Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Understanding the Driving Force for Molecular Recognition of S_6-Corona[3]arene[3]pyridazine toward Organic Ammonium Cations

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1. HRMS (ESI-ion trap) of the host guest complexes

[**1**+**G1**-PF_6]$^+$ = [$C_{61}H_{66}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1280.3088 Found, m/z = 1280.30765

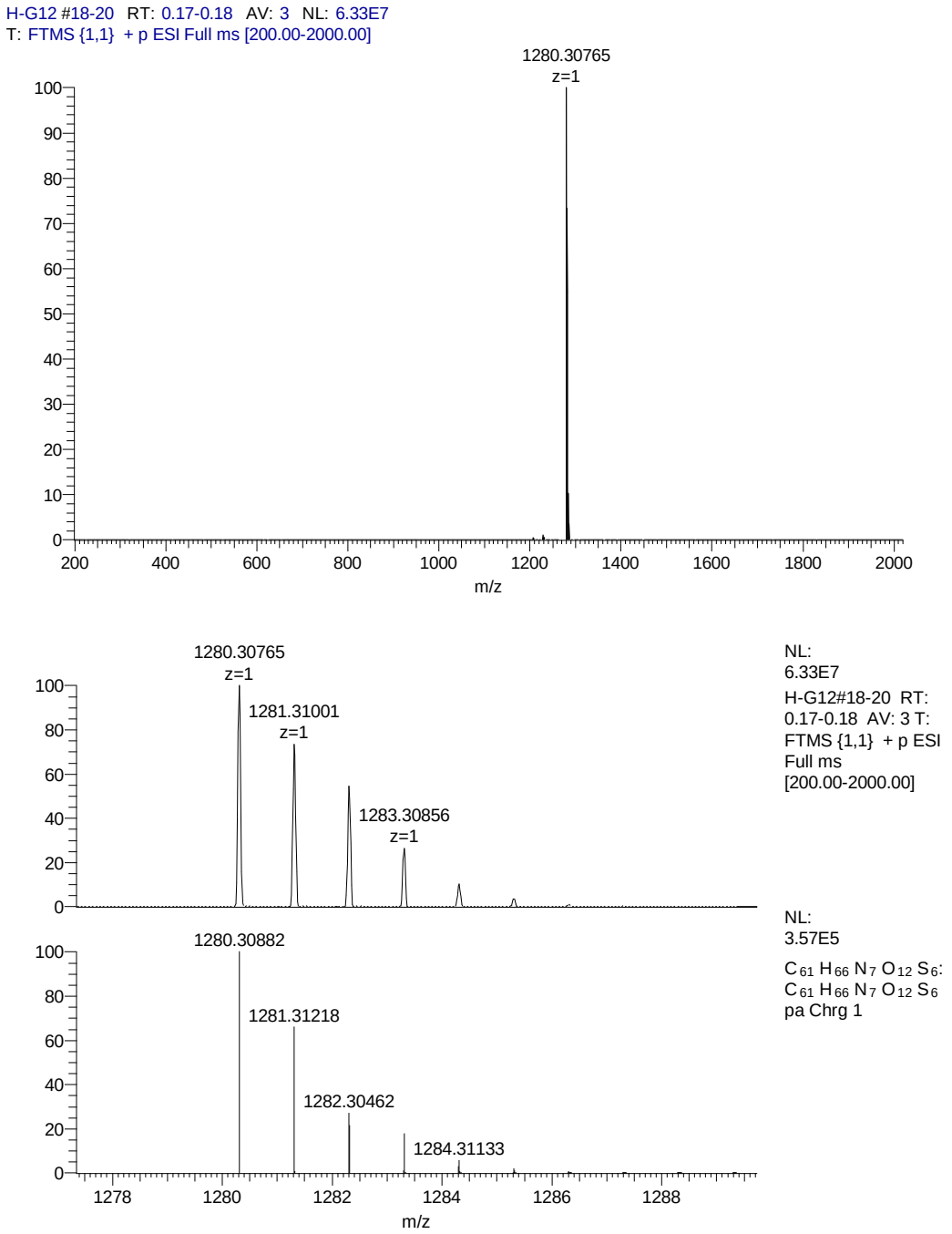


Figure S1. HRMS of **1+G1**

[**1**+**G2**-PF_6]$^+$ = [$C_{62}H_{68}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1294.3245 Found, m/z = 1294.32351

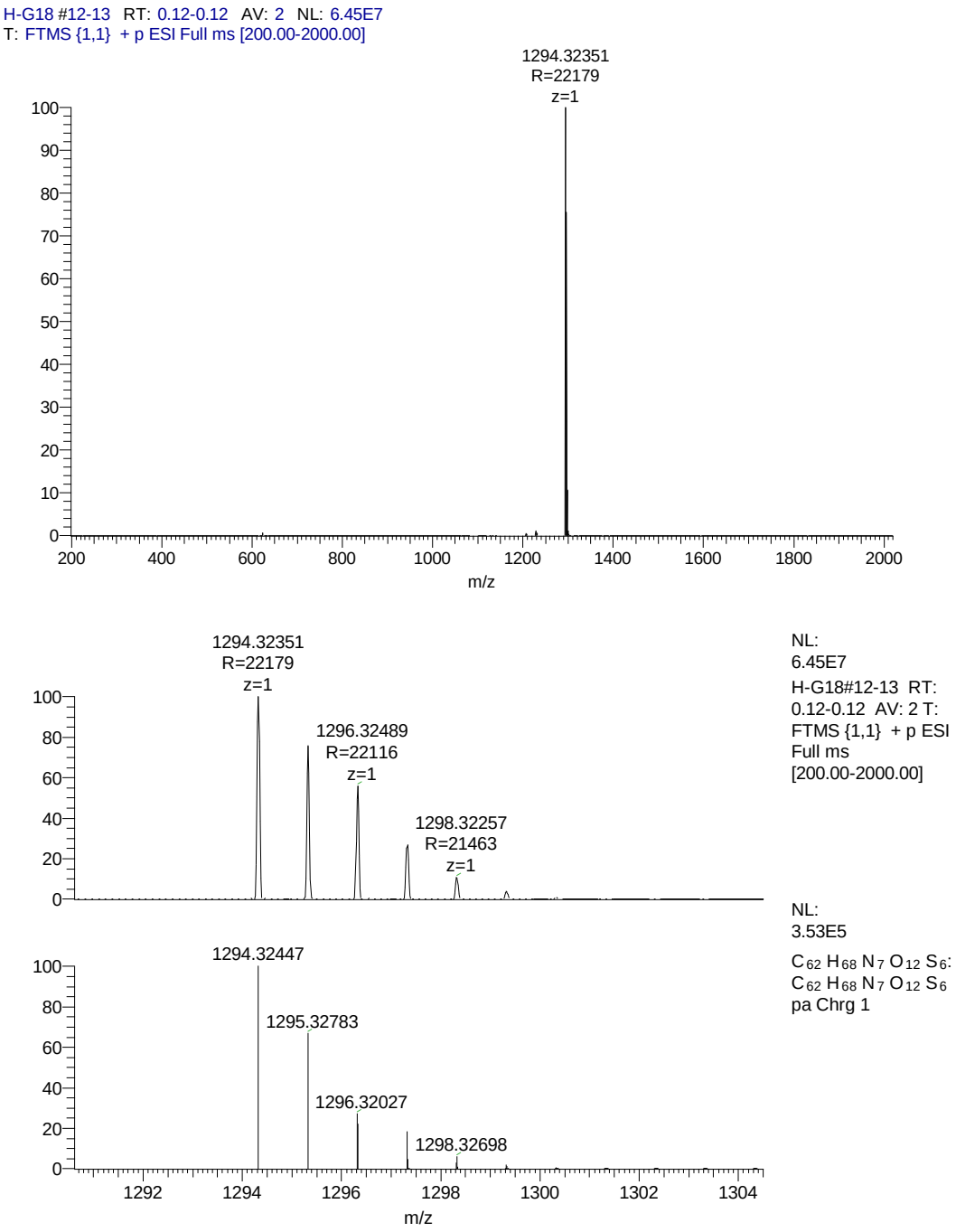


Figure S2. HRMS of **1+G2**

[**1**+**G3**-PF_6]$^+$ = [$C_{64}H_{72}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1322.3558 Found, m/z = 1322.35355

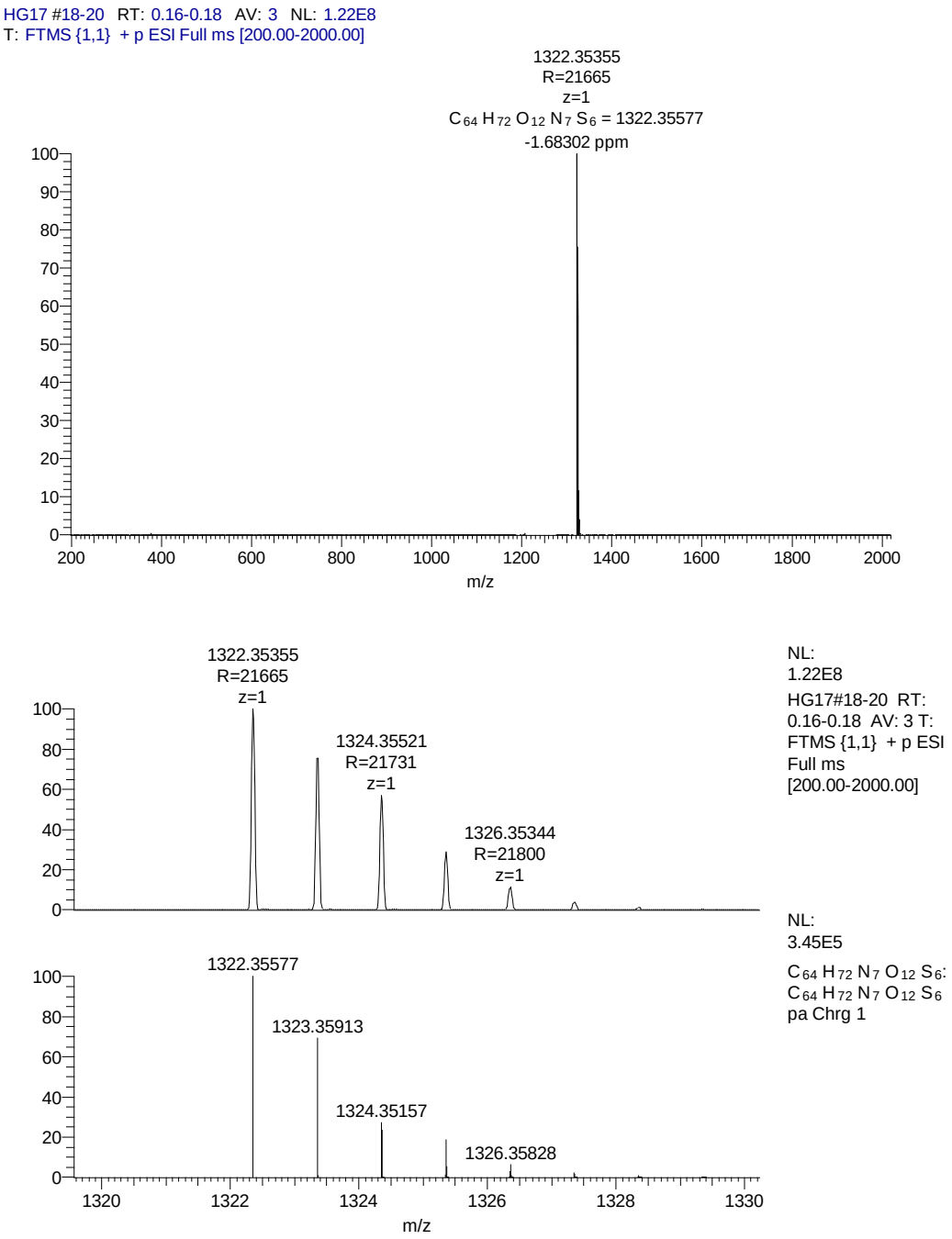


Figure S3. HRMS of **1+G3**

[**1**+**G4**-PF_6]$^+$ = [$C_{66}H_{76}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1350.3871 Found, m/z=1350.38635

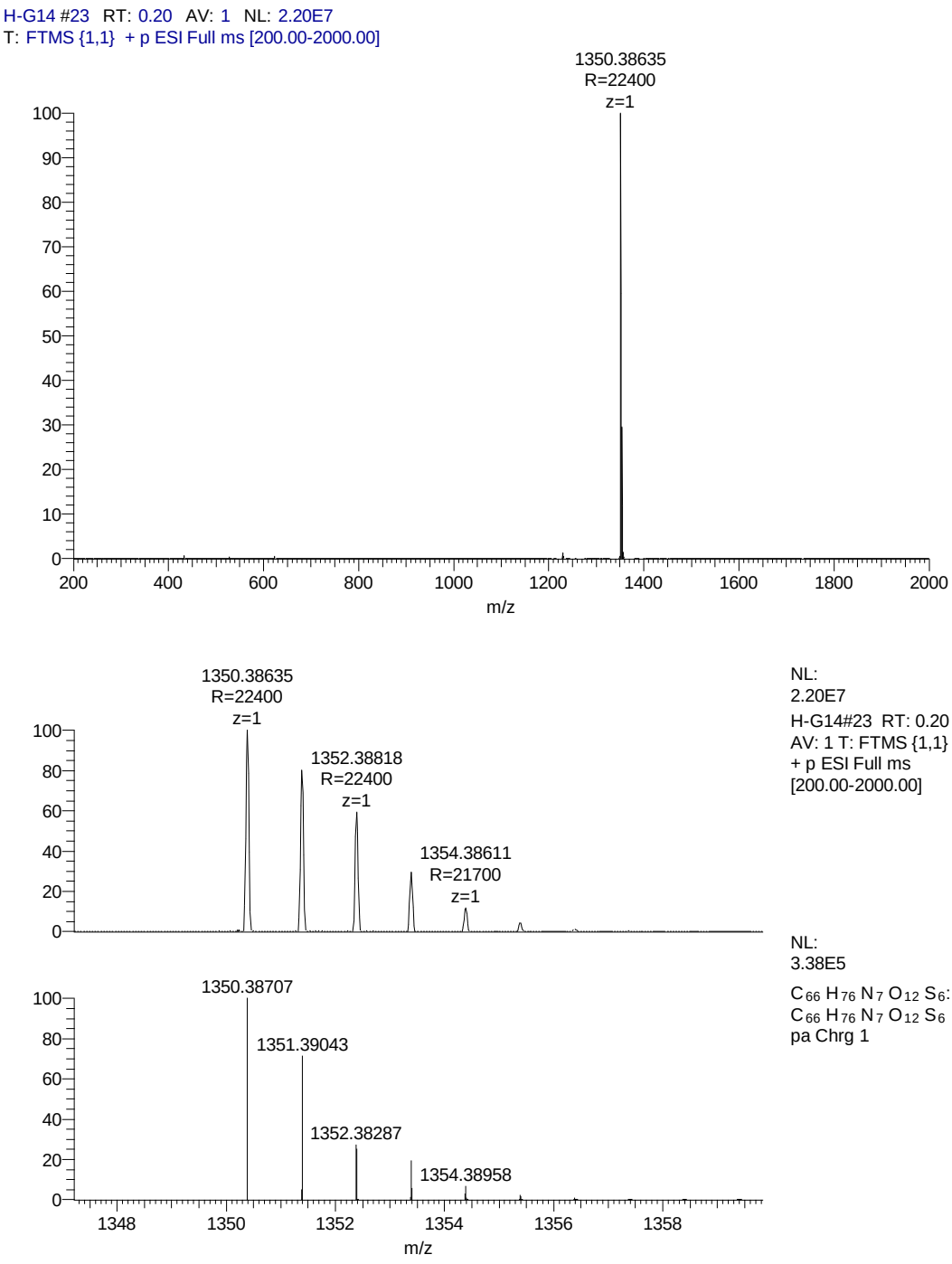


Figure S4. HRMS of **1+G4**

[**1**+**G5**-PF_6]$^+$ = [$C_{66}H_{68}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1342.3245 Found, m/z = 1342.32407

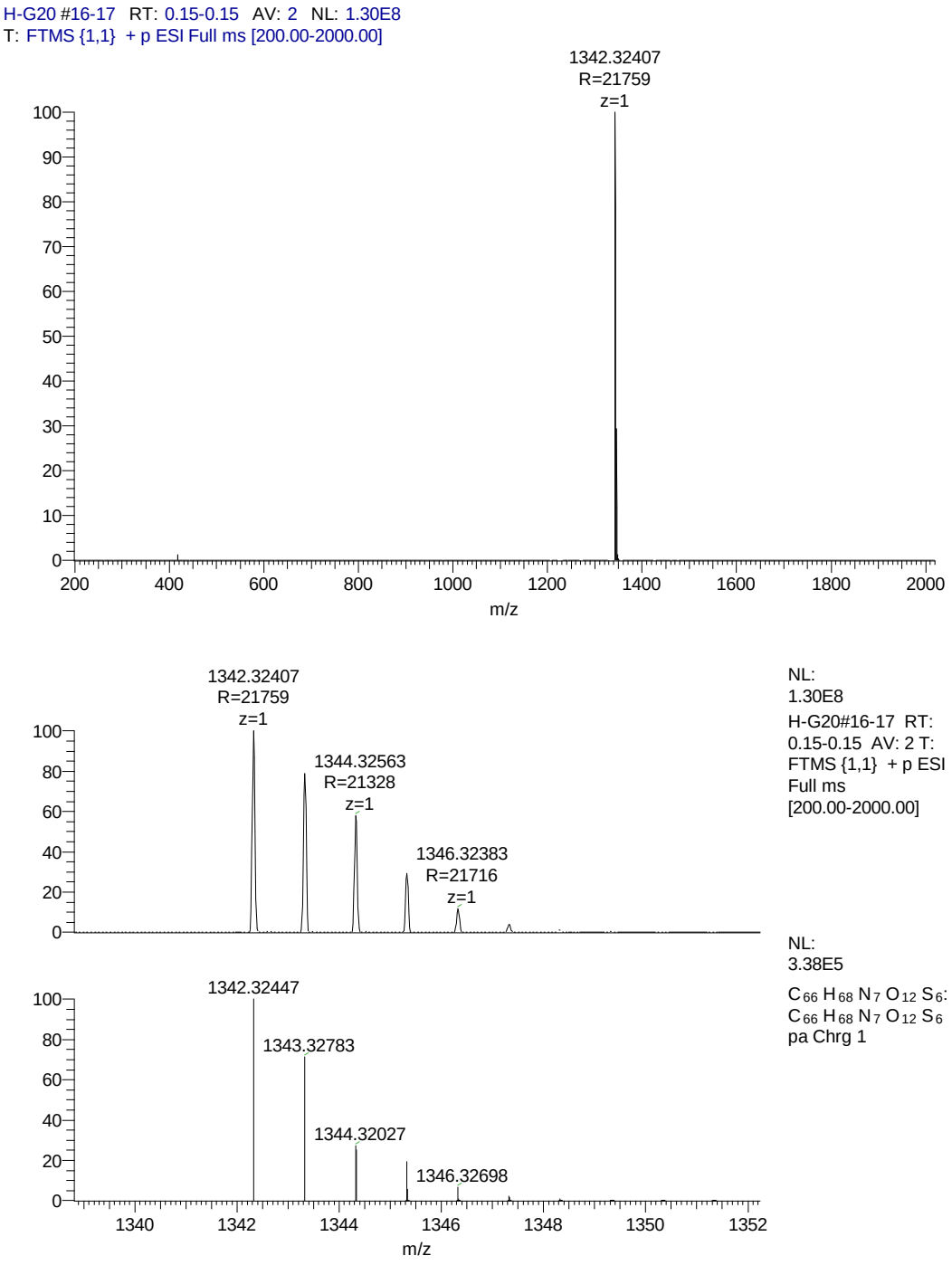


Figure S5. HRMS of **1+G5**

[**1**+**G6**-PF_6]$^+$ = [$C_{67}H_{70}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1356.3401 Found, m/z = 1356.33889

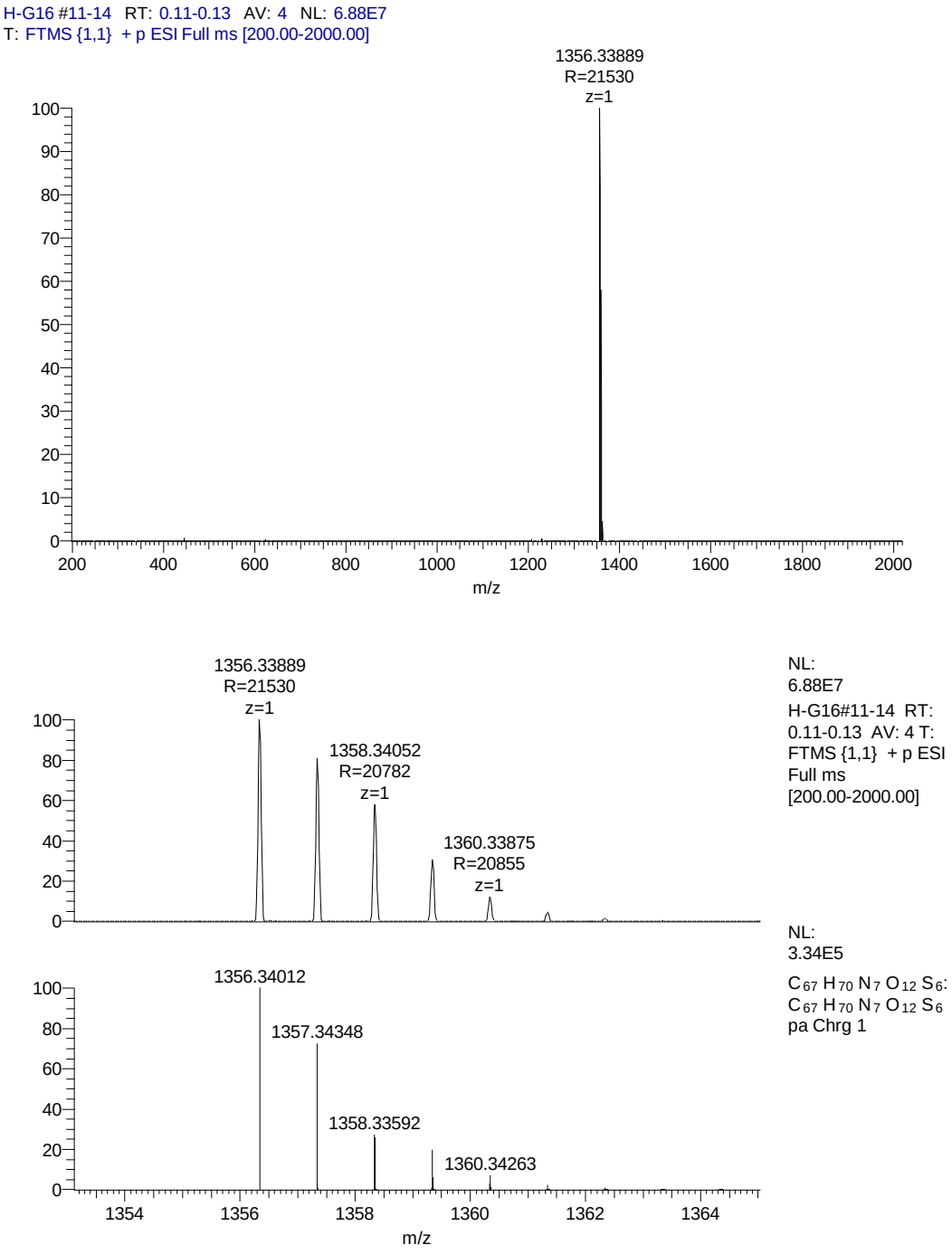


Figure S6. HRMS of **1+G6**

[**1**+**G7**-PF_6]$^+$ = [$C_{68}H_{72}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1370.3558 Found, m/z = 1370.35511

