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Preparation of perinones via a novel multicomponent synthesis of isoindole scaffold

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ABSTRACT

A convenient procedure for the preparation of isoindole derivatives is described. The method is based on the multicomponent reaction of heterocyclic ketene aminals with dialkyl acetylenedicarboxylates in presence of DMAP. The reaction is very simple from an experimental point of view and allows the creation of a fused isoindole moiety with concomitant formation of benzene and pyrrole ring in a single operation.

1. Introduction

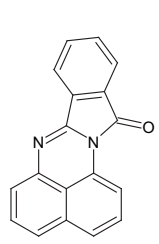
The isoindole moiety has become attractive targets in organic and medicinal chemistry. This heterocyclic framework is an integral part of the structure of some biologically active compounds,[1] dyes and pigments[2] and a few alkaloids.[3] Moreover; isoindoles have been widely used for their fluorescent and electroluminescent properties, which make them attractive candidates for organic light-emitting devices.[4]

Although, the synthesis of heterocycles functionalized with isoindole unit is clearly underdeveloped, recent progress in synthetic organic chemistry has led to the development of new methods for the preparation of diversely substituted isoindoles.[5]

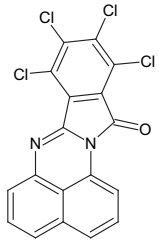
Perinones, fused perimidine compounds of isoindoles, are used as dyes and pigments recommended for a wide range of industrial plastics. They exhibit shades of colour from red to orange, for example, SR 60 and SR 135 are commercial perinone dyes. Moreover SR 180 has been desired with superior heat stability and strength compared to the others perinone dyes.[6] According to literature, these dyes are usually constructed via harsh conditions starting from naphthalene-1,8-diamine and phthalic anhydride derivatives.[2d,7]

As important intermediates, heterocyclic ketene aminals (HKAs), also known as cyclic 1,1-enediamines, have shown great potential for the synthesis of a wide variety of heterocyclic and fused heterocyclic compounds.[8,9] Literature survey revealed that multicomponent reactions (MCRs) constitute an especially attractive synthetic strategy, since they provide easy and rapid access to large libraries of organic compounds with diverse substitution patterns and there are few reports about MCRs of HKAs connotating that reaction of aldehydes and active methylene compounds with HKAs to give pyridinone[8b] and naphthpyridine[10] derivatives.

As part of our current studies on the MCRs to synthesize novel functional heterocycles,[11] we report herein a facile multicomponent synthesis of isoindoles fused perimidine via the reaction between 2-acylmethylene substituted perimidines as HKAs and dialkyl acetylenedicarboxylates (DAAC) in the presence of dimethyl amino pyridine (DMAP).



Solvent Orange 60



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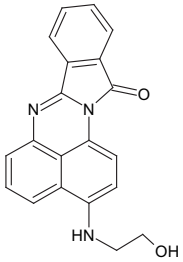

Solvent Red 180

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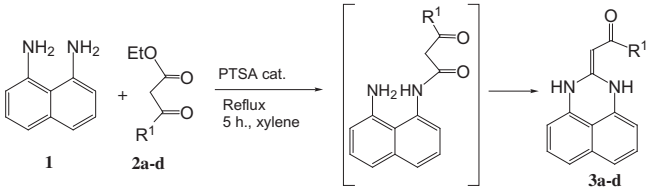
2. Results and discussions

The starting materials, 1*H*-perimidin-2(3*H*)-ylidenes (**3a**,**b**), have been previously reported from the reactions of the corresponding diketene or 3,3-dichloroacryloyl chloride with naphthalene-1,8-diamine.[12] However, compounds **3a**,**b** and the new derivatives **3c**,**d**, have been prepared from **1** via a new method (Scheme 1) starting from the corresponding β-keto esters **2a**–**d** in xylene at reflux in good yields (56–73%). Short reaction times resulted in the isolation of significant amounts of the corresponding amides together with the perimidines.



2a, **3a**: R^1 = Me **2b**, **3b**: R^1 = Ph
2c, **3c**: R^1 = 4-(MeO)Ph **2d**, **3d**: R^1 = 3,4-$(MeO)_2$Ph

Scheme 1. Synthesis of compound **3**.

