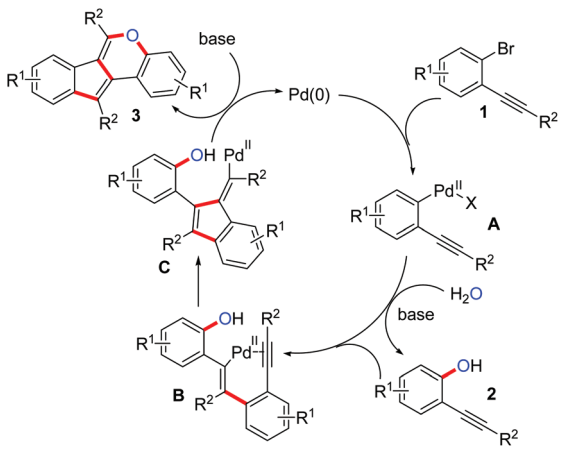
[a] Reaction conditions: 2-alkynylbromobenzene **1a** (0.4 mmol), water (2.5 equiv.), palladium catalyst (5 mol%), ligand (10 mol%), base (2.0 equiv.), solvent (2.0 mL). [b] Isolated yield based on 2-alkynylbromobenzene **1a**.



Scheme 3 The synthesis of indeno[1,2-*c*]chromenes *via* a palladium-catalyzed reaction of 2-alkynylbromobenzenes **1** with water.



Scheme 4 The synthesis of indeno[1,2-*c*]chromenes *via* a palladium-catalyzed reaction of 2-alkynylbromobenzenes **1** with water.



Scheme 5 A possible mechanism for the palladium-catalyzed reaction of 2-alkynylbromobenzenes **1** with water.

attached on the triple bond, only a trace amount of product **3y** was detected. Further investigation revealed that the substituents on the aromatic ring of 2-alkynylbromobenzene **1** were also crucial for the successful transformation. Methyl-substituted 2-alkynylbromobenzene worked well in the reaction. The reaction failed when chloro-substituted 2-alkynylbromobenzene was employed under the standard conditions. Therefore, to expand the utility of this conversion, we re-explored the conditions for the reactions of electron-deficient 2-alkynylbromobenzenes.

1-(2-(2-Bromophenyl)ethynyl)-4-chlorobenzene was selected for reaction development (Scheme 4). The parameters of the palladium catalyst, ligand, base, solvent and temperature were re-screened. We finally identified that the reaction proceeded smoothly when phosphine **L5** was utilized as the ligand in the presence of *t*-BuONa, leading to the desired product **3y** in 56% yield. The reaction of 2-alkynylbromobenzene with an acetyl group was studied in the meantime, which gave rise to the expected product **3z** in 25% yield.

A possible mechanism was proposed, which is presented in Scheme 5. We reasoned that an oxidative addition of Pd(0) to 2-alkynylbromobenzenes **1** would take place to afford Pd(II) **A**. Then, hydroxylation would occur in the presence of water to produce 2-alkynylphenol **2**, which would enter into the reaction with Pd(II) **A** to generate intermediate **B**. Intramolecular coordination and insertion of a triple bond would afford intermediate **C**, which would undergo a C–O coupling to give the desired indeno[1,2-*c*]chromene **3**.

In conclusion, we have described a facile assembly of indeno-[1,2-*c*]chromenes *via* a palladium-catalyzed tandem reaction of 2-alkynylbromobenzenes with 2-alkynylphenol. The reaction works efficiently with excellent selectivity. Additionally, the scaffold of indeno[1,2-*c*]chromene could be constructed *via* a palladium-catalyzed reaction of 2-alkynylbromobenzene with water, in which four bonds are formed with high efficiency. The related library construction is currently ongoing.

Experimental section

General experimental procedure for palladium-catalyzed reaction of 2-alkynylbromobenzenes 1 with 2-alkynylphenols 2

2-Alkynylbromobenzene (0.20 mmol) was added to a mixture of $Pd(OAc)_2$ (5 mol%), tricyclohexylphosphine (10 mol%), *t*-BuONa (0.8 mmol) and 2-alkynylphenol (0.24 mmol) in 1,4-dioxane (2.0 mL). The mixture was heated to reflux. After completion of the reaction, as indicated by TLC, the reaction was cooled and the solvent was diluted by EtOAc (10 mL), washed with saturated brine (2 × 10 mL) and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the indeno[1,2-*c*]chromenes **3**.

