

Supporting Information for

[2]Pseudorotaxane formation between rigid Y-shaped 2,4,5-triphenylimidazolium axles and [24]crown-8 ether wheels

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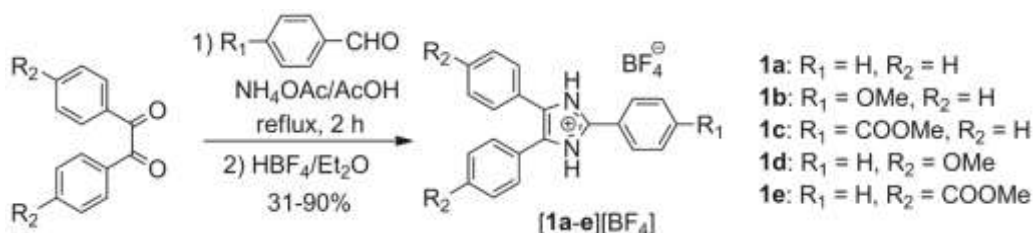
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General Comments

4,4'-Bis(methyloxycarbonyl)benzil was synthesized according to literature procedures.^[S1] All association constant (K_a) values were determined using the single point method.^[S2] All chemicals were obtained from Sigma-Aldrich and used without further purification. The solvents were dried using an Innovative Technologies Solvent Purification System. ^1H , ^{13}C and 2D NMR spectra were recorded on a Bruker Avance 500 instrument. High resolution mass spectra (HR-MS) were performed on a Micromass LCT electrospray ionization (ESI) time-of-flight (ToF) spectrometer. Melting points were recorded on a Stanford Research Systems, Opti Melt MPA100 instrument. FT-IR spectra ($4000 - 400\text{ cm}^{-1}$) were measured as thin films on a Bruker Alpha FT-IR instrument equipped with a Platinum single reflection diamond ATR module. The single crystal X-ray data were collected on a Bruker D8 Venture dual source diffractometer with a Photon 100 detector operated at 50 kV and 30 mA using $\text{CuK}\alpha$ radiation. Crystallographic data for the X-ray structure have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 990746. Copies of the data can be obtained free of charge on application to CCDC at email: deposit@ccdc.cam.ac.uk.

Experimental procedure:

Procedure for the Synthesis of 2,4,5-triphenylimidazolium salts [1a-1e][BF₄].



The corresponding 4,4' substituted benzil (2.38 mmol, 1 eq.), *p*-substituted benzaldehyde (2.83 mmol, 1 eq.) and ammonium acetate (35.7 mmol, 15 eq.) were dissolved in acetic acid (9 mL). The reaction mixture was heated to 100 °C and stirred for 2 h. It was then cooled and neutralized with NH₄OAc and water (4 mL). The resulting solid was filtered, washed with water and dried under vacuum. The pure 2,4,5-triphenylimidazole was dissolved in a minimum

amount of THF (7 mL) and tetrafluoroboric acid - diethyl ether complex (2.38 mmol, 1 eq.) was added. The mixture was stirred for 10 min and of diethyl ether (10 mL) was added. The resulting solid precipitated from solution and was collected by filtration, washed with ether and air dried.

[1a][BF₄]: (R₁ = R₂ = H, Yield 88 %): MP 172-174 °C (dec). ¹H NMR (CD₃NO₂, 500 MHz, 293 K): δ (ppm) = 12.51 (s, 2H), 8.05 (d, 2H, *J* = 7.0 Hz) 7.75-7.68 (m, 3H), 7.58 (d, 4H, *J* = 7.5 Hz), 7.52-7.47 (m, 6H); ¹³C NMR (CD₃CN, 125 MHz, 294 K): δ (ppm) = 140.5, 128.7, 125.9, 125.8, 125.7, 125.1, 124.3, 122.9, 122.7, 118.6; IR (neat) = 3209, 1647, 1598, 1491, 1467, 1445, 1324, 1280, 1201, 996, 776, 764, 695, 597, 517, 502 cm⁻¹; HR-MS (ESI-ToF) *m/z* found: 297.1404 [M+H]⁺, [C₂₁H₁₇N₂]⁺, calc: 297.1392.

[1b][BF₄]: (R₁ = OMe, R₂ = H, Yield 89 %): MP 260-264 °C (dec). ¹H NMR (CD₃NO₂, 500 MHz, 294 K): δ (ppm) = 12.32 (s, 2H), 8.01 (d, 2H, *J* = 9.0 Hz), 7.56 (d, 4H, *J* = 7.5 Hz), 7.51-7.46 (m, 6H), 7.20 (d, 2H, *J*=9.0 Hz), 3.91 (s, 3H); ¹³C NMR (CD₃NO₂, 125 MHz, 295 K): δ (ppm) = 159.6, 140.6, 126.1, 125.2, 124.9, 124.8, 124.3, 122.5, 111.2, 109.9, 51.2; IR (neat): 3303, 1645, 1610, 1506, 1443, 1303, 1266, 1189, 1026, 989, 958, 834, 770, 735, 692, 511 cm⁻¹; HR-MS (ESI-ToF) *m/z* found: 327.1496 [M+H]⁺, [C₂₂H₁₉N₂O]⁺, calc: 327.1497.

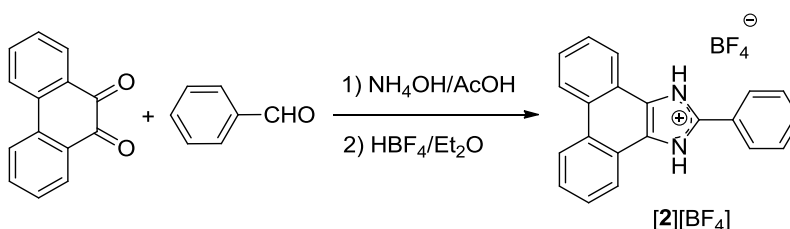
[1c][BF₄]: (R₁ = COOMe, R₂ = H, Yield 95 %): MP 272-275 °C (dec). ¹H NMR (CD₃NO₂, 500 MHz, 295 K): δ (ppm) = 12.97 (s, 2H), 8.26 (d, 2H, *J* = 8.5 Hz), 8.16 (d, 2H, *J* = 8.5 Hz), 7.59(d, 4H, *J* = 8.0 Hz), 7.54-7.47 (m, 6H), 3.94 (s, 3H). ¹³C NMR (CD₃NO₂, 125 MHz, 295 K): δ (ppm) = 161.8, 139.2, 129.9, 126.4, 126.3, 126.1, 125.2, 124.4, 123.1, 122.2, 121.7, 48.0; IR (neat) = 3275, 1720, 1651, 1430, 1277, 1015, 862, 765, 722, 699, 520 cm⁻¹; HR-MS *m/z* found: 355.1453 [M+H]⁺, [C₂₃H₁₉N₂O₂]⁺, calc: 355.1447.

[1d][BF₄]: (R₁ = H, R₂ = OMe, Yield 85 %): MP 255-258 °C (dec). ¹H NMR (CD₃NO₂, 500 MHz, 294 K): δ (ppm) 12.19 (s, 2H), 8.01 (d, 2H, *J* = 7.0 Hz), 7.73-7.66 (m, 3H), 7.50 (d, 4H, *J* = 9.0 Hz), 7.02 (d, 4H, *J* = 9.0 Hz), 3.84 (s, 6H); ¹³C NMR (CD₃NO₂, 125 MHz, 295 K): δ (ppm) = 157.0, 139.7, 128.9, 125.8 (2 peaks), 124.8, 122.8, 118.0, 114.6, 110.5, 50.8; IR "(neat) = 3238, 1648, 1613,

1503, 1301, 1254, 1182, 1031, 836, 804, 777, 701, 689, 584, 533, 500, 417 cm^{-1} ; HR-MS (ESI-ToF) m/z found: 357.1604 $[\text{M}+\text{H}]^+$, $[\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_2]^+$, calc: 357.1603.

[1e][BF₄]: ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{COOMe}$, Yield 31 %): MP 285-289 °C (dec). ¹H NMR (CD_3NO_2 , 500 MHz, 295 K): δ (ppm) = 12.86 (s, 2H), 8.09-8.06 (m, 6H), 7.77-7.69 (m, 7H), 3.91 (s, 6H); ¹³C NMR (DMSO, 125 MHz, 294 K): δ (ppm) = 165.9, 145.3, 132.3, 132.2, 130.4, 130.0, 129.7, 129.6, 129.2, 127.6, 123.8, 52.6; IR (neat) = 3197, 2953, 1714, 1645, 1611, 1436, 1279, 1196, 1113, 1059, 987, 955, 863, 777, 721, 702, 684 cm^{-1} ; HR-MS (ESI-ToF) m/z found: 413.1521 $[\text{M}+\text{H}]^+$, $[\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_4]^+$, calc: 413.1501.

2-Phenyl-1H-phenanthro[9,10-d]imidazolium salt [2][BF₄]:



The procedure for **[2][BF₄]** is the same as described above for **[1a][BF₄]** but uses 9,10-phenanthrenequinone (1.50 g, 7.20 mmol) as the starting material. It should be noted that 2-phenyl-1H-phenanthro[9,10-d]imidazole and its corresponding imidazolium salt are known compounds previously prepared by a different method.^[S3] Our spectroscopic characterization was consistent with the original published data for the charged **[2]⁺** species in solution. However, the tetrafluoroborate salt **[2][BF₄]** is a new compound. The crude product was recrystallized from nitromethane. Yield: 2.10 g, 76%, MP 253-256 °C. ¹H NMR (CD_3CN , 500 MHz, 293 K): δ (ppm) = 13.04 (s, 2H), 8.85 (d, 2H, $J = 8.0$ Hz), 8.40 (d, 2H, $J = 7.5$ Hz), 8.19 (d, 2H, $J = 7.5$ Hz), 7.85-7.78 (m, 7H). ¹³C NMR (CD_3CN , 125 MHz, 294 K): δ (ppm) = 147.6, 134.5, 130.9, 129.7, 129.3, 129.0, 128.8, 126.9, 124.9, 123.0, 122.7, 120.5; IR (neat) = 3245, 1654, 1562, 1462, 995, 956, 754, 721, 697, 614, 517, 484, 426 cm^{-1} . HR-MS (ESI-ToF) m/z found: 295.1239 $[\text{M}+\text{H}]^+$, $[\text{C}_{21}\text{H}_{16}\text{N}_2]^+$, calc = 295.1235.

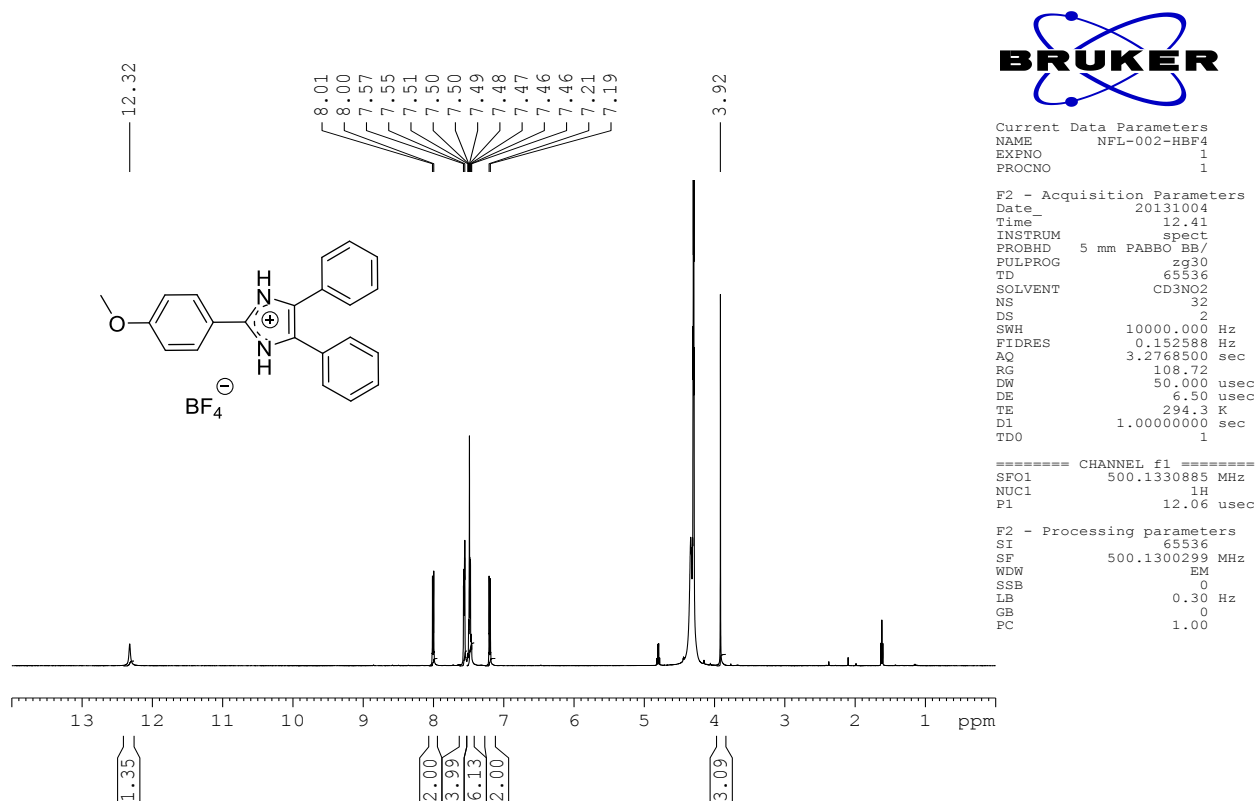


Figure S3. ¹H NMR spectrum of [1b][BF₄] in CD₃NO₂.

