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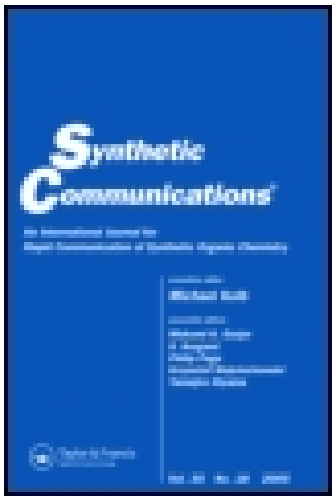

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CERIUM (IV) MEDIATED OXIDATIVE DIMERIZATION OF 3-OXOACID ANILIDES AND THEIR CYCLIZATIONS

B. Zaleska [a] & S. Lis [a]

[a] Department of Organic Chemistry , Jagiellonian University , Ingardena 3, Cracow, PL, 30-060, Poland

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CERIUM (IV) MEDIATED OXIDATIVE DIMERIZATION OF 3-OXOACID ANILIDES AND THEIR CYCLIZATIONS

B. Zaleska* and S. Lis

Department of Organic Chemistry, Jagiellonian University,
PL 30-060 Cracow, Ingardena 3, Poland

ABSTRACT

Investigation of the behavior of several anilides of 3-oxoacids in oxidation reaction with ceric ammonium nitrate has shown that selective intermolecular C-C bond formation, which led to their dimers, is typical of these compounds. These dimeric species were cyclized in two routes, A and B, leading to 3-[2′-(1′-aniline-3′-oxo)-indene]-quinoline-2-on derivatives with $HCl_{(g)}$ (Route A), and with application of H_2SO_4 as a cyclization agent, gave furane-3,4-dicarboxylic acid derivatives (Route B).

For some years we have been employing anilides of 3-oxoacids as starting material for the synthesis of several biologically active heterocyclic systems, such as 1,4-thiazepine (1), pyridine (2), pyrrolidine (3), pyrrolo[2,3-*c*]pyridine (4), and thiophene (5).

Although oxidative dimerization of 1,3-dicarbonyl compounds by ceric ammonium nitrate (CAN) was investigated (5), there is only scant information available on C-C bond forming reactions of 3-oxoacid derivatives (6).

* To whom correspondence should be addressed.

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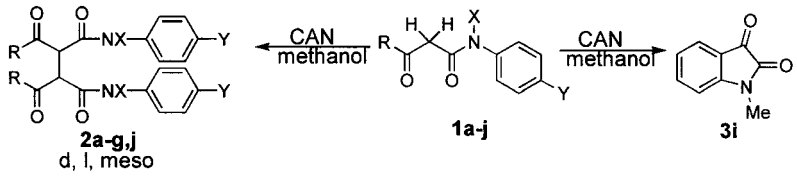

a - R=Me, X=H, Y=H; **b** - R=Me, X=H, Y=Cl; **c** - R=Ph, X=H, Y=H; **d** -R=p-CH_3-C_6H_4, X=H, Y=H; **e** - R=Ph, X=H, Y=Me; **f** - R=Ph, X=H,Y=OMe; **g** - R=Ph, X=H, Y=Cl; **h** - R=Ph, X=H, Y=NO_2; **i** - R=Ph, X=Me,Y=H; **j** - R=Ph, X=Et, Y=H

Scheme 1.

We have initiated studies in this area and our preliminary results on CAN mediated dimerization of various anilides of 3-oxoacids and further cyclisation of dimeric species are reported here.

We have found that treatment of 3-oxoacid anilides **1** with 2 mol equiv. of CAN in methanol gave excellent isolated yields of the dimeric product **2** (Scheme 1). A different course was observed only for N-methylanilide of benzoylacetic acid **1i**, where oxidative cyclization product, N-methyl isatine **3i** was formed. Whereas, in the case of p-nitroanilide of benzoylacetic acid **1h** in this oxidation process, mono p-nitroanilide of oxalyl acid was isolated.

This CAN mediated C-C bond forming reaction leading to compounds **2** proceeded with a change of color from light yellow to deep orange, which indicated complexation with metal. Based on an already proposed mechanism (7,8), change of color suggests that dimers **2** formation is of radical type that occurs after the complexation of ceric (IV) ion with 1,3-dicarbonyl system of 3-oxoacid anilides.

