# $NiFe_2O_4$ nanoparticles: A green and reusable heterogeneous catalyst for the synthesis of spiro[indole-3,2'-pyrrole]-2,5'(1*H*,1'*H*)-diones

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NiFe<sub>2</sub>O<sub>4</sub> nanoparticles were used as an efficient catalyst for the preparation of spiro[indole-3,2'-pyrrole]-2,5'(1*H*,1'*H*)-diones by the multicomponent condensation reaction of arylamines, acetylenedicarboxylates and isatins under reflux conditions in ethanol.

Keywords: spiro[indole-3,2'-pyrrole]-2,5'(1H,1'H)-dione; isatin; NiFe<sub>2</sub>O<sub>4</sub> nanoparticles; One-pot; robust catalyst

### Introduction

Spirooxindoles represent an important class of compounds owing to their wide range of biological activities such as antiproliferative,1 anticancer,2 MDM2 inhibitors3 and can also serve as synthetic intermediates for many kinds of pharmaceuticals or drug precursors.4 Therefore, the development of simple methods for the synthesis of spirooxindoles is a major challenge and an interesting field in chemistry. Multicomponent reaction is one of the most common methods that have been utilised for the synthesis of a variety of biologically active compounds. Undoubtedly, the synthesis of spirooxindoles through multicomponent reactions (MCR) has been paid much attention due to experimental simplicity, excellent synthetic efficiency, inherent atom economy, and low environmental impact.<sup>5,6</sup> The synthesis of spirooxindoles has been reported in the presence of diverse catalysts including DBU,<sup>7</sup> piperidine,<sup>8</sup> ZnS nanoparticle,<sup>9</sup> BF<sub>3</sub>·OEt<sub>2</sub>,<sup>10</sup> *p*-toluenesulfonic acid<sup>11,12</sup> and NaHCO<sub>2</sub>.<sup>13</sup> However, some of the reported methods tolerate disadvantages including long reaction times, harsh reaction conditions and use of toxic and non-reusable catalyst. Consequently, to avoid these limitations, the searching of an efficient, easily available catalyst with high catalytic activity for the preparation of spirooxindoles is still favoured. Ideally, utilising environmental and green catalysts which can be simply recycled at the end of reactions has

received important attention in recent years. To overcome the separation limitations of the nanocatalysts, magnetic materials have used as recoverable catalysts.<sup>14,15</sup>

Herein we wish to report the synthesis of spiro[indole-3,2'-pyrrole]-2,5'(1*H*,1'*H*)-diones by the multi-component condensation reaction of arylamines, acetylenedicarboxylates and isatins in the presence of NiFe<sub>2</sub>O<sub>4</sub> nanoparticles under reflux conditions in ethanol (Scheme 1).

#### **Results and discussion**

To optimise the reaction conditions, the condensation reaction of 4-methylaniline, dimethyl acetylenedicarboxylate and isatin was selected as a model study to examine the effects of the catalyst and solvent for the synthesis of spiro[indole-3,2'pyrrole]-2,5'(1*H*,1'*H*)-diones (Scheme 2). A wide variety of catalysts including piperidine, ZnCl<sub>2</sub>, NiCl<sub>2</sub>, NiO, FeCl<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> NPs were employed to test their efficacy for the synthesis of spiro[indole-3,2'-pyrrole]-2,5'(1*H*,1'*H*)-diones. Then, we optimised the amount of NiFe<sub>2</sub>O<sub>4</sub> NPs required; the optimum amount was found to be 0.3 mol%. Also, we examined the reaction in different solvents including water DMF, acetonitrile and ethanol. Ethanol was found to be the best solvent, in which the product was obtained in 93% yield (Table 1). Unfortunately, when the model reaction was carried out in water, the desired product was only obtained in 60% yield.



Scheme 1 Synthesis of spiro[indole-3,2'-pyrrole]-2,5'(1H,1'H)-diones using NiFe<sub>2</sub>O<sub>4</sub> NPs.



