Electronic Supplementary Material (ESI) for CrystEngComm.

Stoichiometry of Adamantylamine-Trinitrophloroglucinol Salts Controlled by Solvate Formation

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Supporting Information

Table S1 Crystallographic data for all of the prepared compounds

Compound	**I**	**II**	**III**	**IV**	**V**
Formula	(H**aa**)$_3$ **tnpg** · 0.5 EtOH · 0.5 H_2O	(H**aa**)$_3$ **tnpg** · tfEtOH	(H**aa**)$_3$ **tnpg** · H_2O	(H**aa**)$_3$ **tnpg** · 0.5 MeOH · 0.5 H_2O	(H**aa**)$_5$ **tnpg** H**tnpg** · 3 MeOH · H_2O
Empirical formula	$C_{18.5}H_{28.75}N_3O_5$	$C_{76}H_{112}F_6N_{12}O_{20}$	$C_{36}H_{54}N_6O_{10}$	$C_{73}H_{114}N_{12}O_{20}$	$C_{66}H_{106}N_{11}O_{23}$
MW/ gmol^{-1}	373.19	1627.77	729.93	1479.76	1421.61
Temp./ K	293	298	293(2)	293(2)	293(2)
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	*P* $2_1/c$	*P* $na2_1$	*P* $2_1/c$	*P* $2_1/c$	*P bca*
a/Å	18.805(5)	18.370(3)	14.4004(12)	18.9589(6)	16.1105(14)
b/Å	15.975(4)	16.060(2)	16.1041(9)	16.0224(7)	26.198(3)
c/Å	27.184(6)	27.340(3)	18.7528(10)	26.5928(13)	35.156(5)
α/°	90.00(2)	90	90	90	90
β/°	92.65(2)	90	105.420(7)	93.164(4)	90
γ/°	90.00(2)	90	90	90	90
Volume/Å^3	8158(4)	8066(2)	4192.3(5)	8065.7(6)	14838(3)
Z	16	4	4	4	8
ρ_{calcg}/cm^3	1.215	1.34	1.158	1.219	1.273
μ/mm-1	0.089	0.106	0.085	0.089	0.096
F(000)	3212	3464	1568	3184	6104
λ/ Å	0.71073	0.71073	0.71073	0.71073	0.71073
2*Θ* range /°	8.076 - 51.998	8.138 - 51.992	8.3 - 52	8.236 - 51.998	8.284 - 60
Index ranges	$-21 \le h \le 22$ $-19 \le k \le 19$ $-33 \le l \le 19$	$-22 \le h \le 15$ $-19 \le k \le 19$ $-33 \le l \le 18$	$-17 \le h \le 17$ $-19 \le k \le 17$ $-23 \le l \le 21$	$-22 \le h \le 23$ $-19 \le k \le 19$ $-32 \le l \le 32$	$-22 \le h \le 18$ $-36 \le k \le 15$ $-49 \le l \le 15$
Refl. collected	25978	39378	19184	39384	54282
Indep. refl.	15598	11843	8204	15797	21581
R_{int}	0.1654	0.3454	0.0618	0.1047	0.3323
R_{sigma}	0.1749	0.3713	0.106	0.1644	0.4962
Data/ restraints/ parameters	15598/12/999	11843/528/1052	8204/14/520	15797/8/995	21581/144/905
Goof on F2	1.158	0.918	1.133	1.047	1.031
Final *R* indexes [I>=2σ (I)]	*R1* = 0.1473 wR2 = 0.3581	*R1* = 0.1162 *wR2* = 0.2320	*R1* = 0.1270 *wR2* = 0.3476	*R1* = 0.1308 *wR2* = 0.3404	*R1* = 0.1870 *wR2* = 0.2427
Final *R* indexes [all data]	*R1* = 0.2687 wR2 = 0.4625	*R1* = 0.3594 wR2 = 0.3382	*R1* = 0.2161 wR2 = 0.4080	*R1* = 0.2569 wR2 = 0.4229	*R1* = 0.4234 wR2 = 0.3325
Largest diff. peak/hole / e Å^{-3}	0.86/-0.90	0.35/-0.32	1.18/-0.42	1.31/-0.77	0.87/-0.48
Flack parameter	n/a	-0.2(10)	n/a	n/a	n/a

Compound	**VI**	**VII**	**VIII**	**IX**	**X**
Formula	(H**aa**)$_3$ **tnpg** · PrOH	(H**aa**)$_2$ H**tnpg** · tfEtOH	H**aa** H_2**tnpg**	(H**aa**)$_2$ H**tnpg** · **thf**	(H**aa**)$_3$ **tnpg** · 3 **dmso** · H_2O
Empirical formula	$C_{78}H_{124}N_{12}O_{20}$	$C_{56}H_{78}F_6N_{10}O_{20}$	$C_{16}H_{20}N_4O_9$	$C_{34}H_{54}N_5O_{11}$	$C_{42}H_{76}N_6O_{14}S_3$
MW/ gmol^{-1}	1549.88	1326.29	412.36	708.82	985.26
Temp./ K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	triclinic
Space group	Pna21	$P2_1/n$	Pbca	C2/c	P-1
a/Å	18.4656(11)	17.5039(7)	11.1478(3)	14.445(5)	11.5708(6)
b/Å	16.0811(11)	18.8674(6)	22.3581(8)	17.0130(19)	14.8651(9)
c/Å	27.4522(18)	20.3861(7)	29.9866(12)	15.845(4)	17.1263(8)
α/°	90	90	90	90	101.650(4)
β/°	90	103.005(4)	90	108.81(4)	108.206(5)
γ/°	90	90	90	90	107.592(5)
Volume/Å^3	8151.9(9)	6559.9(4)	7474.0(4)	3686.1(17)	2520.5(3)
Z	4	4	4	4	2
ρ_{calcg}/cm^3	1.263	1.342	1.466	1.277	1.300
μ/mm^{-1}	0.091	0.113	0.121	0.096	0.214
F(000)	3344	2792	3456	1524	1062
λ/ Å	0.71073	0.71073	0.71073	0.71073	0.71073
2Θ range /°	8.34 - 65.33	8.304 - 49.998	8.27 - 53.998	7.648 - 54	8.326 - 53.99
Index ranges	-27 ≤ h ≤ 26 -23 ≤ k ≤ 24 -41 ≤ l ≤ 39	-20 ≤ h ≤ 20 -22 ≤ k ≤ 22 -24 ≤ l ≤ 24	-14 ≤ h ≤ 11 -28 ≤ k ≤ 23 -17 ≤ l ≤ 38	-18 ≤ h ≤ 18 -21 ≤ k ≤ 21 -20 ≤ l ≤ 20	-14 ≤ h ≤ 14 -18 ≤ k ≤ 18 -21 ≤ l ≤ 21
Refl. collected	96385	90384	22536	18527	22840
Indep. refl.	27308	11479	8128	4000	10941
R_{int}	0.186	0.0728	0.0282	0.1142	0.0331
R_{sigma}	0.2277	0.0429	0.0331	0.1932	0.0549
Data/ restraints/ parameters	27308/13/1037	11479/38/765	8128/0/529	4000/52/240	10941/9/651
Goof on F2	0.929	1.405	1.043	1.035	1.027
Final *R* indexes [I>=2σ (I)]	*R1* = 0.0902 *wR2* = 0.1472	*R1* = 0.1245 *wR2* = 0.3587	*R1* = 0.0648 *wR2* = 0.1525	*R1* = 0.1214 *wR2* = 0.2835	*R1* = 0.0909 *wR2* = 0.2368
Final *R* indexes [all data]	*R1* = 0.2896 *wR2* = 0.2102	*R1* = 0.1750 *wR2* = 0.3987	*R1* = 0.0963 *wR2* = 0.1697	*R1* = 0.3389 *wR2* = 0.3957	*R1* = 0.1316 *wR2* = 0.2678
Largest diff. peak/hole / e Å^{-3}	0.36/-0.27	1.18/-0.71	0.41/-0.27	0.67/-0.34	1.70/-0.50
Flack parameter	-0.7(9)	n/a	n/a	n/a	n/a

