Supporting Information

Pseudorotaxane Orientational Stereoisomerism Driven by $\pi$-Electron Density

Carmine Gaeta,* Carmen Talotta, and Placido Neri*

Dipartimento di Chimica e Biologia, Università di Salerno,
Via Giovanni Paolo II 132, I-84084 Fisciano (Salerno), Italy
E-mail: neri@unisa.it, cgaeta@unisa.it
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GENERAL COMMENTS

ESI(+)–MS measurements were performed on a triple quadrupole mass spectrometer equipped with electrospray ion source, using a mixture of H$_2$O/CH$_3$CN (1:1) and 5% HCOOH as solvent. All chemicals were reagent grade and were used without further purification. Anhydrous solvents were purchased from Aldrich. When necessary compounds were dried in vacuo over CaCl$_2$. Reaction temperatures were measured externally. Reactions were monitored by TLC on Merck silica gel plates (0.25 mm) and visualized by UV light, or by spraying with H$_2$SO$_4$–Ce(SO$_4$)$_2$.

Derivatives 1, 2+, 4a+, 11e+, and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, were synthesized according to literature procedures.¹

NMR spectra were recorded on a Bruker Avance-600 spectrometer [600 (¹H) and 150 MHz (¹³C)], Bruker Avance-400 spectrometer [400 (¹H) and 100 MHz (¹³C)], Bruker Avance-300 spectrometer [300 (¹H) and 75 MHz (¹³C)], or Bruker Avance-250 spectrometer [250 (¹H) and 63 MHz (¹³C)]; chemical shifts are reported relative to the residual solvent peak (CHCl$_3$: δ 7.26, CDCl$_3$: δ 77.23; CD$_3$OH: δ 4.87, CD$_3$OD: δ 49.0). A standard pulse program, provided by the manufacturer, was used for 2D COSY experiments.

Full geometry optimizations have been carried out with the B3LYP density functional with the standard 6-31G(d,p) basis set with the Gaussian 09 package.² All calculations included Grimme’s dispersion³ correction, present in Gaussian 09, using IOp(3/124 = 3). Single-point calculations were carried out at M06/6-31+G(d,p) level of theory. GaussianView 5.0.8W was used in the calculation of ESP at the B3LYP/6-31G(d,p) level. The input structures for ESP calculations were optimized at the B3LYP/6-31G(d,p) level of theory.

Chart S1

2⁺·TFPB⁻  3⁺·TFPB⁻  4⁺·TFPB⁻

X  

a) NO₂  a) H  
b) CN  b) Cl  
c) Me  c) OMe  
d) OMe  d) OH  
e) Me  e) Me

TFPB⁻ Anion

S3
General procedure for the synthesis of 3a-d⁺·TFPB⁻ salts

To a solution of aldehyde 5a-d (5.0 mmol) in CHCl₃ (5 mL) was added benzylamine 6 (5.0 mmol). The reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated to give the imine intermediate in quantitative yield as a yellow solid. The solid was used for the next step without further purification. The imine was dissolved in dry MeOH (50 mL) under a nitrogen atmosphere and NaBH₄ (50.0 mmol) was added at 0 °C and then the mixture was allowed to warm at room temperature. The solution was kept under stirring for 4 h. The solvent was removed under reduced pressure and the residue partitioned between AcOEt (100 mL) and a saturated aqueous solution of NaHCO₃ (100 mL). The organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure, to give secondary amine 7a-d as a yellow solid. The solid was used for the next step without further purification. The crude product was dissolved in MeOH at room temperature and an aqueous solution of HCl (37% w/w, 10 mmol) was added dropwise. The mixture was kept under stirring for 1 h, until a white precipitate was formed. The solid was collected by filtration, washed with MeOH (10 mL) and CH₃CN (10 mL), and dried under vacuum to give salt 8a-d⁺·Cl⁻ as a white solid. Derivative 8a-d⁺·Cl⁻ (2.0 mmol) was dissolved in warm dry MeOH (20 mL), then a solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (2.0 mmol) in dry MeOH (10 mL) was added. The mixture was kept under stirring overnight in the dark. The solvent was removed and deionized water was added, obtaining a brown precipitate that was filtered off and dried under vacuum to give salt 3a-d⁺·TFPB⁻.
**Derivative 8a⁺·Cl⁻**: (1.19 g, 4.3 mmol, 86%). **ESI(+) MS**: m/z = 267.2 (M⁺). **¹H NMR** (300 MHz, CD₃OD, 298 K): δ 4.03 (s, 2H, Hₐ), 4.04 (s, 2H, Hₐ), 7.45-7.52- (overlapped, 5H, Hₑ₋ₐ), 7.76 (d, J = 6Hz, 2H, Hₐ), 8.29 (d, J = 6Hz, 2H, Hₐ); **¹³C NMR** (75 MHz, CD₃OD, 298 K): δ 49.8, 51.3, 123.8, 129.1, 129.6, 129.9, 130.9, 131.2, 138.2, 148.8. Anal. Calcd for C₁₄H₁₅ClN₂O₂: C, 60.33; H, 5.42. Found: C, 60.41; H, 5.33.

