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Gold-Catalyzed Cascade Friedel–Crafts/Furan-Yne Cyclization/ Heteroenyne Metathesis for the Highly Efficient Construction of Phenanthrene Derivatives

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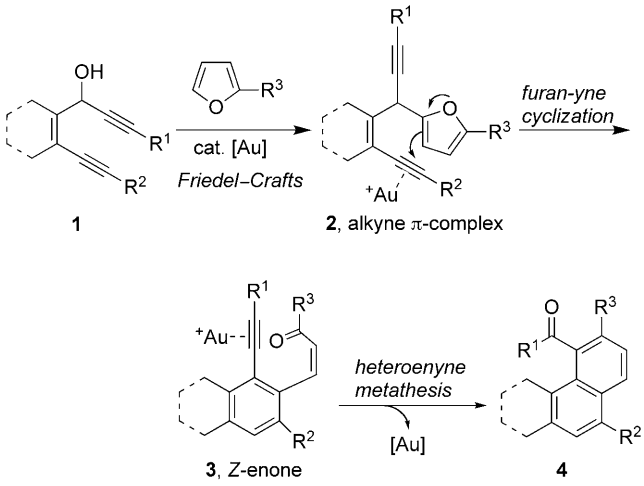
Abstract: A rapid access to highly substituted phenanthrenyl ketones through gold-catalyzed cyclization of 1,6-diyn-4-en-3-ols with furans has been developed. Gold catalysts are effective to catalyze three cascade processes involving Friedel–Crafts/furan-yne cyclization/heteroenyne metathesis through C–O bond and alkyne activation. This method offers several advantages such as high selectivities and easily accessible starting materials.

Keywords: annulation; cascade reactions; gold catalysis; heteroenyne metathesis; phenanthrene

Introduction

Transition metal-catalyzed cascade reactions are among the most powerful strategic tools for the rapid assembly of complex structures.[1] These processes enable multiple bond-forming and bond-cleaving events to occur in one sequence which greatly enhances the synthetic efficiency, while producing less waste and minimizing handling. Although much progress has been achieved in this field, metal-catalyzed cascades involving three or more than three reactions are still a major challenge in synthetic organic chemistry. In recent years, gold complexes and salts are emerging as promising catalysts due to their unique ability to activate alkynes, allenes, and alkenes towards nucleophilic attack.[2] Recently, we have developed a new domino approach for the synthesis of (*Z*)-enones with excellent stereoselectivity through gold(I)-catalyzed reactions of enynols with furans.[3,4] The gold catalyst was found to be quite efficient to catalyze both the Friedel–Crafts and the furan/alkyne[5,6] cyclization reactions in a highly regioselective manner of *endo*-cyclization. The resulting Z-enones enable the possibility of further facile cyclizations with unsaturated moieties. We envisioned that if an alkynyl group was introduced at the alcoholic position in enynol substrates such as diyne **1** shown in Scheme 1, the newly formed (*Z*)-enone **3** might undergo further heteroenyne metathesis reactions with the alkyne moiety located on the proximal reaction site through a π-complex. This would eventually lead to the polycyclic aromatic ketones such as phenanthrenyl ketone **4**, which are very important subunits in material science[7] and which occur in numerous natural products.[8] The alkyne-carbonyl metathesis is an attractive method for the construction of cyclic enones, it also serves as an alternative to the Wittig reaction in carbonyl olefinations due to the efficient construction of new C–C bond and C–O bonds at the



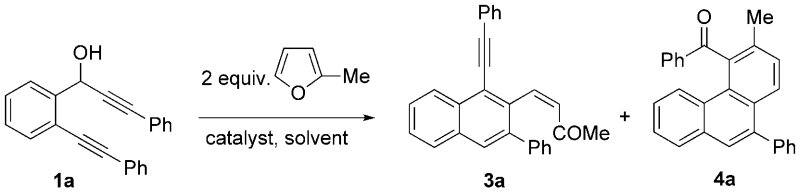
Scheme 1. Proposed formation of phenanthrene derivatives.

same time.[9,10] However, incorporation of this metathesis strategy into a cascade sequence is quite rare.[10o] In this contribution, we report our study of this novel transformation as shown in Scheme 1 directly from the readily available 1,6-diyn-4-en-3-ols and furans catalyzed by gold, which involves the three key steps of Friedel–Crafts/furan-yne cyclization/heteroenyne metathesis, affording multi-substituted phenanthrenyl ketones in a one-pot procedure.

Results and Discussion

In the proposed process, three independent reactions should occur sequentially by a single-set catalyst, and how to avoid the undesired side reactions becomes a big challenge. We began our investigations with easily accessible 3-phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol **1a**, which has previously been shown to undergo gold-catalyzed intramolecular 6-*endo-dig* cyclization without addition of any nucleophiles to form naphthyl ketones (Table 1).[11a] An initial study was conducted by treatment of **1a** and 2 equivalents of 2-methylfuran in DCE with 5 mol% of PPh_3AuNTf_2. It was found that enone **3a** was obtained in 48% yield with a high level of (*Z*)-olefin selectivity (*Z*/*E* = 100:3), together with 23% of the naphthyl ketone derived by intramolecular 6-*endo-dig* cyclization[11a] (Table 1, entry 1). To our delight, performing the reaction at 80 °C resulted in the formation of the target phenanthren-4-one **4a** in 53% yield (entry 2). PPh_3AuSbF_6 was also effective to afford a moderate yield of **4a** at 80 °C (entry 3). The use of $AuCl_3$ afforded mainly Friedel–Crafts product **2a** at room tempera-

Table 1. Optimization studies for the formation of phenanthrenyl ketones.

