

**Supporting Information**  
**for**  
**Synthesis and fluorosolvatochromism of 3-  
arylnaphtho[1,2-*b*]quinolizinium derivatives**

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**Experimental and analytical data**

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# 1 Experimental Section

## 1.1 General

NMR spectra were recorded with a Bruker Avance 400 ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 100 MHz) at room temperature (approximately 22 °C) or with a Varian VNMR-S 600 ( $^1\text{H}$ : 600 MHz,  $^{13}\text{C}$ : 150 MHz) at 25 °C or 35 °C ( $\text{DMSO}-d_6$ ). Spectra were analysed with the software ACD/NMR Processor Academic Edition 12.02 and referenced to the solvent  $\text{DMSO}-d_6$  ( $^1\text{H} = 2.50$ ,  $^{13}\text{C} = 39.5$ ). The chemical shifts are given in ppm. Absorption spectra were recorded with a Cary 100 bio spectrophotometer in quartz cells (10 mm x 10 mm) with baseline correction. Emission spectra were collected in quartz cells (10 mm x 10 mm) with a Cary Eclipse spectrophotometer at 20 °C. Elemental analyses data were determined with a HEKAtech EUROEA combustion analyzer by Mr. Rochus Breuer (Universität Siegen, Organische Chemie I). Mass spectra (ESI) were recorded on a Finnigan LCQ Deca ( $U = 6$  kV; working gas: argon; auxiliary gas: nitrogen; temperature of the capillary: 200 °C). The melting points were measured with a Büchi 545 (Büchi, Flawil, CH) and they are uncorrected.

## 1.2 Synthesis

### *1-[(6-Bromonaphth-2-yl)methyl]-2-(1,3-dioxolan-2-yl)pyridinium bromide (3)*

A solution of 2-bromo-6-(bromomethyl)naphthalene (**2**) (2.38 g, 7.99 mmol) and 2-(1,3-dioxolane-2-yl)pyridine (1.33 g, 8.80 mmol) in DMSO (60 mL) was stirred under an inert gas atmosphere for 7 d at room temperature. The reaction mixture was added dropwise under vigorous stirring to EtOAc (1 L). The white precipitate was filtered, washed with EtOAc (50 mL) and  $\text{Et}_2\text{O}$  (50 mL) and dried in vacuo to give the pure product as white amorphous solid which was used without further purification (2.81 g, 6.23 mmol, 78%). For analytical purposes a sample was recrystallized from MeOH/EtOAc to give the product **3** as bright beige-colored microcrystalline solid; mp = 193–195 °C (dec.). –  $^1\text{H}$ -NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 4.11\text{--}4.13$  (m, 4 H, 2 x  $\text{CH}_2$ ), 6.16 (s, 2 H,  $\text{CH}_2$ ), 6.56 (s, 1 H, CH), 7.55 (dd,  $^3J = 8.8$  Hz,  $^4J = 1.8$  Hz, 1 H, 3-H), 7.69 (dd,  $^3J = 8.8$  Hz,  $^4J = 2.0$  Hz, 1 H, 7-H), 7.87 (s, 1 H, 1-H), 7.90 (d,  $^3J = 8.8$  Hz, 1 H, 8-H), 7.99 (d,  $^3J = 8.8$  Hz, 1 H, 4-H), 8.20–8.23 (m, 1 H, 5'-H), 8.27 (d,  $^4J = 1.8$  Hz, 1 H, 5-H), 8.36 (dd,  $^3J = 7.9$  Hz,  $^4J = 1.2$  Hz, 1 H, 3'-H), 8.73–8.77 (m, 1 H, 4'-H), 9.11 (dd,  $^3J = 6.1$  Hz,  $^4J = 0.9$  Hz, 1 H, 6'-H). –  $^{13}\text{C}$ -NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 59.9$  ( $\text{CH}_2$ ), 65.7 (2 x  $\text{CH}_2$ ), 97.2 (CH), 120.2 (6-C), 126.1 (3'-C), 126.6 (3-C), 127.5 (1-C), 128.1 (4-C), 128.7 (5'-C), 129.6 (5-C), 129.8 (7-C), 130.3 (8-C), 131.2 (8a-C), 132.1 (2-C), 133.9 (4a-C), 147.3 (4'-C), 147.4 (6'-C), 152.2 (2'-C). – MS (ESI $^+$ ):  $m/z = 370$  (100) [ $\text{M}-\text{Br}$ ] $^+$  – EI. Anal. for  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{NO}_2$  (451.16), calcd (%): C 50.58, H 3.80, N 3.10, found (%): C 50.54, H 3.75, N 3.04.

### *3-Bromonaphtho[1,2-b]quinolizinium bromide (4)*

A solution of pyridinium derivative **3** (2.80 g, 6.21 mmol) in aq. HBr (48%, 28 mL) was stirred under reflux for 4.5 h. After cooling to room temperature, THF (50 mL) was added to the reaction mixture and the orange-colored precipitate was collected, washed with THF (25 mL) and Et<sub>2</sub>O (25 mL). The analytically pure product **4** was obtained by two-fold recrystallization from MeOH as fine shiny yellow needles (1.75 g, 4.49 mmol, 73%); mp > 300 °C (dec.). – <sup>1</sup>H-NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 8.08–8.10 (m, 1 H, 10-H), 8.10 (dd, <sup>3</sup>*J* = 8.8 Hz, <sup>4</sup>*J* = 2.4 Hz, 1 H, 2-H), 8.13 (br. s, 2 H, 5-H, 6-H), 8.27 (ddd, <sup>3</sup>*J* = 7.6 Hz, <sup>3</sup>*J* = 6.8 Hz, <sup>4</sup>*J* = 0.8 Hz, 1 H, 11-H), 8.43 (d, <sup>4</sup>*J* = 2.4 Hz, 1 H, 4-H), 8.64 (d, <sup>3</sup>*J* = 8.8 Hz, 1 H, 12-H), 8.99 (d, <sup>3</sup>*J* = 8.8 Hz, 1 H, 1-H), 9.40 (d, <sup>3</sup>*J* = 6.8 Hz, 1 H, 9-H), 10.05 (s, 1 H, 13-H), 10.29 (s, 1 H, 7-H). – <sup>13</sup>C-NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 120.7 (13-C), 122.9 (10-C), 124.7 (6-C), 125.4 (3-C, 6a-C), 125.6 (13b-C), 126.9 (12-C), 127.1 (1-C), 131.3 (5-C), 131.5 (4-C), 131.7 (2-C), 133.3 (11-C), 134.7 (9-C), 134.7 (13a-C), 134.9 (4a-C), 137.5 (7-C), 138.9 (12a-C). – MS (ESI<sup>+</sup>): *m/z* = 308 (100) [M-Br]<sup>+</sup>. – El. Anal. for C<sub>17</sub>H<sub>11</sub>Br<sub>2</sub>N x H<sub>2</sub>O (407.11), calcd (%): C 50.16, H 3.22, N 3.44, found (%): C 50.10, H 3.23, N 3.48.

