Electronic Supplementary Material (ESI) for Green Chemistry.

[*Supporting Information*]

Catalyst-free nucleophilic addition reactions of silyl glyoxylates in water

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1. General information

Chemicals and analytical grade solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. General ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Chemical shifts were reported in ppm and the coupling constants *J* are given in Hz. $CHCl_3$ (δ = 7.26 ppm) served as an internal standard for ^{1}H NMR; while $CDCl_3$ (δ = 77.0 ppm) was used as an internal standard for ^{13}C NMR. HRMS data were obtained on a Bruker Apex II mass instrument (ESI).

Thiols were purchased from commercial suppliers. Silyl glyoxylates were prepared according to the literature procedures.[1]

Reference

1. (*a*) S. N. Greszler and J. S. Johnson, *Angew. Chem., Int. Ed.*, 2009, **48**, 3689; (*b*) T. Toma, J. Shimokawa and T. Fukuyama, *Org. Lett.*, 2007, **9**, 3195; (*c*) A. G. Myers, B. Zheng and M. Movassaghi, *J. Org. Chem.*, 1997, **62**, 7507.

2. Filtration-based procedure for 3f

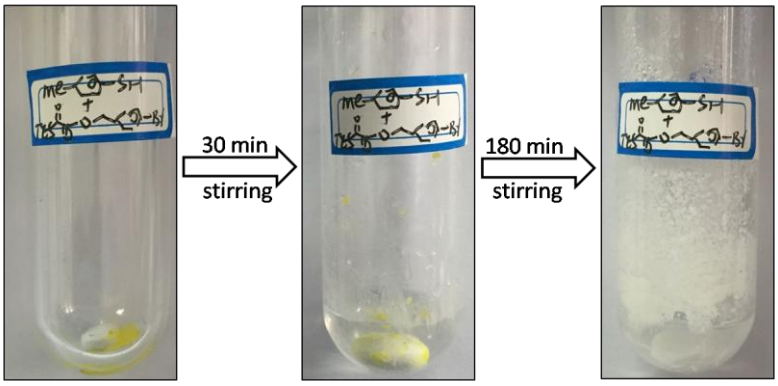
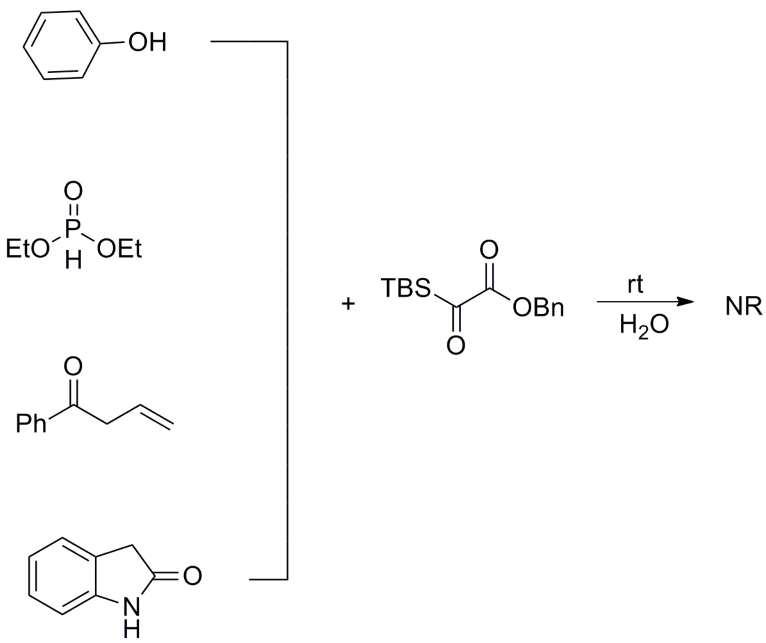


Figure 1. The appearance of the reaction for **3f**.

The mixture of 4-methylbenzenethiol (0.3 mmol) and 4-bromobenzyl 2-oxo-2-(triethylsilyl)acetate (0.2 mmol) in 1 mL H_2O were stirred at room temperature. After stirring for 3 hours, the mixture was filtrated and washed with water to afford the desired product **3f**.

3. Other nucleophile investigation



4. Mechanistic investigation

(1) Control experiments in homogeneous reaction condition.

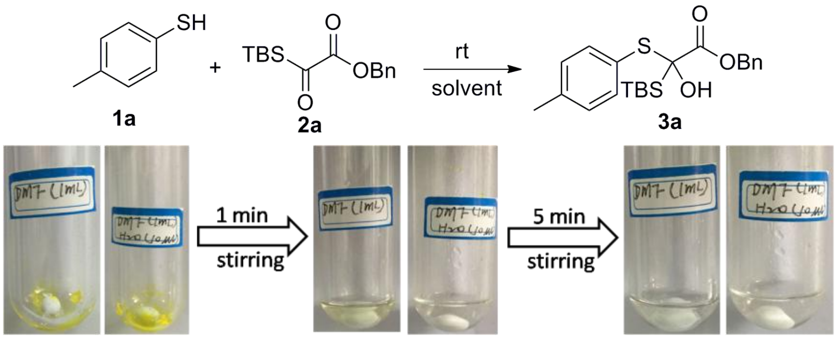


Figure 2. The appearance of the reaction in homogeneous reaction conditions.

The starting material of silyl glyoxylate is yellow oil and the reaction progress can be monitored approximately by visualization of the change of color (the yellow oil disappeared). The reaction between **1a** and **2a** was conducted under homogenous conditions and the reaction phenomenon have shown that the reaction rates order is: DMF/H_2O (100:1) > DMF. The ratio of addition product to Brook rearrangement product (41:1) in DMF/H_2O is also better than the reaction (11:1) in DMF. These results suggested that the solvent polarity and hydrogen bonding may be important for rate acceleration.

(2) Control experiments of nucleophilies

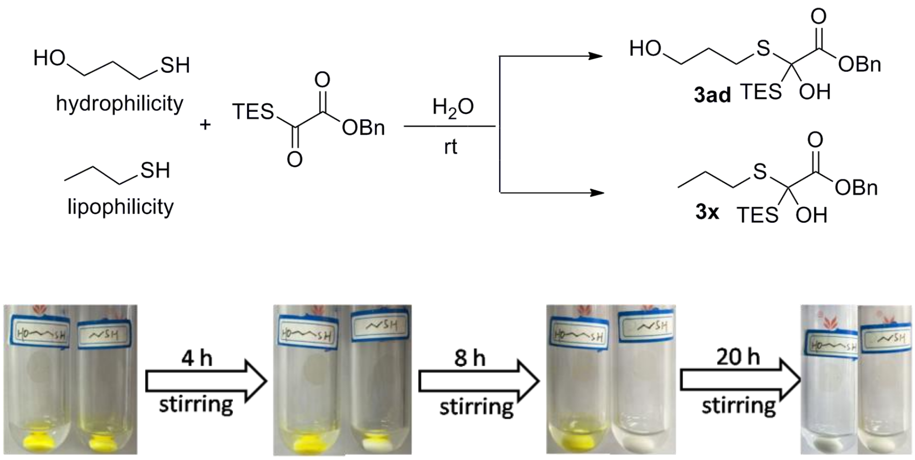


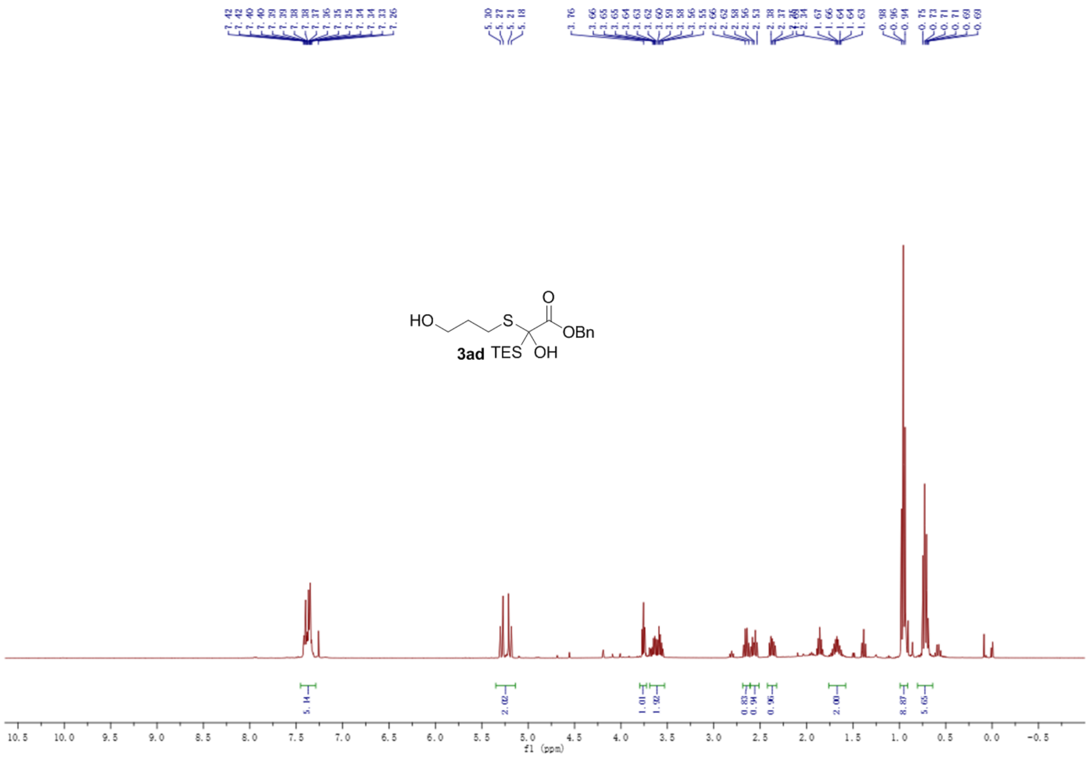
Figure 3. The appearance of the reaction with different nucleophilies

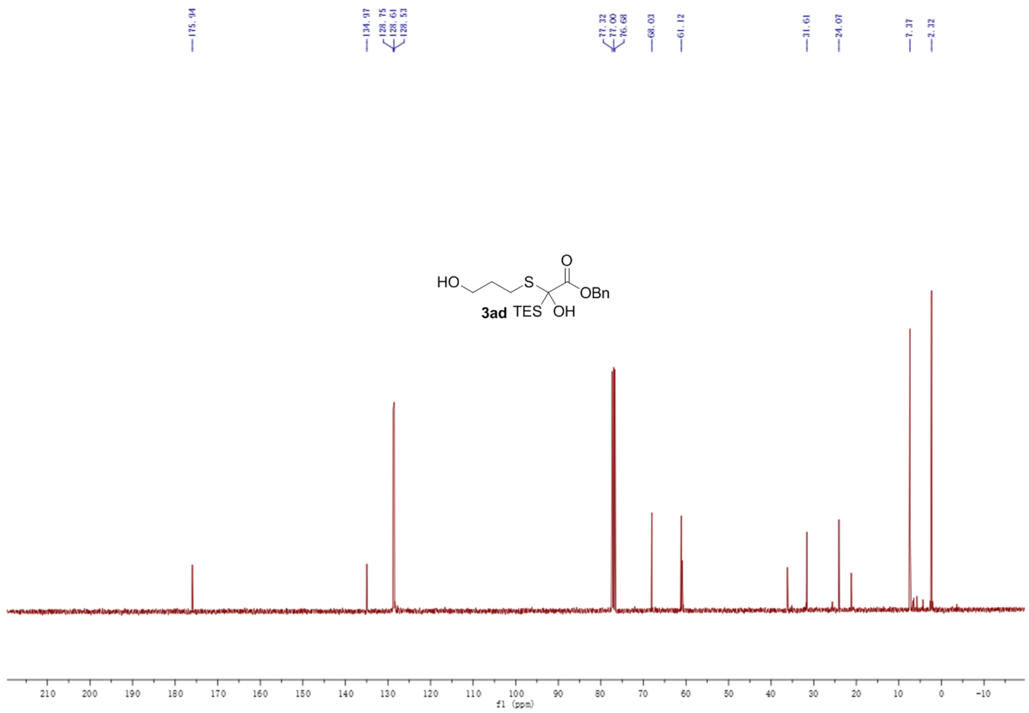
The starting material of silyl glyoxylate is yellow oil and the reaction progress can be monitored approximately by visualization of the change of color (the yellow oil disappeared). The reaction phenomenon have shown that the reaction rates with *n*-propylthiol (lipophilicity) as the nucleophilie is obviously faster than the reaction with 3-mercaptopropanol (hydrophilicity) as the nucleophilie.

From two sets of control experiments, we can see that the rate acceleration and the higher ratio of addition product to Brook rearrangement product were observed when the reaction was performed in water or in DMF/H_2O. However, where the chemistry occurs at the interface or in an oil phase is currently unclear.

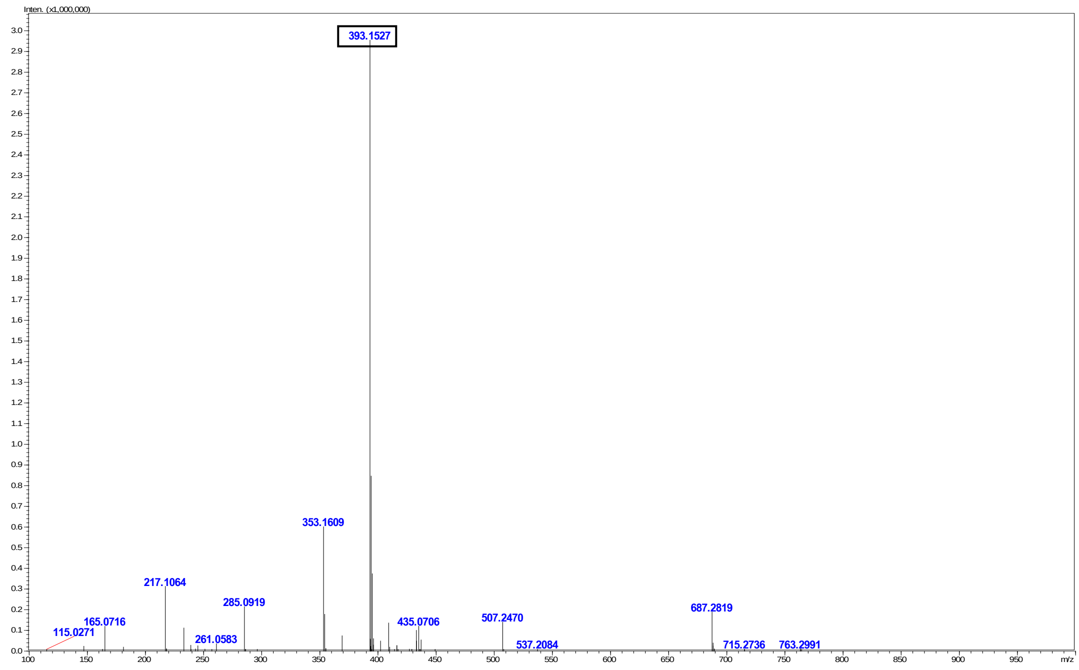
The procedure for 3ad

A mixture of 3-mercaptopropanol (0.2 mmol) and 4-bromobenzyl 2-oxo-2-(triethylsilyl)acetate (0.1 mmol) in H_2O (1 mL) were stirred at room temperature. After stirring for 20 hours, the mixture was extracted with EtOAc and washed with water to afford the desired product **3ad**. Note: the product **3ad** was not stable when the reaction mixture was purified by silica gel chromatography. However, the desired product could be purified by extraction and the crude product was identified by ^{1}H NMR, ^{13}C NMR and HRMS.



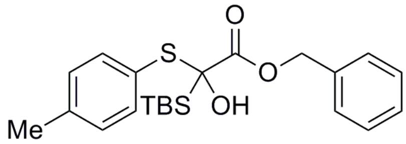


3ad: HRMS calcd. for $[M+Na]^+$ 393.1532, found 393.1527.



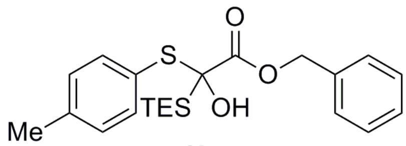
5. General procedure for catalyst-free nucleophilic addition reactions of silyl glyoxylates with thiols in water

The mixture of thiols **1** (0.2 mmol), silyl glyoxylates **2** (0.1 mmol) in 1 mL H_2O were stirred at room temperature. After stirring for the indicated time, the mixture was further purified by silica gel chromatography to afford the desired product **3**.



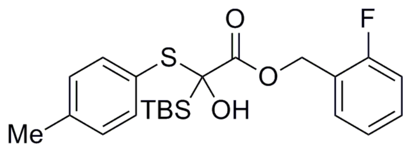
3a

3a: 81% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (s, 5H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.04 (dd, *J* = 12.0, 20.0 Hz, 2H), 3.59 (s, 1H), 2.33 (s, 3H), 0.94 (s, 9H), 0.33 (s, 3H), 0.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 139.4, 136.2, 134.8, 129.6, 128.8, 128.6, 128.5, 125.9, 80.8, 67.8, 27.2, 21.3, 18.5, -5.9, -6.2; **HRMS (ESI)**: calcd. for $[C_{22}H_{30}O_3SSi+Na]^+$ 425.1583, found 425.1575.



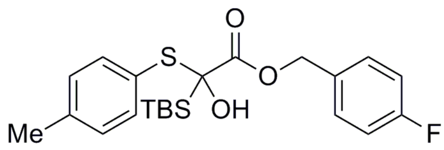
3b

3b: 83% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.44 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.08 (s, 2H), 3.57 (s, 1H), 2.32 (s, 3H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.78–0.84 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 139.3, 136.0, 129.6, 128.9, 128.5, 126.1, 80.3, 67.8, 21.2, 7.4, 2.5; **HRMS (ESI)**: calcd. for $[C_{22}H_{30}O_3SSi+NH_4]^+$ 420.2029, found 420.2020.



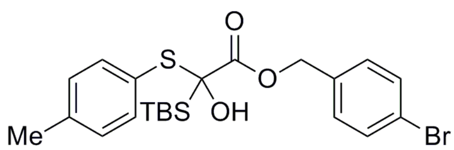
3c

3c: 90% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.0, 12.0 Hz, 1H), 7.15–7.20 (m, 3H), 7.04–7.09 (m, 4H), 5.02 (dd, *J* = 12.0, 32.0 Hz, 2H), 3.56 (s, 1H), 2.32 (s, 3H), 0.94 (s, 9H), 0.34 (s, 3H), 0.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 162.8 (d, *J* = 245 Hz), 139.5, 137.2 (d, *J* = 7 Hz), 129.6, 125.9, 124.2 (d, *J* = 3 Hz), 115.5 (q, *J* = 12 Hz), 80.8, 66.8, 27.2, 21.2, 18.5, -5.9, -6.6; **HRMS (ESI)**: calcd. for $[C_{22}H_{29}FO_3SSi+Na]^+$ 443.1488, found 443.1480.



3d

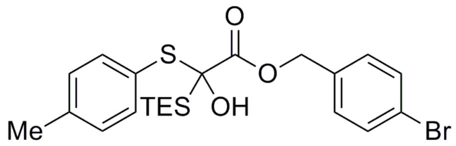
3d: 83% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.38 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.03–7.10 (m, 4H), 5.01 (dd, *J* = 16.0, 20.0 Hz, 2H), 3.56 (s, 1H), 2.32 (s, 3H), 0.93 (s, 9H), 0.32 (s, 3H), 0.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 162.8 (d, *J* = 246 Hz), 139.5, 136.1, 130.9 (d, *J* = 8 Hz), 129.6, 125.9, 115.5 (d, *J* = 21 Hz), 80.7, 67.0, 27.2, 21.3, 18.5, -5.9, -6.6; **HRMS (ESI)**: calcd. for $[C_{22}H_{29}FO_3SSi+NH_4]^+$ 438.1934, found 438.1917.



3e

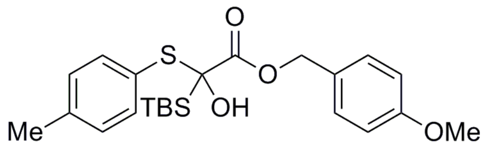
3e: 74% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.37 (m, 2H), 7.02–7.12 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 4.79 (dd, *J* = 12.0, 32.0 Hz, 2H), 3.35 (s, 1H), 2.13 (s, 3H), 0.75 (s, 9H), 0.13 (s, 3H), 0.00 (s, 3H); **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 174.7, 139.5, 136.1, 133.9, 131.8, 130.5, 129.6, 126.0, 122.7, 80.7, 66.9, 27.2, 21.2, 18.5, -5.9, -6.6; H**RMS (ESI)**: calcd. for $[C_{22}H_{29}BrO_3SSi+Na]^+$ 503.0688, found 503.0685.



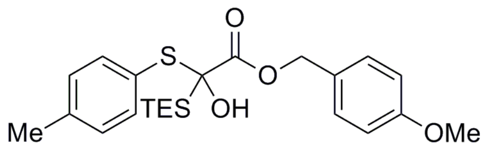
3f

3f: 76% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44–7.50 (m, 2H), 7.20–7.26 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.99 (dd, *J* = 12.0, 24.0 Hz, 2H), 3.50 (s, 1H), 2.30 (s, 3H), 1.00 (t, *J* = 8.0 Hz, 9H), 0.82–0.75 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 139.4, 135.8, 134.0, 131.7, 130.5, 129.6, 126.1, 122.7, 80.2, 66.9, 21.2, 7.4, 2.5; H**RMS (ESI)**: calcd. for $[C_{22}H_{29}BrO_3SSi+NH_4]^+$ 498.1134, found 498.1129.



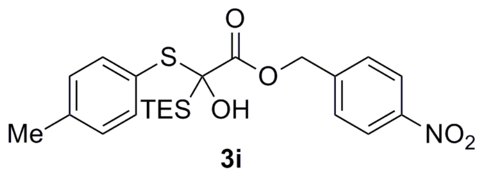
3g

3g: 71% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.35 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.87–6.92 (m, 2H), 7.98 (s, 2H), 3.84 (s, 3H), 3.60 (s, 1H), 2.32 (s, 3H), 0.93 (s, 9H), 0.31 (s, 3H), 0.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 159.8, 139.4, 136.3, 130.6, 129.6, 127.0, 126.0, 113.9, 80.8, 67.6, 55.3, 27.3, 21.3, 18.5, -5.9, -6.6; **HRMS (ESI)**: calcd. for $[C_{23}H_{32}O_4SSi+H]^+$ 433.1869, found 433.1862.



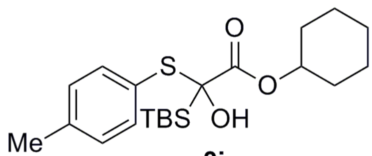
3h

3h: 69% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.35 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.88–6.92 (m, 2H), 5.01 (dd, *J* = 11.6, 12.8 Hz, 2H), 3.84 (s, 3H), 3.56 (s, 1H), 2.32 (s, 3H), 1.01 (t, *J* = 8.0 Hz, 9H), 0.76–0.83 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 159.9, 139.2, 136.0, 130.7, 129.5, 127.2, 126.2, 113.9, 80.3, 67.6, 55.3, 21.2, 7.4, 2.5; **HRMS (ESI)**: calcd. for $[C_{23}H_{32}O_4SSi+Na]^+$ 455.1688, found 455.1653.



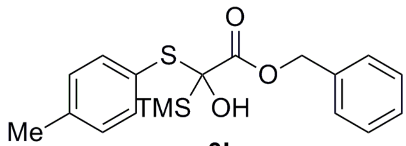
3i

3i: 76% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.42 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 2H), 3.56 (s, 1H), 2.32 (s, 3H), 1.01 (t, *J* = 8.0 Hz, 9H), 0.77–0.84 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 139.3, 136.0, 135.0, 129.6, 128.9, 128.5, 126.1, 80.3, 67.8, 21.2, 7.4, 2.5; **HRMS(ESI)**: calcd. for $[C_{22}H_{29}NO_5SSi +Na]^+$ 470.1433, found 470.1431.



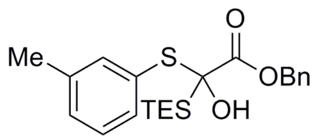
3j

3j: 70% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.61–4.67 (m, 2H), 3.66 (s, 1H), 2.32 (s, 3H), 1.72–1.81 (m, 4H), 1.45–1.56 (m, 3H), 1.29–1.37 (m, 3H), 0.99 (s, 9H), 0.35 (s, 3H), 0.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 139.2, 136.0, 129.5, 126.4, 80.3, 75.3, 31.7, 31.5, 27.4, 25.3, 23.7, 21.2, 18.7, -6.0, -6.4; **HRMS (ESI)**: calcd. for $[C_{21}H_{34}O_3SSi+NH_4]^+$ 412.2342, found 412.2341.



