

Supporting Information for

Copper-Mediated Arylation of Thioethers with Boronic Acids

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CONTENTS

1. General Information	S2
2. Optimization of the Reaction Conditions	S3
3. Procedures for preparation of substrates	S3
4. Procedures for preparation of aryl sulfonium salts	S15
5. UV absorption and Thermogravimetric analysis of 3a , 3d , 3e , 3t	S30
6. Proposed mechanism	S32
7. References	S32
8. NMR Spectra	S33

1. General information: Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in flame-dried glassware under air unless otherwise noted. NMR spectra were recorded on Bruker-400 spectrometers. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale (CHCl_3 : δ 7.26 for proton and δ 77.16 for carbon). Multiplicities were given as: s (singlet); d (doublet); dd (doublet of doublets); t (triplet); Coupling constants are reported as a J value in Hz. High-resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. Thermogravimetric analyses (TGA) were carried out on NETZSCH TG 209 thermal gravimetric analyzer (NETZSCH, Selb, Germany). UV absorption spectra were measured using a Hitachi UH5300 double-beam UV-vis spectrophotometer. The heat source used for the reaction is an oil bath. Column chromatography was performed on 300-400 mesh silica gel using petroleum ether-ethyl acetate or dichloromethane-methanol gradient system. TLC visualization was carried out using UV light (254 nm and 366 nm) where applicable, and otherwise by iodine vapor staining.

2. Optimization of the Reaction Conditions

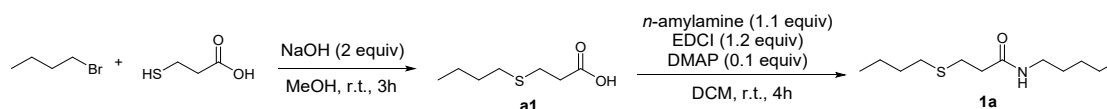
Entry	Deviation from standard conditions	3a (%) ^a
1	none	94
2	In HFIP	57(87)
3	In MeOH	21
4	In DCE	80
5	In THF	67
6	In toluene	52
7	In MeCN	<15
8	In DMSO	<15
9	In DMF	<15
10	Under argon atmosphere	72
11	1a (1.5 equiv) with 2a (1 equiv)	83
12	1a (1 equiv) with 2a (2 equiv)	76
13	Cu(OTf) ₂ (1.5 equiv)	91
14	Cu(OAc) ₂ instead of Cu(OTf) ₂	31
15	CuSO ₄ ·5H ₂ O instead of Cu(OTf) ₂	30
16	CuBr ₂ instead of Cu(OTf) ₂	<15
17	CuCl ₂ instead of Cu(OTf) ₂	<15
18	Cu(OTf) ₂ (10 mol%) with NFSI (1.5 equiv)	<15
19	Cu(OTf) ₂ (10 mol%) with PIDA (1.5 equiv)	<15
20	Cu(OTf) ₂ (10 mol%) with selectfluor (1.5 equiv)	<15
21	Cu(OTf) ₂ (10 mol%) with LPO (1.5 equiv)	<15

^aThe reaction of **1a** (0.6 mmol), **2a** (0.3 mmol), and Cu(OTf)₂ (0.6 mmol) was carried out in trifluoroethanol (1 mL) at 60 °C for 4h under air unless otherwise noted.

3. Procedures for preparation of substrates

Most of the boronic acids (**2a-2o**) were commercially available and used directly without further purification. Boronic acid **2ai** was prepared according to the known procedure.¹

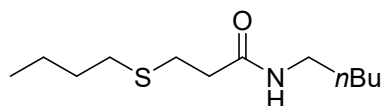
Substrates 1p - 1z were prepared analogously to **1a**:



Step 1: To a solution of 1-bromobutane (2.6 g, 18.8 mmol, 1.0 equiv) and 3-mercaptopropanoic acid (2.0 g, 18.8 mmol, 1.0 equiv) (2-mercaptoacetic acid was used for substrates **3t**, **3u**, **3v**) in MeOH (15 mL) was added NaOH (1.5 g, 37.6 mmol, 2.0 equiv) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. After completion of the reaction as monitored by TLC, the mixture was concentrated under reduced pressure. The residue was acidified with 1 M aqueous HCl and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (300 - 400 mesh, eluting with DCM/MeOH = 20 : 1) to afford compound **a1** (2.0 g, 67% yield).

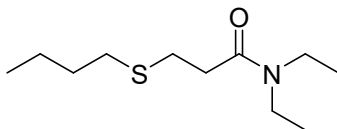
Step 2: To a stirred solution of compound **a1** (1.62 g, 10.0 mmol, 1.0 equiv) in DCM (15 mL) were added EDCI (2.30 g, 12.0 mmol, 1.2 equiv) and DMAP (122 mg, 1.0 mmol, 0.1 equiv) at 0 °C. Subsequently, a solution of *n*-amylamine (0.96 g, 11.0 mmol, 1.1 equiv) in DCM (2 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Upon completion as monitored by TLC, the reaction mixture was diluted with DCM (30 mL) and washed sequentially with 1 M aqueous HCl (3 × 20 mL) and brine (20 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (300 - 400 mesh, eluting with PE/EtOAc = 2 : 1) to afford the product **1a** (1.98 g, 86% yield).

3-(butylthio)-N-pentylpropanamide (1a):



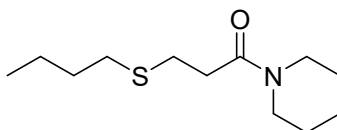
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.5. Yield: 93% (2.15 g scale); ¹H NMR (400 MHz, CDCl₃) δ 6.12 (s, 1H), 3.23 – 3.12 (m, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.51 – 2.44 (m, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 1.55 – 1.41 (m, 4H), 1.39 – 1.30 (m, 2H), 1.29 – 1.18 (m, 4H), 0.89 – 0.79 (m, 6H).; ¹³C NMR (101 MHz, CDCl₃) δ 171.3, 39.6, 36.9, 32.1, 31.7, 29.3, 29.1, 28.0, 22.4, 22.0, 14.0, 13.7.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₁₂H₂₆NOS⁺, 232.1730. Found. 232.1733.

3-(butylthio)-N,N-diethylpropanamide (1p):



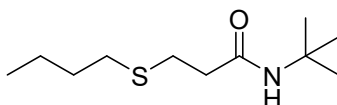
Yellow oily liquid. PE/EtOAc = 2 : 1, R_f = 0.8. Yield: 77% (1.66 g scale); ¹H NMR (400 MHz, CDCl₃) δ 3.33 – 3.17 (m, 4H), 2.78 – 2.68 (m, 2H), 2.54 – 2.40 (m, 4H), 1.55 – 1.42 (m, 2H), 1.38 – 1.23 (m, 2H), 1.13 – 0.98 (m, 6H), 0.81 (t, *J* = 7.3 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 170.3, 41.8, 40.1, 33.6, 32.1, 31.7, 27.6, 21.9, 14.2, 13.6, 13.0.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₁₁H₂₄NOS⁺, 218.1573. Found. 218.1579.

3-(butylthio)-1-(piperidin-1-yl)propan-1-one (1q):



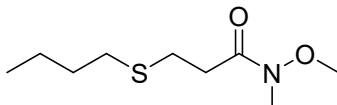
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.7. Yield: 90% (1.27 g scale); ¹H NMR (400 MHz, CDCl₃) δ 3.51 – 3.43 (m, 2H), 3.36 – 3.29 (m, 2H), 2.77 – 2.70 (m, 2H), 2.56 – 2.50 (m, 2H), 2.49 – 2.43 (m, 2H), 1.61 – 1.54 (m, 2H), 1.54 – 1.42 (m, 6H), 1.38 – 1.28 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 169.4, 46.5, 42.7, 33.7, 32.1, 31.7, 27.6, 26.4, 25.5, 24.5, 21.9, 13.7.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₁₂H₂₄NOS⁺, 230.1573. Found. 230.1580.

N-(tert-butyl)-3-(butylthio)propanamide (1r):



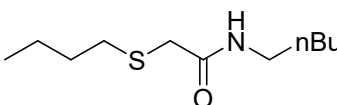
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.7. Yield: 71% (0.95 g scale); ¹H NMR (400 MHz, CDCl₃) δ 2.77 – 2.72 (m, 2H), 2.53 – 2.47 (m, 2H), 2.36 – 2.30 (m, 2H), 1.58 – 1.49 (m, 2H), 1.41 – 1.33 (m, 2H), 1.32 (s, 9H), 0.87 (t, *J* = 7.3 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 170.7, 51.4, 37.9, 32.2, 31.8, 28.9, 27.9, 22.0, 13.7.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₁₁H₂₄NOS⁺, 218.1573. Found. 218.1580.

3-(butylthio)-N-methoxy-N-methylpropanamide (1s):



Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.6. Yield: 86% (1.23 g scale); ¹H NMR (400 MHz, CDCl₃) δ 3.66 (s, 3H), 3.15 (s, 3H), 2.79 – 2.74 (m, 2H), 2.72 – 2.64 (m, 2H), 2.53 – 2.48 (m, 2H), 1.58 – 1.49 (m, 2H), 1.42 – 1.31 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 61.3, 32.6, 32.1, 31.7, 26.9, 22.0, 13.7.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₉H₂₀NO₂S⁺, 206.1209. Found. 206.1213.

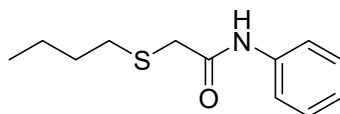
2-(butylthio)-N-pentylacetamide(1t):



colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.6. Yield: 88% (1.29 g scale); ¹H NMR (400 MHz, CDCl₃) δ 6.95 (s, 1H), 3.23 – 3.17 (m, 2H), 3.12 (s, 2H), 2.49 – 2.42 (m, 2H), 1.53 – 1.41

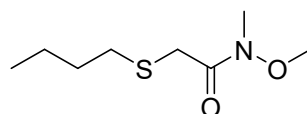
(m, 4H), 1.37 – 1.28 (m, 2H), 1.28 – 1.20 (m, 4H), 0.87 – 0.79 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 39.7, 36.2, 32.8, 31.2, 29.2, 29.0, 22.3, 21.8, 13.9, 13.5. HRMS (ESI) m/z : $(\text{M}+\text{H})^+$ Calc. for: $\text{C}_{11}\text{H}_{24}\text{NOS}^+$, 218.1573. Found. 218.1571.

2-(butylthio)-N-phenylacetamide (1u):



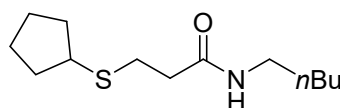
Yellow oily liquid. PE/EtOAc = 2 : 1, R_f = 0.6. Yield: 91% (1.38 g scale); ^1H NMR (400 MHz, CDCl_3) δ 8.82 (s, 1H), 7.63 – 7.49 (m, 2H), 7.38 – 7.27 (m, 2H), 7.17 – 7.07 (m, 1H), 3.34 (s, 2H), 2.65 – 2.54 (m, 2H), 1.68 – 1.53 (m, 2H), 1.49 – 1.32 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.3, 137.6, 129.1, 124.6, 119.8, 37.1, 32.9, 31.2, 21.9, 13.6.; HRMS (ESI) m/z : $(\text{M}+\text{H})^+$ Calc. for: $\text{C}_{12}\text{H}_{18}\text{NOS}^+$, 224.1104. Found. 224.1106.

2-(butylthio)-N-methoxy-N-methylacetamide (1v):



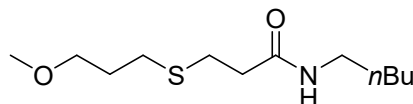
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.6. Yield: 73% (0.97 g scale); ^1H NMR (400 MHz, CDCl_3) δ 3.68 (s, 3H), 3.28 (s, 2H), 3.13 (s, 3H), 2.63 – 2.55 (m, 2H), 1.57 – 1.46 (m, 2H), 1.39 – 1.28 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 61.4, 32.2, 32.1, 31.6, 31.2, 21.8, 13.6.; HRMS (ESI) m/z : $(\text{M}+\text{H})^+$ Calc. for: $\text{C}_8\text{H}_{18}\text{NO}_2\text{S}^+$, 192.1053. Found. 192.1054.

3-(cyclopentylthio)-N-pentylpropanamide (1w):



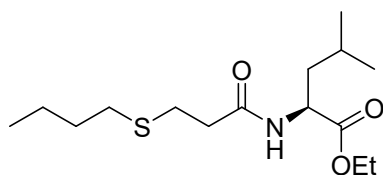
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.5. Yield: 91% (1.27 g scale); ^1H NMR (400 MHz, CDCl_3) δ 6.04 (s, 1H), 3.25 – 3.14 (m, 2H), 3.12 – 3.00 (m, 1H), 2.83 – 2.74 (m, 2H), 2.46 – 2.36 (m, 2H), 2.03 – 1.87 (m, 2H), 1.78 – 1.61 (m, 2H), 1.58 – 1.37 (m, 6H), 1.32 – 1.20 (m, 4H), 0.84 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.4, 44.1, 39.6, 36.9, 33.8, 29.3, 29.1, 27.7, 24.8, 22.4, 14.0.; HRMS (ESI) m/z : $(\text{M}+\text{H})^+$ Calc. for: $\text{C}_{13}\text{H}_{26}\text{NOS}^+$, 244.1730. Found. 244.1733.

3-((3-methoxypropyl)thio)-N-pentylpropanamide (1x):



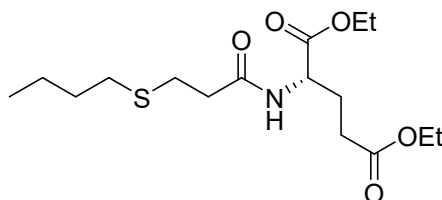
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.2. Yield: 94% (1.30 g scale); ^1H NMR (400 MHz, CDCl_3) δ 6.20 (s, 1H), 3.37 (t, J = 6.1 Hz, 2H), 3.24 (s, 3H), 3.15 (dd, J = 13.0, 7.1 Hz, 2H), 2.72 (t, J = 7.3 Hz, 2H), 2.53 (t, J = 7.3 Hz, 2H), 2.37 (t, J = 7.3 Hz, 2H), 1.82 – 1.68 (m, 2H), 1.47 – 1.35 (m, 2H), 1.28 – 1.16 (m, 4H), 0.81 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.3, 71.0, 58.5, 39.6, 36.7, 29.5, 29.2, 29.0, 28.8, 27.9, 22.3, 14.0.; HRMS (ESI) m/z : $(\text{M}+\text{H})^+$ Calc. for: $\text{C}_{12}\text{H}_{26}\text{NO}_2\text{S}^+$, 248.1679. Found. 248.1682.

ethyl (3-(butylthio)propanoyl)-L-leucinate (1y):



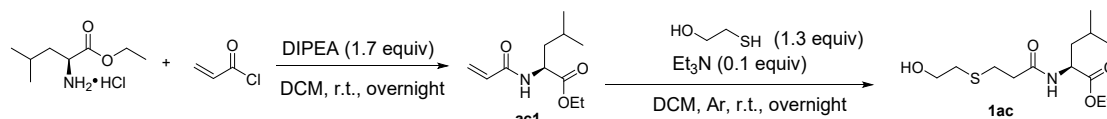
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.6. Yield: 81% (1.53 g scale); ¹H NMR (400 MHz, CDCl₃) δ 6.31 (d, *J* = 8.2 Hz, 1H), 4.61 – 4.53 (m, 1H), 4.18 – 4.08 (m, 2H), 2.79 – 2.71 (m, 2H), 2.51 – 2.41 (m, 4H), 1.69 – 1.55 (m, 2H), 1.55 – 1.44 (m, 3H), 1.39 – 1.29 (m, 2H), 1.25 – 1.19 (m, 3H), 0.92 – 0.82 (m, 9H).; ¹³C NMR (126 MHz, CDCl₃) δ 173.2, 171.1, 61.3, 50.8, 41.7, 36.6, 32.0, 31.7, 27.6, 24.9, 22.8, 22.0, 21.9, 14.2, 13.7.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₁₅H₃₀NO₃S⁺, 304.1941. Found. 304.1946.

diethyl (3-(butylthio)propanoyl)-L-glutamate (1z):



Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.6. Yield: 67% (1.44 g scale); ¹H NMR (400 MHz, CDCl₃) δ 6.57 (d, *J* = 7.8 Hz, 1H), 4.59 – 4.49 (m, 1H), 4.18 – 4.10 (m, 2H), 4.09 – 4.02 (m, 2H), 2.77 – 2.69 (m, 2H), 2.52 – 2.40 (m, 4H), 2.39 – 2.24 (m, 2H), 2.17 – 2.08 (m, 1H), 1.98 – 1.87 (m, 1H), 1.55 – 1.45 (m, 2H), 1.38 – 1.28 (m, 2H), 1.25 – 1.15 (m, 6H), 0.87 – 0.80 (m, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 171.9, 171.3, 61.6, 60.7, 51.7, 36.6, 32.0, 31.6, 30.3, 27.6, 27.3, 21.9, 14.2, 14.1, 13.6.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₁₆H₃₀NO₅S⁺, 348.1839. Found. 348.1843.

Substrates 1aa, 1ab were prepared analogously to 1ac:

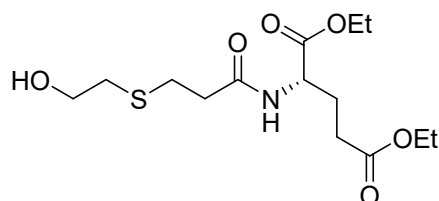


Step 1: To a stirred solution of L-leucine ethyl ester hydrochloride (4.30 g, 22.0 mmol, 1.1 equiv) and DIPEA (4.39 g, 34.0 mmol, 1.7 equiv) in DCM (20 mL) was added dropwise acryloyl chloride (1.81 g, 20.0 mmol, 1.0 equiv) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight. After completion of the reaction as monitored by TLC, the mixture was washed with brine (30 mL), and the aqueous phase was extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (300 - 400 mesh, eluting with PE/EtOAc = 2 : 1) to afford compound **ac1** (3.42 g, 80% yield).

Step 2: Under an argon atmosphere, a mixture of compound **ac1** (2.13 g, 10.0 mmol,

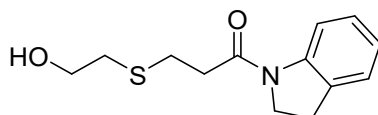
1.0 equiv), 2-mercaptoethanol (1.02 g, 13.0 mmol, 1.3 equiv), and Et₃N (0.10 g, 1.0 mmol, 0.1 equiv) in DCM (15 mL) was stirred at room temperature overnight. After completion of the reaction as monitored by TLC, the mixture was washed with brine (30 mL), and the aqueous phase was extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (300 - 400 mesh, eluting with PE/EtOAc = 1 : 1) to afford compound **1ac** (2.06 g, 71% yield).

diethyl (3-((2-hydroxyethyl)thio)propanoyl)-L-glutamate (1aa):



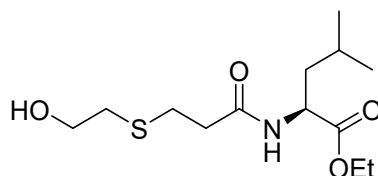
Colorless oily liquid. DCM/MeOH = 20 : 1, R_f = 0.4. Yield: 69% (4.60 g scale); ¹H NMR (400 MHz, CDCl₃) δ 7.03 (d, *J* = 7.9 Hz, 1H), 4.46 – 4.37 (m, 1H), 4.06 – 3.99 (m, 2H), 3.99 – 3.92 (m, 2H), 3.64 – 3.54 (m, 3H), 2.71 – 2.65 (m, 2H), 2.58 – 2.52 (m, 2H), 2.42 – 2.35 (m, 2H), 2.30 – 2.20 (m, 2H), 2.06 – 1.97 (m, 1H), 1.85 – 1.76 (m, 1H), 1.14 – 1.06 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 171.7, 171.4, 61.3, 60.9, 60.4, 51.5, 36.1, 34.7, 30.1, 27.3, 26.9, 13.9, 13.8.; HRMS (ESI) *m/z* : (M-H)⁻ Calc. for: C₁₄H₂₄NO₆S⁻, 334.1330. Found. 334.1325.

3-((2-hydroxyethyl)thio)-1-(indolin-1-yl)propan-1-one (1ab):



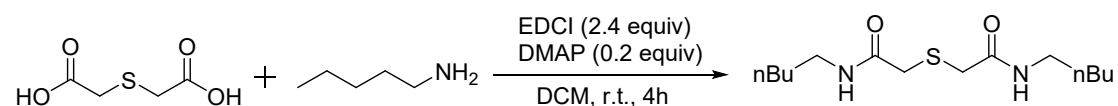
White solid. DCM/MeOH = 20 : 1, R_f = 0.6. Yield: 63% (1.90 g scale); **Melting point:** 139 – 140 °C ; ¹H NMR (400 MHz, CDCl₃) δ 8.22 – 8.17 (m, 1H), 7.19 – 7.13 (m, 2H), 7.02 – 6.97 (m, 1H), 4.02 – 3.96 (m, 2H), 3.79 – 3.76 (m, 2H), 3.18 – 3.12 (m, 2H), 2.96 – 2.90 (m, 3H), 2.78 – 2.74 (m, 2H), 2.70 – 2.66 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 169.4, 142.7, 131.2, 127.5, 124.6, 123.8, 117.0, 61.0, 47.9, 36.3, 35.6, 27.9, 26.4.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₁₃H₁₈NO₂S⁺, 252.1053. Found. 252.1054.

ethyl (3-((2-hydroxyethyl)thio)propanoyl)-L-leucinate (1ac):



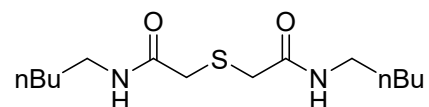
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.1. Yield: 71% (2.06 g scale); ¹H NMR (400 MHz, CDCl₃) δ 6.24 (d, *J* = 8.1 Hz, 1H), 4.65 – 4.58 (m, 1H), 4.22 – 4.13 (m, 2H), 3.78 – 3.70 (m, 2H), 2.90 – 2.80 (m, 3H), 2.75 – 2.70 (m, 2H), 2.55 – 2.48 (m, 2H), 1.71 – 1.59 (m, 2H), 1.57 – 1.48 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.96 – 0.90 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 173.4, 171.1, 61.6, 61.0, 51.0, 41.8, 36.7, 35.6, 27.4, 25.0, 22.9, 22.1, 14.3.; HRMS (ESI) *m/z* : (M-H)⁻ Calc. for: C₁₃H₂₄NO₄S⁻, 290.1432. Found. 290.1429.

Preparation of Substrate 1ad:



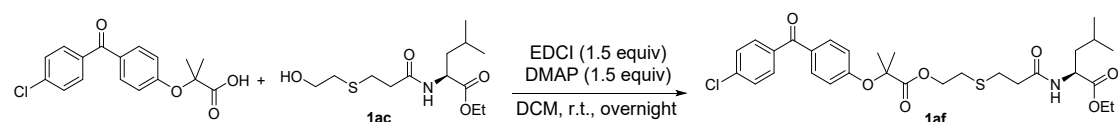
To a stirred solution of thiodiglycolic acid (600.6 mg, 4.0 mmol, 1.0 equiv) in DCM (10 mL) were added EDCI (1.84 g, 9.6 mmol, 2.4 equiv) and DMAP (98.0 mg, 0.8 mmol, 0.2 equiv) at 0 °C. Subsequently, a solution of *n*-amylamine (767.0 mg, 8.8 mmol, 2.2 equiv) in DCM (1 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Upon completion as monitored by TLC, the reaction mixture was diluted with DCM (30 mL) and washed sequentially with 1 M aqueous HCl (3 × 20 mL) and brine (20 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (300 - 400 mesh, eluting with DCM/MeOH = 20 : 1) to afford the product **1ad** (1.07 g, 93% yield).

2,2'-thiobis(*N*-pentylacetamide) (**1ad**) :



White solid. DCM/MeOH = 20 : 1, R_f = 0.6. Yield: 93% (1.07 g scale); **Melting point**: 111 – 112 °C.; **¹H NMR** (400 MHz, CDCl₃) δ 7.25 – 7.18 (m, 2H), 3.23 – 3.16 (m, 8H), 1.53 – 1.44 (m, 4H), 1.32 – 1.23 (m, 8H), 0.88 – 0.82 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 168.9, 40.0, 35.9, 29.2, 29.1, 22.4, 14.0.; **HRMS (ESI)** m/z : (M)⁺ Calc. for: C₁₄H₂₉N₂O₂S⁺, 289.1944. Found. 289.1947.

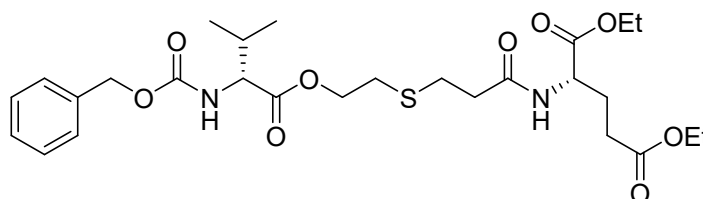
Substrates 1ae, 1ah were prepared analogously to 1af:



To a stirred solution of fenofibric acid (1.12 g, 3.5 mmol, 1.0 equiv) and compound **1ac** (1.02 g, 3.5 mmol, 1.0 equiv) in DCM (15 mL) at 0 °C were added sequentially EDCI (1.01 g, 5.25 mmol, 1.5 equiv) and DMAP (0.64 g, 5.25 mmol, 1.5 equiv). The ice bath was then removed, and the mixture was allowed to warm to room temperature and stirred overnight. The reaction progress was monitored by TLC until complete

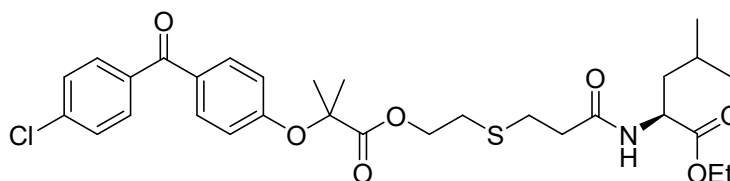
consumption of the starting materials. Upon completion, the reaction was quenched with 1 M aqueous HCl, and the mixture was extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (300 - 400 mesh, PE/EtOAc = 1 : 1) to afford the target compound **1af** (1.9 g, 92% yield).

diethyl (3-((2-(((benzyloxy)carbonyl)-D-valyl)oxy)ethyl)thio)propanoyl)-L-glutamate (1ae):



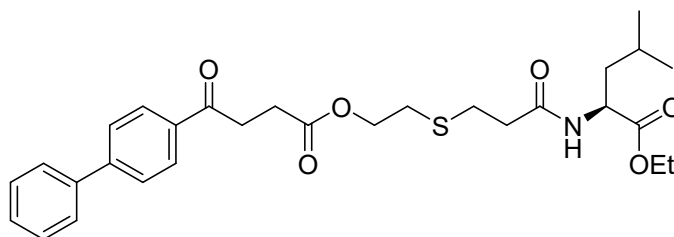
Colorless oily liquid. DCM/MeOH = 50 : 1, R_f = 0.5. Yield: 95% (1.62 g scale); ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.30 (m, 4H), 7.30 – 7.27 (m, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.56 (d, *J* = 9.0 Hz, 1H), 5.08 – 5.06 (m, 1H), 4.60 – 4.53 (m, 1H), 4.28 – 4.22 (m, 3H), 4.18 – 4.12 (m, 2H), 4.11 – 4.05 (m, 3H), 2.86 – 2.78 (m, 2H), 2.75 – 2.70 (m, 2H), 2.49 – 2.42 (m, 2H), 2.40 – 2.30 (m, 2H), 2.18 – 2.11 (m, 2H), 1.97 – 1.89 (m, 1H), 1.26 – 1.20 (m, 6H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 172.0, 171.9, 170.9, 156.4, 136.3, 128.6, 128.2, 128.1, 67.0, 64.3, 61.7, 60.7, 59.2, 51.7, 36.6, 31.1, 30.6, 30.4, 27.8, 27.3, 19.1, 17.6, 14.2, 14.1.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₂₇H₄₁N₂O₉S⁺, 569.2527. Found. 569.2528.

ethyl (3-((2-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)ethyl)thio)propanoyl)-L-leucinate (1af):



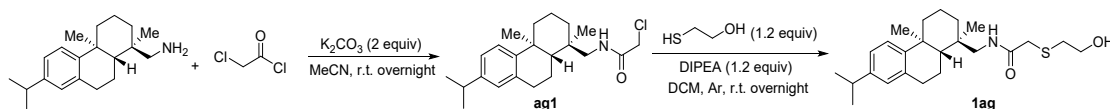
Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.3. Yield: 92% (1.90 g scale); ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.66 (m, 4H), 7.45 – 7.40 (m, 2H), 6.90 – 6.83 (m, 2H), 6.25 (d, *J* = 8.2 Hz, 1H), 4.62 – 4.55 (m, 1H), 4.32 – 4.26 (m, 2H), 4.19 – 4.11 (m, 2H), 2.82 – 2.75 (m, 2H), 2.72 – 2.66 (m, 2H), 2.48 – 2.39 (m, 2H), 1.66 (s, 6H), 1.64 – 1.47 (m, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.94 – 0.87 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.4, 173.6, 173.1, 170.7, 159.6, 138.5, 136.3, 132.1, 131.3, 130.5, 128.6, 117.4, 79.5, 64.4, 61.4, 50.9, 41.7, 36.6, 30.6, 27.7, 25.6, 25.5, 24.9, 22.9, 22.0, 14.2.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₃₀H₃₉ClNO₇S⁺, 592.2130. Found. 592.2153.

ethyl (3-((2-((4-([1,1'-biphenyl]-4-yl)-4-oxobutanoyl)oxy)ethyl)thio)propanoyl)-L-leucinate (1ah):



Yellow oily liquid. PE/EtOAc = 2 : 1, R_f = 0.1. Yield: 87% (1.61 g scale); ¹H NMR (500 MHz, CDCl₃) δ 8.07 – 8.02 (m, 2H), 7.70 – 7.65 (m, 2H), 7.63 – 7.59 (m, 2H), 7.48 – 7.43 (m, 2H), 7.41 – 7.36 (m, 1H), 6.31 (d, *J* = 8.3 Hz, 1H), 4.65 – 4.58 (m, 1H), 4.30 – 4.24 (m, 2H), 4.18 – 4.12 (m, 2H), 3.38 – 3.32 (m, 2H), 2.90 – 2.85 (m, 2H), 2.81 – 2.75 (m, 4H), 2.59 – 2.48 (m, 2H), 1.70 – 1.57 (m, 2H), 1.54 – 1.47 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 6.1 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 197.8, 173.1, 172.8, 170.8, 146.0, 139.8, 135.2, 129.0, 128.7, 128.3, 127.3, 77.4, 64.0, 61.4, 50.9, 41.7, 36.8, 33.4, 30.7, 28.3, 27.9, 24.9, 22.9, 22.0, 14.2.; HRMS (ESI) *m/z* : (M+H)⁺ Calc. for: C₂₉H₃₈NO₆S⁺, 528.2414. Found. 528.2421.

The preparation of **1ag** :

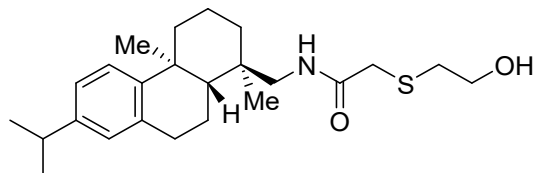


Step 1: To a stirred solution of dehydroabietylamine (2.85 g, 10 mmol, 1 equiv) and K₂CO₃ (2.76 g, 20 mmol, 2 equiv) in MeCN (20 mL) was added dropwise chloroacetyl chloride (1.13 g, 10 mmol, 1 equiv) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight. After completion of the reaction as monitored by TLC, the mixture was washed with brine (30 mL), and the aqueous phase was extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (300 - 400 mesh, eluting with PE/EtOAc = 5 : 1) to afford compound **ag1** (1.36 g, 38% yield).

Step 2: Under an argon atmosphere, a mixture of compound **ag1** (1.35 g, 3.7 mmol, 1.0 equiv), 2-mercaptoethanol (344 mg, 4.4 mmol, 1.2 equiv), and DIPEA (569 mg, 4.4 mmol, 1.2 equiv) in DCM (10 mL) was stirred at room temperature overnight. After completion of the reaction as monitored by TLC, the mixture was washed with brine (30 mL), and the aqueous phase was extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (300

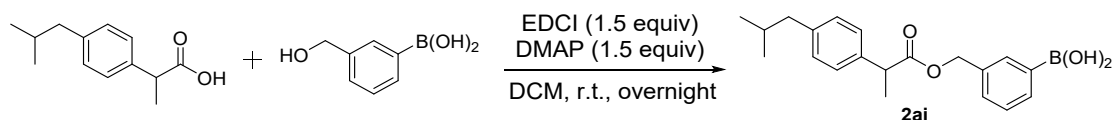
- 400 mesh, eluting with DCM/MeOH = 20 : 1) to afford compound **1ag** (1.25 g, 84% yield).

2-((2-hydroxyethyl)thio)-N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)acetamide (1ag):



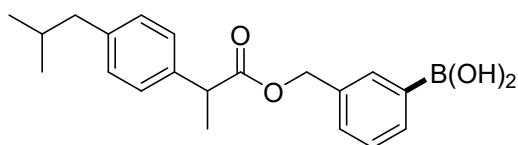
Colorless oily liquid. DCM/MeOH = 20 : 1, R_f = 0.4. Yield: 83% (1.25g scale); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.18 – 7.15 (m, 1H), 7.01 – 6.97 (m, 1H), 6.89 (s, 1H), 6.86 – 6.78 (m, 1H), 3.70 – 3.65 (m, 2H), 3.31 – 3.26 (m, 1H), 3.25 (s, 2H), 3.14 – 3.08 (m, 1H), 2.96 – 2.89 (m, 1H), 2.86 – 2.78 (m, 2H), 2.70 – 2.65 (m, 2H), 2.40 (br, 1H), 2.32 – 2.27 (m, 1H), 1.93 – 1.86 (m, 1H), 1.80 – 1.71 (m, 2H), 1.70 – 1.66 (m, 1H), 1.47 – 1.27 (m, 4H), 1.23 – 1.20 (m, 9H), 0.95 (s, 3H).; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.4, 147.2, 145.9, 134.9, 127.0, 124.3, 124.0, 61.3, 50.3, 45.4, 38.5, 37.6, 37.5, 36.4, 36.2, 33.6, 30.2, 25.3, 24.1, 24.0, 19.1, 18.9, 18.7.; **HRMS (ESI)** m/z : $(\text{M}+\text{H})^+$ Calc. for: $\text{C}_{24}\text{H}_{38}\text{NO}_2\text{S}^+$, 404.2618. Found. 404.2616.

The preparation of 2ai :



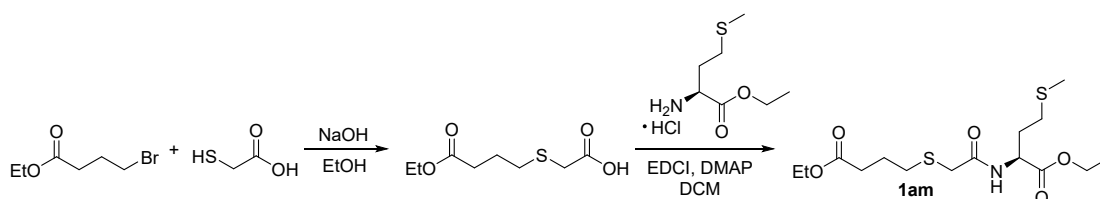
To a stirred solution of ibuprofen (1.03 g, 5.0 mmol, 1.0 equiv) and 3-(hydroxymethyl)phenylboronic acid (0.76 g, 5.0 mmol, 1.0 equiv) in DCM (15 mL) at 0 °C were added sequentially EDCI (1.44 g, 7.5 mmol, 1.5 equiv) and DMAP (0.92 g, 7.5 mmol, 1.5 equiv). The ice bath was then removed, and the mixture was allowed to warm to room temperature and stirred overnight. The reaction progress was monitored by TLC until complete consumption of the starting materials. Upon completion, the mixture was acidified with 1 M aqueous HCl and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (300 - 400 mesh, PE/EtOAc = 2 : 1) to afford the target compound **2ai** (1.24 g, 73% yield).

(3-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)phenyl)boronic acid (2ai):



Colorless oily liquid. PE/EtOAc = 2 : 1, R_f = 0.5. Yield: 73% (1.24 g scale); ¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.19 (m, 1H), 8.17 (s, 1H), 7.53 – 7.47 (m, 2H), 7.31 – 7.27 (m, 2H), 7.15 – 7.12 (m, 2H), 5.33 – 5.22 (m, 2H), 3.89 – 3.82 (m, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.93 – 1.82 (m, 1H), 1.61 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 6H).; ¹³C NMR (101 MHz, CDCl₃) δ 174.6, 140.6, 137.7, 135.9, 135.5, 135.1, 132.4, 129.4, 129.3, 128.3, 127.3, 66.4, 45.3, 45.1, 30.2, 22.5, 18.6.; HRMS (ESI) *m/z* : (M+Na)⁺ Calc. for: C₂₀H₂₅BNaO₄⁺, 363.1738. Found. 363.1744.

Substrates 1ak, 1al were prepared analogously to 1am:

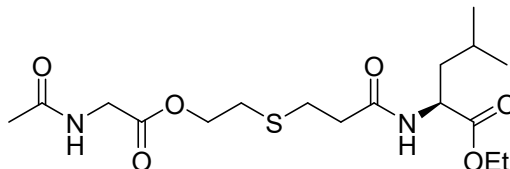


Step 1: To a solution of mercaptoacetic acid (2.77 g, 30.0 mmol, 1.0 equiv) and ethyl 4-bromobutyrate (5.85 g, 30.0 mmol, 1.0 equiv) in EtOH (20 mL) was added NaOH (2.40 g, 60 mmol, 2.0 equiv) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. After completion of the reaction as monitored by TLC, the mixture was concentrated under reduced pressure. The residue was acidified with 1 M aqueous HCl and extracted with DCM (3 × 20 mL) and water. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (300–400 mesh, eluting with DCM/MeOH = 20 : 1) to afford the product (4.27 g, 69% yield).

Step 2: To a stirred solution of 2-((4-ethoxy-4-oxobutyl)thio)acetic acid (1.03 g, 5.0 mmol, 1.0 equiv) in DCM (15 mL) were added EDCI (1.44 g, 7.5 mmol, 1.5 equiv) and DMAP (0.92 g, 7.5 mmol, 1.5 equiv) at 0 °C. Subsequently, a solution of L-Methionine ethyl ester hydrochloride (1.07 g, 5.0 mmol, 1.0 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Upon completion as monitored by TLC, the reaction mixture was diluted with DCM (30 mL) and washed sequentially with 1 M aqueous HCl (3 × 20 mL) and brine (20 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under

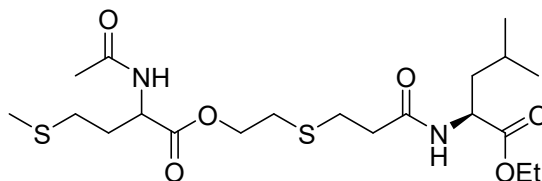
reduced pressure. The residue was purified by silica gel column chromatography (300–400 mesh, eluting with PE/EtOAc = 2 : 1) to afford the product **1am** (1.36 g, 75% yield).

ethyl (3-((2-((acetylglycyl)oxy)ethyl)thio)propanoyl)-L-leucinate (1ak):



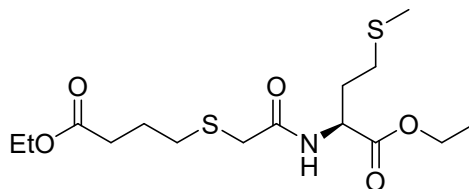
Colorless oily liquid. DCM/MeOH = 20 : 1, R_f = 0.5. Yield: 97% (1.33 g scale); ¹H NMR (500 MHz, CDCl₃) δ 6.75 – 6.68 (m, 1H), 6.59 – 6.54 (m, 1H), 4.57 – 4.51 (m, 1H), 4.30 – 4.23 (m, 2H), 4.15 – 4.10 (m, 2H), 3.98 (d, *J* = 5.5 Hz, 2H), 2.86 – 2.79 (m, 2H), 2.75 – 2.71 (m, 2H), 2.50 – 2.45 (m, 2H), 1.99 (s, 3H), 1.65 – 1.54 (m, 2H), 1.52 – 1.46 (m, 1H), 1.24 – 1.21 (m, 3H), 0.89 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 173.2 , 171.0 , 170.7 , 170.0 , 64.8 , 61.3 , 50.9 , 41.5 , 41.4 , 36.7 , 30.6 , 28.0 , 24.9 , 22.8 , 22.7 , 21.9 , 14.2.; HRMS (ESI) *m/z* : (M)⁺ Calc. for: C₁₇H₃₁N₂O₆S⁺, 391.1897. Found. 391.1902.

ethyl (3-((2-((acetylmethionyl)oxy)ethyl)thio)propanoyl)-L-leucinate (1al):



Yellow oily liquid. DCM/MeOH = 20 : 1, R_f = 0.5. Yield: 87% (1.42 g scale); ¹H NMR (500 MHz, CDCl₃) δ 6.85 – 6.77 (m, 1H), 6.59 – 6.51 (m, 1H), 4.67 – 4.61 (m, 1H), 4.57 – 4.51 (m, 1H), 4.34 – 4.19 (m, 2H), 4.16 – 4.09 (m, 2H), 2.89 – 2.79 (m, 2H), 2.76 – 2.71 (m, 2H), 2.53 – 2.46 (m, 4H), 2.14 – 2.06 (m, 1H), 2.04 (s, 3H), 1.98 (s, 3H), 1.96 – 1.90 (m, 1H), 1.66 – 1.54 (m, 2H), 1.52 – 1.46 (m, 1H), 1.25 – 1.20 (m, 3H), 0.89 (d, *J* = 6.3 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 173.2 , 172.0 (d, *J* = 4.8 Hz), 171.0 , 170.4 (d, *J* = 1.4 Hz), 64.9 (d, *J* = 9.9 Hz), 61.4 , 51.8 (d, *J* = 9.0 Hz), 50.9 (d, *J* = 1.6 Hz), 41.5 , 36.7 , 31.5 (d, *J* = 1.3 Hz), 30.5 , 30.1 , 27.9 (d, *J* = 1.9 Hz), 24.9 , 23.0 , 22.8 , 22.0 (d, *J* = 1.6 Hz), 15.5 , 14.1.; HRMS (ESI) *m/z* : (M)⁺ Calc. for: C₂₀H₃₇N₂O₆S₂⁺, 465.2088. Found. 465.2093.

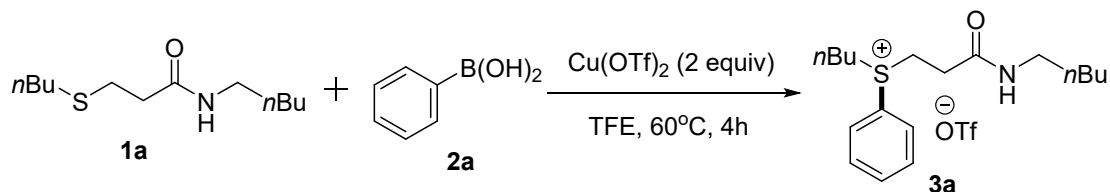
ethyl (2-((4-ethoxy-4-oxobutyl)thio)acetyl)-L-methioninate (1am):



Yellow oily liquid. PE/EtOAc = 2 : 1, R_f = 0.6. Yield: 75% (1.36 g scale); ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 8.0 Hz, 1H), 4.65 – 4.60 (m, 1H), 4.18 – 4.12 (m, 2H), 4.09 – 4.04 (m, 2H), 3.19 (s, 2H), 2.60 – 2.55 (m, 2H), 2.49 – 2.44 (m, 2H), 2.39 – 2.33 (m, 2H), 2.16 – 2.08 (m, 1H), 2.04 (s, 3H), 2.01 – 1.93 (m, 1H), 1.91 – 1.84 (m, 2H), 1.25 – 1.17 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 172.8 , 171.6 , 168.8 , 61.7 , 60.5 , 51.8 , 35.7 , 32.9 , 32.1 , 31.6 , 30.0 ,

24.2 , 15.5 , 14.2 , 14.1.; **HRMS (ESI)** m/z : (M)⁺ Calc. for: C₁₅H₂₈NO₅S₂⁺, 366.1403. Found. 366.1409.

4. Procedures for preparation of aryl sulfonium salts (**3a** - **3aj**):

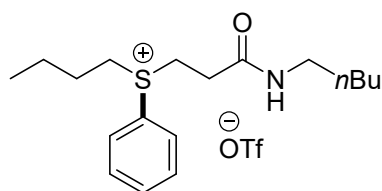


A mixture of **1a** (138.6 mg, 0.60 mmol, 2 equiv) and phenylboronic acid **2a** (36.6 mg, 0.30 mmol, 1 equiv) in TFE (1.0 mL) was stirred at room temperature. Cu(OTf)₂ (217 mg, 0.60 mmol, 2 equiv) was added in one portion, and the resulting mixture was stirred at 60 °C for 4 h under air. The reaction progress was monitored by TLC until complete consumption of the starting materials. Upon completion, the mixture was allowed to cool to room temperature. After completed, the reaction mixture was subjected to silica gel column chromatography (300 - 400 mesh silica gel; DCM/MeOH = 20 : 1) to afford the product **3a**.

Scale-up synthesis of **3a**:

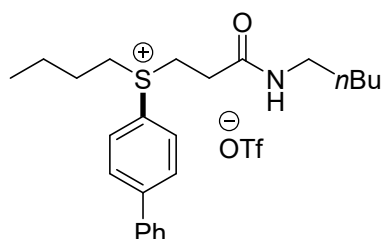
A mixture of **1a** (1.39 g, 6.0 mmol, 2 equiv) and phenylboronic acid (366 mg, 3.0 mmol, 1 equiv) in TFE (10 mL) was stirred at room temperature. Cu(OTf)₂ (2.17 g, 6.0 mmol, 2.0 equiv) was added in one portion, and the resulting mixture was stirred at 60 °C for 4 h. The reaction progress was monitored by TLC until complete consumption of the starting materials. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (300 - 400 mesh silica gel; DCM/MeOH = 20 : 1) to afford the product **3a** (1.27 g, 93% yield).

butyl(3-oxo-3-(pentylamino)propyl)(phenyl)sulfonium trifluoromethanesulfonate (3a):



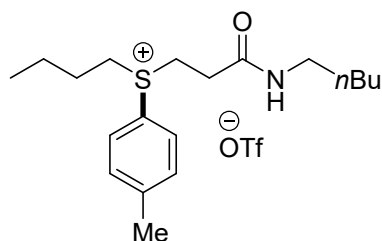
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 94% (86.2 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.76 – 7.69 (m, 1H), 7.68 – 7.61 (m, 2H), 7.34 – 7.27 (m, 1H), 4.05 – 3.94 (m, 1H), 3.89 – 3.81 (m, 1H), 3.80 – 3.71 (m, 2H), 3.14 – 3.03 (m, 2H), 2.94 – 2.83 (m, 1H), 2.74 – 2.64 (m, 1H), 1.63 – 1.46 (m, 2H), 1.46 – 1.38 (m, 4H), 1.28 – 1.19 (m, 4H), 0.89 – 0.80 (m, 6H).; ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 134.9, 131.6, 131.4, 122.1, 44.1, 42.2, 39.9, 30.2, 29.1, 28.8, 26.7, 22.3, 21.3, 14.0, 13.3.; HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₈H₃₀NOS⁺, 308.2043. Found. 308.2043.

[1,1'-biphenyl]-4-yl(butyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3b):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 80% (85.0 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 7.99 (m, 2H), 7.90 – 7.80 (m, 2H), 7.64 – 7.56 (m, 2H), 7.51 – 7.40 (m, 3H), 7.37 – 7.28 (m, 1H), 4.11 – 3.99 (m, 1H), 3.98 – 3.87 (m, 1H), 3.84 – 3.73 (m, 2H), 3.17 – 3.07 (m, 2H), 3.00 – 2.90 (m, 1H), 2.82 – 2.70 (m, 1H), 1.68 – 1.52 (m, 2H), 1.51 – 1.41 (m, 4H), 1.28 – 1.20 (m, 4H), 0.93 – 0.87 (m, 3H), 0.86 – 0.80 (m, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 169.1, 148.0, 138.3, 132.1, 129.9, 129.3, 129.2, 127.5, 120.0, 44.1, 42.3, 40.0, 30.3, 29.1, 28.8, 26.7, 22.4, 21.4, 14.0, 13.4.; HRMS (ESI) m/z : (M)⁺ Calc. for: C₂₄H₃₄NOS⁺, 384.2356. Found. 384.2355.

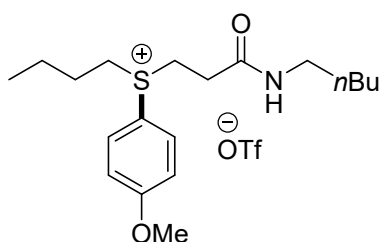
butyl(3-oxo-3-(pentylamino)propyl)(p-tolyl)sulfonium trifluoromethanesulfonate (3c):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.5. Yield: 80% (113.6 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.76 (m, 2H), 7.46 – 7.38 (m, 2H), 7.32 – 7.27 (m, 1H), 3.98 – 3.88 (m, 1H), 3.84 – 3.75 (m, 1H), 3.74 – 3.66 (m, 2H), 3.11 – 3.03 (m, 2H), 2.88 – 2.78 (m, 1H), 2.69 – 2.60 (m, 1H), 2.42 (s, 3H), 1.60 – 1.45 (m, 2H), 1.44 – 1.37 (m, 4H), 1.26 – 1.18 (m, 4H), 0.86 – 0.79 (m, 6H).; ¹³C NMR (101 MHz, CDCl₃) δ 168.8, 146.4, 132.1, 131.4, 118.1, 44.0, 42.1, 39.8, 30.1, 29.0, 28.8, 26.6, 22.3, 21.7, 21.3, 13.9, 13.3.; HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₉H₃₂NOS⁺, 322.2199. Found. 322.2189.

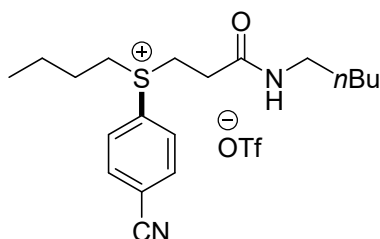
butyl(4-methoxyphenyl)(3-oxo-3-(pentylamino)propyl)sulfonium

trifluoromethanesulfonate (3d):



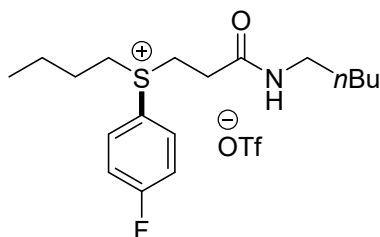
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.5. Yield: 55% (79.8 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.82 (m, 2H), 7.34 – 7.27 (m, 1H), 7.15 – 7.08 (m, 2H), 3.96 – 3.89 (m, 1H), 3.87 (s, 3H), 3.84 – 3.75 (m, 1H), 3.71 – 3.63 (m, 2H), 3.14 – 3.06 (m, 2H), 2.88 – 2.79 (m, 1H), 2.70 – 2.61 (m, 1H), 1.60 – 1.46 (m, 2H), 1.46 – 1.39 (m, 4H), 1.27 – 1.20 (m, 4H), 0.89 – 0.81 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 164.8, 133.6, 117.0, 110.7, 56.0, 44.1, 42.2, 39.9, 30.2, 29.1, 28.8, 26.6, 22.3, 21.3, 14.0, 13.3.; HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₉H₃₂NO₂S⁺, 338.2148. Found. 338.2151.

butyl(4-cyanophenyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3e):



Reaction was conducted for 8h. Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 65% (94.0 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.17 (m, 2H), 7.97 – 7.90 (m, 2H), 7.24 – 7.16 (m, 1H), 4.09 – 3.99 (m, 1H), 3.97 – 3.89 (m, 1H), 3.88 – 3.75 (m, 2H), 3.12 – 3.02 (m, 2H), 2.99 – 2.89 (m, 1H), 2.77 – 2.67 (m, 1H), 1.68 – 1.47 (m, 2H), 1.45 – 1.37 (m, 4H), 1.28 – 1.18 (m, 4H), 0.90 – 0.81 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 134.5, 132.7, 128.3, 118.5, 116.7, 44.7, 42.5, 39.9, 30.2, 29.0, 28.8, 26.8, 22.3, 21.4, 14.0, 13.3.; HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₉H₂₉N₂OS⁺, 333.1995. Found. 333.1992.

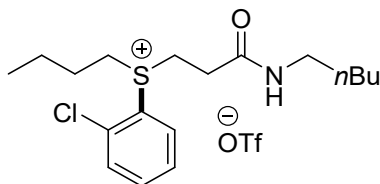
butyl(4-fluorophenyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3f):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 69% (98.4 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 7.99 (m, 2H), 7.39 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 4.03 – 3.92 (m, 1H), 3.90 – 3.81 (m, 1H), 3.80 – 3.69 (m, 2H), 3.14 – 3.02 (m, 2H), 2.95 – 2.83 (m, 1H), 2.72 – 2.63 (m, 1H), 1.63 – 1.47 (m, 2H), 1.45 – 1.36 (m, 4H), 1.28 – 1.17 (m, 4H), 0.90 – 0.78 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 166.4 (d, J = 259.4 Hz), 134.6 (d, J = 9.7 Hz), 119.0 (d, J = 23.0 Hz), 117.4 (d, J = 3.2 Hz), 44.4, 42.5, 39.9, 30.2, 29.1, 28.8, 26.7, 22.3, 21.3, 14.0, 13.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -78.51, -100.60.; HRMS (ESI) m/z : (M)⁺ Calc. for:

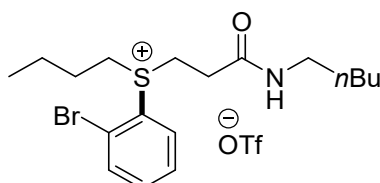
C₁₈H₂₉FNOS⁺, 326.1948. Found. 326.1959.

butyl(2-chlorophenyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3g):



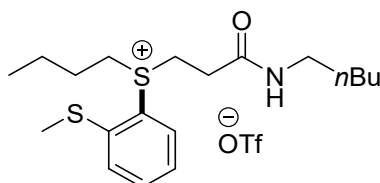
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 65% (96.4 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.18 (m, 1H), 7.68 – 7.63 (m, 2H), 7.62 – 7.58 (m, 1H), 7.32 – 7.26 (m, 1H), 4.13 – 4.03 (m, 1H), 3.93 – 3.81 (m, 3H), 3.13 – 3.06 (m, 2H), 2.99 – 2.89 (m, 1H), 2.85 – 2.75 (m, 1H), 1.63 – 1.51 (m, 2H), 1.50 – 1.40 (m, 4H), 1.28 – 1.19 (m, 4H), 0.91 – 0.81 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.6, 137.8, 135.7, 132.0, 131.6, 130.4, 122.1, 44.6, 41.9, 39.9, 30.3, 29.0, 28.8, 26.6, 22.3, 21.4, 14.0, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₈H₂₉ClNOS⁺, 342.1653. Found. 342.1653.