### **General procedure for the Suzuki–Miyaura coupling of 3-bromonaphtho[1,2-b]quinolizinium bromide with arylboronic acids (GP 1)<sup>[1]</sup>**

Under an inert gas atmosphere, a suspension of 3-bromonaphtho[1,2-b]quinolizinium bromide (**4**) (1.00 mmol), the corresponding arylboronic acid (1.10 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (30.0 μmol) or Pd(dppf)<sub>2</sub>Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (30.0 μmol) and KF (4.00 mmol) in DME/MeOH/H<sub>2</sub>O (2/1/1; 12 mL) was stirred at 80 °C for 18–24 h (reaction monitored by TLC). MeOH (20 mL) was added to the reaction mixture and the precipitated palladium-black was removed by hot filtration. After cooling the filtrate to room temperature, the yellow precipitate was collected, washed with EtOAc and Et<sub>2</sub>O (5 mL). The analytically pure product was isolated by recrystallization of the precipitate from MeOH.

### *3-Phenylnaphtho[1,2-b]quinolizinium bromide (6a)*

According to GP 1, the naphthoquinolizinium **4** (389 mg, 1.00 mmol) was made to react with phenyl boronic acid (**5a**) (134 mg, 1.10 mmol) for 20 h using Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (21.1 mg, 30.0 μmol) as catalyst. The product **6a** was obtained as dark orange colored, microcrystalline solid (97.3 mg, 252 μmol, 25%); mp > 300 °C. – <sup>1</sup>H-NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 7.49–7.52 (m, 1 H, 4'-H), 7.58–7.61 (m, 2 H, 3'-H, 5'-H), 7.96–7.98 (m, 2 H, 2'-H, 6'-H), 8.04–8.07 (m, 1 H, 10-H), 8.15 (d, <sup>3</sup>*J* = 8.8 Hz, 1 H, 6-H), 8.24–8.29 (m, 2 H, 5-H, 11-H), 8.33 (dd, <sup>3</sup>*J* =

8.4 Hz,  $^4J = 2.0$  Hz, 1 H, 2-H), 8.54 (d,  $^4J = 2.0$  Hz, 1 H, 4-H), 8.65 (d,  $^3J = 8.8$  Hz, 1 H, 12-H), 9.18 (d,  $^3J = 8.8$  Hz, 1 H, 1-H), 9.37 (d,  $^3J = 6.8$  Hz, 1 H, 9-H), 10.08 (s, 1 H, 13-H), 10.26 (s, 1 H, 7-H). –  $^{13}\text{C}$ -NMR (150 MHz, DMSO- $d_6$ ):  $\delta = 120.4$  (13-C), 122.6 (10-C), 123.6 (6-C), 125.7 (6a-C), 125.8 (1-C), 125.8 (13b-C), 126.8 (12-C), 126.9 (4-C), 127.2 (2'-C, 6'-C), 127.4 (2-C), 128.6 (4'-C), 129.1 (3'-C, 5'-C), 132.8 (5-C), 132.9 (11-C), 134.0 (4a-C), 134.6 (9-C), 135.1 (13a-C), 137.3 (7-C), 138.4 (1'-C), 138.8 (12a-C), 143.0 (3-C). – MS (ESI $^+$ ):  $m/z = 306$  (100)  $[\text{M}-\text{Br}]^+$ . – El. Anal. for  $\text{C}_{23}\text{H}_{16}\text{BrN}$  (385.9), calcd (%): C 71.51, H 4.18, N 3.63, found (%): C 71.68, H 4.10, N 3.60.

### *3-(4-Methylphenyl)naphtho[1,2-b]quinolizinium bromide (6b)*

According to GP 1, the naphthoquinolizinium **4** (389 mg, 1.00 mmol) was made to react with 4-methylphenyl boronic acid (**5b**) (150 mg, 1.10 mmol) for 20 h using  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (21.1 mg, 30.0  $\mu\text{mol}$ ) as catalyst. The product **6b** was obtained as dark yellow fine needles (67.4 mg, 168  $\mu\text{mol}$ , 17%); mp > 300 °C. –  $^1\text{H}$ -NMR (600 MHz, DMSO- $d_6$ ):  $\delta = 2.41$  (s, 3 H,  $\text{CH}_3$ ), 7.38–7.40 (m, 2 H, 3'-H, 5'-H), 7.85–7.87 (m, 2 H, 2'-H, 6'-H), 8.03–8.05 (m, 1 H, 10-H), 8.12 (d,  $^3J = 8.8$  Hz, 1 H, 6-H), 8.23–8.26 (m, 2 H, 5-H, 11-H), 8.28 (dd,  $^3J = 8.4$  Hz,  $^4J = 2.0$  Hz, 1 H, 2-H), 8.49 (d,  $^4J = 2.0$  Hz, 1 H, 4-H), 8.63 (d,  $^3J = 8.8$  Hz, 1 H, 12-H), 9.12 (d,  $^3J = 8.8$  Hz, 1 H, 1-H), 9.35 (d,  $^3J = 6.8$  Hz, 1 H, 9-H), 10.05 (s, 1 H, 13-H), 10.25 (s, 1 H, 7-H). –  $^{13}\text{C}$ -NMR (150 MHz, DMSO- $d_6$ ):  $\delta = 20.8$  (4'- $\text{CH}_3$ ), 120.3 (13-C), 122.6 (10-C), 123.7 (6-C), 125.6 (13b-C), 125.7 (6a-C), 125.8 (1-C), 126.5 (4-C), 126.9 (12-C), 127.1 (2'-C, 6'-C), 127.2 (2-C), 129.8 (3'-C, 5'-C), 132.8 (5-C), 133.0 (11-C), 134.1 (4a-C), 134.7 (9-C), 135.2 (13a-C), 135.5 (1'-C), 137.4 (7-C), 138.3 (4'-C), 138.9 (12a-C), 142.9 (3-C). – MS (ESI $^+$ ):  $m/z = 320$  (100)  $[\text{M}-\text{Br}]^+$ . – El. Anal. for  $\text{C}_{24}\text{H}_{18}\text{BrN}$  (400.3), calcd (%): C 72.01, H 4.53, N 3.50, found (%): C 71.84, H 4.48, N 3.52.

