

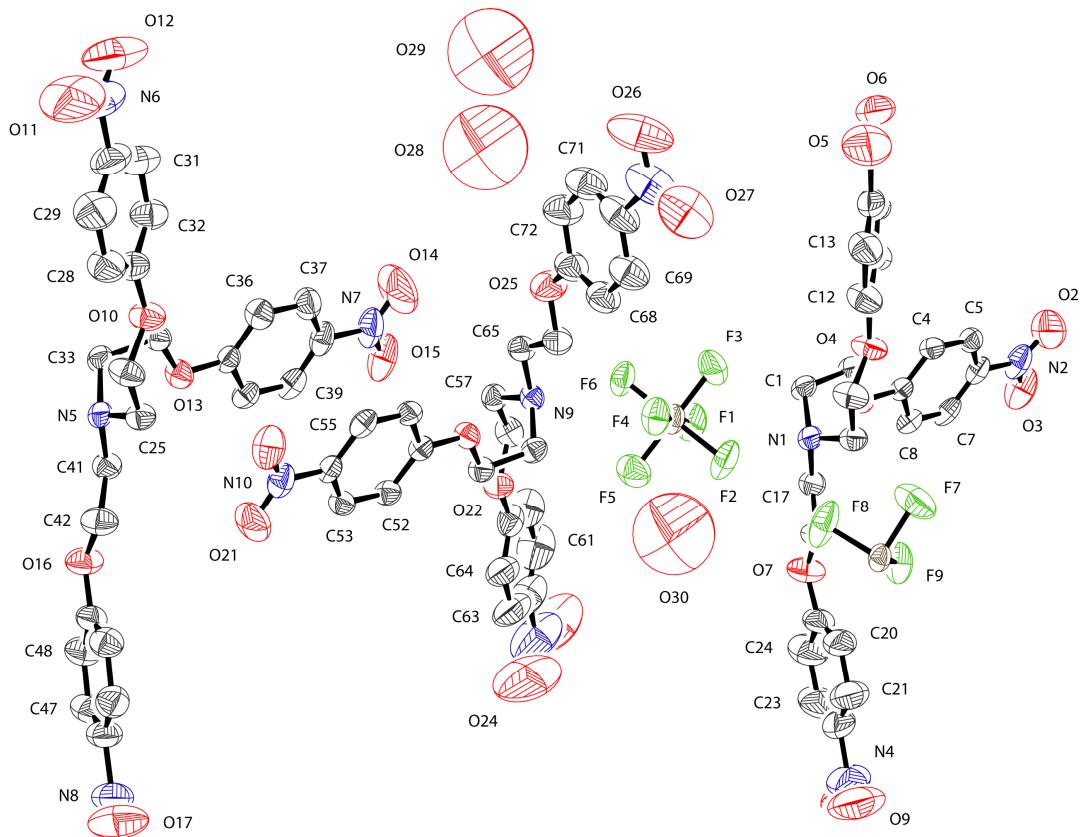
Supplementary Information for:

A subtle interplay of C-H hydrogen bonds in complexation of  
anions of varied dimensionality by a nitro functionalized  
tripodal podand

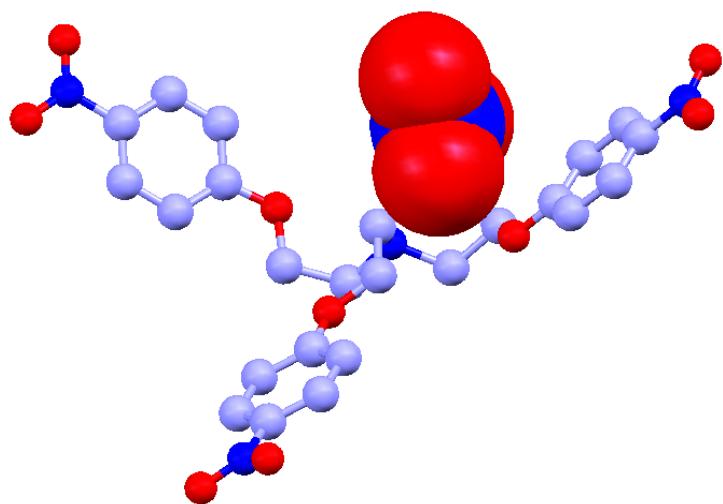
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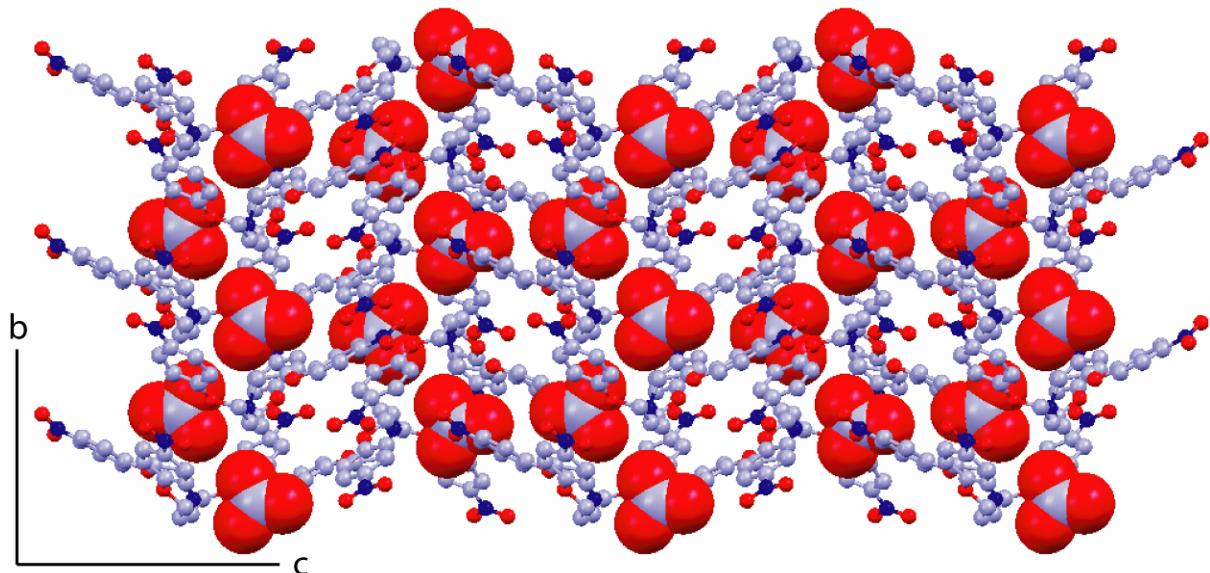
E-mail: [gdas@iitg.ernet.in](mailto:gdas@iitg.ernet.in)



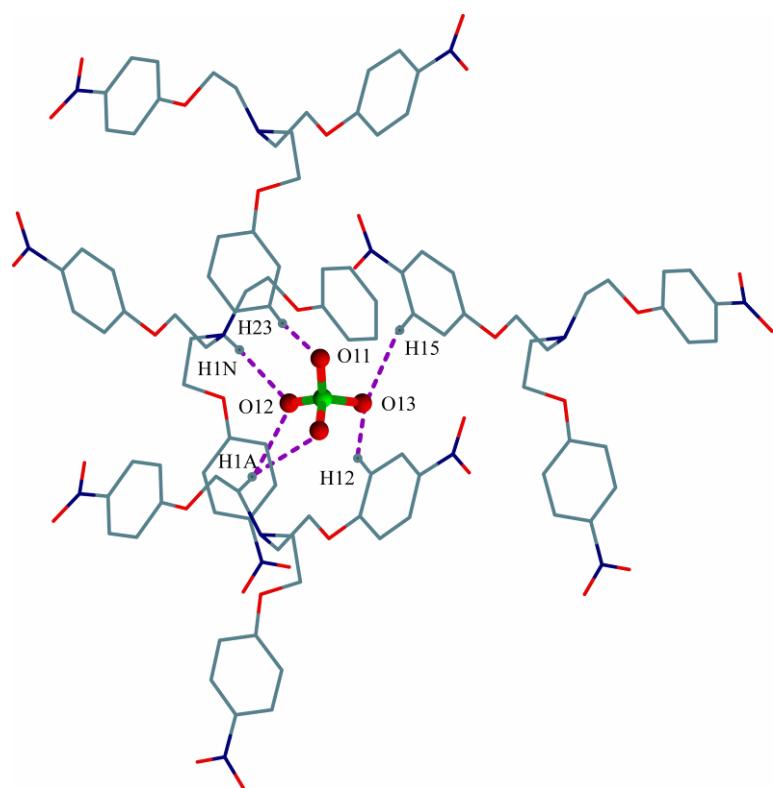
**Figure S1.** ORTEP plot (50 % probability ellipsoids) of  $[\text{HL}^+]\bullet[\text{SiF}_6^-]\bullet1.3\text{ H}_2\text{O}$  (**6**) along with atom numbering scheme.



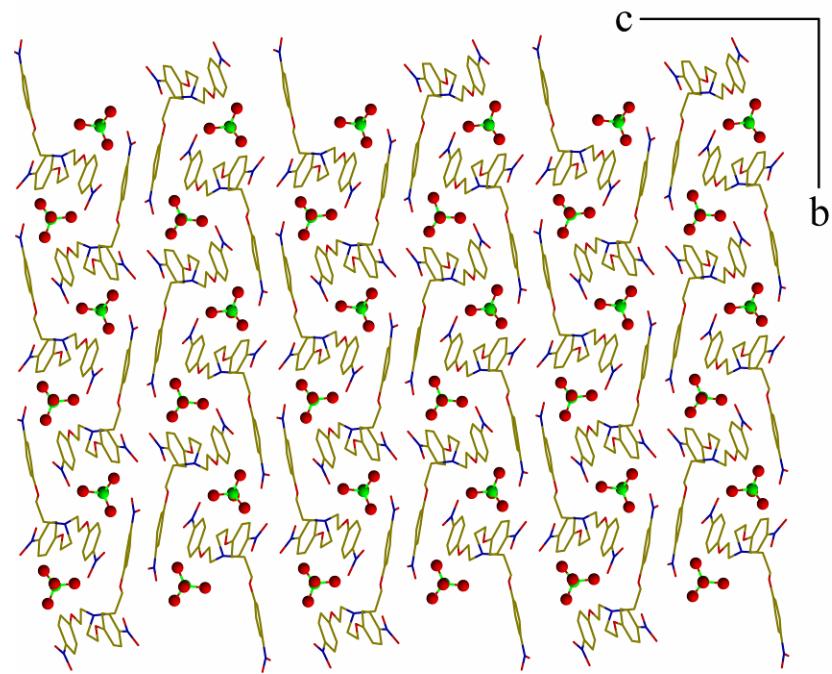
**Figure S2.** Crystal structure of  $[HL^+]\bullet[NO_3^-]$  (**3**) depicting the tripodal cleft shaped cavity in  $HL^+$  unit with the nitrate being placed within the tripodal cleft.