Compound	**XI**	**XII**	**XIII**	**XIV**
Formula	H**aa pic** · H_2O	(H**aa**)$_2$ **stph** · 2 **dmso**	$(MeNH_3)_3$ **tnpg**	$(t\text{-}BuNH_3)_3$ **tnpg** · MeOH · H_2O
Empirical formula	C16H22N4O8	C30H49N5O10.03S2	C6H12N4O6	C37H82N12O22
MW/ gmol^{-1}	398.37	703.86	236.2	1047.14
Temp./ K	293(2)	293(2)	293(2)	295
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P21/n	C2/c	P21/c	P21/c
a/Å	12.7841(9)	14.2574(9)	10.2615(7)	21.8759(13)
b/Å	6.8465(4)	17.0725(7)	17.7734(10)	16.7522(8)
c/Å	21.4945(14)	15.8640(9)	8.8411(7)	15.7197(10)
α/°	90	90	90	90
β/°	105.996(7)	113.279(7)	113.363(8)	110.086(7)
γ/°	90	90	90	90
Volume/Å^3	1808.5(2)	3547.1(4)	1480.25(19)	5410.4(6)
Z	8	4	6	4
ρ_{calcg}/cm^3	1.463	1.318	1.59	1.286
μ/mm-1	0.119	0.21	0.142	0.105
F(000)	840	1504	744	2256
λ/ Å	0.71073	0.71073	0.71073	0.71073
2*Θ* range /°	8.394 - 65.586	8.7 - 53.988	8.42 - 59.99	8.632 - 53.996
Index ranges	-18 ≤ h ≤ 16 -10 ≤ k ≤ 8 -32 ≤ l ≤ 29	-18 ≤ h ≤ 16 -21 ≤ k ≤ 21 -20 ≤ l ≤ 20	-14 ≤ h ≤ 13 -14 ≤ k ≤ 25 -12 ≤ l ≤ 12	-27 ≤ h ≤ 27 -21 ≤ k ≤ 21 -19 ≤ l ≤ 20
Refl. collected	10793	16527	9552	48405
Indep. refl.	5998	3864	4308	11754
R_{int}	0.0291	0.0298	0.0216	0.1102
R_{sigma}	0.0565	0.0265	0.0301	0.1257
Data/ restraints/ parameters	5998/5/280	3864/0/218	4308/0/223	11754/0/675
Goof on F2	1.057	1.036	1.035	1.089
Final *R* indexes [I>=2σ (I)]	*R1* = 0.0862 *wR2* = 0.1759	*R1* = 0.0664 *wR2* = 0.1657	*R1* = 0.0443 *wR2* = 0.1133	*R1* = 0.1141 *wR2* = 0.1863
Final *R* indexes [all data]	*R1* = 0.1510 *wR2* = 0.2078	*R1* = 0.0881 *wR2* = 0.1807	*R1* = 0.0594 *wR2* = 0.1228	*R1* = 0.2168 *wR2* = 0.2265
Largest diff. peak/hole / e Å^{-3}	0.46/-0.32	0.43/-0.40	0.33/-0.23	0.44/-0.34
Flack parameter	n/a	n/a	n/a	n/a

Table S2 Geometric parameters for the hydrogen bonds in the crystal structure of compound **I**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	*d*(H...A)/ Å	*d*(D...A)/ Å	*α*(D-H...A)/°
N10	O107	1.85	2.720(10)	166
N10	O208	2.27	3.156(11)	172
N10	O205	2.11	2.987(9)	169
N10	O206	2.43	3.058(9)	128
N10	N202	2.62	3.448(8)	155
N20	O102	2.52	3.192(9)	133
N20	O103	1.94	2.818(9)	171
N20	N101	2.59	3.441(9)	160
N20	O204	2.01	2.837(7)	154
N20	O108	2.21	2.902(12)	134
N20	O109	2.5	3.327(6)	156
N30	O301	2.08	2.955(10)	169
N30	O206	2.3	2.774(9)	113
N30	O207	1.87	2.729(8)	161
N30	O201	1.94	2.806(8)	163
N40	O101	2.04	2.915(8)	166
N40	O102	2.56	3.159(9)	125
N40	O203	2.23	3.096(11)	163
N40	O104	1.92	2.762(8)	157
O401	O204	2.00	2.798(4)	156
N50	O106	2.06	2.928(9)	166
N50	O207	1.95	2.824(8)	167
N50	O201	1.92	2.740(7)	153
N50	O202	2.41	3.056(9)	130
N60	O104	1.89	2.756(6)	162
N60	O101	1.86	2.728(5)	164
N60	O401	1.89	2.7508(10)	163
O301	O107	1.94	2.761(10)	179
C49	O108	2.49	3.323(13)	144
C61	O401	2.54	3.279(10)	132

Table S3 Geometric parameters for the hydrogen bonds in the crystal structure of compound **II**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O103	2.17	3.00(2)	154
N10	O107	1.93	2.81(2)	167
N10	O203	2.31	3.13(2)	153
N10	O204	2.08	2.748(19)	132
N20	O105	2.07	2.952(17)	172
N20	O205	2.09	2.97(3)	173
N20	O206	2.57	3.25(3)	133
N20	O25A	2.13	2.88(4)	142
N20	O201	1.88	2.73(2)	161
N30	O4	2.25	3.12(2)	165
N30	O207	1.87	2.730(19)	163
N30	O208	2.30	2.76(2)	112
N30	O101	1.85	2.72(2)	163
N40	O207	1.91	2.78(2)	164
N40	O101	1.90	2.750(18)	159
N40	O102	2.52	3.12(2)	125
N40	O202	2.20	3.05(2)	161
N50	O104	1.95	2.82(2)	165
N60	O106	2.26	2.72(2)	112
N60	O107	1.87	2.716(18)	159
C13	F4	2.50	3.33(2)	143
C15	O205	2.60	3.52(3)	159
C46	O101	2.59	3.30(3)	129
N10	O103	2.17	3.00(2)	154
N10	O107	1.93	2.81(2)	167
N10	O203	2.31	3.13(2)	153
N10	O204	2.08	2.748(19)	132
N20	O105	2.07	2.952(17)	172
N20	O205	2.09	2.97(3)	173
N20	O206	2.57	3.25(3)	133

Table S4 Geometric parameters for the hydrogen bonds in the crystal structure of compound **III**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O107	1.87	2.756(6)	173
N10	O2	2.57	3.05(2)	114
N10	O101	1.91	2.742(6)	156
N10	O102	2.28	2.779(6)	115
N10	O10	1.93	2.811(9)	172
N20	O101	1.94	2.825(6)	171
N20	O105	2.25	3.074(7)	154
N20	O3	2.16	3.026(18)	164
N20	O106	2.45	3.141(7)	134
N20	O107	1.97	2.783(6)	151
N30	O104	1.86	2.735(7)	165
N30	O108	2.16	3.021(7)	163
N30	O109	2.48	3.227(6)	142
N30	O1	2.55	3.387(19)	158
N30	O2	1.94	2.740(14)	150
N30	O102	2.36	3.036(7)	132
N30	O103	2.15	3.034(7)	171
N30	N101	2.62	3.469(7)	160
C15	O4	2.17	3.11(3)	165
C27	O105	2.48	3.294(9)	141
C28	O108	2.60	3.528(9)	160
C31	O1	2.57	3.431(17)	148
C31	O3	2.50	3.32(2)	142