**Derivative 3a⁺·TFPB⁻**: (1.97 g, 1.78 mmol, 89%). **ESI(+) MS**: m/z = 267.2 (M⁺). **¹H NMR** (400 MHz, CD₃OD, 298 K): 4.28 (s, 2H, Hₐ), 4.38 (s, 2H, Hₐ), 7.47 (overlapped, 5H, Hₑ₋ₐ), 7.58 (overlapped, 12H, ArHₜₕₕₚₛ), 7.72 (d, J = 8.4Hz, 2H, Hₐ), 8.31 (d, J = 8.4Hz, 2H, Hₐ); **¹³C NMR** (100 MHz, CD₃OD, 298 K): δ 49.7, 51.2, 117.1, 120.3, 123.0, 123.7, 125.7, 128.4, 128.9, 129.2, 129.4, 129.6, 130.8, 130.9, 134.4, 138.1, 148.6, 160.7, 161.2, 161.7, 162.2. Anal. Calcd for C₄₆H₂₇BF₂₄N₂O₂: C, 49.93; H, 2.46. Found: C, 50.02; H, 2.39.
Derivative 8b⁺·Cl⁻: (1.19 g, 4.6 mmol, 92%). ESI(+) MS: m/z = 222.6 (M⁺). ¹H NMR (300 MHz, CD₃OD, 298 K): δ 4.30-4.35 (overlapped, 4H, Hₐ,d), 7.45-7.80 (overlapped, 9H, Hₑ-g Hₐ+ Hₜ); ¹³C NMR (75 MHz, CD₃OD, 298 K): δ 49.9, 51.2, 113.3, 129.1, 129.6, 129.9, 130.8, 132.7, 136.4. Anal. Calcd for C₁₅H₁₅ClN₂: C, 69.63; H, 5.84. Found: C, 69.72; H, 5.75.