Simply heating an EtOAc solution of HKAs (**3**), 2 equiv of DAAD, and 1.2 equiv of DMAP led to the formation of 2-phenyl substituted perimidine derivatives as intermediate products. Subsequent intramolecular reaction of the intermediate products led to polyfunctionalized 8-alkyl-12-oxo-12*H*-isoindolo[2,1-*a*]perimidine-9,10,11-tricarboxylate derivatives (**5**) in good yield (Table 1). In the event that there is 1 equiv of DAAD used, the reactions gave the same products. When MeCN was used as solvent, the final products were obtained in similar yields. All crude products can be purified by crystallization.

The ^{1}H NMR spectrum of **5a** showed three methoxy protons at δ 4.11, 4.02, 3.36 ppm, and a methyl proton at 2.84 ppm. The ^{13}C NMR showed four carbonyl carbons at δ 167.4, 165.9, 164.6 and 160.9 ppm, a methyl carbon at 15.7 ppm and three methoxy carbons at δ 53.4, 53.3, 53.1 ppm. In the ^{13}C NMR spectra of **5a**, new aromatic carbon signals along with carbon signals of perimidine moiety were clearly observed.

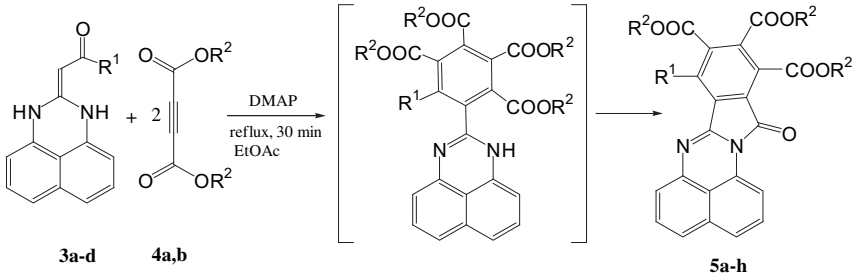
Unambiguous evidence for the structure of **5c** was obtained by using X-ray analysis (Fig. 1).[13] The compound crystallizes in the triclinic space group *P*-1. Dihedral angle between the isoindolo plane [Cg1: N(2)–C(5)–C(6)–C(7)–C(13)–C(14)–C(15)–C(18)–C(19)] and the perimidine plane [Cg2: N(2)–C(5)–N(1)–C(4)–C(3)–C(2)–C(1)–C(20)–C(25)–C(24)–C(23)–C(22)–C(21)] is equal to 3.93°, which indicates that the two ring systems are almost coplanar. However, the isoindolo ring and the phenyl ring are not coplanar, the dihedral angle being 59.89°.

A possible reaction scenario (outlined in Scheme 2) is as follows: the tandem addition of a carbanion, generated from heterocyclic ketene aminal by DMAP, to C≡C bounds of two acetylenic esters, would generate a species, which can transform into an aromatic system well-disposed to undergo electrocyclization to afford a dihydrobenzene derivative, and the latter would undergo dehydration to deliver polysubstituted phenyl ring. It is similar that the formation of a phenyl ring from the MCR of β-keto esters with DMAP and DAAD was previously reported.[14] Finally, the reaction is completed with nucleophilic attack of an N-atom of perimidine ring on the C═O of corresponding ester attached to phenyl ring.

3. Conclusion

In conclusion we have achieved an efficient process for the synthesis of isoindolo[2,1-*a*]perimidin-12-one derivatives starting from readily available reagents. The reaction is very simple from an experimental point of view and allows the creation of a fused

