Supplementary Information

New approach for the synthesis of mono- and A1/A2-dihydroxy-substituted pillar[5]arenes and their complexation with alkyl alcohols in solution and in solid state

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Single crystal X-ray diffraction data:

Table 1S. Summary on the nature of the crystals and various crystallographic parameters of **Pilla-1a**, **Pillar-3a**, and **Pillar-4a**.

Crystal Name	**Pillar-1a**	**Pillar-3a**	**Pillar-4a**
Crystal Dimension/mm	0.20 X 0.13 X 0.06	0.21 X 0.16 X 0.12	0.22 X 0.20 X 0.17
Crystal Color, Habit	colorless, block	colorless, block	colorless, block
Formula	$C_{57}H_{65}NO_{12}$	$C_{59}H_{62}O_{10}Cl_2$	$C_{43}H_{46}O_{10}$
Crystal system	triclinic	triclinic	monoclinic
Space group(no.)	P-1 (#2)	P-1 (#2)	C 2 (#5)
T/K	150	150	150
a/Å	11.1032(19)	13.895(2)	21.155(10)
b//Å	12.108(2)	16.972(2)	12.211(5)
c/Å	22.115(4)	23.680(2)	17.858(9)
α	81.852(6)	72.585(5)	90
β	77.004(6)	87.742(7)	98.777(7)
γ	63.908(5)	87.878(7)	90
V/ Å^3	2598.7(8)	5322.5(9)	4559(4)
Z	2	4	4
μ(CuKα) / mm^{-1}	0.085	0.180	0.074
ρ_{calcd}/g cm^{-3}	1.222	1.250	1.053
θ_{max}/deg	26.37	26.37	26.37
Reflections collected	22648	47687	17028
Unique reflections	10565	21645	4839
R_{int}	0.0624	21645	0.0571
R (I > 2σ)	0.0724	0.0618	0.0535
R (all data)	0.1347	0.0947	0.0768
R_w(all data)	0.2276	0.1939	0.2000
$\lvert\Delta\rho\rvert_{max}$e Å^{-3}	0.51	0.88	0.162

Table 2S. Summary on the nature of the crystals and various crystallographic parameters of **Pillar-1b-4b**.

Crystal Name	**Pillar-1b**	**Pillar-2b**	**Pillar-3b**	**Pillar-4b**
Crystal Dimension/mm	0.30 X 0.25 X 0.20	0.09 X 0.07 X 0.03	0.22 X 0.18 X 0.03	0.22 X 0.19 X 0.17
Crystal Color, Habit	colorless, block	colorless, platelet	colorless, platelet	colorless, block
Formula	$C_{80}H_{112}O_{10}Cl_2$	$C_{71}H_{102}O_{10}$	$C_{87}H_{120}O_{10}$	$C_{69}H_{96}O_{10}Cl_2$
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group(no.)	P-1 (#2)	P 21/c (#14)	P-1 (#2)	P-1 (#2)
T/K	150	150	150	150
a/Å	12.2915(5)	17.2159(13)	12.259(7)	12.9562(14)
b//Å	14.3465(6)	23.5570(17)	14.997(8)	16.8936(18)
c/Å	22.0563(16)	16.0651(10)	21.960(11)	17.2373(16)
α	90.367(6)	90	90.762(8)	74.643(5)
β	90.635(6)	97.159(6)	91.801(11)	70.786(5)
γ	104.150(7)	90	103.438(8)	68.798(5)
V/ Å^3	3771.0(3)	6464.5(8)	3924.(4)	3275.7(6)
Z	2	4	2	2
μ(CuKα) / mm^{-1}	0.142	0.075	0.071	0.155
ρ_{calcd}/g cm^{-3}	1.149	1.146	1.122	1.172
θ_{max}/deg	26.34	25.03	25.03	25.03
Reflections collected	33355	24460	29842	25305
Unique reflections	15257	11163	13508	11501
R_{int}	0.0194	0.1096	0.0752	0.0274
R (I > 2σ)	0.1311	0.0934	0.1369	0.0879
R (all data)	0.1564	0.2040	0.2526	0.1089
R_w(all data)	0.4293	0.2804	0.4310	0.2668
$\lvert\Delta\rho\rvert_{max}$e Å^{-3}	1.609	0.560	0.493	0.943

Table 3S. Summary on the nature of the crystals and various crystallographic parameters of **DMP5 ⊃ octanol (G3).**

Crystal Name	**DMP5 ⊃ octanol (G3)**
Crystal Dimension/mm	0.21 X 0.20 X 0.17
Crystal Color, Habit	colorless, block
Formula	$C_{53}H_{68}O_{11}$
Crystal system	triclinic
Space group(no.)	P-1 (#2)
T/K	150
a/Å	12.2468(7)
b//Å	20.1135(12)
c/Å	22.5815(16)
α	80.311(6)
β	76.326(5)
γ	83.145(6)
V/ Å^3	5309.3(6)
Z	4
μ(CuKα) / mm^{-1}	0.076
ρ_{calcd}/g cm^{-3}	1.102
θ_{max}/deg	25.01
Reflections collected	40566
Unique reflections	18559
R_{int}	0.0432
R (I > 2σ)	0.0944
R (all data)	0.1688
R_w(all data)	0.3254
$\lvert\Delta\rho\rvert_{max}$e Å^{-3}	0.819

Table 4S. Summary on the nature of the crystals and various crystallographic parameters of inclusion complexes.

Crystal Name	**Pillar-2a ⊃ Hexanol**	**Pillar-2a ⊃ heptanol**	**Pillar-2a ⊃ octanol**
Crystal Dimension/mm	0.12 X 0.11 X 0.03	0.20 X 0.18 X 0.02	0.20 X 0.16 X 0.03
Crystal Color, Habit	colorless, platelet	colorless, platelet	colorless, platelet
Formula	$C_{50}H_{62}O_{11}$	$C_{51}H_{64}O_{11}$	$C_{52}H_{66}O_{11}$
Crystal system	triclinic	triclinic	triclinic
Space group(no.)	P-1 (#2)	P-1 (#2)	P-1 (#2)
T/K	150	150	150
a/Å	11.032(2)	11.423(11)	11.4704(9)
b//Å	12.204(2)	12.053(11)	12.0826(10)
c/Å	19.541(3)	19.397(12)	19.3426(15)
α	84.688(6)	93.07(2)	92.797(6)
β	87.523(7)	91.52(3)	91.136(6)
γ	63.365(5)	117.76(4)	117.996(8)
V/ Å^3	2341.8(5)	2356(4)	2361.4(3)
Z	2	2	2
μ(CuKα) / mm^{-1}	0.083	0.083	0.084
ρ_{calcd}/g cm^{-3}	1.190	1.202	1.219
θ_{max}/deg	25.02	26.06	26.41
Reflections collected	17319	20144	20597
Unique reflections	8183	9201	9525
R_{int}	0.1107	0.0998	0.0579
R (I > 2σ)	0.0806	0.1025	0.0799
R (all data)	0.2702	0.1446	0.1244
R_w(all data)	0.2678	0.3499	0.2560
$\lvert\Delta\rho\rvert_{max}$e Å^{-3}	0.17	0.55	0.576

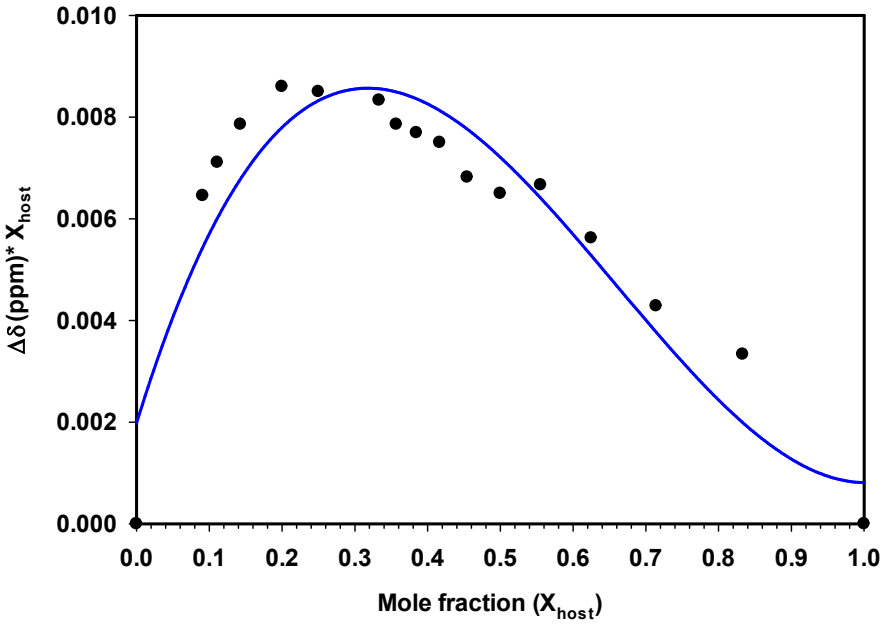

Figure S1. Job's plot for complexation of host **Pillar-2a** with hexanol guest **G1**, determined from ^{1}HNMR titration in $CDCl_3$ at 25 ^{o}C.

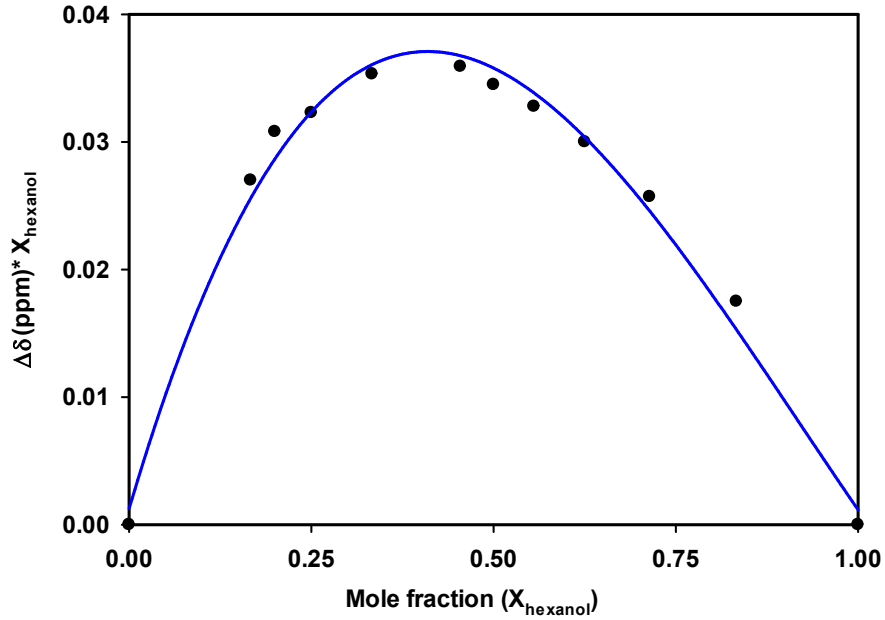

Figure S2. Job's plot for complexation of host **DMP5** with hexanol guest **G3**, determined from ^{1}HNMR titration in $CDCl_3$ at 25 ^{o}C.

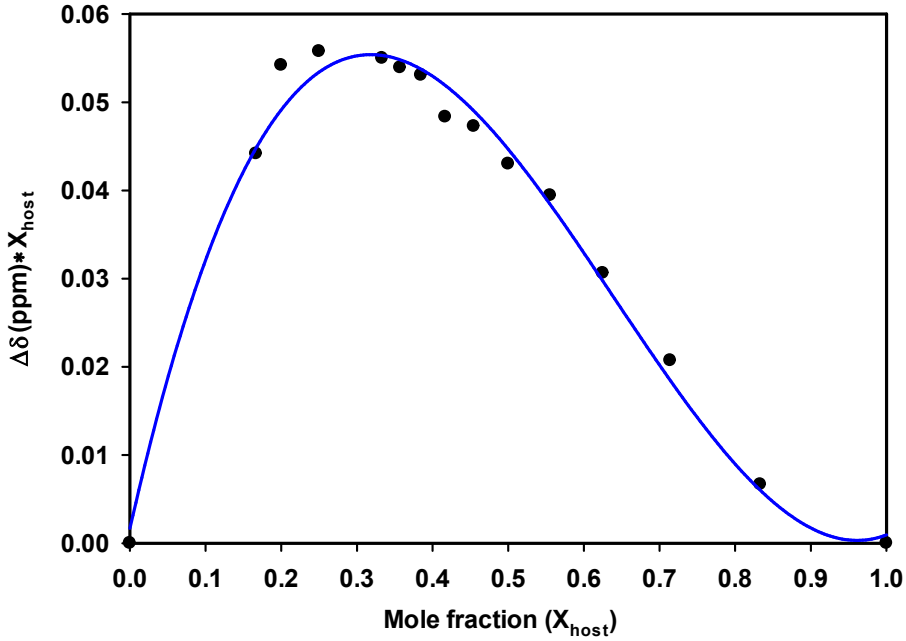

Figure S3. Job's plot for complexation of host **Pillar-2a** with heptanol guest **G2**, determined from ^{1}HNMR titration in $CDCl_3$ at 25 ^{o}C.

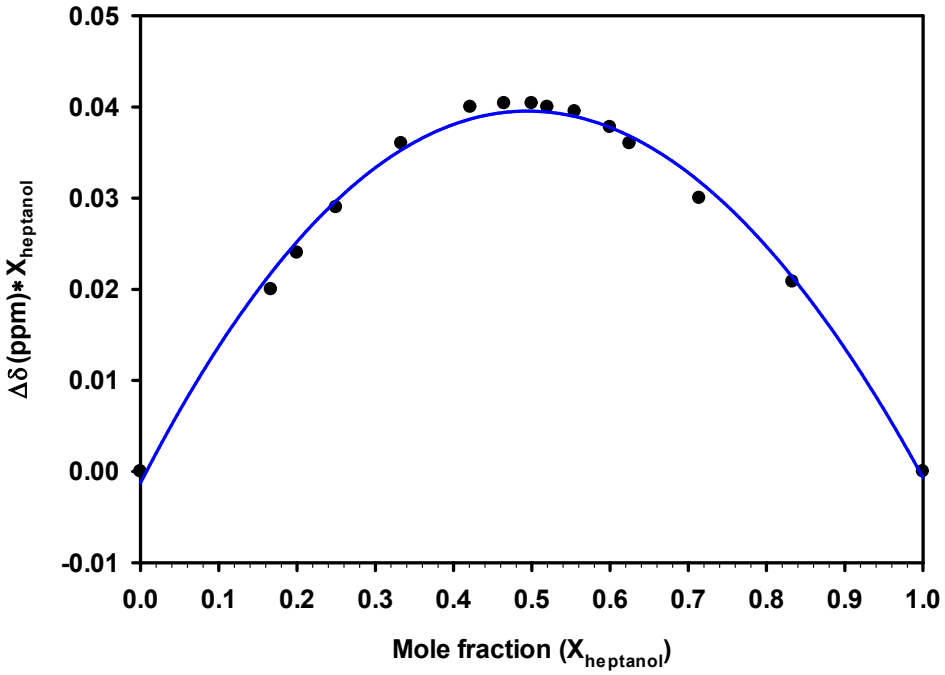

Figure S4. Job's plot for complexation of host **DMP5** with heptanol guest **G2**, determined from ^{1}HNMR titration in $CDCl_3$ at 25 ^oC.