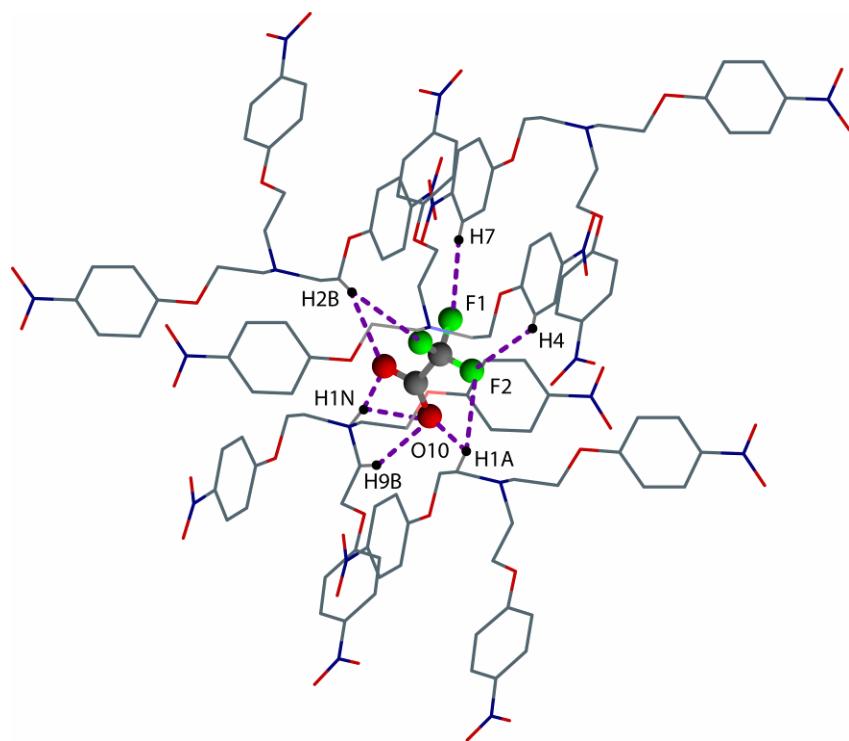
**Figure S3.** Crystal packing diagram of  $[HL^+]\bullet[NO_3^-]$  (**3**) as viewed down the crystallographic *a*-axis showing the zigzag arrangement of the nitrate anions along *b*-axis.



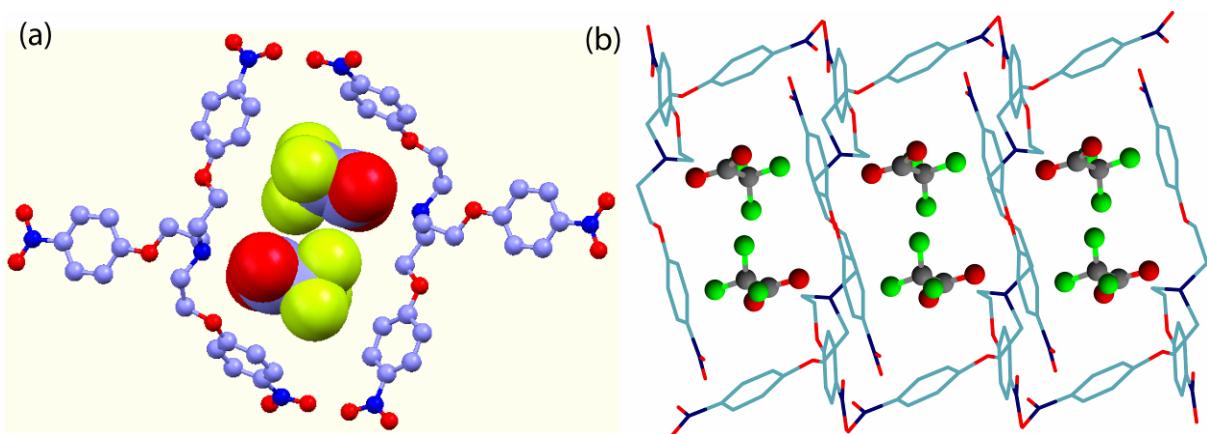
**Figure S4.** Close-up view of perchlorate binding by four encircling  $HL^+$  tripodal receptor molecules in complex  $[HL^+]\bullet[ClO_4^-]$  (**4**).



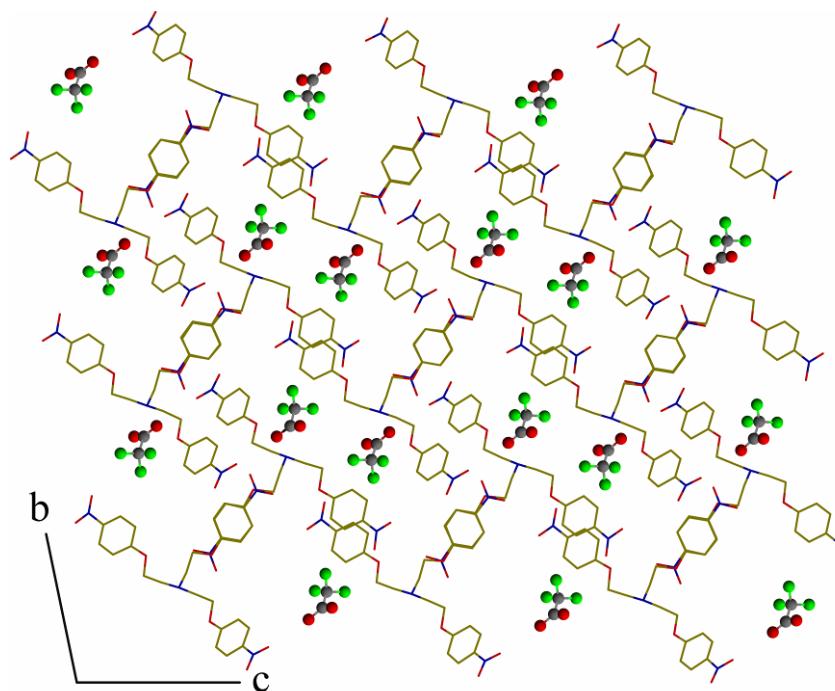
**Figure S5.** Crystal packing diagram of  $[HL^+][ClO_4^-]$  (4) as viewed down the crystallographic *a*-axis showing the zigzag arrangement of the perchlorate anions along *b*-axis.



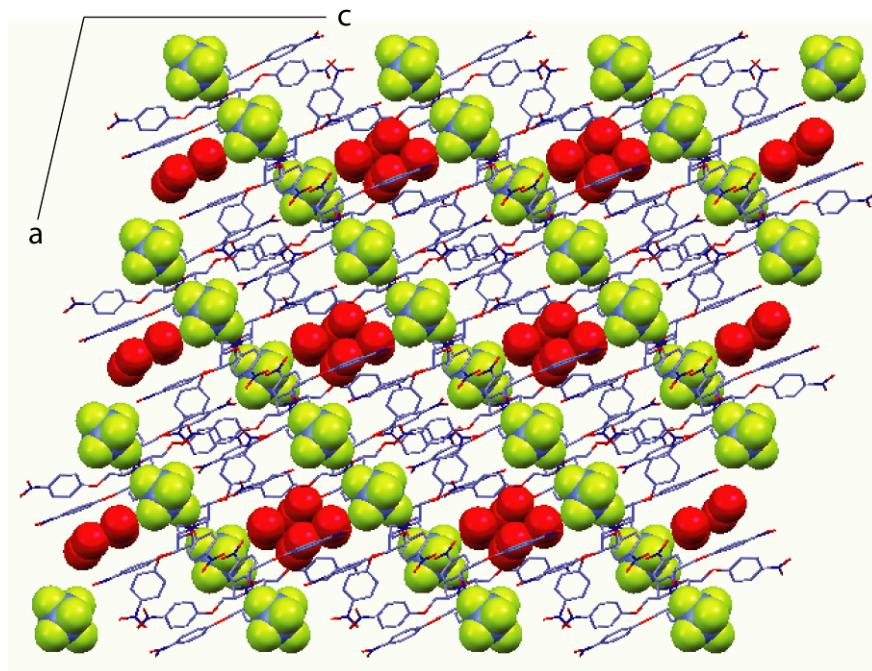
**Figure S6.** Close-up view for binding of trifluoroacetate by five encircling cationic  $HL^+$  tripodal receptor molecules in complex  $[HL^+][CF_3COO^-]$  (5).



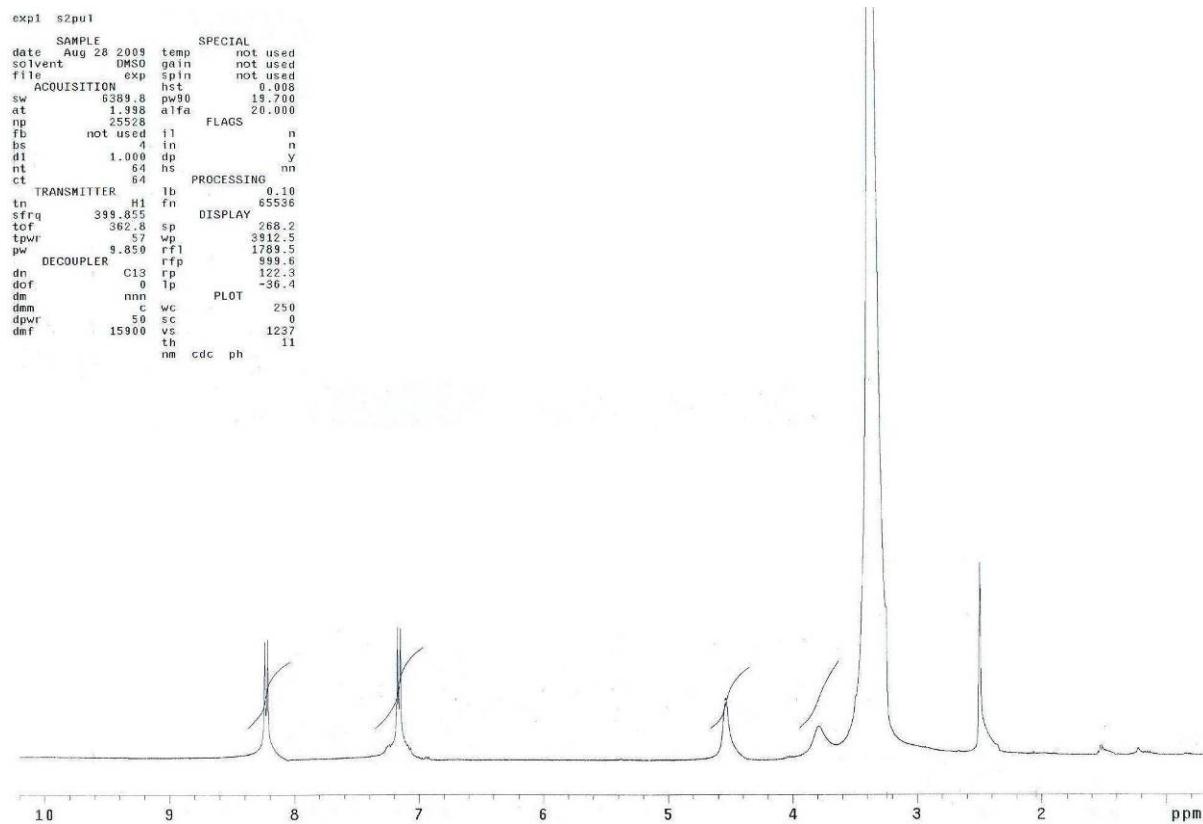
**Figure S7.** Close-up views for the encapsulation of dimeric trifluoroacetate anions within the tripodal cleft of  $\text{HL}^+$  units in  $[\text{HL}^+] \cdot [\text{CF}_3\text{COO}^-]$  (**5**) (Ball and stick representation).



