# Photoinduced Chlorine Atom-transfer Cyclization/Photohydrolysis of 3-Acyl-2-chloro-*N*-(ω-phenylalkynyl) pyrroles: Alkyne was Converted to Ketone.

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### **Supporting Information**

Content	page
General remark	S2
Experimental procedures	S2-S4
References	S4
Analytical data for compounds 1a-6i	S5-S11
Analytical data for compounds 2a-8	S11-S14
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra	S15-S33

#### General remark:

All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh).

Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. <sup>1</sup>H NMR and <sup>13</sup>C NMR (300 or 400 MHz and 75 or 100MHz, respectively) spectra were recorded in CDCl<sub>3</sub>. Chemical shifts ( $\delta$ ) are reported in ppm using TMS as internal standard and spin-spin coupling contants (*J*) are given in Hz. EI-MS spertra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI.

#### **Experimental procedures:**

The preparation of 3,5-Dichloropyrrole-2,4-dicarbaldehyde.<sup>1</sup> N-Acetylglycine (0.5 g, 4.27 mmol) was dissolved in dry DMF (5mL) and cooled to 0  $^{\circ}$ C in an ice bath and POCl<sub>3</sub> (1.46 mL, 15.66 mmol) was added dropwise over 30min. The resulting mixture was stirred for 1h at room temperature then 4h at 90  $^{\circ}$ C. The contents of the fask were then poured, with stirring, onto a mixture of crushed ice (50 mL), sodium acetate (1.46 g) and water (5 mL). The product was extracted with ether (5 × 20mL) and dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was puried by column chromatographyonsilica, eluting with ethylacetate to give a red solid (0.36 g, 44%).

#### The preparation of 2-Bromo-1*H*-indole-3-carbaldehyde.<sup>2</sup>

To a solution of dimethylformamide (3.6 mL, 46 mmol) in dichloromethane (12 mL) was added dropwise a solution of phosphorus oxybromide (11.1g, 36.6 mmol) in dichloromethane (20mL) at  $0^{\circ}$ C. The white thick mixture was refluxed during 15 min, and then oxindole (2.053g, 15.42 mmol) was added portionwise. Then mixture was stirred at reflux during 1h. The reaction was quenched by addition of crushed ice to the media. The mixture was stirred for 20 min, then the two layers were separated. The aqueous layer was neutralized with solid potassiun carbonate. The pale yellow precipitate which appeared was washed with cold water and cold dichloromethane then triturated with evaporation 2was acetone. After of solvent. pure bromo-1H-indole-3-carbaldehyde was obtained as 3.44 g (15.35 mmol) of pale yellow solid

(98%).

#### The preparation of 3-Acetyl-2-chloroindole.<sup>3</sup>

POCl<sub>3</sub> (5.51mL) was added to a mixture of DMA (5.7mL) and CHCl<sub>3</sub> (20mL). A solution of oxindole (2.7 g; 18mmol) in CHCl<sub>3</sub> (20mL) was then added. The mixture was boiled for 5 h, cooled and poured onto water. The organic layer was extracted, and the PH of the aqueous layer was adjusted to PH=7 with sodium acetate. The mixture was left at room temperature overnight and then the solid was collected by filtration and washed with water. Yield 79%.

#### The preparation of 2-Chloro-1*H*-indole-3-carbaldehyde.

This compound was obtained by the modification of The preparation of 3-acetyl-2-chloroindole.<sup>3</sup> POCl<sub>3</sub> (5.51 mL) was added to a mixture of DMF (5.7 mL) and CHCl<sub>3</sub> (20 mL). A solution of oxindole (2.7 g; 18 mmol) in CHCl<sub>3</sub> (20 mL) was then added. The mixture was boiled for 18 h, cooled and poured onto water. Then the PH of the mixture was adjusted to PH=7 with sodium carbonate. The whole was extracted with dichloromethane. The organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The products were separated by column chromatography (silica gel, hexane–acetone, 10:1) to afford the title compound (65%).

### General procedure for the preparation of *N*-alkylated-3,5-Dichloropyrrole-2,4dicarbaldehyde derives:



**Method A<sup>4</sup>**: Potassium carbonate (3mmol) was added to a solution of 3,5-Dichloropyrrole-2,4dicarbaldehyde (1 mmol) and the alkynyl halide (2 mmol) in CH<sub>3</sub>CN (25 mL). The mixture was heated to reflux for 10h. When the starting materials were consumed completely monitored by TLC, the reaction mixture was concentrated by vacuum and then the product was isolated by silica gel column chromatography. The identity and purity of the product was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis.



**Method B<sup>5</sup>**: to a mixture of 3,5-Dichloropyrrole-2,4- dicarbaldehyde (0.5 mmol), the alkynyl alcohol (0.6 mmol), and PPh<sub>3</sub> (0.75mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) was added diethyl azodicarboxylate (0.75 mmol) at 0 °C. The resulting mixture was flushed with Ar and stirred at room temperature for 24h. The mixture was concentrated and the residue was purified by chromatography on a silica gel column. The identity and purity of the product was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis.

