Supporting Information


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# Table of Contents

General Remarks and Materials .................................................. 2  
Synthesis and Characterisation of F ........................................ 3  
Synthesis and Characterisation of H ........................................ 10  
Guttman-Beckett Plot ............................................................... 13  
NMR Characterisation of $\text{P}[F(pC)\supset\text{DOV}]_2\text{OTs}$ ........ 14  
Spectrophotometric Titration of $\text{P}[F(pC)\supset\text{DOV}]_2\text{OTs}$ ... 17  
NMR Characterisation of $\text{P}[F(C)\supset\text{DOV}]_2\text{I}$ ............... 18  
Competition Studies ................................................................. 21  
NMR Spectra of Compounds 3 ..................................................... 23  
References ................................................................................. 38
• **General Remarks and Materials**

All chemicals those syntheses are not reported hereafter were purchased from commercial sources and used as received. Solvents were dried and stored over molecular sieves previously activated in an oven (450 °C overnight). Column chromatography was performed on silica gel 60 (70-230 mesh). NMR spectra were recorded on a Bruker 400 MHz and JEOL 600 MHz using solvents as internal standards (7.26 ppm for $^1$H NMR and 77.00 ppm for $^{13}$C-NMR for CDCl$_3$). The terms m, s, d, t, q and quint represent multiplet, singlet, doublet, triplet, quadruplet and quintuplet respectively, and the term br means a broad signal. Exact masses were recorded on a LTQ ORBITRAP XL Thermo Mass Spectrometer (ESI source). Spectrophotometric titration (air-equilibrated CH$_2$Cl$_2$, room temperature) were performed with a JASCO V-750 UV-visible spectrophotomer by adding small aliquots (typically 10 μL) of a concentrated solution of calixarene TSA F to a dilute solution of dioctyliovologen salt. The titration curves were fitted according to a 1:1 association model by using the SPECFIT/32 software.¹ TSA calixarenes A-G and sulfonamide H were synthesized according to a known procedure.²⁻⁴ Nitroalkenes 1 were purchased from commercially available sources or synthesized following common routes.⁵
Synthesis and Characterisation of F

In a two-necked round bottomed flask, under N₂ atmosphere, Pd/C (10 mol %) was added to a suspension of A (395 mg, 0.3 mmol) in EtOH (100 ml). Subsequently, NH₂NH₂•H₂O (6 mmol, 20 eq.) was added dropwise and the reaction placed in an oil-bath where it was refluxed at 100 °C for 24 hs. After completion determined by TLC analysis, the reaction was cooled down to room temperature, and then filtered through a Celite pad to remove the Pd/C catalyst. The mixture was concentrated at reduced pressure and water (30 ml) was added. After extraction with CH₂Cl₂ (3 x 30 ml), organic phases were dried over Na₂SO₄ and concentrated at reduced pressure to afford a pale yellow solid. The crude was dissolved with dry CH₂Cl₂ (15 ml) under N₂ atmosphere and TEA (1.2 mmol, 4.0 eq.) was added. Subsequently, the mixture was cooled down at -78 °C and trifluoromethanesulfonic anhydride (1.0 mmol, 3.5 eq.) was added as a CH₂Cl₂ solution (5 ml) over 30 mins. The reaction was stirred for 4 hs. After completion, H₂O (20 ml) was added and the mixture extracted with CH₂Cl₂ (3 x 30 ml). The organic layers were dried over Na₂SO₄, concentrated at reduced pressure and the crude purified by column chromatography on silica gel (n-Hex/AcOEt: 80:20) yielding TSA F (345 mg, 71%) as a white solid. M. p. = 100-103 °C. ¹H NMR pseudo cone conformer (400 MHz, CDCl₃) δ = 7.28 (s, 6H), 6.90 (s, 3H, NH), 4.49 (d, J = 15.3 Hz, 6H), 3.92 (t, J = 6.5 Hz, 6H), 3.49 (d, J = 15.5 Hz, 6H), 2.51 (bs, 9H), 1.95 – 1.83 (m, 6H), 1.62 – 1.51 (m, 6H), 1.38 – 1.28 (m, 24H), 1.35 (d, J = 20.9 Hz, 4H), 0.99 – 0.86 (m, 9H). ¹³C NMR pseudo cone conformer (101 MHz, CDCl₃) δ = 154.4 (C₆), 153.9 (C₆), 146.9 (C₆), 136.5 (C₆), 132.5 (C₆), 128.4 (C₆), 128.1 (CH), 123.3 (CH), 119.5 (q, JCF =322 Hz, C₆), 73.4 (CH₂), 60.1 (CH₃), 34.2 (C₆), 31.9 (CH₃), 31.5 (CH₃), 30.4 (CH₃), 30.2 (CH₃), 29.6 (CH₃), 29.3 (CH₃), 26.2 (CH₃), 22.7 (CH₃), 14.1 (CH₃). ¹⁹F NMR (565 MHz, CDCl₃) δ = -75.20. HR-MS (ESI) m/z: [M+NH₄⁺]⁺ calcd. for C₈₄H₁₁₈F₉N₄O₁₂S₃: 1641.77647; found 1641.77625.
TSA F ($^1$H-NMR, 400 MHz, CDCl$_3$)

