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The First Formation of (1*Z*)-1-Alkylidene-1*H*-isobenzofuranium Amides and 1*H*-Inden-1-ones: Acid-Promoted 5-*exo* Cyclization and Hydration/Aldol Condensation Reactions of *o*-Ethynylbenzophenones

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(1Z)-1-(2,2-Dimethylpropylidene)-1*H*-isobenzofuranium bis(trifluoromethylsulfonyl)amides were synthesized through 5-*exo* cyclization reactions between sterically encumbered *o*-alkynylbenzophenones and bis(trifluoromethylsulfonyl)imide (Tf_2NH). It was confirmed that the five-membered-ring isobenzofuranium amide isomerized to give the corresponding benzopyrylium amide, the six-membered-ring framework compound, in quantitative yield. Treatment of less encumbered *o*-alkynylbenzophenones with Tf_2NH at ambient temperature resulted in acid-promoted hydration and sequential intramolecular aldol condensation reactions to afford 3-aryl-1*H*-inden-1-one derivatives in good yields. The proposed reaction mechanism was strongly supported by the reaction behaviour of 4-chloro- and 5-methoxy-2-ethynylbenzophenone derivatives as substrates with Tf_2NH, leading to the formation of the corresponding 3-aryl-1*H*-inden-1-ones.

Introduction

Electrophilic cyclization reactions of *o*-alkynylphenyl carbonyl compounds have attracted much attention as powerful tools for the syntheses of oxygen-containing heterocycles.[1] Lewis-acid-induced electrophilic cyclization of *o*-alkynyl-substituted benzene derivatives such as benzaldehyde,[2] acetophenone,[3] benzamide,[4] benzoic acid,[5] methyl benzoate,[6] and benzophenone[7] has been investigated,[8] and it was demonstrated that these synthetic methodologies are one of the most useful methods affording access to heterocycles. Swager's group demonstrated that 6-*endo-dig* cyclization of *o*-alkynylbenzophenones with the aid of electrophiles such as TfOH and HBF_4 is an effective strategy for formation of benzo[*c*]pyrylium salts.[7a] In that report, however, it was also revealed that the reaction could not work well in the case of a substrate bearing an *n*-butyl group at the alkynyl terminus, with no evidence of formation of the corresponding benzo[*c*]pyrylium salt being obtained.[7a] Certain challenges, such as protonation-induced electrophilic cyclization reactions of ethynylbenzophenones, therefore still remain. Here we would like to describe the formation of new (1*Z*)-1-alkylidene-1*H*-isobenzofuranium salts through Brønsted-acid-promoted 5-*exo* cyclization reactions, as well as the unprecedented formation of 1*H*-inden-1-ones through hydration/aldol condensation reactions of *o*-ethynylbenzophenones.

Results and Discussion

The synthetic route to ethynylbenzophenone substrates **4a**–**d** is shown in Scheme 1. Treatment of commercially available 2-iodobenzoic acid with thionyl chloride at 70 °C for 5 h, followed by Friedel–Crafts reactions with 1,3,5-triisopropylbenzene, mesitylene, or benzene in the presence of aluminum chloride, afforded 2-iodo-2′,4′,6′-triisopropylbenzophenone (**1**), 2-iodo-2′,4′,6′-trimethylbenzophenone (**2**) or 2-iodobenzophenone (**3**) in yields of 43%, 64%, or 78%, respectively.

Sonogashira cross-coupling between **1** and *p*-tolylacetylene in the presence of $[PdCl_2(PPh_3)_2]$, copper iodide, and diisopropylamine gave ethynylbenzophenone **4a** in 63% yield. Similarly, cross-coupling between **1**–**3** and 3,3-dimethylbut-1-yne afforded **4b**–**d** in quantitative, 68%, or 51% yields, respectively.

We focused on protonation/intramolecular cyclization reactions between ethynylbenzophenones **4a**–**d** and bis(trifluoromethylsulfonyl)imide (Tf_2NH) as a Brønsted acid, because Tf_2NH is known to work as a better protonation reagent toward alkynyl species.[9] Intramolecular cyclization between **4a** and Tf_2NH in dichloromethane at room temperature afforded the corresponding benzo[*c*]pyrylium bis(trifluoromethylsulfonyl)amide **5a** as the sole product, in 58% isolated yield (Table 1, Entry 1). The solid-state structure of **5a** was determined by X-ray crystallographic analysis [Figure 1(a)].[10] The results are similar to other reported

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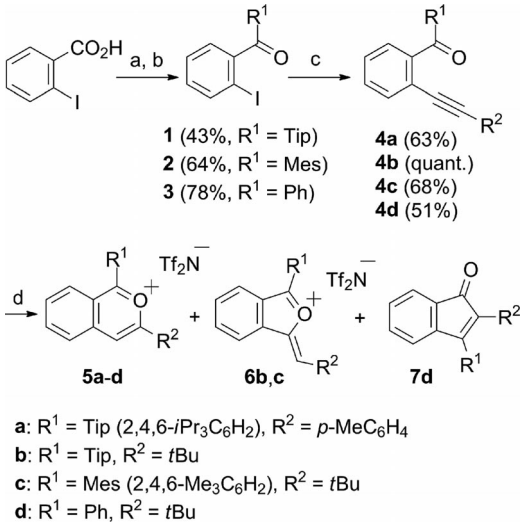


Scheme 1. Reactions between **4a**–**d** and Tf_2NH. Reagents and conditions: (a) $SOCl_2$, 70 °C, 5 h; (b) 1,3,5-(iPr)$_3C_6H_3$ (for **1**), 1,3,5-$Me_3C_6H_3$ (for **2**), C_6H_6 (for **3**), $AlCl_3$, reflux; (c) *p*-tolylacetylene for **4a**, 3,3-dimethylbut-1-yne for **4b**–**d**, $PdCl_2(PPh_3)_2$, CuI, iPr_2NH, THF, reflux; (d) Tf_2NH (1.1 equiv.), CH_2Cl_2.

findings,[7] indicating that protonation-induced 6-*endo* cyclization of **4a** occurs to form the 2,6-diarylbenzo[*c*]pyrylium derivative.

Table 1. Reactions between **4a**–**c** and Tf_2NH in dichloromethane.

