Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Super-Base-Derived Hypergolic Ionic Fuels with Remarkably Improved Thermal Stability

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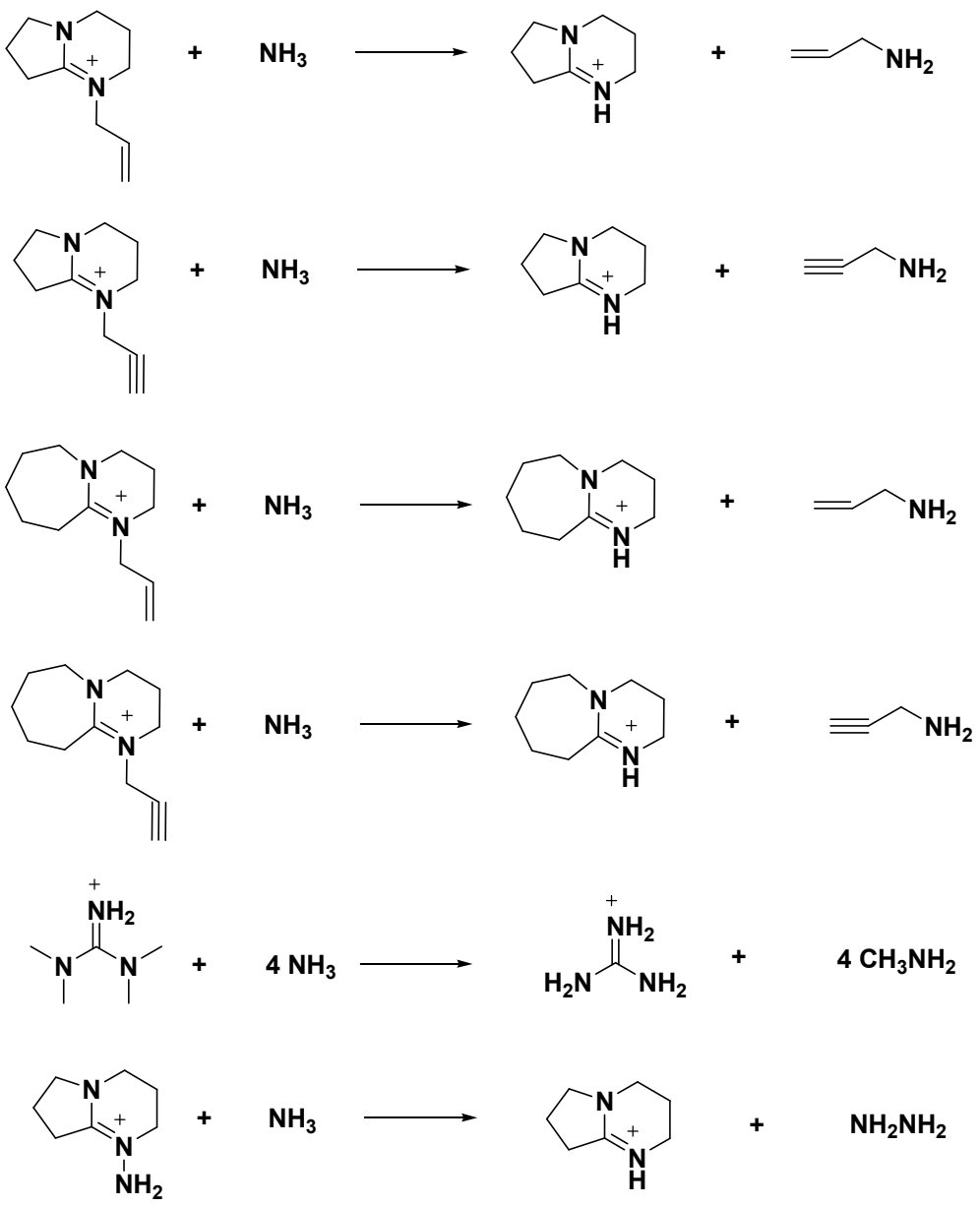


Scheme S1. Isodesmic reactions of seven super-base-derived cations

Table S1. Enthalpies of the gas-phase species for part cations (C^+) and anions (A^-) (G2 method)

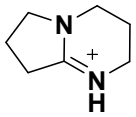
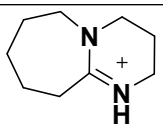
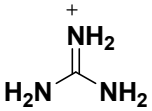
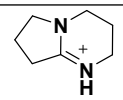
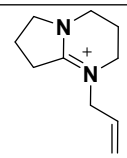
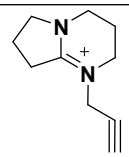
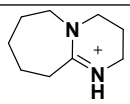
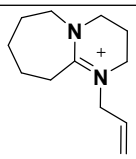
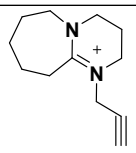
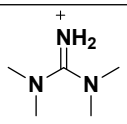
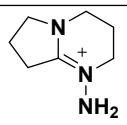
ions	ΔH_f^o (kJ mol^{-1})
	+559.69
	+512.98
	+573.23
$[N(CN)_2]^-$	+121.98
$[BH_3CN]^-$	-92.83

Table S2. Enthalpies of the gas-phase species of eight cations based on isodesmic reactions

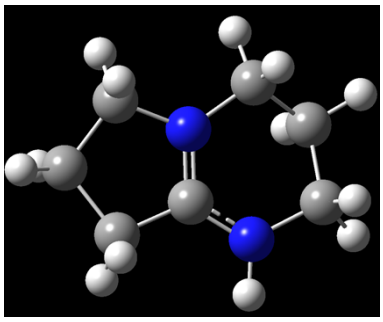
Cations	E(MP2)[a]	ZPE[b]	TCH[c]	ΔHcorr	ΔH_f^{od} (kJ mol^{-1})
	-382.825493	0.202261	0.211132	-382.62	559.69
	-499.192487	0.263392	0.275958	-498.93	626.73
	-497.955777	0.239356	0.251664	-497.71	803.73
	-461.220043	0.260521	0.271393	-460.96	512.98
	-577.581076	0.321841	0.336354	-577.26	596.00
	-576.345015	0.297824	0.312084	-576.04	771.36
	-362.015649	0.202000	0.213478	-361.81	539.78
	-438.012427	0.218346	0.228698	-437.79	647.57

[a] Total energy calculated by B3LYP/6-31+G**//MP2/6-311++G** method (Hartree/Particle); [b] zero-point correction (Hartree/Particle); [c]thermal correction to enthalpy (Hartree/Particle); [d] heat of formation (kJ/mol).

Table S3. The calculated enthalpies of fourteen new HILs

Compounds	ΔH_{cation}(kJ/mol)	ΔH_{anion}(kJ/mol)	U_{pot}(kJ/mol)	ΔH_{Lat}(kJ/mol)	ΔH_{salt}(kJ/mol)
1	626.73	121.98	438.71	443.67	305.04
2	803.73	121.98	442.14	447.09	478.62
3	647.57	121.98	459.29	464.24	305.31
4	559.69	121.98	464.55	469.51	212.16
5	596.00	121.98	425.23	430.18	287.80
6	771.36	121.98	428.20	433.16	460.18
7	512.98	121.98	454.65	459.61	175.34
8	626.73	-92.83	440.13	445.08	88.82
9	803.73	-92.83	444.06	449.01	261.89
10	559.69	-92.83	467.34	472.30	-5.43
11	596.00	-92.83	426.36	431.32	71.85
12	771.36	-92.83	429.14	434.09	244.44
13	512.98	-92.83	453.14	458.10	-37.95
14	539.78	-92.83	463.86	468.82	-21.87

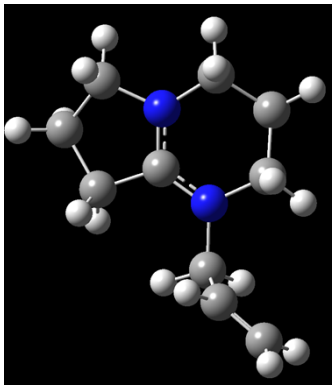
The geometries and XYZ coordinates of eight cations are in the follows.



2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium XYZ orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.504952	0.004877	0.277000
2	6	0	1.629474	1.195923	-0.161338
3	6	0	1.640825	-1.241192	-0.030722
4	6	0	0.246001	-0.678460	-0.044287
5	1	0	2.705212	0.064294	1.349948
6	1	0	1.855942	-1.661164	-1.021609
7	1	0	1.833929	1.522343	-1.187847
8	1	0	3.462858	-0.014846	-0.244035
9	1	0	1.711603	2.061729	0.500079
10	1	0	1.752770	-2.046933	0.699854
11	7	0	-0.875189	-1.385447	-0.048092
12	6	0	-0.965380	1.451408	-0.179545
13	6	0	-2.205938	-0.752858	-0.148466
14	1	0	-0.806256	-2.393807	-0.007110
15	6	0	-2.137409	0.666610	0.421345
16	1	0	-1.146127	1.709735	-1.230104
17	1	0	-0.796339	2.381523	0.369190

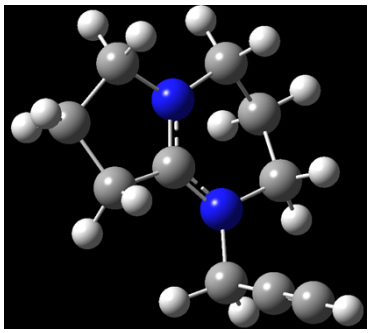
18	**1**	**0**	**-2.519215**	**-0.748189**	**-1.198544**
19	**1**	**0**	**-2.913209**	**-1.365450**	**0.414243**
20	**1**	**0**	**-3.072801**	**1.189758**	**0.208020**
21	**1**	**0**	**-2.027600**	**0.620593**	**1.509863**
22	**7**	**0**	**0.258629**	**0.642955**	**-0.089890**



1-allyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	**6**	**0**	**-2.515992**	**-1.761653**	**-0.170105**
2	**6**	**0**	**-2.824182**	**-0.394005**	**0.461907**
3	**6**	**0**	**-0.972624**	**-1.836916**	**-0.192085**
4	**6**	**0**	**-0.555156**	**-0.385703**	**-0.125058**
5	**1**	**0**	**-2.903962**	**-1.796622**	**-1.191515**
6	**1**	**0**	**-0.569651**	**-2.362186**	**0.682910**
7	**1**	**0**	**-2.985819**	**-0.450713**	**1.545453**
8	**1**	**0**	**-2.963444**	**-2.585447**	**0.387538**
9	**1**	**0**	**-3.684617**	**0.107347**	**0.011773**

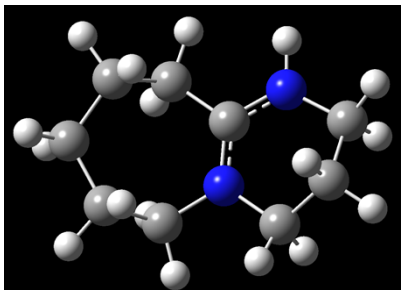
10	**1**	**0**	**-0.587348**	**-2.339687**	**-1.081625**
11	**7**	**0**	**0.667894**	**0.092153**	**-0.312491**
12	**6**	**0**	**-1.505439**	**1.830299**	**0.389137**
13	**6**	**0**	**0.933953**	**1.540339**	**-0.141664**
14	**6**	**0**	**-0.322458**	**2.363517**	**-0.418709**
15	**1**	**0**	**-1.394078**	**2.043270**	**1.459919**
16	**1**	**0**	**-2.445246**	**2.278459**	**0.055573**
17	**1**	**0**	**1.311114**	**1.711319**	**0.872609**
18	**1**	**0**	**1.733047**	**1.807607**	**-0.837239**
19	**1**	**0**	**-0.135750**	**3.408096**	**-0.156934**
20	**1**	**0**	**-0.561990**	**2.330554**	**-1.486981**
21	**7**	**0**	**-1.597156**	**0.381165**	**0.190040**
22	**6**	**0**	**1.839959**	**-0.769474**	**-0.603562**
23	**1**	**0**	**1.476027**	**-1.778491**	**-0.805907**
24	**1**	**0**	**2.306829**	**-0.396682**	**-1.521523**
25	**6**	**0**	**2.834588**	**-0.782121**	**0.529108**
26	**6**	**0**	**4.108956**	**-0.408296**	**0.397148**
27	**1**	**0**	**2.468807**	**-1.151530**	**1.486807**
28	**1**	**0**	**4.804759**	**-0.468445**	**1.227879**
29	**1**	**0**	**4.506529**	**-0.045996**	**-0.548269**



1-(prop-2-yn-1-yl)-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium XYZ orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.075593	-2.007211	-0.193961
2	6	0	-2.516474	-0.746594	0.570236
3	6	0	-0.552749	-1.828272	-0.390217
4	6	0	-0.360506	-0.338802	-0.246216
5	1	0	-2.573591	-2.047863	-1.166136
6	1	0	0.034548	-2.332317	0.387803
7	1	0	-2.550861	-0.893694	1.656507
8	1	0	-2.318558	-2.922938	0.346438
9	1	0	-3.484661	-0.358452	0.244297
10	1	0	-0.203965	-2.202166	-1.355550
11	7	0	0.745107	0.341743	-0.533198
12	6	0	-1.550538	1.653724	0.585550
13	6	0	0.836053	1.782478	-0.201167
14	6	0	-0.543894	2.435180	-0.259147
15	1	0	-1.364657	1.779561	1.659447
16	1	0	-2.573433	1.981875	0.382570
17	1	0	1.291155	1.885452	0.791045
18	1	0	1.510533	2.242914	-0.927144
19	1	0	-0.473881	3.462597	0.106851
20	1	0	-0.889314	2.479353	-1.297427
21	7	0	-1.454780	0.229321	0.246949
22	6	0	2.001318	-0.341479	-0.914596
23	1	0	1.759118	-1.264838	-1.445470

