Supporting Information

Inclusion of Amine Isomers with Open-Chain Hosts Having a Partial Structure of *p-tert*-Butylthiacalixarene

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Powder X-ray diffraction (PXRD) analysis of inclusion crystals

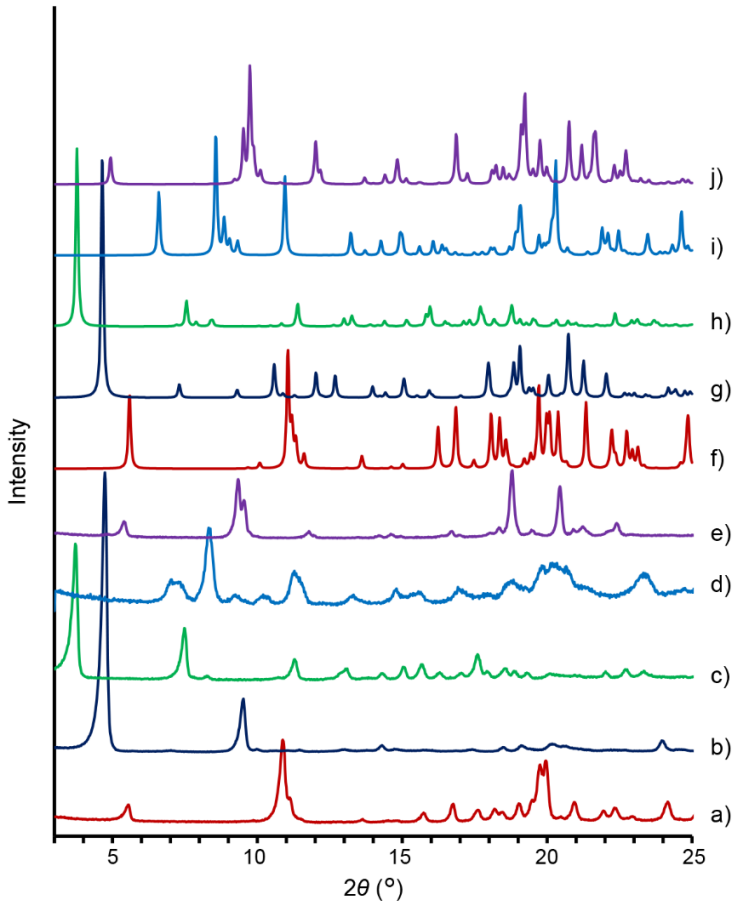

Figure S1. Comparison of the PXRD patterns of inclusion crystals prepared by inclusion experiments using single guest amines with those simulated from single-crystal XRD data for the corresponding single crystals: PXRD patterns measured for the inclusion crystals of diacid **2** with (a) 3-methylpyridine, (b) 4-methylpyridine, (c) 2-methylquinoline, and (d) 6-methylquinoline and the inclusion crystal of monoester **3** with (e) *trans*-4-methylcyclohexanamine. PXRD patterns simulated from the single-crystal XRD data of (f) **2**·3-methylpyridine, (g) **2**·4-methylpyridine·toluene$_{0.5}$, (h) **2**·2-methylquinoline·toluene$_{0.5}$, (i) **2**·6-methylquinoline·toluene, and (j) **3**·*trans*-4-methylcyclohexanamine.

Crystal structure of 2·6-methylquinoline·acetonitrile

Single crystal **2**·6-methylquinoline·acetonitrile was prepared by leaving a solution containing diacid **2** (3.0 mg, 6.72 μmol) and 6-methylquinoline (1.6 mg, 16.8 μmol) in acetonitrile (1 mL) at room temperature. The crystal belongs to the triclinic system with the $P\bar{1}$ space group (Z = 2). Diacid **2** forms a 1:1 salt with 6-methylquinoline (Figure S2a). Two 1:1 salts related by an inversion center are gathered to form a 2:2 self-inclusion complex so as to include each other's phenol units in their concaves (Figure S2b); a couple of complementary CH–π interactions are observed between a *tert*-butyl group of one host and a benzene ring of the other and vice versa. Two adjacent self-inclusion complexes are connected through a couple of complementary hydrogen bonds between carboxy and carboxylato groups, thereby forming an infinite columnar structure along the *b*-axis (Figure S2c). The columnar structures are arranged along the *c*-axis to form a layer parallel to the *b*–*c* plane; between adjacent columnar structures, a π–π interaction and two hydrogen bonds are observed between each amine molecule in one column and a neighboring host molecule in the other column and vice versa. The layer piles up along the *a*-axis in such a way that amine molecules in the upper and lower layers are stacked alternately along the *b*-axis (Figure S2d); between adjacent layers, each amine molecule is connected to a neighboring host molecule through a CH–π interaction and a hydrogen bond. Between adjacent layers, there are disconnected spatial voids, each of which is filled with two acetonitrile molecules, thereby realizing tight packing; the crystal density is 1.248 g/cm^3.

