

Research Letter

Synthesis of Benzo[*b*]fluorenone Nuclei of Stealthins

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Two routes, one based on a Michael-initiated aldol condensation and the other on an intramolecular carbonyl-ene reaction, have been found to be feasible for an entry to benzo[*b*]fluorenones. Reaction of 4,9-dimethoxybenz[*f*]indenone with nitromethane in the presence of DBU gave the corresponding Michael adduct, which afforded 2-methyl-5,10-dimethoxybenzo[*b*]fluorenone on reaction with methacrolein under a variety of basic conditions. Similarly, 2-methallyl-4,9-dimethoxybenz[*f*]indenone reacted with nitromethane to give the corresponding Michael adduct, Nef reaction of which furnished 3-formyl-2-methyl-4,9-dimethoxybenz[*f*]indanone. This underwent ene-cyclization under the influence of SnCl₄·5H₂O, and yielded 2-methyl-5,10-dimethoxybenzo[*b*]fluorenone.

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1. Introduction

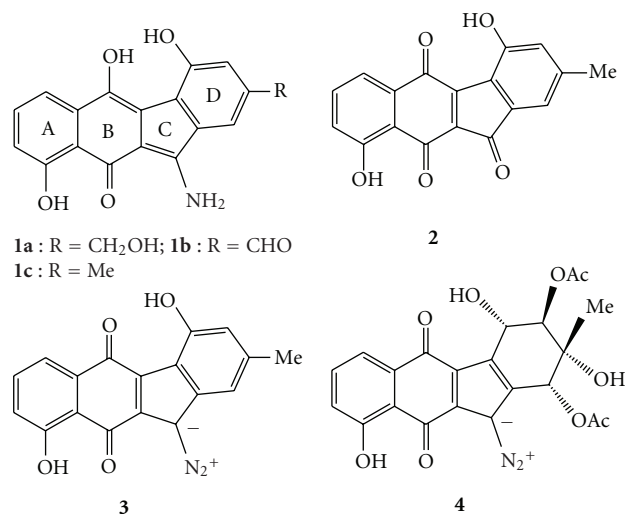
Stealthins A (**1a**) and B (**1b**), isolated from *Streptomyces viridochromogenes* as potent radical scavengers, are the first known members of natural benzo[*b*]fluorenones [1]. Interest in this group of compounds grew considerably due to the identification of structurally allied natural products, stealthin C (**1c**) [2], kinafluorenone (**2**) [3], prekinamycin (**3**) [4], and kinamycin antibiotics (e.g., kinamycin D, **4**) [5] (Figure 1). Their synthesis became an active area of research since 1996 [6–19]. In line with the Ishikawa approach [19], we intended to explore the chemistry of benz[*f*]indenones (e.g., **5b**) to establish new synthetic routes to functionalized benzo[*b*]fluorenones [20]. Herein, we report regioselective construction of the D-ring of benzo[*b*]fluorenones (e.g., **6**) from the corresponding benz[*f*]indenones.

2. Results and Discussion

Initial studies were focused on the utilization of the readily accessible benz[*f*]indenones **5a** and **5b** [21]. DBU-promoted Michael addition of nitromethane to the indenones furnished indenones **7a** and **7b**, respectively. The intended annulation of **7b** with methacrolein was then studied with

different base-solvent systems (Scheme 1). But, none of the attempts gave desired product **8**. Instead, most of the methods produced benzo[*b*]fluorenone **6** in low yields. The best yield was 25%, which was obtained with DBU in benzene. The presence of singlet at δ 2.23 for Ar-CH₃ in ¹H NMR spectrum was indicative of the structure **6**. It is probable that the compound **6** was formed from tetracycle **8** through elimination of HNO₂. Considering the fact that even a weak base such as *n*-Bu₃P caused the elimination of NO₂ group, we examined the route (Scheme 2), involving an acid-catalyzed cyclization. The d⁴ Synchron equivalent **9** was prepared in two steps from methacrolein by adaptation of Miyakoshi protocol [22] (Scheme 2). Conjugate addition of the reagent **9** to benz[*f*]indenone **5b** in the presence of DBU provided **10** in good yield. ¹H NMR spectrum of the product indicated the formation of a 1:1 mixture of diastereomers. When treated with 1 N HCl, the mixture afforded the expected product **8** in trace amount, the major product being **6** (25%). Repeated attempts to optimize the transformation of **10** into **8** were of no avail.

