Supporting Information

Discovery of neat silica gel as catalyst: an example of S→O acetyl migration reaction†

Yu Jin,‡[a] Jiachen Li,‡[a] Li Peng,[a] Chao Gao*[a]

[a] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, P. R. China. Tel: +86-571-87952088; E-mail: chaogao@zju.edu.cn

† This work is supported by the National Natural Science Foundation of China (No. 21325417, No. 51173162).

Table of Content

S1. Experimental

S1.1 Chemicals:

Silica gel 70-230 mesh and 230-400 mesh were purchased from J&K Scientific Co., 200-300 mesh from Aladdin Industrial Co., 100-200 mesh, 200-300 mesh and 300-400 mesh from Sinopharm Chemical Reagent Co., Ltd, and 300-400 mesh from Qingdao Haiyang Chemical Co., Ltd. Propylene oxide (99%), 1,2-epoxybutane (99%), tertbutyl glycidyl ether (99%), butyl glycidyl ether (98%), glycidyl phenyl ether (99%), glycidyl benzyl ether (98%), epichlorohydrin (99%), epibromohydrin (97%), glycidol (96%), glycidyl methacrylate (97%), allylglycidyl ether (99%) and thioacetic acid (97.5%) were purchased from J&K Scientific Co., propargylglycidyl ether (94%) was obtained from Da Tang Pharmacy Co. All the reagents above were used as received.

S1.2 Measurements:

Fourier transform infrared (FT-IR) spectra were recorded on a PE Paragon 1000 spectrometer (film or KBr disk). XPS was performed using a PHI 5000C ESCA system operated at 14.0KV. BET measurement was performed by nitrogen adsorption on a Quantachrome NOVA 2000 surface analyzer. SEM image was taken on a Hitachi S4800 field-emission SEM system. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy were carried out on a Varian Mercury plus 400 NMR spectrometer with $CDCl_3$ as the solvent at 20 ℃.

S2. General procedure for the synthesis of thiol compounds

S2.1 General procedure for generating latent sulfur intermediates b from thiol-epoxy reactions between epoxy compounds a and thioacetic acid

The reaction of thioacetic acid with epichlorohydrin was chosen as a model reaction. In a specific experiment, epichlorohydrin (5.0g, 54.0mmol), deionized water (30mL), and thioacetic acid (4.73g, 62.2mmol) were added into a round-bottomed flask (50mL) equipped with a magnet. After vigorous stirring for 2d at room temperature in nitrogen atmosphere, the oily product was extracted by 250mL ethyl acetate, washed with saturated $NaHCO_3$ aqueous solution and deionized water, then dried by anhydrous $MgSO_4$ for half an hour. After filtration, all volatiles were removed by the reduced pressure distillation and vacuum drying, affording the latent sulfur intermediates in nearly quantitative yield.

S2.2 General procedure to transform b into thiol compounds c from S→O acetyl migration reactions

The prepared product (1.7g) was dissolved in ethyl acetate, then the solution was added slowly into a silica gel chromatography column. After reacting at room temperature for 9-14h, the oily product was eluted out by ethyl acetate and hexane (1:6), and evaporated by a rotary evaporation to obtain a pure corresponding thiol compound.

