Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Substituent Effects Direct Anion Transport in Aryl-Triazole Derivatives

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1. General materials.

All starting materials were obtained from commercial suppliers and were used without further purification unless otherwise stated. All air- or moisture-sensitive reactions were performed using oven-dried or flame-dried glassware under an inert atmosphere of dry argon. Air- or moisture-sensitive liquids and solutions were transferred via syringe. Tetrahydrofuran (THF) was distilled from sodium benzophenone; dichloromethane was distilled from calcium hydride; triethylamine (TEA) was redistilled and stored over KOH pellets prior to use. Egg yolk phosphatidylcholine (EYPC) was obtained from Avanti Polar lipids as a solution in chloroform (25 mg·mL^{-1}). Lucigenin dye and Trixon-100 were obtained from Sigma-Aldrich and used without further purification.

2. Characterizations.

Proton and carbon nuclear magnetic resonance spectra (^{1}H, ^{13}C NMR) were recorded on a Bruker Avance 400/600 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from the Me_4Si resonance which was used as the internal standard when recording ^{1}H NMR spectra. Mass spectra were recorded on a Micromass GCTTM and a Micromass LCTTM. Fluorescence measurements were performed on a Varian Cary Eclipses fluorescence spectrometer equipped with a stirrer and a temperature controller (kept at 25 °C unless otherwise noted). A Mini-Extruder used for the preparation of large unilamellar vesicles (LUVs) was purchased from Avanti Polar lipids. The size of EYPC vesicles was determined using a Delsa™ Nano Submicron Particle Size and Zeta Potential Particle Analyzer (Beckman Coulter Inc., USA).

3. Synthesis of compounds.

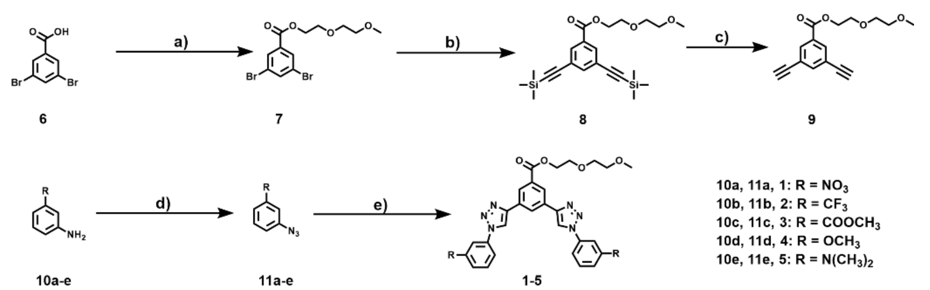


Figure S1 Synthetic route for compounds 1-5. Regeants and reaction conditions: a), diethylene glycol monomethyl ether, DCM, EDCI, DMAP; b), trimethylsilylacetylene, TEA, CuI, trans-dichlorobis (triphenyl-phosphine) palladium(II); c), TBAF, THF; d), $NaNO_2$, 2M HCl, azidotrimethylsilane; e), sodium ascorbate, $CuSO_4 \cdot 5H_2O$, THF, H_2O.

Preparation of 7: To a solution of 3, 5-dibromobenzoic acid (5 g, 17.99 mmol) and 2-(2-methoxyethoxy) ethanol (4.32 g, 35.98 mmol) in 100 mL dry dichloromethane (DCM) was added 4-dimethylaminopyridine (DMAP, 1.05 g, 8.995 mmol). The mixture was stirred at 0°C for 15 min and then added 1-Ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDCI, 3.36 g, 17.99 mmol). The reaction solution was stirred at room temperature for 12 h and then concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed with brine, dried over anhydrous Na_2SO_4. After removing of the solvent, the crude product was purified by column chromatography on silica gel to afford 7 as a colorless oil. Yield 92%; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.12 (d, J=1.8 Hz, 2H), 7.85 (t, J=1.8 Hz, 1H), 4.53-4.46 (m, 2H), 3.87-3.80 (m, 2H), 3.72-3.66 (m, 2H), 3.61-3.54 (m, 2H), 3.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.39, 143.20, 143.18, 138.48, 136.56, 136.00, 135.98, 135.76, 135.43, 135.24, 128.24, 128.05, 127.82, 76.46, 74.83, 73.28, 70.05, 63.30, 60.12, 45.29, 45.17, 45.03, 44.89, 44.75, 44.62, 44.48, 44.34; LR-MS (ESI): Calcd. For $C_{12}H_{14}Br_2O_4Na$ $[M+Na]^+$: 402.9. Found: 402.9.

Preparation of 8: Compound 7 (1 g, 2.63 mmol) was dissolved in dry trimethylamine (TEA, 8 mL) containing $Pd(PPh_3)_2Cl_2$ (0.106 g, 0.15 mmol) and CuI (12 mg, 0.057 mmol) and stirred for 5 min, trimethylsilylacetylene (1.88 mL, 12.53 mmol) was then added to above solution and stirred at 60°C for 72 h. DCM was added to the mixture and washed with saturated NH_4Cl, HCl (10%) and NaCl, respectively. The organic phase was dried with Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel to afford 8 as a brown oil. Yield 80%; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.83 (d, J=1.6 Hz, 2H), 7.53-7.47 (m, 1H), 4.26 (dd, J=5.8,3.8 Hz, 2H), 3.61 (dd, J=5.8,4.0 Hz, 2H), 3.50-3.43 (m, 2H), 3.38-3.31 (m, 2H), 3.17 (s, 3H), 0.00 (s, 18H); LR-MS (ESI): Calcd. For $C_{22}H_{32}O_4Si_2Na$ $[M+Na]^+$: 439.2. Found: 439.2.

Preparation of 9: To a solution of 8 (2g, 7.35 mmol) in 40 mL tetrahydrofuran (THF) was added tetra-n-butylammonium fluoride (TBAF, 11.53g, 44.27 mmol) after stirring for 1 min. The mixture was stirred at room temperature and the reaction progress was measured by thin layer chromatography. DCM was added to the mixture and washed with water, then the organic phase was dried over anhydrous Na_2SO_4. After removing of the solvent, the crude product was purified by column chromatography on silica gel to afford 9 as a white solid. Yield 50%; ^1H NMR (400 MHz, DMSO-d_6) δ ppm 7.97 (d, J=1.6 Hz, 2H), 7.86 (t, J=1.6 Hz, 1H), 4.45 (s, 2H), 4.42-4.38 (m, 2H), 3.79-3.72 (m, 2H), 3.62-3.55 (m, 2H), 3.48-3.42 (m, 2H), 3.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 169.28, 143.81, 137.47, 128.28, 88.23, 86.47, 76.44, 74.81, 73.31, 69.82, 63.29, 45.08 (d, J=20.9 Hz); LR-MS (ESI): Calcd. For $C_{16}H_{16}O_4Na$ $[M+Na]^+$: 295.1. Found: 295.1.

Preparation of 11a, 11b, 11d and 11e: The synthesis of these compounds followed similar procedures, as exemplified by the preparation of compound 11a.To a vented and stirred solution of 3-nitroaniline (10a, 1 g, 6.21 mmol) in 12.5 mL 2M HCl at 0 ºC was syringed sodium nitrite (0.5 g, 7.45 mmol) in water dropwise. The reaction was allowed to proceed for 1 h at room temperature and azidotrimethylsilane (1.75 g, 15.21 mmol) was added dropwise. The obtained deep brown solution was stirred for a further 2 hours at room temperature. The reaction was extracted with DCM. After removing the solvent, the obtained crude was used directly for the click reaction without any purification.

Preparation of 11c: To a solution of methyl 3-aminobenzoate (10c, 1g, 7.35 mmol) in 20 mL acetonitrile (MeCN) was added tert-Butyl nitrite (0.91g, 8.82 mmol). The reaction was allowed to proceed for 1 h at room temperature and azidotrimethylsilane (1.27 g, 11.02 mmol) was added dropwise. The solution was stirred for a further 2 hours at room temperature. The solvent was removed under vacuum and the product was directly used for the next reaction.

