Water-Soluble Fluorescent Chemosensor for Sorbitol based on a Dicationic Diboronic Receptor. Crystal Structure and Spectroscopic Studies

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GENERAL CONDITIONS

Reagents and solvents were purchased as reagent grades and used without further purification. Compounds **9** and **10** were synthesized based on previously reported procedures.[1] On the other hand, **11**-**13** were obtained with methodologies described in the literature with slight modification (*vide infra*).[2,3] NMR spectra were recorded on a Bruker 300 with solvent peaks as the internal reference. ^{1}H and ^{13}C NMR spectra were obtained for solutions in $(CD_3)_2SO$, D_2O and/or CD_3CN; ^{11}B spectra were acquired for solutions in CD_3OD or mixtures as specificized in the footnotes. The assignments were confirmed by two-dimensional NMR experiments (COSY ^{1}H-^{1}H, HSQC ^{1}H-^{13}C, and HMBC ^{1}H-^{13}C). High-Resolution Electrospray Ionization mass with positive scan spectra for bromide salts of **11-13** and **11** and in the presence of sorbitol were obtained with a Bruker Micro TOF II.

Combustion analysis were recorded by a vario MICRO cube Elemental Analyzer Analysensysteme GmbH in CHNS modus.

Fluorescence Lifetime. A time-correlated single photon counting system coupled to a custom-built confocal microscope was used to acquire the fluorescence lifetimes. A 354 nm picosecond laser pulsed at 10 MHz (LDH-DC-405, PicoQuant) was focused into a 1 cm quartz cell with a 0.85 NA microscope objective. The fluorescence collected with the same objective was passed through a 366 nm long-pass dichroic mirror (Chroma T510lpxrxt), a 364 nm notch flter (Chroma ZET405nf), and a 425 nm long pass emission flter (Chroma ET425lp) and was focused to an avalanche photodiode (PD-050-CTE, MPD). The laser controller (PDL-800-D, PicoQuant) and the APD were connected to a TCSPC card (PicoHarp 300, PicoQuant). The power of irradiation was controlled to obtain less than 1% of the detection events in order to avoid pile-up effects on the recorded histogram. Allura Red (analytical standard) was used to obtain the IRF under the same conditions of irradiation. All data wer obtained and treated in SymphoTime software (PicoQuant).

Synthesis of N^2,N^6-di(quinolin-6-yl)pyridin-2,6-dicarboxamide, ***9***

The nucleophilic addition of *6-aminoquinoline* (500.0 mg, 3.47 mmol) into *2,6-pyridinedicarbonyl dichloride* was achieved in dry toluene (40 mL) under reflux for 4 hours in N_2 atmosphere. The bright-yellow precipitate was collected by vacuum filtration and washed twice with acetone. Then, the compound was neutralized with 3% $NaHCO_3$ aqueous solution to give a pale-yellow powder that corresponds to the desired compound after drying. The compound **9** was obtained at high purity according to ^1H and ^{13}C NMR spectra in 96% yield.

Synthesis of N-(quinolin-6-yl)benzamide, ***10****.*

6-aminoquinoline (500.0 mg, 3.47 mmol) and *benzoyl chloride* (3.47 mmol) were combined in dry toluene (40ml) and stirred at reflux for 2 hours. The yellow precipitate was isolated by filtration and then slurred in acetone for 2 hours and filtered again in a vacuum, and washed with extra cold acetone (30 mL). The solid was suspended in deionized water (10 mL), and a 3% $NaHCO_3$ aqueous solution was added to neutralize it. A pale-yellow powder was obtained and isolated by vacuum filtration and washed with two portions of 100 mL of distilled water. The solid was dried up in the air and then under vacuum (95% yield). The compound was identified by ^1H and ^{13}C NMR spectroscopy.

Synthesis 6,6'-((pyridine-2,6-dicarbonyl)bis(azanediyl))bis(1-benzylquinolin-1-ium) dibromide, ***12****.*

The compound **9** (100.0 mg, 0.238 mmol) was dissolved in 5 mL of anhydrous dimethylformamide (DMF). Then, a slight excess of bromomethyl-benzene (122.3 mg, 0.715 mmol) was added and stirred for 24 hours at room temperature under an N_2 atmosphere. The volume of solvent was halved under vacuum at 50 °C on a rotary evaporator; thus, a yellow precipitate was obtained. The yellow solid was isolated by vacuum filtration and washed twice with 10 mL of ethyl acetate/acetone mixture (1:3) and finally with 10 mL of diethyl ether. The yellow solid was dried under reduced pressure to give the bromide salt **11** in 87% yield (158.0 mg). The compound was identified by ^1H and ^{13}C NMR spectroscopy techniques.

*Cristal structure of **11-SO₄***

Table S1.** Crystal data and structure refinement for **11-SO₄

Empirical formula	$C_{45}H_{57.41}N_5O_{16.21}S_4B_2$
Formula weight	1077.52
Temperature/K	273(2)
Crystal system	Triclinic
Space group	P-1
a/Å	11.5675(8)
b/Å	14.3355(10)
c/Å	15.8991(11)
α/°	95.8776(14)
β/°	100.6117(14)
γ/°	102.3371(14)
Volume/Å^3	2503.8(3)
Z	2
ρ_{calc}g/cm^3	1.429
μ/mm^{-1}	0.265
F(000)	1132.0
Crystal size/mm^3	0.303 × 0.267 × 0.261
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.648 to 54.89
Index ranges	$-15 \le h \le 15$, $-18 \le k \le 18$, $-20 \le l \le 20$
Reflections collected	107739
Independent reflections	11433 [R_{int} = 0.0417, R_{sigma} = 0.0196]
Data/restraints/parameters	11433/146/745
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1044
Final R indexes [all data]	R_1 = 0.0467, wR_2 = 0.1105
Largest diff. peak/hole / e Å^{-3}	0.71/-0.65

Table S2. *Hydrogen Bonds for* ***11-SO₄***

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	**H2A**	**S1**	0.841(10)	2.919(13)	3.7131(13)	158(2)
O2	**H2A**	**O7**	0.841(10)	1.942(11)	2.7662(18)	166(2)
O3	**H3A**	**S1**	0.843(10)	2.829(14)	3.5981(14)	153(2)
O3	**H3A**	**O10**	0.843(10)	1.862(10)	2.7045(18)	179(3)
O5	**H5**	**S1**	0.840(10)	2.851(14)	3.6447(14)	158(2)
O5	**H5**	**O10**	0.840(10)	1.877(11)	2.7064(18)	169(3)
O6	**H6**	**S1**	0.837(10)	2.856(14)	3.6274(13)	154(2)
O6	**H6**	**O8**	0.837(10)	1.842(11)	2.6712(17)	170(2)
N2	**H2N**	**N1**	0.846(9)	2.25(2)	2.6751(18)	111.2(16)
N2	**H2N**	**O11**	0.846(9)	2.268(15)	2.9924(17)	143.7(19)
N4	**H4N**	**O11**	0.852(9)	2.171(12)	2.9794(17)	158.4(19)
O11	**H11A**	**O9**	0.827(10)	1.965(11)	2.7739(17)	166(2)
O11	**H11B**	**O12**	0.829(9)	2.017(10)	2.8400(18)	172(2)
O12	**H12A**	**S2**	0.848(10)	2.911(12)	3.7343(16)	164(2)
O12	**H12A**	**O15**	0.848(10)	1.916(12)	2.746(2)	166(3)
O12	**H12A**	**S2A**	0.848(10)	2.778(18)	3.567(11)	156(3)
O12	**H12A**	**O15A**	0.848(10)	2.17(3)	2.97(3)	157(3)
O12	**H12B**	**S3**	0.846(10)	3.011(14)	3.8027(15)	157(2)
O12	**H12B**	**O16**	0.846(10)	1.951(11)	2.793(2)	173(3)
O13	**H13A**	**O12**	0.843(10)	1.937(12)	2.771(2)	170(4)
O13	**H13B**	**S4**	0.841(10)	2.71(3)	3.310(2)	129(3)
O13	**H13B**	**O17**	0.841(10)	2.135(16)	2.941(2)	160(4)
O14	**H14A**	**O7**	0.840(10)	2.080(18)	2.901(3)	165(6)
O14	**H14B**	**O7**	0.840(10)	2.17(3)	2.925(3)	150(5)
O14	**H14B**	**O14**	0.840(10)	2.32(5)	2.847(6)	121(5)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x+1,-y+1,-z

Table S3. *Bond Lengths for boronic acid moieties in* ***11-SO₄***

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O5	B1	1.353(2)	O2	B2	1.357(2)
O6	B1	1.356(2)	O3	B2	1.360(2)
C36	B1	1.578(3)	C19	B2	1.577(3)

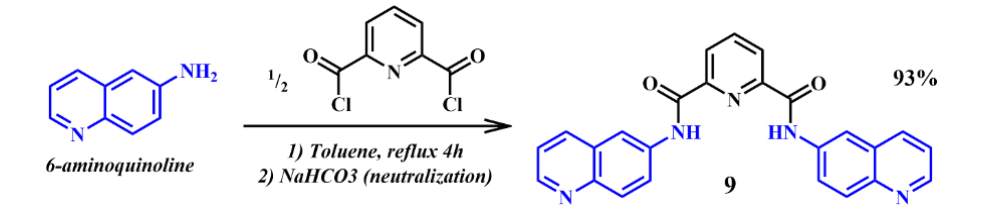
Table S4. *Bond Angles for boronic acid moieties in* ***11-SO₄***

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	B1	O6	125.02(17)	O2	B2	O3	124.51(17)
O5	B1	C36	117.38(16)	O2	B2	C19	117.97(15)
O6	B1	C36	117.59(15)	O3	B2	C19	117.51(16)

