Supporting Information

Three Switchable Orthogonal Dynamic Covalent Reactions and Complex Networks Based on the Control of Dual Reactivity

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^{1}H NMR and ^{13}C NMR spectra

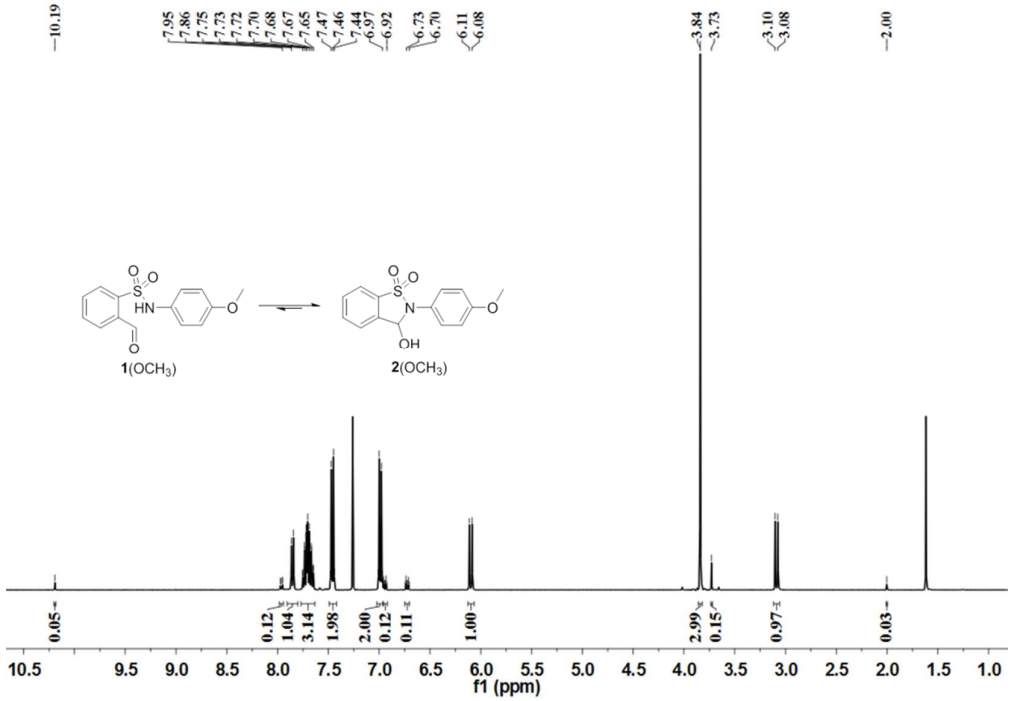


Figure S1. ^{1}H NMR spectrum of **2**(OCH_3) in $CDCl_3$. The ratio of **1**(OCH_3) and **2**(OCH_3) is 1:20.

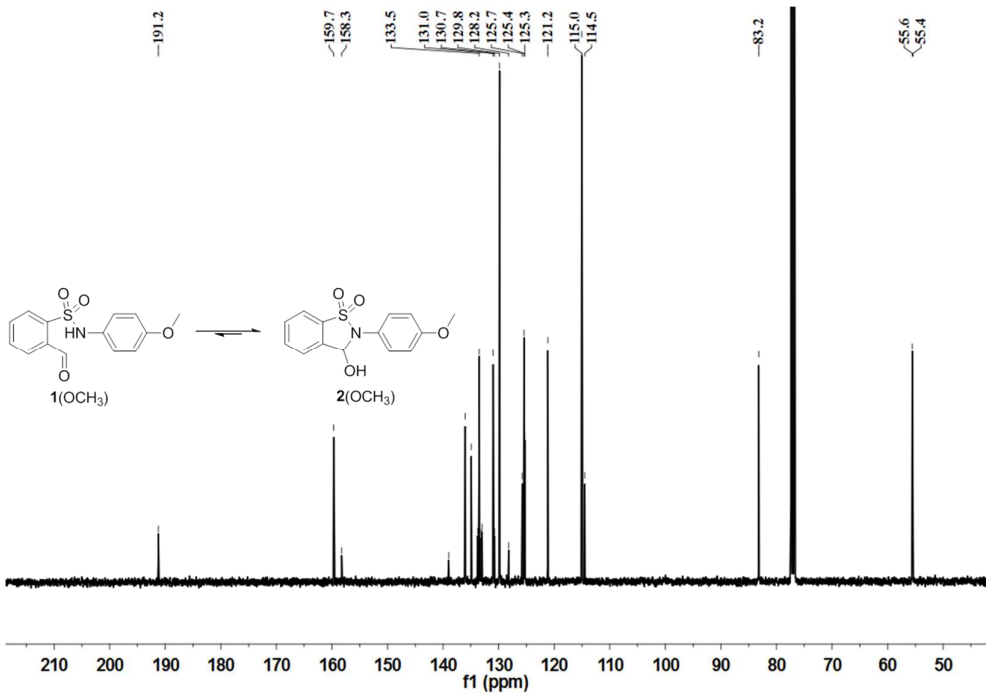


Figure S2. ^{13}C NMR spectrum of **2**(OCH_3) in $CDCl_3$.

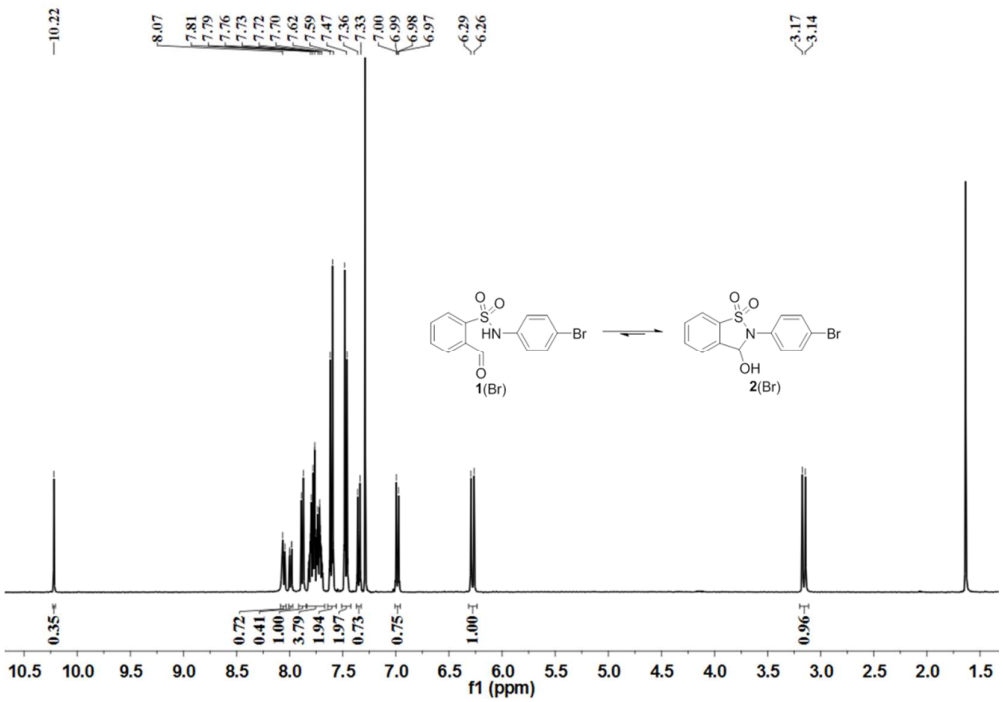


Figure S3. ^{1}H NMR spectrum of **2**(Br) in $CDCl_3$. The ratio of **1**(Br) and **2**(Br) is 7:20.

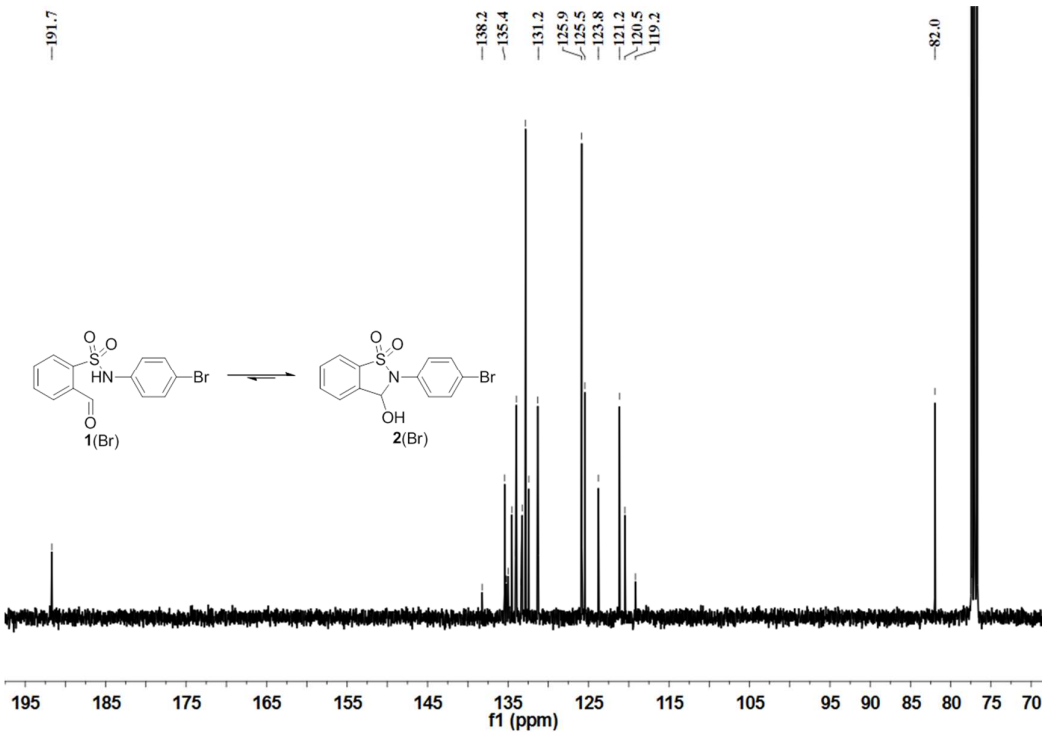


Figure S4. ^{13}C NMR spectrum of **2**(Br) in $CDCl_3$.

Regulation of 1 and 2

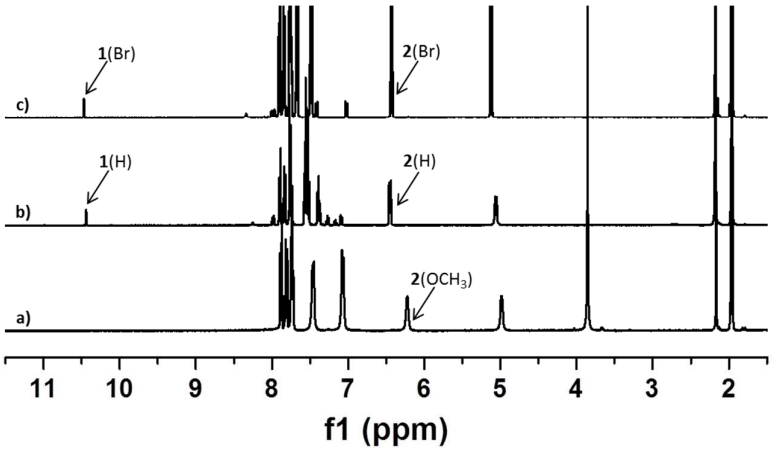


Figure S5. (a) ^{1}H NMR spectrum of the equilibrium between **1**(OCH_3) and **2**(OCH_3) in CD_3CN; (b) ^{1}H NMR spectrum of the equilibrium between **1**(H) and **2**(H) in CD_3CN; (c) ^{1}H NMR spectrum of the equilibrium between **1**(Br) and **2**(Br) in CD_3CN.

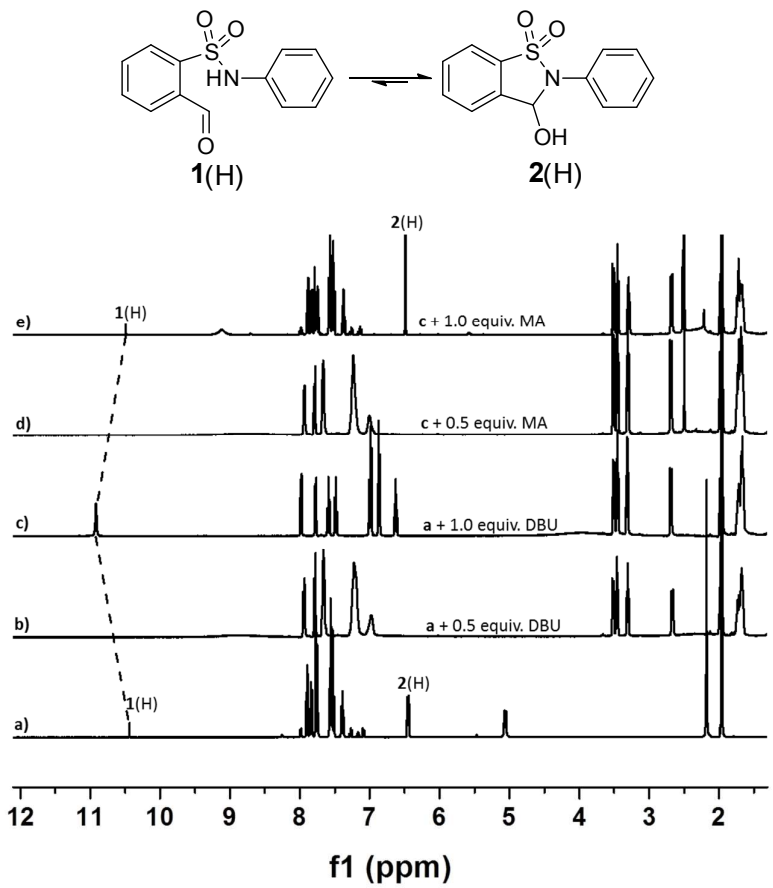


Figure S6. ^{1}H NMR spectra of **2**(H) (a) as well as the titration of 0.5 equiv. (b) and 1.0 equiv. (c) of DBU. To the solution in panel c, was then added 0.5 equiv. (d) and 1.0 equiv. (e) of MA. This figure shows the details and full spectra of Figure 2C in the main text.

2. Dynamic Covalent Reactions (DCRs)

DCRs with RNH_2

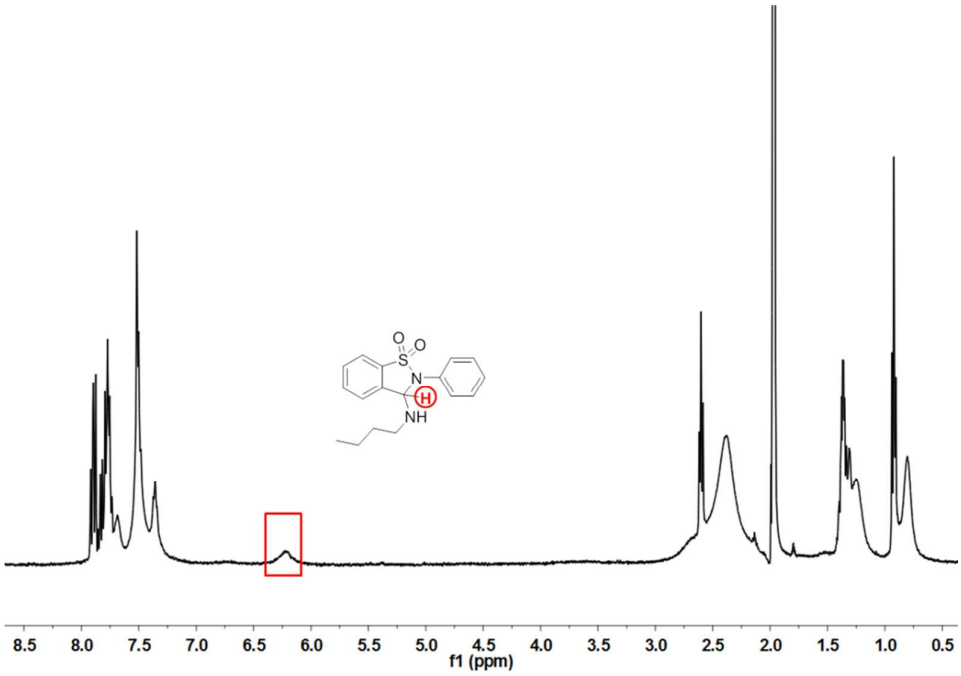
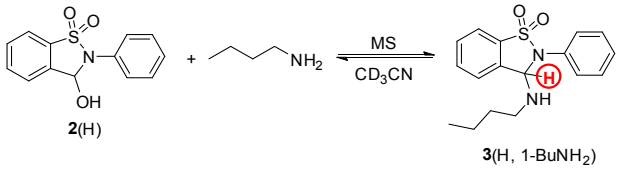


Figure S7. ^{1}H NMR spectrum of the reaction of **2**(H) and 1-butylamine in CD_3CN.



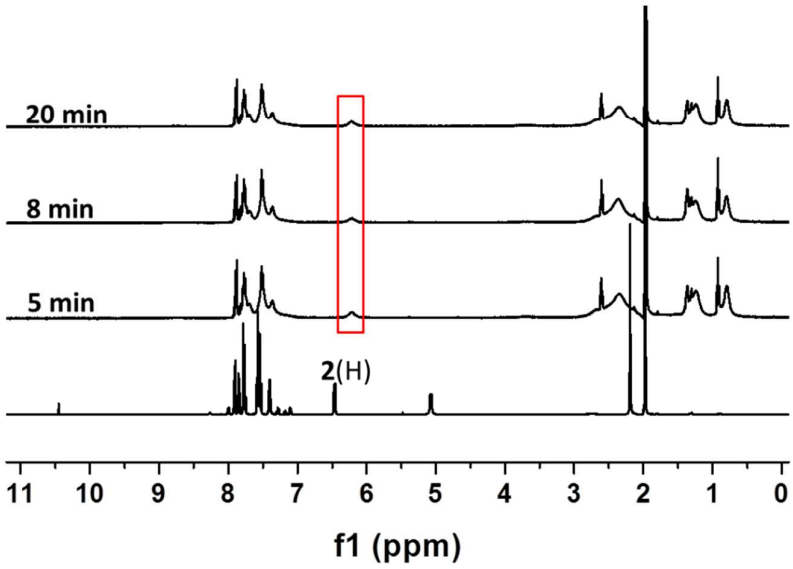


Figure S8. ^{1}H NMR spectra of the reaction of **2**(H) and 1-butylamine in CD_3CN at varied time.

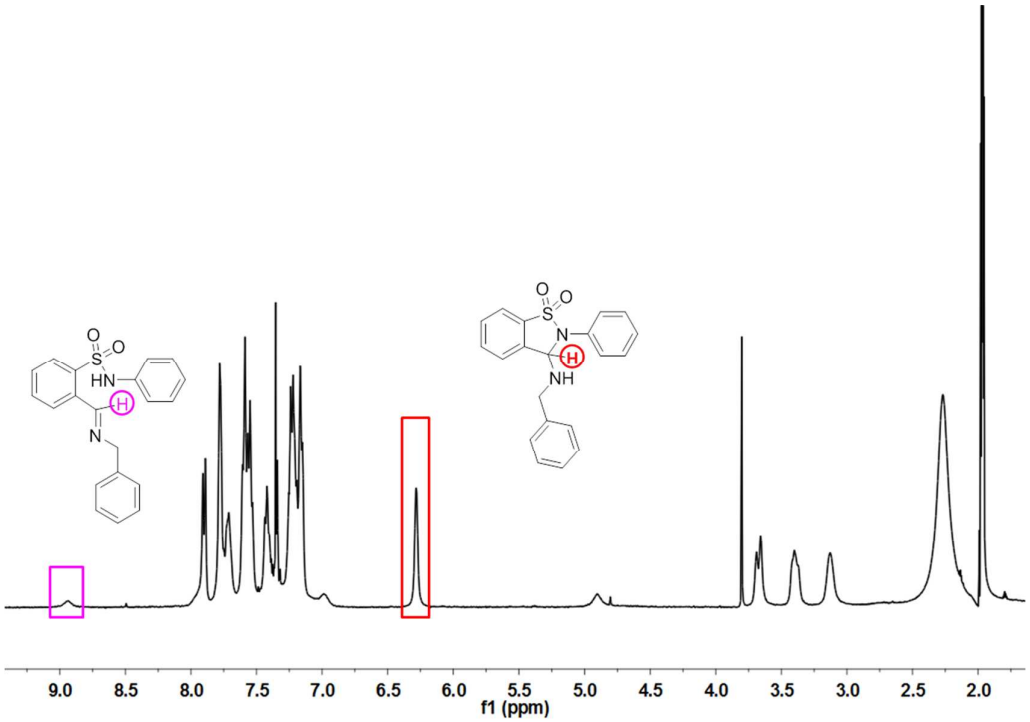


Figure S9. ^{1}H NMR spectrum of the reaction of **2**(H) and benzylamine in CD_3CN.

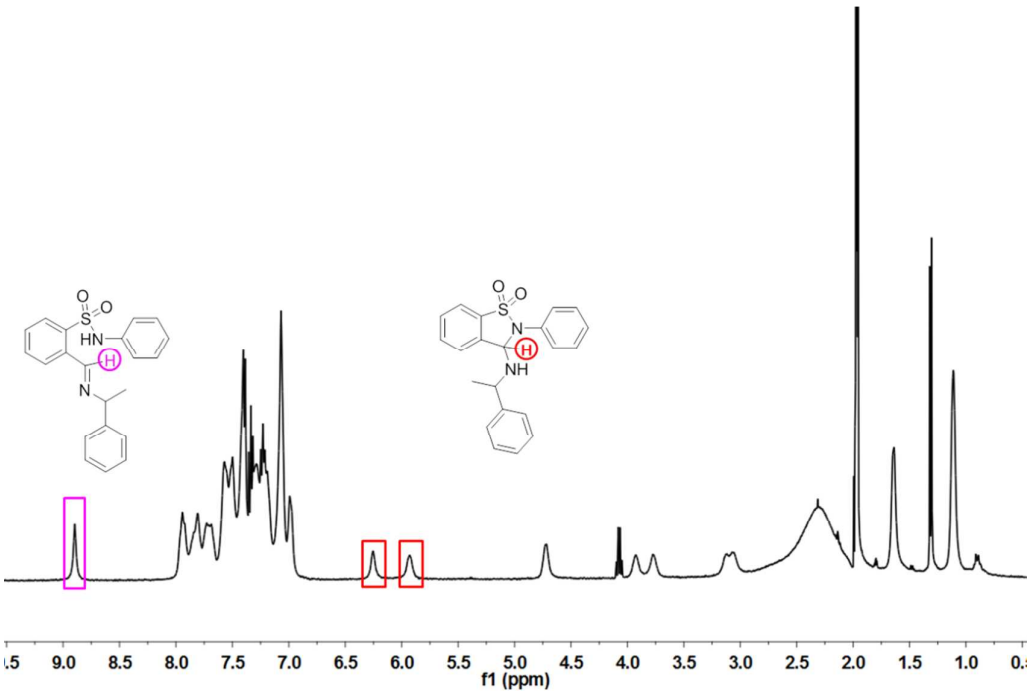


Figure S10. ^{1}H NMR spectrum of the reaction of **2**(H) and 1-phenylethylamine in CD_3CN.

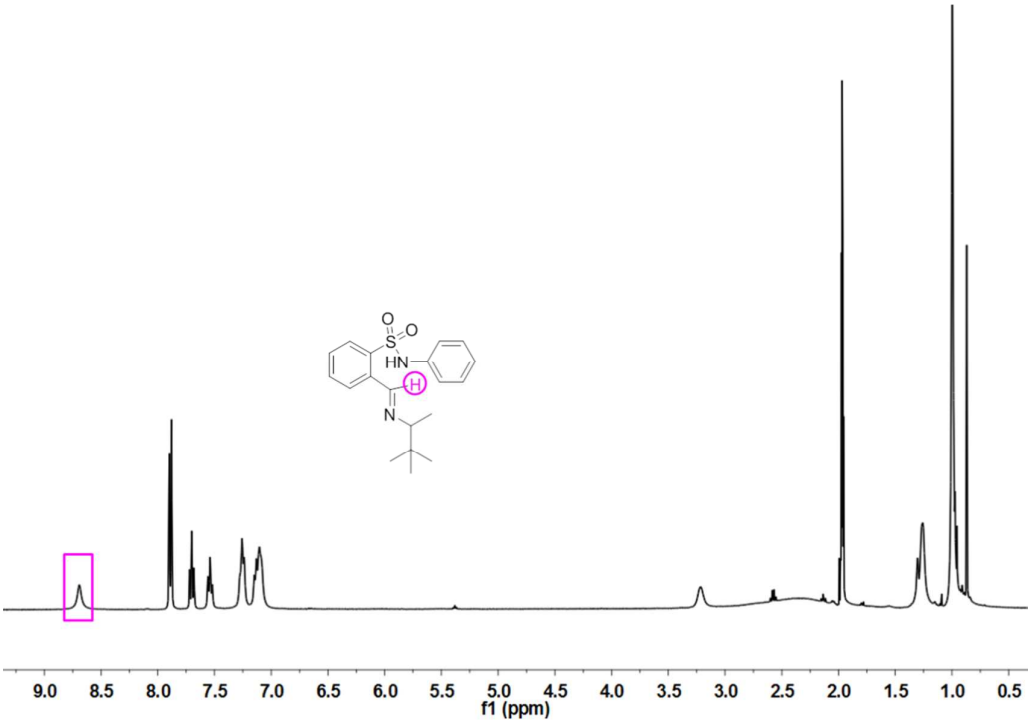


Figure S11. ^{1}H NMR spectrum of the reaction of **2**(H) and 3,3-dimethyl-2-butylamine in CD_3CN.

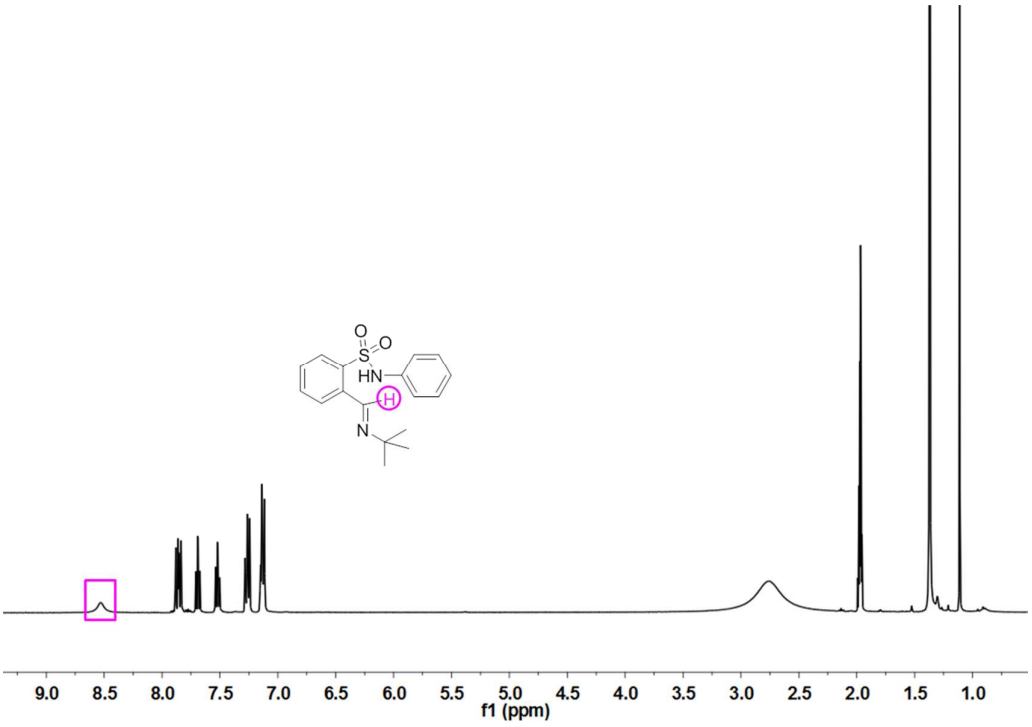


Figure S12. ^{1}H NMR spectrum of the reaction of **2**(H) and *t*-butylamine in CD_3CN.

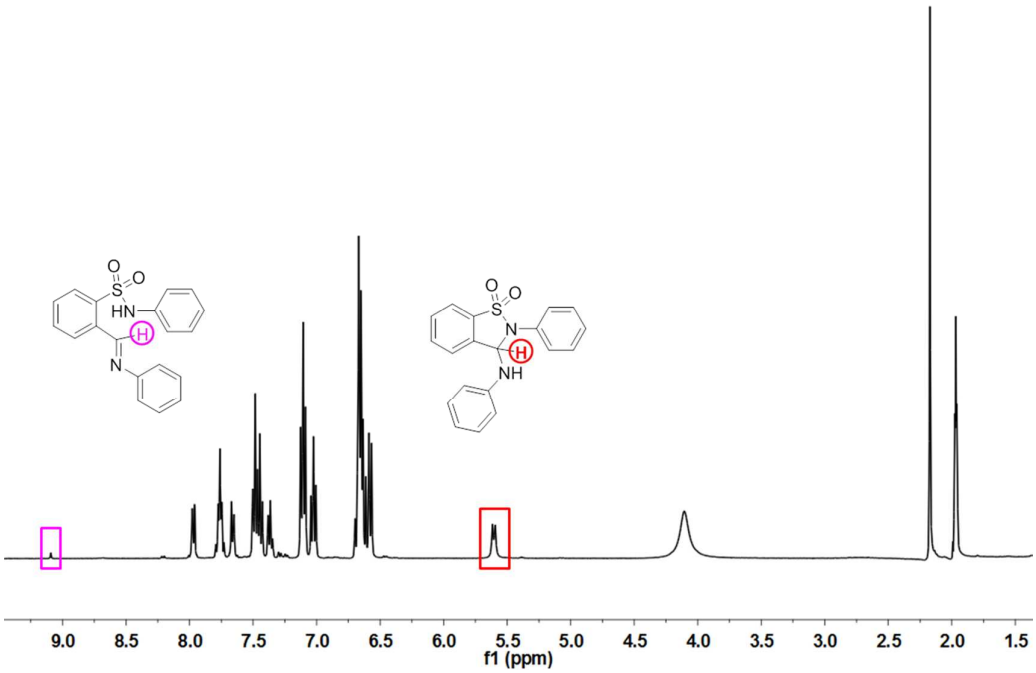


Figure S13. ^{1}H NMR spectrum of the reaction of **2**(H) (1.0 equiv.) and aniline (3.0 equiv.) in CD_3CN.

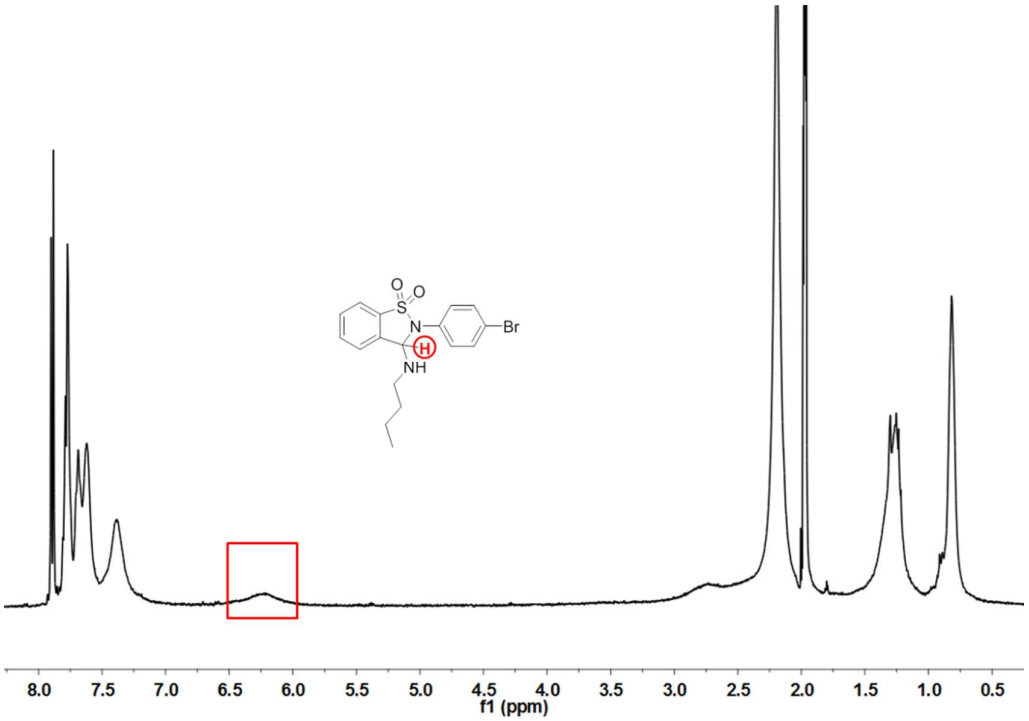


Figure S14. ^{1}H NMR spectrum of the reaction of **2**(Br) and 1-butylamine in CD_3CN.

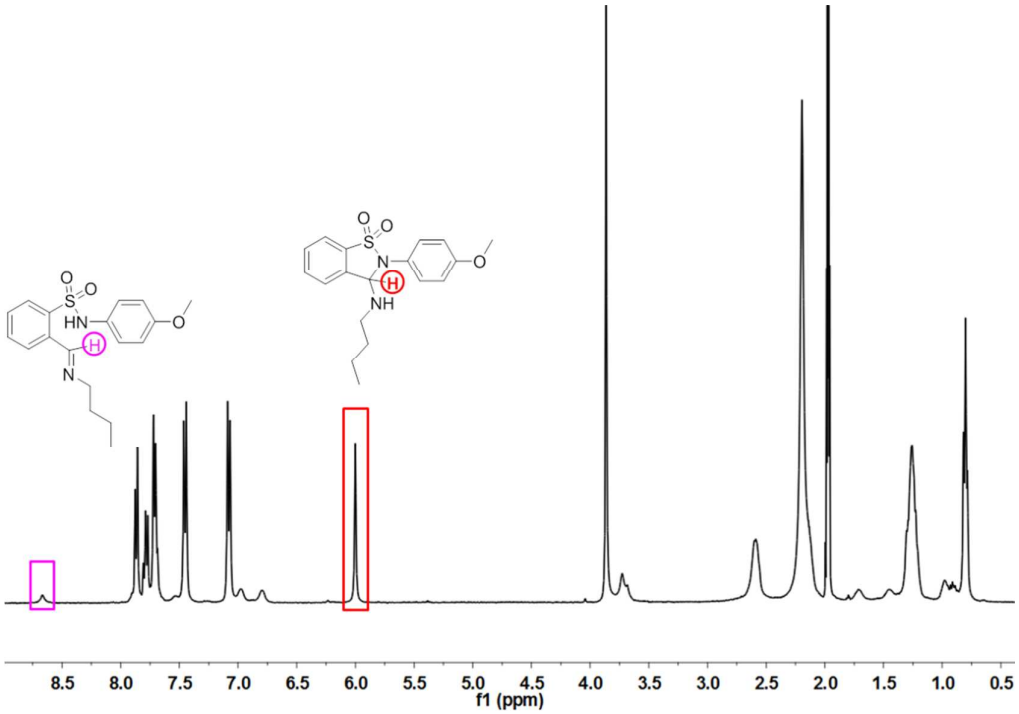


Figure S15. ^{1}H NMR spectrum of the reaction of **2**(OCH_3) and 1-butylamine in CD_3CN.