As an alternative avenue, the strategy (Scheme 3) based upon the intramolecular carbonyl-ene reaction [23] of **11** was undertaken. Preparation of the key precursor **11** as depicted in Scheme 3. LDA-promoted allylation of **12** [21]

FIGURE 1: Naturally occurring benzo[*b*]fluorenones.

with allyl bromide **13a** furnished **14a**. Characteristic multiplets at δ 5.6 and two doublets at δ 5.1 and δ 4.87 in ¹H NMR spectrum were in complete agreement with the structure **14a**. The *cis*-relationship between the angular allyl group and the methano bridge was inferred by comparing the NMR signals of C-4a H of an angularly methylated analog [24]. Flash vacuum pyrolysis (FVP) of the adduct **14a** at 475°C/0.01 mm gave enone **5c** in sufficiently pure form for the next use. It was then subjected to conjugate addition with nitromethane in the presence of DBU to produce allylated nitro adduct **15a** as a single isomer in 92% yield (Scheme 3). Similarly, precursor **15b** was obtained in three steps from **12**. Methallylation of **12** with methallyl iodide **13b** in the presence of LDA gave **14b** (91%), FVP of which furnished **5d**. Addition of nitromethane to **5d** in the presence of DBU furnished intermediate **15b** in 80% yield. Nef reaction [25] of **15b** with NaOMe and TiCl₃-buffer provided aldehyde **11** in moderate yield (50%). The singlet at δ 9.94 in ¹H NMR spectrum and the band at 1718 cm⁻¹ in IR spectrum confirmed the presence of CHO functionality in **11**. When a solution of the aldehyde in dichloromethane was treated with SnCl₄·5H₂O [26], D-ring aromatized compound **6** was formed in 45% yield.

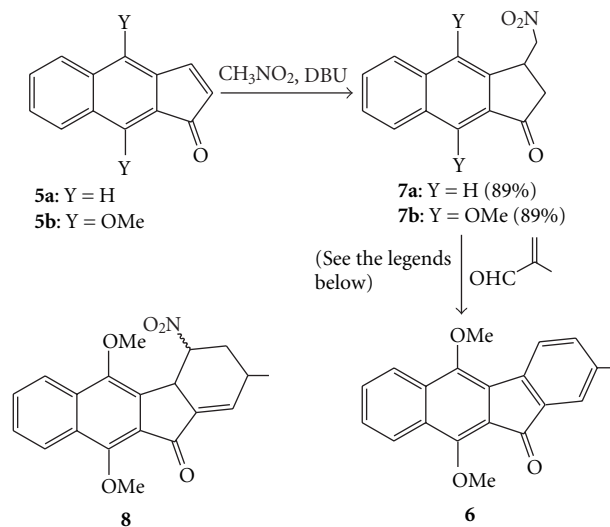
3. Conclusion

We have validated two synthetic routes to benzo[*b*]fluoren-11-ones from benz[*f*]indenones **5**. The intramolecular carbonyl-ene reaction of the intermediate **11** (Scheme 3) proved to be better pathway than the tandem Michael-aldol route (Scheme 2) to benzo[*b*]fluoren-11-one **6**.

4. Experimental

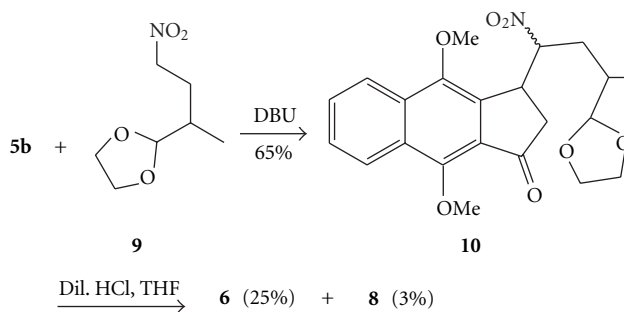
The general experimental is described in [27].

