Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Benzimidazolium-based Synthetic Chloride and Calcium Transporters in Bacterial Membranes

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Contents

GENERAL INFORMATIONS

4-iodobenzoïc acid, borane in tetrahydorfuran (BH_3 in THF), phosphorus tribromide (PBr_3) were obtained from Aldrich. Tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile (CH_3CN), hexane and ethyl acetate (EtOAc) were purchased from EMD. ^{1}H-NMR spectra were recorded on a Bruker spectrometer at 300 and 75 MHz, respectively, in the indicated solvent. Chemical shifts are reported in ppm with internal reference to TMS. High-resolution mass spectra (HRMS) were recorded on a LC-MSD-Tof instrument from Agilent technologies in positive electrospray mode in general. Protonated molecular ions $(M+H)^+$ were used for empirical formula confirmation. Phospholipids used to prepare liposomes were purchased from Avanti Polar Lipids. Size-exclusion chromatography was performed using Sephadex G-25. Lucigenin were purchased from Molecular Probes. Liposome fluorimetric assays were recorded using a Varian Cary Eclipse Fluorescence spectrophotometer.

GENERAL PROCEDURES

Synthesis. The (4-phenylethynyl)benzyl bromide (**c**) has been obtained from 4-iodobenzoïc acid (**3a**) reduced to 4-iodobenzyl alcohol (**b**) using BH_3 in THF overnight at room temperature, then to react with benzylacetylene using PPh_3, $PdCl_2(PPh_3)_2$, CuI in dry THF with Et_3N overnight at 50 °C (Scheme 1). The (*N,N'* Diphenylethynylbenzyl)benzimidazolium bromide salt (**1**) has been synthesized from benzimidazole using (4-phenylethynyl)benzyl bromide (**d**) in THF at 25°C during 12 hours (Scheme 2). The compounds **2-4** have been synthesized by a counter ion metathesis from compound **1** (Scheme 3).

4-Iodobenzyl alcohol (b) : 4-Iodobenzoïc acid (0.02 mol) diluted in 40 mL THF was added to 40 mL of a solution of BH_3 in THF 1.0 M and the mixture was stirred overnight at room temperature. The reaction was quenched with 100 mL of HCl 2 N and extracted with 3 × 140 mL of DCM. The combined organic layers were washed with 2 × 80 mL of saturated $NaHCO_3$, 2 × 80 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the pure product as a white solid in a 99 % isolated yield. Mp 68 – 70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, 2H, J = 8.2 Hz), 7.06 (d, 2H, J = 8.0 Hz), 4.58 (s, 2H), 2.04 (b, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 137.4, 128.7, 92.9, 64.4. HRMS (ESI) calcd for $C_7H_7AgIO^+$ $[M+Ag]^+$: 340.8587, found 340.8591.

(4-Phenylethynyl)benzyl alcohol (c) : To a carefully degassed solution of 4-iodobenzyl alcohol **b** (4.3 mmol), PPh_3 (0.085 mmol), and $PdCl_2(PPh_3)_2$ (0.026 mmol) in 10 mL of dry THF and 5 mL of dry triethylamine was added CuI (0.085 mmol). The mixture was degassed for 5 min and a solution of phenylacetylene (4.3 mmol) in 2 mL of dry THF was added dropwise. The reaction was stirred overnight at 50 °C under nitrogen atmosphere. The mixture was added to 50 mL of iced water and the organic phase was recovered, dried over $MgSO_4$. The solvent was removed under reduced pressure to give the pure product as a white solid in 99 % isolated yield. Mp. 118 – 120 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.50 (m, 4H), 7.37-7.24 (m, 5H), 4.66 (s, 2H), 2.00 (b, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 131.7, 131.5, 128.3, 128.2, 126.7, 123.1, 122.3, 89.3, 89.1, 64.8. HRMS (ESI) calcd for $C_{15}H_{13}O^+$ $[M+H]^+$: 209.0961, found 209.0969.

(4-Phenylethynyl)benzyl bromide (d) : (4-Phenylethynyl)benzyl alcohol (**c**) (1.44 mmol) was dissolved in 5 mL of DCM. The mixture was put at 0 °C and phosphorus tribromide was added dropwise. Then the mixture was stirred 2 hours at 0 °C and the solvent was removed under reduced pressure. The product was purified by flash chromatography (Hexane/EtOAc, 60:40) to afford the compound **d** as a white solid in 100 % isolated yield. Mp 94 – 96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.48 (m, 4H), 7.37-7.24 (m, 5H), 4.48 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 131.9, 131.5, 129.0, 128.3, 128.2, 123.3, 122.9, 90.2, 88.8, 32.9. HRMS (ESI) calcd for $C_{15}H_{12}Br^+$ $[M+H]^+$: 271.0117, found 271.0109.

(*N,N'*-Diphenylethynylbenzyl)benzimidazolium bromide (1) : 503 mg (4.3 mmols) of benzimidazole and 464 mg (19.3 mmols) of sodium hydride are diluted in 10 mL of THF. After 5 minutes at room temperature, 1270 mg (4.68 mmols) of (4-phenylethynyl)benzyl bromide **d** is added to the mixture. The solution is stirred at room temperature for 12 hrs and the solvent is removed in vacuuo. 30 mL of water are added to the crude product and extracted with 3 X 30 mL of DCM. The organic phase is separated, washed with 2 x 30 mL of water, of $NaHCO_3$ and $NaCl_{(sat.)}$ and then dried on $MgSO_4$. The solvent is removed in vacuuo to yield 1060 mg of the intermediate (4 -Phenylethynylbenzyl)benzimidazole. This compound is then used without further purification: 745 mg (2.41 mmols) of (4-Phenylethynylbenzyl)benzimidazole and 0.6535 mg (2.41 mmols) of (4-phenylethynyl)benzyl bromide **d** are disolved in 30 mL of THF. The mixture is stirred 72 hrs at 70^{o}C and the resulting precipitate is filtered, washed with 10 mL of THF, and dried in vacuuo. 880

