Supplementary Material (ESI) for PCCP

Supplementary Information

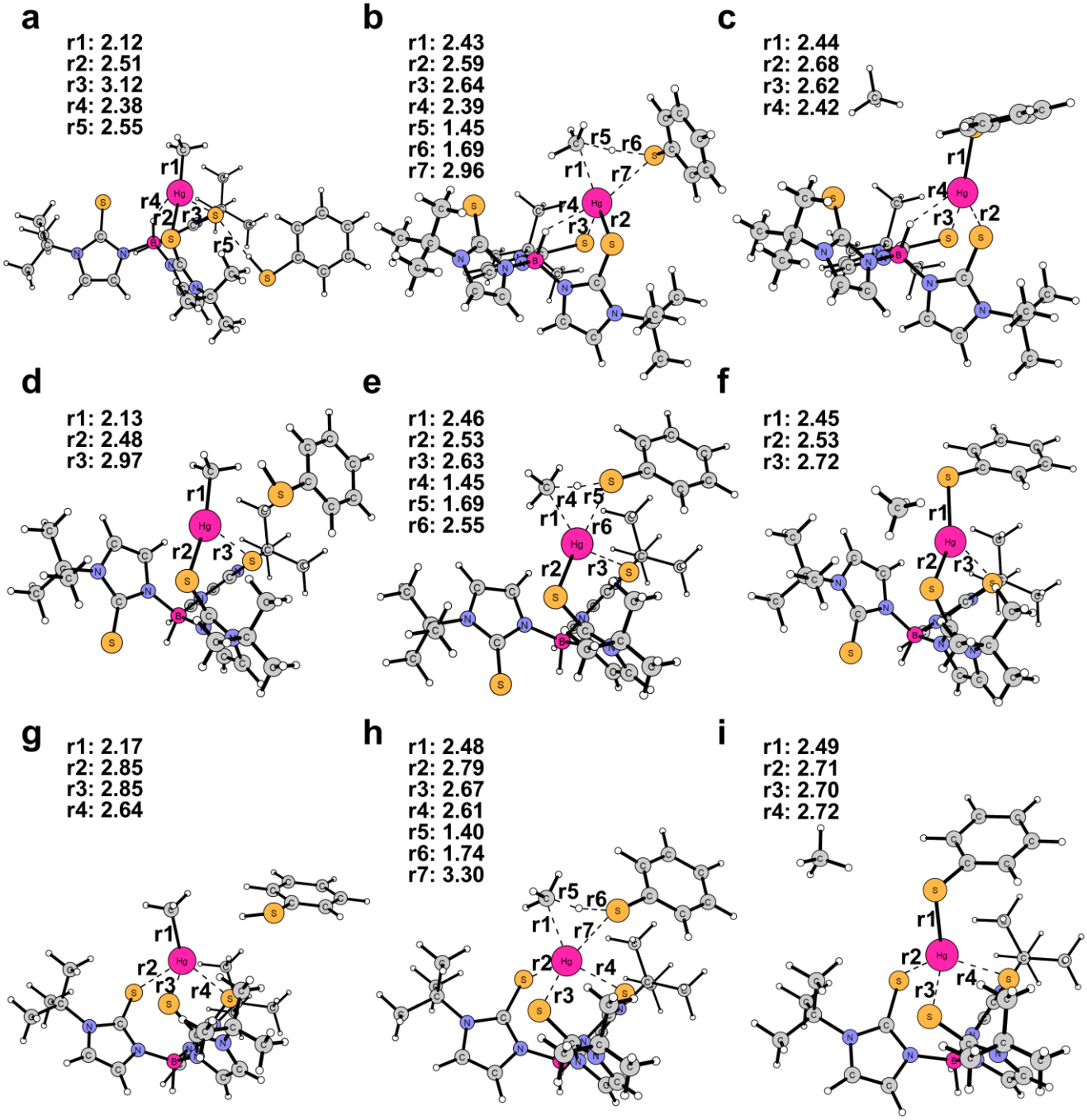

Fig. 1 Structures of the frontside attack pathway featuring four-center TS. (a), (d), and (g): RE for $[\kappa^1/\kappa^2/\kappa^3\text{-Tm}^{t\text{-Bu}}]$HgMe complexes, respectively. (b), (e), and (h): the corresponding TS. (c), (f), and (i): the corresponding PRO.

