Supplementary Material

Semirotaxanes and unsymmetrical rotaxanes from substituted benzylammonium salts and dibenzo-24-crown-8

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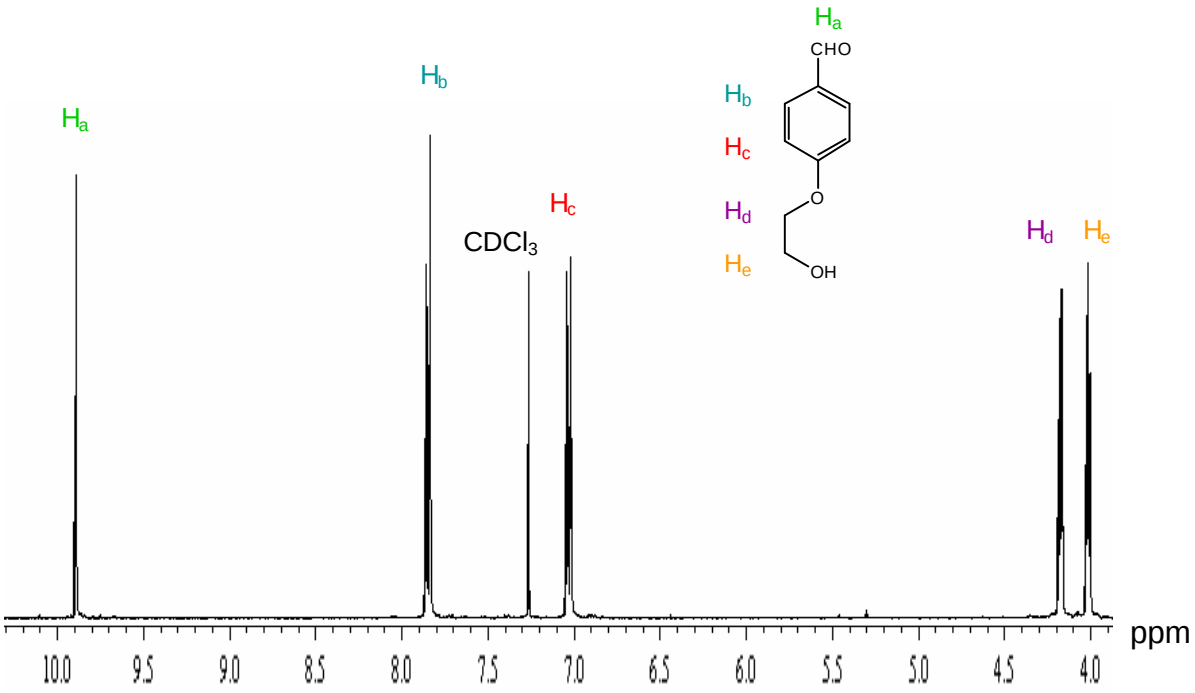


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, ambient T) of *p*-(2'-hydroxyethoxy)benzaldehyde (**2**).

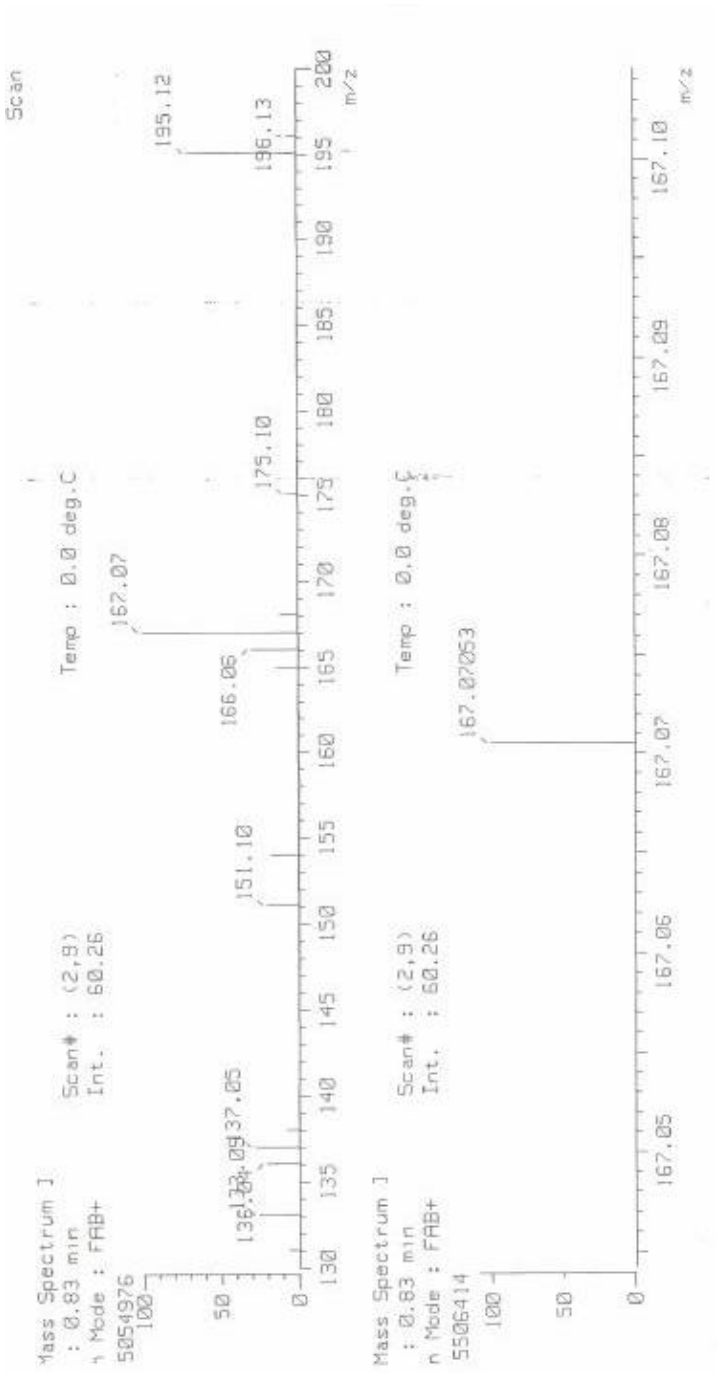


Figure S2. HR FAB mass spectrum of *p*-(2'-hydroxyethoxy)benzaldehyde (**2**).

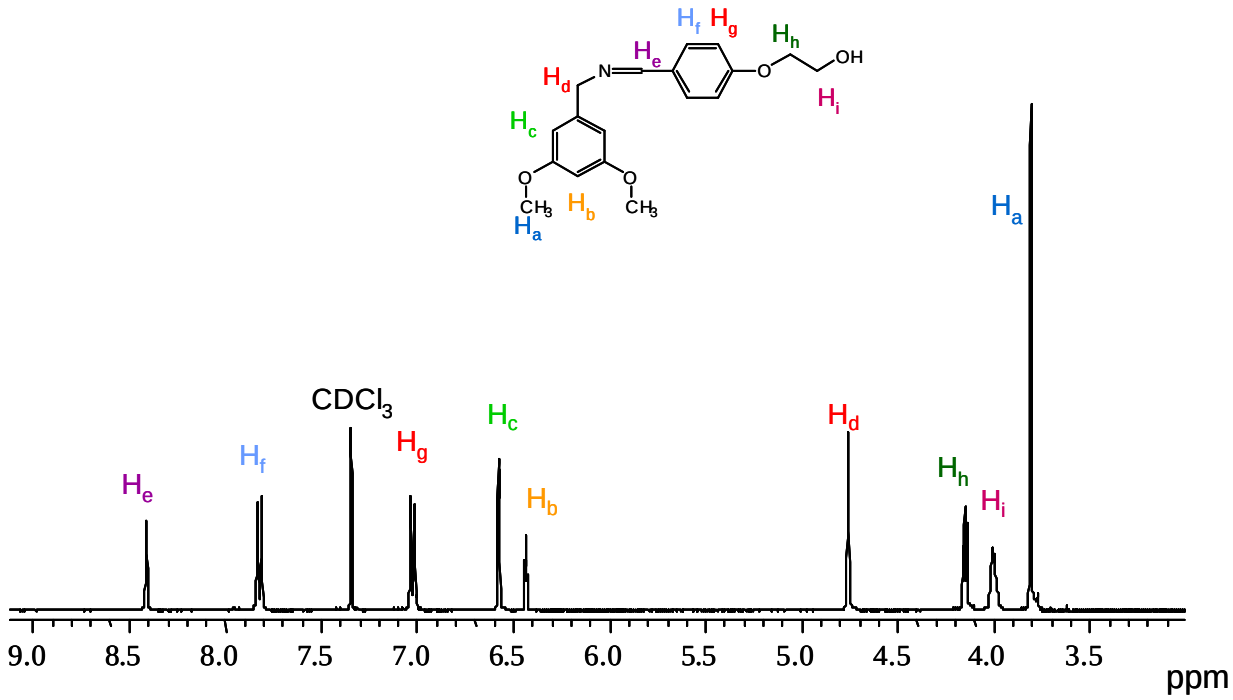


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, ambient T) of *p*-(2'-hydroxyethoxy)benzylidene-3",5"-dimethoxybenzylamine (Schiff base **3**).

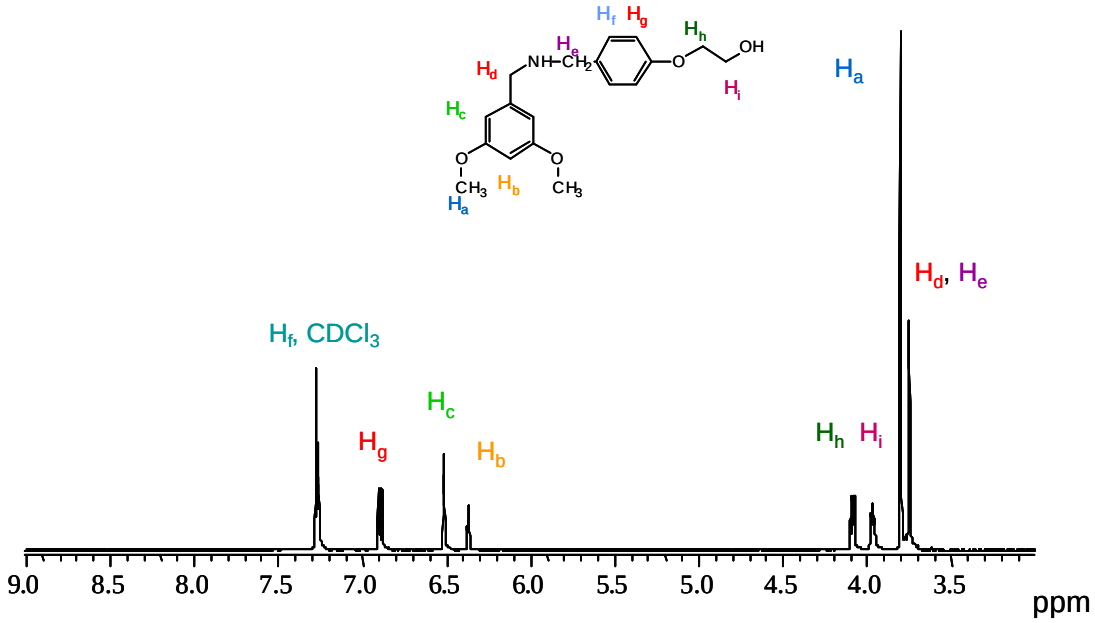


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, ambient T) of N-[*p*-(2'-hydroxyethoxy)benzyl]-3",5"-dimethoxybenzylamine (**4**).