Entry	Substrate	Conditions	Products	Total yield **5+6**	Ratio **5/6**
1	**4a**	r.t., 1.5 h	**5a**	88%	–
2	**4b**	r.t., 2.0 h	**5b+6b**	77%	31:69
3	**4b**	0 °C, 2.0 h	**5b+6b**	66%	38:62
4	**4b**	reflux, 2.0 h	**5b+6b**	73%	33:67
5	**4c**	r.t., 2.0 h	**5c+6c**	91%	29:71

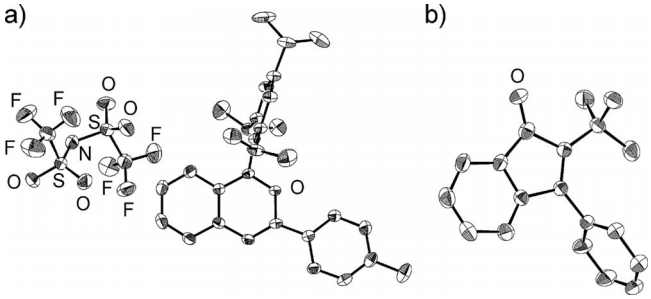


Figure 1. Molecular structures of a) **5a**, and b) **7d** with thermal ellipsoid plots (30% probability). All hydrogen atoms are omitted for clarity.

In contrast, treatment of **4b**, featuring a *tert*-butyl group on the ethynyl unit, with Tf_2NH in dichloromethane at room temperature for 2 h gave not only the expected benzo[*c*]pyrylium amide **5b**, but also the unexpected product (1*Z*)-1-(2,2-dimethylpropylidene)-1*H*-isobenzofuranium bis(trifluoromethylsulfonyl)amide **6b**, in 77% total yield and in the ratio of 31:69 (Entry 2).[11] To the best of our knowledge, this result represents the first formation of a (1*Z*)-1-alkylideneisobenzofuranium framework. The ratio of the 6-*endo* to 5-*exo*-cyclized products in this reaction did not dramatically change when the reaction was carried out at reflux or 0 °C (Entries 3 and 4). Similarly, the reaction between **4c**, bearing a mesityl group, and Tf_2NH was carried out under the same conditions as for **4b** to give benzo[*c*]pyrylium amide **5c** and isobenzofuranium amide **6c** in 91% total yield and in a ratio of 29:71 (Entry 5).

The ^1H NMR spectra of **5b** and **6b** in CD_3CN showed characteristic singlet signals at δ = 8.43 and 7.80 ppm, respectively, attributable in each case to a hydrogen atom derived from Tf_2NH, as judged by integration of the spectrum. The former signal is similar to those of protons at the 4-position in benzo[*c*]pyrylium derivatives (e.g., 8.91 ppm for **5a**, 8.41 ppm for **5c**), and the latter can be attributed to a proton of the *exo*-alkene moiety of **6b**. Moreover, by means of NOESY NMR experiment, cross peaks between the protons as shown in Figure 2 were visible. These indicate that **6b** has the *Z* configuration in the *exo*-alkene unit. In its ^{13}C NMR spectrum, **6b** exhibited characteristic peaks at δ = 196.8 and 149.8 ppm, attributable to C_C and C_D (Figure 2), respectively. These chemical shifts are not within the range of C_A and C_B of benzo[*c*]-pyrylium derivatives [e.g.; 185.5 (C_A) and 164.4 (C_B) ppm for **5a**, 186.7 (C_A) and 175.6 (C_B) ppm for **5b**, 185.2 (C_A) and 175.7 (C_B) ppm for **5c**].

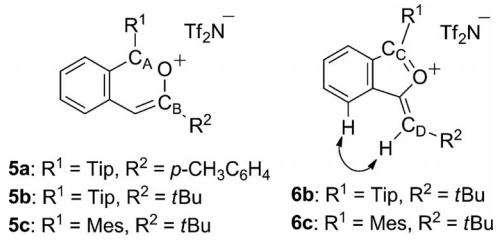
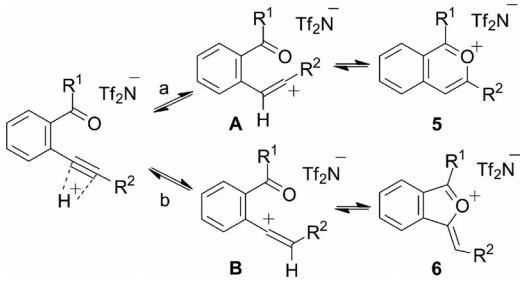


Figure 2. Structures of compounds **5a**–**c** and **6b**–**c**. The arrow shows the observed enhancement in the NOESY spectrum.

The reaction mechanism is considered to be as follows (Scheme 2). Protonation of the alkyne moiety of ethynylbenzophenone **4** might give carbocation intermediates **A** and **B**, followed by nucleophilic attack by the carbonyl oxygen atom at the cationic carbon in a 6-*endo* fashion (path a in Scheme 2) to afford 2,6-disubstituted benzo[*c*]pyrylium system **5**.[7] In contrast, in the case of nucleophilic attack by the carbonyl oxygen at the proton-activated alkyne moiety in a 5-*exo* mode (path b in Scheme 2), the cyclization reaction would result in the formation of the new (1*Z*)-1-alkylidene-1*H*-isobenzofuranium amide **6**. In cases in which an alkyl group was present at the ethynyl terminus, as in compounds **4b** or **4c**, more stable cations of type **B** might undergo a 5-*exo* cyclization process to form furanium salts **6b** or **6c** as the major products. The stabilities of the intermediates are thus an important factor determining the reaction outcomes in the presence of a Brønsted acid.



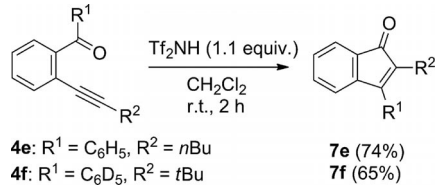
Scheme 2. Plausible mechanism for the formation of 6-*endo*- and 5-*exo*-cyclized products.

We next focused on the properties of (1*Z*)-1-alkylidene-1*H*-isobenzofuranium amide **6b**. After an acetic acid solution of a mixture of **5b** and **6b** had been stirred at room temperature for 1 h, the ^{1}H NMR spectrum of the reaction mixture showed exclusive formation of **5b**, indicating that thermal isomerization from **6b** to **5b**, a thermally stable structural isomer, readily occurs under the reaction conditions. We consider that the cyclization reactions of **4b**–**c** with Tf_2NH can be said to be under kinetic control and that **5b**, **5c**, **6b** and **6c** are all likely to equilibrate thermally under these reaction conditions.