Table S5. *π – π interactions measured for* ***11-SO₄***

Atoms of 1st plane	Atoms of 2nd plane	Angle/°	Centroid-centroid distance/Å	Shift distance/Å
[C7-C8-C9-C10-C14-C15]	[N3-C11-C12-C13-C14-C10]	3.907	3.523	0.930
[C24-C27-C28-C32-C33-C25]	[C24-C27-C28-C32-C33-C25]	0.000	3.800	1.721
[C24-C27-C28-C32-C33-C25]	[N1-C5-C4-C3-C2-C1]	5.542	3.635	1.270
[C24-C27-C28-C32-C33-C25]	[N5-C32-C28-C29-C31-C30]	0.590	3.496	0.883
[C17-C18-C19-C20-C21-C22]	[C17-C18-C19-C20-C21-C22]	0.000	3.755	1.276

^{1}H and ^{13}C NMR spectra of N^2,N^6-di(quinolin-6-yl)pyridin-2,6-dicarboxamide, ***9****.*



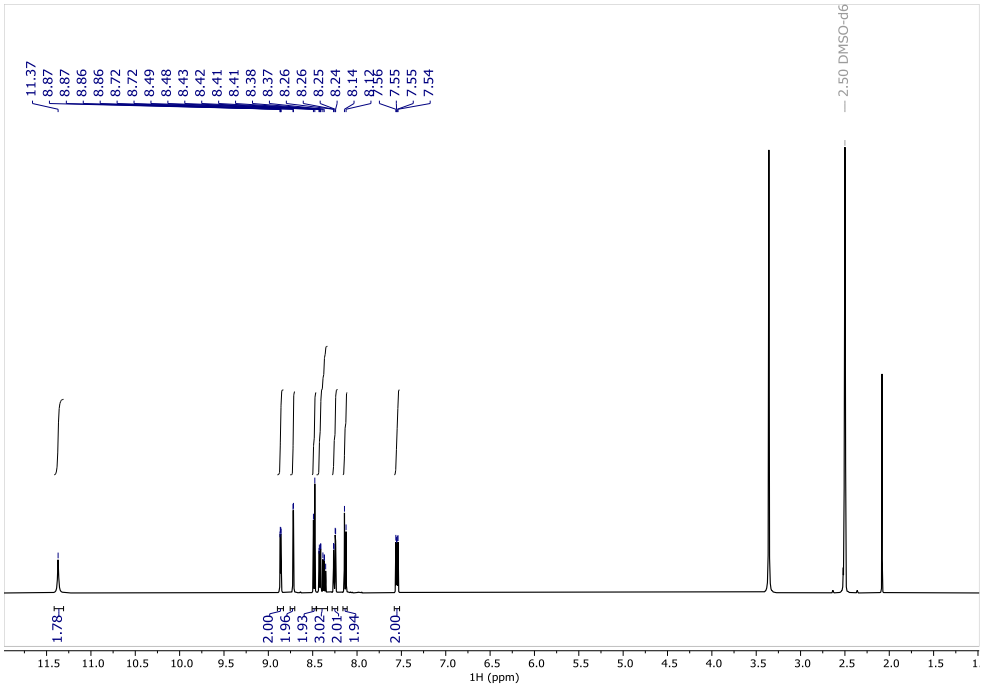


Fig. S1. *^{1}H NMR spectrum of compound* ***9*** *(500 MHz, DMSO-d_6, 300 K)*

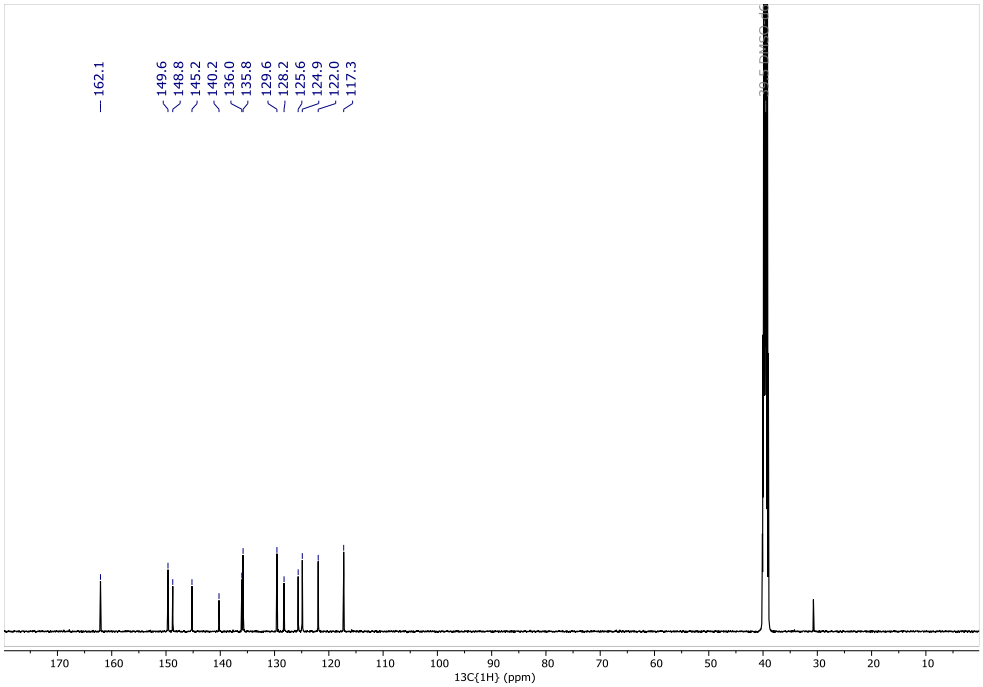
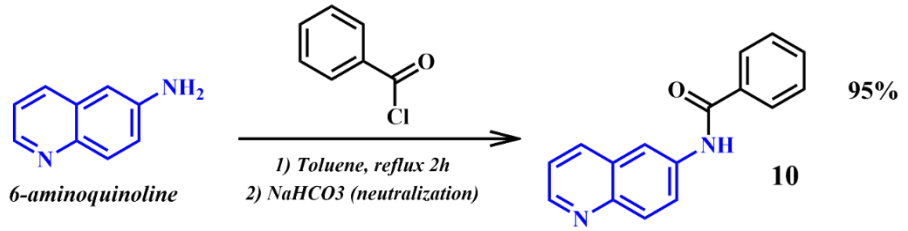


Fig. S2. *$^{13}C\{^{1}H\}$NMR spectrum of compound* ***9*** *(125.7 MHz, DMSO-d_6, 297 K)*

