Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Structure determination of liquid molecules by encapsulation in an aromatic cavity with hydrogen bonding and enhanced C–H···π interactions

Shu-Qin Qin, Wei Xu, Wen-Cai Ye*, Ren-Wang Jiang*

Guangdong Province Key Laboratory of Pharmacodynamic Constituents of TCM and New Drugs Research, College of Pharmacy, Jinan University, Guangzhou 510632, P. R. China.

e-mails: trwjiang@jnu.edu.cn, chywc@aliyun.com

Tel: 8620-85221016; Fax: 8620-85221559

Outline

1. Spectra of as-synthesized host

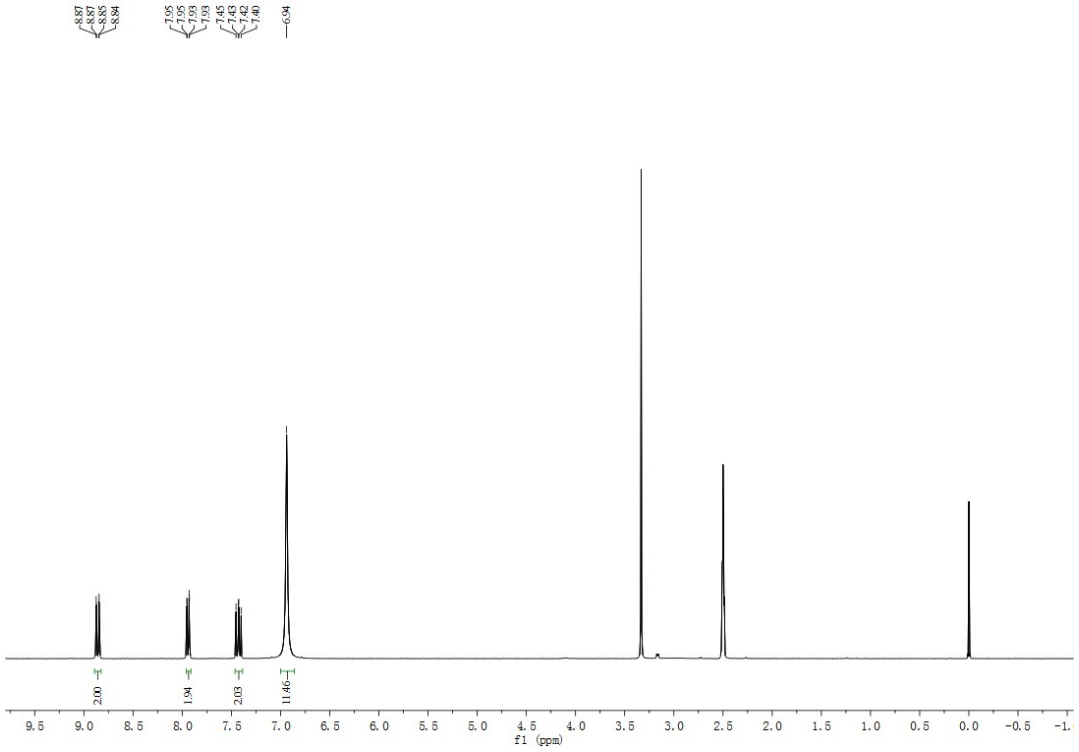

Fig. S1a ^{1}H-NMR spectra of guanidinium−naphthalenedisulfonic acid (GNPS) (400 MHz, DMSO).

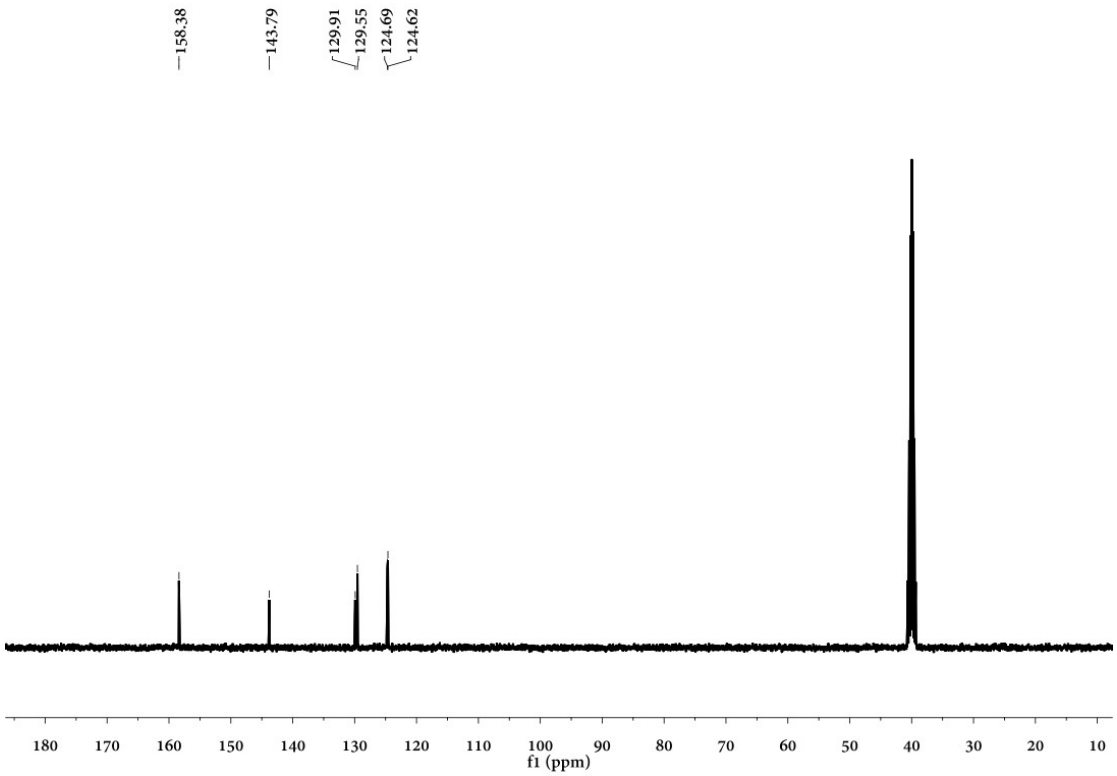

Fig. S1b ^{13}C-NMR spectra of guanidinium−biphenyldisulfonic acid (GNPS) (100 MHz, DMSO).

2. Crystallization methods.

Crystallization of GNPS ⊃1. Slow evaporation of 1 mL methanol solution containing 1.7 μL (0.01 mmol) of (-)-isopulegol and 4.08 mg (0.01 mmol) of Guanidinium−naphthalenedisulfonic acid (GNPS) apohost in a 2 mL transparent glass vial afforded colourless block-shaped single crystals within 1 day with the formula GNPS⊃(-)-isopulegol (**GNPS⊃1**).

Crystallization of GNPS ⊃2. Slow evaporation of 1 mL methanol solution containing 2.1 μL (0.01 mmol) of (-)-menthyl acetate and 4.08 mg (0.01 mmol) of Guanidinium−naphthalenedisulfonic acid (GNPS) apohost in a 2 mL transparent glass vial afforded colourless needle-shaped single crystals within 1 day with the formula GNPS⊃(-)-menthyl acetate (**GNPS⊃2**).

Crystallization of GNPS ⊃3. Slow evaporation of 1 mL methanol solution containing 1.5 μL (0.01 mmol) of isoeugenol and 4.08 mg (0.01 mmol) of Guanidinium−naphthalenedisulfonic acid (GNPS) apohost in a 2 mL transparent glass vial afforded colourless needle-shaped single crystals within 3 day with the formula GNPS⊃ isoeugenol (**GNPS⊃3**).

Crystallization of GNPS ⊃4. Slow evaporation of 1 mL methanol solution containing 1.3 μL (0.01 mmol) of 2,6-dimethylaniline and 4.08 mg (0.01 mmol) of Guanidinium−naphthalenedisulfonic acid (GNPS) apohost in a 2 mL transparent glass vial afforded colourless block-shaped single crystals within 1 day with the formula GNPS⊃ 2,6-dimethylaniline (**GNPS⊃4**).

Crystallization of GNPS ⊃5. Slow evaporation of 1 mL methanol solution containing 1.8 μL (0.01 mmol) of methyleugenol and 4.08 mg (0.01 mmol) of Guanidinium−naphthalenedisulfonic acid (GNPS) apohost in a 2 mL transparent glass vial afforded colourless needle-shaped single crystals within 3 day with the formula GNPS⊃ methyleugenol (**GNPS⊃5**).

Crystallization of GNPS ⊃6. Slow evaporation of 1 mL methanol solution containing 1.9 μL (0.01 mmol) of 2,6-diisopropylaniline and 4.08 mg (0.01 mmol) of Guanidinium−naphthalenedisulfonic acid (GNPS) apohost in a 2 mL transparent glass vial afforded colourless block-shaped single crystals within 1 day with the formula GNPS⊃ 2,6-diisopropylaniline (**GNPS⊃6**).

Crystallization of GNPS ⊃7. Slow evaporation of 1 mL methanol solution containing 1.3 μL (0.01 mmol) of methyl salicylate and 4.08 mg (0.01 mmol) of

Guanidinium−naphthalenedisulfonic acid (GNPS) apohost in a 2 mL transparent glass vial afforded colourless block-shaped single crystals within 1 day with the formula GNPS⊃ methyl salicylate (**GNPS⊃7**).

Crystallization of GNPS ⊃8. Slow evaporation of 1 mL methanol solution containing 1.6 μL (0.01 mmol) of L(-)-carvone and 4.08 mg (0.01 mmol) of Guanidinium−naphthalenedisulfonic acid (GNPS) apohost in a 2 mL transparent glass vial afforded colourless block-shaped single crystals within 1 day with the formula GNPS⊃ L(-)-carvone (**GNPS⊃8**).