We performed theoretical calculations on model molecules **5b′** and **6b′**, in which the counter anions in **5b** and **6b** are omitted, in order to understand the electronic structures of **5b** and **6b**.[12,13] We found that **5b′** was thermally more stable than **6b′** by 10.8 kcal mol^{-1}, which is consistent with the experimentally observed relative stabilities of **5b** and **6b**.

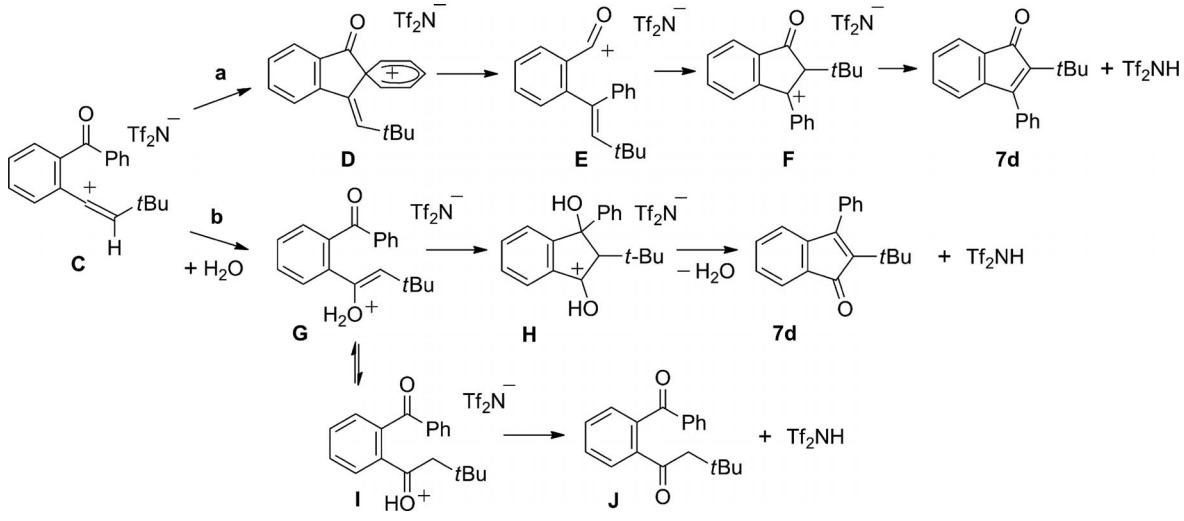
On the other hand, the reaction between **4d**, containing a phenyl group, and Tf_2NH in dichloromethane at room temperature unprecedentedly afforded 2-*tert*-butyl-3-phenyl-1*H*-inden-1-one (**7d**, Scheme 1) together with a small amount of 6-*endo* cyclization product **5d**. The **7d**/**5d** ratio was estimated from the ^{1}H NMR spectrum to be 91:9, and compound **7d** was isolated in 78% yield. The molecular structure of **7d** was fully characterized by spectroscopic and X-ray crystallographic analysis [Figure 1(b)].[10] The result suggests two reaction pathways as follows (Scheme 3). (1) One reaction proceeds by formal addition of a carbonyl–phenyl bond to an alkynyl moiety and is a unique aryl migration reaction (path a in Scheme 3), although it has been reported that transition-metal-catalyzed cyclizations of *o*-alkynyl-substituted benzene derivatives proceeded similarly, with methoxy, benzyl, silyl, and sulfonyl migrations.[14] (2) The other reaction consists of stereoselective acid-catalyzed hydration of the alkyne unit in **4d**, followed by intramolecular aldol condensation of the resulting 1,4-diketone equivalent **G** to give 1*H*-inden-1-one **7d** (path b in Scheme 3).

We next synthesized compounds **4e** (Scheme 4), possessing an *n*-butyl group at the ethynyl terminus, and **4f**, containing a perdeuterated phenyl group. It was confirmed that the reactions of **4e** and **4f** with Tf_2NH also proceeded smoothly to afford the corresponding 1*H*-inden-1-ones **7e** and **7f** in 74% and 65% yields, respectively. In order to find out whether the reaction occurs in an intramolecular or intermolecular fashion, we performed crossover experiment. On treatment of a 1:1 mixture of **4e** and **4f** with Tf_2NH under the standard conditions, normal products **7e** and **7f** were obtained and no crossover products were detected by GC-MS or NMR spectroscopy (Scheme 5). The reaction should thus proceed in an intramolecular manner.

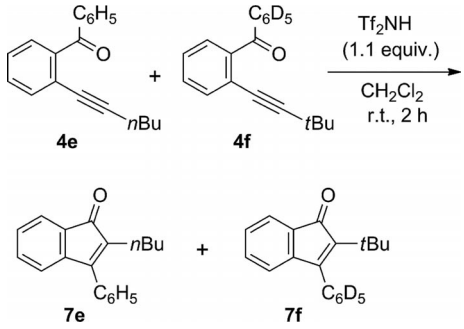


Scheme 4. Syntheses of compounds **7e** and **7f**.

We next examined the reaction behavior of 4-chloro-2-ethynylbenzophenone (**4g**, Scheme 6) and 2-ethynyl-5-methoxybenzophenone (**4h**, Scheme 7, below) in the presence of a Brønsted acid to ascertain the reaction mechanism. Treat-

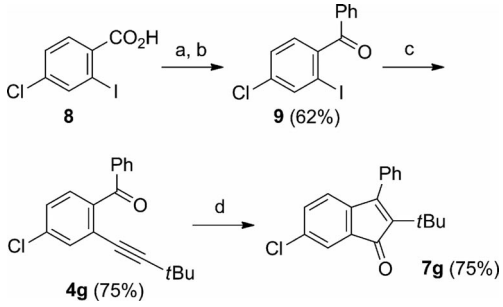


Scheme 3. Plausible mechanism for the formation of the 1*H*-inden-1-one derivative.



Scheme 5. Crossover reaction with compounds **4e** and **4f**.

ment of chlorobenzoic acid **8** with $SOCl_2$ and a subsequent Friedel–Crafts reaction gave 4-chloro-2-iodobenzophenone (**9**) in moderate yield. Compound **9** was treated with 3,3-dimethylbut-1-yne in the presence of a palladium catalyst to afford **4g** in 75% yield. Treatment of **4g** with 1.1 equiv. of Tf_2NH at room temperature afforded 2-*tert*-butyl-3-phenylindenone (**7g**), with a chlorine atom at the 6-position, in 75% yield (Scheme 6).



