Supplementary Material

Generation and reactions of thiirenium ions by the cation pool method

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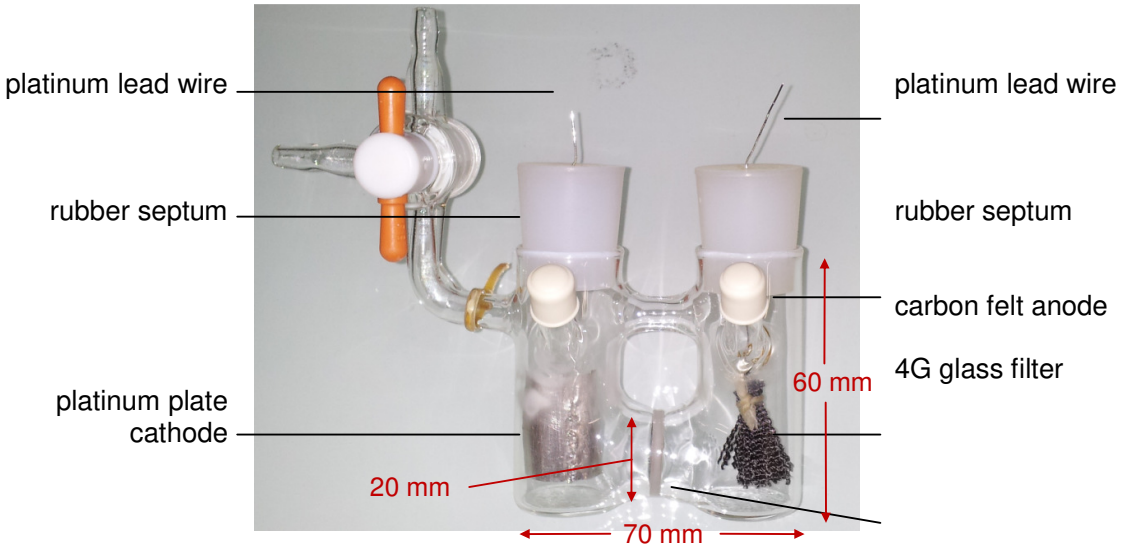

Figure S1. An H-type divided cell for electrolysis.

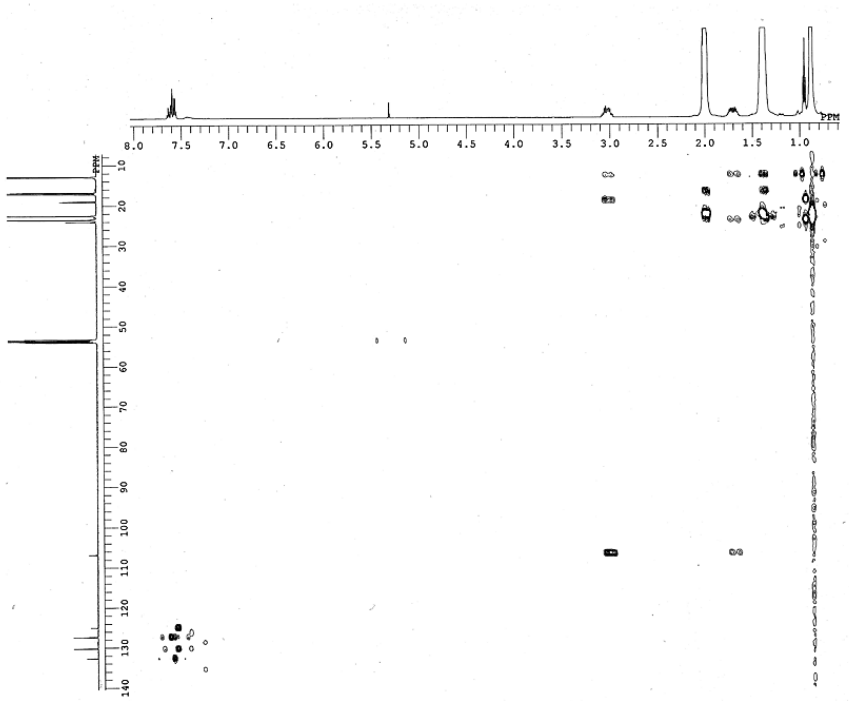

Figure S2. The ^{1}H-^{13}C HMQC spectrum of thionium ion **1a** at −78 °C.

