Supporting Information

Synthesis of alkynyl sulfides via base-promoted nucleophilic ring-opening of α-bromostyrene sulfonium salt

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Table of contents

1. General Information

All solvents were dried over molecular sieves. Unless otherwise noted, all materials obtained from commercial suppliers were used without further purification. The products were isolated by column chromatography on silica gel (300-400 mesh) by using petroleum ether (PE, 30-60 °C) and ethyl acetate (EA) as eluents. Silica gel for column chromatography was purchased from Anhui Liang Chen Chemical Co, Lt. All yields described herein are the isolated yields after column chromatography. Reaction progress and product mixtures were routinely monitored by TLC using TLC SiO_2 sheets, and compounds were visualized under ultraviolet light. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400 MHz or 500 MHz spectrometer. Chemical shifts are reported in ppm with the residual solvent signal as the internal standard. For ^{1}H NMR: $CDCl_3$, δ 7.26; CD_3OD, δ 3.31; DMSO-d_6, δ 2.50. For ^{13}C NMR: $CDCl_3$, δ 77.00; CD_3OD, δ 49.00; DMSO-d_6, δ 39.50. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), brs (broad singlet). High–Resolution Mass Spectra (HRMS) were recorded on Agilent 1290UPLC-QTOF-MS (6546). Melting points were measured with a melting point instrument (Shanghai Yidian Physical Optical Instrument Co., Ltd., SGW, and X-4A) and were uncorrected. Known compound *o*-hydroxybenzyl alcohol was prepared by the literature procedure and spectral data in agreement with literature values.[1]

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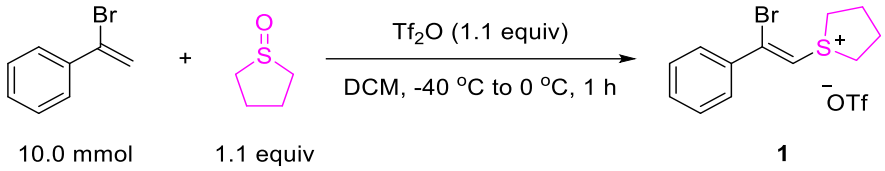
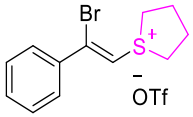
2. Synthesis of *α*-Bromostyrene Sulfonium Salt



10.0 mmol 1.1 equiv **1**

General experimental procedures for the synthesis of *α*-bromostyrene sulfonium salt 1: Under an argon atmosphere, tetramethylene sulfoxide (1.1 equiv, 11.0 mmol) and anhydrous DCM (50 mL) were added to a 100 mL round bottom flask at -40 °C. The Tf_2O (1.1 equiv, 11.0 mmol) was added dropwise under argon, then *α*-bromostyrene (1.0 equiv, 10.0 mmol) was added gradually. The reaction mixture was stirred at -40 °C for 15 min before warming to 0 °C. Upon completion monitored by the TLC, the solvent was removed under reduced pressure. The resulted crude product was dissolved in a small amount of anhydrous DCM, which was slowly dropped into anhydrous ether to precipitate out the alkenyl sulfonium salts solid. The white solid was collected by filtration and washed three times with ether to afford the sulfonium salts **1**.

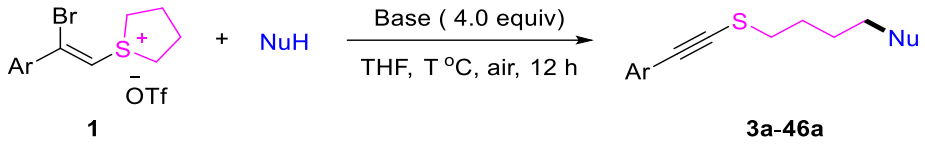


1a

(*Z*)-1-(2-bromo-2-phenylvinyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1): Sulfonium salt **1** was synthesized following the general procedure on 10.0 mmol scale and was obtained as a white solid in 81% (3.4 g). M.p. = 108–110 °C **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.48 – 7.39 (m, 4H), 3.96 – 3.89 (m, 2H), 3.78 – 3.71 (m, 2H), 2.57 – 2.49 (m, 2H), 2.45 – 2.38 (m, 2H). The data is in accordance with the literature.[2]

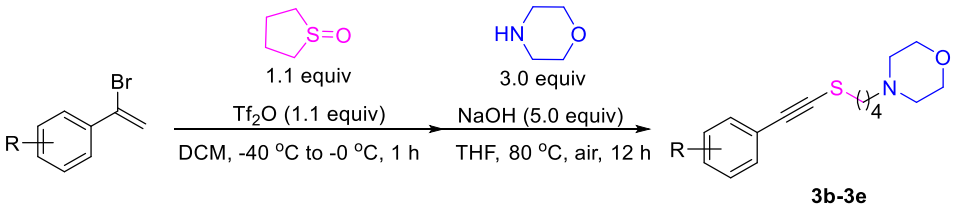
3. General Procedures for the Products

3.1 General Procedures A for the Products



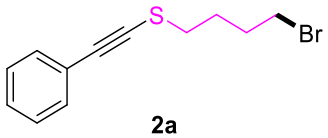
General procedure A for the synthesis of alkynyl sulfides 3a-46a: A 10.0 mL schlenk tube with a stirring bar was added *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 1.0 equiv), nucleophiles (0.9 mmol or 0.6 mmol, 3.0 equiv or 2.0 equiv), NaOH or Cs_2CO_3 (1.2 mmol, 4.0 equiv) and THF (2.0 mL). The reaction mixture was stirred at T ℃ (80 ℃ or 100 ℃) for 12 h in air. After complete consumption of the *α*-bromostyrene sulfonium salt **1a** (monitored by the TLC), the resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA, from 30:1 to 1:1) to afford desired alkynyl sulfide products **3a-46a**.

3.2 General Procedures B for the Products



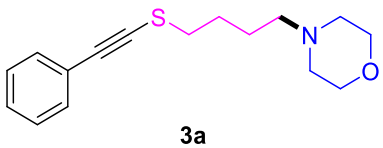
General procedure B for the synthesis of alkynyl sulfides 3b-3e: Under an argon atmosphere, tetramethylene sulfoxide (1.1 equiv, 0.55 mmol) and anhydrous DCM (4.0 mL) were added to a 25.0 mL Schlenk tube at -40 ℃. The Tf_2O (1.1 equiv, 0.55 mmol) was added dropwise under argon, then *α*-bromostyrene [3] (1.0 equiv, 0.5 mmol) was added gradually. The reaction mixture was stirred at -40 ℃ for 15 min before warming to 0 ℃. After stirring for 1 h, the reaction solvent was removed under reduced pressure. Then NaOH (5.0 equiv, 2.5 mmol), morpholine (3.0 equiv, 1.5 mmol), and THF (3.0 mL) were added. The reaction mixture was stirred at 80 ℃ for 12 h in air. The resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA = 1:1) to afford desired alkynyl sulfide products **3b-3e**.

4. Characterization Data of Products



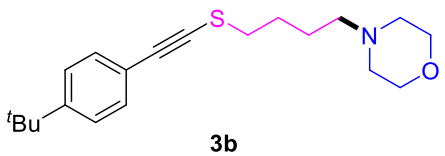
2a

4-Bromobutyl)(phenylethynyl)sulfane (2a): Following the general procedure A, compound **2** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 15:1) as a yellow oil in 85% yield (68.6 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.31 – 7.26 (m, 3H), 3.47 (t, *J* = 6.5 Hz, 2H), 2.83 (t, *J* = 6.8 Hz, 2H), 2.09– 2.03 (m, 2H), 2.02– 1.96 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 131.4, 128.3, 128.1, 123.3, 93.3, 78.9, 34.7, 32.9, 31.0, 27.7. **HRMS** m/z (ESI) calcd for $C_{12}H_{14}SBr$ $(M+H)^+$ 268.9994, found 268.9993.