Scheme 2 The model reaction for the preparation of 4d.

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Table 1 Optimisation of reaction conditions using different catalysts<sup>a</sup>

Entry	Solvent (reflux)	Catalyst/mol%	Time/h	Yield/% <sup>b</sup>
1	EtOH		14	trace
2	EtOH	piperidine (2)	10	28
3	EtOH	$ZnCl_{2}(3)$	6	37
4	EtOH	$\text{NiCl}_{2}(4)$	5	45
5	EtOH	NiO (3)	4	55
6	EtOH	FeCl <sub>3</sub> (4)	4	40
7	EtOH	Fe <sub>3</sub> 0 <sub>4</sub> (3)	4	51
8	H <sub>2</sub> 0	NiFe <sub>2</sub> O <sub>4</sub> NPs (0.3)	1.5	60
9	DMF	NiFe <sub>2</sub> 0 <sub>4</sub> NPs (0.3)	1.5	74
10	CH <sub>3</sub> CN	NiFe <sub>2</sub> 0 <sub>4</sub> NPs (0.3)	1.5	81
11	EtOH	$NiFe_2O_4 NPs$ (0.2)	1.5	91
12	EtOH	NiFe <sub>2</sub> O <sub>4</sub> NPs (0.3)	1.5	93
13	EtOH	$NiFe_2O_4 NPs (0.4)$	1.5	93

<sup>a</sup>4-methylaniline (4 mmol), dimethyl acetylenedicarboxylate (2 mmol) and isatin (2 mmol).

<sup>b</sup>Isolated yield.

The above results obviously show the present catalytic procedure is extendable to a wide variety of substrates to construct a diversity-oriented library of spiro[indole-3,2'-pyrrole]-2,5'(1H,1'H)-diones (Table 2). An important feature of this method is that both electron-releasing and withdrawing groups give excellent yields.

The recoverability of the nano-NiFe<sub>2</sub>O<sub>4</sub> catalyst was examined for the synthesis of product **4d** and it was found that product yields decreased to a small extent on each reuse (run 1, 93%; run 2, 93%; run 3, 92%; run 4, 92%; run 5, 91%). In the recycling procedure of NiFe<sub>2</sub>O<sub>4</sub> NPs, after completion of the reaction, 10 mL ethanol was added and magnet was introduced into the mixture in the form of a magnetic stirrer bar and catalyst was separated magnetically.

In conclusion, we have developed a straightforward and efficient approach to synthesis of spiro[indole-3,2'-pyrrole]-2,5'(1*H*,1'*H*)-diones by the multi-component condensation reaction of arylamines, acetylenedicarboxylates and isatins in the presence of NiFe<sub>2</sub>O<sub>4</sub> nanoparticles under reflux conditions in ethanol. The method offers several advantages including rapid assembly of heterocyclic molecules, cleaner reaction profiles, high yields, shorter reaction times, simple experimental, reusability of the catalyst and little catalyst loading.

#### **Experimental**

The products were isolated and characterised by physical and spectral data. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as internal standard. The IR spectra were recorded on FTIR Magna 550 apparatus using with KBr plates. Melting points were determined on Electro thermal 9200, and are not corrected. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyser. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with monochromatised Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). Microscopic morphology of products was visualised by SEM (MIRA 3 TESCAN).

#### $Preparation of NiFe_2O_4$ nanoparticles

The NiFe<sub>2</sub>O<sub>4</sub> nanoparticles were prepared according to the procedure reported in the literature.<sup>16</sup> 3 M solution of sodium hydroxide (as the precipitating agent) was slowly mixed with salt solutions of 0.4 M ferric chloride (FeCl<sub>2</sub>. 6H<sub>2</sub>O) and 0.2 M nickel chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O). The pH of the solution was constantly monitored as the NaOH solution was added dropwise. The reactants were constantly stirred using a magnetic stirrer until a pH level of >12 was achieved. A specified amount of oleic acid (2-3 drops for total reacting solution of 75 mL) was added to the solution as the surfactant. The liquid precipitate was then brought to a reaction temperature of 80 °C and stirred for 40 min. The product was cooled to room temperature and then washed twice with distilled water and ethanol to remove unwanted impurities and the excess surfactant from the prepared sample. The sample was centrifuged for 15 min at 2000 rpm and then dried overnight at above 80 °C. The acquired substance was then grinded into a fine powder and then annealed for 10 h at 600 °C.