The structure of the dimerization products **2**, as a mixture of meso and d,l pair of 2,3-dibenzoylsuccinic acid anilides, is clear from their spectral data.

The ^{13}C nmr spectra of compounds **2** confirmed the presence of C2-C3 bond of succinic acid anilide **2**, because the diagnostic signal at 60.4 ppm of **2a** corresponds to sp^3 hybridized carbon atoms. This signal assignment was supported by ^1H nmr spectra of compound **2a**, which show in the place of the two characteristic signals for anilide **1a** at 3.55 ppm and 4.95 ppm (tautomeric equilibrium) one at 4.64 ppm (2 × CH). Additionally, this fact was confirmed by DEPT 135 and HETCOR nmr spectra of compound **2a**. Electron impact (MS/EI) spectra of **2** display diagnostic peaks m/z of M^+ ions, which indicates dimerization of 3-oxoacid anilides **1**.

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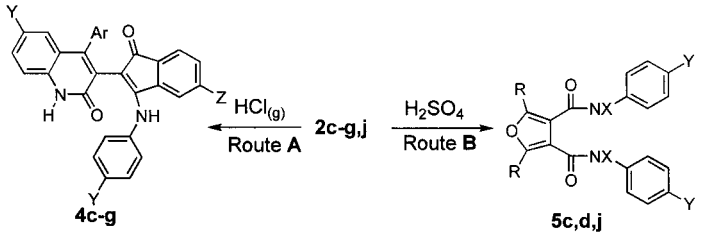

Scheme 2.

Intramolecular Cyclization of Compounds 2 to Quinoline Derivatives 4 (*Route A*)

The saturation of an ethanolic suspension of the anilides of 2,3-disubstituted succinic acid **2** with $HCl_{(g)}$ at 50°C (3 h) gave, almost quantitatively, new quinoline derivatives **4** (Scheme 2). During this intramolecular cyclization of compounds **2**, one fragment gave a quinoline ring system, but the other formed the indene-2-on (9), present as the substituent at position 3 of the quinoline-2-on.

The structure of obtained new compounds **4** was elucidated on the basis of their spectroscopic data. The ir spectrum showed two intensive absorption peaks of carbonyl groups at 1749 cm^{-1} attributed to indene system and at 1680 cm^{-1} of quinoline-2-on.

The analysis of ^{13}C nmr data of compound **4c** clearly indicates the presence of two different carbons of carbonyl group at 169 ppm of C-2 quinoline ring and at 187 ppm of indene-2-on.

The MS spectra of **4c** show peaks assigned to M^+ ion as well as 1/2 M^+ (**A**) ion. Characteristic fragmentation of quinoline-4-on system confirmed the presence of ions **B**, present in all spectra of compound **4**, formed due to the α and β cleavages of the heterocyclic ring (Figure 1). Indene-2-on fragmentation give ions **D**.

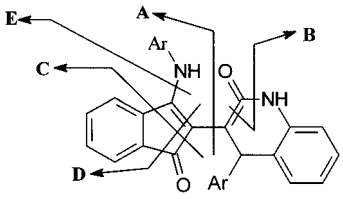

Figure 1.

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Intramolecular Cyclization of Compounds 2 to Furan Derivatives 5 (*Route B*)

Other type of cyclization process of dimers **2** took place, when conc. H_2SO_4 was used as cyclization agent (Scheme 2). In this case intramolecular ring closure led to 3,4-dicarboxylic acid of 2,5-diphenyl-furane **5**. Analysis of the ir, nmr as well as ms (10) spectra confirmed proposed structure of furan derivatives **5**.