*Benz[*f*]inden-1-one 5c*. This compound was prepared from **14a**. Mp: 80–85°C; yellow; yield 93%; IR (cm⁻¹): 1684; ¹H



- (i) DBU, 0°C-rt, 24 h, **6**, 25%;
- (ii) Et₃N, CHCl₃, 0°C-rt, 24 h, **6**, 18%;
- (iii) *i*-Pr₂NH, CHCl₃, reflux, 6 h, **6**, 15%;
- (iv) *n*-Bu₃P, C₆H₆, 24 h, 0°C-rt, **6**, 18%;
- (v) *t*-BuOLi, THF, -65°C-rt, intractable mixture;
- (vi) *t*-BuOK, *t*-BuOH, 0°C-rt, intractable mixture

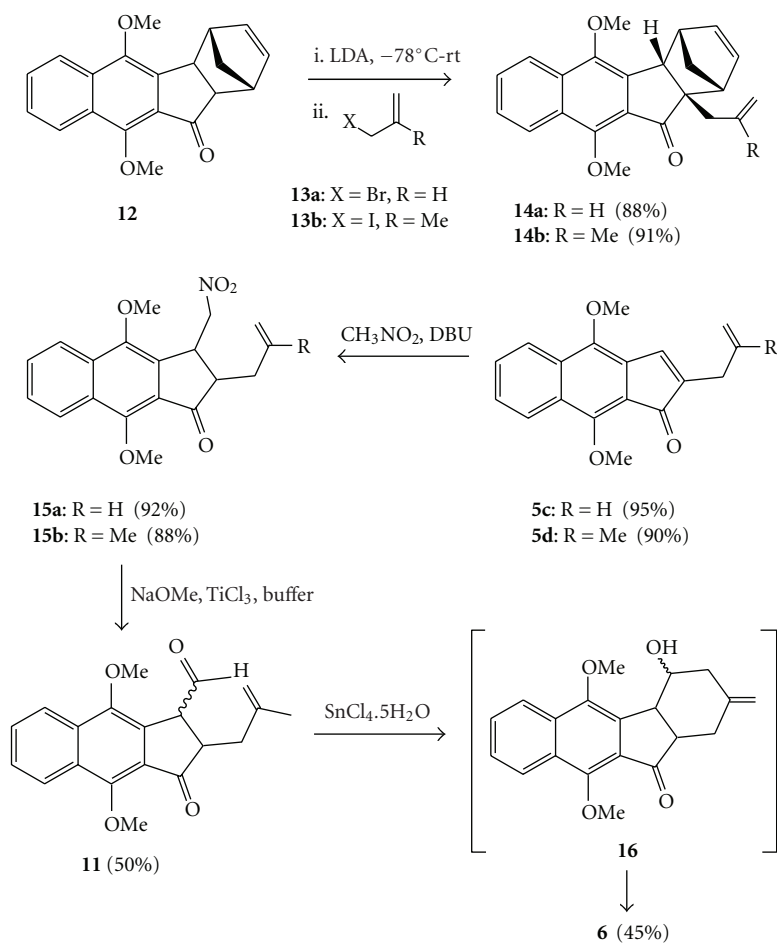
SCHEME 1: Michael-aldol sequence.



SCHEME 2: Michael-aldol sequence.

NMR (200 MHz), 8.20 (d, 1H, *J* = 8.1), 7.97 (d, 1H, *J* = 8.1), 7.57–7.41 (m, 3H), 6.01–5.88 (m, 1H), 5.23–5.12 (m, 2H), 4.28 (s, 3H), 4.02 (s, 3H), 3.11–3.07 (m, 2H); ¹³C NMR (50 MHz): 193.99, 152.2, 144.6, 141.5, 139.8, 134.5, 132.9, 131.1, 129.4, 127.1, 126.2, 125.7, 123.0, 117.1, 115.5, 62.8, 62.7, 29.5; MS (*m/z*): 280 (M⁺, 100%), 265, 250, 223, 178, 165.

