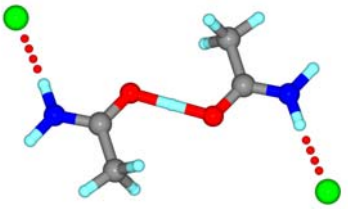
Table S1. Amide salts from CSD. 1-46 are O-protonated; 47-50 are N-protonated. SHB indicates shortest hydrogen bond in the crystal.

No	REFCODE	C=O /Å	C=N /Å	O(N)-H/ /Å	SHB/ Å
1	ACAMBR02	1.268	1.303	--	2.439
2	ACAMCL	1.265	1.305	1.225	2.450
3	AFEGAT	1.272	1.302	---	2.446
4	BOPDUF	1.283	1.309	---	2.434
5	BOZGAY	1.268 1.269	1.307 1.303	--- ---	2.435 2.423
6	BZAMTI01	1.254 1.271 1.274	1.311 1.301 1.298	--- --- ---	2.422 2.422 2.407
7	BIFKEG	1.297	1.306	0.965	2.481
9	BIFKIK	1.299	1.300	0.873	2.534
10	BADCIS10	1.277 1.291	1.328 1.313	--- ---	2.424 2.442
11	CAPNIC	1.275	1.302	---	2.432
12	CAPRLC	1.299 1.303	1.293 1.295	1.060 1.112	2.862 2.879
13	CUGMOG	1.302 1.293	1.301 1.302	0.776 0.850	2.636 2.621
14	CRBAMP06	1.295	1.323	1.176	2.420
15	DAHRAF	1.275 1.274	1.319 1.324	1.116 1.317	2.420 2.420
16	ENANLC	1.307	1.294	0.958	2.922
17	FAJHUT	1.287 1.260	1.237 1.297	--- ---	2.448 2.448
18	FUVMUE	1.308	1.295	0.886	2.922
19	FAMXIA	1.268 1.271	1.302 1.307	--- ---	2.430 2.430
20	HEKYAX	1.298	1.287	0.798	2.889
21	HIRLIE	1.283	1.316	---	2.448
22	JIJRUP	1.268	1.313	1.212	2.424
23	MACMHC	1.304	1.290	0.915	2.869
24	MACMNO	1.287	1.292	1.116	2.566
25	MIJTAB	1.270 1.272	1.330 1.308	1.169 ---	2.453 2.453
26	POCKOH	1.250 1.269	1.341 1.346	--- ---	2.438 2.438
27	PHACHI10	1.254	1.303	---	2.464
28	PELAHC	1.275	1.305	---	2.432
29	SATBAR	1.279	1.310	0..830	2.494

30	SUCABT	1.255 1.263	1.326 1.310	--- ---	2.451 2.451
31	SOYQED	1.294	1.292	0.981	2.463
32	UFAKUH	1.308	1.312	0.862	2.577
33	UFALAO	1.303 1.319	1.323 1.317	0.787 0.797	2.557 2.568
34	UREANT	1.303	1.297	0.988	2.597
35	VAYLEM	1.302	1.307	0.825	2.561
36	VAYLAI	1.279 1.255	1.298 1.319	0.980 ---	2.495 2.495
37	VOPXOO	1.283	1.301	0.814	2.530
38	VOPXUU	1.282	1.302	0.840	2.577
39	VOPYEF	1.271	1.316	0.830	2.413
40	VOPYIJ	1.291	1.298	0.861	2.522
41	VOPYOP	1.325	1.319	0.745	2.642
42	VOPZIK	1.293	1.301	0.855	2.572
43	VOPZOQ	1.290	1.290	0.898	2.567
44	VOCPUY	1.287	1.307	1.177	2.551
45	XIZQAY	1.272 1.282	1.313 1.310	1.220 ---	2.440 2.440
46	Dutasteride salt[a]	1.277	1.291	0.833	2.411
47	NEKPAV	1.168 1.192	1.483 1.524	0.931 0.931	2.789 2.793
48	ja101690u-002[b]	1.201	1.492	0.931	2.721
49	ja101690u-003[b]	1.198	1.490	0.863	2.684
50	ja101690u-004[b]	1.192	1.502	0.892	2.682

[a]present study; [b]reference 10c in the main paper.

O-protonation of amides



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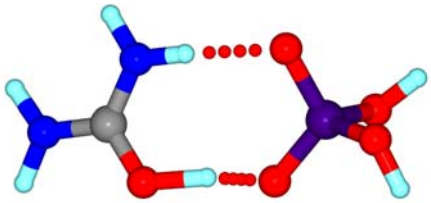