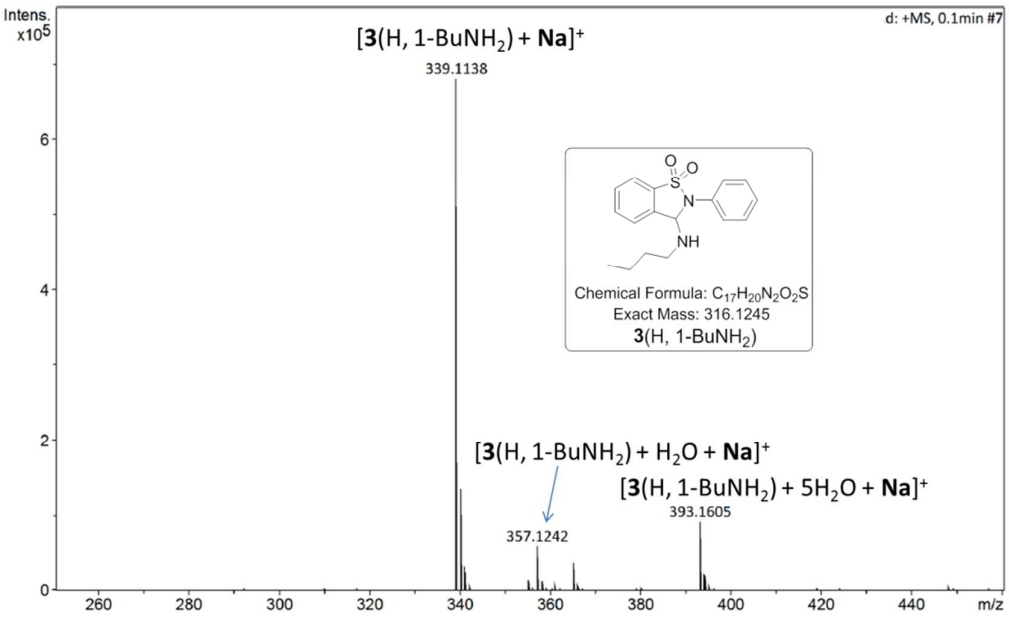


Figure S16. ESI mass spectrum of the reaction of **2**(H) and 1-butylamine in CD_3CN.

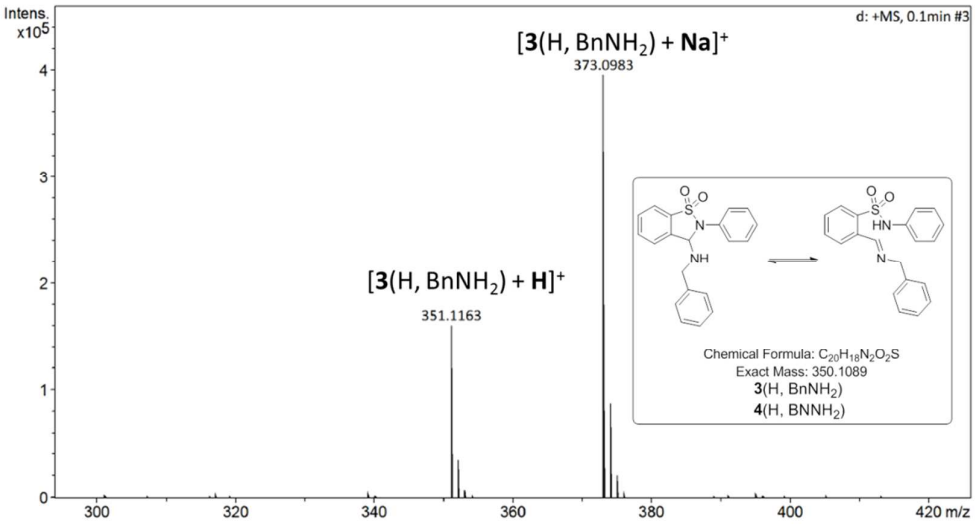


Figure S17. ESI mass spectrum of the reaction of **2**(H) and benzylamine in CD_3CN.

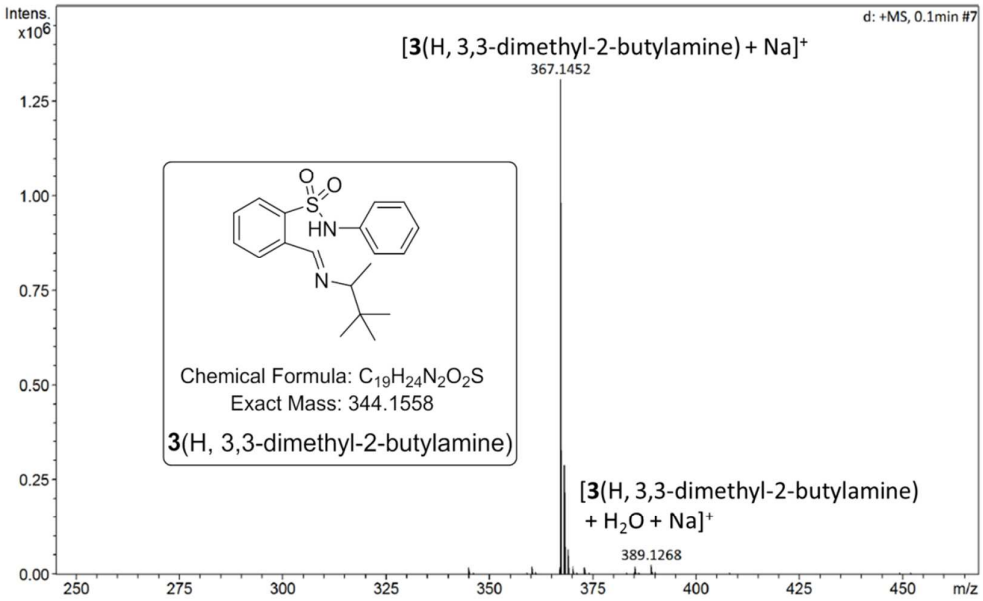


Figure S18. ESI mass spectrum of the reaction of **2**(H) and 3,3-dimethyl-2-butylamine in CD_3CN.

DCRs with R^1R^2NH

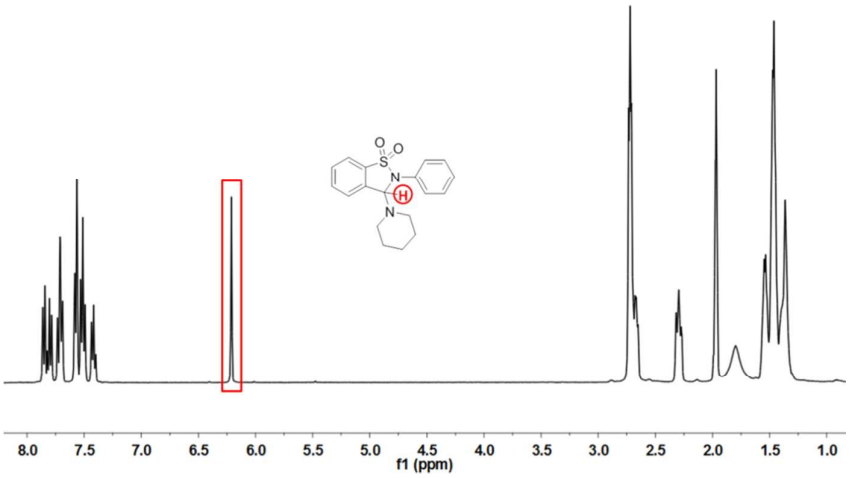


Figure S19. ^{1}H NMR spectrum of the reaction of **2**(H) and piperidine in CD_3CN.

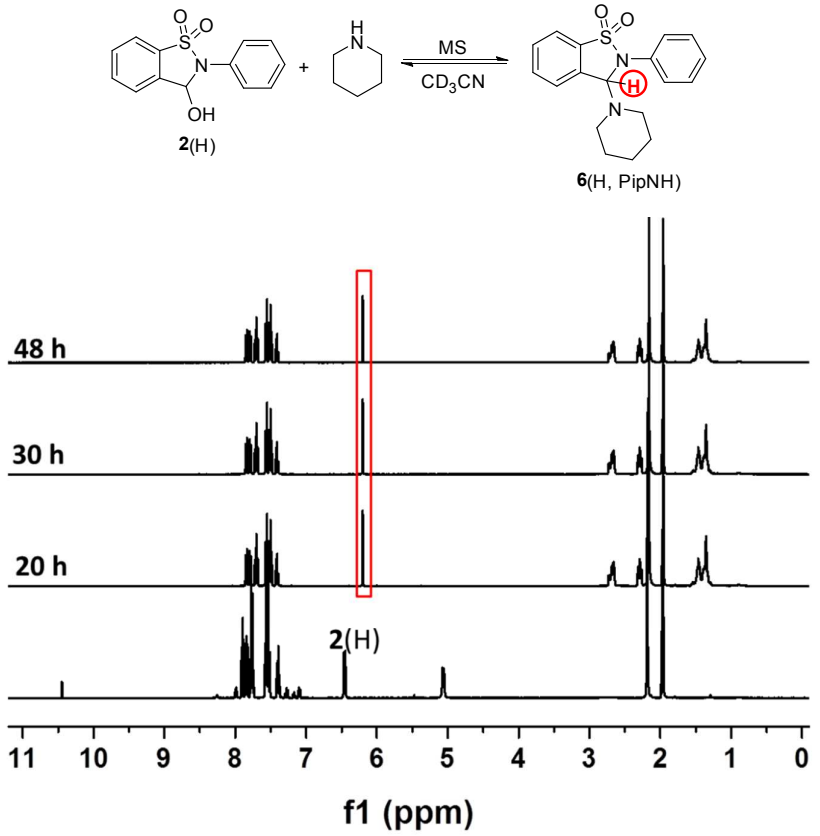


Figure S20. ^{1}H NMR spectra of the reaction of **2**(H) (1.0 equiv.) and piperidine (1.2 equiv.) in CD_3CN at varied time.

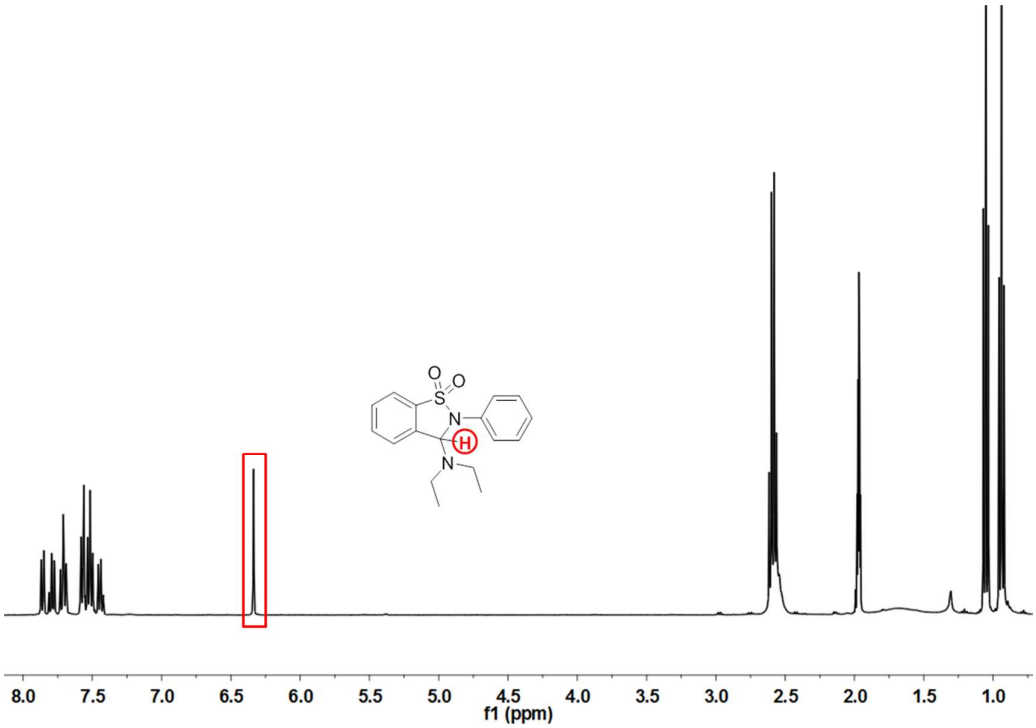


Figure S21. ^{1}H NMR spectrum of the reaction of **2**(H) and diethylamine in CD_3CN.

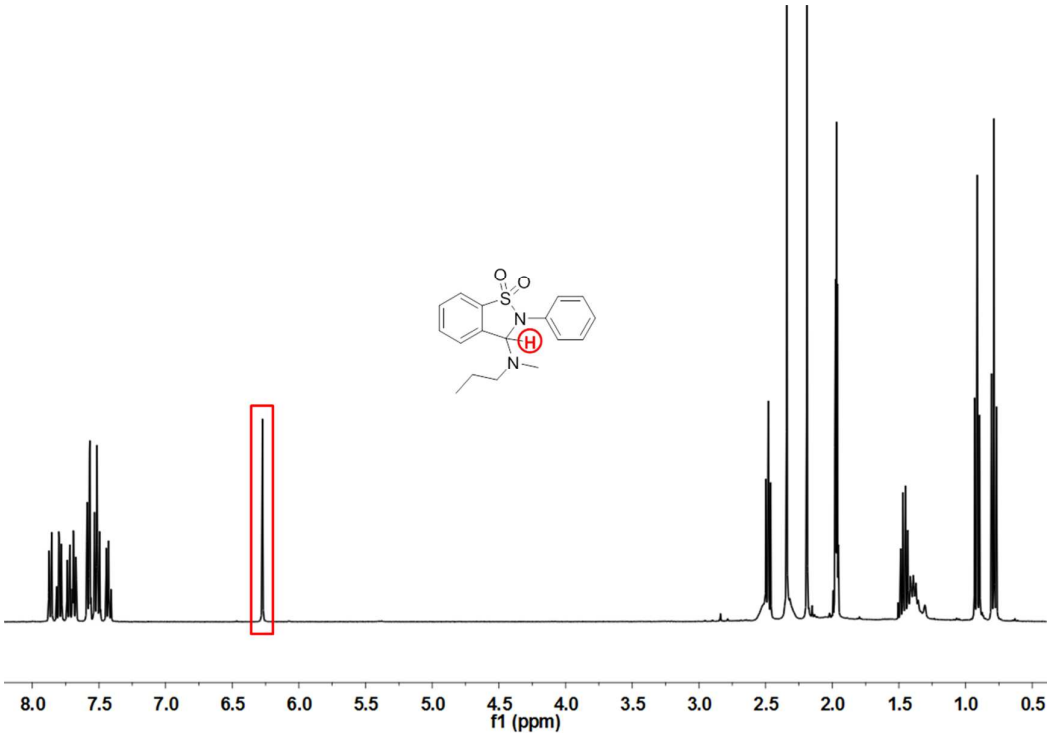


Figure S22. ^{1}H NMR spectrum of the reaction of **2**(H) and *N*-methyl-1-propylamine in CD_3CN.

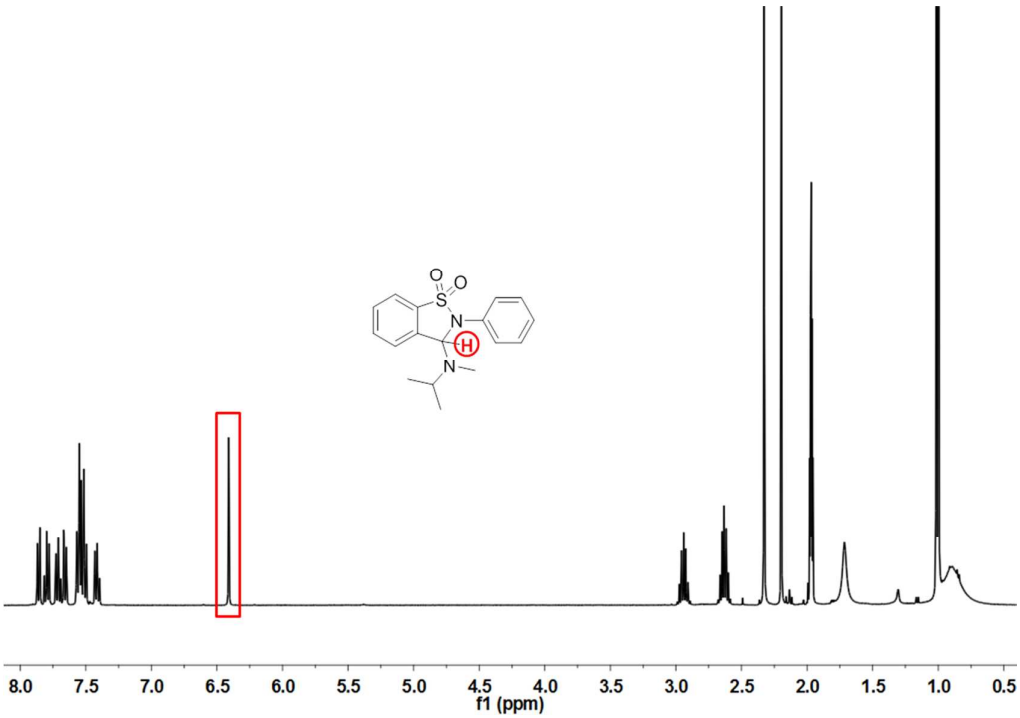


Figure S23. ^{1}H NMR spectrum of the reaction of **2**(H) and *N*-methyl-2-propylamine in CD_3CN.

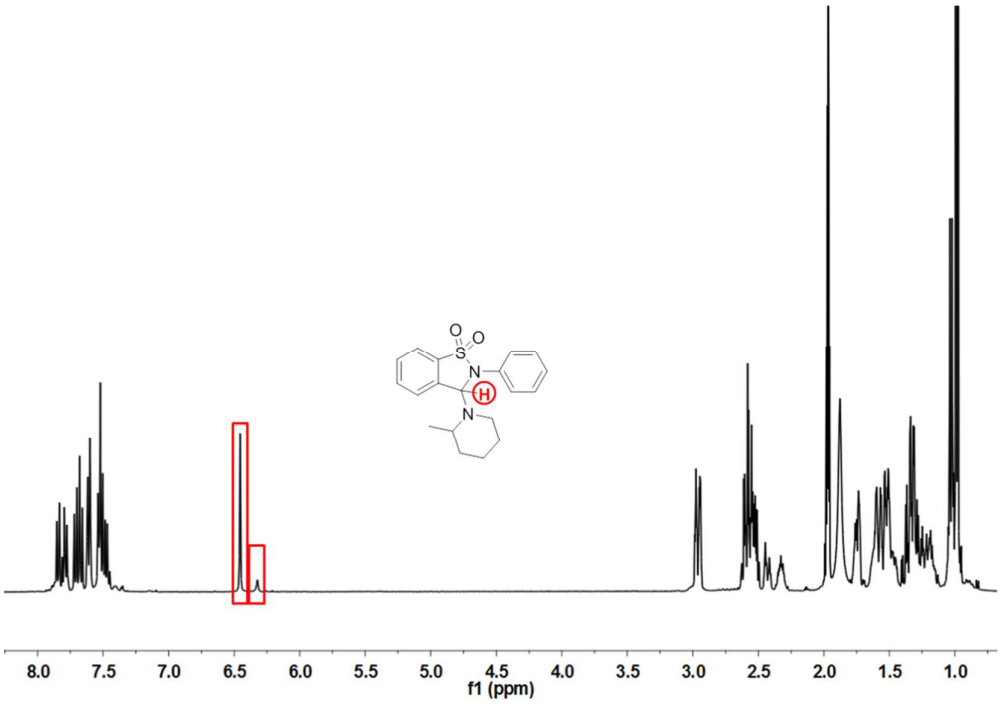


Figure S24. ^{1}H NMR spectrum of the reaction of **2**(H) and 2-methylpiperidine in CD_3CN.

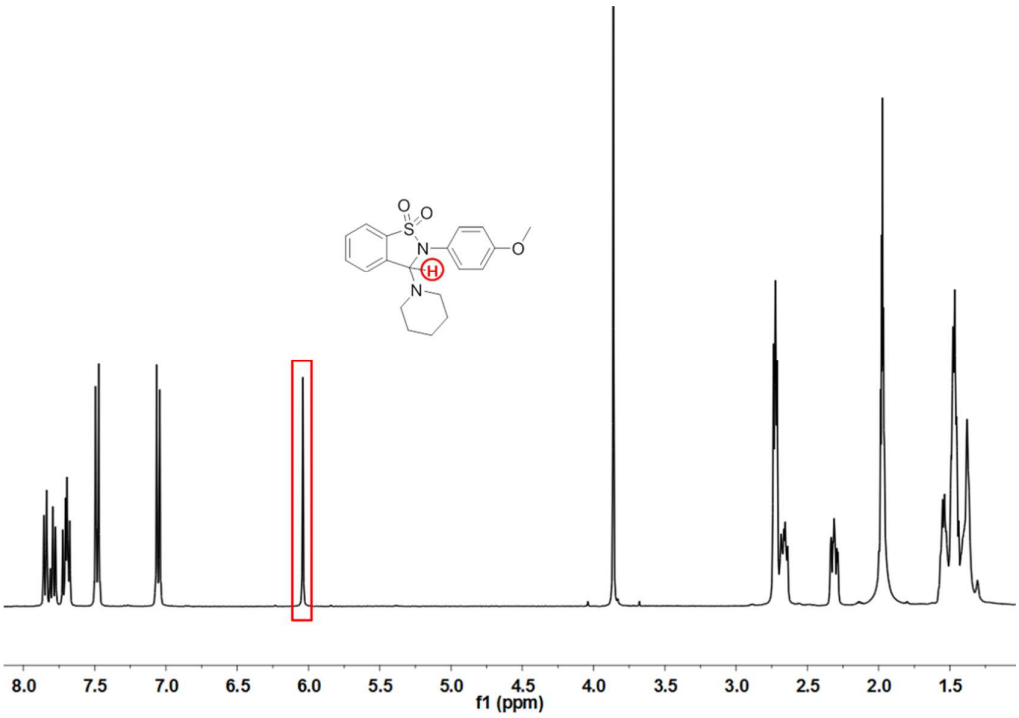


Figure S25. ^{1}H NMR spectrum of the reaction of **2**(OCH_3) and piperidine in CD_3CN.

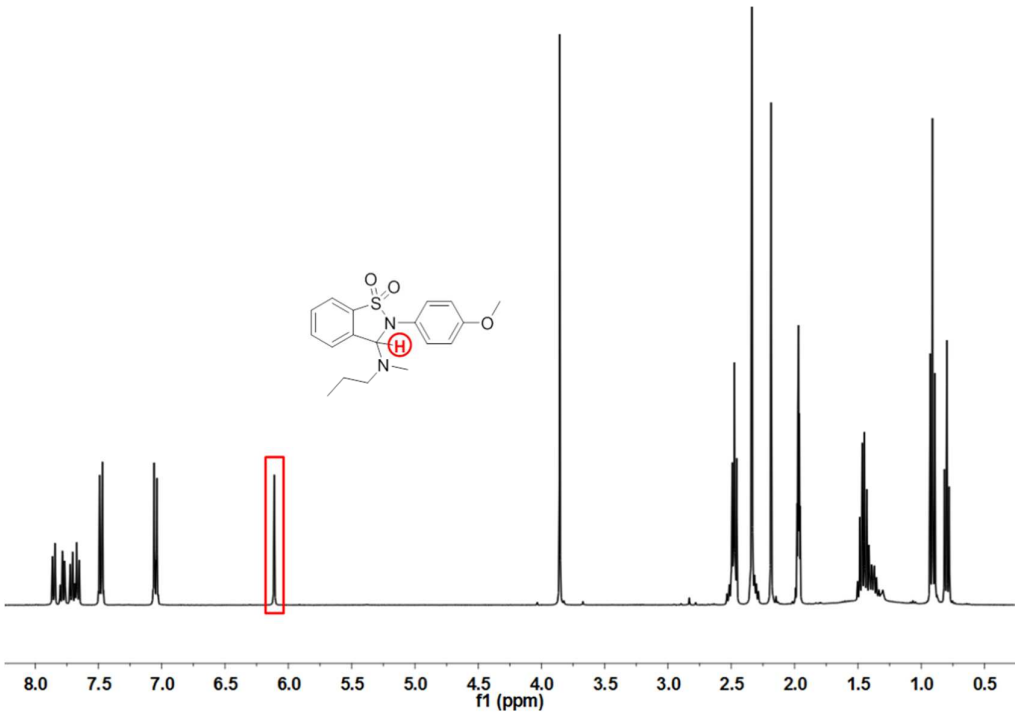


Figure S26. ^{1}H NMR spectrum of the reaction of **2**(OCH_3) and *N*-methyl-1-propylamine in CD_3CN.

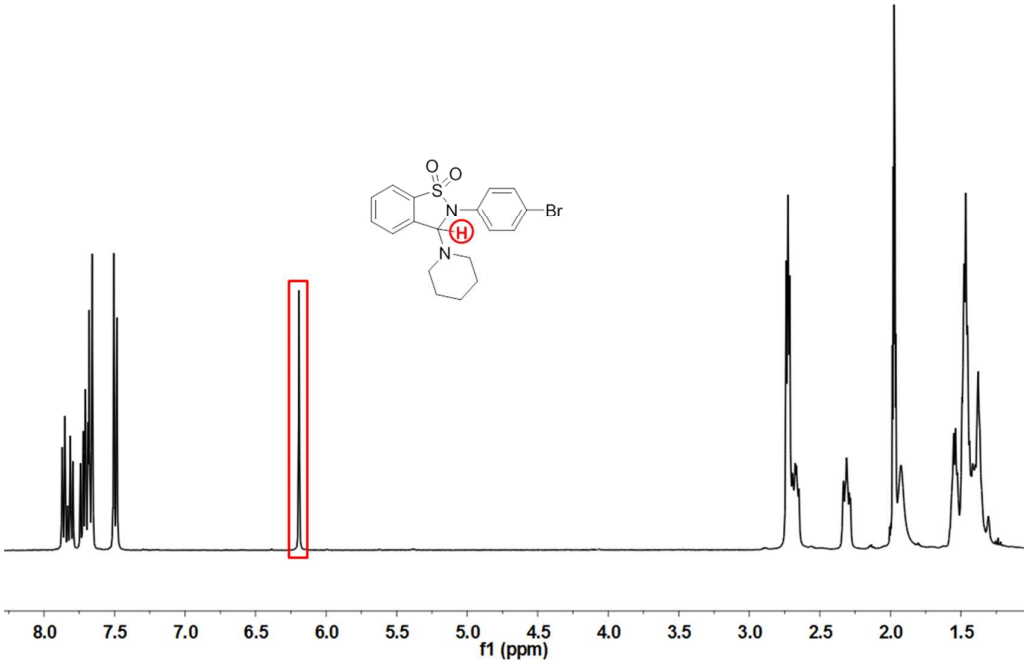


Figure S27. ^{1}H NMR spectrum of the reaction of **2**(Br) and piperidine in CD_3CN.

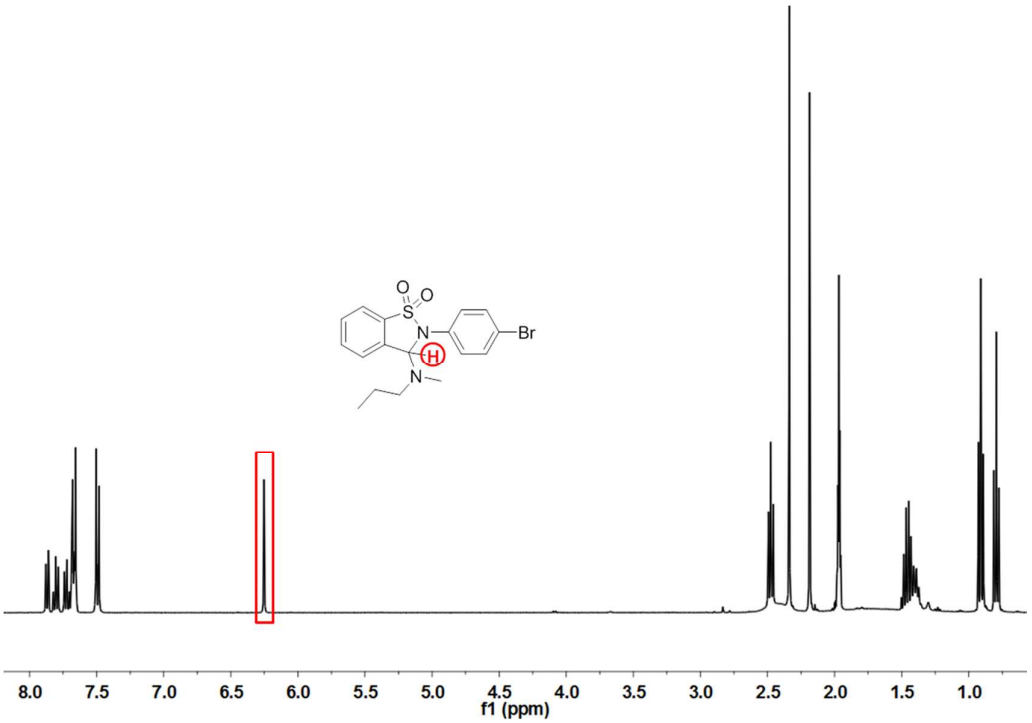


Figure S28. ^{1}H NMR spectrum of the reaction of **2**(Br) and *N*-methyl-1-propylamine in CD_3CN.

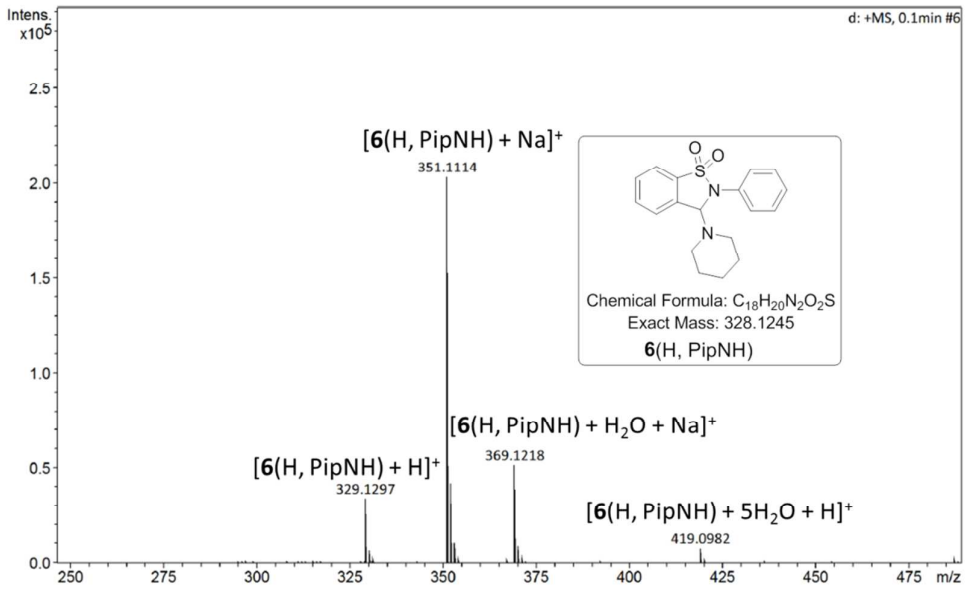


Figure S29. ESI mass spectrum of the reaction of **2**(H) and piperidine in CD_3CN.

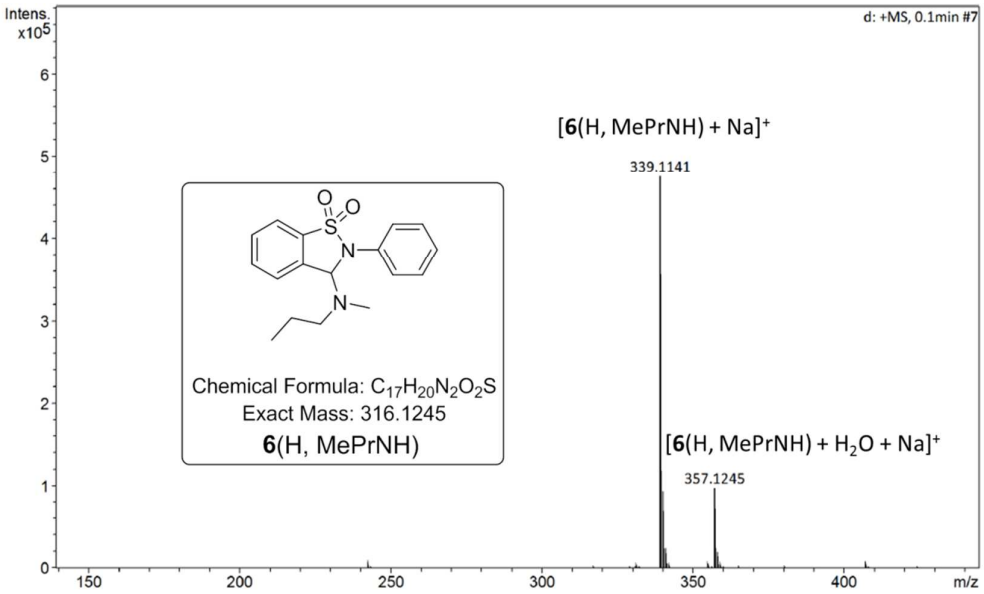


Figure S30. ESI mass spectrum of the reaction of **2**(H) and *N*-methyl-1-propylamine in CD_3CN.