3a

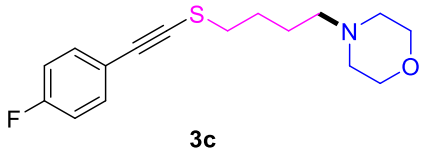
4-(4-((Phenylethynyl)thio)butyl)morpholine (3a): Following the general procedure A, compound **3** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), morphine (0.9 mmol, 78.4 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 2:1) as a yellow oil in 92% yield (75.9 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.31 – 7.27 (m, 3H), 3.71 – 3.69 (m, 4H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.44 – 2.42 (m, 4H), 2.39 – 2.36 (m, 2H), 1.88 – 1.82 (m, 2H), 1.69 – 1.63 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 131.4, 128.3, 128.0, 123.5, 93.0, 79.3, 67.0, 58.6, 53.7, 35.6, 27.1, 25.0. **HRMS** m/z (ESI) calcd for $C_{16}H_{22}NOS$ $(M+H)^+$ 276.1417, found 276.1414.



3b

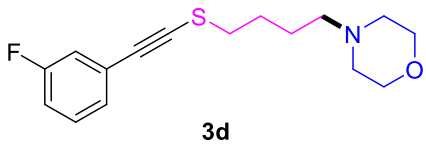
4-(4-(((4-(Tert-butyl)phenyl)ethynyl)thio)butyl)morpholine (3b) : Following the general procedure B, tetramethylene sulfoxide (0.55 mmol, 49.4 μL) and anhydrous DCM (4.0 mL) were added at -40 ℃. The Tf_2O (0.55 mmol, 92.4 μL) and 1-(1-bromovinyl)-4-(tert-butyl)benzene (0.5 mmol, 119.6 mg) were added gradually at -40 ℃ for 15 min before warming to -0 ℃. After stirring for 1 h, the reaction mixture solvent was removed under reduced pressure. Then NaOH (2.5 mmol,

100.0 mg), morpholine (1.5 mmol, 131.2 μL), and THF (3.0 mL) were added at 80 ℃ for 12 h in air. The residue was purified through a silica gel flash column (PE/EA = 1:1) as a yellow oil in 73% yield (121.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 3.70 – 3.68 (m, 4H), 2.79 (t, *J* = 7.1 Hz, 2H), 2.44 – 2.40 (m, 4H), 2.40 – 2.36 (m, 2H), 1.86 – 1.79 (m, 2H), 1.69 – 1.62 (m, 2H), 1.28 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 131.4, 125.3, 120.5, 93.1, 78.4, 66.9, 58.3, 53.7, 35.7, 31.2, 27.2, 25.0. **HRMS** m/z (ESI) calcd for $C_{20}H_{30}NOS$ $(M+H)^+$ 332.2043, found 332.2042.



3c

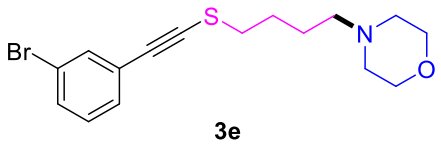
4-(4-(((4-Fluorophenyl)ethynyl)thio)butyl)morpholine (3c)： Following the general procedure B, tetramethylene sulfoxide (0.55 mmol, 49.4 μL) and anhydrous DCM (4.0 mL) were added at -40 ℃. The Tf_2O (0.55 mmol, 92.4 μL) and 1-(1-bromovinyl)-4-fluorobenzen (0.5 mmol, 100.7 mg) were added gradually at -40 ℃ for 15 min before warming to -0 ℃. After stirring for 1 h, the reaction mixture solvent was removed under reduced pressure. Then NaOH (2.5 mmol, 100.0 mg), morpholine (1.5 mmol, 131.2 μL), and THF (3.0 mL) were added at 80 ℃ for 12 h in air. The residue was purified through a silica gel flash column (PE/EA = 1:1) as a yellow oil in 68% yield (99.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 6.99 – 6.93 (m, 2H), 3.68 – 3.66 (m, 4H), 2.79 (t, *J* = 7.1 Hz, 2H), 2.42 – 2.39 (m, 4H), 2.37 – 2.33 (m, 2H), 1.84 – 1.74 (m, 2H), 1.67 – 1.59 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 249.6 Hz), 133.3 (d, *J* = 8.3 Hz), 119.5 (d, *J* = 3.6 Hz), 115.5 (d, *J* = 22.0 Hz), 91.7, 79.0, 66.8, 58.2, 53.6, 35.5, 27.1, 24.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.9. **HRMS** m/z (ESI) calcd for $C_{16}H_{21}FNOS$ $(M+H)^+$ 294.1322, found 294.1317.



3d

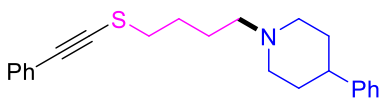
4-(4-(((3-Fluorophenyl)ethynyl)thio)butyl)morpholine (3d)： Following the general procedure B, tetramethylene sulfoxide (0.55 mmol, 49.4 μL) and anhydrous DCM (4.0 mL) were added at -40 ℃. The Tf_2O (0.55 mmol, 92.4 μL) and 1-(1-bromovinyl)-3-fluorobenzene (0.5 mmol, 100.7 mg) were added gradually at -40 ℃ for 15 min before warming to -0 ℃. After stirring for 1 h, the reaction mixture solvent was removed under reduced pressure. Then NaOH (2.5 mmol, 100.0 mg), morpholine (1.5 mmol, 131.2 μL), and THF (3.0 mL) were added at 80 ℃ for 12 h in air. The residue

was purified through a silica gel flash column (PE/EA = 1:1) as a yellow oil in 67% yield (98.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 1H), 7.21 – 7.19 (m, 1H), 7.13 – 7.10 (m, 1H), 7.05 – 7.00 (m, 1H), 3.76 – 3.73 (m, 4H), 2.87 (t, *J* = 7.1 Hz, 2H), 2.50 – 2.47 (m, 4H), 2.45 – 2.41 (m, 2H), 1.92 – 1.85 (m, 2H), 1.75 – 1.67 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.6 Hz), 129.8 (d, *J* = 8.7 Hz), 127.0 (d, *J* = 3.0 Hz), 125.2 (d, *J* = 9.6 Hz), 117.9 (d, *J* = 22.8 Hz), 115.2 (d, *J* = 21.3 Hz), 91.8, 80.9, 66.8, 58.2, 53.6, 35.5, 27.1, 24.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.9. **HRMS** m/z (ESI) calcd for $C_{16}H_{21}FNOS$ $(M+H)^+$ 294.1322, found 294.1321.



3e

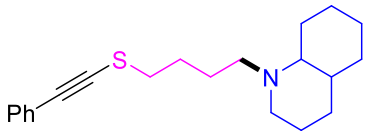
4-(4-(((3-Bromophenyl)ethynyl)thio)butyl)morpholine (3e): Following the general procedure B, tetramethylene sulfoxide (0.55 mmol, 49.4 μL) and anhydrous DCM (4.0 mL) were added at -40 ℃. The Tf_2O (0.55 mmol, 92.4 μL) and 1-bromo-3-(1-bromovinyl)benzene (0.5 mmol, 131.0 mg) were added gradually at -40 ℃ for 15 min before warming to -0 ℃. After stirring for 1 h, the reaction mixture solvent was removed under reduced pressure. Then NaOH (2.5 mmol, 100.0 mg), morpholine (1.5 mmol, 131.2 μL), and THF (3.0 mL) were added at 80 ℃ for 12 h in air. The residue was purified through a silica gel flash column (PE/EA = 1:1) as a colorless oil in 74% yield (131.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 1.7 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.30 – 7.27 (m, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 3.71 – 3.68 (m, 4H), 2.81 (t, *J* = 7.1 Hz, 2H), 2.45 – 2.43 (m, 4H), 2.40 – 2.36 (m, 2H), 1.86 – 1.79 (m, 2H), 1.69 – 1.62 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.8, 131.0, 129.6, 125.4, 122.0, 91.5, 81.4, 66.8, 58.2, 53.6, 35.5, 27.1, 24.8. **HRMS** m/z (ESI) calcd for $C_{16}H_{21}BrNOS$ $(M+H)^+$ 354.0522, found 354.0520.