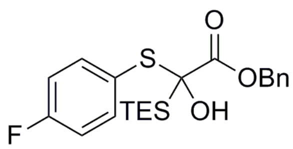
3k

3k: 41% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.41 (m, 5H), 7.22–7.26 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.10 (dd, *J* = 12.0, 32.0 Hz, 2H), 3.53 (s, 1H), 2.33 (s, 3H), 0.20 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 139.4, 136.0, 135.1, 129.6, 128.7, 128.6, 128.5, 126.1, 80.1, 67.8, 21.2, -3.3; **HRMS (ESI)**: calcd. for $[C_{19}H_{24}O_3SSi+NH_4]^+$ 378.1559, found 378.1547.



3m

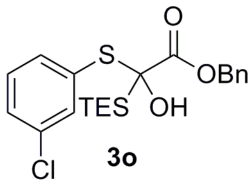
3m: 92% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.42 (m, 5H), 7.19 (s, 1H), 7.10–7.14 (m, 3H), 5.06 (s, 2H), 3.61 (s, 1H), 2.27 (s, 3H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.78-0.84 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 138.5, 136.6, 134.9, 132.8, 130.0, 128.7, 128.6, 80.4, 67.8, 21.2, 7.4, 2.5; **HRMS (ESI)**: calcd. for $[C_{22}H_{30}O_3SSi+H]^+$ 425.1583, found 425.1583.



3n

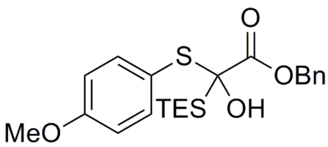
3n: 66% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.42 (m, 5H), 7.21–7.25 (m, 2H), 6.86–6.91 (m, 2H), 5.09 (dd, *J* = 12.0, 28.0 Hz, 2H), 3.58 (s, 1H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.78–0.84 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 163.3

(d, J = 210 Hz), 138.0 (d, J = 9 Hz), 134.8, 129.0, 128.7, 128.6, 125.0, 115.8 (d, J = 22 Hz), 80.3, 67.9, 7.4, 2.5; **HRMS (ESI)**: calcd. for $[C_{21}H_{27}FO_3SSi+Na]^+$ 429.1332, found 429.1337.



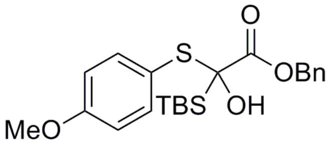
3o

3o: 74% yield; yellow oil; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.41 (m, 6H), 7.28–7.31 (m, 1H), 7.12–7.19 (m, 2H), 5.07 (d, J = 4.0 Hz, 2H), 3.67 (s, 1H), 1.01 (t, J = 8.0 Hz, 9H), 0.76–0.84 (m, 6H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 174.3, 135.3, 134.7, 134.2, 133.7, 132.0, 129.7, 129.3, 128.9, 128.7, 128.6, 80.6, 68.1, 7.4, 2.4; **HRMS (ESI)**: calcd. for $[C_{21}H_{27}ClO_3SSi+H]^+$ 423.1217, found 423.1212.



3p

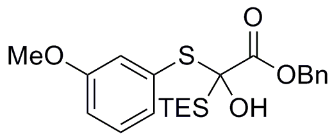
3p: 82% yield; yellow oil; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.39 (m, 5H), 7.19–7.23 (m, 2H), 6.72–6.77 (m, 2H), 5.09 (dd, J = 12.0, 16.0 Hz, 2H), 3.78 (s, 3H), 3.52 (s, 1H), 1.01 (t, J = 8.0 Hz, 9H), 0.77–0.83 (m, 6H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 174.5, 160.6, 137.7, 135.0, 128.9, 128.6, 120.2, 114.3, 80.4, 67.8, 55.2, 7.5, 2.5; **HRMS(ESI)**: calcd. for $[C_{22}H_{30}O_4SSi+H]^+$ 419.1712, found 419.1716.



3q

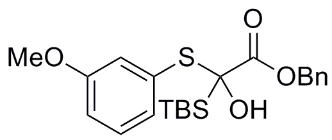
3q: 70% yield; yellow oil; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.44 (m, 5H), 7.20–

7.24 (m, 2H), 6.74–6.78 (m, 2H), 5.06 (dd, *J* = 12.0, 28.0 Hz, 2H), 3.78 (s, 3H), 3.58 (s, 1H), 0.95 (s, 9H), 0.34 (s, 3H), 0.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 160.6, 137.9, 134.9, 128.8, 128.6, 128.5, 120.0, 114.3, 80.8, 67.8, 55.2, 27.2, 18.5, -5.9, -6.6; **HRMS(ESI)**: calcd. for $[C_{22}H_{30}O_4SSi+H]^+$ 419.1712, found 419.1716.



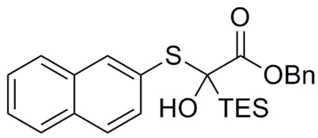
3r

3r: 72% yield; light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.37 (m, 5H), 7.12-7.19 (m, 1H), 7.04–7.07 (m, 2H), 6.81–6.84 (m, 1H), 5.51 (s, 1H), 5.12 (dd, *J* = 12.0, 24.0 Hz, 2H), 3.74 (s, 3H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.62 (dd, *J* = 8.0, 16.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 159.5, 135.3, 132.9, 128.5, 128.3, 125.9, 118.6, 114.7, 78.6, 67.1, 55.2, 6.5, 4.6; **HRMS (ESI)**: calcd. for $[C_{22}H_{30}O_4SSi+Na]^+$ 441.1532, found 441.1523.



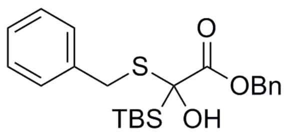
3s

3s: 74% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.42 (m, 5H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.87–6.96 (m, 3H), 5.02 (dd, *J* = 12.0, 20.0 Hz, 2H), 3.71 (s, 4H), 0.96 (s, 9H), 0.35 (s, 3H), 0.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 159.4, 134.8, 130.9, 129.4, 128.6, 128.5, 128.4, 128.1, 120.8, 115.5, 81.1, 67.8, 55.2, 27.2, 18.5, -5.9, -6.6; **HRMS (ESI)**: calcd. for $[C_{22}H_{30}O_4SSi+Na]^+$ 441.1532, found 441.1523.



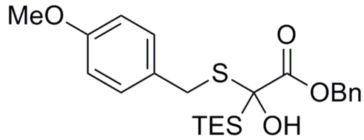
3t

3t: 85% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.79–7.81 (m, 1H), 7.67–7.72 (m, 2H), 7.45–7.50 (m, 2H), 7.31–7.49 (m, 6H), 5.02 (dd, *J* = 12.0, 12.0 Hz, 2H), 3.68 (s, 1H), 1.05 (t, *J* = 8.0 Hz, 9H), 0.80–0.88 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 135.7, 134.9, 133.4, 133.3, 132.4, 128.8, 128.6, 128.2, 127.9, 127.7, 127.4, 126.8, 126.3, 80.8, 67.9, 7.5, 2.5; **HRMS (ESI)**: calcd. for $[C_{25}H_{30}O_3SSi+Na]^+$ 461.1583, found 461.1547.



3u

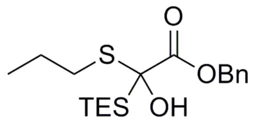
3u: 67% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.38 (m, 5H), 7.16–7.24 (m, 5H), 5.01 (dd, *J* = 12.0, 12.0 Hz, 2H), 3.85 (s, 1H), 3.73 (d, *J* = 12.0 Hz, 1H), 3.46 (d, *J* = 12.0 Hz, 1H), 0.92 (s, 9H), 0.23 (s, 3H), 0.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 137.2, 129.3, 128.6, 128.3, 127.0, 78.1, 67.9, 31.9, 27.3, 18.5, -6.2, -6.7; **HRMS (ESI)**: calcd. for $[C_{22}H_{30}O_2SSi+Na]^+$ 425.1583, found 425.1575.



3v

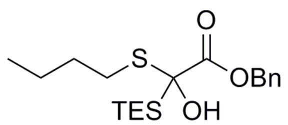
3v: 72% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.39 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 5.07 (dd, *J* = 12.0, 20.0 Hz, 2H), 3.81 (s, 1H), 3.75 (s, 3H), 3.71 (d, *J* = 12.0 Hz, 1H), 3.43 (d, *J* = 12.0 Hz, 1H), 0.96 (t, *J* = 8.0

Hz, 9H), 0.70–0.76 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.7, 158.6, 135.1, 130.3, 129.0, 128.6, 128.5, 113.8, 77.8, 67.9, 55.2, 31.5, 7.4, 2.3; **HRMS(ESI)**: calcd. for $[C_{23}H_{32}O_4SSi+Na]^+$ 455.1688, found 455.1647.



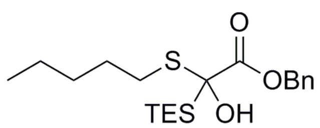
3w

3w: 67% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.43 (m, 5H), 5.24 (dd, J = 12.0, 36.0 Hz, 2H), 3.71 (s, 1H), 2.43–2.50 (m, 1H), 2.15–2.22 (m, 1H), 1.41–1.50 (m, 2H), 0.97 (t, J = 8.0 Hz, 9H), 0.87 (t, J = 8.0 Hz, 3H), 0.70–0.77 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 135.0, 128.7, 128.6, 128.5, 67.9, 67.2, 29.4, 22.5, 13.6, 7.4, 2.3; **HRMS (ESI)**: calcd. for $[C_{18}H_{30}O_3SSi+Na]^+$ 377.1583, found 377.1594.



3x

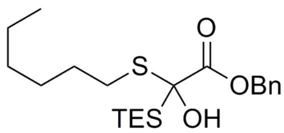
3x: 72% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.42 (m, 5H), 5.24 (dd, J = 12.0, 36.0 Hz, 2H), 3.71 (s, 1H), 2.47–2.53 (m, 1H), 2.16–2.23 (m, 1H), 1.38–1.46 (m, 2H), 1.23–1.33 (m, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.83 (t, J = 8.0 Hz, 3H), 0.67–0.77 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 135.1, 128.7, 128.6, 128.5, 77.4, 68.0, 31.1, 27.1, 22.2, 13.6, 7.4, 2.4; **HRMS (ESI)**: calcd. for $[C_{19}H_{32}O_3SSi+H]^+$ 369.1920, found 369.1902.



3y

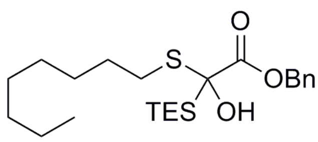
3y: 76% yield; yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.42 (m, 5H), 5.24

(dd, J = 12.0, 36.0 Hz, 2H), 3.71 (s, 1H), 2.46–2.53 (m, 1H), 2.15–2.21 (m, 1H), 1.40–1.48 (m, 2H), 1.22–1.27 (m, 4H), 0.96 (t, J = 8.0 Hz, 9H), 0.83–0.86 (m, 3H), 0.69–0.77 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 135.0, 128.7, 128.6, 128.5, 77.5, 67.9, 31.3, 28.7, 27.4, 22.2, 13.9, 7.4, 2.4; **HRMS (ESI)**: calcd. for $[C_{20}H_{34}O_3SSi+H]^+$ 383.2076, found 338.2075.



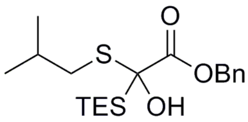
3z

3z: 74% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.43 (m, 5H), 5.24 (dd, J = 12.0, 36.0 Hz, 2H), 3.71 (s, 1H), 2.46–2.53 (m, 1H), 2.15–2.22 (m, 1H), 1.39–1.47 (m, 2H), 1.16–1.30 (m, 6H), 0.97 (t, J = 8.0 Hz, 9H), 0.86 (t, J = 8.0 Hz, 3H), 0.70–0.76 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 135.1, 128.7, 128.6, 128.5, 77.4, 67.9, 31.3, 29.0, 28.8, 27.4, 22.5, 14.0, 7.4, 2.4; **HRMS (ESI)**: calcd. for $[C_{21}H_{36}O_3SSi+H]^+$ 397.2233, found 397.2254.



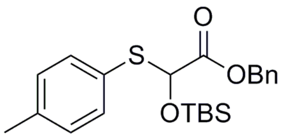
3aa

3aa: 46% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.42 (m, 5H), 5.24 (dd, J = 12.0, 36.0 Hz, 2H), 3.70 (s, 1H), 2.46–2.52 (m, 1H), 2.15–2.21 (m, 1H), 1.37–1.47 (m, 2H), 1.21–1.30 (m, 12H), 0.96 (t, J = 8.0 Hz, 9H), 0.87 (t, J = 8.0 Hz, 3H), 0.69–0.75 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 135.1, 128.7, 128.6, 128.5, 77.5, 67.9, 31.8, 27.5, 22.6, 14.1, 7.4, 2.4; **HRMS(ESI)**: calcd. for $[C_{23}H_{40}O_3SSi+Na]^+$ 447.2365, found 447.2356.



3ab

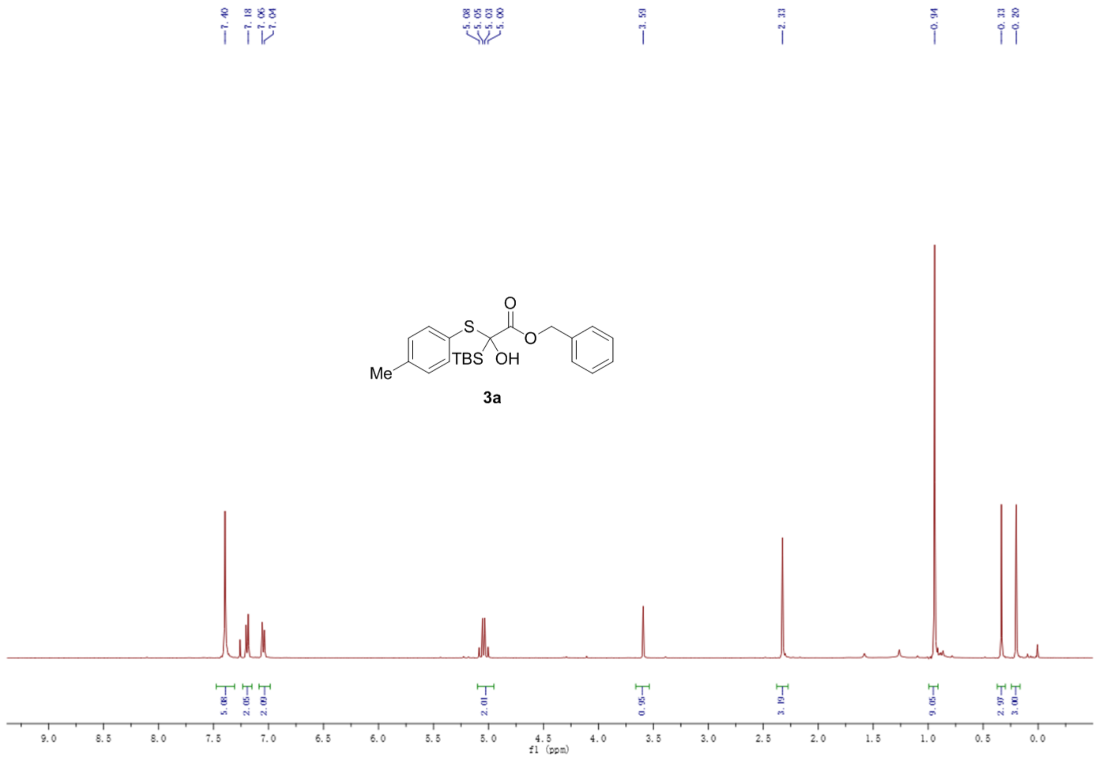
3ab: 64% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.43 (m, 5H), 5.24 (dd, *J* = 12.0, 52.0 Hz, 2H), 3.68 (s, 1H), 2.36 (t, *J* = 8.0, 12.0 Hz, 1H), 2.06 (t, *J* = 8.0, 12.0 Hz, 1H), 1.60–1.67 (m, 1H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.87 (t, *J* = 8.0 Hz, 6H), 0.70–0.76 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 135.1, 128.7, 128.6, 128.5, 77.1, 67.9, 36.0, 28.3, 22.2, 22.1, 7.4, 2.4; **HRMS(ESI)**: calcd. for $[C_{19}H_{32}O_3SSi+H]^+$ 369.1920, found 369.1911.

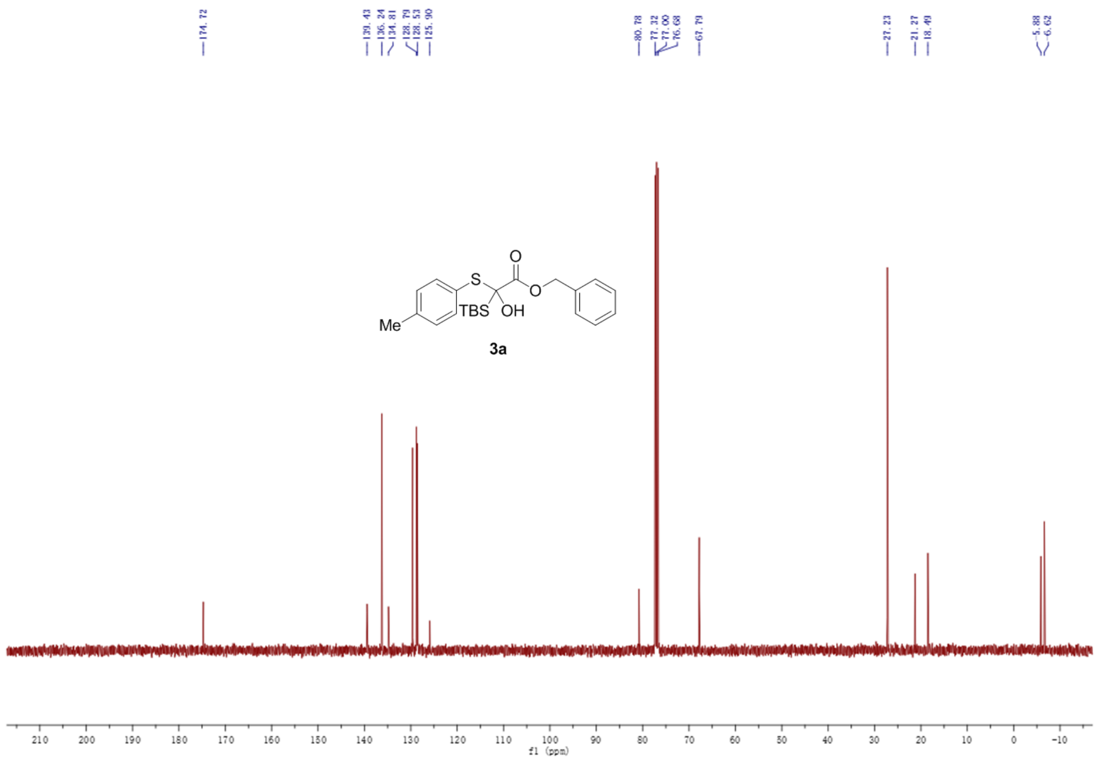


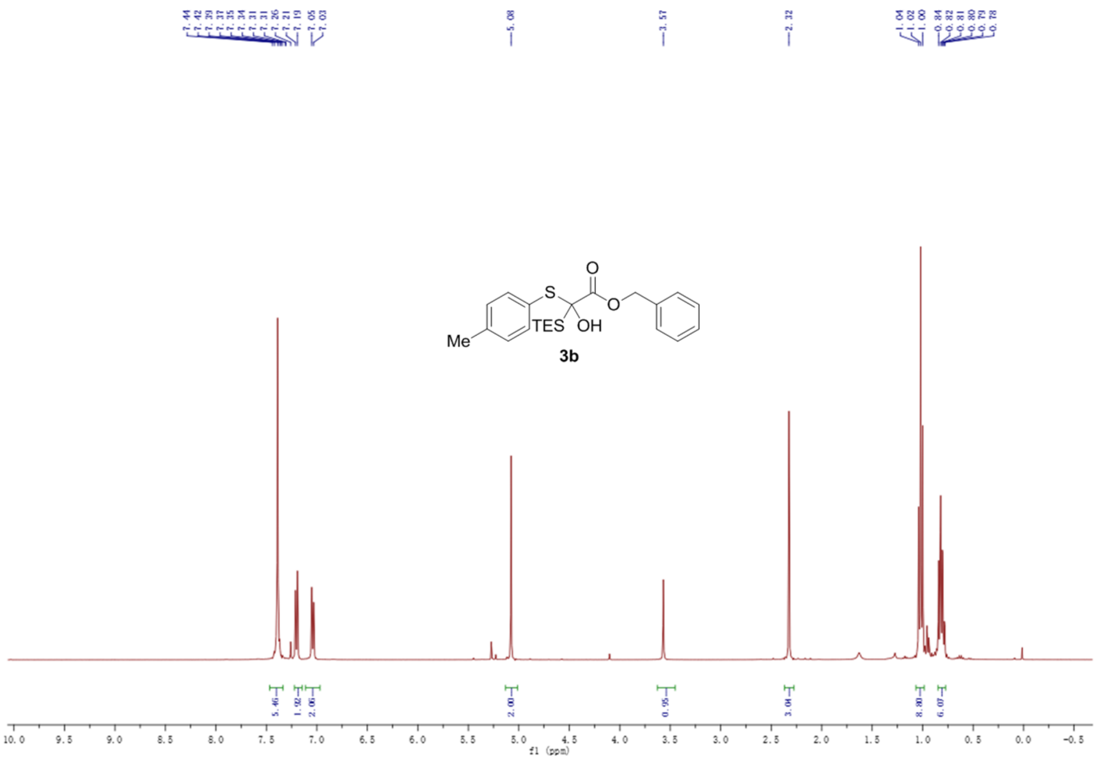
4a

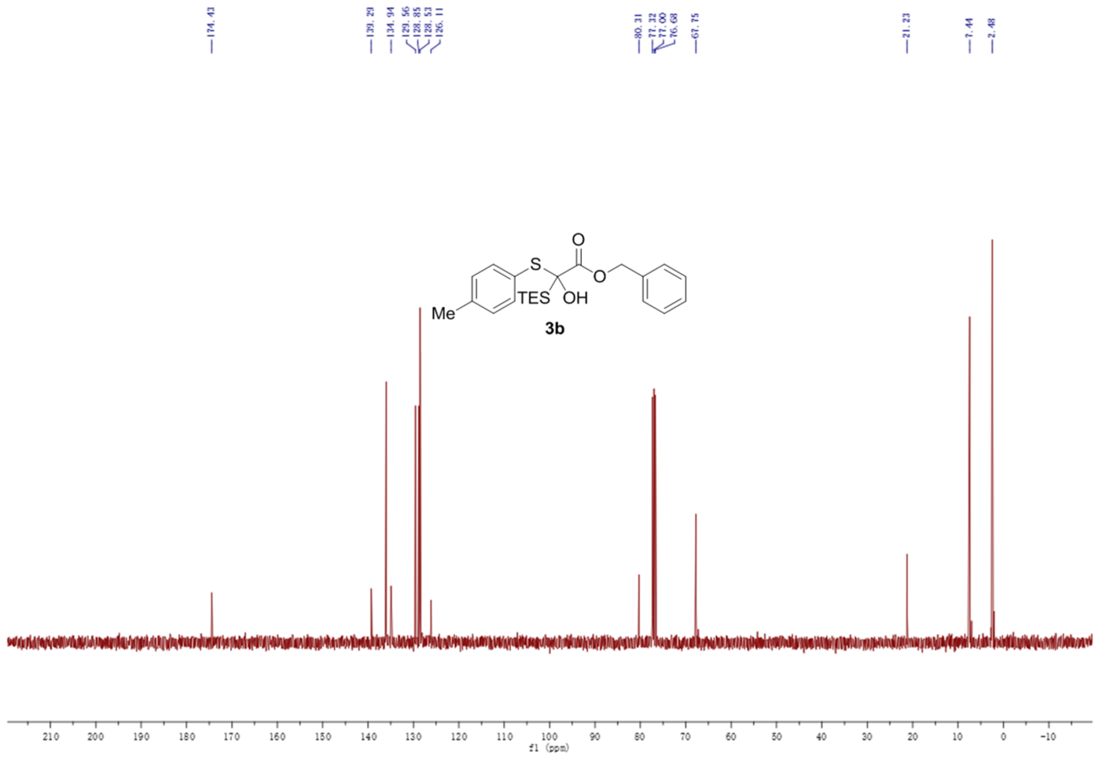
4a: colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.40 (m, 7H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.44 (s, 1H), 5.11 (dd, *J* = 12.0, 40.0 Hz, 2H), 2.32 (s, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 138.8, 135.3, 134.8, 129.5, 128.4, 128.3, 127.6, 78.9, 67.0, 25.5, 21.2, 18.1, -4.8, -5.5; **HRMS(ESI)**: calcd. for $[C_{22}H_{30}O_3SSi+NH_4]^+$ 420.2029, found 420.2027.

