Supporting Information

Rh/DuanPhos Catalyzed Asymmetric Hydrogenation of β-Acetylamino Vinylsulfides: An Approach to Chiral β-Acetylamino Sulfides

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Table of Contents

General Information.....S2

General Procedure For the Synthesis of Compound 1a-1p.....S2

General Procedure for Asymmetric Hydrogenation of compound 1 .....S11

General Procedure for Asymmetric Hydrogenation of compound 1o S18

General Procedure for Oxidation of compound 2a and 2p. S19

The investigation of the influence of Z/E ratio to enantioselectivity S20

References.....S21

NMR and HPLC of 1, 2 and 3. .....S22

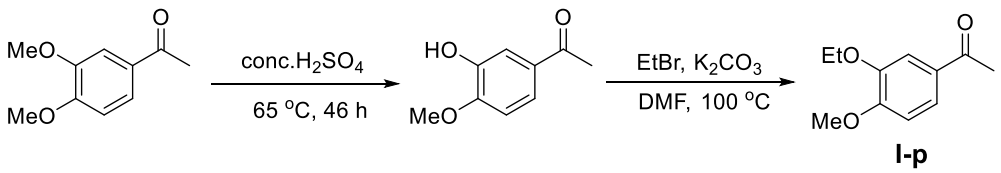
General Information

All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen or in the nitrogen-filled glovebox. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on Bruker ADVANCE III (400 MHz) spectrometers for ^{1}H NMR and ^{13}C NMR. $CDCl_3$ was the solvent used for the NMR analysis, with tetramethylsilane as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for ^{1}H NMR and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR. Optical rotation was determined using a Perkin Elmer 343 polarimeter. HPLC analysis was conducted on an Agilent 1260 Series instrument. Column Chromatography was performed with silica gel Merck 60 (300-400 mesh). All new products were further characterized by HRMS. A positive ion mass spectrum of sample was acquired on a Thermo LTQ-FT mass spectrometer with an electrospray ionization source.

General Procedure For the Synthesis of Compound 1a-1p

The route for the synthesis of compound **1** was listed below. If not mentioned, the starting materials were purchased from commercial suppliers.

Preparation of ketone **I-p**[1]



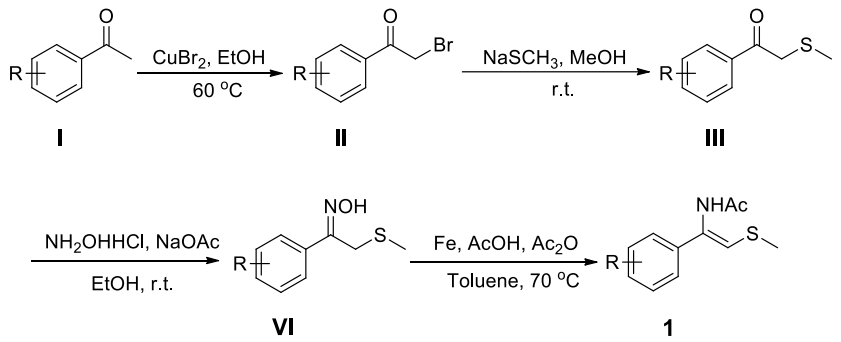
A solution of ketone (15 g, 83 mmol) in conc. H_2SO_4 (75 mL) was stirred at 65 ^{o}C for 46 h. After cooling to ambient temperature, the reaction mixture was poured on ice (300 g) and the mixture stirred at room temperature for 1 h. The precipitate was filtered off then, washed with water, and redissolved in NaOH (0.19 mol, 190mL of a

1 mol/L solution in water). The mixture was extracted with CH_2Cl_2 (80 mL). The aqueous layer was acidified (cooling with ice/water bath) with conc. HCl (30 mL), stirred for 1.5 h, and the precipitate filtered off to give corresponding phenol as a light brown solid (8.3g, 61% yield).

A suspension of phenol (4.00 g, 24.1 mmol) and K_2CO_3 (4.77 g, 48.1 mmol) in DMF(20 mL) was heated at 100 ^oC for 30 min and then cooled to room temperature. Ethyl bromide (5.25 g, 48.1 mmol) was slowly added dropwise, and the reaction mixture heated at 100 ^oC for 6 h. After cooling to ambient temperature and removal of the solvent, the residue was dissolved in water (40 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined extracts were dried ($MgSO_4$), filtered and concentrated. The crude product was recrystallized from 2-propanol (25 mL) to give the target ketone as fine colorless needles (4.09 g, 88% yield).

Preparation of **1**[2,3]

1 was synthesized as follows, the preparation of **1a** was taken as an example.



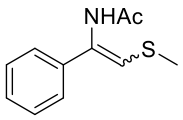
A solution of $CuBr_2$ (3.35 g, 15 mmol) and acetophenone (1.2 g, 10 mmol) in ethanol (50 mL) was stirred at 60 ^oC. After completion of the reaction, as monitored by TLC, the mixture was cooled to room temperature and then filtered. The filtrate was evaporated in vacuo and recrystallized in petroleum ether to afford pure products 2-bromo-1-phenylethan-1-one (white solid, 1.52 g, 77% yield).

2-bromo-1-phenylethan-1-one (0.98 g, 5.0 mmol) was added in portions to a solution of $NaSCH_3$ (842 mg, 6.0 mmol, 50%) in methanol (30 mL). Within a few minutes the color of the solution turned to orange. After the addition was completed, the mixture was stirred at room temperature for 15 min and water was then added to

the mixture. The product was extracted with CH_2Cl_2 (3×30 mL), the organic layer was washed, dried over $MgSO_4$, filtered and evaporated in vacuo, The residue was purified by flash chromatography (petroleum ether:CH_2Cl_2=5:1) to afford the 2-bromo-1-phenylethan-1-one (light yellow oil, 0.63 g, 76% yield).

A methanol solution of the 2-bromo-1-phenylethan-1-one (1.66 g, 10 mmol, 1.0equiv.), hydroxylamine hydrochloride (1.04 g, 15 mmol, 1.5 equiv.), and NaOAc (2.05 g, 25 mmol, 2.5 equiv.) was stirred at ambient temperature for 12 h. Then diluted with water. The resultant layer was extracted with diethyl ether several times. The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 5/1-2/1) to give oxime as a white solid (1.66 g, 90% yield).

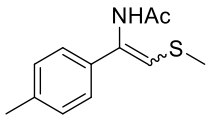
Acetic anhydride (1.53 g, 15 mmol, 3.0 equiv.) was added, in portions, to a solution of oxime (0.905 g, 5.0 mmol, 1.0 equiv.) obtained from above step in toluene (1.3 M) under a nitrogen atmosphere. Acetic acid (0.9 g, 15 mmol, 3.0 equiv.) was then added, followed by Fe powder (0.56 g, 10 mmol, 2.0 equiv.). The mixture was then heated to 70 °C overnight. The reaction was then cooled to room temperature and filtered through celite to remove solid residues, which were then washed with ethyl acetate. The combined filtrate was washed with brine. The organic phase was separated, dried by Na_2SO_4 and evaporated. The crude material was purified by flash chromatography (*n*-hexane/ ethyl acetate 5:1-2:1) to afford the product **1a** as white solid (0.36 g, 35% yield).



N-(2-(methylthio)-1-phenylvinyl)acetamide 1a

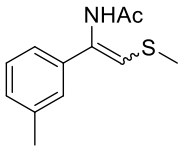
White solid, 35% yield; mixture of Z& E isomers (ratio: 2:1). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.20 (m, 5H), 6.91 (brs, 1H), 6.21 (s, 1H), 2.38 (s, 3H), 2.15 (s, 3H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.20 (m, 5H), 6.63 (brs, 1H), 6.42 (s, 1H), 2.43 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$)

mixture of isomers: δ 173.2, 168.3, 136.6, 132.5, 128.9, 128.4, 128.0, 127.7, 126.0, 125.0, 124.7, 121.6, 23.4, 21.1, 17.3, 17.0; ESI-HRMS Calculated for $C_{11}H_{14}NOS^+$ ($[M+H]^+$): 208.0791, found: 208.0789; $C_{11}H_{13}NOSNa^+$ ($[M+Na]^+$): 230.0610, found: 230.0608.



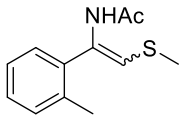
N-(2-(methylthio)-1-(p-tolyl)vinyl)acetamide 1b

White solid, 34% yield; mixture of Z& E isomers (ratio: 2:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.18 (m, 2H), 7.15-7.05 (m, 2H), 6.89 (brs, 1H), 6.14 (s, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.14 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 2H), 7.15-7.05 (m, 2H), 6.60 (brs, 1H), 6.35 (s, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.2, 138.1, 137.6, 134.3, 133.8, 133. 7, 132.8, 129.6, 129.2, 125.0, 124.6, 120.2, 23.5, 21.2, 17.4, 17.0; ESI-HRMS Calculated for $C_{12}H_{16}NOS^+$ ($[M+H]^+$): 222.0947, found: 222.0944; $C_{12}H_{15}NOSNa^+$ ($[M+Na]^+$): 244.0767, found: 244.0763.



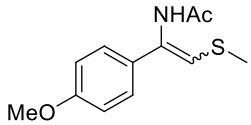
N-(2-(methylthio)-1-(m-tolyl)vinyl)acetamide 1c

White solid, 47% yield; mixture of Z& E isomers (ratio: 2:1); Major isomer:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.02 (m, 4H), 6.84 (brs, 1H), 6.19 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 2.16 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 6.97 (m, 4H), 6.59 (brs, 1H), 6.40 (s, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 173.3, 168.3, 138.6, 137.9, 137.0, 136.6, 132.3, 131.5, 128.8, 128.5, 128.3, 125.7, 125.3, 122.2, 121.7, 121.55, 23.33, 21.5, 21.0, 17.30, 17.0; ESI-HRMS Calculated for $C_{12}H_{16}NOS^+$ ($[M+H]^+$): 222.0947, found: 222.0945; $C_{12}H_{15}NOSNa^+$ ($[M+Na]^+$): 244.0767, found: 244.0763.



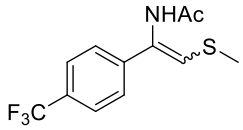
N-(2-(methylthio)-1-(o-tolyl)vinyl)acetamide 1d

White solid, 50% yield; mixture of Z& E isomers (ratio: 9:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 7.17 (s, 1H), 6.60 (brs, 1H), 2.32 (s, 3H), 2.23 (s, 3H), 2.01 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.32 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 6.60 (brs, 1H), 6.05 (s, 1H), 2.35 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.2, 136.6, 136.0, 131.2, 130.6, 129.5, 129.1, 126.3, 115.3, 24.4, 19.10, 17.7; ESI-HRMS Calculated for $C_{12}H_{16}NOS^+$ ([M+H]$^+$): 222.0947, found: 222.0944.



N-(1-(4-methoxyphenyl)-2-(methylthio)vinyl)acetamide 1e

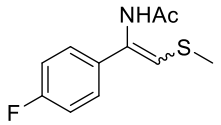
White solid, 46% yield; mixture of Z& E isomers (ratio: 2:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.19 (m, 2H), 6.91 (brs, 1H), 6.90-6.75 (m, 2H), 6.06 (s, 1H), 3.80 (s, 3H), 2.36 (s, 3H), 2.14 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.44 – 7.19 (m, 2H), 6.90-6.75 (m, 2H), 6.63 (brs, 1H), 6.24 (s, 1H), 3.80 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 173.3, 168.3, 159.3, 132.6, 129.4, 126.4, 126.1, 123.2, 119.1, 114.3, 113.3, 55.3, 23.4, 21.07, 17.4, 17.0; ESI-HRMS Calculated for $C_{12}H_{16}NO_2S^+$ ([M+H]$^+$): 238.0896, found: 238.0893; $C_{12}H_{15}NO_2SNa^+$ ([M+Na]$^+$): 260.0716, found: 60.0712.



N-(2-(methylthio)-1-(4-(trifluoromethyl)phenyl)vinyl)acetamide 1f

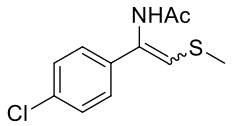
White solid, 30% yield; mixture of Z& E isomers (ratio: 4.3:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.51 (m, 2H), 7.46-7.36 (m, 2H), 6.88 (brs, 1H), 6.30 (s, 1H), 2.42 (s, 3H), 2.16 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.59-7.51 (m, 2H), 7.46-7.36 (m, 2H), 6.64 (s, 2H), 2.47 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.9, 139.7, 130.3, 130.0, 129.1, 128.5, 125.4, 125.0, 122.6, 121.1, 24.0, 23.2, 18.4, 17.2; ESI-HRMS Calculated for $C_{12}H_{13}F_3NOS^+$ ([M+H]$^+$): 276.0664, found: 276.0661.



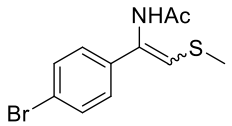
N-(1-(4-fluorophenyl)-2-(methylthio)vinyl)acetamide 1g

White solid, 34% yield; mixture of Z& E isomers (ratio: 3.3:1); Major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.22 (m, 2H), 7.02 (m, 2H), 6.94 (brs, 1H), 6.10 (s, 1H), 2.38 (s, 3H), 2.14 (s, 3H); Minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.21 (m, 2H), 7.11 – 6.95 (m, 2H), 6.65 (brs, 1H), 6.35 (s, 1H), 2.42 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.4, 163.6, 161.1, 132.8, 131.9, 126.7, 126.7, 126.4, 120.9, 116.0, 115.8, 115.4, 115.2, 31.0, 23.4, 21.1, 17.3; ESI-HRMS Calculated for $C_{11}H_{13}FNOS^+$ ([M+H]$^+$): 226.0696, found: 226.0693.



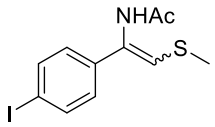
N-(1-(4-chlorophenyl)-2-(methylthio)vinyl)acetamide 1h

White solid, 50% yield; mixture of Z& E isomers (ratio: 2.7:1). Major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.13 (m, 4H), 6.84 (brs, 1H), 6.18 (s, 1H), 2.39 (s, 3H), 2.15 (s, 3H).Minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ7.50 – 7.13 (m, 4H), 6.57 (brs, 1H), 6.45 (s, 1H), 2.44 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.4, 135.1, 133.3, 131.6, 129.1, 128.6, 126.2, 125.8, 122.1, 23.4, 21.0, 17.3; ESI-HRMS Calculated for $C_{11}H_{13}ClNOS^+$ ([M+H]$^+$): 242.0401, found: 242.0397.



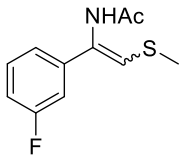
N-(1-(4-bromophenyl)-2-(methylthio)vinyl)acetamide 1i

White solid, 50% yield; mixture of Z& E isomers (ratio: 3.1:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.29 (m, 2H), 7.24-7.12 (m, 2H), 6.96 (brs, 1H), 6.19 (s, 1H), 2.38 (s, 3H), 2.13 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.55 – 7.29 (m, 2H), 7.24-7.12 (m, 2H), 6.65 (s, 1H), 6.47 (s, 1H), 2.43 (s, 1H), 1.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.4, 135.5, 132.1, 131.5, 126.5, 126.1, 122.2, 121.5, 23.4, 17.3; ESI-HRMS Calculated for $C_{11}H_{13}BrNOS^+$ ([M+H]$^+$): 285.9896, found: 285.9891.



N-(1-(4-iodophenyl)-2-(methylthio)vinyl)acetamide 1j

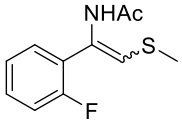
White solid, 46% yield; mixture of Z& E isomers (ratio: 2.5:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.54 (m, 2H), 7.20-7.00 (m, 2H), 6.78 (brs, 1H), 6.18 (s, 1H), 2.39 (s, 3H), 2.15 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.54 (m, 2H), 7.20-7.00 (m, 2H), 6.47 (s, 2H), 2.39 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.5, 138.0, 137.4, 136.1, 131.5, 130.2, 127.5, 126.7, 126.3, 122.5, 93.0, 23.3, 17.3; ESI-HRMS Calculated for $C_{11}H_{13}INOS^+$ ([M+H]$^+$): 333.9757, found: 333.9751.



N-(1-(3-fluorophenyl)-2-(methylthio)vinyl)acetamide 1k

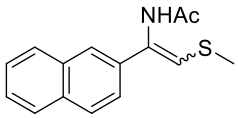
White solid, 44% yield; mixture of Z& E isomers (ratio: 3:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.14 (m, 1H), 7.16-7.05 (m, 1H), 7.04 – 6.88 (m, 3H), 6.28 (s, 1H), 2.39 (s, 3H), 2.13 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.36 – 7.14 (m, 1H), 7.16-7.05 (m, 1H), 7.04 – 6.88 (m, 2H), 6.69 (brs, 1H), 6.53 (s, 1H), 2.44 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.4, 138.0, 137.4, 136.1, 131.6, 127.5, 126.7, 126.3, 122.4, 93.1, 23.4, 21.0, 18.9,

17.3; ESI-HRMS Calculated for $C_{11}H_{13}FNOS^+$ ([M+H]$^+$): 226.0696, found: 226.0693.



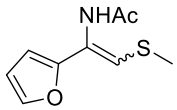
N-(1-(2-fluorophenyl)-2-(methylthio)vinyl)acetamide 1l

White solid, 46% yield; mixture of Z& E isomers (ratio: 3.8:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 1H), 7.17-7.05 (m, 2H), 7.05-6.93 (m, 1H), 6.70 (s, 1H), 6.20 (s, 1H), 2.36 (s, 3H), 2.07 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.30 – 7.17 (m, 1H), 7.17-7.05 (m, 2H), 7.05-6.93 (m, 1H), 2.42 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 168.2, 160.6, 158.1, 129.0, 129.0, 128.7, 128.6, 127.8, 124.8, 124.7, 124.3, 124.3, 124.1, 124.1, 115.8, 115.6, 23.2, 17.3; ESI-HRMS Calculated for $C_{11}H_{13}FNOS^+$ ([M+H]$^+$): 226.0696, found: 226.0693.



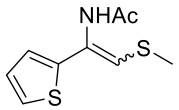
N-(2-(methylthio)-1-(naphthalen-2-yl)vinyl)acetamide 1m

Brown solid, 26% yield; mixture of Z& E isomers (ratio: 2:1); Major isomer:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.68 (m, 4H), 7.47 (m, 3H), 7.04 (brs, 1H), 6.35 (s, 1H), 2.39 (s, 3H), 2.16 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.68 (m, 4H), 7.58-7.37 (m, 3H), 6.73 (brs, 1H), 6.59 (s, 1H), 2.44 (s, 1H), 1.82 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 173.4, 168.4, 134.0, 133.4, 133.0, 132.9, 132.3, 128.8, 128.2, 128.0, 127.8, 127.7, 127.6, 127.1, 126.8, 126.6, 126.5, 126.3, 126.0, 125.6, 125.5, 123.6, 123.4, 123.2, 122.6, 118.2, 24.3, 23.4, 18.4, 17.4; ESI-HRMS Calculated for $C_{15}H_{16}NOS^+$ ([M+H]$^+$): 258.0947, found: 258.0943.



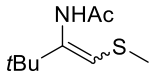
N-(1-(furan-2-yl)-2-(methylthio)vinyl)acetamide 1n

White solid, 53% yield; mixture of Z& E isomers (ratio: 1.7:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.39 (m, , 1H), 6.89 (brs, 1H), 6.53 (s, 1H), 6.43-6.30 (m, 1H), 6.26 – 6.12 (m, 1H), 2.38 (s, 3H), 2.15 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.39 (m, 1H), 6.67 (s, 1H), 6.53 (brs, 1H), 6.43-6.30 (m, 1H), 6.26 – 6.12 (m, 1H), 2.43 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 173.3, 168.3, 150.9, 142.7, 142.1, 127.0, 123.1, 122.2, 111.6, 111.4, 105.5, 105.2, 23.2, 19.9, 17.3, 16.9; ESI-HRMS Calculated for $C_9H_{12}NO_2S^+$ ($[M+H]^+$): 198.0583, found: 198.0581.



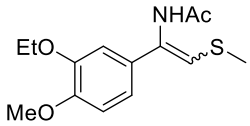
N-(2-(methylthio)-1-(thiophen-2-yl)vinyl)acetamide 1o

White solid, 38% yield; mixture of Z& E isomers (ratio: 2:1); Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.04 (m, 1H), 7.13 (brs, 1H), 7.01-6.86 (m, 2H), 6.35 (s, 1H), 2.36 (s, 3H), 2.13 (s, 3H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.22 – 7.04 (m, 1H), 7.01-6.86 (m, 2H), 6.76 (brs, 1H), 6.48 (s, 1H), 2.42 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 173.2, 168.3, 141.4, 127.9, 127.5, 126.6, 126.1, 124.9, 124.3, 123.0, 122.8, 23.2, 20.3, 17.3, 16.9; ESI-HRMS Calculated for $C_9H_{12}NOS_2^+$ ($[M+H]^+$): 214.0355, found: 214.0352.



N-(3,3-dimethyl-1-(methylthio)but-1-en-2-yl)acetamide 1p

White solid, 45% yield; mixture of Z& E isomers (ratio: 2:1); Major isomer:^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (brs, 1H), 5.92 (s, 1H), 2.27 (s, 3H), 2.11 (s, 3H), 1.10 (s, 9H); Minor isomer: 1H NMR (400 MHz, CDCl3) δ 6.51 (brs, 1H), 5.95 (s, 1H), 2.31 (s, 3H), 2.01 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.17, 167.75, 139.77, 138.47, 124.58, 121.60, 37.54, 36.95, 28.03, 27.96, 23.20, 19.79, 16.96, 16.61.

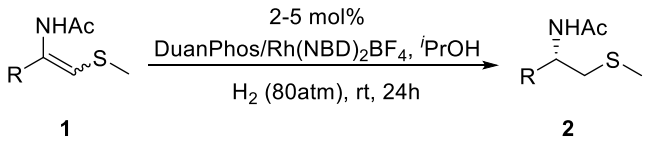


N-(1-(3-ethoxy-4-methoxyphenyl)-2-(methylthio)vinyl)acetamide 1q

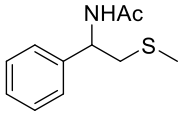
White solid, 30% yield; mixture of Z& E isomers (ratio: 2:1); Major isomer: ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.03-6.72 (m, 4H), 6.08 (s, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.88 (s, 1H), 2.38 (s, 3H), 2.17 (s, 3H), 1.81 (s, 3H), 1.47 (t, *J* = 6.9 Hz, 3H); Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.72 (m, 3H), 6.55 (brs, 1H), 6.21 (s, 1H), 2.17 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) mixture of isomers: δ 173.3, 168.3, 149.3, 148.5, 148.1, 132.6, 131.7, 129.7, 123.1, 119.5, 117.8, 117.6, 111.4, 111.2, 110.0, 109.2, 64.4, 56.0, 23.5, 21.1, 17.3, 17.0, 14.8; ESI-HRMS Calculated for $C_{14}H_{20}NO_3S^+$ ($[M+H]^+$): 282.1158, found: 282.1156.

General Procedure for Asymmetric Hydrogenation of compound 1



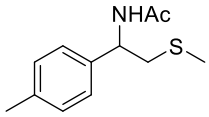
A stock solution was made by mixing $[Rh(NBD)_2]BF_4$ with (*S*c,*R*p)-Duanphos in a 1:1.1 molar ratio in CH_2Cl_2 at room temperature for 30 min in a nitrogen-filled glovebox. An aliquot of the catalyst solution (0.5mL, 0.0005 mmol) was transferred by syringe into the vials charged with different substrates (0.05 mmol for each) in anhydrous ^{i}PrOH (3 mL). The vials were subsequently transferred into an autoclave into which hydrogen gas was charged. The reaction was then stirred under H_2 (80 atm) at room temperature for 24 h. The hydrogen gas was released slowly and carefully. The solution was concentrated and passed through a short column of silica gel (eluent: EtOAc) to yield the desired products. The ee values of compounds **2** were determined by HPLC analysis on a chiral stationary phase.



N-(2-(methylthio)-1-phenylethyl)acetamide 2a

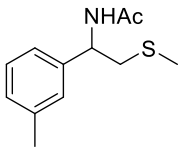
White solid, 10.4 mg, 97% yield; 98% ee; $[\alpha]_D^{20}$ = -50.60 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane:

isopropanol = 95: 5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 32.2 min (minor), 39.3 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.26 (m, 5H), 6.14 (brs, 1H), 5.19 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.92 (d, *J* = 6.6 Hz, 2H), 2.04 (s, 1H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 140.7, 128.8, 127.8, 126.5, 52.1, 40.3, 23.4, 16.0; ESI-HRMS Calculated for $C_{11}H_{16}NOS^+$ ($[M+H]^+$): 210.0947, found: 210.0944.



N-(2-(methylthio)-1-(p-tolyl)ethyl)acetamide 2b

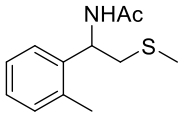
White solid, 11.4 mg, 93% yield; 97% ee; $[\alpha]_D^{20}$ = -56.60 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 10.7 min (minor), 11.7 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.13 (m, 4H), 6.06 (brs, 1H), 5.15 (dd, *J* = 14.2, 6.8 Hz, 1H), 3.26 – 2.68 (m, 2H), 2.33 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 137.6, 137.5, 129.5, 126.4, 51.8, 40.2, 23.5, 21.1, 16.0; ESI-HRMS Calculated for $C_{12}H_{18}NOS^+$ ($[M+H]^+$): 224.1104, found: 224.1100.



N-(2-(methylthio)-1-(m-tolyl)ethyl)acetamide 2c

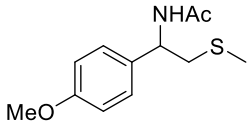
White solid, 10.5 mg, 94% yield; 94% ee; $[\alpha]_D^{20}$ = -67.00 (c = 0.5, CHCl3); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 10.9 min (minor), 14.1 min (major); ^{1}H NMR (400 MHz, CDCl3) δ 7.25-7.18 (m, 1H), 7.14-7.04 (m, 3H), 6.08 (brs, 1H), 5.14 (dd, J = 14.2, 6.9 Hz, 1H), 2.91 (d, J = 6.8 Hz, 1H), 2.35 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 140.6, 138.5, 128.7, 128.6, 127.3, 123.4, 52.1, 40.3, 23.4, 21.5, 16.0; ESI-HRMS

Calculated for $C_{12}H_{18}NOS^+$ ([M+H]$^+$): 224.1104, found: 224.1101.



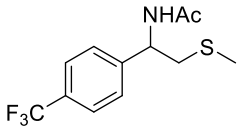
N-(2-(methylthio)-1-(o-tolyl)ethyl)acetamide 2d

White solid, 11.0 mg, 99% yield; 86% ee; $[\alpha]_D^{20}$ = -28.20 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 95: 5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 22.5 min (minor), 30.8 min (major);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 4H), 6.00 (brs, 1H), 5.41 (dd, *J* = 14.3, 7.1 Hz, 1H), 2.99 – 2.62 (m, 2H), 2.42 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 138.95, 136.0, 130.9, 127.7, 126.4, 125.1, 48.3, 39.3, 23.4, 19.4, 16.0; ESI-HRMS Calculated for $C_{12}H_{18}NOS^+$ ([M+H]$^+$): 224.1104, found: 224.1102.



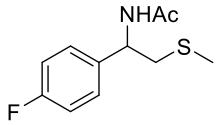
N-(1-(4-methoxyphenyl)-2-(methylthio)ethyl)acetamide 2e

White solid, 11.5 mg, 96% yield; 94% ee; $[\alpha]_D^{20}$ = -77.40 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 230 nm; t_R = 30.5 min (minor), 43.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 6.90-6.83 (m, 1H), 6.10 (brs, 1H), 5.13 (dd, *J* = 13.9, 6.8 Hz, 1H), 3.79 (s, 3H), 3.07 – 2.79 (m, 2H), 2.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 159.1, 132.7, 127.7, 114.1, 55.3, 51.6, 40.2, 23.5, 16.0; ESI-HRMS Calculated for $C_{12}H_{18}NO_2S^+$ ([M+H]$^+$): 240.1053, found: 240.1049.



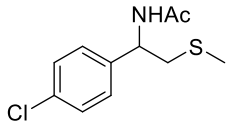
N-(2-(methylthio)-1-(4-(trifluoromethyl)phenyl)ethyl)acetamide 2f

White solid, 12.4mg, 93% yield; 89% ee; $[\alpha]_D^{20}$ = +21.80 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 9.9 min (minor), 11.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.56 (m, 2H), 7.47-7.40 (m, 2H), 6.25 (brs, 1H), 5.21 (q, *J* = 6.8 Hz, 1H), 3.05 – 2.79 (m, 2H), 2.06 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 143.9, 129.0, 128.7, 125.8, 124.7, 124.7, 124.7, 124.6, 50.7, 39.1, 22.3, 14.9; ESI-HRMS Calculated for $C_{12}H_{15}F_3NOS^+$ ($[M+H]^+$): 278.0821, found: 278.0819.



N-(1-(4-fluorophenyl)-2-(methylthio)ethyl)acetamide 2g

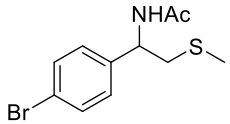
White solid, 10.0 mg, 88% yield; 98% ee; $[\alpha]_D^{20}$ = -40.20 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 14.1 min (minor), 15.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.10 – 6.98 (m, 2H), 6.14 (brs, 1H), 5.16 (dd, J = 13.9, 6.7 Hz, 1H), 2.90 (d, J = 6.5 Hz, 2H), 2.04 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 168.6, 162.4, 159.9, 135.53, 127.1, 127.1, 114.7, 114.5, 50.4, 39.2, 22.34, 15.0; ESI-HRMS Calculated for $C_{11}H_{15}FNOS^+$ ($[M+H]^+$): 228.0853, found: 228.0852.



N-(1-(4-chlorophenyl)-2-(methylthio)ethyl)acetamide 2h

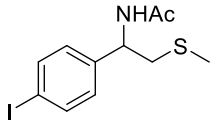
White solid, 12.0 mg, 98% yield; 98% ee; $[\alpha]_D^{20}$ = -43.60 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 28.5 min (minor), 34.9 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.26 –

7.21 (m, 2H), 6.13 (brs, 1H), 5.15 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.89 (d, *J* = 6.5 Hz, 2H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 139.3, 133.5, 128.9, 127.9, 51.5, 40.2, 23.4, 16.0; ESI-HRMS Calculated for $C_{11}H_{15}ClNOS^+$ ($[M+H]^+$): 244.0557, found: 244.0555.



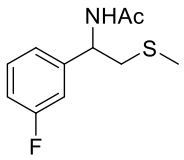
N-(1-(4-bromophenyl)-2-(methylthio)ethyl)acetamide 2i

White solid, 14.1 mg, 98% yield; 99% ee; $[\alpha]_D^{20}$ = -48.80 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 16.6 min (minor), 22.6 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.27-7.14 (m, 2H), 6.15 (brs, 1H), 5.13 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.88 (d, *J* = 6.5 Hz, 2H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 139.9, 131.8, 128.2, 121.6, 51.5, 40.1, 23.4, 16.0; ESI-HRMS Calculated for $C_{11}H_{15}BrNOS^+$ ($[M+H]^+$): 288.0052, found: 288.0049.



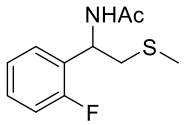
N-(1-(4-iodophenyl)-2-(methylthio)ethyl)acetamide 2j

White solid, 16.3 mg, 98% yield; 97% ee; $[\alpha]_D^{20}$ = -48.80 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95: 5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 23.7 min (minor), 32.5 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.60 (m, 2H), 7.14 – 6.98 (m, 2H), 6.15 (brs, 1H), 5.11 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.87 (d, *J* = 6.5 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 140.6, 137.8, 128.5, 93.2, 51.62 40.06, 23.4, 16.0; ESI-HRMS Calculated for $C_{11}H_{15}INOS^+$ ($[M+H]^+$): 335.9914, found: 335.9908.



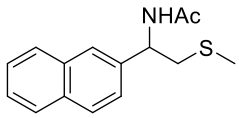
N-(1-(3-fluorophenyl)-2-(methylthio)ethyl)acetamide 2k

White solid, 11.0 mg, 96% yield; 94% ee; $[\alpha]_D^{20}$ = -47.20 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 95: 5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 25.8 min (minor), 28.1 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 1H), 7.12-7.06 (m, 1H), 6.03-6.93 (m, 2H), 6.16 (brs, 1H), 5.18 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.97 – 2.78 (m, 2H), 2.06 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 164.2, 161.8, 143.5, 143.5, 130.3, 130.2, 122.2, 122.1, 114.7, 114.5, 113.5, 113.3, 51.6, 40.2, 23.3, 16.0; ESI-HRMS Calculated for $C_{11}H_{15}FNOS^+$ ($[M+H]^+$): 228.0853, found: 228.0851.



N-(1-(2-fluorophenyl)-2-(methylthio)ethyl)acetamide 2l

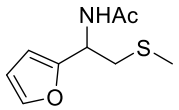
White solid, 10.6 mg, 94% yield; 96% ee; $[\alpha]_D^{20}$ = -24.40 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 9.0 min (minor), 10.2 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.35-7.24 (m, 1H), 6.19 (brs, 1H), 5.36 (dd, *J* = 15.3, 6.9 Hz, 1H), 3.03 – 2.80 (m, 2H), 2.05 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 129.5, 129.5, 129.0, 128.9, 127.7, 127.5, 124.4, 124.4, 116.0, 115.8, 48.7, 39.1, 23.4, 15.7; ESI-HRMS Calculated for $C_{11}H_{15}FNOS^+$ ($[M+H]^+$): 228.0853, found: 228.0851.



N-(2-(methylthio)-1-(naphthalen-2-yl)ethyl)acetamide 2m

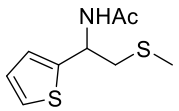
White solid, 9.8 mg, 76% yield (80% conv.); 92% ee; $[\alpha]_D^{20}$ = +2.00 (c = 0.5, $CHCl_3$);

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 20.6 min (minor), 29.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 3H), 7.78-7.73 (m, 1H), 7.53 – 7.43 (m, 2H), 7.41 (m, 1H), 6.23 (brs, 1H), 5.36 (dd, *J* = 14.1, 6.8 Hz, 1H), 3.01 (d, *J* = 6.5 Hz, 2H), 2.06 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 137.0, 132.2, 131.8, 127.6, 126.9, 126.6, 125.3, 125.0, 124.3, 123.5, 51.1, 39.1, 22.4, 15.0; ESI-HRMS Calculated for $C_{15}H_{18}NOS^+$ ($[M+H]^+$): 260.1104, found: 260.1101.



N-(1-(furan-2-yl)-2-(methylthio)ethyl)acetamide 2n

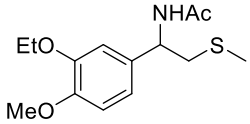
White solid, 10.0 mg, 99% yield; 99% ee; $[\alpha]_D^{20}$ = -58.60 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column, hexane: isopropanol = 95: 5; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 60.1 min (minor), 60.8 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 1H), 6.34 (m, 1H), 6.25 (m, 1H), 6.09 (brs, 1H), 5.33 (dd, *J* = 8.5, 6.2 Hz, 1H), 2.99 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.90 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.04 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 151.7, 141.0, 109.54, 106.0, 45.5, 37.0, 22.3, 14.8; ESI-HRMS Calculated for $C_9H_{14}NO_2S^+$ ($[M+H]^+$): 200.0740, found: 200.0738.



N-(2-(methylthio)-1-(thiophen-2-yl)ethyl)acetamide 2o

White solid, 11.0 mg, 99% yield; 97% ee; $[\alpha]_D^{20}$ = -89.60 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 15.5 min (minor), 17.3 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 1H), 7.06 – 6.92 (m, 2H), 6.11 (brs, 1H), 5.51 (dd, *J* = 14.6, 6.3 Hz, 1H), 2.99 (d, *J* = 6.3 Hz, 2H), 2.08 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 144.3, 127.0, 124.80,

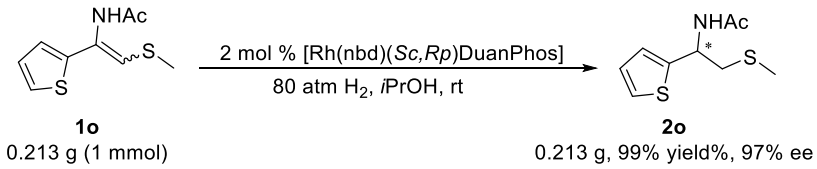
124.7, 48.1, 40.7, 23.3, 16.2; ESI-HRMS Calculated for $C_9H_{14}NOS_2^+$ ($[M+H]^+$): 216.0511, found: 216.0509.



N-(1-(3-ethoxy-4-methoxyphenyl)-2-(methylthio)ethyl)acetamide 2q

White solid, 14.0 mg, 99% yield; 96% ee; The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 21.5 min (major), 25.3 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 – 6.77 (m, 3H), 5.99 (brs, 1H), 5.12 (dd, *J* = 14.2, 6.7 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.86 (s, 3H), 3.04 – 2.72 (m, 2H), 2.04 (s, 3H), 2.02 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 147.8, 147.4, 132.1, 117.4, 110.6, 110.4, 63.4, 54.9, 50.9, 39.1, 22.4, 15.0, 13.8; ESI-HRMS Calculated for $C_{14}H_{22}NO_3S^+$ ($[M+H]^+$): 284.1315, found: 284.1313.

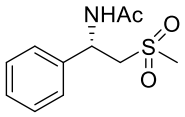
General Procedure for Asymmetric Hydrogenation of compound 1o



A stock solution was made by mixing $[Rh(NBD)_2]BF_4$ (7.5 mg) with (*Sc*,*Rp*)-Duanphos (8.4 mg) in a 1:1.1 molar ratio in CH_2Cl_2 (1 mL) at room temperature for 5-10 min in a nitrogen-filled glovebox. The catalyst solution was transferred by syringe into the vials charged with **1o** (0.213 g, 1mmol) in anhydrous ^{i}PrOH (60 mL). The vials were subsequently transferred into an autoclave into which hydrogen gas was charged. The reaction was then stirred under H_2 (80 atm) at room temperature for 24 h. The hydrogen gas was released slowly and carefully. The solution was concentrated and passed through a short column of silica gel (eluent: PE/EtOAc=2/1) to yield the desired products. The ee values of compounds **2o** were determined by HPLC analysis on a chiral stationary phase.

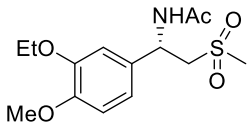
General Procedure for Oxidation of compound 2a and 2q.[4]

A mixture of sulfide **2a** or **2q** (1.0 mmol), tantalumchloride (7.1 mg, 0.02 mmol), and 30% hydrogen peroxide (0.5 mL, 5 mmol) in MeOH (2 mL) was stirred at 45 ^{o}C. When **2a** or **2q** disappeared from the TLC, saturated aqueous sodium thiosulfate (15 mL) is added to the reaction mixture, followed by extraction with ethyl acetate (3×20 mL). The combined organic phase is washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel gave pure products **3a** or **3q**.



(S)-N-(2-(methylsulfonyl)-1-phenylethyl)acetamide 3a

White solid, 78% yield; 96% ee; $[\alpha]^{D}_{20}$ = 18.0 (c = 0.3, CH_2Cl_2); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 85: 15; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 14.7 min (minor), 18.2 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.33 (m, 5H), 6.86 (d, *J* = 8.0, 1H), 5.61 (q, *J* = 7.2 Hz, 1H), 3.67 (dd, *J* = 7.2, 15.2 Hz, 1H), 3.47 (dd, *J* = 4.8, 14.8 Hz, 1H), 2.63 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 138.4, 129.2, 128.5, 126.5, 59.4, 49.0, 41.9, 23.3.



(S)-N-(1-(3-ethoxy-4-methoxyphenyl)-2-(methylsulfonyl)ethyl)acetamide 3q

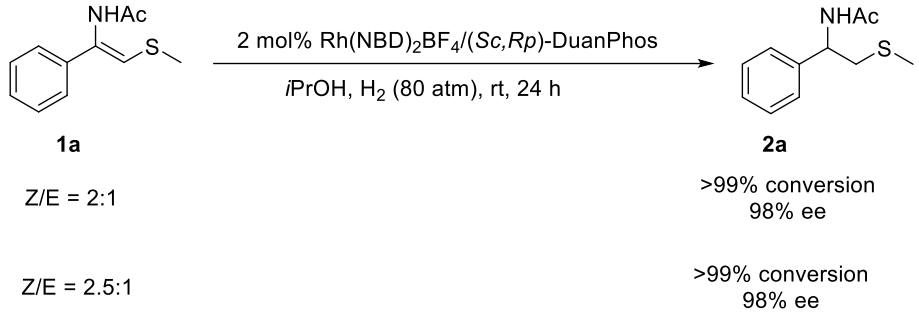
White solid, 50% yield; 94% ee; The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 85: 15; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 18.0 min (minor), 19.3 min (major);^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 – 6.70 (m, 3H), 6.61 (brs, 1H), 5.51 (dd, *J* = 13.4, 6.4 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.87 (s, 3H), 3.64 (dd, *J* = 14.9, 6.5 Hz, 1H), 3.45 (dd, *J* = 14.9, 5.0 Hz, 1H), 2.62 (s, 3H), 2.06 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 168.9, 148.3, 147.7, 129.7, 117.5, 110.6, 110.3, 63.6, 58.4, 55.0, 47.9, 40.9, 22.3, 13.4.

