# Diiron hexacarbonyl complexes as potential CO-RMs: their CO-releasing initiated by the substitution reaction with cysteamine and structural correlation to the bridging linkage

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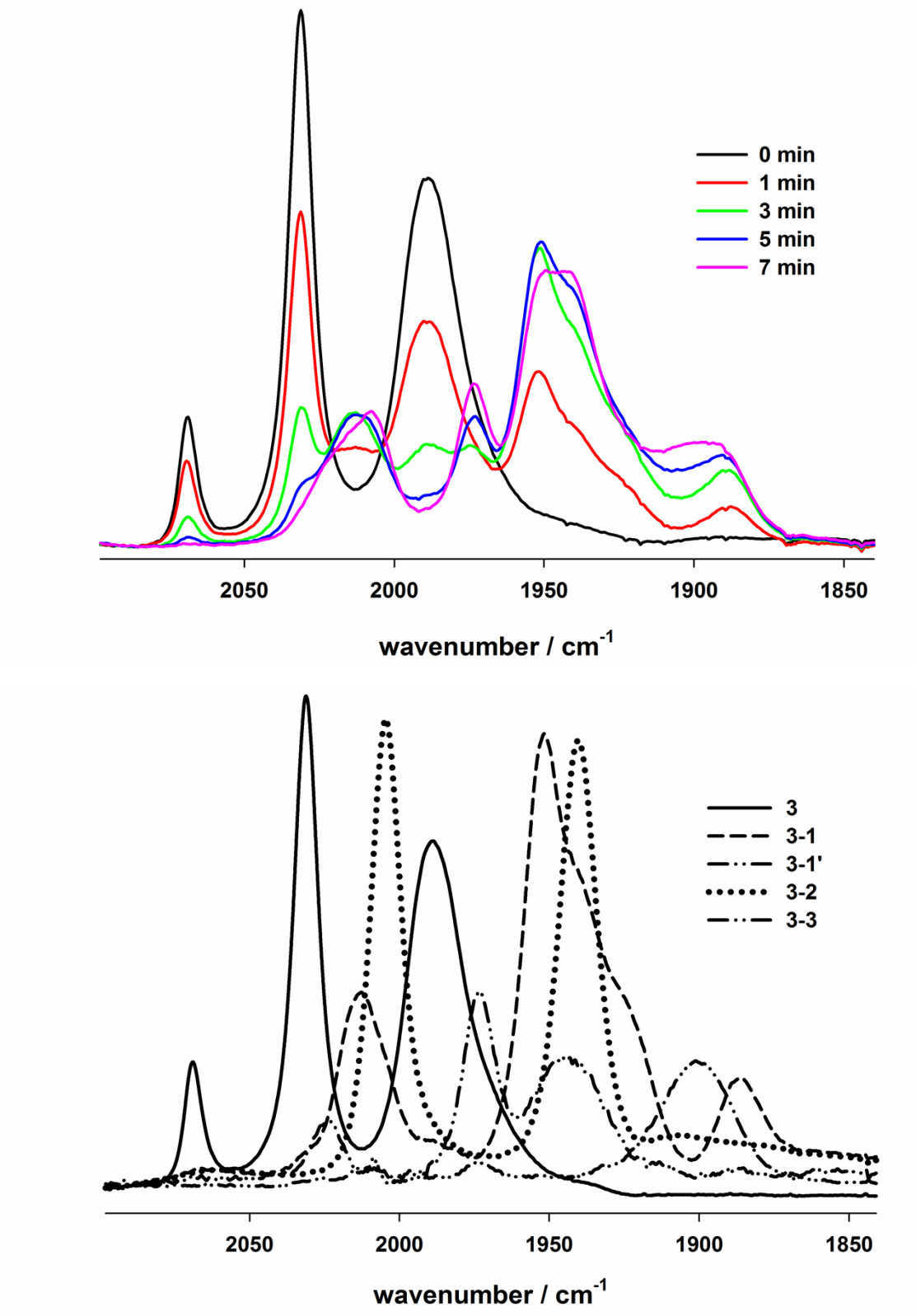



Fig. S1 Infrared spectral variation during the CO-releasing process of complex **3** ([**3**] = 0.011 mol $L^{-1}$ and [**CysA**] = 0.066 mol $L^{-1}$) (top) and the intermediates in the reaction mixture (bottom), when the reaction proceeded from 1 min to 7 min in

DMSO at 37 ˚C.