Table 1
Synthesis of heterocyclic keten aminals **5a**–**h**



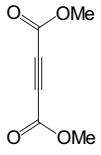
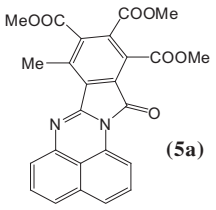
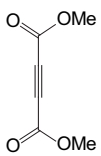
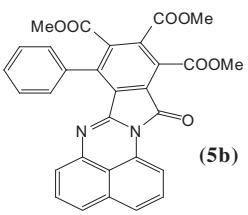
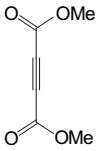
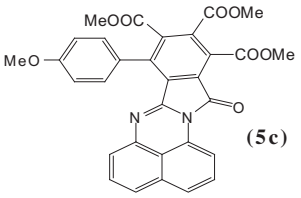
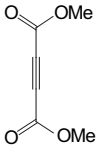
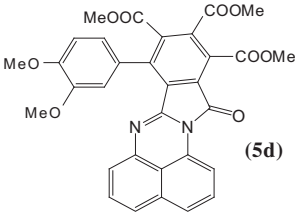
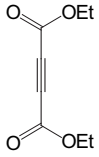
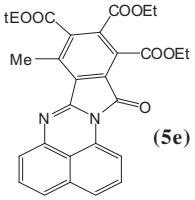
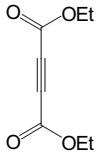
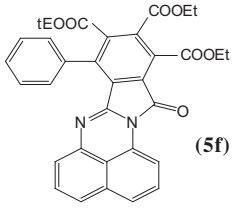
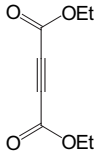
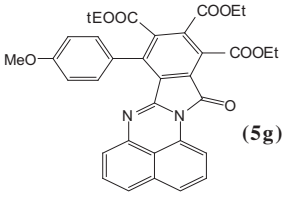
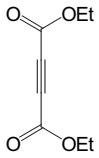
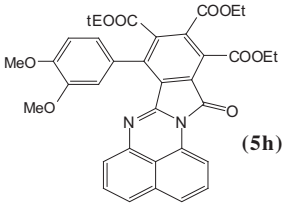
Entry	HKA	DAAD	Product	Recrystallization solvent	Yield[a] (%)
1	**3a**		 **(5a)**	Acetonitrile	68
2	**3b**		 **(5b)**	Acetonitrile	70

Table 1 (*continued*)

Entry	HKA	DAAD	Product	Recrystallization solvent	Yield[a] (%)
3	**3c**		 **(5c)**	Acetonitrile	75
4	**3d**		 **(5d)**	Ethyl acetate	65
5	**3a**		 **(5e)**	Ethyl acetate	78
6	**3b**		 **(5f)**	2-Propanol	69
7	**3c**		 **(5g)**	2-Propanol	62
8	**3d**		 **(5h)**	2-Propanol	72

[a] Isolated yield of analytically pure compound.

isoindole moiety with concomitant formation of benzene and pyrrole ring in a single operation.

4. Experimental

4.1. General

Melting points were measured on an Electrothermal 9100 apparatus and uncorrected. Elemental analyses for C, H and N were performed using a LECO-932 CHNS-O Elemental Analyzer. ^{1}H and ^{13}C NMR spectra were measured with Bruker Avance 400 spectrometer using $CDCl_3$ or DMSO-d_6 solvents. The IR spectra were obtained in potassium bromide pellets using a Jasco FTIR-460 Plus spectrometer. Diffraction data for **5c** were collected with a Bruker AXS APEX[15a] CCD diffractometer. Diffraction data were collected over the full sphere and were corrected for absorption. The crystal structures were solved by direct methods and refined by using SHELXS-97 and SHELXL-97 crystallographic software packages.[15b,c] All nonhydrogen atoms were refined anisotropically using reflections I[2r (I). Hydrogen atoms were located in ideal positions. Geometric calculations and visualizations were done using PLATON,[15d] MERCURY.[15e]

