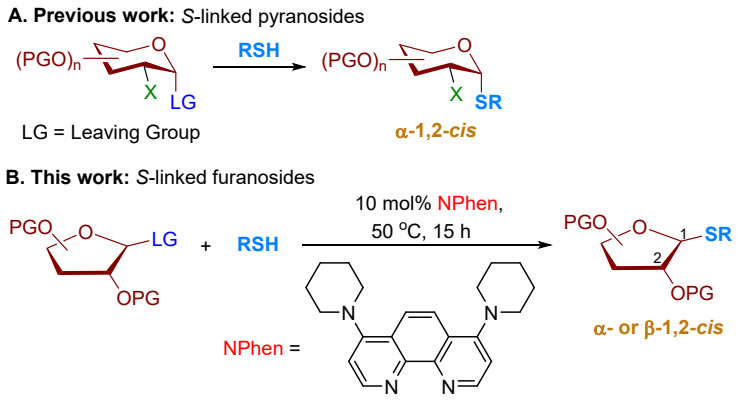
**Scheme 1**. Stereoselective construction of β-*S*-linked pyranosides and furanosides




**Scheme 2**. Preliminary studies with readily available 4,7-diphenyl-1,10-phenanthroline (BPhen) catalyst

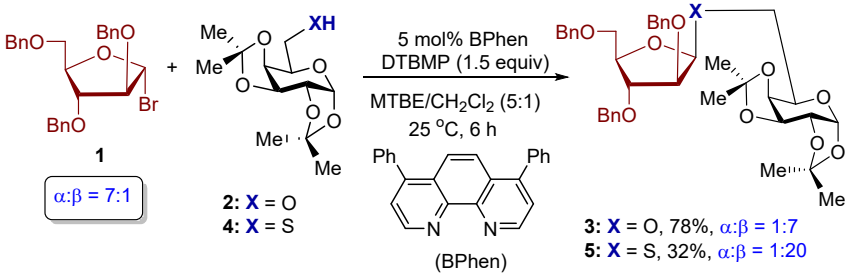
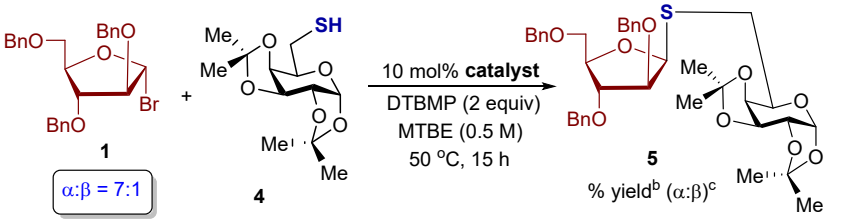
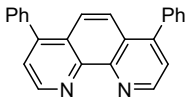
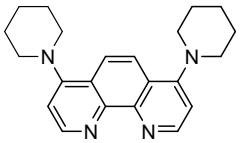
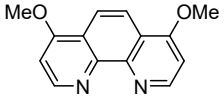
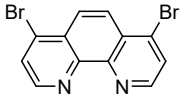
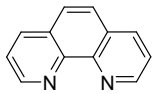
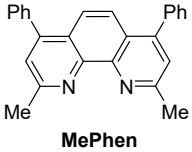
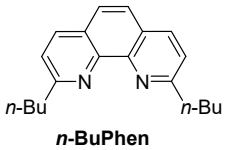
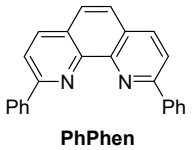
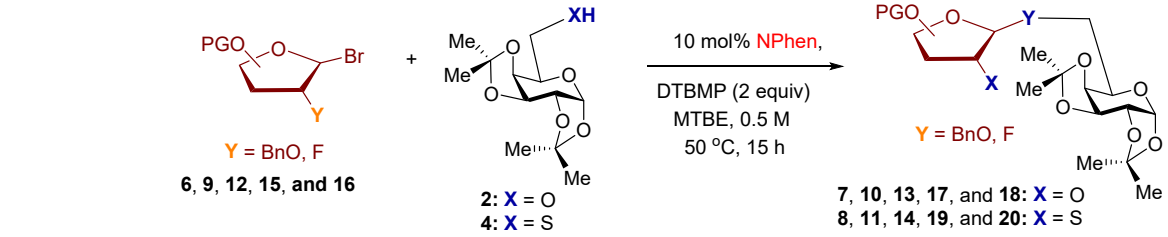



