Electronic Supplementary Information for Anion recognition by silanetriol in acetonirile

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General

All reagents used were of analytical grade. Acetonitrile was distilled over calcium hydride. NMR spectra were measured on a JEOL ECA-500 (500 MHz) spectrometer. UV-vis spectra were recorded on a Shimadzu UV-2500PC spectrometer with a thermal regulator (± 0.5 ºC). Fluorescence spectra were recorded on a Horiba Jobin Yvon Fluoromax 3 spectrofluorometer. FT-IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analysis was performed with Yanaco MT-5. Column chromatography was performed by using Silica Gel 60N from Kanto Reagents. Melting points were determined with a Yanaco MP-J3 micro melting point apparatus and are uncorrected.

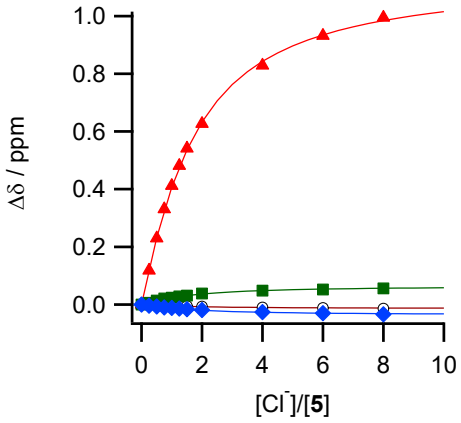

Fig. S1. Chemical shift changes of receptor **5** upon the addition of Cl^- in MeCN-d_3 at 298 K. [**5**] = 5.0×10^{-3} mol dm^{-3}. SiOH (▲), 3- and 5-CH (♦), CH of 2- and 6-iPr (■), and CH of 4-iPr (●). Curved lines indicate theoretical binding isotherms from curve-fitting anlysis.

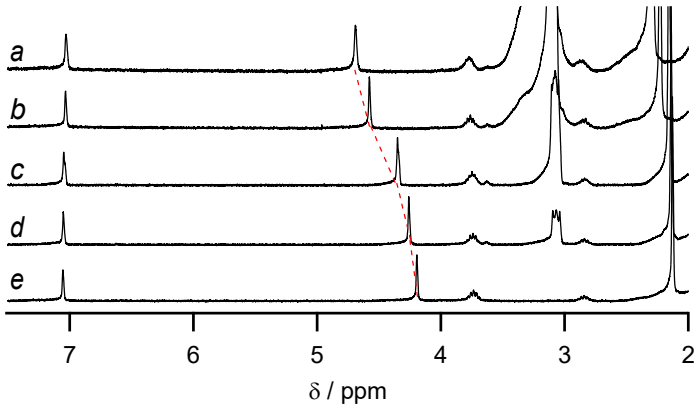

Fig. S2. ^{1}H NMR titration of receptor **5** with TBABr in MeCN-d_3 at 298 K. [**5**] = 5.0×10^{-3} mol dm^{-3}. [Br^-]/[**5**] = 14.0 (*a*), 8.0 (*b*), 2.0 (*c*), 0.75 (*d*), and 0 (*e*) equiv.

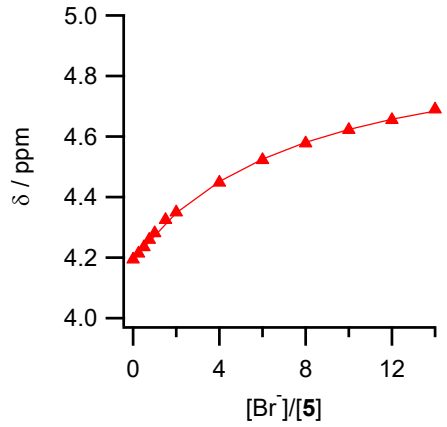

Fig. S3. Chemical shift changes of the silanol OH proton of receptor **5** upon the addition of Br^- in MeCN-d_3 at 298 K. [**5**] = 5.0×10^{-3} mol dm^{-3}.