S3. Characteristics of the silica gel fixed-bed catalyst

S3.1 FT-IR spectra data of the silica gel

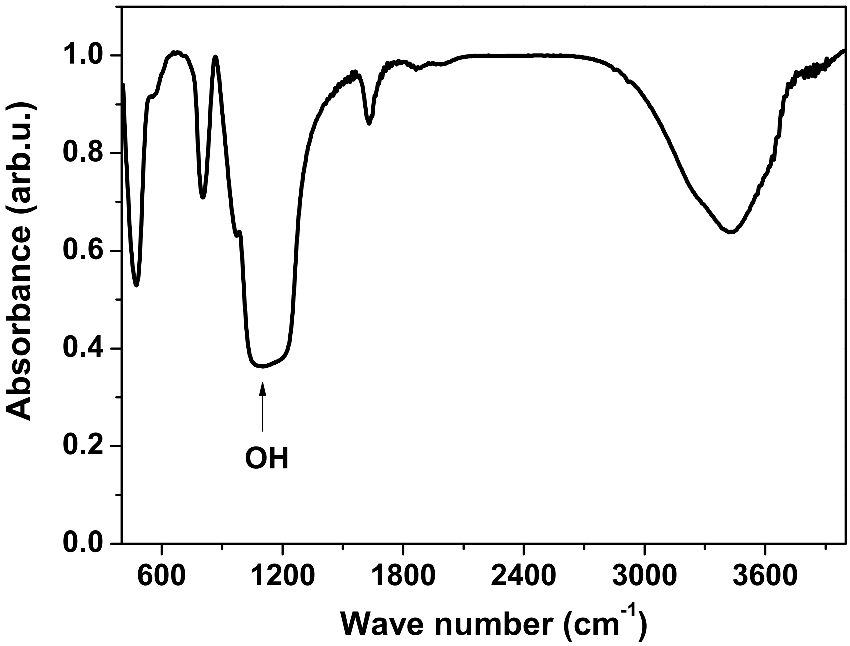


Figure S1. FT-IR Spectra of the silica gel

S3.2 XPS spectra data of the silica gel

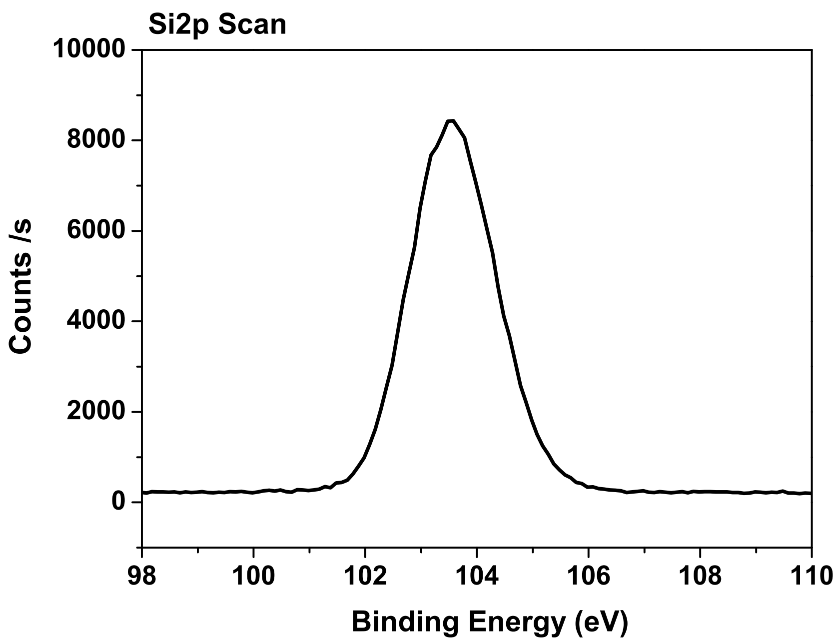


Figure S2. XPS Spectra of the silica gel

S3.3 BET profile of the silica gel

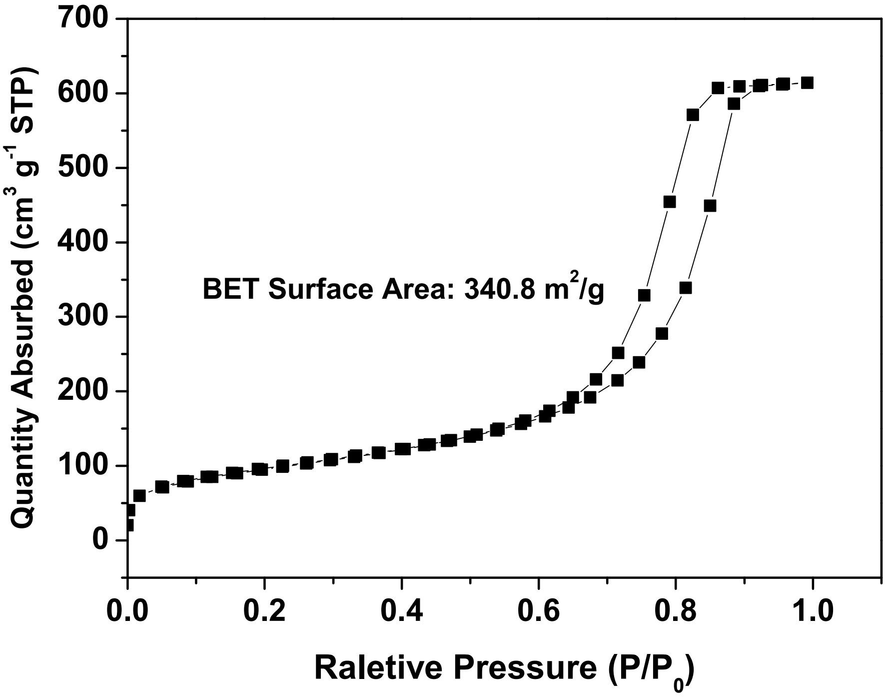


Figure S3. BET profile of the silica gel (300-400 mesh) fixed-bed catalyst

S3.4 SEM images of the silica gel

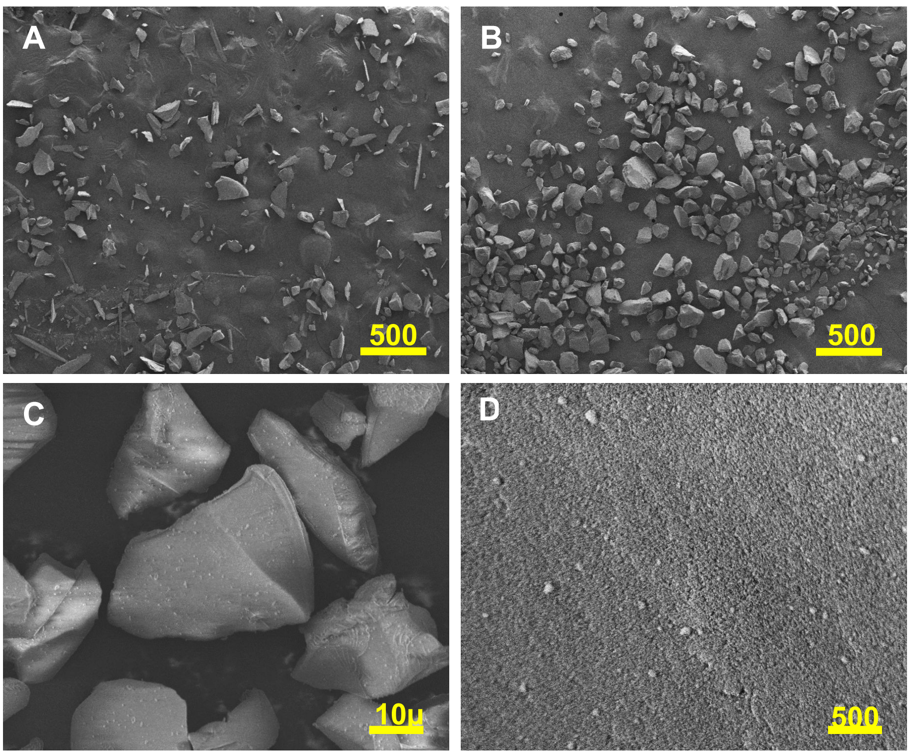
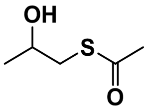


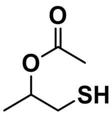
Figure S4. SEM images of Silica gel with 300-400 meshes (A, B) and its porous surface (C, D).

S4. ^{1}H and ^{13}C NMR data of the intermediates and the corresponding thiol compounds

1b. 

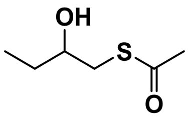
^{1}H NMR (400 MHz, $CDCl_3$, 303 K): δ (ppm) 1.25-1.22 (d, 3H), 2.0-2.3 (m, H), 3.98-3.88 (m, H), 3.11-2.85 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 22.42, 67.29, 37.92, 196.56, 30.42.

1c. 

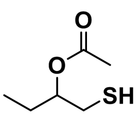
^{1}H NMR (400 MHz, 303 K): δ (ppm) 1.29-1.27 (d, 3H), 4.93-4.87 (m, H), 2.70-2.57 (m, 2H), 1.41-1.37 (t, H), 2.03 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 19.16, 72.18, 30.26, 171.03, 21.80.

2b. 

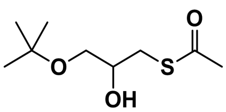
^{1}H NMR (400 MHz, 303 K): δ (ppm) 0.99-0.95 (t, 3H), 1.61-1.48 (m, 2H), 3.71-3.62 (m, H), 3.16-2.87 (m, 2H), 2.37 (s, 3H), 2.34 (s, H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 9.86, 29.08, 72.22, 35.85, 196.46. 30.50

2c. 

^{1}H NMR (400 MHz, 303 K): δ (ppm) 0.89-0.93 (t, 3H), 1.37-1.42 (t, H), 1.62-1.77 (d, H), 2.09 (s, 3H), 2.64-2.74 (m, 2H), 4.80-4.86 (m, H).

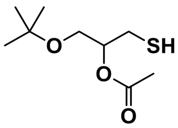
^{13}C NMR (400 MHz, 303 K): δ (ppm) 170.49, 76.00, 27.48, 25.32, 21.13, 9.59.

3b. 

^{1}H NMR (400 MHz, 303 K): δ (ppm) 1.19 (s, 9H), 3.33-3.29 (m, 2H), 3.43-3.40 (m, H), 3.14-3.09 (m, 2H), 2.36 (s, 3H), 3.03-2.94 (m, H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 27.45, 30.47, 69.84, 73.33, 64.25, 196.08, 32.44.

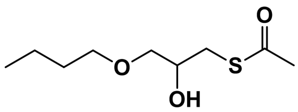
3c.



^{1}H NMR (400 MHz, 303 K): δ (ppm) 1.18 (s, 9H), 3.57-3.47 (m, 2H), 4.95-4.89 (m, H), 2.88-2.69 (m, 2H), 1.45-1.40 (t, H), 2.08 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 21.02, 25.00, 74.04, 73.24, 60.76, 170.36, 27.41.

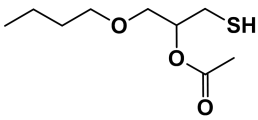
4b.



^{1}H NMR (400 MHz, 303 K): δ (ppm) 0.97-0.88 (t, 3H), 1.42-1.33 (m, 2H), 1.61-1.52 (m, 2H), 3.51-3.36 (m, 2H), 3.47 (s, 2H), 3.94-3.85 (d, H), 3.15-2.97 (m, 2H), 2.88-2.83 (s, 3H), 2.39-2.33 (s, H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 13.65, 19.26, 31.60, 69.47, 73.06, 71.21, 32.36, 196.07, 30.52.

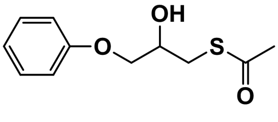
4c.



^{1}H NMR (400 MHz, 303 K): δ (ppm) 0.97-0.88 (t, 3H), 1.40-1.30 (m, 2H), 1.59-1.50 (m, 2H), 3.52-3.39 (m, 2H), 3.67-3.55 (m, 2H), 5.02-4.95 (m, H), 2.87-2.69 (m, 2H), 1.47-1.40 (t, H), 2.14-2.07 (s, 3H).

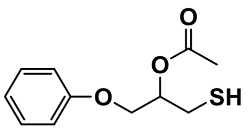
^{13}C NMR (400 MHz, 303 K): δ (ppm) 13.75, 21.02, 31.55, 69.59, 71.39, 73.64, 24.88, 170.32, 19.23.

5b.