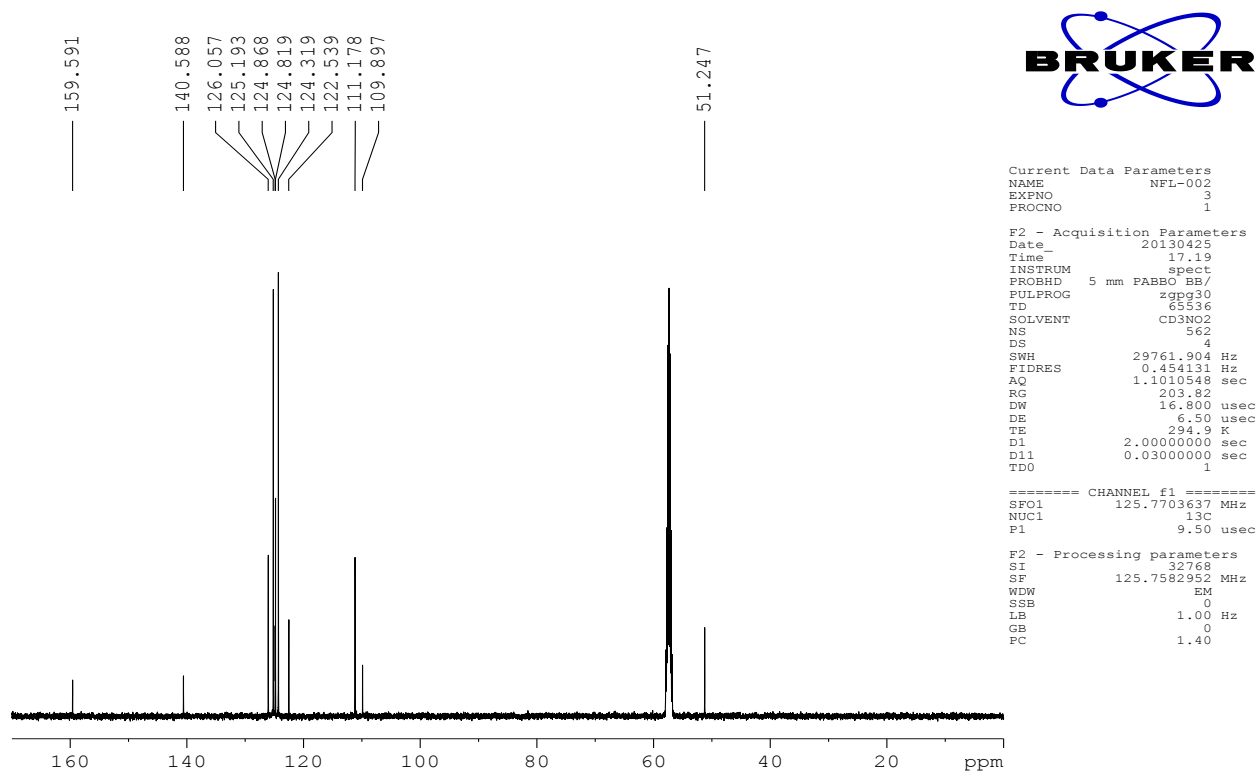


Figure S4. ¹³C NMR spectrum of [1b][BF₄] in CD₃NO₂.

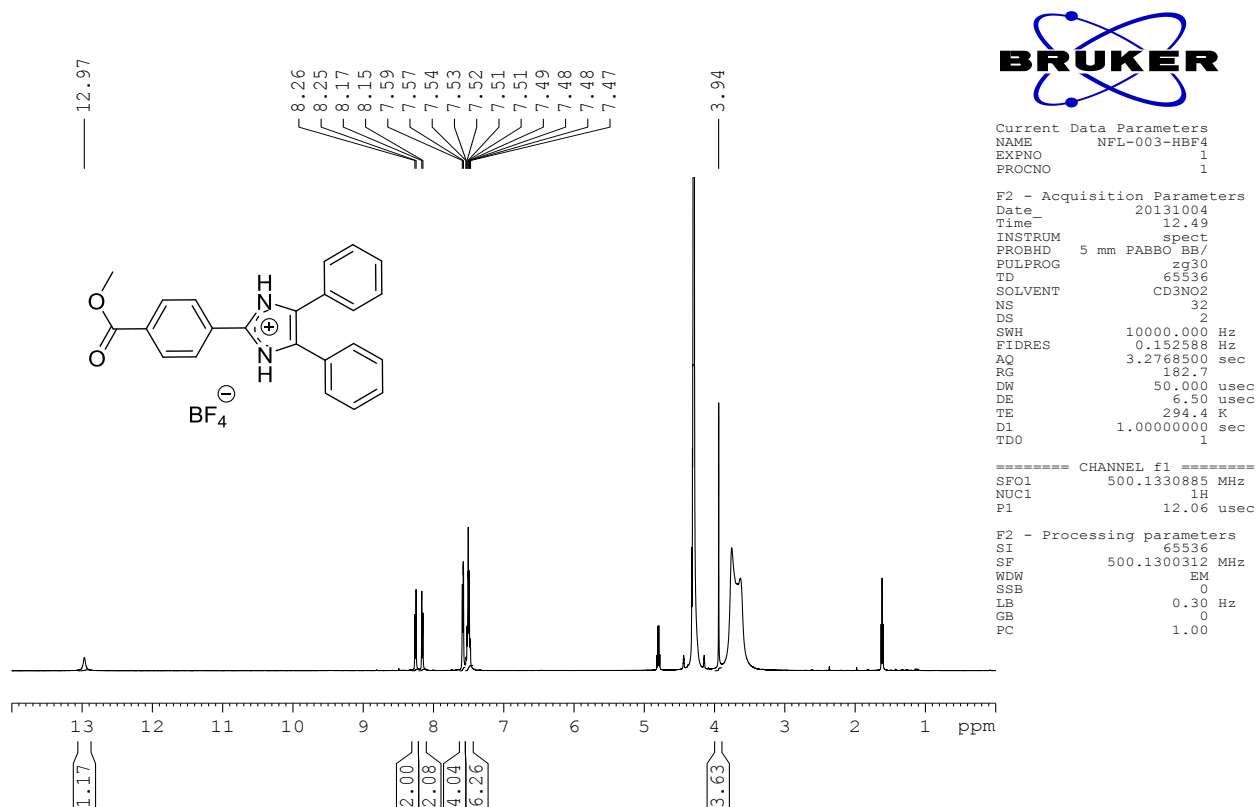


Figure S5. ^1H NMR spectrum of $[1\text{c}][\text{BF}_4]$ in CD_3NO_2 .

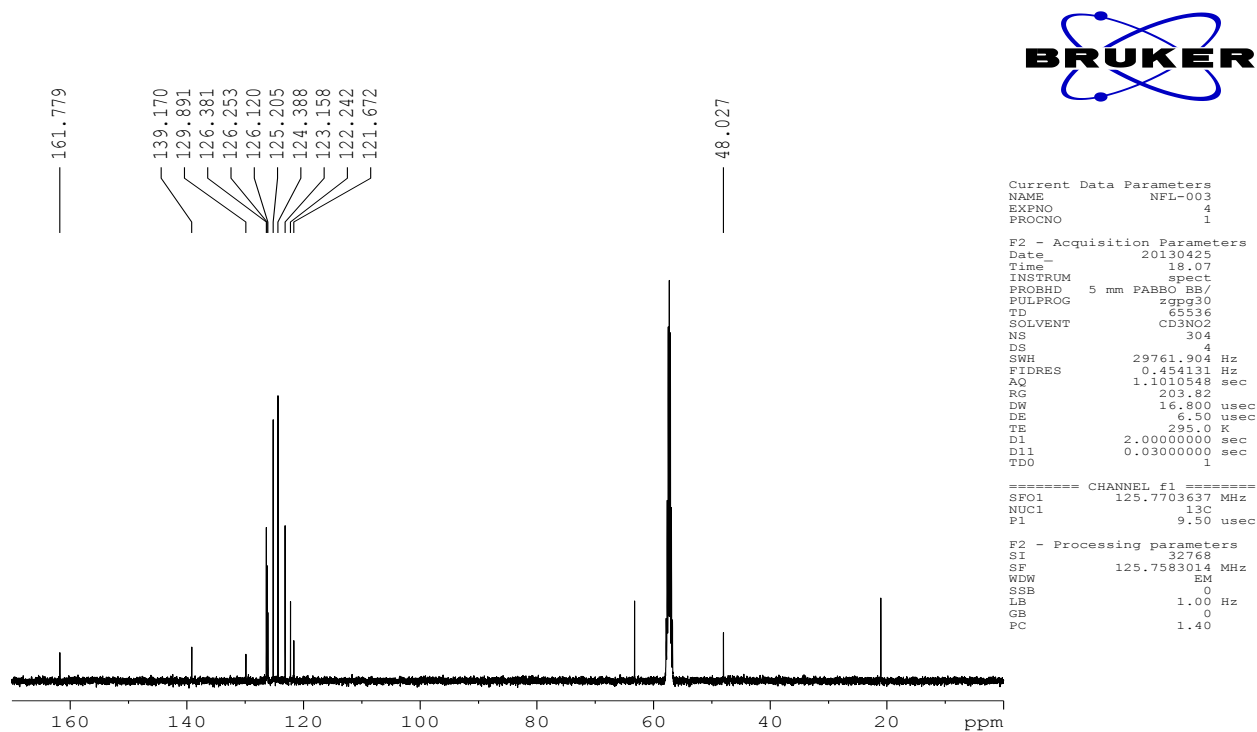


Figure S6. ^{13}C NMR spectrum of $[1\text{c}][\text{BF}_4]$ in CD_3NO_2 .