General experimental procedure for palladium-catalyzed reaction of 2-alkynylbromobenzenes 1 with water

2-Alkynylbromobenzene (0.40 mmol) was added to a mixture of $Pd(OAc)_2$ (5 mol%,), X-Phos (10 mol%) and KOH (0.8 mmol) in 1,4-dioxane (2.0 mL with 5 equiv. water). The mixture was heated to reflux. After completion of the reaction, as indicated by TLC, the reaction was cooled and the solvent was diluted by EtOAc (10 mL), washed with saturated brine (2 × 10 mL) and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the indeno[1,2-*c*]chromenes **3**.

6,11-Diphenylindeno[1,2-*c*]chromene (3a). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.87 (m, 2H), 7.69 (dd, J = 8.0, 1.2 Hz, 1H), 7.62–7.44 (m, 10H), 7.38–7.29 (m, 3H), 7.11–7.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 150.1, 144.4, 136.6, 133.8, 130.5, 130.0, 129.7, 129.5, 128.9, 128.8, 127.7, 127.4, 126.7, 126.5, 124.9, 124.3, 123.8, 122.8, 121.5, 120.1, 119.3, 117.7, 117.3. HRMS (ESI) calculated for $C_{28}H_{18}O$ $[M + H]^+$ 371.1436, found 371.1424.

6-Phenyl-11-(*p*-tolyl)indeno[1,2-*c*]chromene (3b). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.75–7.73 (m, 1H), 7.63–7.60 (m, 3H), 7.50–7.43 (m, 4H), 7.39–7.35 (m, 3H), 7.33–7.29 (m, 2H), 7.10–7.05 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 150.1, 144.5, 137.1, 133.9, 133.5, 130.5, 129.8, 129.6, 129.5, 128.8, 127.6, 126.65, 126.60, 124.9, 124.2, 123.6, 122.7, 121.4, 120.2, 119.4, 117.6, 117.3, 21.5. HRMS (ESI) calculated for $C_{29}H_{20}O$ $[M + H]^+$ 385.1592, found 385.1599.

11-(4-Methoxyphenyl)-6-phenylindeno[1,2-*c*]chromene (3c). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.73

(dd, J = 8.0, 1.2 Hz, 1H), 7.64–7.62 (m, 3H), 7.52–7.49 (m, 3H), 7.46–7.44 (m, 1H), 7.39–7.31 (m, 3H), 7.12–7.07 (m, 4H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 134.2, 131.1, 130.5, 129.5, 128.7, 127.6, 126.7, 124.8, 124.2, 122.7, 121.4, 119.3, 117.7, 114.3, 55.3. HRMS (ESI) calculated for $C_{29}H_{20}O_2$ $[M + H]^+$ requires 401.1542, found 401.1530.

11-(4-Chlorophenyl)-6-phenylindeno[1,2-*c*]chromene (3d). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.86 (m, 2H), 7.66 (dd, J = 8.4, 1.2 Hz, 1H), 7.62–7.60 (m, 3H), 7.54–7.49 (m, 5H), 7.46–7.44 (m, 1H), 7.35–7.32 (m, 3H), 7.11–7.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 150.1, 143.9, 135.1, 133.7, 133.2, 131.4, 130.6, 129.7, 129.5, 129.2, 128.8, 127.9, 126.8, 125.0, 124.7, 124.4, 124.1, 122.9, 121.5, 119.8, 119.0, 117.8, 117.2. HRMS (ESI) calculated for $C_{28}H_{17}ClO$ $[M + H]^+$ 405.1046, found 405.1045.