Table S5 Geometric parameters for the hydrogen bonds in the crystal structure of compound **IV**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O101	1.88	2.729(6)	158
N10	O109	2.43	3.049(8)	127
N10	O203	2.07	2.932(12)	163
N10	O22A	2.50	3.34(6)	157
N10	O23A	2.60	3.41(4)	152
N10	O104	1.96	2.827(5)	164
N20	O401	2.02	2.911(7)	173
N20	O104	1.90	2.759(6)	162
N20	O105	2.32	2.805(6)	114
N20	O12A	2.44	3.009(15)	122
N20	O101	1.96	2.818(6)	160
N30	O207	2.06	2.914(6)	162
N30	O208	2.45	3.080(7)	128
N30	O108	2.18	3.041(9)	163
N30	O201	1.93	2.787(6)	161
N40	O107	2.04	2.887(7)	160
N40	O205	2.52	3.311(8)	148
N40	O206	2.10	2.877(7)	146
N40	N202	2.61	3.472(6)	163
N40	O208	2.41	3.210(6)	150
N40	O209	1.99	2.820(5)	154
N40	N203	2.58	3.463(6)	177
N50	O201	1.92	2.789(7)	164
N50	O207	1.90	2.748(6)	159
N50	O301	2.02	2.891(10)	164
N60	O204	1.79	2.662(7)	166
N60	O12A	2.09	2.845(13)	142
N60	O103	2.25	3.138(7)	173
N60	O105	2.35	3.018(7)	132
N60	O106	2.15	3.032(7)	172
N60	N102	2.62	3.463(7)	159
O401	O204	2.03	2.724(7)	142
C35	O206	2.58	3.392(9)	142
C58	O22A	2.40	3.30(5)	154
C65	O23A	2.36	3.23(4)	149

Table S6 Geometric parameters for the hydrogen bonds in the crystal structure of compound **V**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O104	1.87	2.719(6)	158
N10	O106	2.46	3.004(8)	119
N10	O107	2.43	3.191(7)	144
N10	O208	2.15	2.994(7)	158
N10	O209	1.86	2.747(7)	171
N20	O101	2.54	3.145(7)	126
N20	O107	1.93	2.785(7)	162
N20	O108	1.93	2.814(9)	171
N20	O1	1.90	2.775(7)	167
N20	O101	2.55	3.085(7)	120
N30	O102	1.91	2.793(9)	171
N30	O3	1.88	2.770(9)	173
N30	O4	2.55	2.968(9)	110
N30	O204	1.99	2.778(15)	148
N40	O205	1.87	2.754(7)	173
N40	O207	2.45	2.917(7)	113
N40	O208	2.51	3.186(7)	134
N40	O105	2.12	3.004(7)	170
N40	O106	2.02	2.902(7)	170
N50	O109	2.56	2.879(8)	102
N50	O103	1.95	2.828(11)	169
N50	O2	1.85	2.725(7)	169
N50	O103	2.40	2.879(8)	114
O63	O104	1.74	2.460(8)	145
O63	O209	2.40	2.831(8)	114
O81	N203	1.92	2.645(7)	146
C11	O209	2.56	3.352(9)	139
C47	O206	2.54	3.506(9)	171

Table S7 Geometric parameters for the hydrogen bonds in the crystal structure of compound **VI**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O401	2.08	2.949(6)	166
N10	O204	1.92	2.782(7)	164
N10	O22A	2.44	3.010(18)	122
N10	O101	1.90	2.748(6)	158
N10	O109	2.29	2.782(7)	115
N20	O206	2.13	2.993(6)	163
N20	O104	1.92	2.763(6)	158
N20	O105	2.51	3.124(6)	126
N20	O201	1.97	2.828(7)	161
N20	O202	2.57	3.200(6)	128
N30	O103	2.09	2.982(8)	177
N30	O12A	2.11	2.84(2)	138
N30	O208	2.11	2.998(7)	176
N30	O209	2.50	3.092(7)	125
N30	O107	1.89	2.762(7)	167
N40	O104	1.97	2.788(7)	153
N40	O12A	2.41	3.02(3)	127
N40	O201	1.85	2.724(6)	169
N40	O209	2.35	2.788(7)	110
N40	O301	2.05	2.929(7)	168
N50	O207	1.86	2.724(7)	163
N50	O202	2.59	3.275(7)	135
N50	O203	2.05	2.935(9)	171
N50	O22A	1.97	2.774(17)	149
N50	O108	2.15	3.037(7)	176
N50	O109	2.41	3.050(7)	129
N50	N101	2.61	3.448(7)	156
N60	O204	1.89	2.765(6)	168
O301	O107	1.86	2.683(5)	176
O401	O207	1.87	2.692(5)	175
C51	O23A	2.56	3.44(2)	151

Table S8 Geometric parameters for the hydrogen bonds in the crystal structure of compound **VII**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O205	2.14	3.014(5)	166
N10	O207	2.24	2.763(5)	117
N10	O103	2.44	2.924(5)	114
N10	O104	1.97	2.857(4)	173
N10	O103	2.59	2.924(5)	103
N10	O109	2.29	3.148(5)	162
N20	O107	1.88	2.755(5)	168
N20	O202	2.25	3.101(12)	160
N20	O203	2.49	3.243(12)	143
N20	O1	2.56	3.326(12)	144
N20	O4	2.03	2.886(12)	160
N20	O105	2.30	3.116(6)	153
N20	O106	2.44	3.265(6)	155
N30	O204	1.94	2.802(5)	163
N30	O207	2.08	2.779(5)	135
N30	O209	2.39	3.210(5)	153
N30	O104	1.97	2.851(5)	173
N40	O208	2.59	3.299(7)	137
N40	O209	2.23	3.117(6)	171
O101	O102	1.79	2.473(4)	139
O101	N101	2.37	2.804(5)	114
O201	O202	2.02	2.698(11)	139
O201	O4	1.80	2.419(12)	131
C1	O201	2.56	3.196(12)	123
C1	O206	2.60	3.291(10)	129
C4	O101	2.49	3.226(7)	133
C18	O108	2.52	3.255(8)	133
C31	O209	2.57	3.404(7)	144

Table S9 Geometric parameters for the hydrogen bonds in the crystal structure of compound **VIII**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O201	2.00	2.864(3)	165
N10	O101	1.95	2.801(3)	159
N10	O106	2.57	3.262(3)	135
N10	O206	2.38	2.999(3)	127
N20	O101	2.16	2.960(2)	149
N20	O201	1.93	2.813(3)	172
N20	O208	2.42	2.932(3)	117
N20	O108	2.33	2.912(3)	123
O104	O105	1.83	2.536(4)	143
O104	N102	2.44	2.869(4)	113
O107	O106	1.81	2.525(3)	144
O107	N102	2.42	2.853(3)	114
O204	O205	1.75	2.459(3)	144
O204	N202	2.40	2.837(3)	114
O207	O208	1.75	2.469(3)	146
O207	N203	2.35	2.806(3)	116
C24	O103	2.57	3.294(3)	131

Table S10 Geometric parameters for the hydrogen bonds in the crystal structure of compound **IX**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	*d*(H...A)/ Å	*d*(D...A)/ Å	*α*(D-H...A)/°
N10	O102	1.90	2.782(7)	172
N10	O1	1.91	2.794(8)	174
N10	O102	1.97	2.832(7)	162
N10	O101	2.46	3.020(9)	121
O105	O2	1.90	2.483(9)	127
O105	O103	2.46	3.060(5)	131