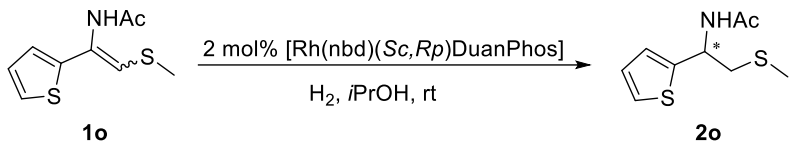
The investigation of the influence of Z/E ratio to enantioselectivity.

In order to investigate the effect of Z/E ratio to the enantioselectivity, we added some experiments to elucidate their relationship.

(1) Hydrogenation of **1a** with different Z/E ratio



(2)Control experiment for asymmetric hydrogenation of **1o**



Entry	H_2 (atm)	Time (h)	Conv. (%)[a]		Ee (%)
			Z[b,c]	E[b,c]	
1	10	24	63(94)	30(89)	97
2	10	12	52(79)	19(57)	97
3	5	24	42(63)	8(25)	97
4	80	24	67(100)	33(100)	97

[a] The conversion is calculated by ^{1}H NMR. [b] the conversion is based on the mixture of **1o**. [b] the conversion in parentheses is based on the corresponding isomer of **1o.**

These experiment results clearly identified that the Z/E ratio have no influence on the enantioselectivity for this reaction.

References

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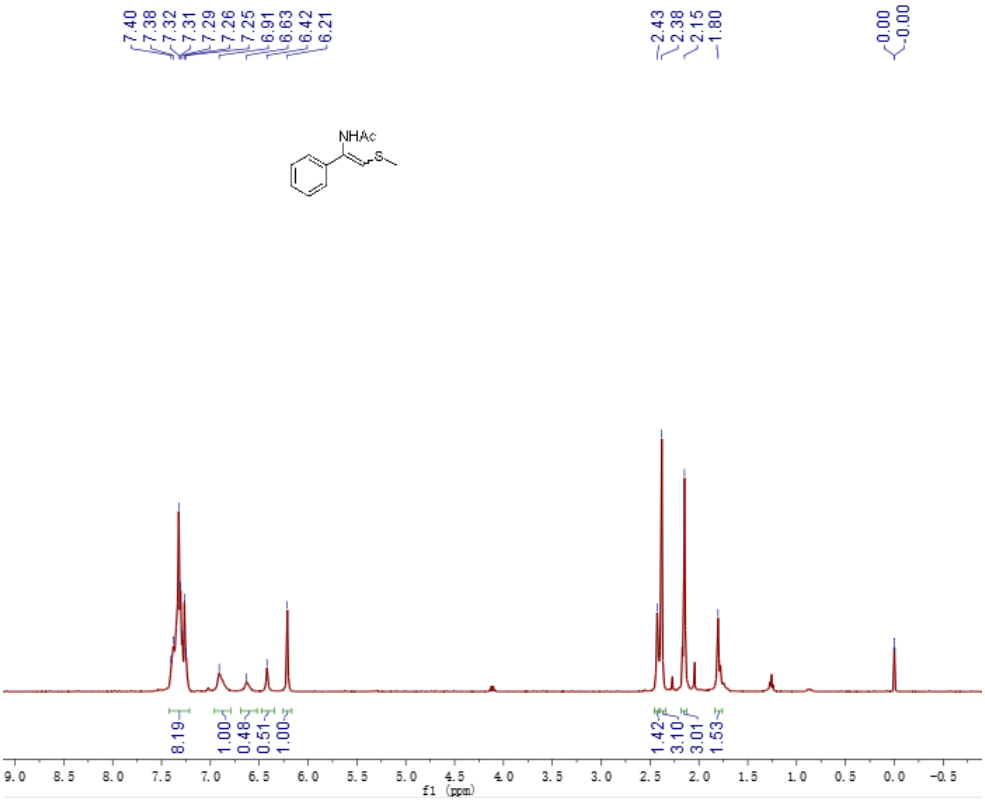
2. Su, Q.; Zhao, Z.-J.; Xu, F.; Lou, P.-C.; Zhang, K.; Xie, D.-K.; Shi, L.; Cai, Q.-Y.; Peng, Z.-H.; An, D.-L. *Eur. J. Org. Chem.* **2013**, *8*, 1551.

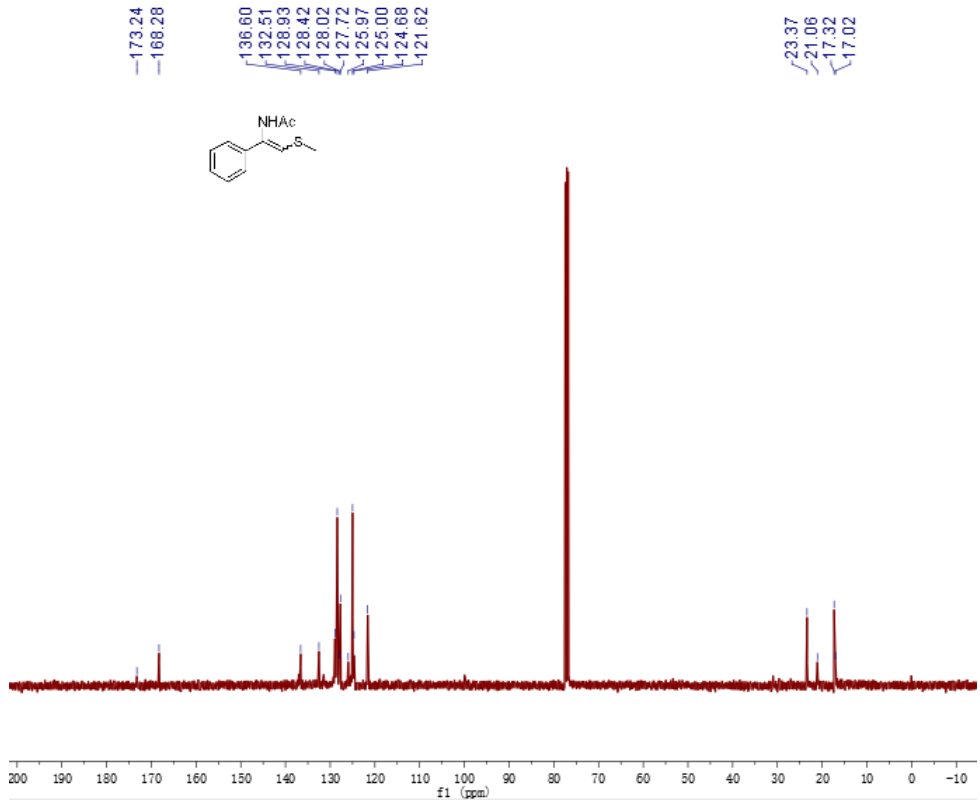
3. Burk, M. J.; Casy, G.; Johnson, N. B. *J. Org. Chem*. **1998**, *63*, 6084-6085.

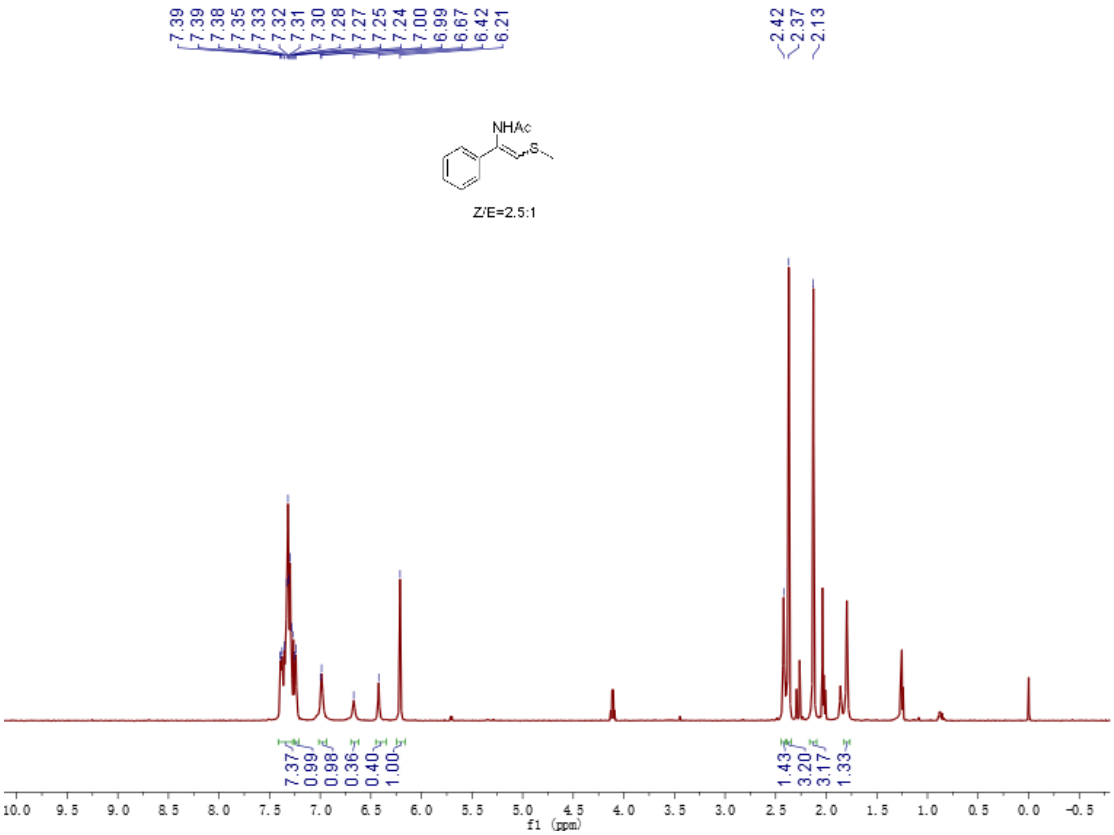
4. Kirihara, M.; Yamamoto, J.; Noguchi, T.; Hirai, Y. *Tetrahedron Lett* **2009**, *50*, 1180.

NMR and HPLC of 1, 2 and 3.

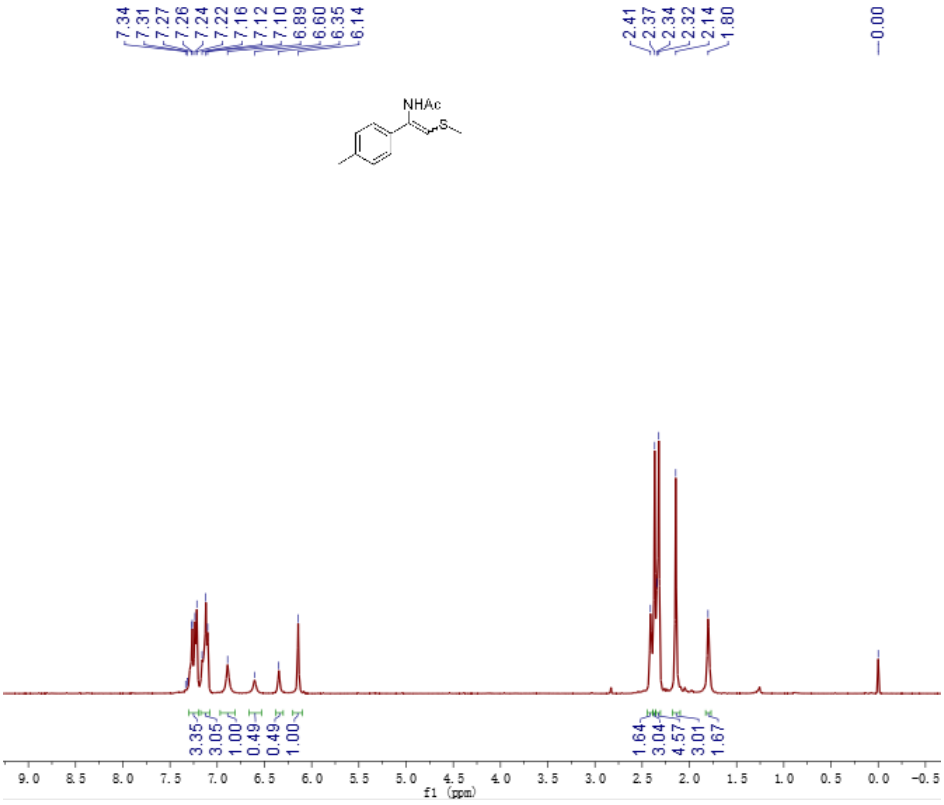
^{1}H NMR and ^{13}C NMR of 1a

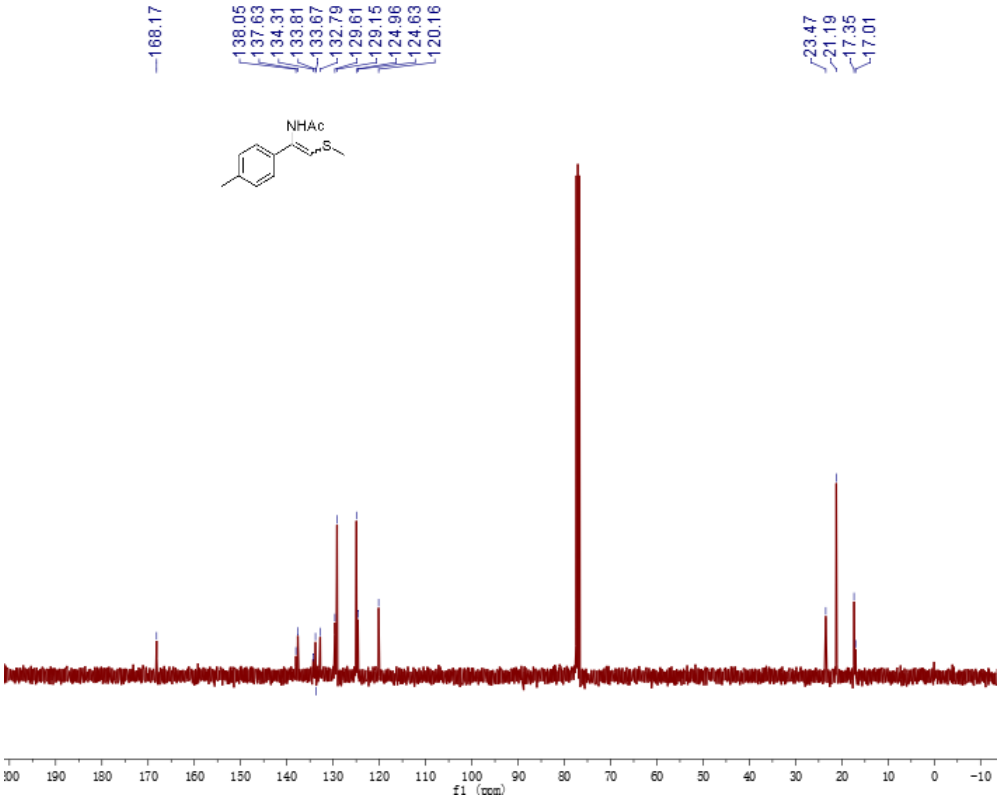




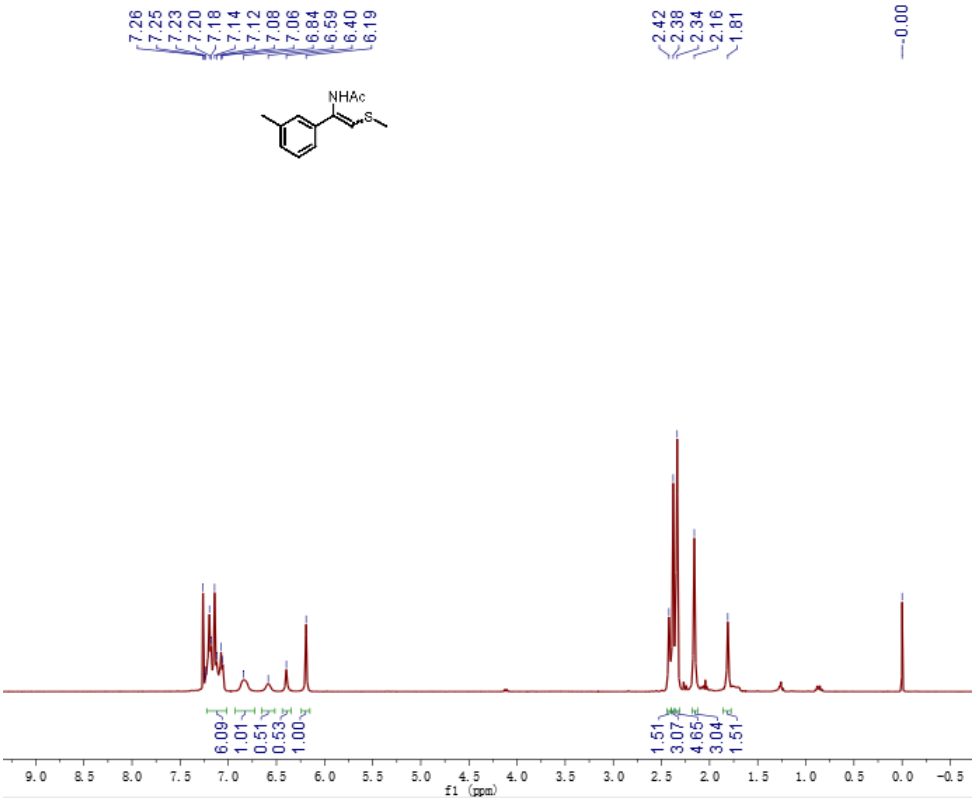

7.39
7.39
7.38
7.35
7.33
7.32
7.31
7.30
7.28
7.27
7.25
7.24
7.00
6.99
6.67
6.42
6.21
2.42
2.37
2.13
NHAc
S
Z/E=2.5:1
7.37
0.99
0.98
0.36
0.40
1.00
1.43
3.20
3.17
1.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