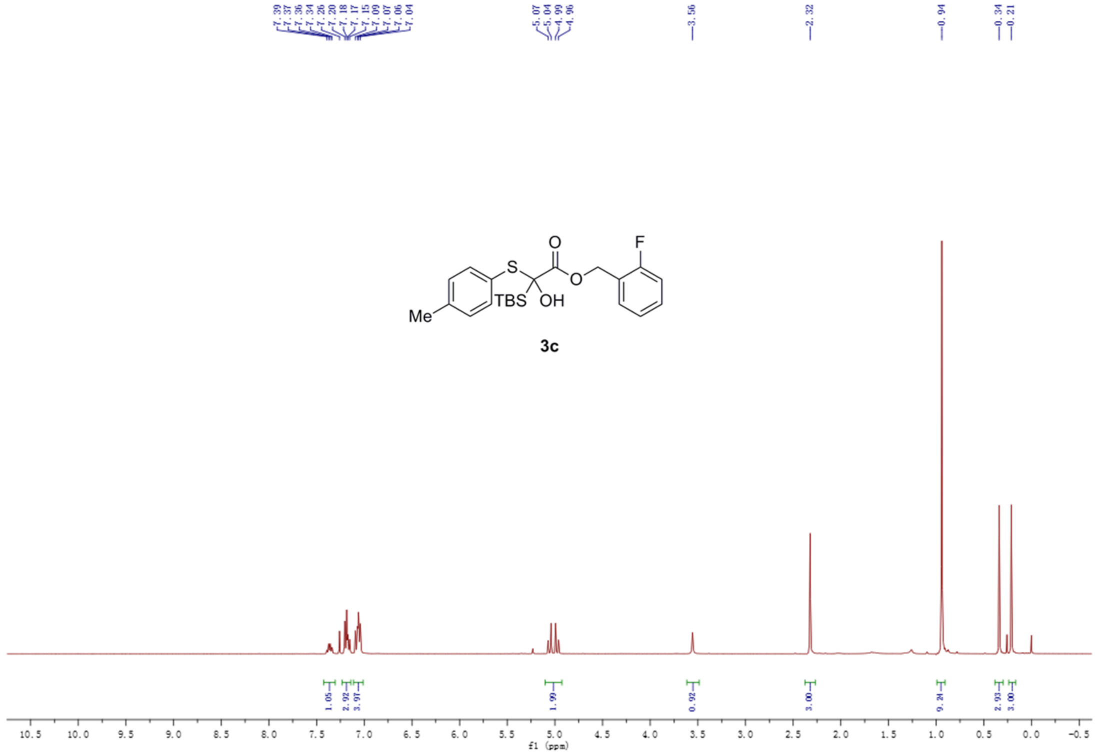
6. NMR spectra

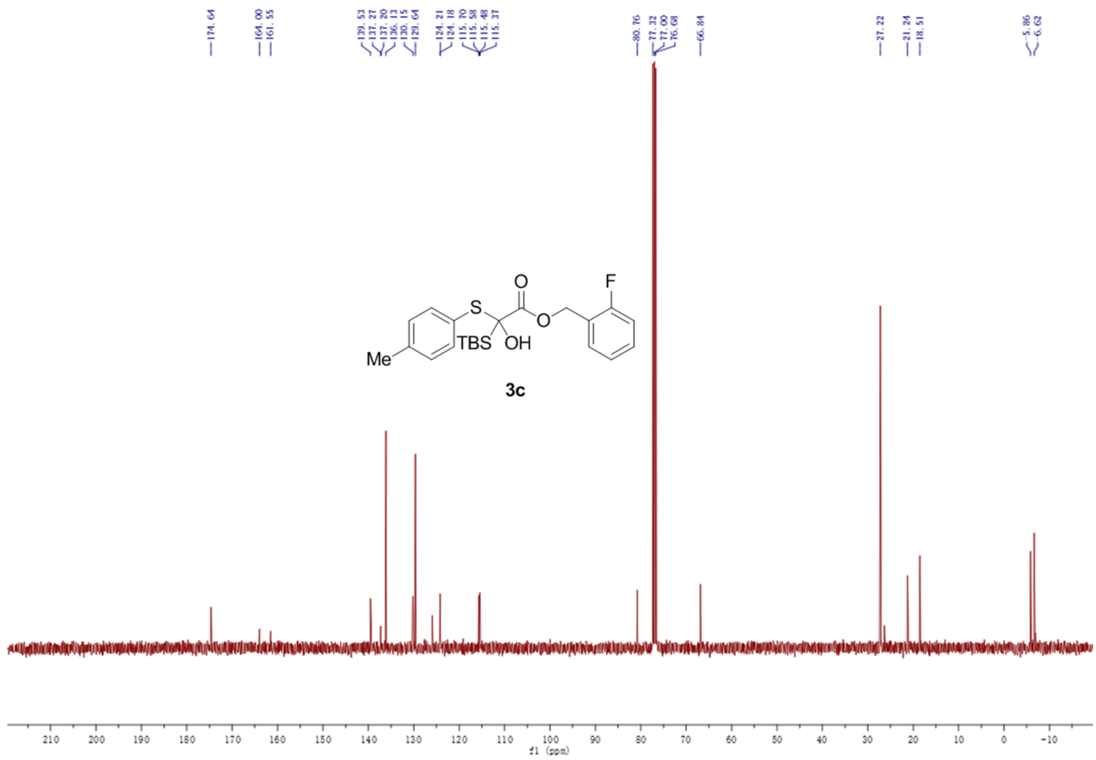


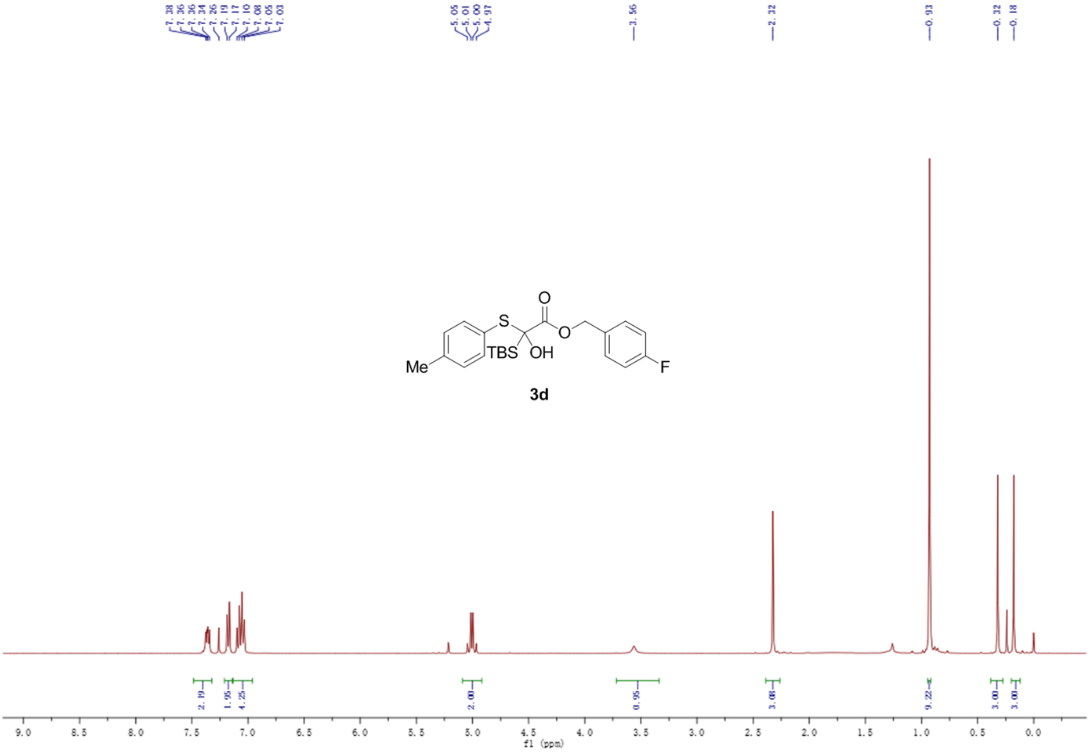


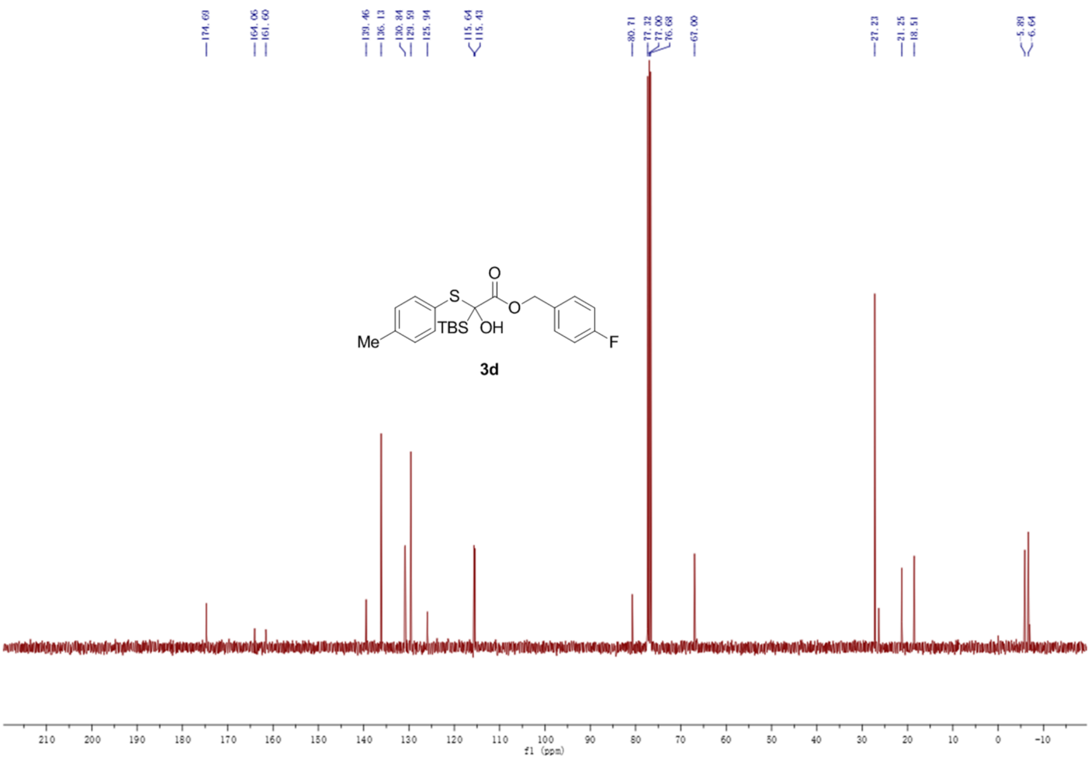


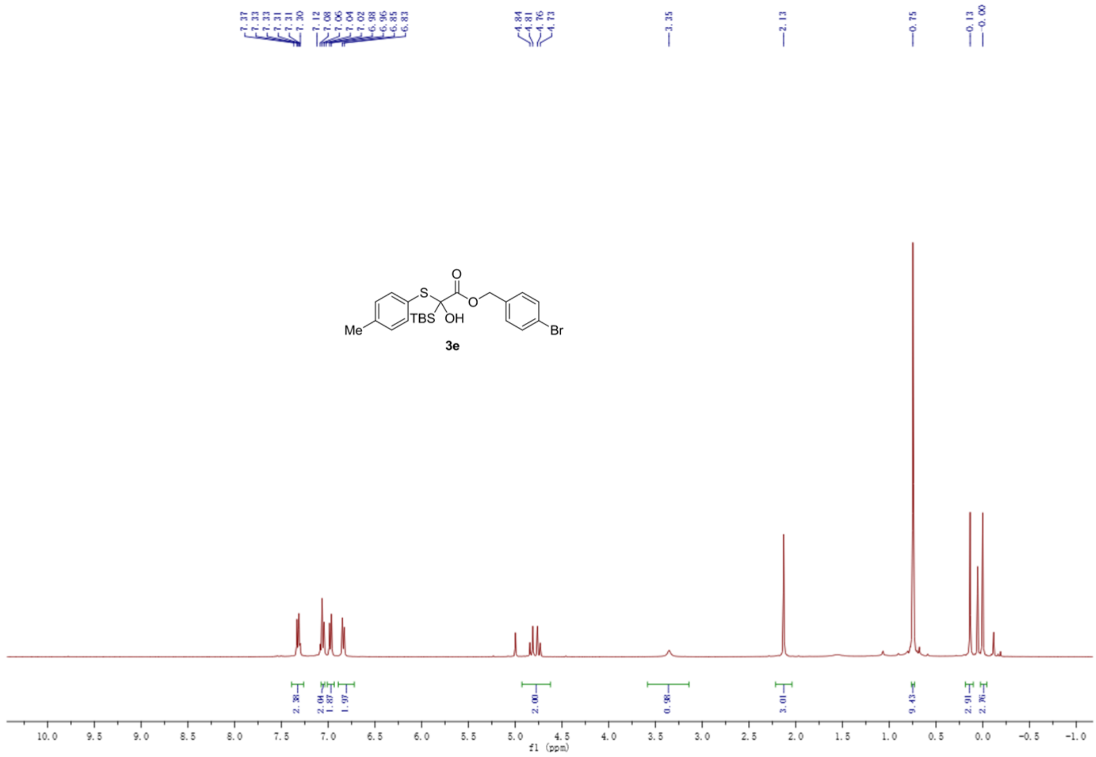


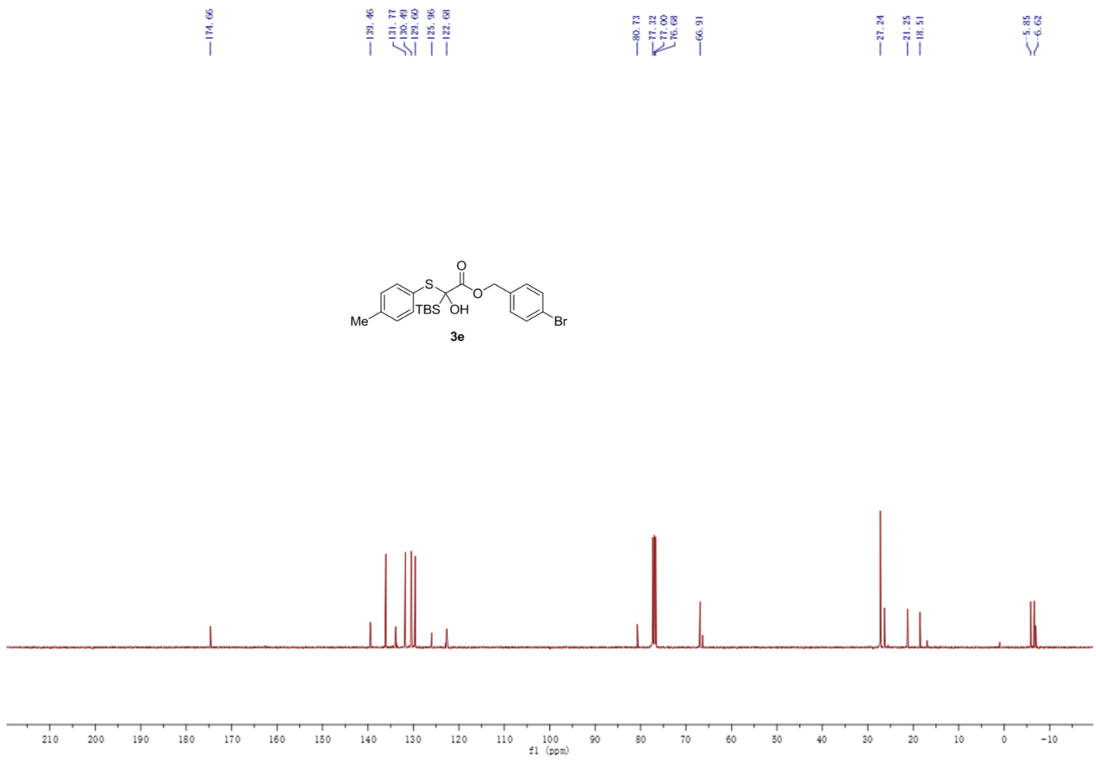


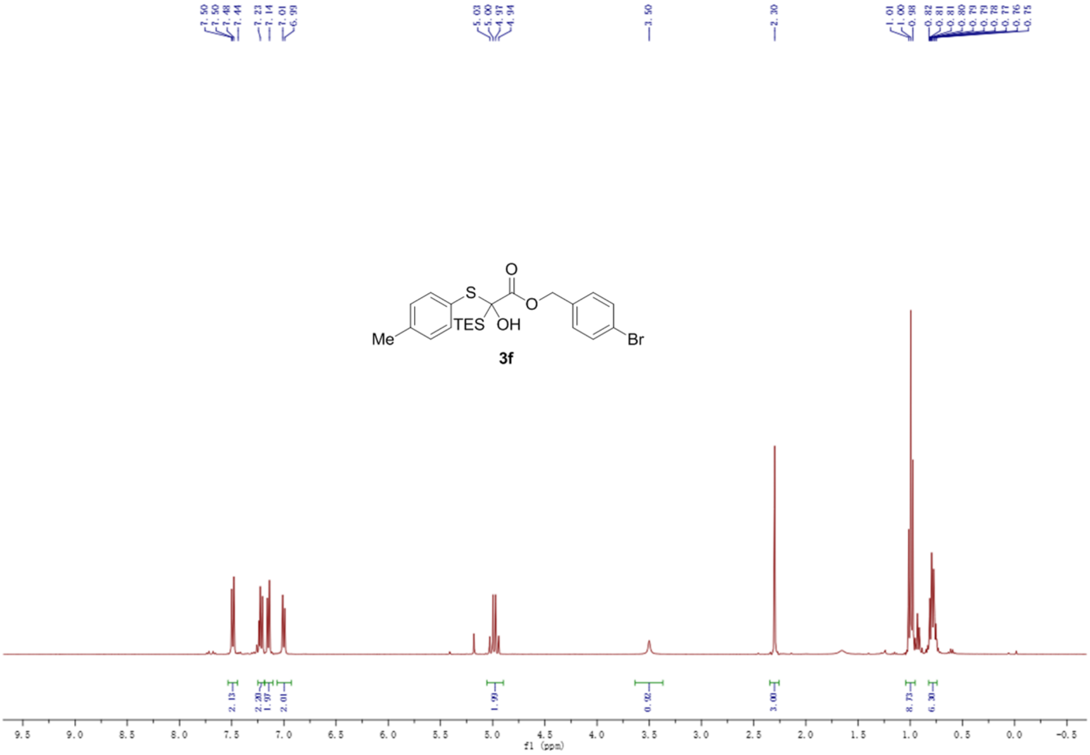












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2.30
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1.00
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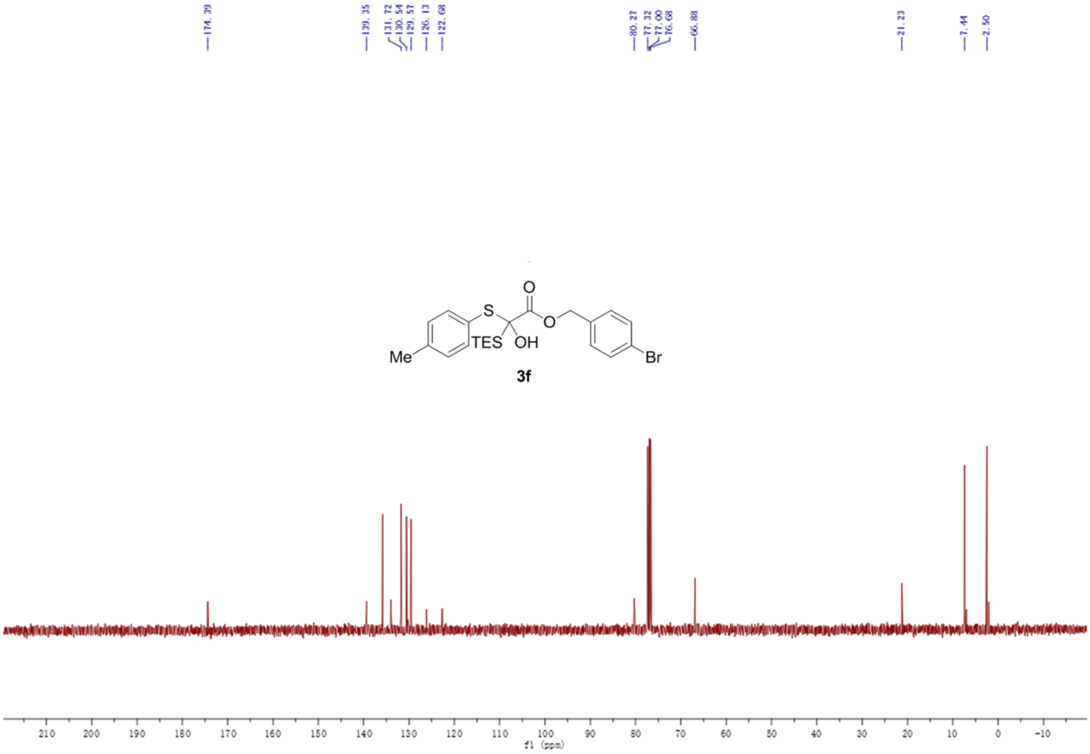
f1 (ppm)