Preparation of compounds 1-5: The synthesis of these compounds followed similar procedures, as exemplified by the preparation of compound 1. A THF: water (V/V= 1/1, 5 mL) solution containing 9 (0.5 g, 1.84 mmol), 11a (0.093 g, 1.84 mmol), sodium ascorbate (18.34 mg, 0.092 mmol) and copper (II) sulfate pentahydrate (11.59 mg, 0.051 mmol) was stirred at 60 °C for 5 h. After removal of the solvents in vacuum, the crude product was purified by column chromatography to afford 1 as white solid. Yield 75%; ^1H NMR (400 MHz, DMSO-d_6) δ ppm 9.88 (s, 2H), 8.93-8.85 (m, 3H), 8.60-8.51 (m, 4H), 8.39 (dd, J=8.4, 2.0 Hz, 2H), 7.98 (t, J=8.2 Hz, 2H), 4.57-4.50 (m, 2H), 3.87-3.81 (m, 2H), 3.64 (dd, J=5.7, 3.7 Hz, 2H), 3.52-3.45 (m, 2H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 165.73, 146.62, 138.12, 132.42, 132.01 (d, J = 10.1 Hz), 126.72, 125.98, 123.02, 121.29, 119.43, 71.74, 70.15, 68.82, 64.93, 58.57; HR-MS (ESI): Calcd. For $C_{28}H_{24}N_8O_8Na$ $[M+Na]^+$: 623.1609. Found: 623.1614.

Compound 2: ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.68 (s, 2H), 8.84 (t, J = 1.7 Hz, 1H), 8.53 (d, J = 1.6 Hz, 2H), 8.29 (t, J = 2.0 Hz, 2H), 8.09 (ddd, J = 8.2, 2.1, 1.0 Hz, 2H), 7.75 (ddd, J = 8.1, 2.0, 1.0 Hz, 2H), 7.62 (t, J = 8.1 Hz, 2H), 4.55-4.48 (m, 2H), 3.86-3.79 (m, 2H), 3.67-3.60 (m, 2H), 3.51-3.44 (m, 2H), 3.24 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 165.72, 146.72, 137.48, 131.93 (d, J=8.3 Hz), 131.08 (d, J=33.2 Hz), 126.69, 125.94 (d, J=25.9 Hz), 125.00, 124.36, 123.20, 121.40, 117.10, 71.74, 70.16, 69.82, 64.93, 58.55; HR-MS (ESI): Calcd. For $C_{30}H_{24}F_6N_6O_4Na$ $[M+Na]^+$: 669.1655. Found: 669.1660.

Compound 3: ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.75 (s, 2H), 8.87 (t, J = 1.7 Hz, 1H), 8.56 (d, J = 1.6 Hz, 4H), 8.34 (ddd, J = 8.2, 2.4, 1.1 Hz, 2H), 8.10 (dt, J = 7.8, 1.3 Hz, 2H), 7.83 (t, J = 8.0 Hz, 2H), 4.52 (dd, J = 5.8, 3.8 Hz, 2H), 3.95 (s, 6H), 3.84 (dd, J = 5.7, 3.8 Hz, 2H), 3.67-3.61 (m, 2H), 3.52-3.45 (m, 2H), 3.24 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 165.74 (d, J=4.2 Hz), 146.71, 137.23, 131.85 (d, J=20.8 Hz), 131.10, 129.63, 125.93, 124.79, 121.09, 120.47, 71.74, 70.17, 68.82, 64.87, 58.56, 53.08; HR-MS (ESI): Calcd. For $C_{32}H_{31}N_6O_8$ $[M+H]^+$: 627.2198. Found: 627.2202.

Compound 4: ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.62 (s, 2H), 8.84 (t, J = 1.7 Hz, 1H), 8.54 (d, J = 1.6 Hz, 2H), 7.62 (dq, J = 9.7, 2.0, 1.5 Hz, 3H), 7.60-7.52 (m, 3H), 7.11 (ddd, J = 8.2, 2.4, 1.2 Hz, 2H), 4.56-4.49 (m, 2H), 3.90 (s, 6H), 3.83 (dd, J = 5.7, 3.7 Hz, 2H), 3.67-3.60 (m, 2H), 3.52-3.45 (m, 2H), 3.24 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d6) δ ppm 170.52, 165.46, 151.22, 142.79, 136.82, 136.08, 130.60, 125.76, 119.77, 117.16, 110.76, 76.49, 74.91, 73.57, 69.63, 63.30, 60.88; HR-MS (ESI): Calcd. For $C_{30}H_{31}N_6O_6$ $[M+H]^+$: 571.2300. Found: 571.2342.

Compound 5: ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.54 (s, 2H), 8.83 (d, J=1.8 Hz, 1H), 8.54 (d, J=1.6 Hz, 2H), 7.41 (t, J=8.4 Hz, 2H), 7.28-7.22 (m, 4H), 6.85 (d, J=8.5 Hz, 2H), 4.51 (d, J=5.0 Hz, 2H), 3.83 (s, 2H), 3.63 (dd, J=5.6, 3.8 Hz, 2H), 3.48 (t, J=4.8 Hz, 3H), 3.24 (d, J=1.3Hz, 3H), 3.03 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 165.85, 151.71, 146.32, 137.97, 132.24, 131.78, 130.68, 126.82, 125.80, 120.93, 112.77, 107.67, 103.67, 71.73, 70.17, 68.83, 58.55; HR-MS (ESI): Calcd. For $C_{32}H_{37}N_8O_4$ $[M+H]^+$: 597.2932. Found: 597.2939.

4. Optimization of molecular structures and calculation of ion binding energy.

Gaussian 09 program was employed for optimization of molecular structures and calculation of ion binding energy. Under the conditions of the B3LYP functional and 6-31G (d, p) basis set, the optimized structures of compounds 1−5 and their chloride ion binding energies were obtained.

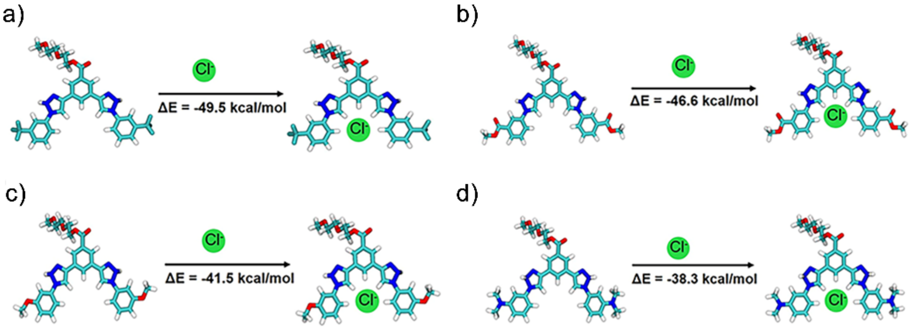


Figure S2 Structure optimization and binding energy calculation of a) compound 2 and [2+Cl⁻] complex, b) compound 3 and [3+Cl⁻] complex, c) compound 4 and [4+Cl⁻] complex, and d) compound 5 and [5+Cl⁻] complex.

5. Anions Binding assay determined by ^{1}H NMR.

All ion binding constants were measured by ^{1}H NMR titrations in a Bruker AVIII 400 spectrometer at 400 MHz and 298 K. All titration experiments were conducted in deuterated $CDCl_3$ or CD_3CN with a compound concentration at 2.0~7.0 mM. Tetrabutylammonium chloride (TBACl) was added incrementally at varying molar ratios. After each addition, the corresponding ^{1}H NMR spectrum was recorded. The data was analyzed by a global fit procedure using the Bindfit program, in which non-linear least squares analysis was applied for the best fit between observed and calculated chemical shifts for the 1:1 binding stoichiometry. The binding constant K was determined from three independent titration experiments and is reported as the mean ± standard deviation.

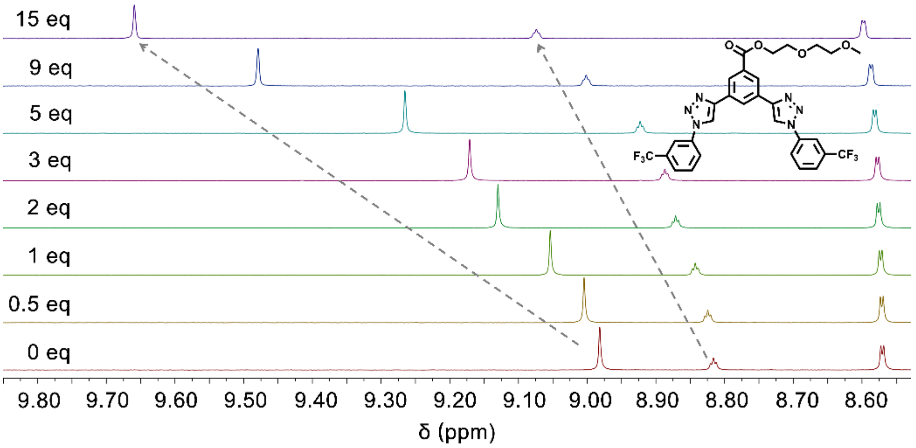


Figure S3 Representative partial ^{1}H NMR spectral changes of compound 2 (2 mM) with tetrabutylammonium chloride (TBACl, 0–15 eq) in deuterated CD_3CN (400 MHz, 298 K).