Scheme 6. Reaction between **4g** and Tf_2NH. Reagents and conditions: (a) $SOCl_2$, 80 °C, 2 h; (b) C_6H_6, $AlCl_3$, reflux, 2 h; (c) 3,3-dimethylbut-1-yne, $PdCl_2(PPh_3)_2$, CuI, iPr_2NH, THF, reflux, 3 h; (d) Tf_2NH (1.1 equiv.), CH_2Cl_2, room temperature, 2 h.

Moreover, 2-bromo-5-methoxybenzoic acid (**10**, Scheme 7) was converted into ethynylbenzophenone **4h** by way of bromobenzophenone **11** and iodobenzophenone **12**. The reaction between **4h** and Tf_2NH gave 2-*tert*-butyl-5-methoxy-3-phenylinden-1-one (**7h**) in 42% yield together with the corresponding hydration product – 1,4-diketone **7′h** – in 49% yield. Fortunately, single crystals of **7h** were obtained and the molecular structure was confirmed by X-ray crystallographic analysis (Figure 3),[10] which shows the methoxy group of **7h** located at the 5-position.

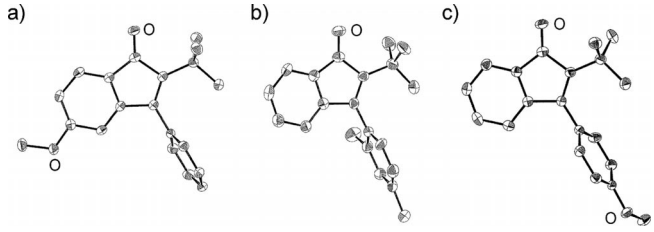
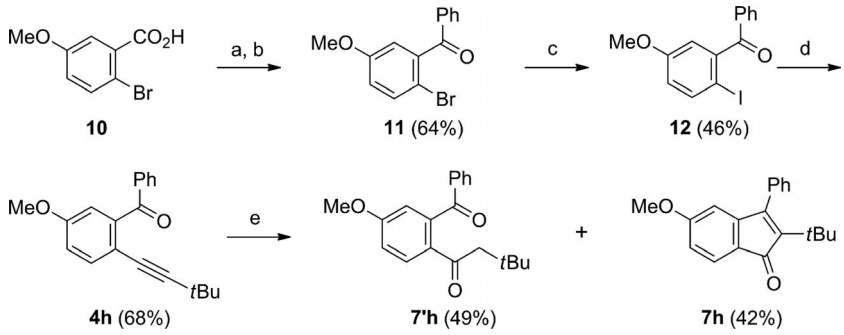


Figure 3. Molecular structures of a) **7h**, b) **7i**, and c) **7k** with thermal ellipsoid plots (50% probability). All hydrogen atoms are omitted for clarity.

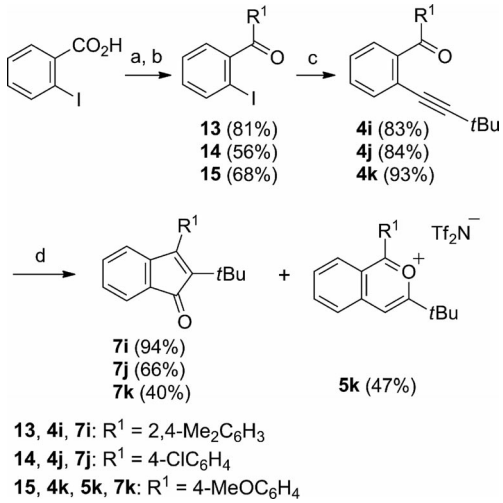
These results thus clearly reveal that the formation of 6-chloro- and 5-methoxy-1*H*-inden-1-ones **7g** and **7h** can be explained in terms of acid-promoted hydration and subsequent intramolecular aldol condensation reactions of **4g** and **4h**, respectively (path b in Scheme 3). Furthermore, the reaction mechanism was also supported by previous research into protonation of phenylacetylene to give vinyl cationic species[15] and into selective Tf_2NH-catalyzed hydration of internal alkynes.[16] Numerous reports on the acid-catalyzed hydration of internal alkynes have appeared; most of them require severe reaction conditions, such as formic acid at 100 °C for 60 h,[17a] PTSA/EtOH at 78 °C for 60 h,[17b] Tf_2NH at 100 °C for 40 h,[16] or HCl/EtOH at reflux for 8 h.[17c] In contrast, we found that this transformation of *o*-ethynylbenzophenones into 1*H*-inden-1-ones could be smoothly carried out under mild conditions.

Next, several substituted benzophenone derivatives bearing electron-donating or -withdrawing groups were tested; the results are shown in Scheme 8. Introduction of dimethyl, chloro, and methoxyphenyl groups was also achieved through Friedel–Crafts reactions with *m*-xylene, chlorobenzene, and anisole, respectively, affording compounds **4i**–**k** in good yields (Scheme 8).

Reactions between **4i**–**k** and Tf_2NH were performed under standard conditions. In the cases of **4i** and **4i**, the ^1H and ^{13}C NMR spectra of the reaction mixtures showed the corresponding 1*H*-inden-1-ones **7i** and **7j** along with the starting materials. Chromatographic purification afforded



Scheme 7. Reaction between **4h** and Tf_2NH. Reagents and conditions: (a) $SOCl_2$, 80 °C, 2 h; (b) C_6H_6, $AlCl_3$, reflux, 1 h; (c) NaI, CuI, *N*,*N*′-dimethylethylenediamine, dioxane, in a sealed tube, 110 °C, 22 h; (d) 3,3-dimethylbut-1-yne, $PdCl_2(PPh_3)_2$, CuI, iPr_2NH, THF, reflux, 17 h; (e) Tf_2NH (1.1 equiv.), CH_2Cl_2, room temperature, 2 h.

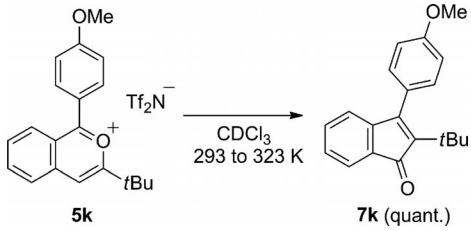


Scheme 8. Syntheses of compounds **7i**, **7j**, and **7k**. Reagents and conditions: (a) $SOCl_2$, 70–80 °C, 8–24 h; (b) *m*-xylene (for **13**), chlorobenzene (for **14**), anisole (for **15**), $AlCl_3$, 70–80 °C, 2–24 h; (c) 3,3-dimethylbut-1-yne, $PdCl_2(PPh_3)_2$, CuI, *i*Pr_2NH, THF, 70–80 °C, 4–17 h; (d) Tf_2NH (1.1 equiv.), CH_2Cl_2, room temperature, 2 h.