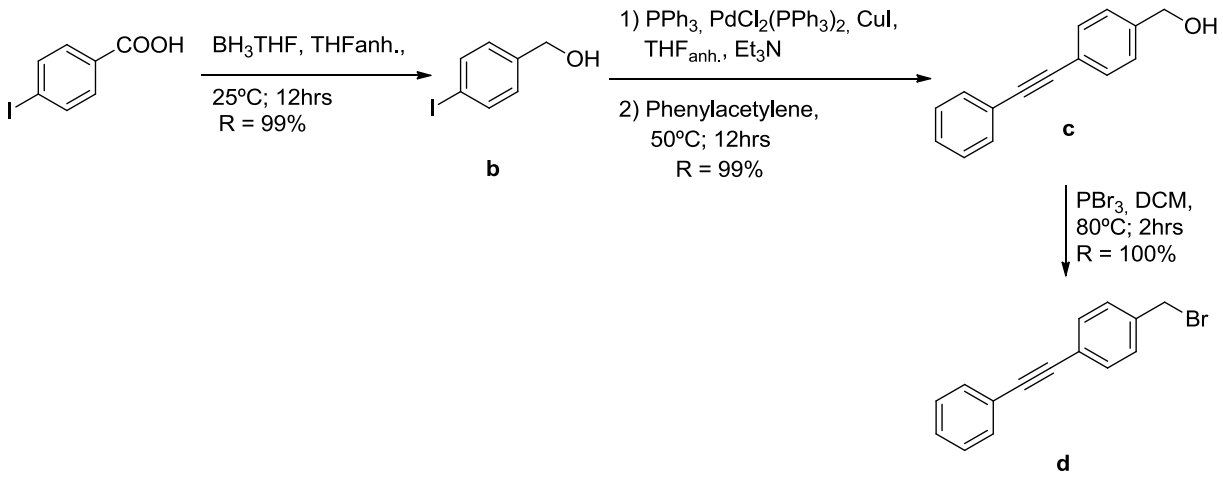
mg of **1** were obtained. Yield 63 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 9.97 (s, 1 H), 7.90 - 7.96 (m, 1 H), 7.52 (m, 14 H), 7.38 - 7.45 (m, 7 H), 5.81 (s, 4 H). MS (ESI): m/z Calcd for $C_{37}H_{27}N_2$ [M-Br]+: 499.22, found 499.22.

(*N,N'*-Diphenylethynylbenzyl)imidazolium Tetrafluoroborate (2) : 150 mg (0.26 mmoles) of (N,N'-Diphenylethynylbenzyl)imidazolium boride (**1**) are dissolved in a mixture of MeOH/ACN (50 :50). Then, 71 mg (0.65 mmoles) of $NaBF_4$ are added to 10 mL of methanol before being poured onto the solution containing the imidazolium salt. The resulting mixture is then brought to 80°C and stirred with a magnetic stir bar during 12 hours. After evaporating the solvent under reduced pressure, 40mL of distilled water are added to the powder obtained. The mixture is heated to 100ºC for 12 hours under magnetic stirring, and then filtered on a fritted glass. The raw product is then dried at 80°C for 2 hours, in order to obtain 137 mg of a white powder (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 9.97 (s, 1 H), 7.90 - 7.96 (m, 1 H), 7.52 (m, 14 H), 7.38 - 7.45 (m, 7 H), 5.81 (s, 4 H). MS (ESI): m/z Calcd for $C_{37}H_{27}N_2$ [M- BF_4]+: 499.22, found 499.22. (ESI): m/z Calcd for BF_4^-: 87.00, found 87.00.

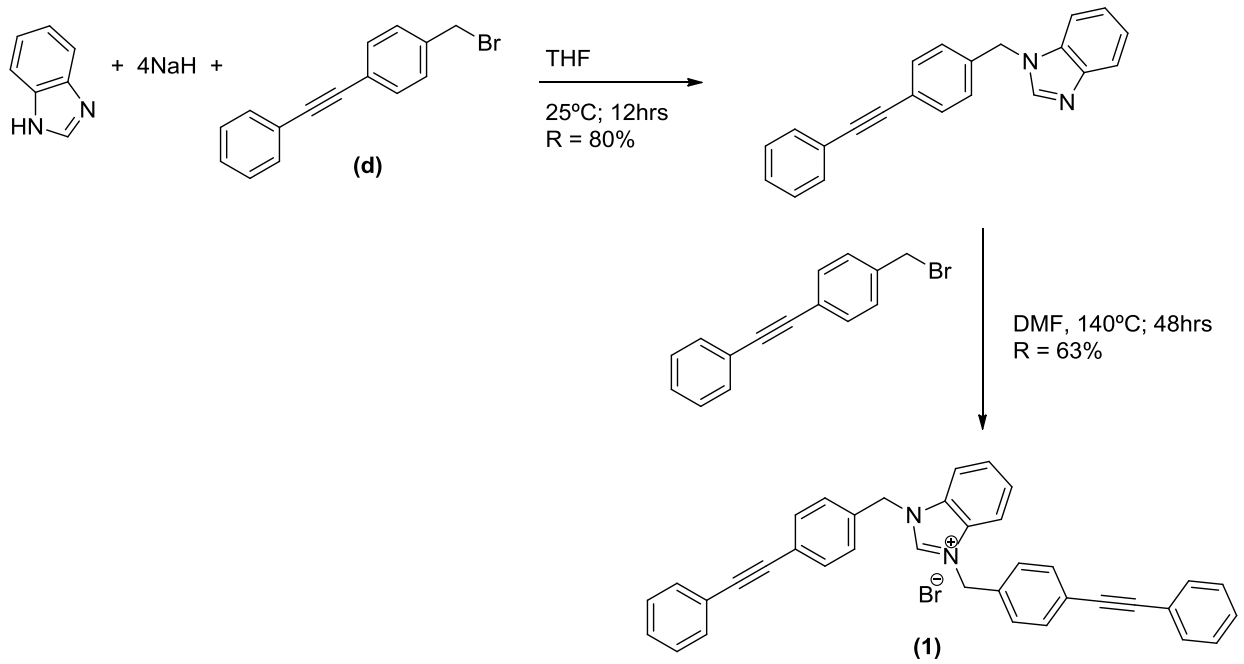
(*N,N'*-Diphenylethynylbenzyl)imidazolium Hexafluorophosphate (3) : 150 mg (0.26 mmoles) of (N,N'-Diphenylethynylbenzyl)imidazolium bromide are dissolved in a mixture of MeOH/ACN (50 :50). Then, 106 mg (0.65 mmoles) of NH_4PF_6 are added to 10 mL of methanol before being poured onto the solution containing the imidazolium salt. The resulting mixture is then brought to 80°C and stirred with a magnetic stir bar during 12 hours. After evaporating the solvent under reduced pressure, 40mL of distilled water are added to the powder obtained. The mixture is heated to 100ºC for 12 hours under magnetic stirring, and then filtered on a fritted glass. The raw product is then dried at 80°C for 2 hours, in order to obtain 167 mg of a white powder (99% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 9.97 (s, 1 H), 7.90 - 7.96 (m, 1 H), 7.52 (m, 14 H), 7.38 - 7.45 (m, 7 H), 5.81 (s, 4 H). MS (ESI): m/z Calcd for $C_{37}H_{27}N_2$ [M- PF_6]+: 499.22, found 499.22. (ESI): m/z Calcd for PF_6^-: 144.96, found 144.96.