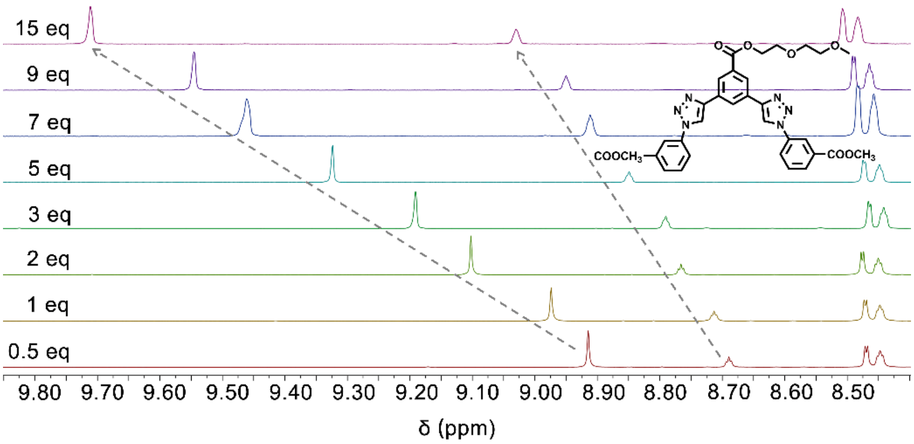


Figure S4 Representative partial ^{1}H NMR spectral changes of compound 3 (3 mM) with tetrabutylammonium chloride (TBACl, 0–15 eq) in deuterated CD$_3$CN (400 MHz, 298 K).

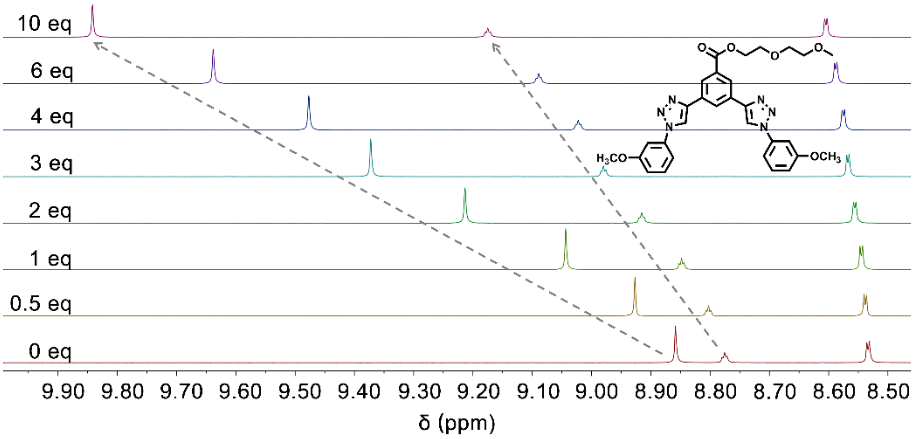


Figure S5 Representative partial ^{1}H NMR spectral changes of compound 4 (7 mM) with tetrabutylammonium chloride (TBACl, 0–10 eq) in deuterated CD$_3$CN (400 MHz, 298 K).

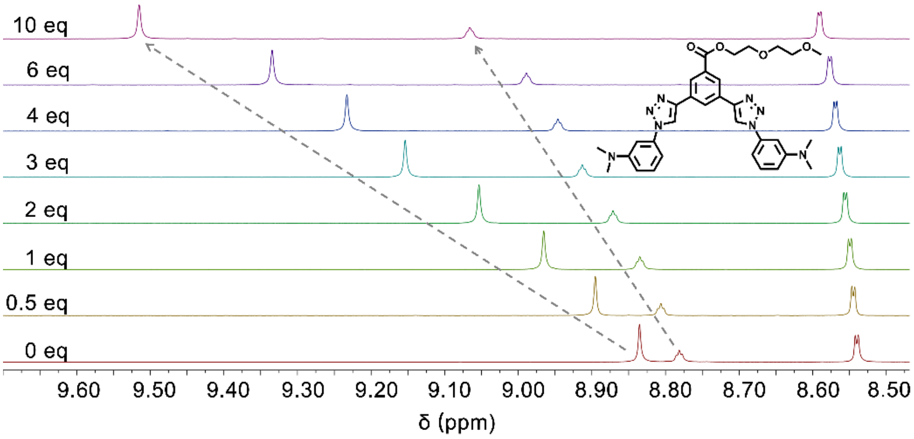
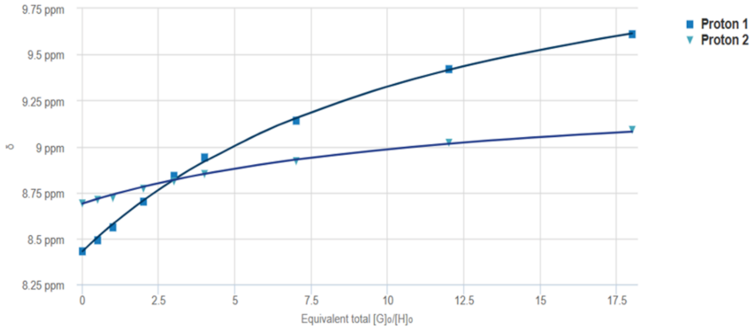
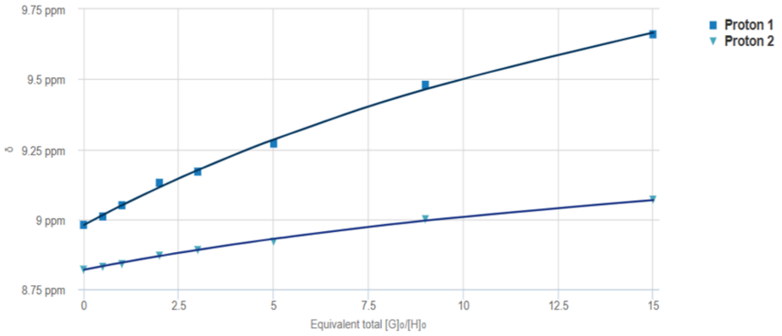


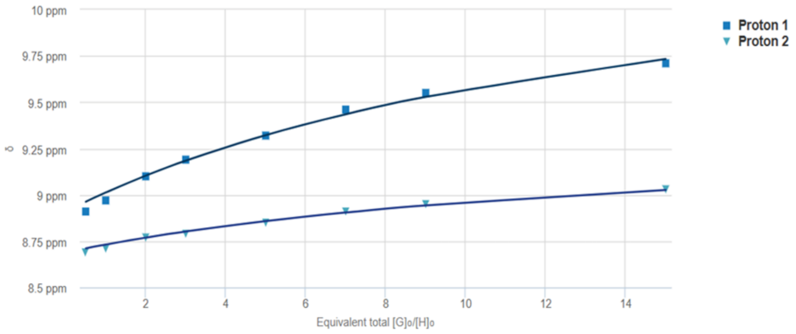
Figure S6 Representative partial ^{1}H NMR spectral changes of compound 5 (7 mM) with tetrabutylammonium chloride (TBACl, 0–10 eq) in deuterated CD$_3$CN (400 MHz, 298 K).