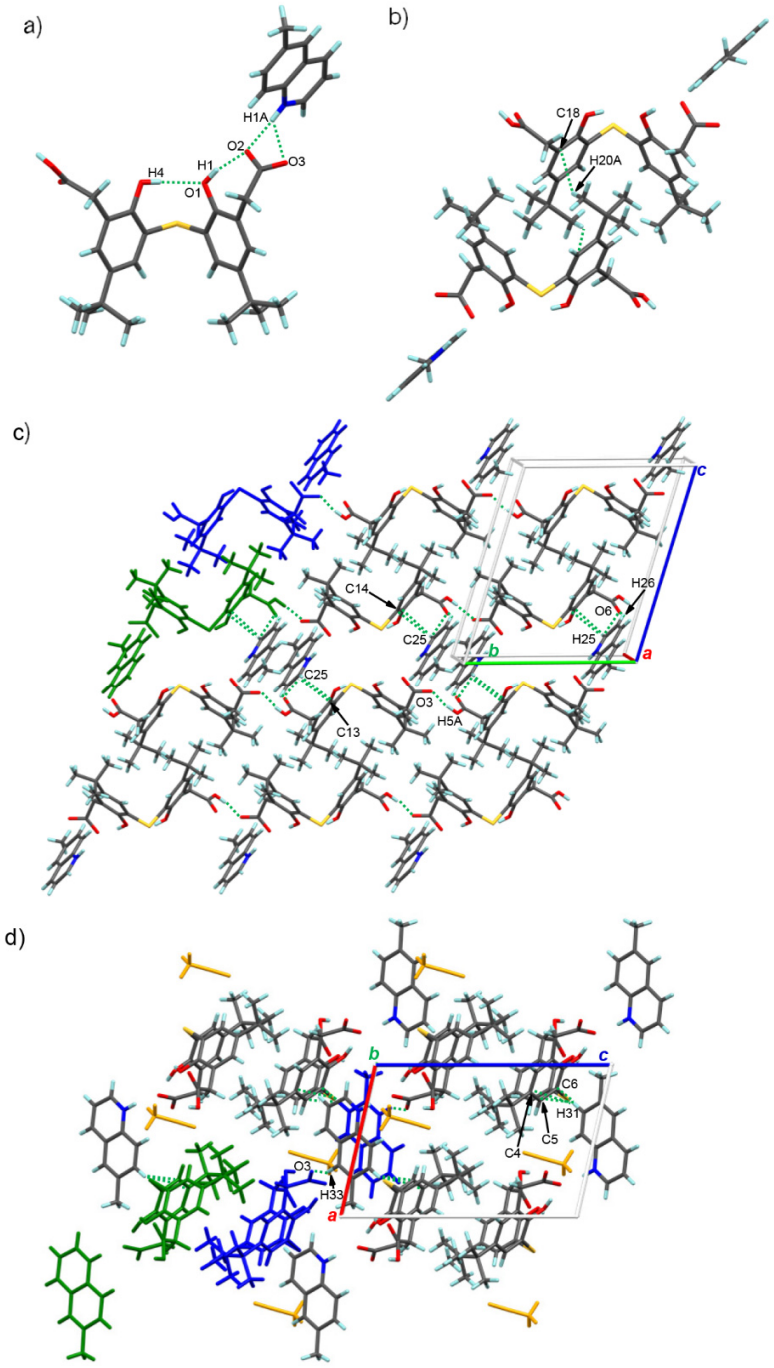

Figure S2. X-ray structure of **2**·6-methylquinoline·acetonitrile: (a) a 1:1 salt between **2** and 6-methylquinoline, (b) a 2:2 self-inclusion complex, (c) a parallel cross-section to the *b*–*c* plane, and (d) a parallel cross-section to the *a*–*c* plane. In (c) and (d), a pair of 1:1 salts are color-corded. In (d), solvent molecules are colored orange and interactions from solvent molecules are omitted for clarity. Selected distances: a) O1···H4 (2.088 Å), O2···H1 (1.767 Å), O2···H1A (1.860 Å), O3···H1A (2.553 Å), b) C18···H20A (2.886 Å), c) O3···H5A (1.734 Å), C13···C25 (3.134 Å), C14···C25 (3.246 Å), O6···H25 (2.487 Å), O6···H26 (2.628 Å). d) C4···H31 (2.876 Å), C5···H31 (2.734 Å), C6···H31 (2.771 Å), O3···H33(2.598 Å).