(*N,N'*-Diphenylethynylbenzyl)imidazolium Bis(trifluoromethane)sulfonimide (4) : 150 mg (0,19 mmoles) of (N,N'-Diphenylethynylbenzyl)imidazolium bromide are dissolved in a mixture of MeOH/ACN (50 :50). Then, 187 mg (0.65 mmoles) of $LiNTf_2$ are added to 10 mL of methanol before being poured onto the solution containing the imidazolium salt. The resulting mixture is then brought to 80°C and stirred with a magnetic stir bar during 12 hours. After evaporating the solvent under reduced pressure, 40mL of distilled water are added to the powder obtained. The mixture is heated to 100ºC for 12 hours under magnetic stirring, and then filtered on a fritted glass. The raw product is then dried at 80°C for 2 hours, in order to obtain 182 mg of a white powder (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 9.97 (s, 1 H), 7.90 - 7.96 (m, 1 H), 7.52 (m, 14 H), 7.38 - 7.45 (m, 7 H), 5.81 (s, 4 H). MS (ESI): m/z Calcd for $C_{37}H_{27}N_2$ [M- NTf_2]+: 499.22, found 499.22. (ESI): m/z Calcd for NTf_2^-: 279.92, found 279.92.

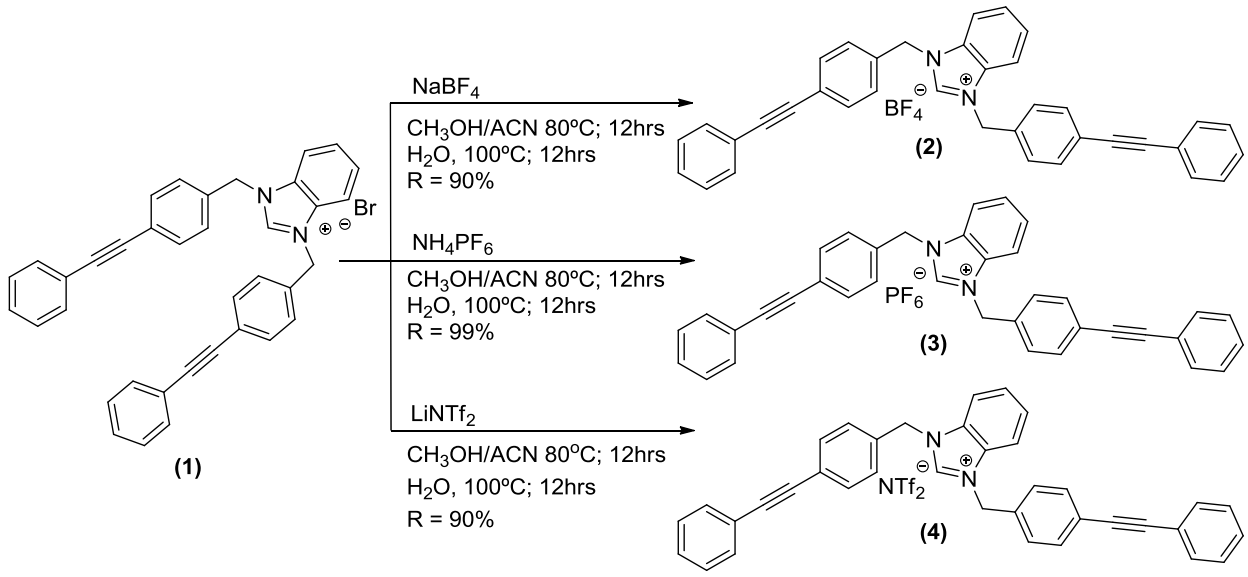
Scheme 1. : Synthesis of (4-Phenylethynyl)benzyl bromide



Scheme 2 : Synthesis of (*N,N'*-Diphenylethynylbenzyl)imidazolium bromide (**1**)



Scheme 3. : Counter anion metathesis



Preparation of EYPC liposomes for Lucigenin-based assays. A stock solution of egg-yolk phosphatidylcholine (EYPC) in $CHCl_3$ (100 mg) was evaporated under reduced pressure on the water bath at room temperature to produce a thin film that was dried *in vacuo* for 2 h at 35 ^{o}C. This lipid film was hydrated with 1 mL of 10 mM sodium phosphate (pH =6,4) containing sodium chloride, [NaCl] = 100 mM, and 2 mM Lucigenin[1]. Freeze/thaw cycles were repeated at least 30 times until no solid particles were visible. The frozen solution was warmed to 37^{o}C before every freeze cycle. The mixture was also placed on a vortexer 10 times for 1 min to facilitate hydration. The cloudy solution was extruded through a 100 nm polycarbonate membrane at least 20 times until the solution was transparent. This solution was passed down a Sephadex G-25 column (15 cm x 1 cm) to remove extravesicular lucigenin dye. The eluant was free of lucigenin and contained 10 mM phosphate buffer and 100 mM NaCl. The 2,6 mL of solution isolated from gel filtration was 50 mM in lipid, assuming all EYPC was incorporated into the liposomes. Each stock solution of liposomes was used that same day for any ion transport assays.

Preparation of DPPC liposomes for Lucigenin-based assays. DPPC (50 mg) was dissolved in 5 mL of a chloroform/methanol mixture (5 % MeOH), and the resulting solution was then evaporated under reduced pressure at 45^{o}C to produce a thin film that was then dried *in vacuo* for 2 h. The lipid film was hydrated with 1mL of 10 mM sodium phosphate containing sodium chloride, [NaCl] = 100 mM, and 2 mM Lucigenin. After 15 freeze/thaw cycles (thawing, and then warming to 45^{o}C) the liposomes were extruded through a 100 nm polycarbonate membrane 21 times at temperature between 45-55^{o}C (fluid state lipid). This solution was passed down a Sephadex G-25 column (15 cm x 1 cm) to remove extravesicular lucigenin dye. The eluant was free of lucigenin and contained 10 mM phosphate buffer and 100 mM NaCl. The 2,6 mL of solution isolated from gel filtration was 26,2 mM in lipid, assuming all DPPC was incorporated into the liposomes. Each stock solution of liposomes was used that same day for any ion transport assays.