3. Figures for the NMR and interactions of inclusion complexes

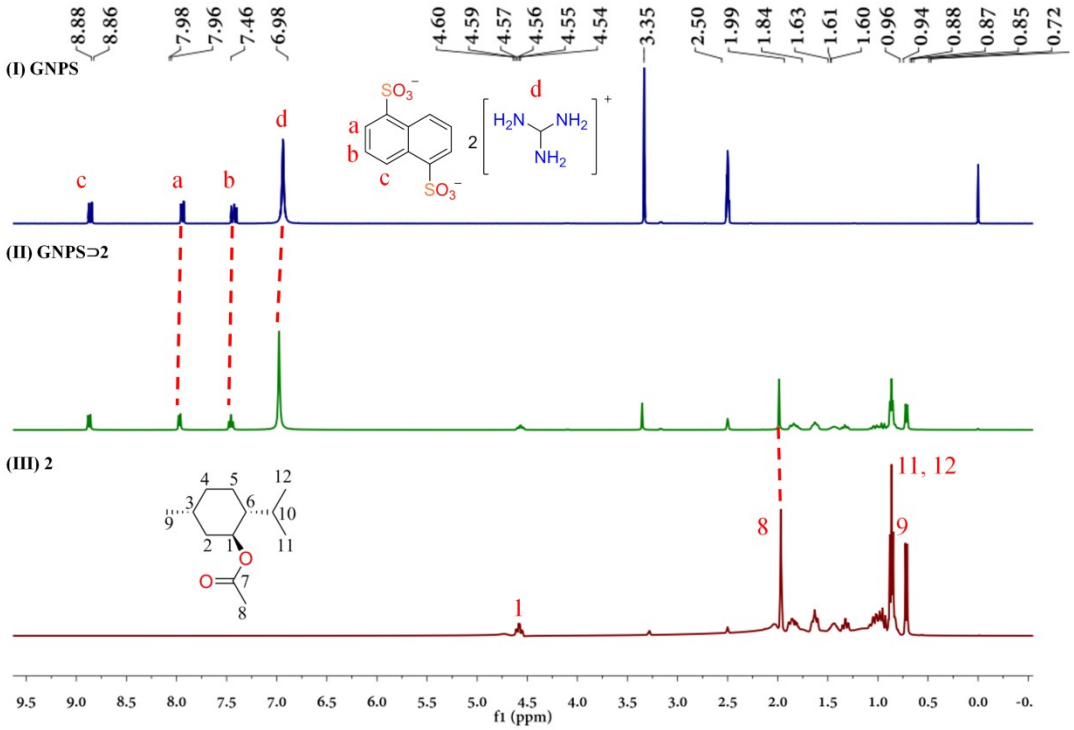

Fig. S2a ^{1}H-NMR of (I) GNPS, (II) GNPS ⊃**2** and (III)**2** (400 MHz, DMSO)

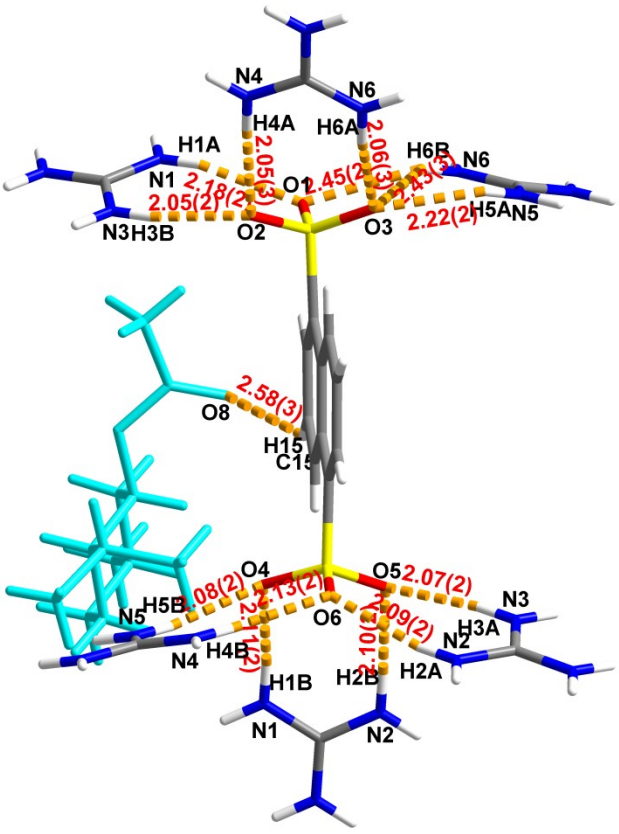

Fig. S2b N–H···O and C–H···O hydrogen bonds in GNPS ⊃**2**

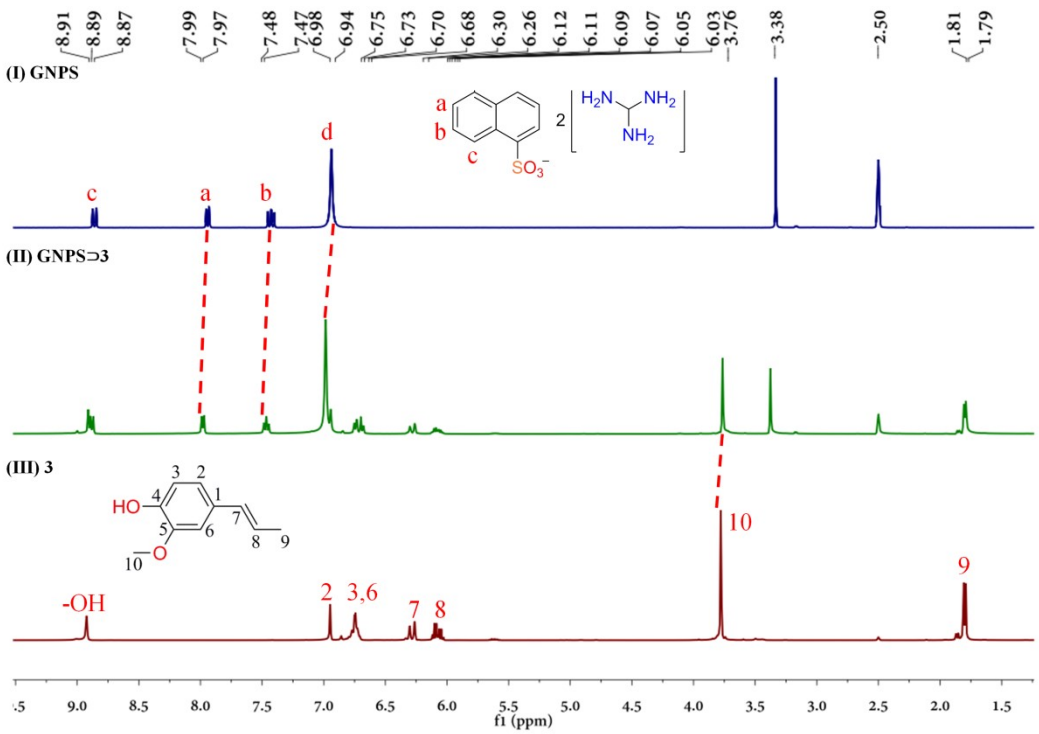

Fig. S3a ^{1}H-NMR of (I) GNPS, (II) GNPS ⊃**3** and (III)**3** (400 MHz, DMSO)

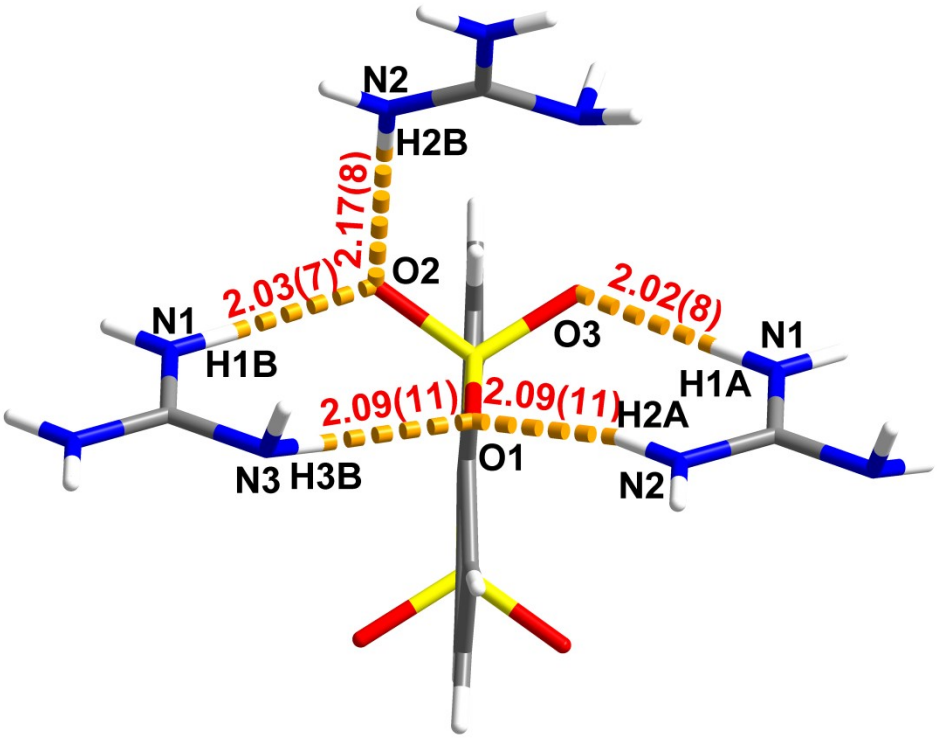

Fig. S3b N–H···O hydrogen bonds in GNPS ⊃**3**

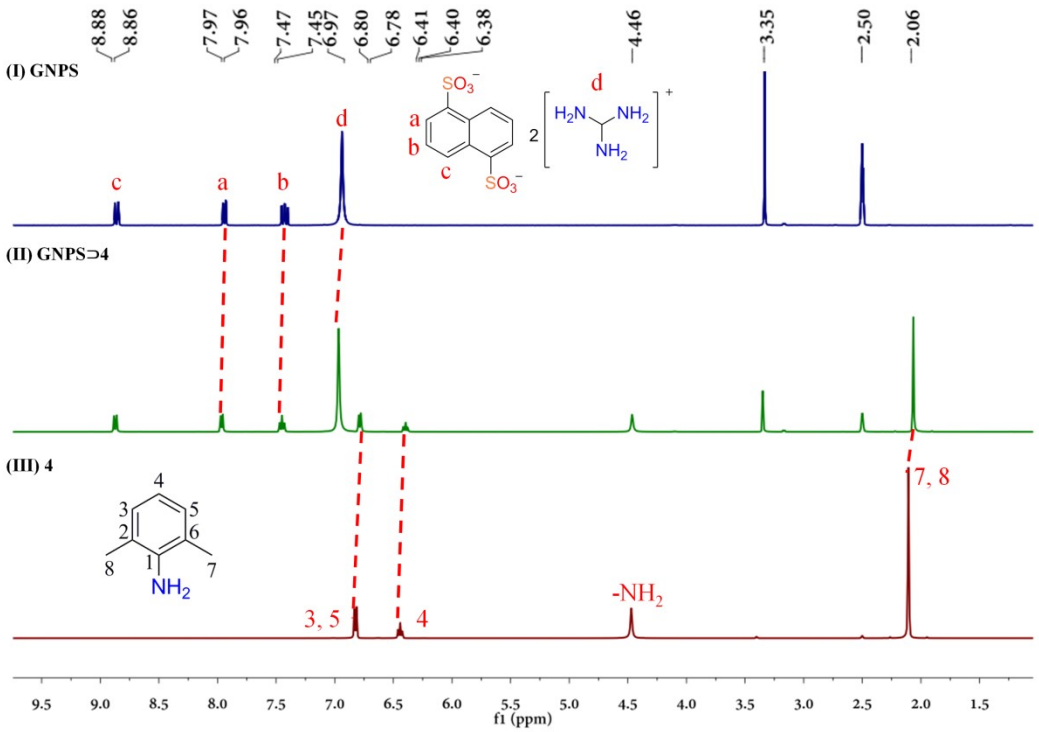

Fig. S4a ^{1}H-NMR of (I) **GNPS**, (II) **GNPS⊃4** and (III)**4** (400 MHz, DMSO)