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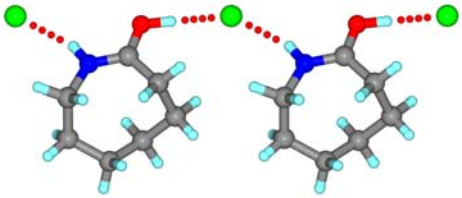
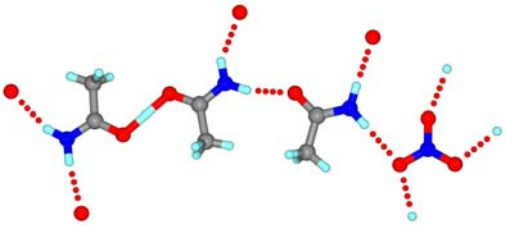
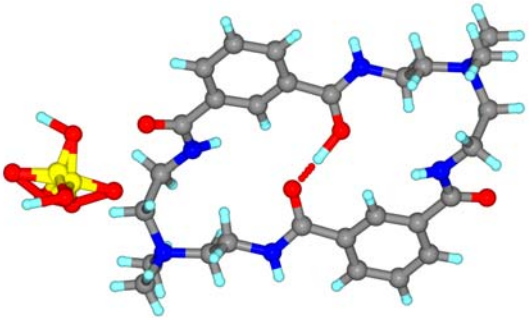


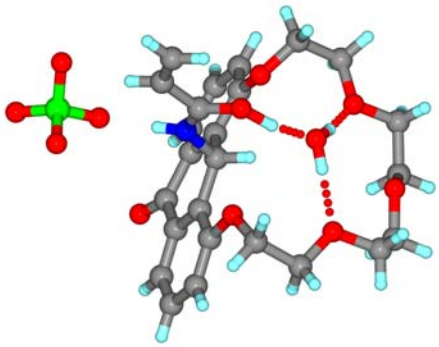
ENANLC



FAMXIA

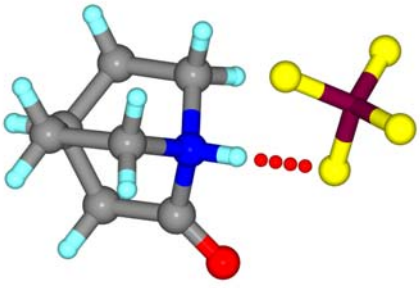


MIJTAB

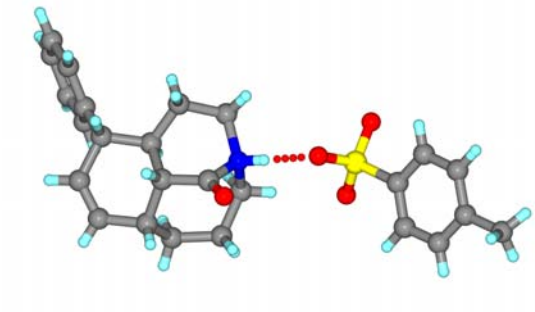


VOPYEF

N-Protonation of amides



NEKPAV



ja101690u-002

Figure S1. Selected literature examples of amide salts.

Complete structural refinement details: Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 9822 reflections in the range of $2.27 < \theta < 20.57°$ for hemihydrate and 3522 reflections in the range of $2.33 < \theta < 24.24°$ for dutasteride salt. Integration and scaling of intensity data were accomplished using SAINT program. The structure was solved by direct methods using SHELXS97 and refinement was carried out by full-matrix least-squares technique using SHELXL97. Anisotropic displacement parameters were included for all non-hydrogen atoms. N-bound H atoms of the dutasteride molecules and H atoms of water molecules of hemihydrate and salt were located in difference Fourier maps and their positions and isotropic displacement parameters were refined. Distance restraints were applied to N-H & O-H of hemihydrate and water O-H of salt, with a set values of 0.84(2) Å for N-H and 0.89(2) Å for O-H, respectively. All other H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.98 Å and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(c) for other H atoms]. The methyl groups were allowed to rotate but not to tip. The fluorine atoms (F4A-F6A, F1B-F3B & F4B-F6B) of the trifluoromethyl (CF3) groups of hemihydrate were disordered over two sites, with occupancies of 0.502(9) and 0.498(9). Similarly, the fluorine atoms (F4-F6) of CF3 group of salt were also disordered over two sites, with occupancies of 0.537(11) and 0.463(9). The anisotropic displacement parameters of the major and minor components were restrained to be similar with SIMU and SAME instructions (SHELXL97, Sheldrick, 2008). The C-F distances of the disordered trifluoromethyl (CF3) groups were restrained to be 1.33(2) Å and the F…F distances to be 2.10(2) Å for hemihydrate. The ethanol solvate in the salt was disordered over two sites (C30/C31/O3 & C301/C311/O31) with site occupancies of 0.727(10) and 0.273(10). Distance restraints were applied to C-C and C-O of the ethanol solvate, with a set value of 1.55(2) and 1.44(2) Å, respectively. The O-bound H atom of ethanol solvate was located in difference Fourier maps and found to be shared by disordered atoms O3 and O31. Their positions and isotropic displacement parameters were refined. **References**: Bruker, SAINT Version 6.28a and SMART version 5.625, Bruker AXS Inc, Madison, Wisconsin, USA, 2000. (e) G. M. Sheldrick, SHELXS97 and SHELXL97, 1997, University of Göttingen, Gernany.