Electronic Supplementary Material (ESI) for CrystEngComm.

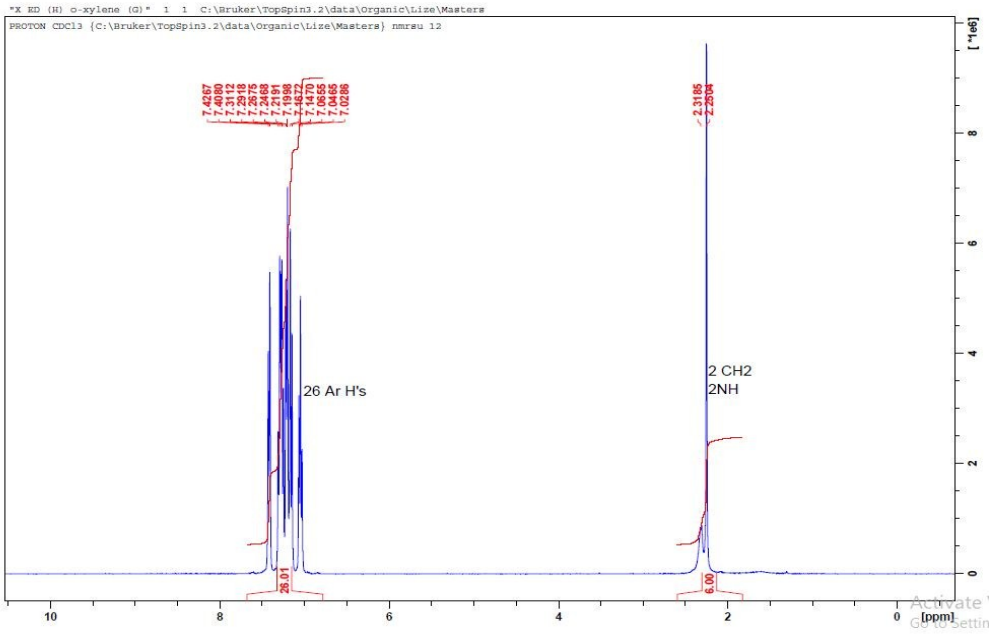
Supplementary Information

Minor modifications afford improved host selectivities in xanthenyl-type host systems

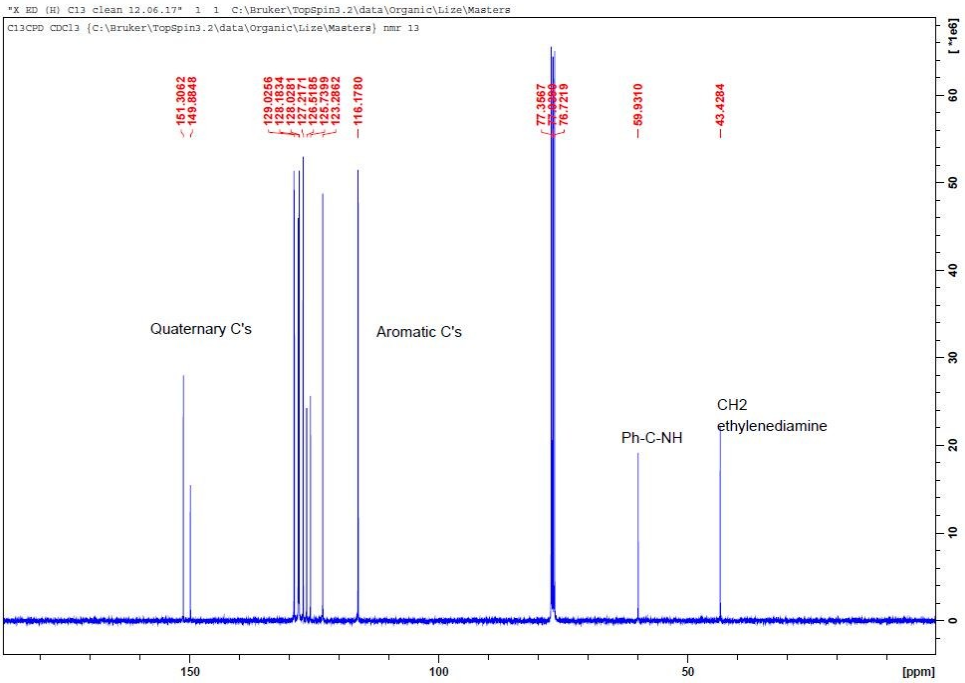
Benita Barton,*[1] Lize de Jager,*[2] and Eric C. Hosten

Department of Chemistry, PO Box 77000, Nelson Mandela University, Port Elizabeth, 6031, South Africa. E-mail: benita.barton@mandela.ac.za;[1] s213337665@mandela.ac.za*[2]*

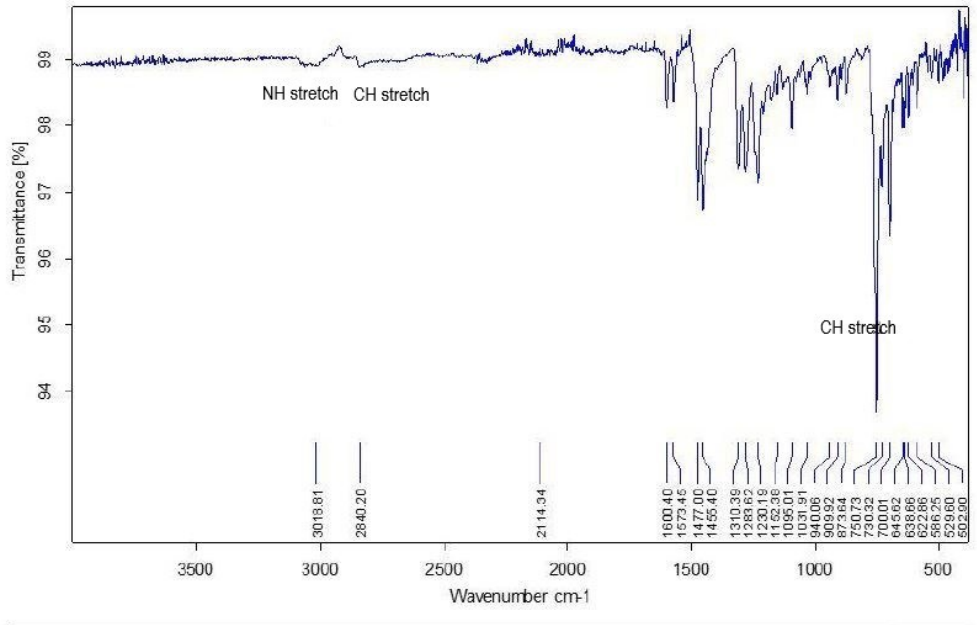
(a)