**Figure S8.** Crystal packing diagram of  $[\text{HL}^+] \cdot [\text{CF}_3\text{COO}^-]$  (**5**) as viewed down the crystallographic *a*-axis.

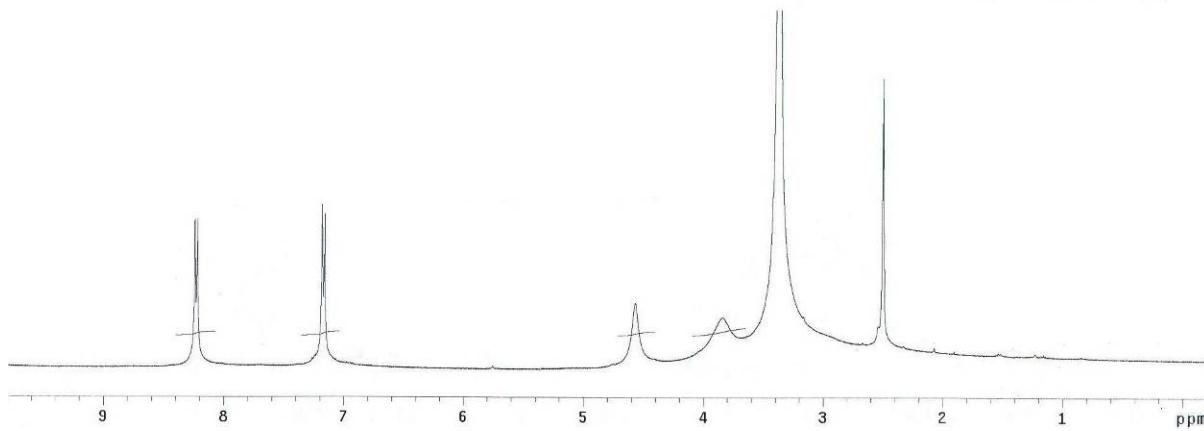


**Figure S9.** Crystal packing diagram of  $[2\text{HL}^+]\cdot[\text{SiF}_6^{-2}]\cdot 2 \text{H}_2\text{O}$  (**6**) as viewed down the crystallographic *b*-axis showing the linear arrangement of  $\text{SiF}_6^-$  ions diagonally along the ac-plane and cluster of water molecules are positioned in the available space between the adjacent tripodal arrays.



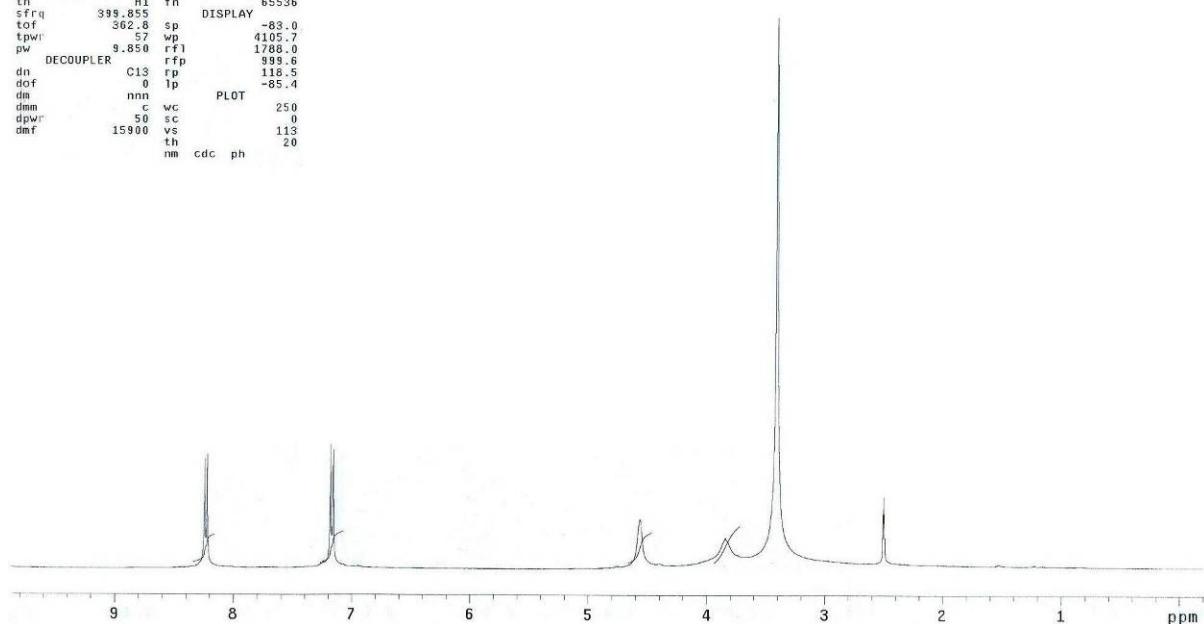
**Figure S10.**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{DMSO}-d_6$ ) of  $[\text{HL}^+]\cdot[\text{Cl}^-]$  (**1**) in  $\text{DMSO}-d_6$ .

```
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solvent DMSO gain not used
file exp spin not used
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sw 6389.8 pw90 19.700
at 1.998 alfa 20.000
np 25528 FLAGS
fb not used il n
bs 4 in n
d1 1.000 dp y
nt 128 hs nn
ct 128 PROCESSING
TRANSMITTER H1 lb 0.10
tn 399.855 fn 65536
sfrq 399.855 DISPLAY
tof 362.8 sp -99.8
tpwr 57 wp 4089.0
pw 9.850 rfl 1788.0
DECOUPLER C13 rfp 899.6
dn C13 rp 120.1
dof 0 lp -95.7
dm nnn PLOT
dmm c wc 250
dpwr 50 sc 0
dmf 15900 vs 749
th nm cdc ph 11
```



**Figure S11.**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{DMSO}-d_6$ ) of  $[\text{HL}^+]\cdot[\text{Br}^-]$  (**2**) in  $\text{DMSO}-d_6$ .

```
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SAMPLE SPECIAL
date Jul 29 2009 temp not used
solvent DMSO gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 6389.8 pw90 19.700
at 1.998 alfa 20.000
np 25528 FLAGS
fb not used il n
bs 4 in n
d1 1.000 dp y
nt 128 hs nn
ct 128 PROCESSING
TRANSMITTER H1 lb 0.10
tn 399.855 fn 65536
sfrq 399.855 DISPLAY
tof 362.8 sp -83.0
tpwr 57 wp 4105.7
pw 9.850 rfl 1788.0
DECOUPLER C13 rfp 899.6
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dpwr 50 sc 0
dmf 15900 vs 113
th nm cdc ph 20
```

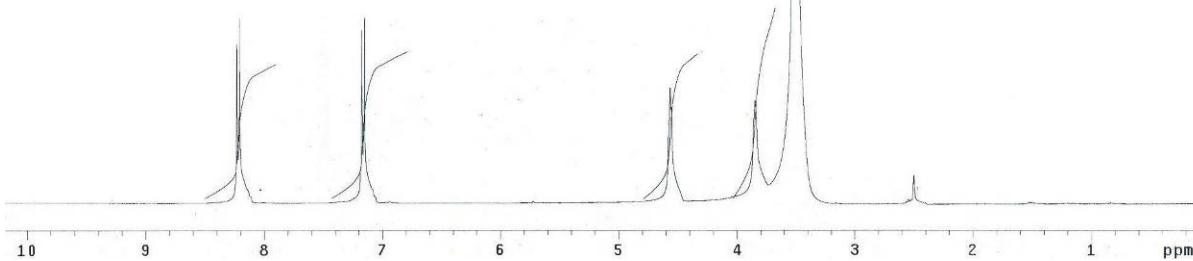


**Figure S12.**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{DMSO}-d_6$ ) of  $[\text{HL}^+]\cdot[\text{NO}_3^-]$  (**3**) in  $\text{DMSO}-d_6$ .

```

exp1 s2pul
SAMPLE SPECIAL
date Oct 21 2009 temp not used
solvent DMSO gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 6389.8 pw90 19.700
at 1.998 alfa 20.000
np 25528 FLAGS
fb not used il n
bs 4 in n
d1 1.000 dp y
nt 64 hs nn
ct 64 PROCESSING
TRANSMITTER 1b 0.10
tn H1 fn 65536
sfrq 399.855 DISPLAY
tof 362.8 sp 34.8
tpwr 57 wp 4105.7
pw 9.850 rfl 1788.0
DECOUPLER rfp 999.6
dn C13 rfp 157.4
dof 0 lp -104.6
dm nnn PLOT
dmm c wc 250
dpwr 50 sc 0
dmf 15900 vs 134
nm cdc ph 16

