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AuCl-catalyzed reaction of *ortho*-alkynyl(oxo)benzene with benzenediazonium 2-carboxylate as a synthetic method towards anthracene, triptycene, and phthalazine derivatives

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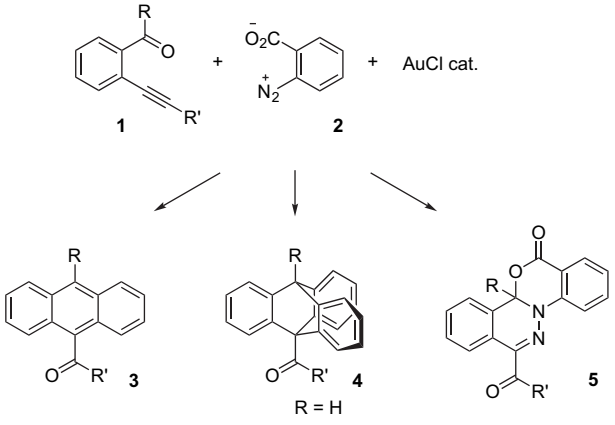
Abstract

The AuCl-catalyzed benzannulation of *ortho*-alkynylphenyl ketones with benzenediazonium 2-carboxylate proceeded efficiently at 40 °C in $(CH_2Cl)_2$ and a variety of anthracene derivatives, having a ketone group at 9-position, were produced in good to high yields. On the other hand, the reaction of *ortho*-alkynylbenzaldehydes with benzenediazonium 2-carboxylate afforded triptycyl ketones. The reactions most probably proceed through the formation of a zwitterionic intermediate by the gold-induced electrophilic cyclization of *ortho*-alkynyl(oxo)benzenes, followed by the cycloaddition of benzyne. In contrast, when the above reaction was carried out at rt in 1,4-dioxane, phthalazine derivative was produced without the generation of benzyne.

Keywords: Gold catalyst; Anthracene; Benzyne; Benzannulation

1. Introduction

It is well known that benzynes are important reactive intermediates and many studies on their reactions have been undertaken in synthetic organic chemistry.[1] Particularly, pericyclic cycloadditions using benzyne, such as the Diels–Alder reaction, are one of the most important methods for the construction of polyaromatic compounds.[2] Due to its extraordinary reactive ability, the reaction is observed with a very wide range of dienes including simple benzene derivatives or other aromatic compounds. The transition metal-catalyzed synthetic methods of polyaromatics with benzynes have also been studied well. However, to the best of our knowledge, there is no research on the Lewis acid-catalyzed Diels–Alder reaction with benzyne. As a benzyne precursor, benzenediazonium 2-carboxylate **2** has been often used in organic synthesis[3] (*caution*: when dry, benzenediazonium 2-carboxylate detonates violently on being scraped or heated). We recently have communicated the gold-catalyzed benzannulations between *ortho*-alkynylphenyl ketone **1** and **2**, which afforded anthryl ketone product **3** in good to high yields (Scheme 1).[4] While exploring the scope of this reaction, we found that the reaction of *ortho*-



Scheme 1. Gold-catalyzed reaction of **1** with **2**.

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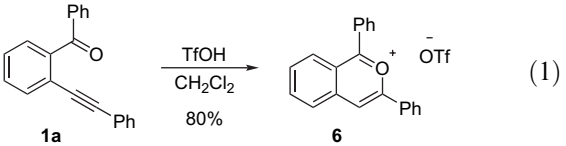
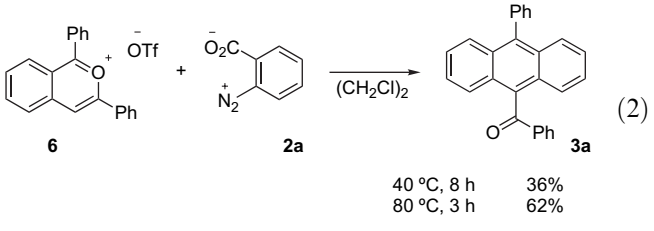
alkynylbenzaldehyde **1** (R=H) with **2** afforded triptycyl ketone **4** but not anthryl ketone **3**. In both reactions, benzyne would be generated via a thermal decomposition of **2**, which reacted with **1** to give anthracenes **3** or triptycenes **4**. Interestingly, however, we noticed that the gold-catalyzed reaction of **1** with **2** proceeded even without generation of benzyne under lower temperatures and the corresponding phthalazine product **5** was produced. In this paper, we detail the synthetic method of anthryl ketone **3** together with unprecedented synthetic approaches to triptycyl ketone **4** and phthalazine derivative **5**.[5]

2. Results and discussion

2.1. Benzannulation with benzo[c]pyrylium salt

Recently, we have reported that gold-catalyzed [4+2] benzannulations between *ortho*-alkynyl(oxo)benzenes and alkynes proceeded smoothly in both inter- and intramolecular ways to give naphthalene compounds in good to high yields.[6,7] The reaction likely proceeds through the formation of a benzopyrylium type intermediate, followed by the Diels–Alder addition of alkynes. It occurred to us that benzyne may be utilized as a partner in the benzannulation reactions. As a preliminary experiment, we initially examined the reaction of benzyne with an isolable benzo[*c*]pyrylium salt.[8,9] The requisite substrate **6** was easily prepared from the corresponding *ortho*-alkynyl(oxo)benzene **1a** according to the Swager's procedure.[10] Treatment of **1a** with excess amount of TfOH in CH_2Cl_2, followed by addition of ether produced **6** in 80% yield (Eq. 1). Then, the benzannulation reaction of **6** was undertaken with benzenediazonium 2-carboxylate **2a** as a precursor of benzyne. As expected, when **6** was treated with 1.8 equiv of **2a** in $(CH_2Cl)_2$ at 40 °C for 8 h, the reaction proceeded and an anthracene product **3a**, bearing a ketone group at the C9-position, was obtained in 36% yield (Eq. 2). It seems that the low yield of **3a** is due to the low reactivity as well as the insolubility of **6** to the solvent. Indeed, the chemical yield was increased up to 62% by just conducting the reaction at 80 °C for 3 h. These results clearly showed that benzyne worked as a dienophile in the Diels–Alder reaction with benzo[*c*]pyrylium salt **6** and this is a novel synthetic approach to anthracene compounds.

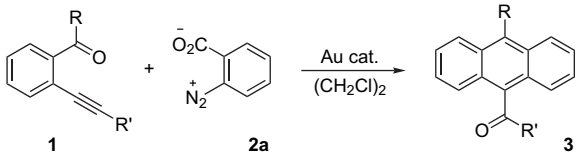




2.2. Gold-catalyzed benzannulation

Since the model study proceeded smoothly, we next examined the Lewis acid-catalyzed direct benzannulation between *ortho*-alkynyl(oxo)benzenes **1** and benzyne and the results are summarized in Table 1. When the reaction of (2-phenylethynyl-phenyl)-*p*-tolylmethanone **1b** (R=*p*-MeC_6H_4, R′=Ph) was carried out with 1.8 equiv of **2a** in the presence of 10 mol % of $AuBr_3$ in $(CH_2Cl)_2$, the reaction proceeded smoothly at 60 °C for 2 h and the anthracene derivative **3b** was obtained in 55% yield as a sole product (entry 1). Optimization experiments revealed that the chemical yield was increased up to 81% when the reaction was conducted in the presence of AuCl catalyst at 40 °C (entries 2–5). Other Lewis and Brønsted acids, such as $Cu(OTf)_2$, $PtCl_2$, and TfOH, were not effective. The AuCl-catalyzed reaction also proceeded well with other differently substituted substrates **1a**,**c**–**f** (entries 6–10). Interestingly, the reaction of **1a** with **2a** produced **3a** in 72% yield (entry 6), which is higher than that of the model reaction mentioned in Eq. 2. Compared with **1b**, the reactions of **1a** and **1c** gave the corresponding products in lower yields (entries 5–7). These results would be ascribed to the fact that an intermediate **8** in Scheme 2 can be stabilized effectively by an electron-donating ability of R group (vide infra). The reaction of **1d**, having a propyl group instead of an aryl group at the terminus of alkyne, afforded anthracene derivative **3d** in 87% yield (entry 8). The reaction proceeded well even with the sterically bulky *tert*-butyl group (entry 9). When the reaction of **1a** was performed in the absence of gold catalyst, no benzannulation products were obtained at all. This blank test clearly indicates that a Lewis acid, such as AuCl, is an essential catalyst for the current transformation.