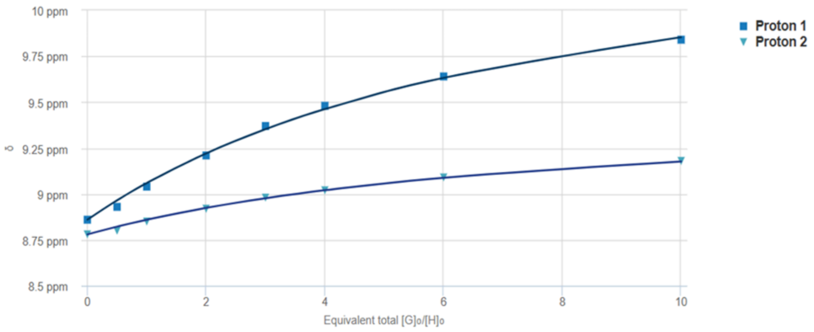
Then, a curve was plotted with Δδ against Cl⁻ concentration, and the ion complexation constant between compound and Cl⁻ was obtained by fitting with the curves. The obtained binding constant K values were summarized in Table 1.

Taking the titration experiment of compound 1 with Cl⁻ as an example:









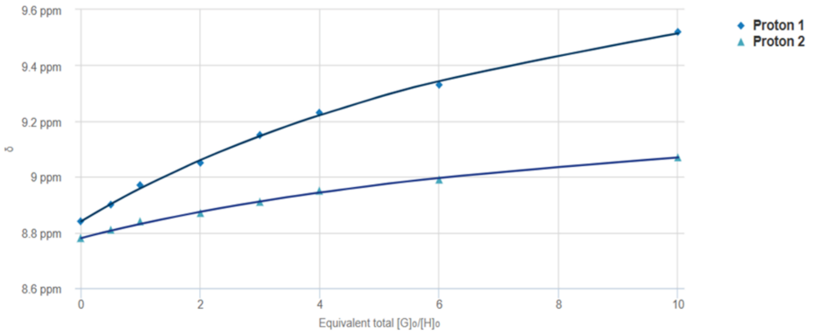


Figure S7 Representative values of Δδ ($H_a/H_{a'}$) and Δδ (H_b) as a function of the host-guest concentration ratio ($[G]_0/[H]_0$) in ^{1}H NMR titration experiments for compound 1-5 (from up to down), and the corresponding fitting curves.

6. Ion transporting activity studied by LUV⊃HPTS assay.

6.1 Preparation of LUVs vesicle enwrapped with HPTS (LUVs⊃HPTS).

To an EYPC solution (10.0 mg, 400 μL, 25.0 mg mL^{-1} in $CHCl_3$) was added cholesterol (1.0 mg, 100 μL, 10.0 mg mL^{-1} in $CHCl_3$). The solvent was evaporated by a slow stream of nitrogen, followed by drying under vacuum for 12 h. The lipid membrane was hydrated with 500 μL HEPES buffer (1 mM HPTS, 10 mM HEPES, 100 mM NaCl, pH = 7.0) and stirred in a shaker for 2 h (37 °C, 180 rad min^{-1}). Then, the suspension was subjected to seven freeze-thaw cycles and allowed to age for 30 min at room temperature before extruding 21 times through a 100 nm polycarbonate membrane. The mixture was purified with size exclusion column chromatography (SephadexG-25) and further diluted to 12.9 mL with HEPES buffer (10 mM HEPES, 100 mM NaCl, pH = 7.0) to afford vesicle stock solution with a total lipid concentration of 1.0 mM, assuming 100% retention of lipid during the gel filtration process.

6.2 Ion transport activity.

In a typical experiment, 2900 μL of HEPES buffer (10 mM HEPES, 100 mM NaCl, pH = 7.0) was transferred to a quartz cuvette followed by addition of 100 μL of LUV⊃HPTS vesicle stock solution. The cuvette was placed in the fluorescence instrument with a slow stirring condition by a magnetic stirrer equipped in the instrument (at t = 0 s). The time-dependent change in fluorescence intensity (λ_{em} = 510 nm) was monitored at two excitation wavelengths simultaneously (I_{450}: λ_{ex} = 450 nm, I_{405}: λ_{ex} = 405 nm), during the addition of base (30 μL, 0.5 M NaOH, ΔpH = 0.8) at t = 50 s, transporter (10 μL stock solution in DMSO) at t = 100 s, and 60 μL of 5% Triton X-100 aqueous solution at t = 400 s. All the temperature was kept at 25 ºC by a stirrer and a temperature controller. Time courses of fluorescence intensity I_F were obtained by ratiometric analysis ($R = I_{450}/I_{405}$) and normalization according to Equation S1,

$$I_F = \frac{R - R_{100}}{R_{\infty} - R_{100}} \quad Eq.S1$$

where R_{100} is the R before addition of transporter and R_{∞} is the R after addition of Triton X-100. The solvent DMSO (10 μL) was also monitored as the background. Finally, I_F at 400 s just before the addition of Triton X-100 was defined as the normalized transmembrane activity Y ($Y = I_F - I_{DMSO}$).

For clarity, the data before the addition of transporter was deleted and time (X-axis) was changed to start from the point of transporter addition (i.e. t = 100 s was normalized to t = 0 s) to the end point of experiment (i.e. t = 400 s was normalized to t = 300 s). The detailed data processing was illustrated in Figure S8 and three independent experiments were repeated for each concentration. The concentration-dependent dynamic curve was investigated until the activity achieved the maximum or the appearance of precipitation in the test process.

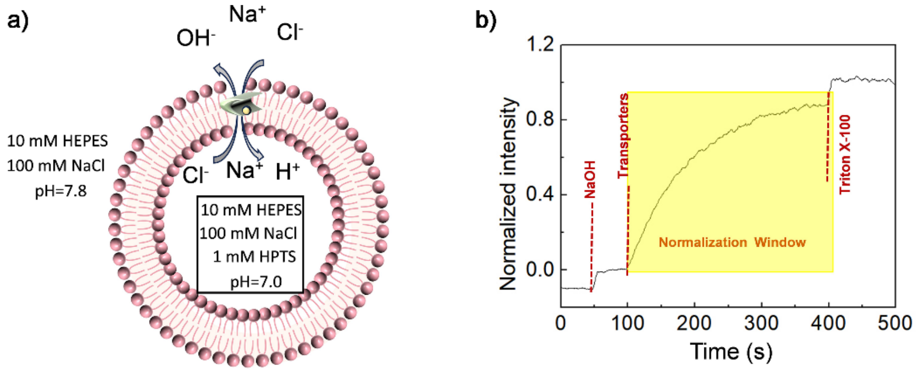


Figure S8 a) Schematic illustration of LUVs⊃HPTS assay and b) representative fluorescence kinetics for the experimental process.

Then, the obtained normalized transmembrane activities were analyzed with Hill Equation S2 to give effective concentration EC_{50} (the effective concentration required for 50% activity) and the Hill coefficient n,

$$Y = Y_{\infty} + \frac{Y_0 - Y_{\infty}}{1 + \left(\frac{c}{EC_{50}}\right)^n} \quad Eq.S2$$

Where Y_0 is Y in absence of transporter (normally defined as 0), $Y_{□}$ is Y with excess transporter (normally defined as 1) and c is the transporter concentration.

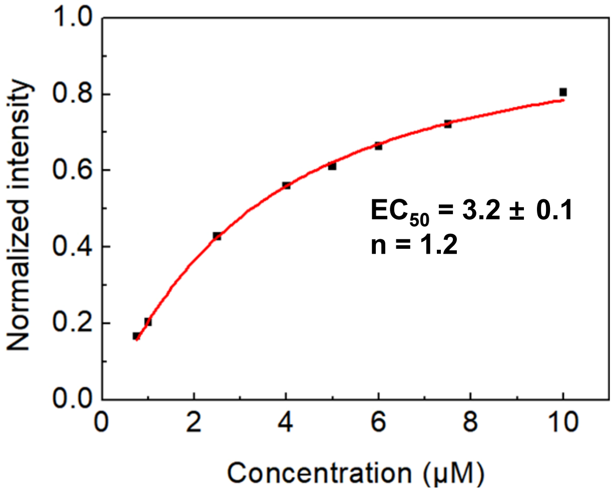


Figure S9 The corresponding Hill equation fitting of the concentration-activity curve of compound 1.