### *3-(Naphth-1-yl)naphtho[1,2-b]quinolizinium bromide (6c)*

According to GP 1, the naphthoquinolizinium **4** (389 mg, 1.00 mmol) was made to react with naphthalene-1-boronic acid (**5c**) (189 mg, 1.10 mmol) for 20 h using  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (21.1 mg, 30.0  $\mu\text{mol}$ ) as catalyst. In deviation from GP 1, the solvent of the filtrate was removed *in vacuo*, the residue was redissolved in DMSO (2 mL) and added dropwise to EtOAc (150 mL). The yellow precipitate was collected, washed with  $\text{H}_2\text{O}$  (5 mL), EtOAc (2 x 20 mL) and  $\text{Et}_2\text{O}$  (2 x 20 mL). The analytically pure product **6c** was separated by two-fold recrystallization of the precipitate from MeOH and obtained as ocher-colored, amorphous solid (117 mg, 268  $\mu\text{mol}$ , 27%); mp > 300 °C. –  $^1\text{H}$ -NMR (600 MHz, DMSO- $d_6$ ):  $\delta = 7.55$ –7.57 (m, 1 H, 7'-H), 7.60–7.63 (m, 1 H, 6'-H), 7.65 (dd,  $^3J = 6.8$  Hz,  $^4J = 1.2$  Hz, 1 H, 2'-H), 7.68–7.70 (m, 1 H, 3'-H), 7.89 (d,  $^3J = 8.4$  Hz, 1 H, 8'-H), 8.08–8.11 (m, 3 H, 10-H, 4'-H, 5'-H), 8.13 (dd,  $^3J = 8.0$  Hz,  $^4J = 1.6$  Hz, 1 H, 2-H), 8.19 (d,  $^3J = 8.8$  Hz, 1 H, 6-H), 8.27–8.29 (m, 1 H, 11-H), 8.31

(d,  $^3J = 9.2$  Hz, 1 H, 5-H), 8.36 (d,  $^4J = 2.0$  Hz, 1 H, 4-H), 8.69 (d,  $^3J = 8.8$  Hz, 1 H, 12-H), 9.27 (d,  $^3J = 8.8$  Hz, 1 H, 1-H), 9.42 (d,  $^3J = 6.8$  Hz, 1 H, 9-H), 10.17 (s, 1 H, 13-H), 10.33 (s, 1 H, 7-H). –  $^{13}\text{C}$ -NMR (150 MHz, DMSO- $d_6$ ):  $\delta = 120.6$  (13-C), 122.8 (10-C), 123.8 (6-C), 125.0 (8'-C), 125.4 (1-C), 125.6 (3'-C), 125.8 (6a-C), 125.9 (13b-C), 126.2 (6'-C), 126.9 (7'-C), 127.0 (12-C), 127.6 (2'-C), 128.6 (4'-C, 5'-C), 130.4 (4-C), 130.6 (8a'-C), 130.8 (2-C), 132.7 (5-C), 133.1 (11-C), 133.5 (4a'-C), 133.7 (4a-C), 134.8 (9-C), 135.3 (13a-C), 137.5 (7-C), 138.1 (1'-C), 139.0 (12a-C), 143.4 (3-C). – MS (ESI $^+$ ):  $m/z = 356$  (100)  $[\text{M}-\text{Br}]^+$ . – EI. Anal. for  $\text{C}_{27}\text{H}_{18}\text{BrN} \times \text{H}_2\text{O}$  (454.4), calcd (%): C 71.37, H 4.44, N 3.08, found (%): C 71.38, H 4.23, N 3.07.

### *3-(Naphth-2-yl)naphtho[1,2-b]quinolizinium bromide (6d)*

According to GP 1, the naphthoquinolizinium **4** (389 mg, 1.00 mmol) was made to react with naphthalene-2-boronic acid (**5d**) (189 mg, 1.10 mmol) for 18 h using  $\text{Pd}(\text{dppf})_2\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$  (24.5 mg, 30.0  $\mu\text{mol}$ ) as catalyst. The product **6d** was obtained as yellow, amorphous solid (214 mg, 490  $\mu\text{mol}$ , 49%); mp > 300 °C. –  $^1\text{H}$ -NMR (600 MHz, DMSO- $d_6$ ):  $\delta = 7.58$ –7.63 (m, 2 H, 6'-H, 7'-H), 8.00–8.01 (m, 1 H, 5'-H), 8.04–8.06 (m, 1 H, 10-H), 8.08–8.09 (m, 1 H, 8'-H), 8.12 (br. s, 2 H, 3'-H, 4'-H), 8.16 (d,  $^3J = 8.8$  Hz, 1 H, 6-H), 8.24–8.27 (m, 1 H, 11-H), 8.32 (d,  $^3J = 9.2$  Hz, 1 H, 5-H), 8.47 (dd,  $^3J = 8.4$  Hz,  $^4J = 2.0$  Hz, 1 H, 2-H), 8.54 (br. s, 1 H, 1'-H), 8.65 (d,  $^3J = 8.4$  Hz, 1 H, 12-H), 8.68 (d,  $^4J = 2.0$  Hz, 1 H, 4-H), 9.21 (d,  $^3J = 8.4$  Hz, 1 H, 1-H), 9.36 (d,  $^3J = 6.8$  Hz, 1 H, 9-H), 10.08 (s, 1 H, 13-H), 10.26 (s, 1 H, 7-H). –  $^{13}\text{C}$ -NMR (150 MHz, DMSO- $d_6$ ):  $\delta = 120.4$  (13-C), 122.6 (10-C), 123.7 (6-C), 124.9 (3'-C), 125.7 (6a-C), 125.8 (13b-C), 125.9 (1-C), 126.3 (1'-C), 126.6 (7'-C), 126.7 (6'-C), 126.9 (12-C), 127.2 (4-C), 127.5 (5'-C), 127.6 (2-C), 128.3 (8'-C), 128.7 (4'-C), 132.7 (4a'-C), 132.8 (5-C), 132.9 (11-C), 133.2 (8a'-C), 134.1 (4a-C), 134.7 (9-C), 135.2 (13a-C), 135.7 (2'-C), 137.4 (7-C), 138.9 (12a-C), 142.8 (3-C). – MS (ESI $^+$ ):  $m/z = 356$  (100)  $[\text{M}-\text{Br}]^+$ . – EI. Anal. for  $\text{C}_{27}\text{H}_{18}\text{BrN} \times \text{H}_2\text{O}$  (454.4), calcd (%): C 71.37, H 4.44, N 3.08, found (%): C 71.26, H 4.01, N 3.08.