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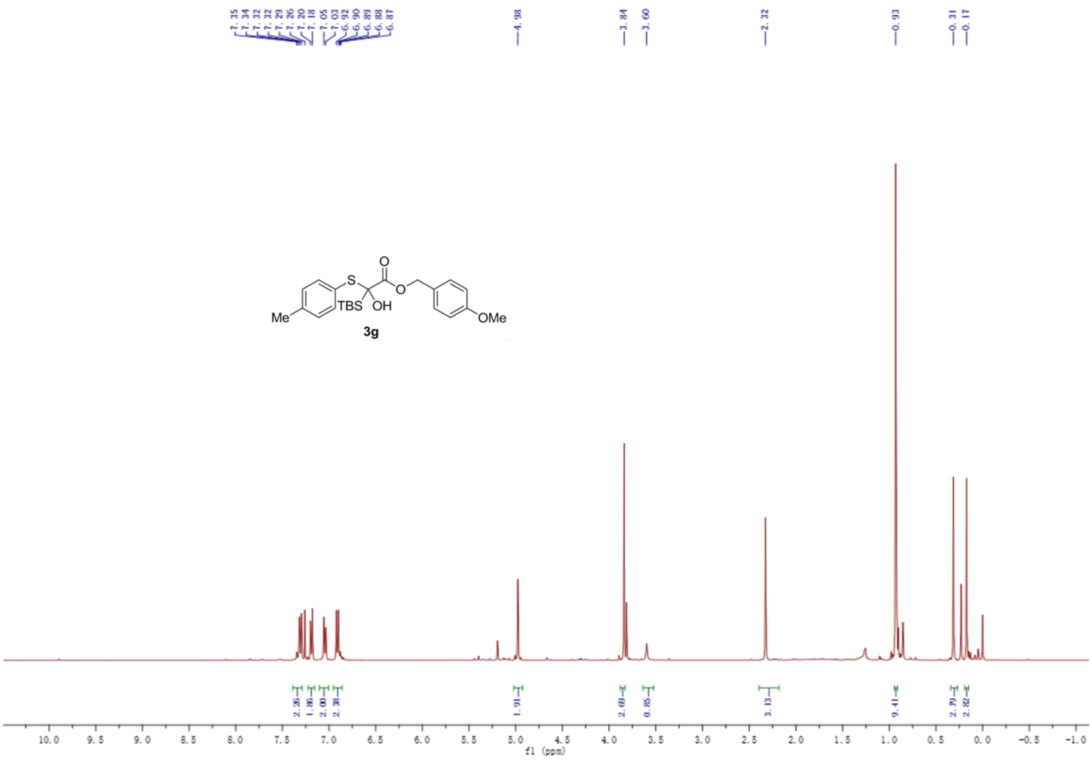
3f
f1 (ppm)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3.84 3.60
2.32
0.93
0.31 0.17
Me
S
TBS
OH
O
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OMe
3g
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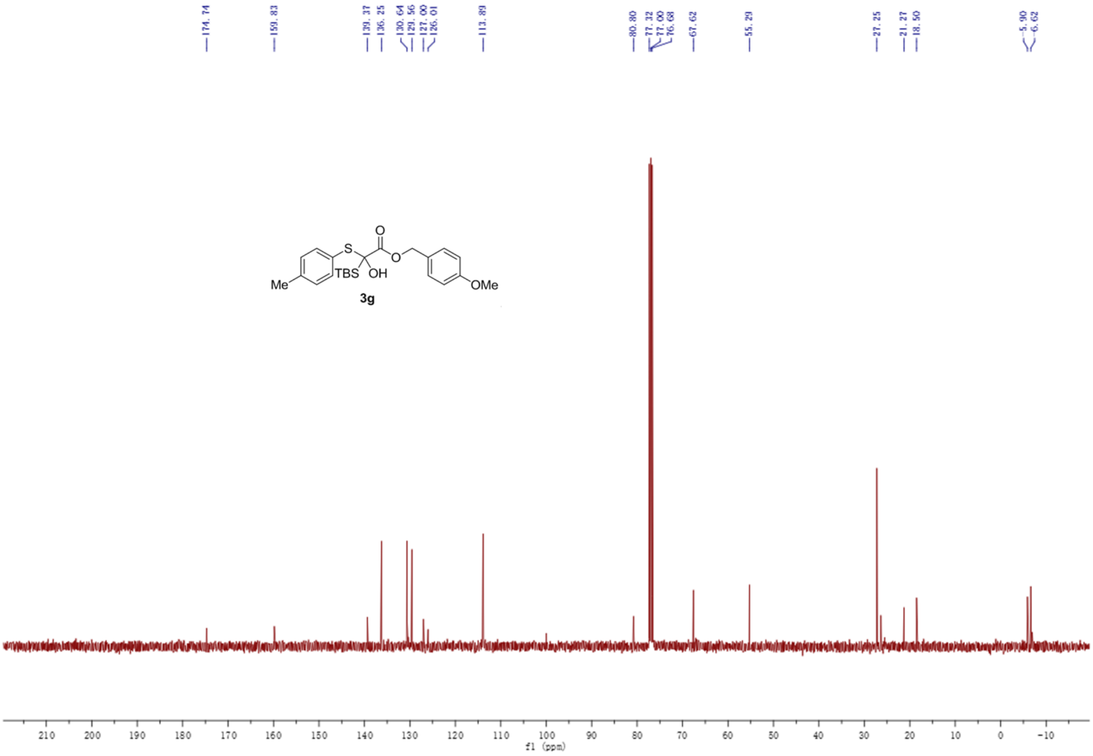
f1 (ppm)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OH
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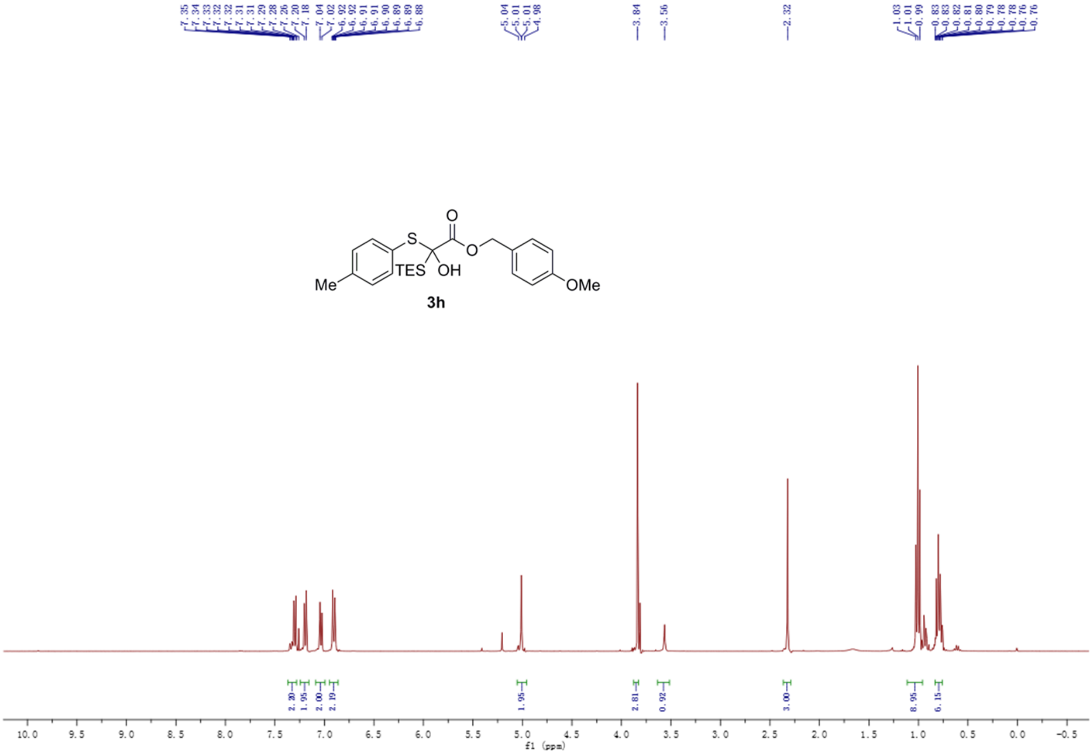
3g
f1 (ppm)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5.04 5.01 5.01 4.98
3.84 3.56
2.32
1.03 1.01 0.99 0.83 0.83 0.82 0.81 0.80 0.79 0.78 0.76 0.76
S
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Me
OMe
3h
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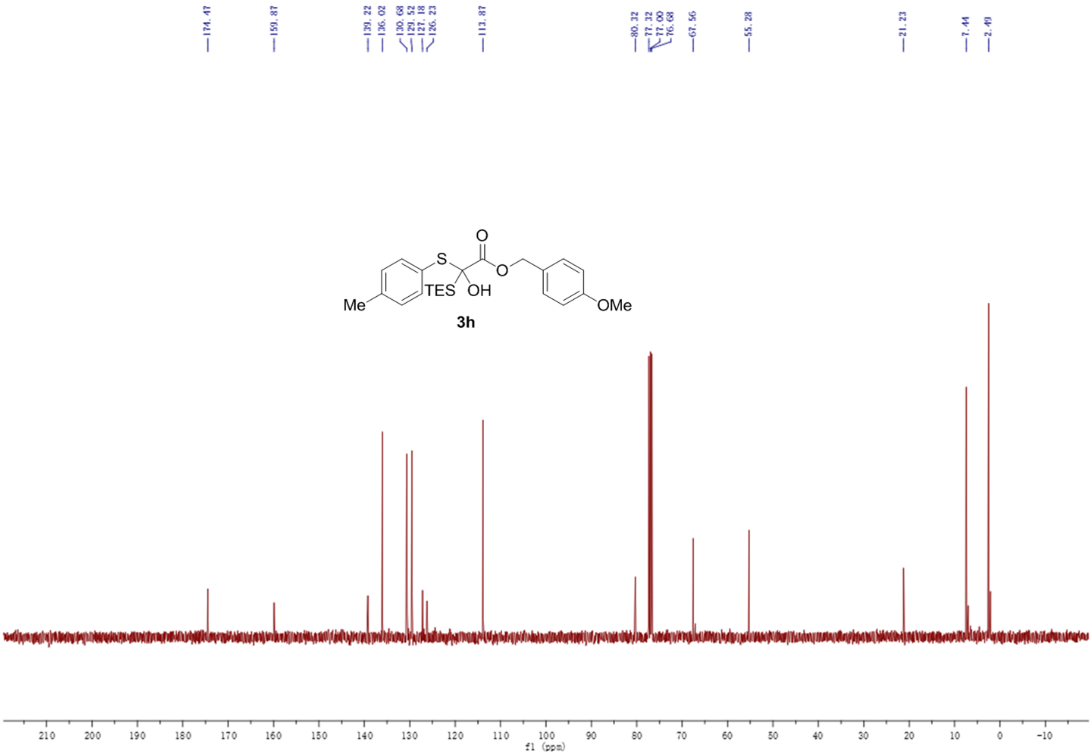
f1 (ppm)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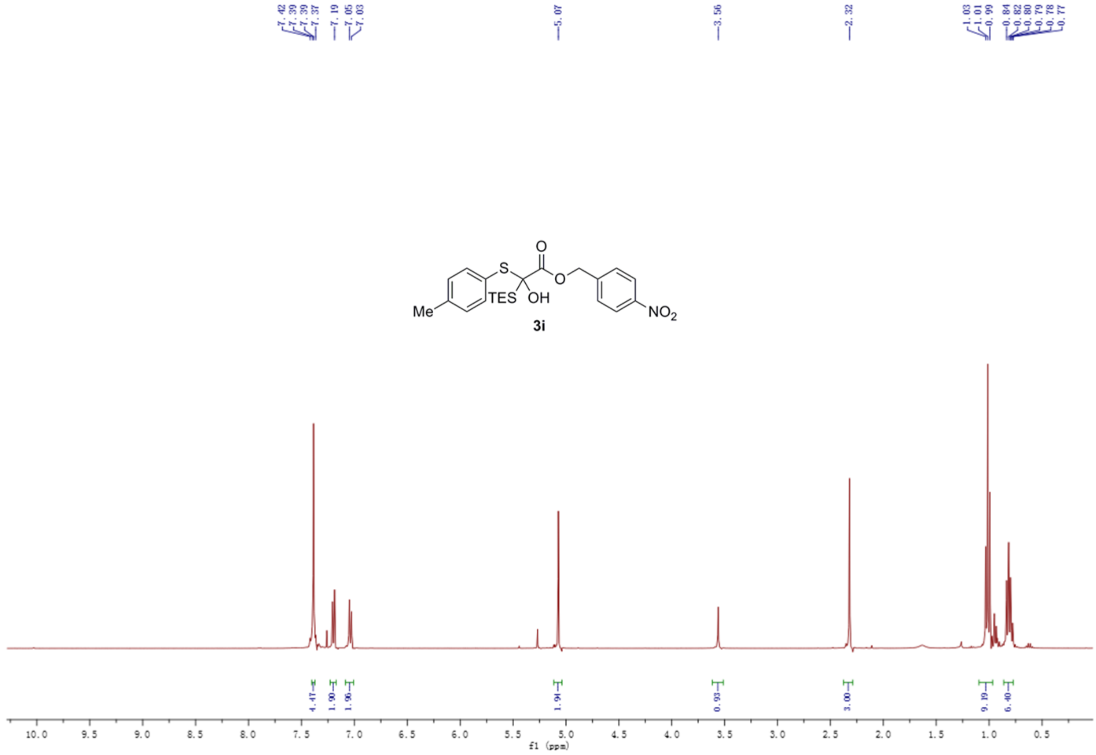
f1 (ppm)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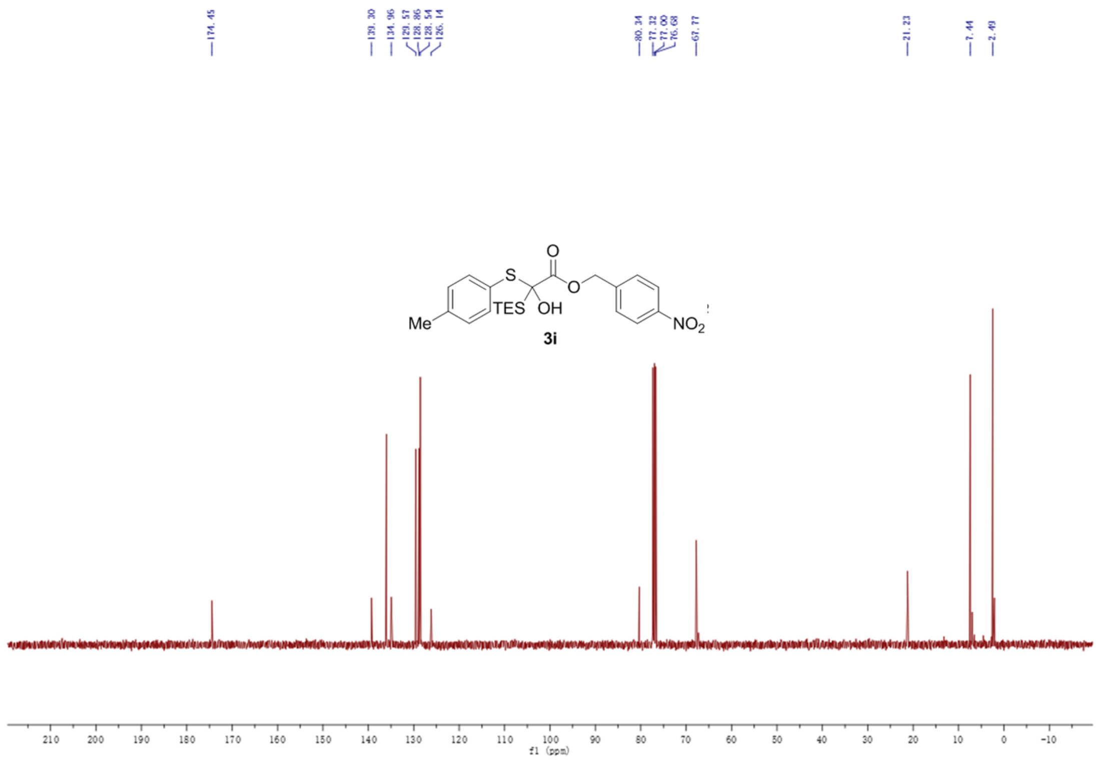
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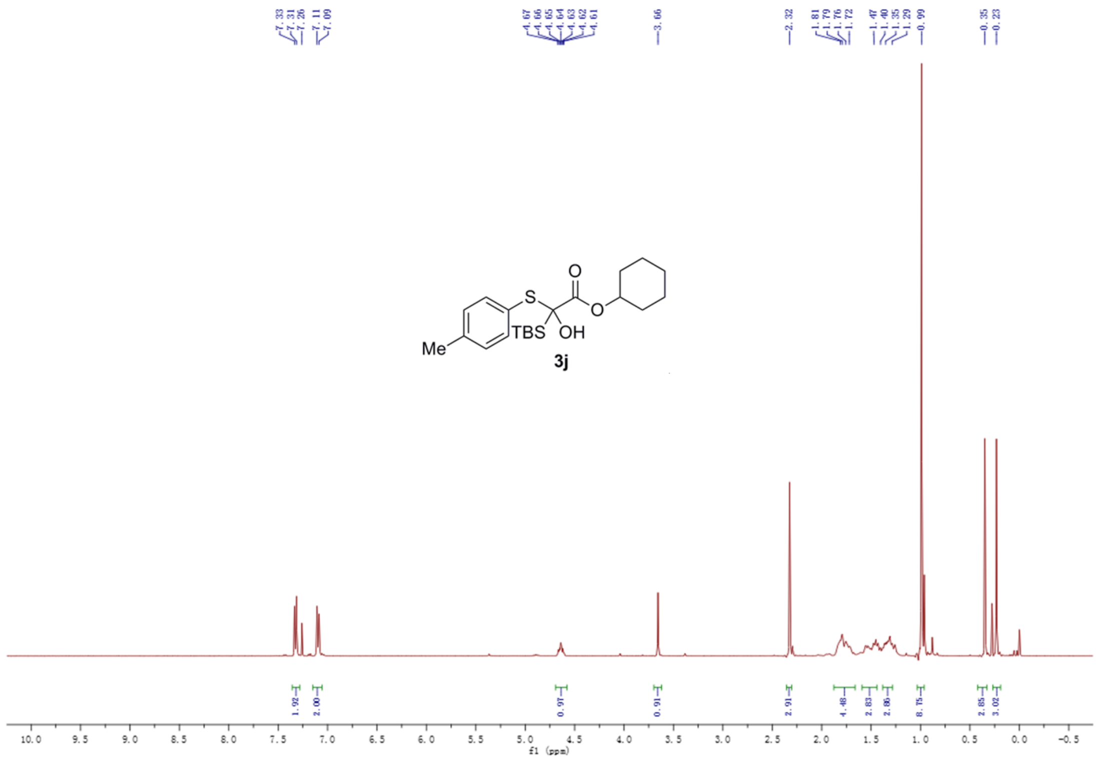
3i
f1 (ppm)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1.72
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S
O
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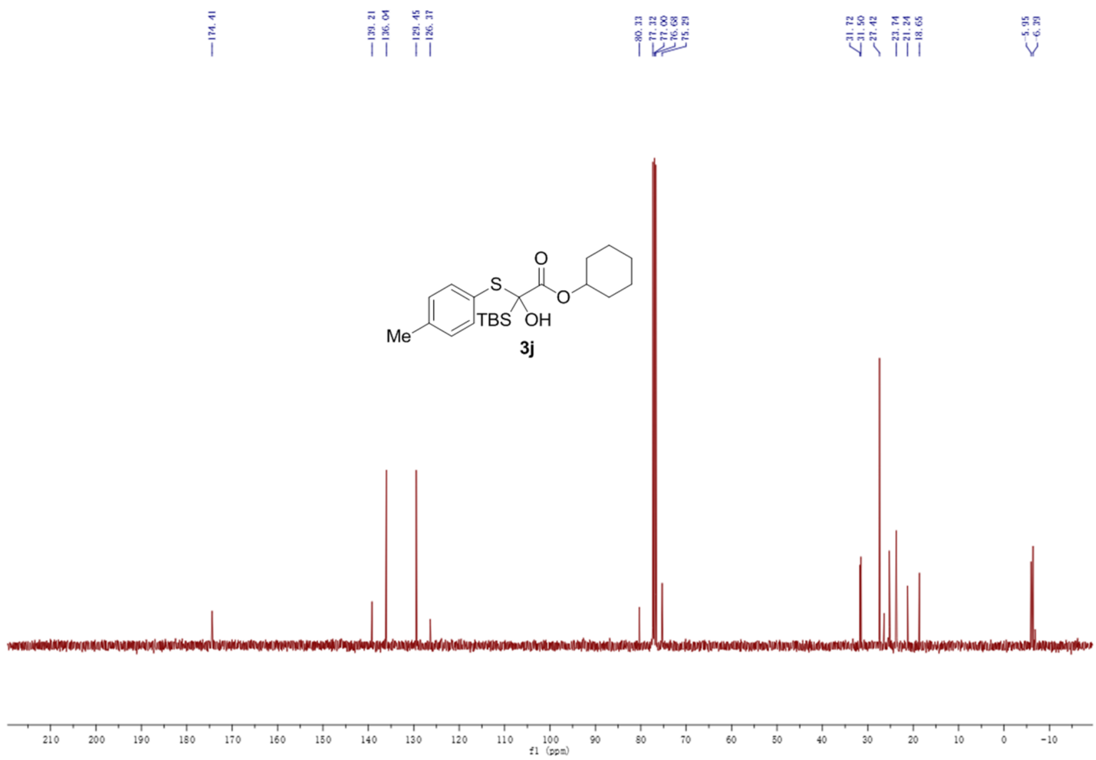
OH
3j
f1 (ppm)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S
O
O
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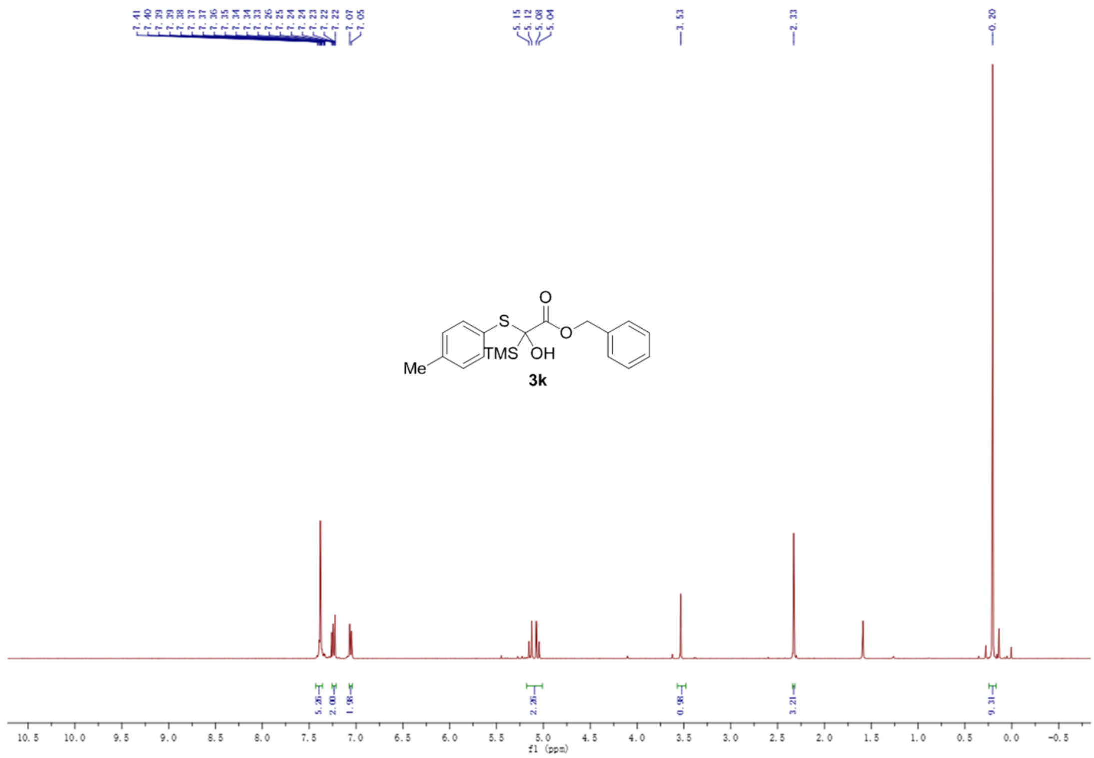
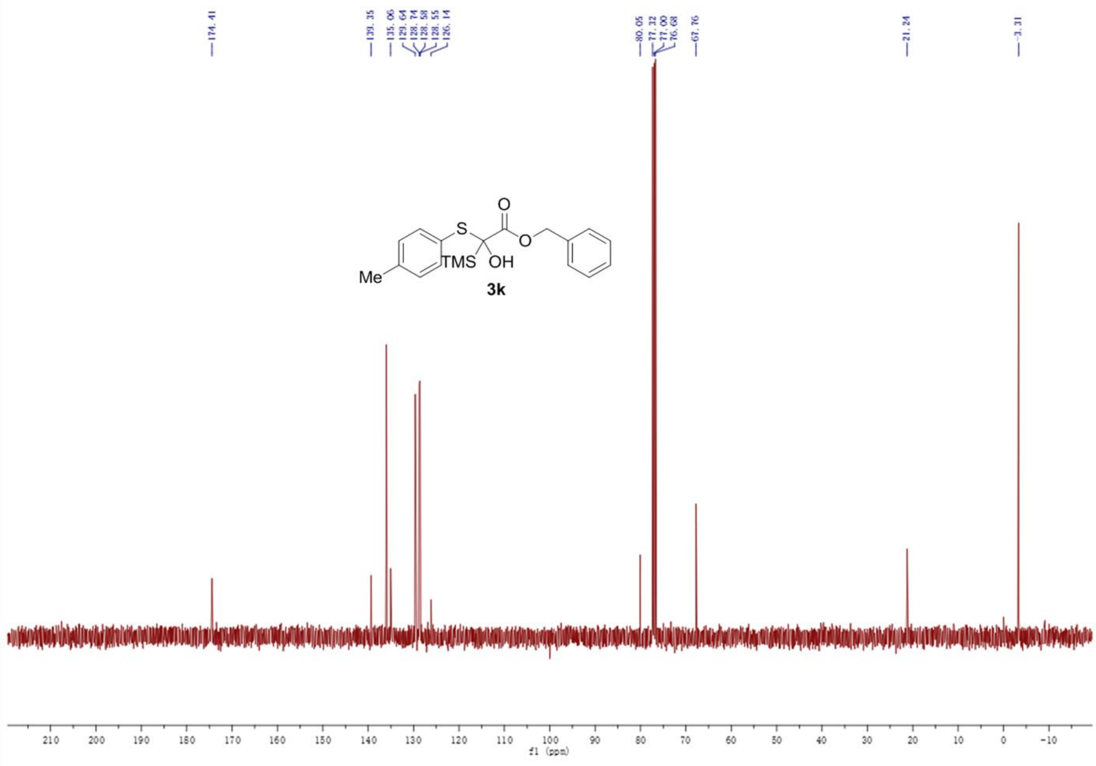
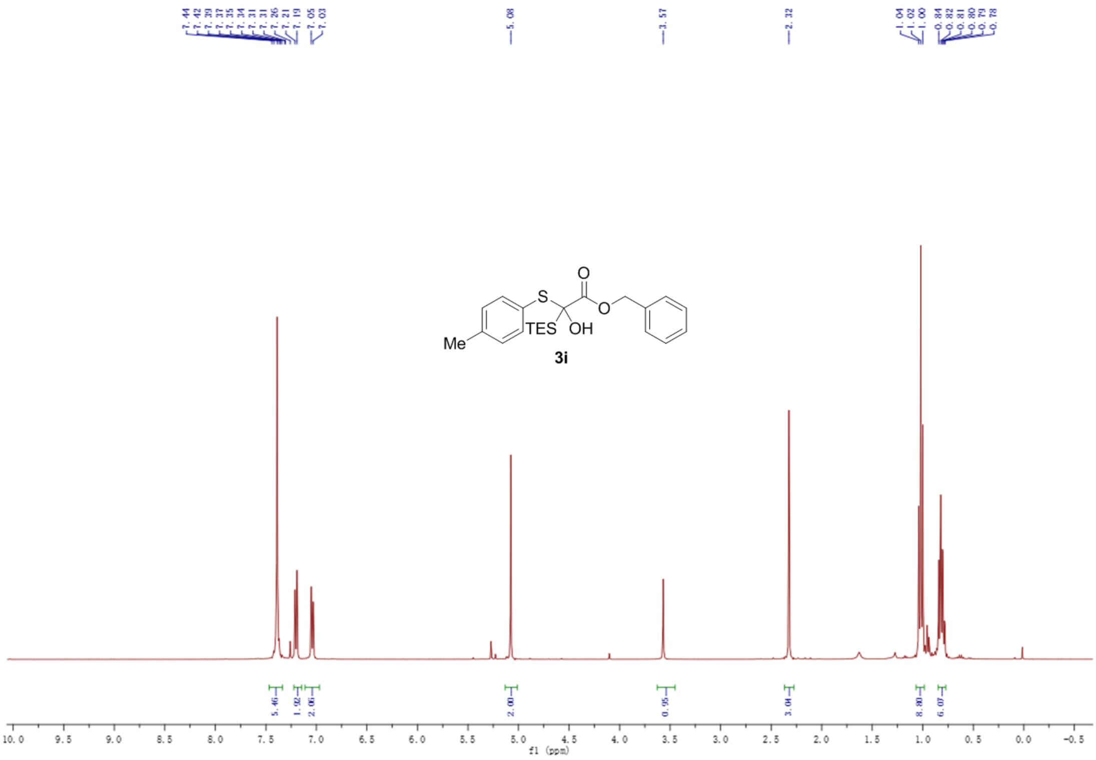
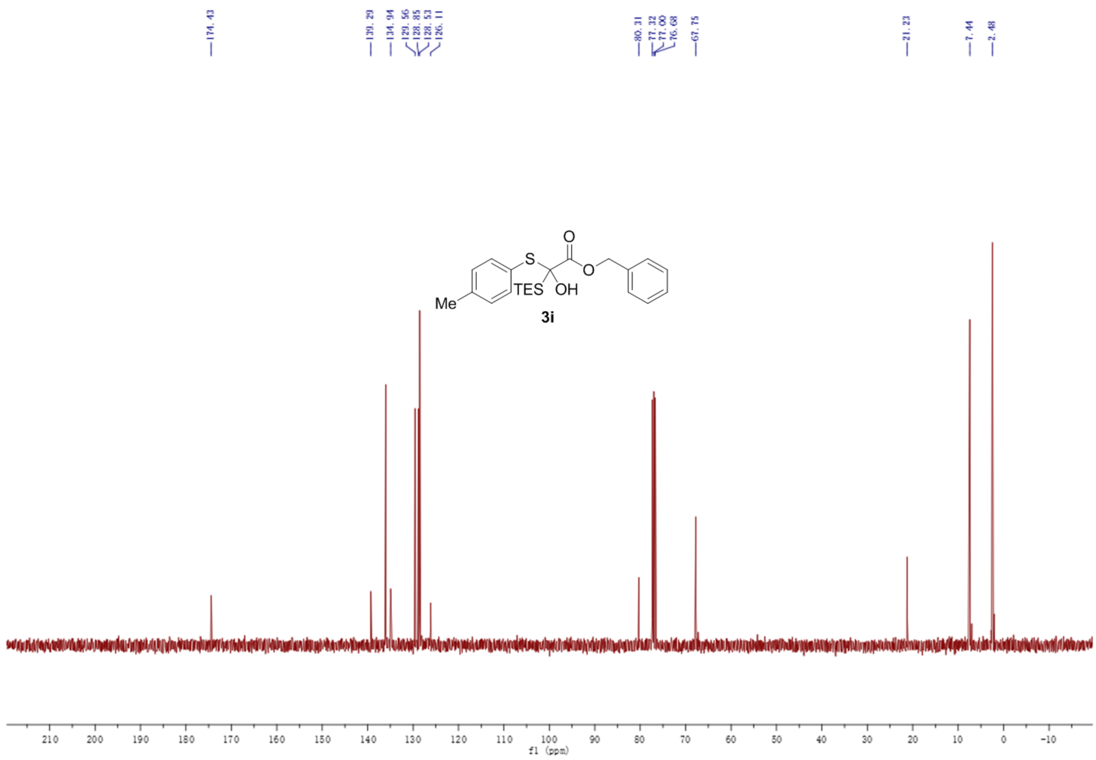
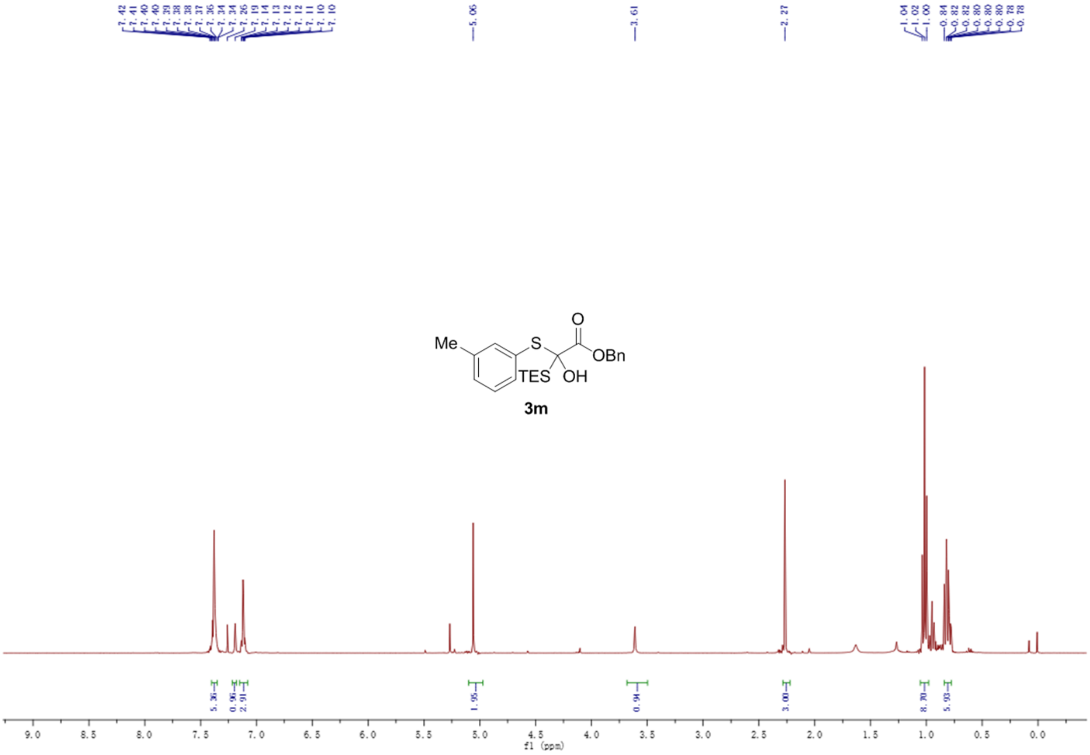
OH
3j
f1 (ppm)