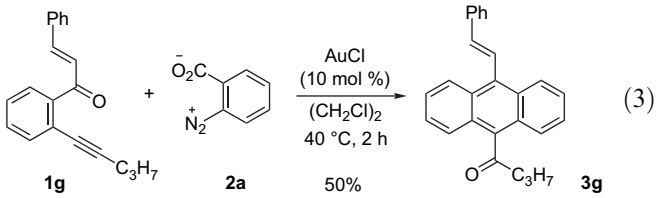
Table 1
The gold-catalyzed benzannulation between *ortho*-alkynyl(oxo)benzenes **1** and benzenediazonium 2-carboxylate **2a**[a]



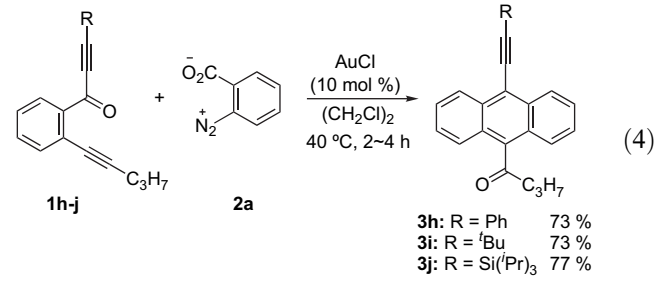
Entry	1	R	R′	Lewis acid	Conditions	3	Yield %[b]
1	**1b**	*p*-MeC_6H_4	Ph	$AuBr_3$	60 °C, 2 h	**3b**	55
2	**1b**	*p*-MeC_6H_4	Ph	$AuCl_3$	60 °C, 2 h	**3b**	62
3	**1b**	*p*-MeC_6H_4	Ph	AuCl	60 °C, 1 h	**3b**	74
4[c]	**1b**	*p*-MeC_6H_4	Ph	AuCl-PPh_3	60 °C, 2 h	**3b**	52
5	**1b**	*p*-MeC_6H_4	Ph	AuCl	40 °C, 7 h	**3b**	81
6	**1a**	Ph	Ph	AuCl	40 °C, 8 h	**3a**	72
7	**1c**	*p*-$CF_3C_6H_4$	Ph	AuCl	40 °C, 9 h	**3c**	62
8	**1d**	*p*-MeC_6H_4	C_3H_7	AuCl	40 °C, 4 h	**3d**	87
9	**1e**	Ph	^{t}Bu	AuCl	40 °C, 9 h	**3e**	73
10	**1f**	2-Benzofuranyl	C_3H_7	AuCl	40 °C, 9 h	**3f**	65

[a] All reactions were carried out with **1** (1 equiv) and **2a** (1.8 equiv) in the presence of gold catalyst (10 mol %) in $(CH_2Cl)_2$.
[b] Isolated yield.
[c] Starting material **1b** was recovered in 25% yield.

Introduction of alkenyl and alkynyl groups at C10-position on the anthracene skeleton was also examined. Treatment of α,β-unsaturated ketone derivative **1g** with **2a** in the presence of AuCl catalyst under the standard condition resulted in the formation of a styrenyl substituted anthracene product **3g** in 50% yield (Eq. 3). The reactions of **1h–j**, bearing alkynyl group at the carbonyl group, with **2a** also proceeded smoothly and alkynyl substituted anthracene products **3h–j** were obtained in good yields, respectively (Eq. 4).



(3)



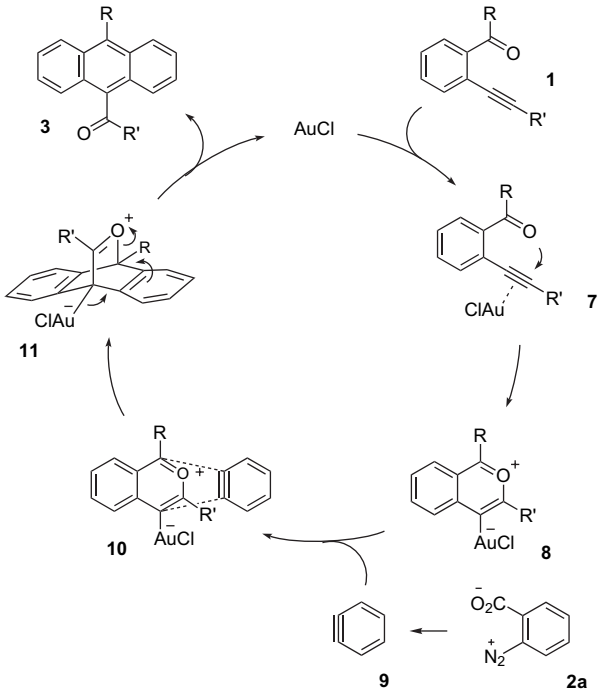
(4)

2.3. Reaction mechanism of benzannulation

A plausible mechanism for the present benzannulation is shown in Scheme 2. The coordination of the triple bond of **1** to AuCl enhances the electrophilicity of alkyne, and the subsequent nucleophilic attack (as shown in **7**) of the carbonyl oxygen to the electron-deficient alkyne would form the ate complex **8**. The reverse electron demand-type Diels–Alder reaction between **8** and benzyne **9**, derived from **2a**, would generate the intermediate **11** through **10**. The subsequent bond rearrangement, as shown in **11**, would afford the anthranyl ketones **3** and regenerate AuCl.[11] Due to the instability of benzyne **9**, it is necessary that **9** should be trapped by the intermediate **8** as soon as it is generated from the precursor **2a**. Probably, the generation speed of **8** is faster than that of benzyne **9** under the optimized reaction condition, which could keep the catalytic cycle effective.

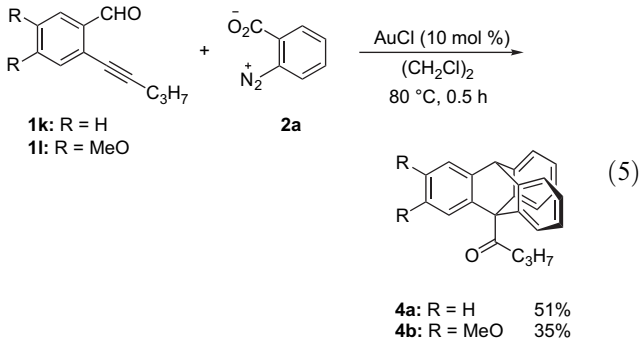
2.4. Triptycene synthesis

Triptycene[12] and its derivatives form an interesting class of compounds due to their three-dimensional rigid frameworks. They have been found to have unique electrochemical and photochemical properties,[13] interesting reactivities,[14] potential pharmaceutical properties,[15] and attractive applications in supramolecular chemistry[16] and materials science.[17] Moreover, they have also been shown to be useful building blocks in



Scheme 2. A plausible mechanism of the gold-catalyzed benzannulation.

constructing molecular devices and synthetic molecular machines.[18] It is well known that Diels–Alder reaction between anthracene and benzyne is an established protocol for preparation of triptycene.[19] However, in the present benzannulation, such triptycene products were not obtained at all even though excess amount of benzyne precursor **2a** was used toward *ortho*-alkynylphenyl ketone **1**. On the other hand, the reaction of 9-acetylanthracene with benzyne has been reported to give 9-acetyltriptycene in moderate yield.[20] These results suggest that the substituent at C10-position on the anthracene skeleton hampers the approach of benzyne due to its steric hindrance. It occurred to us that the reaction of *ortho*-alkynylbenzaldehyde **1** would produce triptycene since the anthracene product derived from such substrate has no substituents at the C10-position. Then, we prepared **1k** and examined the reaction with 3.5 equiv of benzyne precursor **2a**. As we anticipated, the reaction proceeded at 80 °C for 0.5 h and 9-triptycyl ketone **4a** was obtained in 51% yield as a sole product. Dimethoxy-substituted triptycene **4b** was also obtained from **1l** in 35% yield by the present one-pot procedure.



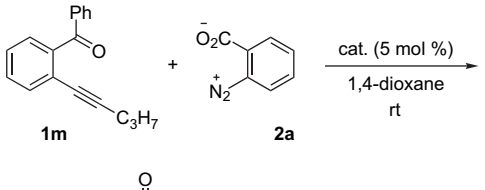
(5)

2.5. Phthalazine derivatives synthesis

Nitrogen-containing heterocyclic compounds are widespread in nature, and their applications to biologically active pharmaceuticals, agrochemicals, and functional materials are becoming more and more important.[21] The development of new efficient methods to synthesize *N*-heterocycles with structural diversity is of major interest to modern synthetic organic chemists.[22] While exploring the scope of the benzannulation with benzyne, we examined the AuCl-catalyzed reaction of **1m** with **2a** in 1,4-dioxane at rt. To our surprise, the reaction gave a small amount of phthalazine derivative **5a** together with anthryl ketone **3k**. It is clear that **5a** was produced from **1m** and **2a** directly without the generation of benzyne via the thermal decomposition of **2a**. Only a few papers have been reported on the synthetic utility of **2a**, excluding the usefulness as a benzyne precursor.[23] Therefore, this result prompted us to investigate the present cycloaddition reaction as a novel synthetic approach to phthalazine derivatives and the results are summarized in Table 2. When the reaction was carried out with 1.1 equiv of **2a** in the presence of 5 mol % of AuCl in 1,4-dioxane at rt, the reaction proceeded for 24 h and **5a** was obtained in 17% yield. Besides **5a**, anthryl ketone **3k** and hydrated product **12** were obtained in 11 and 17% yields, respectively (entry 1). The chemical yield of **5a** was increased up to 40% with $AuCl_3$ catalyst instead of AuCl (entry 2). However, other catalysts, such as $AuBr_3$, $Cu(OTf)_2$, $PtCl_2$, and $Pd(OAc)_2$, were less effective (entries 3–6).

Interestingly, the chemical yield of phthalazine derivative was increased dramatically when the reaction was carried out with *ortho*-alkynylnaphthyl ketone **1n** instead of **1m**. Indeed, the reaction of **1n** with **2a** in the presence of AuCl catalyst proceeded at rt for 2 days and benzo[*g*]phthalazine derivative **5b** was obtained in 88% yield (Eq. 6). Other aryne precursors **2b**,**c** were also suitable for the current cycloaddition reaction and the corresponding products **5c**,**d** were obtained in 77 and 91% yields, respectively (Eqs. 7 and 8). The structure of **5b** was unambiguously confirmed by X-ray analysis (Fig. 1).