Derivative 3b⁺·TFPB⁻: (2.13 g, 1.96 mmol, 98%). ESI(+) MS: m/z = 222.6 (M⁺). ¹H NMR (400 MHz, CD₃OD, 298 K): δ 4.24 (s, 2H, Hₜ), 4.32 (s, 2H, Hₐ), 7.47 (overlapped, 5H, Hₑ-g), 7.58 (overlapped, 12H, ArTFPB), 7.64 (d, J = 9.2Hz, 2H, Hₜ), 7.82 (d, J = 9.2Hz, 2H, Hₜ); ¹³C NMR (100 MHz, CD₃OD, 298 K): δ; 51.4, 52.6, 114.6, 118.4, 118.9, 121.7, 124.4, 127.1, 129.8, 129.9, 130.3, 130.4, 130.6, 130.8, 131.0, 131.9, 132.3, 134.0, 135.8, 137.8, 162.1, 162.6, 163.1, 163.6. Anal. Calcd for C₄₇H₂₇BF₂₄N₂: C, 51.96; H, 2.50. Found: C, 52.05; H, 2.42.
Derivative 8c⁺·Cl⁻: (1.00 g, 4.05 mmol, 81%). ESI(+) MS: \( m/z = 211.7 \) (M⁺). \(^1\)H NMR (400 MHz, CD₃OD, 298 K): \( \delta \) 2.36 (s, 3H, H_d), 4.18 (s, 2H, H_e), 4.20 (s, 2H, H_a), 7.27 (d, \( J = 8\) Hz, 2H, H_c), 7.36 (d, \( J = 8\) Hz, 2H, H_b), 7.45-7.46 (overlapped, 5H, H_f-h); \(^1^3\)C NMR (63 MHz, CD₃OD, 298 K): \( \delta \) 38.3, 49.9, 50.4, 115.3, 123.9, 130.0, 130.4, 130.9, 132.3, 132.6. Anal. Calcd for C₁₅H₁₈ClN: C, 72.71; H, 7.32. Found: C, 72.80; H, 7.23.

Derivative 3c⁺·TFPB⁻: (1.85 g, 1.72 mmol, 86%). ESI(+) MS: \( m/z = 211.7 \) (M⁺). \(^1\)H NMR (250 MHz, CD₃OD, 298 K): \( \delta \) 2.34 (s, 3H, H_d), 4.16 (s, 2H, H_e), 4.19 (s, 2H, H_a), 7.28-7.36 (overlapped, 4H, H_c,b), 7.36 (overlapped, 5H, H_f-h), 7.59 (overlapped, 12H, Ar_{TFPB}⁻); \(^1^3\)C NMR (63 MHz, CD₃OD, 298 K): \( \delta \) 21.2, 51.8, 51.9, 118.5, 119.3, 123.6, 127.9, 129.4, 129.7, 130.3, 130.7, 130.9, 132.2, 132.6, 135.8, 141.0, 161.6, 162.4, 163.2, 164.0. Anal. Calcd for C₄₇H₃₆BF₂₄N: C, 52.49; H, 2.81. Found: C, 52.58; H, 2.73.
**Derivative 8d⁺·Cl⁻**: (1.10 g, 4.2 mmol, 84%). ¹H NMR (400 MHz, CD₃OD, 298 K): δ 3.80 (s, 3H, H₃), 4.18 (s, 2H, H₄), 4.21 (s, 2H, H₅), 6.98 (broad, 2H, H₆), 7.44-7.52 (overlapped, 7H, H₇+H₈); ¹³C NMR (100 MHz, CD₃OD, 298 K): δ 51.6, 51.7, 55.8, 115.5, 124.1, 130.3, 130.6, 131.1, 132.5, 132.7, 162.1. Anal. Calcd for C₁₅H₁₈ClNO: C, 68.30; H, 6.88. Found: C, 68.40; H, 6.97.

**Derivative 3d⁺·TFPB⁻**: (2.07 g, 1.90 mmol, 95%). ESI(+) MS: m/z = 227.7 (M⁺). ¹H NMR (250MHz, CD₃OD, 298 K): δ 3.66 (s, 3H, H₃), 4.20 (s, 2H, H₄), 4.22 (s, 2H, H₅), 7.48-7.63 (overlapped, 21H, H₇+H₈+ArTFPB); ¹³C NMR (63 MHz, CD₃OD, 298 K): δ 52.4, 52.5, 55.3, 119.0, 119.8, 124.1, 128.4, 130.0, 130.8, 131.2, 131.39, 131.43, 132.7, 133.1, 136.3, 141.5, 162.1, 162.9, 163.7, 164.5. Anal. Calcd for C₄₇H₃₀BF₂₄NO: C, 51.72; H, 2.77. Found: C, 51.81; H, 2.68.
**Synthesis of 4b-e⁺·TFPB⁻ salts**