### *3-(Phenanthrene-9-yl)naphtho[1,2-b]quinolizinium bromide (6e)*

According to GP 1, the naphthoquinolizinium **4** (195 mg, 500  $\mu\text{mol}$ ) was made to with phenanthrene-9-boronic acid (**5e**) (117 mg, 525  $\mu\text{mol}$ ) for 24 h using  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (10.5 mg, 15.0  $\mu\text{mol}$ ) as catalyst. In deviation from GP 1, the solvent of the filtrate was removed *in vacuo*, the residue was redissolved in DMSO (4 mL) and added dropwise to EtOAc (100 mL). The yellow precipitate was collected, washed with  $\text{H}_2\text{O}$  (5 mL), EtOAc (20 mL) and  $\text{Et}_2\text{O}$  (20 mL) and dried *in vacuo*. The product **6e** was obtained as yellow, amorphous solid (48.9 mg, 100  $\mu\text{mol}$ , 20%); mp > 215 °C (dec.). –  $^1\text{H}$ -NMR (600 MHz, DMSO- $d_6$ ):  $\delta = 7.62$ –7.64 (m, 1 H, 7'-H), 7.68–7.70 (m, 1 H, 2'-H), 7.73–7.77 (m, 2 H, 3'-H, 6'-H), 7.87 (d,  $^3J = 8.4$  Hz, 1 H, 8'-H), 7.94 (s, 1 H, 10'-H), 8.05–8.09 (m, 2 H, 1'-H, 10-H), 8.12–8.14 (m, 2 H, 2-H, 6-H),

8.25–8.29 (m, 2 H, 11-H, 5-H), 8.37 (s, 1 H, 4-H), 8.69 (d,  $^3J = 8.4$  Hz, 1 H, 12-H), 8.87 (d,  $^3J = 8.0$  Hz, 1 H, 4'-H), 8.95 (d,  $^3J = 8.0$  Hz, 1 H, 5'-H), 9.25 (d,  $^3J = 8.0$  Hz, 1 H, 1-H), 9.41 (d,  $^3J = 6.0$  Hz, 1 H, 9-H), 10.13 (s, 1 H, 13-H), 10.32 (s, 1 H, 7-H). –  $^{13}\text{C}$ -NMR (150 MHz, DMSO- $d_6$ ): = 120.5 (13-C), 122.7 (10-C), 122.7 (4'-C), 123.4 (5'-C), 123.7 (6-C), 125.3 (1-C), 125.7 (6a-C), 125.9 (8'-C), 125.9 (13b-C), 126.9 (12-C), 127.0 (6'-C), 127.1 (7'-C), 127.2 (2'-C), 127.3 (3'-C), 128.1 (10'-C), 128.8 (1'-C), 129.5 (4a'-C), 129.7 (8a'-C), 130.1 (4b'-C), 130.2 (4-C), 130.6 (2-C), 130.8 (10a'-C), 132.6 (5-C), 132.9 (11-C), 133.7 (4a-C), 134.6 (9-C), 135.1 (13a-C), 136.6 (9'-C), 137.3 (7-C), 138.8 (12a-C), 143.3 (3-C). – MS (ESI $^+$ ):  $m/z = 406$  (100)  $[\text{M}-\text{Br}]^+$ . – El. Anal. for  $\text{C}_{31}\text{H}_{20}\text{BrN} \times 2 \text{H}_2\text{O}$  (522.44), calcd (%): C 71.27, H 4.63, N 2.68, found (%): C 71.39, H 4.13, N 2.87.

### 1.3 Determination of fluorescence quantum yields

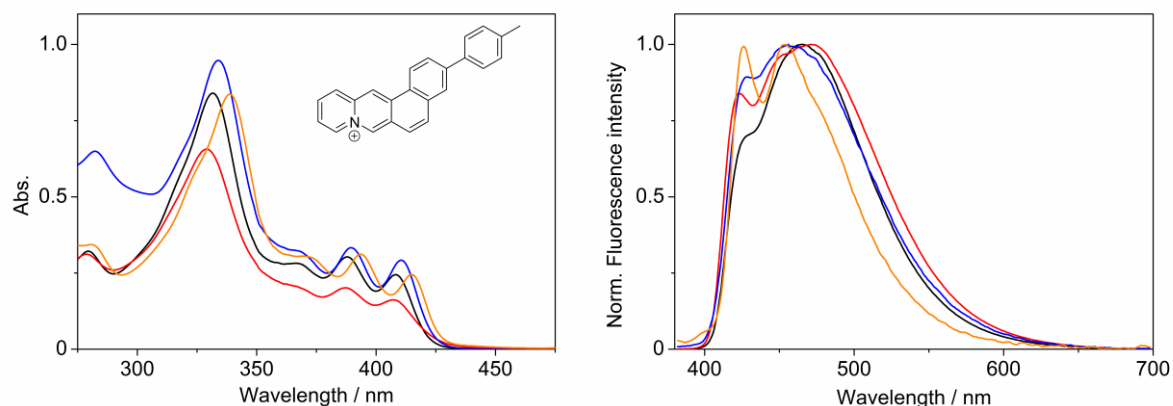
Solutions were prepared for each measurement from stock solutions in a suitable solvent (MeOH for **6a–d**,  $\text{CHCl}_3$  for **6e**;  $c = 1.00$  mM). For experiments in different solvents, aliquots of the stock solution were evaporated under a stream of nitrogen and redissolved in the respective solvent. In general, absorption spectra were determined with a detection speed of  $120 \text{ nm min}^{-1}$  in a range from 275 to 450 nm and subsequently smoothed in the Origin software with the function “adjacent-averaging” (factor of 10).

For the detection of emission spectra the excitation and emission slits were adjusted to 5 nm. The detection speed was  $120 \text{ nm min}^{-1}$  and the detector voltage was adjusted between 500 V and 600 V depending on the fluorescence emission intensity. The spectra were smoothed with the implemented moving-average function by a factor of 5. The relative fluorescence quantum yields of the aryl-substituted naphtho[1,2-*b*]quinolizinium derivatives were determined under identical conditions, i.e. the same cuvettes were used and the measurements were performed at a constant temperature with the same settings on the spectrometer (detection wavelength, excitation wavelength, detector voltage, slit bandwidths, collection rate). Coumarin 1 ( $\Phi_F = 0.73$  in EtOH)<sup>[2]</sup> (for **6a** and **6b**) and Coumarin 153 ( $\Phi_F = 0.38$  in EtOH)<sup>[2]</sup> (for **6c–e**) were used as standards. The emission spectra were collected from solutions with Abs = 0.10 at the respective excitation wavelength. After integration of the fluorescence band, the relative fluorescence quantum yields were calculated according to Eq. 1.<sup>[3,4]</sup>