```

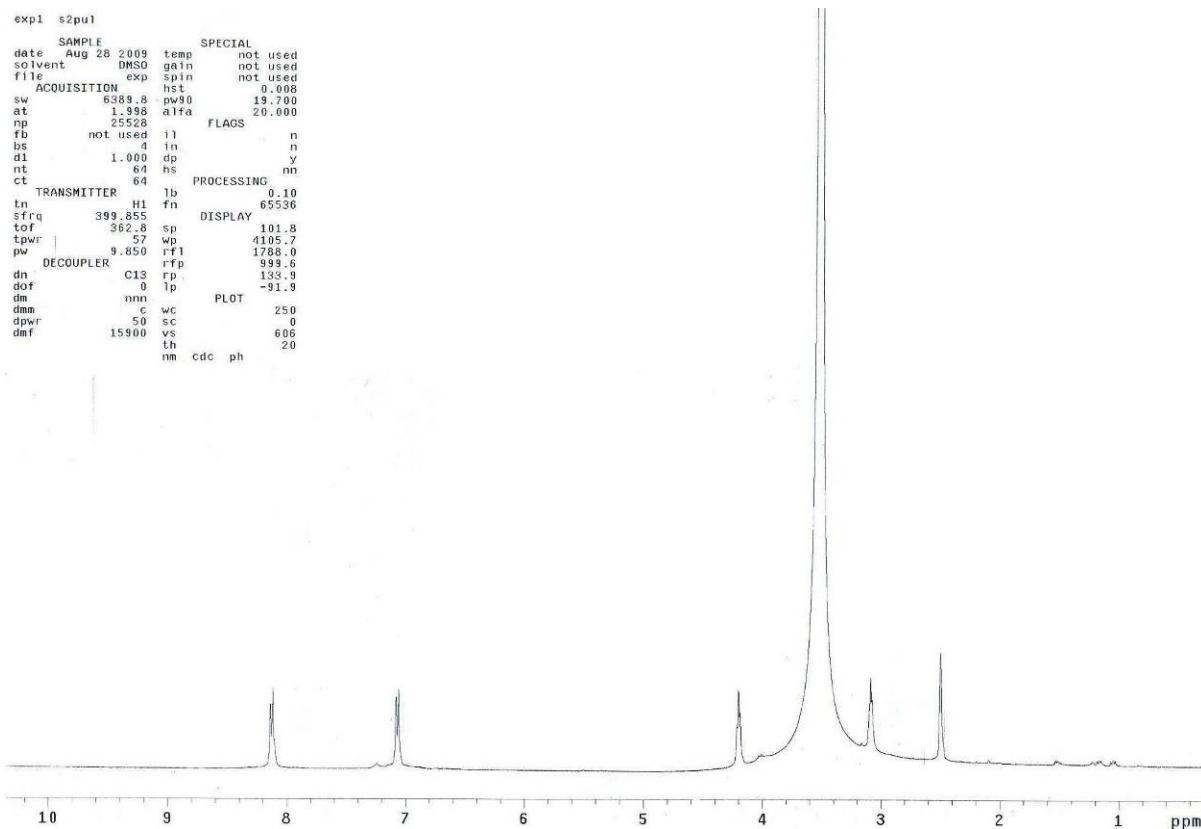


**Figure S13.**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{DMSO}-d_6$ ) of  $[\text{HL}^+]\text{[ClO}_4^-$ ] (**4**) in  $\text{DMSO}-d_6$ .

```

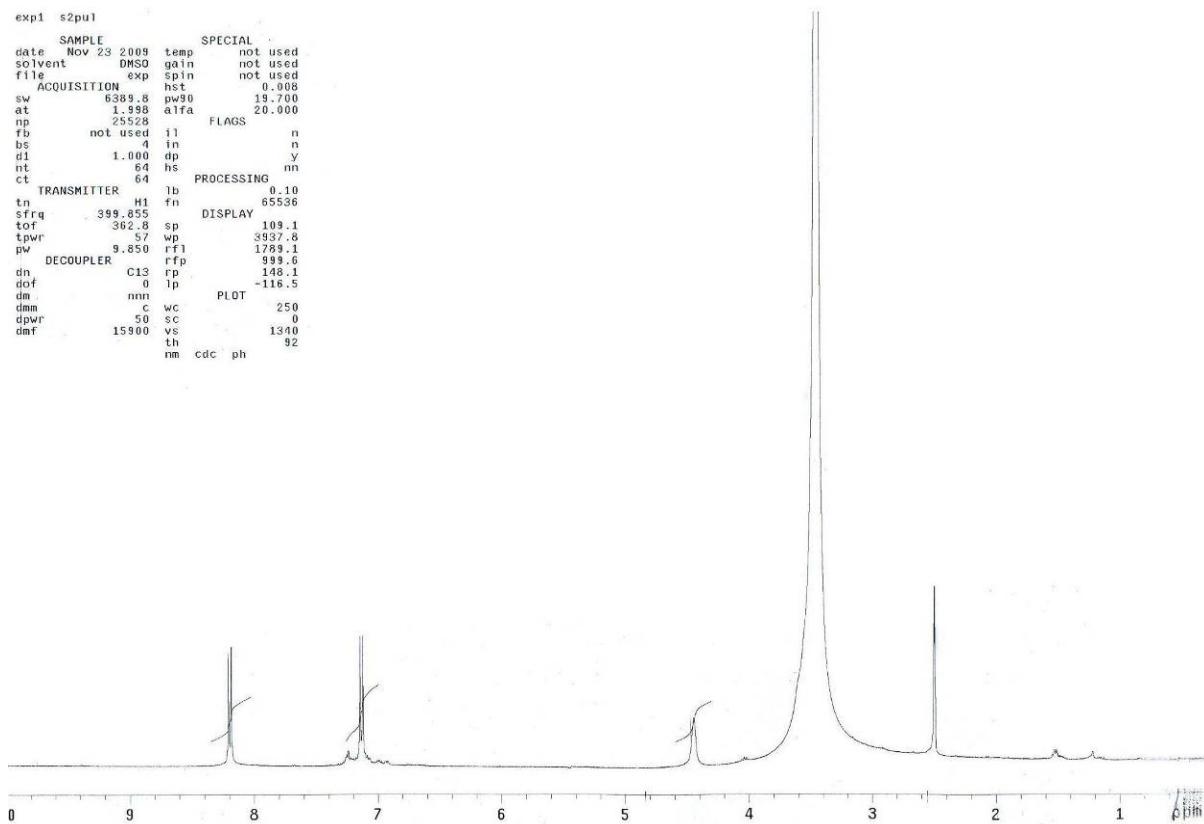
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solvent DMSO gain not used
file exp spin not used
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at 1.998 alfa 20.000
np 25528 FLAGS
fb not used il n
bs 4 in n
d1 1.000 dp y
nt 64 hs nn
ct 64 PROCESSING
TRANSMITTER 1b 0.10
tn H1 fn 65536
sfrq 399.855 DISPLAY
tof 362.8 sp 101.8
tpwr 57 wp 4105.7
pw 9.850 rfl 1788.0
DECOUPLER rfp 999.6
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dm nnn PLOT
dmm c wc 250
dpwr 50 sc 0
dmf 15900 vs 608
nm cdc ph 20

```



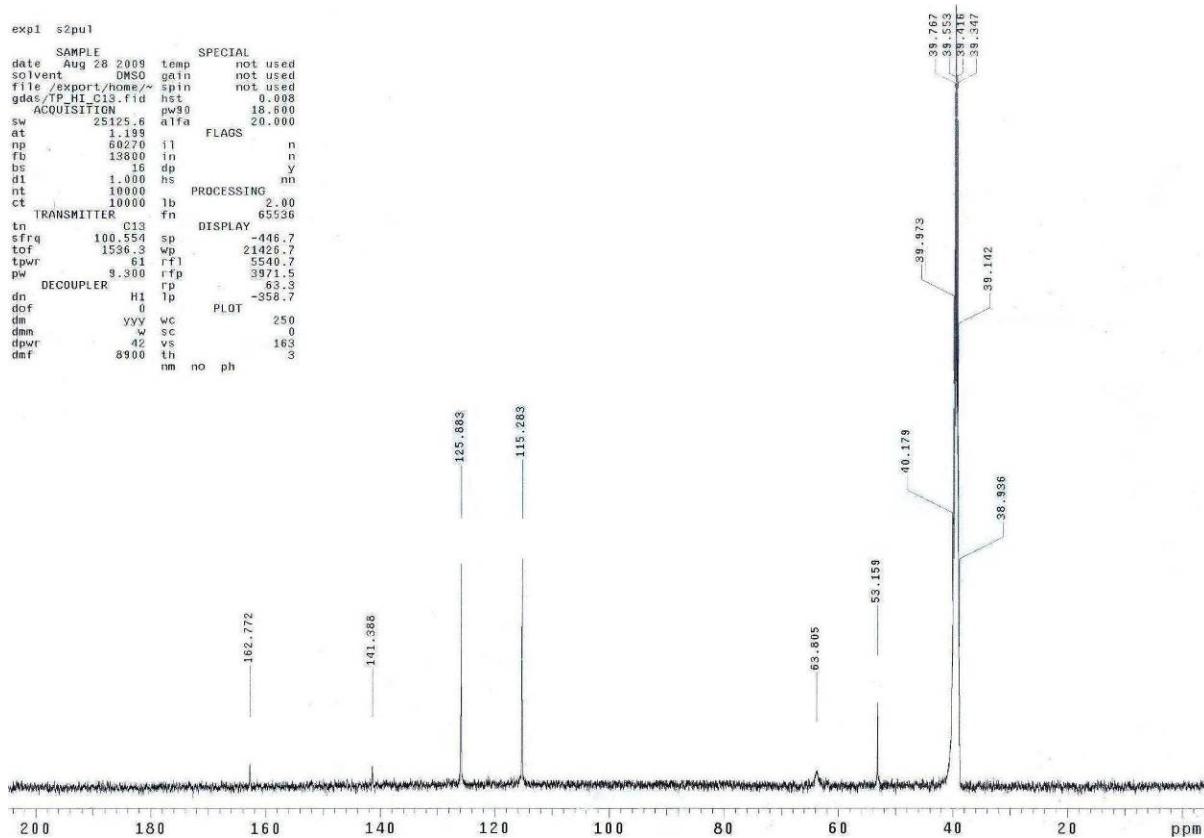
**Figure S14.**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{DMSO}-d_6$ ) of  $[\text{HL}^+]\text{[CF}_3\text{COO}^-$ ] (**5**) in  $\text{DMSO}-d_6$ .

```
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date Nov 23 2009 temp    not used
solvent   DMSO gain     not used
file      /export/home/ spin    not used
gdas/TP_HI_C13.fid hst     0.008
ACQUISITION pw90    19.700
sw       6389.6 pw90    19.700
at       1.988 alfa   20.000
np      25528  FLAGS
fb      not used  i1      n
bs        4      in      n
d1      1.000 dp      y
nt      64      hs      nn
ct      64      PROCESSING
tn      H1      lb      0.10
fn      65536
sfrq   399.855 DISPLAY
tof     362.8 sp      109.1
tpwr   9.850 wp      3897.8
pw     9.850 rfp     1789.1
DECOUPLER C13      rfp     993.6
dn      C13      rp      148.1
dof     0        lp      -116.5
dm      nnn      PLOT
dmm    c        wc      250
dpwr   50       sc      0
dmf    15900    vs      1340
th      nm      cdc    ph      92
nm      cdc    ph
```



**Figure S15.**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{DMSO}-d_6$ ) of  $[\text{HL}^+]\cdot[\text{SiF}_6^-]$  (**6**) in  $\text{DMSO}-d_6$ .

```
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SAMPLE          SPECIAL
date Aug 28 2009 temp    not used
solvent   DMSO gain     not used
file      /export/home/ spin    not used
gdas/TP_HI_C13.fid hst     0.008
ACQUISITION pw90    18.600
sw       25125.6 alfa   20.000
at       1.988 FLAGS
np      60270  i1      n
fb      13800  in      n
bs        16     dp      y
d1      1.000 hs      nn
nt      10000  PROCESSING
ct      10000  lb      2.00
tn      C13      fn      65536
sfrq   100.554 DISPLAY
tof     1536.3 sp      -446.7
tpwr   61       wp      21425.7
pw     9.300 rfp     5540.7
DECOUPLER H1      rp      63.3
dn      0        lp      -358.7
dof     VVV      PLOT
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dmm    W      sc      0
dpwr   42       vs      163
dmf    8900    th      s
nm      no      ph
```