7.41
7.40
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.07
7.05
5.15
5.12
5.08
5.04
3.53
2.33
0.20
S
O
O
TMS
OH
Me
3k
5.26
2.00
1.98
2.26
0.98
3.21
9.31
f1 (ppm)

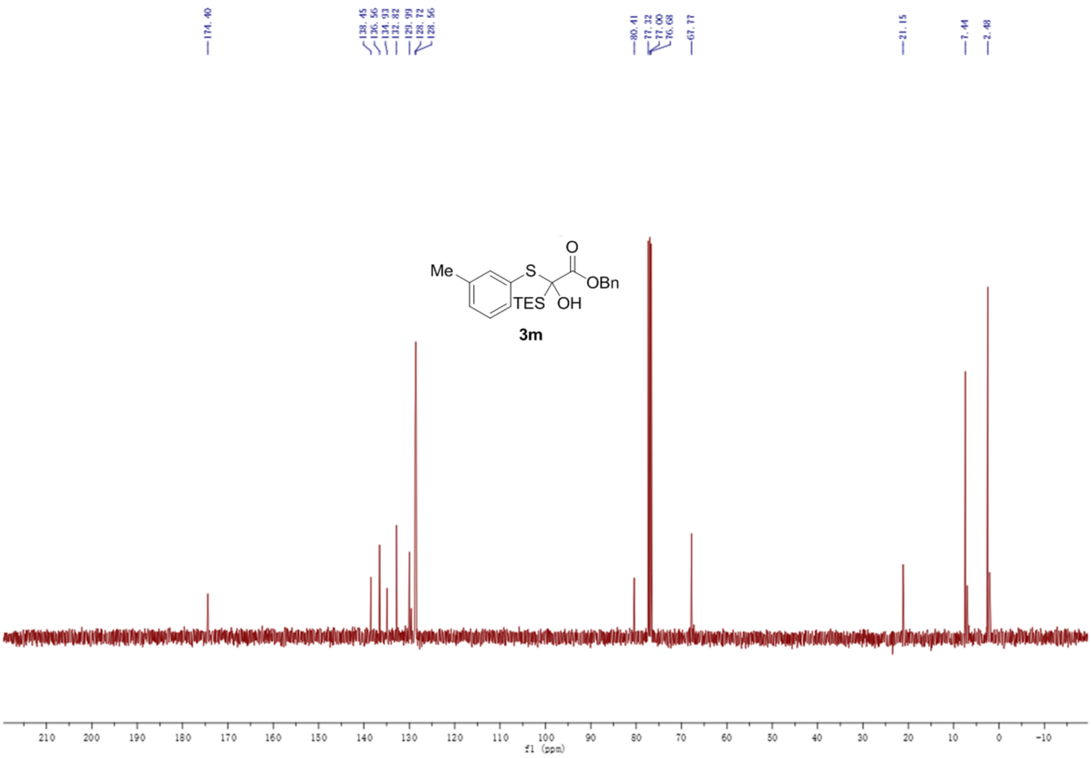

174.41
139.35
135.06
129.64
128.74
128.58
128.55
126.14
80.05
77.32
77.00
76.68
67.76
21.24
-3.31
S
O
O
TMS
OH
Me
3k
f1 (ppm)



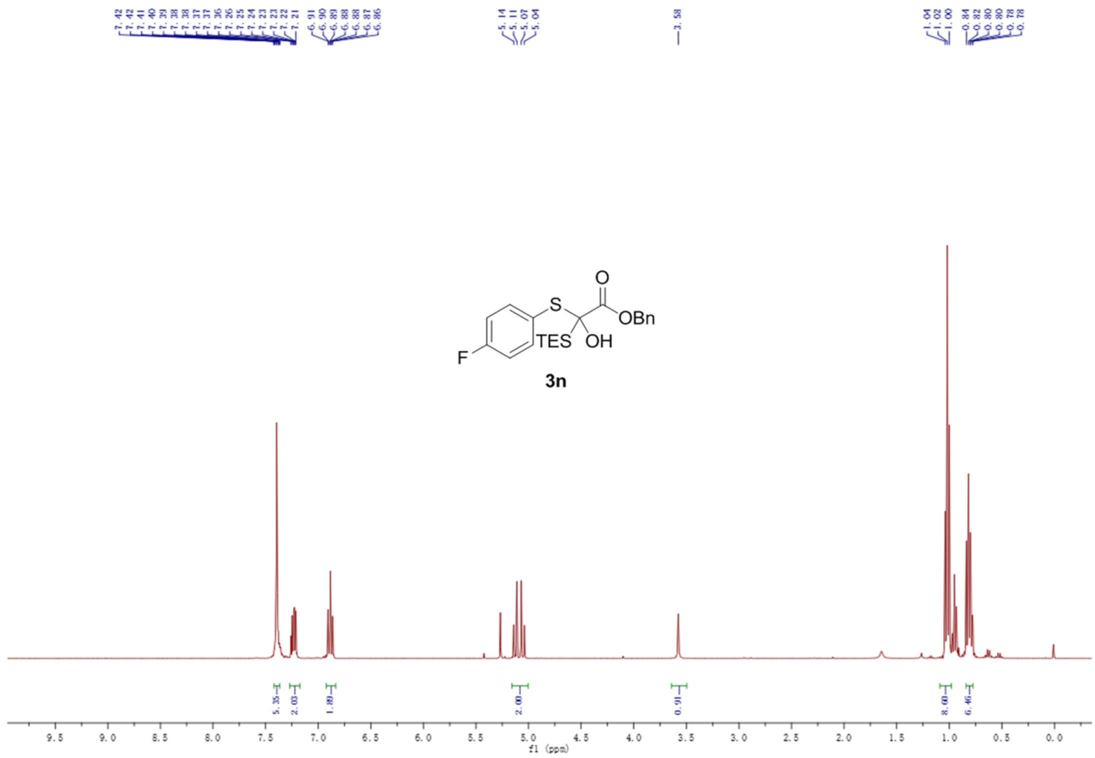




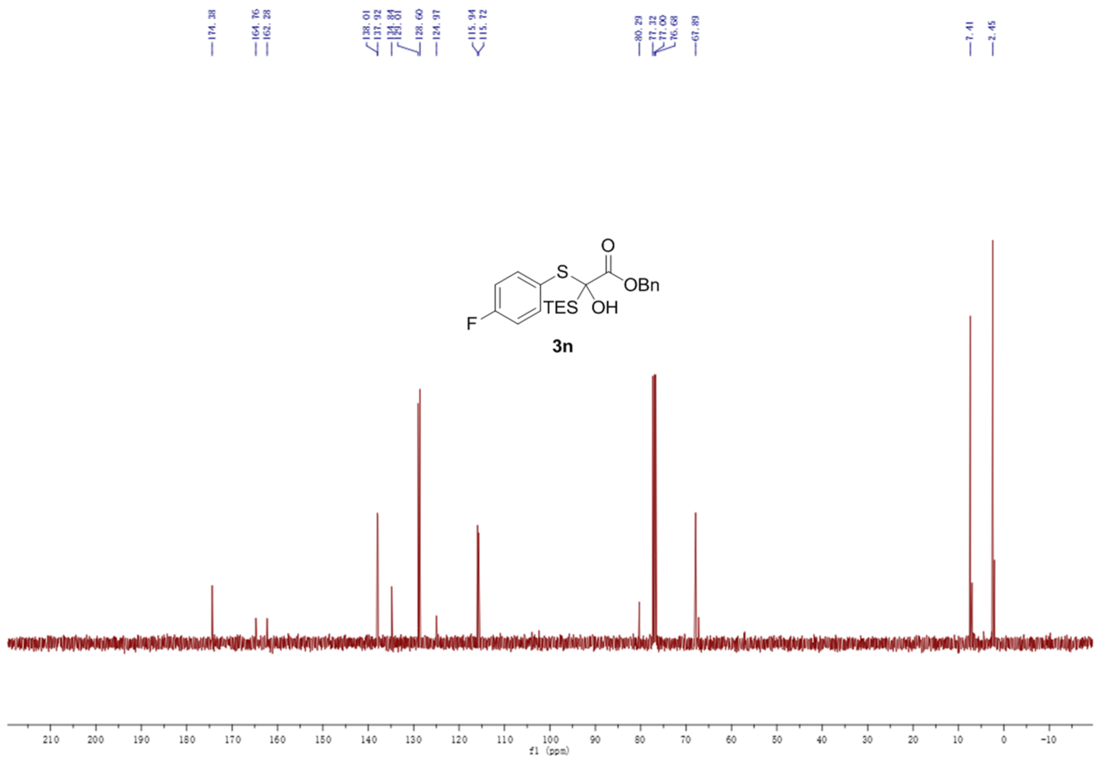
Me
S
O
OBn
TES
OH
3m
5.06
3.61
2.27
f1 (ppm)



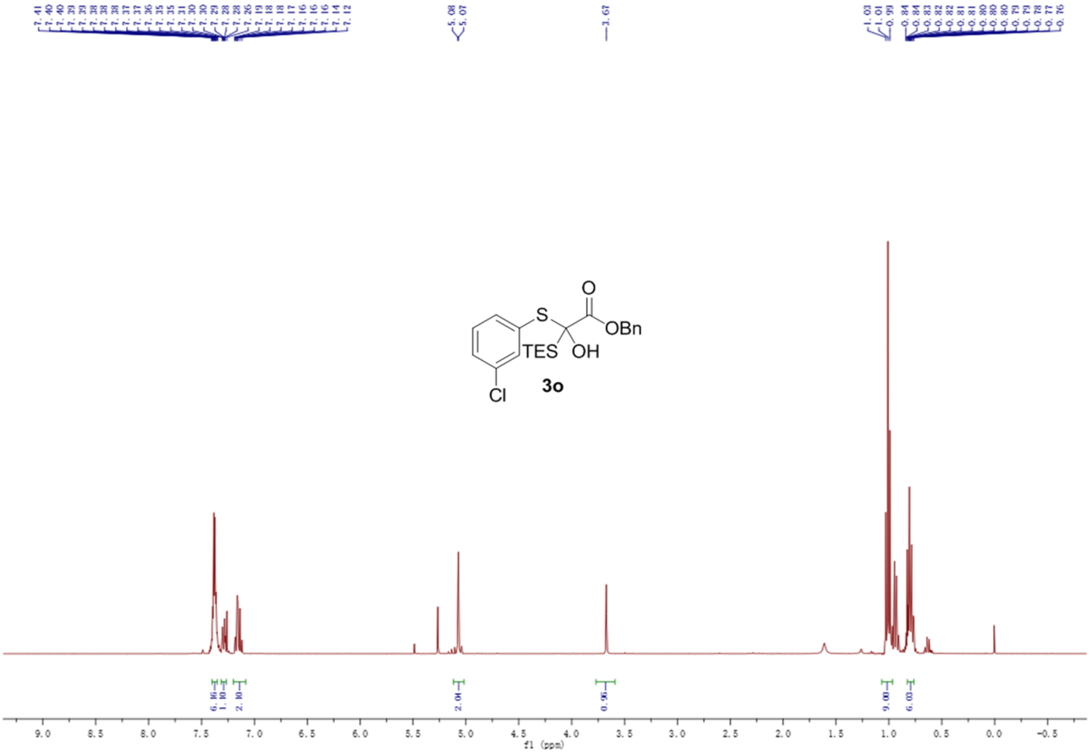
174.40
80.41
67.77
21.15
7.44
2.48
Me
S
O
OBn
TES
OH
3m
f1 (ppm)

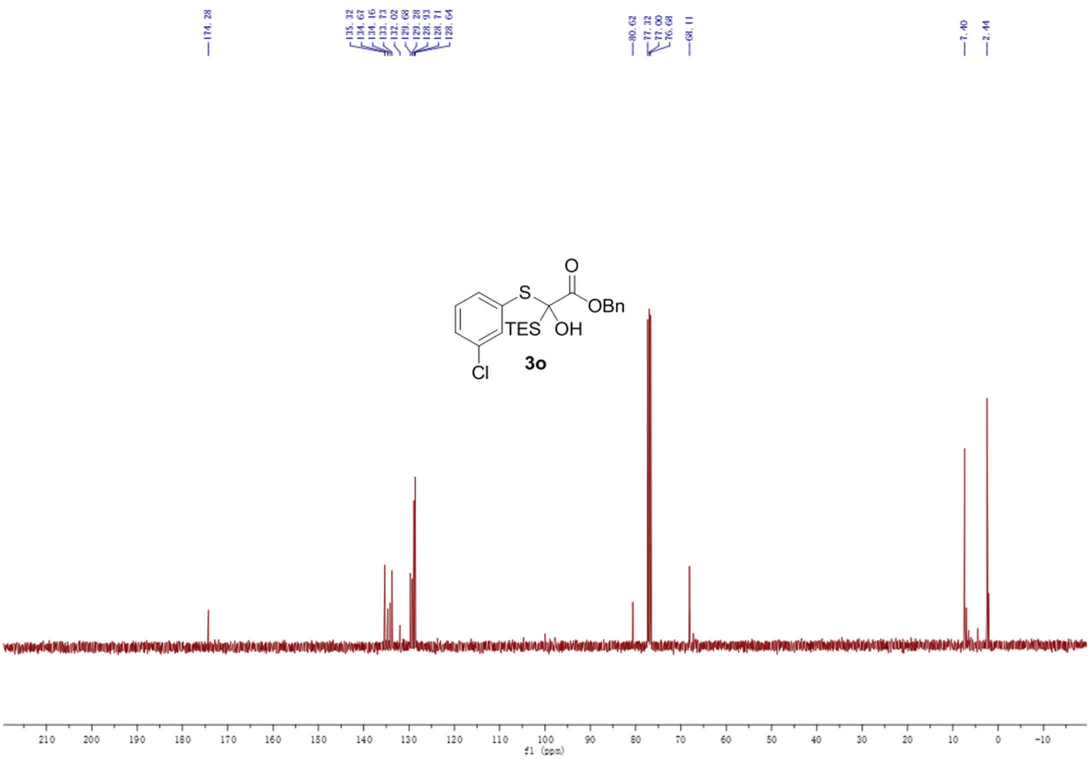


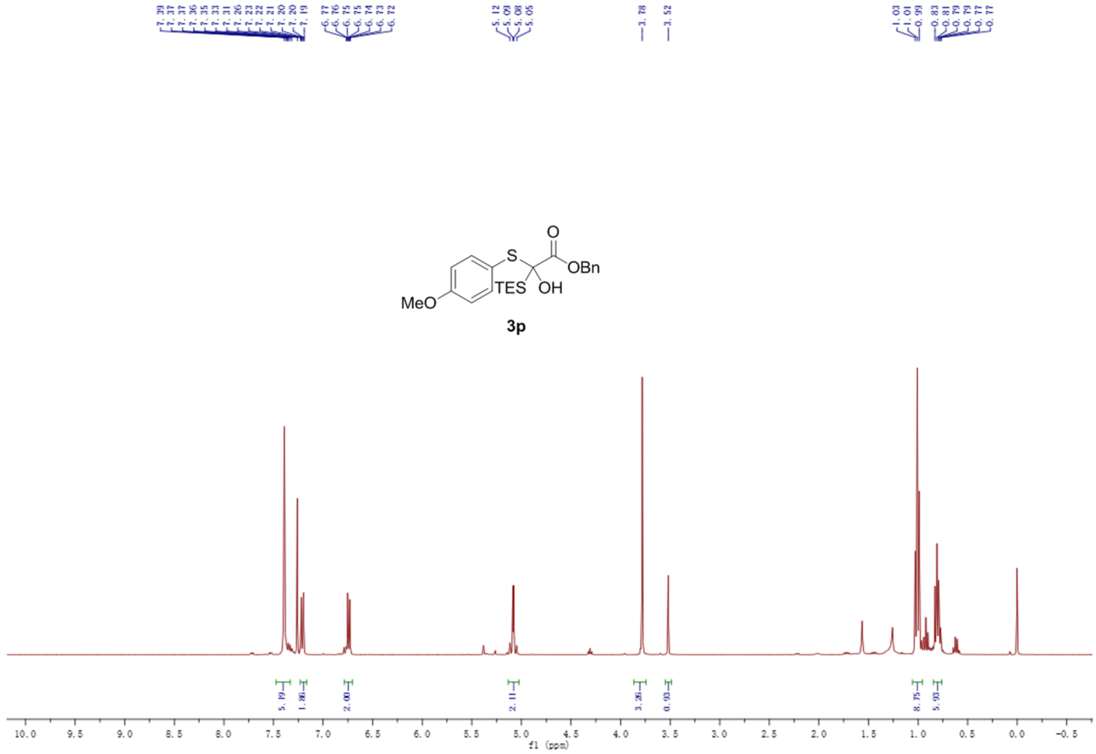
3n
f1 (ppm)