Table 2
The gold-catalyzed synthesis of phthalazine derivatives[a]



Entry	Cat.	Time (h)	Yield %[b]			
			5a	**3k**	**12**	**1m**
1	AuCl	24	17	11	17	12
2	$AuCl_3$	12	40	0	22	0
3	$AuBr_3$	24	24	4	29	0
4	$Cu(OTf)_2$	12	0	0	0	62
5	$PtCl_2$	24	0	7	5	50
6	$Pd(OAc)_2$	12	23	15	6	6

[a] All reactions were carried out with **1m** (1 equiv) and **2a** (1.1 equiv) in the presence of catalyst (5 mol %) in 1,4-dioxane at rt.
[b] Determined by ^1H NMR spectra using *p*-xylene as an internal standard.

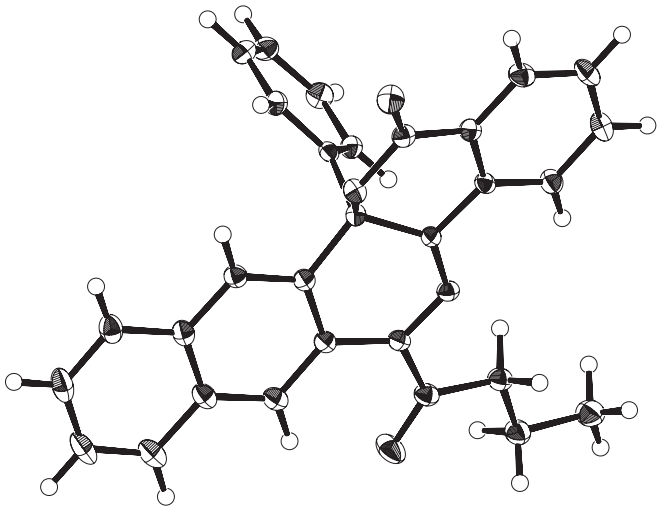
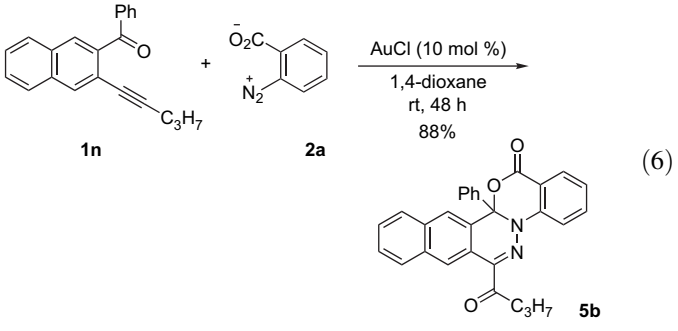


Figure 1. X-ray structure of **5b**.



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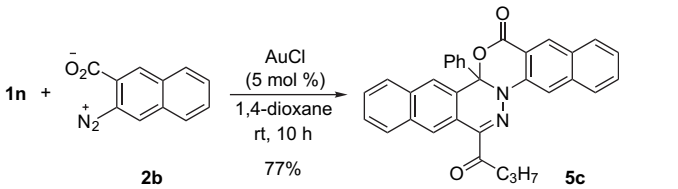

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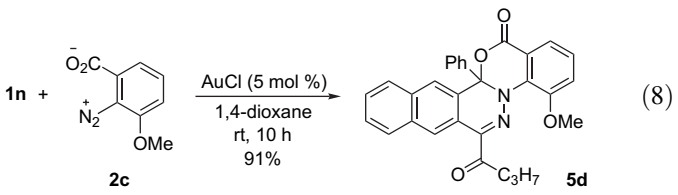
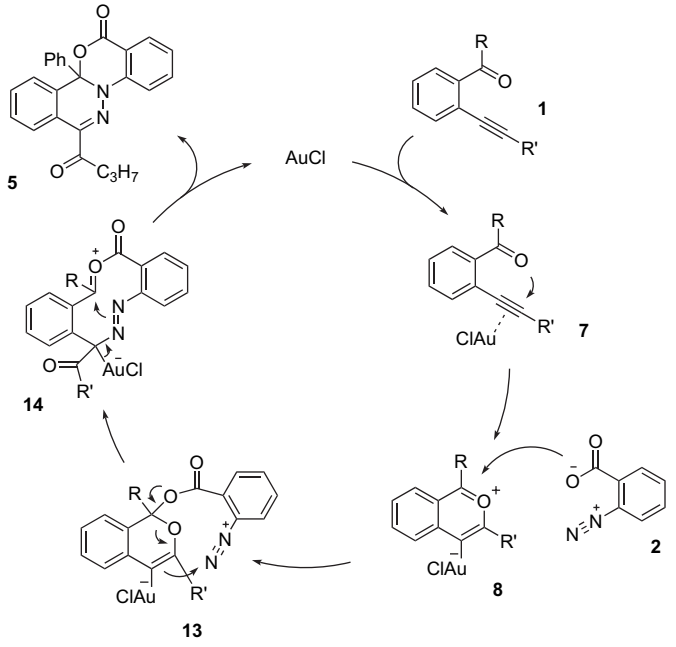


(8)

2.6. Reaction mechanism of cycloaddition

A plausible mechanism for the current transformation is shown in Scheme 3. After the formation of the key

intermediate **8**, the carboxylate moiety of **2** attacks **8** to give **13**. The subsequent intramolecular addition of the enol moiety of **13** to the diazonium group, followed by cleavage of the carbon–enol oxygen bond, as shown in **13**, affords 10-membered cyclized intermediate **14**. The attack of nitrogen to the electron-deficient benzyl carbon results in a second cyclization to afford the phthalazine **5** and regenerate AuCl. Probably, the generation of a benzyne from **2** is sluggish at rt in 1,4-dioxane and the electrophilicity of the intermediate **8** is high enough to react with **2** under the optimized conditions. Obviously, compared to benzo[*c*]pyrylium intermediate **8** derived from **1m**, benzo[*g*]isochromenium intermediate derived from **1n** would be more stable due to its superior resonance effect. This might be the reason why phthalazine derivatives **5b–d** were obtained in higher yields than that of **5a**.



Scheme 3. A plausible mechanism of the cycloaddition for the synthesis of phthalazine derivatives.

3. Conclusion

We are now in a position to synthesize functionalized anthracene derivatives from *ortho*-alkynylphenyl ketones **1** and benzenediazonium 2-carboxylate **2** in good to high yields. The reaction most probably proceeds through the inverse electron demand-type Diels–Alder reaction between the intermediate **8** and benzyne **9**. The protocol can be applied to the synthesis of triptycyl ketones **4** by using *ortho*-alkynylbenzaldehyde. The direct cycloaddition between **1** and **2** proceeds under lower temperatures without the generation of benzyne, leading to phthalazine derivatives **5**. Further studies to elucidate the precise mechanism of these reactions and to extend the scope of synthetic utility are in progress in our laboratory.

4. Experimental

4.1. General

NMR spectra were measured at 400 MHz for ^{1}H and 100 MHz for ^{13}C by JEOL JNM-AL 400 spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane with reference to internal residual $CHCl_3$ (δ=7.26) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard (δ=77.0) in $CDCl_3$. High-resolution mass spectra (HRMS) were performed on BRUKER DALTONICS APEX III spectrometer. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (Kieselgel 60 F_{254}, 0.2 mm) were used. The products were purified by flash column chromatography on silica gel 60N (KANTO, 40–50 μm). All manipulations were carried out under argon atmosphere using standard Schlenk techniques.

4.2. Typical procedure for preparation of anthryl ketone *3*

The preparation of **3b** is representative. To a mixture of AuCl (12 mg, 10 mol %) and **1b** (148 mg, 0.5 mmol) in 1,2-dichloroethane (3.5 mL) was added a creamy white solid of benzenediazonium 2-carboxylate **2a** (133 mg, 0.9 mmol) at rt under Ar atmosphere. After the reaction mixture was stirred for 7 h at 40 °C, the resulting solution was filtered through a short pad of silica gel. The filtrate was evaporated under reduced pressure to give the crude product, which was purified by silica gel column chromatography with hexane/ether as eluent to give **3b** (151 mg, 0.405 mmol) in 81% yield as a white solid.

4.3. Typical procedure for preparation of triptycyl ketone *4*

The preparation of **4a** is representative. To a mixture of AuCl (7.0 mg, 10 mol %) and **1k** (51.6 mg, 0.30 mmol) in 1,2-dichloroethane (2.0 mL) was added a creamy white solid of benzenediazonium 2-carboxylate **2a** (155 mg, 1.05 mmol) at rt under Ar atmosphere. The mixture was warmed to 80 °C and stirred for 0.5 h. After cooling, the resulting solution was filtered through a short pad of silica gel. The filtrate was evaporated under reduced pressure to give the crude product, which was recrystallized from hexane/ether/CH_2Cl_2 to give **4a** (49.6 mg, 0.15 mmol) in 51% yield as a white solid.

4.4. Typical procedure for preparation of phthalazine derivatives *5*

The preparation of **5b** is representative. To a mixture of AuCl (7.0 mg, 10 mol %) and **1n** (107 mg, 0.36 mmol) in 1,4-dioxane (2.1 mL) was added a creamy white solid of benzenediazonium 2-carboxylate **2a** (44 mg, 0.30 mmol) at rt under Ar atmosphere. After the reaction mixture was stirred for 48 h at rt, the resulting solution was filtered through a short pad of silica gel. The filtrate was evaporated under reduced pressure to give the crude product, which was recrystallized from hexane/

ether/CH_2Cl_2 to give **5b** (118 mg, 0.26 mmol) in 88% yield as a light yellow solid.

4.5. Characterization data

4.5.1. Phenyl(2-(2-phenylethynyl)phenyl)methanone (*1a*)

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (m, 2H), 7.63–7.43 (m, 7H), 7.24–7.18 (m, 3H), 7.04 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.9, 141.5, 137.3, 133.0, 132.5, 131.3, 130.21, 130.20, 128.6, 128.3, 128.1, 128.0, 122.5, 121.8, 95.1, 87.4. IR (KBr): 3063, 2216, 1668, 1595, 1315, 843, 694, 638 cm^{-1}. MS (EI) *m/z* 282 (M^+, 88). HRMS calcd for $C_{21}H_{14}ONa$ ($[M+Na]^+$): 305.0937, found: 305.0937. Mp=49–50 °C.