(b)



(c)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CH stretch
CH stretch
Transmittance [%]
Wavenumber cm-1
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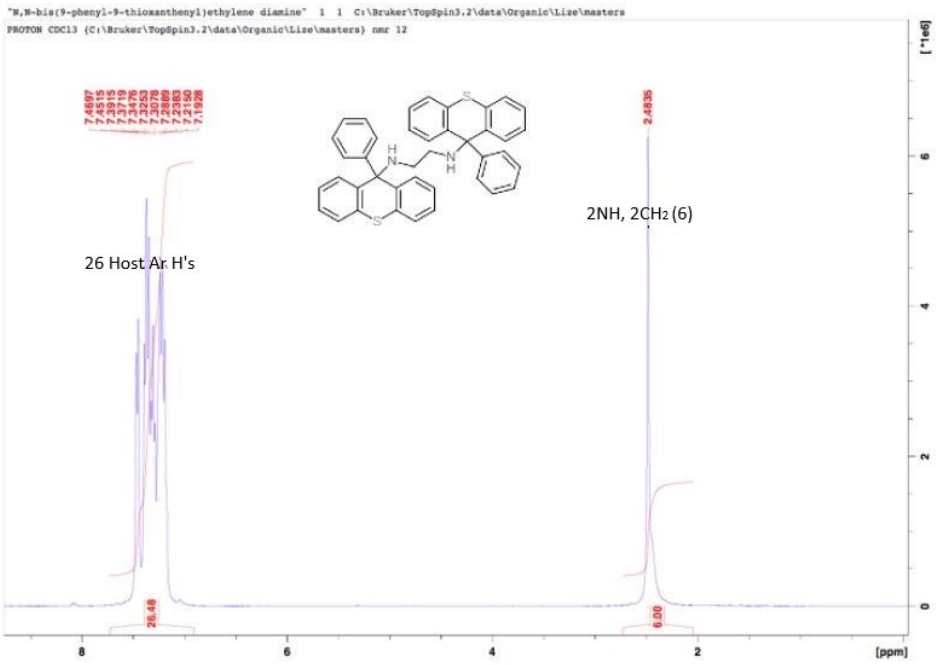
2840.20
2114.34
1600.40
1573.45
1477.00
1455.40
1310.39
1283.62
1230.19
1152.36
1095.01
1031.91
940.06
909.92
873.64
750.73
730.32
700.01
645.62
638.66
622.96
606.25
529.19
502.90

(d)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26 Host Ar H's
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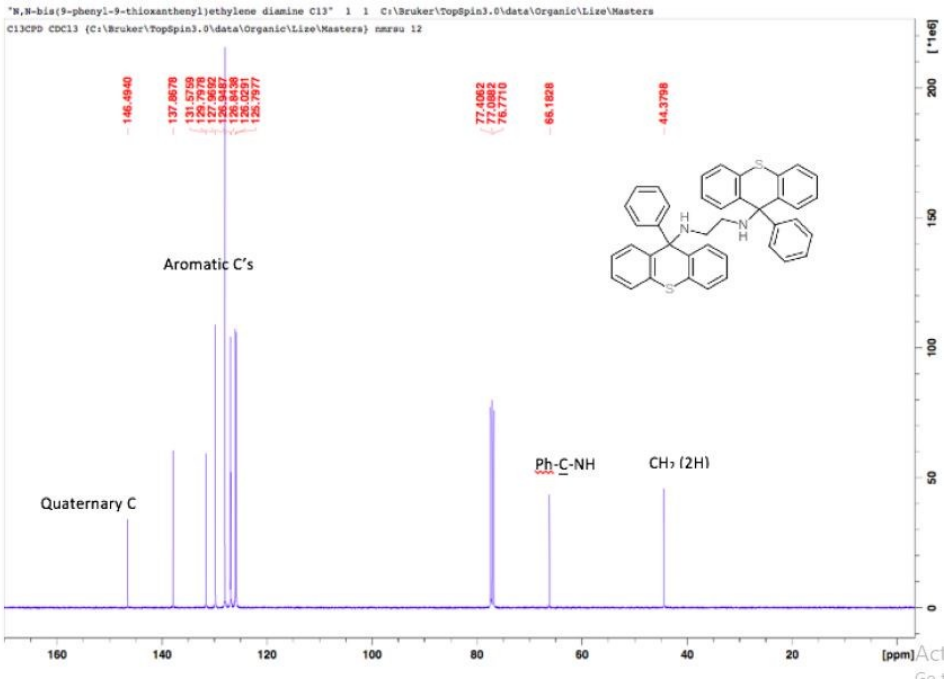
6.00
[ppm]

(e)



(f)