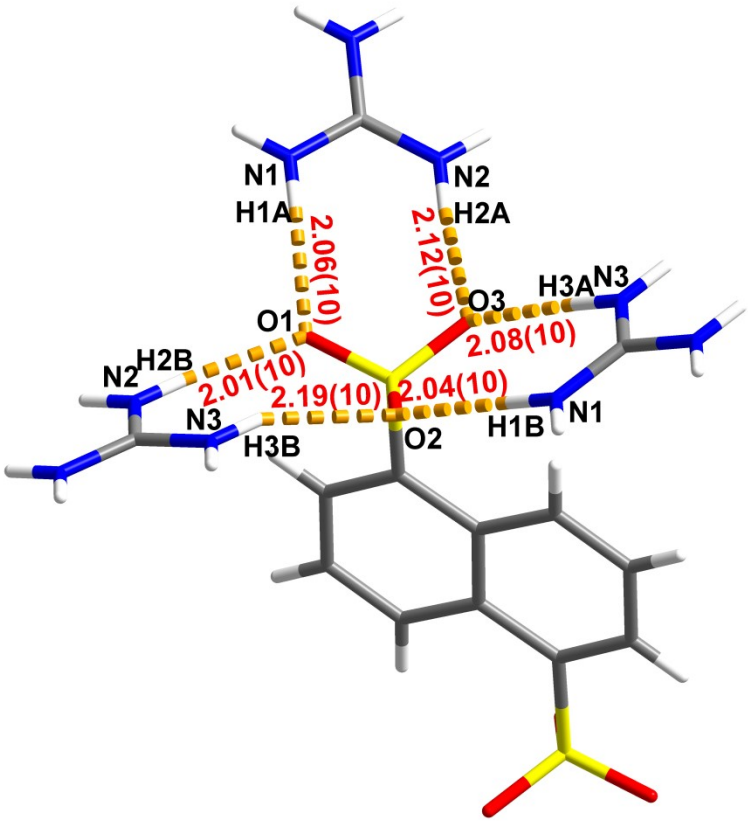

Fig. S4b N–H···O interactions in GNPS ⊃**4**

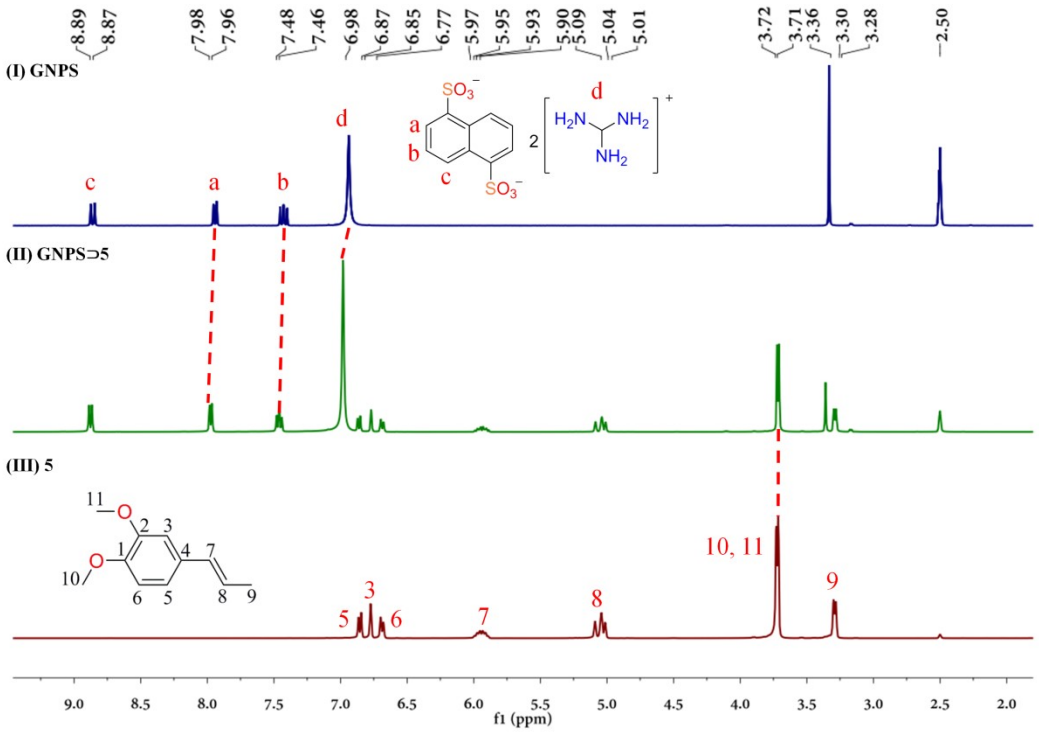

Fig. S5a ^{1}H-NMR of (I)**GNPS**, (II)**GNPS ⊃5** and (III)**5** (400 MHz, DMSO).

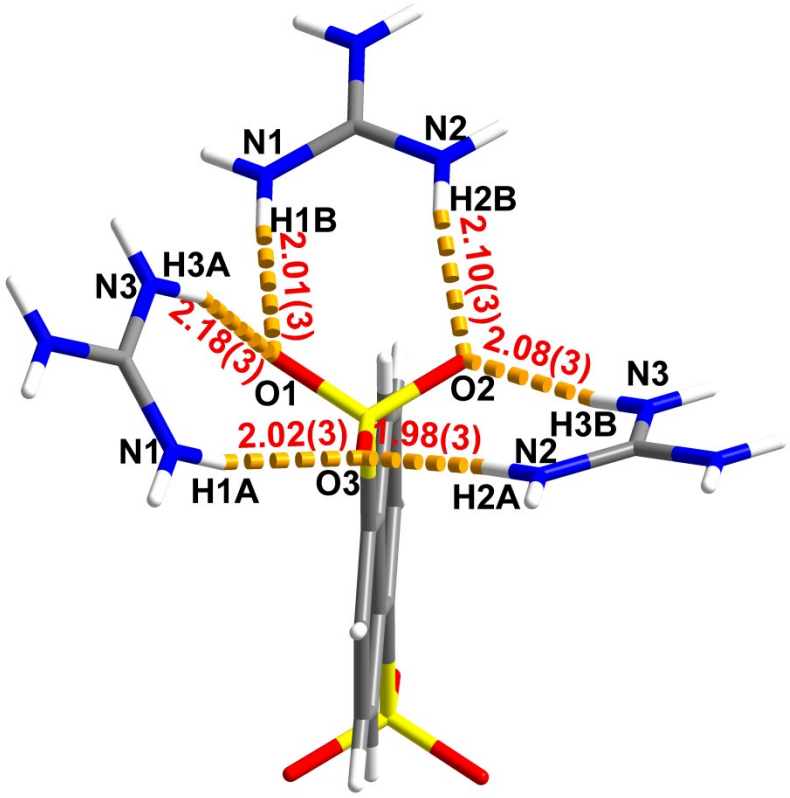

Fig. S5b N–H···O hydrogen bonds in GNPS ⊃ **5**

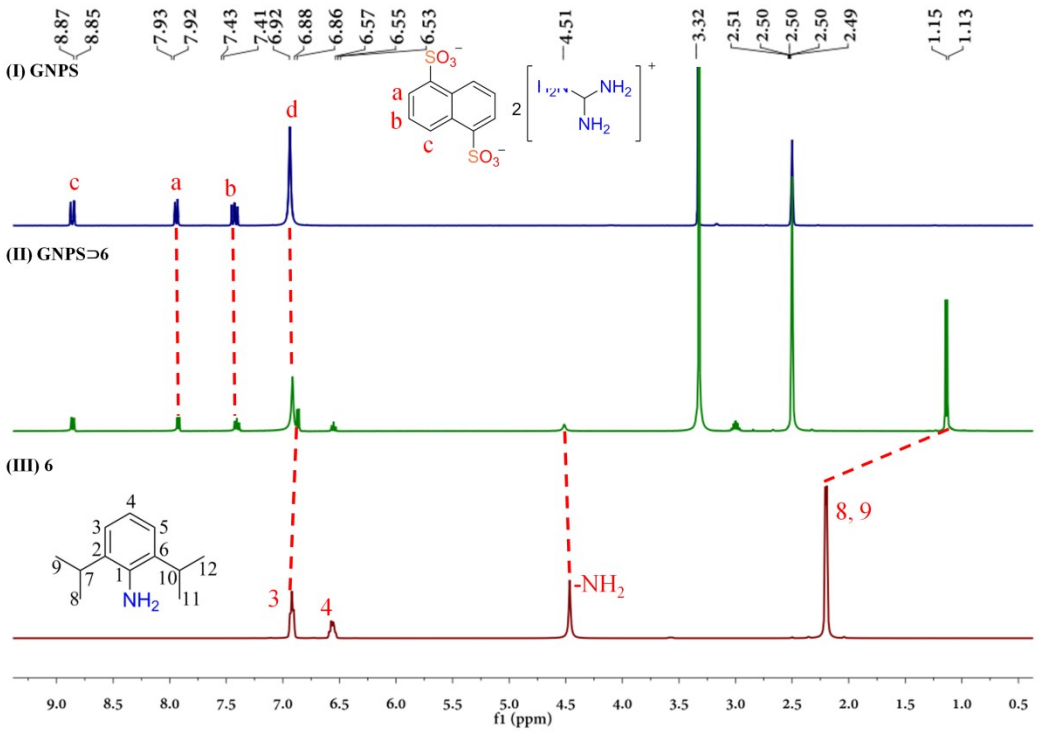

Fig. S6a ^{1}H-NMR of (I) **GNPS**, (II) **GNPS ⊃6** and (III)**6** (400 MHz, DMSO)