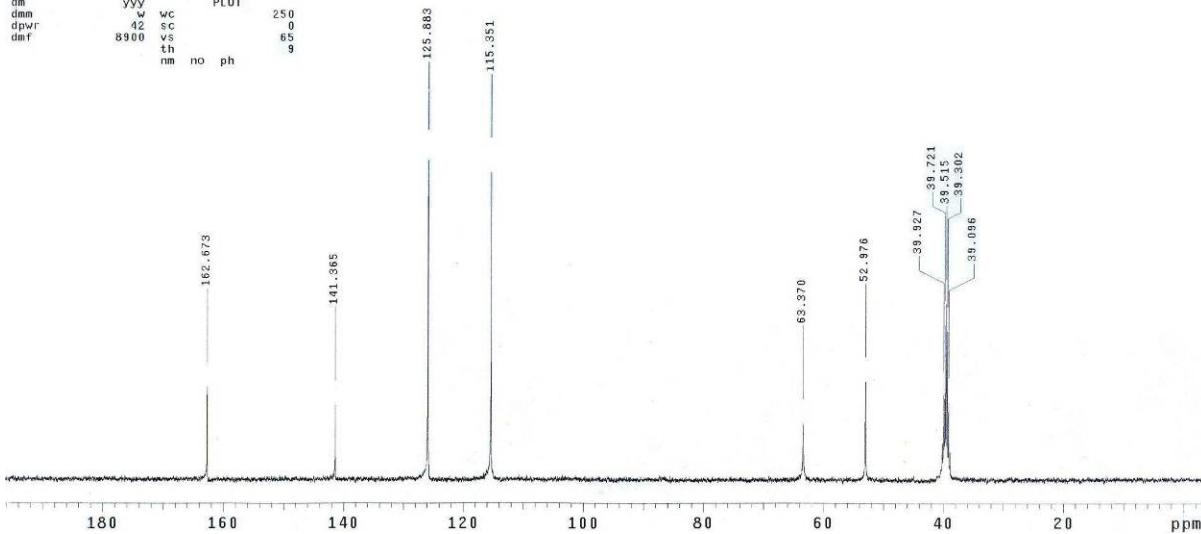


**Figure S16.**  $^{13}\text{C}$ -NMR spectrum (100 MHz,  $\text{DMSO}-d_6$ ) of  $[\text{HL}^+]\cdot[\text{Cl}^-]$  (**1**) in  $\text{DMSO}-d_6$ .

```

expl s2pul
SAMPLE          SPECIAL
date Jul 29 2009 temp not used
solvent   DMSO gain  not used
file      exp spin  not used
ACQUISITION hst    0.008
sw       25125.6 pw90  18.600
at       1.189 alfa   20.000
np       60270   FLAGS
fb       13800   i1     n
bs       16      in    n
d1      1.000   dp    y
nt      10000   hs    mn
ct      1188    PROCESSING
TRANSMITTER 1b    2.00
tn      C13   fn    65536
sfrq   100.553 DISPLAY
tof     1536.3 sp    -401.5
tpwr   61     wp    20462.9
pw     9.300  rfp   5539.9
DECOUPLER rfp   3971.5
dn      H1    rfp   18.7
dof    0     l1p   -321.4
dm      VVY   PLOT
dmm    w    wc    250
dpwr   42    sc    0
dmf    8900   vs    65
th      nm no ph

```

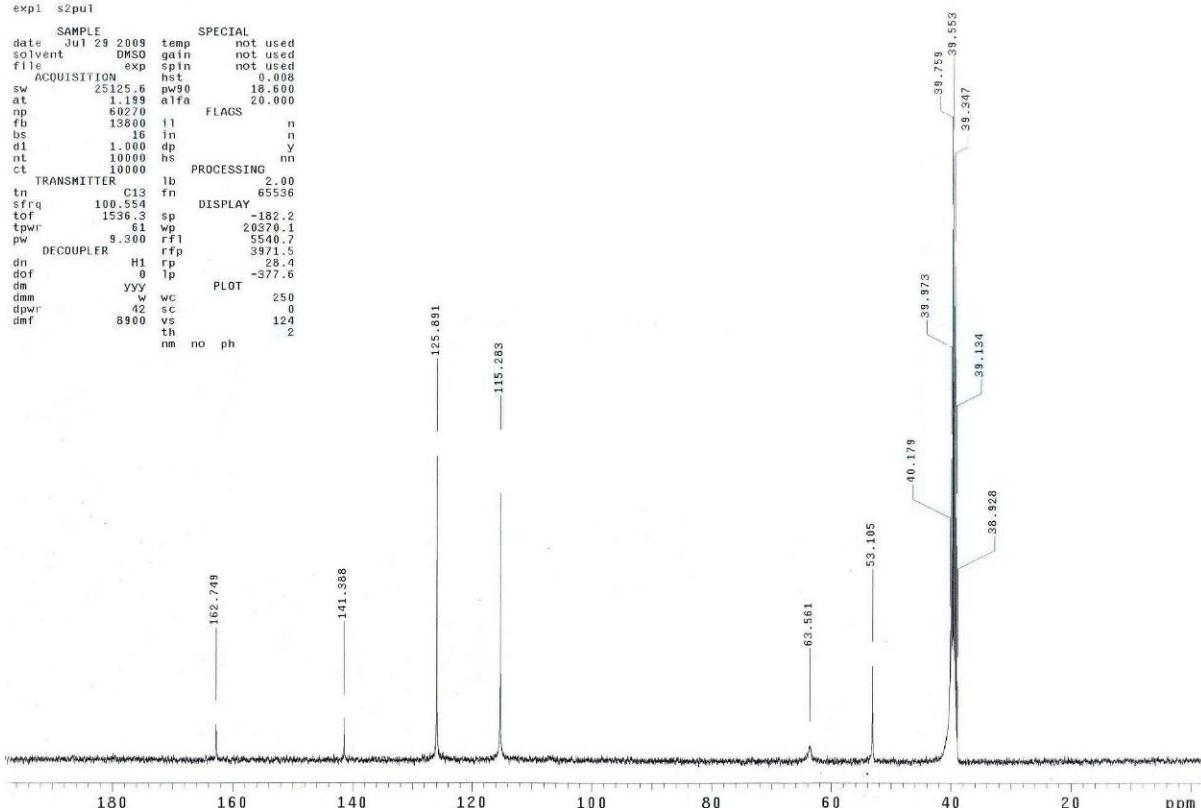


**Figure S17.**  $^{13}\text{C}$ -NMR spectrum (100 MHz, DMSO- $d_6$ ) of  $[\text{HL}^+]\text{*[Br}^-]$  (**2**) in DMSO- $d_6$ .

```

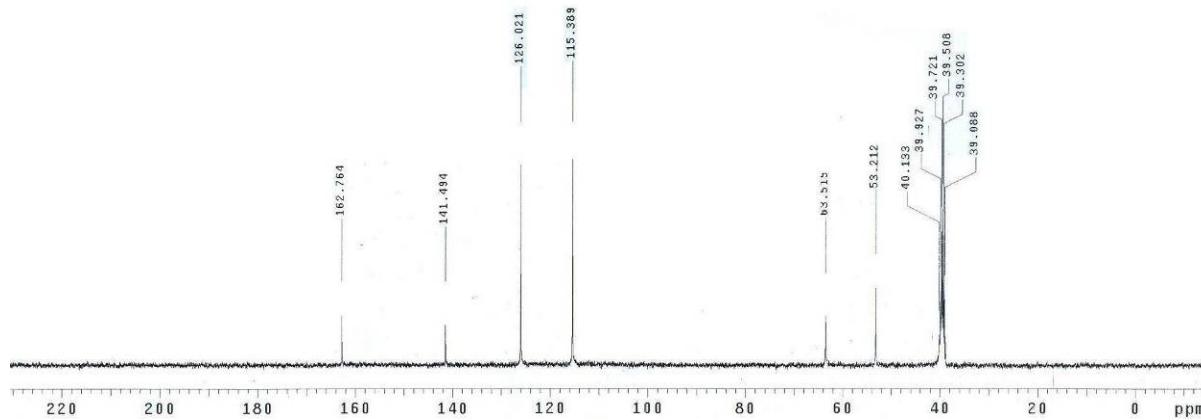
expl s2pul
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date Jul 29 2009 temp not used
solvent   DMSO gain  not used
file      exp spin  not used
ACQUISITION hst    0.008
sw       25125.6 pw90  18.600
at       1.189 alfa   20.000
np       60270   FLAGS
fb       13800   i1     n
bs       16      in    n
d1      1.000   dp    y
nt      10000   hs    mn
ct      10000   PROCESSING
TRANSMITTER 1b    2.00
tn      C13   fn    65536
sfrq   100.554 DISPLAY
tof     1536.3 sp    -182.2
tpwr   61     wp    20460.1
pw     9.300  rfp   5540.7
DECOUPLER rfp   3971.5
dn      H1    rfp   28.4
dof    0     l1p   -377.6
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th      nm no ph

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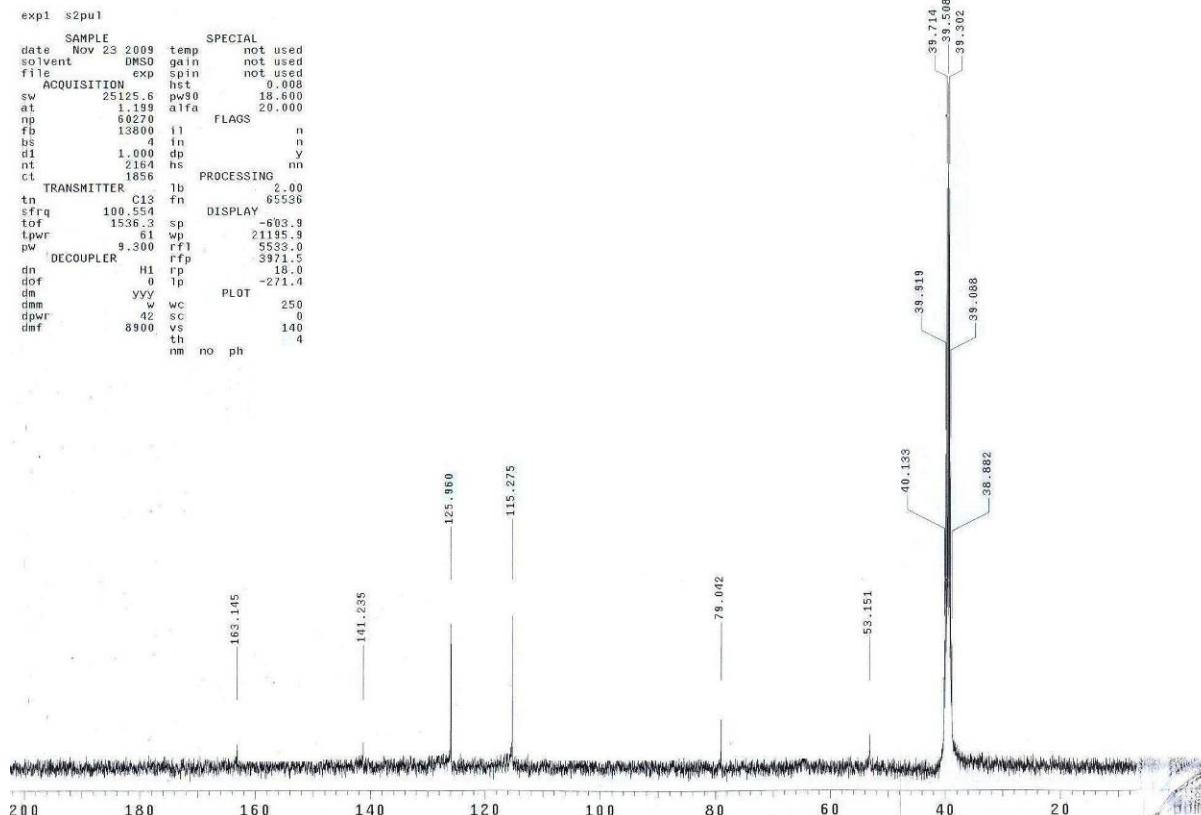
**Figure S18.**  $^{13}\text{C}$ -NMR spectrum (100 MHz, DMSO- $d_6$ ) of  $[\text{HL}^+]\text{*[NO}_3^-]$  (**3**) in DMSO- $d_6$ .