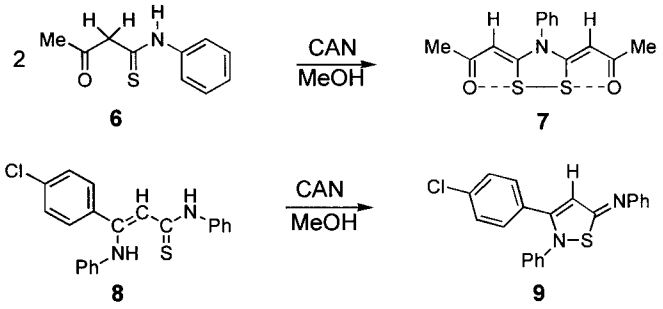
Cyclization of 3-Oxoacid Thioanilides to 1,2,4-Dithiazol 7 and Isothiazol 8 Derivatives

Our experience with the CAN promoted C-C bond formation described above prompted us to test the possibility of exploiting this procedure to prepare heterocyclic compounds starting from 3-oxoacid tioanilide **6**. Oxygenation of benzoylthioacetic acid anilide **6** with CAN led to 1,2,4-ditiazol derivatives 7 (11), by intermolecular S-S bond formation. This cyclization to heterocyclic system **7** took place with elimination of one molecule of aniline (Scheme 3).

Usage of 3-aminothiocinnamic acid anilides **8** allows formation of isothiazol derivatives **9** (11) by N-S intermolecular bond formation.

Although the chemistry of 1,2,4-dithiazol **7** as well as isothiazol **9** is well researched (11), this method of their preparation is novel.

In conclusion, oxidation of 3-oxoacid anilides promoted by ceric ammonium nitrate leads to intermolecular C2-C2 bond formation, typical to 1,3-dioxocompounds. Dimeric species **2** are valuable intermediates for synthesis of new, pharmacologically interesting, heterocyclic derivatives such as quinoline **4**, substituted in position 3 with indene, and furan 3,4-dicarboxylic acid derivatives **5**, known as drugs (12).



Scheme 3.

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All the methods of synthesis described here are very efficient, and can be applied conveniently for the preparation of new compounds **4** and **5** as well as **7** and **8**.

EXPERIMENTAL

General Procedure for the Preparation of 2,3-Disubstituted Succinic Acid Anilide 2

A solution of CAN (2 mmol) in methanol (10 mL) was added dropwise to an ice-cold solution of 3-oxoacid anilide **1** (1 mmol) in methanol (10 mL) and stirred for 3 h. The reaction mixture was left for 12 h, and after this time it was diluted with water (100 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The colorless precipitate was filtered off and washed with water.

2a. Yield 60%; m.p. 231–232°C; $C_{20}H_{20}N_2O_4 \cdot H_2O$, MW = 370 a.u., **CHN** requires: C-64.86%, H-5.94%, N-7.57%; found: C-64.66%, H-5.29%, N-7.60%; **ir** (KBr, cm^{-1}): 1651, 1680 ($\nu_{C=O}$), 3052 ($\nu_{C\text{-}H}$), 3251 ($\nu_{N\text{-}H}$); **^{1}H nmr** (DMSO-d_6, ppm) 2.24 (s, 6H, C**H**$_3$-), 4.64 (s, 2H, C**H**), 7.02–7.58 (m, 10H, C(Ar)), 10.72 (s, 2H, N**H**); **^{13}C nmr** (DMSO-d_6, ppm) 29.22 (**C**H$_3$), 60.37 (-**C**H-), 119.46, 123.90, 128.95, 138.67 (C(Ar)), 164.84, 201.93 (**C**=O); **MS-EI** (70 eV, m/e): 352 (8.15%), 334 (19.24%), 309 (30.66%), 292 (3.35%), 259 (9.59%), 241 (24.46%), 216 (53.73%) 173 (47.12%), 93 (100%), 77 (22.11%).

2b. Yield 58%; m.p. 198°–199°C; $C_{20}H_{18}N_2O_4Cl_2 \cdot H_2O$, MW = 421 a.u.; **CHN** requires: C-57.0%, H-4.3%, N-6.6% ; found: C-57.2%, H-4.0%, N-6.9%; **ir** (KBr, cm^{-1}): 1648, 1683 ($\nu_{C=O}$), 3058 ($\nu_{C\text{-}H}$), 3268 ($\nu_{N\text{-}H}$); **^{1}H nmr** (DMSO-d_6, ppm) 2.28 (s, 6H, C**H**$_3$-), 4.64 (s, 2H, C**H**), 7.34–7.57 (m, 8H, C(Ar)), 10.88 (s, 2H, N**H**); **^{13}C nmr** (DMSO-d_6, ppm) 29.00 (**C**H$_3$), 60.52 (-**C**H-), 120.81; 127.55; 128.79; 137.39 (C(Ar)), 164.75; 201.31 (**C**=O).

