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Indium(III)-Catalyzed Tandem Reaction with Alkynylbenzaldehydes and Alkynylanilines to Heteroaromatic Compounds

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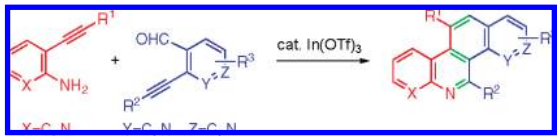
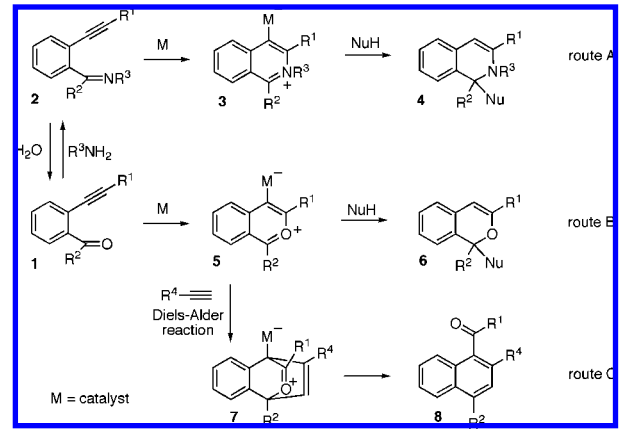


Starting from *ortho*-alkynylbenzaldehydes and *ortho*-alkynylanilines, $In(OTf)_3$-catalyzed synthesis of ring-condensed heteroaromatic compounds was developed via a domino intramolecular nucleophilic attack/intermolecular cycloaddition/dehydration reaction.

Substituted phenanthridine alkaloids constitute an attractive class of compounds from the viewpoint of their biological and pharmaceutical activities, which are attributed to their special affinity toward DNA. There have recently been a lot of interesting applications.[1] However, a little efficient synthetic method that is applicable to various phenanthridines has been developed.[2] Development of short and diverse synthetic methods is important for further study. On the other hand, electrophilic cyclization of phenylacetylenes bearing a carbonyl group or an imino group in the *ortho* position is currently a popular research topic and important method from the viewpoint of synthetic potential. As shown in Scheme 1, the reaction with *ortho*-alkynylcarbonyl compounds **1** usually produces imines **2** in the presence of amines, and then the coordination of a catalyst to the alkynyl moiety of **2** occurs to produce **3**. The addition of nucleophiles to **3** results in the formation of 1,2-dihydroisoquinolines **4** (route A).[3] In the reaction of compound **1** with no amines, benzannulation would proceed to give compounds **6** via intermediates **5** in the presence of nucleophiles (route B).[4] When dienophilic alkynes are added instead of nucleophiles, Diels−Alder-type cycloaddition reactions would occur with active dienes **5** to produce naphthyl ketone derivatives **8** via intermediates **7** (route C).[5,6]

SCHEME 1



On the basis of these results, we planned to apply π-acidic metal-catalyzed tandem reaction to rapidly access phenanthridine structures. We envisaged that Lewis acid catalyzed annulation of *ortho*-alkynylbenzaldehydes with *ortho*-alkynylanilines might successively proceed to form one carbon−nitrogen and two carbon−carbon bonds of benzophenanthridine derivatives in one step. An overview of our strategy is summarized in Scheme 2.

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(6) Very recently, Iwasawa et al. reported the synthesis of naphthalene derivatives through platinum(II)-catalyzed reaction of 2-alkynylbenzoate with vinyl ethers. In this report, they believe the [3 + 2]-cycloaddition mechanism is reasonable at least in platinum(II)-catalyzed benzannulation. (a) Kusama, H.; Funami, H.; Iwasawa, N. *Synthesis* **2007**, 2014. (b) Kusama, H.; Miyashita, Y.; Takaya, J.; Iwasawa, N. *Org. Lett.* **2006**, *8*, 289. (c) Straub, B. F. *Chem. Commun.* **2004**, 1726.