3-aryl-2-*tert*-butyl-1*H*-inden-1-ones **7i** and **7j** in 94% and 66% yields, respectively. In the case of **4k**, 1*H*-inden-1-one **7k** and 6-*endo* cyclization product **5k** were isolated in 40% and 47% yields, respectively (Scheme 8). The molecular structures of **7i** and **7k** were confirmed by X-ray crystallographic analysis (Figure 3).[10]

We had found that these substituents of **4i**–**k** were able to tolerate the formation of **7i**–**k**. It may therefore be assumed that the sterically hindered 2,4,6-triisopropylphenyl and trimethylphenyl groups at R^1 in **4b** and **4c** prevent the intramolecular aldol condensation from proceeding, whereas the less bulky groups C_6H_5, 2,4-$Me_2C_6H_3$, 4-ClC_6H_4, and 4-$CH_3OC_6H_4$ allow the intramolecular aldol condensation, leading to the formation of 1*H*-inden-1-ones **7d**–**k** in good yields.

After a $CDCl_3$ solution of benzo[*c*]pyrylium amide **5k** had been allowed to stand with exclusion of light, gradual formation of 1*H*-inden-1-one **7k** as a single product was detected by NMR spectroscopy; the half-life of **5k** (8.70 mol L^{-1} in a $CDCl_3$ solution) at 20, 30, 40, and 50 °C was estimated to be 7.89×10^4, 4.50×10^4, 2.85×10^4, and 2.05×10^4 s, respectively (Scheme 9). Plots of the logarithm of the concentration of **5k** against time (Figure 4) show linear decay of **5k** through >90% consumption in $CDCl_3$ solution at 20–50 °C, indicating that the transformation is first-order with respect to the concentration of the substrate, with observed rate constants $k = 8.78 \times 10^{-6}$, 1.54×10^{-5}, 2.43×10^{-5}, and 3.38×10^{-5} s^{-1} at 20, 30, 40, and 50 °C, respectively. The active parameters were estimated from the Eyring plot shown in Figure 4 to be $\Delta H^{\ddagger}$ = +8.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ = –51 cal mol^{-1} K^{-1}, and $\Delta G^{\ddagger}$ (293 K) = +24 kcal mol^{-1}. The estimated $\Delta G^{\ddagger}$ value is similar to those reported for acid-catalyzed hydration processes of arylacetylenes in the literature.[15a] The characteristic negative value of $\Delta S^{\ddagger}$ observed in the reaction of **5k** might be interpreted as follows: the rate-determining step should be the hydration of the alkyne moiety of **5k**, similarly to the case of hydration of arylacetylenes.[15] The exclusive conversion of **5k** into 1*H*-inden-1-one **7k**, in contrast to the robust natures of benzo[*c*]pyrylium amides **5b** and **5c**, is unprecedented and unique.



Scheme 9. Transformation of **5k** into **7k**.

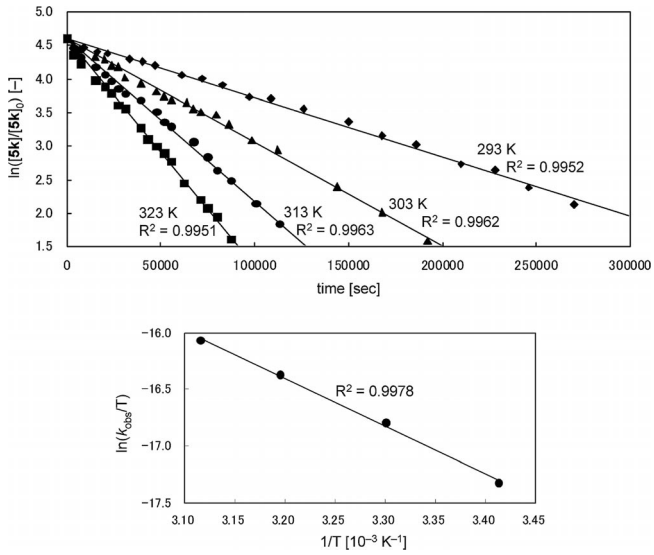
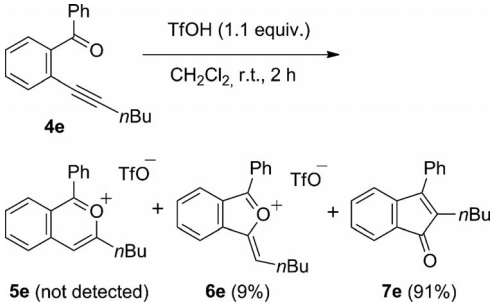


Figure 4. Top: First-order kinetic plot of the transformation of **5k** in $CDCl_3$ solution (8.70 mol L^{-1}) over a range from 293 to 323 K. The lines are least-squares fits to the data points over three half-lives. Bottom: Eyring plot of the transformation of **5k** over a range from 293 to 323 K.

In 1999, Swager and co-worker reported that the reaction between **4e** and TfOH resulted in no formation of the corresponding six-membered-ring pyrylium trifluoromethanesulfonate **5e**, but at least two compounds were detected, although characterization of these was not achieved.[7a] With reactivity of *o*-ethynylbenzophenones toward a Brønsted acid now established, a check on the reaction between **4e** and TfOH at room temperature was also made (Scheme 10). NMR spectra of the reaction mixture revealed the formation of the corresponding 5-*exo*-cyclized product **6e** and 1*H*-inden-1-one **7e** in a ratio of 9:91. On separation of the mixture, compound **7e** was isolated in 73% yield. We have thus confirmed that the reaction of an *o*-ethynylbenzophenone possessing an alkyl group at the ethynyl terminus afforded not the 6-*endo* cyclization product but the 5-*exo* cyclization product and the 1*H*-inden-1-one derivative.



Scheme 10. Reaction between **4e** and TfOH.