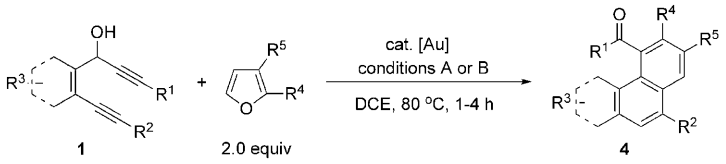


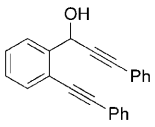
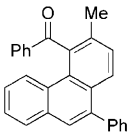
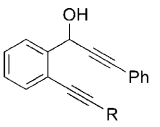
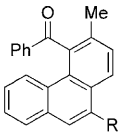
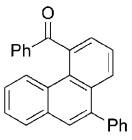
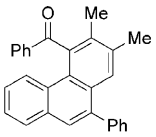
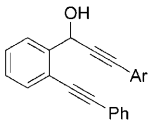
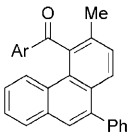
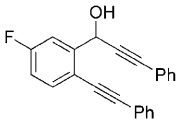
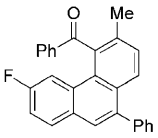
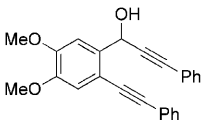
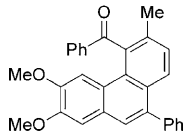
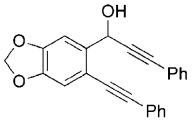
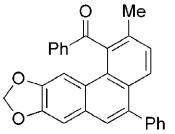
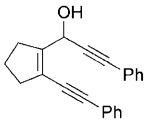
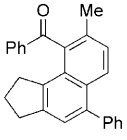
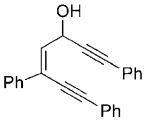
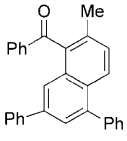
1a **3a** **4a**

Entry	catalyst (mol%)	Time [h]	Solvent	Temp. [°C]	Yield of **3a** [%][a]	Yield of **4a** [%][a]
1	PPh_3AuNTf_2 (5)	0.75	DCE	r.t.	48[b]	-
2[c]	PPh_3AuNTf_2 (5)	4	DCE	80	-	53
3[c]	PPh_3AuSbF_6 (5)	5	DCE	80	-	62
4	$AuCl_3$ (5)	1.5	DCE	r.t.	12[d]	
5[c]	$AuCl_3$ (5)	5	DCE	80	52[e]	-
6	PPh_3AuSbF_6 (5)	1	DCE	r.t.	58	-
7[c]	$AuCl_3$ (5)/$AgSbF_6$ (15)	1	DCE	80	-	50
8[f]	$AuCl_3$ (5)/$AgSbF_6$ (15)	10	DCE	50	-	54
9[f]	$AuCl_3$ (5)/$AgSbF_6$ (15)	1	toluene	80	-	50
10[c,f]	$AuCl_3$ (5)/$AgSbF_6$ (15)	9	MeCN	80	-	58
11[c,f]	$AuCl_3$ (5)/$AgSbF_6$ (15)	1	DCM	80	-	62
12[c,f]	$AuCl_3$ (5)/$AgSbF_6$ (15)	2	DCE	80	-	65
13[c]	AuCl (5)/$AgSbF_6$ (5)	10	DCE	80	-	25[g]
14[h]	10% HCl	7	DCE	r.t.	-	-

[a] Isolated yields.
[b] *Z*/*E* = 100:3. Phenyl(2-phenylnaphthalen-1-yl)methanone was also obtained in 23% yield.
[c] In a sealed tube.
[d] NMR yield. The product **2a** of a Friedel–Crafts reaction was also obtained in 60% NMR yield.
[e] A mixture of *cis/trans* isomers was obtained in a ratio of 2.5:1.
[f] The reaction was stirred at room temperature for 1–1.5 h with $AuCl_3$ until most of **1a** was converted to Friedel–Crafts product **2a**, then $AgSbF_6$ was added and the mixture was heated up to 80 °C.
[g] Containing 12% of impurity. In addition, **2a** was also obtained in 35% yield.
[h] HCl was used as a 2.1 M solution in ether. **1a** was recovered quantitatively.

Table 2. Synthesis of phenanthrenyl ketones through cascade reactions.



Entry	Substrate	Conditions/Product[a]	Entry	Substrate	Conditions/Product[a]
1			8		
	1a	A, **4a**, 65%		**1h**, R = *p*-MeC$_6$H$_4$	A, **4h**, 62%
2	**1a**		9	**1i**, R = *p*-ClC$_6$H$_4$	A, **4i**, 66%
		4b, 72%[b]			
3	**1a**		10	**1j**, R = n-C$_4$H$_9$	B, **4j**, 73%
		A, **4c**, 72%[c]			
4			11		
	1d, Ar = *p*-MeC$_6$H$_4$	A, **4d**, 63%		**1k**	A, **4k**, 58%
5	**1e**, Ar = *p*-ClC$_6$H$_4$	A, **4e**, 67%	12		
				1l	A, **4l**, 46%
6	**1f**, Ar = *p*-BrC$_6$H$_4$	B, **4f**, 51%	13		
				1m	A, **4m**, 52%
7	**1g**, Ar = 2-thienyl	B, **4g**, 54%	14		
				1n	B, **4n**, 76%
			15		
				1o	B, **4o**, 48%

[a] Isolated yields. Unless noted, all the reactions were carried out with 2-methylfuran. *Conditions A:* $AuCl_3$ (5 mol%), room temperature, 1.0–2.5 h, then $AgSbF_6$ (15 mol%) and heated up to 80 °C. *Conditions B:* 5 mol% PPh_3AuCl and 5 mol% $AgSbF_6$.