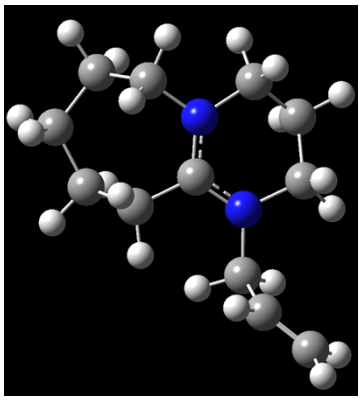
24	1	0	2.517715	0.305933	-1.630982
25	6	0	2.861255	-0.617551	0.237708
26	6	0	3.580195	-0.837483	1.183548
27	1	0	4.213160	-1.036801	2.021068



2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium XYZ orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.042404	-1.299585	0.365253
2	6	0	-2.836714	0.013655	0.354998
3	6	0	-1.999553	1.285677	0.545891
4	6	0	-0.951222	-1.382086	-0.710037
5	6	0	-0.920070	1.512230	-0.541551
6	6	0	0.328374	0.689850	-0.347085
7	1	0	-1.590245	-1.474574	1.350020
8	1	0	-3.383746	0.089507	-0.594753
9	1	0	-1.525073	1.291429	1.535366
10	1	0	-1.335092	1.295700	-1.533929
11	1	0	-1.324204	-1.028279	-1.677469
12	1	0	-2.734920	-2.130815	0.191121
13	1	0	-3.597944	-0.025760	1.141171

14	1	0	-2.667164	2.152782	0.520538
15	1	0	-0.638422	-2.417146	-0.856371
16	1	0	-0.626817	2.565720	-0.557268
17	7	0	1.471556	1.342752	-0.125081
18	6	0	1.502162	-1.449157	-0.104602
19	6	0	2.772189	0.695339	0.098743
20	1	0	1.427401	2.352341	-0.110403
21	6	0	2.526001	-0.675278	0.720907
22	1	0	1.922359	-1.771153	-1.065094
23	1	0	1.178933	-2.343060	0.434052
24	1	0	3.305615	0.612724	-0.855295
25	1	0	3.358326	1.336684	0.760427
26	1	0	3.459402	-1.242094	0.764210
27	1	0	2.164123	-0.555123	1.747621
28	7	0	0.290571	-0.636001	-0.373354

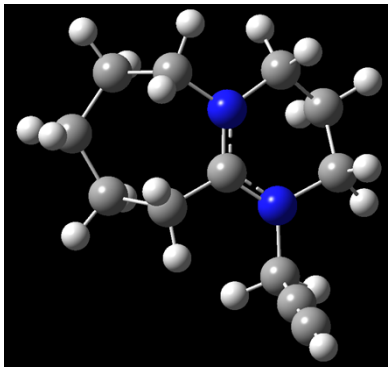


1-allyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium XYZ orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	**6**	**0**	**-3.284123**	**-0.029874**	**-0.055196**
2	**6**	**0**	**-3.077462**	**-1.534124**	**-0.275373**
3	**6**	**0**	**-1.661519**	**-1.937366**	**-0.709195**
4	**6**	**0**	**-2.319913**	**0.588622**	**0.966398**
5	**6**	**0**	**-0.552251**	**-1.528656**	**0.295606**
6	**6**	**0**	**-0.088842**	**-0.097178**	**0.147346**
7	**1**	**0**	**-3.200257**	**0.518291**	**-1.002662**
8	**1**	**0**	**-3.322472**	**-2.064366**	**0.655176**
9	**1**	**0**	**-1.429451**	**-1.525418**	**-1.699355**
10	**1**	**0**	**-0.916574**	**-1.659717**	**1.321542**
11	**1**	**0**	**-2.226962**	**-0.044795**	**1.854441**
12	**1**	**0**	**-4.303990**	**0.137374**	**0.309244**
13	**1**	**0**	**-3.792875**	**-1.888960**	**-1.024757**
14	**1**	**0**	**-1.623446**	**-3.026462**	**-0.812684**
15	**1**	**0**	**-2.702508**	**1.550123**	**1.313286**
16	**1**	**0**	**0.297347**	**-2.199994**	**0.205352**
17	**7**	**0**	**1.157657**	**0.186123**	**-0.254063**
18	**6**	**0**	**-0.687521**	**2.311664**	**0.196357**
19	**6**	**0**	**1.638517**	**1.584388**	**-0.245218**
20	**6**	**0**	**0.521457**	**2.510338**	**-0.702771**
21	**1**	**0**	**-0.542021**	**2.790849**	**1.171999**
22	**1**	**0**	**-1.581881**	**2.747944**	**-0.257348**
23	**1**	**0**	**1.982804**	**1.839380**	**0.764137**
24	**1**	**0**	**2.500035**	**1.643706**	**-0.911302**
25	**1**	**0**	**0.848433**	**3.552343**	**-0.653851**
26	**1**	**0**	**0.265689**	**2.292775**	**-1.745317**

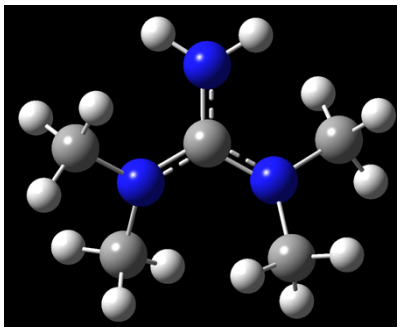
27	7	0	-0.965187	0.875117	0.425569
28	6	0	2.176927	-0.830357	-0.630933
29	1	0	1.671835	-1.722613	-1.002174
30	1	0	2.730480	-0.416434	-1.478176
31	6	0	3.117038	-1.154131	0.501446
32	6	0	4.438546	-0.976782	0.439713
33	1	0	2.665029	-1.573861	1.399811
34	1	0	5.085424	-1.250597	1.267051
35	1	0	4.922929	-0.567509	-0.444044



1-(prop-2-yn-1-yl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium XYZ orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.118958	-0.113554	0.056072
2	6	0	-2.869616	-1.581910	-0.313153
3	6	0	-1.468147	-1.885402	-0.860090
4	6	0	-2.122410	0.451120	1.077678
5	6	0	-0.314496	-1.513135	0.108937
6	6	0	0.070505	-0.052705	0.059658
7	1	0	-3.110325	0.521430	-0.839409

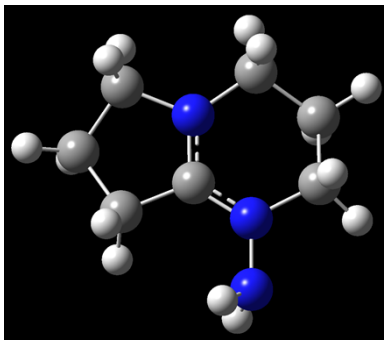
8	**1**	**0**	**-3.039840**	**-2.203046**	**0.576871**
9	**1**	**0**	**-1.313329**	**-1.385639**	**-1.824879**
10	**1**	**0**	**-0.603099**	**-1.751413**	**1.139285**
11	**1**	**0**	**-1.949269**	**-0.256918**	**1.894519**
12	**1**	**0**	**-4.121619**	**-0.023598**	**0.488947**
13	**1**	**0**	**-3.614662**	**-1.897782**	**-1.050963**
14	**1**	**0**	**-1.393558**	**-2.959795**	**-1.055922**
15	**1**	**0**	**-2.521273**	**1.357897**	**1.535092**
16	**1**	**0**	**0.557465**	**-2.130149**	**-0.090372**
17	**7**	**0**	**1.265297**	**0.321583**	**-0.426235**
18	**6**	**0**	**-0.589263**	**2.309882**	**0.407572**
19	**6**	**0**	**1.700120**	**1.733280**	**-0.361626**
20	**6**	**0**	**0.506504**	**2.647784**	**-0.589866**
21	**1**	**0**	**-0.344543**	**2.675395**	**1.412208**
22	**1**	**0**	**-1.535253**	**2.768833**	**0.108449**
23	**1**	**0**	**2.171067**	**1.919393**	**0.611582**
24	**1**	**0**	**2.457353**	**1.883543**	**-1.132743**
25	**1**	**0**	**0.805193**	**3.692227**	**-0.468006**
26	**1**	**0**	**0.139803**	**2.526419**	**-1.614718**
27	**7**	**0**	**-0.814878**	**0.848347**	**0.489932**
28	**6**	**0**	**2.299163**	**-0.652771**	**-0.859446**
29	**1**	**0**	**1.838689**	**-1.440946**	**-1.459438**
30	**1**	**0**	**2.965726**	**-0.113061**	**-1.537568**
31	**6**	**0**	**3.065971**	**-1.214421**	**0.253040**
32	**6**	**0**	**3.704111**	**-1.675653**	**1.169517**
33	**1**	**0**	**4.277633**	**-2.087386**	**1.971432**



bis(dimethylamino)methaniminium XYZ orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.000008	0.495886	0.000043
2	7	0	1.175962	-0.159804	0.025362
3	7	0	0.000010	1.845606	0.000104
4	1	0	0.798286	2.369885	0.325234
5	1	0	-0.798264	2.370022	-0.324807
6	7	0	-1.175943	-0.159760	-0.025477
7	6	0	-2.423798	0.485906	0.409290
8	1	0	-2.949685	0.955776	-0.430817
9	1	0	-3.075074	-0.281038	0.834036
10	1	0	-2.219589	1.226896	1.183084
11	6	0	-1.343184	-1.450512	-0.713356
12	1	0	-0.441527	-1.706318	-1.267143
13	1	0	-1.579288	-2.249036	-0.003998
14	1	0	-2.169504	-1.357778	-1.424321

15	6	0	2.423764	0.485890	-0.409524
16	1	0	2.949638	0.955953	0.430496
17	1	0	3.075094	-0.281100	-0.834098
18	1	0	2.219461	1.226720	-1.183438
19	6	0	1.343209	-1.450419	0.713498
20	1	0	0.441748	-1.705811	1.267824
21	1	0	1.578712	-2.249252	0.004278
22	1	0	2.169891	-1.357718	1.424043



1-amino-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium XYZ orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.579151	0.380858	0.274634
2	6	0	-2.044368	-0.992421	-0.172558
3	6	0	-1.415606	1.359303	-0.010007

4	**6**	**0**	**-0.214275**	**0.452771**	**-0.028060**
5	**1**	**0**	**-2.797690**	**0.365888**	**1.345602**
6	**1**	**0**	**-1.509071**	**1.840021**	**-0.992753**
7	**1**	**0**	**-2.317197**	**-1.242797**	**-1.204844**
8	**1**	**0**	**-3.493219**	**0.658916**	**-0.251418**
9	**1**	**0**	**-2.359905**	**-1.812750**	**0.476594**
10	**1**	**0**	**-1.323103**	**2.155977**	**0.731957**
11	**7**	**0**	**1.058178**	**0.841933**	**-0.031401**
12	**6**	**0**	**0.380142**	**-1.929211**	**-0.194481**
13	**6**	**0**	**2.162089**	**-0.139499**	**-0.128888**
14	**6**	**0**	**1.715247**	**-1.496112**	**0.416773**
15	**1**	**0**	**0.487485**	**-2.206018**	**-1.250657**
16	**1**	**0**	**-0.035399**	**-2.789636**	**0.336425**
17	**1**	**0**	**2.477113**	**-0.202811**	**-1.176953**
18	**1**	**0**	**2.994187**	**0.268793**	**0.446424**
19	**1**	**0**	**2.480575**	**-2.243909**	**0.194281**
20	**1**	**0**	**1.618021**	**-1.442886**	**1.506426**
21	**7**	**0**	**-0.577715**	**-0.822198**	**-0.083565**
22	**7**	**0**	**1.444386**	**2.192964**	**-0.042476**
23	**1**	**0**	**1.057870**	**2.692476**	**-0.837767**
24	**1**	**0**	**1.221921**	**2.655707**	**0.834303**

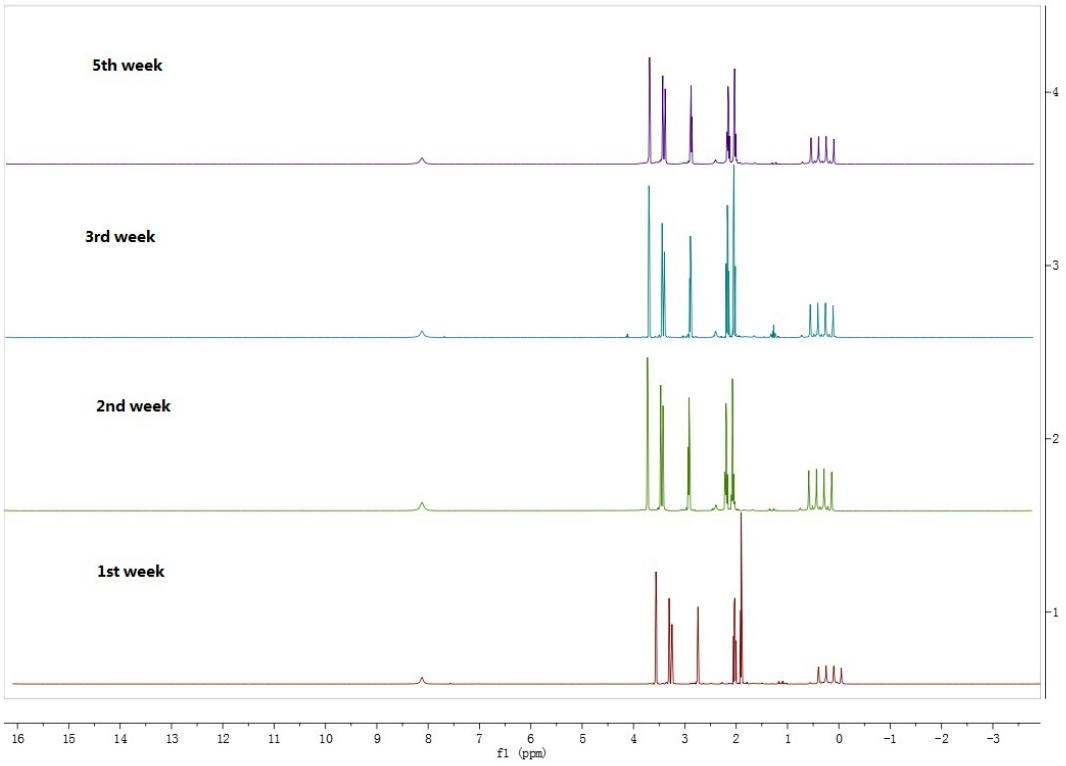


Figure S1. Stability study of **IL10;** The ^{1}H NMR changes of **IL10** dissolved in CD_3CN are dependent on the time.