2c. Yield 84%; m.p. 247°–248°C; $C_{30}H_{24}N_2O_4 \cdot H_2O$, MW = 494 a.u., **CHN** requires: C-72.9%, H-5.3%, N-5.7%; found: C-73.13%, H-5.37%, N-5.61%; **ir** (KBr, cm^{-1}): 1661, 1686 ($\nu_{C=O}$), 3062, 3132 ($\nu_{C\text{-}H}$), 3243, 3330 ($\nu_{N\text{-}H}$); **^{1}H nmr** (DMSO-d_6, ppm): 5.60 (s, 2H, C**H**), 6.98–8.22 (m, 20H, C(Ar)), 10.64, 10.86 (2 × s, 2H, N**H**); **^{13}C nmr** (DMSO-d_6, ppm): 55.45 (-**C**H-), 119.35, 124.05, 128.63, 128.76, 129.00, 133.95, 135.44, 138.16 (C(Ar)), 165.33, 193.42 (**C**=O), MS-EI (70 eV, m/e): 476 (1.26%), 458 (4.54%), 348 (8.57%), 371 (23.34%), 365 (10.04%), 291 (11.09%), 278 (23.39%), 265 (9.89%), 119 (6.80%), 105 (100%), 93 (40.97%), 77 (35.09%).

2d. Yield 75%; m.p. 248°–249°C; $C_{32}H_{28}N_2O_4 \cdot H_2O$, MW = 522 a.u., **CHN** requires: C-73.5%, H-5.8%, N-5.4%; found: C-74.06%, H-5.22%, N-5.17%; **ir** (KBr, cm^{-1}): 1643, 1693 ($\nu_{C=O}$), 3049, 3124 ($\nu_{C\text{-}H}$), 3243 ($\nu_{N\text{-}H}$); **^{1}H nmr** (DMSO-d_6, ppm): 2.16 (s, 6H, C**H**$_3$), 5.58 (s, 2H, C**H**), 6.87–8.96 (m, 18H, C(Ar)), 10.50, 10.76 (2 × s, 2H, N**H**); **^{13}C nmr** (DMSO-d_6, ppm): 20.63 (**C**H$_3$), 56.71

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(-**C**H-), 120.04, 128.69, 129.20, 129.26, 133.34, 134.13, 135.76, 135.98 (C(Ar)), 165.36, 193.75 (**C**=O); **MS-EI** (70 eV, m/e): 504 (2.25%), 486 (11.50%), 468 (6.49%), 399 (30.93%), 397 (12.52%), 379 (68.22%), 353 (14.89%), 333 (13.15%) 293 (2.59%) 292 (15.83%), 266 (11.58%), 133 (12.77%), 107 (100%), 105 (24.39%).

2e. Yield 89%; m.p. 244°–245°C; $C_{32}H_{28}N_2O_4 \cdot H_2O$, MW = 522 a.u., **CHN** requires: C-69.31%, H-5.42%, N-5.05%; found: C-69.27%, H-5.18%, N-5.33%; **ir** (KBr, cm^{-1}): 1649, 1680 ($\nu_{C=O}$), 2916, 2973, 3036, 3130 (ν_{C-H}), 3256, 3337 (ν_{N-H}); **^{1}H nmr** (DMSO-d_6, ppm): 2.37 (s, 6H, C**H**$_3$), 5.54 (s, 2H, C**H**), 6.96–8.13 (m, 18H, C(Ar)), 10.82 (s, 2H, N**H**); **^{13}C nmr** (DMSO-d_6, ppm): 21.07 (**C**H$_3$), 56.28 (-**C**H-), 119.62, 123.63, 126.03, 126.79, 128.54, 129.22, 137.40, 144.39 (C(Ar)), 165.41, 192.77 (**C**=O); **MS-EI** (70 eV, m/e): 504 (1.18%), 486 (3.14%), 412 (6.49%), 385 (12.03%), 319 (9.66%), 293 (12.40%), 266 (14.76%), 119 (100%), 93 (23.49%).

