New Tandem Cyclo- and/or Addition Reactions between *N*-Arylisoindolines with Benzyne and Dimethyl Acetylenedicarboxylate

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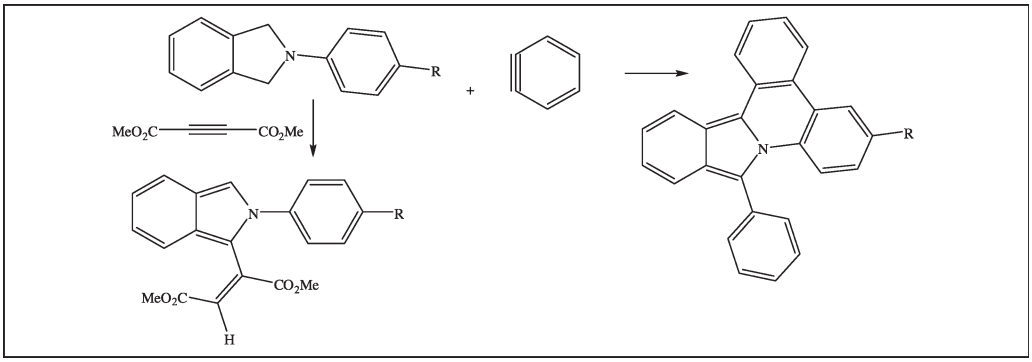

Reaction of *N*-arylisoindolines with benzyne afforded predominantly 10-arylisoindolo[2,1-*f*]phenanthridines. On the other hand, *N*-arylisoindolines react with dimethyl acetylenedicarboxylate to give dimethyl 2-(2-aryl-2*H*-isoindol-1-yl)fumarates. Possible reaction mechanisms are discussed.

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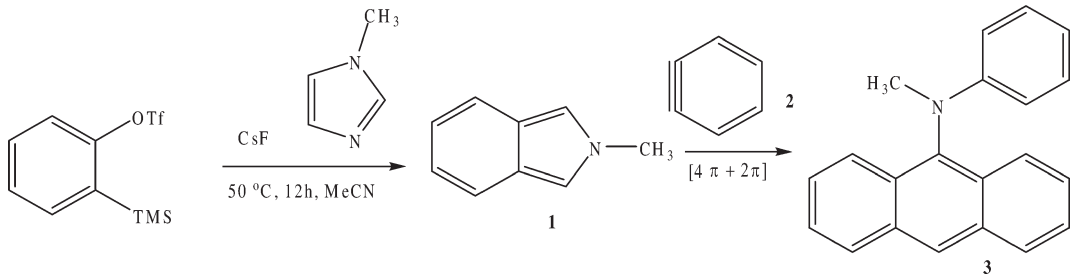
INTRODUCTION

Previously, it was demonstrated that *N*-arylisoindolines underwent charge-transfer complexation [1,2] and deep seated chemical transformations with 1,4-benzo- or 1,4-naphthoquinones [2] under initial α-H-atom abstraction to give α-oxygenated products [3,4]. Also and in a multistep reaction, 3,3′-(2-aryl-2*H*-isoindol-1,3-ylene)-di-(1,4-naphthoquinone-2-carbonitriles) have been formed in 25–61% yield from a series of *N*-aryl-isoindolines with (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile in aerated pyridine [5]. On the other side, *N*-arylisoindolines react with ethenetetracarbonitrile (TCNE) in aerated benzene with the formation of [3-(2-aryl-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-ylidene)-2-aryl-2,3-dihydro-1*H*-isoindol-1-ylidene]propanedinitriles, *N*-aryl-3-dicyanomethylene-isoindol-2-ones, and *N*-aryl-phthalimides as well as ethanetetracarbonitrile [4,6]. The highly reactive parent system, benzyne, reacts with imine compounds to give (*o*-anilinobenzyhydryl)-aniline [7] and phenanthridine derivatives [8] as well as acridines [8] *via* [2π + 2π] and/or [4π + 2π] cycloaddition reactions. We investigated the cycloaddition reactions of aromatic diimines [9], azomethine compounds having [2.2]paracyclophane [10] and ethenyl-[2.2]-paracyclophanes [11] with selected dienophiles including benzyne aiming to synthesize various heterocycles and heterophanes. Synthesis of biologically active heterocycles has also been one of our interests [12,13]. Aryne chemistry has been applied to the synthesis of aryl amines in a tandem reaction including two Diels-Alder reactions, with three benzyne molecules reacting with one imidazole molecule (Scheme 1) [14]. The reaction proceeds *via* formation of 2-methyl-2*H*-isoindole (**1**), which reacted with two more molecules of benzyne (**2**) to give the corresponding *N*-methyl-*N*-phenylanthracen-9-amine (**3**, Scheme 1) [14]. Accordingly, we were encouraged to investigate the reaction of *N*-arylisoindolines **4a–d** [2,15] with benzyne (**2**) and dimethyl acetylenedicarboxylate (DMAD, **11**).