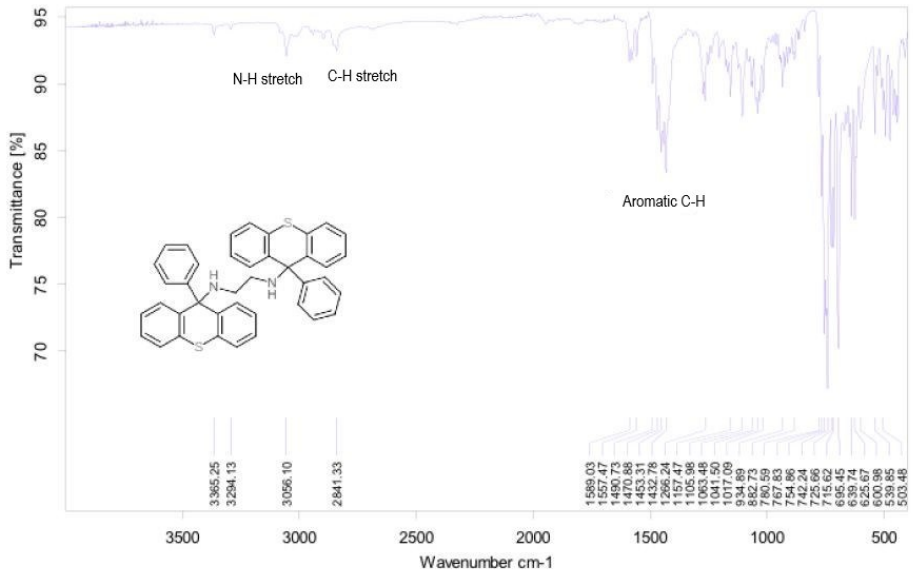


Figure S1. Characterization spectra for (a) ^{1}H-NMR spectrum for $\mathbf{H_2}$, (b) ^{13}C-NMR spectrum for $\mathbf{H_2}$, (c) IR spectrum for $\mathbf{H_2}$, (d) ^{1}H-NMR spectrum for $\mathbf{H_1}$, (e) ^{13}C-NMR spectrum for $\mathbf{H_1}$ and (f) IR spectrum for $\mathbf{H_1}$.

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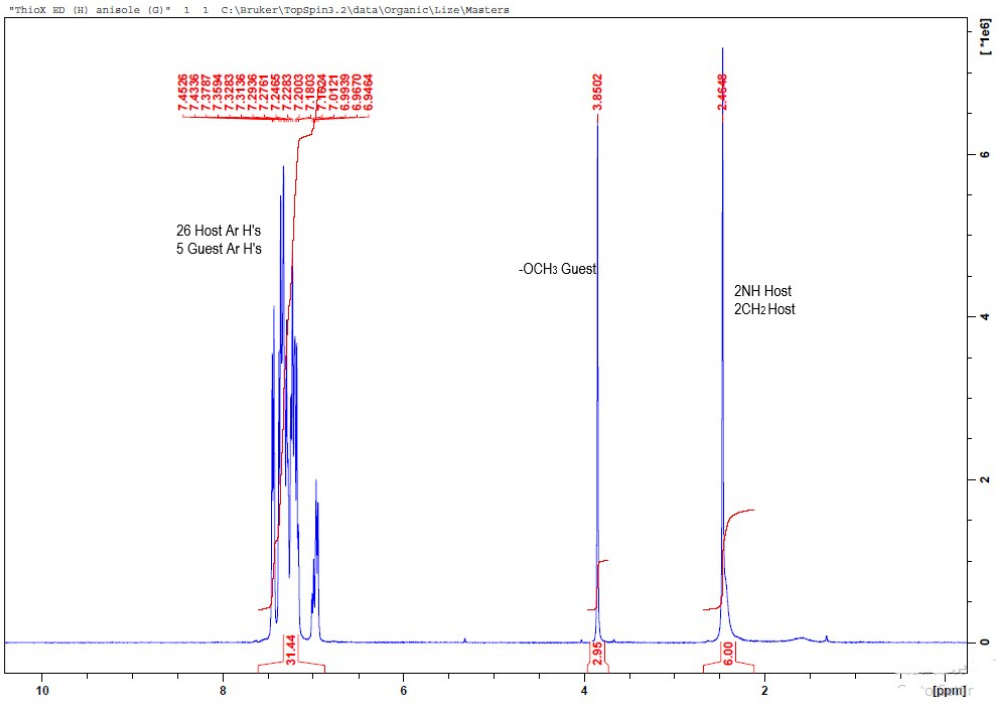
(a)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7.3777
7.3594
7.3283
7.3136
7.2936
7.2761
7.2585
7.2283
7.2003
7.1803
7.1624
7.0121
6.9838
6.9670
6.9464
3.8502
2.4648
26 Host Ar H's
5 Guest Ar H's
-OCH3 Guest
2NH Host
2CH2 Host
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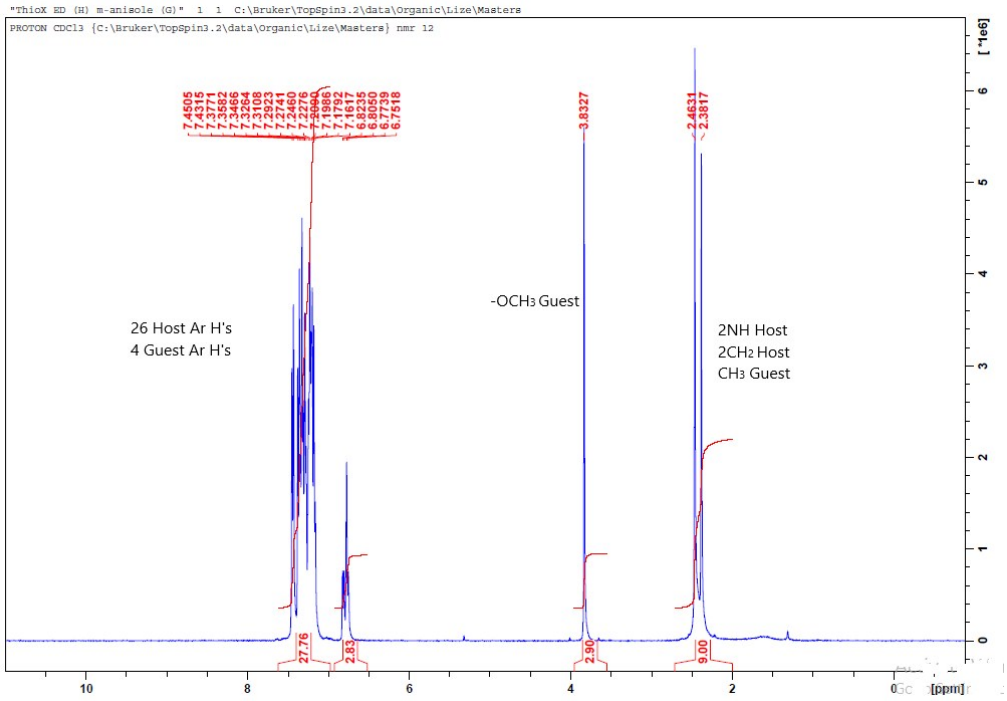
2.95
6.00
[*1e6]
[ppm]