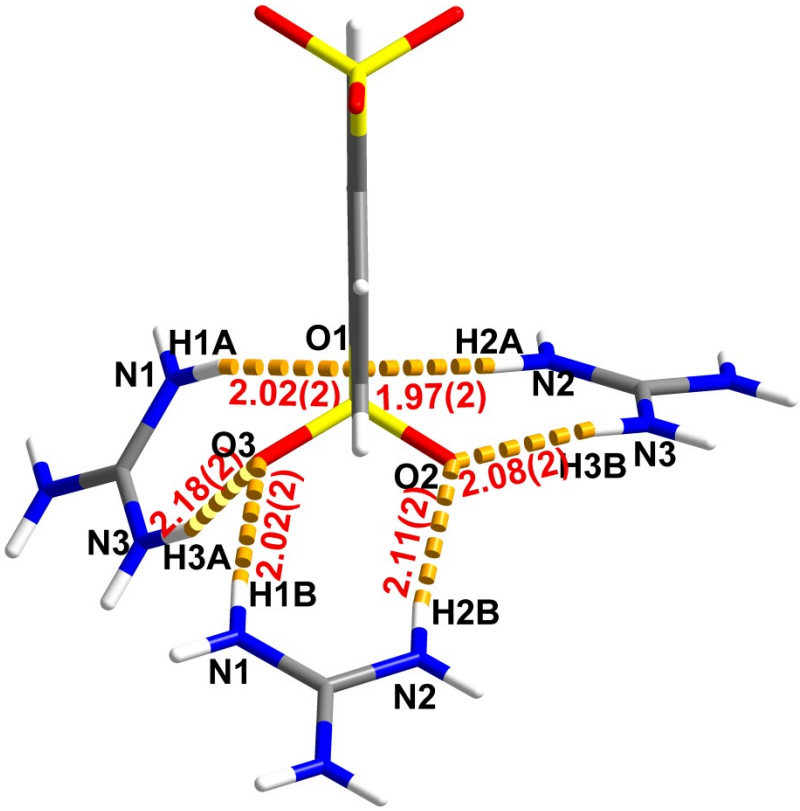

Fig. S6b N–H···O hydrogen bonds in GNPS ⊃ **6**

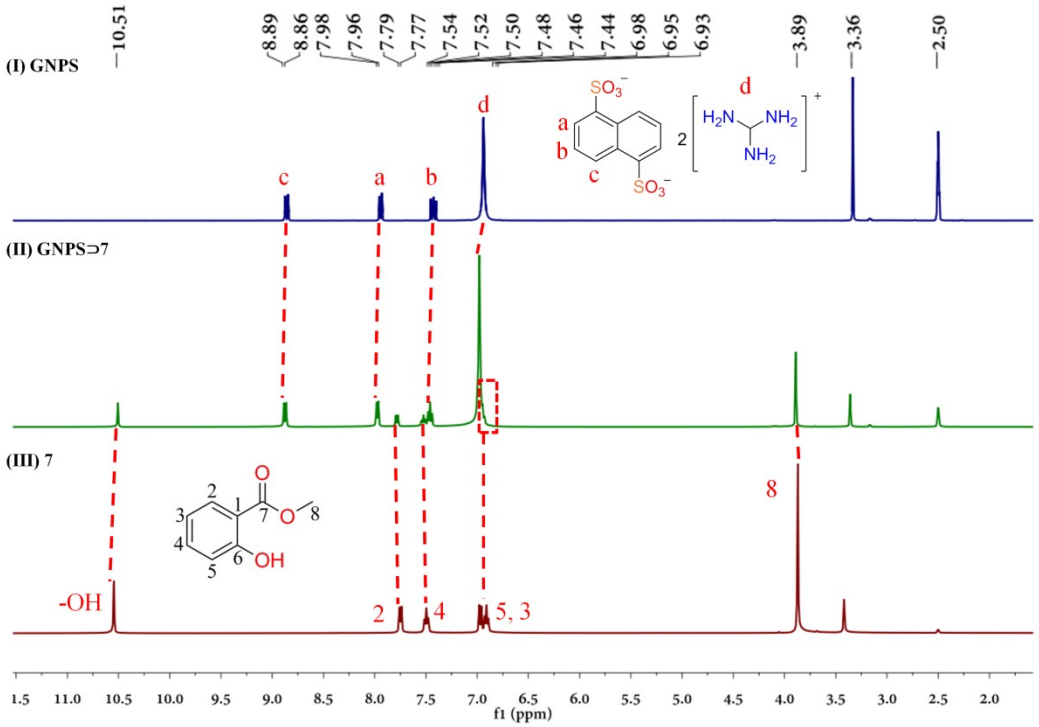

Fig. S7a ^{1}H-NMR of (I) **GNPS**, (II) **GNPS ⊃7** and (III)**7** (400 MHz, DMSO)

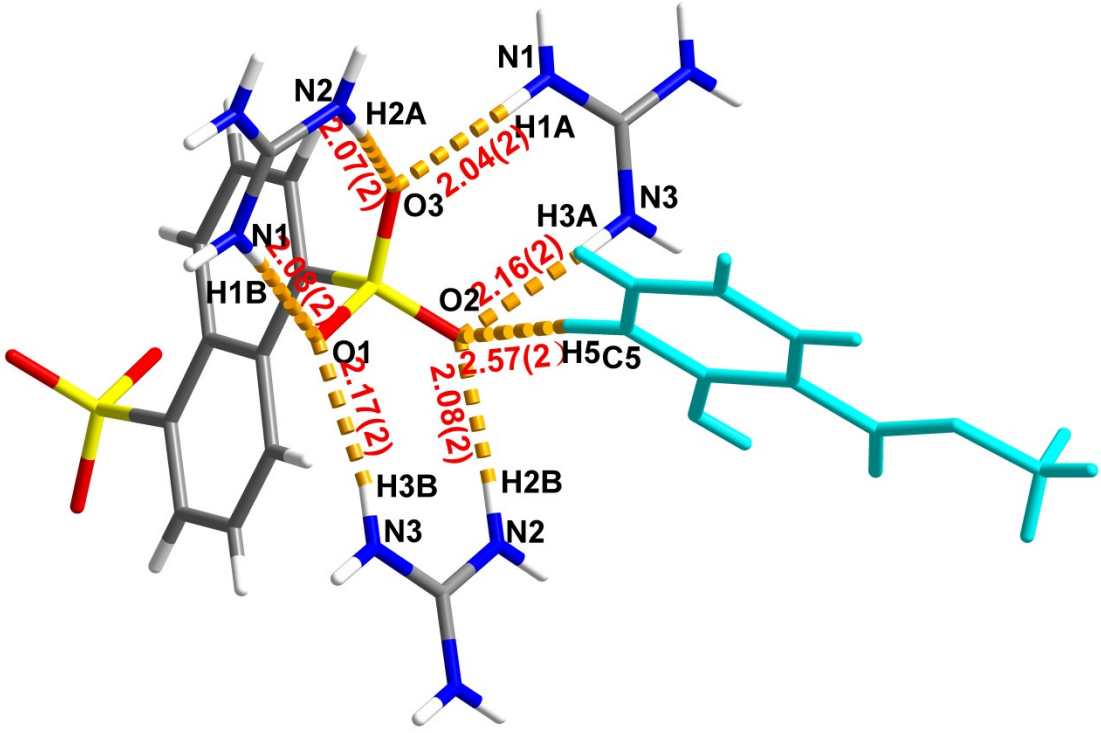

Fig. S7b N–H···O and C–H···O hydrogen bonds in GNPS ⊃ **7**

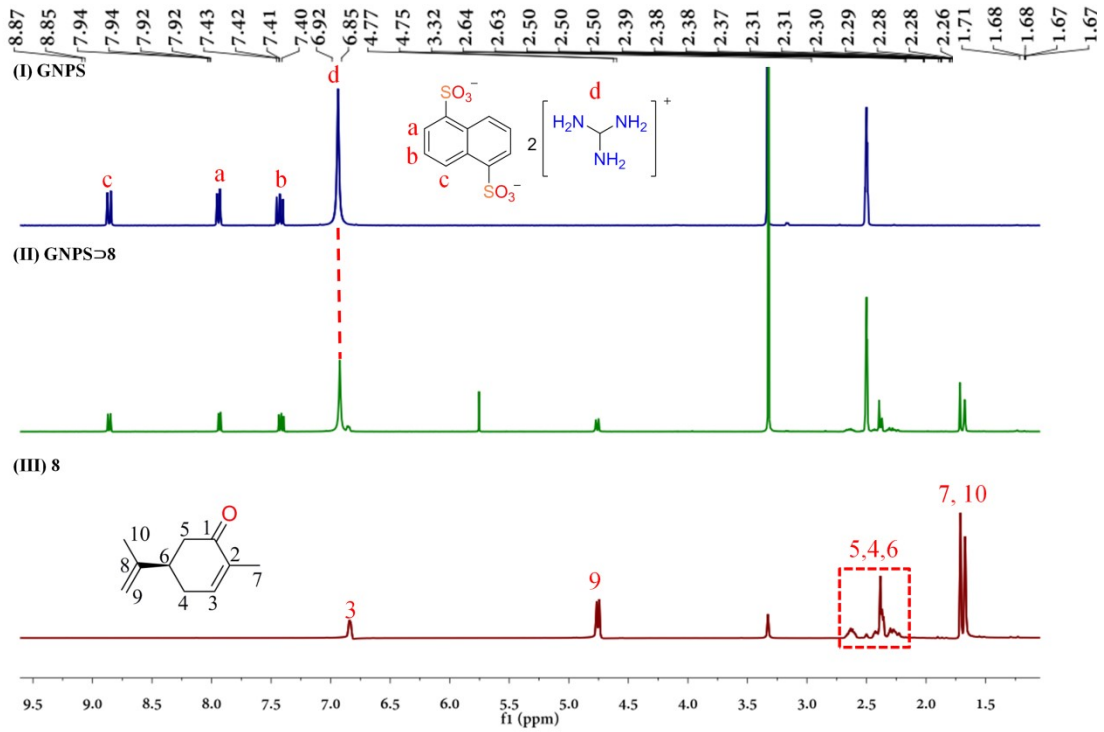

Fig. S8a ^{1}H-NMR of (I) **GNPS**, (II) **GNPS ⊃8** and (III)**8** (400 MHz, DMSO)

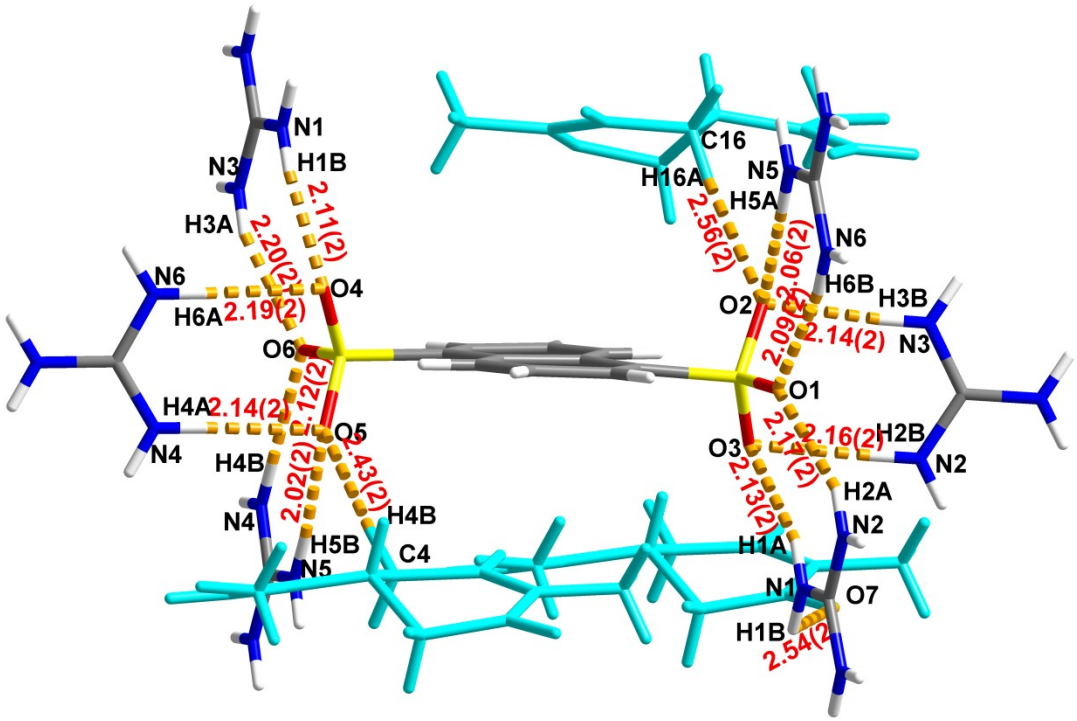

Fig. S8b N–H···O and C–H···O hydrogen bonds in GNPS ⊃ **8**

4. Supplementary Tables

Table S1. Changes of ^{1}H-NMR chemical shifts of GNPS

δ/ppm	GNPS	GNPS⊃1	GNPS⊃2	GNPS⊃3	GNPS⊃4	GNPS⊃5	GNPS⊃6	GNPS⊃7	GNPS⊃8
Ha	7.95	7.98(0.03)	7.98(0.03)	7.99(0.04)	7.98(0.03)	7.98(0.03)	7.94(-0.01)	7.93(-0.02)	7.97(0.02)
Hb	7.43	7.46(0.03)	7.46(0.03)	7.47(0.04)	7.46(0.03)	7.46(0.03)	7.42(-0.01)	7.41(-0.02)	7.45(0.02)
Hc	8.87	8.88(0.01)	8.89(0.02)	8.89(0.02)	8.88(0.01)	8.89(0.02)	8.87(0.00)	8.87(0.00)	8.88(0.01)
Hd	6.94	6.98(0.04)	6.98(0.04)	6.98(0.04)	6.98(0.04)	6.98(0.04)	6.92(-0.02)	6.92(-0.02)	7.97(0.03)