RESULTS AND DISCUSSION

Herein, we report the cycloaddition reactions of *N*-arylisoindolines **4a–d** with benzyne (dehydrobenzene, **2**), which was generated by diazotization of 1,2-anthranilic acid [11,16–19]. We chose *N*-arylisoindolines **4a–d** bearing electron donating and withdrawing substituents on the benzene ring, to examine their effect on the course of reaction. Scheme 2 outlines the reaction of **4a–d** with **2** in dry acetonitrile under N_2 atmosphere.

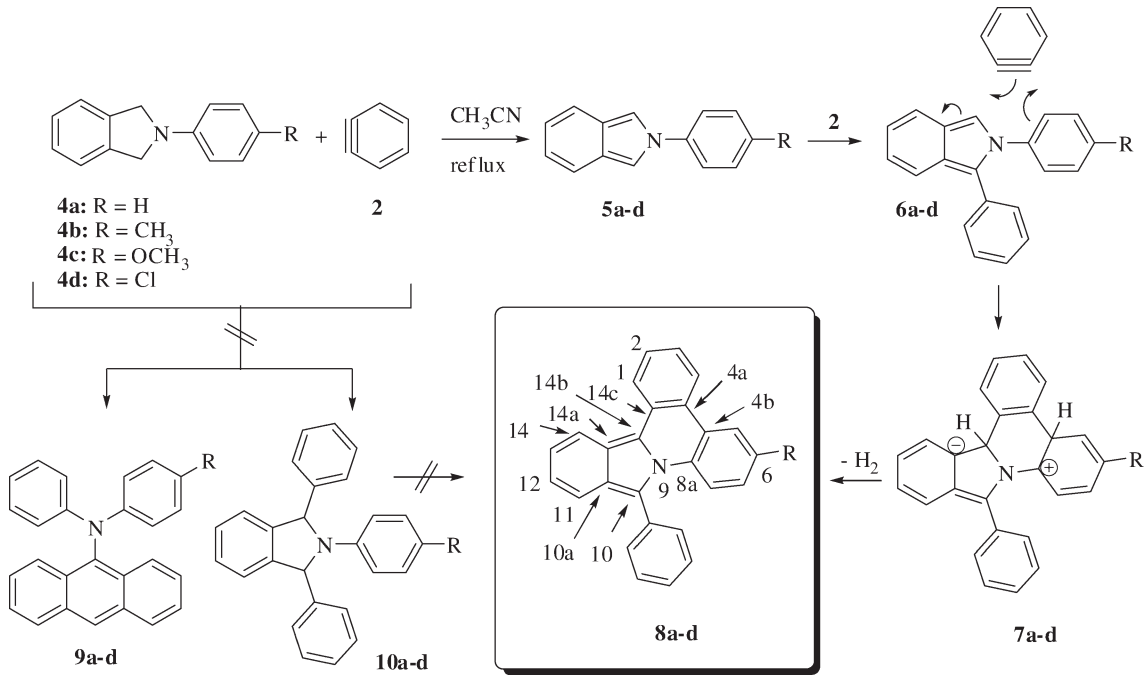
Scheme 1. Reaction of *N*-methylisoindolone with benzene.