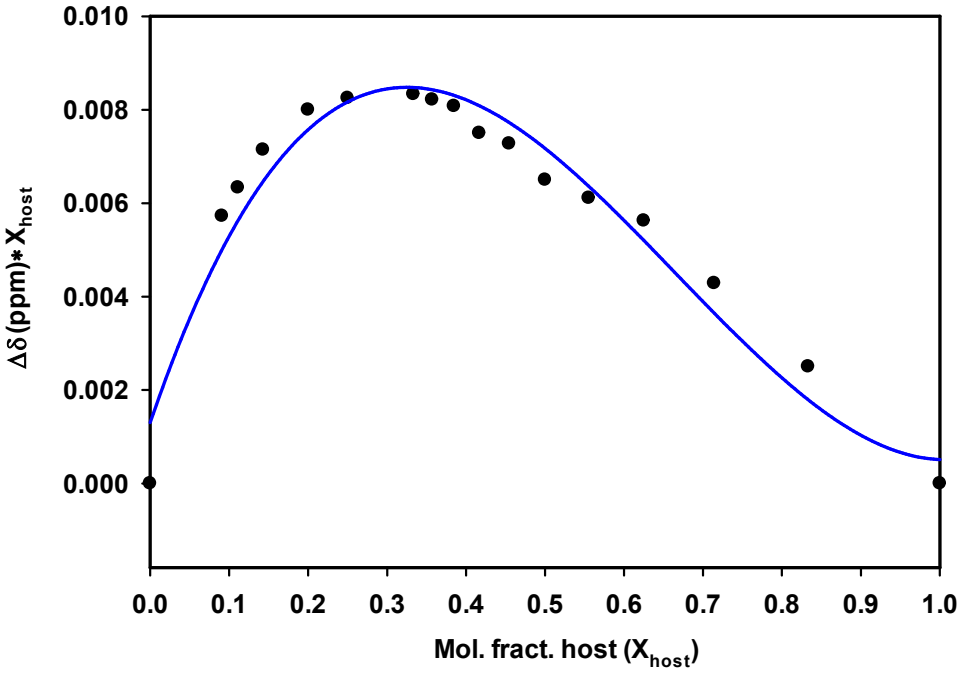

Figure S5. Job's plot for complexation of host **Pillar-2a** with octanol guest **G3**, determined from ^{1}HNMR titration in $CDCl_3$ at 25 ^oC.

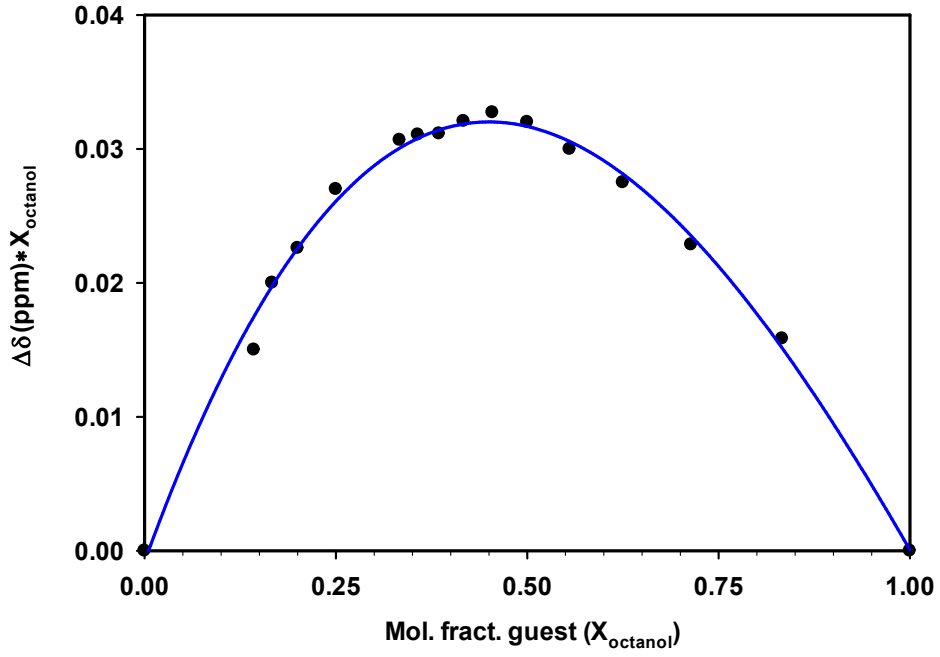

Figure S6. Job's plot for complexation of host **DMP5** with octanol guest **G3**, determined from ^{1}HNMR titration in $CDCl_3$ at 25 ^{o}C.

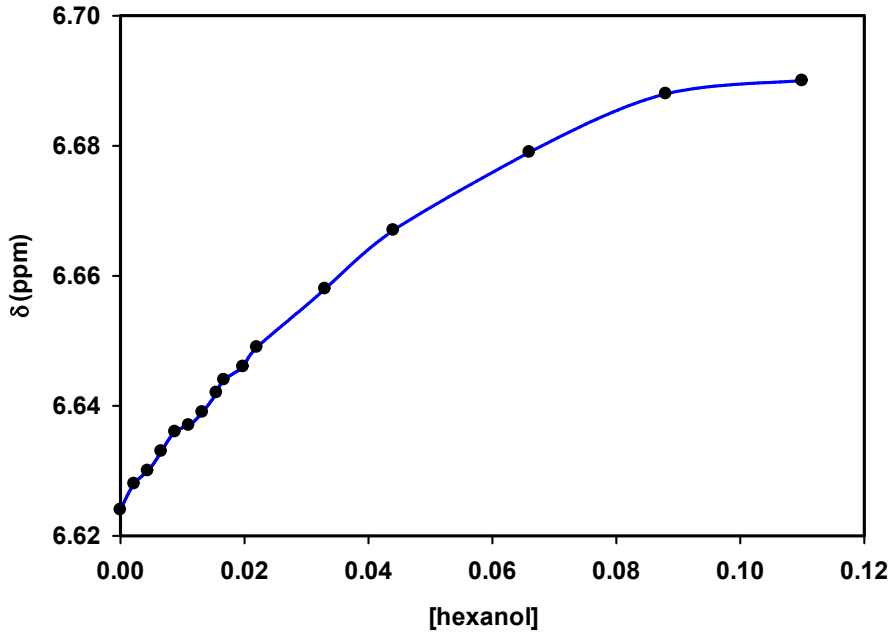

Figure S7. Plot of chemical shift (δ) changes for the host (**Pillar-2a**) proton aromatic region as function of guest (hexanol) concentration in $CDCl_3$ at 25 ^{o}C.

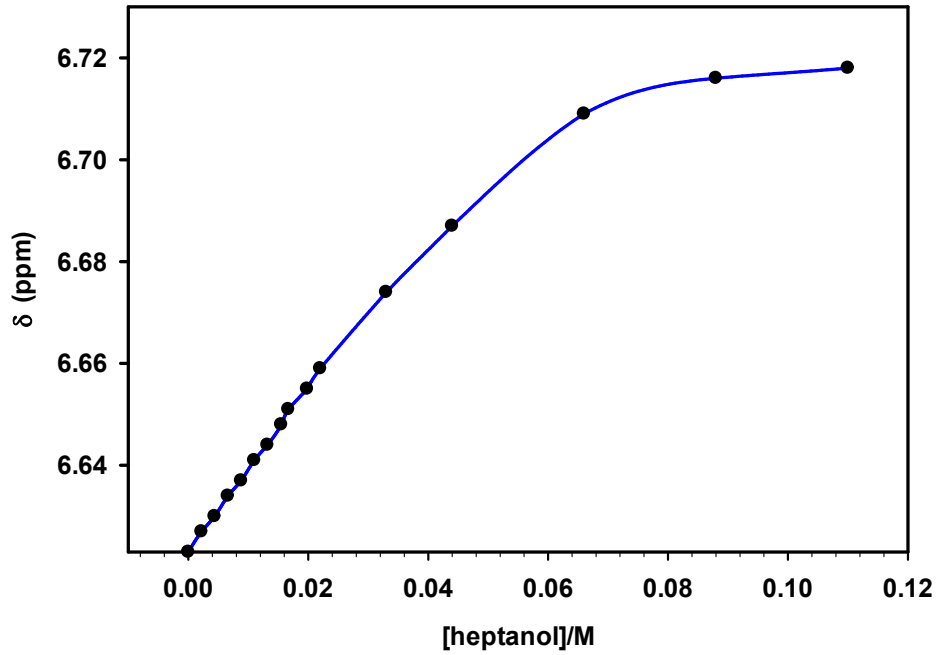

Figure S8. Plot of chemical shift (δ) changes for the host (**Pillar-2a**) proton aromatic region as function of guest (heptanol) concentration in $CDCl_3$ at 25 °C.

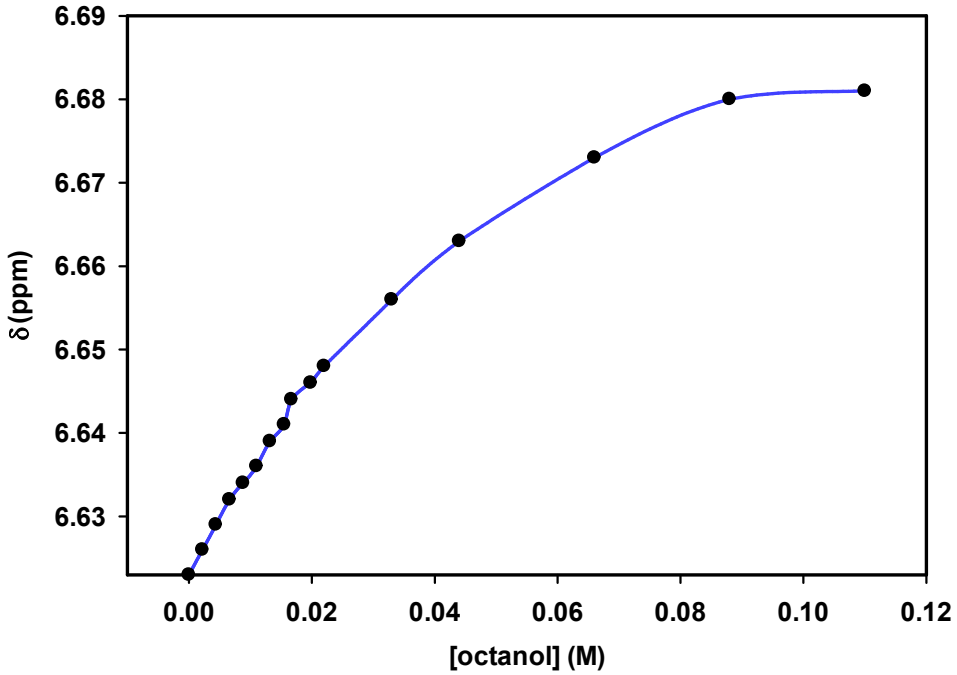

Figure S9. Plot of chemical shift (δ) changes for the host (**Pillar-2a**) proton aromatic region as function of guest (octanol) concentration in $CDCl_3$ at 25 °C.

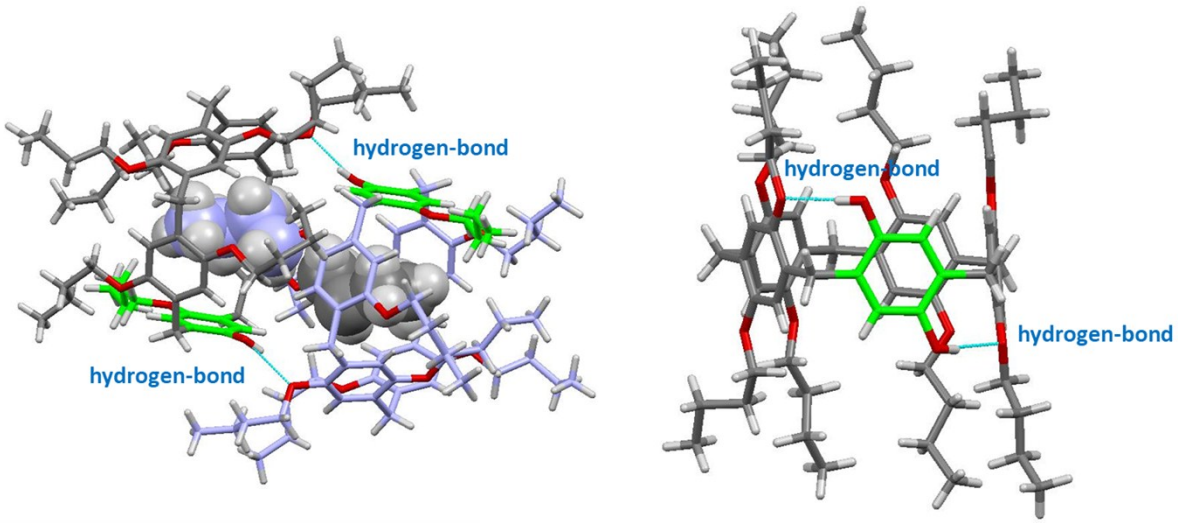

Figure S10. Mode of hydrogen-bonding attractions of **Pillar-2b** and **Pillar-4b**.

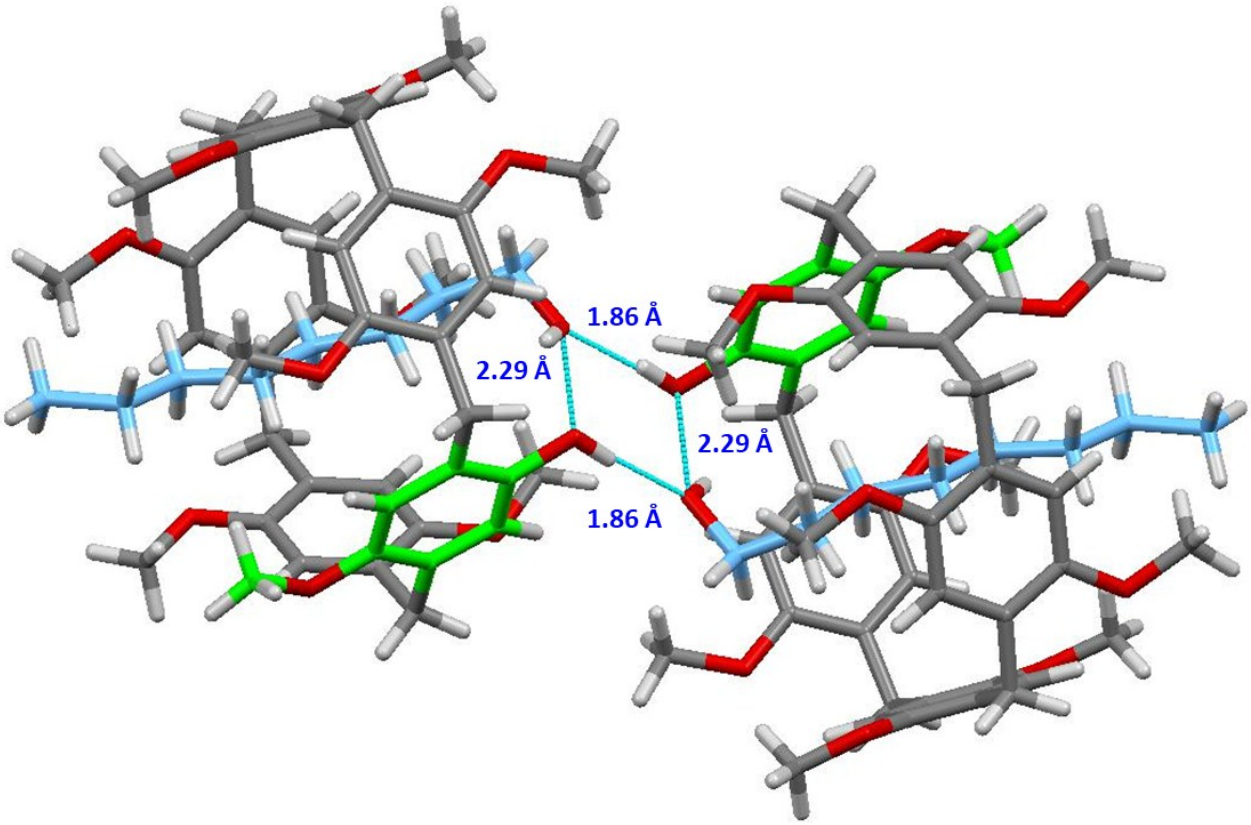

Figure S11. Representative example of supramolecular dimeric head-to-head assembly induced by hydrogen-bonding interactions **Pilar-2a** ⊃ **G3**.