2f. Yield 68%; m.p. 246°–247°C; $C_{32}H_{28}N_2O_6 \cdot H_2O$, MW = 554 a.u., **CHN** requires: C-69.31%, H-5.42%, N-5.05%; found: C-69.04%, H-5.30%, N-5.21%; **ir** (KBr, cm^{-1}): 1649, 1687 ($\nu_{C=O}$), 2835, 2961, 3055, 3130 (ν_{C-H}), 3243 (ν_{N-H}); **^{1}H nmr** (DMSO-d_6, ppm): 3.65 (s, 6H, C**H**$_3$), 5.54 (s, 2H, C**H**), 6.76–8.22 (m, 18H, C(Ar)), 10.70 (s, 2H, N**H**); **^{13}C nmr** (DMSO-d_6, ppm) 55.8 (**C**H$_3$), 56.28 (-**C**H-), 113.75, 121.23, 128.35, 128.88, 131.26, 133.80, 135.44, 155.68 (C(Ar)), 164.81, 193,46 (**C**=O).

2g. Yield 87%; m.p. 244°–245°C; $C_{30}H_{20}N_2O_4Cl_2 \cdot H_2O$, MW = 561 a.u., **CHN** requires: C-64.17%, H-3.92%, N-4.99%; found: C-64.26%, H-3.67%, N-5.14%; **ir** (KBr, cm^{-1}): 1649, 1687 ($\nu_{C=O}$), 3049, 3117 (ν_{C-H}), 3237, 3318 (ν_{N-H}); **^{1}H nmr** (DMSO-d_6, ppm): 5.56 (s, 2H, C**H**), 7.23–8.19 (m, 18H, C(Ar)), 10.99 (s, 2H, N**H**); **^{13}C nmr** (DMSO-d_6, ppm): 56.79 (-**C**H-), 121.49, 128.17, 128.79, 129.04, 129.49, 134.49, 135.76, 137.43 (C(Ar)), 165.93, 193.55 (**C**=O); **MS-EI** (70 eV, m/e): 546 (2.19%), 544 (3.84%), 528 (4.63%), 526 (6.96%), 441 (24.85%), 439 (37.54%), 418 (20.22%), 312 (26.93%), 286 (36.19%), 265 (25.05%), 155 (9.49%), 153 (33.20%), 129 (28.29%), 127 (93.08%), 105 (100%).

2j. Yield 92%; m.p. 195°–196%°C; $C_{34}H_{32}N_2O_4$, MW = 532 a.u.; **CHN** requires: C-76.7%, H-6.1%, N-5.3%; found: C-76.18%, H-5.88%, N-5.13%; **ir** (KBr, cm^{-1}): 1636, 1680 ($\nu_{C=O}$), 2973, 3061 (ν_{C-H}), 3431 (ν_{N-H}); **^{1}H nmr** ($CDCl_3$, ppm): 0.69 (t, 3H, C**H**$_3$), 1.16 (t, 3H, C**H**$_3$), 3.12 (m, 1H, C**H**$_2$), 3.65 (m, 2H, C**H**$_2$), 3.90 (m, 1H, C**H**$_2$), 5.46 (s, 1H, C**H**), 5.58 (s, 1H, C**H**), 6.40–7.55 (m, 20H, C(Ar)); **^{13}C nmr** ($CDCl_3$, ppm): 12.34, 12.83 (**C**H$_3$), 45.01, 45.05 (**C**H), 53.16, 53.53 (**C**H$_2$), 127.65, 127.96, 128.10, 129.02, 129.14, 129.58, 132.70, 132.73, 136.07, 136.92, 140.84, 141.11 (C(Ar)), 165.67, 167.07 (**C**=O), 196.33, 196.84 (**C**=O); **MS-EI** (70 eV, m/e): 532 (1.16%), 514 (1.39%), 427 (33.59%), 412 (100%), 306 (36.31%), 291 (31.65%), 148 (46.67%), 120 (6.42%), 105 (26.86%).

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Procedure for Preparation of 3-[2′-(1′-Aniline-3′-oxo)-indene]-4-phenyl-2-oxo-quinoline 4c (*Route A*)

A suspension of apropriate compound **2** (3 mmol) in 10 mL of methanol was stirred at 50°C and saturated with $HCl_{(g)}$ (3 h). Red crystalline compound **4c** was filtered off.