DCRs with ROH

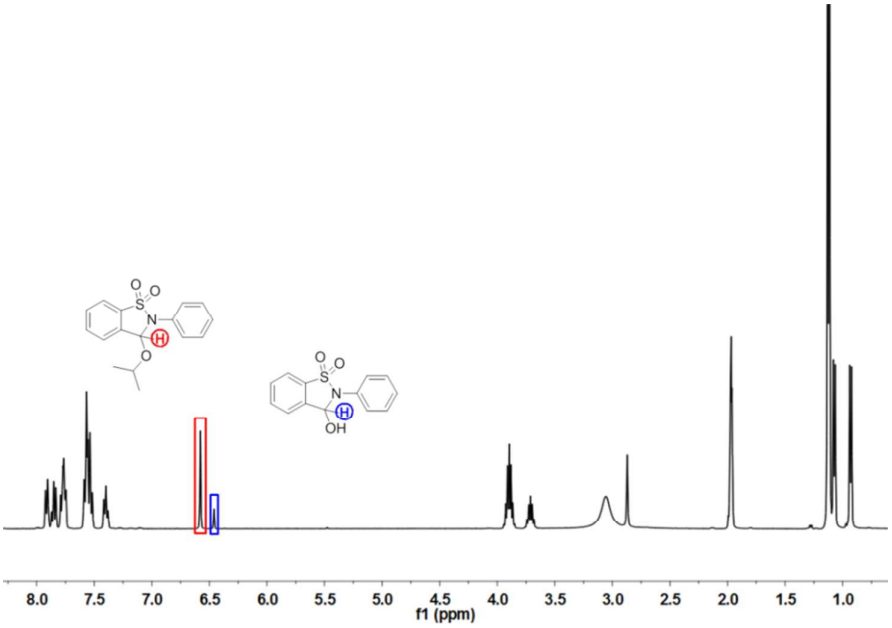
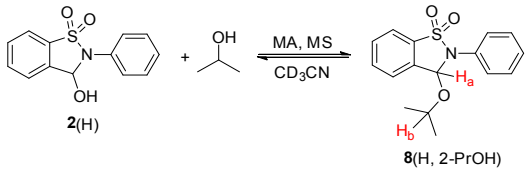


Figure S31. ^{1}H NMR spectrum of the reaction of **2**(H) and 2-propanol in CD_3CN.



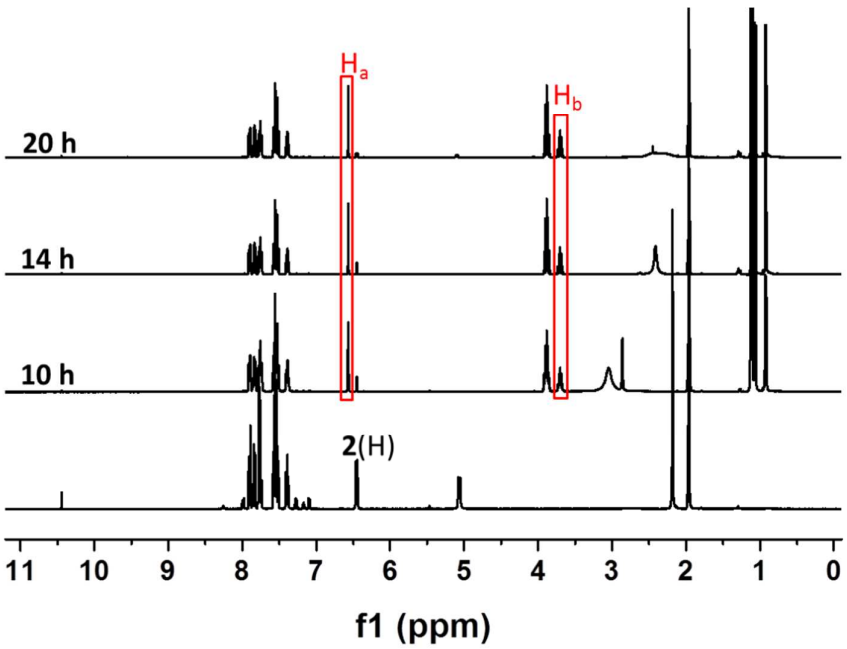


Figure S32. ^{1}H NMR spectra of the reaction of **2**(H) and 2-propanol in CD_3CN at varied time.

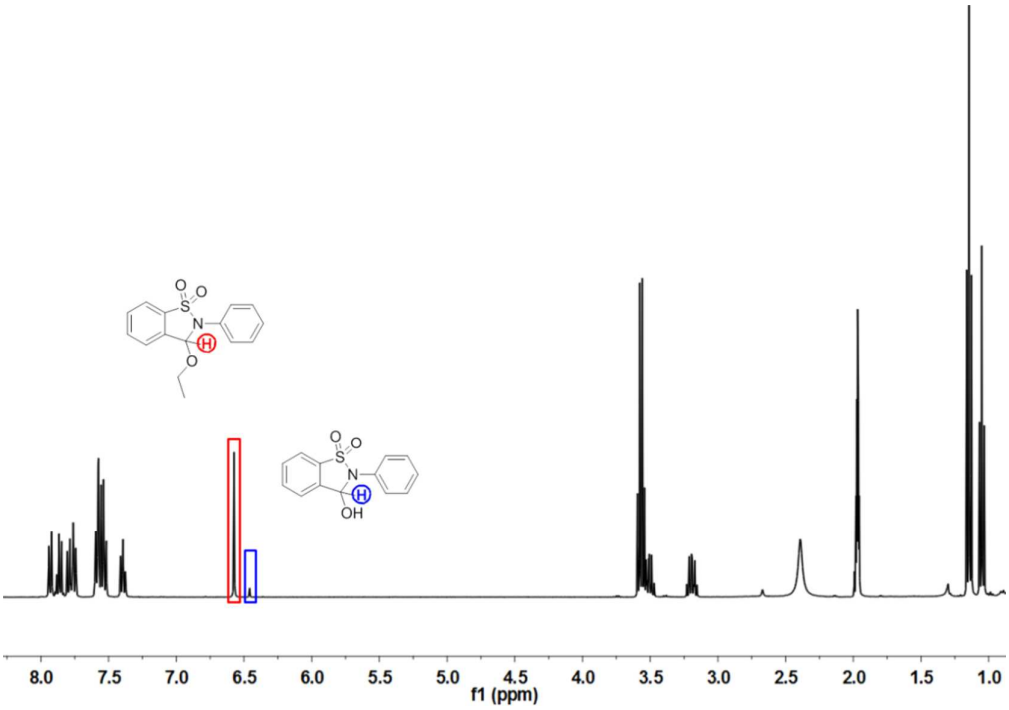


Figure S33. ^{1}H NMR spectrum of the reaction of **2**(H) and ethanol in CD_3CN.

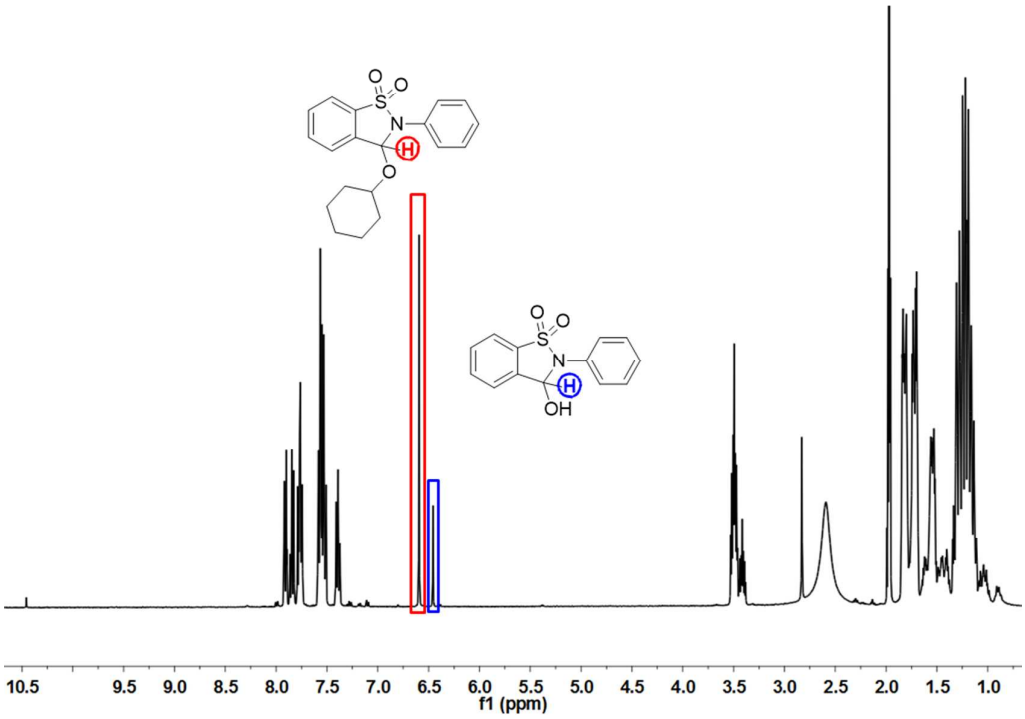


Figure S34. ^{1}H NMR spectrum of the reaction of **2**(H) and cyclohexanol in CD_3CN.

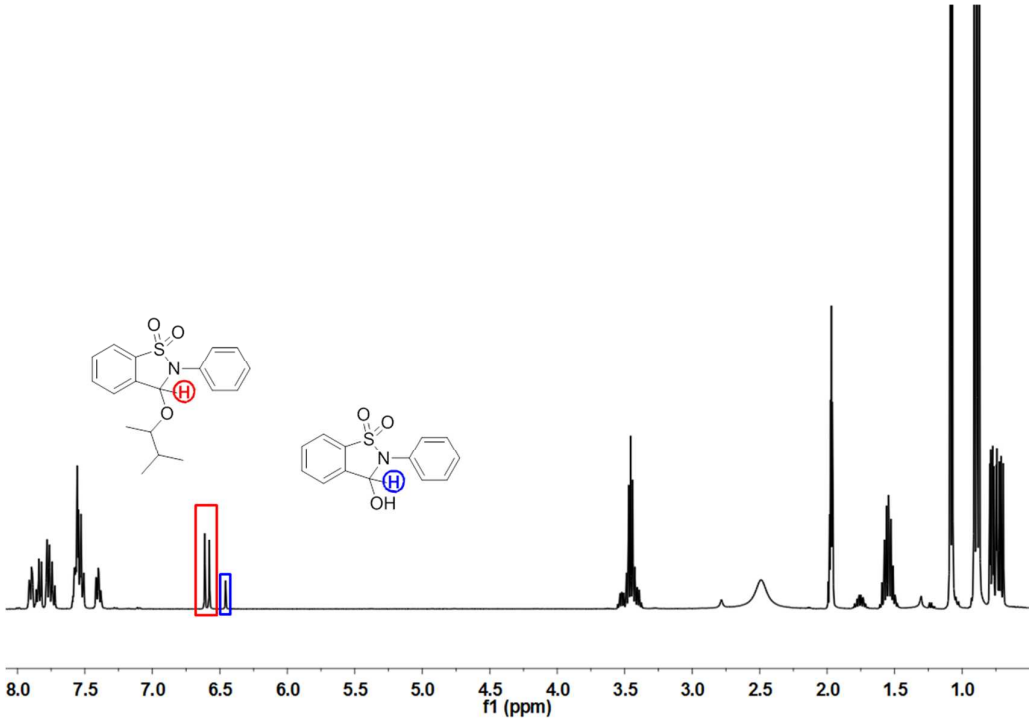


Figure S35. ^{1}H NMR spectrum of the reaction of **2**(H) and 3-methyl-2-butanol in CD_3CN.

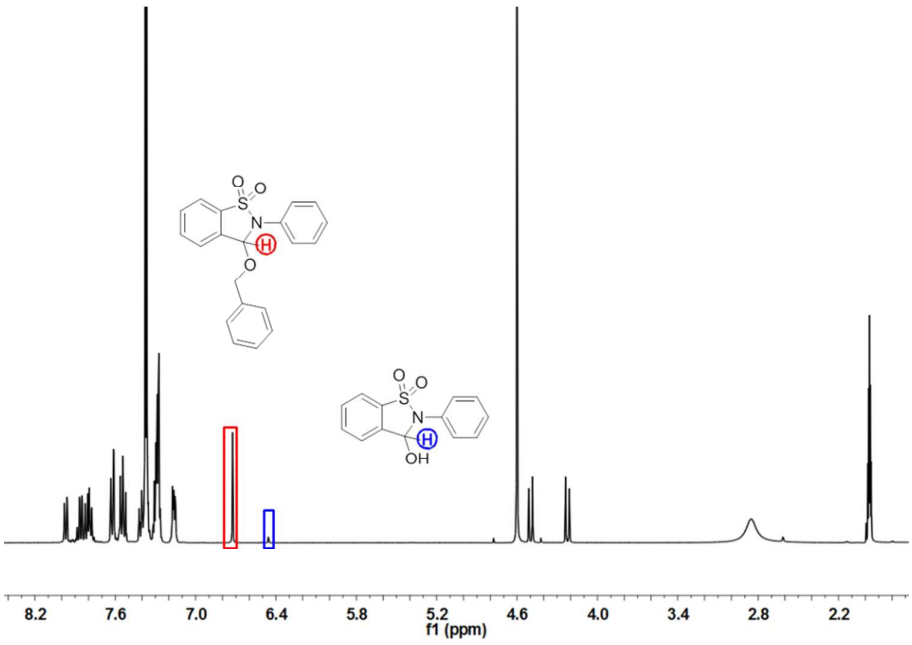


Figure S36. ^{1}H NMR spectrum of the reaction of **2**(H) and benzylalcohol in CD_3CN.

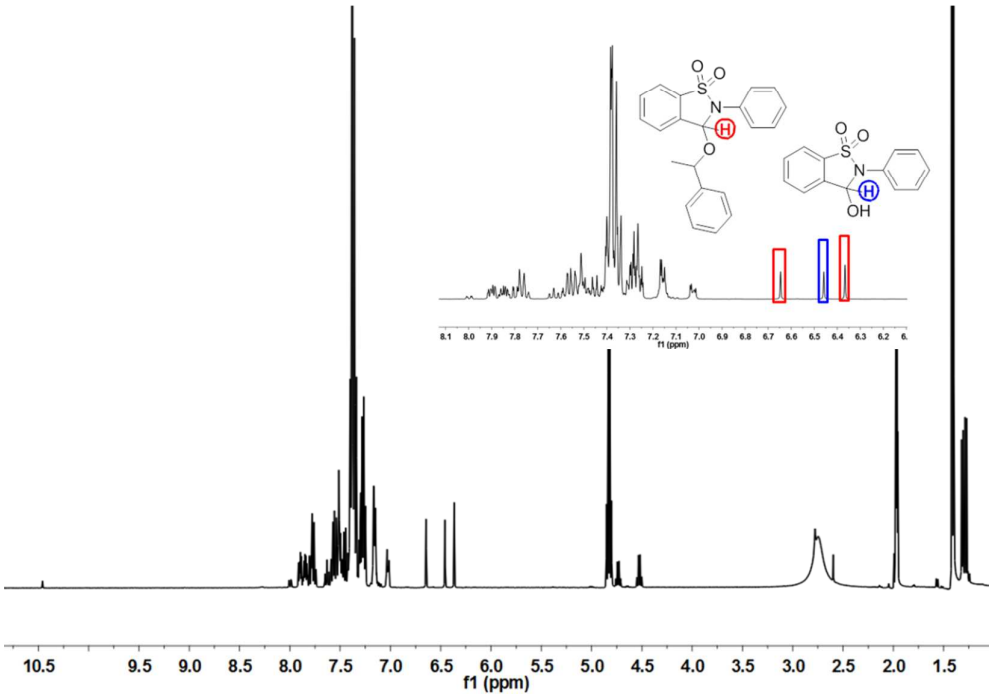


Figure S37. ^{1}H NMR spectrum of the reaction of **2**(H) and 1-phenylethanol in CD_3CN.

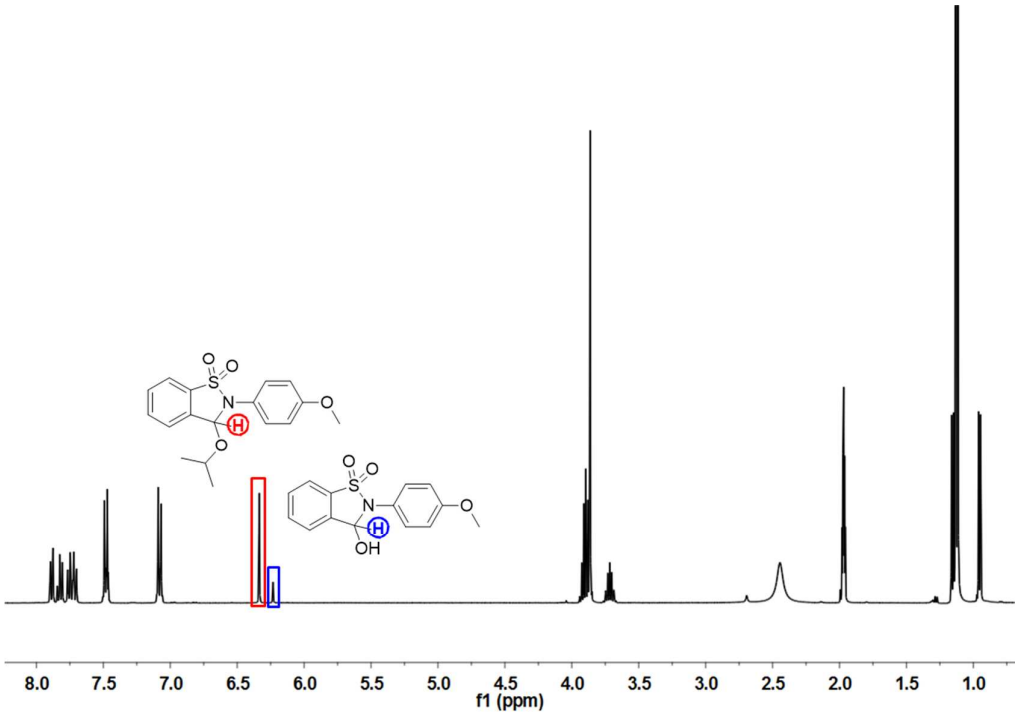


Figure S38. ^{1}H NMR spectrum of the reaction of **2**(OCH_3) and 2-propanol in CD_3CN.

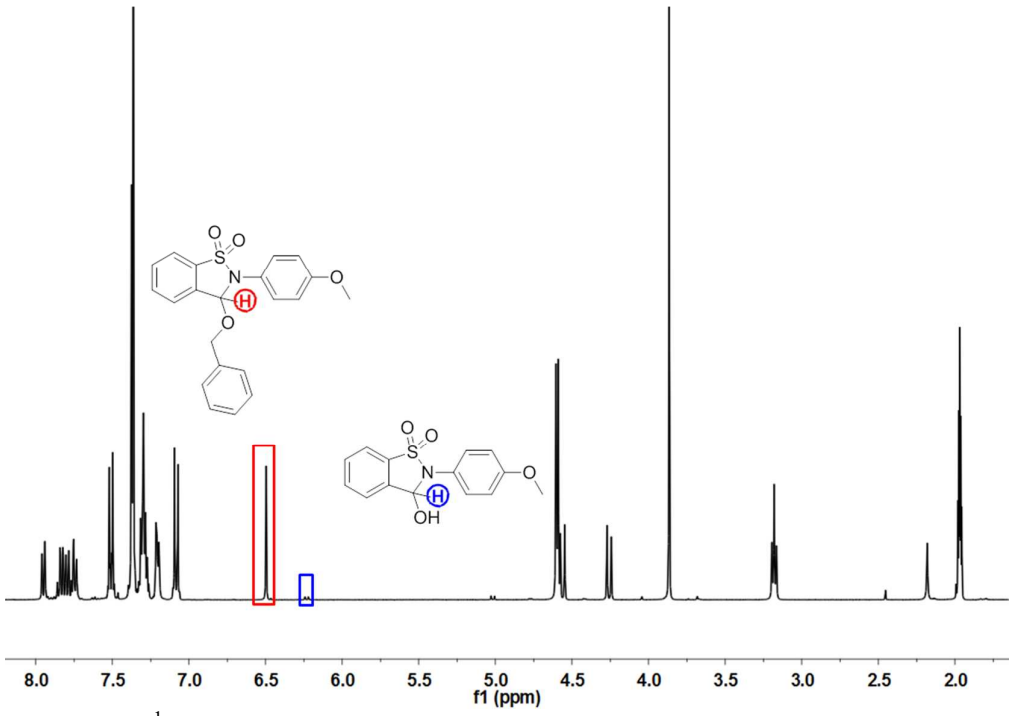


Figure S39. ^{1}H NMR spectrum of the reaction of **2**(OCH_3) and benzylalcohol in CD_3CN.

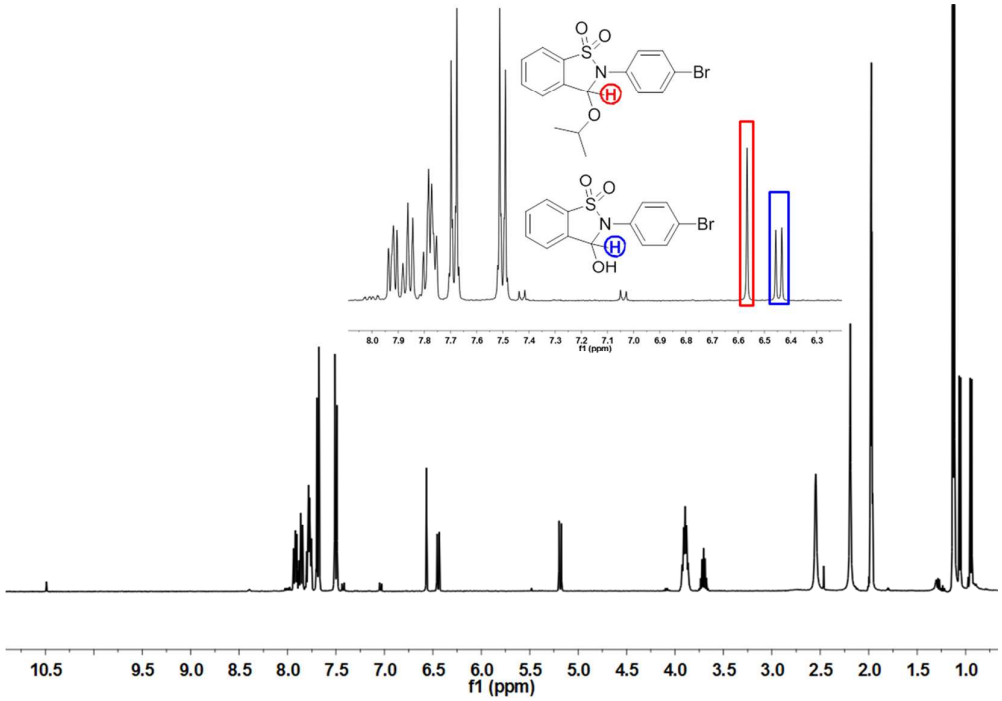


Figure S40. ^{1}H NMR spectrum of the reaction of **2**(Br) and 2-propanol in CD_3CN.

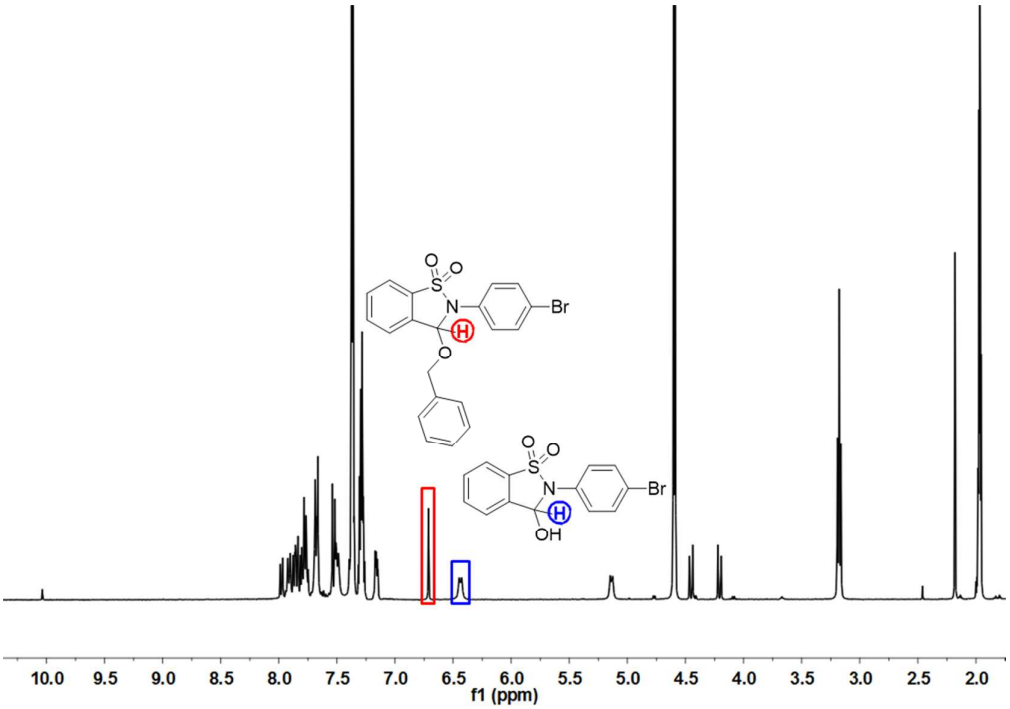


Figure S41. ^{1}H NMR spectrum of the reaction of **2**(Br) and benzylalcohol in CD_3CN.

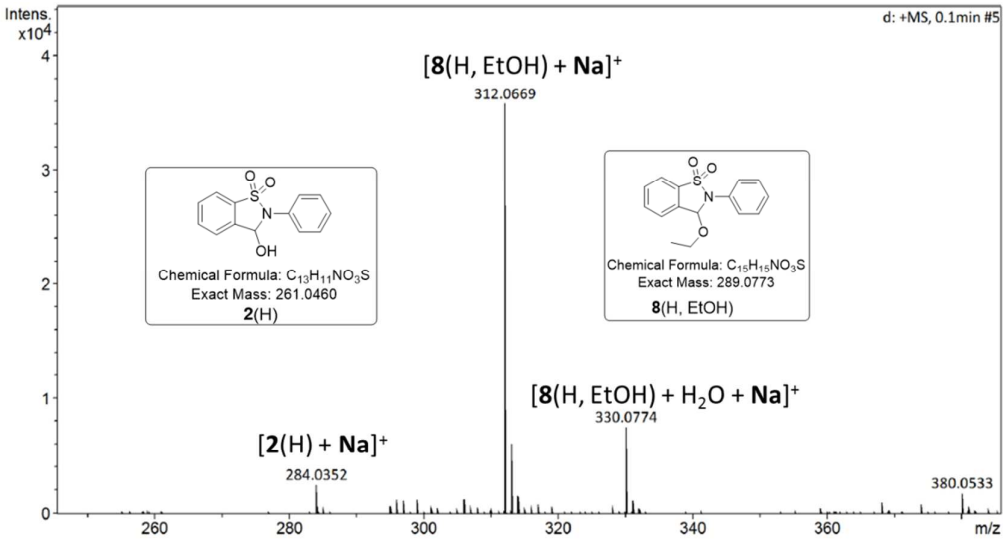


Figure S42. ESI mass spectrum of the reaction of **2**(H) and ethanol in CD_3CN.

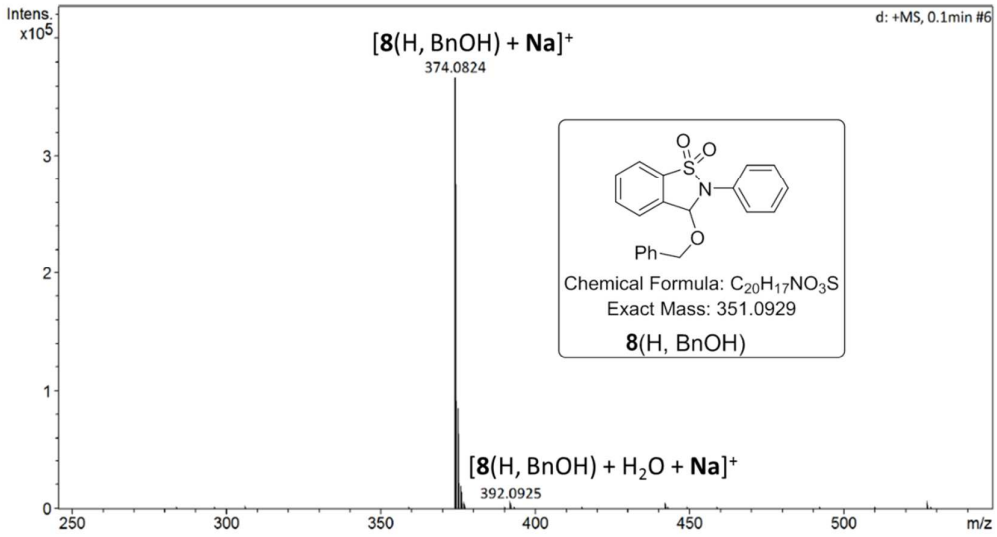


Figure S43. ESI mass spectrum of the reaction of **2**(H) and benzylalcohol in CD_3CN.

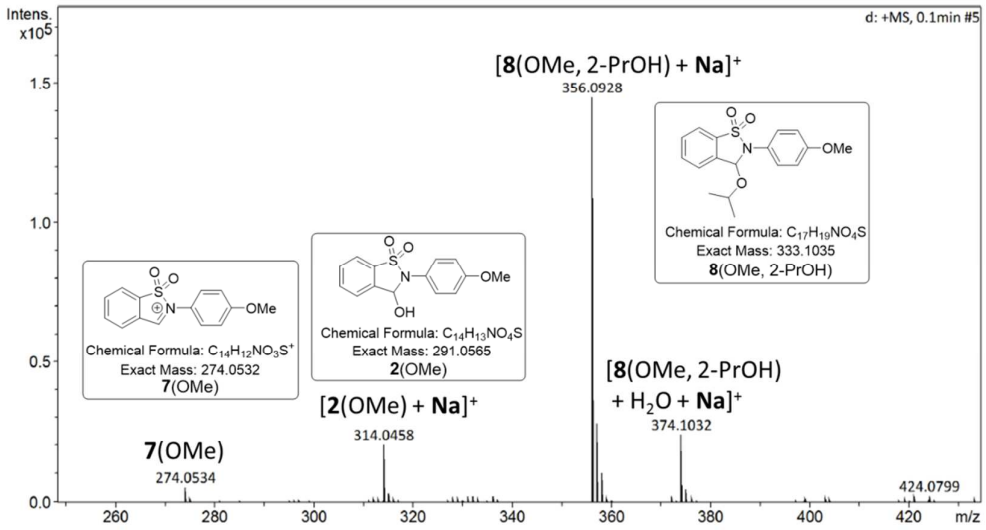


Figure S44. ESI mass spectrum of the reaction of **2**(OCH_3) and 2-propanol in CD_3CN.

DCRs with RSH

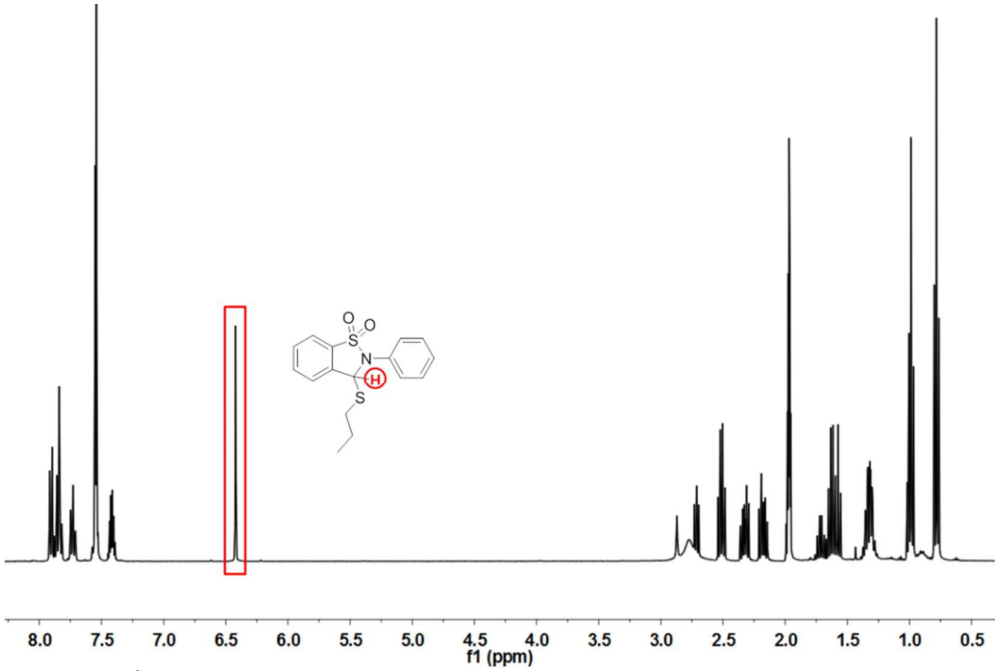


Figure S45. ^{1}H NMR spectrum of the reaction of **2**(H) and 1-propanethiol in CD_3CN.

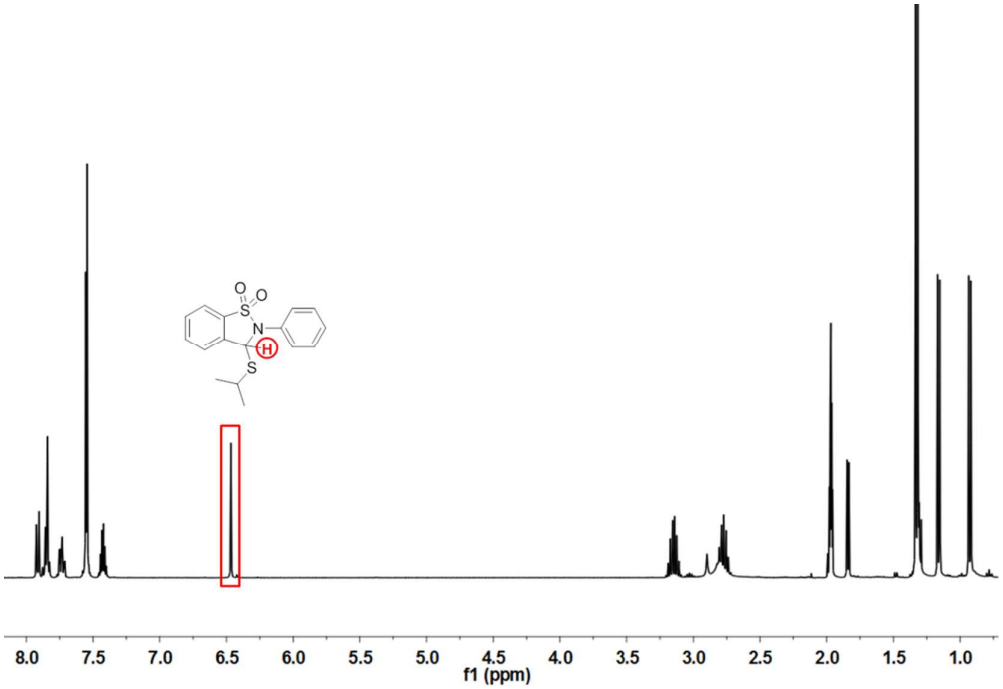


Figure S46. ^{1}H NMR spectrum of the reaction of **2**(H) and 2-propanethiol in CD_3CN.