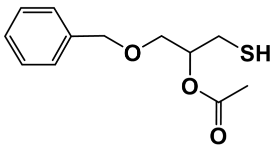
^{1}H NMR (400 MHz, 303 K): δ (ppm) 7.28-7.24 (t, H), 6.96-6.93 (t, 2H), 6.89-6.87 (d, 2H), 4.00-3.90 (m, 2H), 4.14-4.07 (m, H), 3.24-3.08 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 121.31, 129.57, 114.61, 158.41, 70.37, 69.39, 32.50, 196.4, 30.57.

5c. 

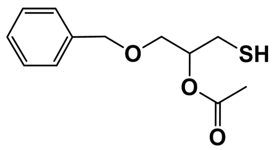
^{1}H NMR (400 MHz, 303 K): δ (ppm) 6.98-6.95 (t, H), 7.30-7.25 (m, 2H), 6.92-6.90 (d, 2H), 4.22-4.10 (m, 2H), 5.20-5.15 (m, H), 2.97-2.81 (m, 2H), 1.50-1.46 (t, H), 2.10 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 121.33, 129.57, 114.63, 158.40, 66.61, 72.93, 24.81, 170.39, 21.04.

6b. 

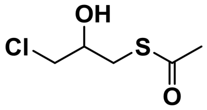
^{1}H NMR (400 MHz, 303 K): δ (ppm) 2.34 (s, 3H), 3.15-2.97 (m, 2H), 3.96-3.89 (d, H), 3.56-3.42 (m, 2H), 4.54 (s, 2H), 7.38-7.26 (m, 5H), 2.78-2.73 (d, H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 30.54, 196.08, 32.66, 69.78, 73.36, 72.63, 137.62, 127.87, 128.50, 127.80.

6c. 

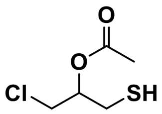
^{1}H NMR (400 MHz, 303 K): δ (ppm) 1.41-1.35 (t, H), 2.88-2.70 (m, 2H), 4.63-4.49 (m, H), 3.72-3.59 (m, 2H), 5.05-4.97 (m, 2H), 7.38-7.26 (m, 5H), 2.09(s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 32.66, 73.41, 69.82, 72.67, 137.62, 127.89, 128.48, 127.80, 196.08, 30.54.

7b. 

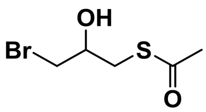
^{1}H NMR (400 MHz, 303 K): δ (ppm) 3.67-3.55 (m, 2H), 4.02-3.93 (m, H), 3.20-3.06 (m, 2H), 2.38 (s, 3H), 2.88-2.87 (d, H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 32.99, 70.49, 48.00, 196.42, 30.49.

7c. 

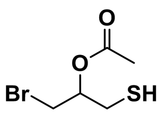
^{1}H NMR (400 MHz, 303 K): δ (ppm) 3.79-3.77 (d, 2H), 5.07-5.02(m, H), 2.87-2.82 (m, 2H), 1.49-1.45 (t, H), 2.12(s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 77.44, 73.32, 43.47, 169.98, 25.14.

8b. 

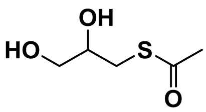
^{1}H NMR (400 MHz, 303 K): δ (ppm) 3.55-3.44 (m, 2H), 3.96(s, H), 3.20-3.16 (m, 2H), 2.38 (s, 3H), 3.13-3.08 (m, H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 33.86, 70.17, 37.44, 196.31, 30.55.

8c. 

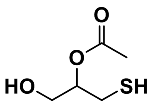
^{1}H NMR (400 MHz, 303 K): δ (ppm) 3.65-3.64 (d, 2H), 5.03-4.98 (m, H), 2.87-2.83 (m, 2H), 1.51-1.46 (t, H), 2.12 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 72.87, 31.95, 26.25, 170.02, 20.89.

9b. 

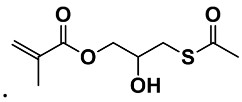
^{1}H NMR (400 MHz, 303 K): δ (ppm) 3.67-3.56 (m, 2H), 4.02-3.95 (m, H), 3.20-3.04 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 48.06, 70.55, 32.99, 196.31, 30.55.

9c. 

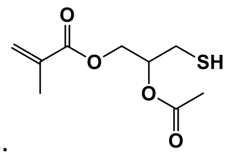
^{1}H NMR (400 MHz, 303 K): δ (ppm) 3.80-3.78 (d, 2H), 5.07-5.02 (m, H), 2.86-2.82 (m, 2H), 1.50-1.46 (t, H), 2.11 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 43.51, 73.31, 25.17, 170.07, 20.91.

10b. 

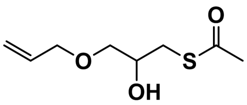
^{1}H NMR (400 MHz, 303 K): δ (ppm) 5.62 (s, H), 6.16 (s, H), 1.96 (s, 3H), 3.18-3.02 (m, 2H), 4.05-3.98 (m, H),4.21-4.19 (m, 2H), 2.37 (s, 2H), 3.27-3.26 (d, H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 126.30, 135.80, 18.27, 167.38, 68.96, 66.94, 32.52, 196.16, 30.52.

10c. 

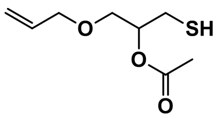
^{1}H NMR (400 MHz, 303 K): δ (ppm) 6.11 (s, H), 5.60 (m, H), 1.96-1.94 (d, 3H), 4.44-4.28 (m, 2H), 5.16-5.10 (m, H), 2.79-2.75 (m, 2H), 1.55-1.50 (t, H), 2.09 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 125.18, 134.82, 17.25, 165.77, 62.38, 71.32, 23.76, 169.12, 19.90.

11b. 

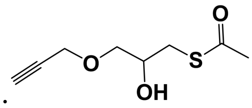
^{1}H NMR (400 MHz, 303 K): δ (ppm) 5.30-5.18 (m, 2H), 5.94-5.85 (m, H), 4.02-4.01 (d, 2H), 3.52-3.38 (m, 2H), 3.95-3.88 (m, H), 3.15-2.96 (m, 2H), 2.36 (s, 3H), 2.68-2.67 (d, H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 117.28, 134.28, 72.24, 72.66, 69.54, 32.45, 196.08, 30.45.

11c. 

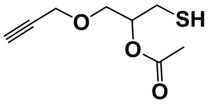
^{1}H NMR (400 MHz, 303 K): δ (ppm) 5.29-5.18 (m, 2H), 5.93-5.83 (m, H), 4.06-3.96 (m, 2H), 3.68-3.58 (m, 2H), 5.02-4.96 (m, H), 2.86-2.68 (m, 2H), 1.48-1.43 (t, H), 2.09 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 117.29, 134.24, 68.81, 72.19, 73.49, 24.78, 170.27, 21.01.

12b. 

^{1}H NMR (400 MHz, 303 K): δ (ppm) 2.50-2.48 (m, H), 4.20-4.19 (d, 2H), 3.53-3.59 (m, 2H), 3.97.3.89 (m, H), 3.15-2.98 (m, 2H), 2.37 (s, 3H), 2.94-2.88 (m, H).

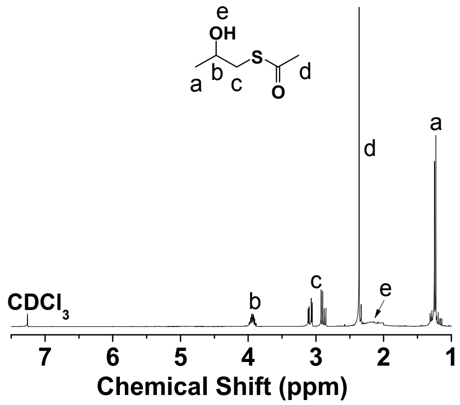
^{13}C NMR (400 MHz, 303 K): δ (ppm) 117.42, 134.32, 69.56, 72.68, 72.26, 32.43, 196.17, 30.50.

12c. 

^{1}H NMR (400 MHz, 303 K): δ (ppm) 2.50-2.49 (t, H), 4.20-4.18 (t, 2H), 3.80-3.69 (m, 2H), 5.03-4.98 (m, H), 2.86-2.70 (m, 2H), 1.51-1.47 (t, H), 2.10 (s, 3H).