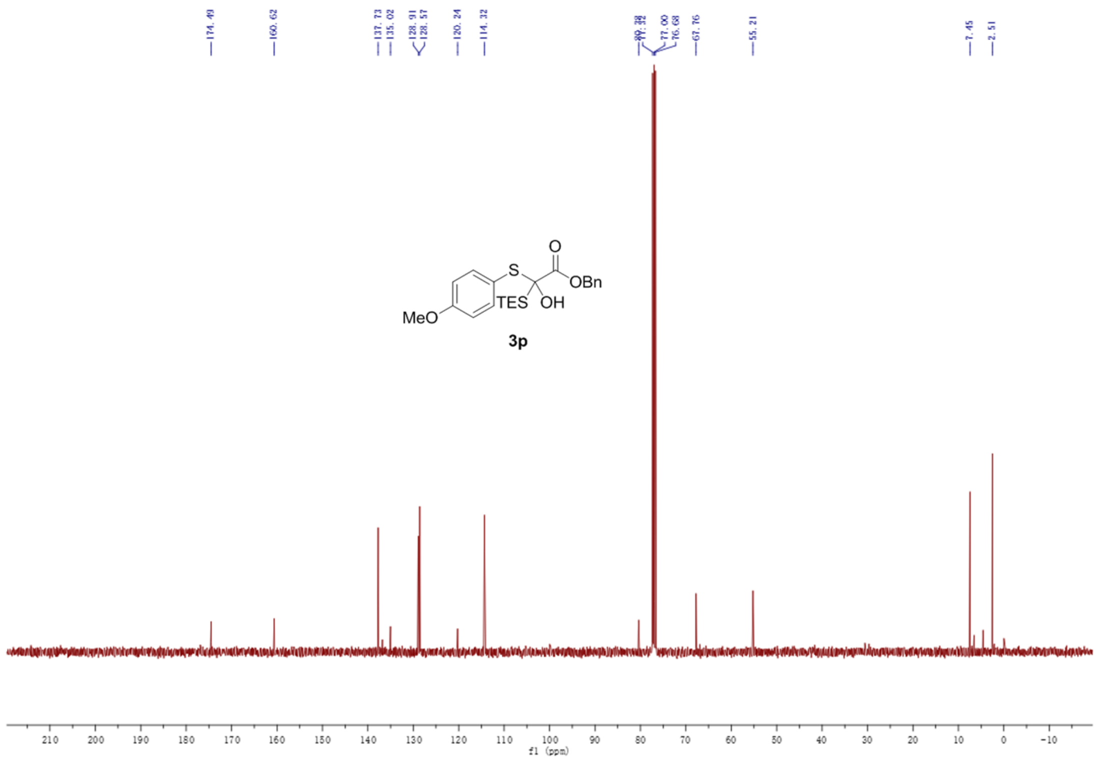


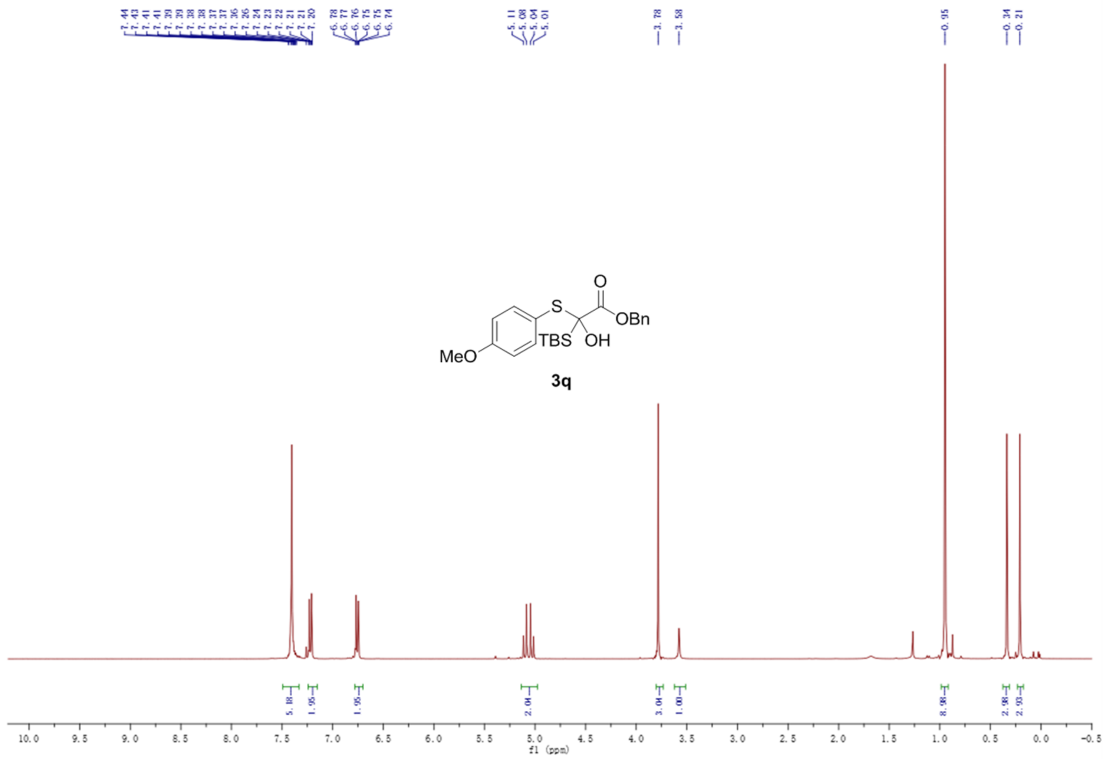
3n
f1 (ppm)

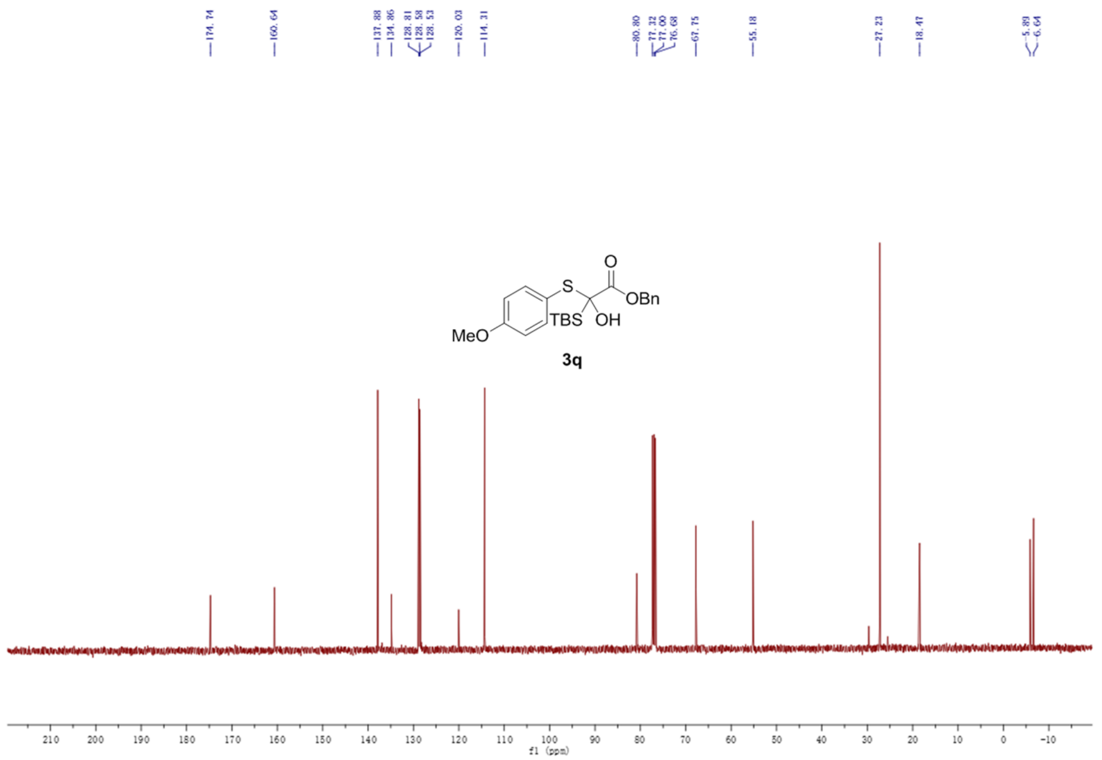


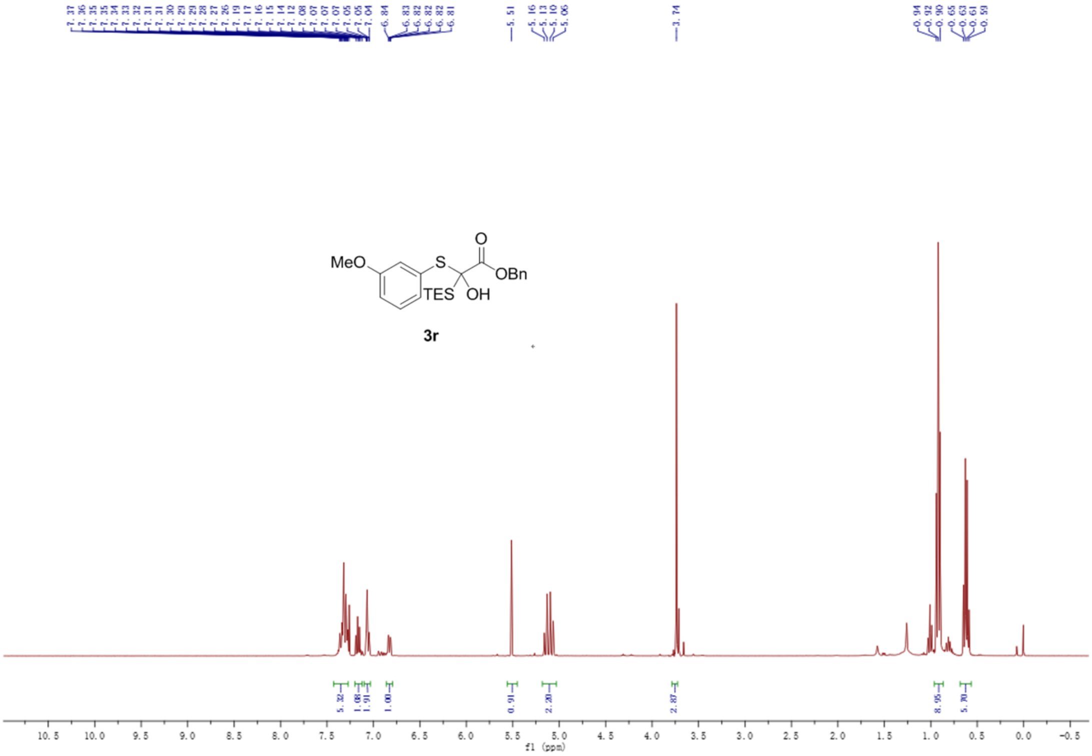


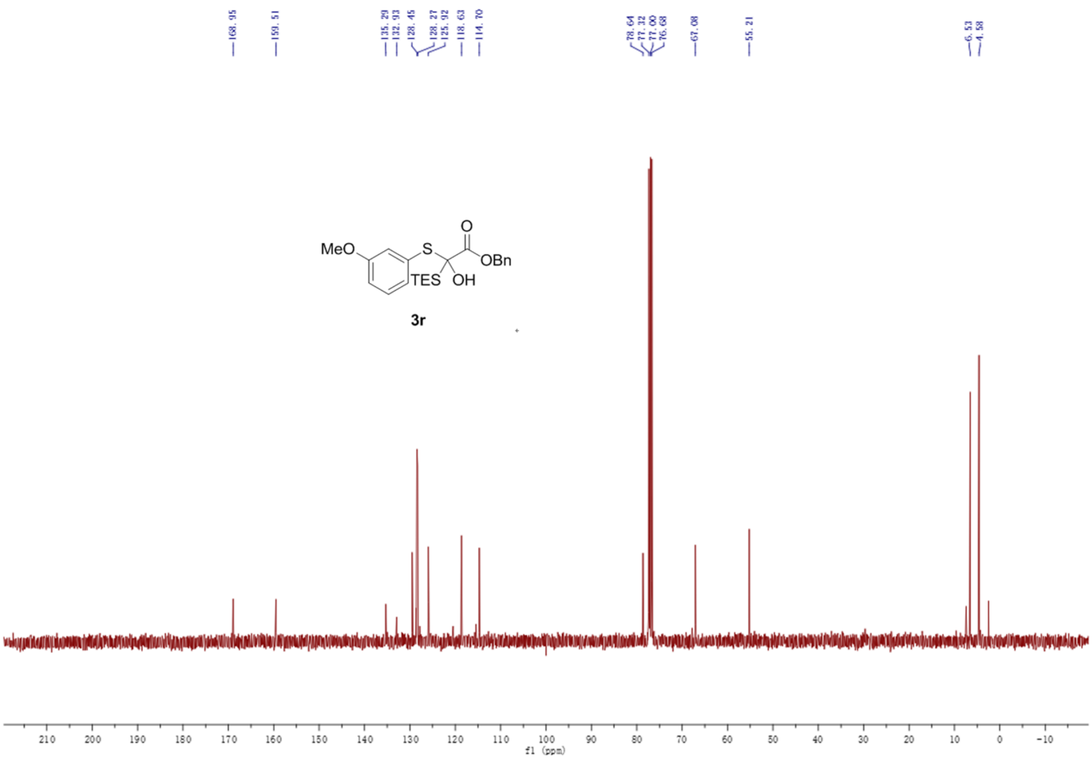


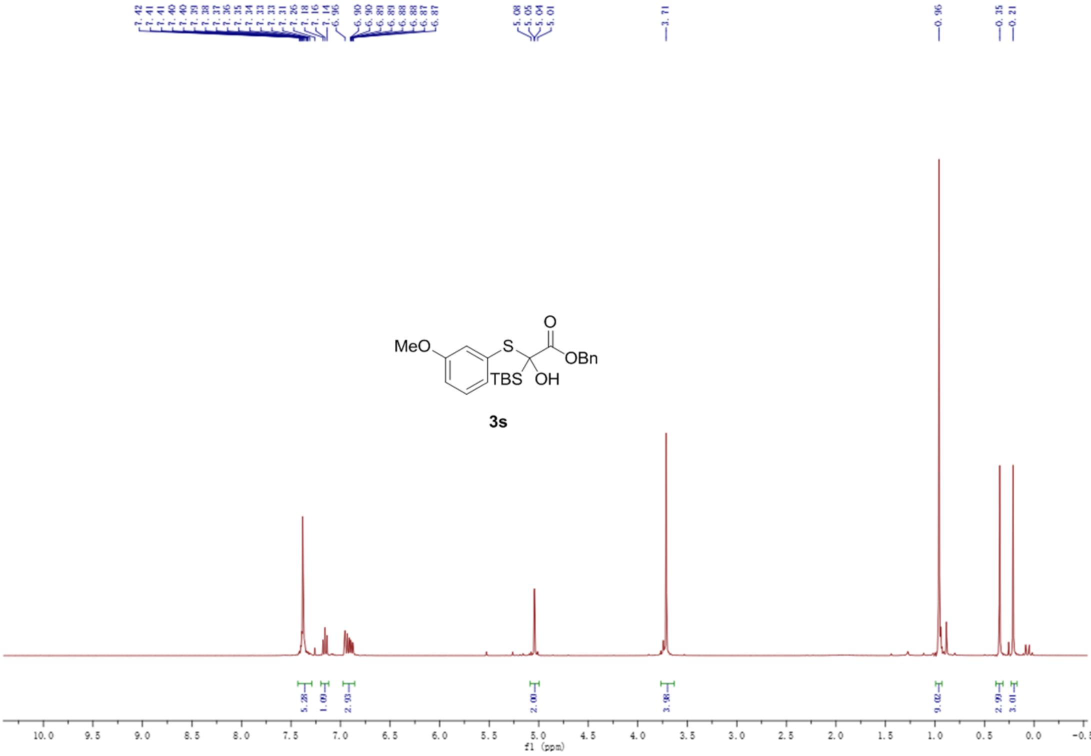




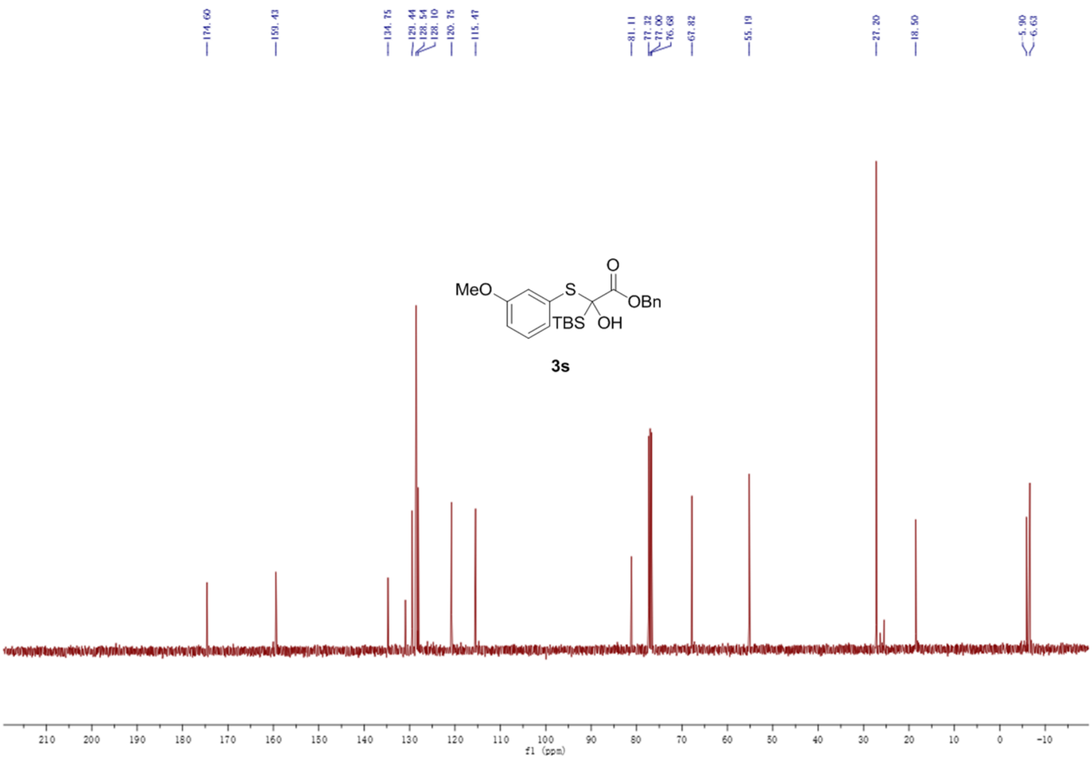



MeO
S
O
OBn
TES
OH
3r
f1 (ppm)


MeO
S
O
OBn
TES
OH
3r
f1 (ppm)


MeO
S
O
OBn
TBS
OH
fl (ppm)

3s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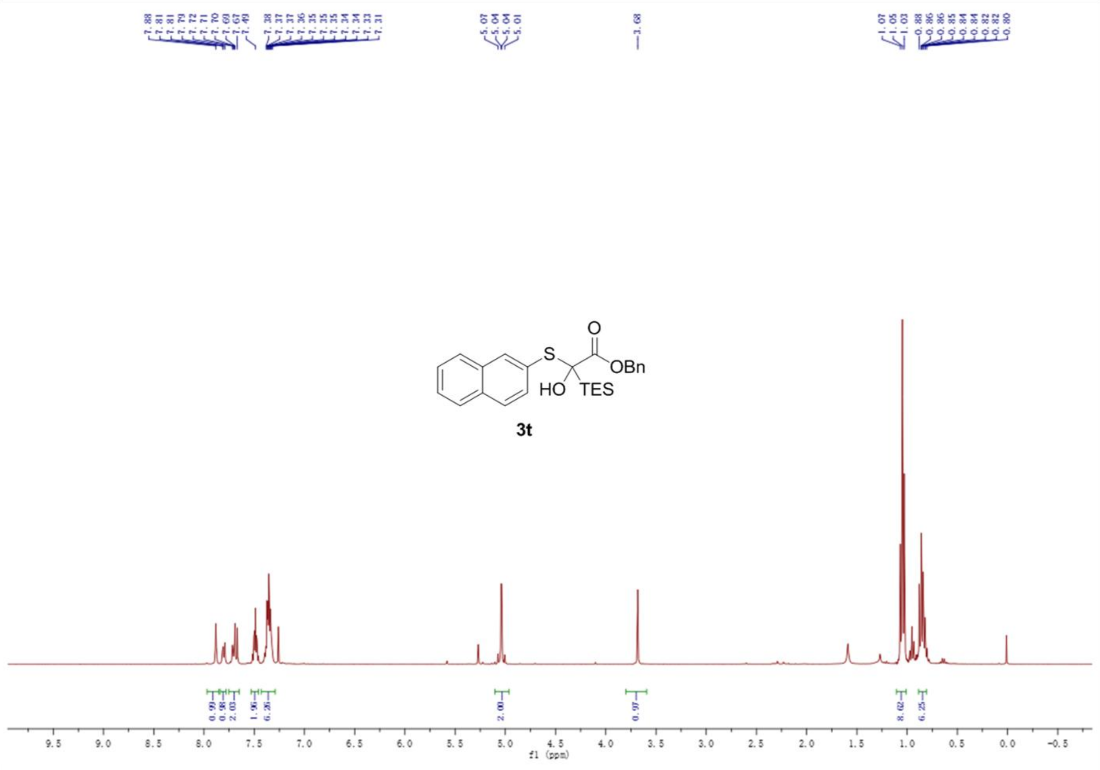
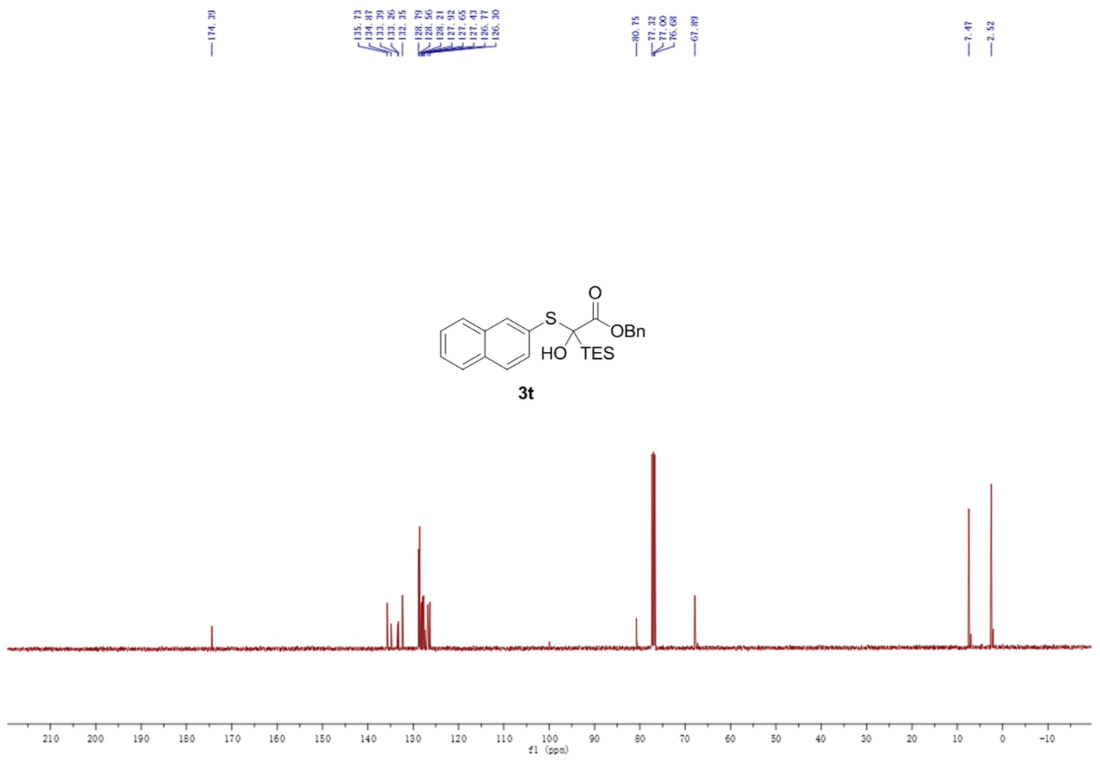
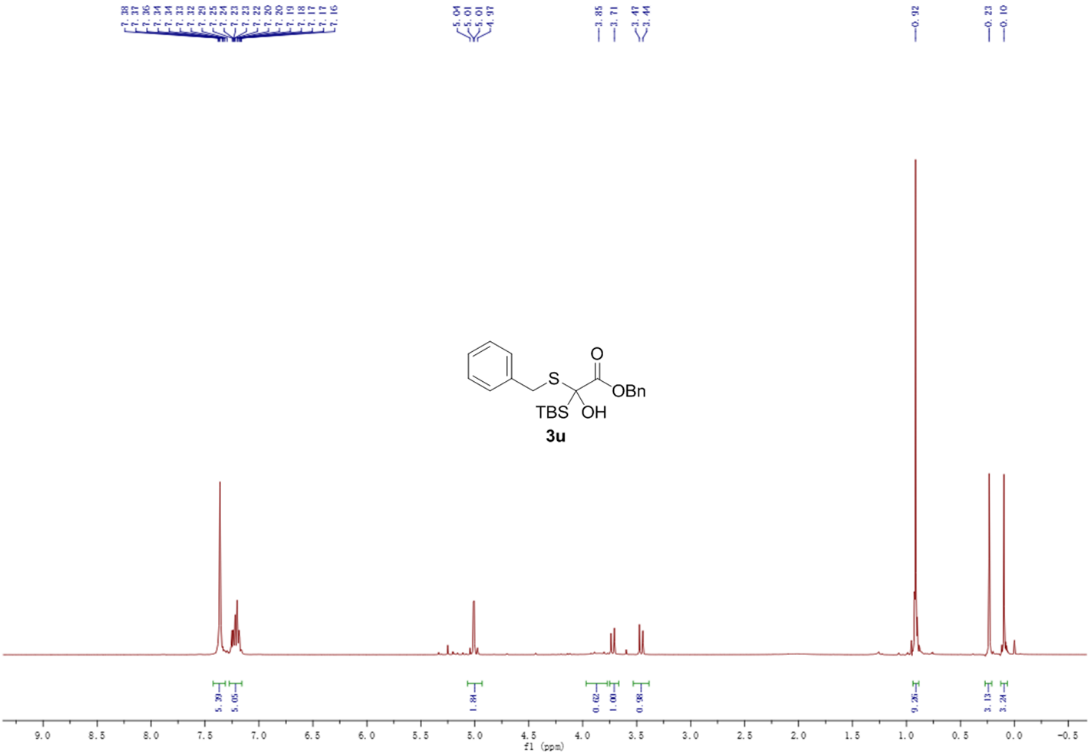
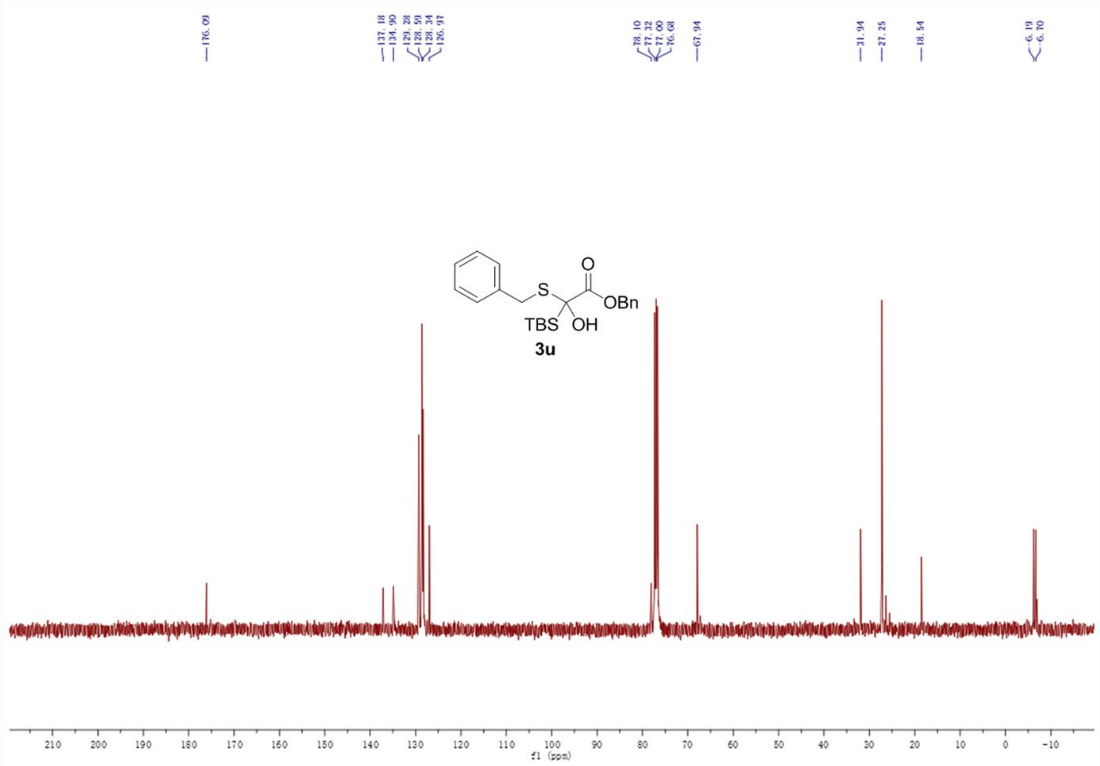
159.43
134.75
129.44
128.54
128.10
120.75
115.47
81.11
77.32
77.00
76.68
67.82
55.19
27.20
18.50
-5.90
-6.63
MeO
S
O
OBn
TBS
OH
fl (ppm)