6-Butyl-11-phenylindeno[1,2-*c*]chromene (3e). Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.55–7.51 (m, 4H), 7.47–7.27 (m, 6H), 7.05–7.00 (m, 1H), 3.23 (t, J = 7.6 Hz, 2H), 1.99–1.91 (m, 2H), 1.61–1.55 (m, 2H), 1.02 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 149.9, 144.1, 136.8, 130.1, 129.8, 128.8, 127.4, 127.3, 125.9, 125.2, 124.9, 124.1, 123.4, 122.9, 121.5, 120.2, 119.5, 117.4, 116.2, 32.4, 29.6, 22.7, 13.9. HRMS (ESI) calculated for $C_{26}H_{22}O$ $[M + H]^+$ 351.1749, found 351.1746.

6-Butyl-11-(*p*-tolyl)indeno[1,2-*c*]chromene (3f). Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 1H), 7.69 (dd, J = 8.0, 0.9 Hz, 1H), 7.44–7.32 (m, 8H), 7.29–7.25 (m, 1H), 7.04–7.01 (m, 1H), 3.21 (t, J = 7.6 Hz, 2H), 2.47 (s, 3H), 1.97–1.90 (m, 2H), 1.59–1.53 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 149.9, 144.2, 136.8, 133.7, 129.9, 129.8, 129.5, 127.3, 125.9, 125.2, 124.9, 124.0, 123.2, 122.8, 121.5, 120.3, 119.6, 117.4, 116.3, 32.3, 29.6, 22.7, 21.4, 14.0. HRMS (ESI) calculated for $C_{27}H_{24}O$ $[M + H]^+$ 365.1905, found 365.1890.

11-Phenyl-6-(*p*-tolyl)indeno[1,2-*c*]chromene (3g). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.68 (dd, J = 8.0, 1.2 Hz, 1H), 7.60–7.53 (m, 5H), 7.48–7.40 (m, 4H), 7.37–7.28 (m, 3H), 7.11–7.03 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 150.1, 144.3, 140.8, 136.7, 130.9, 130.0, 129.8, 129.45, 129.43, 128.9, 127.6, 127.4, 126.6, 126.3, 124.8, 124.2, 123.8, 122.7, 121.5, 120.1, 119.3, 117.7, 117.0, 21.7. HRMS (ESI) calculated for $C_{29}H_{20}O$ $[M + H]^+$ 385.1592, found 385.1579.

11-(4-Chlorophenyl)-6-(*p*-tolyl)indeno[1,2-*c*]chromene (3h). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.66 (dd, J = 8.0, 1.2 Hz, 1H), 7.58–7.56 (m, 1H), 7.56–7.52 (m, 4H), 7.47–7.41 (m, 3H), 7.36–7.32 (m, 3H), 7.12–7.10 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 150.2, 143.9, 140.9, 135.2, 134.2, 133.2, 131.5, 130.8, 129.8, 129.5, 129.4, 129.2, 127.9, 126.6, 124.7, 124.3, 122.8, 121.6, 119.8, 119.0, 117.8, 117.0, 21.7. HRMS (ESI) calculated for $C_{29}H_{19}ClO$ $[M + H]^+$ 419.1203, found 419.1178.

2-Methyl-11-phenyl-6-(*p*-tolyl)indeno[1,2-*c*]chromene (3i). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.60–7.52 (m, 5H), 7.47–7.44 (m, 2H), 7.41–7.37 (m, 3H), 7.34–7.29 (m, 2H), 7.11–7.07 (m, 2H), 2.50 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 148.3, 144.2, 140.7, 136.7, 133.6, 131.0, 130.0, 129.8, 129.4, 128.73, 128.67, 127.4, 126.4, 125.9, 124.8, 124.0, 122.5, 121.4, 119.7, 119.2, 117.4, 116.9, 21.6, 21.2. HRMS (ESI) calculated for $C_{30}H_{22}O$ $[M + H]^+$ 399.1749, found 399.1760.