Table S2. C-H···π intermolecular interactions in Host and Guest

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
GNPS⊃1	C_9-H_9A···Cg2 [a]	2.98(1)	155	3.87(6)

Symmetry codes: [a] 1-X,-1/2+Y,3/2-Z; Cg2 is the centroid of C15, C16, C17, C18, C19 and C20.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
GNPS⊃2	C_3-H_3···Cg2 [a]	2.59(1)	162	3.54(3)
	C_4-H_4A···Cg1 [b]	2.61(1)	164	3.56(3)

Symmetry codes: [a] -1+X,Y,Z; [b] -X,-1/2+Y,1/2-Z;Cg1 is the centroid of C13, C14, C15, C16, C17 and C18. Cg2 is the centroid of C17, C18, C19, C20, C21 and C22.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
GNPS⊃3	C_7-H_7···Cg2 [a]	2.39(1)	154	3.25(3)

Symmetry codes: [a] X,Y,-1+Z; Cg2 is the centroid of C11, C12, C13, C13, C12 and C11;

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
GNPS⊃4	C_3-H_3···Cg1 [a]	2.90(1)	150	3.73(6)
	C_9-H_9···Cg4 [a]	2.80(1)	124	3.41(6)

Symmetry codes: [a] 1/2+X,1/2-Y,1-Z; Cg4 is the centroid of C9, C10, C11, C11, C12 and C13; Cg4 is the centroid of C1, C2, C3, C4, C5 and C6.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
GNPS⊃5	C_{16}-H_{16}···Cg4 [a]	2.81(0)	148	3.64(4)
	C_9-H_9A···Cg5 [b]	2.99(1)	122	3.59(2)
	C_{11}-$H_{11}B$···Cg5 [c]	2.71(1)	144	3.53(12)

Symmetry codes: [a] X,1+Y,Z; [b] 5/2-X,-1/2+Y,Z; [c] 3/2-X,-1/2+Y,Z;Cg4 is the centroid of C1, C2, C3, C4, C5 and C6; Cg5 is the centroid of C12, C13, C14, C14, C15 and C16.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
GNPS⊃6	C_{14}-H_{14}···Cg2 [a]	2.81(2)	149	3.64(3)
	C_8-H_8B···Cg1 [b]	2.97(2)	148	3.82(14)
	C_9-H_9B···Cg1 [c]	2.66(2)	171	3.62(9)

Symmetry codes: [a] 3/2-X,1/2+Y,Z; [b] X,Y,Z; [b] X,Y,Z; [c] 1-X,1-Y,1-Z; Cg1 is the centroid of C13, C14, C15, C16, C17 and C17. Cg2 is the centroid of C1, C2, C3, C4, C5 and C6.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
GNPS⊃7	C_{14}-H_{14}C···Cg1 [a]	3.23(1)	153	4.11(37)

Symmetry codes: [a] 1/2+X,1/2-Y,1-Z; Cg4 is the centroid of C1, C2, C3, C3, C4 and C5.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
GNPS⊃8	C_{10}-H_{10}C···Cg2 [b]	2.90(0)	131	3.60(3)

Symmetry codes: [a] 1/2-X,-Y,1/2+Z; Cg2 is the centroid of C15, C16, C17, C18, C19 and C20.

Table S3. Geometric parameters of the N–H···O, O–H···O, C–H···N and C–H···O hydrogen bonding interactions in the co-crystals

H-G	Interactions	D−H (Å)	D···A (Å)	H···A (Å)	D-H···A (deg)	Symmetry code
GNPS	N_1-H_1A···O_2W	0.860	2.14(5)	2.91(6)	148	1-x,1-y,2-z
	N_1-H_1B···O_1	0.860	2.09(4)	2.92(7)	164	1+x,y,z
	N_2-H_2A···O_2W	0.860	2.15(4)	2.91(6)	148	1-x,1-y,2-z
	N_2-H_2B···O_1	0.860	2.15(4)	3.01(7)	171	x, y, z
	N_3-H_3A···O_3	0.860	2.22(4)	3.05(7)	163	1+x,y,z
	N_3-H_3B···O_2	0.860	2.04(4)	2.88(7)	168	x, y, z
	O_1W-H_1WA···O_3	0.850	2.01(4)	2.84(5)	165	x, y, z
	O_1W-H_1WB···O_3	0.850	2.08(4)	2.91(6)	164	-x,1-y,1-z
	O_2W-H_2WA···O_1W	0.850	1.97(4)	2.80(6)	168	x, y, z
	O_2W-H_2WB···O_1W	0.850	2.12(5)	2.92(6)	156	-x,-y,1-z
GNPS⊃1	N_1-H_1A···O_7	0.860	2.07(3)	2.93(4)	175	-1/2+x,3/2-y,1-z
	N_1-H_1B···O_6	0.860	2.04(4)	2.88(4)	168	-x,1/2+y,3/2-z
	N_2-H_2A···O_5	0.860	2.15(3)	3.00(4)	168	-x,1/2+y,3/2-z
	N_2-H_2B···O_1	0.860	2.11(2)	2.96(4)	169	x, y, z
	N_3-H_3A···O_3	0.860	2.17(3)	2.99(4)	161	-1/2+x,3/2-y,1-z
	N_3-H_3B···O_2	0.860	2.02(3)	2.86(4)	166	x, y, z
	N_4-H_4A···O_1W	0.860	2.07(3)	2.90(5)	164	x, y, z
	N_4-H_4B···O_5	0.860	2.26(2)	3.09(4)	162	-1/2-x,1-y,-1/2+z

	N_5-$H_5A\cdots O_7$	0.860	2.05(3)	2.83(4)	150	x, y, z
	N_5-$H_5B\cdots O_4$	0.860	2.08(3)	2.94(4)	174	-x,-1/2+y,3/2-z
	N_6-$H_6A\cdots O_6$	0.860	2.05(3)	2.90(4)	169	-x,-1/2+y,3/2-z
	N_6-$H_6B\cdots O_4$	0.860	2.26(2)	3.10(4)	166	-1/2-x,1-y,-1/2+z
	O_1W-$H_1WA\cdots O_2$	0.850	2.04(3)	2.86(4)	160	x, y, z
	O_1W-$H_1WB\cdots O_1$	0.850	2.22(2)	3.06(4)	172	-1/2+x,3/2-y,1-z
	O_7-$H_7\cdots O_3$	0.820	1.94(3)	2.75(4)	171	x, y, z
GNPS⊃2	N_1-$H_1A\cdots O_1$	0.860	2.18(2)	2.99(3)	157	x, y, z
	N_1-$H_1B\cdots O_4$	0.860	2.11(2)	2.94(3)	161	1/2-x,1-y,1/2+z
	N_2-$H_2A\cdots O_6$	0.860	2.09(2)	2.93(3)	166	1-x,-1/2+y,1/2-z
	N_2-$H_2B\cdots O_5$	0.860	2.10(2)	2.94(4)	168	1/2-x,1-y,1/2+z
	N_3-$H_3A\cdots O_5$	0.860	2.07(2)	2.92(3)	173	1-x,-1/2+y,1/2-z
	N_3-$H_3B\cdots O_2$	0.860	2.05(2)	2.90(3)	169	x, y, z
	N_4-$H_4A\cdots O_2$	0.860	2.05(3)	2.89(4)	169	x, y, z
	N_4-$H_4B\cdots O_6$	0.860	2.13(2)	2.97(3)	166	3/2-x,1-y,1/2+z
	N_5-$H_5A\cdots O_3$	0.860	2.22(2)	2.99(3)	148	1/2+x,3/2-y,1-z
	N_5-$H_5B\cdots O_4$	0.860	2.08(2)	2.92(3)	166	3/2-x,1-y,1/2+z
	N_6-$H_6A\cdots O_3$	0.860	2.06(3)	2.91(5)	171	x, y, z
	N_6-$H_6B\cdots O_1$	0.860	2.45(2)	3.18(3)	142	1/2+x,3/2-y,1-z
	N_6-$H_6B\cdots O_3$	0.860	2.43(3)	3.14(4)	142	1/2+x,3/2-y,1-z
	C_{15}-$H_{15}\cdots O_8$	0.930	2.58(3)	3.24(4)	129	x, y, z
GNPS⊃3	N_1-$H_1A\cdots O_3$	0.860	2.02(8)	2.88(15)	175	x, y, z
	N_1-$H_1B\cdots O_2$	0.860	2.03(7)	2.89(15)	175	x,y,-1+z
	N_2-$H_2A\cdots O_1$	0.860	2.09(11)	2.93(15)	164	x, y, z
	N_2-$H_2B\cdots O_2$	0.860	2.17(8)	2.99(14)	158	1/2+x,-1/2-y,-1/2+z
	N_3-$H_3B\cdots O_1$	0.860	2.09(11)	2.93(14)	165	x,y,-1+z
GNPS⊃4	N_1-$H_1A\cdots O_1$	0.860	2.06(10)	2.92(17)	176	1/2-x,1/2+y,z
	N_1-$H_1B\cdots O_2$	0.860	2.04(10)	2.90(17)	178	1-x,1/2+y,3/2-z
	N_2-$H_2A\cdots O_3$	0.860	2.12(10)	2.97(16)	167	1/2-x,1/2+y,z
	N_2-$H_2B\cdots O_1$	0.860	2.01(10)	2.87(17)	172	x, y, z
	N_3-$H_3A\cdots O_3$	0.860	2.08(10)	2.95(16)	176	1-x,1/2+y,3/2-z
	N_3-$H_3B\cdots O_2$	0.860	2.19(10)	3.01(16)	159	x, y, z
GNPS⊃5	N_1-$H_1A\cdots O_3$	0.860	2.02(3)	2.85(5)	162	-1/2+x,y,1/2-z
	N_1-$H_1B\cdots O_1$	0.860	2.01(3)	2.86(4)	174	2-x,-1/2+y,1/2-z
	N_2-$H_2A\cdots O_3$	0.860	1.98(3)	2.84(4)	176	x, y, z
	N_2-$H_2B\cdots O_2$	0.860	2.10(3)	2.94(4)	164	2-x,-1/2+y,1/2-z
	N_3-$H_3A\cdots O_1$	0.860	2.18(3)	2.99(4)	158	-1/2+x,y,1/2-z
	N_3-$H_3B\cdots O_2$	0.860	2.08(3)	2.94(5)	172	x, y, z
GNPS⊃6	N_1-$H_1A\cdots O_1$	0.860	2.02(2)	2.85(2)	163	-1/2+x,y,3/2-z
	N_1-$H_1B\cdots O_3$	0.860	2.02(2)	2.87(3)	174	1-x,1/2+y,3/2-z
	N_2-$H_2A\cdots O_1$	0.860	1.97(2)	2.83(3)	177	x, y, z
	N_2-$H_2B\cdots O_2$	0.860	2.11(2)	2.94(2)	164	1-x,1/2+y,3/2-z
	N_3-$H_3A\cdots O_3$	0.860	2.18(2)	2.99(3)	157	-1/2+x,y,3/2-z