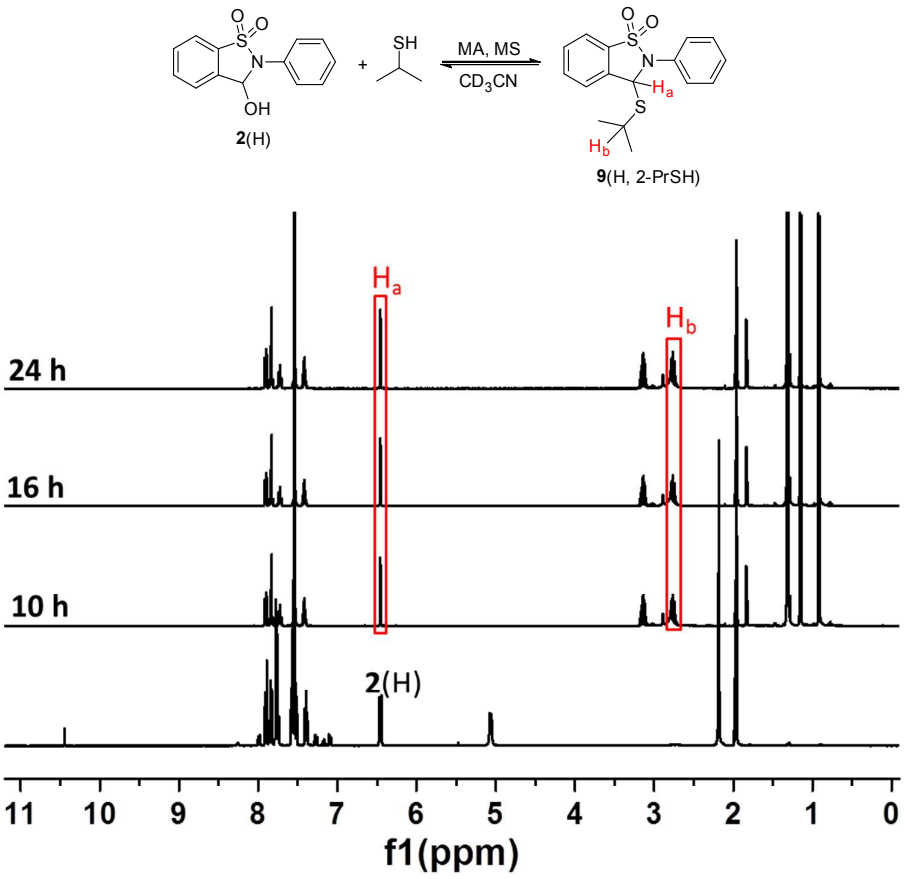


Figure S47. ^{1}H NMR spectra of the reaction of **2**(H) and 2-propanethiol in CD_3CN at varied time.

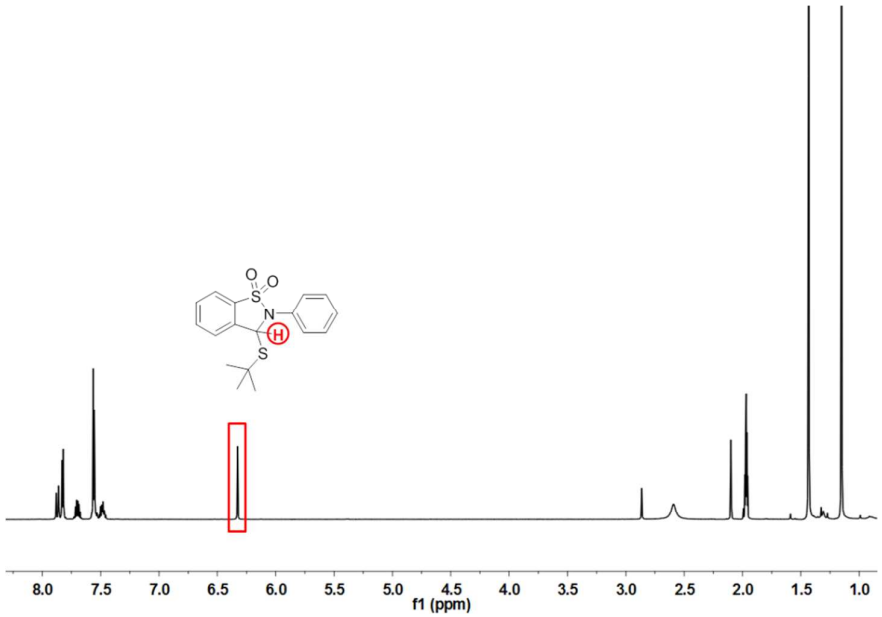


Figure S48. ^{1}H NMR spectrum of the reaction of **2**(H) and *t*-butanethiol in CD_3CN.

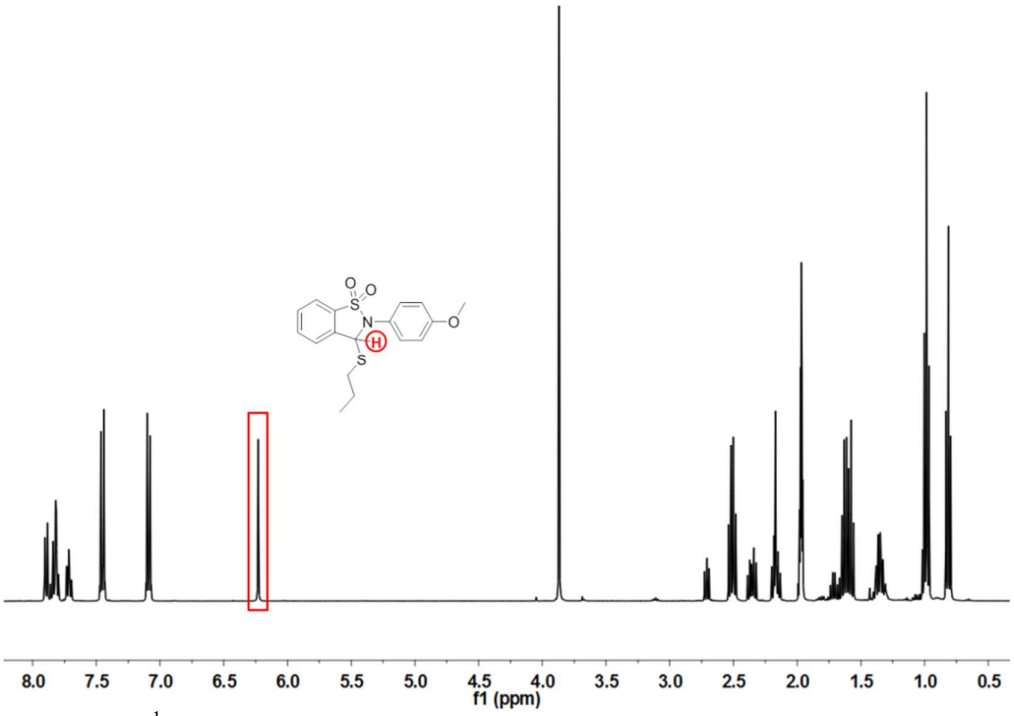


Figure S49. ^{1}H NMR spectrum of the reaction of **2**(OCH_3) and 1-propanethiol in CD_3CN.

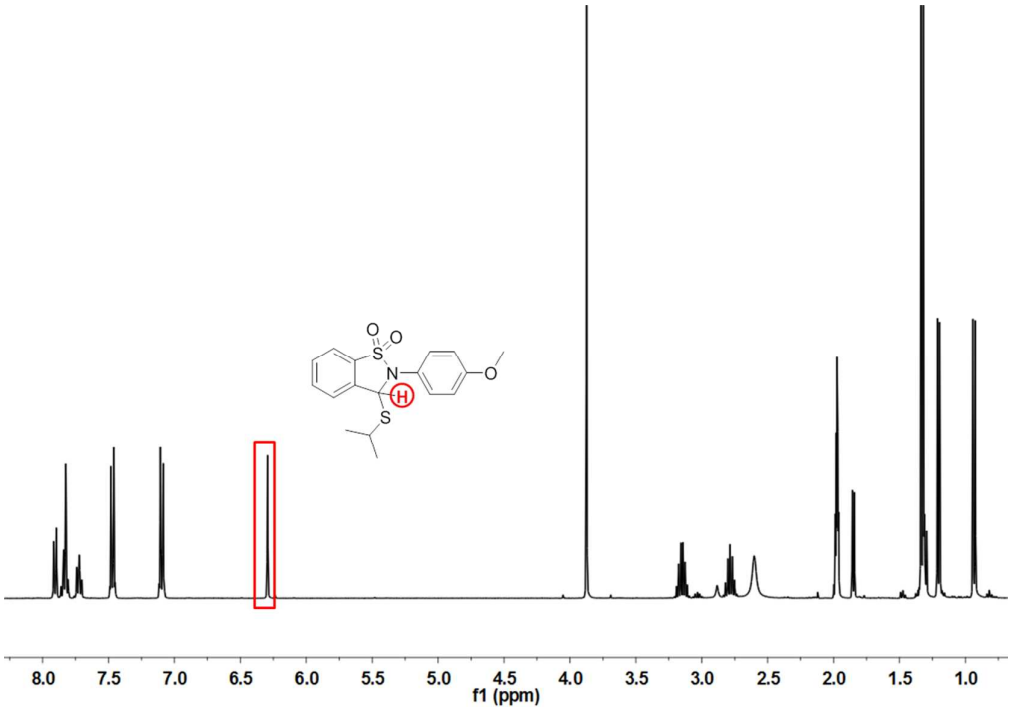


Figure S50. ^{1}H NMR spectrum of the reaction of **2**(OCH_3) and 2-propanethiol in CD_3CN.

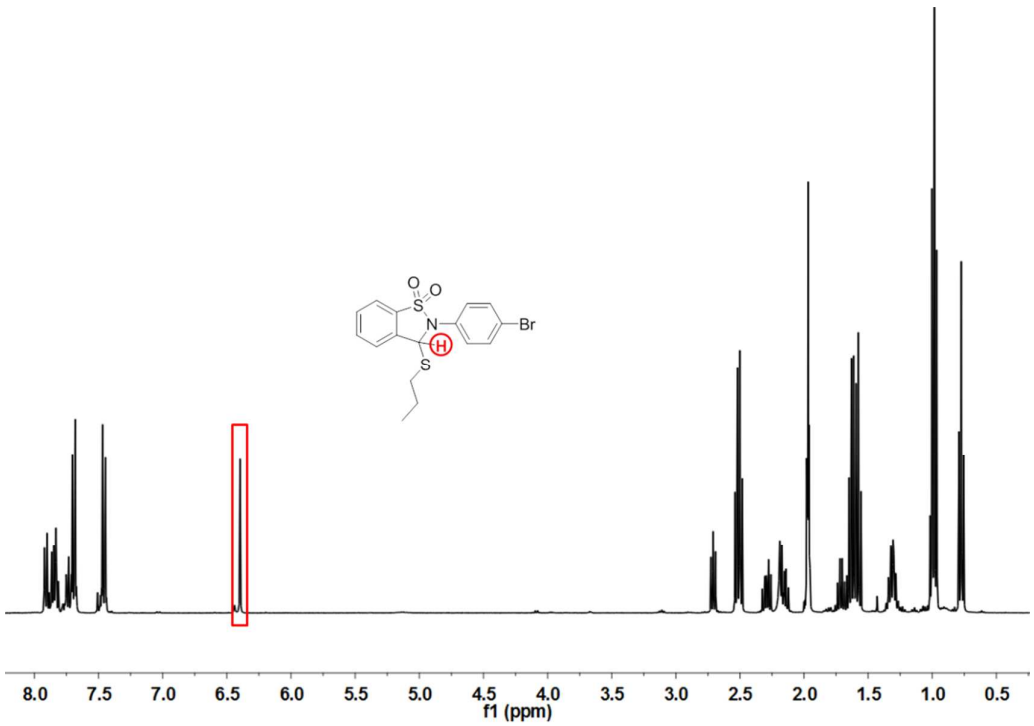


Figure S51. ^{1}H NMR spectrum of the reaction of **2**(Br) and 1-propanethiol in CD_3CN.

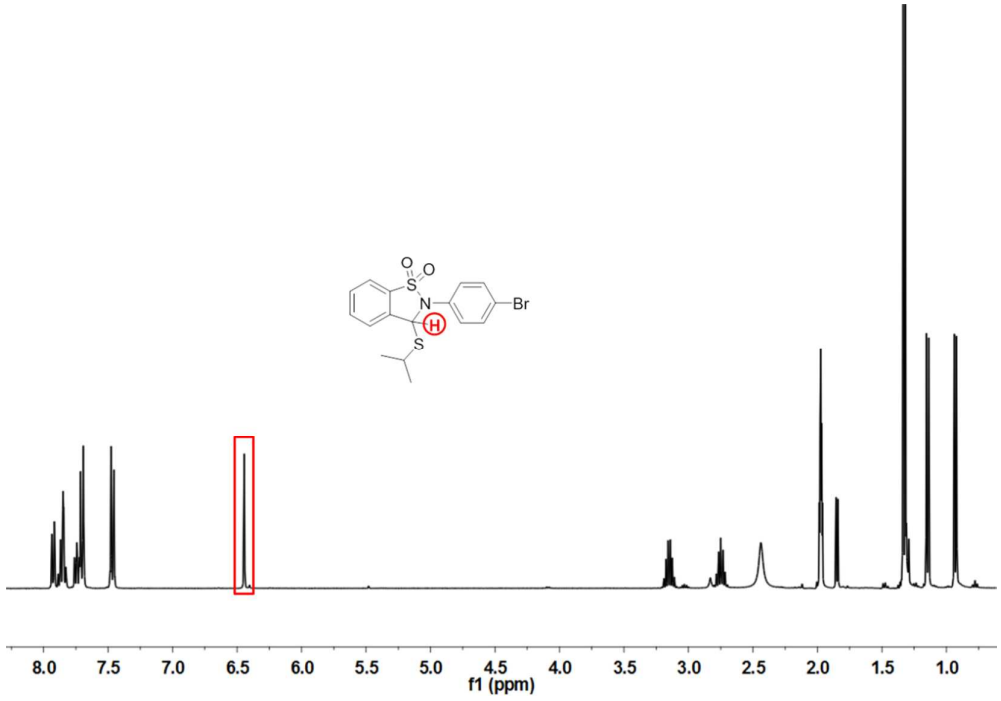


Figure S52. ^{1}H NMR spectrum of the reaction of **2**(Br) and 2-propanethiol in CD_3CN.

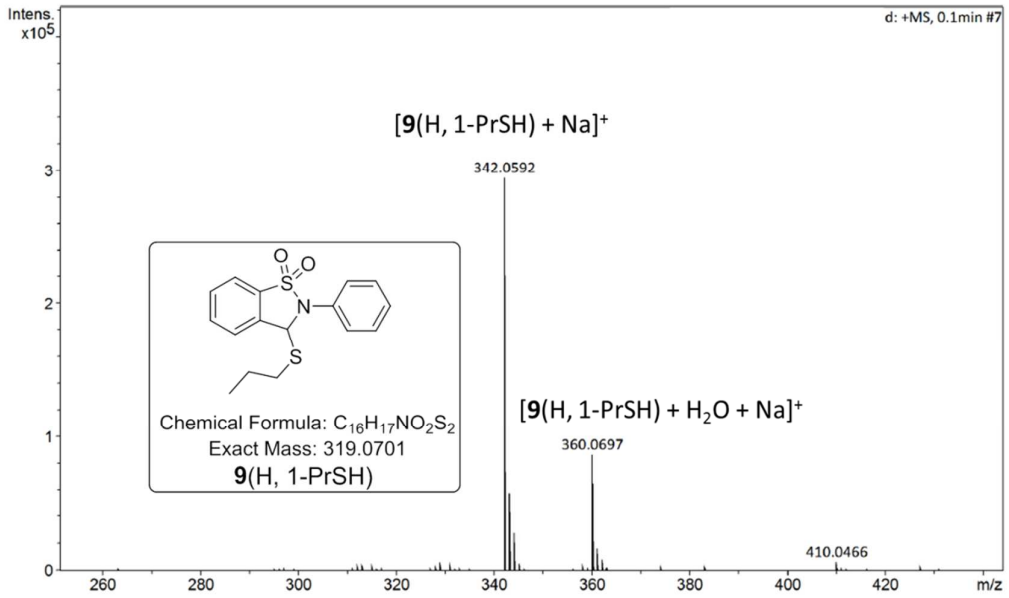


Figure S53. ESI mass spectrum of the reaction of **2**(H) and 1-propanethiol in CD_3CN.

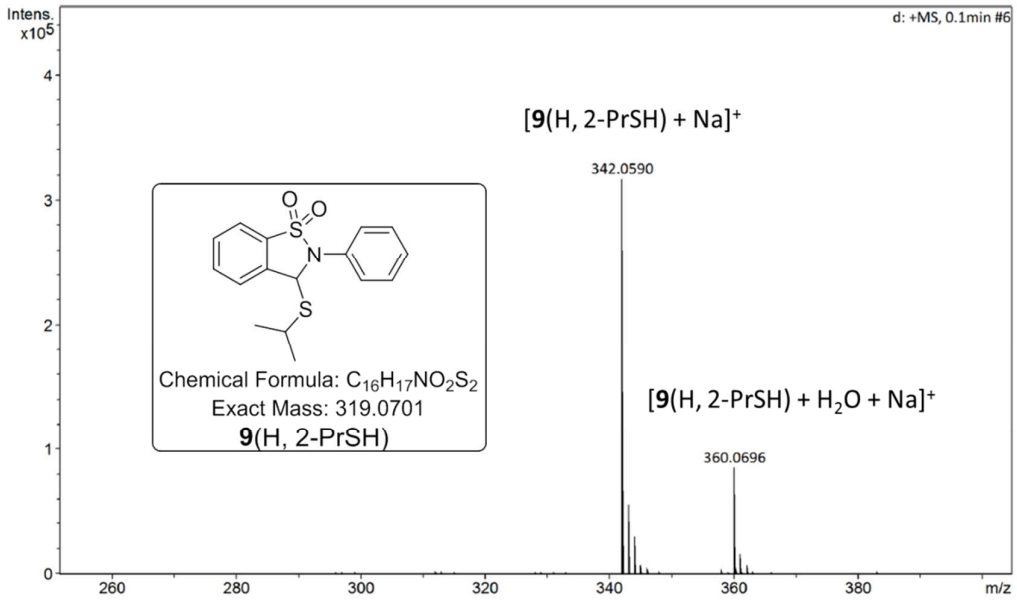


Figure S54. ESI mass spectrum of the reaction of **2**(H) and 2-propanethiol in CD_3CN.

3. Dynamic Mixtures

Two-component Exchange

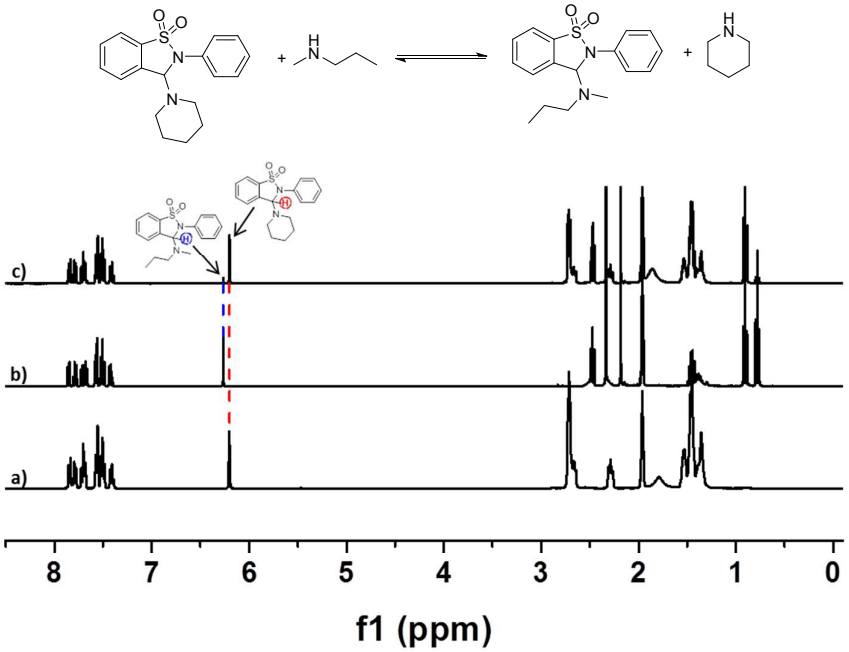


Figure S55. Dynamic amine exchange (c) between piperidine (a) and *N*-methyl-1-propylamine (b) derived assemblies. This figure shows the details and full spectra of Figure 3A in the main text.

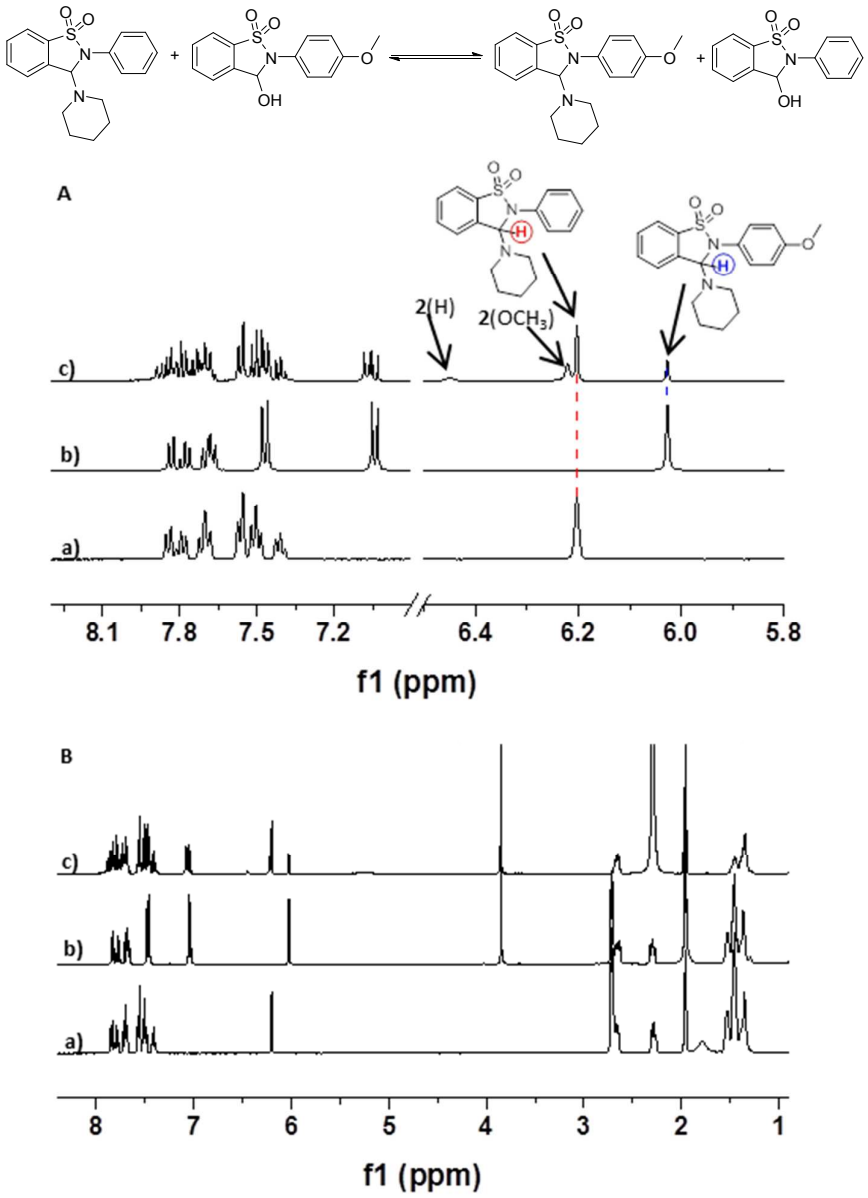


Figure S56. (A) Dynamic aldehyde exchange (c) between **2**(H) (a) and **2**(OMe) (b) derived assemblies with piperidine. (B) The full ^{1}H NMR spectra of A. This figure shows the details and full spectra of Figure 3A in the main text.

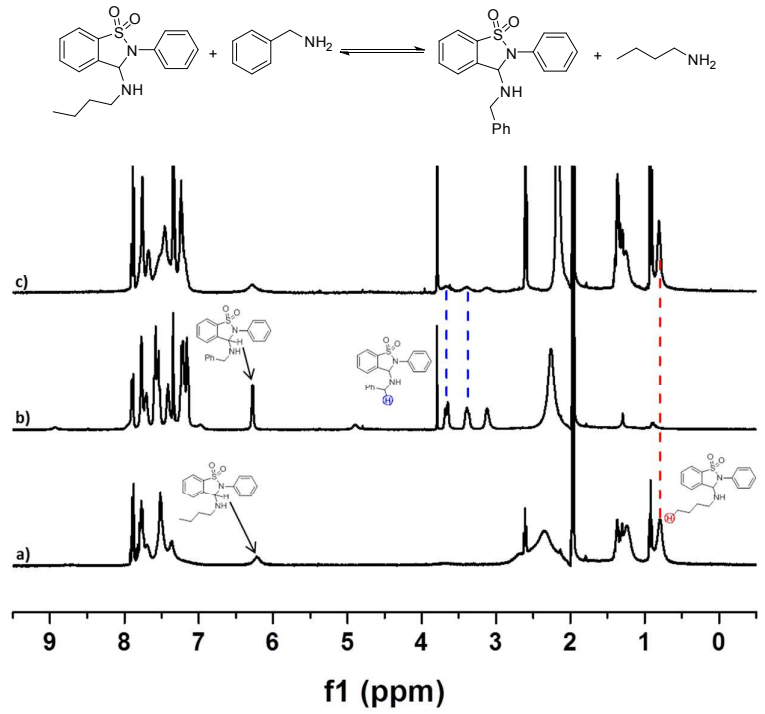


Figure S57. Dynamic amine exchange (c) between 1-butylamine (a) and benzylamine (b) derived assemblies. Due to overlapping of the methine peaks of **3**(H, 1-BuNH_2) and **3**(H, BnNH_2), the peaks of methyl and benzyl protons are marked in red and blue, respectively.

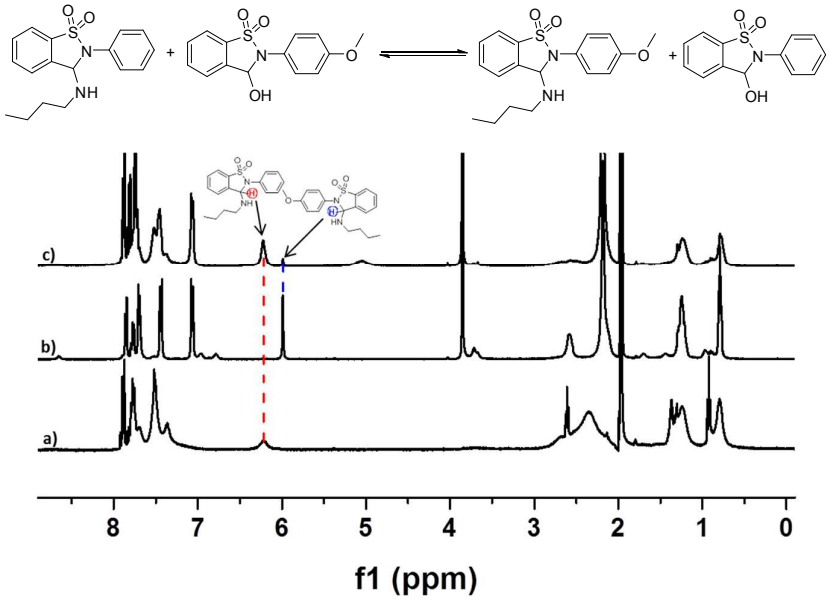


Figure S58. Dynamic aldehyde exchange (c) between **2**(H) (a) and **2**(OMe) (b) derived assemblies with 1-butylamine.

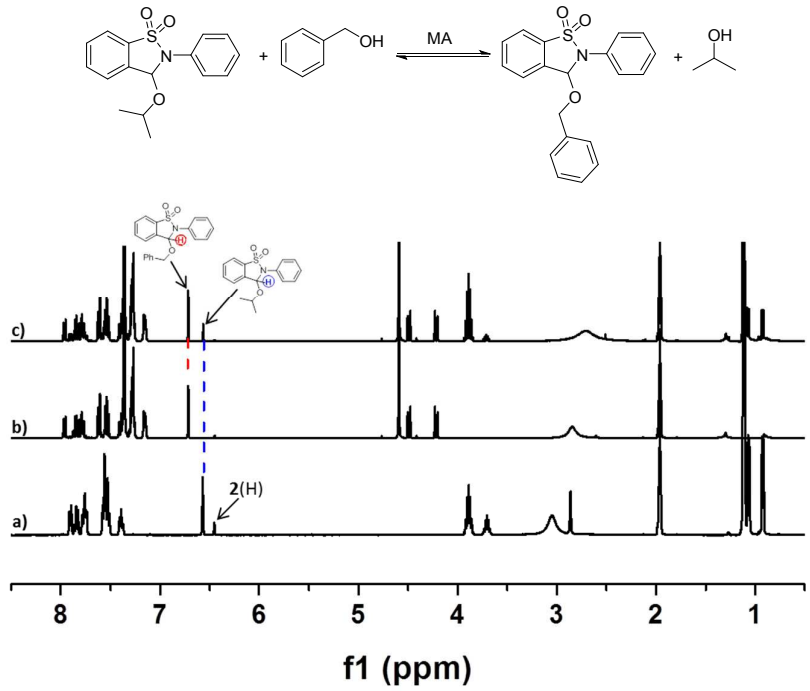


Figure S59. Dynamic alcohol exchange (c) between 2-propanol (a) and benzylalcohol (b) derived assemblies.

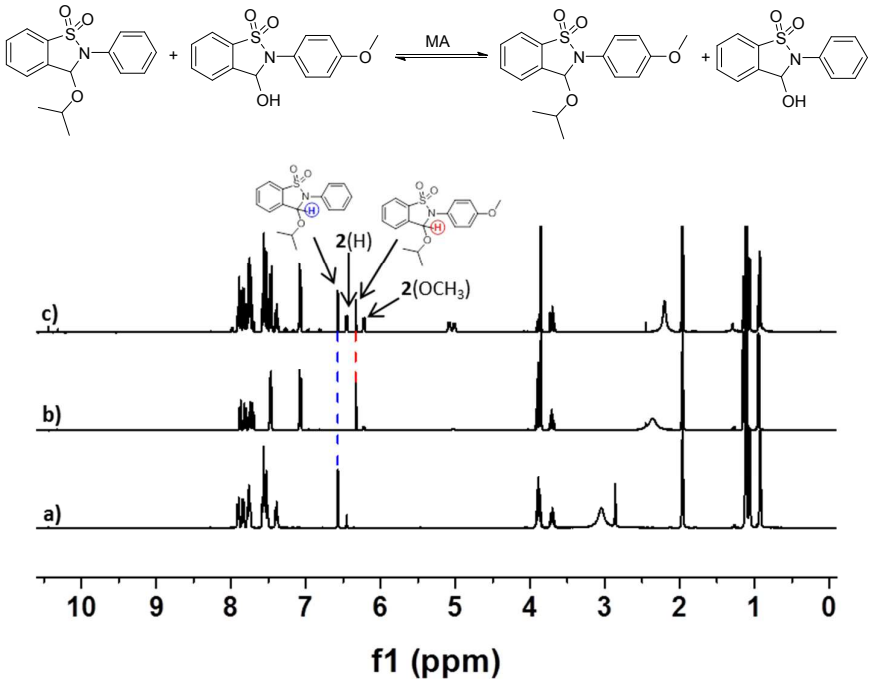


Figure S60. Dynamic aldehyde exchange (c) between **2**(H) (a) and **2**(OMe) (b) derived assemblies with 2-propanol.

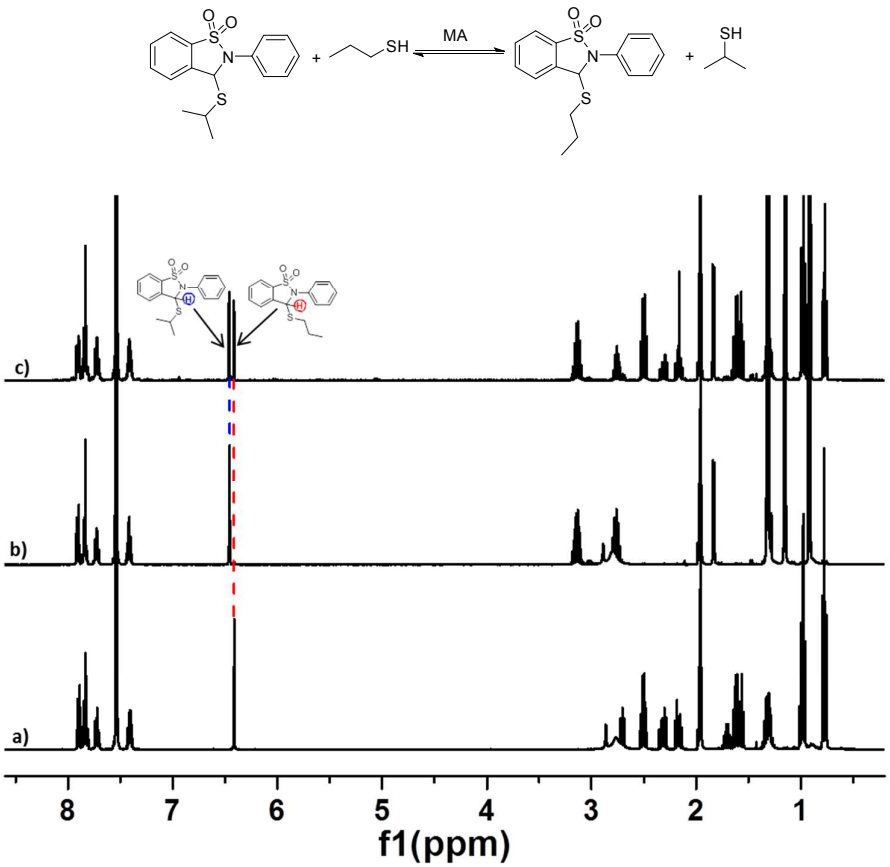


Figure S61. Dynamic thiol exchange (c) between 1-propanethiol (a) and 2-propanethiol (b) derived assemblies.