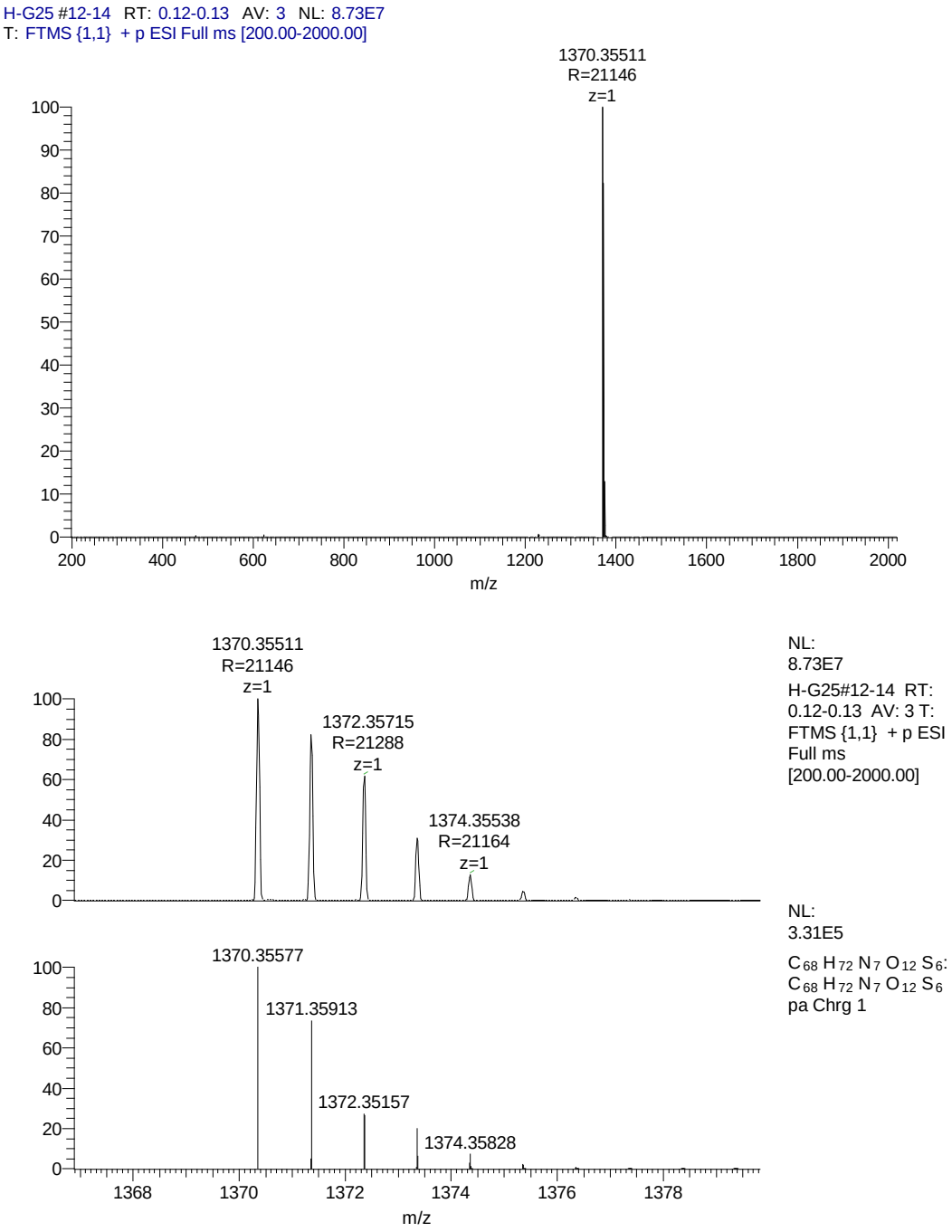


Figure S7. HRMS of **1+G7**

[**1**+**G8**-PF_6]$^+$ = [$C_{64}H_{70}N_7O_{14}S_6$]$^+$ Calcd. m/z = 1352.32995 Found, m/z = 1352.32802

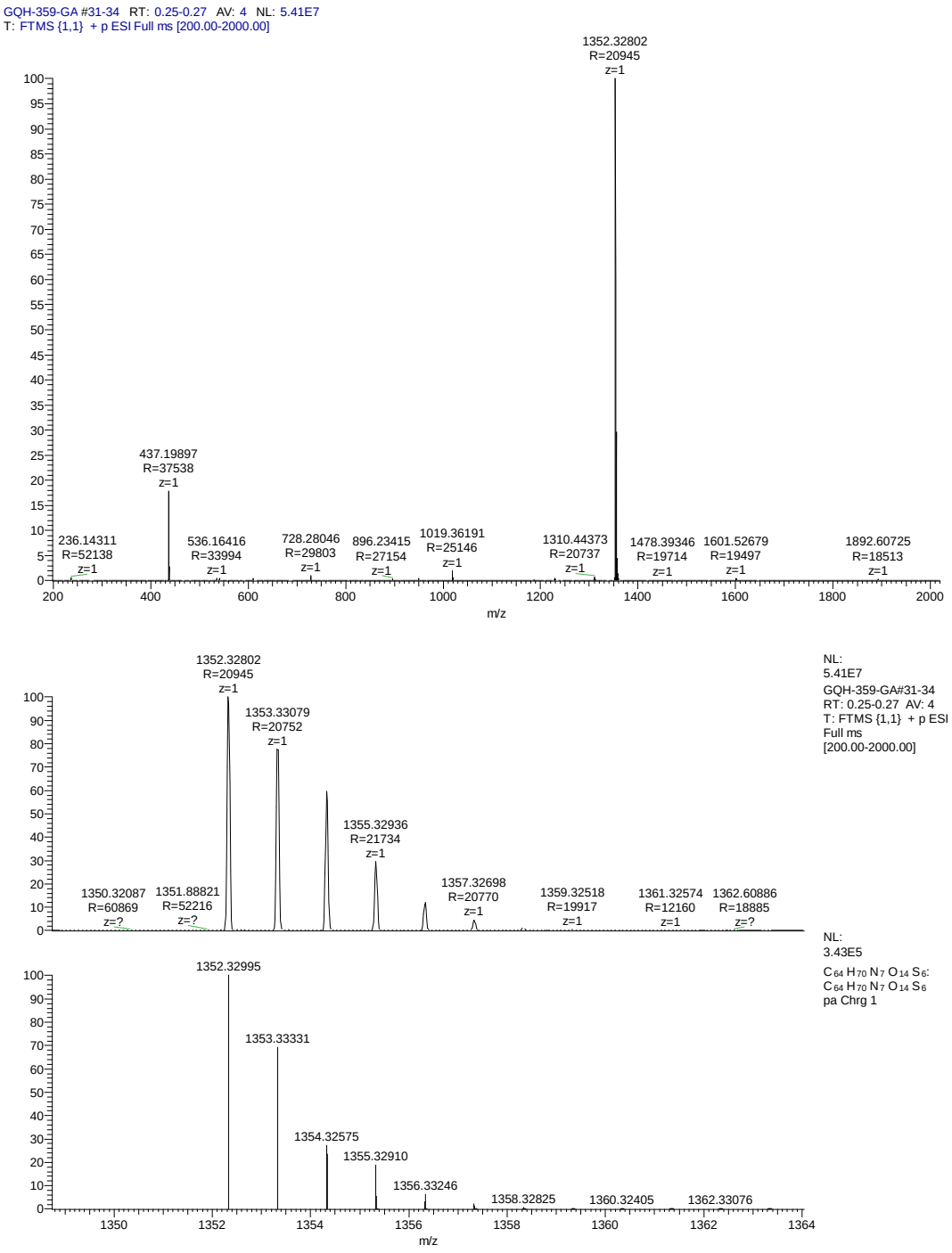


Figure S8. HRMS of **1+G8**

[**1**+**G9**-PF_6]$^+$ = [$C_{71}H_{75}N_7O_{12}S_6Fe$]$^+$ Calcd. m/z = 1465.3142 Found, m/z = 1465.30522

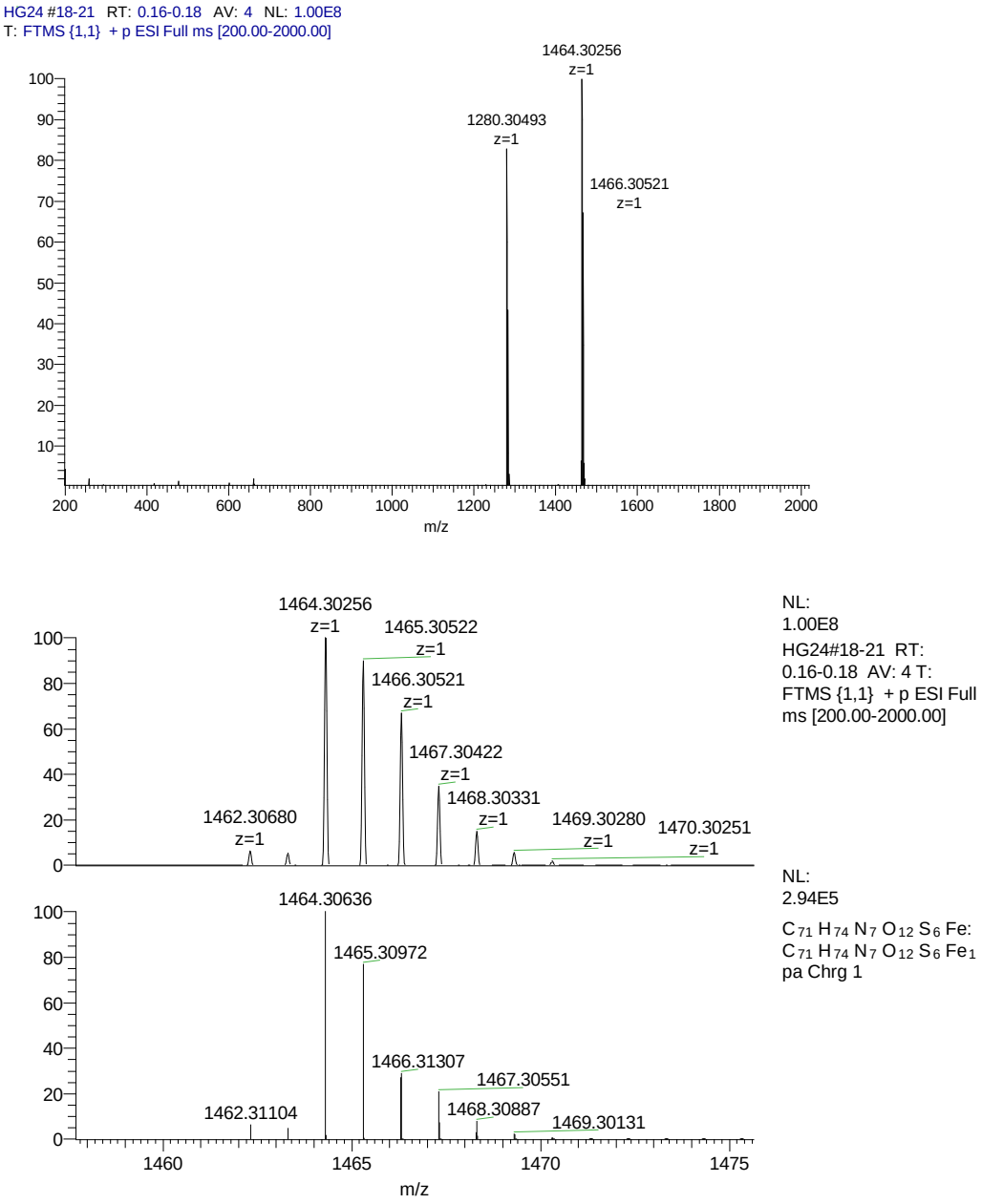


Figure S9. HRMS of **1+G9**

[**1**+**G10**-PF_6]$^+$ = [$C_{70}H_{78}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1400.4027 Found, m/z = 1400.40112

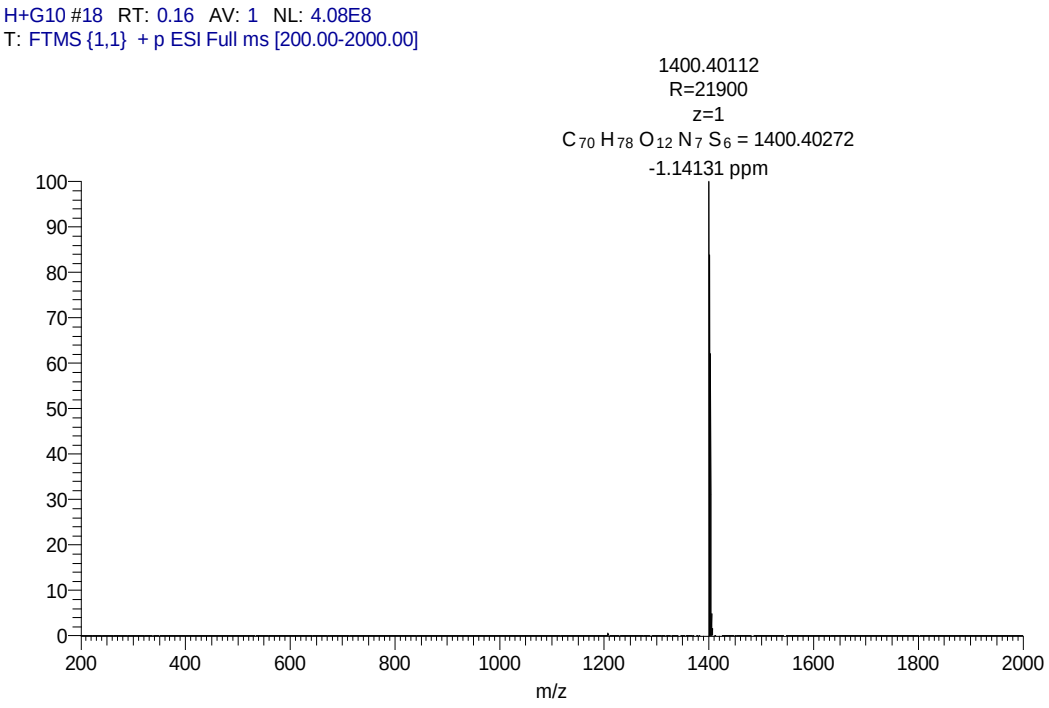


Figure S10. HRMS of **1+G10**

[**1**+**G11**-PF_6]$^+$ = [$C_{64}H_{69}N_{10}O_{12}S_6$]$^+$ Calcd. m/z = 1361.34 Found, m/z = 1361.33984：

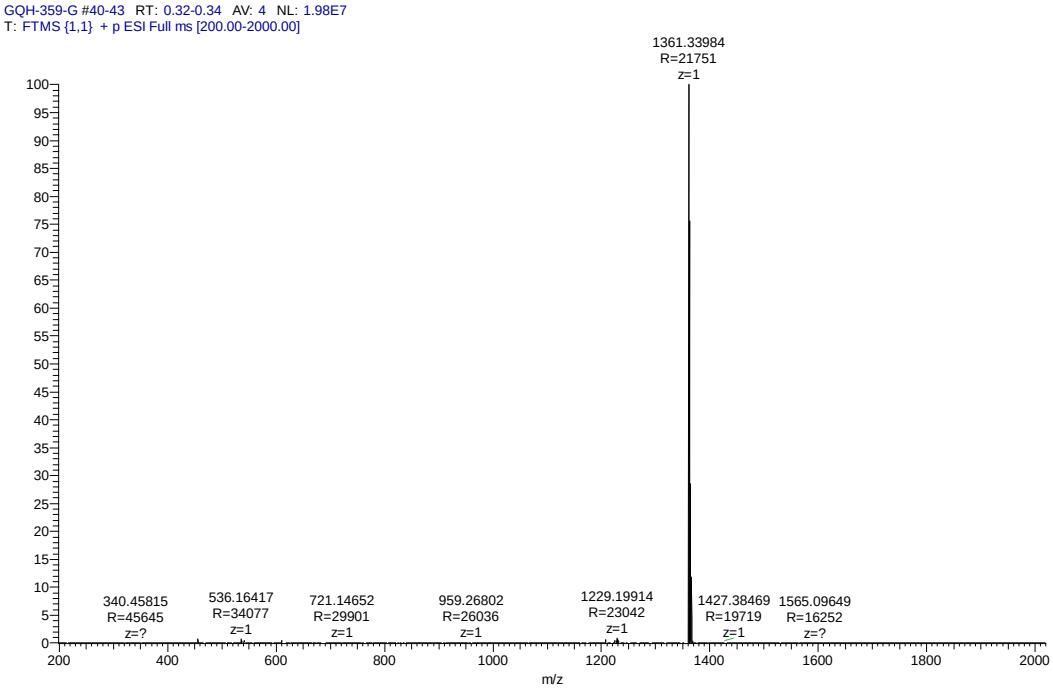


Figure S11. HRMS of **1+G11**

[**1**+**G12**-PF_6]$^+$ = [$C_{70}H_{73}N_{10}O_{12}S_6$]$^+$ Calcd. m/z = 1437.3728 Found, m/z = 1437.37161

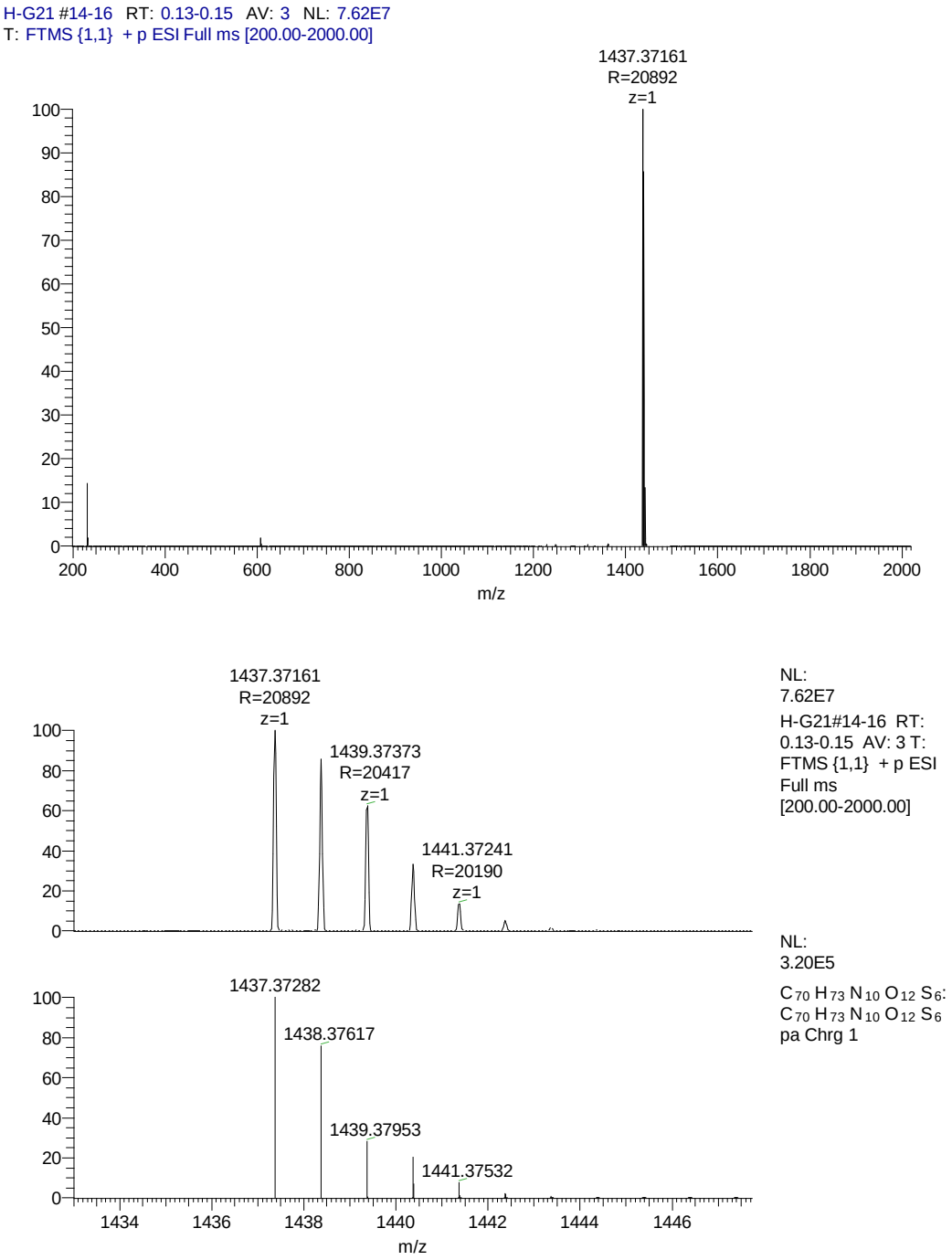


Figure S12. HRMS of **1+G12**

[**1**+**G13**-PF_6]$^+$ = [$C_{70}H_{72}N_8O_{12}S_6$]$^+$ Calcd. m/z = 1409.3667 Found, m/z = 1409.36206

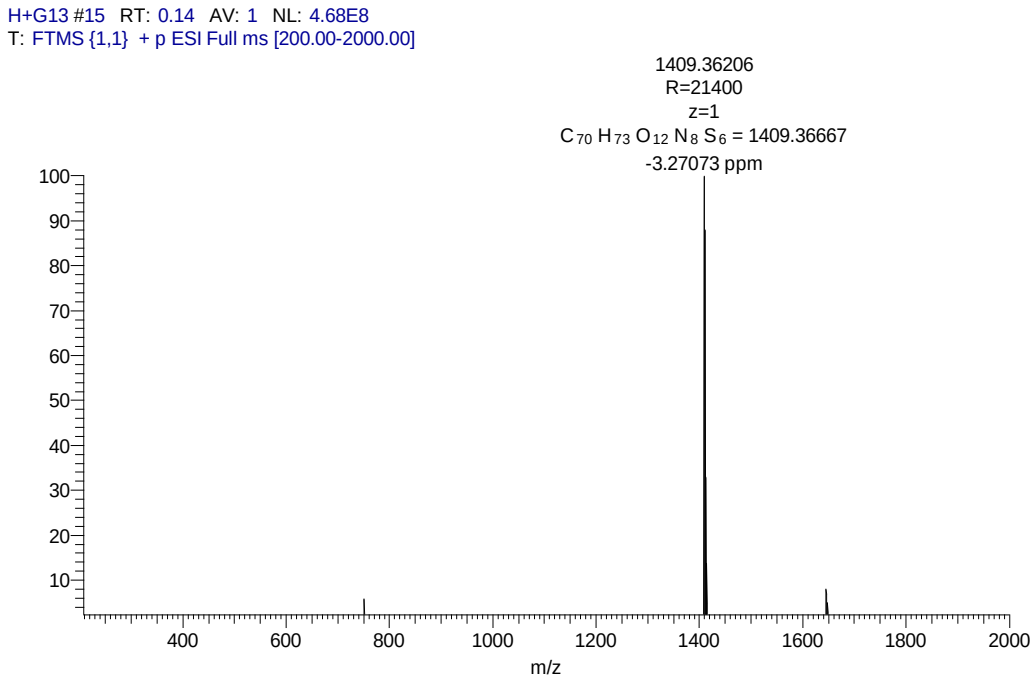


Figure S13. HRMS of **1+G13**

[**1**+**G14**-PF_6]$^+$ = [$C_{71}H_{70}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1404.3401 Found, m/z = 1404.33903