(2-bromophenyl)(butyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3h):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 77% (123.1 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.16 (m, 1H), 7.79 – 7.74 (m, 1H), 7.73 – 7.67 (m, 1H), 7.60 – 7.54 (m, 1H), 7.31 – 7.26 (m, 1H), 4.11 – 4.02 (m, 1H), 3.91 – 3.79 (m, 3H), 3.13 – 3.06 (m, 2H), 2.97 – 2.88 (m, 1H), 2.84 – 2.74 (m, 1H), 1.63 – 1.51 (m, 2H), 1.49 – 1.39 (m, 4H), 1.27 – 1.20 (m, 4H), 0.90 – 0.85 (m, 3H), 0.85 – 0.80 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.6, 135.8, 134.9, 132.0, 131.0, 127.4, 124.3, 44.9, 42.2, 39.9, 30.3, 29.0, 28.8, 26.6, 22.3, 21.5, 14.0, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₈H₂₉BrNOS⁺, 386.1148. Found. 386.1143.

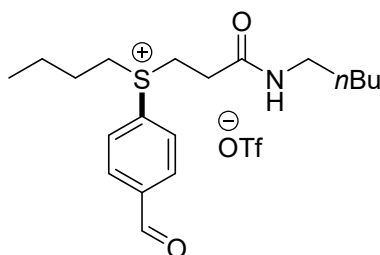
butyl(2-(methylthio)phenyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3i):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 57% (85.8 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.98 (m, 1H), 7.65 – 7.60 (m, 1H), 7.51 – 7.41 (m, 2H), 7.31 – 7.26 (m, 1H), 4.06 – 3.96 (m, 1H), 3.85 – 3.73 (m, 3H), 3.15 – 3.06 (m, 2H), 2.90 – 2.81 (m, 1H), 2.80 – 2.71 (m, 1H), 2.54 (s, 3H), 1.63 – 1.52 (m, 2H), 1.49 – 1.40 (m, 4H), 1.27 – 1.19 (m, 4H), 0.90 – 0.80 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.6, 144.8, 134.9, 130.7, 128.7, 128.6, 121.0, 44.2, 41.6, 39.9, 30.3, 29.0, 28.8, 26.6, 22.3, 21.4, 17.0, 14.0, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₉H₃₂NOS₂⁺, 354.1920. Found. 354.1919.

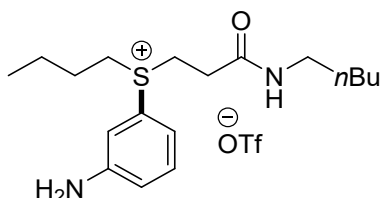
butyl(4-formylphenyl)(3-oxo-3-(pentylamino)propyl)sulfonium

trifluoromethanesulfonate (3j):



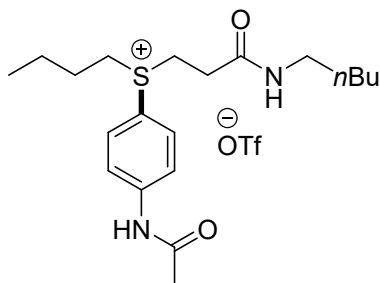
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 72% (104.3 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 10.10 (s, 1H), 8.24 – 8.19 (m, 2H), 8.16 – 8.10 (m, 2H), 7.26 – 7.21 (m, 1H), 4.09 – 4.01 (m, 1H), 3.97 – 3.91 (m, 1H), 3.87 – 3.80 (m, 2H), 3.10 – 3.04 (m, 2H), 2.97 – 2.89 (m, 1H), 2.75 – 2.67 (m, 1H), 1.64 – 1.49 (m, 2H), 1.45 – 1.38 (m, 4H), 1.25 – 1.19 (m, 4H), 0.87 – 0.80 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 190.6, 168.9, 140.3, 132.6, 131.7, 128.5, 44.5, 42.4, 39.9, 30.2, 29.0, 28.8, 26.8, 22.3, 21.4, 14.0, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₉H₃₀NO₂S⁺, 336.1992. Found. 336.1990.

(3-aminophenyl)(butyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3k):



Yellow oily liquid. DCM/MeOH = 10 : 1, R_f = 0.3. Yield: 58% (81.8 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 7.36 (s, 1H), 7.25 – 7.20 (m, 1H), 7.17 – 7.11 (m, 1H), 6.98 – 6.92 (m, 2H), 4.59 (br, 2H), 3.84 – 3.76 (m, 1H), 3.75 – 3.68 (m, 1H), 3.65 – 3.58 (m, 2H), 3.14 – 3.07 (m, 2H), 2.83 – 2.73 (m, 1H), 2.67 – 2.57 (m, 1H), 1.61 – 1.49 (m, 2H), 1.47 – 1.38 (m, 4H), 1.28 – 1.20 (m, 4H), 0.89 – 0.81 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.8, 151.0, 131.3, 121.5, 121.2, 120.5, 113.5, 44.0, 41.7, 39.9, 30.1, 29.1, 28.9, 26.6, 22.4, 21.4, 14.0, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₈H₃₁N₂OS⁺, 323.2152. Found. 323.2162.

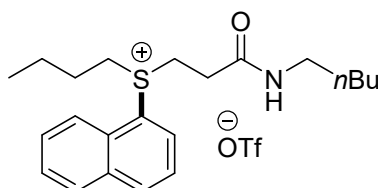
(4-acetamidophenyl)(butyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3l):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.3. Yield: 68% (104.6 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 9.62 (s, 1H), 7.96 – 7.89 (m, 2H), 7.83 – 7.76 (m, 2H), 7.26 – 7.22 (m, 1H), 3.94 – 3.78 (m, 2H), 3.73 – 3.60 (m, 2H), 3.13 – 3.06 (m, 2H), 2.84 – 2.73 (m, 1H), 2.70 – 2.59 (m, 1H), 2.16 (s, 3H), 1.59 – 1.46 (m, 2H), 1.44 – 1.35 (m, 4H), 1.26 – 1.17 (m, 4H), 0.87 – 0.77 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 170.7, 168.8, 145.3, 132.4, 121.6, 113.2,

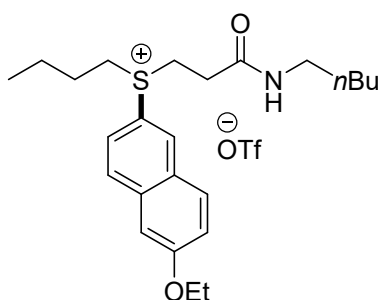
44.6, 41.9, 40.0, 30.2, 29.1, 28.8, 26.6, 24.4, 22.3, 21.3, 13.9, 13.3. **HRMS (ESI)** m/z : (M)⁺ Calc. for: C₂₀H₃₃N₂O₂S⁺, 365.2257. Found. 365.2246.

butyl(naphthalen-1-yl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3m):



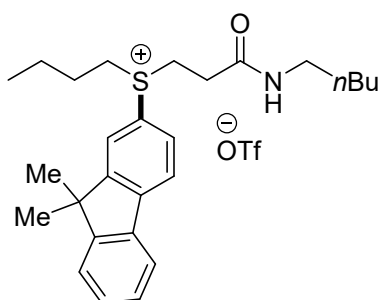
Yellow oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 63% (95.2 mg scale); **¹H NMR** (400 MHz, CDCl₃) δ 8.49 – 8.44 (m, 1H), 8.32 – 8.27 (m, 1H), 8.22 – 8.18 (m, 1H), 8.02 – 7.97 (m, 1H), 7.82 – 7.72 (m, 2H), 7.70 – 7.64 (m, 1H), 7.26 – 7.21 (m, 1H), 4.20 – 4.10 (m, 1H), 4.02 – 3.87 (m, 3H), 3.09 – 3.01 (m, 2H), 2.98 – 2.89 (m, 1H), 2.75 – 2.67 (m, 1H), 1.62 – 1.46 (m, 2H), 1.44 – 1.35 (m, 4H), 1.25 – 1.16 (m, 4H), 0.83 – 0.78 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 168.7, 135.3, 134.1, 133.2, 130.6, 129.7, 129.5, 128.2, 127.0, 122.3, 118.8, 44.6, 42.4, 39.8, 30.3, 29.0, 28.8, 26.7, 22.3, 21.5, 14.0, 13.3. **HRMS (ESI)** m/z : (M)⁺ Calc. for: C₂₂H₃₂NOS⁺, 358.2199. Found. 358.2198.

butyl(6-ethoxynaphthalen-2-yl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3n):



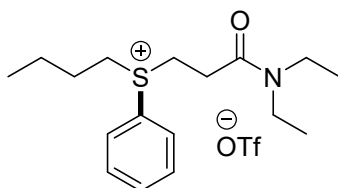
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 65% (107.7 mg scale); **¹H NMR** (400 MHz, CDCl₃) δ 8.42 – 8.37 (m, 1H), 7.99 – 7.94 (m, 1H), 7.92 – 7.82 (m, 2H), 7.31 – 7.26 (m, 2H), 7.18 – 7.15 (m, 1H), 4.19 – 4.12 (m, 2H), 4.05 – 3.97 (m, 1H), 3.95 – 3.86 (m, 1H), 3.85 – 3.74 (m, 2H), 3.08 – 3.00 (m, 2H), 2.93 – 2.84 (m, 1H), 2.75 – 2.66 (m, 1H), 1.52 – 1.45 (m, 5H), 1.44 – 1.33 (m, 4H), 1.24 – 1.15 (m, 4H), 0.87 – 0.78 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 168.9, 160.5, 137.7, 134.7, 130.8, 130.7, 128.4, 124.2, 121.8, 114.4, 106.8, 64.1, 44.0, 42.2, 39.9, 30.3, 29.1, 28.8, 26.7, 22.3, 21.4, 14.6, 14.0, 13.3. **HRMS (ESI)** m/z : (M)⁺ Calc. for: C₂₄H₃₆NO₂S⁺, 402.2461. Found. 402.2476.

butyl(9,9-dimethyl-9H-fluoren-2-yl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3o):



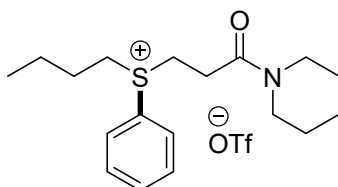
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 61% (104.3 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 8.06 (m, 1H), 7.95 – 7.88 (m, 2H), 7.79 – 7.75 (m, 1H), 7.49 – 7.41 (m, 2H), 7.40 – 7.34 (m, 2H), 4.11 – 4.03 (m, 1H), 3.95 – 3.88 (m, 1H), 3.85 – 3.78 (m, 2H), 3.15 – 3.09 (m, 2H), 3.00 – 2.91 (m, 1H), 2.80 – 2.70 (m, 1H), 1.59 – 1.49 (m, 8H), 1.47 – 1.40 (m, 4H), 1.25 – 1.20 (m, 4H), 0.88 – 0.80 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 156.9, 154.6, 146.3, 136.5, 131.0, 129.9, 127.7, 125.6, 123.0, 122.3, 121.5, 119.0, 47.8, 44.1, 42.5, 39.9, 30.3, 29.1, 28.8, 26.7, 26.6, 22.3, 21.3, 14.0, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: C₂₇H₃₈NOS⁺, 424.2669. Found. 424.2672.

butyl(3-(diethylamino)-3-oxopropyl)(phenyl)sulfonium trifluoromethanesulfonate (3p):



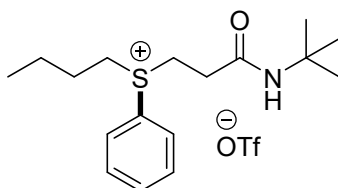
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 90% (119.8 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.75 – 7.69 (m, 1H), 7.68 – 7.61 (m, 2H), 4.04 – 3.96 (m, 1H), 3.95 – 3.87 (m, 1H), 3.84 – 3.73 (m, 2H), 3.36 – 3.24 (m, 2H), 3.23 – 3.12 (m, 2H), 3.09 – 3.00 (m, 1H), 2.80 – 2.70 (m, 1H), 1.63 – 1.53 (m, 1H), 1.51 – 1.37 (m, 3H), 1.07 – 0.99 (m, 6H), 0.89 – 0.82 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.1, 134.8, 131.7, 131.4, 122.7, 45.0, 42.4, 42.1, 40.5, 28.5, 26.8, 21.3, 13.9, 13.3, 12.9. HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₇H₂₈NOS⁺, 294.1886. Found. 294.1902.

butyl(3-oxo-3-(piperidin-1-yl)propyl)(phenyl)sulfonium trifluoromethanesulfonate (3q):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 99% (135.1 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.75 – 7.69 (m, 1H), 7.68 – 7.62 (m, 2H), 4.06 – 3.97 (m, 1H), 3.93 – 3.85 (m, 1H), 3.85 – 3.72 (m, 2H), 3.51 – 3.38 (m, 2H), 3.30 – 3.24 (m, 2H), 3.11 – 3.01 (m, 1H), 2.84 – 2.73 (m, 1H), 1.64 – 1.51 (m, 4H), 1.51 – 1.39 (m, 6H), 0.91 – 0.82 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 134.8, 131.6, 131.4, 123.0, 46.5, 45.0, 43.1, 42.7, 28.6, 26.8, 26.1, 25.4, 24.2, 21.3, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: C₁₈H₂₈NOS⁺, 306.1886. Found. 306.1895.

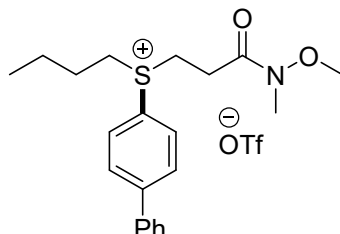
butyl(3-(tert-butylamino)-3-oxopropyl)(phenyl)sulfonium trifluoromethanesulfonate (3r):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 94% (124.5 mg scale); ¹H NMR

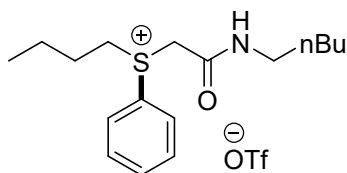
(400 MHz, CDCl₃) δ 7.98 – 7.91 (m, 2H), 7.76 – 7.70 (m, 1H), 7.68 – 7.62 (m, 2H), 6.86 (s, 1H), 3.99 – 3.91 (m, 1H), 3.85 – 3.71 (m, 3H), 2.89 – 2.79 (m, 1H), 2.69 – 2.60 (m, 1H), 1.62 – 1.52 (m, 1H), 1.50 – 1.39 (m, 3H), 1.25 (s, 9H), 0.9 (t, *J* = 6.9 Hz, 3H).. ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 134.9, 131.5, 131.4, 122.1, 51.6, 44.0, 42.1, 30.9, 28.5, 26.7, 21.3, 13.3. **HRMS (ESI)** *m/z* : (M)⁺ Calc. for: C₁₇H₂₈NOS⁺, 294.1886. Found. 294.1893.

[1,1'-biphenyl]-4-yl(butyl)(3-(methoxy(methyl)amino)-3-oxopropyl)sulfonium trifluoromethanesulfonate (3s):



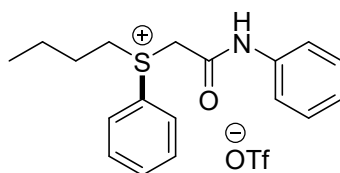
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 89% (134.9 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.05 (m, 2H), 7.91 – 7.84 (m, 2H), 7.64 – 7.57 (m, 2H), 7.51 – 7.42 (m, 3H), 4.14 – 4.05 (m, 1H), 4.04 – 3.96 (m, 1H), 3.94 – 3.83 (m, 2H), 3.63 (s, 3H), 3.19 – 3.14 (m, 4H), 2.97 – 2.89 (m, 1H), 1.70 – 1.55 (m, 2H), 1.55 – 1.28 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H).. ¹³C NMR (101 MHz, CDCl₃) δ 170.0, 147.9, 138.3, 132.2, 129.9, 129.3, 129.2, 127.4, 120.4, 61.6, 45.2, 41.8, 32.2, 27.6, 26.8, 21.4, 13.4. **HRMS (ESI)** *m/z* : (M)⁺ Calc. for: C₂₁H₂₈NO₂S⁺, 358.1835. Found. 358.1845.

butyl(2-oxo-2-(pentylamino)ethyl)(phenyl)sulfonium trifluoromethanesulfonate (3t):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 86% (114.7 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.99 (m, 2H), 7.95 – 7.89 (m, 1H), 7.80 – 7.74 (m, 1H), 7.71 – 7.65 (m, 2H), 4.98 (d, *J* = 14.7 Hz, 1H), 4.74 (d, *J* = 14.7 Hz, 1H), 3.74 (t, *J* = 7.4 Hz, 2H),, 3.21 – 3.05 (m, 2H), 1.67 – 1.53 (m, 2H), 1.52 – 1.43 (m, 2H), 1.42 – 1.35 (m, 2H), 1.28 – 1.22 (m, 2H), 1.20 – 1.13 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 3H).. ¹³C NMR (101 MHz, CDCl₃) δ 161.3, 135.3, 131.6, 121.0, 49.1, 44.1, 40.5, 28.9, 28.6, 26.5, 22.3, 21.4, 14.0, 13.3. **HRMS (ESI)** *m/z* : (M)⁺ Calc. for: C₁₇H₂₈NOS⁺, 294.1886. Found. 294.1884.

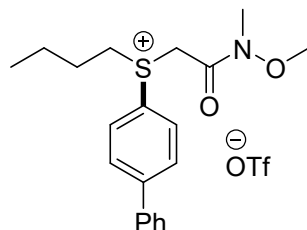
butyl(2-oxo-2-(phenylamino)ethyl)(phenyl)sulfonium trifluoromethanesulfonate (3u):



Yellow oily liquid. DCM/MeOH = 10 : 1, R_f = 0.6. Yield: 80% (108.2 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 9.86 (s, 1H), 8.05 – 7.98 (m, 2H), 7.76 – 7.70 (m, 1H), 7.68 – 7.62 (m, 2H), 7.52 – 7.47 (m, 2H), 7.26 – 7.20 (m, 2H), 7.11 – 7.05 (m, 1H), 5.23 (d, *J* = 15.2 Hz, 1H),

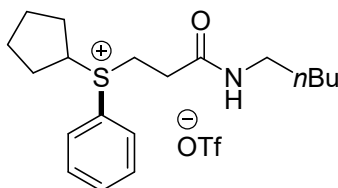
4.95 (d, $J = 15.2$ Hz, 1H), 3.81 – 3.74 (m, 2H), 1.65 – 1.52 (m, 2H), 1.47 – 1.43 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.9, 137.2, 135.4, 131.6, 131.5, 129.1, 125.3, 120.9, 120.3, 50.0, 44.3, 26.5, 21.4, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: $\text{C}_{18}\text{H}_{22}\text{NOS}^+$, 300.1417. Found. 300.1412.

[1,1'-biphenyl]-4-yl(butyl)(2-(methoxy(methyl)amino)-2-oxoethyl)sulfonium trifluoromethanesulfonate (3v):



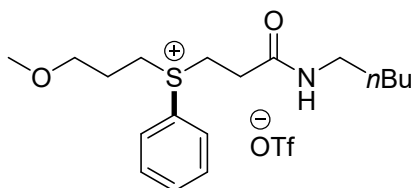
Colorless oily liquid. DCM/MeOH = 10 : 1, $R_f = 0.6$. Yield: 85% (126.2 mg scale); ^1H NMR (400 MHz, CDCl_3) δ 8.21 – 8.13 (m, 2H), 7.90 – 7.83 (m, 2H), 7.63 – 7.56 (m, 2H), 7.51 – 7.40 (m, 3H), 5.43 (d, $J = 16.7$ Hz, 1H), 5.03 (d, $J = 16.7$ Hz, 1H), 4.10 – 4.01 (m, 1H), 3.95 – 3.86 (m, 1H), 3.82 (s, 3H), 3.16 (s, 3H), 1.67 – 1.54 (m, 2H), 1.53 – 1.44 (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.2, 148.0, 138.3, 132.2, 129.9, 129.3, 129.2, 127.4, 119.7, 62.4, 50.0, 43.8, 32.3, 26.6, 21.3, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: $\text{C}_{20}\text{H}_{26}\text{NO}_2\text{S}^+$, 344.1679. Found. 344.1688.

cyclopentyl(3-oxo-3-(pentylamino)propyl)(phenyl)sulfonium trifluoromethanesulfonate (3w):



Colorless oily liquid. DCM/MeOH = 10 : 1, $R_f = 0.3$. Yield: 77% (107.8 mg scale); ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.91 (m, 2H), 7.75 – 7.68 (m, 1H), 7.66 – 7.58 (m, 2H), 7.26 – 7.20 (m, 1H), 4.51 – 4.40 (m, 1H), 4.01 – 3.92 (m, 1H), 3.89 – 3.79 (m, 1H), 3.10 – 3.02 (m, 2H), 2.85 – 2.76 (m, 1H), 2.49 – 2.45 (m, 1H), 2.43 – 2.34 (m, 1H), 2.03 – 1.92 (m, 1H), 1.89 – 1.77 (m, 3H), 1.72 – 1.61 (m, 2H), 1.51 – 1.37 (m, 3H), 1.25 – 1.16 (m, 4H), 0.81 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 134.9, 131.9, 131.3, 122.1, 56.6, 40.8, 39.8, 30.6, 29.9, 29.8, 29.0, 28.8, 25.4, 24.8, 22.3, 13.9. HRMS (ESI) m/z : (M)⁺ Calc. for: $\text{C}_{19}\text{H}_{30}\text{NOS}^+$, 320.2043. Found. 320.2049.

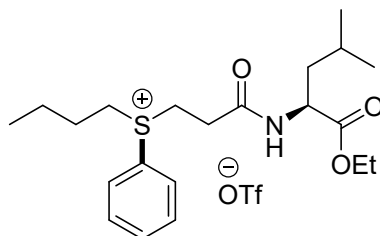
(3-methoxypropyl)(3-oxo-3-(pentylamino)propyl)(phenyl)sulfonium trifluoromethanesulfonate (3x):



Yellow oily liquid. DCM/MeOH = 10 : 1, $R_f = 0.3$. Yield: 99% (141.3 mg scale); ^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.88 (m, 2H), 7.72 – 7.66 (m, 1H), 7.64 – 7.58 (m, 2H), 7.26 – 7.20 (m, 1H), 3.96 – 3.74 (m, 4H), 3.45 – 3.35 (m, 2H), 3.19 (s, 3H), 3.09 – 3.01 (m, 2H), 2.86 –

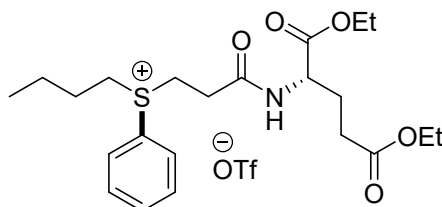
2.76 (m, 1H), 2.64 – 2.56 (m, 1H), 1.93 – 1.79 (m, 2H), 1.45 – 1.34 (m, 2H), 1.24 – 1.16 (m, 4H), 0.80 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 134.7, 131.5, 131.2, 122.4, 69.8, 58.5, 42.8, 42.3, 39.8, 30.2, 29.0, 28.8, 25.1, 22.3, 13.9. HRMS (ESI) m/z : (M)⁺ Calc. for: $\text{C}_{18}\text{H}_{30}\text{NO}_2\text{S}^+$, 324.1992. Found. 324.2006.

butyl(3-(((S)-1-ethoxy-4-methyl-1-oxopentan-2-yl)amino)-3-oxopropyl)(phenyl)sulfonium trifluoromethanesulfonate (3y):



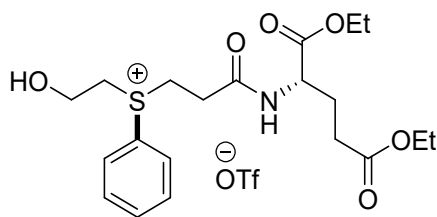
Colorless oily liquid. DCM/MeOH = 10 : 1, $R_f = 0.5$. Yield: 82% (130.2 mg scale); ^1H NMR (400 MHz, CDCl_3) δ 8.00 – 7.91 (m, 2H), 7.76 – 7.69 (m, 1H), 7.68 – 7.61 (m, 2H), 7.55 – 7.43 (m, 1H), 4.38 – 4.28 (m, 1H), 4.14 – 4.06 (m, 2H), 4.05 – 3.96 (m, 1H), 3.89 – 3.81 (m, 1H), 3.80 – 3.71 (m, 2H), 3.00 – 2.88 (m, 1H), 2.79 – 2.68 (m, 1H), 1.64 – 1.50 (m, 4H), 1.49 – 1.36 (m, 3H), 1.23 – 1.17 (m, 3H), 0.90 – 0.81 (m, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.5 (d, $J = 6.0$ Hz), 169.3 (d, $J = 12.0$ Hz), 134.9 (d, $J = 2.3$ Hz), 131.5, 131.4 (d, $J = 2.1$ Hz), 121.8 (d, $J = 13.7$ Hz), 61.2 (d, $J = 4.2$ Hz), 51.5 (d, $J = 2.3$ Hz), 43.9 (d, $J = 2.3$ Hz), 42.0 (d, $J = 2.8$ Hz), 40.2 (d, $J = 5.9$ Hz), 30.0, 26.6, 24.7, 22.7, 21.6 (d, $J = 5.1$ Hz), 21.2, 14.1, 13.3. HRMS (ESI) m/z : (M)⁺ Calc. for: $\text{C}_{21}\text{H}_{34}\text{NO}_3\text{S}^+$, 380.2254. Found. 380.2266.

butyl(3-(((S)-1,5-diethoxy-1,5-dioxopentan-2-yl)amino)-3-oxopropyl)(phenyl)sulfonium trifluoromethanesulfonate (3z):



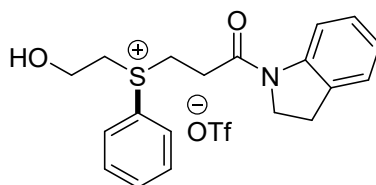
Colorless oily liquid. DCM/MeOH = 10 : 1, $R_f = 0.4$. Yield: 80% (137.4 mg scale); ^1H NMR (400 MHz, CDCl_3) δ 8.00 – 7.92 (m, 2H), 7.75 – 7.69 (m, 1H), 7.67 – 7.62 (m, 2H), 7.62 – 7.55 (m, 1H), 4.41 – 4.33 (m, 1H), 4.14 – 4.03 (m, 4H), 4.03 – 3.96 (m, 1H), 3.91 – 3.81 (m, 1H), 3.80 – 3.72 (m, 2H), 3.00 – 2.89 (m, 1H), 2.80 – 2.67 (m, 1H), 2.40 – 2.29 (m, 2H), 2.18 – 2.07 (m, 1H), 2.01 – 1.88 (m, 1H), 1.61 – 1.51 (m, 1H), 1.50 – 1.37 (m, 3H), 1.23 – 1.16 (m, 6H), 0.84 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.7 (d, $J = 7.8$ Hz), 171.3 (d, $J = 3.6$ Hz), 169.3 (d, $J = 9.5$ Hz), 135.0 (s), 131.6 (s), 131.4 (s), 121.7 (d, $J = 10.1$ Hz), 61.5 (d, $J = 3.6$ Hz), 60.6 (d, $J = 1.8$ Hz), 52.2 (d, $J = 4.0$ Hz), 43.9 (s), 41.8 (s), 30.3 (s), 30.0 (s), 26.6 (s), 26.4 (s), 21.2 (s), 14.1 (s), 14.0 (s), 13.3 (s). HRMS (ESI) m/z : (M)⁺ Calc. for: $\text{C}_{22}\text{H}_{34}\text{NO}_5\text{S}^+$, 424.2152. Found. 424.2159.

(3-(((S)-1,5-diethoxy-1,5-dioxopentan-2-yl)amino)-3-oxopropyl)(2-hydroxyethyl)(phenyl)sulfonium trifluoromethanesulfonate (3aa):



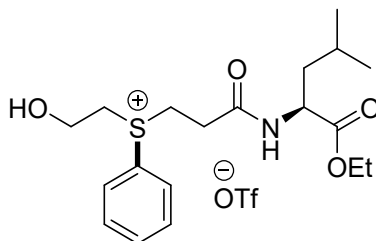
Yellow oily liquid. DCM/MeOH = 10 : 1, Rf = 0.4. Yield: 72% (121.2 mg scale); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 – 7.89 (m, 2H), 7.75 – 7.68 (m, 1H), 7.67 – 7.59 (m, 2H), 7.57 – 7.46 (m, 1H), 4.71 – 4.47 (m, 1H), 4.44 – 4.32 (m, 1H), 4.12 – 4.03 (m, 6H), 3.91 – 3.70 (m, 3H), 3.07 (br, 1H), 2.96 – 2.86 (m, 1H), 2.79 – 2.66 (m, 1H), 2.38 – 2.27 (m, 2H), 2.15 – 2.03 (m, 1H), 1.99 – 1.86 (m, 1H), 1.23 – 1.16 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.9 (d, $J = 11.5$ Hz), 171.6 (d, $J = 11.6$ Hz), 169.3 (d, $J = 8.0$ Hz), 134.8, 131.6, 131.3, 122.1, 61.7 (d, $J = 7.7$ Hz), 60.8, 56.5, 52.2, 48.7, 41.3, 30.3, 30.2, 26.5, 14.1, 14.0. **HRMS (ESI)** m/z : (M) $^+$ Calc. for: $\text{C}_{20}\text{H}_{30}\text{NO}_6\text{S}^+$, 412.1788. Found. 412.1800.

(2-hydroxyethyl)(3-(indolin-1-yl)-3-oxopropyl)(phenyl)sulfonium trifluoromethanesulfonate (3ab):



Thioether (0.3 mmol) and boronic acid (0.6 mmol) were used for this reaction. Yellow oily liquid. DCM/MeOH = 10 : 1, Rf = 0.3. Yield: 77% (110.8 mg scale); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 – 7.86 (m, 3H), 7.71 – 7.65 (m, 1H), 7.64 – 7.57 (m, 2H), 7.17 – 7.01 (m, 2H), 6.99 – 6.91 (m, 1H), 4.56 (s, 1H), 4.30 – 4.14 (m, 2H), 4.13 – 4.05 (m, 1H), 3.99 – 3.89 (m, 1H), 3.87 – 3.67 (m, 4H), 3.12 – 2.91 (m, 3H), 2.89 – 2.70 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.0, 142.2, 134.7, 131.7, 131.6, 131.3, 127.4, 124.9, 124.4, 122.7, 116.7, 56.6, 49.3, 47.8, 41.3, 30.9, 27.8. **HRMS (ESI)** m/z : (M) $^+$ Calc. for: $\text{C}_{19}\text{H}_{22}\text{NO}_2\text{S}^+$, 328.1366. Found. 328.1370.

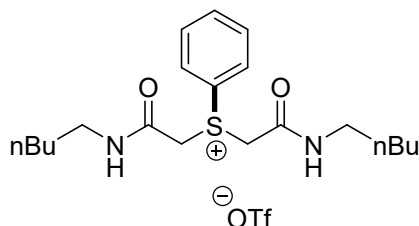
(3-(((S)-1-ethoxy-4-methyl-1-oxopentan-2-yl)amino)-3-oxopropyl)(2-hydroxyethyl)(phenyl)sulfonium trifluoromethanesulfonate (3ac):



Colorless oily liquid. DCM/MeOH = 10 : 1, Rf = 0.2. Yield: 82% (127.2 mg scale); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 – 7.89 (m, 2H), 7.75 – 7.68 (m, 1H), 7.67 – 7.60 (m, 2H), 7.39 – 7.26 (m, 1H), 4.51 (br, 1H), 4.39 – 4.30 (m, 1H), 4.14 – 4.05 (m, 4H), 3.92 – 3.83 (m, 1H), 3.82 – 3.69 (m, 2H), 2.95 – 2.85 (m, 1H), 2.80 – 2.69 (m, 1H), 1.67 – 1.57 (m, 1H), 1.56 – 1.51 (m, 2H), 1.27 – 1.17 (m, 4H), 0.90 – 0.81 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.9 (d, $J = 14.9$ Hz), 169.2 (d, $J = 10.6$ Hz), 134.8 (d, $J = 2.9$ Hz), 131.5, 131.4, 122.2 (d, $J = 4.7$ Hz), 61.4 (d, $J = 9.0$ Hz), 56.5 (d, $J = 3.8$ Hz), 51.5 (d, $J = 5.2$ Hz), 48.6 (d, $J = 9.7$ Hz), 41.4 (d, $J = 6.1$

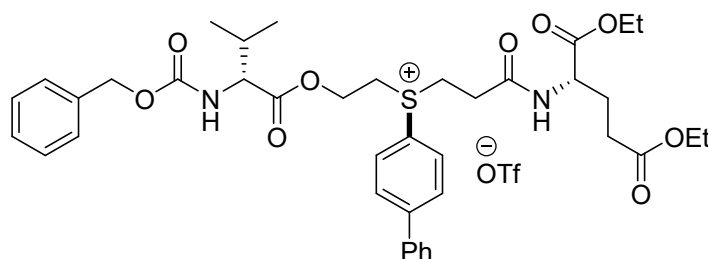
Hz), 40.4 (d, $J = 6.3$ Hz), 30.2 (d, $J = 10.3$ Hz), 24.8, 22.7 (d, $J = 2.5$ Hz), 21.7 (d, $J = 8.5$ Hz), 14.1. **HRMS (ESI) m/z** : (M)⁺ Calc. for: C₁₉H₃₀NO₄S⁺, 368.1890. Found. 368.1898.

bis(2-oxo-2-(pentylamino)ethyl)(phenyl)sulfonium trifluoromethanesulfonate (3ad) :



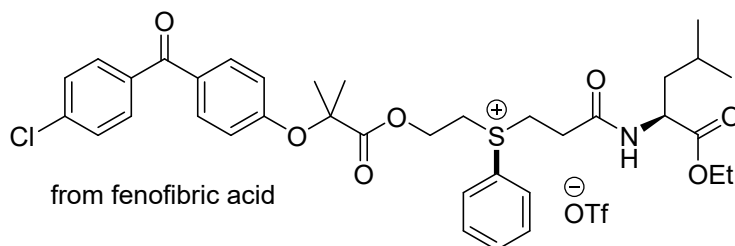
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.7. Yield: 86% (133.1 mg scale); **¹H NMR** (400 MHz, CDCl₃) δ 8.06 – 8.00 (m, 2H), 7.72 – 7.65 (m, 3H), 7.62 – 7.56 (m, 2H), 4.93 – 4.77 (m, 4H), 3.13 – 2.99 (m, 4H), 1.35 – 1.27 (m, 4H), 1.21 – 1.13 (m, 4H), 1.11 – 1.03 (m, 4H), 0.81 – 0.74 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 161.7, 134.6, 131.2, 130.9, 122.4, 48.5, 40.3, 28.7, 28.5, 22.2, 13.8.; **HRMS (ESI) m/z**: (M)⁺ Calc. for: C₂₀H₃₃N₂O₂S⁺, 365.2257. Found. 365.2275.

(5R,15S)-10-([1,1'-biphenyl]-4-yl)-15-(ethoxycarbonyl)-5-isopropyl-3,6,13,18-tetraoxo-1-phenyl-2,7,19-trioxa-10-thia-4,14-diazahenicosan-10-ium trifluoromethanesulfonate (3ae):



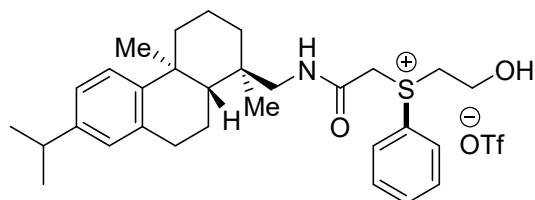
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.3. Yield: 71% (184.2 mg scale); **¹H NMR** (400 MHz, *d*-DMSO) δ 8.51 (d, $J = 7.5$ Hz, 1H), 8.18 – 7.99 (m, 3H), 7.82 – 7.62 (m, 3H), 7.57 – 7.41 (m, 3H), 7.38 – 7.23 (m, 6H), 5.06 – 4.99 (m, 2H), 4.35 – 4.14 (m, 4H), 4.11 – 3.96 (m, 6H), 3.86 – 3.73 (m, 1H), 2.83 – 2.69 (m, 1H), 2.61 – 2.49 (m, 1H), 2.38 – 2.23 (m, 2H), 2.00 – 1.69 (m, 4H), 1.19 – 1.08 (m, 6H), 0.88 – 0.71 (m, 6H). **¹³C NMR** (101 MHz, *d*-DMSO) δ 172.0, 171.3, 168.8, 164.8, 156.4, 146.0, 137.7, 136.9, 132.5, 131.0, 129.2, 129.1, 129.0, 128.8, 128.4, 127.9, 127.8, 127.3, 127.2, 126.4, 126.0, 65.7, 60.7, 60.6, 60.0, 59.4, 58.9, 51.4, 51.3, 29.8, 29.4, 29.2, 26.1, 18.9, 17.9, 14.0, 13.9. **HRMS (ESI) m/z** : (M)⁺ Calc. for: C₃₉H₄₉N₂O₉S⁺, 721.3153. Found. 721.3158.

(5S)-15-(4-(4-chlorobenzoyl)phenoxy)-5-isobutyl-15-methyl-4,7,14-trioxa-10-phenyl-3,13-dioxa-10-thia-6-azahexadecan-10-ium trifluoromethanesulfonate (3af):



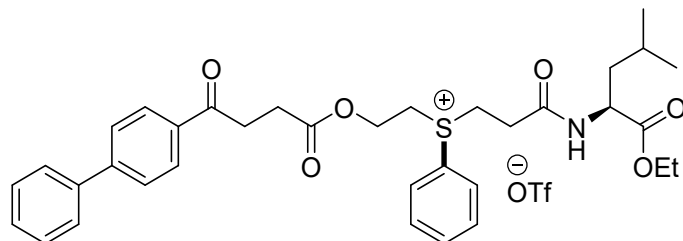
Yellow oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 93% (227.1 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.83 (m, 2H), 7.73 – 7.67 (m, 5H), 7.64 – 7.56 (m, 2H), 7.45 – 7.43 (m, 1H), 7.43 – 7.41 (m, 1H), 6.82 – 6.80 (m, 1H), 6.80 – 6.77 (m, 1H), 4.63 – 4.55 (m, 1H), 4.39 – 4.30 (m, 1H), 4.26 – 4.18 (m, 2H), 4.12 – 4.07 (m, 2H), 3.94 – 3.84 (m, 1H), 3.04 – 2.92 (m, 1H), 2.78 – 2.67 (m, 1H), 1.72 – 1.62 (m, 1H), 1.60 – 1.51 (m, 8H), 1.28 – 1.17 (m, 6H), 0.90 – 0.81 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 194.3 , 173.1 , 172.6 (d, *J* = 11.6 Hz), 169.2 (d, *J* = 15.2 Hz), 159.3 , 138.7 , 136.2 , 135.1 (d, *J* = 4.9 Hz), 132.2 , 131.7 , 131.5 (d, *J* = 3.4 Hz), 131.3 , 130.9 , 128.7 , 117.6 , 79.3 , 61.3 (d, *J* = 6.5 Hz), 59.3 (d, *J* = 6.0 Hz), 51.5 (d, *J* = 5.6 Hz), 44.4 (d, *J* = 5.8 Hz), 42.5 (d, *J* = 9.4 Hz), 40.4 (d, *J* = 12.4 Hz), 30.1, 29.8, 25.5 (d, *J* = 9.3 Hz), 25.1 (d, *J* = 10.9 Hz), 24.8, 22.7 (d, *J* = 2.6 Hz), 21.7 (d, *J* = 11.3 Hz), 14.2. HRMS (ESI) *m/z* : (M)⁺ Calc. for: C₃₆H₄₃ClNO₇S⁺, 668.2443. Found. 668.2458.

(2-hydroxyethyl)(2-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)amino)-2-oxoethyl)(phenyl)sulfonium trifluoromethanesulfonate (3ag):



White solid. DCM/MeOH = 10 : 1, R_f = 0.5. Yield: 83% (156.9 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.89 (m, 2H), 7.66 – 7.51 (m, 3H), 7.43 – 7.35 (m, 1H), 7.14 – 7.05 (m, 1H), 7.01 – 6.93 (m, 1H), 6.89 – 6.75 (m, 1H), 4.99 – 4.83 (m, 2H), 4.12 – 3.98 (m, 2H), 3.74 (br, 4H), 2.97 – 2.67 (m, 4H), 2.25 – 2.11 (m, 1H), 1.80 – 1.67 (m, 1H), 1.65 – 1.50 (m, 3H), 1.28 – 1.19 (m, 8H), 1.15 – 1.07 (m, 4H), 1.01 – 0.93 (m, 1H), 0.82 (s, 1H), 0.68 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.1, 147.1, 145.7, 145.5, 134.8, 131.3, 131.1, 127.0, 124.2, 123.9, 121.6, 56.4, 51.4, 48.1, 45.9, 38.3, 37.7, 37.4, 36.0, 33.5, 30.0, 29.8, 25.3, 24.1, 24.0, 19.1, 18.5, 17.9. [The product was obtained as a mixture of isomers, and the NMR spectra are complex (see the provided spectra). ¹H NMR integrations are reported for the mixture, while only the major isomer is annotated in the ¹³C NMR spectrum]. HRMS (ESI) *m/z* : (M)⁺ Calc. for: C₃₀H₄₂NO₂S⁺, 480.2931. Found. 480.2938.

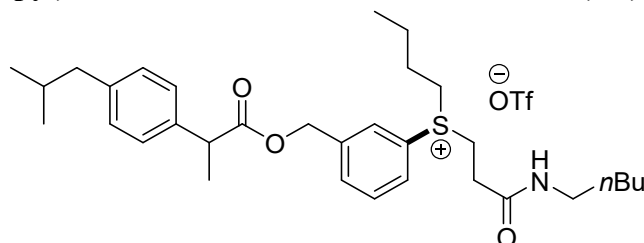
(5S)-17-([1,1'-biphenyl]-4-yl)-5-isobutyl-4,7,14,17-tetraoxo-10-phenyl-3,13-dioxo-10-thia-6-azaheptadecan-10-ium trifluoromethanesulfonate (3ah):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 90% (203.4 mg scale); ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.98 (m, 4H), 7.73 – 7.63 (m, 5H), 7.62 – 7.58 (m, 2H), 7.52 – 7.35 (m, 4H), 4.59 – 4.49 (m, 1H), 4.43 – 4.33 (m, 1H), 4.29 – 4.20 (m, 2H), 4.19 – 4.13 (m, 2H), 4.12 – 4.06 (m, 2H), 4.01 – 3.91 (m, 1H), 3.30 – 3.23 (m, 2H), 3.08 – 2.94 (m, 1H), 2.83 – 2.72 (m, 1H), 2.64 – 2.56 (m, 2H), 1.68 – 1.60 (m, 1H), 1.59 – 1.52 (m, 2H), 1.22 – 1.17 (m, 3H), 0.90 – 0.82 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 197.7 (d, *J* = 2.0 Hz), 172.6 (d, *J* = 9.1

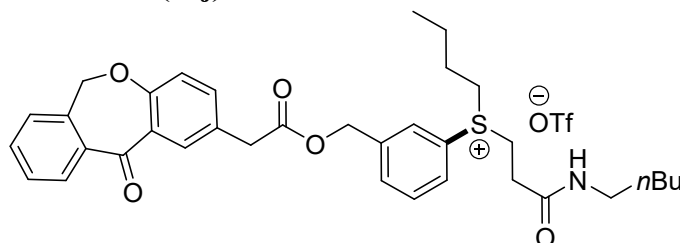
Hz), 172.4, 169.2 (d, $J = 11.4$ Hz), 146.1, 139.7, 135.0, 131.7, 131.3 (d, $J = 2.0$ Hz), 129.0, 128.7, 128.4, 127.3, 127.2, 122.2, 122.0 (d, $J = 11.1$ Hz), 61.2 (d, $J = 6.8$ Hz), 58.2, 51.5 (d, $J = 6.3$ Hz), 44.8, 41.9, 40.3 (d, $J = 6.9$ Hz), 33.3, 30.1, 27.8, 24.7, 22.7 (d, $J = 2.3$ Hz), 21.7 (d, $J = 9.6$ Hz), 14.1. **HRMS (ESI)** m/z : (M)⁺ Calc. for: C₃₅H₄₂NO₆S⁺, 604.2727. Found. 604.2746.

butyl(3-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)phenyl)(3-oxo-3-(pentylamino)propyl)sulfonium trifluoromethanesulfonate (3ai):



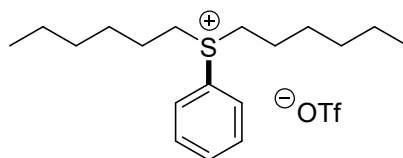
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.4. Yield: 74% (150.4 mg scale); **¹H NMR** (400 MHz, CDCl₃) δ 7.92 – 7.87 (m, 1H), 7.79 (s, 1H), 7.57 – 7.51 (m, 1H), 7.48 – 7.43 (m, 1H), 7.35 – 7.30 (m, 1H), 7.19 – 7.14 (m, 2H), 7.09 – 7.04 (m, 2H), 5.20 – 5.14 (m, 2H), 4.02 – 3.93 (m, 1H), 3.85 – 3.66 (m, 4H), 3.13 – 3.05 (m, 2H), 2.92 – 2.83 (m, 1H), 2.72 – 2.64 (m, 1H), 2.43 – 2.39 (m, 2H), 1.86 – 1.76 (m, 1H), 1.51 – 1.46 (m, 4H), 1.45 – 1.36 (m, 5H), 1.27 – 1.19 (m, 4H), 0.88 – 0.81 (m, 12H). **¹³C NMR** (101 MHz, CDCl₃) δ 174.2, 168.8, 140.8, 140.2, 137.4, 137.3, 133.5, 131.5, 130.6, 130.3, 130.2, 129.4, 127.2, 122.4, 64.6, 45.0, 44.1, 44.0, 42.2, 39.8, 30.2, 29.0, 28.8, 26.6, 22.4, 22.3, 21.3, 18.3, 13.9, 13.2. **HRMS (ESI)** m/z : (M)⁺ Calc. for: C₃₂H₄₈NO₃S⁺, 526.3349. Found. 526.3384.

butyl(3-oxo-3-(pentylamino)propyl)(3-(((2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetoxy)methyl)phenyl)sulfonium trifluoromethanesulfonate (3aj):



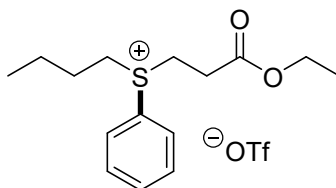
Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.5. Yield: 65% (144.3 mg scale); **¹H NMR** (400 MHz, CDCl₃) δ 8.09 – 8.05 (m, 1H), 7.96 – 7.89 (m, 2H), 7.84 – 7.78 (m, 1H), 7.67 – 7.59 (m, 2H), 7.55 – 7.50 (m, 1H), 7.46 – 7.38 (m, 2H), 7.35 – 7.27 (m, 2H), 7.01 – 6.97 (m, 1H), 5.20 (s, 2H), 5.14 (s, 2H), 4.05 – 3.95 (m, 1H), 3.91 – 3.82 (m, 1H), 3.81 – 3.73 (m, 2H), 3.71 (s, 2H), 3.11 – 3.04 (m, 2H), 2.94 – 2.84 (m, 1H), 2.73 – 2.65 (m, 1H), 1.60 – 1.45 (m, 2H), 1.44 – 1.36 (m, 4H), 1.25 – 1.18 (m, 4H), 0.85 – 0.79 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 190.8, 171.1, 168.8, 160.6, 140.3, 139.9, 136.5, 135.6, 134.1, 133.0, 132.4, 131.6, 131.0, 130.6, 129.4, 129.3, 127.9, 127.4, 125.2, 122.6, 121.2, 73.6, 65.1, 44.2, 42.2, 40.0, 39.8, 30.2, 29.0, 28.8, 26.6, 22.3, 21.3, 13.9, 13.2. **HRMS (ESI)** m/z : (M)⁺ Calc. for: C₃₅H₄₂NO₅S⁺, 588.2778. Found. 588.2788.

dihexyl(phenyl)sulfonium trifluoromethanesulfonate (3a'):



Colorless oily liquid. DCM/MeOH = 10 : 1, R_f = 0.7. Yield: 39% (49.7 mg scale); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 – 7.96 (m, 2H), 7.81 – 7.74 (m, 1H), 7.74 – 7.66 (m, 2H), 3.86 – 3.73 (m, 4H), 1.67 – 1.57 (m, 2H), 1.56 – 1.47 (m, 2H), 1.44 – 1.36 (m, 4H), 1.24 – 1.16 (m, 8H), 0.84 – 0.76 (m, 6H).; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 135.1, 131.7, 131.6, 121.1, 44.6, 31.0, 27.7, 24.7, 22.2, 13.8.; **HRMS (ESI)** m/z : (M)⁺ Calc. for: $\text{C}_{18}\text{H}_{31}\text{S}^+$, 279.2141. Found. 279.2148.

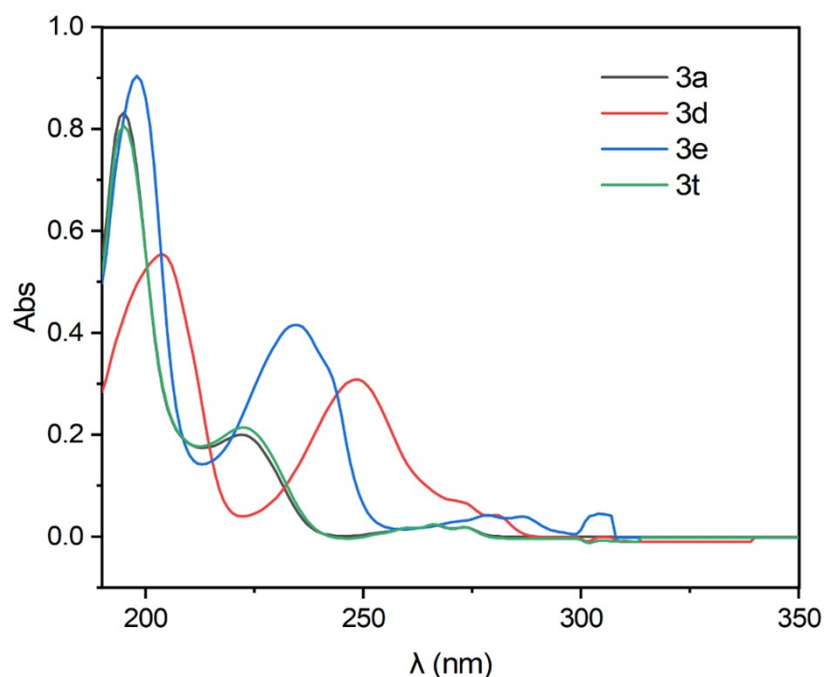
butyl(3-ethoxy-3-oxopropyl)(phenyl)sulfonium trifluoromethanesulfonate (3a''):



Yellow oily liquid. DCM/MeOH = 10 : 1, R_f = 0.7. Yield: 61% (75.6 mg scale); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06 – 7.96 (m, 2H), 7.80 – 7.73 (m, 1H), 7.72 – 7.64 (m, 2H), 4.12 – 4.04 (m, 3H), 4.02 – 3.94 (m, 1H), 3.90 – 3.80 (m, 2H), 2.90 – 2.80 (m, 1H), 2.76 – 2.66 (m, 1H), 1.67 – 1.56 (m, 1H), 1.54 – 1.39 (m, 3H), 1.23 – 1.16 (m, 3H), 0.89 – 0.83 (m, 6H).; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.9, 135.2, 131.8, 131.6, 121.3, 61.9, 44.8, 40.7, 29.4, 26.6, 21.3, 14.0, 13.3.; **HRMS (ESI)** m/z : (M)⁺ Calc. for: $\text{C}_{15}\text{H}_{23}\text{O}_2\text{S}^+$, 267.1413. Found. 267.1419.

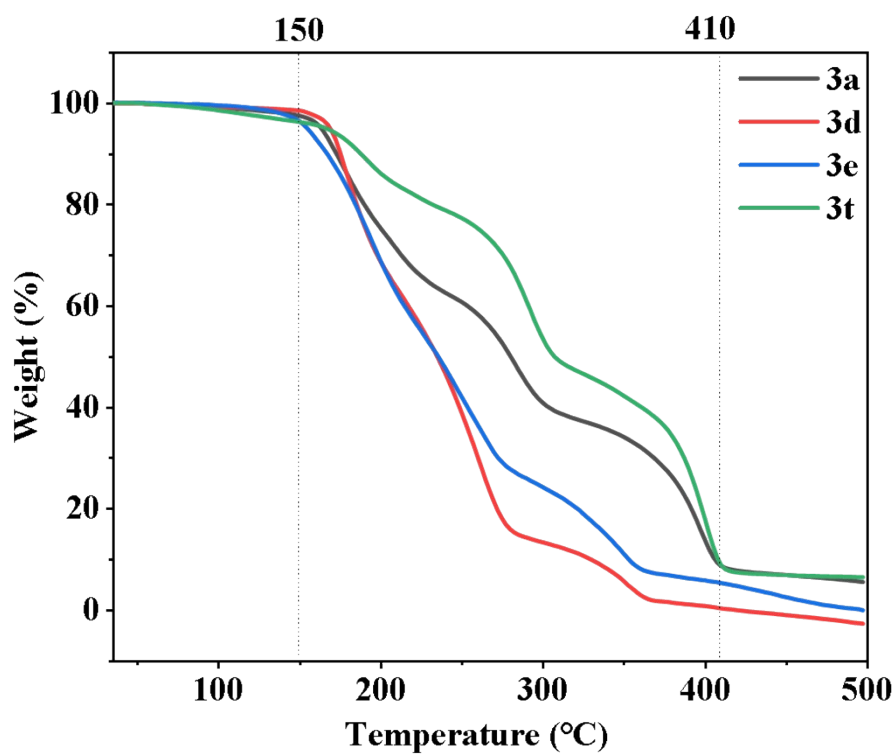
5. UV absorption and Thermogravimetric analysis of 3a, 3d, 3e, 3t:

1) The four aryl sulfonium salts were dissolved in acetonitrile to prepare solutions at a concentration of 2.0×10^{-5} mol/L. UV absorption spectra were measured over a scanning range of 190 - 400 nm using a Hitachi UH5300 double-beam UV-vis spectrophotometer.



compounds	UV	
	λ_{\max} (nm)	Abs
3a	195	0.832
3d	204, 248	0.554, 0.308
3e	198, 235	0.904, 0.415
3t	195	0.806

2) The TGA measurements were performed on a Netzsch TG209 instrument under a nitrogen atmosphere. The temperature range was set from 30 °C to 500 °C with a heating rate of 10 K/min. The TGA curves illustrate the weight changes of the samples as a function of temperature.