Crystal structure of 2·(*trans*-4-methylcyclohexanamine)$_3$

Single crystal **2**·(*trans*-4-methylcyclohexaneamine)$_3$ was prepared by leaving a solution containing monoester **3** (2.0 mg, 4.48 μmol) and *trans*-4-cyclohexanamine (30.4 mg, 0.269 mmol) in benzene (2 mL) at 30 °C. The crystal belongs to the triclinic system with the $P\bar{1}$ space group (Z = 2). In the crystal, diacid **2** with a syn conformation forms a 1:3 salt with three amine molecules using the two carboxy groups and a hydroxy group (Figure S3a). One of the amine molecules connected with a carboxyl group (amine A) is embedded in the concave of the host molecule, while the other two amine molecules connected with another carboxy group (amine B) and a hydroxy group (amine C) are placed outside the cavity; the inclusion of amine A is stabilized by a hydrogen bond between its ammonio group and another hydroxy group and a CH–π interaction between its methylene hydrogen at the 2-position [6-position] and a benzene ring. Two 1:3 salts related by an inversion center are connected through two couples of complementary hydrogen bonds between the ammonio groups of amines A and B in one 1:3 salt and the two carboxylato groups in the other 1:3 salt and vice versa, thereby forming a 2:6 inclusion complex (Figure S3b); a couple of complementary hydrogen bonds are also observed between methylene hydrogens at the 6-position [2-position] of amine A and carboxylato groups. Two adjacent 2:6 inclusion complexes are connected through a couple of complementary hydrogen bonds between the ammonio groups of amine B and the carboxylato groups paired with amine A, thereby forming an infinite columnar structure along the *b*-axis (Figures S3c and S4). The columnar structures are arranged along the *a*-axis to form a layer parallel to the *a*–*b* plane. Each molecule of amine C tightly connects two adjacent columns through hydrogen bonds between its ammonio group and two carboxylato groups paired with amine A and amine B in different 2:6 complexes and CH–π interactions between its hydrogen atoms at the 2- and 4-positions and a benzene ring; between adjacent columns, CH–S interactions are also observed between hydrogen atoms of amine A at the 5-position [3-position] and a sulfur atom. The layer piles up along the *c*-axis (Figure S3d). There are no spatial voids in the crystal.