#### **Photochemical Reactions; General Procedure:**

**1a** (0.096 g, 0.3 mmol) was dissolved in 25 mL acetone containing 0.1 mL H<sub>2</sub>O. The solution was deaerated by bubbling Ar for 30 min and irradiated at  $\lambda > 300$  nm with a medium-pressure mercury lamp (500 W) at ambient temperature. The progress of reaction was monitored by TLC at regular intervals. After the solvent was removed under reduced pressure, the residue was separated by column chromatography on silica gel eluted by hexane–ethyl acetate 6 : 1 ( v/v ) to afford product **2a**.

#### **References:**

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- (3) A. Monge, J. Palop, C. Ramirez, M. Font, E. F. Alvarez, J. Med. Chem. 1991, 26, 179.
- (4) A. P. Dobbs, K. Jones, K. T. Veal, Tetrahedron 1998, 54, 2149.
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Analytical data for compounds 1a-4i:



**3,5-dichloro-1-(4-phenylbut-3-ynyl)pyrrole-2,4-dicarbaldehyde (1a).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.98 (s, 1H), 9.83 (s, 1H), 7.27-7.32 (m, 5H), 4.69 (t, J = 6.4 Hz, 2H), 2.89 (t, J = 6.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 182.2, 177.4, 132.3, 131.4, 128.2, 128.1, 127.66, 126.2, 122.7, 117.1, 84.2, 83.4, 44.6, 20.8; ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>11</sub>Cl<sub>2</sub>NO<sub>2</sub>+H<sup>+</sup>: 320.0240, found 320.0243.



**3,5-dichloro-1-(4-p-tolylbut-3-ynyl)pyrrole-2,4-dicarbaldehyde (1b).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.97 (s, 1H), 9.82 (s, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 4.68 (t, *J* = 6.6 Hz, 2H), 2.87 (t, *J* = 6.6 Hz, 2H), 2.32 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 182.2, 177.4, 138.3, 132.3, 131.3, 129.0, 127.6, 126.2, 119.6, 117.0, 83.5, 83.4, 44.6, 21.4, 20.8; ESI-HRMS: m/z Calcd for C<sub>17</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub>+H<sup>+</sup>: 334.0396, found 334.0399.



**3,5-dichloro-1-(4-(4-methoxyphenyl)but-3-ynyl)pyrrole-2,4-dicarbaldehyde (1c).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.98 (s, 1H), 9.82 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.68 (t, *J* = 6.4 Hz, 2H), 3.79 (s, 3H), 2.87 (t, *J* = 6.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 182.3, 177.4, 159.5, 132.8, 132.4, 127.7, 126.2, 117.0, 114.9, 113.9, 83.3, 82.6, 55.2, 44.7, 20.8; ESI-HRMS: m/z Calcd for C<sub>17</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>3</sub>+H<sup>+</sup>: 350.0345, found 350.0340.



**3,5-dichloro-1-(4-(4-chlorophenyl)but-3-ynyl)pyrrole-2,4-dicarbaldehyde** (1d). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.97 (s, 1H), 9.82 (s, 1H), 7.21-7.27 (m, 4H), 4.68 (t, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 182.2, 177.4, 134.2, 132.6, 132.1, 128.6, 127.7, 126.1, 121.1, 116.9, 85.3, 82.3, 44.4, 20.7; ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>10</sub>Cl<sub>3</sub>NO<sub>2</sub> + H<sup>+</sup>: 353.9850, found 353.9853.



**3,5-dichloro-1-(5-(4-methoxyphenyl)pent-4-ynyl)pyrrole-2,4-dicarbaldehyde** (1e). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.92 (s, 1H), 9.81 (s, 1H), 7.30 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 4.61 (t, J = 6.9 Hz, 2H), 3.80 (s, 3H), 2.50 (t, J = 6.9 Hz, 2H), 1.98-2.07 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 182.2, 177.3, 159.2, 132.8, 131.7, 127.5, 126.1, 116.9, 115.4, 113.8, 85.9, 81.4, 55.2, 45.5, 28.8, 16.8; ESI-HRMS: m/z Calcd for C<sub>18</sub>H<sub>15</sub>Cl<sub>2</sub>NO<sub>3</sub>+H<sup>+</sup>: 364.0502, found 364.0500.



**3,5-dichloro-1-(5-(4-chlorophenyl)pent-4-ynyl)pyrrole-2,4-dicarbaldehyde (1f).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.93 (s, 1H), 9.82 (s, 1H), 7.24-7.32 (m, 4H), 4.61 (t, *J* = 7.2 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.99-2.08 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 182.2, 177.3, 133.8, 132.7, 132.5, 128.5, 127.5, 126.1, 121.7, 116.9, 88.6, 80.5, 45.4, 28.6, 16.7; ESI-HRMS: m/z Calcd for C<sub>17</sub>H<sub>12</sub>Cl<sub>3</sub>NO<sub>2</sub>+H<sup>+</sup>: 368.0007, found 368.0011.