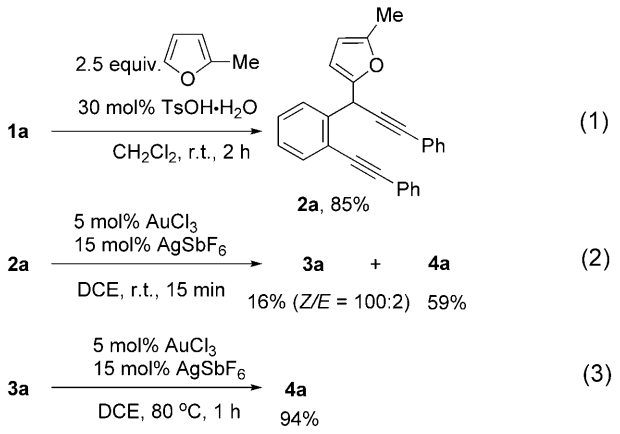
[b] PPh_3AuNTf_2 (5 mol%) and 5 equiv. of furan were used.

[c] 2,3-Dimethylfuran was used.

ture,[12] and enone **3a** as a mixture of *Z*/*E* isomers in a ratio of 2.5:1 at 80 °C, respectively (entries 4 and 5). Further screening of catalysts and reaction conditions revealed that stepwise addition of $AuCl_3$ and $AgSbF_6$ was the optimal set of conditions, in which the yield of **4a** could be improved to 65% (entry 12). The results indicated that to achieve good reaction yields, it is crucial to first complete the Friedel–Crafts alkylation of 2-methylfuran before the sequential cyclization/metathesis reactions (compare entry 7 and entry 12). When 10% HCl was used, the desired products were not observed (entry 14).

Having established the effective catalytic system for this novel cascade annulation reaction, we proceeded to explore the scope of this method under the optimal reaction conditions (Table 2). In addition to 2-methylfuran, furan and 2,3-dimethylfuran could also be used, furnishing the corresponding phenanthrenes **4b** and **4c** in the same yield of 72% (Table 2, entries 2 and 3). It is noted that the reaction with furan was found to be efficient only with PPh_3AuNTf_2. Next, the diyne substrates containing different R^1 and R^2 groups at the alkyne terminus were examined. The reaction tolerated both electron-rich and electron-poor aryl substituents as R^1 and R^2, furnishing the corresponding phenanthrenyl ketones **4d**–**4f**, **4h** and **4i** in 51–67% yields (entries 4–6, 8 and 9). As the aryl substituent R^1 became more electron-deficient (**4f**, entry 6), the reaction efficiency decreased, this might due to the lower stability of the cationic intermediate formed in the metathesis step. A thienyl group as R^1 was also suitable in this domino reaction, producing **4g** in 54% yield (entry 7). The reaction with the alkyl (R^2)-substituted diyne **1j** was also satisfactory, as it afforded desired **4j** in 73% yield (entry 10). In addition, the substituted parent phenyl rings with F or OR functionalities were compatible for this transformation, and moderate yields were realized for all cases (entries 11–13), especially, the reaction of the diyne **1m** substituted with a strong electron-donating methylenedioxy group afforded the ketone **4m** without problems in 52% yield (entry 13). The structure of **4m** was unambiguously determined by X-ray crystallography.[13] The reaction has also been successfully extended to enynols without the fused aromatic rings. Enynol **1n** fused with a 5-membered carbocycle readily participated in this domino reaction to generate the naphthyl ketone **4n** in a good yield of 76% (entry 14). A trisubstituted (*Z*)-enynol underwent cyclization smoothly with 2-methylfuran to give the desired ketone **4o** in 48% yield (entry 15). It was noted that, in some cases, the use of PPh_3AuSbF_6 afforded better results than those with $AuCl_3/AgSbF_6$.

To understand the mechanism, the Friedel–Crafts product **2a** and enone **3a** were isolated under controlled reaction conditions [Scheme 2, Eq. (1) and Eq. (2)]. In order to obtain the pure Friedel–Crafts product **2a**, we screened various acid catalysts. Gratifyingly, we found that **2a** could be formed cleanly using 30 mol% $TsOH{\cdot}H_2O$. Treatment of **2a** with gold catalyst resulted in the formation of **3a** and **4a** in 16% and 59% yields, respectively.

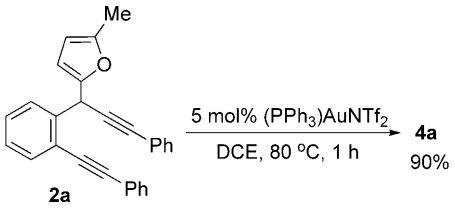


Scheme 2. Determination and transformation of the intermediates.

