Electronic Supplementary Material (ESI) for Chemical Communications.

Discrimination and quantitation of halobenzoic acid isomers upon Th(IV) coordination by mass spectrometry

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1) Experimental and Computational Section

Reagents. *o*-, *m*- and *p*-halobenzoic acids ($C_6H_4XCO_2H$, X = F, Cl and Br) were purchased from Macklin. All chemicals were used without further purification. The $ThCl_4$ stock solution was prepared by dissolving $ThCl_4$ (99.99%) powder in boiling hydrochloric acid, which was then diluted by Milli-Q ultrapure water at ambient temperature. The thorium isotope employed was ^{232}Th.

Mass Spectrometry. All the experiments were performed on a Bruker Daltonics (Bremen, Germany) SolariX XR 7.0T Fourier transform ion cyclotron resonance mass spectrometer (FTICR MS) equipped with a heated electrospray ionization source. The acetonitrile solutions of 0.05 mM $ThCl_4$ and 0.15 mM *o*-, *m*- or *p*-$C_6H_4XCO_2H$ (X = F, Cl and Br) mixture were prepared for negative ion mode ESI experiments to generate suitable thorium chloride halobenzoate anions with the general formula of $ThCl_{5-x}(C_6H_4XCO_2)_x^-$. These anions were readily identified via the isotopic patterns mainly arising from 75.77% ^{35}Cl and 24.23% ^{37}Cl as well as 50.69% ^{79}Br and 49.31% ^{81}Br in some cases. The first isotope of $ThCl_4(C_6H_4XCO_2)^-$ was selected for precursor to subject CID experiment. High purity nitrogen gas for nebulization and drying in the ESI source was supplied from the boil-off of a liquid nitrogen Dewar. The pressure inside the ICR cell is about $5.00 \times 10^{-10} \sim 5.00 \times 10^{-9}$ mbar. Detailed instrumental parameters: syringe pump flow rate 4.00 μL/min, capillary 4.0 kV, end plate offset -0.5 kV, nebulizer 2 bar, dry gas 1 bar, dry temperature 200 °C, capillary exit 220.0 V, deflector plate 2 V, funnel 1 150.0 V, skimmer 1 15 V, funnel RF amplitude 150.0 Vpp, collision voltage 2.5 V, DC extract bias -0.5 V, the time of flight 0.6ms. MS/MS analyses were acquired via sustained off-resonance irradiation collision-induced dissociation (SORI-CID) with the following parameters: isolation power 15%, SORI power 0.4~1.0%, pulse length 0.2s, frequency offset -500 Hz. Mass spectra were collected with an acquisition size of 1 M (mass resolving power more than 100000 at m/z 500) in the range between 21.5 and 1000 Da. Ions were accumulated in the ICR cell for 0.3s and 30 scans were averaged for each spectrum.

Quantitative analysis. The acetonitrile solutions of 0.05 mM $ThCl_4$ and 0.15 mM FBA were prepared for negative ion mode ESI, in which FBA represents binary *o*-FBA/*m*-FBA, *o*-FBA/*p*-FBA or *m*-FBA/*p*-FBA mixtures with the mole ratios of 4:1, 3:2, 2:3 and 1:4. The MS/MS analyses of $ThCl_4(C_6H_4FCO_2)^-$ were carried out as described above with the SORI power fixed at 0.8%. Each sample was analyzed ten times in order to ensure good repeatability, and the percentage of $ThFCl_4^-$ in the fragmentation products can be calculated using the equation below. A linear relationship between the proportion of $ThFCl_4^-$ in the CID spectrum and the fraction of a certain isomer in the solution can be established.

$$ThFCl_4^-\% = \frac{Intensity\ of\ ThFCl_4^-}{Intensity\ of\ ThFCl_4^- + Intensity\ of\ ThCl_4(C_6H_4F)^-}$$

In the case of ternary mixtures, the acetonitrile solutions of 0.05 mM $ThCl_4$ and 0.15 mM ternary *o*-FBA/*m*-FBA/*p*-FBA with different mole ratios were prepared for the ESI/CID experiments. The MS/MS analyses of $ThCl_4(C_6H_4FCO_2)^-$ were carried out at a SORI power of 1.0%, under which condition three CID products, namely $ThFCl_4^-$, $ThCl_3(C_6H_3F)^-$ and $ThCl_4(C_6H_4F)^-$, were obtained. A linear relationship between the proportion of $ThCl_3(C_6H_3F)^-$ among the fragmentation products and the fraction of *p*-FBA in the solution was therefore established (Fig. S5a), and $ThCl_3(C_6H_3F)^-$ is mainly

generated from $ThCl_4(p\text{-}C_6H_4FCO_2)^-$. A linear relationship between the proportion of $ThFCl_4^-$ and the fraction of *o*-FBA (Fig. S5b) can be established similarly.

Computational methods Density functional theory (DFT) calculations on the species with singlet ground states discussed in this work were performed with the Gaussian 09 package using the hybrid B3LYP density functional.[1-3] The 60 electron core pseudopotential basis sets were used for Th,[4] and the 6-311++G(d,p) basis set was used for all the remaining atoms (C, H, O, F, Cl).[5-9] All the geometrical parameters were fully optimized, and zero-point energy (ZPE) corrections were included in the relative energies. Vibrational frequencies were calculated for all optimized structures to check that they correspond to the local minima (no imaginary frequency) or transition states (one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structures and minima.[10,11]

Reference

1 Gaussian 09, Revision A.01. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr.Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, Klene, M. J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, **2009**.

2 C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

3 A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

4 T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294-301.

5 R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650-654.

6 A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639-5648.

7 M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654-3665.

8 T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294-301.

9 G. W. Spitznagel, T. Clark, P. v. R. Schleyer, W. J. Hehre, *J. Comput. Chem.* **1987**, *8*, 1109-1116.

10 K. Fukui, *J. Phys. Chem.* **1970**, *74*, 4161-4163.

11 K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363-368.

2) Additional Tables and Figures

Table S1. Experimental and calculated mass-to-charge ratios (m/z) of relevant species.