^{13}C NMR (400 MHz, 303 K): δ (ppm) 73.28, 75.09, 58.47, 68.46, 79.21, 24.61, 170.31, 21.01.

S5. ^{1}H and ^{13}C NMR figures of the latent sulfur intermediates and its counterpart thiol compounds



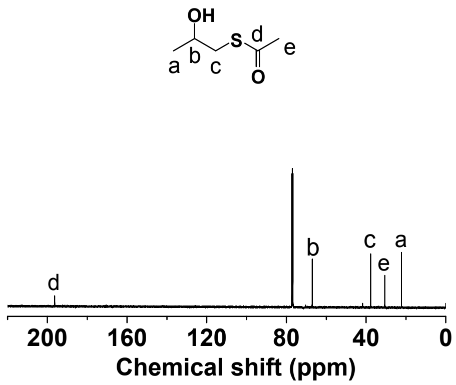
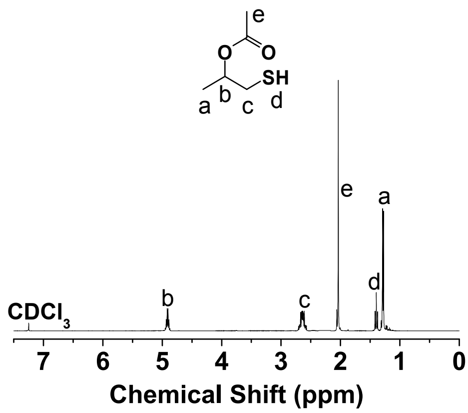


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of **1b**.



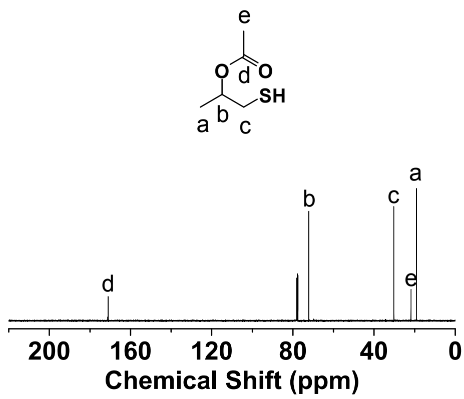
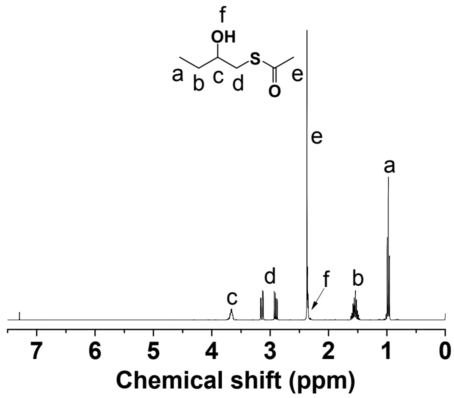


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of **1c**.



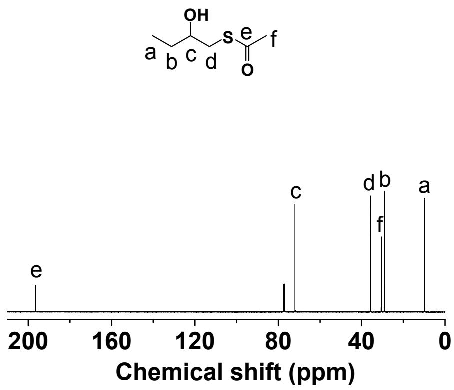
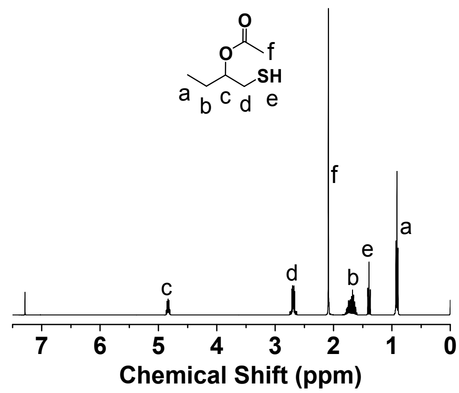


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of **2b**.



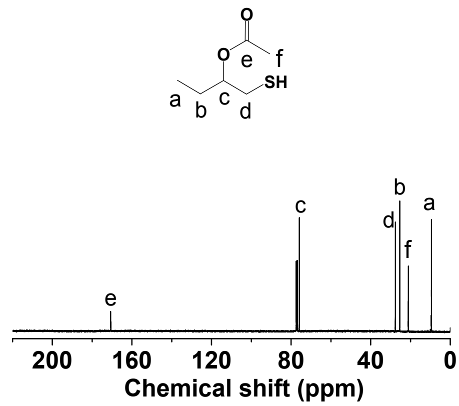


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of **2c**.

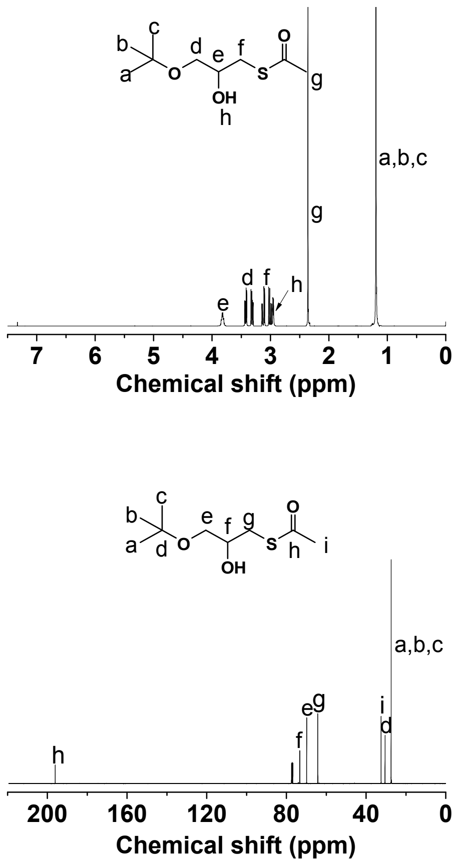
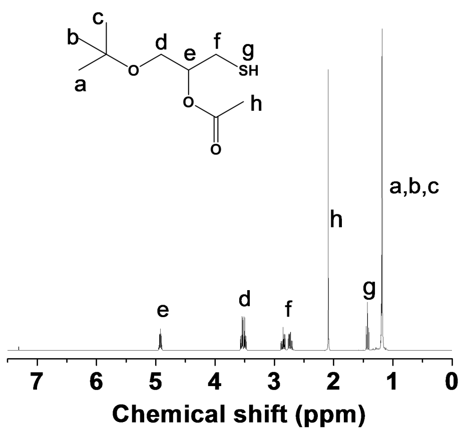


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of **3b**.



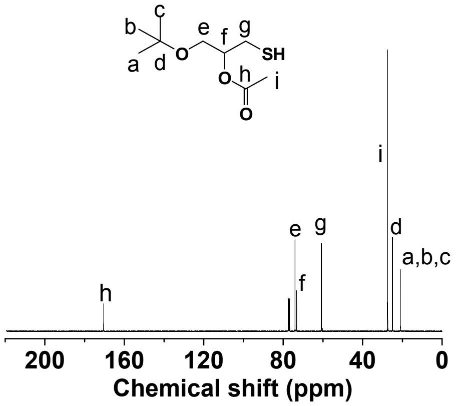


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of **3c**.