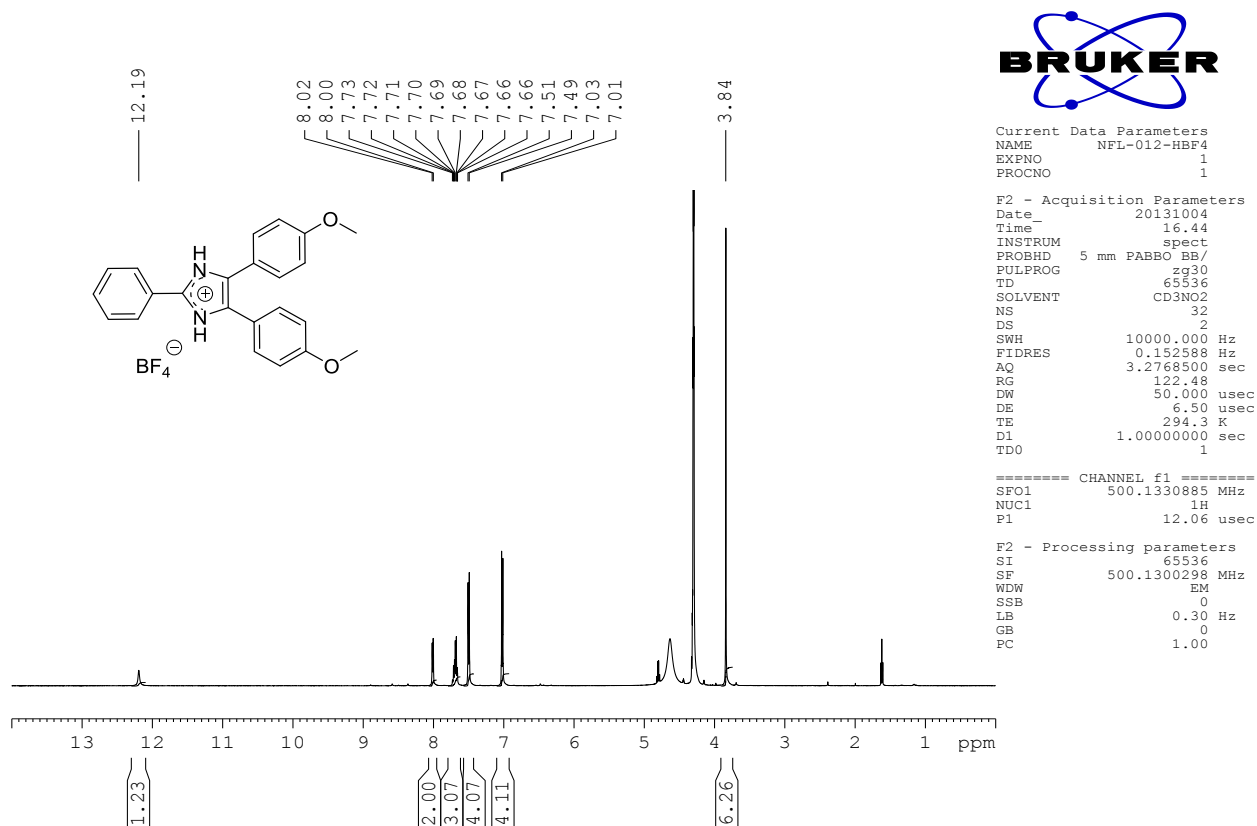


Figure S7. ^1H NMR spectrum of $[\mathbf{1d}][\text{BF}_4]$ in CD_3NO_2 .

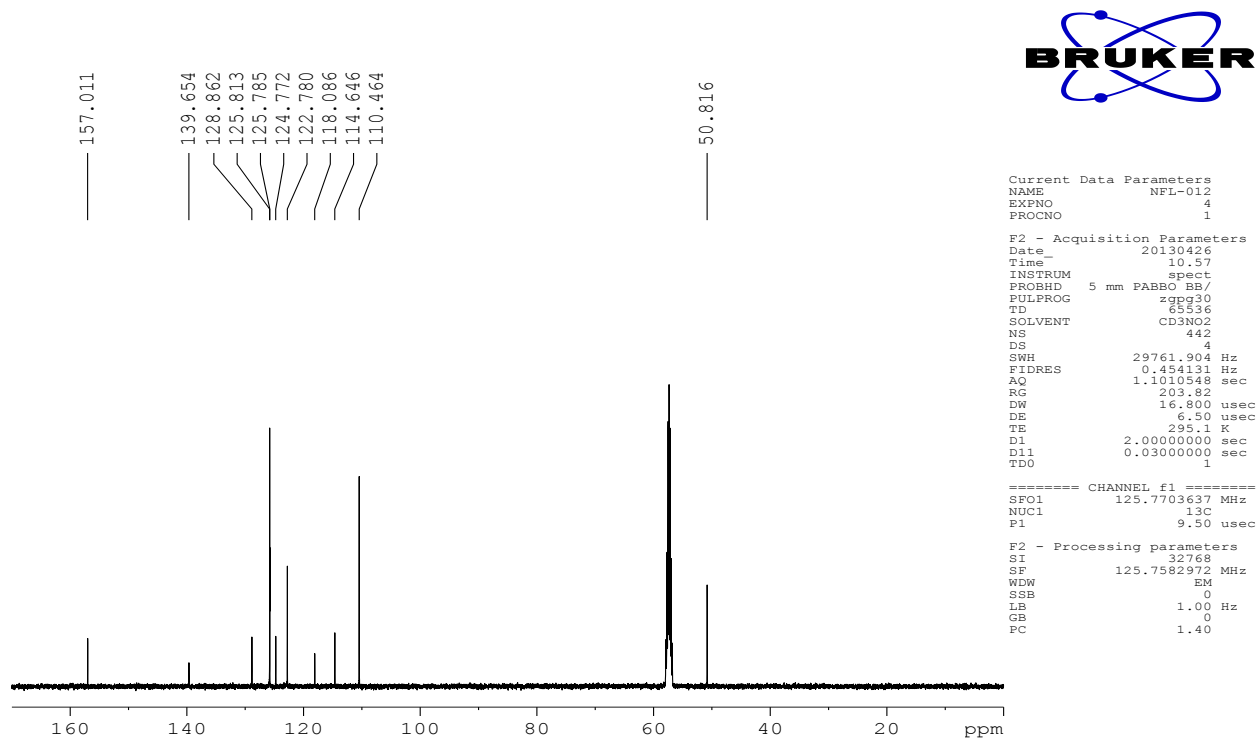


Figure S8. ^{13}C NMR spectrum of $[\mathbf{1d}][\text{BF}_4]$ in CD_3NO_2 .

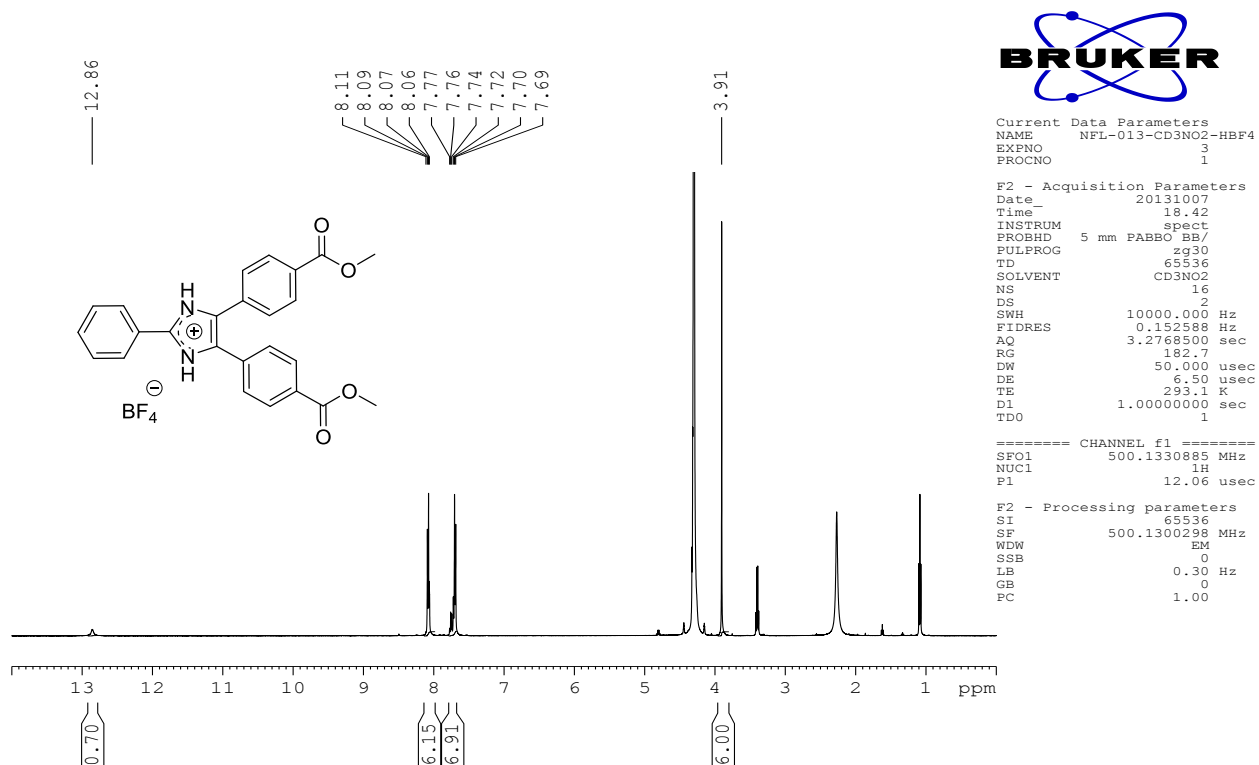


Figure S9. ^1H NMR spectrum of $[1\text{e}][\text{BF}_4]$ in CD_3NO_2 .

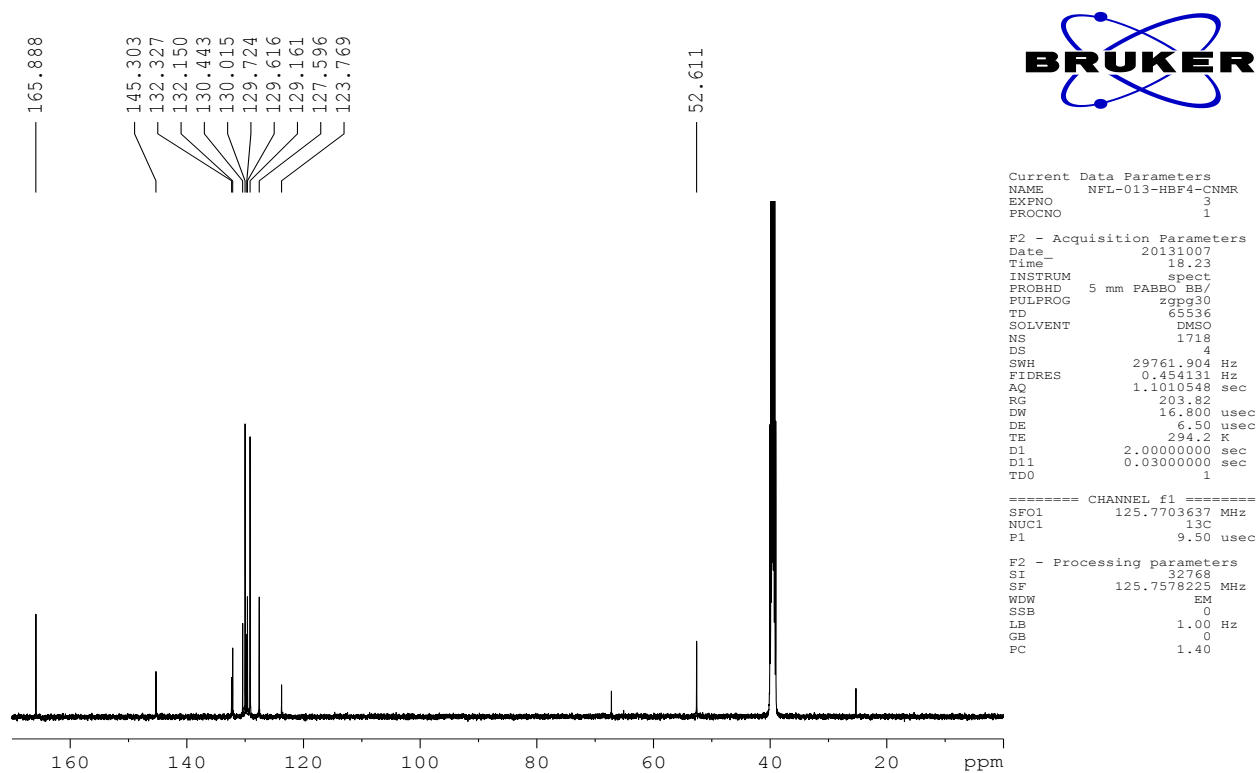


Figure S10. ^{13}C NMR spectrum of $[1\text{e}][\text{BF}_4]$ in $\text{DMSO}-d_6$.