4a

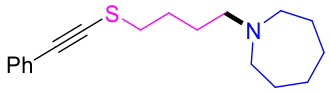
4-Phenyl-1-(4-((phenylethynyl)thio)butyl)piperidine (4a): Following the general procedure A, compound **4a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 4-phenylpiperidine (0.9 mmol, 145.1 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 2:1) as a colorless oil in 72% yield (75.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.45 – 7.40 (m, 2H), 7.32 – 7.28 (m, 5H), 7.24

– 7.18 (m, 3H), 3.08 – 3.05 (m, 2H), 2.85 (t, J = 7.2 Hz, 2H), 2.53 – 2.46 (m, 1H), 2.45 – 2.41 (m, 2H), 2.05 (td, J = 11.4, 3.3 Hz, 2H), 1.90 – 1.78 (m, 6H), 1.76 – 1.69 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.4, 131.4, 128.4, 128.2, 127.9, 126.8, 126.1, 123.5, 93.0, 79.5, 58.4, 54.4, 42.7, 35.7, 33.5, 27.4, 25.7. **HRMS** m/z (ESI) calcd for $C_{23}H_{28}NS$ $(M+H)^+$ 350.1937, found 350.1936.



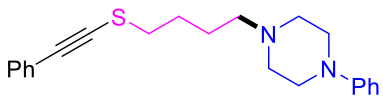
5a (mixture)

1-(4-((Phenylethynyl)thio)butyl)decahydroquinoline (5a): Following the general procedure A, compound **5a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), decahydroquinoline (cis+trans, 0.9 mmol, 125.3 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a colorless oil in 77% yield (75.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.29 – 7.26 (m, 3H), 2.93 – 2.88 (m, 1H), 2.80 (t, J = 7.2 Hz, 2H), 2.75 – 2.68 (m, 1H), 2.51 – 2.44 (m, 1H), 2.22 – 2.16 (m, 1H), 2.06 – 2.02 (m, 1H), 1.78 – 1.69 (m, 4H), 1.63 – 1.53 (m, 7H), 1.29 – 1.04 (m, 4H), 1.02 – 0.90 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.4, 128.2, 127.9, 123.5, 92.9, 79.4, 65.8, 53.5, 52.3, 42.0, 35.7, 33.1, 32.6, 30.2, 27.6, 25.9, 25.8, 25.8, 23.3. **HRMS** m/z (ESI) calcd for $C_{21}H_{30}NS$ $(M+H)^+$ 328.2093, found 328.2095.



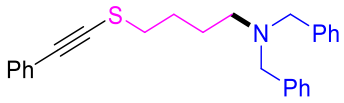
6a

1-(4-((Phenylethynyl)thio)butyl)azepane (6a): Following the general procedure A, compound **6a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), azepane (0.9 mmol, 89.3 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 2:1) as a colorless oil in 69% yield (59.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.30 – 7.27 (m, 3H), 2.82 (t, J = 7.2 Hz, 2H), 2.62 – 2.60 (m, 4H), 2.52 – 2.48 (m, 2H), 1.85 – 1.78 (m, 2H), 1.66 – 1.54 (m, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.4, 128.2, 127.9, 123.5, 92.9, 79.6, 57.6, 55.5, 35.8, 28.1, 27.4, 27.0, 26.2. **HRMS** m/z (ESI) calcd for $C_{18}H_{26}NS$ $(M+H)^+$ 288.1780, found 288.1781.



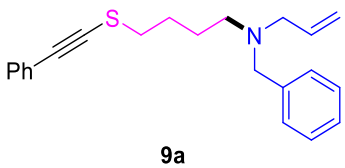
7a

1-Phenyl-4-(4-((phenylethynyl)thio)butyl)piperazine (7a): Following the general procedure A, compound **7a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 1-phenylpiperazine (0.9 mmol, 146.0 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 3:1) as a colorless oil in 85% yield (89.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.28 – 7.22 (m, 5H), 6.91 – 6.88 (m, 2H), 6.85 – 6.82 (m, 1H), 3.18 – 3.16 (m, 4H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.59 – 2.57 (m, 4H), 2.44 – 2.41 (m, 2H), 1.88 –1.83 (m, 2H), 1.72 –1.66 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.3, 131.4, 129.0, 128.2, 127.9, 119.6, 115.9, 93.0, 79.4, 57.9, 53.2, 49.1, 35.6, 27.2, 25.4. **HRMS** m/z (ESI) calcd for $C_{22}H_{27}N_2S$ $(M+H)^+$ 351.1889, found 351.1889.



8a

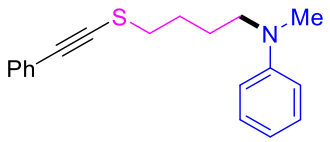
***N,N*-Dibenzyl-4-((phenylethynyl)thio)butan-1-amine (8a):** Following the general procedure A, compound **8a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 1-dibenzylamine (0.9 mmol, 177.6 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 82% yield (94.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 6H), 7.29 –7.25 (m, 7H), 7.22 – 7.18 (m, 2H), 3.54 (s, 4H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 6.8 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.69 – 1.62 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 131.4, 128.8, 128.2, 128.8, 127.9, 126.8, 123.5, 92.9, 79.5, 58.3, 52.4, 35.4, 26.8, 25.5. **HRMS** m/z (ESI) calcd for $C_{26}H_{28}NS$ $(M+H)^+$ 386.1937, found 386.1933.



9a

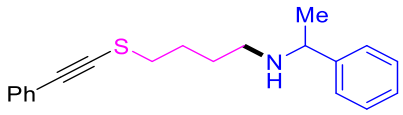
***N*-Allyl-*N*-benzyl-4-((phenylethynyl)thio)butan-1-amine (9a):** Following the general procedure A, compound **9a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg),

N-benzylprop-2-en-1-amine (0.9 mmol, 132.5 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 4:1) as a colorless oil in 81% yield (81.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.32 – 7.25 (m, 7H), 7.22 – 7.19 (m, 1H), 5.92 – 5.82 (m, 1H), 5.20 – 5.10 (m, 2H), 3.55 (s, 2H), 3.06 (d, *J* = 6.3 Hz, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.46 (t, *J* = 7.0 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.67 – 1.60 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 136.0, 131.4, 128.8, 128.2, 128.1, 127.9, 126.7, 123.6, 117.1, 92.9, 79.6, 58.2, 56.7, 52.5, 35.6, 27.0, 25.6. **HRMS** m/z (ESI) calcd for $C_{22}H_{26}NS$ $(M+H)^+$ 336.1780, found 336.1783.



10a

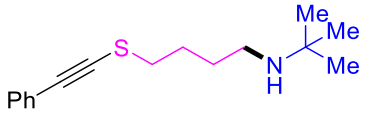
***N*-Methyl-*N*-(4-((phenylethynyl)thio)butyl)aniline (10a):** Following the general procedure A, compound **10a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), *N*-methylaniline (0.9 mmol, 87.4 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 67% yield (59.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.27 – 7.26 (m, 3H), 7.22 – 7.18 (m, 2H), 6.70 – 6.65 (m, 3H), 3.34 (t, *J* = 7.1 Hz, 2H), 2.91 (s, 3H), 2.79 (t, *J* = 7.0 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.76 – 1.69 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 131.4, 129.1, 128.2, 123.4, 116.2, 112.2, 93.2, 79.3, 52.2, 38.3, 35.6, 27.0, 25.5. **HRMS** m/z (ESI) calcd for $C_{19}H_{22}NS$ $(M+H)^+$ 296.1467, found 296.1463.