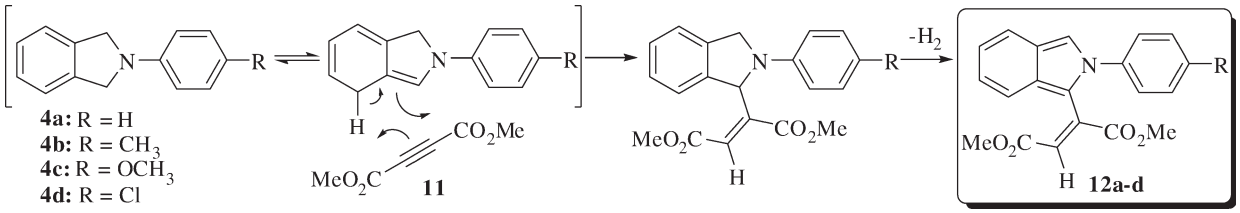
The reaction proceeded to yield, after chromatographic purification and recrystallization, compounds **8a–d** (58–68%) (Scheme 2). The NMR and mass spectra, and elemental analyses, confirm the addition of two molecules of **2** to **4** (Scheme 2).

NMR spectra confirmed the absence of the isoindoline CH_2 protons and their corresponding carbons. In **8a**, a double-doublet at $\delta_H = 8.46$ corresponded to H-11 ($J =$ 7.8, 1.2 Hz). Another multiplet at $\delta_H = 8.40$–8.34 was assigned to H-8,12,13,14. Another two double-doublets at $\delta_H = 8.00$ and 7.76 corresponded to H-5 and H-4 ($J =$ 7.8, 1.2 Hz), respectively. The ^{13}C NMR spectrum of **8a** showed C-14b, C-10a, C-4a, C-8a at $\delta_C = 150.2$, 141.0, 137.4, and 131.0, respectively. The absence of the symmetrical anthracene ring system from the ^{13}C NMR spectra [20] excluded the formation of compounds **9a-d**. One can also envision that the regioisomers **10a–d** might be formed. Of compounds **10a–d,** 1,2,3-triphenylisoindole (**10a**) is known [21]. However, the NMR spectra of **10a** should show the molecular symmetry, which is absent from **8a**. Autoxidation of **10a** is reported to give ring opening, not closure to **8a** [22]; thus, we exclude **10a–d** as intermediates in our pathways leading to **8a–d**. Published syntheses of isoindoles from isoindolines proceed *via N*-oxidation, followed by *O*-acylation and elimination [17,23]. However, benzyne is reported to oxidize dihydropyridines to pyridines [24], presumably by a hydrogen-transfer mechanism like a diimide reduction. We, therefore, propose that **2** oxidizes isoindolines **4a–d** to the corresponding isoindoles **5a–d**, which undergo electrophilic substitution by **2,** selectively at C-1 [25], to give compounds **6a–d**. (The order of these steps may be reversed: see below) Subsequently, compounds **6a–d** react with a second molecule of **2** by intermolecular cycloaddition, followed by oxidation *in situ* to produce the stable heterocyclic compounds **8a–d**. Interestingly, the reaction of isoindolines having electron-donating substituents in the arylidene groups, such as **4b** and **4c**, with

Scheme 2. Reaction of *N*-arylisoindolines **4a–d** with benzyne (**2**). **8a**: 6 h, 62%; **8b**: 8 h, 64%; **8c**: 4 h, 68%; **8d**: 10 h, 58%.



Scheme 3. Reaction of *N*-arylisoindolines **4a–d** with DMAD (11). **12a**: 14 h, 82%; **12b**: 14 h, 82%; **12c**: 12 h, 87%; **12d**: 18 h, 78%.