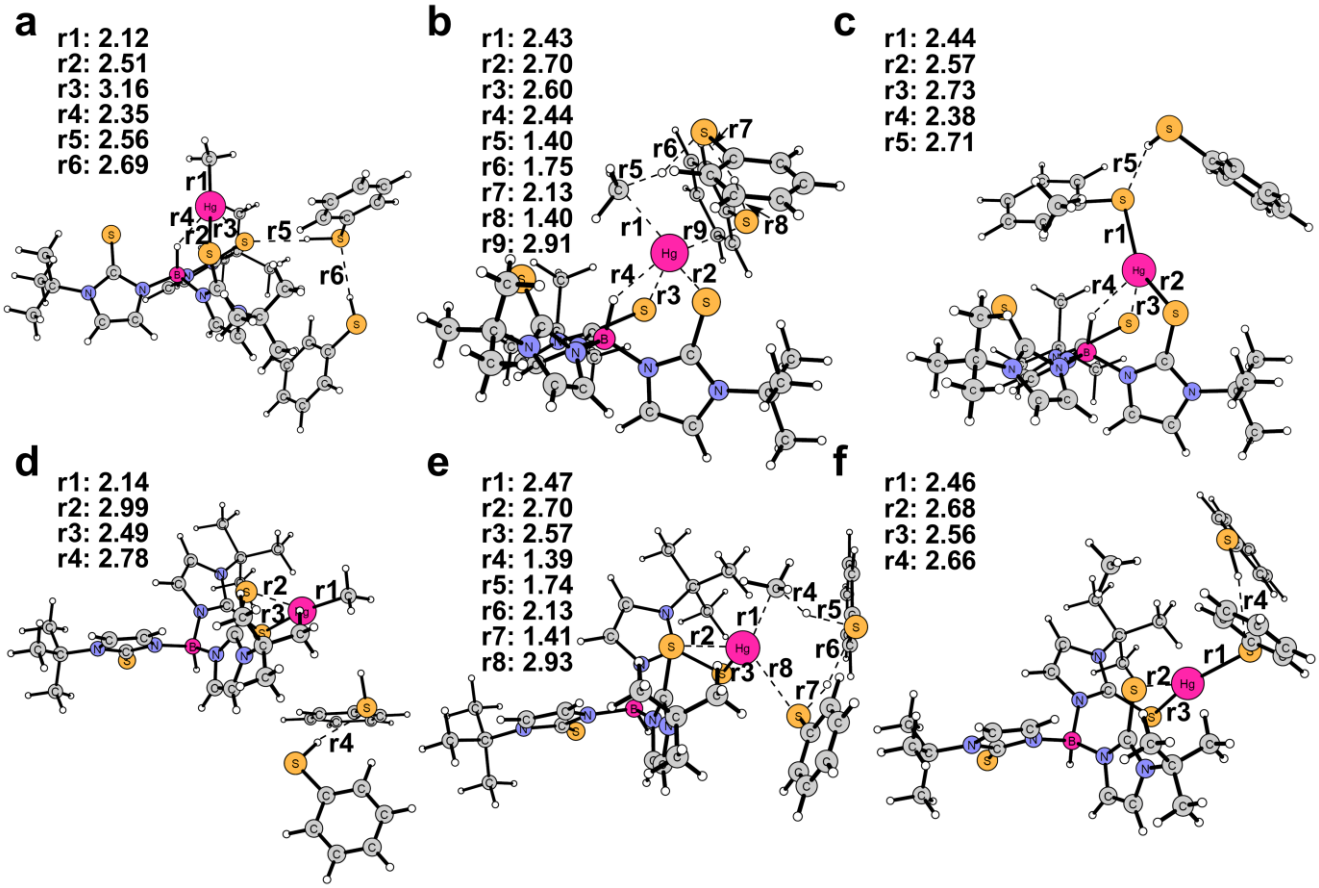

Fig. 2 Structures of the frontside attack pathway featuring six-center TS. (a), (d), and (g): RE for $[\kappa^1/\kappa^2\text{-Tm}^{t\text{-Bu}}]$HgMe complexes, respectively. (b), (e), and (h): the corresponding TS. (c), (f), and (i): the corresponding PRO.

