

**Supplementary Table 1b** Statistics for competitiveness for ether oxygen<sup>\*</sup> relative to other groups. (HB acceptor: Z-O-Z, HB donor: Z-H excluding methyl donors). Footnotes same as described in Table 1a.

	<b>Acceptor - 1</b> (HB group for evaluating competitiveness) <sup>@</sup>	<b>Acceptor- 2</b> (co-existing HB group) <sup>@</sup>	Fragments in CSD (N1)	Hydrogen-bonded fragments <sup>§</sup> (N2)	Exclusive hydrogen-bonded fragments <sup>§</sup> (N3)	<b>ASC<sup>§</sup></b> (%)	<b>RSC<sup>§</sup></b> (%)	<b>ESC<sup>§</sup></b> (%)	Mean H...A distance(Å) /D-H...A angle(°) <sup>#</sup>
a)	Carbonyl	-	70454	41408	-	59	-	-	2.26/151
b)	One-ether	-	64928	18682	-	29	-	-	2.41/149
c)	Two-ether	-	33933	10878	-	32	-	-	2.41/149
d)	Three-ether	-	14889	4974	-	33	-	-	2.42/149
e)	Carbonyl in ester	Ether	30429	15070	11699	50	78	38	2.36/149
f)	Ether in ester	Carbonyl	30429	4412	540	14	22	2	2.48/149
g)	Ether excluding ester	-	34499	12041	-	35	-	-	2.39/149
h)	One-ether	Pyridine	2521	778	422	31	44	17	2.44/148
i)	Two-ether	Pyridine	1126	383	212	34	48	19	2.45/148
j)	Three-ether	Pyridine	449	194	110	43	57	24	2.44/149
k)	Pyridine	One-ether	2521	998	586	40	56	23	2.25/157
l)	Pyridine	Two-ether	1126	412	200	37	52	18	2.30/155
m)	Pyridine	Three-ether	449	150	44	33	43	10	2.31/155
n)	One-ether	=N-	13498	3687	2303	27	51	17	2.42/148
o)	Two-ether	=N-	5913	1903	1239	32	58	21	2.42/149
p)	Three-ether	=N-	2348	783	543	33	62	23	2.41/149
q)	=N-	One-ether	13498	3492	1951	26	49	14	2.30/154
r)	=N-	Two-ether	5913	1361	589	23	42	10	2.34/153
s)	=N-	Three-ether	2348	480	170	20	38	7	2.34/153

**Supplementary Table 1c** Statistics for competitiveness for ether oxygen\* relative to other groups. (HB acceptor: C-O-C, HB donor: Z-H). Footnotes same as described in Table 1a.

	<b>Acceptor - 1</b> (HB group for evaluating competitiveness) <sup>@</sup>	<b>Acceptor- 2</b> (co-existing HB group) <sup>@</sup>	Fragments in CSD (N1)	Hydrogen-bonded fragments <sup>§</sup> (N2)	Exclusive hydrogen-bonded fragments <sup>§</sup> (N3)	<b>ASC<sup>§</sup></b> (%)	<b>RSC<sup>§</sup></b> (%)	<b>ESC<sup>§</sup></b> (%)	Mean H...A distance(Å) /D-H...A angle(°) <sup>#</sup>
a)	One-COC	-	57385	23450	-	41	-	-	2.43 / 149
b)	Two-COC	-	30229	15257	-	50	-	-	2.44 / 149
c)	Three-COC	-	13255	7867	-	59	-	-	2.44 / 149
d)	One-COC	Pyridine	2190	863	424	39	45	19	2.46 / 148
e)	Two-COC	Pyridine	1026	481	255	47	52	25	2.46 / 148
f)	Three-COC	Pyridine	413	259	143	63	61	35	2.45 / 148
g)	Pyridine	One-COC	2190	1045	606	48	55	28	2.28 / 156
h)	Pyridine	Two-COC	1026	453	227	44	48	22	2.33 / 155
i)	Pyridine	Three-COC	413	171	55	41	39	13	2.33 / 155
j)	One-COC	=N-	11239	4070	2612	36	54	23	2.43 / 149
k)	Two-COC	=N-	4805	2304	1550	48	63	32	2.44 / 149
l)	Three-COC	=N-	1851	1017	712	55	68	38	2.43 / 149
m)	=N-	One-COC	11239	3433	1975	31	46	18	2.33 / 154
n)	=N-	Two-COC	4805	1362	608	28	37	13	2.37 / 153
o)	=N-	Three-COC	1851	479	174	26	32	9	2.39 / 152