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SCHEME 2. Synthetic Strategy

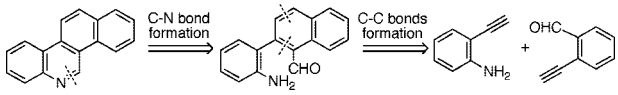
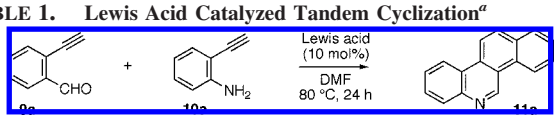


TABLE 1. Lewis Acid Catalyzed Tandem Cyclization[a]



entry	Lewis acid	yield[b] (%)
1	$In(OTf)_3$	93[c]
2	$InBr_3$	76
3	$Sc(OTf)_3$	92
4	$Sm(OTf)_3$	84
5	$Yb(OTf)_3$	85
6	$Yb(NTf_2)_3$	89
7	$Fe(OTf)_3$	92
8	$AuClPPh_3$	13
9	AgOTf	35
10	$Cu(OTf)_2$	0[d]
11	$Pd(OAc)_2$	0[d]
12	TfOH	0

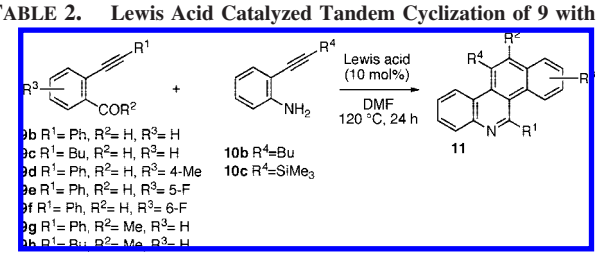
[a] The reaction was carried out in DMF (3 mL) using **9a** (1 mmol) and **10a** (1 mmol) in the presence of Lewis acid (10 mol %). [b] Determined by ^{1}H NMR using 1,4-di-*tert*-butylbenzene as an internal standard. [c] Isolated yield. [d] Complex mixture was formed.

Various *ortho*-alkynylbenzaldehydes and *ortho*-alkynylanilines can be readily synthesized by Sonogashira reaction. In this report, we describe a new effective indium(III)-catalyzed tandem reaction with *ortho*-alkynylbenzaldehydes and *ortho*-alkynylanilines to produce ring-condensed heteroaromatic compounds.

In the reaction of *ortho*-alkynylbenzaldehydes and *ortho*-alkynylanilines, there was the possibility that the three routes A, B, and C in Scheme 1 would occur. First, we turned our attention to the desired domino reaction in the presence of a metal catalyst. Fortunately, the reaction of **9a** with **10a** afforded benzo[*i*]phenanthridine **11a**[2g] in 93% yield with 10 mol % of indium triflate, $In(OTf)_3$, in DMF at 80 °C (Table 1, entry 1). The structure of compound **11a** was unambiguously confirmed by X-ray crystallography.[7] In the absence of $In(OTf)_3$ in DMF, the reaction did not take place at all. The reaction with $In(OTf)_3$ in water gave **11a** (10% yield) and toluene (33% yield). Reaction with $InBr_3$, $Sc(OTf)_3$, $Sm(OTf)_3$, $Yb(OTf)_3$, $Yb(NTf_2)_3$, and $Fe(OTf)_3$ also produced the condensed aromatic product **11a** in good yields (entries 2−7). In contrast to these results, $AuClPPh_3$ and AgOTf[3a,e] gave **11a** in low yield, and $Cu(OTf)_2$[3e,5c,e] and $Pd(OAc)_2$[4b] were ineffective[8] to produce desired product but complex mixture (entries 8−11). Brønsted acid, TfOH (30 mol %), did not catalyze this tandem cyclization reaction (entry 12).