Figure S2-S29. ^{1}H NMR and ^{13}C NMR spectra of HILs **1-14** in CD_3CN

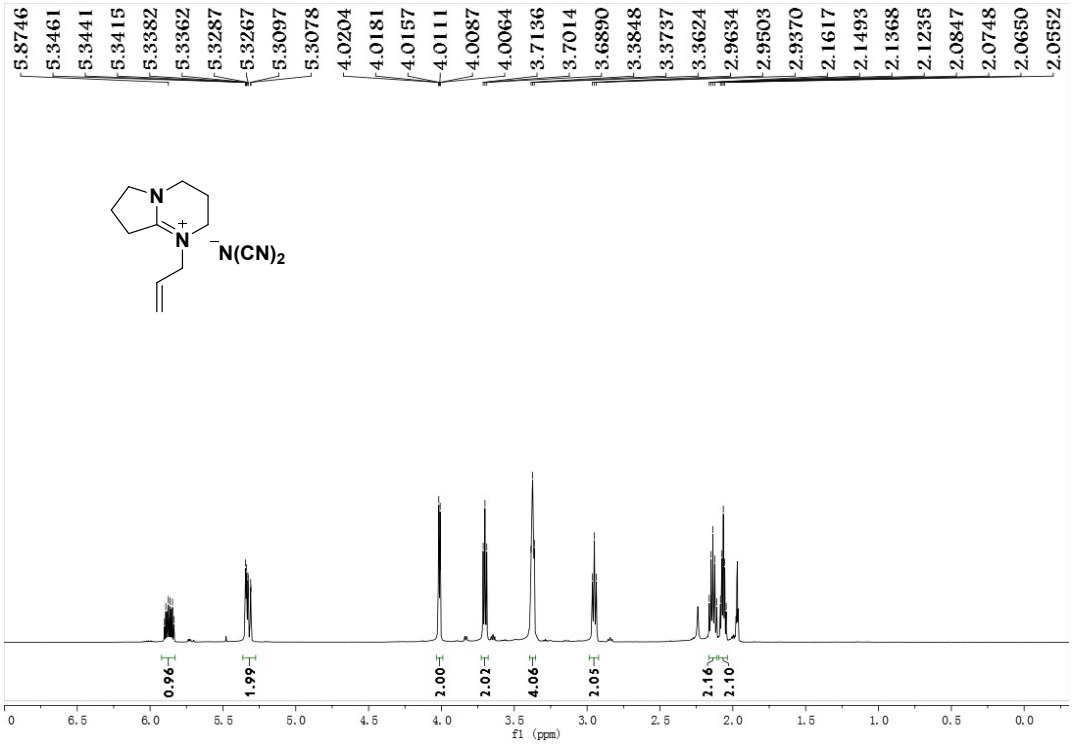


Figure S2. ^{1}H NMR of **IL1**

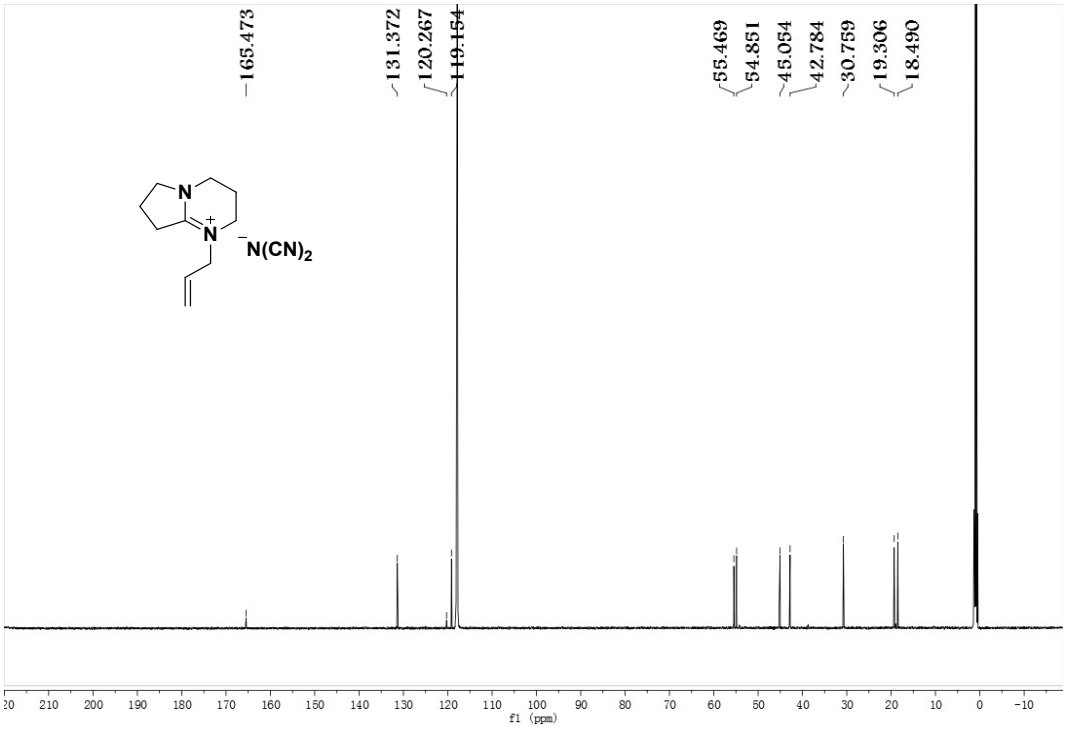


Figure S3. ^{13}C NMR of **IL1**

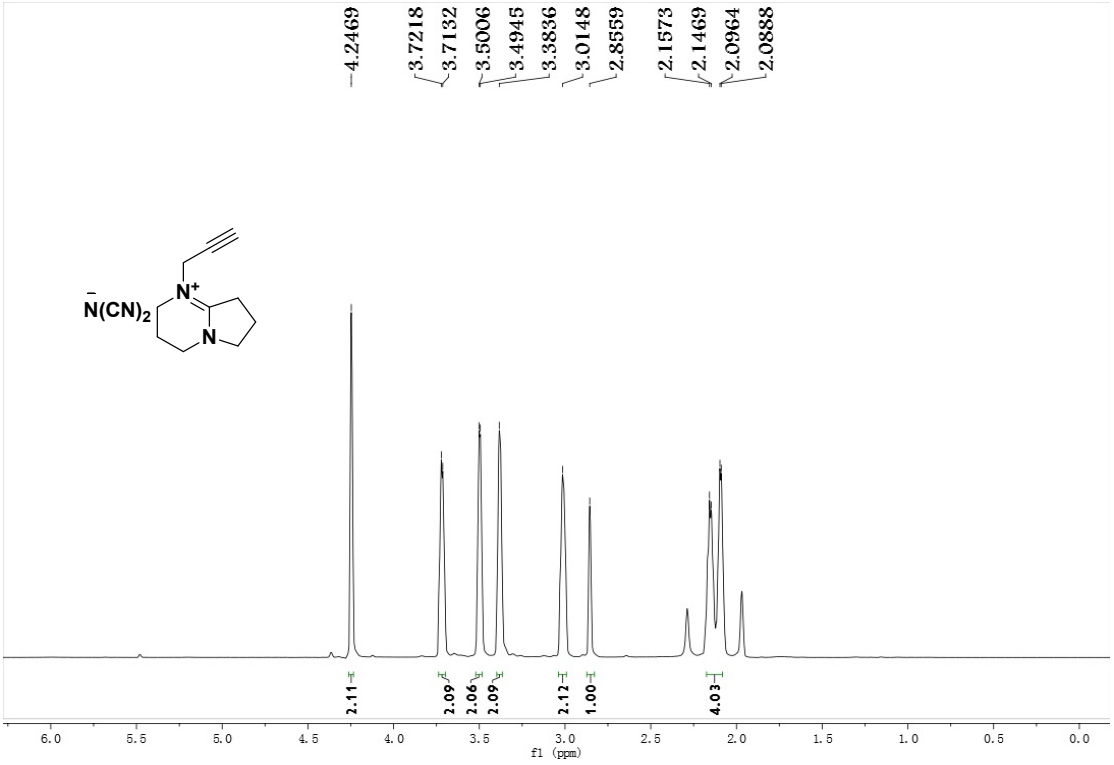


Figure S4. ^{1}H NMR of **IL2**

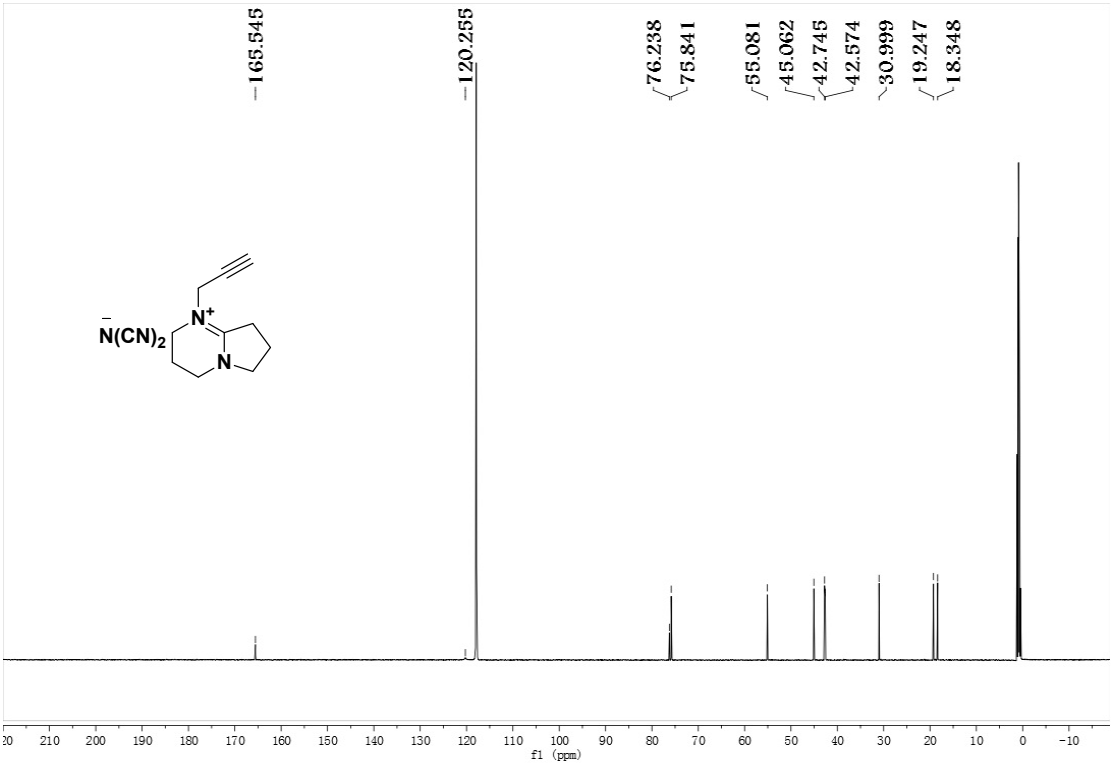


Figure S5. ^{13}C NMR of **IL2**