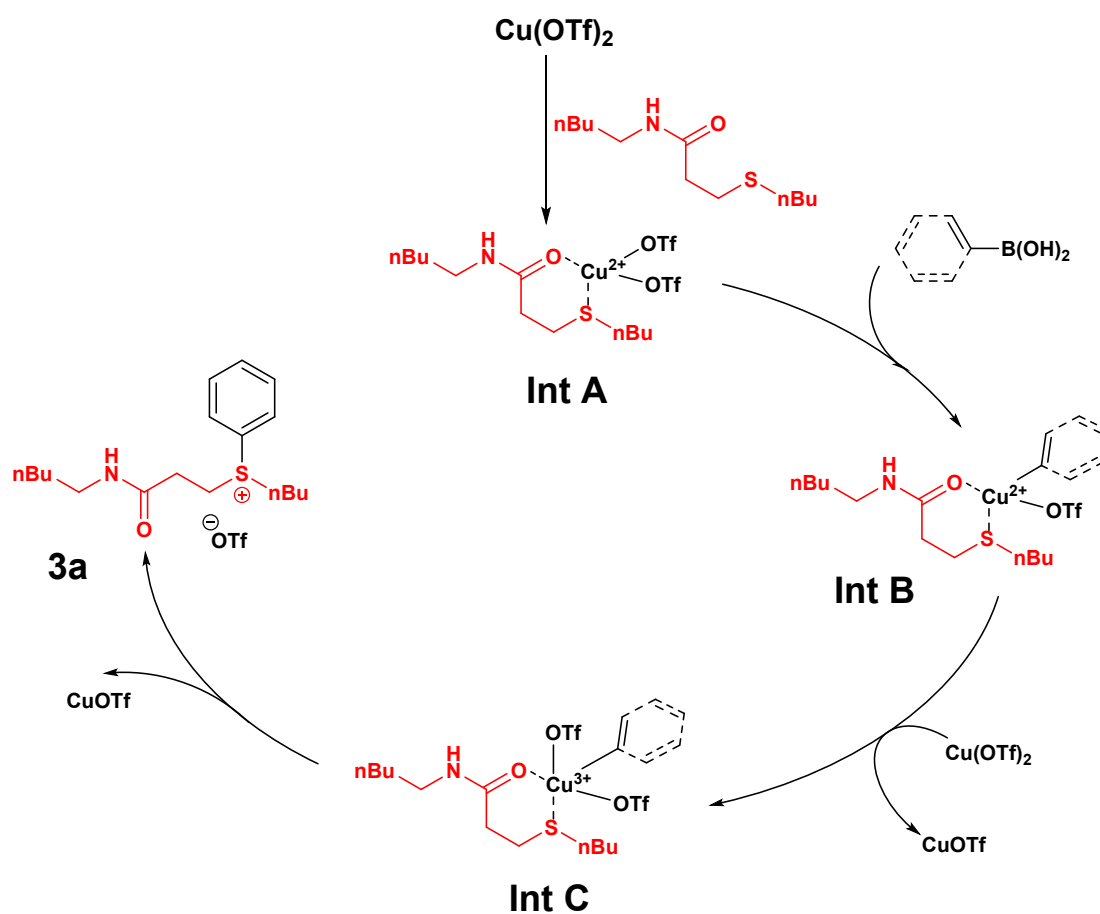


TGA

compounds	^a T _{2wt%} /°C	^b T _{5wt%} /°C	^c T _{50wt%} /°C	residual mass T _{500°C} /wt%
3a	140.74	163.37	280.10	5.53
3d	155.59	168.71	234.62	0.16
3e	137.74	154.41	235.13	0.14
3t	112.40	166.37	307.00	6.47

^aweight loss of 2%. ^bweight loss of 5%. ^cweight loss of 10%

6. Proposed mechanism



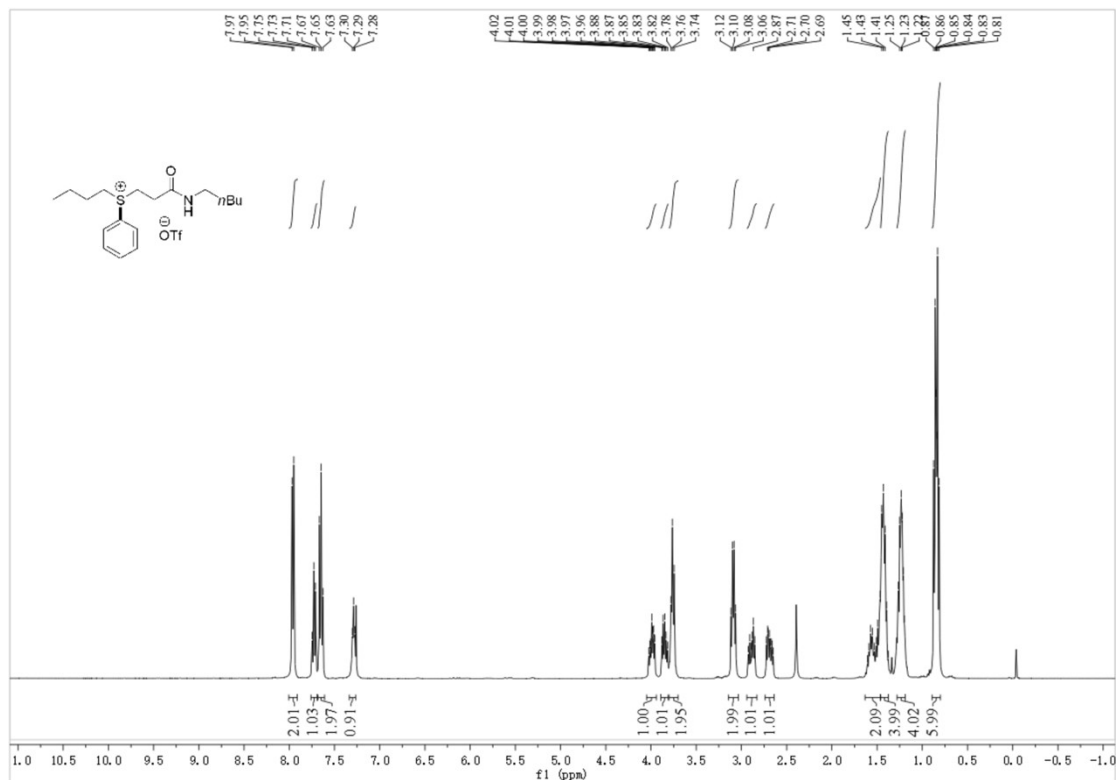
Based on the previous studies,² the synergistic coordination of both the thioether and the amide to copper is crucial for facilitating the transformation, or at least helps avoid the use of high loadings of the thioether. After transmetalation with boron compounds, disproportionation of **Int B** with another Cu^{2+} species is suggested to generate Cu^{3+} species **Int C**, followed by reductive elimination to form the sulfonium salt **3a**.

7. Reference:

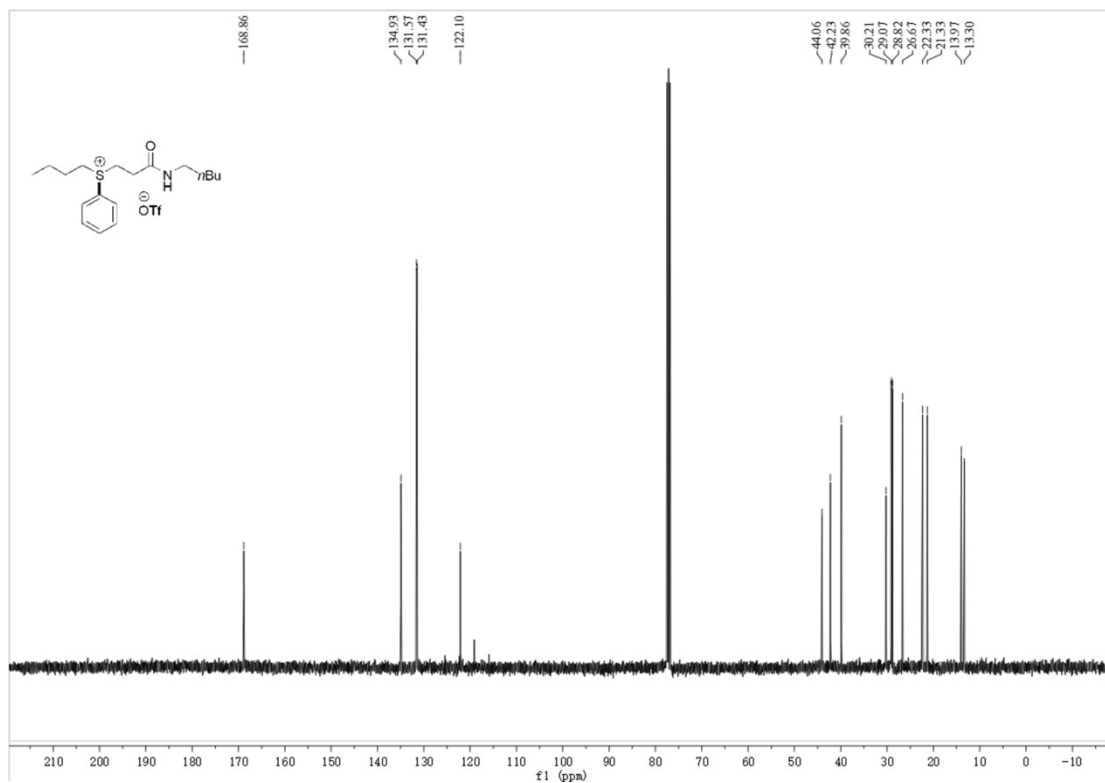
- (1) Li, Y.; Han, D.; Luo, Z.; Lv, X.; Liu, B. The Chan–Lam-Type Synthesis of Thioimidazolium Salts for Thiol–(Hetero)arene Conjugation. *Chem. Commun.* **2024**, *60*, 4675.
- (2) Wang, G.; Han, D.; Li, Y.; Nie, Y.; Muthusamy, S.; Luo, Z.; Liu, B. Copper-Mediated Deconstructive Ring Cleavage of Cyclic Thioethers with Boron Compounds. *Org. Lett.* **2023**, *25*, 3522–3526.

Spectra Data

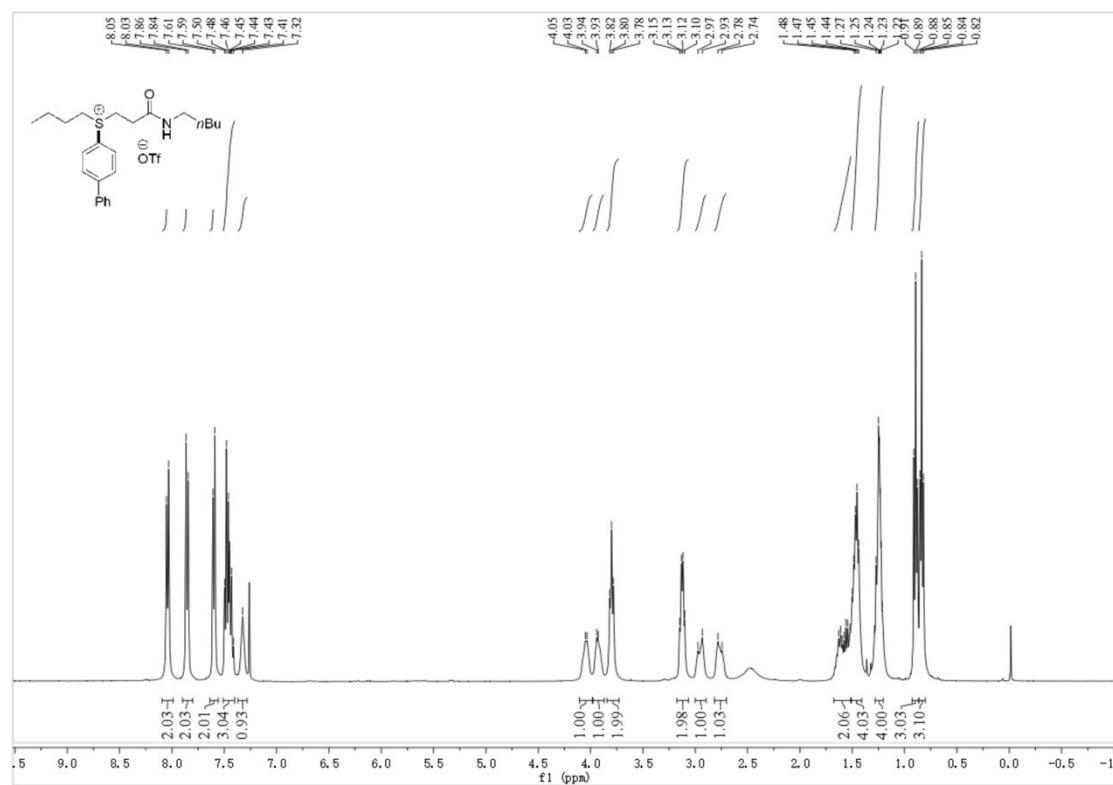
^1H NMR spectrum of **3a** (CDCl_3 , 400 MHz)



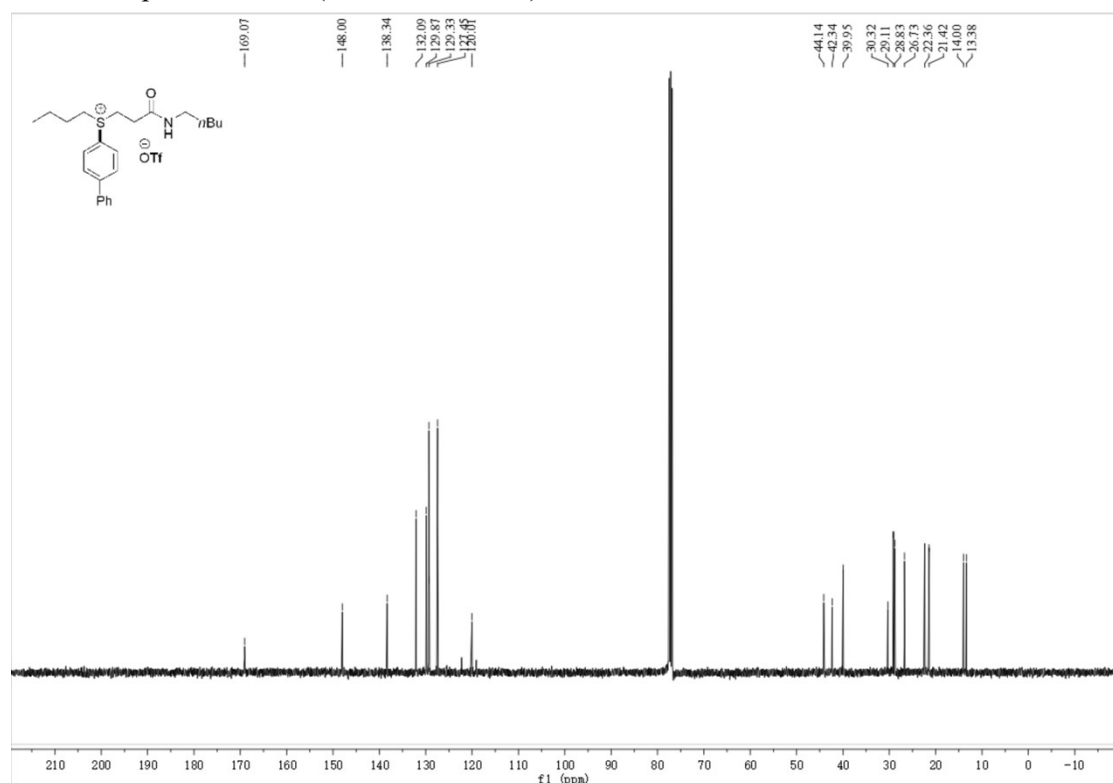
^{13}C NMR spectrum of **3a** (CDCl_3 , 101 MHz)



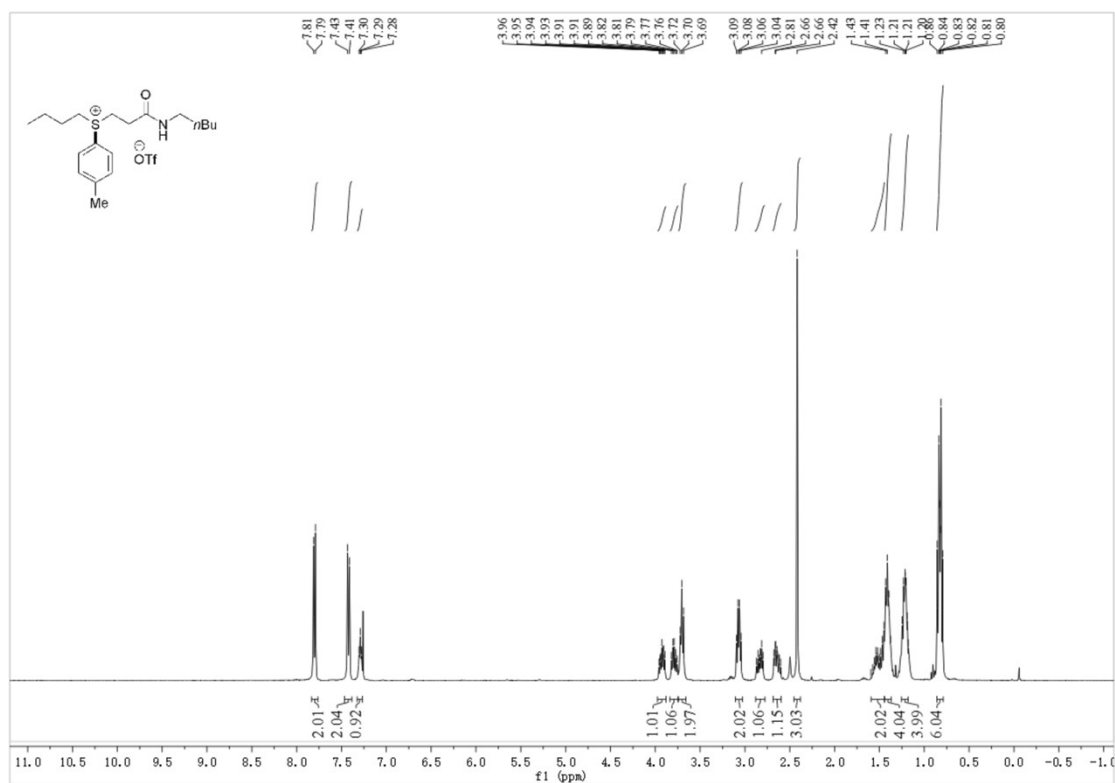
^1H NMR spectrum of **3b** (CDCl_3 , 400 MHz)



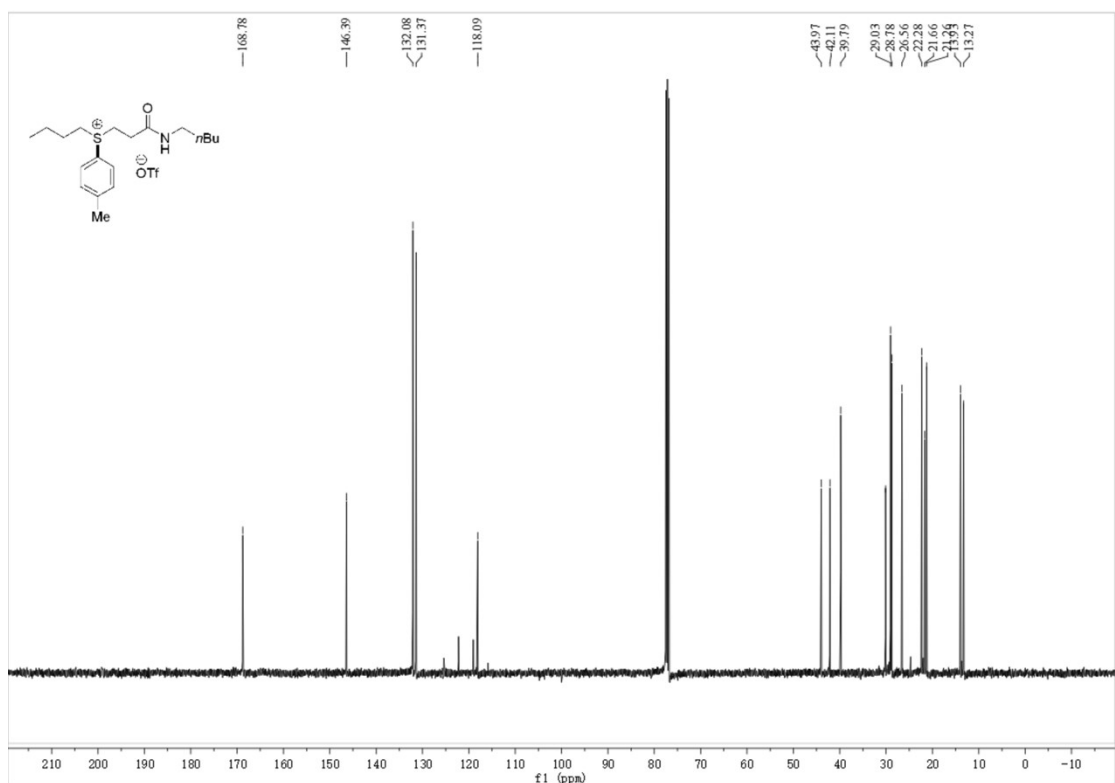
^{13}C NMR spectrum of **3b** (CDCl_3 , 101 MHz)



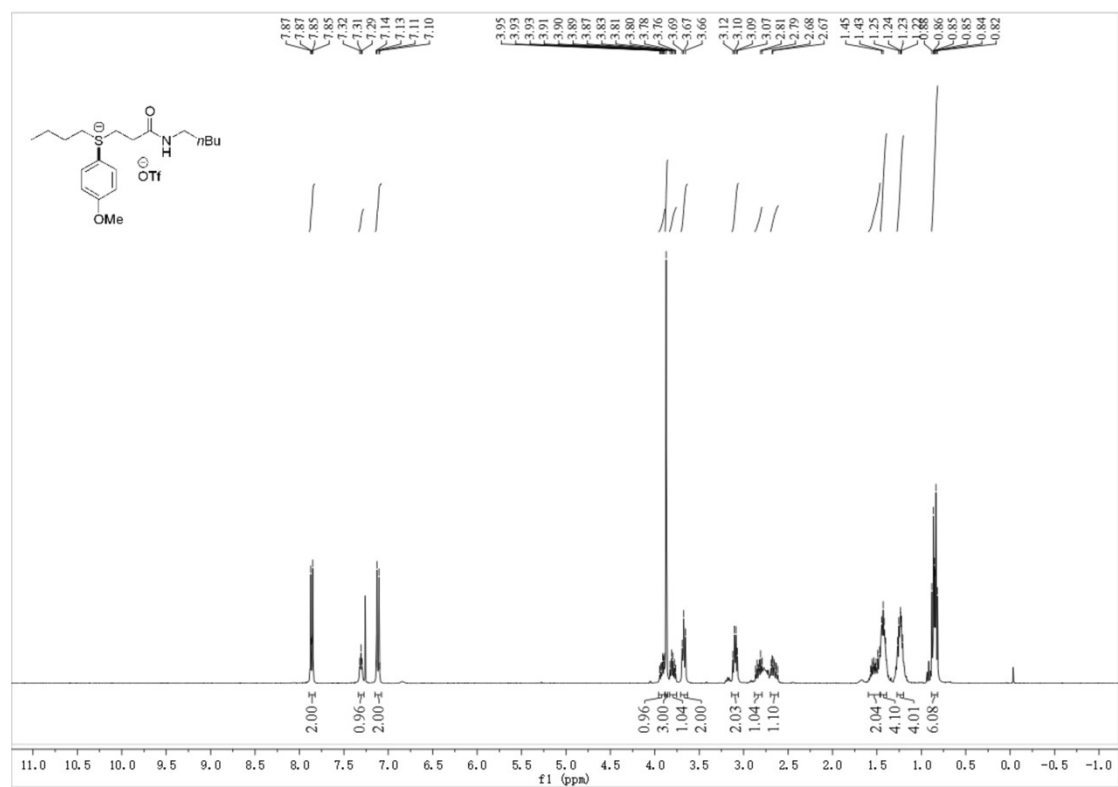
^1H NMR spectrum of **3c** (CDCl_3 , 400 MHz)



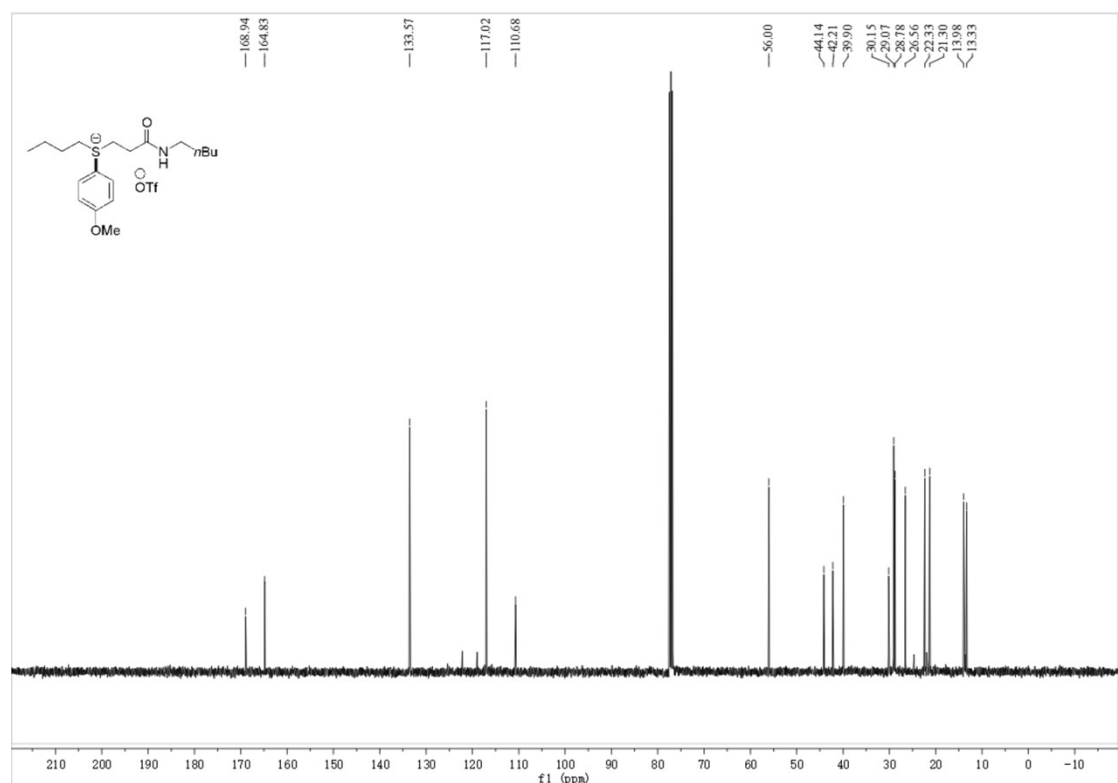
^{13}C NMR spectrum of **3c** (CDCl_3 , 101 MHz)



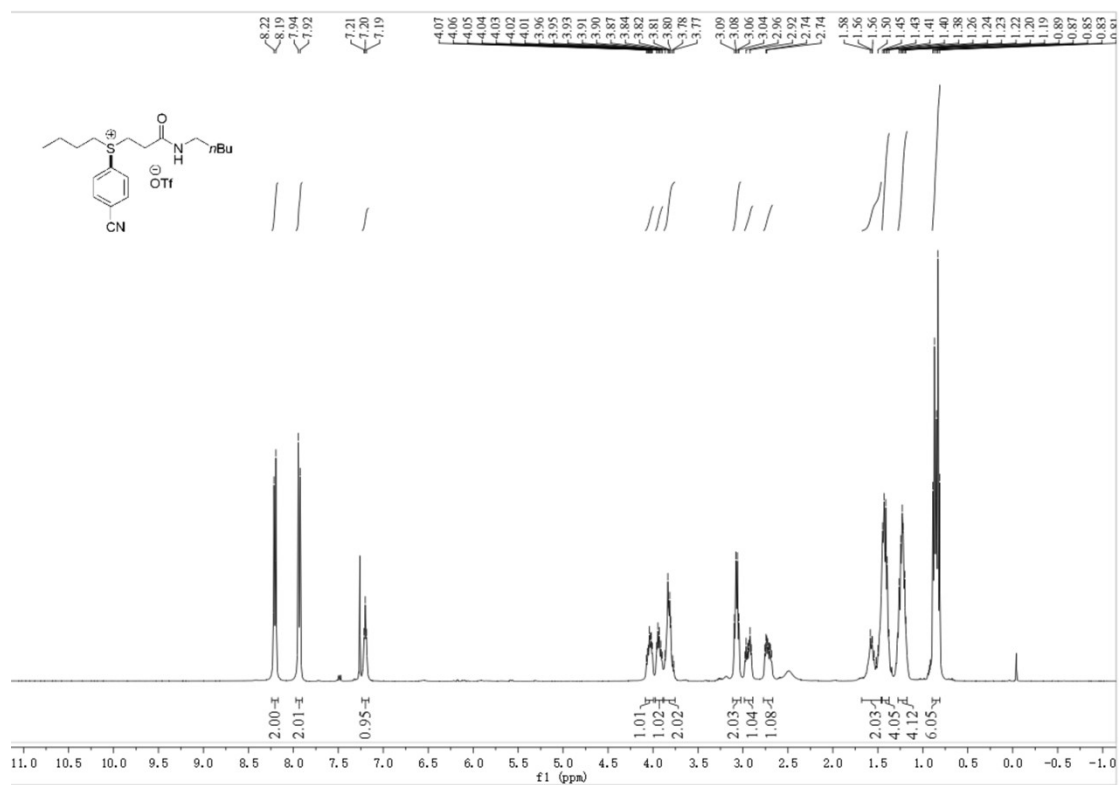
¹H NMR spectrum of **3d** (CDCl₃, 400 MHz)



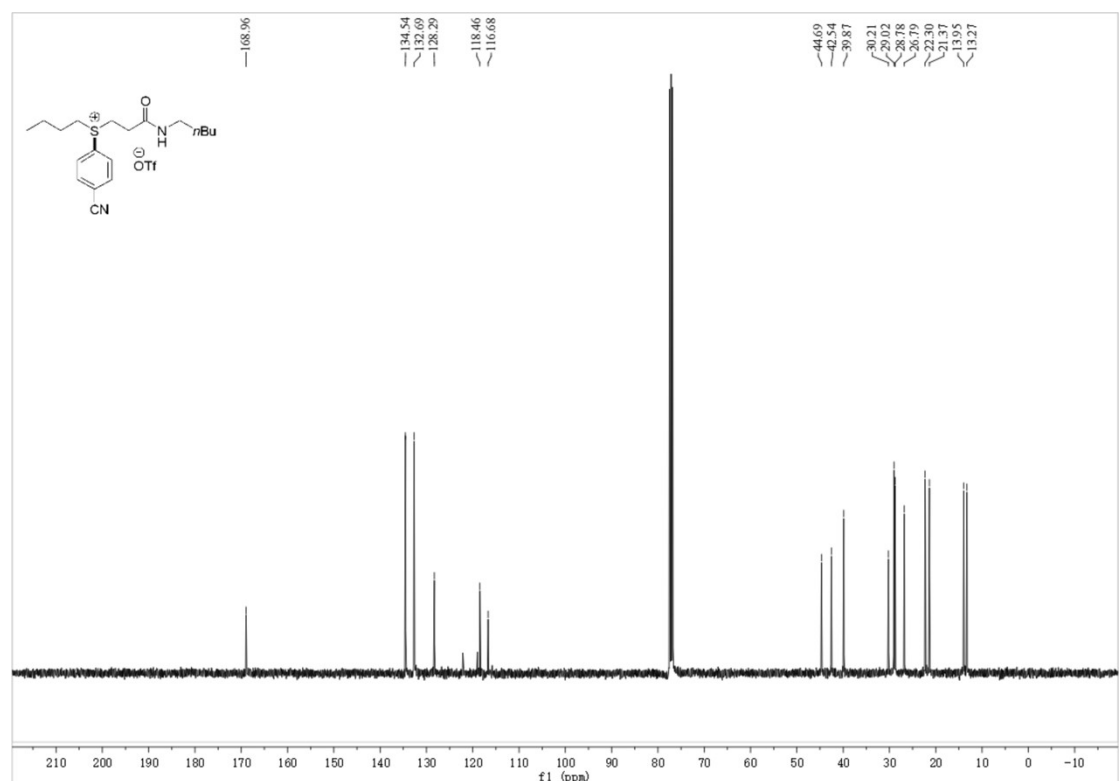
¹³C NMR spectrum of **3d** (CDCl₃, 101 MHz)



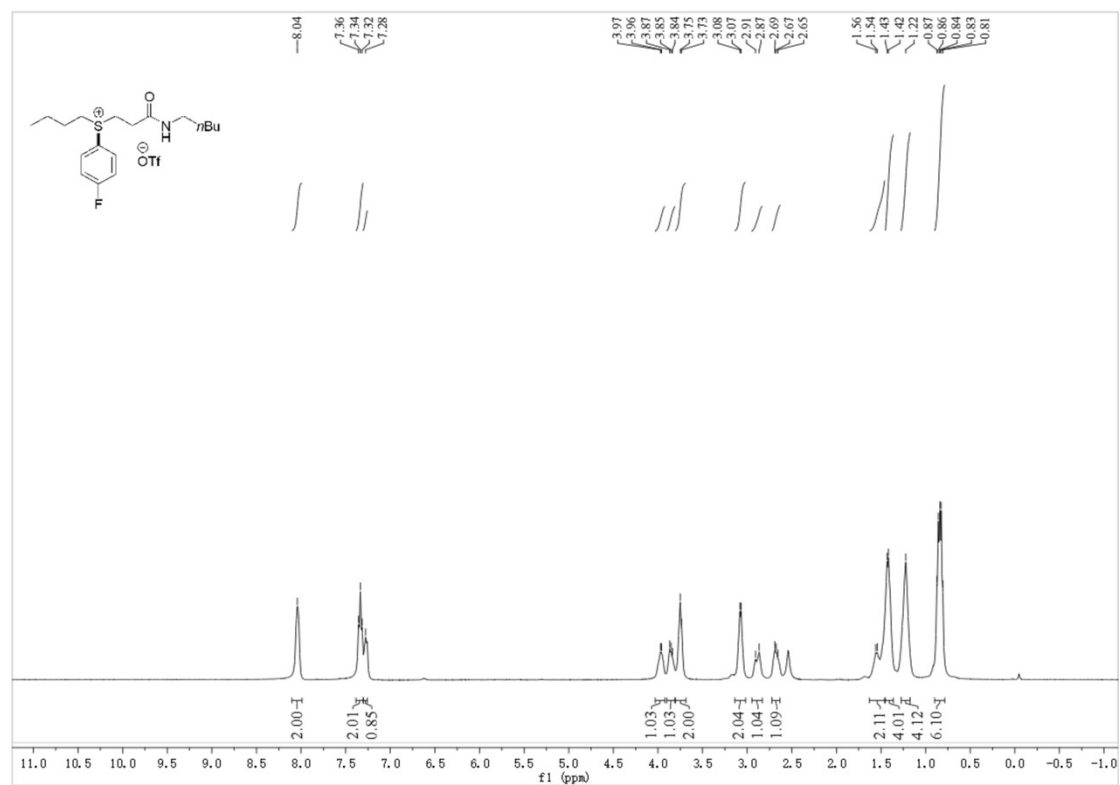
¹H NMR spectrum of **3e** (CDCl₃, 400 MHz)



¹³C NMR spectrum of **3e** (CDCl₃, 101 MHz)

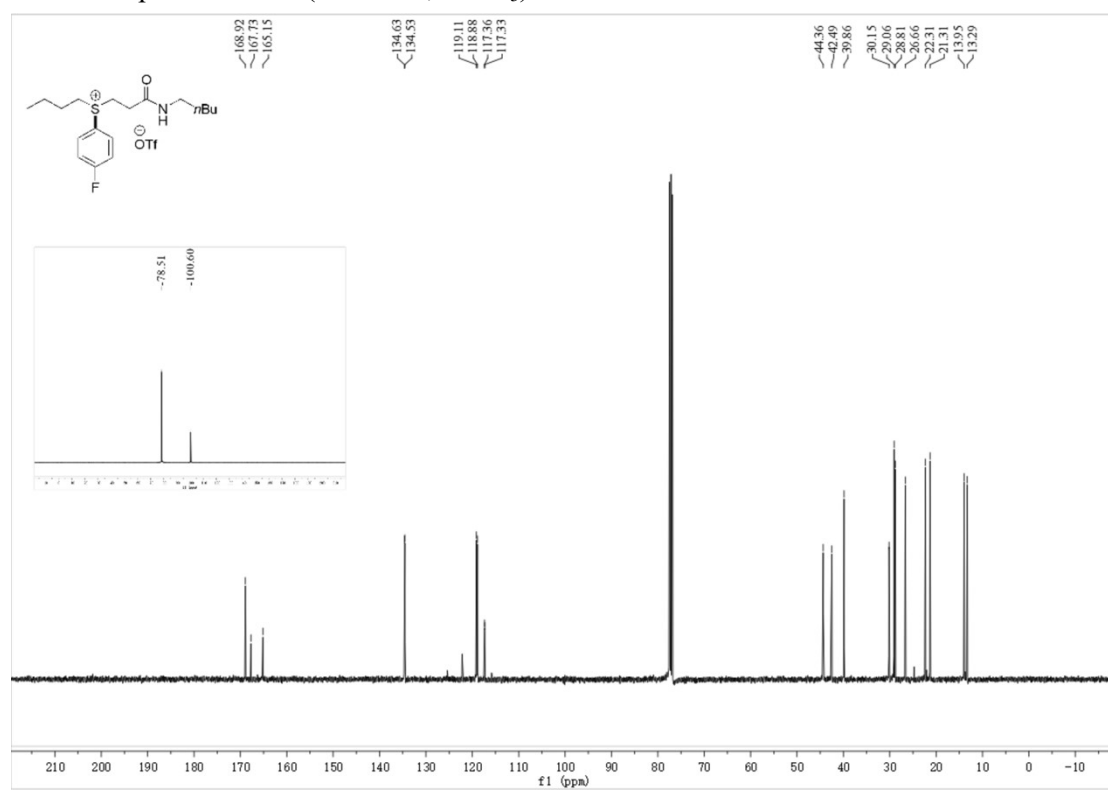


^1H NMR spectrum of **3f** (CDCl_3 , 400 MHz)

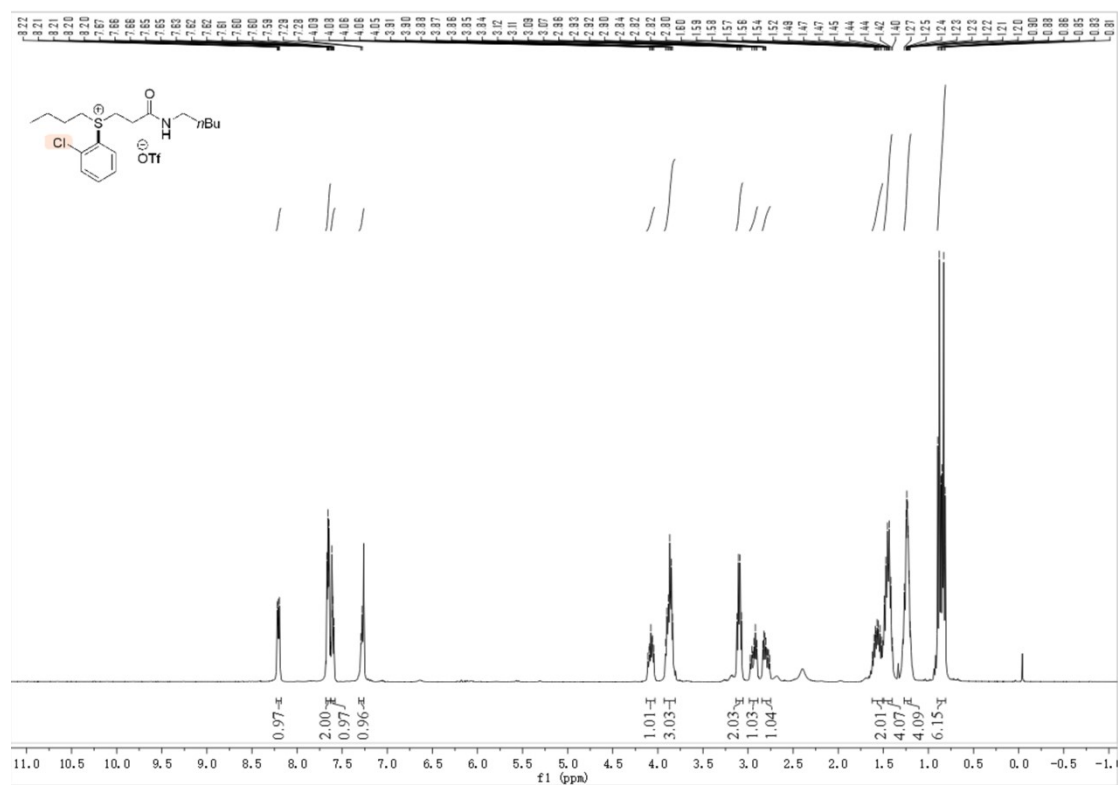


^{13}C NMR spectrum of **3f** (CDCl_3 , 101 MHz)

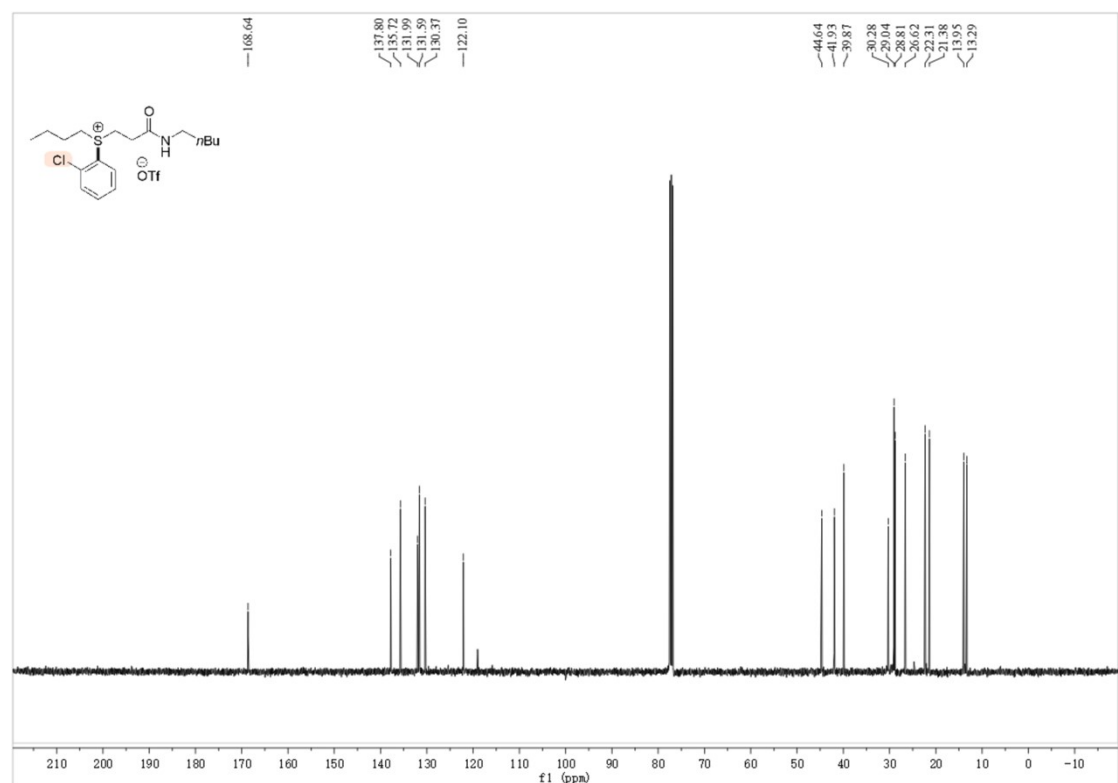
^{19}F NMR spectrum of **3f** (376 MHz, CDCl_3)



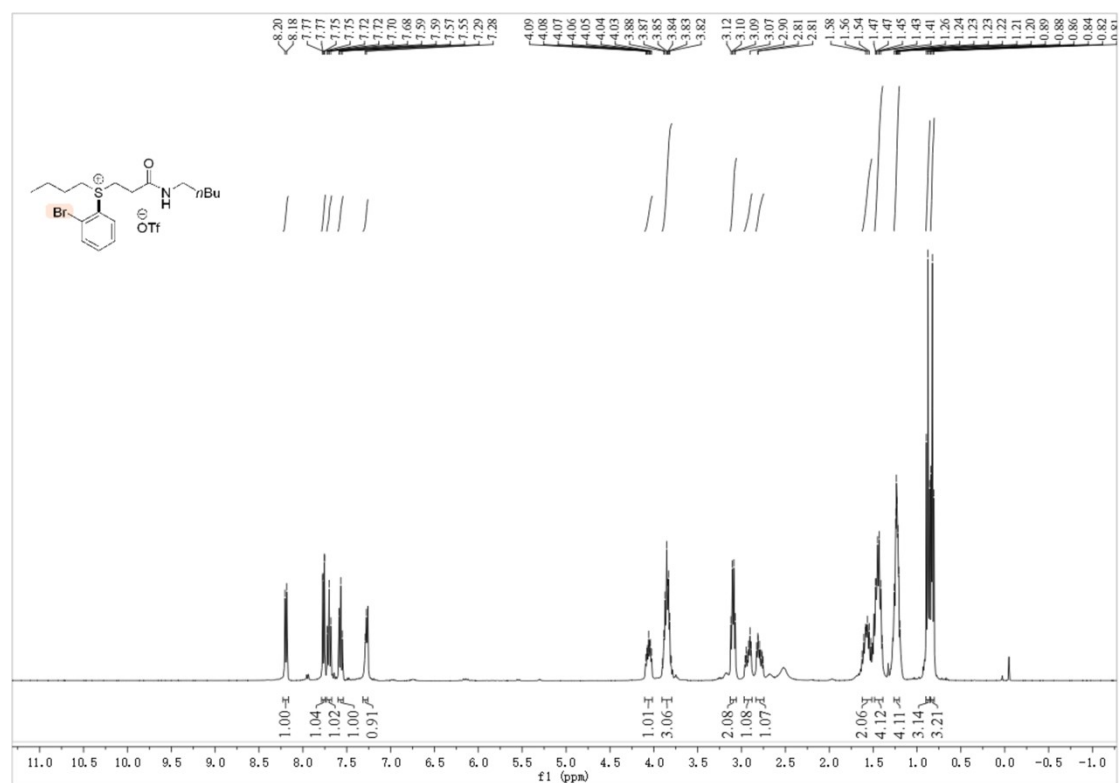
^1H NMR spectrum of **3g** (CDCl_3 , 400 MHz)



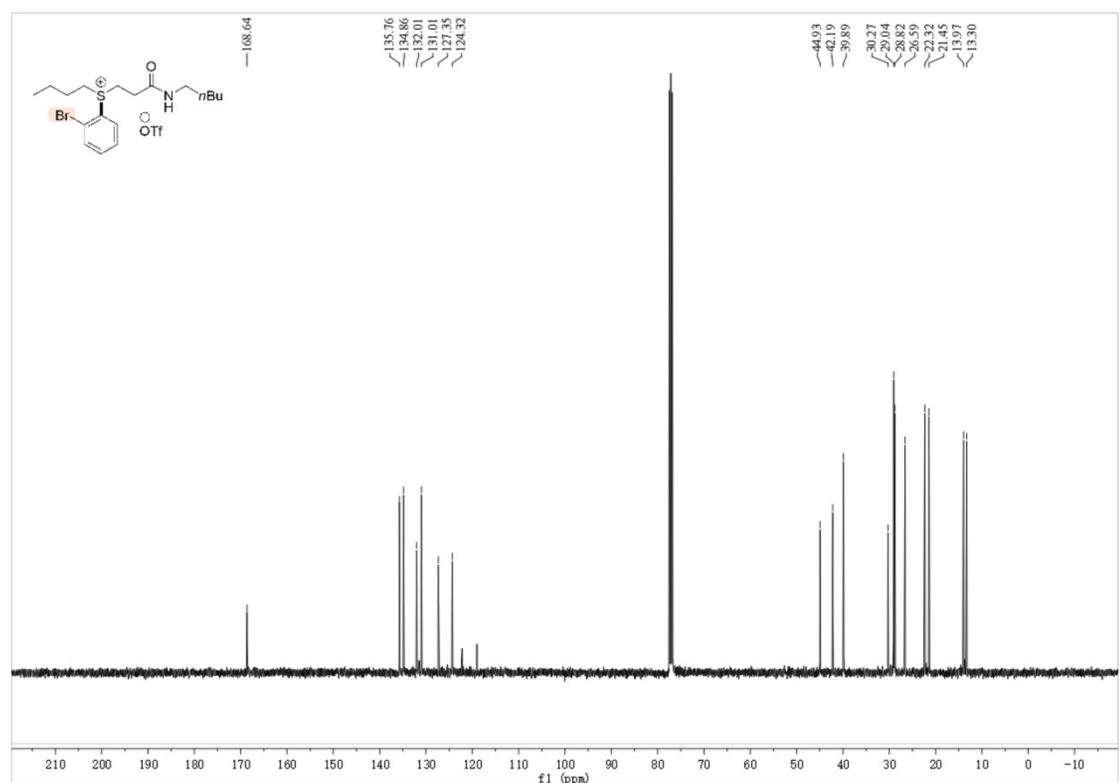
^{13}C NMR spectrum of **3g** (CDCl_3 , 101 MHz)



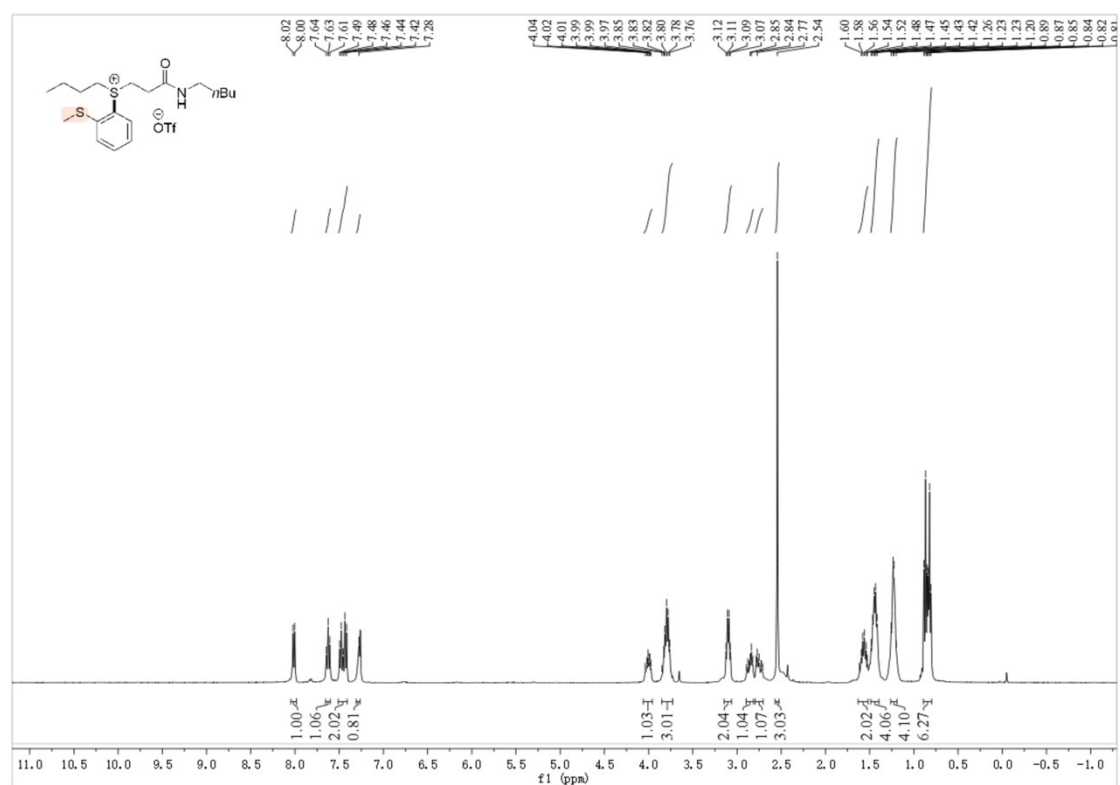
^1H NMR spectrum of **3h** (CDCl_3 , 400 MHz)



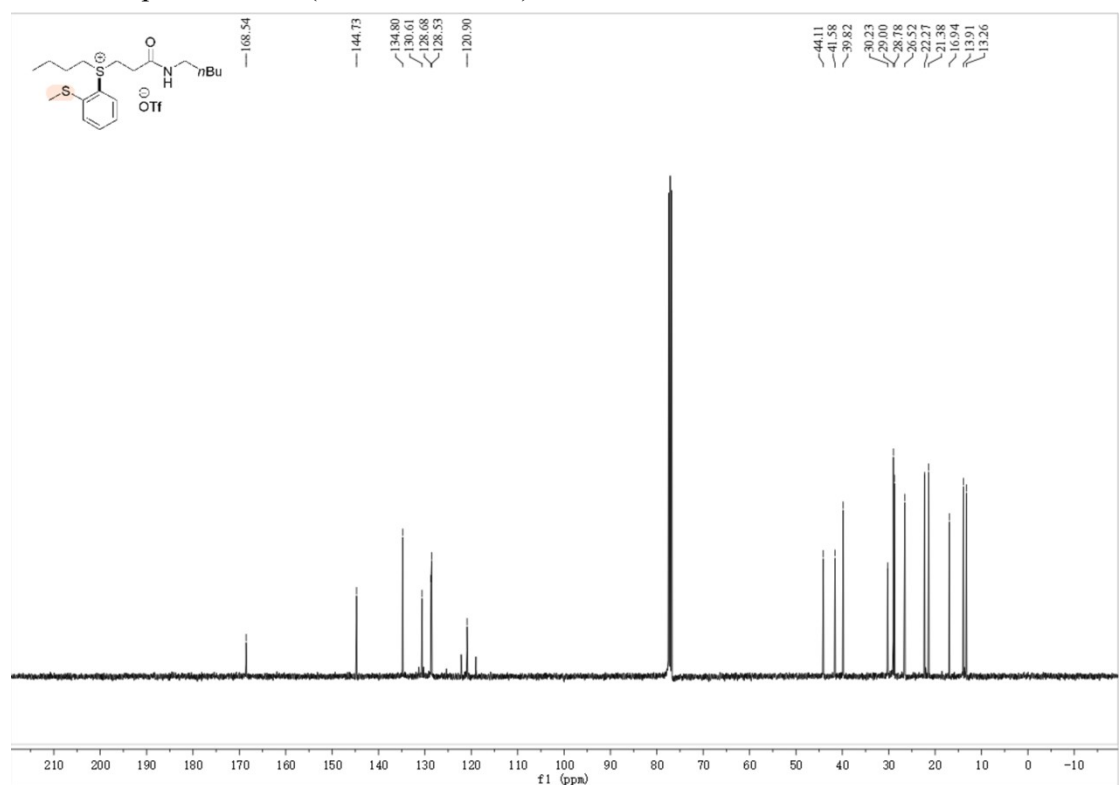
^{13}C NMR spectrum of **3h** (CDCl_3 , 101 MHz)