With these results in hand, we set out to define the scope of this methodology. A variety of *ortho*-alkynylbenzaldehydes **9** and *ortho*-alkynylanilines **10** were investigated. The reaction of aldehyde bearing phenyl-substituted alkyne **9b** with amine

TABLE 2. Lewis Acid Catalyzed Tandem Cyclization of 9 with 10



entry	9	10	Lewis acid	time (h)	11	yield (%)[a]
1	**9b**	**10a**	$In(OTf)_3$	24	**11b**	71
2	**9b**	**10a**	$Sc(OTf)_3$	24	**11b**	69
3	**9b**	**10a**	$Fe(OTf)_3$	24	**11b**	25
4	**9c**	**10a**	$In(OTf)_3$	24	**11c**	51
5	**9d**	**10a**	$In(OTf)_3$	24	**11d**	73
6	**9e**	**10a**	$In(OTf)_3$	13	**11e**	62
7	**9f**	**10a**	$In(OTf)_3$	14	**11f**	75
8	**9g**	**10a**	$In(OTf)_3$	24	—	0[b]
9	**9h**	**10a**	$In(OTf)_3$	24	—	0[b]
10	**9a**	**10b**	$In(OTf)_3$	24	**11g**	30
11	**9e**	**10b**	$In(OTf)_3$	22	**11h**	54
12	**9a**	**10c**	$In(OTf)_3$	72	**11a**, **11i**	33,24

[a] Isolated yield. [b] Complex mixture was formed.

10a at 80 °C by $In(OTf)_3$ provided **11b** in low yield. However, this problem was resolved by changing the reaction temperature from 80 to 120 °C (Table 2, entry 1). $Sc(OTf)_3$ and $Fe(OTf)_3$ catalysts also catalyzed this reaction (entries 2 and 3). We selected $In(OTf)_3$ as a more effective and lower cost catalyst. The reactions of aldehydes **9c**, **9d**, **9e**, and **9f** with amine **10a** also proceeded smoothly to give **11c**, **11d**, **11e**, and **11f** (entries 4−7). Reactions of the substrate bearing an electron-withdrawing substituent on the aromatic ring of aldehyde **9** were faster than that of an analogous substrate containing an electron-donating substituent (entries 5−7). The reaction of acetophenone derivatives **9g** and **9h** with **10a** gave only a complex mixture (entries 8 and 9). From these results, it is clear that aldehyde function of compound **9** is important for this reaction. Compound **9a** with aniline-bearing butyl-substituted alkyne **10b** also provided the desired compound **11g** but in low yield (entry 10). Therefore, we tried the reaction of aldehyde **9e** bearing an electron-withdrawing group on the aromatic ring with amine **10b**. The yield of the desired product was moderately but not greatly improved (entry 11). The reaction with **9a** and trimethylsilylethynylaniline **10c** afforded the desired compound **11i** accompanied by desilylated condensed aromatic compound **11a** in 57% total yield (entry 12).

This indium(III)-catalyzed tandem reaction also allows for the synthesis of benzophenanthroline derivatives **11j** and **11k**, naphthophenanthridine derivative **11l**, and naphthonaphthyridine derivative **11m** in moderatly high isolated yields.

A proposed mechanism for this indium(III)-catalyzed tandem reaction is shown in Scheme 3. Coordination of the triple bond of **9** to $In(OTf)_3$ enhances the electrophilicity of alkyne,[9] and the subsequent nucleophilic attack of the carbonyl oxygen to the electron-deficient alkyne would result in the formation of the 6-*endo*-*dig*-cyclized pyrylium cation intermediate **B**.[4,5]

(7) CCDC 658463 contains 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.

