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Hg−C bond protonolysis by a functional model of bacterial enzyme organomercurial lyase MerB

Ramesh Karri,[b] Ranajit Das,[b] Rakesh Kumar Rai,[b] Anaswara Gopalakrishnan,[b] and Gouriprasanna Roy*[a]

[a]*Department of Chemistry, Indian Institute of Technology Tirupati (IIT-Tirupati), Tirupati, A.P. - 517506, India. E-mail: gproy@iittp.ac.in*
[b]*Department of Chemistry, School of Natural Sciences, Shiv Nadar University, NH91, Dadri, Gautam Buddha Nagar, UP 201314, India.*

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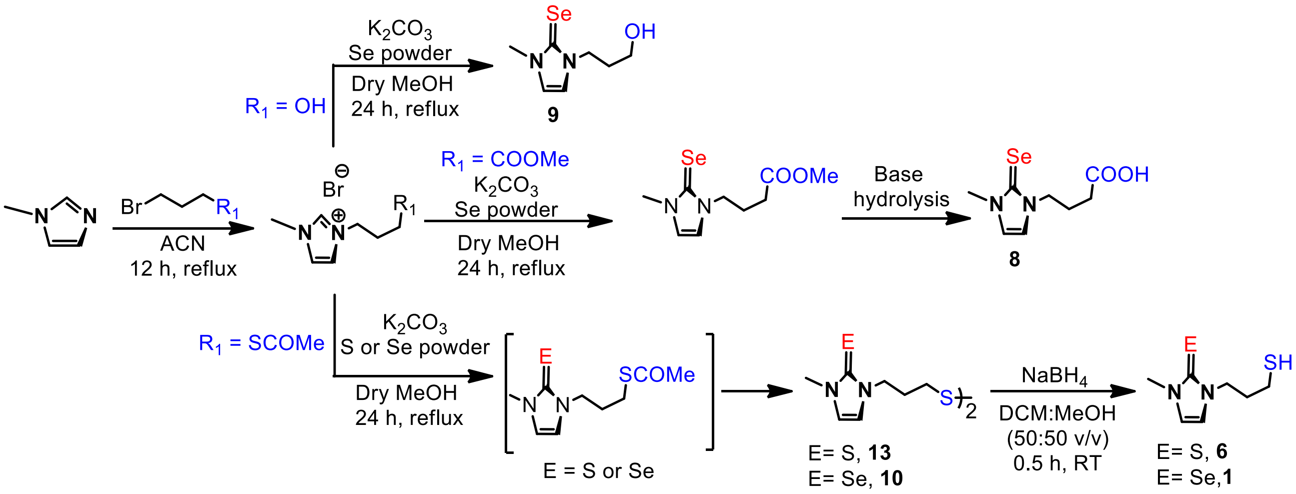
1. Experimental Section

General Procedure. Imidazole, 1-methylimidazole, 4-Bromo butyrate, 3-Bromopropanol, 1, 3-dibromo propane, 1, 2-dibromoethane, potassium thioacetate, ethylmercury chloride, thiosalicylic acid and methylmercury iodide were purchased from Alfa Aesar. Methylmercury chloride, 4-chloromercuric benzoic acid, mercurymercury chloride, sulfur powder, and selenium powder, were purchased from Sigma-Aldrich and other chemicals were purchased from local companies. All the experiments were performed under anhydrous and anaerobic conditions using standard Schlenk techniques for the synthesis of ligands and crystals. Ultra-performance liquid chromatography (UPLC) was carried out using an Agilent 6540 accurate–mass Q-TOF LC/MS (Agilent Technologies,U.S.A.). Mass spectra data were acquired in the positive ion mode by scanning from 100 to 1500 in the mass to charge ratio (m/z). ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{199}Hg (71.6 MHz) NMR, ^{77}Se (76.3 MHz) spectra were obtained on a Bruker Advance 400 NMR spectrometer using the solvent as an internal standard for ^{1}H and ^{13}C. Chemical shifts (^{1}H, ^{13}C) were cited with respect to tetramethylsilane (TMS). ^{199}Hg NMR spectra were reported in ppm relative to neat Me_2Hg ($\delta = 0$ ppm) and $HgCl_2$ ($\delta = -1501$ ppm for 1 M solution in DMSO-d_6) was used as external standard.[1] The chemical shifts of ^{77}Se NMR are reported using a solution of Ph_2Se_2 in DMSO-d_6 ($\delta = 470$) as an external standard with respect to relative to neat Me_2Se ($\delta = 0$) chemical shift.[2]

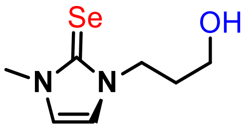
CAUTION! *Organomercurials are extremely toxic to humans, and thus appropriate safety precautions must be taken in handling these toxic chemicals. All the experimentation involving these reagents should be carried out in a well- vented fume hood.*

A. Synthetic procedures for *N,N'*–disubstituted thiones and selones:

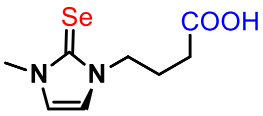
The *N*-substituted imidazole-based selone and thione were synthesized in good yields by *in-situ* generation of carbene of *N, N'*- disubstituted imidazolinium or benzimidazolinium salts with potassium carbonate followed by the addition of elemental selenium or sulfur powder. Ligands **4**, **5**, 1-methyl benzimidazole, 1-benzyl imidazole,[3] **11**,[4] 2-bromothioacetate and 3-bromothioacetate are synthesized by following literature procedures.[5]



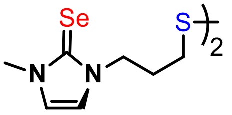
Scheme S1: Synthesis of *N*,*N'*–disubstituted thiones and selones via *in situ* generation of N–heterocyclic carbenes from the corresponding imidazolium salts.



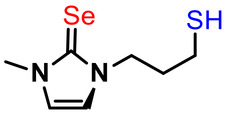
Synthesis of 1-(3-hydroxypropyl)-3-methyl-1*H*-imidazole-2(3H)-selenone (9) : In a 50 mL round-bottomed flask, fitted to a reflux condenser, a mixture of 1-methyl imidazole (1 g, 0.012 mmol) and 3-bromopropanol (1.35 mL, 0.015 mmol) was added into 20 mL of acetonitrile and stirred at the reflux temperature for 12 hrs. The reaction mixture was cooled and washed with EtOAc to get ionic liquid. Which is further transferred into 100 mL round-bottomed flask fitted to a reflux condenser, and treated with 50 mL of dry MeOH, anhydrous potassium carbonate (2.07 g, 0.015 mmol), and selenium (1.18 g, 0.015 mmol) under an inert atmosphere and the reaction mixture was stirred at reflux temperature for 24 hrs. After completion of the reaction, the solution was filtered through celite. The solvent was evaporated under reduced pressure to yield light brown crude product, which was further purified by column chromatography packed with silica, Ethylacetate / hexane as mobile phase (30%). The desired compound **9** was obtained as brownish liquid. Yield: 1.89 (82 %). ^{1}H NMR (400 MHz, DMSO) δ = 7.39 (d, *J* = 1.9 Hz, 2H), 7.30 (d, *J* = 1.9 Hz, 2H), 4.91 (t, *J* = 5.2 Hz, 2H), 4.09 (dd, *J* = 8.4, 6.2 Hz, 4H), 3.67 (dd, *J* = 10.9, 5.5 Hz, 2H), 2.26 – 2.11 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ = 153.9, 120.8, 118.9, 58.7, 51.2, 46.1, 28.4. ^{77}Se NMR (76.3): δ = 16.0 ppm; HRMS (TOF): m/z calculated for $[M+H]^+$ $C_7H_{12}N_2OSe$: 221.0188; found: 221.0172.



Synthesis of 4-(3-methyl-2-selenoxo-2,3-dihydro-1*H*-imidazol-1-yl) butanoic acid (8): The synthesis of **8** was a two-step process, initially synthesis of the ester compound followed by hydrolysis in basic medium. The compound **8** was synthesized following similar procedure to that of ligand **9**, except 4-bromo butyrate (1.35 mL, 0.015 mmol) was added in place of 3-bromopropanol. The obtained pure compound was further proceeded to base hydrolysis using 6 M aq. KOH and followed by hydrolysis with 1N HCl solution to get white solid of **8**. Which was filtered and dried under high vacuum for 2 h. Yield: 1.76 g (58 %).^{1}H NMR (400 MHz, DMSO) δ 7.98 (d, *J* = 2.4 Hz, 4H), 7.59 (d, *J* = 2.4 Hz, 4H), 6.63 (t, *J* = 6.7 Hz, 4H), 3.70 (s, 12H), ^{13}C NMR (101 MHz, DMSO) δ 150.7, 123.1, 121.6, 59.9, 37.5. HR-ESIMS (m/z): calculated for $[M+H]^+$ $C_8H_{12}N_2O_2Se$ = 249.0137, found: 249.0166.

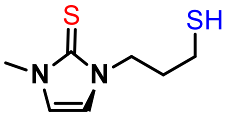


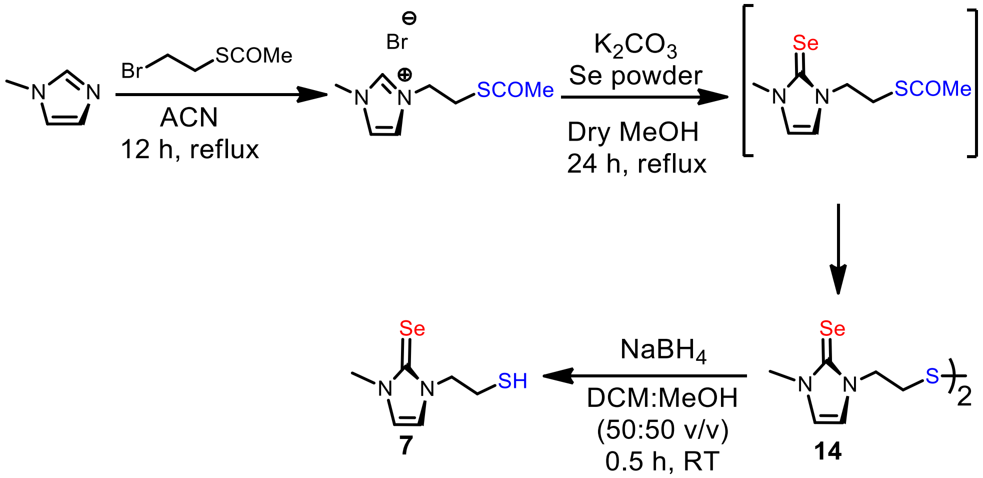
Synthesis of 1-(3-mercaptopropyl)-3-methyl-1*H*-imidazole-2(3*H*)-selenone (1): The synthesis of **1** was also a two-step process, initially synthesis of the thio-ester compound followed by reduction with $NaBH_4$. In first step the compound **10** was synthesized following similar procedure to that of ligand **9**, except 3-bromo thioacetae (2.95 g, 0.015 mmol) was added in place of 3-bromopropanol. In basic medium thio-acetate compound was converted into the disulfide. After completion of the reaction, the solution was filtered through celite. The solvent was evaporated under reduced pressure to yield crude product, which was further purified by column chromatography packed with silica, Ethylacetate / hexane as mobile phase (60 %). The desired compound **10** was obtained as half white solid. Yield: 3.7 g (65 %). ^{1}H NMR (400 MHz, DMSO) δ 7.35 (d, *J* = 1.8 Hz, 2H), 4.11 (t, *J* = 7.0 Hz, 2H), 3.55 (s, 3H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.16 – 1.99 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 154.6, 120.7, 119.4, 47.4, 36.3, 34.7, 28.4. ^{77}Se NMR (76.3): δ = 21.26 ppm; HRMS (TOF): m/z calculated for $[M+K]^+$ $C_{14}H_{24}N_4S_2Se_2$: 508.9415 ; found: 508.9456.



In the second step: The compound **10** (1.00 g, 0.0021 mmol) was dissolved in 10 mL of dichloromethane: methanol (1:1 v/v) and add the $NaBH_4$ pellets (0.25 g, 0.006 mmol) in portion wise then stirred at the room temperature for 30 min. After completion of the reaction, the reaction solution was diluted with 25 mL of dichloromethane and quenched with 5 mL of 1N aq. HCl then extracted the organic phase. The solvent was evaporated under reduced pressure to yield pure colorless liquid product **1**. Yield: 0.45 g (90 %). ^{1}H NMR (400 MHz, DMSO) δ 7.34 (s, 2H), 4.12 (t, *J* = 6.8 Hz, 2H), 3.55 (s, 3H), 2.68 (t, *J* = 7.9 Hz, 1H), 2.41 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.98 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 154.5, 120.8, 119.4, 47.2, 36.4, 32.8, 20.7.^{77}Se NMR (76 MHz, DMSO) δ 20.13; HRMS (TOF): m/z calculated for $C_7H_{12}N_2SSe$: 236.9969 $[M+H]^+$; found: 236.9965.

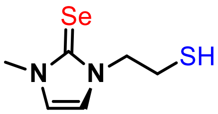
Synthesis of 1-(3-mercaptopropyl)-3-methyl-1H-imidazole-2(3*H*)-thione (6): The compound **6** was synthesized following similar procedure to that of ligand **1**, except sulphur powder (0.48g, 0.015 mmol) was added in place of selenium powder. ^{1}H NMR (400 MHz, DMSO) δ 7.14 (s, 2H), 4.03 (t, *J* = 6.8 Hz, 2H), 3.46 (s, 3H), 2.64 (t, *J* = 7.9 Hz, 1H), 2.41 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.94 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 161.4, 118.5, 117.1, 45.3, 34.4, 32.6, 20.7. HRMS (TOF): m/z calculated for $C_7H_{12}N_2S_2$: 189.0515 $[M+H]^+$; found: 189.0499.

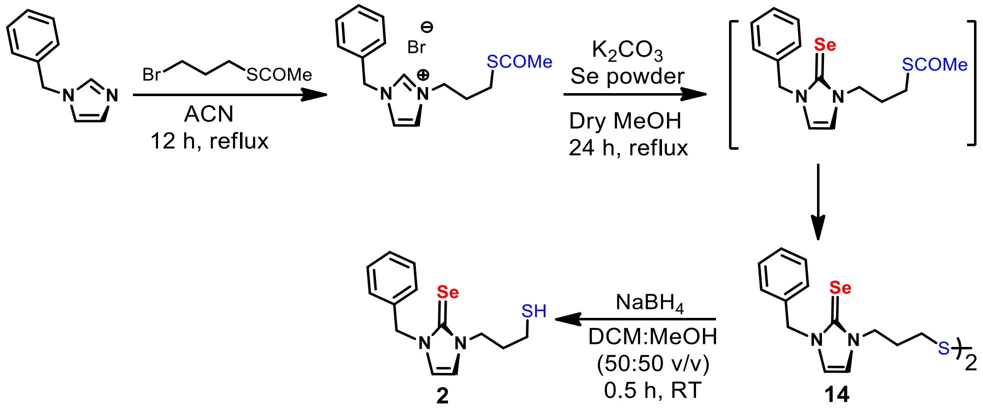




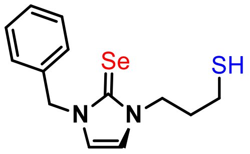
Scheme S2: Synthetic scheme for **7**.

Synthesis of 1-(2-mercaptoethyl)-3-methyl-1*H*-imidazole-2(3*H*)-selenone (7): The compound 7 was synthesized following similar procedure to that of ligand **1**, except 2-bromoethylthioacetate (2.75 g, 0.015 mmol) was added in place of 3-bromopropylthioacetate. Yield: 1.85 g (70 %). ^{1}H NMR (400 MHz, DMSO) δ 7.35 (d, *J* = 2.2 Hz, 1H), 7.33 (d, *J* = 2.2 Hz, 1H), 4.20 – 4.13 (m, 2H), 3.55 (s, 3H), 2.85 (dd, *J* = 14.6, 7.6 Hz, 2H), ^{13}C NMR (101 MHz, DMSO) δ 154.4, 120.3, 119.9, 51.3, 36.3, 22.5. ^{77}Se NMR (76.3): δ = 21.7 ppm; HR-ESIMS (m/z): m/z calculated for $C_6H_{10}N_2SSe$: 222.9802 $[M+H]^+$; found: 222.9836.

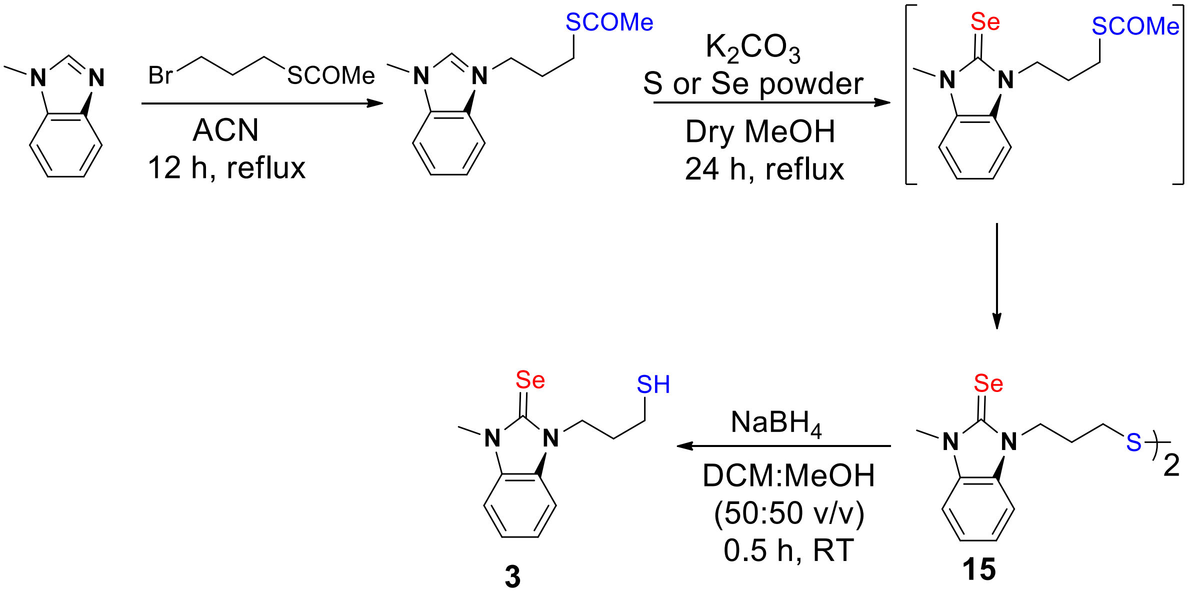




Scheme S3: Synthetic scheme for **2.**

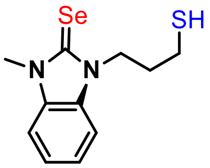


1-benzyl-3-(3-mercaptopropyl)-1*H*-imidazole-2(3*H*)-selenone (2): The compound 2 was synthesized following similar procedure to that of ligand **1**, except 1-benzyl imidazole (1.89 g, 0.012 mmol) was added in place of 1-methylimidazole. Yield: 1.98 g (53 %).^{1}H NMR (400 MHz, DMSO) δ 7.49 – 7.22 (m, 7H), 5.32 (s, 2H), 4.18 (t, *J* = 6.8 Hz, 2H), 3.34 (s, 2H), 2.72 (t, *J* = 8.1 Hz, 1H), 2.43 (dd, *J* = 14.9, 7.1 Hz, 2H), 2.01 (p, *J* = 6.9 Hz, 2H.^{13}C NMR (101 MHz, DMSO) δ 155.02 (s), 136.76 (s), 128.52 (s), 127.73 (d, *J* = 8.8 Hz), 120.1, 119.9, 51.4, 47.3, 32.8, 20.7. ^{77}Se NMR (76.3): δ = 19.1 ppm; HR-ESIMS (m/z): calcd for [M]$^+$ $C_{13}H_{16}N_2SSe$ = 313.0272,found: 313.0265.



Scheme S4: Synthetic scheme for **3**.

1-(3-mercaptopropyl)-3-methyl-1*H*-benzo[*d*]imidazole-2(3*H*)-selenone (3): The compound **3** was synthesized following similar procedure to that of ligand **1**, except 1-methyl benimidazole (1.58 g, 0.012 mmol) was added in place of 1-methylimidazole. Yield: 860 mg (83 %).^{1}H NMR (400 MHz, DMSO) δ 7.59 (ddd, *J* = 14.8, 6.1, 3.1 Hz, 2H), 7.38 – 7.26 (m, 2H), 4.49 (t, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 2.75 – 2.62 (m, 1H), 2.53 (d, *J* = 7.2 Hz, 2H), 2.04 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 165.4, 133.1, 132.3, 123.2, 110.3, 110.0, 44.5, 32.9, 32.0, 21.0. HR-ESIMS (m/z): m/z calculated for $C_{11}H_{14}N_2SSe$: 287.0115 $[M+H]^+$; found: 287.0115.



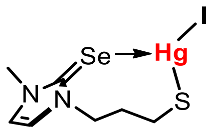
B. Synthetic procedures for thiol conjugated organomercurials:

Synthesis of MeHgCys: The MeHgCys was synthesized by following modified literature procedure.[3b-c,6] with mTo a solution of methylmercury chloride (100 mg, 0.40 mmol) in 5 mL of water / acetonitrile mixture (1:1), sodium hydroxide (16 mg, 0.40 mmol) was added and stirred for 30 min at 37°C. After that, supernatant solution was transfer into a 5ml solution of L-cysteine (48 mg, 0.40 mmol) in water/acetonitrile mixture (1:1), and stirred for 4 h at 37°C to obtain the white precipitate. The precipitate was washed thoroughly with water/acetonitrile mixture and dried in air to yield white solid powder. Yield: 107 mg (80 %). ^{1}H NMR (400 MHz, DMSO) δ 3.66 – 3.57 (m, 2H), 0.54 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 172.1, 57.3, 30.6, 13.6, 9.0.

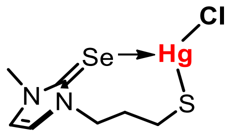
Synthesis of EtHgCys: The compound EtHgCys was synthesized following similar procedure to that of compound MeHgCys, except ethylmercury chloride (106 mg, 0.40 mmol) was added in place of methylmercury chloride. Yield: 121 mg (86 %). ^{1}H NMR (400 MHz, DMSO) δ 3.81 (t, *J* = 4.6 Hz, 4H), 1.40 (dd, *J* = 15.5, 7.0 Hz, 3H), 1.30 (t, *J* = 7.5 Hz, 5H). ^{13}C NMR (101 MHz, DMSO) δ 170.2, 55.7, 27.9, 26.3, 14.0.

Synthesis of Thimerosal: The compound thimerosal was synthesized following similar procedure to that of compound EtHgCys, except thiosalicylicacid (62 mg, 0.40 mmol) was added in place of L-cysteine. Yield: 126 mg (78 %). ^{1}H NMR (400 MHz, DMSO) δ 7.82 (d, *J* = 4.4 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.09 (m, 1H), 1.62 (q, *J* = 7.7 Hz, 3H), 1.25 (t, *J* = 7.8 Hz, 4H).^{13}C NMR (101 MHz, DMSO) δ 137.9, 131.8, 124.5, 22.88, 13.8.

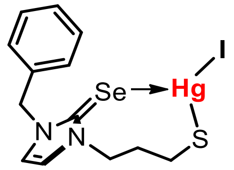
C. Synthetic procedures for isolated complexes:



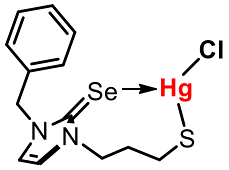
Synthesis of [(1)HgI]: A solution of **1** (50 mg, 0.21 mmol) in 10 mL of dichloromethane and methanol (1:1) solution was treated with methylmercury iodide (73 mg, 0.21 mmol) and stirred at room temperature for 15 h to observed a pale yellow coloured precipitate. The mixture was filtered and the volatile components were removed in vacuum to afford a crude product which was purified to afford [(**1**)HgI] as a pale yellow colour floppy compound. Yield: 42 mg (36 %). ^{1}H NMR (400 MHz, DMSO) δ 7.62 (s, 2H), 4.29 (t, J = 6.7 Hz, 2H), 3.72 (s, 3H), 2.65 (t, J = 6.6 Hz, 2H), 2.11 (p, J = 6.7 Hz, 2H. ^{13}C NMR (101 MHz, DMSO) δ 145.8, 123.2, 121.5, 47.8, 37.4, 33.3. HR-ESIMS (m/z): m/z calculated for $C_7H_{11}N_2SSeHgI$: 434.9499 $[M-I]^+$; found: 434.9954.



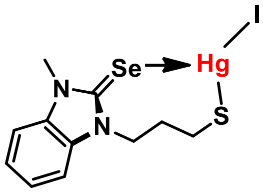
Synthesis of [(1)HgCl]: The compound [(1)HgCl] was synthesized following the similar procedure of [(**1**)HgI], except methylmercury chloride (52.8 mg, 0.21 mmol) was added in place of methylmercury iodide. The reaction mixture was stirred at room temperature for 48 h to obtain [(**1**)HgCl] as a white colour precipitate. Yield: 36 mg (36 %). ^{1}H NMR (400 MHz, DMSO) δ 7.80 – 7.63 (m, 2H), 7.45 – 7.27 (m, 5H), 5.40 (s, 2H), 4.34 (dt, J = 14.8, 6.9 Hz, 2H), 2.85 (dt, J = 14.2, 6.9 Hz, 2H), 2.20 (dd, J = 13.0, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 143.3, 135.5, 128.7, 128.5, 127.9, 122.5, 52.7, 47.9, 33.9. HR-ESIMS (m/z): m/z calculated for $C_7H_{11}N_2SSeHgCl$: 434.9499 $[M-Cl]^+$; found: 434.9954.



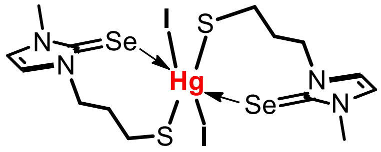
Synthesis of [(2)HgI]: A solution of **2** (50 mg, 0.16 mmol) in 10 mL dichloromethane and methanol (1:1) solution was treated with methylmercury iodide (55 mg, 0.16 mmol) and stirred at room temperature for 24 h. The mixture was filtered and the volatile components were removed filtarate in vacuo to afford [(**2**)HgI] as a pale yellow colour floppy compound. Yield: 48 mg (47 %). ^{1}H NMR (400 MHz, DMSO) δ 7.75 – 7.60 (m, 2H), 7.44 – 7.25 (m, 5H), 5.40 (s, 2H), 4.34 (t, J = 6.7 Hz, 2H), 2.71 (t, J = 6.0 Hz, 2H), 2.29 – 2.06 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 135.6, 128.7, 128.1, 122.3, 122.1, 52.7, 47.8, 33.4. HR-ESIMS (m/z): m/z calculated for $C_{13}H_{15}N_2SSeHgI$: 510.9814 $[M-I]^+$; found: 510.9819.