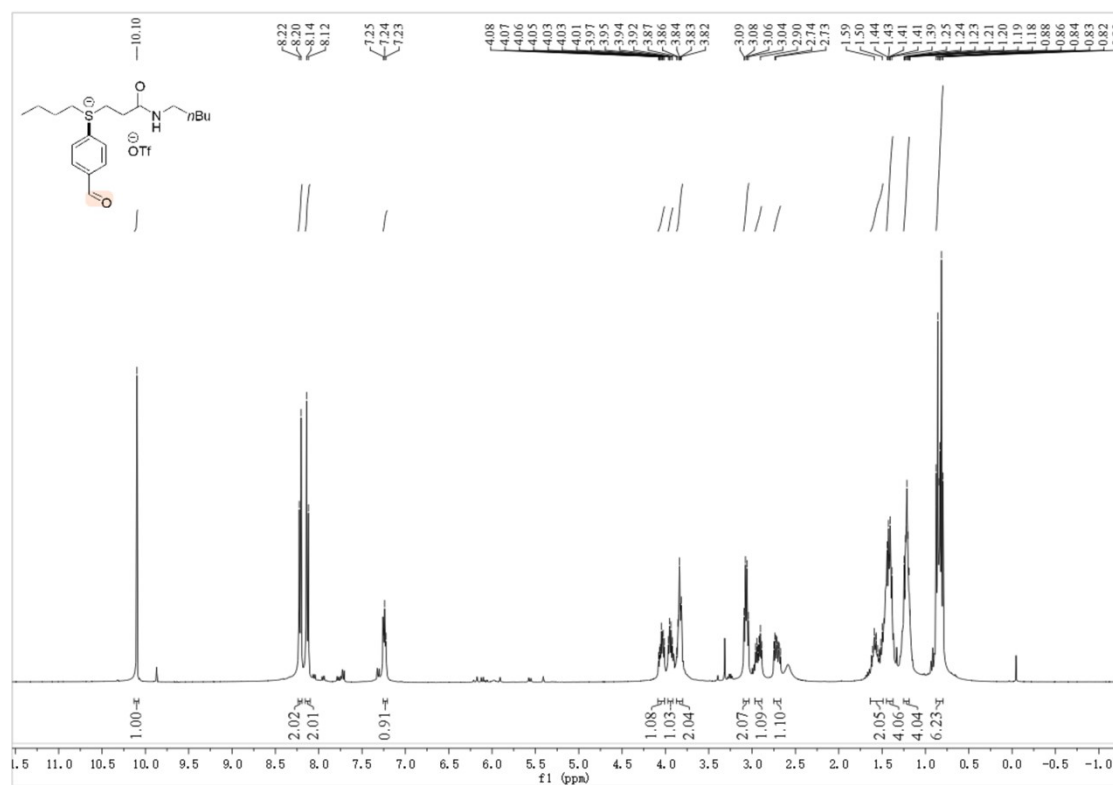
^1H NMR spectrum of **3i** (CDCl_3 , 400 MHz)



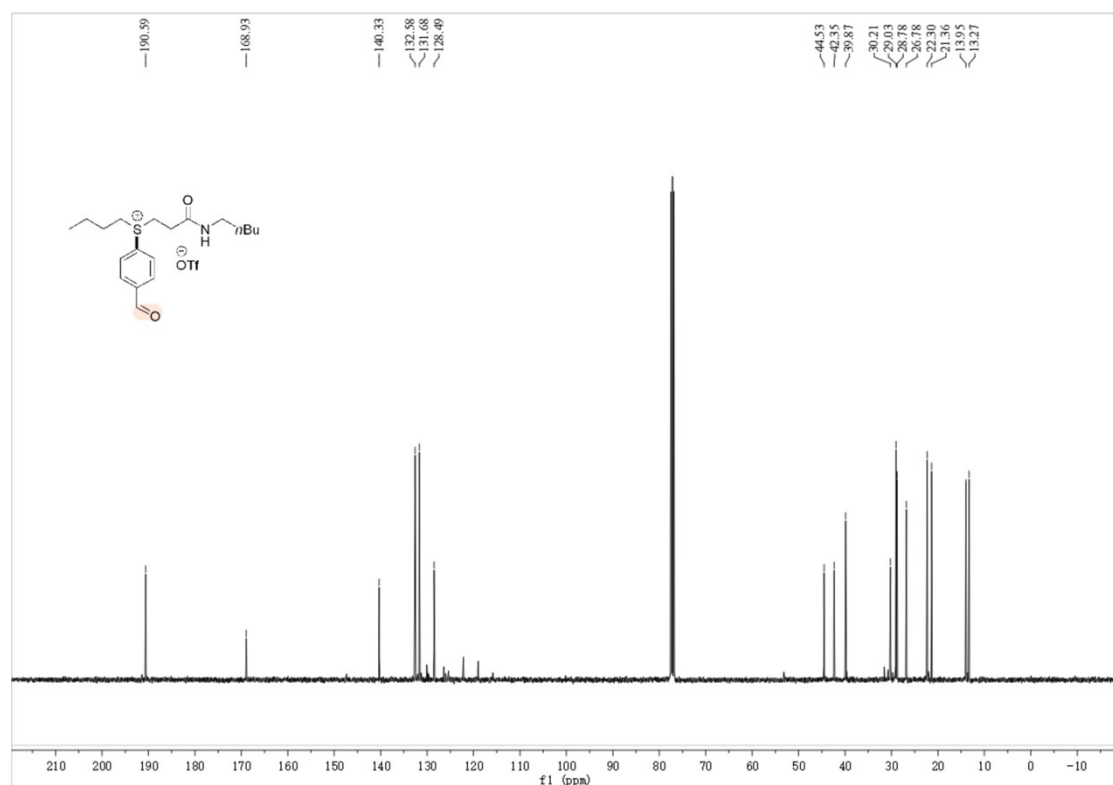
^{13}C NMR spectrum of **3i** (CDCl_3 , 101 MHz)



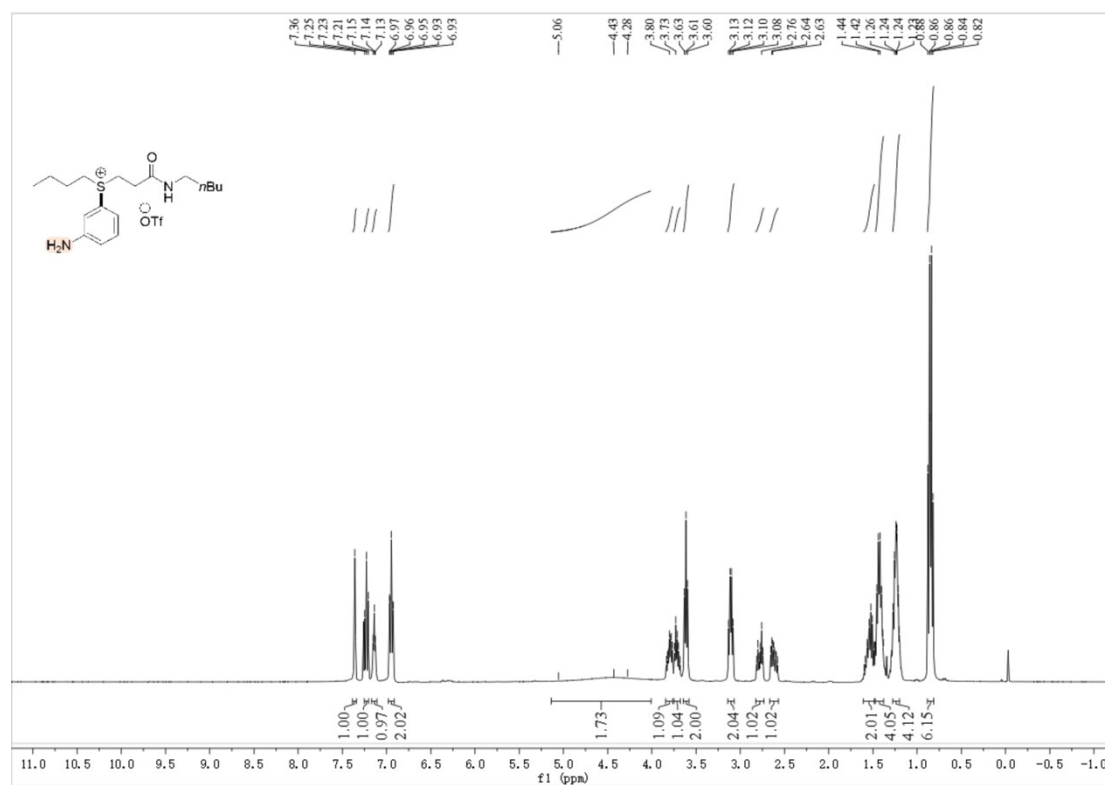
^1H NMR spectrum of **3j** (CDCl_3 , 400 MHz)



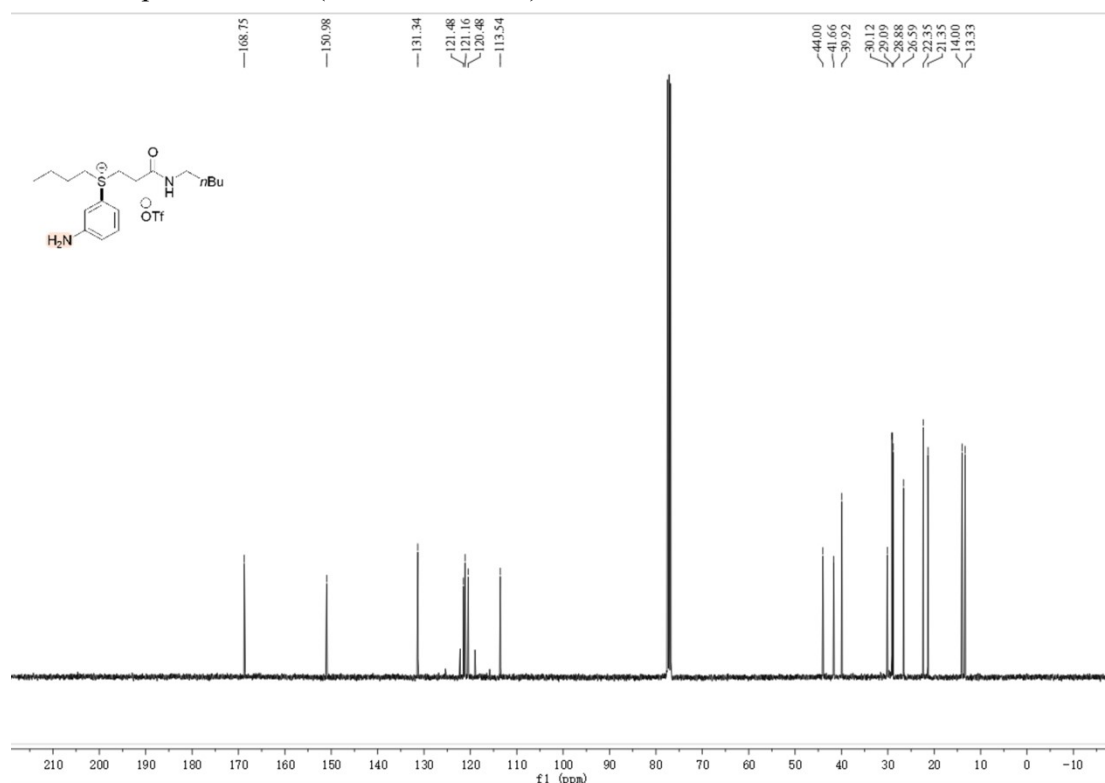
^{13}C NMR spectrum of **3j** (CDCl_3 , 101 MHz)



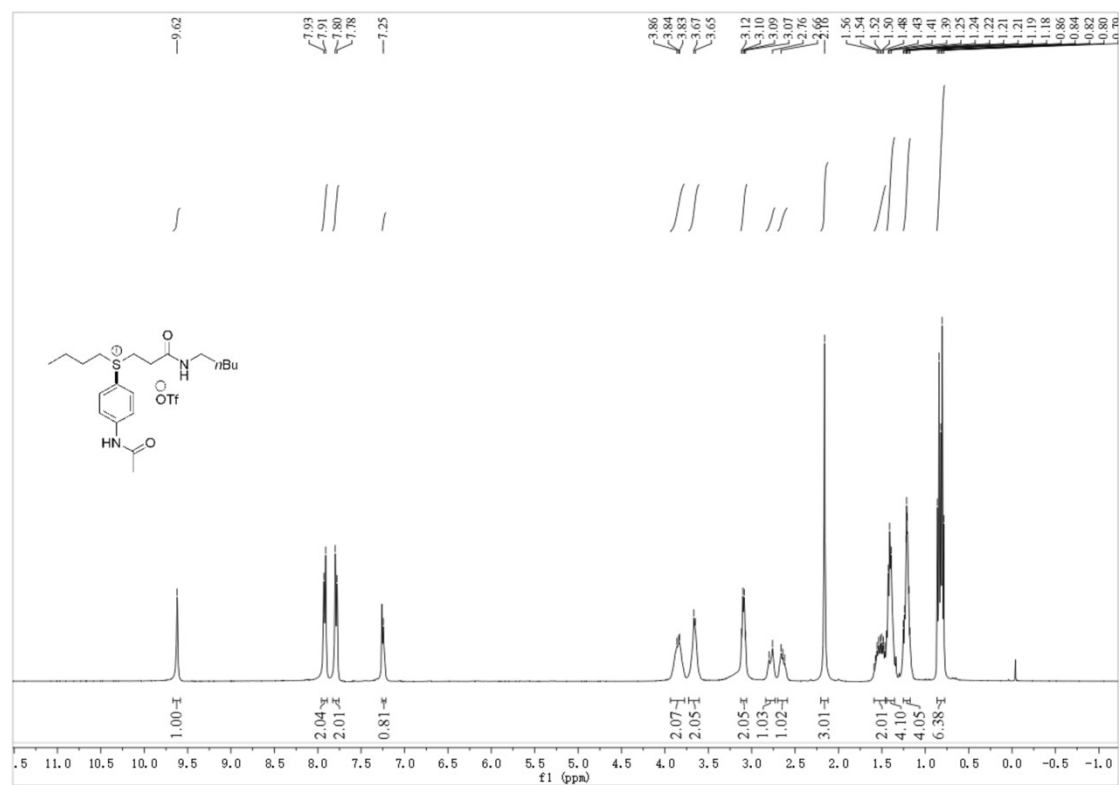
^1H NMR spectrum of **3k** (CDCl_3 , 400 MHz)



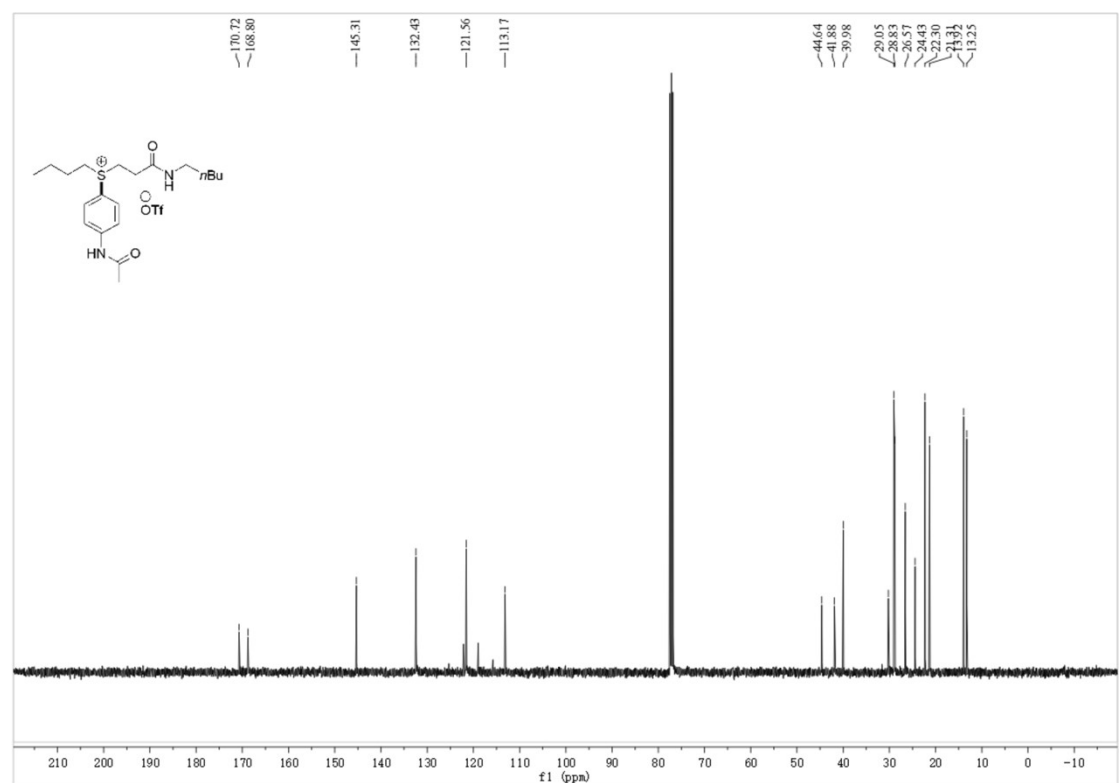
^{13}C NMR spectrum of **3k** (CDCl_3 , 101 MHz)



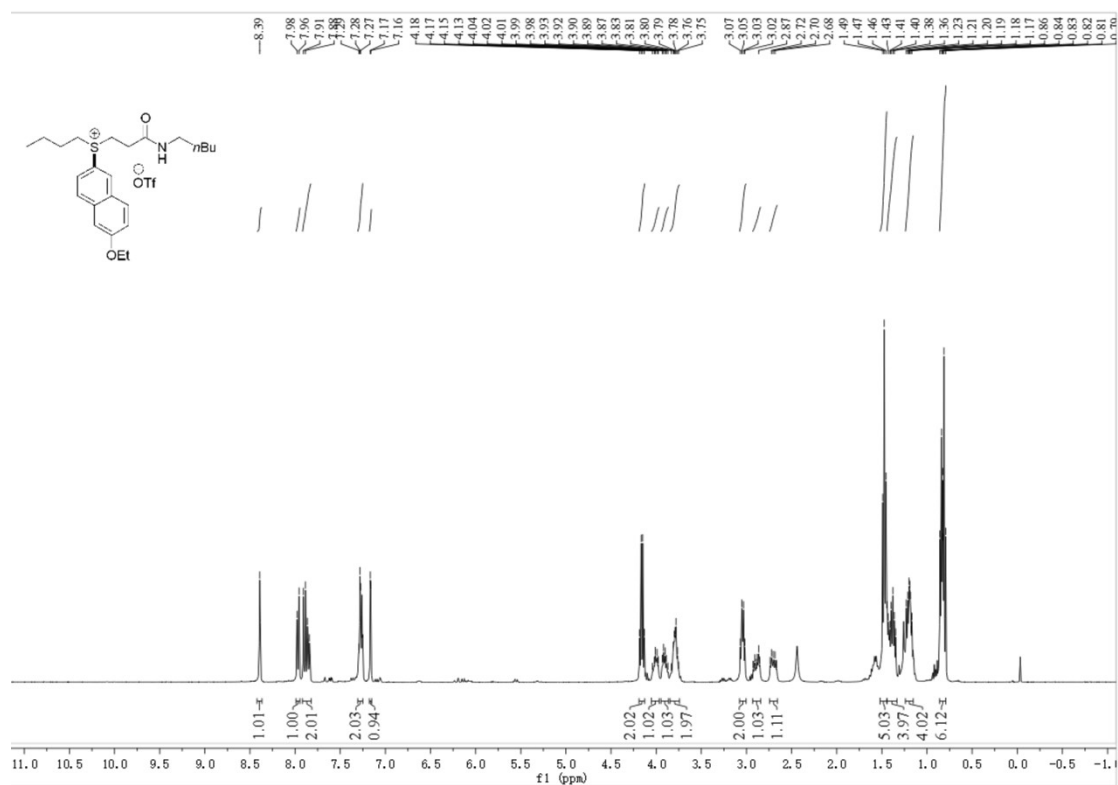
^1H NMR spectrum of **31** (CDCl_3 , 400 MHz)



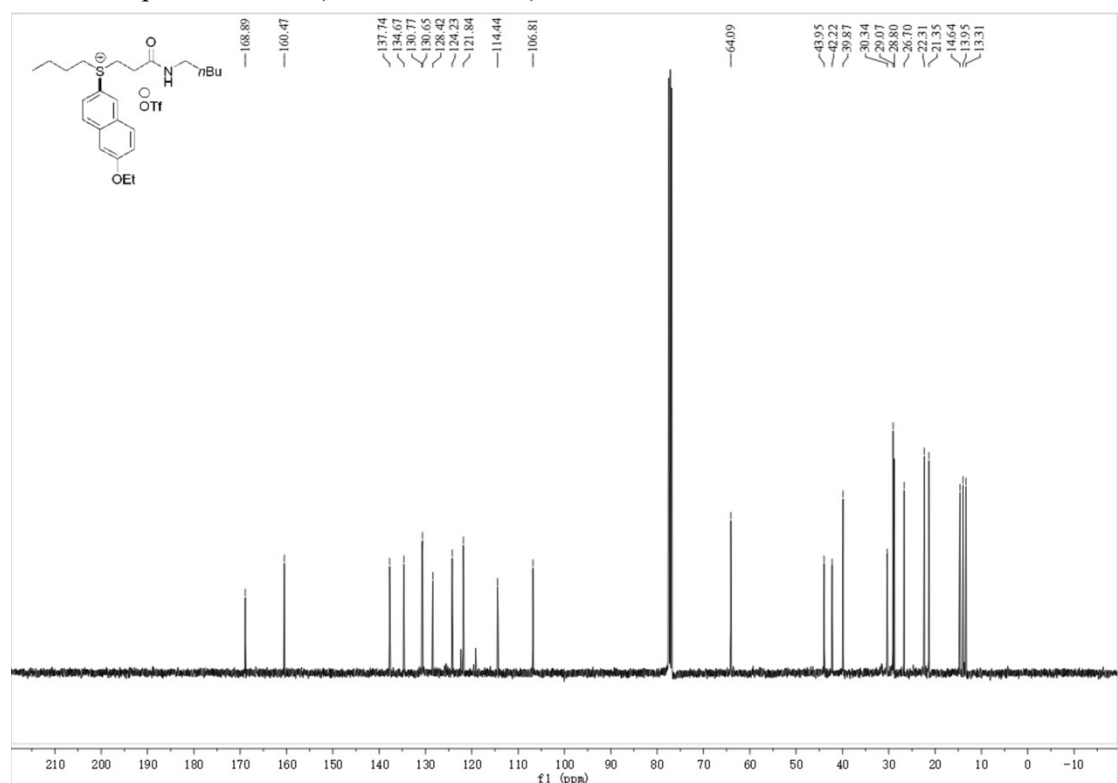
^{13}C NMR spectrum of **31** (CDCl_3 , 101 MHz)



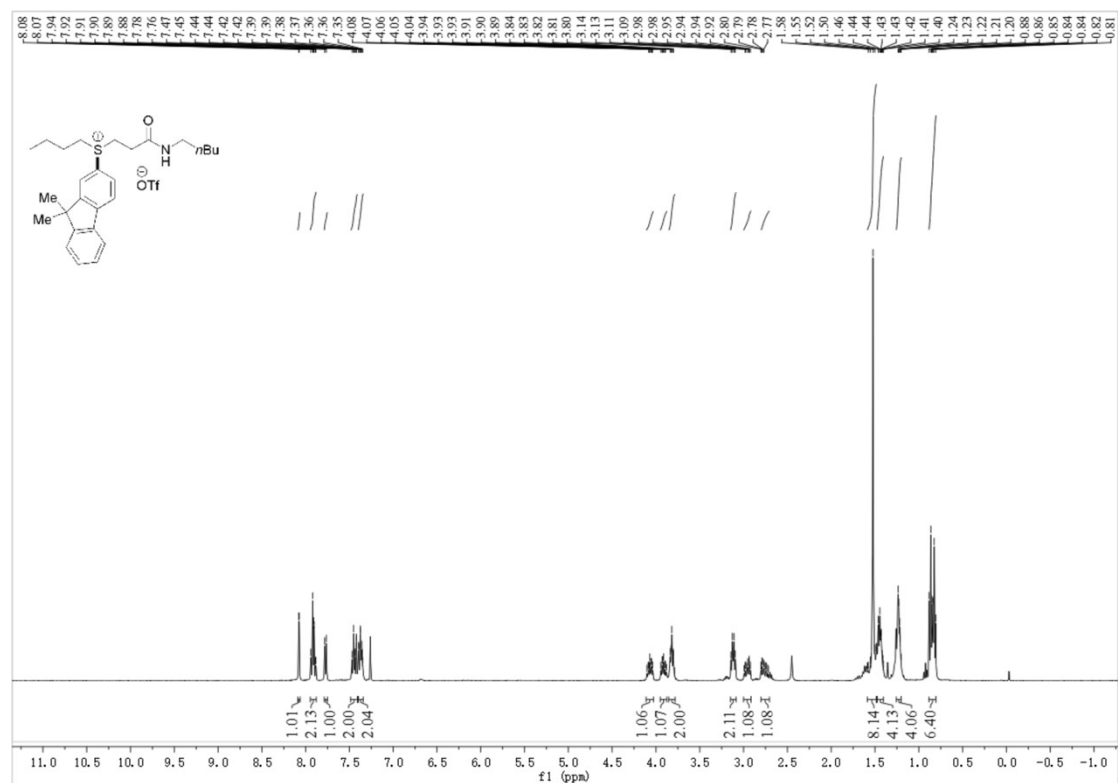
¹H NMR spectrum of **3n** (CDCl₃, 400 MHz)



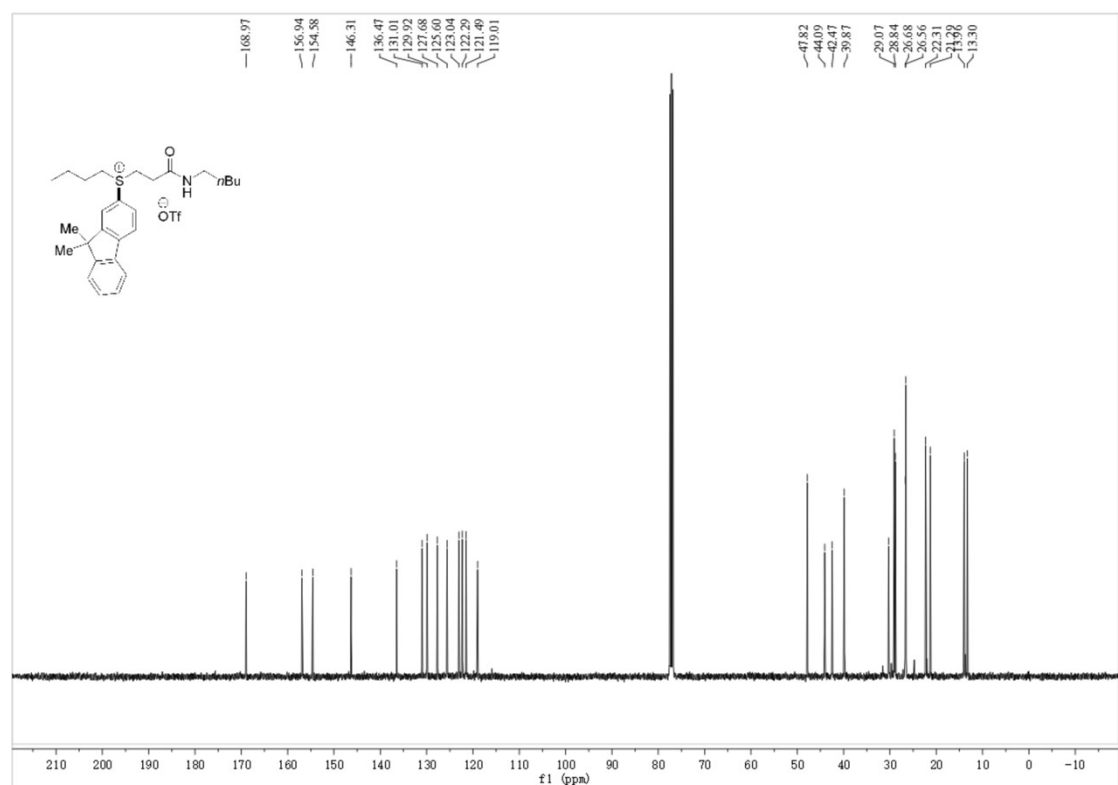
¹³C NMR spectrum of **3n** (CDCl₃, 101 MHz)



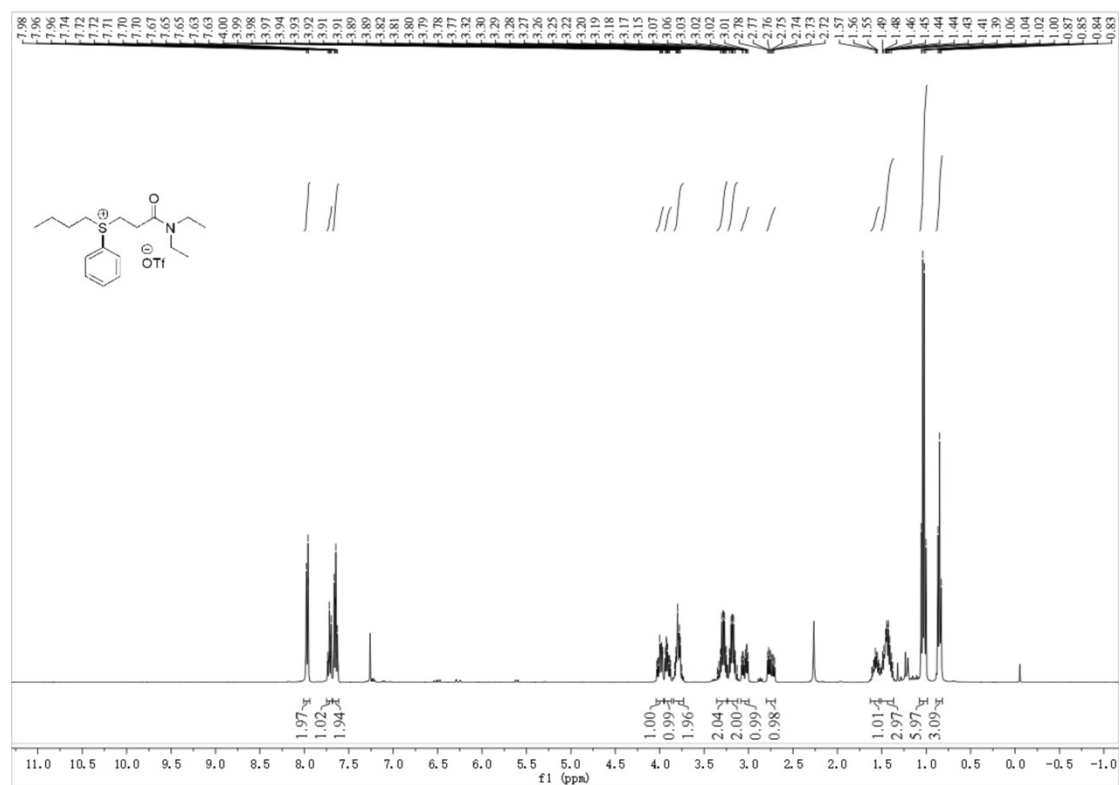
^1H NMR spectrum of **3o** (CDCl_3 , 400 MHz)



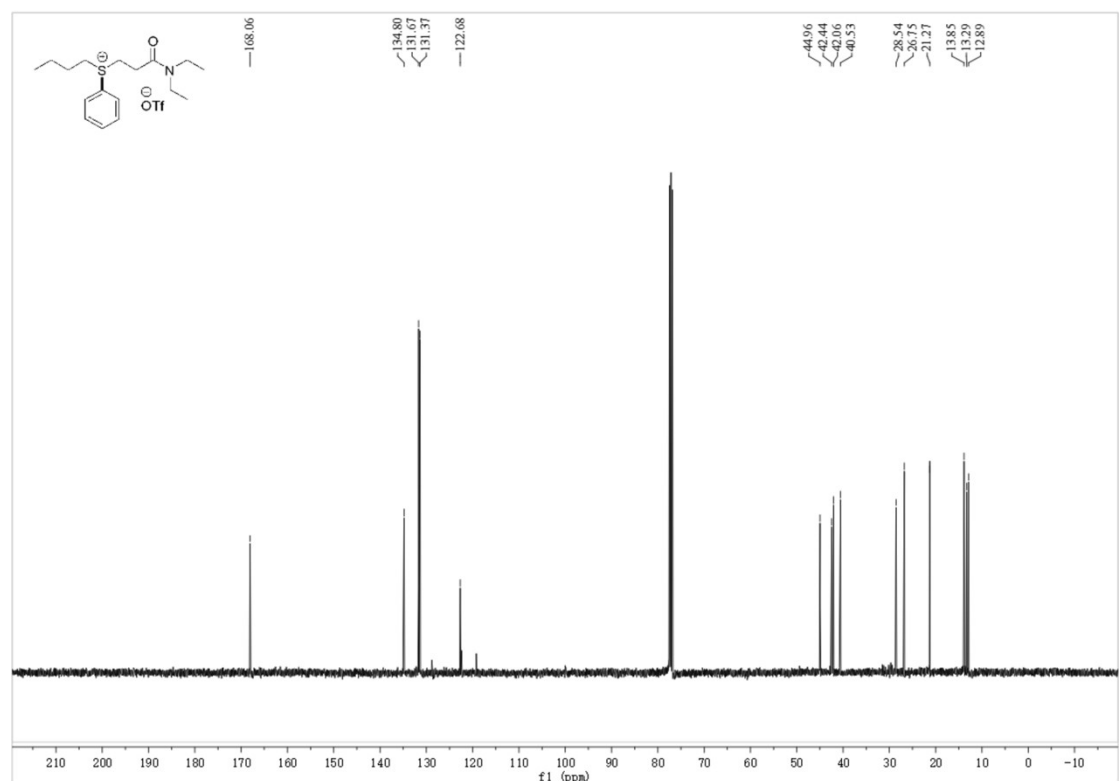
^{13}C NMR spectrum of **3o** (CDCl_3 , 101 MHz)



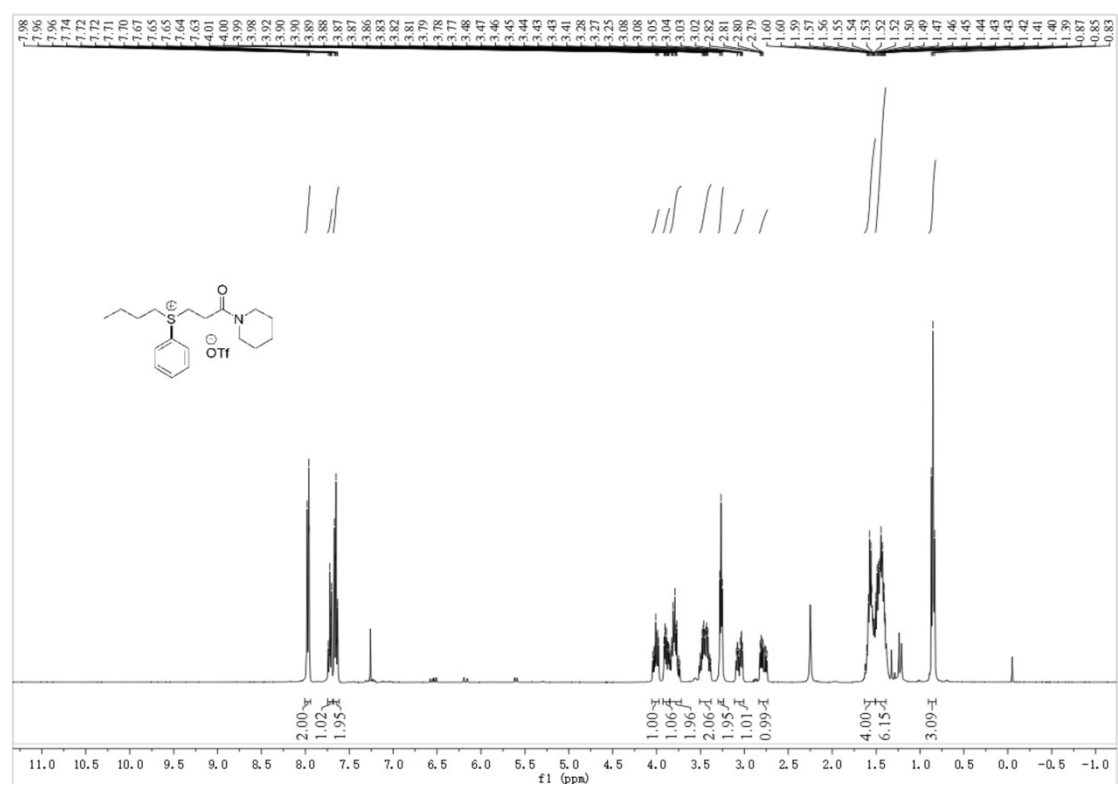
¹H NMR spectrum of **3p** (CDCl₃, 400 MHz)



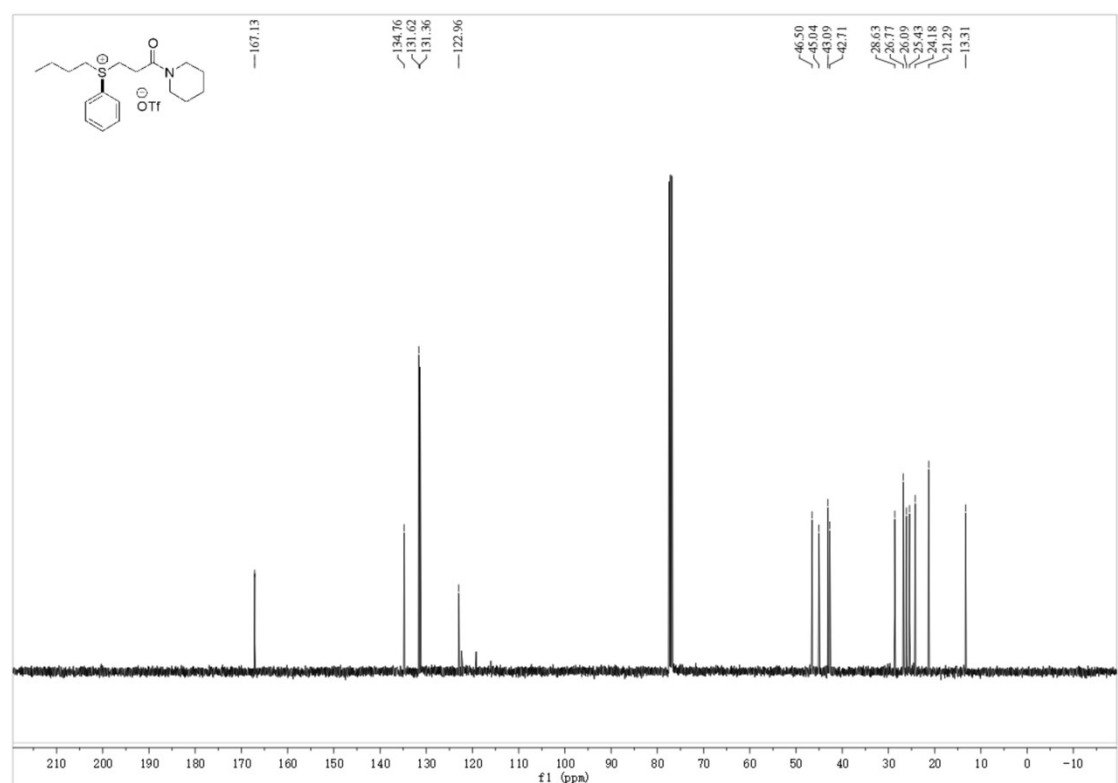
¹³C NMR spectrum of **3p** (CDCl₃, 101 MHz)



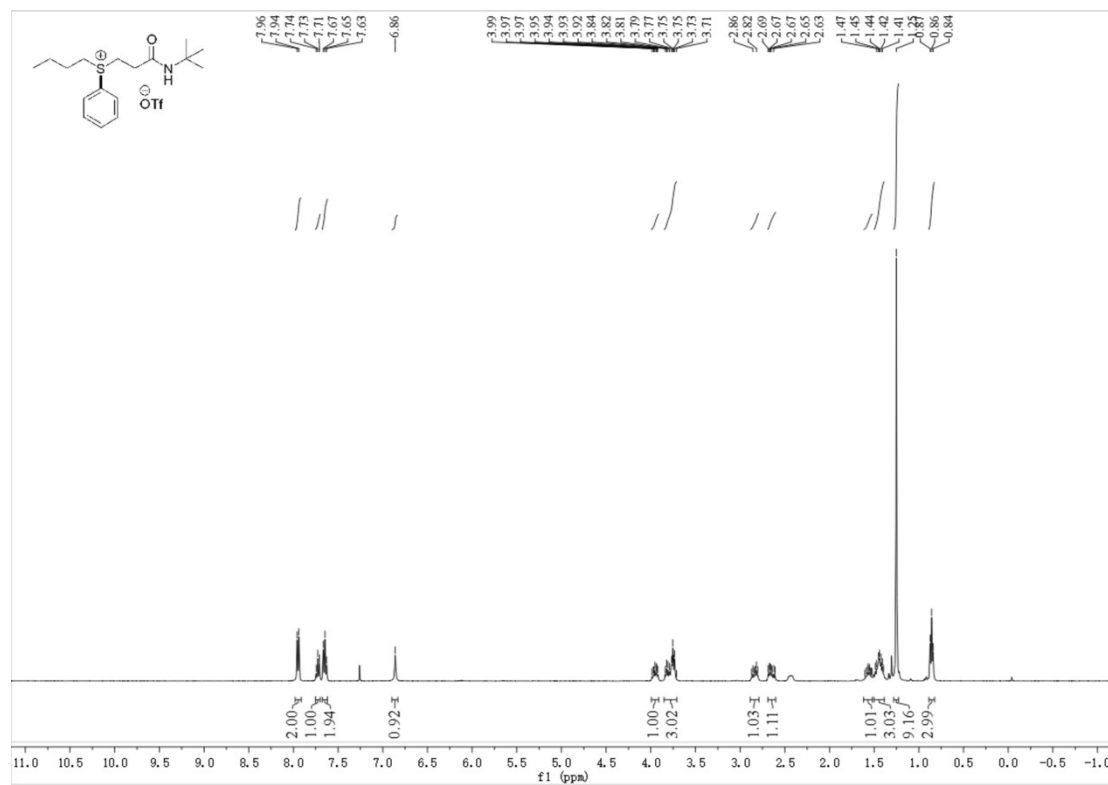
^1H NMR spectrum of **3q** (CDCl_3 , 400 MHz)



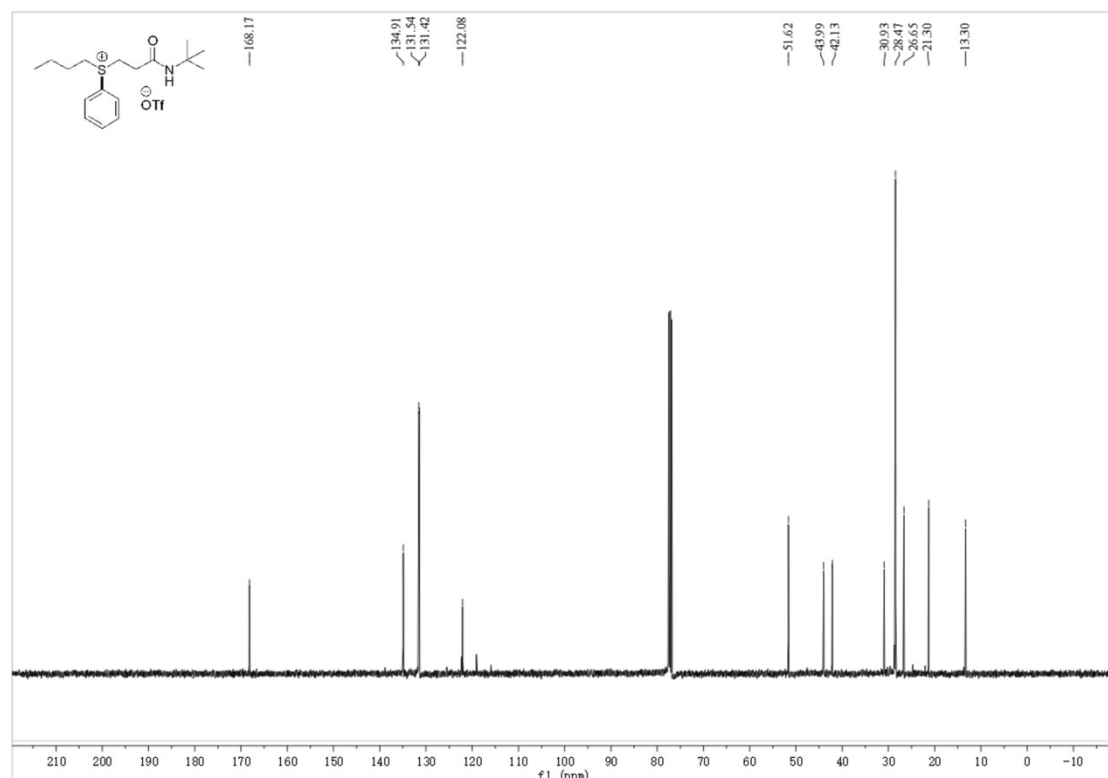
^{13}C NMR spectrum of **3q** (CDCl_3 , 101 MHz)



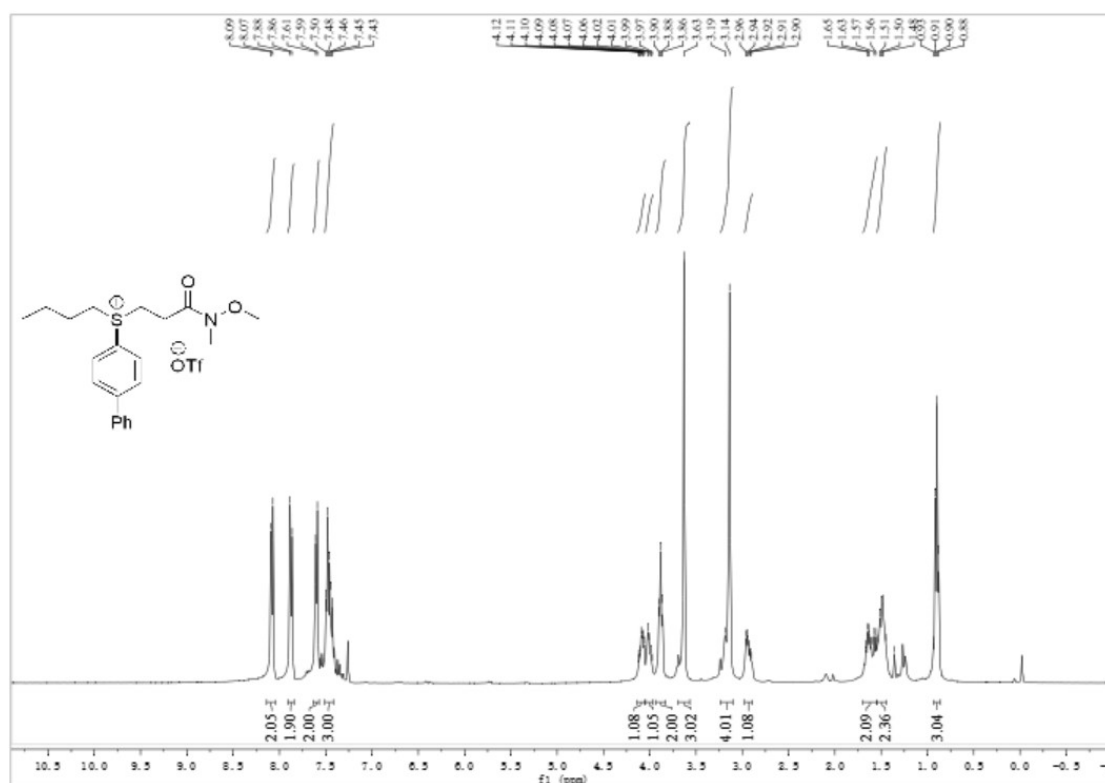
^1H NMR spectrum of **3r** (CDCl_3 , 400 MHz)



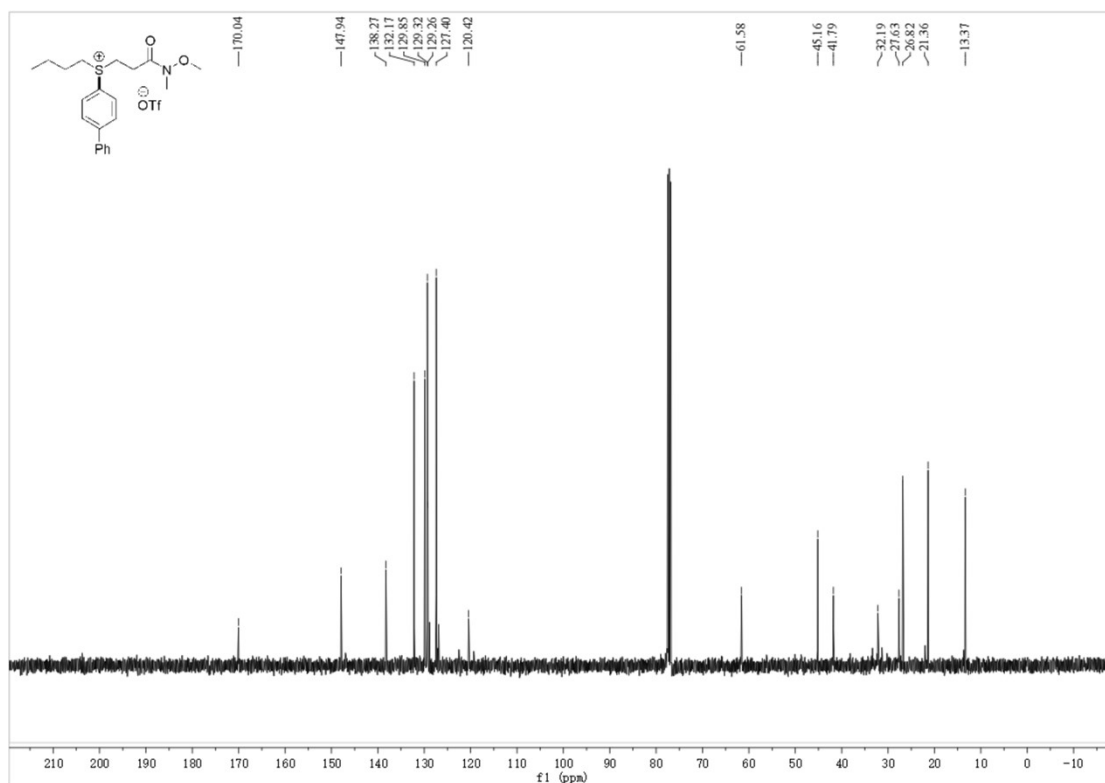
^{13}C NMR spectrum of **3r** (CDCl_3 , 101 MHz)



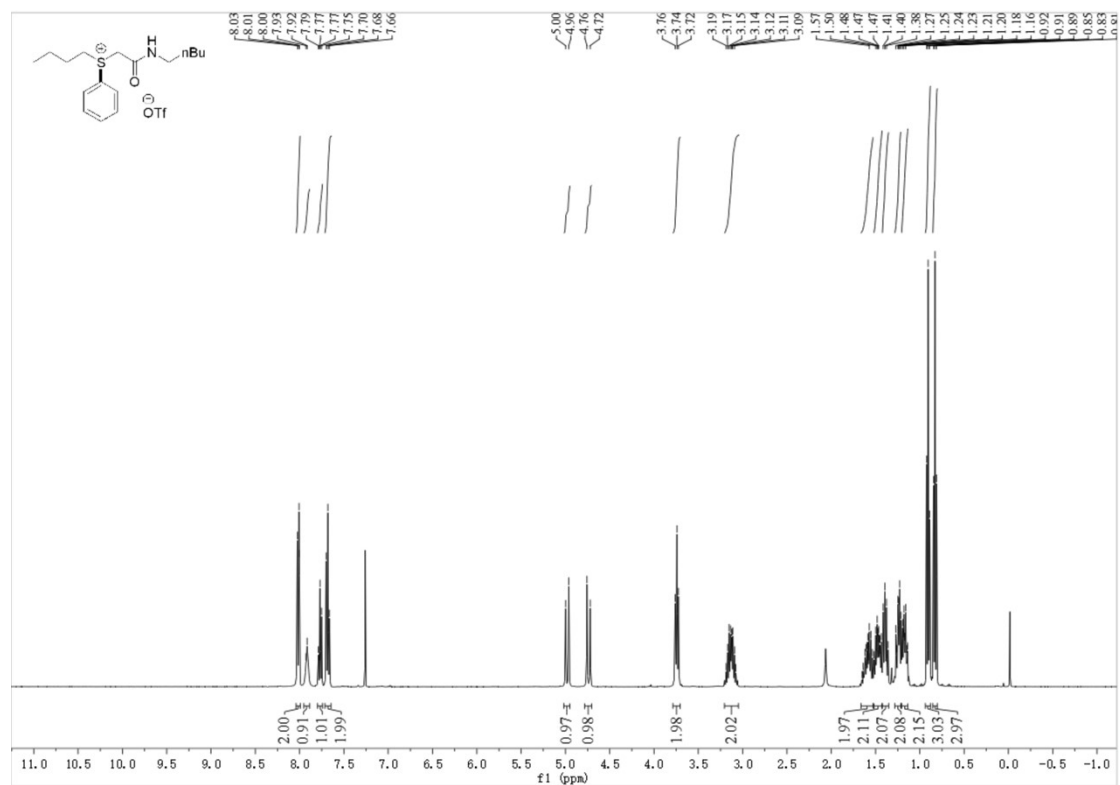
^1H NMR spectrum of **3s** (CDCl_3 , 400 MHz)