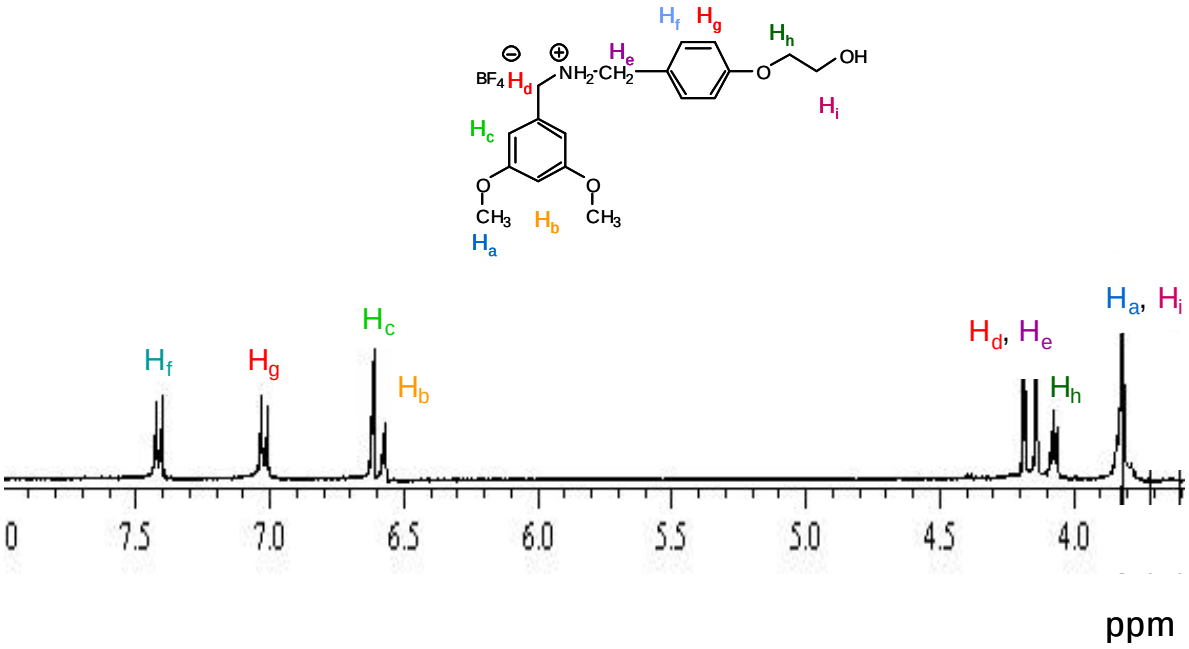


Figure S5. ^{1}H NMR spectrum (400 MHz, CD_3CN, ambient T) of N-[*p*-(2'-hydroxyethoxy)benzyl]-3",5"-dimethoxybenzyl ammonium tetrafluoroborate (**5a**).

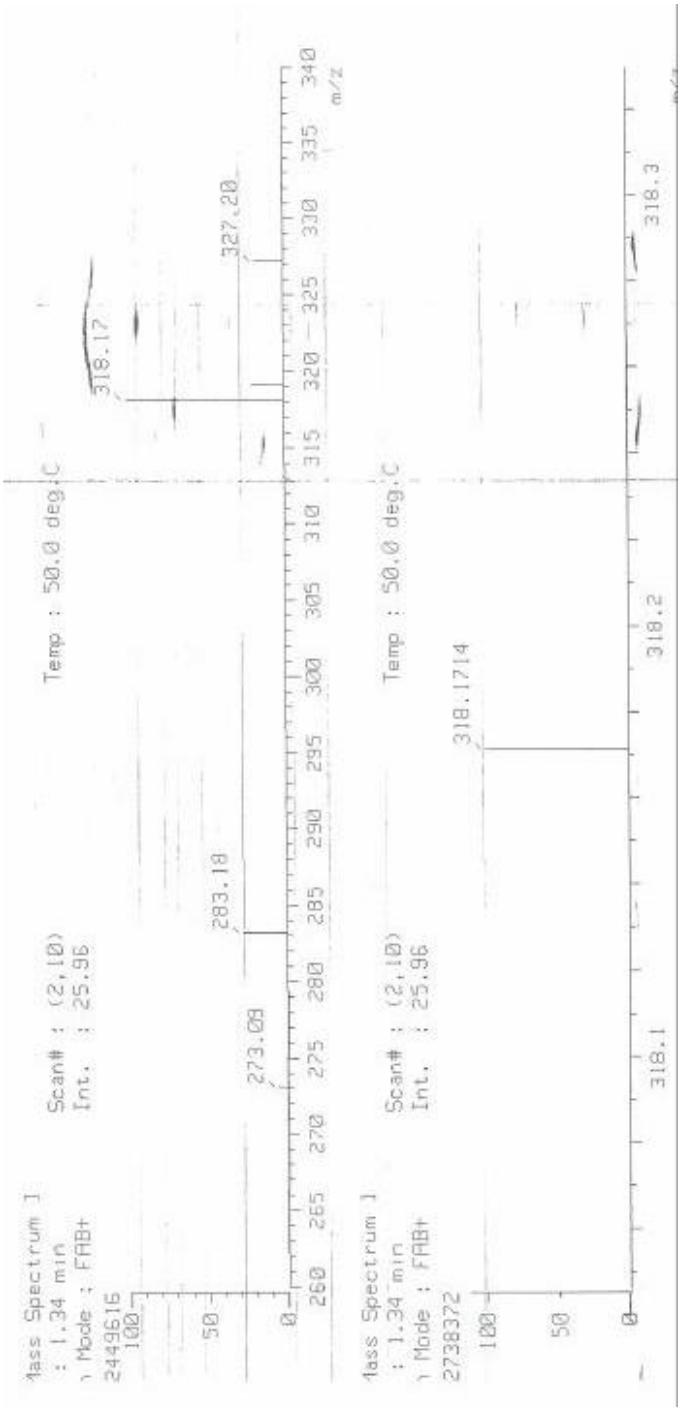


Figure S6. HR FAB mass spectrum of N-[*p*-(2'-hydroxyethoxy)benzyl]-3",5"-dimethoxybenzyl ammonium tetrafluoroborate (**5a**).

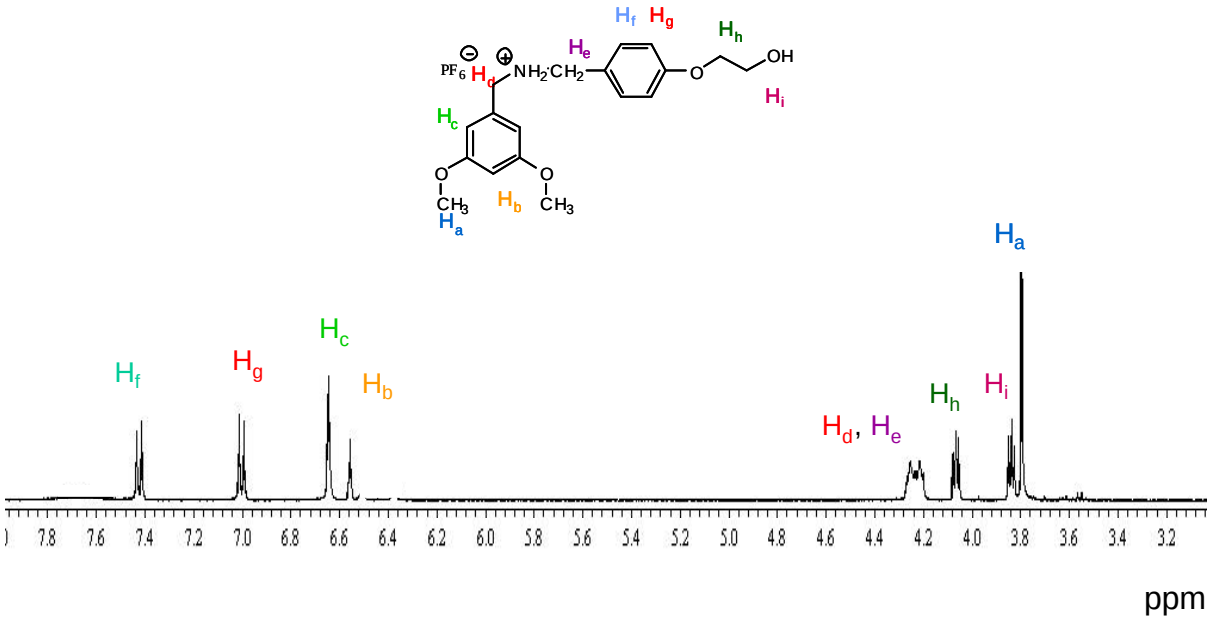


Figure S7. ^{1}H NMR spectrum (400 MHz, CD_3CN, ambient T) of N-[*p*-(2'-hydroxyethoxy)benzyl]-3",5"-dimethoxybenzyl ammonium hexafluorophosphate (**5b**).

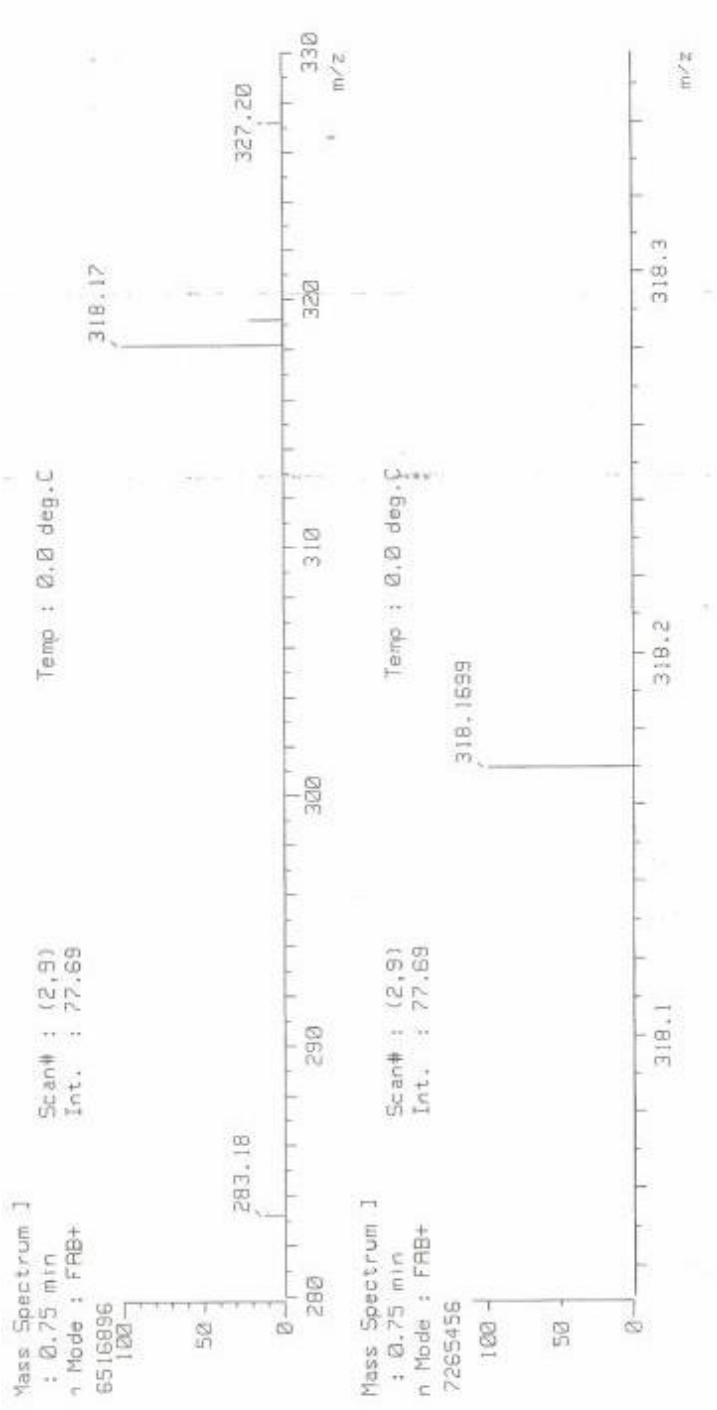


Figure S8. HR FAB mass spectrum of N-[*p*-(2'-hydroxyethoxy)benzyl]-3",5"-dimethoxybenzyl ammonium hexafluorophosphate (**5b**).