[1]H and [13]C NMR spectra of N-(quinolin-6-yl)benzamide, ***10****.*



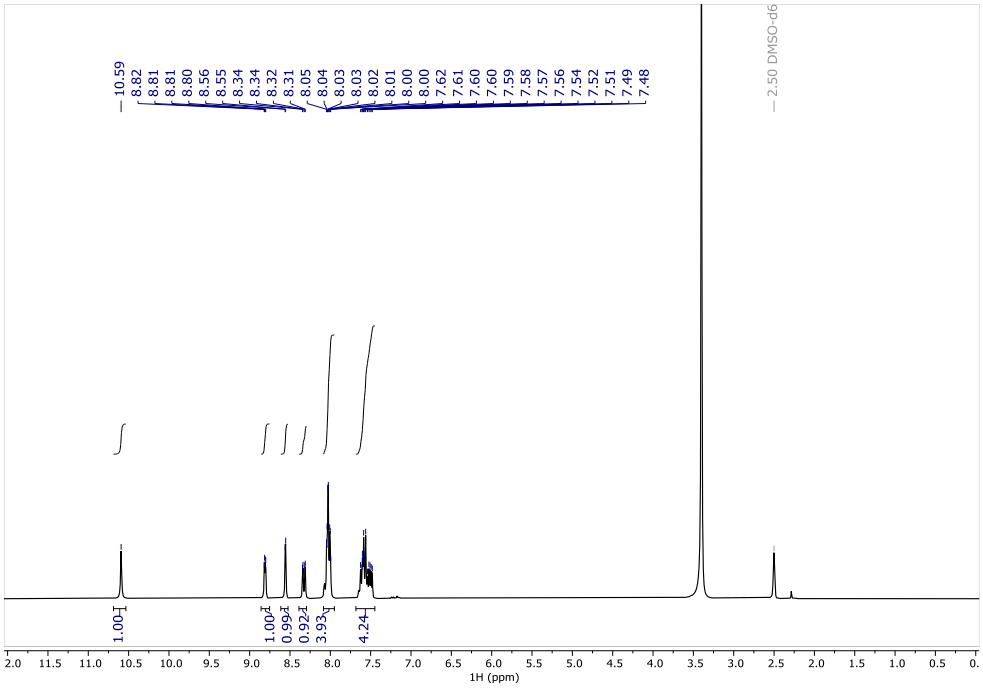


Fig. S3. *[1]H NMR spectrum of compound* ***10*** *(300 MHz, DMSO-d$_6$, 297 K)*

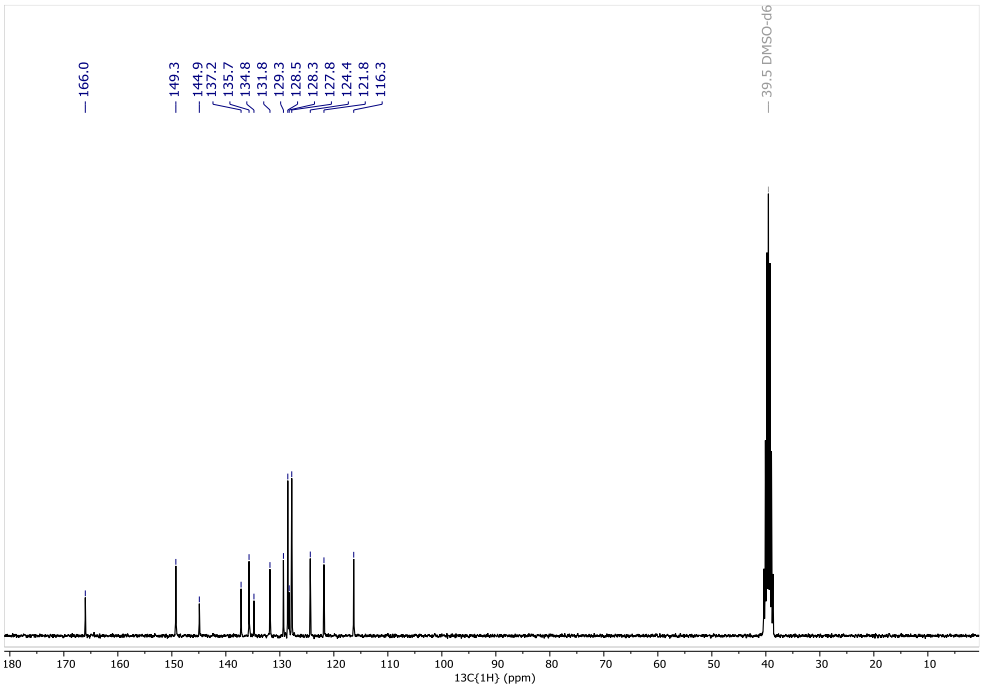
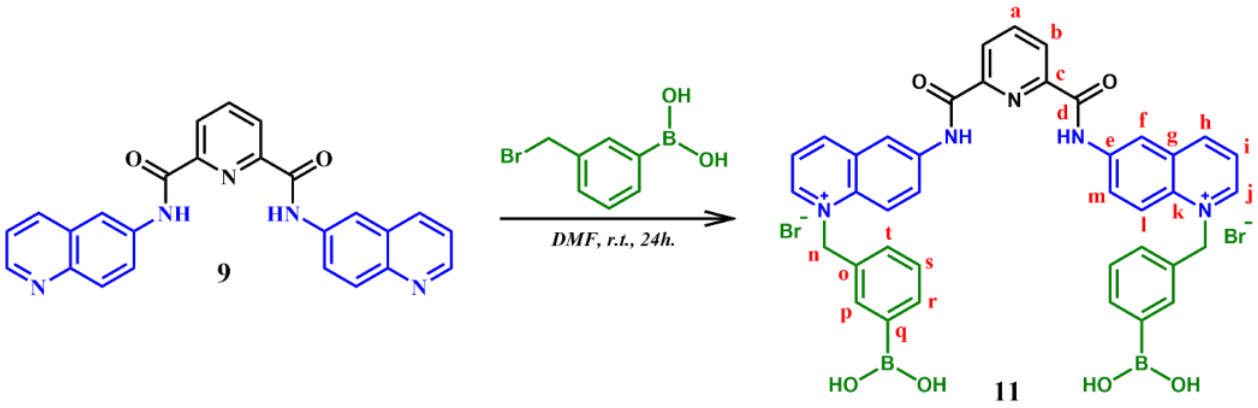


Fig. S4. *[13]C{[1]H }NMR spectrum of compound* ***10*** *(75.45 MHz, DMSO-d$_6$, 297 K)*

Characterization of 3,3'-((pyridine-2,6-dicarbonyl)bis(azanediyl))bis(1-(3-boronobenzyl)quinolin-1-ium) dibromide, ***11****.*



^{1}H NMR (300 MHz, 298 K, DMSO-d_6); δ 11.61 (s, 2H, $NH_{(amide)}$), 9.62 (d, $^{3}J_{HH}$ = 5.7 Hz, 2H, H_j), 9.22 ($^{3}J_{HH}$ = 8.7 Hz, 2H, H_h), 8.61-8.50 (m, 6H, $H_{i, m, l}$) 8.41 (m, 1H, H_a) 8.30 (*pseudo*-t, $^{3}J_{HH}$ = 6.9 Hz, 2H, H_b), 8.19 (*broad*-s, 4H, *BOH*), 7.78 (d, $^{3}J_{HH}$ = 7.2Hz, 2H, H_r), 7.68 (s, 2H, H_p), 7.48 (d, $^{3}J_{HH}$ = 7.5Hz, 2H, H_t), 7.40 (t, $^{3}J_{HH}$ = 7.5Hz, 2H, H_s), 6.37 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** (100 MHz, 298 K, DMSO-d_6); δ 163.1 (*carbonyl*-C_d), 149.2 (C_j), 148.5 (C_c), 148.0 (C_h), 142.0 (C_a), 139.4 (C_e), 135.6 (C_q), 135.3 (C_k), 135.0 (C_r), 133.5 (C_o), 132.9 (C_p), 131.7 (C_g), 130.6 (C_i), 129.6 (C_t), 128.9 (C_s), 126.6 (C_m), 123.4 (C_b), 120.8 (C_l), 118.5 (C_f), 60.7 (*methylene*-C_n); **^{11}B NMR** (96.3 MHz, 298 K, CD_3OD) δ 27.4 (*broad signal*); **HRMS-ESI^{+}** (*m/z*): calculated for $[C_{39}H_{33}B_2N_5O_6Br]^{+}$: 768.179484, found: 768.179957. **ATR-IR** ν (cm^{-1}): 3218*br*, 1546*s*, 1378*s*, 1333*s*, 771*m* and 714*m*. **UV-absorptions** λ_{max} (Buffer MOPS pH 7.4)/nm (log ε): 274 (4.57), 350 (3.87). **Fluorescence emission** λ_{max} (Buffer MOPS pH 7.4)/nm: 463.

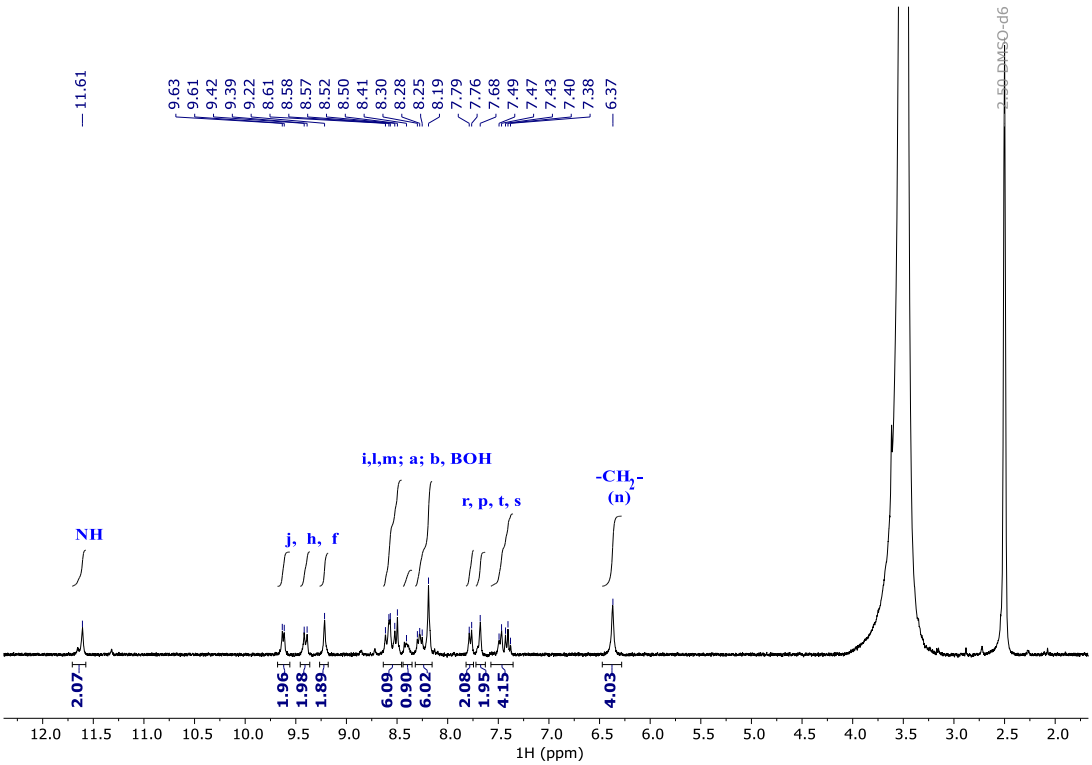


Fig. S5. *^{1}H NMR spectrum (300 MHz) of compound **11** in DMSO-d_6 at 298 K.*

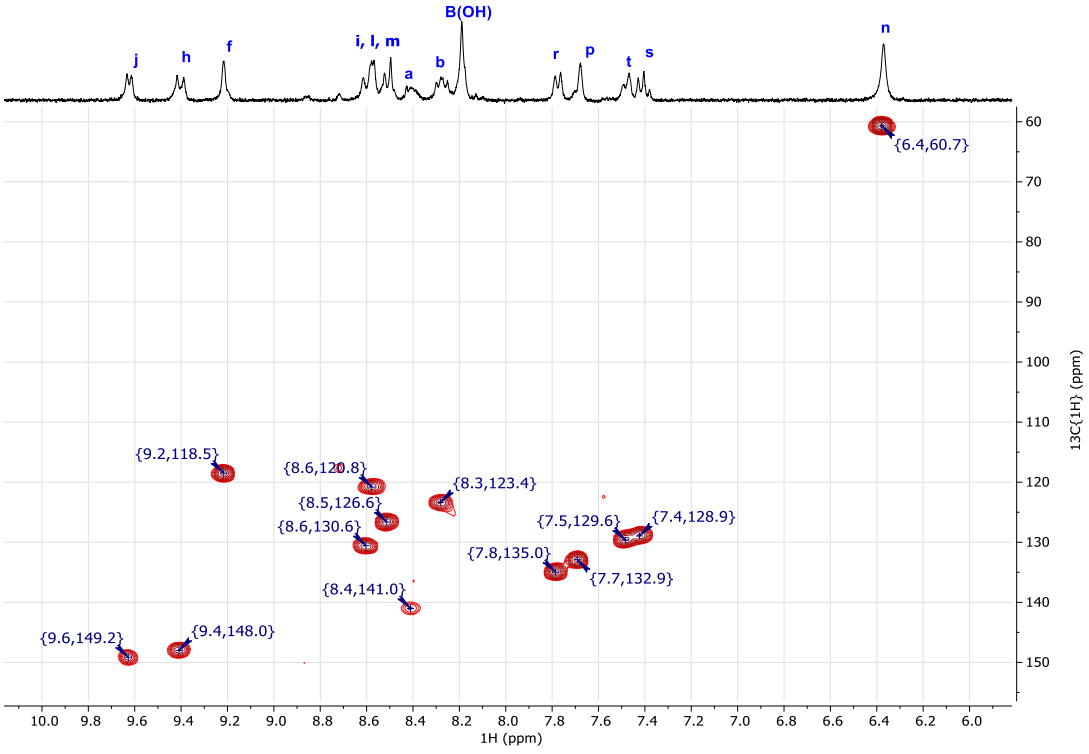


Fig. S6. *HSQC ^{1}H-^{13}C 2D-NMR spectrum of compound **11** in DMSO-d_6 at 298 K.*