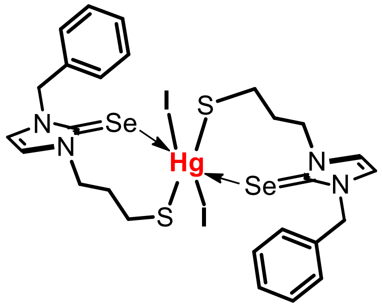
Synthesis of [(2)HgCl]: The compound [(**2**)HgCl] was synthesized following the similar procedure of [(**2**)HgI], except methylmercury chloride (40 mg, 0.16 mmol) was added in place of methylmercury iodide. The reaction mixture was stirred at room temperature for 48 h. The mixture was filtered and the volatile components were removed in vacuo to give [(**2**)HgCl] as a white colour precipitate. Yield: 36 mg (36 %). ^{1}H NMR (400 MHz, DMSO) δ 7.80 – 7.63 (m, 2H), 7.45 – 7.27 (m, 5H), 5.40 (s, 2H), 4.34 (dt, *J* = 14.8, 6.9 Hz, 2H), 2.85 (dt, *J* = 14.2, 6.9 Hz, 2H), 2.20 (dd, *J* = 13.0, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 143.3, 135.5, 128.7, 128.53, 127.9, 122.5, 52.8, 47.9, 33.9. HR-ESIMS (m/z): m/z calculated for $C_{13}H_{15}N_2SSeHgCl$: 510.9814 $[M-Cl]^+$; found: 510.9819.



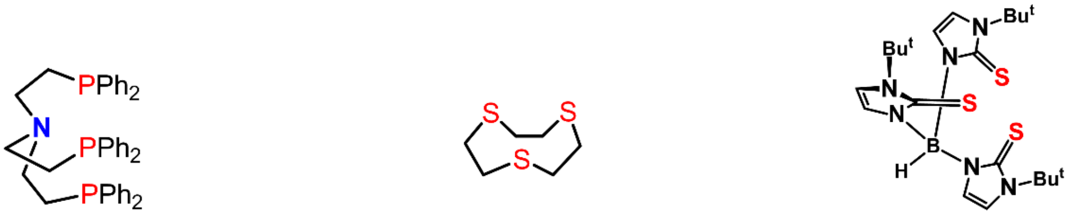
Synthesis of [(3)HgI]: A solution of **3** (50 mg, 0.18 mmol) in 10 mL dichloromethane and methanol (1:1) solution was treated with methylmercury iodide (62 mg, 0.18 mmol) and stirred at room temperature for 24 h. After this period, the formation pale yellow coloured precipitate was observed. The mixture was filtered and the volatile components were removed filtarate in vacuo to afford [(**3**)HgI]. Yield: 25 mg (28 %). ^{1}H NMR (400 MHz, DMSO) δ 7.84 – 7.63 (m, 2H), 7.47 – 7.36 (m, 2H), 4.61 (t, *J* = 6.9 Hz, 2H), 3.92 (s, 3H), 2.83 (d, *J* = 6.5 Hz, 2H), 2.13 (dd, *J* = 13.6, 6.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 143.1, 133.6, 132.7, 124.8, 111.8, 45.8, 34.6, 33.6.



Synthesis of [(1)$_2$HgI$_2$]: A solution of **1** (100 mg, 0.42 mmol) in 10 mL dichloromethane and methanol (1:1) solution was treated with methylmercury iodide (145 mg, 0.42 mmol) and stirred at room temperature for 5 days. After this period, the formation pale yellow coloured precipitate was observed. The mixture was washed with ethyl acetate (2 x 5 mL) then filtered and the volatile components were removed in vacuo to give [(**1**)$_2$HgI$_2$] as yellow coloured viscous liquid compound. Yield: 120 mg (32 %). ^{1}H NMR (400 MHz, DMSO) δ 7.63 (d, *J* = 6.0 Hz, 2H), 4.37 – 4.15 (m, 2H), 3.76 (s, 3H), 2.85 (t, *J* = 6.7 Hz, 2H), 2.27 – 2.09 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 145.6, 123.2, 121.6, 48.6, 37.4, 35.2, 28.8. HR-ESIMS (m/z): m/z calculated for $C_{14}H_{22}N_4S_2Se_2HgI_2$: 796.836 $[M-I]^+$; found: 796.8457.



Synthesis of [(2)$_2$HgI$_2$]: The compound [(**2**)$_2$HgI$_2$] was synthesized following the similar procedure of [(**1**)$_2$HgI$_2$, except compound **2** (130 mg, 0.42 mmol) was added in place of compound **1**. The reaction mixture was stirred at room temperature for 5 to 6 days. After this period, the formation yellow colour precipitate was observed. The precipitate was washed with ethyl acetate (2 x 5 mL) and filtered. The volatile components were removed in vacuo to give (**2**)$_2$HgI$_2$ as a yellow colour precipitate. Yield: 150 mg (36 %). ^{1}H NMR (400 MHz, DMSO) δ 7.72 – 7.59 (m, 2H), 7.41 – 7.26 (m, 5H), 5.46 (s, 2H), 4.36 – 4.23 (m, 2H), 2.85 (t, *J* = 7.0 Hz, 2H), 2.28 – 2.12 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 136.0, 129.2, 128.5, 122.8, 53.2, 49.2, 35.7, 29.2. HR-ESIMS (m/z): m/z calculated for $C_{26}H_{30}N_4S_2Se_2HgI_2$: 948.899 [M-I]$^+$; found: 948.8923.



np$_3$ *Inorg. Chem.* **1994**, *33*, 6163–6170

[9]aneS$_3$ *Eur. J. Inorg. Chem.* **2004**, 2301–2312

TM$^{Bu^t}$ *Science* **2007**, *317*, 225–227

Figure S1: Reported model compounds used for Hg–C bond cleavage in the presence of excess Brønsted acids (CF_3SO_3H, CF_3CO_2H) or excess thiols (C_6H_5SH, *p*-$CH_3C_6H_4SH$).[7]

2. NMR Data Analyses:

The Hg–C protonolysis reactions of MeHgX (X = SPh, Cl or I) by **1** or any other –SH containing selones (**2, 7, 3**) or thione (**6**) were monitored by ^{1}H NMR spectroscopy in DMSO-*d*$_6$, or in any other deuterated NMR solvents. All experiments were performed in a sealed NMR tubes at 21 °C. ^{1}H NMR spectra were recorded at various time intervals and rate of demethylation of MeHgX was calculated with respect to mesitylene (12 mM) as an external standard.[8,9] Integral values of singlet resonance of methyl protons (-CH$_3$) of MeHgX (at various time points) with respect to the aromatic singlet resonance of mesitylene (which is considered as one proton and this signal does not interfere with other signals) were used for calculating the initial rate of the reaction. Initial value at 0 min was considered as 100 % of MeHgX (0.1 M) and first 10-15% of demethylation was considered as the initial rate of the reaction. Likewise, the Hg–C protonolysis reactions of other organomercurials like EtHgCl by **1** or any other –SH containing selones (**2**, **7, 3)** or thione (**6**) were monitored by ^{1}H NMR spectroscopy in DMSO-*d*$_6$, or in any other deuterated NMR solvents as mentioned in the manuscript at 21 °C.

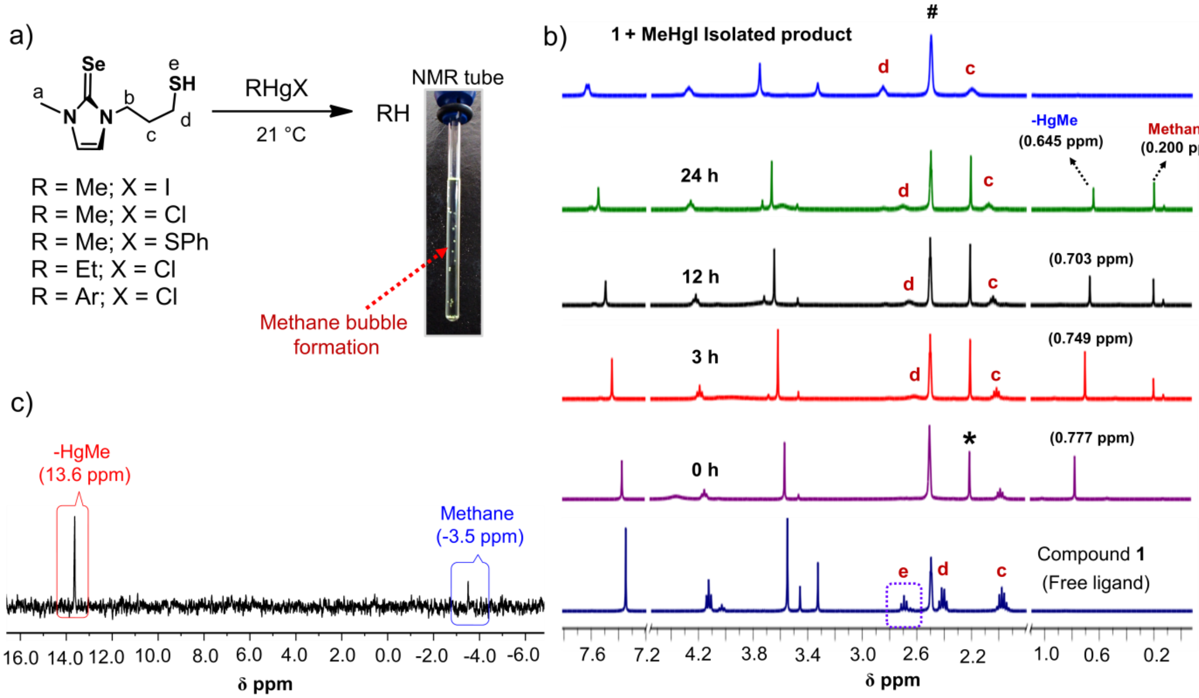


Figure S2: a) Synthetic scheme for the cleavage of Hg–C bonds of RHgX by **1**. b) ^{1}H NMR stack spectra showing the degradation of MeHgI and formation of methane by **1** at 21 °C.[10] (* = mesitylene, external standard and [RHgX] = [**1**] = 25 mM). c) ^{13}C NMR spectrum showing the methane and –HgMe peaks of 1:1 adduct.

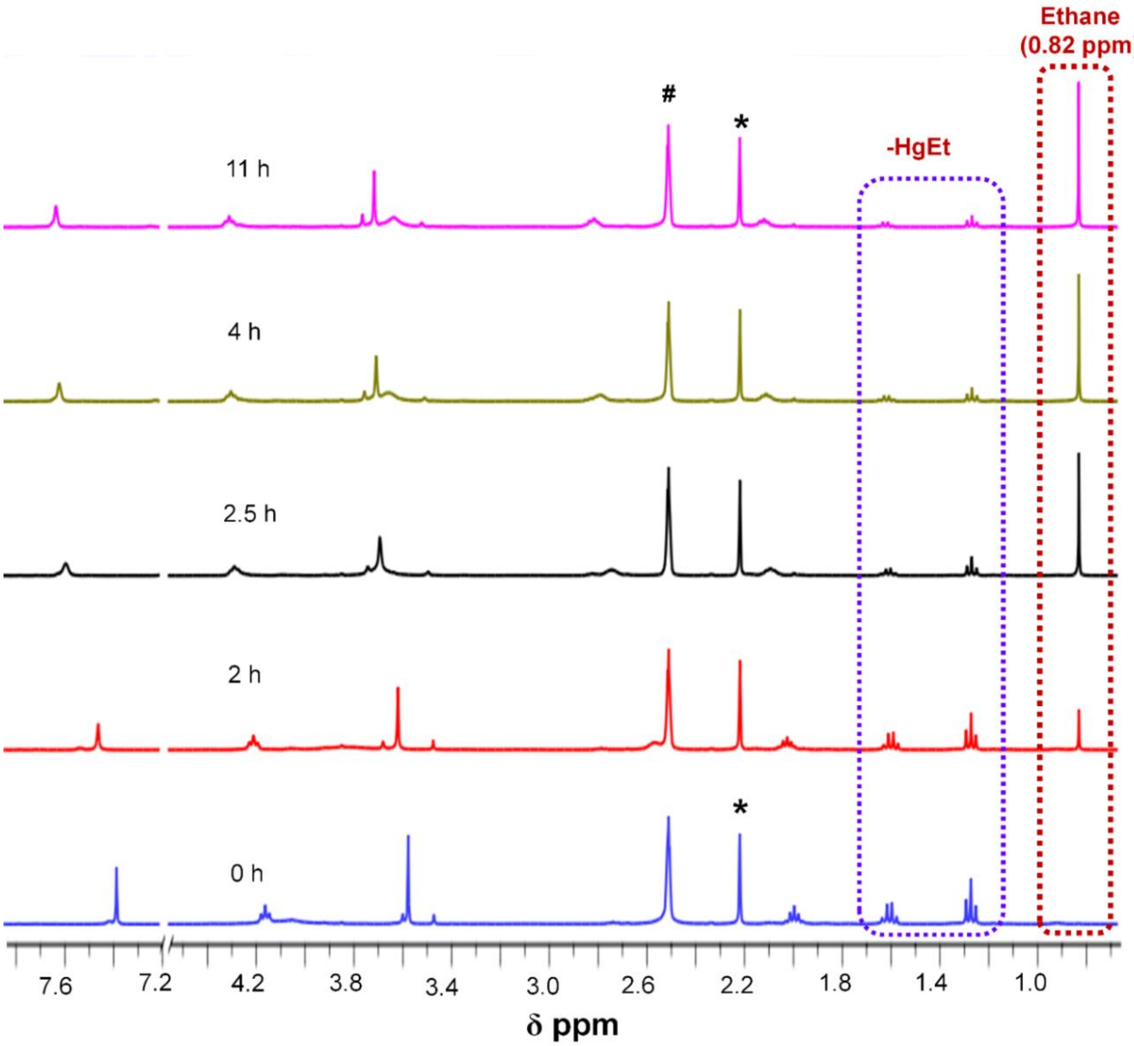


Figure S3. ^{1}H NMR stack spectra showing the degradation of EtHgCl and formation of ethane by treatment of **1** at 21 °C.[11] (# = DMSO-d_6, * = mesitylene, external standard and [EtHgCl] = [**1**] = 25 mM).

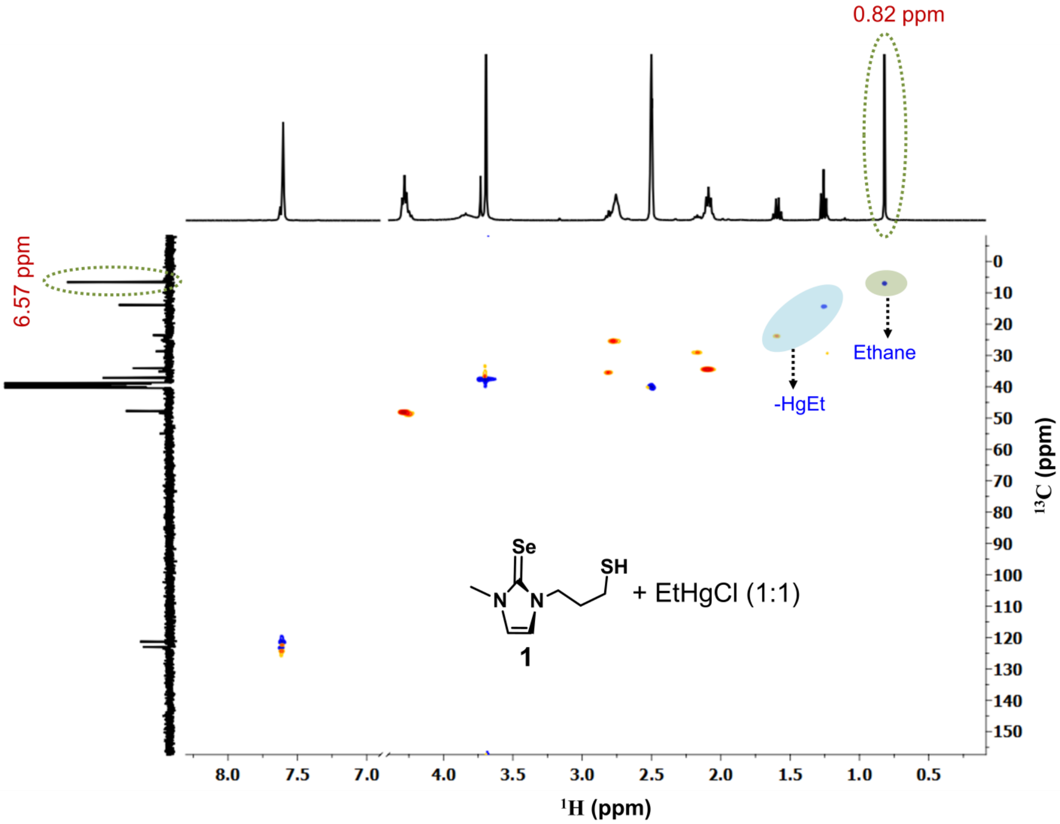


Figure S4: HSQC spectrum of ethane formation by treatment of EtHgCl and **1** in DMSO-*d*6.

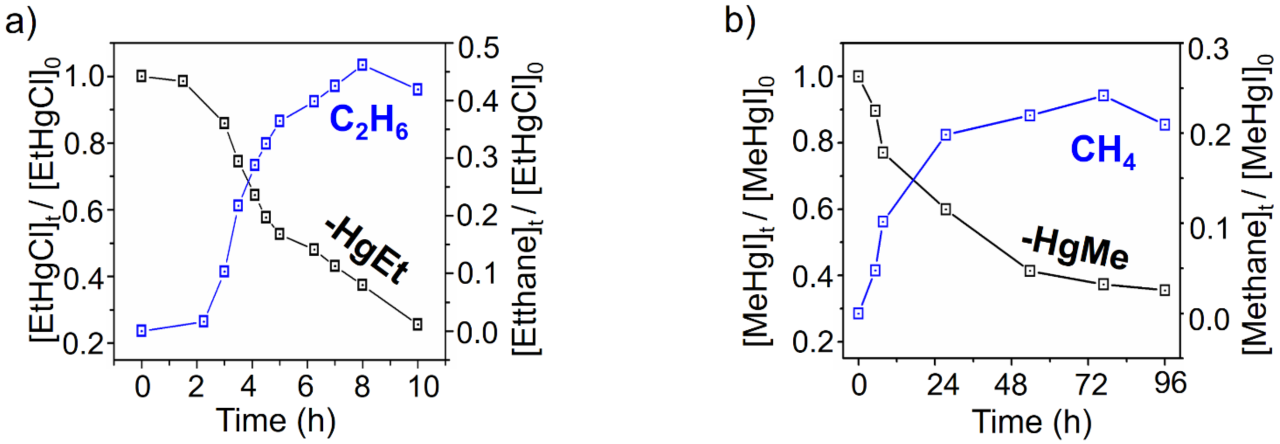


Figure S5: Graphs showing the gradual degradation of EtHgCl (a) and MeHgI (b) by compound **1** and the gradual formation of dissolved C_2H_6 and CH_4 in NMR solution (DMSO-*d*6), respectively, at 21 °C.

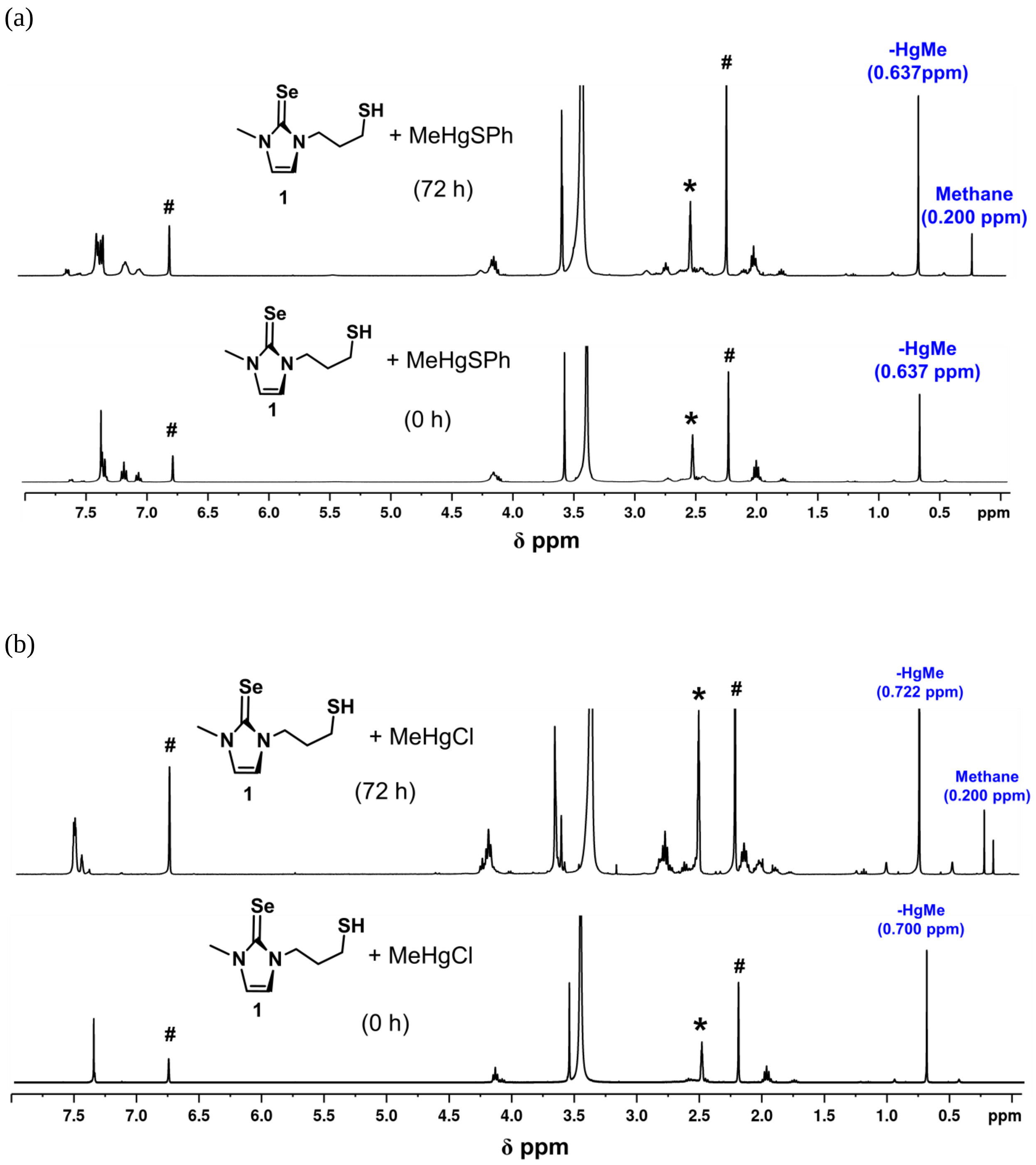


Figure S6: (a) ^{1}H NMR stack spectra showing the degradation of MeHgSPh and formation of methane by **1** at 21 °C. (* = DMSO-*d*$_{6}$, # = mesitylene, external standard and [MeHgSPh] = [**1**] = 25 mM). (b) ^{1}H NMR stack spectra showing the degradation of MeHgCl and formation of methane by **1** at 21 °C. (* = DMSO-*d*$_{6}$, # = mesitylene, external standard and [MeHgCl] = [**1**] = 25 mM).

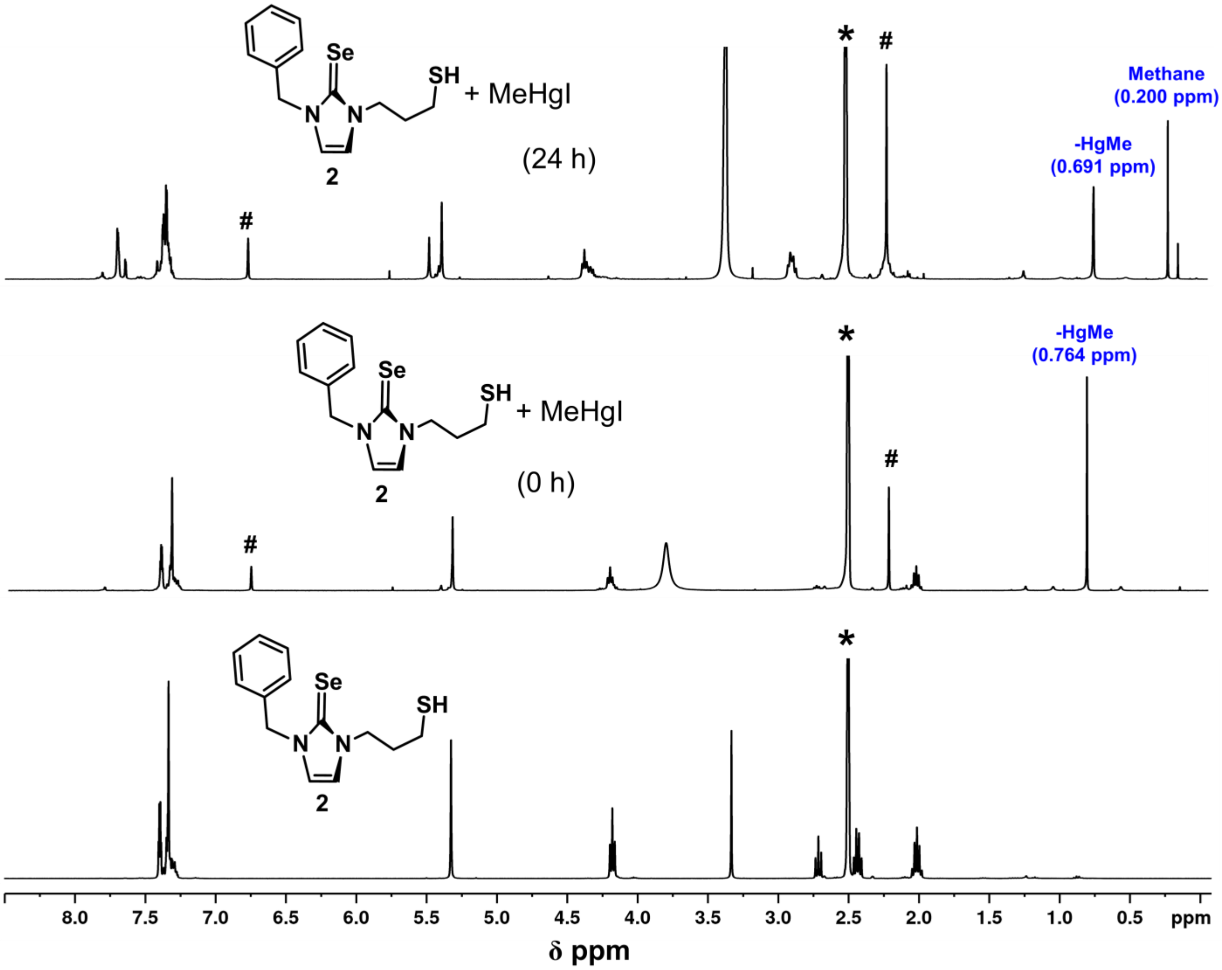


Figure S7: ^{1}H NMR stack spectra showing the degradation of MeHgI and formation of methane by **2** at 21 °C. (* = DMSO-d_6, # = mesitylene, external standard and [MeHgI] = [**2**] = 25 mM).