Lucigenin-based ion transport assays. A 20 µL aliquot of the stock solution of liposomes was added to a cuvette containing 2,5 mL of a solution of salt $NaNO_3$ (100 mM) in phosphate buffer (10 mM) to give a 0.4 mM solution of phospholipid. The fluorescence of intravesicular dye was monitored by excitation at 372 nm and the emission at 503 nm was recorded. For assays in EYPC liposomes, some time within the first 100 s of the experiment, an 400 µL aliquot of a 0,25 mM

solution of benzimidazoliums **1, 2, 3** and **4** in MeOH was injected to give a solution that was less than 0,035 mM in benzimidazolium. At the end of the experiment, 10% aqueous Triton-X was injected to lyse the liposomes. The temperature was set to 37 ^{o}C. For kinetic analysis in EYPC liposomes, some time within the first 100 s of the experiment, seven 400 µL aliquots of 0,025 mM to 0,31 mM solutions of benzimidazolium **4** in MeOH were injected to give solutions that were 3 µM to 43 µM in benzimidazolium respectively. The temperature was set to 37 ^{o}C. For assays in DPPC liposomes, some time within the first 100 s of the experiment, an 400 µL aliquot of a 0,25 mM solution of benzimidazolium **4** in MeOH was injected to give a solution that was less than 0,035 mM in benzimidazolium. The temperature was set to 20^{o}C, 25^{o}C, 30^{o}C, 35^{o}C, 40^{o}C, 45^{o}C successively.

Initial rate and the rate constant calculations

Fluorescence assays were run at different **4**/EYPC ratios: 1-12.5%. The initial rate were determined at t=50s when the transporter is injected, following the Stern-Volmer equation.

$$\left(\frac{F_0}{F}\right) = 1 + K_{SV}[Cl^-]$$

with F_0 : maximum fluorescence intensity in absence of quencher

F : fluorescence intensity

K_{SV} : Stern-Volmer constant, here $K_{SV} = 142M^{-1}$

$[Cl^-]$: intravesicular chloride concentration

From this equation, we can deduce:

At t=0, $$-\left(\frac{d[Cl^-]}{dt}\right) = \left(\frac{F_0}{K_{SV}}\right) \bullet \left(\frac{1}{F^2}\right) \bullet \left(\frac{dF}{dt}\right)_{t=0} = V_0$$

With V_0 : initial rate

According to equation 1, the initial rate of ion flow (V_0) is expected to have a dependence on the pseudo first ordre constant (k_{obsd}) and $[Cl^-]$ the total initial intravesicular chloride concentration (77mM).

$$V_0 = k_{obsd}\,[Cl^-]_{t=0}$$

Table S1. Determination of V_0 and k_{obds} at different 4/EYPC ratios

mol% 4/EYPC	[4] (mM)	(dF/dt) (s^{-1})	V_0 (mM/s)	V_0 average (mM/s)	K_{obsd} (s^{-1})	Standard deviation
1,0	0,003	0,067	1,075	0,419	0,006	3,55E-03
		0,006	0,095			
		0,005	0,087			
1,6	0,005	0,131	2,103	1,389	0,019	4,69E-03
		0,038	0,607			
		0,091	1,458			
2,5	0,009	0,047	0,750	1,278	0,018	5,17E-03
		0,139	2,231			
		0,053	0,854			
5,0	0,017	0,118	1,900	2,376	0,033	2,73E-03
		0,154	2,472			
		0,172	2,757			
7,0	0,024	0,397	6,373	5,506	0,075	6,75E-03
		0,364	5,849			
		0,268	4,297			
10,0	0,034	0,517	8,300	10,232	0,140	1,22E-02
		0,634	10,177			
		0,761	12,218			
12,5	0,043	0,767	12,309	13,756	0,188	1,21E-02
		0,994	15,957			
		0,810	13,003			

Table S2. Determination of activity of 4 at different 4/EYPC ratios

mol% 4/EYPC	Log(mol% 4/EYPC)	% of Rmax at 250 s	Average % of Rmax at 250 s	Standard deviation
1,0	0,0000	29,52	32,44	4,19
		30,57		
		37,24		
1,6	0,1987	42,30	46,71	6,05
		44,23		
		53,61		
2,5	0,3979	55,07	56,41	1,31
		56,45		
		57,69		
5,0	0,6990	87,34	86,65	2,56
		83,81		
		88,80		
7,0	0,8451	100,30	102,21	6,31
		109,25		
		97,07		
10,0	1,0000	104,33	102,17	2,18
		99,98		
		102,21		
12,5	1,0969	104,58	101,33	13,03
		86,97		
		112,43		

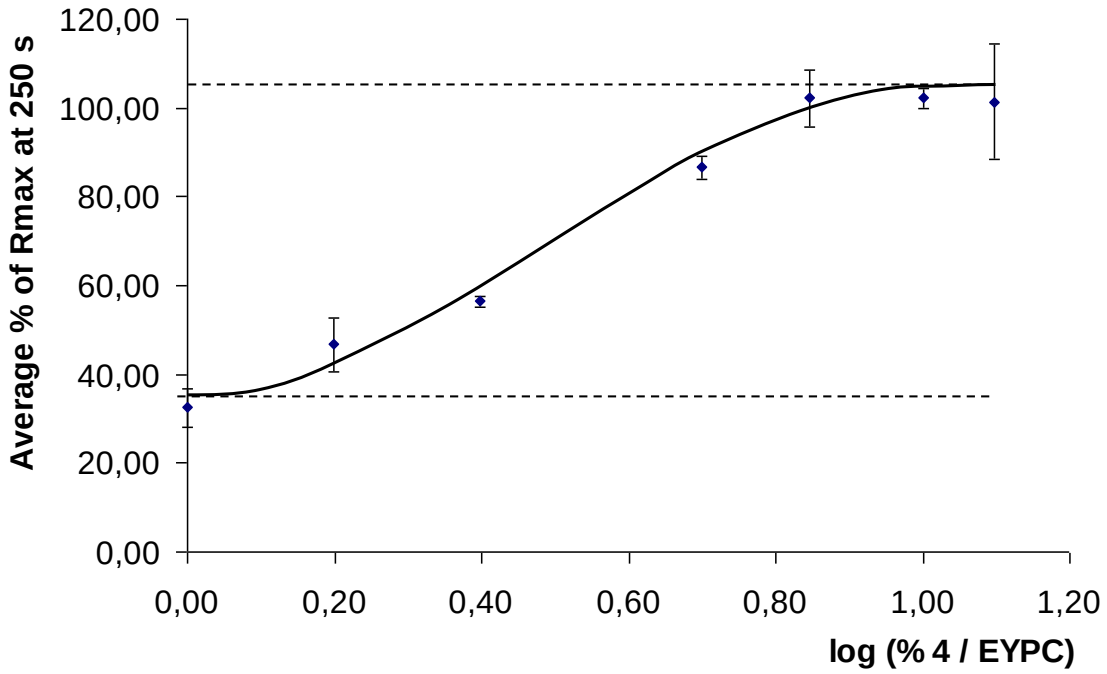


Figure S1_ Dose response curve for determination of the EC_{50} for imidazolium **4**. The data at each mol% is the average of 3 runs, with the standard deviation. The Log(mol% **4**/EYPC) that provokes a response half way between the baseline (32.44%) and maximum response (102.21%) has a value of 0.475. This corresponds to a mol% **4**/EYPC of 2.99%. Hill coefficient *n* was estimated with a curve fitting from the GraphPad Prism 6.00 for Windows (GraphPad Software, Inc.) at 2.092