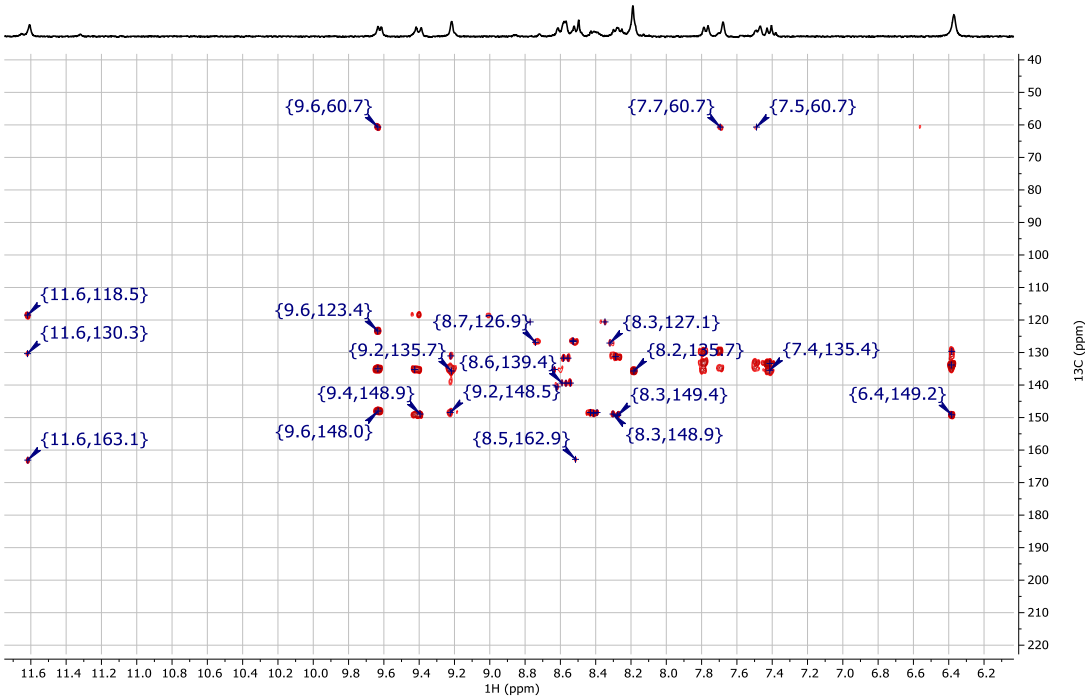


Fig. S7. *HMBC ^{1}H-^{13}C 2D-NMR spectrum of compound **11** in DMSO-d_6 at 298 K.*

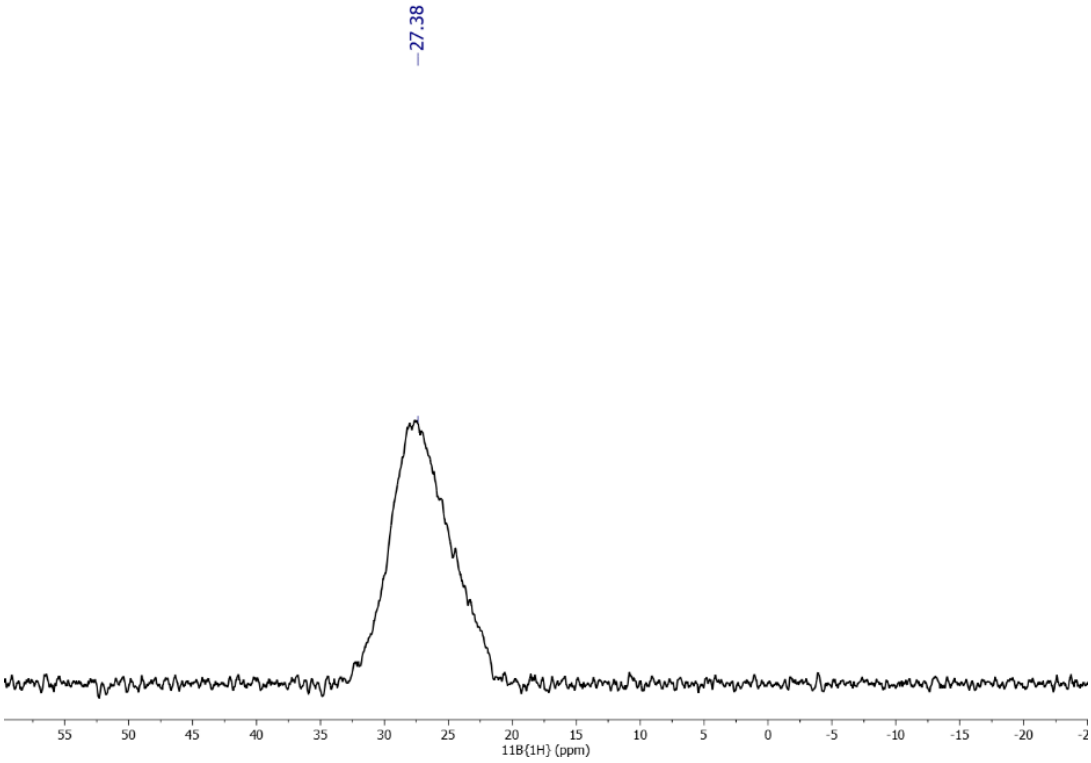


Fig. S8. *^{11}B NMR spectrum (96.3 MHz) of compound **11** in Methanol-d_4 at 298 K. Smoothing by average movement method, factor 5.*