11a

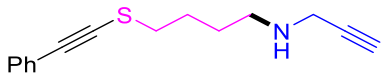
***N*-(1-Phenylethyl)-4-((phenylethynyl)thio)butan-1-amine (11a):** Following the general procedure A, compound **11a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), *α*-methylbenzylamine (0.9 mmol, 109.1 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a colorless oil in 65% yield (60.3 mg).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.31 – 7.22 (m, 8H), 3.76 (q, *J* = 6.6 Hz, 1H), 2.75 (t, *J* = 7.2 Hz, 2H), 2.58 – 2.52 (m, 1H), 2.49 – 2.43 (m,

1H), 1.88 – 1.72 (m, 2H), 1.70 – 1.56 (m, 2H), 1.35 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 131.4, 128.4, 128.2, 127.9, 126.9, 126.5, 123.5, 93.0, 79.4, 58.3, 47.0, 35.6, 28.7, 27.1, 24.2. **HRMS** m/z (ESI) calcd for $C_{20}H_{24}NS$ $(M+H)^+$ 310.1624, found 310.1625.



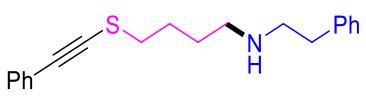
12a

***N*-(Tert-butyl)-4-((phenylethynyl)thio)butan-1-amine (12a):** Following the general procedure A, compound **12a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), *tert*-butylamine (0.9 mmol, 65.9 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 60% yield (47.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.30 – 7.27 (m, 3H), 2.81 (t, J = 7.3 Hz, 2H), 2.59 (t, J = 7.3 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.65 – 1.57 (m, 2H), 1.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.4, 128.2, 127.9, 123.5, 93.0, 79.5, 50.2, 42.0, 35.7, 29.8, 29.0, 27.4. **HRMS** m/z (ESI) calcd for $C_{16}H_{24}NS$ $(M+H)^+$ 262.1624, found 262.1627.



13a

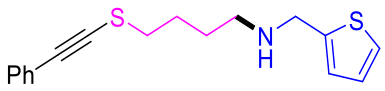
4-((Phenylethynyl)thio)-*N*-(prop-2-yn-1-yl)butan-1-amine (13a): Following the general procedure A, compound **13a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), propargylamine (0.9 mmol, 49.6 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 66% yield (48.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.30 – 7.26 (m, 3H), 3.44 (d, J = 2.4 Hz, 2H), 2.82 (t, J = 7.2 Hz, 2H), 2.75 (t, J = 7.2 Hz, 2H), 2.22 (t, J = 2.4 Hz, 1H), 2.02 (brs, 1H), 2.02 – 1.83 (m, 2H), 1.71 – 1.63 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.4, 128.2, 127.9, 123.4, 93.0, 81.8, 79.3, 71.5, 47.8, 38.0, 35.5, 28.1, 27.0. **HRMS** m/z (ESI) calcd for $C_{15}H_{18}NS$ $(M+H)^+$ 244.1154, found 244.1159.



14

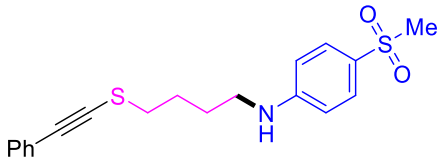
***N*-Phenethyl-4-((phenylethynyl)thio)butan-1-amine (14a):** Following the general procedure A,

compound **14a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), *β*-phenylethylamine (0.9 mmol, 109.1 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 2:1) as a colorless oil in 61% yield (56.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.23 – 7.20 (m, 3H), 2.89 (t, *J* = 6.9 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 4H), 2.68 (t, *J* = 7.2 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.68 – 1.61 (m, 2H), 1.33 (brs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 131.3, 128.6, 128.4, 128.2, 127.9, 126.1, 123.5, 93.0, 79.4, 51.1, 49.2, 36.4, 35.6, 28.6, 27.1. **HRMS** m/z (ESI) calcd for $C_{20}H_{24}NS$ $(M+H)^+$ 310.1624, found 310.1628.



15a

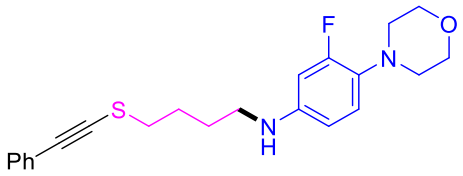
4-((Phenylethynyl)thio)-*N*-(thiophen-2-yl-methyl)butan-1-amine (15a): Following the general procedure A, compound **15a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 2-thiophenemethylamine (0.9 mmol, 101.9 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a yellow oil in 56% yield (50.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.30 – 7.28 (m, 3H), 7.20 (d, *J* = 5.0 Hz, 1H), 6.95 – 6.91 (m, 2H), 4.00 (s, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.1 Hz, 2H), 1.91 – 1.84 (m, 2H), 1.72 – 1.65 (m, 2H), 1.45 (brs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 131.4, 128.2, 127.9, 126.6, 124.7, 124.2, 123.5, 93.0, 79.4, 48.5, 48.4, 35.7, 28.5, 27.1. **HRMS** m/z (ESI) calcd for $C_{17}H_{20}NS_2$ $(M+H)^+$ 302.1032, found 302.1031.



16a

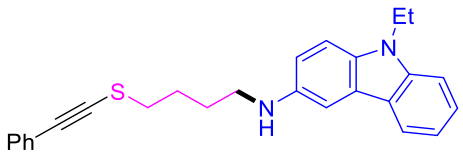
4-(Methylsulfonyl)-*N*-(4-((phenylethynyl)thio)butyl)aniline (16a): Following the general procedure A, compound **16a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 4-(methylsulfonyl)aniline (0.9 mmol, 154.1 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 1:1) as a white solid in 56% yield (60.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.8 Hz, 2H),

7.38 (dd, J = 6.6, 3.0 Hz, 2H), 7.30 – 7.27 (m, 3H), 6.58 (d, J = 8.8 Hz, 2H), 4.42 (s, 1H), 3.24 – 3.20 (m, 2H), 2.98 (s, 3H), 2.83 (t, J = 6.8 Hz, 2H), 1.94 – 1.89 (m, 2H), 1.85 – 1.78 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 131.3, 129.3, 128.3, 128.1, 127.1, 123.2, 111.7, 93.3, 78.9, 45.0, 42.7, 35.2, 27.5, 26.5. **HRMS** m/z (ESI) calcd for $C_{19}H_{22}NO_2S_2$ $(M+H)^+$ 360.1086, found 360.1087.



17a

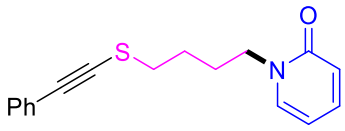
3-Fluoro-4-morpholino-*N*-(4-((phenylethynyl)thio)butyl)aniline (17a): Following the general procedure A, compound **17a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 3-fluoro-4-morpholinoaniline (0.9 mmol, 176.6 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 4:1) as a yellow oil in 75% yield (86.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 –7.39 (m, 2H), 7.31 – 7.28 (m, 3H), 6.81 (t, J = 9.0 Hz, 1H), 6.36 – 6.29 (m, 2H), 3.86 – 3.84 (m, 4H), 3.10 (t, J = 6.9 Hz, 2H), 2.97 – 2.95 (m, 4H), 2.83 (t, J = 7.0 Hz, 2H), 1.95 – 1.88 (m, 2H), 1.80 – 1.73 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 1567.0 (d, J = 244.7 Hz), 145.0 (d, J = 10.3 Hz), 131.2, 130.4(d, J = 9.8 Hz), 128.2, 127.9, 123.2, 120.3 (d, J = 4.5 Hz), 108.1 (d, J = 2.6 Hz), 101.2 (d, J = 24.3 Hz), 93.2, 79.1, 77.2, 67.0, 51.73, 51.71, 43.6, 35.2, 27.8, 26.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.7. **HRMS** m/z (ESI) calcd for $C_{22}H_{26}FN_2OS$ $(M+H)^+$ 385.1744, found 385.1743.