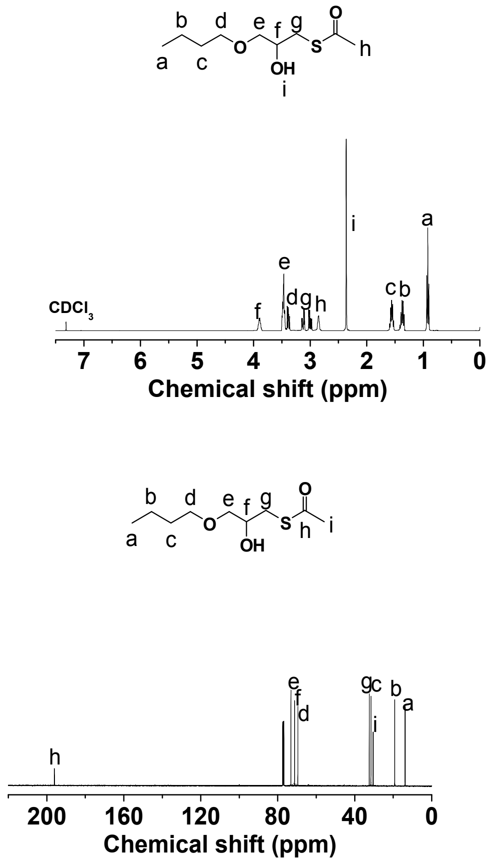
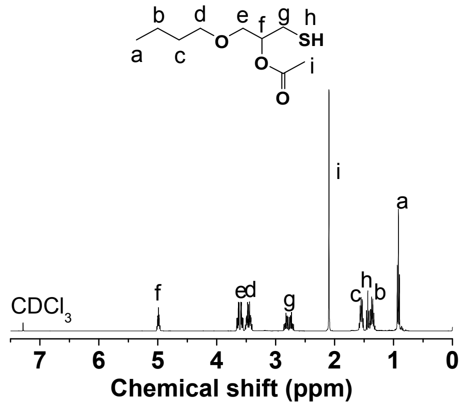


Figure S11. ^{1}H NMR and ^{13}C NMR spectra of **4b**.



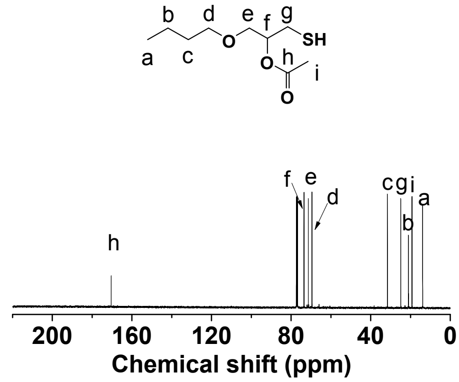
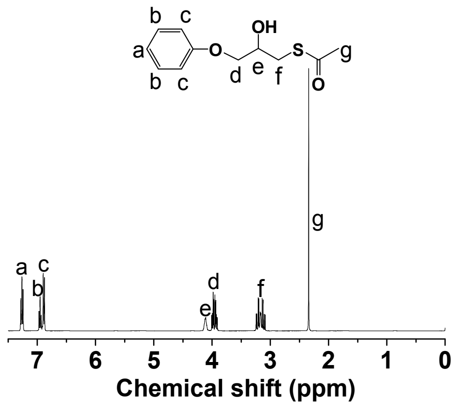


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of **4c**.



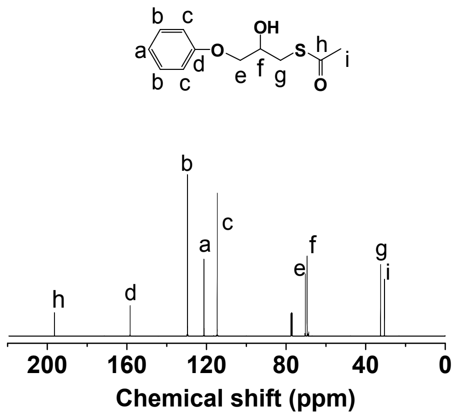


Figure S13. ^{1}H NMR and ^{13}C NMR spectra of **5b**.

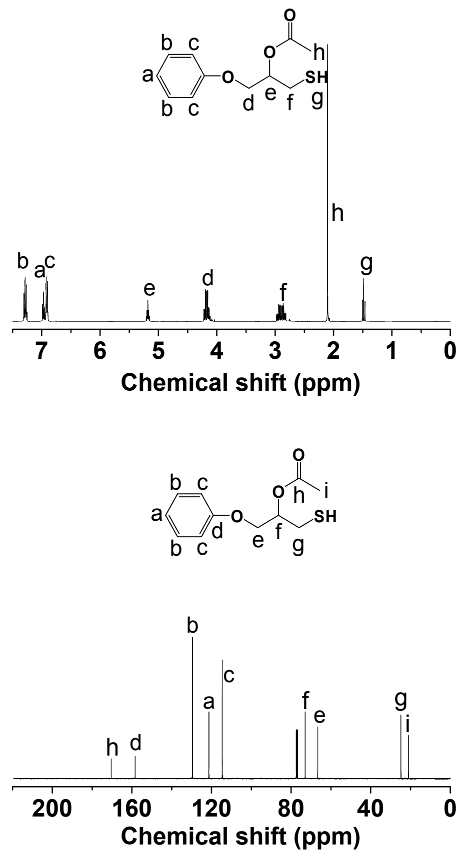
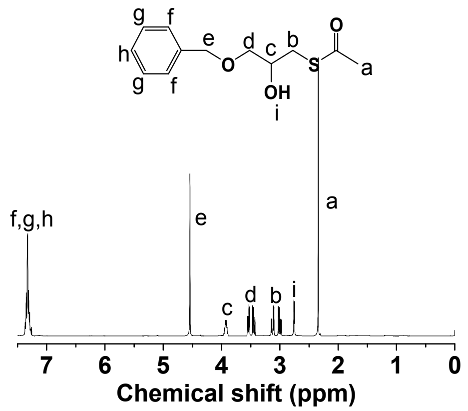


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of **5c**.



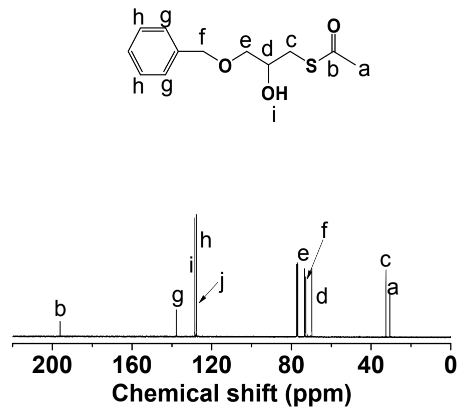
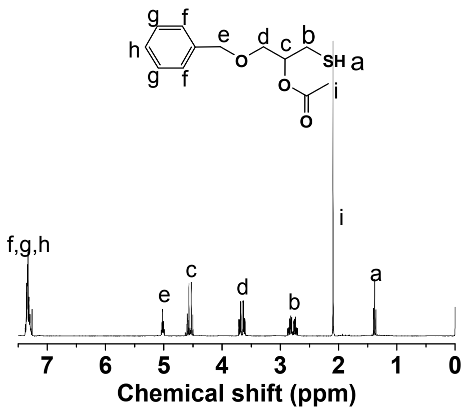


Figure S15. ^{1}H NMR and ^{13}C NMR spectra of **6b**.



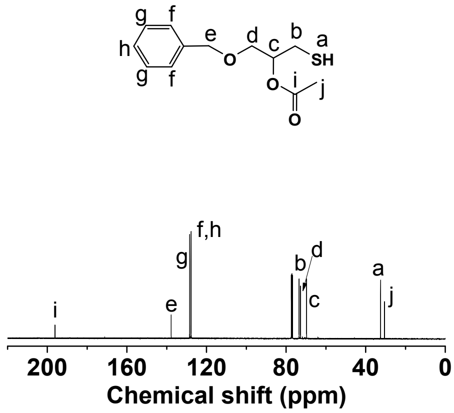
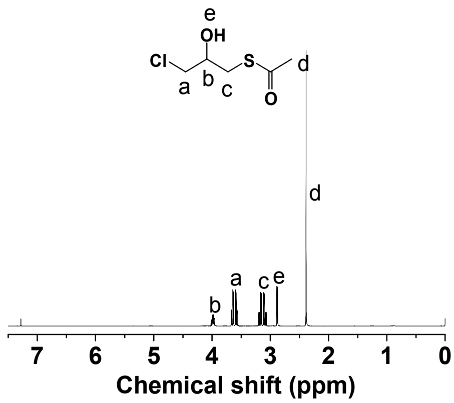


Figure S16. ^{1}H NMR and ^{13}C NMR spectra of **6c**.