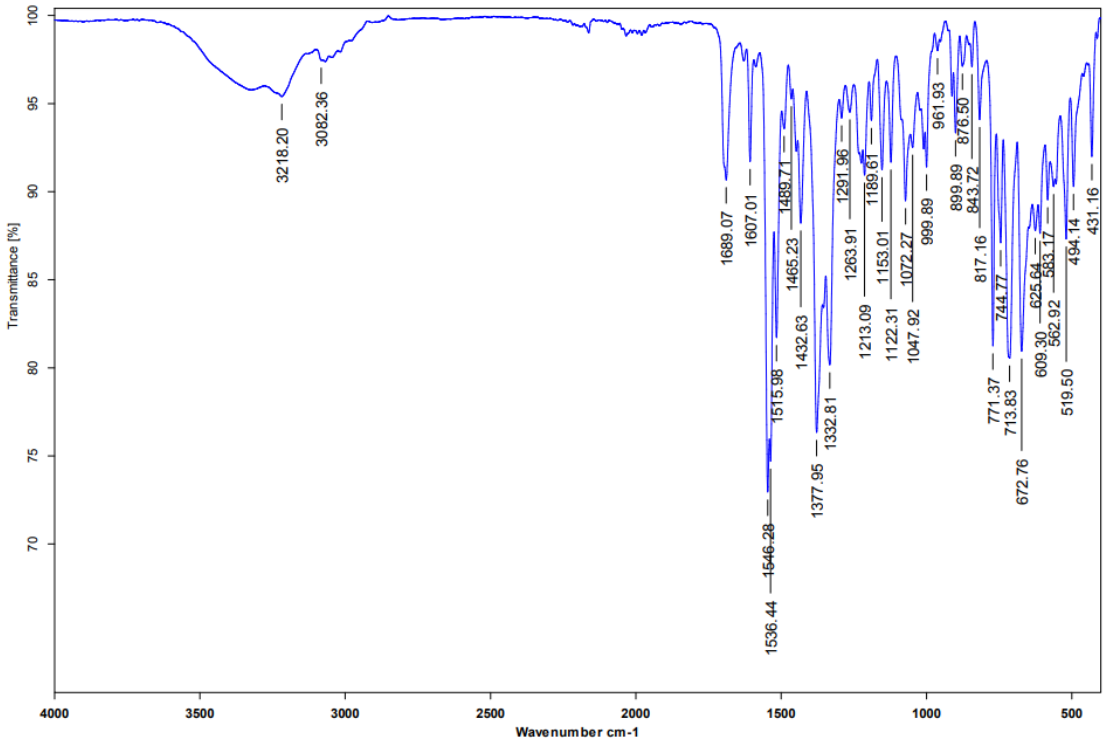


Fig. S9. *Infrared spectrum (ATR) of compound* ***11*** *at room temperature.*

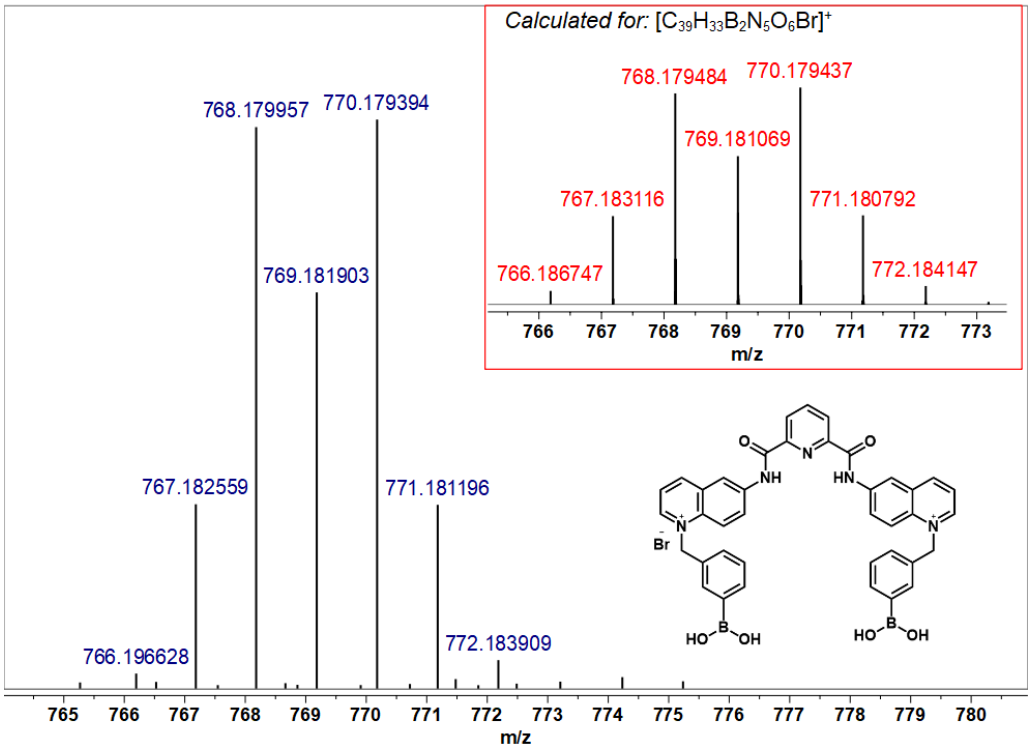
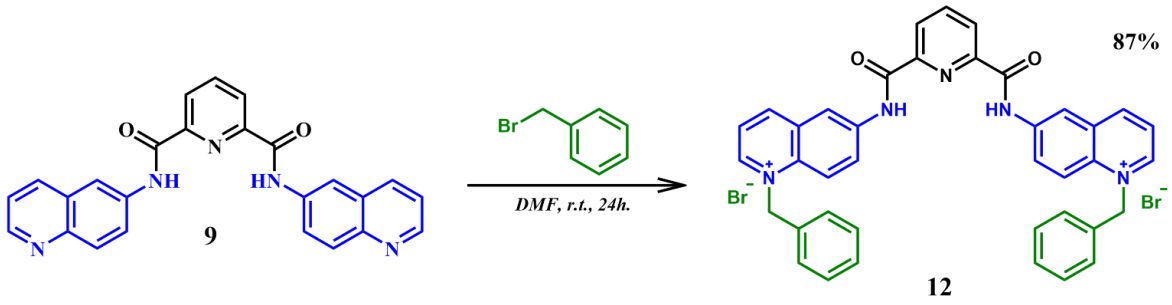


Fig. S10. *HRMS-ESI*$^{+}$ *isotopic pattern positive scan for* ***11****. Inset: calculated isotopic pattern for* $[C_{39}H_{33}B_2N_5O_6Br]^{+}$

Characterization of 6,6'-((pyridine-2,6-dicarbonyl)bis(azanediyl))bis(1-benzylquinolin-1-ium) dibromide, ***12****.*



^{1}H NMR (700 MHz, 298 K, DMSO-d_6 (with TMS as internal reference δ 0.00); δ 11.59 (s, 2H), 9.65 (dd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.4 Hz, 2H), 9.43 (dd, $^3J_{HH}$ = 9.1 Hz, $^4J_{HH}$ = 1.4 Hz, 2H), 8.62 (m, 3H), 8.52 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 8.42 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.7 Hz, 1H), 8.29 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 5.6 Hz, 2H), 7.43–7.39 (m, 10H), 6.39 (br. s, 4H); **HSQC ^{1}H – ^{13}C NMR** (700 MHz–175 MHz, 298 K, DMSO-d_6) the carbons attached to the hydrogen atoms in **12** were indirectly detected by an HSQC pulse sequence because its low solubility; δ 149.0, 147.9, 141.0, 130.5, 129.6, 129.2, 127.9, 126.6, 123.3, 120.5, 118.3, 60.4. **HRMS-ESI$^+$** (*m/z*): calculated for $[C_{39}H_{31}N_5O_2Br]^+$ 682.16352, found 682.163278. **ATR-IR** ν (cm^{-1}): 3406*br*. 2339*br*, 3037*br*, 1545*s*, 1516*s*, 1369*m*, 722*m* and 648*m*. **UV-absorptions** λ_{max} (Buffer MOPS pH 7.4)/nm (log ε): 272 (4.76), 355 (4.00). **Fluorescence emission** λ_{max} (Buffer MOPS pH 7.4)/nm: 464.

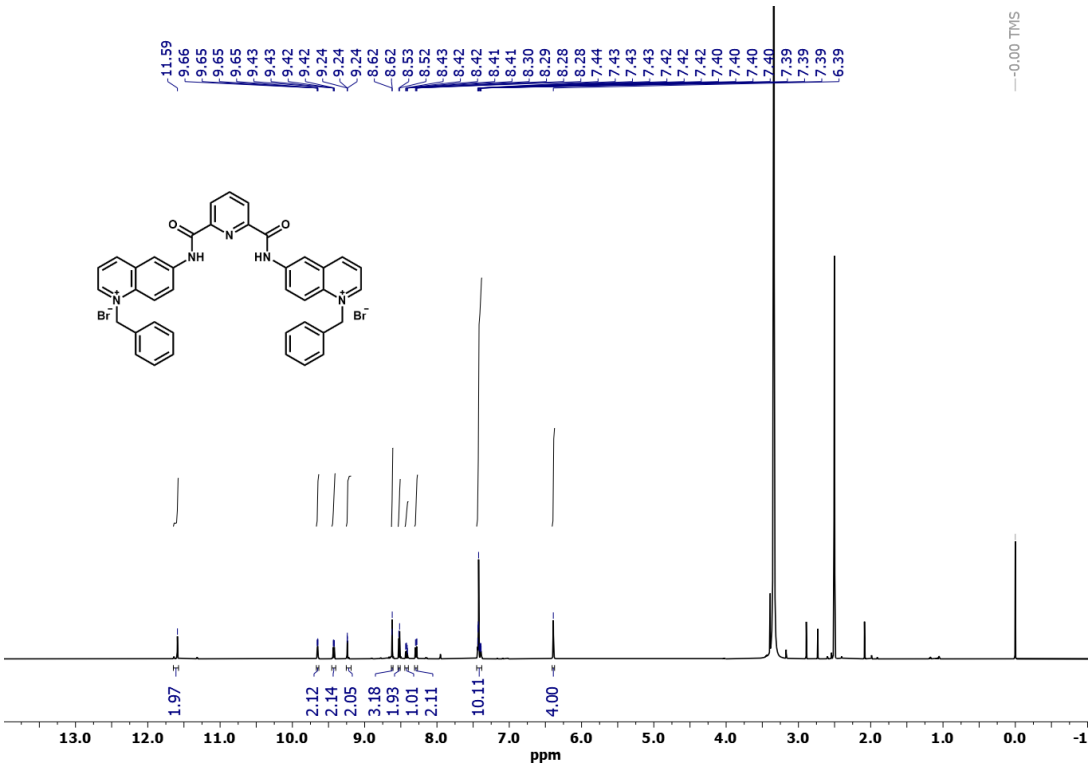


Fig. S11. *^{1}H NMR spectrum (700 MHz) of **12**in DMSO-d_6 at 298 K.*

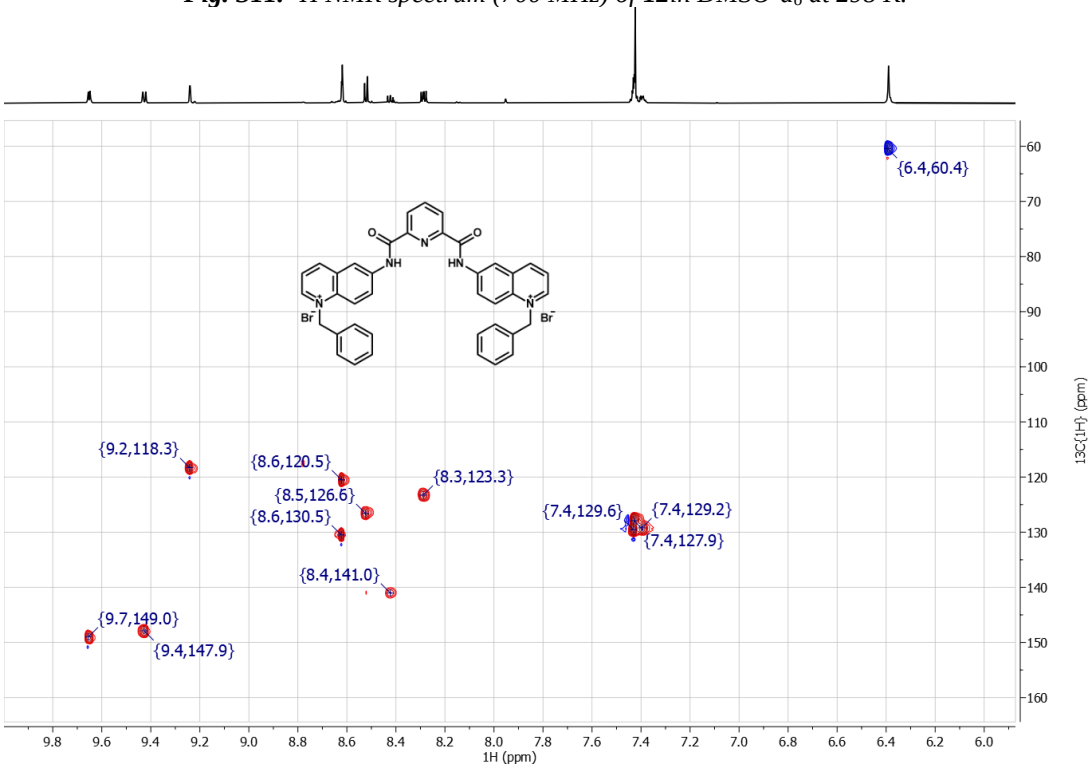


Fig. S12. *2D-NMR HSQC ^{1}H – ^{13}C{^{1}H} (700 MHz – 175 MHz) spectrum of **12** in DMSO-d_6 at 298 K.*