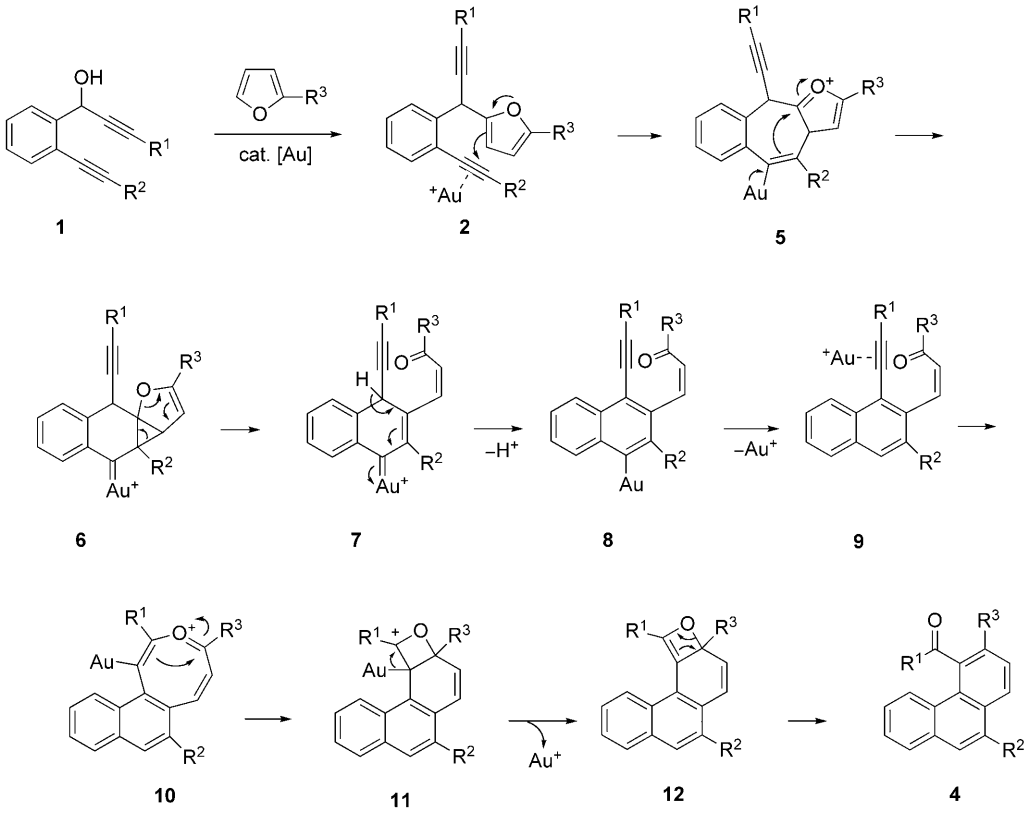
The intramolecular alkyne-carbonyl metathesis of **3a** catalyzed by $AuCl_3/AgSbF_6$ proceeded smoothly to provide the same product **4a** as observed in the tandem process [Scheme 2, Eq. (3)]. These results strongly supported our assumption that phenanthrene was formed through the tandem sequence involving the key intermediates **2a** and **3a**.

To our delight, we found that when Friedel–Crafts product **2a** was used as a starting material, the phenanthrenyl ketone **4a** could be obtained in a high yield of 90% in the presence of 5 mol% $(PPh_3)AuNTf_2$ (Scheme 3). The results clearly indicate that the domino furan/yne and carbonyl-yne cyclization reactions are highly efficient under gold catalysis.

Based on the above results, we propose the following reaction mechanism for this cascade sequence (Scheme 4).[3,5o] The reaction is initiated by gold-catalyzed Friedel–Crafts reaction with 2-substituted furan through the nucleophilic attack of furan C-5 on the benzyl cationic intermediate[14] to afford the arylated diyne **2**. Intramolecular furan/yne cyclization takes place in a highly regioselective 7-*endo*-*dig* manner to form a cyclopropyl gold carbenoid **6**.[15] Rearrangement of **6** followed by aromatization/deauration *via* **8**



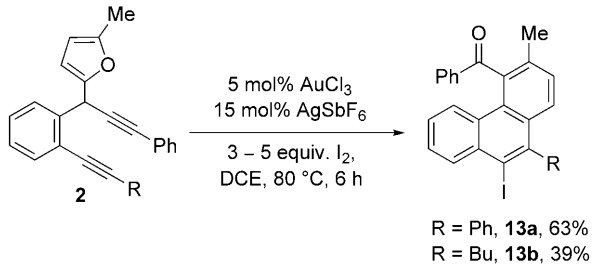
Scheme 3. Gold-catalyzed tandem reaction of **2a**.



Scheme 4. Proposed mechanism for the gold-catalyzed domino reaction.

leads to *Z*-enone **9**. Addition of the carbonyl oxygen to the gold-alkyne complex in **9** results in the formation of oxetene intermediate **12** *via* oxonium **10** and cationic gold species **11**. Ring opening of **12** give the final product **4**.

We also tried the gold-catalyzed reaction of **2** in the presence of I_2 (Scheme 5). It was found that the iodinated phenanthrenyl ketones **13** were formed in 39–63% yields. This result supports the formation of a naphthyl gold intermediate **8** in the domino process.



Scheme 5. Formation of iodinated phenanthrenes.

Conclusions

In conclusion, we have developed a gold-catalyzed tandem Friedel–Crafts/furan-yne cyclization/heterenyne metathesis to form phenanthrenyl ketones with high diversity and in a regioselective manner. Gold catalysts are effective to catalyze all the three processes through C–O bond and alkyne activation. A variety of diyne substrates turned out to be applicable to this catalytic system. Further studies to extend the scope and synthetic utility of this Au-catalyzed cascade reactions are in progress in our laboratory.