## Synthesis of spiro[indole-3,2'-pyrrole]-2,5'(1H,1'H)-diones (**4a-h**); general procedure

A solution of arylamine (4 mmol), and isatin (2.0 mmol), acetylenedicarboxylate (2.0 mmol) and NiFe<sub>2</sub>O<sub>4</sub> NPs (0.3 mol%) as catalyst in 10 mL ethanol was refluxed for about 90 min. After completion of the reaction, 10 mL ethanol added and magnet was introduced into the mixture in the form of a magnetic stirrer bar and catalyst was separated magnetically. The precipitated solid was filtered and washed with ethanol to give the pure product.

*Methyl* 4'-(3-nitroanilino)-1'-(3-nitrophenyl)-2,5'-dioxo-1,1',2,5'tetrahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (**4a**): Yellow solid; m.p. 236–238 °C, (lit.<sup>11</sup> 238–240 °C); IR  $v_{max}$ /cm<sup>-1</sup> (KBr): 3345, 3277, 3115, 2949, 1727, 1693, 1652, 1615, 1526, 1482, 1265; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  3.31 (3H, s, OCH<sub>3</sub>), 6.84 (d, J = 7.8 Hz, 1H, ArH), 6.95 (t, J = 8 Hz, 1H, ArH), 7.12–7.15 (m, 2H, ArH), 7.97–8.05 (m, 2H, ArH), 7.42 (s, 1H, ArH), 7.50–7.53 (m, 3 H, ArH), 7.97–8.05 (m, 2H, ArH), 8.15 (s, 1, ArH), 9.20 (s, 1H, NH), 10.90 (s, 1H, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  51.2, 70.9, 109.8, 110.5, 115.8, 117.9, 120.6, 122.5, 124.5, 124.8, 127.8, 129.2, 130.6, 130.7, 132.5, 136.0, 140.5, 141.0, 143.2, 147.6, 147.9, 161.7, 165.5, 173.5 ppm; Anal.

Table 2	Synthesis	of spiro	[indole-3.	2'-pyrrole	1-2,5'(	1 <i>H</i> ,1'H	)-diones	4 a-h	) <sup>a</sup>
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Entry	Ar	К	R'	Product	l ime/min	Yield/%	M.p./ °C Found	M.p./°C ref Reported
1	3-N0 <sub>2</sub> C <sub>6</sub> H4	CH3	Н	4a	100	89	236-238	238-240 11
2	4-CH <sub>3</sub> C <sub>6</sub> H4	CH <sub>3</sub>	NO <sub>2</sub>	4b	90	95	276-278	-
3	4-0CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	CI	4c	90	94	256-258	254-256 11
4	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	Н	4d	90	93	229-231	229-231 11
5	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Et	Н	4e	93	92	228-230	-
6	$4-CH_3C_6H_4$	Et	CI	4f	93	94	248-250	247-249 11
7	$4-CH_3C_6H_4$	CH <sub>3</sub>	CH <sub>3</sub>	4g	96	91	249-251	249-250 11
8	$4-CH_3C_6H_4$	CH <sub>3</sub>	CI	4h	90	94	256-258	258-260 11

<sup>a</sup>Arylamines, acetylenedicarboxylates and isatins with NiFe<sub>2</sub>O<sub>4</sub>NPs (0.3 mol%). <sup>b</sup>Isolated yield. calcd for  $C_{25}H_{17}N_5O_8$ : C, 58.26; H, 3.32; N, 13.59; found: C, 58.32; H, 3.38; N, 13.68%.