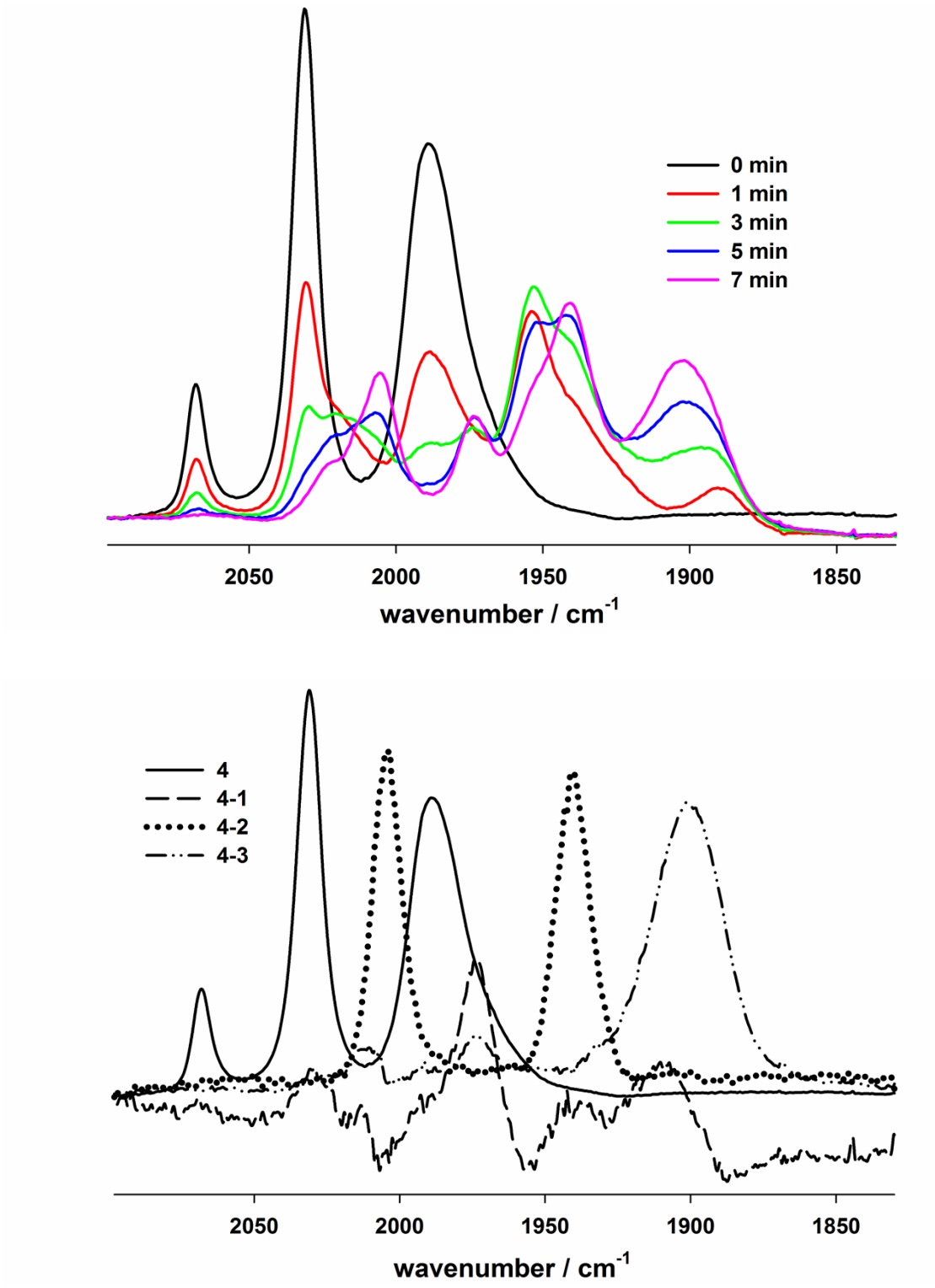



Fig. S2 Infrared spectral variation during the CO-releasing process of complex **4** ([**4**] = 0.011 mol $L^{-1}$ and [**CysA**] = 0.066 mol $L^{-1}$) (top) and the intermediates in the

reaction mixture (bottom), when the reaction proceeded for 1 min (4-1), 3 min (4-2) and 7 min (4-3), respectively, in DMSO at 37 ˚C.