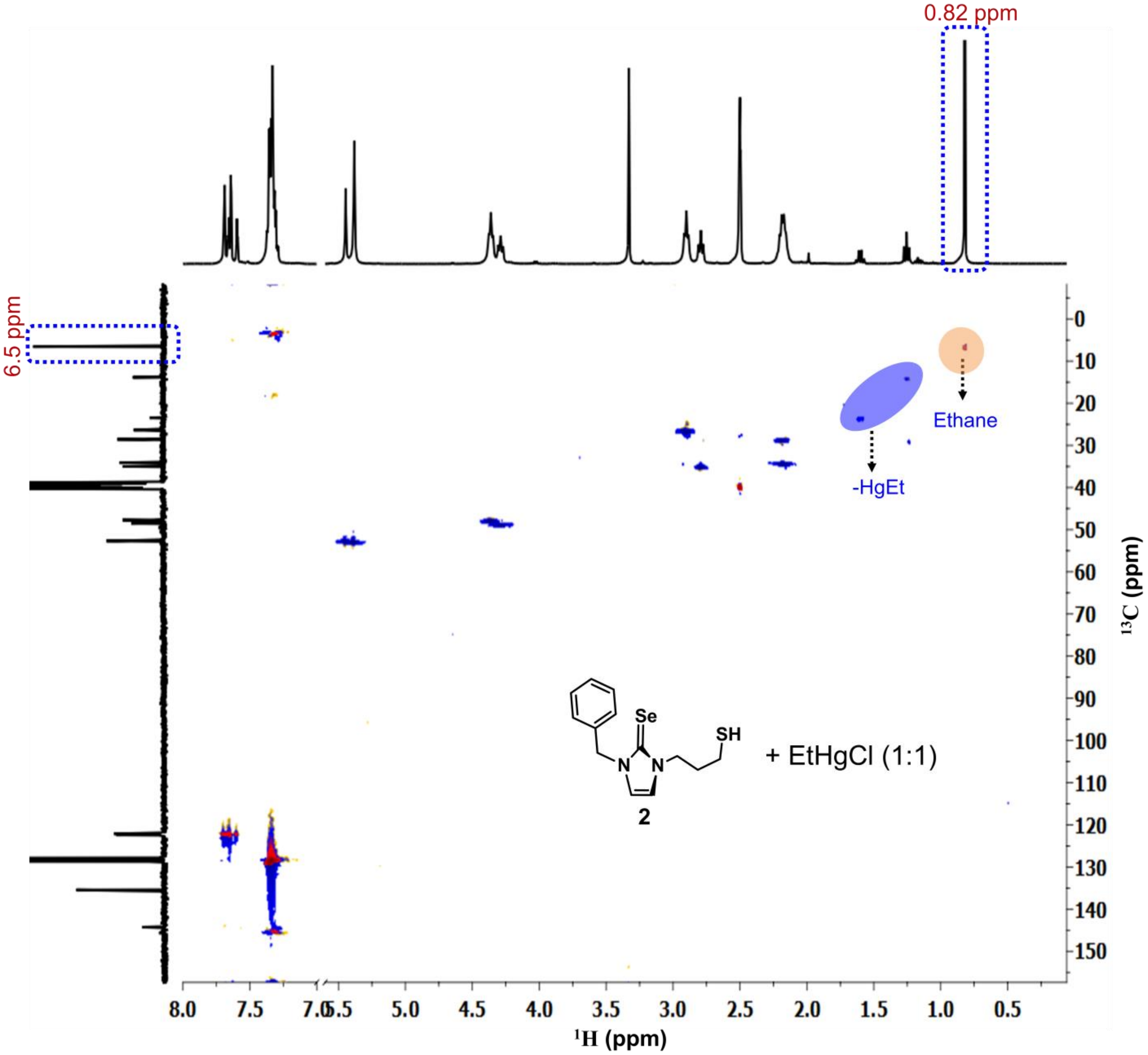


Figure S8: HSQC spectrum of ethane formation by treatment of EtHgCl and **2** in DMSO-*d*$_6$.

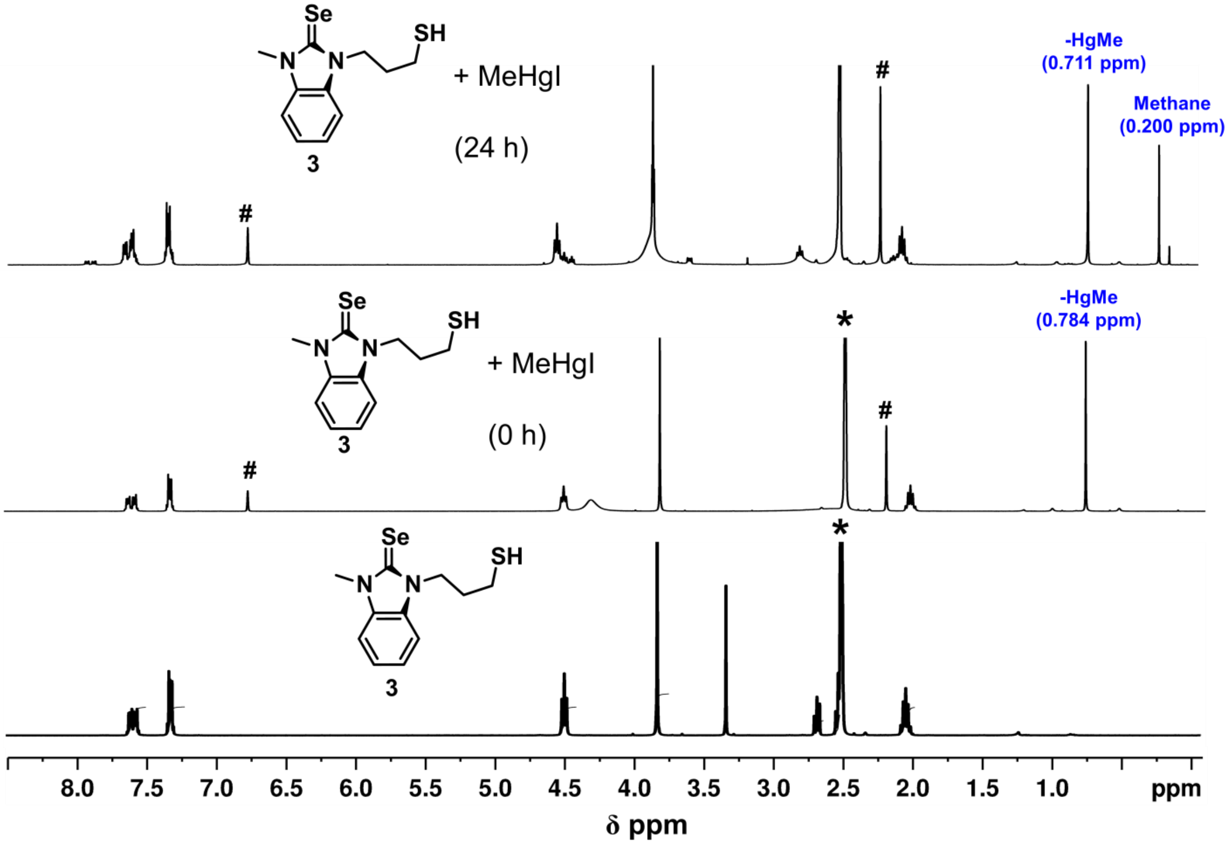


Figure S9: ^{1}H NMR stack spectra showing the degradation of MeHgI and formation of methane by **3** in a 1:1 molar ratio at 21 °C. (* = DMSO-d_6, # = mesitylene, external standard and [MeHgI] = [**3**] = 25 mM).

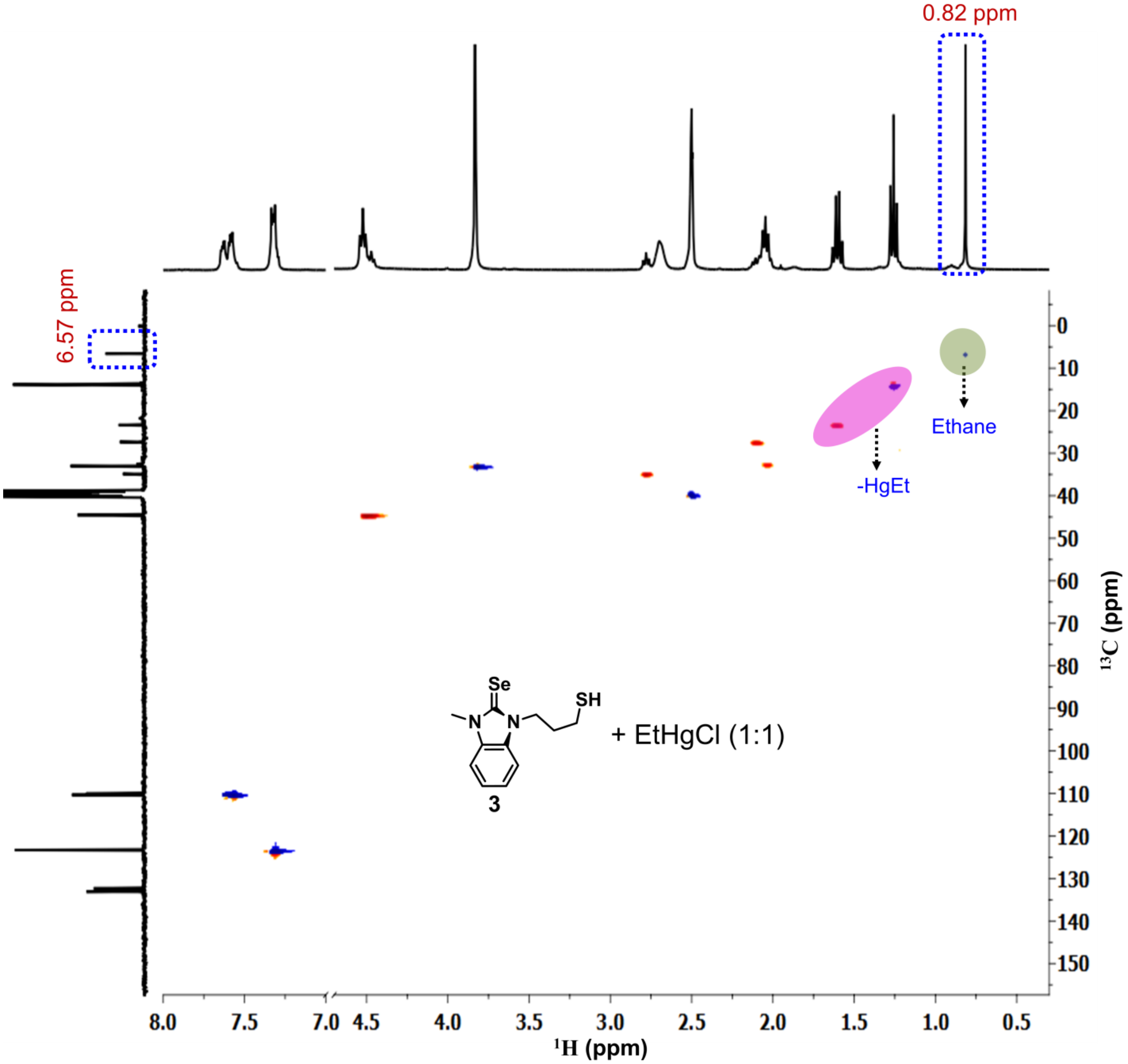


Figure S10:. HSQC spectrum of ethane formation by treatment of EtHgCl and **3** in DMSO-d_6.

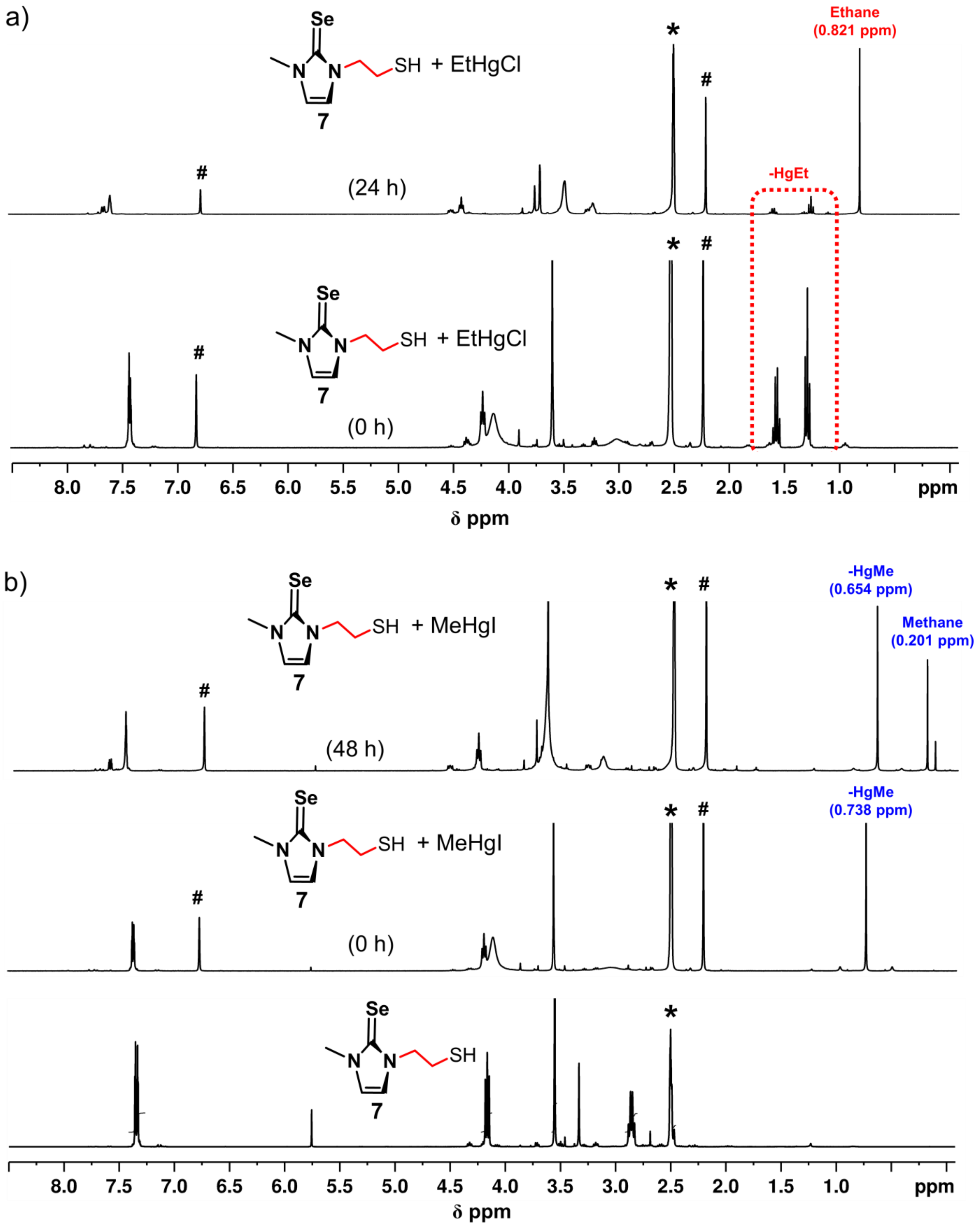


Figure S11: ^{1}H NMR stack spectra showing the cleavage of Hg–C bond of EtHgCl (a) and MeHgI (b) induced by **7**, in 1:1 molar ratio, at 21 °C. (* = DMSO-d_6, # = mesitylene, external standard and [EtHgCl] = [MeHgI] = [7] = 25 mM).

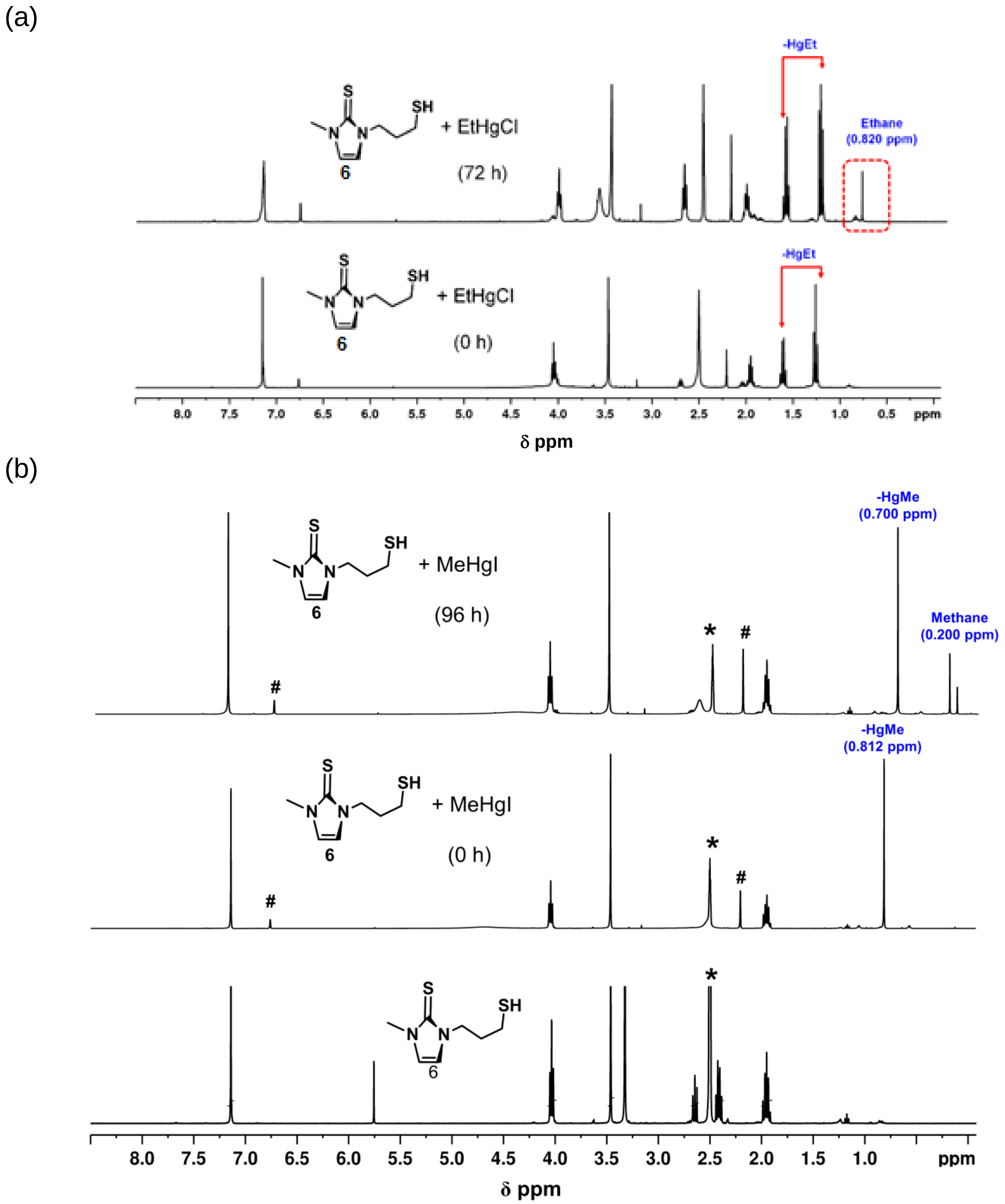


Figure S12: ^{1}H NMR stack spectra in DMSO-d$_6$ showing the degradation of EtHgCl (a) MeHgI (b) by 100 mM of **6**, used in 1:1 molar ratio, and showing the formation of the corresponding ethane and methane, respectively. (* = DMSO-d_6, # = mesitylene, external standard and [MeHgI] = [EtHgCl] = [**6**] = 100 mM).

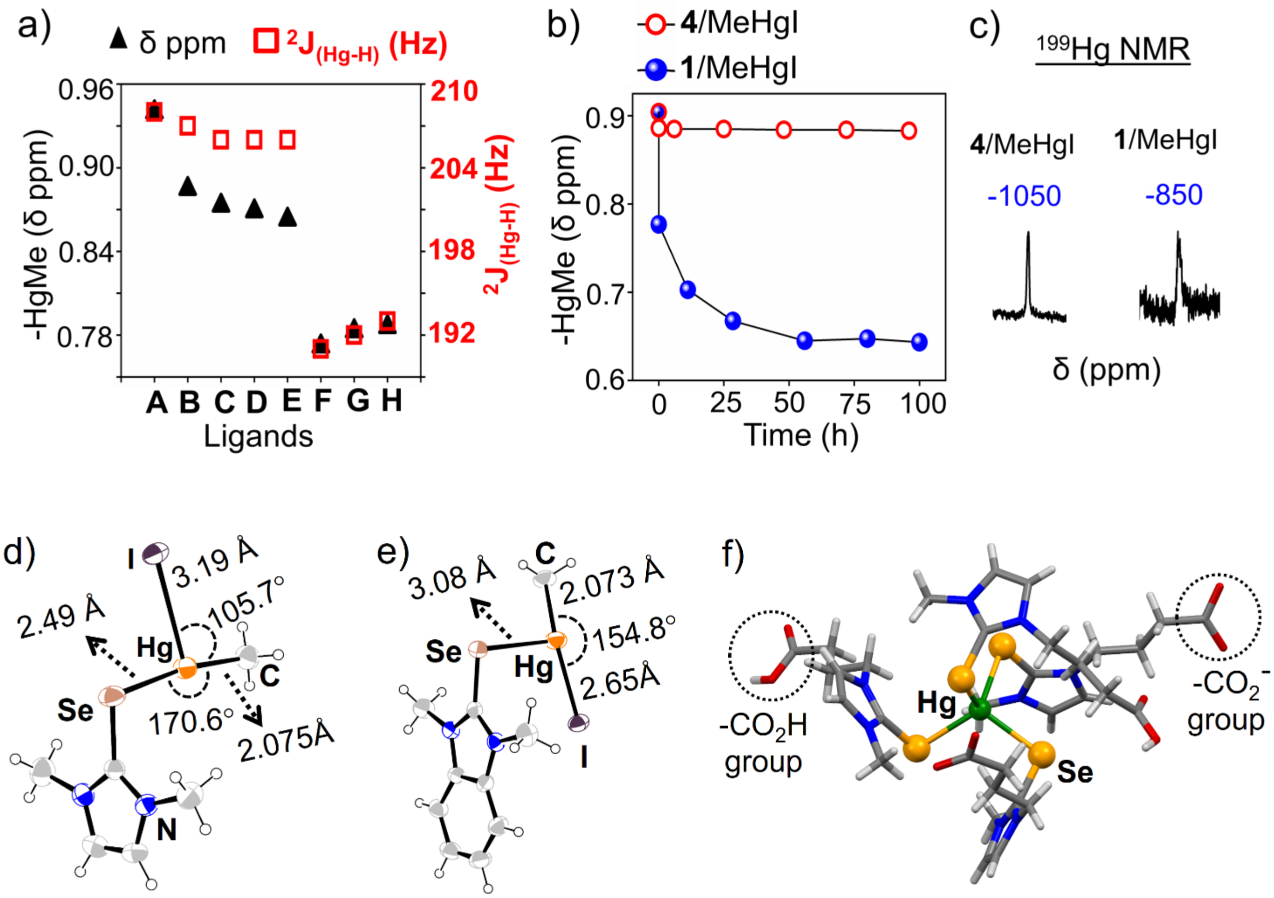


Figure S13: (a) ^{1}H resonances and ^{2}J(Hg-H) coupling constant values of –HgMe of MeHgI in the presence of 1 equiv. of various ligands (25 mM) in DMSO-d_6 ; A: MeHgI only (no ligand), B: Compound 4, C: Compound 8, D: Compound 9, E: Compound 10, F: Compound 1, G: Compound 2, H: Compound 3. b) The change of ^{1}H resonances of MeHgI (25 mM) in the presence of 1 equiv of 1 or 4 over time. c) ^{199}Hg NMR spectra of a 1:1 solution of 4/MeHgI (25 mM) and 1/MeHgI in DMSO-d_6 at 21 °C. X-ray structures of **4**.MeHgI (d), **5**.MeHgI (e), and **12** (f).

To understand the activation of Hg–C bond by selones we have carried out detailed ^{1}H NMR study. The ^{1}H resonance of methyl group of MeHg$^+$ in the presence or absence of a chelating ligand (selone) provides very useful information on the extent of Hg–C bond activation by ligand. Addition of selones to a solution of MeHgI, in 1:1 molar ratio, led to significant up-field shift of –HgMe ^{1}H resonance, ranging from 0.94 to 0.772 ppm (Δδ = 0.168) depending upon the type of selone added to the solution of MeHgI, (Figure S13, left panel, Δ δ ppm; Note: the ^{1}H resonance of MeHgI appeared at 0.94 ppm in DMSO-d_6). Interestingly, the selones with an –N(CH$_2$)$_3$SH moiety such as compounds **1**, **2**, and **3** exhibited significant amount of –HgMe ^{1}H resonance shift (Δδ = 0.168 – 0.154 ppm) than the selones without an –N(CH_2)$_3$SH moiety (Δδ = 0.071 – 0.041 ppm). Moreover, among –N(CH_2)$_3$SH containing selones, addition of compound 1 to a solution of MeHgI resulted maximum up-field shift of –HgMe ^{1}H resonance (Δδ for **1** is 0.168 ppm, where the Δδ values for **2** and **3** are 0.157 and 0.154 ppm, respectively). In fact, the –HgMe ^{1}H resonance of MeHgI gradually up-field shifted over time after addition of 1 equiv of compound **1** shifted from 0.94 ppm to 0.67 ppm in 24 h (Δδ = 0.27 ppm), whereas only a slight –HgMe ^{1}H resonance shift (Δδ = 0.06 ppm) was observed in the case of compound **4** (Figure S13e).