```
exp1 s2pul
SAMPLE          SPECIAL
date Oct 21 2009 temp not used
solvent   DMSO gain not used
file     exp spin not used
ACQUISITION hst    0.008
sw      25125.6 pw90 18.600
at      1.189 alfa 20.000
np      60270   FLAGS
fb      13800 i1    n
bs      4      in    n
di      1.000 dp    y
nt      2000 hs   nn
ct      644    PROCESSING
tn      C13 fn   65536
sfrq   100.554 DISPLAY
t0f    1536.3 sp   -1555.4
tpwr   61      wp   25124.9
pw     9.300 r1f  5527.7
DECOUPLER H1    rfp  39.515
dn      H1    rp   57.1
dof    0     lp   -363.8
dm      YYY   PLOT
dmm    w    wc   250
dpwr   42    sc    0
dmf    8900 vs   42
th      nm no ph   5
```



**Figure S19.**  $^{13}\text{C}$ -NMR spectrum (100 MHz, DMSO- $d_6$ ) of  $[\text{HL}^+]\text{[ClO}_4^-$ ] (**4**) in DMSO- $d_6$ .

```
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SAMPLE          SPECIAL
date Nov 23 2009 temp not used
solvent   DMSO gain not used
file     exp spin not used
ACQUISITION hst    0.008
sw      25125.6 pw90 18.600
at      1.199 alfa 20.000
np      60270   FLAGS
fb      13800 i1    n
bs      4      in    n
di      1.000 dp    y
nt      2184 hs   nn
ct      1856   PROCESSING
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sfrq   100.554 DISPLAY
t0f    1536.3 sp   -603.9
tpwr   61      wp   21195.9
pw     9.300 r1f  5533.0
DECOUPLER H1    rfp  3971.5
dn      H1    rp   18.0
dof    0     lp   -271.4
dm      YYY   PLOT
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dpwr   42    sc    0
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th      nm no ph   4
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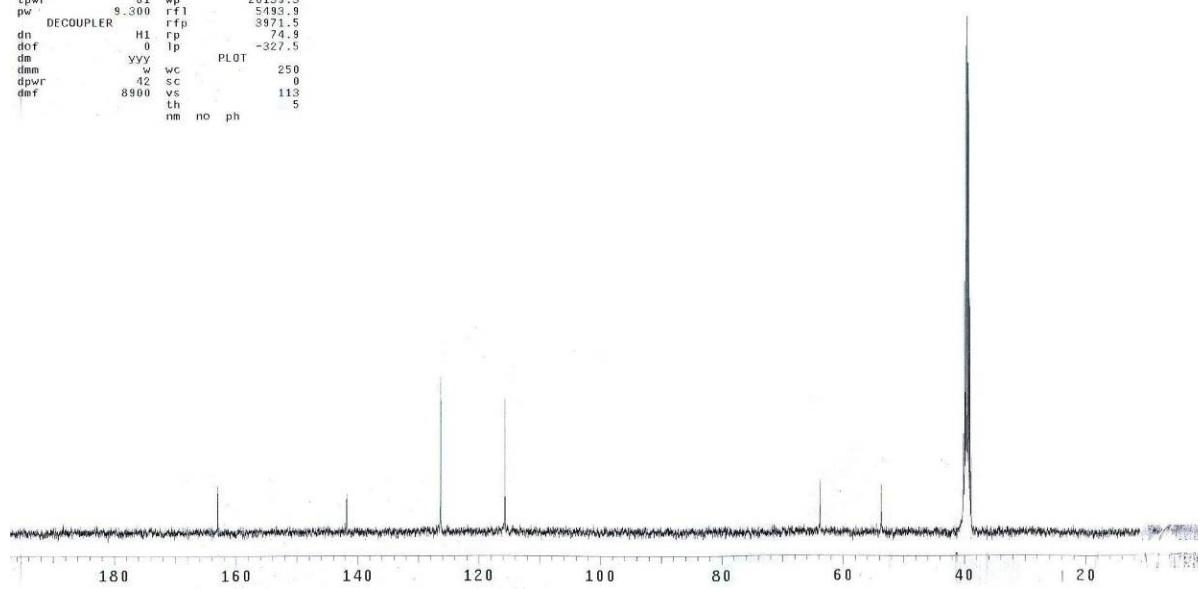


**Figure S20.**  $^{13}\text{C}$ -NMR spectrum (100 MHz, DMSO- $d_6$ ) of  $[\text{HL}^+]\text{[CF}_3\text{COO}^-$ ] (**5**) in DMSO- $d_6$ .

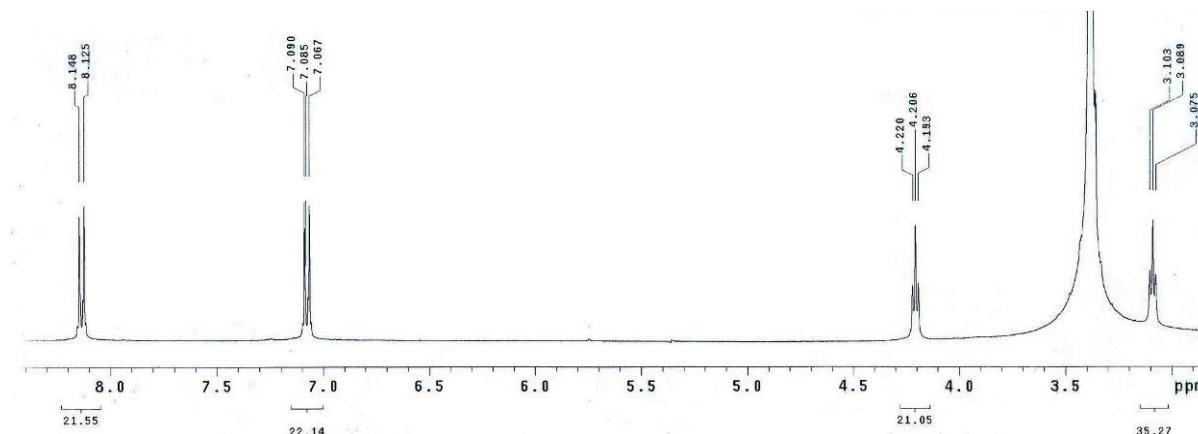
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solvent DMSO gain not used
file   exp Spin not used
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at   1.190 alfa 20.000
np   60270   FLAGS
fb   13800 i1 n
bs      4 in n
d1   1.000 dp y
nt   2000 hs nn
ct   1080   PROCESSING
| TRANSMITTER 1b 2.00
tn   C13 fn 65536
sfrq 100.554   DISPLAY
t0f 1536.3 sp -36.5
tpwr 61 wp 2039.3
pw 9.300 rf1 5493.9
DECOUPLER H1 rfp 3971.5
dn   0 rp 74.9
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dm   VVY wcp 250
dmm  w wcp 0
dpwr 42 sec 0
dmf  8900 vs 113
th   nm no ph 5