Species	Experimental m/z [a]	Calculated m/z [a]	Error in ppm
$C_6H_4FCO_2^-$	139.02001	139.02008	0.50
$C_6H_4F^-$	95.03028	95.03025	-0.32
$ThCl_4(C_6H_4FCO_2)^-$	510.93403	510.93355	-0.95
$ThCl_4(C_6H_4F)^-$	466.94267	466.94372	0.42
$ThCl_3(C_6H_3F)^-$	430.96626	466.96704	0.45
$ThFCl_4^-$	390.91274	390.91242	-0.81
$C_6H_4ClCO_2^-$	154.99061	154.99053	-0.20
$C_6H_4Cl^-$	111.00100	111.00070	-0.52
Cl^-	34.96936	34.96940	1.14
$ThCl_4(C_6H_4ClCO_2)^-$	526.90472	526.90400	-1.24
$ThCl_4(C_6H_4Cl)^-$	482.91379	482.91307	-1.56
$ThCl_3(C_6H_3Cl)^-$	446.93805	446.93749	-1.39
$ThCl_5^-$	406.88234	406.88177	-1.27
$C_6H_4BrCO_2^-$	198.94035	198.94002	-1.66
$C_6H_4Br^-$	154.95037	154.95019	-1.16
Br^-	78.91901	78.91889	-1.52
$ThCl_4(C_6H_4BrCO_2)^-$	570.85420	570.85348	-1.26
$ThCl_4(C_6H_4Br)^-$	526.86332	526.86256	-1.43
$ThCl_3(C_6H_3Br)^-$	490.88744	490.88698	-0.95
$ThBrCl_4^-$	450.83202	450.83126	-1.67

[a] For the most abundant isotopomer.

Table S2. Actual and measured compositions of binary FBA isomer mixtures (relative error in italic).[a]

Actual compositions	Measured compositions				
	relative error δ				
50%/50% *o*-FBA/*p*-FBA	51.22%/48.78%	48.89%/51.11%	51.38%/48.62%	49.18%/50.82%	49.35%/50.65%
			2.07%		
50%/50% *m*-FBA/*o*-FBA	51.42%/48.58%	50.89%/49.11%	49.39%/50.61%	49.55%/50.45%	52.15%/47.85%
			2.21%		
50%/50% *p*-FBA/*m*-FBA	51.37%/48.63%	50.53%/49.47%	48.66%/51.34%	52.34%/47.66%	51.30%/48.70%
			2.75%		

[a] Each sample was analyzed five times. The relative error δ = average value of $|$measured fraction of a certain isomer – actual fraction of a certain isomer$|$/actual fraction of a certain isomer × 100%.

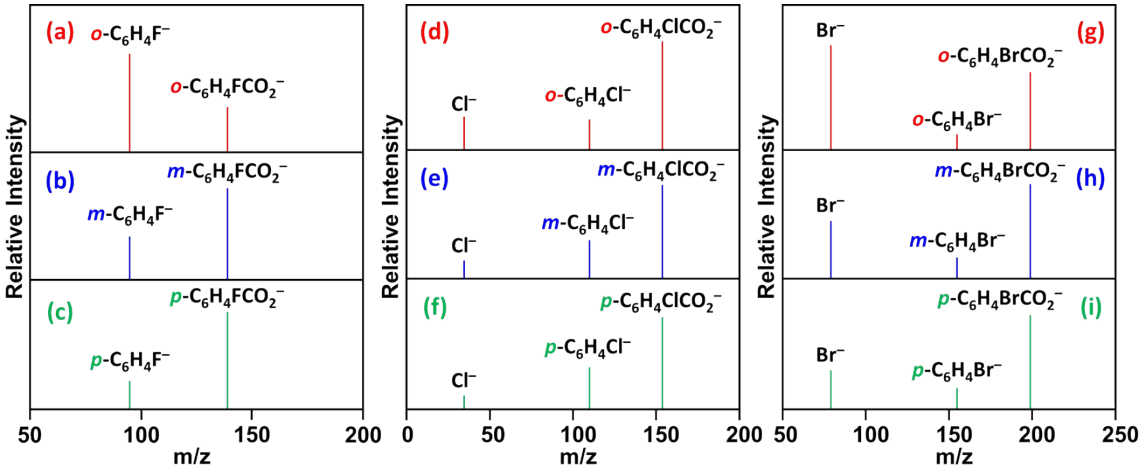

Fig. S1 CID mass spectra of (a) *o*-, (b) *m*- and (c) *p*-$C_6H_4FCO_2^-$, (d) *o*-, (e) *m*- and (f) *p*-$C_6H_4ClCO_2^-$, (g) *o*-, (h) *m*- and (i) *p*-$C_6H_4BrCO_2^-$. A single isotopomer was mass selected (SORI power 0.4%).