4.5.2. (2-(2-Phenylethynyl)phenyl)(p-tolyl)methanone (*1b*)

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, J=8.0 Hz, 2H), 7.61 (ddd, J=0.7, 1.2, 7.8 Hz, 1H), 7.52–7.42 (m, 3H), 7.28–7.18 (m, 5H), 7.06 (ddd, J=2.4, 3.9, 8.3 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.5, 143.9, 141.8, 134.8, 132.4, 131.3, 130.4, 130.0, 129.0, 128.4, 128.3, 128.0, 128.0, 122.7, 121.7, 94.8, 87.5, 21.8. IR (KBr): 1948, 1665, 1491, 930, 835, 777, 608, 515 cm^{-1}. MS (EI) *m/z* 296 (M^+, 94). HRMS calcd for $C_{22}H_{16}ONa$ ($[M+Na]^+$): 319.1093, found: 319.1092. Mp=89–90 °C.

4.5.3. (2-(2-Phenylethynyl)phenyl)(4-(trifluoromethyl)-phenyl)methanone (*1c*)

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J=8.0 Hz, 2H), 7.73 (d, J=8.0 Hz, 2H), 7.63 (ddd, J=0.7, 1.2, 7.6 Hz, 1H), 7.59 (ddd, J=0.7, 1.2, 7.6 Hz, 1H), 7.55 (ddd, J=1.2, 7.3, 7.6 Hz, 1H), 7.48 (ddd, J=1.2, 7.3, 7.6 Hz, 1H), 7.28–7.18 (m, 3H), 6.97 (ddd, J=1.2, 1.5, 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.8, 140.3, 134.3, 134.0, 132.7, 131.2, 131.0, 130.3, 129.0, 128.6, 128.4, 128.1, 125.3, 124.9, 122.2, 122.0, 96.0, 87.3. IR (KBr): 3072, 1672, 1410, 1331, 1067, 932, 756, 691 cm^{-1}. MS (EI) *m/z* 350 (M^+, 100). HRMS calcd for $C_{22}H_{13}F_3ONa$ ($[M+Na]^+$): 373.0811, found: 373.0809. Mp=62–63 °C.

4.5.4. (2-(Pent-1-ynyl)phenyl)(p-tolyl)methanone (*1d*)

Light yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (ddd, J=1.0, 1.2, 8.1 Hz, 2H), 7.47 (ddd, J=1.0, 1.2, 7.8 Hz, 1H), 7.43–7.33 (m, 3H), 7.23 (d, J=8.1 Hz, 2H), 2.42 (s, 3H), 2.11 (t, J=6.8 Hz, 2H), 1.27 (tt, J=6.8, 7.3 Hz, 2H), 0.78 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.7, 143.7, 141.9, 134.6, 132.4, 130.2, 129.6, 128.8, 127.7, 127.1, 122.2, 96.0, 78.6, 21.7 (×2), 21.3, 13.3. IR (neat): 2963, 2235, 1666, 1607, 1312, 1151, 928, 758 cm^{-1}. MS (EI) *m/z* 262 (M^+, 2). HRMS calcd for $C_{19}H_{18}ONa$ ($[M+Na]^+$): 285.1250, found: 285.1250.

4.5.5. (2-(3,3-Dimethylbut-1-ynyl)phenyl)(phenyl)-methanone (*1e*)

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (ddd, J=0.7, 1.4, 7.8 Hz, 2H), 7.56 (ddd, J=7.3, 7.6 Hz, 1H), 7.47–7.36 (m, 6H), 0.92 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.4, 141.7, 137.4, 132.8, 132.1, 130.1, 129.9, 128.2, 128.1, 127.5, 122.3, 104.8, 77.2, 30.3, 27.8. IR (KBr): 2964, 2239, 1560, 1472, 1362, 1028, 806, 440 cm^{-1}. MS (EI) *m/z* 262 (M^+, 15). HRMS calcd for $C_{19}H_{18}ONa$ ($[M+Na]^+$): 285.1250, found: 285.1250. Mp=64–66 °C.

4.5.6. Benzofuran-2-yl(2-(pent-1-ynyl)phenyl)-methanone (*1f*)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (ddd, J=0.8, 1.2, 7.6 Hz, 1H), 7.62 (ddd, J=0.7, 1.0, 8.8 Hz, 1H), 7.55 (ddd, J=1.2, 7.6, 8.8 Hz, 2H), 7.50 (dd, J=1.2, 7.3 Hz, 1H), 7.46 (dd, J=1.4, 7.6 Hz, 1H), 7.39 (ddd, J=1.4, 7.3, 7.6 Hz, 1H), 7.34 (d, J=1.0 Hz, 1H), 7.31 (ddd, J=1.0, 7.3, 7.3 Hz, 1H), 2.16 (t, J=6.8 Hz, 2H), 1.30 (tt, J=6.8, 7.6 Hz, 2H), 0.78 (t, J=7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.5, 156.0, 152.3, 140.3, 132.9, 130.4, 128.3, 127.9, 127.1, 127.0, 123.7, 123.2, 122.7, 117.0, 112.4, 96.0, 78.2, 21.7, 21.3, 13.2. IR (KBr): 2963, 2233, 1614, 1553, 1300, 1128, 974, 754 cm^{-1}. MS (EI) *m/z* 288 (M^+, 9). HRMS calcd for $C_{20}H_{16}O_2Na$ ($[M+Na]^+$): 311.1043, found: 311.1044.

4.5.7. (*E*)-1-(2-(Pent-1-ynyl)phenyl)-3-phenylprop-2-en-1-one (*1g*)

Light yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (m, 4H), 7.51 (dd, J=1.1, 7.8 Hz, 1H), 7.40 (m, 6H), 2.32 (t, J=7.1 Hz, 2H), 1.47 (qt, J=7.1, 7.3 Hz, 2H), 0.92 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.2, 144.0, 142.0, 134.9, 133.1, 130.4, 130.3, 128.8, 128.3, 128.2, 127.5, 126.0, 122.3, 96.9, 79.2, 22.0, 21.6, 13.5. IR (neat): 2963, 2232, 1607, 1576, 1448, 1333, 1207, 758 cm^{-1}. MS (EI) *m/z* 274 (M^+, 2). HRMS calcd for $C_{20}H_{18}ONa$ ($[M+Na]^+$): 297.1250, found: 297.1251. Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.55; H, 6.48.

4.5.8. 1-(2-(Pent-1-ynyl)phenyl)-3-phenylprop-2-yn-1-one (*1h*)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (dd, J=1.2, 7.8 Hz, 1H), 7.65 (m, 2H), 7.54 (dd, J=1.2, 7.8 Hz, 1H), 7.50–7.45 (m, 2H), 7.42–7.37 (m, 3H), 2.42 (t, J=7.1 Hz, 2H), 1.63 (tt, J=7.1, 7.3 Hz, 2H), 1.05 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.7, 138.5, 134.5, 133.0, 132.2, 131.1, 130.5, 128.5, 127.1, 123.8, 120.4, 97.3, 92.9, 88.2, 79.2, 22.1, 22.0, 13.7. IR (neat): 2963, 2197, 1647, 1560, 1489, 1204, 995, 756 cm^{-1}. MS (EI) *m/z* 272 (M^+, 48). HRMS calcd for $C_{20}H_{16}ONa$ ($[M+Na]^+$): 295.1093, found: 295.1092.

4.5.9. 4,4-Dimethyl-1-(2-(pent-1-ynyl)phenyl)-pent-2-yn-1-one (*1i*)

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J=7.8 Hz, 1H), 7.50 (d, J=7.3 Hz, 1H), 7.44 (dd, J=7.3, 7.3 Hz, 1H), 7.35 (dd, J=7.3, 7.8 Hz, 1H), 2.45 (t, J=7.1 Hz, 2H), 1.68 (tt, J=7.1, 7.3 Hz, 2H), 1.35 (s, 9H), 1.09 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.9, 138.5, 134.4, 131.8, 131.4, 126.9, 123.5, 103.3, 96.5, 79.4, 79.2, 30.2, 28.0, 22.1, 22.0, 13.7. IR (neat): 2970, 2210, 1653, 1562, 1477, 1225, 756, 691 cm^{-1}. MS

(EI) *m/z* 252 (M^+, 86). HRMS calcd for $C_{18}H_{20}ONa$ ($[M+Na]^+$): 275.1406, found: 275.1407.

*4.5.10. 1-(2-(Pent-1-ynyl)phenyl)-3-(triisopropylsilyl)-prop-2-yn-1-one (**1j**)*

Orange oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.17 (dd, J=1.4, 7.8 Hz, 1H), 7.52 (dd, J=1.4, 7.8 Hz, 1H), 7.46 (ddd, J=1.4, 7.6, 7.8 Hz, 1H), 7.36 (ddd, J=1.4, 7.6, 7.8 Hz, 1H), 2.46 (t, J=7.1 Hz, 2H), 1.68 (tt, J=7.1, 7.3 Hz, 2H), 1.16 (m, 3H), 1.15 (d, J=4.9 Hz, 18H), 1.09 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 137.8, 134.7, 132.2, 132.1, 127.0, 123.7, 103.8, 97.2, 96.8, 79.5, 22.1, 22.0, 18.6, 13.7, 11.2. IR (neat): 2866, 2233, 2149, 1653, 1560, 1229, 1013, 883, 754 cm^{-1}. MS (EI) *m/z* 309 ($M^+-C_3H_7$, 100). HRMS calcd for $C_{23}H_{32}OSiNa$ ($[M+Na]^+$): 375.2115, found: 375.2115.