6-(4-Methoxyphenyl)-11-phenylindeno[1,2-*c*]chromene (3j). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.63–7.53 (m, 5H), 7.48–7.42 (m, 2H), 7.38–7.28 (m, 3H), 7.13–7.10 (m, 3H), 7.07–7.03 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 152.7, 150.1, 144.2, 136.7, 131.1, 130.0, 129.9, 128.9, 127.6, 127.4, 126.5, 126.0, 124.8, 124.1, 123.9, 122.6, 121.4, 120.1, 119.3, 117.6, 116.8, 114.1, 113.5, 55.4. HRMS (ESI) calculated for $C_{29}H_{20}O_2$ $[M + H]^+$ 401.1542, found 401.1525.

6-(4-Methoxyphenyl)-11-(*p*-tolyl)indeno[1,2-*c*]chromene (3k). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.73 (dd, J = 8.0, 1.2 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.47–7.45 (m, 2H), 7.43–7.26 (m, 6H), 7.11–7.03 (m, 4H), 3.90 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 152.6, 150.1, 144.3, 136.9, 133.6, 131.1, 129.8, 129.6, 127.5, 126.5, 126.2, 126.1, 124.8, 124.1, 123.8, 122.6, 121.4, 120.2, 119.3, 117.6, 116.9, 114.1, 55.4, 21.4. HRMS (ESI) calculated for $C_{30}H_{22}O_2$ $[M + H]^+$ 415.1698, found 415.1694.

11-(4-Chlorophenyl)-6-(4-methoxyphenyl)-2-methylindeno-[1,2-*c*]chromene (3l). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2H), 7.61–7.59 (m, 1H), 7.53 (m, 4H), 7.47 (s, 1H), 7.37–7.32 (m, 3H), 7.16–7.10 (m, 4H), 3.95 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 153.1, 148.3, 143.8, 135.3, 133.8, 133.1, 131.5, 131.1, 129.8, 128.9, 126.5, 126.0, 124.5, 124.4, 124.2, 122.7, 121.4, 119.5, 118.9, 117.5, 116.6, 114.1, 55.5, 21.3. HRMS (ESI) calculated for $C_{30}H_{21}ClO_2$ $[M + H]^+$ 449.1308, found 449.1326.

6-(4-Chlorophenyl)-11-phenylindeno[1,2-*c*]chromene (3m). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2H), 7.67 (dd, J = 8.0, 1.2 Hz, 1H), 7.60–7.56 (m, 6H), 7.52–7.42 (m, 3H), 7.37–7.30 (m, 3H), 7.14–7.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 150.0, 144.5, 136.7, 136.5, 132.2, 130.9, 129.9, 129.5, 129.1, 128.9, 127.8, 127.5, 126.92, 126.86, 124.9, 124.4, 123.7, 122.9, 121.3, 119.9, 119.5, 117.6. HRMS (ESI) calculated for $C_{28}H_{17}ClO$ $[M + H]^+$ 405.1046, found 405.1024.

6-(4-Chlorophenyl)-11-(*p*-tolyl)indeno[1,2-*c*]chromene (3n). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.72 (dd, J = 8.0, 1.2 Hz, 1H), 7.60–7.58 (m, 2H), 7.51–7.41 (m, 4H), 7.37–7.29 (m, 5H), 7.13–7.06 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151, 150.0, 144.6, 137.2, 136.6, 134.2, 133.3, 132.2, 131.0, 129.7, 129.6, 129.1, 128.8, 127.7, 126.9, 124.9, 124.3, 123.5, 122.9, 121.3, 120.1, 119.5, 117.6, 21.5. HRMS (ESI) calculated for $C_{29}H_{19}ClO$ $[M + H]^+$ 419.1203, found 419.1191.

6-(4-Chlorophenyl)-2-methyl-11-phenylindeno[1,2-*c*]chromene (3o). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.60–7.56 (m, 6H), 7.51–7.45 (m, 3H), 7.39–7.32

(m, 3H), 7.14–7.09 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 148.2, 144.4, 136.5, 133.9, 132.3, 130.9, 129.9, 129.54, 129.51, 129.1, 128.8, 127.5, 126.8, 126.5, 124.8, 123.8, 122.8, 121.3, 119.6, 119.4, 117.3, 21.2. HRMS (ESI) calculated for $C_{29}H_{19}ClO$ $[M + H]^+$ 419.1203, found 419.1178.