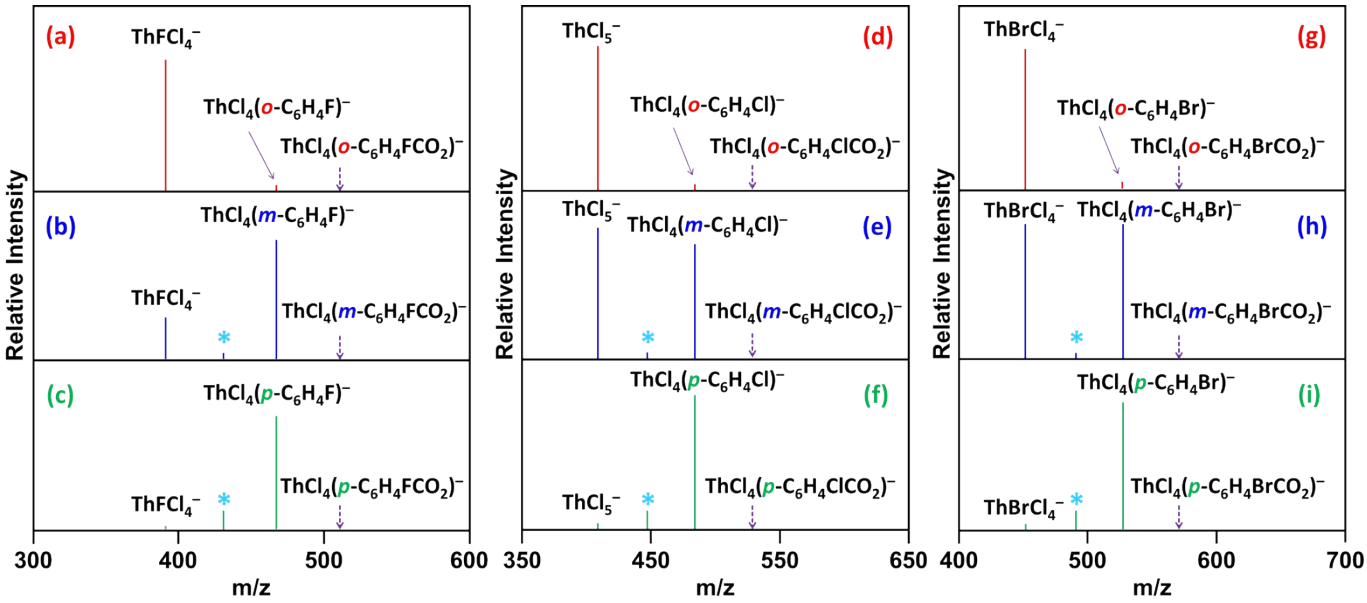

Fig. S2 CID mass spectra of (a) *ortho*, (b) *meta* and (c) *para* isomers of $ThCl_4(C_6H_4FCO_2)^-$, (d) *ortho*, (e) *meta* and (f) *para* isomers of $ThCl_4(C_6H_4ClCO_2)^-$, (g) *ortho*, (h) *meta* and (i) *para* isomers of $ThCl_4(C_6H_4BrCO_2)^-$. The asterisks denote $ThCl_3(C_6H_3X)^-$ (X = F, Cl and Br), and the dotted arrows indicate the $ThCl_4(C_6H_4XCO_2)^-$ parent ions which completely dissociate. A single isotopomer was mass selected (SORI power 1.0%).

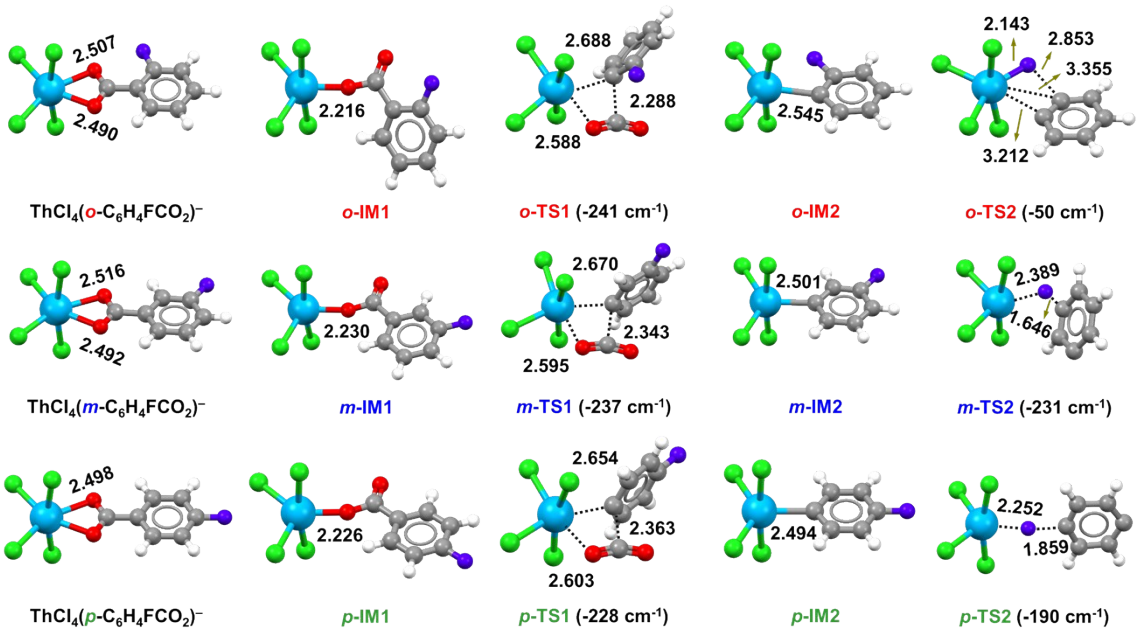

Fig. S3 The structures and selected bond lengths (Å) of ions involved in the decarboxylation and fluoride transfer pathways of $ThCl_4(C_6H_4FCO_2)^-$ at the B3LYP/6-311++G(d,p)/SDD level of theory. Th cyan, C gray, H white, O red, Cl green, F blue.