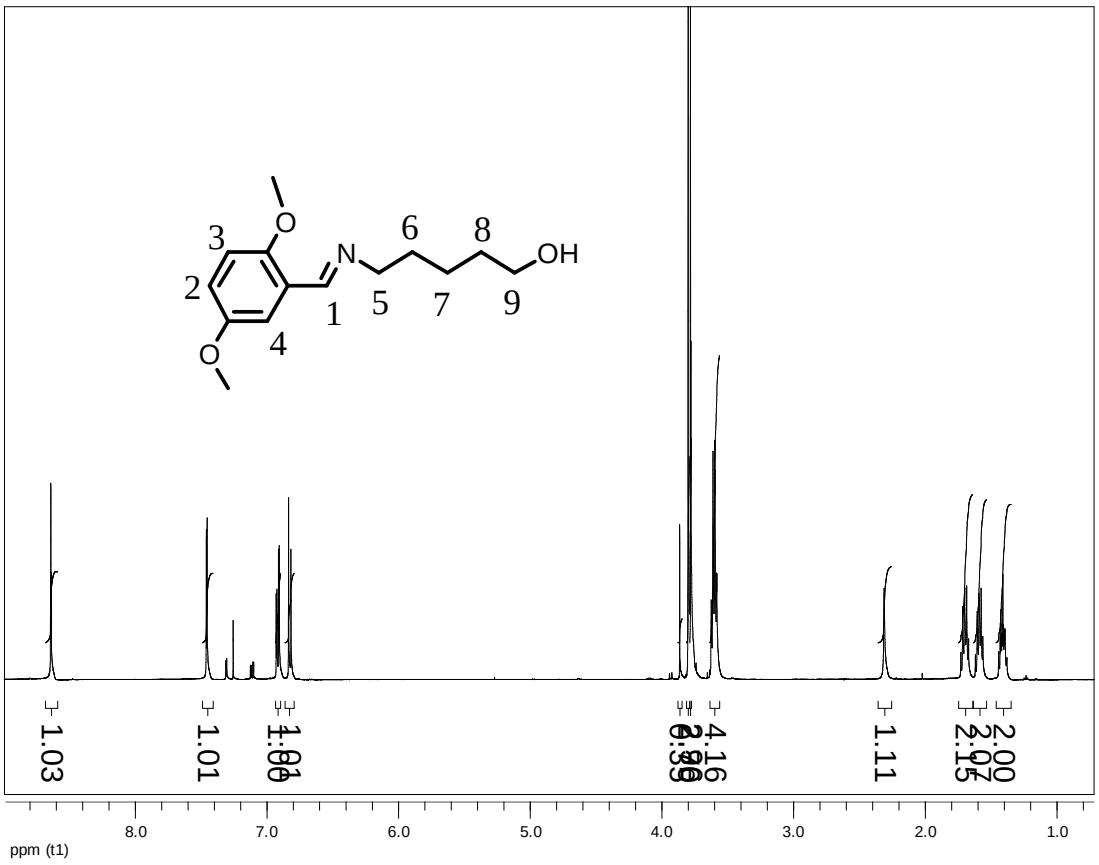


Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, ambient T) of 5-[(2',5'-dimethoxybenzylidene)amino]pentanol (**7**). Solvent impurity peaks are noted between 7.0 and 7.4 ppm and at 2.1 ppm.

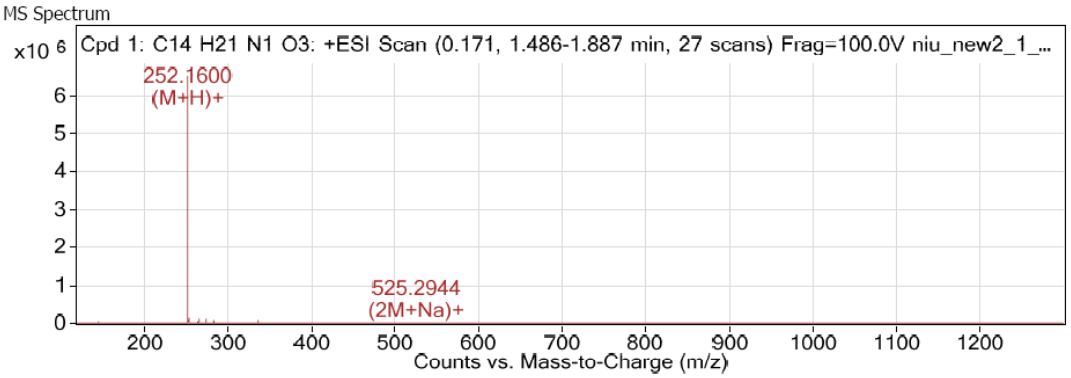


Figure S10. ESI TOF mass spectrum of 5-[(2',5'-dimethoxybenzylidene)amino]pentanol (**7**).

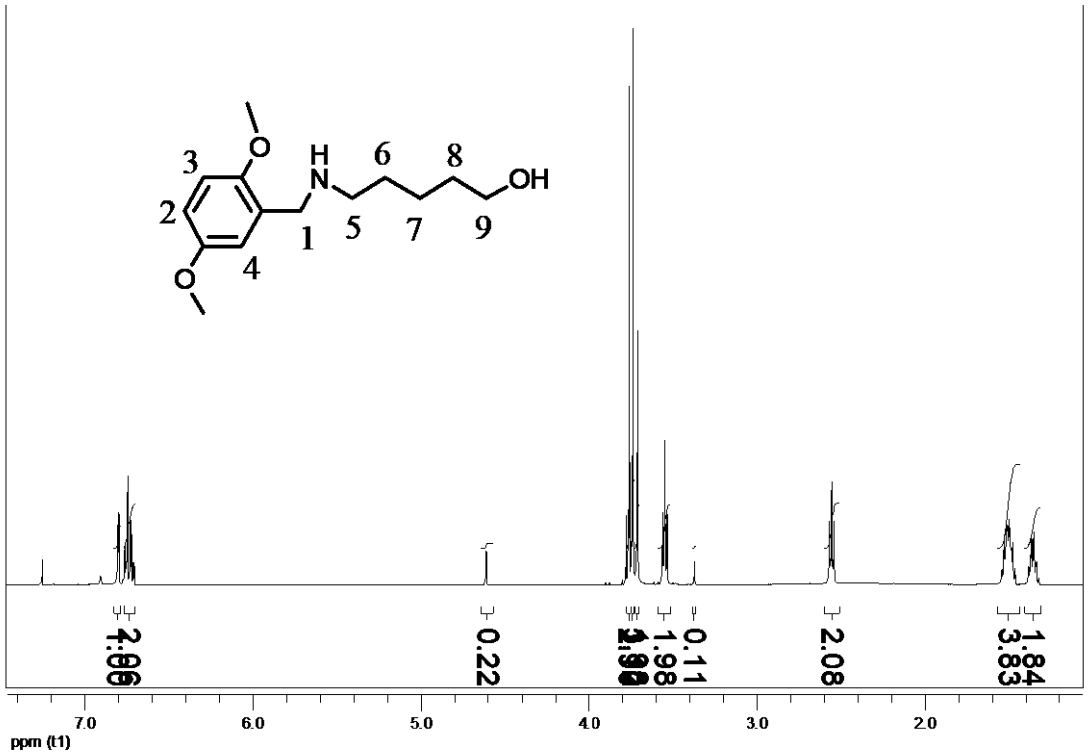


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, ambient T) of 5-[(2',5'-dimethoxybenzyl)amino]pentanol (**8**).

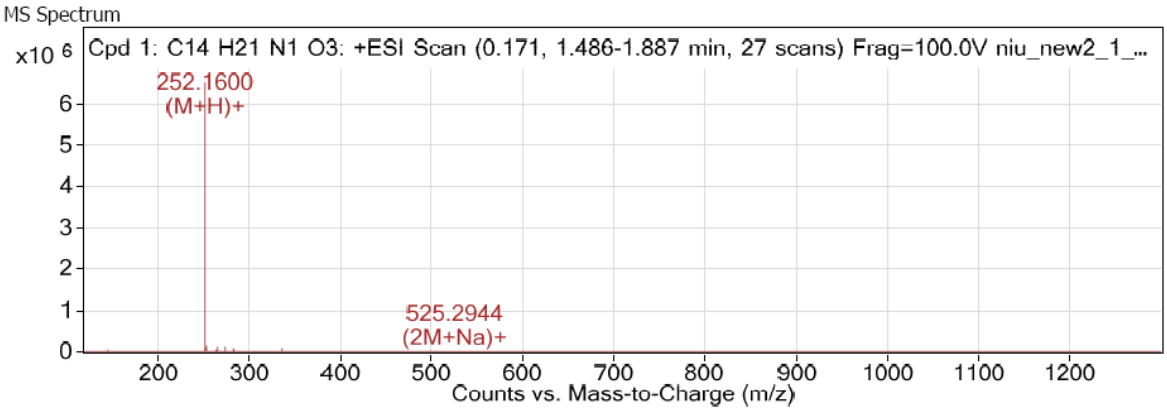


Figure S12. ESI TOF mass spectrum of 5-[(2',5'-dimethoxybenzyl)amino]pentanol (**8**).