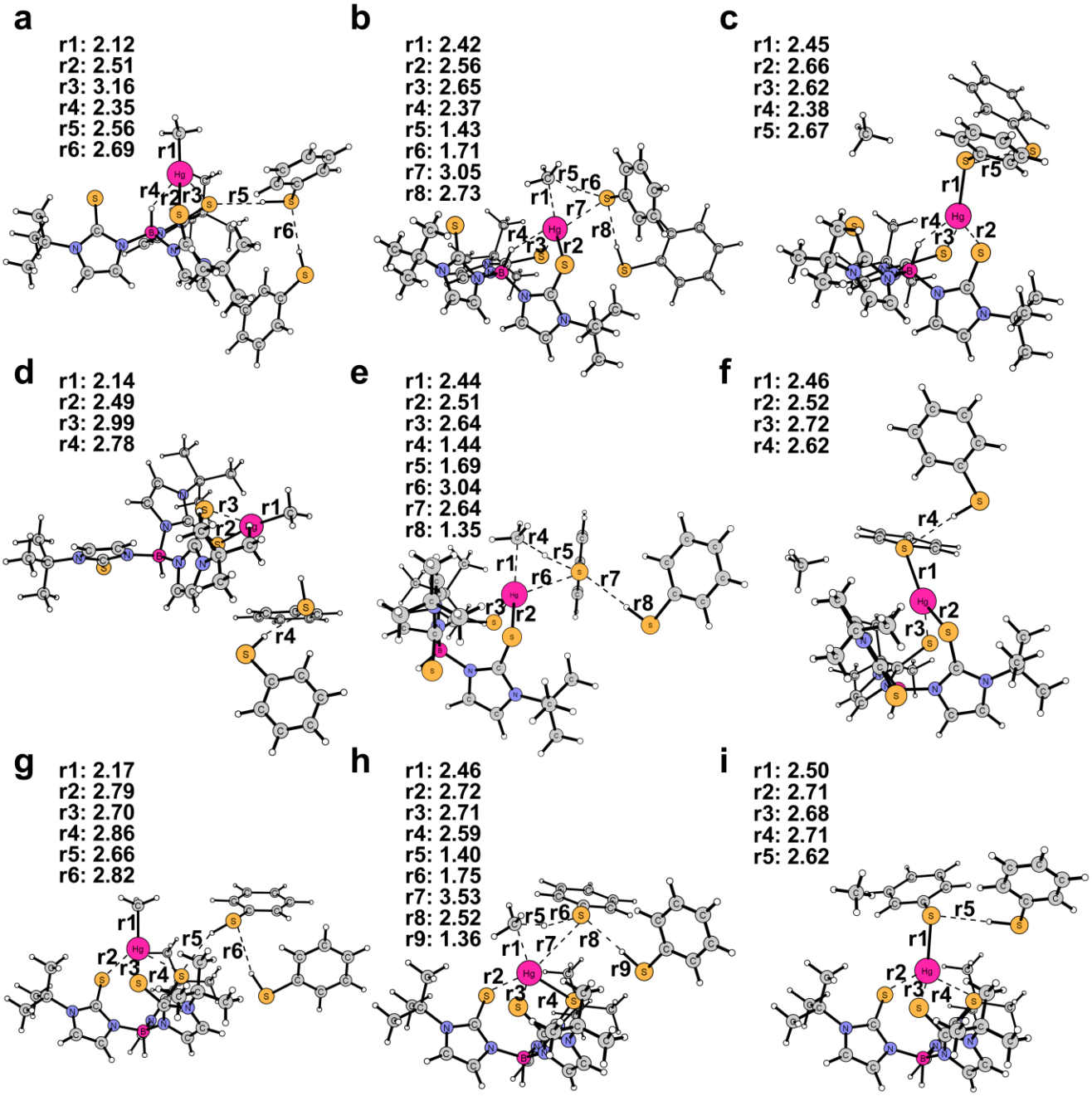

Fig. 3 Structures of the frontside attack pathway featuring HB-assisted four-center TS. (a), (d), and (g): RE for [$\kappa^1/\kappa^2/\kappa^3$-Tm$^{t\text{-Bu}}$]HgMe complexes, respectively. (b), (e), and (h): the corresponding TS. (c), (f), and (i): the corresponding PRO.