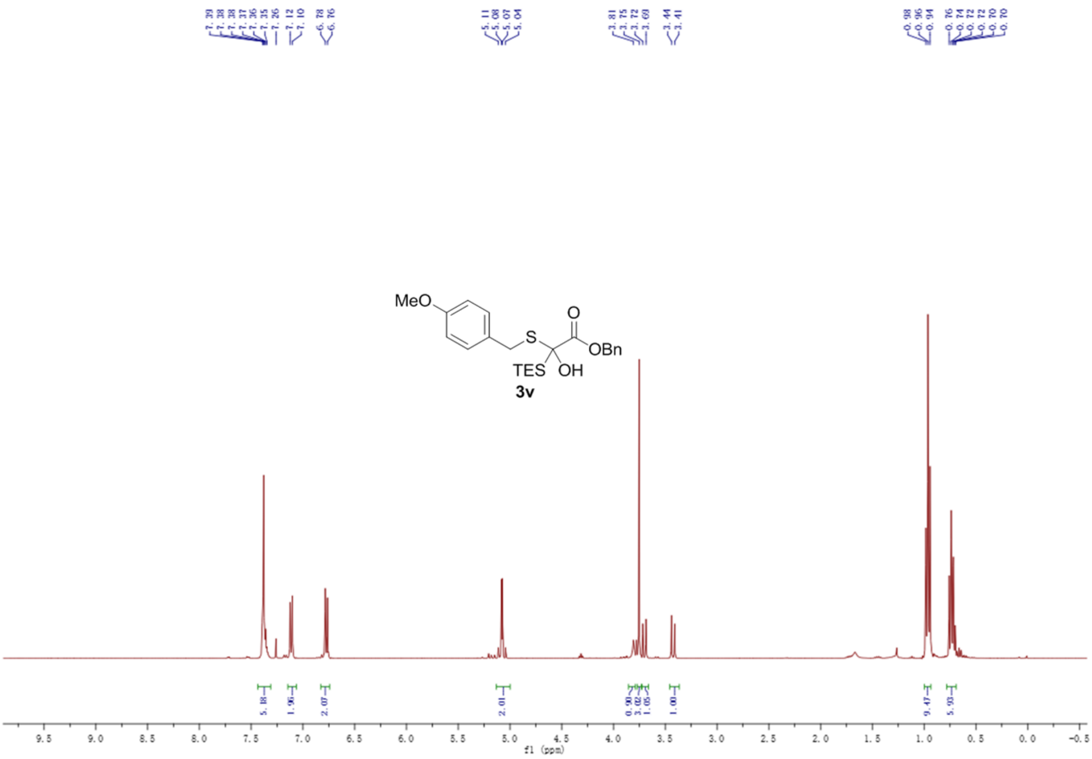
3s



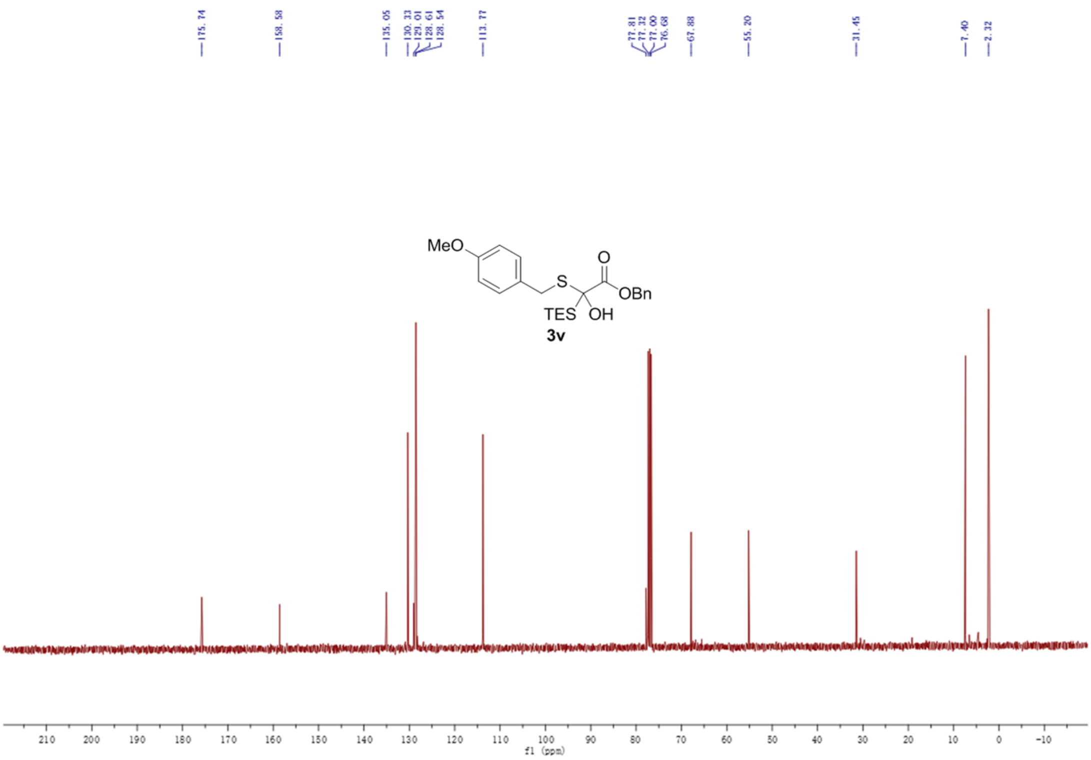




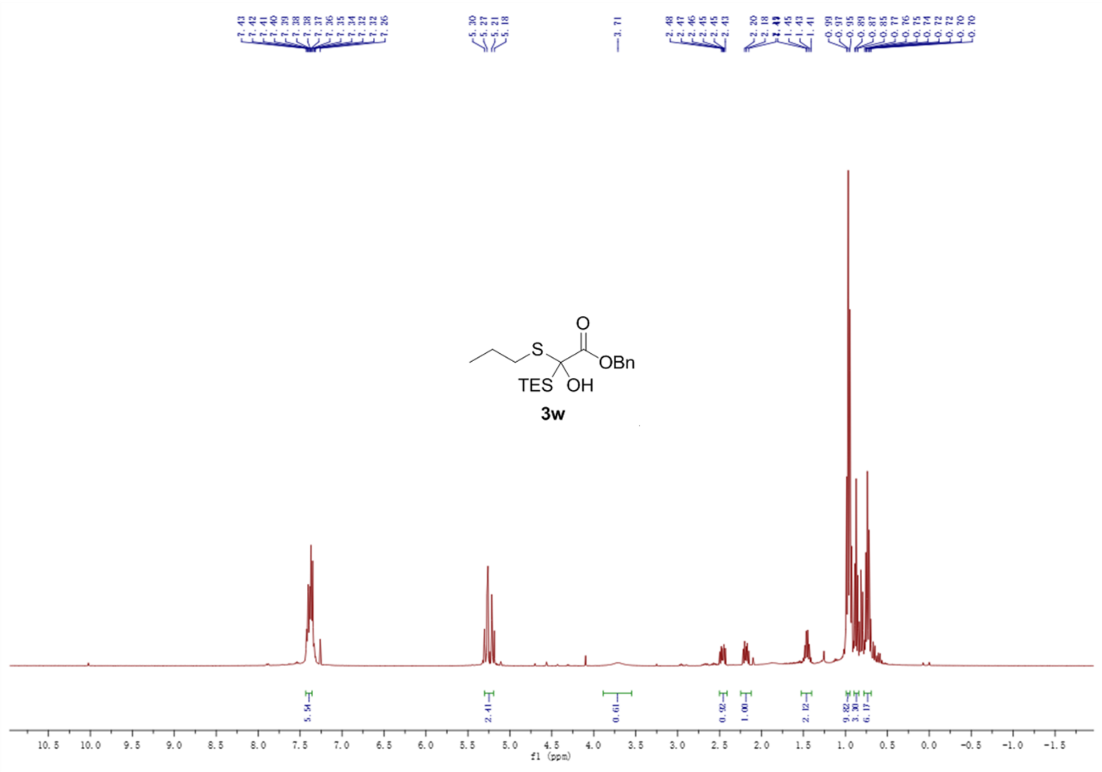


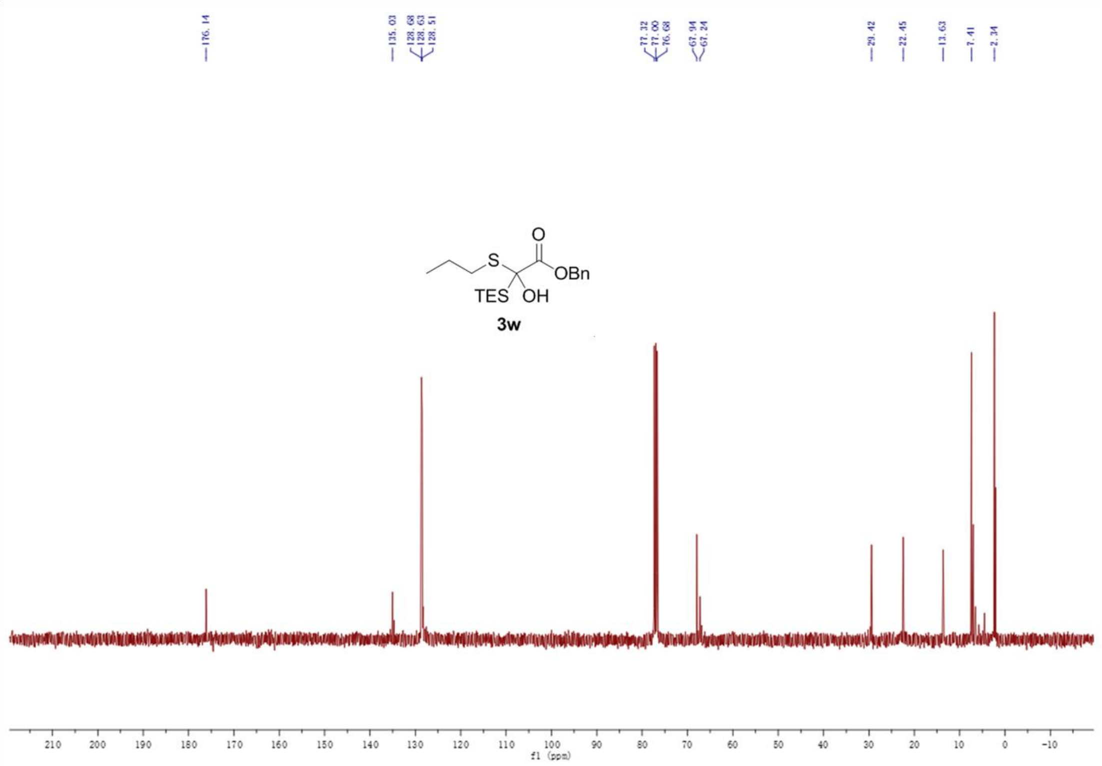


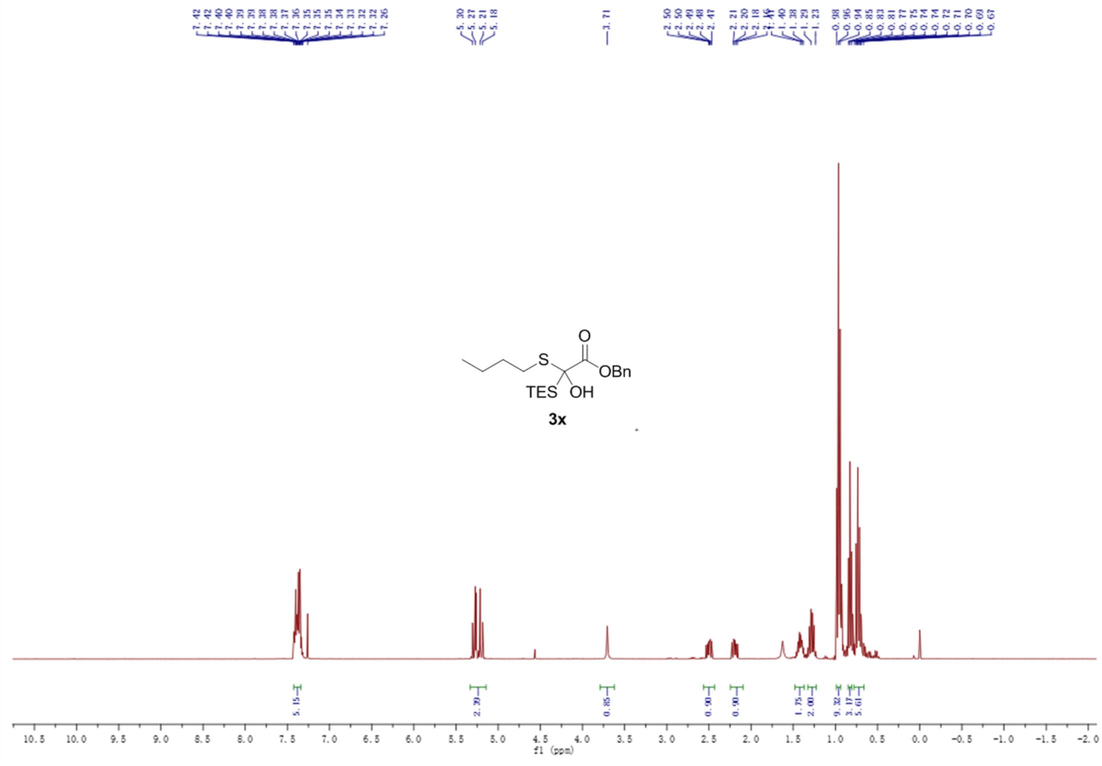
MeO
S
O
OBn
TES OH
3v
f1 (ppm)



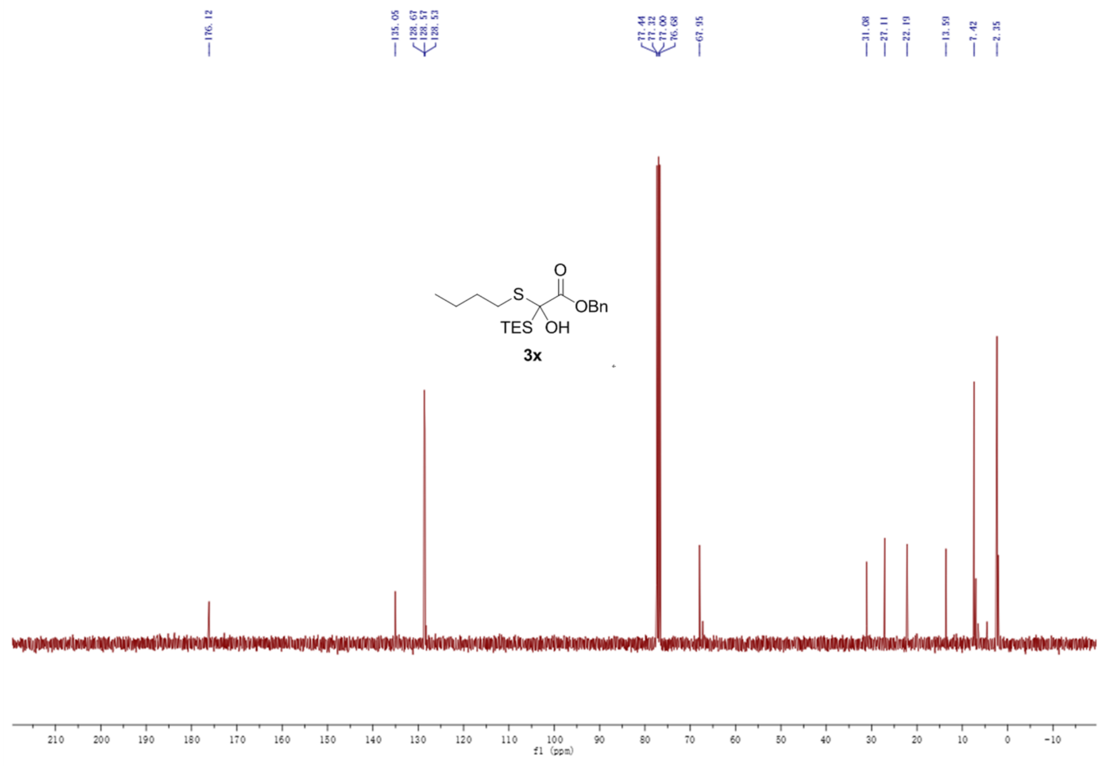
MeO
S
O
OBn
TES OH
3v
f1 (ppm)



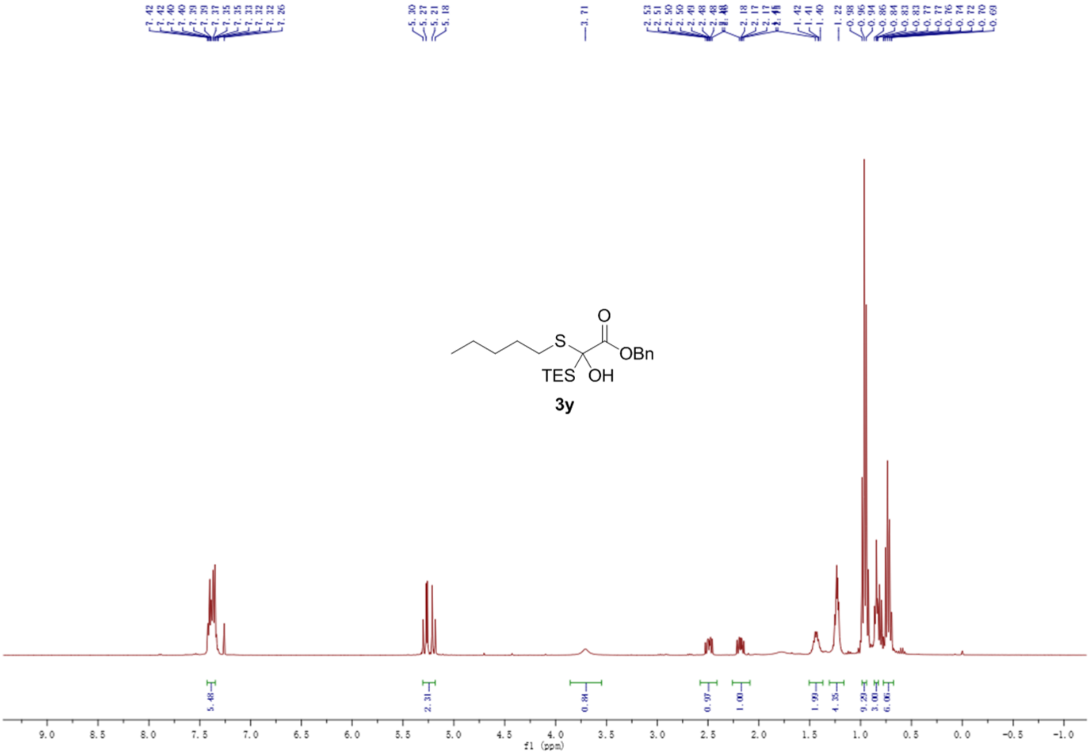




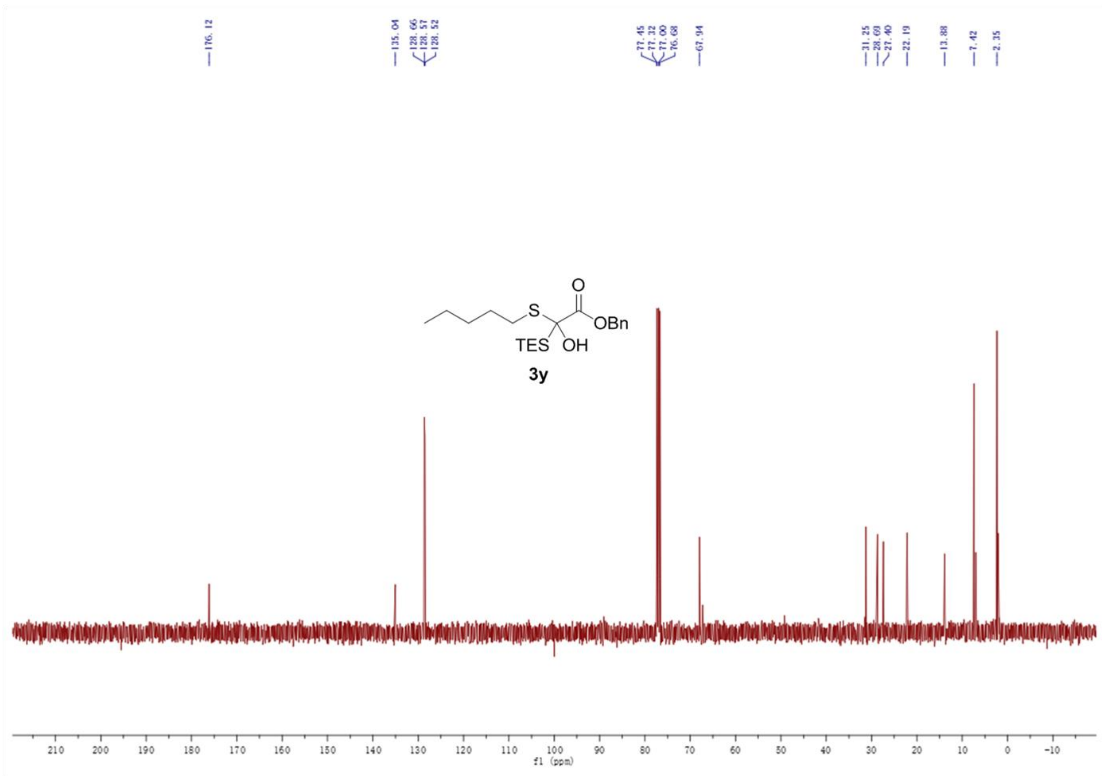
TES
OH
OBn
O
S
3x
f1 (ppm)