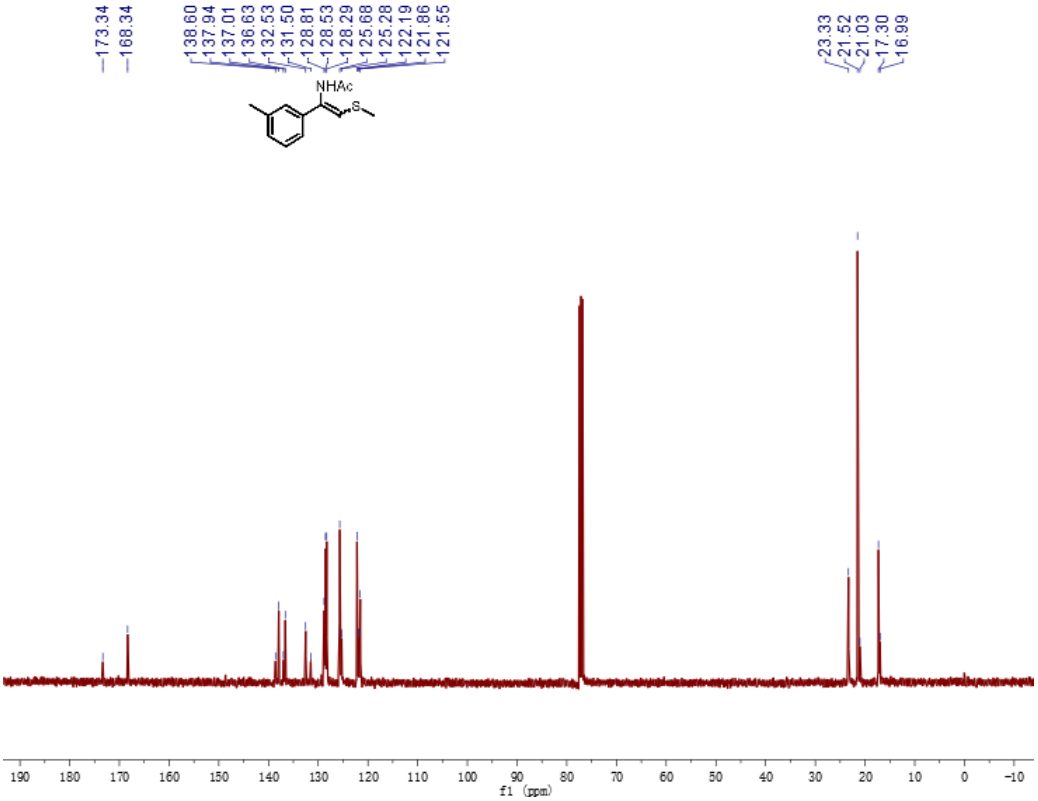
^{1}H NMR and ^{13}C NMR of 1b



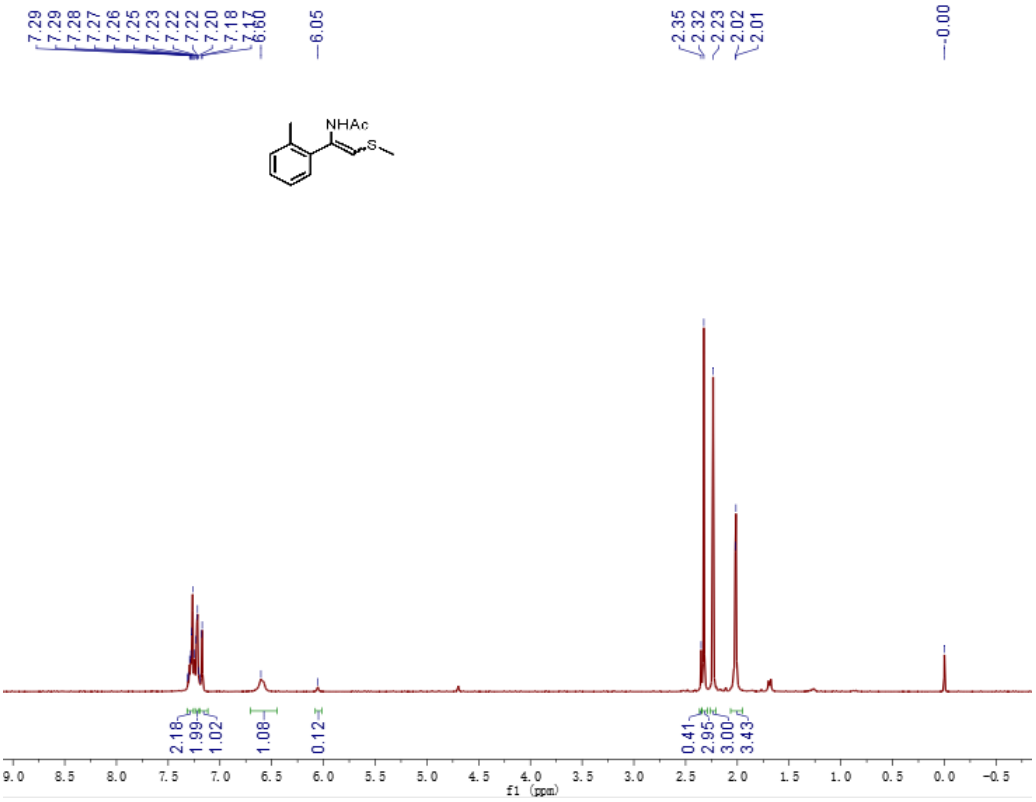


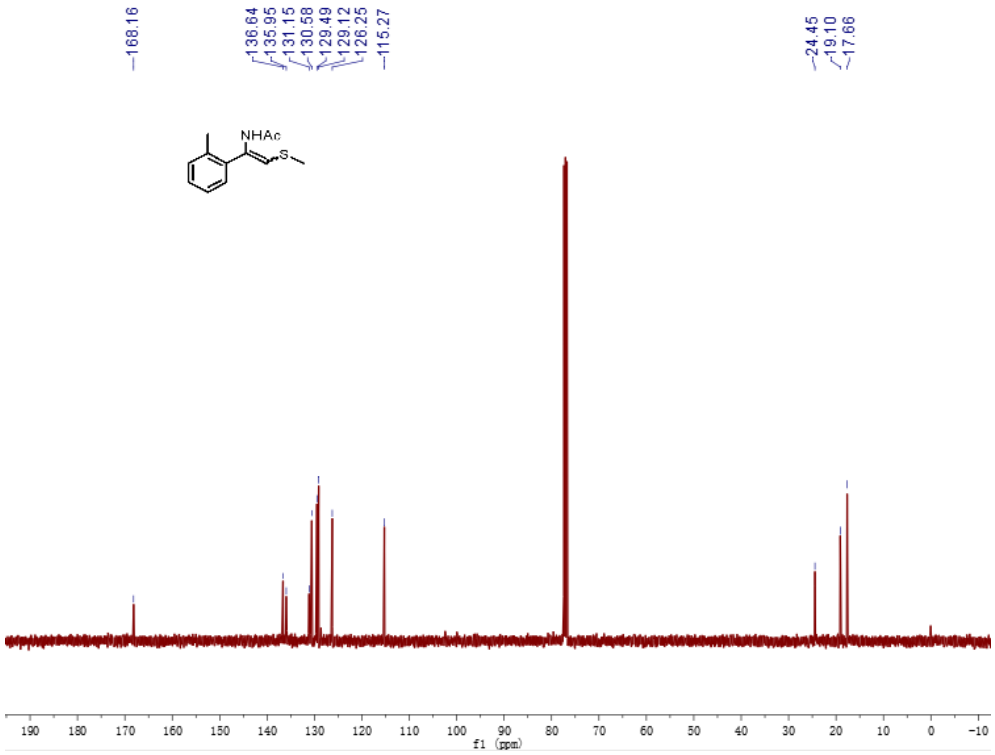
^{1}H NMR and ^{13}C NMR of 1c



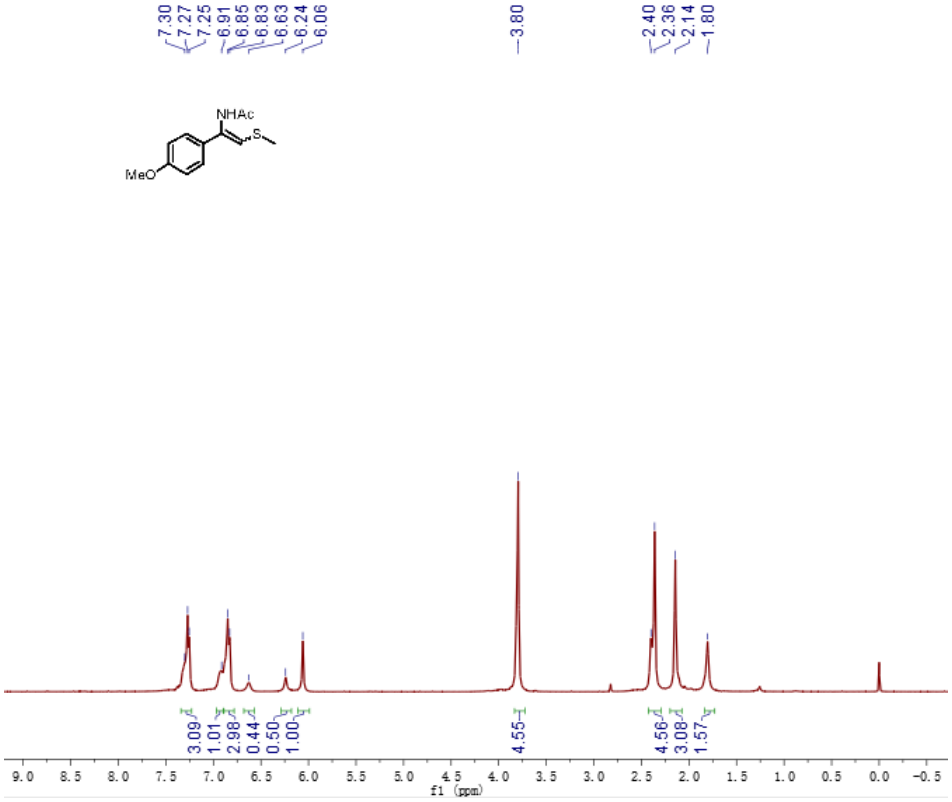


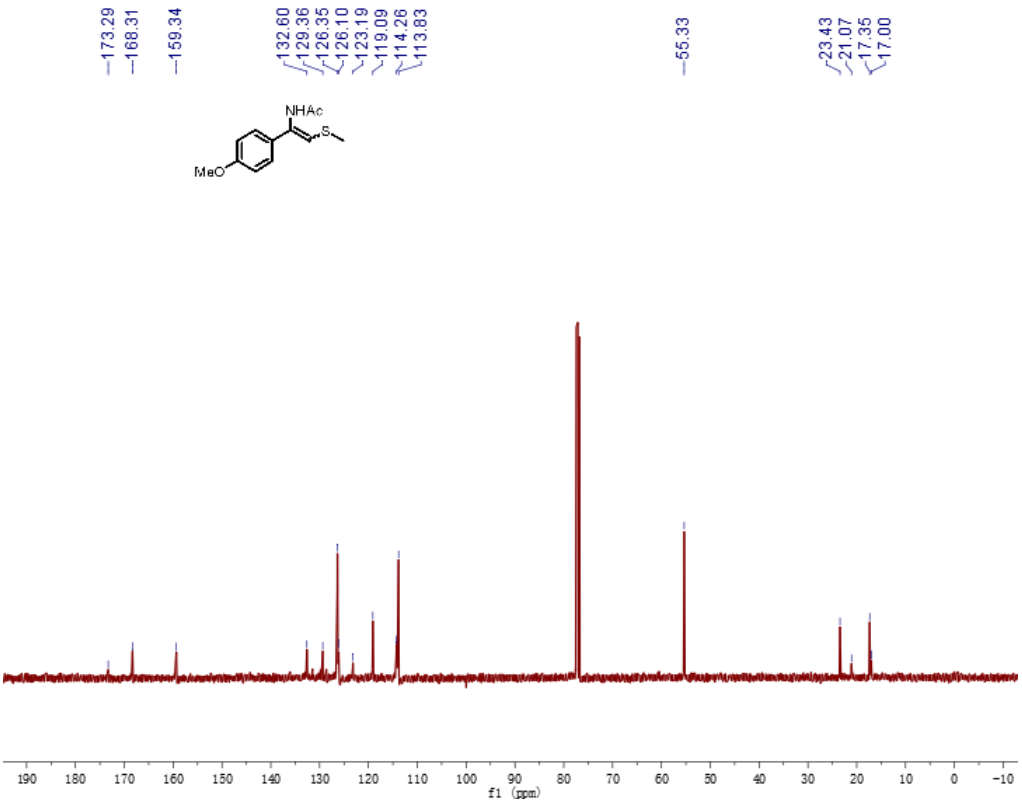
^{1}H NMR and ^{13}C NMR of 1d



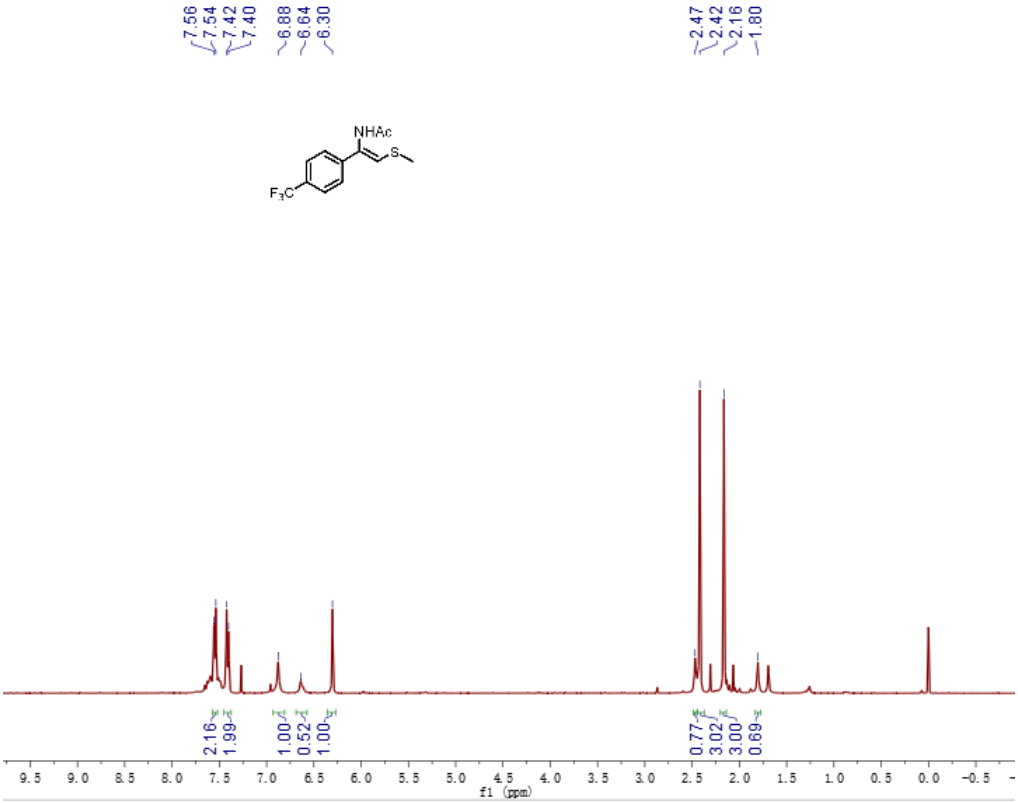


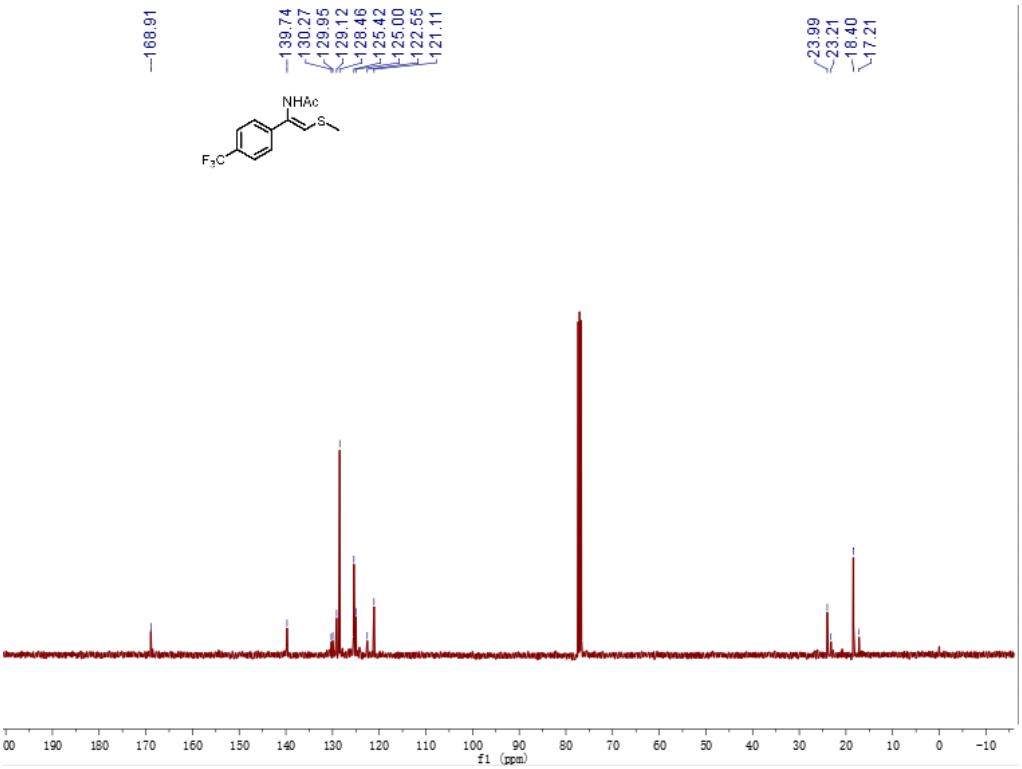
^{1}H NMR and ^{13}C NMR of 1e



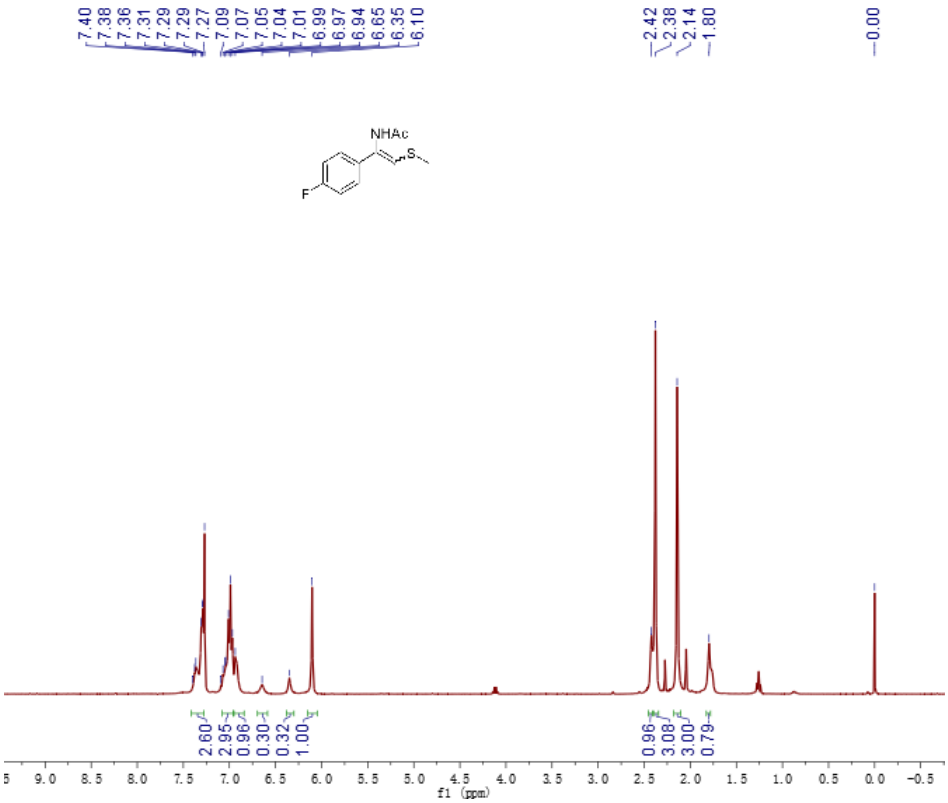


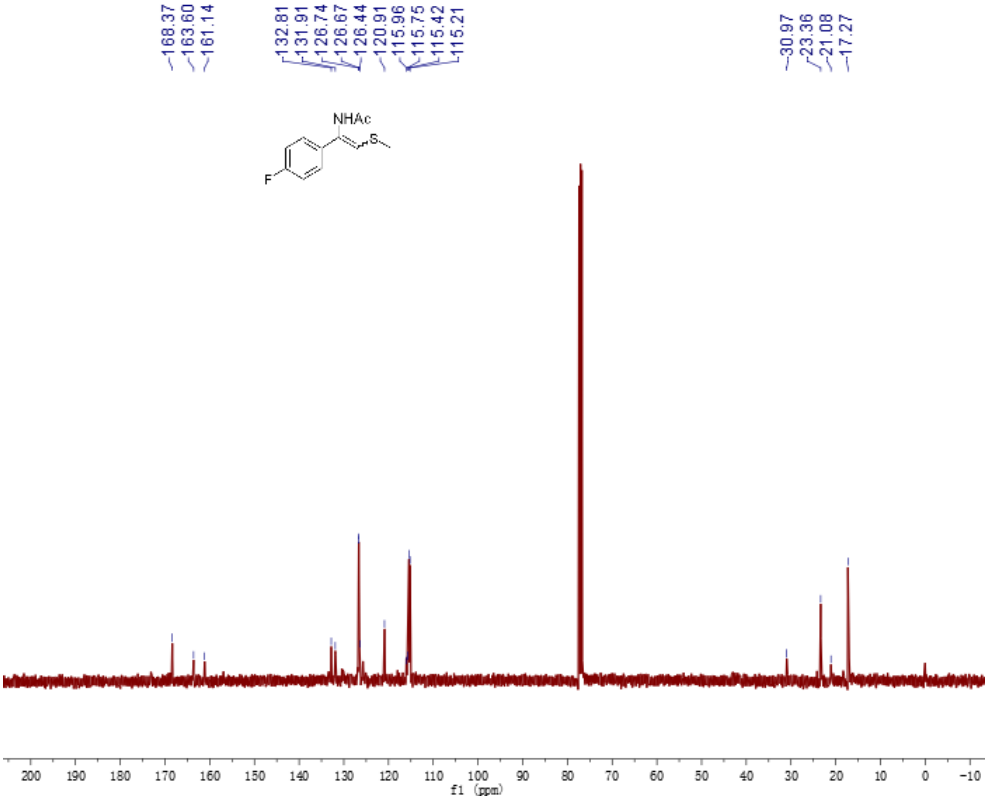
^{1}H NMR and ^{13}C NMR of 1f



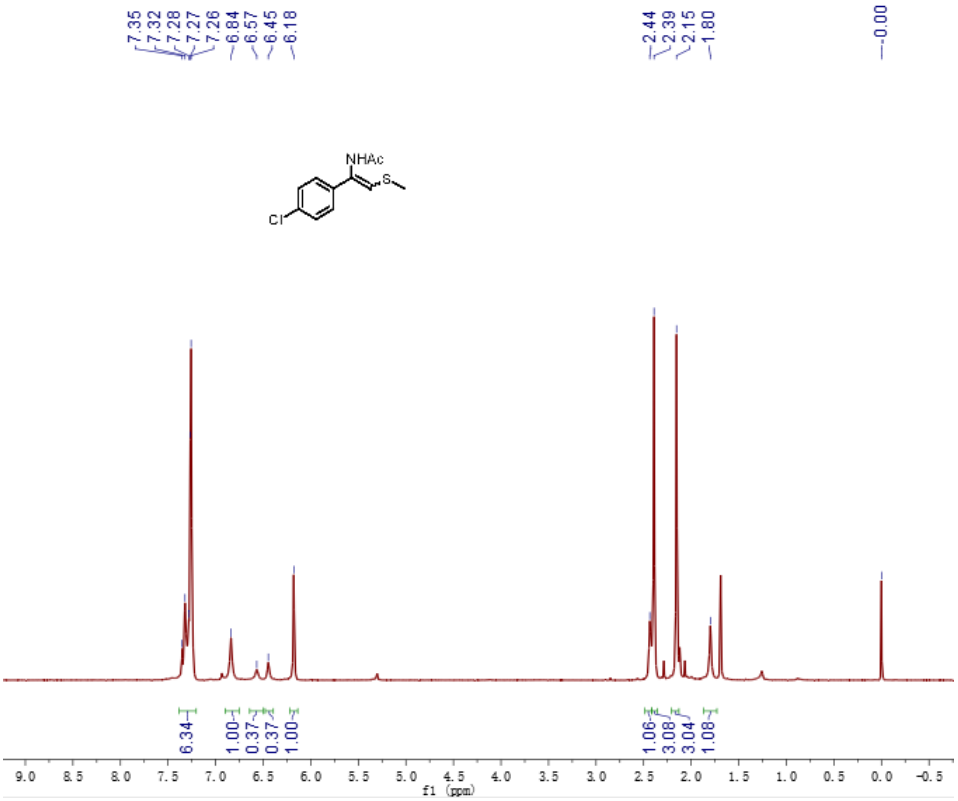


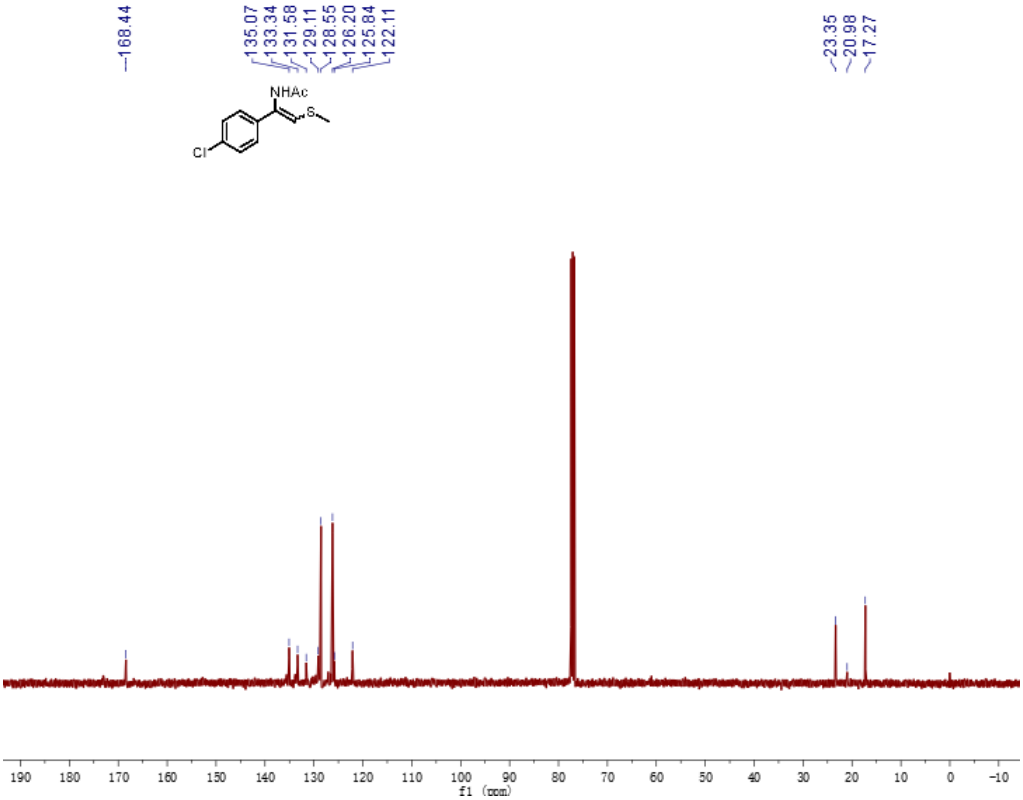
^{1}H NMR and ^{13}C NMR of 1g



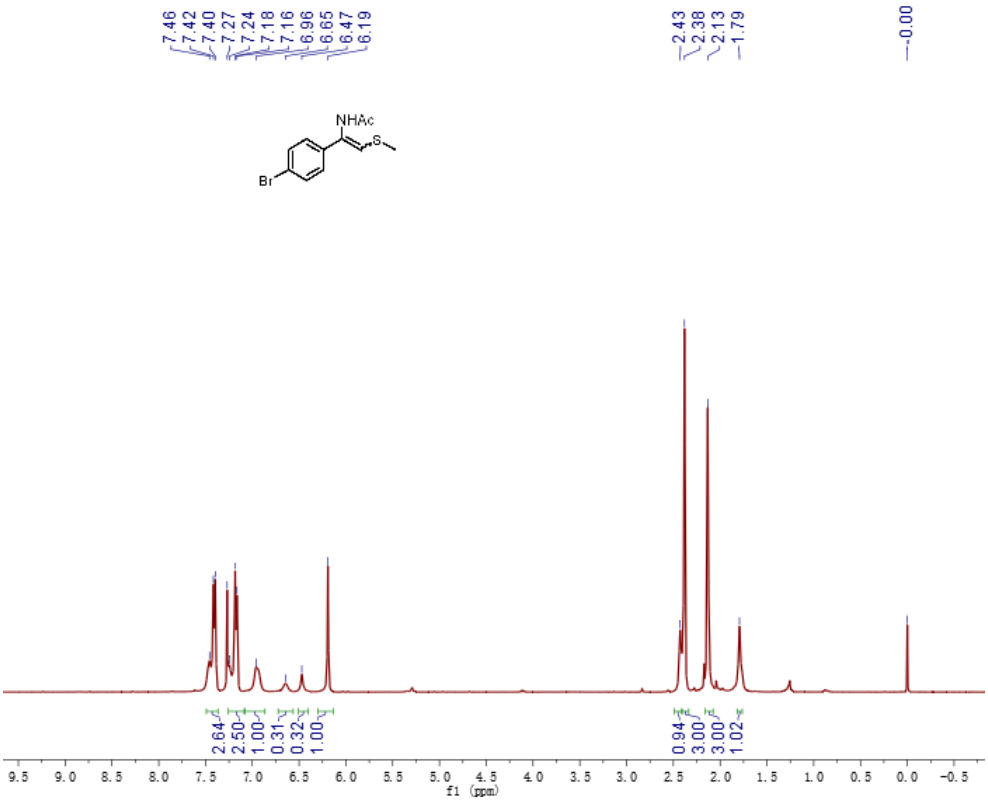


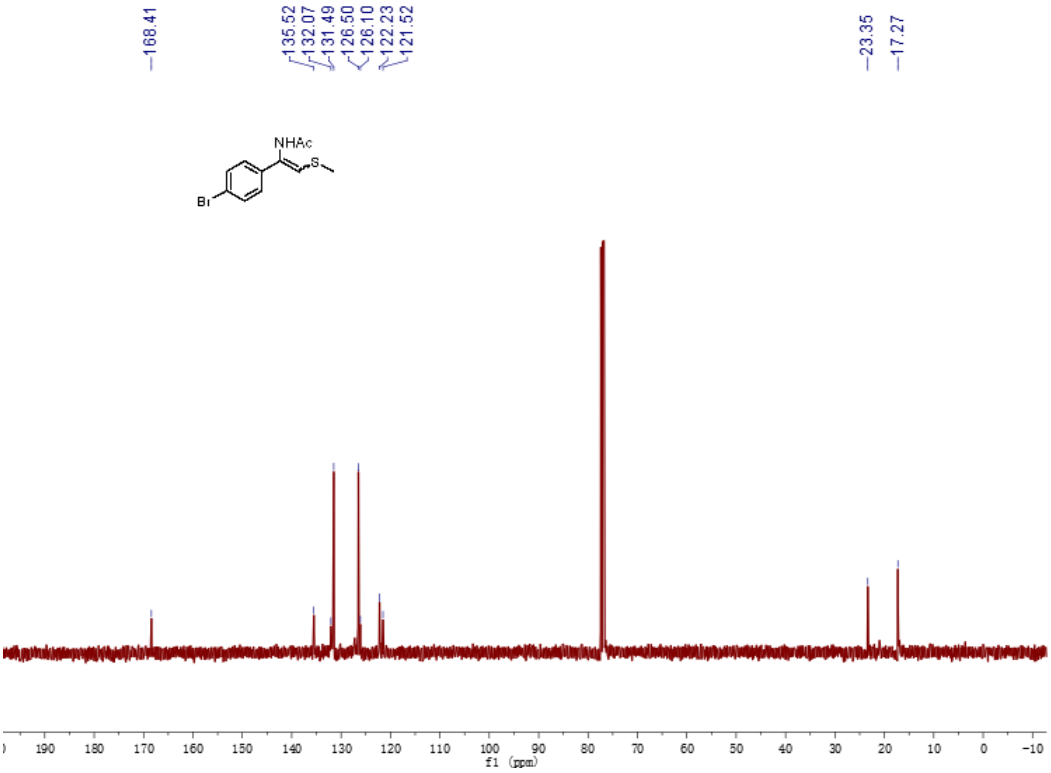
^{1}H NMR and ^{13}C NMR of 1h



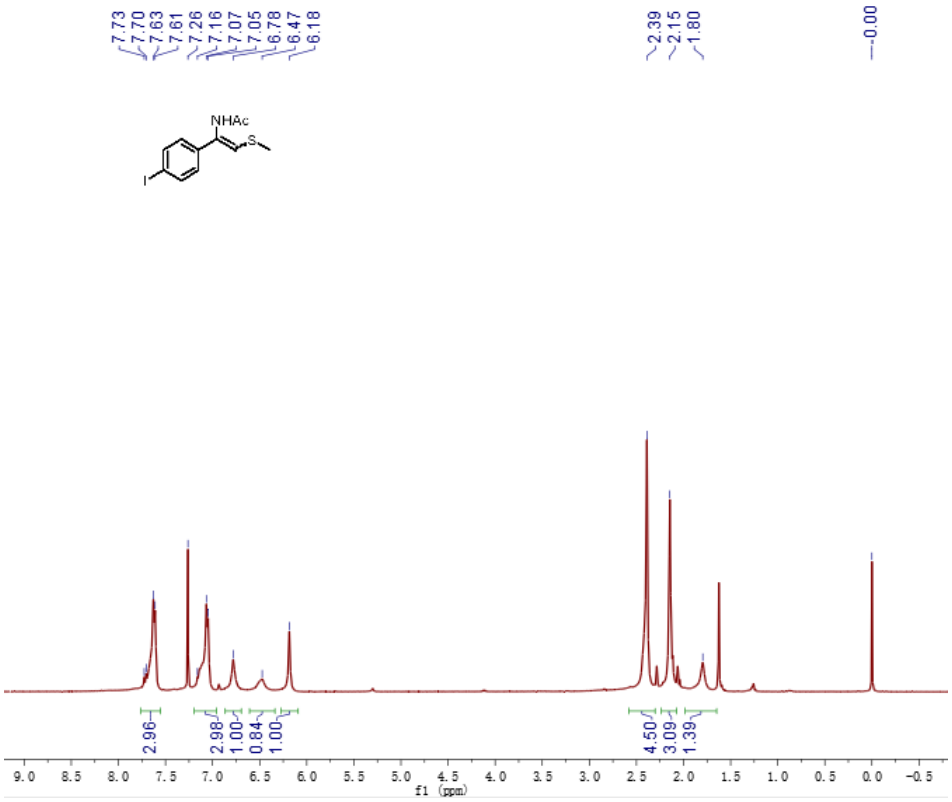


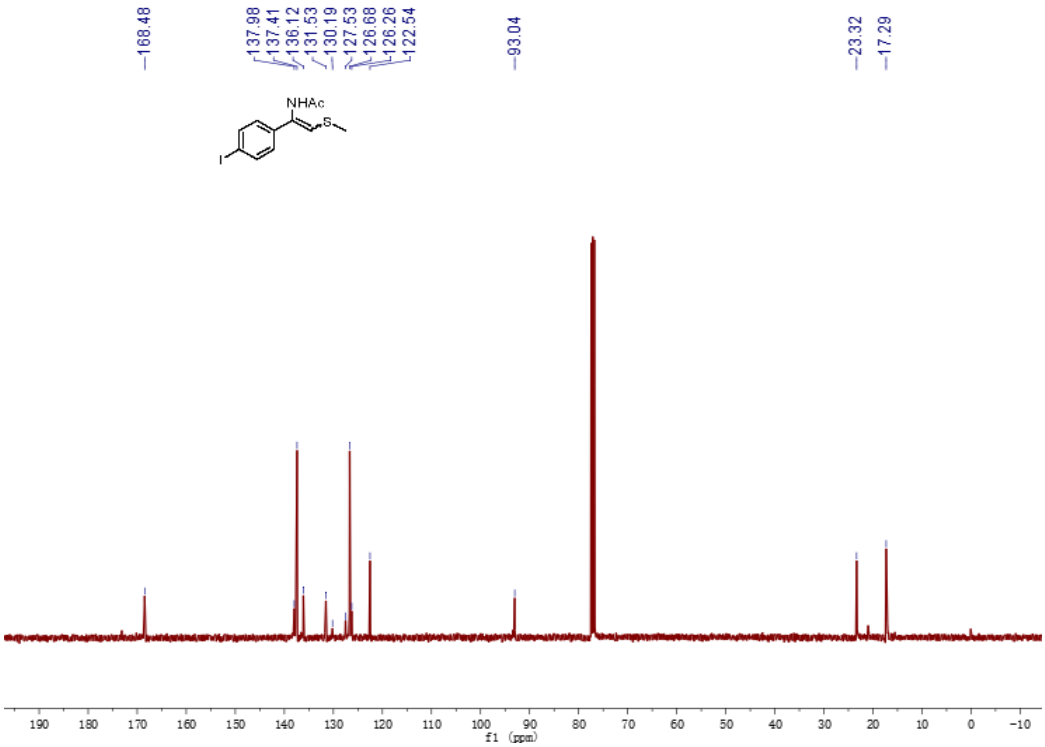
^{1}H NMR and ^{13}C NMR of 1i



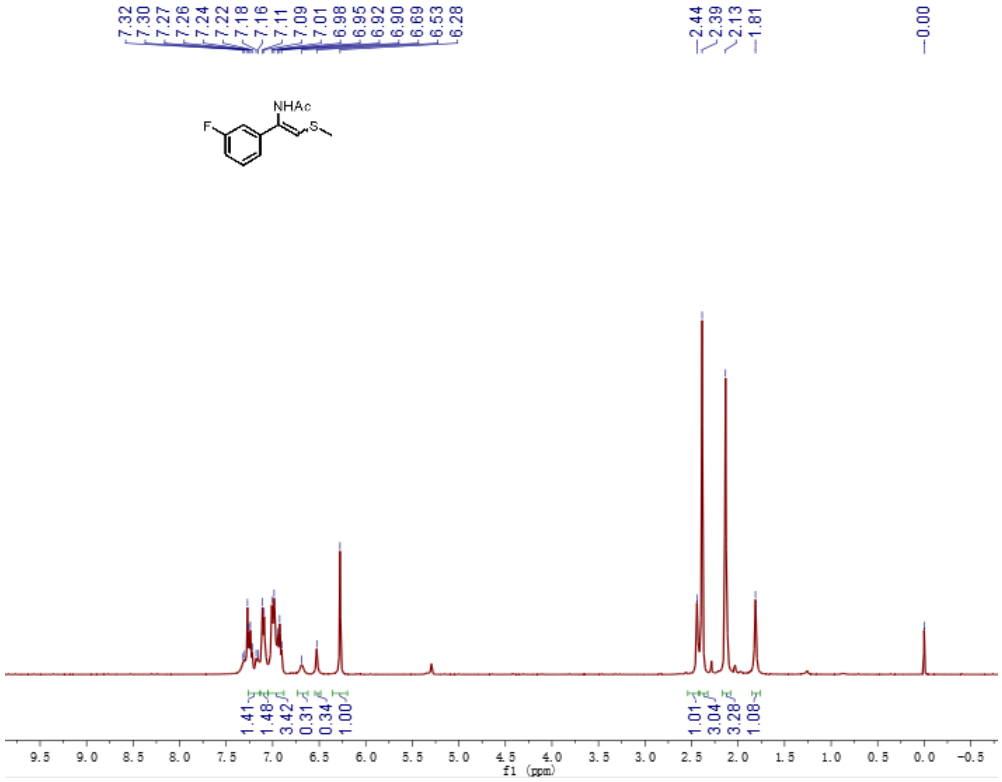


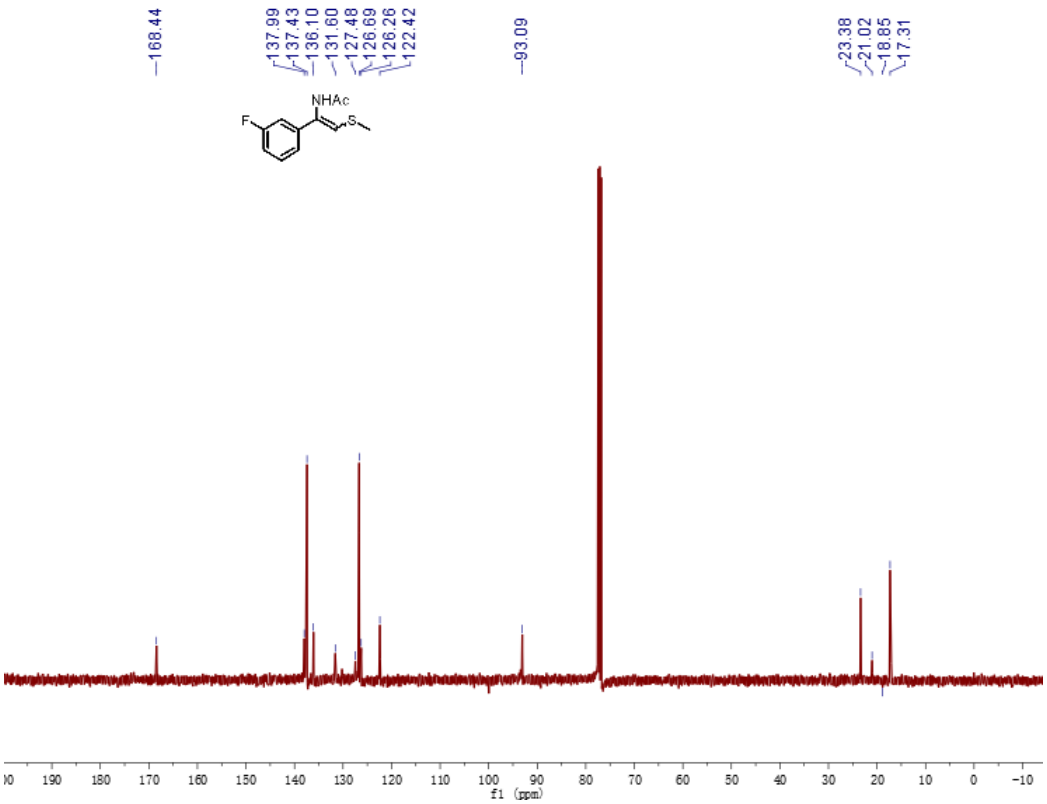
^{1}H NMR and ^{13}C NMR of 1j



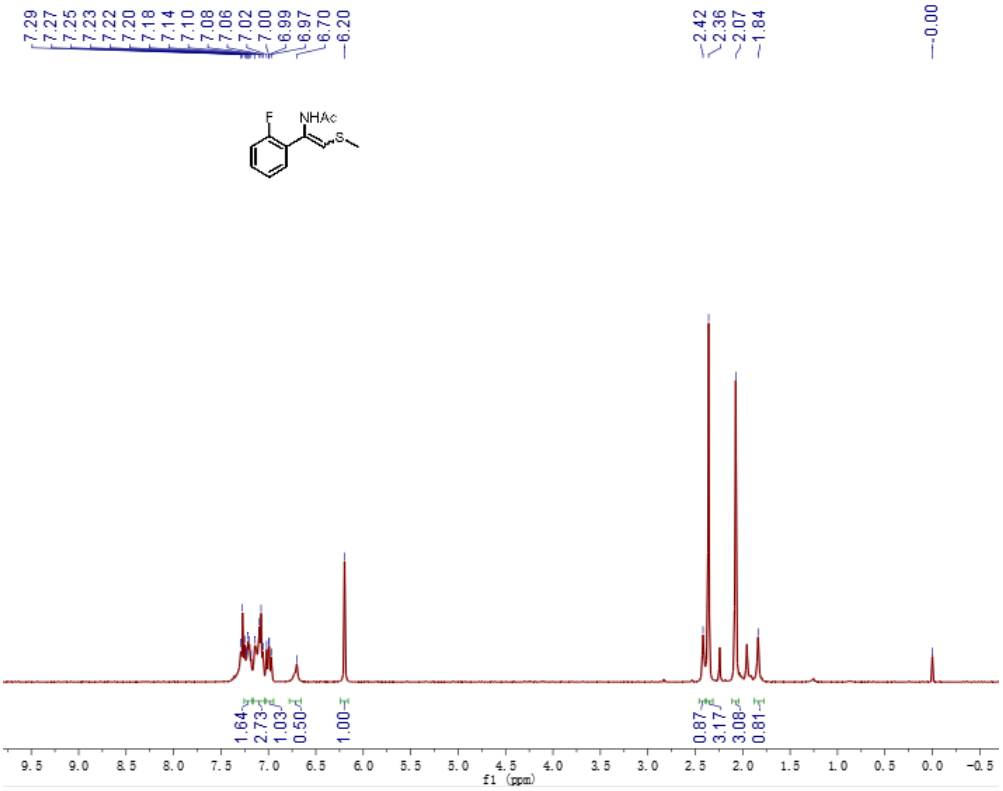


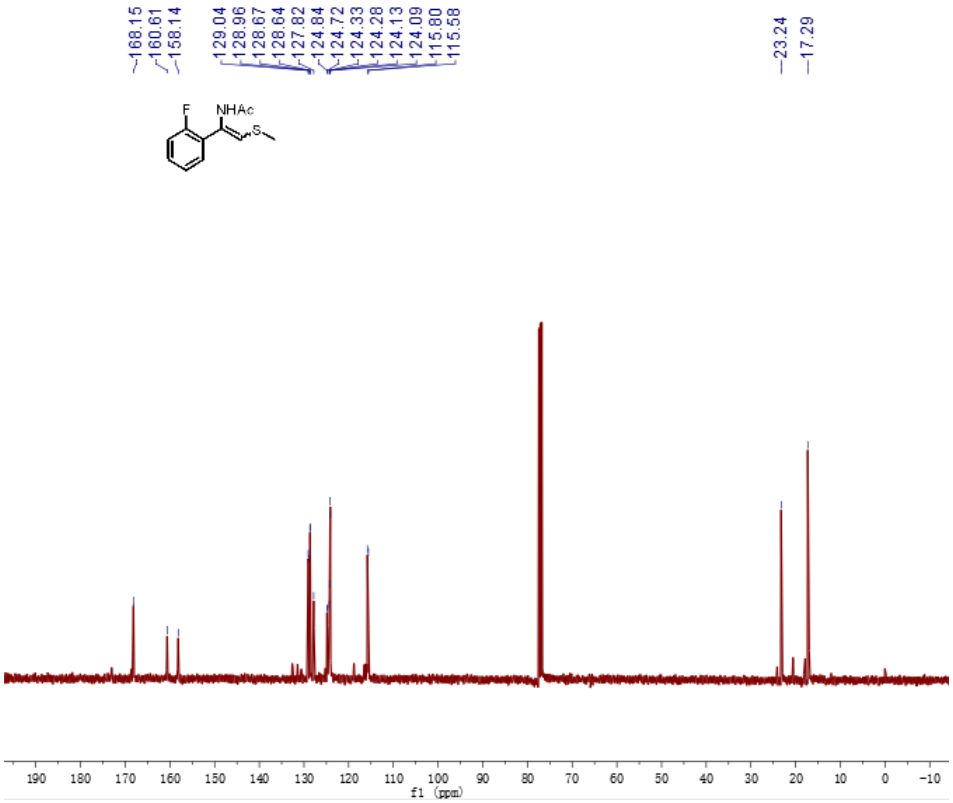
^{1}H NMR and ^{13}C NMR of 1k



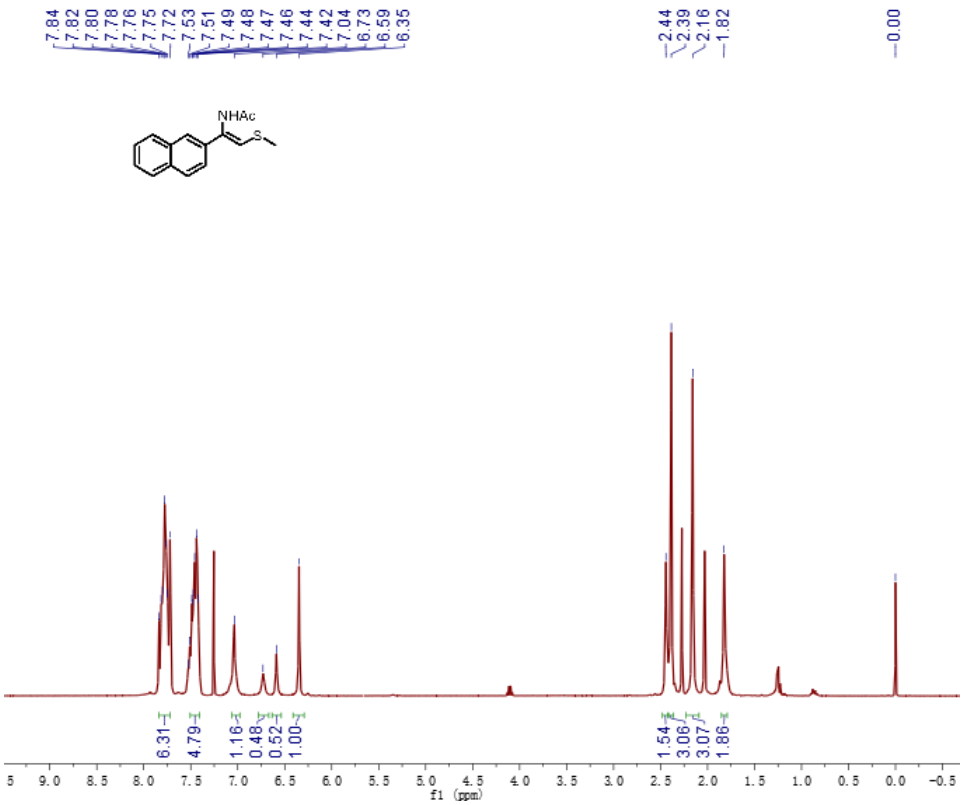