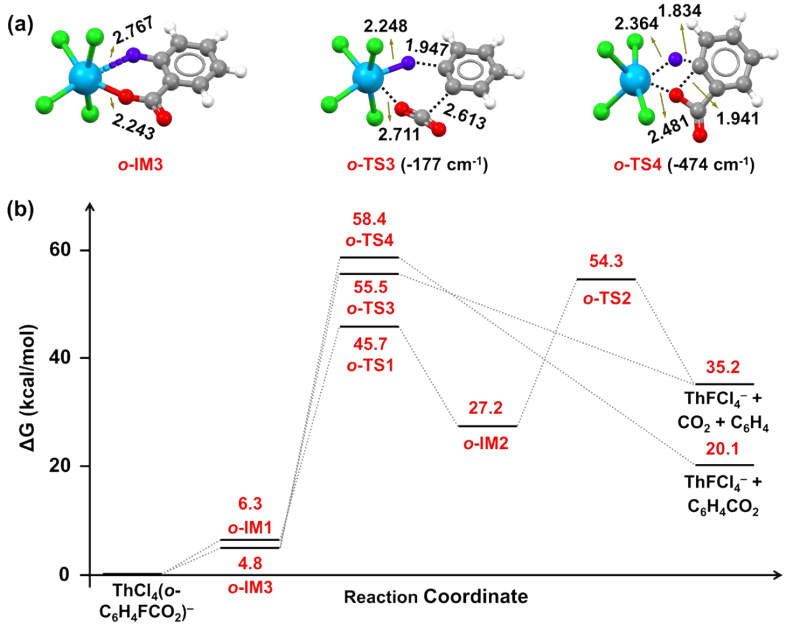

Fig. S4 (a) The structures and selected bond lengths (Å) of ions involved in the concerted CO_2/C_6H_4 elimination and lactone loss pathways of $ThCl_4(o\text{-}C_6H_4FCO_2)^-$ at the B3LYP/6-311++G(d,p)/SDD level of theory. Th cyan, C gray, H white, O red, Cl green, F blue. (b) The Gibbs free energies (kcal/mol) for the sequential and concerted CO_2/C_6H_4 elimination as well as the $C_6H_4CO_2$ lactone loss pathways of $ThCl_4(o\text{-}C_6H_4FCO_2)^-$.

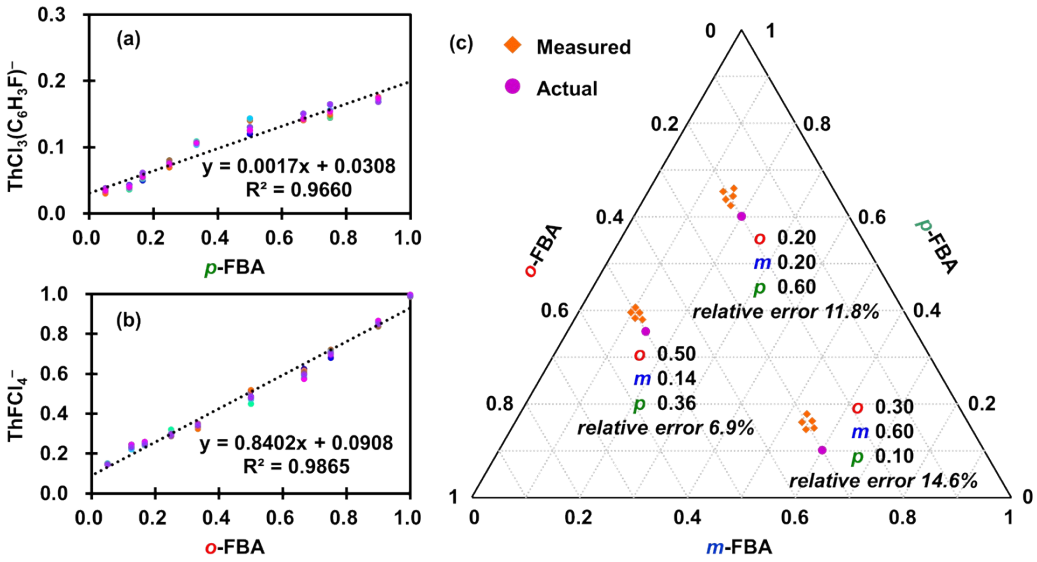

Fig. S5 Linear relationships between (a) the proportion of $ThCl_3(C_6H_3F)^-$ and the fraction of *p*-FBA, (b) the proportion of $ThFCl_4^-$ and the fraction of *o*-FBA in the acetonitrile solution of ternary FBA mixtures. (c) Actual (magenta solid circle) and measured (orange diamond) compositions of three ternary FBA isomer mixtures, each of which was analyzed five times.

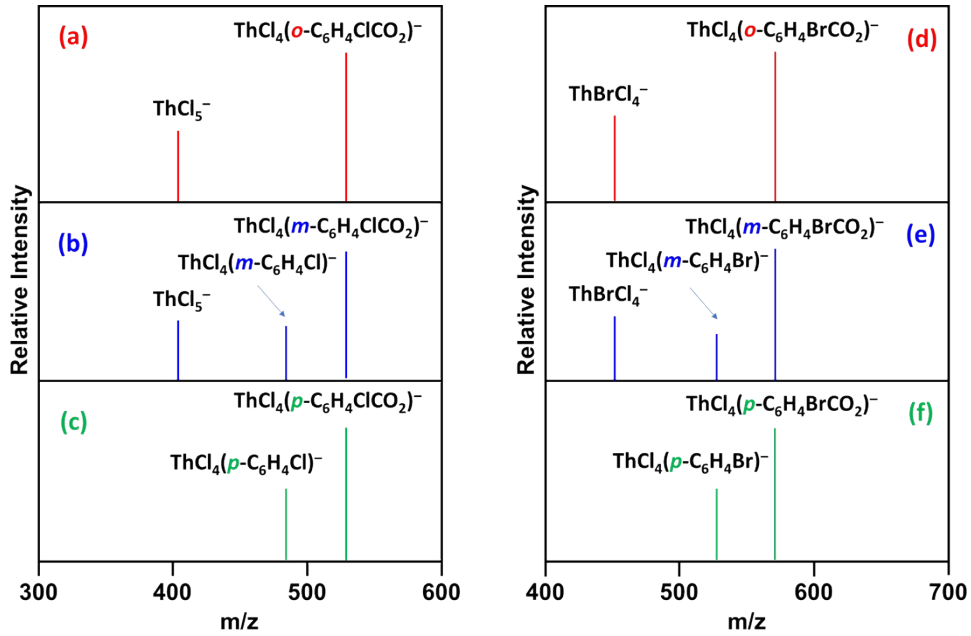

Fig. S6 CID mass spectra of (a) *ortho*, (b) *meta*, (c) *para* isomers of $ThCl_4(C_6H_4ClCO_2)^-$, and (d) *ortho*, (e) *meta*, (f) *para* isomers of $ThCl_4(C_6H_4BrCO_2)^-$. A single isotopomer was mass selected (SORI power 0.8%).