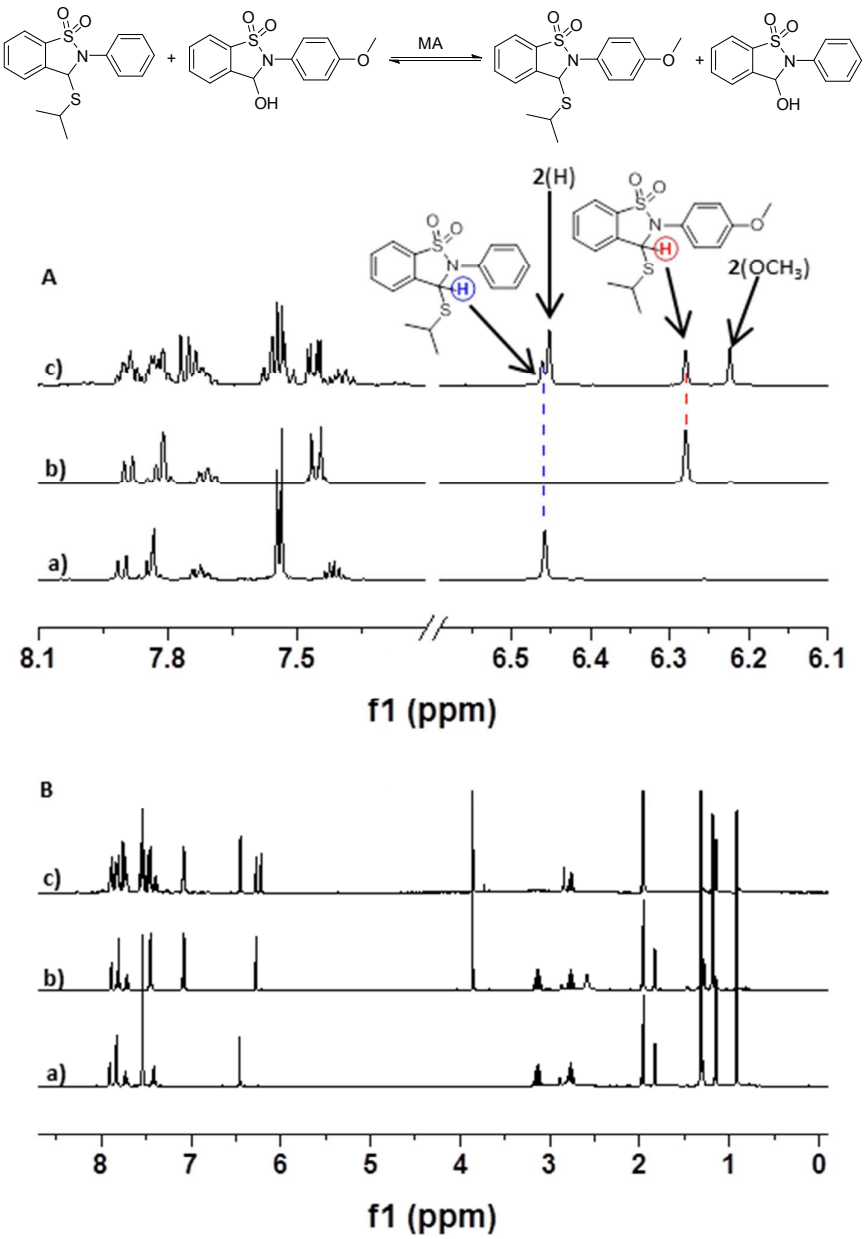
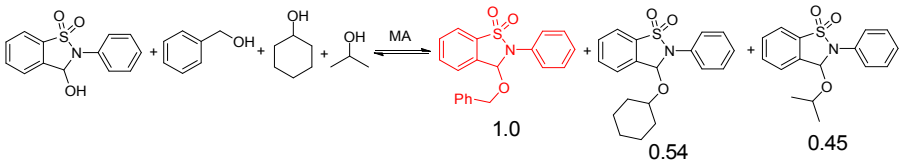


Figure S62. (A) Dynamic aldehyde exchange (c) between **2**(H) (a) and **2**(OMe) (b) derived assemblies with 2-propanethiol. (B) The full ^{1}H NMR spectra of A.

Multi-component Exchange



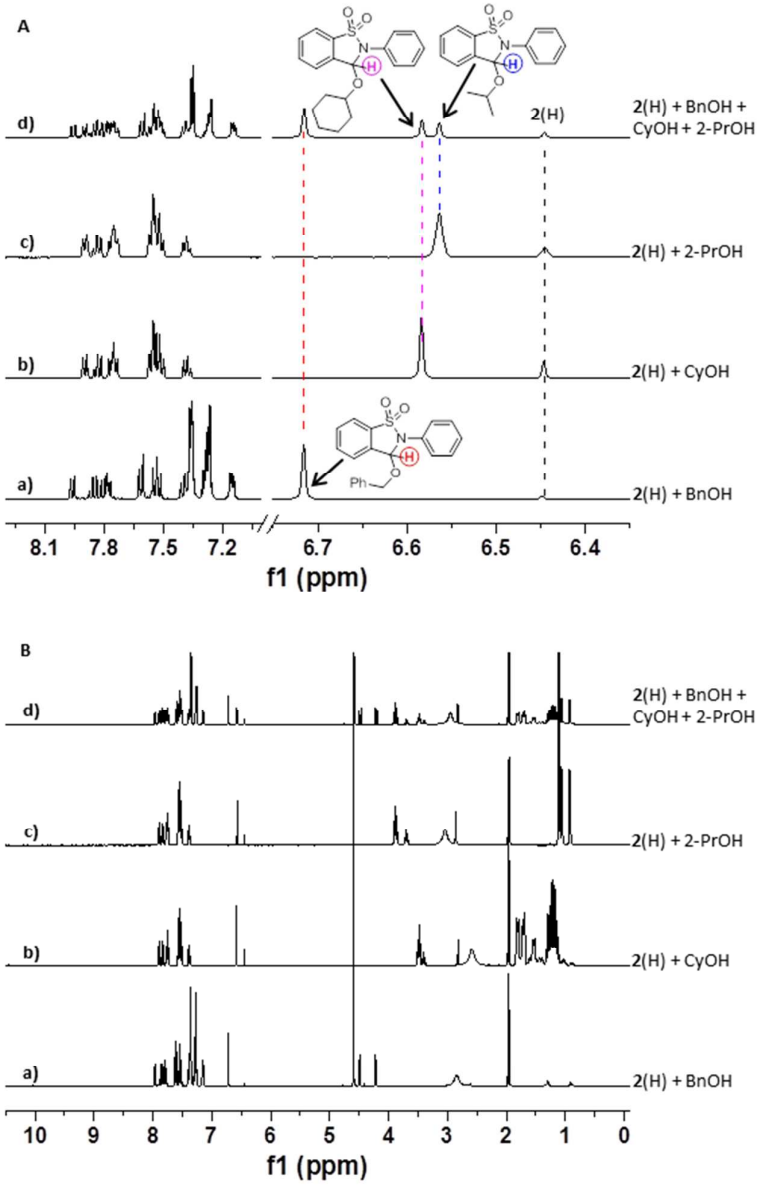


Figure S63. (A) The competition (d) between benzylalcohol (1.0 equiv.), cyclohexanol (1.0 equiv.), and 2-propanol (1.0 equiv.) for the reaction with **2**(H) (1.0 equiv.). The single individual DCR is shown in panels a-c for the comparison. (B) The full ^{1}H NMR spectra of A. The integrals are listed, and the most populated product is highlighted in red. This figure shows the details and full spectra of Figure 3B in the main text.

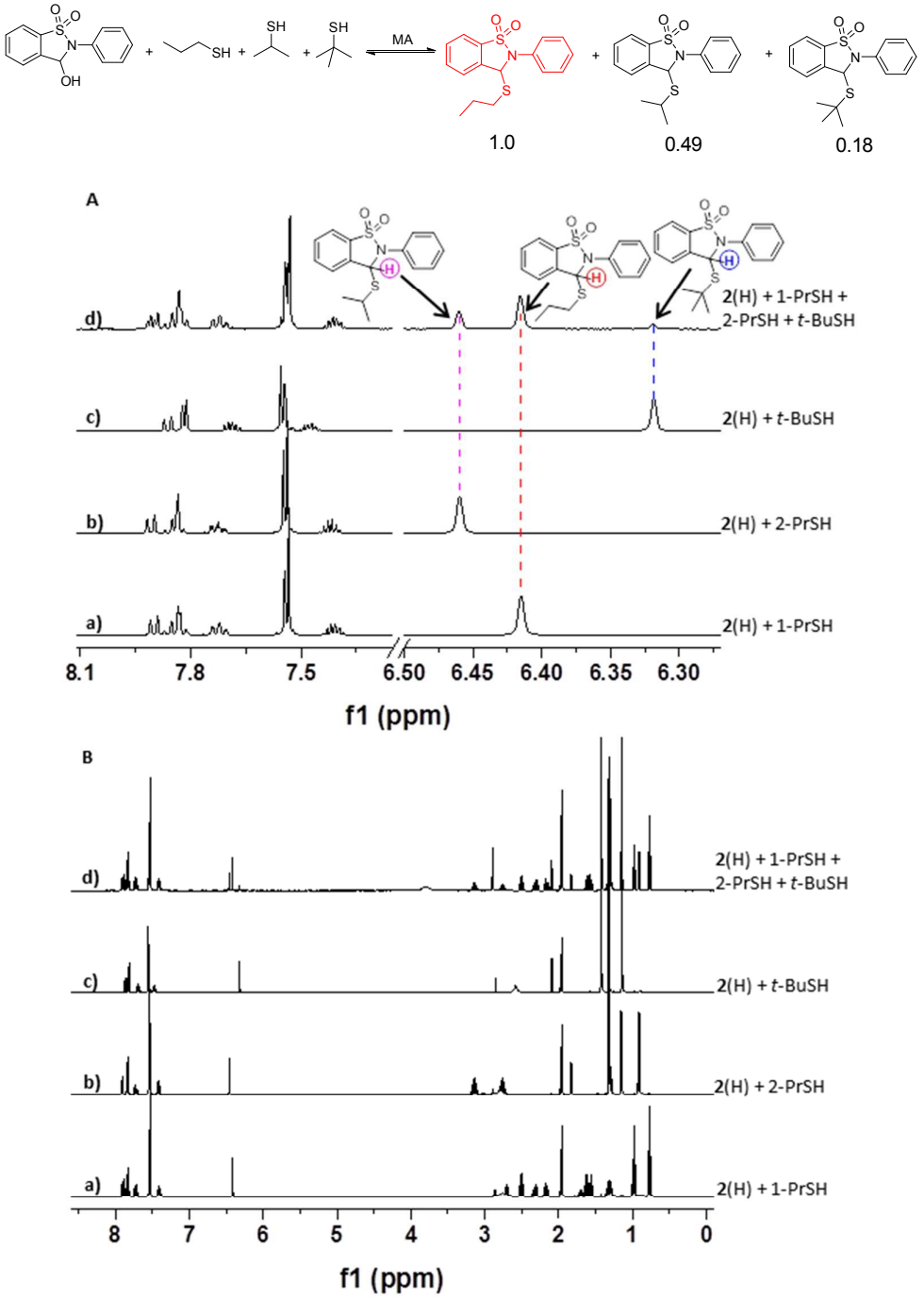


Figure S64. (A) The competition (d) between 1-propanethiol (1.0 equiv.), 2-propanethiol (1.0 equiv.), and *t*-butanethiol (1.0 equiv.) for the reaction with **2**(H) (1.0 equiv.). The single individual DCR is shown in panels a-c for the comparison. (B) The full ^{1}H NMR spectra of A. The integrals are listed, and the most populated product is highlighted in red.

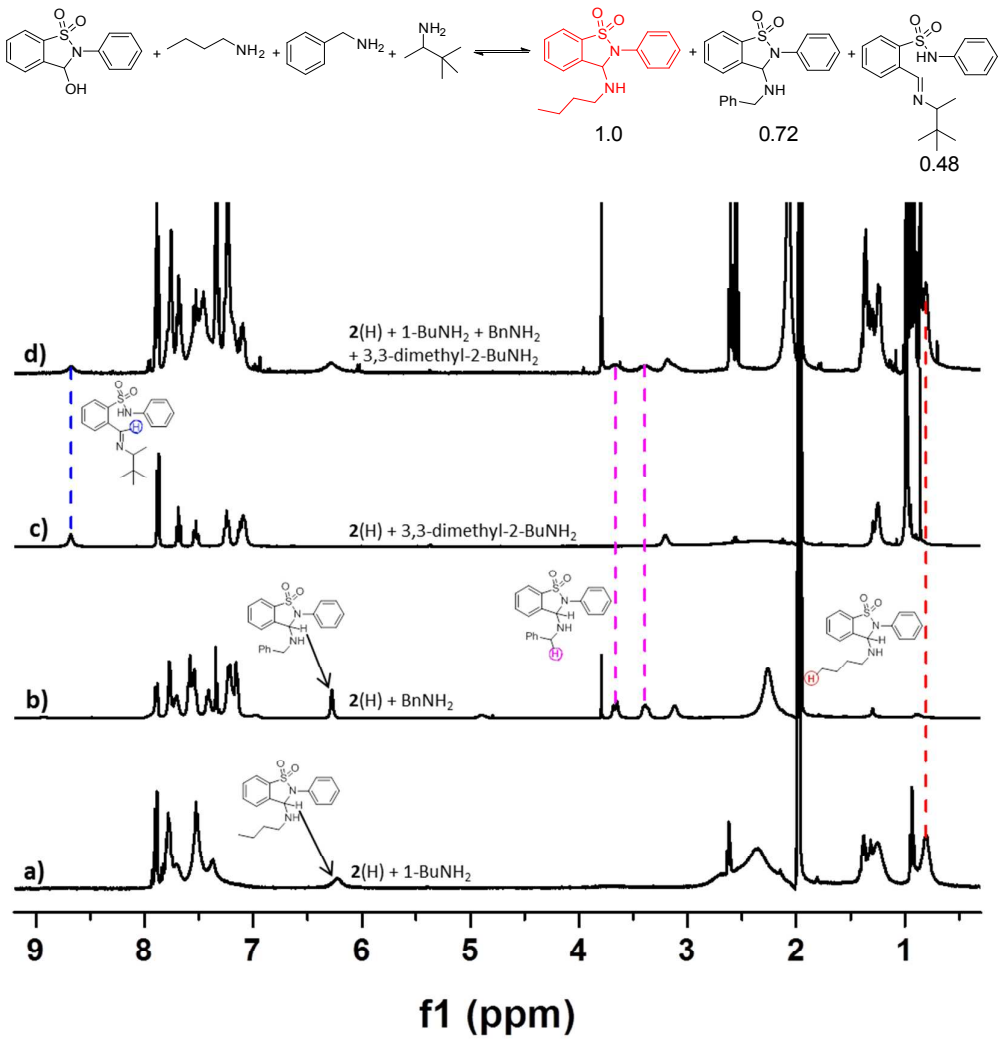


Figure S65. The competition (d) between 1-butylamine (1.0 equiv.), benzylamine (1.0 equiv.), and 3,3-dimethyl-2-butylamine (1.0 equiv.) for the reaction with **2**(H) (1.0 equiv.). The single individual DCR is shown in panels a-c for the comparison. Due to overlapping of the methine peaks of **3**(H, 1-BuNH$_2$) and **3**(H, BnNH$_2$), the peaks of methyl and benzyl protons are marked in red and pink, respectively. The integrals are listed, and the most populated product is highlighted in red.

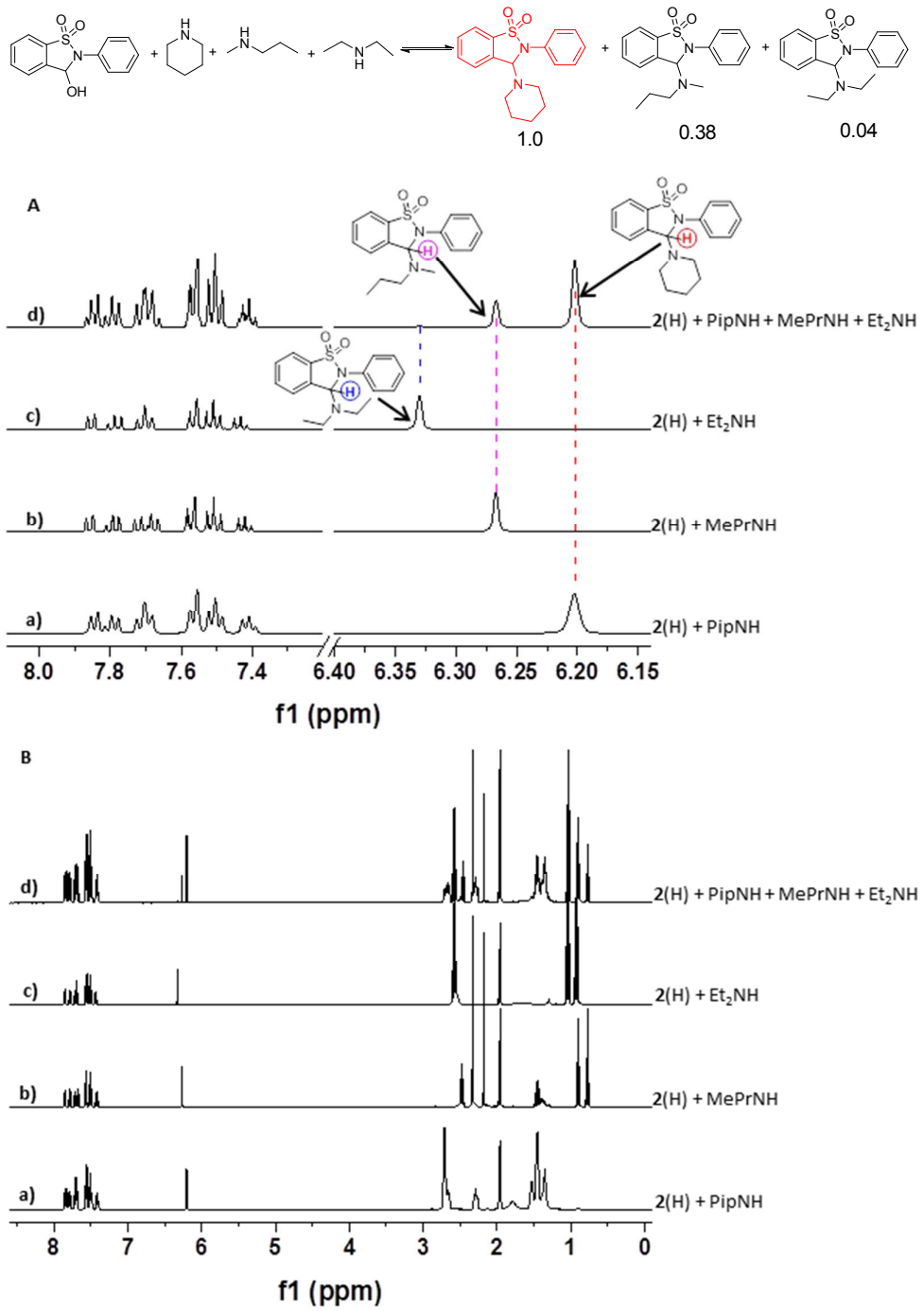


Figure S66. (A) The competition (d) between piperidine (1.0 equiv.), *N*-methyl-1-propylamine (1.0 equiv.), and diethylamine (1.0 equiv.) for the reaction with **2**(H) (1.0 equiv.). The single individual DCR is shown in panels a-c for the comparison. (B) The full ^{1}H NMR spectra of A. The integrals are listed, and the most populated product is highlighted in red.

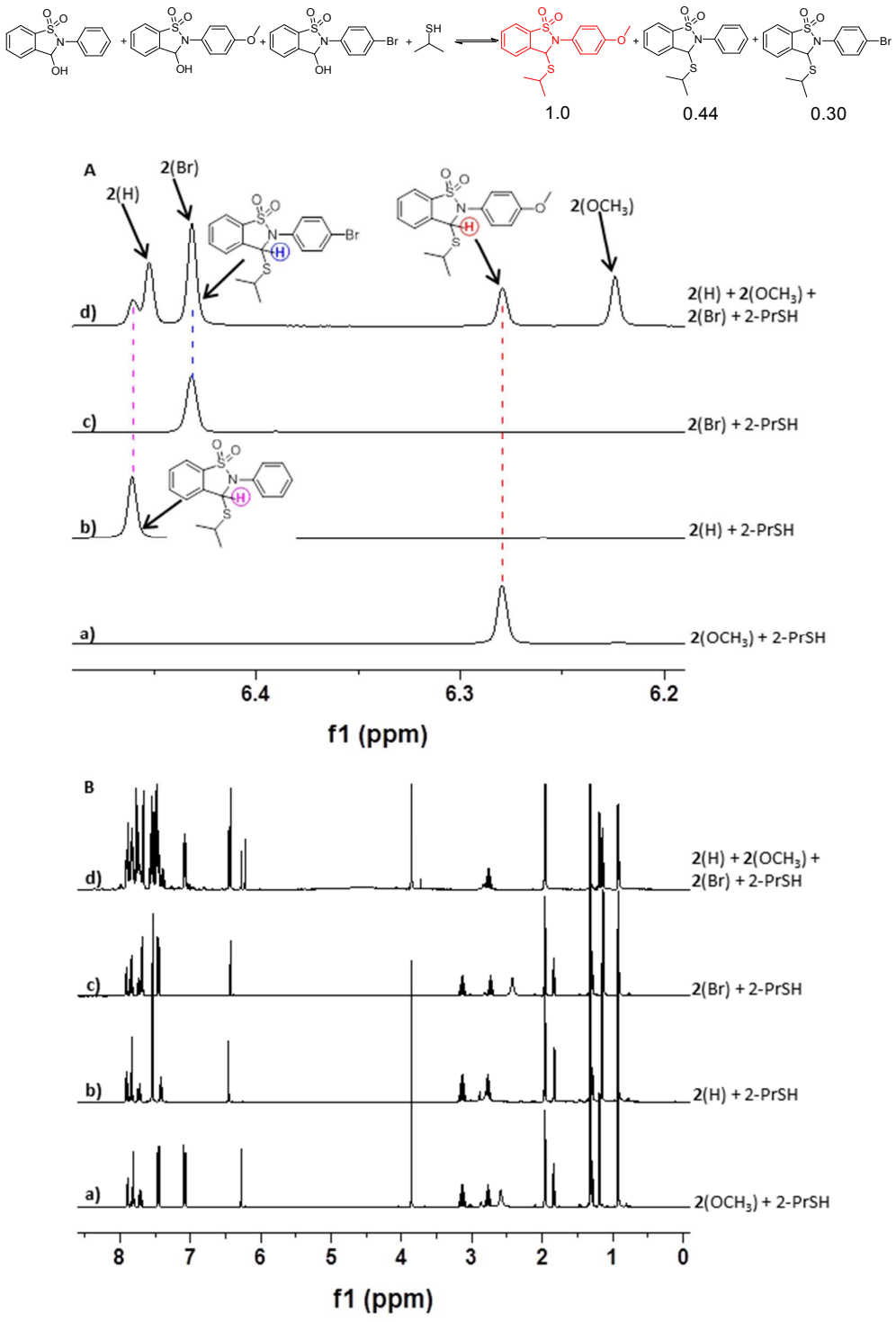


Figure S67. (A) The competition (d) between **2**(OCH_3) (1.0 equiv.), **2**(H) (1.0 equiv.), and **2**(Br) (1.0 equiv.) for the reaction with 2-propanethiol (1.0 equiv.). The single individual DCR is shown in panels a-c for the comparison. (B) The full ^{1}H NMR spectra of A. The integrals are listed, and the most populated product is highlighted in red. This figure shows the details and full spectra of Figure 3C in the main text.

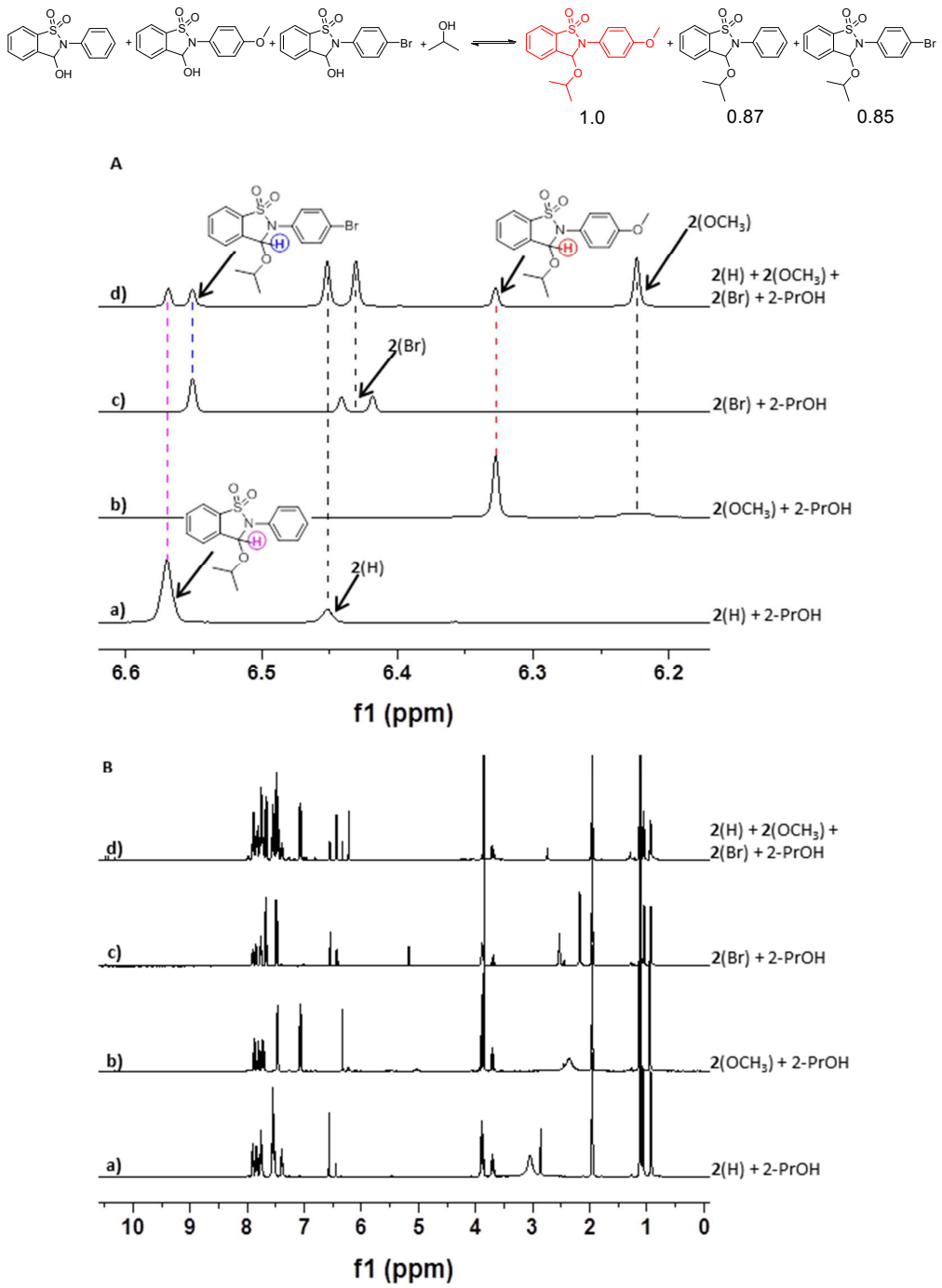


Figure S68. (A) The competition (d) between **2**(H) (1.0 equiv.), **2**(OCH_3) (1.0 equiv.), and **2**(Br) (1.0 equiv.) for the reaction with 2-propanol (1.0 equiv.). The single individual DCR is shown in panels a-c for the comparison. (B) The full ^{1}H NMR spectra of A. The integrals are listed, and the most populated product is highlighted in red.

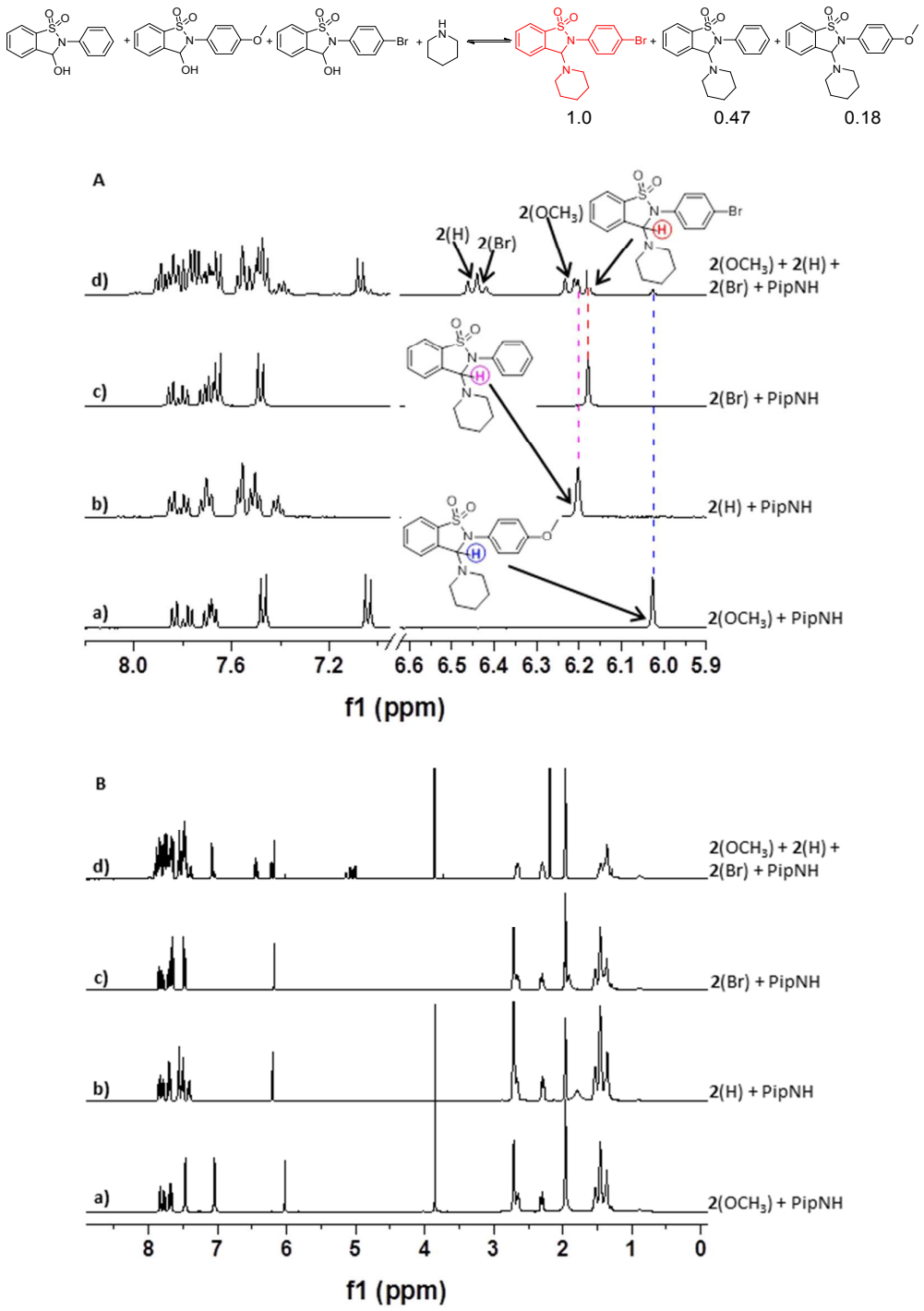


Figure S69. (A) The competition (d) between **2**(OCH_3) (1.0 equiv.), **2**(H) (1.0 equiv.), and **2**(Br) (1.0 equiv.) for the reaction with piperidine (1.0 equiv.). The single individual DCR is shown in panels a-c for the comparison. (B) The full ^{1}H NMR spectra of A. The integrals are listed, and the most populated product is highlighted in red. This figure shows the details and full spectra of Figure 3D in the main text.

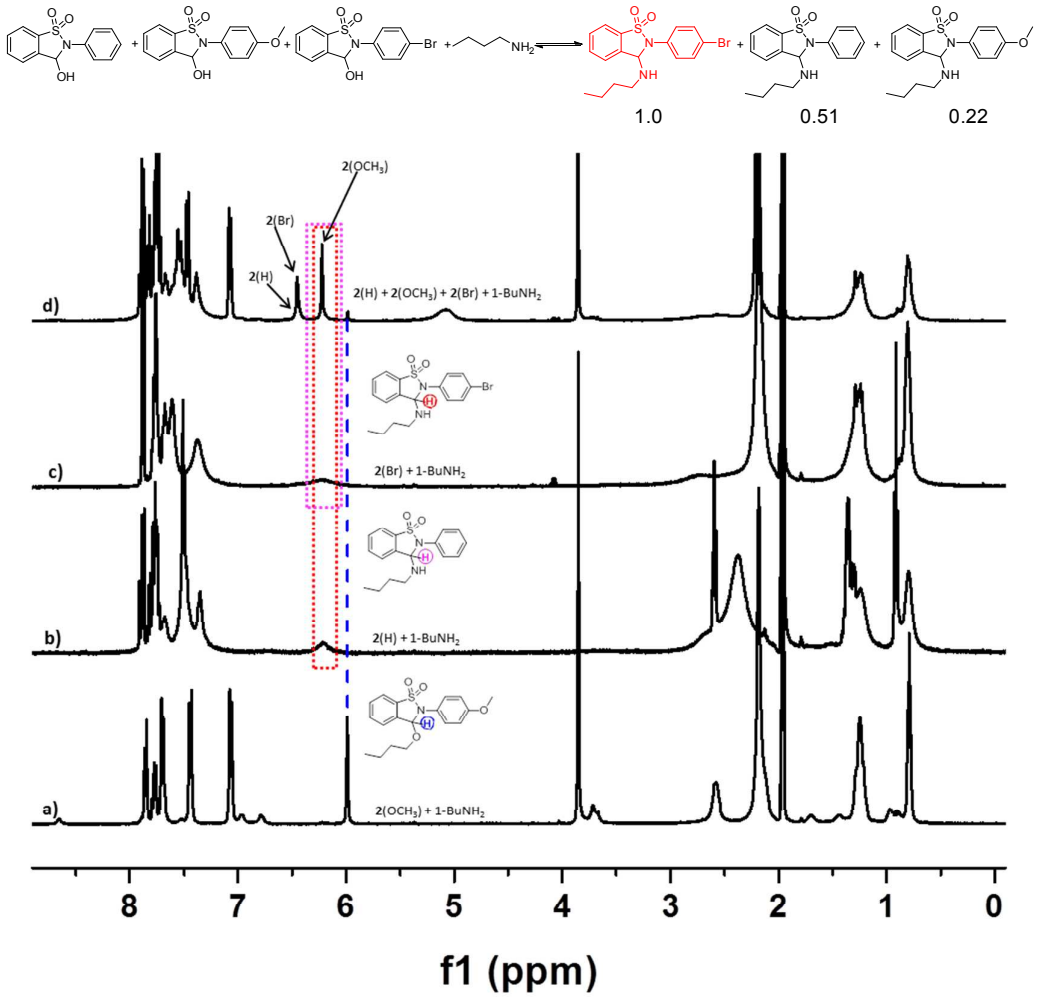


Figure S70. The competition (d) between **2**(OCH_3) (1.0 equiv.), **2**(H) (1.0 equiv.), and **2**(Br) (1.0 equiv.) for the reaction with 1-butylamine (1.0 equiv.). The single individual DCR is shown in panels a-c for the comparison. The integrals are listed, and the most populated product is highlighted in red.