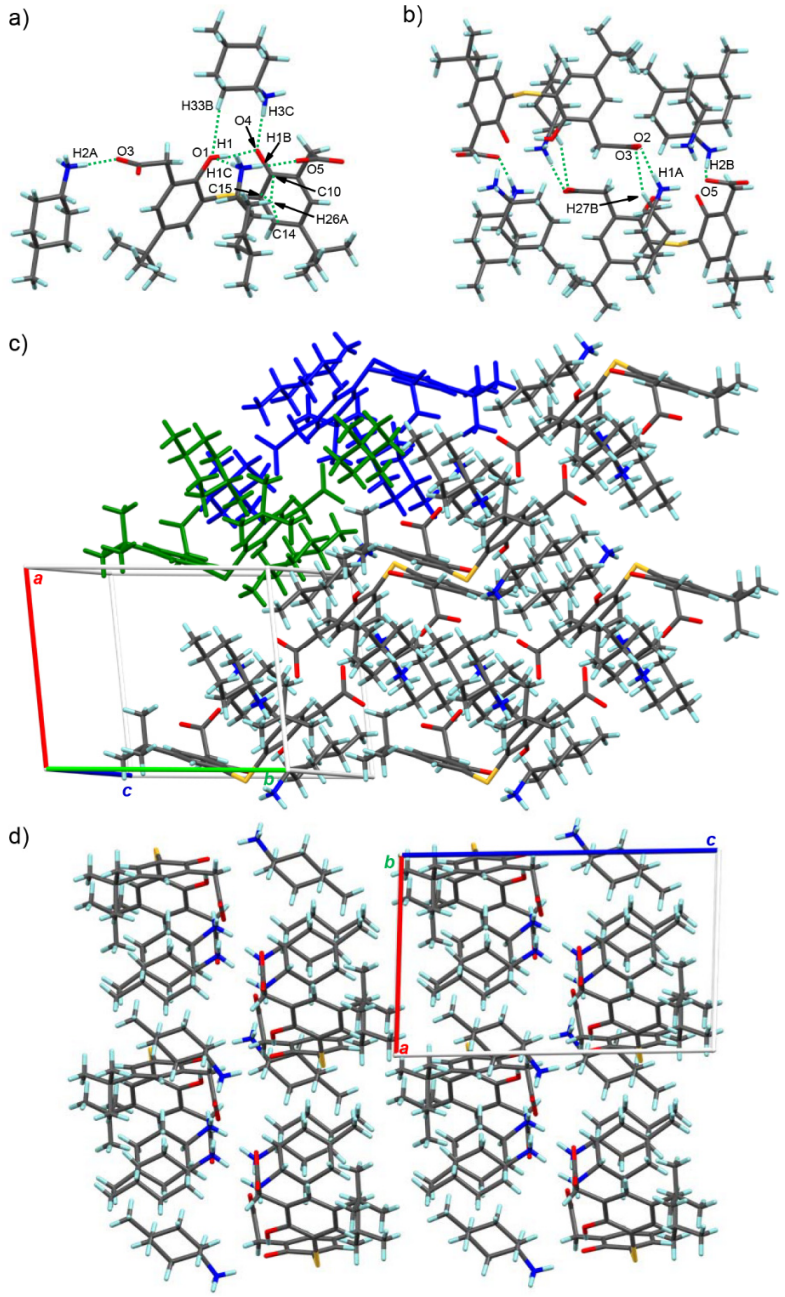

Figure S3. X-ray structure of **2**·(*trans*-4-methylcyclohexanamine)$_3$: (a) a 1:3 salt between **2** and *trans*-4-methylcyclohexanamine, (b) a 2:6 inclusion complex, (c) a parallel cross-section to the *a*–*b* plane. and (d) a parallel cross-section to the *a*–*c* plane. In (c) and (d), a pair of 1:3 salts are color-corded. Selected distances: a) O4···H1 (1.595 Å), O5···H1B (1.838 Å), O3···H2A (1.819 Å), O4···H3C (1.821 Å), O1···H33B (2.535 Å), O1···H1C (2.040 Å), C10···H26A (2.690 Å), C14···H26A (2.832 Å), C15···H26A (2.560 Å), b) O2···H1A (1.836 Å), O5···H2B (1.927 Å), O3···H27B (2.692 Å).