A mixture of appropriate aldehyde 5c-f (2 mmol), hexamethyldisilazane (HMDS, 4 mmol), and LiClO₄ (2 mmol) was heated for 30 min at 50 °C. The reaction mixture was cooled at 0 °C and a solution of NaBH₄ (10 mmol) in methanol (5 mL) was slowly added over a period of 15 min. The reaction mixture was allowed to warm at room temperature and then stirred for 2 h. Methanol was removed under reduced pressure, the residue was quenched with a saturated aqueous solution of NaHCO₃ (50 mL) and extracted with AcOEt (50 mL). The combined organic extract was washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was dissolved in MeOH at room temperature and an aqueous solution of HCl (37% w/w, 3 mmol) was added dropwise. The mixture was kept under stirring for 15 min until a white precipitate was formed. The solid was collected by filtration, washed with MeOH (20 mL) and CH₃CN (20 mL), and dried under vacuum, to give solid salts 10b-e⁺·Cl⁻. Each salt 10b-e⁺·Cl⁻ (1.0 mmol) was dissolved in warm dry MeOH (50 mL), then a solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1.0 mmol) in dry MeOH (25 mL) was added. The mixture was kept under stirring overnight in the dark. The solvent was removed and deionized water was added, obtaining a brown precipitate that was filtered off and dried under vacuum to give salts 4b-e⁺·TFPB⁻.
Derivative $4b^{+}\cdot$TFPB$^-$: (1.05 g, 0.93 mmol, 93%). ESI(+ MS: $m/z = 265.6$ (M$^+$). $^1$H NMR (400 MHz, CD$_3$OD, 298 K): $\delta$ 4.23 (s, 4H, H$_a$), 7.48 (s, 12H, ArH$_{\text{TFPB}}$), 7.60-7.63 (overlapped, 8H, H$_{b+c}$); $^{13}$C NMR (100 MHz, CD$_3$OD, 298 K): $\delta$ 53.0, 120.0, 123.2, 126.0, 128.6, 131.3, 131.5, 131.8, 132.0, 132.1, 132.5, 132.8, 133.9, 134.2, 137.3, 138.4, 163.7, 164.2, 164.7, 165.2. Anal. Calcd for C$_{46}$H$_{26}$BCl$_2$F$_{24}$N: C, 48.88; H, 2.32. Found: C, 48.99; H, 2.23.

Derivative $10c^{+}\cdot$Cl$: (0.37 g, 1.28 mmol, 64%) ESI(+) MS: $m/z = 257.7$ (M$^+$). $^1$H NMR (600 MHz, CD$_3$OD, 298 K): 3.83 (s, 6H, H$_d$), 4.17 (s, 4H, H$_a$), 7.02 (d, $J = 7.8$Hz, 4H, H$_b$), 7.43 (d, $J = 7.8$Hz, 4H, H$_c$); $^{13}$C NMR (150 MHz, CD$_3$OD, 298 K): $\delta$ 51.3, 55.8, 115.5, 124.2, 132.6, 162.1. Anal. Calcd for C$_{16}$H$_{20}$ClNO$_2$: C, 65.41; H, 6.86. Found: C, 65.50; H, 6.78.
Derivative 4c-TFPB`: (1.02 g, 0.91 mmol, 91%). ESI(+) MS: m/z = 257.7 (M`). ¹H NMR (600 MHz, CD₃OD, 298 K): 3.82 (s, 6H, H₆), 4.15 (s, 4H, H₄), 7.02 (d, J = 9Hz, 4H, H₃), 7.39 (d, J = 9Hz, 4H, H₂), 7.61-7.63 (overlapped, 12H, ArHTFPB); ¹³C NMR (150 MHz, CD₃OD, 298 K): δ 55.5, 62.0, 116.5, 117.9, 119.8, 122.0, 123.4, 126.9, 129.4, 130.0, 130.5, 131.8, 135.2, 155.5, 161.4, 162.0, 162.8, 163.4. Anal. Calcd for C₄₈H₃₂BF₂₄NO₂: C, 51.40; H, 2.88. Found: C, 51.48; H, 2.79.