TSA F (DEPT, 100 MHz, CDCl$_3$)
TSA F ($^{19}$F-NMR, 576 MHz, CDCl$_3$)

TSA F (HSQC, 400, 100 MHz, CDCl$_3$)
Figure S1. (Top) HR-MS (TOF) spectrum of TSA F, and (Down) expansion showing its isotopical pattern.
**Figure S2.** 1D-ROESY spectra of TSA F recorded with selective irradiation of axial methylene protons of “distorted” cone conformation at 4.12 (blue spectrum) and OCH$_3$ signal of pseudo-cone conformation at 2.51 (green spectrum) ppm. Their interchanges are highlighted with blue and green dotted line respectively, showing a slow exchange at the NMR time scale of the two conformers.
Figure S3. $^1$H-NMR spectra of a 0.04 M solution of TSA F in CDCl$_3$ (top). To this solution sequential additions of CD$_3$OD were carried out to evaluate the interchange of distorted pseudo cone and pseudo cone conformers.
Synthesis and Characterisation of H

In a two-necked round bottomed flask, under N₂ atmosphere, Pd/C (10 mol %) was added to a suspension of 1-nitro-4-(octyloxy)benzene[4] (502 mg, 2.0 mmol) in EtOH (100 ml). Subsequently, NH₂NH₂•H₂O (20.0 mmol, 10 eq.) was added dropwise and the reaction placed in an oil-bath where it was refluxed at 100 °C for 4 hrs. After completion determined by TLC analysis, the reaction was cooled-down to room temperature, and then filtered through a Celite pad to remove the Pd/C catalyst. The mixture was concentrated at reduced pressure and water (30 ml) was added. After extraction with CH₂Cl₂ (3 x 30 ml), organic phases were dried over Na₂SO₄ and concentrated at reduced pressure to afford a pale yellow solid. The crude was dissolved with dry CH₂Cl₂ (50 ml) under N₂ atmosphere and TEA (4.0 mmol, 2.0 eq.) was added. Subsequently, the mixture was cooled down at -78 °C and trifluoromethanesulfonic anhydride (3.0 mmol, 1.5 eq.) was added as a CH₂Cl₂ solution (15 ml) over 30 mins. The reaction was stirred for 2 hrs. After completion, H₂O (50 ml) was added and the mixture extracted with CH₂Cl₂ (3 x 50 ml). The organic layers were dried over Na₂SO₄, concentrated at reduced pressure and the crude purified by column chromatography on silica gel (n-Hex/AcOEt: 80:20) yielding H (562 mg, 80%) as a pale yellow solid. M. p. = 42-45 °C. ¹H NMR (400 MHz, CDCl₃) δ = 7.28 – 7.19 (m, 2H), 6.93 – 6.89 (m, 2H), 6.88 (bs, 1H), 3.97 (t, J = 6.5 Hz, 2H), 1.80 (dt, J = 14.5, 6.6 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.41 – 1.24 (m, 8H), 0.98 – 0.86 (m, 3H). ¹³C NMR (600MHz, CDCl₃) δ = 159.2 (Cₘ), 127.3 (CH), 125.5 (Cₛ), 120.0 (q, J_C-F = 323 Hz, Cₙ), 115.4 (CH), 68.5 (CH₂), 31.9 (CH₃), 29.4 (CH₃), 29.3 (CH₂), 29.2 (CH₂), 26.1 (CH₂), 22.7 (CH₃), 14.1 (CH₃). ¹⁹F NMR (565 MHz, CDCl₃) δ = -75.00. HR-MS (ESI) m/z: [M+H]+ calcd. for C₁₅H₂₃F₃NO₃S: 354.1351; found 353.1348.
(565 MHz, CDCl₃)
**Guttman-Beckett Plot**

*Figure S4.* Titration Results for a Series of Trisulfonamides (TSA A-F) and monomeric trifluoromethyl-analogue H with Et₃PO (5mM in C₆D₆) monitored by ³¹P NMR.