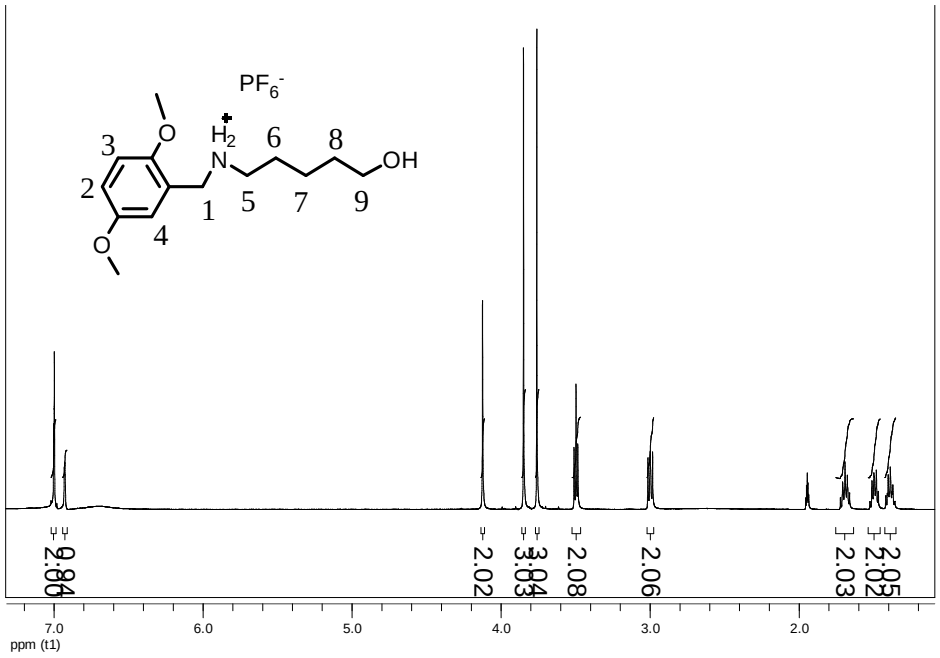


Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, ambient T) of N-(5'-hydroxypentyl)-2,5-dimethoxybenzylammonium hexafluorophosphate (**9**).

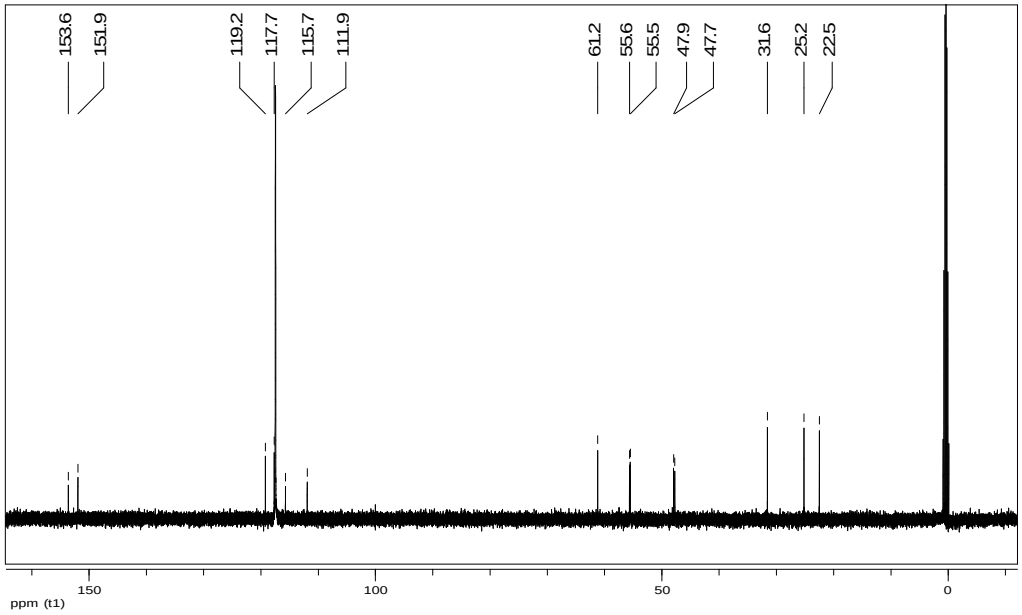


Figure S14. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, ambient T) of N-(5'-hydroxypentyl)-2,5-dimethoxybenzylammonium hexafluorophosphate (**9**).

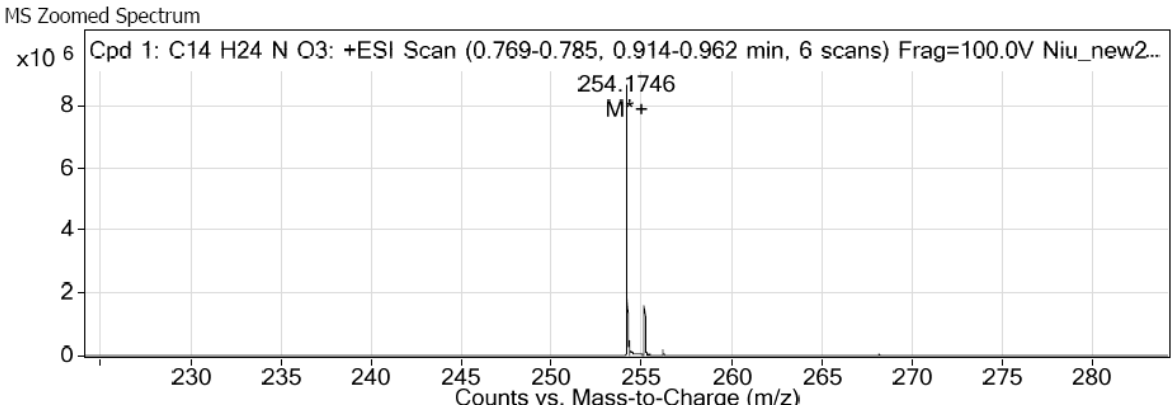


Figure S15. ESI TOF mass spectrum of of N-(5'-hydroxypentyl)-2,5-dimethoxybenzylammonium hexafluorophosphate (**9**).

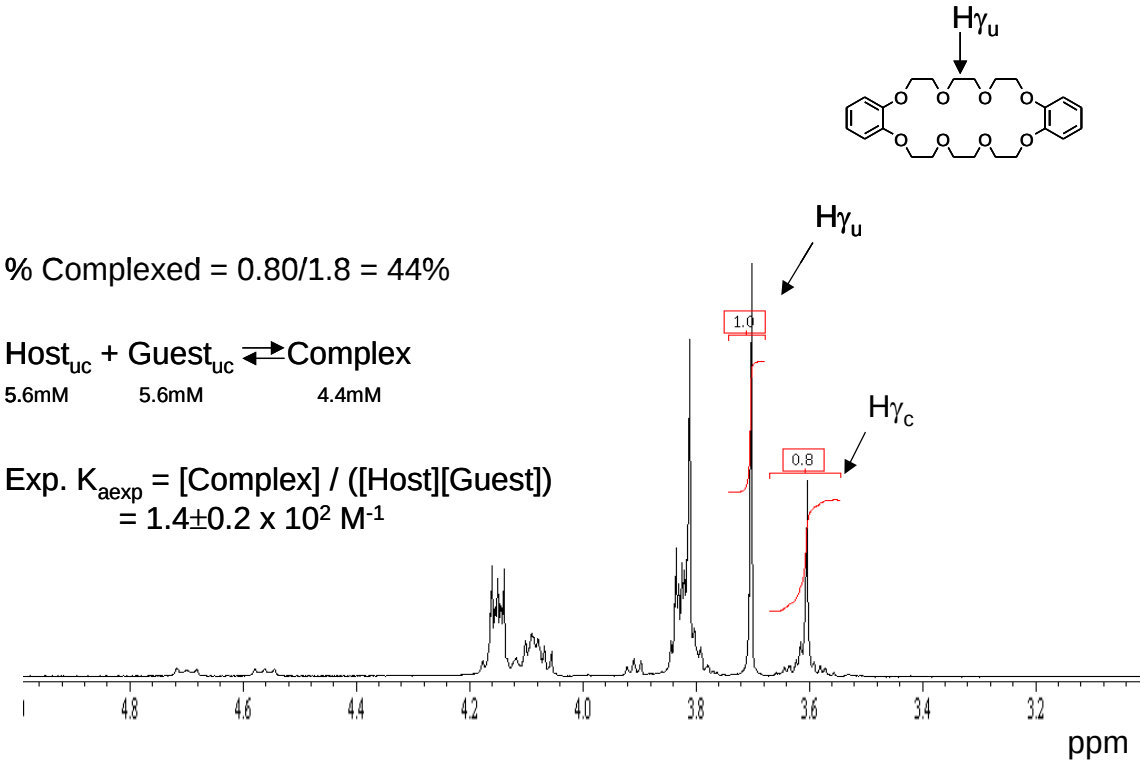


Figure S16. Expanded partial ^{1}H NMR spectrum (400 MHz, ambient T, CD_3CN) of **DB24C8** and **5b** (10 mM each). Determination of K_a for formation of semirotaxane **11**.

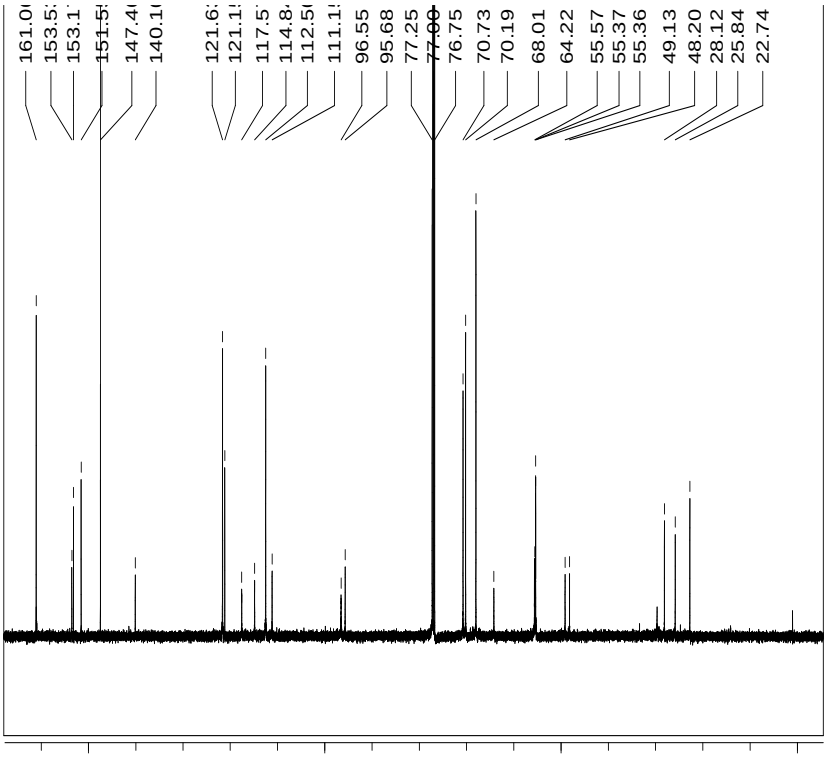


Figure 17. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, ambient T) of an equimolar (10 mM) solution of **DB24C8** and **9**, containing semirotaxane **12**.