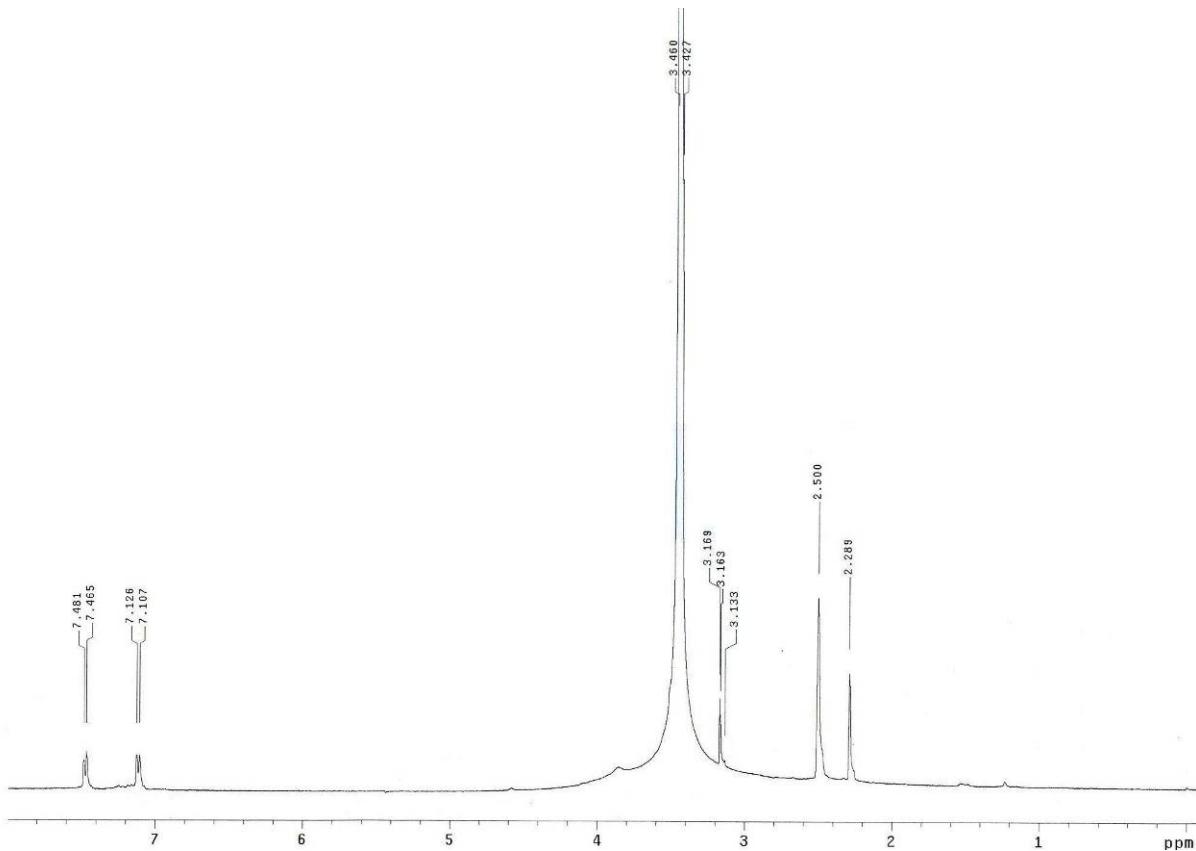
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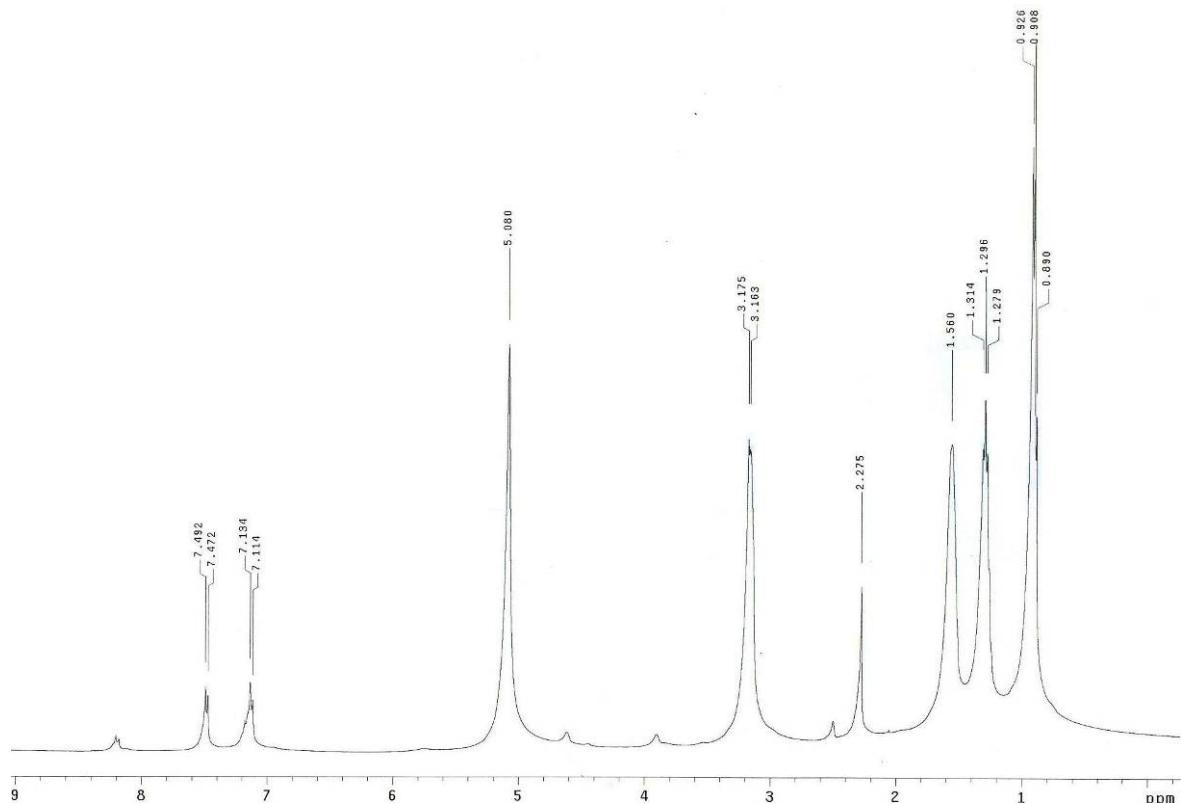
**Figure S21.**  $^{13}\text{C}$ -NMR spectrum (100 MHz, DMSO- $d_6$ ) of  $[\text{HL}^+]\bullet[\text{SiF}_6^-]$  (**6**) in DMSO- $d_6$ .



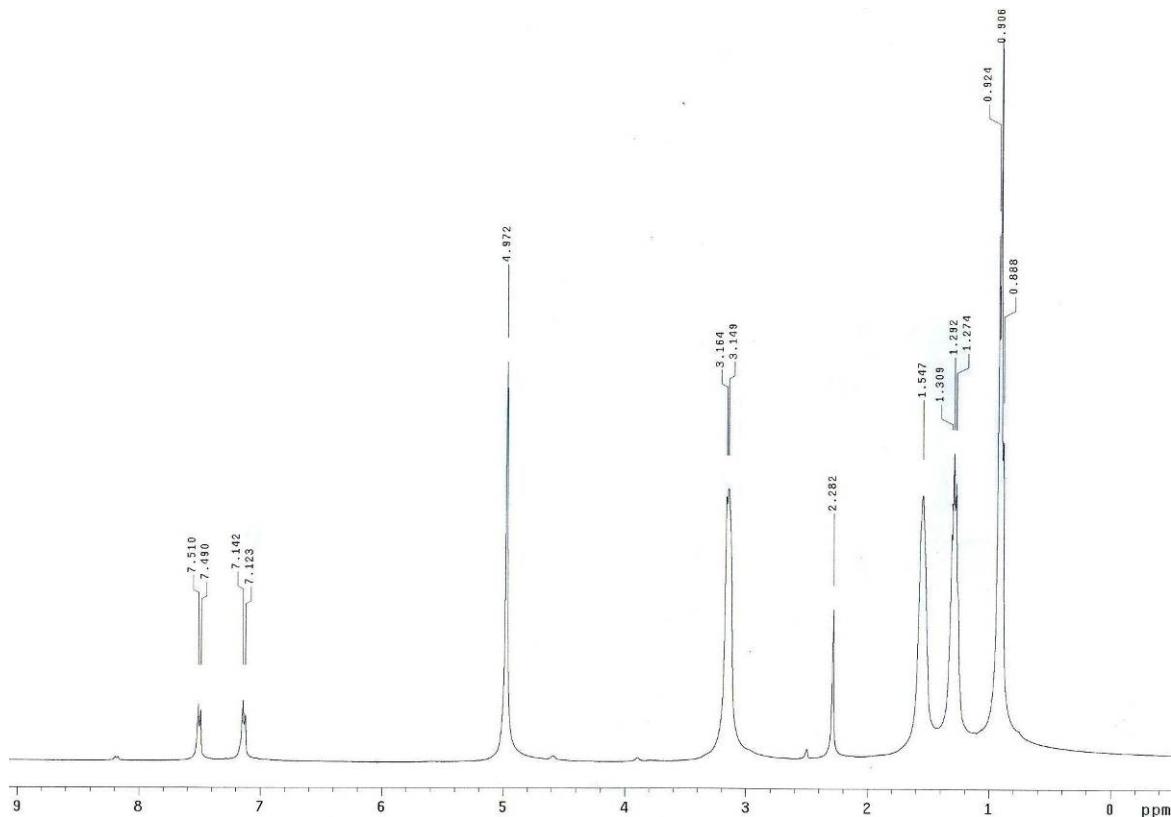
**Figure S22.** Selected region of the  $^1\text{H}$ -NMR (400 MHz, DMSO- $d_6$ ) spectrum of receptor **L**.



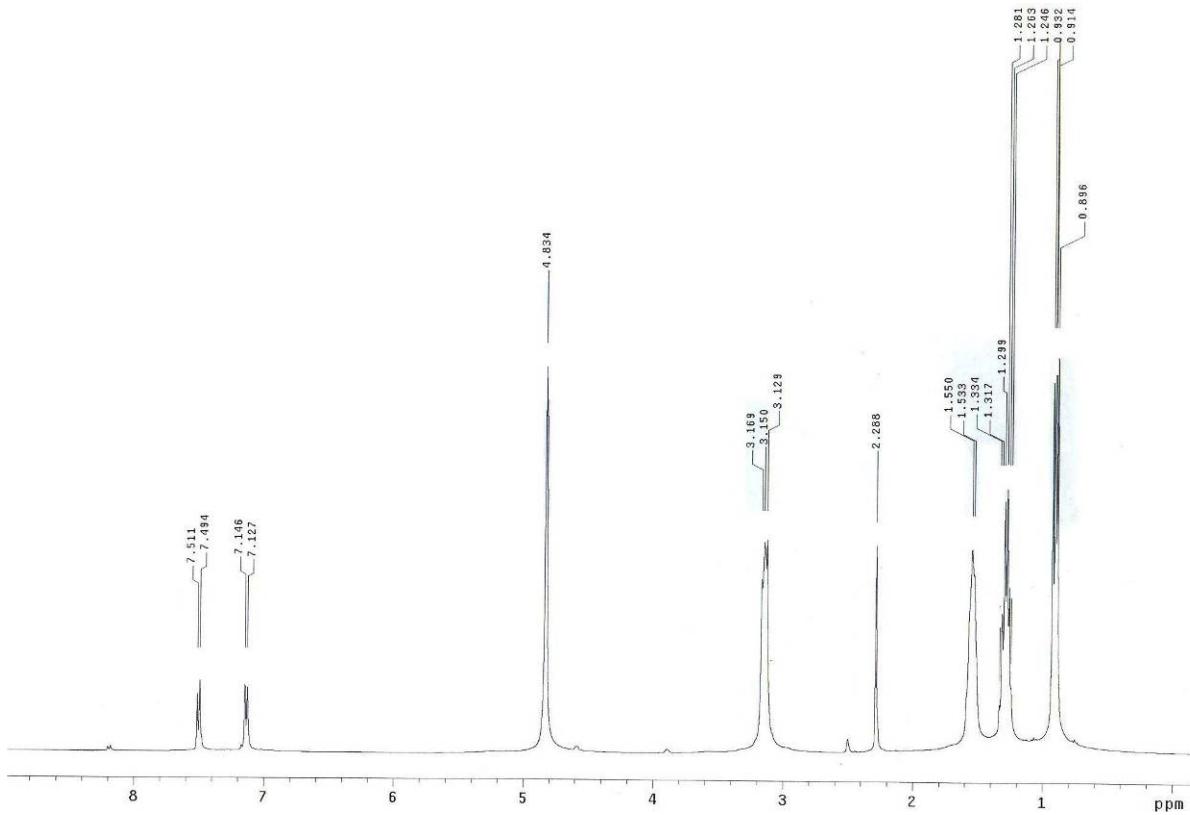
**Figure S23.** <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of receptor **L** with 1 equivalent of *p*-toluenesulphonic acid (PTSA), [HL<sup>+</sup>]•[OTs] salt.