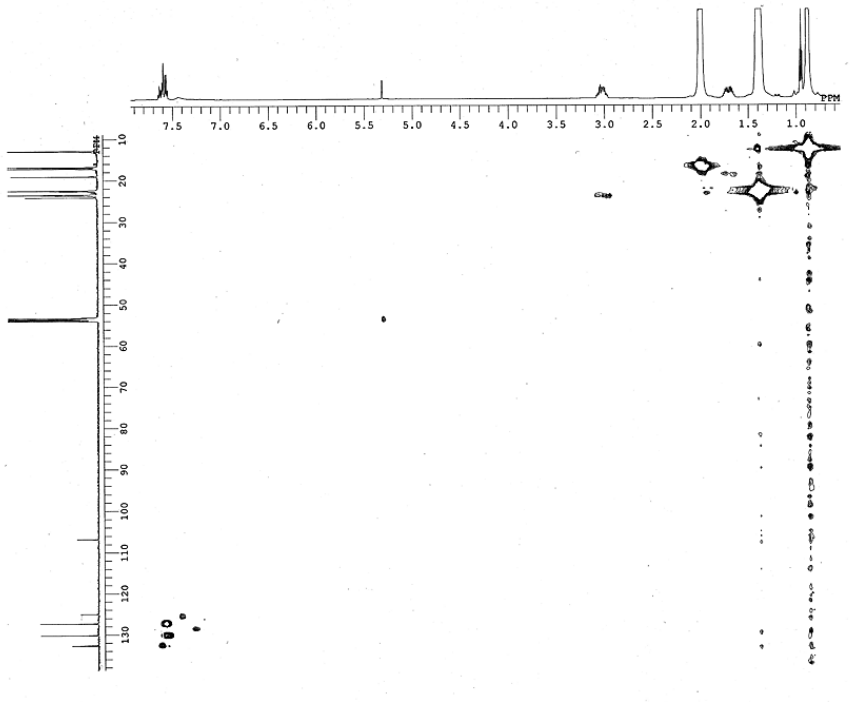

Figure S3. The ^{1}H-^{13}C HMBC spectrum of thionium ion **1a** at −78 °C.

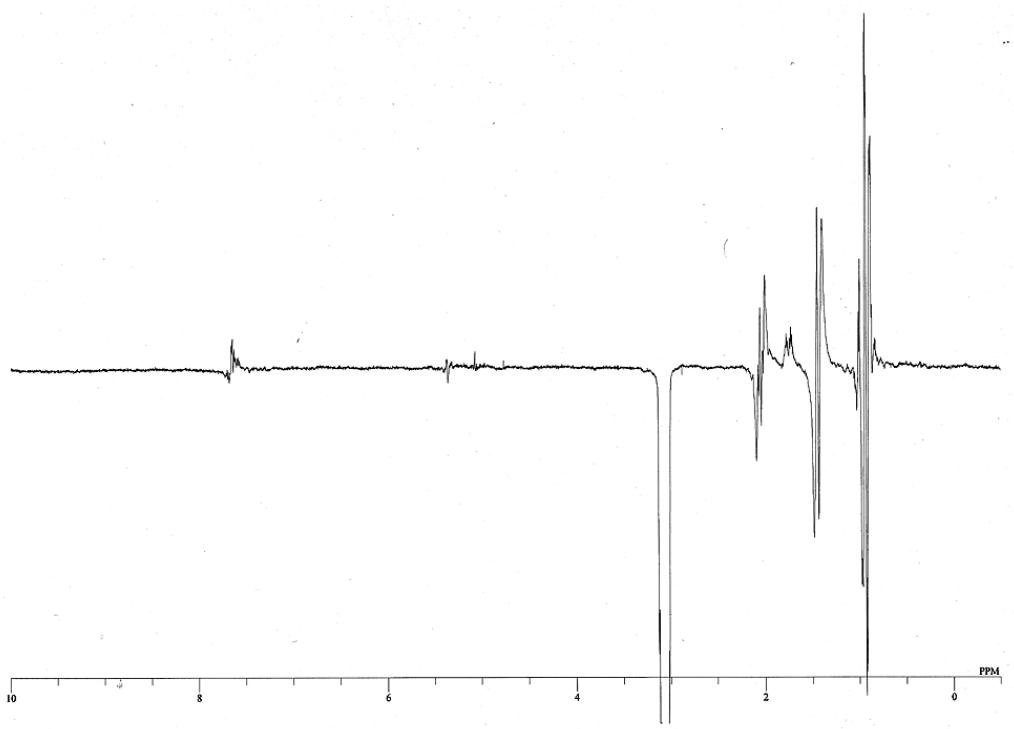

Figure S4. Differential NOE spectrum of thionium ion **1a** at −78 °C.