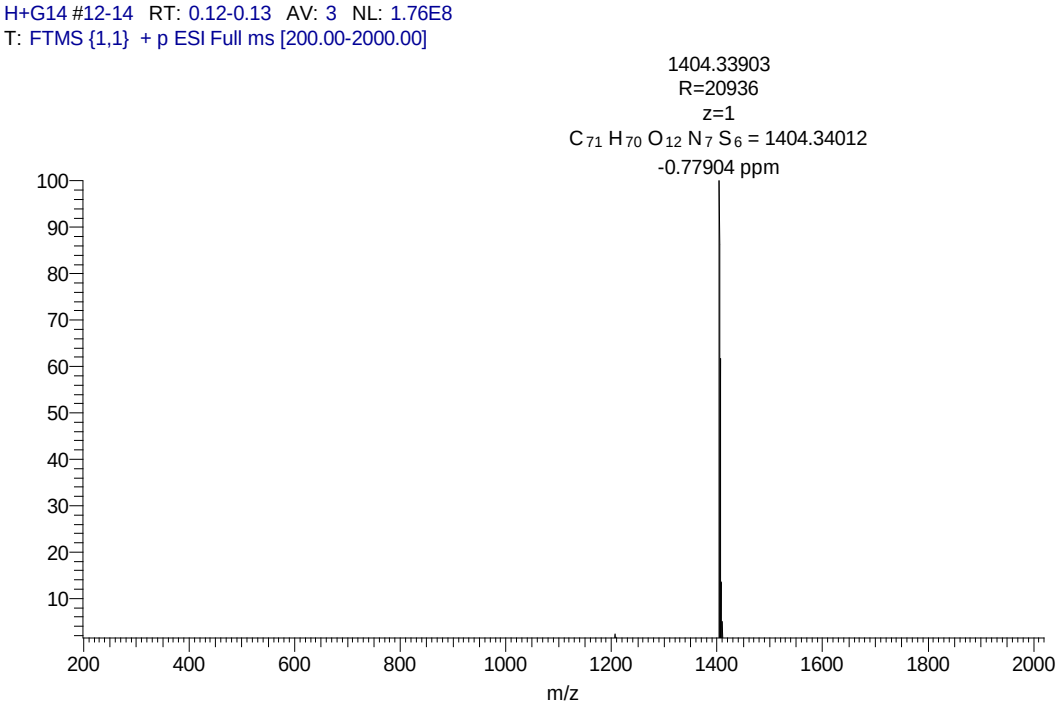


Figure S14. HRMS of **1+G14**

[**1**+**G15**-PF_6]$^+$ = [$C_{63}H_{62}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1300.2775 Found, m/z = 1300.27723

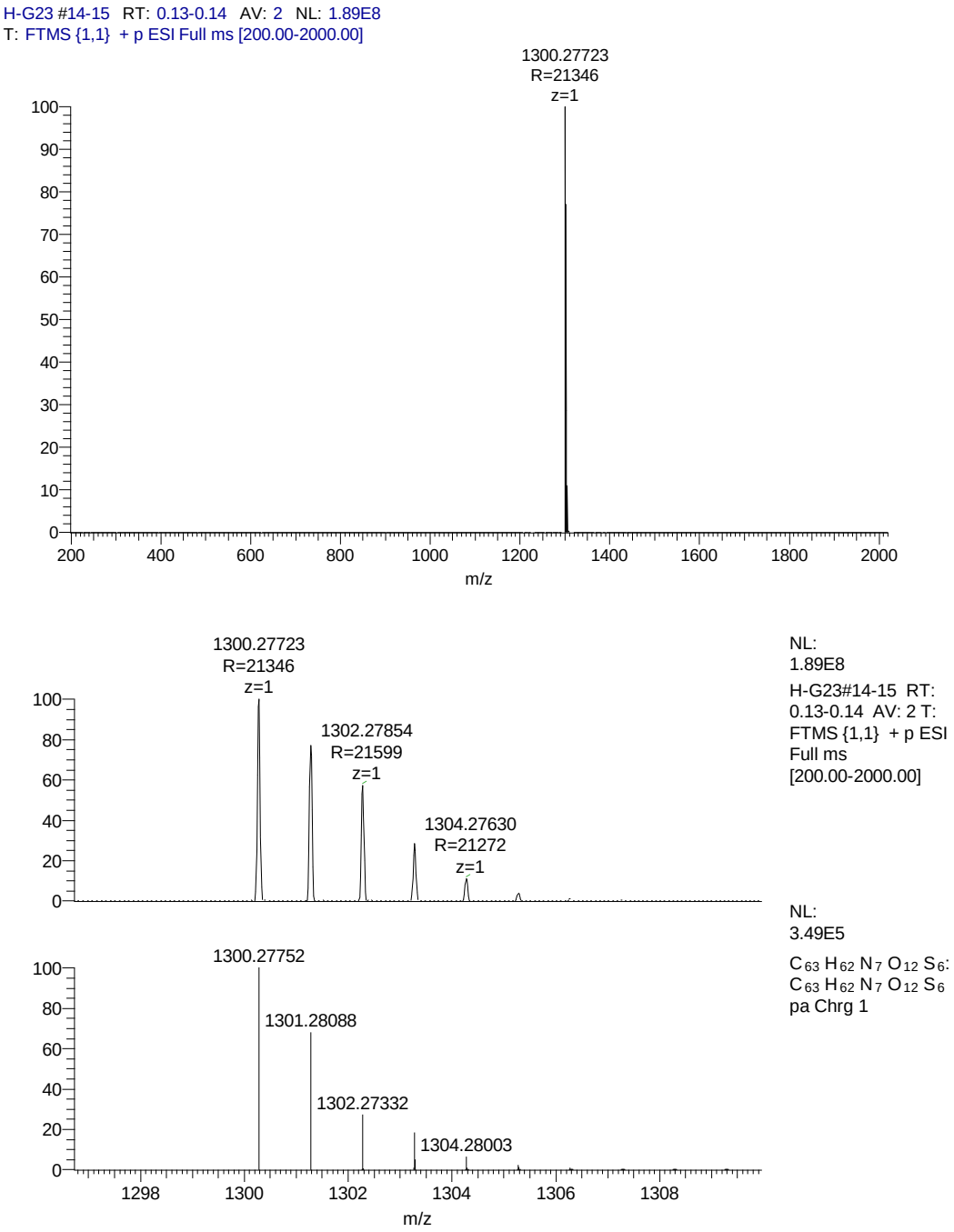


Figure S15. HRMS of **1+G15**

[**1**+**G16**-PF_6]$^+$ = [$C_{67}H_{64}N_7O_{12}S_6$]$^+$ Calcd. m/z = 1350.2932 Found, m/z = 1350.29262

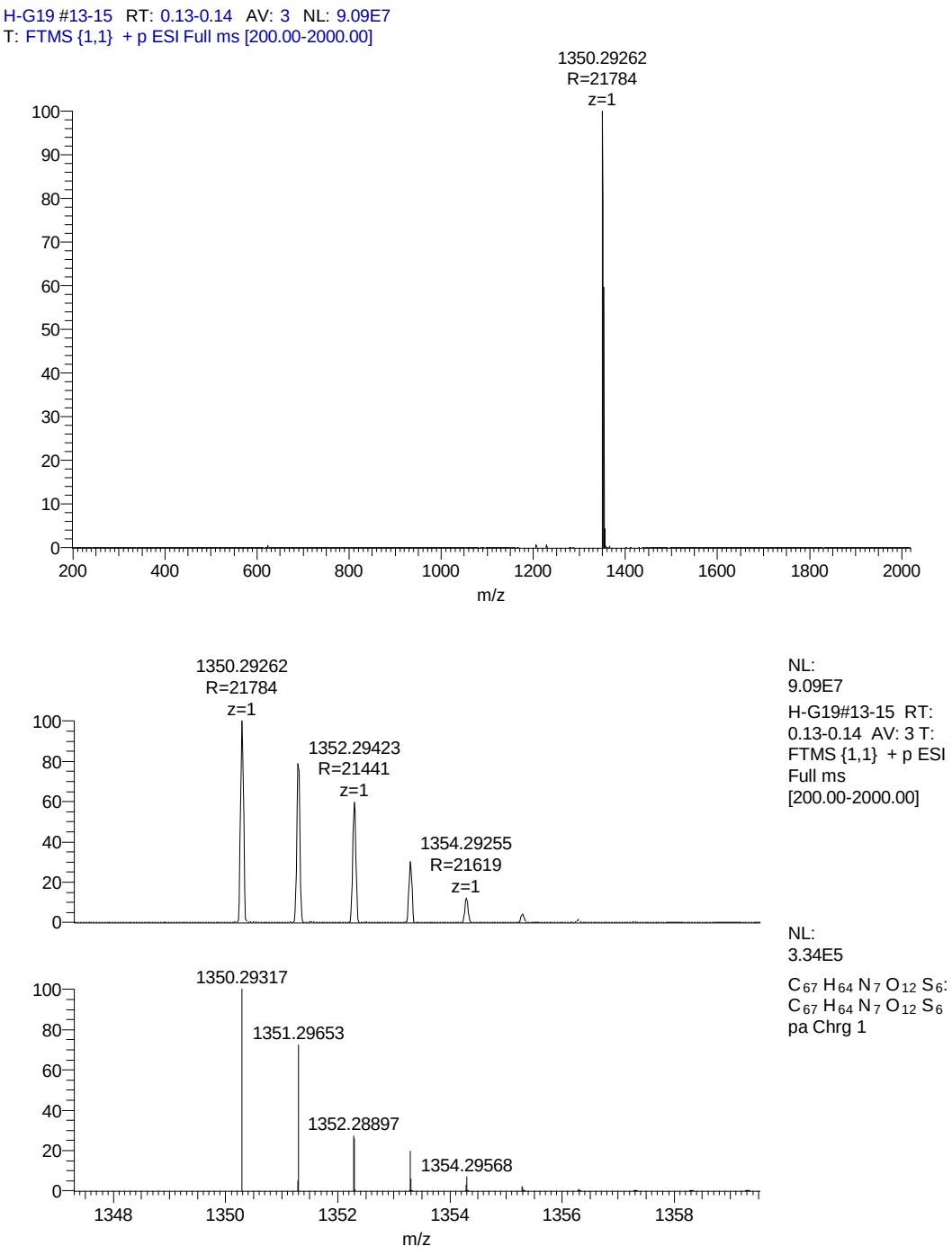
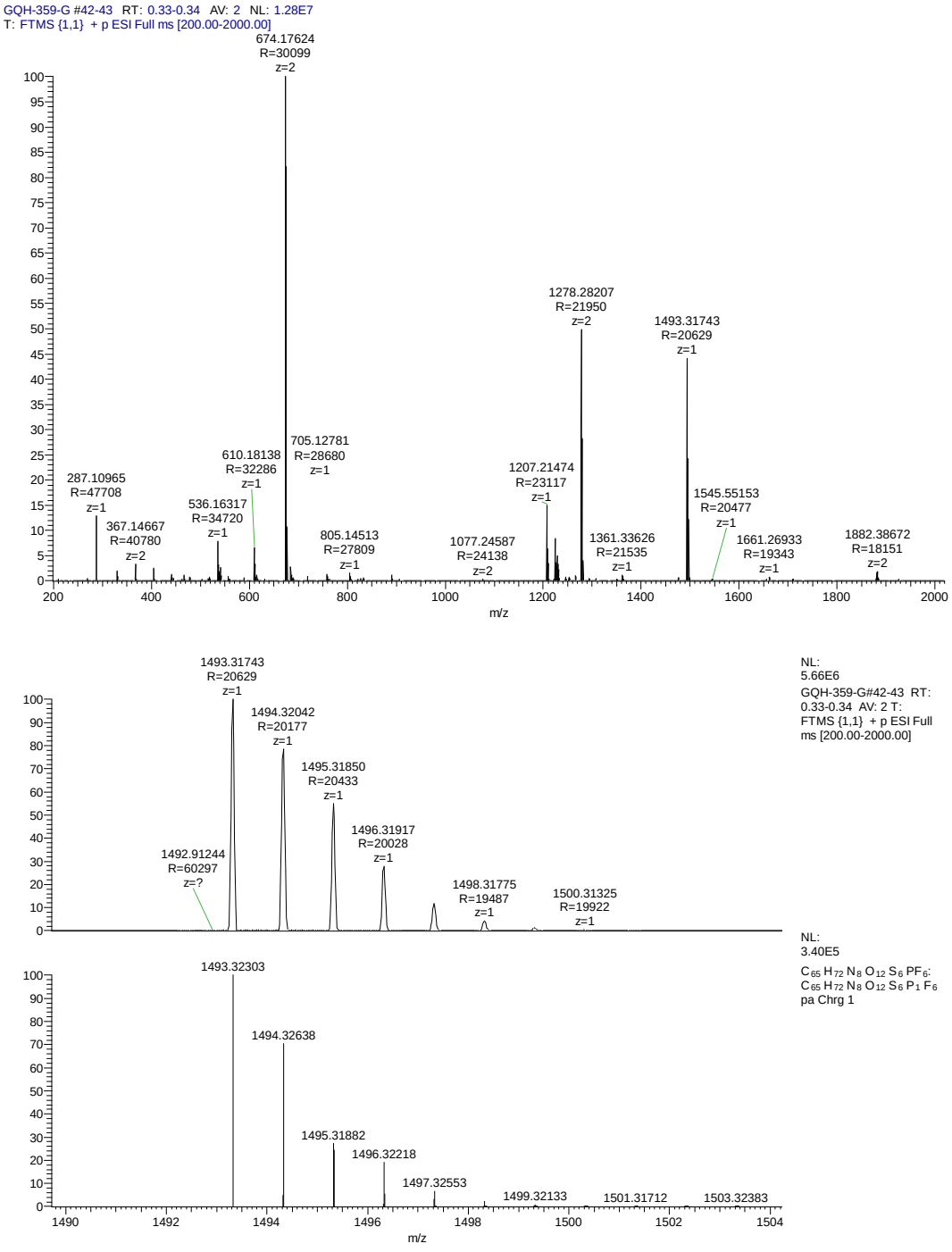


Figure S16. HRMS of **1+G16**

[**1**+**G17**-2PF_6]$^{2+}$ = [$C_{65}H_{72}N_8O_{12}S_6$]$^{2+}$ Calcd. m/z = 674.1791 Found, m/z = 674.17624

[**1**+**G17**-PF_6]$^{+}$ = [$C_{65}H_{72}N_8O_{12}S_6$]$^{2+}$[PF_6]$^{-}$ Calcd. m/z = 1493.3230 Found, m/z = 1493.31743


GQH-359-G #42-43 RT: 0.33-0.34 AV: 2 NL: 1.28E7
T: FTMS {1,1} + p ESI Full ms [200.00-2000.00]
674.17624
R=30099
z=2
1278.28207
R=21950
z=2
1493.31743
R=20629
z=1
705.12781
R=28680
z=1
610.18138
R=32286
z=1
287.10965
R=47708
z=1
1207.21474
R=23117
z=1
1545.55153
R=20477
z=1
536.16317
R=34720
z=1
367.14667
R=40780
z=2
805.14513
R=27809
z=1
1077.24587
R=24138
z=2
1361.33626
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1661.26933
R=19343
z=1
1882.38672
R=18151
z=2
m/z
1493.31743
R=20629
z=1
1494.32042
R=20177
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1498.31775
R=19487
z=1
1500.31325
R=19922
z=1
NL:
5.66E6
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0.33-0.34 AV: 2 T:
FTMS {1,1} + p ESI Full
ms [200.00-2000.00]
1493.32303
1494.32638
1495.31882
1496.32218
1497.32553
1499.32133
1501.31712
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3.40E5
C65 H72 N8 O12 S6 PF6:
C65 H72 N8 O12 S6 P1 F6
pa Chrg 1
m/z

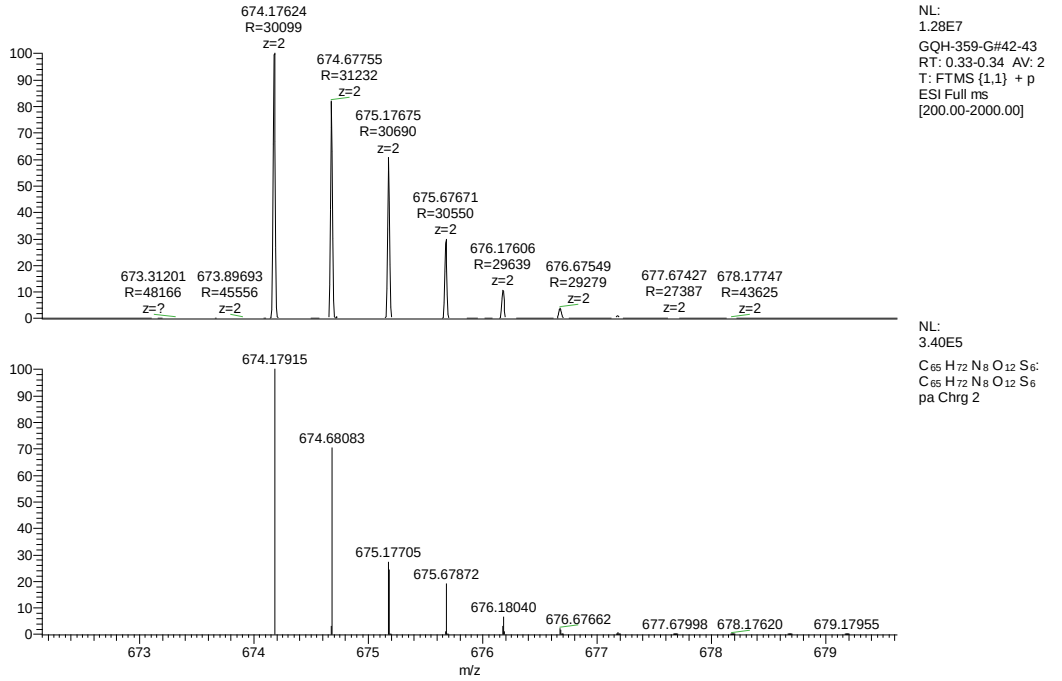
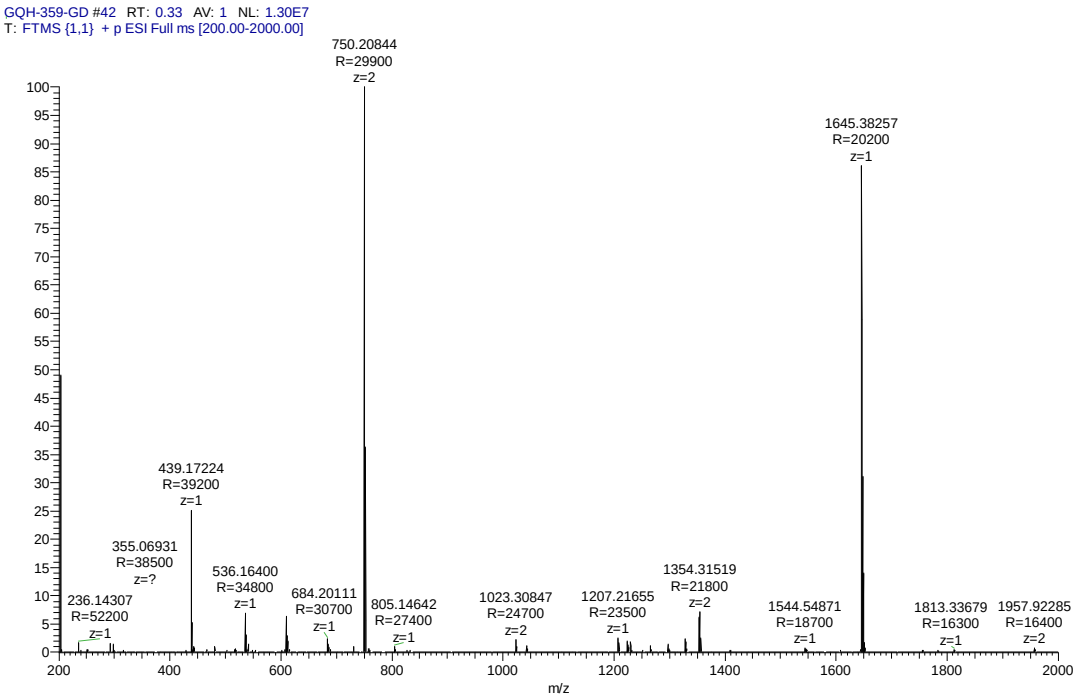


Figure S17. HRMS of **1+G17**

[**1**+**G18**-2PF_6]$^{2+}$ = [$C_{77}H_{80}N_8O_{12}S_6$]$^{2+}$ Calcd. m/z = 750.2104 Found, m/z = 750.20644

[**1**+**G18**-PF_6]$^{+}$ = [$C_{77}H_{80}N_8O_{12}S_6$]$^{2+}$[PF6]$^{-}$ Calcd. m/z = 1645.3856 Found, m/z = 1645.38257



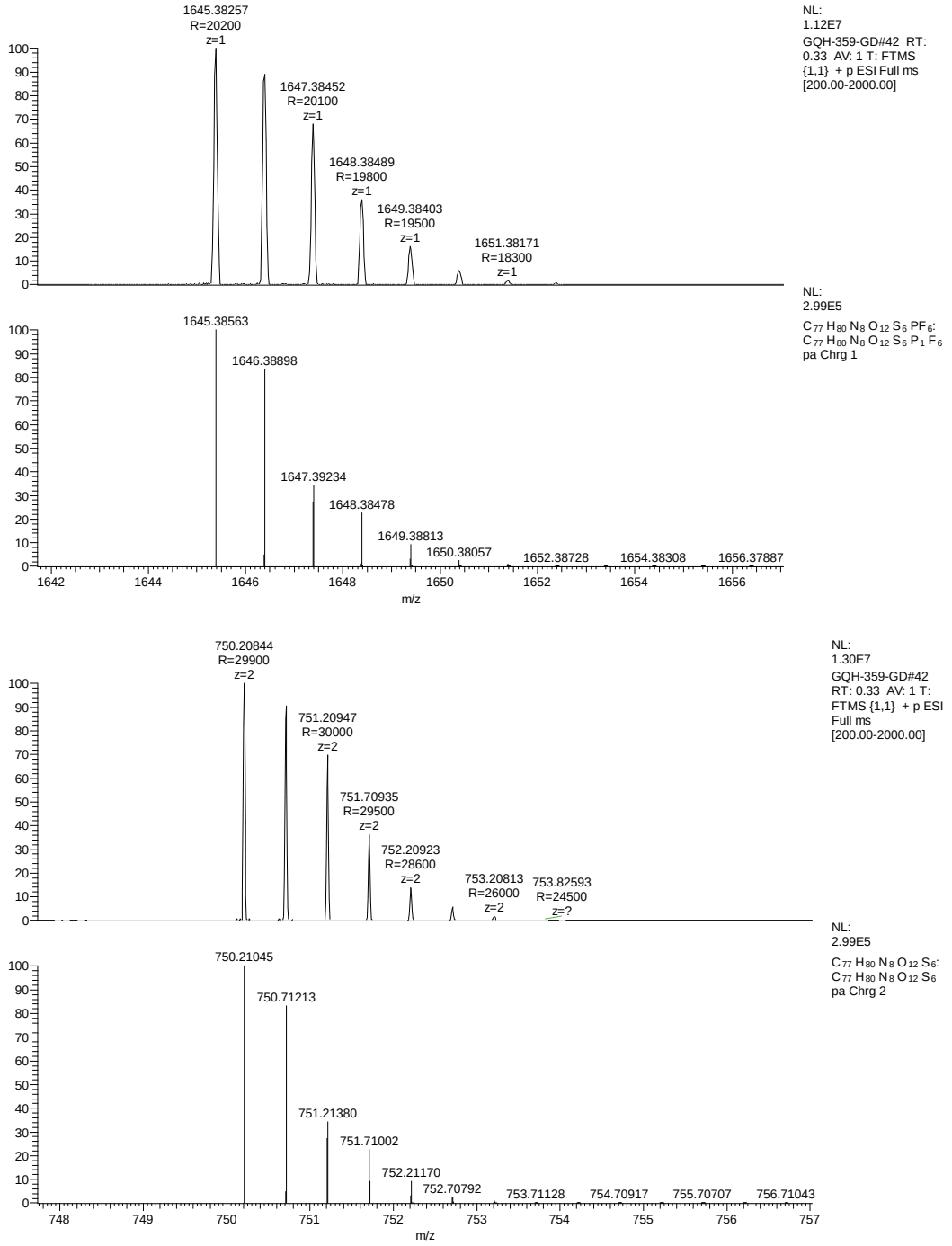


Figure S18. HRMS of **1+G18**

[**1**+**G19**-2PF_6]$^{2+}$ = [$C_{69}H_{66}N_8O_{12}S_6$]$^{2+}$ Calcd. m/z = 695.1557 Found, m/z = 695.15292