4. Orthogonal DCRs

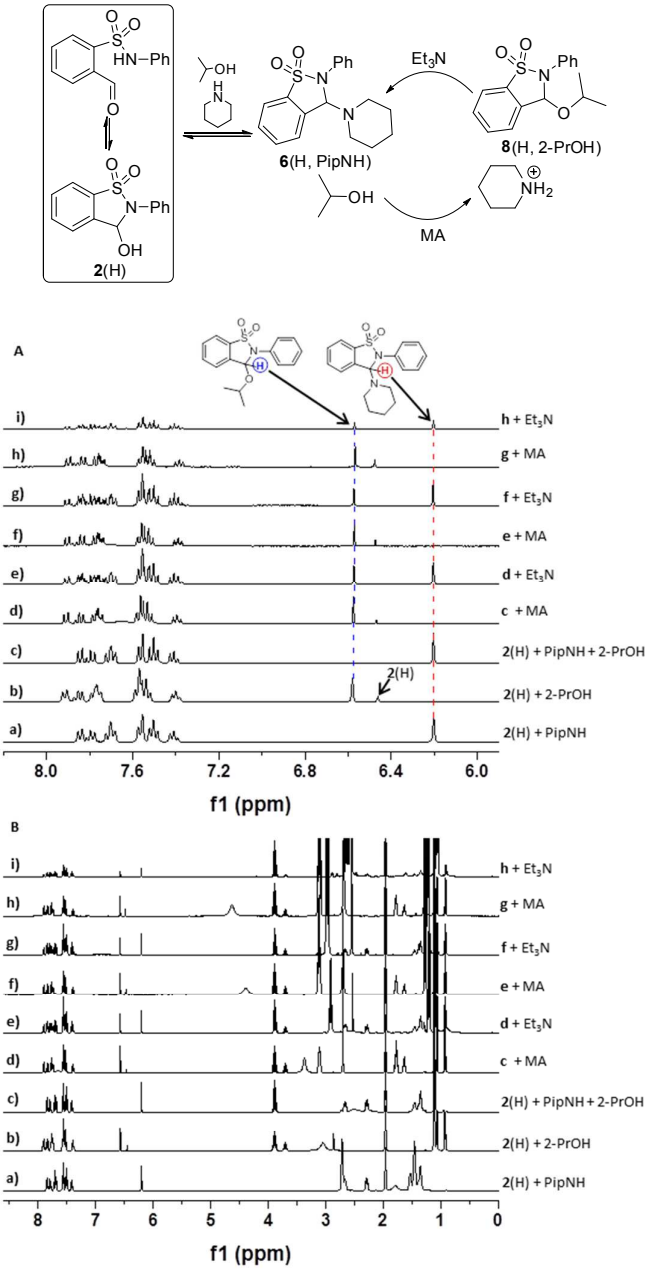


Figure S71. The switch between the assemblies incorporating piperidine and 2-propanol. (A) (a) The reaction of **2**(H) with piperidine; (b) the reaction of **2**(H) with 2-propanol; (c) the reaction of **2**(H) (1.0 equiv.), piperidine (1.2 equiv.), and 2-propanol (3.0 equiv.); (d) the addition of MA (1.8 equiv.) into panel c; (e) the addition of Et_3N (2.0 equiv.) into panel d; (f) the addition of MA (2.0 equiv.) into panel e; (g) the addition of Et_3N (2.2 equiv.) into panel f; (h) the addition of MA (2.2 equiv.) into panel g; (i) the addition of Et_3N (2.4 equiv.) into panel h. (B) The full ^1H NMR spectra of A. This figure shows the details and full spectra of Figure 4A in the main text.

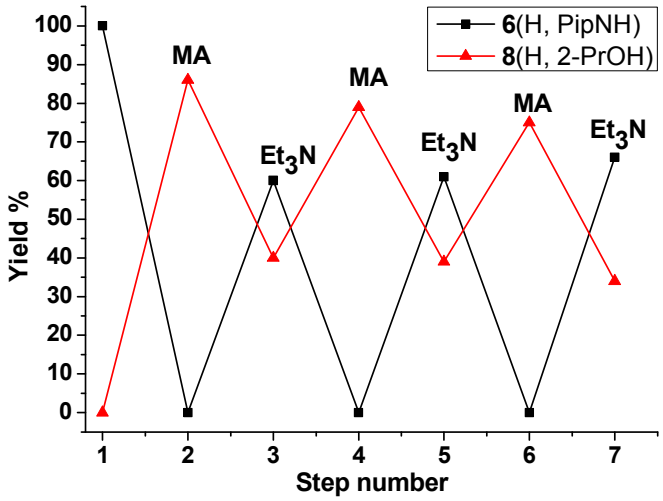


Figure S72. The efficiency of the switch in Figure S71 (from panel c to panel i).

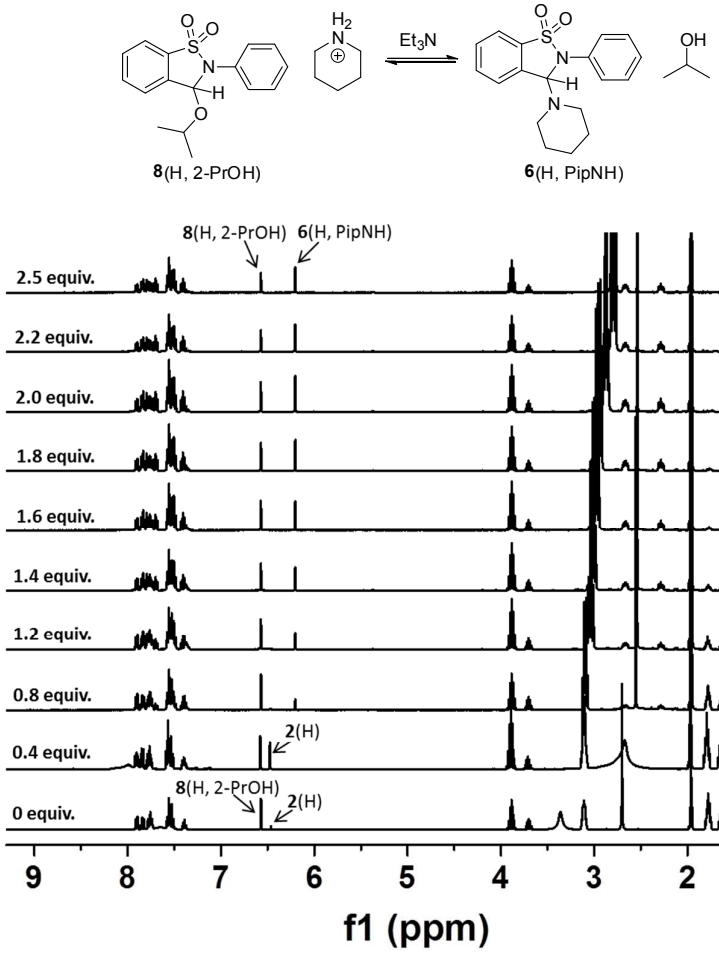


Figure S73. ^{1}H NMR spectra of the titration of Et_3N for the switch from **8**(H, 2-PrOH) to **6**(H, PipNH). **8**(H, 2-PrOH) was created *in situ*, as illustrated in panel b of Figure 3A. This figure shows the details and full spectra of panel d of Figure 4A in the main text.

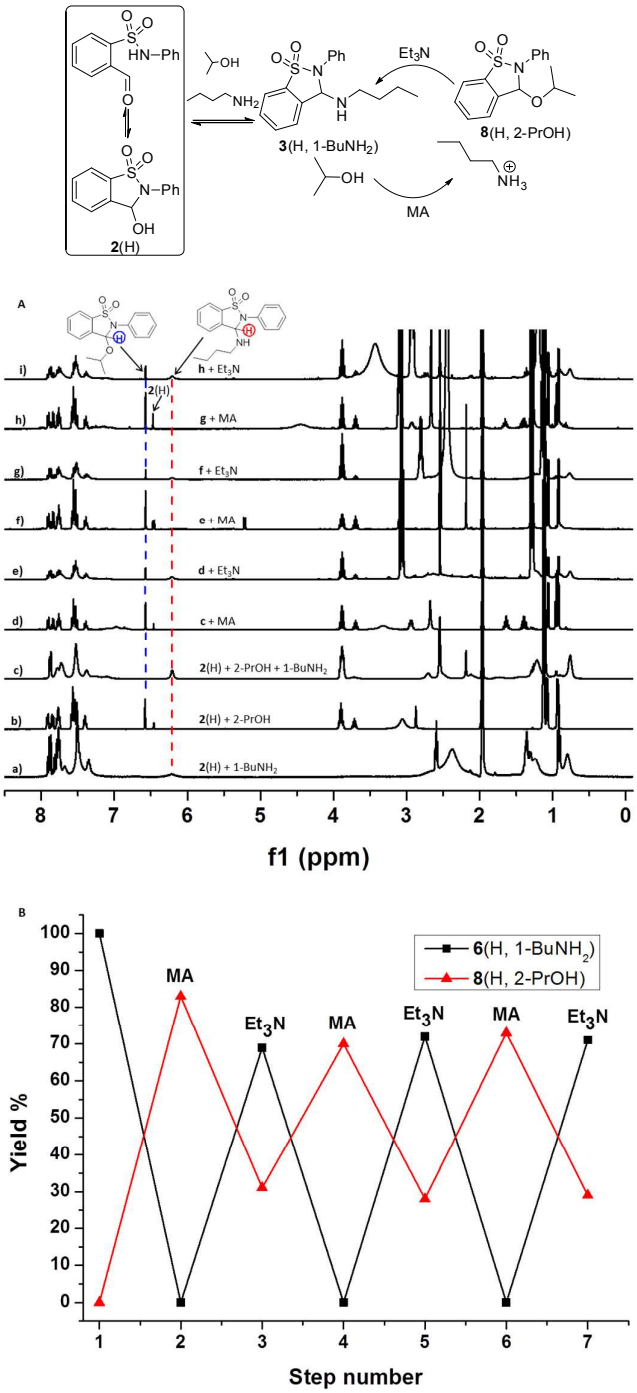


Figure S74. The switch between the assemblies incorporating 1-butylamine and 2-propanol. (A) (a) The reaction of **2**(H) with 1-butylamine; (b) the reaction of **2**(H) with 2-propanol; (c) the reaction of **2**(H) (1.0 equiv.), 1-butylamine (1.2 equiv.), and 2-propanol (3.0 equiv.); (d) the addition of MA (1.8 equiv.) into panel c; (e) the addition of Et_3N (2.0 equiv.) into panel d; (f) the addition of MA (2.0 equiv.) into panel e; (g) the addition of Et_3N (2.2 equiv.) into panel f; (h) the addition of MA (2.2 equiv.) into panel g; (i) the addition of Et_3N (2.4 equiv.) into panel h. (B) The efficiency of the switch in part A (from panel c to panel i).

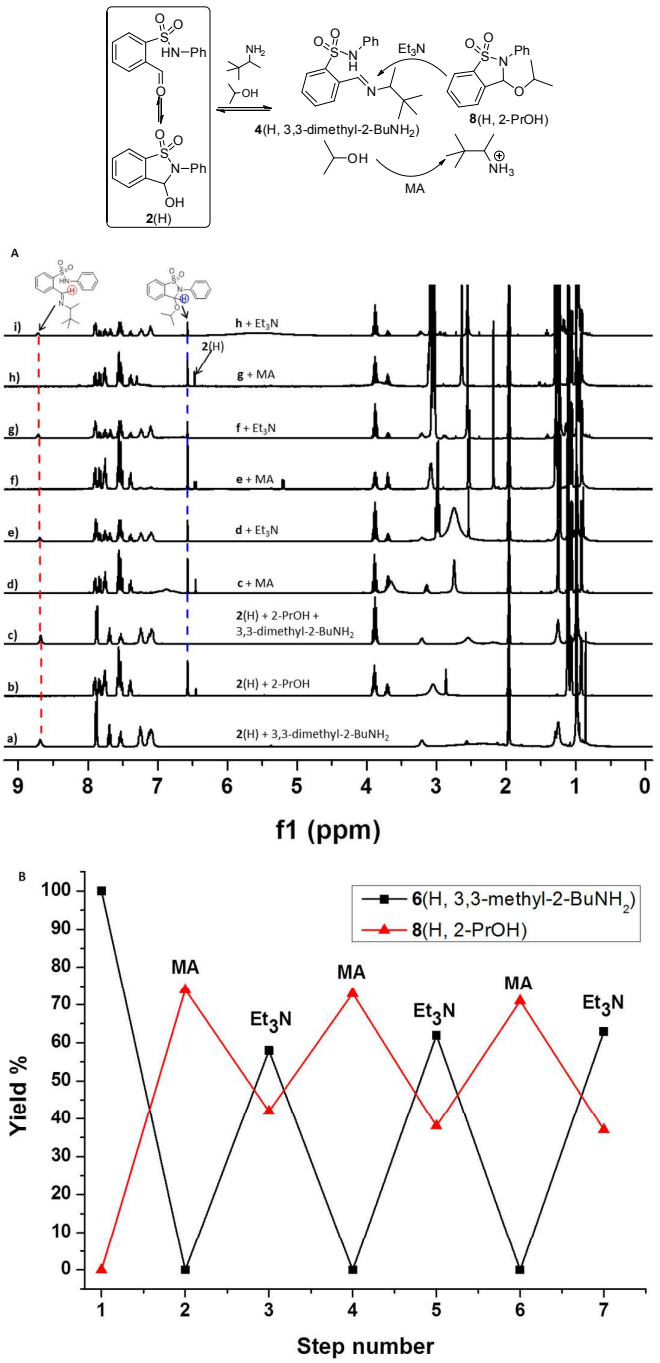


Figure S75. The switch between the assemblies incorporating 3,3-dimethyl-2-butylamine and 2-propanol. (A) (a) The reaction of **2**(H) with 3,3-dimethyl-2-butylamine; (b) the reaction of **2**(H) with 2-propanol; (c) the reaction of **2**(H) (1.0 equiv.), 3,3-dimethyl-2-butylamine (1.2 equiv.), and 2-propanol (3.0 equiv.); (d) the addition of MA (1.8 equiv.) into panel c; (e) the addition of Et_3N (2.0 equiv.) into panel d; (f) the addition of MA (2.0 equiv.) into panel e; (g) the addition of Et_3N (2.2 equiv.) into panel f; (h) the addition of MA (2.2 equiv.) into panel g; (i) the addition of Et_3N (2.4 equiv.) into panel h. (B) The efficiency of the switch in part A (from panel c to panel i).

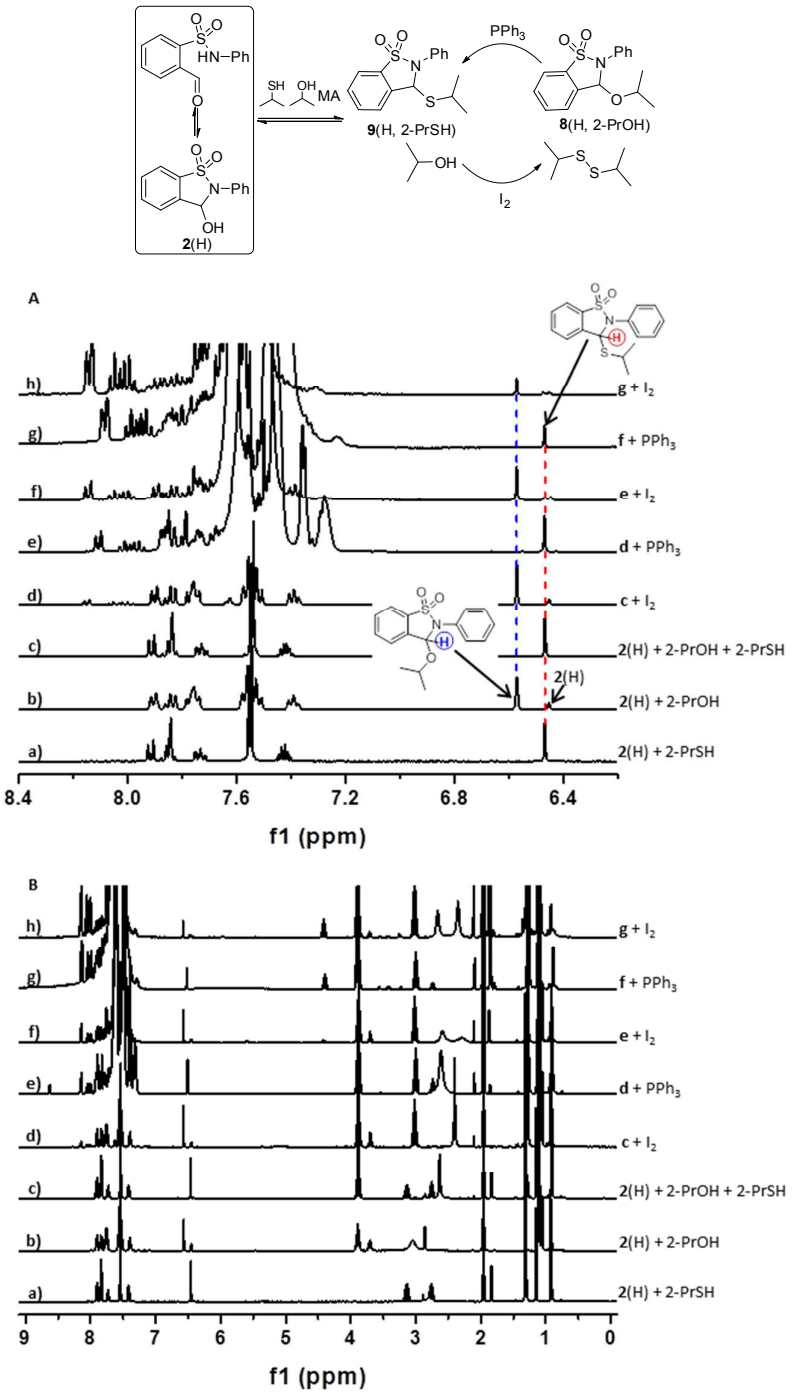


Figure S76. The switch between the assemblies incorporating 2-propanethiol and 2-propanol. (A) (a) The reaction of **2**(H) with 2-propanethiol; (b) the reaction of **2**(H) with 2-propanol; (c) the reaction of **2**(H) (1.0 equiv.), 2-propanethiol (3.0 equiv.), and 2-propanol (3.0 equiv.), and MA (0.4 equiv.); (d) the addition of I_2 (1.5 equiv.) into panel c; (e) the addition of PPh_3 (3.0 equiv.) into panel d; (f) the addition of I_2 (1.5 equiv.) into panel e; (g) the addition of PPh_3 (3.0 equiv.) into panel f; (h) the addition of I_2 (1.5 equiv.) into panel g. (B) The full ^{1}H NMR spectra of A. This figure shows the details and full spectra of Figure 4B in the main text.

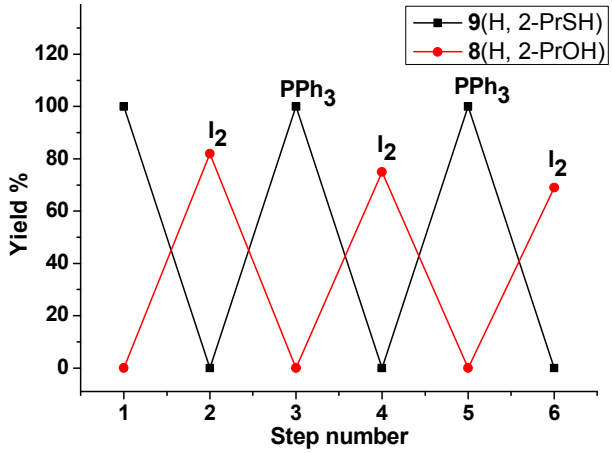


Figure S77. The efficiency of the switch in Figure S76 (from panel c to panel h).

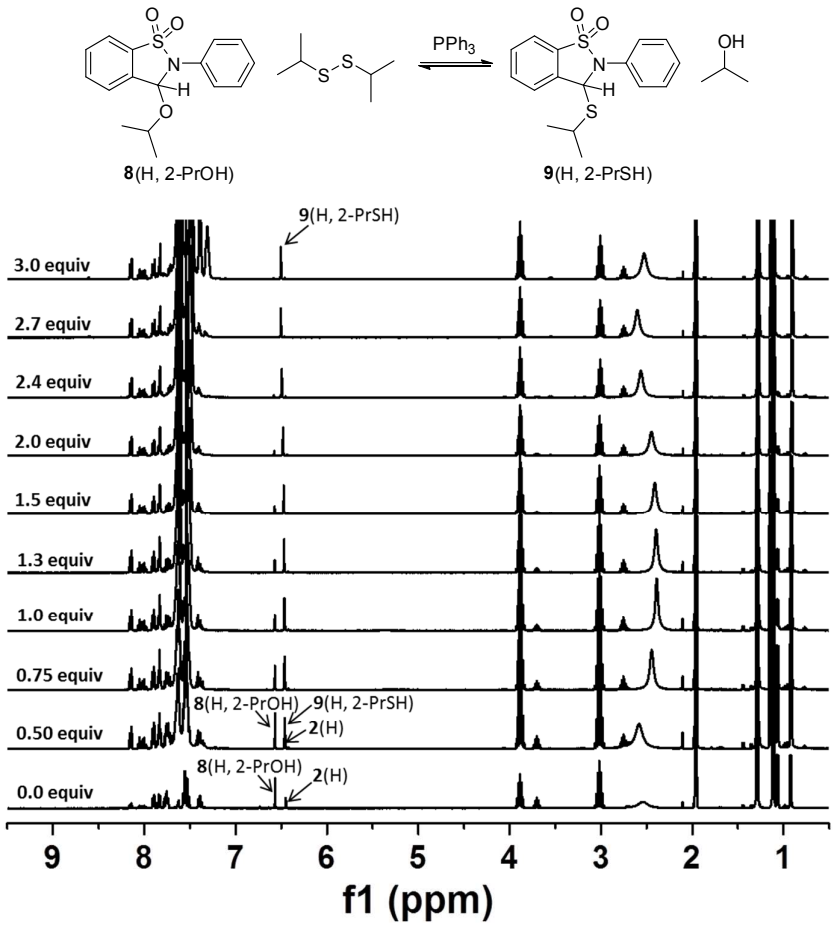


Figure S78. ^{1}H NMR spectra of the titration of PPh_3 for the switch from **8**(H, 2-PrOH) to **9**(H, 2-PrSH). **8**(H, 2-PrOH) was created *in situ*, as illustrated in panel b of Figure 3B. This figure shows the details and full spectra of panel d of Figure 4B in the main text.

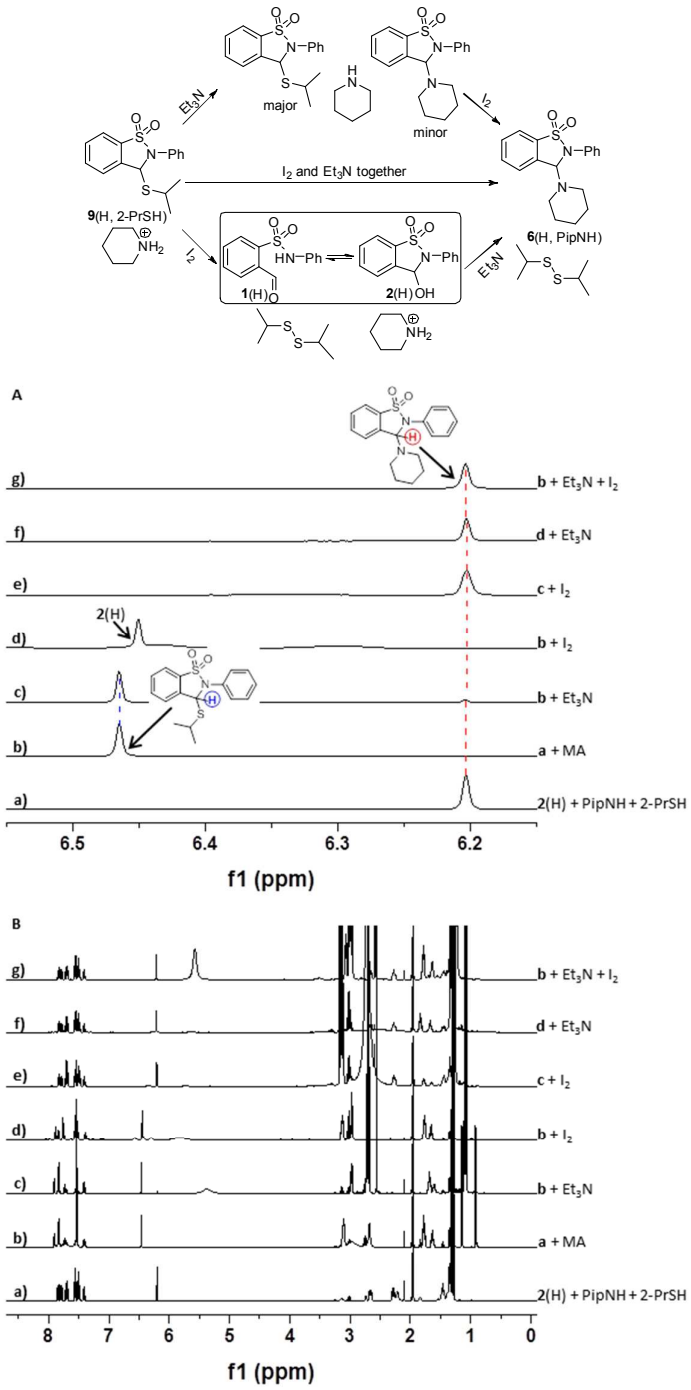


Figure S79. The effect of the sequence of the addition of Et_3N and I_2 on the conversion from **9** to **6**. (A) (a) the reaction of **2**(H) (1.0 equiv.), piperidine (1.2 equiv.), and 2-propanethiol (3.0 equiv.); (b) the addition of MA (2.0 equiv.) into panel a; (c) the addition of Et_3N (5.0 equiv.) into panel b; (d) the addition of I_2 (1.5 equiv.) into panel b; (e) the addition of I_2 (1.5 equiv.) into panel c; (f) the addition of Et_3N (5.0 equiv.) into panel d; (g) the addition of I_2 (1.5 equiv.) and Et_3N (5.0 equiv.) into panel b. (B) The full ^1H NMR spectra of A. This figure shows the details and full spectra of Figure 4C in the main text.

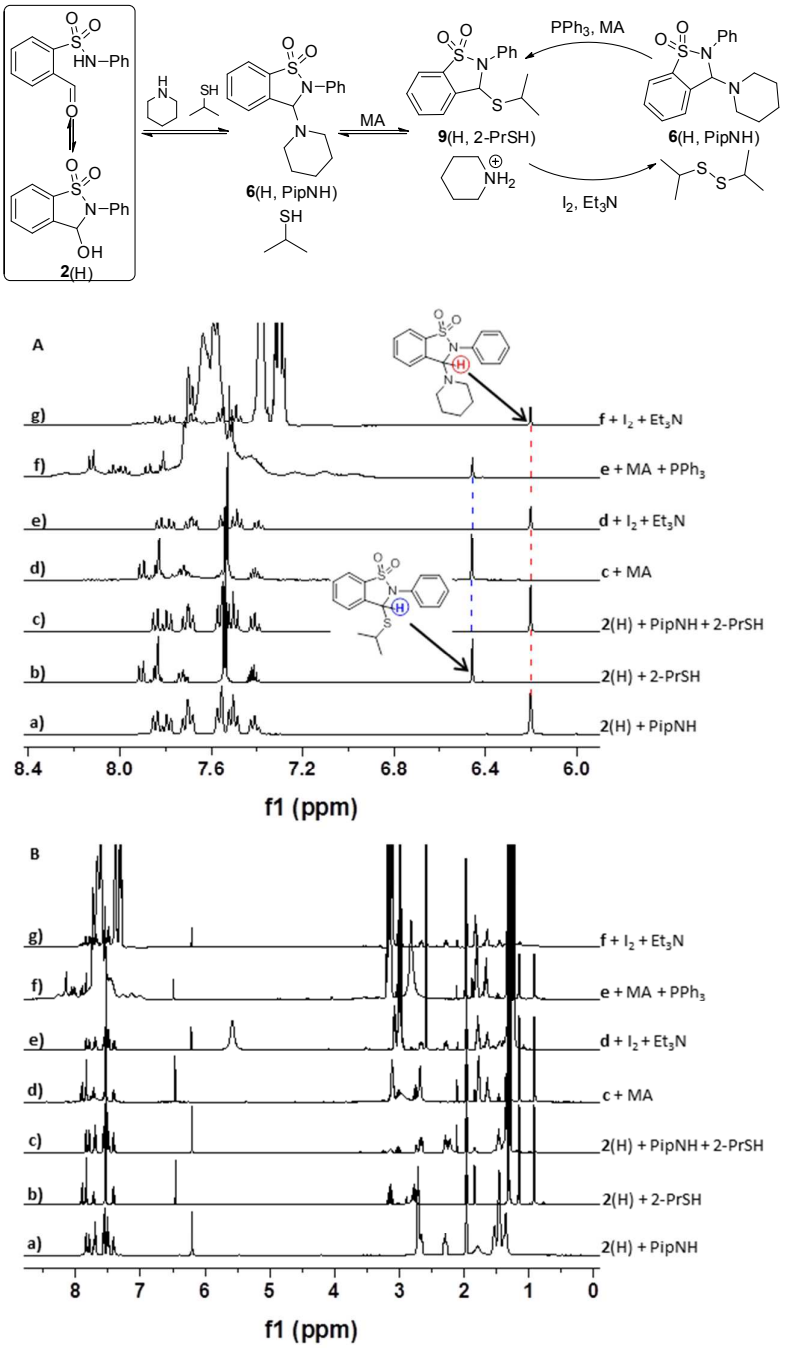


Figure S80. The switch between the assemblies incorporating piperidine and 2-propanethiol. (A) (a) The reaction of **2**(H) with piperidine; (b) the reaction of **2**(H) with 2-propanethiol; (c) the reaction of **2**(H) (1.0 equiv.), piperidine (1.2 equiv.), and 2-propanethiol (3.0 equiv.); (d) the addition of MA (2.0 equiv.) into panel c; (e) the addition of I_2 (1.5 equiv.) and Et_3N (5.0 equiv.) into panel d; (f) the addition of PPh_3 (3.0 equiv.) and MA (2.0 equiv.) into panel e; (g) the addition of I_2 (1.5 equiv.) and Et_3N (5.0 equiv.) into panel f. (B) The full ^1H NMR spectra of A. This figure shows the details and full spectra of Figure 4C in the main text.

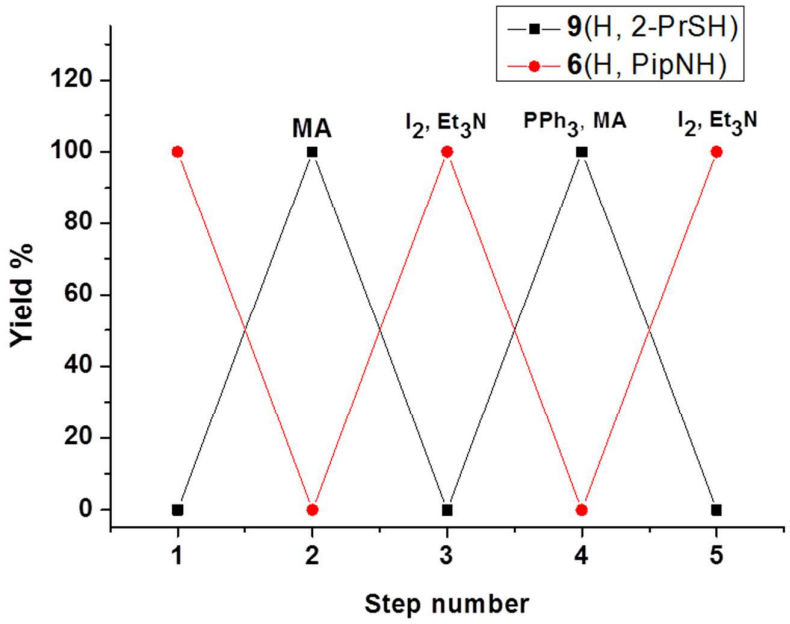


Figure S81. The efficiency of the switch in Figure S80 (from panel c to panel g).