**Table 1**. Evaluation of Phenanthroline Catalysts for Stereoselective *S*-Furanosylation.




| | | |
|---|---|---|
|  **BPhen** 69% (α:β = 1:20) |  **NPhen** 79% (α:β = 1:25) |  **MeOPhen** 71% (α:β = 1:20) |
|  **BrPhen** 76% (α:β = 1:15) |  **Phen** 69% (α:β = 1:17) | |
|  **MePhen** 50% (α:β = 1:14) |  ***n*-BuPhen** 74% (α:β = 1:6) |  **PhPhen** 71% (α:β = 1:15) |

**Scheme 3.** Reactivity and stereoselectivity differences between *O*-furanosides and *S*-furanosides



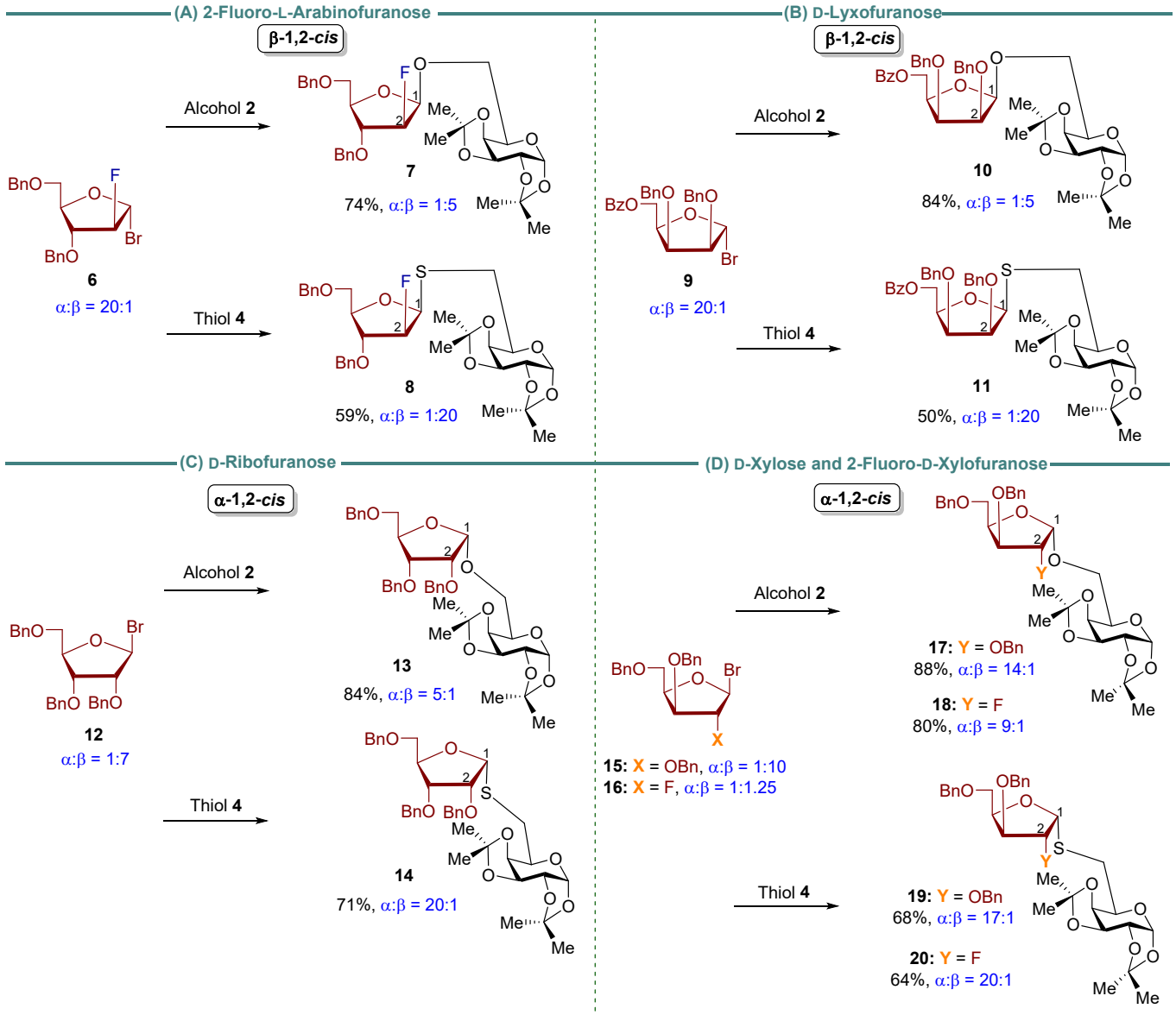
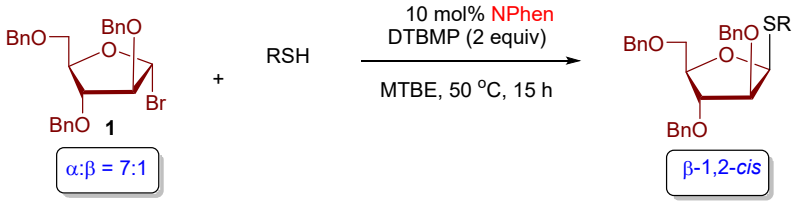
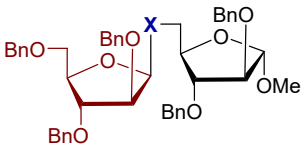
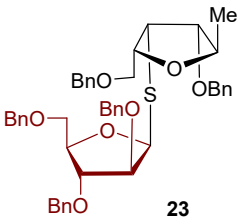