2 yielded the main products **8b**,**c** in higher percentage yields compared with **8d**.

Surprisingly, the reactions of **4a–d** with dimethyl acetylenedicarboxylate (DMAD, **11**), in refluxing ethanol, afforded dimethyl 2(2-aryl-2*H*-isoindole-1-yl)fumarates **12a–d** (Scheme 3). Structure **12a** has formula $C_{20}H_{17}NO_4$, consistent with the molecular ion of m/z = 335. The ^{1}H NMR spectrum of **12a** showed the two methyl esters as two singlets at δ_H = 3.86 and 3.78. Another singlet at δ_H = 7.00 denoted the vinylic H of the ethylenic bond. The ^{13}C NMR spectrum of **12a** showed two carbonyl carbons at δ_C = 170.0 and 168.5. The remaining carbons of **12a** showed signals at δ_C = 138.9, 138.4, 127.6, 123.2, 120.5, 120.0, 118.8, 116.2, 115.2, 112.8, 102.0, 52.0, and 51.7 corresponding to (Ar-C—N), (vinylic-C-2′), (Ar-CH-6), (Ar-CH-7), (Ar-CH-5), (C-1), (Ar-CH-4), (CH-3), (C-3a), (vinylic-CH-1′), (C-7a), (ester-CH3) and (ester-CH_3), respectively. Formally, compounds **12a–d** arise by ene reaction between **11** and a tautomer of **4a–d**, followed by oxidation (Scheme 3). The same kind of sequence can be written for reaction of **4a–d** with benzyne, which would lead the substitution invoked above (Scheme 2) to occur before oxidation.

CONCLUSIONS

In conclusion, *N*-arylisoindolines react with benzyne to form arylisoindolophenanthridines and with DMAD to form (2-aryl-2*H*-isoindol-1-yl)fumarates. The mechanisms of these transformations are uncertain but appear to involve both concerted reactions and oxidations.

EXPERIMENTAL SECTION

General. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured in deuterochloroform solutions on Bruker AM-400 or AV-400 spectrometers (400.13 MHz for 1H and 100.6 MHz for 13C). The AV-400 was purchased with assistance from the National Science Foundation (CHE 03-42251). For preparative thin layer chromatography (PLC), glass plates (20 × 48 cm) were covered with a slurry of silica gel Merck PF_{254} and air-dried using the solvents listed for development. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm UV light. Elemental analyses were carried in Assiut Microanalysis Center of Assiut University. Mass spectroscopy was performed with a Finnigan Mat 8430 spectrometer at 70 eV Institute of Organic Chemistry, TU-Braunschweig. Germany. IR spectra were run on a Shimadzu 470 spectrometer using KBr pellets.

Starting materials. 2-Aryl-2,3-dihydro-1*H*-isoindoles **4a–d** were prepared according to published procedures [2,15]. Dimethyl acetylene-dicarboxylate (DMAD, **10**) was bought from Fluka.

Reaction of isoindolines 4a-d with benzyne (2). Benzenediazonium carboxylate was prepared by the procedure described in [16–19]. Under nitrogen atmosphere, 6 mmol of benzyne (**2**) precursor was slowly added to the stirred and refluxed solutions of **4a–d** (2 mmol) in dry acetonitrile (250 mL) for 1 h. The reaction mixture was refluxed till the consumption of the starting materials was completed (reaction progress monitored by TLC analysis) in 4–10 h. The solvent was concentrated and the residue was filtered off. The precipitate was washed with dichloromethane (200 mL). The filtrate was then concentrated in vacuum and the residue was applied to PLC using toluene as an eluent. The migrating zones contained the products **8a–d** were recrystallized from the stated solvents. All zones were extracted with acetone and the products recovered.