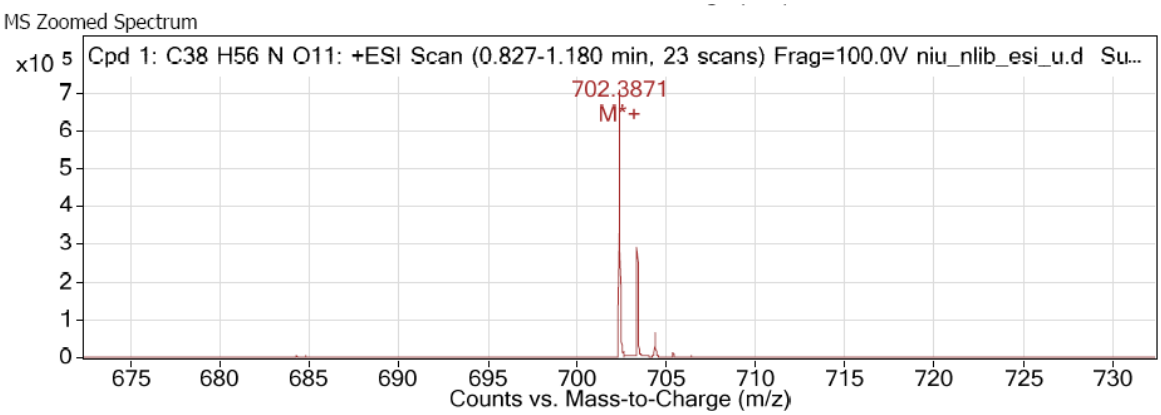


Figure S18. ESI TOF mass spectrum of an equimolar solution of **DB24C8** and **9**, containing semirotaxane **12**.

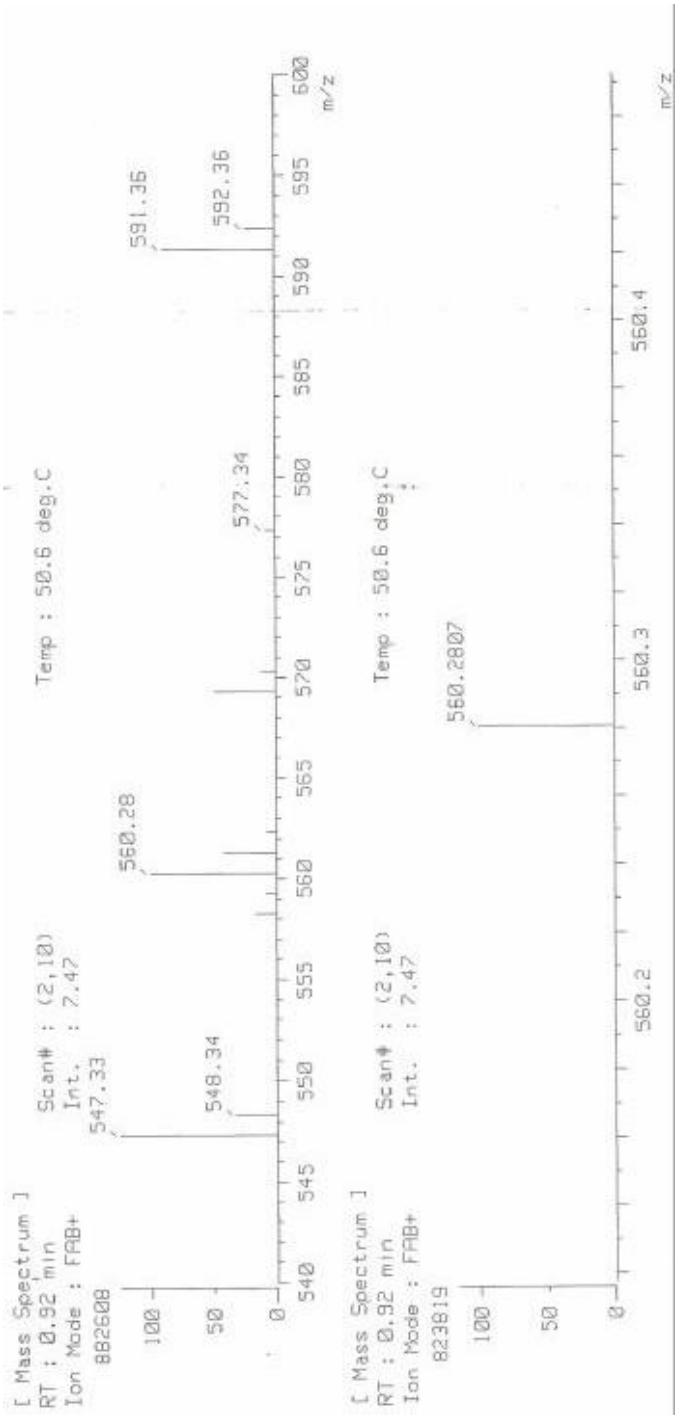


Figure S19. HR FAB mass spectrum of N-*p*-(2'-triphenylmethoxyethoxy)benzyl-3",5"-dimethoxybenzylamine (**13**).

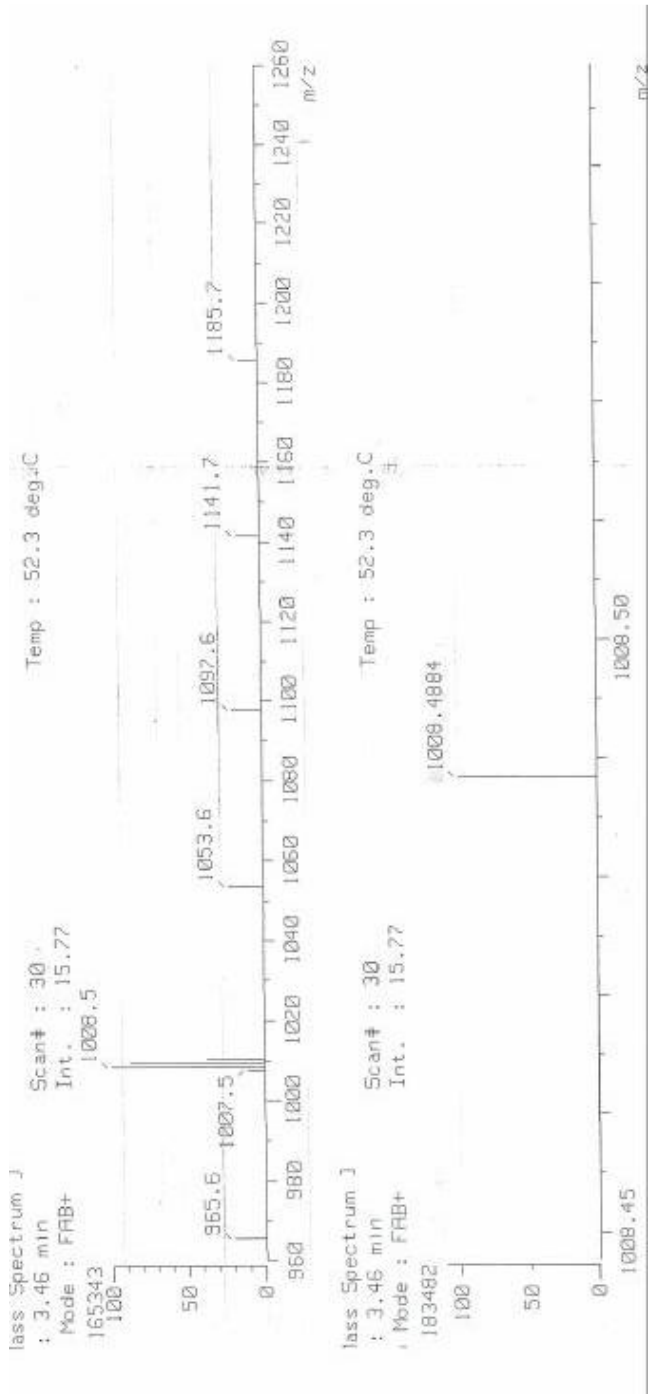


Figure S20. HR FAB mass spectrum of [2]rotaxane **14**.

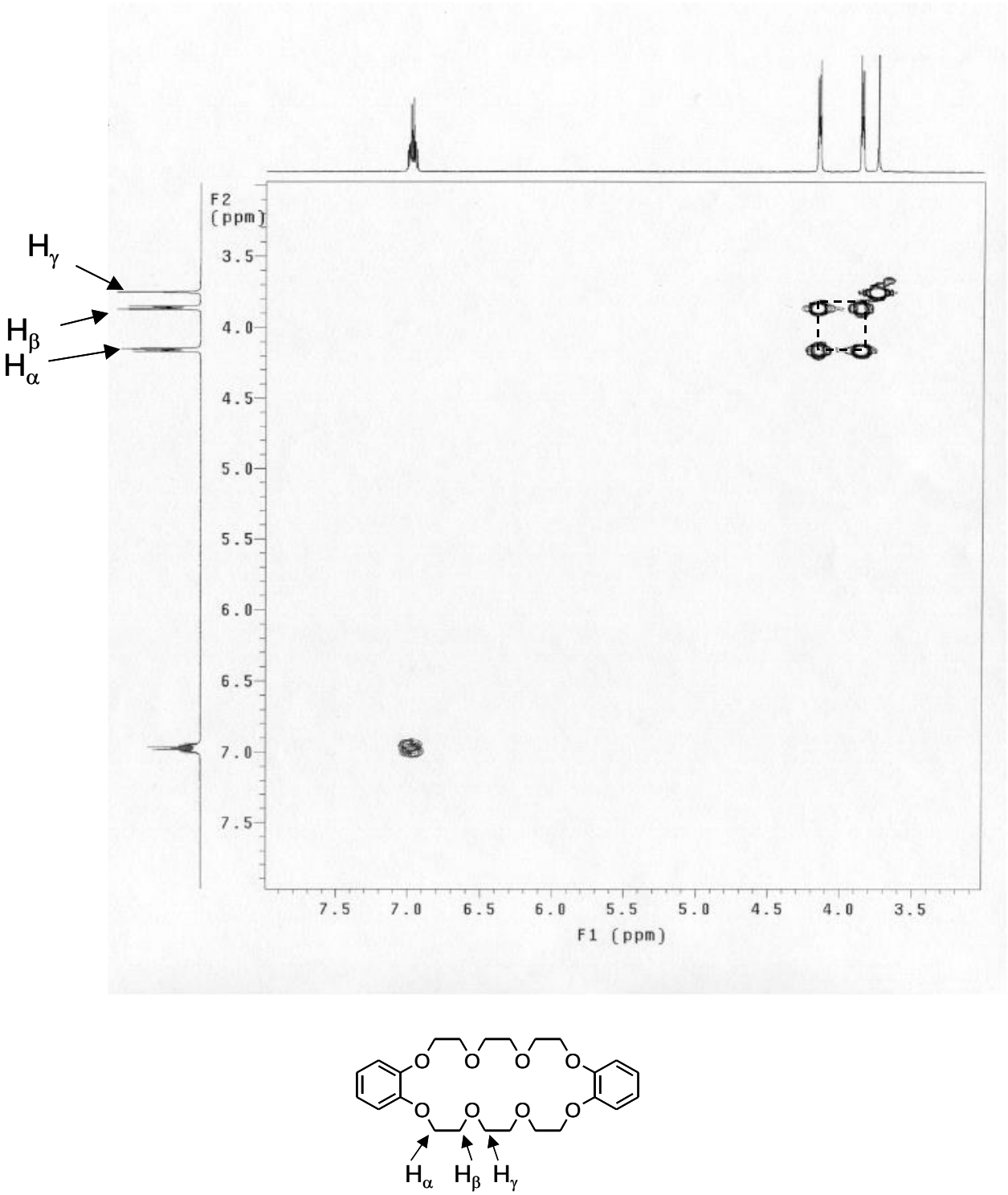
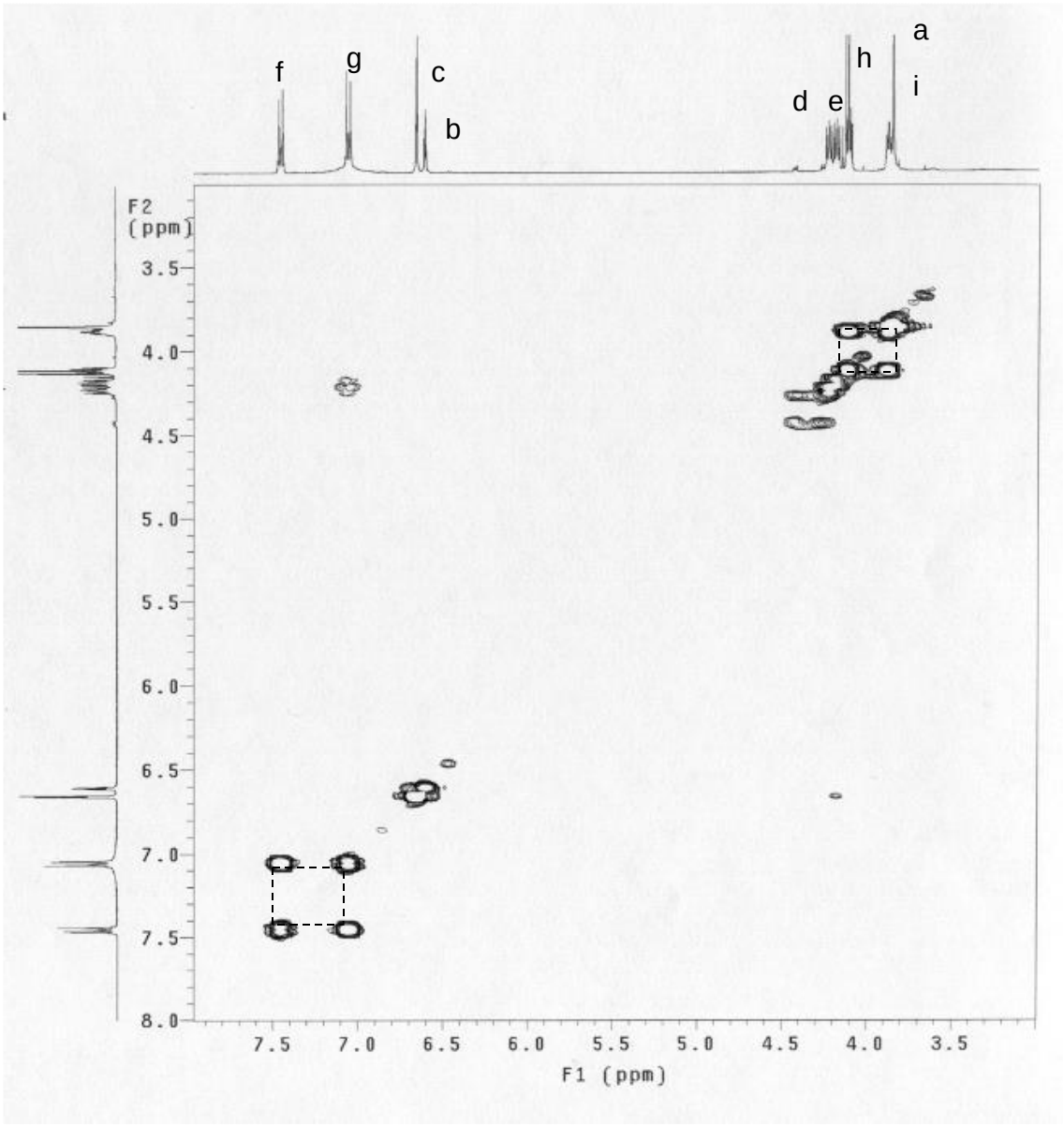