The $^2J(^{199}Hg–^1H)$ coupling constants are also a good indicator of the nature of coordination in solution.[7c] The 1:1 solutions of MeHgI/**1** (207 Hz), MeHgI/**9** (206 Hz), and MeHgI/**8** (206 Hz) showed higher $^2J(^{199}Hg–^1H)$ coupling constant values, almost close to MeHgI (209 Hz), than the 1:1 solutions of MeHgI/**1**(191 Hz), MeHgI/**2** (192 Hz), and MeHgI/**3** (193 Hz), (Figure S13, right panel, $^2J_{(Hg-H)}$ Hz). Furthermore, the ^{199}Hg NMR of a 1:1 solution of MeHgI/**4** (0.1 M) showed a resonance at -1050 ppm in DMSO-d_6 (^{199}Hg of MeHgI appeared at -1153 ppm), whereas a MeHgI/**1** (0.1 M) solution showed a large shift at -850 ppm, Figure 5f. These observations clearly indicate that the selones, having an –N(CH_2)$_3$SH moiety, activate Hg–C bond strongly through formation of a higher coordinated species than the selones without –N(CH_2)$_3$SH moiety.

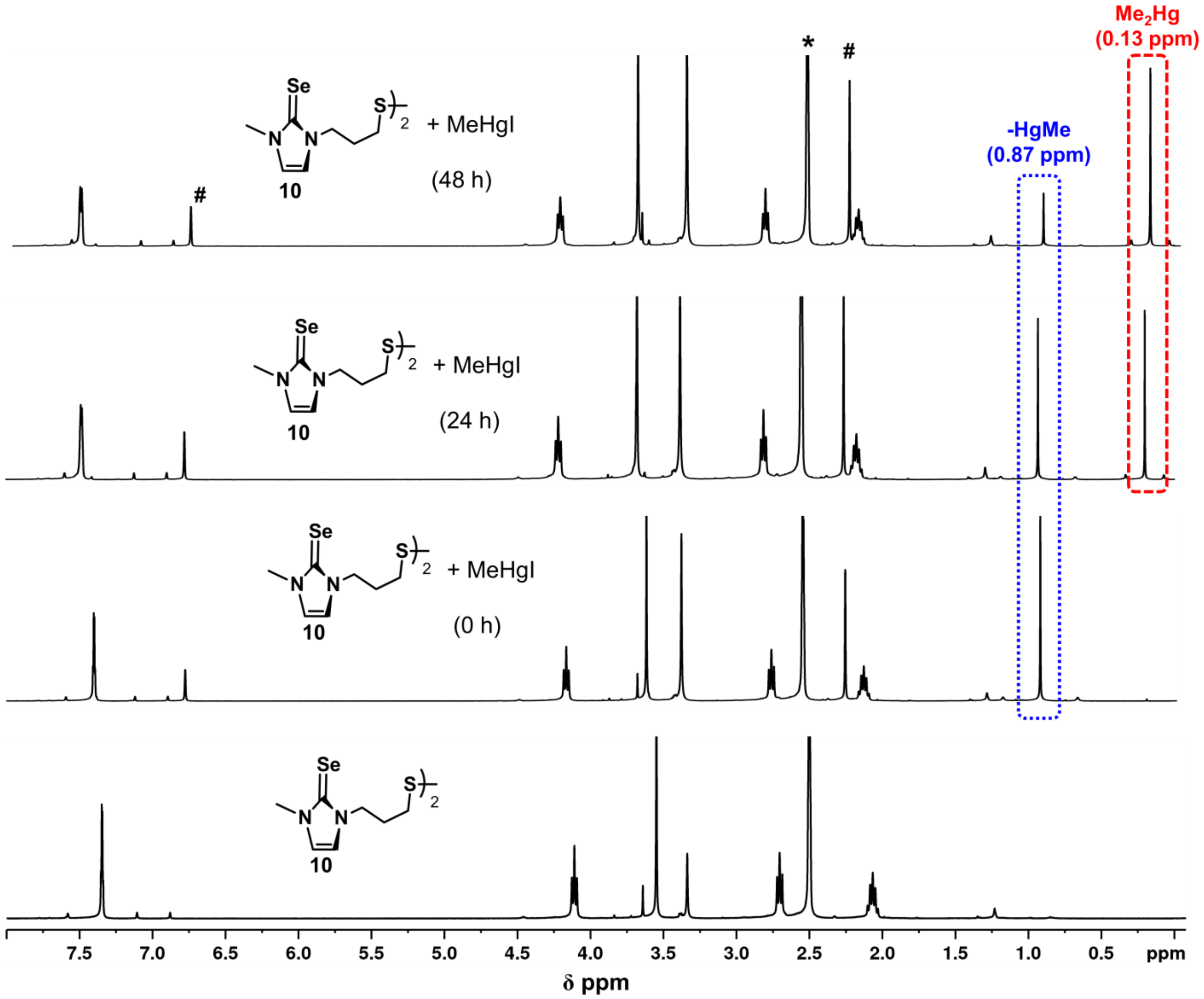


Figure S14: ^{1}H NMR stack spectra in DMSO-d$_6$ showing the degradation of MeHgI and formation of Me$_2$Hg by treatment of **10** in a 1:1 molar ratio. (* = DMSO-*d$_6$*, # = mesitylene, external standard and [MeHgI] = [**10**] = 25 mM).

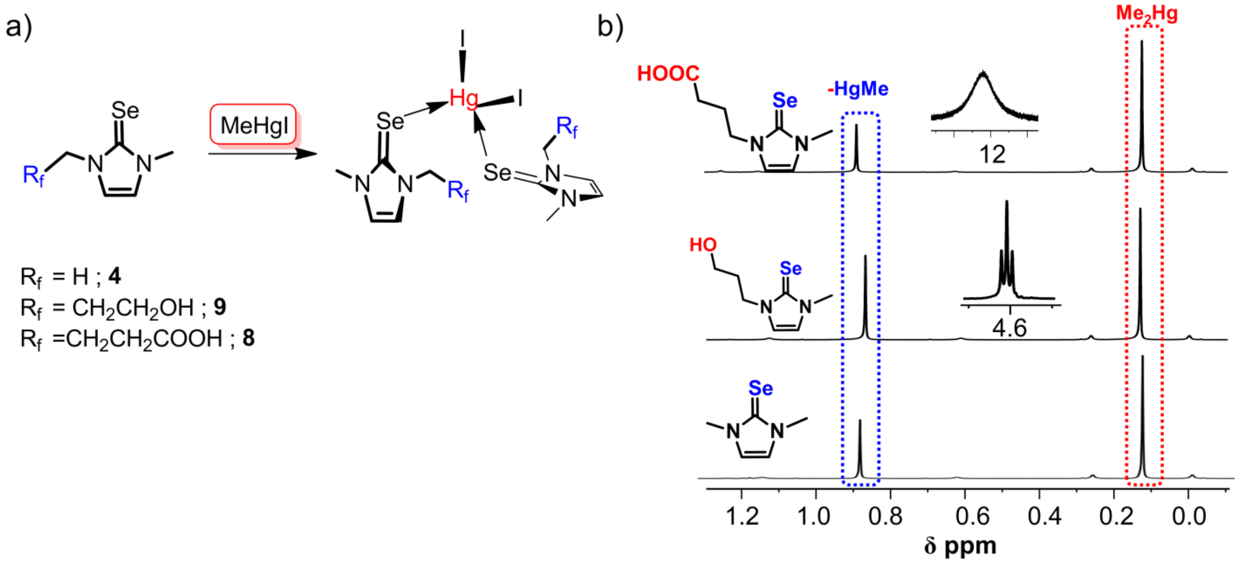


Figure S15: (a) Synthetic route of Hg–C bond cleavage of MeHgI by compounds **4**, **9**, and **8** showing the formation of Me_2Hg *via* 4-membered intermediate.[9a] (b) ^1H NMR stack spectra showing the conversion of MeHgI (25 mM) to Me_2Hg induced by compound **4**, **9**, **8** (1:1 molar ratio), recorded in DMSO-d_6 at 21 °C.

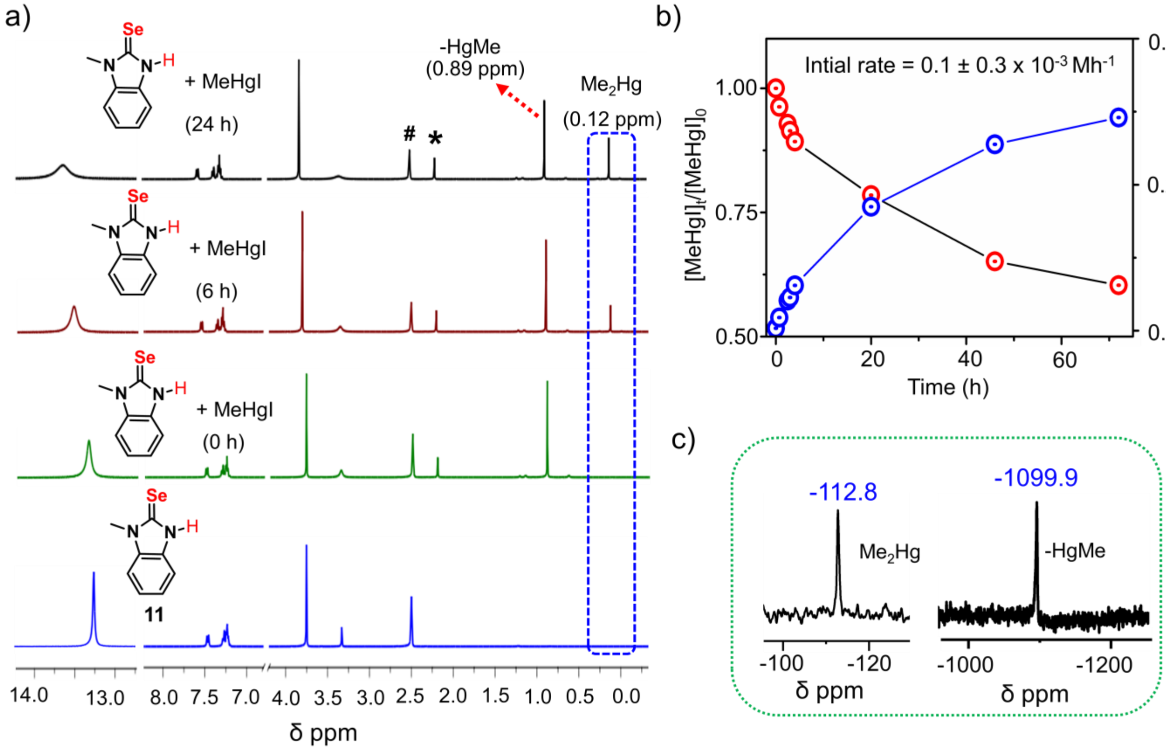


Figure S16: (a) ^1H NMR stack spectra showing the conversion of MeHgI (50 mM) to Me_2Hg induced by **11** (1:1 molar ratio), recorded in DMSO-d_6 at 21 °C (# = DMSO-d_6, * = mesitylene, external standard). (b) Graph showing the degradation of MeHgI and the corresponding Me_2Hg formation via 4-membered intermediate (Figure S16) over time induced by **11**. (c) ^{199}Hg NMR spectra of Me_2Hg and 1:1 adduct [**11**.MeHgI].

Recently, Parkin *et al.* in their pioneer work reported the protolytic Hg−C bond cleavage of MeHgX (X = Cl or I) by **11** via an unknown reaction mechanism, when mercury alkyls MeHgX were heated with excess amount of **11** for overnight at high temperature (100 °C).[12] Unfortunately, N center being a hard base is unlikely to coordinate to the Hg center in the presence of mercurophilic Se center in the molecule and, as a result, **11** produces toxic Me_2Hg, instead of CH_4, in reaction with MeHgX at 21 °C (Fig. S16). It is noteworthy to mention here that imidazole-based biomolecule selenoneine, with two N–H protons in the heterocycle, was reported to detoxify $MeHg^+$ in a different pathway, i.e., through conversion of biologically inert HgSe species.[13] Recently, we have also shown that the imidazole-based thione/selone, having an $–N(CH_2)_2OH$ substituent, degrades various RHgOH *via* the formation of HgS/HgSe species.[14]

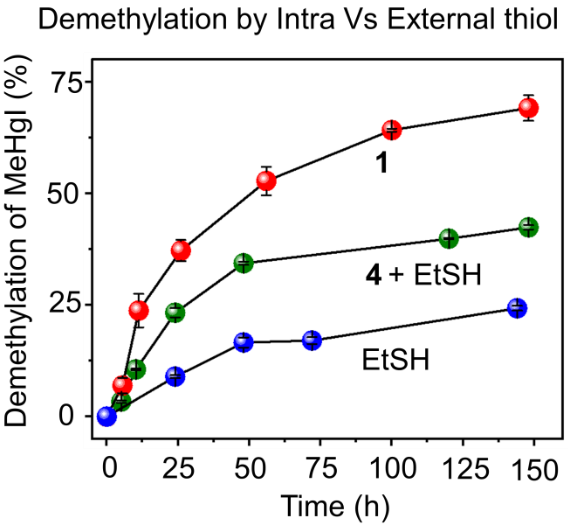


Figure S17: Demethylation of MeHgI in the presence of compound **1** or EtSH or the mixture of (**4** + EtSH).

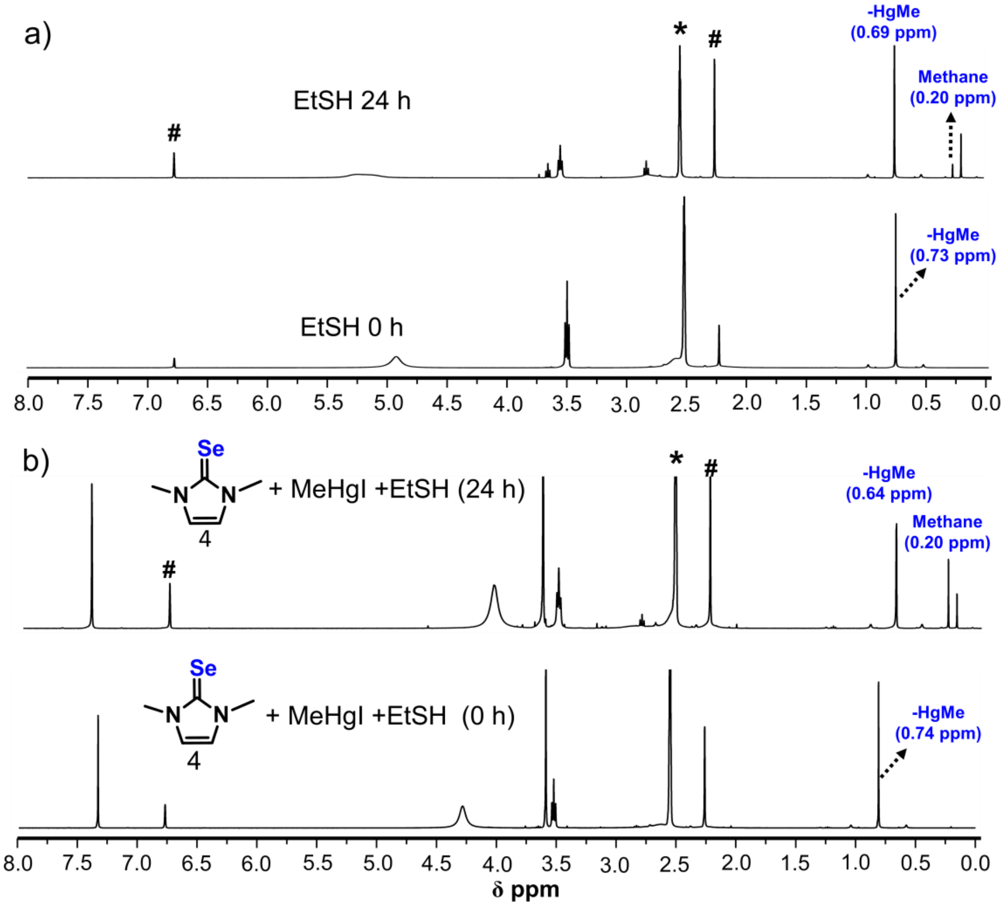


Figure S18: ^{1}H NMR stack spectra in DMSO-d_6 showing the degradation of MeHgI by treatment of (a) EtSH, in a 1:1 molar ratio, and (b) EtSH + **4**, in 1:1:1 molar ratio. (* = DMSO-d_6, # = mesitylene, external standard).

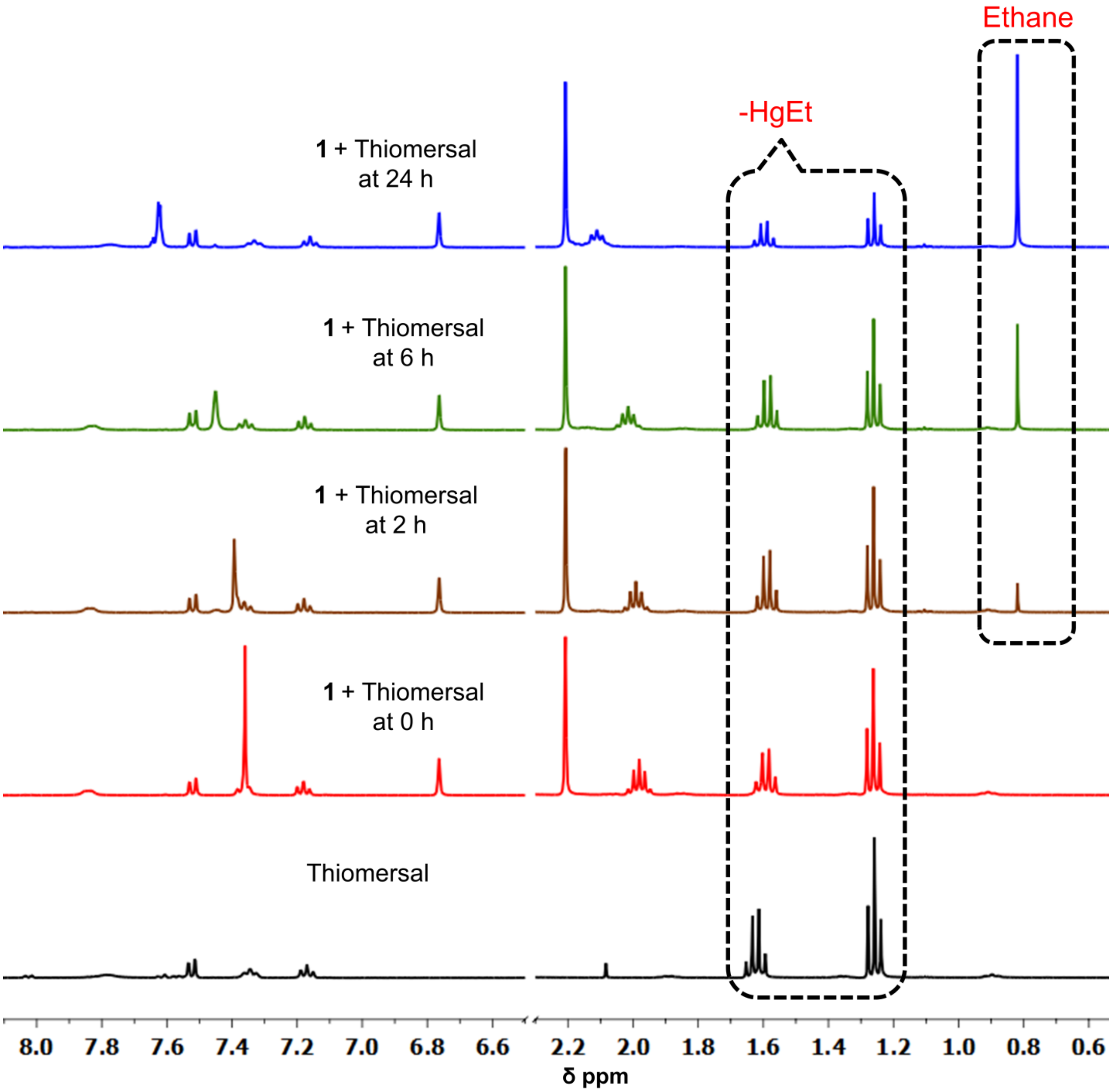


Figure S19: ^{1}H NMR stack spectra showing the degradation of thimerosal and formation of ethane by treatment of compound **1** at 21 °C. ([Thimerosal] = [**1**] = 25 mM).

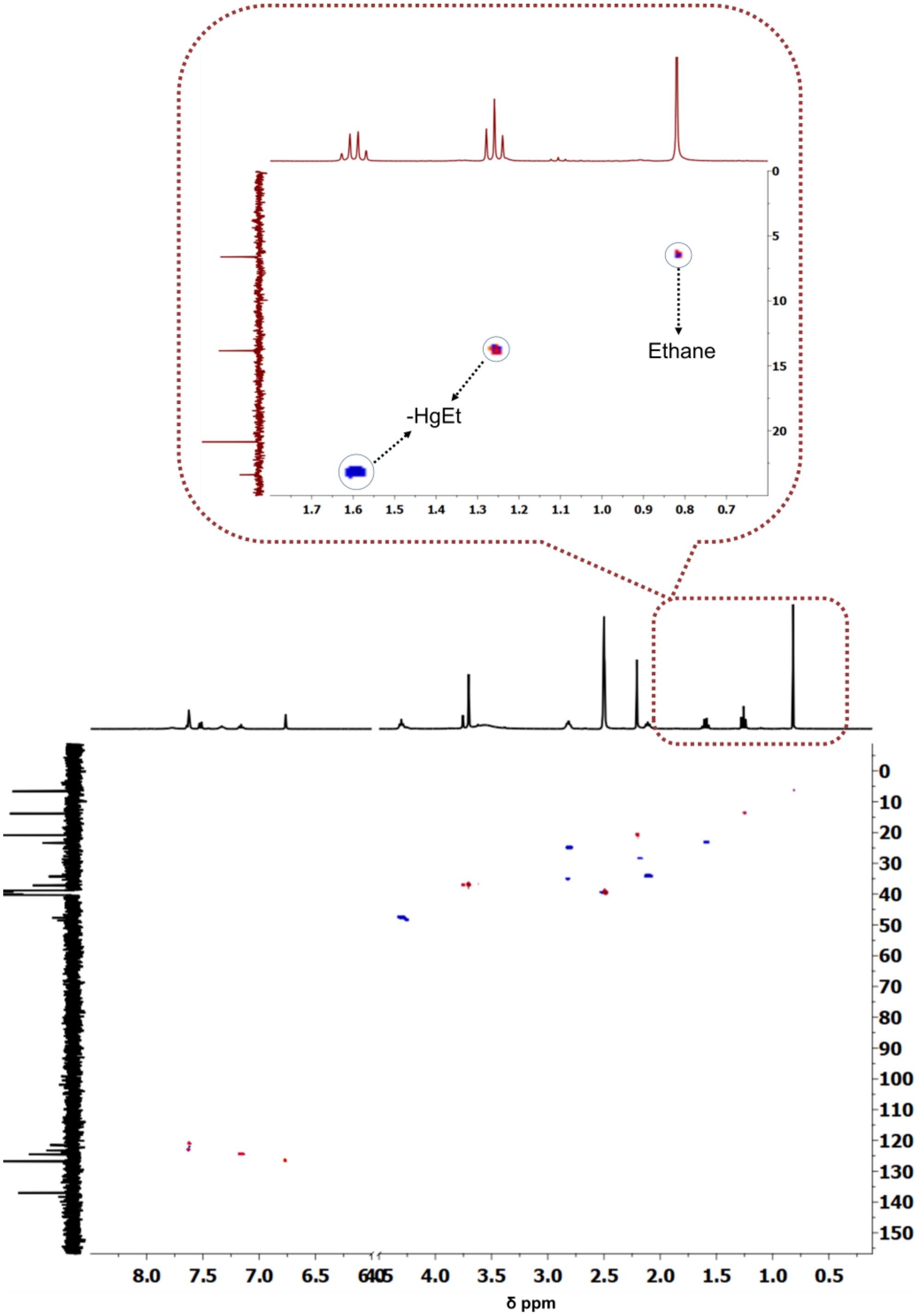


Figure S20: HSQC spectrum of ethane formation by treatment of thimerosal and **1** in DMSO-*d*₆.