**methyl 2-(5-(2,4-dichloro-3,5-diformylpyrrol-1-yl)pent-1-ynyl)benzoate (1g).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.92 (s, 1H), 9.81 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.42-7.52 (m, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 4.67 (t, *J* = 6.9 Hz, 2H), 3.90 (s, 3H), 2.61 (t, *J* = 6.9 Hz, 2H), 2.05-2.10 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 182.2, 177.3, 167.8, 134.2, 131.6, 131.5, 131.5, 130.2, 127.5, 126.1, 123.9, 116.8, 116.8, 93.1, 80.3, 52.1, 45.5, 28.6, 17.2; ESI-HRMS: m/z Calcd for C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub>NO<sub>4</sub>+H<sup>+</sup>: 392.0451, found 392.0455.



**4,5-dichloro-1-(4-phenylbut-3-ynyl)pyrrole-2-carbaldehyde (1h).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.39 (s, 1H), 7.27-7.32 (m, 5H), 6.93 (s, 1H), 4.63 (t, J = 6.9 Hz, 2H), 2.87 (t, J = 6.9 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 178.0, 132.3, 130.3, 128.2, 127.9, 125.2, 121.2, 119.9, 110.7, 84.7, 83.6, 45.1, 21.4; ESI-HRMS: m/z Calcd for C<sub>15</sub>H<sub>11</sub>Cl<sub>2</sub>NO+H<sup>+</sup>: 292.0291, found 292.0295.



**4,5-dichloro-1-(4-p-tolylbut-3-ynyl)pyrrole-2-carbaldehyde (1i).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ ppm 9.40 (s, 1H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 6.92 (s, 1H), 4.64 (t, *J* = 6.9

Hz, 2H), 2.85 (t, J = 6.9 Hz, 2H), 2.38 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 178.0, 138.0, 131.3, 129.2, 128.9, 126.1, 122.3, 119.9, 111.7, 84.1, 83.0, 45.1, 21.4, 21.1; ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>13</sub>Cl<sub>2</sub>NO+H<sup>+</sup>:306.0447, found 306.0443.

**4,5-dichloro-1-(4-(4-methoxyphenyl)but-3-ynyl)pyrrole-2-carbaldehyde** (**1***j*). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.38 (s, 1H), 7.27 (d, *J* = 9.3 Hz, 2H), 6.91 (s, 1H), 6.80 (d, *J* = 9.3 Hz, 2H), 4.62 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 2.83 (t, *J* = 6.9 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 178.0, 159.2, 132.8, 129.1, 123.1, 122.2, 115.1, 113.8, 111.6, 83.3, 82.7, 55.2, 44.1, 21.1; ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub>+H<sup>+</sup>:322.0396, found 322.0398.



**1-(5-phenylpent-4-ynyl)pyrrole-2-carbaldehyde (1m).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ ppm 9.52 (s, 1H), 7.40-7.43 (m, 2H), 7.26-7.29 (m, 3H), 7.01 (s, 1H), 6.92-6.93 (m, 3H), 6.20-6.22 (m, 3H), 4.46 (t, J = 6.6 Hz, 2H), 2.34 (t, J = 7.2 Hz, 2H), 2.19-2.07 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ ppm 179.1, 131.7, 131.4, 131.1, 128.1, 127.6, 126.10, 124.9, 123.5, 109.4, 88.4, 81.5, 47.6, 29.0, 16.2; ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>15</sub>Cl<sub>3</sub>NO+H<sup>+</sup>: 238.1235, found 238.1228.



**2-chloro-1-(4-phenylbut-3-ynyl)indole-3-carbaldehyde (4a).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 10.12 (s, 1H), 8.29-8.32 (m, 1H), 7.41-7.43 (m, 1H), 7.31-7.34 (m, 2H), 7.23-7.27 (m, 5H), 4.47 (t, J = 7.2 Hz, 2H), 2.93 (t, J = 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 184.0, 136.1, 135.3, 131.4, 128.2, 128.1, 124.4, 124.1, 123.5, 122.7, 121.4, 113.2, 109.7, 86.4, 83.4, 42.5, 20.3; ESI-HRMS: m/z Calcd for C<sub>19</sub>H<sub>14</sub>ClNO+H<sup>+</sup>:308.0837, found 308.0833.



**2-chloro-1-(4-p-tolylbut-3-ynyl)indole-3-carbaldehyde (4b).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 10.13 (s, 1H), 8.29-8.32 (m, 1H), 7.42-7.45 (m, 1H), 7.29-7.35 (m, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.49 (t, *J* = 6.9 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H), 2.32 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 184.0, 138.3, 136.2, 135.4, 131.3, 129.0, 124.5, 124.1, 123.5, 121.4, 119.6, 113.2, 109.7, 83.8, 83.5, 42.6, 21.4, 20.4; ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>16</sub>CINO+H +:322.0993, found 322.0996.