3) Calculated Cartesian coordinates, energies (Hartree) and frequencies (for transition states) of the relevant species obtained at the B3LYP/SDD/6-311++G(d,p) level of theory.

$ThCl_4(o\text{-}C_6H_4FCO_2)^-$

Th	1.24678400	-0.01663900	0.00172700
Cl	0.97563700	-0.42780200	-2.63257700
Cl	2.74142400	2.15816900	-0.31348500
Cl	2.92209500	-2.06362400	0.29430200
Cl	0.97976200	0.33594300	2.64446200
O	-0.95768300	-1.16302100	0.16808300
O	-1.03357000	1.01547700	-0.14494600
C	-1.62614100	-0.09022900	0.01329300
C	-3.11942000	-0.18397900	0.02133000
C	-3.70668800	-1.45097500	0.15015700
C	-3.97952000	0.91298000	-0.09220600
C	-5.08558200	-1.61660300	0.16271300
H	-3.03793300	-2.29747900	0.23934900
C	-5.36172100	0.76871200	-0.07982500
C	-5.91545300	-0.50087400	0.04733500
H	-5.51182300	-2.60801700	0.26195000
H	-5.97828700	1.65466800	-0.16989600
H	-6.99382300	-0.61590500	0.05633800
F	-3.50146000	2.16274900	-0.21565900

Sum of electronic and zero-point Energies = -2768.670462

$ThCl_4(o\text{-}C_6H_4FCO_2)^-$ *o*-IM1

Th	-1.32402900	-0.02045300	0.02452900
Cl	-0.63410000	-2.26423400	-1.29720900
Cl	-1.93018900	-1.41386200	2.20118700
Cl	-3.29418900	0.44213500	-1.69404200
Cl	-1.73959900	2.29136600	1.28160400
O	2.08850400	2.04295100	-1.30797200
O	0.80098600	0.54832800	-0.24489900
C	1.96542800	1.04186900	-0.63874300
C	3.14651800	0.20619500	-0.21007900
C	3.02590100	-1.18582600	-0.10056000
C	4.40549700	0.75987600	0.03432900
C	4.12029500	-1.98474900	0.21643300
H	2.05845400	-1.63576700	-0.28726600
C	5.50597700	-0.01603300	0.37092700
C	5.36225400	-1.39852700	0.45495900
H	3.99985600	-3.05986700	0.27978500
H	6.45304500	0.47352900	0.56301500
H	6.21928900	-2.01197600	0.71060900
F	4.58801800	2.09620800	-0.01895400

Sum of electronic and zero-point Energies = -2768.658950

***o*-TS1** (-241 cm^{-1})

Th	-0.81850400	-0.10757700	0.03988200
Cl	-0.97579900	0.44542800	-2.59000000
Cl	-1.24870900	-2.68637800	-0.38287900
Cl	-3.20676400	0.94100900	0.50665100
Cl	-0.33810400	-0.45428100	2.62883200
O	2.06111500	2.86066900	-0.90420800
O	0.02244300	2.33977300	0.04414200
C	1.12495400	2.34496400	-0.43211700
C	1.83667800	0.17638800	-0.26587100
C	2.20088100	-0.65044700	-1.35027200
C	2.77214100	0.22418700	0.76530000
C	3.38332000	-1.39315200	-1.36334400
H	1.54166700	-0.71609300	-2.21082000
C	3.95841600	-0.49318000	0.79919000
C	4.26137600	-1.31676400	-0.28397400
H	3.61674000	-2.02556700	-2.21331400
H	4.62199100	-0.40049900	1.65111100
H	5.18228300	-1.89032600	-0.28237800
F	2.54300600	1.06452400	1.81875800

Sum of electronic and zero-point Energies = -2768.598932

$ThCl_4(o\text{-}C_6H_4F)^-$ *o*-IM2

Th	0.69148400	-0.04239600	0.00471400
Cl	0.46299700	0.27495900	2.64718100
Cl	2.06500700	-2.29883900	0.27659100
Cl	2.05938200	2.23091200	-0.26692000
Cl	0.47736200	-0.35807800	-2.63942900
C	-1.82571600	-0.41329100	0.03586800
C	-2.44274200	0.81458200	-0.07444000
C	-2.71547000	-1.49771700	0.13016300
C	-3.80168900	1.07064700	-0.09707900
C	-4.10161000	-1.31894900	0.11304900
H	-2.32567900	-2.50884900	0.21807300
C	-4.64549300	-0.03736800	0.00042400
H	-4.76146100	-2.17804700	0.18705700
H	-5.72121700	0.10275600	-0.01227900
H	-4.18221800	2.08147700	-0.18632700

F	-1.57193100	1.90873900	-0.17498600

Sum of electronic and zero-point Energies = -2579.975284

***o*-TS2** (-50 cm^{-1})

Th	0.76942200	0.00000600	-0.10064000
Cl	0.47226400	-2.67772300	-0.14085200
Cl	0.47290200	2.67782200	-0.13984700
Cl	0.21293600	-0.00041900	2.54226000
Cl	3.41907700	-0.00028000	-0.32326200
C	-2.39587700	0.00017300	0.44339400
C	-3.46806600	-0.00036700	1.32492600
C	-2.51182700	0.00061800	-0.79611900
C	-4.69423100	-0.00033300	0.63288800
H	-3.39543800	-0.00078000	2.40446700
C	-3.62703000	0.00067300	-1.59788700
C	-4.77284300	0.00017400	-0.77355300
H	-5.61709100	-0.00072900	1.20502900
H	-3.66433200	0.00104500	-2.67831600
H	-5.75034100	0.00017000	-1.24647200
F	0.02071000	0.00048400	-2.10889700