**Table 2.** Reaction of thiol nucleophiles with L-arabinofuranosyl bromide

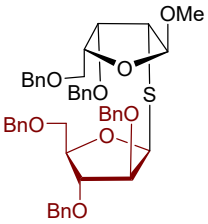


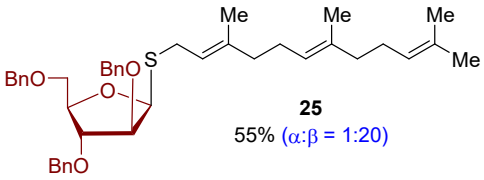

**21:** **X** = S 55% (α:β = 1:20)
**22:** **X** = O 88% (α:β = 1:5)



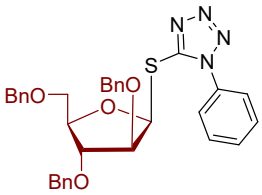

**23**
57% (α:β = 1:20)



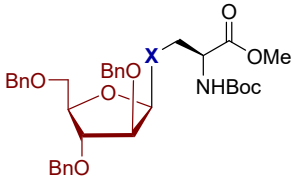

**24**
55% (α:β = 1:15)



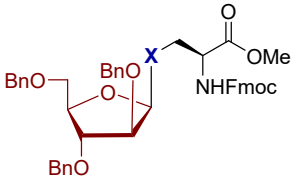

**25**
55% (α:β = 1:20)



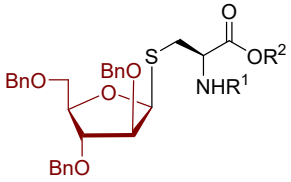

**26**
77% (α:β = 1:20)



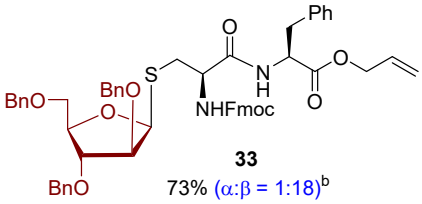

**27:** **X** = S 78% (α:β = 1:25)
**28:** **X** = O 84% (α:β = 1:1)



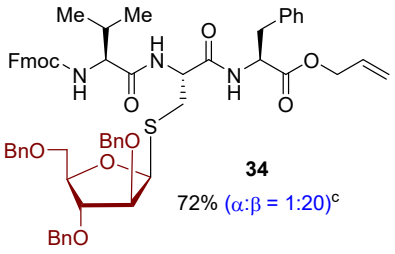

**29:** **X** = S 72% (α:β = 1:20)
**30:** **X** = O 75% (α:β = 1:4)




**31:** $R^1$ = Boc, $R^2$ = Allyl 58% (α:β = 1:25)
**32:** $R^1$ = Fmoc, $R^2$ = Allyl 70% (α:β = 1:15)

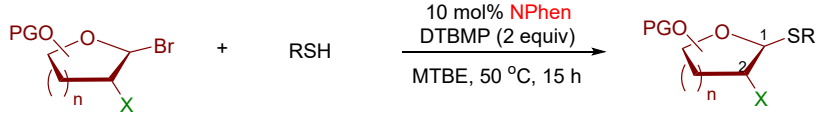



**33**
73% (α:β = 1:18)[b]




**34**
72% (α:β = 1:20)[c]

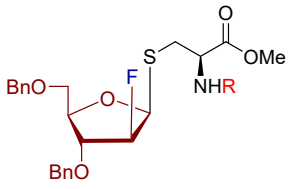
**Table 3.** Reaction of furanosyl and pyranosyl bromide donor with cysteine residues




X = BnO, F and n = 1 or 2

1,2-*cis* Products