(b)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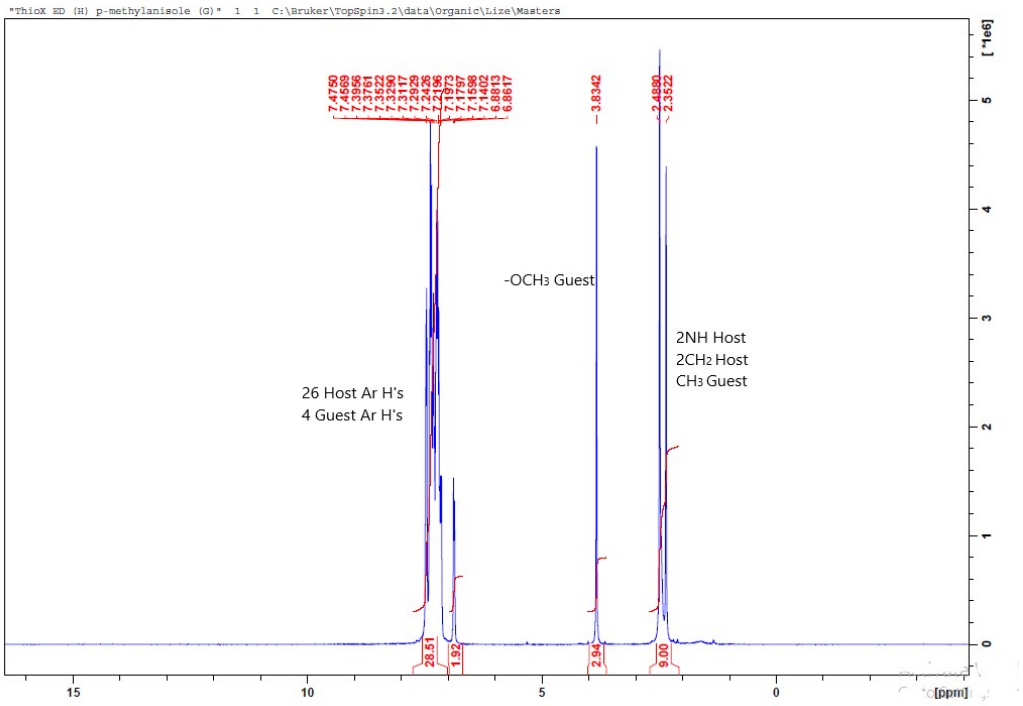
7.4315
7.3771
7.3582
7.3466
7.3264
7.3108
7.2923
7.2741
7.2460
7.2276
7.1986
7.1792
7.1617
6.8235
6.8050
6.7739
6.7518
3.8327
2.4631
2.3817
26 Host Ar H's
4 Guest Ar H's
-OCH3 Guest
2NH Host
2CH2 Host
CH3 Guest
27.76
2.83
2.90
9.00
[*1e6]
[ppm]

(c)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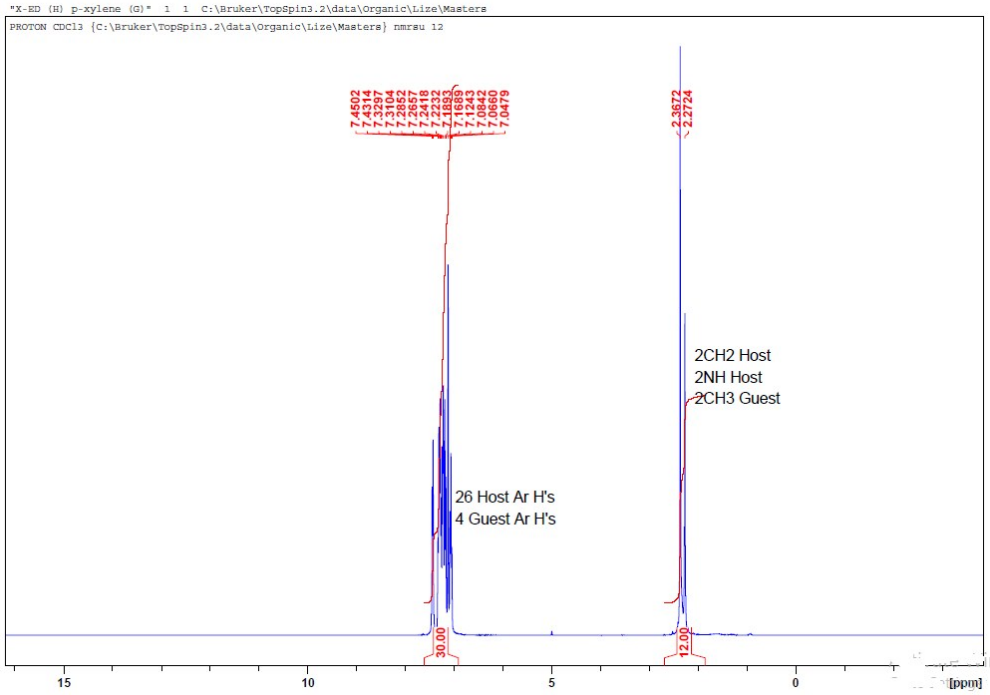
7.4569
7.3956
7.3761
7.3522
7.3360
7.3117
7.2929
7.2426
7.2196
7.1973
7.1797
7.1598
7.1402
6.8813
6.8617
3.8342
2.4880
2.3522
-OCH3 Guest
2NH Host
2CH2 Host
CH3 Guest
26 Host Ar H's
4 Guest Ar H's
28.51
1.92
2.94
9.00
[1e6]
[ppm]