18a

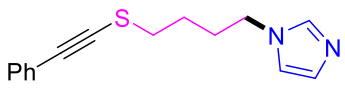
9-Ethyl-*N*-(4-((phenylethynyl)thio)butyl)-9*H*-carbazol-3-amine (18a): Following the general procedure A, compound **18a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 3-amino-9-ethylcarbazole (0.9 mmol, 189.3 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a dark oil in 65% yield (77.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.8 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.37 (dd, J = 5.2, 2.9 Hz, 2H), 7.34 – 7.32 (m, 3H), 7.26 (d, J = 8.6 Hz, 1H), 7.22 – 7.18 (m, 1H), 6.89 (dd, J = 8.6, 2.3 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 3.31 (t, J = 7.0 Hz,

2H), 2.90 (t, J = 7.1 Hz, 2H), 2.05 – 1.99 (m, 2H), 1.92 – 1.86 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.6, 140.2, 134.0, 131.4, 128.3, 128.0, 125.2, 123.6, 123.4, 122.6, 120.3, 117.8, 114.5, 109.1, 108.3, 103.3, 93.2, 79.3, 45.0, 37.4, 35.4, 28.2, 26.9, 13.8. **HRMS** m/z (ESI) calcd for $C_{26}H_{27}N_2S$ $(M+H)^+$ 399.1889, found 399.1887.



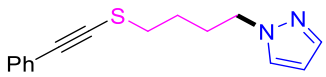
19a

1-(4-((Phenylethynyl)thio)butyl)pyridin-2(1*H*)-one (19a): Following the general procedure A, compound **19a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 2-thiophenemethylamine (0.9 mmol, 101.9 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 82% yield (70.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.29 – 7.24 (m, 5H), 6.54 (d, J = 9.1 Hz, 1H), 6.13 – 6.09 (m, 1H), 3.97 (t, J = 7.0 Hz, 2H), 2.82 (t, J = 6.8 Hz, 2H), 1.97 – 1.82 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 139.2, 137.2, 131.3, 128.1, 127.9, 123.2, 121.0, 105.9, 93.2, 78.9, 48.9, 35.0, 27.6, 26.1. **HRMS** m/z (ESI) calcd for $C_{17}H_{18}NOS$ $(M+H)^+$ 284.1104, found 284.1107.



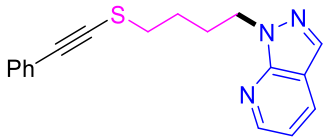
20a

1-(4-((Phenylethynyl)thio)butyl)-1*H*-imidazole (20a): Following the general procedure A, compound **20a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), imidazole (0.6 mmol, 40.8 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 °C for 12 h. The residue was purified through a silica gel flash column (PE/EA = 2:1) as a colorless oil in 64% yield (49.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.38 – 7.36 (m, 2H), 7.29 – 7.26 (m, 3H), 7.03 (s, 1H), 6.90 (s, 1H), 3.97 (t, J = 7.0 Hz, 2H), 2.76 (t, J = 6.9 Hz, 2H), 1.98 – 1.91 (m, 2H), 1.82 – 1.75 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 131.3, 129.4, 128.2, 128.1, 123.1, 118.6, 93.3, 78.6, 46.4, 34.9, 29.4, 26.1. **HRMS** m/z (ESI) calcd for $C_{15}H_{17}N_2S$ $(M+H)^+$ 257.1107, found 257.1108.



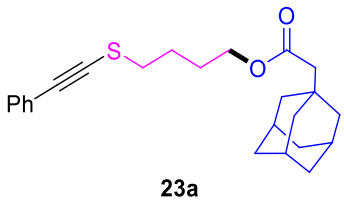
21a

1-(4-((Phenylethynyl)thio)butyl)-1*H*-pyrazole (21a): Following the general procedure A, compound **21a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), pyrazole (0.6 mmol, 40.8 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 1:1) as a colorless oil in 56% yield (43.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 1.5 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.31 – 7.27 (m, 3H), 6.22 (t, *J* = 2.1 Hz, 1H), 4.19 (t, *J* = 6.9 Hz, 2H), 2.78 (t, *J* = 7.1 Hz, 2H), 2.09 – 2.02 (m, 2H), 1.84 – 1.77 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 131.4, 128.9, 128.2, 128.0, 123.4, 105.4, 93.3, 79.0, 51.45, 35.09, 28.91, 26.31. **HRMS** m/z (ESI) calcd for $C_{15}H_{17}N_2S$ $(M+H)^+$ 257.1107, found 257.1102.



22a

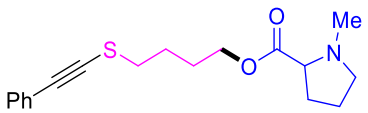
1-(4-((Phenylethynyl)thio)butyl)-1*H*-pyrazolo[3,4-b]pyridine (22a) : Following the general procedure A, compound **22a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 1*H*-pyrazolo[3,4-b]pyridine (0.6 mmol, 71.5 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 1:1) as a colorless oil in 62% yield (57.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 4.2, 1.7 Hz, 1H), 7.97 (d, *J* = 1.7 Hz, 1H), 7.95 – 7.94 (m, 1H), 7.34 – 7.30 (m, 2H), 7.29 – 7.25 (m, 3H), 7.01 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.50 (t, *J* = 6.9 Hz, 2H), 2.80 (t, *J* = 7.0 Hz, 2H), 2.28 – 2.20 (m, 2H), 1.86 – 1.79 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3, 151.2, 131.3, 129.5, 128.2, 128.0, 123.1, 122.5, 117.6, 113.8, 93.3, 78.7, 53.6, 34.8, 28.7, 26.1. **HRMS** m/z (ESI) calcd for $C_{18}H_{18}N_3S$ $(M+H)^+$ 308.1216, found 308.1220.



23a

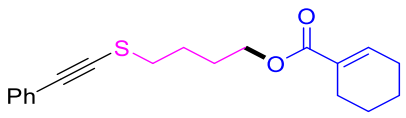
4-((Phenylethynyl)thio)butyl 2-(adamantan-1-yl)acetate (23a): Following the general procedure

A, compound **23a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 1-adamantaneacetic acid (0.9 mmol, 174.9 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 20:1) as a colorless oil in 71% yield (81.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.30 –7.27 (m, 3H), 4.10 (t, *J* = 6.3 Hz, 2H), 2.83 (t, *J* = 7.0 Hz, 2H), 2.05 (s, 2H), 1.97 –1.93 (m, 3H), 1.92 – 1.88 (m, 2H), 1.84 – 1.79 (m, 2H), 1.70 – 1.59 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.8, 131.4, 128.2, 128.0, 123.4, 93.1, 79.0, 63.2, 48.9, 42.4, 36.7, 35.2, 32.7, 28.5, 27.3, 25.9. **HRMS** m/z (ESI) calcd for $C_{24}H_{31}O_2S$ $(M+H)^+$ 383.2039, found 383.2037.



24a

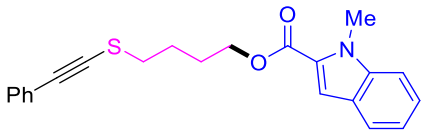
4-((Phenylethynyl)thio)butyl methylprolinate (24a): Following the general procedure A, compound **24a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), *N*-methyl-L-proline (0.9 mmol, 116.2 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 2:1) as a yellow oil in 60% yield (57.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.29 – 7.27 (m, 3H), 4.21– 4.17 (m, 2H), 3.13 – 3.08 (m, 1H), 2.97 – 2.93 (m, 1H), 2.81 (t, J = 6.7 Hz, 2H), 2.39 (s, 3H), 2.32 – 2.26 (m, 1H), 2.15 – 2.05 (m, 1H), 1.98 – 1.81(m, 6H), 1.77 – 1.69 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 131.3, 128.2, 127.9, 123.3, 93.1, 79.0, 67.4, 63.8, 56.2, 40.8, 35.1, 29.6, 27.2, 25.8, 23.0. **HRMS** m/z (ESI) calcd for $C_{18}H_{24}NO_2S$ $(M+H)^+$ 318.1522, found 318.1518.