**L-2-Fluoro-Arabinofuranose**

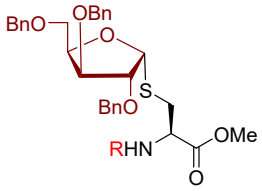



**donor:** α:β = 20:1

**35:** R = Boc, 53%, α:β = 1:25[b]

**36:** R = Fmoc, 48%, α:β = 1:20

**D-Xylofuranose**

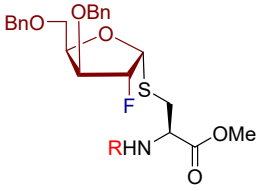



**donor:** α:β = 1:10

**37:** R = Boc 67%, α:β = 25:1[b]

**38:** R = Fmoc 68%, α:β = 20:1

**D-2-Fluoro-Xylofuranose**

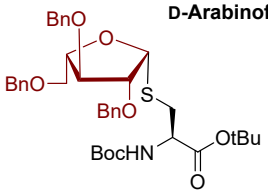



**donor:** α:β = 1:1.25

**39:** R = Boc 60%, α:β = 25:1[b]

**40:** R = Fmoc 68%, α:β = 20:1

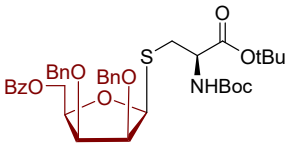
**D-Arabinofuranose**




**donor:** α:β = 7:1

**41:** 62% (α:β = 1:15)

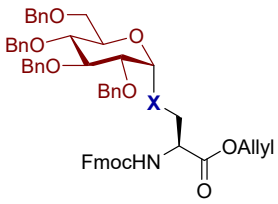
**D-Lyxofuranose**




**donor:** α:β = 20:1

**42:** 52% (α:β = 1:25)

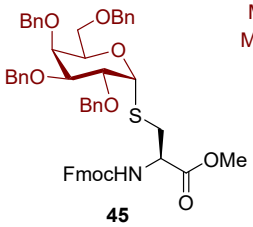
**D-Glucose**




**43:** **X** = O, 73%, α:β = 18:1[b]

**44:** **X** = S, 70%, α:β = 25:1[b]

**D-Galactose**

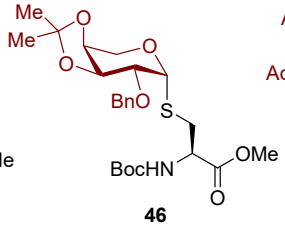



**45**

61%

(α:β = 20:1)

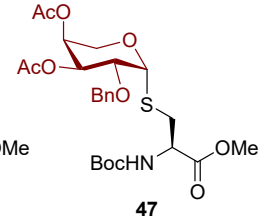
**L-Arabinopyranose**




**46**

60%

(α:β = 25:1)[b]

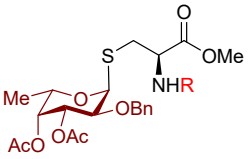



**47**

60%

(α:β = 20:1)[b]