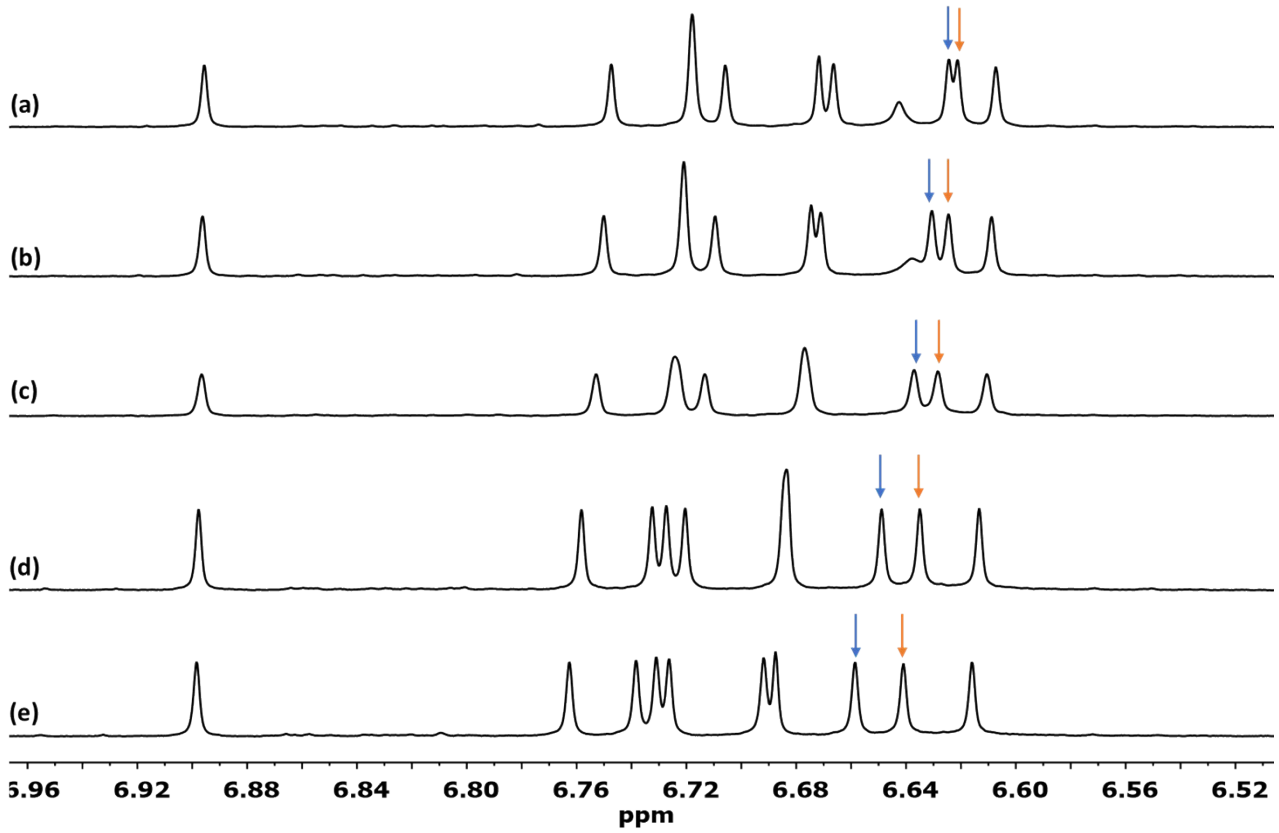

Figure S12. Partial ^{1}H NMR spectra (600 MHz, chloroform-*d*, 25 °C) of **Pilar-2a** and hexanol (**G1**) (a); 10 mM **Pilar-2a** (b); 10 mM **Pilar-2a** and 4 mM **G1** (c); 10 mM **Pilar-2a** and 10 mM **G1** (d); 10 mM **Pilar-2a** and 20 mM **G1** (e); 10 mM **Pilar-2a** and 30 mM **G1**.

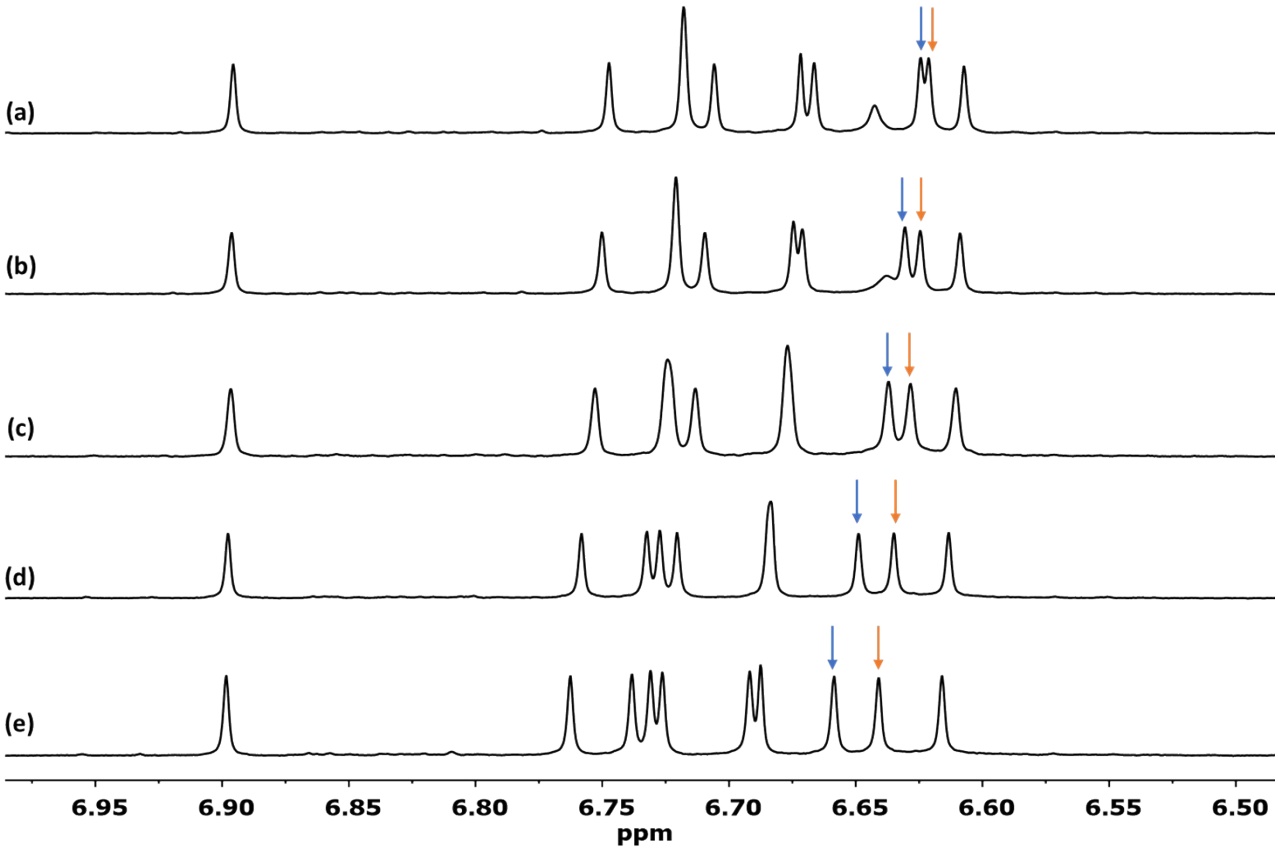

Figure S13. Partial ^{1}H NMR spectra (600 MHz, chloroform-*d*, 25 °C) of **Pilar-2a** and heptanol (**G2**) (a); 10 mM **Pilar-2a** (b); 10 mM **Pilar-2a** and 4 mM **G2** (c); 10 mM **Pilar-2a** and 10 mM **G2** (d); 10 mM **Pilar-2a** and 20 mM **G2** (e); 10 mM **Pilar-2a** and 30 mM **G2**.

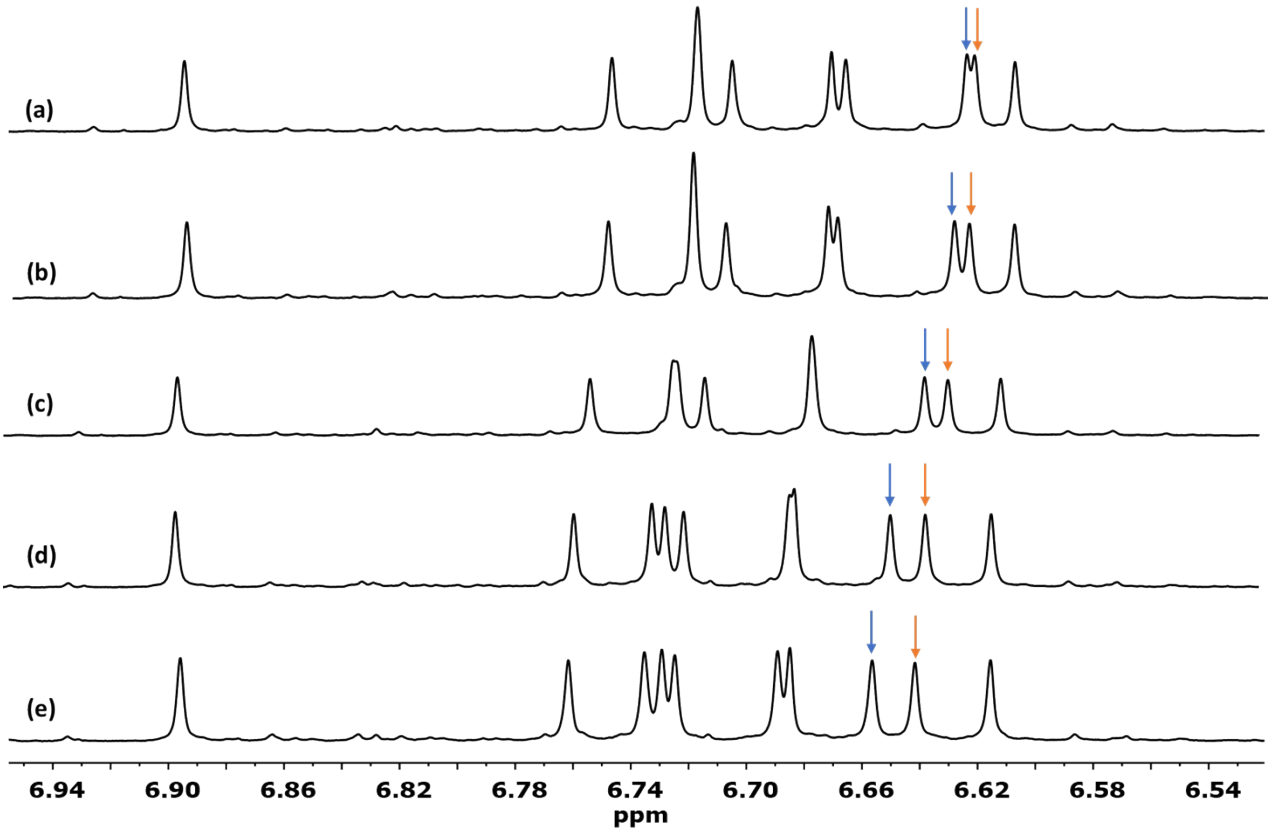

Figure S14. Partial ^{1}H NMR spectra (600 MHz, chloroform-*d*, 25 °C) of **Pilar-2a** and octanol (**G3**) (a); 10 mM **Pilar-2a** (b); 10 mM **Pilar-2a** and 4 mM **G3** (c); 10 mM **Pilar-2a** and 10 mM **G3** (d); 10 mM **Pilar-2a** and 20 mM **G3** (e); 10 mM **Pilar-2a** and 30 mM **G3**.

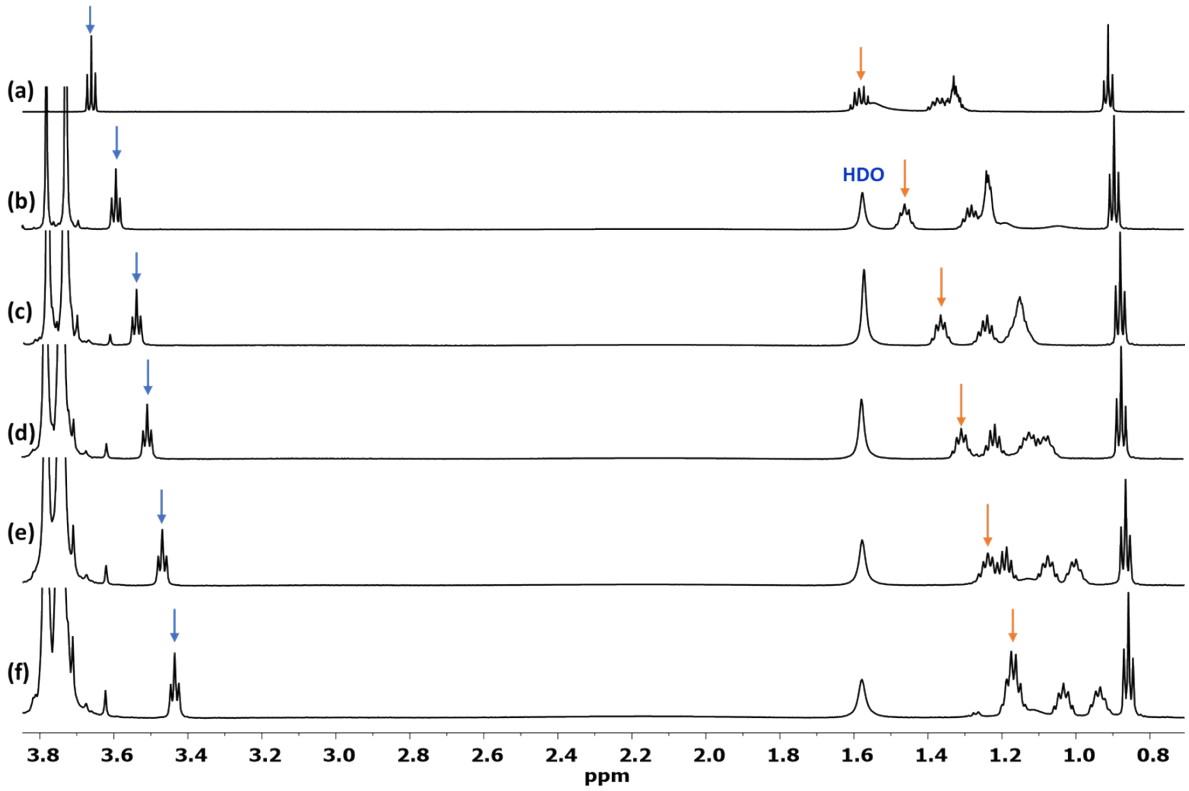

Figure S15. Partial ^{1}H NMR spectra (600 MHz, chloroform-*d*, 25 °C) of **DMP5** and hexanol (**G1**) (a); 7.5 mM **G1** (b); 7.5 mM **DMP5** and 7.5 mM **G1** (c); 15 mM **DMP5** and 7.5 mM **G1** (d); 22.5 mM **DMP5** and 7.5 mM **G1** (e); 30 mM **DMP5** and 7.5 mM **G1** (f); 37.5 mM **DMP5** and 7.5 mM **G1**.

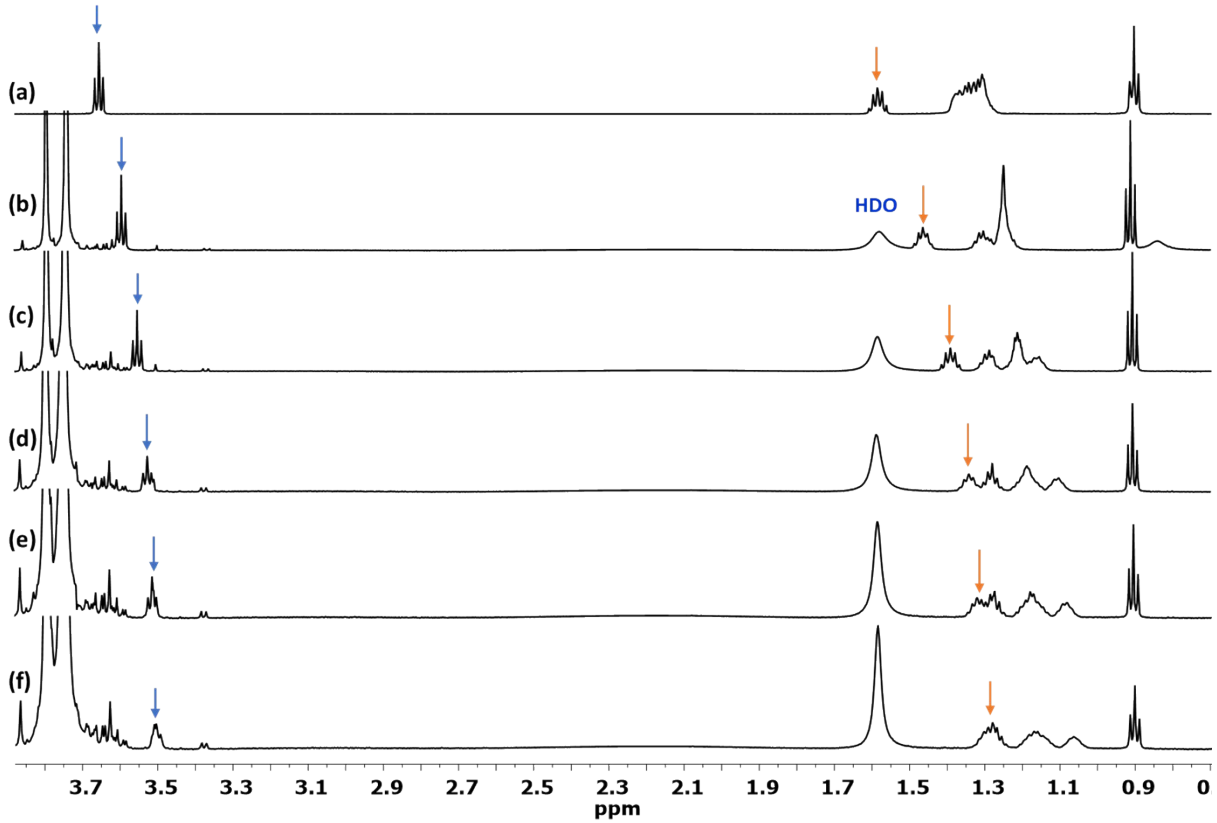

Figure S16. Partial ^{1}H NMR spectra (600 MHz, chloroform-*d*, 25 °C) of **DMP5** and heptanol (**G2**) (a); 7.5 mM **G2** (b); 7.5 mM **DMP5** and 7.5 mM **G2** (c); 15 mM **DMP5** and 7.5 mM **G2** (d); 22.5 mM **DMP5** and 7.5 mM **G2** (e); 30 mM **DMP5** and 7.5 mM **G2** (f); 37.5 mM **DMP5** and 7.5 mM **G2**.