*4.5.11. 2-(Pent-1-ynyl)benzaldehyde (**1k**)*

Light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.54 (s, 1H), 7.89 (ddd, J=1.0, 1.0, 7.8 Hz, 1H), 7.51 (m, 2H), 7.38 (m, 1H), 2.47 (t, J=7.1 Hz, 2H), 1.68 (qt, J=7.1, 7.3 Hz, 2H), 1.08 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.1, 135.9, 133.6, 133.2, 127.9, 127.8, 126.8, 98.0, 76.5, 22.1, 21.6, 13.7. IR (neat): 3065, 3032, 2905, 2745, 2233, 1653, 1429, 1339, 1296, 1159, 637 cm^{-1}. MS (EI) *m/z* 172 (M^+, 2). HRMS calcd for $C_{12}H_{12}ONa$ ($[M+Na]^+$): 195.0780, found: 195.0779.

*4.5.12. 4,5-Dimethoxy-2-(pent-1-ynyl)benzaldehyde (**1l**)*

Light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.38 (s, 1H), 7.36 (s, 1H), 6.92 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 2.45 (t, J=6.9 Hz, 2H), 1.67 (tq, J=6.9, 6.9 Hz, 2H), 1.07 (t, J=6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.8, 153.5, 149.1, 130.1, 122.7, 114.4, 107.9, 96.4, 76.2, 56.2, 56.1, 22.1, 21.6, 13.7. IR (neat): 2963, 2936, 2835, 1682, 1593, 1506, 1352, 1283, 1221, 1124, 1009 cm^{-1}. MS (EI) *m/z* 232 (M^+, 11). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.19; H, 6.90.

*4.5.13. (2-(Pent-1-ynyl)phenyl)(phenyl)methanone (**1m**)*

Light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.82 (m, 2H), 7.56 (m, 1H), 7.49–7.34 (m, 6H), 2.08 (t, J=7.3 Hz, 2H), 1.26 (tq, J=7.3, 7.3 Hz, 2H), 0.77 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.2, 141.6, 137.2, 132.9, 132.5, 130.0, 129.9, 128.1, 128.0, 127.2, 122.4, 96.4, 78.7, 21.7, 21.3, 13.4. IR (neat): 2963, 2235, 1668, 1597, 1450, 1317, 1288, 928 cm^{-1}. MS (EI) *m/z* 248 (M^+, 2). HRMS calcd for $C_{18}H_{16}ONa$ ($[M+Na]^+$): 271.1093, found: 271.1093.

*4.5.14. (3-(Pent-1-ynyl)naphthalen-2-yl)(phenyl)-methanone (**1n**)*

Light yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.99 (s, 1H), 7.92 (s, 1H), 7.84 (m, 4H), 7.59–7.52 (m, 3H), 7.45 (dd, J=7.6, 7.6 Hz, 2H), 2.14 (t, J=7.1 Hz, 2H), 1.31 (tq, J=7.3, 7.1 Hz, 2H), 0.82 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.9, 138.7, 137.5, 135.0, 133.5, 132.8, 132.3, 131.4, 130.1, 128.4, 128.1, 127.7, 127.3, 127.0, 119.4, 95.8, 79.0, 21.8, 21.4, 13.5. IR (neat): 2963, 2232, 1668, 1597, 1448, 1217, 893, 750 cm^{-1}. MS (EI) *m/z* 298 (M^+, 8). Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.47; H, 6.04.

*4.5.15. Phenyl(9-phenylanthracen-10-yl)methanone (**3a**)*

Light yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J=7.7 Hz, 2H), 7.76 (dd, J=1.2, 8.6 Hz, 2H), 7.71 (dd, J=1.0, 8.3 Hz, 2H), 7.64–7.55 (m, 4H), 7.47 (m, 4H), 7.38 (ddd, J=1.5, 6.5, 7.7 Hz, 2H), 7.34 (ddd, J=1.4, 6.5, 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.3, 138.9, 138.3, 138.1, 134.1, 133.9, 131.0, 130.0, 129.6, 128.8, 128.4, 128.2, 128.1, 127.6, 127.3, 126.1, 125.3. IR (KBr): 1665, 1518, 1389, 1227, 1070, 851, 710, 644 cm^{-1}. MS (EI) *m/z* 358 (M^+, 100). HRMS calcd for $C_{27}H_{18}ONa$ ($[M+Na]^+$): 381.1250, found: 381.1249. Mp=215–219 °C.

*4.5.16. Phenyl(9-p-tolylanthracen-10-yl)methanone (**3b**)*

Yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, J=7.1 Hz, 2H), 7.75 (m, 4H), 7.60 (ddd, J=1.2, 1.2, 7.3 Hz, 1H), 7.46–7.31 (m, 10H), 2.55 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.4, 139.1, 138.1, 137.3, 135.2, 133.9, 130.9, 130.0, 129.7, 129.1, 128.8, 128.2, 127.4, 126.1, 125.3, 125.2, 21.5. IR (KBr): 3912, 1665, 1443, 1312, 1225, 930, 820, 729 cm^{-1}. MS (EI) *m/z* 372 (M^+, 100). HRMS calcd for $C_{28}H_{20}ONa$ ($[M+Na]^+$): 395.1406, found: 395.1406. Mp=258–262 °C.

*4.5.17. Phenyl(9-(4-(trifluoromethyl)phenyl)anthracen-10-yl) methanone (**3c**)*

Light yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.90 (m, 4H), 7.78 (m, 2H), 7.61 (m, 5H), 7.46 (dd, J=7.3, 8.0 Hz, 2H), 7.40 (ddd, J=1.7, 6.6, 6.6 Hz, 2H), 7.37 (ddd, J=1.7, 6.6, 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.1, 142.4, 138.0, 137.0, 134.8, 134.0, 131.5, 130.2, 130.0, 129.9, 129.4, 128.9, 128.1, 126.7, 126.3, 125.8, 125.5, 122.9. IR (KBr): 3062, 1668, 1325, 1227, 930, 708, 685, 448 cm^{-1}. MS (EI) *m/z* 426 (M^+, 100). HRMS calcd for $C_{28}H_{17}F_3ONa$ ($[M+Na]^+$): 449.1124, found: 449.1125. Mp=329–331 °C.

*4.5.18. 1-(9-p-Tolylanthracen-10-yl)butan-1-one (**3d**)*

Light yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, J=8.8 Hz, 2H), 7.66 (d, J=8.8 Hz, 2H), 7.44 (dd, J=7.1, 8.0 Hz, 2H), 7.36–7.21 (m, 6H), 3.07 (t, J=7.3 Hz, 2H), 2.49 (s, 3H), 1.92 (tt, J=7.3, 7.3 Hz, 2H), 1.08 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.5, 138.8, 137.2, 136.7, 135.1, 130.8, 129.7, 129.0, 127.5, 126.5, 126.2, 125.1, 124.3, 48.5, 21.4, 17.4, 14.0. IR (KBr): 2870, 1695, 1512, 1159, 808, 766, 665, 611 cm^{-1}. MS (EI) *m/z* 338 (M^+, 35). HRMS calcd for $C_{25}H_{22}ONa$ ($[M+Na]^+$): 361.1563, found: 361.1562. Mp=141–144 °C.

*4.5.19. 2,2-Dimethyl-1-(9-phenylanthracen-10-yl)-propan-1-one (**3e**)*

Light yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, J=8.8 Hz, 2H), 7.69 (d, J=8.8 Hz, 2H), 7.63–7.54 (m, 3H), 7.50–7.46 (m, 3H), 7.40–7.33 (m, 3H), 1.40 (s, 9H). ^{13}C

NMR ($CDCl_3$, 100 MHz) δ 218.5, 138.3, 138.1, 136.5, 131.2, 130.8, 129.5, 128.3, 128.3, 127.6, 127.3, 126.9, 125.7, 125.5, 125.2, 46.3, 28.3. IR (KBr): 2967, 1686, 1474, 1443, 1084, 1028, 932, 700, 611 cm^{-1}. MS (EI) *m/z* 338 (M^+, 9). HRMS calcd for $C_{25}H_{22}ONa$ ($[M+Na]^+$): 361.1563, found: 361.1564. Mp=201–205 °C.

*4.5.20. 1-(9-(Benzofuran-2-yl)anthracen-10-yl)-butan-1-one (**3f**)*

Light yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.00 (ddd, *J*=1.0, 1.2, 8.8 Hz, 2H), 7.84 (ddd, *J*=1.0, 1.2, 8.8 Hz, 2H), 7.77 (m, 1H), 7.63 (dd, *J*=1.2, 8.8 Hz, 1H), 7.53 (ddd, *J*=1.2, 6.6, 8.8 Hz, 2H), 7.47 (ddd, *J*=1.2, 6.6, 8.8 Hz, 2H), 7.42 (ddd, *J*=1.2, 7.3, 7.3 Hz, 1H), 7.38 (ddd, *J*=1.2, 7.3, 7.3 Hz, 1H), 7.08 (d, *J*=1.2 Hz, 1H), 3.09 (t, *J*=7.3 Hz, 2H), 1.96 (tt, *J*=7.3, 7.6 Hz, 2H), 1.13 (t, *J*=7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.9, 155.3, 152.2, 139.2, 130.9, 128.6, 128.5, 126.7, 126.5, 126.4, 126.3, 124.5, 123.0, 121.0, 111.4, 109.5, 109.5, 48.3, 17.3, 13.9. IR (KBr): 2963, 1699, 1558, 1452, 1256, 1134, 810, 438 cm^{-1}. MS (EI) *m/z* 364 (M^+, 46). HRMS calcd for $C_{26}H_{20}O_2$ Na ($[M+Na]^+$): 387.1356, found: 387.1357. Mp=130–133 °C.