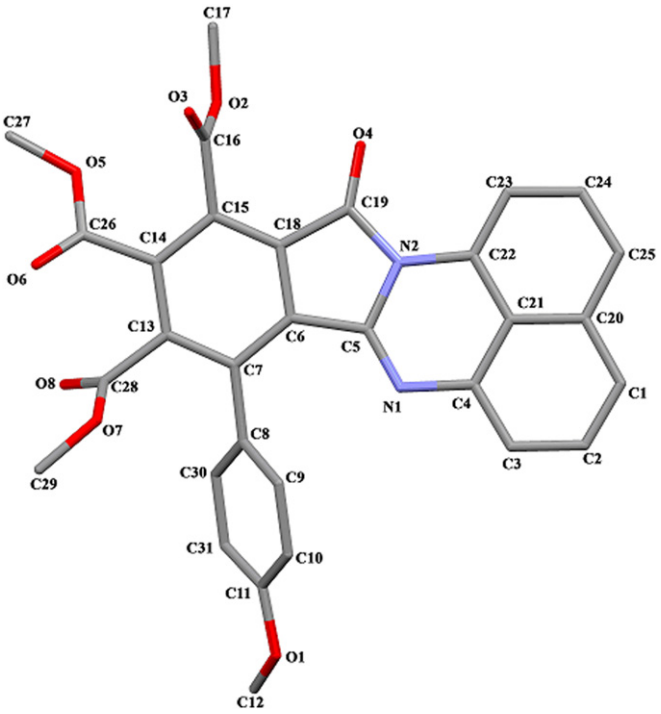


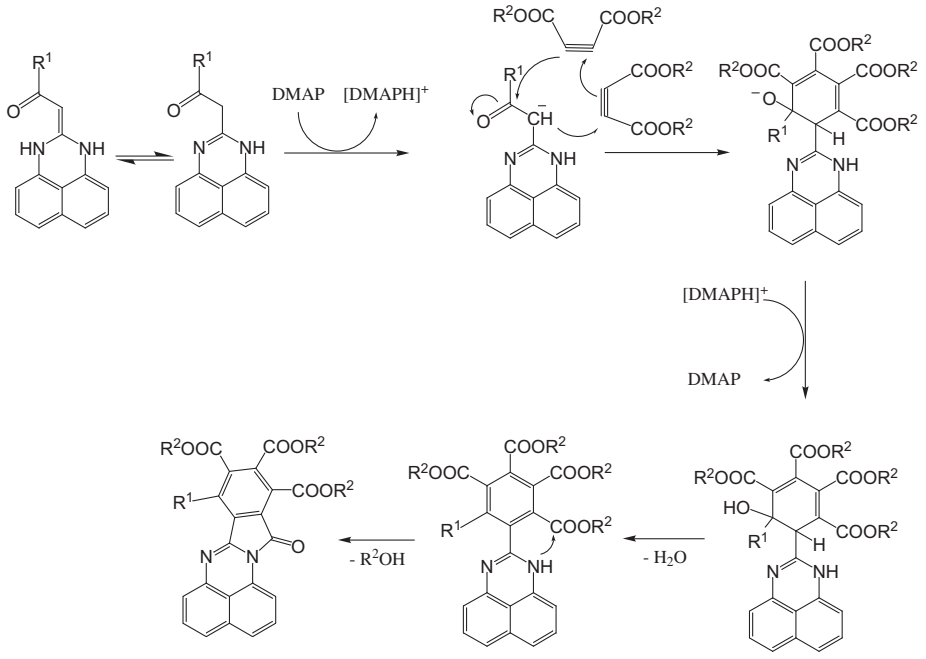
Fig. 1. Molecular structure of **5c** (Hydrogen atoms have been omitted for clarity).

^{13}C NMR (DMSO-d_6): 191.5 (C=O), 152.4 (*C*=CHCOMe), 135.1, 134.6, 134.2, 128.8, 128.7, 119.3, 118.7, 116.3, 105.8, 105.1 (C=C, aro.), 80.5 (C=*C*HCOMe), 29.0 ppm (CH_3). Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.83; H, 5.33; N, 12.59%.

*4.2.2. 2-(1H-Perimidin-2(3H)-ylidene)-1-phenylethanone (**3b**).* Brown crystals, yield: 0.172 g, 60%; mp 246 °C. FT-IR (KBr): ν_{max}: 3295 (NH), 1649 (C=O), 1633 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): 13.80, 10.73 (s, 2H, NH), 7.84–6.59 (m, 11H, Ar–H), 5.59 (s, 1H,=CH) ppm; ^{13}C NMR (DMSO-d_6): 184.5 (C=O), 153.9 (*C*=CHCOPh), 140.5, 135.1, 134.7, 134.1, 130.9, 128.8, 126.6, 119.7, 119.0, 116.7, 106.2, 105.3 (C=C, aro.), 77.9 ppm (C=*C*HCOPh). Anal. Calcd for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.84; H, 4.99; N, 9.61%.

*4.2.3. 1-(4-Methoxyphenyl)-2-(1H-perimidin-2(3H)-ylidene)ethanone (**3c**).* Brown crystals, yield 0.193 g, 61%; mp 300 °C. FT-IR (KBr): ν_{max}: 3290 (NH), 1647 (C=O), 1631 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): NH, not detected, 7.84–6.59 (m, 10H, Ar–H), 5.53 (s, 1H,=CH), 3.80 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6): 184.0 (C=O), 153.5 (*C*=CHCOPh), 161.6, 134.7, 132.9, 128.7, 128.4, 119.1, 116.5, 114.0, 105.6 (C=C, aro.), 77.1 ppm (C=*C*HCOPh), 55.7 (OCH_3). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.81; H, 5.10; N, 8.72%.