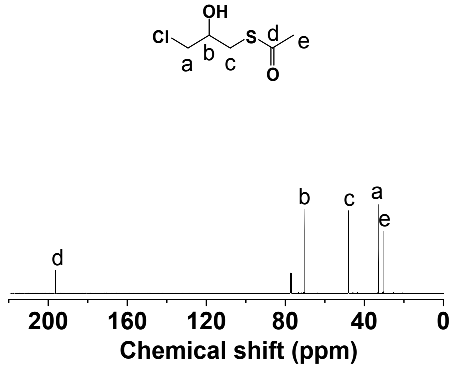


Figure S17. ^{1}H NMR and ^{13}C NMR spectra of **7b**.

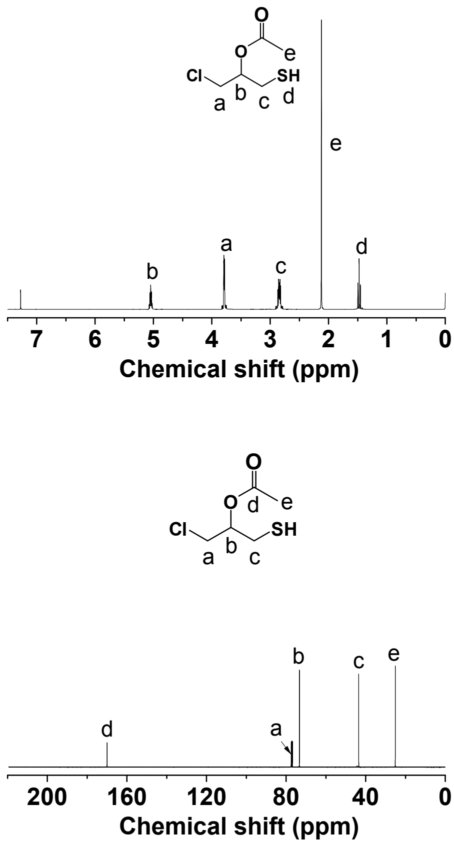


Figure S18. ^{1}H NMR and ^{13}C NMR spectra of **7c**.

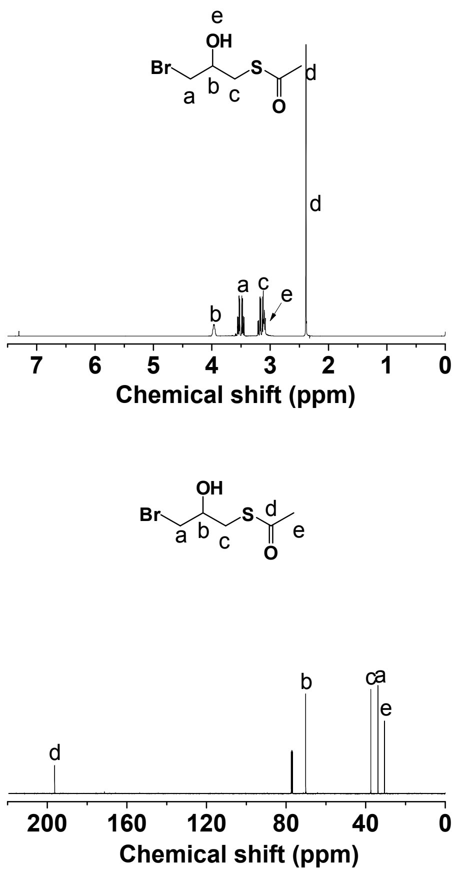


Figure S19. ^{1}H NMR and ^{13}C NMR spectra of **8b**.

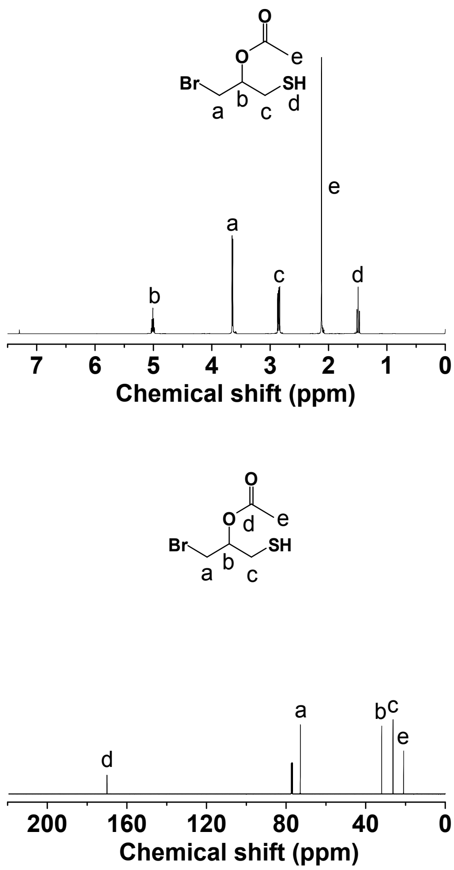
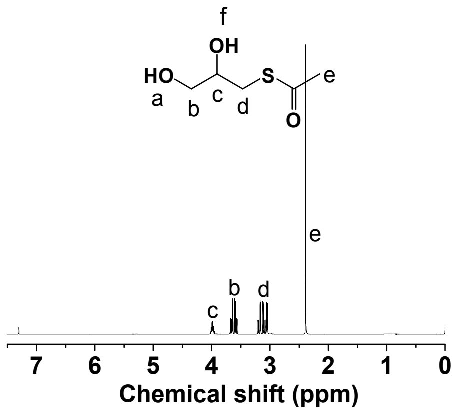


Figure S20. ^{1}H NMR and ^{13}C NMR spectra of **8c**.



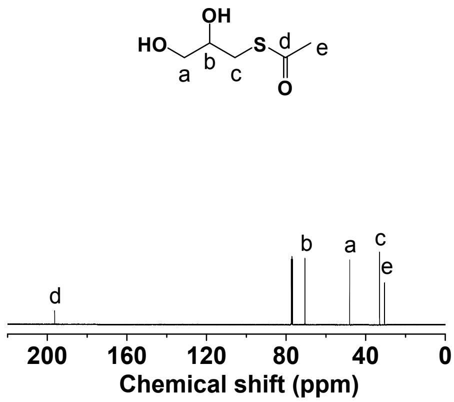
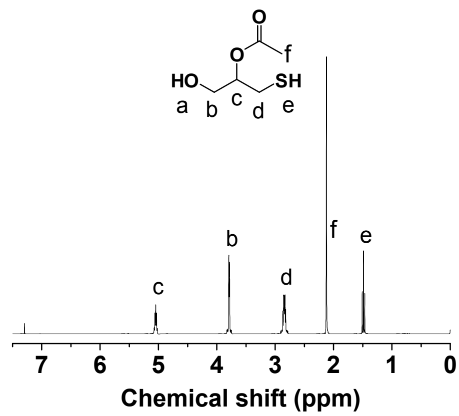


Figure S21. ^{1}H NMR and ^{13}C NMR spectra of **9b**.



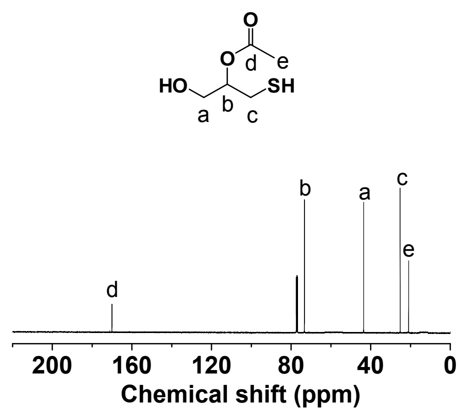


Figure S22. ^{1}H NMR and ^{13}C NMR spectra of **9c**.