4c. Yield 65%; m.p. > 300°C; $C_{30}H_{20}N_2O_2 \cdot HCl$, MW = 440 a.u.; **CHN** requires: C-75.51%, H-4.20%, N-5.88%, found: C-75.18%, H-4.88%, N-5.67%; **ir** (KBr, cm^{-1}): 1680, 1749 ($\nu_{C=O}$), 3397 ($\nu_{N\text{-}H}$); **^{1}H nmr** (D_2SO_4, ppm): 7.02–8.15 (m, 18H, C(Ar)); **^{13}C nmr** (D_2SO_4, ppm): 125.86 (=**C**-); 127.44, 132.10, 132.65, 133.54, 133.79, 134.89, 140.35, 140.73, 147.87 (C(Ar)), 148.49 (**C**-NH), 169.18, 187.02 (**C**=O); **MS-EI** (70 eV, m/e): 440 (100%), 413 (11.81%, **B**), 364 (12.75%), 348 (5.3%), 220 (3.60%), 180 (30.50%), 105 (7.07%).

4d. Yield 70%; m.p. > 300°C; $C_{32}H_{24}N_2O_2 \cdot HCl$, MW = 468 a.u.; **CHN** requires: C-76.19%, H-4.96%, N-5.56%, found: C-76.08%, H-4.75%, N-5.71%; **ir** (KBr, cm^{-1}): 1680, 1762 ($\nu_{C=O}$), 3419 ($\nu_{N\text{-}H}$); **^{1}H nmr** (D_2SO_4, ppm): 2.46 (s, 3H, C**H**$_3$), 3.17 (s, 3H, C**H**$_3$), 7.03–8.11 (m, 16H, C(Ar)); **^{13}C nmr** (D_2SO_4, ppm): 23.15, 37.48 (**C**H$_3$), 125.86 (=**C**-); 127.44, 132.11, 132.45, 133.64, 133.39, 134.59, 140.45, 140.73, 147.87 (C(Ar)), 148.60 (**C**-NH), 169.60, 187.96 (**C**=O); **MS-EI** (70 eV, m/e): 468 (100%), 454 (7.32%), 440 (1.81%), 379 (22.07%), 361 (1.3%), 234 (3.84%), 194 (25.73%), 105 (7.07%).

4e. Yield 82%; m.p. > 300°C; $C_{32}H_{24}N_2O_2 \cdot HCl$, MW = 468 a.u.; **CHN** requires: C-76.19%, H-4.96%, N-5.56%, found: C-76.27%, H-4.83%, N-5.42%; **ir** (KBr, cm^{-1}): 1662, 1680, ($\nu_{C=O}$), 3437 ($\nu_{N\text{-}H}$); **^{1}H nmr** (D_2SO_4, ppm): 2.56 (s, 3H, C**H**$_3$), 3.16 (s, 3H, C**H**$_3$), 7.33–7.88 (m, 16H, C(Ar)); **^{13}C nmr** (D_2SO_4, ppm): 25.81, 37.48 (**C**H$_3$), 123.41 (=**C**-), 127.44, 132.11, 132.45, 134.50, 135.01, 135.20, 136.03, 140.73, 141.24 (C(Ar)), 166.30 (**C**-NH), 170.00, 184.62 (**C**=O); **MS-EI** (70 eV, m/e): 468 (100%), 440 (1.62%), 376 (1.32%), 234 (1.42%), 194 (19.95%), 119 (3.94%).

4f. Yield 63%; m.p. >300°C; $C_{32}H_{24}N_2O_4 \cdot HCl$, MW = 500 a.u.; **CHN** requires: C-71.64%, H-4.66%, N-5.22%, found: C-71.53%, H-4.33%, N-5.57%; **ir** (KBr, cm^{-1}): 1680, 1721 ($\nu_{C=O}$), 2835, 2961, 3017 ($\nu_{C\text{-}H}$), 3431 ($\nu_{N\text{-}H}$).