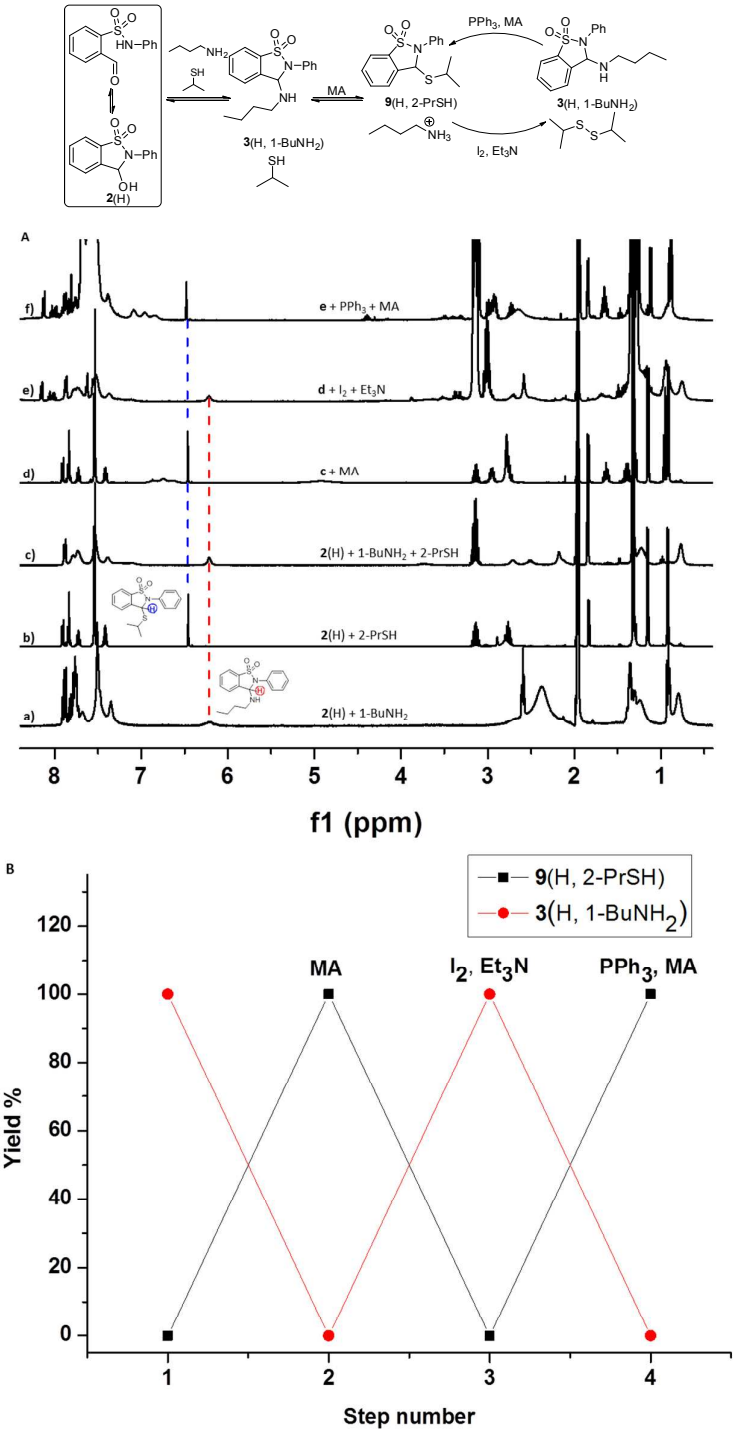


Figure S82. The switch between the assemblies incorporating 1-butylamine and 2-propanethiol. (A) (a) The reaction of **2**(H) with 1-butylamine; (b) the reaction of **2**(H) with 2-propanethiol; (c) the reaction of **2**(H) (1.0 equiv.), 1-butylamine (1.2 equiv.), and 2-propanethiol (3.0 equiv.); (d) the addition of MA (2.0 equiv.) into panel c; (e) the addition of I_2 (1.5 equiv.) and Et_3N (5.0 equiv.) into panel d; (f) the addition of PPh_3 (3.0 equiv.) and MA (2.0 equiv.) into panel e. (B) The efficiency of the switch in part A (from panel c to panel f).

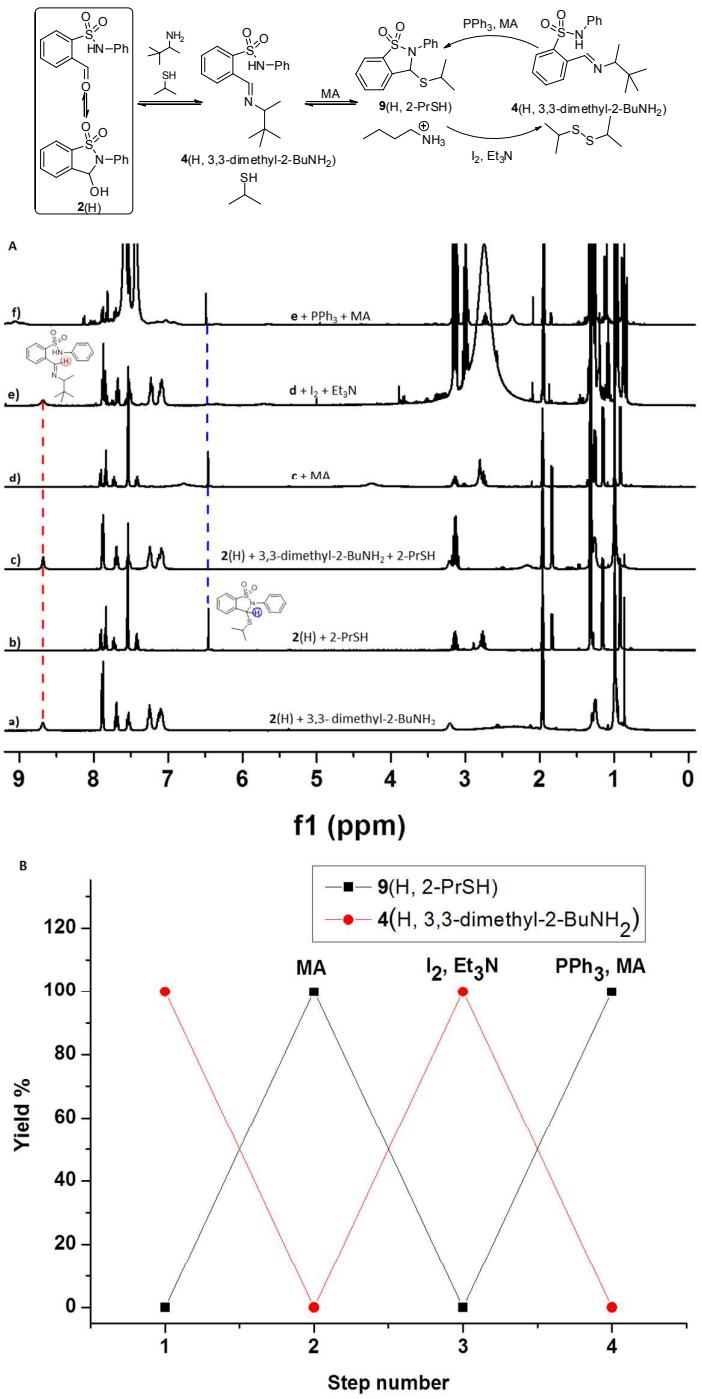


Figure S83. The switch between the assemblies incorporating 3,3-dimethyl-2-butylamine and 2-propanethiol. (A) (a) The reaction of **2**(H) with 3,3-dimethyl-2-butylamine; (b) the reaction of **2**(H) with 2-propanethiol; (c) the reaction of **2**(H) (1.0 equiv.), 3,3-dimethyl-2-butylamine (1.2 equiv.), and 2-propanethiol (3.0 equiv.); (d) the addition of MA (2.0 equiv.) into panel c; (e) the addition of I_2 (1.5 equiv.) and Et_3N (5.0 equiv.) into panel d; (f) the addition of PPh_3 (3.0 equiv.) and MA (2.0 equiv.) into panel e. (B) The efficiency of the switch in part A (from panel c to panel f).

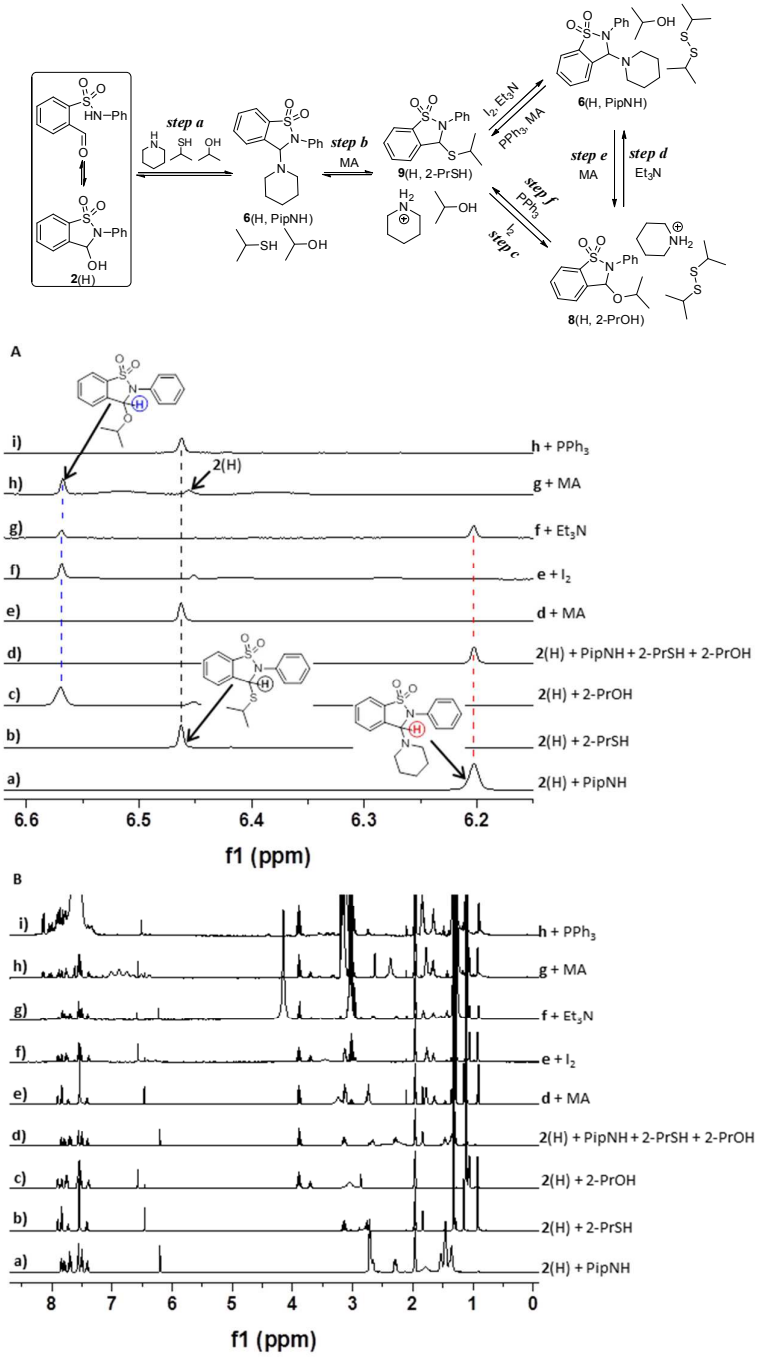


Figure S84. The switch between the assemblies incorporating piperidine, 2-propanol, and 2-propanethiol. (A) (a) The reaction of **2**(H) with piperidine; (b) the reaction of **2**(H) with 2-propanethiol; (c) The reaction of **2**(H) with 2-propanol; (d) the reaction of **2**(H) (1.0 equiv.), piperidine (1.2 equiv.), 2-propanol (3.0 equiv.), and 2-propanethiol (3.0 equiv.); (e) the addition of MA (1.8 equiv.) into panel d; (f) the addition of I_2 (1.5 equiv.) into panel e; (g) the addition of Et_3N (4.8 equiv.) into panel f; (h) the addition of MA (1.8 equiv.) into panel g; (i) the addition of PPh_3 (3.0 equiv.) into panel h. (B) The full ^1H NMR spectra of A. This figure shows the details and full spectra of Figure 5 in the main text.

5. Control Experiments

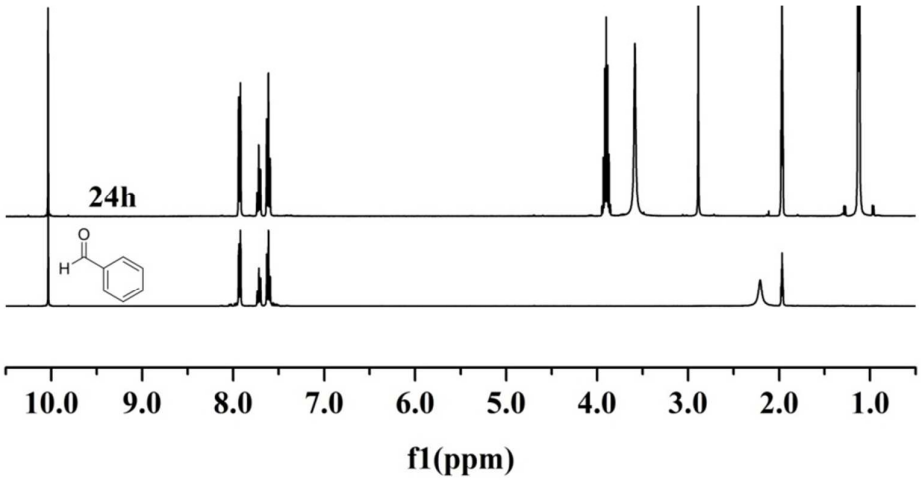


Figure S85. ^{1}H NMR spectra of benzaldehyde (bottom) and its reaction (1.0 equiv.) with 2-propanol (3.0 equiv.) in the presence of MA (1.0 equiv.) after 24 h. No reaction was detected.

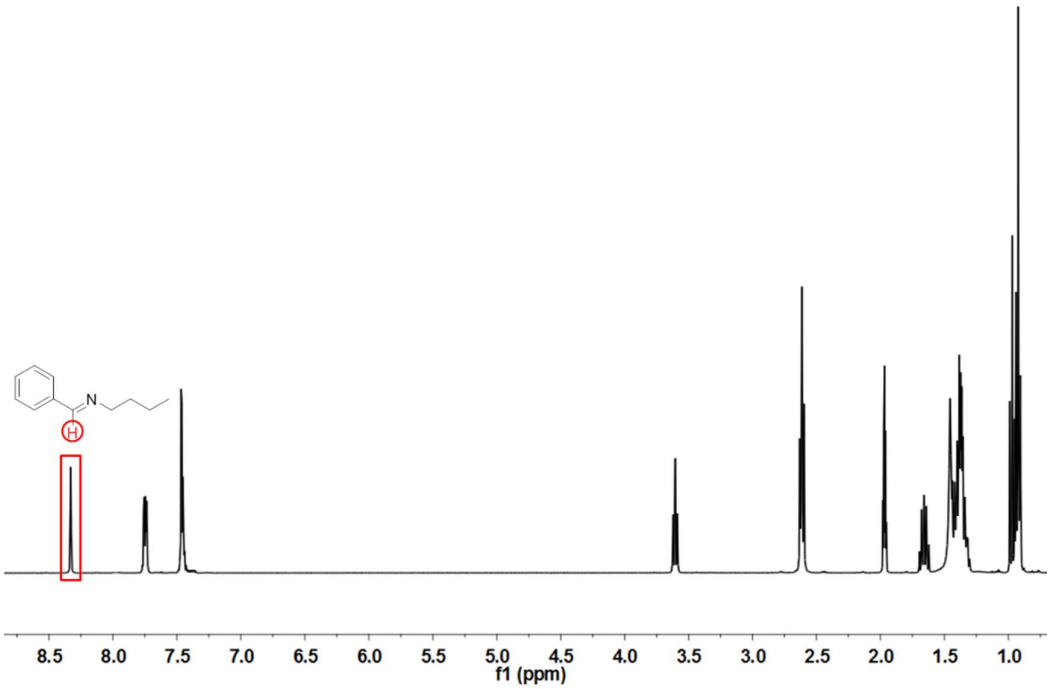


Figure S86. ^{1}H NMR spectrum of the reaction of benzaldehyde (1.0 equiv.) and 1-butylamine (3.0 equiv.) in CD_3CN.

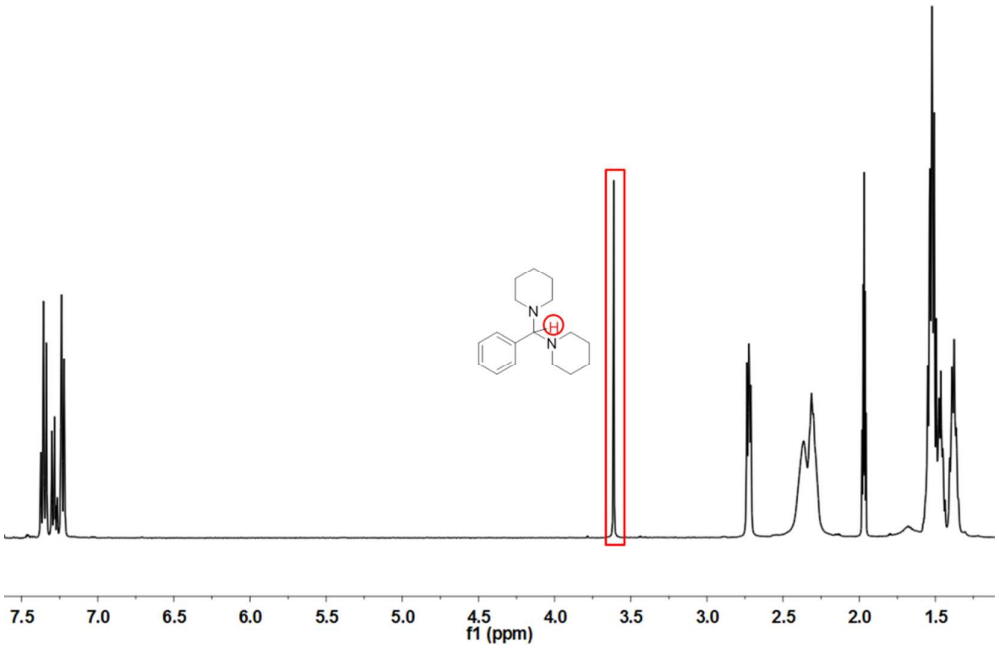


Figure S87. ^{1}H NMR spectrum of the reaction of benzaldehyde (1.0 equiv.) and piperidine (3.0 equiv.) in CD_3CN.

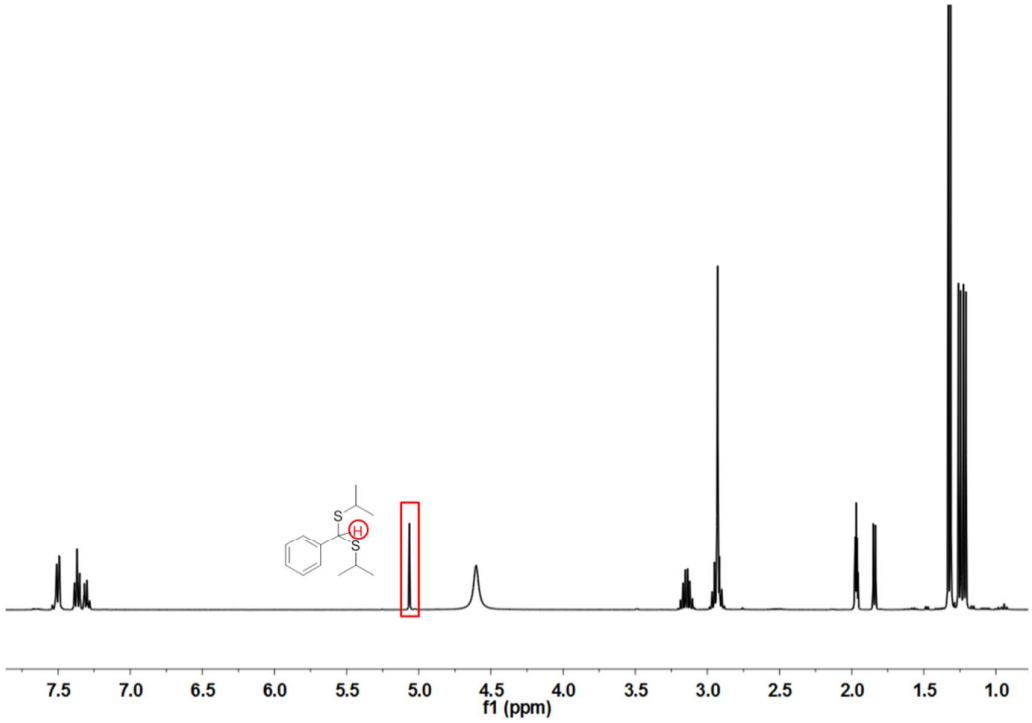


Figure S88. ^{1}H NMR spectrum of the reaction of benzaldehyde (1.0 equiv.) and 2-propanethiol (3.0 equiv.) in the presence of MA (1.0 equiv.) in CD_3CN.

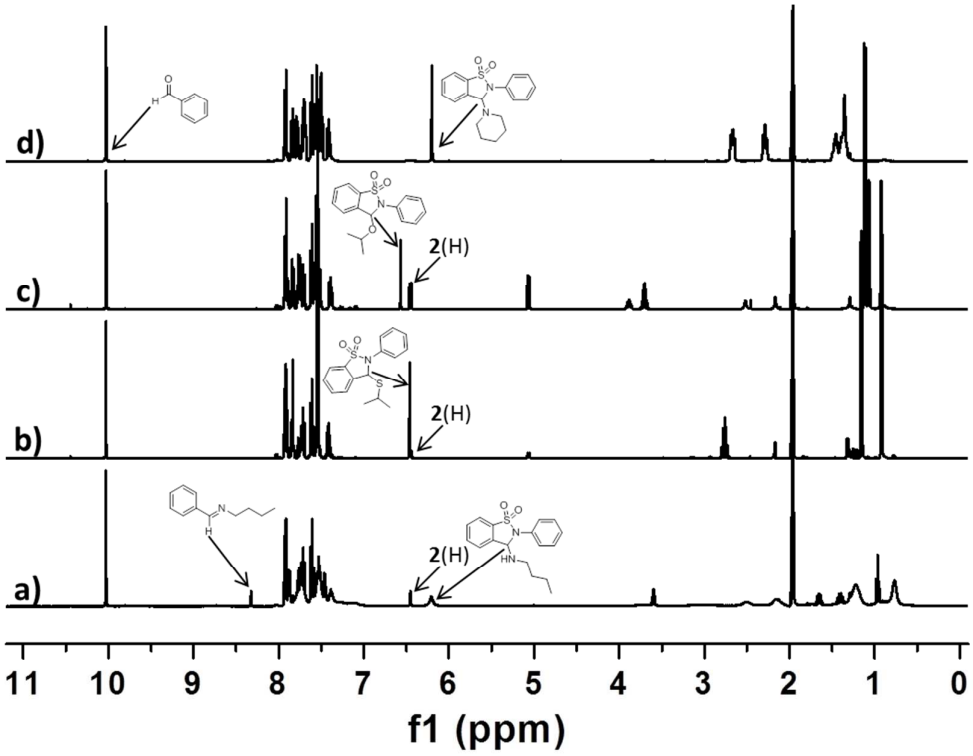


Figure S89. The competition between **2**(H) and benzaldehyde for DCRs with 1-butylamine (a), 2-propanethiol (b), 2-propanol (c), and piperidine (d). This figure shows the details and full spectra of Figure 6 in the main text.

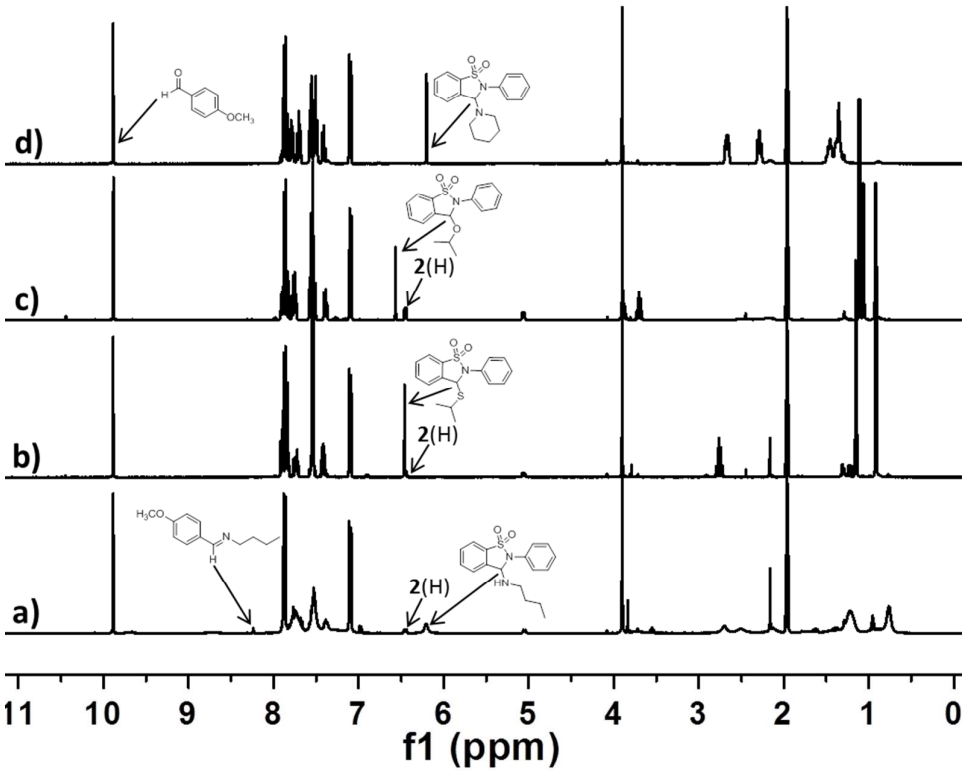


Figure S90. The competition between **2**(H) and 4-methoxybenzaldehyde for DCRs with 1-butylamine (a), 2-propanethiol (b), 2-propanol (c), and piperidine (d). This figure shows the details and full spectra of Figure 6 in the main text.

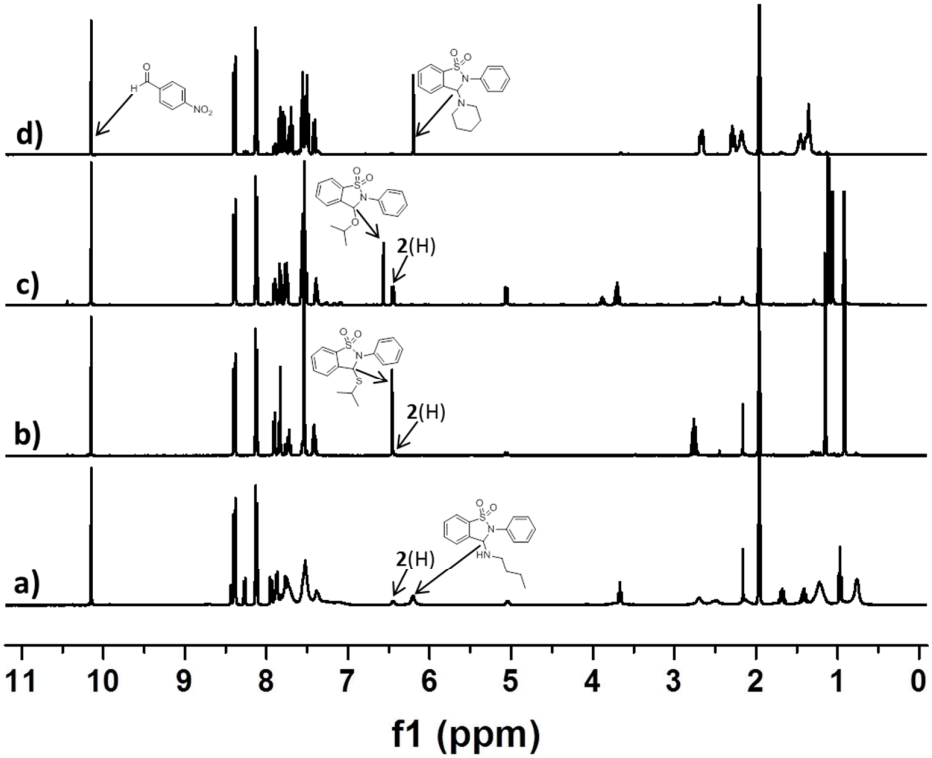


Figure S91. The competition between **2**(H) and 4-nitrobenzaldehyde for DCRs with 1-butylamine (a), 2-propanethiol (b), 2-propanol (c), and piperidine (d). This figure shows the details and full spectra of Figure 6 in the main text.

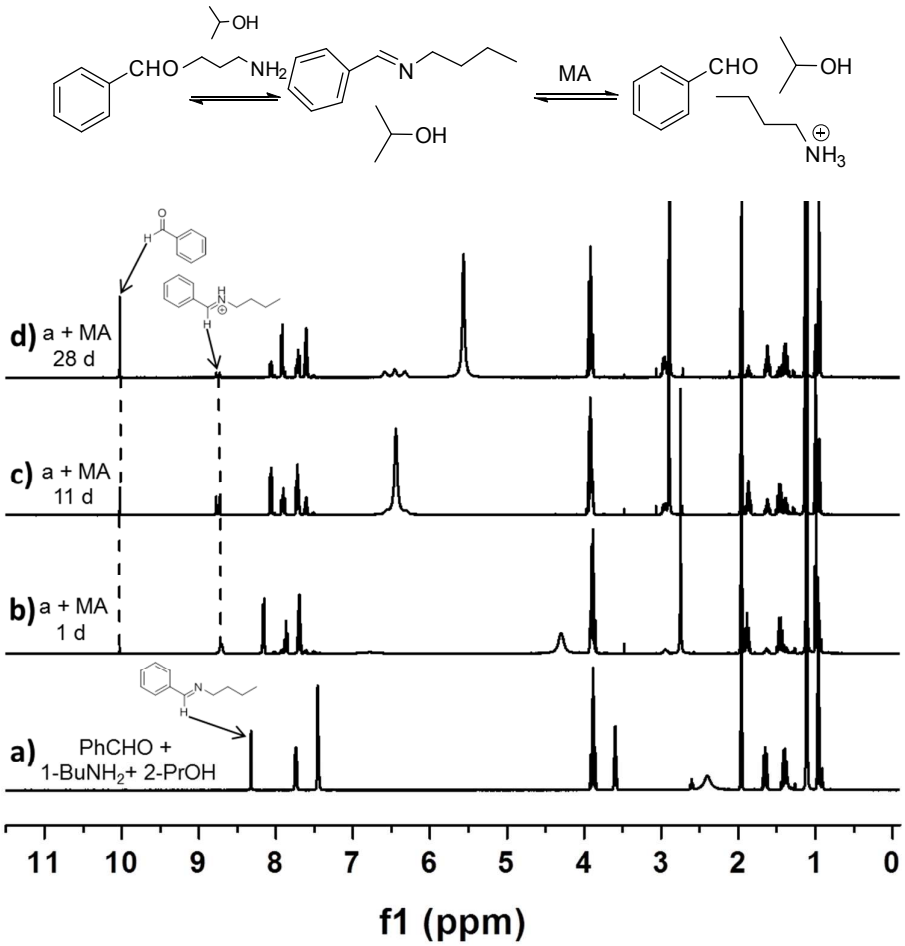


Figure S92. Orthogonal DCC with benzaldehyde. (a) The reaction of benzaldehyde (1.0 equiv.), 1-butylamine (1.2 equiv.), and 2-propanol (3.0 equiv.); (b) the addition of MA (2.4 equiv.) into panel a after 1 day; (c) the addition of MA (2.4 equiv.) into panel a after 11 days; (d) the addition of MA (2.4 equiv.) into panel a after 28 days. This figure shows the details and full spectra of Figure 7A in the main text.

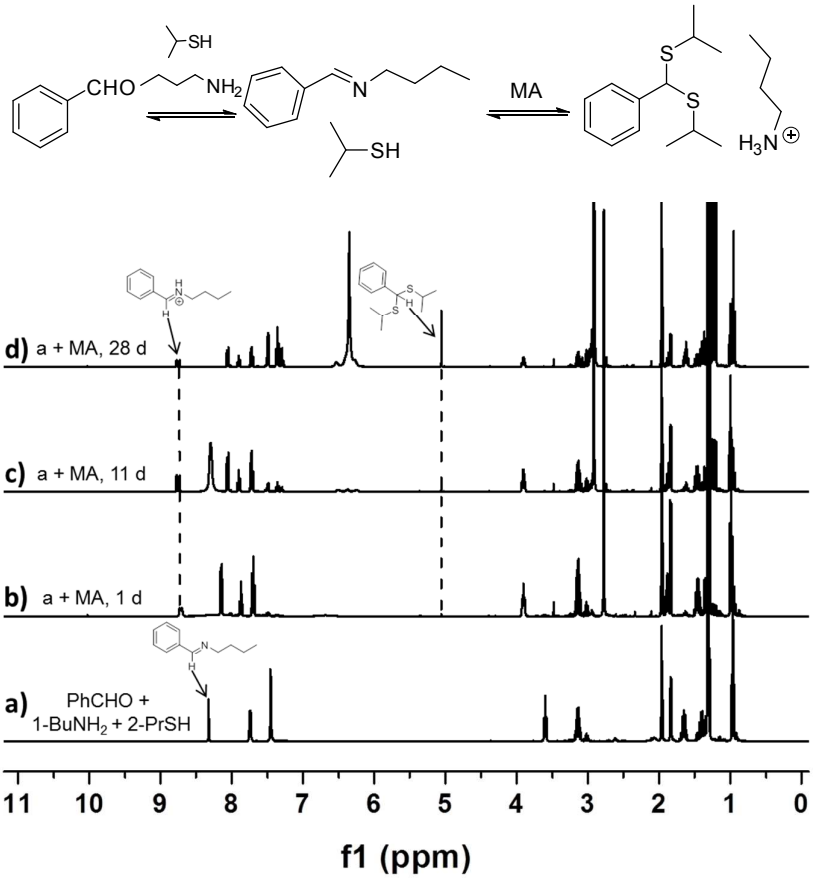


Figure S93. Orthogonal DCC with benzaldehyde. (a) The reaction of benzaldehyde (1.0 equiv.), 1-butylamine (1.2 equiv.), and 2-propanethiol (3.0 equiv.); (b) the addition of MA (2.4 equiv.) into panel a after 1 day; (c) the addition of MA (2.4 equiv.) into panel a after 11 days; (d) the addition of MA (2.4 equiv.) into panel a after 28 days. This figure shows the details and full spectra of Figure 7B in the main text.