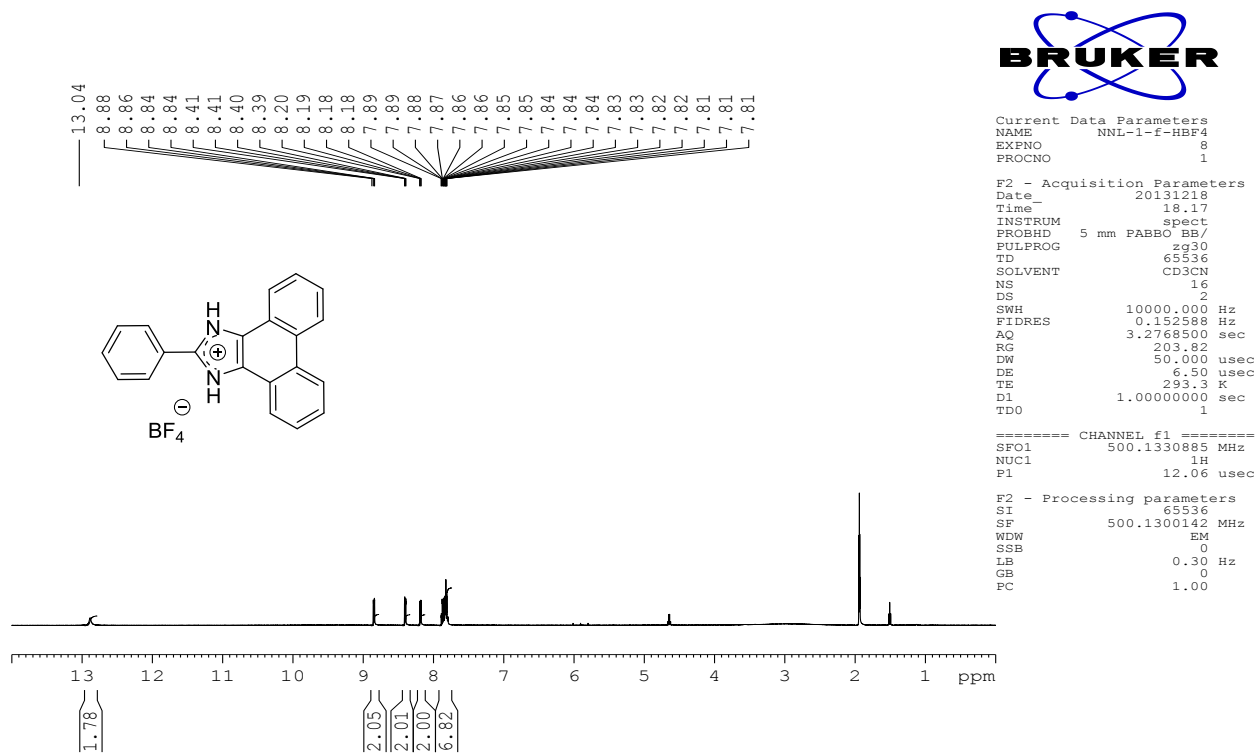


Figure S11. ¹H NMR spectrum of [2][BF₄] in CD₃CN.

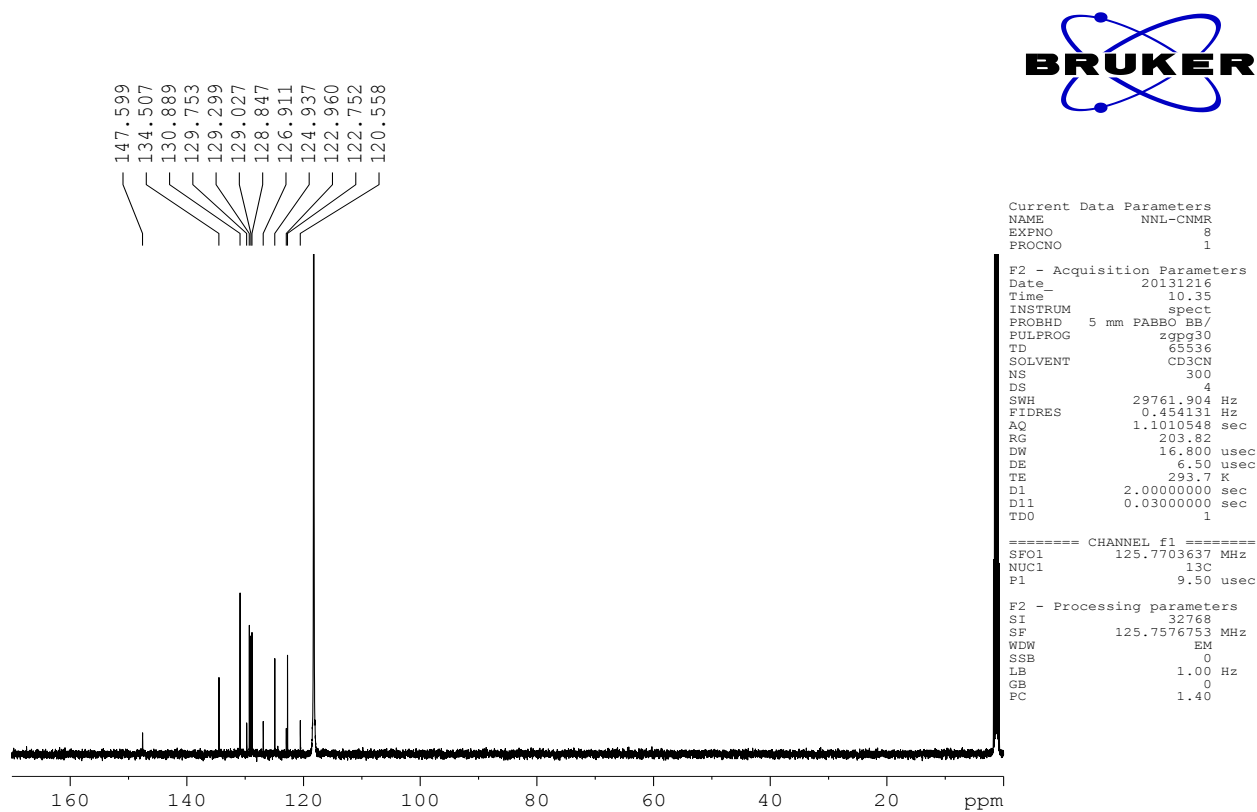


Figure S12. ¹³C NMR spectrum of [2][BF₄] in CD₃CN.

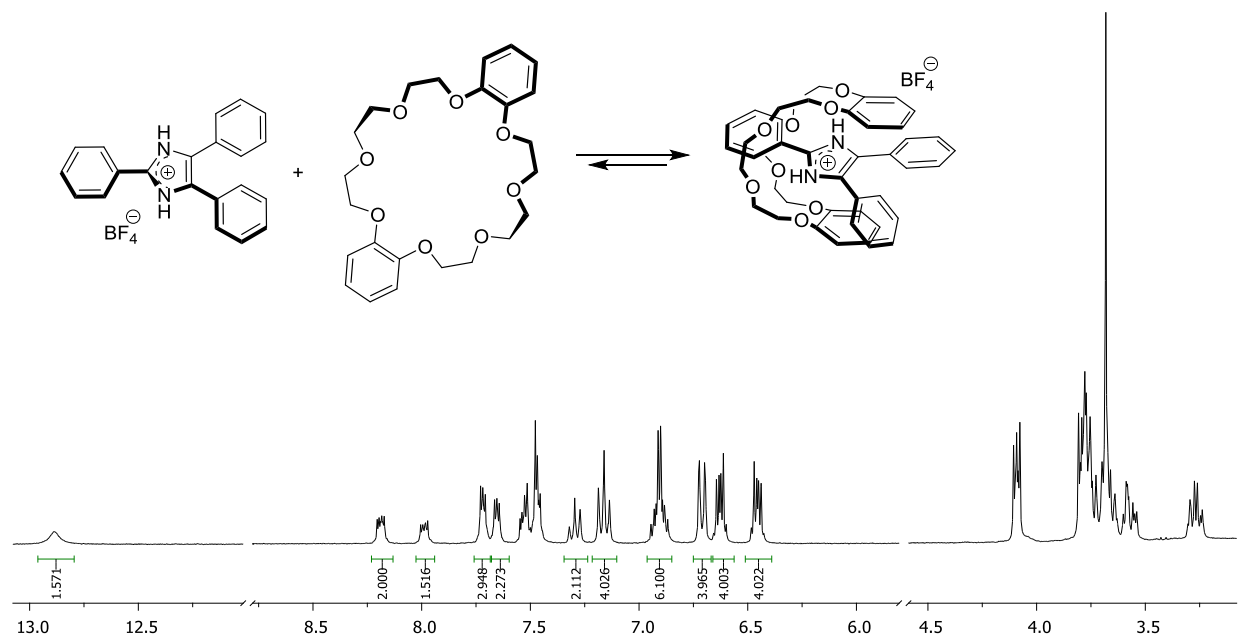


Figure S13. ¹H NMR spectra in CD₃CN: 1.0 x 10⁻² M solution of **[1a][BF₄]** with 1 eq. of **DB24C8** showing formation of [2]pseudorotaxane **[1a $\subset$ DB24C8][BF₄]**.

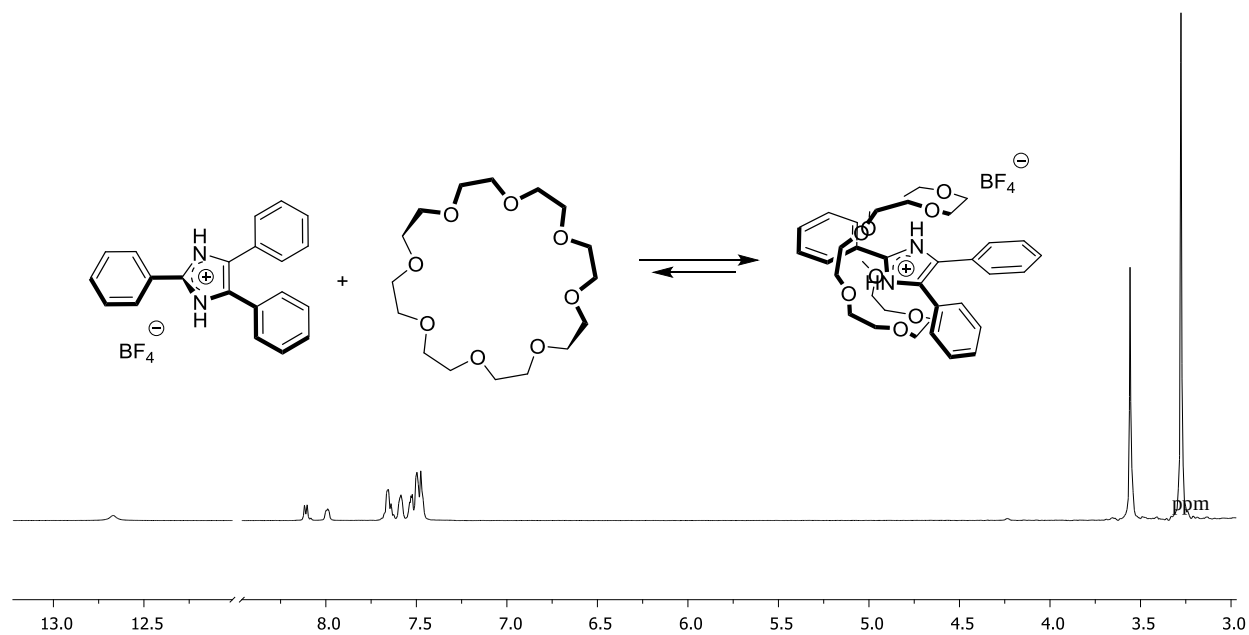


Figure S14. ¹H NMR spectra in CD₃CN: 1.0 x 10⁻² M solution of **[1a][BF₄]** with 1 eq. of **24C8** showing formation of [2]pseudorotaxane **[1a $\subset$ 24C8][BF₄]**.