Experimental Section

Typical Procedure for Gold-Catalyzed Cascade Reaction for the Synthesis of Phenanthrenyl Ketone Derivatives

Method A: All the reactions were carried out on a 0.2 or 0.3 mmol scale. To a solution of 3-phenyl-1-[2-(phenylethynyl)phenyl]prop-2-yn-1-ol (**1a**) (92.5 mg, 0.3 mmol) and 2-methylfuran (49.3 mg, 54 μL, 0.6 mmol) in DCE (3 mL) was added $AuCl_3$ (0.3 mL, 0.015 mmol, used as a 0.05 M solution in MeCN). The resulting solution was stirred at room temperature for 1.5 h until most of the diyne **1a** was converted to Friedel–Crafts product as monitored by thin-layer chromatography. Then $AgSbF_6$ (0.9 mL, 0.045 mmol, used as a 0.05 M solution in MeCN) was added. The flask was sealed and immersed in an oil bath at 80 °C. After stirring for 2 h, the mixture was cooled down. The solvent was evaporated under the reduced pressure and the residue was purified by

chromatography on silica gel (petroleum ether:dichloromethane = 2:1) to afford (3-methyl-10-phenylphenanthren-4-yl)-(phenyl)methanone **4a** as a yellow solid; yield: 72.4 mg (65%); mp 178–179 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 2.32 (s, 3H), 7.24–7.28 (m, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.39–7.54 (m, 8H), 7.64 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 7.2 Hz, 2H), 7.92 (d, J = 8.8 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): δ = 20.28, 126.02, 126.67, 126.95, 127.41, 127.88, 127.93, 128.32, 128.41, 128.65, 128.82, 128.85, 129.06, 129.46, 130.06, 130.34, 132.70, 133.64, 133.80, 136.69, 137.46, 138.68, 140.76, 202.32; HR-MS (EI): m/z = 372.1513, calcd. for $C_{28}H_{20}O$: 372.1514.

Method B: To a solution of 3-(4-bromophenyl)-1-[2-(phenylethynyl)-phenyl]prop-2-yn-1-ol (**1f**) (116.2 mg, 0.3 mmol) and 2-methylfuran (49.3 mg, 54 μL, 0.6 mmol) in DCE (3 mL) were added PPh_3AuCl (7.4 mg, 0.015 mmol) and $AgSbF_6$ (0.3 mL, 0.015 mmol, used as a 0.05 M solution in MeCN) subsequently. The flask was sealed and immersed in an oil bath at 80 °C. After stirring for 4 h, the mixture was cooled down. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether: dichloromethane = 2:1) to afford (4-bromophenyl)(3-methyl-10-phenylphenanthren-4-yl)methanone **4f** as a sticky yellow oil; yield: 69.5 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 2.32 (s, 3H), 7.25–7.30 (m, 1H), 7.40–7.52 (m, 9H), 7.64 (s, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.79 (dd, J = 1.6, 8.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 8.30 (dd, J = 0.8, 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): δ = 20.24, 126.10, 126.75, 126.82, 127.47, 128.01, 128.10, 128.32, 128.34, 128.49, 128.91, 128.99, 129.13, 130.04, 130.33, 130.88, 132.21, 132.71, 133.84, 135.96, 136.24, 138.68, 140.61, 201.22; HR-MS (EI): m/z = 450.0616, calcd. for $C_{28}H_{19}OBr$: 450.0619.

Phenyl(10-phenylphenanthren-4-yl)methanone (4b)

To a solution of 3-phenyl-1-[2-(phenylethynyl)phenyl]prop-2-yn-1-ol (**1a**) (61.7 mg, 0.2 mmol) and furan (68.1 mg, 1 mmol) in DCE (2 mL) was added PPh_3AuNTf_2 (7.4 mg, 0.01 mmol). The flask was sealed and immersed in an oil bath at 80 °C. After stirring for 2 h, the mixture was cooled down. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether:ethyl acetate = 50:1) to afford **4b** as a yellow oil; yield: 51.5 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 7.29 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.43–7.55 (m, 9H), 7.71 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 7.2 Hz, 2H), 8.04 (t, J = 4.8 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): δ = 125.37, 126.03, 126.98, 127.10, 127.44, 127.51, 128.33, 128.36, 128.57, 128.66, 128.71, 128.84, 130.06, 130.24, 132.15, 132.44, 133.49, 137.07, 138.21, 138.62, 140.51, 200.36; HR-MS (EI); m/z = 358.1360, calcd. for $C_{27}H_{18}O$: 358.1358.

(2,3-Dimethyl-10-phenylphenanthren-4-yl)(phenyl)-methanone (4c)

Method A and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a sticky yellow oil; yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 2.22 (s, 3H), 2.37 (s, 3H), 7.24 (t, J = 8.0 Hz, 1H), 7.33–7.41 (m, 3H), 7.46–7.53 (m, 6H), 7.61 (s, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.80 (s, 1H), 7.86 (d, J = 7.2 Hz, 2H), 8.35 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): δ = 16.95, 20.73, 125.96, 126.21, 126.63, 126.68, 127.34, 128.08, 128.32, 128.38, 128.61, 128.84, 128.86, 129.50, 130.06, 130.30, 132.37, 132.92, 133.62, 135.82, 136.82, 137.80, 138.36, 140.96, 203.07; HR-MS (EI): m/z = 386.1669, calcd. for $C_{29}H_{22}O$: 386.1671.