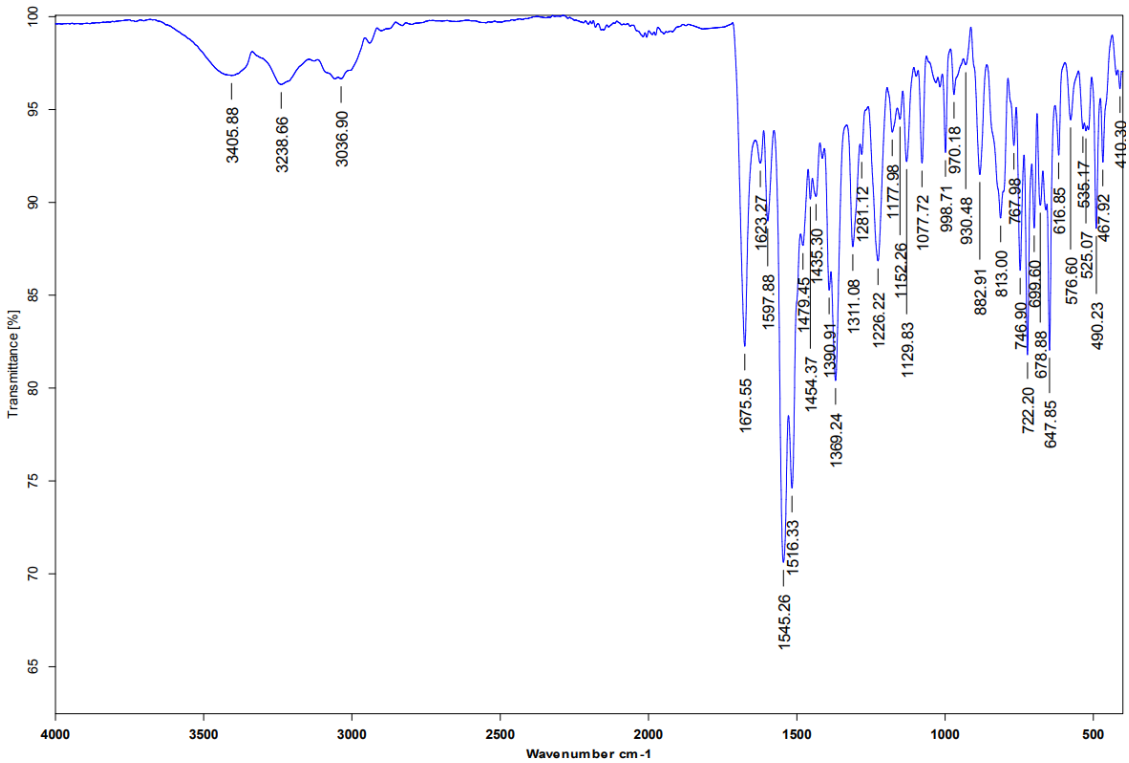
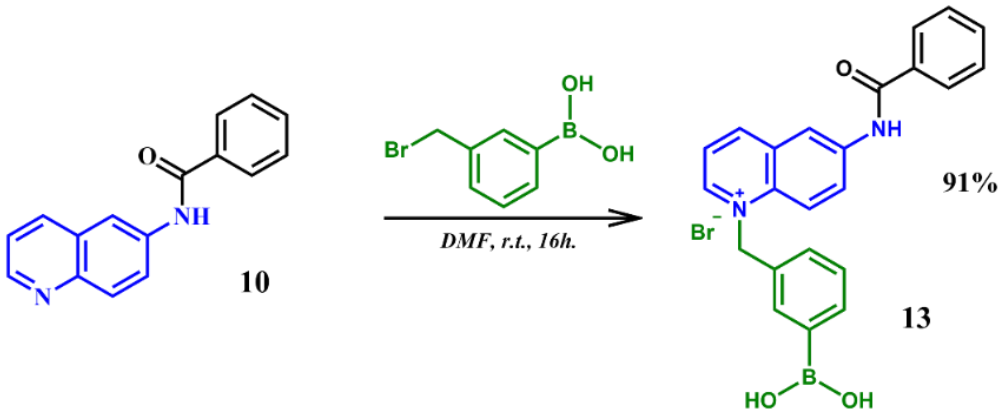


Fig. S13*. Infrared spectrum (ATR) of compound* ***12****.*

Characterization of 6-benzamido-1-(3-boronobenzyl)quinolin-1-ium bromide, ***13****.*



^{1}H NMR (400 MHz, 298 K, D_2O/CD_3CN); δ 9.17 (dd, $^{3}J_{HH}$ = 6.0 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H), 9.97 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H), 8.59 (d, $^{3}J_{HH}$ = 2.4 Hz, 1H), 8.23 (d, $^{3}J_{HH}$ = 9.6 Hz, 1H), 8.15 (dd, $^{3}J_{HH}$ = 9.6 Hz, $^{3}J_{HH}$ = 2.4 Hz, 1H), 7.97 (dd, $^{3}J_{HH}$ = 8.4 Hz, $^{3}J_{HH}$ = 6.0 Hz, 1H), 7.76 (d, $^{3}J_{HH}$ = 6.8 Hz, 2H), 7.69 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H), 7.61 (s, 1H), 7.49 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.41 – 7.36 (m, 4H), 6.11 (s, 2H). **^{13}C{^{1}H} NMR** (100.6 MHz, 298 K, DMSO-d_6); δ 169.4, 148.8, 148.6, 140.1, 135.8, 135.6, 134.0, 133.7, 133.4, 133.2, 132.1, 130.9, 130.6, 129.9, 129.7, 128.5, 123.4, 120.6, 119.6, 62.0; **^{11}B NMR** (160 MHz, 297 K, methanol-d_4); δ 28.6; **HRMS-ESI^{+}** (m/z): calculated for $[C_{51}H_{53}B_2BrN_5O_6]^{+}$ 383.15615, found 383.156633. **ATR-IR** ν (cm^{-1}): 3354*br*, 1667*m*, 1548*s*, 1357*s*, 1330*s*, 1257*s*, 705*s* and 637*m*. **UV-absorptions** λ_{max} (Buffer MOPS pH 7.4)/nm (log ε): 271 (4.80), 325 (4.01), 350 (3.80). **Fluorescence emission** λ_{max} (Buffer MOPS pH 7.4)/nm: 473.

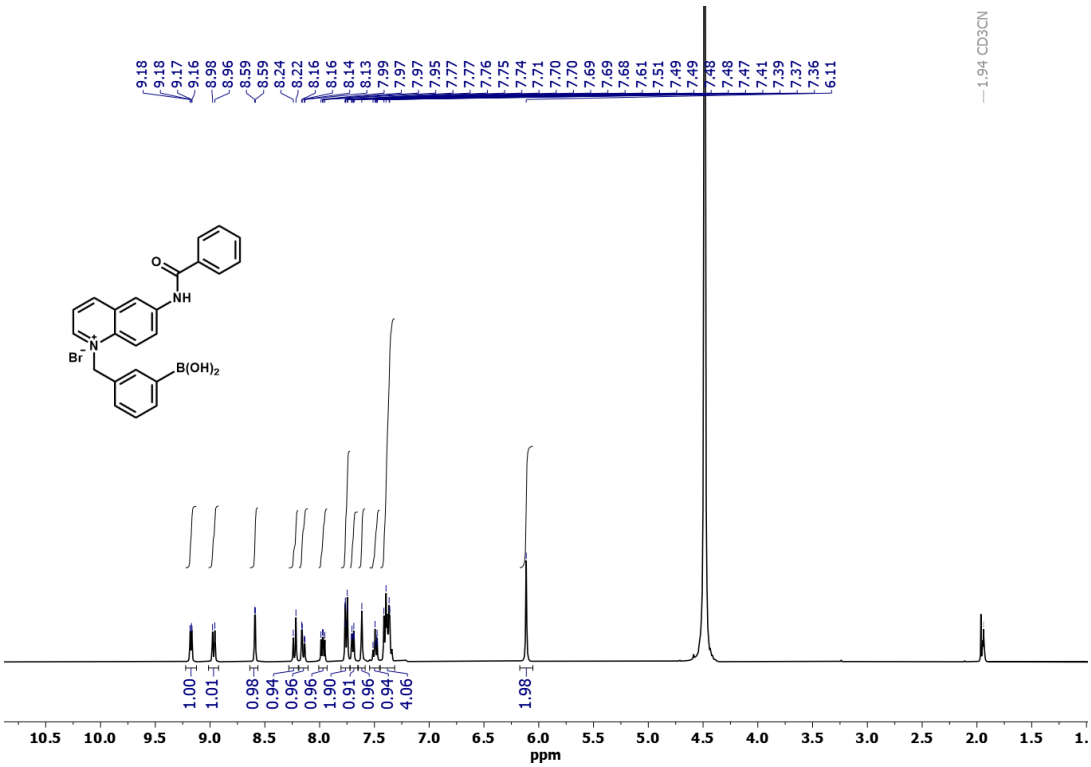


Fig. S14. *^{1}H NMR spectrum of compound **13** in acetonitrile-d_3/D_2O (1:3) at 298 K*