OCH-

**2-chloro-1-(4-(4-methoxyphenyl)but-3-ynyl)indole-3-carbaldehyde (4c).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 10.10 (s, 1H), 8.28-8.32 (m, 1H), 7.42-7.51 (m, 1H), 7.29-7.34 (m, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 4.48 (t, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.91 (t, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 184.1, 159.4, 135.4, 132.8, 124.5, 124.1, 124.1, 123.5, 121.4, 114.8, 113.9, 113.2, 109.7, 83.3, 83.1, 55.2, 42.7, 20.4; ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>16</sub>ClNO<sub>2</sub>+H<sup>+</sup>:338.0943, found 338.0946.



**1-(2-chloro-1-(4-phenylbut-3-ynyl)indol-3-yl)ethanone (4d).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.38-8.41 (m, 1H), 7.37-7.42 (m, 1H), 7.26-7.32 (m, 7H), 4.48 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.67 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 192.9, 134.9, 131.4, 130.9, 128.2, 128.1, 125.9, 123.6, 123.0, 122.8, 122.2, 113.6, 109.4, 84.9, 83.2, 42.5, 30.8, 20.3; ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>16</sub>ClNO+H<sup>+</sup>: 322.0993, found 322.0990.



**1-(2-chloro-1-(4-p-tolylbut-3-ynyl)indol-3-yl)ethanone (4e).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.38-8.40 (m, 1H), 7.40-7.42 (m, 1H), 7.28-7.31 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.50 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.68 (s, 3H), 2.32 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 192.9, 138.2, 135.0, 131.4, 130.9, 129.0, 126.0, 123.7, 123.1, 122.3, 119.8, 113.8, 109.4, 84.1, 83.4, 42.7, 30.4, 20.4, 14.0; ESI-HRMS: m/z Calcd for C<sub>21</sub>H<sub>18</sub>CINO+H<sup>+</sup>: 336.1150, found 336.1155.



**1-(2-chloro-1-(4-(4-chlorophenyl)but-3-ynyl)indol-3-yl)ethanone** (**4f**). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.38-8.41 (m, 1H), 7.32-7.41 (m, 1H), 7.28-7.31 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.48 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.67 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 192.9, 135.0, 134.1, 132.6, 130.8, 128.5, 125.9, 123.6, 123.1, 122.3, 121.2, 113.7, 109.3, 86.0, 82.2, 42.4, 30.8, 20.3; ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>15</sub>Cl<sub>2</sub>NO+H<sup>+</sup>: 356.0604, found 356.0607.



**2-bromo-1-(4-phenylbut-3-ynyl)indole-3-carbaldehyde (4g).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 10.04 (s, 1H), 8.31-8.34 (m, 1H), 7.43-7.46 (m, 1H), 7.26-7.33 (m, 7H), 4.51 (t, *J* = 7.2 Hz,

2H), 2.93 (t, J = 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 185.4, 136.7, 131.4, 128.2, 128.1, 125.5, 125.3, 124.1, 123.6, 122.7, 121.2, 115.5, 109.9, 84.7, 83.4, 43.8, 20.4; ESI-HRMS: m/z Calcd for C<sub>19</sub>H<sub>14</sub>BrNO+H<sup>+</sup>: 352.0332, found 352.0335.

**2-bromo-1-(4-p-tolylbut-3-ynyl)indole-3-carbaldehyde (4h).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 10.03 (s, 1H), 8.31-8.33 (m, 1H), 7.40-7.44 (m, 1H), 7.28-7.32 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 4.49 (t, *J* = 6.6 Hz, 2H), 2.91 (t, *J* = 6.6 Hz, 2H), 2.31 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 185.4, 138.2, 136.7, 131.3, 129.0, 125.5, 125.3, 124.1, 123.4, 121.2, 119.6, 115.5, 109.9, 83.9, 83.5, 43.9, 21.4, 20.4; ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>16</sub>BrNO + H<sup>+</sup>: 366.0488, found 366.0485.



**1-(2-chloro-1-(5-phenylpent-4-ynyl)indol-3-yl)ethanone (4i**). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.37-8.39 (m, 1H), 7.40-7.43 (m, 3H), 7.27-7.32(m, 5H), 4.42 (t, J = 7.2 Hz, 2H), 2.67 (S, 3H), 2.49 (t, J = 6.6 Hz, 2H), 2.08-2.16 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 192.8, 135.0, 131.57, 131.0, 128.3, 127.9, 125.9, 123.5, 123.3, 122.9, 122.2, 113.4, 109.3, 88.0, 81.9, 42.7, 30.7, 28.2, 16.9; ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>18</sub>ClNO+H<sup>+</sup>: 336.1150, found 336.1153.