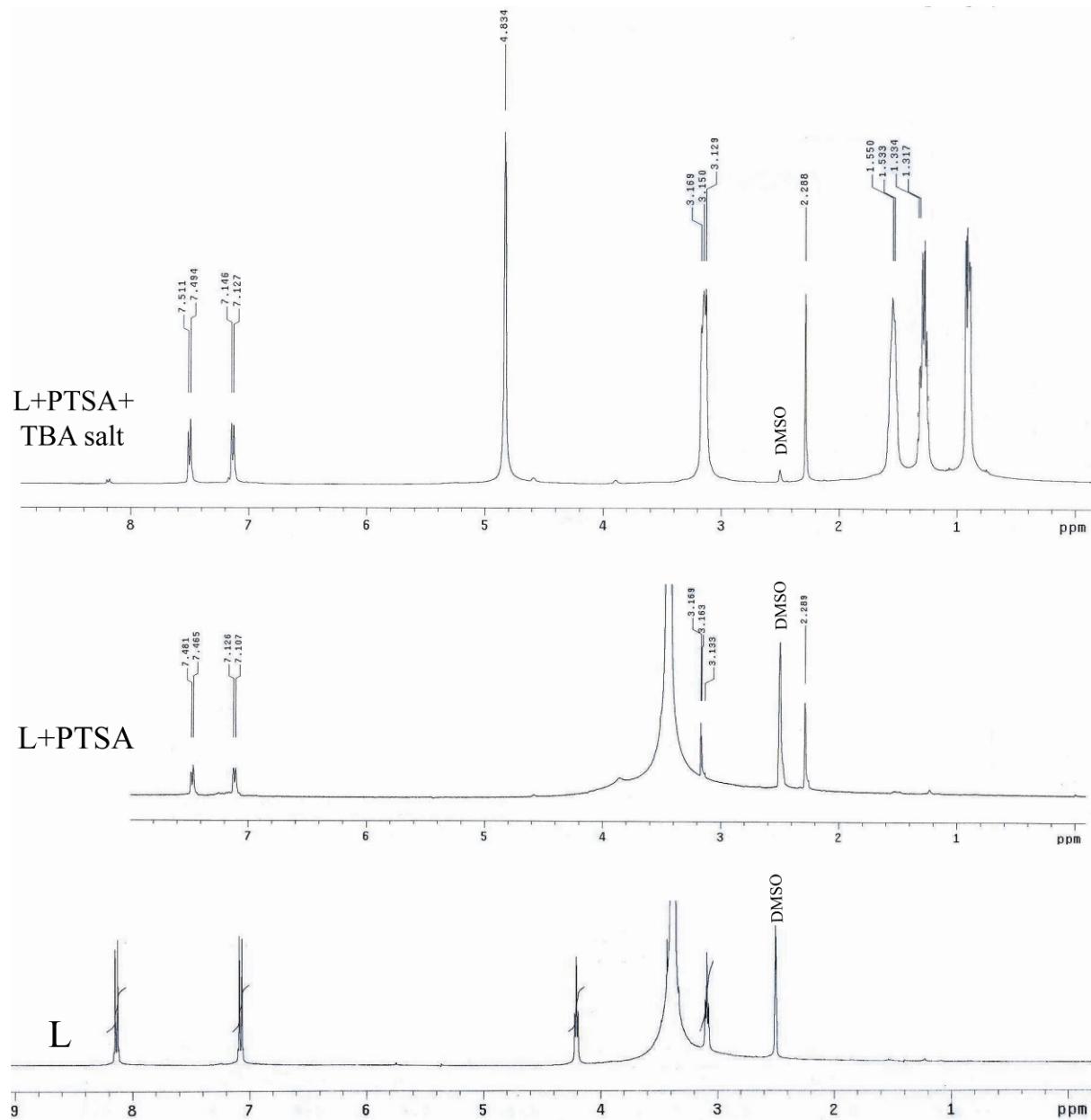
**Figure S24.** <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of [HL<sup>+</sup>]•[OTs] salt, doped with 1.2 equivalent of tetrabutyl ammonium bromide.



**Figure S25.** <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) spectrum of [HL<sup>+</sup>][OTs] salt, doped with 1.2 equivalent of tetrabutyl ammonium nitrate.



**Figure S26.** <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) spectrum of [HL<sup>+</sup>][OTs] salt, doped with 1.2 equivalent of tetrabutyl ammonium perchlorate.



**Figure S27.** <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) spectra of receptor **L** (below), **L** with 1 equivalent of *p*-toluene sulphonic acid (PTSA), [HL<sup>+</sup>]•[OTs] salt (middle) and [HL<sup>+</sup>]•[OTs] with 1.2 equivalent of tetrabutyl ammonium (TBA) salt of inorganic anions (above).

**Table S1.** Selected interligand non-covalent interactions among  $\text{LH}^+$  units in anionic complexes **1-6**.

D-H $\cdots$ A	$d(\text{H}\cdots\text{A})$ (Å)	$d(\text{D}\cdots\text{A})$ (Å)	$\angle(\text{DHA})$ (°)
$[\text{HL}^+]\bullet[\text{Cl}^-]$ ( <b>1</b> )			
C16-H16 $\cdots$ O2	2.51	3.390	156
C2-H2B $\cdots$ O3	2.60	3.229	121
C10-H10A $\cdots$ O3	2.59	3.560	178
C8-H8 $\cdots$ O3	2.33	3.222	160
C17-H17B $\cdots$ O5	2.70	3.349	124
C20-H20 $\cdots$ O6	2.52	3.428	164
C7-H7 $\cdots$ C2g	3.037	3.970	157
C1g $\cdots$ C1g		4.183	
C3g $\cdots$ C3g		3.610	
C1g $\cdots$ C3g		3.858	
$[\text{HL}^+]\bullet[\text{Br}^-]$ ( <b>2</b> )			
C24-H24 $\cdots$ O3	2.63	3.499	162
C2-H2A $\cdots$ O5	2.55	3.559	172
C10-H10A $\cdots$ O5	2.59	3.263	125
C16-H16 $\cdots$ O5	2.42	3.328	163
C8-H8 $\cdots$ O6	2.52	3.415	160
C23-H23 $\cdots$ O9	2.70	3.504	150
C3g $\cdots$ C3g		3.601	
C3g $\cdots$ C2g		3.906	
C15-H15 $\cdots$ C1g	3.056	3.924	156
$[\text{HL}^+]\bullet[\text{NO}_3^-]$ ( <b>3</b> )			
C1-H1B $\cdots$ O3	2.70	3.594	152
C24-H24 $\cdots$ O3	2.60	3.323	134
C2-H2A $\cdots$ O5	2.60	3.472	148
C17-H17B $\cdots$ O5	2.67	3.644	175
C4-H4 $\cdots$ O6	2.48	3.399	168
C10-H10A $\cdots$ O6	2.58	3.256	126
C8-H8 $\cdots$ O9	2.40	3.089	130
$[\text{HL}^+]\bullet[\text{ClO}_4^-]$ ( <b>4</b> )			
C17-H17A $\cdots$ O2	2.54	3.367	142
C10-H10B $\cdots$ O3	2.71	3.594	151
C17-H17B $\cdots$ O3	2.33	3.235	154
C9-H9B $\cdots$ O5	2.51	3.373	147
C24-H24 $\cdots$ O6	2.54	3.431	
C8-H8 $\cdots$ O8	2.68	3.563	157
$[\text{HL}^+]\bullet[\text{CF}_3\text{COO}^-]$ ( <b>5</b> )			
C9-H9A $\cdots$ O2	2.56	3.324	135
C10-H10A $\cdots$ O3	2.67	3.620	164
C17-H17B $\cdots$ O5	2.68	3.615	160
C17-H17B $\cdots$ O6	2.66	3.497	143
C20-H20 $\cdots$ O6	2.56	3.155	121
C1g $\cdots$ C1g		3.726	
C2g $\cdots$ C2g		3.518	
$[2\text{HL}^+]\bullet[\text{SiF}_6^{2-}]\bullet2\text{H}_2\text{O}$ ( <b>6</b> )			
C9-H9B $\cdots$ O3	2.55	3.372	149
C33-H33A $\cdots$ O3	2.60	3.364	135
C50-H50A $\cdots$ O5	2.66	3.592	159
C1-H1B $\cdots$ O6	2.57	3.290	131
C53-H53 $\cdots$ O9	2.67	3.413	136
C55-H55 $\cdots$ O11	2.60	3.521	169
C50-H50B $\cdots$ O12	2.60	3.348	133
C1-H1A $\cdots$ O15	2.61	3.371	135
C65-H65A $\cdots$ O15	2.58	3.487	154
C16-H16 $\cdots$ O17	2.56	3.381	146
C25-H25B $\cdots$ O20	2.46	3.339	149

C49-H49B···O20	2.69	3.405	130
C68-H68···O21	2.51	3.380	155
C34-H34A···O24	2.65	3.605	166
C69-H69···O27	2.71	3.546	149
C1g···C1g		3.688	
C1g···C5g		3.544	
C5g···C7g		3.671	
C7g···C7g		3.507	
C4g···C4g		3.629	

C1g = Centroid of ring C3-C8  
 C2g = Centroid of ring C11-C16  
 C3g = Centroid of ring C19-C24

\*C4g = Centroid of ring C27-C32  
 \*C5g = Centroid of ring C35-C40  
 \*C7g = Centroid of ring C51-C56  
 \* = Present only in complex **6**

**Table S2.** Molecular conformation: Relevant Torsion Angles in anion complexes **1-6** ( $\tau_{\text{ether}}$  = atoms involving N<sub>amino</sub>-C-C-O<sub>ether</sub> and  $\tau_{\text{amino}}$  = atoms involving C-N<sub>amino</sub>-C-C).

Complexes	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
(a) $\tau_{\text{ether}}$						
N1-C1-C2-O1	-161.67	60.29	-70.56	-55.88	-83.38	72.40
N1-C9-C10-O4	-58.78	160.80	56.50	168.30	80.23	-77.81
N1-C17-C18-O7	-79.42	79.01	90.27	-65.60	-74.81	166.97
(b) $\tau_{\text{amino}}$						
C1-N1-C9-C10	-54.64	58.73	48.06	56.86	65.14	56.19
C1-N1-C17-C18	50.78	179.95	-59.10	157.30	174.07	-178.68
C9-N1-C1-C2	-57.98	52.65	63.95	174.10	52.08	54.66
C9-N1-C17-C18	178.33	-50.86	169.58	-75.56	-57.34	50.36
C17-N1-C1-C2	67.36	-177.41	-62.41	-57.43	178.66	-74.07
C17-N1-C9-C10	177.07	-67.64	177.70	-72.54	-60.42	-175.05