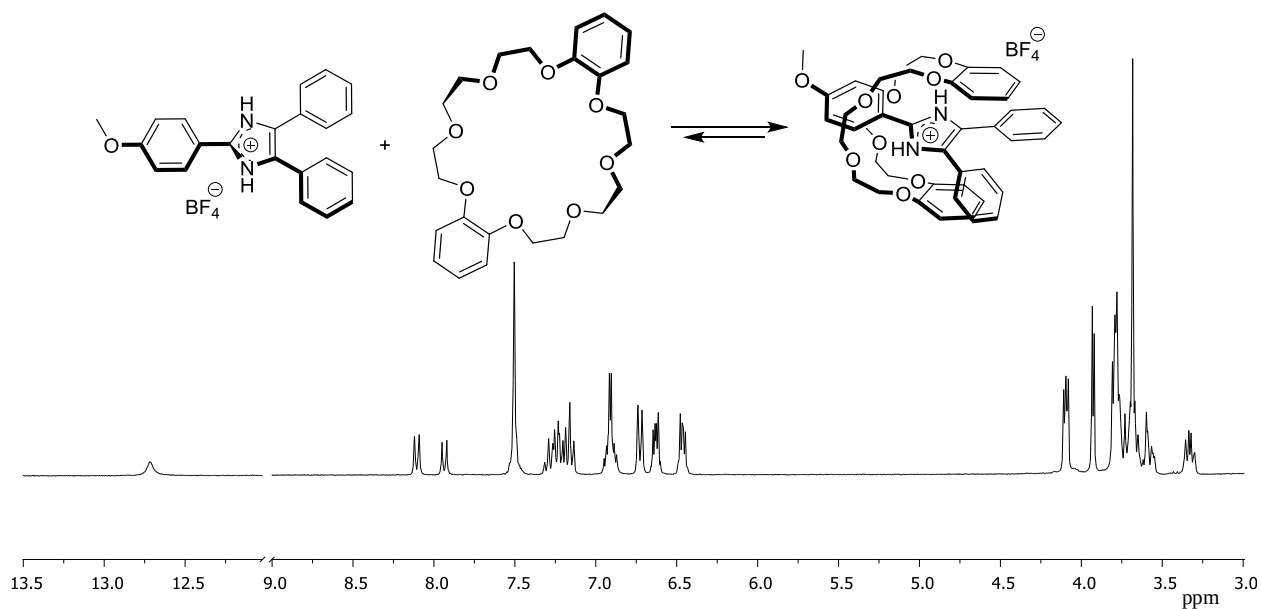


Figure S15. ¹H NMR spectra in CD₃CN: 1.0 x 10⁻² M solution of [1b][BF₄] with 1 eq. of DB24C8 showing formation of [2]pseudorotaxane [1b-DB24C8][BF₄].

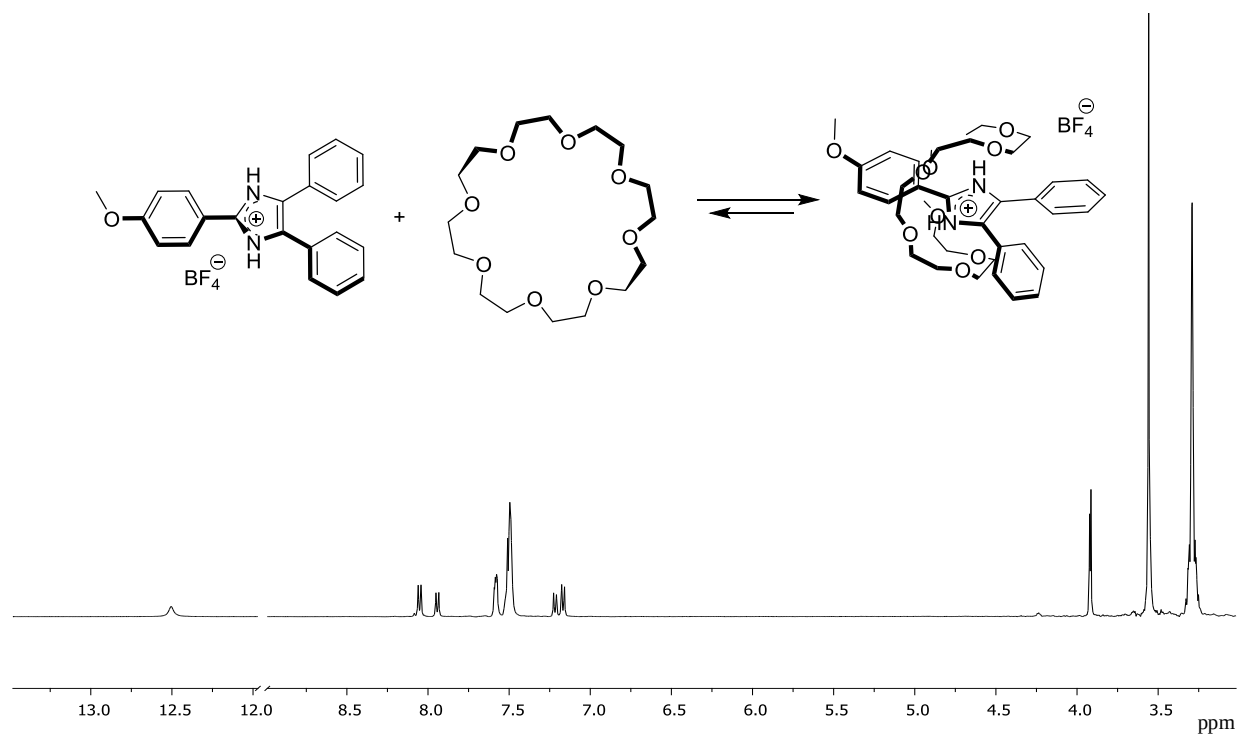


Figure S16. ¹H NMR spectra in CD₃CN: 1.0 x 10⁻² M solution of [1b][BF₄] with 1 eq. of 24C8 showing formation of [2]pseudorotaxane [1b-24C8][BF₄].

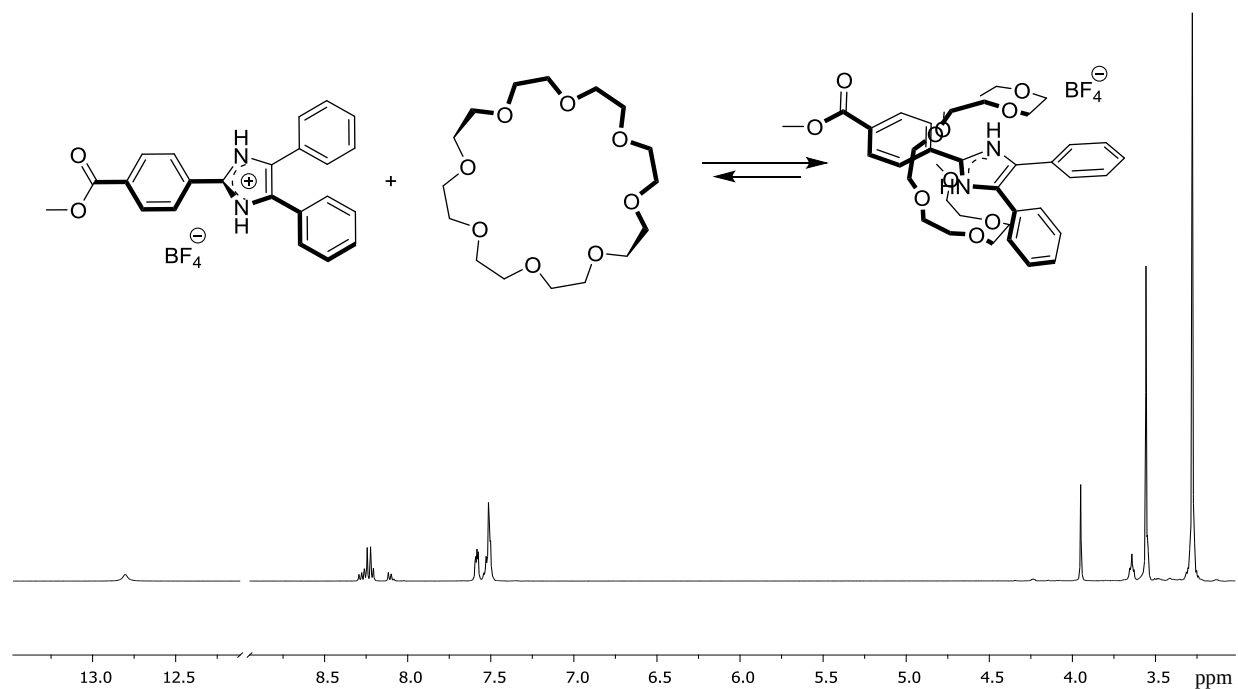


Figure S17. ^1H NMR spectra in CD_3CN : 1.0×10^{-2} M solution of **[1c]** $[\text{BF}_4]$ with 1 eq. of **24C8** showing formation of [2]pseudorotaxane **[1c-24C8]** $[\text{BF}_4]$.

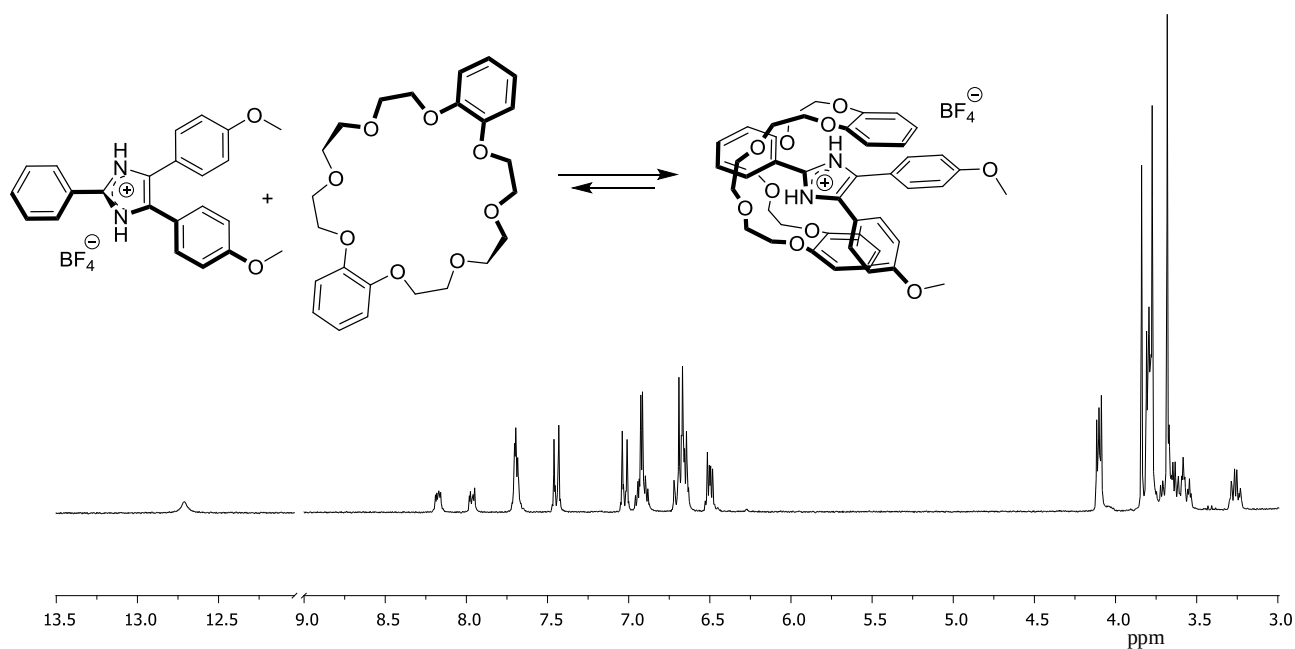


Figure S18. ^1H NMR spectra in CD_3CN : 1.0×10^{-2} M solution of **[1d]** $[\text{BF}_4]$ with 1 eq. of **DB24C8** showing formation of [2]pseudorotaxane **[1d-DB24C8]** $[\text{BF}_4]$.