Figure S21. COSY ^{1}H NMR spectrum of **DB24C8** (CD_3CN, 400 MHz, ambient T).



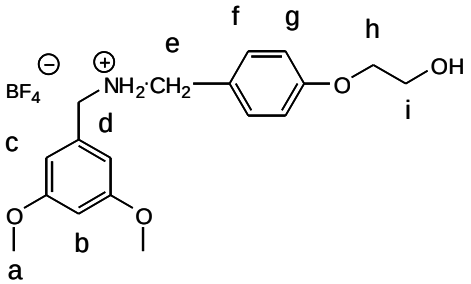


Figure S22. COSY ^{1}H NMR spectrum of BF_4 salt **5a** (CD_3CN, 400 MHz, ambient T).

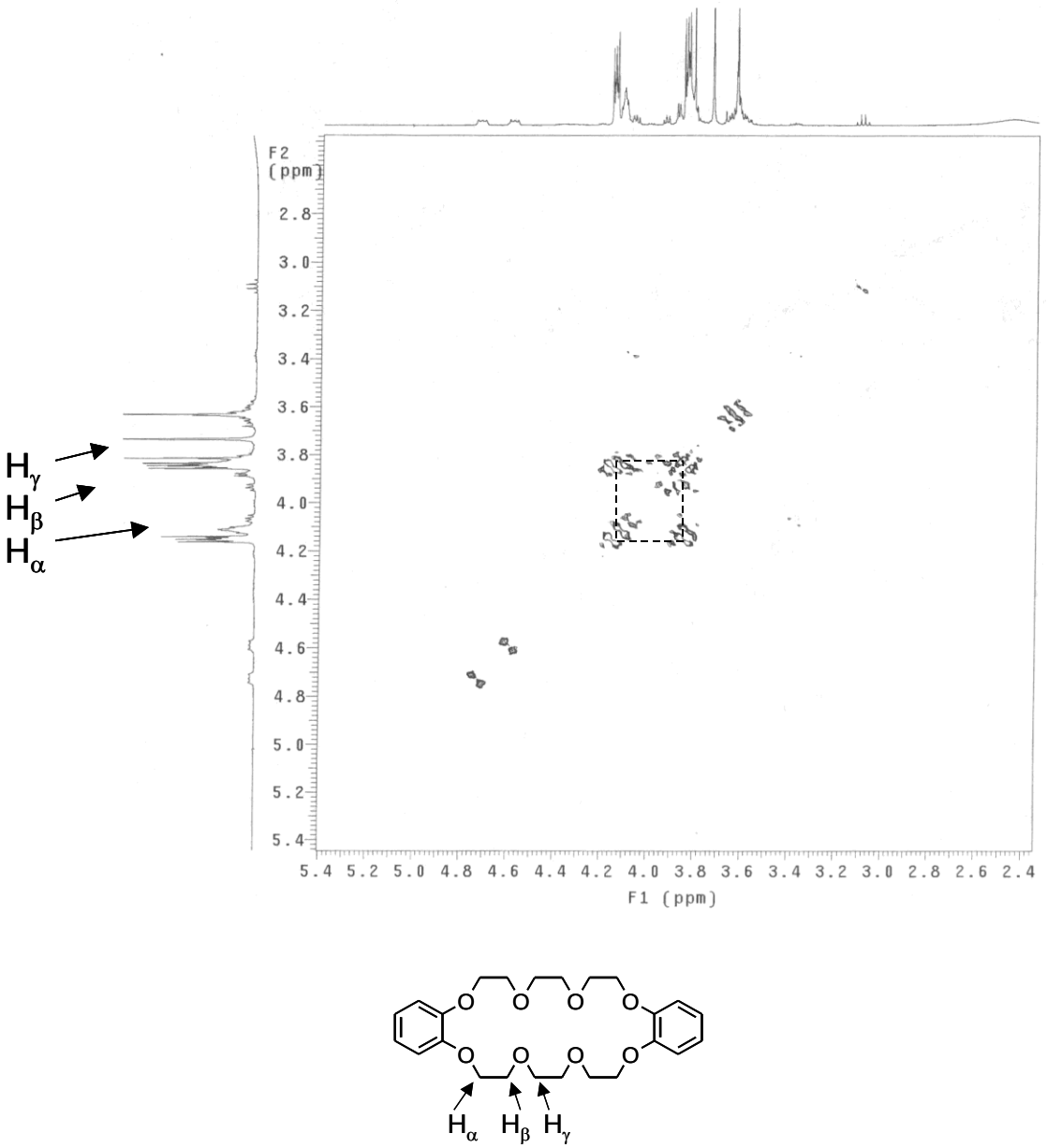


Figure S23. Partial COSY ^{1}H NMR spectrum of [2]rotaxane **14** (2:3 $CD_3CN/CDCl_3$, 400 MHz, ambient T).

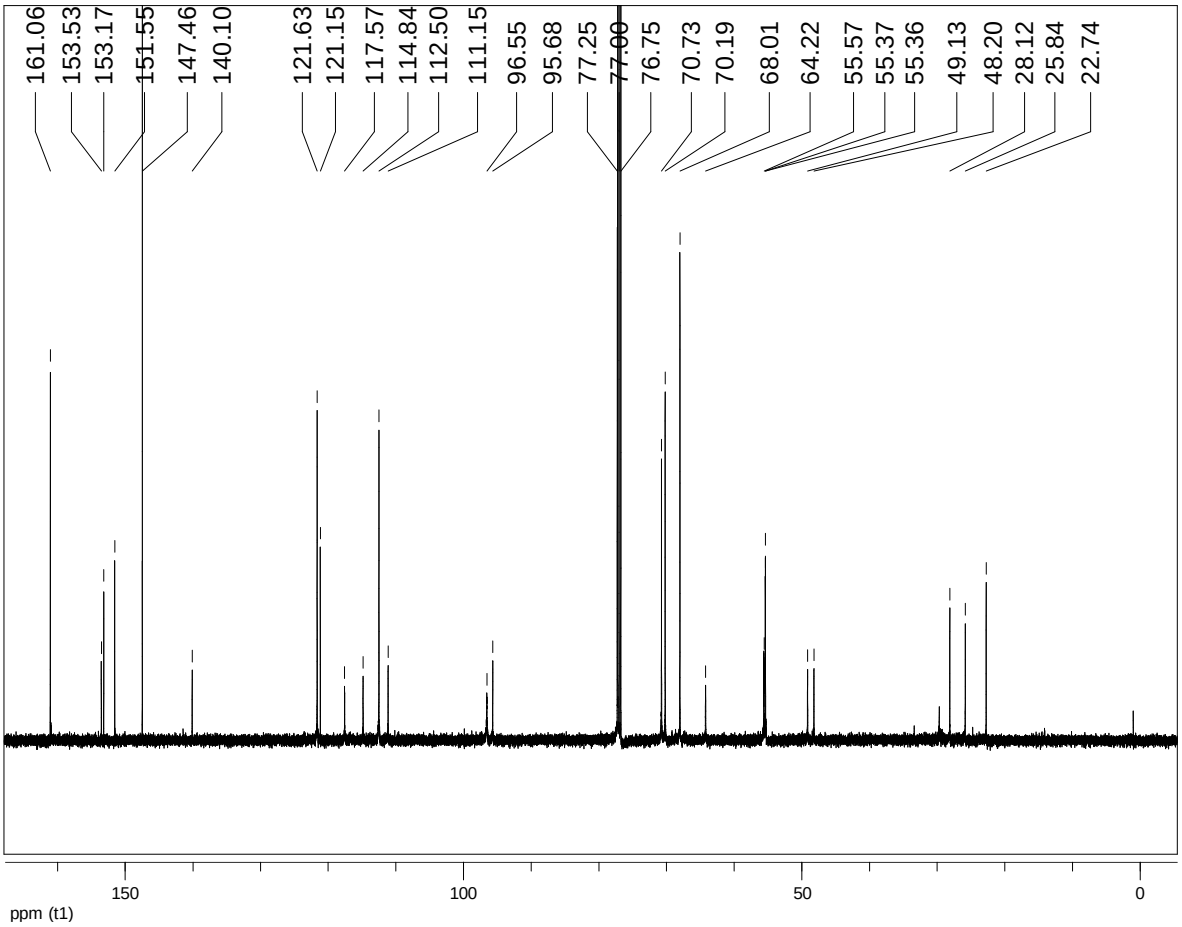


Figure S24. ^{13}C NMR spectrum of [2]rotaxane **15**.