Derivative 10d⁺-Cl⁻: (0.32 g, 1.20 mmol, 60%). ESI(+) MS: m/z = 229.6 (M`). ¹H NMR (400 MHz, CD₃OD, 298 K): 4.11(s, 4H, H₄), 6.87 (d, J = 8.8Hz, 4H, H₃), 7.32 (d, J = 8.8Hz, 4H, H₂); ¹³C NMR (100 MHz, CD₃OD, 298 K): δ 51.3, 116.9, 122.9, 132.6, 159.9. Anal. Calcd for C₁₄H₁₆ClNO₂: C, 63.28; H, 6.07. Found: C, 63.35; H, 6.15.
**Derivative 4d\textsuperscript{+}-TFPB\textsuperscript{−}:** (0.96 g, 0.88 mmol, 88%). **ESI(+) MS:** $m/z = 229.6$ (M\textsuperscript{+}). **\textsuperscript{1}H NMR** (300 MHz, CD\textsubscript{3}OD, 298 K): 4.10 (s, 4H, H\textsubscript{a}), 6.87 (d, $J = 8.4$Hz, 4H, H\textsubscript{c}), 7.30 (d, $J = 8.4$ Hz, 4H, H\textsubscript{b}), 7.62 (overlapped, 12H, ArH\textsubscript{TFPB}); **\textsuperscript{13}C NMR** (75 MHz, CD\textsubscript{3}OD, 298 K): $\delta$ 51.4, 117.0, 118.4, 118.49, 118.54, 120.4, 122.8, 124.0, 127.6, 129.9, 130.24, 130.28, 130.66, 130.69, 130.73, 131.2, 132.6, 135.8, 160.0, 161.9, 162.6, 162.9, 163.2, 163.9. Anal. Calcd for C\textsubscript{46}H\textsubscript{28}BF\textsubscript{24}NO\textsubscript{2}: C, 50.53; H, 2.58. Found: C, 50.62; H, 2.49.

**Derivative 10e\textsuperscript{+}-Cl\textsuperscript{−}:** (0.46 g, 1.76 mmol, 88%). **ESI(+) MS:** $m/z = 225.7$ (M\textsuperscript{+}). **\textsuperscript{1}H NMR** (250 MHz, CD\textsubscript{3}OD, 298 K): 2.37 (s, 6H, H\textsubscript{d}), 4.17 (s, 4H, H\textsubscript{a}), 7.29 (d, $J = 7.7$Hz, 4H, H\textsubscript{b}), 7.35 (d, $J = 7.7$ Hz, 4H, H\textsubscript{c}); **\textsuperscript{13}C NMR** (63 MHz, CDCl\textsubscript{3}, 298 K): $\delta$ 19.8, 50.2, 127.9, 129.4, 129.6, 139.5. Anal. Calcd for C\textsubscript{16}H\textsubscript{20}ClN: C, 73.41; H, 7.70. Found: C, 73.50; H, 7.78.
Derivative $4e^+\cdot\text{TFPB}^-$: (1.00 g, 0.92 mmol, 92%). ESI(+) MS: $m/z = 225.7$ (M$^+$). $^1$H NMR (250 MHz, CD$_3$OD, 298 K): 2.36 (s, 6H, $H_d$), 4.14 (s, 4H, $H_a$), 7.29 (d, $J = 8.2$, 4H, $H_b$), 7.32 (d, $J = 8.2$ Hz, 4H, $H_c$), 7.59 (overlapped, 12H, ArH$^{\text{TFPB}}$); $^{13}$C NMR (75 MHz, CD$_3$OD, 298 K): δ 22.6, 53.5, 119.81, 119.86, 119.92, 121.8, 125.4, 128.9, 129.8, 131.2, 131.6, 131.65, 131.69, 132.0, 132.03, 132.07, 132.1, 132.5, 133.3, 134.3, 137.2, 141.5, 163.3, 163.9, 164.6, 165.3. Anal. Calcd for C$_{48}$H$_{32}$BF$_{24}$N: C, 52.91; H, 2.96. Found: C, 53.00; H, 2.88.
$^1$H and $^{13}$C NMR spectra of 8a-d$^+\cdot$Cl$^-$ salts