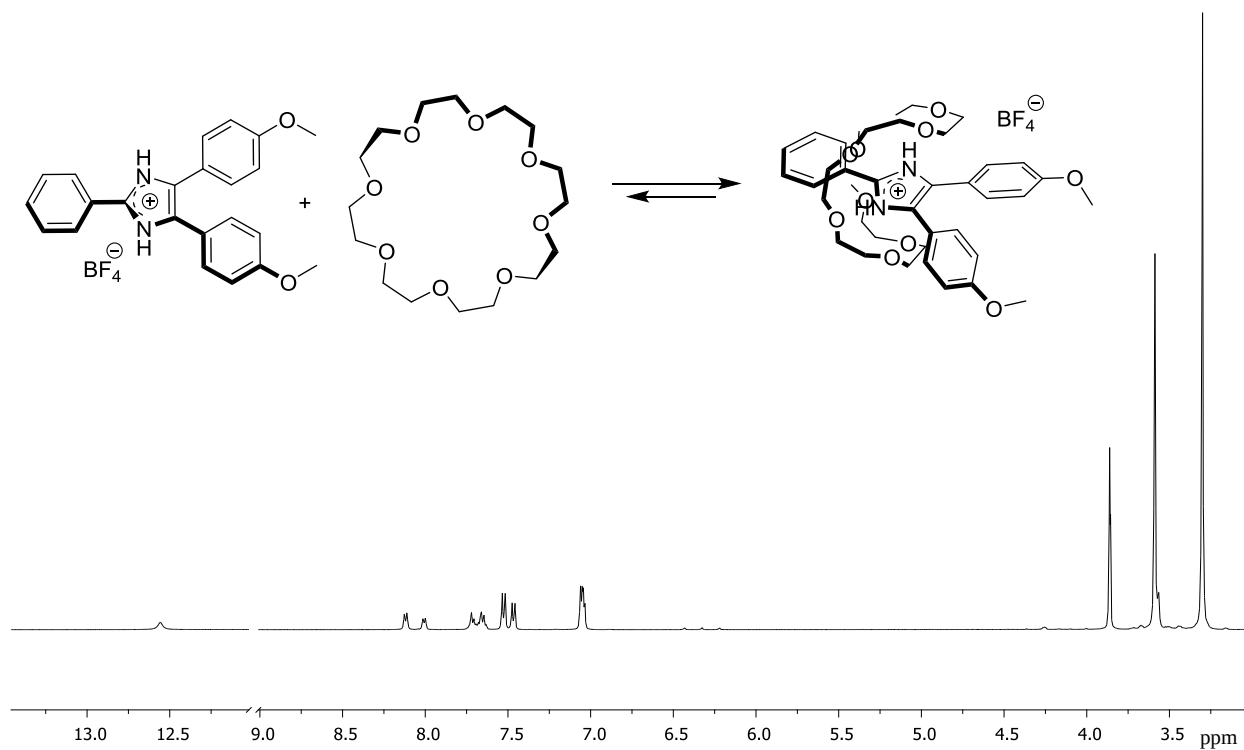


Figure S19. ^1H NMR spectra in CD_3CN : 1.0×10^{-2} M solution of $[1\text{d}][\text{BF}_4]$ with 1 eq. of **24C8** showing formation of [2]pseudorotaxane $[1\text{d} \subset 24\text{C8}][\text{BF}_4]$.

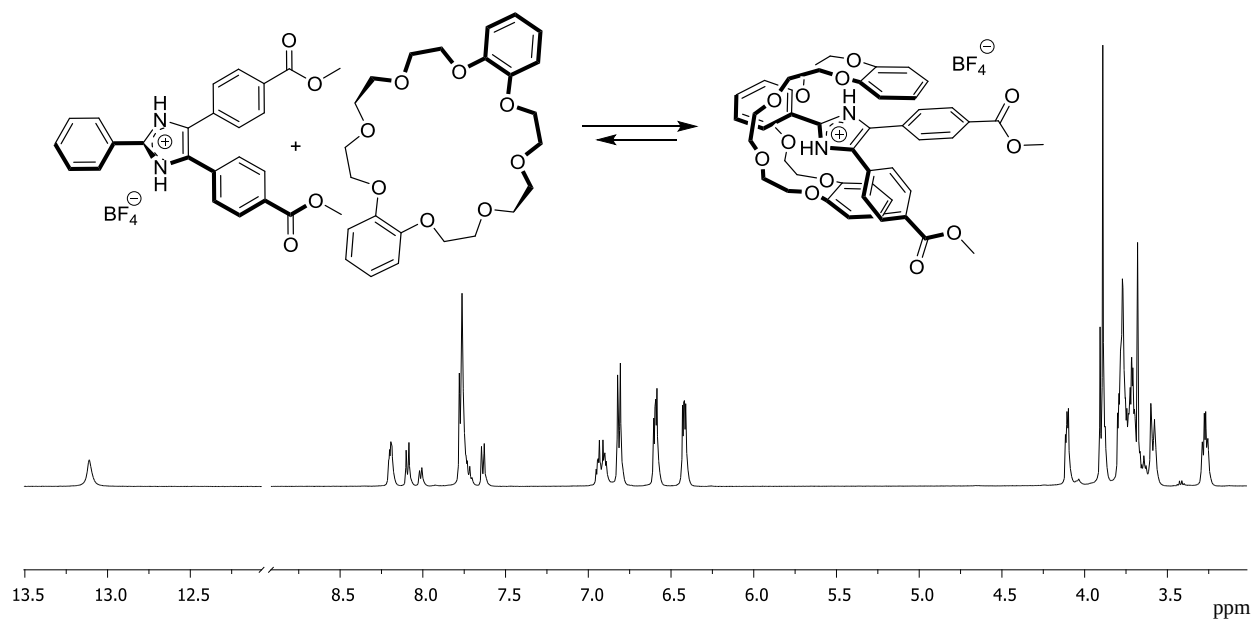


Figure S20. ^1H NMR spectra in CD_3CN : 1.0×10^{-2} M solution of $[1\text{e}][\text{BF}_4]$ with 1 eq. of **DB24C8** showing formation of [2]pseudorotaxane $[1\text{e} \subset \text{DB24C8}][\text{BF}_4]$.

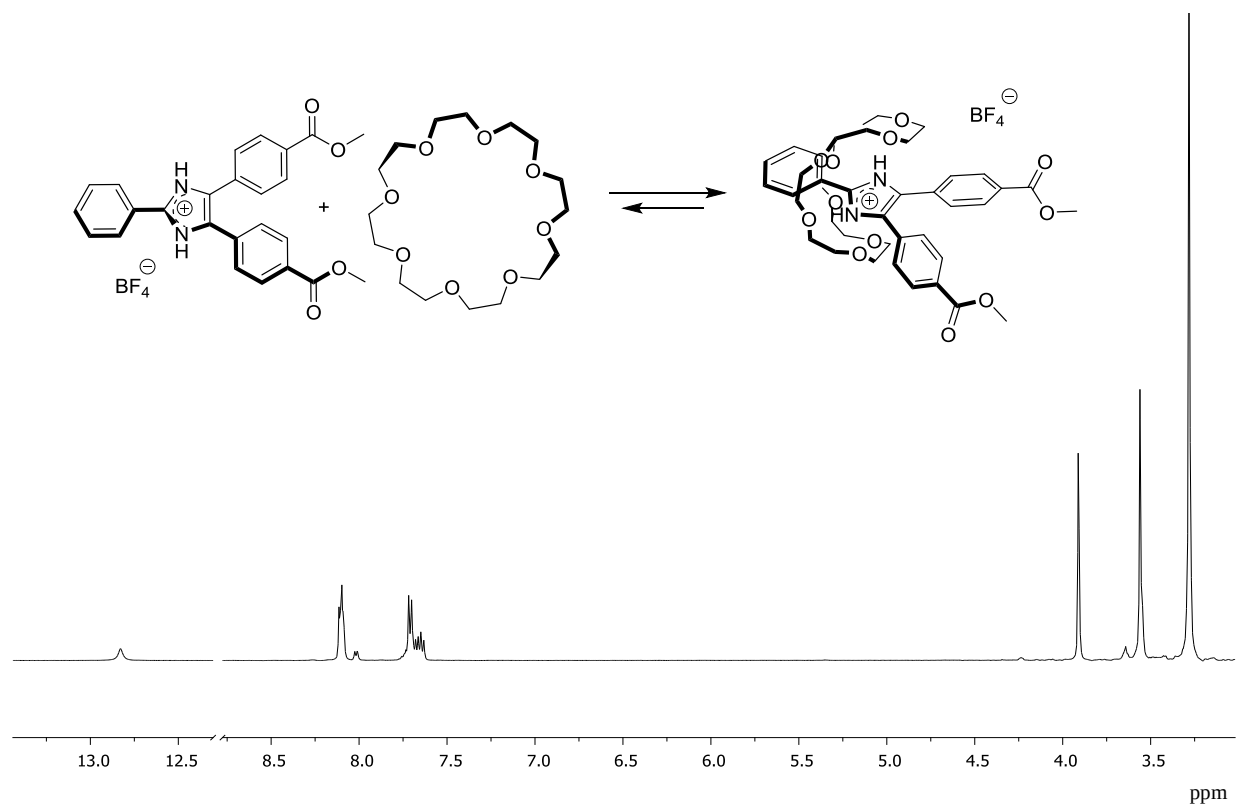


Figure S21. ^1H NMR spectra in CD_3CN : 1.0×10^{-2} M solution of $[1e][\text{BF}_4]$ with 1 eq. of **24C8** showing formation of [2]pseudorotaxane $[1e \subset 24C8][\text{BF}_4]$.

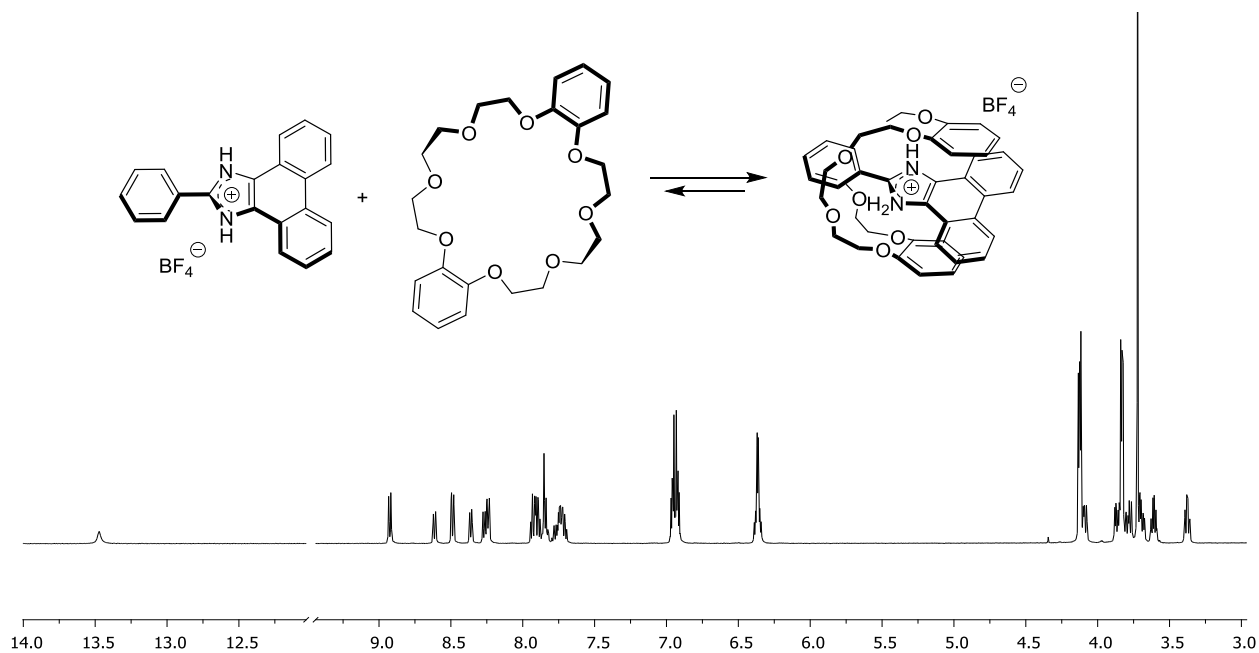


Figure S22. ^1H NMR spectra in CD_3CN : 1.0×10^{-2} M solution of $[2][\text{BF}_4]$ with 1 eq. of **DB24C8** showing formation of [2]pseudorotaxane $[2 \subset \text{DB24C8}][\text{BF}_4]$.