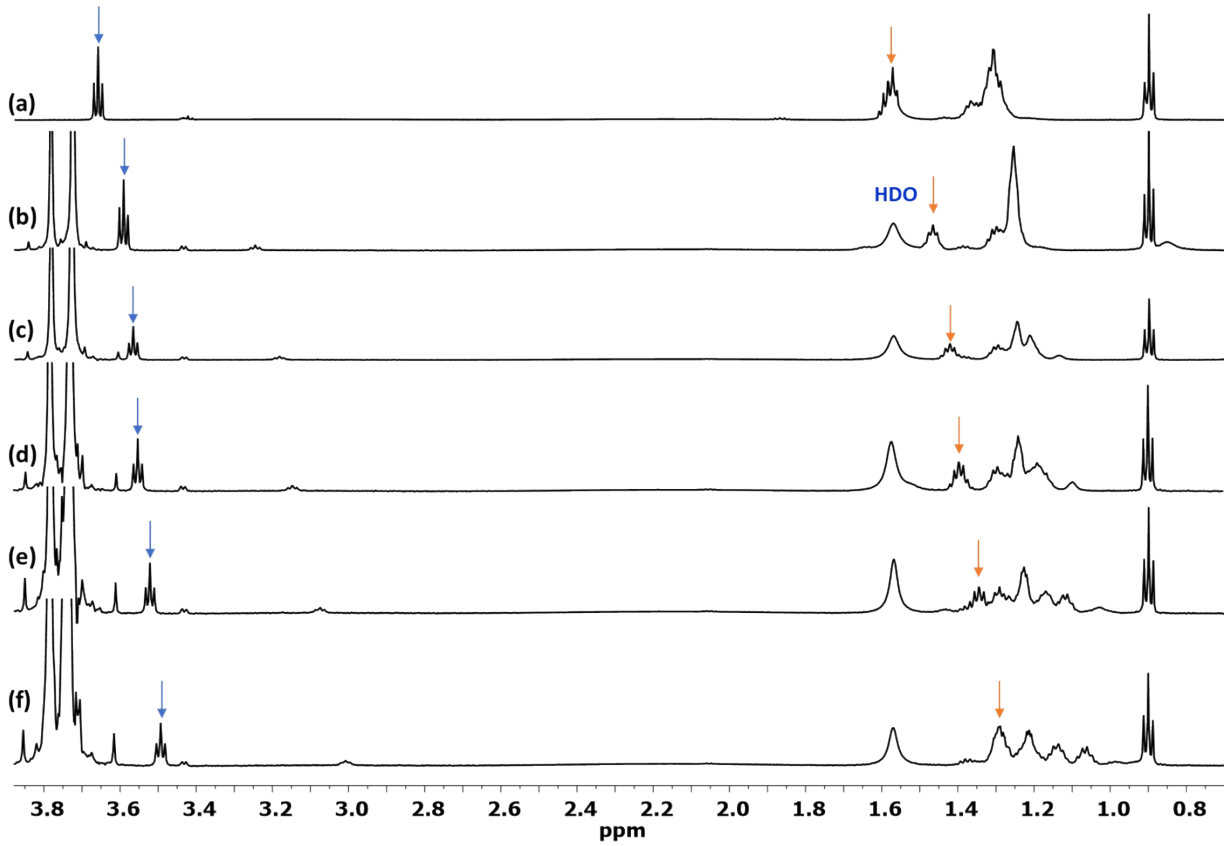

Figure S17. Partial ^{1}H NMR spectra (600 MHz, chloroform-*d*, 25 °C) of **DMP5** and octanol (**G3**) (a); 7.5 mM **G3** (b); 7.5 mM **DMP5** and 7.5 mM **G3** (c); 15 mM **DMP5** and 7.5 mM **G3** (d); 22.5 mM **DMP5** and 7.5 mM **G3** (e); 30 mM **DMP5** and 7.5 mM **G3** (f); 37.5 mM **DMP5** and 7.5 mM **G3**.

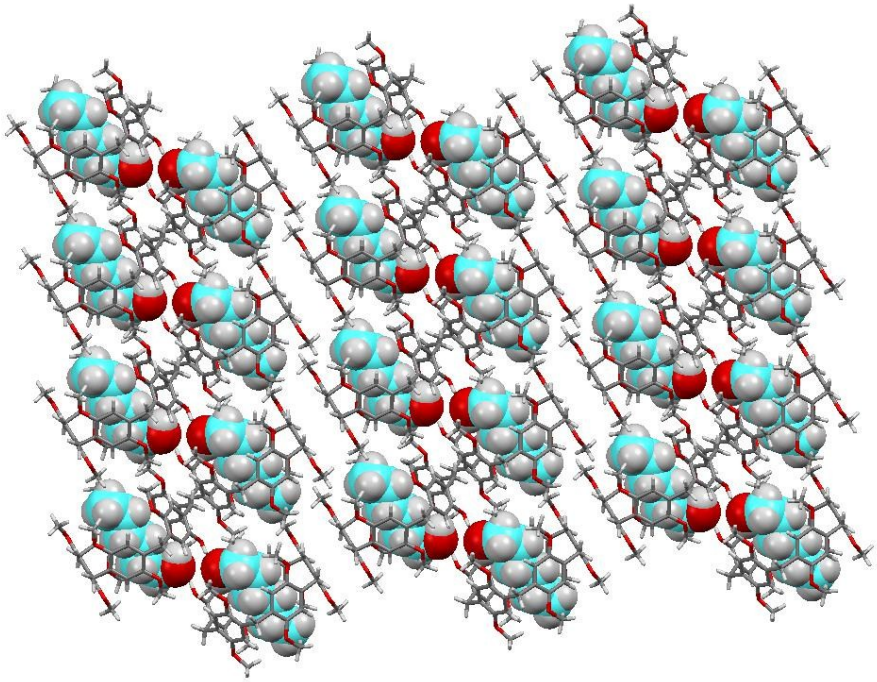

Figure S18. Three-dimensional packing of inclusion-complex **Pillar-2a** with hexanol (**G1**), crystals viewing along its b-direction.

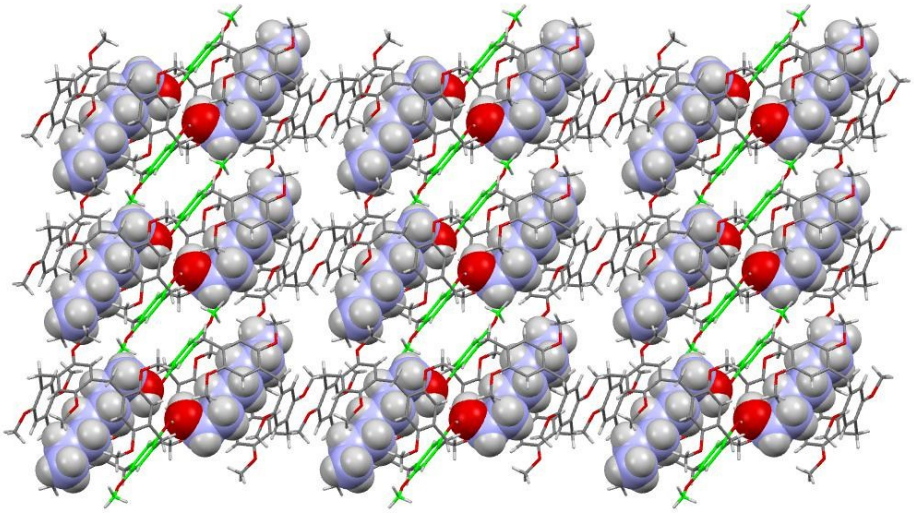

Figure S19. Three-dimensional packing of inclusion-complex **Pillar-2a** with heptanol (**G2**), crystals viewing along its b-direction.

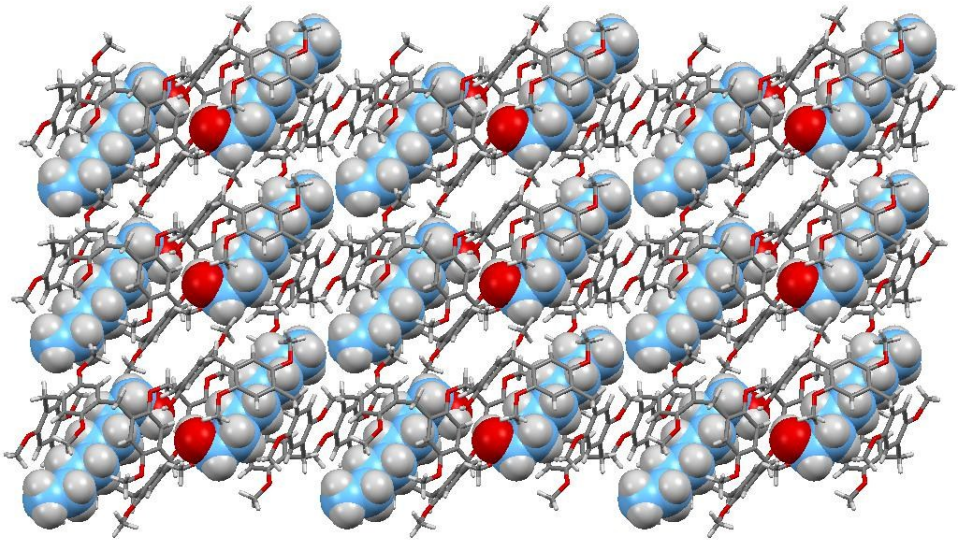

Figure S20. Three-dimensional packing of inclusion-complex **Pillar-2a** with octanol (**G3**), crystals viewing along its b-direction.

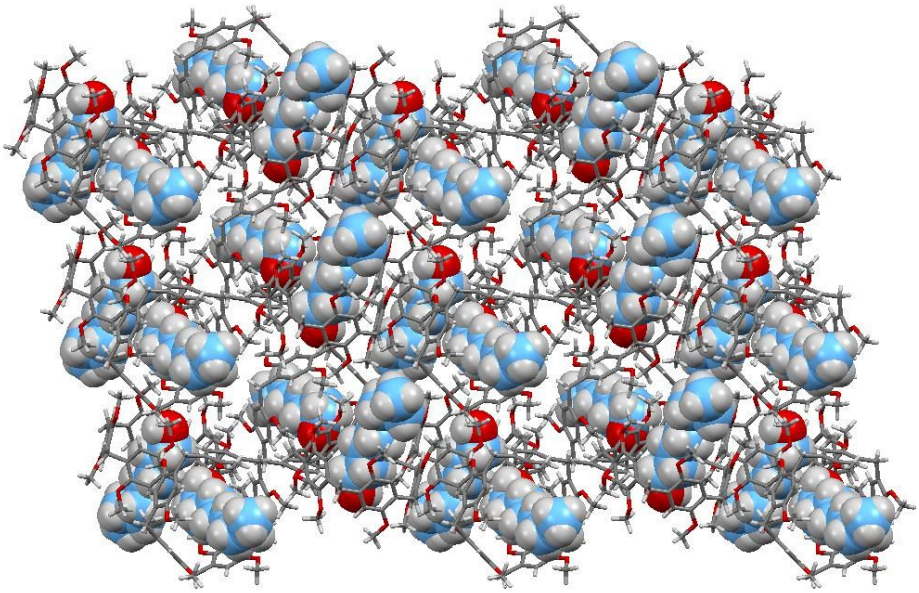

Figure S21. Three-dimensional packing of inclusion-complex **DMP5** with octanol (**G3**), crystals viewing along its b-direction.

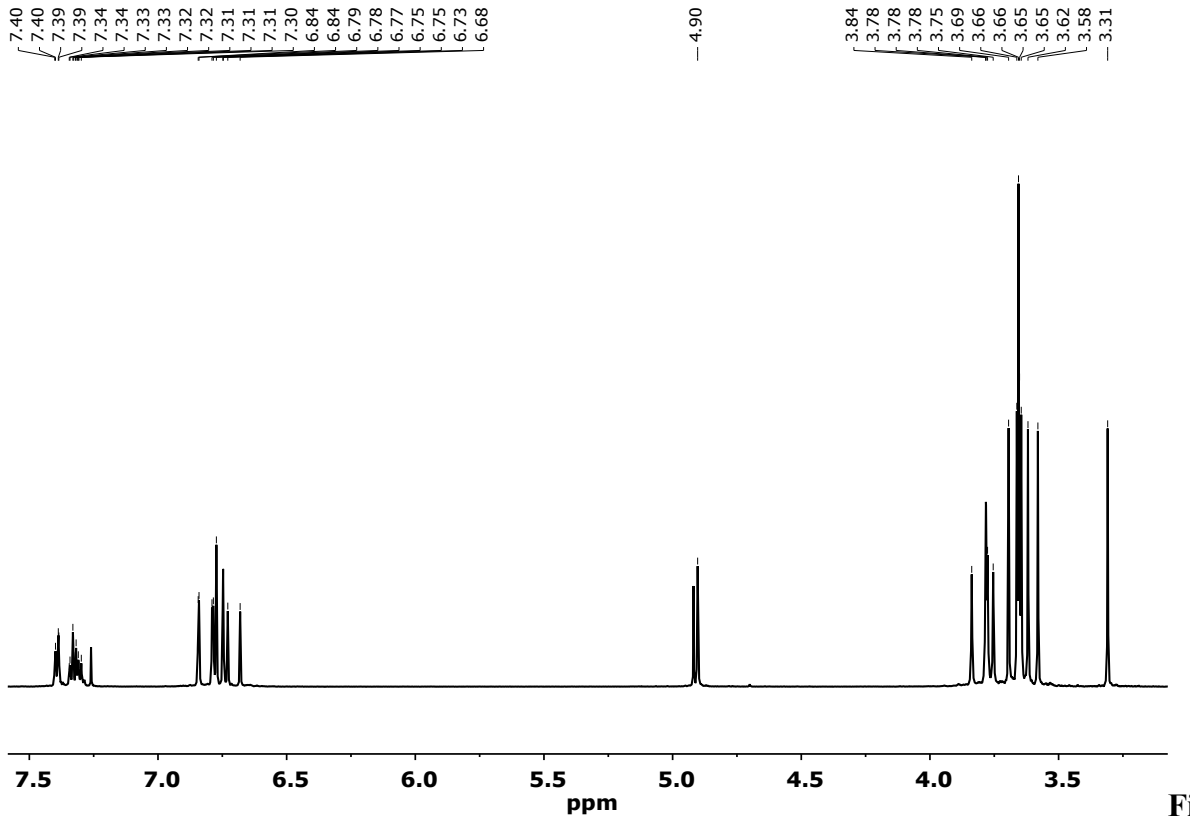

Figure S22. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-1a**.