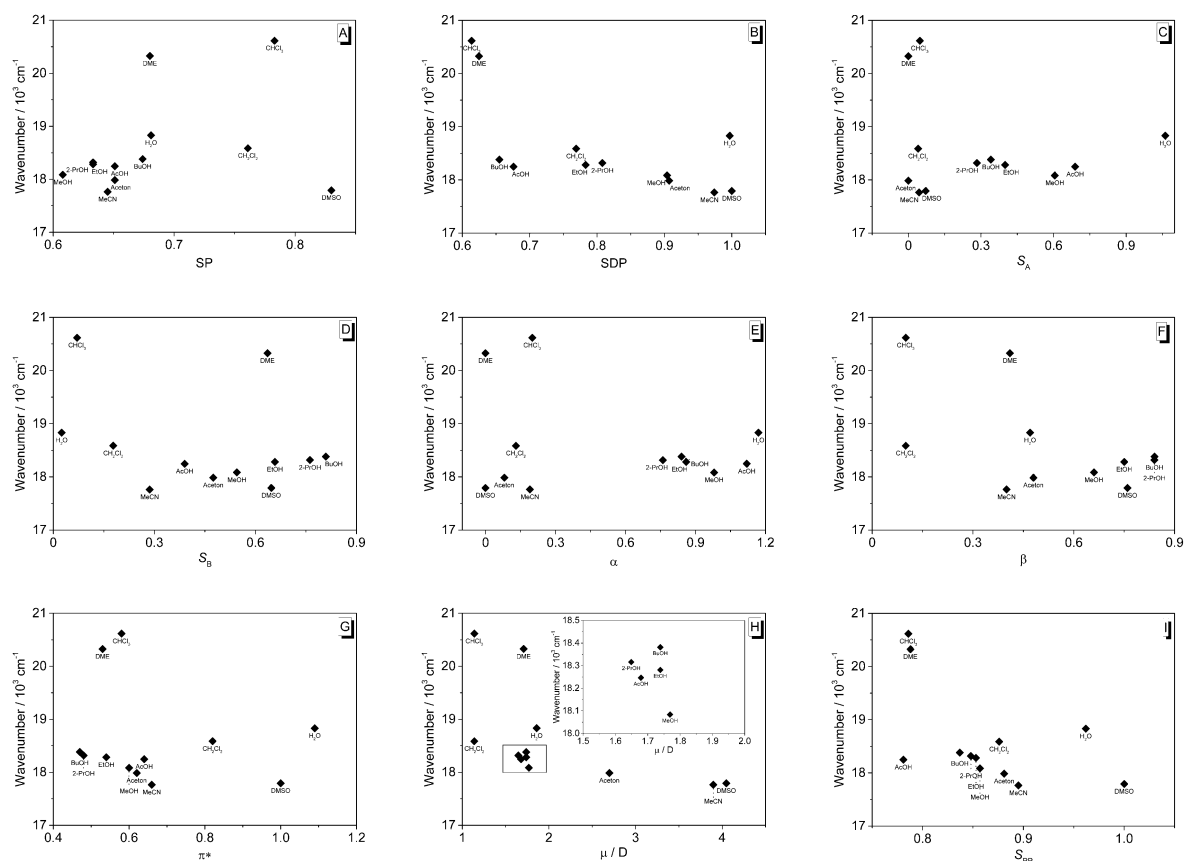
$$\phi_F = \frac{J_x(1-T_s)}{J_s(1-T_x)} \cdot \frac{n_x^2}{n_s^2} \cdot \phi_{F,s} \quad (\text{Eq. 1})$$

The subscripts “x” and “s” refer to the substance under investigation and a reference compound, respectively;  $J = \int I_F(\lambda) d\lambda$  is the emission integral over the area of interest;  $T$  is the optical transmittance of the sample solution at the excitation wavelength,  $\lambda_{ex}$ ;  $n$  is the refractive index of the sample or standard solution; however the quotient of the refractive indexes was neglected because it does not differ significantly from 1.

## 2 Additional spectroscopic data

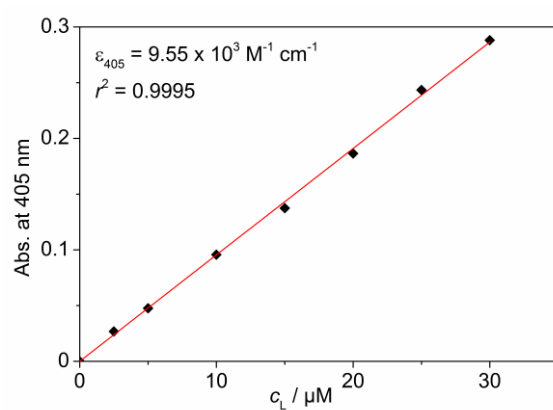


**Figure S1:** Absorption (left) and normalized emission spectra (right) of **6b** ( $c = 20 \mu\text{M}$ ) in different solvents:  $\text{H}_2\text{O}$  (red),  $\text{MeOH}$  (black),  $\text{DMSO}$  (blue),  $\text{CHCl}_3$  (orange).