10-Phenylisoindolo[2,1-f]phenathridines (8a). Yellow crystals (0.213 g, 62%), mp 240°C (ethanol); [Found: C, 90.80; H, 4.90; N, 4.00. $C_{26}H_{17}NO$ requires C, 90.93; H, 4.99; N, 4.08%]; ν_{max} (potassium bromide) 3030–3000 (m, Ar-CH), 1580 (m, olefinic-CH) cm^{-1}; δ_H = 8.46 (dd, J = 7.8, 1.2 Hz, 1H, H-11), 8.40–8.34 (m, 4H, H-8,12,13,14), 8.00 (dd, J = 7.8, 1.2 Hz, 1H, H-5), 7.76 (dd, J = 7.8, 1.2 Hz, 1H, H-4), 7.60–7.58 (m, 6H, Ar-H), 7.50–7.38 (m, 4H, Ar-H); δ_C = 150.2 (C-14b), 141.0 (C-10a), 137.4 (C-4a), 133.4 (Ph-C), 131.0 (C-8a), 130.0 (Ar-CH-*p*), 129.2 (Ar-CH-*p*), 128.6 (Ar-2CH-*m*), 128.4 (Ar-2CH-*o*), 128.0, 127.6, 127.4, 127.0, 126.6 (Ar-CH), 126.4 (C-14a), 125.9, 125.6 (Ar-CH), 124.8 (C-4b), 124.0 (CH-11), 123.4 (CH-12), 123.0 (CH-13), 122.8 (CH-14), 118.0 (C-14c), 116.8 (C-10); m/z (70 eV, EI): 343 [M$^+$] (100), 266 (30), 242 (18), 192 (20), 168 (28), 92 (20), 78 (24%).

6-Methyl-10-phenylisoindolo[2,1-f]phenathridines (8b). Yellow crystals **8b** (0.229 g, 64%), mp 260°C (methanol); [Found: C, 90.60; H, 5.39; N, 4.08. $C_{27}H_{19}N$ requires C, 90.72; H, 5.36; N, 3.92%]; ν_{max} (potassium bromide): 3065–3008 (m, Ar-CH), 2980–2870 (w, aliph.—CH), 1582 (m, olefinic-CH) cm^{-1}; δ_H = 8.38 (dd, J = 7.6, 1.2 Hz, 2H, H-11,14), 8.40–8.28 (m, 2H, H-12,13), 7.86 (m, 2H, H-5,4), 7.76–7.52 (6H, m), 7.40–7.30 (4H, m), 2.34 (s, 3H, CH_3); δ_C = 149.6 (C-14b), 141.2 (C-10a), 137.0 (C-4a), 133.0, 132.6 (Ar-C), 128.9 (C-8a), 128.4 (Ar-CH-*p*), 127.6 (Ar-2CH-*m*), 127.0 (Ar-2CH-*o*), 126.9 (C-14a), 126.6, 126.2, 125.8, 125.6, 125.4, 125.0, 124.8 (Ar-CH), 124.4 (C-4b), 124.0 (CH-11),

123.6 (CH-12), 123.2 (CH-13), 122.6 (CH-14), 118.2 (C-14c), 116.6 (C-10), 21.8 (CH_3); m/z (70 eV, EI): 357 [M+] (100), 342 (26), 264 (28), 242 (28), 190 (26), 168 (32), 92 (32), 78 (44%).