#### Analytical data for compounds 2a-7:



Colorless solid, mp 113-115 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.81 (s, 1H), 9.76 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.64 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 5.27 (dd, *J* = 10.0 Hz, 4.0 Hz, 1H), 4.38-4.51 (m, 2H), 2.94-3.04 (m, 1H), 2.58-2.65 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 196.6, 183.2, 177.3, 146.1, 135.3, 133.9, 128.8, 128.8, 127.7, 124.8, 116.1, 48.6, 45.5, 32.0; MS m/z (relative intensity, %): 303 (32.3), 301 (100), 254 (30.8), 228 (11.2), 146 (8.9), 127 (13.6), 99 (6.4), 75 (8.9); ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>12</sub>ClNO<sub>3</sub>+H<sup>+</sup>: 302.0579, found 302.0577.



Colorless solid, mp 125-126 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.80 (s, 1H), 9.76 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.24 (dd, *J* = 10.0 Hz, 4.0 Hz, 1H), 4.38-4.51 (m, 2H), 2.91-3.01 (m, 1H), 2.57-2.64 (m, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm

196.2, 183.2, 177.4, 146.0, 145.0, 132.8, 129.5, 129.0, 127.7, 124.8, 116.1, 48.7, 45.3, 32.0, 21.6; MS m/z (relative intensity, %): 317 (32.3), 315 (100), 275 (30.8), 238 (11.6), 136 (12.1), 129 (11.6), 99 (9.4), 75 (9.3); ESI-HRMS: m/z Calcd for  $C_{17}H_{14}CINO_3+H^+$ : 316.0735, found 316.0737.



Colorless solid, mp 160-161 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.81 (s, 1H), 9.77 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.23 (dd, *J* = 9.6 Hz, 3.6 Hz, 1H), 4.40-4.53 (m, 2H), 3.90 (s, 3H), 2.91-3.00 (m, 1H), 2.58-2.66 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 195.2, 183.4, 177.4, 164.3, 146.5, 131.3, 128.3, 127.9, 124.9, 116.2, 114.1, 55.6, 48.8, 45.1, 32.2; MS m/z (relative intensity, %): 333 (32.1), 331 (100), 128 (17.9), 104 (9.7), 100 (6.9), 39 (9.5); ESI-HRMS: m/z Calcd for C<sub>17</sub>H<sub>14</sub>CINO<sub>4</sub>+H<sup>+</sup>: 332.0684, found 332.0688.



Colorless solid, mp 138-139 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.81 (s, 1H), 9.77 (s, 1H), 7.99 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 5.22 (dd, J = 10.0 Hz, 4.0 Hz, 1H), 4.41-4.53 (m, 2H), 2.93-3.03 (m, 1H), 2.58-2.65 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 195.7, 183.4, 177.5, 145.7, 140.6, 133.7, 130.2, 129.2, 127.9, 124.9, 116.1, 48.7, 45.3, 32.0; MS m/z (relative intensity, %): 339 (11.2), 337 (67.2), 335 (100), 238 (36.2), 127 (22.8), 100 (12.4), 63 (8.9); ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>11</sub>Cl<sub>2</sub>NO<sub>3</sub>+H<sup>+</sup>: 336.0189, found 336.0186.



Colorless solid, mp 151-152 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.84 (s, 1H), 9.82 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.38 (dd, *J* = 6.8 Hz, 3.6 Hz, 1H), 4.68 (dt, *J* = 14.4 Hz, 4.0 Hz, 1H), 4.10-4.17 (m, 1H), 3.89 (s, 3H), 2.02-2.14 (m, 3H), 1.90-2.01 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 196.2, 184.1, 177.7, 163.8, 140.9, 130.9, 129.1, 128.0, 126.0, 117.8, 114.1, 55.5, 46.0, 41.6, 22.6, 18.8; MS m/z (relative intensity, %): 347 (35.6), 345 (100), 271 (69.6), 254 (34.3), 127 (54.8), 40 (64.6); ESI-HRMS: m/z Calcd for C<sub>18</sub>H<sub>16</sub>CINO<sub>4</sub>+H<sup>+</sup>: 346.0841, found 346.0845.



Colorless solid, mp 149-150 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.84 (s, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 5.34 (dd, J = 6.8 Hz, 2.4 Hz, 1H), 4.68 (dt, J = 14.4 Hz, 4.0 Hz, 1H), 4.12-4.21 (m, 1H), 2.11-2.14 (m, 1H), 1.96-2.05 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):

δ ppm 196.6, 184.2, 177.8, 140.1, 140.0, 133.4, 130.0, 129.2, 129.1, 126.1, 117.9, 45.9, 41.8, 22.3, 18.8; MS m/z (relative intensity, %): 353 (11.0), 351 (66.7), 349 (100), 271 (69.6), 127 (54.8), 40 (64.6); ESI-HRMS: m/z Calcd for  $C_{17}H_{13}Cl_2NO_3+H^+$ : 350.0345, found 350.0348.