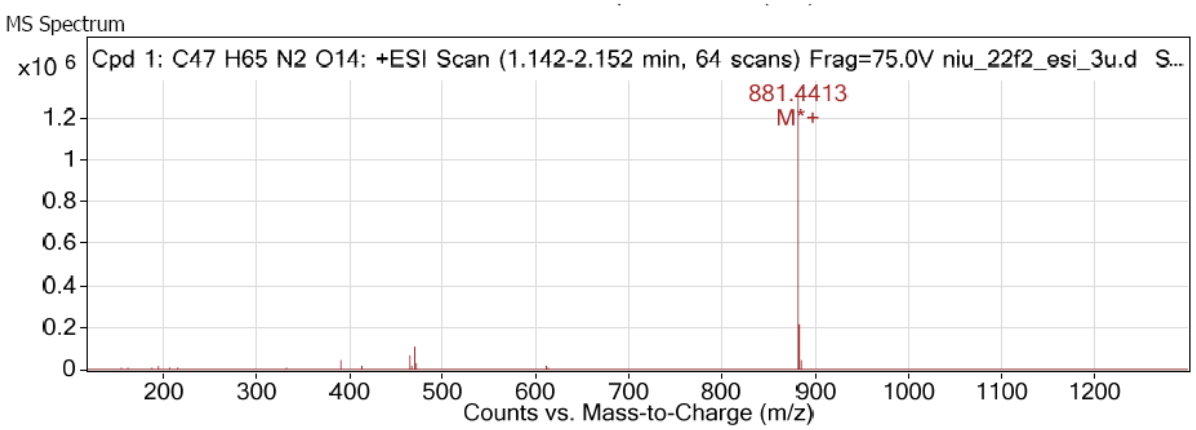


Figure S25. ESI TOF mass spectrum of [2]rotaxane **15**.

CRYSTALLOGRAPHIC DATA FOR SEMIROTAXANE 12.

Experimental

A colorless rod (0.06 x 0.14 x 0.70 mm^3) was centered on the goniometer of an Oxford Diffraction Gemini E Ultra diffractometer operating with MoKα radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.[1] Preliminary unit cell determination suggested a monoclinic C-lattice with unit cell volume, V = 8910 $Å^3$, but data merging statistics (R_{int} = 0.56) proved this assignment wrong. Consequently, the cell was transformed to the primitive lattice with V = 4455 $Å^3$ and solved in the triclinic space group P-1 (R_{int} = 0.072). The structure was solved using SHELXS-97[2] and refined using SHELXL-97[3] via the OLEX2 Program System.[4] The asymmetry unit comprises 2 crystallographically unique host-guest complexes and 2 unique acetone solvates. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms. A riding model was used for all hydrogen atoms, except the hydroxyl hydrogen atom positions that are potentially involved in hydrogen bonding. Analysis of this tricinic P-1 structure (viewed down the b-axis) shows pseudo-inversion symmetry between the two crystallographically unique host, PF_6^- and acetone entities. The two guest molecules, however, have distinctly different geometry, breaking this symmetry. In addition, the ADDSYMM subroutine of the PLATON program package suggests the absence of any higher symmetry in the final model.[5]

Table 1. Crystal data and structure refinement for cs1553.

Identification code	NiuC29-1
Empirical formula	$[C_{24}H_{32}O_8 \bullet C_{14}H_{24}NO_3][PF_6] \bullet C_3H_6O$
Formula weight	905.89
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 13.3554(5) Å □= 113.419(4)°.
	b = 19.7295(8) Å □= 101.358(3)°.
	c = 19.7284(8) Å □ = 101.260(3)°.
Volume	4455.3(3) $Å^3$
Z	4
Density (calculated)	1.351 Mg/m^3
Absorption coefficient	0.147 mm^{-1}
F(000)	1920
Crystal size	0.70 x 0.14 x 0.06 mm^3
Theta range for data collection	3.57 to 27.48°.

(1) CrysAlisPro v171.33.31, Oxford Diffraction: Wroclaw, Poland, 2009.
(2) Sheldrick, G. M. "A short history of SHELX". *Acta Cryst.* **2008**, *A64*, 112-122.
(3) Sheldrick, G. M. "A short history of SHELX". *Acta Cryst.* **2008**, *A64*, 112-122.
(4) Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.
(5) [5] Spek, A. L. "PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands." *J.Appl.Cryst.*, **2003,** *36*, 7-13.

Index ranges	-17<=h<=17, -25<=k<=25, -25<=l<=25
Reflections collected	81645
Independent reflections	20368 [R(int) = 0.0728]
Completeness to theta = 27.48°	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20368 / 0 / 1113
Goodness-of-fit on F^2	0.727
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0685
R indices (all data)	R1 = 0.1070, wR2 = 0.0768
Largest diff. peak and hole	0.429 and -0.316 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for cs1553.

P(1)-F(4)	1.5938(13)	C(15)-C(16)	1.472(3)	O(18)-C(52)	1.376(2)
P(1)-F(5)	1.5986(13)	C(17)-C(18)	1.485(3)	O(18)-C(56)	1.429(2)
P(1)-F(3)	1.6001(11)	C(19)-C(20)	1.498(2)	O(19)-C(62)	1.425(2)
P(1)-F(2)	1.6005(12)	C(21)-C(22)	1.500(2)	N(1)-C(58)	1.498(2)
P(1)-F(6)	1.6008(12)	C(23)-C(24)	1.506(2)	N(1)-C(57)	1.509(2)
P(1)-F(1)	1.6142(12)	O(9)-C(25)	1.382(2)	C(49)-C(54)	1.389(2)
P(2)-F(7)	1.5924(13)	O(9)-C(37)	1.438(2)	C(49)-C(50)	1.396(2)
P(2)-F(8)	1.5958(12)	O(10)-C(38)	1.430(2)	C(50)-C(51)	1.388(2)
P(2)-F(9)	1.5967(12)	O(10)-C(39)	1.432(2)	C(50)-C(57)	1.501(2)
P(2)-F(12)	1.5987(11)	O(11)-C(40)	1.429(2)	C(51)-C(52)	1.390(2)
P(2)-F(11)	1.6026(12)	O(11)-C(41)	1.430(2)	C(52)-C(53)	1.390(2)
P(2)-F(10)	1.6045(13)	O(12)-C(31)	1.375(2)	C(53)-C(54)	1.387(3)
O(1)-C(1)	1.392(2)	O(12)-C(42)	1.438(2)	C(58)-C(59)	1.518(3)
O(1)-C(13)	1.440(2)	O(13)-C(26)	1.378(2)	C(59)-C(60)	1.503(3)
O(2)-C(14)	1.417(2)	O(13)-C(43)	1.426(2)	C(60)-C(61)	1.542(3)
O(2)-C(15)	1.429(2)	O(14)-C(44)	1.415(2)	C(61)-C(62)	1.521(3)
O(3)-C(17)	1.418(2)	O(14)-C(45)	1.432(2)	O(20)-C(64)	1.374(2)
O(3)-C(16)	1.421(2)	O(15)-C(47)	1.416(2)	O(20)-C(69)	1.431(2)
O(4)-C(7)	1.375(2)	O(15)-C(46)	1.446(2)	O(21)-C(66)	1.378(2)
O(4)-C(18)	1.432(2)	O(16)-C(32)	1.389(2)	O(21)-C(70)	1.428(2)
O(5)-C(2)	1.376(2)	O(16)-C(48)	1.441(2)	O(22)-C(75)	1.428(2)
O(5)-C(19)	1.443(2)	C(25)-C(30)	1.378(2)	N(2)-C(72)	1.500(2)
O(6)-C(22)	1.428(2)	C(25)-C(26)	1.402(2)	N(2)-C(71)	1.509(2)
O(6)-C(20)	1.428(2)	C(26)-C(27)	1.386(2)	C(63)-C(65)	1.384(2)
O(7)-C(23)	1.429(2)	C(27)-C(28)	1.393(2)	C(63)-C(64)	1.396(2)
O(7)-C(21)	1.430(2)	C(28)-C(29)	1.375(3)	C(63)-C(71)	1.503(2)
O(8)-C(8)	1.374(2)	C(29)-C(30)	1.395(3)	C(64)-C(68)	1.391(2)
O(8)-C(24)	1.436(2)	C(31)-C(36)	1.394(2)	C(65)-C(66)	1.388(2)
C(1)-C(6)	1.370(3)	C(31)-C(32)	1.396(3)	C(66)-C(67)	1.388(2)
C(1)-C(2)	1.395(3)	C(32)-C(33)	1.381(3)	C(67)-C(68)	1.385(3)
C(2)-C(3)	1.392(2)	C(33)-C(34)	1.401(3)	C(72)-C(73)	1.521(2)
C(3)-C(4)	1.381(3)	C(34)-C(35)	1.366(3)	C(73)-C(74)	1.523(2)
C(4)-C(5)	1.361(3)	C(35)-C(36)	1.388(3)	C(74)-C(76)	1.538(3)
C(5)-C(6)	1.390(3)	C(37)-C(38)	1.509(2)	C(75)-C(76)	1.499(3)
C(7)-C(12)	1.383(2)	C(39)-C(40)	1.492(2)	O(23)-C(81)	1.214(3)
C(7)-C(8)	1.410(2)	C(41)-C(42)	1.487(3)	C(80)-C(81)	1.484(4)
C(8)-C(9)	1.376(2)	C(43)-C(44)	1.499(3)	C(81)-C(82)	1.479(3)
C(9)-C(10)	1.395(3)	C(45)-C(46)	1.473(3)	O(24)-C(78)	1.215(3)
C(10)-C(11)	1.379(3)	C(47)-C(48)	1.490(2)	C(77)-C(78)	1.487(3)
C(11)-C(12)	1.387(3)	O(17)-C(49)	1.376(2)	C(78)-C(79)	1.490(3)
C(13)-C(14)	1.486(3)	O(17)-C(55)	1.434(2)		