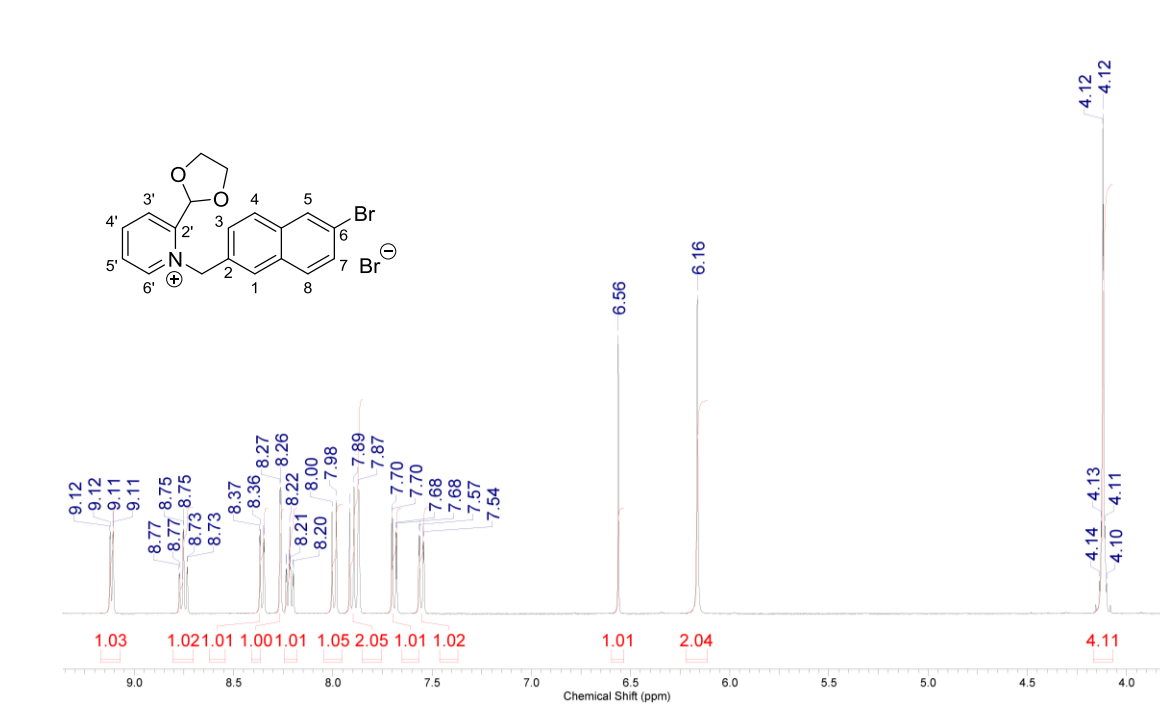
**Figure S2:** Plot of the emission maximum of **6e** in different solvents versus the polarizability, SP (A),<sup>[5]</sup> the dipolarity SDP (B),<sup>[5]</sup> the acidity,  $S_A$  (C),<sup>[6]</sup> the basicity,  $S_B$  (D),<sup>[6]</sup> the hydrogen bond (HB) donating properties,  $\alpha$  (E),<sup>[6]</sup> the HB accepting properties,  $\beta$  (F),<sup>[6]</sup> the Taft parameter  $\pi^*$  (G),<sup>[6]</sup> the dipole moment,  $\mu$  (H),<sup>[6]</sup> the dipolarity and polarizability  $S_{PP}$  (I).<sup>[6]</sup>



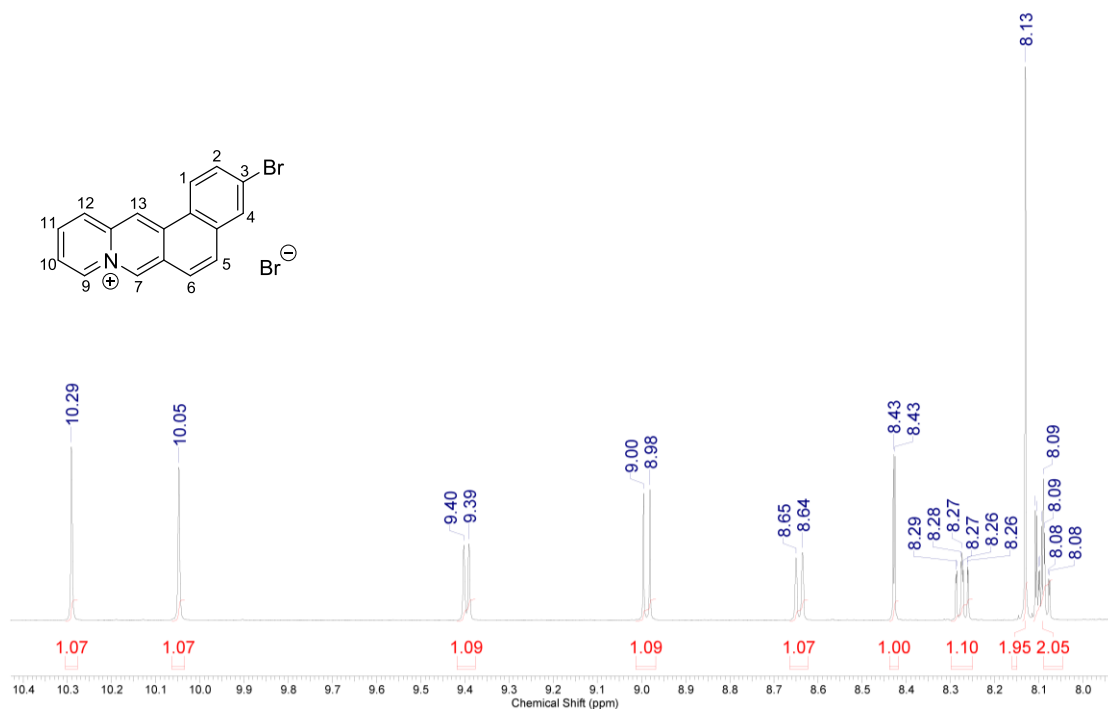


**Figure S3:** Plot of the absorbance of **6c** in H<sub>2</sub>O at  $\lambda = 405 \text{ nm}$  *versus* concentration.

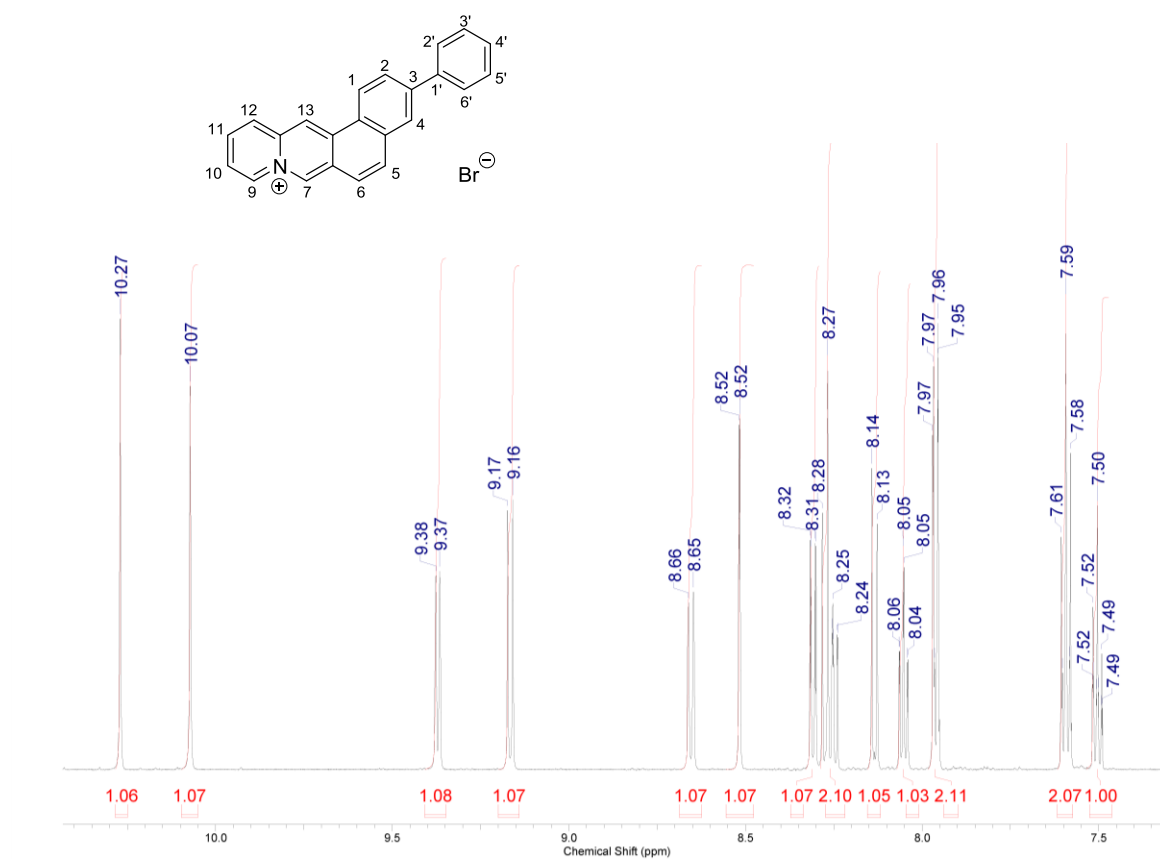
### 3 $^1\text{H}$ -NMR spectra of derivatives 3, 4 and 6a–e