Conclusions

We have succeeded in the first syntheses of (1*Z*)-1-(2,2-dimethylpropylidene)-1*H*-isobenzofuranium bis(trifluoromethylsulfonyl)amides **6b**–**c** through protonation-induced 5-*exo* cyclization reactions between *o*-alkynylbenzophenones **4b**–**c** and Tf_2NH. In reactions between **4d**–**k** and Tf_2NH, however, stereospecific acid-promoted hydration of the alkyne units in **4d**–**k** and intramolecular aldol condensation gave 1*H*-inden-1-ones **7d**–**k** in good yields at room temperature. In particular, the results with substituted ethynylbenzophenones **4g** and **4h** as substrates provided strong evidence in support of the proposed reaction mechanism. The formation of 1*H*-inden-1-ones is thus noteworthy in terms not only of the unique acid-catalyzed hydration and subsequent intramolecular aldol condensation of *o*-ethynylbenzophenones, but also of the development of a new synthetic method for 2,3-disubstituted 1*H*-inden-1-one derivatives.

Experimental Section

General: All solvents were purified by standard methods. Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 Hz) spectra were measured in $CDCl_3$ or CD_3CN with a Varian Mercury 400 plus spectrometer and use either of $CHCl_3$ (δ_H = 7.26 ppm) and $CDCl_3$ (δ_C = 77.0 ppm) or of CHD_2CN (δ_H = 2.10 ppm) and CD_3CN (δ_C = 1.79 ppm) as internal standards for ^{1}H and ^{13}C NMR spectra, respectively. ^{19}F NMR (376 MHz) spectra were measured in $CDCl_3$ or CD_3CN with a Varian Mercury 400 plus spectrometer and use of $CFCl_3$ (δ_F = 0.00 ppm) as an external standard. EI and ESI-TOF mass spectroscopic data were obtained with a JEOL JMS-gcmateII and a JEOL JMS-T100CS spectrometer, respectively. Infrared spectra were obtained with a PerkinElmer Spectrum One spectrometer. Elemental analyses were performed with a Yanaco MT-5 CHN-corder. All melting points were determined with a Yanaco micro melting point apparatus or a Mettler Toledo MP90 melting point system and are uncorrected. All experiments were performed under argon unless otherwise noted.

Synthesis of 2-Iodo-2′,4′,6′-triisopropylbenzophenone (1): A mixture of 2-iodobenzoic acid (2.01 g, 8.06 mmol) and thionyl chloride (15 mL) was warmed at 70 °C for 5 h and then allowed to cool to room temperature. After removal of thionyl chloride, acetonitrile (20 mL), 1,3,5-triisopropylbenzene (4.11 g, 20.2 mmol), and aluminum chloride (1.41 g, 19.5 mmol) were added to the residue. The reaction mixture was heated at reflux for 3 h and then allowed to cool to room temperature. After the mixture had been poured into water, it was extracted with dichloromethane. The organic layer was washed with saturated sodium hydrogen carbonate solution and brine. The organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated to afford a yellow solid. Purification of the crude product by column chromatography on silica gel (elution with hexane/dichloromethane 1:2) gave compound **1** (1.51 g, 3.47 mmol, 43%) as yellow crystals, m.p. 129.1–129.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 8.0, 1.2 Hz, 1 H, ArH), 7.39 (dd, *J* = 7.6, 1.6 Hz, 1 H, ArH), 7.31 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H, ArH), 7.10 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1 H, ArH), 7.04 (s, 2 H, ArH), 2.93 (sept, *J* = 7.2 Hz, 1 H, CH), 2.67 (sept, *J* = 6.8 Hz, 2 H, CH), 1.28 (d, *J* = 7.2 Hz, 6 H, CH_3), 1.29 (br, 12 H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.49, 150.27, 145.46, 142.50, 140.54, 134.89, 132.89, 132.82, 127.75, 127.74, 121.14, 121.13, 93.15, 34.61, 34.49, 31.34, 24.39, 24.25 ppm. MS (EI): *m*/*z* = 434 $[M]^+$. $C_{22}H_{27}IO$: C 60.83, H 6.27; found C 60.78, H 6.21.

Synthesis of 2-Iodobenzophenone (3): The mixture of 2-iodobenzoic acid (10.0 g, 40.3 mmol) and thionyl chloride (45 mL) was warmed to 70 °C for 5 h and then allowed to cool to room temperature. After removal of thionyl chloride, benzene (40 mL, 451 mmol) and aluminum chloride (3.27 g, 45.3 mmol) were added to the residue. The reaction mixture was heated at reflux for 4 h and then allowed to cool to room temperature. After the mixture had been poured into water, it was extracted with dichloromethane. The organic layer was washed with saturated sodium hydrogen carbonate solution and brine. The organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated to afford compound **3** (9.68 g, 31.4 mmol, 78%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 7.2, 1.2 Hz, 1 H, ArH), 7.81 (dd, *J* = 7.2, 1.2 Hz, 2 H, ArH), 7.60 (dd, *J* = 7.4, 2.6 Hz, 1 H, ArH), 7.48–7.42 (m, 3 H, ArH), 7.29 (dd, *J* = 7.6, 1.6 Hz, 1 H, ArH), 7.18 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1 H, ArH) ppm.

Synthesis of 2-(*p*-Tolylethynyl)-2′,4′,6′-triisopropylbenzophenone (4a): Bis(triphenylphosphine)palladium dichloride (163 mg, 0.232 mmol) was added at room temperature to a degassed solution of compound **1** (2.04 g, 4.70 mmol), *p*-tolylacetylene (684 mg, 5.89 mmol), and copper iodide (89 mg, 0.47 mmol) in tetrahydrofuran (20 mL) and triethylamine (10 mL). The solution was stirred at reflux for 17 h and then allowed to cool to room temperature. After saturated ammonium chloride solution had been added, the reaction mixture was extracted with diethyl ether. The organic layer was washed with water. The organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated to afford a yellow oil. Purification of the crude product by column chromatography on silica gel (elution with dichloromethane/hexane 3:1) gave compound **4a** (1.25 g, 2.96 mmol, 63%) as a pale yellow solid, m.p. 92.8–94.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.6 Hz, 2 H, ArH), 7.48 (dd, *J* = 7.6, 7.5 Hz, 1 H, ArH), 7.35–7.30 (m, 3 H, ArH), 7.11 (d, *J* = 7.6 Hz, 2 H, ArH), 7.63 (s, 2 H, ArH), 2.89 [sept, *J* = 6.9 Hz, 1 H, C*H*$(CH_3)_2$], 2.75 [sept, *J* = 6.7 Hz, 2 H, C*H*$(CH_3)_2$], 2.35 (s, 3 H, CH_3), 1.25 [d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.14 [d, *J* = 6.7 Hz, 12 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.2, 149.7, 145.2, 139.6, 138.5, 136.3, 134.8, 132.0, 131.8, 131.2, 128.9, 127.6, 123.3, 121.1, 120.2, 95.4, 87.8, 34.3, 31.1, 24.2, 23.9, 21.5 ppm. MS (EI): *m*/*z* = 422 $[M]^+$. $C_{31}H_{34}O$: C 88.10, H 8.11; found C 88.05, H 7.93.