[**1**+**G19**-PF_6]$^{+}$ = [$C_{69}H_{66}N_8O_{12}S_6$]$^{2+}$[PF_6]$^{-}$ Calcd. m/z = 1535.2761 Found, m/z = 1535.27058

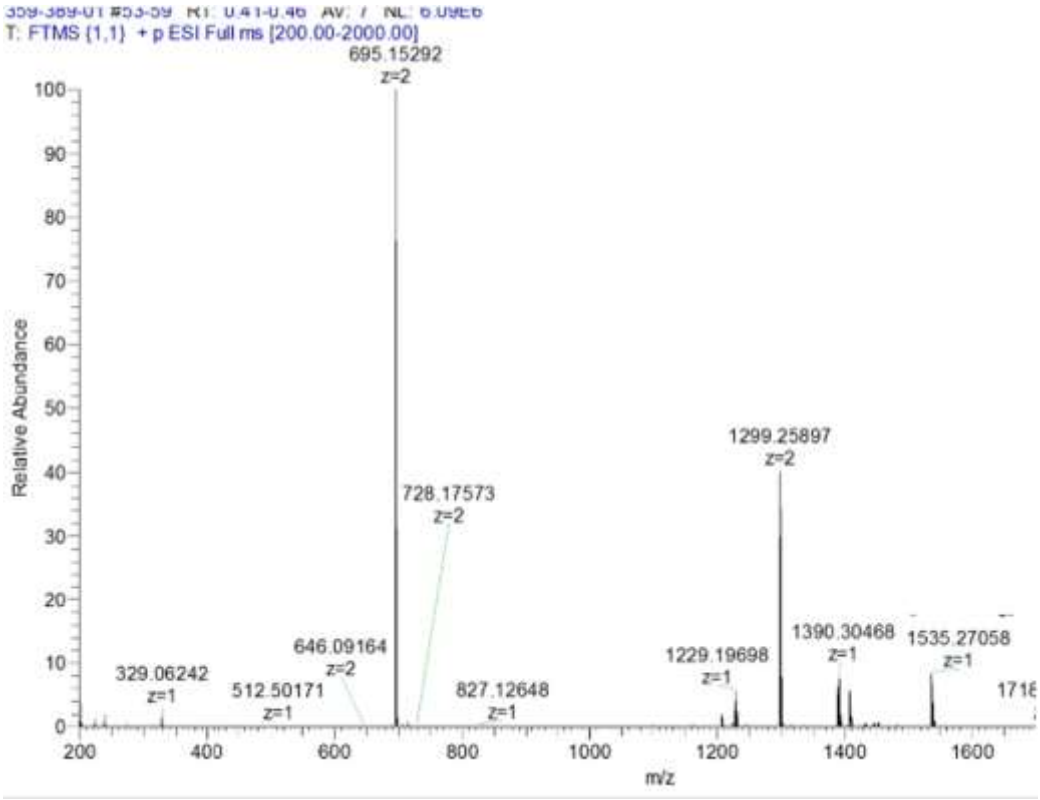


Figure S19. HRMS of **1+G19**

[**1**+**G20**-2PF_6]$^{2+}$ = [$C_{72}H_{68}N_8O_{12}S_6$]$^{2+}$ Calcd. m/z = 714.1635 Found, m/z = 714.14231

[**1**+**G20**-PF_6]$^{+}$ = [$C_{72}H_{68}N_8O_{12}S_6$]$^{2+}$[PF_6]$^{-}$ Calcd. m/z = 1573.2917 Found, m/z = 1573.29023

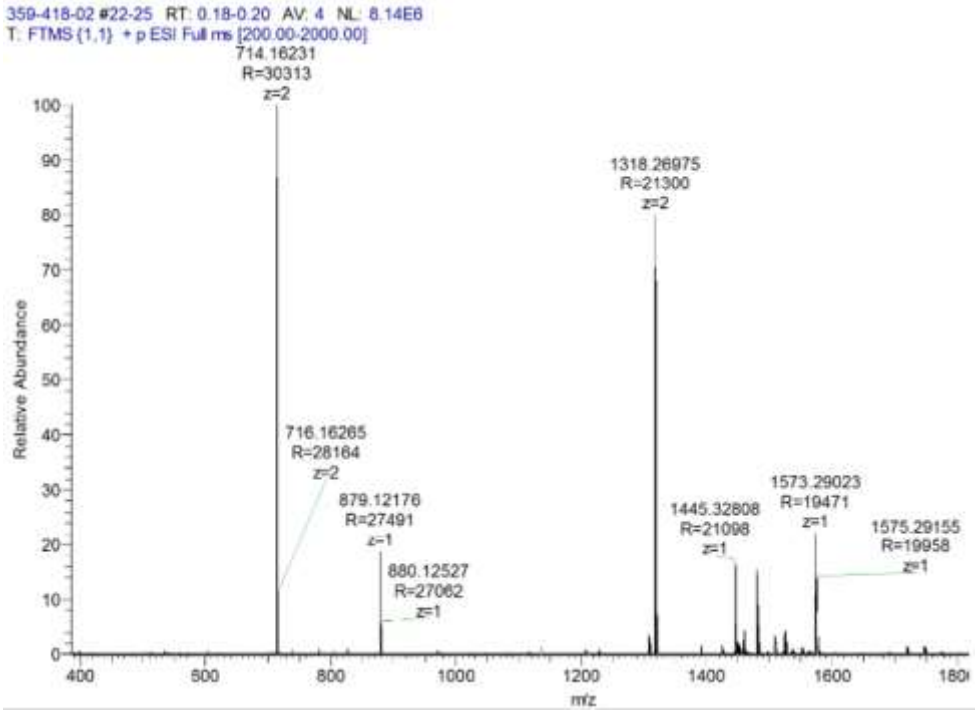


Figure S20. HRMS of **1+G20**

[**1**+**G21**-2PF_6]$^{2+}$ = [$C_{71}H_{66}N_8O_{12}S_6$]$^{2+}$ Calcd. m/z = 707.1557 Found, m/z = 707.15243

[**1**+**G21**-PF_6]$^{+}$ = [$C_{71}H_{66}N_8O_{12}S_6$]$^{2+}$[PF_6]$^{-}$ Calcd. m/z = 1559.2761 Found, m/z = 1559.26912

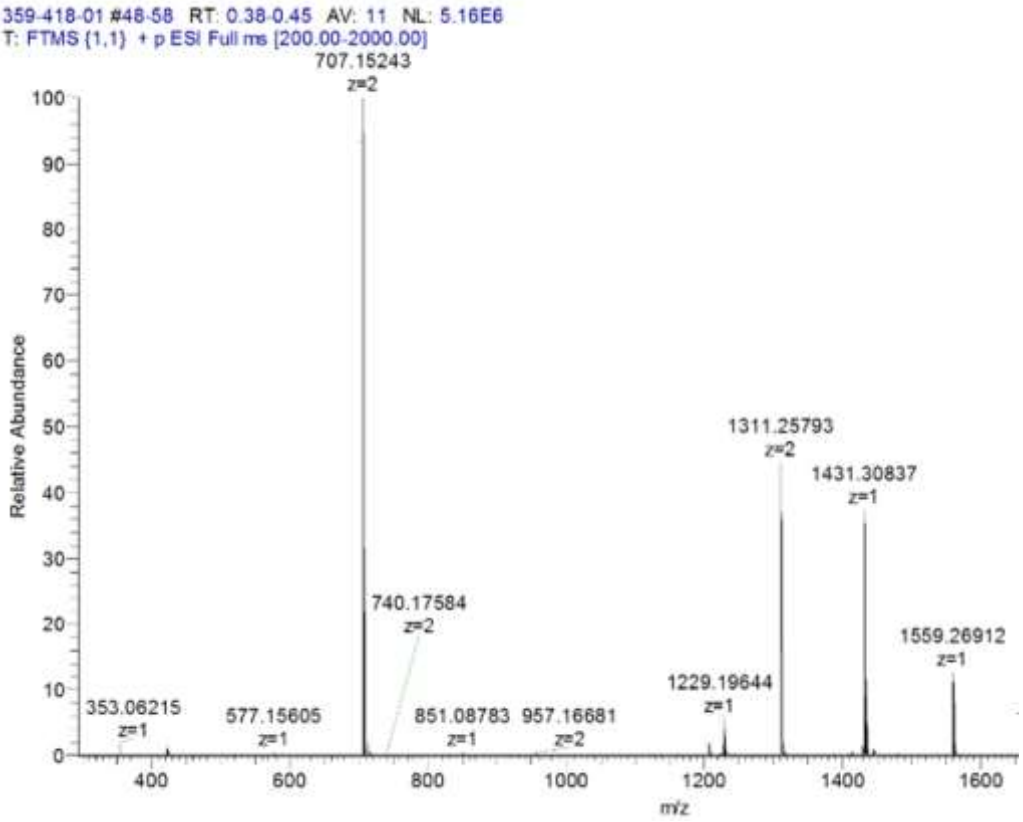


Figure S21. HRMS of **1**+**G21**

2. ITC titration results

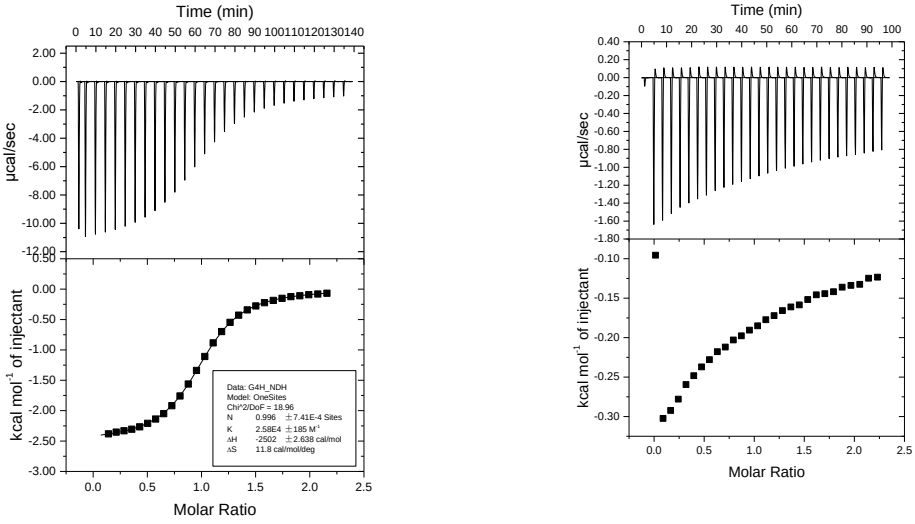


Figure S22. ITC titration of 0.994 mM host **1** with 29×10 μL 9.993 mM guest **G11**. Ka = (2.50± 0.09)×10^4 , T=298.15K

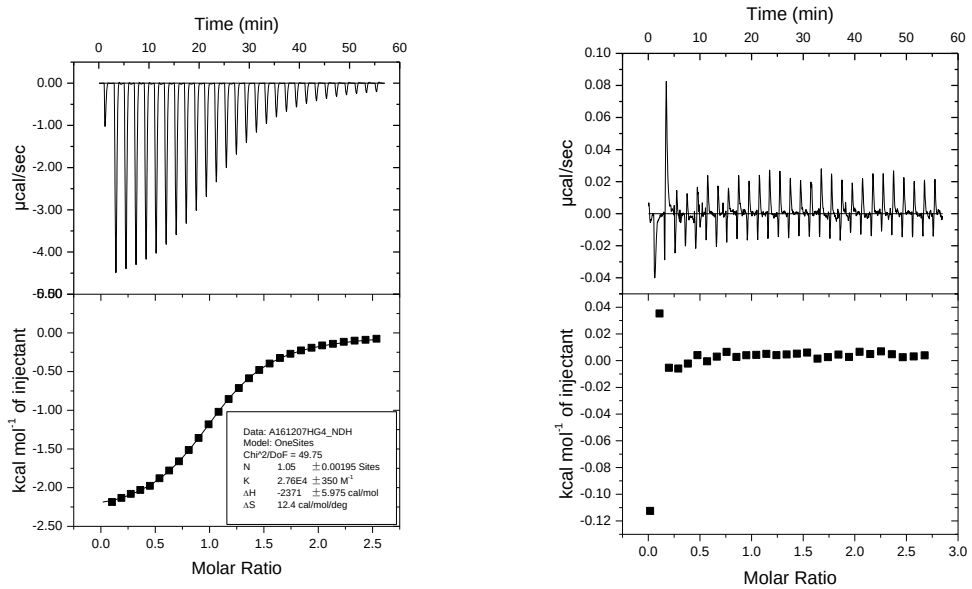


Figure S23. ITC titration of 0.4131 mM guest **G11** with 29×10 μL 5.0373 mM host **1**, Ka = (2.70± 0.06)×10^4 M^{-1}, T=298.15K

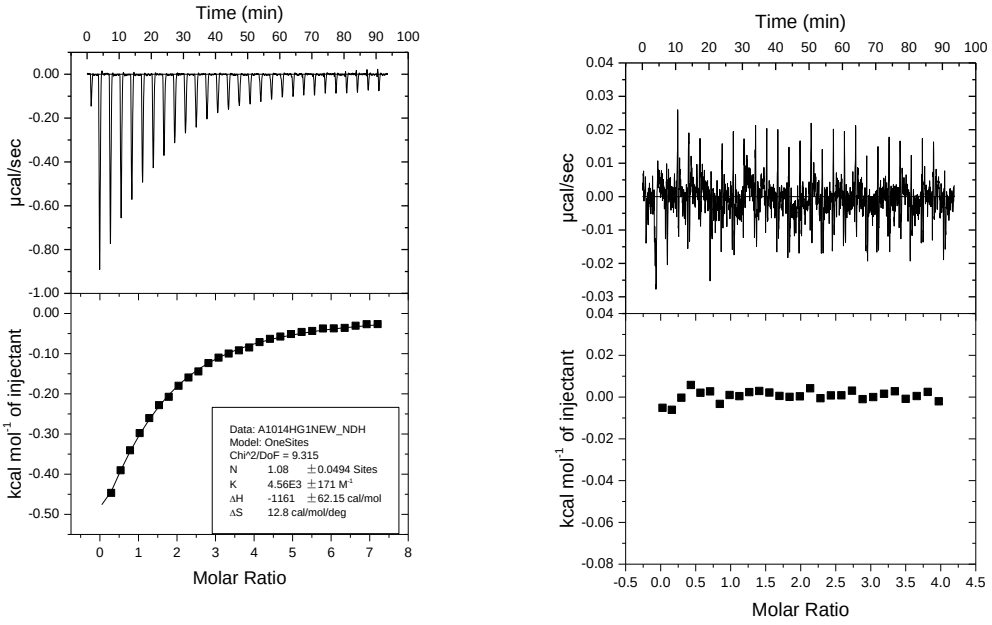


Figure S24. ITC titration of 0.1446 mM guest **G1** with 29×10 μL 5.0108 mM host **1** , T=298.15K

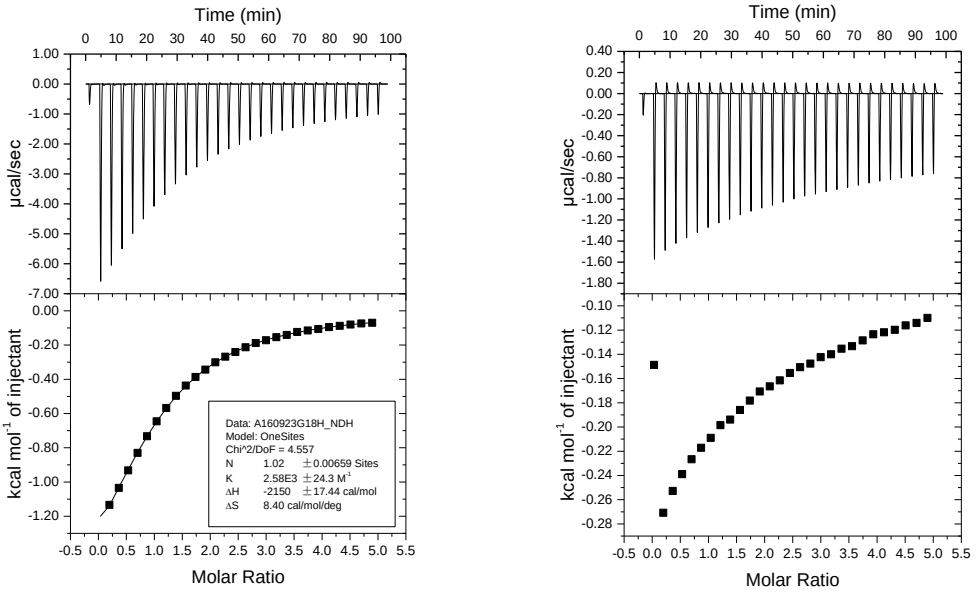


Figure S25. ITC titration of 0.4921 mM host **1** with 29×10 µL 11.5580 mM **G2**, T=298.15K

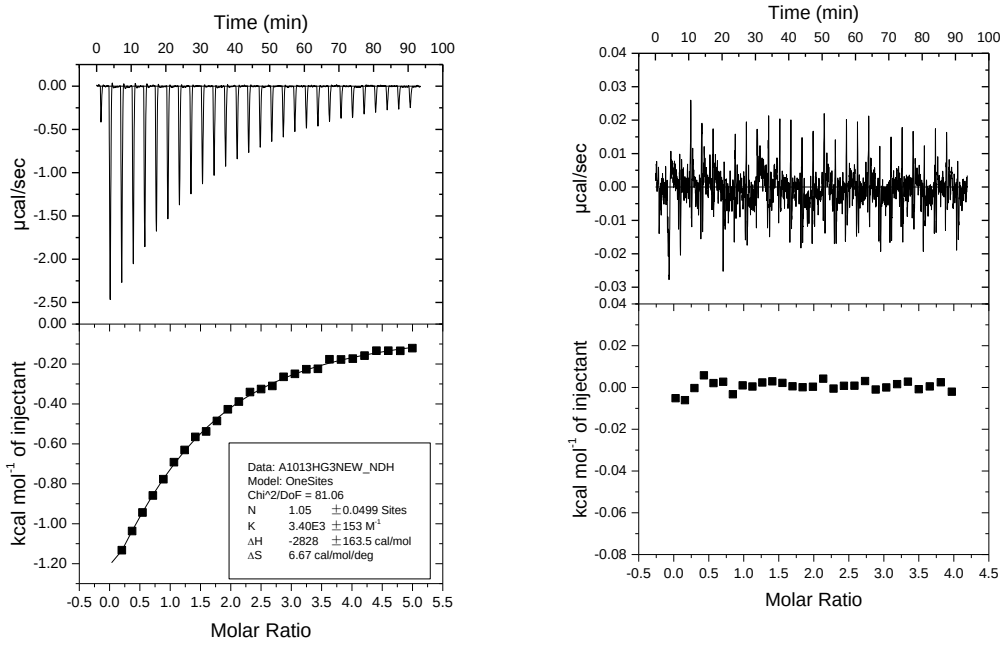


Figure S26. ITC titration of 0.2085 mM guest **G3** with 29×10 µL 5.0108 mM host **1**, T=298.15K

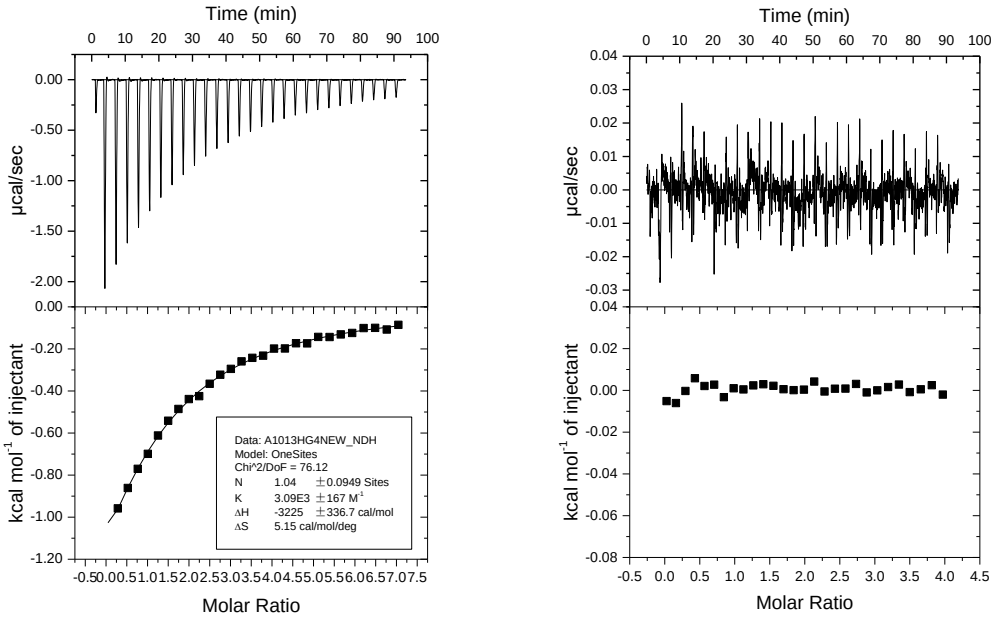


Figure S27. ITC titration of 0.1479 mM guest **G4** with 29×10 μL 5.0108 mM host **1**, T=298.15K