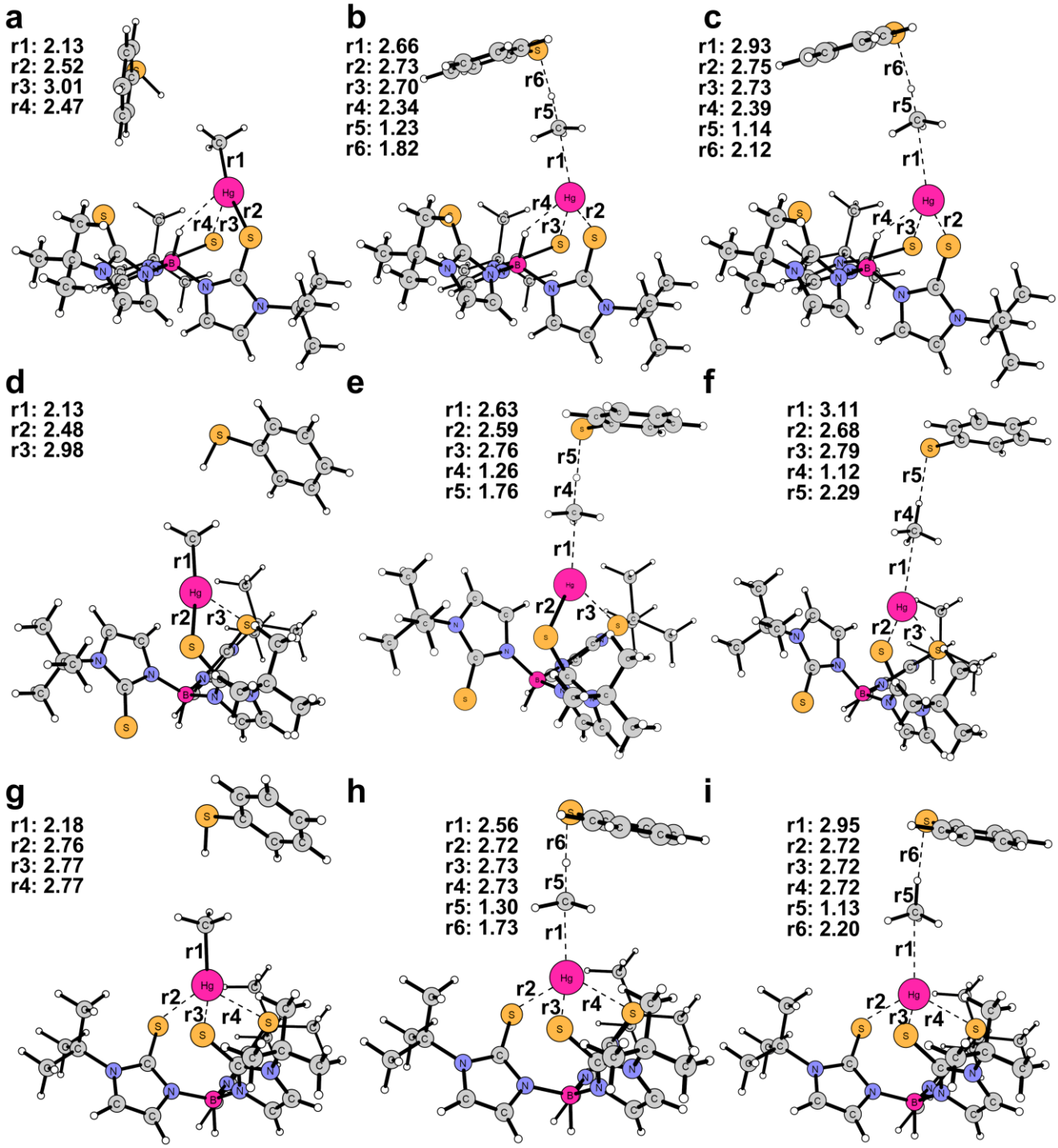

Fig. 4 Structures of the backside attack pathway involving one PhSH molecule. (a), (d), and (g): RE for [$\kappa^1/\kappa^2/\kappa^3$-Tm$^{t\text{-Bu}}$]HgMe complexes, respectively. (b), (e), and (h): the corresponding TS. (c), (f), and (i): the corresponding PRO.