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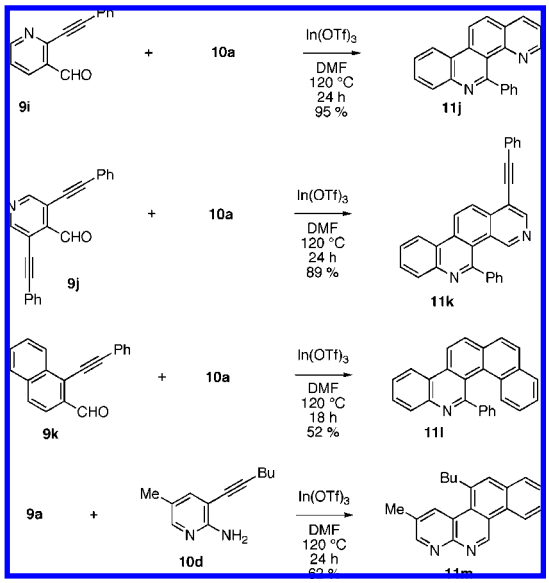
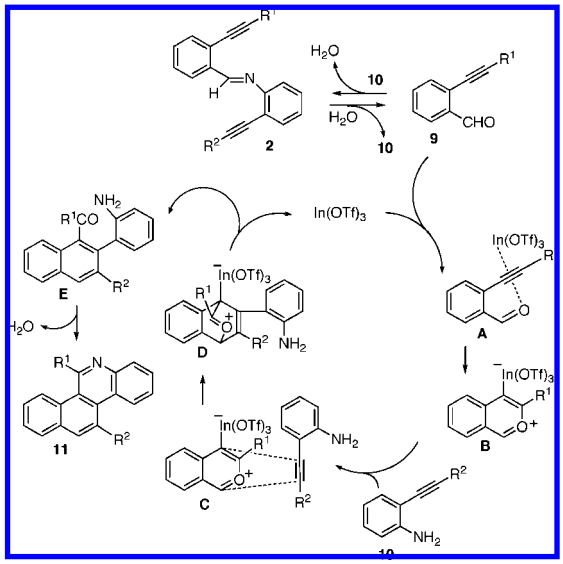


The Diels−Alder-type cycloaddition of **B** with *ortho*-alkynylaniline **10** would occur as shown in **C** to give the intermediate **D** with the same high regioselectivity.[5c,e,f] The subsequent bond rearrangement would proceed to afford **E** with regeneration of $In(OTf)_3$. Dehydration of **E** would produce ring-condensed heteroaromatic compound **11**. To obtain further information, ^1H NMR spectroscopic analysis between 9 and 11 ppm was performed using the reaction of **9a** with **10a** in the presence of 10 mol % of $In(OTf)_3$ in DMF-d_6. First, the aldehyde proton signal (δ 10.5) of **9a** gradually decreased, and a new aldehyde proton signal (δ 10.1) of perhaps compound **E** ($R^1 = H$) and an imine proton signal (δ 9.0) of compound **2** ($R^1 = R^2 = H$) gradually increased (Figure 1). After 2 h at 50 °C, the C*H*N proton signal (δ 10.2) of the desired cyclic product **11a** appeared in the same proton signal region. The imine proton signal gradually decreased in conjunction with generation of **11a** and water and then disappeared after 2 h at 80 °C. Finally, after 24 h at 80 °C, there was only the C*H*N proton signal of **11a**, with no signal of starting aldehyde **9a** or aldehyde **E**.

In the reaction of **9a** with **10c** (Table 2, entry 12), byproduct **12** was obtained in 4% yield (eq 1). It is thought that byproduct

SCHEME 3. Proposed Mechanism



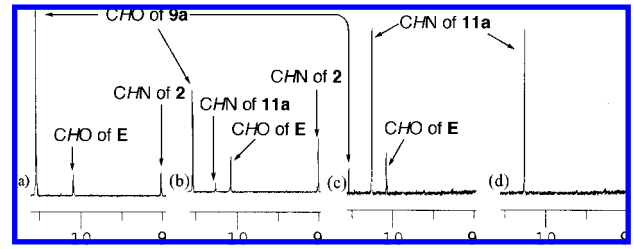
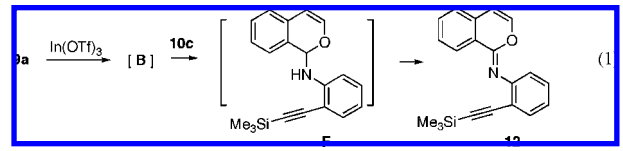


FIGURE 1. ^1H NMR spectra (DMF-d_6, 300 MHz) of the reaction of **9a** with **10a**: (a) at 50 °C, 30 min; (b) at 50 °C, 2 h; (c) at 80 °C, 2 h; (d) at 80 °C, 24 h.