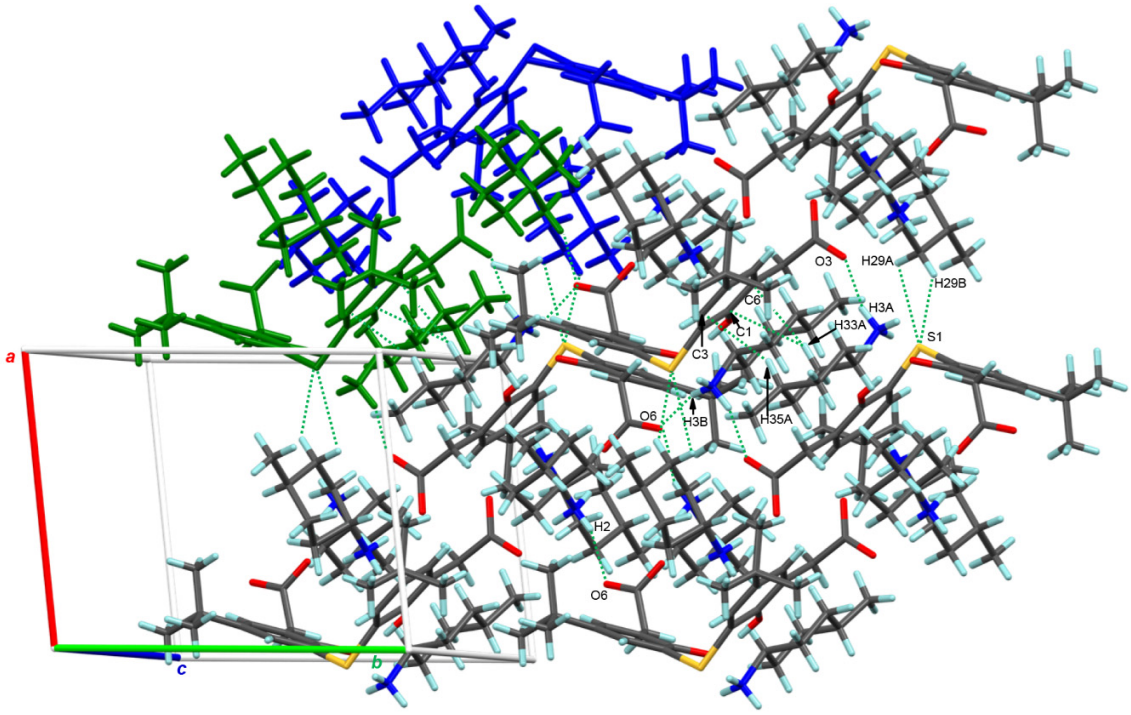

Figure S4. Expansion of Figure S3(c). Selected distances: O6···H2 (1.968 Å), O6···H3B (1.946 Å), O3···H3A (1.864 Å), C1···H33A (2.869 Å), C6···H33A (2.747 Å), C3···H35A (2.801 Å), S1···H29A (2.988 Å), S1···H29B (2.928 Å).

Crystallographic data for inclusion crystals

Table S1. Crystallographic Data for the Inclusion Crystals of Diacid **2** with 3- and 4-Methylpyridine

	2·3-methylpyridine	**2**·4-methylpyridine·toluene$_{0.5}$
Empirical formula	$C_{30}H_{37}NO_6S$	$C_{33.5}H_{41}NO_6S$
Formula weight	539.66	585.73
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, b, c / Å	9.637(3), 9.748(4), 16.361(6)	19.389(4), 15.669(3), 10.438(2)
α, β, γ / °	86.333(5), 75.287(5), 69.792(5)	90, 101.635(3), 90
V / Å^3	1394.6(9)	3106.2(10)
Z	2	4
F(000)	576	1252
T / K	100(2)	100(2)
ρ_{calc} / gcm^{-3}	1.285	1.253
Reflections collected	8065	17673
Independent reflections	6113 [R_{int} = 0.0453]	7075[R_{int} = 0.0701]
μ (Mo Kα) / mm^{-1}	0.160	0.149
Data / restraints / parameters	6113 / 4 / 359	7075 / 200 / 437
R_1, wR_2 ($I > 2\sigma(I)$)	0.0737, 0.1617	0.0577, 0.1063
R_1, wR_2 (all data)	0.1570, 0.2164	0.1222, 0.1321
Goodness-of-fit on F^2	1.010	1.010
Largest diff. peak and hole / e·Å^3	0.420 and -0.396	0.421 and -0.369

Table S2. Crystallographic Data for the Inclusion Crystals of Diacid **2** with 2- and 6-Methylquinoline.

	2·2-methylquinoline·toluene$_{0.5}$	**2**·6-methylquinoline·toluene	**2**·6-methylquinoline·acetonitrile
Empirical formula	$C_{75}H_{36}N_2O_{12}S_2$	$C_{41}H_{47}NO_6S$	$C_{36}H_{42}N_2O_6S$
Formula weight	1271.57	681.85	630.77
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, b, c / Å	19.965(3), 13.086(3), 23.497(5)	11.4571(16), 12.8125(18), 14.789(2)	9.589(3), 12.356(3), 15.066(4)
α, β, γ / °	92.721(3), 93.698(3), 110.195(3)	72.1642(17), 67.7107(16), 71.2796(17)	104.914(4), 101.789(4), 92.677(4)
V / Å^3	3435.9(12)	1859.8(4)	1679.2(8)
Z	2	2	2
F(000)	1356	728	672
T / K	100(2)	100(2)	100(2)
ρ_{calc} / gcm^{-3}	1.229	1.218	1.248
Reflections collected	19775	10683	9667
Independent reflections	15022[R_{int} = 0.0186]	8094[R_{int} = 0.0160]	7324[R_{int} = 0.0282]
μ (Mo Kα) / mm^{-1}	0.140	0.134	0.144
Data / restraints / parameters	15022 / 219 / 933	8094 / 262 / 500	7324 / 4 / 423
R_1, wR_2 ($I > 2\sigma(I)$)	0.0637, 0.1524	0.0410, 0.1042	0.0569, 0.1282
R_1, wR_2 (all data)	0.0900, 0.1717	0.0486, 0.1104	0.0908, 0.1491
Goodness-of-fit on F^2	1.030	1.029	1.019
Largest diff. peak and hole / e·Å^3	1.369 and -0.481	0.326 and -0.343	0.575 and -0.558