*Methyl* 4'-(4-*methylanilino*)-1'-(4-*methylphenyl*)-5-*nitro*-2,5'-*dioxo*-1,1',2,5'-*tetrahydrospiro* [*indole*-3,2'-*pyrrole*]-3'-*carboxylate* (4b): Yellow solid; m.p. 276–278 °C; IR  $v_{max}$ /cm<sup>-1</sup> (KBr): 3325, 3257, 2947, 1722, 1691, 1650, 1612, 1523, 1480, 1350; <sup>1</sup>H NMR (400 MHz, DMSO- $d_o$ ): δ 2.24 (s, 3H, CH<sub>3</sub>), 2.28 (s, 3H, CH<sub>3</sub>), 3.28 (3H, s, OCH<sub>3</sub>), 6.74 (d, *J* = 7.8 Hz, 1H, ArH), 6.95 (d, *J* = 8 Hz, 2H, ArH), 7.02–7.20 (m, 6H, ArH), 7.56 (d, *J* = 8 Hz, 1H, ArH), 7.96 (s, 1H, ArH), 9.21 (s, 1H, NH), 10.85 (s, 1H, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO- $d_o$ ): δ 20.4, 20.5, 50.7, 70.6, 104.7, 111.4, 122.3, 124.6, 126.3, 126.9, 128.5, 129.5, 129.6, 129.7, 132.3, 133.2, 137.1, 137.5, 142.1, 142.3, 162.4, 165.2, 174.2 ppm; Anal. calcd for C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub>: C, 65.05; H, 4.45; N, 11.24; found: C, 65.15; H, 4.51; N, 11.32%.

*Methyl* 5-chloro-4'-(4-methoxyanilino)-1'-(4-methoxyphenyl)-2,5'dioxo-1,1',2,5'-tetrahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (**4c**): Yellow solid; m.p. 256–258 °C, (lit.<sup>11</sup> 254–256 °C); IR v<sub>max</sub>/cm<sup>-1</sup> (KBr): 3331, 3250, 2953, 2835, 1730, 1624, 1510, 1475, 1360, 1302; <sup>1</sup>H NMR (400 MHz, DMSO- $d_{o}$ ): δ 3.26 (s, 3H, OCH<sub>3</sub>), 3.67 (s, 3H, OCH<sub>3</sub>), 3.74 (s, 3H, OCH<sub>3</sub>), 6.74 (d, *J* = 7.8 Hz, 2H, ArH), 6.92–7.05 (m, 4H, ArH), 7.14 (m, 2H, ArH), 7.25 (d, *J* = 8 Hz, 2H, ArH), 7.56 (d, *J* = 7.6 Hz, 1H, ArH), 9.06 (s, 1H, NH), 10.83 (s, 1H, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO- $d_{o}$ ): δ 50.7, 55.1, 55.2, 70.7, 103.2, 111.3, 113.1, 114.2, 124.3, 124.6, 126.2, 127.1, 128.3, 128.5, 129.7, 132.5, 142.2, 142.6, 156.2, 158.7, 162.3, 165.3, 174.2 ppm; Anal. calcd for C<sub>27</sub>H<sub>22</sub>ClN<sub>3</sub>O<sub>6</sub>: C, 62.37; H, 4.26; N, 8.08; found: C, 62.45; H, 4.34; N, 8.02%.