*4.5.21. (E)-1-(10-Styrylanthracen-9-yl)butan-1-one (**3g**)*

Light green solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.38 (d, *J*=8.5 Hz, 2H), 7.90 (d, *J*=16.6 Hz, 1H), 7.80 (d, *J*=8.1 Hz, 2H), 7.68 (d, *J*=7.6 Hz, 2H), 7.49 (m, 6H), 7.37 (dd, *J*=7.3, 7.3 Hz, 1H), 6.93 (d, *J*=16.6 Hz, 1H), 3.07 (t, *J*=7.3 Hz, 2H), 1.93 (qt, *J*=7.3, 7.6 Hz, 2H), 1.08 (t, *J*=7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.6, 137.9, 136.9, 136.5, 134.5, 129.1, 128.8, 128.2, 126.62, 126.58, 126.3, 125.4, 124.7, 124.4, 48.5, 17.4, 14.0. IR (KBr): 2962, 2927, 1689, 1445, 1182, 1134, 966, 750, 692, 669 cm^{-1}. MS (EI) *m/z* 350 (M^+, 70). HRMS calcd for $C_{26}H_{22}ONa$ ($[M+Na]^+$): 373.1563, found: 373.1562. Mp=154.5 °C.

*4.5.22. 1-(9-(2-Phenylethynyl)anthracen-10-yl)-butan-1-one (**3h**)*

Yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.71 (d, *J*=8.5 Hz, 2H), 7.79 (ddd, *J*=1.2, 7.6, 8.5 Hz, 4H), 7.62 (ddd, *J*=1.2, 6.6, 6.8 Hz, 2H), 7.55 (ddd, *J*=1.2, 6.6, 6.8 Hz, 2H), 7.49–7.43 (m, 3H), 3.05 (t, *J*=7.3 Hz, 2H), 1.93 (tt, *J*=7.3, 7.3 Hz, 2H), 1.10 (t, *J*=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 Hz) δ 209.9, 137.5, 131.9, 131.6, 128.7, 128.5, 127.4, 126.8, 126.5, 126.5, 124.8, 123.2, 119.1, 85.8, 77.2, 48.4, 17.3, 13.9. IR (KBr): 2873, 2365, 1695, 1493, 1441, 1132, 760, 692 cm^{-1}. MS (EI) *m/z* 348 (M^+, 38). HRMS calcd for $C_{26}H_{20}ONa$ ($[M+Na]^+$): 371.1406, found: 371.1407. Mp=125–128 °C.

*4.5.23. 1-(9-(3,3-Dimethylbut-1-ynyl)anthracen-10-yl)-butan-1-one (**3i**)*

Yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.61 (d, *J*=8.5 Hz, 2H), 7.79 (d, *J*=8.5 Hz, 2H), 7.58 (dd, *J*=7.3, 8.5 Hz, 2H), 7.52 (dd, *J*=7.3, 8.5 Hz, 2H), 3.02 (t, *J*=7.6 Hz, 2H), 1.92 (tt, *J*=7.3, 7.6 Hz, 2H), 1.57 (s, 9H), 1.09 (t, *J*=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.0, 136.5, 131.7, 127.4, 126.6, 126.4, 126.1, 124.6, 120.1, 111.5, 75.5, 48.3, 31.3, 28.9, 17.3, 13.9. IR (KBr): 2964, 2208, 1701, 1560, 1396, 1132, 932, 806, 768 cm^{-1}. MS (EI) *m/z* 328 (M^+, 41). HRMS calcd for $C_{24}H_{24}ONa$ ($[M+Na]^+$): 351.1719, found: 351.1720. Mp=134–137 °C.

*4.5.24. 1-(9-(2-(Triisopropylsilyl)ethynyl)anthracen-10-yl)-butan-1-one (**3j**)*

Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.69 (dd, *J*=1.0, 8.6 Hz, 2H), 7.80 (dd, *J*=1.0, 8.6 Hz, 2H), 7.62 (ddd, *J*=1.0, 6.6, 8.6 Hz, 2H), 7.54 (ddd, *J*=1.0, 6.6, 8.6 Hz, 2H), 3.03 (t, *J*=7.3 Hz, 2H), 1.92 (tt, *J*=7.3, 7.6 Hz, 2H), 1.30 (m, 3H), 1.29 (d, *J*=5.1 Hz, 18H), 1.10 (t, *J*=7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.7, 137.5, 132.3, 127.4, 126.7, 126.6, 126.4, 124.7, 119.3, 104.2, 102.8, 48.4, 18.9, 17.3, 13.9, 11.6. IR (neat): 2864, 2141, 1701, 1462, 1412, 1134, 883, 766 cm^{-1}. MS (EI) *m/z* 428 (M^+, 100). HRMS calcd for $C_{29}H_{36}OSiNa$ ($[M+Na]^+$): 451.2428, found: 451.2427.

*4.5.25. 1-(10-Phenylanthracen-9-yl)butan-1-one (**3k**)*

White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, *J*=8.8 Hz, 2H), 7.68 (d, *J*=8.8 Hz, 2H), 7.58 (m, 3H), 7.51 (m, 2H), 7.42 (m, 2H), 7.37 (m, 2H), 3.17 (t, *J*=7.6 Hz, 2H), 1.98 (qt, *J*=7.3, 7.6 Hz, 2H), 1.13 (t, *J*=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.6, 138.6, 138.2, 136.8, 131.0, 129.6, 128.3, 127.6, 127.4, 126.4, 126.2, 125.5, 124.3, 48.5, 17.4, 14.0. IR (neat): 2966, 1697, 1443, 1161, 1123, 1026, 706, 610 cm^{-1}. MS (EI) *m/z* 324 (M^+, 33). HRMS calcd for $C_{24}H_{20}ONa$ ($[M+Na]^+$): 347.1406, found: 347.1407. Mp=118.5 °C.

*4.5.26. 1-(9-Triptycyl)butan-1-one (**4a**)*

White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.73 (m, 3H), 7.43 (m, 3H), 7.06 (m, 6H), 5.38 (s, 1H), 3.16 (m, 2H), 2.17 (tq, *J*=7.2, 7.2 Hz, 2H), 1.18 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.4, 146.3, 143.5, 125.4, 124.9, 123.8, 123.6, 66.4, 54.9, 46.8, 18.5, 14.3. IR (KBr): 2972, 2929, 1705, 1456, 1417, 1350, 1136, 1112, 1062, 966, 748, 633 cm^{-1}. MS (EI) *m/z* 324 (M^+, 40). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.80; H, 6.24. Mp=189.5 °C.

*4.5.27. 1-(2,3-Dimethoxy-9-triptycyl)butan-1-one (**4b**)*

White solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.57 (m, 4H), 7.40 (m, 2H), 7.03 (m, 3H), 6.98 (s, 1H), 5.26 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.14 (m, 2H), 2.14 (tq, *J*=7.2, 7.2 Hz, 2H), 1.15 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.8, 146.6, 145.9, 145.4, 143.9, 139.7, 136.1, 125.4, 124.8, 123.4, 123.3, 109.3, 107.9, 66.1, 56.2, 56.0, 54.5, 46.8, 18.6, 14.3. IR (KBr): 2958, 2933, 1703, 1499, 1456, 1286, 1221, 1196, 1150, 1113, 1057, 880, 750, 621 cm^{-1}. MS (EI) *m/z* 384 (M^+, 84). Anal. Calcd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.13; H, 6.23. Mp=153.5 °C.

*4.5.28. 1,2-Dihydrophthalazine derivative (**5a**)*

Light yellow solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.52 (dd, *J*=0.7, 7.6 Hz, 1H), 7.94 (d, *J*=7.6 Hz, 2H), 7.85 (dd, *J*=0.7,

7.6 Hz, 1H), 7.66 (dt, J=1.5, 7.3 Hz, 1H), 7.51 (dt, J=1.1, 7.6 Hz, 1H), 7.44 (dt, J=1.5, 7.2 Hz, 1H), 7.32 (m, 2H), 7.21 (m, 3H), 7.13 (t, J=7.6 Hz, 1H), 3.23 (dt, J=7.3, 17.1 Hz, 1H), 3.15 (dt, J=7.3, 17.1 Hz, 1H), 1.86 (ddq, J=7.3, 7.3, 7.3 Hz, 2H), 1.10 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.4, 160.7, 143.7, 141.9, 137.9, 135.9, 131.4, 131.3, 130.3, 129.3, 129.1, 129.0, 125.9, 125.4, 124.4, 123.7, 119.8, 116.2, 115.5, 90.3, 40.7, 18.3, 14.1. IR (KBr): 3960, 1740, 1682, 1607, 1582, 1479, 1313, 1140, 1074, 1012, 752 cm^{-1}. MS (EI) *m/z* 396 (M^+, 15). Anal. Calcd for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.08; N, 7.07. Found: C, 75.67; H, 5.16; N, 7.03. Mp=197.5 °C.