	N_3-$H_3B\cdots O_2$	0.860	2.08(2)	2.94(3)	172	x, y, z
GNPS⊃7	N_1-$H_1A\cdots O_3$	0.880	2.04(2)	2.90 (3)	176	x, y, z
	N_1-$H_1B\cdots O_1$	0.880	2.08(2)	2.94(2)	170	3/2-x,1/2+y,z
	N_2-$H_2A\cdots O_3$	0.880	2.07(2)	2.93(3)	172	3/2-x,1/2+y,z
	N_2-$H_2B\cdots O_2$	0.880	2.08(2)	2.94(3)	176	1-x,1/2+y,3/2-z
	N_3-$H_3A\cdots O_2$	0.880	2.16(2)	2.99(3)	165	x, y, z
	N_3-$H_3B\cdots O_1$	0.880	2.17(2)	3.02(3)	169	1-x,1/2+y,3/2-z
	C_5-$H_5\cdots O_2$	0.930	2.57(2)	3.44(4)	155	1-x,-1/2+y,3/2-z
GNPS⊃8	N_1-$H_1A\cdots O_3$	0.860	2.13(2)	2.96(3)	162	1-x,1/2+y,1/2-z
	N_1-$H_1B\cdots O_4$	0.860	2.11(2)	2.94(3)	164	x, y, z
	N_1-$H_1B\cdots O_7$	0.860	2.54(2)	2.97(3)	112	1/2+x,1/2-y,1-z
	N_2-$H_2A\cdots O_1$	0.860	2.17(2)	2.99(3)	160	1-x,1/2+y,1/2-z
	N_2-$H_2B\cdots O_3$	0.860	2.16(2)	2.99(3)	163	1/2-x,1-y,1/2+z
	N_3-$H_3A\cdots O_6$	0.860	2.20(2)	2.98(3)	150	x, y, z
	N_3-$H_3B\cdots O_2$	0.860	2.14(2)	2.96(3)	159	1/2-x,1-y,1/2+z
	N_4-$H_4A\cdots O_5$	0.860	2.14(2)	2.97(4)	162	-1/2+x,1/2-y,1-z
	N_4-$H_4B\cdots O_6$	0.860	2.12(2)	2.97(3)	171	x, y, z
	N_5-$H_5A\cdots O_2$	0.860	2.06(2)	2.92(3)	177	1-x,-1/2+y,1/2-z
	N_5-$H_5B\cdots O_5$	0.860	2.02(2)	2.88(3)	174	x, y, z
	N_6-$H_6A\cdots O_4$	0.860	2.19(2)	3.01(4)	159	-1/2+x,1/2-y,1-z
	N_6-$H_6B\cdots O_1$	0.860	2.09(2)	2.94(3)	170	1-x,-1/2+y,1/2-z
	C_4-$H_4A\cdots O_2$	0.970	2.56(2)	3.51(4)	168	1/2+x,1/2-y,1-z
	C_4-$H_4B\cdots O_5$	0.970	2.43(2)	3.38(4)	167	3/2-x,-y,1/2+z

5. Calculation of the Nucleus-independent chemical shift (NICS)

All calculations were carried out using the Gaussian 09 program.[1] All structures were fully optimized at B3LYP/6-31G(d)[2] theoretical level. Vibrational analyses at the same level of theory were performed to confirm each stationary point to a local minimum.[3] Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP-GIAO/6-31G(d) level.

Molecular Geometries and Energies

B3LYP/6-31G(d) Cartesian coordinates and energies in Hartree

biphenyldisulfonic acid

C	0.00000000	0.00000000	0.00000000

C	0.00000000	0.00000000	1.40729132
C	1.25081179	0.00000000	2.05183646
C	2.44193722	-0.00455432	1.32680587
C	2.42335968	-0.01222843	-0.07006705
C	1.19005261	-0.00623179	-0.72652768
H	-0.95004069	0.03850066	-0.52852720
H	1.28525945	-0.01802793	3.13899543
H	3.40254005	0.00757917	1.83306568
H	1.18018789	0.02280814	-1.81202031
C	-1.26965147	0.01036126	2.18140486
C	-2.40587569	-0.68887643	1.73415799
C	-1.38727260	0.72811037	3.38617470
C	-3.59843066	-0.67559878	2.45672719
H	-2.34244657	-1.26811335	0.81552444
C	-2.57843508	0.74111471	4.11079142
H	-0.53892712	1.31017552	3.73960184
C	-3.69523212	0.03614239	3.65493918
H	-4.47368512	-1.20854612	2.09742123
H	-2.66837644	1.32111273	5.02443672
S	-5.23290732	0.00078455	4.63376560
O	-5.06479413	-1.16402525	5.54657939
O	-5.25118057	1.31793566	5.32966020
S	3.97867696	-0.08452624	-1.01851713
O	4.96855351	0.60922153	-0.14771736
O	4.24004792	-1.54051984	-1.19183992
O	-6.30744876	-0.17632003	3.61718878
O	3.66406974	0.62962990	-2.28756935
Bq	1.21769355	-0.00383576	0.66488982
Bq	1.21625068	-1.00383080	0.66768988

B3LYP/6-31G(d) Total Energy: -1709.792815

1,5-naphthalenedisulfonic acid

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38070492
C	1.25040942	0.00000000	2.08857471
C	2.49291000	0.00000000	1.33111206
C	2.42349579	0.00000000	-0.08986063
C	1.20516009	0.00000000	-0.72988507
H	0.38621705	0.00000000	4.05836823
H	-0.95194893	-0.00000000	-0.52195941
C	1.31982363	0.00000000	3.50954741
C	3.74331942	0.00000000	2.03898185
H	3.35710237	0.00000000	-0.63868145
H	1.16893873	0.00000000	-1.81915966
C	3.74331942	0.00000000	3.41968677
C	2.53815933	-0.00000000	4.14957185
H	4.69526835	0.00000000	3.94164618
H	2.57438069	0.00000000	5.23884643
S	5.45025032	0.00000000	1.31785373
O	6.05313264	1.24769700	1.86543055
O	6.05313032	-1.24770000	1.86542570
S	-1.70693090	0.00000000	2.10183305
O	-2.30981197	1.24769900	1.55426014
O	-2.30981209	-1.24769800	1.55425815
O	-1.59457010	0.00000000	3.58934288
O	5.33788952	-0.00000000	-0.16965610
Bq	1.22866256	0.00000000	0.66344100
Bq	1.22866256	-1.00000000	0.66344100

B3LYP/6-31G(d) Total Energy: -1632.347428

6. Guest volume calculations

The volume of guests were performed at 6-311++G(d,p) level using the Gaussian 09 program. The length and width of the guests and host are measured by diamond.

Cartesian coordinates (Å) for the optimized geometries of **1**

C	-2.02270000	-0.53480000	-1.11620000
C	-1.48970000	-1.66540000	-0.21880000
C	0.04430000	-1.73710000	-0.27130000
C	0.67220000	-0.39270000	0.13330000
C	0.14330000	0.72740000	-0.76550000
C	-1.38230000	0.80610000	-0.71750000
O	0.67970000	1.96130000	-0.34860000
C	-3.55630000	-0.45460000	-1.04940000
C	2.19110000	-0.44140000	0.15790000
C	2.87700000	-0.08560000	1.25700000
C	2.91780000	-0.88000000	-1.09180000
H	-1.73460000	-0.76050000	-2.17410000
H	-1.81820000	-1.49380000	0.83330000
H	-1.92160000	-2.64260000	-0.54150000
H	0.40810000	-2.54580000	0.40660000
H	0.34880000	-2.00830000	-1.30920000
H	0.31490000	-0.17080000	1.17000000
H	0.46920000	0.57390000	-1.81950000
H	-1.70960000	1.08070000	0.31290000
H	-1.73640000	1.61410000	-1.40080000
H	0.43320000	2.64260000	-0.97820000
H	-4.02330000	-1.41570000	-1.36430000

H	-3.90390000	-0.22970000	-0.01570000
H	-3.94680000	0.34340000	-1.72140000
H	3.97640000	-0.11070000	1.28230000
H	2.36860000	0.24680000	2.17410000
H	2.68430000	-1.94060000	-1.33280000
H	2.63570000	-0.24550000	-1.96050000
H	4.02330000	-0.81030000	-0.98570000

Cartesian coordinates (Å) for the optimized geometries of **2**

C	-0.85260000	-0.62000000	-0.57720000
C	0.57590000	-0.65240000	-0.01490000
C	1.33250000	0.65930000	-0.31140000
C	0.50620000	1.84410000	0.23480000
C	-0.90550000	1.89290000	-0.36330000
C	-1.66160000	0.58660000	-0.07280000
C	1.75390000	0.80980000	-1.79900000
O	0.49350000	-0.86800000	1.36670000
C	2.38890000	2.18070000	-2.10590000
C	2.75160000	-0.28250000	-2.23660000
C	1.42110000	-1.56400000	2.08790000
C	2.57980000	-2.17390000	1.31470000
O	1.32870000	-1.70140000	3.29030000
C	-3.06560000	0.61190000	-0.69820000
H	-0.82020000	-0.59820000	-1.69100000
H	-1.38340000	-1.56350000	-0.30430000
H	1.06800000	-1.52720000	-0.48870000
H	2.28950000	0.65380000	0.26860000
H	1.02840000	2.81400000	0.07730000
H	0.41440000	1.75820000	1.34380000
H	-0.84640000	2.06300000	-1.46280000

H	-1.46590000	2.75670000	0.06740000
H	-1.78320000	0.49100000	1.03570000
H	0.85080000	0.71760000	-2.45010000
H	2.77660000	2.22650000	-3.14890000
H	1.65590000	3.01360000	-2.02550000
H	3.24140000	2.39080000	-1.42090000
H	3.08010000	-0.13330000	-3.29030000
H	2.31530000	-1.30400000	-2.20200000
H	3.66350000	-0.27380000	-1.59770000
H	2.23430000	-3.01360000	0.67090000
H	3.13310000	-1.42110000	0.71310000
H	3.32290000	-2.60770000	2.02180000
H	-3.66350000	1.46770000	-0.30960000
H	-3.01240000	0.70950000	-1.80620000
H	-3.62640000	-0.32190000	-0.46500000

Cartesian coordinates (Å) for the optimized geometries of **3**

C	-1.90210000	-0.35830000	0.00080000
C	-0.55340000	-0.28440000	0.00050000
C	0.16800000	0.85310000	0.00040000
C	-0.53460000	1.99740000	0.00060000
C	-1.87350000	1.96310000	0.00080000
C	-2.57490000	0.81610000	0.00100000
O	-3.93080000	0.91440000	0.00100000
O	-2.42680000	-1.63310000	0.00080000
C	1.51610000	0.78950000	0.00020000
C	2.38690000	1.81360000	0.00000000
C	3.88400000	1.63310000	-0.00030000
C	-3.80940000	-1.88380000	0.00040000
H	-0.01790000	-1.25160000	0.00040000