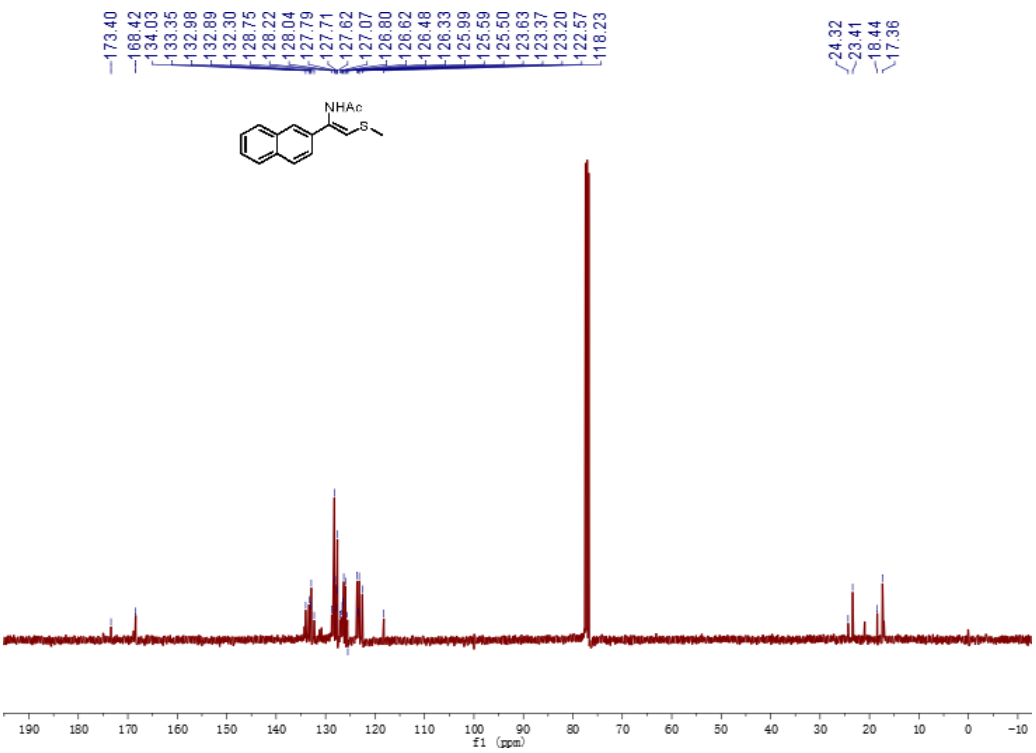
^{1}H NMR and ^{13}C NMR of 1l



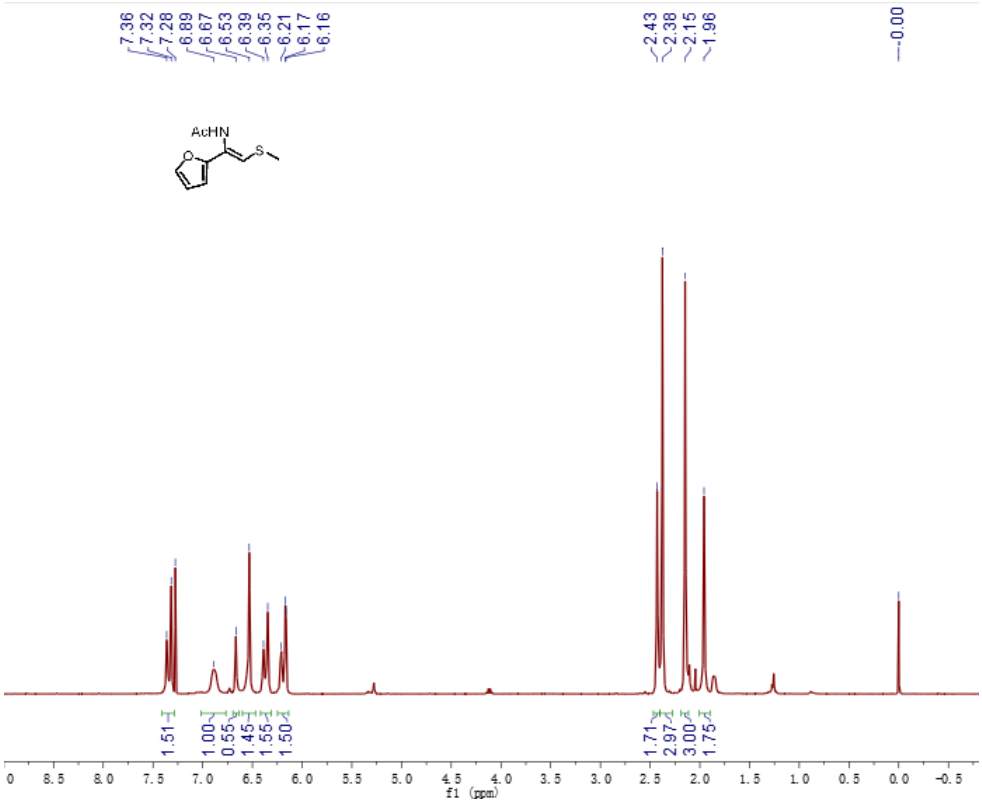


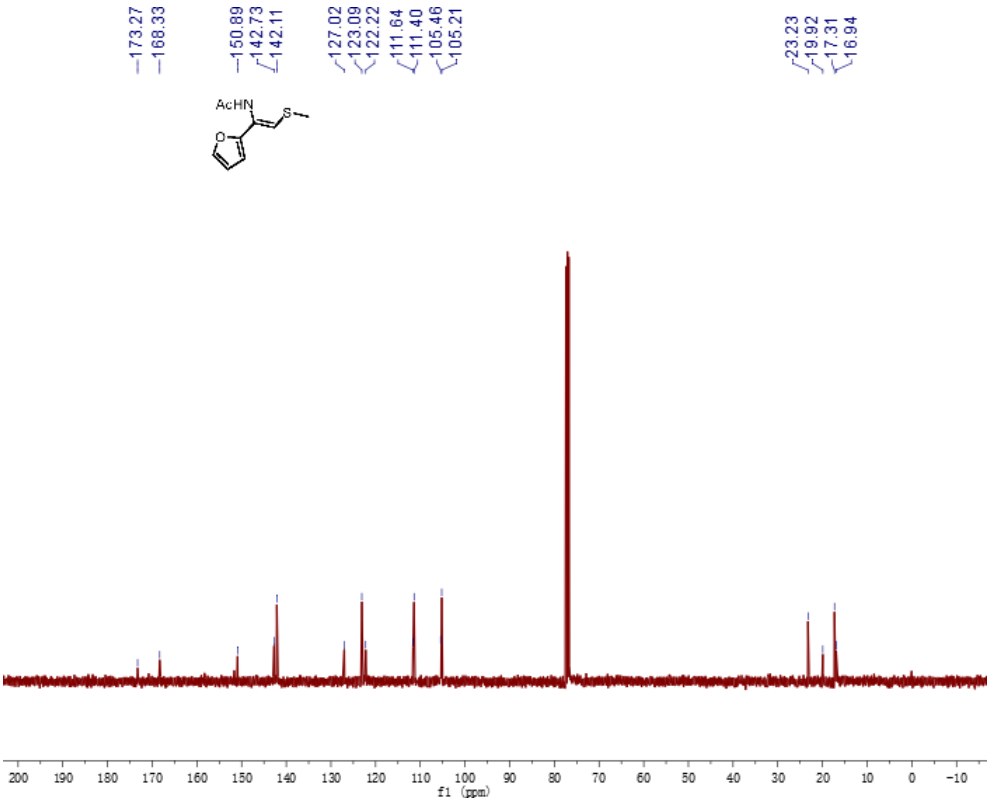
^{1}H NMR and ^{13}C NMR of 1m



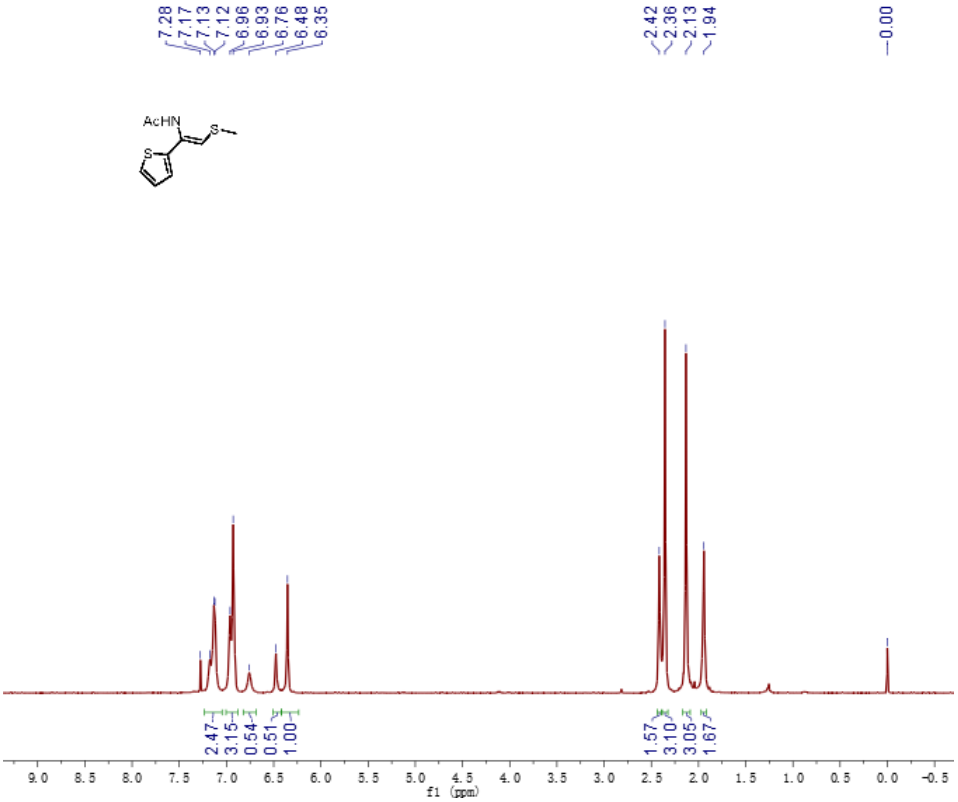


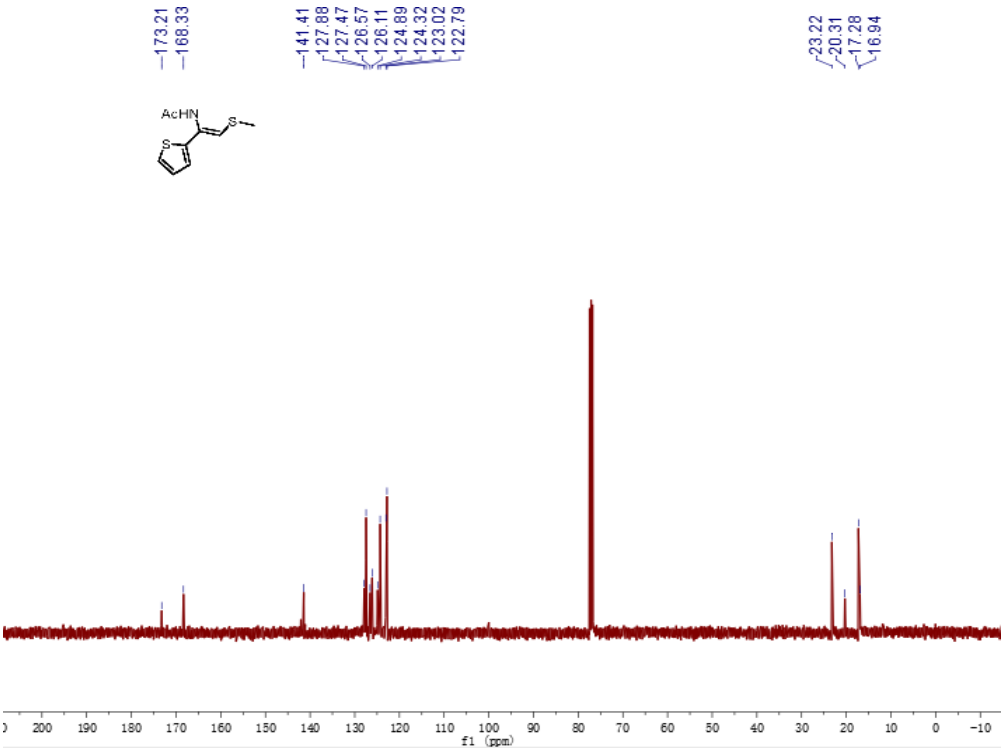
^{1}H NMR and ^{13}C NMR of 1n



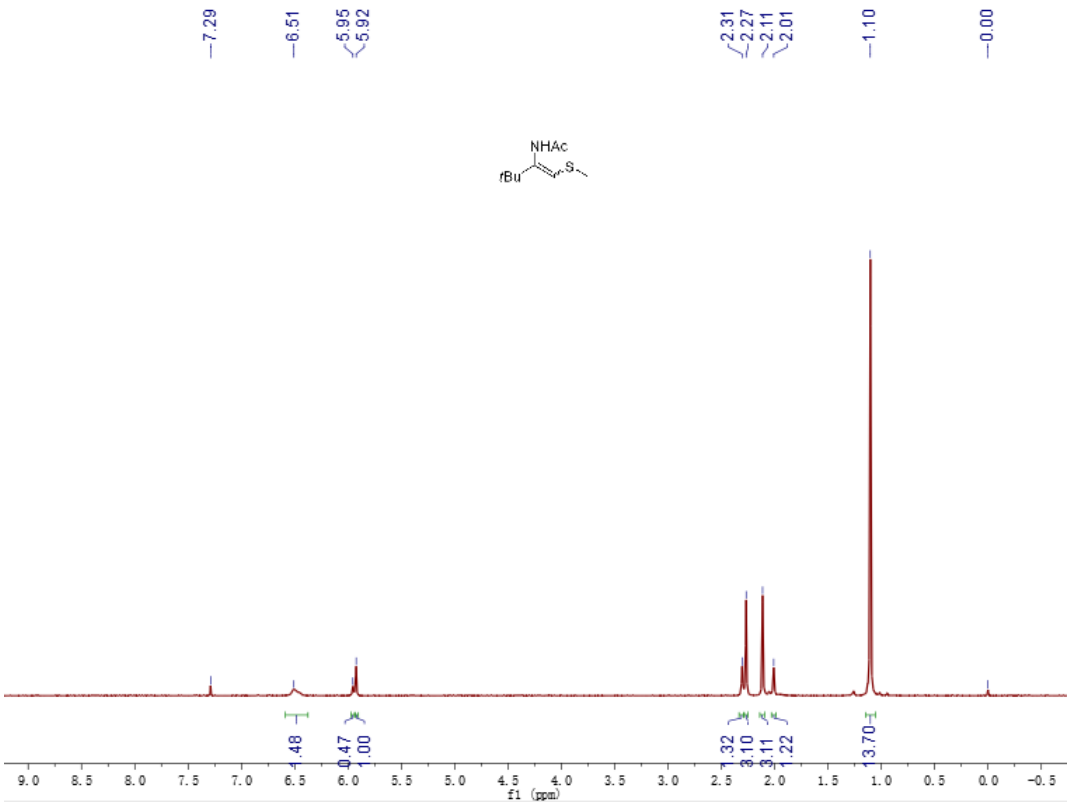


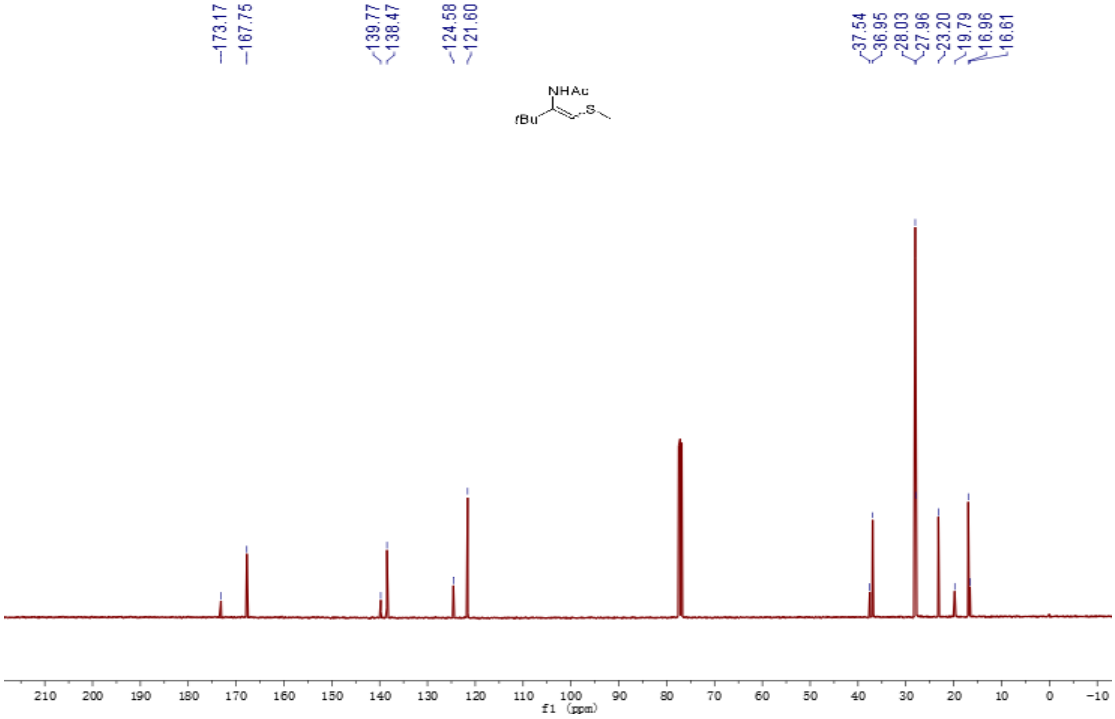
^{1}H NMR and ^{13}C NMR of 1o



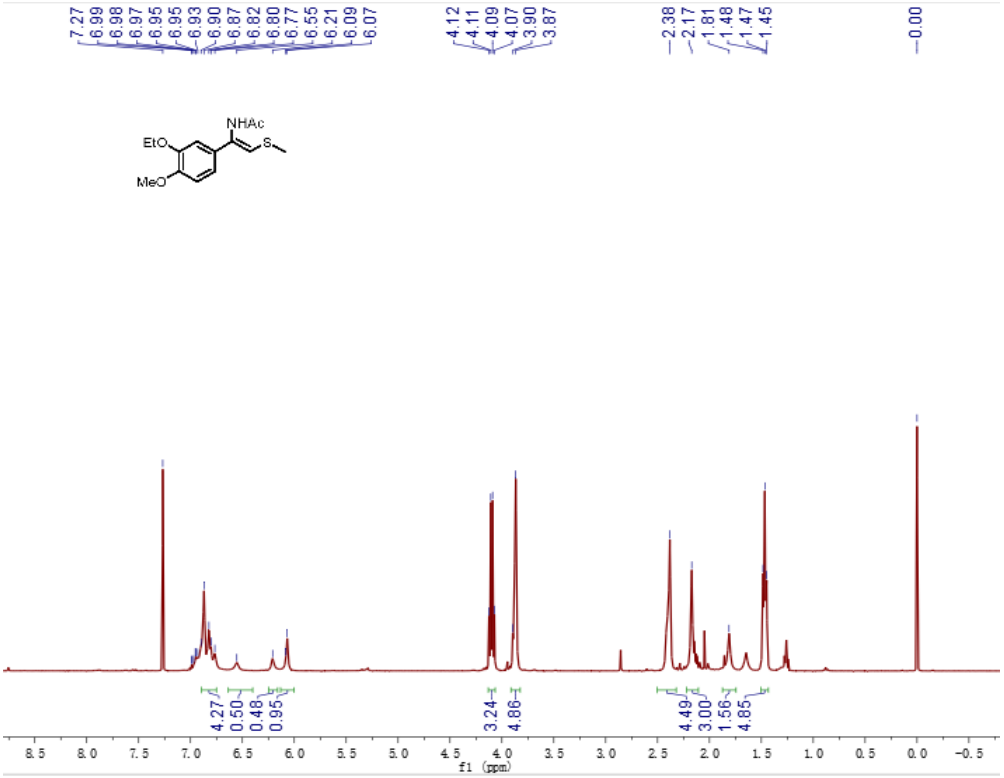


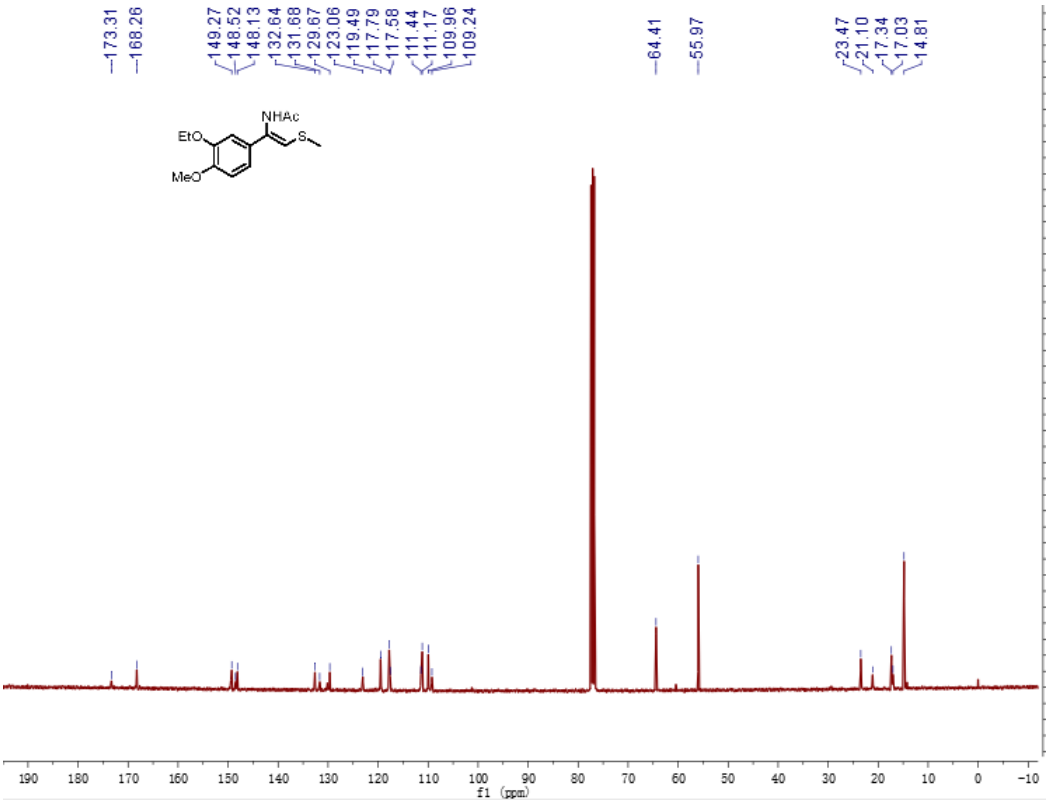
^{1}H NMR and ^{13}C NMR of 1p



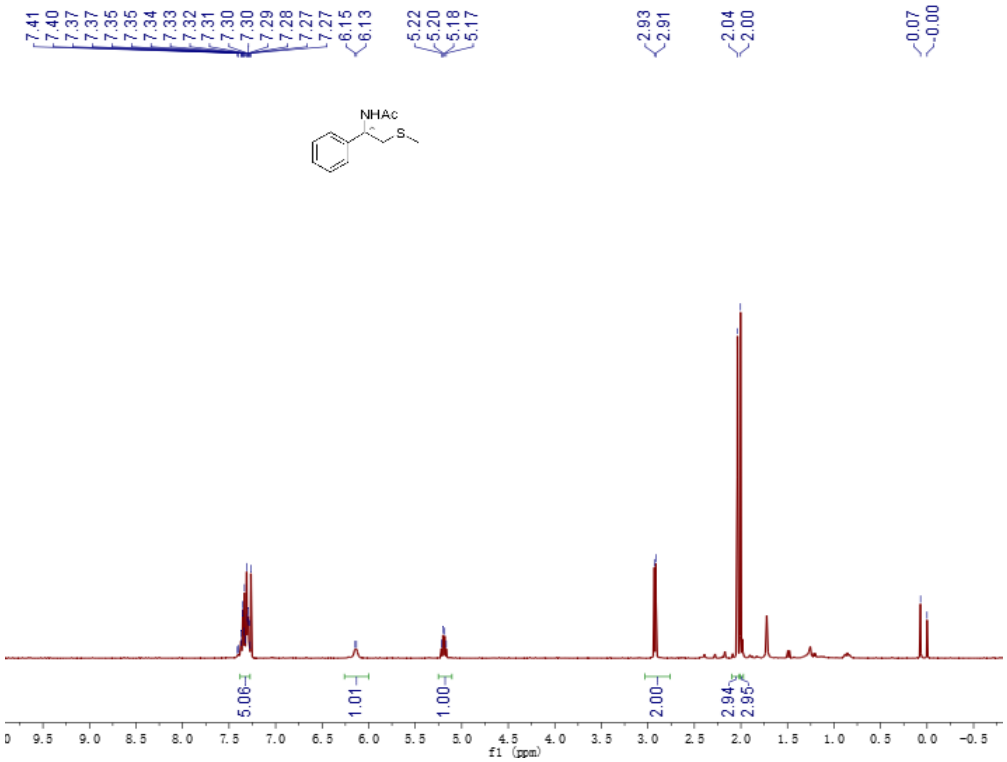


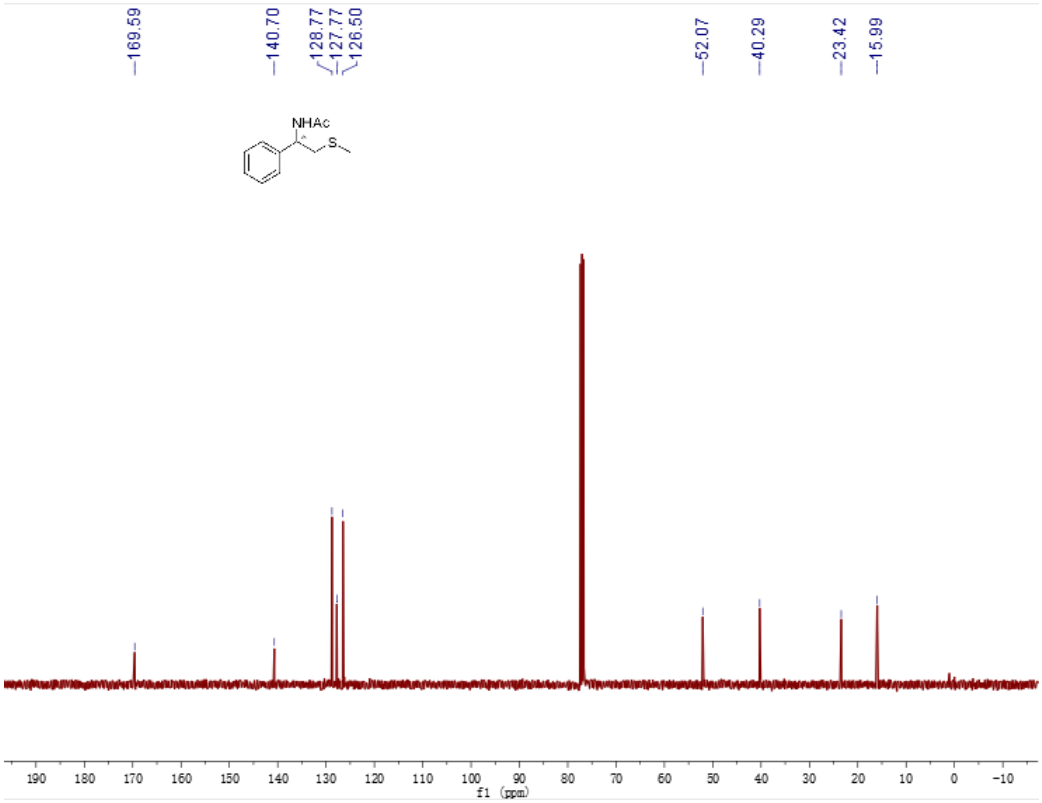
^{1}H NMR and ^{13}C NMR of 1q



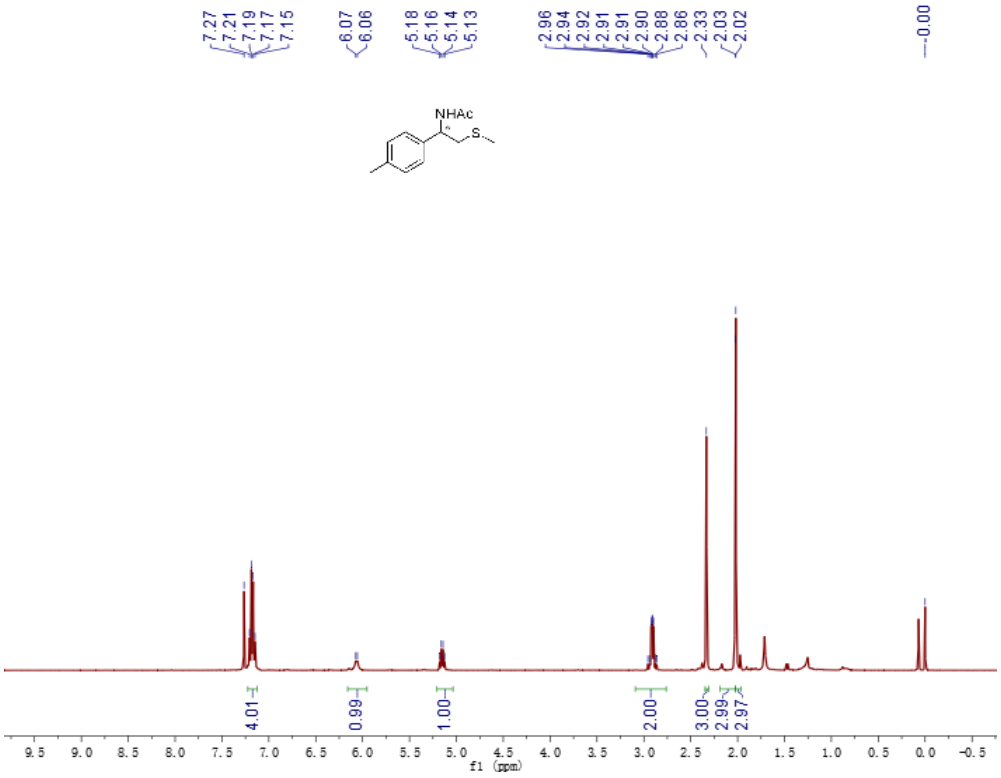


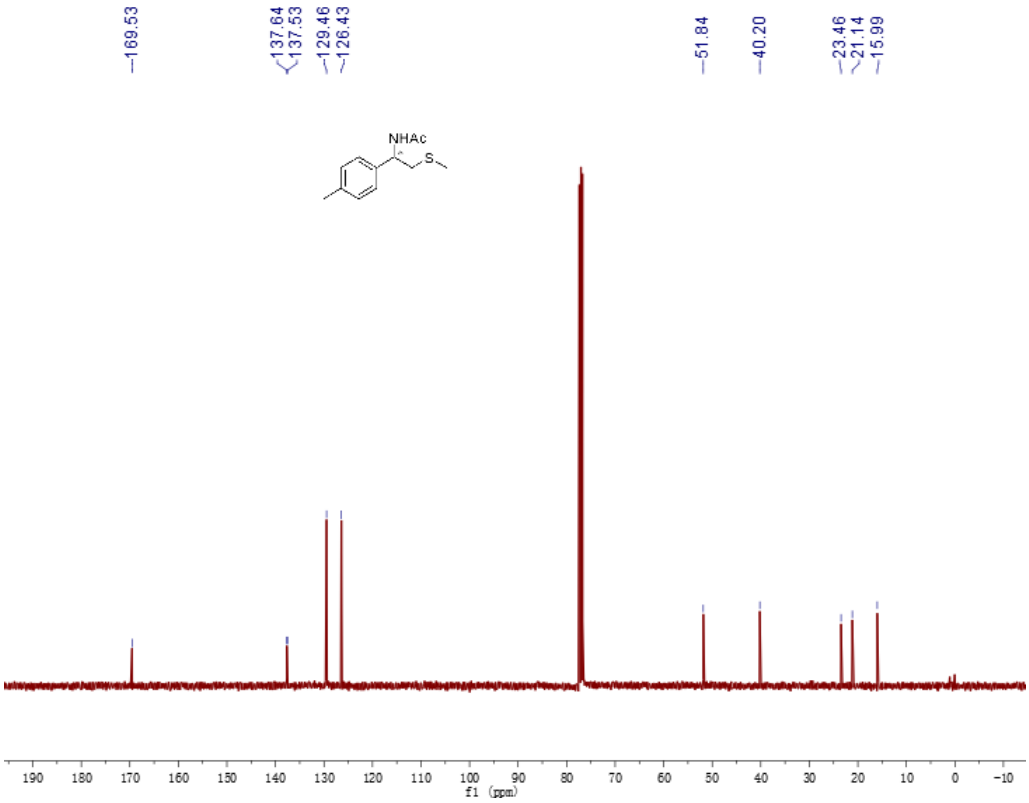
^{1}H NMR and ^{13}C NMR of 2a





^{1}H NMR and ^{13}C NMR of 2b





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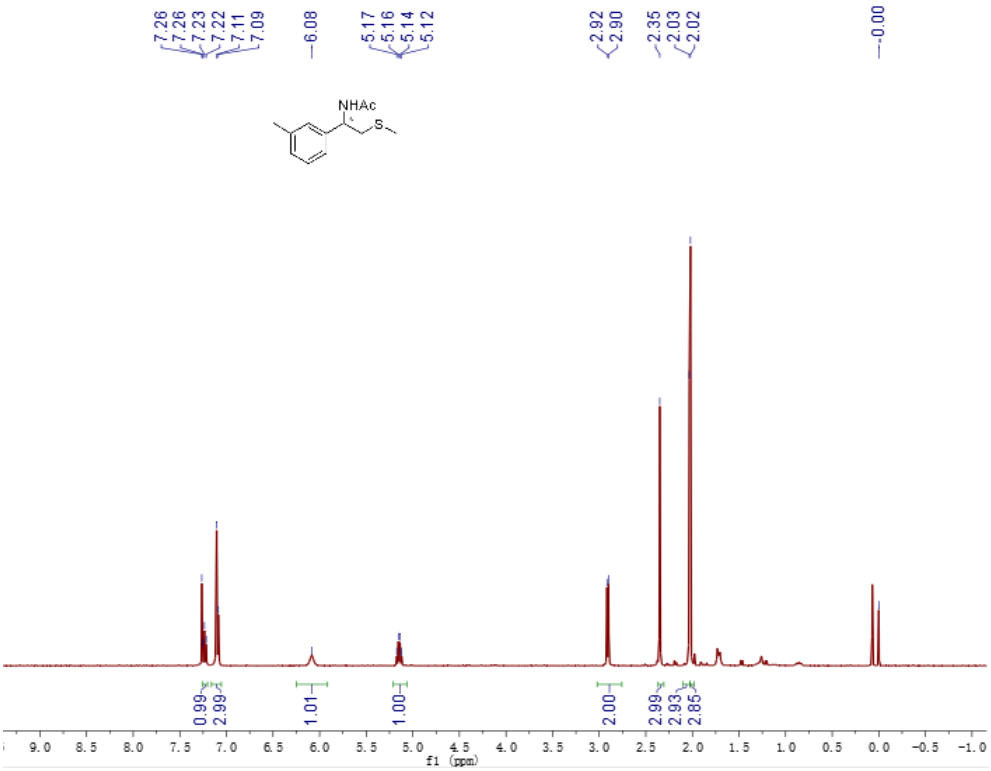
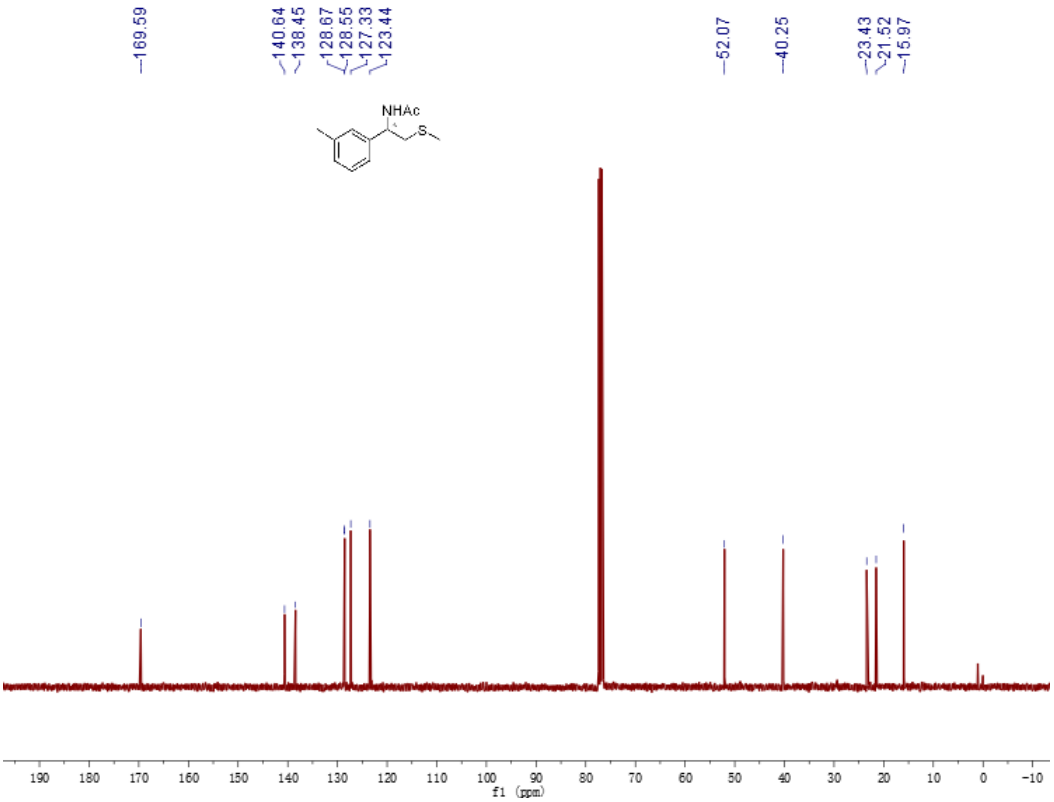
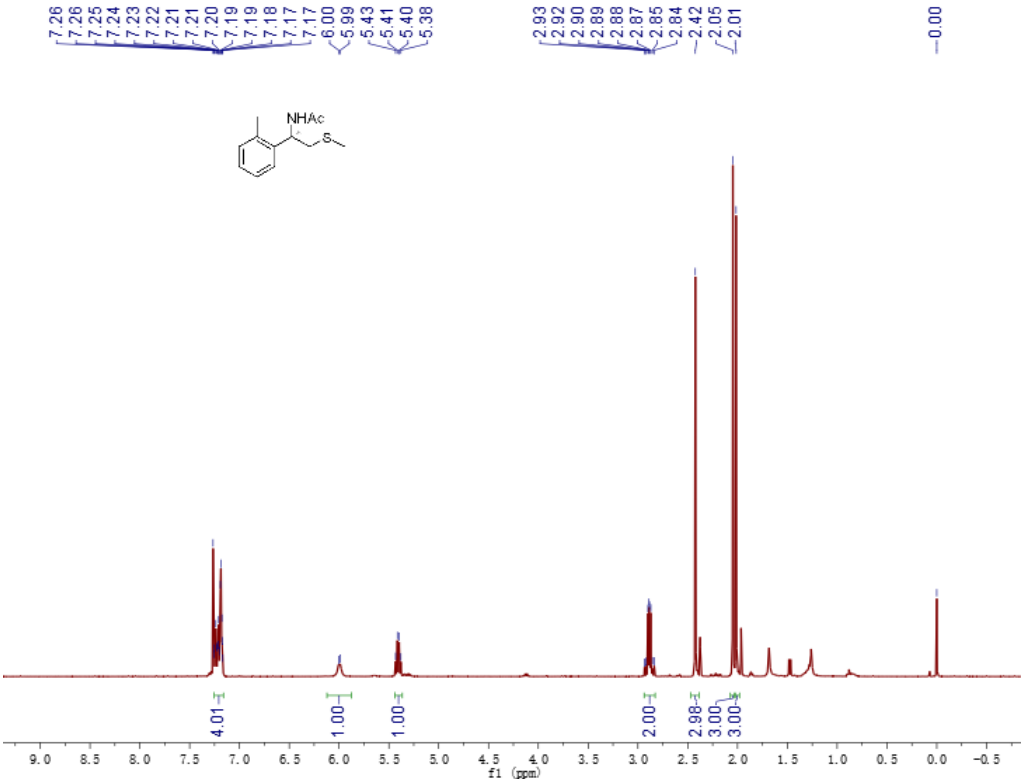
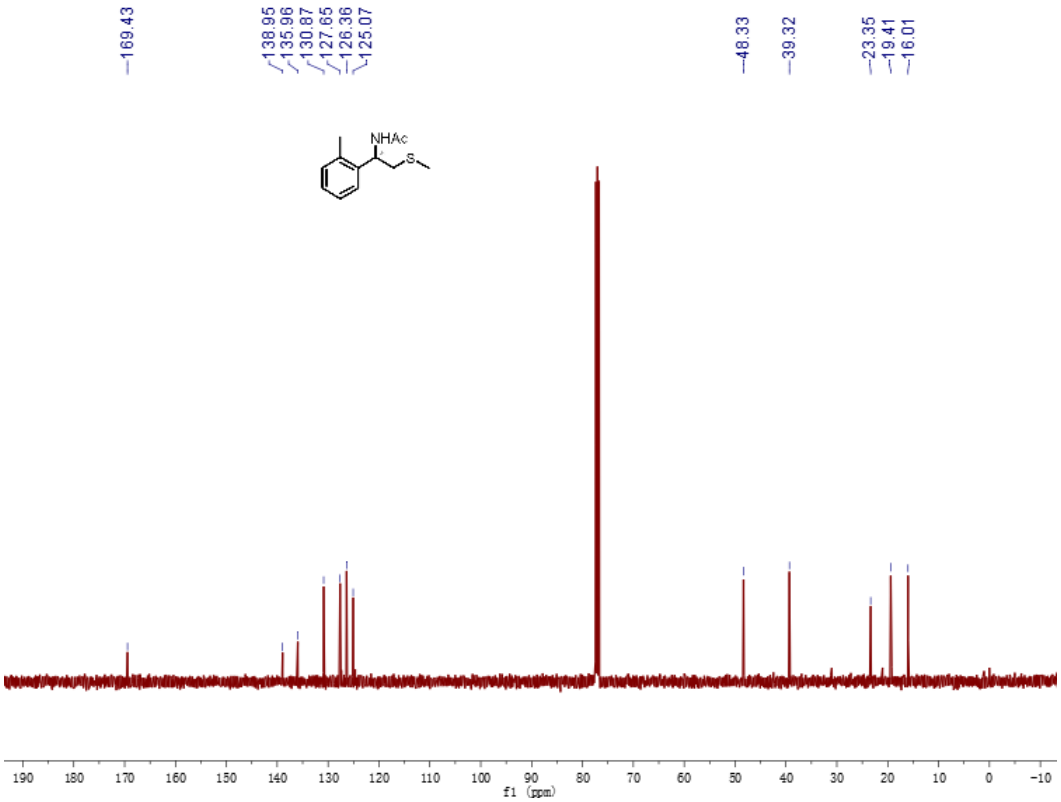




^{1}H NMR and ^{13}C NMR of 2d





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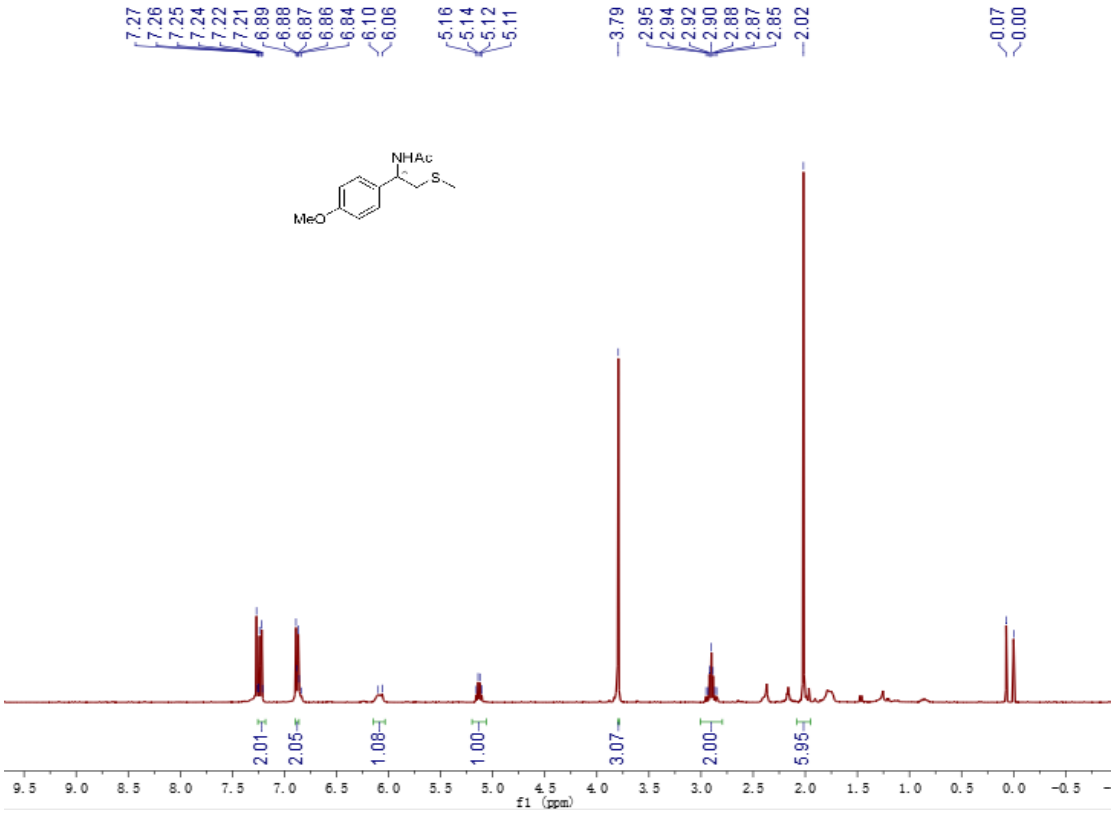