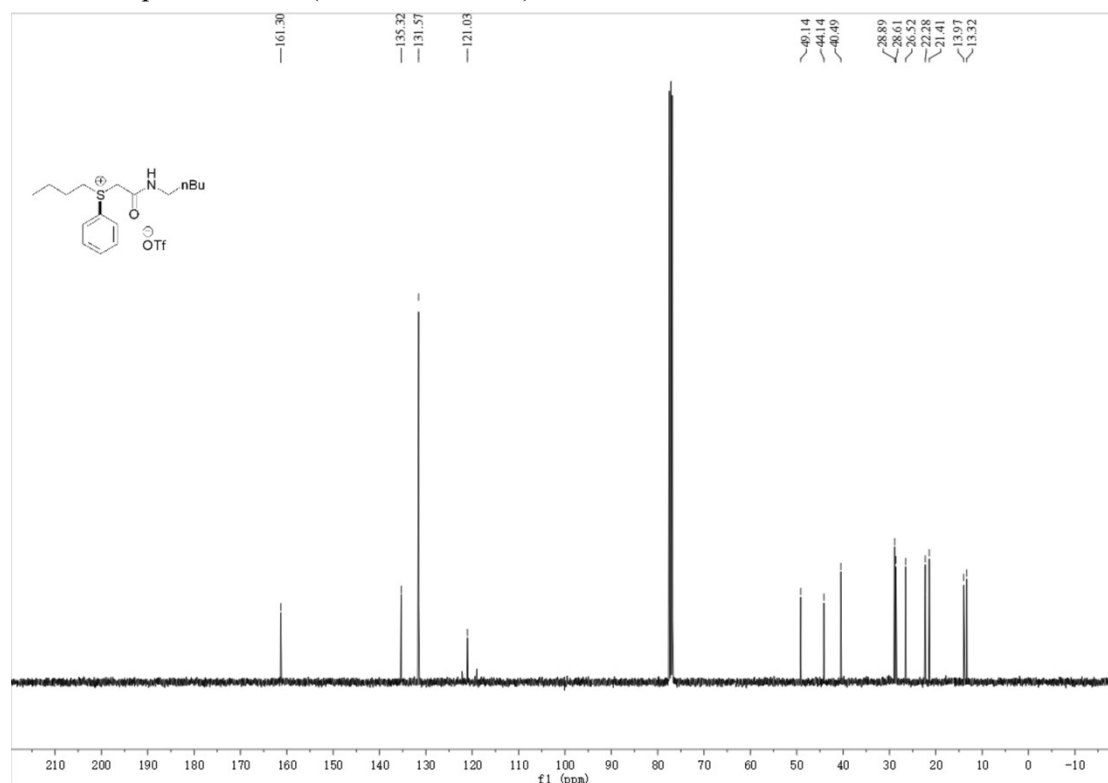
^{13}C NMR spectrum of **3s** (CDCl_3 , 101 MHz)



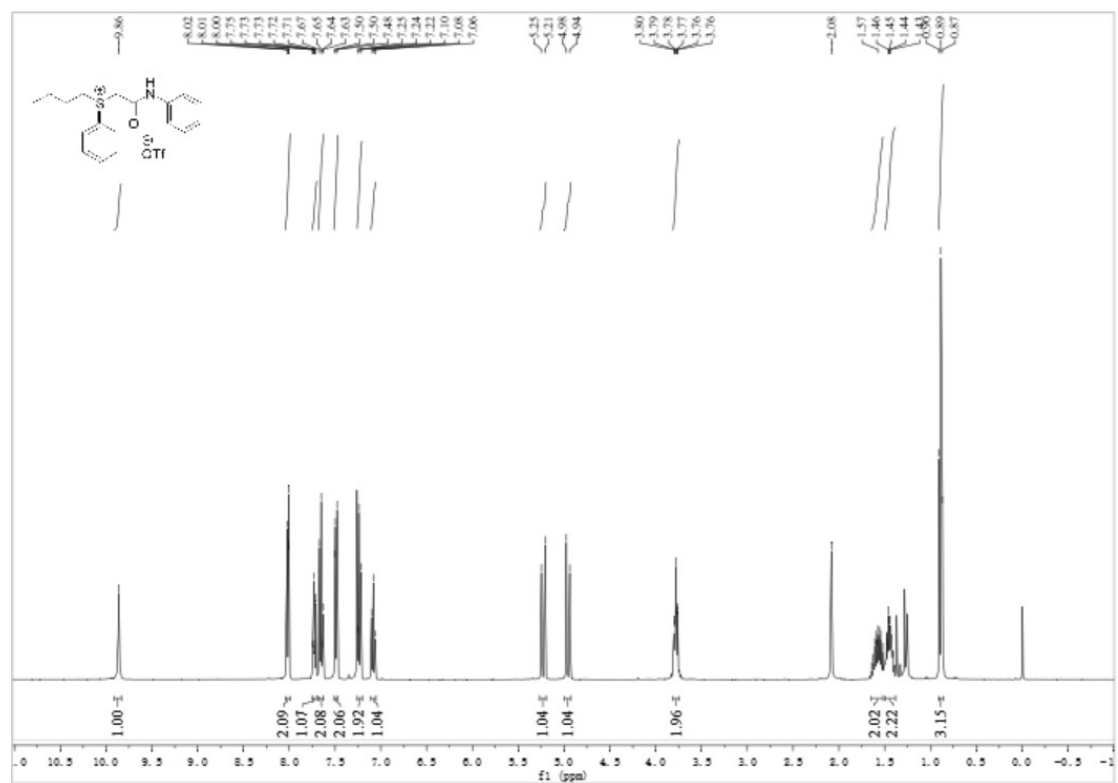
¹H NMR spectrum of **3t** (CDCl₃, 400 MHz)



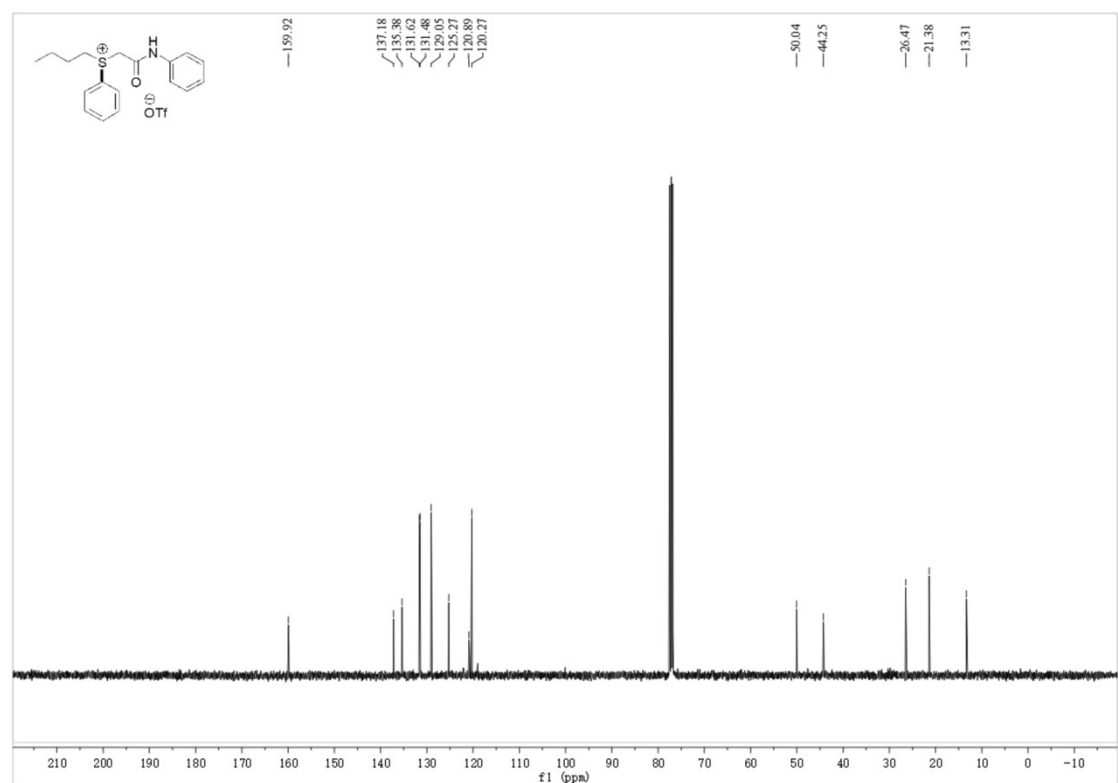
¹³C NMR spectrum of **3t** (CDCl₃, 101 MHz)



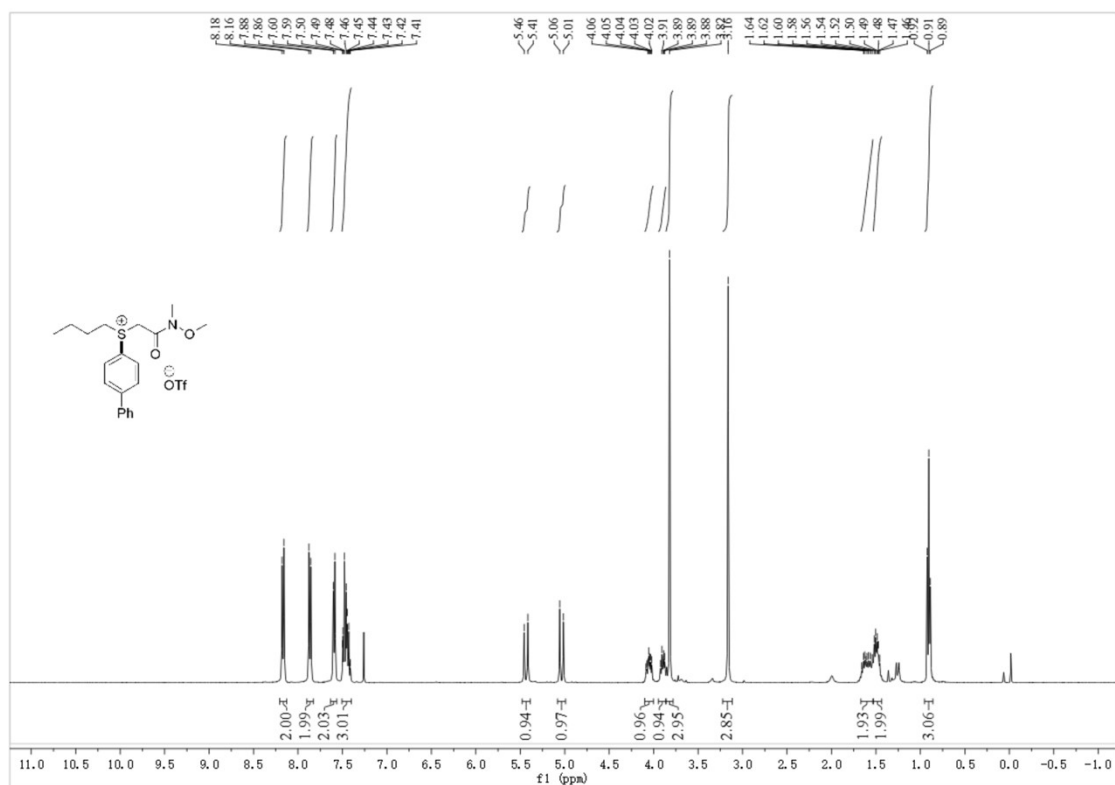
^1H NMR spectrum of **3u** (CDCl_3 , 400 MHz)



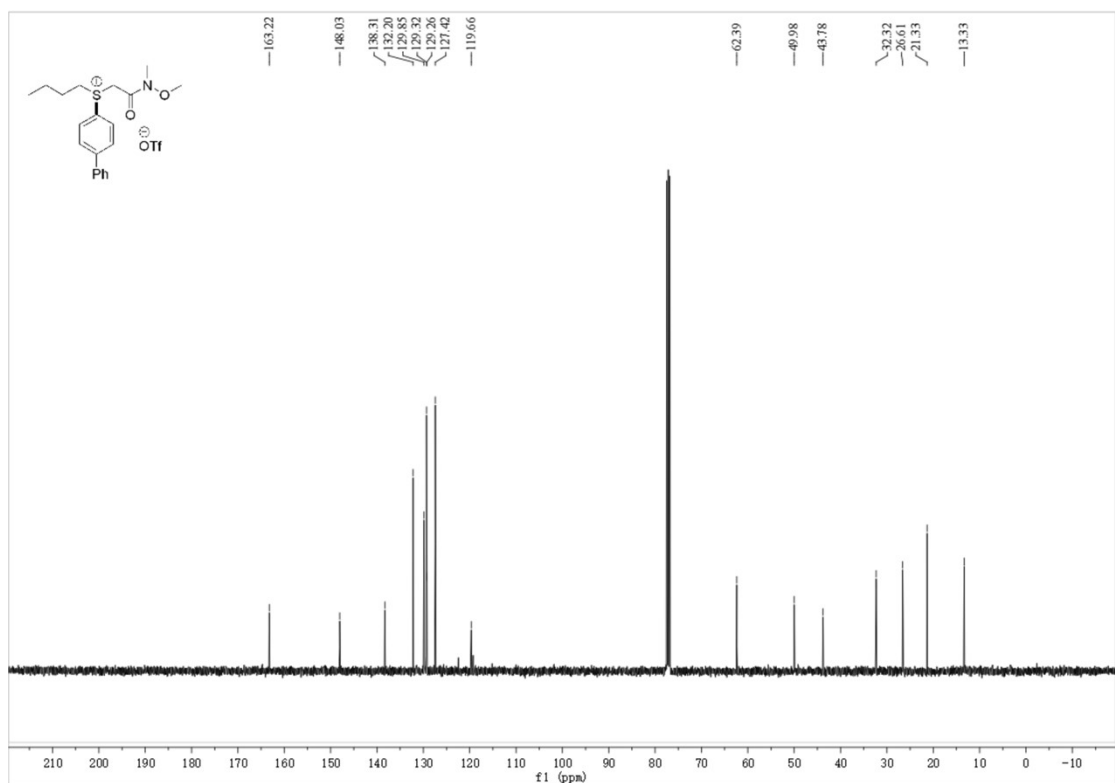
^{13}C NMR spectrum of **3u** (CDCl_3 , 101 MHz)



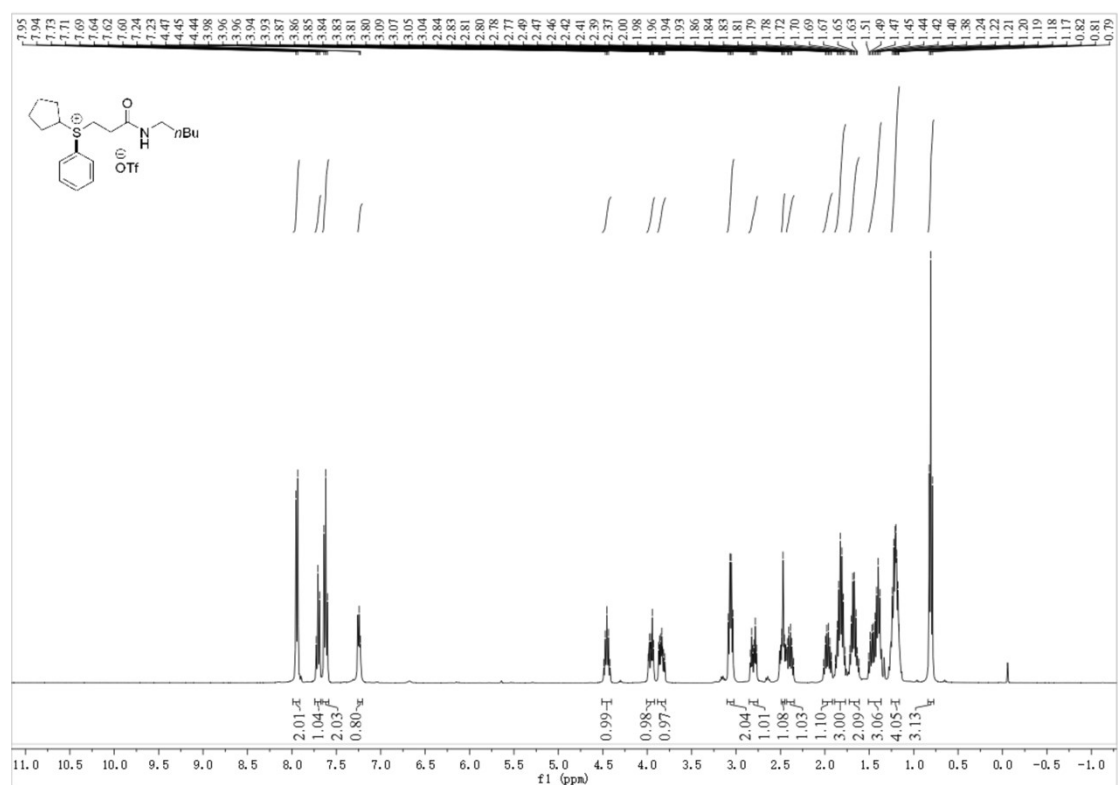
^1H NMR spectrum of **3v** (CDCl_3 , 400 MHz)



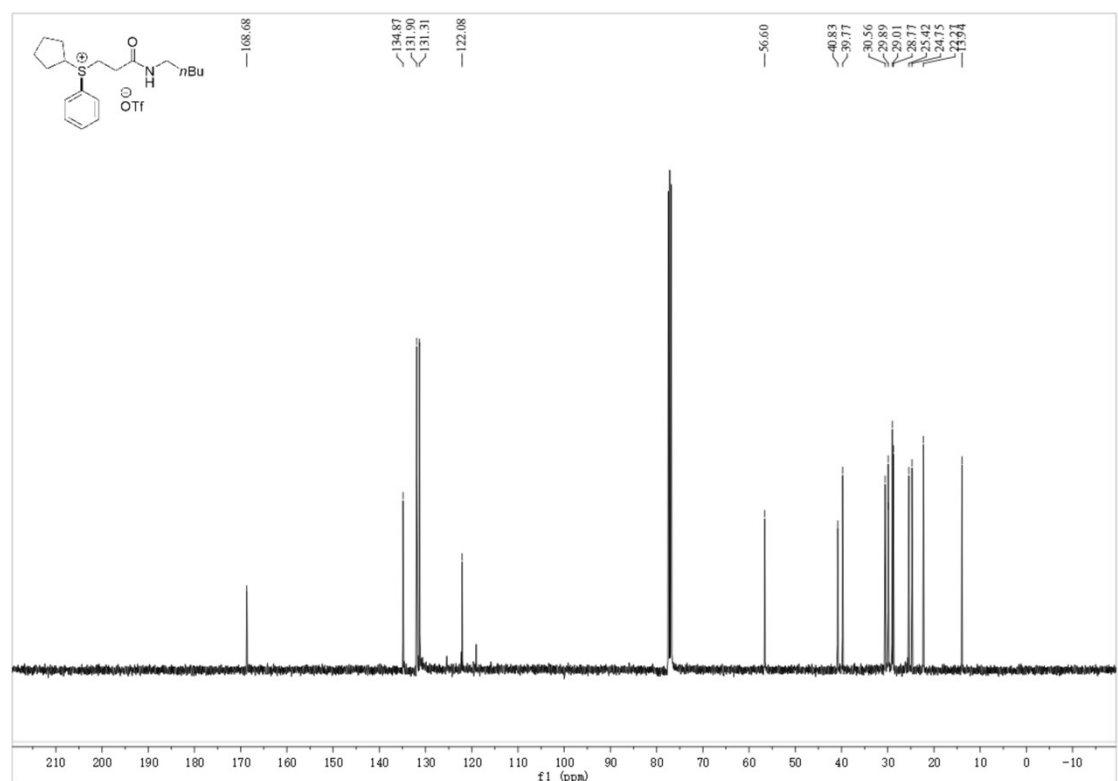
^{13}C NMR spectrum of **3v** (CDCl_3 , 101 MHz)



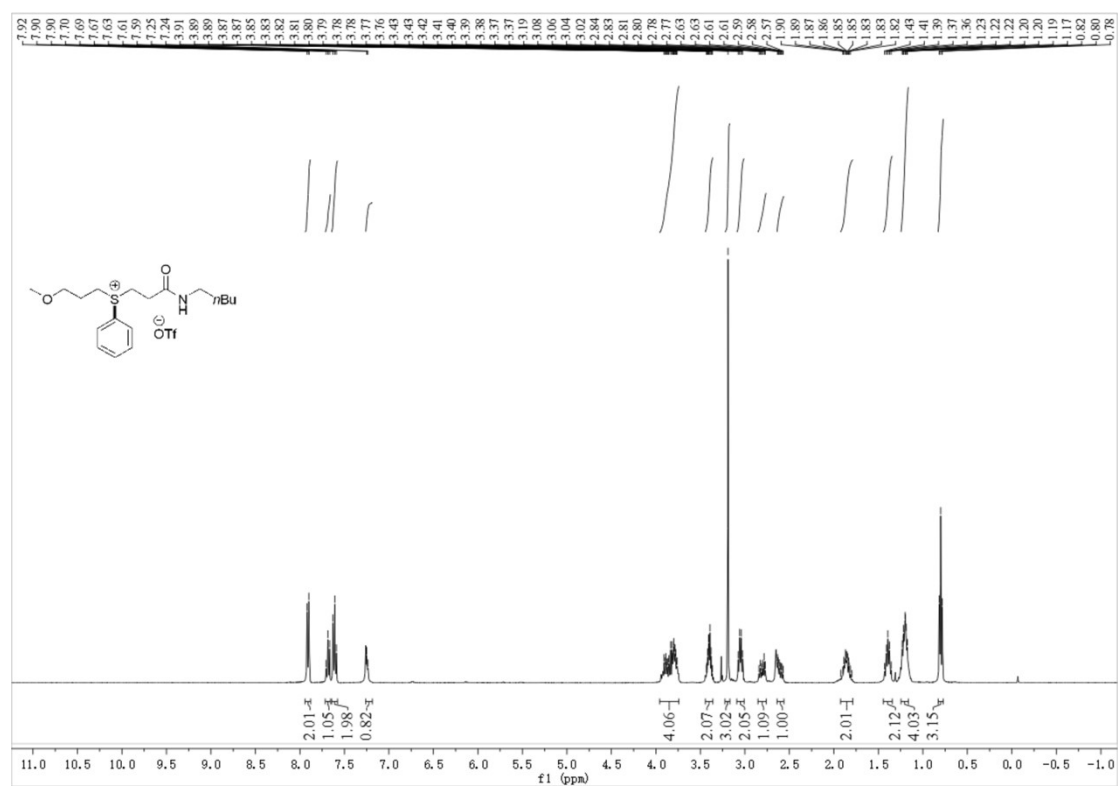
^1H NMR spectrum of **3w** (CDCl_3 , 400 MHz)



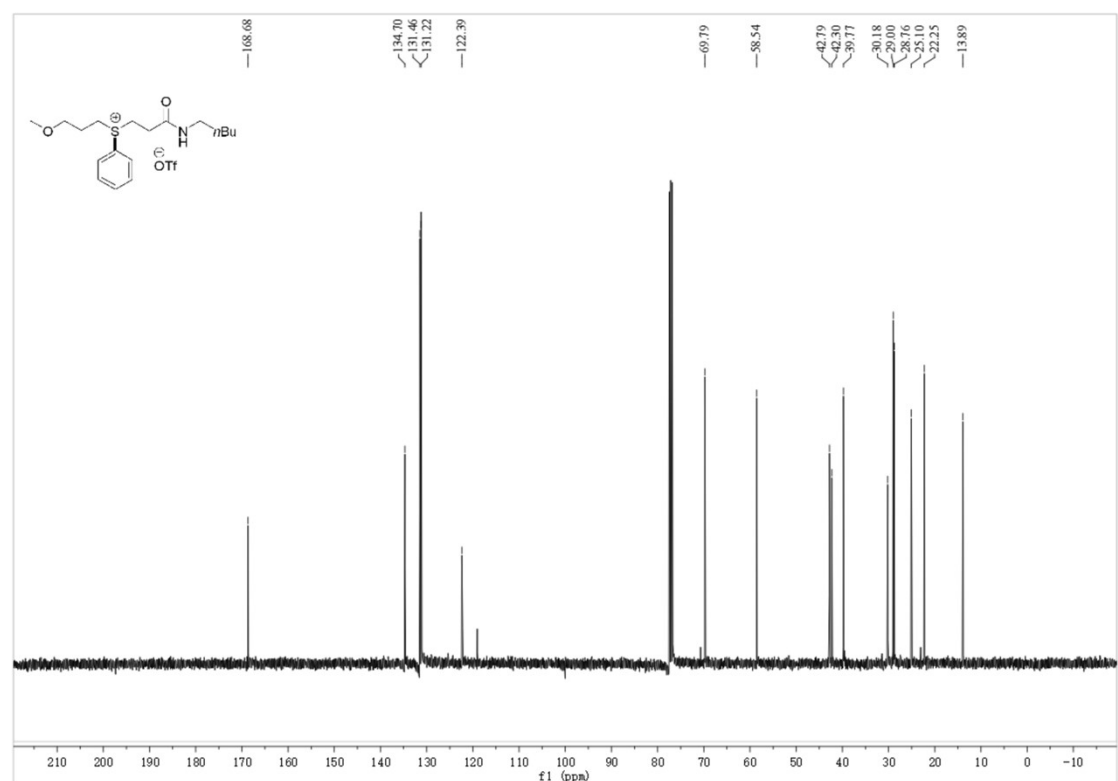
^{13}C NMR spectrum of **3w** (CDCl_3 , 101 MHz)



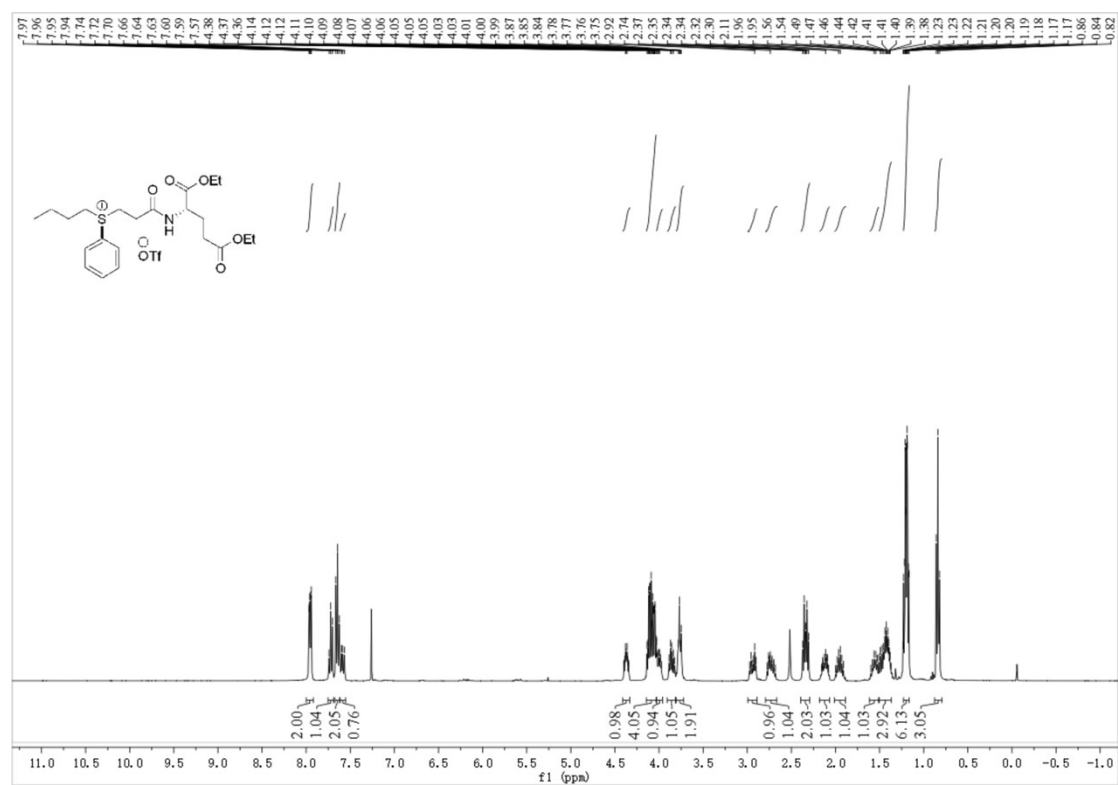
^1H NMR spectrum of **3x** (CDCl_3 , 400 MHz)



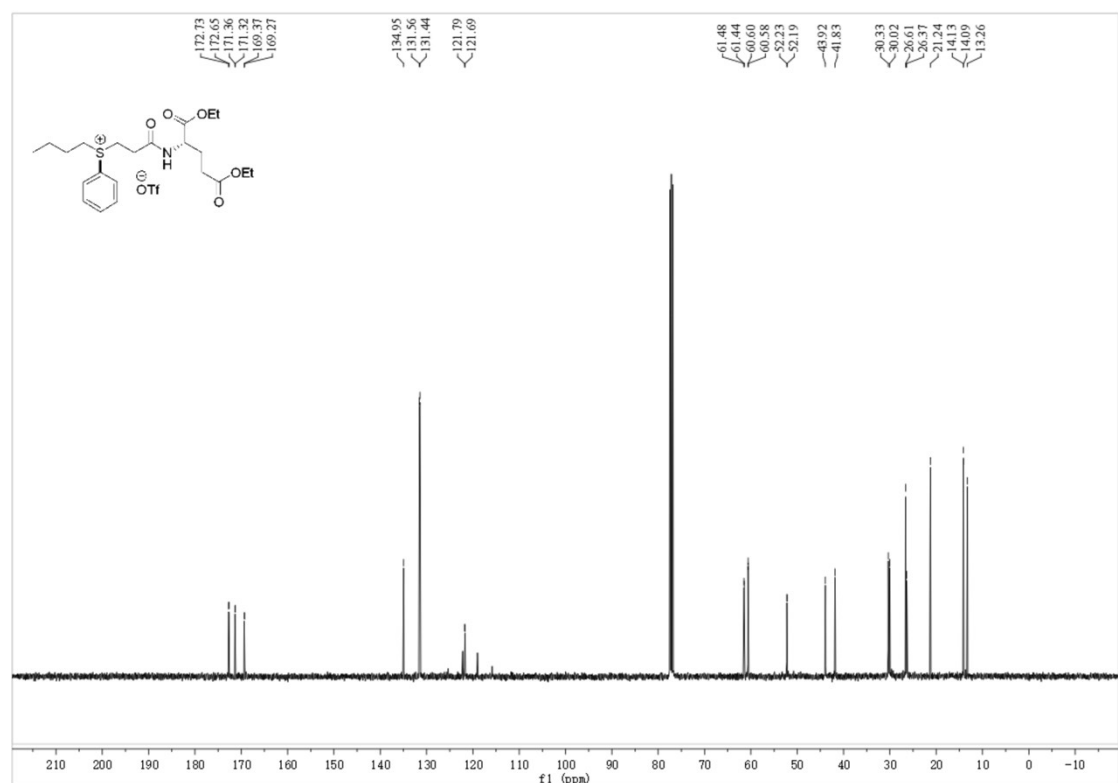
^{13}C NMR spectrum of **3x** (CDCl_3 , 101 MHz)



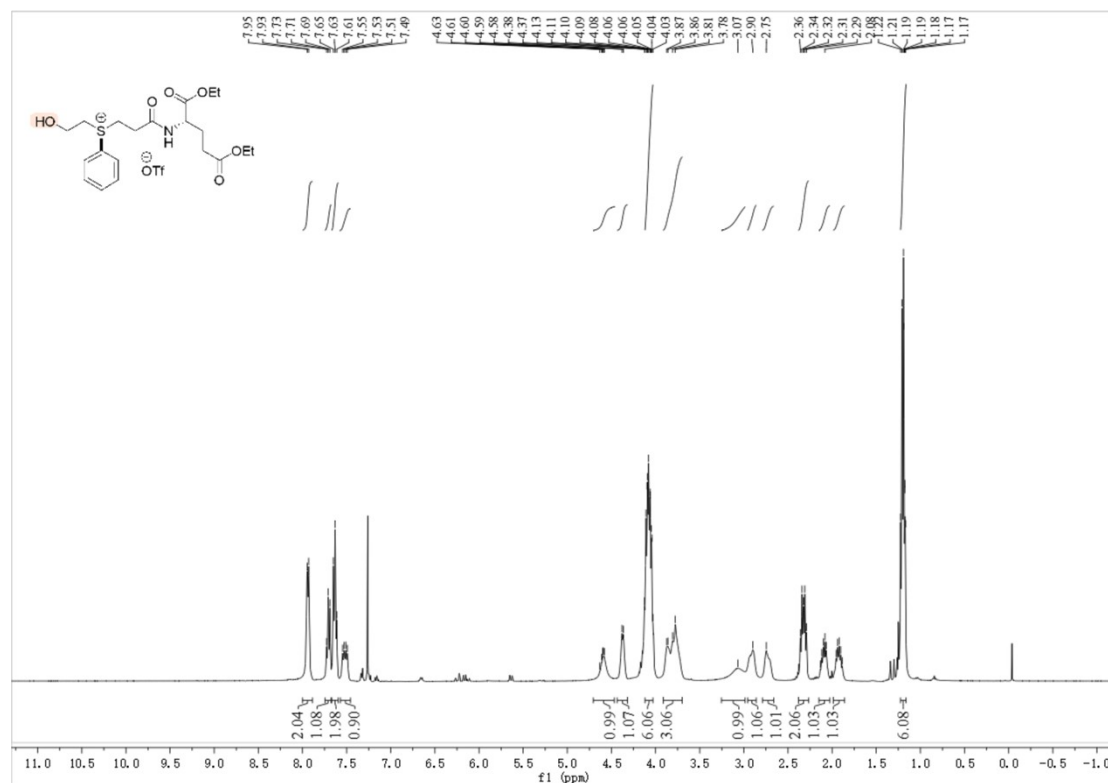
^1H NMR spectrum of **3z** (CDCl_3 , 400 MHz)



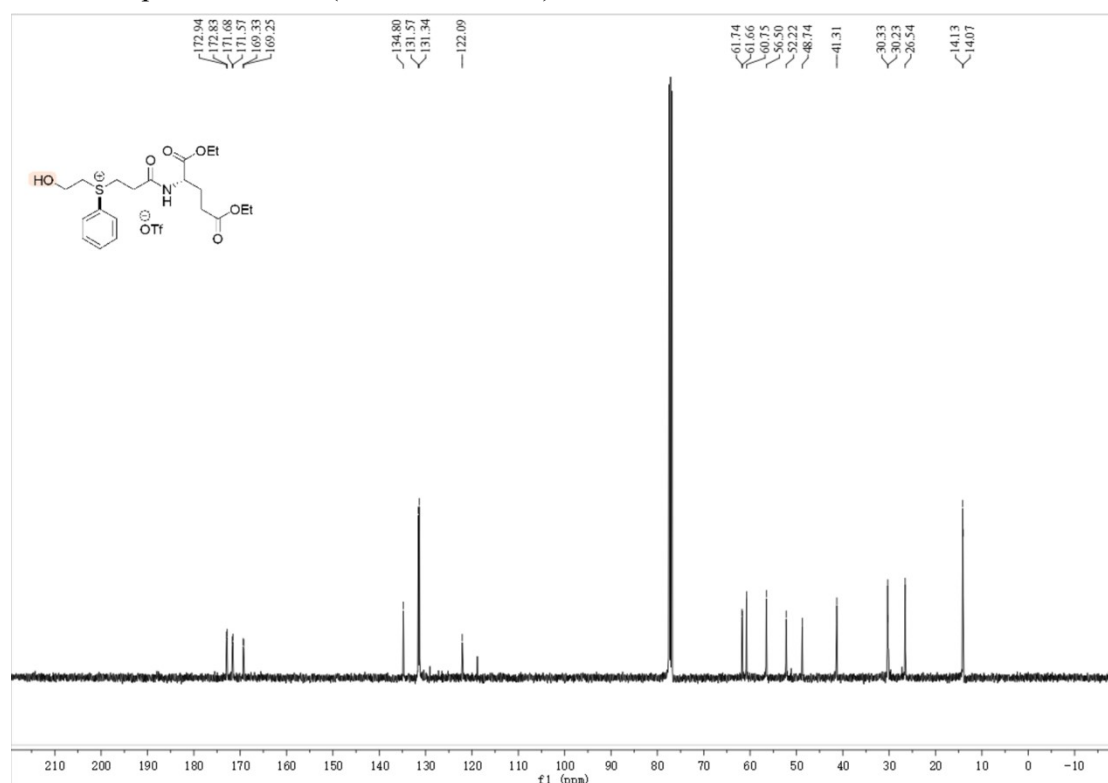
^{13}C NMR spectrum of **3z** (CDCl_3 , 101 MHz)



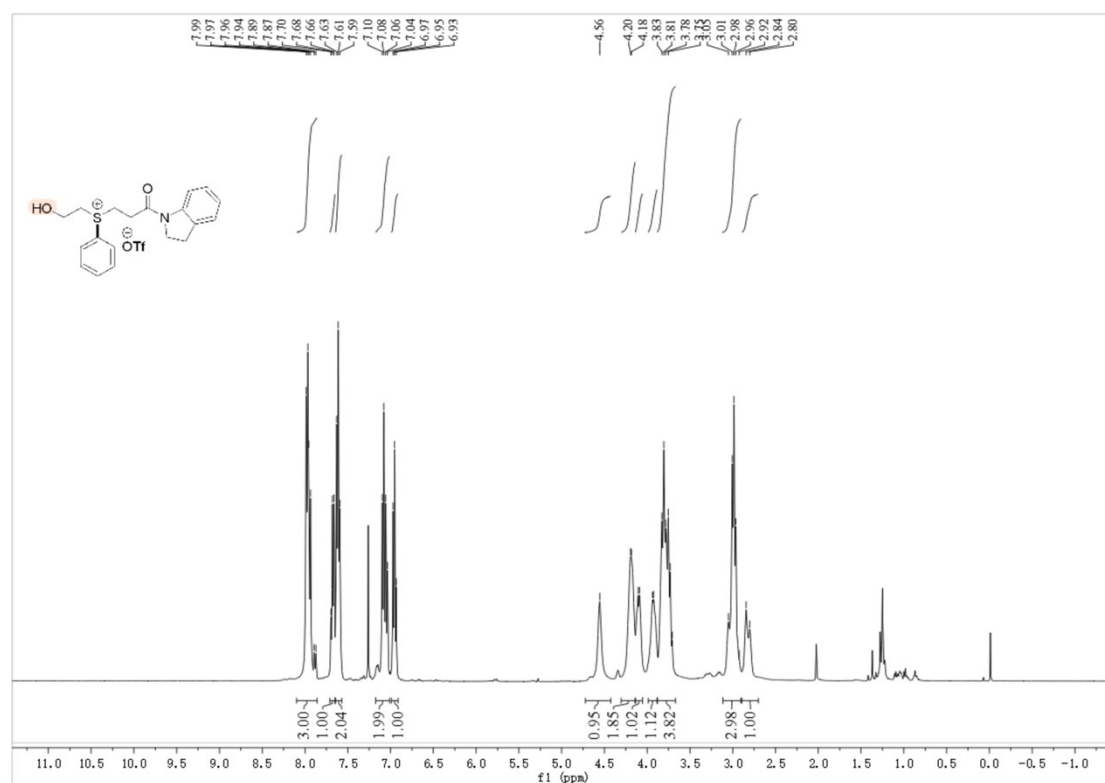
^1H NMR spectrum of **3aa** (CDCl_3 , 400 MHz)



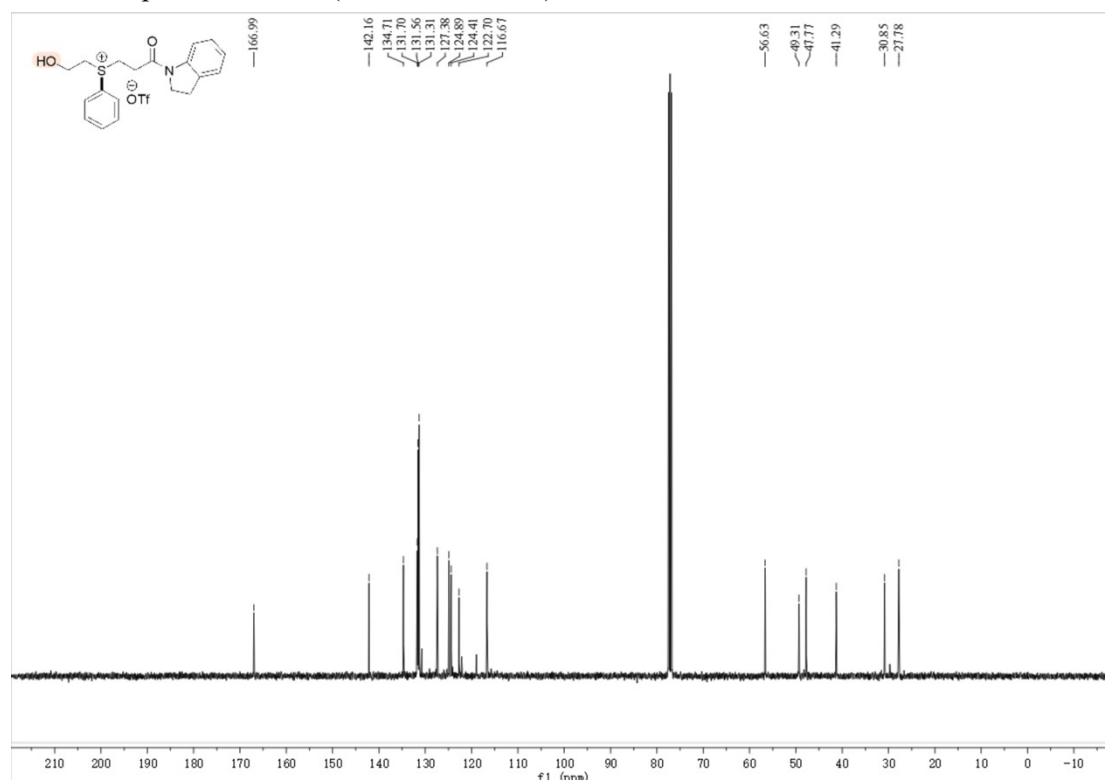
^{13}C NMR spectrum of **3aa** (CDCl_3 , 101 MHz)



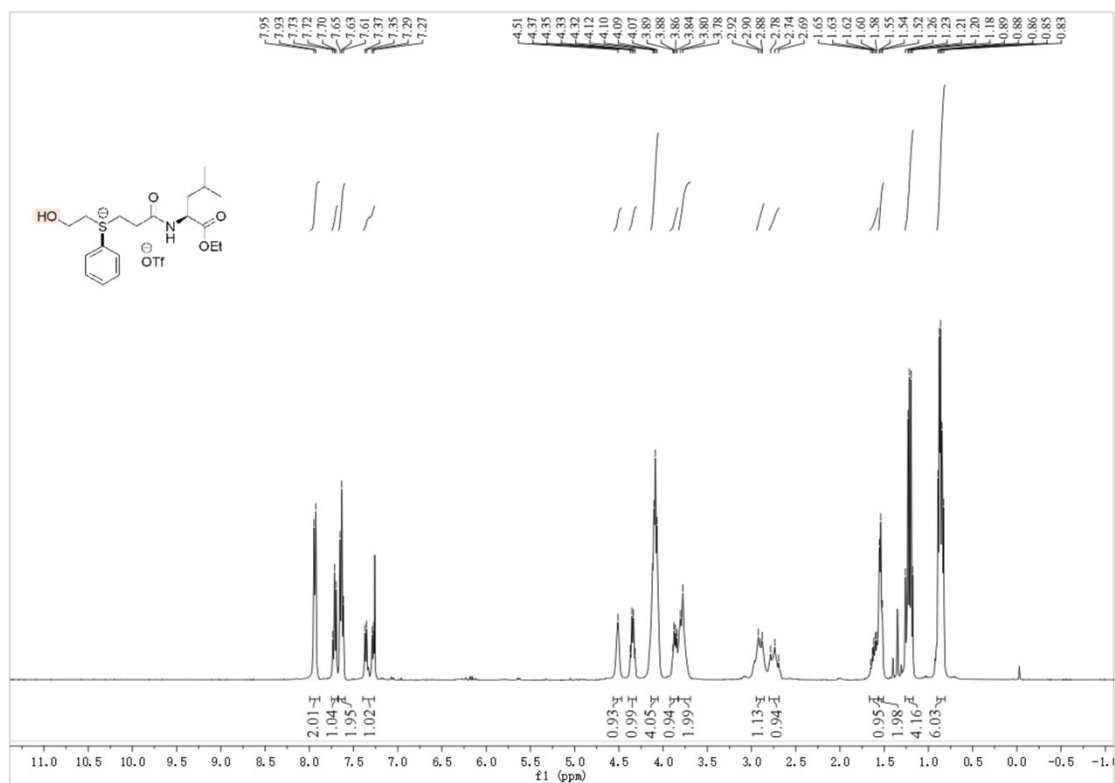
¹H NMR spectrum of **3ab** (CDCl₃, 400 MHz)



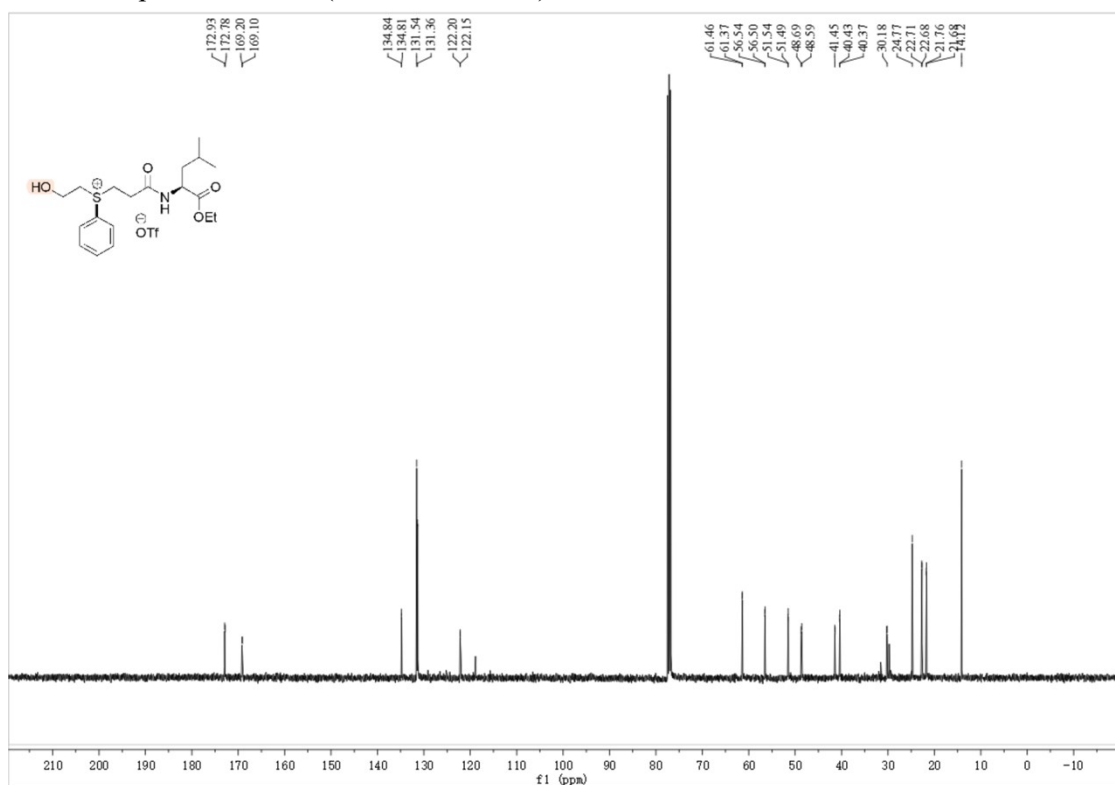
¹³C NMR spectrum of **3ab** (CDCl₃, 101 MHz)



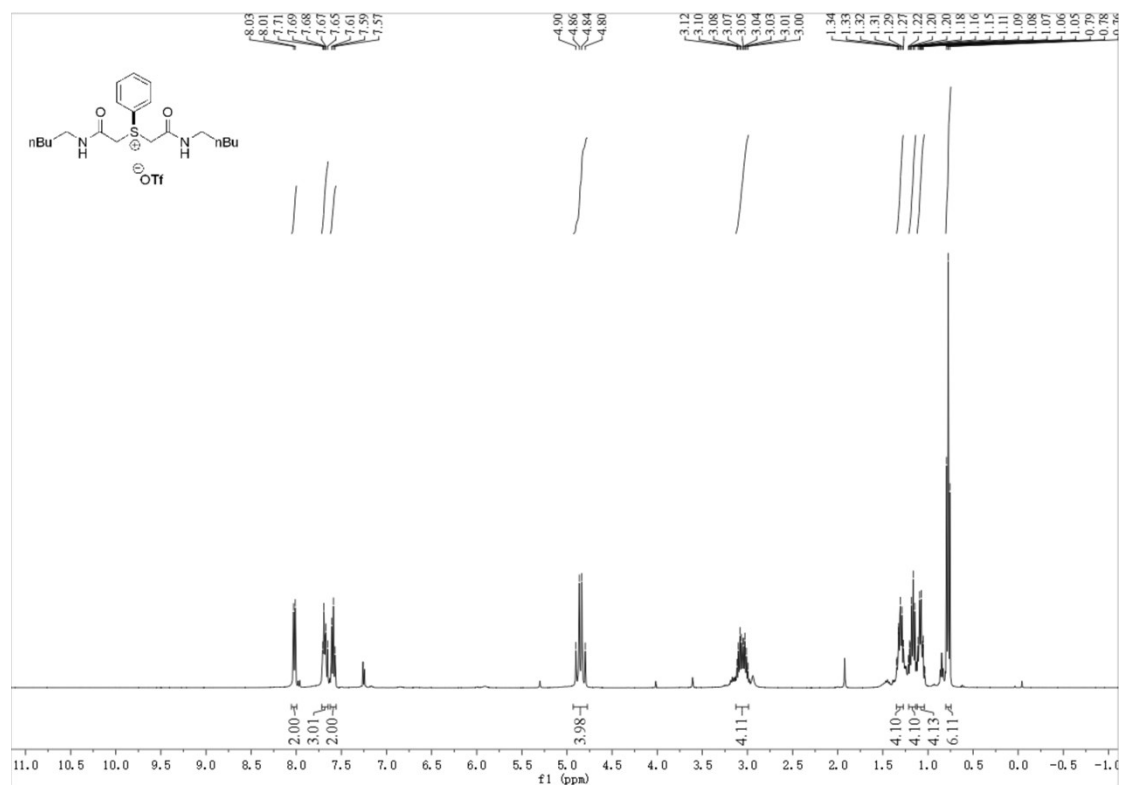
¹H NMR spectrum of **3ac** (CDCl₃, 400 MHz)



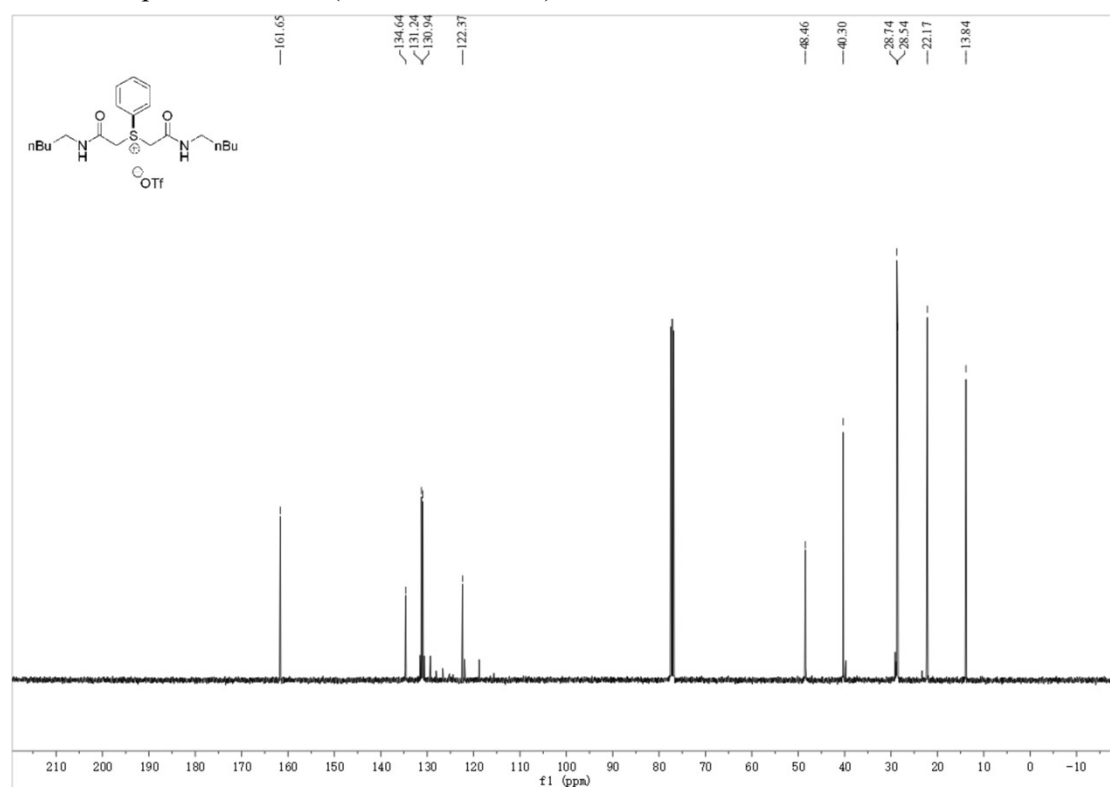
¹³C NMR spectrum of **3ac** (CDCl₃, 101 MHz)



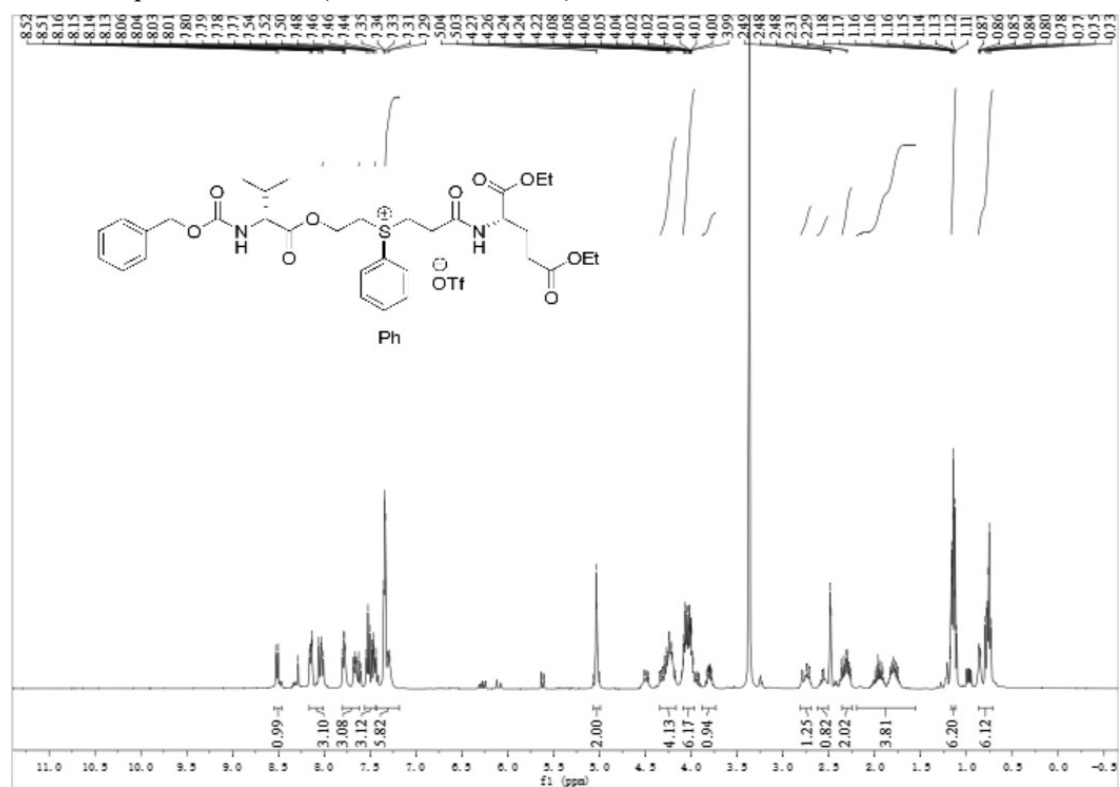
^1H NMR spectrum of **3ad** (CDCl_3 , 400 MHz)