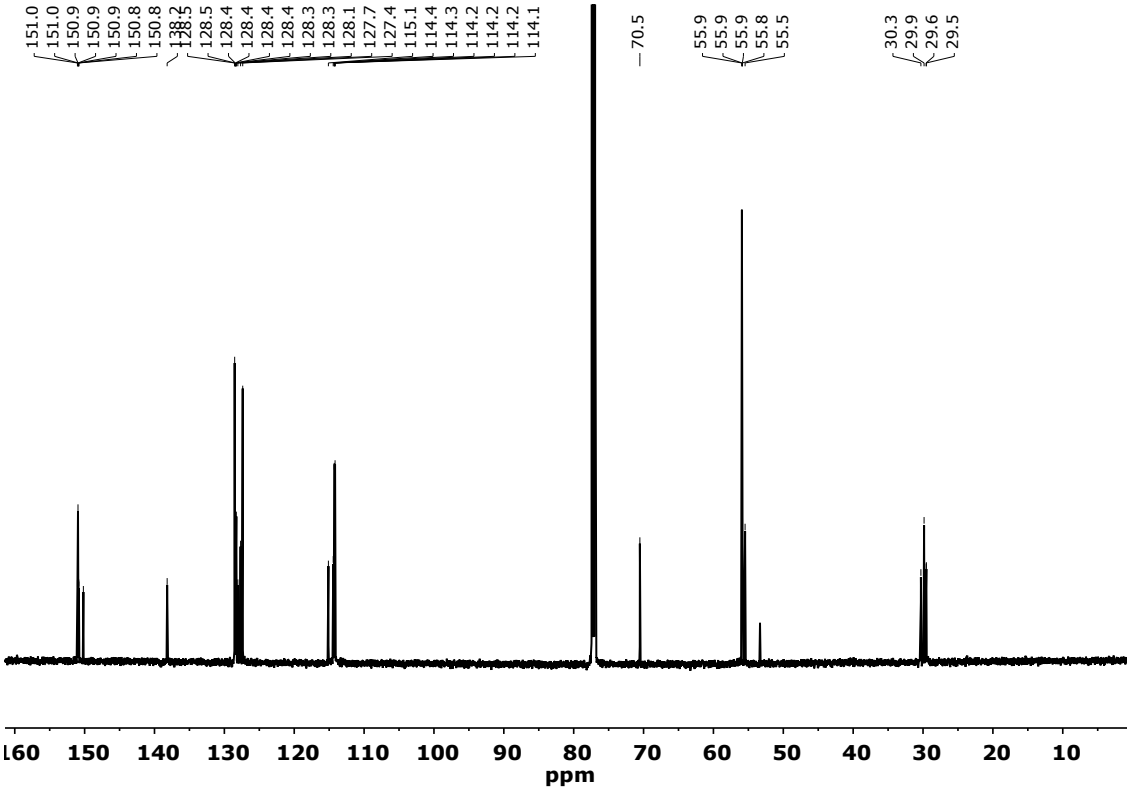

Figure S23. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-1a**.

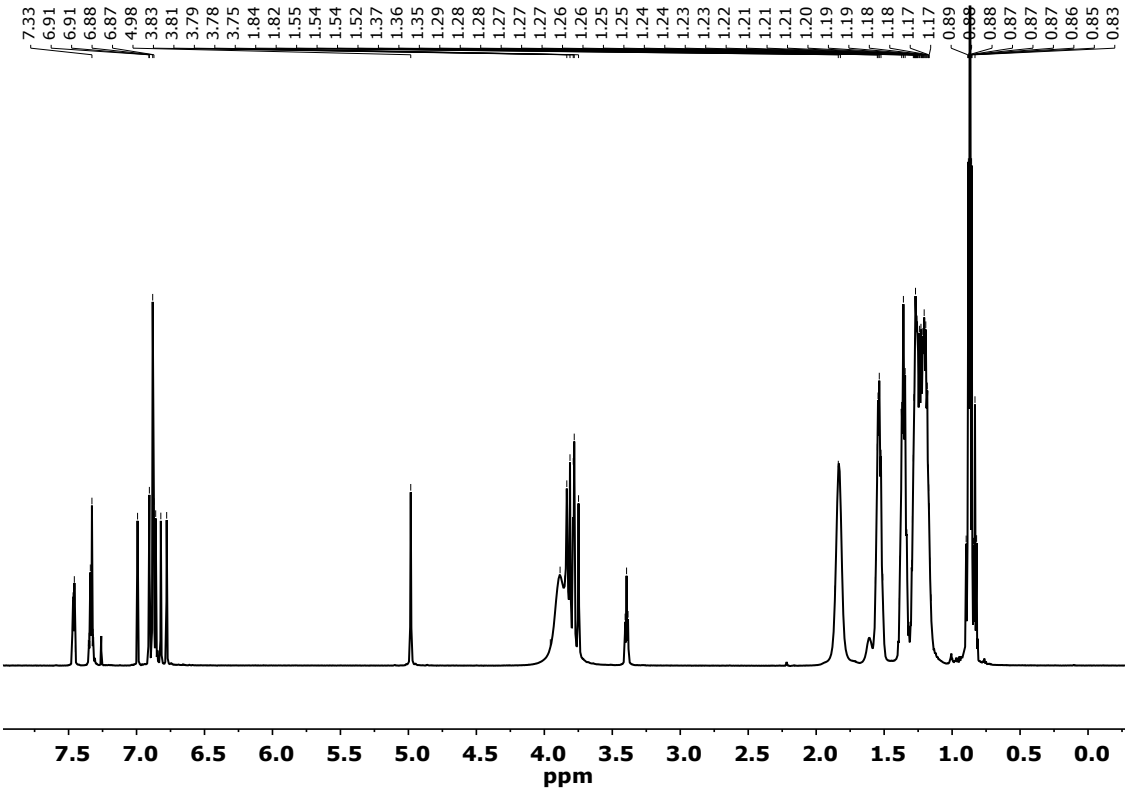

Figure S24. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-1b**.

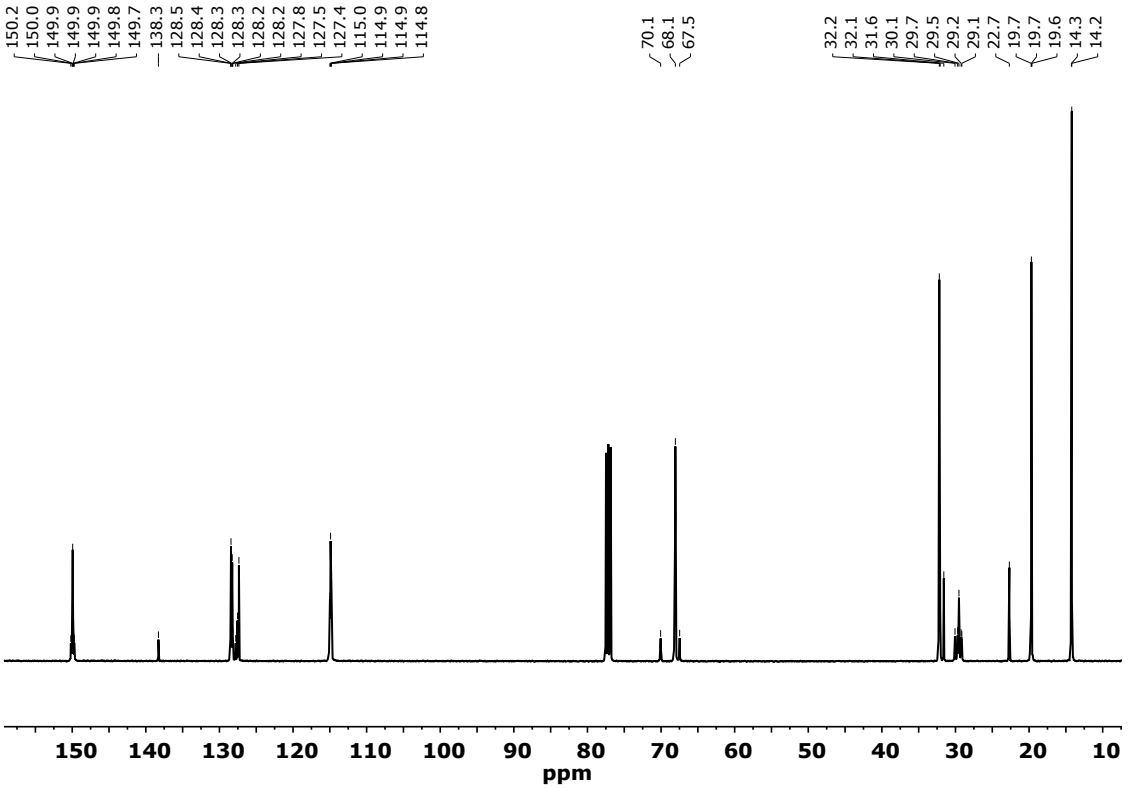

Figure S25. ^{13}CNMR (100 MHz, $CDCl_3$) spectrum of **Pillar-1b**.

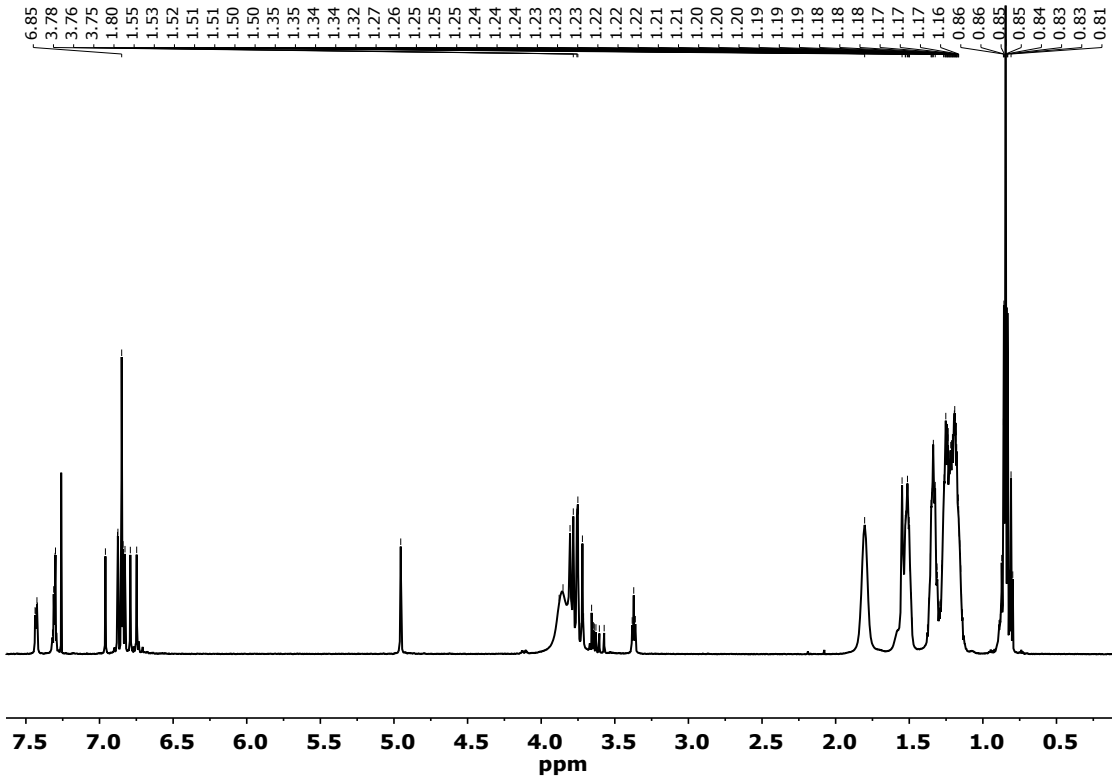

Figure S26. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-1c**.

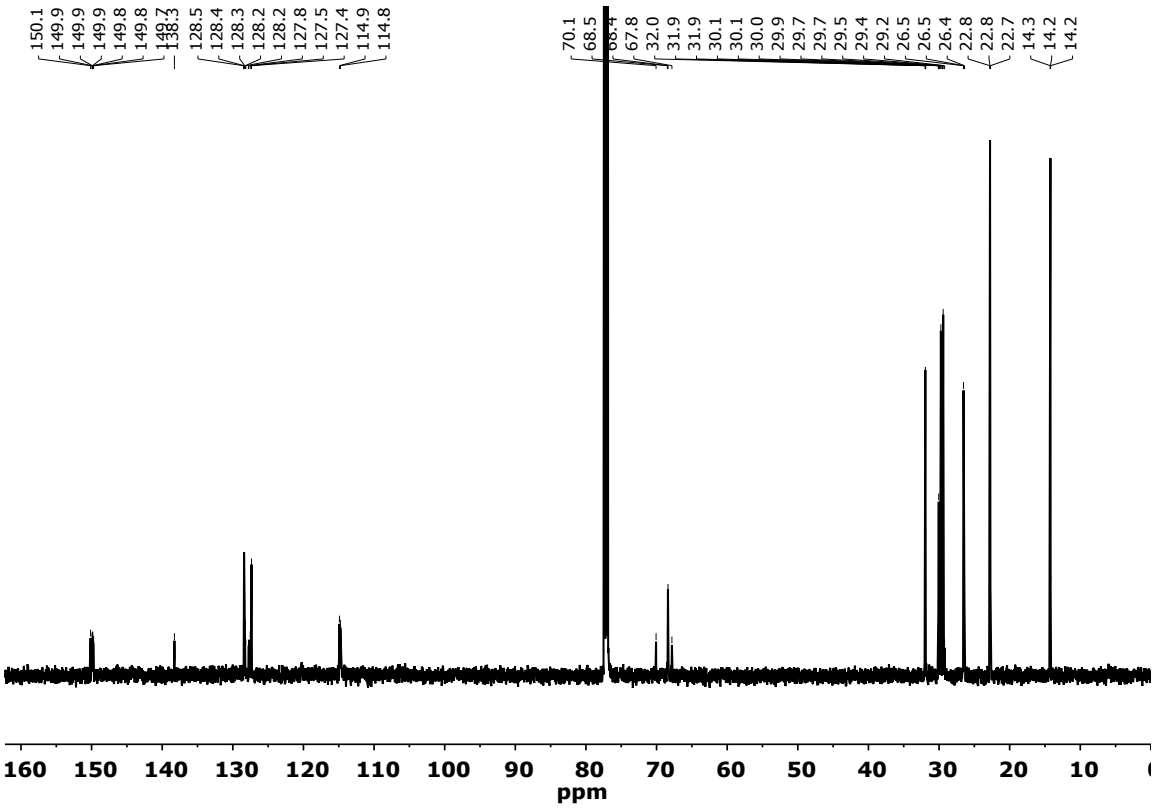

Figure S27. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-1c**.

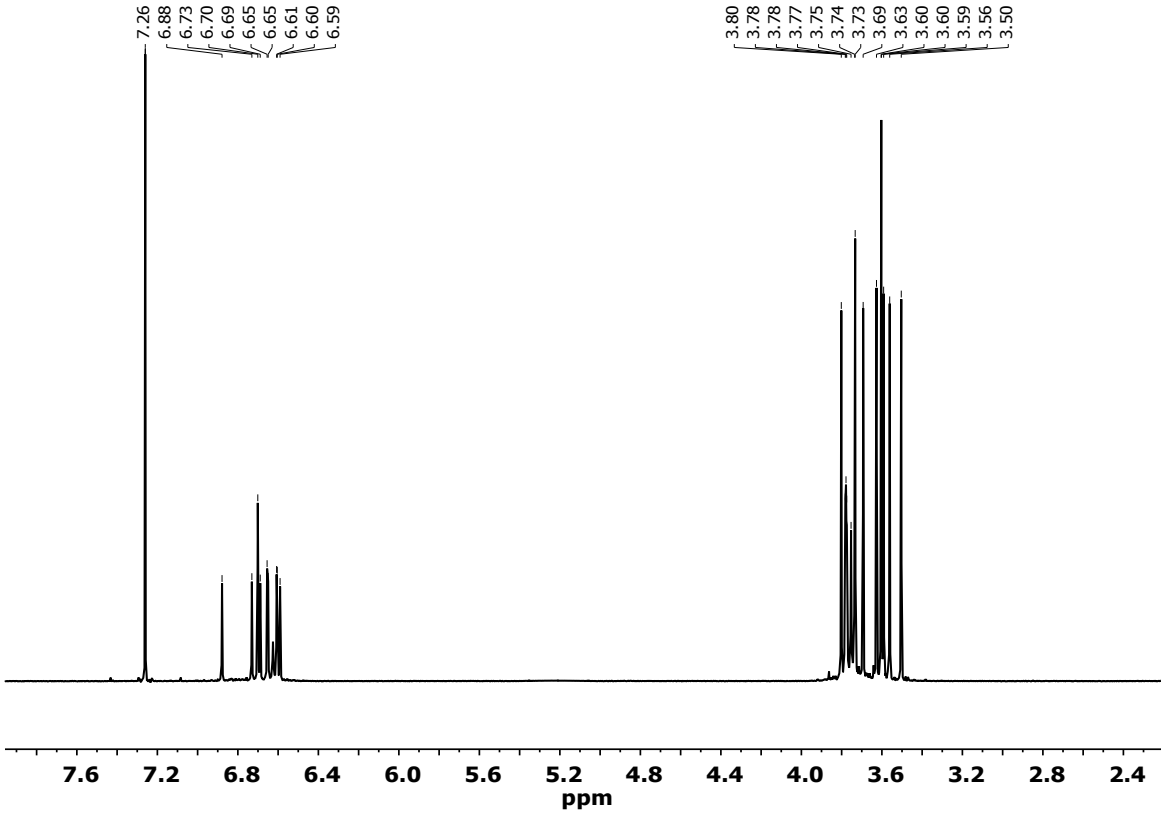

Figure S28. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-2a**.