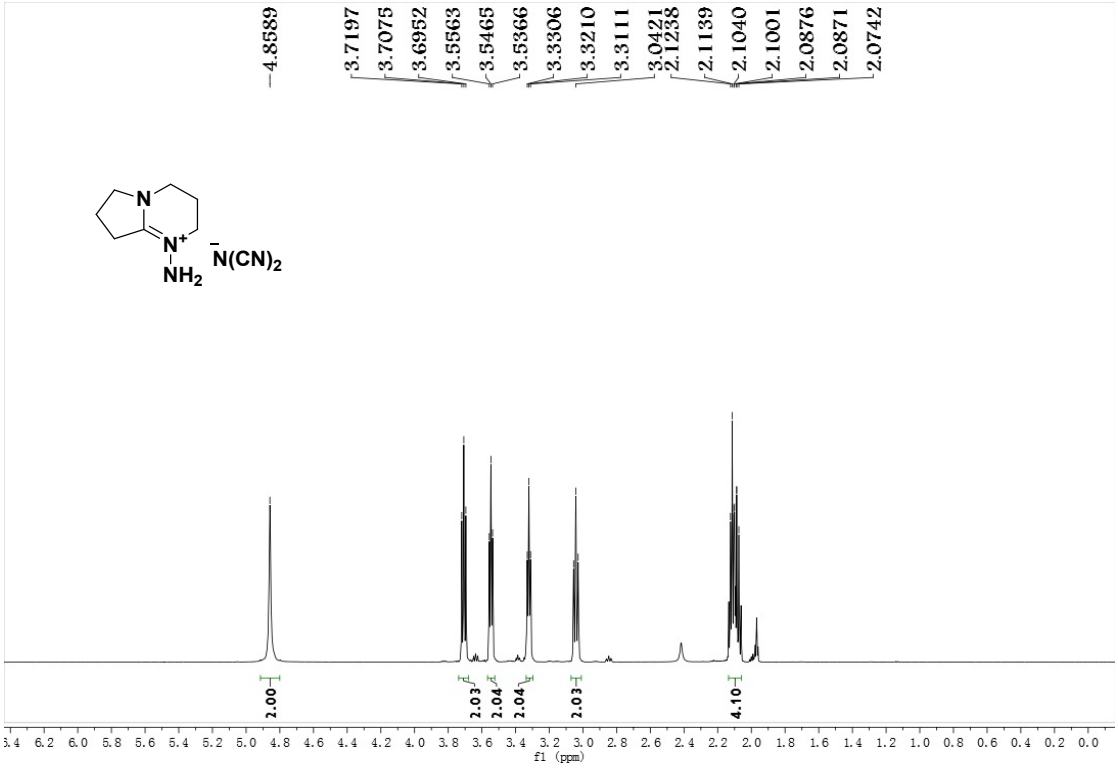


Figure S6. ^{1}H NMR of **IL3**

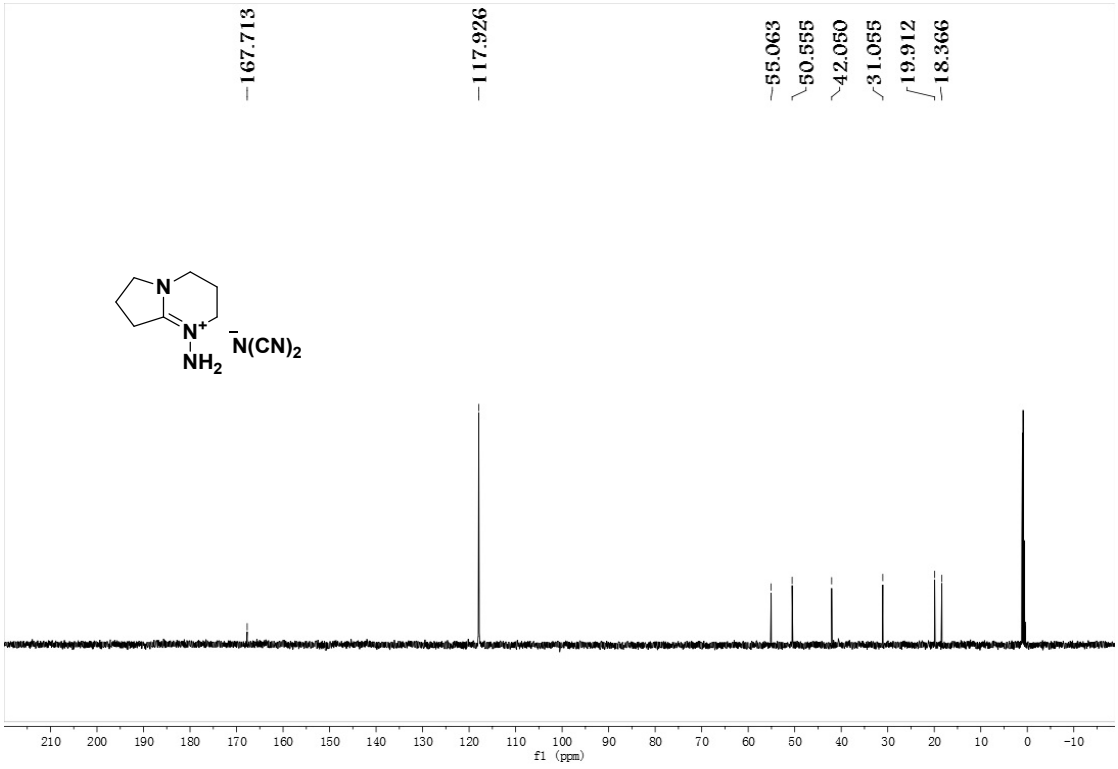


Figure S7. ^{13}C NMR of **IL3**

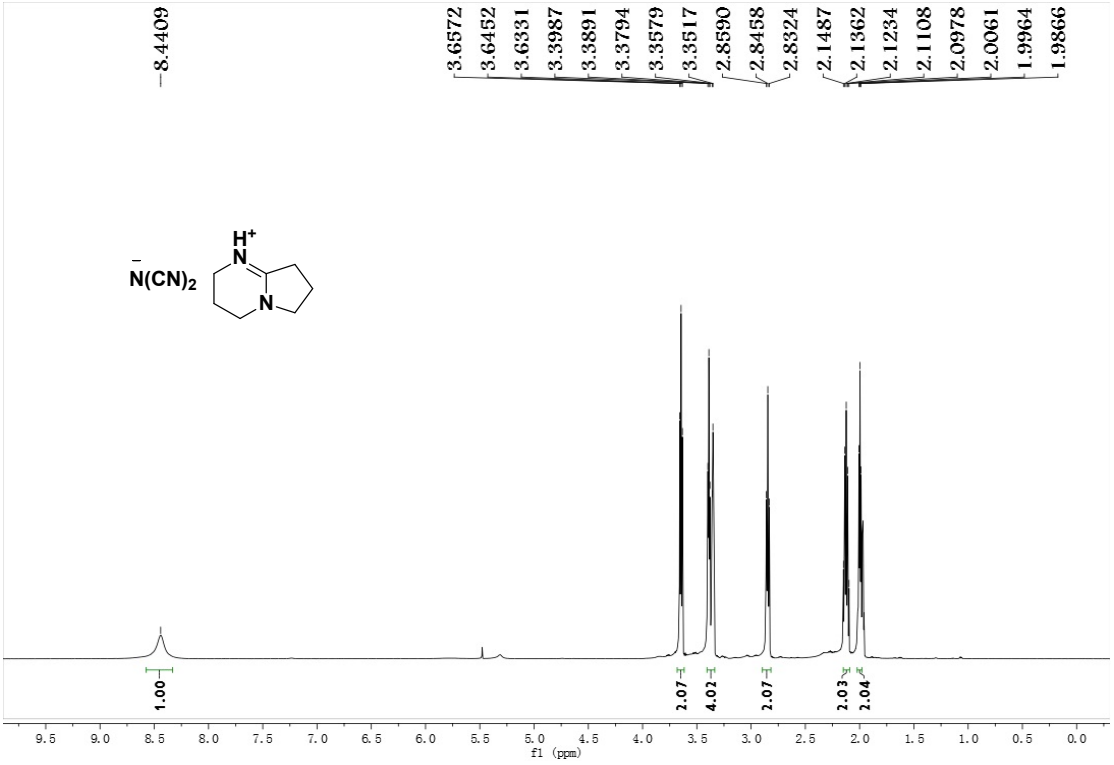


Figure S8. ^{1}H NMR of **IL4**

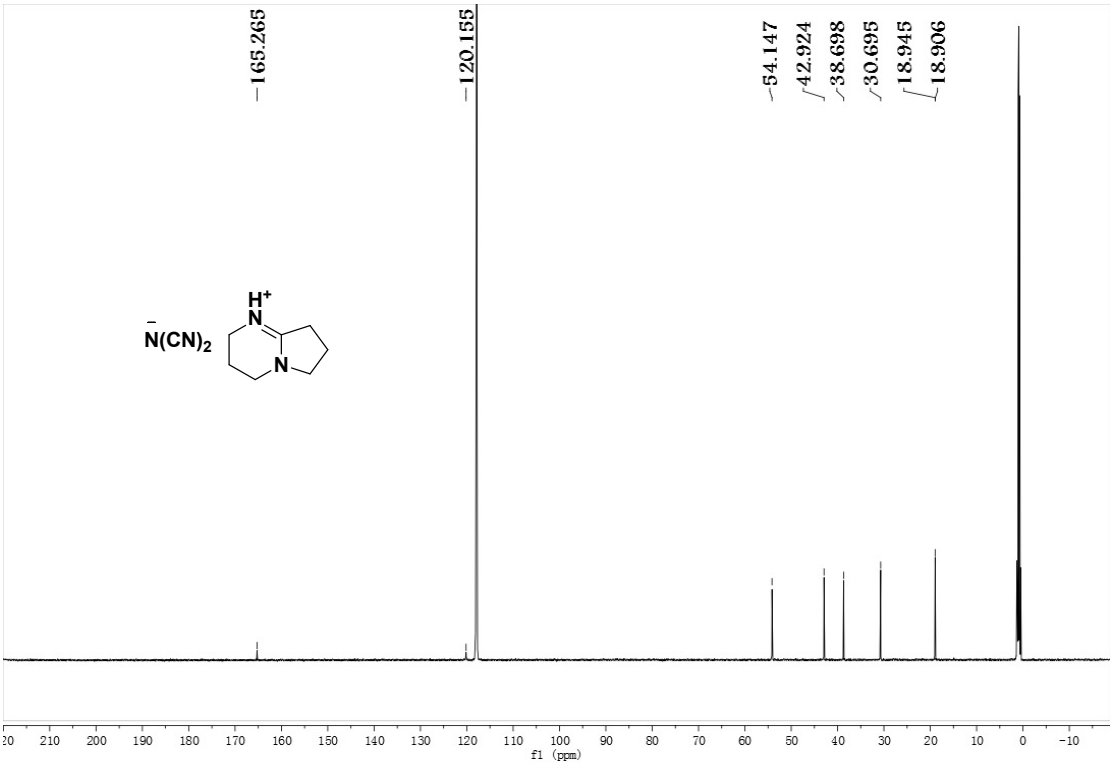


Figure S9. ^{13}C NMR of **IL4**

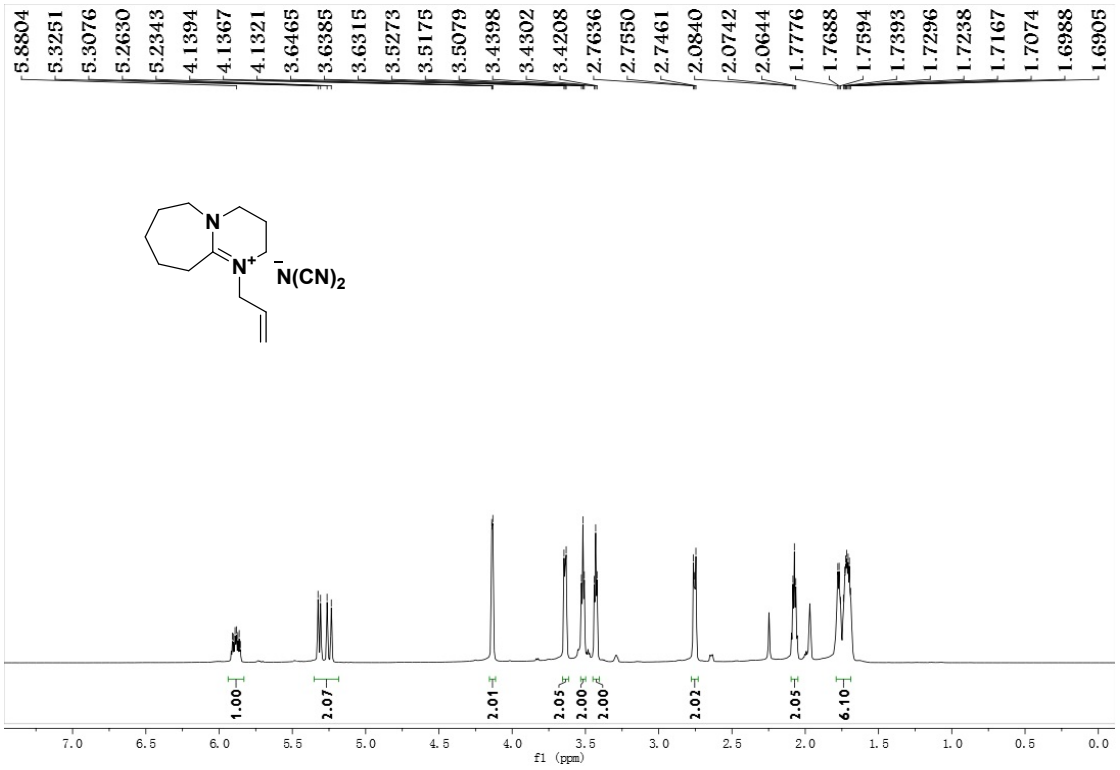


Figure S10. ^{1}H NMR of **IL5**