12 would be produced through air oxidation of compound **F** formed by the reaction of **9a** with **10c** through route B in Scheme 1. This supports the formation of intermediate **B**.



In conclusion, starting from readily available *ortho*-alkynylanilines and *ortho*-alkynylbenzaldehydes, we have developed a new atom-economical $In(OTf)_3$-catalyzed synthesis of ring-condensed heteroaromatic compounds via a domino intramolecular nucleophilic attack/intermolecular cycloaddition/dehydration reaction. Further studies on the mechanism and to extend the scope of synthetic utility are in progress.

Experimental Section

General Procedure for Preparation of Compound 11a. $In(OTf)_3$ (56.2 mg, 0.1 mmol) was added to a solution of ethynylbenzaldehyde **9a** (130 mg, 1 mmol) with ethynylaniline **10a** (117 mg, 1 mmol) in DMF (3 mL), and the mixture was stirred for 24 h at 80 °C. DMF was evaporated under reduced pressure. The mixture was filtered through a plug of Celite and concentrated in vacuo. Chromatography over silica gel using 20% AcOEt in hexane afforded the desired benzo[*i*]phenanthridine **11a** (213 mg, 93%) as yellow plates.

Benzo[*i*]phenanthridine (11a).[2h] Yellow plates; mp 181−182 °C (from Hex−AcOEt); ^1H NMR (600 MHz, $CDCl_3$) δ = 10.23 (s, 1H), 8.91 (d, J = 8.2 Hz, 1H), 8.66 (d, J = 8.2 Hz, 1H), 8.60 (d, J = 8.9 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 8.18 (d, J = 8.9 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.81 (dd, J = 8.2, 6.9 Hz, 1H), 7.79 (dd, J = 8.2, 6.9 Hz, 1H), 7.73 (dd, J = 8.2, 6.9 Hz, 1H), 7.69 (dd, J = 7.6, 6.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 147.8, 145.2, 132.1, 132.0, 130.0, 130.0, 128.9, 128.8, 128.1, 127.1, 127.1, 124.3, 122.7, 122.1, 121.7, 119.8; IR ($CHCl_3$, cm^{-1}) 3011, 1502, 1203, 787, 775, 725, 698; MS (EI) m/z = 229 (M^+, 100); HRMS (EI) m/z calcd for $C_{17}H_{11}N$ 229.0891, found 229.0885.

5-Phenylbenzo[*i*]phenanthridine (11b). The residue was chromatographed on silica gel [AcOEt−hexane (1:10)] to afford **11b** as yellow prisms: mp 142−144 °C (from Hex−AcOEt); ^1H NMR (600 MHz, $CDCl_3$) δ = 8.66 (d, J = 8.2 Hz, 2H), 8.28 (d, J = 7.6 Hz, 1H), 8.17 (d, J = 8.9 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.85−7.76 (m, 2H), 7.70 (dd, J = 7.6, 7.6 Hz, 1H), 7.64−7.60 (m, 2H), 7.54−7.46 (m, 4H), 7.21 (dd, J = 7.9, 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.3, 144.5, 144.0, 134.3, 133.2, 132.3, 130.2, 129.9, 129.1, 129.0, 128.8, 128.4, 128.4, 128.3, 126.8, 126.4, 125.8, 123.6, 122.4, 121.4, 119.9; IR ($CHCl_3$, cm^{-1}) 3011, 2965, 1611, 1574, 1558, 1468, 1423, 1362, 1350, 1315, 1298, 1240, 1207, 829, 725, 698; MS (EI) m/z = 305 (M^+, 66.8); HRMS (EI) m/z calcd for $C_{23}H_{15}N$ 305.1204, found 305.1198.