Synthesis of 2-(3,3-Dimethylbut-1-ynyl)-2′,4′,6′-triisopropylbenzophenone (4b): Bis(triphenylphosphine)palladium dichloride (65 mg, 0.093 mmol) was added at room temperature to a degassed solution of compound **1** (674 mg, 1.55 mmol), 2,2-dimethylbut-1-yne

(140 mg, 1.70 mmol), and copper iodide (50 mg, 0.26 mmol) in tetrahydrofuran (20 mL) and diisopropylamine (10 mL). The solution was stirred at reflux for 12 h and then allowed to cool to room temperature. After saturated ammonium chloride solution had been added, the reaction mixture was extracted with diethyl ether. The organic layer was washed with water, dried with anhydrous magnesium sulfate, filtered, and concentrated to afford a yellow oil. Purification of the crude product by column chromatography on silica gel (elution with dichloromethane/hexane 1:1) gave compound **4b** (602 mg, 1.55 mmol, quant.) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.0 Hz, 2 H, ArH), 7.40 (dd, J = 8.0, 8.0 Hz, 1 H, ArH), 7.24 (dd, J = 7.6, 7.6 Hz, 1 H, ArH), 7.03 (s, 2 H, ArH), 2.91 (sept, J = 6.8 Hz, 1 H, CH), 2.75 (sept, J = 6.8 Hz, 2 H, CH), 1.27 (d, J = 6.8 Hz, 6 H, CH_3), 1.23 [s, 9 H, $C(CH_3)_3$], 1.13 (br, 12 H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.42, 149.64, 145.05, 140.29, 136.51, 134.77, 131.54, 130.70, 126.89, 121.09 (2 C), 104.21, 77.99, 34.35 (2 C), 30.92, 30.75, 28.18, 23.99 ppm. MS (EI): m/z = 388 $[M]^+$. $C_{28}H_{36}O$: C 86.54, H 9.34; found C 86.32, H 9.34.

Synthesis of 2-(3,3-Dimethylbut-1-ynyl)benzophenone (4d): Bis(triphenylphosphine)palladium dichloride (68 mg, 0.097 mmol) was added at room temperature to a degassed solution of compound **3** (3.02 g, 9.80 mmol), 2,2-dimethylbut-1-yne (884 mg, 10.8 mmol), and copper iodide (200 mg, 1.05 mmol) in tetrahydrofuran (20 mL) and diisopropylamine (10 mL). The solution was stirred at reflux for 15 h and then allowed to cool to room temperature. After saturated ammonium chloride solution had been added, the reaction mixture was extracted with diethyl ether. The organic layer was washed with water, dried with anhydrous magnesium sulfate, filtered, and concentrated to afford a yellow oil. Purification of the crude product by column chromatography on silica gel (elution with dichloromethane/hexane 1:1) gave compound **4d** (1.31 g, 5.00 mmol, 51%) as a pale yellow powder, m.p. 79.8–80.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 7.2 Hz, 2 H, ArH), 7.54 (t, J = 7.6 Hz, 1 H, ArH), 7.38–7.45 (m, 6 H, ArH), 0.90 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.43, 141.89, 137.33, 132.84, 132.08, 130.03, 129.89, 128.13, 128.06, 127.47, 122.20, 104.63, 77.24, 30.12, 27.58 ppm. MS (EI): m/z = 262 $[M]^+$. $C_{19}H_{18}O$: C 86.99, H 6.92; found C 86.79, H 7.07.

Synthesis of 3-*p*-Tolyl-1-(2,4,6-triisopropylphenyl)isochromenium Bis(trifluoromethylsulfonyl)amide (5a): A solution of bis(trifluoromethylsulfonyl)imide (481 mg, 1.71 mmol) in dichloromethane (20 mL) was added at room temperature to a solution of compound **4a** (553 mg, 1.31 mmol) in dichloromethane (35 mL). After the solution had been stirred at room temperature for 1.5 h, the solvent was removed under reduced pressure. Hexane (10 mL) was added to the residue, and the solution was cooled to 0 °C. The resulting suspension was filtered and washed with cold hexane to give compound **5a** (809 mg, 1.15 mmol, 88%) as yellow crystals, m.p. 113.2–114.2 °C. ^{1}H NMR (400 MHz, CD_3CN): δ = 8.91 (s, 1 H, ArH), 8.44–8.48 (m, 4 H, ArH), 8.36 (d, J = 8.4 Hz, 1 H, ArH), 8.04 (d, J = 8.4 Hz, 2 H, ArH), 7.98–7.97 (m, 2 H, ArH), 7.51 (d, J = 8.4 Hz, 2 H, ArH), 7.43 (s, 2 H, ArH), 3.10 [sept, J = 6.9 Hz, 1 H, $CH(CH_3)_2$], 2.47 (s, 3 H, CH_3), 2.21 [sept, J = 6.7 Hz, 2 H, $CH(CH_3)_2$], 1.36 [d, J = 6.9 Hz, 6 H, $CH(CH_3)_2$], 1.12 [d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$], 1.07 [d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$] ppm. ^{13}C NMR (101 MHz, CD_3CN): δ = 185.5, 164.4, 155.9, 149.9, 146.0, 145.5, 145.2, 134.2, 132.6, 131.8, 129.3, 127.8, 127.4, 127.0, 124.0, 123.4, 120.9 (quart, $J_{F,C}$ = 321 Hz, CF_3), 117.4, 35.4, 33.0, 25.2, 24.0, 23.5, 21.7 ppm. ^{19}F NMR (376 MHz, CD_3CN): δ = –80.6 (s) ppm. MS (EI): m/z = 423 $[M – (CF_3SO_2)_2N]^+$. $C_{33}H_{35}F_6NO_5S_2$: C 56.32, H 5.01, N 1.99; found C 56.40, H 5.05, N 2.30.