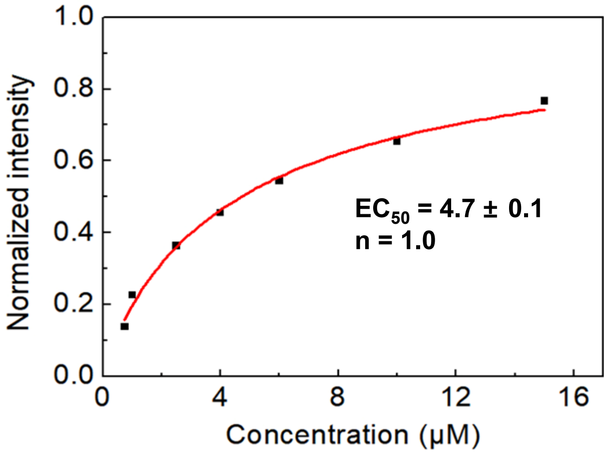


Figure S10 The corresponding Hill equation fitting of the concentration-activity curve of compound 2.

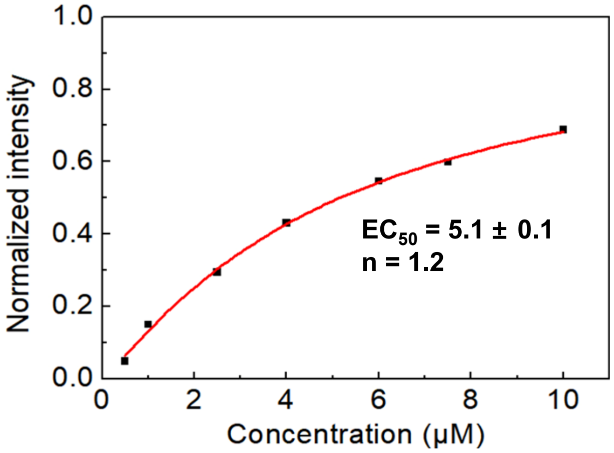


Figure S11 The corresponding Hill equation fitting of the concentration-activity curve of compound 3.

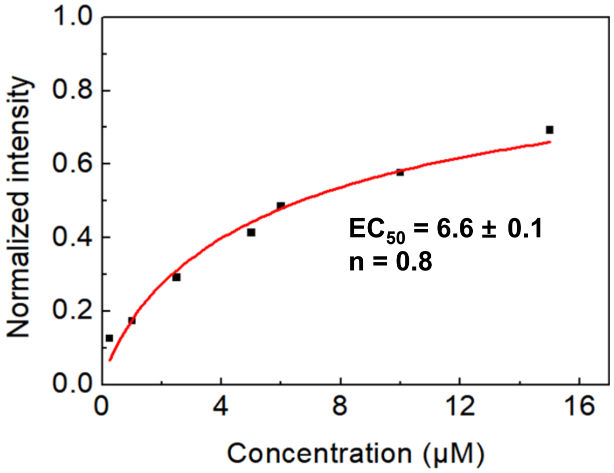


Figure S12 The corresponding Hill equation fitting of the concentration-activity curve of compound 4.

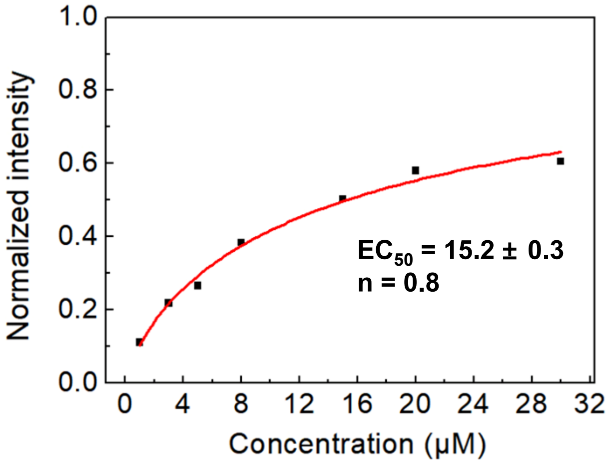


Figure S13 The corresponding Hill equation fitting of the concentration-activity curve of compound 5.

6.3 Cation selectivity assay.

100 μL of LUVs⊃HPTS solution (10 mM HEPES, 100 mM NaCl, 1 mM HPTS, pH = 7.0) and 2900 μL of HEPES buffer solution (10 mM HEPES, 100 mM MCl, pH = 7.0, $M^+ = Cs^+, K^+, Li^+, Rb^+, Na^+$) were added into the cuvette. At 50 s, the corresponding MOH (30 μL, 0.5 M MOH, ΔpH = 0.8, $M^+ = Cs^+, K^+, Li^+, Rb^+, Na^+$) was added into the cuvette as the base. At 100 s, compound 1 (10 μL DMSO, final concentration of 4.0 μM) was introduced. Finally, the fluorescence activity before adding Triton X-100 at 400 s was compared, and the data graph of cation selectivity was summarized.

6.4 Anion selectivity assay.

100 μL of LUVs⊃HPTS solution (10 mM HEPES, 100 mM NaCl, 1 mM HPTS, pH = 7.0) and 2900 μL of HEPES buffer solution (10 mM HEPES, 100 mM NaX, pH

= 7.0, $X^- = F^-, Cl^-, Br^-, I^-, SO_4^{2-}$) were added into the cuvette. At 50 s, compound 1 (10 μL DMSO, final concentration of 4.0 μM) was introduced and finally Triton X-100 was added to balance the ion gradient at 350 s. The data from 50 s to 350 s was selected for the normalization process using Eq S1.

6.5 FCCP assay.

The experimental protocol was similar to that described in section 4.3.2), except that at t = 75 s, FCCP solution (10 μL, final concentration of 0.01 μM) was added. All other experimental conditions and data processing methods were consistent with those in section 4.3.2).

7. LUVs⊃Lucigenin assay for Cl^- transport.

The protocol for preparing lucigenin encapsulated large unilamellar vesicles (LUV⊃Lucigenin) follows the standard LUV preparation method, with the following modifications. Hydration was carried out using a buffer containing 2 mM Lucigenin, 225 mM $NaNO_3$, and 5 mM PB (pH = 7.2). Finally, the purified vesicles were diluted with a PB buffer (225 mM $NaNO_3$, 5 mM PB, pH = 7.2) to achieve a final lipid concentration of 0.4 mM, assuming complete lipid retention during gel filtration.

In a typical experiment (Figure S14), 2900 μL of vesicle stock solution as prepared above was transferred to a quartz cuvette. The fluorescence at 506 nm under 368 nm excitation was monitored. At 50 s, 30 μL of PB buffer containing of 4 M NaCl and 225 mM $NaNO_3$ was added. Then, a MeCN solution (10 μL) containing compound 1 was added at 100 s. After 400 s, 60 μL of 5% Triton-X detergent was added to lyse the vesicles. The detected fluorescent intensity was normalized into $I_F = F/F_0$ (F_0, the fluorescent intensity before the addition of compound 1). For clarity, the data before the addition of transporter was deleted and time (X-axis) was changed to start from the point of transporter addition (i.e. t = 100 s was normalized to t = 0 s) to the end point of experiment (i.e. t = 400 s was normalized to t = 300 s).

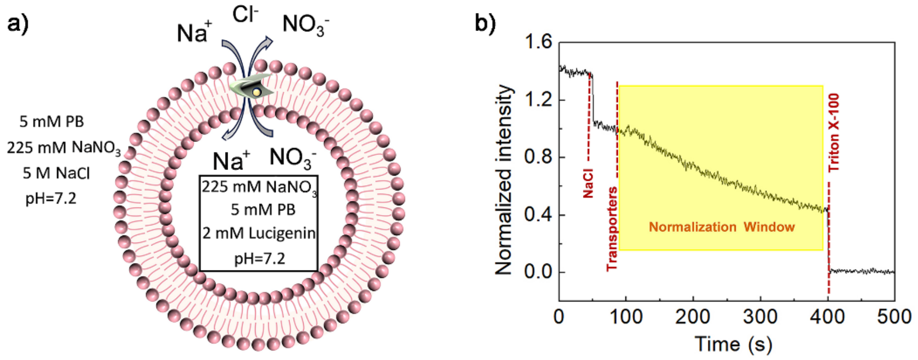


Figure S14 a) Schematic illustration of LUVs⊃ Lucigenin assay and b) representative fluorescence kinetics for the experimental process.