6-Methoxy-10-phenylisoindolo[2,1-f]phenathridines (8c). Yellow crystals (0.254 g, 68%), mp 290°C (acetonitrile); [Found: C, 86.70; H, 5.10; N, 3.68. $C_{27}H_{19}NO$ requires C, 86.84; H, 5.13; N, 3.75%]; ν_{max} (potassium bromide) 3080–3012 (m, Ar-CH), 2988–2860 (m, aliph.—CH), 1590 (s, olefinic-CH) cm^{-1}; δ_H = 8.38 (dd, J = 7.6, 1.0 Hz, 2H, H-11,14), 8.30–8.20 (m, 2H, H-12,13), 7.94 (t, J = 7.8 Hz, 1H, H-8), 7.90 (dd, J = 7.8, 1.2 Hz, 1H, H-1), 7.80 (dd, J = 7.8, 1.2 Hz, 2H, H-5,4), 7.52–7.40 (6H, m), 7.30–7.18 (2H, m), 3.90 (s, 3H, OCH_3); δ_C = 158.0 (H_3CO-Ar-C), 148.0 (C-14b), 141.2 (C-10a), 135.8 (C-4a), 133.2 (Ph-C), 128.6 (Ph-CH-*p*), 128.0 (Ph-2CH-*m*), 127.2 (Ph-2CH-*o*), 127.0 (C-8a), 126.9 (C-14a), 126.8, 126.6, 126.0, 125.4, 125.0 (Ar-CH), 124.6 (C-4b), 123.8 (CH-11), 123.6 (CH-12), 123.0 (CH-13), 122.8 (CH-14), 122.6 (CH-7), 117.6 (C-14c), 115.0 (C-10), 104.0 (CH-5), 55.8 (OCH_3); m/z (70 eV, EI): 373 [M^+] (100), 356 (18), 342 (26), 264 (28), 242 (30), 190 (34), 168 (22), 109 (22), 92 (30), 78 (34%).

6-Chloro-10-phenylisoindolo[2,1-f]phenathridines (8d). Yellow crystals (0.219 g, 58%), mp 250°C (ethyl acetate); [Found: C, 82.50; H, 4.20; Cl, 9.50; N, 3.62. $C_{26}H_{16}ClN$ requires C, 82.64; H, 4.27; Cl, 9.38; N, 3.71%]; ν_{max} (potassium bromide) 3060–3009 (m, Ar-CH), 1585 (s, olefinic-CH) cm^{-1}; δ_H = 8.45 (dd, J = 7.8, 1.2 Hz, 2H, H-8), 8.30 (t, J = 7.6 Hz, 1H, H-14), 8.20 (t, J = 7.6 Hz, 1H, H-11), 8.08 (t, J = 7.6 Hz, 1H, H-13), 8.04 (dd, J = 7.6, 1.2 Hz,, 1H, H-5), 7.90–7.64 (10H, m); δ_C = 149.0 (C-14b), 141.6 (C-10a), 136.2 (C-4a), 133.4 (Ph-C), 130.6 (CH-3), 131.2 (CH-7), 130.0 (CH-8), 129.6 (CH-2), 129.4 (C-8a), 129.2 (Ar-2CH-*m*), 128.6 (CH-1), 128.4 (Ar-CH-*p*), 128.0 (CH-1), 127.8 (Ar-2CH-*o*), 127.0 (Ar-C—Cl), 126.6 (C-14a), 125.8 (C-4b), 124.0 (CH-14), 123.6 (CH-5), 123.2 (CH-11), 123.0 (CH-12), 122.8 (CH-13), 119.2 (C-14c), 116.0 (C-10); m/z (70 eV, EI): 378 [M+1] (30), 377 [M^+] (100), 344 (23), 342 (34), 266 (28), 242 (20), 192 (26), 168 (30), 112 (28), 92 (20), 78 (24%).

Reaction of isoindolines 4a–d with dimethyl acetylenedicarboxylate (DMAD, 11). A mixture of **4a–d** (1 mmol) with **11** (0.142 g, 1 mmol) in absolute ethanol (50 mL) was refluxed for 12–18 h (the reaction was followed by TLC analysis). The solvent was removed under vacuum. The residue was applied on column chromatography (silica gel) using dichloromethane as eluent. The separated products **12a–d** were recrystallized from the stated solvents.