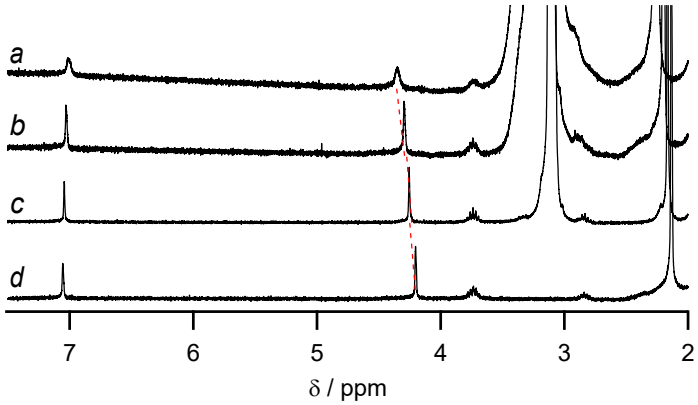

Fig. S4. ^{1}H NMR titration of receptor **5** with TBAI in MeCN-d_3 at 298 K. [**5**] = 5.0×10^{-3} mol dm^{-3}. $[I^-]/[5]$ = 60.0 (*a*), 30.0 (*b*), 12.0 (*c*), and 0 (*d*) equiv.

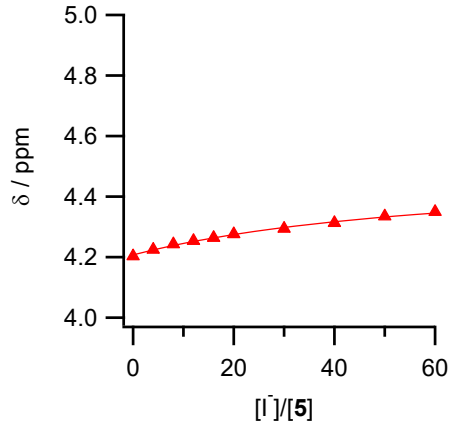

Fig. S5. Chemical shift changes of the silanol OH proton of receptor **5** upon the addition of I^- in MeCN-d_3 at 298 K. [**5**] = 5.0×10^{-3} mol dm^{-3}.

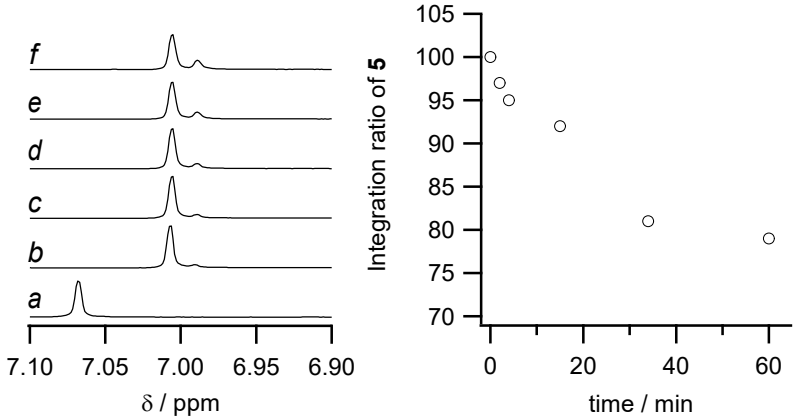

Fig. S6. ^{1}H NMR spectra of receptor **5** in the presence of 1 equiv. of AcO^- in MeCN-d_3 at 298 K. [**5**] = [AcO^-] = 5.0×10^{-3} mol dm^{-3}. Left: (*a*) In the absence of AcO^-; (*b*) 2 min, (*c*) 4 min, (*d*) 15 min, (*e*) 34 min, and (*f*) 60 min after addition of AcO^-. Right: Time course of the integration ratio of the peak corresponding to 3- and 5-CH of Tip moiety of **5**·AcO^- and a newly formed peak in the upfield region.

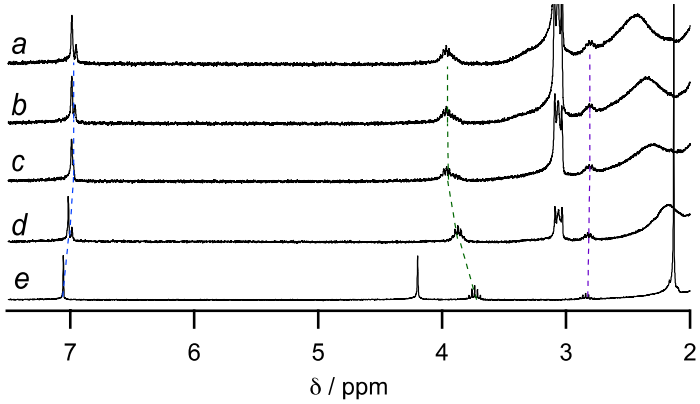

Fig. S7. ^{1}H NMR titration of receptor **5** with TBAAcO in MeCN-d_3 at 298 K. [**5**] = 5.0×10^{-3} mol dm^{-3}. [AcO^-]/[**5**] = 2.0 (*a*), 1.5 (*b*), 1.0 (*c*), 0.5 (*d*), and 0 (*e*) equiv.

