

SCHEME 1: Experimental GA Ladder Together with Computational Data and AN pK_a Values^{a-i}

No	Acid	Directly measured ΔGA	GA exp	GA ^b calc	PA calc	pK _a Acetonitrile
1	(CF ₃ CO) ₂ NH		307.5	(303.4), 308.4, 308.5 ^c	(311.2), 316.2	
2	(CF ₃ CO) ₂ CHF	1.3, 1.9, 3.1	306.6	(300.6), 308.2	(308.2), 315.5	
3	(C ₃ F ₇ CO) ₂ CH ₂	5.8	305.6	(304.5)	(311.9)	
4	(2-C ₁₀ F ₇) ₂ CHCN	3.0	304.2	(298.7)	(306.1)	
5	(4-Cl-C ₆ H ₄ -SO ₂) ₂ NH	2.5	302.6	(304.2)	(311.6)	10.20 ^d
6	C ₆ (CN) ₅ CH ₃	5, 1.5	301.6	(300.4), 304.7	(308.5), 311.2	20.14 ^e
7	Tos-NH-SO ₂ -C ₆ H ₄ -4-NO ₂ ^f	1.8	301.2	(304.7)	(310.5)	10.04 ^d
8	C ₆ (CF ₃) ₅ SH	0.8	300.9	(288.2)	(294.7)	10.10
9	(CF ₃ SO ₂) ₂ CH ₂	2.6	300.6	(297.9), 297.9, 297.4 ^c	(305.6), 305.3	
10	C ₆ H ₅ -CH(Tf) ₂ ^g	1.8, 1.9, 1.6, 0.3, 0.8	300.0	(300.3), 297.4	(307.7), 305.0	7.85 ^d
11	Tos-NH-SO ₂ -C ₆ H ₃ -4-Cl-3-NO ₂	1.7, 4.1, 0.7, 3.5	299.8	(301.9)	(308.3)	9.71
12	C ₆ (CF ₃) ₅ OH	1.4, 0.4	299.0	(290.2) ^h	(297.8)	10.46 ^h
13	4-CH ₃ -C ₆ H ₄ -S(=NTf) ₂ NH ₂	1.9, 1.4, 0.4, 2.8	298.8	(297.9)	(306.9)	
14	2,4,6-Tf ₃ -C ₆ H ₂ -NHOH	1.9, 2.0, 3.9, 3.8	297.5	(298.3)	(305.5)	
15	4-Cl-C ₆ H ₄ -SO ₂ -NH-SO ₂ -C ₆ H ₄ -4-NO ₂	2.0	297.0	(298.2)	(305.3)	9.17 ^e
16	4-Cl-C ₆ H ₄ -SO ₂ -NH-SO ₂ -C ₆ H ₃ -4-Cl-3-NO ₂	0.8, 2.8	296.1	(297.8)	(304.5)	8.80
17	C ₆ F ₅ -SO ₂ -NH-SO ₂ -C ₆ H ₄ -4-Cl	-3.6, 3.1, 5.8	296.0	(297.2)	(304.5)	7.57
18	4-Cl-C ₆ H ₄ -SO ₂ -NH-Tf	3.0, 5.8	294.8	(296.1)	(303.4)	5.33 ^e
19	(3-NO ₂ -C ₆ H ₄ -SO ₂) ₂ NH	4.3	293.3	(293.8)	(301.2)	8.15
20	3-NO ₂ -C ₆ H ₄ -SO ₂ -NH-SO ₂ -C ₆ H ₃ -4-Cl-3-NO ₂	2.3, 0.7, 3.5	291.1	(289.5)	(297.2)	7.88
21	(4-NO ₂ -C ₆ H ₄ -SO ₂) ₂ NH	0.7, 3.5	291.1	(290.9)	(298.7)	8.19 ^e
22	C ₆ F ₅ -SO ₂ -NH-SO ₂ -C ₆ H ₄ -3-NO ₂	-1.8, 3.0	290.3	(292.7)	(298.5)	6.73
23	C ₆ F ₅ -SO ₂ -NH-SO ₂ -C ₆ H ₄ -4-NO ₂	3.3, 1.7	289.2	(291.4)	(299.0)	6.60
24	C ₆ F ₅ -SO ₂ -NH-SO ₂ -C ₆ H ₃ -4-Cl-3-NO ₂	-1.5, 2.4	287.8	(290.8)	(298.2)	6.20
25	(C ₆ F ₅ SO ₂) ₂ NH	1.3, 1	287.5	(289.4)	(296.5)	5.40
26	Tf ₂ NH	1.3, 1	286.5	(286.4), 285.9, 283.3 ⁱ	(294.0), 294.1	
27	Tf-NH-SO ₂ C ₂ F ₅	-2.2, 1.4	285.2	(283.9), 285.3	(291.1), 293.1	
28	CF ₂ (CF ₂ SO ₂) ₂ NH	1.5, 1.6, 2.6, 2.8, 2.8	284.2	(284.1), 283.3	(291.3), 290.5	
29	(C ₂ F ₅ SO ₂) ₂ NH	0.4	283.7	(284.3), 284.2	(291.1), 291.0	

^a All data from this work, unless indicated otherwise. See the Supporting Information for computational methods. ^b Without parentheses: G3(MP2). In parentheses: DFT B3LYP 6-311+G**. ^c Ref 6. ^d Ref 12. ^e Ref 13. ^f Tos denotes the 4-CH₃-C₆H₄-SO₂- group. ^g Tf denotes the CF₃SO₂- group. ^h Ref 5. ⁱ Ref 14, DFT B3LYP 6-31+G*.