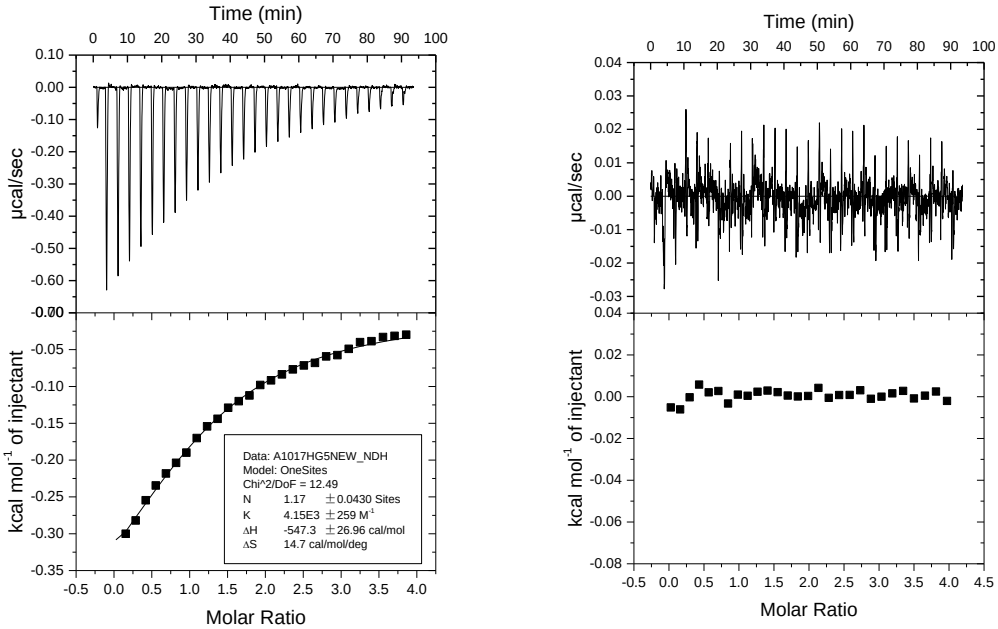


Figure S28. ITC titration of 0.2700 mM **G5** with 29×10 μL 5.0108 mM host **1**, T=298.15K

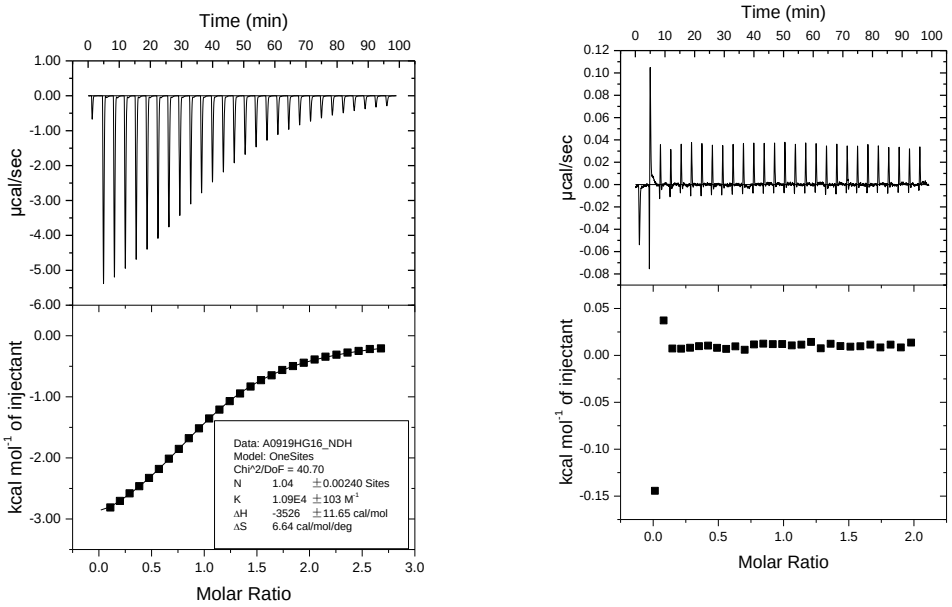


Figure S29. ITC titration of 0.3821 mM **G6** with 29×10 µL 4.9213 mM host **1**, T=298.15K

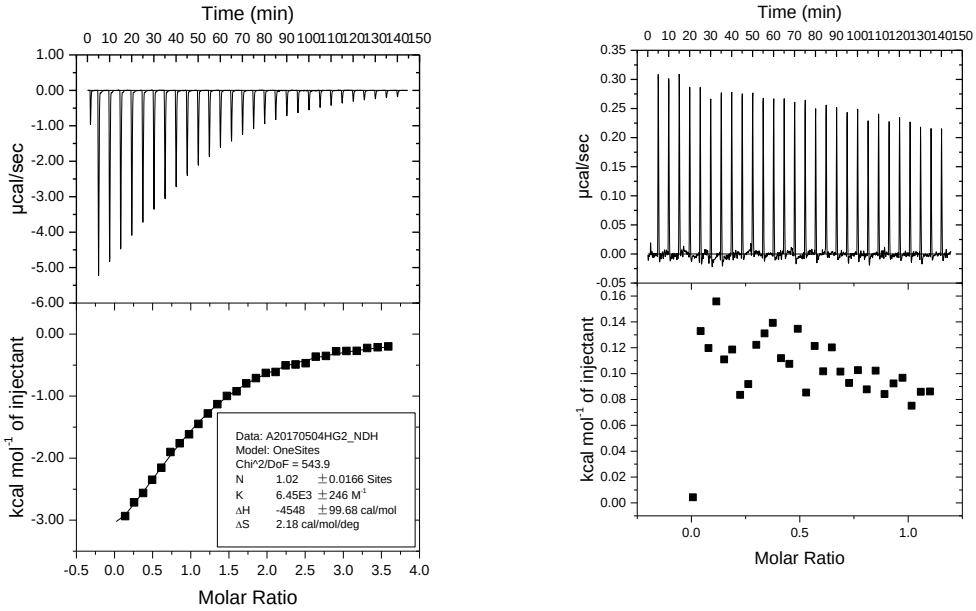


Figure S30. ITC titration of 0.3066 mM **G7** with 29×10 µL 5.1036 mM host **1**, T=298.15K

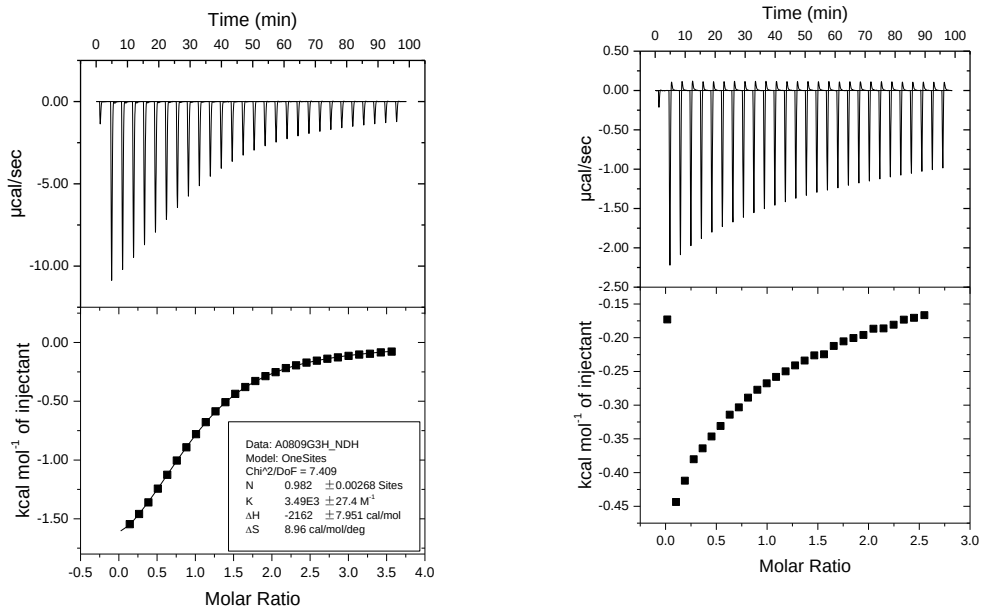


Figure S31. ITC titration of 0.8534 mM host **1** with 29×10 µL 14.6291 mM **G8**, T=298.15K

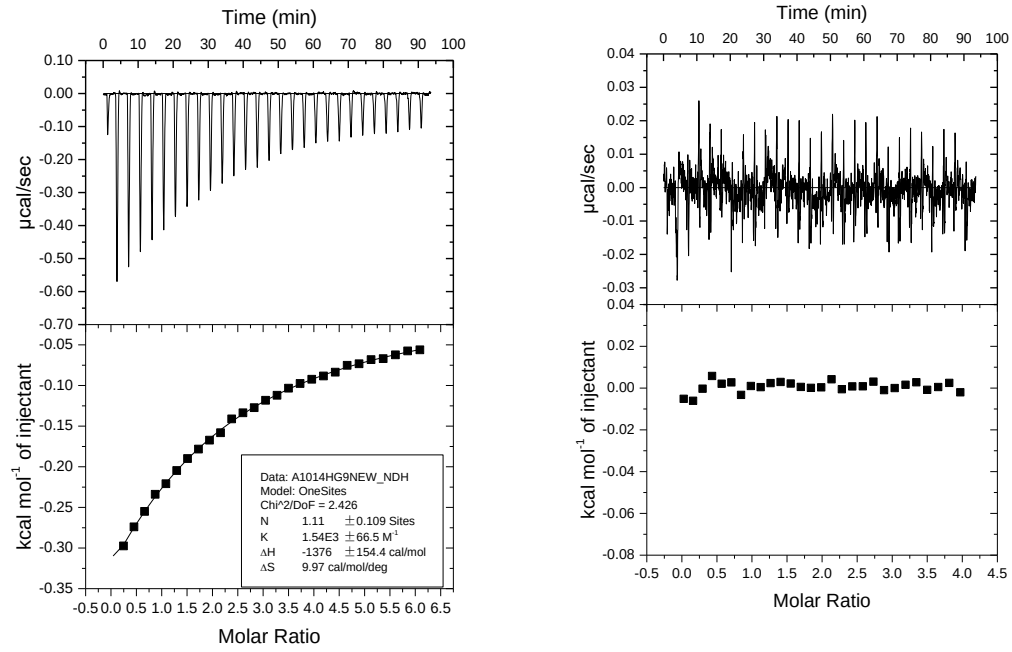


Figure S32. ITC titration of 0.1711 mM **G9** with 29×10 µL 5.0108 mM host **1**, T=298.15K

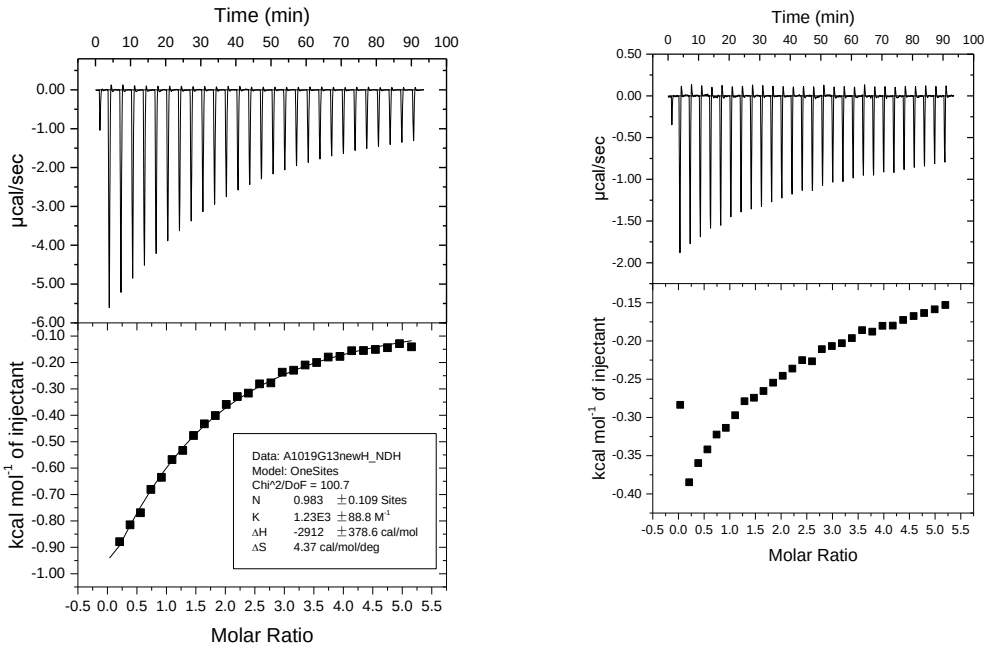


Figure S33. ITC titration of 0.4009 mM host **1** with 29×10 µL 9.9425 mM **G13**, T=298.15K

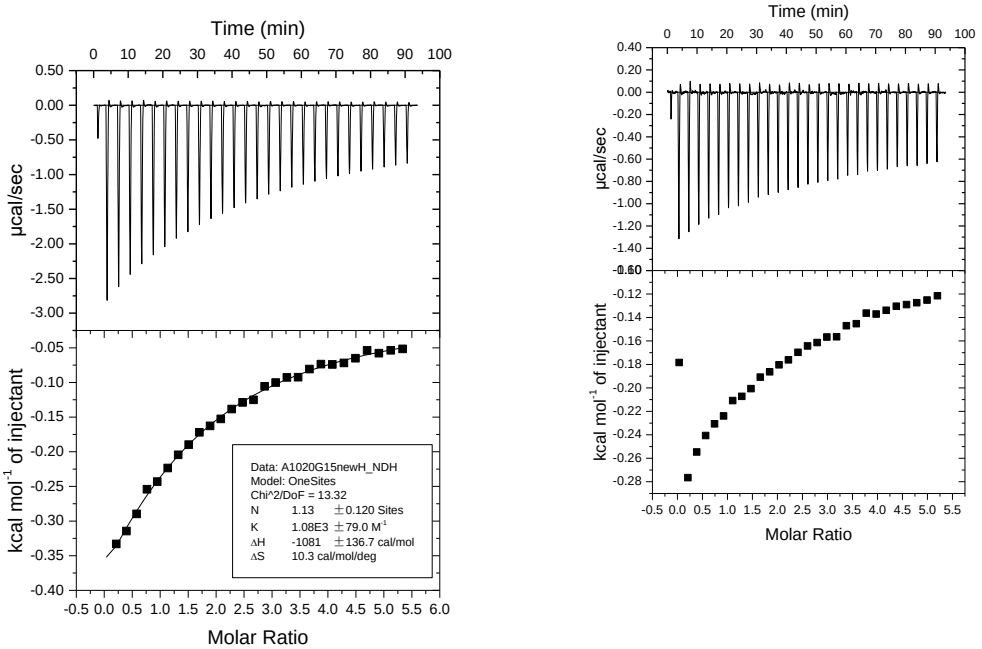


Figure S34. ITC titration of 0.4009 mM host **1** with 29×10 µL 10.2843 mM **G15**, T=298.15K

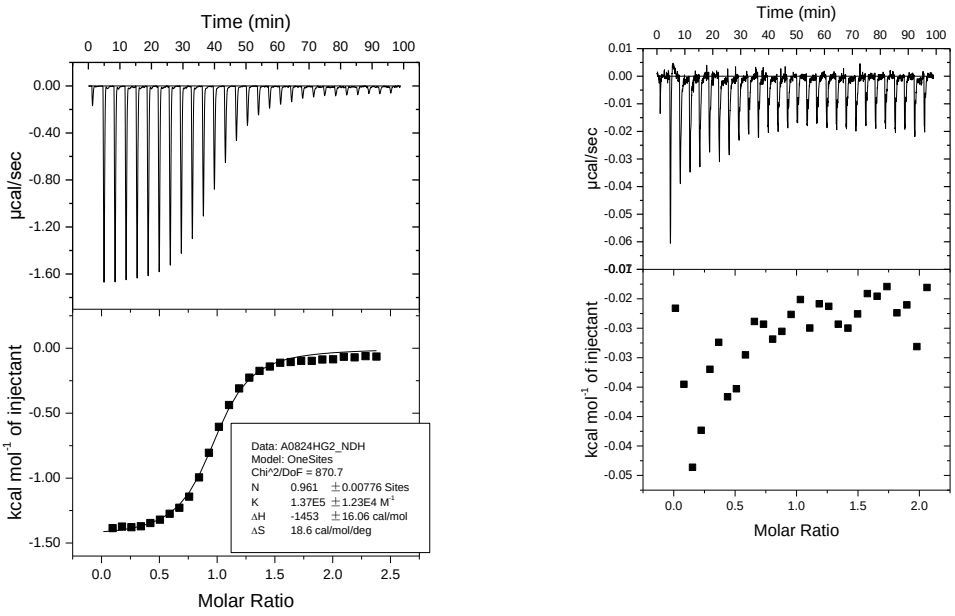


Figure S35. ITC titration of 0.3067 mM guest **18** with 29×10 µL 3.0406 mM host **1**, T=298.15K

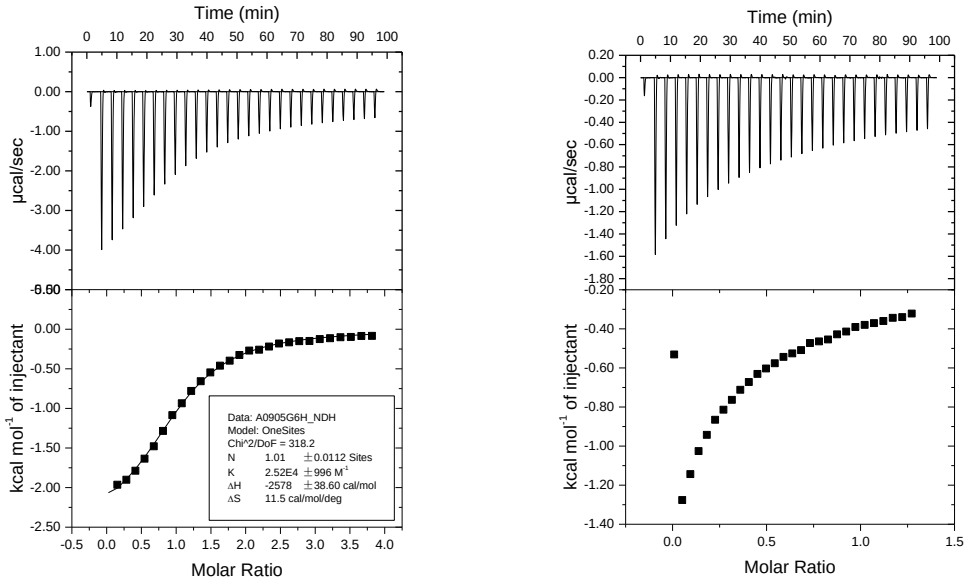


Figure S36. ITC titration of 0.1620 mM host **1** with 29×10 µL 2.9725 mM **G19** , T=298.15K

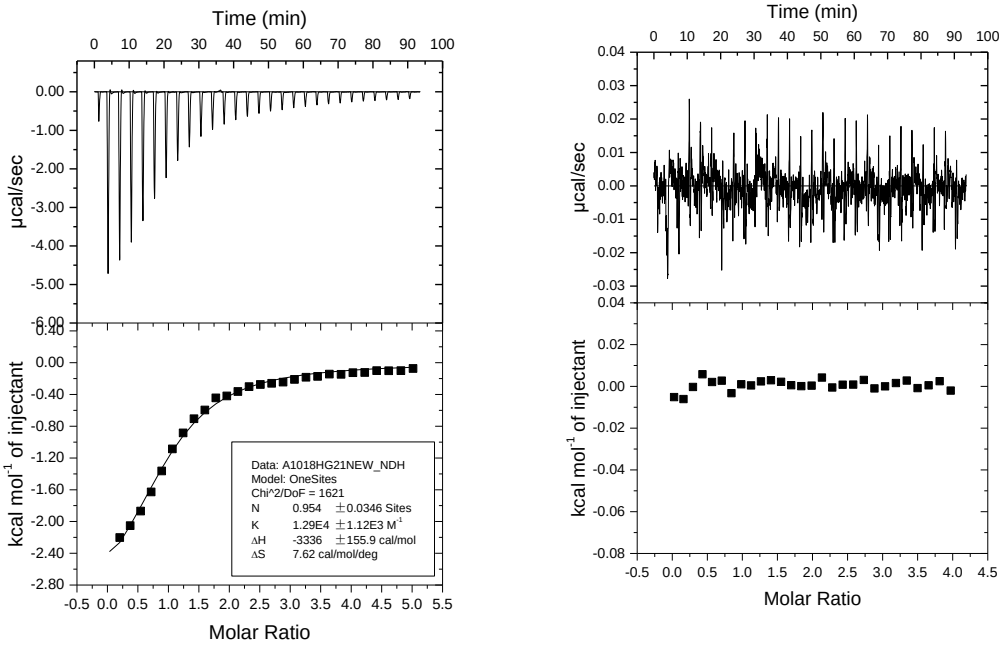


Figure S37. ITC titration of 0.2078 mM **G20** with 29×10 µL 5.0108 mM host **1**, T=298.15K

3. ^{1}H NMR Job's Plot

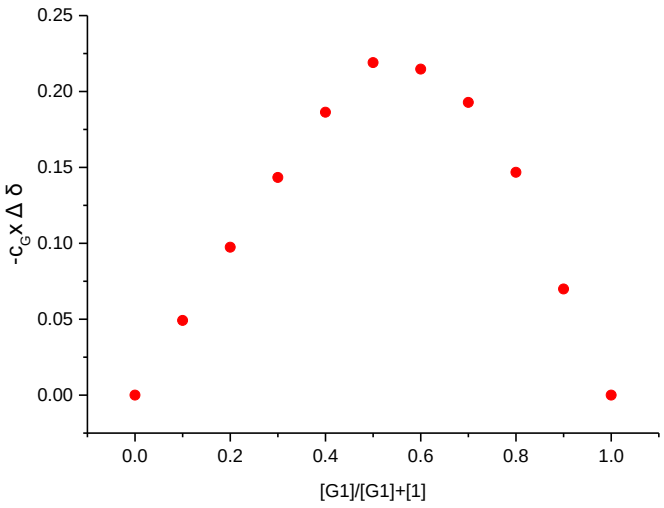


Figure S38. Job's Plot of **G1**. ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ºC

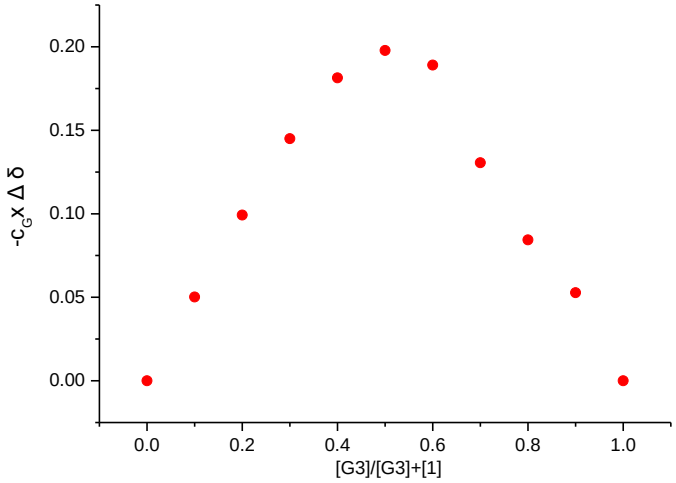


Figure S39. Job's Plot of **G3**. ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ^{o}C

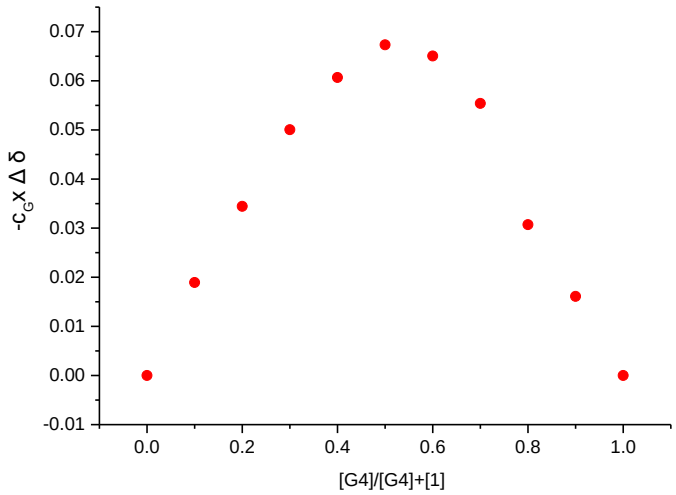


Figure S40. Job's Plot of **G4**. ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ^{o}C