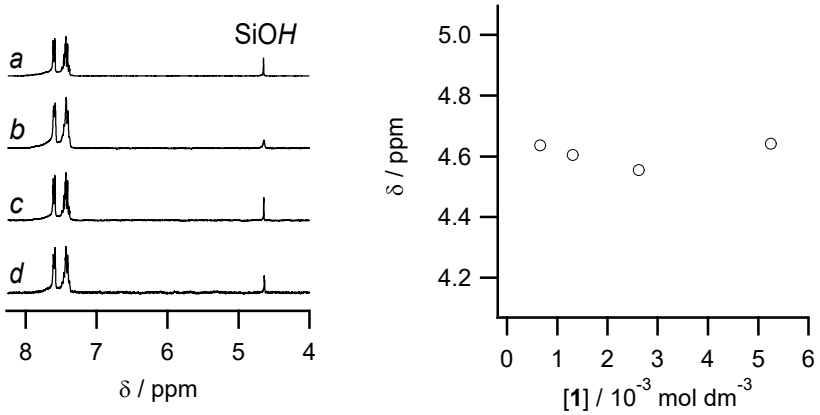

Fig. S8. Dilution experiment of receptor **1** by ^{1}H NMR spectroscopy in MeCN-d_3. [**5**] = 5.25 (*a*), 2.62 (*b*), 1.31 (*c*), and 0.66 mM (*d*).

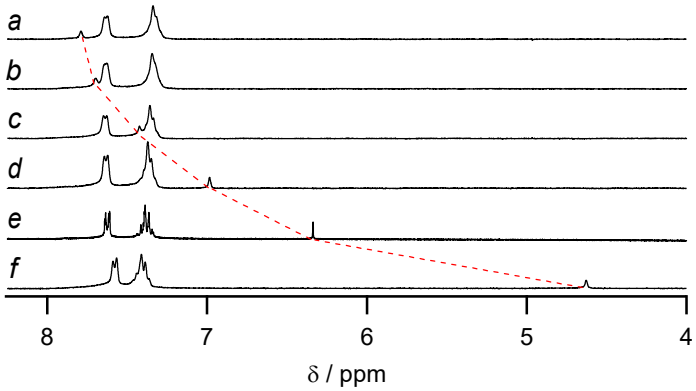

Fig. S9. ^{1}H NMR titrations of receptor **1** with Cl^{-} in MeCN-d_3 at 298 K. [**1**] = 5.0×10^{-3} mol dm^{-3}. [Cl^{-}]/[**1**] = 40.0 (*a*), 33.0 (*b*), 21.0 (*c*), 12.0 (*d*), 6.0 (*e*), and 0 (*f*) equiv.

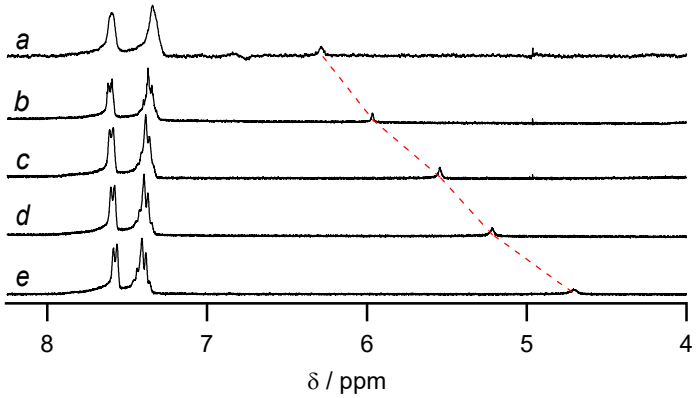

Fig. S10. ^{1}H NMR titrations of receptor **1** with Br^{-} in MeCN-d_3 at 298 K. [**1**] = 5.0×10^{-3} mol dm^{-3}. [Br^{-}]/[**1**] = 80.0 (*a*), 40.0 (*b*), 20.0 (*c*), 10.0 (*d*), and 0 (*e*) equiv.