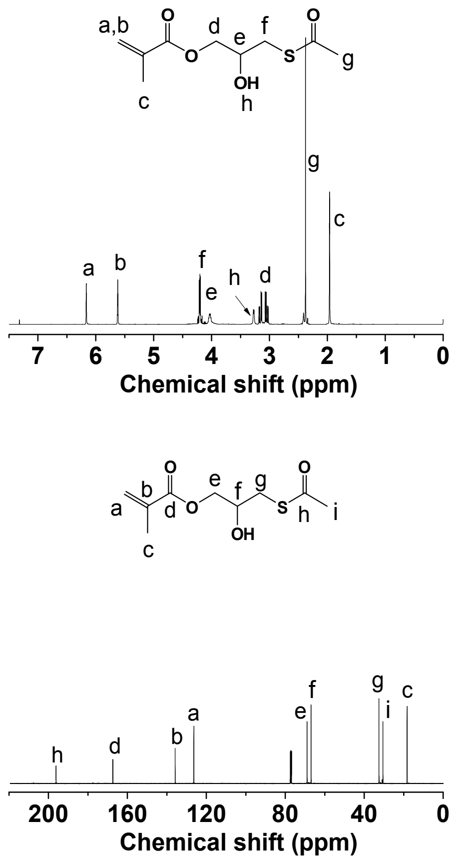


Figure S23. ^{1}H NMR and ^{13}C NMR spectra of **10b**.

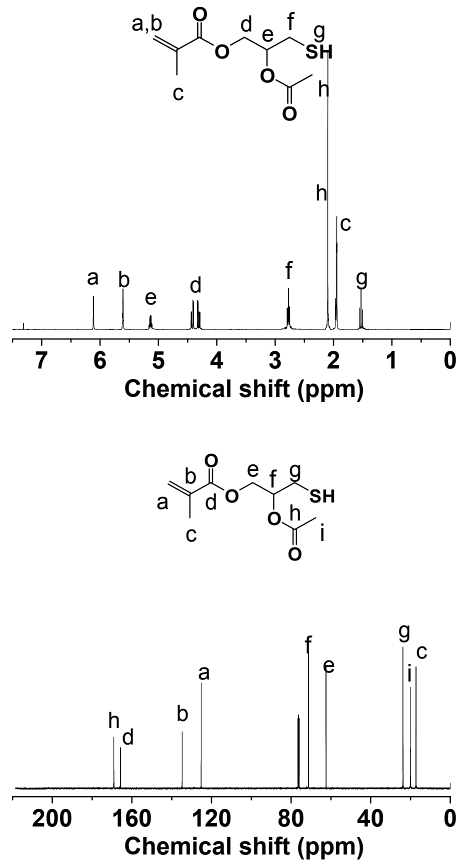


Figure S24. ^{1}H NMR and ^{13}C NMR spectra of **10c**.

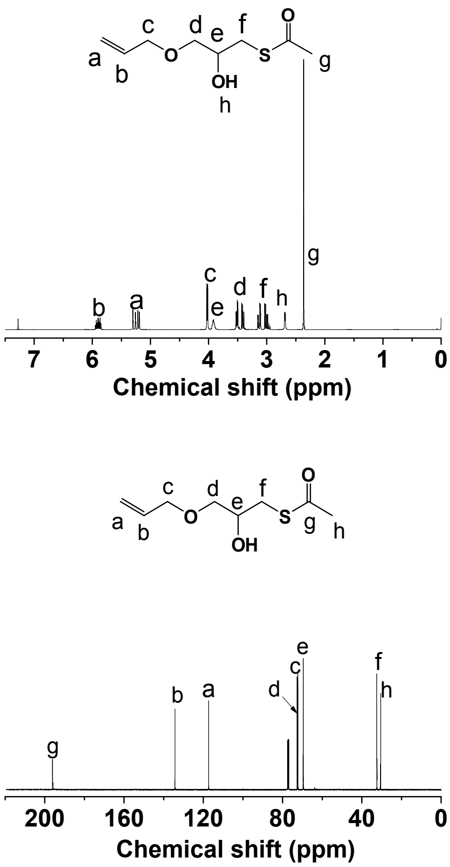


Figure S25. ^{1}H NMR and ^{13}C NMR spectra of **11b**.

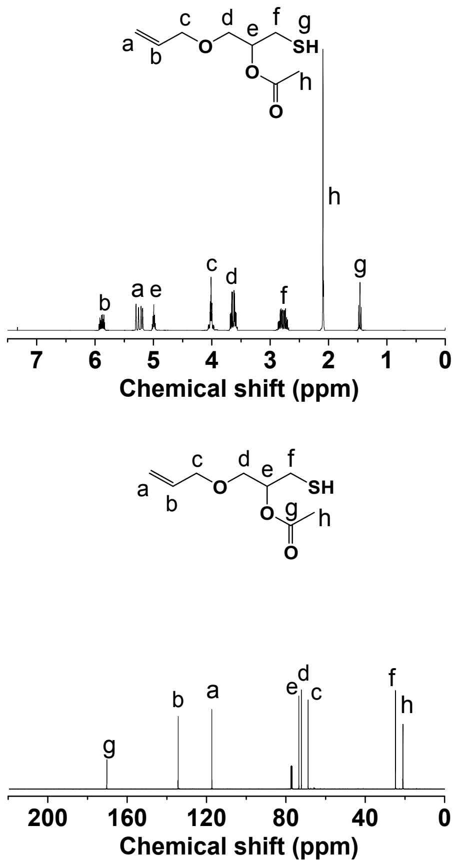


Figure S26. ^{1}H NMR and ^{13}C NMR spectra of **11c**.

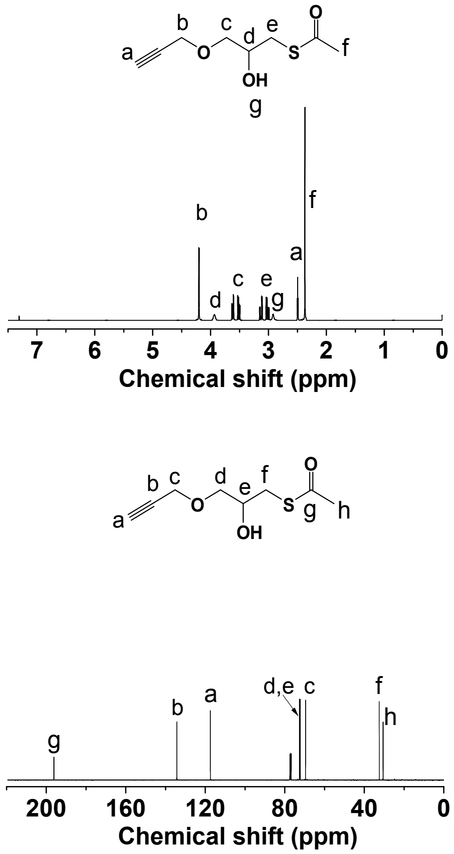
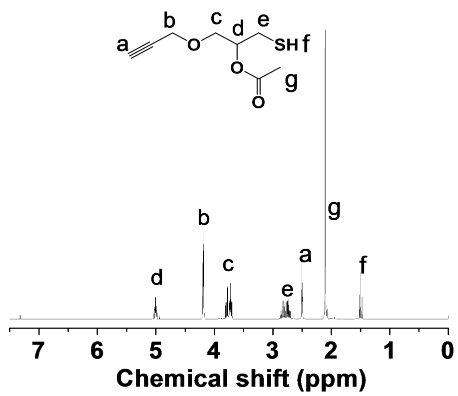


Figure S27. ^{1}H NMR and ^{13}C NMR spectra of **12b**.



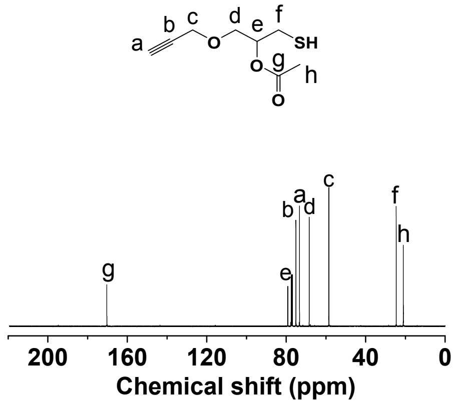


Figure S28. ^{1}H NMR and ^{13}C NMR spectra of **12c**.