Colorless solid, mp 200-202 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.88 (s, 1H), 9.84 (s, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.66 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.57 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 5.22 (d, *J* = 5.6 Hz, 1H), 4.76 (dt, *J* = 17.2 Hz, 2.8 Hz, 1H), 4.03-4.11 (m, 1H), 3.83 (s, 3H), 2.20-2.32 (m, 2H), 1.93-2.03 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 199.5, 184.3, 177.8, 167.9, 139.7, 139.0, 132.2, 131.3, 131.2, 129.6, 129.1, 128.1, 126.1, 118.2, 55.5, 46.1, 44.7, 20.9, 18.5; MS m/z (relative intensity, %): 375 (35.6), 373 (100), 291 (79.6), 274 (34.3), 117 (54.8), 47 (64.6); ESI-HRMS: m/z Calcd for C<sub>19</sub>H<sub>16</sub>CINO<sub>5</sub>+H<sup>+</sup>: 374.0790, found 374.0794.

Colorless solid, mp 131-132 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.41 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 6.84 (s, 1H), 5.01 (dd, *J* = 9.6 Hz, 4.4 Hz, 1H), 4.41-4.52 (m, 2H), 2.93-3.02 (m, 1H), 2.75-2.82 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 196.6, 178.2, 140.1, 135.5, 133.9, 128.9, 128.8, 127.7, 123.5, 107.5, 47.9, 43.6, 32.9; MS m/z (relative intensity, %): 275 (32.3), 273 (100), 146 (8.9), 127 (13.6), 99 (6.4), 75 (8.9); ESI-HRMS: m/z Calcd for C<sub>15</sub>H<sub>12</sub>CINO<sub>2</sub>+H<sup>+</sup>: 274.0630, found 274.0634.



Colorless solid, mp 134-135 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.41 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 4.98 (dd, *J* = 8.8 Hz, 4.0 Hz, 1H), 4.39-4.52 (m, 2H), 2.90-2.99 (m, 1H), 2.73-2.80 (m, 1H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 196.2, 178.2, 145.0, 140.4, 133.0, 129.5, 129.1, 127.7, 123.6, 107.5, 48.0, 43.4, 33.0, 21.7; MS m/z (relative intensity, %): 289 (30.8), 287 (100), 146 (8.9), 127 (13.6), 99 (6.4), 75 (8.9); ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>14</sub>CINO<sub>2</sub>+H<sup>+</sup>: 288.0786, found 288.0789.



Colorless solid, mp 154-155 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.40 (s, 1H), 8.05 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.83 (s, 1H), 4.97 (dd, J = 9.2 Hz, 4.4 Hz, 1H), 4.39-4.52 (m,

2H), 3.91 (s, 3H), 2.89-2.98 (m, 1H), 2.74-2.81 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 195.0, 178.2, 164.2, 140.5, 131.3, 128.4, 127.6, 123.6, 114.0, 107.4, 55.5, 48.0, 43.1, 33.0; MS m/z (relative intensity, %): 303 (32.3), 301 (100), 228 (11.2), 146 (9.9), 127 (33.6), 99 (9.4), 75 (9.9); ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>14</sub>CINO<sub>3</sub>+H<sup>+</sup>: 304.0735, found 304.0738.



Colorless solid, mp 164-165 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 10.56 (s, 1H), 9.86 (s, 1H), 7.52 (d, *J* = 6.8 Hz, 1H), 7.43-7.46 (m, 3H), 4.36 (t, *J* = 6.8 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 185.2, 178.4, 142.2, 137.7, 129.8, 129.7, 128.7, 128.5, 128.5, 127.3, 125.6, 115.8, 47.6, 36.3; MS m/z (relative intensity, %): 323 (11.2), 321 (66.7) 319 (100), 105 (36.5), 77 (32.8); ESI-HRMS: m/z Calcd for C<sub>16</sub>H<sub>11</sub>Cl<sub>2</sub>NO<sub>2</sub>+H<sup>+</sup>: 320.0240, found 320.0244.



Colorless solid, mp 157-158 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.72 (s, 1H), 8.16-8.19 (m, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.64 (tt, J = 7.6 Hz, 1.2 Hz, 1H), 7.52 (t, J = 7.2 Hz, 2H), 7.25-7.31 (m, 3H), 5.30 (dd, J = 9.2 Hz, 4.0 Hz, 1H), 4.26-4.32 (m, 1H), 4.12-4.18 (m, 1H), 2.99-3.08 (m, 1H), 2.78-2.86 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 197.3, 183.4, 151.4, 135.4, 134.0, 133.1, 129.9, 129.0, 128.8, 123.1, 122.8, 121.3, 110.5, 110.3, 44.8, 44.2, 32.9; MS m/z (relative intensity, %): 289 (100), 184 (44.7), 105 (98.2), 77 (54.8); ESI-HRMS: m/z Calcd for C<sub>19</sub>H<sub>15</sub>NO<sub>2</sub>+H<sup>+</sup>: 290.1176, found 290.1179.