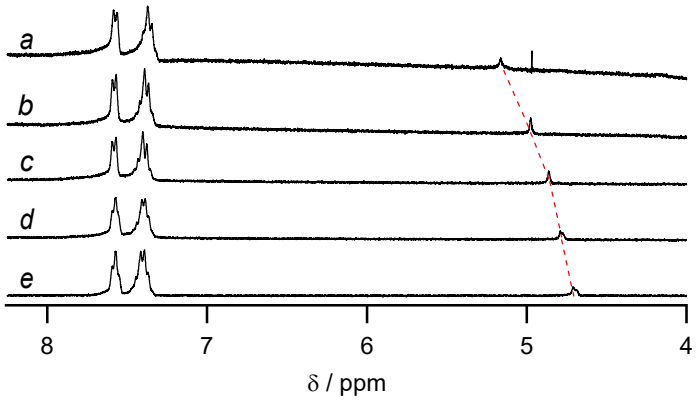

Fig. S11. ^{1}H NMR titrations of receptor **1** with I^{-} in MeCN-d_3 at 298 K. [**1**] = 5.0×10^{-3} mol dm^{-3}. [I^{-}]/[**1**] = 80.0 (*a*), 40.0 (*b*), 20.0 (*c*), 10.0 (*d*), and 0 (*e*) equiv.

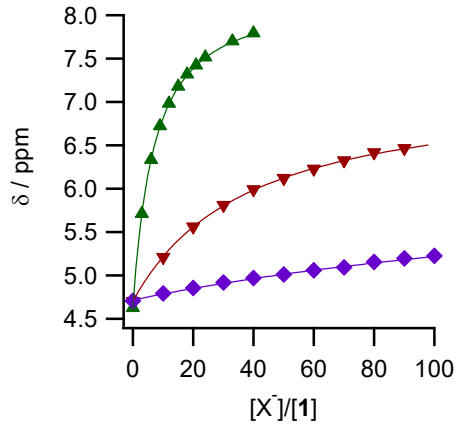

Fig. S12. Chemical shift changes of silanol OH proton upon the addition of X^-. [**1**] = 5.0×10^{-3} mol dm^{-3}.

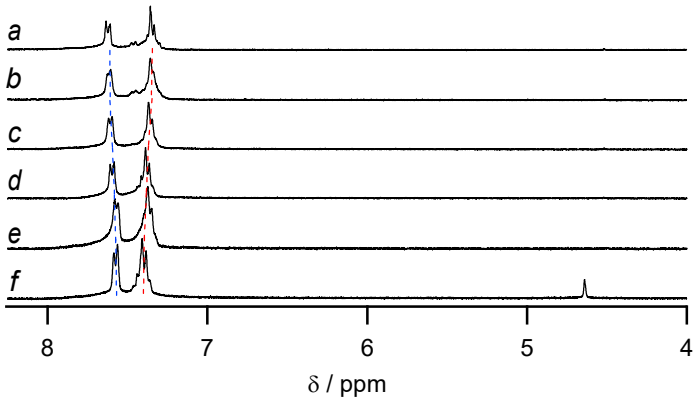

Fig. S13. ^{1}H NMR titrations of receptor **1** with AcO^- in MeCN-d_3 at 298 K. [**1**] = 5.0×10^{-3} mol dm^{-3}. [AcO^-]/[**1**] = 4.5 (*a*), 3.0 (*b*), 1.5 (*c*), 0.8 (*d*), 0.4 (*e*), and 0 (*f*) equiv.

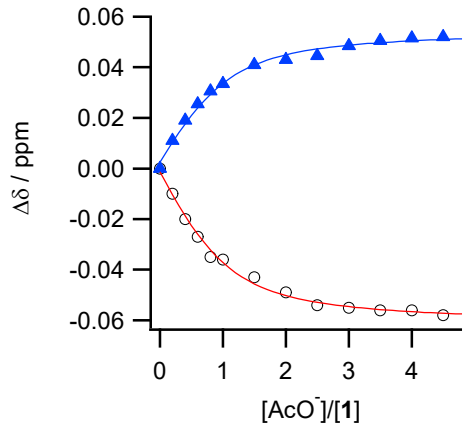

Fig. S14. Chemical shift changes of *o*-CH (▲) and *m*-CH (●) protons upon the addition of AcO^-. [**1**] = 5.0×10^{-3} mol dm^{-3}.