Dimethyl 2-(2-phenyl-2H-isoindol-1-yl)fumarate (12a). Yellow crystals (0.275 g, 82%), mp 220°C (methanol); [Found: C, 71.50; H, 5.08; N, 4.18. $C_{20}H_{17}NO_4$ requires C, 71.63; H, 5.11; N, 4.18%]; ν_{max} (potassium bromide): 3090–3008 (m, Ar-CH), 2980–2860 (m, aliph.—CH), 1730–1712 (br, s, CO), 1586 (s, olefinic-CH) cm^{-1}; δ_H = 8.38 (t, J = 7.6 Hz, 1H, H-4), 8.30 (t, J = 7.8 Hz, 1H, H-6), 8.10 (dd, J = 7.8, 1.2 Hz, 1H, H-5), 8.06 (dd, J = 7.6, 1.2 Hz, 1H, H-5), 7.36–7.20 (5H, m), 7.00 (s, 1H, vinylic-H-2′), 6.96 (s, 1H, H-3), 3.86 (s, 3H, CH_3-ester), 3.78 (s, 3H, CH_3-ester); δ_C = 170.0 (CO-ester), 168.5 (CO-ester), 138.9 (Ar-C—N), 138.4 (vinylic-C-2′), 129.0 (Ph-2CH-*m*), 126.8 (Ar-CH-*p*), 127.6 (Ar-CH-6), 122.4 (Ar-2CH-*o*), 123.2 (Ar-CH-7), 120.5 (Ar-CH-5), 120.0 (C-1), 118.8 (Ar-CH-4), 116.2 (CH-3), 115.2 (C-3a), 112.8 (vinylic-CH-1′), 102.0 (C-7a), 52.0 (ester-CH_3), 51.7 (ester-CH_3); m/z (70 eV, EI): 335 [M^+] (100), 320 (22), 305 (24), 277 (18), 266 (30), 250 (18), 212 (40), 192 (20), 168 (28), 92 (20), 78 (24%).

Dimethyl 2-(2-(4′-methylphenyl)-2H-isoindol-1-yl)fumarate (12b). Yellow crystals (0.293 g, 84%), mp 240°C (ethanol); [Found: C, 72.30; H, 5.34; N, 4.00. $C_{21}H_{19}NO_4$ requires C, 72.19; H, 5.48; N, 4.01%]; ν_{max} (potassium bromide) 3085–3008 (m, Ar-CH), 2982–2840 (m, aliph.—CH), 1728–1715 (br, s, CO), 1586 (s, olefinic-CH) cm^{-1}; δ_H = 8.36 (t, J = 7.8 Hz, 1H, H-4), 8.32 (t, J = 7.6 Hz, 1H, H-6), 8.08 (dd, J = 7.8, 1.2 Hz, 1H, H-5), 8.00 (dd, J = 7.8, 1.2 Hz, 1H, H-5), 7.36 (d, J = 7.7 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 7.10 (s, 1H, vinylic-H-2′), 6.90 (s, 1H, H-3), 3.90 (s, 3H, CH_3-ester), 3.86 (s, 3H, CH_3-ester), 2.34 (s, 3H, CH_3-Ar); δ_C = 169.4 (CO-ester), 168.8 (CO-ester), 138.6 (Ar-C—N), 138.2 (vinylic-C-2′), 135.4 (Ar-C), 129.2 (Ph-2CH-m), 127.2 (Ar-CH-6), 124.4 (Ar-2CH-*o*), 123.2 (Ar-CH-7), 120.5 (Ar-CH-5), 120.2 (C-1), 119.2 (Ar-CH-4), 116.4 (CH-3), 115.4 (C-3a), 113.0 (vinylic-CH-1′), 102.2 (C-7a), 52.2 (ester-CH3), 51.2 (ester-CH_3), 22.4 (Ar-CH_3) m/z (70 eV, EI): 349 [M^+] (100), 335 (24), 320 (20), 304 (18), 276 (26), 266 (30), 250 (18), 207 (34), 192 (20), 168 (28), 92 (40), 78 (34%).