(d)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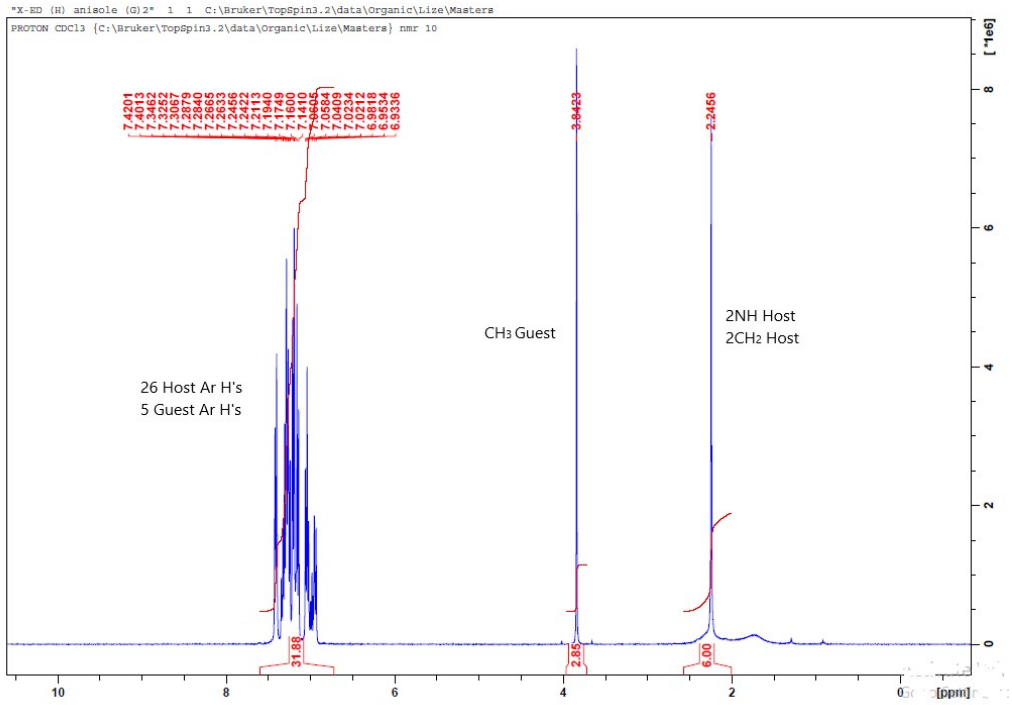
7.4314
7.3297
7.3104
7.2852
7.2657
7.2418
7.2232
7.1893
7.1693
7.1443
7.0842
7.0660
7.0479
2.3672
2.2724
2CH2 Host
2NH Host
2CH3 Guest
26 Host Ar H's
4 Guest Ar H's
30.00
12.00
[ppm]

(e)



(f)

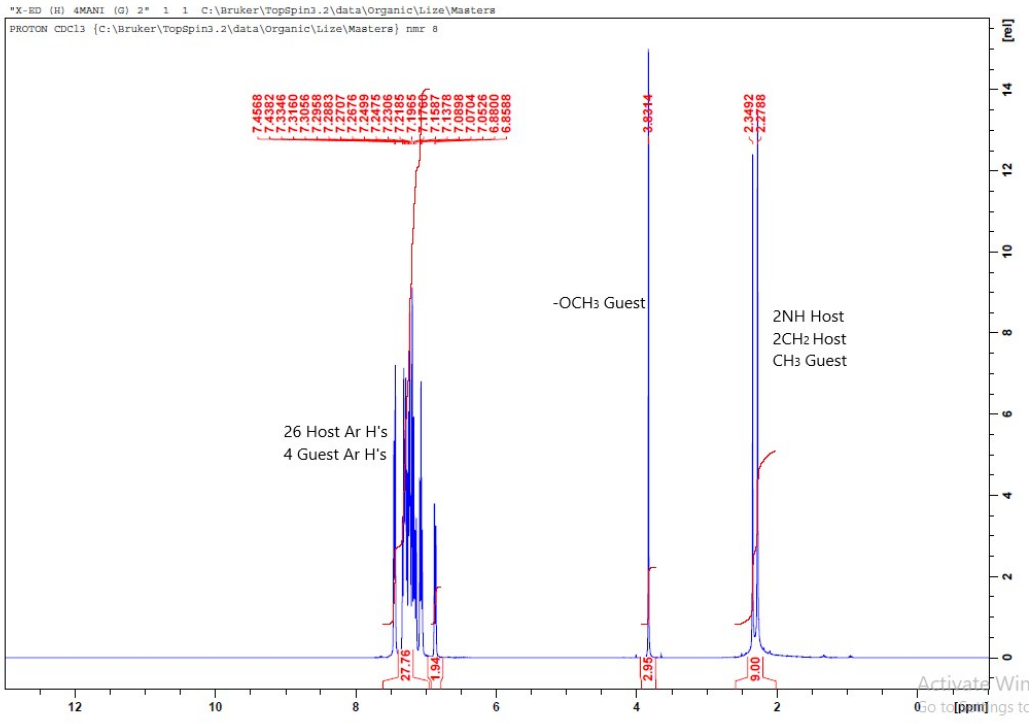


Figure S2. Individual inclusion spectra for (a) ^{1}H-NMR for ANI with $\mathbf{H_1}$, (b) ^{1}H-NMR for 3MANI with $\mathbf{H_1}$, (c) ^{1}H-NMR for 4MANI with $\mathbf{H_1}$, (d) ^{1}H-NMR for *p*-Xy with $\mathbf{H_2}$, (e) ^{1}H-NMR for ANI with $\mathbf{H_2}$ and (f) ^{1}H-NMR for 4MANI with $\mathbf{H_2}$.