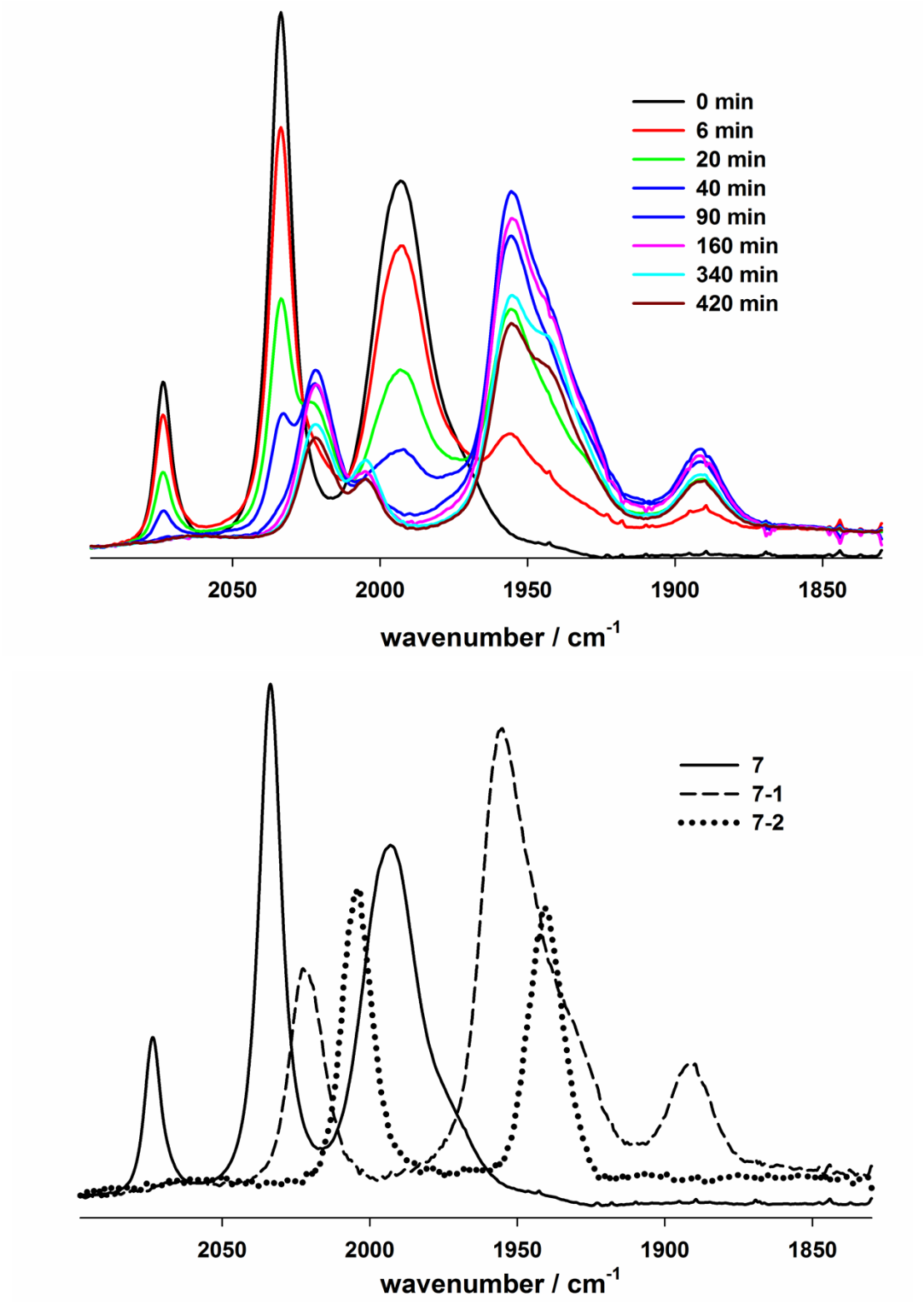



Fig. S3 Infrared spectral variation during the CO-releasing process of complex **7** ([**7**]

= 0.011 mol $L^{-1}$ and [**CysA**] = 0.066 mol $L^{-1}$) (top) and the intermediates in the reaction mixture (bottom), when the reaction proceeded for 260 min (7-1) and 320 min (7-2), respectively, in DMSO at 37 ˚C.