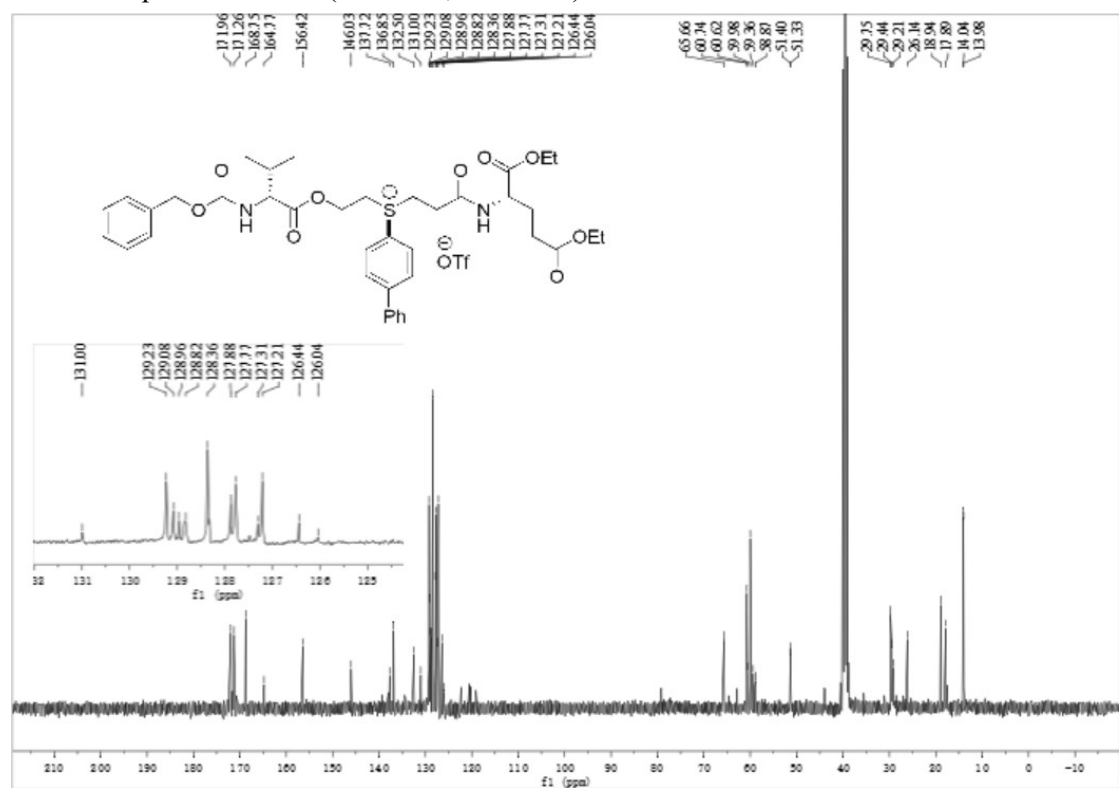
^{13}C NMR spectrum of **3ad** (CDCl_3 , 101 MHz)



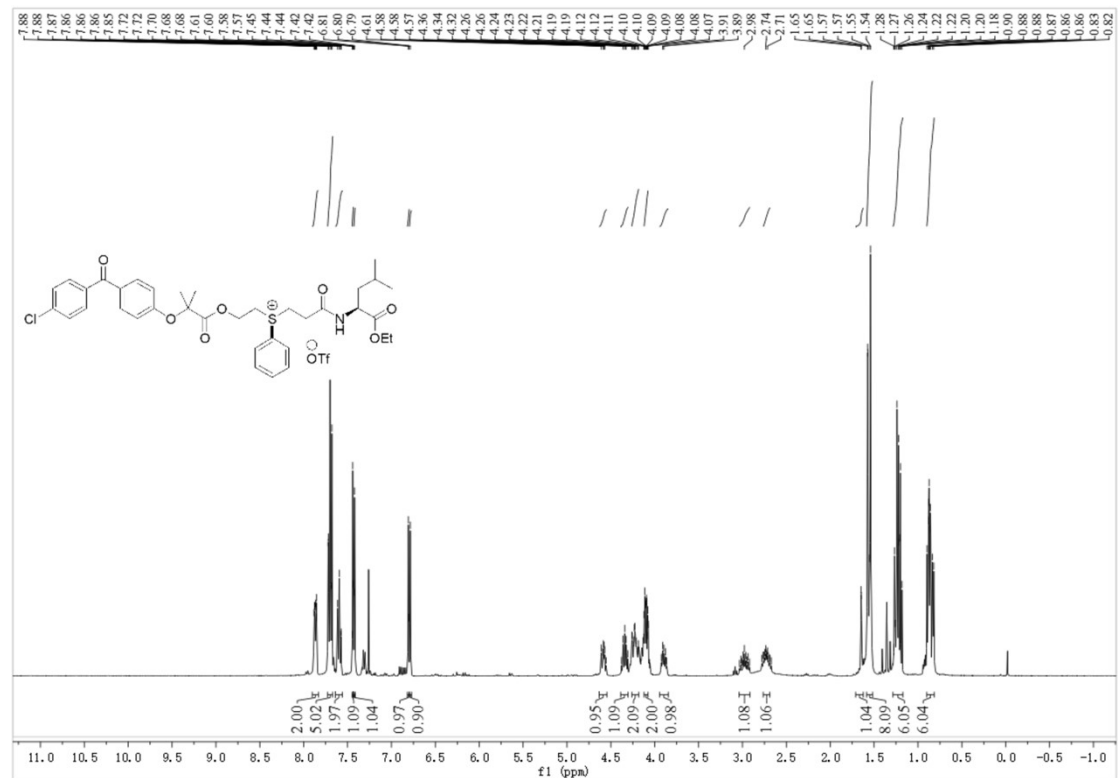
¹H NMR spectrum of **3ae** (*d*-DMSO, 400 MHz)



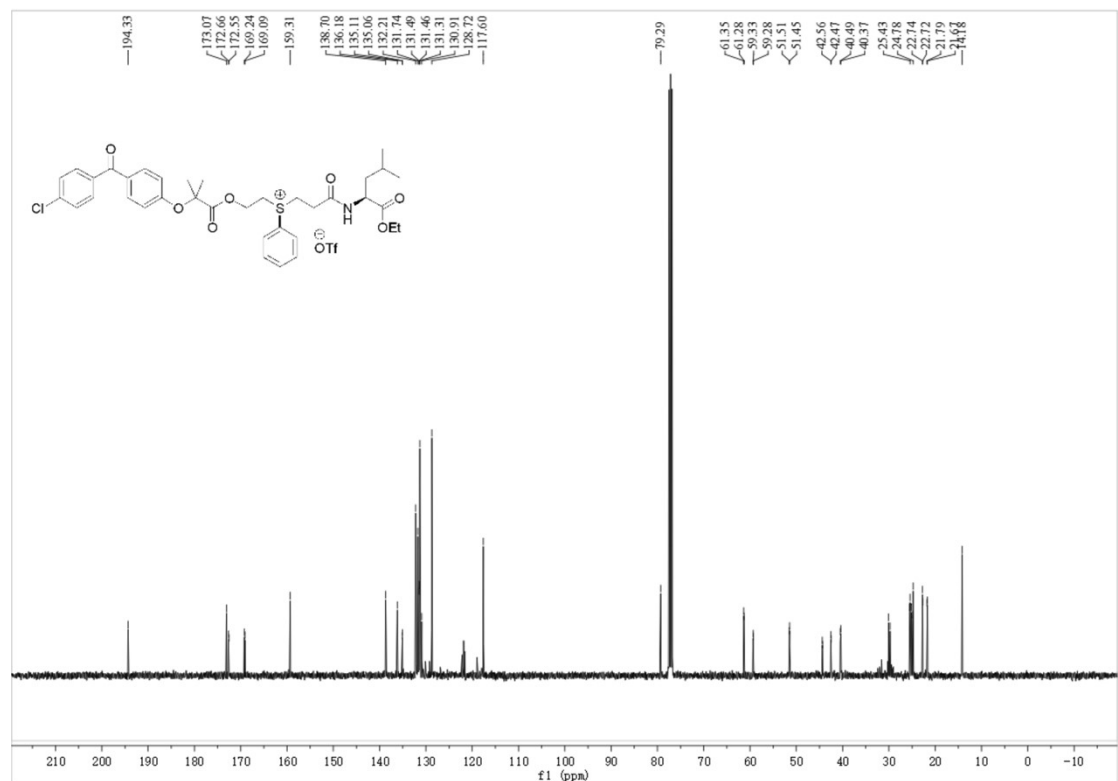
¹³C NMR spectrum of **3ae** (*d*-DMSO, 101 MHz)



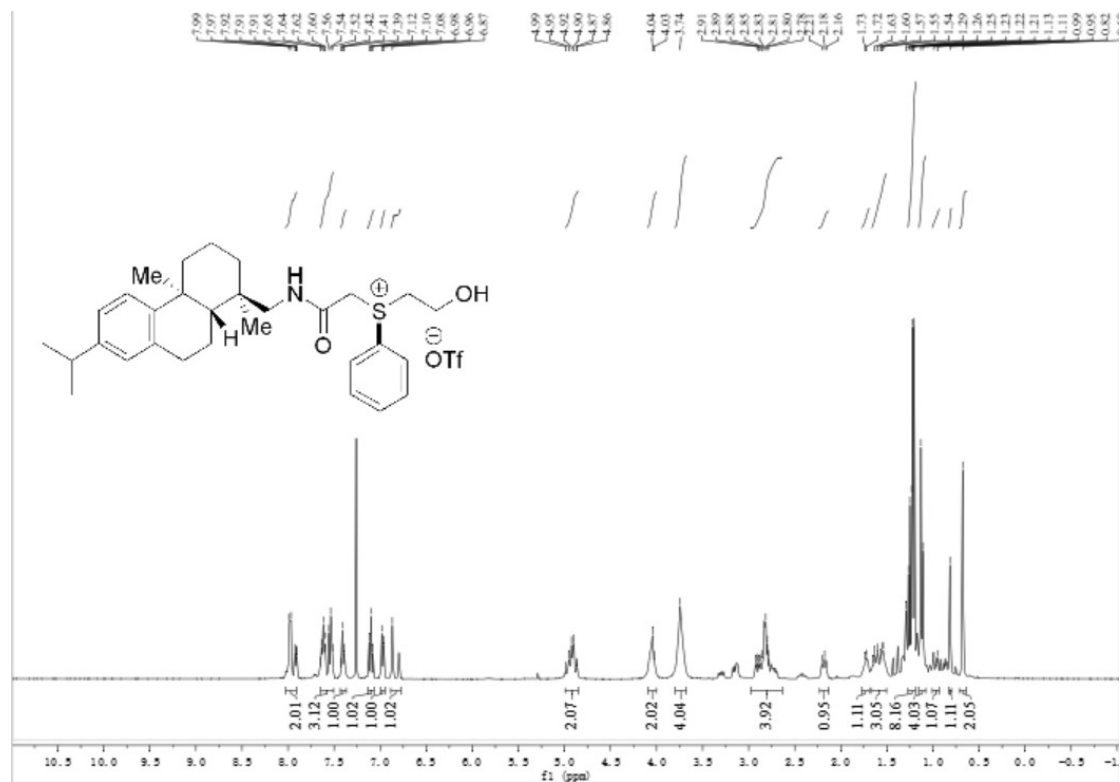
^1H NMR spectrum of **3af** (CDCl_3 , 400 MHz)



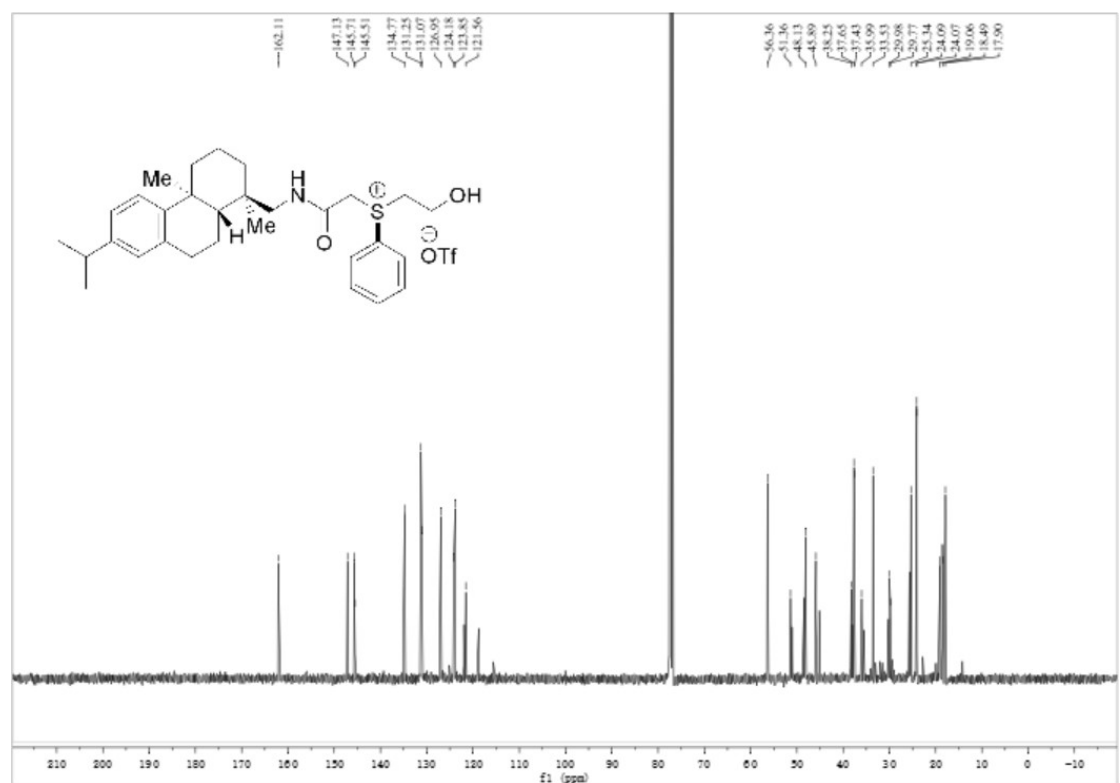
^{13}C NMR spectrum of **3af** (CDCl_3 , 101 MHz)



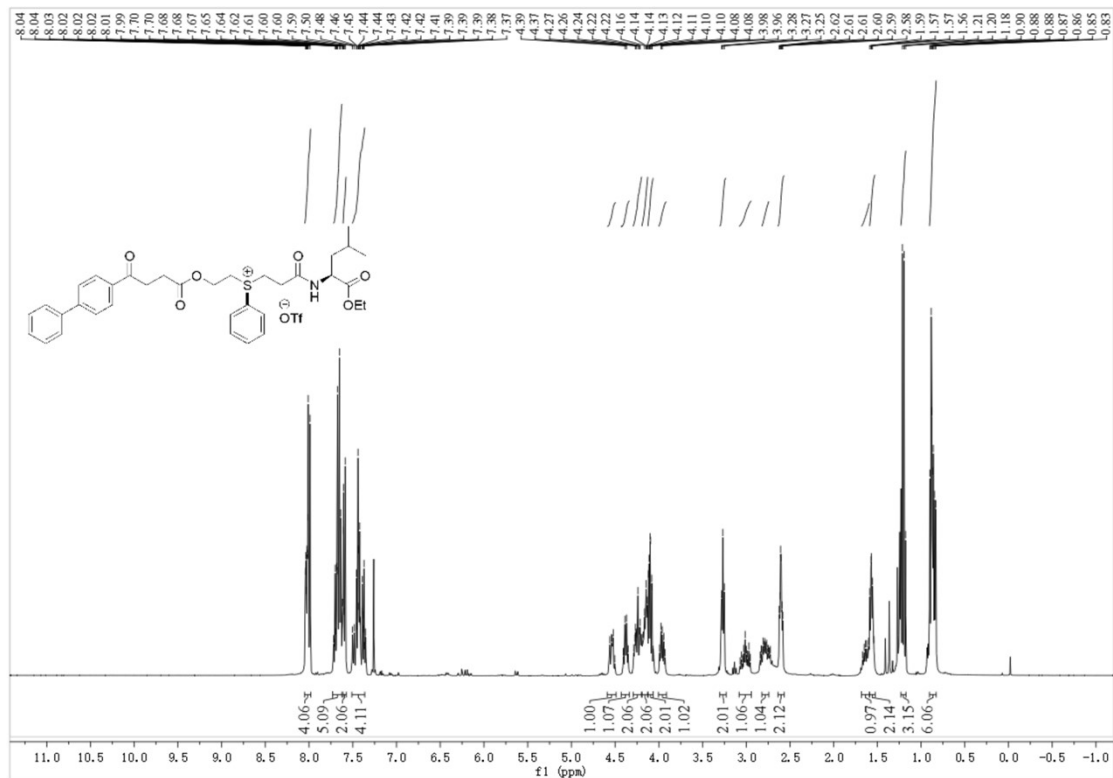
^1H NMR spectrum of **3ag** (CDCl_3 , 400 MHz)



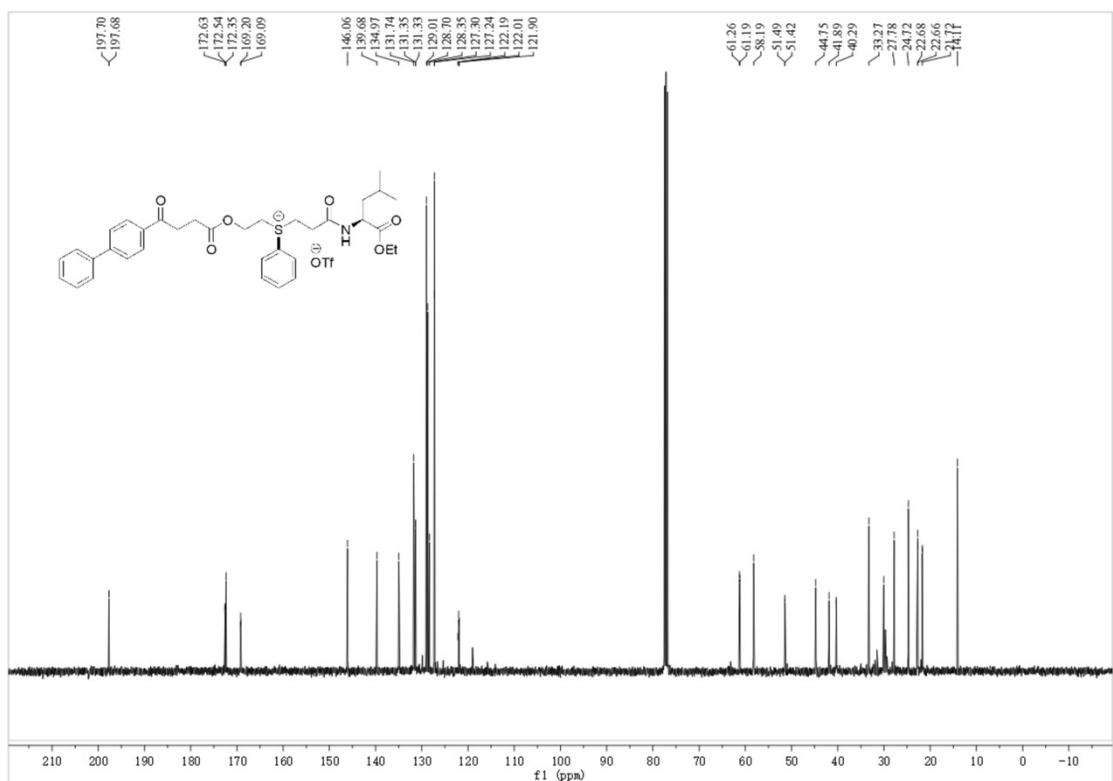
^{13}C NMR spectrum of **3ag** (CDCl_3 , 101 MHz)



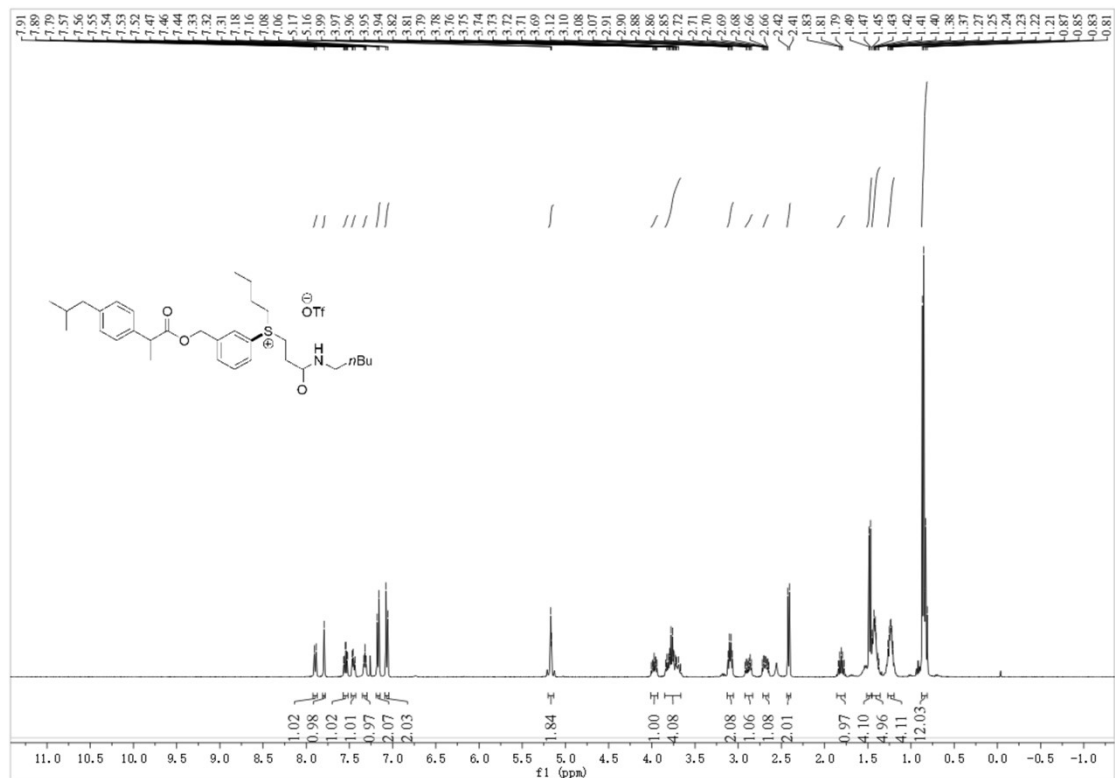
^1H NMR spectrum of **3ah** (CDCl_3 , 400 MHz)



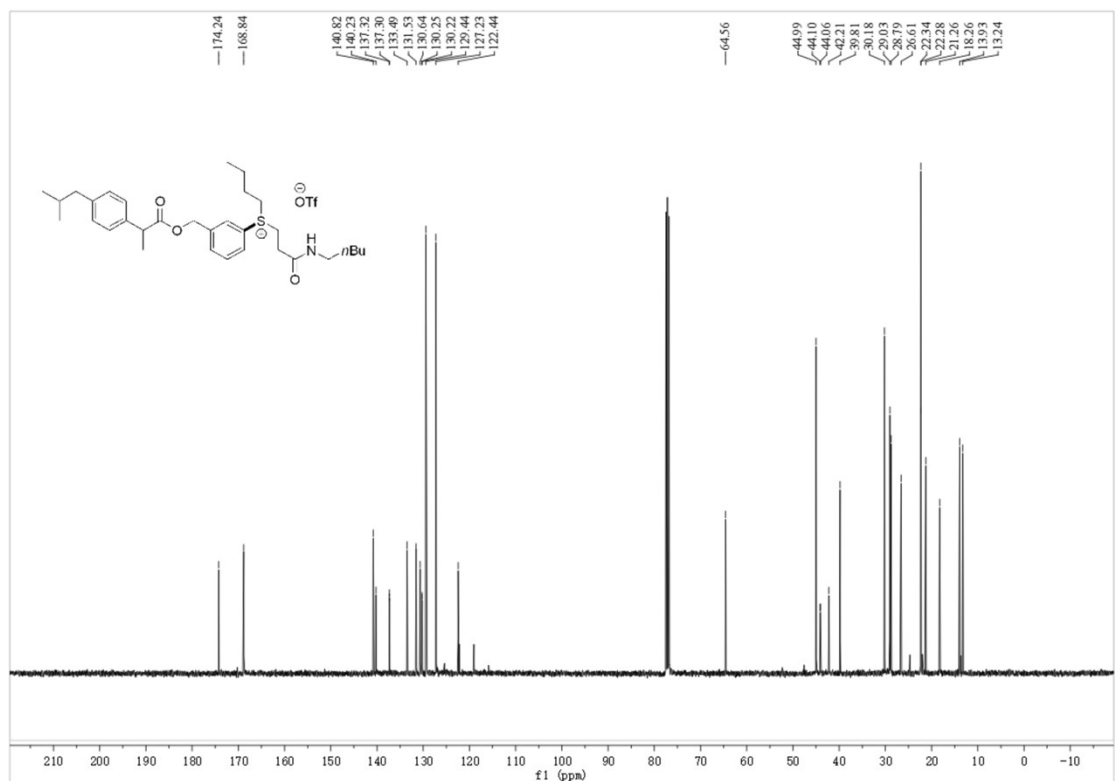
^{13}C NMR spectrum of **3ah** (CDCl_3 , 101 MHz)



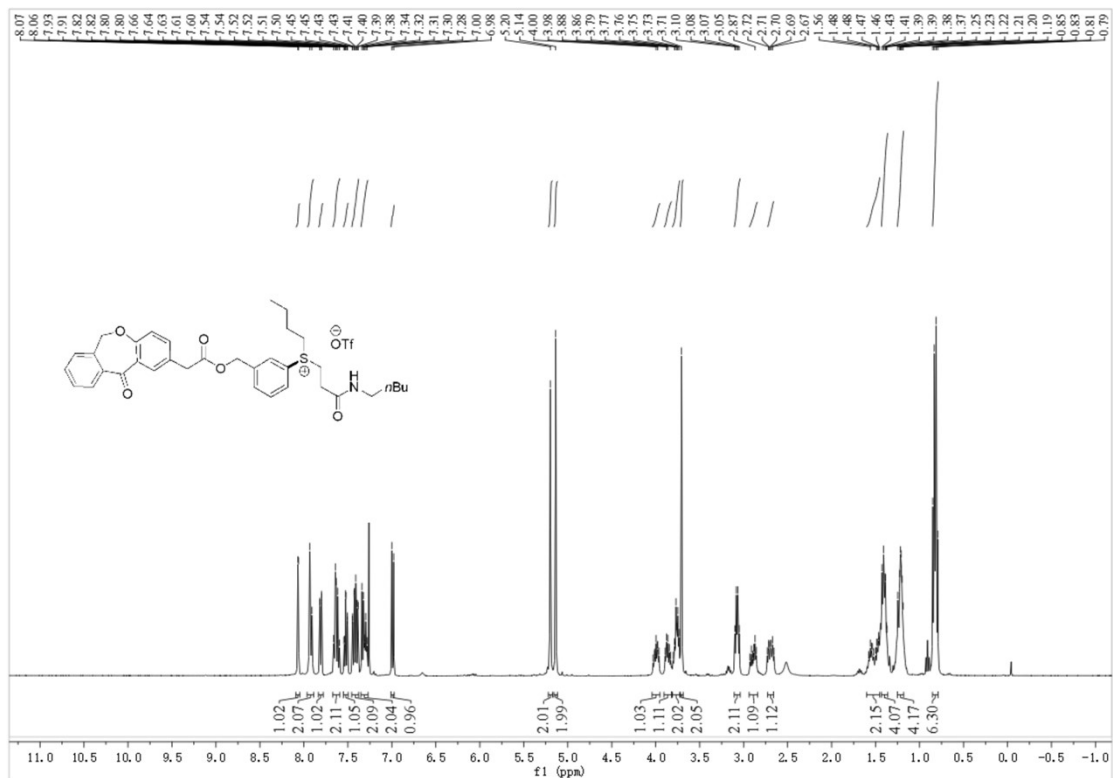
^1H NMR spectrum of **3ai** (CDCl_3 , 400 MHz)



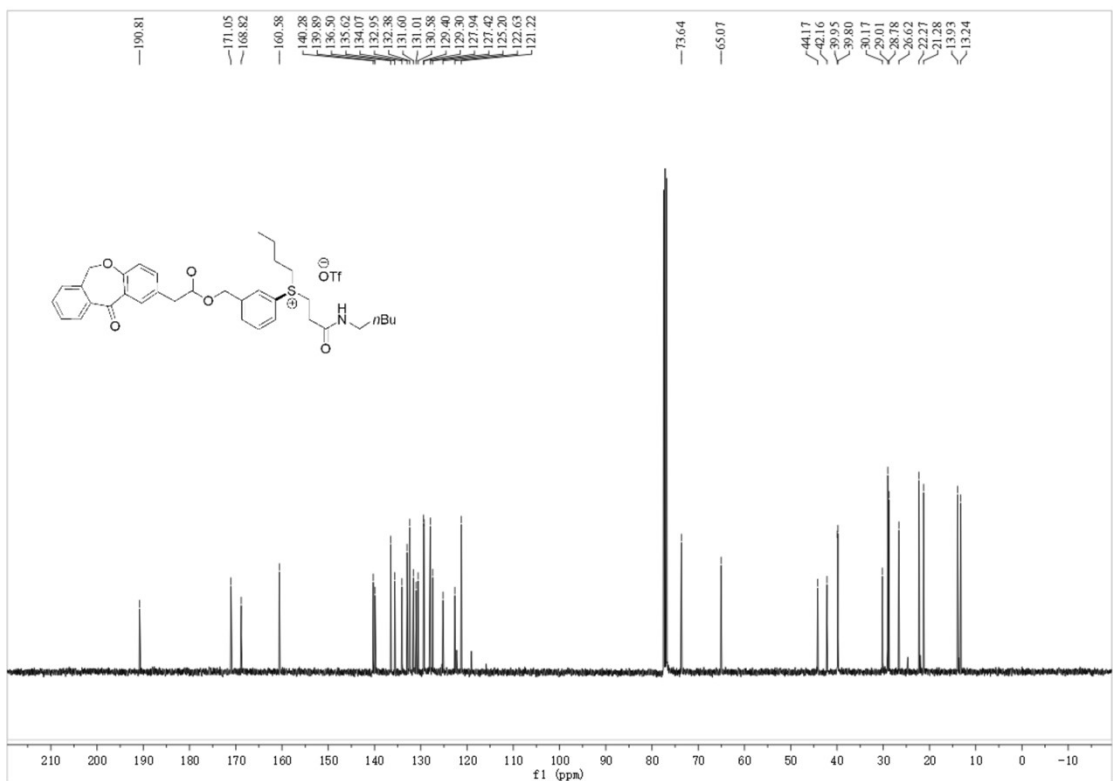
^{13}C NMR spectrum of **3ai** (CDCl_3 , 101 MHz)

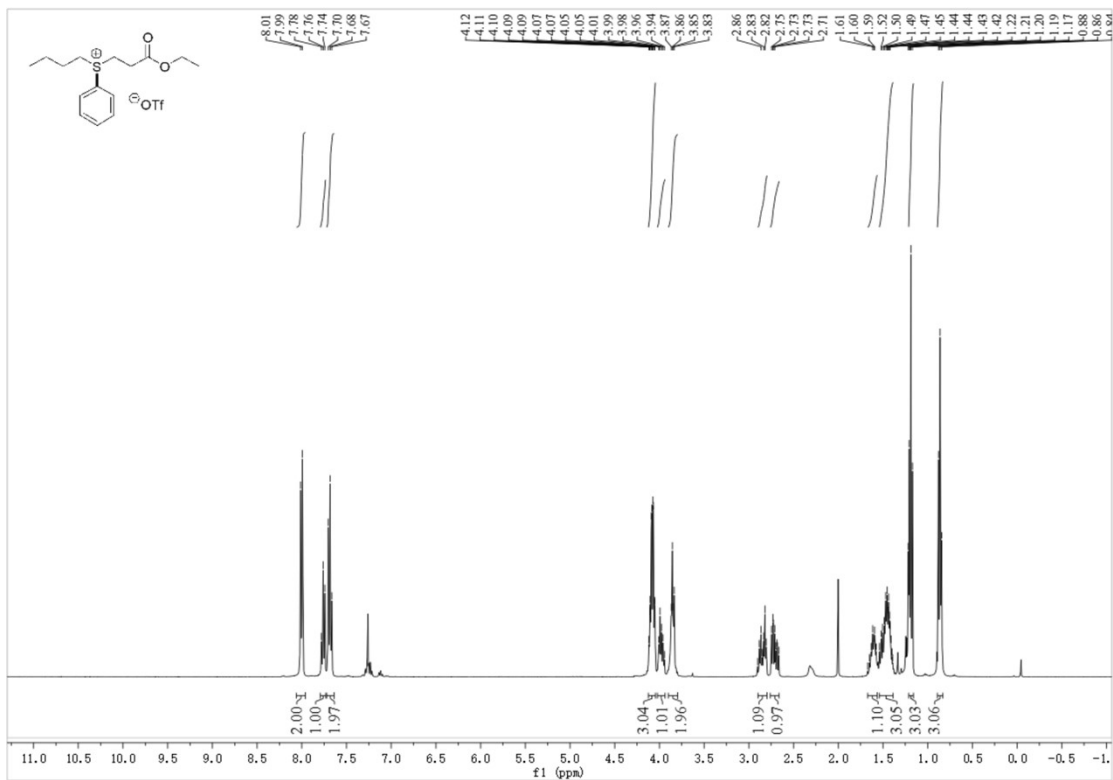


^1H NMR spectrum of **3aj** (CDCl_3 , 400 MHz)

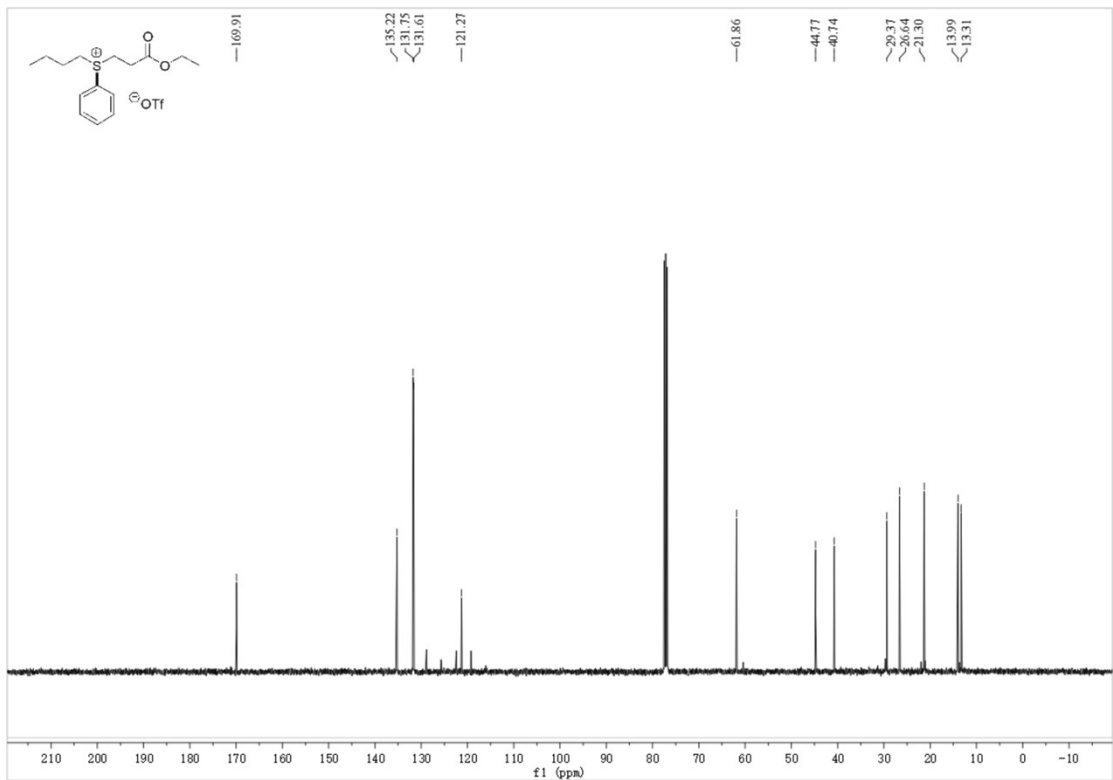


^{13}C NMR spectrum of **3aj** (CDCl_3 , 101 MHz)

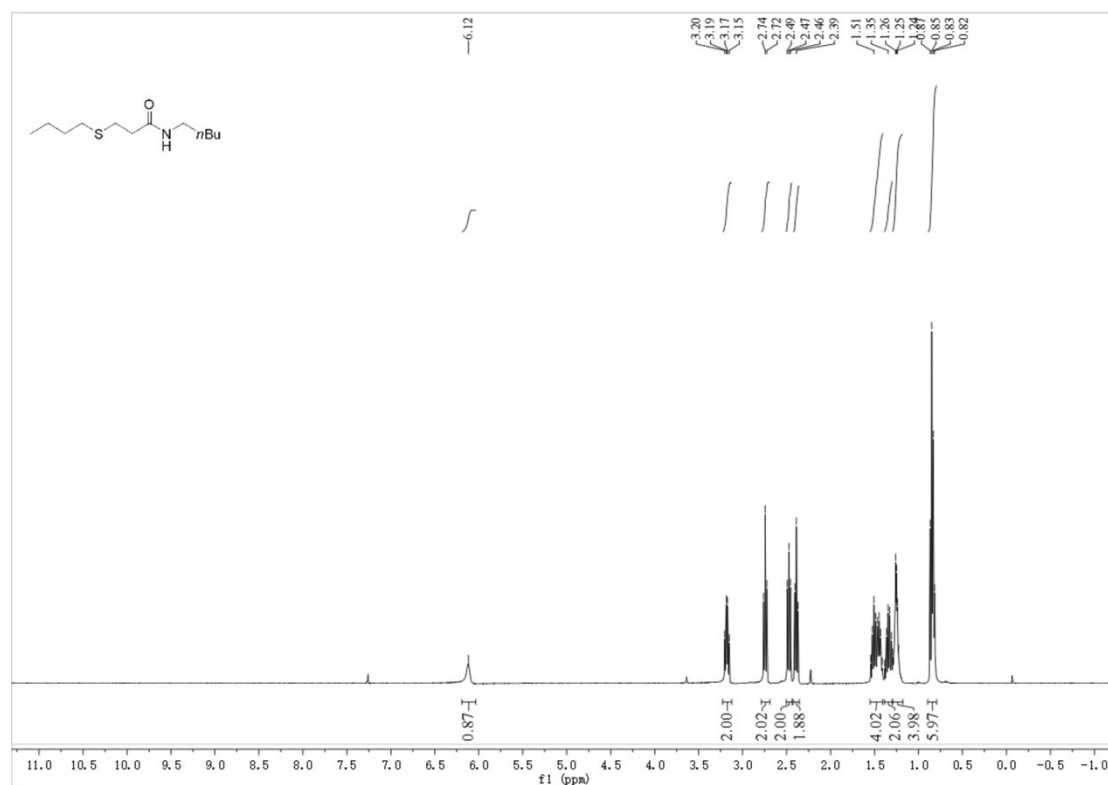




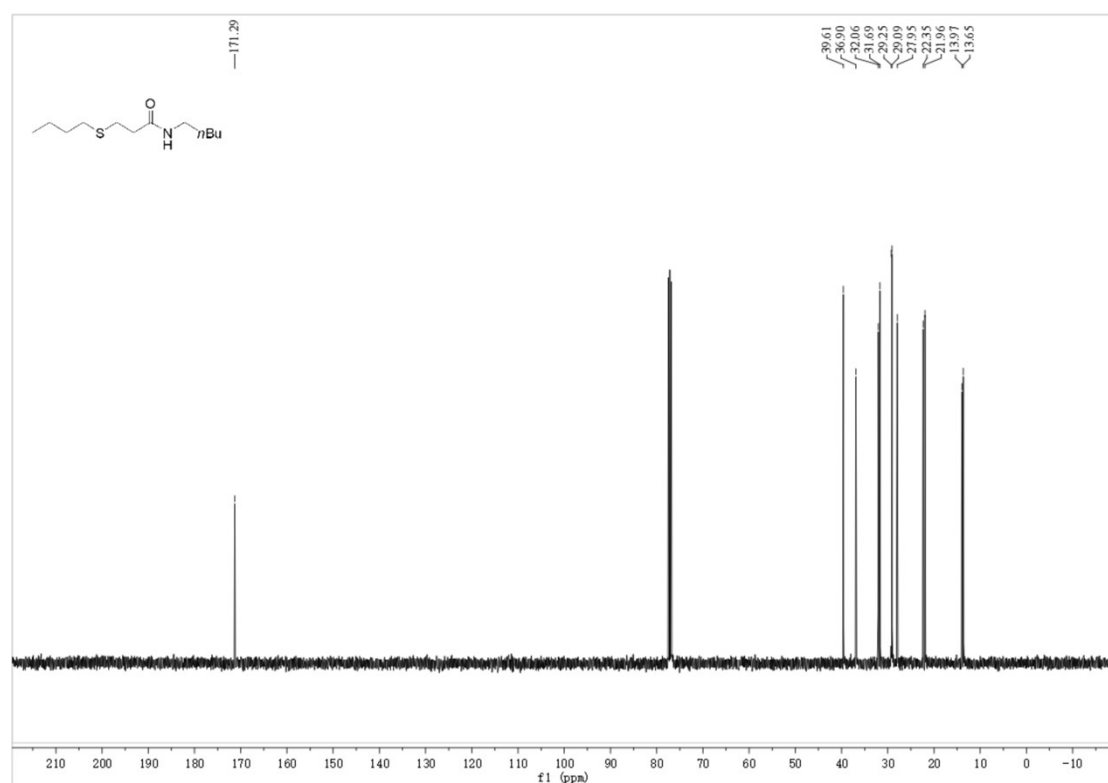
¹³C NMR spectrum of 1a''' (CDCl₃, 101 MHz)



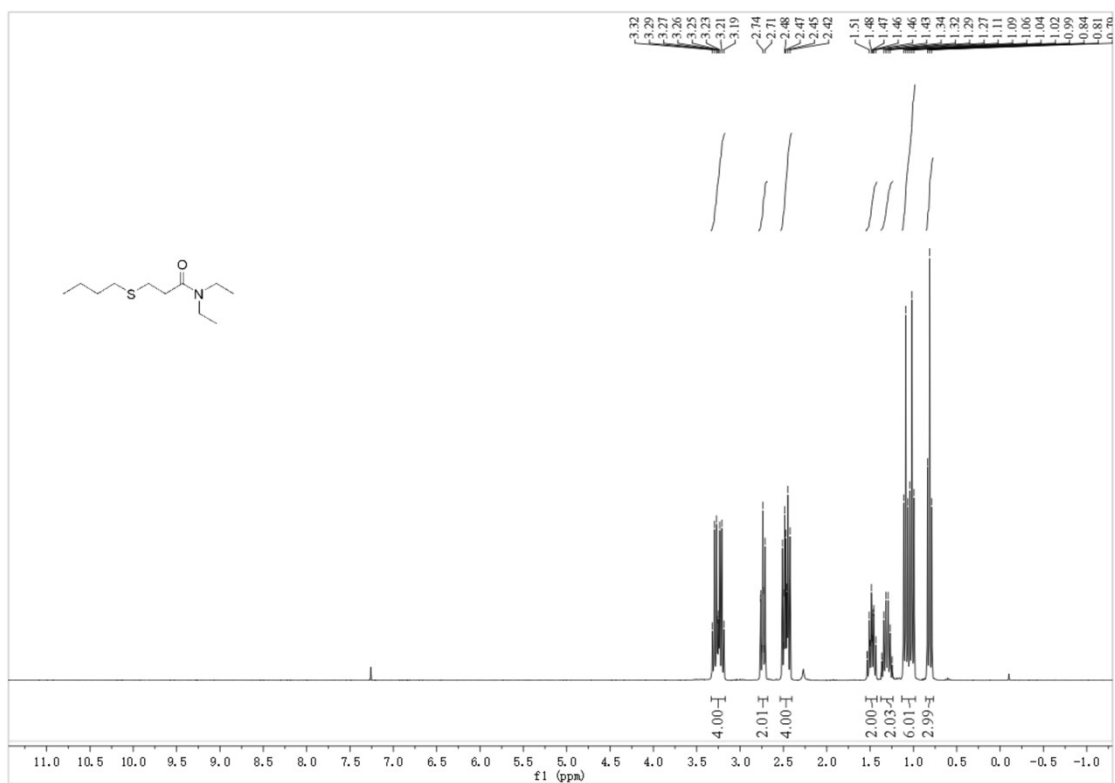
^1H NMR spectrum of **1a** (CDCl_3 , 400 MHz)



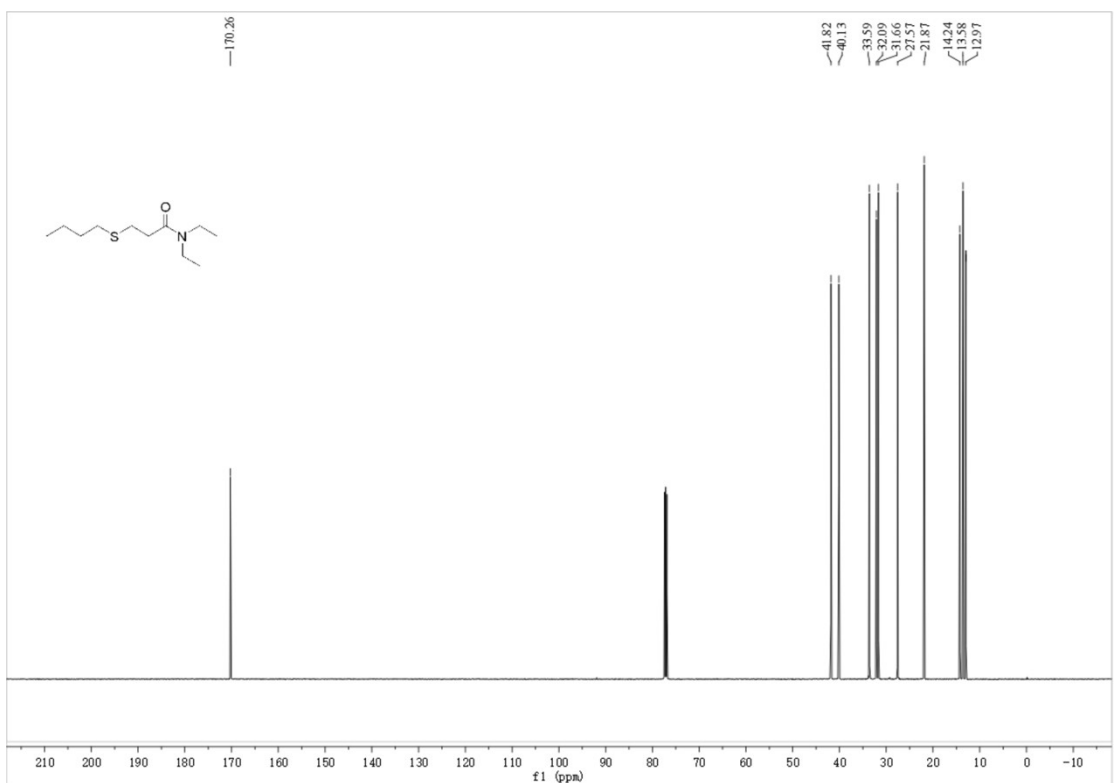
^{13}C NMR spectrum of **1a** (CDCl_3 , 101 MHz)



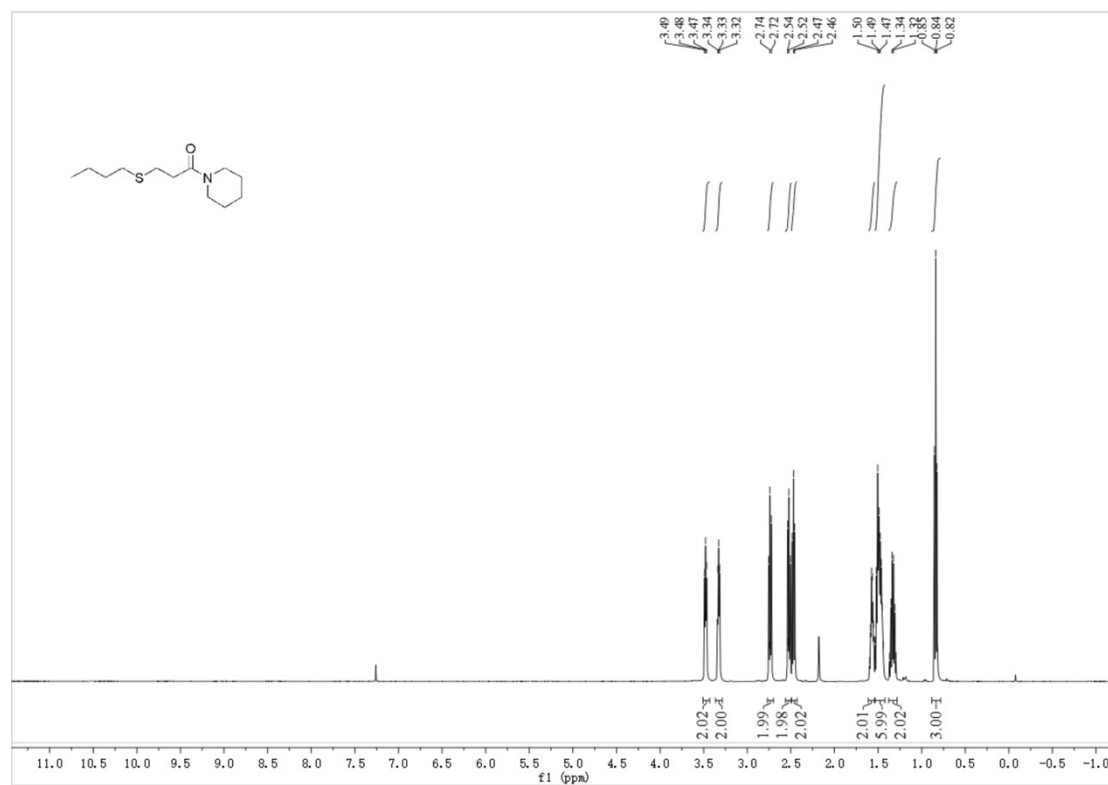
^1H NMR spectrum of **1p** (CDCl_3 , 400 MHz)



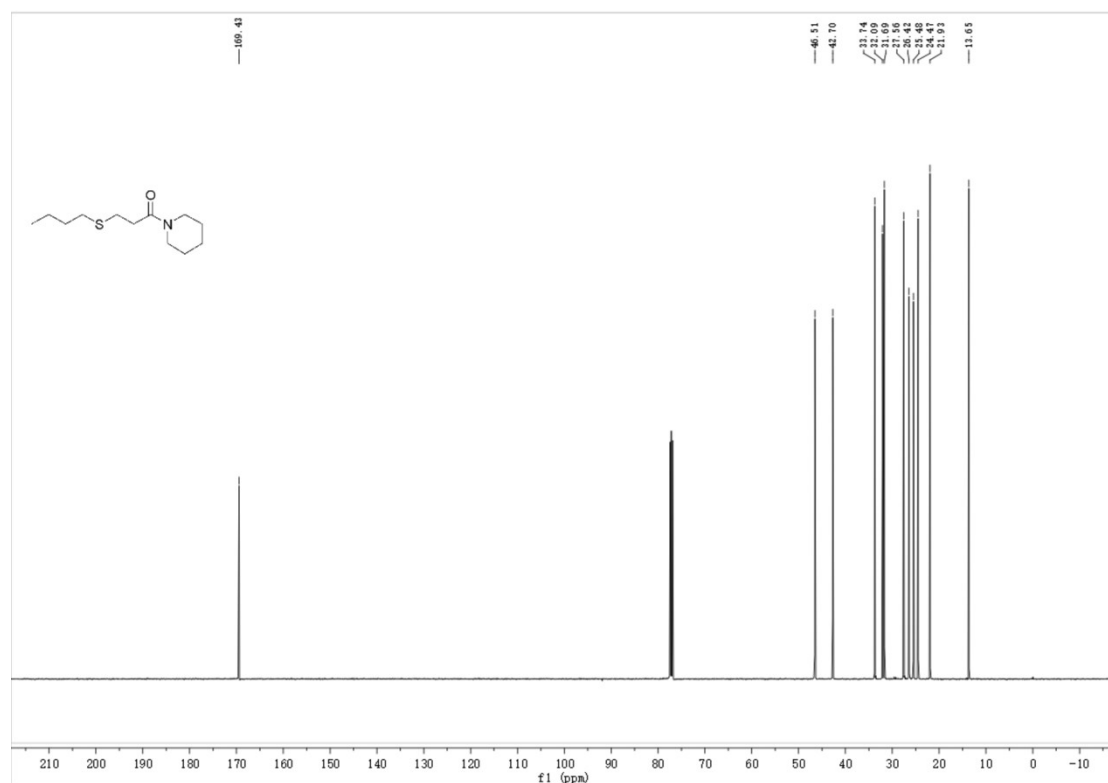
^{13}C NMR spectrum of **1p** (CDCl_3 , 101 MHz)