Sum of electronic and zero-point Energies = -2579.944857

$ThCl_4$(*o*-$C_6H_4FCO_2$)$^-$ ***o*-IM3**

Th	0.04578600	1.09328000	0.00000000
Cl	-0.10060100	0.73015600	2.65326800
Cl	1.60892500	3.22852700	0.00000000
Cl	-2.45796800	2.01567200	0.00000000
Cl	-0.10060100	0.73015600	-2.65326800
O	2.85416900	-2.38796700	0.00000000
O	1.36383800	-0.72162400	0.00000000
C	1.70899700	-1.97952800	0.00000000
C	0.56046400	-2.97688700	0.00000000
C	0.87952600	-4.34228200	0.00000000
C	-0.79752000	-2.66630400	0.00000000
C	-0.10060100	-5.32647900	0.00000000
H	1.93301700	-4.59360500	0.00000000
C	-1.80265000	-3.61980200	0.00000000
C	-1.44825900	-4.96474200	0.00000000
H	0.18323100	-6.37268600	0.00000000
H	-2.83527700	-3.29455600	0.00000000
H	-2.22310100	-5.72300100	0.00000000
F	-1.22979800	-1.36168500	0.00000000

Sum of electronic and zero-point Energies = -2768.663449

***o*-TS3** (-177 cm^{-1})

Th	-1.05280100	-0.14048200	-0.00001700
Cl	-0.70823500	0.15322500	2.63782600
Cl	-3.00078100	1.67422700	0.00068900
Cl	-2.45836100	-2.37867400	-0.00066600
Cl	-0.70853600	0.15494300	-2.63771500
O	2.51190800	3.34724600	0.00012800
O	0.64792800	1.97102900	0.00049700
C	1.66315200	2.55675300	0.00028600
C	3.23863200	0.47213200	0.00000200
C	4.64383700	0.62027300	0.00014200
C	2.88197300	-0.76065000	-0.00021200
C	5.44828000	-0.52739300	0.00004800
H	5.10564900	1.60503500	0.00032100
C	3.48784300	-1.98192900	-0.00033200
C	4.88452300	-1.81287900	-0.00018400
H	6.52974300	-0.42592200	0.00015700
H	2.99378900	-2.94282600	-0.00051200
H	5.52217900	-2.69064200	-0.00025200
F	0.96923400	-1.12328600	-0.00043600

Sum of electronic and zero-point Energies = -2768.579708

***o*-TS4** (-474 cm^{-1})

Th	0.99764900	-0.04723800	-0.02345500
Cl	1.05948500	2.19811900	-1.46088500
Cl	2.55438200	0.89195000	1.90954100
Cl	2.68135200	-1.33172700	-1.62452200
Cl	0.37074100	-2.28794900	1.35284500
O	-2.12758000	2.83509900	0.86730700
O	-1.19748900	0.73732500	0.82651300
C	-2.15142500	1.67787200	0.56511000
C	-3.16178600	0.79448500	-0.06907300
C	-4.54745800	0.75608600	-0.17970900
C	-2.45695200	-0.38919400	-0.12802800
C	-5.15395800	-0.49666100	-0.30406400
H	-5.13011000	1.66576700	-0.08468900
C	-2.98612900	-1.65060900	-0.11766700
C	-4.38671100	-1.66583700	-0.23731400
H	-6.23075700	-0.57192300	-0.39921300
H	-2.38192100	-2.54502700	-0.07969700
H	-4.87865100	-2.63065600	-0.30418200
F	-0.98014200	-0.59996600	-1.19511500

Sum of electronic and zero-point Energies = -2768.570340

$ThFCl_4^-$

Th	0.00000000	0.00000000	0.13406100
Cl	0.00000000	2.68484300	0.24925900
Cl	0.00000000	-2.68484300	0.24925900
Cl	-2.31123700	0.00000000	-1.20156000
Cl	2.31123700	0.00000000	-1.20156000
F	0.00000000	0.00000000	2.25697400

Sum of electronic and zero-point Energies = -2349.045984

CO_2

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16080000
O	0.00000000	0.00000000	-1.16080000

Sum of electronic and zero-point Energies = -188.635227

***o*-C_6H_4**

C	-0.70293900	1.05683800	0.00029000
C	-1.45873300	-0.13466600	-0.00014200
C	-0.62167900	-1.23473100	0.00014500
C	0.62296000	-1.23467300	-0.00002400
C	1.45869700	-0.13348700	-0.00050800
C	0.70198200	1.05735900	0.00008900
H	-1.22953500	2.00586700	0.00076600
H	-2.54094000	-0.13724500	0.00021000
H	2.54092100	-0.13524300	-0.00048300
H	1.22782600	2.00679200	0.00041200

Sum of electronic and zero-point Energies = -230.897891

$C_6H_4CO_2$ lactone

O	-2.23839600	1.82480400	0.00000000
O	-1.77184600	-0.49106000	0.00000000
C	-1.46359200	0.93908100	0.00000000
C	0.00000000	0.61855000	0.00000000
C	1.31945700	1.01638500	0.00000000
C	-0.38358300	-0.71365500	0.00000000
C	2.25206100	-0.03835300	0.00000000
H	1.63246900	2.05281500	0.00000000
C	0.48832700	-1.77128500	0.00000000
C	1.84461100	-1.37604000	0.00000000
H	3.31129000	0.18775200	0.00000000
H	0.18860400	-2.81038100	0.00000000
H	2.60588800	-2.14823200	0.00000000