Reaction between Ethynylbenzophenone 4b and Bis(trifluoromethylsulfonyl)imide: A solution of bis(trifluoromethylsulfonyl)imide (126 mg, 0.448 mmol) in dichloromethane (1.5 mL) was added at room temperature to a solution of compound **4b** (159 mg, 0.409 mmol) in dichloromethane (5 mL). After the solution had been stirred at room temperature for 2 h, the solvent was removed under reduced pressure. Hexane (ca. 10 mL) was added to the residue, and the solution was cooled to 0 °C. The resulting suspension was filtered and washed with cold hexane to afford a mixture of benzo[*c*]pyrylium amide **5b** and alkylideneisobenzofuranium amide **6b** (208 mg, 2.97 mmol, 77%, **5b/6b** 31:69) as yellow crystals, m.p. 105–119 °C (**5b/6b** 31:69). ^{19}F NMR (376 MHz, CD_3CN): δ = –80.6 (s) ppm. MS (ESI): m/z = 389 $[M – (CF_3SO_2)_2N]^+$. $C_{30}H_{37}F_6NO_5S_2$: C 53.80, H 5.57, N 2.09; found C 53.73, H 5.36, N 2.36.

Compound 5b: Yellow crystals, m.p. 141.4–143.2 °C. ^{1}H NMR (400 MHz, CD_3CN): δ = 8.50 (ddd, J = 8.3, 6.2, 1.9 Hz, 1 H, ArH), 8.43 (s, 1 H, ArH), 8.33–8.39 (m, 1 H, ArH), 8.03–7.97 (m, 2 H, ArH), 7.41 (s, 2 H, ArH), 3.09 (sept, J = 6.9 Hz, 1 H, CH), 2.05 (sept, J = 6.7 Hz, 2 H, CH), 1.54 [s, 9 H, $C(CH_3)_3$], 1.34 (d, J = 6.9 Hz, 6 H, CH_3), 1.12 (d, J = 6.7 Hz, 6 H, CH_3), 1.03 (d, J = 6.7 Hz, 6 H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.80, 175.66, 154.87, 148.39, 144.65, 143.47, 133.09, 131.48, 129.38, 125.69, 122.65, 122.27, 121.46, 119.86 (quart, $J_{F,C}$ = 321 Hz, CF_3), 118.26, 116.50, 37.63, 34.61, 32.46, 30.61, 28.18, 24.74, 23.73, 23.44 ppm.

Compound 6b: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.33–8.39 (m, 2 H, ArH), 8.05 (br. d, J = 8.2 Hz, 1 H, ArH), 7.93 (ddd, J = 8.2, 6.3, 1.8 Hz, 1 H, ArH), 7.80 [s, 1 H, =C*H*-$C(CH_3)_3$], 7.45 (s, 2 H, ArH), 3.08 (sept, J = 6.9 Hz. 1 H, CH), 2.54 (sept, J = 6.7 Hz, 2 H, CH), 1.49 [s, 9 H, $C(CH_3)_3$], 1.51 (d, J = 6.9 Hz, 6 H, CH_3), 1.18 (d, J = 6.7 Hz, 6 H, CH_3), 1.16 (d, J = 6.7 Hz, 6 H, CH_3) ppm. 2D NOESY NMR (400 MHz, CD_3CN): a singlet signal at δ = 7.80 ppm correlates to a multiplet signal between 8.33 to 8.39 ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.84, 156.58, 152.04, 151.15, 149.37, 144.37, 144.11, 133.13, 131.48, 127.96, 123.90, 122.79, 119.86 (quart, $J_{F,C}$ = 321 Hz, CF_3), 119.26, 115.07, 37.33, 34.76, 32.61, 30.16, 25.15, 23.54 ppm.

Reaction between Ethynylbenzophenone 4d and Bis(trifluoromethylsulfonyl)imide: A solution of bis(trifluoromethylsulfonyl)imide (765 mg, 2.74 mmol) in dichloromethane (10 mL) was added at room temperature to a solution of compound **4d** (625 mg, 2.38 mmol) in dichloromethane (40 mL). After the solution had been stirred at room temperature for 2 h, the solvent was removed under reduced pressure to afford a mixture of benzo[*c*]pyrylium amide **5d** and 1*H*-inden-1-one **7d** (**5d/7d** 9:91) as an orange oil. Hexane (10 mL) was added to the residue, and the solution was allowed to stand at room temperature for several minutes. The resulting supernatant was then removed. This process was repeated five times, and the combined hexane solution was concentrated under reduced pressure to give 1*H*-inden-1-one **7d** as yellow crystals. The hexane-insoluble orange oil was benzo[*c*]pyrylium amide **5d**.

Compound 5d: Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, J = 8.1 Hz, 1 H, ArH), 8.58 (d, J = 8.3 Hz, 2 H, ArH), 8.29 (d, J = 8.1 Hz, 1 H, ArH), 8.22 (dd, J = 7.8, 8.1 Hz, 1 H, ArH), 8.01–7.97 (m, 1 H, ArH), 7.96 (dd, J = 7.8, 8.1 Hz, 1 H, ArH), 7.88 (t, J = 8.3 Hz, 2 H, ArH), 7.38 (s, 1 H, ArH), 1.58 [s, 9 H, $C(CH_3)_3$] ppm. ^{19}F NMR (376 MHz, CD_3CN): δ = –80.6 (s) ppm. MS (ESI): m/z = 263 $[M – (CF_3SO_2)_2N]^+$.

Compound 7d: Yellow crystals, m.p. 111.8–112.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.37 (m, 4 H, ArH), 7.27–7.24 (m, 2 H, ArH), 7.23–7.19 (m, 1 H, ArH), 7.17–7.13 (m, 1 H, ArH), 6.49

(d, J = 7.1 Hz, ArH), 1.16 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.41, 153.96, 147.65, 141.46, 135.32, 133.32, 129.86, 128.18, 128.06, 127.89, 127.84, 121.72, 120.36, 33.63, 30.64 ppm. MS (EI): m/z = 262 $[M]^+$. $C_{19}H_{18}O$: C 86.99, H 6.92; found C 87.08, H 6.99.

Supporting Information (see footnote on the first page of this article): Other experimental information, spectroscopic data, crystallographic analyses, theoretical calculations, and copies of ^1H and ^{13}C NMR spectra of the reported compounds.

Acknowledgments

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[10] CCDC-907192 (for **5a**), -925633 (for **7d**), -962364 (for **7h**), -962363 (for **7i**), and -962362 (for **7k**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] It is difficult to separate the mixture of **5b** and **6b** even by common separation methods such as thin-layer chromatography, gel-permeation liquid chromatography, or recrystallization.

[12] All theoretical calculations were carried out by use of the Gaussian 03 program at the B3LYP/6–311+G(2d,p) level.

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