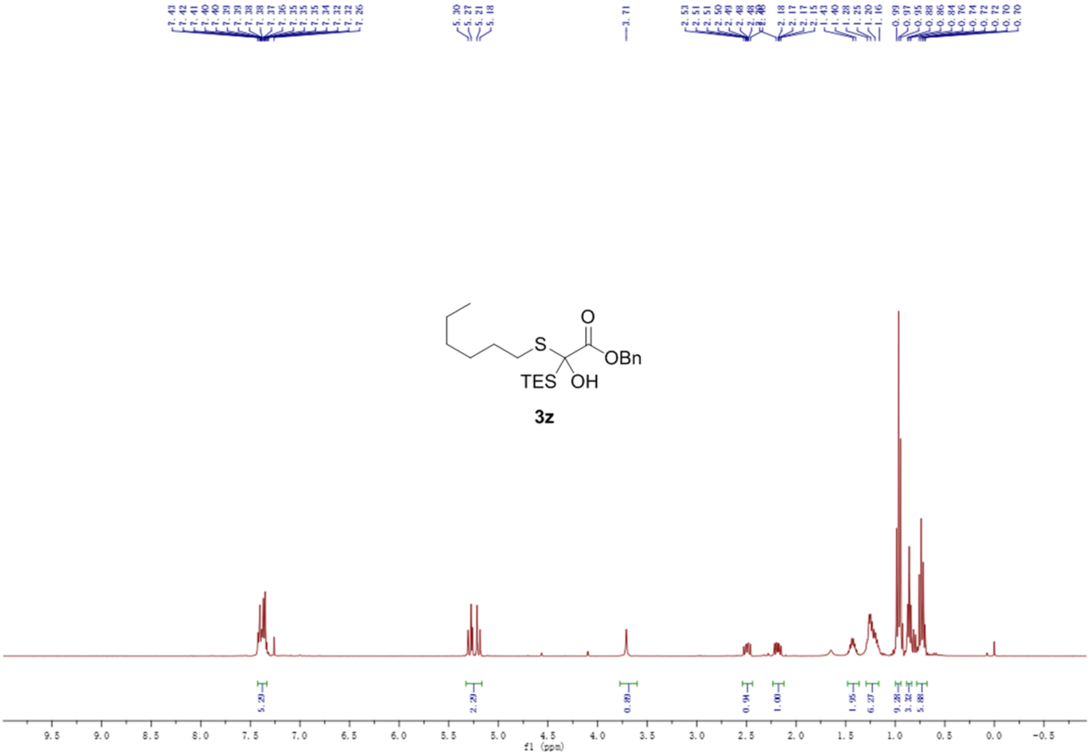
176.12
135.05
128.67
128.57
128.53
77.44
77.32
77.00
76.68
67.95
31.08
27.11
22.19
13.59
7.42
2.35
TES
OH
OBn
O
S
3x
f1 (ppm)

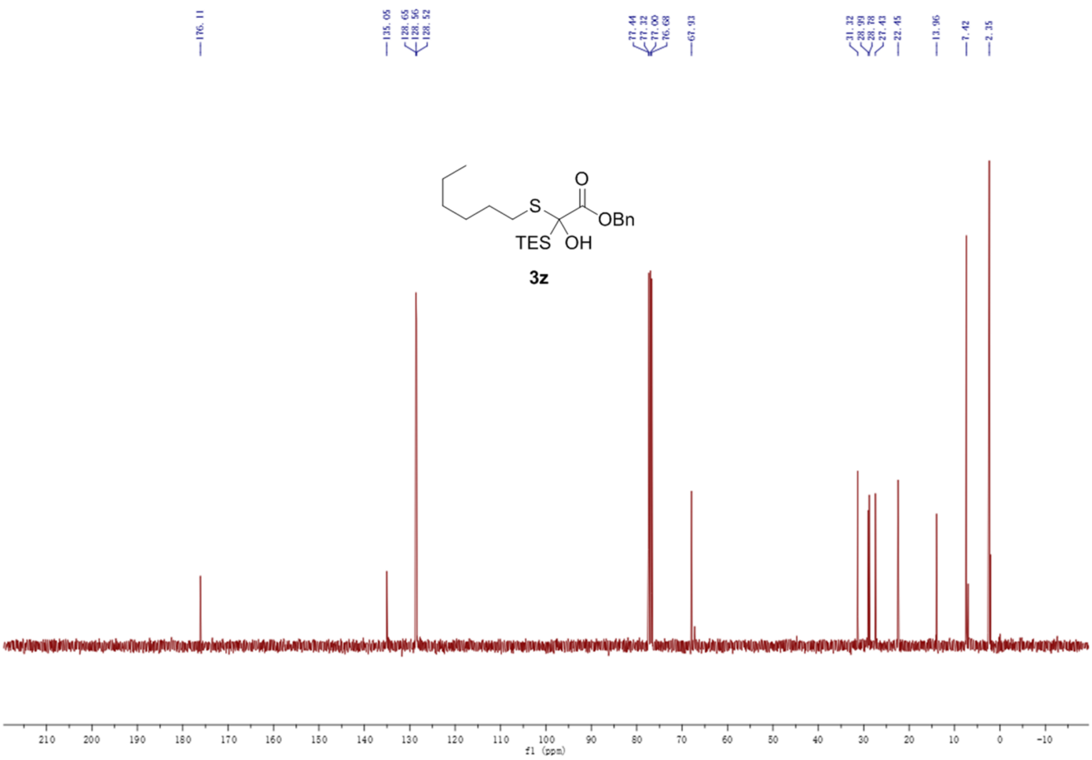


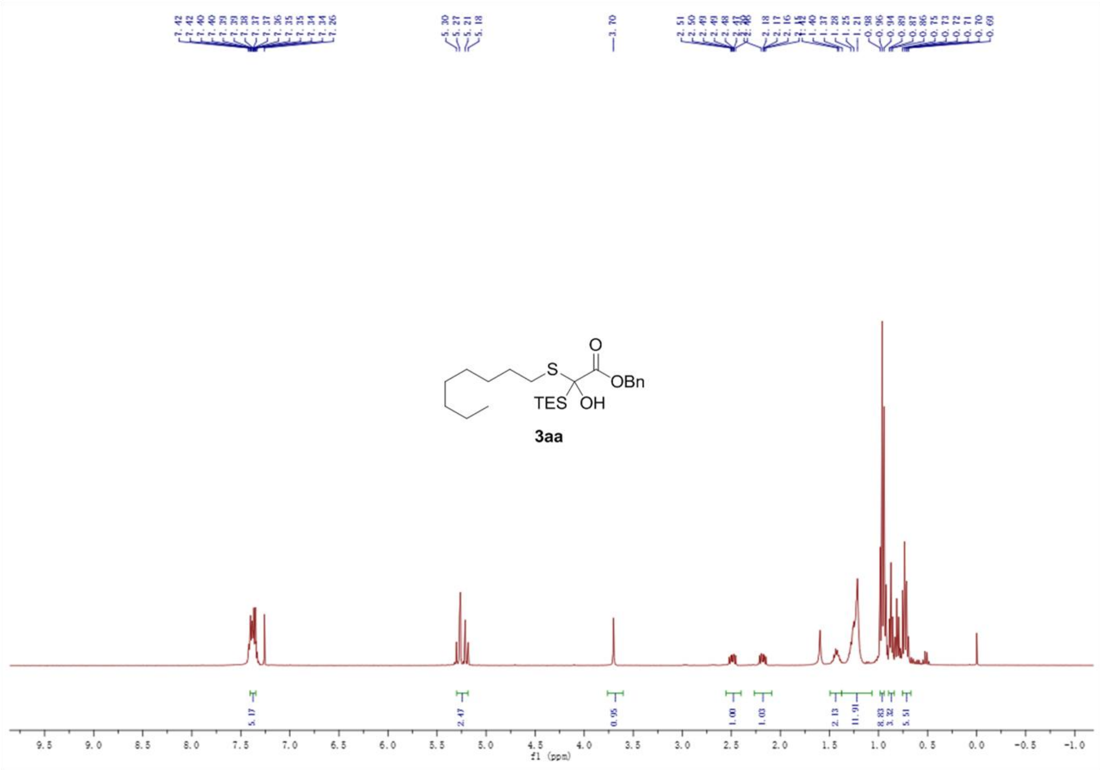
3y
fl (ppm)

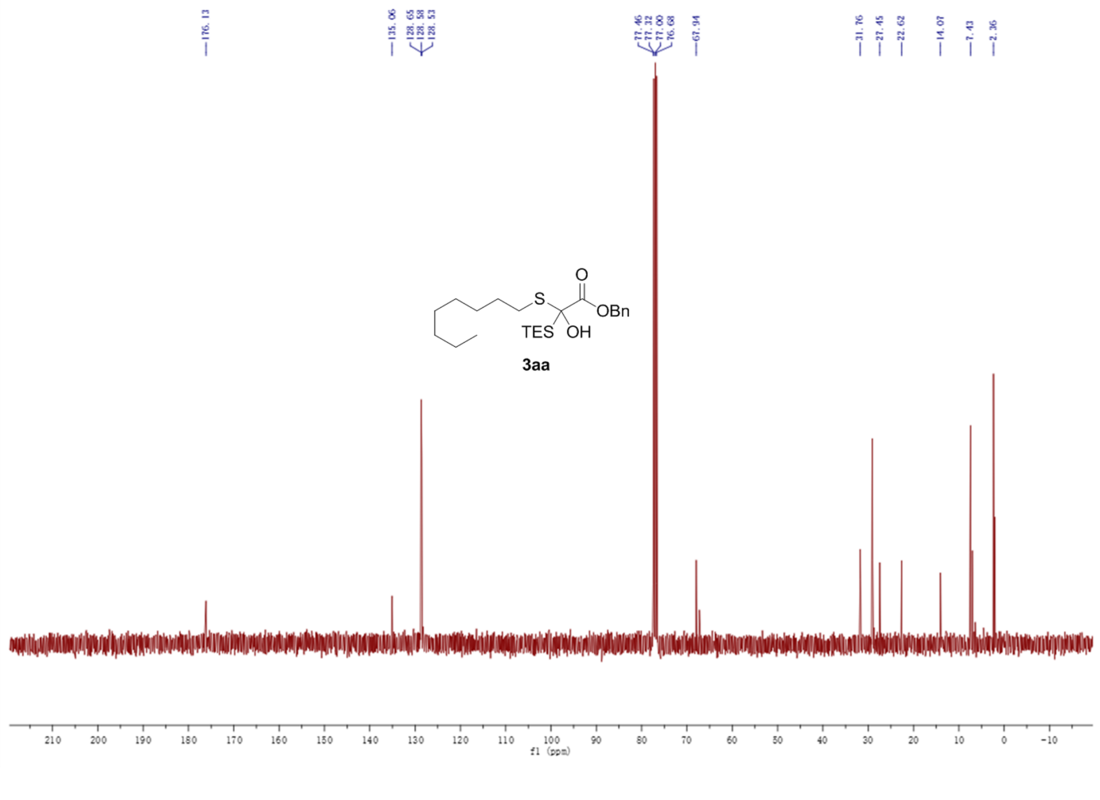


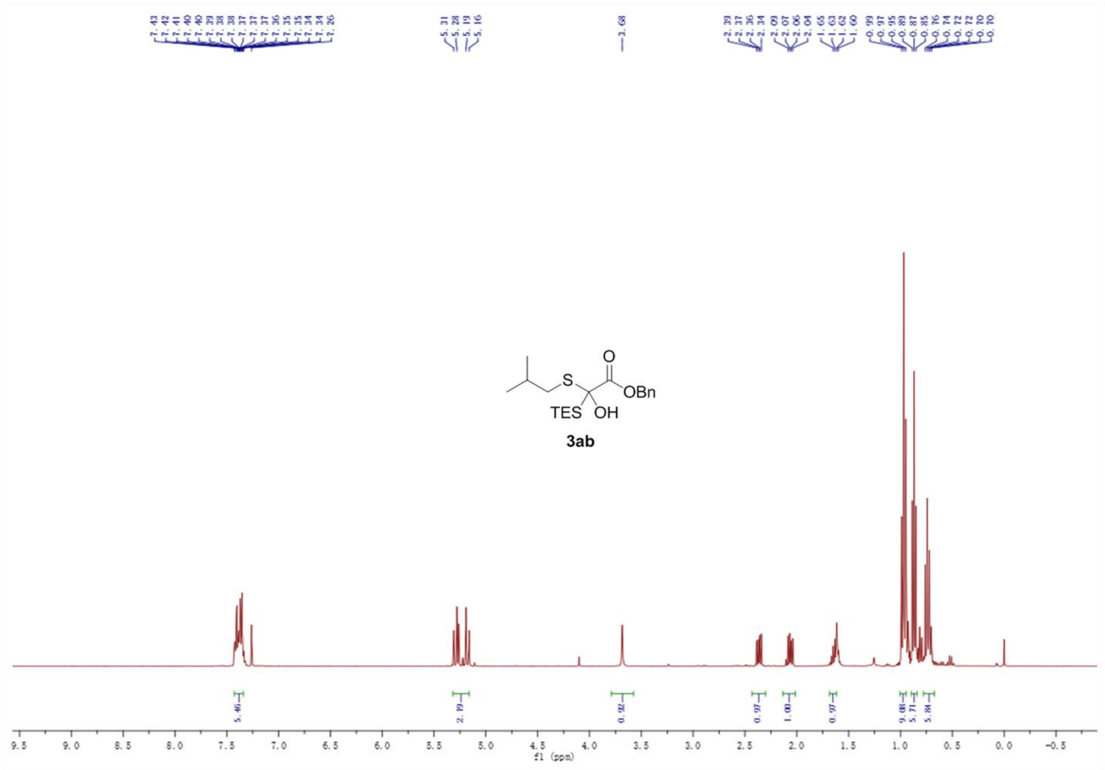
3y
fl (ppm)

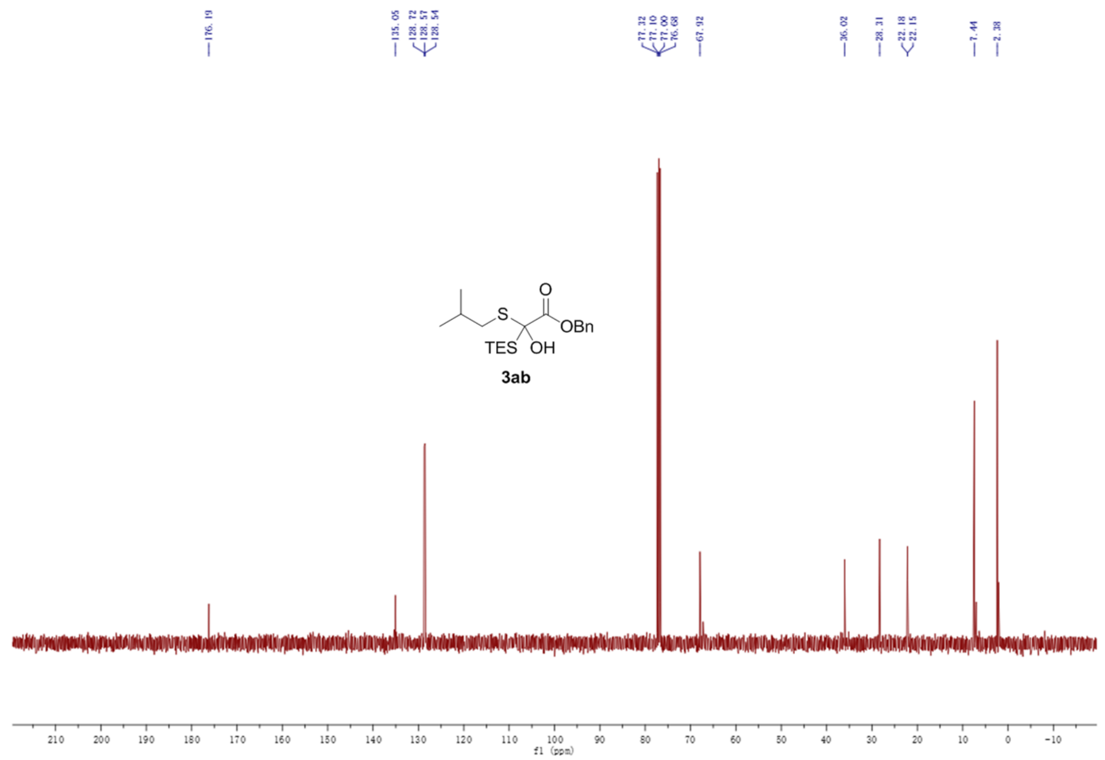


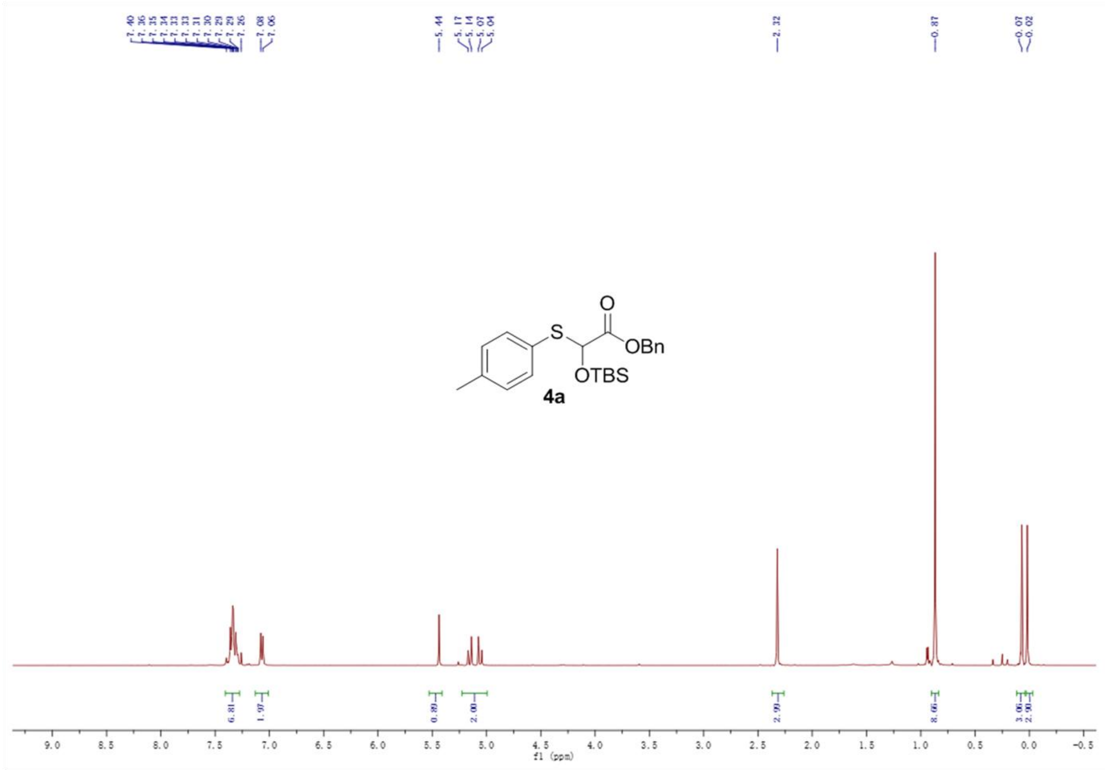


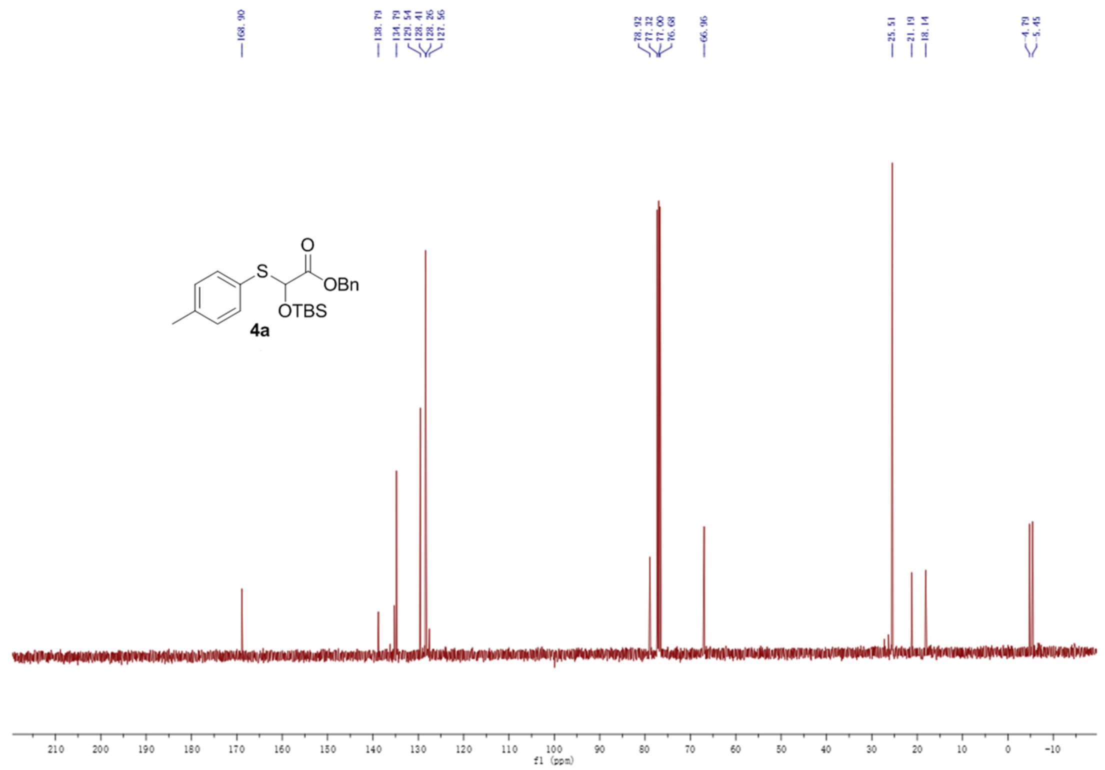

S
O
OBn
TES
OH
3aa


S
O
OBn
TES
OH
3aa






OBn
OTBS
4a
f1 (ppm)


OBn
OTBS
4a
f1 (ppm)