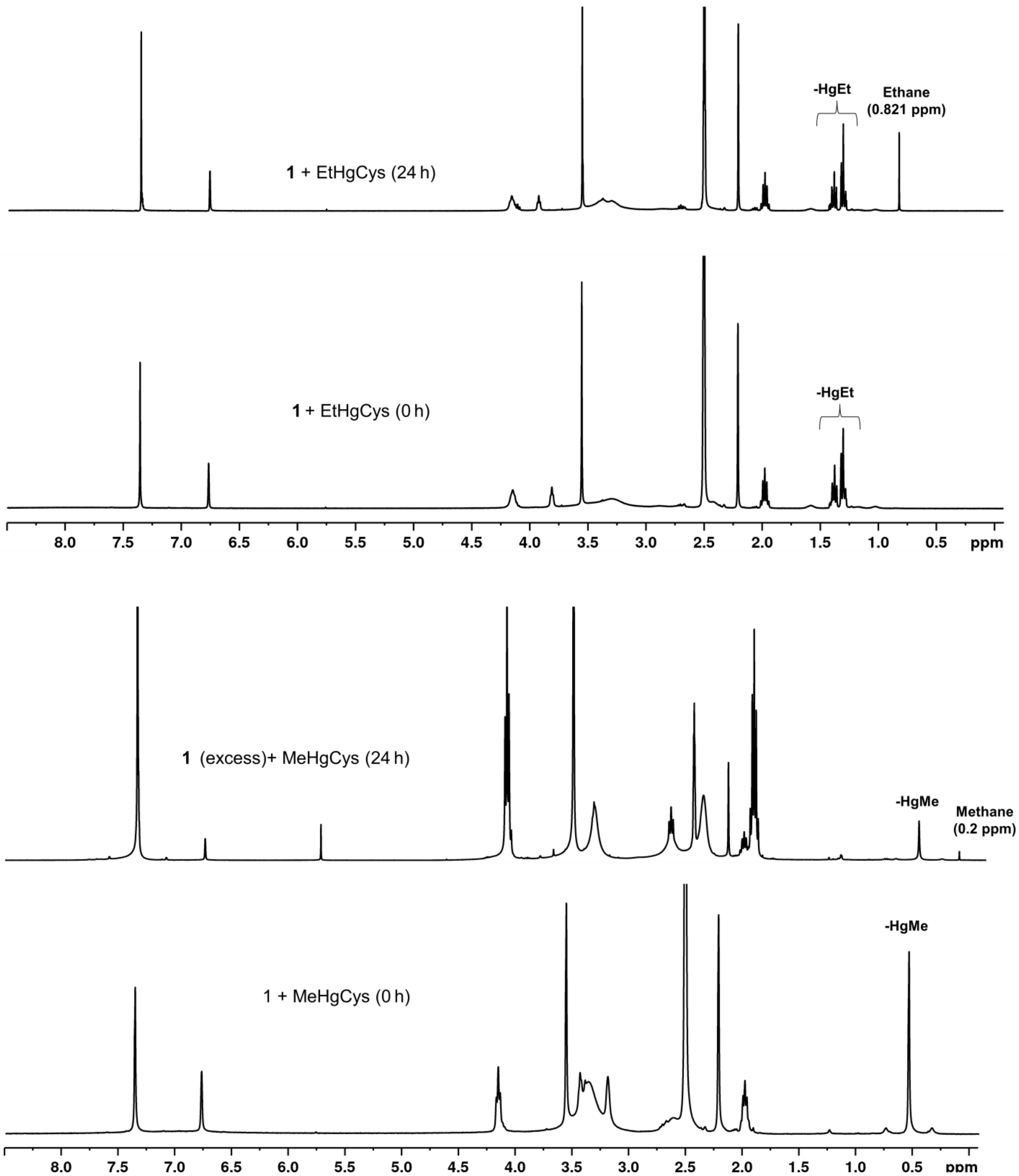


Figure S21: ^{1}H NMR stack spectra showing the degradation of MeHgCys, EtHgCys and corresponding formation of methane, ethane by treatment of **1** at 21 °C in DMSO-d_6. ([MeHgCys] = [EtHgCys] = [**1**] = 25 mM).

Solvent assisted Hg–C bond Cleavage:

In order to investigate the solvent assistance in protolytic cleavage of Hg–C bond in RHgX, we have performed a reaction of **1** (or **2**) with MeHgI in 1:1 ratio at 21°C in different protic solvents namely D_2O, Methanol-d_4 and Acetic acid- d_4. Formation of CH_3D in the 1:1 solution of MeHgI/**2** (25 mM) in DMSO-d_6 and in the mixture of DMSO-d_6 /MeOH-d_4 solvents was observed in NMR tube.[15] Total volume of NMR solution was maintained 0.6 mL for all experiments. Separate experiments were performed for comparison purpose using different solvent ratio like DMSO-d_6 : H_2O-d_2 = 5:1, 9.2 mM of D_2O, DMSO-d_6 : MeOH-d_4 = 5:1, 5.2 mM of MeOH-d_4, DMSO-d_6 : AcOD-d_4 = 5:1, 2.8 mM of AcOH-d_4, and DMSO-d_6 : MeOH-d_4 : AcOD-d_4 = 4:1:1.

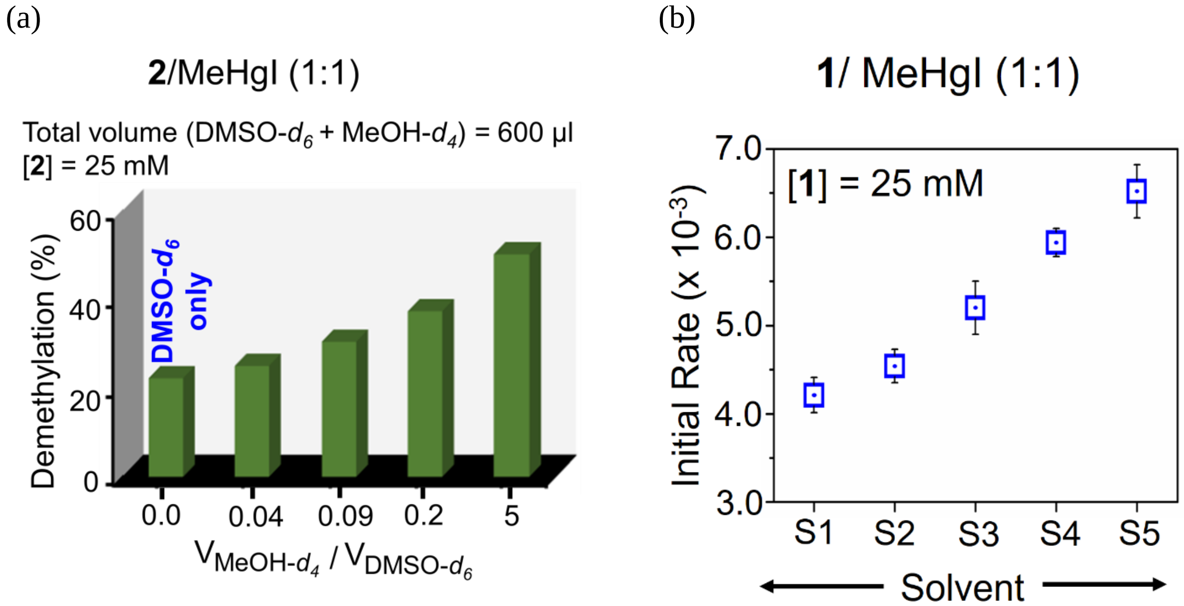


Figure S22: (a) Percentage of demethylation of MeHgI (25 mM) by **2** (in 1:1 molar ratio) in DMSO-d_6 and in the mixture of DMSO-d_6 /MeOH-d_4 solvents. (b) Protonolysis rates of MeHgI by 1 at 21 °C in DMSO-d_6 (S1) and in other solvent mixture, S2 (DMSO-d_6 : H_2O-d_2 = 5:1; [H_2O-d_2] = 5.5 mM), S3 (DMSO-d_6 : MeOH-d_4 = 5:1; [MeOH-d_4] = 3.1 mM), S4 (DMSO-d_6 : AcOH-d_4 = 5:1; [AcOH-d_4] = 1.7 mM), S5 (DMSO-d_6 : MeOH-d_4 : AcOH-d_4 = 4:1:1).

The Hg─C bond protonolysis of MeHgI by **2** rate increases with addition of protic solvent into the reaction solution of DMSO-d_6, in the NMR tube (Figures S22-S27).[16] The protonolysis rate also increases with decreasing the pK_a value of the protic solvent added into the reaction mixture (Initial rates ($M.h^{-1}$): $4.21 \pm 0.21 \times 10^{-3}$ in DMSO-d_6 only; $4.54 \pm 0.19 \times 10^{-3}$ in H_2O-d_2/DMSO-d_6; $5.20 \pm 0.20 \times 10^{-3}$ in MeOH-d_4/DMSO-d_6; $5.94 \pm 0.16 \times 10^{-3}$ in AcOH-d_4/DMSO-d_6). A significant increase of rate ($6.52 \pm 0.3 \times 10^{-3}$ $M.h^{-1}$) is also observed when the reaction is performed in a mixture of protic solvents, AcOH-d 4 and MeOH-d 4 (Figure 6b/Figure S22b).

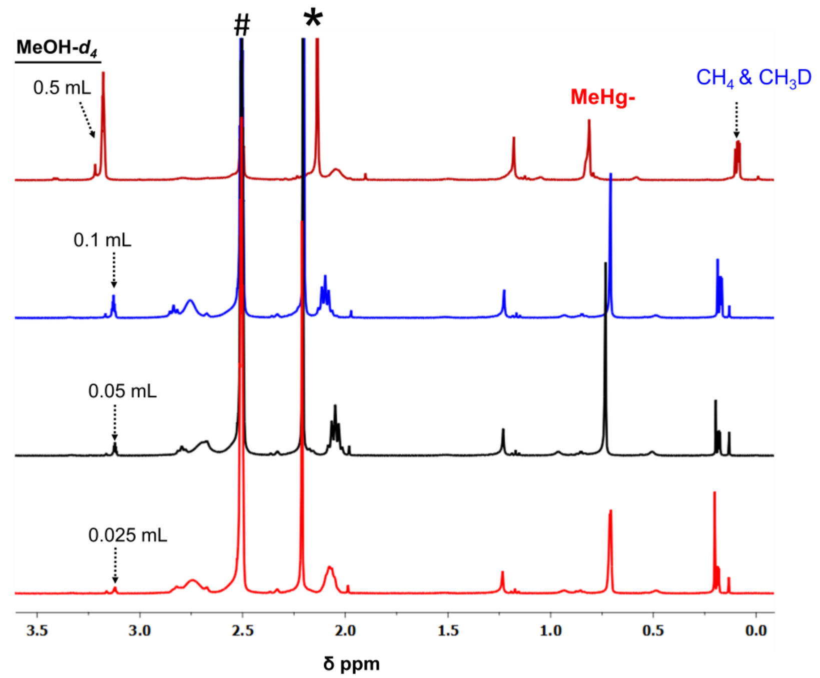


Figure S23: ^{1}H NMR stack spectra showing the cleavage of Hg–C bond of MeHgI and formation of CH_3D induced by **2**,[15] in 1:1 molar ratio, at 21 °C in mixed solvent system of DMSO-d_6 and MeOH-d_4 upto 0.6 mL of total volume. (* = DMSO-d_6, # = mesitylene, external standard and [MeHgI] = [**2**] = 25 mM).

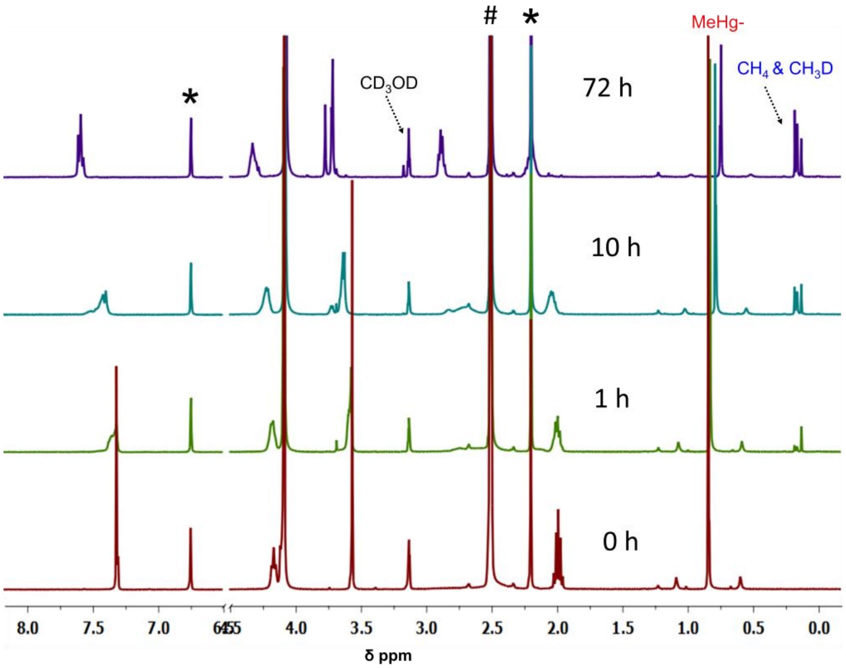


Figure S24: ^{1}H NMR stack spectra showing protolytic cleavage of MeHgI induced by **1** (1:1 molar ratio; 25 mM) in DMSO-d_6 : MeOH-d_4 = 5:1, 5.2 mM of MeOH-d_4 at 21 °C. (* = DMSO-d_6, # = mesitylene, external standard).

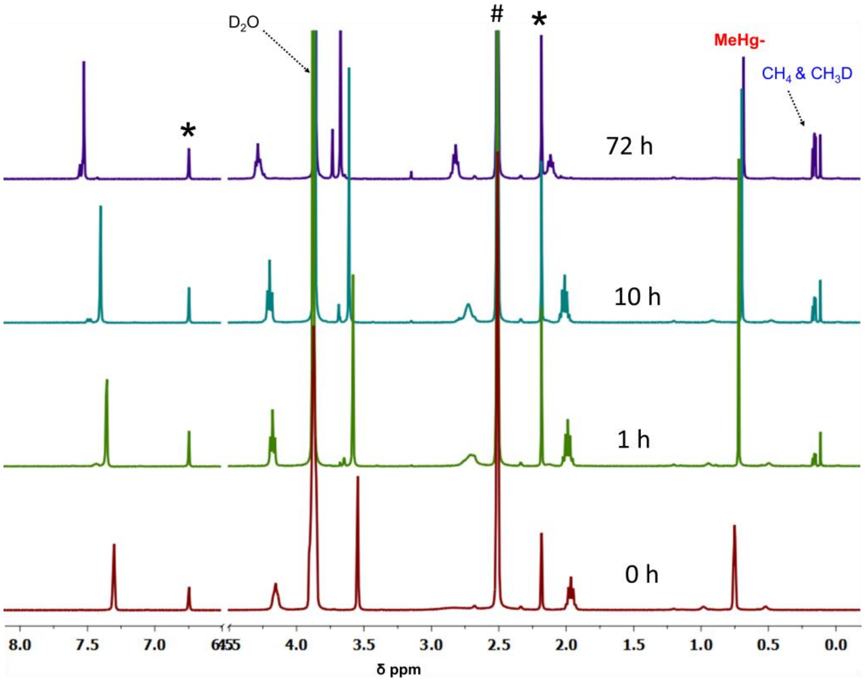


Figure S25: ^{1}H NMR stack spectra showing protolytic cleavage of MeHgI induced by **1** (1:1 molar ratio; 25 mM) in DMSO-*d*$_6$: H$_2$O-*d*$_2$ = 5:1, 9.2 mM of D$_2$O at 21 °C. (* = DMSO-*d*$_6$, # = mesitylene, external standard).

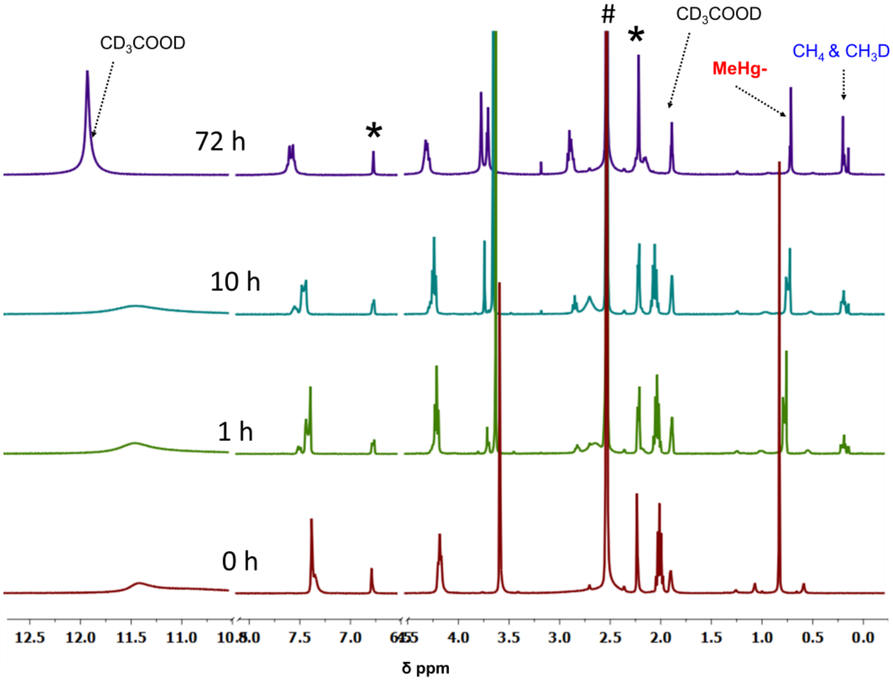


Figure S26: ^{1}H NMR stack spectra showing protolytic cleavage of MeHgI induced by **1** (1:1 molar ratio; 25 mM) in DMSO-*d*$_6$: AcOD-*d*$_4$ = 5:1, 2.8 mM of AcOH-*d*$_4$ at 21 °C. (* = DMSO-*d*$_6$, # = mesitylene, external standard).

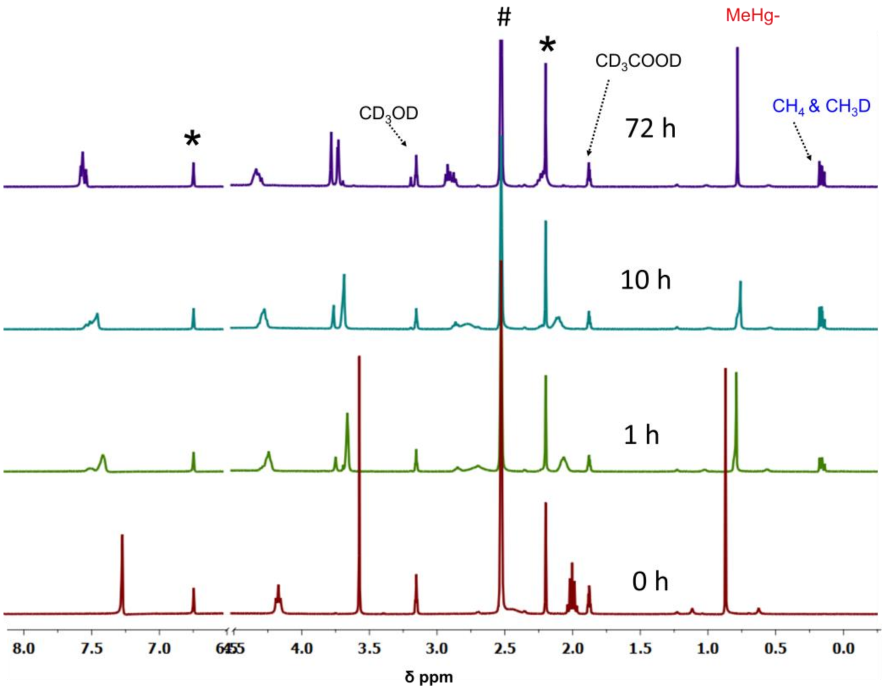


Figure S27: ^{1}H NMR stack spectra showing protolytic cleavage of MeHgI induced by **1** (1:1 molar ratio; 25 mM) in DMSO-d_6 : MeOH-d_4 : AcOD-d_4 = 4:1:1 at 21 °C. (* = DMSO-d_6, # = mesitylene, external standard).

3. HRMS Analyses:

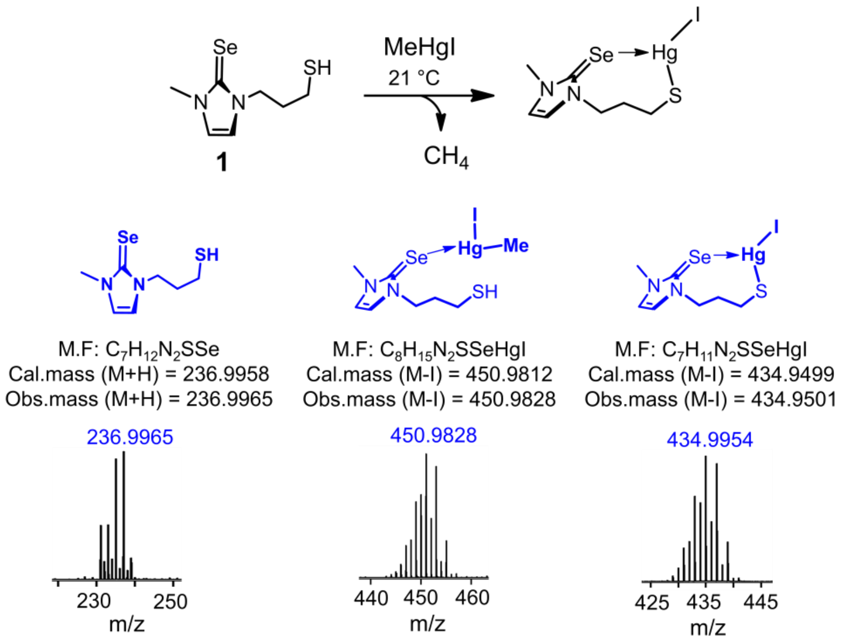


Figure S28: Mass spectra of products obtained over the course of the reactions between **1** (25 μM) and MeHgI, in 1:1 molar ratio, at 21 °C.

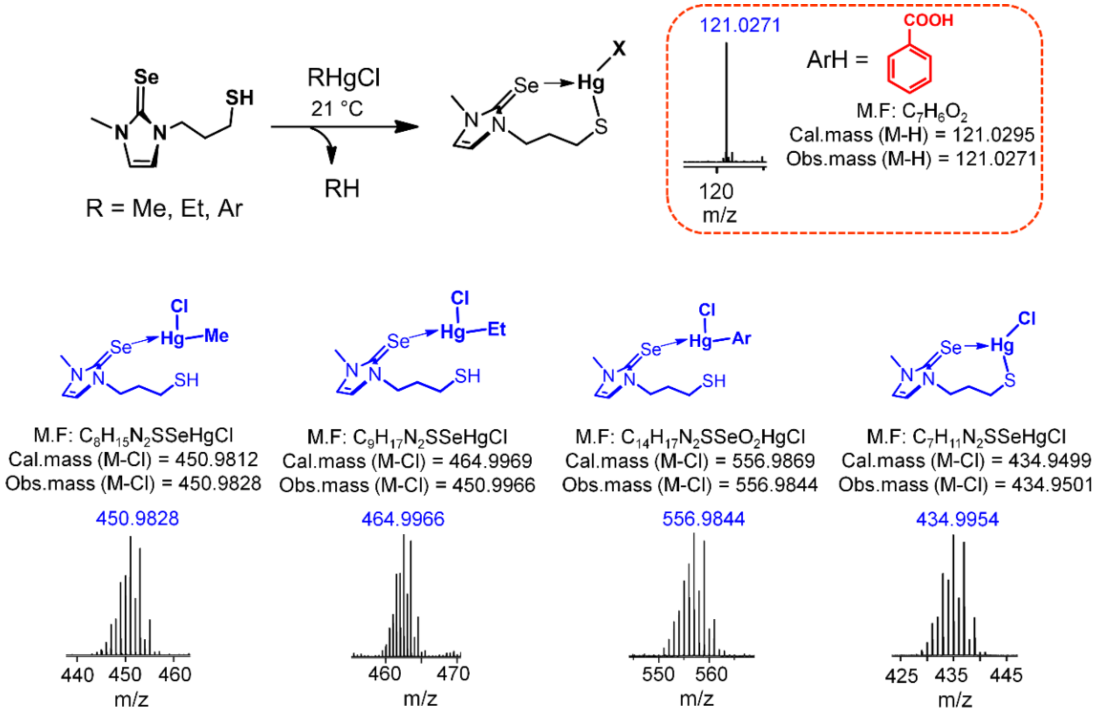


Figure S29: Mass spectra of products obtained during the course of the reactions between **1** (25 μM) and RHgCl (where R = Me, Et or Ar), in 1:1 molar ratio, at 21 °C.

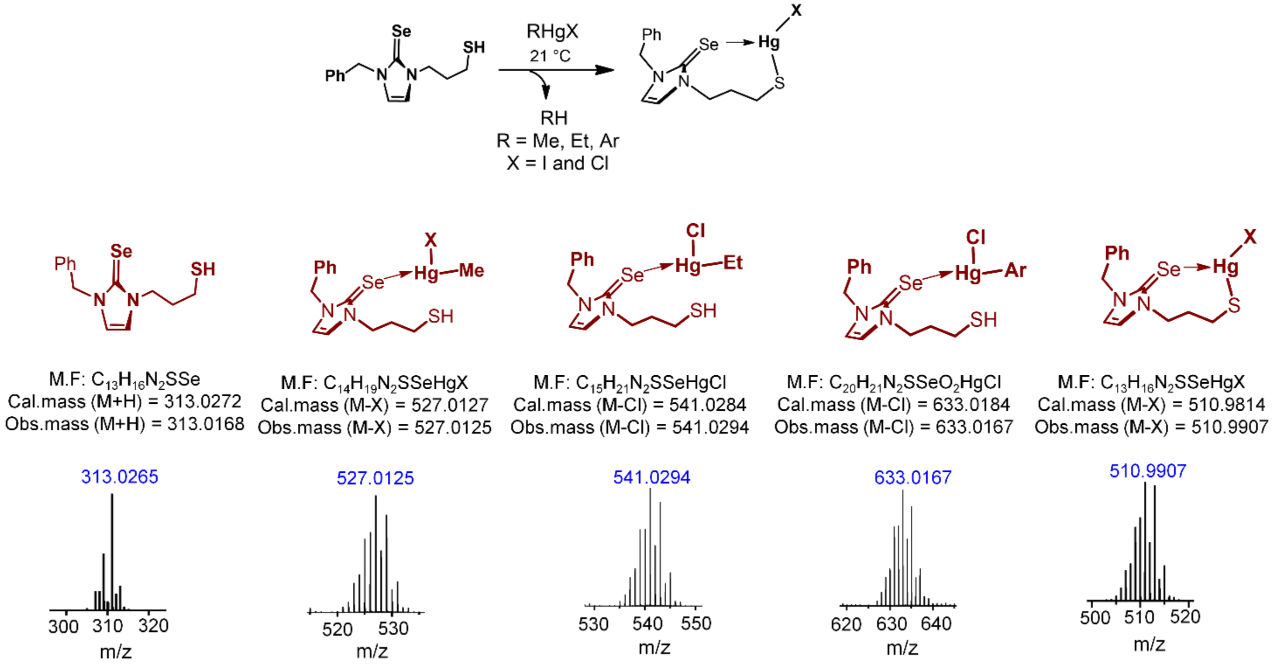


Figure S30: Mass spectra of products obtained over the course of the reactions between **2** (25 μM) and RHgX (where R = Me, Et or Ar; X = Cl or I), in 1:1 molar ratio, at 21 °C.