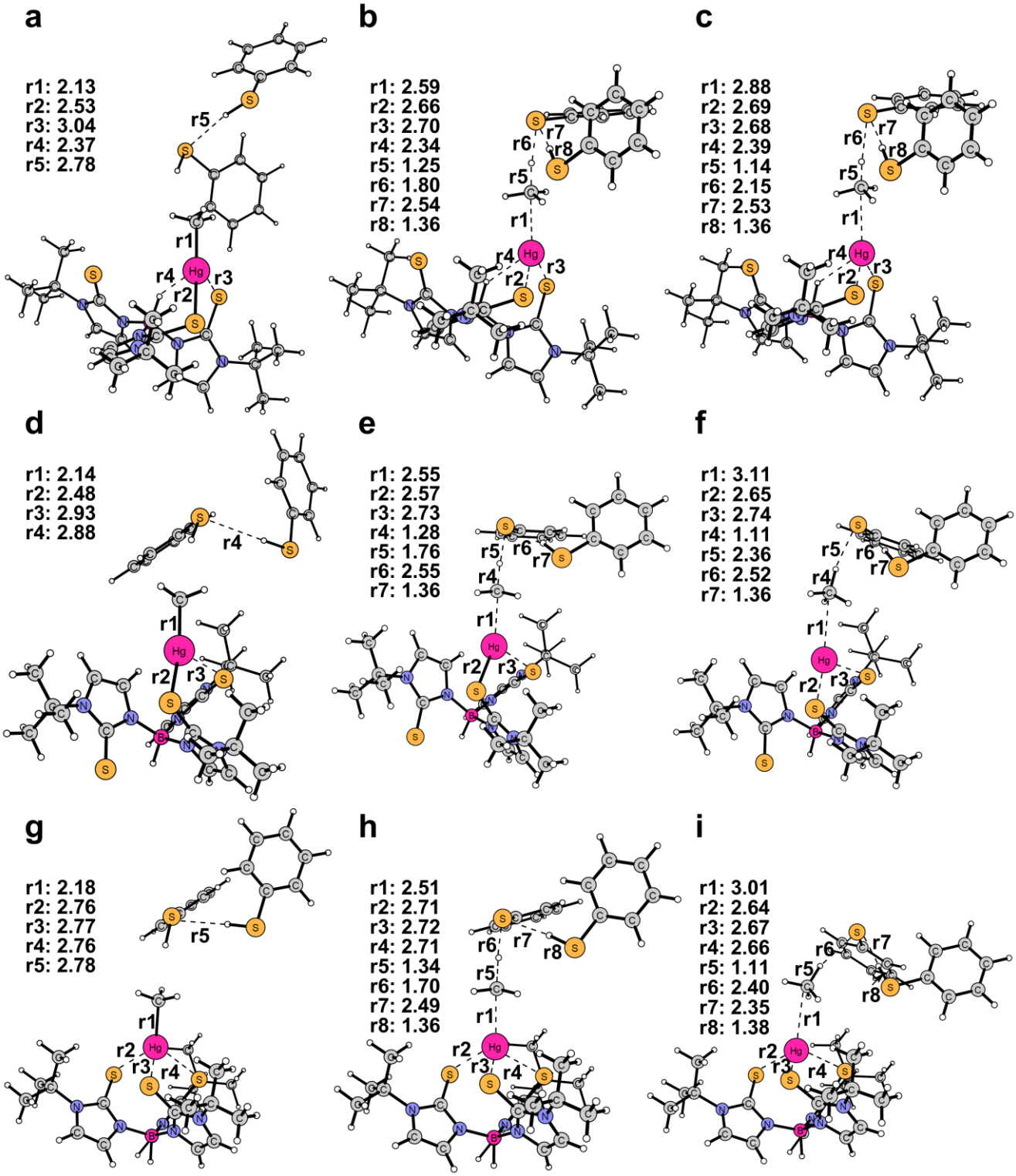

Fig. 5 Structures of the backside attack pathway involving two PhSH molecules. (a), (d), and (g): RE for [$\kappa^1/\kappa^2/\kappa^3$-Tm$^{t\text{-Bu}}$]HgMe complexes, respectively. (b), (e), and (h): the corresponding