4.5.29. 1,2-Dihydrobenzo[g]phthalazine derivative (**5b**)

Light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.09 (s, 1H), 8.38 (s, 1H), 7.96 (m, 3H), 7.88 (d, J=7.6 Hz, 1H), 7.69 (ddd, J=8.2, 7.2, 1.2 Hz, 1H), 7.53 (m, 2H), 7.38 (d, J=7.2 Hz, 2H), 7.21 (dd, J=8.2, 6.8 Hz, 2H), 7.16 (d, J=6.8 Hz, 1H), 7.12 (d, J=7.6 Hz, 1H), 3.31 (dt, J=16.4, 7.6 Hz, 1H), 3.23 (dt, J=16.4, 7.2 Hz, 1H), 1.91 (dddq, J=7.6, 7.2, 7.2, 2.0 Hz, 2H), 1.13 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.5, 160.8, 143.9, 141.6, 138.3, 136.0, 134.0, 132.8, 130.3, 129.4, 129.3, 129.0, 128.0, 127.9, 127.3, 126.9, 124.9, 124.4, 123.4, 117.1, 115.6, 114.8, 90.5, 40.8, 18.3, 14.1. IR (KBr): 2961, 1747, 1686, 1481, 1362, 1312, 1240, 1202, 1053, 887 cm^{-1}. MS (EI) *m/z* 446 (M^+, 33). Anal. Calcd for $C_{29}H_{22}N_2O_3$: C, 78.01; H, 4.97; N, 6.27. Found: C, 78.08; H, 5.03; N, 6.29. Mp=239.5 °C.

4.5.30. 1,2-Dihydrobenzo[g]phthalazine derivative (**5c**)

Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.12 (s, 1H), 8.58 (s, 1H), 8.38 (s, 1H), 8.26 (s, 1H), 7.96–7.83 (m, 4H), 7.60 (ddd, J=8.0, 6.8, 1.2 Hz, 1H), 7.55 (ddd, J=8.8, 6.8, 2.0 Hz, 1H), 7.52 (ddd, J=8.4, 6.8, 1.6 Hz, 1H), 7.43 (m, 3H), 7.18 (m, 2H), 7.10 (m, 1H), 3.39 (dt, J=16.4, 7.6 Hz, 1H), 3.30 (dt, J=16.4, 7.6 Hz, 1H), 1.96 (ddq, J=7.6, 7.6, 7.2 Hz, 2H), 1.18 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.7, 161.5, 141.9, 139.4, 138.2, 137.1, 133.9, 133.0, 132.9, 129.8, 129.5, 129.4, 129.3, 129.2, 129.0, 129.0, 128.1, 127.9, 127.4, 127.3, 126.8, 125.7, 125.0, 124.5, 117.2, 115.1, 112.5, 90.9, 40.8, 18.4, 14.2. IR (KBr): 2967, 1734, 1672, 1628, 1558, 1063, 934, 546, 467 cm^{-1}. Anal. Calcd for $C_{33}H_{24}N_2O_3$: C, 79.82; H, 4.87; N, 5.64. Found: C, 79.53; H, 4.93; N, 5.58. Mp=236.5 °C.

4.5.31. 1,2-Dihydrobenzo[g]phthalazine derivative (**5d**)

Orange solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.26 (s, 1H), 7.99 (d, J=8.0 Hz, 1H), 7.70–7.47 (m, 8H), 7.33–7.17 (m, 4H), 3.99 (s, 3H), 3.14 (dt, J=16.0, 7.6 Hz, 1H), 3.00 (dt, J=16.0, 7.8 Hz, 1H), 1.82 (ddq, J=7.8, 7.6, 7.2 Hz, 2H), 1.03 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.3, 162.0, 152.6, 141.6, 140.0, 133.5, 133.5, 133.2, 129.4, 129.3, 128.7, 128.5, 128.1, 127.6, 127.5, 127.4, 127.4, 126.7, 126.5, 123.6, 120.7, 117.9, 117.2, 91.3, 56.5, 40.7, 18.2, 14.1. IR (KBr): 2945, 1869, 1684, 1636, 1522, 1489, 1364, 1053, 756, 519 cm^{-1}. Anal. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88. Found: C, 75.88; H, 5.10; N, 5.86. Mp=241.5 °C.

4.6. X-ray crystallographic analysis

4.6.1. X-ray crystallographic analysis of **5b**

Single crystals of **5b** suitable for X-ray diffraction study were obtained by recrystallization from hexane/ether/CH_2Cl_2 at rt. X-ray data were collected on a Rigaku Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ 0.71070 Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using the CrystalStructure crystallographic software package.[24,25]

4.6.2. Crystal data of 1,2-dihydrobenzo[g]phthalazine derivative (**5b**)

$C_{29}H_{22}N_2O_3$, M_w=446.50, colorless prism, 0.40×0.30×0.10 mm, monoclinic, space group $P2_1/n$ (no. 14), a=11.824(5) Å, b=9.473(4) Å, c=19.655(9) Å, β=94.7817(15)°, V=2193.8(16) Å^3, T=173 K, Z=4, μ(Mo Kα)=0.881 cm^{-1}, 27,676 reflections measured, 4874 unique (R_{int}=0.043). The final $R1$ and $wR2$ were 0.0371 ($I>2.00\sigma(I)$) and 0.0810 (for all data), respectively. Crystallographic data (excluding structure factors) for the structure of **5b** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 654091. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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References and notes

1. For reviews, see: (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, NY, 1967; (b) Biehl, E. R.; Khanapure, S. P. *Acc. Chem. Res.* **1989**, *22*, 275–281; (c) Kessar, S. V. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, NY, 1991; Vol. 4, pp 483–515; (d) Buchward, S. L.; Broene, R. D. *Comprehensive Organometallic Chemistry II*; Able, E. W., Stone, F. G. A., Willkinson, G., Eds.; Pergamon: Oxford, UK, 1995; Vol. 12, pp 771–784; (e) Pellissier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701–730; (f) Wenk, H. H.; Winkler, M.; Sander, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 502–528.
2. For recent examples, see: (a) Schuster, I. I.; Craciun, L.; Ho, D. M.; Pascal, R. A., Jr. *Tetrahedron* **2002**, *58*, 8875–8882; (b) Duong, H. M.; Bendikov, M.; Steiger, D.; Zhang, Q.; Sonmez, G.; Yamada, J.; Wudl, F. *Org. Lett.* **2003**, *5*, 4433–4436; (c) Lu, J.; Ho, D. M.; Vogelaar, N. J.; Kraml, C. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2004**, *126*, 11168–11169; (d) Ikadai, J.; Yoshida, H.; Ohshita, J.; Kunai, A. *Chem. Lett.* **2005**, *34*, 56–57; (e) Hayes, M. E.; Shinokubo, H.; Danheiser, R. L. *Org. Lett.* **2005**, *7*, 3917–3920; (f) Dockendorff, C.; Sahli, S.; Olsen, M.; Milhau, L.; Lautens, M. *J. Am. Chem. Soc.* **2005**, *127*, 15028–15029; (g) Shou, W.-G.; Yang, Y.-Y.; Wang, Y.-G. *J. Org. Chem.* **2006**, *71*, 9241–9243.
3. Logullo, F. M.; Seitz, A. H.; Friedman, L. *Org. Synth.* **1973**, *Coll. Vol. V*, 54–59.