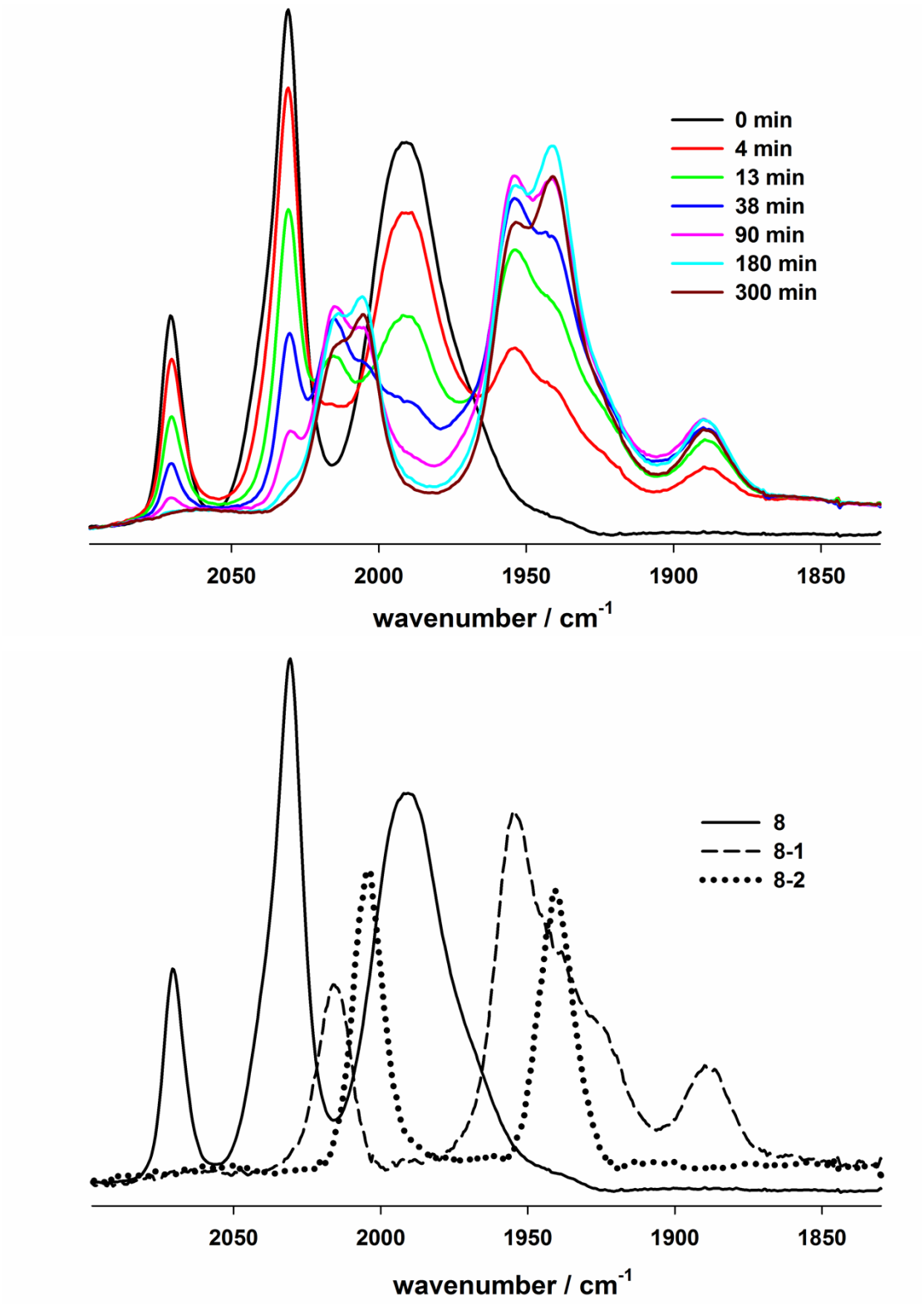



Fig. S4 Infrared spectral variation during the CO-releasing process of complex **8** ([**8**]

= 0.011 mol $L^{-1}$ and [**CysA**] = 0.066 mol $L^{-1}$) (top) and the intermediates in the reaction mixture (bottom), when the reaction proceeded for 260 min (8-1) and 320 min (8-2), respectively, in DMSO at 37 ˚C.