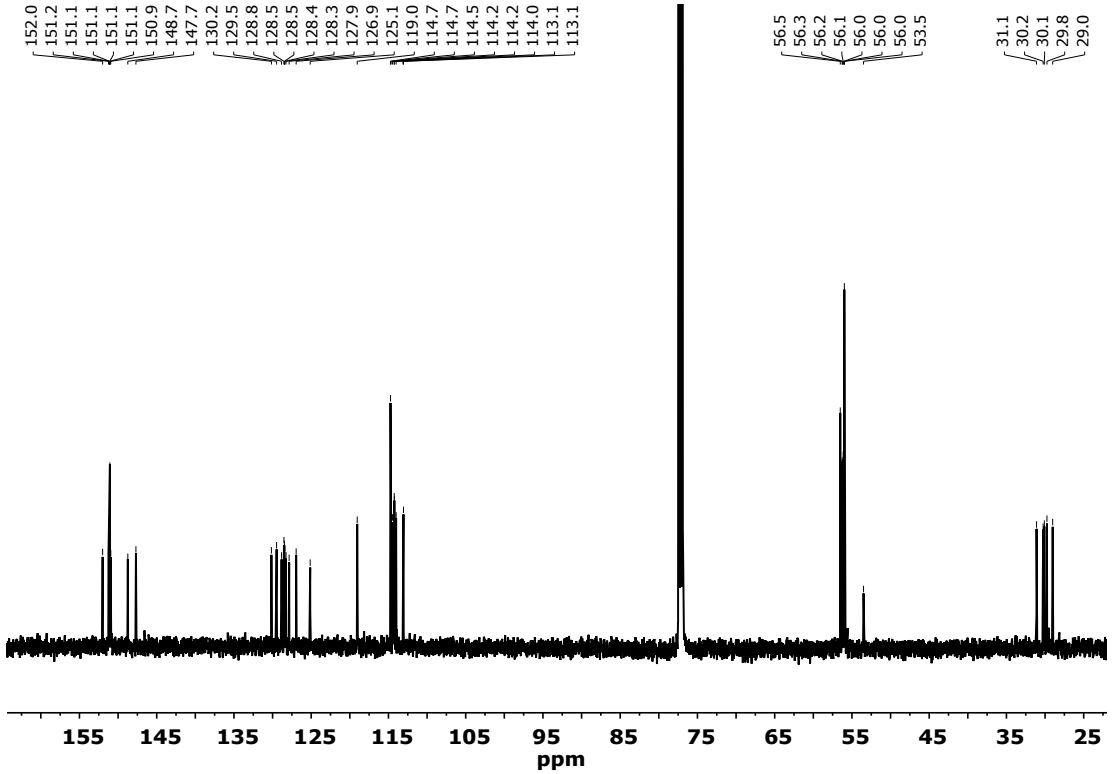

Figure S29. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-2a**.

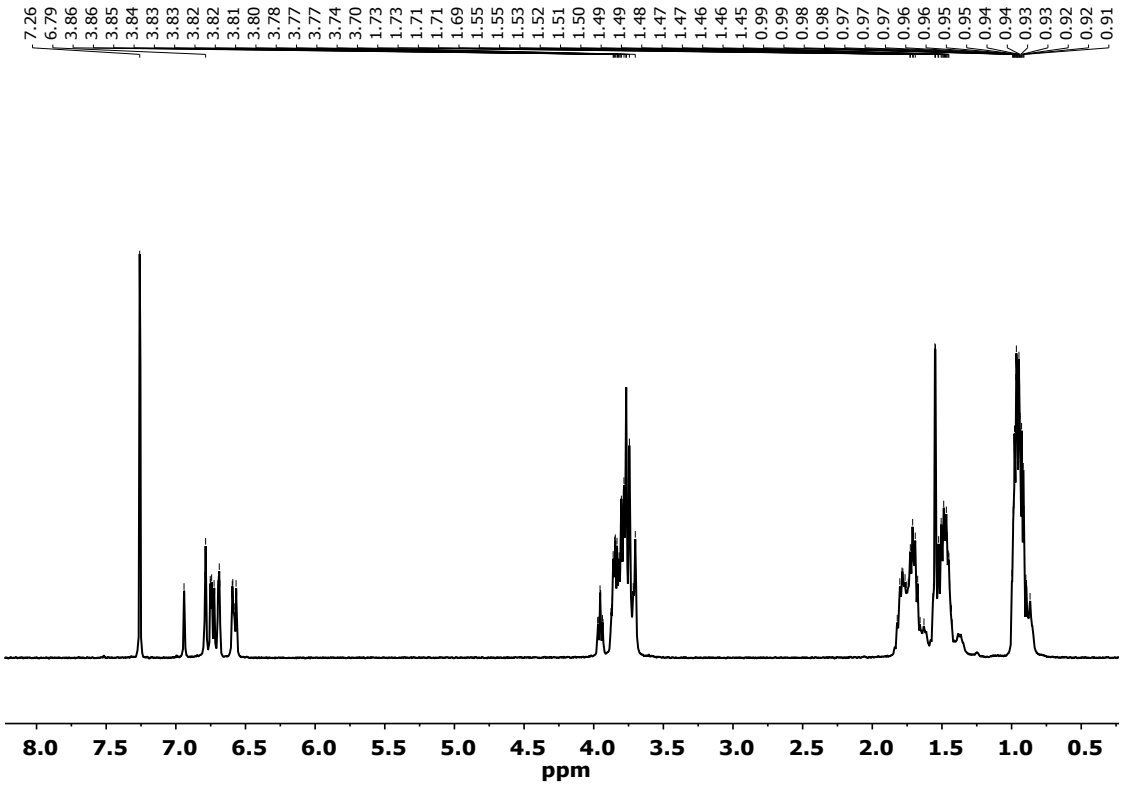

Figure S30. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-2b**.

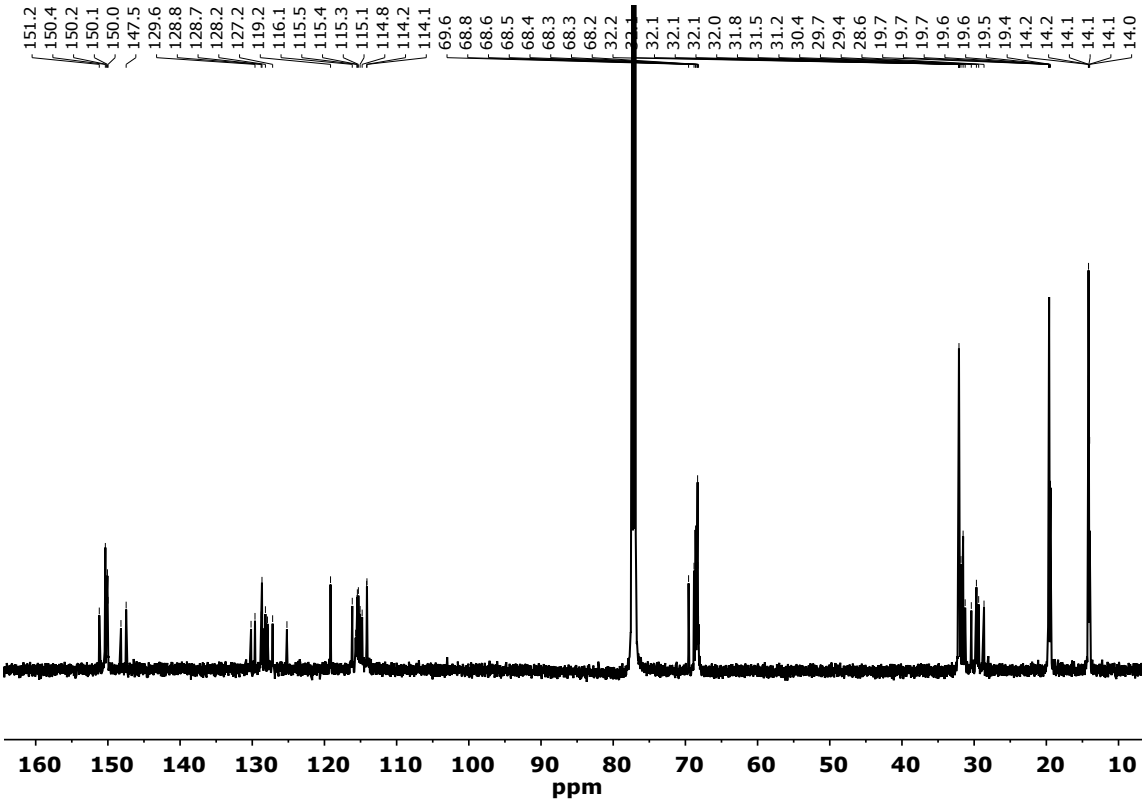

Figure S31. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-2b**.

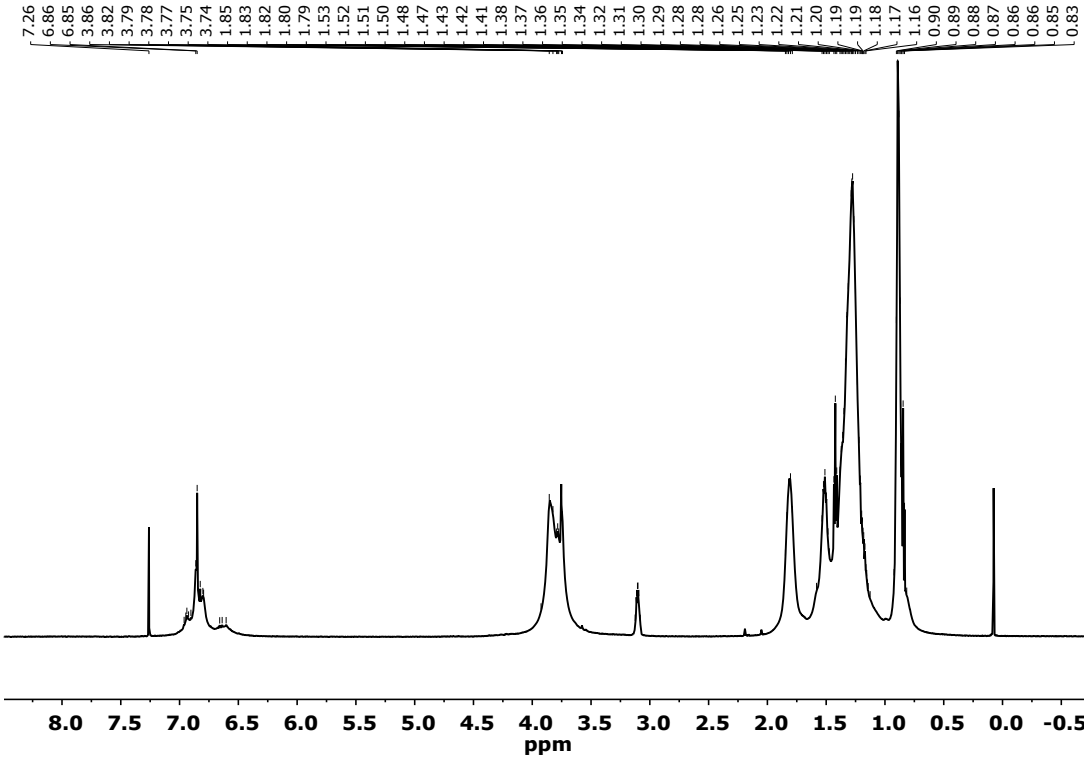

Figure S32. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-2c**.

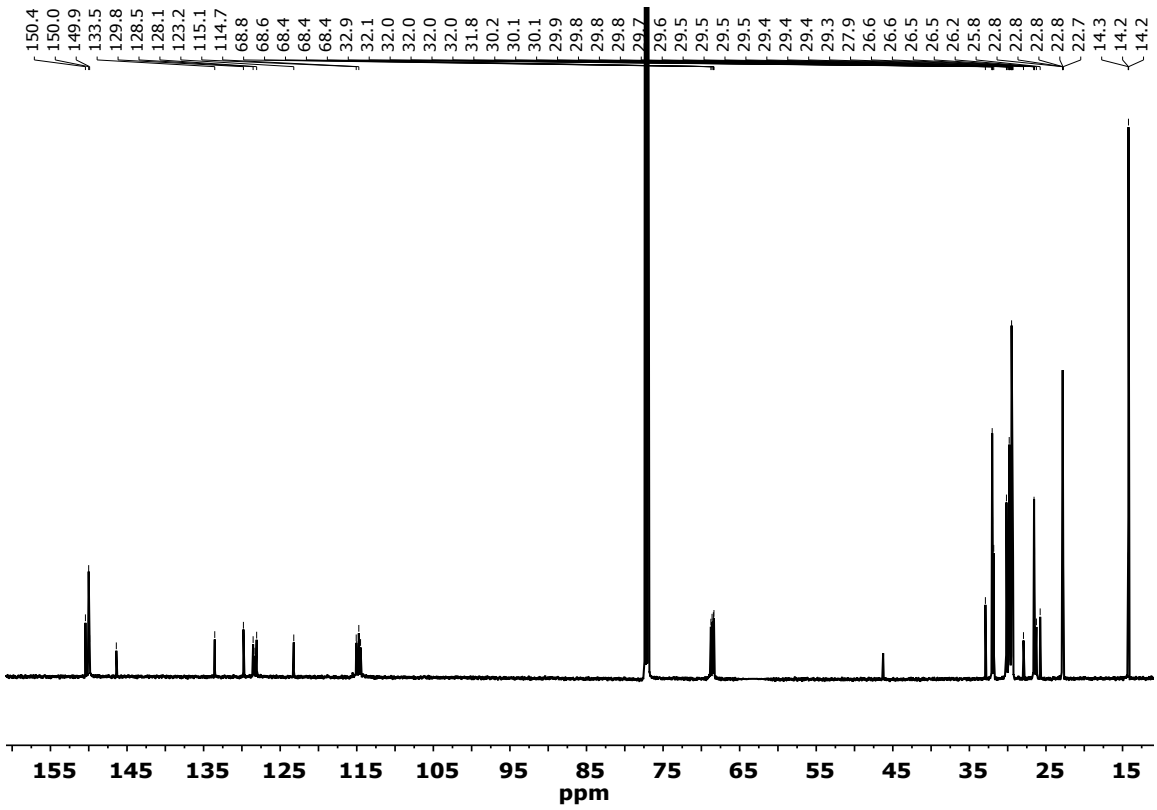

Figure S33. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-2c**.