*4.2.4. 1-(3,4-Dimethoxyphenyl)-2-(1H-perimidin-2(3H)-ylidene) ethanone (**3d**).* Orange crystals, yield 0.253 g, 73%; mp 228 °C. FT-IR (KBr): ν_{max}: 3332 (NH), 1621 (C=O) cm^{-1}; ^{1}H NMR (DMSO-d_6): 13.78, 10.65 (s, 2H, NH), 7.41–6.58 (m, 9H, Ar–H), 5.55 (s, 1H,=CH), 3.80 (s, 6H, 2× OCH_3); ^{13}C NMR (DMSO-d_6): 184.0 (C=O), 153.4 (*C*=CHCOPh), 151.3, 148.8, 135.2, 134.7, 134.1, 133.1, 128.8, 126.4, 119.8, 119.5, 118.8, 116.5, 111.4, 109.9, 106.0, 105.2 (C=C, aro.), 77.2 ppm (C=*C*HCOPh), 56.0, 55.7 (2× OCH_3). Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.94; H, 5.19; N, 8.24%.



Scheme 2. A proposed mechanism for the pseudomulticomponent reaction of HKAs.

4.2. General procedure for the preparation of 3

A solution of β-keto ester **2** (1 mmol) and naphthalene-1, 8-diamine (**1**) (0.158 g, 1 mmol) in the presence of PTSA (catalytic amount) in xylene (50 mL) was refluxed for 5 h. After removal of the solvent, the residue was crystallized from xylene to give pure **3a**–**d**.

*4.2.1. 1-(1H-Perimidin-2(3H)-ylidene)acetone (**3a**).* Grey crystals, yield 0.125 g, 56%; mp 260 °C. FT-IR (KBr): ν_{max}: 3124 (NH), 1658 (C=O), 1631 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): 13.33, 10.41 (s, 2H, NH), 7.26–6.52 (m, 6H, Ar–H), 4.82 (s, 1H,=CH), 1.91 ppm ($COCH_3$);

4.3. General procedure for the preparation of products 5

To stirred solution of **3** (1 mmol) and the corresponding dialkyl acetylenedicarboxylates (2 mmol) in EtOAc (30 mL) was added

dropwise DMAP (1.2 mmol) in EtOAc (10 mL), and the mixture was stirred at rt for 1 min. Later the mixture was heated at reflux for 30 min. The solvent was removed under reduced pressure, and the residue was treated with the petroleum ether to give corresponding products **5**, which were filtered off and recrystallized from the proper solvent and dried (P_2O_5).

*4.3.1. Trimethyl 8-methyl-12-oxo-12H-isoindolo[2,1-a]perimidine-9,10,11-tricarboxylate (**5a**).* Red crystals, yield 0.313 g, 68%; mp 249 °C. FT-IR (KBr): ν_{max}: 1721 (br, C=O), 1639 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): 8.39–7.27 (m, 6H, Ar–H), 4.11, 4.02, 3.96 (3× s, 9H, OMe), 2.84 ppm (s, 3H, Ar–Me); ^{13}C NMR ($CDCl_3$): 167.4, 165.9, 164.6, 160.9 (C=O), 147.4, 140.2, 138.5, 136.7, 133.6, 132.0, 131.1, 129.4, 129.4, 128.0, 127.8, 127.6, 126.6, 123.5, 123.4, 117.9, 110.4 (Ar–C=C, C=N), 53.4, 53.3, 53.1 (3× OMe), 15.7 ppm (Me). Anal. Calcd for $C_{25}H_{18}N_2O_7$ (458 g/mol): C, 65.50; H, 3.96; N, 6.11. Found: C, 65.24; H, 3.87; N, 6.13%.