(3-Methyl-10-phenylphenanthren-4-yl)(*p*-tolyl)-methanone (4d)

Method A and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a sticky yellow oil; yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 2.31 (s, 6H), 7.13 (d, J = 7.8 Hz, 2H), 7.26 (t, J = 7.8 Hz, 1H), 7.37–7.52 (m, 7H), 7.62 (s, 1H), 7.75 (t, J = 8.7 Hz, 3H), 7.90 (d, J = 8.7 Hz, 1H), 8.40 (d, J = 8.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si): δ = 20.24, 21.68, 126.00, 126.60, 126.95, 127.37, 127.73, 127.88, 128.29, 128.33, 128.67, 128.78, 129.02, 129.57, 129.60, 130.03, 130.30, 132.65, 133.71, 135.07, 136.91, 138.65, 140.76, 144.61, 202.00; HR-MS (EI): m/z = 386.1667, calcd. for $C_{29}H_{22}O$: 386.1671.

(4-Chlorophenyl)(3-methyl-10-phenylphenanthren-4-yl)methanone (4e)

Method A and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as sticky yellow oil; yield: 67%. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 2.31 (s, 3H), 7.27 (dt, J = 1.8, 7.8 Hz, 1H), 7.38–7.51 (m, 9H), 7.64 (s, 1H), 7.65 (d, J = 8.7 Hz, 2H), 7.78 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 20.23, 126.08, 126.70, 126.78, 127.44, 127.98, 128.06, 128.27, 128.32, 128.43, 128.89, 128.98, 129.11, 130.00, 130.27, 130.85, 132.17, 132.67, 133.80, 135.91, 136.16, 138.62, 140.55, 201.22; HR-MS (EI): m/z = 406.1122, calcd. for $C_{28}H_{19}OCl$: 406.1124.

(3-Methyl-10-phenylphenanthren-4-yl)(thien-2-yl)-methanone (4g)

Method B and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a sticky yellow oil; yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 2.45 (s, 3H), 6.87 (t, J = 4.0 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.40–7.53 (m, 7H), 7.62 (d, J = 4.2 Hz, 1H), 7.64 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): δ = 20.21, 126.15, 126.77, 126.81, 127.43, 127.92, 128.13, 128.16, 128.30, 128.33, 128.66, 128.76, 128.99, 130.06, 130.27, 132.63, 134.23, 134.77, 135.14, 136.25, 138.55, 140.68, 145.31, 194.49; HR-MS (EI): m/z = 378.1074, calcd. for $C_{26}H_{18}OS$: 378.1078.

(3-Methyl-10-*p*-tolylphenanthren-4-yl)(phenyl)-methanone (4h)

Method A and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a sticky yellow oil; yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 2.32 (s, 3H), 2.45 (s, 3H), 7.24 (t, J = 8.0 Hz, 1H), 7.30–7.48 (m, 9H), 7.62 (s, 1H), 7.76 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$,

Me_4Si): $\delta = 20.24$, 21.23, 125.90, 126.61, 126.90, 127.85, 127.92, 128.38, 128.55, 128.77, 128.82, 128.99, 129.01, 129.43, 129.91, 130.44, 132.73, 133.61, 133.70, 136.63, 137.08, 137.42, 137.75, 138.64, 202.35; HR-MS (EI): $m/z = 386.1674$, calcd. for $C_{29}H_{22}O$: 386.1671.

[10-(4-Chlorophenyl)-3-methylphenanthren-4-yl]-(phenyl)methanone (4i)

Method A and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a sticky yellow oil; yield: 66%. It could be solidified as a foamy solid by the treatment with hot hexane; mp 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 2.31$ (s, 3H), 7.25 (t, $J = 7.2$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 2H), 7.38–7.45 (m, 7H), 7.58 (s, 1H), 7.75 (d, $J = 7.6$ Hz, 1H), 7.81–7.84 (m, 3H), 8.38 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): $\delta = 20.24$, 126.22, 126.75, 126.91, 127.49, 128.01, 128.41, 128.51, 128.70, 128.84, 129.18, 129.40, 130.01, 131.33, 132.50, 133.45, 133.66, 133.98, 136.78, 137.35, 137.37, 139.12, 202.13; HR-MS (EI): $m/z = 406.1128$, calcd. for $C_{28}H_{19}OCl$: 406.1124.

(10-Butyl-3-methylphenanthren-4-yl)(phenyl)-methanone (4j)

Method B and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) to afford the title product as a sticky yellow oil; yield: 73%. It could be solidified as a foamy solid by the treatment with hot hexane; mp 99–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 1.00$ (t, $J = 7.2$ Hz, 3H), 1.48–1.54 (m, 2H), 1.78–1.83 (m, 2H), 2.33 (s, 3H), 3.08–3.15 (m, 2H), 7.16–7.20 (m, 1H), 7.29 (t, $J = 7.2$ Hz, 2H), 7.35–7.39 (m, 1H), 7.42–7.46 (m, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.54 (s, 1H), 7.71 (dd, $J = 1.6$, 8.0 Hz, 1H), 7.77 (d, $J = 6.8$ Hz, 2H), 8.12 (d, $J = 8.4$ Hz, 1H), 8.31 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): $\delta = 14.02$, 20.22, 22.89, 32.35, 33.40, 125.26, 126.37, 126.49, 126.89, 128.14, 128.34, 128.57, 128.75, 129.03, 129.41, 130.41, 133.11, 133.28, 133.51, 136.64, 136.97, 137.48, 202.40; HR-MS (EI): $m/z = 352.1822$, calcd. for $C_{26}H_{24}O$: 352.1827.