Table S3. (a) Duplicate data for equimolar competition experiments of anisole and methylanisole isomers with $\mathbf{H_1}$

Combination:	Batch 1	Batch 2	Average	e.s.d.'s
ANI 2MANI	98.29:1.71	94.09:5.91	96.19:3.54	(2.10): (2.10)
ANI 3MANI	54.40: 45.60	57.88:42.12	56.14:43.86	(1.74): (1.74)
ANI 4MANI	35.59:64.42	36.04:63.97	35.82:64.20	(0.23): (0.23)
23 MANI	11.58:88.42	14.91:85.09	13.25:86.76	(1.67): (1.67)
34 MANI	40.14:59.86	40.56:59.44	40.35:59.65	(0.21): (0.21)
24 MANI	3.75:96.25	4.18:95.82	3.79:96.04	(0.22): (0.22)
ANI 23MANI	35.10:8.12:56.78	38.56:7.89:53.55	36.83:8.01:55.17	(1.73): (0.12): (1.62)
ANI 34MANI	27.36:32.73:39.91	29.54:29.97:40.49	28.45:31.38:40.20	(1.09): (1.41): (0.29)
ANI 24MANI	36.31:4.51:59.18	35.69:3.03:61.28	36.00:3.77:60.23	(0.31): (0.74): (1.05)
234 MANI	4.50:40.89:54.60	3.12:43.39:53.46	3.18:42.14:54.03	(0.69): (1.25): (0.57)
ANI 234MANI	31.06:2.88:19.59:46.47	27.02:3.04:24.10:45.85	29.04:2.96:21.85:46.16	(2.02): (0.08): (2.26): (0.31)

Table S3. (b) Duplicate data for equimolar competition experiments of anisole and methylanisole isomers with $\mathbf{H_2}$

Combination:	Batch 1	Batch 2	Average	e.s.d.'s (%)
ANI 2MANI	97.47:2.54	95.07:4.93	96.27:3.73	(1.20): (1.20)
ANI 3MANI	91.80:8.20	89.91:10.09	90.86:9.14	(0.95): (0.95)
ANI 4MANI	14.54:85.46	14.08:85.92	14.31:85.69	(0.23): (0.23)
23 MANI	[a]	[a]	–	–
34 MANI	6.55:93.45	6.20:93.80	6.37:93.63	(0.18): (0.18)
24 MANI	3.88:96.12	3.50:96.50	3.69:96.31	(0.19): (0.19)
ANI 23MANI	[a]	[a]	–	–
ANI 34MANI	11.25:4.77:83.98	9.81:4.17:86.02	10.53:4.47:85.00	(0.72): (0.30): (1.02)
ANI 24MANI	10.11:1.76:88.13	11.73:2.36:85.91	10.92:2.06:87.02	(0.81): (0.30): (1.11)
234 MANI	1.25:3.95:94.80	2.17:5.65:92.18	1.71:4.80:93.49	(0.46): (0.85): (1.31)
ANI 234MANI	11.58:1.15:5.28:81.99	11.09:1.76:3.89:83.26	11.34:1.46:4.59:82.63	(0.25): (0.31): (0.70): (0.64)

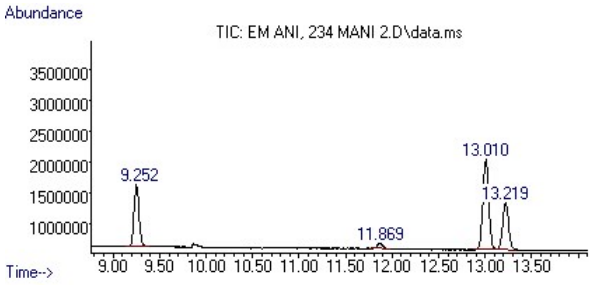
[a]Did not crystallize

Table S3. (c) Duplicate data for equimolar competition experiments of ethylbenzene and xylene isomers with $\mathbf{H_2}$

Combination:	Batch 1	Batch 2	Average	e.s.d.'s
p,o–xylene	96.66:3.34	96.79:3.21	96.73:3.27	(0.07): (0.07)
p,m–xylene	96.09:3.91	96.39:3.61	96.24:3.76	(0.15): (0.15)
m,o–xylene	[a]	[a]	-	-
p,m,o–xylene	96.85:1.60:1.55	96.12:2.16:1.72	96.49: 1.88: 1.63	(0.37): (0.28): (0.09)
p–xyl and EB	91.94:8.06	92.63:7.37	92.29:7.71	(0.35): (0.35)
o–xyl and EB	[a]	[a]	-	-
m–xyl and EB	[a]	[a]	-	-
p,o–xyl and EB	92.77:1.89:5.35	92.75:2.18:5.08	92.76: 2.04:5.22	(0.01): (0.15): (0.14)
p,m–xyl and EB	90.94:2.85:6.22	92.02:1.97:6.01	91.48:2.41:6.12	(0.54): (0.44): (0.11)
o,m–xyl and EB	[a]	[a]	-	-
p,m,o–xyl and EB	91.42:1.51:1.86:5.21	92.61:1.04:1.11:5.25	92.02:1.28:1.49:5.23	(0.60): (0.24): (0.38): (0.02)

[a]No inclusion occurred

(a)



(b)

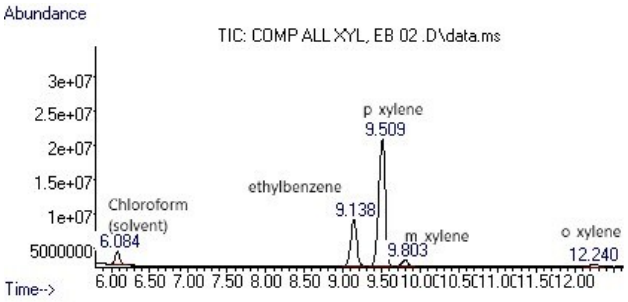


Figure S4 Chromatograph of standards for guests (a) anisoles and methylanisole isomers and (b) ethylbenzene and xylene isomers.