Table S11 Geometric parameters for the hydrogen bonds in the crystal structure of compound **X**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
O2	O232	2.03(4)	2.874(7)	169(8)
N10	O232	2.05	2.937(6)	177
N10	O101	1.82	2.694(4)	167
N10	O222	1.98	2.865(4)	171
N20	O103	2.41(2)	2.932(5)	120(3)
N20	O104	1.98(2)	2.798(4)	161(3)
N20	O210	2.044(12)	2.935(5)	159.5(10)
N20	O104	1.940(19)	2.784(3)	156.4(13)
N20	O105	2.39(2)	2.994(4)	125.0(10)
N30	O107	2.408(15)	3.011(4)	129.2(11)
N30	O108	2.234(12)	3.026(5)	156.9(13)
N30	O107	2.122(18)	2.802(4)	146(2)
N30	O2	1.864(17)	2.877(7)	175(2)
N30	O2A	1.76(2)	2.643(15)	142.9(18)
O301	O101	1.985(12)	2.744(5)	169.0(14)
C15	O102	2.46	3.290(7)	143
C221	O109	2.47	3.378(9)	159
C230	O2A	2.57	3.435(16)	151
C39	O106	2.43	3.358(5)	159

Table S12 Geometric parameters for the hydrogen bonds in the crystal structure of compound **XI**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O10	1.89	2.775(3)	171
N10	O101	2.17	2.809(3)	128
N10	O107	2.44	3.295(13)	162
N10	O1	2.30	3.130(16)	155
N10	O10	2.52	3.062(3)	120
O10	O101	2.08(2)	2.822(3)	147(2)
O10	O102	2.38(2)	3.062(3)	140(2)
O10	O105	2.14(3)	2.880(3)	147(3)
C18	O1	2.56	3.37(2)	141
C105	O2	2.26	2.59(2)	100

Table S13 Geometric parameters for the hydrogen bonds in the crystal structure of compound **XII**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O3	1.93	2.807(2)	168
N10	O3	2.00	2.862(3)	161
N10	O4	2.52	3.103(3)	123
N10	O20	1.93	2.804(3)	167
C20	O2	2.51	3.439(6)	163

Table S14 Geometric parameters for the hydrogen bonds in the crystal structure of compound **XIII**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O103	2.13	2.9688(16)	157
N10	O104	2.37	2.9725(16)	125
N10	O106	1.93	2.8195(15)	174
N10	O107	2.39	2.7343(17)	103
N10	O102	2.56	2.9832(16)	110
N10	O103	1.99	2.8758(15)	176
N20	O104	2.03	2.8784(18)	159
N20	O101	2.41	2.9757(19)	122
N20	O109	1.76	2.6186(19)	162
N20	O108	2.10	2.9107(18)	150
N20	O109	2.45	3.1211(19)	133
N30	O107	2.53	2.9247(16)	108
N30	O103	2.17	3.0273(16)	162
N30	O102	2.04	2.8739(17)	155
N30	O105	2.25	2.9276(17)	133
N30	O106	1.95	2.7613(17)	150
C20	O101	2.50	3.389(2)	153

Table S15 Geometric parameters for the hydrogen bonds in the crystal structure of compound **XIV**. Distances between selected atoms in a contact are denoted as *d*, while the corresponding angle is marked with α

Donor atom	Acceptor atom	d(H...A)/ Å	d(D...A)/ Å	α(D-H...A)/°
N10	O102	2.20	2.985(5)	147
N10	O205	2.44	2.847(5)	108
N10	O206	1.91	2.797(5)	176
N10	O205	2.48	2.847(5)	105
N10	O108	2.52	3.359(6)	157
N10	O302	2.53	3.041(5)	117
N20	O301	1.95	2.838(7)	172
N20	O101	2.54	3.086(5)	120
N20	O109	1.93	2.809(5)	170
N20	O103	2.09	2.934(4)	157
N20	O104	2.30	2.952(4)	130
N30	O303	1.97	2.838(5)	164
N30	O203	1.96	2.829(4)	167
N30	O201	2.43	3.020(4)	124
N30	O209	1.98	2.845(5)	164
O303	O106	2.23	2.745(5)	119
O304	O105	2.20	2.660(5)	114
O304	O207	2.09	2.829(6)	145
O304	O208	2.46	3.159(6)	140
N40	O106	1.90	2.792(5)	180
N40	O201	2.16	3.028(5)	166
N40	O202	2.52	3.033(4)	117
N40	O304	2.1	2.969(5)	167
N50	O304	2.08	2.957(5)	170
N50	O209	2.03	2.909(4)	168
N50	O202	2.26	2.783(5)	117
N50	O203	1.90	2.773(5)	166
O302	O107	2.56	3.053(5)	120
C22	O103	2.59	3.366(5)	138
C52	O204	2.53	3.484(8)	170

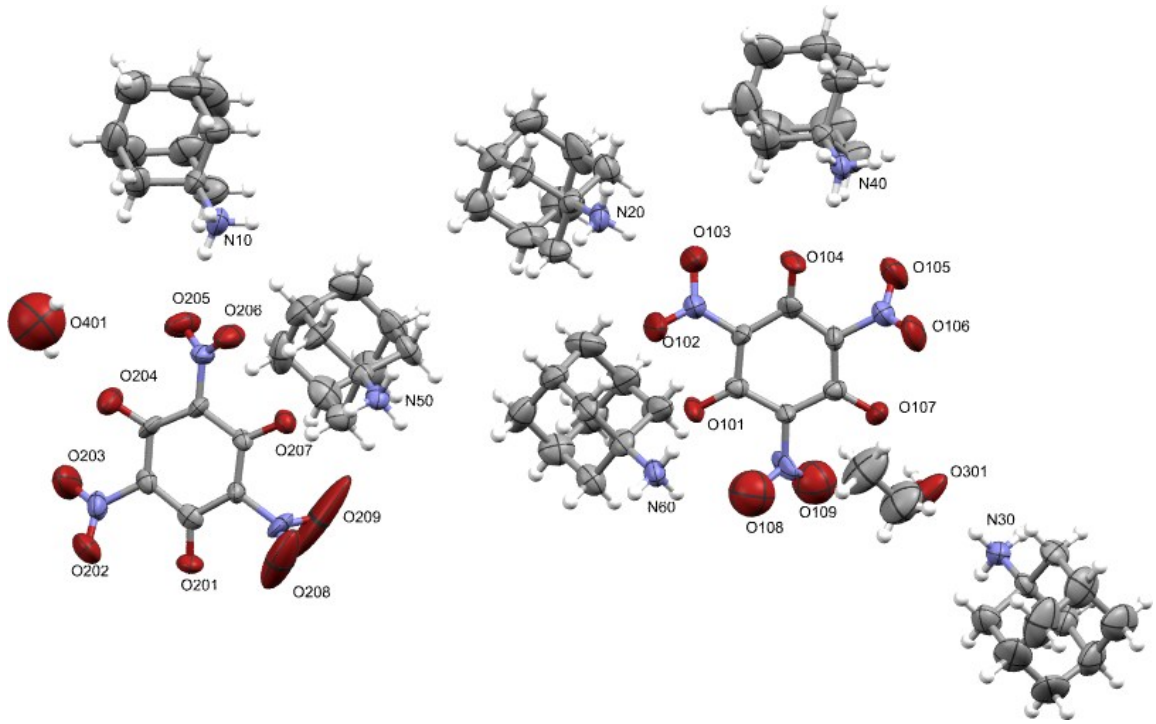

Figure S1 Asymmetric unit of compound **I** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