Colorless solid, mp 155-156 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.73 (s, 1H), 8.16-8.19 (m, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25-7.29 (m, 3H), 5.30 (dd, *J* = 9.2 Hz, 4.0 Hz, 1H), 4.28-4.34 (m, 1H), 4.12-4.18 (m, 1H), 2.97-3.07 (m, 1H), 2.80-2.87 (m, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 196.9, 183.4, 151.7, 145.1, 133.1, 133.0, 129.90, 129.70, 129.0, 123.10, 122.8, 121.4, 110.5, 110.3, 44.7, 44.3, 33.0, 21.7; MS m/z (relative intensity, %): 303 (100), 225 (44.7), 107 (63.3), 77 (64.8); ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>2</sub>+H<sup>+</sup>: 304.1332, found 304.1334.



Colorless solid, mp 164-165 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 9.79 (s, 1H), 8.16-8.18 (m, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.28-7.32 (m, 3H), 7.00 (d, *J* = 8.8 Hz, 1H), 5.37 (dd, *J* = 9.2 Hz, 4.0 Hz, 1H), 4.35-4.42 (m, 1H), 4.18-4.24 (m, 1H), 3.90 (s, 3H), 3.00-3.09 (m, 1H), 2.85-2.93 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 195.8, 183.4, 164.3, 151.8, 133.1, 131.3, 129.9, 128.3, 123.2, 122.8, 121.4, 114.2, 110.5, 110.2, 55.6, 44.4, 44.3, 33.1; MS m/z (relative intensity, %): 319

(100), 284 (74.7), 107 (23.6), 77 (54.8); ESI-HRMS: m/z Calcd for  $C_{19}H_{15}NO_2+H^+$ : 320.1281, found 320.1285.

Colorless solid, mp 194-195 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.10 (d, J = 7.2 Hz, 2H), 8.00 (d, J = 7.2 Hz, 1H), 7.63 (t, J = 7.2 Hz, 1.2 Hz, 1H), 7.53 (t, J = 7.2 Hz, 2H), 7.27-7.34 (m, 3H), 5.45 (dd, J = 9.6 Hz, 3.6 Hz, 1H), 4.17-4.31 (m, 2H), 3.02-3.11 (m, 1H), 2.66-2.73 (m, 1H), 2.50 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 198.1, 192.6, 150.4, 136.0, 133.5, 132.9, 129.9, 128.8, 128.7, 122.2, 122.1, 121.3, 110.4, 110.4, 46.0, 43.7, 32.8, 29.8; MS m/z (relative intensity, %): 303 (100), 225 (44.7), 107 (63.3), 77 (64.8); ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>2</sub>+H<sup>+</sup>: 304.1332, found 304.1336.



Colorless solid, mp 211-212 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.00-8.02 (m, 3H), 7.30-7.34 (m, 3H), 7.24-7.29 (m, 2H), 5.47 (dd, J = 9.6 Hz, 3.6 Hz, 1H), 4.20-4.34 (m, 2H), 3.02-3.12 (m, 1H), 2.66-2.74 (m, 1H), 2.50 (s, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 197.7, 192.6, 150.5, 144.5, 133.5, 133.0, 130.0, 129.5, 129.0, 122.2, 122.1, 121.3, 110.5, 110.4, 45.9, 43.8, 33.0, 29.8, 21.7; MS m/z (relative intensity, %): 317 (100), 271 (69.6), 254 (34.3), 127 (54.8), 40 (64.6); ESI-HRMS: m/z Calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>2</sub>+H<sup>+</sup>: 318.1489, found 318.1486.

![](_page_12_Picture_6.jpeg)

Colorless solid, mp 223-225 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.06 (d, J = 8.8 Hz, 2H), 7.94 (dd, J = 6.8 Hz, 2.0 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.35 (dd, J = 6.8 Hz, 2.0 Hz, 1H), 7.27-7.32 (m, 2H), 5.45 (dd, J = 9.6 Hz, 4.0 Hz, 1H), 4.31-4.37 (m, 1H), 4.19-4.30 (m, 1H), 3.02-4.12 (m, 1H), 2.67-2.75 (m, 1H), 2.55 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 197.3, 192.8, 150.3, 140.1, 134.6, 133.0, 130.3, 129.7, 129.1, 122.2, 122.2, 121.1, 110.6, 110.3, 45.7, 43.8, 32.8, 29.9; MS m/z (relative intensity, %): 339 (33.1), 337 (100), 254 (34.3), 127 (54.8), 77 (64.6); ESI-HRMS: m/z Calcd for C<sub>20</sub>H<sub>16</sub>CINO<sub>2</sub>+H<sup>+</sup>: 338.0943, found 338.0945.