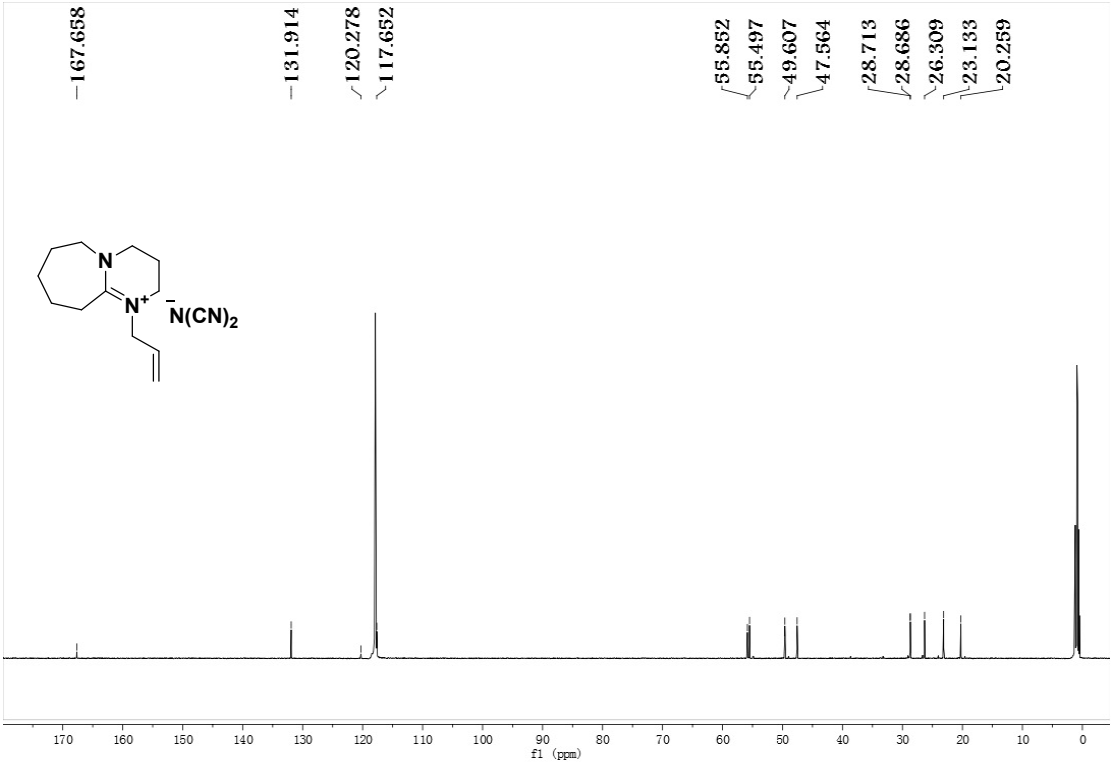


Figure S11. ^{13}C NMR of **IL5**

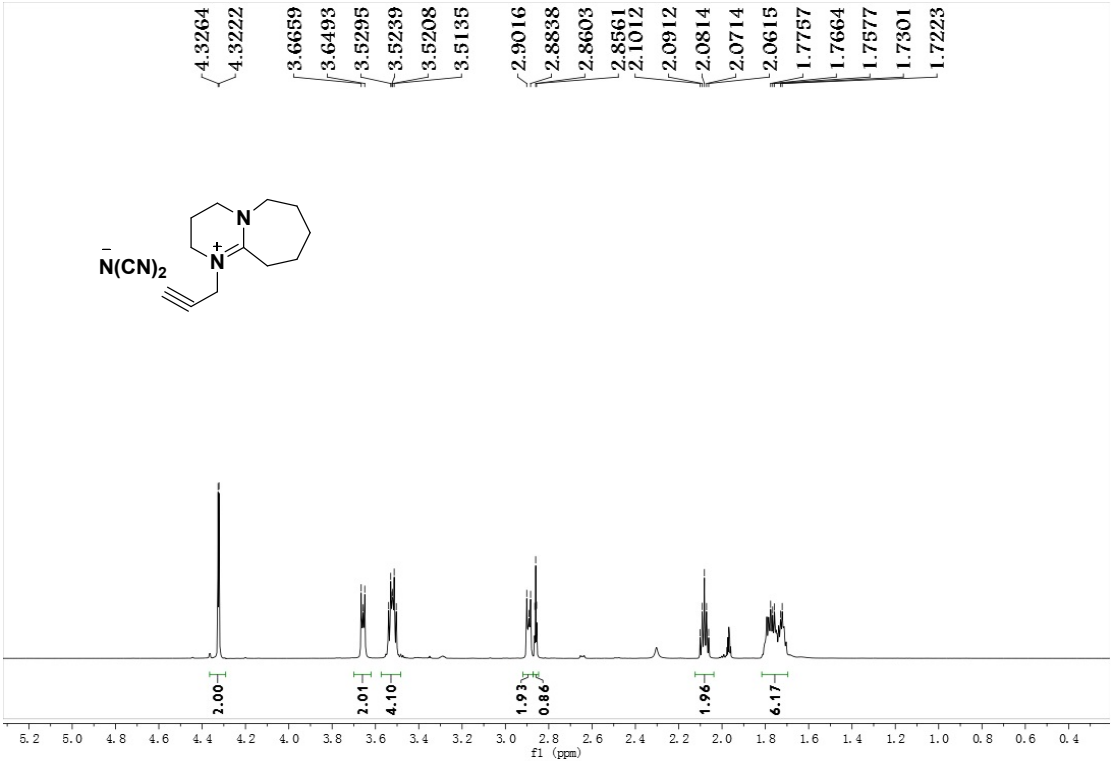


Figure S12. ^{1}H NMR of **IL6**

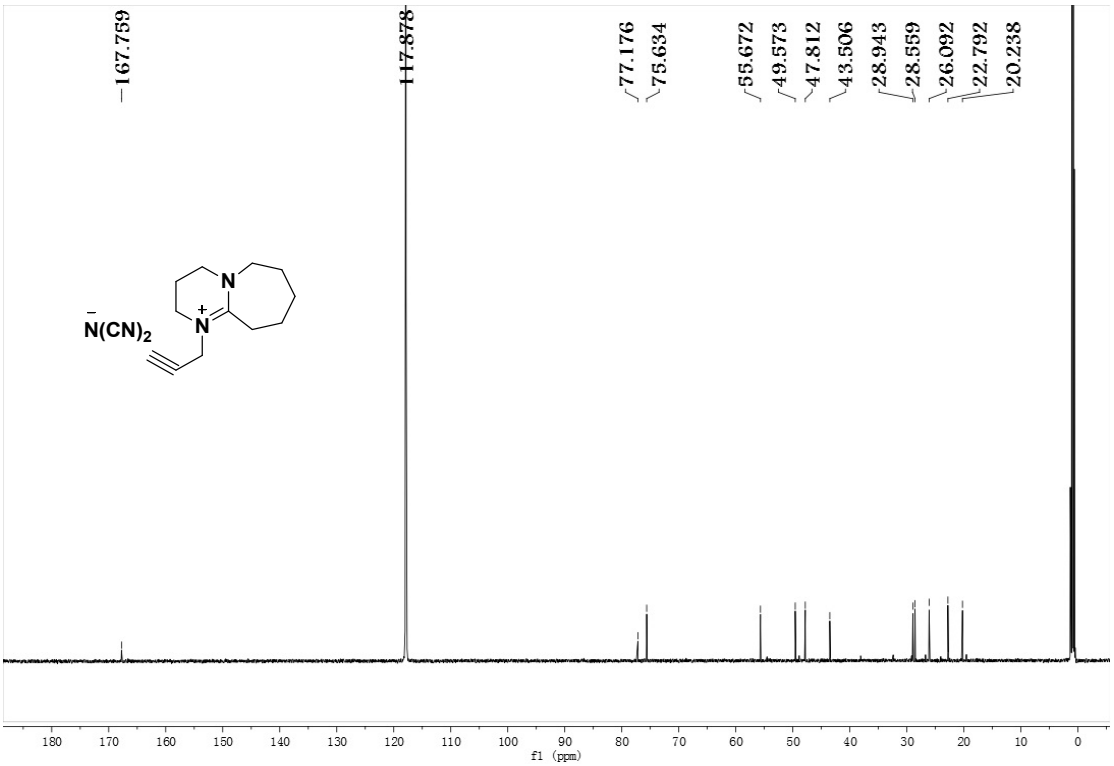


Figure S13. ^{13}C NMR of **IL6**

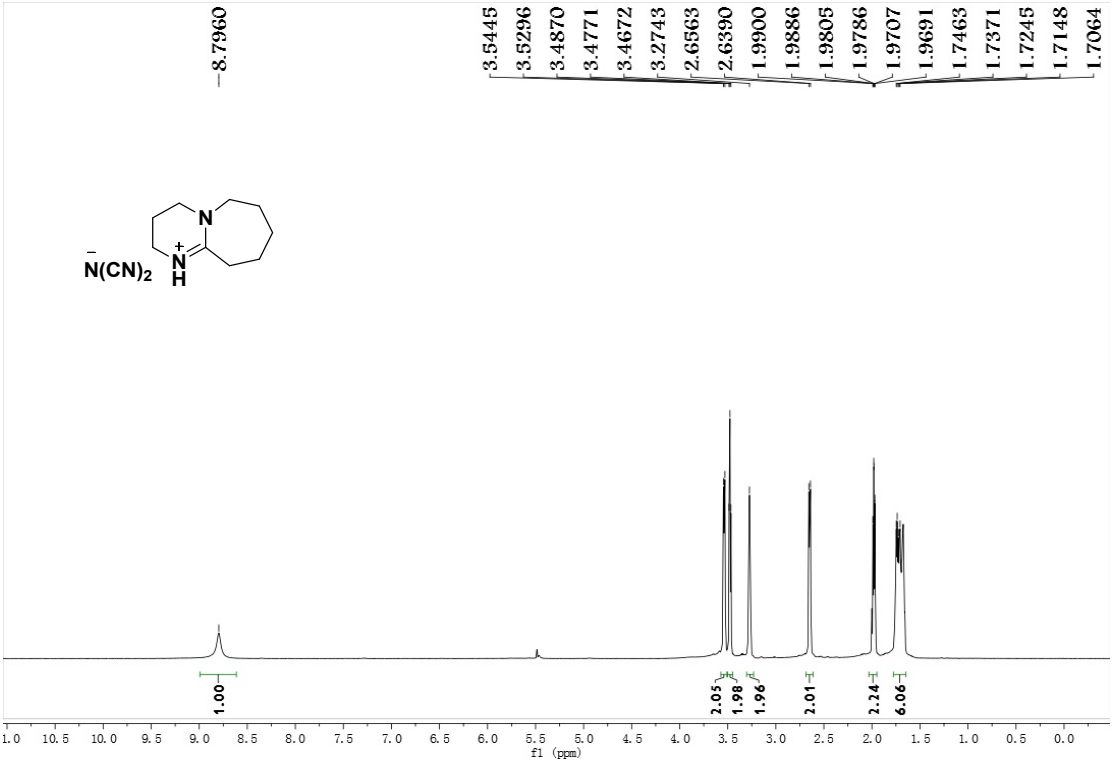


Figure S14. ^{1}H NMR of **IL7**

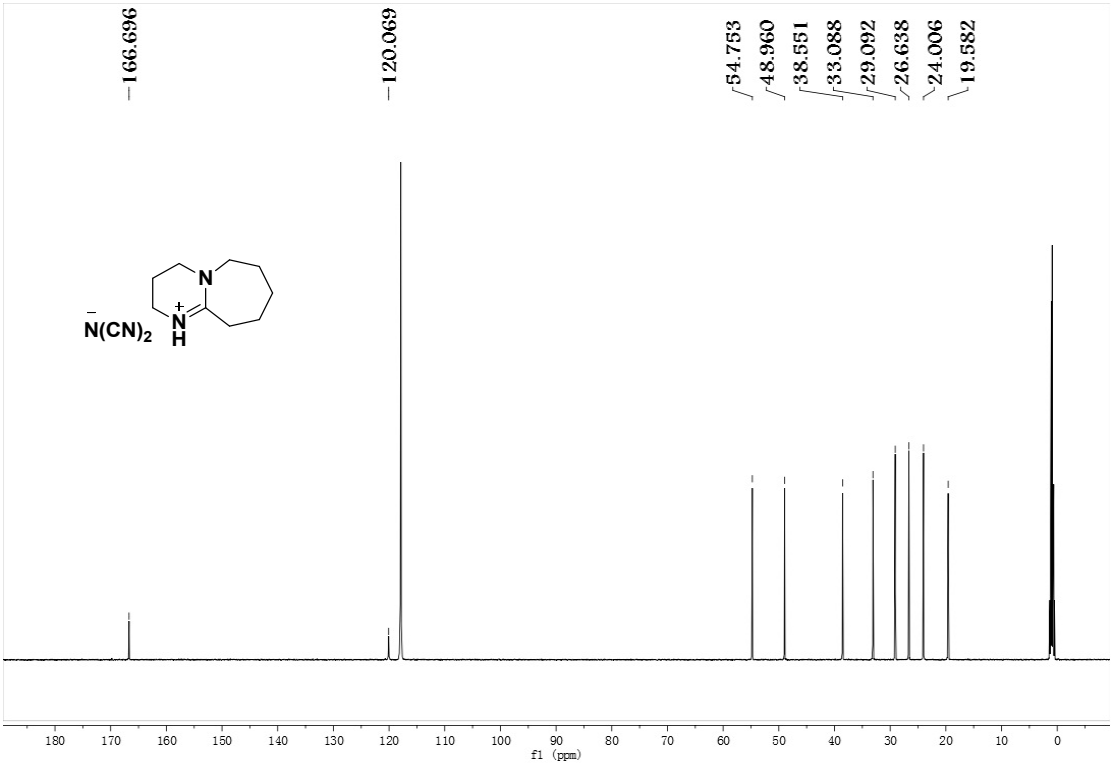