Derivative 8a$^+\cdot$Cl$^-$

Figure S1. $^1$H NMR spectrum of derivative 8a$^+\cdot$Cl$^-$ (300 MHz, CD$_3$OD, 298 K).
Figure S2. $^{13}$C NMR spectrum of derivative $8a^+\cdot Cl^-$ (75 MHz, CD$_3$OD, 298 K).
Derivative 8b⁺·Cl⁻

Figure S3. ¹H NMR spectrum of derivative 8b⁺·Cl⁻ (300 MHz, CD₃OD, 298 K).
Figure S4. $^{13}$C NMR spectrum of derivative 8b$^+\cdot$Cl$^-$ (75 MHz, CD$_3$OD, 298 K).
Figure S5. $^1$H NMR spectrum of derivative 8e•Cl$^-$ (400 MHz, CD$_3$OD, 298 K).
Figure S6. $^1$H NMR spectrum of derivative 8c·Cl$^-$ (100 MHz, CDCl$_3$, 298 K).
Figure S7. $^1$H NMR spectrum of derivative $8d^\dagger\cdot\text{Cl}^-$ (400 MHz, CD$_3$OD, 298 K).
Figure S8. $^{13}$C NMR spectrum of derivative $8d^\ast\cdot Cl^-$ (100 MHz, CD$_3$OD, 298 K).
$^1$H and $^{13}$C NMR spectra of 3a-d$^+\cdot$TFPB$^-$ salts

Derivative 3a$^+\cdot$TFPB$^-$

Figure S9. $^1$H NMR spectrum of derivate 3a$^+\cdot$TFPB$^-$ (400 MHz, CD$_3$OD, 298 K).
Figure S10. $^{13}$C NMR spectrum of derivative $3a^+\cdot$TFPB$^-$ (100 MHz, CD$_3$OD, 298 K).
Figure S11. $^1$H NMR spectrum of derivate 3b$^+\cdot$TFPB$^-$ (400 MHz, CD$_3$OD, 298 K).
Figure S12. $^{13}$C NMR spectrum of derivative $3b\cdot{\text{TFPB}}^-$ (100 MHz, CD$_3$OD, 298 K).
Derivative 3c⁺·TFPB⁻

Figure S13. ¹H NMR spectrum of derivate 3c⁺·TFPB⁻ (250 MHz, CD₃OD, 298 K).
Figure S14. $^{13}$C NMR spectrum of derivative 3c·TFPB$^-$ (63 MHz, CD$_3$OD, 298 K).
Figure S15. $^1$H NMR spectrum of derivate $3d^+\cdot$TFPB$^-$ (250 MHz, CD$_3$OD, 298 K).
Figure S16. $^{13}$C NMR spectrum of derivative $3d^{+}$·TFPB$^-$ (63 MHz, CD$_3$OD, 298 K).
$^1$H and $^{13}$C NMR spectra of 10c-e$^+$·Cl$^-$ salts

Figure S17. $^1$H NMR spectrum of derivative 10c$^+$·Cl$^-$ (600 MHz, CD$_3$OD, 298 K).
Figure S18. $^{13}$C NMR spectrum of derivative $10e^+\cdot Cl^-$ (150 MHz, CD$_3$OD, 298 K).
Figure S19. $^1$H NMR spectrum of derivative 10d$^+$-$\text{Cl}^-$ (400 MHz, CD$_3$OD, 298 K).
Figure S20. $^{13}$C NMR spectrum of derivative 10d$^+\cdot$Cl$^-$ (100 MHz, CD$_3$OD, 298 K).
Figure S21. $^1$H NMR spectrum of derivative $10e^+\cdot\text{Cl}^-$ (250 MHz, CD$_3$OD, 298 K).
Figure S22. $^{13}$C NMR spectrum of derivative $10e^+\cdot Cl^-$ (63 MHz, CD$_3$OD, 298 K).
$^1$H and $^{13}$C NMR spectra of 4b-f$^+$·TFPB$^-$ salts

Figure S23. $^1$H NMR spectrum of derivative 4b$^+$.TFPB$^-$ (400 MHz, CD$_3$OD, 298 K).