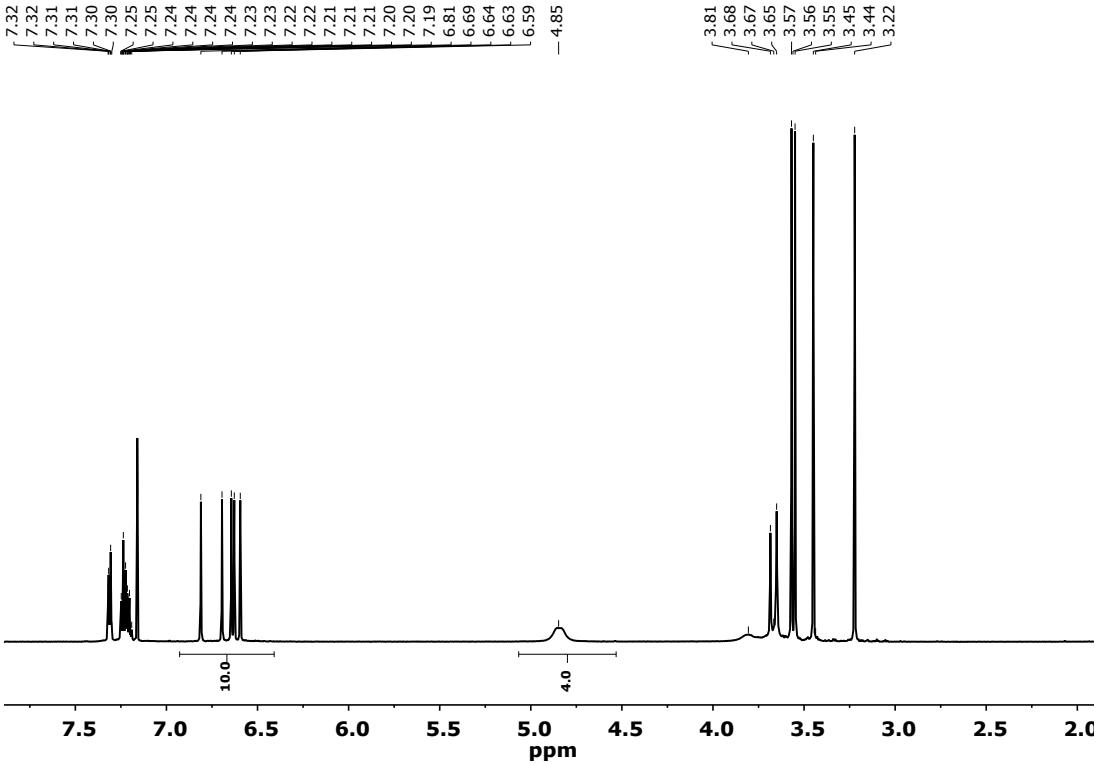

Figure S34. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-3a**.

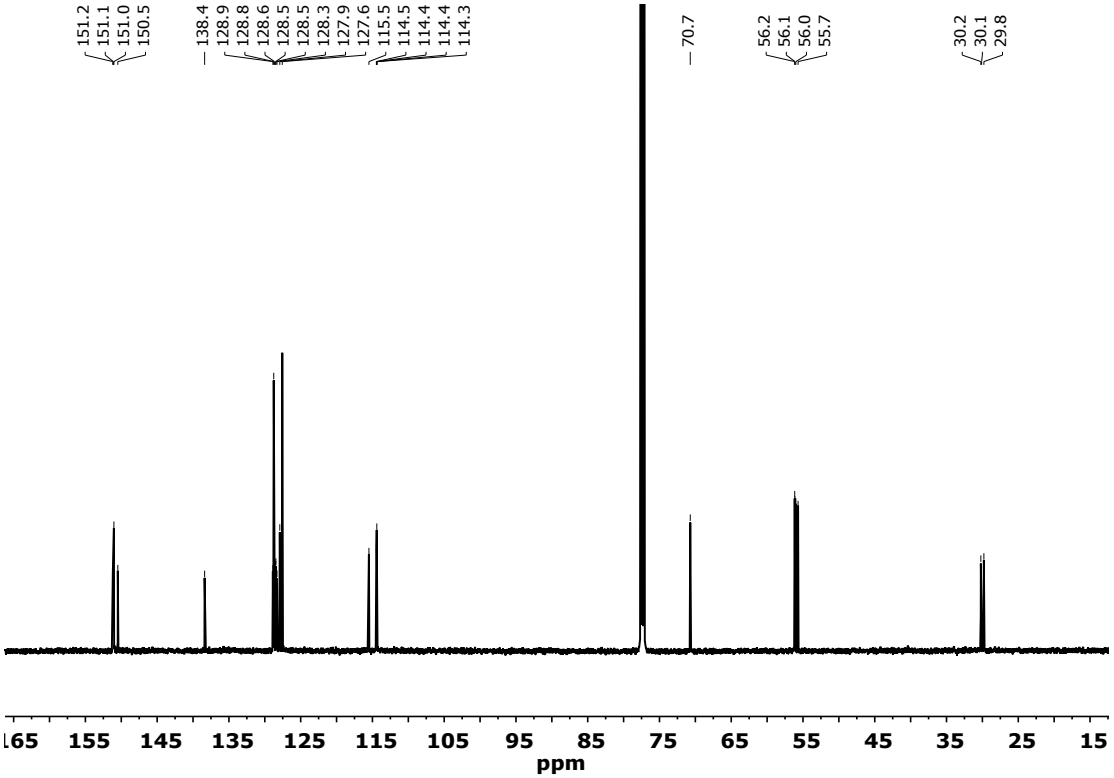

Figure S35. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-3a**.

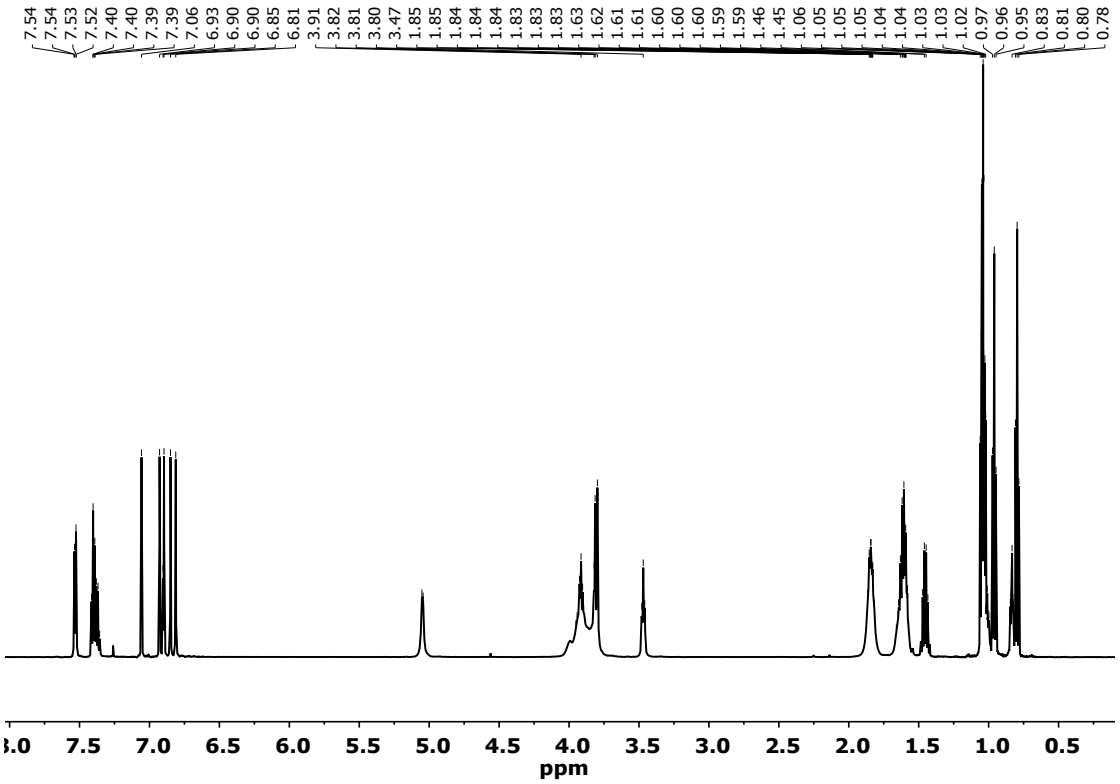

Figure S36. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-3b.**

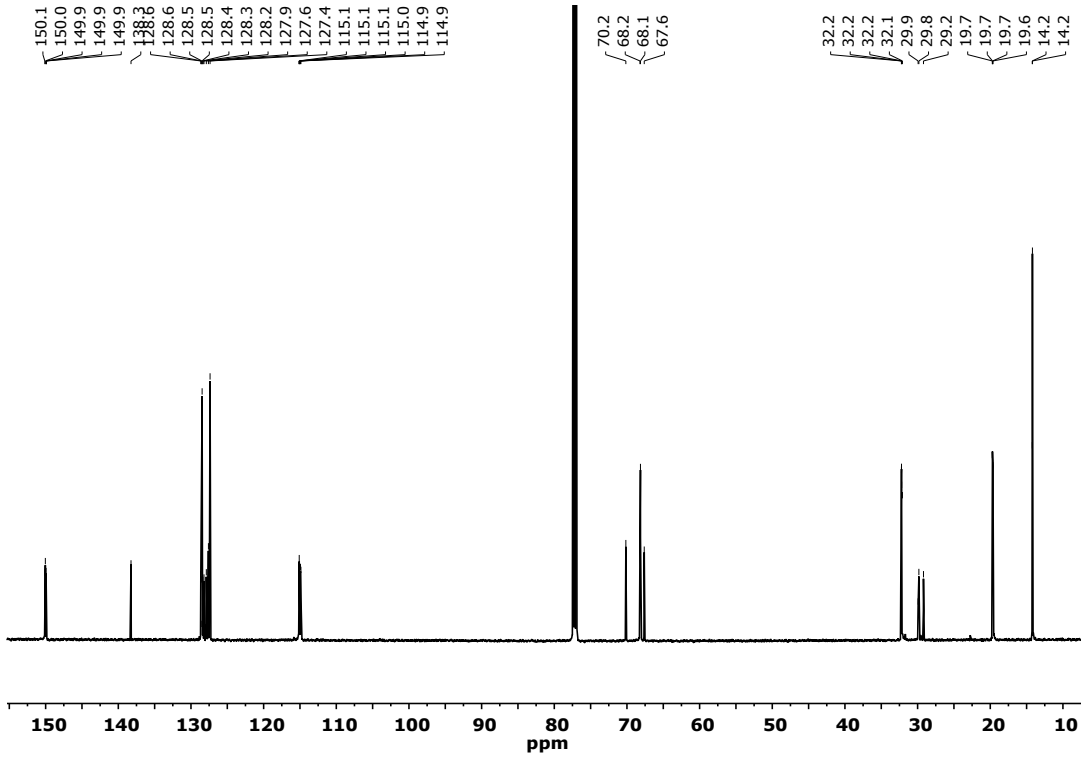

Figure S37. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-3b**.

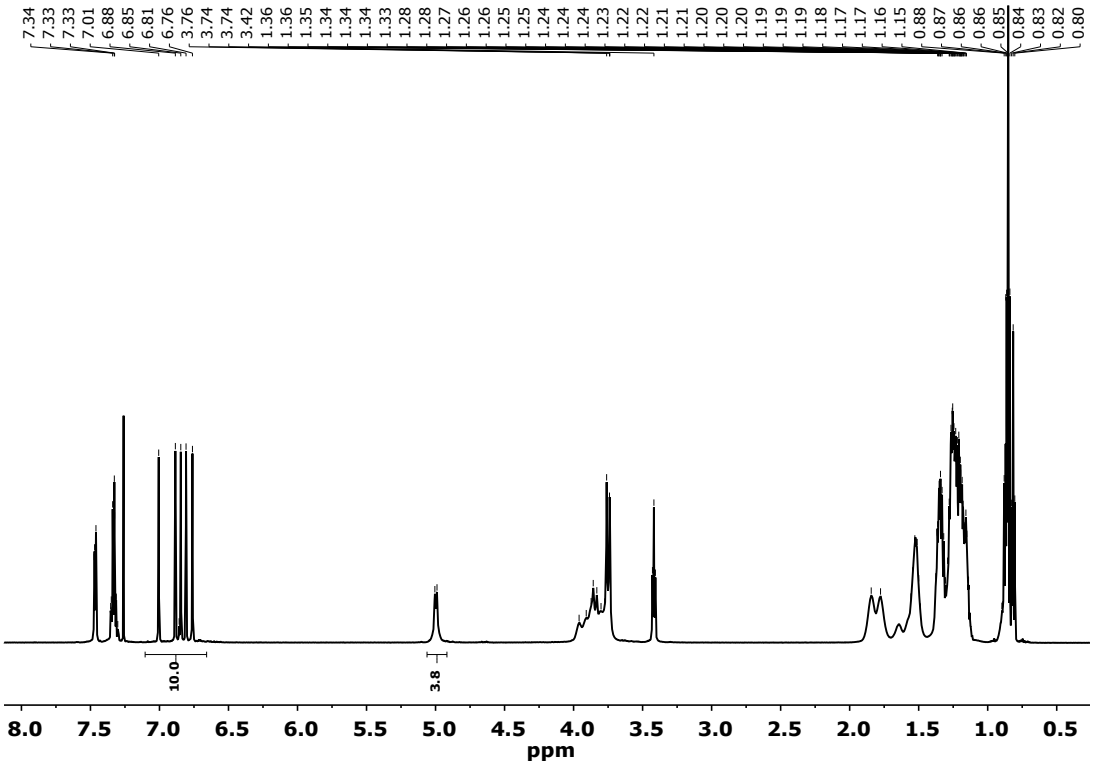

Figure S38. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-3c.**

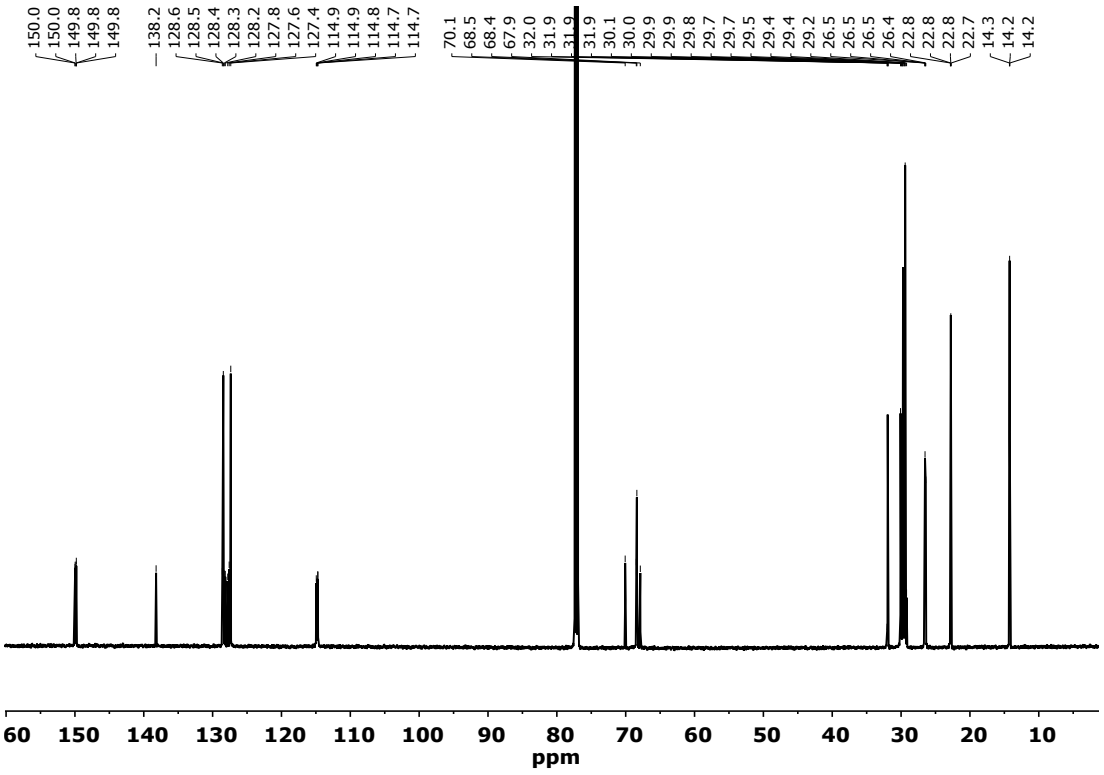

Figure S39. ^{13}CNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-3c**.