![](_page_12_Picture_8.jpeg)

Colorless solid, mp 104-105 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.67 (d, J = 8.0 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.45-7.49 (m, 2H), 7.36 (td, J = 5.6 Hz, 2.4 Hz, 1H), 4.26 (t, J = 6.0 Hz, 2H), 3.25 (t, J = 6.0 Hz,

2H), 2.33-2.39 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 138.7, 135.4, 129.4, 126.6, 126.5, 126.4, 125.5, 124.0, 123.3, 123.2, 123.1, 122.0, 121.1, 119.9, 111.7, 109.0, 40.7, 24.1, 22.1; MS m/z (relative intensity, %): 293 (32.3), 291 (100), 254 (30.8), 228 (11.2), 146 (8.9), 127 (13.6), 99 (6.4), 75 (8.9); ESI-HRMS: m/z Calcd for C<sub>19</sub>H<sub>14</sub>ClN+H<sup>+</sup>: 292.0888, found 292.0891.

![](_page_13_Picture_2.jpeg)

Colorless solid, mp 146-147 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.44 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.40-7.46 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 4.59 (t, *J* = 7.2 Hz, 2H), 3.91 (t, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 148.7, 138.3, 130.8, 128.8, 128.1, 126.6, 125.6, 124.4, 123.59, 123.58, 123.5, 122.9, 122.4, 119.7, 110.6, 106.6, 47.5, 33.4; MS m/z (relative intensity, %): 279 (28.9), 277 (100), 241 (43.7), 213 (9.3), 120 (18.9), 106 (10.9); ESI-HRMS: m/z Calcd for C<sub>18</sub>H<sub>12</sub>ClN+H<sup>+</sup>: 278.0731, found 278.0733.

![](_page_14_Figure_1.jpeg)

![](_page_14_Figure_2.jpeg)

![](_page_15_Figure_1.jpeg)

 $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) and  $^{13}$ C NMR spectra (100 MHz, CDCl<sub>3</sub>) of **2b.** 

![](_page_16_Figure_1.jpeg)

 $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>) and  $^{13}\text{C}$  NMR spectra (100 MHz, CDCl<sub>3</sub>) **2c.** 

![](_page_17_Figure_1.jpeg)

 $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>) and  $^{13}\text{C}$  NMR spectra (100 MHz, CDCl<sub>3</sub>) of **2d.** 

![](_page_18_Figure_1.jpeg)

 $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) and  $^{13}$ C NMR spectra (100 MHz, CDCl<sub>3</sub>) of **2e.** 

![](_page_19_Figure_1.jpeg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR spectra (100 MHz, CDCl<sub>3</sub>) **2f.** 

![](_page_20_Figure_1.jpeg)

 $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>) and  $^{13}\text{C}$  NMR spectra (100 MHz, CDCl<sub>3</sub>) of **2g.** 

![](_page_21_Figure_1.jpeg)

![](_page_21_Figure_2.jpeg)

![](_page_22_Figure_1.jpeg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR spectra (100 MHz, CDCl<sub>3</sub>) of **2i**.

![](_page_23_Figure_1.jpeg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR spectra (100 MHz, CDCl<sub>3</sub>) of **2j.** 

![](_page_24_Figure_1.jpeg)

 $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>) and  $^{13}\text{C}$  NMR spectra (100 MHz, CDCl<sub>3</sub>) of **3.** 

![](_page_25_Figure_1.jpeg)

![](_page_25_Figure_2.jpeg)

![](_page_26_Figure_1.jpeg)

![](_page_26_Figure_2.jpeg)

![](_page_27_Figure_1.jpeg)

 $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>) and  $^{13}\text{C}$  NMR spectra (100 MHz, CDCl<sub>3</sub>) of **5c.** 

![](_page_28_Figure_1.jpeg)

## $^1\text{H}$ NMR (400 MHz, CDCl<sub>3</sub>) and $^{13}\text{C}$ NMR spectra (100 MHz, CDCl<sub>3</sub>) of **5d.**

![](_page_29_Figure_1.jpeg)

![](_page_29_Figure_2.jpeg)

![](_page_30_Figure_1.jpeg)

### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR spectra (100 MHz, CDCl<sub>3</sub>) of **5f.**

![](_page_31_Figure_1.jpeg)

# $^1\text{H}$ NMR (400 MHz, CDCl<sub>3</sub>) and $^{13}\text{C}$ NMR spectra (100 MHz, CDCl<sub>3</sub>) of **6.**

9.5 9.0

8.5 8.0 7.5 7.0 6.5

1.00

0.99

![](_page_32_Figure_1.jpeg)

6.0 5.5

5.0 4.5 4.0

2.07

3.5 3.0 2.5 2.0

1.5

1.0 0.5

ppm

# $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) and $^{13}$ C NMR spectra (100 MHz, CDCl<sub>3</sub>) of **7.**

![](_page_32_Figure_3.jpeg)

2.06

![](_page_33_Figure_1.jpeg)

![](_page_33_Figure_2.jpeg)