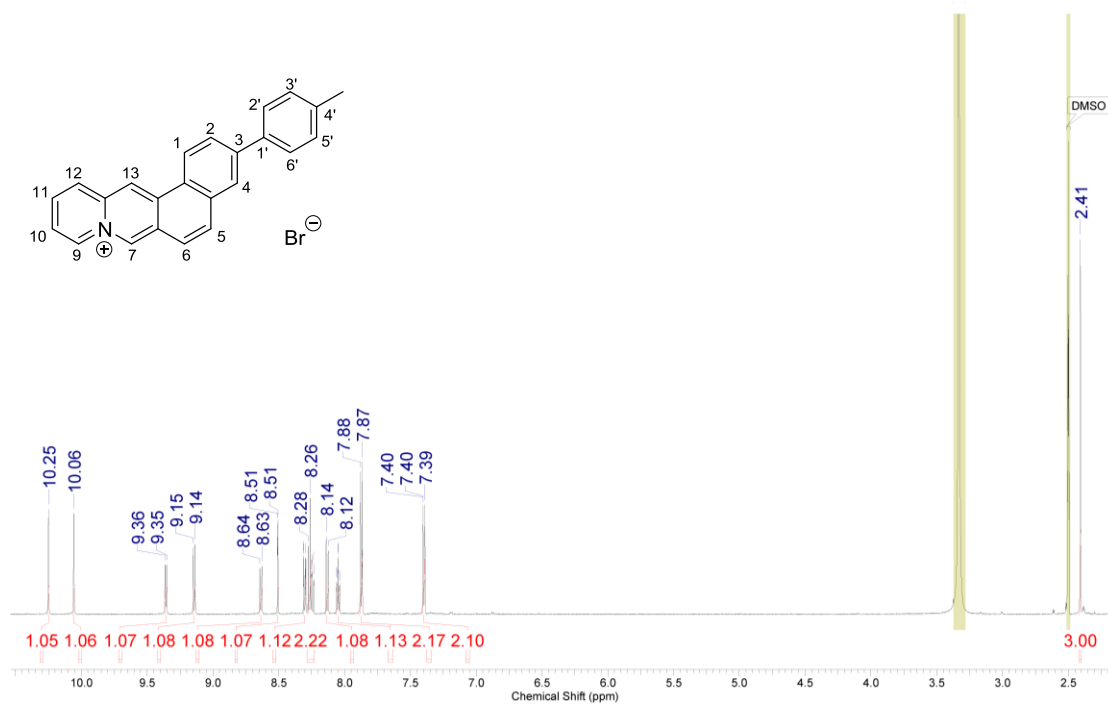
**Figure S4:**  $^1\text{H}$  NMR spectrum of 1-[(6-bromonaphth-2-yl)methyl]-2-(1,3-dioxolan-2-yl)pyridinium bromide (3).



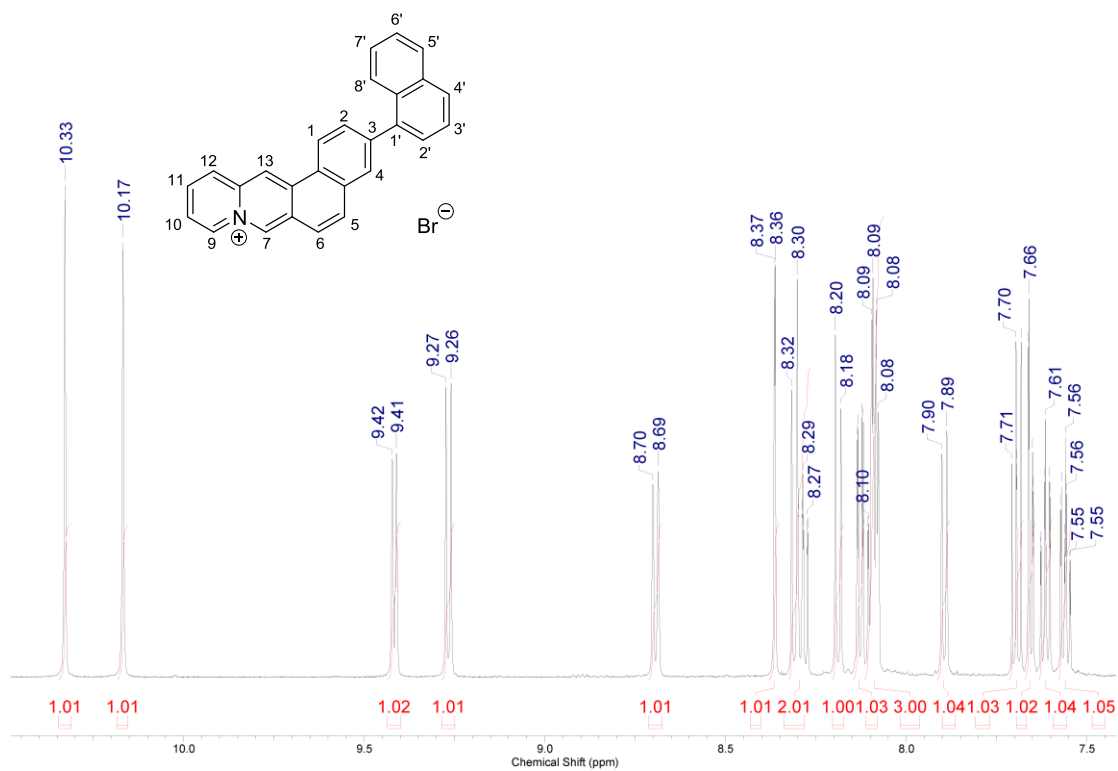
**Figure S5:**  $^1\text{H}$  NMR spectrum of 3-bromonaphtho[1,2-*b*]quinolizinium bromide (4).