6,11-Bis(4-chlorophenyl)-2-methylindeno[1,2-*c*]chromene (3p). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.61–7.59 (m, 2H), 7.55–7.46 (m, 6H), 7.36–7.33 (m, 3H), 7.18–7.10 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 148.2, 144.1, 136.6, 135.0, 134.1, 133.3, 132.2, 131.4, 130.9, 129.4, 129.13, 129.09, 129.07, 126.9, 124.9, 124.6, 124.1, 122.9, 121.4, 119.4, 119.1, 117.5, 21.3. HRMS (ESI) calculated for $C_{29}H_{18}Cl_2O$ $[M + H]^+$ 453.0813, found 453.0780.

2-Chloro-6-(4-chlorophenyl)-11-phenylindeno[1,2-*c*]chromene (3q). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 2H), 7.62–7.51 (m, 9H), 7.38–7.36 (3H), 7.28–7.27 (m, 1H), 7.17–7.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 136.8, 135.6, 134.3, 131.9, 130.9, 129.7, 129.5, 129.2, 129.1, 127.9, 127.7, 127.1, 124.2, 123.4, 121.4, 121.3, 119.8, 118.9. HRMS (ESI) calculated for $C_{28}H_{16}Cl_2O$ $[M + H]^+$ 439.0656, found 439.0635.

8-Methyl-6,11-diphenylindeno[1,2-*c*]chromene (3r). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.67–7.53 (m, 8H), 7.47–7.41 (m, 2H), 7.31–7.21 (m, 3H), 7.16–7.14 (m, 1H), 7.06–7.02 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 150.0, 142.1, 136.8, 133.9, 132.4, 130.5, 130.1, 129.9, 129.6, 128.8, 128.7, 127.8, 127.5, 127.4, 126.5, 124.7, 124.2, 123.0, 121.9, 120.2, 119.1, 117.6, 117.3, 21.8. HRMS (ESI) calculated for $C_{29}H_{20}O$ $[M + H]^+$ 385.1592, found 385.1590.

8-Chloro-6,11-diphenylindeno[1,2-*c*]chromene (3s). Red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.67–7.66 (m, 4H), 7.59–7.56 (m, 4H), 7.51–7.45 (m, 3H), 7.36–7.32 (m, 1H), 7.30–7.25 (m, 2H), 7.10–7.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 150.1, 142.6, 136.2, 134.3, 133.3, 130.9, 129.9, 129.4, 128.98, 128.95, 128.5, 127.9, 127.6, 126.7, 125.8, 124.8, 124.5, 124.2, 121.4, 120.1, 119.9, 117.7, 116.5. HRMS (ESI) calculated for $C_{28}H_{17}ClO$ $[M + H]^+$ 405.1046, found 405.1033.

6,11-Bis(4-methoxyphenyl)indeno[1,2-*c*]chromene (3t). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.8 Hz, 2H), 7.73–7.71 (m, 1H), 7.61–7.59 (m, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.44–7.42 (m, 1H), 7.38–7.36 (m, 1H), 7.29 (d, J = 6.9 Hz, 2H), 7.12–7.05 (m, 6H), 3.93 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 158.9, 152.5, 150.2, 144.5, 131.1, 129.9, 128.8, 127.5, 126.5, 126.1, 125.9, 124.8, 124.1, 123.8, 122.6, 121.4, 120.3, 119.3, 117.6, 114.3, 114.1, 113.8, 55.4, 55.3. HRMS (ESI) calculated for $C_{30}H_{23}O$: 431.1647 $(M + H^+)$, found 431.1640.

6,11-Di-*p*-tolylindeno[1,2-*c*]chromene (3u). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (m, 3H), 7.56 (d, J = 7.8 Hz, 1H), 7.48–7.45 (m, 2H), 7.42–7.39 (m, 2H), 7.36–7.35 (m, 3H), 7.33–7.30 (m, 3H), 7.09–7.06 (m, 2H), 2.51 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 150.2, 144.4, 140.7, 137.0, 133.6, 131.0, 129.8, 129.6, 129.4, 128.4, 127.6, 126.5, 126.4, 124.9, 124.1, 123.7, 122.7, 121.5, 120.3, 119.3, 117.6, 117.1, 21.6, 21.5. HRMS (ESI) calculated for $C_{30}H_{23}O$: 399.1749 $(M + H^+)$, found 399.1758.