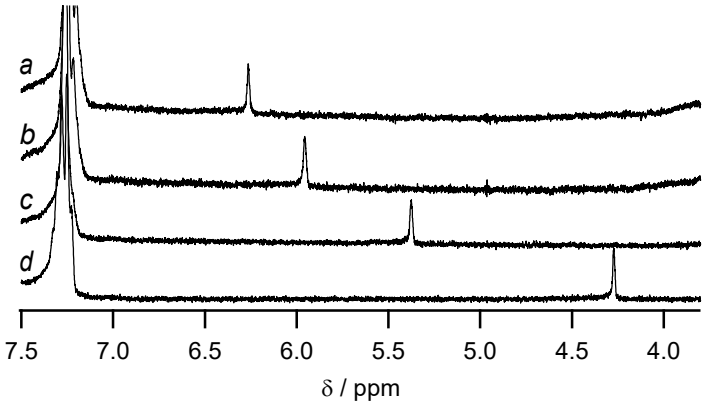

Fig. S15. ^{1}H NMR titrations of receptor **6** (Ph_3COH) with Cl^- in MeCN-d_3 at 298 K. [**6**] = 5.0×10^{-3} mol dm^{-3}. [Cl^-]/[**6**] = 60.0 (*a*), 40.0 (*b*), 20.0 (*c*), and 0 (*d*) equiv.

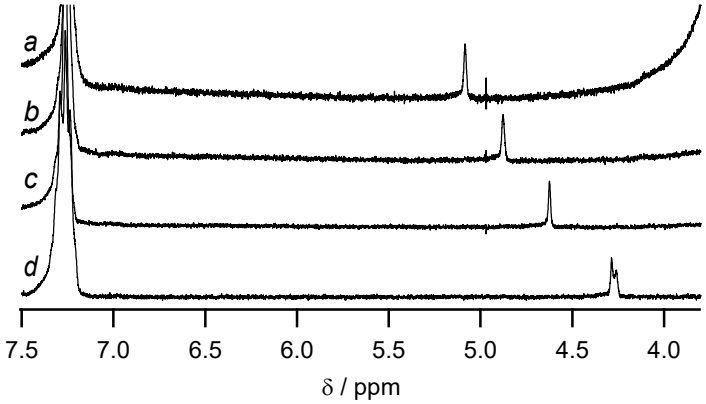

Fig. S16. ^{1}H NMR titrations of receptor **6** (Ph_3COH) with Br^- in MeCN-d_3 at 298 K. [**6**] = 5.0×10^{-3} mol dm^{-3}. [Br^-]/[**6**] = 60.0 (*a*), 40.0 (*b*), 20.0 (*c*), and 0 (*d*) equiv.

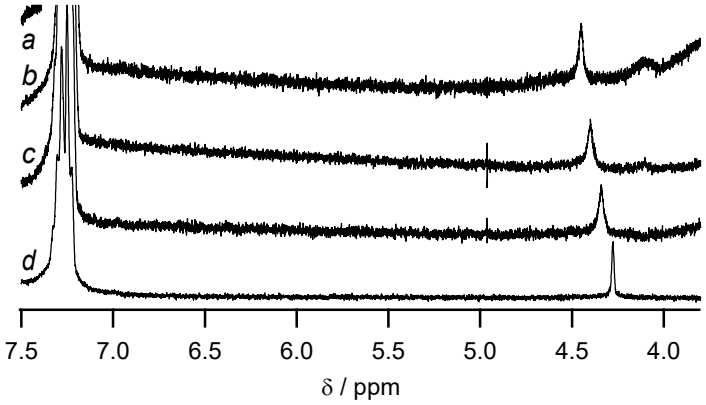

Fig. S17. ^{1}H NMR titrations of receptor **6** (Ph_3COH) with I^- in MeCN-d_3 at 298 K. [**6**] = 5.0×10^{-3} mol dm^{-3}. [I^-]/[**6**] = 60.0 (*a*), 40.0 (*b*), 20.0 (*c*), and 0 (*d*) equiv.