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Figure S24. $^{13}$C NMR spectrum of derivative $4b^{+}$·TFPB$^{-}$ (100 MHz, CD$_3$OD, 298 K).
Figure S25. $^1$H NMR spectrum of derivative 4c$^+\cdot$TFPB$^-$ (600 MHz, CD$_3$OD, 298 K).
Figure S26. $^{13}$C NMR spectrum of derivative 4c·TFPB$^-$ (100 MHz, CD$_3$OD, 298 K).
Figure S27. $^1$H NMR spectrum of derivative 4d$^\text{+}$·TFPB$^\text{−}$ (300 MHz, CD$_3$OD, 298 K).
Figure S28. $^{13}$C NMR spectrum of derivative $4d^+ \cdot \text{TFPB}^-$ (75 MHz, CD$_3$OD, 298 K).
Figure S29. $^1$H NMR spectrum of derivative 4e$^+\cdot$TFPB$^-$ (250 MHz, CD$_3$OD, 298 K).
Figure S30. $^{13}$C NMR spectrum of derivative $4e^+\cdot$TFPB$^-$ (75 MHz, CD$_3$OD, 298 K).
Preparation of pseudorotaxanes 6a-e$^+$ and 7a-d$^+$

Calixarene derivative 1 (2.0·10$^{-3}$ mmol) was dissolved in 0.4 mL of CDCl$_3$ (5.0·10$^{-3}$ M solution), then tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salt 3a-d$^+$ or 4a-e$^+$ (2.0·10$^{-3}$ mmol, 5·10$^{-3}$ M) was added and the mixture was stirred for 15 min at 40 °C. After cooling, the solution was transferred in a NMR tube for 1D and 2D NMR spectra acquisition.

Determination of pseudorotaxane $K_{ass}$ values by quantitative NMR analysis

Each sample was prepared by dissolving 1 (2.45 × 10$^{-3}$ mmol) and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salt 3a-d$^+$ or 4a-e$^+$ (2.45 × 10$^{-3}$ mmol) in CDCl$_3$ (0.4 mL) containing 2 μL of 1,1,2,2-tetrachloroethane (d = 1.59 g/mL) as internal standard. The complex concentration [complex] was evaluated by integration of the $^1$H NMR signal of CHCl$_2$CHCl$_2$ vs the ArCH$_2$Ar signals of the complex. The following equation was used to obtain the moles of the complex:

$$\frac{G_a}{G_b} = \frac{F_a}{F_b} \times \frac{N_a}{N_b} \times \frac{M_a}{M_b}$$

where

- $G_a$ = grams of 1,1,2,2-tetrachloroethane;
- $G_b$ = grams of complex
- $F_a$ and $F_b$ = areas of the signals of 1,1,2,2-tetrachloroethane and ArCH$_2$Ar signal of the complex.
- $N_a$ and $N_b$ = numbers of nuclei which cause the signals ($N_a$ for 1,1,2,2-tetrachloroethane; $N_b$ for complex)
- $M_a$ and $M_b$ = molecular masses of 1,1,2,2-tetrachloroethane (a) and complex (b)
$^1$H NMR spectrum of pseudorotaxane $6b^+ \cdot$TPFB$^-$

Figure S31. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar solution of $4b^+ \cdot$TPFB$^-$ and 1 (5.0·10$^{-3}$ M).
$^1$H NMR spectrum of pseudorotaxane 6c$^+$·TFPB$^-$