**L-Fucose**




**48:** R = Boc, 53%, α:β = 20:1[b]

**49:** R = Fmoc, 64%, α:β = 18:1[b]

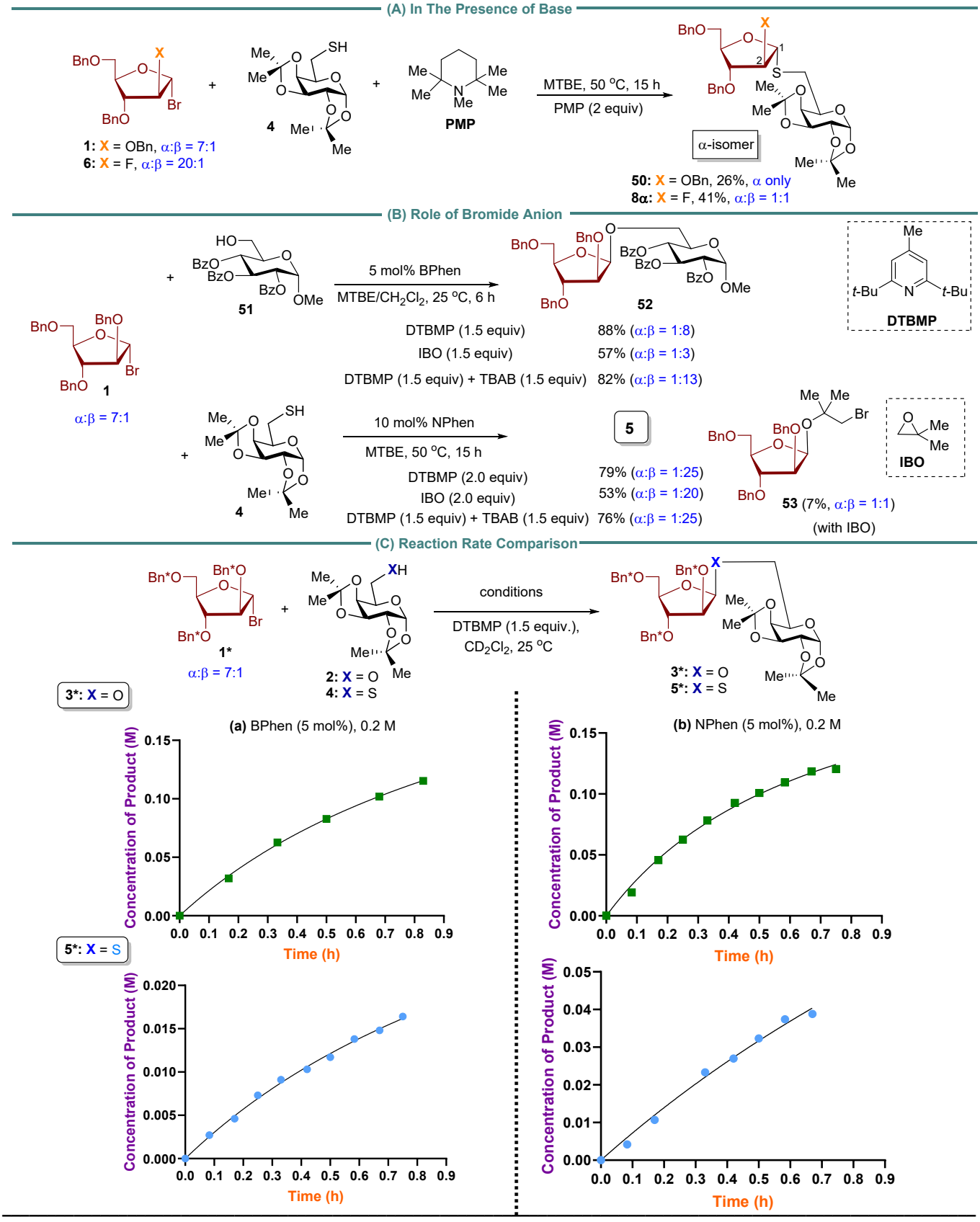



**Figure 2. (A)** Control experiment with the bulk base, penta-methylpiperidine (PMP). (**B**) Studies the role of bromide ion in influencing reaction selectivity difference between alcohol and thiol. (**C**) Reaction rate comparison between alcohol and thiol