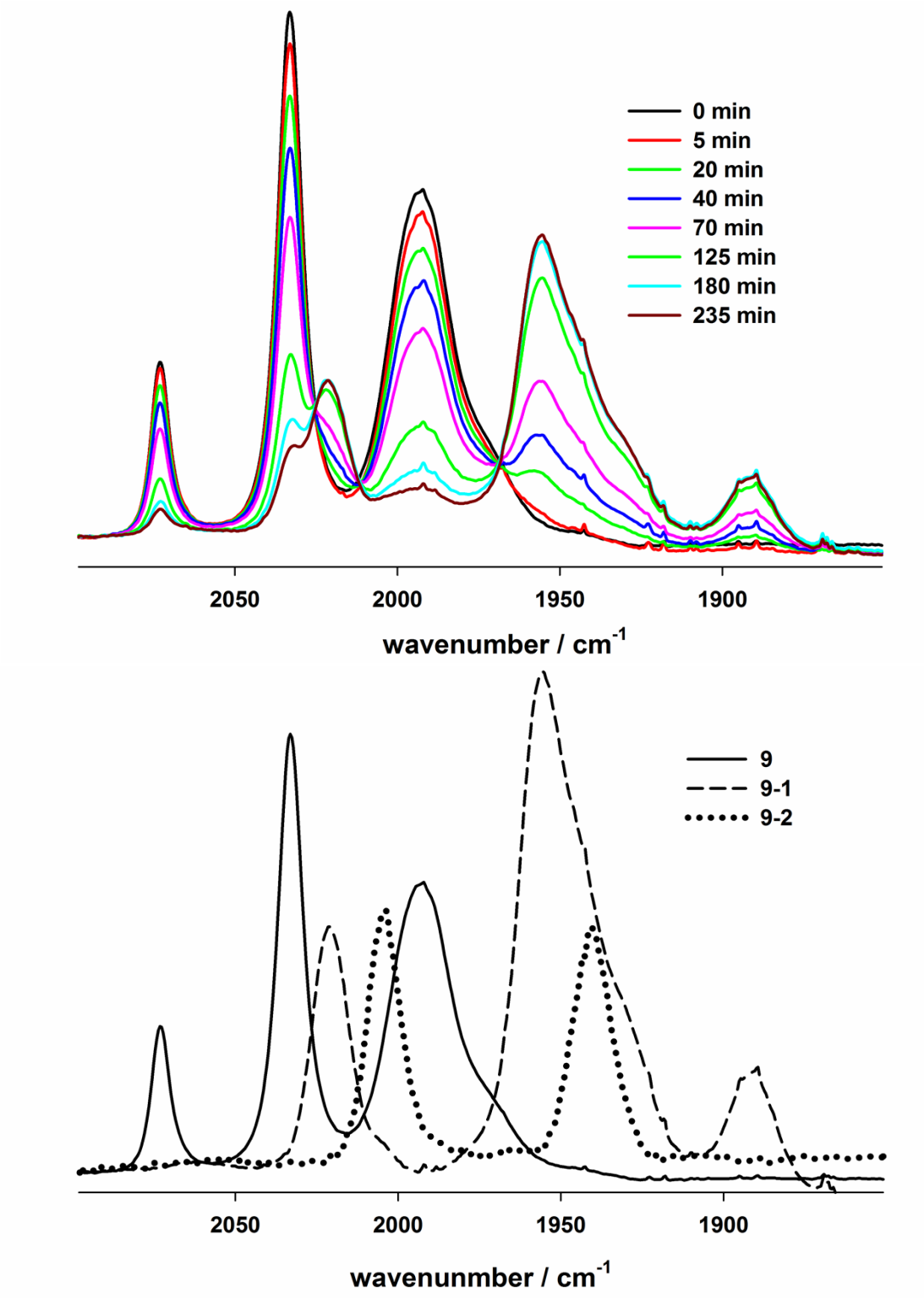



Fig. S5 Infrared spectral variation during the CO-releasing process of complex **9** ([**9**]

= 0.011 mol $L^{-1}$ and [**CysA**] = 0.066 mol $L^{-1}$) (top) and the intermediates in the reaction mixture (bottom), when the reaction proceeded for 70 min (9-1) and 235 min (9-2), respectively, in DMSO at 37 ˚C.

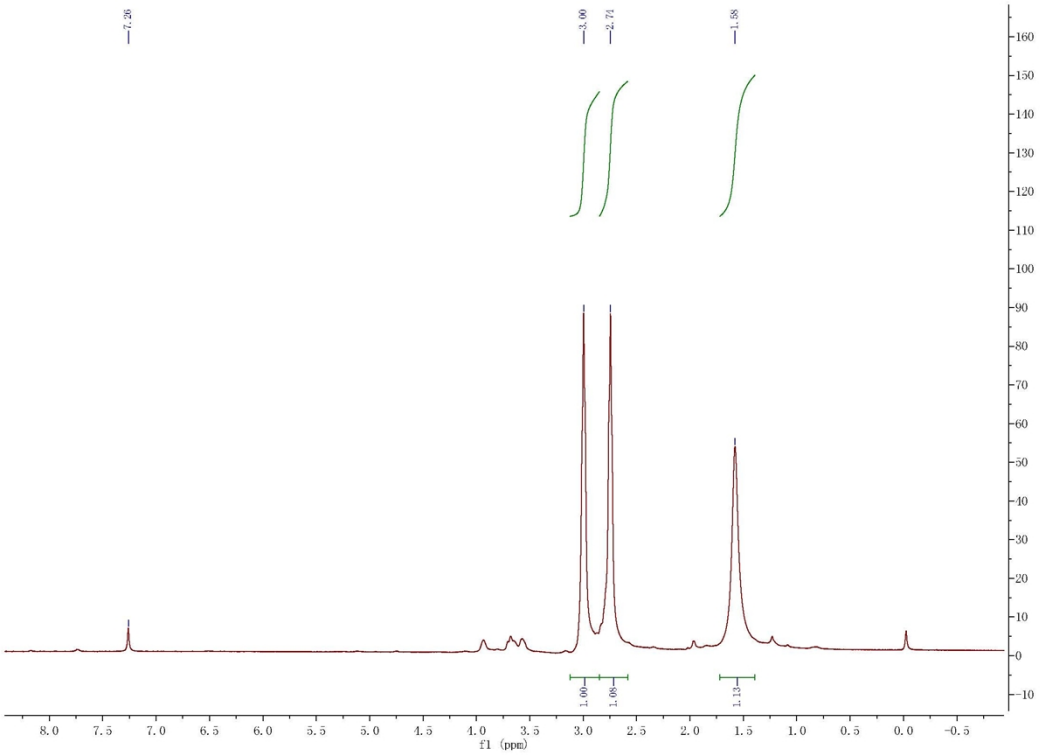



Fig. S6 $^{1}$H NMR spectra of the final decomposition product for complex **4** ($CD_3Cl$).

