Supporting information for

Unexpected formation of *N*-(1-(2-aryl-hydrazono)isoindolin-2-yl)benzamides and their conversion into 1,2-(bis-1,3,4-oxadiazol-2-yl)benzenes

by

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Figure S 1 ROESY full-spectrum of 10Ca



Formula	C ₂₈ H ₃₀ N ₄ O ₈
FW (g·mol ⁻¹)	550.56
Temperature (K)	293(2)
Wavelength (Å)	0,56080
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
a (Å)	10,2036(18)
b (Å)	14,2650(15)
c (Å)	18,965(3)
α(°)	90,00
β (°)	97,125(11)
γ (°)	90,00
$V(A^3)$	2739,1(7)
Ζ	4
Density (g·cm ⁻³)	1,335
$\mu (\mathrm{mm}^{-1})$	0,061
F (000)	1160
Fit quality for F ²	1,021
R_1 final, $wR^2 [I > 2(I)]$	0,0786; 0,1725
R ₁ , wR ² (for all data)	0,1378; 0,2002
Maximum difference peak and hole (e Å ⁻³)	0,457; -0,266

Table S 1 Crystallographic data for 10Ca-Z

between the supramolecular chains

Figure S 2 Crystal packing of 10C-Z (view along *a* axis) with illustration of the C–H---O contacts

General experimental procedures, ¹H NMR and MS spectra of crude reactions for condensations of

ortho-phthalaldehyde and hydrazide 9a



Table S 2 Reaction conditions for condensation of ortho-phthaldehyde and hydrazide 9a

Entry	Solvent	Reaction time (h)	Temperature (°C)	Catalyst
1	EtOH	24	78	-
2	EtOH	4/12	78/rt	-
3	CHCl ₃	24	rt	-
4	CHCl ₃	24	63	AcOH
5	CHCl ₃	4/12	63/rt	АсОН
6	toluene	1	110	-

Entry 1

Hydrazide **9a** (3 mmol) and *ortho*-phthalaldehyde (1,5 mmol, 0.201 g) were refluxed for 24 h in ethanol (50 mL). The solvent was removed under vacuum, the residue was dried and ¹H NMR spectrum recorded (Figure S3).

Entry 2

Hydrazide **9a** (3 mmol) and *ortho*-phthalaldehyde (1,5 mmol, 0.201 g) were refluxed for 4 h in ethanol (50 mL). The mixture was then stirred at room temperature for 12 h. The solvent was removed under vacuum, the residue (denoted R2-**10a**) was dried and ¹H NMR spectrum (Figure S4) were recorded.

Entry 3

Hydrazide **9a** (3 mmol) and *ortho*-phthalaldehyde (1.5 mmol, 0.201 g) were stirred at room temperature for 24 h in chloroform (50 mL). The solvent was removed under vacuum, the residue (denoted R3-10a) was washed with cold ethyl ether, filtered and washed again with cold methanol. After drying ¹H NMR spectrum was recorded (Figure S5).

Entry 4

Hydrazide **9a** (3 mmol) and *ortho*-phthalaldehyde (1.5 mmol, 0.201 g) were refluxed for 24 h in chloroform (50 mL) and a few drops of acetic acid. The solvent was removed under vacuum, the residue (denoted R4-**10a**) was dried and ¹H NMR spectrum recorded (Figure S6).

Entry 5

Hydrazide **9a** (3 mmol) and *ortho*-phthalaldehyde (1.5 mmol, 0.201 g) were refluxed for 4 h in chloroform (50 mL) and a few drops of acetic acid added. The mixture was then stirred at room temperature for 12 h. The solvent was removed under vacuum, the residue was dried and ¹H NMR spectra and RP-HPLC performed. The solvent was removed under vacuum, the residue (denoted R5-**10a**) was washed with cold ethyl ether, filtered and washed again with cold methanol. After drying ¹H NMR spectrum was recorded (Figure S7).

Entry 6

Hydrazide **9a** (3 mmol) and *ortho*-phthalaldehyde (1.5 mmoli, 0.201 g) were refluxed for 1 h in toluene (50 mL). The solution was concentrated under vacuum, cooled to room temperature and the resulted white residue (denoted R6-**10a**) was dried and ¹H NMR spectrum recorded (Figure S8).





Figure S 4 ¹H NMR spectrum of crude condensation reaction corresponding to entry 2 in Table S2





Figure S 5 ¹H NMR spectrum of crude condensation reaction corresponding to entry 3 in Table S2

ppm (t1)



Figure S 6 ¹H NMR spectrum of crude condensation reaction corresponding to entry 4 in Table S2

13



ppm (t1)



Figure S 8 ¹H NMR spectrum of crude condensation reaction corresponding to entry 6 in Table 3

15

Optimisation of the cyclisation reaction and ¹H NMR spectra of the isolated product 5a in each

reaction

Table S 3 Reaction conditions used to prepare 10a (various isomers ratios) that were assessed as

Entry	Starting material	Isolated yield of 5a
1	10C resulted from reaction preformed according to entry 6 in Table 3	35%
2	10A + 10C resulted from reaction preformed according to entry 5 in Table 3	33%
3	10A + 10C resulted from reaction preformed according to entry 4 in Table 3	34%

precursors of the 1,3,4-oxadiazoles

Figure S 9¹H NMR spectrum of the product 5a when optimising cyclisation reaction conditions



Figure S 10 UV-Vis and fluorescence spectra of compounds 5b Solvent: CH_2Cl_2 , $\lambda_{ex}=270$ nm, $c=8,58\cdot10^{-5}$ mole/L, A=0,29, $\lambda_A=270$ nm, $c=2,5\cdot10^{-6}$ mole/L, $\lambda_F=383$ nm, $\Delta\phi=113$ nm