4g. Yield 78%; m.p. > 300°C; $C_{30}H_{18}N_2O_2Cl_2 \cdot HCl$, MW = 509 a.u.; **CHN** requires: C-66.06%, H-3.49%, N-5.14%, found: C-66.43%, H-3.71%, N-5.01%; **ir** (KBr, cm^{-1}): 1660, 1687 ($\nu_{C=O}$), 3049, 3092 ($\nu_{C\text{-}H}$), 3450 ($\nu_{N\text{-}H}$); **^{1}H nmr** (D_2SO_4, ppm): 6.73–7.68 (m, 16H, C(Ar)); **^{13}C nmr** (D_2SO_4, ppm): 125.65 (=**C**-), 129.46, 131.16, 131.94, 132.83, 133.09, 134.07, 134.21, 134.51, 140.58, 142.98 (C(Ar)), 149.14 (**C**-NH), 168.61, 187.36 (**C**=O), **MS-EI** (70 eV, m/e): 510 (100%), 398 (1.75%), 216 (30.50%), 129 (7.25%).

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Procedure for Preparation of Dianilides of 2,5-Diphenyl-furane-3,4-dicarboxylic Acid 5 (*Route B*)

A mixture of (3 mmol) of compound **2** and 5 mL of conc. H_2SO_4 in 10 mL of ethanol was stirred for 1 h at room temp. After 1 h, 10 mL of water was added. Crystalline compound **5** was filtered off. The product was purified by Al_2O_3 column ($CHCl_3$), giving colorless compound **5**.

5c. Yield 92%; m.p. 219°–220°C; $C_{30}H_{22}N_2O_3$, MW = 458 a.u.; **CHN** requires: C-78.60%, H-4.80%, N-6.11%, found: C-78.46%, H-4.74%, N-6.21%; **ir** (KBr, cm^{-1}): 1624 ($\nu_{C=O}$), 3080 ($\nu_{C\text{-}H}$), 3205, 3318 ($\nu_{N\text{-}H}$); **^{1}H nmr** ($CDCl_3$, ppm): 7.05–8.72 (m, 20H, C(Ar)), 10.32 (s, 2H, N**H**); **^{13}C nmr** ($CDCl_3$, ppm): 117.93 (**C**=C), 119.62, 124.42, 124.98, 127.22, 127.80, 128.60, 129.51, 133.51 (C(Ar)), 137.62 (O-**C**=C), 162.10 (**C**=O); **MS-EI** (70 eV, m/e): 458 (26.23%), 366 (100%), 247 (1.85%), 105 (22.81%).

5d. Yield 95%; m.p. 214°–215°C; $C_{32}H_{26}N_2O_3$, MW = 486 a.u.; **CHN** requires: C-79.01%, H-5.35%, N-5.76%, found: C-78.94%, H-5.21%, N-5.71%; **ir** (KBr, cm^{-1}): 1647 ($\nu_{C=O}$), 2863, 3052 ($\nu_{C\text{-}H}$), 3188, 3240 ($\nu_{N\text{-}H}$); **^{1}H nmr** ($CDCl_3$, ppm): 2.32 (s, 6H, C**H**$_3$), 6.89–7.93 (m, 18H, C(Ar)), 8.93 (s, 2H, N**H**); **^{13}C nmr** ($CDCl_3$, ppm): 20.91 (**C**H$_3$), 117.98 (**C**=C), 119.23, 120.43, 125.82, 127.58, 128.33, 128.91, 129.51, 134.53 (C(Ar)), 153.49 (O-**C**=C), 162.07 (**C**=O).

5j. Yield 94%; m.p. 186°–187°C; $C_{34}H_{30}N_2O_3$, MW = 514 a.u.; **CHN** requires: C-79.38%, H-5.84%, N-5.45%, found: C-79.45%, H-5.58%, N-5.62%; **ir** (KBr, cm^{-1}): 1667 ($\nu_{C=O}$), 2878, 3082 ($\nu_{C\text{-}H}$); **^{1}H nmr** ($CDCl_3$, ppm): 1.11, 1.29 (t, 6H, C**H**$_3$), 3.88, 4.29 (q, 4H, C**H**$_2$), 6.42–7.72 (m, 20H, C(Ar)), **^{13}C nmr** ($CDCl_3$, ppm): 12.78, 14.10 (**C**H$_3$), 44.06, 44.59 (**C**H$_2$), 107.38 (**C**=C), 119.75, 120.02, 125.83, 127.35, 128.18, 128.70, 129.31, 144.75 (C(Ar)), 155.97 (O-**C**=C), 162.73 (**C**=O), **MS-EI** (70 eV, m/e): 514 (17.20%), 394 (54.93%), 367 (27.14%), 317 (100%), 247 (58.14%), 105 (85.22%).

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