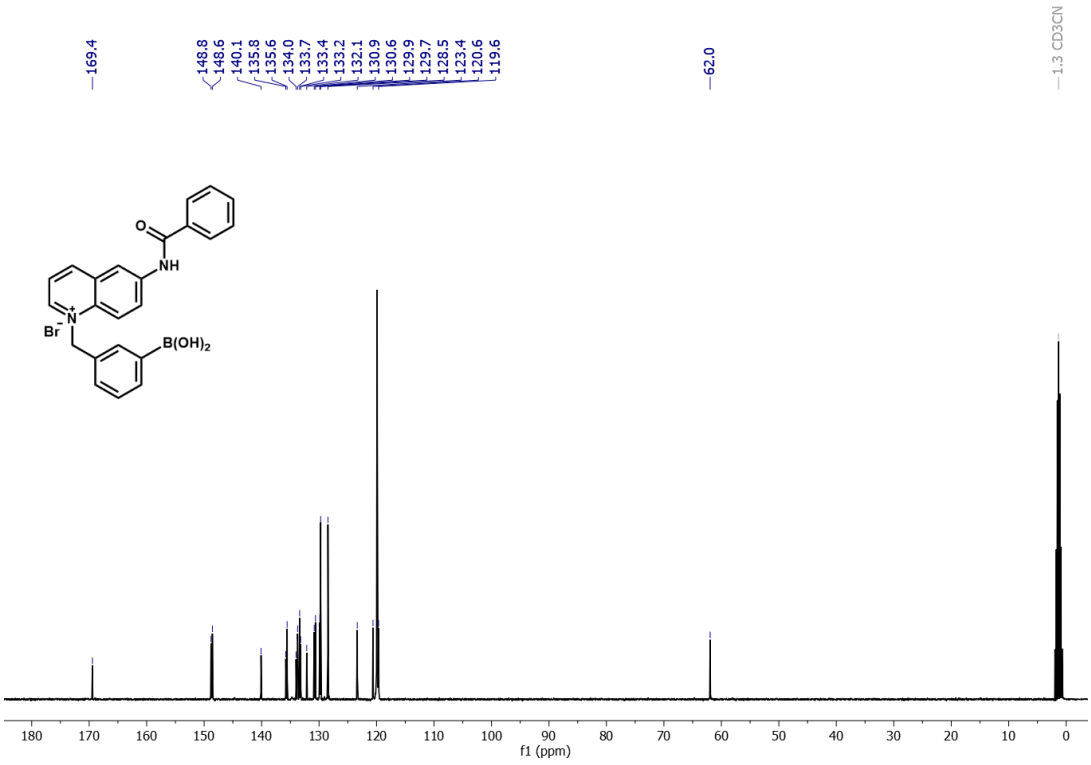


Fig. S15. *$^{13}C\{^{1}H\}$ NMR spectrum of compound **13** in acetonitrile-d_3/D_2O (1:3) at 298 K.*

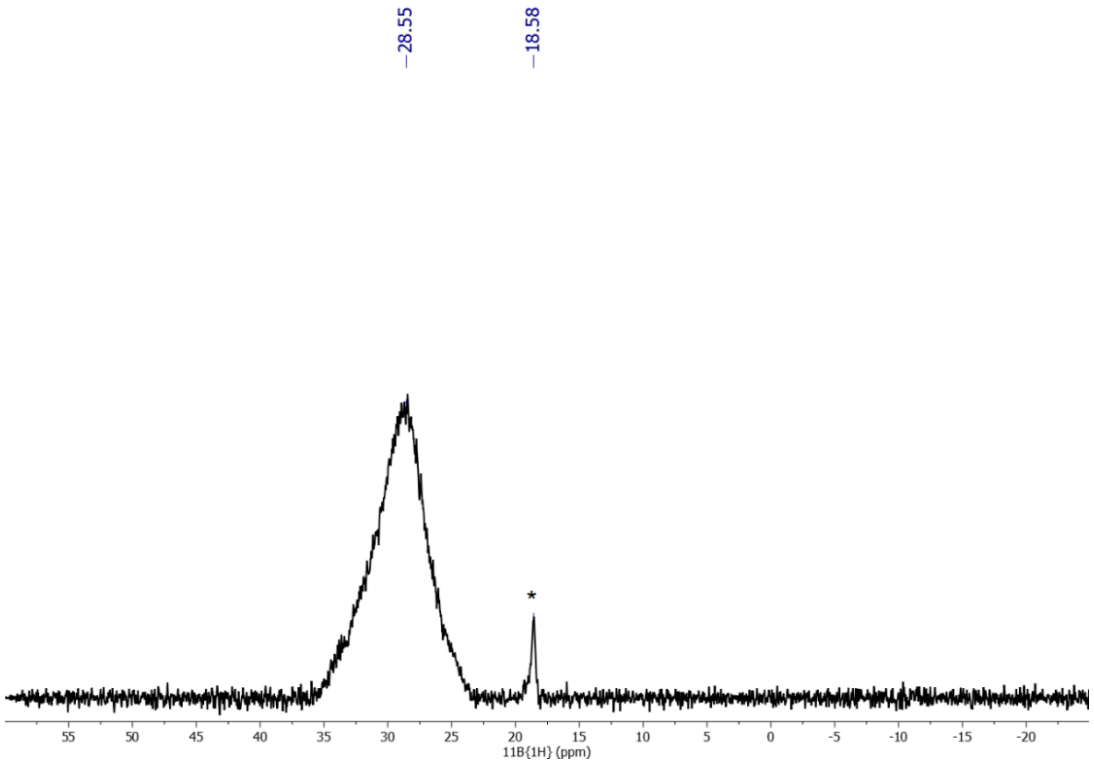


Fig. S16. *^{11}B NMR spectrum (96.3 MHz) of compound **13** in Methanol-d_4 at 297 K. Smoothing by average movement method, factor 5. *Esterified specie.*

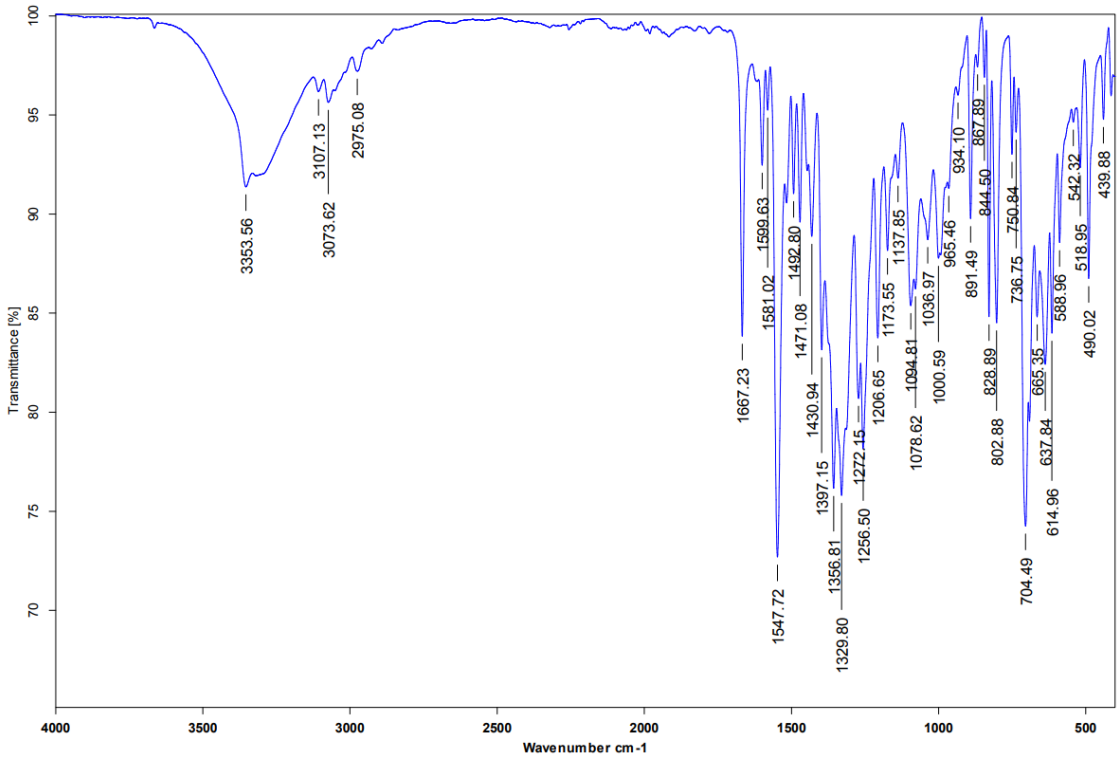


Fig. S17. *Infrared spectrum (ATR) of compound **13**.*

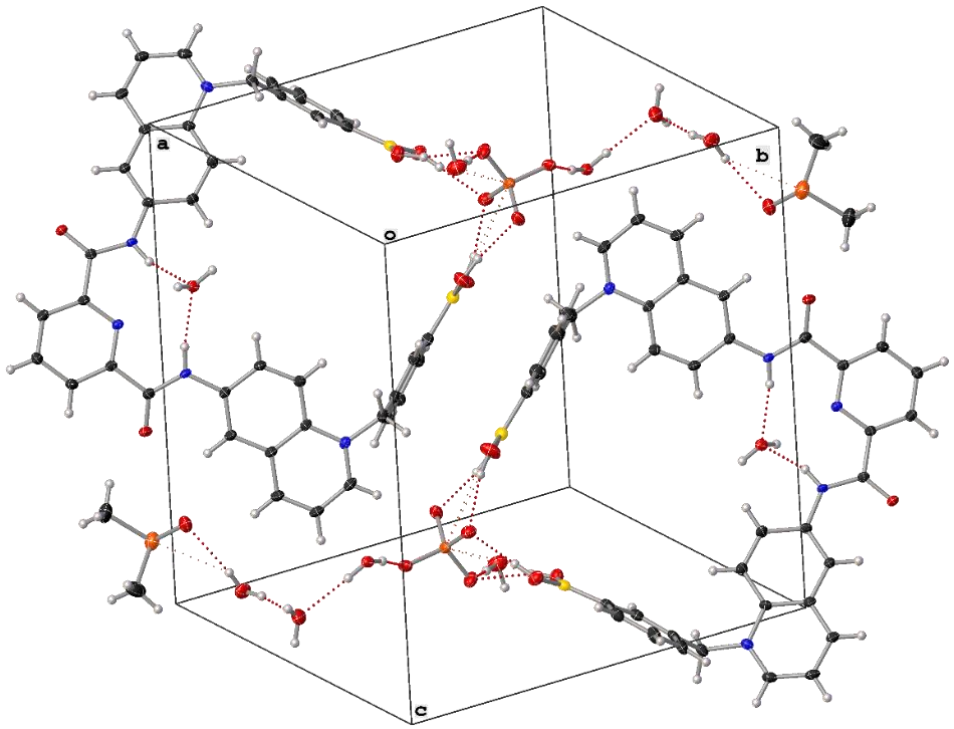


Fig. S18. *ORTEP diagram of the unit cell view along the axes of* ***11-SO₄****. Space group: P-1, volume = 2503.8(3) Å³; Z = 2. Some molecules of DMSO were omitted for clarity*