TS. (c), (f), and (i): the corresponding PRO.

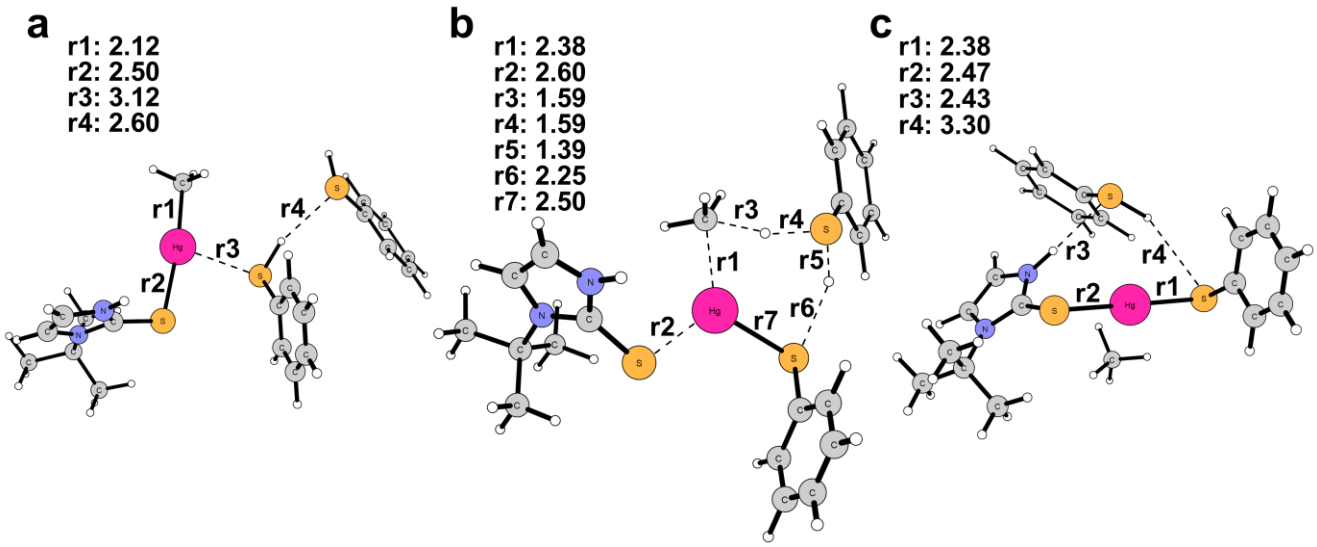

Fig. 6 Structures of the frontside attack pathway featuring six-center TS for $[Hmim^{t\text{-}Bu}]_{n=1}HgMe$ complex. (a), (b), and (c): RE, TS, and PRO, respectively.