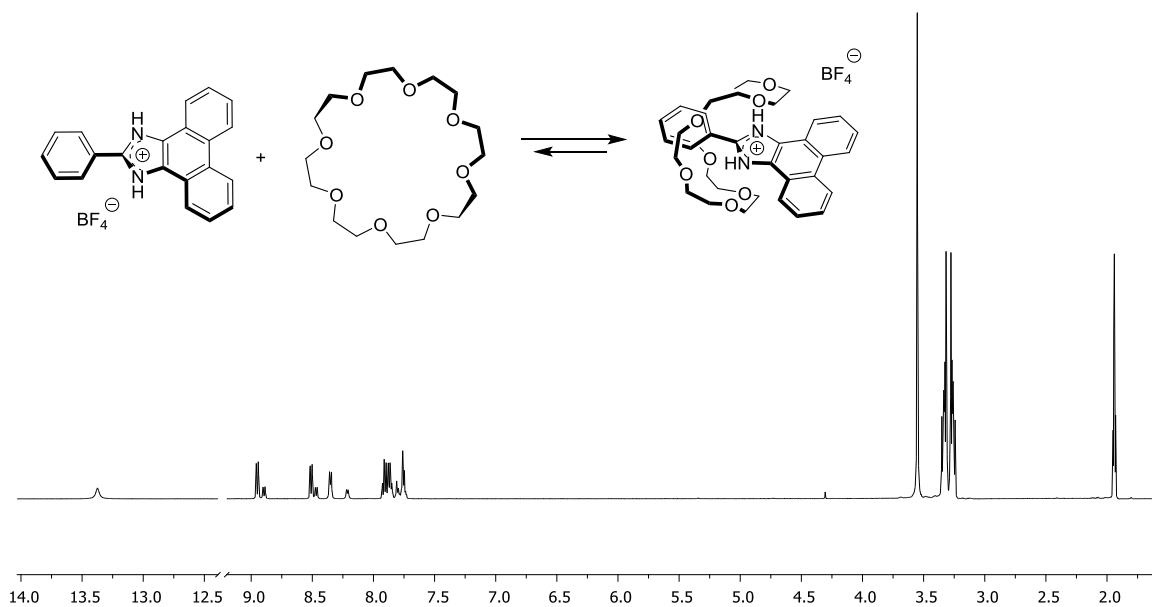


Figure S23. ^1H NMR spectra in CD_3CN : 1.0×10^{-2} M solution of **[2]** $^+$ $[\text{BF}_4]^-$ with 1 eq. of **24C8** showing formation of **[2]**pseudorotaxane **[2-24C8]** $^+$ $[\text{BF}_4]^-$.

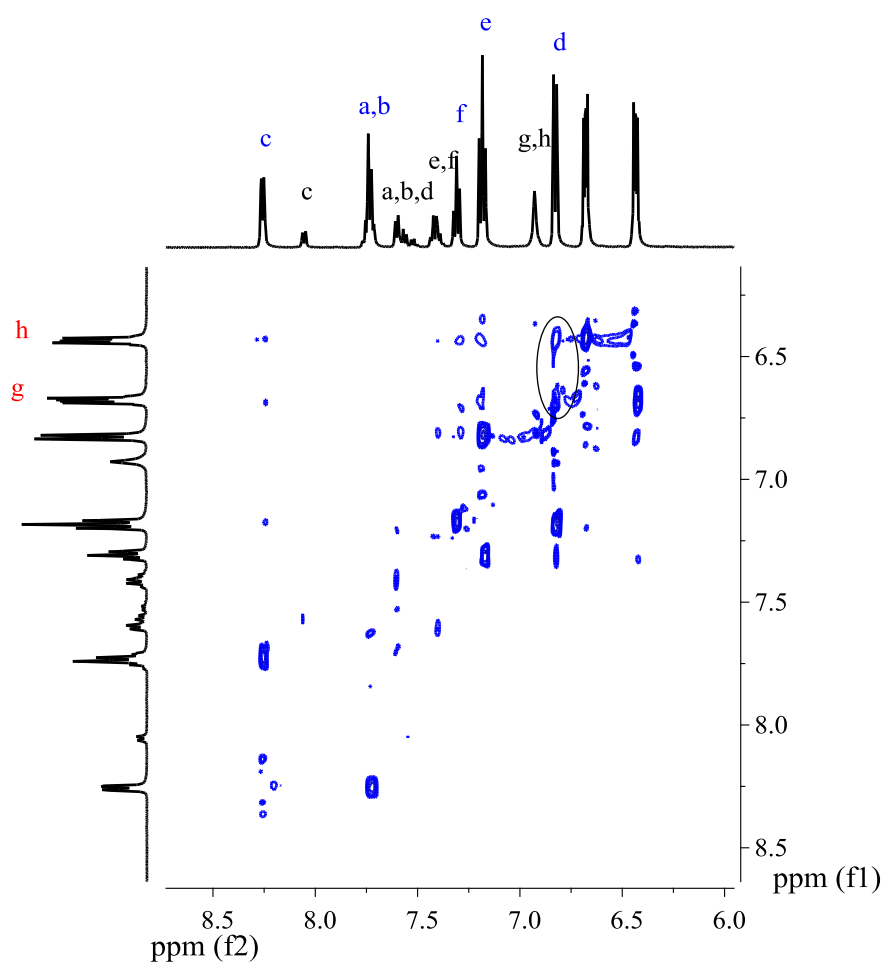
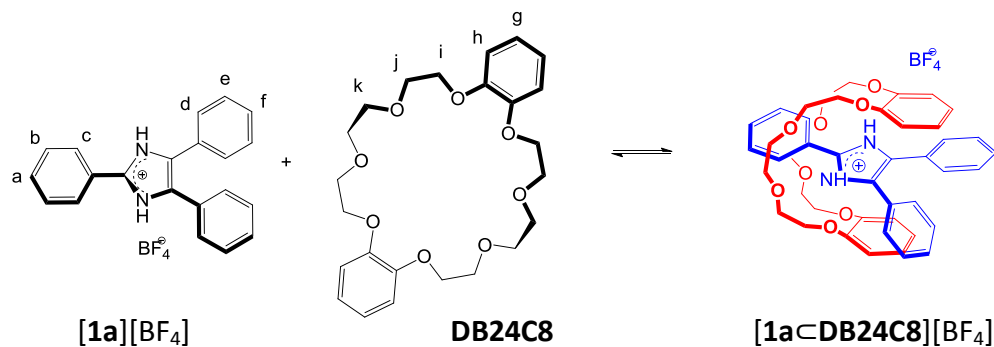


Figure S24. Partial 2D-NOESY spectrum of **[1a⊂DB24C8][BF₄]** (500 MHz, CD₂Cl₂, 298 K). This verifies the interactions between axle and wheel are the same as observed in the X-ray crystal structure.

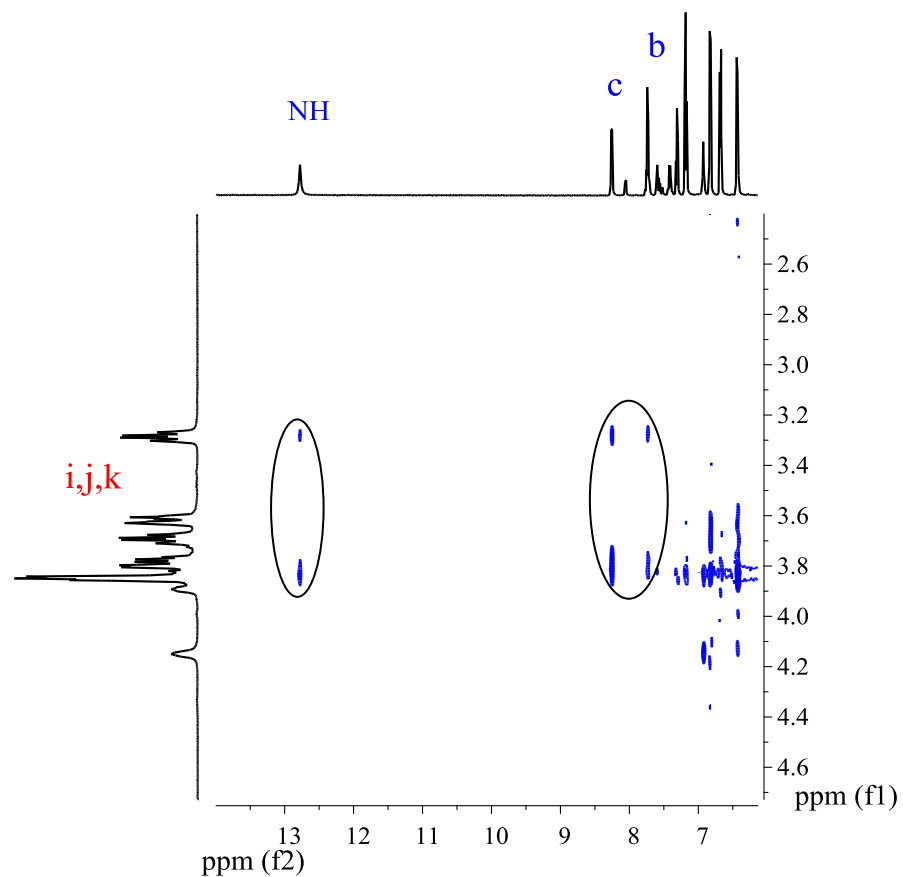
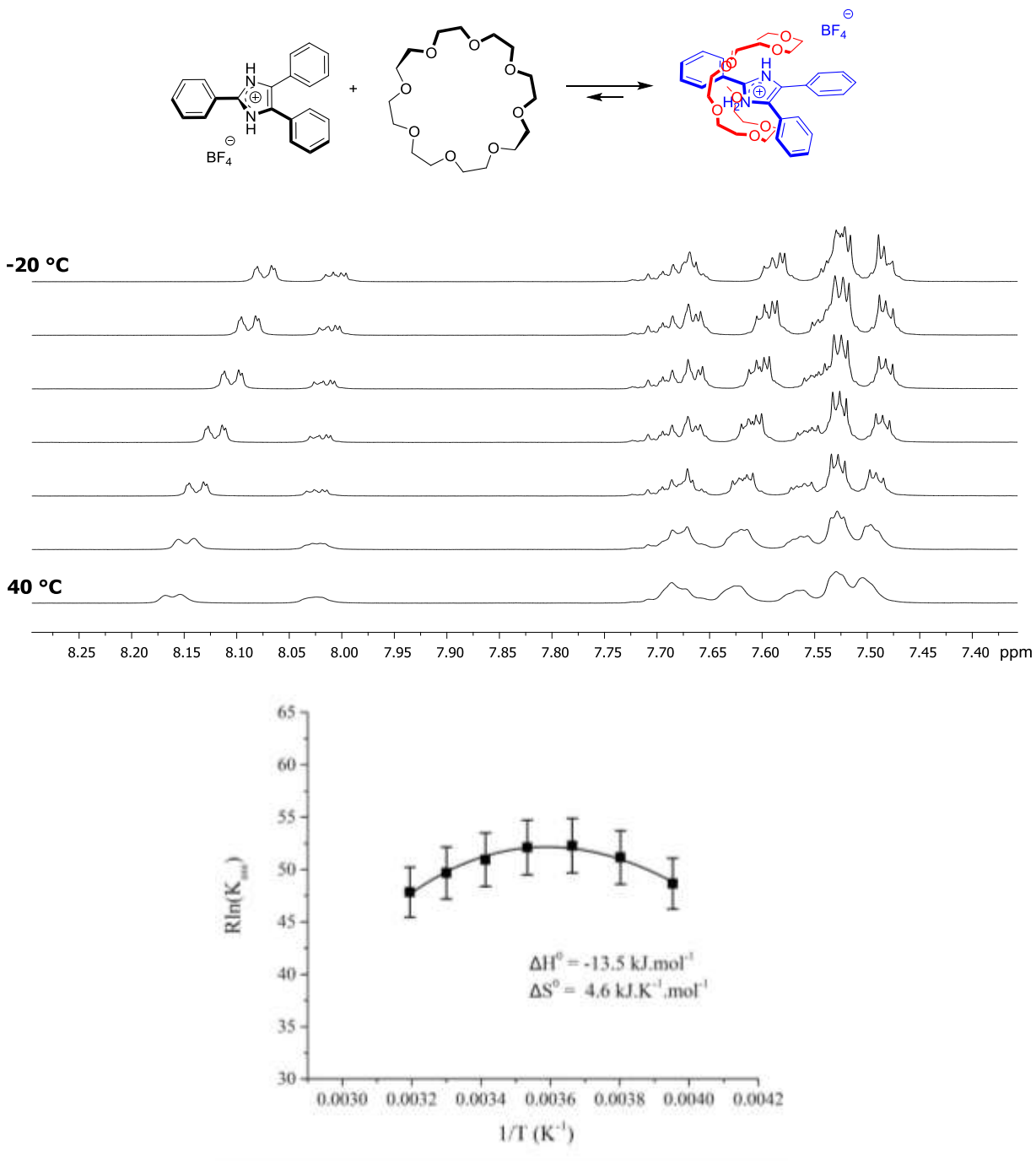


Figure S25. Partial 2D-NOESY spectrum of **[1a-DB24C8][BF₄]** (500 MHz, CD₂Cl₂, 298 K). This verifies the interactions between axle and wheel are the same as observed in the X-ray crystal structure.