From a stock solution of TEPO (5mM in C₆D₆), 400 μl were taken out and added to an NMR tube containing 0.006 mmol of the corresponding analyte (3 equiv). The tube was subsequently analyzed by ³¹P NMR.

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NMR Characterisation of P[F(pC)⇒DOV]2OTs

Figure S5. Expanded region of 2D ROESY-NMR (CDCl₃, 400 MHz, spin-lock = 200 ms) spectrum of P[F(pC)⇒DOV]2OTs showing key ROE contacts between:

- The aromatic CH β of TSA F and OMe S (red)
- The aromatic CH α of TSA F and H₄ (green)
- The aromatic CH δ of TSA F and H₆ (purple)
- The aromatic CH ε of TSA F and H₈ (blue)
- The aromatic CH ε* of DOV with t-Bu (black)
$\text{P[F(pC) }} \supset \text{ DOV}2\text{OTs}$

($^1\text{H-NMR, 400 MHz, CDCl}_3$)

$\text{P[F(pC) }} \supset \text{ DOV}2\text{OTs}$

($\text{HSQC, 400, 100 MHz, CDCl}_3$)
Spectrophotometric Titration of P[F(pC)−DOV]2OTs

![Graph showing the relationship between H/G and Absorbance (270 nm)].
- **NMR Characterisation of P[F(C)→DOV]2I**

**Figure S6.** Expanded region of 2D ROESY-NMR (CDCl$_3$, 400 MHz, spin-lock = 200 ms) spectrum of P[F(C)→DOV]2I showing key ROE contact between the aromatic CH e* of DOV and OMe (red)
$\text{P}[\text{F(C) } \supset \text{ DOV}]_2I$

($^1\text{H-NMR, 400 MHz, CDCl}_3$)

$\text{P}[\text{F(C) } \supset \text{ DOV}]_2I$

($\text{HSQC, 400, 100 MHz, CDCl}_3$)
• Competition Studies

**Figure S7.** Experiment in the presence of a competitive binder (DOV•2OTs).

In a glass tube, \(1a\) (17.9 mg, 0.1 mmol), \(2a\) (35.1 mg, 0.3 mmol), \(F\) (8.2 mg, 5 mol %) and DOV•2OTs (6.5 mg, 10 mol %) were subsequently added. Distilled H\(_2\)O (0.25 ml, 0.4 M) was added and the reaction placed in a pre-heated oil bath at 37°C. After 16 hs CH\(_2\)Cl\(_2\) (10 ml) was added and the mixture passed through a short pad of silica. The mixture was concentrated under reduced pressure and the crude analysed by \(^1\)H-NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard (13.2 mg).
Figure S8. Tentative complexation of nitrostyrene 1a with TSA F

$^1$H-NMR (CDCl$_3$, 400 MHz) of a) nitrostyrene 1a; b) 1:1.5 mixture of TSA F and nitrostyrene 1a.
• NMR Spectra of H and Compounds 3

3aa (CD$_2$Cl$_2$, 400 MHz)

3aa (CD$_2$Cl$_2$, 101 MHz)
3ba (CD$_2$Cl$_2$, 400 MHz)

3ba (CD$_2$Cl$_2$, 101 MHz)
$3ca \ (CD_2Cl_2, \ 400 \ MHz)$

$3ca \ (CD_2Cl_2, \ 150 \ MHz)$
3fa (CD$_2$Cl$_2$, 400 MHz)

3fa (CD$_2$Cl$_2$, 101 MHz)
3ga (CD$_2$Cl$_2$, 400 MHz)

3ga (CD$_2$Cl$_2$, 100 MHz)
$3\text{ha (CD}_2\text{Cl}_2, 400 \text{ MHz)}$

$3\text{ha (CD}_2\text{Cl}_2, 100 \text{ MHz)}$
3bd (CD$_2$Cl$_2$, 400 MHz)

3bd (CD$_2$Cl$_2$, 101 MHz)
3be (CD$_2$Cl$_2$, 400 MHz)

3be (CD$_2$Cl$_2$, 101 MHz)
3ag (CD$_2$Cl$_2$, 400 MHz)
• References