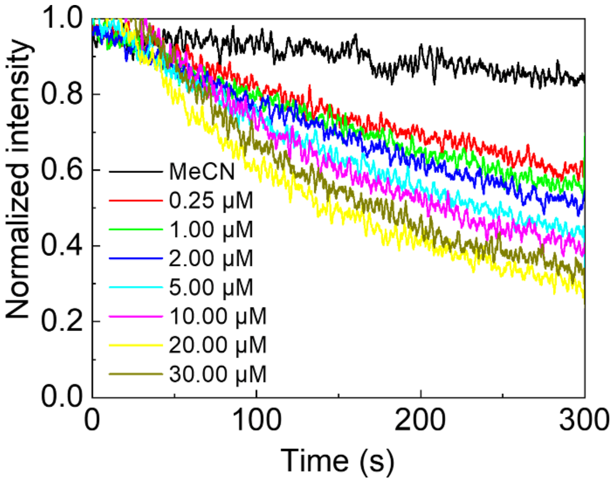


Figure S15 LUVs⊃Lucigenin activity curves of compounds 2 at different concentrations.

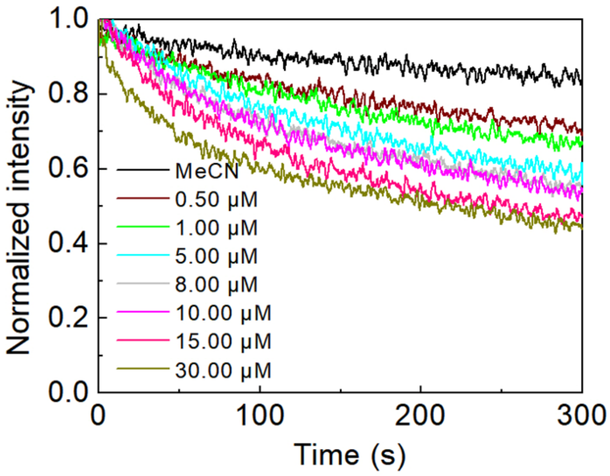


Figure S16 LUVs⊃Lucigenin activity curves of compounds 3 at different concentrations.

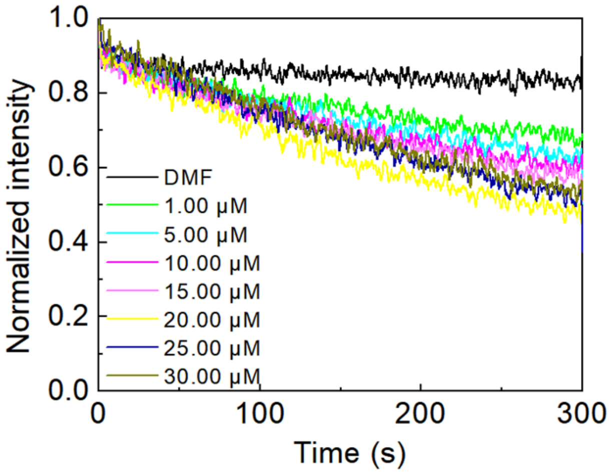


Figure S17 LUVs⊃Lucigenin activity curves of compounds 4 at different concentrations.

8. Appendix: ^{1}H, ^{13}CNMR spectra for compounds 1-5.

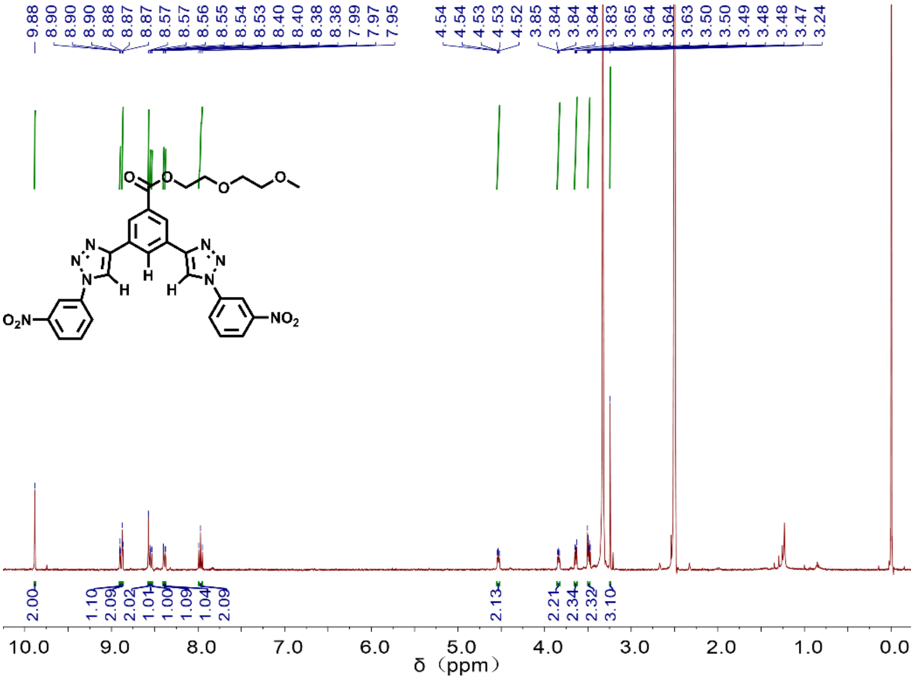


Figure S18 The ^{1}H NMR spectra for compound 1 in d_6-DMSO.

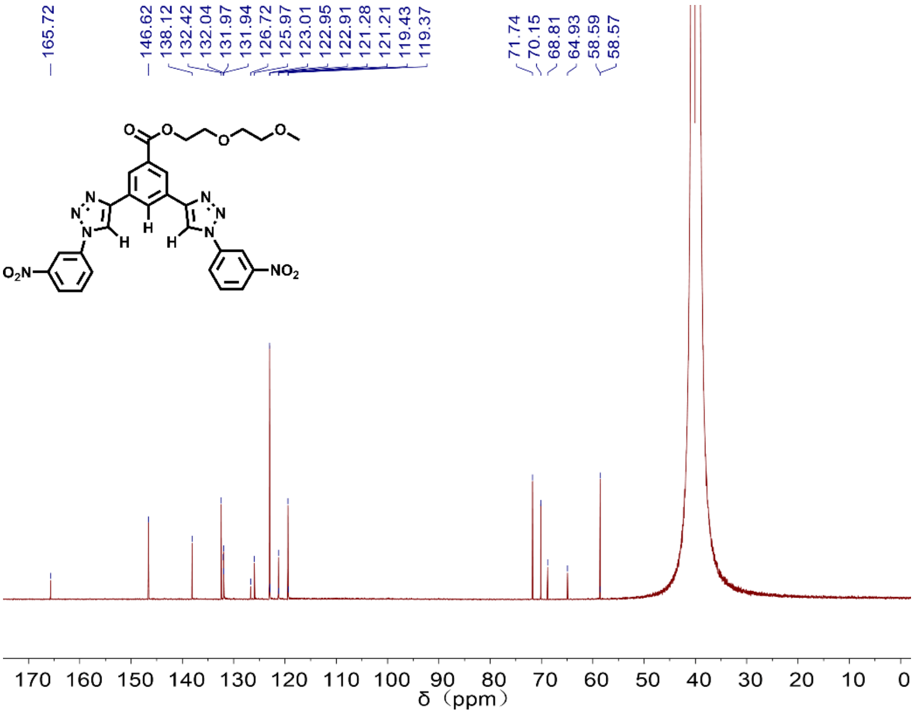


Figure S19 The ^{13}C NMR spectra for compound 1 in d_6-DMSO.

