## **Supplementary Materials**



Figure S1. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2b and thiolsulfonate 3b (CDCl<sub>3</sub>).



Figure S2. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2b and thiolsulfonate 3b (CDCl<sub>3</sub>).



Figure S3. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2c (CDCl<sub>3</sub>).



Figure S4. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2c (CDCl<sub>3</sub>).



Figure S5. <sup>19</sup>F-NMR spectrum of thiolsulfinate 2c (CDCl<sub>3</sub>).



Figure S6. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2d and thiolsulfonate 3d (CDCl<sub>3</sub>).



Figure S7. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2d and thiolsulfonate 3d (CDCl<sub>3</sub>).



Figure S8. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2e (CDCl<sub>3</sub>).



Figure S9. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2e (CDCl<sub>3</sub>).



Figure S10. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2f (CDCl<sub>3</sub>).



Figure S11. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2f (CDCl<sub>3</sub>).



Figure S12. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2g (CDCl<sub>3</sub>).



Figure S13. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2g (CDCl<sub>3</sub>).



Figure S14. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2h (CDCl<sub>3</sub>).



Figure S15. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2h (CDCl<sub>3</sub>).



Figure S16. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2i (CDCl<sub>3</sub>).



Figure S17. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2i (CDCl<sub>3</sub>).



Figure S18. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2j (CDCl<sub>3</sub>).



Figure S19. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2j (CDCl<sub>3</sub>).



Figure S20. <sup>1</sup>H-NMR spectrum of thiolsulfinate 2k (CDCl<sub>3</sub>).



Figure S21. <sup>13</sup>C-NMR spectrum of thiolsulfinate 2k (CDCl<sub>3</sub>).



Figure S22. <sup>1</sup>H-NMR spectrum of thiolsulfinates 4a and 5a (CDCl<sub>3</sub>).



Figure S23. <sup>13</sup>C-NMR spectrum of thiolsulfinates 4a and 5a (CDCl<sub>3</sub>).



Figure S24. <sup>1</sup>H-NMR spectrum of thiolsulfinates 4b and 5b (CDCl<sub>3</sub>).



Figure S25. <sup>13</sup>C-NMR spectrum of thiolsulfinates 4b and 5b (CDCl<sub>3</sub>).



Figure S26. <sup>1</sup>H-NMR spectrum of thiolsulfinate 4c (CDCl<sub>3</sub>).



Figure S27. <sup>13</sup>C-NMR spectrum of thiolsulfinate 4c (CDCl<sub>3</sub>).



Figure S28. <sup>1</sup>H-NMR full spectrum of thiolsulfinates 8–11 from (±)-lipoic acid (CDCl<sub>3</sub>).



Figure S29. <sup>1</sup>H-NMR expanded spectrum of thiolsulfinates 8–11 from (±)-lipoic acid (CDCl<sub>3</sub>).



Figure S30. <sup>13</sup>C-NMR expanded spectrum of thiolsulfinates 8–11 from (±)-lipoic acid (CDCl<sub>3</sub>).



Figure S31. <sup>13</sup>C-NMR full spectrum of thiolsulfinates 8–11 from (±)-lipoic acid (CDCl<sub>3</sub>).



Figure S32. <sup>1</sup>H-NMR spectrum of cystine derivative 12 (CDCl<sub>3</sub>).



Figure S33. <sup>1</sup>H-NMR spectrum of oxidation products of cystine derivative 12 (CDCl<sub>3</sub>).