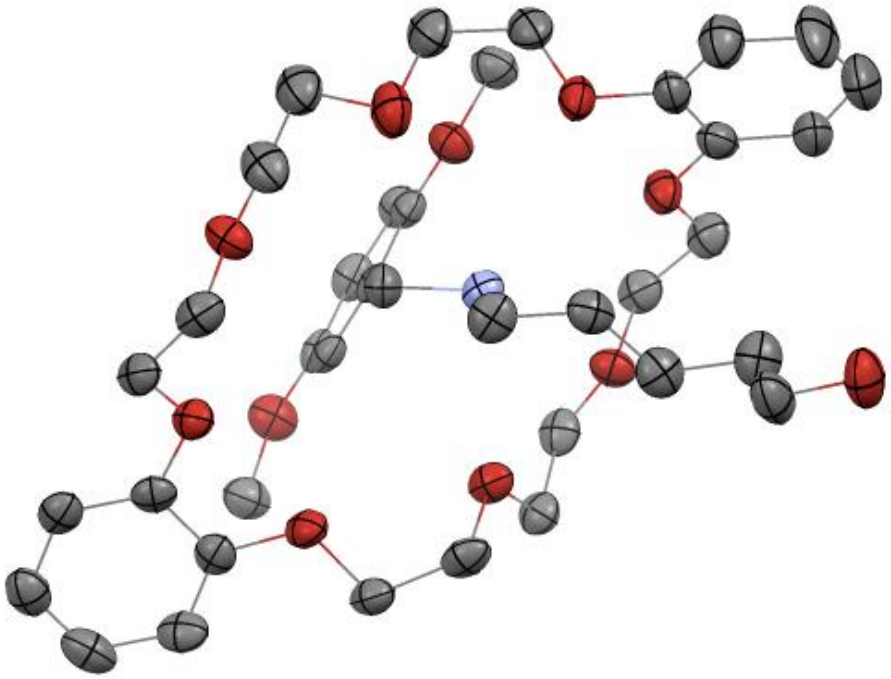
F(4)-P(1)-F(5)	90.42(7)
F(4)-P(1)-F(3)	90.44(6)
F(5)-P(1)-F(3)	90.26(7)
F(4)-P(1)-F(2)	90.42(7)
F(5)-P(1)-F(2)	179.16(8)
F(3)-P(1)-F(2)	89.73(6)
F(4)-P(1)-F(6)	90.07(7)
F(5)-P(1)-F(6)	90.38(7)
F(3)-P(1)-F(6)	179.18(8)
F(2)-P(1)-F(6)	89.63(6)
F(4)-P(1)-F(1)	179.56(7)
F(5)-P(1)-F(1)	89.28(7)
F(3)-P(1)-F(1)	89.88(6)
F(2)-P(1)-F(1)	89.89(6)
F(6)-P(1)-F(1)	89.62(7)
F(7)-P(2)-F(8)	90.30(7)
F(7)-P(2)-F(9)	90.04(7)
F(8)-P(2)-F(9)	90.17(7)
F(7)-P(2)-F(12)	90.50(7)
F(8)-P(2)-F(12)	90.08(7)
F(9)-P(2)-F(12)	179.41(8)
F(7)-P(2)-F(11)	90.40(7)
F(8)-P(2)-F(11)	179.28(8)
F(9)-P(2)-F(11)	90.00(7)
F(12)-P(2)-F(11)	89.75(6)
F(7)-P(2)-F(10)	179.66(8)
F(8)-P(2)-F(10)	89.46(7)
F(9)-P(2)-F(10)	89.72(7)
F(12)-P(2)-F(10)	89.74(7)
F(11)-P(2)-F(10)	89.84(7)
C(1)-O(1)-C(13)	115.04(15)
C(14)-O(2)-C(15)	111.15(14)
C(17)-O(3)-C(16)	110.70(15)
C(7)-O(4)-C(18)	116.05(14)
C(2)-O(5)-C(19)	115.77(14)
C(22)-O(6)-C(20)	111.12(13)
C(23)-O(7)-C(21)	112.50(13)
C(8)-O(8)-C(24)	116.15(13)
C(6)-C(1)-O(1)	123.91(19)
C(6)-C(1)-C(2)	119.72(19)
O(1)-C(1)-C(2)	116.37(17)
O(5)-C(2)-C(3)	124.40(17)
O(5)-C(2)-C(1)	116.67(17)
C(3)-C(2)-C(1)	118.93(18)
C(4)-C(3)-C(2)	120.6(2)
C(5)-C(4)-C(3)	120.2(2)
C(4)-C(5)-C(6)	119.9(2)
C(1)-C(6)-C(5)	120.7(2)
O(4)-C(7)-C(12)	124.65(16)
O(4)-C(7)-C(8)	115.76(16)
C(12)-C(7)-C(8)	119.59(17)
O(8)-C(8)-C(9)	124.79(16)
O(8)-C(8)-C(7)	115.57(16)
C(9)-C(8)-C(7)	119.64(17)
C(8)-C(9)-C(10)	120.25(18)
C(11)-C(10)-C(9)	120.11(19)
C(10)-C(11)-C(12)	120.03(19)
C(7)-C(12)-C(11)	120.35(18)
O(1)-C(13)-C(14)	110.38(16)
O(2)-C(14)-C(13)	111.20(19)
O(2)-C(15)-C(16)	110.14(16)
O(3)-C(16)-C(15)	109.95(17)
O(3)-C(17)-C(18)	110.45(16)
O(4)-C(18)-C(17)	109.24(15)
O(5)-C(19)-C(20)	108.87(14)
O(6)-C(20)-C(19)	109.49(15)
O(7)-C(21)-C(22)	108.74(14)
O(6)-C(22)-C(21)	108.28(15)
O(7)-C(23)-C(24)	112.71(15)
O(8)-C(24)-C(23)	106.82(14)
C(25)-O(9)-C(37)	116.55(13)
C(38)-O(10)-C(39)	112.10(13)
C(40)-O(11)-C(41)	111.43(14)
C(31)-O(12)-C(42)	116.49(14)
C(26)-O(13)-C(43)	116.42(14)
C(44)-O(14)-C(45)	110.80(14)
C(47)-O(15)-C(46)	110.36(14)
C(32)-O(16)-C(48)	115.45(13)
C(30)-C(25)-O(9)	125.09(16)
C(30)-C(25)-C(26)	119.81(17)
O(9)-C(25)-C(26)	115.10(16)
O(13)-C(26)-C(27)	124.42(16)
O(13)-C(26)-C(25)	115.44(16)
C(27)-C(26)-C(25)	120.14(17)
C(26)-C(27)-C(28)	119.63(17)
C(29)-C(28)-C(27)	120.08(18)

C(28)-C(29)-C(30) 120.58(18)
C(25)-C(30)-C(29) 119.76(17)
O(12)-C(31)-C(36) 124.34(17)
O(12)-C(31)-C(32) 116.19(16)
C(36)-C(31)-C(32) 119.47(17)
C(33)-C(32)-O(16) 123.49(17)
C(33)-C(32)-C(31) 120.12(17)
O(16)-C(32)-C(31) 116.39(16)
C(32)-C(33)-C(34) 119.83(19)
C(35)-C(34)-C(33) 120.06(19)
C(34)-C(35)-C(36) 120.63(19)
C(35)-C(36)-C(31) 119.83(19)
O(9)-C(37)-C(38) 106.66(14)
O(10)-C(38)-C(37) 112.96(15)
O(10)-C(39)-C(40) 108.88(14)
O(11)-C(40)-C(39) 108.77(15)
O(11)-C(41)-C(42) 109.30(15)
O(12)-C(42)-C(41) 108.96(15)
O(13)-C(43)-C(44) 109.02(15)
O(14)-C(44)-C(43) 109.76(16)
O(14)-C(45)-C(46) 109.86(16)
O(15)-C(46)-C(45) 109.41(16)
O(15)-C(47)-C(48) 109.84(16)
O(16)-C(48)-C(47) 110.32(15)
C(49)-O(17)-C(55) 118.04(15)
C(52)-O(18)-C(56) 116.55(14)
C(58)-N(1)-C(57) 111.62(13)
O(17)-C(49)-C(54) 125.30(17)
O(17)-C(49)-C(50) 114.74(17)
C(54)-C(49)-C(50) 119.96(17)
C(51)-C(50)-C(49) 119.66(17)
C(51)-C(50)-C(57) 119.97(16)
C(49)-C(50)-C(57) 120.38(17)
C(50)-C(51)-C(52) 120.52(17)
O(18)-C(52)-C(53) 116.22(17)
O(18)-C(52)-C(51) 124.33(17)
C(53)-C(52)-C(51) 119.45(18)
C(54)-C(53)-C(52) 120.46(18)
C(53)-C(54)-C(49) 119.93(18)
C(50)-C(57)-N(1) 111.45(14)
N(1)-C(58)-C(59) 113.73(15)
C(60)-C(59)-C(58) 117.03(17)
C(59)-C(60)-C(61) 112.83(17)
C(62)-C(61)-C(60) 115.43(16)
O(19)-C(62)-C(61) 107.67(16)
C(64)-O(20)-C(69) 118.31(15)
C(66)-O(21)-C(70) 116.05(14)
C(72)-N(2)-C(71) 111.28(13)
C(65)-C(63)-C(64) 120.21(17)
C(65)-C(63)-C(71) 119.39(16)
C(64)-C(63)-C(71) 120.40(16)
O(20)-C(64)-C(68) 125.50(17)
O(20)-C(64)-C(63) 114.82(16)
C(68)-C(64)-C(63) 119.68(17)
C(63)-C(65)-C(66) 120.08(17)
O(21)-C(66)-C(67) 116.35(17)
O(21)-C(66)-C(65) 124.07(17)
C(67)-C(66)-C(65) 119.59(17)
C(68)-C(67)-C(66) 120.75(18)
C(67)-C(68)-C(64) 119.68(18)
C(63)-C(71)-N(2) 111.58(14)
N(2)-C(72)-C(73) 112.86(15)
C(72)-C(73)-C(74) 115.73(15)
C(73)-C(74)-C(76) 112.37(15)
O(22)-C(75)-C(76) 108.65(16)
C(75)-C(76)-C(74) 113.09(16)
O(23)-C(81)-C(82) 120.3(3)
O(23)-C(81)-C(80) 121.0(3)
C(82)-C(81)-C(80) 118.6(3)
O(24)-C(78)-C(77) 121.0(2)
O(24)-C(78)-C(79) 120.9(2)
C(77)-C(78)-C(79) 118.1(2)

Table 3. Hydrogen bonds for cs1553 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(19)-H(19)...O(22)#1	0.88(2)	2.00(2)	2.8237(19)	156(2)
N(1)-H(1B)...O(17)	0.92	2.32	2.8922(19)	119.7
N(1)-H(1B)...O(1)	0.92	2.35	3.1445(19)	144.2
N(1)-H(1B)...O(5)	0.92	2.37	3.1032(19)	136.5
N(1)-H(1A)...O(7)	0.92	2.17	2.9160(18)	138.1
N(1)-H(1A)...O(6)	0.92	2.29	3.0905(19)	144.9
N(2)-H(2A)...O(10)	0.92	2.26	2.9800(18)	134.3
N(2)-H(2A)...O(11)	0.92	2.35	3.1814(19)	150.9
N(2)-H(2B)...O(16)	0.92	2.33	3.1765(18)	153.2
N(2)-H(2B)...O(20)	0.92	2.35	2.8910(19)	117.2
N(2)-H(2B)...O(12)	0.92	2.57	3.2433(19)	130.1

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z-1



Thermal ellipsoid representation at the 80% confidence level; hydrogen atoms deleted for clarity.