25a

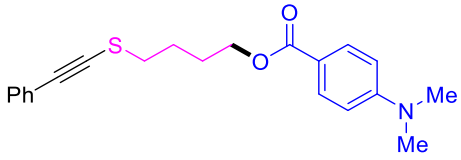
4-((Phenylethynyl)thio)butyl cyclohex-1-ene-1-carboxylate (25a): Following the general procedure A, compound **25a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 1-Cyclohexene-1-carboxylic acid (0.9 mmol, 113.5 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 68% yield (64.1 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.31 – 7.27 (m, 3H), 6.98 – 6.96 (m, 1H), 4.18 (t, *J* = 6.2 Hz, 2H), 2.83 (t, *J* = 7.0 Hz, 2H), 2.26 – 2.22 (m, 2H), 2.16 – 2.12 (m, 2H), 1.96 – 1.90 (m, 2H), 1.89 – 1.82 (m, 2H), 1.65 – 1.55 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 139.7, 131.4, 130.2, 128.2, 128.0, 123.4, 93.2, 79.0, 63.5, 35.2, 27.3, 25.9, 25.7, 24.1, 22.0, 21.4. **HRMS** m/z (ESI) calcd for $C_{19}H_{23}O_2S$ $(M+H)^+$ 315.1314, found 315.1308.



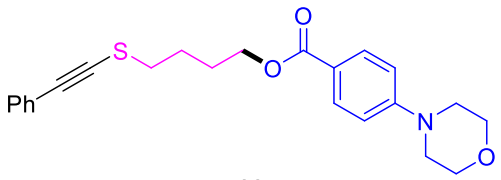
26a

4-((Phenylethynyl)thio)butyl 1-methyl-1*H*-indole-2-carboxylate (26a): Following the general procedure A, compound **26a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 1-methyl-1*H*-indole-2-carboxylic acid (0.9 mmol, 157.7 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 66% yield (72.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.32 (m, 4H), 7.28 (s, 1H), 7.24 – 7.17 (m, 3H), 7.14 – 7.10 (m, 1H), 4.36 (t, *J* = 5.9 Hz, 2H), 4.03 (s, 3H), 2.85 (t, *J* = 6.7 Hz, 2H), 2.04 – 1.91 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 139.6, 131.3, 128.2, 128.0, 127.7, 125.8, 124.9, 123.3, 122.5, 120.5, 110.2, 93.3, 79.0, 63.7, 35.2, 31.5, 27.3, 25.9. **HRMS** m/z (ESI) calcd for $C_{22}H_{22}NO_2S$ $(M+H)^+$ 364.1366, found 364.1364.



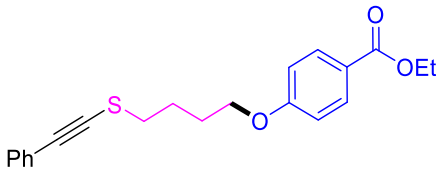
27a

4-((Phenylethynyl)thio)butyl 4-(dimethylamino)benzoate (27a); Following the general procedure A, compound **27a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 4-(dimethylamino)benzoic acid (0.9 mmol, 148.7 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 3:1) as a yellow oil in 67% yield (71.0 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 2H), 7.41 – 7.39 (m, 2H), 7.29 – 7.26 (m, 3H), 6.61 – 6.58 (m, 2H), 4.32 (t, *J* = 6.1 Hz, 2H), 3.00 (s, 6H), 2.86 (t, *J* = 7.0 Hz, 2H), 2.07 – 1.93 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 153.2, 131.4, 131.2, 128.2, 127.9, 123.4, 116.9, 110.6, 93.1, 79.1, 63.4, 40.0, 35.2, 27.4, 26.0. **HRMS** m/z (ESI) calcd for $C_{21}H_{24}NO_2S$ $(M+H)^+$ 354.1522, found 354.1520.



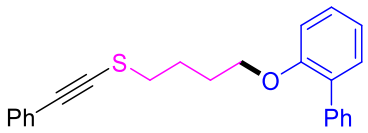
28a

4-((Phenylethynyl)thio)butyl 4-morpholinobenzoate (28a): Following the general procedure A, compound **28a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 4-morpholinobenzoic acid (0.9 mmol, 186.5 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 3:1) as a colorless oil in 65% yield (77.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.40 – 7.36 (m, 2H), 7.30 – 7.24 (m, 3H), 6.83 – 6.74 (m, 2H), 4.33 (t, J = 6.0 Hz, 2H), 3.85 – 3.82 (m, 4H), 3.25 – 3.23 (m, 4H), 2.86 (t, J = 6.8 Hz, 2H), 2.03 – 1.90 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 154.1, 131.4, 131.1, 128.2, 127.9, 123.4, 120.3, 113.4, 93.2, 79.1, 66.5, 63.7, 47.6, 35.2, 27.6, 25.9. **HRMS** m/z (ESI) calcd for $C_{23}H_{26}NO_3S$ $(M+H)^+$ 396.1628, found 396.1630.



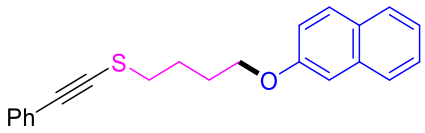
29a

Ethyl 4-(4-((phenylethynyl)thio)butoxy)benzoate (29a): Following the general procedure A, compound **29a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), ethyl 4-hydroxybenzoate (0.6 mmol, 99.7 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a colorless oil in 55% yield (58.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.42 – 7.38 (m, 2H), 7.30 – 7.26 (m, 3H), 6.91 – 6.88 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.06 (t, J = 5.6 Hz, 2H), 2.88 (t, J = 6.6 Hz, 2H), 2.05 – 1.97 (m, 4H), 1.38 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 162.6, 131.5, 131.4, 128.2, 128.0, 123.4, 122.9, 114.0, 93.2, 79.1, 67.4, 60.6, 35.3, 27.6, 25.9, 14.3. **HRMS** m/z (ESI) calcd for $C_{21}H_{23}O_3S$ $(M+H)^+$ 355.1362, found 355.1366.



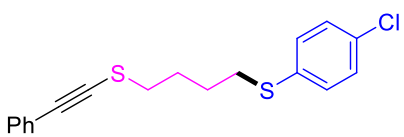
30a

(4-([1,1'-Biphenyl]-2-yloxy)butyl)(phenylethynyl)sulfane (30a): Following the general procedure A, compound **30a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 2-phenylphenol (0.6 mmol, 102.1 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a colorless oil in 72% yield (77.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.1 Hz, 2H), 7.42 – 7.28 (m, 10H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 4.04 – 4.01 (m, 2H), 2.79 – 2.76 (m, 2H), 1.96 – 1.88 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.8, 131.4, 131.1, 130.9, 129.5, 128.5, 128.2, 128.0, 127.8, 126.8, 123.5, 121.0, 112.6, 93.0, 79.4, 67.9, 35.4, 27.7, 26.2. **HRMS** m/z (ESI) calcd for $C_{24}H_{23}OS$ $(M+H)^+$ 359.1464, found 359.1469.



31a

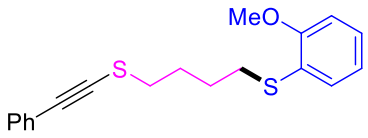
(4-(Naphthalen-2-yloxy)butyl)(phenylethynyl)sulfane (31a): Following the general procedure A, compound **31a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 2-naphthol (0.6 mmol, 86.5 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a yellow oil in 73% yield (72.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 3H), 7.50 – 7.46 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.31 (m, 3H), 7.230 – 7.16 (m, 2H), 4.15 (t, *J* = 5.7 Hz, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 2.14 – 2.02 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.8, 134.5, 131.4, 129.3, 128.9, 128.2, 128.0, 127.6, 126.7, 126.3, 123.5, 123.4, 118.8, 106.6, 93.2, 79.3, 67.2, 35.1, 27.7, 26.0. **HRMS** m/z (ESI) calcd for $C_{22}H_{21}OS$ $(M+H)^+$ 333.1308, found 333.1303.