Table S3. Crystallographic Data for the Inclusion Crystals of Diacid **2** and Monoester **3** with 4-Methylcyclohexanamine

	2·(*trans*-4-methylcyclohexanamine)$_3$	**3**·*trans*-4-methylcyclohexanamine
Empirical formula	$C_{45}H_{75}N_3O_6S$	$C_{68}H_{102}N_2O_{12}S_2$
Formula weight	786.14	1203.62
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, b, c / Å	10.1308(15), 14.411(2), 16.965(2)	12.3387(19), 15.126(2), 18.749(3)
α, β, γ / °	109.550(2), 90.174(2), 96.343(2)	100.1088(19), 103.8252(19), 90.740(2)
V / Å^3	2317.8(6)	3339.7(9)
Z	2	2
F(000)	860	1304
T / K	100(2)	100(2)
ρ_{calc} / gcm^{-3}	1.126	1.197
Reflections collected	26689	19329
Independent reflections	10461 [R_{int} = 0.0304]	14615[R_{int} = 0.0189]
μ (Mo Kα) / mm^{-1}	0.117	0.140
Data / restraints / parameters	10461/ 613 / 716	14615 / 73 / 820
R_1, wR_2 ($I > 2\sigma(I)$)	0.0502, 0.1254	0.0639, 0.1792
R_1, wR_2 (all data)	0.0738, 0.1420	0.0878, 0.1992
Goodness-of-fit on F^2	1.026	1.309
Largest diff. peak and hole / e·Å^3	0.390 and -0.429	1.169 and -0.487

Thermal ellipsoid plots of inclusion crystals

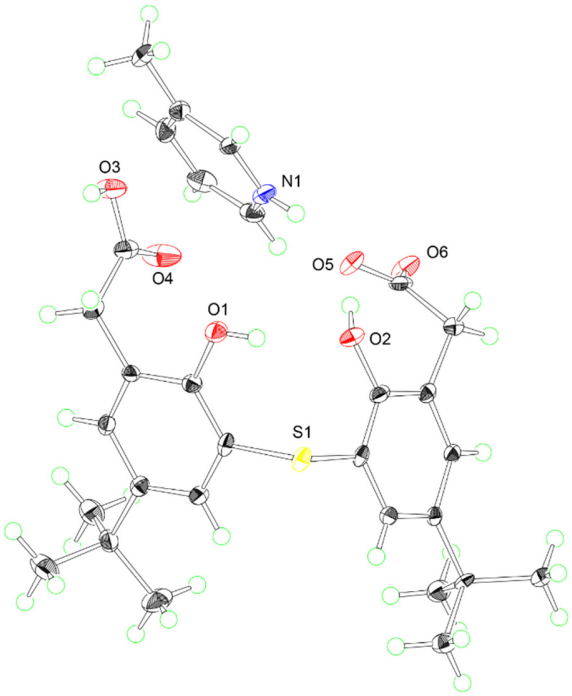

Figure S5. ORTEP drawing of **2**·3-methylpyridine with 50% probability ellipsoids (CCDC 2059346).

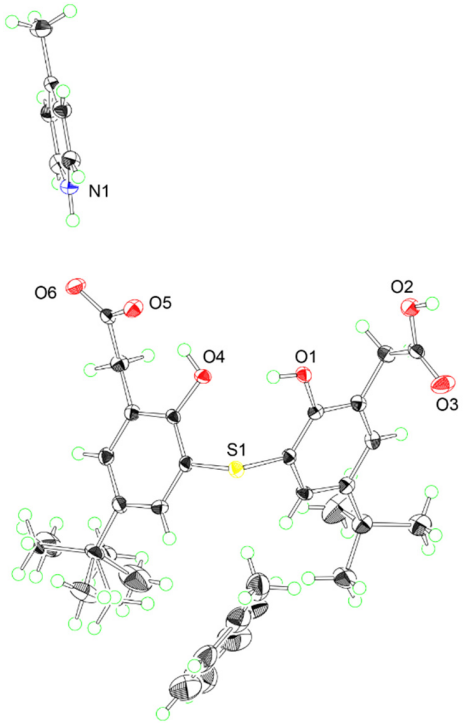

Figure S6. ORTEP drawing of **2**·4-methylpyridine·toluene$_{0.5}$ with 50% probability ellipsoids (CCDC 2059348).