*Benz[*f*]inden-1-one 5d*. This compound was prepared as a yellow oil in 90% yield from **14b**. IR (cm⁻¹): 1689; ¹H NMR (300 MHz): 8.10 (d, 1H, *J* = 8.1), 7.97 (d, 1H, *J* = 8.1), 7.60–7.40 (m, 3H), 4.85 (d, 2H, *J* = 10.8), 4.28 (s, 3H), 4.02 (s, 3H), 3.04 (s, 2H), 1.79 (s, 3H); ¹³C NMR (75 MHz): 192.9, 152.0, 144.5, 142.6, 140.9, 140.4, 132.7, 131.0, 129.3, 127.0, 126.0, 125.6, 122.9, 115.3, 112.5, 62.9, 62.7, 33.3, 22.5; MS (*m/z*): 294 (M⁺, 100%), 279, 263, 236, 165, 152, 139.



SCHEME 3: Intramolecular carbonyl-ene approach.

Benzo[b]fluorenone 6: Method A. To a stirred solution of the nitro compound **7a** (100 mg, 0.33 mmol), and methacrolein (60 mg, 0.86 mmol) in benzene (5 mL) at 0°C was added DBU (10 mg, 0.066 mmol). Stirring was continued for 24 hours at rt. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated sodium bicarbonate solution (10 mL) and then with brine (10 mL). The organic phase was dried (Na₂SO₄) and concentrated. The resulting residue was purified by preparative TLC to give a yellow crystalline solid of **6** (26 mg, 25%).

Method B. To a stirred solution of aldehyde **11** (50 mg, 0.154 mmol) in dichloromethane (6 mL) was added SnCl₄·5H₂O (5 mg) under nitrogen atmosphere. The stirring was continued for 30 hours. After usual work up of the reaction mixture, the residue was purified by preparative TLC to provide **6** (21 mg, 45%). Mp: 150-151°C; IR (cm⁻¹): 1695; ¹H NMR (200 MHz): 8.29 (d, 1H, J = 7.4), 8.04 (d, 1H, J = 7.4), 7.88 (d, 1H, J = 7.7), 7.65–7.36 (m, 4H), 4.28 (s, 3H), 4.00 (s, 3H), 2.42 (s, 3H); ¹³C NMR (50 MHz): 190.4, 153.7, 146.4, 140.0, 138.8, 136.4, 135.4, 133.6, 130.8, 129.4, 127.8, 126.7, 125.5, 124.4, 124.1, 122.4, 119.9, 63.1, 61.1, 21.3; MS (m/z): 304 (M⁺, 100%), 289, 218, 189, 149, 57.

Compound 7a. This was prepared from benzindenone **5a** and nitromethane in 89% yield according to the procedure described earlier [25]. Mp: 124°C; IR (cm⁻¹): 1711; ¹H NMR (200 MHz): 8.37 (s, 1H, ArH) 8.03 (d, 1H, J = 8.1), 7.89–7.87 (m, 2H), 7.68–7.54 (m, 2H), 4.91–4.82 (ABq, 1H, J = 12.8, 5.8), 4.64–4.53 (ABq, 1H, J = 12.8, 5.8), 4.42–4.34 (m, 1H), 3.21–3.07 (ABq, 1H, J = 19.2, 8.2), 2.74–2.63 (ABq, 1H, J = 19.2, 3.9).

Compound 7b. This was prepared from **5b**, following the procedure described for compound **7a**. Mp: 179-180°C; white solid; yield: 89%; IR (cm⁻¹): 1715; ¹H NMR (200 MHz): 8.40 (d, 1H, J = 8.2), 8.10 (d, 1H, J = 8.5), 7.74–7.55 (m, 2H), 5.34–5.29 (m, 1H), 4.43–4.38 (m, 2H), 4.18 (s, 3H), 4.03 (s, 3H) 3.17–3.04 (m, 1H), 2.76–2.65 (m, 1H); ¹³C NMR (50 MHz): 200.4, 152.9, 148.6, 134.1, 132.7, 129.7, 126.9, 125.3, 122.7, 121.8, 77.8, 77.2, 63.4, 61.8, 42.3, 34.4; MS (m/z): 301 (M⁺), 254, 239, 197, 141, 115.