Table S5. (a) All interactions for H_1 with anisole and methylanisole isomers

Non-covalent interaction	**H_1**•ANI	**H_1**•3MANI	**H_1**•4MANI	Symmetry
π···π (H···H and H···G)	4.641(1)–5.989(1) Å	4.527(9)–5.9691(9) Å	4.571(1)–5.998(1) Å	
H···G major	[7] 4.909(1) –5.986(1) Å[a]	[7] 5.028(1)–5.757(1) Å	[6] 4.964(2)–5.535(2) Å	
H···G minor			[7] 5.220(2)–5.869(2) Å	
CH···π (host–host and host–guest)				
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$	2.85 Å, 144°			x, y, 1+z
$C_{(G)}$–$H_{(G)}$···$Cg_{(H)}$		2.78 Å, 170°		1–x, 2–y,1– z
$C_{(G)}$–$H_{(G)}$···$Cg_{(H)}$			2.74 Å, 134°	–1+x, y, z
H-bonding (intramolecular)	Non-classical	Non-classical	Non-classical	
$C_{(H)}$–$H_{(H)}$···$N_{(H)}$	2.62(2) Å, 103°	2.910(2) Å, 102°	2.756(2) Å, 103°	x, y, z
$C_{(H)}$–$H_{(H)}$···$N_{(H)}$	3.443(2) Å, 158°		3.456(2) Å, 155°	x, y, z
$C_{(H)}$–$H_{(H)}$···$N_{(H)}$	2.07(2) Å, 102°	2.763(2) Å, 103°	2.914(2) Å, 102°	x, y, z
$C_{(H)}$–$H_{(H)}$···$N_{(H)}$		3.456(2) Å, 153°		x, y, z
$C_{(H)}$–$H_{(H)}$···$N_{(H)}$	3.455(2) Å, 151°	3.422(2) Å, 151°	3.437(2) Å, 148°	x, y, z
$C_{(H)}$–$H_{(H)}$···$N_{(H)}$	2.768(2) Å, 103°	2.772(2) Å, 103°	2.766(2) Å, 103°	x, y, z
$C_{(H)}$–$H_{(H)}$···$N_{(H)}$	2.898(2) Å, 102°	2.921(2) Å, 101°	2.902(2) Å, 101°	x, y, z
$C_{(H)}$–$H_{(H)}$···$O_{(G)}$			2.55 Å, 132°	1–x, –y, –z
$C_{(H)}$–$H_{(H)}$···$O_{(G)}$–$C_{(G)}$	2.70Å, 127°(<)			1–x, 1–y, 1–z
$N_{(H)}$–$H_{(H)}$···$C_{(H)}$–$C_{(H)}$	2.83Å, 158°(<)			–x, 1–y, 1–z
Short contacts (host/ guest and guest/guest)[b]				
C_{62}–H_{62}···C_{75}–C_{74}	2.87Å, 141°(<)			x, y, 1+z
C_{72}–H_{72}···C_{52}–C_{53}	2.86Å, 143°(<)			–x, 1–y, 1–z
$C_{(H)}$–$H_{(H)}$···$S_{(H)}$–$C_{(H)}$		2.95 Å, 146° (<)		1–x, 2–y, 1–z
$C_{(H)}$–$H_{(H)}$···$H_{(H)}$–$C_{(H)}$		2.35 Å, 128° (<)		1–x, 1–y, 1–z
$C_{(H)}$–$H_{(H)}$···$H_{(G)}$–$C_{(G)}$		2.36 Å, 143° (<)		1–x, 2–y, 1–z
$C_{(H)}$–$H_{(H)}$···$H_{(G)}$–$C_{(G)}$		2.94 Å, 130° (<)		x, 1+y, z
$C_{(H)}$–$H_{(H)}$···$H_{(G)}$–$C_{(G)}$		2.37 Å, 158° (<)		2–x, 2–y, 1–z
$C_{(H)}$–$H_{(H)}$···$H_{(H)}$–$C_{(H)}$			2.38 Å, 127° (<)	2–x, 1–y, –z
$C_{(H)}$–$H_{(H)}$···$H_{(G)}$–$C_{(G)}$			2.27 Å, 158° (<)	2–x, –y, –z
$C_{(G)}$–$H_{(G)}$···$H_{(H)}$–$C_{(H)}$			2.26 Å, 141° (<)	1–x, 1–y, 1–z
$C_{(G)}$–$H_{(G)}$···$H_{(H)}$–$C_{(H)}$			2.25 Å, 141° (<)	1–x, –y, 1–z

[a]Number pf H···G interactions are indicated in parentheses.

[b]Distances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved while those denoted by << is this sum minus 0.2 Å.

Table S5. (b) All interactions for H_2 with anisole and methylanisole isomers

Non-covalent interaction	**H_2**•ANI	**H_2**•4MANI	Symmetry
π···π (H···H and H···G) H···G interactions	4.080(1) – 5.920(1) Å [5] 4.725(1)–5.920(1) Å	4.0427(7) – 5.756(3) Å [H···H only]	
CH···π (host–host)			
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$	2.94 Å, 76°		x, y, z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$	2.57 Å, 97°		x, y, z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$	2.92 Å, 128°		x, 1+y, z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$	2.63 Å, 162°		2–x, 2–y, 2–z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$	2.81 Å, 105°		x, y, z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$	2.92 Å, 128°		1–x, 1–y, 1–z
$C_{(G)}$–$H_{(G)}$···$Cg_{(H)}$	2.90 Å, 137°		x, y, z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$		2.61 Å, 99°	x, y, z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$		2.83 Å, 132°	1+x, y, z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$		2.90 Å, 133°	1–x, –y,1–z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$		2.75 Å, 105°	x, y, z
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$		2.69 Å, 155°	1–x, –y, –z
$C_{(G)}$–$H_{(G)}$···$Cg_{(H)}$		2.78 Å, 135°	–1+x, –1+y, z
H–bonding (intramolecular)	Non-classical	Non-classical	
$C_{(H)}$–$H_{(H)}$···$N_{(H)}$	2.805(3) Å, 102°		x, y, z
$N_{(H)}$–$H_{(H)}$···$C_{(G)}$–$C_{(G)}$		2.63 Å, 156° (<<)	1–x, –y, 1–z
$N_{(H)}$–$H_{(H)}$···$C_{(G)}$–$C_{(G)}$		2.37 Å, 160° (<)	1+x, y, z
$C_{(H)}$–$H_{(H)}$···$O_{(H)}$–$C_{(H)}$	2.64Å, 164°(<)		1+x, 1+y, z
$C_{(H)}$–$H_{(H)}$···$O_{(H)}$–$C_{(H)}$		2.63 Å, 155° (<)	–1+x, –1+y, z
Short contacts (host··· guest and guest···guest)[a,b]			
$C_{(H)}$–$H_{(H)}$···$H_{(G)}$–$C_{(G)}$		2.30 Å, 127° (<)	1+x, 1+y, z

[a]Distances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved while those denoted by << is this sum minus 0.2 Å.