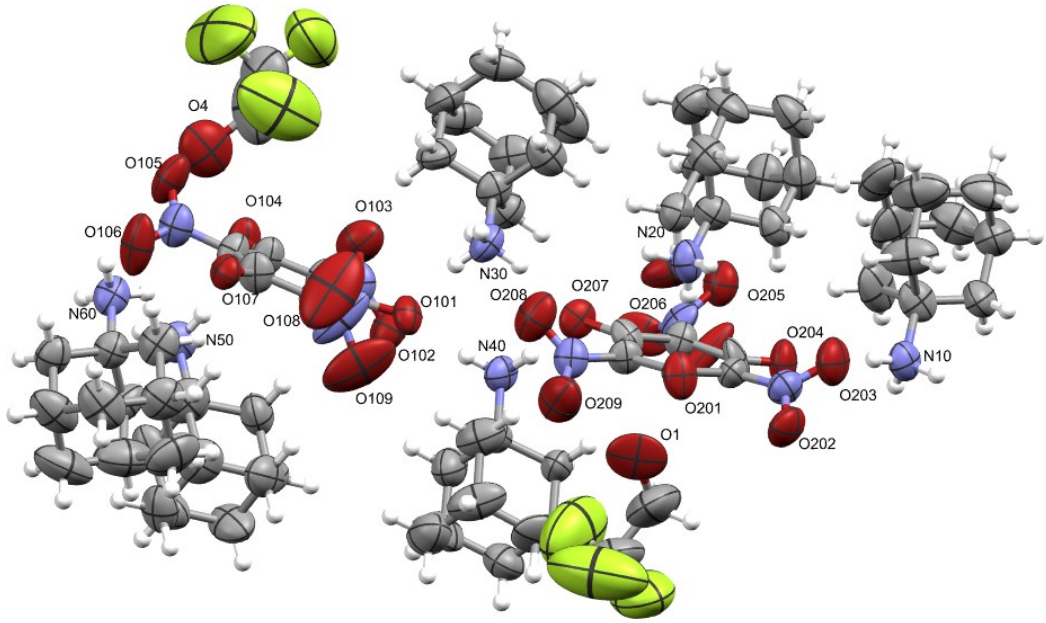

Figure S2 Asymmetric unit of compound **II** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

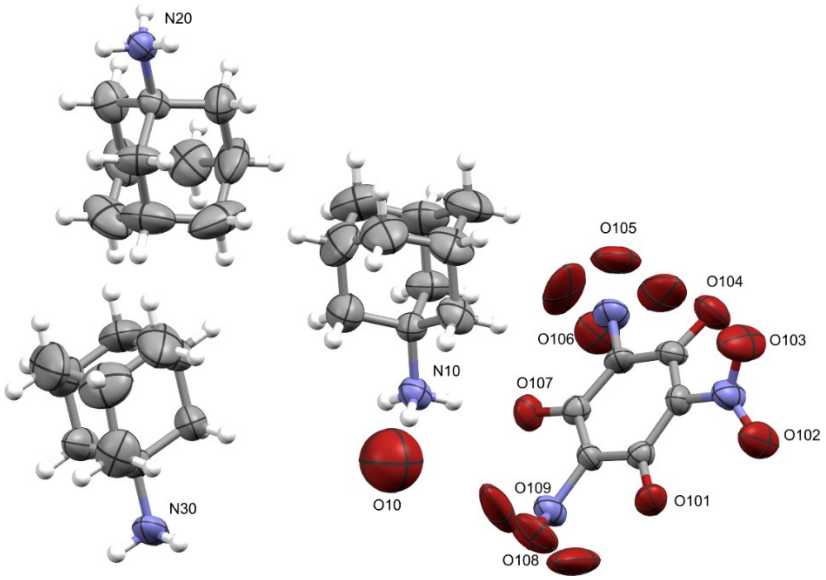

Figure S3 Asymmetric unit of compound **III** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

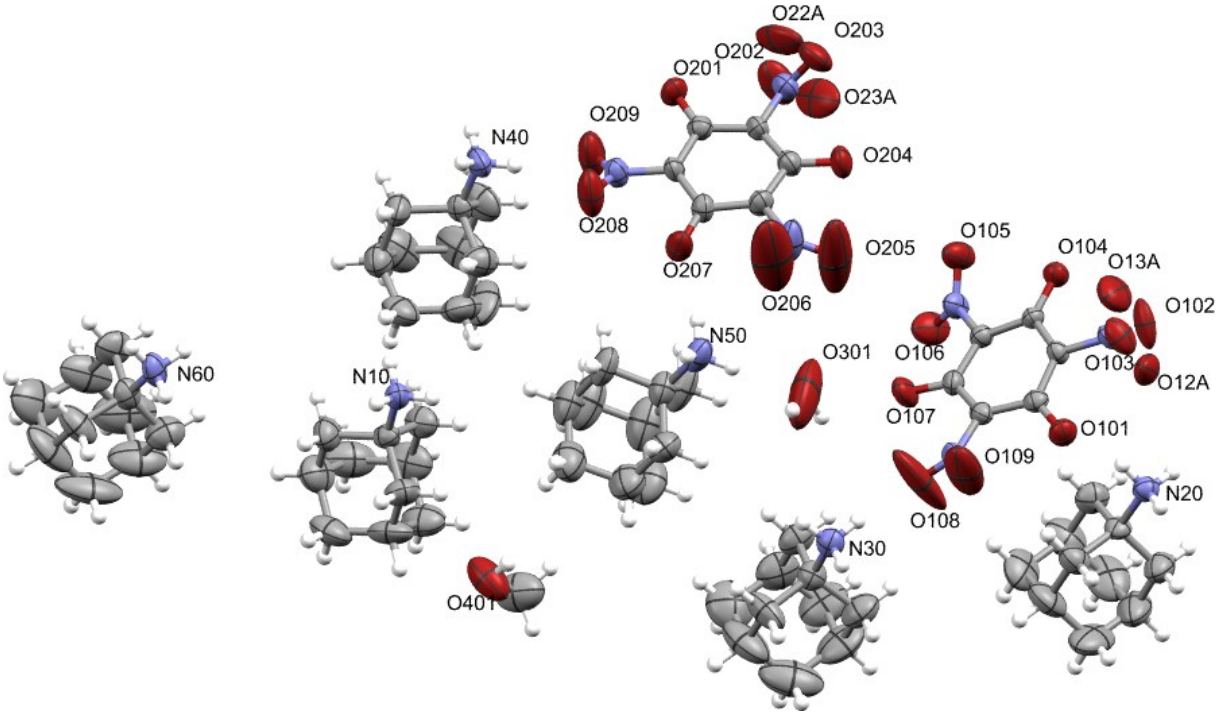

Figure S4 Asymmetric unit of compound **IV** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