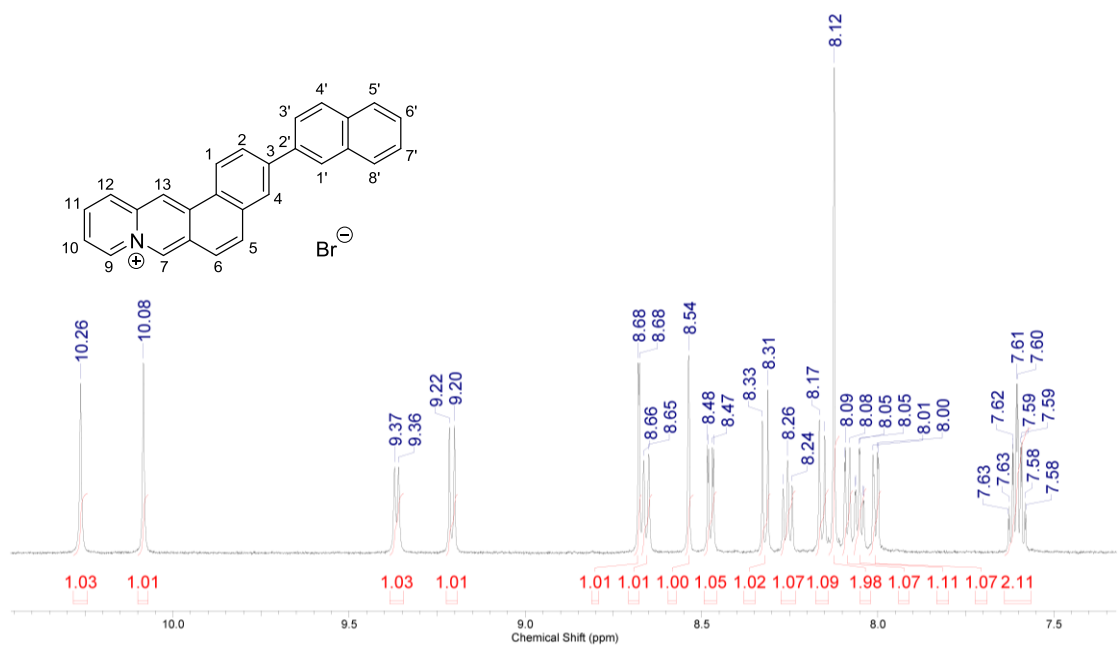
**Figure S6:** <sup>1</sup>H NMR spectrum of 3-phenylnaphtho[1,2-*b*]quinolizinium bromide (**6a**).



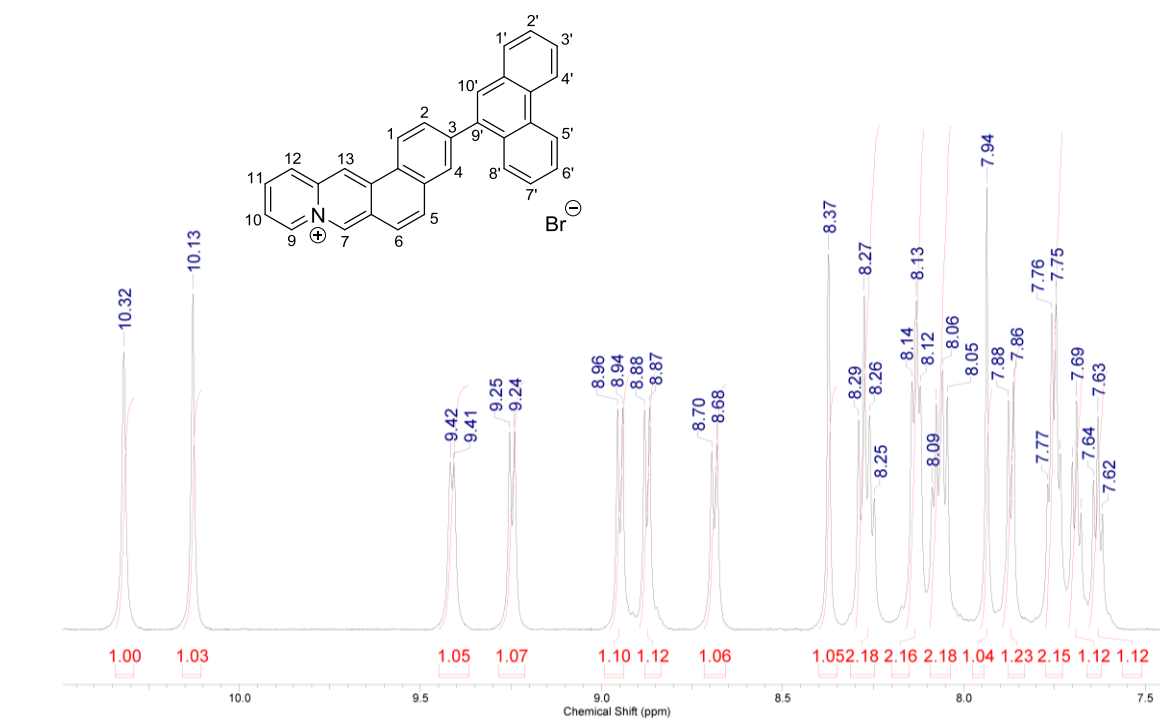
**Figure S7:** <sup>1</sup>H NMR spectrum of 3-(4-methylphenyl)naphtho[1,2-*b*]quinolizinium bromide (**6b**).



**Figure S8:** <sup>1</sup>H NMR spectrum of 3-(naphth-1-yl)naphtho[1,2-*b*]quinolizinium bromide (**6c**).



**Figure S9:** <sup>1</sup>H NMR spectrum of 3-(naphth-2-yl)naphtho[1,2-*b*]quinolizinium bromide (**6d**).



**Figure S10:**  $^1\text{H}$  NMR spectrum of 3-(phenanthrene-9-yl)naphtho[1,2-*b*]quinolizinium bromide (**6e**).

## 4 References

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