*Methyl* 4'-(4-*methylanilino*)-1'-(4-*methylphenyl*)-2,5'-dioxo-1,1',2,5'tetrahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (4d): Yellow solid; m.p. 229–231 °C (lit.<sup>11</sup> 229–231 °C); IR v<sub>max</sub>/cm<sup>-1</sup> (KBr): 3294, 3192, 3091, 2943, 1712, 1674, 1623, 1512, 1474; <sup>1</sup>H NMR (400 MHz, DMSO- $d_o$ ): δ 2.21 (s, 3H, CH<sub>3</sub>), 2.28 (s, 3H, CH<sub>3</sub>), 3.22 (s, 3H, OCH<sub>3</sub>), 6.86 (d, *J* = 7.8 Hz, 1H, ArH), 6.92 (d, *J* = 8 Hz, 2H, ArH), 7.05 (t, *J* = 7.8 Hz, 1H), 7.08–7.15 (m, 6 H, ArH), 7.18 (t, *J* = 8 Hz, 1H, ArH), 7.35 (d, *J* = 7.8 Hz, 1 H, ArH), 9.08 (s, 1H, NH), 10.75 (s, 1H, NH) pm; <sup>13</sup>C NMR (100 MHz, DMSO- $d_o$ ): δ 20.4, 20.5, 50.6, 71.0, 105.7, 110.1, 122.0, 122.1, 124.3, 125.7, 127.0, 128.5, 129.5, 129.9, 132.3, 132.9, 137.3, 137.5, 141.7, 143.2, 162.2, 165.6, 174.1 ppm; Anal. calcd for C<sub>27</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>: C, 71.51; H, 5.11; N, 9.27; found: C, 71.55; H, 5.02; N, 9.38%.

*Ethyl* 4'-(4-methylanilino)-1'-(4-methylphenyl)-2,5'-dioxo-1,1',2,5'tetrahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (**4e**): Yellow solid; m.p. 228–230 °C; IR  $v_{max}$ /cm<sup>-1</sup> (KBr): 3335, 3283, 3032, 2914, 1700, 1544, 1512, 1473, 1442, 1376, 1346, 1293, 1252; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>o</sub>): δ 0.97 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>); 2.19 (s, 3 H, CH<sub>3</sub>), 2.24 (s, 3 H, CH<sub>3</sub>), 3.92–4.02 (m, 2H, OCH<sub>2</sub>), 6.71 (d, *J* = 8 Hz, 1 H, ArH), 6.84 (d, *J* = 8.4 Hz, 2H, ArH), 7.06–7.10 (m, 6H, ArH), 7.17–7.50 (m, 3H), 9.08 (s, 1H, NH), 10.80 (s, 1H, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>o</sub>): δ 13.1, 20.4, 20.5, 59.7, 70.9, 105.2, 111.3, 121.9, 124.8, 126.2, 126.7, 128.2, 128.4, 129.6, 129.7, 132.4, 132.7, 137.1, 137.6, 142.1, 142.2, 161.7, 165.4, 174.1 ppm; Anal. calcd for C<sub>28</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>: C, 71.93; H, 5.39; N, 8.99; found: C, 71.99; H, 5.48; N, 8.85%.