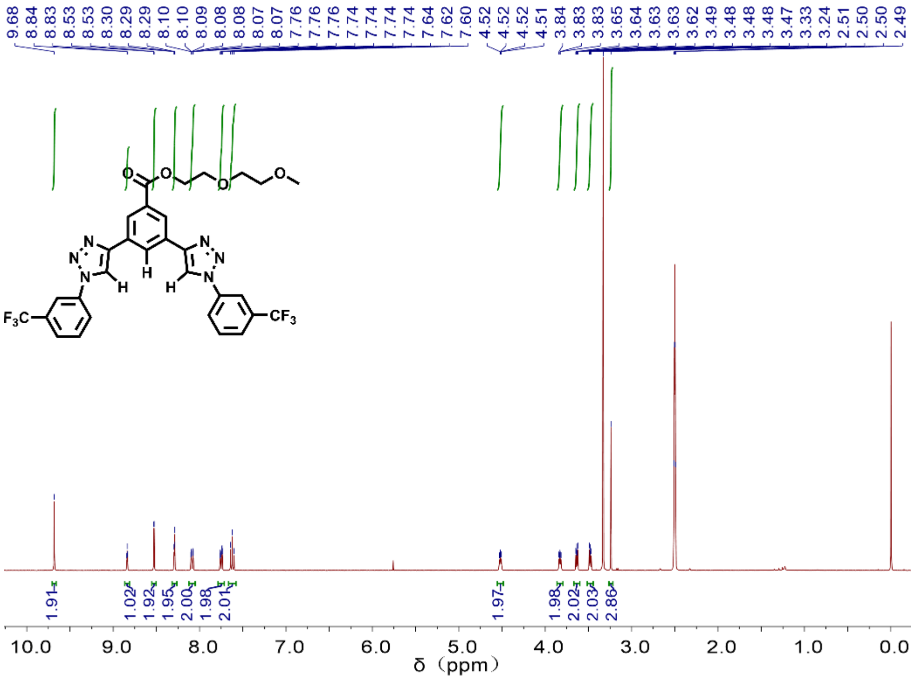


Figure S20 The ^{1}H NMR spectra for compound 2 in d$_6$-DMSO.

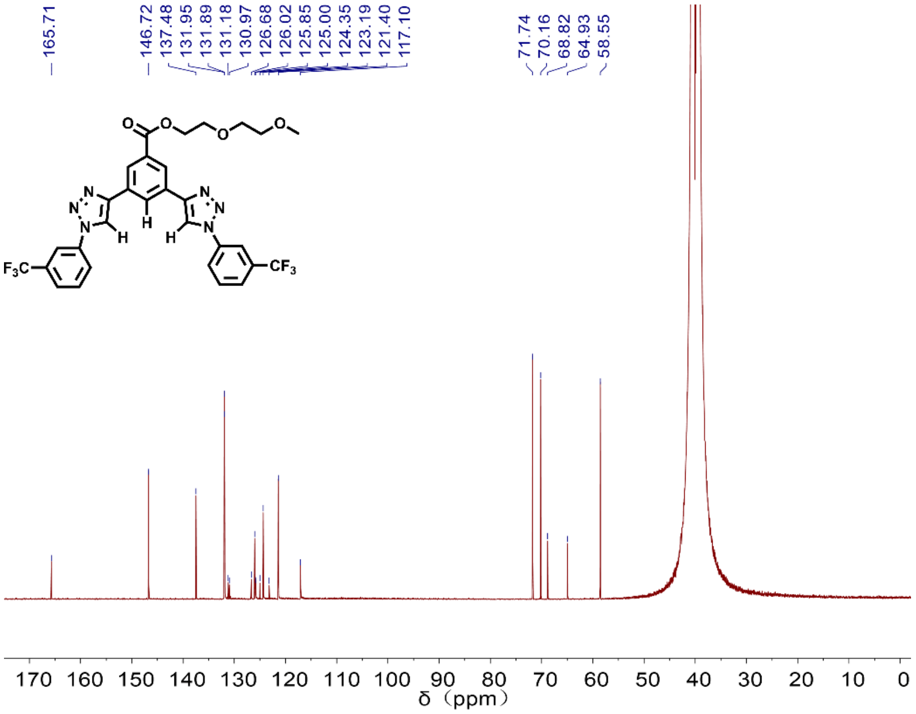


Figure S21 The ^{13}C NMR spectra for compound 2 in d$_6$-DMSO.

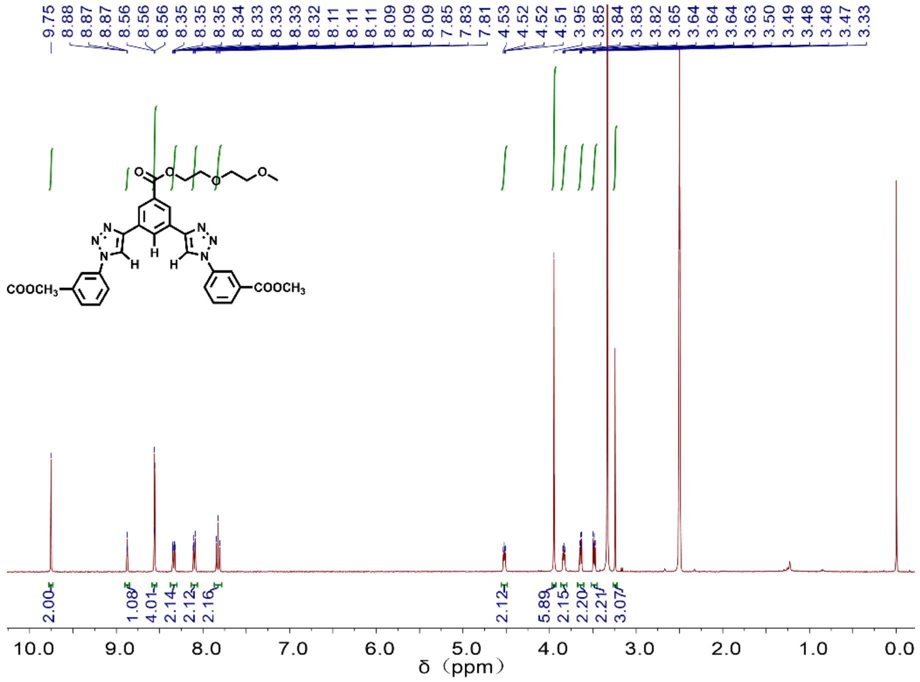


Figure S22 The ^{1}HNMR spectra for compound 3 in d$_6$-DMSO.

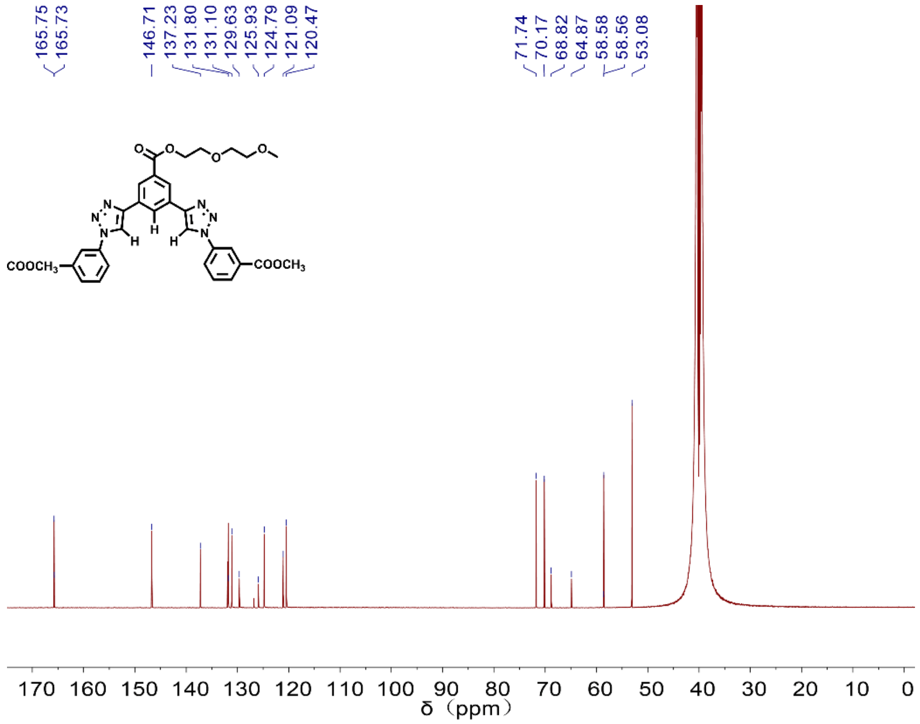


Figure S23 The ^{13}C NMR spectra for compound 3 in d$_6$-DMSO.