Activation of citrine. *E. Coli* containing the pBad plasmid (YFP-Citrine) from frozen stocks were used to inoculate 2 mL of Luria-Bertani (LB) media containing ampicillin (100 mg/ml). The preculture was grown overnight at 37 °C and re-suspended in 75 mL of a fresh LB medium. The culture was grown at 37°C until the OD_{600}=0.5-0.7 and induced at 37°C for 16 hours with 0,02 % (w/v) of arabinose (final concentration).

Ion transport assays with *E. Coli*. A 1.6 mL aliquot of the stock solution of *E.Coli* culture was added to a cuvette containing 1.082 mL of a solution of salt $CaCl_2$ (1 mM). The fluorescence of intracellular citrine non-ratiometric indicator was monitored by excitation at 516 nm and the emission at 529 nm was recorded. Within the first two minutes of the experiment, an 150 µL aliquot of a 4.5 mM solution of benzimidazoliums **4** in MeOH was injected to obtain a 0.24 mM benzimidazolium salt final concentration. For the blank, at t = 2 minutes, an 150 µL aliquot of

MeOH was injected in the cuvette containing 1.6 mL of *E. Coli* culture and 1.082 mL of $CaCl_2$ (1mM). The temperature was set to 37 ^{o}C.

Destruction of YFP-Citrine *E. Coli* membranes. *E.Coli* culture was stirred at 100°C for 3h. An ultrasonic probe was used to destroy the remaining membranes with four cycles of sonication (30 seconds) and relaxation (1 minute).

Optic Density (OD) assay. 800µL of a *E. Coli* culture was added to a cuvette containing 800 µL of 1mM $CaCl_2$ solution and 150µL of transporter **4** or MeOH. The absorbance of the solution was monitored at 600 nm. The absorbance of compound **4** at this wavelength was subtracted.

Université de Montréal

CRYSTAL AND MOLECULAR STRUCTURE OF

C37 H27 Br N2 COMPOUND (SCHM55)

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Structure solved and refined in the laboratory of X-ray diffraction Université de Montréal by Michel Simard.

Table 1. Crystal data and structure refinement for C37 H27 Br N2.

Identification code	SCHM55
Empirical formula	C37 H27 Br N2
Formula weight	579.52
Temperature	100K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.5643(2) Å α = 89.925(1)° b = 9.7254(2) Å β = 80.209(1)° c = 17.4889(4) Å γ = 62.908(1)°
Volume	1421.79(5)Å^3
Z	2
Density (calculated)	1.354 g/cm^3
Absorption coefficient	2.179 mm^{-1}
F(000)	596
Crystal size	0.16 x 0.08 x 0.04 mm
Theta range for data collection	2.57 to 70.95°
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 11$, $-21 \le \ell \le 21$
Reflections collected	27726
Independent reflections	5290 [R_{int} = 0.042]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9165 and 0.6232
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5290 / 0 / 361
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R_1 = 0.0525, wR_2 = 0.1437
R indices (all data)	R_1 = 0.0568, wR_2 = 0.1526
Largest diff. peak and hole	1.562 and -1.166 e/Å^3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for C37 H27 Br N2.

U_{eq} is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U_{eq}
Br(1)	9271(1)	3164(1)	4208(1)	30(1)
N(1)	3764(3)	3171(3)	4839(1)	27(1)
C(2)	2437(4)	3025(4)	5027(2)	28(1)
N(3)	2585(3)	2031(3)	5563(1)	26(1)
C(4)	4100(3)	1490(3)	5750(2)	25(1)
C(5)	4865(4)	429(3)	6260(2)	27(1)
C(6)	6427(4)	111(4)	6271(2)	30(1)
C(7)	7184(4)	846(4)	5803(2)	30(1)
C(8)	6423(4)	1913(3)	5304(2)	28(1)
C(9)	4860(4)	2219(3)	5282(2)	25(1)
C(10)	4015(4)	4182(4)	4257(2)	30(1)
C(11)	4673(4)	3372(3)	3450(2)	26(1)
C(12)	6322(4)	2592(4)	3171(2)	30(1)
C(13)	6918(4)	1807(4)	2434(2)	30(1)
C(14)	5888(4)	1821(4)	1951(2)	29(1)
C(15)	4226(4)	2628(4)	2232(2)	29(1)
C(16)	3640(4)	3375(4)	2972(2)	29(1)
C(17)	6531(4)	1067(4)	1157(2)	33(1)
C(18)	7057(4)	511(4)	537(2)	35(1)
C(19)	7728(4)	-196(4)	-264(2)	30(1)
C(20)	9320(4)	-1380(4)	-481(2)	33(1)
C(21)	9902(4)	-2044(4)	-1238(2)	33(1)
C(22)	8956(4)	-1536(4)	-1801(2)	33(1)
C(23)	7374(4)	-356(4)	-1590(2)	35(1)
C(24)	6770(4)	290(4)	-833(2)	33(1)
C(25)	1336(3)	1614(4)	5916(2)	28(1)
C(26)	563(3)	2350(4)	6738(2)	26(1)
C(27)	-232(4)	1685(4)	7230(2)	32(1)
C(28)	-976(4)	2327(4)	7983(2)	33(1)
C(29)	-939(3)	3651(4)	8264(2)	29(1)
C(30)	-157(4)	4321(4)	7771(2)	29(1)
C(31)	591(4)	3673(4)	7015(2)	28(1)
C(32)	-1707(4)	4340(4)	9059(2)	33(1)
C(33)	-2275(3)	4881(3)	9673(2)	31(1)
C(34)	-2999(4)	5522(4)	10494(2)	28(1)
C(35)	-4081(4)	5099(4)	10941(2)	33(1)
C(36)	-4716(4)	5686(4)	11706(2)	35(1)
C(37)	-4304(4)	6720(4)	12045(2)	35(1)
C(38)	-3249(4)	7171(4)	11600(2)	35(1)
C(39)	-2594(4)	6567(4)	10835(2)	32(1)