Figure S15. ^{13}C NMR of **IL7**

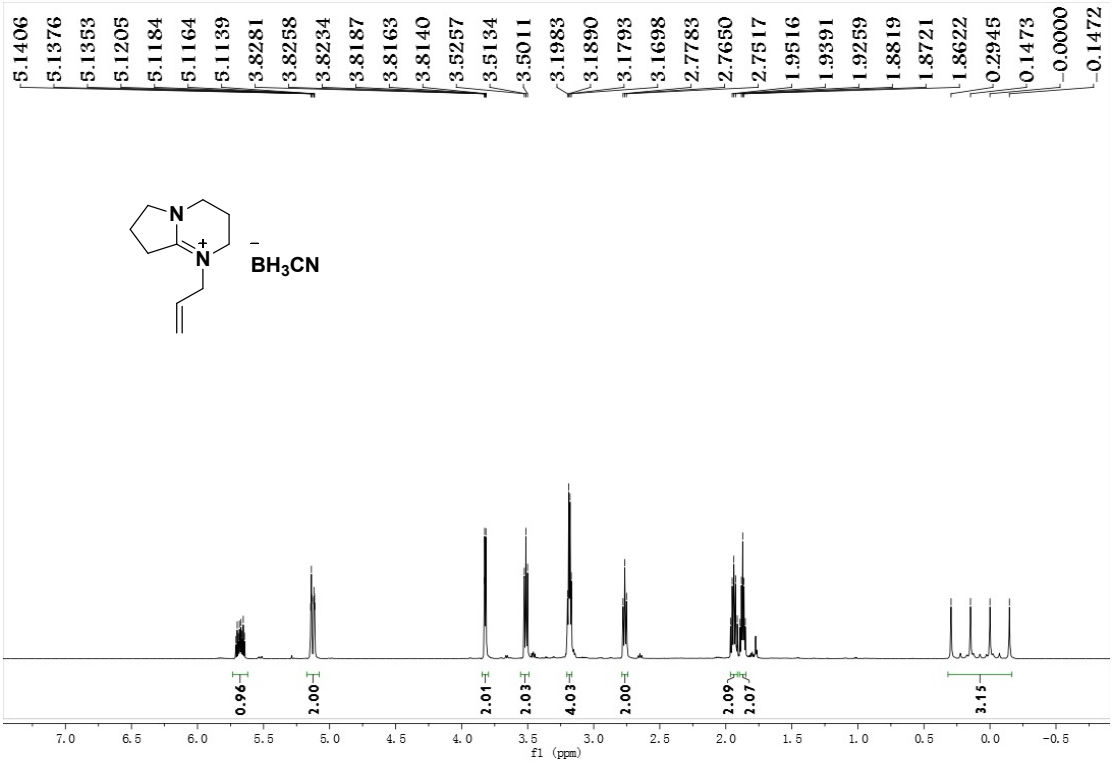


Figure S16. ^{1}H NMR of **IL8**

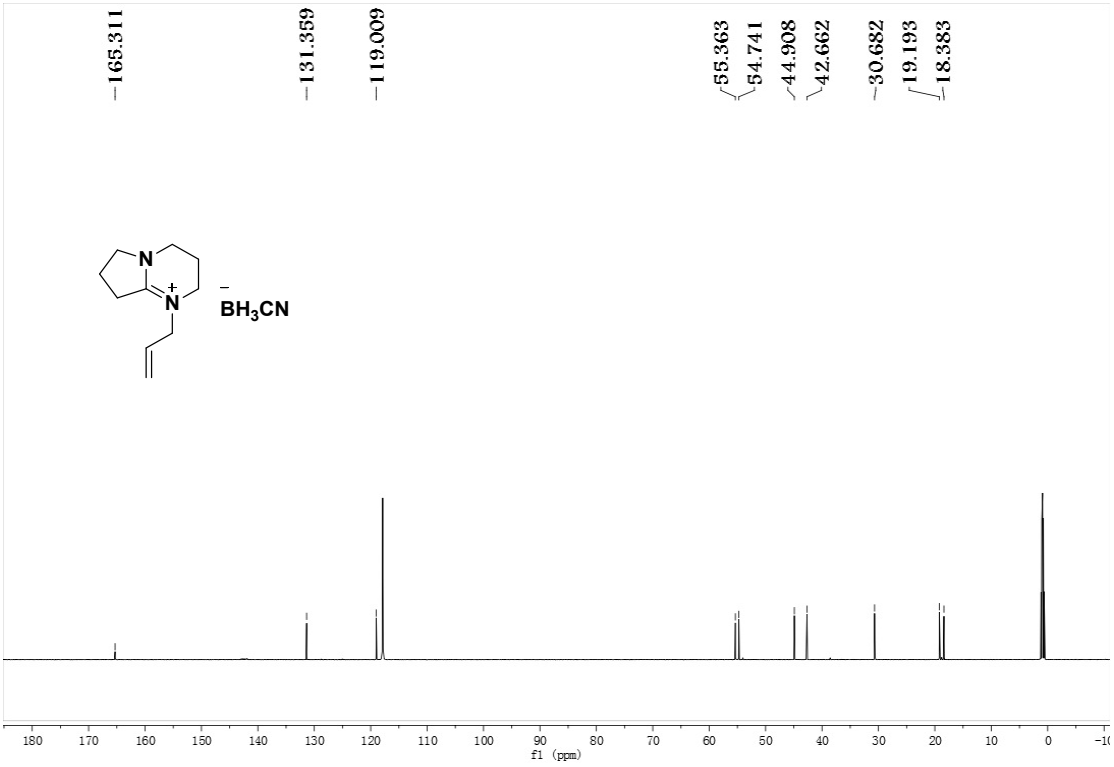


Figure S17. ^{13}C NMR of **IL8**

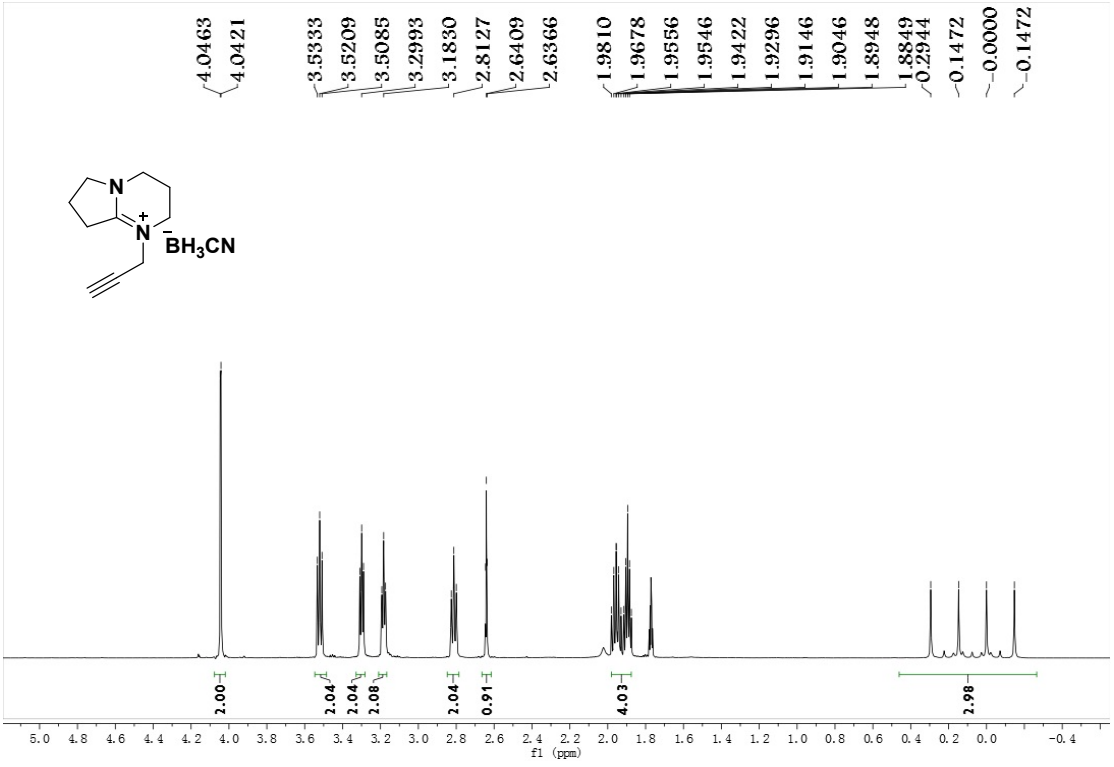


Figure S18. ^{1}H NMR of **IL9**

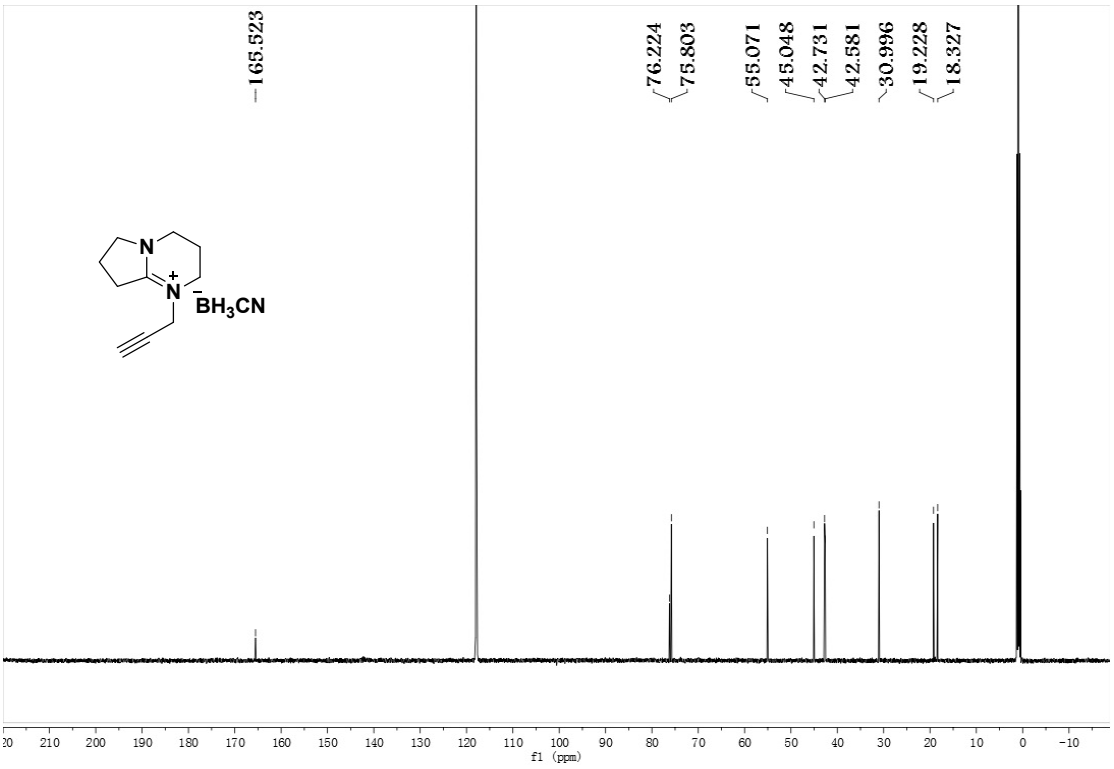


Figure S19. ^{13}C NMR of **IL9**

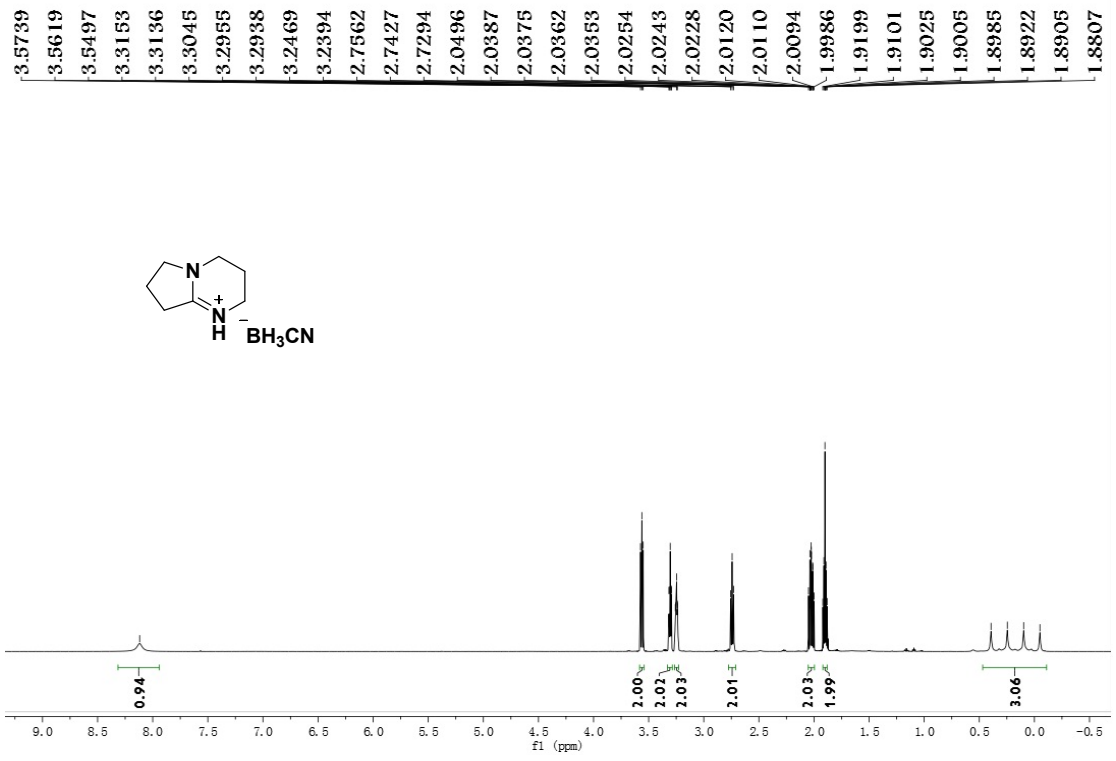