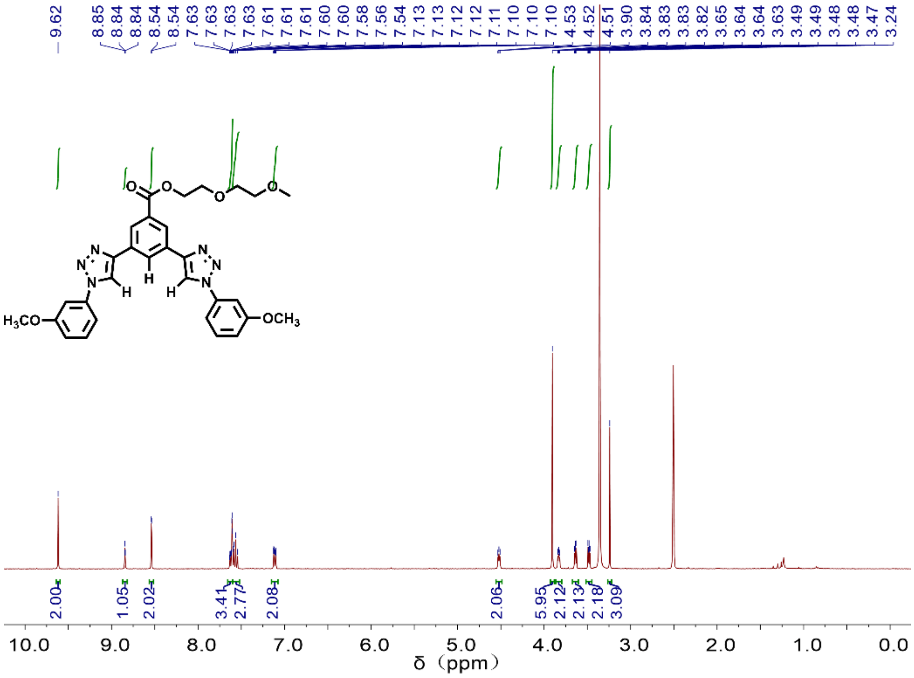


Figure S24 The ^{1}HNMR spectra for compound 4 in d_6-DMSO.

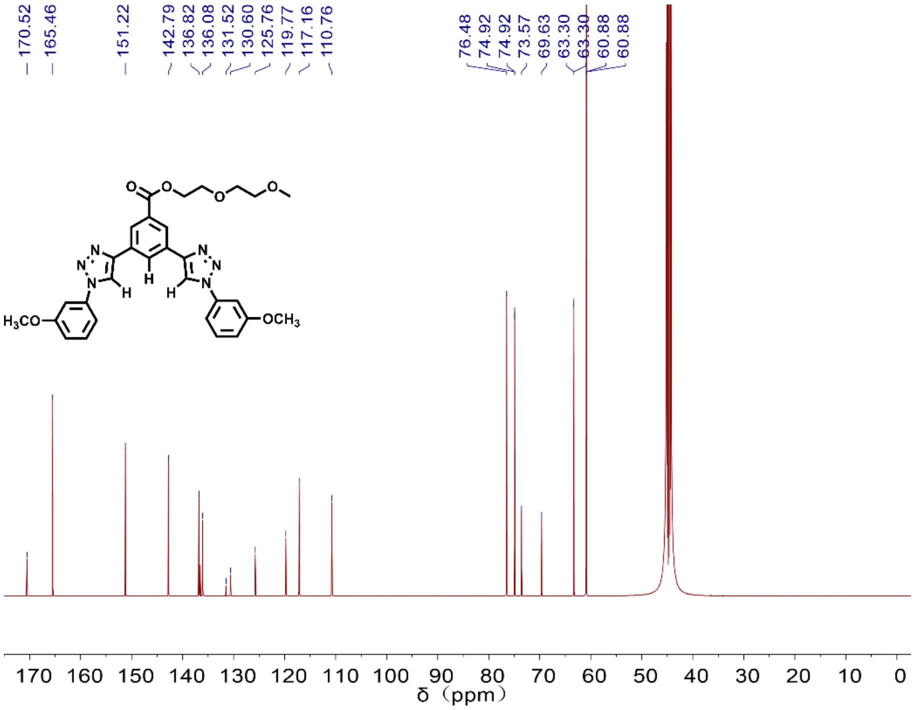


Figure S25 The ^{13}C NMR spectra for compound 4 in d_6-DMSO.

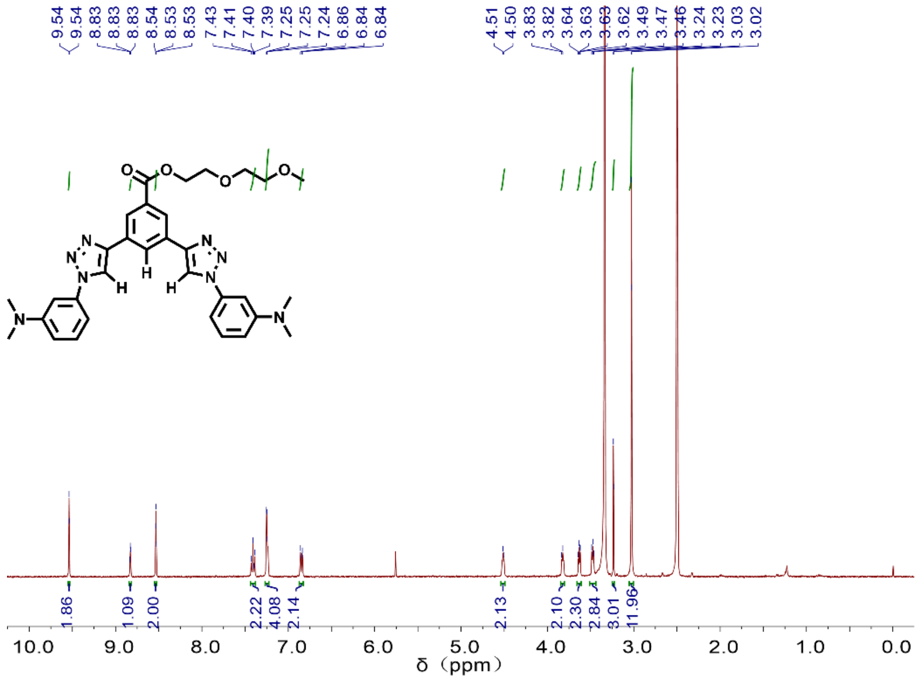


Figure S26 The ^{1}HNMR spectra for compound 5 in d_6-DMSO.

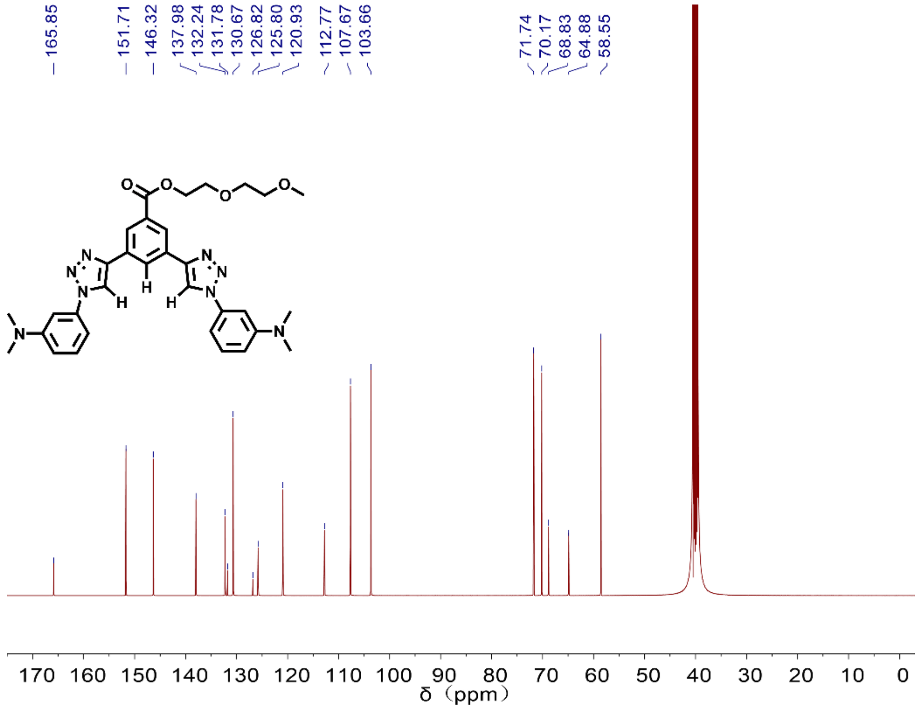


Figure S27 The ^{13}C NMR spectra for compound 5 in d_6-DMSO.