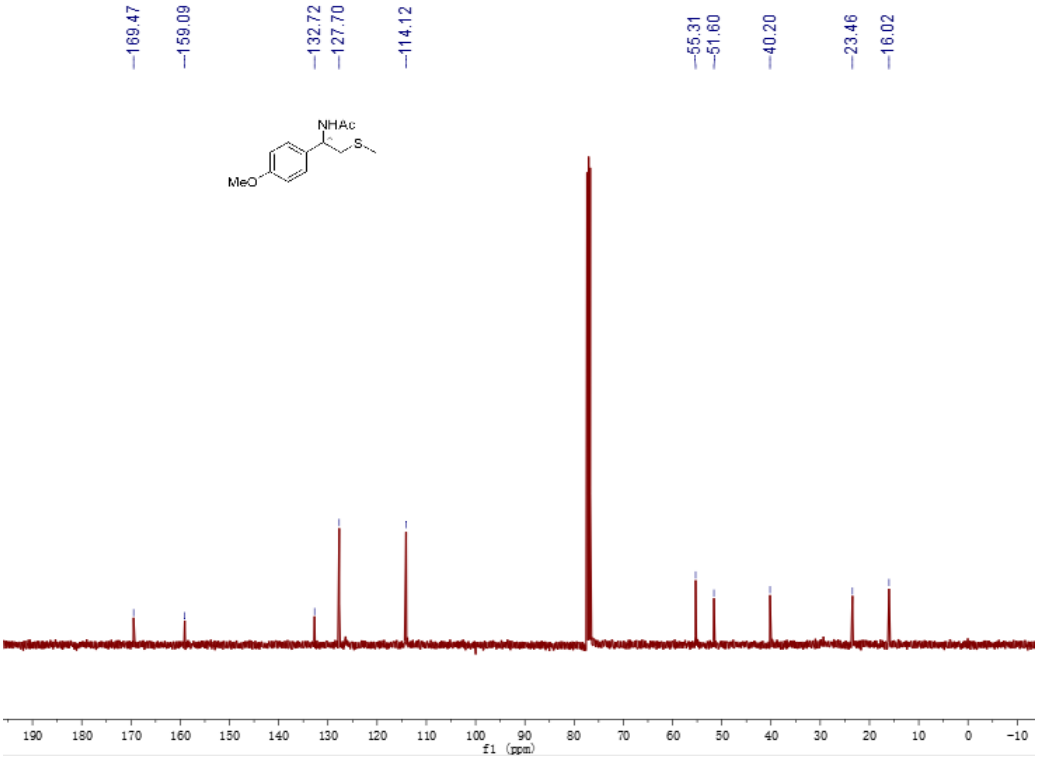

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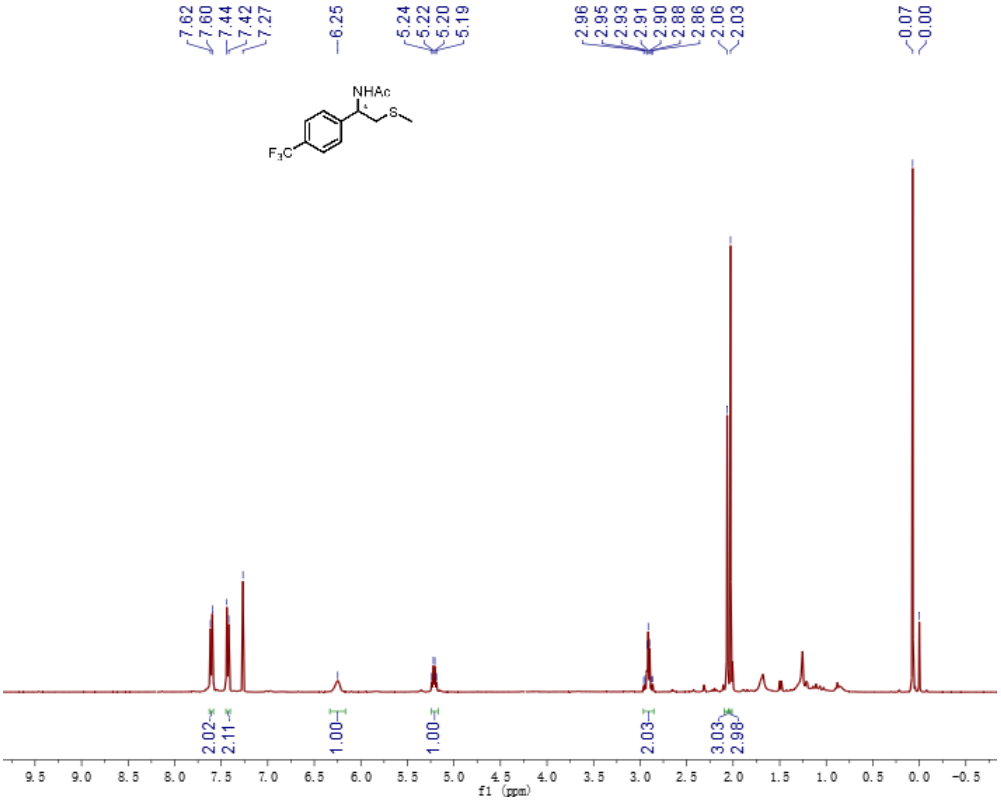
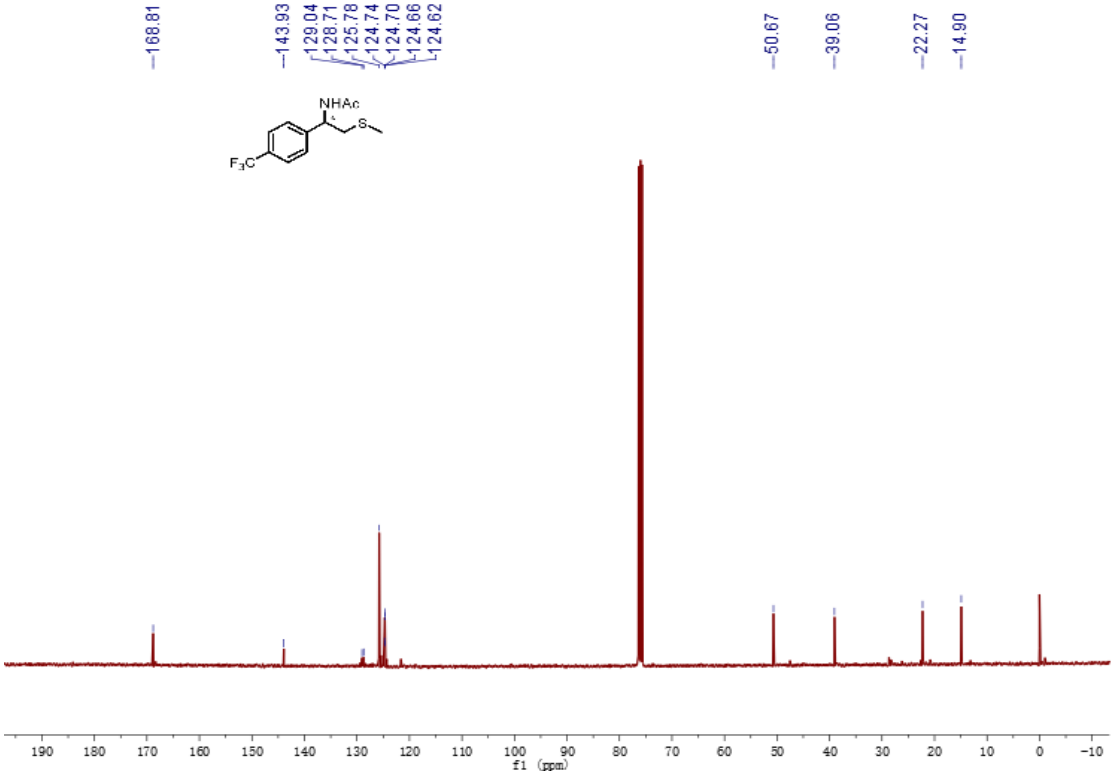
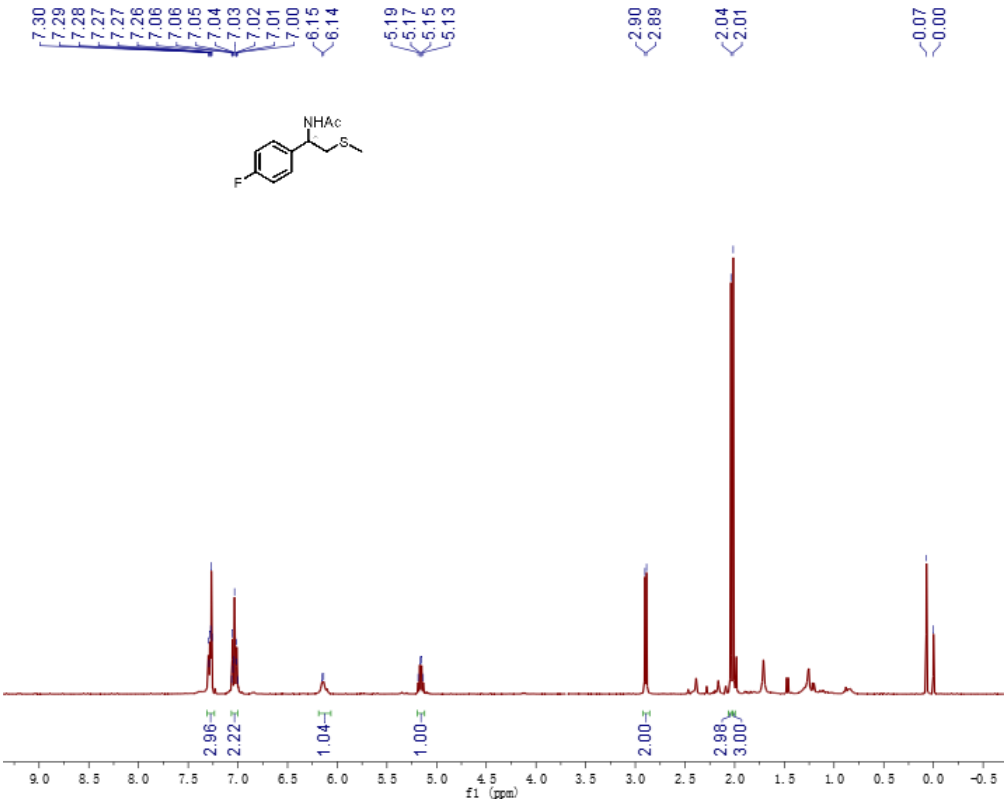
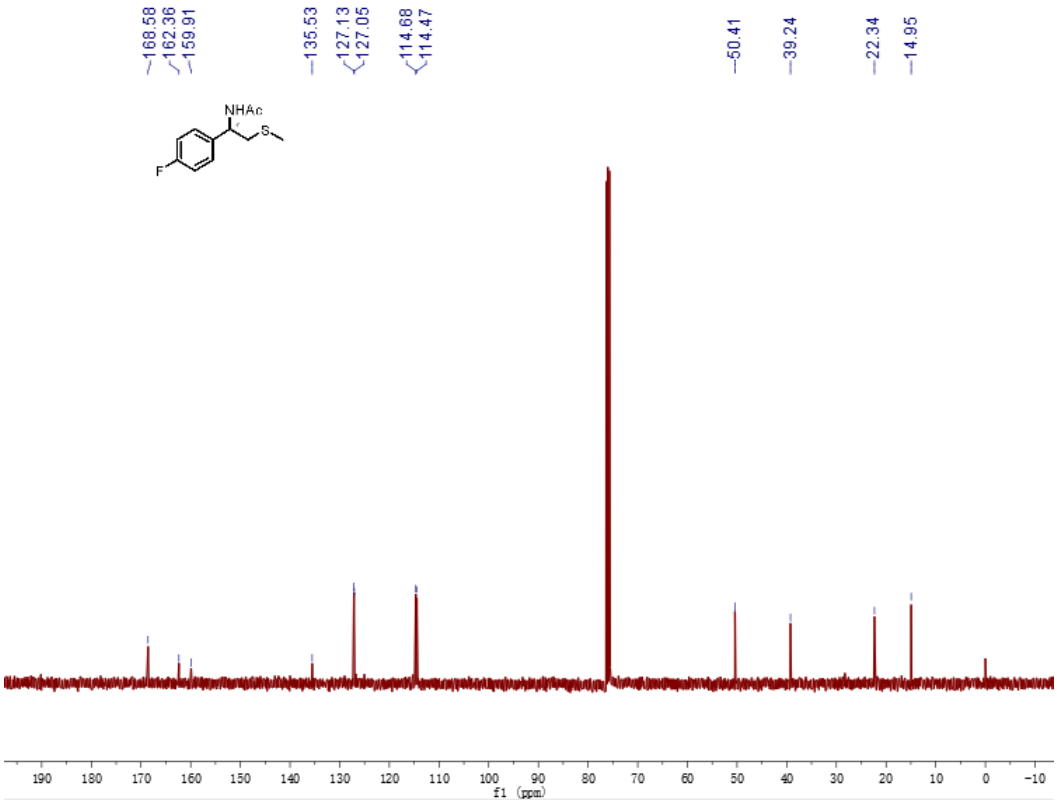