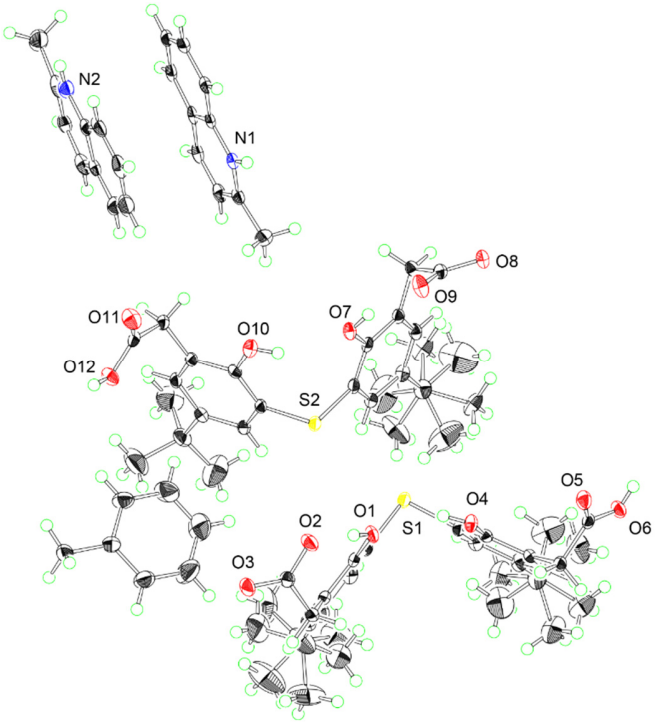

Figure S7. ORTEP drawing of **2**·2-methylquinoline·toluene$_{0.5}$ with 50% probability ellipsoids (CCDC 2059345).

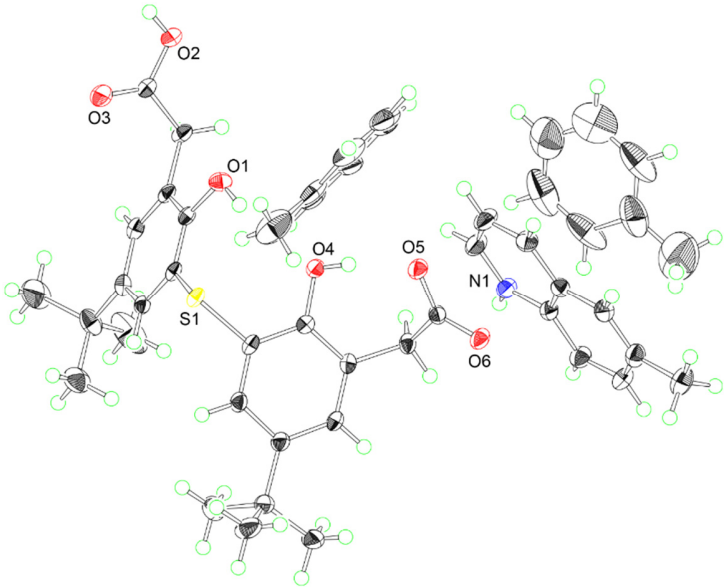

Figure S8. ORTEP drawing of **2**·6-methylquinoline·toluene with 50% probability ellipsoids (CCDC 2059350).