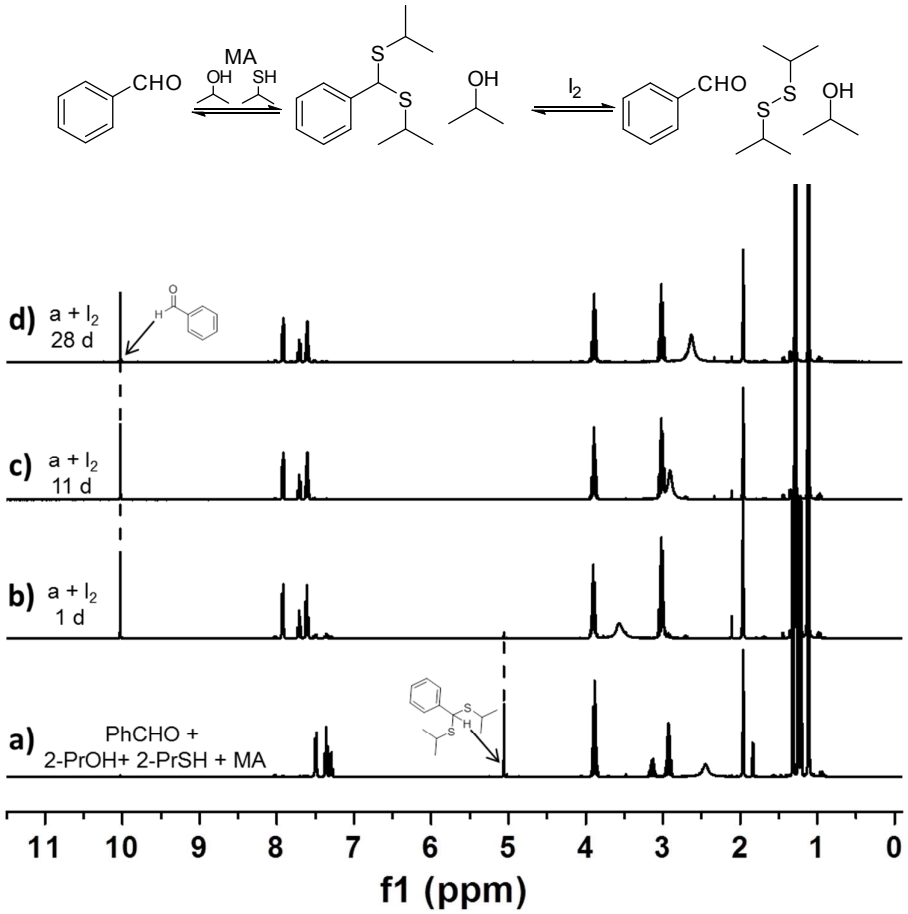


Figure S94. Orthogonal DCC with benzaldehyde. (a) The reaction of benzaldehyde (1.0 equiv.), 2-propanol (3.0 equiv.), 2-propanethiol (3.0 equiv.), and MA (1.0 equiv.); (b) the addition of I_2 (1.5 equiv.) into panel a after 1 day; (c) the addition of I_2 (1.5 equiv.) into panel a after 11 days; (d) the addition of I_2 (1.5 equiv.) into panel a after 28 days. This figure shows the details and full spectra of Figure 7C in the main text.

6. Complex Systems

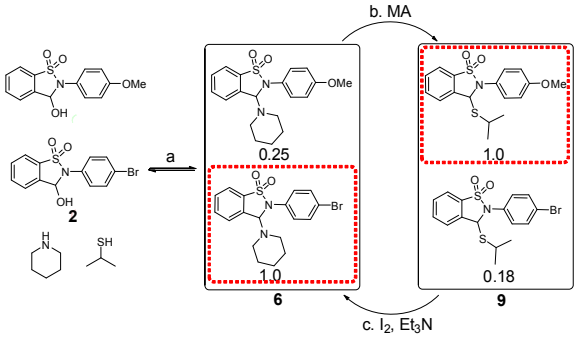


Figure S95. A library created from **2**(Br), **2**(OMe), piperidine, and 2-propanethiol as well as its transformation (a-c). The integrals of products are listed with the favored assemblies highlighted in red. The corresponding ^{1}H NMR spectra are shown in panels e-g of Figure S96.

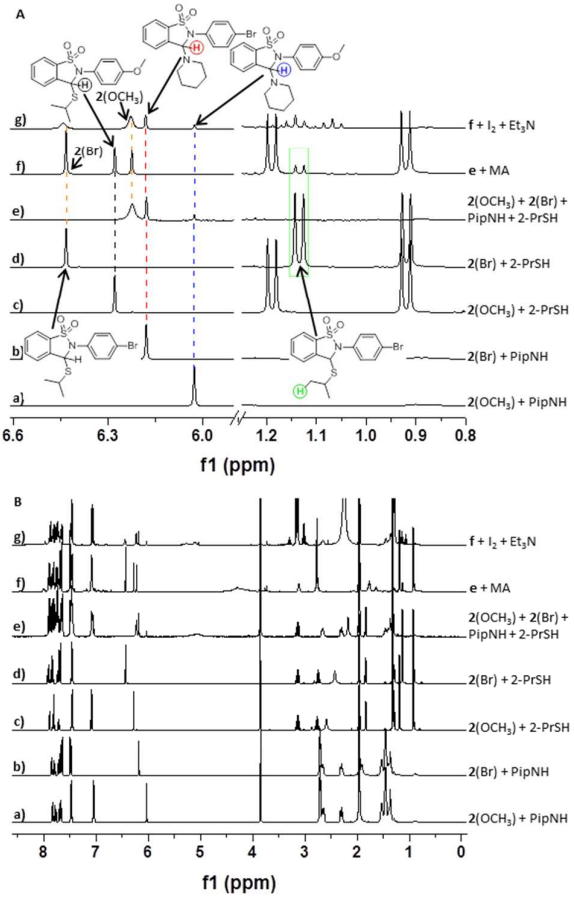


Figure S96. (A) A library created from **2**(Br) (1.0 equiv.), **2**(OMe) (1.0 equiv.), piperidine (0.5 equiv.), and 2-propanethiol (0.5 equiv.) as well as its transformation (e-g). The single individual DCR is shown in panels a-d for the comparison. (B) The full ^{1}H NMR spectra of A. Due to overlapping of the methine peaks of **2**(Br) and **9**(Br, 2-PrSH), the methyl peak of **9**(Br, 2-PrSH) is marked in green. This figure shows the details and full spectra of Figure 8A in the main text.

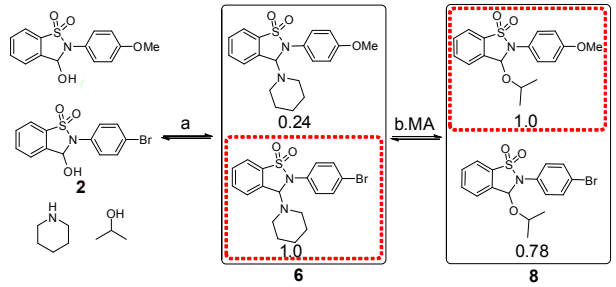


Figure S97. A library created from **2**(Br), **2**(OMe), piperidine, and 2-propanol as well as its transformation (a and b). The integrals of products are listed with the favored assemblies highlighted in red. The corresponding ^{1}H NMR spectra are shown in panel e and f of Figure S98.

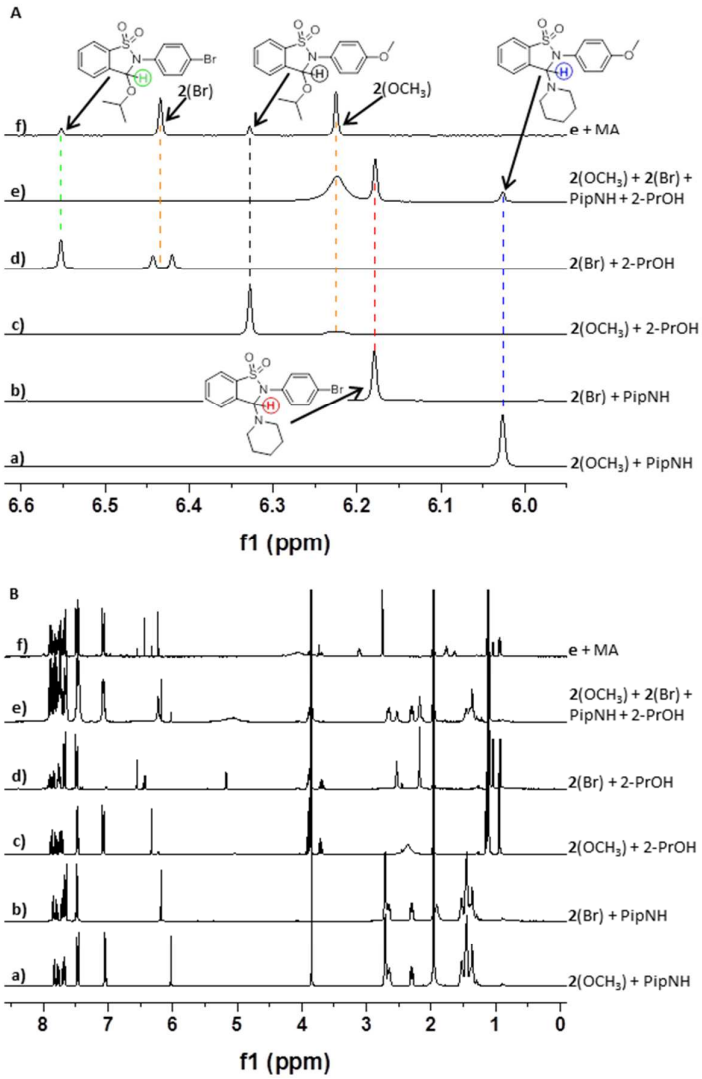


Figure S98. (A) A library created from **2**(Br) (1.0 equiv.), **2**(OMe) (1.0 equiv.), piperidine (0.5 equiv.), and 2-propanol (0.5 equiv.) as well as its transformation (e and f). The single individual DCR is shown in panels a-d for the comparison. (B) The full ^{1}H NMR spectra of A.

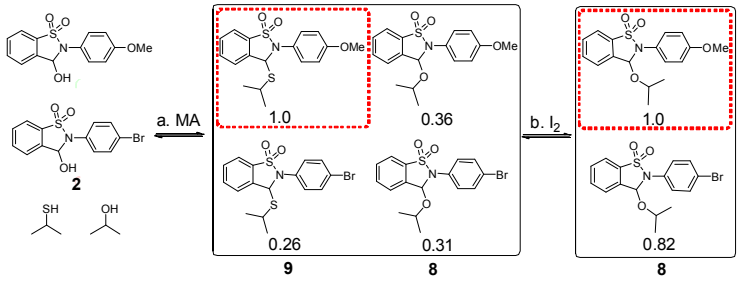


Figure S99. A library created from **2**(Br), **2**(OMe), 2-propanethiol, and 2-propanol as well as its transformation (a and b). The integrals of products are listed with the favored assemblies highlighted in red. The corresponding ^{1}H NMR spectra are shown in panel e and f of Figure S100.

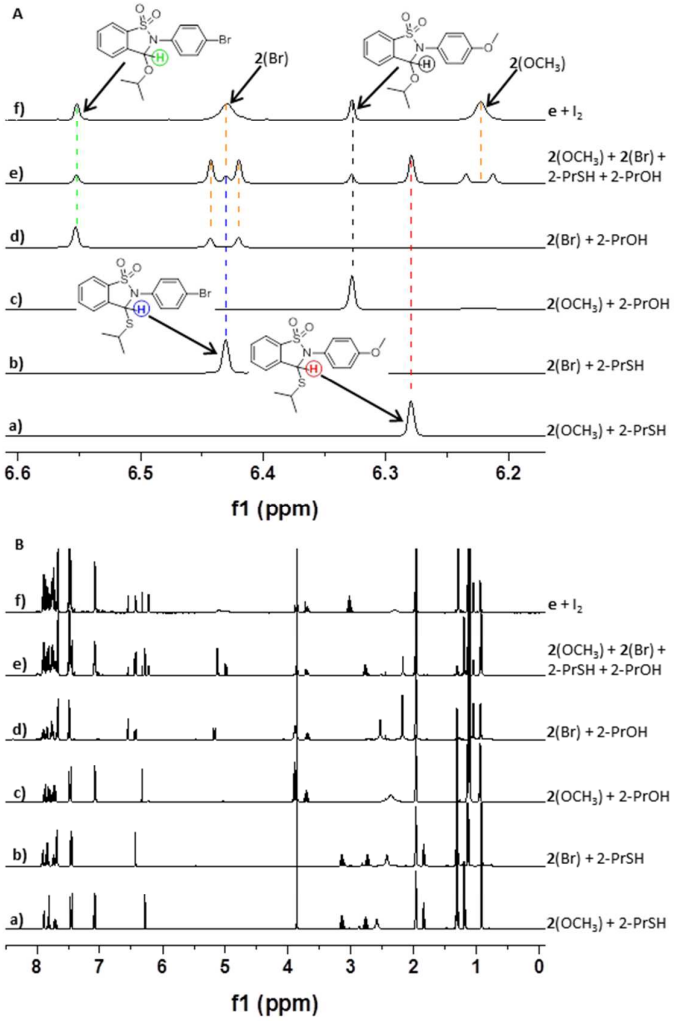


Figure S100. (A) A library created from **2**(Br) (1.0 equiv.), **2**(OMe) (1.0 equiv.), 2-propanethiol (0.5 equiv.), and 2-propanol (0.5 equiv.) as well as its transformation (e and f). The single individual DCR is shown in panels a-d for the comparison. (B) The full ^{1}H NMR spectra of A.

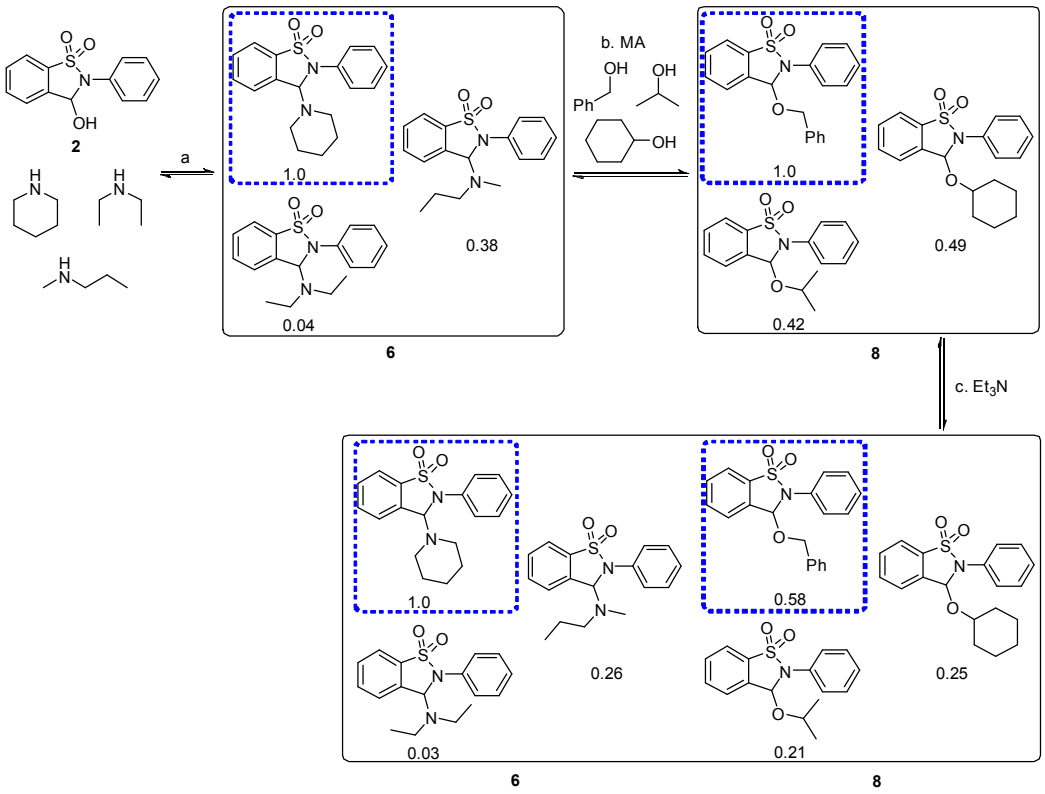


Figure S101. A library created from **2**(H), piperidine, *N*-methyl-1-propylamine, and diethylamine (a) followed by the addition of benzylalcohol, cyclohexanol, 2-propanol, and MA (b) as well as Et_3N (c). The integrals of products are listed with the favored assemblies highlighted in blue. The corresponding ^1H NMR spectra are shown in panels g-i of Figure S102. This figure shows the details of Figure 7B in the main text.

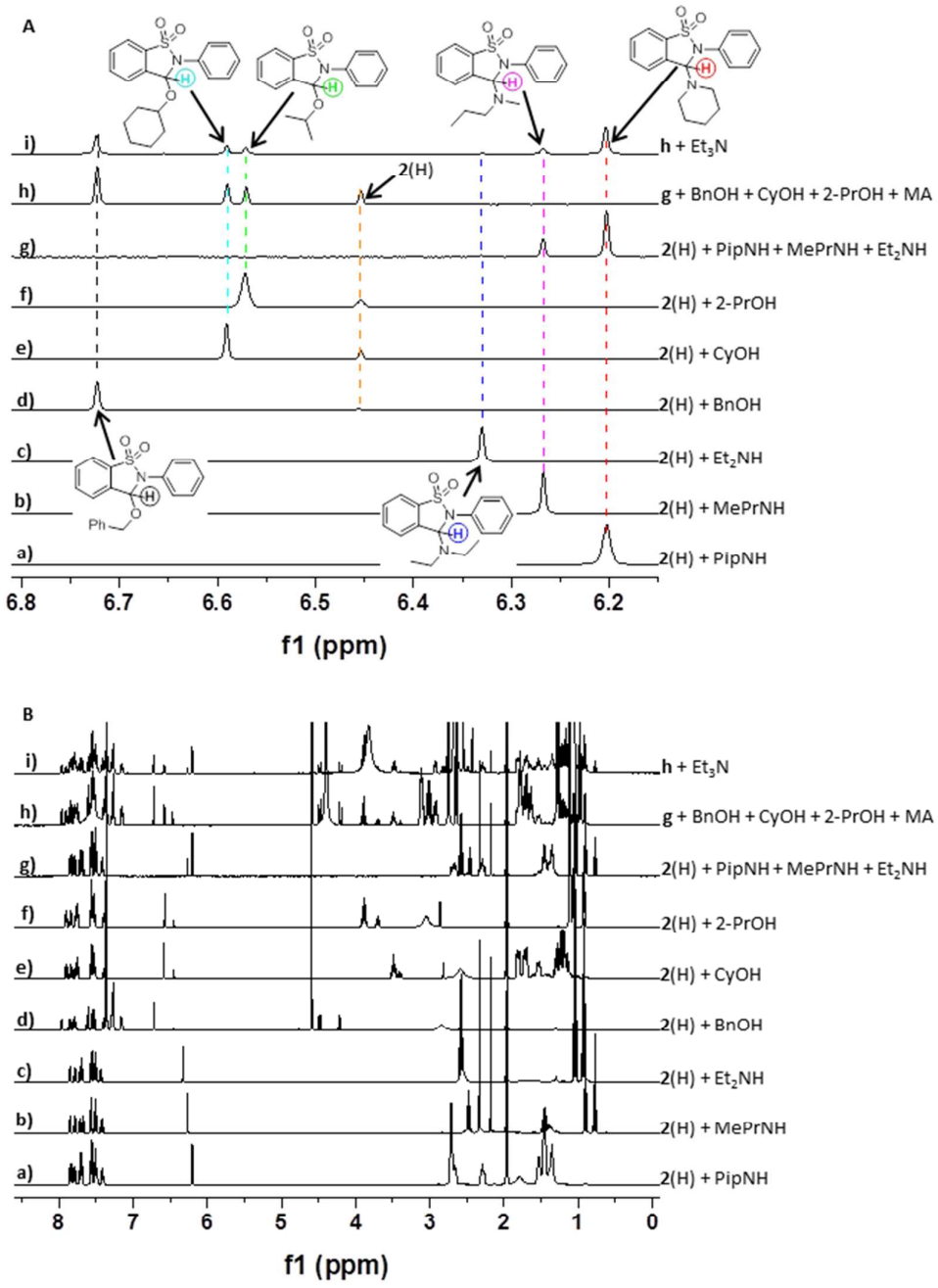


Figure S102. (A) A library created from **2**(H) (1.0 equiv.), piperidine (1.0 equiv.), *N*-methyl-1-propylamine (1.0 equiv.), and diethylamine (1.0 equiv.) (g) followed by the addition of benzylalcohol (1.0 equiv.), cyclohexanol (1.0 equiv.), 2-propanol (1.0 equiv.), and MA (3.8 equiv.) (h) as well as Et_3N (3.8 equiv.) (i). The single individual DCR is shown in panels a-f for the comparison. (B) The full ^1H NMR spectra of A. This figure shows the details and full spectra of Figure 8B in the main text.

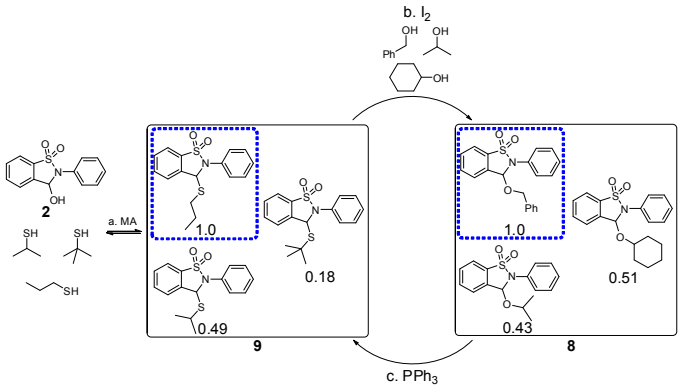


Figure S103. A library created from **2**(H), 1-propanethiol, 2-propanethiol, *t*-butanethiol, and MA (a) followed by the addition of benzylalcohol, cyclohexanol, 2-propanol, and I_2 (b) as well as PPh_3 (c). The integrals of products are listed with the favored assemblies highlighted in blue. The corresponding ^{1}H NMR spectra are shown in panels g-i of Figure S104.

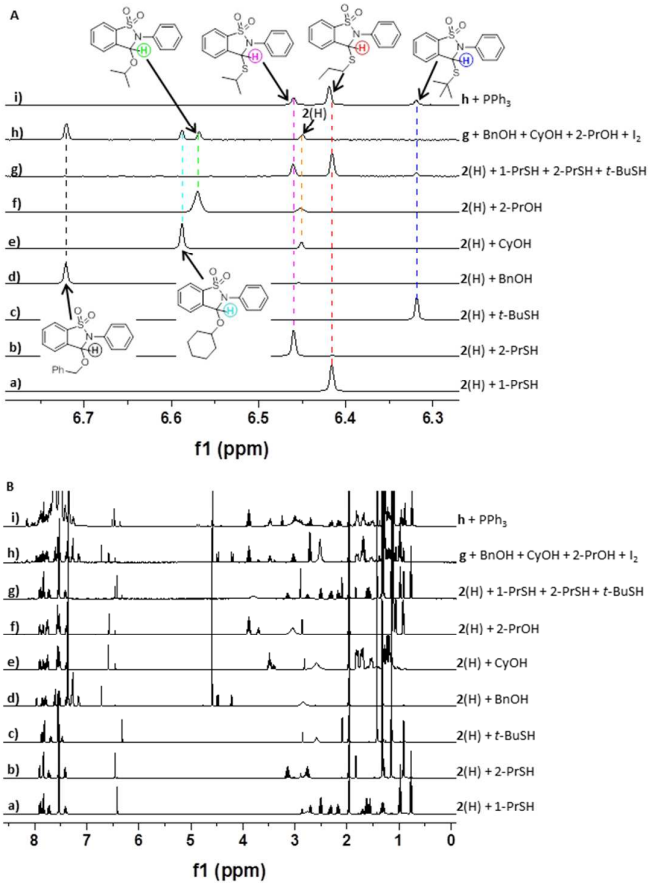


Figure S104. (A) A library created from **2**(H) (1.0 equiv.), 1-propanethiol (1.0 equiv.), 2-propanethiol (1.0 equiv.), *t*-butanethiol (1.0 equiv.), and MA (0.4 equiv.) (g) followed by the addition of benzylalcohol (1.0 equiv.), cyclohexanol (1.0 equiv.), 2-propanol (1.0 equiv.), and I_2 (1.5 equiv.) (h) as well as PPh_3 (3.0 equiv.) (i). The single individual DCR was shown in panels a-f for the comparison. (B) The full ^{1}H NMR spectra of A.

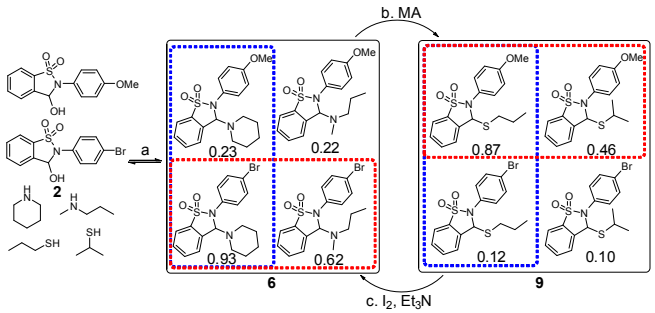


Figure S105. A library created from **2**(OCH_3), **2**(Br), 1-propanethiol, 2-propanethiol, piperidine, and *N*-methyl-1-propylamine as well as its transformation (a-c). The integrals of products are listed, with the favored aldehyde derived assemblies highlighted in red and the favored nucleophile derived assemblies highlighted in blue. The corresponding ^{1}H NMR spectra are shown in panels i-k of Figure S106.

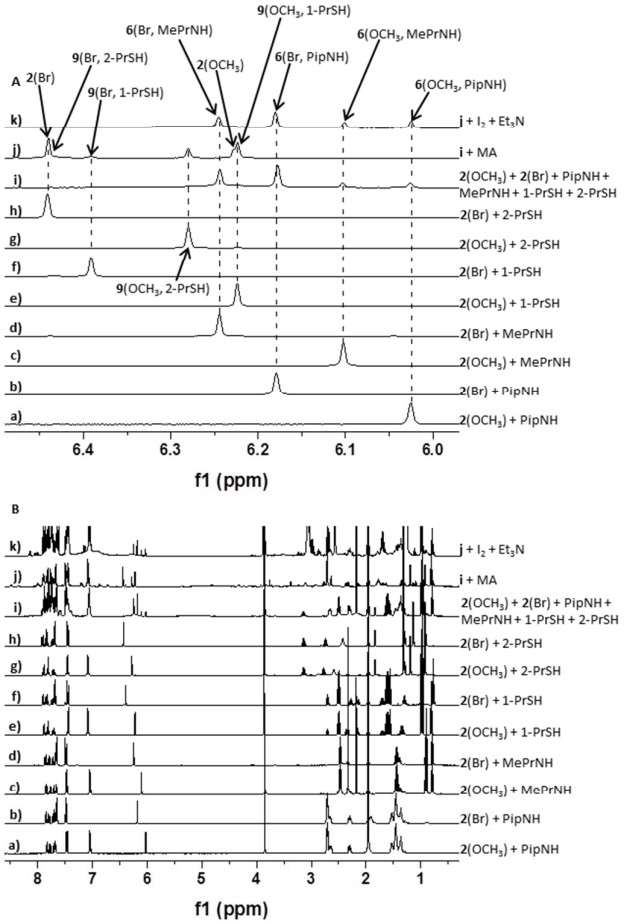


Figure S106. (A) A library created from **2**(OCH_3) (1.0 equiv.), **2**(Br) (1.0 equiv.), 1-propanethiol (0.75 equiv.), 2-propanethiol (0.75 equiv.), piperidine (0.75 equiv.), and *N*-methyl-1-propylamine (0.75 equiv.) as well as its transformation (i-k). The single individual DCR is shown in panels a-h for the comparison. (B) The full ^{1}H NMR spectra of A.

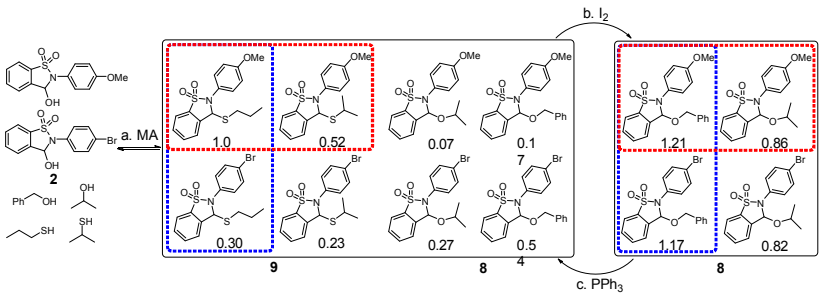


Figure S107. A library created from **2**(OCH_3), **2**(Br), 1-propanethiol, 2-propanethiol, benzylalcohol, and 2-propanol as well as its transformation (a-c). The integrals of products are listed, with the favored aldehyde derived assemblies highlighted in red and the favored nucleophile derived assemblies highlighted in blue. The corresponding ^{1}H NMR spectra are shown in panels i-k of Figure S108.

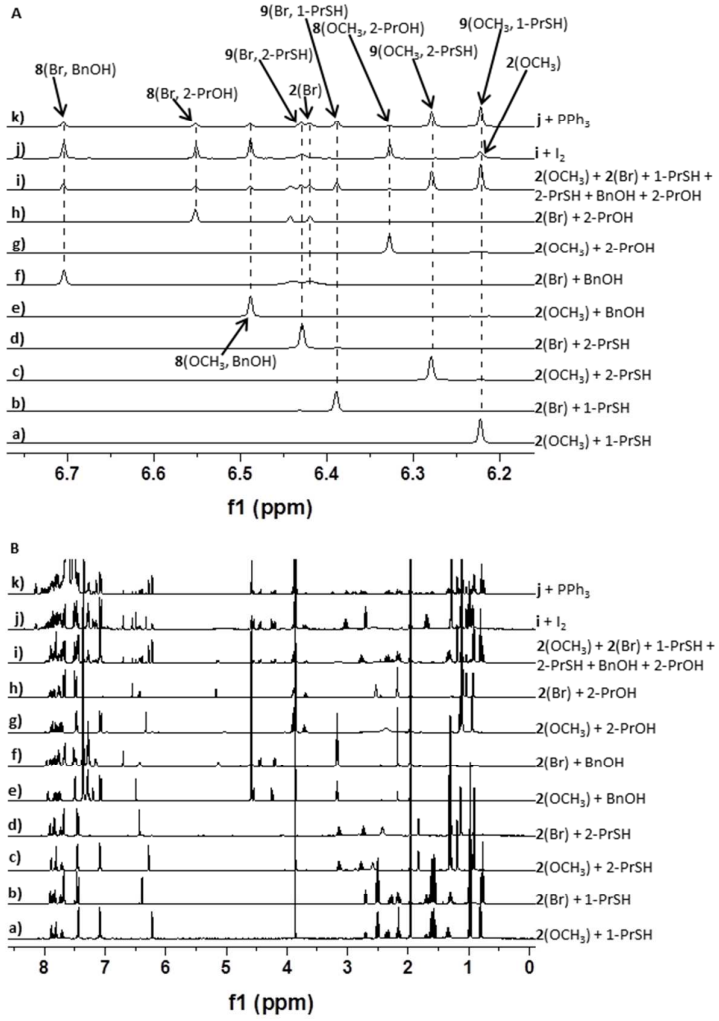


Figure S108. (A) A library created from **2**(OCH_3) (1.0 equiv.), **2**(Br) (1.0 equiv.), 1-propanethiol (0.75 equiv.), 2-propanethiol (0.75 equiv.), benzylalcohol (0.75 equiv.), and 2-propanol (0.75 equiv.) as well as its transformation (i-k). The single individual DCR is shown in panels a-h for the comparison. (B) The full ^{1}H NMR spectra of A.

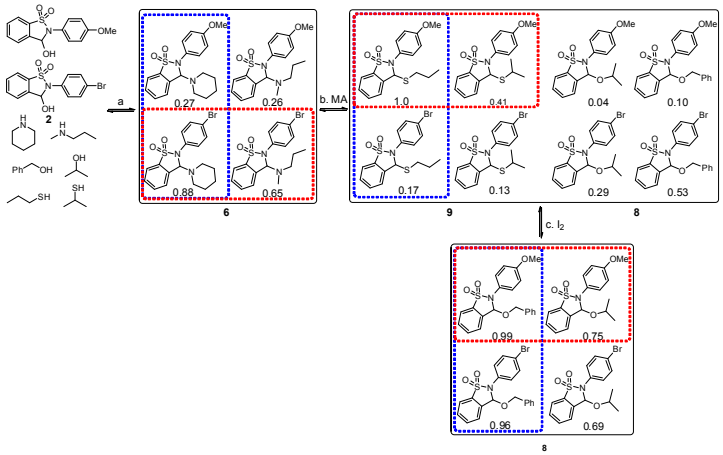


Figure S109. A library created from **2**(OCH_3), **2**(Br), piperidine, *N*-methyl-1-propylamine, 1-propanethiol, 2-propanethiol, benzylalcohol, and 2-propanol as well as its transformation (a-c). The integrals of products are listed, with the favored aldehyde derived assemblies highlighted in red and the favored nucleophile derived assemblies highlighted in blue. The corresponding ^{1}H NMR spectra are shown in panels a-c of Figure S110.

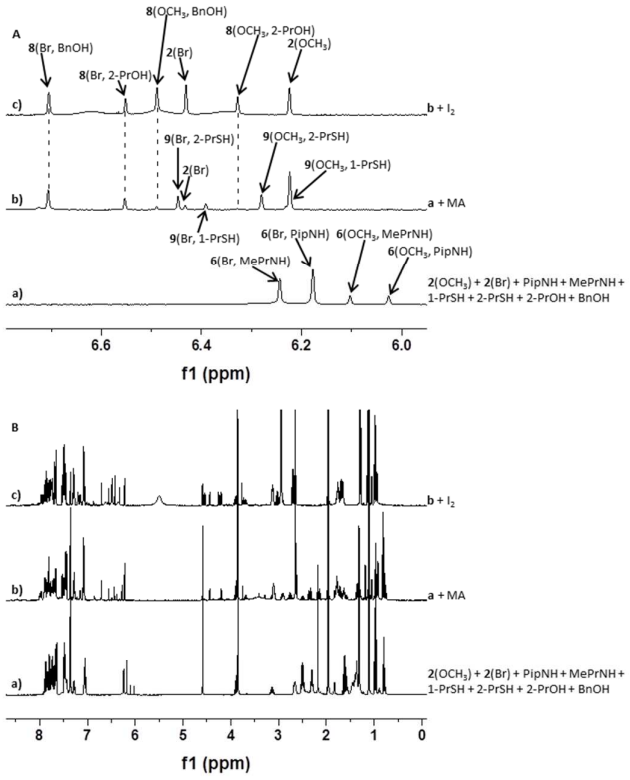


Figure S110. (A) A library created from **2**(OCH_3) (1.0 equiv.), **2**(Br) (1.0 equiv.), piperidine (0.75 equiv.), *N*-methyl-1-propylamine (0.75 equiv.), 1-propanethiol (0.75 equiv.), 2-propanethiol (0.75 equiv.), benzylalcohol (0.75 equiv.), 2-propanol (0.75 equiv.) as well as its transformation (a-c). (B) The full ^{1}H NMR spectra of A. This figure shows the details and full spectra of Figure 8C in the main text.