Figure S 11 UV-Vis and fluorescence spectra of compounds 5g Solvent: CH_2Cl_2 , λ_{ex} =250 nm, c=2,5·10⁻⁴ mole/L, A=0,8, λ_A =301 nm, c=2,5·10⁻⁶ mole/L, λ_F =360 nm, $\Delta \phi$ =59 nm





04 84 32 1H-NMR . . . 101 0 . . • ٠ Ē **11** 0CH₃ 12 13/ 18 14 -OCH3 _ŅH N-\ 19 OCH₃ 16 15\ 2 3 `N∽_` ' NH 9 =0 10Ca 25 20 $H_{3}^{26}CO \xrightarrow{24}$ 21 22 H₃CÓ 27 OCH₃ 28 11 111 -----11 10 9 8 7 6 5 3 4 ppm

Figure S 12 ¹H NMR spectrum of compound 10Ca

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Figure S 14 ¹³C NMR spectrum of compound 10Ca





Figure S 15 H-H COSY NMR spectrum of compound 10Ca

Figure S 16 H-C HMBC NMR spectrum of compound 10Ca



Figure S 17 H-C HSQC NMR spectrum of compound 10Ca



Figure S 18 H-N HMQC NMR spectrum of compound 10Ca





Figure S 19 H-N HMBC NMR spectrum of compound 10Ca

Figure S 20 APCI-HRMS spectrum of compound 10Ca



Figure S 21 ¹H NMR spectrum of compound 10Cb







Figure S 23 H-N HMQC NMR spectrum of compound 10Cb



Figure S 24 APCI-HRMS spectrum of compound 10Cb



Figure S 25 ¹H NMR spectrum of compound 10Cc



Figure S 26 ¹³C NMR spectrum of compound 10Cc





Figure S 27 H-N HMQC NMR spectrum of compound 10Cc



Figure S 28 H-N HMBC NMR spectrum of compound 10Cc

Figure S 29 APCI-HRMS spectrum of compound 10Cc



35

Figure S 30 ¹H NMR spectrum of compound 10Cd



36
Figure S 31 ¹³C NMR spectrum of compound 10Cd



Figure S 32 H-N HMQC NMR spectrum of compound 10Cd





Figure S 33 H-N HMBC NMR spectrum of compound 10Cd

Figure S 34 APCI-HRMS spectrum of compound 10Cd



Figure S 35 ¹H NMR spectrum of compound 10Ce



Figure S 36 ¹³C NMR spectrum of compound 10Ce



Figure S 37 H-N HMQC NMR spectrum of compound 10Ce





Figure S 38 H-N HMBC NMR spectrum of compound 10Ce

Figure S 39 APCI-HRMS spectrum of compound 10Ce



45

Figure S 40 ¹H NMR spectrum of compound 10Cf



Figure S 41 ¹³C NMR spectrum of compound 10Cf





Figure S 42 H-N HMQC NMR spectrum of compound 10Cf



Figure S 43 H-N HMBC NMR spectrum of compound 10Cf



Figure S 44 APCI-HRMS spectrum of compound 10Cf

Figure S 45 ¹H NMR spectrum of compound 10Cg





Figure S 47 APCI HR-MS spectrum of compound 10Cg



Figure S 48 ¹H NMR spectrum of compound 10Ch



54





Figure S 50 H-N HMQC NMR spectrum of compound 10Ch



Figure S 51 H-N HMBC NMR spectrum of compound 10Ch

Figure S 52 APCI-HRMS spectrum of compound 10Ch



Figure S 53 ¹H NMR spectrum of compound 10Ci





Figure S 54 ¹³C NMR spectrum of compound 10Ci



Figure S 55 H-N HMQC NMR spectrum of compound 10Ci



Figure S 56 H-N HMBC NMR spectrum of compound 10Ci

Figure S 57 APCI-HRMS spectrum of compound 10Ci



Figure S 58 ¹H NMR spectrum of compound 5a





Figure S 59 ¹³C NMR spectrum of compound 5a

Figure S 60 APCI-HRMS spectrum of compound 5a



Figure S 61 ¹H NMR spectrum of compound 5b



67

Figure S 62 ¹³C NMR spectrum of compound 5b



Figure S 63 APCI-HRMS spectrum of compound 5b



Figure S 64 ¹H NMR spectrum of compound 5c



Figure S 65 ¹³C NMR spectrum of compound 5c



Figure S 66 APCI-HRMS spectrum of compound 5c



72
Figure S 67 ¹H NMR spectrum of compound 5d



Figure S 68 ¹³C NMR spectrum of compound 5d



Figure S 69 APCI-HRMS spectrum of compound 5d



Figure S 70 ¹H NMR spectrum of compound 5e



Figure S 71 ¹³C NMR spectrum of compound 5e



Figure S 72 APCI-HRMS spectrum of compound 5e



78

Figure S 73 ¹H NMR spectrum of compound 5f



Figure S 74 ¹³C NMR spectrum of compound 5f





Figure S 75 APCI-HRMS spectrum of compound 5f

Figure S 76 ¹H NMR spectrum of compound 5g



Figure S 77 ¹³C NMR spectrum of compound 5g



Figure S 78 APCI-HRMS spectrum of compound 5g



Figure S 79 ¹H NMR spectrum of compound 5h



Figure S 80 ¹³C NMR spectrum of compound 5h



Figure S 81 APCI-HRMS spectrum of compound 5h



Figure S 82 ¹H NMR spectrum of compound 5i



Figure S 83 ¹³C NMR spectrum of compound 5i





Figure S 84 APCI-HRMS spectrum of compound 5i

90