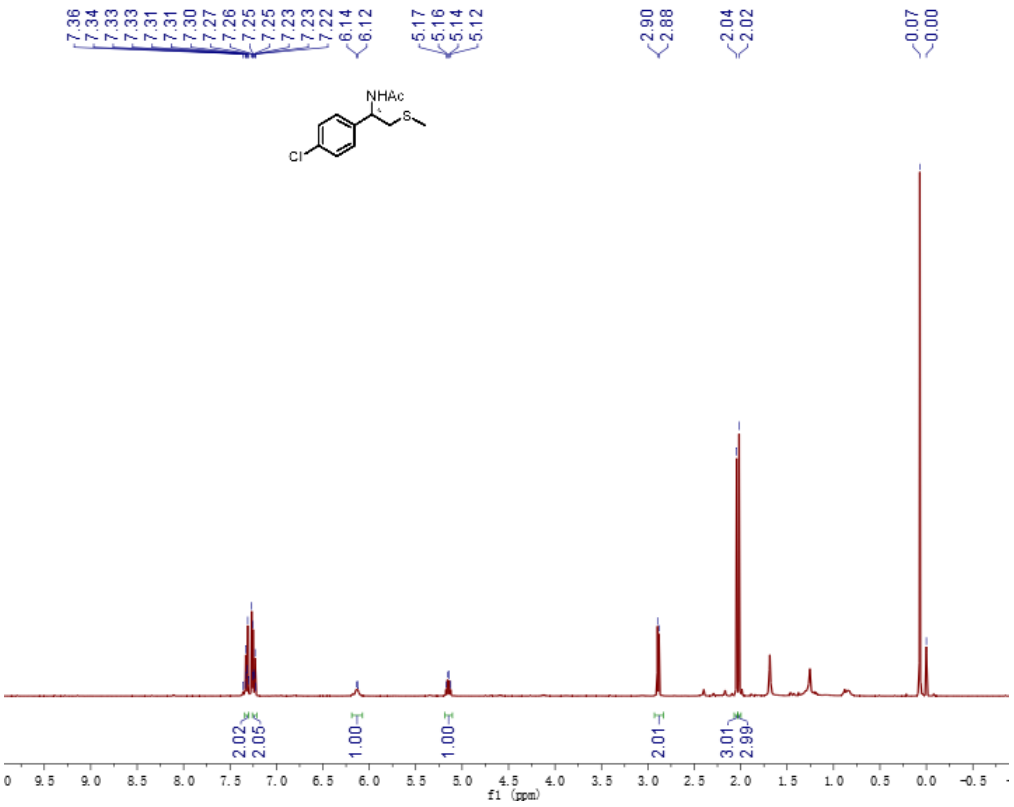


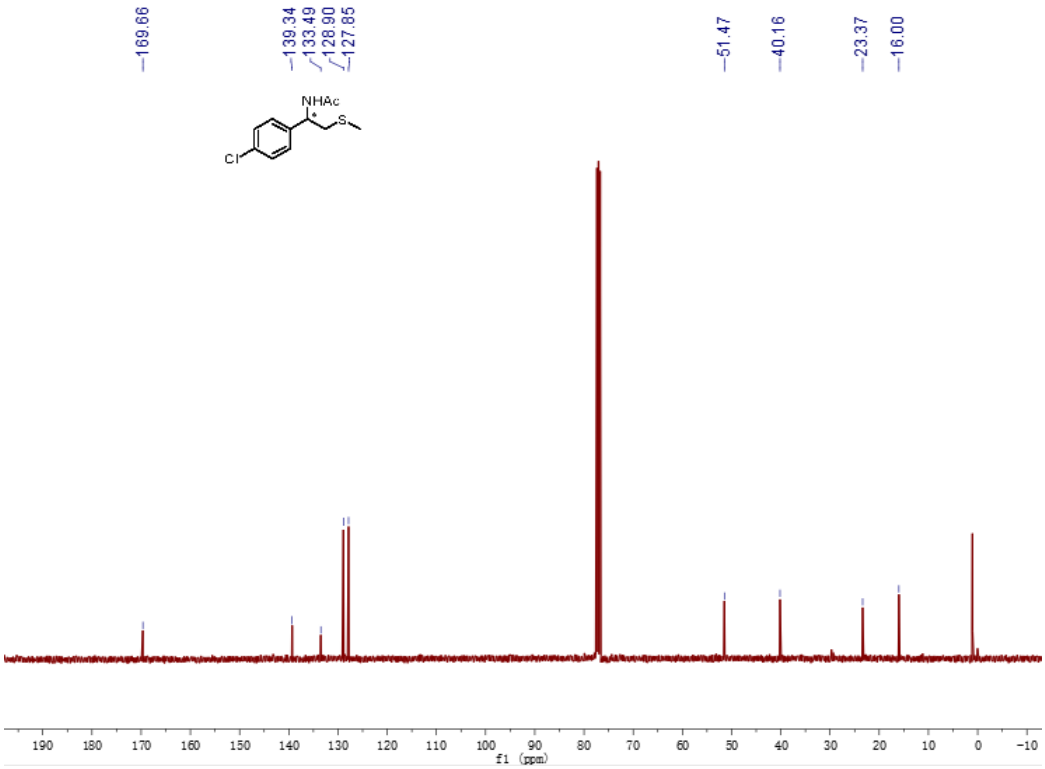
^{1}H NMR and ^{13}C NMR of 2g



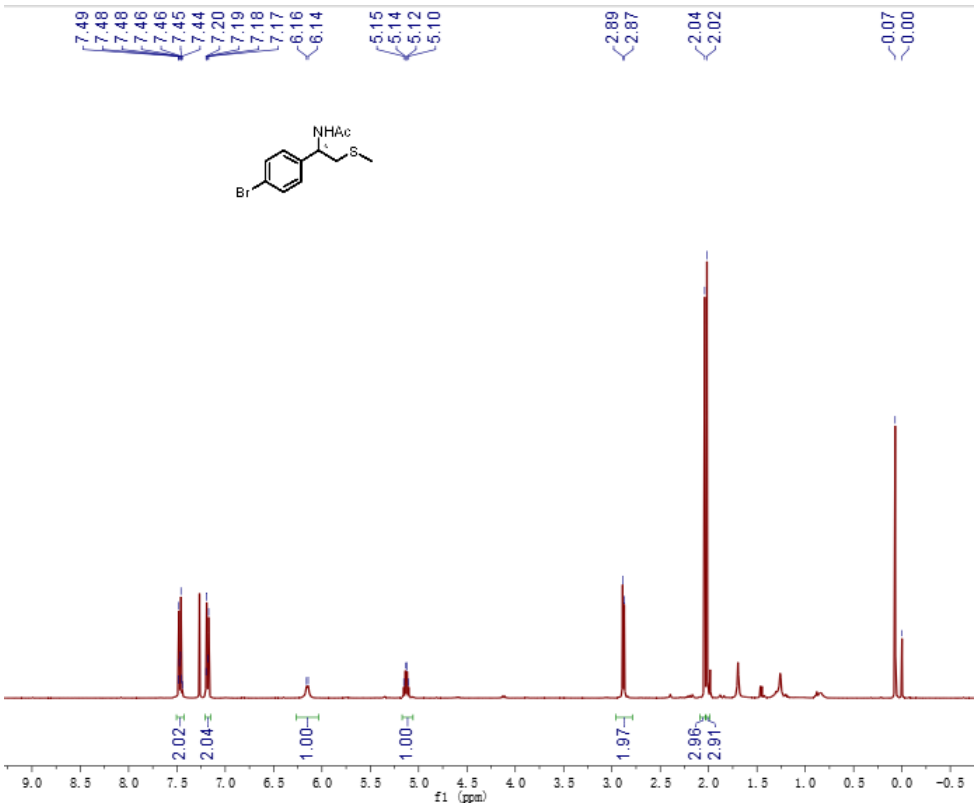


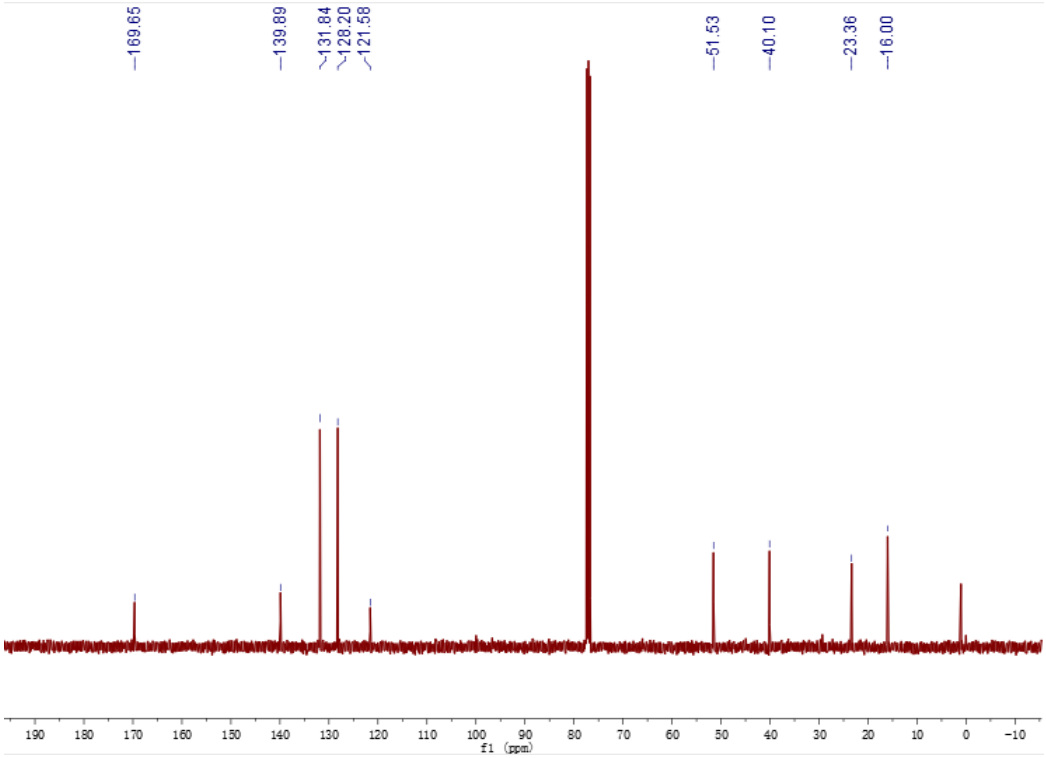
^{1}H NMR and ^{13}C NMR of 2h



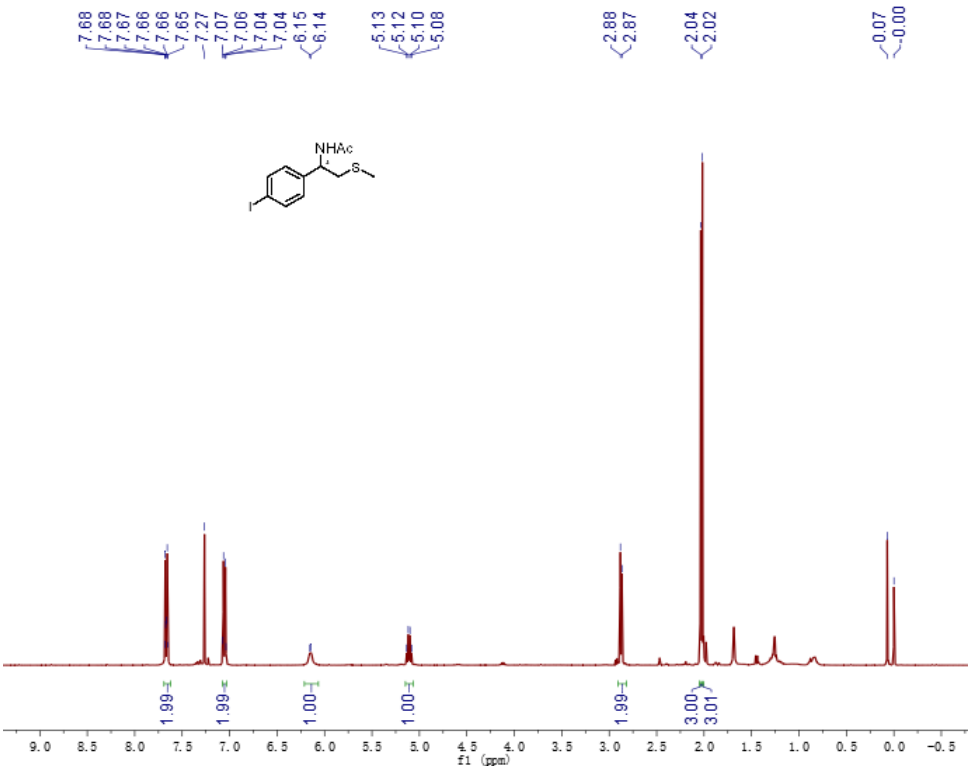


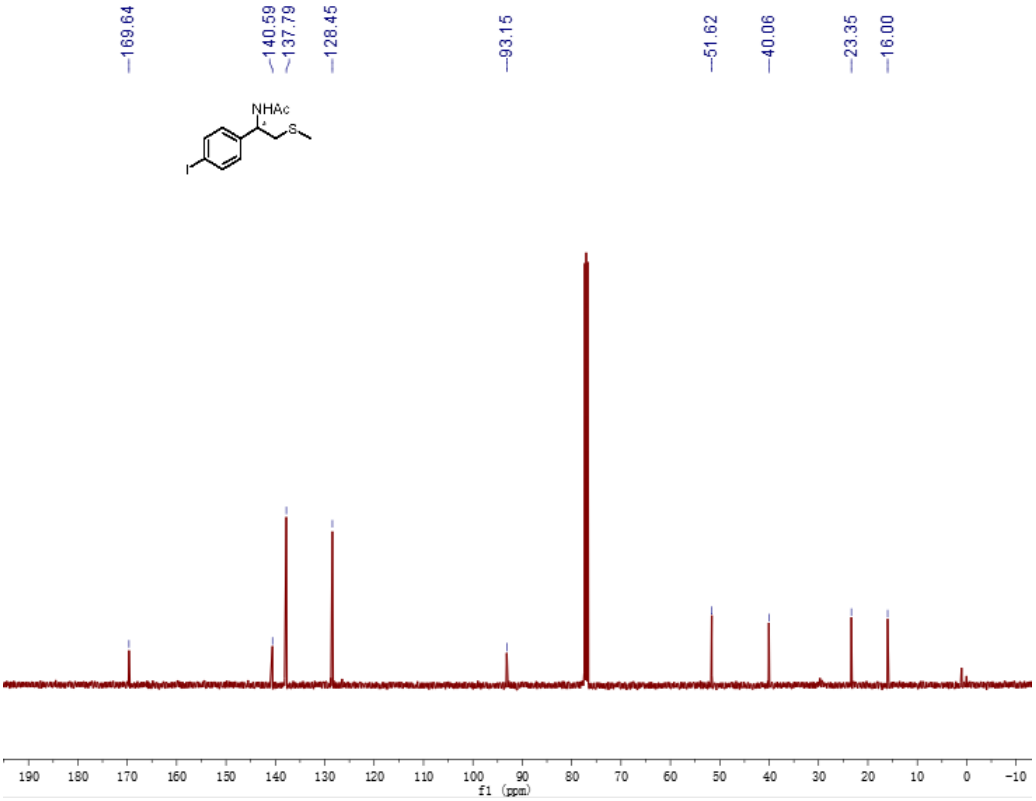
^{1}H NMR and ^{13}C NMR of 2i



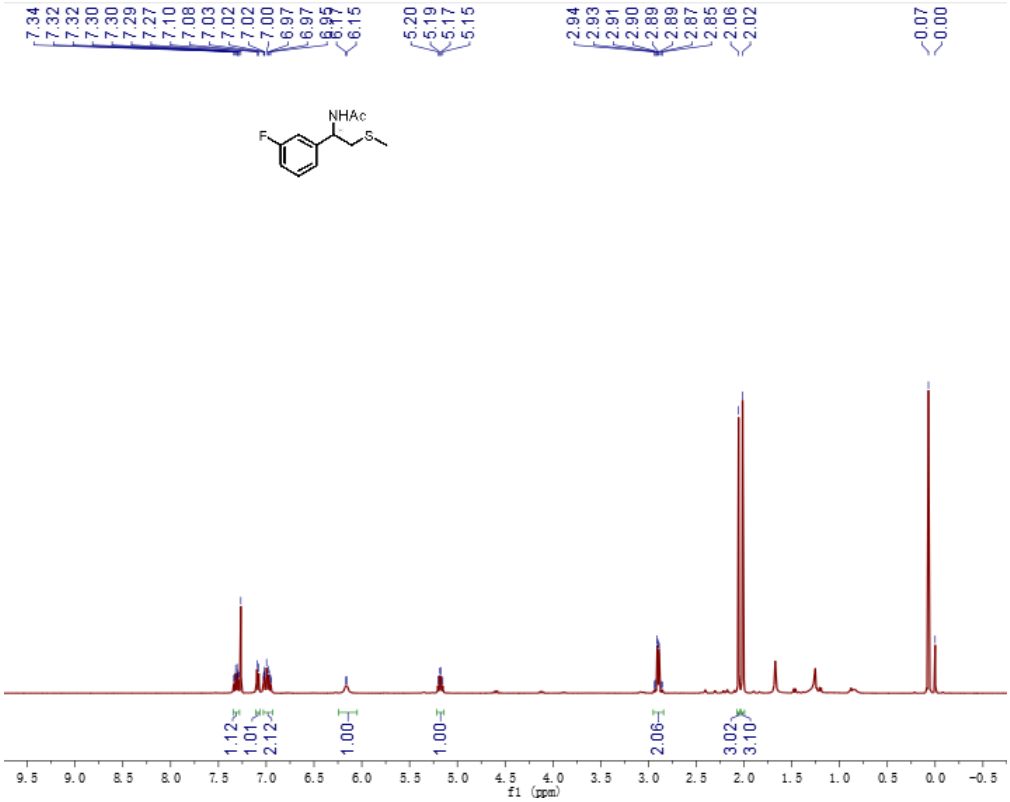


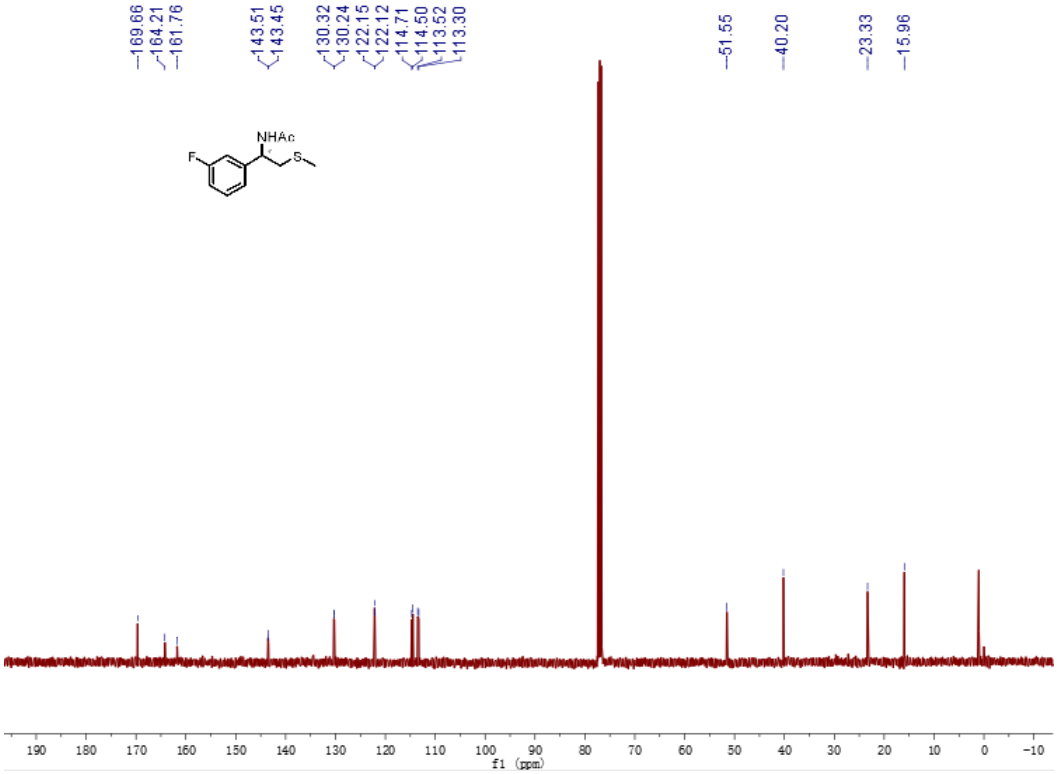
^{1}H NMR and ^{13}C NMR of 2j



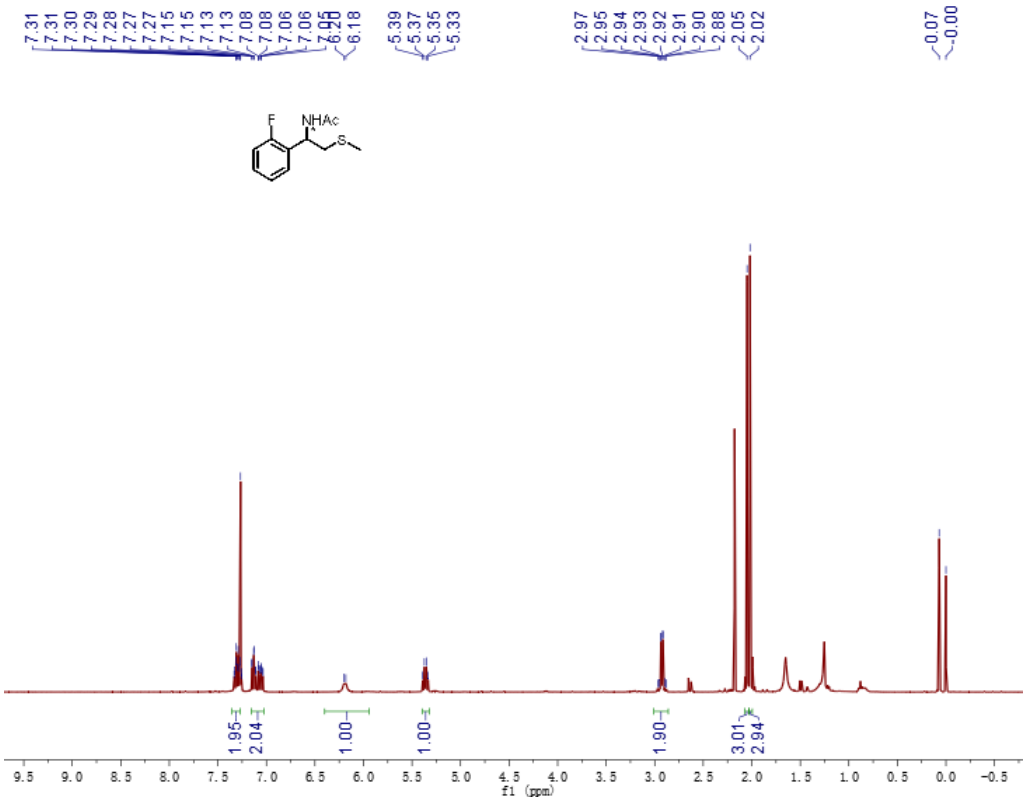


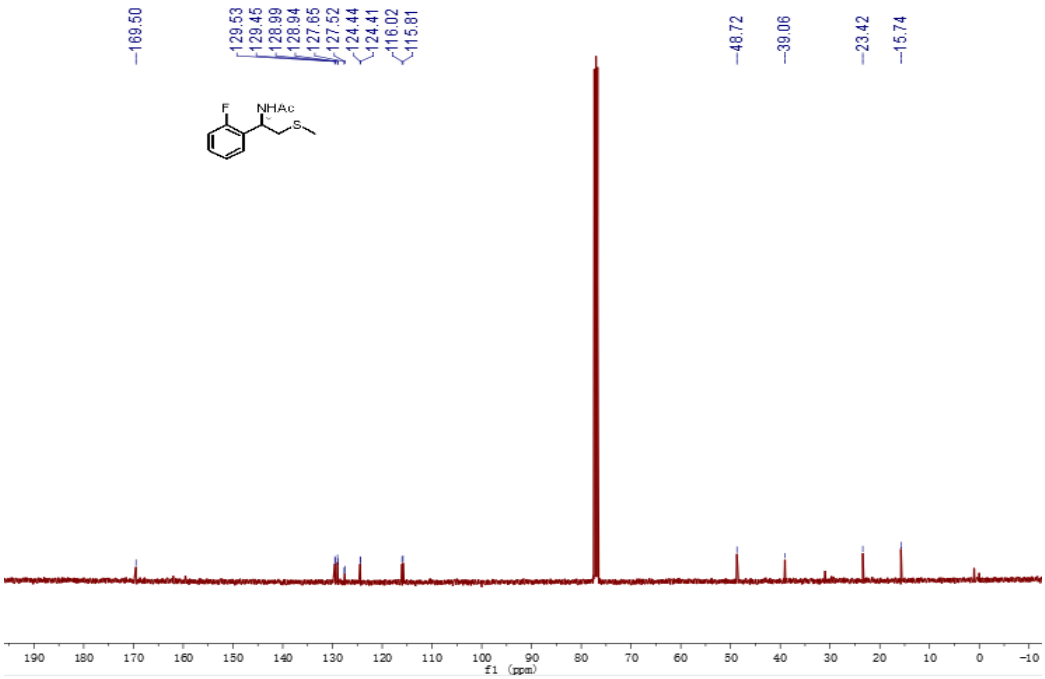
^{1}H NMR and ^{13}C NMR of 2k



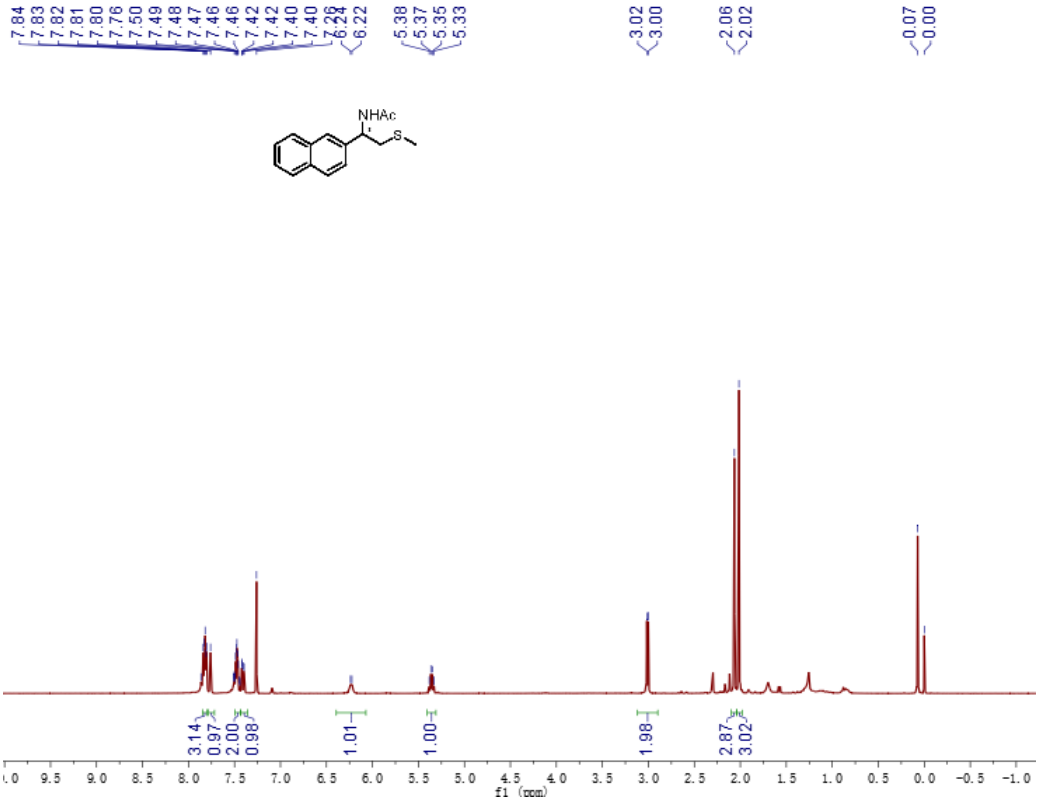


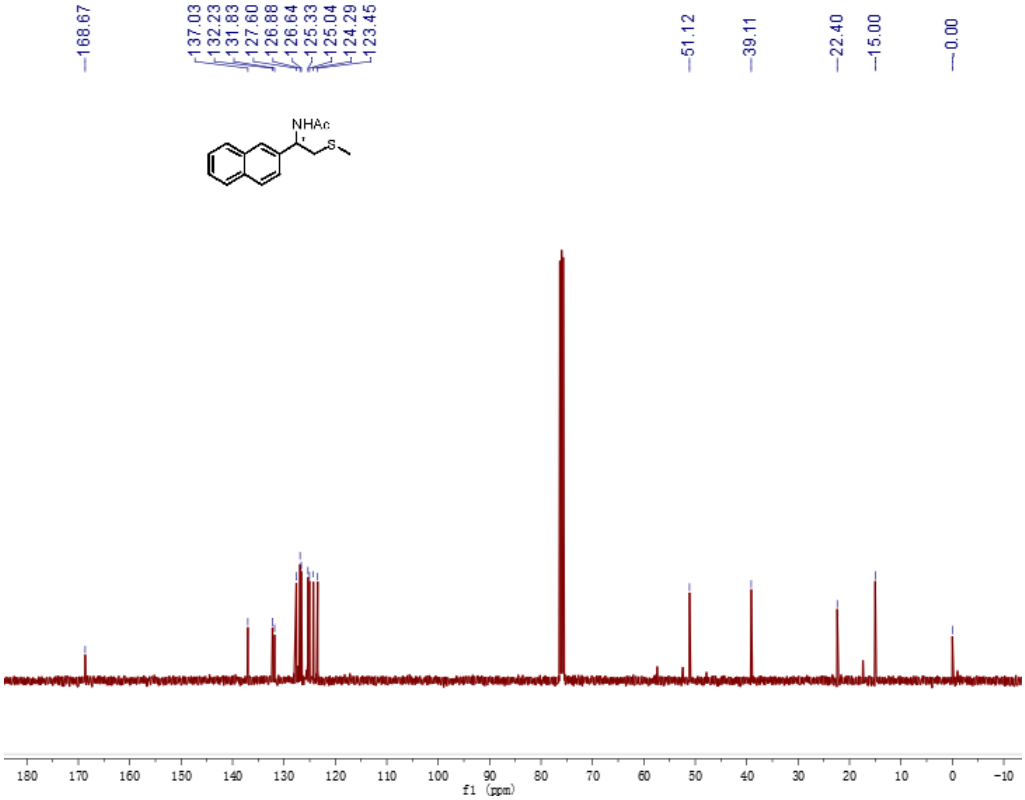
^{1}H NMR and ^{13}C NMR of 2l



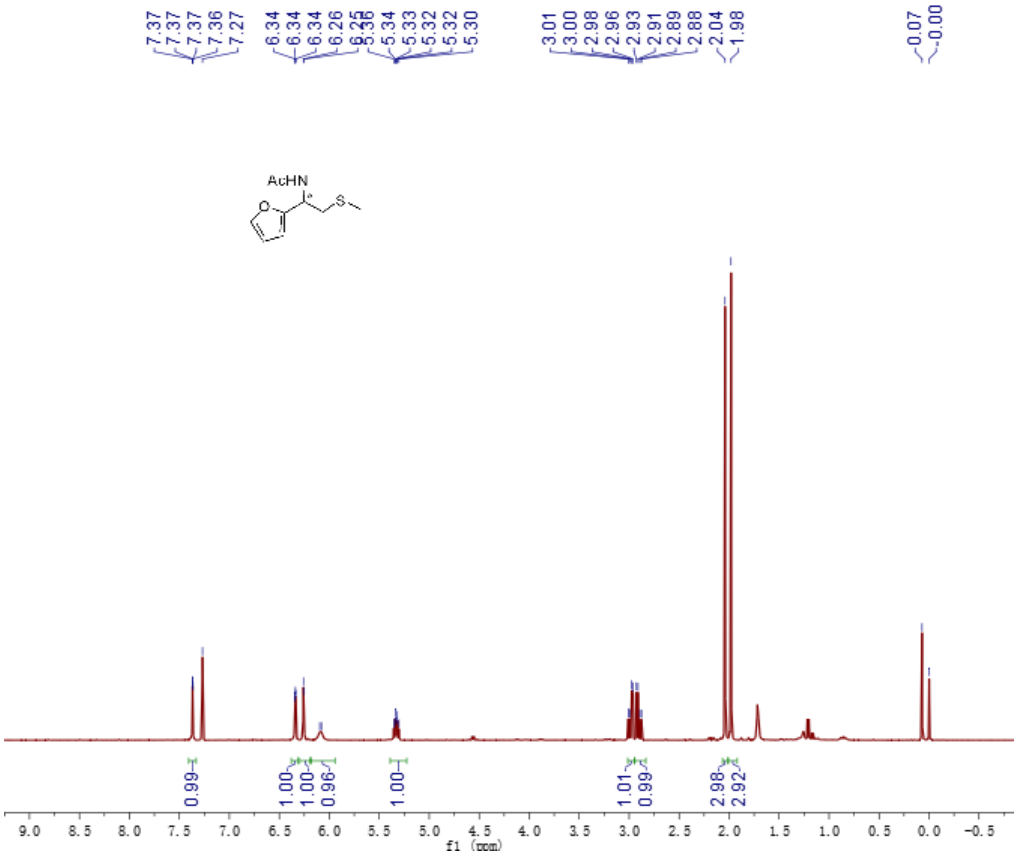


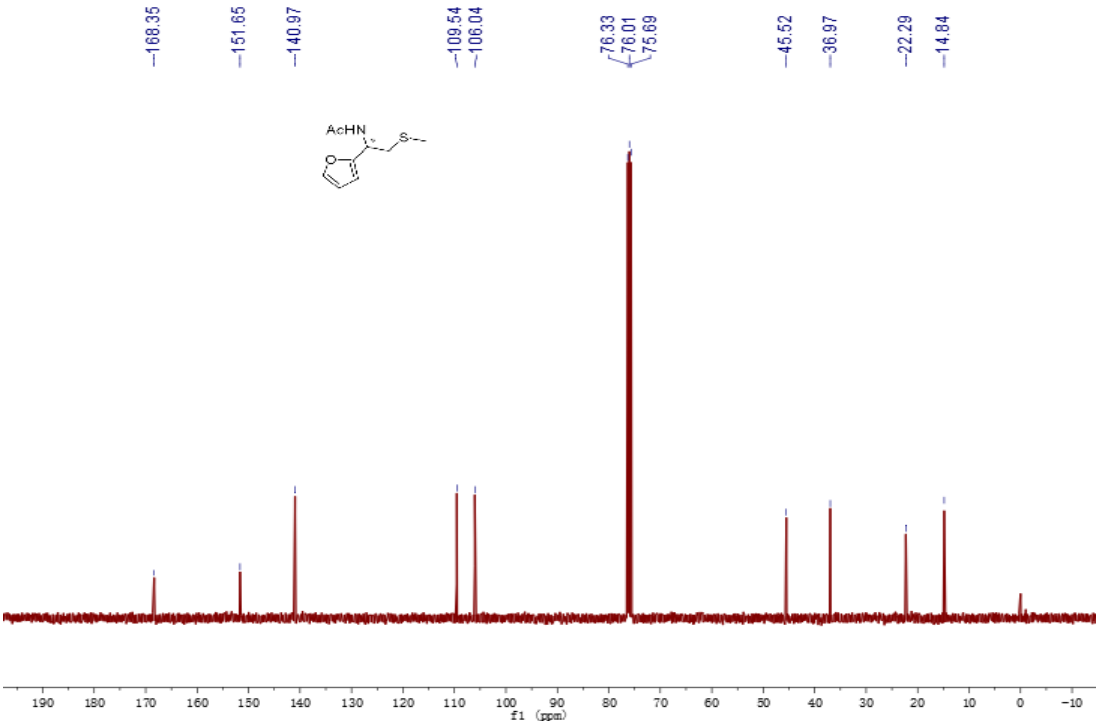
^{1}H NMR and ^{13}C NMR of 2m



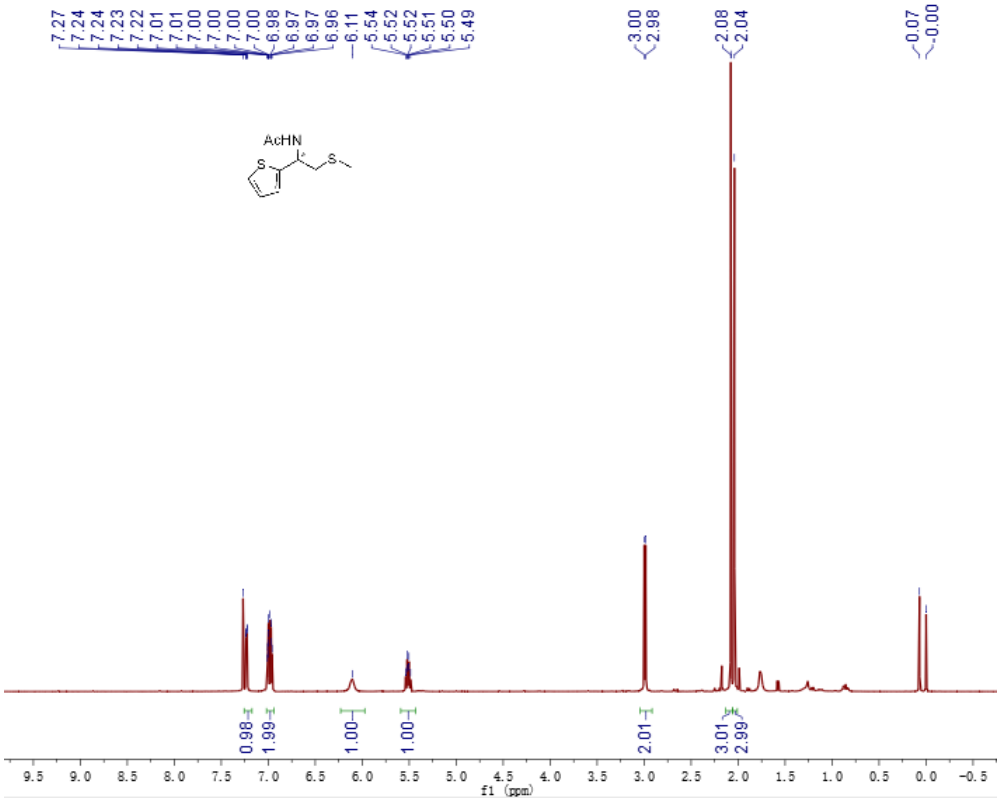


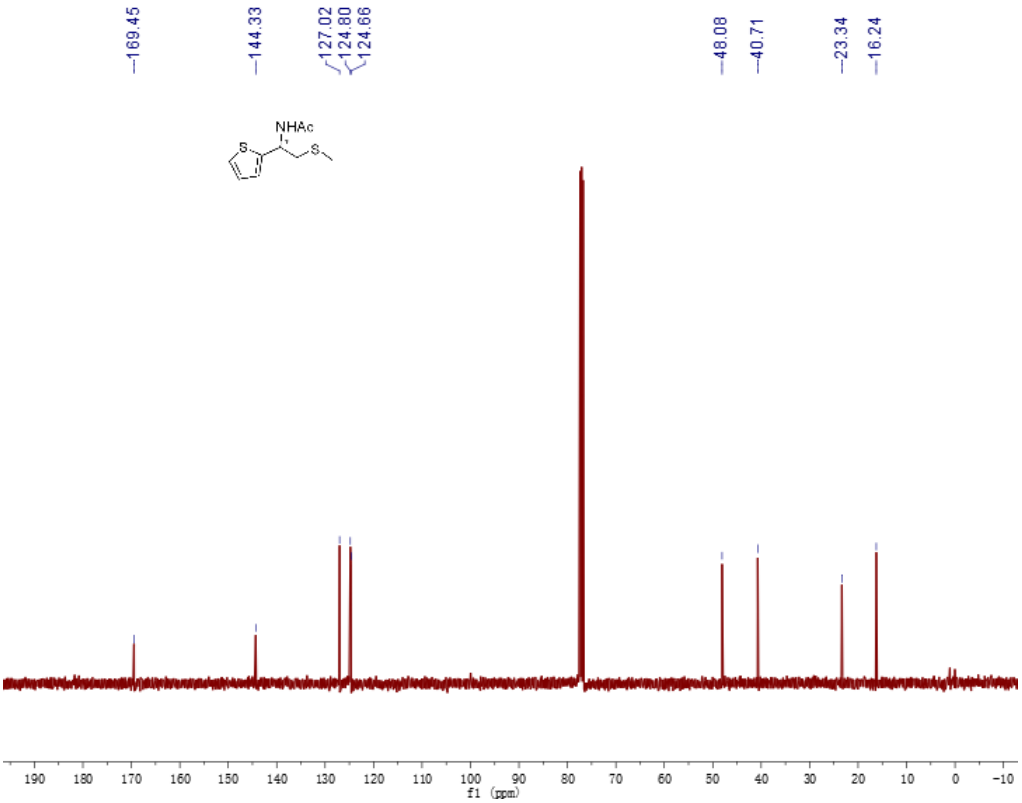
^{1}H NMR and ^{13}C NMR of 2n



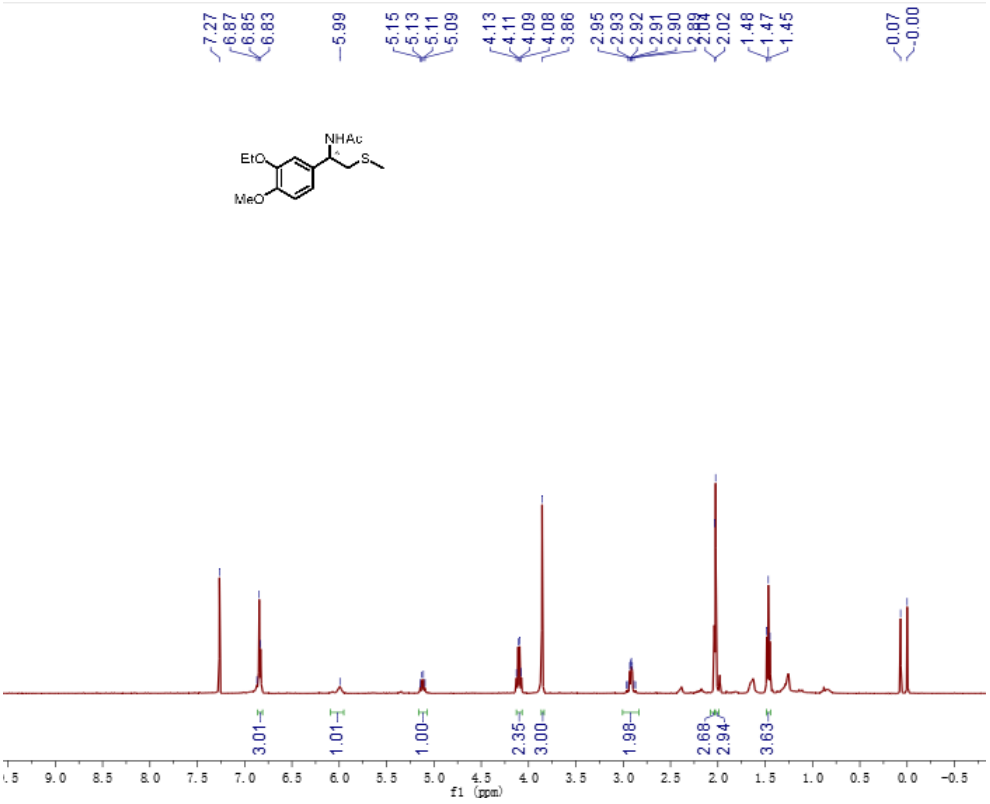


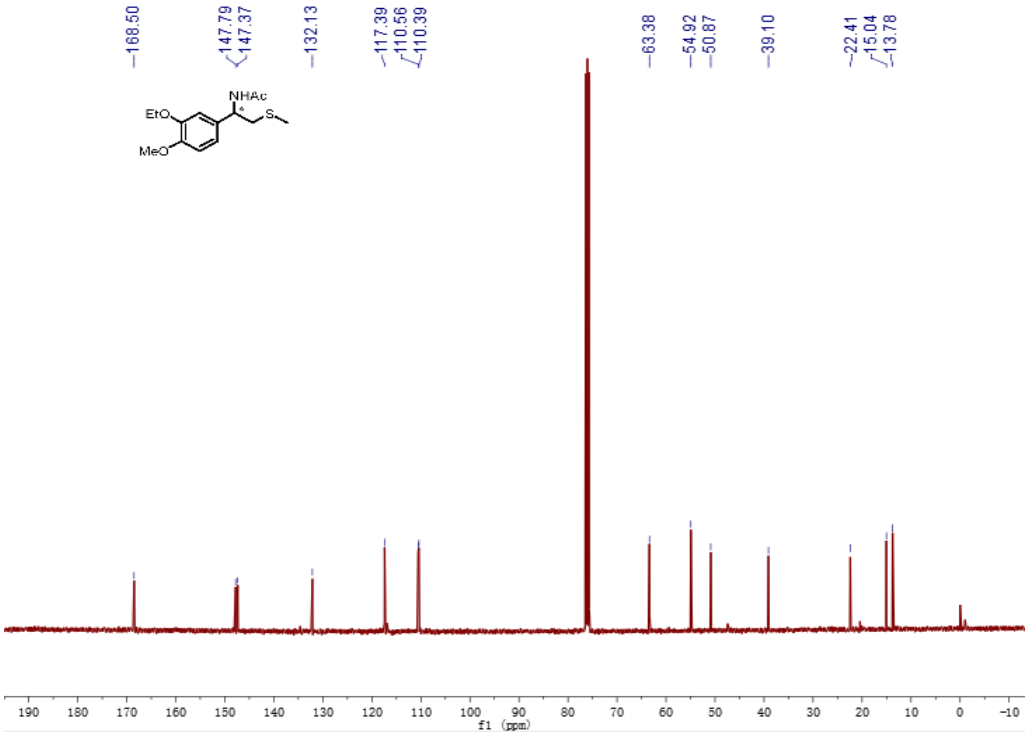
^{1}H NMR and ^{13}C NMR of 2o



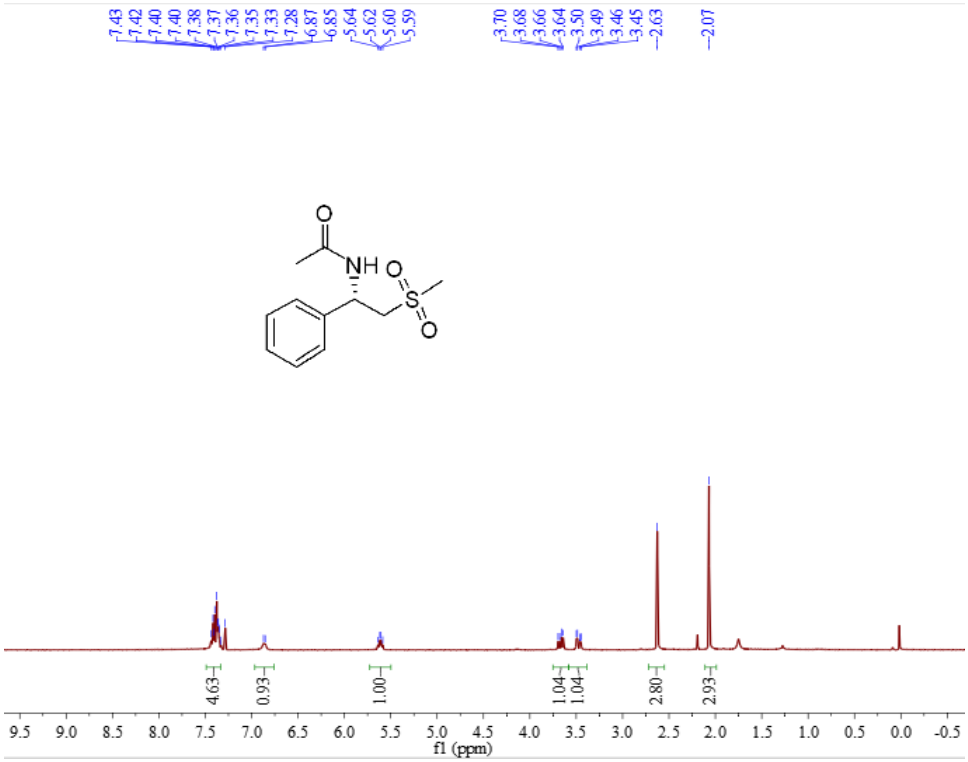


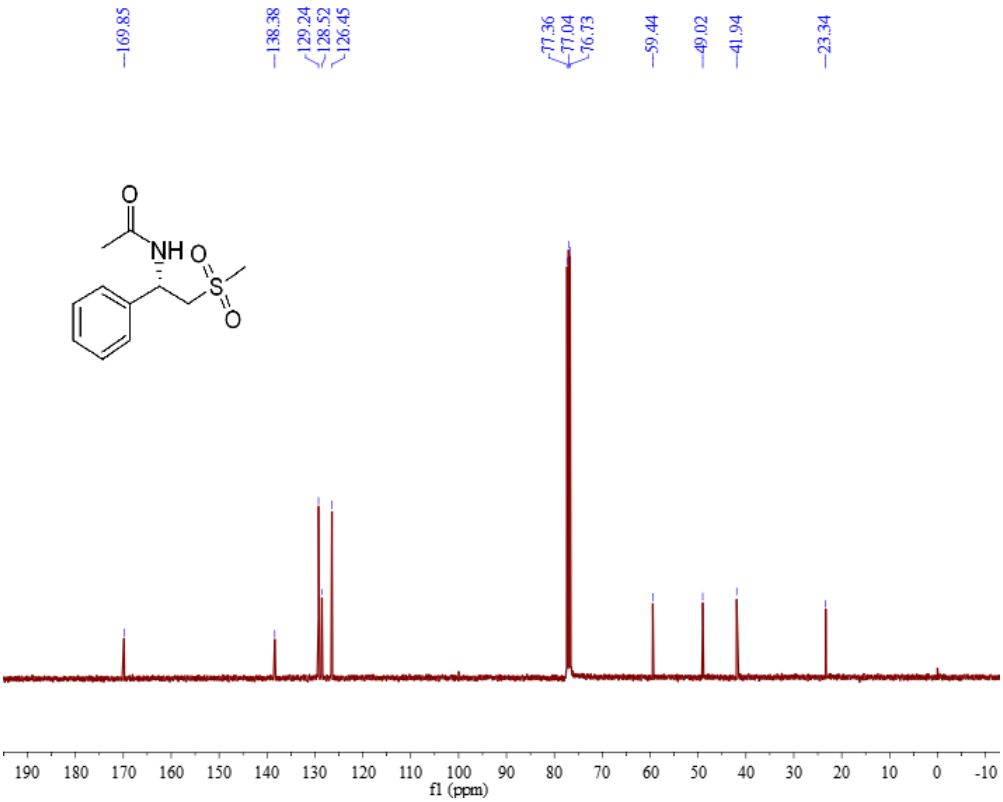
^{1}H NMR and ^{13}C NMR of 2p



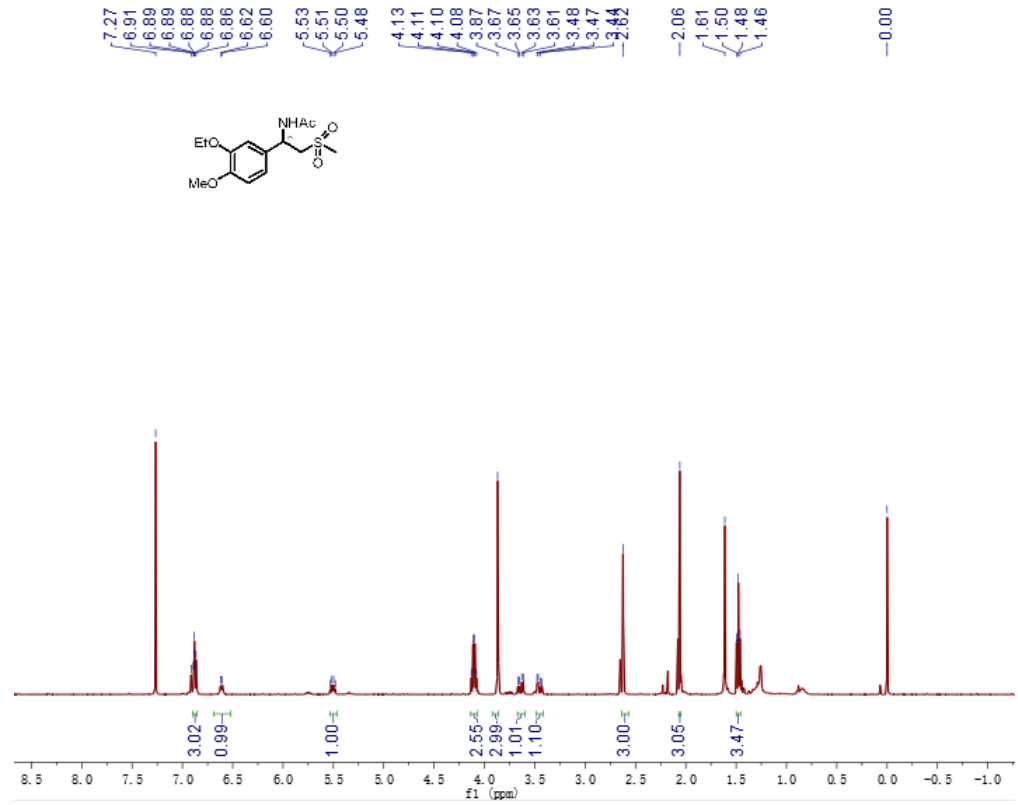


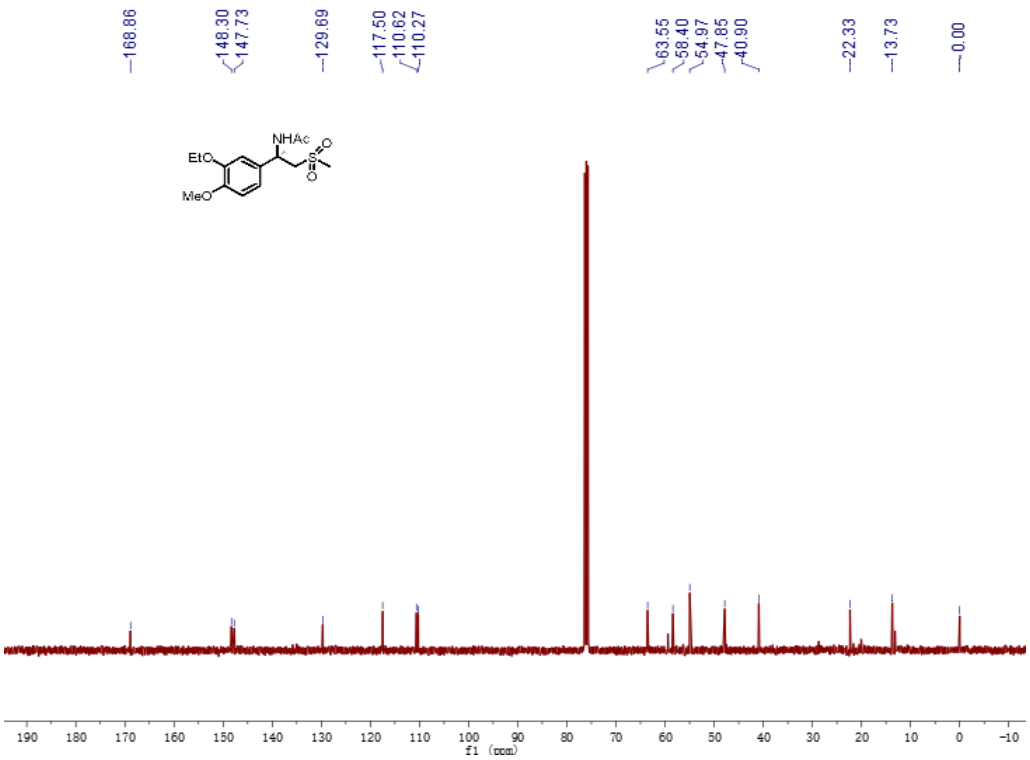
^{1}H NMR and ^{13}C NMR of 3a





^{1}H NMR and ^{13}C NMR of 3p





HPLC of rac-2a

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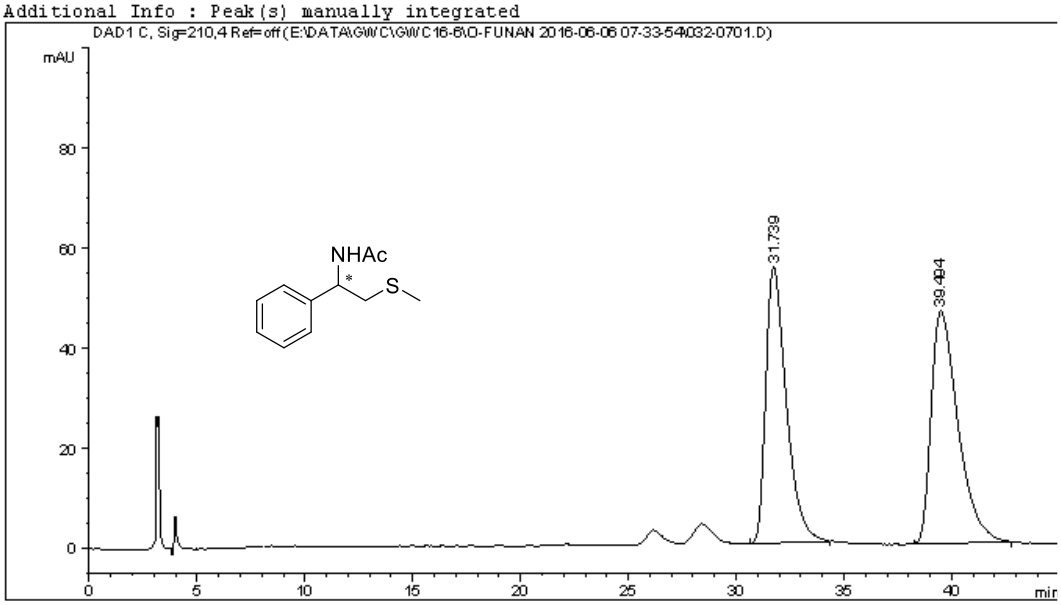
    Acq. Operator   : SYSTEM                          Seq. Line :   7
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 32
    Injection Date  : 6/6/2016 11:12:40 AM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\DAD-ODH-95-5-1ML-205-254
                      -60MIN(1-2).M
    Last changed    : 6/6/2016 10:49:07 AM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\DAD-ODH-95-5-1ML-205-254
                      -60MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:51:59 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  31.739 BB    0.9391 3661.43408   55.25415  47.6953
       2  39.494 BB    1.1513 4015.27832   46.41217  52.3047

    Totals :                  7676.71240  101.66631

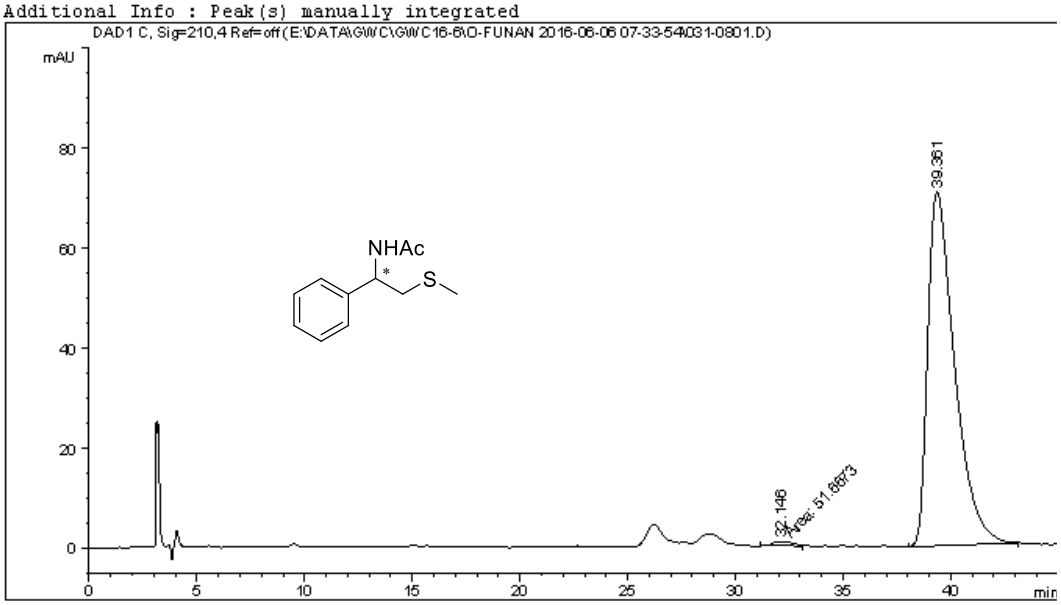

    ==================================================================
                              *** End of Report ***

1260HPLC-DAD 4/10/2017 4:52:12 PM SYSTEM                    Page 1 of 1
```

HPLC of cat-2a

```
Data File E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\031-0801.D
Sample Name: biao-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   8
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 31
    Injection Date  : 6/6/2016 12:13:36 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\DAD-ODH-95-5-1ML-205-254
                      -60MIN(1-2).M
    Last changed    : 6/6/2016 10:49:07 AM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\DAD-ODH-95-5-1ML-205-254
                      -60MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:51:59 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  32.146 MM    1.0056   51.66726 8.56326e-1   0.8337
       2  39.361 BB    1.1991 6145.47559   70.77018  99.1663

    Totals :                  6197.14284   71.62651

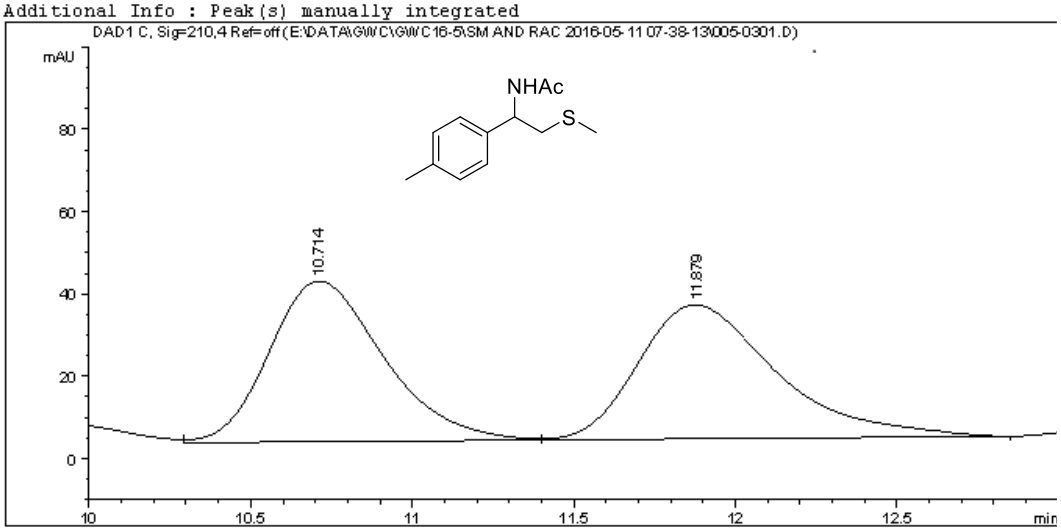

    ==================================================================
                              *** End of Report ***

1260HPLC-DAD 4/10/2017 4:52:01 PM SYSTEM                    Page 1 of 1
```

HPLC of rac-2b

```
Data File E:\DATA\GWC\GWC16-5\SM AND RAC 2016-05-11 07-38-13\005-0301.D
Sample Name: P-Me rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 5
    Injection Date  : 5/11/2016 8:28:01 AM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\SM AND RAC 2016-05-11 07-38-13\DAD-ODH-90-10-AALL-
                      1ML-40MIN(1-2).M
    Last changed    : 5/11/2016 8:52:20 AM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\SM AND RAC 2016-05-11 07-38-13\DAD-ODH-90-10-AALL-
                      1ML-40MIN(1-2).M (Sequence Method)
    Last changed    : 4/12/2017 10:38:52 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.714 VV    0.3790  959.80621   39.01068  49.8430
       2  11.879 VB    0.4505  965.85120   32.51845  50.1570

    Totals :                   1925.65741   71.52913

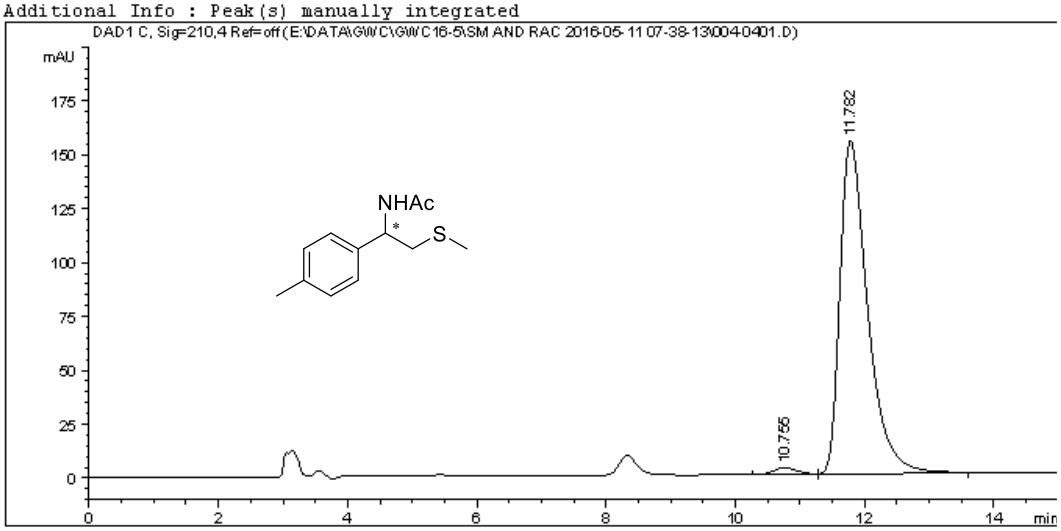

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/12/2017 10:38:58 AM SYSTEM                    Page 1 of 1
```

HPLC of cat-2b

```
Data File E:\DATA\GWC\GWC16-5\SM AND RAC 2016-05-11 07-38-13\004-0401.D
Sample Name: P-Me cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 4
    Injection Date  : 5/11/2016 8:53:57 AM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\SM AND RAC 2016-05-11 07-38-13\DAD-ODH-90-10-AALL-
                      1ML-40MIN(1-2).M
    Last changed    : 5/11/2016 8:54:09 AM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\SM AND RAC 2016-05-11 07-38-13\DAD-ODH-90-10-AALL-
                      1ML-40MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:47:48 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.755 BV    0.3304   75.97803    3.11699   1.6251
       2  11.782 VB    0.4513 4599.30127  154.51550  98.3749

    Totals :                   4675.27930  157.63249

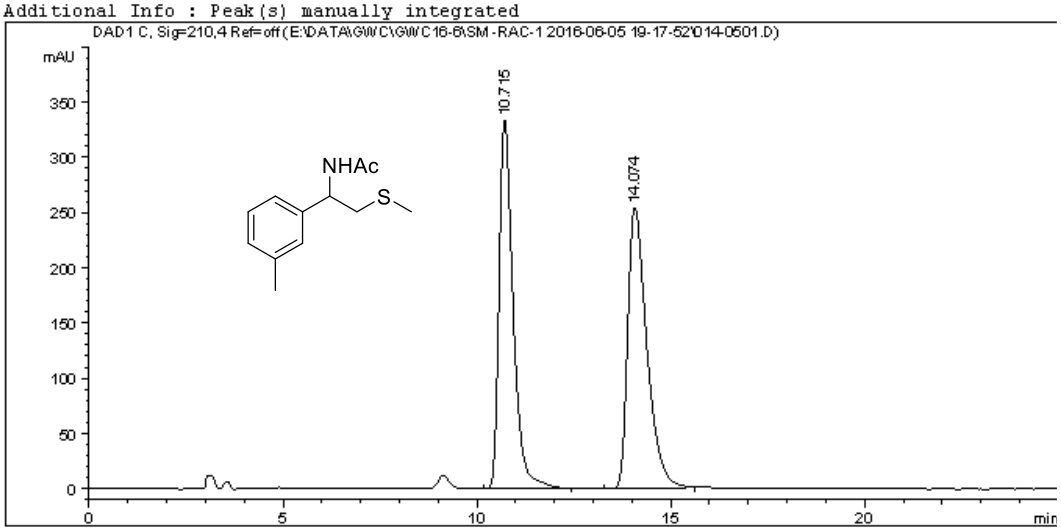

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/10/2017 4:47:53 PM SYSTEM                    Page 1 of 1
```

HPLC of rac-2c

```
Data File E:\DATA\GWC\GWC16-6\SM -RAC-1 2016-06-05 19-17-52\014-0501.D
Sample Name: 3-me-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   5
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 14
    Injection Date  : 6/5/2016 8:42:34 PM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-6\SM -RAC-1 2016-06-05 19-17-52\DAD-ODH-90-10-AALL-1ML
                      -40MIN(1-2).M
    Last changed    : 6/5/2016 8:58:33 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-6\SM -RAC-1 2016-06-05 19-17-52\DAD-ODH-90-10-AALL-1ML
                      -40MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:39:22 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.715 BB    0.3796 8390.31641  333.43802  49.1881
       2  14.074 BB    0.5163 8667.28516  253.88643  50.8119

    Totals :                  1.70576e4   587.32445

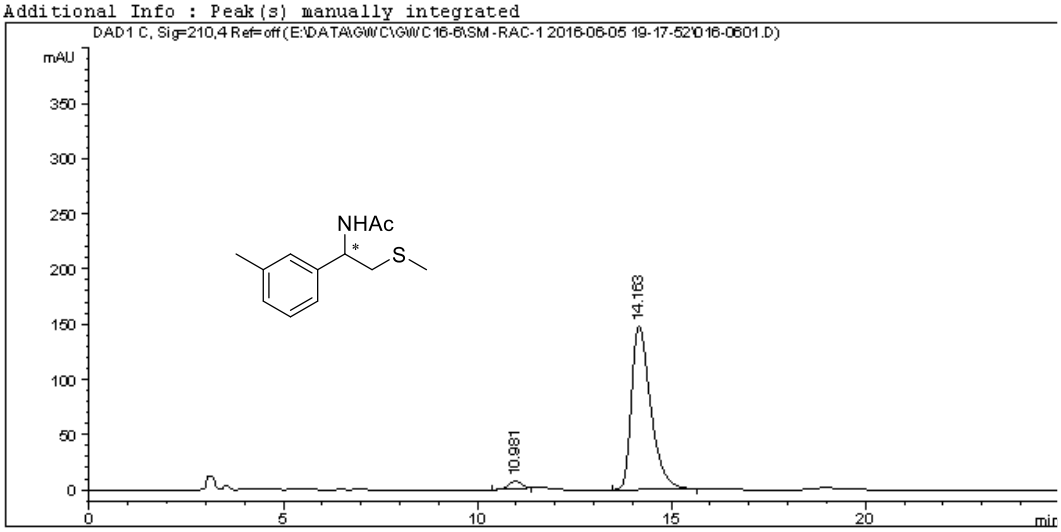

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/10/2017 4:39:29 PM SYSTEM                    Page 1 of 1
```

HPLC of cat-2c

```
Data File E:\DATA\GWC\GWC16-6\SM -RAC-1 2016-06-05 19-17-52\016-0601.D
Sample Name: 3-Me

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   6
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 16
    Injection Date  : 6/5/2016 9:08:30 PM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-6\SM -RAC-1 2016-06-05 19-17-52\DAD-ODH-90-10-AALL-1ML
                      -40MIN(1-2).M
    Last changed    : 6/5/2016 8:58:33 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-6\SM -RAC-1 2016-06-05 19-17-52\DAD-ODH-90-10-AALL-1ML
                      -40MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:39:22 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.981 BB    0.3316  151.89886    6.72197   2.8999
       2  14.163 BB    0.5164 5086.21289  148.20305  97.1001

    Totals :                   5238.11176  154.92502

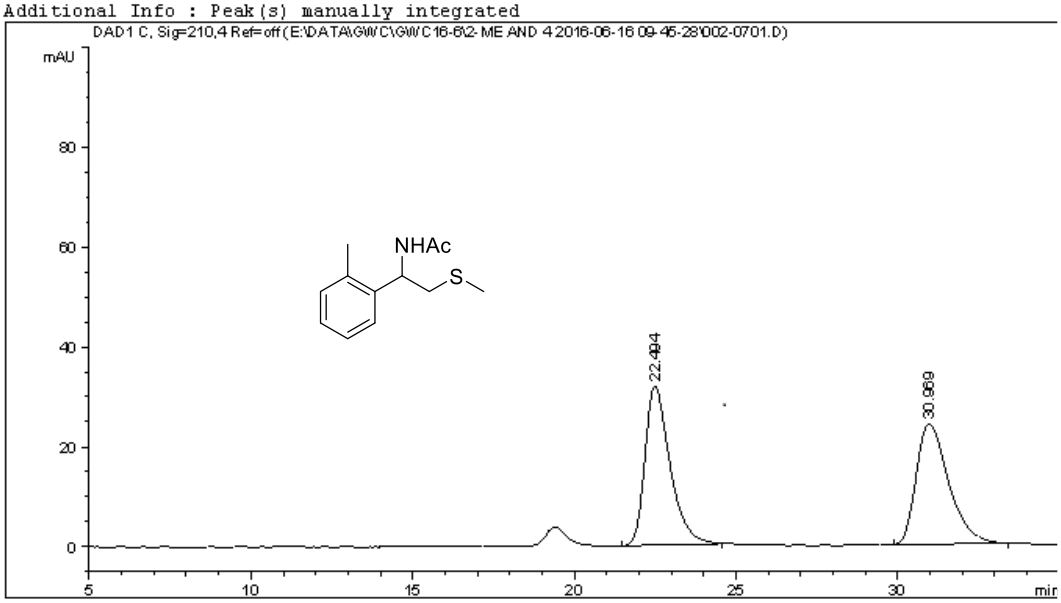

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/10/2017 4:40:39 PM SYSTEM                    Page 1 of 1
```

HPLC of rac-2d

```
Data File E:\DATA\GWC\GWC16-6\2-ME AND 4 2016-06-16 09-45-28\002-0701.D
Sample Name: 2-Me-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   7
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 2
    Injection Date  : 6/16/2016 11:54:11 AM                 Inj :   1
                                                      Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-6\2-ME AND 4 2016-06-16 09-45-28\DAD-ODH-95-5-1ML-205-
                      254-60MIN(1-2).M
    Last changed    : 6/16/2016 12:31:38 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-6\2-ME AND 4 2016-06-16 09-45-28\DAD-ODH-95-5-1ML-205-
                      254-60MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:20:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  22.494 BB    0.7850 1710.75891   31.83483  50.4639
       2  30.969 BB    0.9125 1679.30444   24.11340  49.5361