Table S5. (c) All interactions for H_2 with ethylbenzene and xylene isomers

Non-covalent interaction	**H_2•** *p*-Xy	Symmetry
π–π (H···H and H···G)	4.074(1) – 5.926(1) Å 5H–G 4.781(1)–5.926(1) Å	
CH···π (host–host)		
$C_{(H)}$–$H_{(H)}$···$Cg_{(H)}$	3.00 Å, 127°	x, y, z
$C_{(G)}$–$H_{(G)}$···$Cg_{(H)}$	2.76 Å, 145°	x, 1+y, z
H–bonding	Non-classical	
$N_{(H)}$–$H_{(H)}$···$C_{(G)}$–$C_{(G)}$	2.77 Å, 159° (<)	1–x, 2–y, 1–z
Short contacts (host··· guest and guest···guest)[a,b]		
$C_{(H)}$–$H_{(H)}$···$H_{(G)}$–$C_{(G)}$	2.33 Å, 130° (<)	x, –1+y, z
$C_{(G)}$–$H_{(G)}$···$C_{(H)}$–$C_{(H)}$	2.87 Å, 139° (<)	x, y, z

[a]Distances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved while those denoted by << is this sum minus 0.2 Å.

Summary of H···H interactions of inclusion compounds

Interaction	**H_2•***p*-Xy	
	#	Range
π···π	–	4.047(1)–5.926(1) Å
CH···π	3	2.51–2.80 Å, 102–163˚
Non-classical H-bonding	2	2.811(2)–3.486(2) Å, 102–165˚
Other short contacts	1	2.56 Å, 165˚

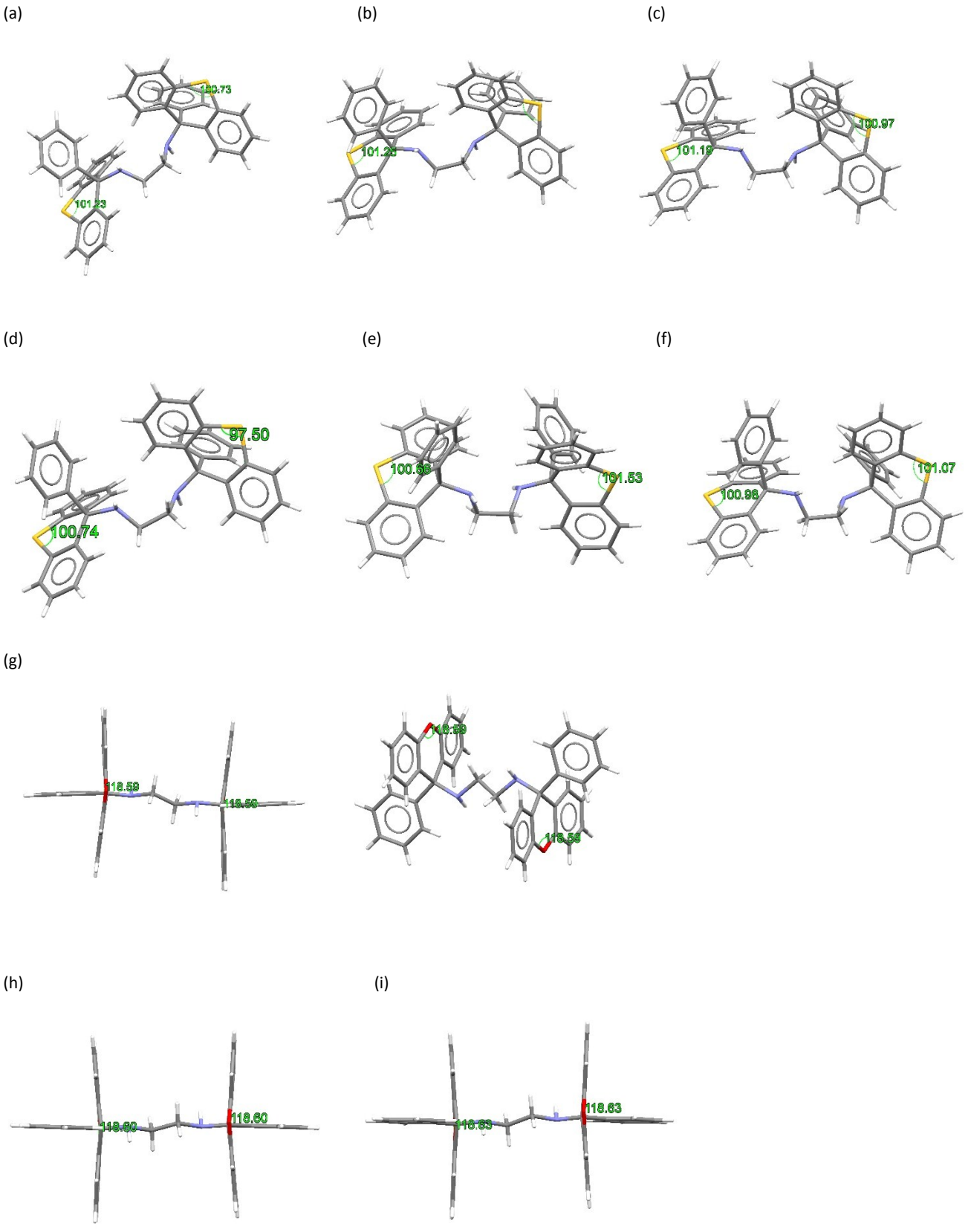


Figure S6. Host geometry within the respective complexes (a) **H$_1$**•*p*-Xy, (b) **H$_1$**•*o*-Xy, (c) **H$_1$**•EB, (d) **H$_1$**•ANI, (e) **H$_1$**•3MANI, (f) **H$_1$**•4MANI, (g) **H$_2$**•*p*-Xy, (h) **H$_2$**•ANI and (i) **H$_2$**•4MANI.