S6. Kinetics of the reaction from 7b to 7c catalyzed by silica gel fixed-bed

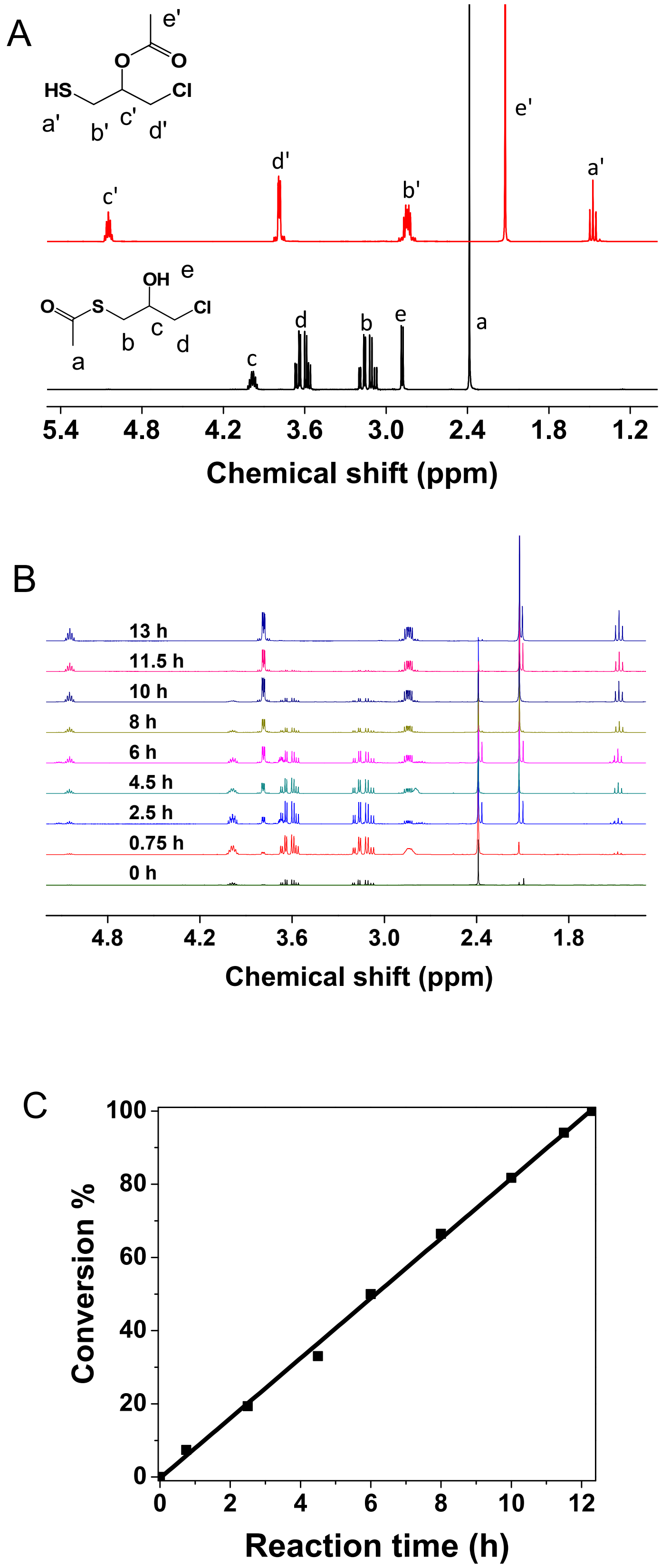


Figure S29. ^{1}H NMR (A) spectra in $CDCl_3$, its kinetics (B) and conversion (C) from 7b to 7c.

S7. The reusability of silica gel fixed-bed in catalyzing the S→O acetyl migration reaction from 7b to 7c

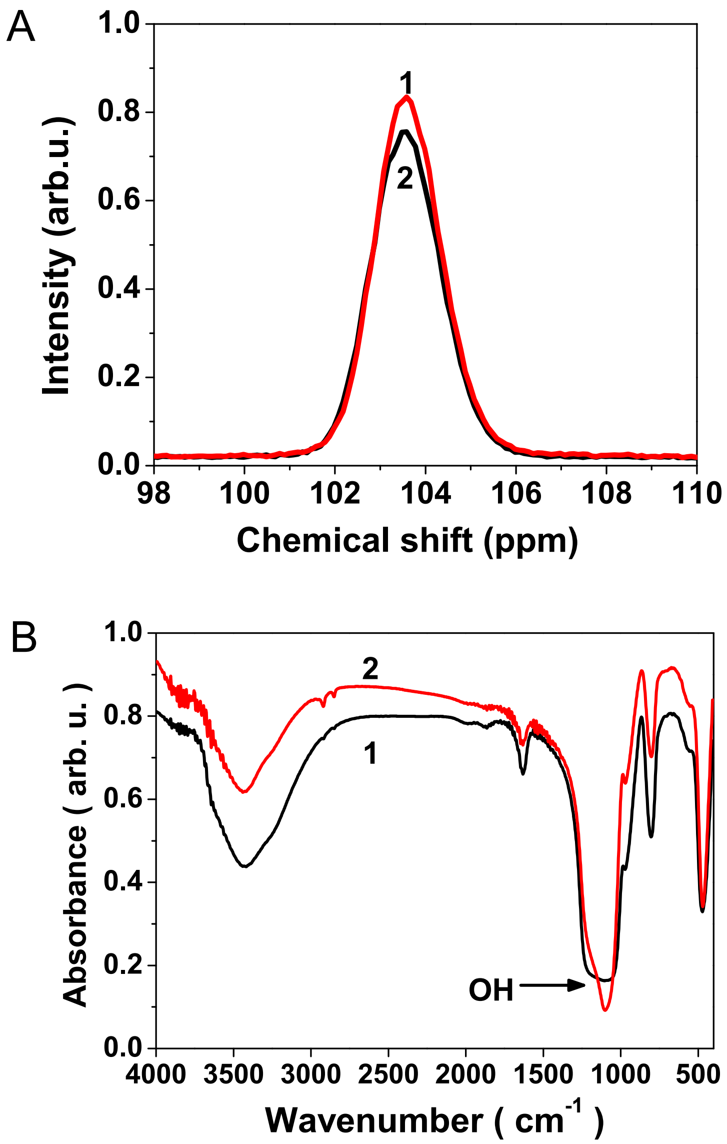


Figure S30. Comparison of the silica gel (300-400 mesh) before (1) and after (2) being reused for 100 times by (A) XPS spectra, (B) IR spectra.

Table S1. The reusability of silica gel (300-400 mesh) in catalyzing the acetyl migration reaction from **7b** to **7c** [A].

Cycles	Conv [B]. /%	Yield [C]/%	Time/h
1	100	97	13
5	100	98	13
10	100	99	13
20	100	96	13
30	100	98	13
50	100	99	13
70	100	94	13
90	100	96	13
100	100	98	13

[A] Unless otherwise noted, all reactions were performed in room temperature with ethyl acetate as the solvent. [B] Conversion was calculated by ^{1}H NMR spectroscopy. [C] The purity was determined by NMR.

S8. Catalytic property comparison of silica gels with different specifications

Table S2. The catalytic property comparison of different silica gel catalyzing the acetyl migration reaction from **7b** to **7c** [A].

No.	Source	Mesh	Time /h	Conv [B]. /%
1	J&K Scientific Co.	70-230	13	91
2	J&K Scientific Co.	230-400	13	98
3	Aladdin Industrial Co.	200-300	13	90
4	Qingdao Haiyang Chemical Co., Ltd.	300-400	13	100

[A] Unless otherwise noted, all reactions were performed in room temperature with ethyl acetate as the solvent. [B] Conversion was calculated by ^{1}H NMR spectroscopy.