5-Butylbenzo[*i*]phenanthridine (11c). The residue was chromatographed on silica gel [AcOEt−hexane (1:10)] to afford **11c** as yellow prisms: mp 83−84 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.80 (d, J = 8.2 Hz, 1H), 8.58 (dd, J = 7.6, 7.6 Hz, 2H), 8.17 (d, J = 8.2 Hz, 1H), 8.10 (d, J = 8.9 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.75 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.71 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.68−7.61 (m, 2H), 3.70 (t, J = 7.9 Hz, 2H), 2.12−2.04 (m, 2H), 1.57 (sext, J = 7.6 Hz, 2H), 1.02 (t, J = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.8, 143.9, 133.8, 133.2, 131.7, 130.2, 129.0, 128.9, 128.8, 127.1, 126.8, 126.3, 126.1, 123.2, 122.7, 122.5, 120.3, 41.3, 31.3, 23.0, 14.0; IR ($CHCl_3$, cm^{-1}) 3063, 3009, 2959, 2932, 2872, 1611, 1562, 1514, 1468, 1454, 1422, 1379, 1360, 1348, 1306, 1279, 1242, 1148, 1132, 1101, 864, 827, 665; MS (EI) m/z = 285 (M^+, 45.0); HRMS (EI) m/z calcd for $C_{21}H_{19}N$ 285.1517, found 285.1513.

3-Methyl-5-phenylbenzo[*i*]phenanthridine (11d). The residue was chromatographed on silica gel [AcOEt−hexane (1:10)] to afford **11d** as yellow prisms: mp 142−144 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.64 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 8.9 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.77 (dd, J = 7.6, 7.6 Hz, 1H), 7.69 (ddd, J = 6.9, 6.9, 1.4 Hz, 1H), 7.62−7.59 (m, 2H), 7.53−7.50 (m, 3H), 7.45 (s, 1H), 7.32 (d, J = 8.2 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.4, 144.6, 144.0, 135.6, 134.4, 132.1, 131.2, 130.3, 129.9, 129.0, 128.9, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 126.7, 123.7, 122.5, 121.1, 118.9, 22.0; IR ($CHCl_3$, cm^{-1}) 3063, 3011, 2963, 2924, 1622, 1612, 1572, 1557, 1468, 1445, 1383, 1356, 1310, 1244, 1223, 1207, 839, 740, 704; MS (EI) m/z = 319 (M^+, 79.9); HRMS (EI) m/z calcd for $C_{24}H_{17}N$ 319.1361, found 319.1358.

2-Fluoro-5-phenylbenzo[*i*]phenanthridine (11e). The residue was chromatographed on silica gel [AcOEt−hexane (1:10)] to afford **11e** as yellow prisms: mp 149−150 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.69 (d, J = 8.9 Hz, 1H), 8.63 (d, J = 8.2 Hz, 1H), 8.27 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 8.9 Hz, 1H), 7.81−7.75 (m, 2H), 7.72 (dd, J = 8.2, 8.2 Hz, 1H), 7.63−7.59 (m, 2H), 7.55 (dd, J = 8.9, 2.7 Hz, 1H), 7.54−7.50 (m, 3H), 6.96 (td, J = 10.0, 2.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.4, 159.7, 144.3, 143.9, 134.6, 133.7, 131.5, 131.4, 130.7, 130.6, 130.0, 129.2, 129.1, 128.8, 128.6, 127.0, 123.4, 122.3, 121.4, 121.1, 115.2, 115.1, 112.1, 112.0; IR ($CHCl_3$, cm^{-1}) 3065, 2963, 1620, 1560, 1516, 1495, 1443, 1431, 1356, 1312, 1294, 1267, 1244, 1207, 1144, 1128, 968, 870, 833, 710, 698, 665; MS (EI) m/z = 323 (M^+, 59.5); HRMS (EI) m/z calcd for $C_{23}H_{14}NF$ 323.1110, found 323.1112.

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Supporting Information Available: Experimental details and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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