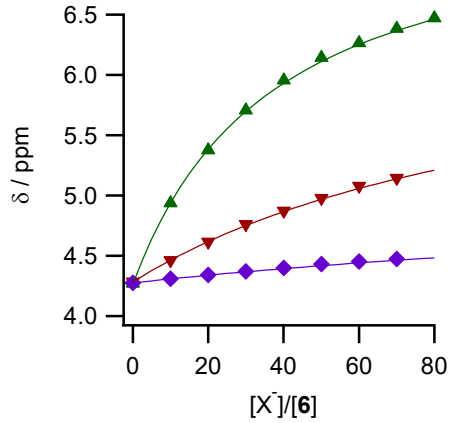

Fig. S18. Chemical shift changes of alcoholic OH group upon the addition of X^-. [**6**] = 5.0×10^{-3} mol dm^{-3}.

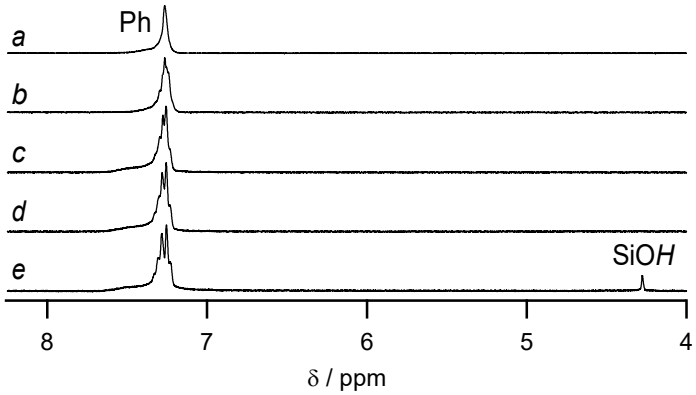

Fig. S19. ^{1}H NMR titrations of receptor **6** (Ph_3COH) with AcO^- in MeCN-d_3 at 298 K. [**6**] = 5.0×10^{-3} mol dm^{-3}. [AcO^-]/[**6**] = 3.0 (*a*), 1.5 (*b*), 0.8 (*c*), 0.4 (*d*), and 0 (*e*) equiv.

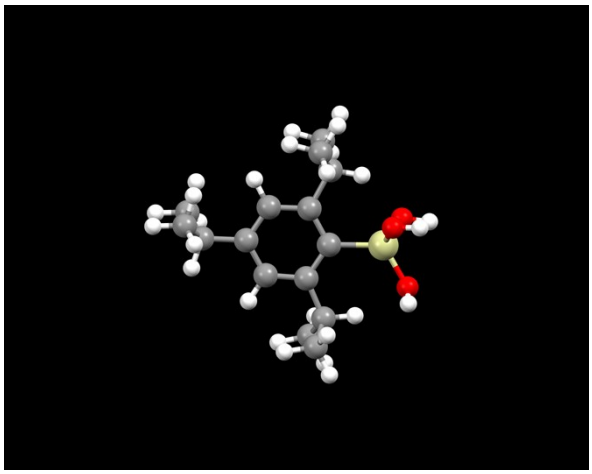

Fig. S20. The optimized structure of **5** by DFT calculation (B3LYP/6-31+G(d) level of theory) in MeCN.

Table S1 Cartesian coordination of the optimized structure of **5** by DFT calculation

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.588	-1.362	-0.073	H	-0.038	2.751	2.134
C	-2.059	1.017	0.022	H	-1.437	3.485	1.326
C	0.107	-0.121	-0.037	H	0.154	4.257	1.213
C	-1.991	-1.369	-0.03	C	-0.446	3.263	-1.304
C	-2.749	-0.199	0.025	H	-0.187	2.707	-2.213
C	-0.661	1.083	-0.01	H	0.075	4.229	-1.337
H	-2.513	-2.323	-0.044	H	-1.523	3.465	-1.326
H	-2.626	1.944	0.043	C	-4.911	0.39	-1.171
C	-0.036	2.483	-0.038	H	-4.542	-0.072	-2.094
H	1.051	2.387	-0.075	H	-4.69	1.464	-1.219
C	-4.271	-0.258	0.073	H	-6.001	0.274	-1.143
H	-4.551	-1.32	0.07	C	-4.831	0.364	1.367
C	0.106	-2.725	-0.154	H	-4.405	-0.117	2.256
H	1.169	-2.561	-0.329	H	-5.921	0.247	1.406
C	-0.022	-3.502	1.173	H	-4.607	1.436	1.424
H	0.385	-2.926	2.013	Si	1.982	0.035	0.022
H	0.525	-4.451	1.115	O	2.472	0.776	-1.39
H	-1.07	-3.733	1.402	H	3.418	0.71	-1.594
C	-0.402	-3.575	-1.337	O	2.333	0.913	1.401
H	-0.313	-3.03	-2.284	H	3.274	1.025	1.61
H	-1.45	-3.874	-1.216	O	2.925	-1.345	0.067
H	0.194	-4.493	-1.419	H	3.041	-1.766	0.933
C	-0.362	3.288	1.236				