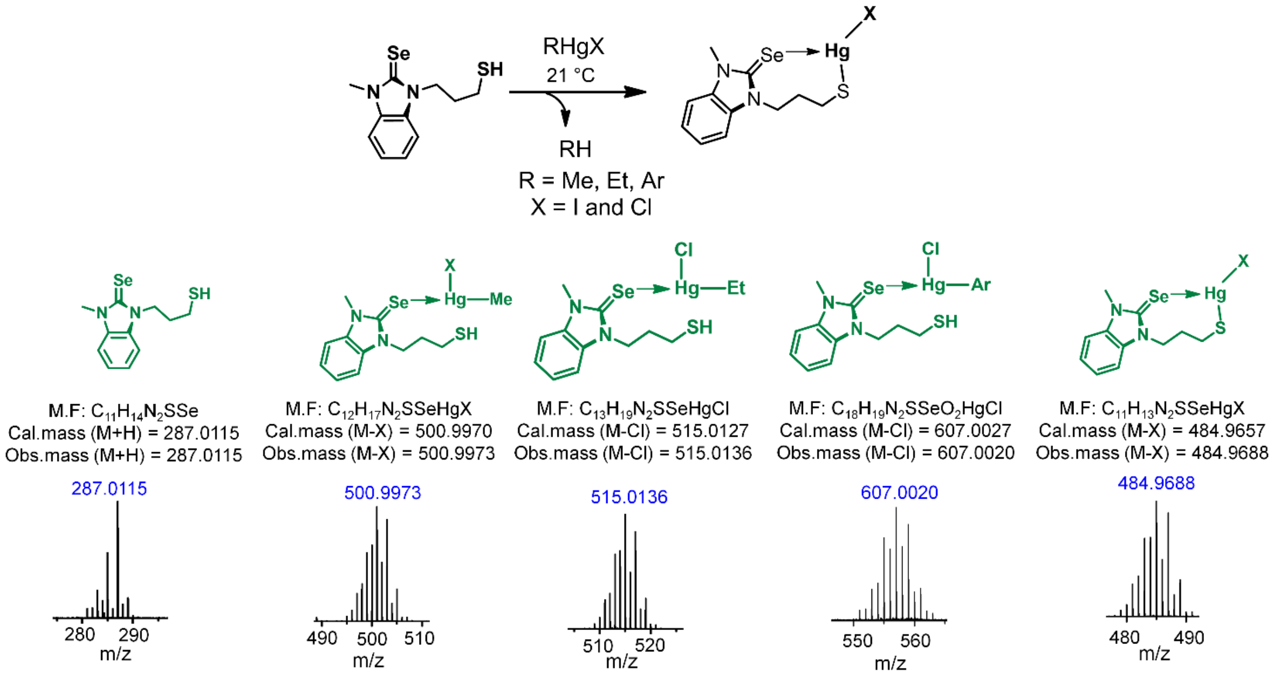


Figure S31: Mass spectra of products obtained over the course of the reactions between **3** (25 µM) and RHgX (where R = Me, Et or Ar; X = Cl or I), in 1:1 molar ratio, at 21 °C.

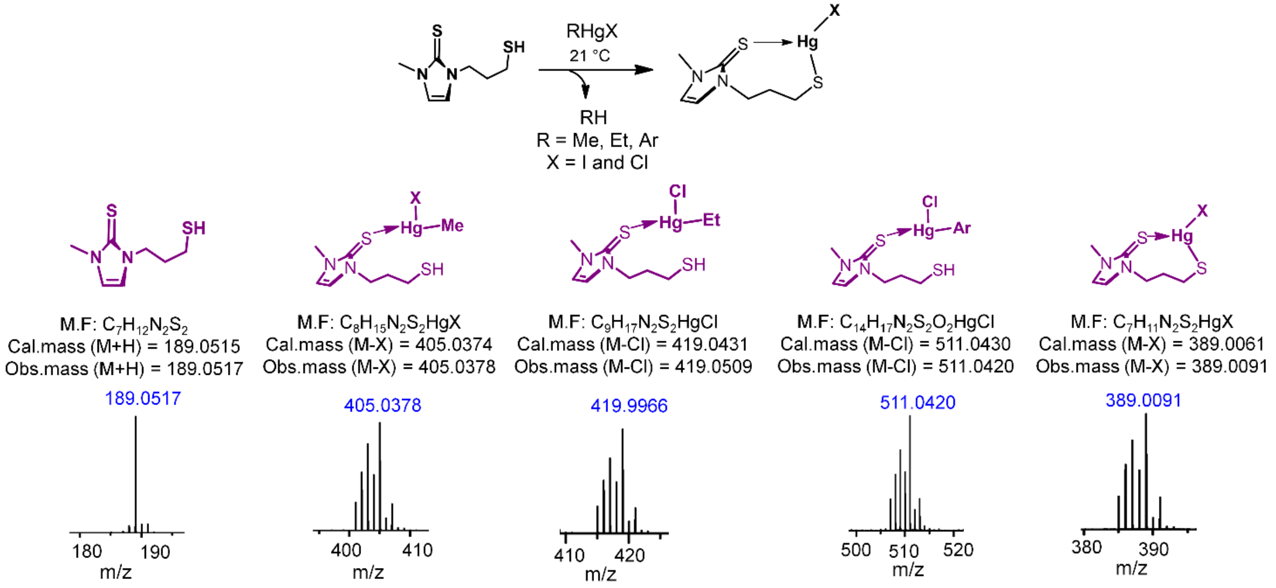


Figure S32: Mass spectra of products obtained over the course of the reaction of **6** (25 µM) and RHgX (where R = Me, Et or Ar; X = Cl or I), in 1:1 molar ratio, at 21 °C.

4. SXRD Analysis:

Single crystal data collections and corrections with D8 Venture Bruker AXS single crystal X-ray diffractometer equipped with CMOS PHOTON 100 detector having monochromatised microfocus sources (Mo-Kα = 0.71073 Å). Single crystals of compounds **10** (CCDC1921791), **14** (CCDC1921792), **2** (CCDC1921788), **3** (CCDC1921787), **12** (CCDC1921793), [**4**.MeHgI] (CCDC1921789), [**5**.MeHgI] (CCDC 1921790) suitable for X-ray diffraction study were obtained from slow evaporation process as described in the experimental section. The structure solution and refinement were performed by using SHELX program implemented in APEX3.[17-20] The non-H atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters. All the hydrogen atoms were placed at the hybridized positions and refined using a riding model with appropriate HFIX commands. The molecular structures were drawn by ORTEP.[21]

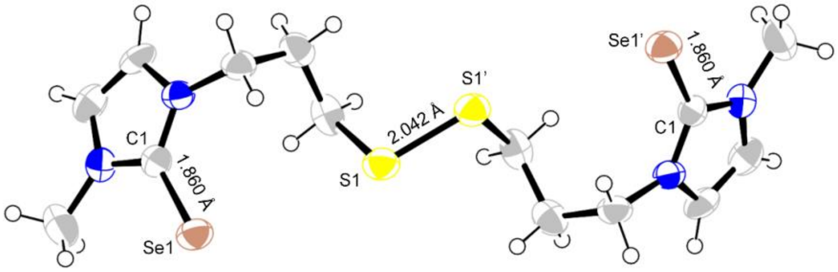


Figure S33: ORTEP diagram of **10**.

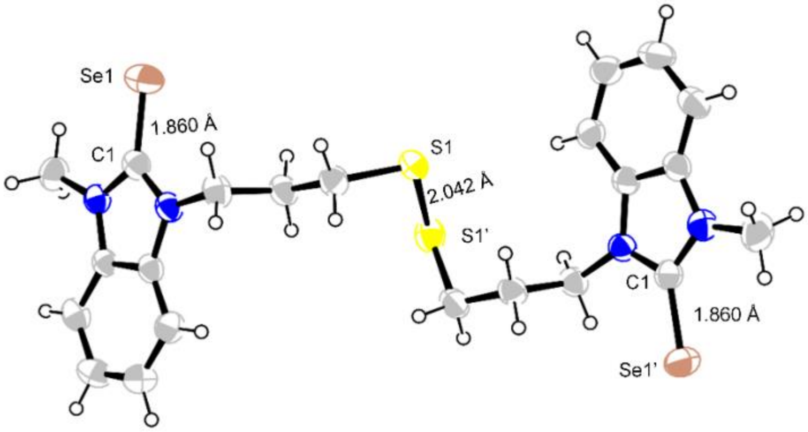


Figure S34: ORTEP diagram of **14**.

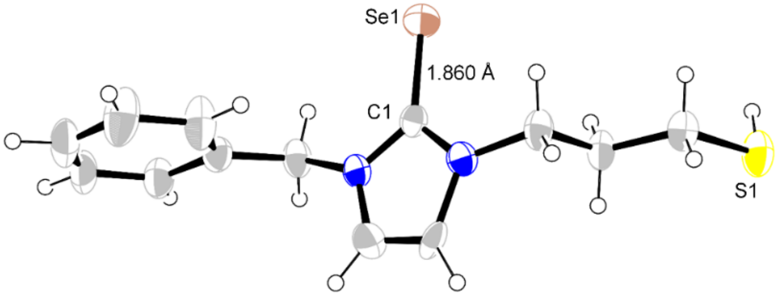


Figure S35: ORTEP diagram of **2**.

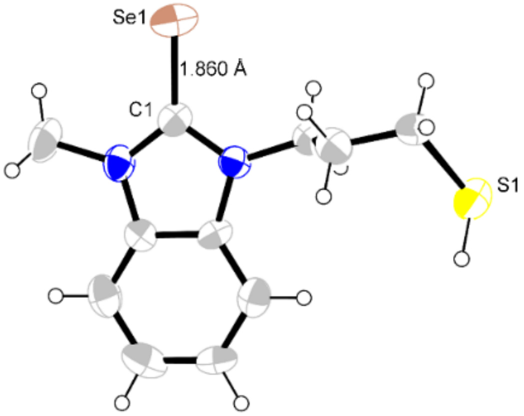


Figure S36: ORTEP diagram of **3**.

Table S1: Crystallographic data for **10**, **14**, **2** and **3**.

	10	**14**	**2**	**3**
CCDC No	1921791	1921792	1921788	1921787
Lattice	Orthorambic	Triclinic	Monoclinic	Orthorambic
Formula	$C_{14}H_{24}N_4S_2O_2Se_2$	$C_{22}H_{26}N_4S_2Se_2$	$C_{13}H_{16}N_4SSe$	$C_{11}H_{14}N_2SSe$
Formula Weight	502.41	568.51	311.30	284.25
Space Group	*P b c n*	*P 1*	*C 2*	$P\,n\,a\,2_1$
a/ A°	34.650(4)	10.3331(9)	19.541(5)	7.3132(5)
b/ A°	4.9196(5)	11.4023(10)	7.5110(18)	15.406(1)
c/ A°	12.0074(14)	12.0379(9)	20.264(5)	10.7773(6)
α/ °	90	64.466(3)	90	90
β/ °	90	79.758(3)	113.102(7)	90
γ/ °	90	68.943(3)	90	90
V/ $A^{\circ 3}$	2046.8(4)	1193.89(18)	2735.7(12)	1214.25(13)
Z	4	2	8	4
Radiation (λ)/A°	0.71073	0.71073	0.71073	0.71073
ρ/ (g cm^{-3})	1.630	1.582	1.512	1.560
μ (Mo K_α) mm^{-1}	3.831	3.289	2.878	3.234
θ_{max}/deg	25.021	25.681	25.679	25.674
Collected reflections	14197	28786	12857	6790
Unique reflections	1804	4518	5184	2289
No of paramaters	114	273	303	138
R_1 [I> 2σI]	0.0556	0.0356	0.0710	0.0592
wR_2 [I> 2σI]	0.1461	0.0868	0.1738	0.1554
R_1 [all data]	0.0559	0.0485	0.1135	0.0691
wR_2 [all data]	0.1362	0.0938	0.2022	0.1622
R_{int} [all data]	0.0648	0.0338	0.0791	0.0219
GOF	1.141	1.034	1.066	1.112

Table S2: Crystallographic data for **12**, [**4**.MeHgI], [**5**.MeHgI].

	12	**4**.MeHgI	**5**.MeHgI
CCDC No	1921793	1921789	1921790
Lattice	Monoclinic	Monoclinic	Monoclinic
Formula	$C_{32}H_{50}HgN_8O_{11}\ Se_4$	$C_6H_{11}HgIN_2Se$	$C_{10}H_{13}HgIN_2Se$
Formula Weight	1239.23	517.62	567.67
Space Group	*C c*	$P\ 2_1/n$	$P\ 2_1/c$
a/ A$^{\circ}$	23.3194(7)	8.9682(5)	8.4028(3)
b/ A$^{\circ}$	14.8183(3)	10.5369(5)	18.7925(6)
c/ A$^{\circ}$	16.3857(4)	11.8452(6)	8.9951(3)
α/ °	90	90	90
β/ °	129.828(1)	91.293(2)	104.092(1)
γ/ °	90	90	90
V/ A$^{\circ 3}$	4348.4(2)	1119.05(10)	1377.67(8)
Z	4	4	4
Radiation (λ)/A$^{\circ}$	0.71073	0.71073	0.71073
ρ/ (g cm^{-3})	1.893	3.072	2.737
μ (Mo K$_{\alpha}$) mm^{-1}	6.950	19.715	16.028
θ$_{max}$/deg	25.681	25.679	26.369
Collected reflections	27813	15180	18642
Unique reflections	8243	2129	2814
No of paramaters	515	103	140
R$_1$ [I> 2σI]	0.0279	0.0353	0.0300
wR$_2$ [I> 2σI]	0.0622	0.0922	0.0638
R$_1$ [all data]	0.0316	0.0376	0.0356
wR$_2$ [all data]	0.0638	0.0946	0.0664
R$_{int}$ [all data]	0.0308	0.0717	0.0368
GOF	1.050	1.084	1.045

5. Computational Details:

All the calculations are performed by using M06-2X level of theory as implemented in the Gaussians 09 package.[22] For geometry optimizations, 6-311++G (2d, p) basis set was used for all atoms except Hg and I. The Stuttgart-Dresden basis set (SDD) was used for Hg and I to treat the (scalar) relativistic effects of the heavier atom and the SDD basis set for the Hg atom was used with the corresponding relativistic effective core potential.[23] Frequency calculations of all the optimized structures were performed to ensure that the optimized structures were the local energy minima without any imaginary frequency, and to obtain zero-point corrections and the Gibbs free energies. Transition states were obtained using Berny optimization algorithm implemented in Gaussian 03 and were in each case verified the presence of a single imaginary vibrational frequency associated with the desired reaction coordinate, and also confirm the nature of transition states to be the transfer of -SH proton to -HgMe carbon. Whereas natural bond orbital calculations was performed in 6-311++G (2d,p) using self-consistent reaction field (SCRF) with SMD model and water as solvent system.[24] The NBO Version 3.1 program implemented in Gaussian 03 was used to perform NPA.[25] All the HOMO and LUMO visualisation files were generated from FCHK file by the help of chemcraft software. The NBO Version 3.1 program implemented in Gaussian 03 was used to perform NPA.[26] Frequency calculations were performed at the optimization level of basis set to confirm the nature of stationary points, and to obtain zero-point corrections and the Gibbs free energies

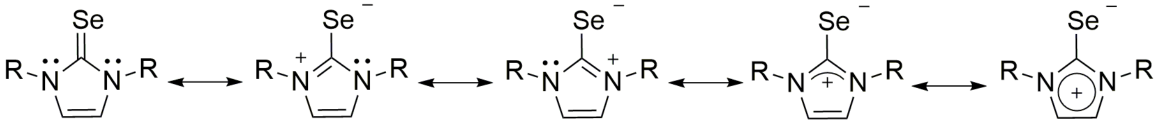
The reaction free energies (ΔG) (the Gibbs free energies i.e., the term of the sum of electronic and thermal free energies) are calculated using the following equation.

$$\Delta G = \mathbf{G_{product}} - \mathbf{G_{reactant}}$$

Similarly, transition state energy calculated as follows

$$\Delta G^{\ddagger} = \mathbf{G_{transition\ state}} - \mathbf{G_{reactant}}$$

Where $G_{product}$ and $G_{reactant}$ are the total energies of products and reactants respectively



Scheme S5. Resonance structures (canonical forms) of *N,N'*–disubstituted imidazole-based selones.[27]

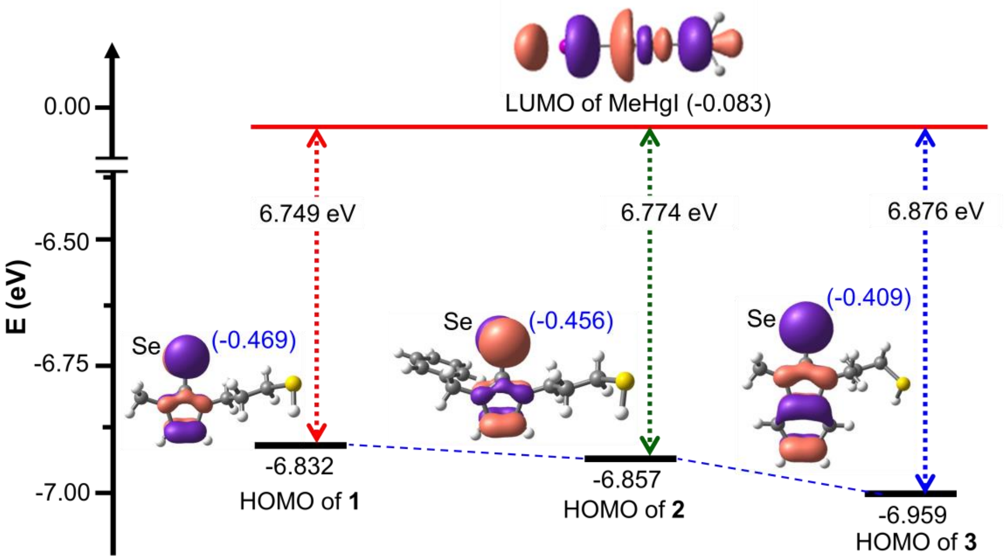


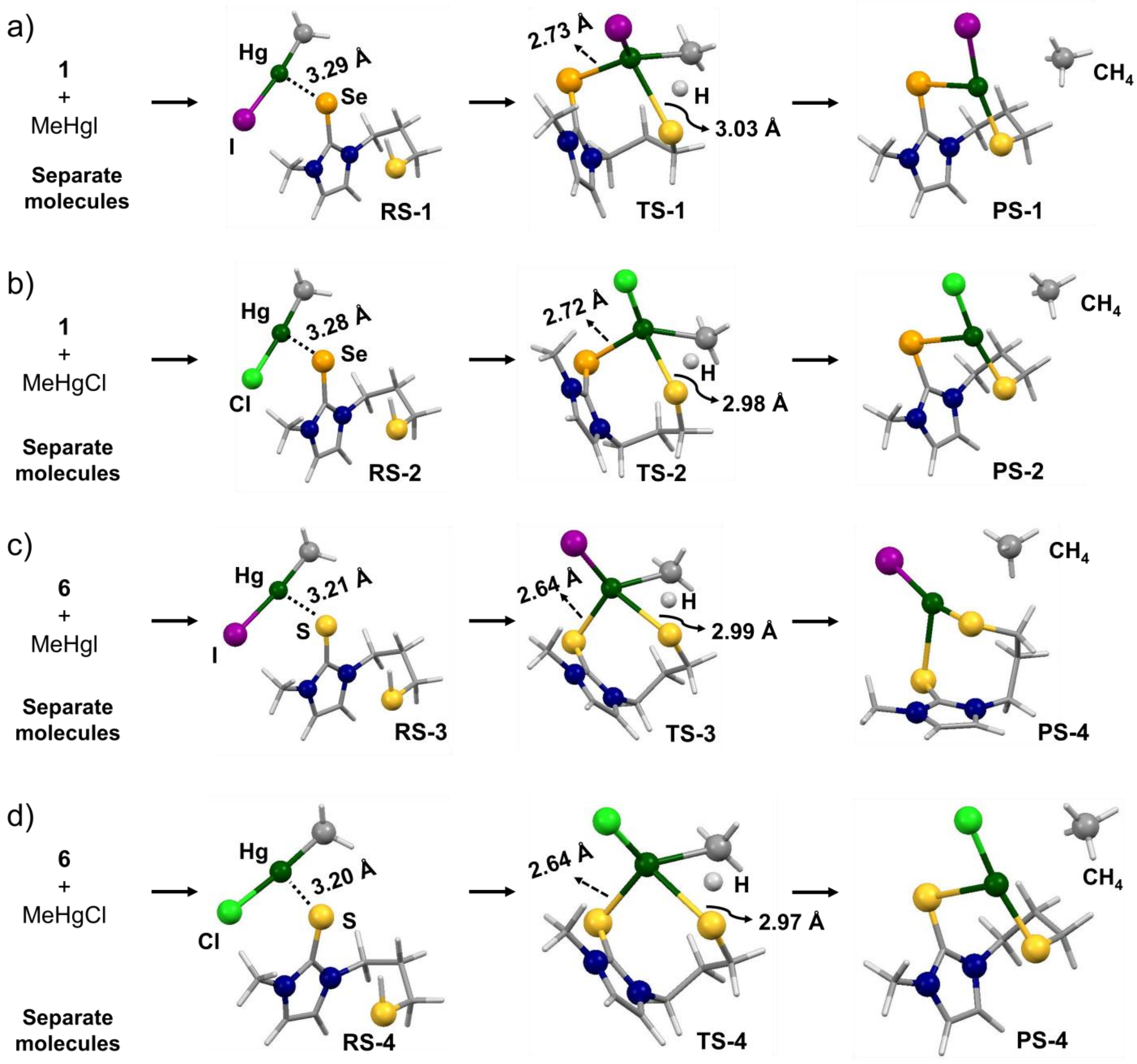
Figure S37: Representation of HOMO-LUMO energy gap between HOMO states of **1**, **2**, or **3** and LUMO of MeHgI.

To understand the protonolysis reactivity of these three selones (**1**, **2**, and **3**) the structures optimization and the Natural Population Analysis (NPA) were performed to compute atomic partial charges, which clearly showed that these selones mostly exist in zwitterionic form with large negative charge on the selenium center and positive charge on the five-membered heterocycle. Interestingly, the Se center of imidazole-based selones **1**(-0.469) and **2** (-0.456) carry more negative charge compared to the Se center of benzimidazole-based selone **3** (-0.409), (Table S3). The HOMO/LUMO analysis of the optimized geometry of selones and MeHgI revealed that the HOMO of **1** is located relatively higher in energy than the HOMO of **2** or **3** in the order of E(**1**) > E(**2**) > E(**3**), (Figure S37). As a result, the energy gap between HOMO of **1** and LUMO of MeHgI is lowest among these three selones.

Table S3: The C–Se bond lengths, bond orders and charge on the Se-atoms of ligands.

Compds.	C–Sebond length (Å) (Calc.) ^{a}	C–Se bond order (Calc.)^{a}	Charge on Se (au)^{a}
1	1.86	1.196	-0.469
2	1.86	1.205	-0.456
3	1.85	1.255	-0.409

^{a}Optimization and NBO analysis were performed at M06-2X /6-311++G(2d,p) level of theory using self-consistent reaction field (SCRF) with SMD model and water as solvent system.



Scheme S6: Reaction pathways of protonolysis of MeHgX (X = I or Cl) by compound **1** or **6**.

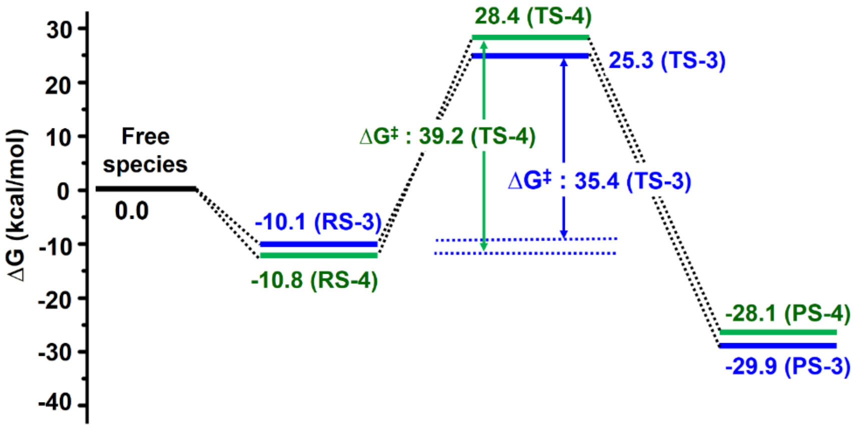


Figure S38: The total energy profile of the reactions between **6** and MeHgX (X = Cl or I). All energies are in kcal mol^{-1}, relative to the starting materials (sum of free species energies). All energies are in kcal mol^{-1}, relative to the free molecules. RS = reactant states; PS = product states; TS = transition states. RS-3, TS-3, and PS-3 correspond to the reaction of **6** and MeHgI. RS-4, TS-4, and PS-4 correspond to the reaction of **6** and MeHgCl.

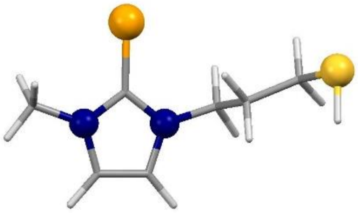
Table S4: Calculated Gibbs free energies and the corresponding K values of for proteolytic cleavage of MeHgX (X = I or Cl) by **1** or **6** at at 298.15 K (in kcal/mol).

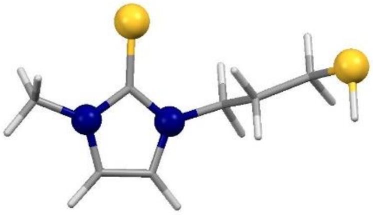
Reactions	ΔG (kcal/mol)	Formation constants
[**1**•••MeHgI] (RS-1) ⟶ **1**.HgI•••CH_4 (PS-1)	-30.77	3.6916 x 10^{22}
[**1**•••MeHgCl] (RS-2) → **1**.HgCl•••CH_4 (PS-2)	-28.90	1.5694 x 10^{21}
[**6**•••MeHgI] (RS-3) → **6**.HgI•••CH_4 (PS-3)	-29.86	7.9398 x 10^{21}
[**6**•••MeHgCl] (RS-4) → **6**.HgCl•••CH_4 (PS-4)	-28.06	3.7989 x 10^{20}

Table S5: Calculated Gibbs free energies of the transition states and the corresponding K values for proteolytic cleavage of MeHgX (X = I or Cl) by **1** or **6** at 298.15 K (in kcal/mol).