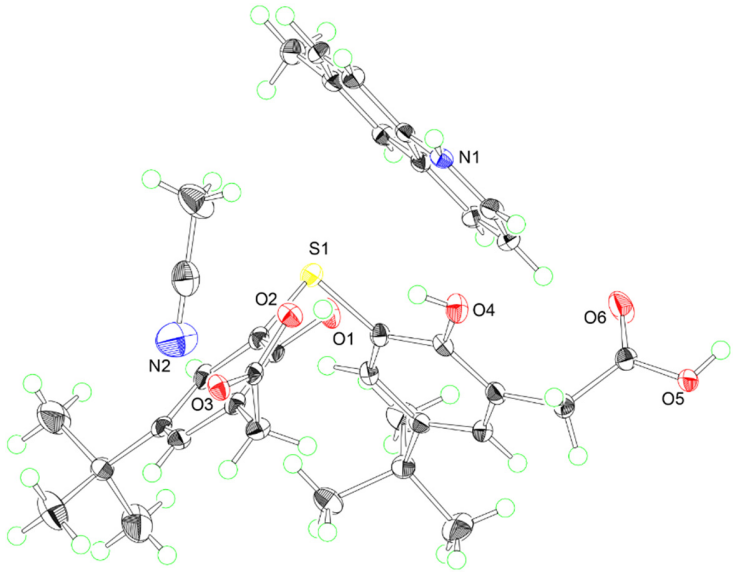

Figure S9. ORTEP drawing of **2**·6-methylquinoline·acetonitrile with 50% probability ellipsoids (CCDC 2059349).

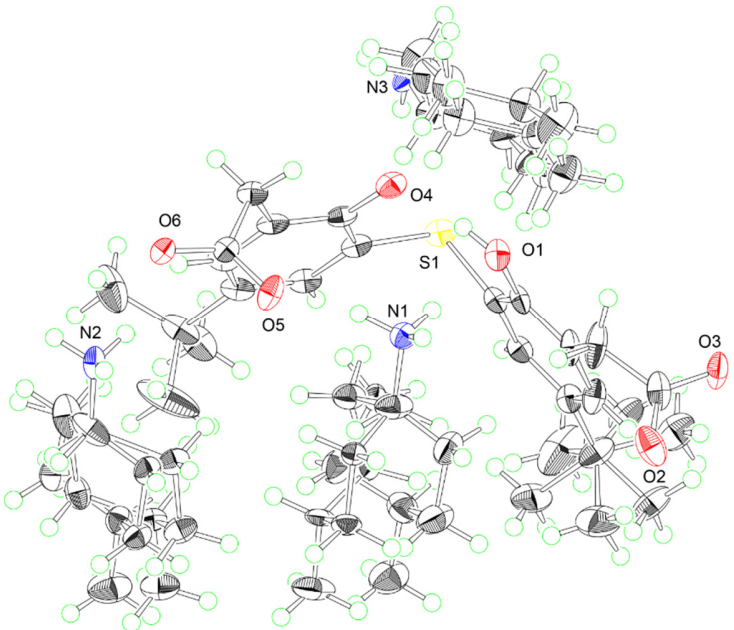

Figure S10. ORTEP drawing of **2**·(*trans*-4-methylcyclohexanamine)$_3$ with 50% probability ellipsoids (CCDC 2059347).

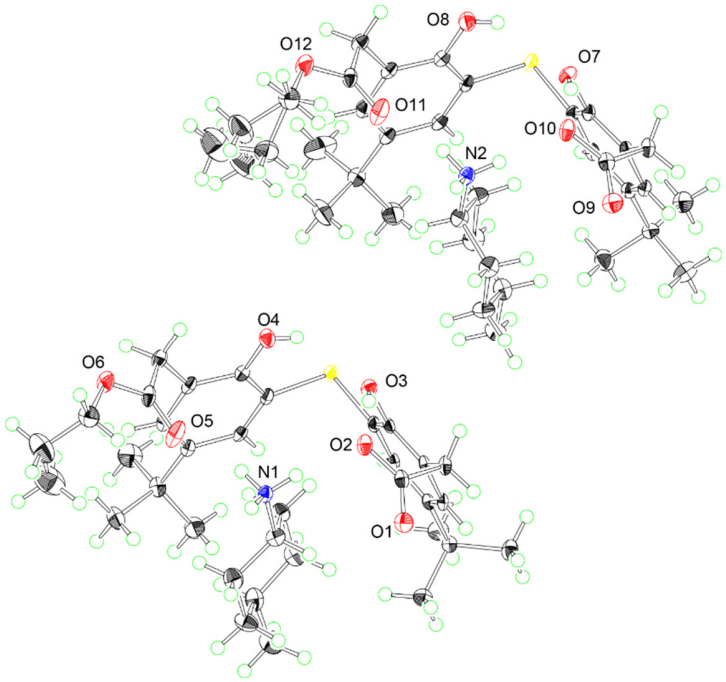

Figure S11. ORTEP drawing of **3**·*trans*-4-methylcyclohexanamine with 50% probability ellipsoids (CCDC 2059351).