    Totals :                  3390.06335   55.94823

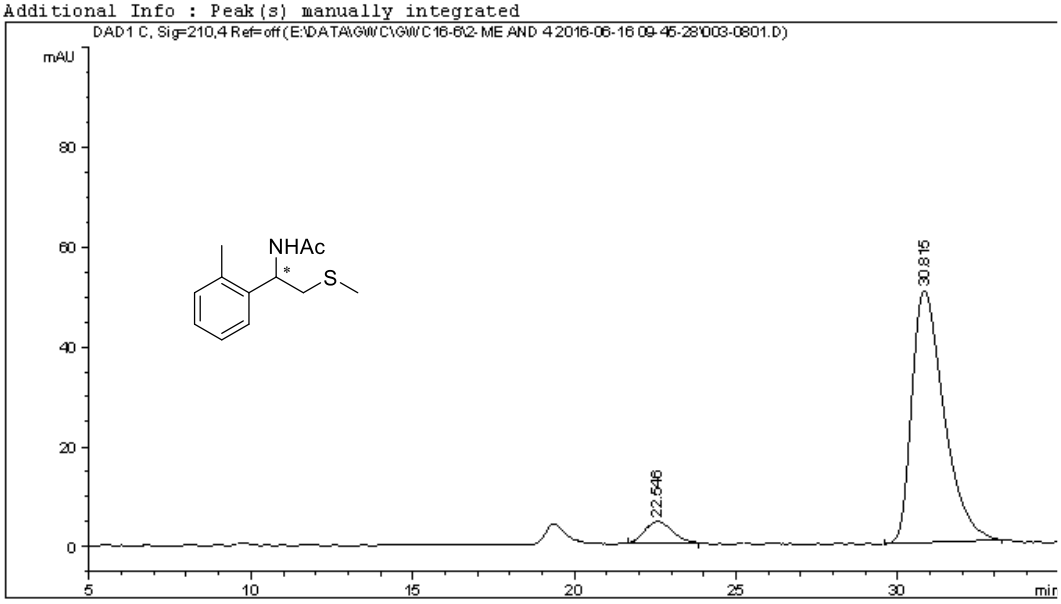

    ==================================================================

1260HPLC-DAD 4/10/2017 4:20:43 PM SYSTEM                          Page 1 of 1
```

HPLC of cat-2d

Data File E:\DATA\GWC\GWC16-6\2-ME AND 4 2016-06-16 09-45-28\003-0801.D
Sample Name: 2-Me-cat

```
==================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   8
Acq. Instrument : 1260HPLC-DAD                     Location : Vial 3
Injection Date  : 6/16/2016 12:33:05 PM                 Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\GWC\GWC16-6\2-ME AND 4 2016-06-16 09-45-28\DAD-ODH-95-5-1ML-205-
                  254-60MIN(1-2).M
Last changed    : 6/16/2016 12:38:03 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\GWC\GWC16-6\2-ME AND 4 2016-06-16 09-45-28\DAD-ODH-95-5-1ML-205-
                  254-60MIN(1-2).M (Sequence Method)
Last changed    : 4/10/2017 4:20:39 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.546 BB    0.6917  247.15256    4.26725   6.6244
   2  30.815 BB    1.0069 3483.79688   50.37363  93.3756

Totals :                  3730.94943   54.64087

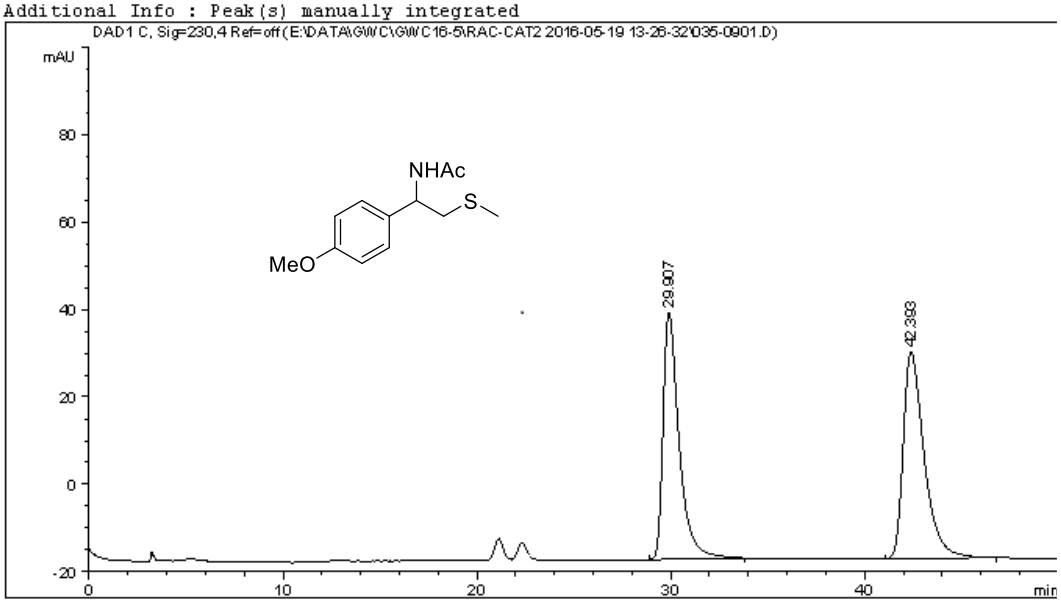

==================================================================
```

1260HPLC-DAD 4/10/2017 4:21:44 PM SYSTEM Page 1 of 1

HPLC of rac-2e

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT2 2016-05-19 13-26-32\035-0901.D
Sample Name: OMe-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   9
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 35
    Injection Date  : 5/19/2016 5:48:54 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT2 2016-05-19 13-26-32\DAD-OJH(1-6)-90-10-210-
                      254-40MIN.M
    Last changed    : 5/19/2016 6:20:00 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT2 2016-05-19 13-26-32\DAD-OJH(1-6)-90-10-210-
                      254-40MIN.M (Sequence Method)
    Last changed    : 4/12/2017 5:14:40 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=230,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|-------|
       1  29.907 BB    0.8482 3247.04150   56.52422  47.8239
       2  42.393 BB    1.0992 3542.53638   47.22276  52.1761

    Totals :                  6789.57788  103.74698

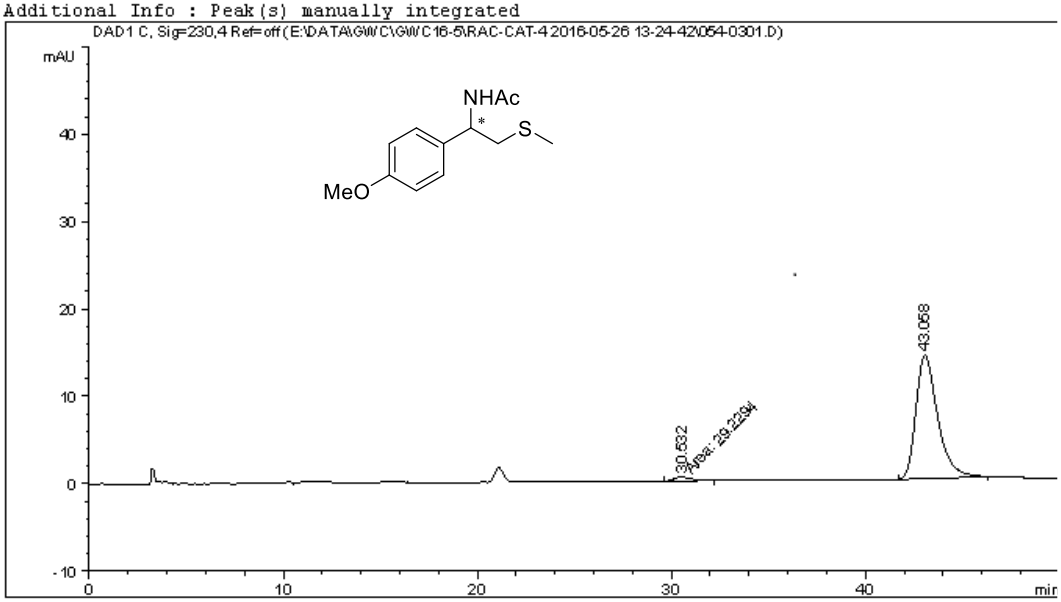

    ==================================================================

1260HPLC-DAD 4/12/2017 5:14:43 PM SYSTEM                          Page 1 of 1
```

HPLC of cat-2e

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT-4 2016-05-26 13-24-42\054-0301.D
Sample Name: OMe-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 54
    Injection Date  : 5/26/2016 1:42:48 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT-4 2016-05-26 13-24-42\DAD-OJH(1-6)-90-10-210
                      -254-40MIN.M
    Last changed    : 5/26/2016 1:44:37 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT-4 2016-05-26 13-24-42\DAD-OJH(1-6)-90-10-210
                      -254-40MIN.M (Sequence Method)
    Last changed    : 4/12/2017 5:12:13 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=230,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  30.532 MM    1.1774   29.22943 4.13752e-1   2.5906
       2  43.058 BB    1.0764 1099.05872   14.08506  97.4094

    Totals :                   1128.28815   14.49881

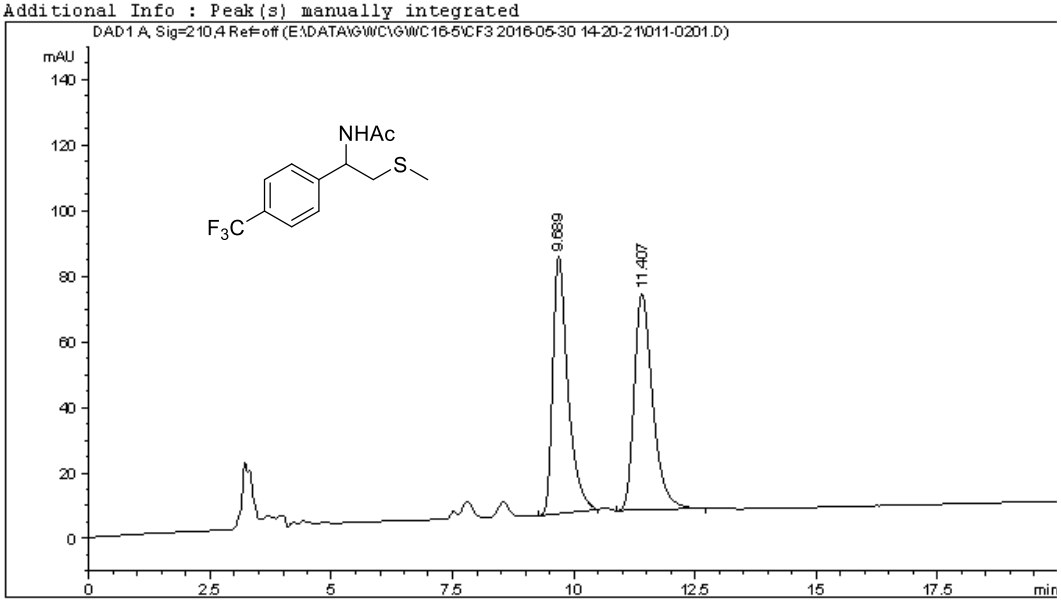

    ==================================================================

1260HPLC-DAD 4/12/2017 5:12:57 PM SYSTEM                          Page 1 of 1
```

HPLC of rac-2f

```
Data File E:\DATA\GWC\GWC16-5\CF3 2016-05-30 14-20-21\011-0201.D
Sample Name: CF3-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 11
    Injection Date  : 5/30/2016 2:32:15 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\CF3 2016-05-30 14-20-21\DAD-0JH(1-6)-90-10-210-254-
                      40MIN.M
    Last changed    : 5/30/2016 3:02:39 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\CF3 2016-05-30 14-20-21\DAD-0JH(1-6)-90-10-210-254-
                      40MIN.M (Sequence Method)
    Last changed    : 4/10/2017 4:59:32 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.689 BB    0.3225 1698.26123   78.46725  49.3365
       2  11.407 BB    0.4028 1743.93982   65.88089  50.6635

    Totals :                   3442.20105  144.34814

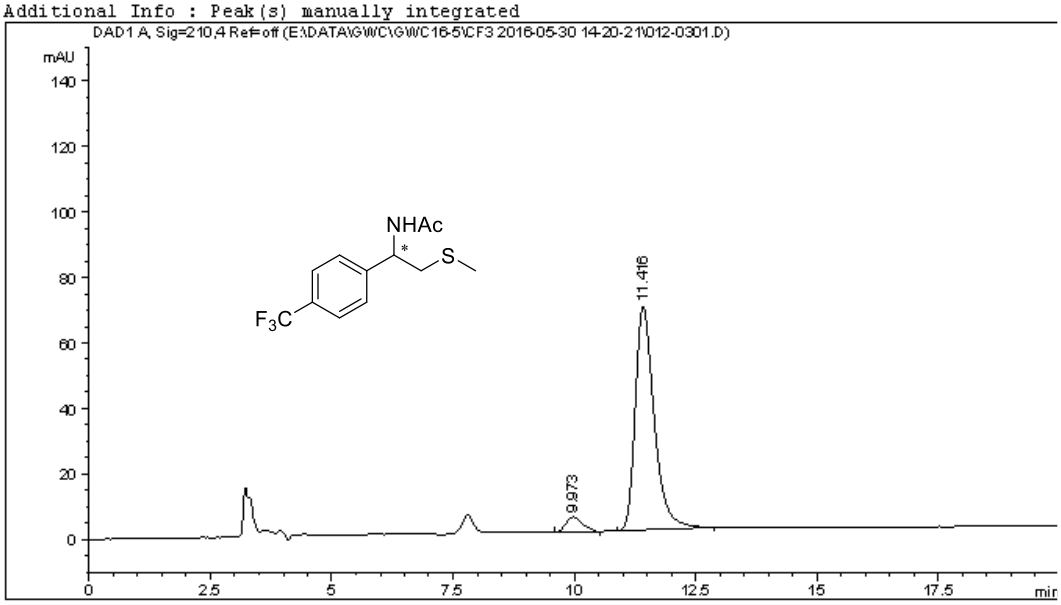

    ==================================================================

1260HPLC-DAD 4/10/2017 4:59:36 PM SYSTEM                          Page 1 of 1
```

HPLC of cat-2f

```
Data File E:\DATA\GWC\GWC16-5\CF3 2016-05-30 14-20-21\012-0301.D
Sample Name: CF3-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 12
    Injection Date  : 5/30/2016 3:08:09 PM                  Inj :   1
                                                      Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\CF3 2016-05-30 14-20-21\DAD-OJH(1-6)-90-10-210-254-
                      40MIN.M
    Last changed    : 5/30/2016 3:02:39 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-5\CF3 2016-05-30 14-20-21\DAD-OJH(1-6)-90-10-210-254-
                      40MIN.M (Sequence Method)
    Last changed    : 4/10/2017 4:59:32 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.973 BB    0.3453  105.92339    4.48940   5.4303
       2  11.416 BB    0.4101 1844.68457   68.08694  94.5697

    Totals :                   1950.60796   72.57634

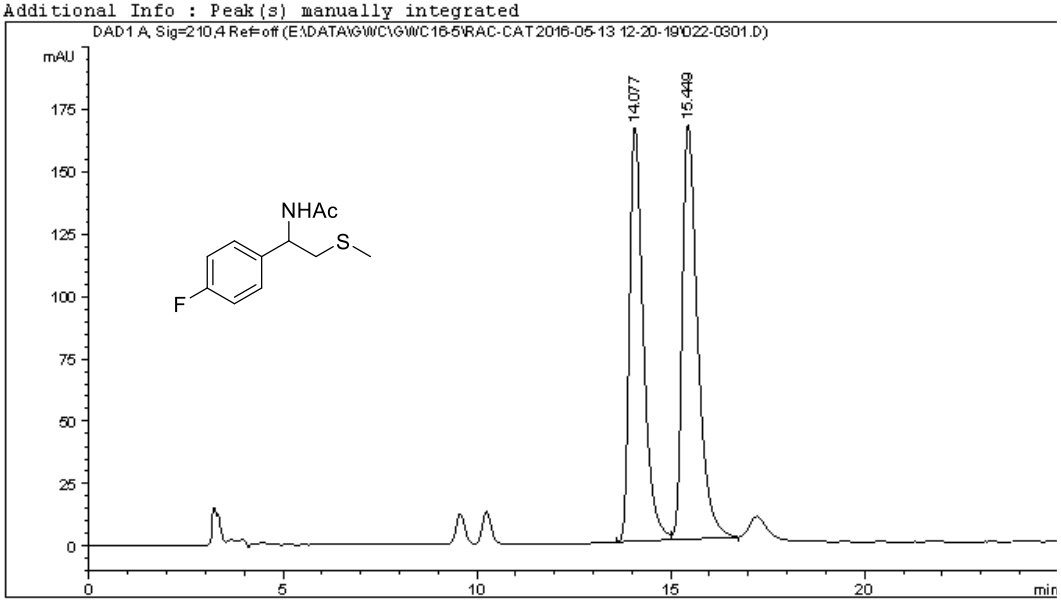

    ==================================================================
                              *** End of Report ***

1260HPLC-DAD 4/10/2017 4:59:49 PM SYSTEM                          Page 1 of 1
```

HPLC of rac-2g

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\022-0301.D
Sample Name: F-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 22
    Injection Date  : 5/13/2016 1:13:04 PM                Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-OJH(1-6)-90-10-210-
                      254-40MIN.M
    Last changed    : 5/13/2016 1:45:33 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-OJH(1-6)-90-10-210-
                      254-40MIN.M (Sequence Method)
    Last changed    : 4/10/2017 4:42:34 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.077 BV    0.3761 4121.92188  165.79160  47.4750
       2  15.449 VB    0.4125 4560.37598  165.98250  52.5250

    Totals :                  8682.29785  331.77409

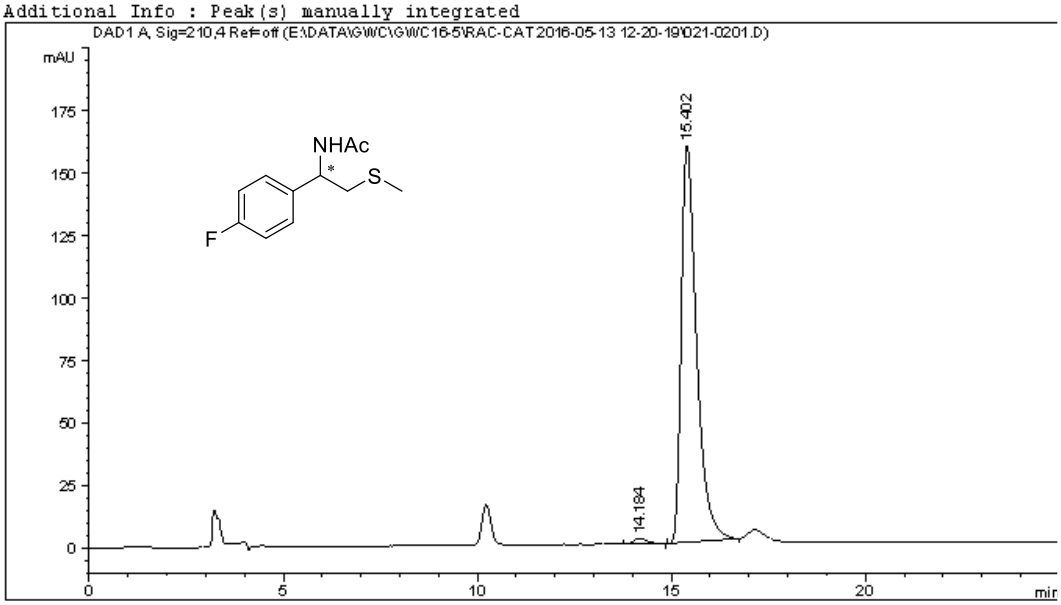

    ==================================================================

1260HPLC-DAD 4/10/2017 4:42:38 PM SYSTEM                          Page 1 of 1
```

HPLC of cat-2g

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\021-0201.D
Sample Name: F-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 21
    Injection Date  : 5/13/2016 12:32:10 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-0JH(1-6)-90-10-210-
                      254-40MIN.M
    Last changed    : 5/13/2016 12:20:19 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-0JH(1-6)-90-10-210-
                      254-40MIN.M (Sequence Method)
    Last changed    : 4/10/2017 4:42:34 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.184 BB    0.3279   56.34747    2.19228   1.2781
       2  15.402 BB    0.4156 4352.48096  158.88470  98.7219

    Totals :                   4408.82842  161.07698

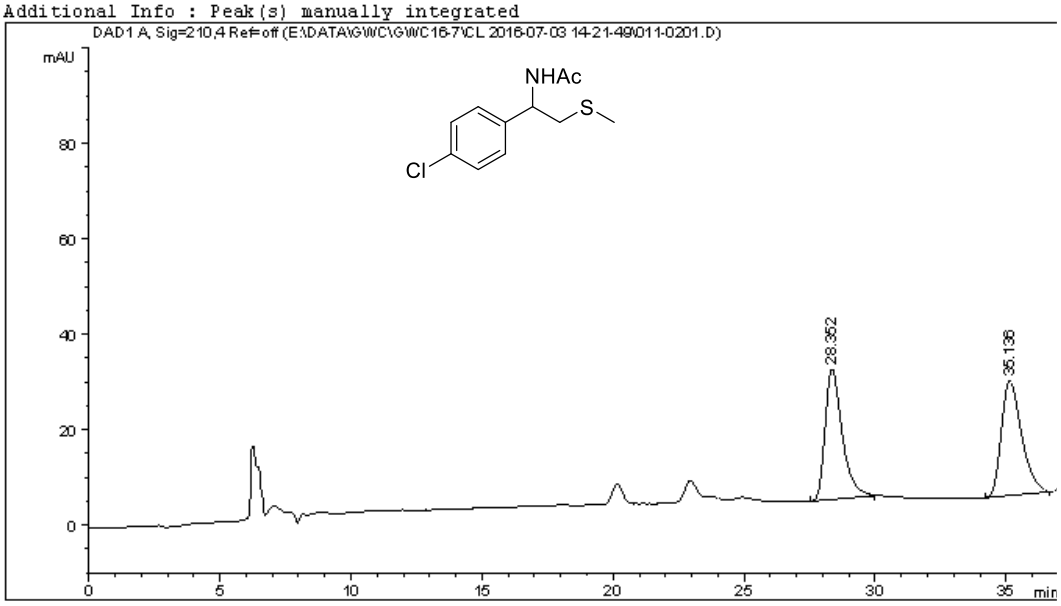

    ==================================================================
                              *** End of Report ***

1260HPLC-DAD 4/10/2017 4:43:49 PM SYSTEM                          Page 1 of 1
```

HPLC of rac-2h

```
Data File E:\DATA\GWC\GWC16-7\CL 2016-07-03 14-21-49\011-0201.D
Sample Name: Cl-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 11
    Injection Date  : 7/3/2016 2:33:47 PM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-7\CL 2016-07-03 14-21-49\DAD-OJH(1-6)-90-10-0.5ML-210-
                      254-80MIN.M
    Last changed    : 7/3/2016 2:21:49 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-7\CL 2016-07-03 14-21-49\DAD-OJH(1-6)-90-10-0.5ML-210-
                      254-80MIN.M (Sequence Method)
    Last changed    : 4/12/2017 10:35:07 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  28.352 BB    0.6484 1239.84961   27.27281  48.9411
       2  35.136 BB    0.7169 1293.50134   23.99518  51.0589

    Totals :                  2533.35095   51.26798

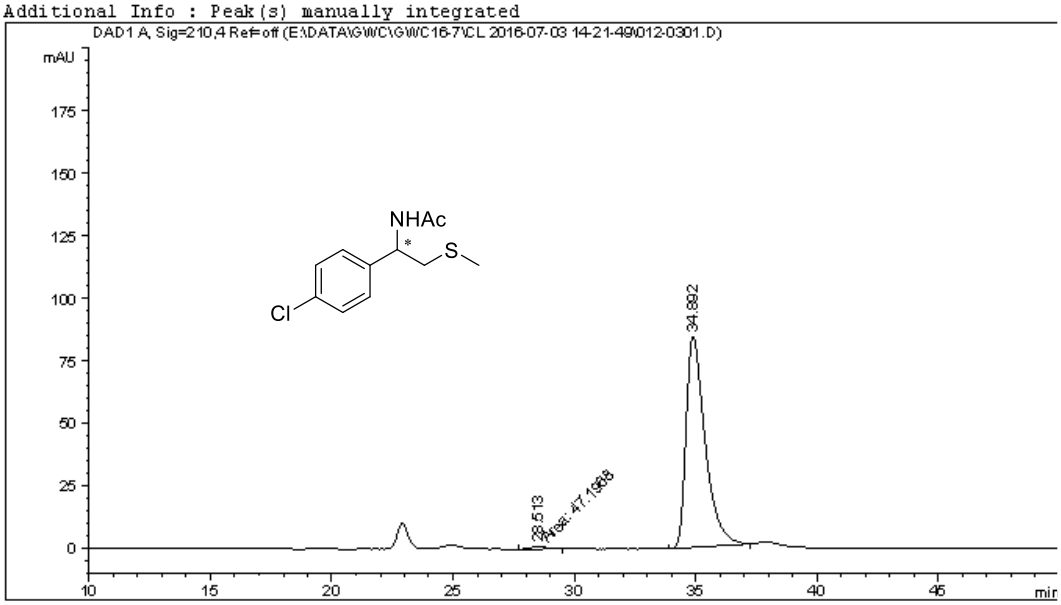

    ==================================================================
                              *** End of Report ***

1260HPLC-DAD 4/12/2017 10:35:14 AM SYSTEM                    Page 1 of 1
```

HPLC of cat-2h

```
Data File E:\DATA\GWC\GWC16-7\CL 2016-07-03 14-21-49\012-0301.D
Sample Name: Cl-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 12
    Injection Date  : 7/3/2016 3:54:42 PM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-7\CL 2016-07-03 14-21-49\DAD-OJH(1-6)-90-10-0.5ML-210-
                      254-80MIN.M
    Last changed    : 7/3/2016 2:21:49 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-7\CL 2016-07-03 14-21-49\DAD-OJH(1-6)-90-10-0.5ML-210-
                      254-80MIN.M (Sequence Method)
    Last changed    : 4/10/2017 5:03:05 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  28.513 MM    0.7780   47.19679    1.01106   1.0116
       2  34.892 BB    0.7966 4618.30859   84.37730  98.9884

    Totals :                   4665.50538   85.38837

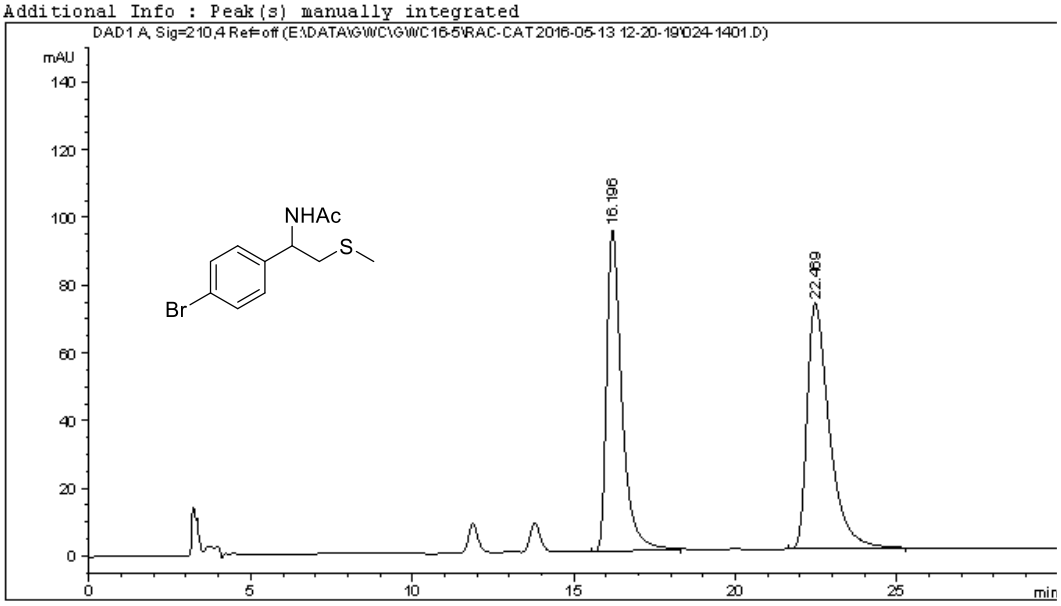

    ==================================================================
                              *** End of Report ***

1260HPLC-DAD 4/10/2017 5:03:12 PM SYSTEM                          Page 1 of 1
```

HPLC of rac-2i

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\024-1401.D
Sample Name: Br-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  14
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 24
    Injection Date  : 5/13/2016 6:34:34 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-0JH(1-6)-90-10-210-
                      254-40MIN.M
    Last changed    : 5/13/2016 12:20:19 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-0JH(1-6)-90-10-210-
                      254-40MIN.M (Sequence Method)
    Last changed    : 4/10/2017 4:56:42 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.196 BB    0.4863 3077.66528   94.91294  46.9937
       2  22.469 BB    0.7089 3471.43066   72.46679  53.0063

    Totals :                  6549.09595  167.37973

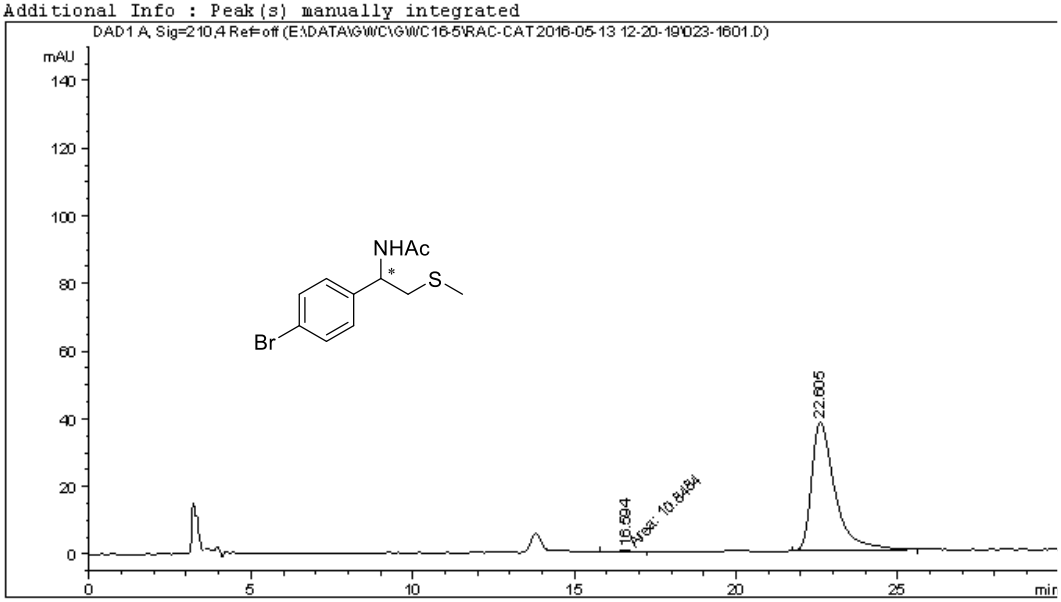

    ==================================================================
                              *** End of Report ***

1260HPLC-DAD 4/10/2017 4:56:49 PM SYSTEM                          Page 1 of 1
```

HPLC of cat-2i

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\023-1601.D
Sample Name: Br-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  16
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 23
    Injection Date  : 5/13/2016 8:06:26 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-0JH(1-6)-90-10-210-
                      254-40MIN.M
    Last changed    : 5/13/2016 8:10:45 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-0JH(1-6)-90-10-210-
                      254-40MIN.M (Sequence Method)
    Last changed    : 4/10/2017 4:56:42 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.594 MM    0.6840   10.84836 2.64318e-1   0.5658
       2  22.605 BB    0.7271 1906.36377   37.88139  99.4342

    Totals :                  1917.21213   38.14571

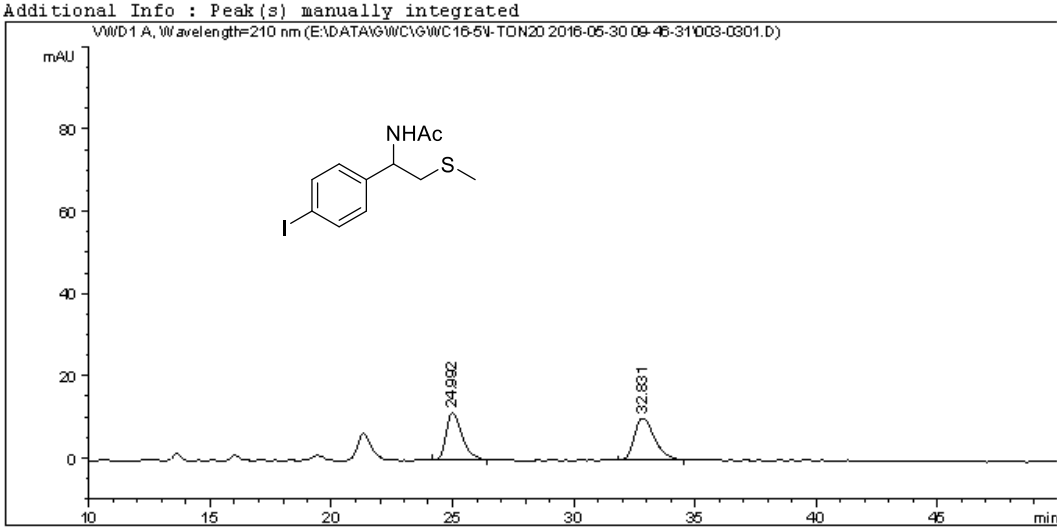

    ==================================================================

1260HPLC-DAD 4/10/2017 4:57:01 PM SYSTEM                          Page 1 of 1
```

HPLC of rac-2j

```
Data File E:\DATA\GWC\GWC16-5\I-TON20 2016-05-30 09-46-31\003-0301.D
Sample Name: I-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 3
    Injection Date  : 5/30/2016 11:08:51 AM                Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\I-TON20 2016-05-30 09-46-31\VWD-ADH(1-6)-95-5-210NM-
                      70MIN.M
    Last changed    : 5/30/2016 12:21:54 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\I-TON20 2016-05-30 09-46-31\VWD-ADH(1-6)-95-5-210NM-
                      70MIN.M (Sequence Method)
    Last changed    : 4/10/2017 5:05:49 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  24.992 BB    0.6863  510.70477   11.40784  46.4463
       2  32.831 BB    0.8841  588.85449   10.19090  53.5537

    Totals :                   1099.55927   21.59874

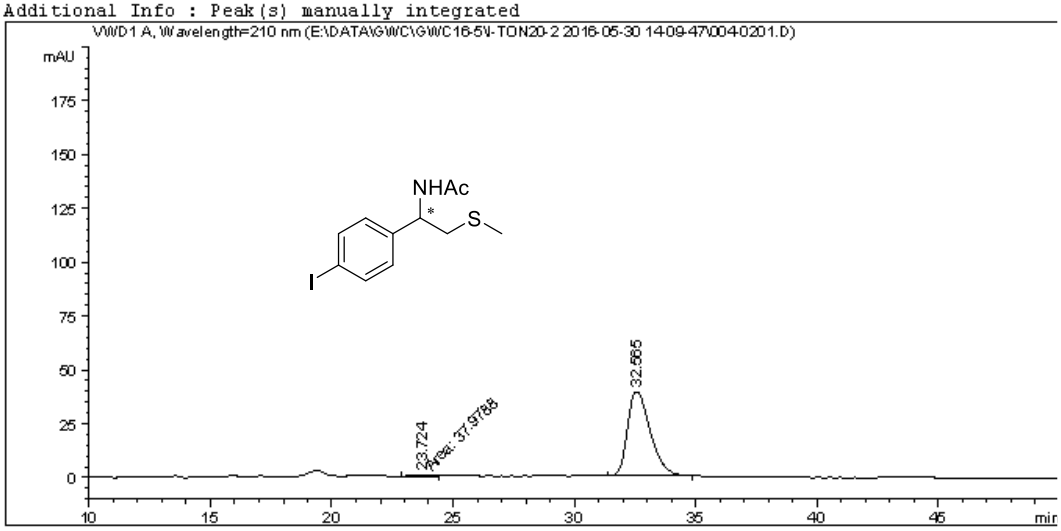

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/10/2017 5:05:58 PM SYSTEM                    Page 1 of 1
```

HPLC of cat-2j

```
Data File E:\DATA\GWC\GWC16-5\I-TON20-2 2016-05-30 14-09-47\004-0201.D
Sample Name: i-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 4
    Injection Date  : 5/30/2016 2:16:17 PM                  Inj :   1
                                                     Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\I-TON20-2 2016-05-30 14-09-47\VWD-ADH(1-6)-95-5-
                      210NM-70MIN-10UL.M
    Last changed    : 5/30/2016 3:18:52 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\I-TON20-2 2016-05-30 14-09-47\VWD-ADH(1-6)-95-5-
                      210NM-70MIN-10UL.M (Sequence Method)
    Last changed    : 4/10/2017 5:06:59 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  23.724 MM    0.8214   37.97881 7.70630e-1   1.4560
       2  32.565 BB    0.9868 2570.37402   39.25983  98.5440

    Totals :                  2608.35283   40.03046

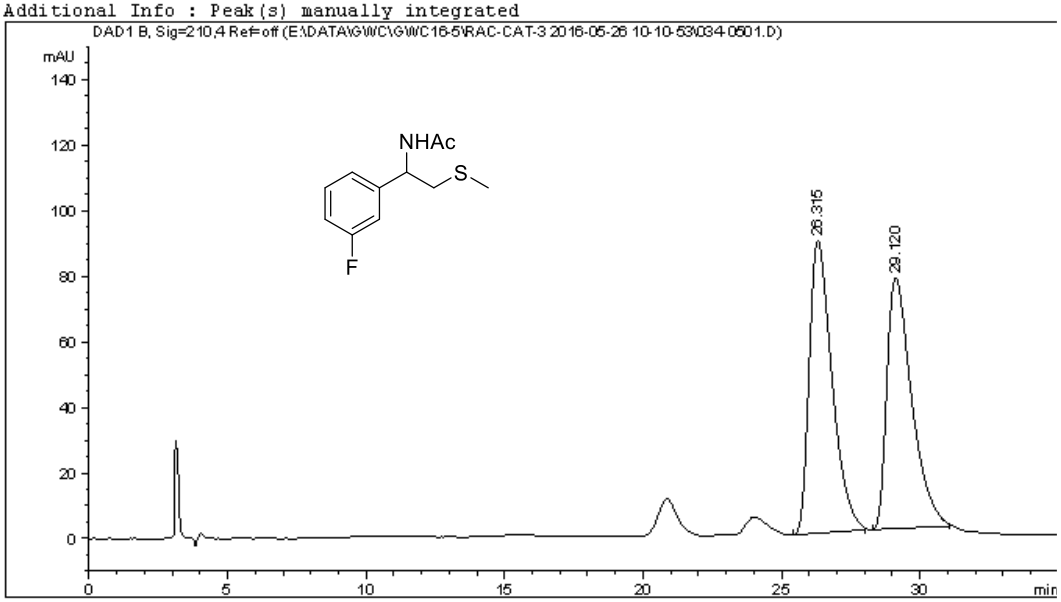

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/10/2017 5:07:05 PM SYSTEM                          Page 1 of 1
```

HPLC of rac-2k

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT-3 2016-05-26 10-10-53\034-0501.D
Sample Name: 3-F-RAC

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   5
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 34
    Injection Date  : 5/26/2016 11:23:07 AM                Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT-3 2016-05-26 10-10-53\DAD-ODH-95-5-1ML-205-
                      254-50MIN(1-2).M
    Last changed    : 5/26/2016 12:21:07 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT-3 2016-05-26 10-10-53\DAD-ODH-95-5-1ML-205-
                      254-50MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:33:21 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  26.315 BB    0.8535 5111.34131   89.33185  51.6618
       2  29.120 BB    0.9369 4782.50586   76.54591  48.3382

    Totals :                  9893.84717  165.87776

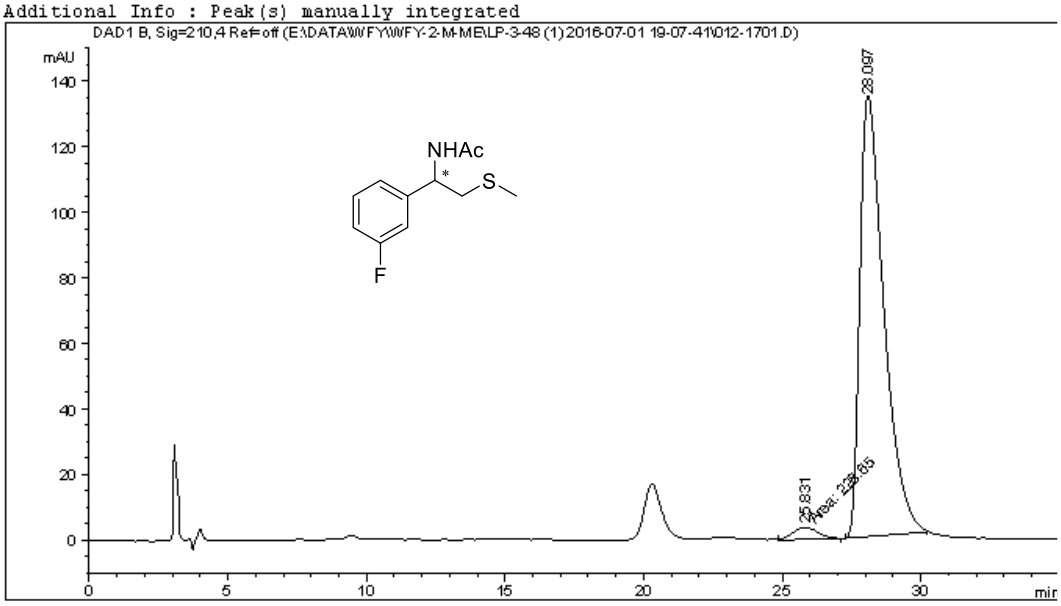

    ==================================================================

1260HPLC-DAD 4/10/2017 4:34:11 PM SYSTEM                          Page 1 of 1
```