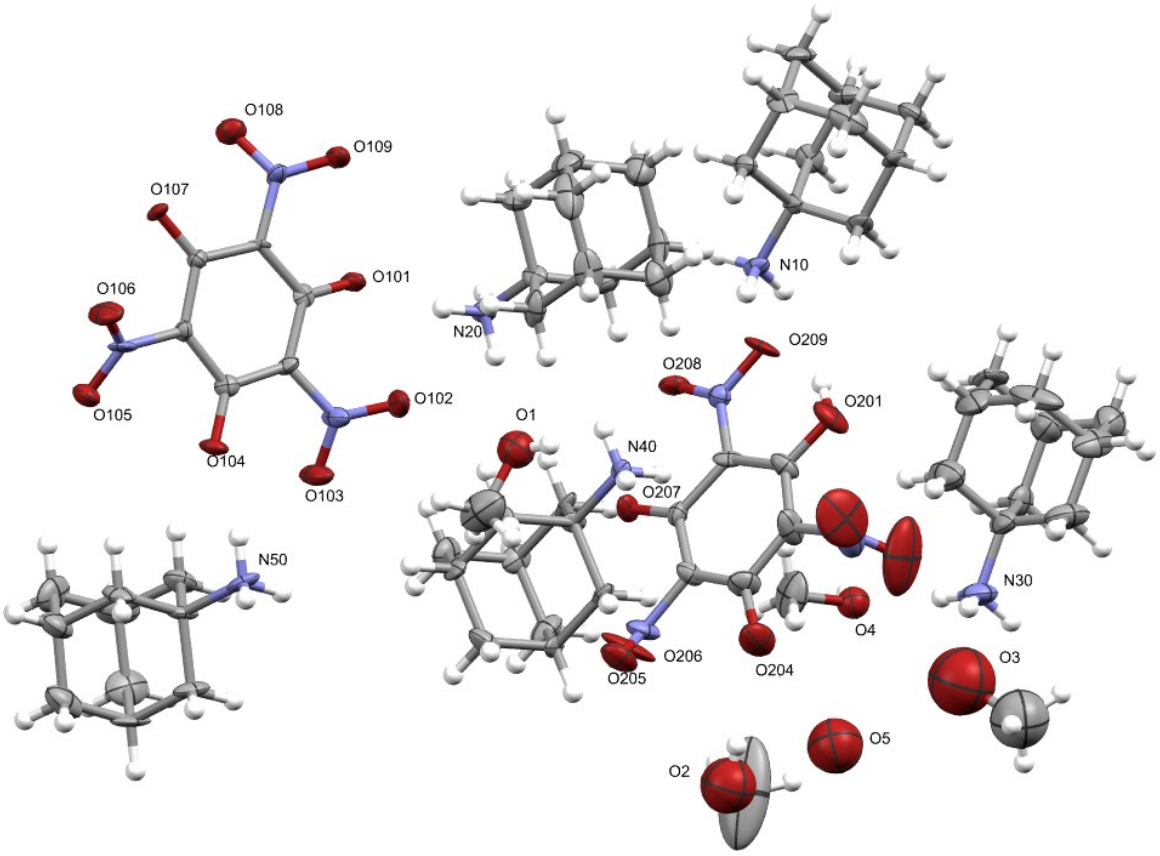

Figure S5 Asymmetric unit of compound **V** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

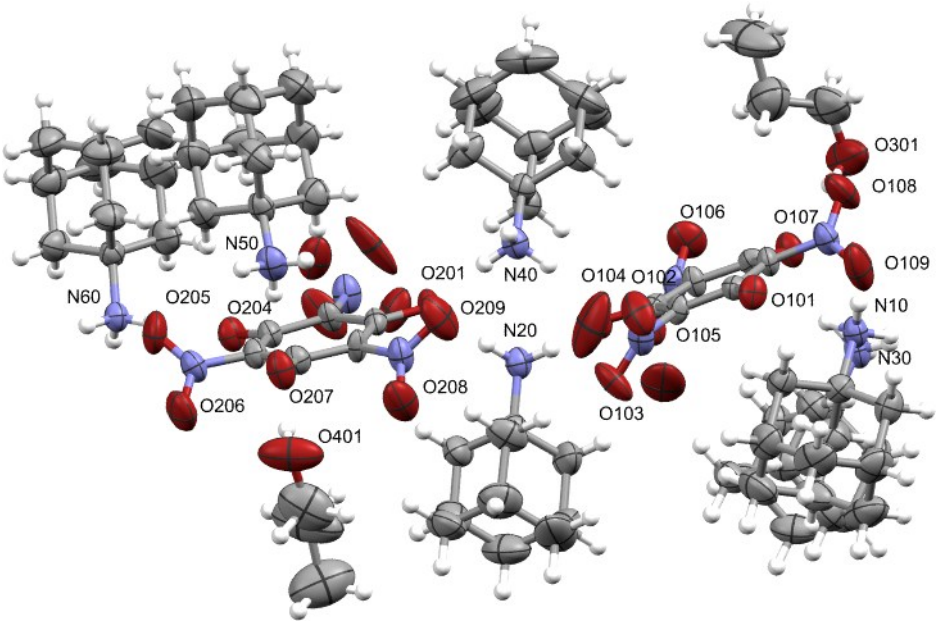

Figure S6 Asymmetric unit of compound **VI** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

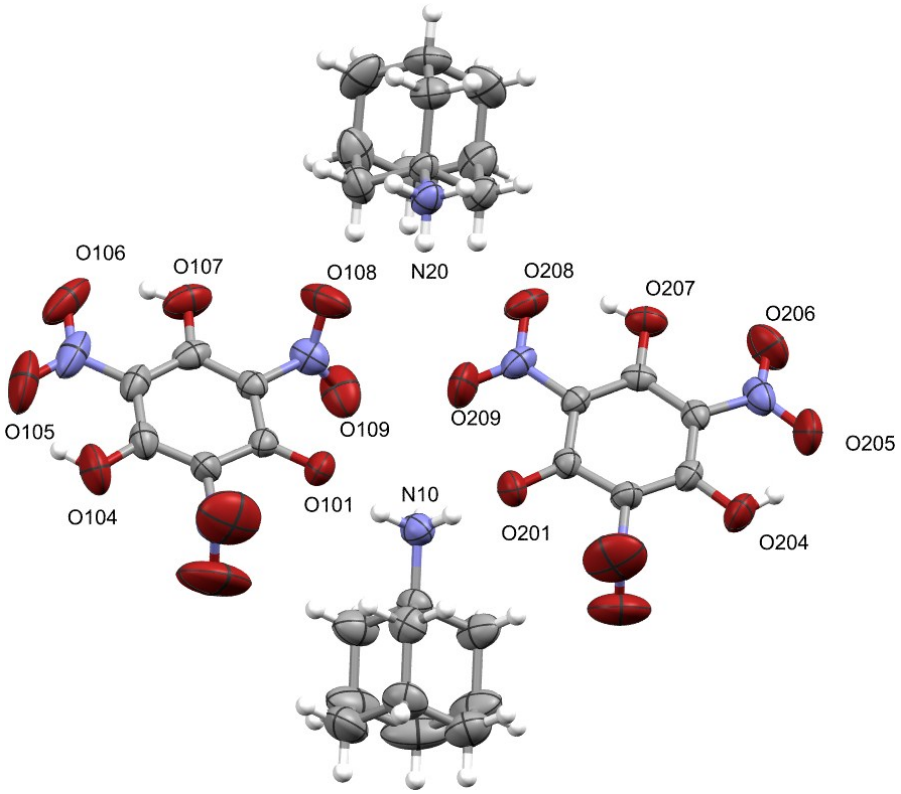

Figure S7 Asymmetric unit of compound **VIII** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

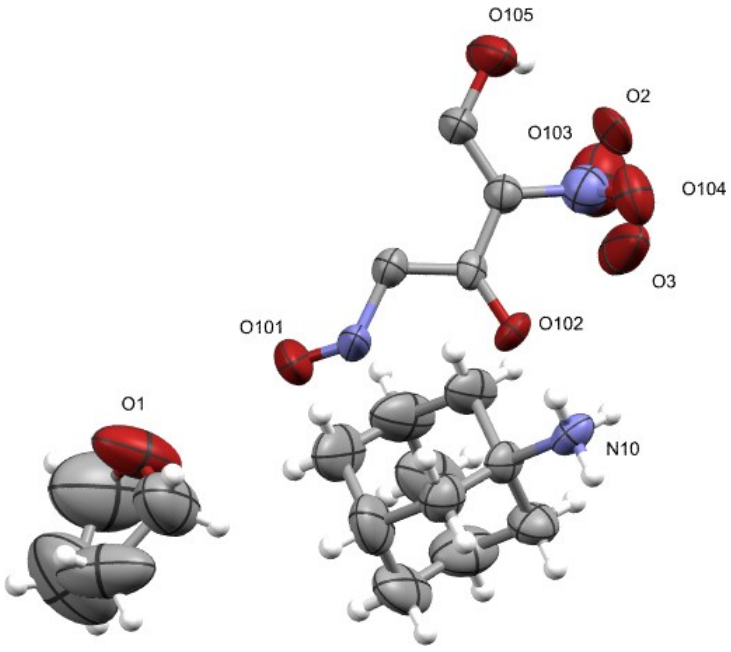

Figure S8 Asymmetric unit of compound **IX** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