Figure S32. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar solution of 4c$^+$·TFPB$^-$ and 1 (5.0·10$^{-3}$ M).
Figure S33. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar solution of 4d$^+$ and 1 (5.0·$10^{-3}$ M).
**1H NMR spectrum of pseudorotaxane 6e⁺·TFPB⁻**

![Diagram of 1H NMR spectrum of pseudorotaxane 6e⁺·TFPB⁻](image)

**Figure S34.** 1H NMR spectrum (400 MHz, CDCl₃, 298 K) of an equimolar solution of 4e⁺ and 1 (5.0·10⁻³ M).
2D COSY spectrum of an equimolar mixture of 1 and 3a$^{+}$

Figure S35. 2D COSY-45 spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar mixture of 3a$^{+}$·TFPB$^-$ and 1 (5.0×10$^{-3}$ M).
2D COSY spectrum of an equimolar mixture of 1 and 3b$^+$

Figure S36. Portion of 2D COSY-45 spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar mixture of 3b$^+$·TFPB$^-$ and 1 (5.0×10$^{-3}$ M).
2D COSY spectrum of an equimolar mixture of 1 and 3c⁺

Figure S37. Portion of 2D COSY-45 spectrum (400 MHz, CDCl₃, 298 K) of an equimolar mixture of 3c⁺·TFPB⁻ and 1 (5.0×10⁻³ M).
2D COSY spectrum of an equimolar mixture of 1 and 3d$^+$

Figure S38. Portion of 2D COSY-45 spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar mixture of 3d$^+\cdot$TFPB$^-$ and 1 (5.0×10$^{-3}$ M).
Hammett-type plot

Figure S39. Hammett correlations between $\log \left( \frac{K_a(6b-e)}{K_a(6a)} \right)$ and $\sigma$. 

Linear Regression: $Y = A + B \times X$

<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
<th>Error</th>
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</thead>
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<td>0.04475</td>
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<tr>
<td>B</td>
<td>2.56956</td>
<td>0.19723</td>
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Details of the optimized structure of *endo*-p-NO$_2$-benzyl-7a$^+$ complex

![Diagram of the optimized structure of endo-p-NO$_2$-benzyl-7a$^+$ complex](image)

**Figure S40.** (Left) Details of the optimized structure of *endo*-p-NO$_2$-benzyl-7a$^+$ complex at the B3LYP/6-31G(d,p) level of theory, indicating the N$^+$···O$_\text{calix}$ and *NH$_2$C-H···centroids$_\text{calix}$ distances (Å). (Right) Particular showing C-H···π interactions between methylene PhCH$_2$NH$_2CH_2$Ph-NO$_2$ hydrogen atoms of 3a$^+$ (in green) and two anisole rings of 1.
Details of the optimized structure of *endo*-benzyl-7a⁺ complex

**Figure S41.** Side view of the optimized structures of the *endo*-benzyl-7a⁺ complex at the B3LYP/6-31G(d,p) level of theory. A mixed CPK/wireframe representation was used for clarity.
Figure S42. (Left) Details of the optimized structure of the *endo*-benzyl-7a$^+$ complex at the B3LYP/6-31G(d,p) level of theory, indicating the N$^+$···O$^{calix}$ and NH$_2$C-H···centroids$^{calix}$ distances (Å). (Right) Particular showing C-H···π interactions between methylene PhCH$_2^+$NH$_2$CH$_2$Ph-\textit{p}-NO$_2$ hydrogen atoms of 3a$^+$ (in green) and two anisole rings of 1.
**1H NMR titration of hexamethoxy-\(p\)-NO\(_2\)-calix[6]arene with 4a\(^{+}\)•TFPB\(^{-}\)**

**Figure S43.** Significant portion of the \(^1\)H NMR spectra (400 MHz, CDCl\(_3\), 298 K) of: (bottom) hexamethoxy-\(p\)-NO\(_2\)-calix[6]arene; (top) 1:1 mixture of hexamethoxy-\(p\)-NO\(_2\)-calix[6]arene and 4a\(^{+}\)•TFPB\(^{-}\).