(6-Fluoro-3-methyl-10-phenylphenanthren-4-yl)-(phenyl)methanone (4k)

Method A and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a sticky yellow oil; yield: 58%. It could be solidified as a foamy solid by the treatment with hot hexane; mp 172–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 2.33$ (s, 3H), 7.15–7.20 (m, 1H), 7.36–7.53 (m, 9H), 7.60 (s, 1H), 7.42 (dd, $J = 6.0$, 8.8 Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 2H), 7.92 (d, $J = 8.8$ Hz, 1H), 8.06 (dd, $J = 2.4$, 12.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): $\delta = 20.07$, 112.17 (d, $J = 24.6$ Hz), 115.68 (d, $J = 23.9$ Hz), 127.28, 127.49, 127.66 (d, $J = 3.7$ Hz), 127.93, 128.37, 128.97, 129.39 (d, $J = 1.5$ Hz), 129.45, 129.60, 129.85 (d, $J = 9.1$ Hz), 130.03, 130.58, 130.69 (d, $J = 9.1$ Hz), 131.85, 133.92, 136.85, 137.23, 138.03 (d, $J = 2.9$ Hz), 140.50, 160.54 (d, $J = 245.4$ Hz), 202.19; HR-MS (EI): $m/z = 390.1421$, calcd. for $C_{28}H_{19}OF$: 390.1420.

(6,7-Dimethoxy-3-methyl-10-phenylphenanthren-4-yl)(phenyl)methanone (4l)

Method A and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a sticky yellow oil; yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 2.32$ (s, 3H), 3.52 (s, 3H), 3.94 (s, 3H), 7.16 (s, 1H), 7.34–7.58 (m, 10H), 7.68 (s, 1H), 7.90–7.92 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): $\delta = 20.18$, 55.35, 55.72, 108.35, 108.50, 123.14, 127.01, 127.23, 127.89, 128.00, 128.06, 128.09, 128.26, 128.98, 129.47, 129.54, 130.16, 133.28, 133.92, 135.80, 137.10, 137.43, 140.99, 148.22, 148.87, 202.44; HR-MS (EI): $m/z = 432.1726$, calcd. for $C_{30}H_{24}O_3$: 432.1725.

(2-Methyl-5-phenylphenanthro[2,3-*d*][1,3]dioxol-1-yl)(phenyl)methanone (4m)

Method A and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) to afford the title product as a sticky yellow oil; yield: 52%. It could be solidified as a foamy solid by the treatment with hot hexane; mp 226–227 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 2.30$ (s, 3H), 5.59 (s, 1H), 5.93 (s, 1H), 7.12 (s, 1H), 7.36 (q, $J = 8.0$ Hz, 3H), 7.45–7.54 (m, 7H), 7.78 (s, 1H), 7.83 (d, $J = 7.2$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): $\delta = 20.30$, 101.26, 105.16, 105.88, 124.60, 127.30, 127.53, 127.87, 128.24, 128.26, 128.30, 128.91, 129.45, 129.50, 129.57, 130.13, 133.44, 133.73, 136.01, 137.17, 137.50, 140.82, 147.25, 147.48, 202.58; HR-MS (EI): $m/z = 416.1410$, calcd. for $C_{29}H_{20}O_3$: 416.1412.

(8-Methyl-5-phenyl-2,3-dihydro-1*H*-cyclopenta[*a*]-naphthalen-9-yl)(phenyl)methanone (4n)

Method B and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a yellow oil; yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 1.85$–1.92 (m, 1H), 1.98–2.05 (m, 1H), 2.21 (s, 3H), 2.50–2.58 (m, 1H), 2.93–3.01 (m, 2H), 3.11–3.19 (m, 1H), 7.18 (d, $J = 8.8$ Hz, 1H), 7.32 (s, 1H), 7.37–7.50 (m, 7H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.87 (d, $J = 8.8$ Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si): $\delta = 19.64$, 24.96, 33.45, 34.66, 124.35, 127.05, 127.22, 127.92, 128.14, 128.26, 128.82, 129.78, 130.13, 132.58, 133.45, 135.06, 136.93, 138.27, 139.53, 141.24, 142.82, 201.63; HR-MS (EI): $m/z = 362.1673$, calcd. for $C_{27}H_{22}O$: 362.1671.

(2-Methyl-5,7-diphenylnaphthalen-1-yl)(phenyl)-methanone (4o)

Method B and column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a yellow oil; yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 2.30$ (s, 3H), 7.28–7.31 (m, 2H), 7.34–7.37 (m, 2H), 7.42–7.47 (m, 3H), 7.49–7.57(m, 7H), 7.65 (d, $J = 2.0$ Hz, 1H), 7.70 (bs, 1H), 7.88–7.92 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): $\delta = 19.66$, 122.28, 126.31, 126.93, 127.43, 127.45, 127.47, 128.34, 128.58, 128.72, 128.88, 129.14, 129.74, 130.03, 131.33, 132.53, 133.88, 136.45, 137.50, 138.81, 140.46, 140.64, 140.98, 200.39. HR-MS (EI): $m/z = 398.1670$, calcd. for $C_{30}H_{22}O$: 398.1671.