HPLC of cat-2k

```
Data File E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\012-1701.D
Sample Name: 3-f-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  17
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 12
    Injection Date  : 7/2/2016 4:06:31 AM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\DAD-ODH-95-5-1ML-
                      205-254-50MIN(1-2).M
    Last changed    : 7/1/2016 9:12:51 PM by SYSTEM
    Analysis Method : E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\DAD-ODH-95-5-1ML-
                      205-254-50MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:35:48 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  25.831 MM    1.0842  228.64955    3.51493   2.7518
       2  28.097 BB    0.8809 8080.56543  134.49971  97.2482

    Totals :                   8309.21498  138.01464

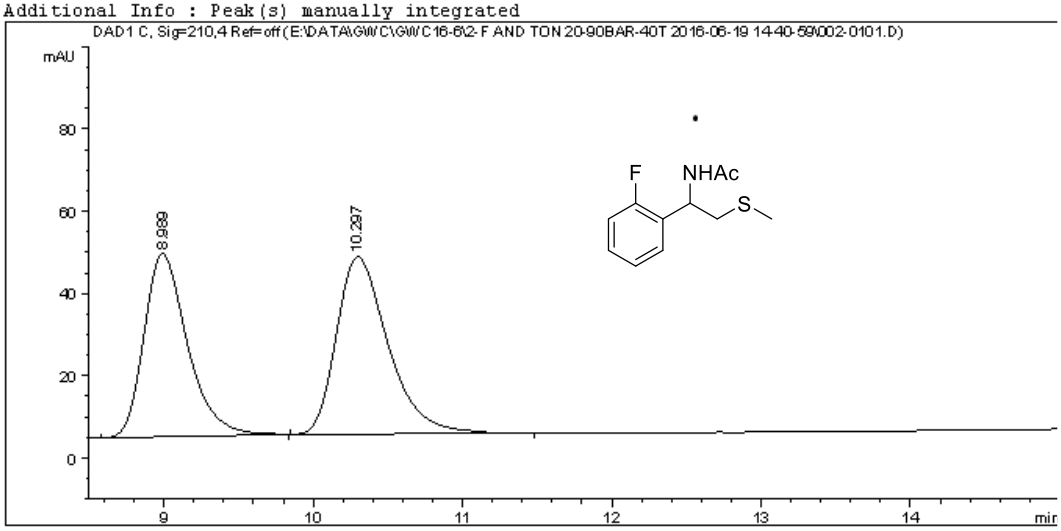

    ==================================================================
                              *** End of Report ***

1260HPLC-VWD 4/10/2017 4:36:00 PM SYSTEM                          Page 1 of 1
```

HPLC of rac-2l

Data File E:\DATA\GWC\GWC16-6\2-F AND TON 20-90BAR-40T 2016-06-19 14-40-59\002-0101.D
Sample Name: 2-F-rac

```
==================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   1
Acq. Instrument : 1260HPLC-DAD                     Location : Vial 2
Injection Date  : 6/19/2016 2:41:49 PM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\GWC\GWC16-6\2-F AND TON 20-90BAR-40T 2016-06-19 14-40-59\DAD-ODH
                  -90-10-AALL-1ML-40MIN(1-2).M
Last changed    : 6/19/2016 2:58:30 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\GWC\GWC16-6\2-F AND TON 20-90BAR-40T 2016-06-19 14-40-59\DAD-ODH
                  -90-10-AALL-1ML-40MIN(1-2).M (Sequence Method)
Last changed    : 4/12/2017 5:31:58 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                          Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.989 BB    0.3079  899.67163   44.48643  46.4772
   2  10.297 BB    0.3668 1036.05652   43.05084  53.5228

Totals :                  1935.72815   87.53727

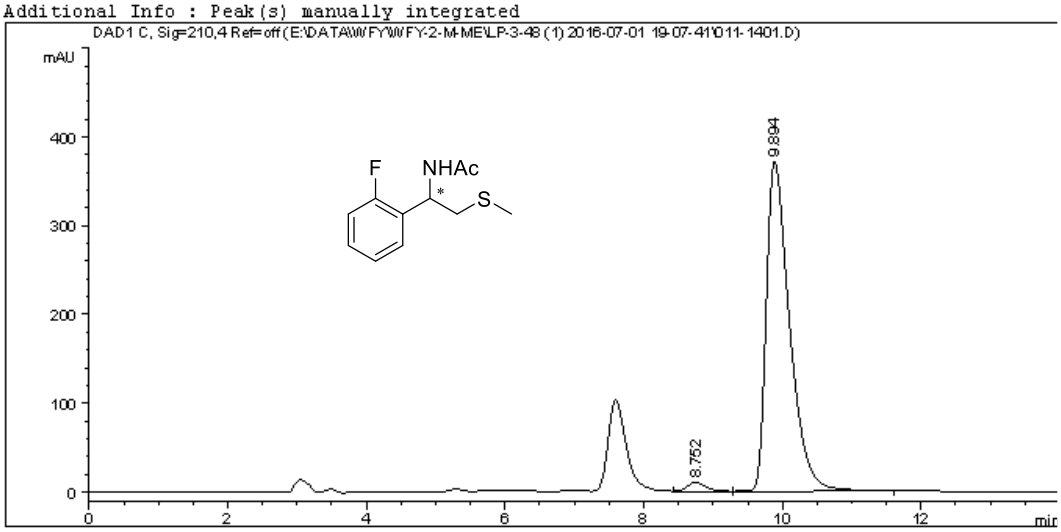

==================================================================
                          *** End of Report ***
```

1260HPLC-DAD 4/12/2017 5:32:03 PM SYSTEM Page 1 of 1

HPLC of cat-2l

```
Data File E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\011-1401.D
Sample Name: 2-f-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  14
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 11
    Injection Date  : 7/2/2016 2:33:34 AM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\DAD-ODH-90-10-
                      AALL-1ML-40MIN(1-2).M
    Last changed    : 7/1/2016 9:12:07 PM by SYSTEM
    Analysis Method : E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\DAD-ODH-90-10-
                      AALL-1ML-40MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 4:29:00 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.752 VB    0.2819  178.53398    9.73975   2.0237
       2   9.894 BB    0.3473 8643.62793  371.66214  97.9763

    Totals :                   8822.16191  381.40189

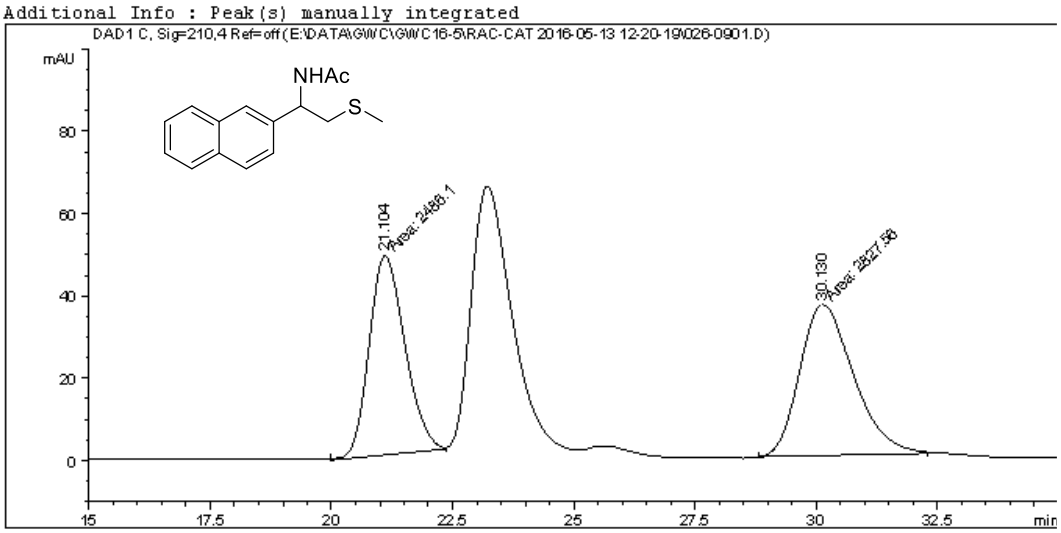

    ==================================================================
                              *** End of Report ***


1260HPLC-VWD 4/10/2017 4:29:02 PM SYSTEM                    Page 1 of 1
```

HPLC of rac-2m

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\026-0901.D
Sample Name: nai-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   9
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 26
    Injection Date  : 5/13/2016 3:53:46 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-ODH-90-10-AALL-1ML-
                      40MIN(1-2).M
    Last changed    : 5/13/2016 4:36:57 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-ODH-90-10-AALL-1ML-
                      40MIN(1-2).M (Sequence Method)
    Last changed    : 12/5/2016 8:29:13 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  21.104 MM    0.8558 2486.09961   48.41458  46.7870
       2  30.130 MM    1.2859 2827.55884   36.64939  53.2130

    Totals :                  5313.65845   85.06397

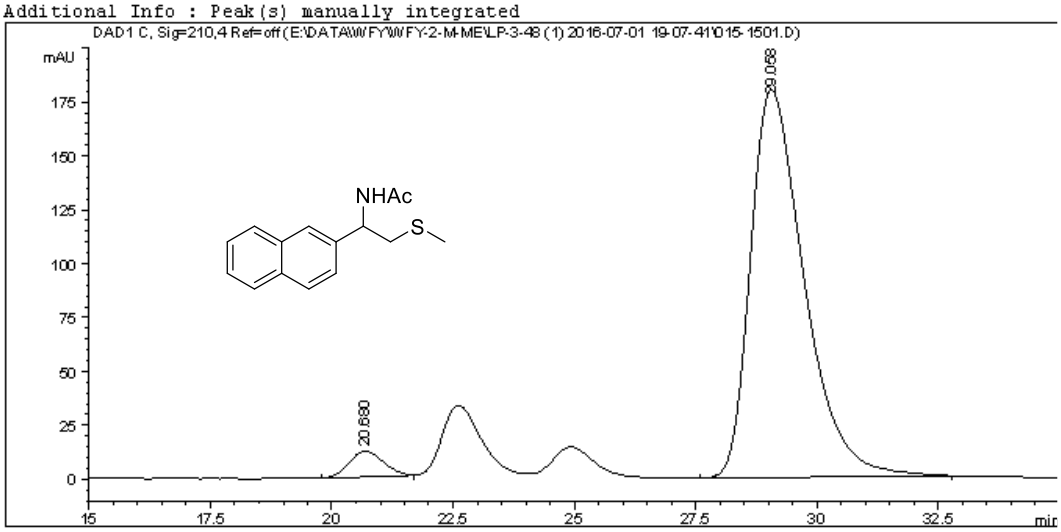

    ==================================================================
                              *** End of Report ***


1260HPLC-VWD 12/5/2016 8:29:17 PM SYSTEM                    Page 1 of 1
```

HPLC of cat-2m

```
Data File E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\015-1501.D
Sample Name: nai-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  15
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 15
    Injection Date  : 7/2/2016 3:14:29 AM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\DAD-ODH-90-10-
                      AALL-1ML-40MIN(1-2).M
    Last changed    : 7/1/2016 9:12:07 PM by SYSTEM
    Analysis Method : E:\DATA\WFY\WFY-2-M-ME\LP-3-48 (1) 2016-07-01 19-07-41\DAD-ODH-90-10-
                      AALL-1ML-40MIN(1-2).M (Sequence Method)
    Last changed    : 12/5/2016 8:26:18 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  20.680 BB    0.5942  586.72400   11.92152   4.0691
       2  29.058 BB    1.1335 1.38324e4   179.80482  95.9309

    Totals :                  1.44191e4   191.72635

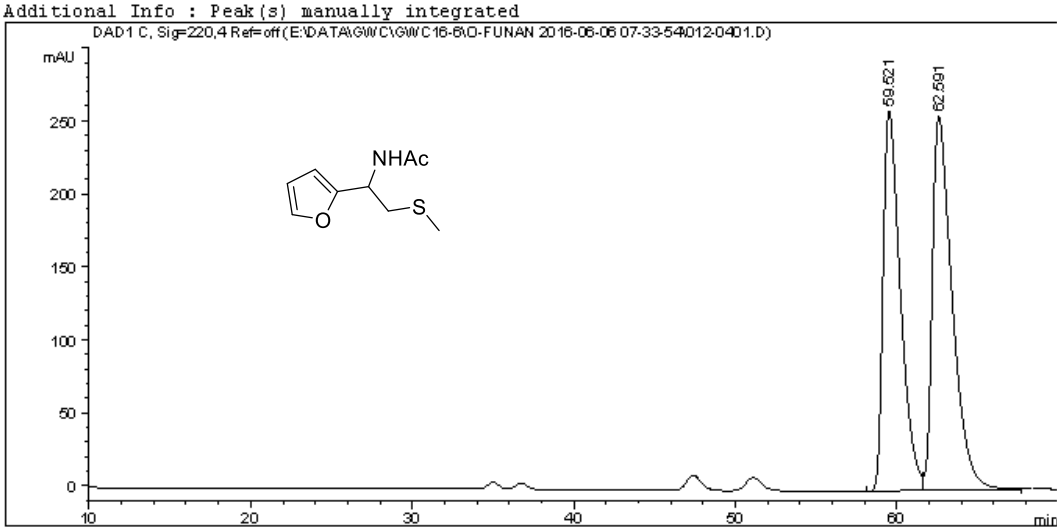

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 12/5/2016 8:26:22 PM SYSTEM                    Page 1 of 1
```

HPLC of rac-2n

```
Data File E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\012-0401.D
Sample Name: 0-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 12
    Injection Date  : 6/6/2016 8:39:41 AM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\DAD-0JH(1-6)-95-5-0.5ML-
                      210-254NM-70MIN.M
    Last changed    : 6/6/2016 8:26:54 AM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\DAD-0JH(1-6)-95-5-0.5ML-
                      210-254NM-70MIN.M (Sequence Method)
    Last changed    : 4/10/2017 5:14:36 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=220,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  59.521 BV    1.1193 1.94013e4   260.37473  46.9302
       2  62.591 VB    1.2308 2.19394e4   256.27975  53.0698

    Totals :                  4.13408e4   516.65448

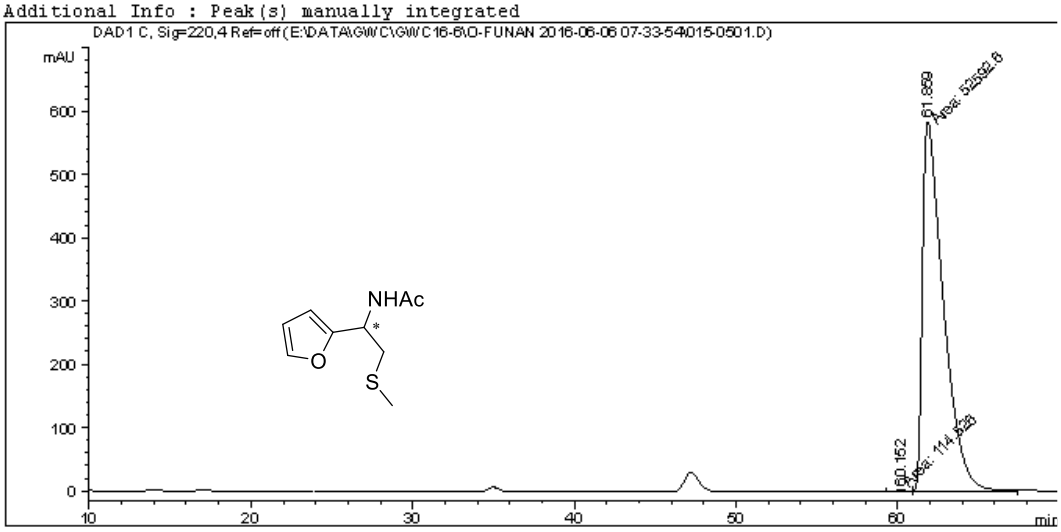

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/10/2017 5:14:40 PM SYSTEM                    Page 1 of 1
```

HPLC of cat-2n

```
Data File E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\015-0501.D
Sample Name: 0-cat

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   5
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 15
    Injection Date  : 6/6/2016 9:50:37 AM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\DAD-0JH(1-6)-95-5-0.5ML-
                      210-254NM-70MIN.M
    Last changed    : 6/6/2016 8:26:54 AM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-6\0-FUNAN 2016-06-06 07-33-54\DAD-0JH(1-6)-95-5-0.5ML-
                      210-254NM-70MIN.M (Sequence Method)
    Last changed    : 4/10/2017 5:15:37 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=220,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  60.152 MM    0.9117  114.52566    2.09357   0.2173
       2  61.859 MM    1.5020 5.25926e4   583.59174  99.7827

    Totals :                  5.27072e4   585.68531

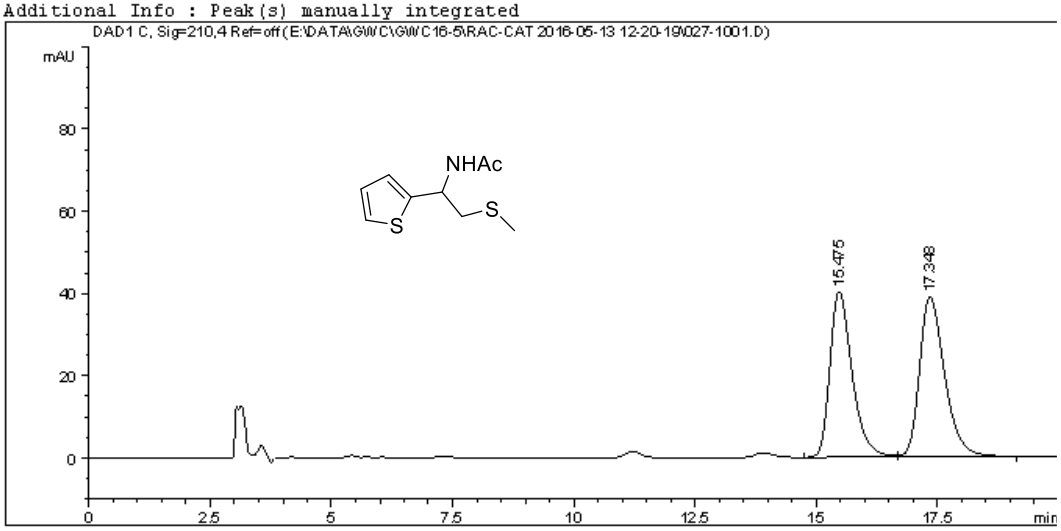

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/10/2017 5:15:41 PM SYSTEM                    Page 1 of 1
```

HPLC of rac-2o

```
Data File E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\027-1001.D
Sample Name: S-rac

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  10
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 27
    Injection Date  : 5/13/2016 4:38:41 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-ODH-90-10-AALL-1ML-
                      40MIN(1-2).M
    Last changed    : 5/13/2016 5:09:45 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-ODH-90-10-AALL-1ML-
                      40MIN(1-2).M (Sequence Method)
    Last changed    : 4/10/2017 5:17:32 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  15.475 BB    0.4778 1268.28577   40.22914  47.8335
       2  17.348 BB    0.5467 1383.17261   38.72876  52.1665

    Totals :                  2651.45837   78.95789

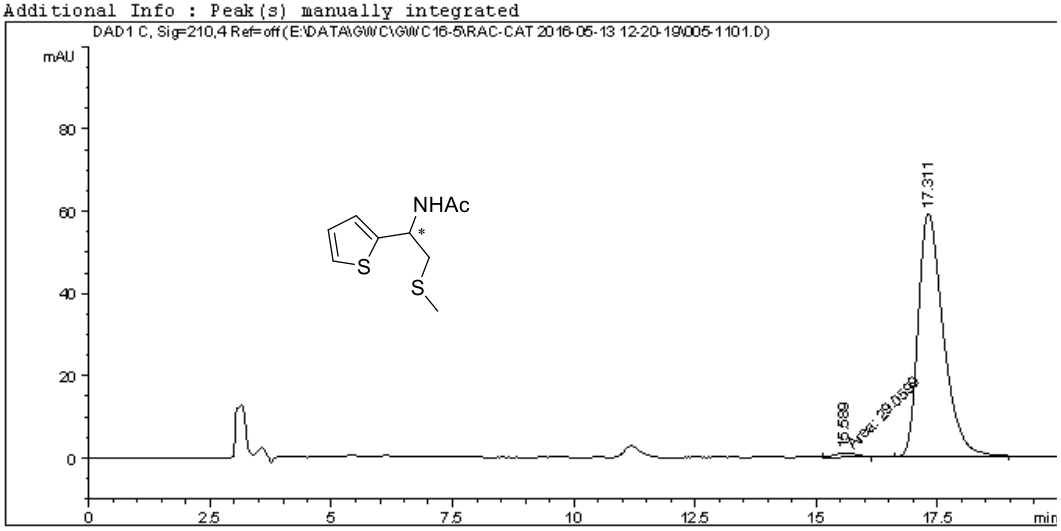

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 4/10/2017 5:17:36 PM SYSTEM                    Page 1 of 1
```

HPLC of cat-2o

Data File E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\005-1101.D
Sample Name: S-cat

```
==================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  11
Acq. Instrument : 1260HPLC-DAD                     Location : Vial 5
Injection Date  : 5/13/2016 5:11:37 PM                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-ODH-90-10-AALL-1ML-
                  40MIN(1-2).M
Last changed    : 5/13/2016 5:13:17 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\GWC\GWC16-5\RAC-CAT 2016-05-13 12-20-19\DAD-ODH-90-10-AALL-1ML-
                  40MIN(1-2).M (Sequence Method)
Last changed    : 4/10/2017 5:18:05 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                          Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.589 MM    0.5166   29.05995 9.37588e-1   1.3552
   2  17.311 BB    0.5455 2115.20801   59.11230  98.6448

Totals :                  2144.26795   60.04989

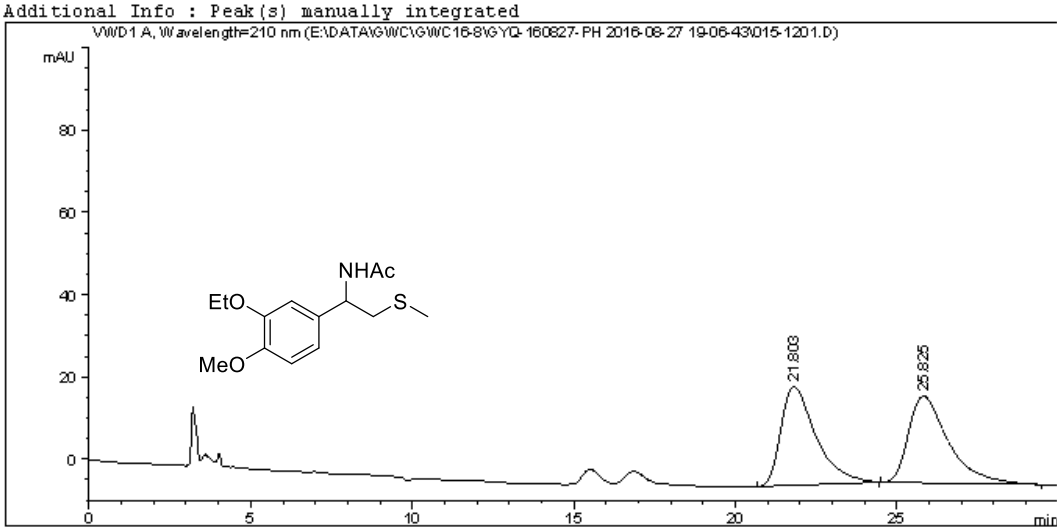

==================================================================
                          *** End of Report ***
```

1260HPLC-DAD 4/10/2017 5:18:09 PM SYSTEM Page 1 of 1

HPLC of rac-2q

```
Data File E:\DATA\GWC\GWC16-8\GYQ-160827-PH 2016-08-27 19-06-43\015-1201.D
Sample Name: RAC

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  12
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 15
    Injection Date  : 8/28/2016 1:36:09 AM                  Inj :   1
                                                      Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-8\GYQ-160827-PH 2016-08-27 19-06-43\VWD-OJ(1-2)-90-10-
                      1ML-40MIN-210NM.M
    Last changed    : 8/27/2016 8:20:13 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-8\GYQ-160827-PH 2016-08-27 19-06-43\VWD-OJ(1-2)-90-10-
                      1ML-40MIN-210NM.M (Sequence Method)
    Last changed    : 4/11/2017 5:43:27 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  21.803 BB    1.1150 1810.98096   23.98081  49.9569
       2  25.825 BB    1.2500 1814.10681   21.12218  50.0431

    Totals :                  3625.08777   45.10299

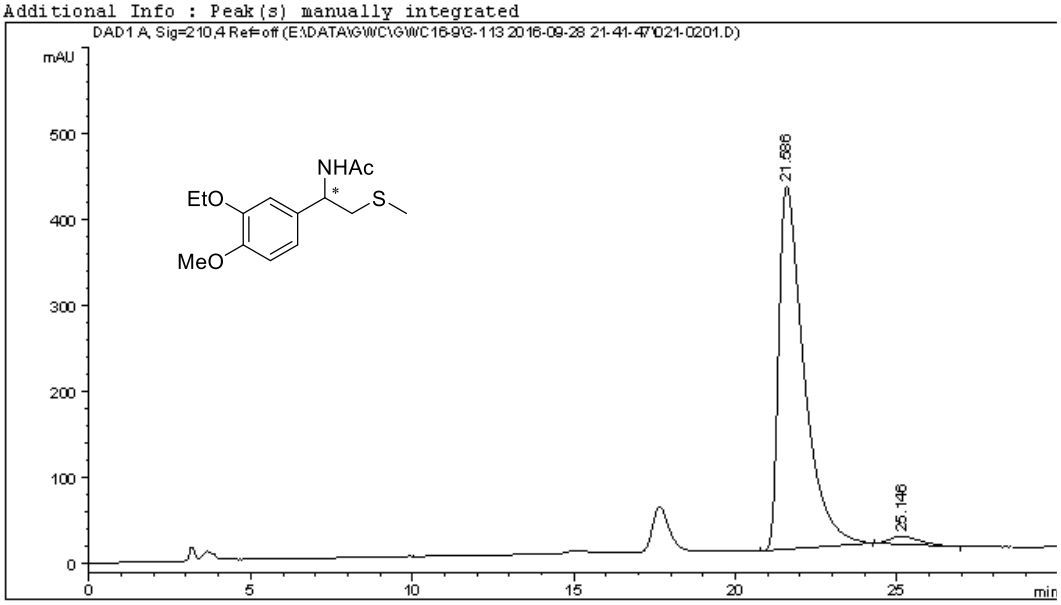

    ==================================================================
                              *** End of Report ***


1260HPLC-VWD 4/11/2017 5:44:28 PM SYSTEM                    Page 1 of 1
```

HPLC of cat-2q

```
Data File E:\DATA\GWC\GWC16-9\3-113 2016-09-28 21-41-47\021-0201.D
Sample Name: S-shuangqudai

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 21
    Injection Date  : 9/28/2016 9:53:39 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-9\3-113 2016-09-28 21-41-47\DAD-OJH(1-6)-90-10-210-254
                      -40MIN.M
    Last changed    : 9/28/2016 9:41:47 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-9\3-113 2016-09-28 21-41-47\DAD-OJH(1-6)-90-10-210-254
                      -40MIN.M (Sequence Method)
    Last changed    : 4/11/2017 5:42:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  21.586 BB    0.7758 2.29420e4   422.27399  97.5213
       2  25.146 BB    0.7372  583.10815    9.30326   2.4787

    Totals :                  2.35251e4   431.57724

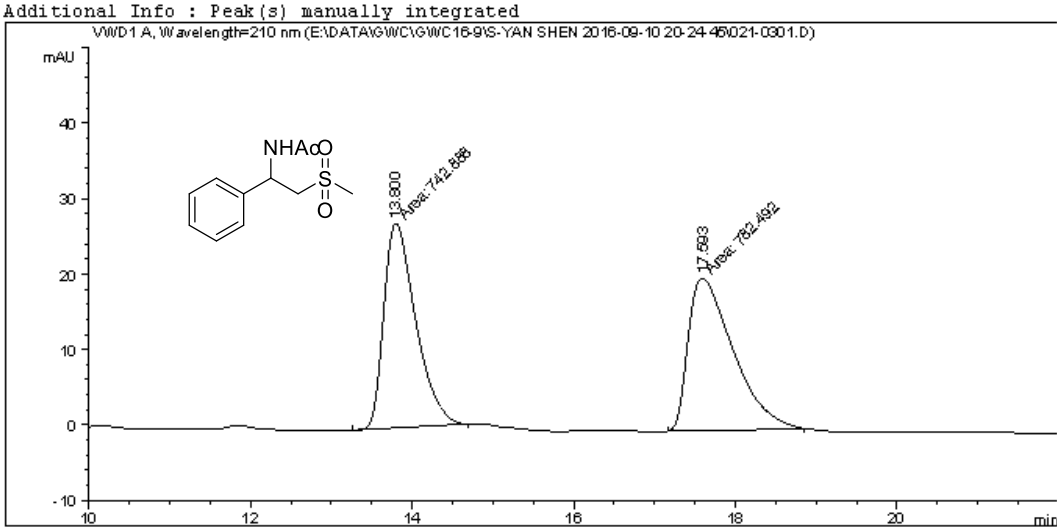

    ==================================================================
                              *** End of Report ***

1260HPLC-VWD 4/11/2017 5:42:46 PM SYSTEM                          Page 1 of 1
```

HPLC of rac-3a

```
Data File E:\DATA\GWC\GWC16-9\S-YAN SHEN 2016-09-10 20-24-45\021-0301.D
Sample Name: S-RAC

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 21
    Injection Date  : 9/10/2016 9:02:02 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GWC\GWC16-9\S-YAN SHEN 2016-09-10 20-24-45\VWD-ADH(1-6)-85-15-
                      210NM-30MIN.M
    Last changed    : 9/10/2016 9:01:05 PM by SYSTEM
    Analysis Method : E:\DATA\GWC\GWC16-9\S-YAN SHEN 2016-09-10 20-24-45\VWD-ADH(1-6)-85-15-
                      210NM-30MIN.M (Sequence Method)
    Last changed    : 10/6/2016 8:15:11 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.800 MM    0.4564  742.88812   27.12571  48.7018
       2  17.593 MM    0.6446  782.49176   20.23214  51.2982

    Totals :                  1525.37988   47.35785

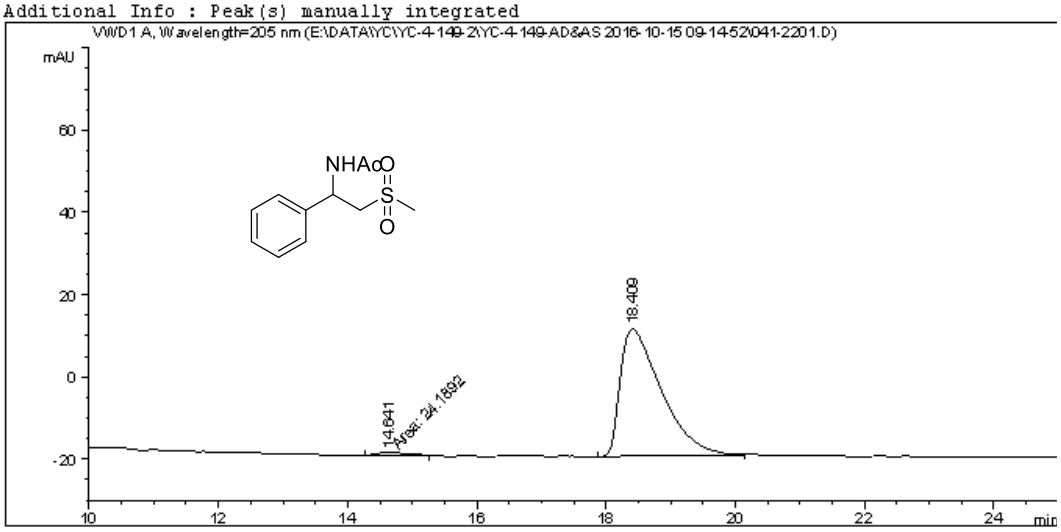

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 10/6/2016 8:15:20 PM SYSTEM                    Page 1 of 1
```

HPLC of cat-3a

```
Data File E:\DATA\YC\YC-4-149-2\YC-4-149-AD&AS 2016-10-15 09-14-52\041-2201.D
Sample Name: S

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  22
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 41
    Injection Date  : 10/15/2016 4:51:21 PM                Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\YC\YC-4-149-2\YC-4-149-AD&AS 2016-10-15 09-14-52\VWD-ADH(1-6)-85
                      -15-205NM-30MIN.M
    Last changed    : 10/15/2016 11:54:07 AM by SYSTEM
    Analysis Method : E:\DATA\YC\YC-4-149-2\YC-4-149-AD&AS 2016-10-15 09-14-52\VWD-ADH(1-6)-85
                      -15-205NM-30MIN.M (Sequence Method)
    Last changed    : 10/16/2016 6:16:45 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=205 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.641 MM    0.5949   24.18923 6.77638e-1   1.7466
       2  18.409 BB    0.6526 1360.77649   30.90807  98.2534

    Totals :                  1384.96572   31.58571

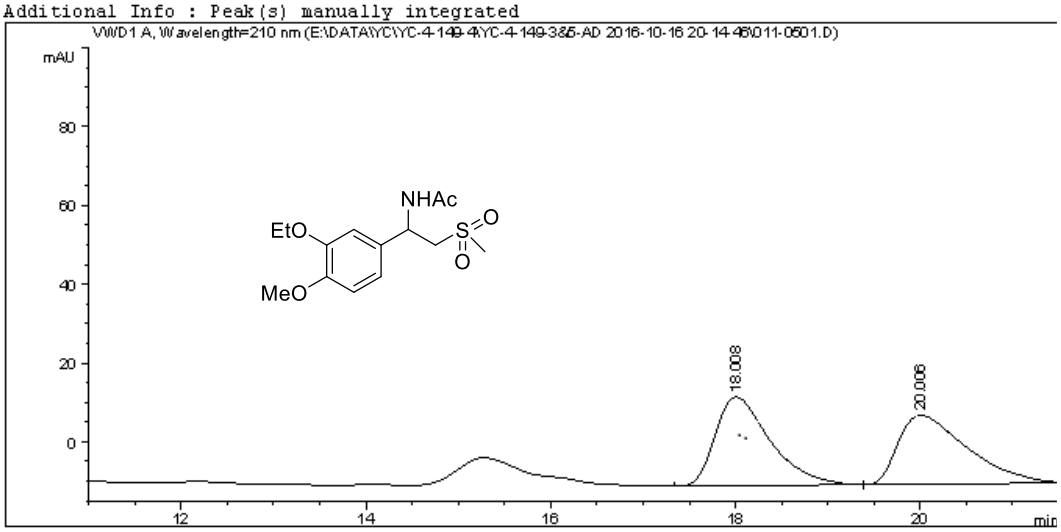

    ==================================================================
                              *** End of Report ***


1260HPLC-DAD 10/16/2016 6:18:05 PM SYSTEM                    Page 1 of 1
```

HPLC of rac-3q

```
Data File E:\DATA\YC\YC-4-149-4\YC-4-149-3&5-AD 2016-10-16 20-14-46\011-0501.D
Sample Name: 1

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   5
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 11
    Injection Date  : 10/16/2016 9:58:35 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\YC\YC-4-149-4\YC-4-149-3&5-AD 2016-10-16 20-14-46\VWD-ADH(1-6)-
                      85-15-210NM-30MIN.M
    Last changed    : 10/16/2016 8:28:04 PM by SYSTEM
    Analysis Method : E:\DATA\YC\YC-4-149-4\YC-4-149-3&5-AD 2016-10-16 20-14-46\VWD-ADH(1-6)-
                      85-15-210NM-30MIN.M (Sequence Method)
    Last changed    : 4/12/2017 10:32:12 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  18.008 BB    0.6255  928.37646   22.53971  50.6550
       2  20.006 BB    0.7779  904.36621   17.47094  49.3450

    Totals :                   1832.74268   40.01065

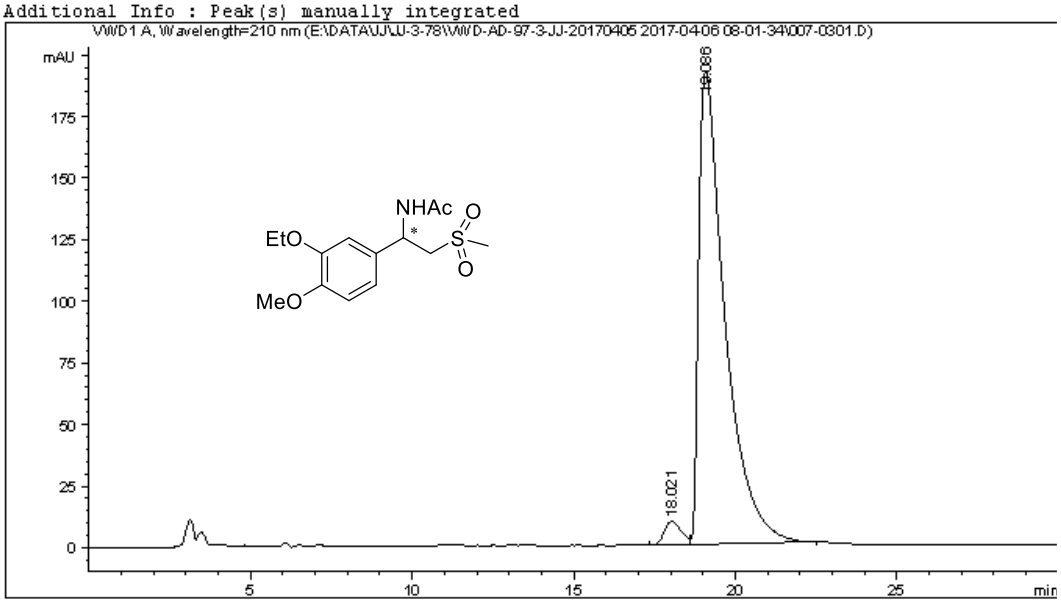

    ==================================================================
                              *** End of Report ***


1260HPLC-VWD 4/12/2017 10:32:20 AM SYSTEM                    Page 1 of 1
```

HPLC of cat-3q

```
Data File E:\DATA\JJ\JJ-3-78\VWD-AD-97-3-JJ-20170405 2017-04-06 08-01-34\007-0301.D
Sample Name: 456

    ==================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 7
    Injection Date  : 4/6/2017 8:55:58 AM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\JJ\JJ-3-78\VWD-AD-97-3-JJ-20170405 2017-04-06 08-01-34\VWD-ADH(1
                      -2)-85-15-205NM-50MIN.M
    Last changed    : 4/6/2017 8:55:13 AM by SYSTEM
    Analysis Method : E:\DATA\JJ\JJ-3-78\VWD-AD-97-3-JJ-20170405 2017-04-06 08-01-34\VWD-ADH(1
                      -2)-85-15-205NM-50MIN.M (Sequence Method)
    Last changed    : 4/6/2017 8:01:34 AM by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                              Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  18.021 BV    0.5571  352.21262    9.50950   3.1448
       2  19.086 VB    0.8289 1.08476e4   192.06339  96.8552

    Totals :                   1.11998e4   201.57288


    ==================================================================
                              *** End of Report ***

1260HPLC-VWD 4/6/2017 9:28:28 AM SYSTEM                          Page 1 of 1
```