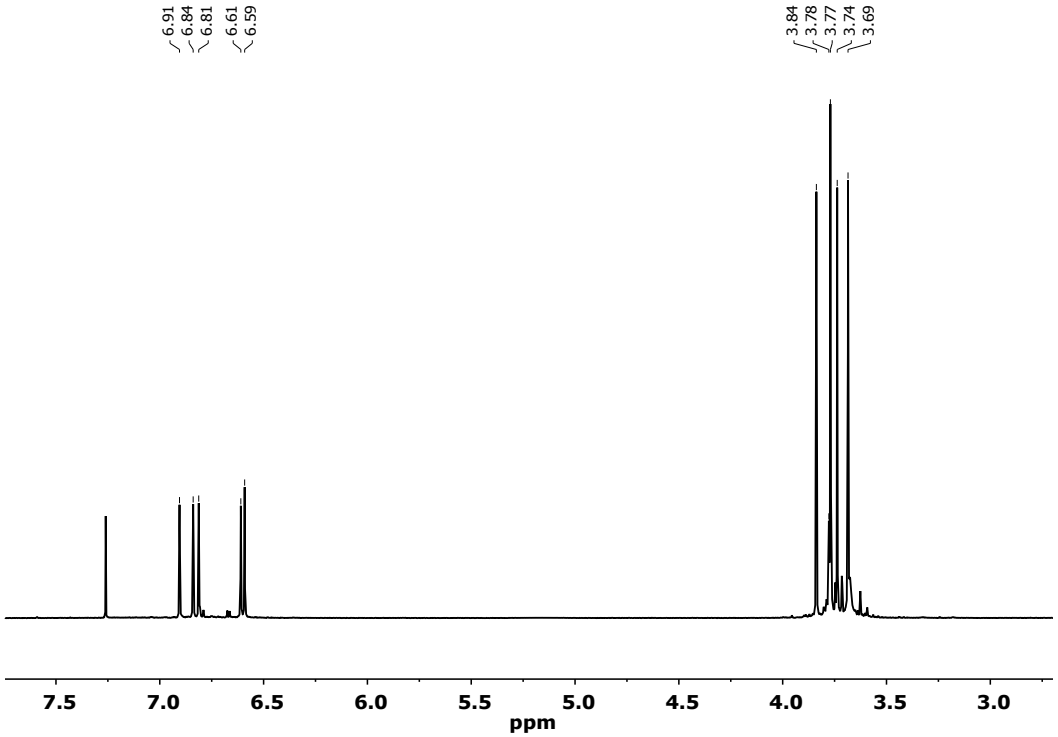

Figure S40. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-4a**.

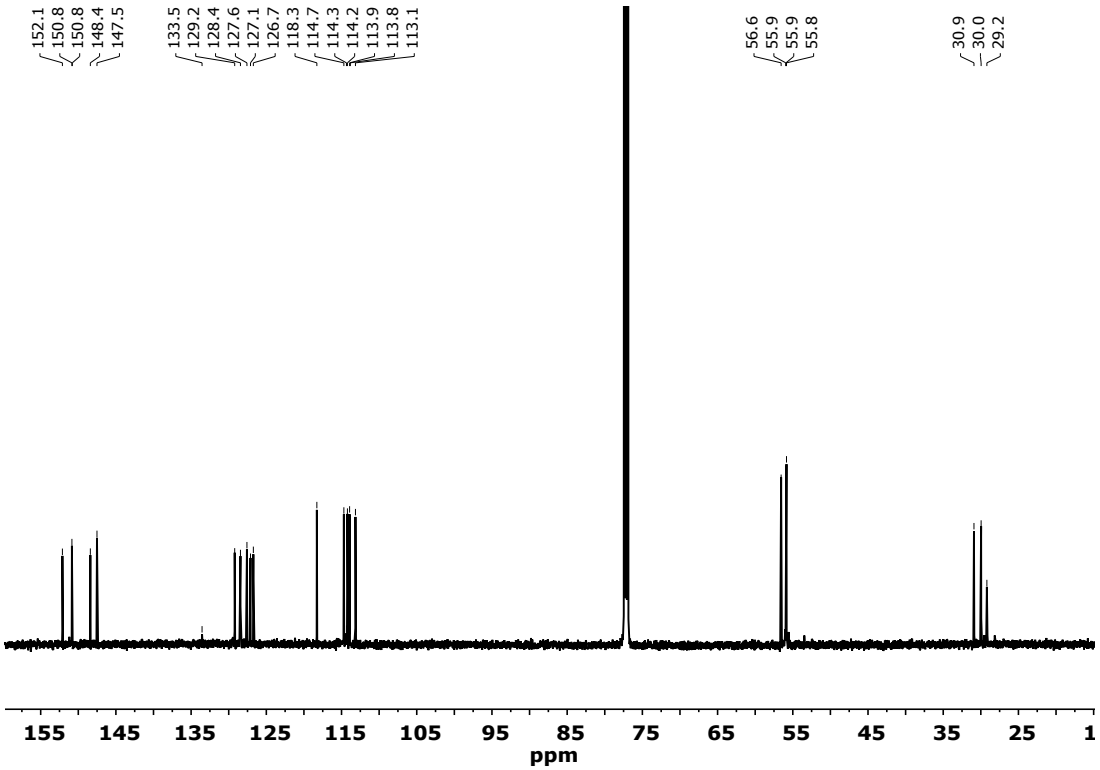

Figure S41. ^{1}HNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-4a**.

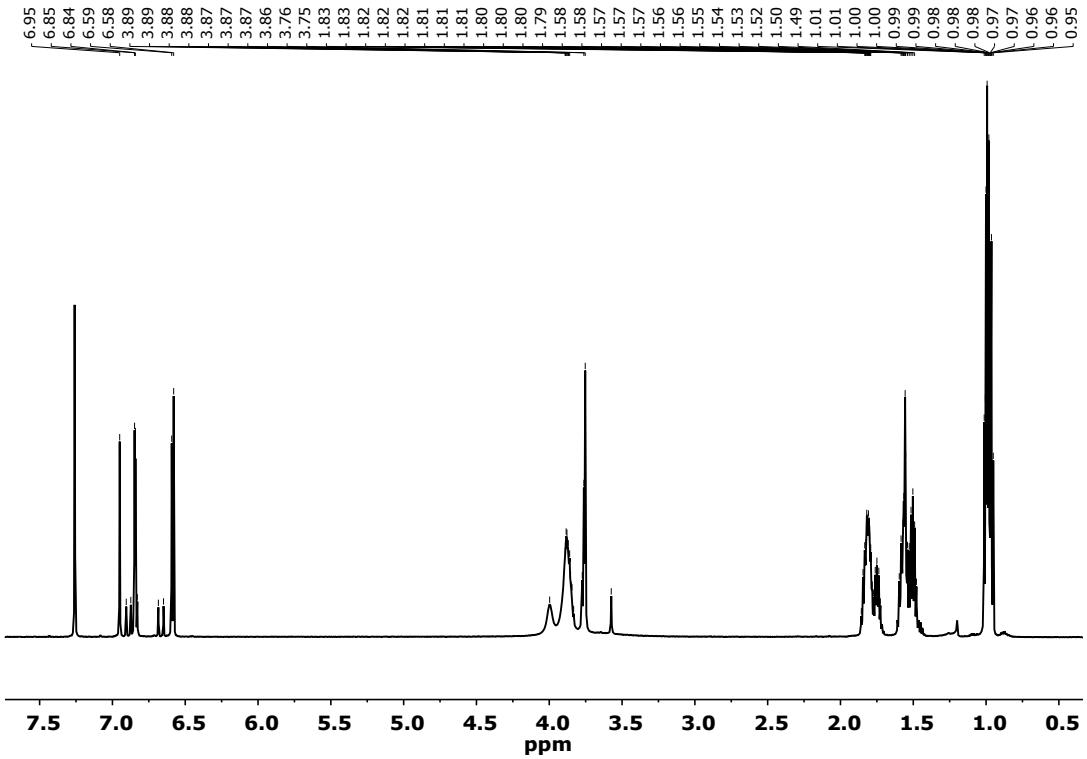

Figure S42. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-4b**.

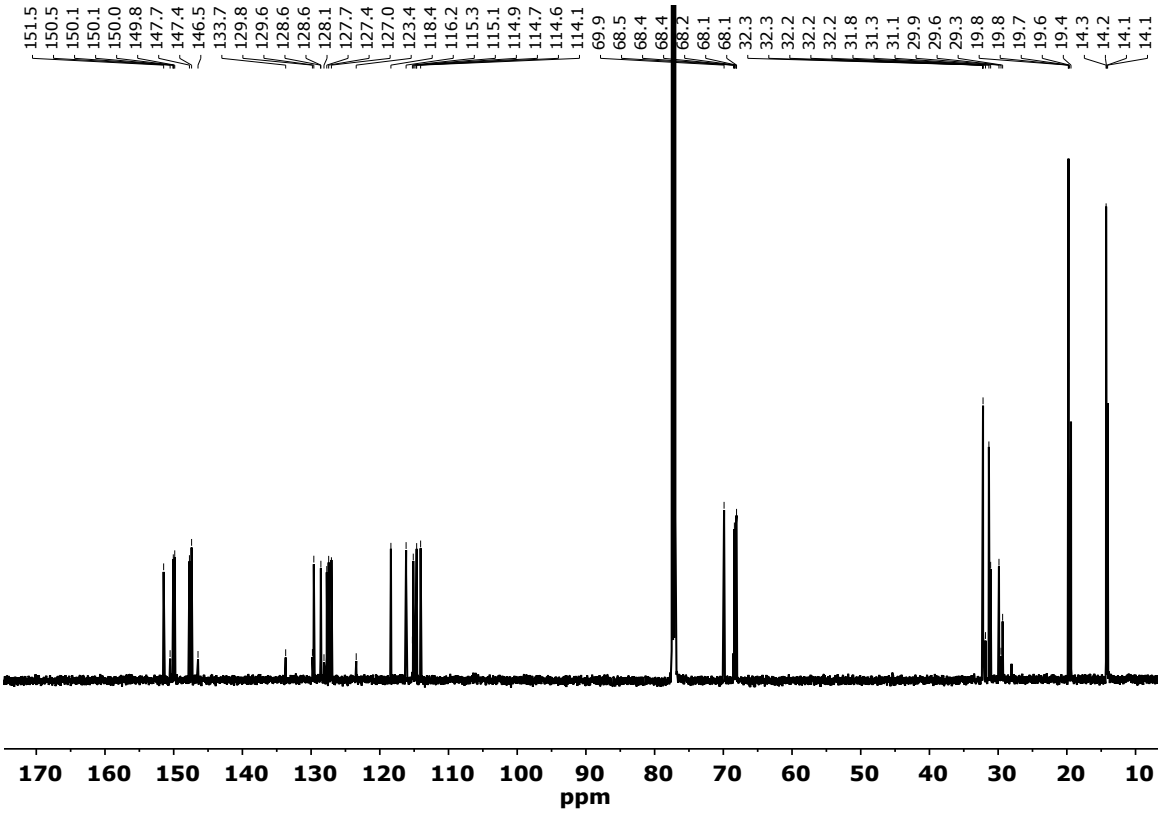

Figure S43. ^{1}HNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-4b**.

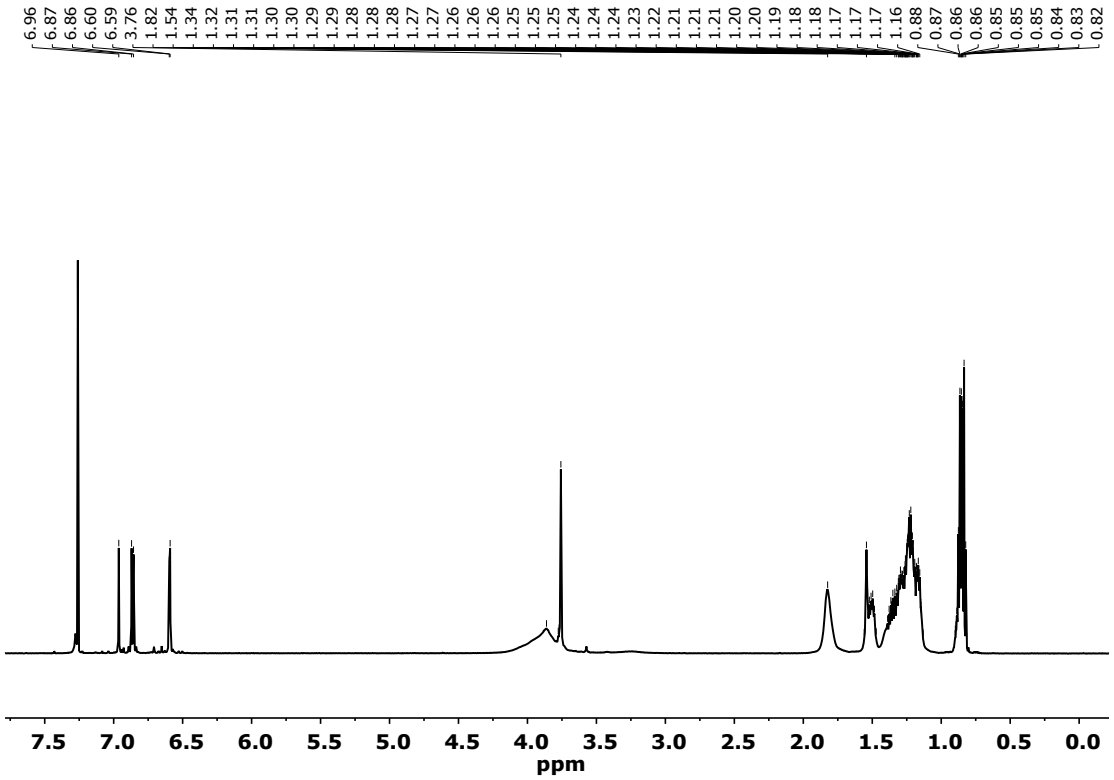

Figure S44. ^{1}HNMR (600 MHz, $CDCl_3$) spectrum of **Pillar-4c**.

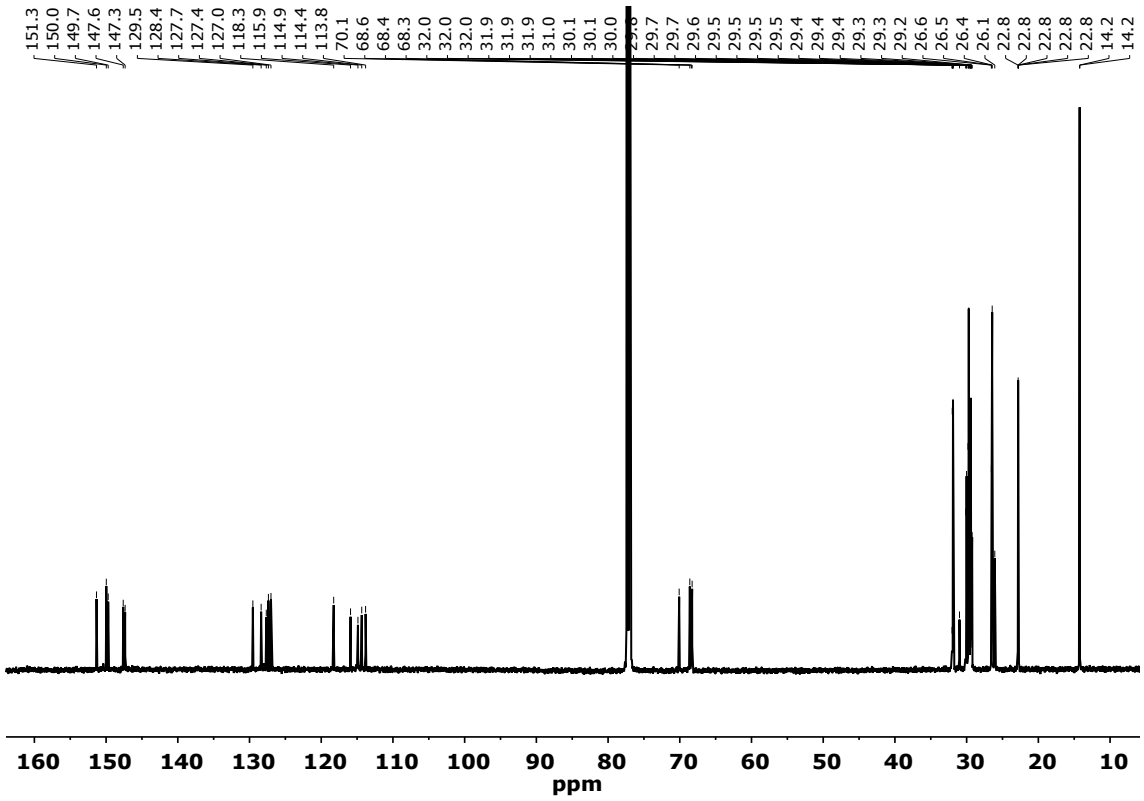

Figure S45. ^{1}HNMR (150 MHz, $CDCl_3$) spectrum of **Pillar-4c**.