Figure S26. Variable Temperature ^1H NMR spectra and van't Hoff Plot for **[1a $\subset$ 24C8]**.



$$R\ln K_a = -(\Delta H_0/T) + \Delta C_p^\circ \ln T + (\Delta S_0 - \Delta C_p^\circ)$$

$$\Delta H_0 = 193.9\text{ KJmol}^{-1}, \Delta S_0 = 4.0\text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \Delta C_p^\circ = -696.2\text{ JK}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ = \Delta H_0 + T \Delta C_p^\circ$$

$$\Delta S^\circ = \Delta S_0 + \Delta C_p^\circ \ln T$$

Figure S27. Variable Temperature ^1H NMR spectra and van't Hoff Plot for $[1\text{a} \subset \text{DB24C8}]$.

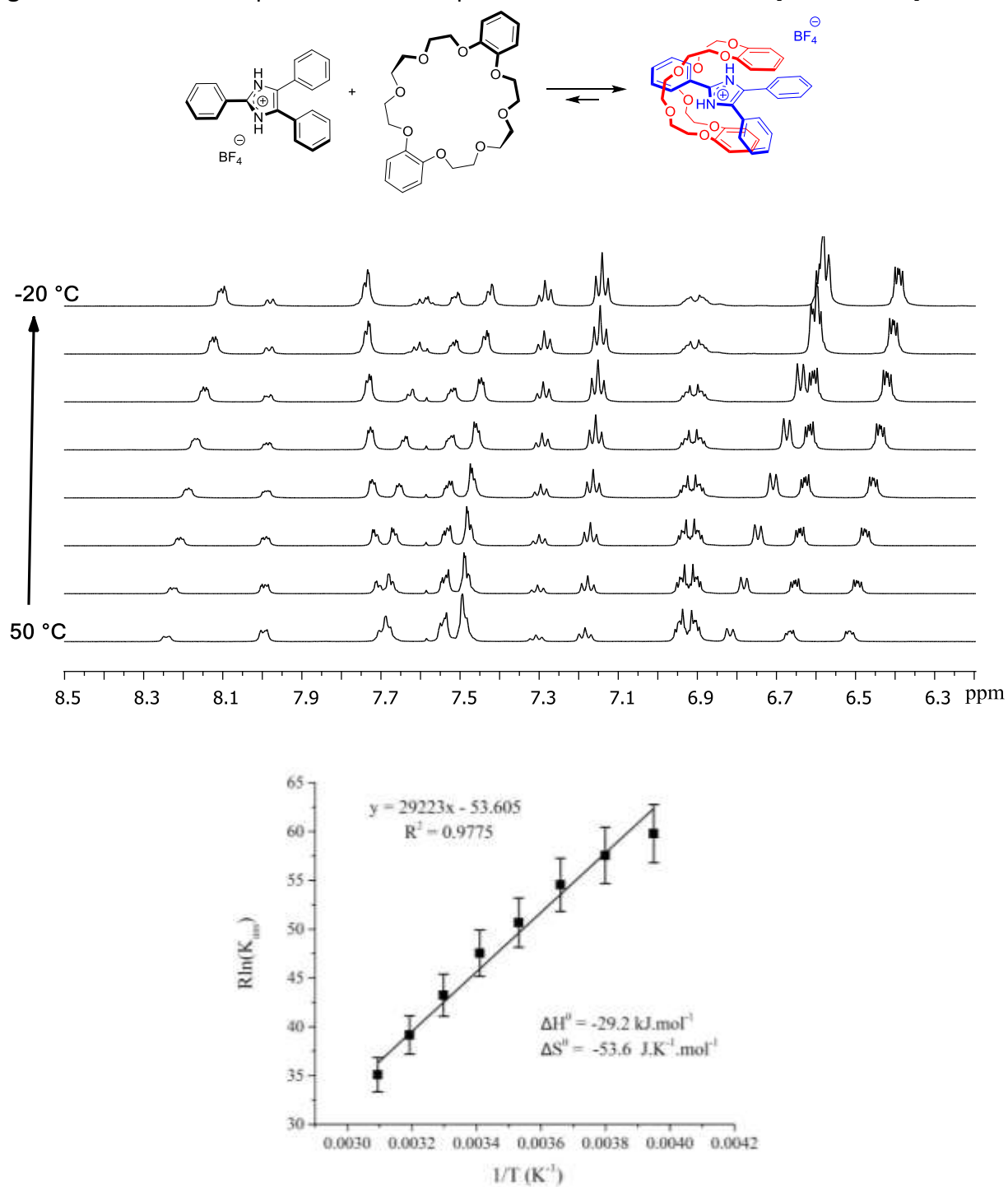


Figure S28. Hammett Plots for **DB24C8** and **24C8** (variation of R_1).

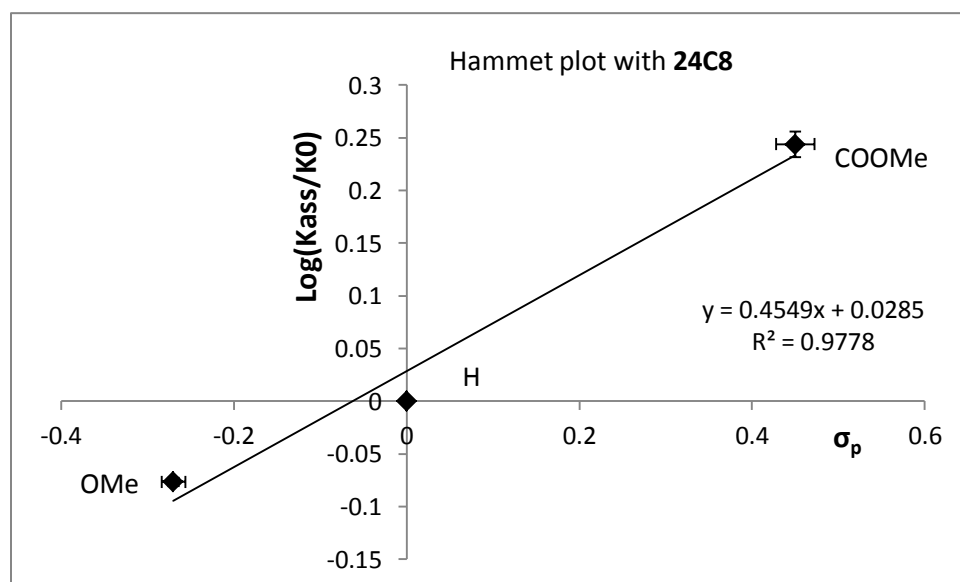
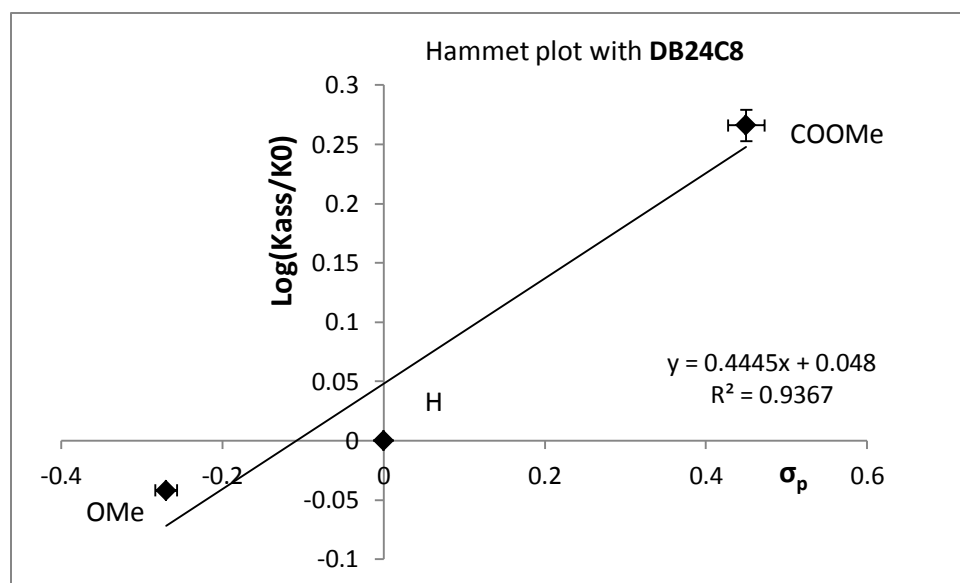
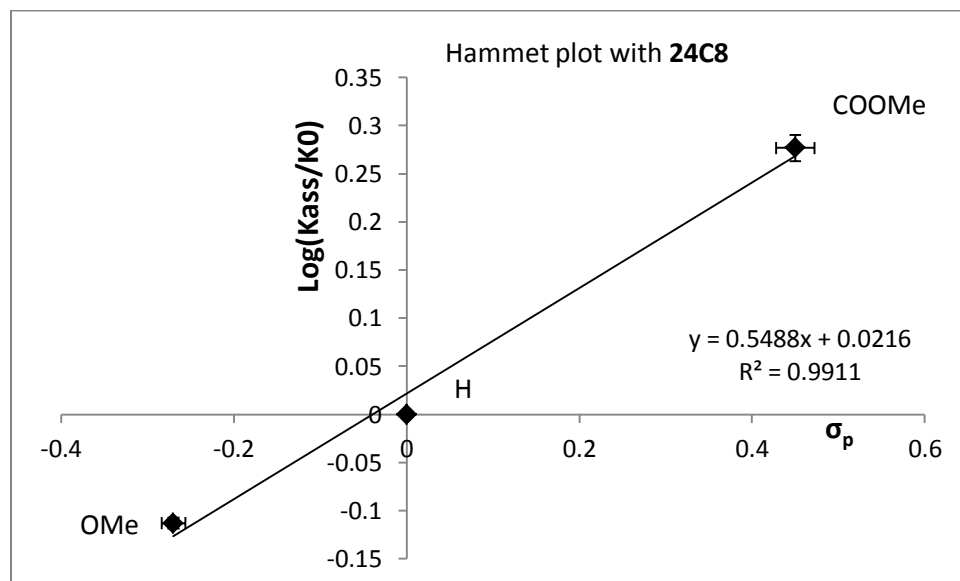
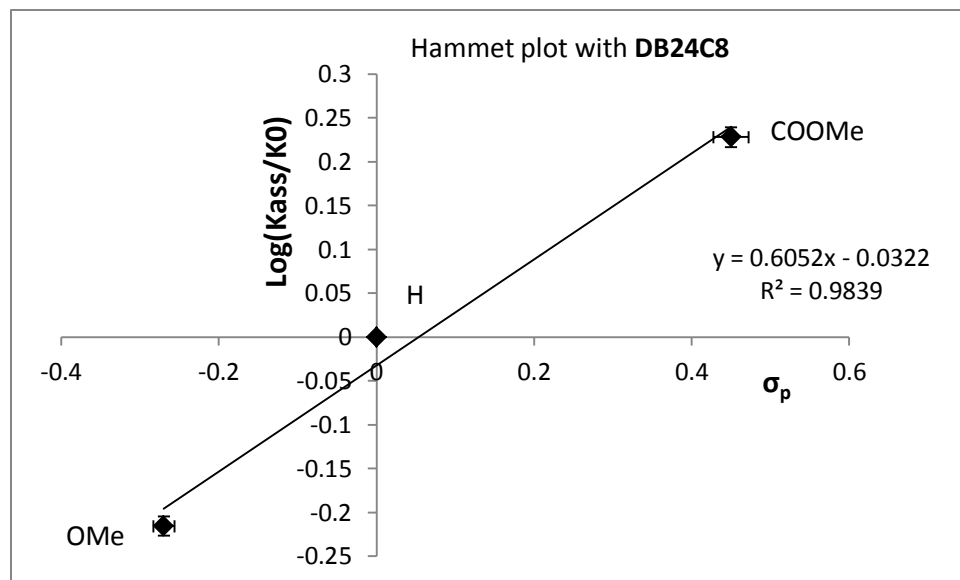


Figure S29. Hammet Plots for **DB24C8** and **24C8** (variation of R_2).



References (cited in this SI section only)

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- [S2] Adrian Jr., J. C.; Wilcox, C. S. *J. Am. Chem. Soc.* **1991**, 113, 678-680.
- [S3] Kishikawa, N.; Wada, M.; Ohba, Y.; Nakashima, K.; Kuroda, N. *J. Chromatogr. A*, **2004**, 1057, 83-88.