4. Asao, N.; Sato, K. *Org. Lett.* **2006**, *8*, 5361–5363.
5. For highlights and reviews on the Au-catalyzed reactions, see: (a) Dyker, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4237–4239; (b) Hashmi, A. S. K. *Gold Bull.* **2003**, *36*, 3–9; (c) Hashmi, A. S. K. *Gold Bull.* **2004**, *37*, 51–65; (d) Arcadi, A.; Di Giuseppe, S. *Curr. Org. Chem.* **2004**, *8*, 795–812; (e) Hoffmann-Röder, A.; Krause, N. *Org. Biomol. Chem.* **2005**, *3*, 387–391; (f) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6990–6993; (g) Ma, S.; Yu, S.; Gu, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 200–203; (h) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271–2296; (i) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936; (j) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333–346; (k) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395–403.
6. (a) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650–12651; (b) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921–10925; (c) Asao, N.; Sato, K.; Menggenbateer; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 3682–3685; (d) Sato, K.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 8977–8981; (e) Asao, N. *Synlett* **2006**, 1645–1656.
7. Other examples of benzannulation with gold catalyst, see: (a) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11553–11554; (b) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *Org. Lett.* **2001**, *3*, 3769–3771; (c) Dankwardt, J. W. *Tetrahedron Lett.* **2001**, *42*, 5809–5812; (d) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *Catal. Today* **2002**, *72*, 19–27; (e) Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556–4575; (f) Hashmi, A. S. K.; Rudolph, M.; Weyrauch, J. P.; Wölfle, M.; Frey, W.; Bats, J. W. *Angew. Chem., Int. Ed.* **2005**, *44*, 2798–2801; (g) Dyker, G.; Hildebrandt, D. *J. Org. Chem.* **2005**, *70*, 6093–6096; (h) Shibata, T.; Fujiwara, R.; Takano, D. *Synlett* **2005**, 2062–2066; (i) Shibata, T.; Ueno, Y.; Kanda, K. *Synlett* **2006**, 411–414; (j) Zhao, J.; Hughes, C. O.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 7436–7437; (k) Lian, J.-J.; Lin, C.-C.; Chang, H.-K.; Chen, P.-C.; Liu, R.-S. *J. Am. Chem. Soc.* **2006**, *128*, 9661–9667; (l) Hildebrandt, D.; Dyker, G. *J. Org. Chem.* **2006**, *71*, 6728–6733; (m) Lian, J.-J.; Liu, R.-S. *Chem. Commun.* **2007**, 1337–1339; (n) Oh, C. H.; Kim, A.; Park, W.; Park, D. I.; Kim, N. *Synlett* **2006**, 2781–2784.
8. Benzo[*c*]pyrylium salts are known to play a diene part in the Diels–Alder reaction with ethyl vinyl ether, see: Kuznetsov, E.; Shcherbakova, I. V.; Balaban, A. T. *Adv. Heterocycl. Chem.* **1990**, *50*, 157–254.
9. For a review, see: Nogradi, M. *Science of Synthesis: Houben–Weyl Methods of Molecular Transformations*; Georg Thieme: Stuttgart, Germany, 2003; Vol. 14, pp 201–273.
10. Tovar, J. D.; Swager, T. M. *J. Org. Chem.* **1999**, *64*, 6499–6504.
11. For examples of reactions with pyrylium intermediates, see: (a) Barluenga, J.; Vázquez-Villa, H.; Ballesteros, A.; González, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 9028–9029; (b) Barluenga, J.; Vázquez-Villa, H.; Ballesteros, A.; González, J. M. *Org. Lett.* **2003**, *5*, 4121–4123; (c) Zhu, J.; Germain, A. R.; Porco, J. A., Jr. *Angew. Chem., Int. Ed.* **2004**, *43*, 1239–1243; (d) Kusama, H.; Funami, H.; Takaya, J.; Iwasawa, N. *Org. Lett.* **2004**, *6*, 605–608; (e) Yue, D.; Ca, N. D.; Larock, R. C. *Org. Lett.* **2004**, *6*, 1581–1584; (f) Sato, K.; Yudha, S. S.; Asao, N.; Yamamoto, Y. *Synthesis* **2004**, 1409–1412; (g) Barluenga, J.; Vázquez-Villa, H.; Ballesteros, A.; González, J. M. *Adv. Synth. Catal.* **2005**, *347*, 526–530; (h) Kusama, H.; Funami, H.; Shido, M.; Hara, Y.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2005**, *127*, 2709–2716; (i) Kim, N.; Kim, Y.; Park, W.; Sung, D.; Gupta, A. K.; Oh, C. H. *Org. Lett.* **2005**, *7*, 5289–5291; (j) Gupta, A. K.; Rhim, C. Y.; Oh, C. H.; Maneb, R. S.; Han, S.-H. *Green Chem.* **2006**, *8*, 25–28; (k) Yue, D.; Cá, N. D.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 3381–3388.
12. Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649–2653.
13. (a) Norvez, S.; Barzoukas, M. *Chem. Phys. Lett.* **1990**, *165*, 41–44; (b) Korth, O.; Wiehe, A.; Kurreck, H.; Röder, B. *Chem. Phys.* **1999**, *246*, 363–372; (c) Beyeler, A.; Belser, P. *Coord. Chem. Rev.* **2002**, *230*, 28–38; (d) Perepichka, D. F.; Bendikov, M.; Meng, H.; Wudl, F. *J. Am. Chem. Soc.* **2003**, *125*, 10190–10191; (e) Satrijo, A.; Swager, T. M. *Macromolecules* **2005**, *38*, 4054–4057.
14. (a) Marks, V.; Nahmany, M.; Gottlieb, H. E.; Biali, S. E. *J. Org. Chem.* **2002**, *67*, 7898–7901; (b) Lu, J.; Zhang, J.; Shen, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 8035–8041; (c) Iiba, E.; Hirai, K.; Tomioka, H.; Yoshioka, Y. *J. Am. Chem. Soc.* **2002**, *124*, 14308–14309; (d) Spyroudis, S.; Xanthopoulou, N. *J. Org. Chem.* **2002**, *67*, 4612–4614; (e) Spyroudis, S.; Xanthopoulou, N. *Tetrahedron Lett.* **2003**, *44*, 3767–3770; (f) Zhu, X. Z.; Chen, C. F. *J. Org. Chem.* **2005**, *70*, 917–924.
15. (a) Perchellet, E. M.; Magill, M. J.; Huang, X.; Brantis, C. E.; Hua, D. H.; Perchellet, J.-P. *Anti-Cancer Drugs* **1999**, *10*, 749–766; (b) Yang, W.; Perchellet, E. M.; Tamura, M.; Hua, D. H.; Perchellet, J. P. *Cancer Lett.* **2002**, *188*, 73–83; (c) Hua, D. H.; Tamura, M.; Huang, X.; Stephany, H. A.; Helfrich, B. A.; Perchellet, E. M.; Sperfslage, B. J.; Perchellet, J.-P.; Jiang, S.; Kyle, D. E.; Chiang, P. K. *J. Org. Chem.* **2002**, *67*, 2907–2912; (d) Perchellet, E. M.; Wang, Y.; Weber, R. L.; Lou, K.; Hua, D. H.; Perchellet, J.-P. H. *Anti-Cancer Drugs* **2004**, *15*, 929–946; (e) Wang, Y.; Perchellet, E. M.; Ward, M. M.; Lou, K.; Zhao, H.; Battina, S. K.; Wiredu, B.; Hua, D. H.; Perchellet, J.-P. H. *Int. J. Oncol.* **2006**, *28*, 161–172.
16. (a) Marc Veen, E.; Postma, P. M.; Jonkman, H. T.; Spek, A. L.; Feringa, B. L. *Chem. Commun.* **1999**, 1709–1710; (b) Yang, J.-S.; Liu, C.-P.; Lee, G.-H. *Tetrahedron Lett.* **2000**, *41*, 7911–7915; (c) Yang, J.-S.; Lee, C.-C.; Yau, S.-L.; Chang, C.-C.; Lee, C.-C.; Leu, J.-M. *J. Org. Chem.* **2000**, *65*, 871–877; (d) Yang, J.-S.; Liu, C.-P.; Lin, B. C.; Tu, C. W.; Lee, G. H. *J. Org. Chem.* **2002**, *67*, 7343–7354; (e) Zhu, X. Z.; Chen, C. F. *J. Am. Chem. Soc.* **2005**, *127*, 13158–13159; (f) Zong, Q. S.; Chen, C. F. *Org. Lett.* **2006**, *8*, 211–214; (g) Han, T.; Chen, C. F. *Org. Lett.* **2006**, *8*, 1069–1072; (h) Zong, Q. S.; Zhang, C.; Chen, C. F. *Org. Lett.* **2006**, *8*, 1859–1862; (i) Peng, X.-X.; Lu, H.-Y.; Han, T.; Chen, C.-F. *Org. Lett.* **2007**, *9*, 895–898; (j) Han, T.; Zong, Q. S.; Chen, C.-F. *J. Org. Chem.* **2007**, *72*, 3108–3111; (k) Zhang, C.; Chen, C.-F. *J. Org. Chem.* **2007**, *72*, 3880–3888.
17. (a) Norvez, S. *J. Org. Chem.* **1993**, *58*, 2414–2418; (b) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321–5322; (c) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873; (d) Yang, J.-S.; Lin, C.-S.; Hwang, C.-Y. *Org. Lett.* **2001**, *3*, 889–892; (e) Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 3826–3827; (f) Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 9670–9671; (g) Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 14113–14119.
18. (a) Iwamura, H.; Mislow, K. *Acc. Chem. Res.* **1988**, *21*, 175–182; (b) Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; Garcia, A.; Lang, F.; Kim, M. H.; Jette, M. P. *J. Am. Chem. Soc.* **1994**, *116*, 3657–3658; (c) Kelly, T. R.; Silva, R. A.; Silva, H. D.; Jasmin, S.; Zhao, Y. *J. Am. Chem. Soc.* **2000**, *122*, 6935–6949; (d) Godinez, C. E.; Zepeda, G.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 4701–4707; (e) Annunziata, R.; Benaglia, M.; Cinquini, M.; Raimondi, L.; Cozzi, F. *J. Phys. Org. Chem.* **2004**, *17*, 749–751.
19. (a) Stiles, M.; Miller, R. G. *J. Am. Chem. Soc.* **1960**, *82*, 3802; (b) Friedman, L.; Logullo, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 1549.
20. Burckhardt, U.; Hintermann, L.; Schnyder, A.; Togni, A. *Organometallics* **1995**, *14*, 5415–5425.
21. (a) Franklin, E. C. *Chem. Rev.* **1935**, *16*, 305–361; (b) Bergstrom, F. W. *Chem. Rev.* **1944**, *35*, 77–277; (c) Lichtenthaler, F. W. *Acc. Chem. Res.* **2002**, *35*, 728–737; (d) Litvinov, V. P. *Russ. Chem. Rev.* **2003**, *72*, 69–85; (e) Xu, Y.; Guo, Q.-X. *Heterocycles* **2004**, *63*, 903–974.
22. (a) Padwa, A.; Waterson, A. G. *Curr. Org. Chem.* **2000**, *4*, 175–203; (b) Orru, R. V. A.; de Greef, M. *Synthesis* **2003**, 1471–1499; (c) Kirsch, G.; Hesse, S.; Comel, A. *Curr. Org. Chem.* **2004**, *1*, 47–63.
23. (a) Yamashita, Y.; Hayashi, T.; Masumura, M. *Chem. Lett.* **1980**, 1133–1136; (b) Compagnini, A.; Lo Vullo, A.; Chiacchio, U.; Corsaro, A.; Purrello, G. *J. Heterocycl. Chem.* **1982**, *19*, 641–643; (c) Atanes, N.; Guitian, E.; Saa, C.; Castedo, L.; Saa, J. M. *Tetrahedron Lett.* **1987**, *28*, 817–820; (d) Al-Rawi, J. M. A.; Khayat, M. A. R. *Magn. Reson. Chem.* **1989**, *27*, 112–116; (e) Agawa, C.; Otsuka, K.; Minoura, M.; Mazaki, Y.; Yamamoto, G. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2273–2281.
24. CrystalStructure 3.7.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC; 9009 New Trails Dr.: The Woodlands, TX 77381, USA, 2000–2005.
25. Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, UK, 1996.