**Supplementary Table 1d** Statistics for competitiveness for ether oxygen<sup>\*</sup> relative to other groups. (HB acceptor: C-S-C, HB donor: Z-H). Footnotes same as described in Table 1a.

	<b>Acceptor - 1</b> (HB group for evaluating competitiveness) <sup>@</sup>	<b>Acceptor- 2</b> (co-existing HB group) <sup>@</sup>	Fragments in CSD (N1)	Hydrogen-bonded fragments (N2)	Exclusive hydrogen-bonded fragments (N3)	<b>ASC<sup>§</sup></b> (%)	<b>RSC<sup>§</sup></b> (%)	<b>ESC<sup>§</sup></b> (%)	Mean H...A distance(Å) /D-H...A angle(°) <sup>#</sup>
a)	One-CSC	-	11562	2735	-	24	-	-	2.80 / 149
b)	Two-CSC	-	3792	1290	-	34	-	-	2.80 / 149
c)	Three-CSC	-	1243	568	-	46	-	-	2.80 / 149
d)	One-CSC	Pyridine	689	190	85	28	36	12	2.80 / 149
e)	Two-CSC	Pyridine	240	96	43	40	44	18	2.80 / 149
f)	Three-CSC	Pyridine	67	31	12	46	42	18	2.80 / 149
g)	Pyridine	One-CSC	689	336	231	49	64	34	2.33 / 155
h)	Pyridine	Two-CSC	240	123	70	51	56	29	2.43 / 154
i)	Pyridine	Three-CSC	67	43	24	64	58	36	2.44 / 153
j)	One-CSC	=N-	3867	683	385	18	31	10	2.80 / 148
k)	Two-CSC	=N-	768	209	131	27	43	17	2.80 / 149
l)	Three-CSC	=N-	131	50	33	38	53	25	2.80 / 151
m)	=N-	One-CSC	3867	1558	1260	40	69	33	2.31 / 156
n)	=N-	Two-CSC	768	274	196	36	57	26	2.40 / 153
o)	=N-	Three-CSC	131	45	28	34	47	21	2.49 / 154

**Supplementary Table 1e** Statistics for competitiveness for ether oxygen\* relative to other groups. (HB acceptor: Z-O-Z, HB donor: C-H). Footnotes same as described in Table 1a.