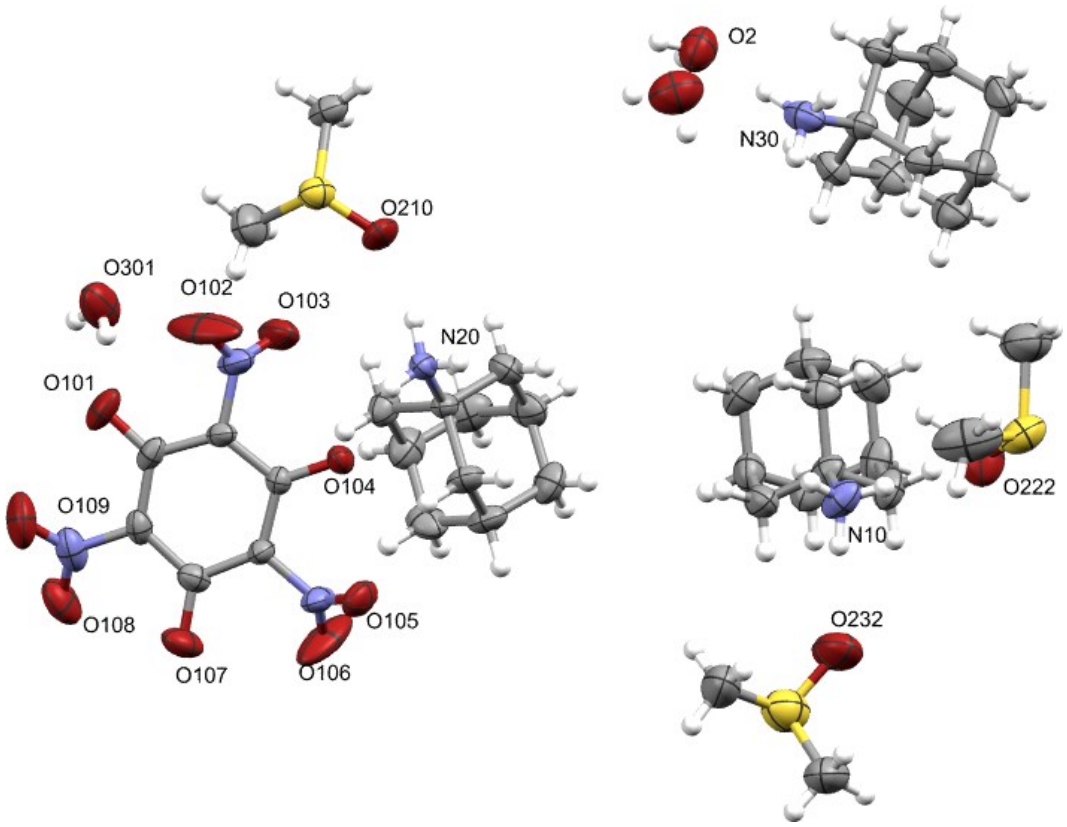

Figure S9 Asymmetric unit of compound **X** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

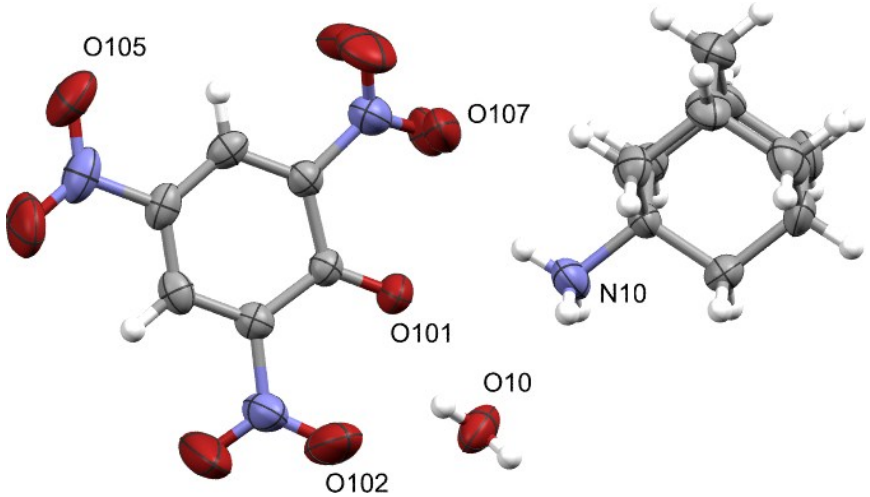

Figure S10 Asymmetric unit of compound **XI** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

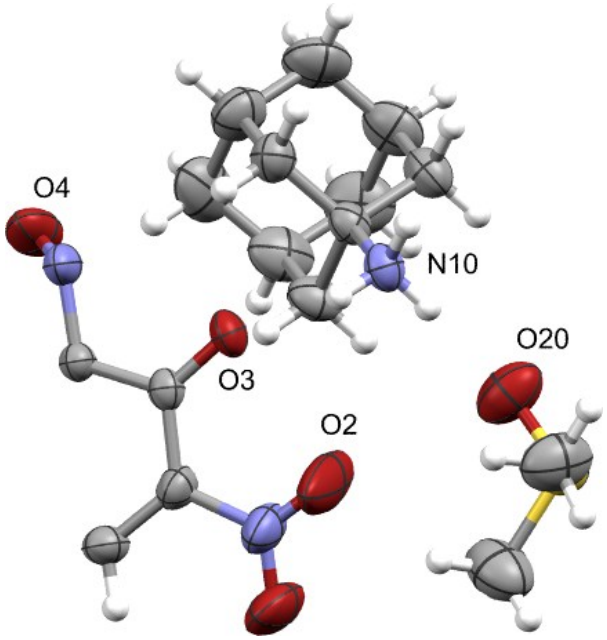

Figure S11 Asymmetric unit of compound **XII** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

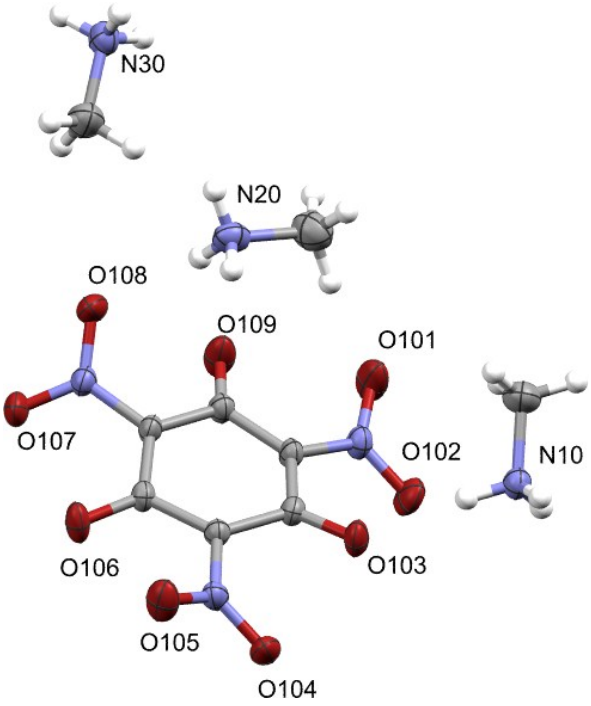

Figure S12 Asymmetric unit of compound **XIII** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