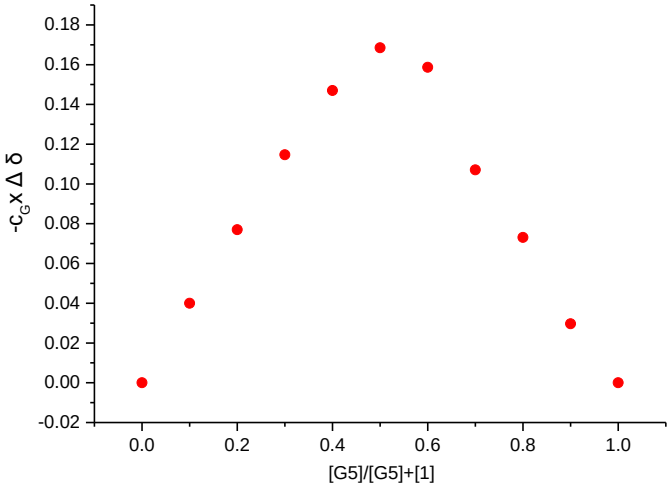


Figure S41. Job's Plot of **G5**. ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ^{o}C

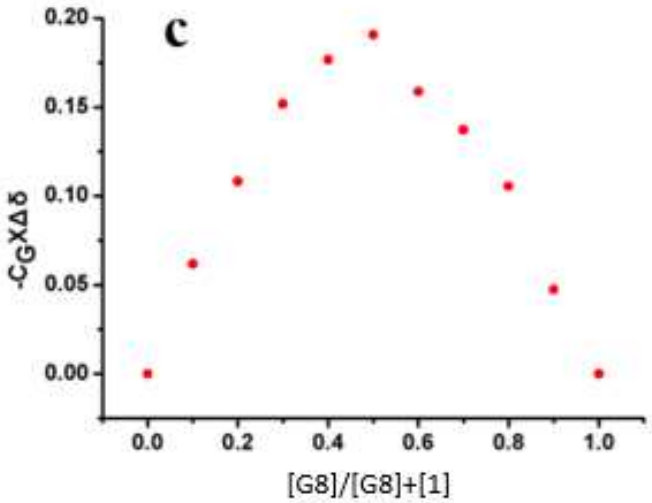


Figure S42. Job's Plot of **G8** (*cf.* Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947)

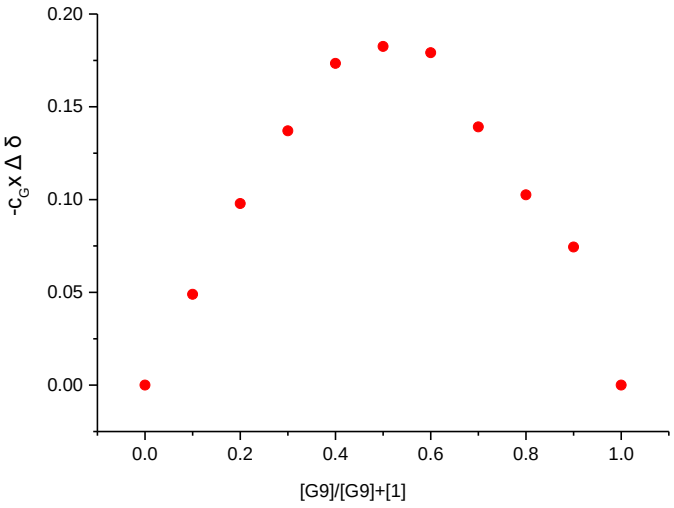


Figure S43. Job's Plot of **G9**. ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ^{o}C

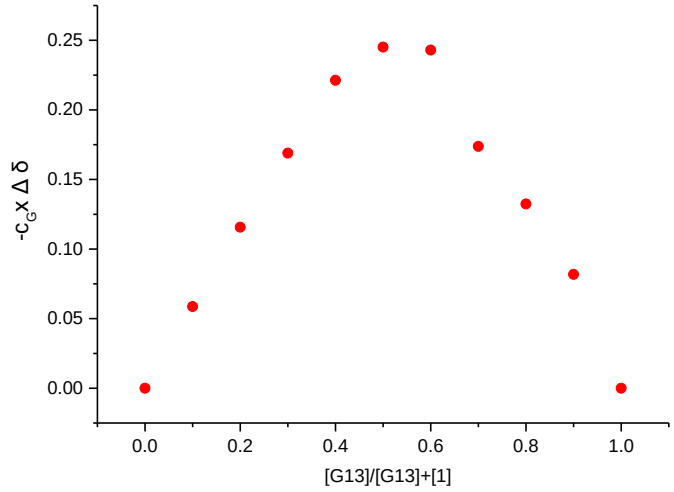


Figure S44. Job's Plot of **G13**. ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ^{o}C

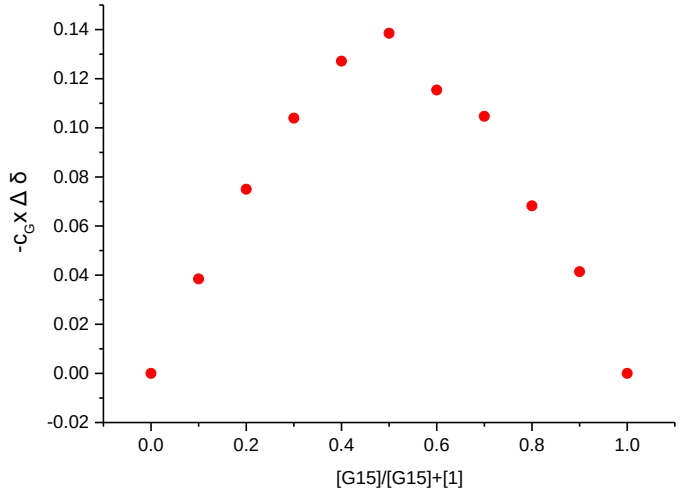


Figure S45. Job's Plot of **G15**. ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ^{o}C

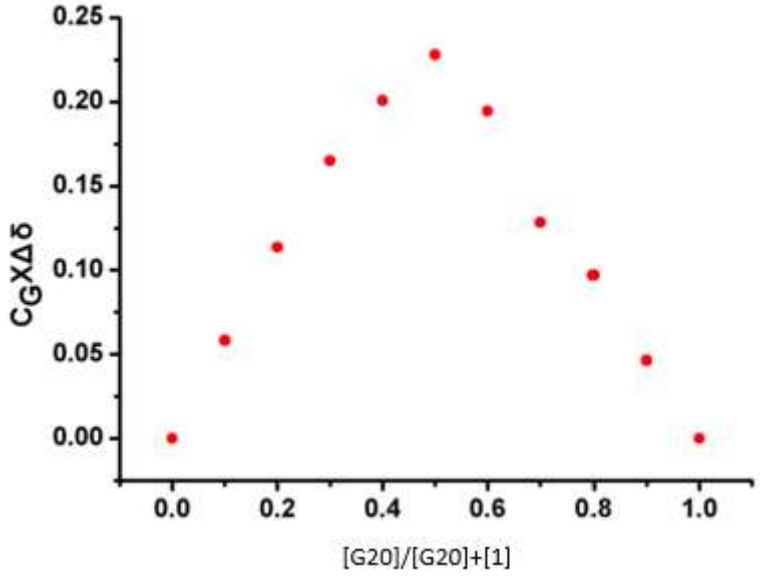


Figure S 46. Job's Plot of **G20** (*cf*. Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J*. **2016**, *22*, 6947).

4. ITC and ^{1}H NMR Job's Plot of G21

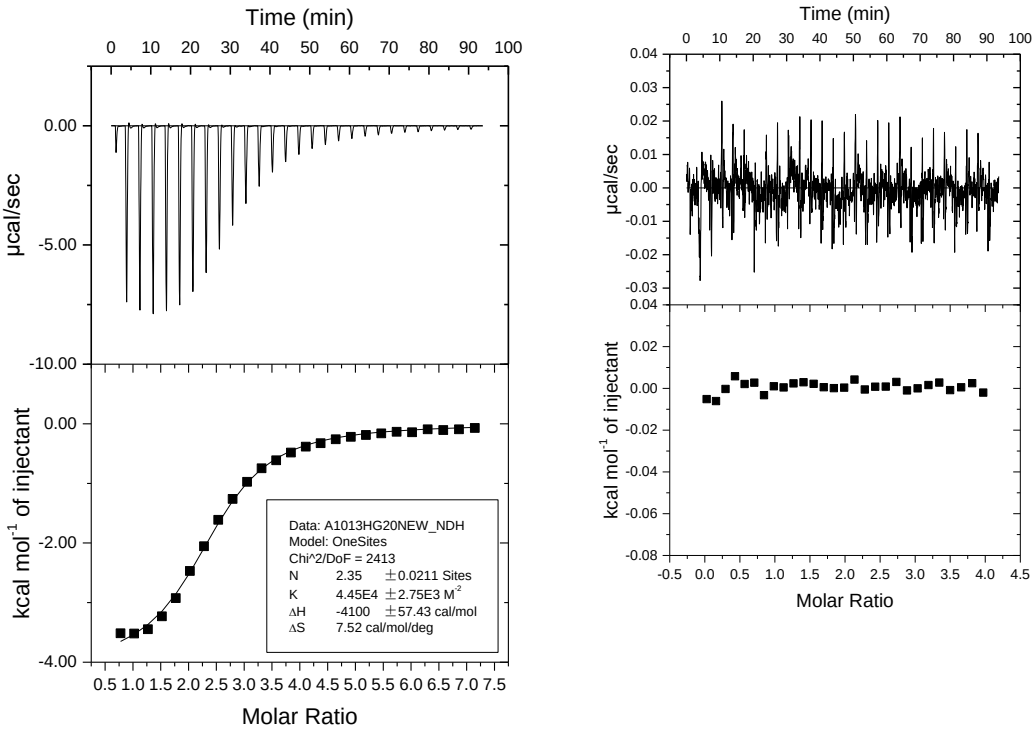


Figure S47. ITC titration of 0.1448 mM guest **G21** with 29×10 µL 5.0108 mM host **1** , T=298.15K

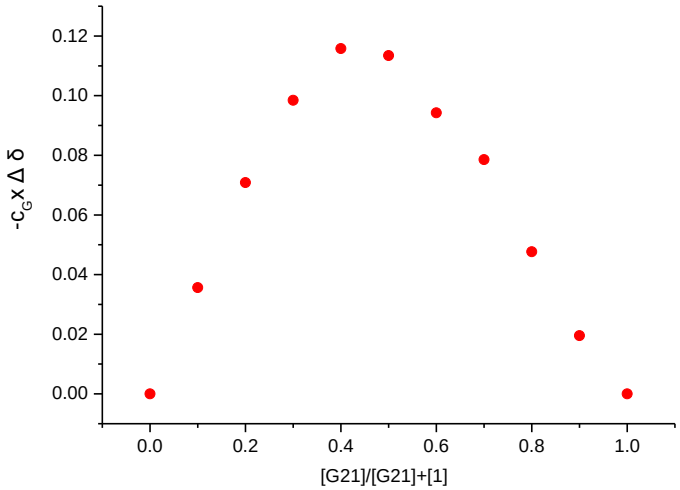


Figure S48 Job's Plot of **G15**. ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ^oC

5. ^{1}H NMR spectra of the host-guest complexes

For ^{1}H NMR spectra of the host-guest complexes of **1** with **G8**, **G11**, **G17-G21**, see: Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947.

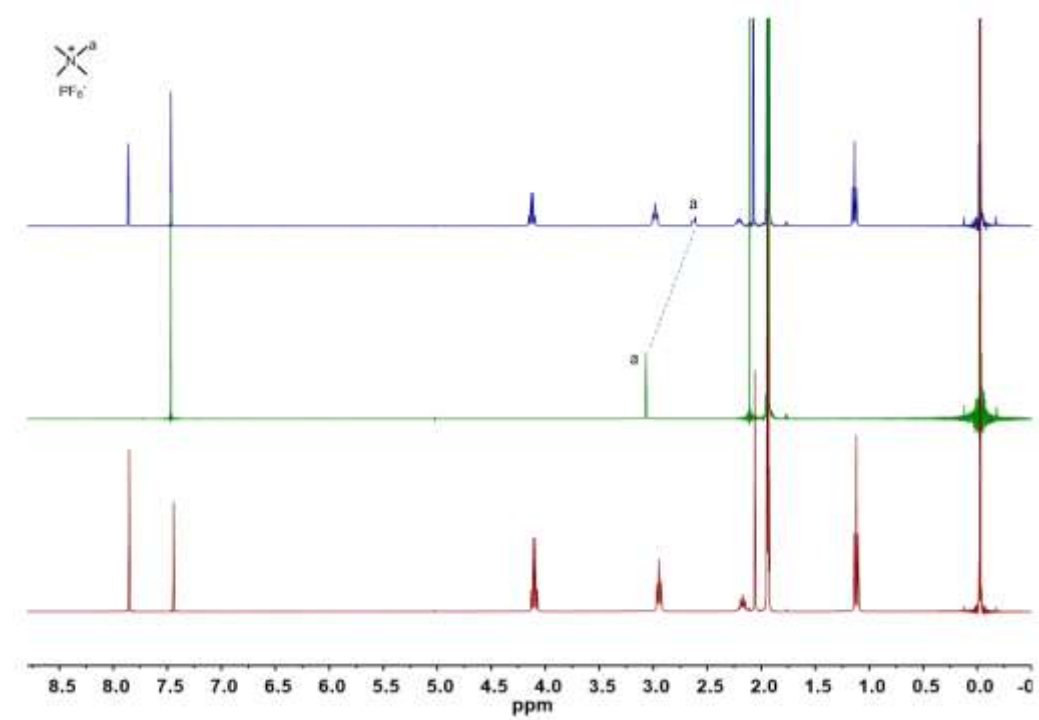


Figure S49. ^{1}H NMR spectra of host **1** (bottom), guest **G1** (middle) and a mixture of **1** and **G1** (top). [**1**] = [**G1**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

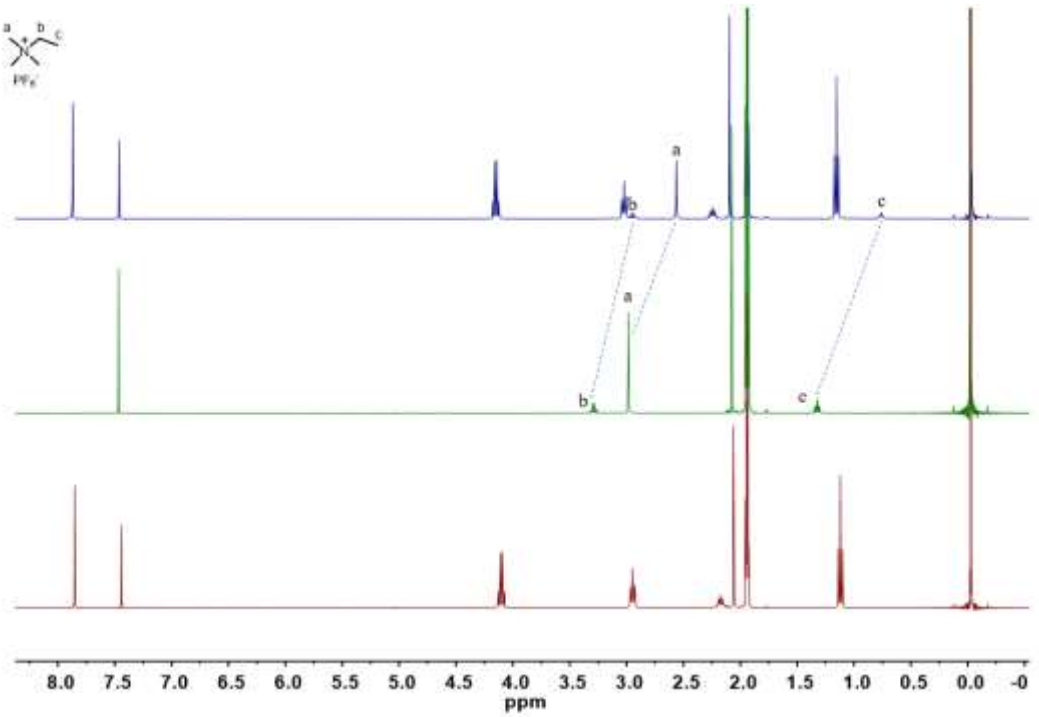


Figure S50. ^{1}H NMR spectra of host **1** (bottom), guest **G2** (middle) and a mixture of **1** and **G2** (top). [**1**] = [**G2**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

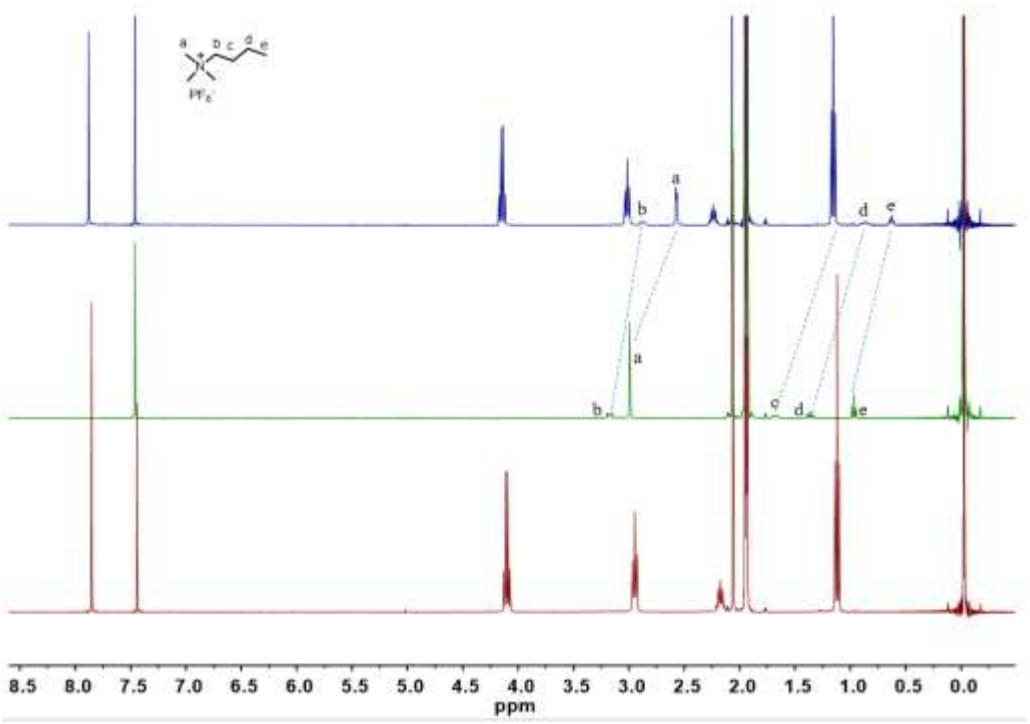


Figure S51. ^{1}H NMR spectra of host **1** (bottom), guest **G3** (middle) and a mixture of **1** and **G3** (top). [**1**] = [**G3**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

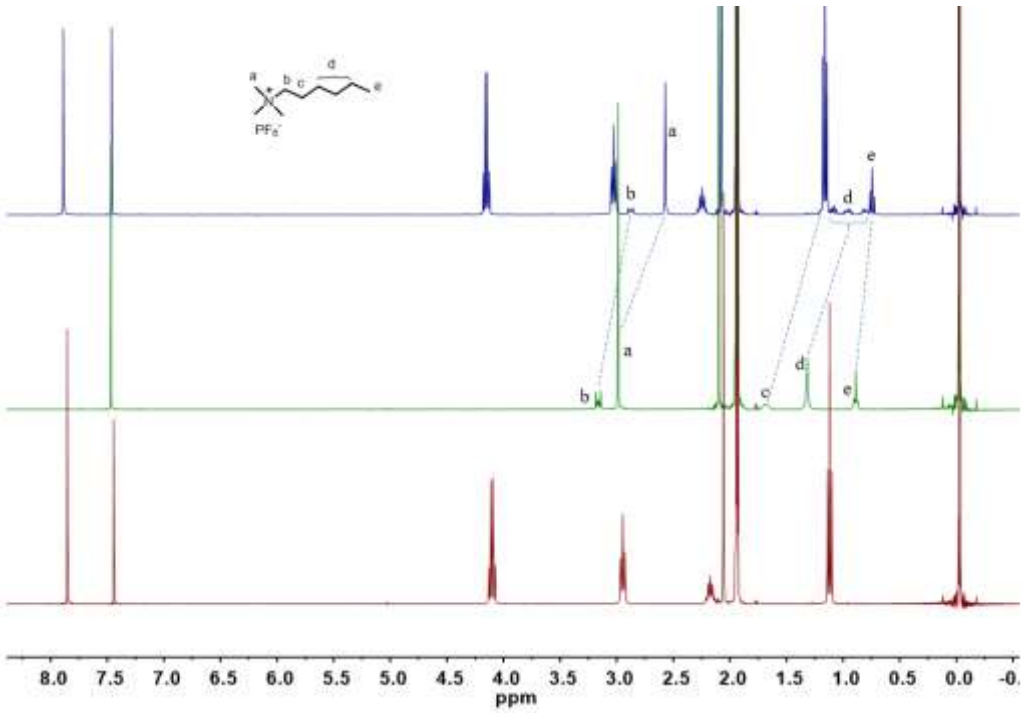


Figure S52. ^{1}H NMR spectra of host **1** (bottom), guest **G4** (middle) and a mixture of **1** and **G4** (top). [**1**] = [**G4**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

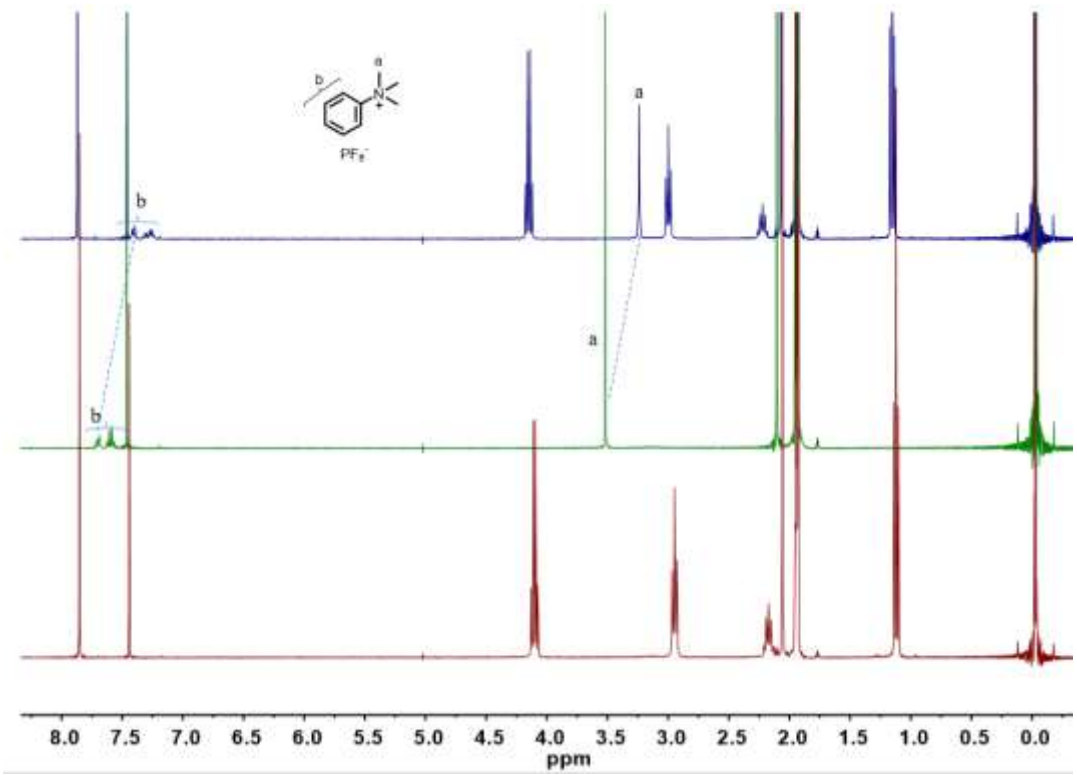


Figure S53. ^{1}H NMR spectra of host **1** (bottom), guest **G5** (middle) and a mixture of **1** and **G5** (top). [**1**] = [**G5**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