Compound 8. To a mixture of enone **5b** (0.178 g, 0.740 mmol) and 1,1-ethanediyldioxy-2-methyl-4-nitrobutane **9** (0.389 g, 2.22 mmol) in CH₂Cl₂ (4 mL) was added DBU (12 mg, 0.078 mmol) and the mixture was stirred at rt

for 6 hours. It was then concentrated and purified by column chromatography to afford **10** as an oil (0.2 g, 65%). ^1H NMR spectrum revealed the presence of two isomers as indicated by three signals δ 4.15, 4.08, and 4.05, corresponding to the methoxy groups. The peak at δ 4.15 was not resolved. The methine hydrogens of CHNO_2 appeared at δ 5.19. To a stirred solution of above nitro acetal **10** (100 mg, 0.24 mmol) in THF (8 mL) was added 10% HCl (1 mL) solution. Stirring was continued for 20 hours. After usual work up of the reaction mixture, the residue was chromatographed to afford **6** (18 mg, 25%) and **8** (2.5 mg, 3%).

Compound 9. Yield: 50%; colorless oil; IR (cm^{-1}): 1541; ^1H NMR (200 MHz): 4.66 (d, 1H, $J = 4$), 4.46 (t, 2H, $J = 6$), 3.98–3.79 (m, 4H), 2.30–1.77 (m, 3H), 1.00 (d, 3H, $J = 6.7$); ^{13}C NMR (50 MHz): 106.8, 74.1, 65.1, 65.0, 34.3, 29.0, 14.7.

Compound 11. This was prepared from compound **15b** by Nef reaction [25]. Yield: 50%; purity > 80%; ^1H NMR (500 MHz): 9.94 (s, 1H), 8.40 (d, 1H, $J = 8.4$), 8.10 (d, 1H, $J = 8.4$), 7.69 (t, 1H, $J = 8.2$), 7.52 (t, 1H, $J = 8.2$), 4.87 (s, 1H), 4.78 (s, 2H), 4.21 (s, 3H), 4.16 (brs, 1H), 4.02 (s, 3H) 3.31–3.27 (m, 1H); 2.78–2.75 (ABq, 1H, $J = 14.0$, 4.3) 1.75 (s, 3H).

Compound 12. ^1H NMR (200 MHz): 8.37 (d, 1H, $J = 8.0$, 1H), 8.05 (d, 1H, $J = 8.0$, 1H), 7.68–7.51 (m, 2H), 6.85 (brs, 1H), 4.80–4.60 (m, 1H), 4.32 (s, 3H), 3.70 (s, 3H), 2.85 (brs, 1H), 2.22–2.15 (m, 1H), 1.5–1.4 (m, 2H), 1.25–1.21 (m, 3H).

Compound 14a. This was prepared as thick brownish oil in 88% yield from pentacycle **12**, following an earlier method [24]. IR (cm^{-1}): 1705; ^1H NMR (300 MHz): 8.33 (d, 1H, $J = 8.7$), 8.06 (d, 1H, $J = 8.4$), 7.61 (m, 1H), 7.49 (m, 1H), 6.05–6.02 (m, 1H), 5.65–5.50 (m, 2H), 5.07 (d, 1H, $J = 16.8$), 4.85 (d, 1H, $J = 10.2$), 4.08 (s, 3H), 4.03 (s, 3H), 3.78 (d, 1H, $J = 4.2$), 3.45 (brs, 1H), 2.89–2.91 (m, 2H), 2.45–2.38 (m, 1H), 2.0 (ABd, 1H, $J = 8.7$), 1.80 (ABd, 1H, $J = 8.7$); ^{13}C NMR (75 MHz): 207.1, 151.2, 147.6, 138.0, 135.2, 135.1, 134.3, 132.4, 128.9, 126.6, 125.8, 125.0, 121.8, 117.5, 63.0, 62.4, 62.1, 50.8, 50.9, 47.0, 46.6, 41.6.