Table 3. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for C37 H27 Br N2.

	x	y	z	U_{eq}
H(2)	1508	3560	4807	34
H(5)	4345	-51	6585	32
H(6)	7003	-625	6603	36
H(7)	8255	599	5832	36
H(8)	6937	2413	4991	33
H(10A)	4766	4527	4406	36
H(10B)	2984	5115	4258	36
H(12)	7036	2597	3487	36
H(13)	8042	1253	2255	37
H(15)	3506	2657	1912	35
H(16)	2518	3899	3160	35
H(20)	9991	-1720	-105	40
H(21)	10964	-2859	-1376	40
H(22)	9374	-1982	-2323	40
H(23)	6718	-2	-1971	42
H(24)	5692	1074	-694	39
H(25A)	1814	473	5922	33
H(25B)	504	1943	5592	33
H(27)	-260	782	7044	38
H(28)	-1514	1866	8311	40
H(30)	-135	5228	7956	35
H(31)	1123	4137	6686	33
H(35)	-4378	4407	10716	39
H(36)	-5440	5387	12007	42
H(37)	-4739	7112	12575	42
H(38)	-2982	7890	11822	42
H(39)	-1863	6861	10536	38

Table 4. Anisotropic parameters ($Å^2$ x 10^3) for C37 H27 Br N2.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$$

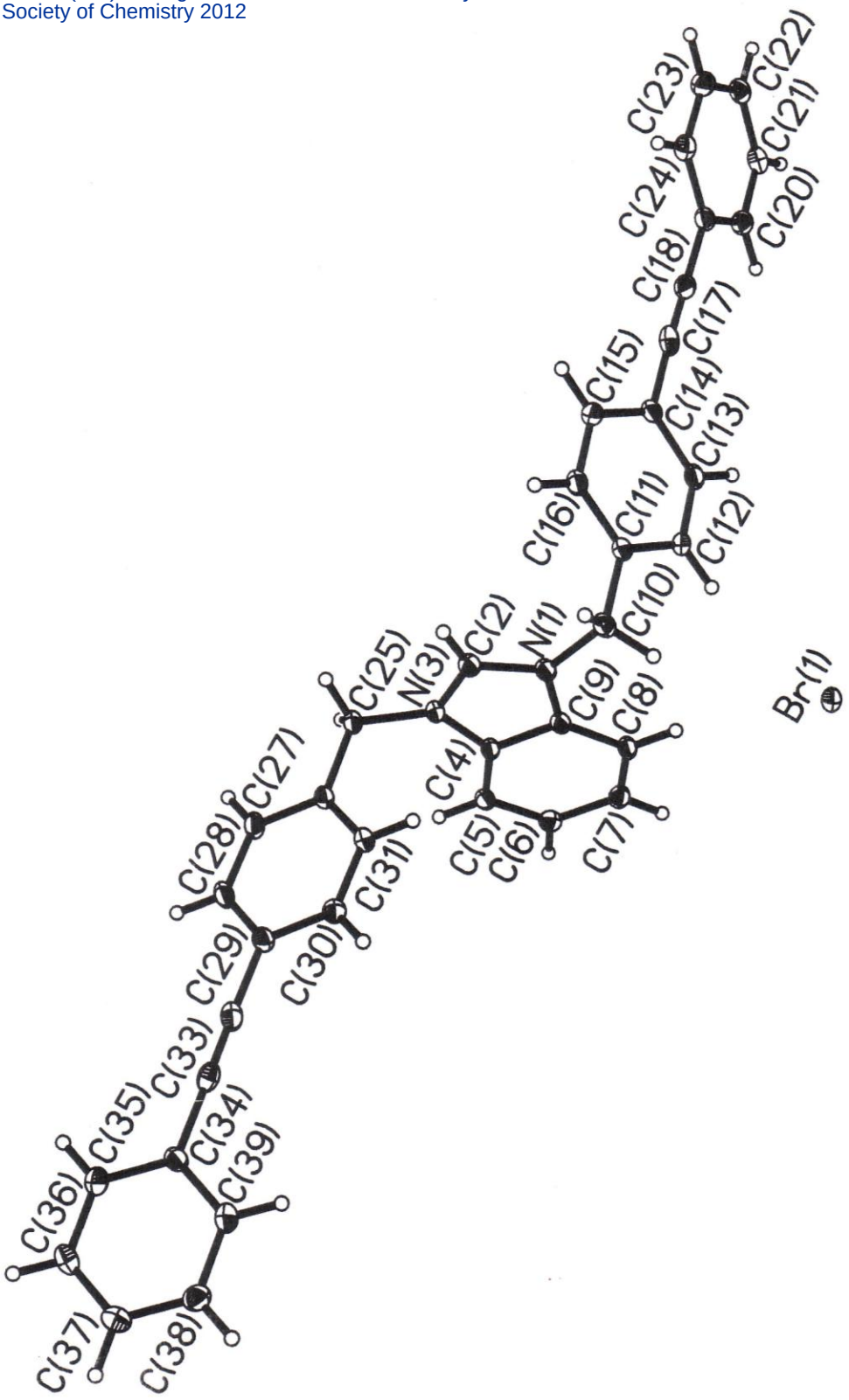
	U11	U22	U33	U23	U13	U12
Br(1)	26(1)	38(1)	32(1)	5(1)	-4(1)	-20(1)
N(1)	29(1)	30(1)	23(1)	0(1)	0(1)	-17(1)
C(2)	29(1)	30(2)	25(1)	0(1)	-2(1)	-16(1)
N(3)	25(1)	34(1)	24(1)	1(1)	0(1)	-18(1)
C(4)	25(1)	29(1)	23(1)	-3(1)	1(1)	-17(1)
C(5)	30(2)	30(2)	23(1)	-1(1)	1(1)	-18(1)
C(6)	30(2)	33(2)	26(1)	0(1)	-5(1)	-14(1)
C(7)	25(1)	35(2)	31(2)	-3(1)	-2(1)	-16(1)
C(8)	29(1)	32(2)	26(1)	-4(1)	4(1)	-20(1)
C(9)	27(1)	27(1)	22(1)	-2(1)	0(1)	-15(1)
C(10)	36(2)	31(2)	27(1)	3(1)	0(1)	-20(1)
C(11)	30(2)	30(2)	24(1)	5(1)	-3(1)	-19(1)
C(12)	30(2)	43(2)	27(1)	6(1)	-5(1)	-26(1)
C(13)	25(1)	38(2)	31(2)	8(1)	-2(1)	-17(1)
C(14)	35(2)	33(2)	24(1)	4(1)	-1(1)	-22(1)
C(15)	31(2)	34(2)	28(1)	6(1)	-8(1)	-20(1)
C(16)	26(1)	33(2)	32(2)	8(1)	-4(1)	-15(1)
C(17)	28(2)	27(2)	44(2)	8(1)	-2(1)	-16(1)
C(18)	45(2)	40(2)	37(2)	16(1)	-16(2)	-31(2)
C(19)	34(2)	32(2)	28(1)	2(1)	-1(1)	-21(1)
C(20)	32(2)	35(2)	37(2)	10(1)	-10(1)	-18(1)
C(21)	30(2)	31(2)	37(2)	4(1)	2(1)	-16(1)
C(22)	41(2)	31(2)	32(2)	1(1)	0(1)	-23(1)
C(23)	40(2)	35(2)	36(2)	4(1)	-10(1)	-21(2)
C(24)	28(2)	34(2)	36(2)	1(1)	-3(1)	-16(1)
C(25)	26(1)	34(2)	27(1)	0(1)	0(1)	-20(1)
C(26)	21(1)	32(2)	26(1)	4(1)	-2(1)	-14(1)
C(27)	30(2)	34(2)	36(2)	1(1)	0(1)	-21(1)
C(28)	31(2)	40(2)	32(2)	4(1)	3(1)	-22(1)
C(29)	22(1)	35(2)	28(1)	2(1)	-2(1)	-12(1)
C(30)	28(1)	30(2)	29(2)	1(1)	-4(1)	-15(1)
C(31)	28(1)	32(2)	26(1)	5(1)	-1(1)	-18(1)
C(32)	26(1)	38(2)	38(2)	11(1)	-6(1)	-18(1)
C(33)	21(1)	26(2)	47(2)	2(1)	-9(1)	-10(1)
C(34)	25(1)	32(2)	25(1)	2(1)	-2(1)	-12(1)
C(35)	32(2)	34(2)	38(2)	4(1)	-5(1)	-20(1)
C(36)	32(2)	35(2)	35(2)	5(1)	4(1)	-16(1)
C(37)	36(2)	33(2)	29(2)	0(1)	-2(1)	-12(1)
C(38)	33(2)	38(2)	34(2)	2(1)	-10(1)	-16(1)
C(39)	28(2)	32(2)	38(2)	8(1)	-5(1)	-16(1)