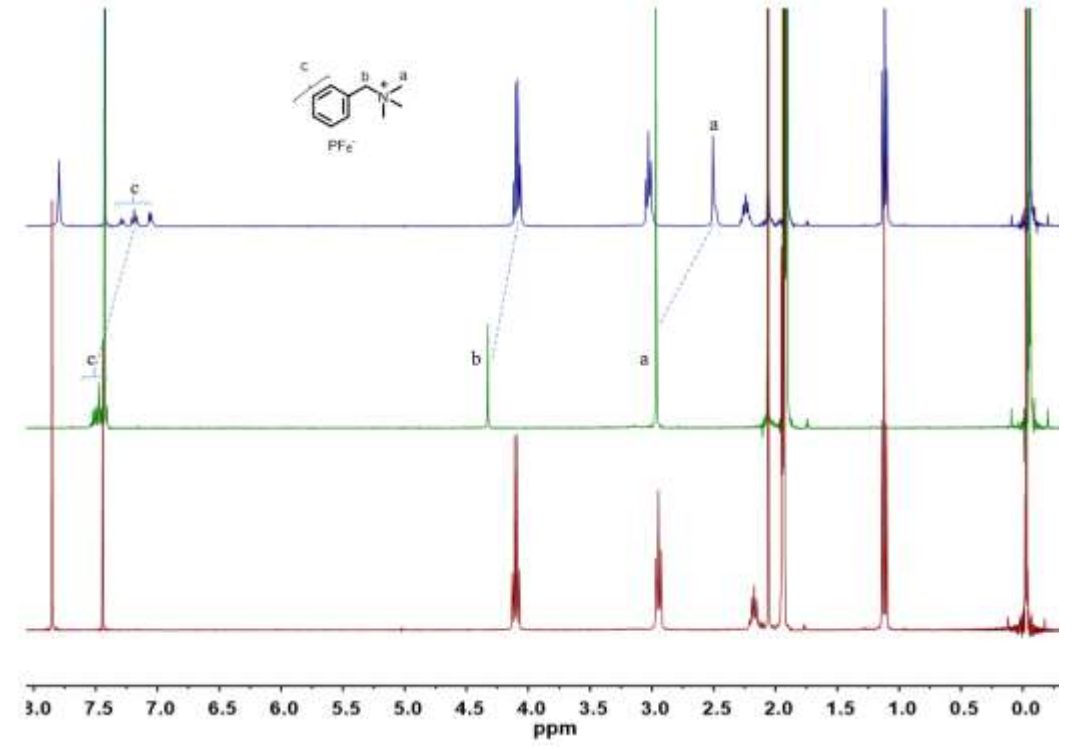


Figure S54. ^{1}H NMR spectra of host **1** (bottom), guest **G6** (middle) and a mixture of **1** and **G6** (top).

[**1**] = [**G6**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 ºC

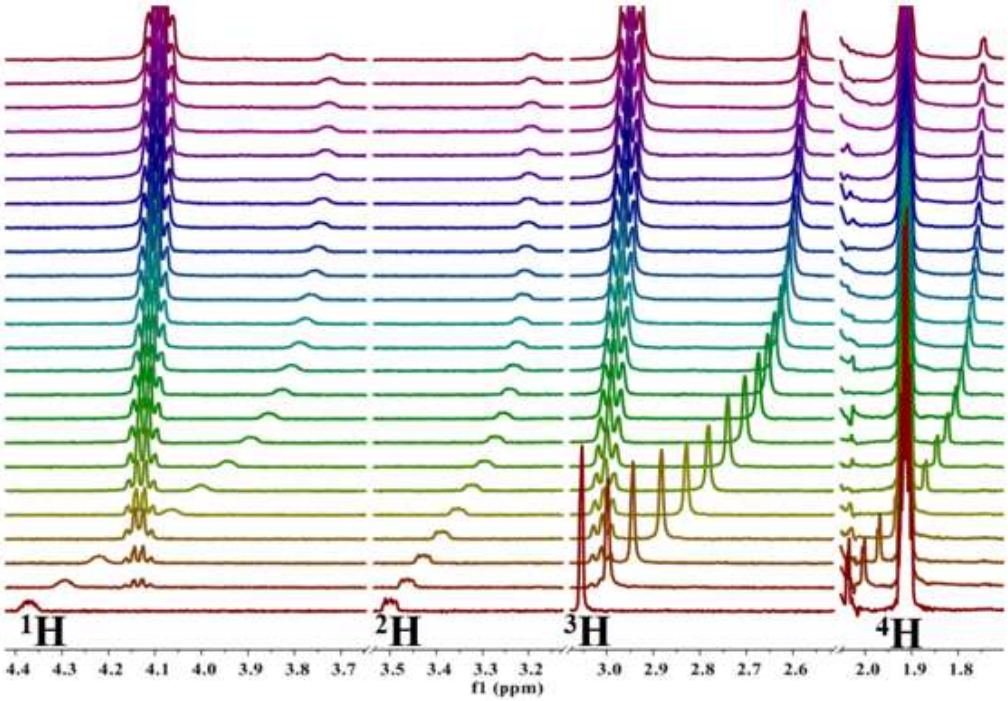


Figure S55. Partial ^{1}H NMR titration spectra of **G8** (1.0 mM) with addition of 0-3.50 equiv. of host **1** (from bottom to top). Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 ºC (*cf*. Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947).

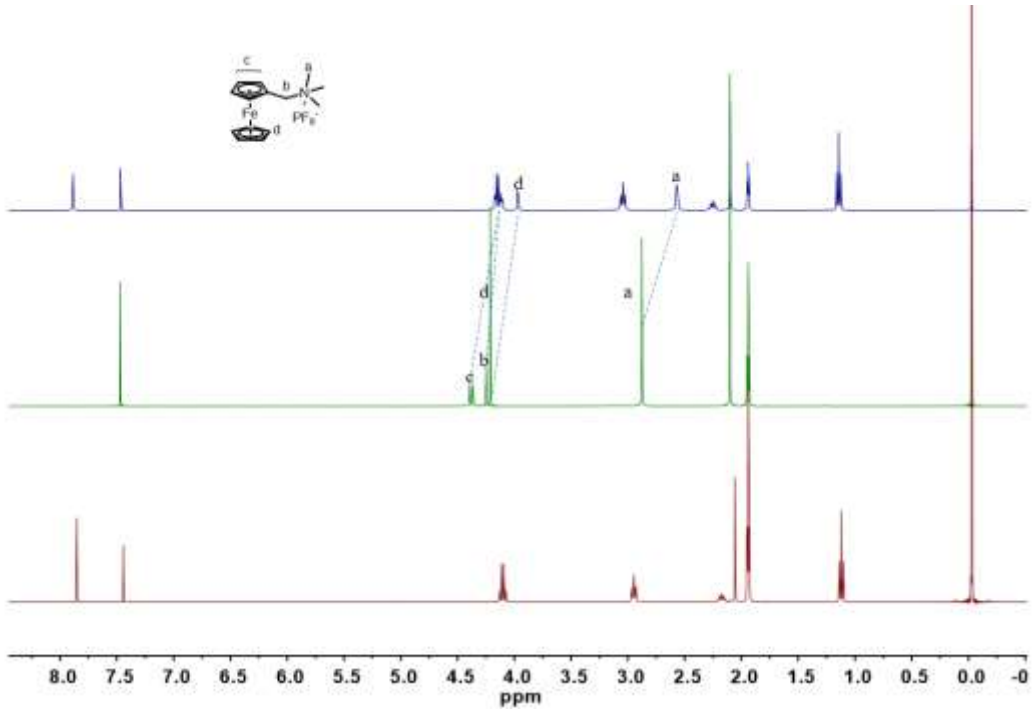


Figure S56. ^{1}H NMR spectra of host **1** (bottom), guest **G9** (middle) and a mixture of **1** and **G9** (top). [**1**] = [**G9**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 ºC

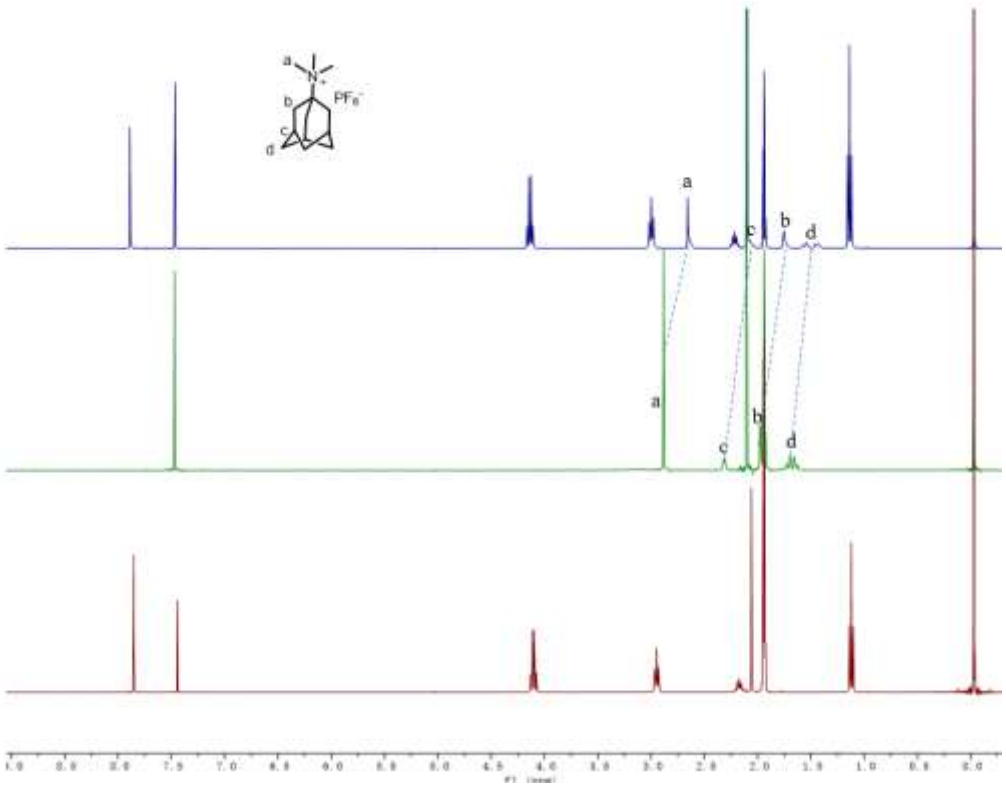


Figure S57. ^{1}H NMR spectra of host **1** (bottom), guest **G10** (middle) and a mixture of **1** and **G10** (top). [**1**] = [**G10**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

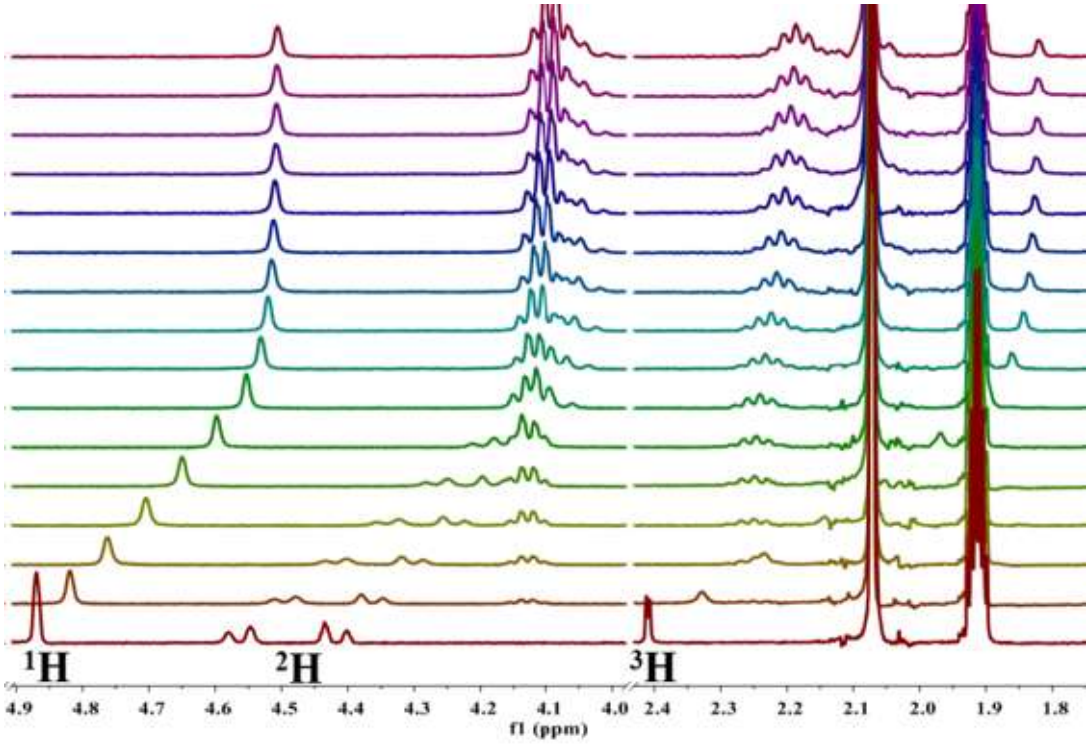


Figure S58. Partial ^{1}H NMR titration spectra of **G11** (1.0 mM) with addition of 0-2.25 equiv. of host **1** (from bottom to top). Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C (*cf.* Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947).

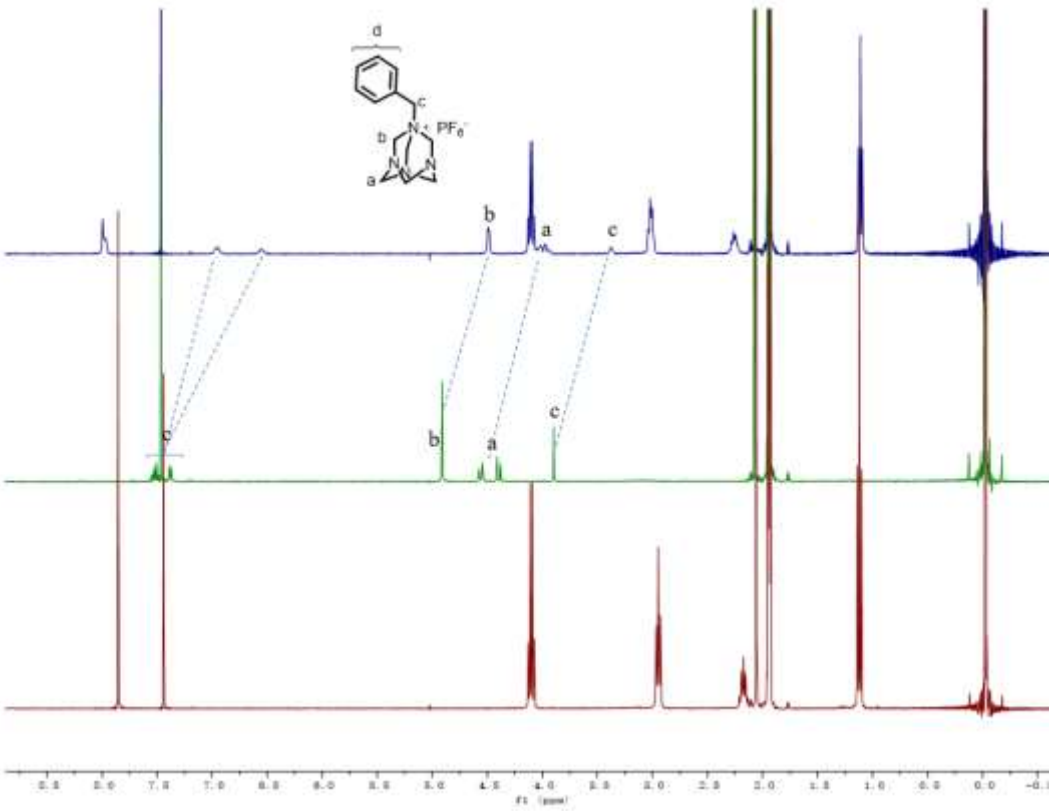


Figure S59. ^{1}H NMR spectra of host **1** (bottom), guest **G12** (middle) and a mixture of **1** and **G12** (top). [**1**] = [**G12**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

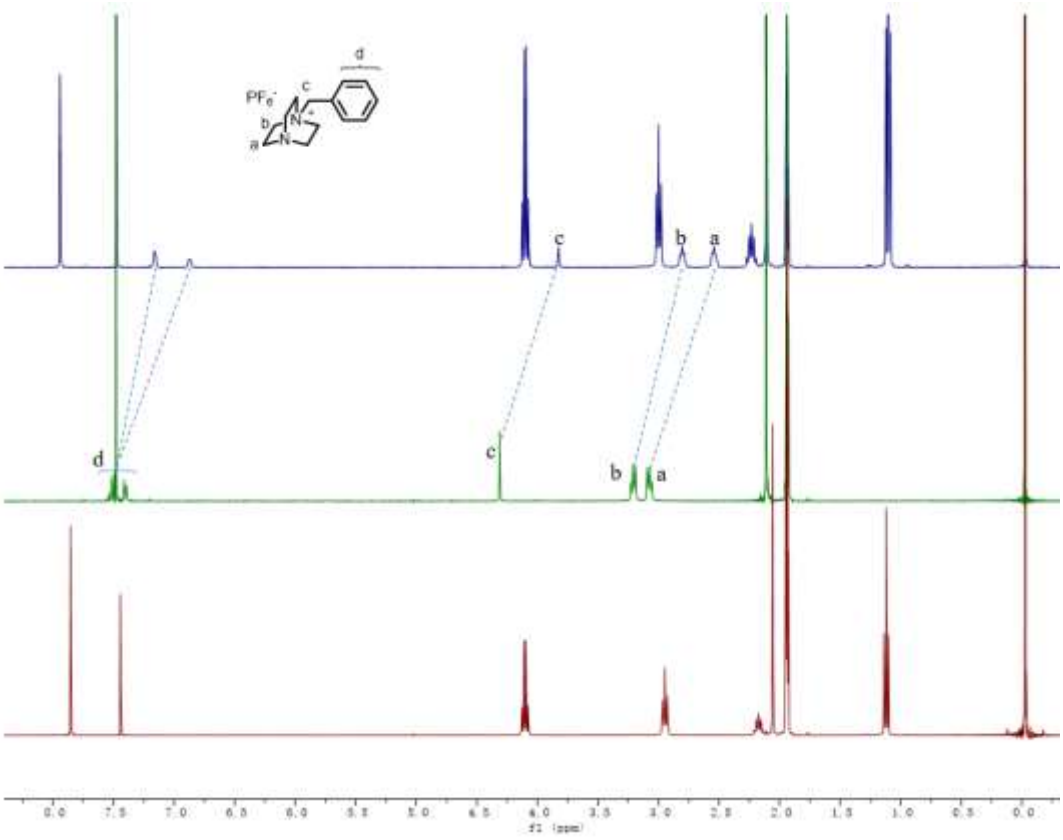


Figure S60. ^{1}H NMR spectra of host **1** (bottom), guest **G13** (middle) and a mixture of **1** and **G13** (top). [**1**] = [**G13**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

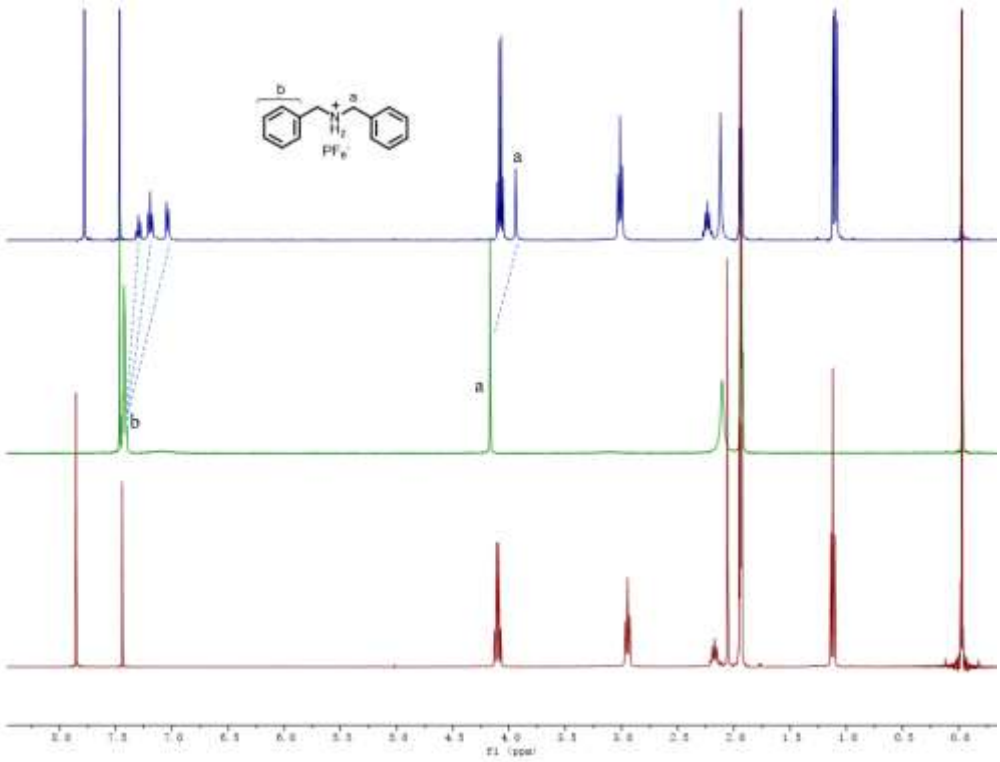


Figure S61. ^{1}H NMR spectra of host **1** (bottom), guest **G14** (middle) and a mixture of **1** and **G14** (top). [**1**] = [**G14**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