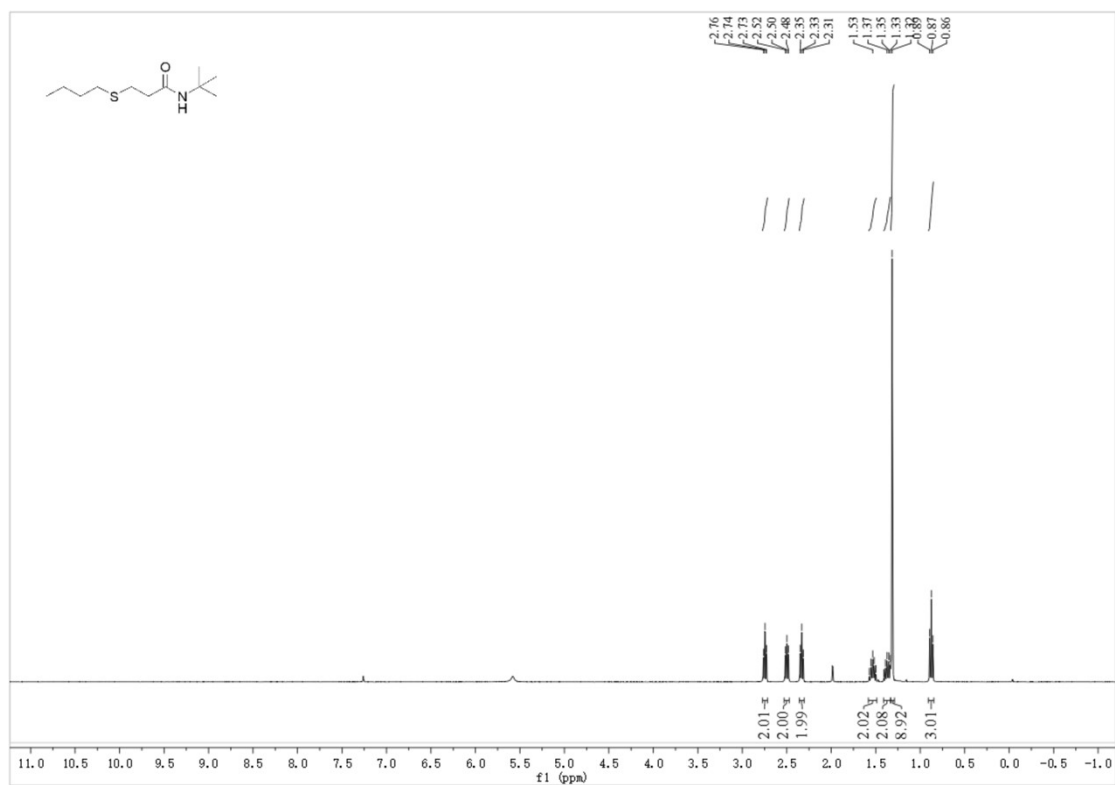
^1H NMR spectrum of **1q** (CDCl_3 , 400 MHz)



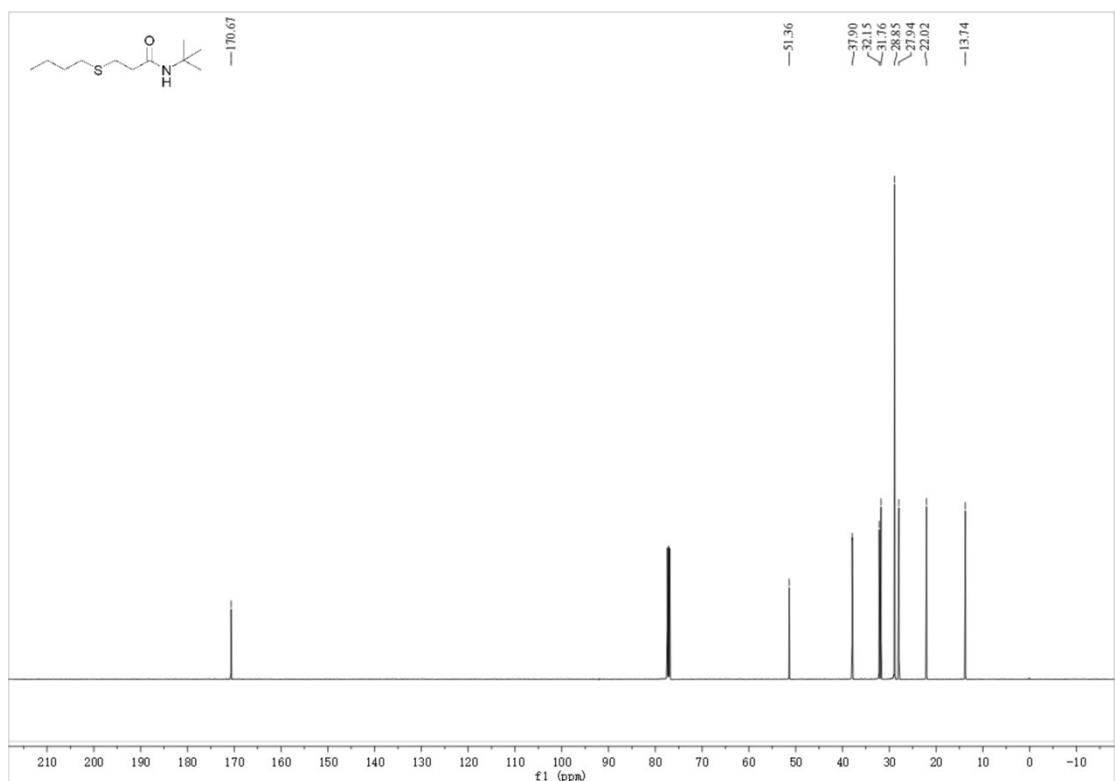
^{13}C NMR spectrum of **1q** (CDCl_3 , 101 MHz)



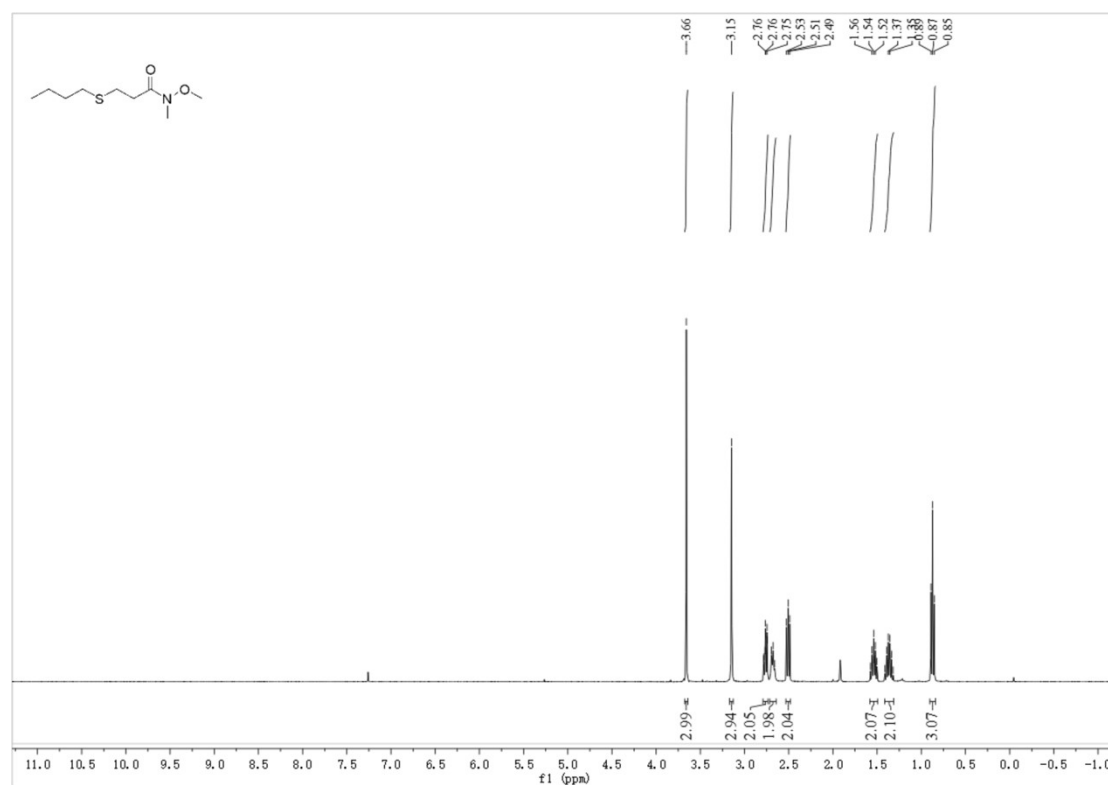
^1H NMR spectrum of **1r** (CDCl_3 , 400 MHz)



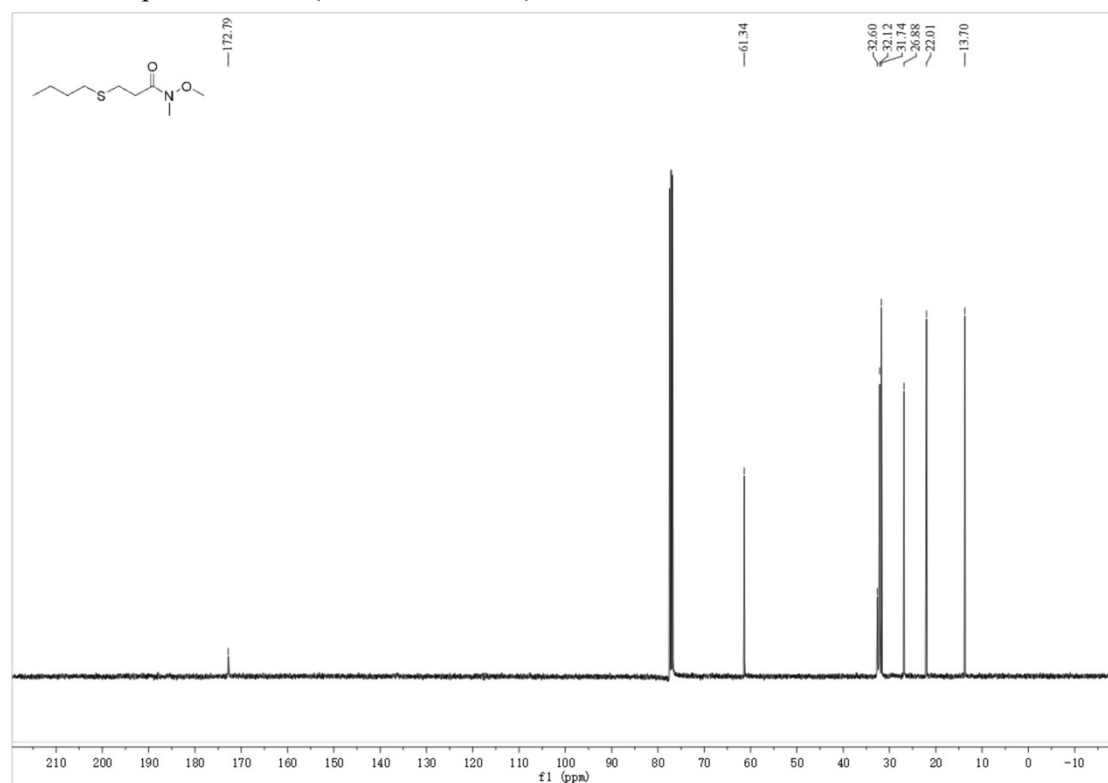
^{13}C NMR spectrum of **1r** (CDCl_3 , 101 MHz)



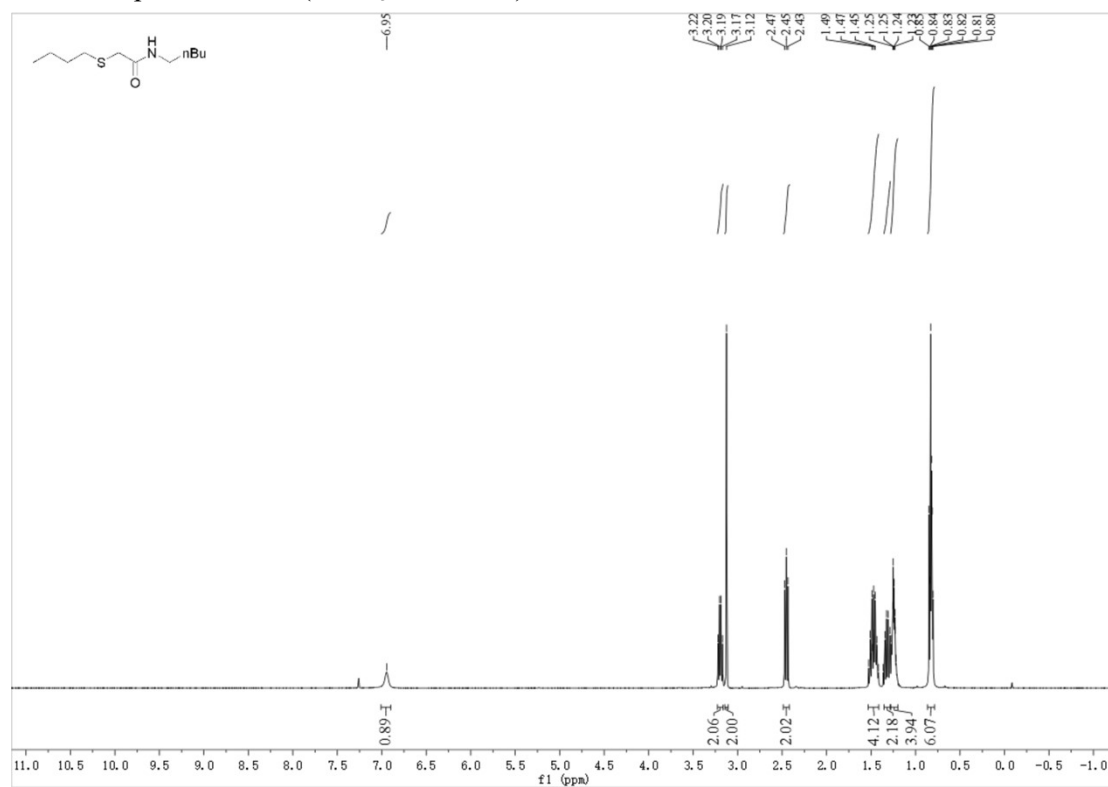
^1H NMR spectrum of **1s** (CDCl_3 , 400 MHz)



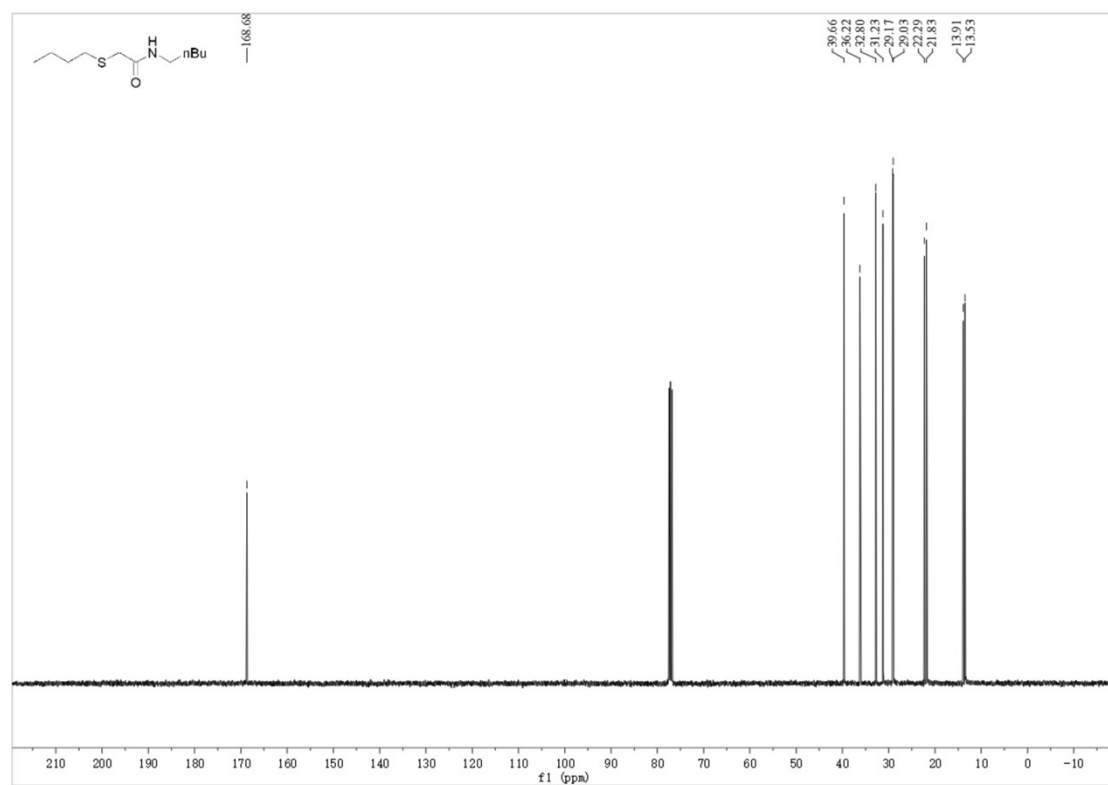
^{13}C NMR spectrum of **1s** (CDCl_3 , 101 MHz)



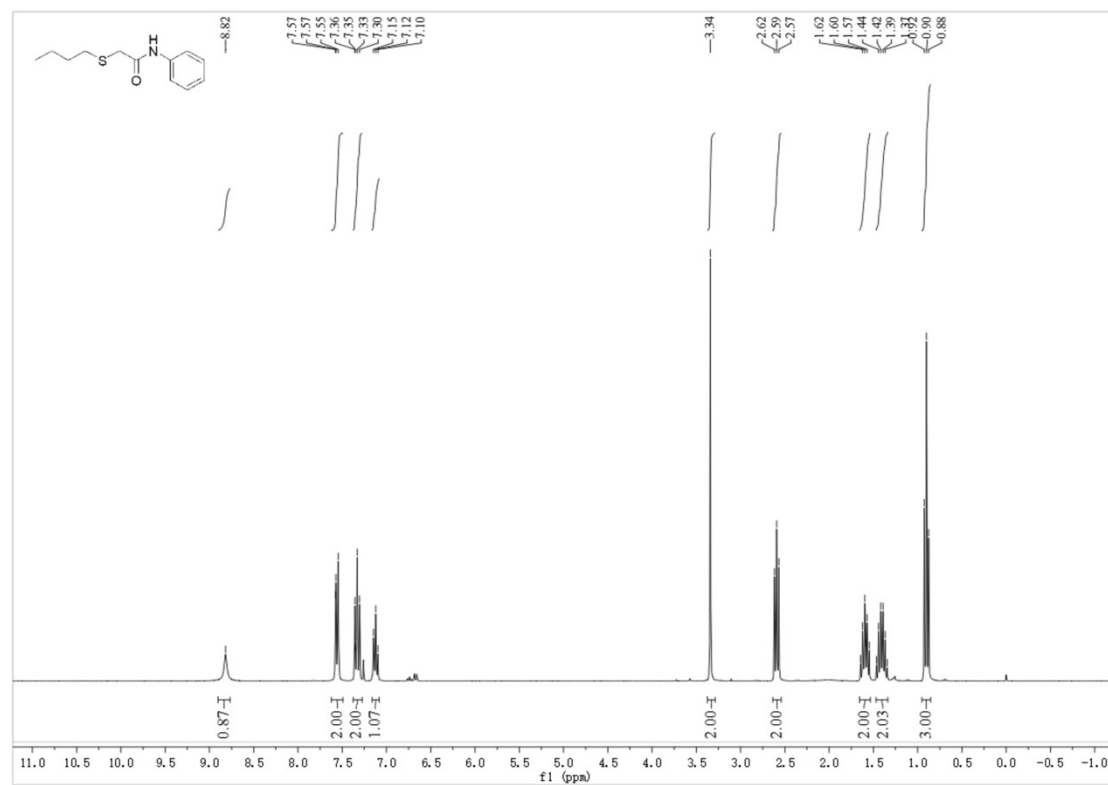
^1H NMR spectrum of **1t** (CDCl_3 , 400 MHz)



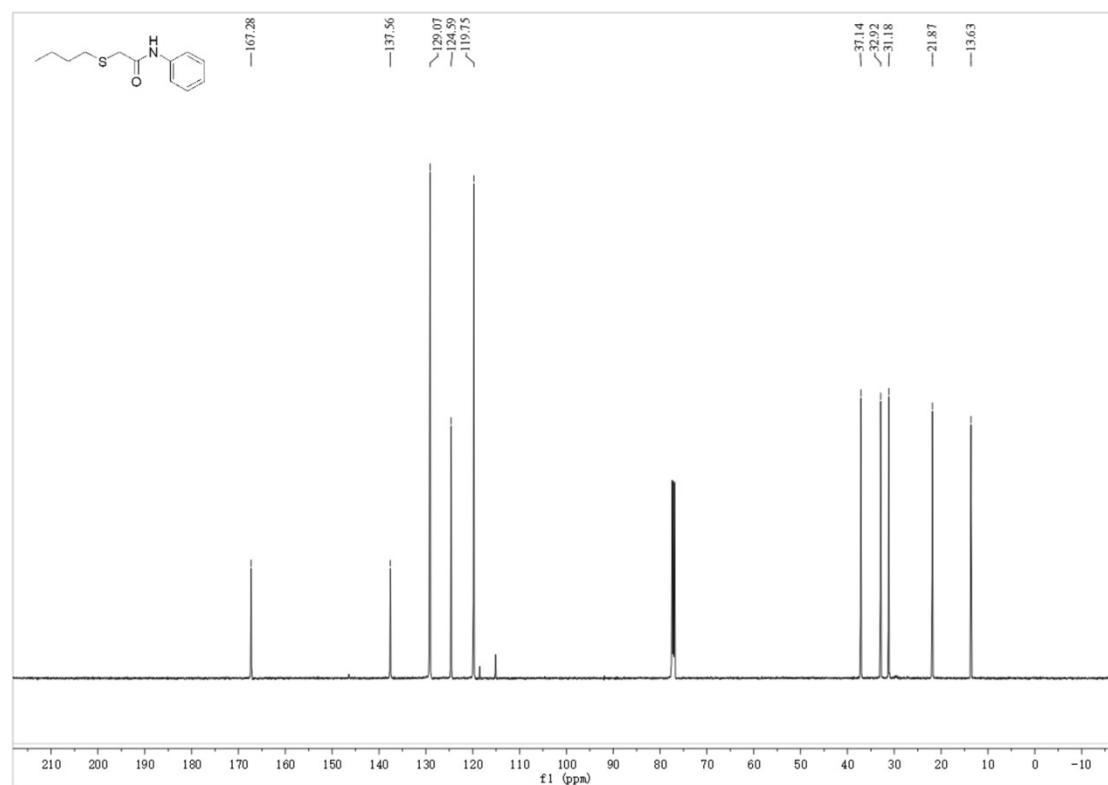
^{13}C NMR spectrum of **1t** (CDCl_3 , 101 MHz)



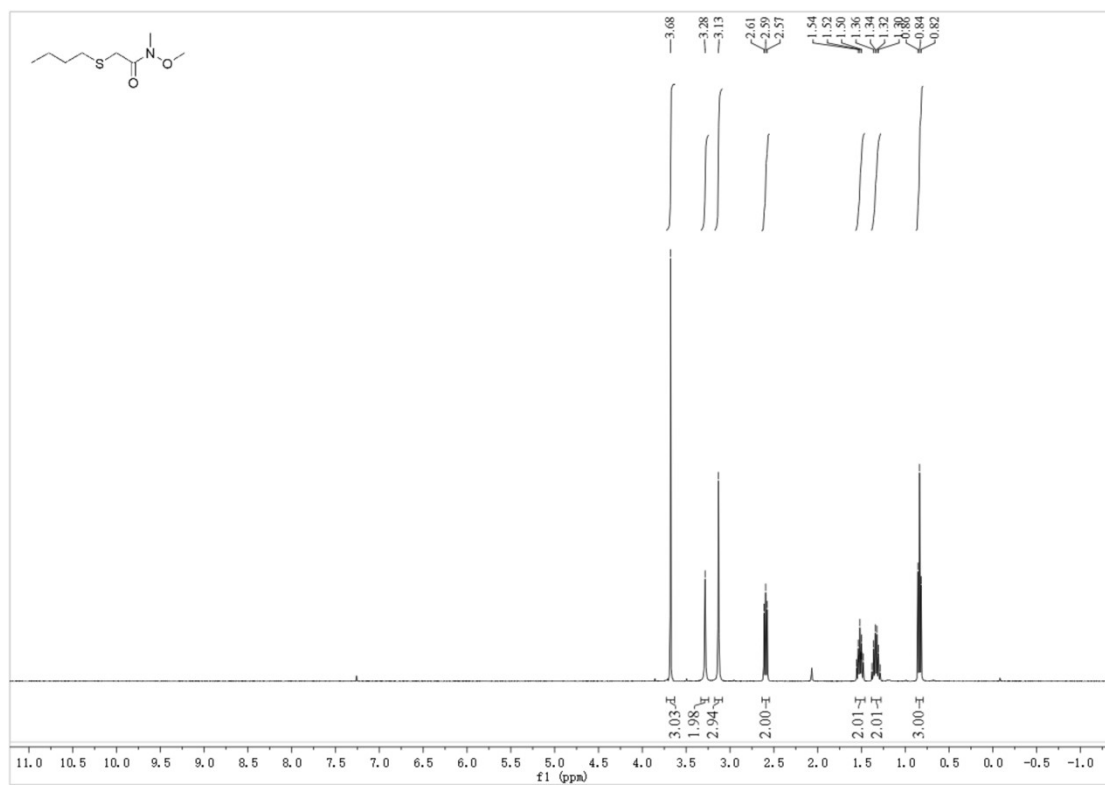
^1H NMR spectrum of **1u** (CDCl_3 , 400 MHz)



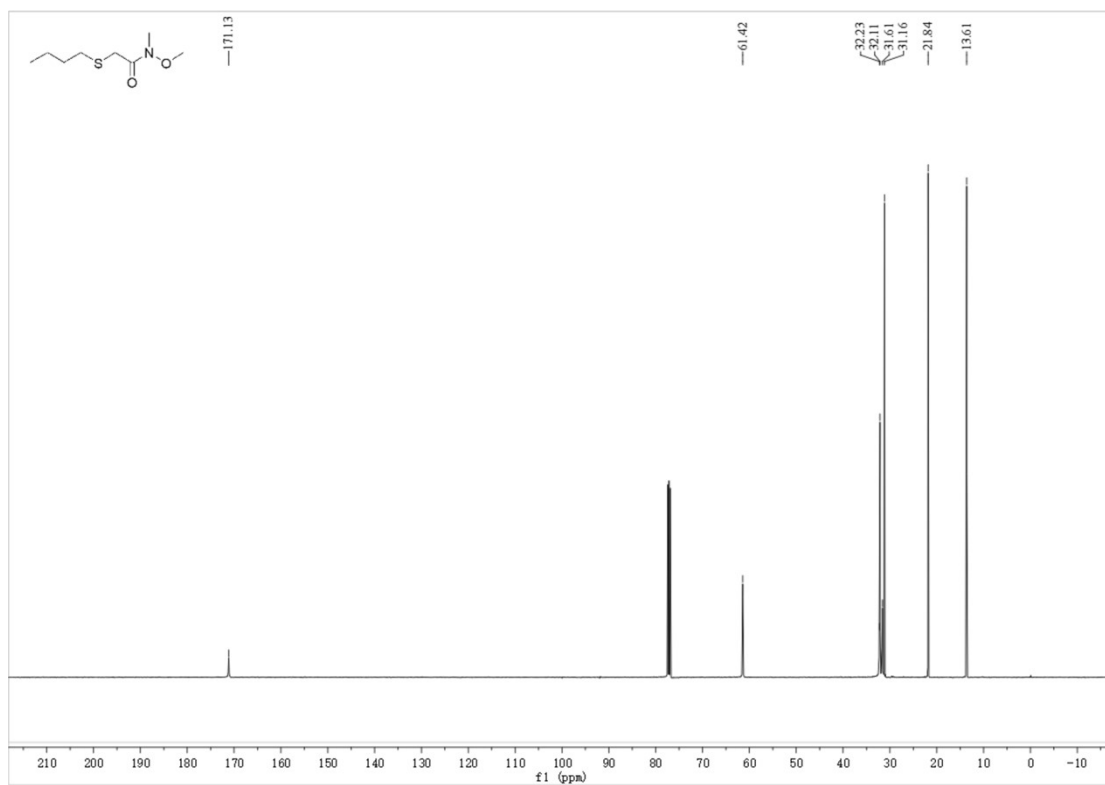
^{13}C NMR spectrum of **1u** (CDCl_3 , 101 MHz)



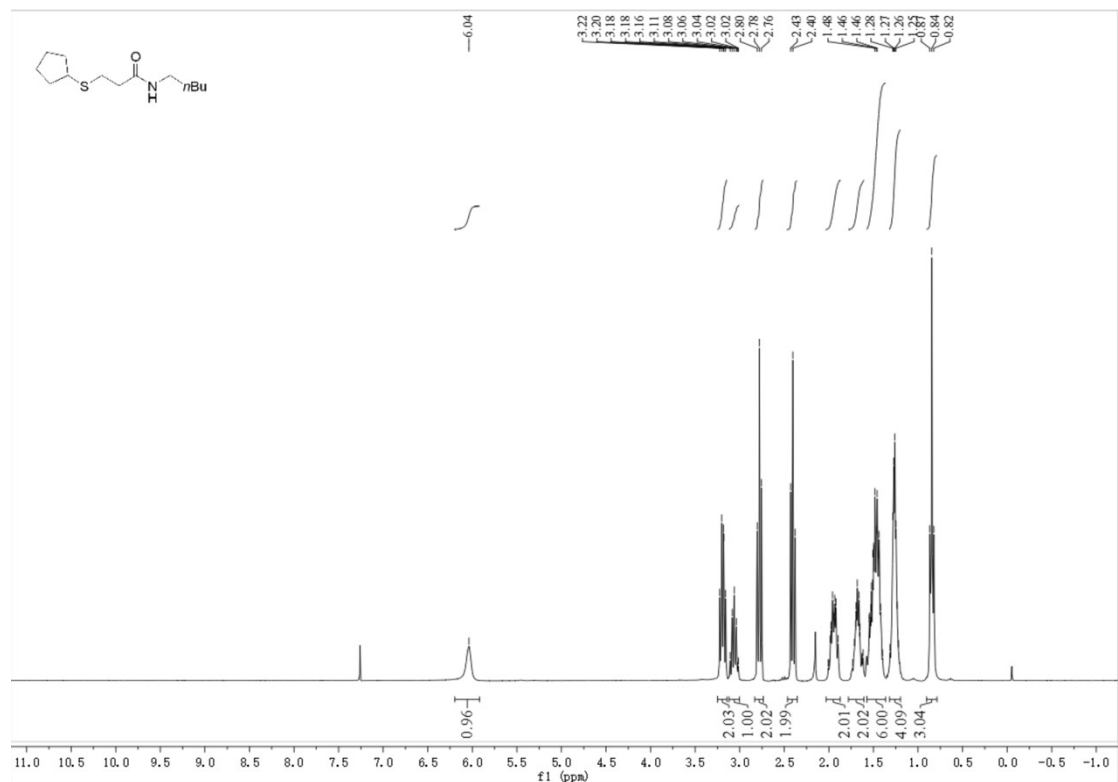
^1H NMR spectrum of **1v** (CDCl_3 , 400 MHz)



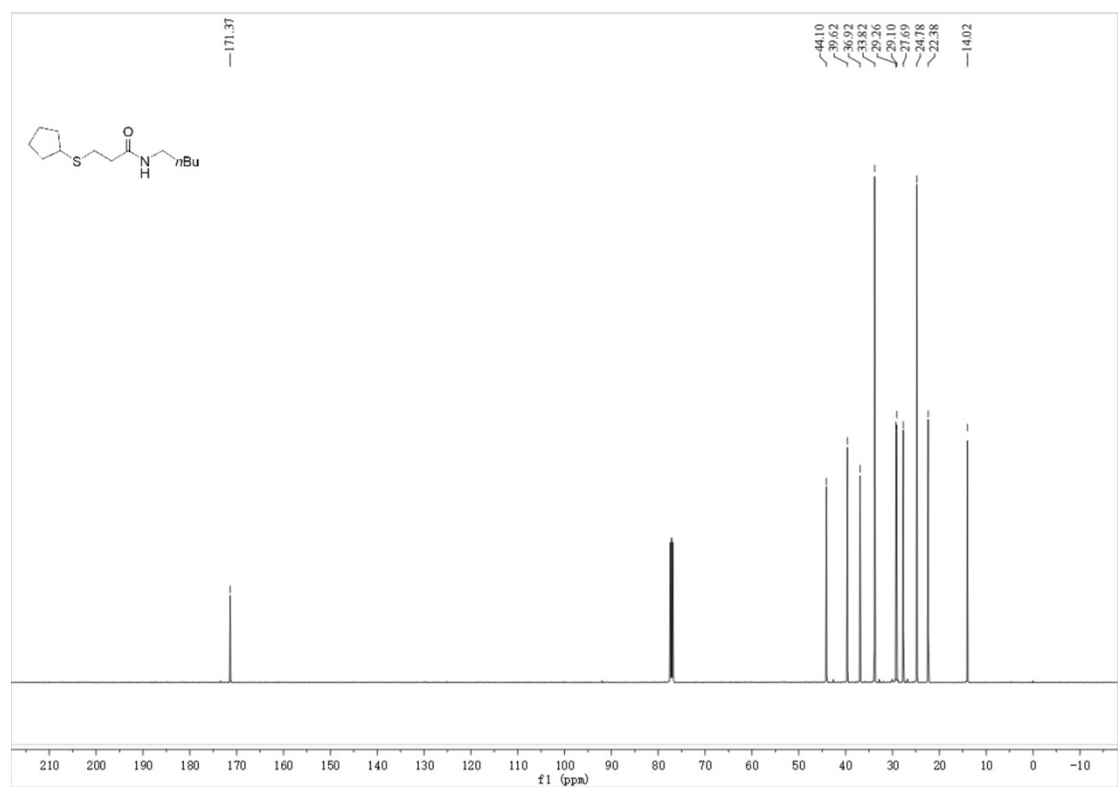
^{13}C NMR spectrum of **1v** (CDCl_3 , 101 MHz)



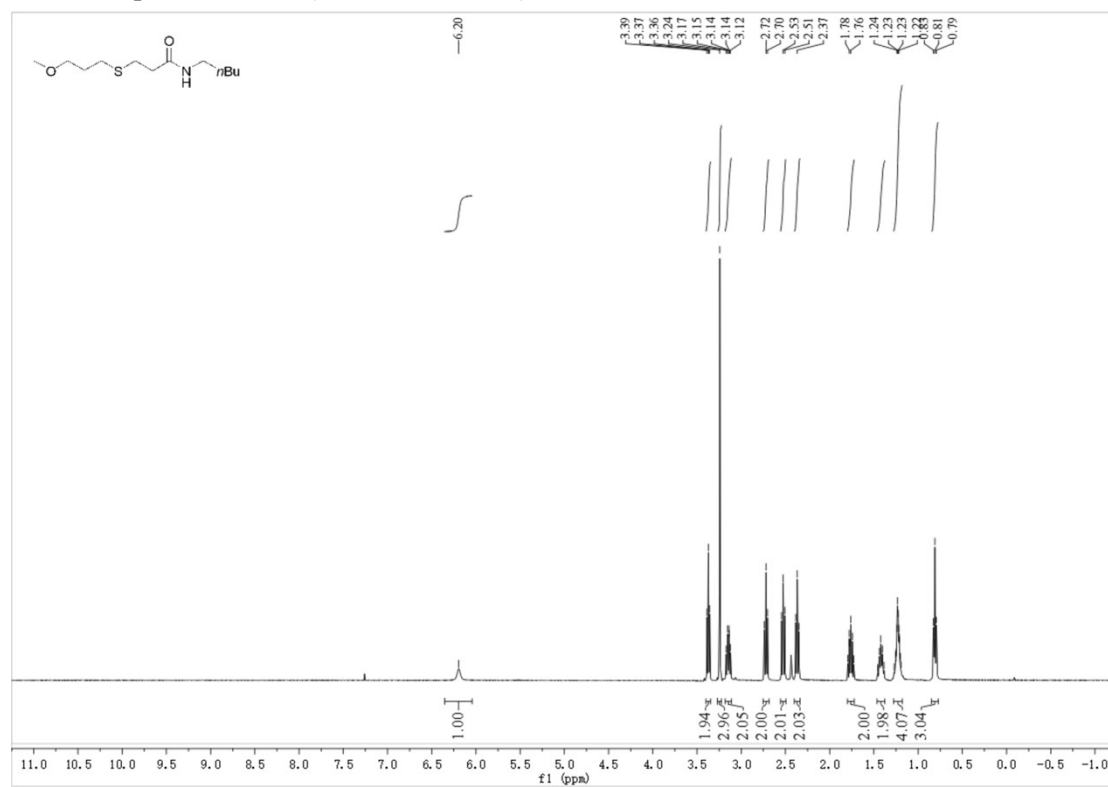
^1H NMR spectrum of **1w** (CDCl_3 , 400 MHz)



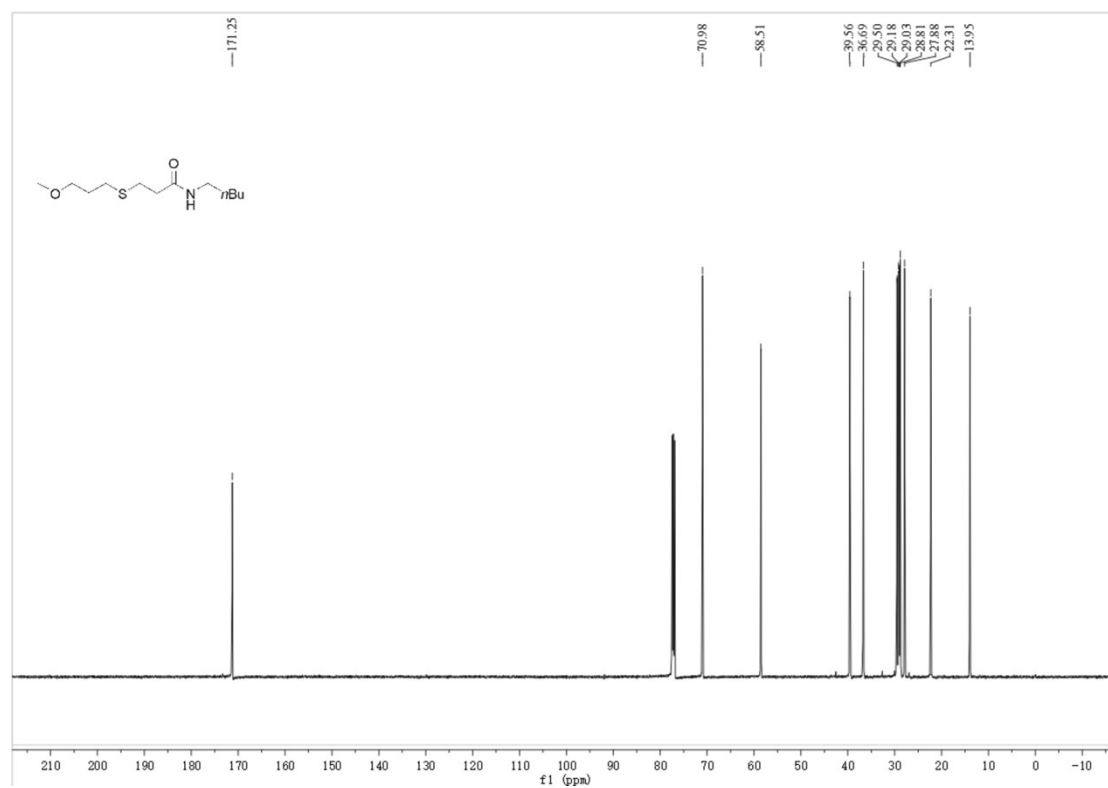
^{13}C NMR spectrum of **1w** (CDCl_3 , 101 MHz)



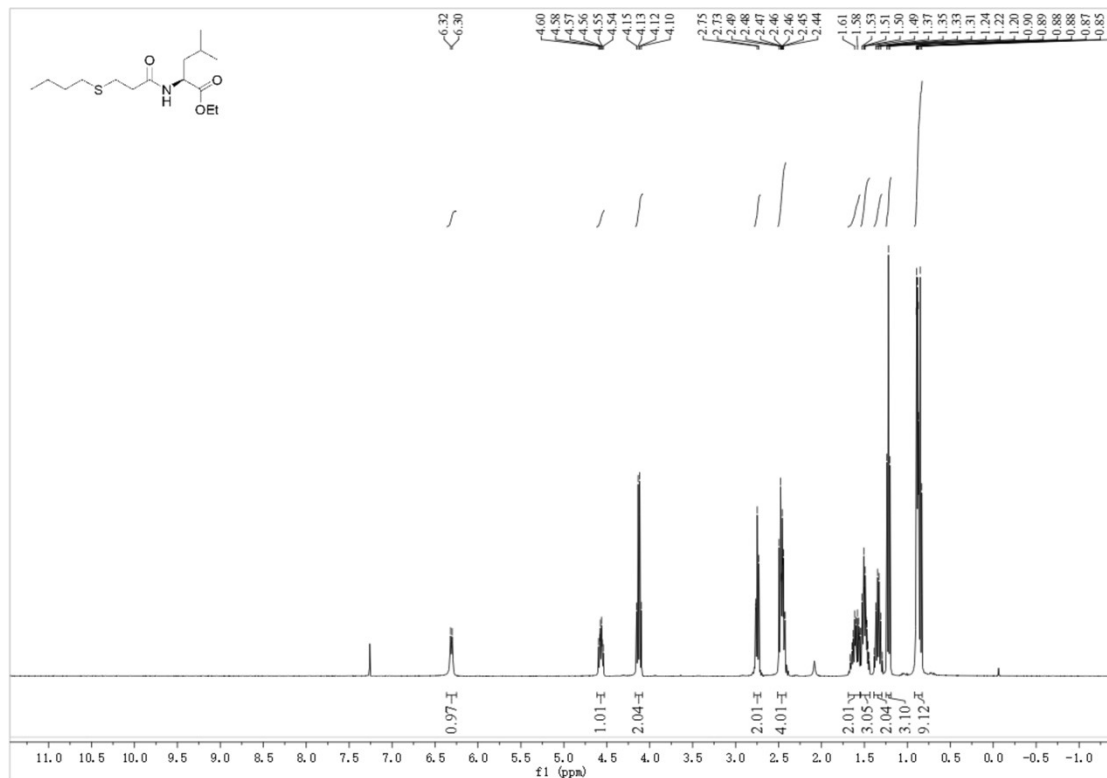
^1H NMR spectrum of **1x** (CDCl_3 , 400 MHz)



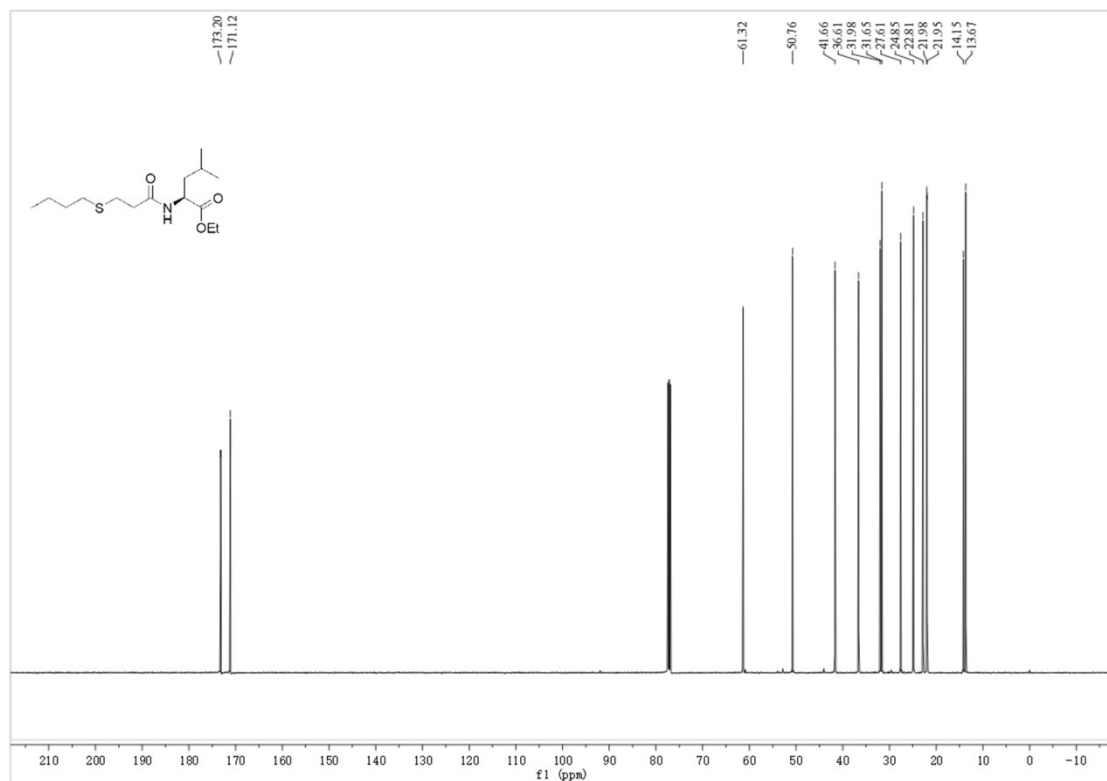
^{13}C NMR spectrum of **1x** (CDCl_3 , 101 MHz)



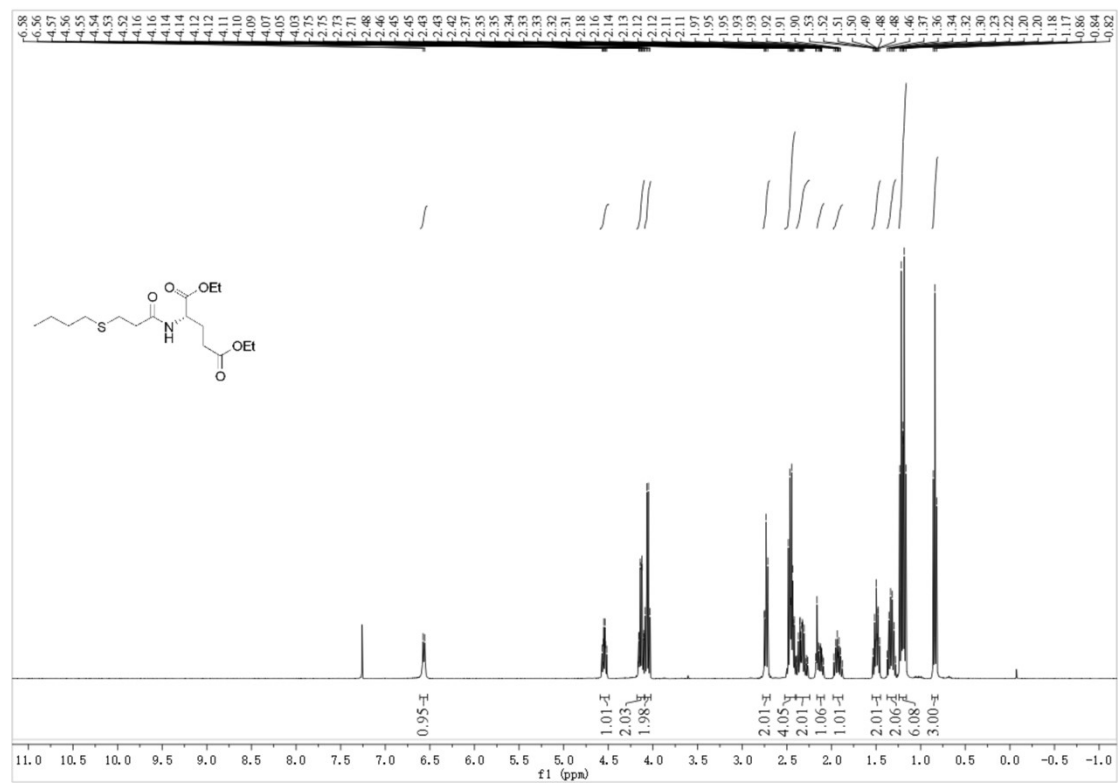
^1H NMR spectrum of **1y** (CDCl_3 , 400 MHz)



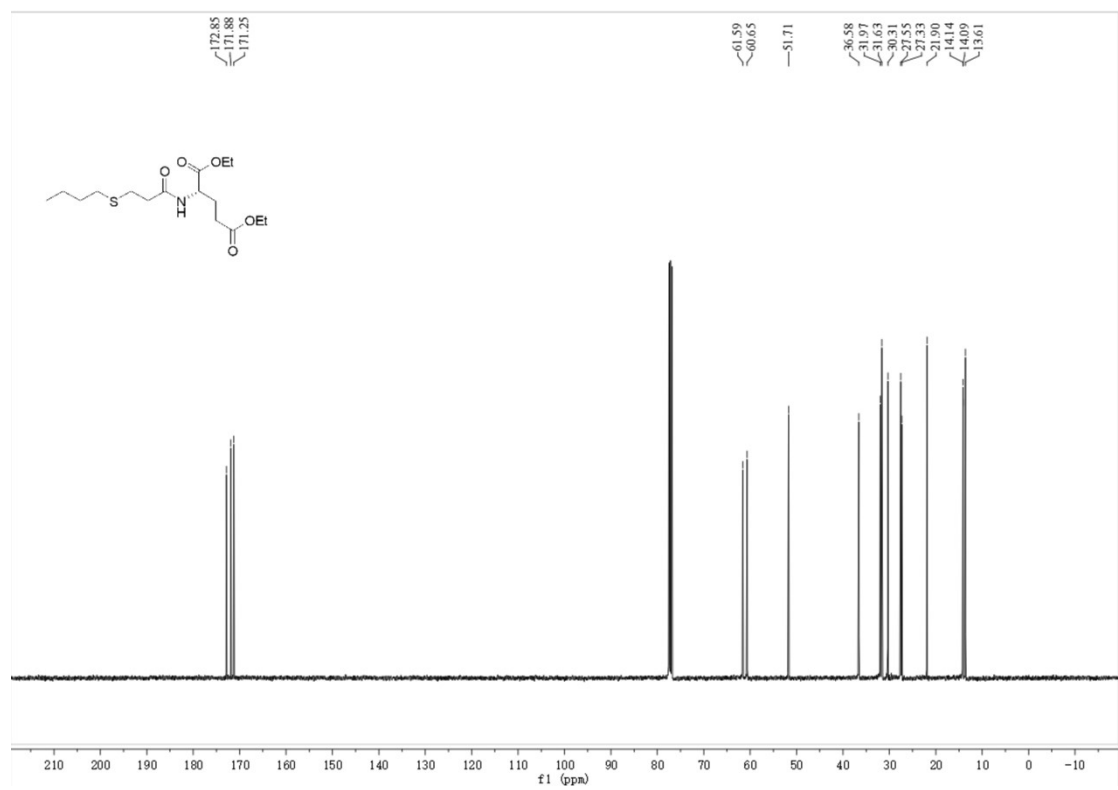
^{13}C NMR spectrum of **1y** (CDCl_3 , 101 MHz)



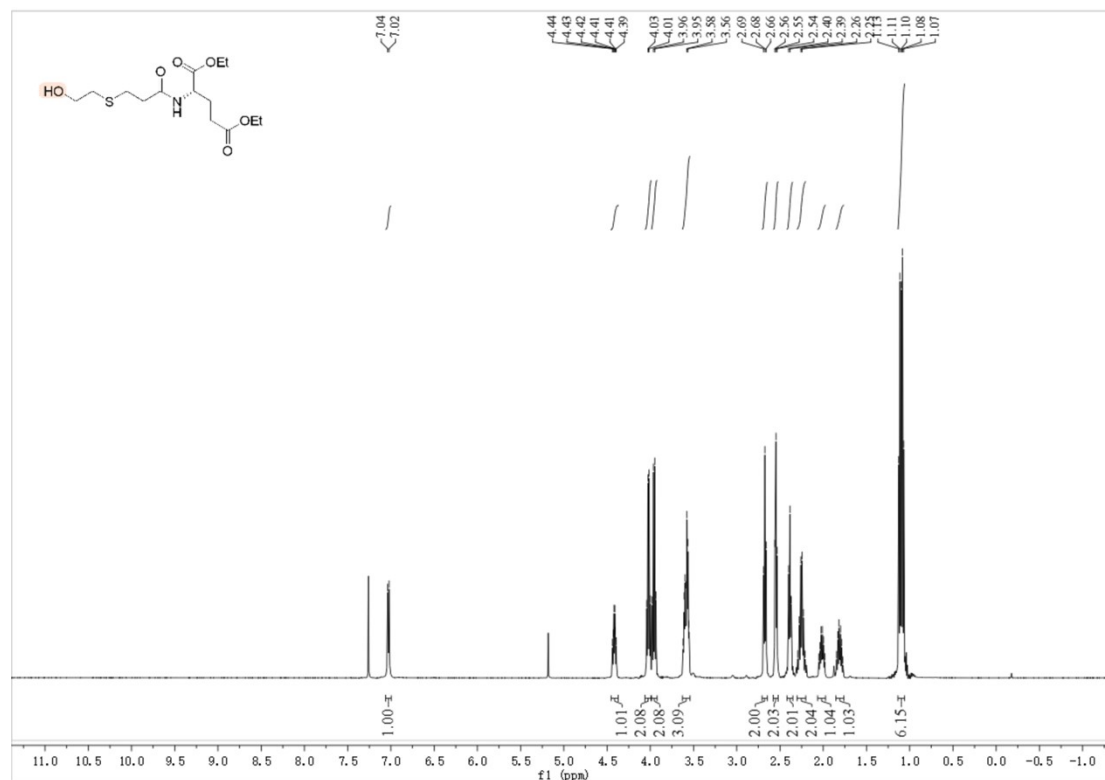
^1H NMR spectrum of **1z** (CDCl_3 , 400 MHz)



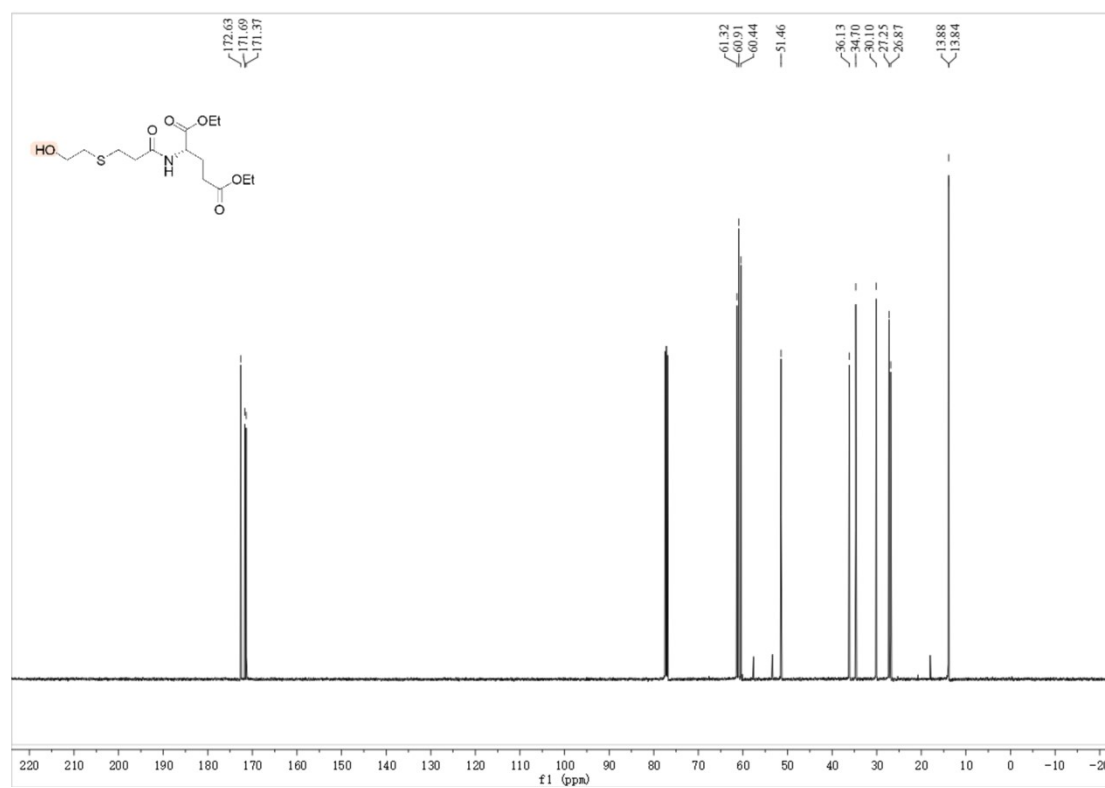
^{13}C NMR spectrum of **1z** (CDCl_3 , 101 MHz)