Table 5. Bond lengths [Å] and angles [°] for C37 H27 Br N2

N(1)-C(2)	1.328(4)	C(5)-C(4)-C(9)	121.7(3)
N(1)-C(9)	1.395(4)	N(3)-C(4)-C(9)	106.2(3)
N(1)-C(10)	1.480(4)	C(6)-C(5)-C(4)	116.3(3)
C(2)-N(3)	1.323(4)	C(5)-C(6)-C(7)	121.8(3)
N(3)-C(4)	1.396(4)	C(8)-C(7)-C(6)	122.1(3)
N(3)-C(25)	1.471(3)	C(7)-C(8)-C(9)	116.4(3)
C(4)-C(5)	1.390(4)	C(8)-C(9)-N(1)	132.1(3)
C(4)-C(9)	1.401(4)	C(8)-C(9)-C(4)	121.7(3)
C(5)-C(6)	1.384(4)	N(1)-C(9)-C(4)	106.2(2)
C(6)-C(7)	1.405(4)	N(1)-C(10)-C(11)	112.3(2)
C(7)-C(8)	1.376(5)	C(16)-C(11)-C(12)	119.2(3)
C(8)-C(9)	1.393(4)	C(16)-C(11)-C(10)	120.3(3)
C(10)-C(11)	1.503(4)	C(12)-C(11)-C(10)	120.5(3)
C(11)-C(16)	1.396(4)	C(13)-C(12)-C(11)	120.0(3)
C(11)-C(12)	1.396(4)	C(12)-C(13)-C(14)	121.0(3)
C(12)-C(13)	1.387(4)	C(13)-C(14)-C(15)	118.6(3)
C(13)-C(14)	1.399(4)	C(13)-C(14)-C(17)	120.4(3)
C(14)-C(15)	1.409(4)	C(15)-C(14)-C(17)	120.9(3)
C(14)-C(17)	1.464(4)	C(16)-C(15)-C(14)	120.2(3)
C(15)-C(16)	1.379(4)	C(15)-C(16)-C(11)	121.0(3)
C(17)-C(18)	1.136(5)	C(18)-C(17)-C(14)	177.6(3)
C(18)-C(19)	1.463(4)	C(17)-C(18)-C(19)	179.7(5)
C(19)-C(24)	1.404(5)	C(24)-C(19)-C(20)	118.6(3)
C(19)-C(20)	1.413(5)	C(24)-C(19)-C(18)	119.6(3)
C(20)-C(21)	1.380(5)	C(20)-C(19)-C(18)	121.7(3)
C(21)-C(22)	1.388(5)	C(21)-C(20)-C(19)	120.1(3)
C(22)-C(23)	1.404(5)	C(20)-C(21)-C(22)	120.8(3)
C(23)-C(24)	1.375(5)	C(21)-C(22)-C(23)	119.4(3)
C(25)-C(26)	1.510(4)	C(24)-C(23)-C(22)	120.3(3)
C(26)-C(31)	1.388(4)	C(23)-C(24)-C(19)	120.7(3)
C(26)-C(27)	1.401(4)	N(3)-C(25)-C(26)	112.7(2)
C(27)-C(28)	1.382(4)	C(31)-C(26)-C(27)	119.1(3)
C(28)-C(29)	1.397(4)	C(31)-C(26)-C(25)	122.4(3)
C(29)-C(30)	1.396(4)	C(27)-C(26)-C(25)	118.6(3)
C(29)-C(32)	1.458(4)	C(28)-C(27)-C(26)	120.8(3)
C(30)-C(31)	1.389(4)	C(27)-C(28)-C(29)	120.1(3)
C(32)-C(33)	1.127(5)	C(30)-C(29)-C(28)	119.1(3)
C(33)-C(34)	1.483(4)	C(30)-C(29)-C(32)	119.9(3)
C(34)-C(35)	1.401(4)	C(28)-C(29)-C(32)	121.0(3)
C(34)-C(39)	1.406(4)	C(31)-C(30)-C(29)	120.6(3)
C(35)-C(36)	1.377(5)	C(26)-C(31)-C(30)	120.3(3)
C(36)-C(37)	1.399(5)	C(33)-C(32)-C(29)	178.5(3)
C(37)-C(38)	1.398(5)	C(32)-C(33)-C(34)	177.4(3)
C(38)-C(39)	1.382(5)	C(35)-C(34)-C(39)	119.1(3)
		C(35)-C(34)-C(33)	121.1(3)
C(2)-N(1)-C(9)	108.4(2)	C(39)-C(34)-C(33)	119.8(3)
C(2)-N(1)-C(10)	125.1(3)	C(36)-C(35)-C(34)	120.1(3)
C(9)-N(1)-C(10)	126.5(2)	C(35)-C(36)-C(37)	120.7(3)
N(3)-C(2)-N(1)	110.7(3)	C(38)-C(37)-C(36)	119.6(3)
C(2)-N(3)-C(4)	108.5(2)	C(39)-C(38)-C(37)	119.8(3)
C(2)-N(3)-C(25)	125.3(3)	C(38)-C(39)-C(34)	120.7(3)
C(4)-N(3)-C(25)	126.2(2)		
C(5)-C(4)-N(3)	132.0(3)		