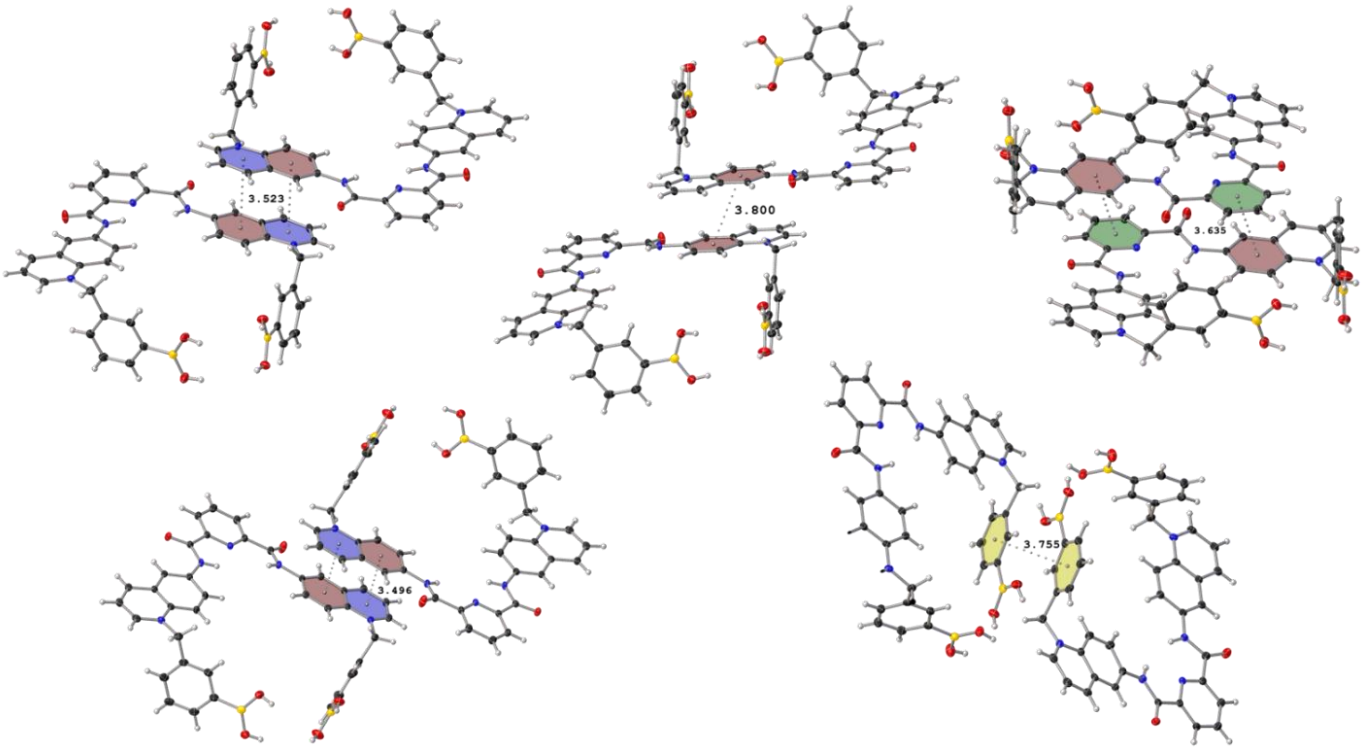


Fig. S19. *Crystal packing perspectives of the π–π stacking interactions for* ***11-SO₄****. Centroid–centroid distances are shown as dotted lines. Solvent molecules and sulfate anion are omitted for clarity.*

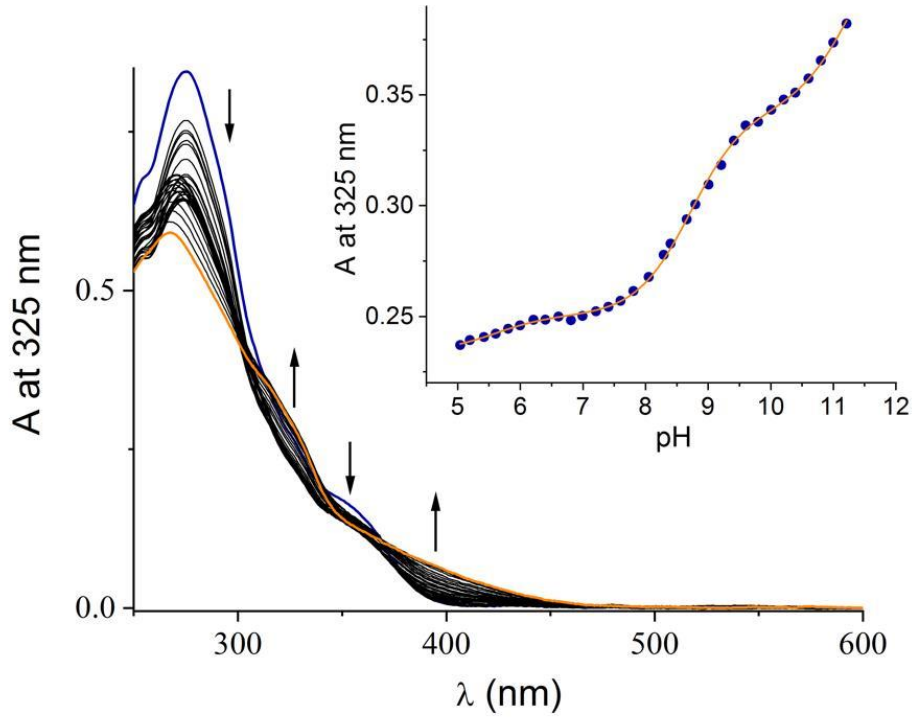


Fig. S20. *UV–vis pH titration of a water solution of* ***11*** *[20 μM] buffered with MOPS, MES and CAPS [10 mM] in presence of D-fructose [10 mM].*

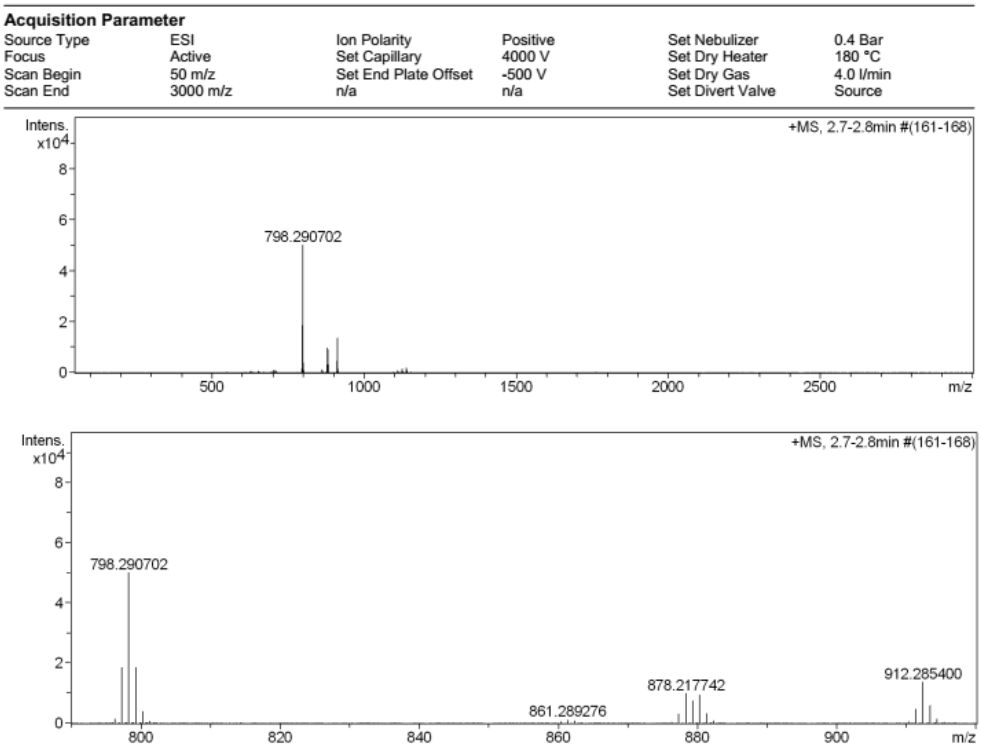


Fig. S21. *ESI-HRMS spectra of* ***11*** *in the presence of 12 equiv. of sorbitol in aqueous methanol.*

(1) Dorazco-González, A.; Alamo, M. F.; Godoy-Alcántar, C.; Höpfl, H.; Yatsimirsky, A. K. Fluorescent Anion Sensing by Bisquinolinium Pyridine-2,6-Dicarboxamide Receptors in Water. *RSC Adv* **2014**, *4* (1), 455–466. https://doi.org/10.1039/C3RA44363A.

(2) Badugu, R.; Lakowicz, J. R.; Geddes, C. D. Wavelength-Ratiometric near-Physiological PH Sensors Based on 6-Aminoquinolinium Boronic Acid Probes. *Talanta* **2005**, *66* (3), 569–574. https://doi.org/https://doi.org/10.1016/j.talanta.2004.11.030.

(3) Valdes-García, J.; Zamora-Moreno, J.; Salomón-Flores, M. K.; Martínez-Otero, D.; Barroso-Flores, J.; Yatsimirsky, A. K.; Bazany-Rodríguez, I. J.; Dorazco-González, A. Fluorescence Sensing of Monosaccharides by Bis-Boronic Acids Derived from Quinolinium Dicarboxamides: Structural and Spectroscopic Studies. *Journal of Organic Chemistry* **2023**, *88* (4). https://doi.org/10.1021/acs.joc.2c02590.