Compound 14b. This was prepared from pentacycle **12**, following the procedure adopted for compound **14a**. Yield: 89%; thick oil; IR (cm^{-1}): 1705; ^1H NMR (400 MHz): 8.32 (d, 1H, $J = 8.1$), 8.07 (d, 1H, $J = 8.1$), 7.62 (br t, 1H), 7.49 (br t, 1H), 6.00 (dd, 1H, $J = 2.8$, 5.6), 5.49 (dd, 1H, $J = 2.8$, 5.6), 4.70 (brs, 1H), 4.66 (brs, 1H), 4.08 (s, 3H), 4.03 (s, 3H), 3.93 (d, 1H, $J = 4$), 3.44 (brs, 1H), 3.05 (ABd, 1H, $J = 13.8$), 2.94 (brs, 1H), 2.41 (ABd, 1H, $J = 13.8$), 1.98 (ABd, 1H, $J = 8.8$), 1.79 (ABd, 1H, $J = 8.8$), 1.46 (s, 3H); ^{13}C NMR (50 MHz): 207.4, 151.0, 147.6, 143.1, 138.3, 135.5, 135.3, 134.6, 132.3, 128.8, 126.7, 125.8, 125.0, 121.8, 114.3, 62.8, 61.8, 61.6, 52.5, 50.8, 46.8, 46.1, 45.7, 23.8.

Compound 15a. This was prepared from **5c**, following the procedure described for compound **7a**. Mp: 98–99°C; white solid; yield: 92%; IR (cm^{-1}): 1712; ^1H NMR (300 MHz): 8.40

(d, 1H, $J = 8.7$), 8.10 (d, 1H, $J = 8.4$), 7.72–7.66 (m, 1H), 7.58 (m, 1H), 5.75–5.61 (m, 1H), 5.23–5.04 (m, 3H), 4.54–4.47 (m, 1H), 4.20 (s, 3H), 4.10 4.05 (m, 1H), 4.01 (s, 3H), 2.83–2.78 (m, 1H); 2.65–2.51 (m, 2H); ^{13}C NMR (75 MHz): 202.7, 153.1, 148.7, 133.8, 133.3, 133.0, 129.8, 127.0, 125.4, 122.3, 121.9, 118.8, 77.7, 77.3, 63.4, 61.8, 52.2, 39.4, 36.1; MS (m/z): 341 (M+), 307, 290, 280 (100%), 265, 165.

Compound 15b. This was prepared from **5d**, following the procedure adopted for compound **7a**. Mp: 122–123°C; white solid; yield: 90%; IR (cm^{-1}): 1707; ^1H NMR (300 MHz): 8.41 (d, 1H, $J = 8.4$), 8.10 (d, 1H, $J = 8.4$), 7.72–7.60 (m, 1H), 7.61–7.55 (m, 1H), 5.07 (dd, 1H, $J = 12.8$, 4.2), 4.88 (s, 1H), 4.76 (s, 1H), 4.59 (dd, 1H, $J = 12.8$, 8.7), 4.20 (s, 3H), 4.15–3.90 (m, 1H), 4.00 (s, 3H), 2.95–2.88 (m, 1H); 2.63 (dd, 1H, $J = 13.8$, 5.1), 2.34 (dd, 1H, $J = 13.8$, 9.0), 1.73 (s, 3H); ^{13}C NMR (75 MHz): 202.8, 153.3, 148.8, 142.5, 133.3, 132.9, 129.9, 129.8, 126.9, 125.3, 122.0, 114.2, 77.8, 63.3, 61.9, 50.8, 40.5, 39.9, 21.9. MS (m/z): 355 (M+), 319, 304, 294 (100%), 279, 265, 253, 236, 223, 165, 152, 139; anal. calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_5$: C, 67.59; H, 5.96; N, 3.94, found C, 67.51; H, 5.93; N, 3.93.

Acknowledgments

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