Table 6. Torsion angles [°] for C37 H27 Br N2.

C(9)-N(1)-C(2)-N(3)	-0.3(3)	C(25)-C(26)-C(27)-C(28)	-179.2(3)
C(10)-N(1)-C(2)-N(3)	179.8(2)	C(26)-C(27)-C(28)-C(29)	-0.2(5)
N(1)-C(2)-N(3)-C(4)	0.5(3)	C(27)-C(28)-C(29)-C(30)	0.6(5)
N(1)-C(2)-N(3)-C(25)	178.8(2)	C(27)-C(28)-C(29)-C(32)	-179.5(3)
C(2)-N(3)-C(4)-C(5)	-178.9(3)	C(28)-C(29)-C(30)-C(31)	-0.7(5)
C(25)-N(3)-C(4)-C(5)	2.9(5)	C(32)-C(29)-C(30)-C(31)	179.5(3)
C(2)-N(3)-C(4)-C(9)	-0.5(3)	C(27)-C(26)-C(31)-C(30)	0.2(5)
C(25)-N(3)-C(4)-C(9)	-178.7(2)	C(25)-C(26)-C(31)-C(30)	179.1(3)
N(3)-C(4)-C(5)-C(6)	177.0(3)	C(29)-C(30)-C(31)-C(26)	0.2(5)
C(9)-C(4)-C(5)-C(6)	-1.2(4)	C(30)-C(29)-C(32)-C(33)	-34(14)
C(4)-C(5)-C(6)-C(7)	1.3(4)	C(28)-C(29)-C(32)-C(33)	146(14)
C(5)-C(6)-C(7)-C(8)	-0.6(5)	C(29)-C(32)-C(33)-C(34)	-108(15)
C(6)-C(7)-C(8)-C(9)	-0.5(4)	C(32)-C(33)-C(34)-C(35)	-54(7)
C(7)-C(8)-C(9)-N(1)	-177.7(3)	C(32)-C(33)-C(34)-C(39)	126(7)
C(7)-C(8)-C(9)-C(4)	0.6(4)	C(39)-C(34)-C(35)-C(36)	-1.0(5)
C(2)-N(1)-C(9)-C(8)	178.5(3)	C(33)-C(34)-C(35)-C(36)	178.8(3)
C(10)-N(1)-C(9)-C(8)	-1.6(5)	C(34)-C(35)-C(36)-C(37)	0.6(5)
C(2)-N(1)-C(9)-C(4)	0.0(3)	C(35)-C(36)-C(37)-C(38)	0.6(5)
C(10)-N(1)-C(9)-C(4)	179.9(2)	C(36)-C(37)-C(38)-C(39)	-1.4(5)
C(5)-C(4)-C(9)-C(8)	0.2(4)	C(37)-C(38)-C(39)-C(34)	1.1(5)
N(3)-C(4)-C(9)-C(8)	-178.4(3)	C(35)-C(34)-C(39)-C(38)	0.1(5)
C(5)-C(4)-C(9)-N(1)	178.9(3)	C(33)-C(34)-C(39)-C(38)	-179.7(3)
N(3)-C(4)-C(9)-N(1)	0.3(3)		
C(2)-N(1)-C(10)-C(11)	-88.5(3)		
C(9)-N(1)-C(10)-C(11)	91.6(3)		
N(1)-C(10)-C(11)-C(16)	87.0(4)		
N(1)-C(10)-C(11)-C(12)	-92.1(3)		
C(16)-C(11)-C(12)-C(13)	-1.1(5)		
C(10)-C(11)-C(12)-C(13)	178.0(3)		
C(11)-C(12)-C(13)-C(14)	1.9(5)		
C(12)-C(13)-C(14)-C(15)	-1.1(5)		
C(12)-C(13)-C(14)-C(17)	176.4(3)		
C(13)-C(14)-C(15)-C(16)	-0.4(4)		
C(17)-C(14)-C(15)-C(16)	-177.9(3)		
C(14)-C(15)-C(16)-C(11)	1.2(5)		
C(12)-C(11)-C(16)-C(15)	-0.4(5)		
C(10)-C(11)-C(16)-C(15)	-179.5(3)		
C(13)-C(14)-C(17)-C(18)	-55(9)		
C(15)-C(14)-C(17)-C(18)	122(9)		
C(14)-C(17)-C(18)-C(19)	-73(81)		
C(17)-C(18)-C(19)-C(24)	-29(80)		
C(17)-C(18)-C(19)-C(20)	152(100)		
C(24)-C(19)-C(20)-C(21)	-0.5(4)		
C(18)-C(19)-C(20)-C(21)	178.6(3)		
C(19)-C(20)-C(21)-C(22)	1.7(4)		
C(20)-C(21)-C(22)-C(23)	-1.5(4)		
C(21)-C(22)-C(23)-C(24)	0.0(5)		
C(22)-C(23)-C(24)-C(19)	1.2(5)		
C(20)-C(19)-C(24)-C(23)	-1.0(4)		
C(18)-C(19)-C(24)-C(23)	179.9(3)		
C(2)-N(3)-C(25)-C(26)	-105.1(3)		
C(4)-N(3)-C(25)-C(26)	72.9(4)		
N(3)-C(25)-C(26)-C(31)	22.0(4)		
N(3)-C(25)-C(26)-C(27)	-159.1(3)		
C(31)-C(26)-C(27)-C(28)	-0.3(5)		



ORTEP view of the C37 H27 Br N2 compound with the numbering scheme adopted. Ellipsoids drawn at 30% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

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