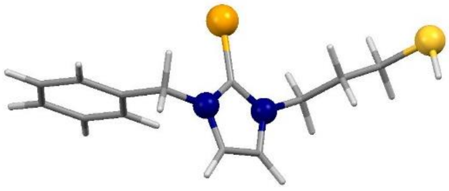
Reactions	$\Delta G^{\ddagger}$ (kcal/mol)	Formation constants
[**1**•••MeHgI] (RS-1) → [**1**.MeHgI]‡ (TS-1)	34.27	7.3645 x 10^{-26}
[**1**•••MeHgCl] (RS-2) → [**1**.MeHgCl]‡ (TS-2)	38.07	1.2091x 10^{-28}
[**6**•••MeHgI] (RS-3) → [**6**.MeHgI]‡ (TS-3)	35.44	1.0117 x 10^{-26}
[**6**•••MeHgCl] (RS-4) → [**6.**MeHgCl]‡ (TS-4)	39.23	1.6822 x 10^{-29}

Table S6: Optimized geometries and coordinates of compounds and complexes**.**

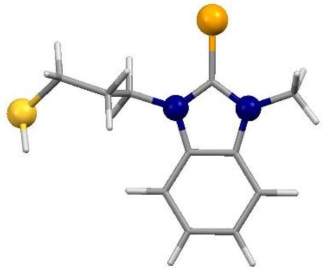
 **1**	34	-1.259247000	-1.712867000	0.146784000
	16	4.501923000	-0.203447000	-0.730209000
	1	4.494395000	1.035058000	-1.242232000
	7	-2.374806000	0.882690000	-0.372788000
	7	-0.440598000	1.027916000	0.572676000
	6	-2.091840000	2.226224000	-0.237644000
	1	-2.780777000	2.984813000	-0.566593000
	6	1.890069000	0.503987000	-0.021882000
	1	1.988942000	1.443102000	-0.573177000
	1	1.525474000	-0.256078000	-0.716551000
	6	3.233679000	0.087691000	0.548217000
	1	3.148155000	-0.864994000	1.073718000
	1	3.609756000	0.825484000	1.256332000
	6	0.875807000	0.688098000	1.099804000
	1	1.171318000	1.498184000	1.766346000
	1	0.774007000	-0.223879000	1.687512000
	6	-0.878219000	2.317345000	0.345976000
	1	-0.289792000	3.172717000	0.631241000
	6	-1.356104000	0.147657000	0.116250000
	6	-3.587318000	0.340218000	-0.964913000
	1	-4.218489000	1.174579000	-1.259311000
	1	-3.337016000	-0.258245000	-1.839250000
	1	-4.110938000	-0.279656000	-0.239393000

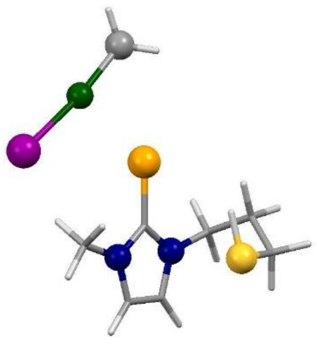
 **6**	16	-4.310433000	0.234983000	-0.681270000
	1	-4.281333000	-0.978148000	-1.244517000
	7	2.667615000	-0.253976000	-0.347681000
	7	0.734196000	-0.728903000	0.500098000
	6	2.553127000	-1.630262000	-0.340266000
	1	3.336993000	-2.271589000	-0.701580000
	6	-1.637495000	-0.337071000	-0.049925000
	1	-1.670350000	-1.208680000	-0.710339000
	1	-1.330376000	0.522321000	-0.648993000
	6	-3.008615000	-0.080725000	0.553539000
	1	-2.987104000	0.824404000	1.163312000

	1	-3.323787000	-0.901277000	1.199613000
	6	-0.600701000	-0.568545000	1.045693000
	1	-0.831234000	-1.464272000	1.626070000
	1	-0.569614000	0.287616000	1.721774000
	6	1.346776000	-1.926372000	0.184266000
	1	0.874807000	-2.875407000	0.367618000
	6	1.542655000	0.317802000	0.165710000
	6	3.796193000	0.517000000	-0.825819000
	1	4.563797000	-0.172404000	-1.170684000
	1	3.479571000	1.166721000	-1.641312000
	1	4.183015000	1.141024000	-0.020962000
	16	1.234889000	1.956197000	0.343389000

 **2**	34	0.119465000	-1.682580000	-0.108174000
	16	6.034797000	-0.320439000	-0.256477000
	1	6.068488000	0.896221000	-0.816372000
	7	-0.791621000	0.940996000	-0.875647000
	7	0.991600000	1.033965000	0.334429000
	6	-3.141013000	0.240509000	-0.526684000
	6	-0.482488000	2.277288000	-0.715050000
	1	-1.089504000	3.053443000	-1.148878000
	6	3.356776000	0.404906000	0.076017000
	1	3.545564000	1.314103000	-0.501748000
	1	3.070241000	-0.384436000	-0.622606000
	6	-4.352776000	-0.234825000	-1.026001000
	1	-4.448567000	-0.439057000	-2.087205000
	6	4.608572000	0.003759000	0.835734000
	1	4.450197000	-0.930783000	1.376227000
	1	4.889000000	0.766480000	1.561677000
	6	-3.020889000	0.499121000	0.833801000
	1	-2.085332000	0.864961000	1.242745000
	6	-4.101723000	0.286492000	1.685054000
	1	-3.996598000	0.490460000	2.743678000
	6	2.210185000	0.662003000	1.044890000
	1	2.447610000	1.483971000	1.719868000
	1	1.992473000	-0.223720000	1.641034000
	6	-5.429698000	-0.446410000	-0.177888000
	1	-6.366004000	-0.816037000	-0.578125000
	6	0.641548000	2.334402000	0.027656000
	1	1.225888000	3.171877000	0.368846000
	6	0.109464000	0.177139000	-0.219439000
	6	-5.306797000	-0.184887000	1.183508000
	1	-6.145710000	-0.350069000	1.848134000
	6	-2.008202000	0.459898000	-1.504675000
	1	-2.296517000	1.202975000	-2.248673000

	1	-1.777385000	-0.466736000	-2.030065000

 **3**	34	-0.842676000	-2.682039000	-0.124390000
	16	4.569833000	0.641420000	-0.246457000
	1	4.405837000	1.633053000	0.641169000
	7	-0.016405000	0.063309000	-0.312910000
	7	-2.154514000	-0.153138000	0.094338000
	6	-0.529939000	1.345434000	-0.196570000
	6	0.079615000	2.589696000	-0.288393000
	1	1.142380000	2.686833000	-0.472061000
	6	2.133222000	-0.279231000	0.830463000
	1	2.022382000	0.681212000	1.342154000
	1	1.671816000	-1.044435000	1.462316000
	6	-1.895816000	1.210205000	0.051821000
	6	1.395891000	-0.238411000	-0.499345000
	1	1.805567000	0.527261000	-1.157654000
	1	1.466303000	-1.197033000	-1.011934000
	6	-1.006637000	-0.837377000	-0.114544000
	6	3.605135000	-0.617337000	0.665448000
	1	3.727562000	-1.533941000	0.085686000
	1	4.074064000	-0.772315000	1.634705000
	6	-0.737701000	3.698160000	-0.128313000
	1	-0.305307000	4.688396000	-0.193209000
	6	-2.715701000	2.320130000	0.210133000
	1	-3.776281000	2.223306000	0.400504000
	6	-3.456779000	-0.765191000	0.300784000
	1	-3.731110000	-1.355761000	-0.571762000
	1	-4.187645000	0.024911000	0.447917000
	1	-3.432192000	-1.404498000	1.181457000
	6	-2.110887000	3.564577000	0.115176000
	1	-2.715711000	4.454502000	0.233335000

 **RS-1**	80	-2.069104000	0.958694000	0.030273000
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	7	2.050801000	-1.770623000	-0.718066000
	6	4.197518000	-1.653195000	-1.145317000
	1	5.239955000	-1.823572000	-1.347961000
	6	3.184688000	-2.520174000	-0.938896000
	1	3.168203000	-3.595081000	-0.929240000
	6	2.344140000	-0.454899000	-0.782933000
	6	0.724296000	-2.289713000	-0.434423000
	1	0.770438000	-3.376081000	-0.437218000
	1	0.020420000	-1.942917000	-1.188994000
	1	0.389173000	-1.931957000	0.538144000
	6	4.446043000	0.845969000	-1.097111000

	1	3.925917000	1.546720000	-1.751542000
	1	5.400822000	0.585631000	-1.557159000
	6	4.671616000	1.491969000	0.268482000
	1	5.386958000	2.304142000	0.108030000
	1	3.742639000	1.953761000	0.606420000
	6	5.222981000	0.575203000	1.356682000
	1	5.995579000	-0.089365000	0.961663000
	1	5.680905000	1.174545000	2.141354000
	16	3.991644000	-0.533903000	2.143968000
	6	-1.675356000	3.022858000	-0.081360000
	1	-1.197487000	3.220456000	-1.038095000
	1	-2.601785000	3.583958000	0.004201000
	1	-0.999290000	3.281695000	0.730209000
	1	2.975438000	0.340768000	2.127072000
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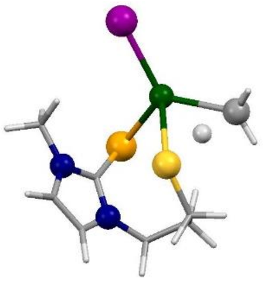 **TS-1**	80	-0.722002000	0.674819000	-0.404137000
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	34	1.021394000	-0.853739000	-1.849048000
	7	3.037116000	-0.876844000	0.213467000
	7	1.412903000	-2.221256000	0.668235000
	6	3.325187000	-1.463573000	1.423391000
	1	4.217204000	-1.223603000	1.973787000
	6	2.307607000	-2.303799000	1.709272000
	1	2.134473000	-2.941361000	2.557585000
	6	1.859239000	-1.336387000	-0.240308000
	6	0.122384000	-2.896769000	0.635554000
	1	-0.616076000	-2.298470000	1.169420000
	1	0.230305000	-3.872347000	1.104375000
	1	-0.191611000	-3.010148000	-0.398810000
	6	3.809474000	0.212617000	-0.384287000
	1	3.924766000	-0.002680000	-1.446082000
	1	4.793470000	0.170816000	0.084824000
	6	3.178505000	1.586971000	-0.178840000
	1	3.918753000	2.309222000	-0.538068000
	1	2.305630000	1.685586000	-0.824904000
	6	2.812821000	1.916390000	1.268845000
	1	3.581592000	1.538254000	1.949050000
	1	2.799518000	2.999462000	1.393406000
	16	1.190787000	1.296901000	1.870653000
	6	-0.303626000	3.078752000	-0.208573000
	1	-0.784763000	3.118508000	-1.192160000
	1	-0.946230000	3.605646000	0.494741000
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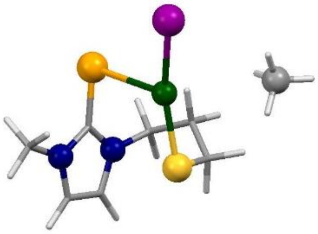 **PS-1**	80	-0.702108000	0.295013000	0.403252000
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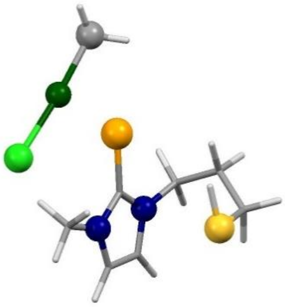
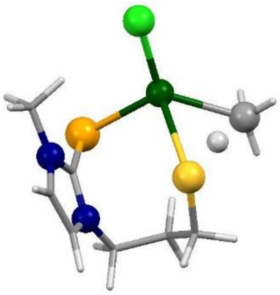
	34	1.037497000	-1.544691000	-1.277584000
	7	3.232566000	0.193077000	-0.563995000
	7	3.000162000	-1.456212000	0.804224000
	6	4.191570000	0.339549000	0.413759000
	1	4.881715000	1.164202000	0.416117000
	6	4.047853000	-0.694100000	1.269316000
	1	4.591356000	-0.951078000	2.160690000
	6	2.491936000	-0.907865000	-0.319648000
	6	2.469932000	-2.649458000	1.439555000
	1	1.443602000	-2.469492000	1.757670000
	1	3.093330000	-2.883843000	2.299025000
	1	2.475574000	-3.475985000	0.731578000
	6	2.985297000	1.155298000	-1.631594000
	1	2.892094000	0.600155000	-2.565622000
	1	3.880988000	1.775794000	-1.686733000
	6	1.749176000	2.029616000	-1.425618000
	1	1.814026000	2.821933000	-2.178604000
	1	0.857369000	1.450246000	-1.669393000
	6	1.605770000	2.684280000	-0.054865000
	1	2.562582000	3.106996000	0.266083000
	1	0.900533000	3.510654000	-0.130850000
	16	1.076279000	1.629140000	1.358233000
	6	-1.911332000	3.308575000	-0.672136000
	1	-2.198550000	4.306553000	-0.999414000
	1	-1.192098000	2.894929000	-1.381373000
	1	-2.789928000	2.666489000	-0.638081000
	1	-1.462165000	3.363660000	0.319801000

 **RS-2**	80	-2.595621000	-0.266401000	-0.101535000
	7	3.202019000	0.298235000	1.041726000
	7	1.785044000	1.823456000	0.475720000
	6	3.894580000	1.487951000	0.970423000
	1	4.948656000	1.547768000	1.175278000
	6	3.006825000	2.441699000	0.619246000
	1	3.133286000	3.497518000	0.460074000
	6	1.901312000	0.503162000	0.728292000
	6	0.541228000	2.466147000	0.086491000
	1	0.731306000	3.527231000	-0.056083000
	1	-0.212875000	2.320508000	0.857081000
	1	0.170663000	2.025464000	-0.837521000
	6	3.809510000	-1.005140000	1.268130000

	1	3.196400000	-1.537235000	1.996633000
	1	4.787161000	-0.812421000	1.713315000
	6	3.955840000	-1.853105000	0.006499000
	1	4.549116000	-2.727053000	0.292033000
	1	2.974551000	-2.223950000	-0.293026000
	6	4.637885000	-1.174325000	-1.178038000
	1	5.490986000	-0.572610000	-0.854280000
	1	5.017172000	-1.929297000	-1.864210000
	16	3.578460000	-0.024194000	-2.135381000
	6	-2.648135000	-2.334156000	0.168668000
	1	-2.329291000	-2.552343000	1.185473000
	1	-3.651867000	-2.715084000	0.000891000
	1	-1.953017000	-2.785012000	-0.536149000
	1	2.472614000	-0.781711000	-2.097907000
	34	0.558370000	-0.764768000	0.661122000
	17	-2.789342000	2.080840000	-0.468896000

 **TS-2**	80	1.308992000	0.228038000	0.142343000
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	7	-2.663083000	-0.202535000	0.006579000
	7	-1.584808000	-1.857548000	-0.862074000
	6	-3.247283000	-0.472150000	-1.208515000
	1	-4.074845000	0.104355000	-1.581559000
	6	-2.572505000	-1.508891000	-1.752316000
	1	-2.697317000	-2.016189000	-2.691909000
	6	-1.640447000	-1.048975000	0.209793000
	6	-0.601124000	-2.916893000	-1.062551000
	1	0.385462000	-2.485890000	-1.236502000
	1	-0.909545000	-3.498858000	-1.927384000
	1	-0.569408000	-3.547884000	-0.177290000
	6	-3.029064000	0.913265000	0.879846000
	1	-3.084259000	0.530510000	1.898626000
	1	-4.030980000	1.214653000	0.570780000
	6	-2.073705000	2.100427000	0.805638000
	1	-2.535807000	2.885952000	1.412920000
	1	-1.132187000	1.844978000	1.293241000
	6	-1.821195000	2.636570000	-0.602307000
	1	-2.752780000	2.643370000	-1.175464000
	1	-1.496583000	3.675238000	-0.532752000
	16	-0.561555000	1.753441000	-1.606919000
	6	1.700550000	2.624490000	0.375149000
	1	2.320905000	2.315404000	1.224290000
	1	2.359587000	3.086959000	-0.357388000
	1	0.994657000	3.357184000	0.771630000
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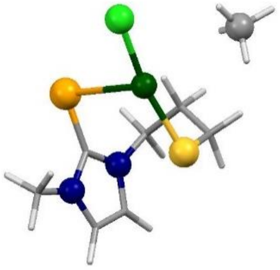 **PS-2**	80	-1.246785000	-0.147111000	0.400900000
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	7	2.818641000	-0.852714000	0.802819000
	6	3.465792000	1.203292000	0.413007000
	1	3.902736000	2.185872000	0.414321000
	6	3.613854000	0.170293000	1.268344000
	1	4.206356000	0.074144000	2.160380000
	6	2.177005000	-0.467104000	-0.321082000
	6	2.632937000	-2.143165000	1.441948000
	1	1.607532000	-2.230915000	1.799915000
	1	3.328529000	-2.214871000	2.274631000
	1	2.819795000	-2.937351000	0.722003000
	6	2.076461000	1.655277000	-1.627842000
	1	2.131112000	1.096275000	-2.562579000
	1	2.768125000	2.496985000	-1.687809000
	6	0.649551000	2.157998000	-1.411177000
	1	0.492065000	2.946356000	-2.154361000
	1	-0.051684000	1.360307000	-1.660741000
	6	0.338542000	2.733411000	-0.032770000
	1	1.145492000	3.396106000	0.293976000
	1	-0.565338000	3.337444000	-0.095988000
	16	0.124719000	1.557443000	1.368515000
	6	-3.241244000	2.319651000	-0.722323000
	1	-3.870962000	3.145976000	-1.048110000
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	1	-3.827657000	1.402303000	-0.690276000
	1	-2.843807000	2.535561000	0.269951000
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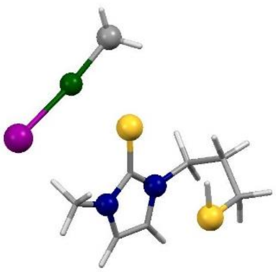 **RS-3**	80	1.931882000	1.012063000	0.030640000
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	7	-2.098528000	-1.705644000	0.714454000
	6	-4.214852000	-1.508736000	1.257372000
	1	-5.249815000	-1.641895000	1.517708000
	6	-3.246656000	-2.411836000	1.001045000
	1	-3.269926000	-3.486688000	0.997799000
	6	-2.338547000	-0.375486000	0.787909000
	6	-0.804439000	-2.265693000	0.374488000
	1	-0.897110000	-3.348191000	0.326636000
	1	-0.066500000	-1.987635000	1.125703000
	1	-0.475657000	-1.876469000	-0.588225000

	6	-4.365376000	1.003914000	1.196825000
	1	-3.785818000	1.687044000	1.819136000
	1	-5.311207000	0.794455000	1.699790000
	6	-4.615997000	1.643162000	-0.167381000
	1	-5.260638000	2.509260000	0.010846000
	1	-3.672707000	2.025369000	-0.560593000
	6	-5.288327000	0.744625000	-1.201620000
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	1	-5.764593000	1.352030000	-1.969183000
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	6	1.434329000	3.046876000	0.215242000
	1	1.008105000	3.197001000	1.204275000
	1	2.319134000	3.663075000	0.081864000
	1	0.690797000	3.277599000	-0.544227000
	1	-3.218576000	0.427866000	-2.337581000
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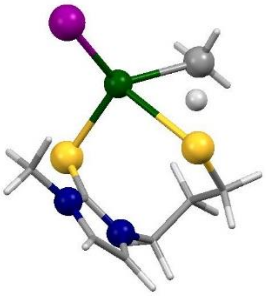 **TS-3**	80	0.602448000	-0.662029000	-0.348240000
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	7	-1.484101000	2.358911000	0.194737000
	6	-3.460232000	1.695285000	0.874034000
	1	-4.397180000	1.523641000	1.373226000
	6	-2.465383000	2.568760000	1.136714000
	1	-2.361813000	3.309809000	1.909069000
	6	-1.857412000	1.362839000	-0.633025000
	6	-0.210008000	3.062564000	0.152527000
	1	0.216055000	2.951631000	-0.841326000
	1	0.475369000	2.634254000	0.883531000
	1	-0.385604000	4.114345000	0.369411000
	6	-3.812309000	-0.175494000	-0.773053000
	1	-3.838590000	-0.063608000	-1.856613000
	1	-4.830155000	-0.081726000	-0.391663000
	6	-3.225449000	-1.530116000	-0.387838000
	1	-3.940409000	-2.276874000	-0.748070000
	1	-2.298379000	-1.696402000	-0.937472000
	6	-3.003226000	-1.724746000	1.112027000
	1	-3.824747000	-1.275336000	1.677348000
	1	-3.020967000	-2.790959000	1.339753000
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	1	0.862950000	-3.489565000	0.692903000
	1	-0.768913000	-3.610719000	-0.025641000
	1	0.586925000	-3.158639000	-1.021972000

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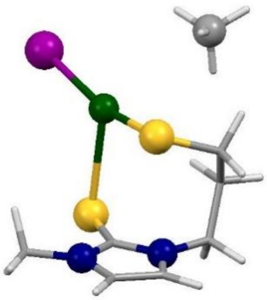 **PS-3**	80	-0.604777000	-0.179625000	-0.378414000
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	7	2.917585000	1.819579000	-0.336417000
	6	4.249396000	0.084410000	-0.197854000
	1	5.009302000	-0.668545000	-0.308980000
	6	4.042211000	1.232745000	-0.874485000
	1	4.587259000	1.680213000	-1.686141000
	6	2.422224000	1.049002000	0.660056000
	6	2.294164000	3.051328000	-0.781706000
	1	1.300853000	2.839507000	-1.177126000
	1	2.917887000	3.490567000	-1.556481000
	1	2.194561000	3.737758000	0.057127000
	6	3.047447000	-1.159794000	1.627715000
	1	2.905338000	-0.781571000	2.640836000
	1	3.976875000	-1.730676000	1.600791000
	6	1.868410000	-2.051416000	1.242810000
	1	1.950445000	-2.948194000	1.865874000
	1	0.939074000	-1.560762000	1.536616000
	6	1.803020000	-2.489662000	-0.217147000
	1	2.791718000	-2.806042000	-0.562738000
	1	1.144848000	-3.353528000	-0.298526000
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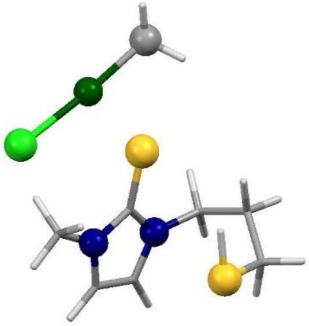	80	-2.473450000	-0.347060000	-0.027610000
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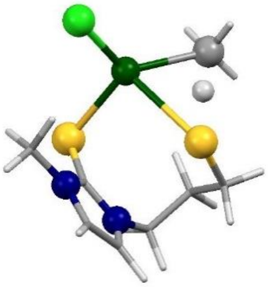
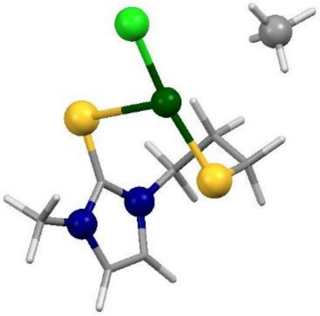
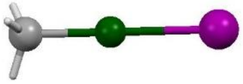
	7	1.780444000	1.820128000	0.406861000
	6	3.878266000	1.481702000	0.952701000
	1	4.930522000	1.538142000	1.167518000
	6	3.012135000	2.425359000	0.530773000
	1	3.160010000	3.466763000	0.308065000
	6	1.869158000	0.512416000	0.742802000
	6	0.549956000	2.449929000	-0.035993000
	1	0.752704000	3.498071000	-0.242669000
	1	-0.215177000	2.361357000	0.732886000

RS-4	1	0.183328000	1.956916000	-0.935135000
	6	3.735666000	-0.988285000	1.417208000
	1	3.113487000	-1.440970000	2.190763000
	1	4.722532000	-0.791003000	1.839669000
	6	3.845061000	-1.945535000	0.231997000
	1	4.402766000	-2.815857000	0.591181000
	1	2.848483000	-2.299275000	-0.035520000
	6	4.552771000	-1.401166000	-1.004975000
	1	5.441271000	-0.826068000	-0.732469000
	1	4.881354000	-2.229392000	-1.630343000
	16	3.550134000	-0.273384000	-2.048416000
	6	-2.381265000	-2.388516000	0.381269000
	1	-1.993504000	-2.512322000	1.389821000
	1	-3.366208000	-2.839519000	0.296527000
	1	-1.695996000	-2.844146000	-0.329958000
	1	2.387056000	-0.919984000	-1.882831000
	17	-2.793302000	1.956556000	-0.539506000
	16	0.625901000	-0.637539000	0.728903000

 **TS-4**	80	-1.253249000	-0.241888000	0.191966000
	7	2.664542000	0.408652000	0.342179000
	7	1.513518000	2.114509000	-0.313047000
	6	3.300935000	0.926283000	-0.761922000
	1	4.197007000	0.486079000	-1.161390000
	6	2.580470000	1.991922000	-1.173011000
	1	2.725126000	2.665528000	-1.998277000
	6	1.563129000	1.134662000	0.609413000
	6	0.450448000	3.106656000	-0.416117000
	1	0.833374000	3.957792000	-0.974108000
	1	0.157745000	3.414624000	0.584720000
	1	-0.416063000	2.680724000	-0.922919000
	6	3.054967000	-0.813475000	1.041785000
	1	3.028799000	-0.607067000	2.111520000
	1	4.089867000	-1.003660000	0.753377000
	6	2.183402000	-2.021081000	0.709267000
	1	2.664946000	-2.875654000	1.195717000
	1	1.205402000	-1.907570000	1.178599000
	6	2.034643000	-2.310536000	-0.784087000
	1	2.988028000	-2.148257000	-1.295053000
	1	1.789627000	-3.364402000	-0.919509000
	16	0.754353000	-1.352478000	-1.689280000
	6	-1.485582000	-2.662958000	0.066316000
	1	-2.171714000	-3.005996000	-0.705179000
	1	-0.736119000	-3.430266000	0.274621000
	1	-2.053385000	-2.546262000	0.996254000

	1	-0.517588000	-2.001796000	-0.757866000
	16	0.440161000	0.859076000	1.885167000
	17	-2.822248000	1.362395000	-0.753283000

 **PS-4**	80	1.153921000	-0.251549000	-0.290464000
	7	-2.662929000	0.622816000	0.633004000
	7	-2.761685000	-1.310399000	-0.323136000
	6	-3.607549000	0.711174000	-0.367448000
	1	-4.143686000	1.621797000	-0.566733000
	6	-3.670654000	-0.496828000	-0.963899000
	1	-4.274775000	-0.846537000	-1.781623000
	6	-2.130769000	-0.622140000	0.658286000
	6	-2.453403000	-2.686635000	-0.661265000
	1	-1.446813000	-2.750705000	-1.075026000
	1	-3.179199000	-3.032069000	-1.393677000
	1	-2.498789000	-3.301111000	0.235671000
	6	-2.215186000	1.734456000	1.459945000
	1	-2.224744000	1.404023000	2.499403000
	1	-2.964491000	2.518631000	1.340976000
	6	-0.828295000	2.270889000	1.108508000
	1	-0.710120000	3.199708000	1.676144000
	1	-0.072694000	1.582171000	1.489266000
	6	-0.574743000	2.579822000	-0.363974000
	1	-1.423302000	3.122261000	-0.791294000
	1	0.295220000	3.230282000	-0.445181000
	16	-0.325437000	1.163383000	-1.513159000
	6	3.033114000	2.442656000	0.401473000
	1	3.581468000	3.362406000	0.598565000
	1	2.233138000	2.343867000	1.137105000
	1	3.705754000	1.590163000	0.485160000
	1	2.611727000	2.480299000	-0.603609000
	16	-0.906505000	-1.217153000	1.670475000
	17	2.974464000	-1.548719000	0.477417000

 MeHgI	80	0.857569000	0.000225000	-0.000498000
	53	-1.816114000	-0.000162000	0.000266000
	6	2.954999000	0.000872000	-0.000888000
	1	3.306333000	-0.889865000	-0.515374000
	1	3.305736000	0.891869000	-0.515336000
	1	3.307142000	0.000946000	1.027465000

	80	-0.190516000	-0.000119000	0.000022000
	6	-2.267748000	0.000504000	-0.000069000

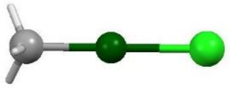
 MeHgCl	1	-2.622830000	0.924075000	-0.450235000
	1	-2.624148000	-0.850771000	-0.574739000
	1	-2.624265000	-0.071188000	1.024336000
	17	2.159943000	0.000256000	-0.000043000

Table S7: Calculated Gibbs free energies and the corresponding transition state energies values of reactions of MeHgI by **1** in solvent methanol (MeOH) or water (H_2O) as proton assistance in top and bottom approach at 298.15 K (in kcal/mol).

