SITE-SELECTIVE ACYLATION OF CARBOHYDRATES DIRECTED BY RECYCLABLE POLYMER-SUPPORTED ISOTHIOUREA CATALYSTS

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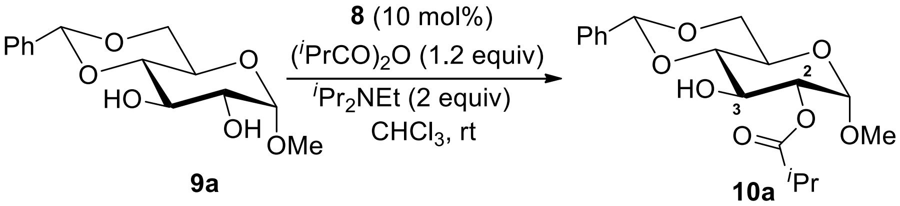
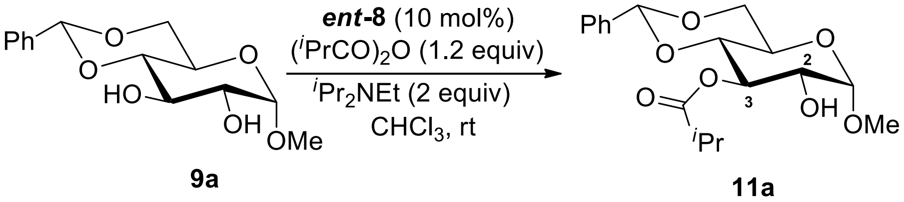
1. The results of the recyclability test of the catalyst

Table S1. The recyclability test for the catalyst **8**



Cycle index	1	2	3	4	5	6	7	8	9	10
Yield (%)	70	70	69	69	68	68	67	66	65	65
Site-selectivity (**C2**/**C3**)	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1

Table S2. The recyclability test for the catalyst ***ent*-8**

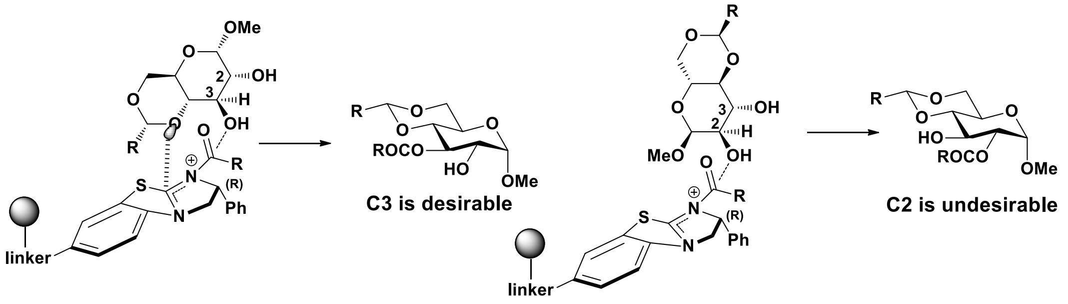


Cycle index	1	2	3	4	5	6	7	8	9	10
Yield (%)	78	78	76	76	75	73	72	72	71	70
Site-selectivity (**C3**/**C2**)	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1

2. The mechanism of the site-selective acylation of carbohydrates

According to previous study, the the cation-*n* interaction between the BTM catalyst and carbohydrate may be the key factor to control the site-selectivity. Herein, the mechanism using polymer-supported BTMs as catalysts should be similar with previous reported because the supporting site cannot influence the transition states for the acylation process. The transition states (TSs) for the acylation of methyl α-D-glucopyranoside featured a stabilizing cation-*n* interaction between the positively charged acylated catalyst and a long pair on OR or OH group of the substrate. For the polystyrene-supported (*R*)-BTM ***ent*-8** as catalyst, the cation-*n* interaction stabilizes the C3-acylation, because the cation-*n* interaction is disrupted by the axial α-OMe group during C2-acylation. As a result, ***ent*-8** prefers C3-acylation products. Switching to polystyrene-supported (*S*)-BTM **8** as catalyst, the stronger cation-*n* interaction with C3-OH favor the C2-acylation. In the polystyrene-supported (S)-BTM **8**-catalyzed C3-acylation, the cation-*n* interaction with C2-OH is disfavored due to steric repulsions with the adjacent axial *α*-OMe group. Thus, polystyrene-supported (*S*)-BTM **8** prefers C2-acylation (Figure S1).

Polystyrene-supported (*R*)-BTM *ent*-8-catalyzed acylation



Polystyrene-supported (*S*)-BTM 8-catalyzed acylation

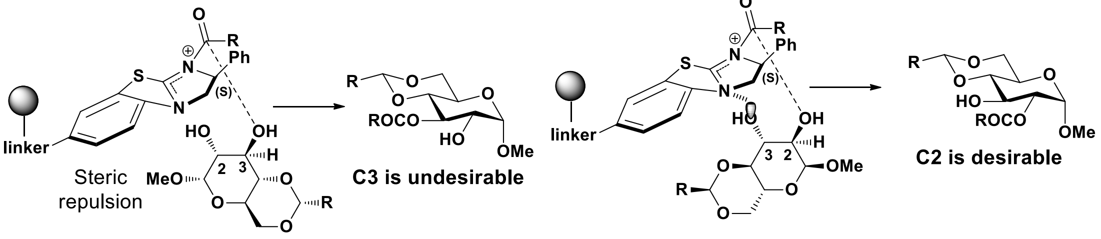


Figure S1. The transition states for the site-selective acylation