32a

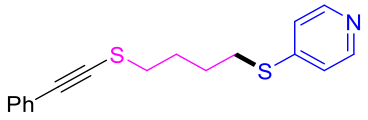
(4-Chlorophenyl)(4-((phenylethynyl)thio)butyl)sulfane (32a): Following the general procedure

A, compound **32a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 4-chlorothiophenol (0.6 mmol, 86.8 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 15:1) as a yellow oil in 67% yield (66.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.30 – 7.27 (m, 3H), 7.25 – 7.20 (m, 4H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.1 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.82 – 1.76 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.9, 131.9, 131.4, 130.6, 129.0, 128.3, 128.0, 123.3, 93.2, 79.0, 35.1, 33.5, 28.2, 27.4. **HRMS** m/z (ESI) calcd for $C_{18}H_{18}ClS_2$ $(M+H)^+$ 333.0533, found 333.0528.



33a

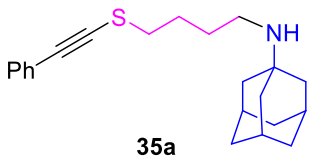
(2-Methoxyphenyl)(4-((phenylethynyl)thio)butyl)sulfane (33a): Following the general procedure A, compound **33a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 2-methoxybenzenethiol (0.6 mmol, 84.1 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 15:1) as a yellow oil in 75% yield (73.9 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.31 – 7.26 (m, 4H), 7.21 – 7.18 (m, 1H), 6.92 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.89 (s, 3H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.01 – 1.95 (m, 2H), 1.86 – 1.80 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.3, 131.4, 129.5, 128.2, 127.9, 127.1, 124.3, 123.4, 121.0, 110.4, 93.1, 79.2, 55.7, 35.2, 31.5, 28.3, 27.4. **HRMS** m/z (ESI) calcd for $C_{19}H_{21}OS_2$ $(M+H)^+$ 329.1028, found 329.1026.



34a

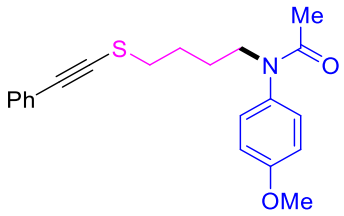
4-((4-((Phenylethynyl)thio)butyl)thio)pyridine (34a): Following the general procedure A, compound **34a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), 4-pyridinethiol (0.6 mmol, 66.7 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 1:1) as a colorless oil in 85% yield (76.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 5.3 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.29 – 7.26 (m, 3H), 7.08 (dd, *J* = 4.7, 1.5 Hz, 2H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.81 (t, *J* = 6.9 Hz, 2H), 2.00

– 1.95 (m, 2H), 1.92– 1.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.1, 148.9, 131.3, 128.2, 128.0, 123.2, 120.6, 93.3, 78.8, 34.9, 30.1, 28.2, 26.8. **HRMS** m/z (ESI) calcd for $C_{17}H_{18}NS_2$ $(M+H)^+$ 300.0875, found 300.0878.



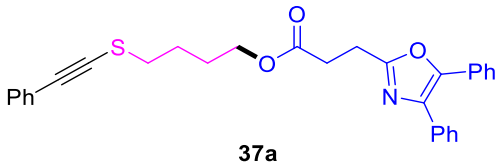
35a

***N*-(4-((Phenylethynyl)thio)butyl)adamantan-1-amine (35a):** Following the general procedure A, compound **35a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Amantadine (0.9 mmol, 136.1 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a white solid in 71% yield (72.3 mg). M.p. = 110-112 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.30 – 7.27 (m, 3H), 6.65 (s, 1H), 2.94 – 2.91 (m, 2H), 2.79 (t, *J* = 6.5 Hz, 2H), 2.17 (s, 3H), 1.95 – 1.85 (m, 10H), 1.71 – 1.63 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.5, 128.2, 128.1, 123.3, 93.4, 78.6, 57.8, 39.8, 38.5, 35.5, 34.8, 29.0, 26.5, 25.4. **HRMS** m/z (ESI) calcd for $C_{22}H_{30}NS$ $(M+H)^+$ 340.2093, found 340.2093.



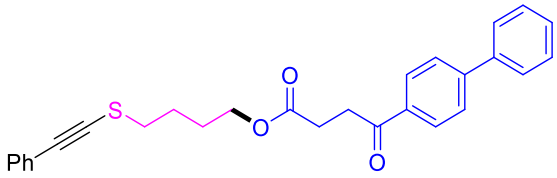
36a

***N*-(4-Methoxyphenyl)-*N*-(4-((phenylethynyl)thio)butyl)acetamide (36a):** Following the general procedure A, compound **36a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Methacetin (0.9 mmol, 148.7 mg), NaOH (1.2 mmol, 48.0 mg) in THF (2.0 mL) at 80 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 4:1) as a yellow oil in 72% yield (76.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.30 – 7.27 (m, 3H), 7.10 – 7.06 (m, 2H), 6.91 – 6.88 (m, 2H), 3.81 (s, 3H), 3.72 (t, *J* = 7.3 Hz, 2H), 2.80 (t, *J* = 7.0 Hz, 2H), 1.87 – 1.80 (m, 5H), 1.71 – 1.63 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 158.9, 135.6, 131.3, 129.0, 128.2, 127.9, 123.4, 114.8, 93.0, 79.4, 55.4, 48.1, 35.4, 26.5, 26.3, 22.6. **HRMS** m/z (ESI) calcd for $C_{21}H_{24}NO_2S$ $(M+H)^+$ 354.1522, found 354.1520.



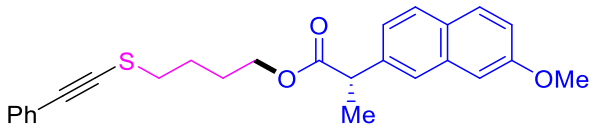
37a

4-((Phenylethynyl)thio)butyl 3-(4,5-diphenyloxazol-2-yl)propanoate (37a); Following the general procedure A, compound **37a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Oxaprozin (0.9 mmol, 264.0 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 54% yield (78.0 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 2H), 7.57 – 7.55 (m, 2H), 7.40 – 7.30 (m, 8H), 7.29 – 7.25 (m, 3H), 4.18 (t, J = 6.2 Hz, 2H), 3.17 (t, J = 7.5 Hz, 2H), 2.90 (t, J = 7.5 Hz, 2H), 2.76 (t, J = 6.8 Hz, 2H), 1.87 – 1.82 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9, 161.6, 145.4, 135.1, 132.4, 131.4, 128.9, 128.6, 128.5, 128.4, 128.2, 128.0, 128.0, 127.8, 126.4, 123.3, 93.2, 79.0, 64.1, 35.1, 31.1, 27.1, 25.7, 23.5. **HRMS** m/z (ESI) calcd for $C_{30}H_{28}NO_3S$ $(M+H)^+$ 482.1784, found 482.1784.



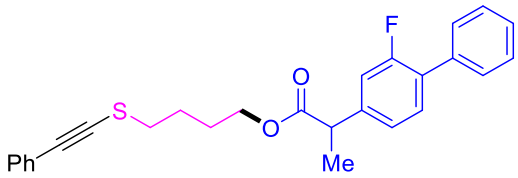
38a

4-((Phenylethynyl)thio)butyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (38a): Following the general procedure A, compound **38a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Fenbufen (0.9 mmol, 228.9 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a yellow oil in 53% yield (70.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 2H), 7.69 – 7.68 (m, 2H), 7.64 – 7.62 (m, 2H), 7.49 – 7.46 (m, 2H), 7.44 – 7.39 (m, 3H), 7.31 – 7.26 (m, 3H), 4.18 (t, J = 6.3 Hz, 2H), 3.32 (t, J = 6.6 Hz, 2H), 2.83 (t, J = 6.9 Hz, 2H), 2.78 (t, J = 6.6 Hz, 2H), 1.94 – 1.81 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 172.7, 145.7, 139.7, 135.1, 131.3, 128.8, 128.5, 128.2, 128.1, 127.9, 127.1, 123.3, 93.1, 79.1, 63.9, 35.1, 33.3, 28.2, 27.1, 25.7. **HRMS** m/z (ESI) calcd for $C_{28}H_{27}O_3S$ $(M+H)^+$ 443.1675, found 443.1679.