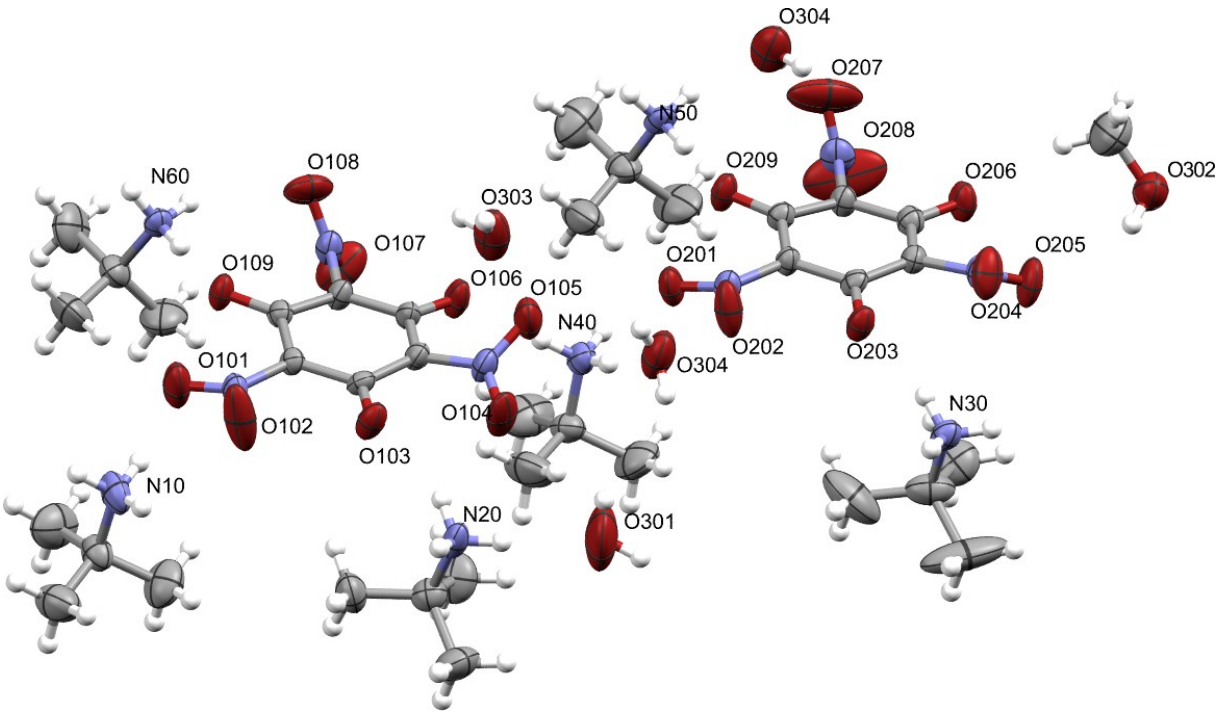

Figure S13 Asymmetric unit of compound **XIV** showing the atom-labelling scheme for hydrogen bond donor and acceptor atoms. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radius.

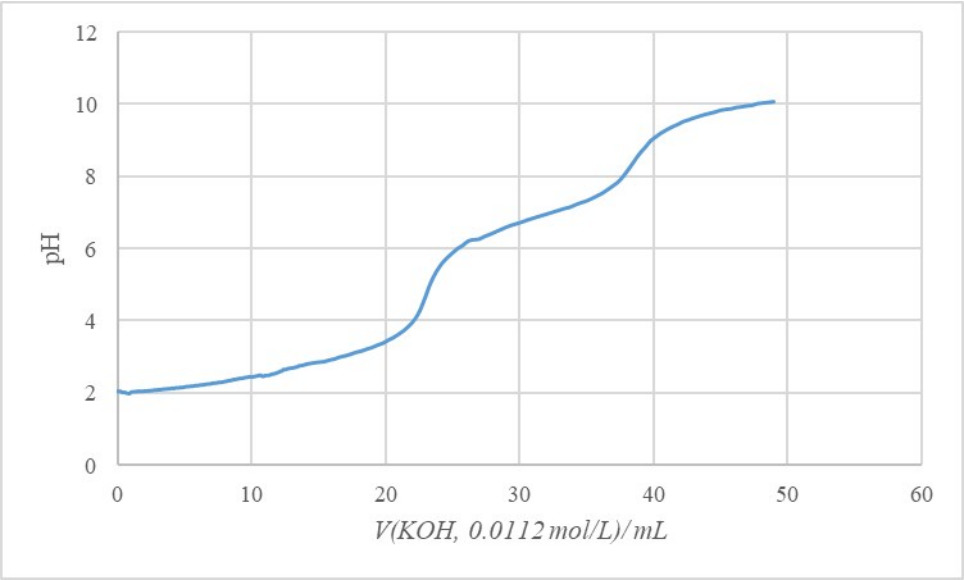

Figure S14 Potentiometric titration curve of an aqueous solution of trinitrophloroglucinol (0.0115 mol/L) with an aqueous solution of potassium hydroxide (0.0112 mol/L) at 22 °C with MettlerToledo EasyFive pH-meter.

Table S16 Atomic coordinates in the optimised structure of **tnpg**$^{3-}$ anion (DFT calculation at the B3LYP/6-311+G(d,p) level of theory).

-2.4017	-1.3260	0.1404	O
2.3526	-1.4119	-0.1375	O
-2.4369	1.4636	0.0846	N
1.2880	-0.7725	0.0029	C
0.0500	2.7559	-0.0039	O
-0.0258	-1.4297	-0.0001	C
2.4884	1.3746	-0.0834	N
-0.0516	-2.8419	-0.0009	N
-1.2237	0.7398	0.0024	C
1.2497	0.6951	-0.0026	C
-2.5414	2.4471	0.8605	O
-1.3151	-0.7254	-0.0022	C
0.0273	1.5062	-0.0020	C
-3.4193	1.1257	-0.6238	O
0.7570	-3.4919	0.7113	O
-0.8835	-3.4612	-0.7136	O
3.4567	1.0023	0.6270	O
2.6293	2.3531	-0.8595	O

Table S17 Atomic coordinates in the optimised structure of H**tnpg**$^{2-}$ anion (DFT calculation at the B3LYP/6-311+G(d,p) level of theory).

1.4433	-2.3386	0.1835	O
1.3643	2.3903	-0.2438	O
-1.3318	-2.4874	0.0288	N
0.7742	1.3151	-0.0756	C
1.4568	0.0419	0.0080	C
-1.4882	2.3833	-0.0452	N
2.8972	0.0817	0.0512	N
-0.6332	-1.2156	0.0132	C
-0.7231	1.2282	-0.0282	C
-2.1503	-2.7143	0.9282	O
0.8424	-1.2601	0.0426	C
-1.3862	-0.0594	-0.0025	C
-1.0709	-3.3066	-0.8539	O
3.4561	0.8314	0.8647	O
3.5428	-0.6414	-0.7209	O
-1.0112	3.5167	0.0671	O
-2.7904	2.2857	-0.1737	O
-2.7218	-0.1442	-0.0356	O
-3.0190	0.8244	-0.1130	H

Table S18 Atomic coordinates in the optimised structure of H_2**tnpg**$^-$ anion (DFT calculation at the B3LYP/6-311+G(d,p) level of theory).

-0.0038	-1.5521	0.0342	C
1.2461	-0.7599	-0.0049	C
1.2286	0.6645	-0.0027	C
0.0036	1.3442	0.0008	C
-1.2251	0.6710	0.0035	C
-1.2500	-0.7534	0.0133	C
2.3496	1.4104	-0.0508	O
3.1353	0.7470	-0.0534	H
-2.3426	1.4228	0.0381	O
-3.1312	0.7633	0.0589	H
-0.0065	-2.8052	0.0909	O
0.0080	2.8008	0.0005	N
-2.4985	-1.4084	0.0239	N
2.4902	-1.4216	-0.0506	N
0.5743	3.3940	0.9628	O
-0.5547	3.3976	-0.9616	O
-3.6078	-0.6703	0.0715	O
-2.6161	-2.6600	-0.0160	O
2.5996	-2.6739	-0.0930	O
3.6044	-0.6893	-0.0527	O