Sum of electronic and zero-point Energies = -419.574551

$ThCl_4$(*m*-$C_6H_4FCO_2$)$^-$

Th	1.33394400	0.01757500	-0.00106800
Cl	1.05878500	-0.36385700	-2.63794500
Cl	2.66017400	2.29989400	-0.28960300
Cl	3.15346700	-1.90769400	0.23626100
Cl	1.06106500	0.30503200	2.64785400
O	-0.81646600	-1.23099400	0.15510500
O	-1.00007800	0.95012900	-0.11654600
C	-1.53470900	-0.19086300	0.02356600
C	-3.02357000	-0.32021400	0.03442300
C	-3.61565700	-1.57995800	0.15870800
C	-3.81553000	0.82577200	-0.08091400
C	-5.00259700	-1.69624900	0.16679500
H	-2.97556400	-2.44807500	0.24647400
C	-5.18971200	0.67502100	-0.06730100
H	-3.35561300	1.80053500	-0.17733400
C	-5.80646900	-0.56169100	0.05354100
H	-5.46571900	-2.67187300	0.26147600
H	-6.88789700	-0.62407700	0.05763900
F	-5.97530600	1.78115300	-0.17724000

Sum of electronic and zero-point Energies = -2768.678952

$ThCl_4$(*m*-$C_6H_4FCO_2$)$^-$ *m*-IM1

Th	-1.43387200	0.01301500	-0.00204400
Cl	-1.27875600	0.23334100	2.65720500
Cl	-1.90336900	2.59707000	-0.35820000
Cl	-3.60582500	-1.50595600	0.20137900
Cl	-1.26729500	-0.49270500	-2.62022000
O	1.91507600	-2.30791500	0.25645700
O	0.75569700	-0.40320600	0.06053600
C	1.87159700	-1.09911100	0.13039800
C	3.13336200	-0.27459700	0.04215600
C	3.10320300	1.11709200	-0.08289800
C	4.36155600	-0.94271000	0.09030200
C	4.29287500	1.83838200	-0.15833200
H	2.14908300	1.62466100	-0.11965800
C	5.52314700	-0.19916400	0.01173100
C	5.52223600	1.18260800	-0.11173600
H	4.26554300	2.91787800	-0.25402300
H	6.46130100	1.71947200	-0.16902700
H	4.38705300	-2.02034200	0.18688400
F	6.72340700	-0.84431600	0.05681300

Sum of electronic and zero-point Energies = -2768.667246

***m*-TS1** (-237 cm^{-1})

Th	-0.89709100	-0.11251000	-0.09772600
Cl	-1.15421900	2.28602000	-1.27064500
Cl	-0.92043300	-1.54300500	-2.32346900
Cl	-3.42932300	-0.01816700	0.70256200
Cl	-0.40022600	-2.13242900	1.59067000
O	1.85496300	1.98736400	2.42833800
O	-0.31363200	1.33442100	1.97553600
C	0.86542600	1.54256400	1.99757900
C	1.70697100	0.44212500	0.10841900
C	2.22151400	1.36220700	-0.83088500
C	2.56027200	-0.61597100	0.49140100
C	3.50030300	1.23041100	-1.37304800
H	1.60930200	2.19694700	-1.15307800
C	3.82711900	-0.72414800	-0.05630800
C	4.32466800	0.17524200	-0.98539700

H	3.86069400	1.95189700	-2.09983100
H	5.32299100	0.04467500	-1.38597100
H	2.24491800	-1.36355100	1.21054100
F	4.63371500	-1.75822500	0.33300800

Sum of electronic and zero-point Energies = -2768.598858

$ThCl_4$(*m*-C_6H_4F)$^-$ *m*-IM2

Th	-0.83367500	0.03180000	0.00172700
Cl	-0.67332900	0.45863300	-2.63088600
Cl	-2.17175400	-2.24711800	-0.36652400
Cl	-1.84425300	2.46986700	0.37781400
Cl	-0.71815000	-0.37474400	2.64038500
C	1.65458300	-0.22274300	-0.01628000
C	2.59939600	0.81530800	0.07769200
C	2.15995300	-1.53146300	-0.13452900
C	3.95450300	0.52950300	0.05288100
H	2.30106800	1.85658600	0.17004900
C	3.52896000	-1.80259000	-0.15890800
H	1.47587400	-2.37602300	-0.20936300
C	4.44999400	-0.75961600	-0.06370200
H	3.88515000	-2.82425100	-0.25102500
H	5.51981000	-0.93038100	-0.07854500
F	4.85464600	1.55875500	0.14634800

Sum of electronic and zero-point Energies = -2579.970097

***m*-TS2** (-231 cm^{-1})

Th	-0.68577000	-0.02267400	0.00264500
Cl	-2.93295000	-0.84367200	-1.05495700
Cl	0.14616100	-2.50390800	0.40748300
Cl	-1.13367400	2.48361900	-0.73833100
Cl	-1.18577000	0.42713400	2.53212700
C	3.64972500	1.41499700	0.74469600
C	2.47988600	1.34345900	-0.06356000
C	4.55477700	0.34090500	0.65291300
C	2.38922500	0.21398900	-0.82852800
H	1.75751600	2.15561000	-0.12289000
C	4.39046900	-0.76929200	-0.18228800
H	5.45560300	0.37017500	1.26699600
C	3.23227700	-0.85697000	-0.96318400
H	5.12856800	-1.56989300	-0.22816400
H	2.99558800	-1.69761500	-1.59861700
F	1.00108800	0.00954200	-1.68923900

Sum of electronic and zero-point Energies = -2579.891315

***m*-C_6H_4**

C	-1.45738700	0.00007300	0.00001800
C	-0.66368400	1.16627300	0.00000400
C	0.66754300	0.80480000	-0.00001400
C	1.74807000	0.00019100	-0.00002600
C	0.66760100	-0.80514400	-0.00000400
C	-0.66358500	-1.16621100	0.00001700
H	-2.54438700	-0.00014600	0.00003300
H	-1.03916500	2.18013500	0.00000500
H	-1.03975300	-2.17984200	0.00003100
H	2.83195700	-0.00004100	-0.00004000