Reactions	ΔG (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)
[**1**•••MeHgI•••MeOH(top)] → **1**.HgI•••Methane•••MeOH]	-39.6	27.35
[**1**•••MeHgI•••MeOH(bottom)] → **1**.HgI•••Methane•••MeOH]	-37.14	33.01
[**1**•••MeHgI•••H_2O(top)] → **1**.HgI•••Methane•••H_2O]	-39.13	30.10
[**1**•••MeHgI•••H_2O (bottom)] → **1**.HgI•••Methane•••H_2O]	-36.64	33.10

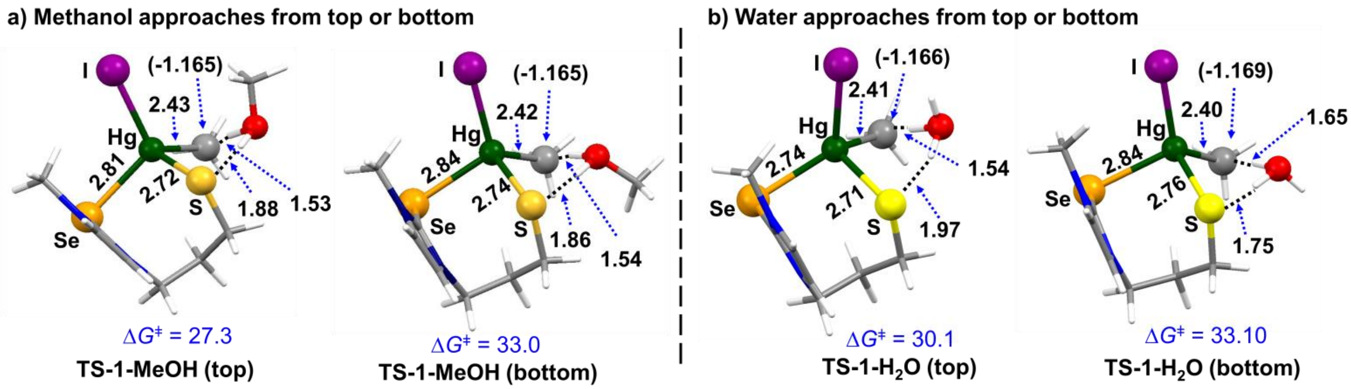


Figure S39: Optimized structures of TS-1-MeOH (top), TS-1- MeOH (bottom), TS-1-H_2O (top), TS-1-H_2O (bottom). In top attack, solvent molecule approaches from the same side of iodine atom as shown in the figure. In bottom attack, solvent molecule approaches from the opposite side of iodine atom as shown in the figure.

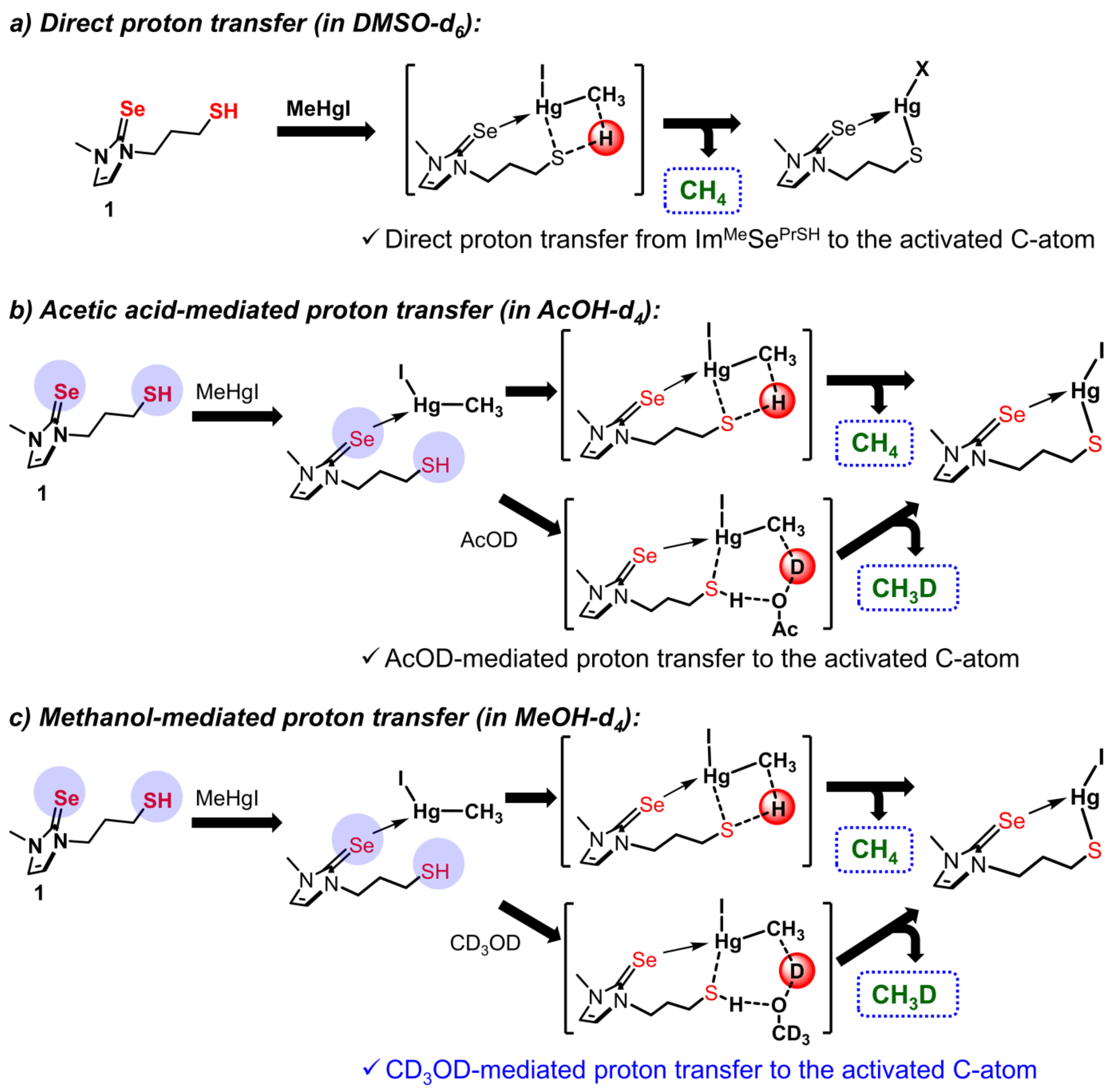


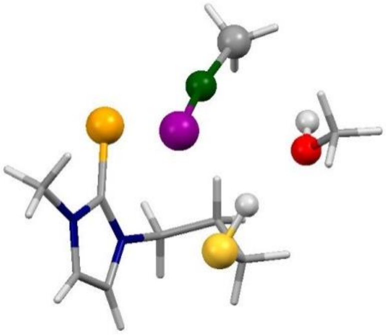
Figure S40: Direct and protic solvent mediated proton transfer to the activated C-atom of MeHgI induced by **1**.

Table S8. Initial rates of Hg–C protonolysis by various selones at 21 °C.

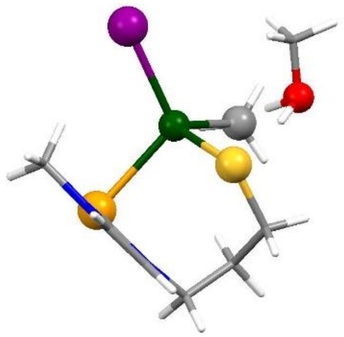
SR NO.	Compd.	RHgX	Initial Rate ($M.h^{-1}$)[a]
1	**1**	Thimerosal	$2.07 \pm 0.2 \times 10^{-3}$
		EtHgCys	$1.2 \pm 0.3 \times 10^{-3}$
		MeHgCys	$0.4 \pm 0.02 \times 10^{-3}$
		MeHgSPh	$0.16 \pm 0.14 \times 10^{-3}$

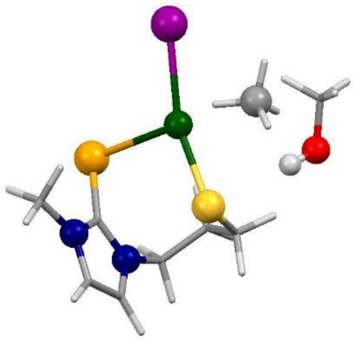
[a] All experiments were carried out in a sealed NMR tube in DMSO-d_6 at 21 °C; [RHgX] = [Compd.] = 25 mM..

Table S9: Optimized geometries and coordinates of compounds and complexes**.**

 **RS-1-MeOH (top)**	80	-1.430884000	0.239620000	-0.757547000
	53	-1.603058000	-1.774430000	1.074845000
	34	1.394977000	-0.202707000	-2.066937000
	7	3.248712000	0.383661000	0.056367000
	7	2.662382000	-1.692551000	0.029876000
	6	3.946400000	-0.247262000	1.063240000
	1	4.621658000	0.285151000	1.709446000
	6	3.582169000	-1.546496000	1.043818000
	1	3.881820000	-2.371546000	1.664744000
	6	2.458654000	-0.507605000	-0.583020000
	6	2.039066000	-2.939930000	-0.381137000
	1	0.962121000	-2.799122000	-0.442975000
	1	2.269424000	-3.696059000	0.365772000
	1	2.421923000	-3.238814000	-1.356533000
	6	3.233792000	1.821764000	-0.179557000
	1	3.255119000	1.976596000	-1.258358000
	1	4.158006000	2.215728000	0.247652000
	6	2.020741000	2.522417000	0.426250000
	1	2.139292000	3.589242000	0.210217000
	1	1.116939000	2.189309000	-0.088884000
	6	1.852193000	2.340127000	1.932086000
	1	2.813152000	2.410793000	2.448238000
	1	1.207936000	3.119889000	2.331869000
	16	1.133827000	0.732837000	2.432261000
	6	-1.797788000	1.897728000	-2.023588000
	1	-0.910614000	2.529183000	-2.003045000
	1	-1.949041000	1.536016000	-3.038220000
	1	-2.680083000	2.450093000	-1.703116000
	8	-1.245368000	2.795155000	1.118339000
	6	-2.489382000	2.511797000	1.747856000
	1	-3.156270000	1.952130000	1.085366000
	1	-2.272071000	1.892443000	2.617197000
	1	-2.986740000	3.426507000	2.077874000
	1	-1.416221000	3.238221000	0.281663000
	1	-0.103783000	1.021821000	2.021671000

	80	-0.586938000	0.325939000	-0.533359000
	53	-2.566174000	-1.415904000	0.460519000
	34	1.602290000	-1.002188000	-1.701402000
	7	3.192060000	-0.072164000	0.525614000
	7	2.150033000	-1.908165000	0.970087000
	6	3.498541000	-0.406846000	1.824572000
	1	4.134367000	0.207939000	2.436450000
	6	2.847667000	-1.557186000	2.102254000
	1	2.809936000	-2.146194000	3.000852000

 **TS-1-MeOH (top)**	6	2.357056000	-0.991979000	0.006928000
	6	1.287355000	-3.075238000	0.832339000
	1	0.248109000	-2.760323000	0.737879000
	1	1.409086000	-3.688005000	1.722130000
	1	1.577233000	-3.635817000	-0.053784000
	6	3.629589000	1.151911000	-0.143462000
	1	3.990959000	0.873972000	-1.133639000
	1	4.473788000	1.522274000	0.440170000
	6	2.556343000	2.230838000	-0.264918000
	1	3.072017000	3.113537000	-0.657980000
	1	1.825993000	1.937649000	-1.020121000
	6	1.850553000	2.613684000	1.032214000
	1	2.581806000	2.743944000	1.834848000
	1	1.367583000	3.581266000	0.890175000
	16	0.580024000	1.431605000	1.659070000
	6	-1.278338000	2.225772000	-1.877424000
	1	-0.544593000	3.013806000	-2.057337000
	1	-1.184115000	1.514092000	-2.701540000
	1	-2.285268000	2.640513000	-1.987240000
	1	-1.450591000	2.554148000	-0.394191000
	8	-1.624677000	3.024914000	0.629760000
	1	-0.846372000	2.564620000	1.169697000
	6	-2.883291000	2.552864000	1.154271000
	1	-3.448799000	2.095493000	0.342213000
	1	-2.697837000	1.800047000	1.920355000
	1	-3.419377000	3.403641000	1.566207000

 **PS-1-MeOH (top)**	80	-0.822036000	-0.008966000	0.108411000
	53	-3.106595000	-0.818915000	-1.085137000
	34	1.347011000	-1.392442000	-1.421136000
	7	3.196026000	-0.150620000	0.424942000
	7	2.493037000	-2.068767000	1.113125000
	6	3.770146000	-0.374935000	1.656203000
	1	4.429616000	0.339682000	2.115490000
	6	3.332316000	-1.576677000	2.086660000
	1	3.538791000	-2.118235000	2.992204000
	6	2.403005000	-1.189401000	0.093253000
	6	1.764531000	-3.324423000	1.173732000
	1	0.693124000	-3.127469000	1.165692000
	1	2.044577000	-3.836481000	2.090990000
	1	2.012891000	-3.935380000	0.308145000
	6	3.337211000	1.084997000	-0.340221000
	1	3.589089000	0.813684000	-1.366112000
	1	4.188397000	1.608979000	0.097048000
	6	2.100293000	1.979346000	-0.334172000
	1	2.412589000	2.926397000	-0.786551000
	1	1.350407000	1.560407000	-1.003527000

	6	1.485493000	2.290190000	1.025174000
	1	2.261677000	2.570042000	1.743512000
	1	0.812968000	3.141419000	0.920737000
	16	0.543043000	0.950709000	1.876985000
	6	-1.076834000	2.632140000	-1.994907000
	1	-0.679786000	3.486320000	-2.542346000
	1	-0.580333000	1.724637000	-2.342861000
	1	-2.145615000	2.537483000	-2.180959000
	8	-1.546239000	3.433030000	1.397644000
	6	-2.895785000	3.144665000	1.082735000
	1	-3.248154000	3.934115000	0.420092000
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	1	-3.526108000	3.130848000	1.976280000
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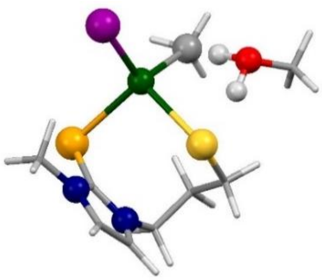 **TS-1-MeOH (bottom)**	80	0.669124000	0.323083000	0.456862000
	53	2.680005000	-1.335685000	-0.545169000
	34	-1.380318000	-1.164854000	1.742285000
	7	-3.139930000	-0.377283000	-0.409869000
	7	-1.979751000	-2.129628000	-0.896625000
	6	-3.477334000	-0.742044000	-1.693474000
	1	-4.185567000	-0.181962000	-2.277286000
	6	-2.751982000	-1.839604000	-1.997355000
	1	-2.709037000	-2.429081000	-2.895430000
	6	-2.213347000	-1.226793000	0.073486000
	6	-1.029351000	-3.229727000	-0.789879000
	1	-1.284656000	-3.846251000	0.069674000
	1	-0.021128000	-2.835367000	-0.667345000
	1	-1.088922000	-3.813940000	-1.704713000
	6	-3.646304000	0.806524000	0.280698000
	1	-3.944114000	0.500805000	1.283885000
	1	-4.539989000	1.109594000	-0.267147000
	6	-2.658891000	1.967187000	0.363416000
	1	-3.225047000	2.801326000	0.792211000
	1	-1.870575000	1.727519000	1.078129000
	6	-2.054572000	2.415482000	-0.963948000
	1	-2.834421000	2.483812000	-1.727876000
	1	-1.661278000	3.425276000	-0.837497000
	16	-0.715132000	1.360871000	-1.668814000
	6	1.140697000	2.285231000	1.798183000
	1	1.245631000	1.566102000	2.614228000
	1	2.044847000	2.900120000	1.872194000
	1	0.267884000	2.899681000	2.028661000
	1	1.330215000	2.613807000	0.303201000
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	6	1.069921000	4.491138000	-0.679929000
	1	1.981096000	5.049249000	-0.478071000
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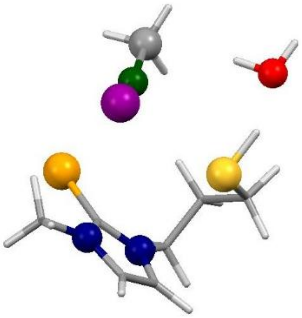
	1	0.333456000	4.681052000	0.102424000

 **RS-1-H_2O (top)**	80	1.138882000	0.720653000	0.566658000
	53	2.154176000	-1.417577000	-0.805142000
	34	-1.435348000	-0.500713000	2.066998000
	7	-2.907225000	-0.540767000	-0.405201000
	7	-1.661778000	-2.289613000	-0.171122000
	6	-3.092855000	-1.325162000	-1.526240000
	1	-3.739917000	-1.024935000	-2.331263000
	6	-2.313562000	-2.416223000	-1.378636000
	1	-2.151145000	-3.258939000	-2.026345000
	6	-2.021072000	-1.134712000	0.430343000
	6	-0.821834000	-3.311084000	0.433349000
	1	-0.044284000	-2.827398000	1.017044000
	1	-0.365129000	-3.895541000	-0.361775000
	1	-1.426620000	-3.946220000	1.081681000
	6	-3.564753000	0.737859000	-0.156095000
	1	-3.872619000	0.744325000	0.889864000
	1	-4.458160000	0.748766000	-0.783461000
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	1	-3.320180000	2.834189000	-0.272160000
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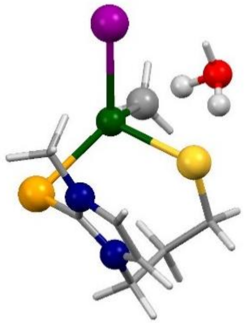
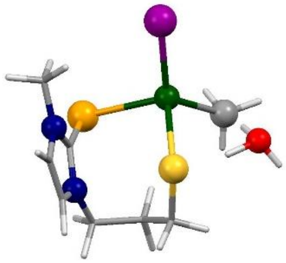
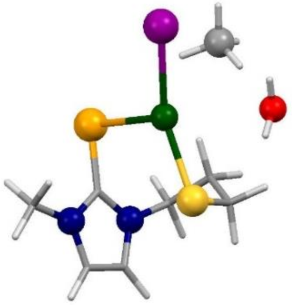
	1	-2.918158000	1.798690000	-2.603306000
	1	-1.755698000	3.017192000	-2.066738000
	16	-0.739351000	0.866529000	-2.150296000
	6	0.925126000	2.545373000	1.634996000
	1	-0.052813000	2.981912000	1.437241000
	1	0.978268000	2.289777000	2.691131000
	1	1.721778000	3.250540000	1.401479000
	8	0.404583000	3.906579000	-1.381769000
	1	0.659095000	3.548383000	-0.523919000
	1	0.145394000	1.805641000	-2.504629000
	1	0.916806000	4.712733000	-1.486219000

	80	-0.551583000	0.486046000	-0.556991000
	53	-2.797962000	-1.019655000	0.475987000
	34	1.502266000	-0.807692000	-1.819969000
	7	3.144859000	-0.275470000	0.504235000
	7	1.961350000	-2.065248000	0.726547000
	6	3.416659000	-0.788245000	1.751038000
	1	4.094853000	-0.303431000	2.430200000

 **TS-1-H$_2$O (top)**	6	2.674458000	-1.908059000	1.890881000
	1	2.580314000	-2.594475000	2.712833000
	6	2.247394000	-1.060162000	-0.117829000
	6	0.953041000	-3.090351000	0.486118000
	1	-0.041126000	-2.643937000	0.542969000
	1	1.061810000	-3.854802000	1.251340000
	1	1.103096000	-3.520990000	-0.500777000
	6	3.628915000	1.018169000	0.021659000
	1	3.957071000	0.886278000	-1.009136000
	1	4.501572000	1.252876000	0.632715000
	6	2.604040000	2.150286000	0.105748000
	1	3.163326000	3.065486000	-0.115420000
	1	1.869100000	2.039437000	-0.692787000
	6	1.895007000	2.317412000	1.448364000
	1	2.621889000	2.271119000	2.264698000
	1	1.449455000	3.311480000	1.482193000
	16	0.581380000	1.082447000	1.830417000
	6	-1.427994000	2.596051000	-1.320620000
	1	-1.124413000	2.254456000	-2.313412000
	1	-2.491878000	2.829283000	-1.417623000
	1	-0.866368000	3.511613000	-1.123366000
	1	-1.744310000	2.377366000	0.166512000
	8	-2.003452000	2.446489000	1.284888000
	1	-1.113081000	2.094311000	1.690873000
	1	-2.646773000	1.726888000	1.435732000

 **TS-1-H$_2$O (bottom)**	80	-0.646833000	0.629421000	-0.391903000
	53	-2.751774000	-0.969261000	0.487661000
	34	1.209013000	-0.931669000	-1.878253000
	7	2.987694000	-0.729517000	0.374773000
	7	1.542877000	-2.308970000	0.644790000
	6	3.226619000	-1.288467000	1.609762000
	1	4.000344000	-0.922407000	2.260672000
	6	2.324206000	-2.276773000	1.777865000
	1	2.156931000	-2.949078000	2.600300000
	6	1.948056000	-1.353772000	-0.214013000
	6	0.438969000	-3.239307000	0.444909000
	1	-0.005650000	-3.045712000	-0.527427000
	1	-0.312858000	-3.074420000	1.214250000
	1	0.820061000	-4.258893000	0.487451000
	6	3.696348000	0.430301000	-0.161888000
	1	3.958179000	0.207172000	-1.196275000
	1	4.617676000	0.509303000	0.417520000
	6	2.915053000	1.739660000	-0.095381000
	1	3.616316000	2.515702000	-0.420684000

	1	2.108343000	1.720417000	-0.828961000
	6	2.369429000	2.114323000	1.279223000
	1	3.136404000	1.962979000	2.043827000
	1	2.143486000	3.181988000	1.279406000
	16	0.866291000	1.210773000	1.847407000
	6	-0.828440000	2.771357000	-1.478694000
	1	-1.044556000	2.175806000	-2.369241000
	1	-1.630968000	3.516327000	-1.462333000
	1	0.127076000	3.269551000	-1.653249000
	1	-0.937025000	2.967873000	0.039631000
	8	-0.942193000	3.326336000	1.128188000
	1	-0.265432000	2.601357000	1.586553000
	1	-0.582695000	4.218319000	1.203733000

 **PS-1-H_2O (top)**	80	0.606076000	0.125906000	-0.436559000
	53	3.166603000	-0.727390000	-0.125479000
	34	-1.129443000	-1.450697000	1.367632000
	7	-3.267283000	0.305250000	0.526394000
	7	-3.123819000	-1.468920000	-0.689376000
	6	-4.237039000	0.400714000	-0.445837000
	1	-4.895426000	1.248428000	-0.511611000
	6	-4.148219000	-0.710165000	-1.207196000
	1	-4.715100000	-1.022857000	-2.065667000
	6	-2.575605000	-0.841121000	0.371052000
	6	-2.638447000	-2.723246000	-1.238336000
	1	-1.646075000	-2.577604000	-1.664447000
	1	-3.332050000	-3.048094000	-2.010134000
	1	-2.575435000	-3.468057000	-0.448068000
	6	-2.955402000	1.361091000	1.486118000
	1	-2.847980000	0.897296000	2.467093000
	1	-3.831815000	2.010376000	1.505625000
	6	-1.701717000	2.168566000	1.154276000
	1	-1.721960000	3.040639000	1.815783000
	1	-0.816305000	1.601525000	1.440871000
	6	-1.570050000	2.663953000	-0.282246000
	1	-2.515041000	3.093088000	-0.628416000
	1	-0.824753000	3.457048000	-0.302554000
	16	-1.116041000	1.432720000	-1.578706000
	6	1.600587000	1.486528000	2.824355000
	1	1.313160000	2.092156000	3.683308000
	1	0.949827000	0.613291000	2.764174000
	1	2.629672000	1.150132000	2.935084000
	8	1.685869000	2.949596000	-0.444768000
	1	1.516246000	2.083006000	1.915049000
	1	2.576261000	2.587335000	-0.519810000
	1	1.284579000	2.832725000	-1.315445000

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