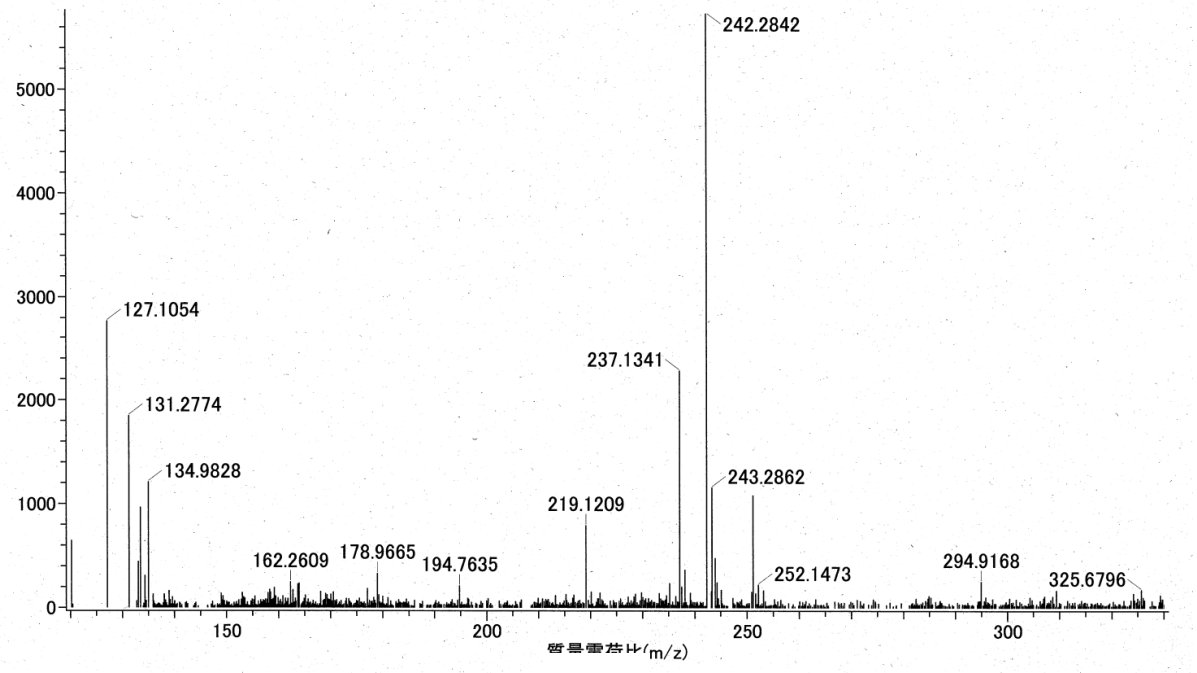

Figure S5. CSI-MA spectrum of **1a** at 0 °C

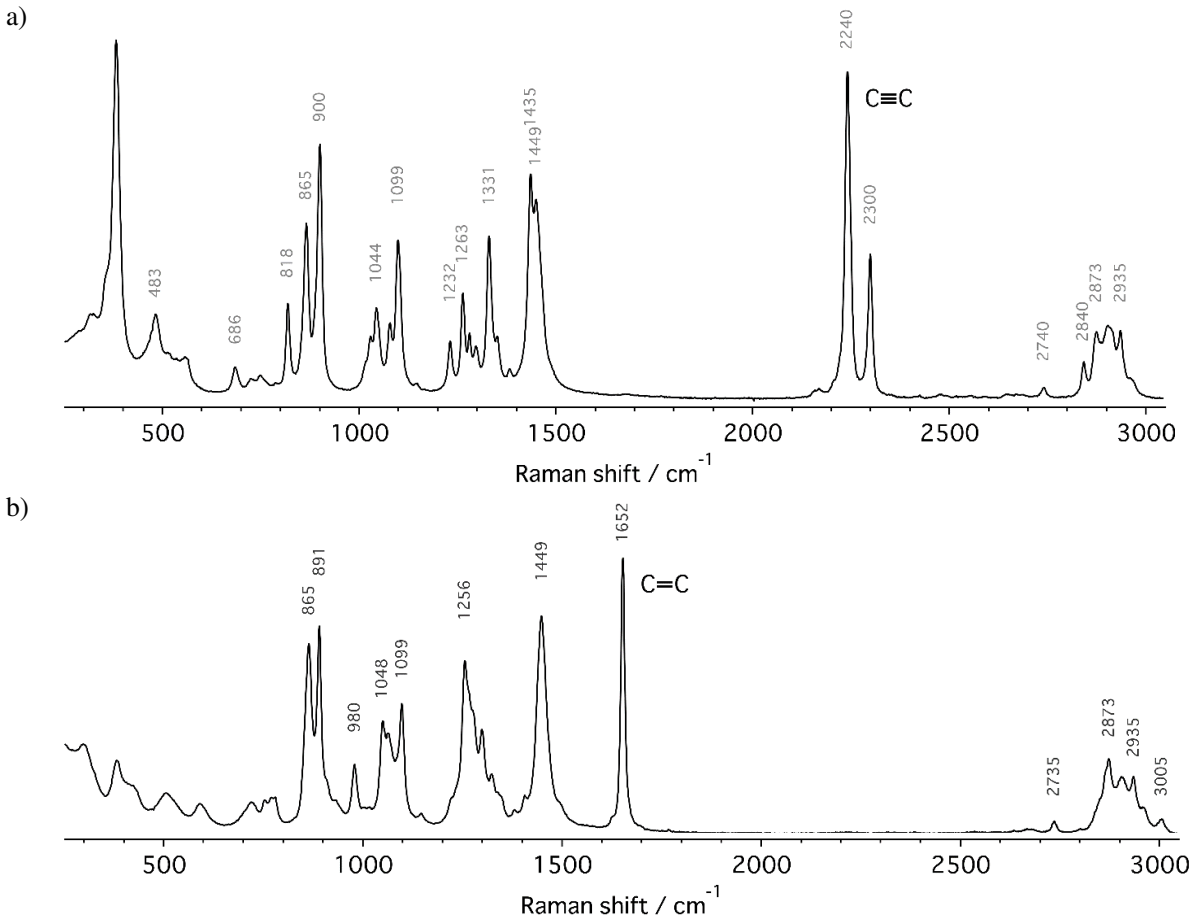

Figure S6. Raman spectra of a) 4-octyne and b) *cis*-4-octene.

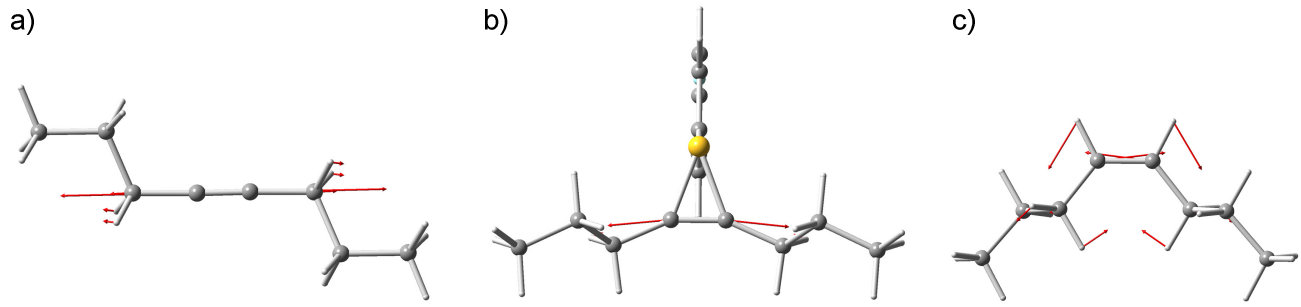

Figure S7. Vibrational modes of a) 4-octyne, b) **1a'**, and c) 4-octene.

DFT Calculations

Table S1. Cartesian coordinates (Å) of the optimized structure of thiirenium ion **1a** calculated at the RB3LYP/6-31G(d) level of theory.

Atom	X	Y	Z	Atom	X	Y	Z
C	-	-	0.646589	H	-	-	1.858382
C	-	-	-	H	2.335588	2.436115	0.000000
C	-	-	-	H	1.566452	4.791052	0.000000
C	-	-	1.998522	H	-	3.469844	0.000000
C	0.317094	1.640930	0.000000	H	-	1.109948	0.000000
C	1.272328	2.661890	0.000000	H	-	5.309054	0.000000
C	0.836396	3.987904	0.000000	H	1.217552	-	2.950179
C	-	4.276278	0.000000	H	0.830982	-	2.320267
C	-	3.241975	0.000000	H	-	-	4.790296
C	-	1.911153	0.000000	H	-	-	4.162394
C	0.410552	-	2.848969	H	0.830982	-	-
C	-	-	4.233908	H	1.217552	-	-
C	0.410552	-	-	H	-	-	-
C	-	-	-	H	-	-	-
H	-	-	-	H	0.729728	-	4.820425
H	-	-	-	H	0.729728	-	-
H	-	-	2.512526	S	1.000474	-	0.000000

Table S2. Cartesian coordinates (Å) of the optimized structure of thiirenium ion **1a'** calculated at the RB3LYP/6-31G(d) level of theory.