*4.3.2. Trimethyl 12-oxo-8-phenyl-12H-isoindolo[2,1-a]perimidine-9,10,11-tricarboxylate (**5b**).* Red crystals, yield 0.365 g, 70%; mp 275 °C. FT-IR (KBr): ν_{max}: 1741, 1728, 1714 (C=O), 1644 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6): 8.34–6.76 (m, 11H, Ar–H), 4.00, 3.88, 3.52 ppm (3× s, 9H, OMe); ^{13}C NMR (DMSO-d_6): 166.5, 165.6, 165.0, 160.6 (C=O), 144.2, 143.4, 139.3, 138.7, 138.6, 133.9, 123.0, 129.9, 129.8, 129.1, 128.7, 128.5, 128.4, 127.9, 126.6, 123.6, 123.1, 118.1, 116.2, 110.1, 109.9 (Ar–C=C, C=N), 54.3, 53.7, 53.2 ppm (3× OMe). Anal. Calcd for $C_{30}H_{20}N_2O_7$ (520 g/mol): C, 69.23; H, 3.87; N, 5.38. Found: C, 69.53; H, 4.16; N, 5.15%.

*4.3.3. Trimethyl 8-(4-methoxyphenyl)-12-oxo-12H-isoindolo[2,1-a]perimidine-9,10,11-tricarboxylate (**5c**).* Red crystals, yield 0.414 g, 75%; mp 211 °C. FT-IR (KBr): ν_{max}: 1741, 1718 (C=O), 1641 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): 8.39–6.93 (m, 10H, Ar–H), 4.14, 3.95, 3.94, 3.36 ppm (4× s, 12H, OMe); ^{13}C NMR ($CDCl_3$): 161.0, 165.9, 164.5, 160.7 (C=O), 160.0, 146.0, 140.7, 138.9, 138.4, 133.5, 132.1, 131.1, 130.9, 130.6, 129.5, 127.9, 127.8, 127.7, 126.5, 125.7, 123.7, 123.4, 118.0, 113.0, 110.5 (Ar–C=C, C=N), 55.4, 53.5, 53.4, 52.7 ppm (4× OMe). Anal. Calcd for $C_{31}H_{22}N_2O_8$ (551 g/mol): C, 67.63; H, 4.03; N, 5.09. Found: C, 67.44; H, 3.89; N, 5.17%.

*4.3.4. Trimethyl 8-(3,4-dimethoxyphenyl)-12-oxo-12H-isoindolo[2,1-a]perimidine-9,10,11-tricarboxylate (**5d**).* Red crystals, yield 0.378 g, 65%; mp 228 °C. FT-IR (KBr): ν_{max}: 1727 (C=O), 1638 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): 8.54–6.93 (m, 9H, Ar–H), 4.14, 4.01, 3.96, 3.88, 3.66 ppm (5× s, 15H, OMe); ^{13}C NMR ($CDCl_3$): 167.0, 165.9, 164.5, 160.9 (C=O), 149.5, 148.1, 146.2, 140.6, 138.8, 138.5, 133.7, 132.1, 131.3, 130.7, 129.8, 128.0, 127.8, 126.7, 125.8, 123.8, 123.6, 122.0, 118.2, 113.6, 110.6, 110.2 (Ar–C=C, C=N), 56.0, 55.9, 53.5, 53.5, 52.8 ppm (5× OMe). Anal. Calcd for $C_{32}H_{24}N_2O_9$ (581 g/mol): C, 66.20; H, 4.17; N, 4.83. Found: C, 66.29; H, 4.24; N, 4.67%.

*4.3.5. Triethyl 8-methyl-12-oxo-12H-isoindolo[2,1-a]perimidine-9,10,11-tricarboxylate (**5e**).* Red crystals, yield 0.390 g, 78%; mp 205 °C. FT-IR (KBr): ν_{max}: 1734, 1723 (C=O), 1637 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6): 8.28–7.35 (m, 6H, Ar–H), 4.43, 4.38, 4.33 (3× q, J=7.2 Hz, 6H, OCH_2), 1.37, 1.29, 1.19 (3× t, J=7.2 Hz, 9H, 3× Me), 2.79 ppm (s, 3H, Ar–Me); ^{13}C NMR (DMSO-d_6): 166.5, 165.0, 164.8, 160.2 (C=O), 147.7, 140.2, 138.9, 136.7, 133.9, 131.1, 130.6, 129.5, 129.4, 128.5, 127.8, 127.7, 126.6, 123.5, 123.2, 118.0, 109.7 (Ar–C=C, C=N), 63.2, 62.7, 62.5 (3× OCH_2), 15.8 (Ar–Me), 14.3, 14.3, 14.1 ppm (3× Me) Anal. Calcd for $C_{28}H_{24}N_2O_7$ (500 g/mol): C, 67.19; H, 4.83; N, 5.60. Found: C, 67.27; H, 4.83; N, 5.51%.