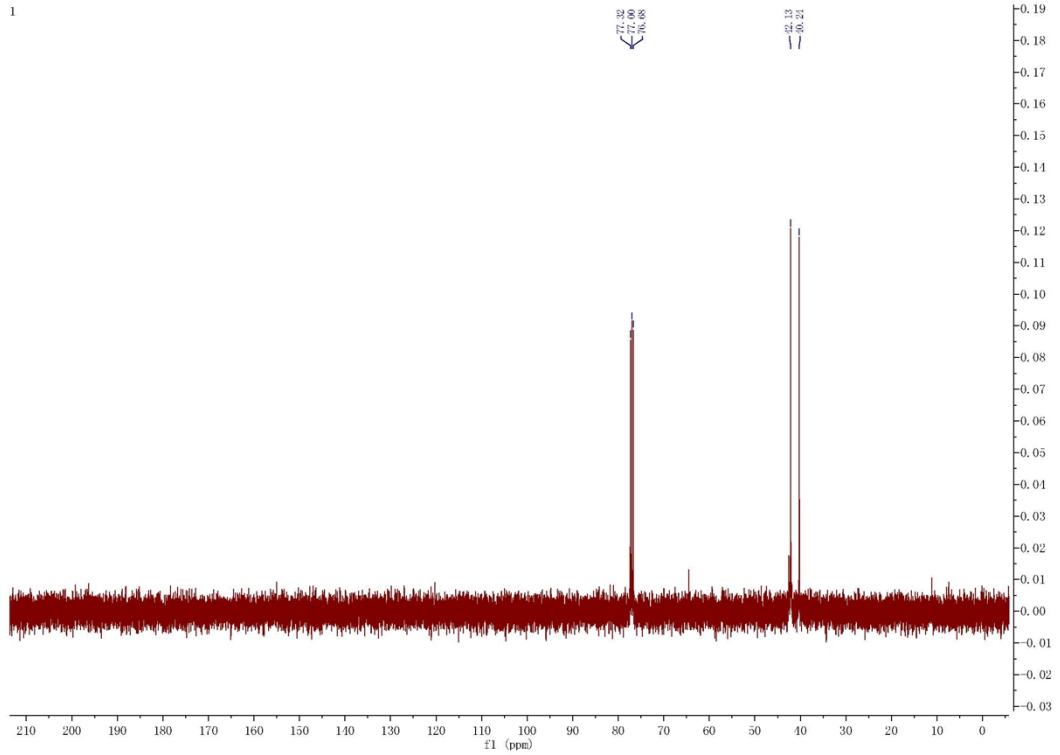



Fig. S7 $^{13}C$ NMR spectra of the final decomposition product for complex **4** ($CD_3Cl$).