Table S2 Cartesian coordination of the optimized structure of **5**·Cl^- by DFT calculation

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.608	-1.386	-0.002	H	-0.099	2.69	2.197
C	-2.064	1.003	0.028	H	-1.472	3.444	1.365
C	0.097	-0.15	0	H	0.124	4.209	1.307
C	-2.013	-1.381	0.01	C	-0.418	3.261	-1.242
C	-2.764	-0.207	0.025	H	-0.138	2.72	-2.153
C	-0.665	1.06	0.015	H	0.102	4.227	-1.246
H	-2.541	-2.332	0.008	H	-1.496	3.463	-1.286
H	-2.624	1.935	0.039	C	-4.894	0.394	-1.221
C	-0.038	2.459	0.02	H	-4.508	-0.074	-2.135
H	1.048	2.363	0.009	H	-4.664	1.466	-1.268
C	-4.287	-0.255	0.038	H	-5.986	0.286	-1.218
H	-4.574	-1.315	0.034	C	-4.871	0.376	1.318
C	0.064	-2.762	-0.018	H	-4.47	-0.104	2.217
H	1.143	-2.624	-0.026	H	-5.963	0.269	1.332
C	-0.269	-3.576	1.25	H	-4.64	1.447	1.376
H	0.012	-3.028	2.158	Si	1.975	0.013	-0.015
H	0.281	-4.526	1.245	O	2.423	0.866	-1.388
H	-1.339	-3.812	1.318	H	3.394	0.976	-1.421
C	-0.292	-3.558	-1.291	O	2.448	0.847	1.361
H	-0.026	-2.998	-2.195	H	3.419	0.957	1.379
H	-1.362	-3.793	-1.343	O	2.808	-1.439	-0.033
H	0.258	-4.508	-1.308	H	3.771	-1.254	-0.04
C	-0.396	3.243	1.299	Cl	5.465	0.437	-0.043

Table S3 Cartesian coordination of the optimized structure of **5**·AcO^- by DFT calculation

Atom	X	Y	Z	Atom	X	Y	Z
C	1.232	1.372	0.046	C	0.714	-3.263	-1.227
C	2.548	-1.096	-0.021	H	0.425	-2.716	-2.132
C	0.457	0.179	0.013	H	0.14	-4.198	-1.198
C	2.634	1.289	0.017	H	1.775	-3.526	-1.314
C	3.317	0.073	-0.026	C	5.367	-0.629	-1.351
C	1.148	-1.07	0.002	H	4.98	-0.126	-2.244
H	3.216	2.207	0.033	H	5.075	-1.685	-1.404
H	3.054	-2.058	-0.034	H	6.463	-0.584	-1.382
C	0.435	-2.427	0.038	C	5.429	-0.648	1.188
H	-0.642	-2.259	0.069	H	5.084	-0.159	2.106
C	4.839	0.034	-0.063	H	6.525	-0.603	1.167
H	5.186	1.076	-0.063	H	5.139	-1.705	1.239
C	0.631	2.778	0.13	Si	-1.431	0.138	-0.047
H	-0.45	2.69	0.211	O	-1.92	-0.803	-1.352
C	1.113	3.537	1.384	H	-2.886	-0.661	-1.471
H	0.898	2.968	2.297	O	-2.003	-0.508	1.377
H	0.597	4.503	1.459	H	-3.003	-0.555	1.368
H	2.19	3.738	1.359	O	-2.162	1.629	-0.288
C	0.915	3.596	-1.147	H	-3.106	1.435	-0.507
H	0.536	3.083	-2.039	H	-7.222	-0.69	0.75
H	1.99	3.768	-1.29	C	-6.721	-0.303	-0.141
H	0.426	4.577	-1.088	H	-7.132	0.682	-0.392
C	0.79	-3.223	1.311	H	-6.932	-0.965	-0.989
H	0.562	-2.646	2.215	C	-5.211	-0.197	0.062
H	1.853	-3.491	1.34	O	-4.531	0.285	-0.905
H	0.211	-4.154	1.348	O	-4.724	-0.589	1.163