	<b>Acceptor - 1</b> (HB group for evaluating competitiveness) <sup>@</sup>	<b>Acceptor- 2</b> (co-existing HB group) <sup>@</sup>	Fragments in CSD (N1)	Hydrogen-bonded fragments (N2)	Exclusive hydrogen-bonded fragments (N3)	<b>ASC<sup>s</sup></b> (%)	<b>RSC<sup>s</sup></b> (%)	<b>ESC<sup>s</sup></b> (%)	Mean H...A distance(Å) /D-H...A angle(°) <sup>#</sup>
a)	Carbonyl	-	70084	49686	-	71	-	-	2.46 / 147
b)	One-ether	-	64779	23562	-	36	-	-	2.49 / 149
c)	two-ether	-	33866	15688	-	46	-	-	2.49 / 149
d)	three-ether	-	14860	8245	-	55	-	-	2.49 / 149
e)	Carbonyl in ester	Ether	30402	20451	15419	67	77	51	2.47 / 147
f)	Ether in ester	Carbonyl	30402	6172	1140	20	23	4	2.50 / 150
g)	Ether excluding ester	-	34377	13748	-	40	-	-	2.48 / 149
h)	One-ether	Pyridine	2521	933	640	37	57	25	2.48 / 148
i)	Two-ether	Pyridine	1126	515	333	46	59	30	2.48 / 148
j)	Three-ether	Pyridine	449	273	179	61	67	40	2.48 / 148
k)	Pyridine	One-ether	2521	713	420	28	43	17	2.51 / 152
l)	Pyridine	Two-ether	1126	356	174	32	41	15	2.50 / 153
m)	Pyridine	Three-ether	449	136	42	30	33	9	2.50 / 153
n)	One-ether	=N-	13440	4485	3394	33	62	25	2.48 / 149
o)	Two-ether	=N-	5876	2622	1973	45	68	34	2.48 / 149
p)	Three-ether	=N-	2327	1214	914	52	71	39	2.48 / 149
q)	=N-	One-ether	13440	2717	1626	20	38	12	2.52 / 151
r)	=N-	Two-ether	5876	1238	589	21	32	10	2.52 / 151
s)	=N-	Three-ether	2327	490	190	21	29	8	2.52 / 151

**Supplementary Table 1f** Statistics for competitiveness for ether oxygen\* relative to other groups. (HB acceptor: Z-O-Z, HB donor: N-H). Footnotes same as described in Table 1a.

	<b>Acceptor - 1</b> (HB group for evaluating competitiveness)@	<b>Acceptor- 2</b> (co-existing HB group)@	Fragments in CSD (N1)	Hydrogen-bonded fragments (N2)	Exclusive hydrogen-bonded fragments (N3)	<b>ASC</b> <sup>§</sup> (%)	<b>RSC</b> <sup>§</sup> (%)	<b>ESC</b> <sup>§</sup> (%)	Mean H...A distance(Å) /D-H...A angle(°)#
a)	Carbonyl	-	23102	14280	-	62	-	-	2.00 / 158
b)	One-ether	-	14405	1397	-	10	-	-	2.21 / 149
c)	Two-ether	-	6444	805	-	12	-	-	2.21 / 150
d)	Three-ether	-	2275	396	-	17	-	-	2.20 / 151
e)	Carbonyl in ester	Ether	7127	2554	2476	36	95	35	2.07 / 155
f)	Ether in ester	Carbonyl	7127	157	79	2	5	1	2.38 / 141
g)	Ether excluding ester	-	7278	1058	-	15	-	-	2.20 / 150
h)	One-ether	Pyridine	737	48	38	7	21	5	2.24 / 149
i)	Two-ether	Pyridine	298	27	22	9	31	7	2.23 / 150
j)	Three-ether	Pyridine	102	15	13	15	47	13	2.22 / 153
k)	Pyridine	One-ether	737	190	180	26	79	24	2.10 / 161
l)	Pyridine	Two-ether	298	59	54	20	69	18	2.13 / 158
m)	Pyridine	Three-ether	102	17	15	17	53	15	2.17 / 155
n)	One-ether	=N-	4267	411	297	10	32	7	2.25 / 145
o)	Two-ether	=N-	1709	211	159	12	39	9	2.23 / 147
p)	Three-ether	=N-	632	88	66	14	45	10	2.23 / 149
q)	=N-	One-ether	4267	911	797	21	68	19	2.11 / 158
r)	=N-	Two-ether	1709	331	279	19	61	16	2.12 / 158
s)	=N-	Three-ether	632	109	87	17	55	14	2.11 / 159

**Supplementary Table 1g** Statistics for competitiveness for ether oxygen<sup>\*</sup> relative to other groups. (HB acceptor: Z-O-Z, HB donor: O-H). Footnotes same as described in Table 1a.