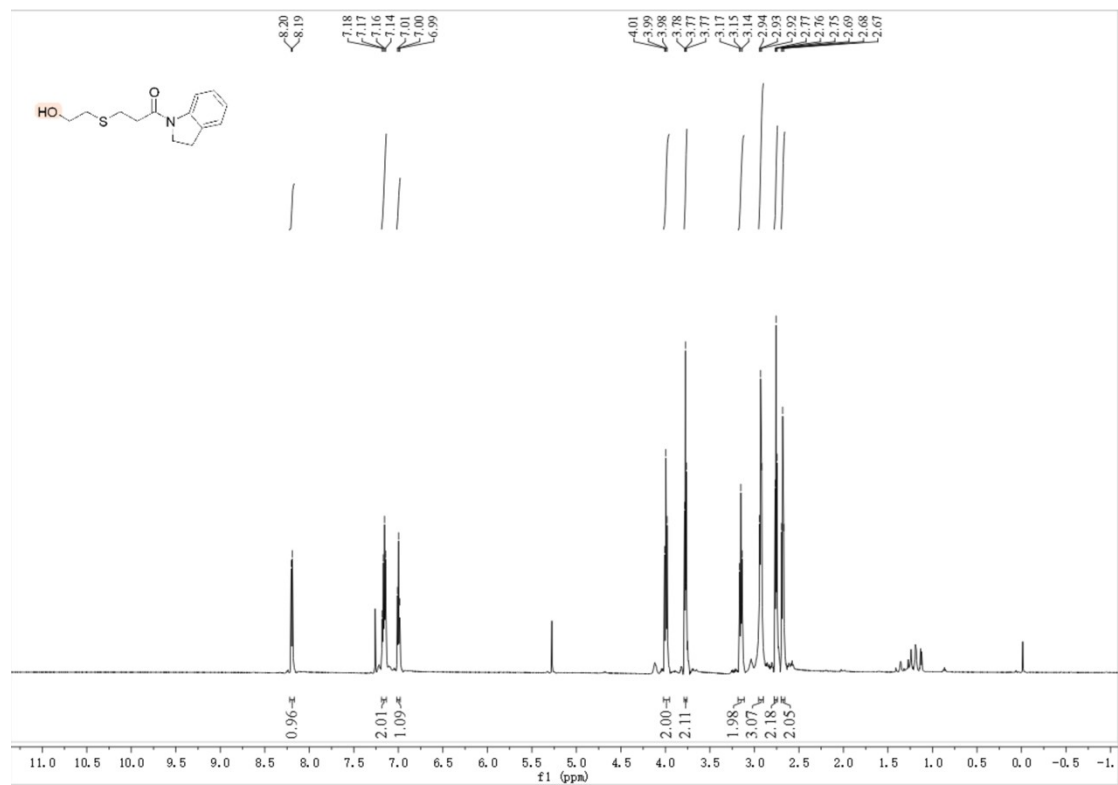
^1H NMR spectrum of **1aa** (CDCl_3 , 400 MHz)



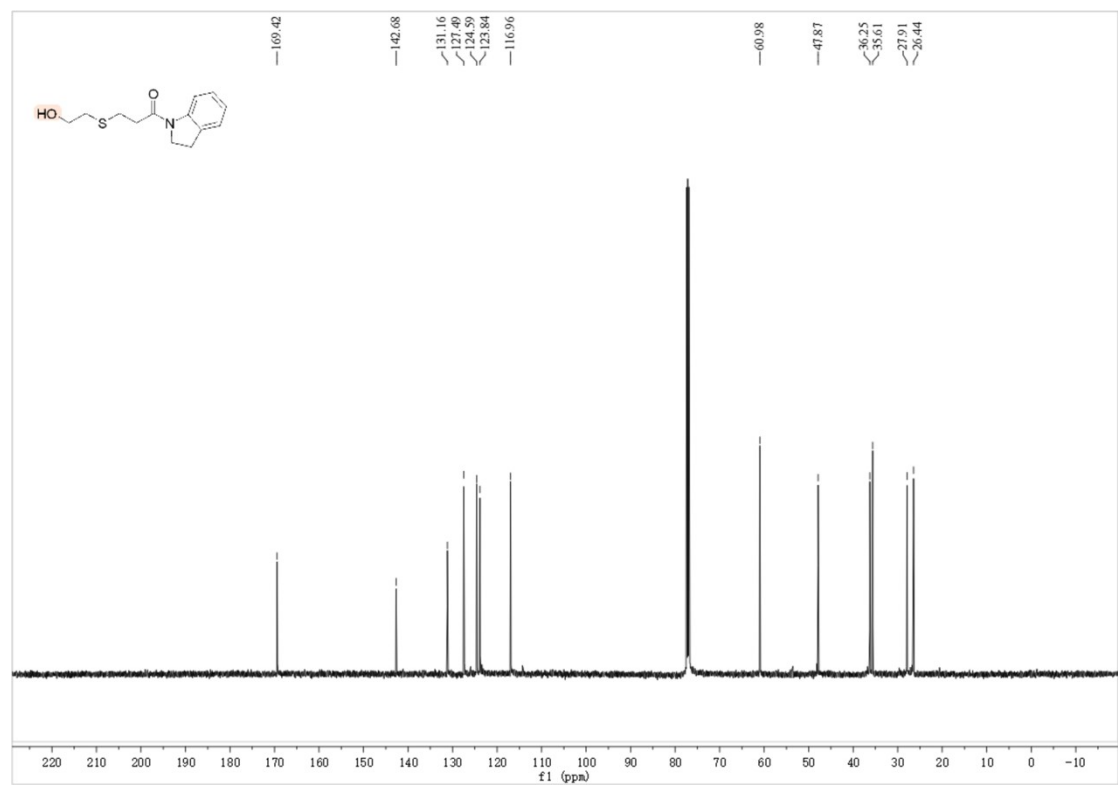
^{13}C NMR spectrum of **1aa** (CDCl_3 , 101 MHz)



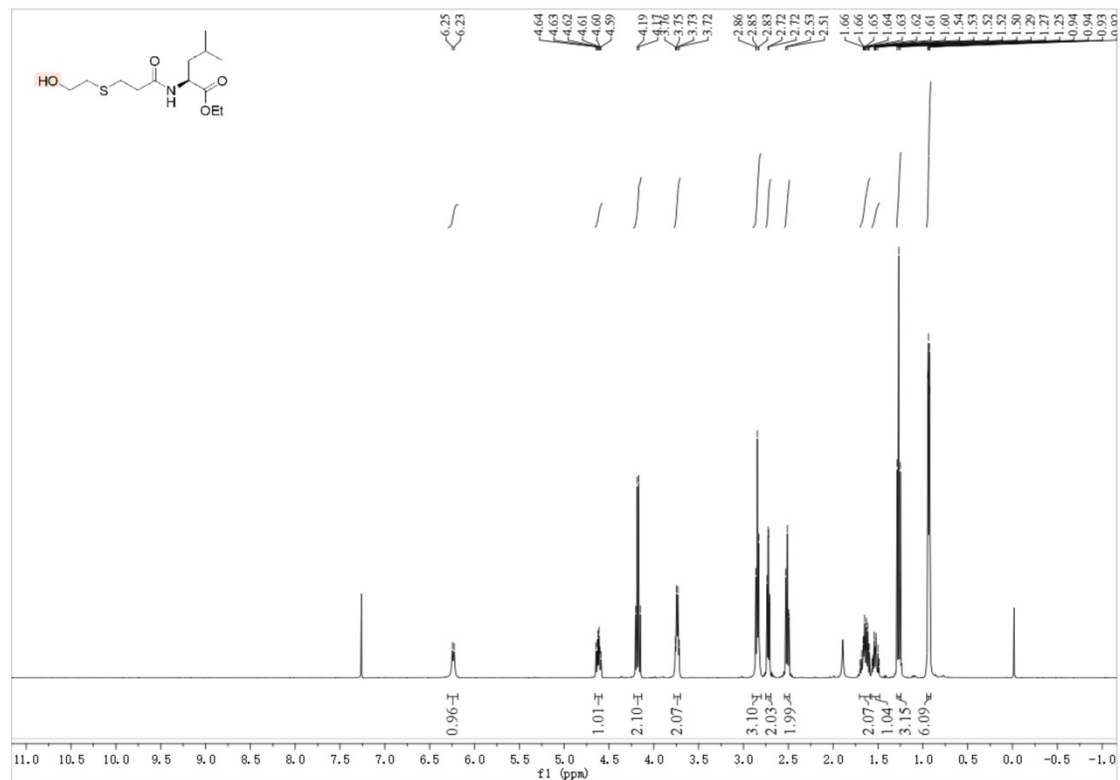
^1H NMR spectrum of **1ab** (CDCl_3 , 400 MHz)



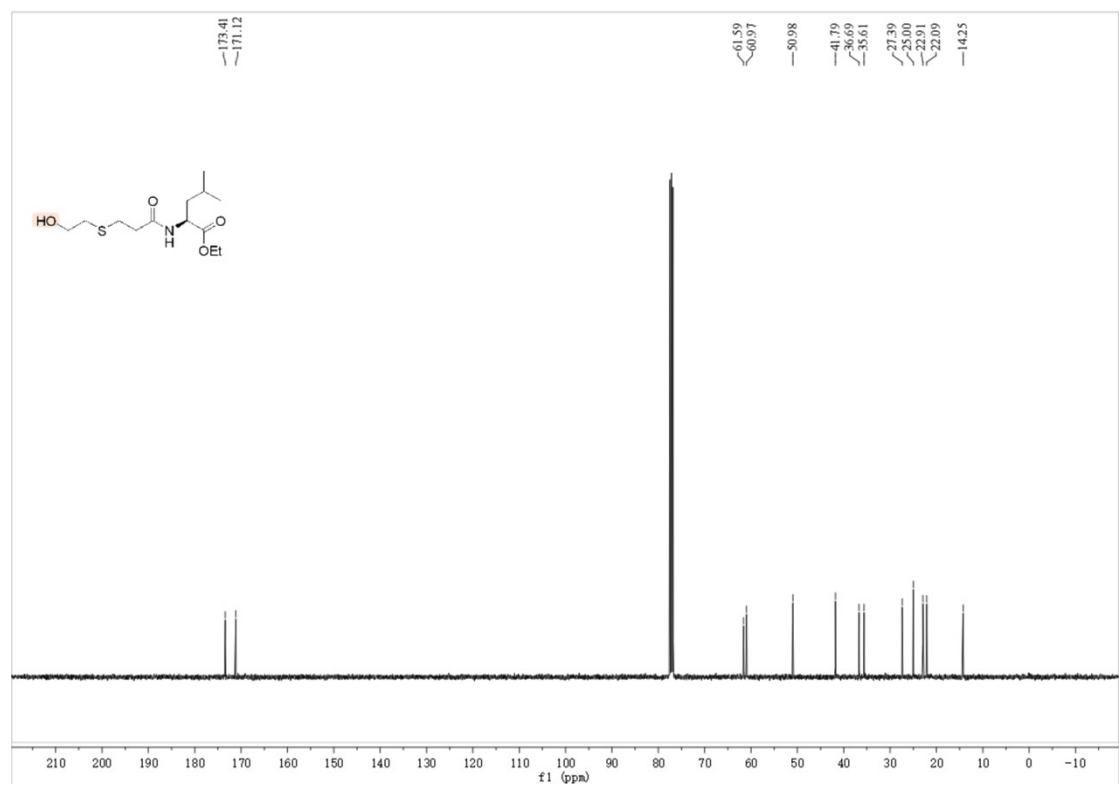
^{13}C NMR spectrum of **1ab** (CDCl_3 , 101 MHz)



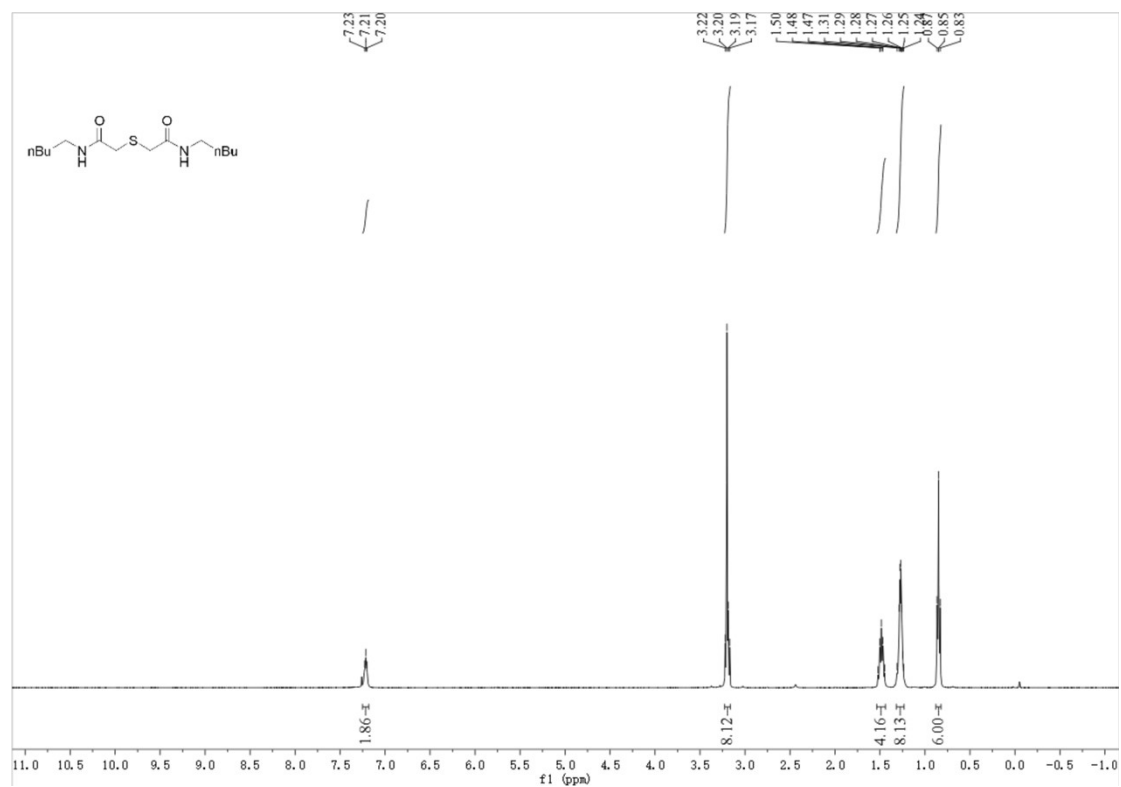
¹H NMR spectrum of **1ac** (CDCl₃, 400 MHz)



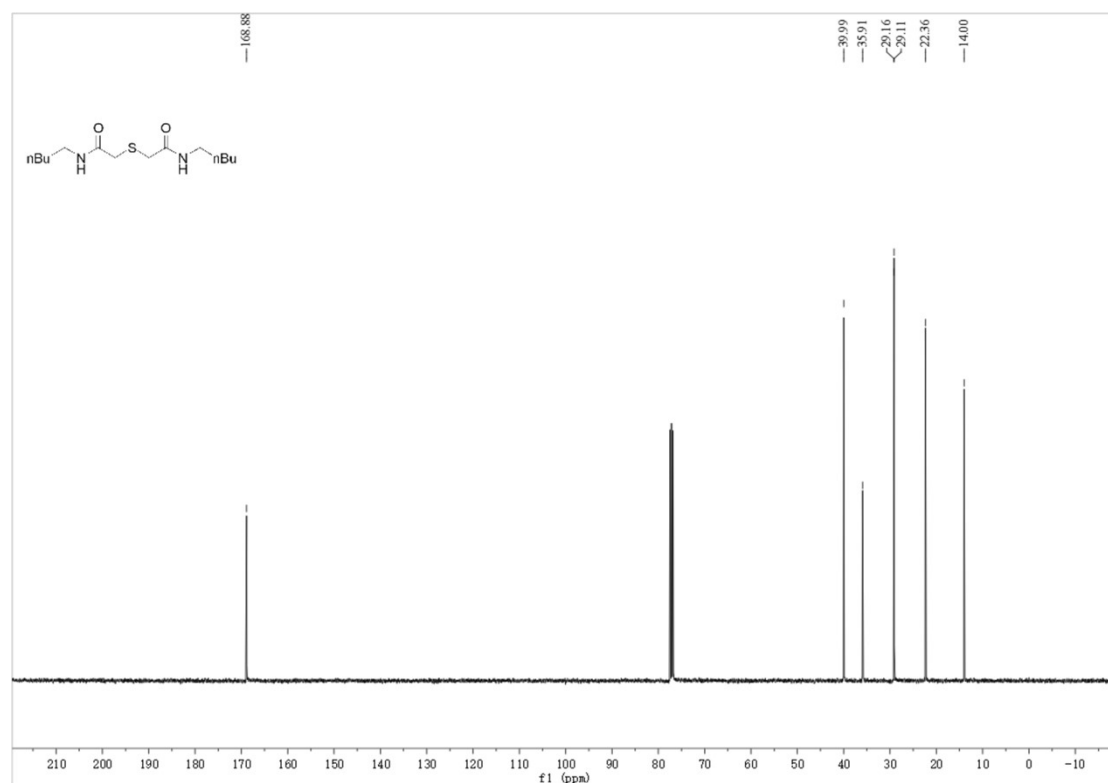
¹³C NMR spectrum of **1ac** (CDCl₃, 101 MHz)



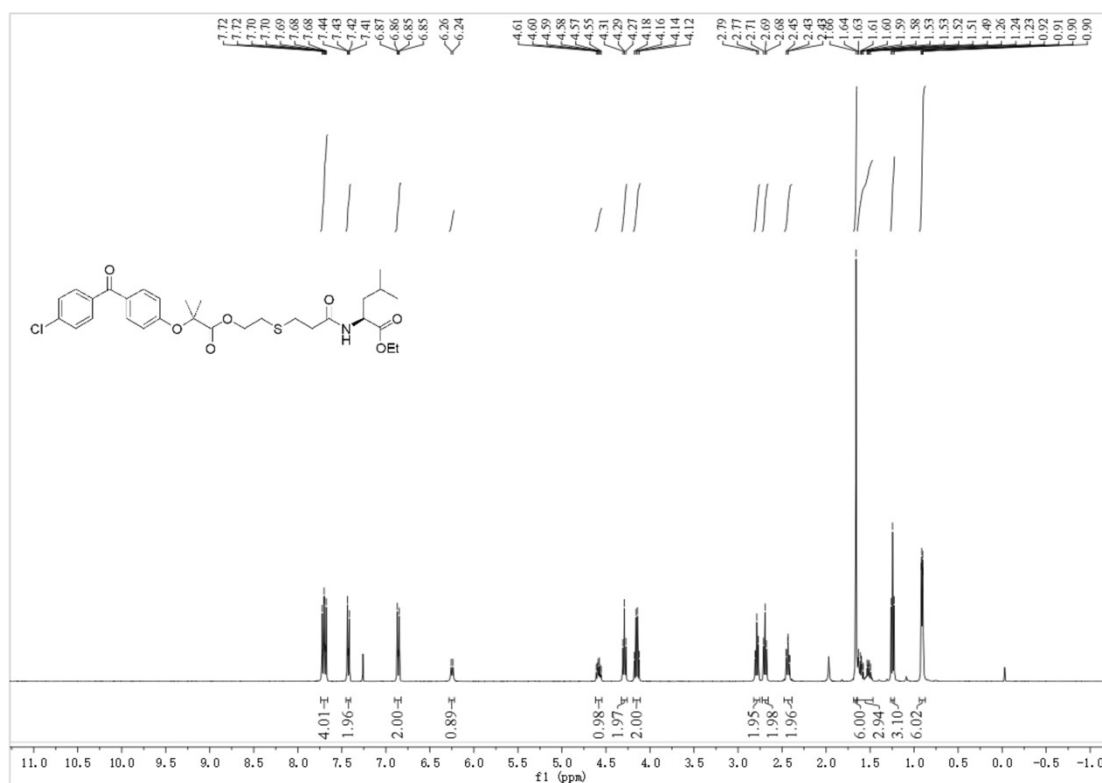
^1H NMR spectrum of **1ad** (CDCl_3 , 400 MHz)



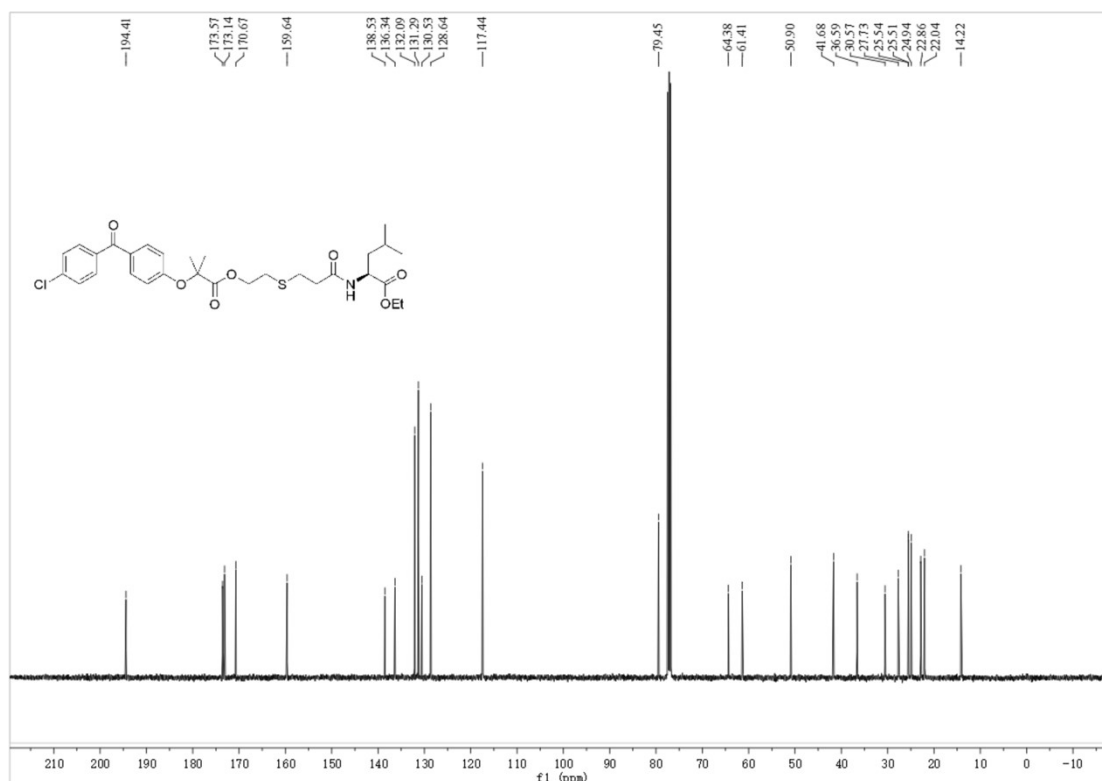
^{13}C NMR spectrum of **1ad** (CDCl_3 , 101 MHz)



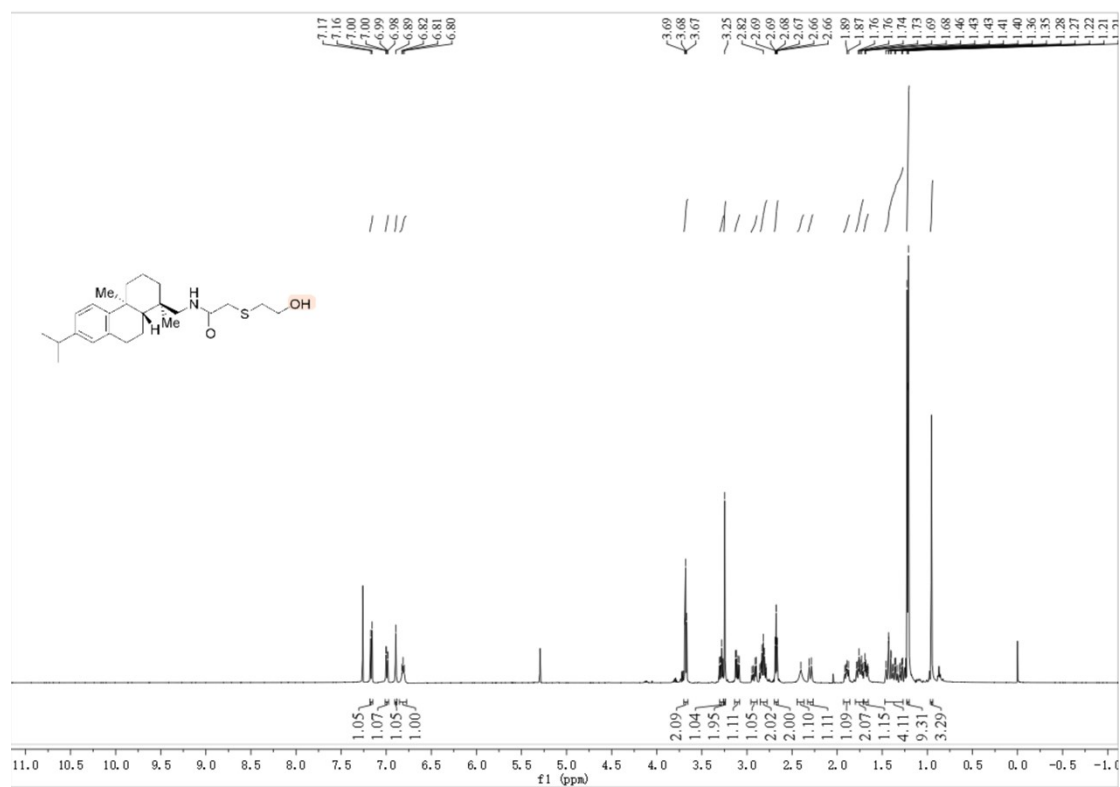
^1H NMR spectrum of **1af** (CDCl_3 , 400 MHz)



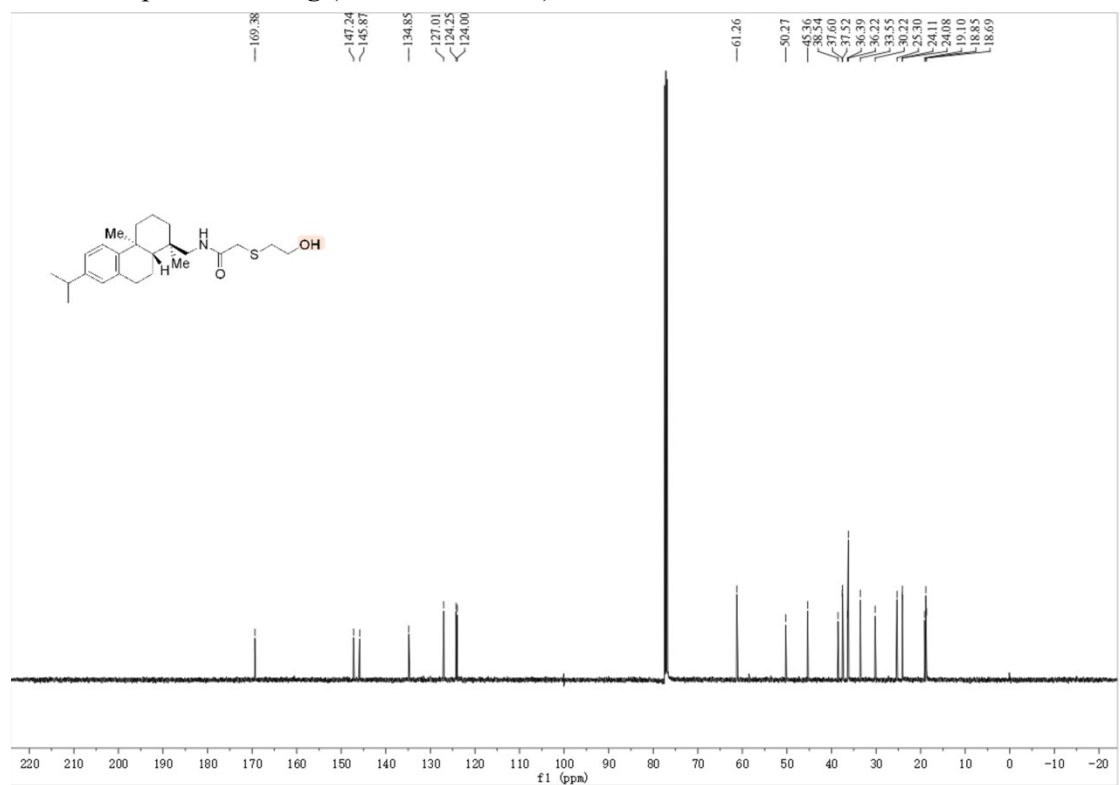
^{13}C NMR spectrum of **1af** (CDCl_3 , 101 MHz)



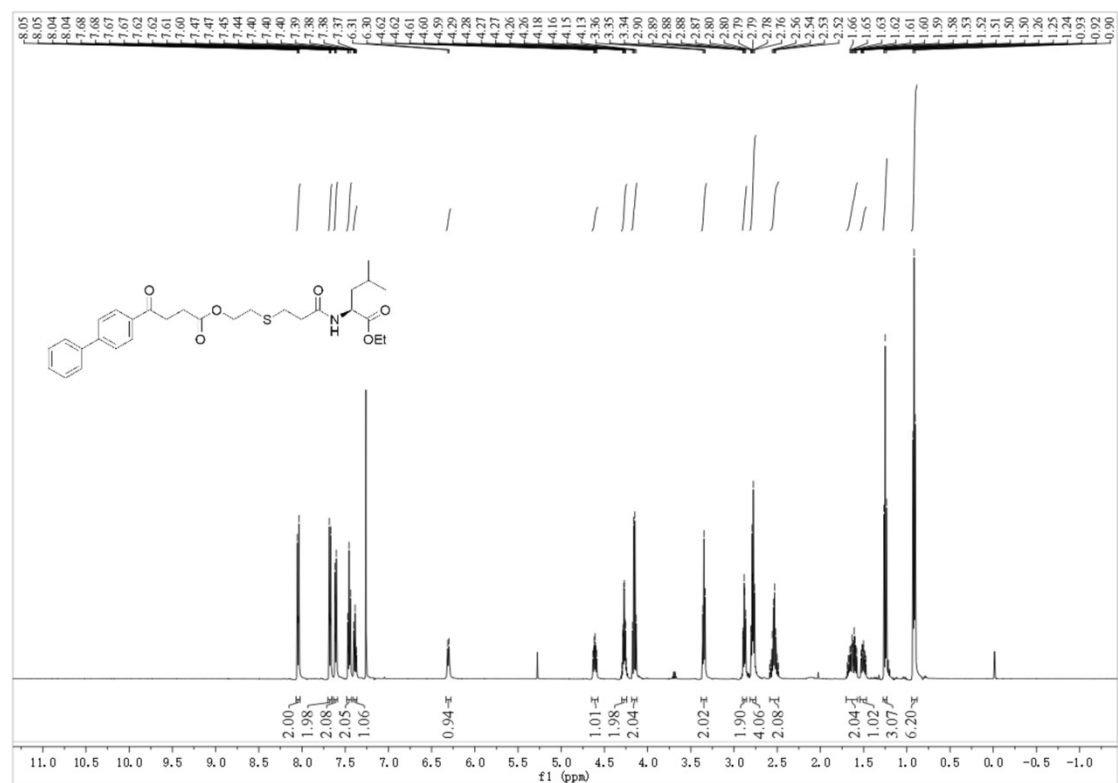
^1H NMR spectrum of **1ag** (CDCl_3 , 400 MHz)



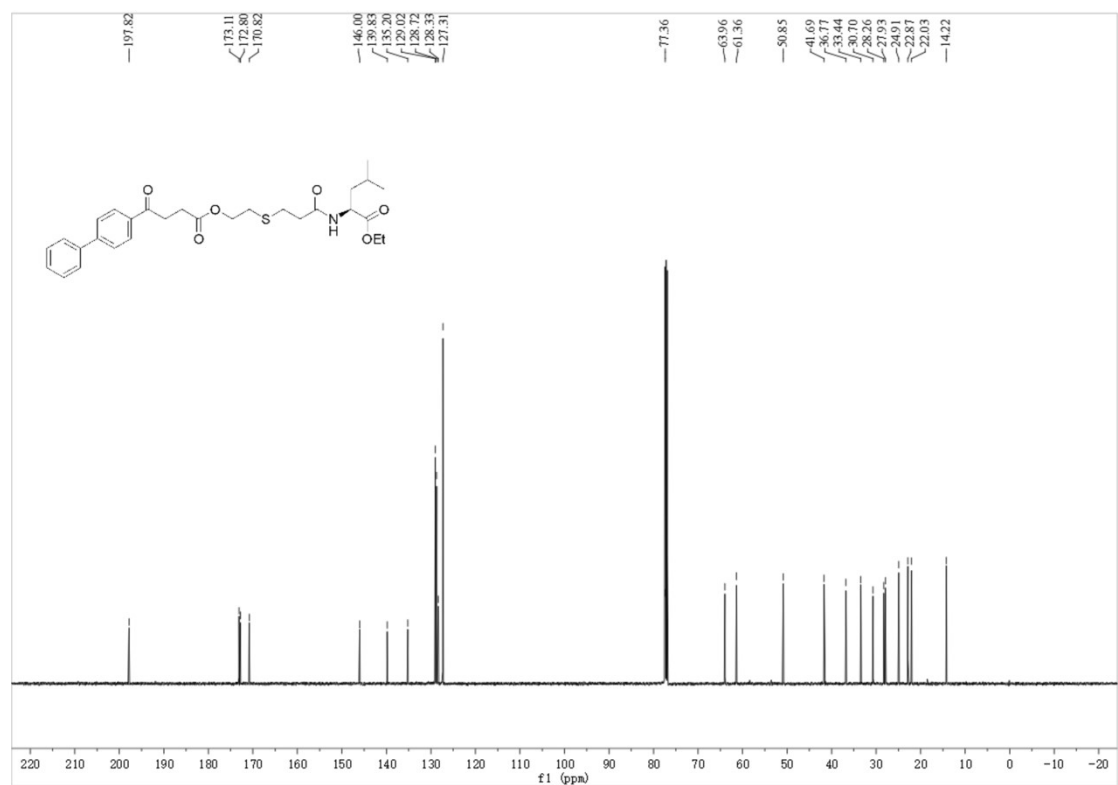
^{13}C NMR spectrum of **1ag** (CDCl_3 , 101 MHz)



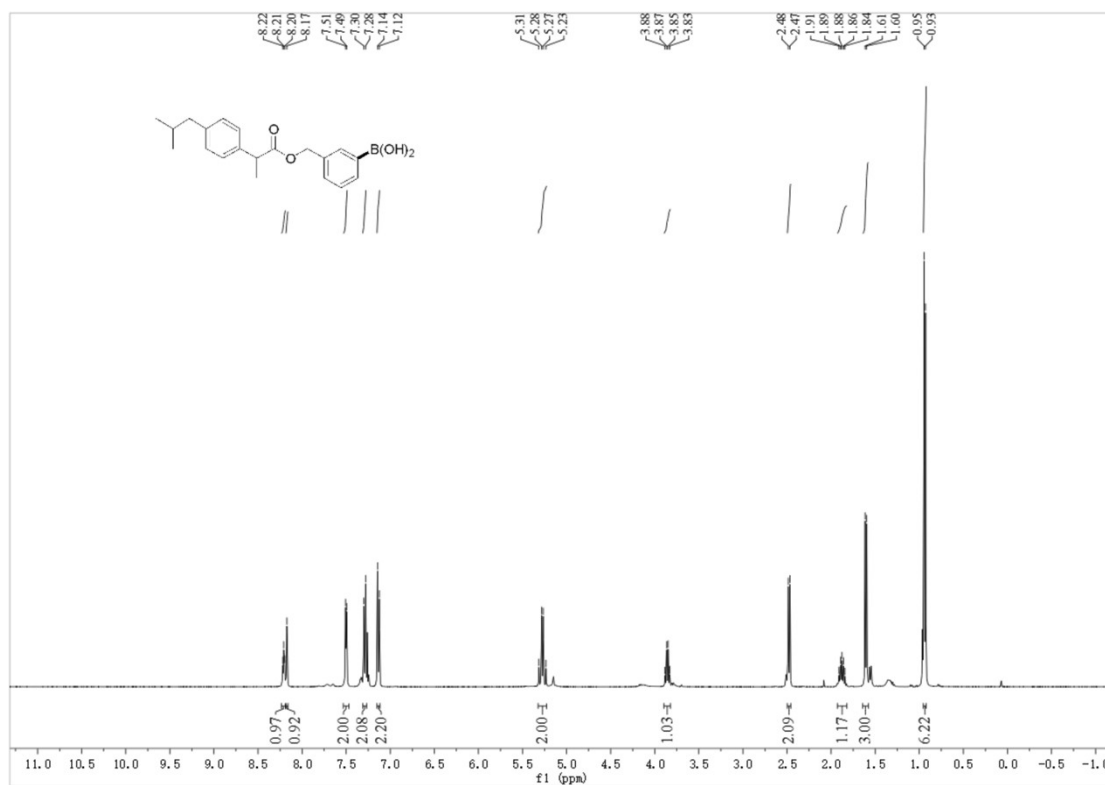
^1H NMR spectrum of **1ah** (CDCl_3 , 400 MHz)



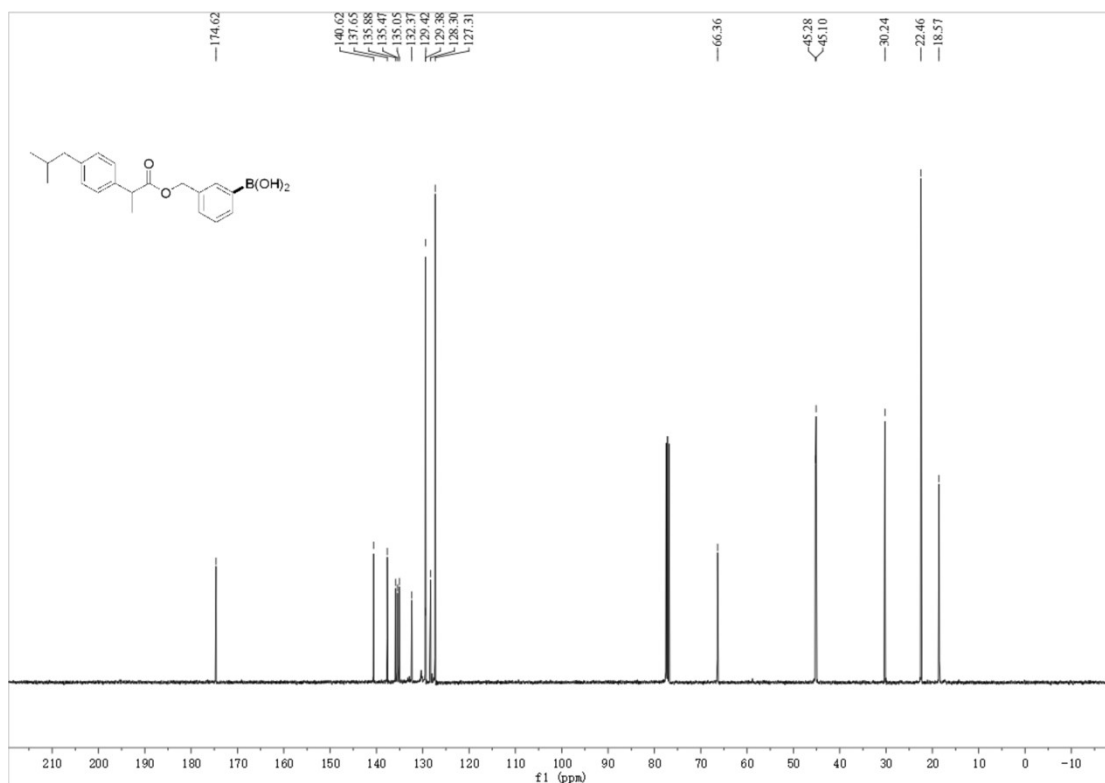
^{13}C NMR spectrum of **1ah** (CDCl_3 , 101 MHz)



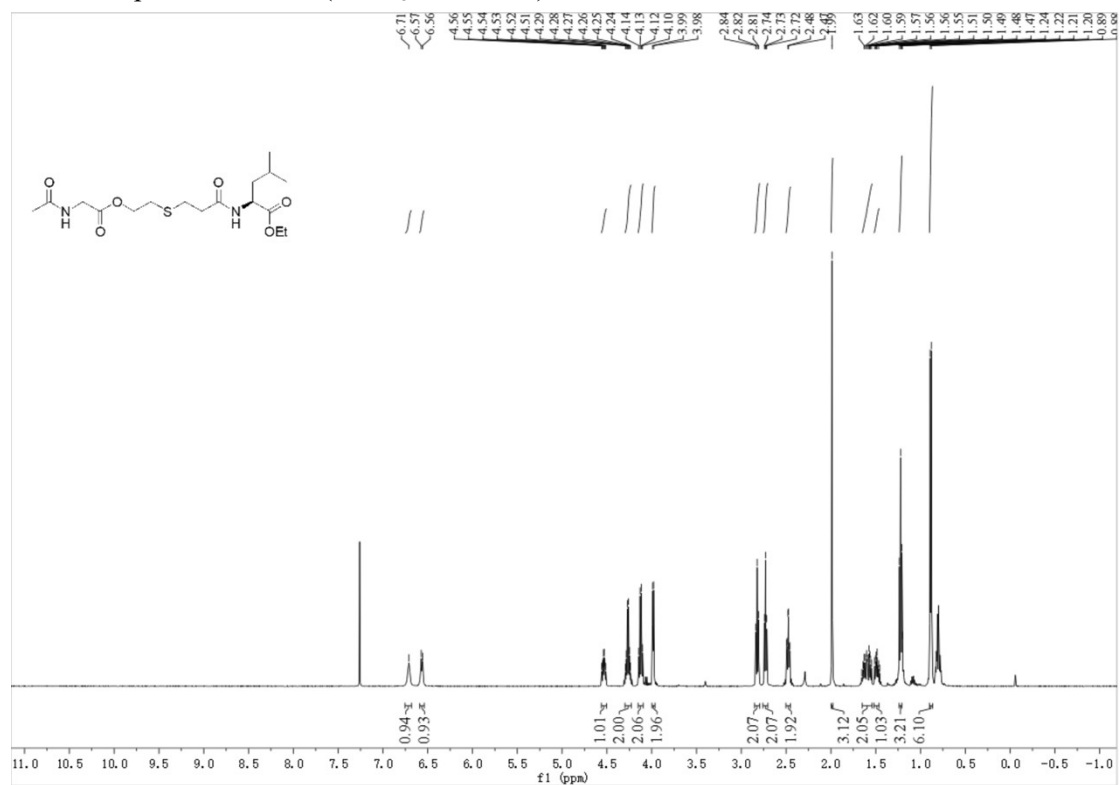
^1H NMR spectrum of **2ai** (CDCl_3 , 400 MHz)



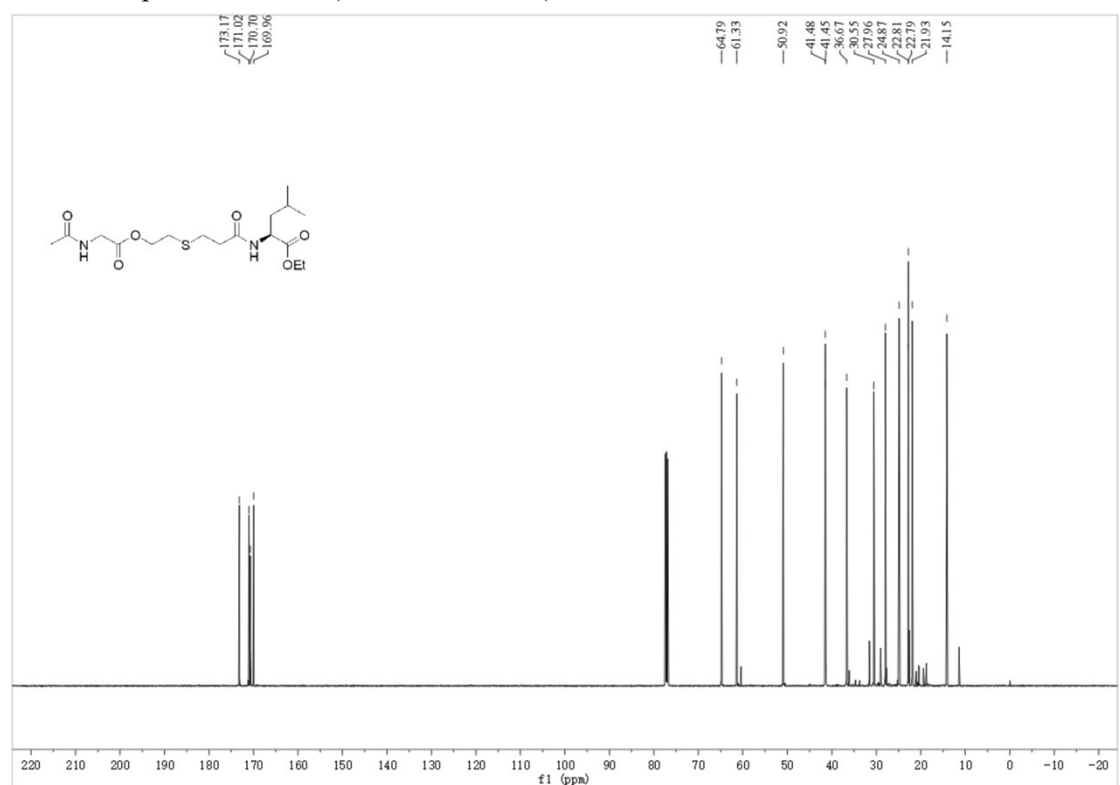
^{13}C NMR spectrum of **2ai** (CDCl_3 , 101 MHz)



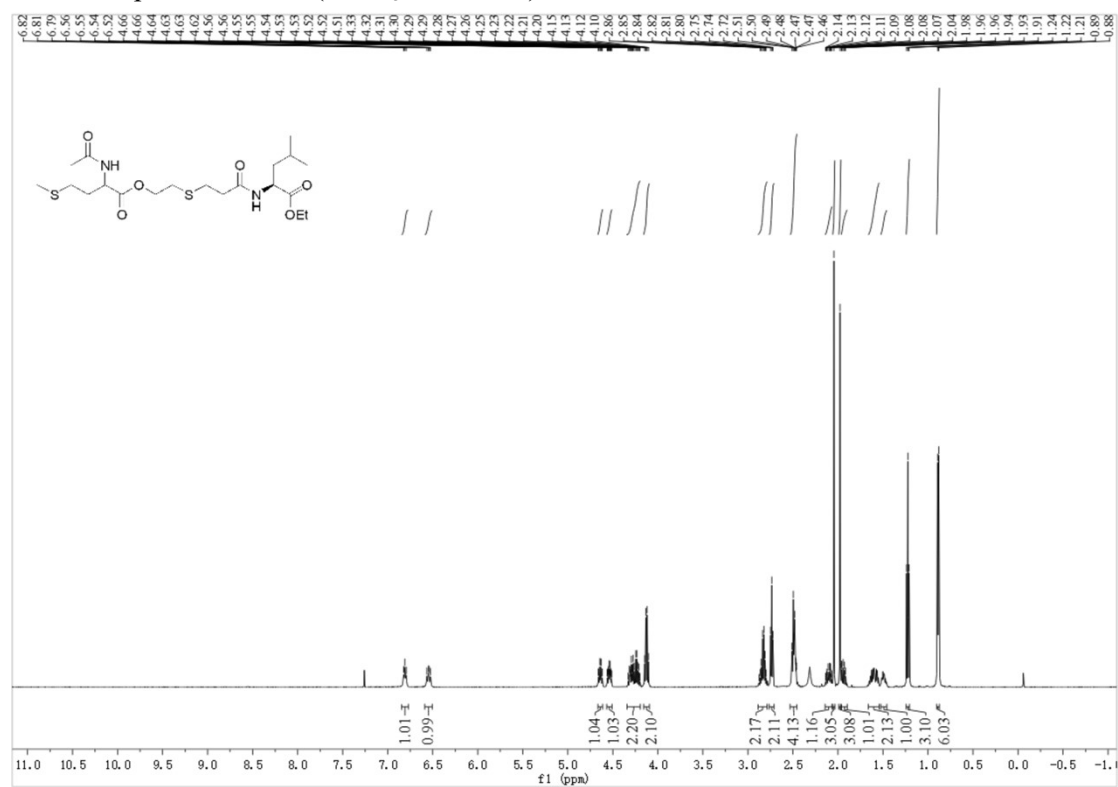
¹H NMR spectrum of **1ak** (CDCl₃, 500 MHz)



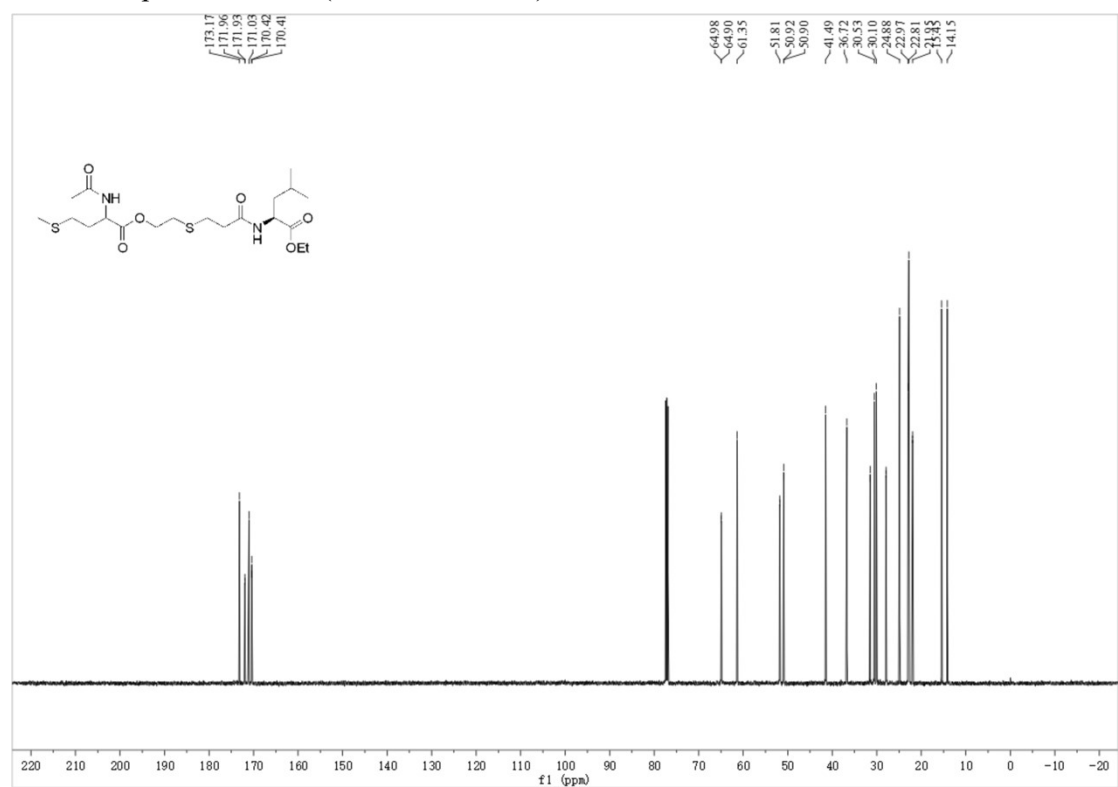
¹³C NMR spectrum of **1ak** (CDCl₃, 126 MHz)



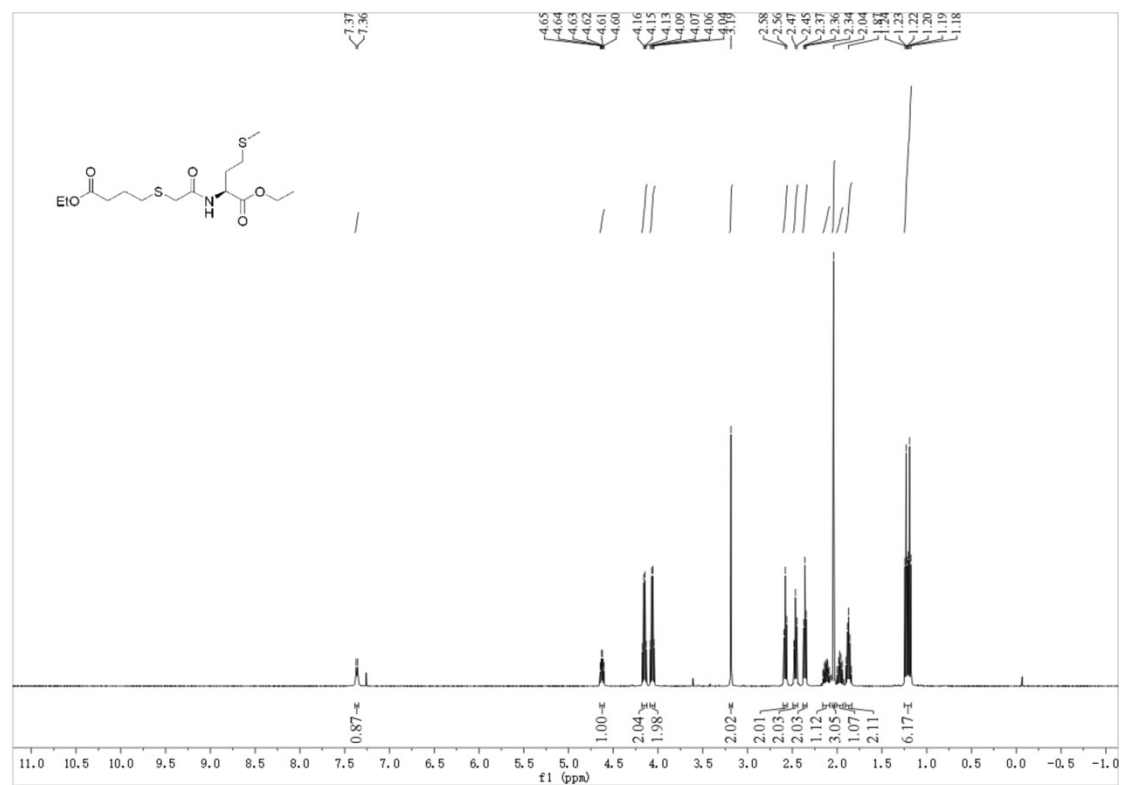
¹H NMR spectrum of **1a1** (CDCl₃, 500 MHz)



¹³C NMR spectrum of **1a1** (CDCl₃, 126 MHz)



^1H NMR spectrum of **1am** (CDCl_3 , 500 MHz)



^{13}C NMR spectrum of **1am** (CDCl_3 , 126 MHz)