*Ethyl* 5-chloro-4'-(4-methylanilino)-1'-(4-methylphenyl)-2,5'-dioxo-1,1',2,5'-tetrahydrospiro [indole-3,2'-pyrrole]-3'-carboxylate (**4f**): Yellow solid; m.p. 248–250 °C; (lit.<sup>11</sup> 247–249 °C); IR  $v_{max}$ /cm<sup>-1</sup> (KBr): 3332, 3281, 3032, 2913, 1703, 1542, 1517, 1477, 1441, 1376, 1346, 1293, 1252, 854, 812, 774; <sup>1</sup>H NMR (400 MHz, DMSO- $d_o$ ): δ 0.66 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); 2.21 (s, 3H, CH<sub>3</sub>), 2.25 (s, 3H, CH<sub>3</sub>), 3.65–3.75 (m, 2H, OCH<sub>2</sub>), 6.75 (d, J = 8 Hz, 1 H, ArH), 6.95 (d, J = 8 Hz, 2H, ArH), 7.05–7.16 (m, 6H), 7.25 (m, 2H) 9.15 (s, 1H, NH), 10.88 (s, 1H, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO- $d_o$ ): δ 13.0, 20.4, 20.5, 59.5, 70.9, 105.1, 111.4, 121.9, 124.7, 126.1, 126.9, 128.1, 128.4, 129.6, 129.8, 132.3, 132.8, 137.0, 137.6, 142.1, 142.3, 161.8, 165.5, 174.2 ppm; Anal. calcd for C<sub>28</sub>H<sub>24</sub>ClN<sub>3</sub>O<sub>4</sub>: C, 67.00; H, 4.82; N, 8.37; found: C, 67.09; H, 4.73; N, 8.24%. *Methyl 5-methyl-4'-(4-methylanilino)-1'-(4-methylphenyl)-2,5'-dioxo-1,1',2,5'-tetrahydro* spiro[indole-3,2'-pyrrole]-3'-carboxylate (4g): Yellow solid, m.p. 249–251 °C; (lit.<sup>11</sup> 249–250 °C); IR  $v_{max}$ /cm<sup>-1</sup> (KBr): 3361, 3273, 3023, 2950, 2912, 1672, 1632, 1545, 1515, 1495, 1432, 1391, 1350, 1290, 1252, 1233, 1197, 1108; <sup>1</sup>H NMR (400 MHz, DMSO- $d_o$ ):  $\delta$  2.21–2.24 (6H, 2 CH<sub>3</sub>), 2.28 (s, 3H, CH<sub>3</sub>), 3.28 (s, 3H, OCH<sub>3</sub>), 6.64 (d, *J* = 7.6 Hz, 1H, ArH), 6.87 (d, *J* = 7.6 Hz, 2H, ArH), 6.98 (d, *J* = 7.8 Hz, 1H, ArH), 7.03 (d, *J* = 7.8 Hz, 2H, ArH), 7.11–7.07 (m, 4H, ArH), 7.14 (s, 1H, ArH), 9.06 (s, 1H, NH), 10.64 (s, 1H, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO- $d_o$ ):  $\delta$  20.4, 20.5, 20.7, 50.7, 71.0, 105.9, 109.8, 122.2, 124.7, 125.6, 126.8, 128.4, 129.5, 130.3, 131.1, 132.4, 132.9, 137.2, 137.4, 140.4, 141.6, 162.3, 165.5, 174.1 ppm; Anal. calcd for C<sub>28</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>: C, 71.93; H, 5.39; N, 8.99; found: C, 72.04; H, 5.48; N, 8.90%.

*Methyl* 5-chloro-4'-(4-methylanilino)-1'-(4-methylphenyl)-2,5'dioxo-1,1',2,5'-tetrahydro spiro[indole-3,2'-pyrrole]-3'-carboxylate (**4h**): Yellow solid; m.p. 256–258 °C; (lit.<sup>11</sup> 258–260 °C); IR v<sub>max</sub>/cm<sup>-1</sup> (KBr): 3343, 3274, 3032, 2950, 2918, 1703, 1544, 1512, 1475, 1440, 1354, 1292, 1254, 1195; <sup>1</sup>H NMR (400 MHz, DMSO- $d_{\delta}$ ):  $\delta$  2.24 (s, 3H, CH<sub>3</sub>), 2.29 (s, 3H, CH<sub>3</sub>), 3.26 (s, 3H, OCH<sub>3</sub>), 6.76 (d, *J* = 7.8 Hz, 1H, ArH), 6.93 (d, *J* = 8 Hz, 2H, ArH), 7.08–7.15 (m, 6H, ArH), 7.25 (m, 2H, ArH), 9.11 (s, 1H, NH), 10.87 (s, 1H, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO- $d_{\delta}$ ):  $\delta$  20.4, 20.5, 50.7, 70.8, 104.8, 111.4, 122.4, 124.7, 126.9, 128.0, 128.4, 129.6, 129.7, 129.8, 132.2, 133.1, 137.0, 137.6, 142.1, 142.2, 162.3, 165.3, 174.1 ppm; Anal. calcd for C<sub>27</sub>H<sub>22</sub>ClN<sub>3</sub>O<sub>4</sub>: C, 66.46; H, 4.54; N, 8.61; found: C, 66.35; H, 4.50; N, 8.50%.

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#### **Electronic Supplementary Information**

The spectral data are available through: stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data

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