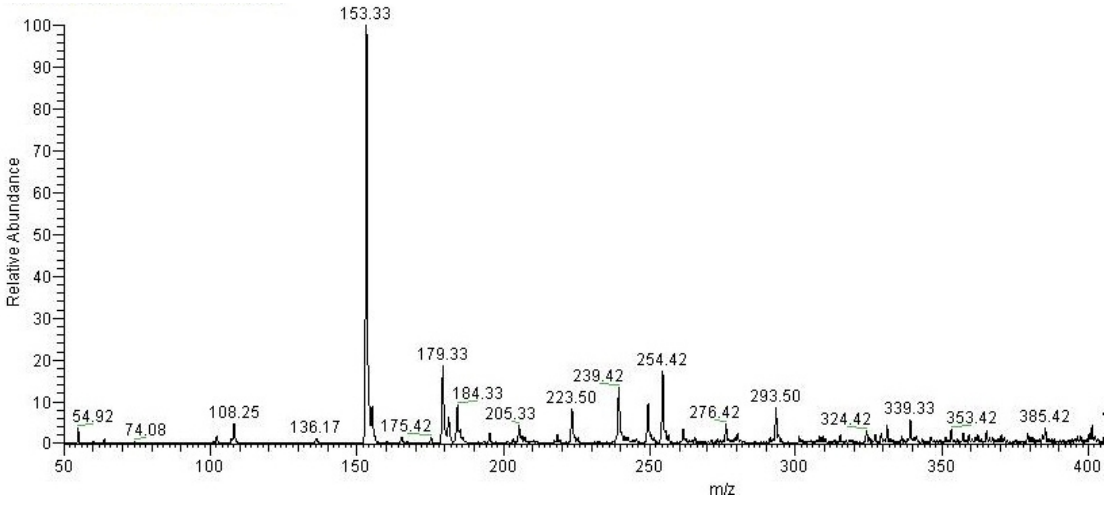
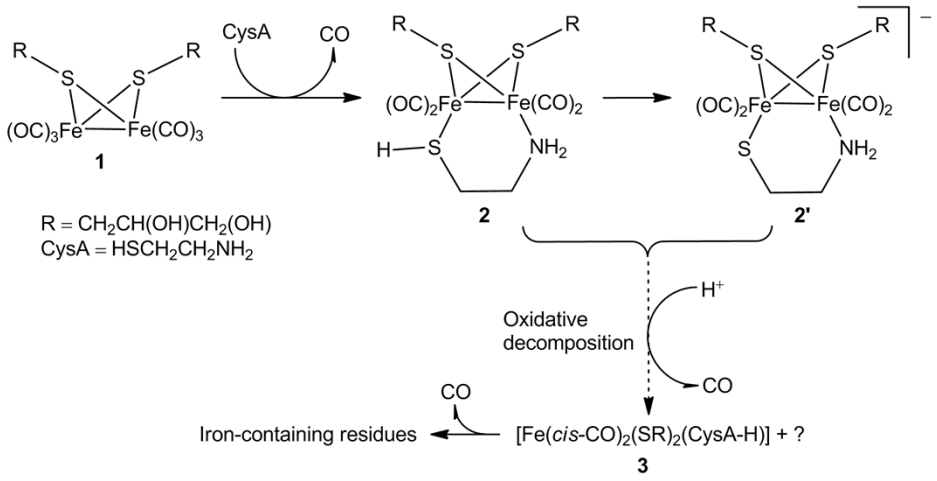



Fig. S8 Mass spectra of the final decomposition product for complex **4** (ESI, cation; the final decomposition product was obtained via the reaction of complex **4** with 6 equivalents of **CysA** under inert atmosphere at room temperature for 24 h).

Table S1 DFT calculation results and the $k_{obs}$ of the compounds

| Complex | Metal centre | $k_{obs}$ | NAP charges (e) |
|---|---|---|---|
| **1** | $\{Fe_2\}$ | | -3.16876 |
| **2** | $\{Fe_2\}$ | 0.806 | -3.17676 |
| **3** | $\{Fe_2\}$ | 0.596 | -3.16479 |
| **4** | $\{Fe_2\}$ | 0.537 | -3.16032 |
| **5** | $\{Fe_2\}$ | 0.319 | -3.20218 |
| **6** | $\{Fe_2\}$ | 0.108 | -3.20754 |
| **7** | $\{Fe_2\}$ | 0.034 | -3.27582 |
| **8** | $\{Fe_2\}$ | 0.026 | -3.26473 |
| **9** | $\{Fe_2\}$ | 0.022 | -3.25846 |




Scheme S1 Possible pathways of substitution-initiated CO-releasing from complex **4** by **CysA** under inert atmosphere [41].