*4.3.6. Triethyl 12-oxo-8-phenyl-12H-isoindolo[2,1-a]perimidine-9,10,11-tricarboxylate (**5f**).* Red crystals, yield 0.389 g, 69%; mp 185 °C. FT-IR (KBr): ν_{max}: 1741, 1719 (C=O), 1640 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): 8.50–6.91 (m, 11H, Ar–H), 4.62, 4.42, 4.05 (3× q, J=7.2 Hz, 6H, OCH_2), 1.51, 1.39, 0.98 ppm (3× t, J=7.2 Hz, 9H, Me); ^{13}C NMR ($CDCl_3$): 166.3, 165.3, 164.2, 160.9 (C=O), 146.2, 140.5, 138.7, 138.5, 133.8, 133.7, 132.0, 131.4, 131.2, 130.1, 129.5, 128.6, 127.9, 127.7, 127.7, 127.5, 126.5, 123.6, 123.4, 118.2, 110.5 (Ar–C=C, C=N), 62.8, 62.6, 61.9 (3× OCH_2), 14.0, 13.8, 13.5 ppm (3 Me). Anal. Calcd for $C_{33}H_{26}N_2O_7$ (563 g/mol): C, 70.45; H, 4.66; N, 4.98. Found: C, 70.53; H, 4.56; N, 5.05%.

*4.3.7. Triethyl 8-(4-methoxyphenyl)-12-oxo-12H-isoindolo[2,1-a]perimidine-9,10,11-tricarboxylate (**5g**).* Red crystals, yield 0.367 g, 62%; mp 117 °C. FT-IR (KBr): ν_{max}: 1721 (br, C=O), 1638 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): 8.50–6.99 (m, 10H, Ar–H), 3.93 (s, 3H, OMe), 4.61, 4.41, 4.09 (3× q, J=7.2 Hz, 6H, OCH_2), 1.50, 1.39, 1.04 ppm (3× t, J=7.2 Hz, 9H, Me); ^{13}C NMR ($CDCl_3$): 166.5, 165.3, 164.2, 160.9 (C=O), 160.0, 146.3, 140.8, 138.7, 138.6, 133.7, 132.1, 131.4, 131.0, 131.0, 130.1, 127.9, 127.7, 126.5, 126.0, 123.7, 123.4, 118.2, 113.0, 110.5 (Ar–C=C, C=N), 62.8, 62.7, 61.9 (3× OCH_2), 55.4 (OMe), 14.0, 13.8, 13.7 ppm (3× Me). Anal. Calcd for $C_{34}H_{28}N_2O_8$ (593 g/mol): C, 68.91; H, 4.76; N, 4.73. Found: C, 69.00; H, 4.76; N, 4.89%.

*4.3.8. Triethyl 8-(3,4-dimethoxyphenyl)-12-oxo-12H-isoindolo[2,1-a]perimidine-9,10,11-tricarboxylate (**5h**).* Red crystals, yield 0.448 g, 72%; mp 90 °C. FT-IR (KBr): ν_{max}: 1722 (br, C=O), 1641 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): 8.54–6.90 (m, 9H, Ar–H), 4.61, 4.41, 4.14 (3× q, J=7.2 Hz, 6H, OCH_2), 4.01, 3.88 (2× s, 6H, 2 OMe), 1.50, 1.39, 1.04 ppm (3× t, J=7.2 Hz, 9H, Me); ^{13}C NMR ($CDCl_3$): 166.6, 165.3, 164.2, 161.0 (C=O), 149.5, 148.1, 140.7, 138.6, 133.7, 131.9, 131.4, 128.0, 127.8, 126.5, 126.1, 123.7, 123.4, 122.1, 113.7, 110.5, 110.2 (Ar–C=C, C=N), 62.8, 62.6, 61.9 (3× OCH_2), 56.0, 56.0 (2× OMe), 14.0, 13.8, 13.7 ppm (3× Me). Anal. Calcd for $C_{35}H_{30}N_2O_9$ (623 g/mol): C, 67.52; H, 4.86; N, 4.50. Found: C, 67.26; H, 4.72; N, 4.39%.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.05.078.

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