H	-0.05550000	2.98840000	0.00050000
H	-2.42480000	2.92000000	0.00080000
H	-4.32560000	0.03370000	-0.00140000
H	1.98390000	-0.21140000	0.00010000
H	2.05360000	2.86310000	0.00010000
H	4.19160000	0.56380000	-0.00030000
H	4.32530000	2.11310000	-0.90340000
H	4.32560000	2.11310000	0.90270000
H	-3.94970000	-2.98840000	0.00070000
H	-4.27510000	-1.48980000	0.93100000
H	-4.27430000	-1.49060000	-0.93100000

Cartesian coordinates (Å) for the optimized geometries of **4**

C	-1.01780000	1.05360000	0.00020000
C	-1.04110000	-0.29120000	0.00020000
C	0.12920000	-0.96450000	0.00030000
C	1.30900000	-0.30900000	0.00030000
C	1.29570000	1.03660000	0.00030000
C	0.14400000	1.72020000	0.00030000
C	-2.37690000	-1.00640000	0.00010000
C	2.66430000	-0.98710000	0.00030000
N	0.08960000	-2.23310000	0.00030000
H	-1.95820000	1.62900000	0.00010000
H	2.24680000	1.59530000	0.00030000
H	0.15220000	2.82310000	0.00030000
H	-3.24230000	-0.30690000	0.00020000
H	-2.48070000	-1.64390000	-0.90730000
H	-2.48080000	-1.64420000	0.90730000
H	2.64160000	-2.09590000	0.00070000
H	3.24200000	-0.68150000	-0.90200000

H	3.24230000	-0.68110000	0.90240000
H	0.95390000	-2.82310000	0.00030000
H	-0.82460000	-2.74570000	0.00020000

Cartesian coordinates (Å) for the optimized geometries of **5**

C	-1.05790000	-1.86570000	0.00040000
C	0.27970000	-1.79050000	0.00060000
C	0.90070000	-0.59990000	0.00500000
C	0.09350000	0.47470000	0.00920000
C	-1.25670000	0.43320000	0.00960000
C	-1.86220000	-0.78280000	0.00410000
O	-3.23290000	-0.88490000	0.00450000
C	2.24940000	-0.55670000	0.00520000
C	3.04010000	0.53040000	0.00950000
C	4.54650000	0.46310000	0.00960000
O	-1.87820000	1.66600000	0.01370000
C	-3.27870000	1.79610000	0.00170000
C	-3.84940000	-2.15140000	0.00730000
H	-1.47670000	-2.88450000	-0.00330000
H	0.85440000	-2.73340000	-0.00280000
H	0.53320000	1.48510000	0.01280000
H	2.79140000	-1.51950000	0.00150000
H	2.62920000	1.55200000	0.01330000
H	4.93380000	-0.58000000	0.00760000
H	4.95080000	0.97670000	-0.89240000
H	4.95040000	0.97310000	0.91380000
H	-3.51290000	2.88450000	0.00120000
H	-3.70420000	1.36550000	-0.93120000
H	-3.72020000	1.36360000	0.92620000
H	-4.95080000	-1.98970000	0.01040000

H	-3.58880000	-2.71340000	-0.91710000
H	-3.58330000	-2.71180000	0.93120000

Cartesian coordinates (Å) for the optimized geometries of **6**

C	-0.83440000	1.07790000	0.31240000
C	-0.84360000	-0.24390000	0.06140000
C	0.34770000	-0.87910000	-0.03500000
C	1.52140000	-0.22940000	0.13430000
C	1.47650000	1.09050000	0.39660000
C	0.31290000	1.74570000	0.48270000
C	-2.17490000	-0.97310000	-0.12500000
C	2.89830000	-0.88800000	0.04270000
N	0.35490000	-2.12110000	-0.29470000
C	3.14040000	-1.93330000	1.14510000
C	3.22190000	-1.40790000	-1.36850000
C	-3.38680000	-0.33350000	0.57950000
C	-2.47130000	-1.13390000	-1.62600000
H	-1.76810000	1.65560000	0.38190000
H	2.40310000	1.67070000	0.54070000
H	0.30010000	2.82930000	0.68930000
H	-2.09470000	-1.98620000	0.34310000
H	3.67490000	-0.10090000	0.23290000
H	1.24370000	-2.66400000	-0.38180000
H	-0.52490000	-2.66780000	-0.44590000
H	4.19250000	-2.29980000	1.12160000
H	2.96380000	-1.49270000	2.15340000
H	2.49050000	-2.82930000	1.05600000
H	4.27500000	-1.76740000	-1.42820000
H	3.10300000	-0.59800000	-2.12490000
H	2.57860000	-2.25550000	-1.68620000

H	-4.27500000	-1.00500000	0.52780000
H	-3.17910000	-0.15060000	1.65890000
H	-3.69860000	0.62490000	0.10790000
H	-3.41590000	-1.70030000	-1.79270000
H	-1.66000000	-1.68470000	-2.15340000
H	-2.57860000	-0.14030000	-2.11810000

Cartesian coordinates (Å) for the optimized geometries of **7**

C	-1.89200000	-0.60350000	1.56210000
C	-1.93140000	-1.93120000	1.40540000
C	-1.08000000	-2.50480000	0.54570000
C	-0.18060000	-1.80380000	-0.17260000
C	-0.14410000	-0.45740000	-0.01080000
C	-1.00540000	0.11430000	0.85770000
C	0.72040000	0.37210000	-0.67870000
O	0.70020000	1.73210000	-0.46310000
O	1.52360000	-0.06730000	-1.47490000
C	1.60500000	2.54780000	-1.17000000
O	0.62120000	-2.52600000	-1.00910000
H	-2.58400000	-0.10950000	2.26480000
H	-2.65270000	-2.54080000	1.97450000
H	-1.12210000	-3.60140000	0.42470000
H	-1.02560000	1.20300000	1.03400000
H	1.42970000	3.60140000	-0.85700000
H	2.65270000	2.27250000	-0.91430000
H	1.42060000	2.46860000	-2.26480000
H	1.25530000	-2.00810000	-1.51810000

Cartesian coordinates (Å) for the optimized geometries of **8**

C	-1.32830000	-0.22090000	-0.74000000

C	-0.48070000	-1.46330000	-1.03130000
C	0.98880000	-1.14730000	-1.02820000
C	1.52510000	0.07000000	-1.22020000
C	0.73100000	1.14790000	-1.46340000
C	-0.77940000	0.96860000	-1.53520000
C	-1.46000000	0.06660000	0.74920000
C	-2.65550000	-0.00140000	1.35990000
C	-0.22650000	0.42650000	1.54330000
O	1.18810000	2.25710000	-1.64140000
C	3.02620000	0.25700000	-1.17280000
H	-2.35880000	-0.43160000	-1.12540000
H	-0.71060000	-2.25710000	-0.28250000
H	-0.71990000	-1.87590000	-2.04050000
H	1.65930000	-2.00740000	-0.85970000
H	-1.29400000	1.90240000	-1.20730000
H	-1.01470000	0.83150000	-2.61860000
H	-2.76510000	0.20200000	2.43540000
H	-3.57360000	-0.26310000	0.81360000
H	0.23510000	1.36090000	1.15520000
H	-0.44960000	0.60490000	2.61860000
H	0.52260000	-0.39470000	1.50570000
H	3.57360000	-0.68980000	-0.96780000
H	3.40330000	0.64770000	-2.14530000
H	3.30370000	0.97350000	-0.36630000

Cartesian coordinates (Å) for the optimized geometries of **α-caryophyllene**

C	-2.77560000	1.05720000	-0.57110000
C	-2.31010000	-0.30090000	-1.03370000
C	-2.07350000	-1.25830000	0.14310000
C	-0.52650000	1.89120000	0.27000000

C	-2.01220000	2.01680000	-0.01330000
C	0.92470000	-1.25110000	1.02230000
C	1.90720000	-0.31830000	0.27750000
C	1.26760000	0.44030000	-0.87690000
C	0.28370000	1.35720000	-0.87990000
C	-1.05230000	-2.31400000	-0.22370000
C	0.24060000	-2.27980000	0.15140000
C	3.07820000	-1.16500000	-0.28190000
C	2.52640000	0.69030000	1.27110000
C	-2.63980000	3.30450000	0.47320000
C	-1.57120000	-3.41400000	-1.12200000
H	-3.85900000	1.24060000	-0.67250000
H	-1.38400000	-0.19050000	-1.63600000
H	-3.05310000	-0.73370000	-1.74390000
H	-1.75180000	-0.68470000	1.03620000
H	-3.02920000	-1.74010000	0.45330000
H	-0.40300000	1.32780000	1.21590000
H	-0.11290000	2.91010000	0.46120000
H	1.47870000	-1.81240000	1.81170000
H	0.19520000	-0.65070000	1.59800000
H	1.70800000	0.22570000	-1.86800000
H	0.03270000	1.81530000	-1.85550000
H	0.89560000	-3.09260000	-0.20610000
H	2.74290000	-1.88820000	-1.05850000
H	3.85900000	-0.52420000	-0.75180000
H	3.57950000	-1.75150000	0.52100000
H	3.07880000	0.16790000	2.08480000
H	3.24650000	1.37020000	0.76140000
H	1.76610000	1.33180000	1.76530000
H	-3.73620000	3.35250000	0.29060000

H	-2.47880000	3.41700000	1.56950000
H	-2.18040000	4.17650000	-0.04510000
H	-0.79880000	-4.17650000	-1.36640000
H	-2.41680000	-3.94500000	-0.62930000
H	-1.93470000	-2.98990000	-2.08480000

Cartesian coordinates (Å) for the optimized geometries of **β-caryophyllene**

C	-0.77580000	0.56340000	0.11850000
C	-0.71580000	-0.57250000	1.14320000
C	0.65020000	-1.27350000	1.24000000
C	1.29780000	-1.46980000	-0.10940000
C	1.30400000	2.11350000	-0.02890000
C	-0.10660000	1.91810000	0.47260000
C	2.34580000	-0.75790000	-0.56280000
C	3.13880000	0.32480000	0.13270000
C	2.39100000	1.48290000	0.81170000
C	1.62820000	2.81310000	-1.12760000
C	0.65990000	-2.54110000	-0.96770000
C	-1.29560000	2.61410000	-0.24530000
C	-2.12810000	1.32680000	-0.00950000
C	-2.96460000	0.88960000	-1.21780000
C	-2.98670000	1.40550000	1.26000000
H	-0.44710000	0.23250000	-0.89410000
H	-1.48120000	-1.32420000	0.83250000
H	-1.01120000	-0.21850000	2.15730000
H	0.53220000	-2.26760000	1.73180000
H	1.32360000	-0.71730000	1.92270000
H	-0.16150000	2.13540000	1.56470000
H	2.72000000	-1.01620000	-1.56990000
H	3.82280000	-0.16740000	0.86400000