Atom	X	Y	Z	Atom	X	Y	Z
C	1.436690	0.538666	0.647012	H	3.043300	0.003334	1.855844
C	1.436690	0.538666	-0.647012	H	-3.008163	1.052776	0.000000
C	2.019203	0.373660	-1.997520	H	-4.689283	-0.791386	0.000000
C	2.019203	0.373660	1.997520	H	-1.537344	-3.704128	0.000000
C	-1.318187	-0.309980	0.000000	H	0.171364	-1.887512	0.000000
C	-2.679673	0.016803	0.000000	H	0.988442	2.037002	2.932232
C	-3.626087	-1.004700	0.000000	H	2.577067	2.447659	2.289430
C	-3.185612	-2.326086	0.000000	H	2.073130	0.700851	4.785479
C	-1.831113	-2.660107	0.000000	H	3.673496	1.115739	4.143474
C	-0.885470	-1.639257	0.000000	H	2.577067	2.447659	-2.289430
C	2.019203	1.675004	2.831197	H	0.988442	2.037002	-2.932232
C	2.633044	1.451321	4.216208	H	3.673496	1.115739	-4.143474
C	2.019203	1.675004	-2.831197	H	2.073130	0.700851	-4.785479
C	2.633044	1.451321	-4.216208	H	2.622730	2.382404	4.790223
H	3.043300	0.003334	-1.855844	H	2.622730	2.382404	-4.790223
H	1.464042	-0.412456	-2.525680	F	-4.088037	-3.307522	0.000000
H	1.464042	-0.412456	2.525680	S	-0.198093	1.101565	0.000000

Table S3. Cartesian coordinates (Å) of the optimized structure of 4-octyne calculated at the RB3LYP/6-31G(d) level of theory.

Atom	X	Y	Z	Atom	X	Y	Z
C	-4.425829	0.002868	0.095326	H	-2.749892	0.998324	1.044428
C	-2.976515	0.495637	0.096088	H	-2.832709	1.244467	-0.692568
C	-1.964795	-0.650962	-0.114768	H	-2.191040	-1.160698	-1.062892
C	-0.570794	-0.201311	-0.117759	H	-2.107507	-1.405988	0.672351
C	0.570794	0.201293	-0.117787	H	2.191049	1.160519	-1.063070
C	1.964796	0.650943	-0.114861	H	2.107502	1.406104	0.672131
C	2.976513	-0.495621	0.096200	H	2.749884	-0.998142	1.044626
C	4.425828	-0.002855	0.095361	H	2.832712	-1.244587	-0.692327
H	-5.125550	0.832491	0.245683	H	5.125547	-0.832452	0.245873
H	-4.681886	-0.480315	-0.855713	H	4.681895	0.480157	-0.855762
H	-4.598791	-0.727680	0.895267	H	4.598786	0.727837	0.895171

Table S4. Cartesian coordinates (Å) of the optimized structure of *cis*-4-octene calculated at the RB3LYP/6-31G(d) level of theory.

Atom	X	Y	Z	Atom	X	Y	Z
C	-2.135846	3.034243	-1.113396	H	-0.268938	2.825071	-0.032964
C	-1.305409	2.471133	0.043919	H	-0.902619	0.540766	-0.852689
C	-1.305409	0.930254	0.089691	H	-2.350218	0.585768	0.142292
C	-0.549416	0.382665	1.271197	H	-0.956201	0.674215	2.241581
C	0.549416	-0.382665	1.271197	H	0.956201	-0.674215	2.241581
C	1.305409	-0.930254	0.089691	H	0.902619	-0.540766	-0.852689
C	1.305409	-2.471133	0.043919	H	2.350218	-0.585768	0.142292
C	2.135846	-3.034243	-1.113396	H	1.690438	-2.860493	0.996837
H	-2.118214	4.130050	-1.121595	H	0.268938	-2.825071	-0.032964
H	-1.753715	2.688065	-2.081738	H	2.118214	-4.130050	-1.121595
H	-3.183913	2.718032	-1.040187	H	1.753715	-2.688065	-2.081738
H	-1.690438	2.860493	0.996837	H	3.183913	-2.718032	-1.040187

NMR spectra