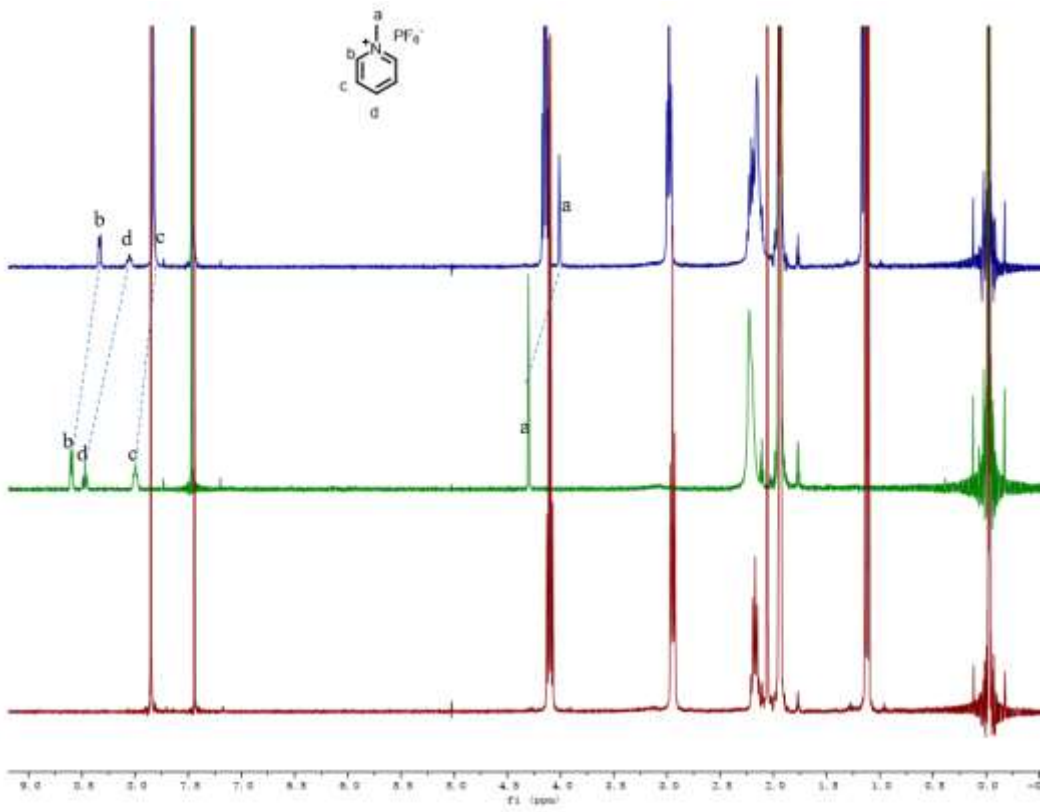


Figure S62. ^{1}H NMR spectra of host **1** (bottom), guest **G15** (middle) and a mixture of **1** and **G15** (top). [**1**] = [**G15**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

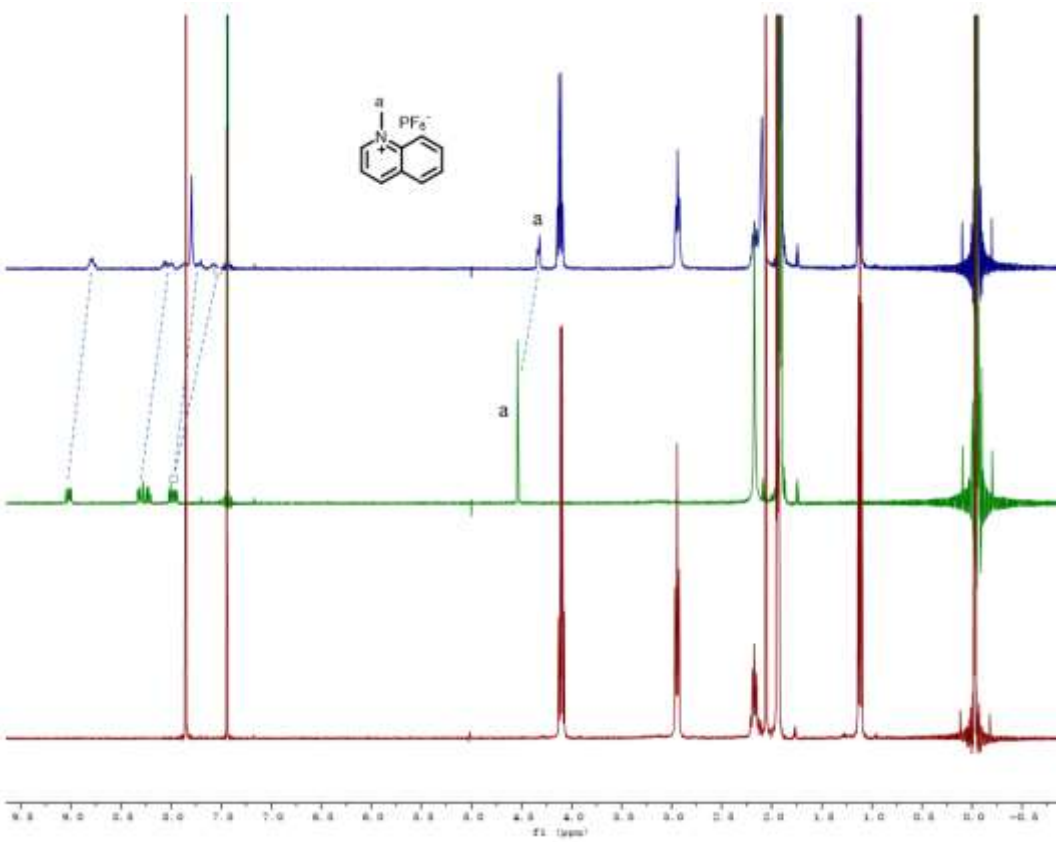


Figure S63. ^{1}H NMR spectra of host **1** (bottom), guest **G16** (middle) and a mixture of **1** and **G16** (top). [**1**] = [**G16**] = 4 mM. Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C

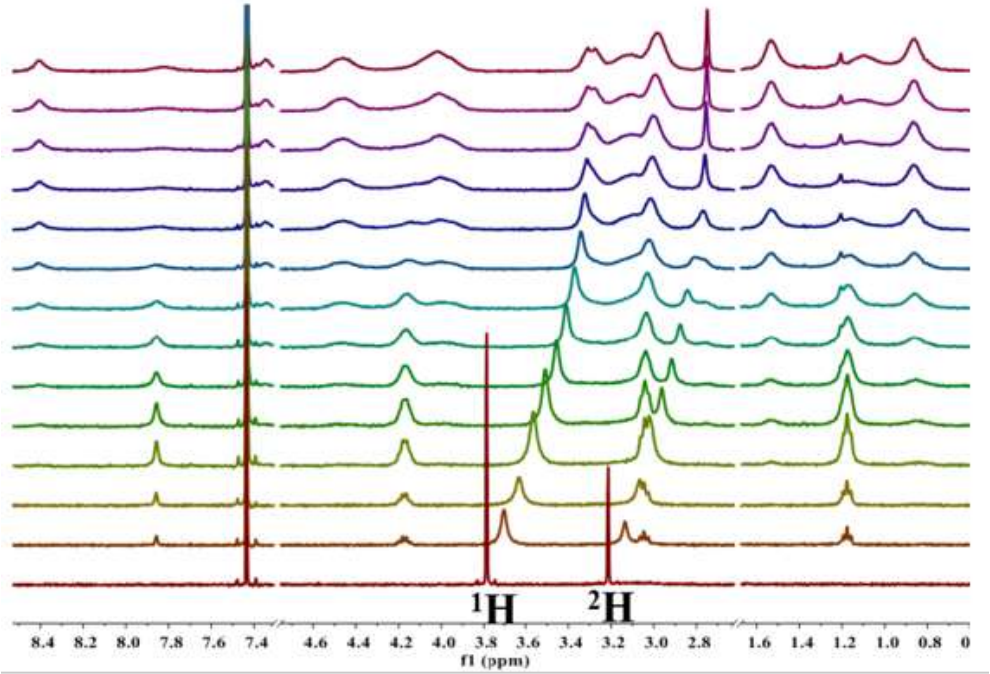


Figure S64. Partial ^{1}H NMR titration spectra of **G17** (1.0 mM) with addition of 0-2.25 equiv. of macrocyclic host **1** (from bottom to top). Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 °C (*cf*. Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947).

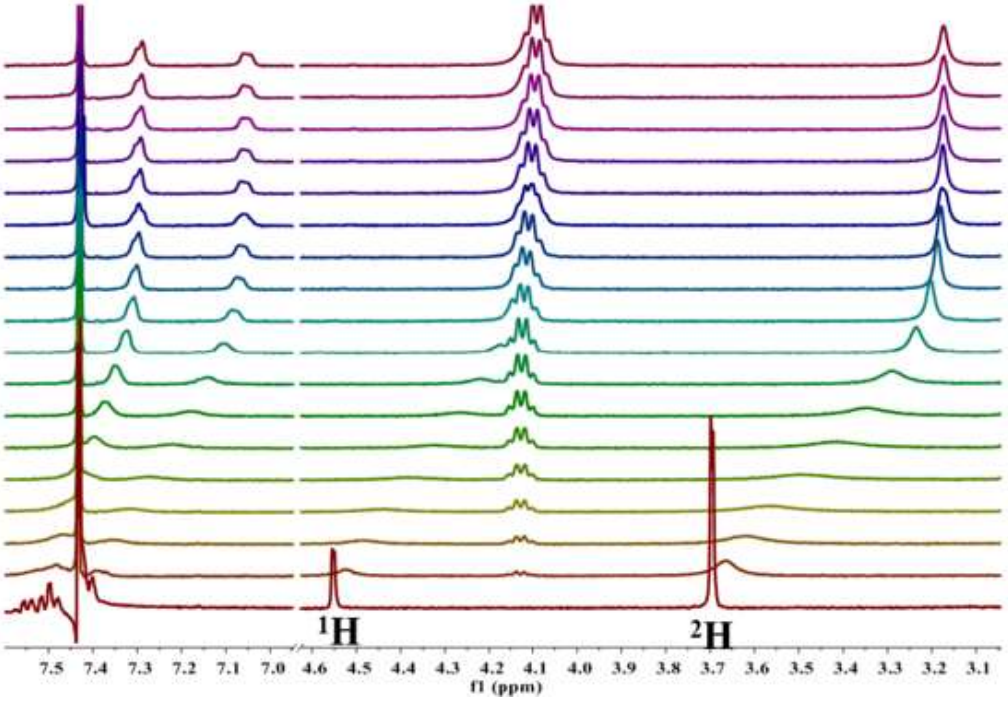


Figure S65. Partial ^{1}H NMR titration spectra of **G18** (1.0 mM) with addition of 0-2.75 equiv. of macrocyclic host **1** (from bottom to top). Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at

20 ºC (*cf*. Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947).

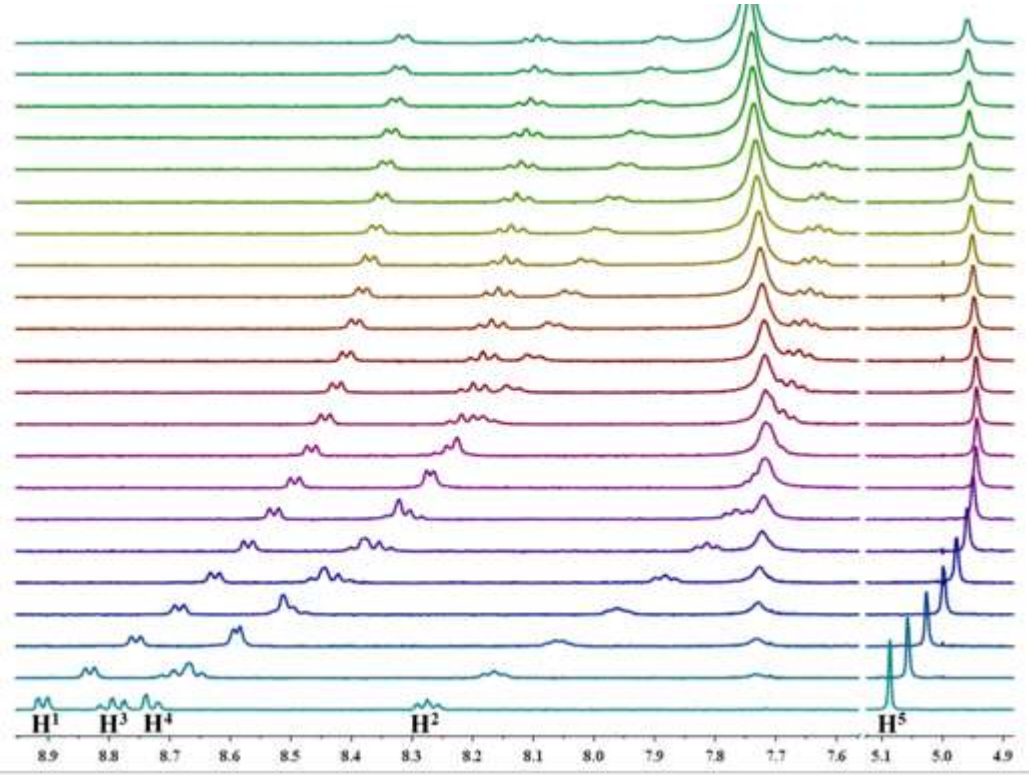


Figure S66. Partial ^{1}H NMR titration spectra of **G19** (1.0 mM) with addition of 0-4.2 equiv. of macrocyclic host **1** (from bottom to top). Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 ºC (*cf*. Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947).

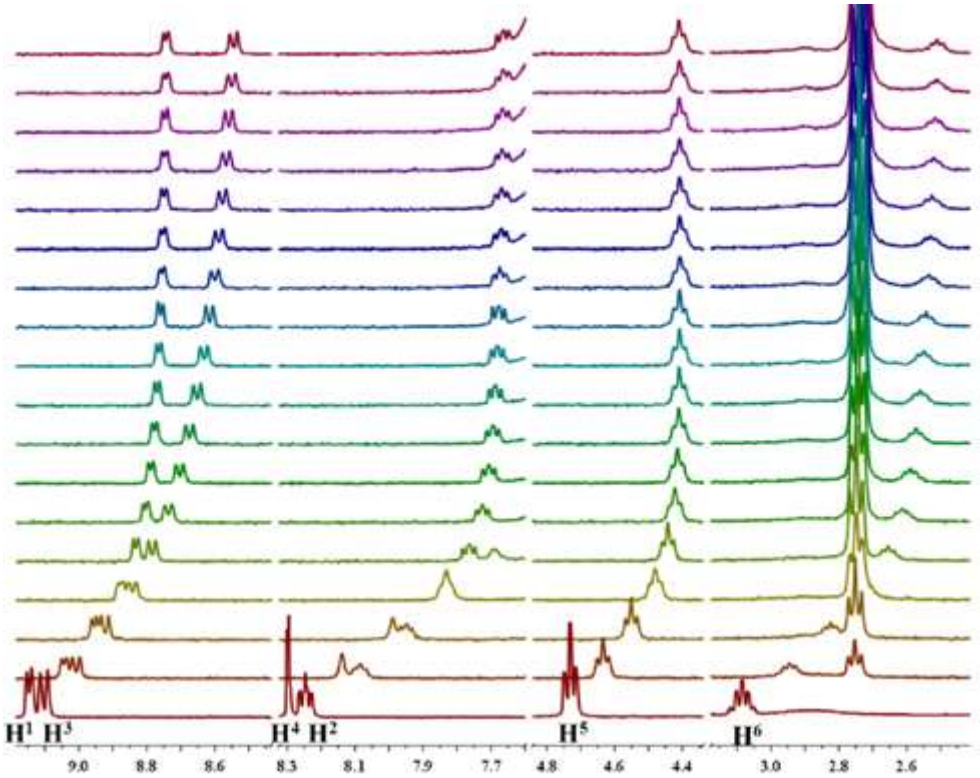


Figure S67. Partial ^{1}H NMR titration spectra of **G20** (2.0 mM) with addition of 0-4.8 equiv. of macrocyclic host **1** (from bottom to top). Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 ºC (*cf*. Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947).

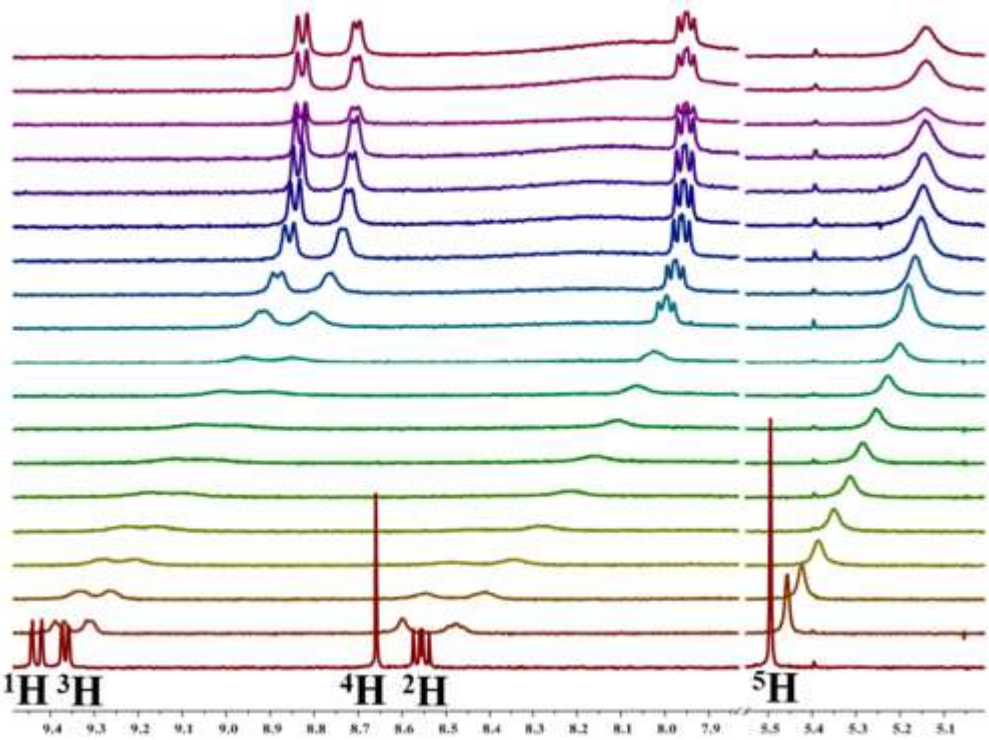


Figure S68. Partial ^{1}H NMR titration spectra of **G21** (1.0 mM) with addition of 0-3.4 equiv. of macrocyclic host **1** (from bottom to top). Measured in a mixture of $CDCl_3$ and CD_3CN (v : v = 1 : 1) at 20 ºC (*cf*. Guo, Q.-H.; Zhao, L.; Wang, M.-X. *Chem. Eur. J.* **2016**, *22*, 6947).

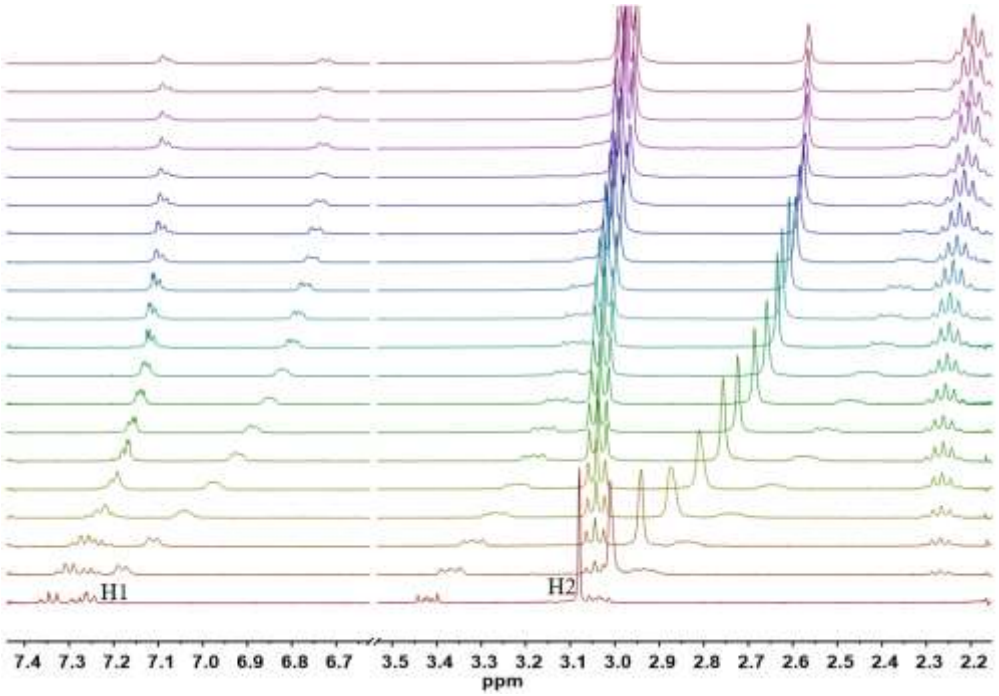
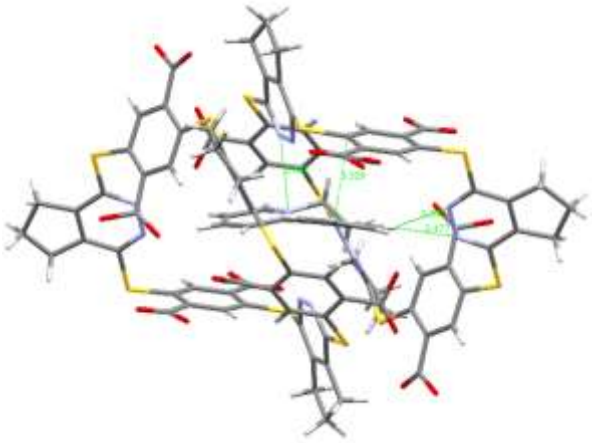


Figure S69. Partial ^{1}H NMR titration spectra of [**G7**](2 mM) with addition of 0-5.85 equiv. of host **1** (from bottom to top). $K_a = 5.16 \times 10^3$ ^{1}H NMR spectra were measured in the mixture of CD_3CN and $CDCl_3$ (V : V = 1:1) at 20 ^{o}C.

6. Crystal data and structure refinement for X-ray molecular structures



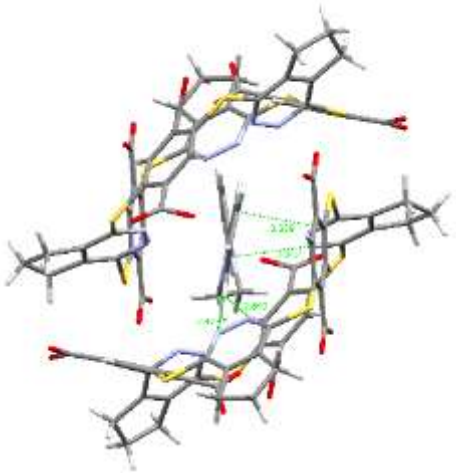


Figure S70. X-ray molecular structure of the complex of **1** with guest **G19** (two different side views). Anions and solvent molecules are omitted for clarity.

Identification code	**1** • 0.5 **G19**
Empirical formula	C65 H63 F6 N8 O12 P S6
Formula weight	1485.56
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 14.180(2) Å b = 16.430(3) Å c = 16.973(2) Å α= 65.700(12)°. β= 71.841(16)°. γ = 79.491(18) °.
Volume	3417.8(10) $Å^3$
Z	2
Density (calculated)	1.444 Mg/m3
Absorption coefficient	0.307 mm-1
F(000)	1540

Crystal size	0.088 x 0.068 x 0.039 mm3
Theta range for data collection	1.751 to 25.200 °.
Index ranges	-16<=h<=16, -19<=k<=19, -20<=l<=20
Reflections collected	40572
Independent reflections	12278 [R(int) = 0.0788]
Completeness to theta = 27.4807 °	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8452
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	12278 / 479 / 1038
Goodness-of-fit on F2	1.207
Final R indices [I>2sigma(I)]	R1 = 0.1451, wR2 = 0.3200
R indices (all data)	R1 = 0.1783, wR2 = 0.3417
Extinction coefficient	n/a
Largest diff. peak and hole	1.215 and -0.589 e.Å^{-3}
CCDC No.	1577768