H	3.80560000	0.77870000	-0.64170000
H	1.99110000	1.19780000	1.80710000
H	3.13090000	2.28240000	1.05960000
H	0.88580000	3.30600000	-1.76720000
H	2.68010000	2.92500000	-1.43050000
H	1.15990000	-2.66490000	-1.95360000
H	0.70510000	-3.52490000	-0.44840000
H	-0.40780000	-2.30190000	-1.17010000
H	-1.67760000	3.52490000	0.26360000
H	-1.14800000	2.78330000	-1.33340000
H	-3.38590000	-0.12720000	-1.04910000
H	-3.81000000	1.59450000	-1.38560000
H	-2.36940000	0.85300000	-2.15730000
H	-3.82280000	2.12680000	1.11670000
H	-3.43600000	0.41510000	1.49760000
H	-2.41390000	1.74570000	2.15030000

Cartesian coordinates (Å) for the optimized geometries of **citronellal**

O	-2.83470000	-2.80240000	-1.03640000
C	-1.88960000	-2.60140000	-1.76420000
C	-0.53570000	-3.24790000	-1.53200000
C	0.62480000	-2.23250000	-1.50970000
C	0.44490000	-1.21990000	-0.35990000
C	1.48960000	-0.09330000	-0.34650000
C	1.16390000	0.92700000	0.71750000
C	0.38020000	2.01080000	0.57250000
C	0.13240000	2.95560000	1.72590000
C	1.96530000	-2.98210000	-1.41400000
C	-0.32530000	2.39040000	-0.70750000
H	-1.98450000	-1.93350000	-2.65310000

H	-0.55090000	-3.82260000	-0.57690000
H	-0.38580000	-3.98330000	-2.35750000
H	0.61260000	-1.67260000	-2.47890000
H	-0.56390000	-0.75060000	-0.44760000
H	0.46680000	-1.75840000	0.61690000
H	2.50880000	-0.49430000	-0.14060000
H	1.54920000	0.38750000	-1.34830000
H	1.59970000	0.72540000	1.71130000
H	0.67210000	2.66060000	2.65310000
H	0.46640000	3.98330000	1.45700000
H	-0.95400000	2.99040000	1.96740000
H	2.83470000	-2.29640000	-1.52260000
H	2.06070000	-3.74280000	-2.22200000
H	2.06150000	-3.50970000	-0.43800000
H	-0.21770000	1.64750000	-1.52510000
H	-1.41750000	2.49930000	-0.51970000
H	0.06350000	3.36450000	-1.08130000

Cartesian coordinates (Å) for the optimized geometries of **citronellol**

O	-4.12940000	-2.15280000	1.79670000
C	-2.90700000	-1.45880000	1.64090000
C	-3.18240000	0.03650000	1.52690000
C	-1.92340000	0.93020000	1.52230000
C	-0.95630000	0.62730000	0.35640000
C	0.18440000	-0.33770000	0.72760000
C	1.10240000	-0.61700000	-0.43780000
C	2.33780000	-1.14310000	-0.35760000
C	3.17420000	-1.37350000	-1.59490000
C	-2.36280000	2.40780000	1.47810000
C	3.00140000	-1.55220000	0.93540000

H	-3.95370000	-3.09530000	1.85390000
H	-2.27950000	-1.69180000	2.52980000
H	-2.42460000	-1.86250000	0.72370000
H	-3.77710000	0.22710000	0.60210000
H	-3.82600000	0.33470000	2.38990000
H	-1.38180000	0.78110000	2.48970000
H	-1.53510000	0.24400000	-0.51560000
H	-0.47400000	1.57550000	0.01680000
H	0.76790000	0.10770000	1.56660000
H	-0.22660000	-1.31270000	1.07280000
H	0.70080000	-0.38120000	-1.43740000
H	2.66410000	-1.05160000	-2.52980000
H	4.12940000	-0.80570000	-1.52190000
H	3.41510000	-2.45560000	-1.69990000
H	-1.49010000	3.09530000	1.56240000
H	-3.04990000	2.65540000	2.31910000
H	-2.89170000	2.64050000	0.52590000
H	2.34390000	-1.46790000	1.82630000
H	3.32490000	-2.61600000	0.87640000
H	3.90190000	-0.92270000	1.11650000

7. Interaction Energies and the energy decomposition analysis (kJ/mol) based on Natural bond orbital (NBO) calculation.

Geometry optimizations of all hydrogen atoms were conducted by DFT using the Gaussian 16 package under the B3LYP-D3/6-311G (d, p) level. All of the heavy atoms were at original X-ray coordinates. Natural bond orbital (NBO) analysis was performed Gaussian NBO Version 3.1. The intermolecular interaction energy and the energy decomposition analysis (EDA) based on SAPT were determined by using the PSI4 1.4 program, and the level of calculation was SAPT0/jun-cc-pVDZ. Five complexes without disorders were included in the calculation. The data of NBO analysis was provided in Table S4

Table S4. Interaction Energies and the energy decomposition analysis (kJ/mol) based on Natural bond orbital (NBO) calculation.

Complex	Electrostatics	Exchange	Induction	Dispersion	Total
GNPS⊃**1**	-55.7683127	68.8908449	-46.16308693	-104.5949559	-124.51298
GNPS⊃**2**	-36.04022071	96.58079187	-15.50921039	-145.9649216	-100.93356
GNPS⊃**4**	-41.53464097	58.93670727	-53.43258083	-87.17874305	-123.20926
GNPS⊃**7**	-22.57516253	58.30971621	-16.69081085	-84.63145939	-65.587717
GNPS⊃**8**	-19.8257027	60.91535765	-12.68499158	-91.12308916	-62.718426

The results of the energy decomposition analysis (kJ/mol) based on Natural bond orbital (NBO) calculation showed that the main interaction between host and guest molecules is the dispersion as attraction effect, similar to C–H···π interactions, suggesting again the important role of C–H···π interactions. Related figures were shown in Fig 9a-9e.

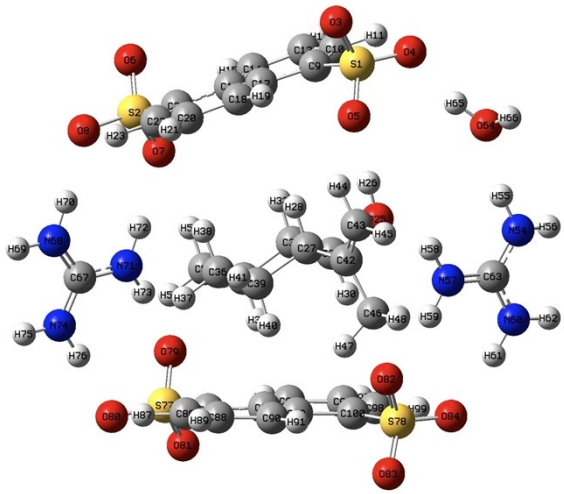

Fig 9a. Extracted structure of the host and guest from GNPS⊃**1**

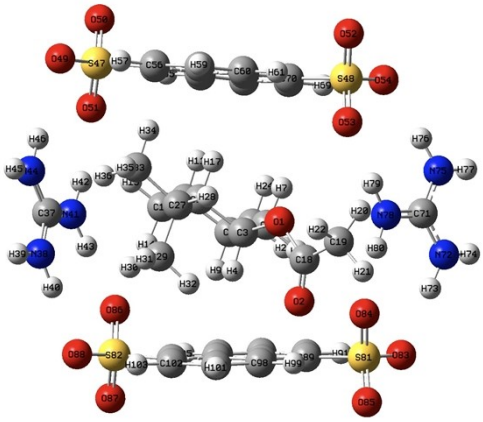

Fig 9b. Extracted structure of the host and guest from GNPS⊃**2**

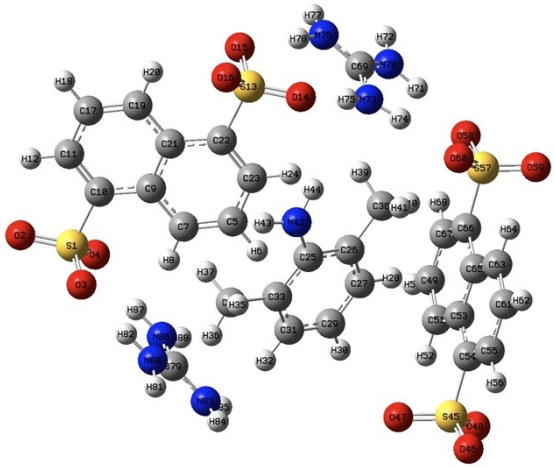

Fig 9c. Extracted structure of the host and guest from GNPS⊃**4**

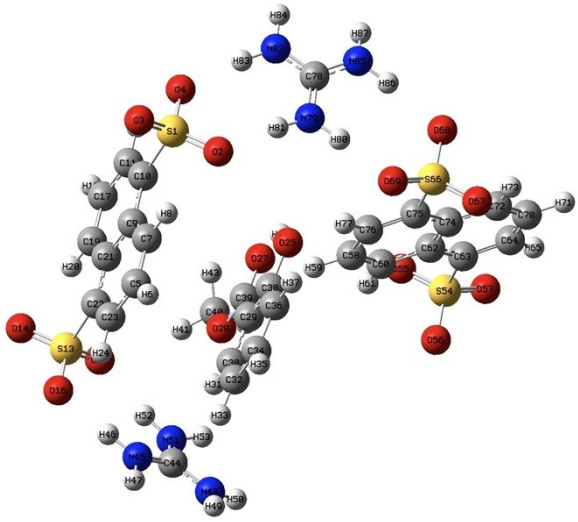

Fig 9d. Extracted structure of the host and guest from GNPS⊃**7**

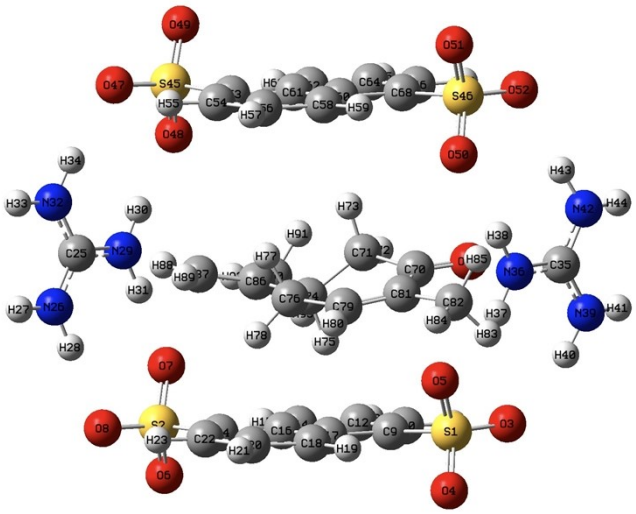

Fig 9e. Extracted structure of the host and guest from GNPS⊃**8**

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C.

Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian Inc. Wallingford CT*, 2009.

2. (a) A. D. J. Becke. *Chem. Phys.* 1993, **98**, 5648-5652. (b) C. Lee, W. Yang, R. G. Parr. *Phys. Rev. B.* 1988, **37**, 785-789. (c) W. J. Hehre, R. Ditchfield, J. A. J. Pople. *Chem. Phys.* 1972, **56**, 2257.

3. R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. J. Truhlar. *Phys. Chem. B*, 2011, **115**, 14556–14562.