Figure S20. ^{1}H NMR of **IL10**

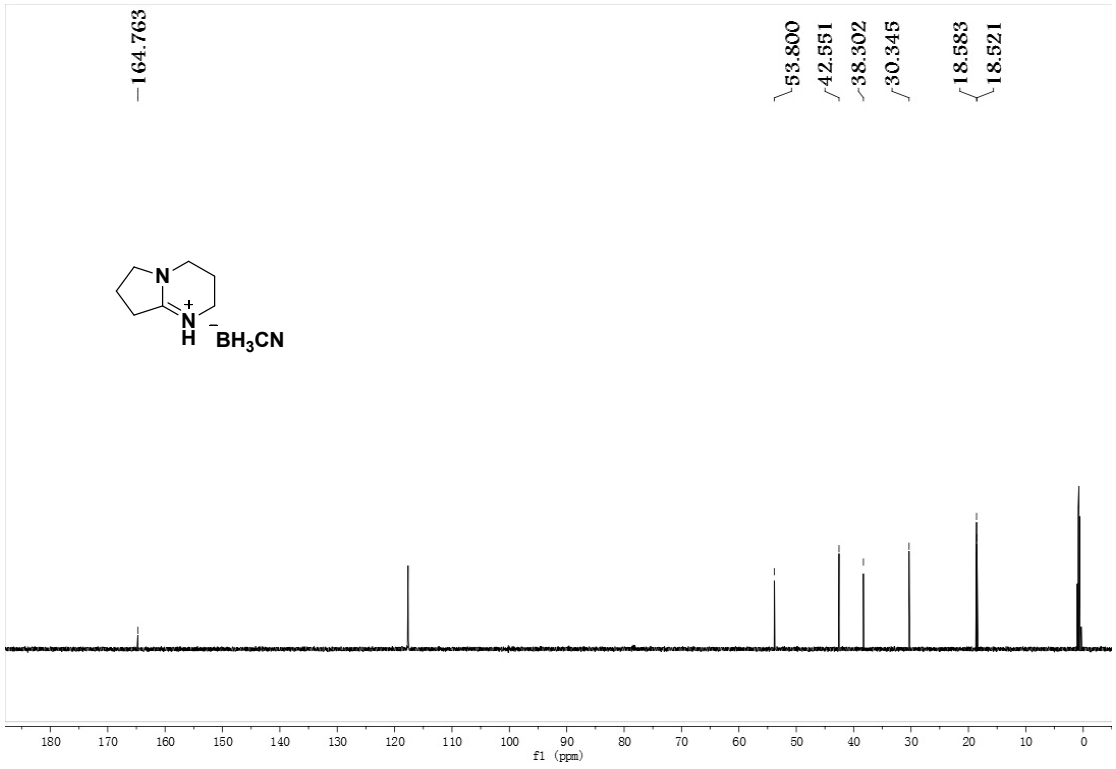


Figure S21. ^{13}C NMR of **IL10**

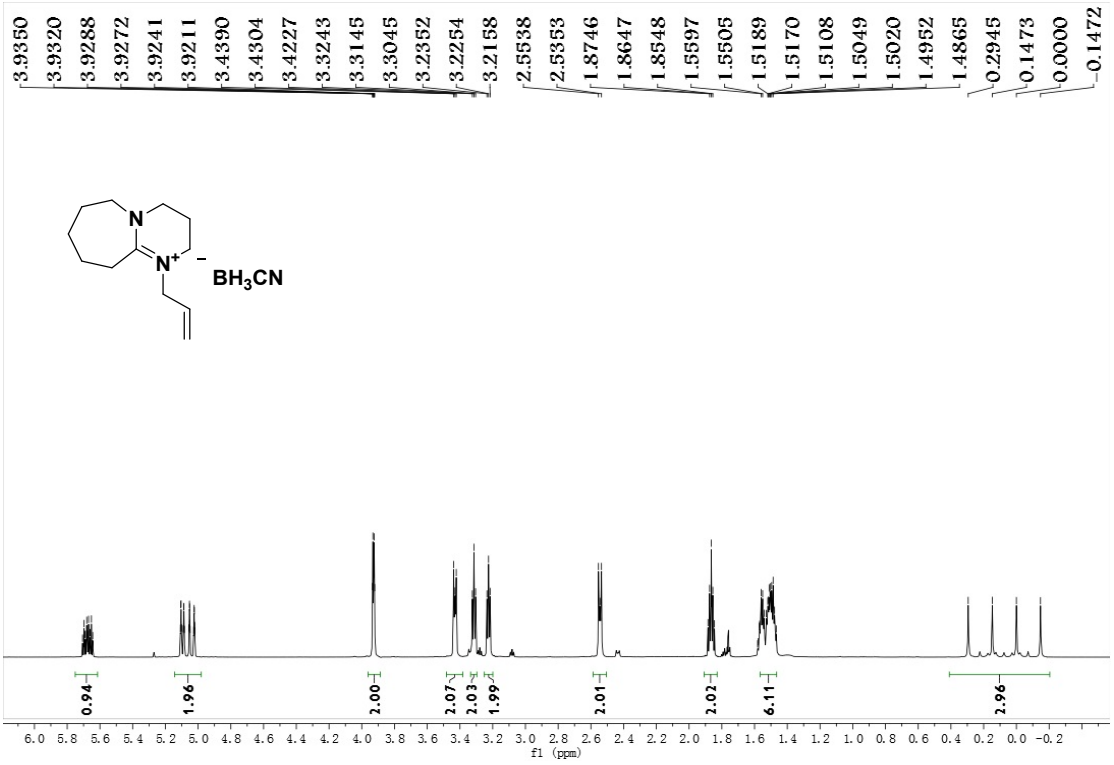


Figure S22. ^{1}H NMR of **IL11**

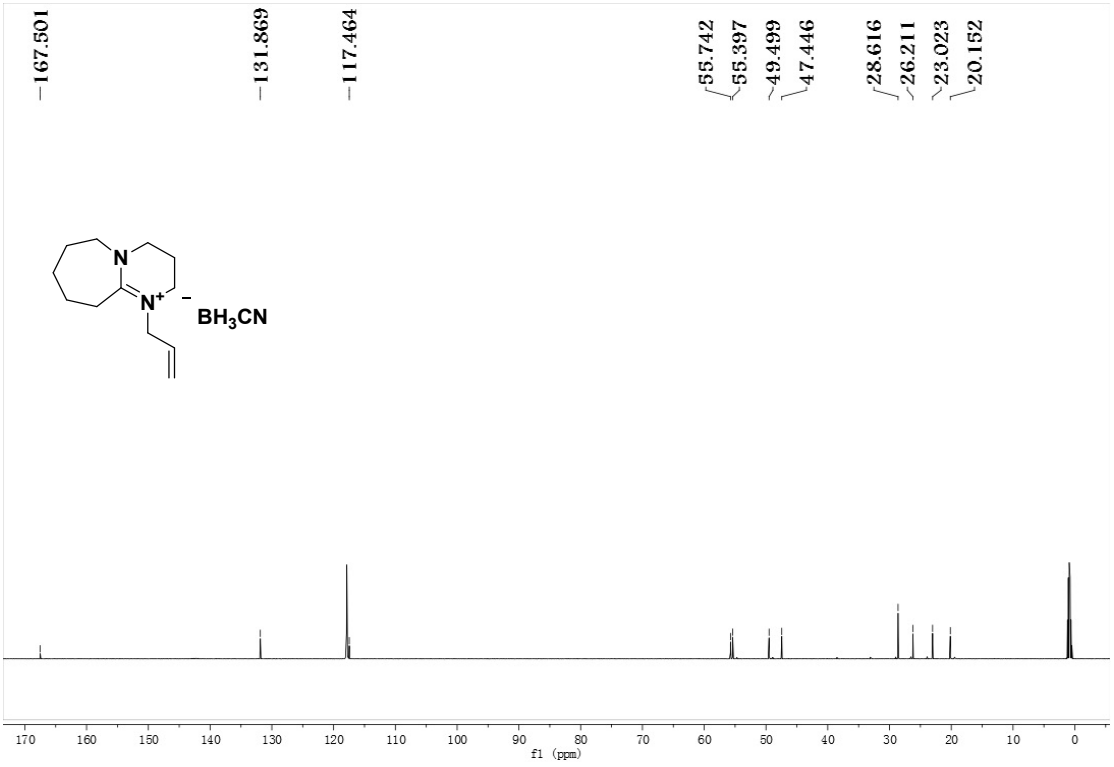


Figure S23. ^{13}C NMR of **IL11**

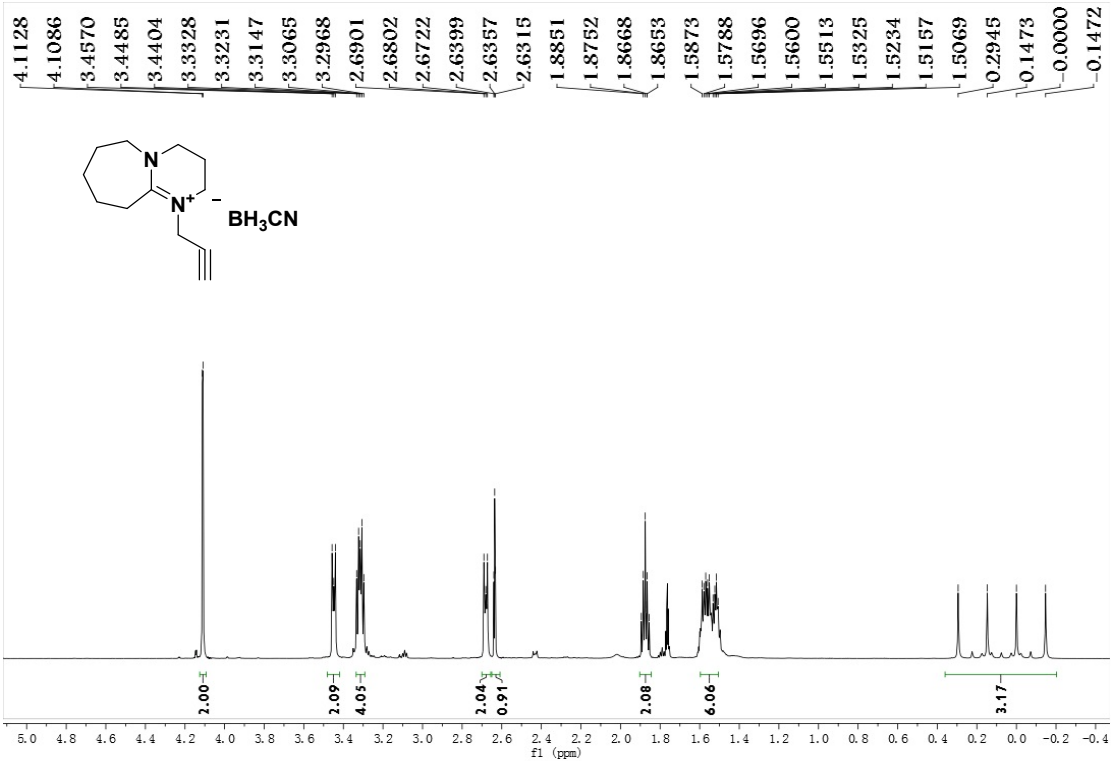


Figure S24. ^{1}H NMR of **IL12**