6,11-Dibutylindeno[1,2-*c*]chromene (3v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.90 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.44–7.41 (m, 2H), 7.34–7.32 (m, 3H), 3.17–3.11 (m, 4H), 1.91–1.88 (m, 2H), 1.74–1.73 (m, 2H), 1.57–1.53 (m, 4H), 1.25 (m, 4H), 1.00 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 149.9, 144.0, 130.1, 126.8, 125.7, 125.0, 124.3, 122.6, 122.2, 121.5, 121.2, 118.4, 117.5, 116.2, 32.1, 31.3, 29.6, 26.1, 23.2, 22.7, 14.2, 13.9. HRMS (ESI) calculated for $C_{24}H_{27}O$: 331.2062 $(M + H^+)$, found 331.2066.

6,11-Dicyclopropylindeno[1,2-*c*]chromene (3w). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67–8.66 (m, 1H), 8.07 (d, J = 7.3 Hz, 1H), 7.93 (d, J = 7.3 Hz, 1H), 7.45–7.42 (m, 1H), 7.33–7.29 (m, 4H), 2.76–2.75 (m, 1H), 2.08–2.07 (m, 1H), 1.39–1.28 (m, 2H), 1.24–1.18 (m, 4H), 0.75–0.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 149.5, 144.3, 130.2, 126.9, 126.7, 125.4, 125.2, 124.2, 123.9, 122.4, 121.5, 120.9, 119.9, 116.8, 116.2, 12.8, 8.2, 7.7. HRMS (ESI) calculated for $C_{22}H_{19}O$: 299.1436 $(M + H^+)$, found 299.1440.

2,8-Dimethyl-6,11-diphenylindeno[1,2-*c*]chromene (3x). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.8 Hz, 3H), 7.52–7.50 (m, 4H), 7.46–7.44 (m, 3H), 7.02 (m, 2H), 6.89 (d, J = 7.3 Hz, 2H), 6.69 (d, J = 7.3 Hz, 2H), 2.19 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 142.4, 140.5, 137.3, 135.5, 134.1, 130.0, 130.3, 129.6, 129.1, 128.6, 128.5, 128.0, 127.9, 127.4, 127.3, 127.0, 122.8, 122.1, 119.0, 117.4, 110.5, 21.4. HRMS (ESI) calculated for $C_{30}H_{23}O$: 399.1749 $(M + H^+)$, found 399.1764.

6,11-Bis(4-chlorophenyl)indeno[1,2-*c*]chromene (3y). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 6.9 Hz, 2H), 7.64–7.60 (m, 3H), 7.55–7.50 (m, 6H), 7.35–7.33 (m, 3H), 7.13–7.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.0, 133.3, 132.1, 131.4, 131.0, 129.2, 128.0, 127.0, 125.4, 124.8, 124.5, 123.1, 121.4, 119.8, 119.2, 117.8. HRMS (ESI) calculated for $C_{28}H_{17}Cl_2O$: 439.0656 $(M + H^+)$, found 439.0648.

1,1′-(Indeno[1,2-*c*]chromene-6,11-diylbis(4,1-phenylene))-diethanone (3z). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.15 (m, 4H), 8.02–8.00 (m, 2H), 7.71–7.69 (m, 3H), 7.51–7.49 (m, 2H), 7.35 (m, 3H), 7.12 (m, 2H), 2.74 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 197.4, 151.5, 150.0, 143.9, 141.9, 138.5, 137.9, 136.2, 130.3, 129.9, 129.4, 129.0, 128.7, 128.2, 127.2, 125.7, 124.8, 124.6, 124.3, 123.3, 121.5, 119.6, 119.2, 117.8, 26.8, 26.7. HRMS (ESI) calculated for $C_{32}H_{23}O_3$: 455.1647 $(M + H^+)$, found 455.1662.

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