Sum of electronic and zero-point Energies = -230.878276

$ThCl_4$(*p*-$C_6H_4FCO_2$)$^-$

Th	1.37566800	-0.00000600	-0.00003900
Cl	1.10552500	2.66642100	-0.00233500
Cl	2.95524600	0.00158100	2.13923800
Cl	2.95656300	-0.00191900	-2.13839400
Cl	1.10507500	-2.66638400	0.00203100
O	-0.86583100	-0.00077300	-1.10288200
O	-0.86583100	0.00117000	1.10262900
C	-1.49711700	0.00025700	-0.00013400
C	-2.98716200	0.00014000	-0.00010700
C	-3.68775400	-0.00109300	-1.20992000
C	-3.68769400	0.00128600	1.20974200
C	-5.07907500	-0.00121900	-1.21771700
H	-3.12675400	-0.00199000	-2.13590600
C	-5.07901300	0.00123500	1.21760800
H	-3.12664500	0.00226600	2.13569800
C	-5.74292200	-0.00002900	-0.00003700
H	-5.64573100	-0.00218800	-2.14059000
H	-5.64562300	0.00213100	2.14051100
F	-7.10317700	-0.00013200	-0.00000200

Sum of electronic and zero-point Energies = -2768.680249

$ThCl_4$(*p*-$C_6H_4FCO_2$)$^-$ *p*-IM1

Th	-1.43220600	0.05639100	-0.00506200
Cl	-1.25343700	0.26161000	2.65520900
Cl	-1.71403100	2.66824500	-0.35802500
Cl	-3.72799600	-1.26756700	0.20355100
Cl	-1.31103700	-0.46114700	-2.62500800
O	1.65912500	-2.55193000	0.25235500
O	0.71392200	-0.53291600	0.05469500
C	1.75086500	-1.34442500	0.13285800
C	3.09126700	-0.66169300	0.06432200
C	3.21180700	0.72620100	-0.05319600
C	4.24797700	-1.44652400	0.12296000
C	4.46687000	1.32798800	-0.11077100
H	2.31810100	1.33393400	-0.09844100
C	5.50889300	-0.86211800	0.06576400
C	5.58885600	0.51777400	-0.04989100
H	4.57942600	2.40136200	-0.20009800

H	6.41570500	-1.45287300	0.10936200
H	4.13703800	-2.51991000	0.21372100
F	6.81946700	1.09760200	-0.10499600

Sum of electronic and zero-point Energies = -2768.667934

***p*-TS1** (-228 cm^{-1})

Th	0.93226200	-0.16169900	-0.00068000
Cl	0.82011500	0.16010300	2.66077400
Cl	0.83574100	-2.80685100	-0.01129100
Cl	3.52587200	0.43582700	0.00184200
Cl	0.82036700	0.18354300	-2.65921900
O	-1.71698300	3.21284200	0.01204700
O	0.44367400	2.39452600	0.01020700
C	-0.73874100	2.57669400	0.01017700
C	-1.66097600	0.40107700	0.00144300
C	-2.37212500	0.15945900	1.19817400
C	-2.37244000	0.16929300	-1.19704000
C	-3.68932700	-0.30176000	1.21138400
H	-1.88706500	0.32659900	2.15378300
C	-3.68963200	-0.29183900	-1.21363900
C	-4.31965300	-0.51799100	-0.00194800
H	-4.21989000	-0.49124400	2.13761100
H	-4.22043700	-0.47383100	-2.14123200
H	-1.88768700	0.34435100	-2.15139000
F	-5.60891900	-0.96845400	-0.00363500

Sum of electronic and zero-point Energies = -2768.599599

$ThCl_4$(*p*-C_6H_4F)$^-$ *p*-IM2

Th	0.00000000	0.00000000	0.87577800
Cl	0.00000000	2.67273900	0.77033800
Cl	-2.40243400	-0.00003000	2.03742200
Cl	2.40243400	0.00003000	2.03742200
Cl	0.00000000	-2.67273900	0.77033800
C	0.00000000	0.00000000	-1.61839900
C	1.19411000	0.00065500	-2.36291200
C	-1.19411000	-0.00065500	-2.36291200
C	1.21272400	0.00066000	-3.76030100
H	2.15635700	0.00119900	-1.85332600
C	-1.21272400	-0.00066000	-3.76030100
H	-2.15635700	-0.00119900	-1.85332600
C	0.00000000	0.00000000	-4.42780100
H	2.13908100	0.00117100	-4.32376600
H	-2.13908100	-0.00117100	-4.32376600
F	0.00000000	0.00000000	-5.79710100

Sum of electronic and zero-point Energies = -2579.969570

***p*-TS2** (-190 cm^{-1})

Th	0.94820000	0.00170000	-0.00330000
Cl	2.68010000	0.06720000	-1.98380000
Cl	0.75700000	2.64850000	0.11060000
Cl	0.57990000	-2.61990000	-0.23020000
Cl	2.11780000	-0.19170000	2.34300000
C	-5.11350000	-1.16250000	0.12070000
C	-3.66840000	-1.18000000	0.02750000
C	-5.89530000	-0.01720000	0.05820000
C	-3.14310000	0.04650000	-0.12680000
H	-3.11470000	-2.10540000	0.07930000
C	-5.18270000	1.16280000	-0.10490000
C	-3.74060000	1.24680000	-0.20610000
H	-5.67070000	2.13450000	-0.16800000
H	-3.24240000	2.19680000	-0.32700000
F	-1.28890000	0.09190000	-0.24590000
H	-5.54320000	-2.15530000	0.24710000

Sum of electronic and zero-point Energies = -2579.862958