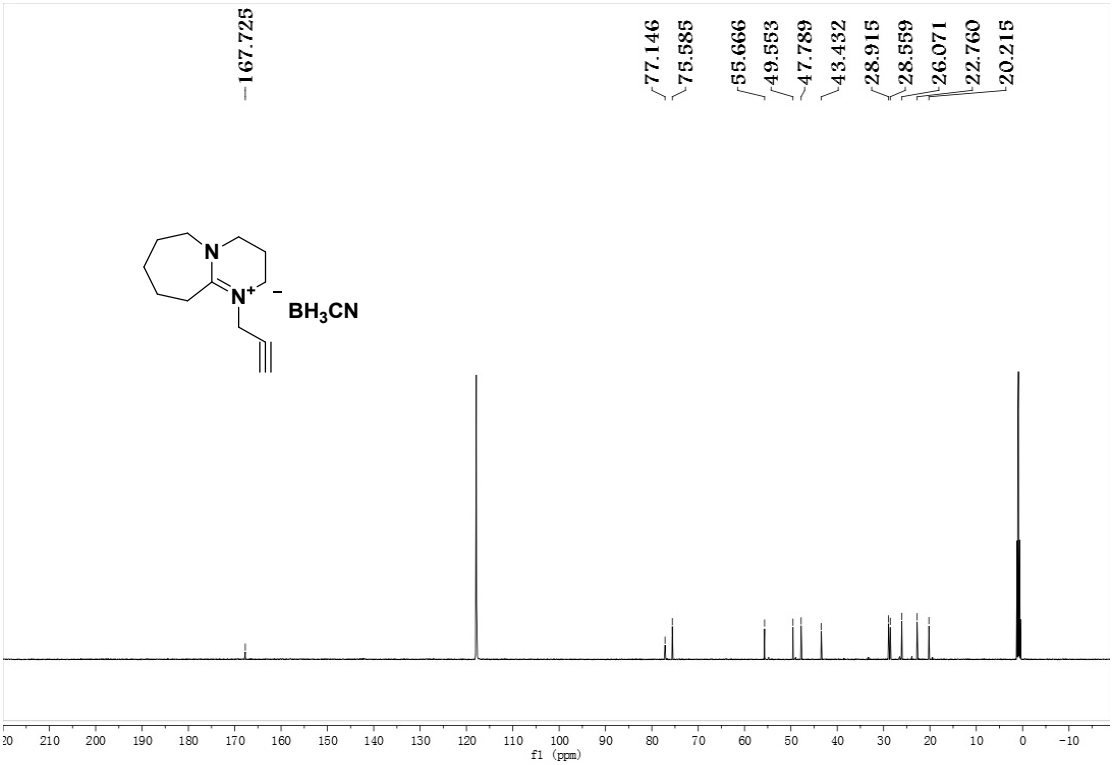


Figure S25. ^{13}C NMR of **IL12**

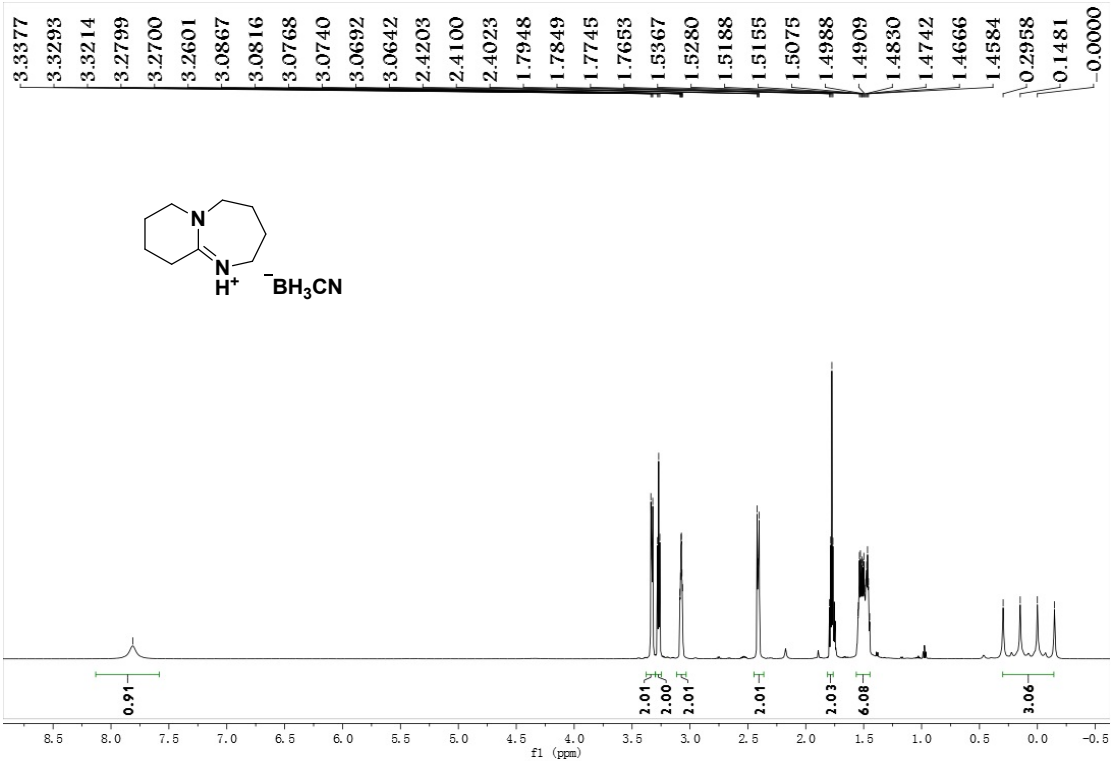


Figure S26. ^{1}H NMR of **IL13**

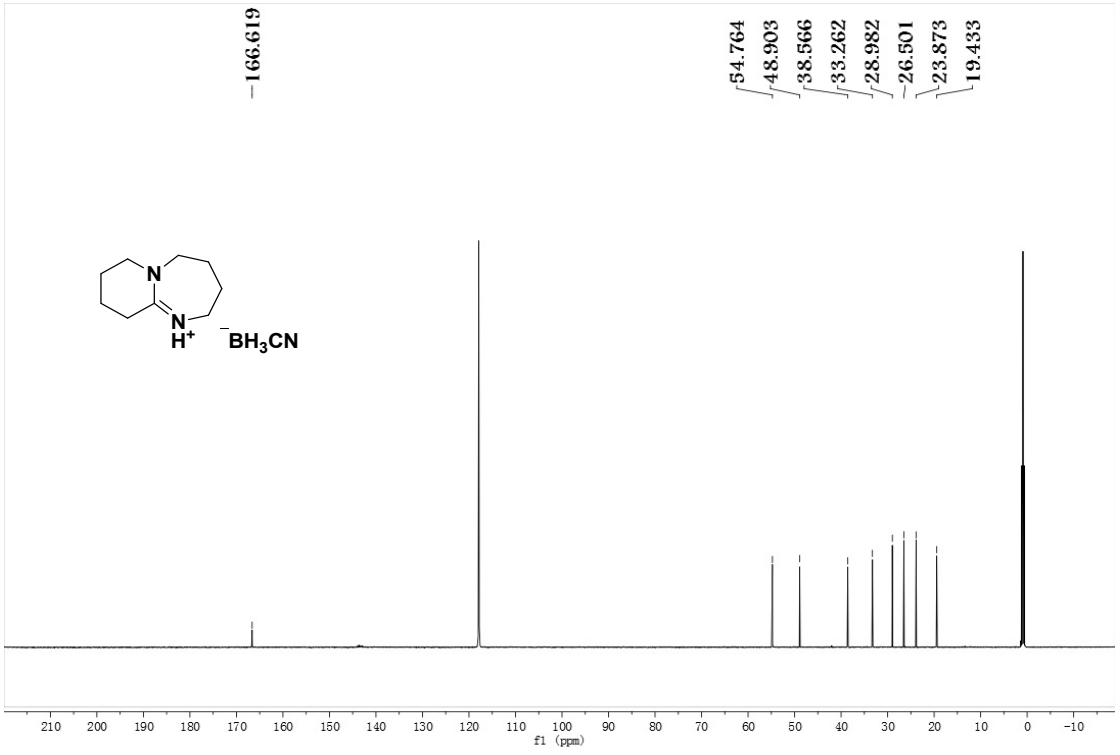


Figure S27. ^{13}C NMR of **IL13**

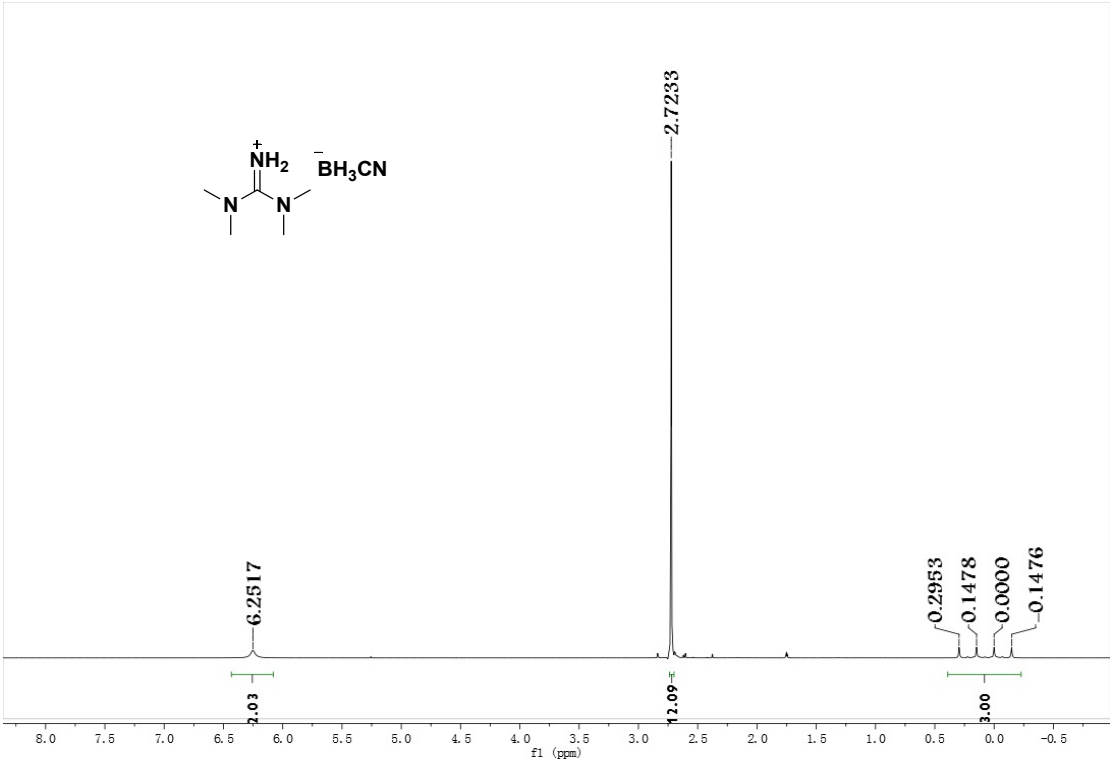


Figure S28. ^{1}H NMR of **IL14**

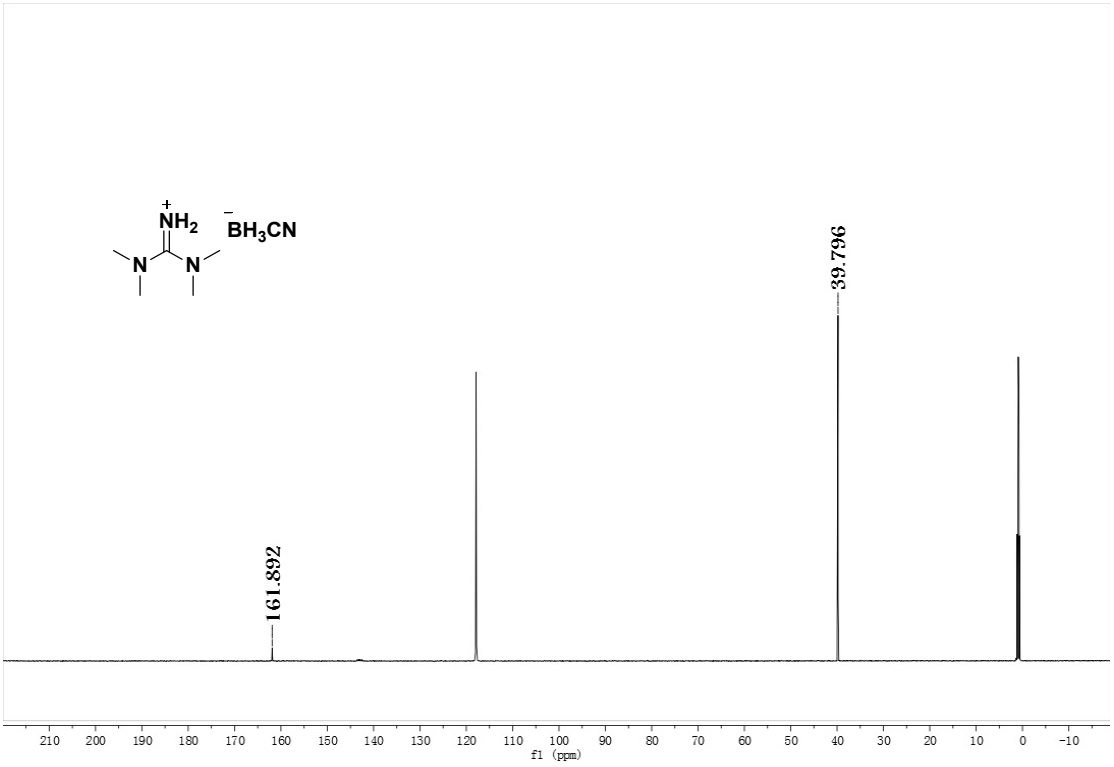


Figure S29. ^{13}C NMR of **IL14**