Typical Procedure for the Synthesis of 2-Methyl-5-{3-phenyl-1-[2-(phenylethynyl)-phenyl]prop-2-ynyl}furan (2a)

To a solution of alcohol **1a** (6.0 mmol, 1.85 g in 90 mL dry CH_2Cl_2) were added 2-methylfuran (15.0 mmol, 1.23 g, 1.35 mL) and $TsOH{\cdot}H_2O$ (1.8 mmol, 342 mg). The mixture was kept at room temperature and the reaction was monitored by TLC. After two hours, the reaction was completed. The solvent was evaporated under vacuum at room temperature. Purification of the crude product by flash column chromatography on silica-gel (petroleum ether:dicloromethane = 10:1) afforded the title compound as a light yellow sticky liquid; yield: 1.91 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 2.22 (s, 3H), 5.86–5.88 (m, 2H), 6.11 (d, J = 2.8 Hz, 1H), 7.23–7.28 (m, 4H), 7.31–7.37 (m, 4H), 7.44–7.47 (m, 2H), 7.52–7.55(m, 3H), 7.68 (dd, J = 1.2, 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): δ = 13.61, 36.03, 83.19, 87.22, 87.83, 94.45, 106.23, 107.49, 122.34, 123.16, 123.29, 127.18, 127.98, 128.09, 128.14, 128.32, 128.36, 128.79, 131.55, 131.74, 132.13, 140.91, 151.26, 151.72; HR-MS (EI): m/z = 372.1511, calcd. for $C_{28}H_{20}O$: 372.1514.

2-{1-[2-(hex-1-ynyl)phenyl]-3-phenylprop-2-ynyl}-5-methylfuran (2b)

This product was obtained according to the procedure described for **2a**. Column chromatography on silica gel (petroleum ether:dichloromethane = 2:1) afforded the title product as a yellow oil; yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.92 (d, J = 7.2 Hz, 3H), 1.44–1.50 (m, 2H), 1.57–1.60 (m, 2H), 2.23 (s, 3H), 2.44 (t, J = 7.2 Hz, 2H), 5.78 (s, 1H), 5.86–5.87 (m, 1H), 6.04 (d, J = 2.8 Hz, 1H), 7.18–7.21 (m, 1H), 7.25–7.29 (m, 4H), 7.41 (d, J = 7.6 Hz, 1H), 7.44–7.46 (m, 2H), 7.61 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): δ = 13.61, 13.62, 19.25, 21.95, 30.75, 35.77, 78.33, 82.82, 88.14, 95.54, 106.10, 107.30, 123.16, 123.39, 127.00, 127.91, 127.92, 127.96, 128.11, 131.72, 132.06, 140.64, 151.49, 151.61; HR-MS (EI): m/z = 352.1831, calcd. for $C_{26}H_{24}O$: 352.1827.

Typical Procedure for the Synthesis of (9-Iodo-3-methyl-10-phenylphenanthren-4-yl)(phenyl)-methanone (13a)

To a solution of 2-methyl-5-{3-phenyl-1-[2-(phenylethynyl)-phenyl]prop-2-ynyl}furan (**2a**) (74.5 mg, 0.2 mmol) in DCE (2 mL) were added I_2 (152.3 mg, 0.6 mmol), $AuCl_3$ (0.2 mL, 0.01 mmol, used as a 0.05 M solution in MeCN) and $AgSbF_6$ (0.6 mL, 0.03 mmol, used as a 0.05 M solution in MeCN) subsequently. The flask was sealed and immersed into an oil bath at 80 °C. After stirring for 6 h, the reaction mixture was quenched at room temperature by saturated aqueous $Na_2S_2O_3$, and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel (petroleum ether:dichloromethane = 1:1) to afford (9-iodo-3-methyl-10-phenylphenanthren-4-yl)(phenyl)methanone (**13a**) as a yellow oil; yield: 62.3 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 2.31 (s, 3H), 7.25–7.39 (m, 6H), 7.44–7.59 (m, 6H), 7.79 (d, J = 7.2 Hz, 2H), 8.35 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 8.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si): δ = 20.47, 106.85, 126.90, 127.28, 127.91, 127.99, 128.46, 128.64, 128.91, 129.47, 129.49, 129.59, 129.68, 130.00, 130.04, 131.36, 133.22, 133.75, 134.72, 134.82, 136.23, 137.33, 145.23, 145.54, 201.86; HR-MS (EI): m/z = 498.0485, calcd. for $C_{28}H_{19}OI$: 498.0481.

(10-Butyl-9-iodo-3-methylphenanthren-4-yl)(phenyl)-methanone (13b)

Five equiv. of I_2 were used. The proudtc was isolated as a brown oil; yield: 39%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 1.07 (t, J = 7.2 Hz, 3H), 1.58–1.67 (m, 2H), 1.74–1.79 (m, 2H), 2.34 (s, 3H), 3.52 (t, J = 8.4 Hz, 2H), 7.20–7.24 (m, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.42–7.47 (m, 2H), 7.53 (d, J = 8.4 Hz, 1H), 7.68 (dd, J = 8.2, 1.2 Hz, 2H), 8.18 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.38 (dd, J = 8.4, 1.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si): δ = 14.02, 20.43, 23.15, 31.60, 40.41, 107.78, 126.08, 126.42, 127.23, 127.68, 128.75, 128.92, 129.16, 129.39, 129.70, 129.93, 133.57, 134.35, 134.61, 136.66, 137.29, 141.85, 201.81; HR-MS (EI): m/z = 478.0798, calcd. for $C_{26}H_{23}IO$: 478.0794.

Supporting Information

Experimental details, spectroscopic characterization of all new compounds and X-ray crystallography of compound **4m** are given in the Supporting Information.

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