Dimethyl 2-(2-(4′-methoxyphenyl)-2H-isoindol-1-yl)fumarate (12c). Yellow crystals (0.318 g, 87%), mp 202°C (methanol); [Found: C, 68.90; H, 5.20; N, 3.90. $C_{21}H_{19}NO_5$ requires C, 69.03; H, 5.24; N, 3.83%]; ν_{max} (potassium bromide) 3090–3006 (m, Ar-CH), 2980–2850 (m, aliph.—CH), 1730–1712 (br, s, CO), 1585 (s, olefinic-CH) cm^{-1}; δ_H = 8.40 (t, J = 7.6 Hz, 1H, H-4), 8.34 (t, J = 7.8 Hz, 1H, H-6), 8.12 (dd, J = 7.6, 1.2 Hz, 1H, H-5), 8.05 (dd, J = 7.6, 1.2 Hz, 1H, H-5), 7.56 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 7.8 Hz, 2H), 6.96 (s, 1H, vinylic-H-2′), 6.90 (s, 1H, H-3), 3.92 (s, 3H, CH3-ester), 3.80 (s, 3H, CH_3-ester), 3.92 (s, 3H, CH_3O-Ar); δ_C = 169.7 (CO-ester), 168.2 (CO-ester), 156.9 (CH3O-Ar-C), 138.5 (Ar-C—N), 139.0 (vinylic-C-2′), 127.2 (Ar-CH-6), 124.4 (Ar-2CH-*o*), 123.4 (Ar-CH-7), 120.5 (Ar-CH-5), 120.2 (C-1), 119.6 (Ar-CH-4), 118.2 (Ar-2CH-*m*), 116.4 (CH-3), 115.4 (C-3a), 113.4 (vinylic-CH-1′), 102.2 (C-7a), 52.0 (ester-CH_3), 51.0 (ester-CH_3), 50.8 (Ar-OCH_3); m/z (70 eV, EI): 365 [M^+] (100), 350 (14), 334 (16), 320 (20), 306 (22), 280 (24), 222 (30), 192 (20), 91 (38), 78 (36%).

Dimethyl 2-(2-(4′-chlorophenyl)-2H-isoindol-1-yl)fumarate (12d). Yellow crystals (0.288 g, 78%), mp 162°C (methanol); [Found: C, 64.96; H, 4.36; Cl, 9.59; N, 3.79. $C_{20}H_{16}ClNO_4$ requires C, 64.80; H, 4.30; Cl, 9.70; N, 3.70%]; ν_{max} (potassium bromide): 3060–3005 (m, Ar-CH), 2980-2770 (m, aliph.—CH), 1732–1710 (br, s, CO), 1586 (s, olefinic-CH) cm^{-1}; δ_H = 8.30–8.26 (m, 2H, H-4,7), 8.12–8.08 (m, 2H, H-6,7), 7.42 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 7.03 (s, 1H, H-3), 6.95 (s, 1H, vinylic-H-2′), 3.95 (s, 3H, CH_3-ester), 3.86 (s, 3H, CH_3-ester); δ_C = 170.0 (CO-ester), 169.2 (CO-ester), 136.5 (Ar-C—N), 138.2 (vinylic-C-2′), 131.0 (Ar-C-Cl), 129.0 (Ar-2CH-*o*), 127.0 (Ar-CH-6), 123.2 (Ar-CH-7), 120.4 (Ar-2CH-*m*), 120.3 (Ar-CH-5), 120.0 (C-1), 119.4 (CH-3), 119.2 (Ar-CH-4), 114.4 (C-3a), 112.0 (vinylic-CH-1′), 101.2 (C-7a), 52.4 (ester-CH3), 51.2 (ester-CH3); m/z (70 eV, EI): 370 [M+1] (32), 369 [M^+] (100), 354 (24), 352 (26), 340 (14), 339 (18), 334 (22), 312 (16), 310 (18), 227 (20), 226 (24), 192 (24), 114 (42), 91 (38), 78 (39%).

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