	Acceptor - 1 (HB group for evaluating competitiveness) @	Acceptor- 2 (co-existing HB group)@	Fragments in CSD (N1)	Hydrogen-bonded fragments (N2)	Exclusive hydrogen-bonded fragments (N3)	ASC <sup>s</sup> (%)	RSC <sup>s</sup> (%)	ESC <sup>s</sup> (%)	Mean H...A distance(Å) /D-H...A angle(°)#
a)	Carbonyl		23397	13911	-	59	-	-	1.86/161
b)	One-ether		18618	3272	-	18	-	-	2.06/151
c)	Two-ether		8934	1932	-	22	-	-	2.08/150
d)	Three-ether		3962	964	-	24	-	-	2.10/148
e)	Carbonyl in ester	Ether	7950	3207	3029	40	91	38	1.94/158
f)	Ether in ester	Carbonyl	7950	286	108	4	9	1	2.22/144
g)	Ether excluding ester	-	10668	2521	-	24	-	-	2.05/151
h)	One-ether	Pyridine	617	71	33	12	19	5	2.12/147
i)	Two-ether	Pyridine	267	36	16	13	25	6	2.21/143
j)	Three-ether	Pyridine	111	24	11	22	37	10	2.22/143
k)	Pyridine	One-ether	617	306	268	50	81	43	1.89/162
l)	Pyridine	Two-ether	267	107	87	40	75	33	1.93/160
m)	Pyridine	Three-ether	111	42	29	38	63	26	1.94/160
n)	One-ether	=N-	3160	425	278	13	30	9	2.10/149
o)	Two-ether	=N-	1283	242	176	19	45	14	2.09/149
p)	Three-ether	=N-	488	103	78	21	51	16	2.10/150
q)	=N-	One-ether	3160	944	797	30	70	25	1.99/158
r)	=N-	Two-ether	1283	289	223	23	55	17	2.00/157
s)	=N-	Three-ether	488	97	72	20	49	15	2.01/157

**Supplementary Table 1h** Statistics for competitiveness for ether oxygen<sup>\*</sup> relative to other groups. (HB acceptor: Z-O-Z, HB donor: methyl group). Footnotes same as described in Table 1a.

	Acceptor - 1 (HB group for evaluating competitiveness) @	Acceptor -2 (co- existing HB group)@	Fragment s in CSD (N1)	Hydrogen- bonded fragments § (N2)	Exclusive hydrogen- bonded fragments § (N3)	ASC \$ (%)	RSC \$ (%)	ESC \$ (%)	Mean H...A distance(Å ) / D-H...A angle(°)#
a)	Carbonyl	-	53830	17332	-	32	-	-	2.48/149
b)	One-ether	-	52855	7648	-	14	-	-	2.50/150
c)	Two-ether	-	29006	6060	-	21	-	-	2.50/149
d)	Three-ether	-	12913	3757	-	29	-	-	2.49/149
e)	Carbonyl in ester	Ether	27392	7900	6813	29	78	25	2.48/149
f)	Ether in ester	Carbonyl	27392	2099	1012	8	22	4	2.51/150
g)	Ether excluding ester	-	25463	3894	-	15	-	-	2.50/150
h)	One-ether	Pyridine	1822	232	203	13	65	11	2.50/148
i)	Two-ether	Pyridine	827	161	137	19	68	17	2.49/148
j)	Three-ether	Pyridine	295	94	79	32	73	27	2.50/147
k)	Pyridine	One-ether	1822	132	103	7	35	6	2.52/153
l)	Pyridine	Two-ether	827	78	54	9	32	7	2.52/155
m )	Pyridine	Three- ether	295	34	19	12	27	6	2.51/156
n)	One-ether	=N-	10411	1331	1186	13	68	11	2.50/149
o)	Two-ether	=N-	4855	947	836	20	74	17	2.50/149
p)	Three-ether	=N-	1950	504	439	26	76	23	2.49/149
q)	=N-	One-ether	10411	646	501	6	32	5	2.55/153
r)	=N-	Two-ether	4855	346	235	7	26	5	2.55/151
s)	=N-	Three- ether	1950	158	93	8	24	5	2.54/151