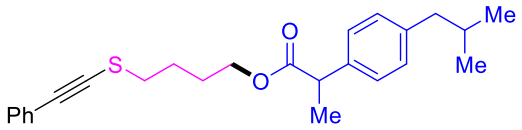
39a

4-((Phenylethynyl)thio)butyl (S)-2-(7-methoxynaphthalen-2-yl)propanoate (39a): Following the general procedure A, compound **39a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Naproxen (0.9 mmol, 207.2 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 5:1) as a colorless oil in 61% yield (88.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.7 Hz, 2H), 7.68 (s, 1H), 7.44 – 7.41 (m, 3H), 7.32 – 7.29 (m, 3H), 7.18 – 7.15 (m, 1H), 7.13 (d, J = 2.6 Hz, 1H), 4.18 – 4.13 (m, 2H), 3.91 (s, 3H), 3.88 – 3.84 (m, 1H), 2.73 (t, J = 6.7 Hz, 2H), 1.84 – 1.75 (m, 4H), 1.60 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 157.5, 135.5, 133.6, 131.3, 129.2, 128.8, 128.2, 128.0, 127.1, 126.1, 125.8, 123.3, 118.9, 105.5, 93.1, 79.1, 64.0, 55.2, 45.4, 35.0, 27.0, 25.7, 18.3. **HRMS** m/z (ESI) calcd for $C_{26}H_{27}O_3S$ $(M+H)^+$ 419.1675, found 419.1674.



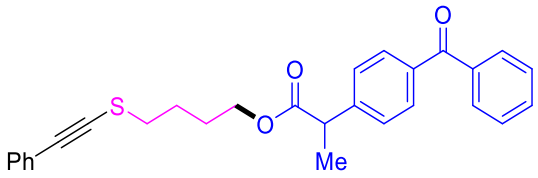
40a

4-((Phenylethynyl)thio)butyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (40a): Following the general procedure A, compound **40a** was synthesized using α-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Flurbiprofen (0.9 mmol, 219.8 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a colorless oil in 56% yield (72.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.47 – 7.36 (m, 6H), 7.32 – 7.29 (m, 3H), 7.17 – 7.13 (m, 2H), 4.22 – 4.16 (m, 2H), 3.77 (q, J = 7.2 Hz, 1H), 2.79 (t, J = 6.7 Hz, 2H), 1.89 – 1.79 (m, 4H), 1.55 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 159.6 (d, J = 248.4 Hz), 141.7 (d, J = 7.7 Hz), 135.4, 131.3, 130.7 (d, J = 3.9 Hz), 128.9 (d, J = 2.9 Hz), 128.4, 128.2, 128.0, 127.8, 127.6, 123.4 (d, J = 3.3 Hz), 123.3, 115.1 (d, J = 23.6 Hz), 93.1, 79.0, 64.3, 45.0 (d, J = 1.4 Hz), 35.1, 27.0, 25.7, 18.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.48. **HRMS** m/z (ESI) calcd for $C_{27}H_{26}FO_2S$ $(M+H)^+$ 433.1632, found 433.1633.



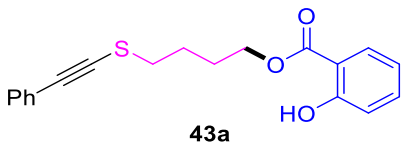
41a

4-((Phenylethynyl)thio)butyl 2-(4-isobutylphenyl)propanoate (41a): Following the general procedure A, compound **41a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), lbuprofen (0.9 mmol, 185.7 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a colorless oil in 48% yield (56.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.32 – 7.29 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.14 (t, *J* = 5.9 Hz, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 2.74 (t, *J* = 6.5 Hz, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.89 – 1.84 (m, 1H), 1.81 – 1.76 (m, 4H), 1.51 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.6, 140.4, 137.6, 131.3, 129.2, 128.2, 127.9, 127.0, 123.3, 93.0, 79.1, 63.9, 45.1, 44.9, 35.1, 30.1, 27.0, 25.7, 22.3, 18.3. **HRMS** m/z (ESI) calcd for $C_{25}H_{31}O_2S$ $(M+H)^+$ 395.2039, found 395.2038.



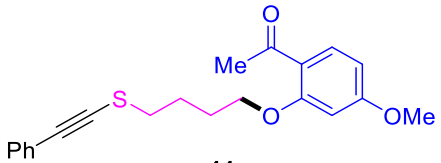
42a

4-((Phenylethynyl)thio)butyl 2-(4-benzoylphenyl)propanoate (42a): Following the general procedure A, compound **42a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), ketoprofen (0.9 mmol, 228.9 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a yellow oil in 55% yield (73.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 2H), 7.75 – 7.74 (m, 1H), 7.67 – 7.64 (m, 1H), 7.60 – 7.46 (m, 5H), 7.39 – 7.37 (m, 2H), 7.28 – 7.26 (m, 3H), 4.16 – 4.08 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 2.76 – 2.72 (m, 2H), 1.81 – 1.73 (m, 4H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3,173.9, 140.8, 137.8, 137.4, 132.4, 131.4, 131.3, 130.0, 129.0, 128.9, 128.5, 128.2, 128.0, 123.3, 93.1, 79.0, 64.2, 45.3, 35.1, 27.0, 25.7, 18.3. **HRMS** m/z (ESI) calcd for $C_{28}H_{27}O_3S$ $(M+H)^+$ 433.1675, found 433.1676.



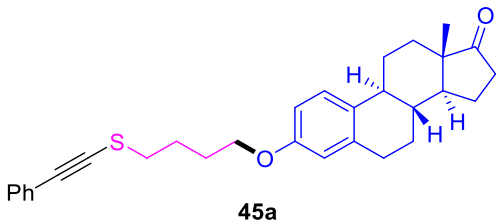
43a

4-((Phenylethynyl)thio)butyl 2-hydroxybenzoate (43a): Following the general procedure A, compound **43a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Aspirin (0.9 mmol, 162.1 mg), Cs_2CO_3 (1.2 mmol, 391.0 mg) in THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 10:1) as a yellow oil in 63% yield (61.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.83 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.40 – 7.38 (m, 2H), 7.30 – 7.27 (m, 3H), 6.98 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.83 – 6.79 (m, 1H), 4.43 – 4.40 (m, 2H), 2.89 – 2.86 (m, 2H), 2.02 – 1.99 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.1, 161.7, 135.7, 131.4, 129.8, 128.3, 128.1, 123.3, 119.1, 117.6, 112.4, 93.3, 78.8, 64.6, 35.1, 27.1, 25.8. **HRMS** m/z (ESI) calcd for $C_{19}H_{19}O_3S$ $(M+H)^+$ 327.1049, found 327.1050.



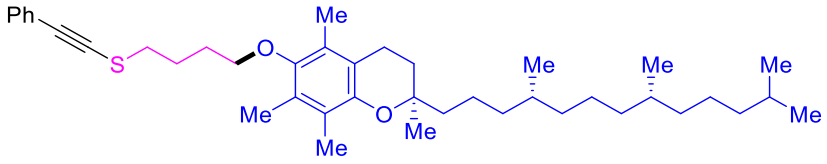
44a

1-(4-Methoxy-2-(4-((phenylethynyl)thio)butoxy)phenyl)ethan-1-one (44a): Following the general procedure A, compound **44a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Paeonol (0.6 mmol, 99.7 mg), NaOH (1.2 mmol, 48.0 mg) in dry THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 3:1) as a colorless oil in 53% yield (56.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.38 (m, 2H), 7.29 – 7.27 (m, 3H), 6.51 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.43 (d, *J* = 2.3 Hz, 1H), 4.09 (t, *J* = 5.7 Hz, 2H), 3.83 (s, 3H), 2.89 – 2.86 (m, 2H), 2.58 (s, 3H), 2.06 – 2.03 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.5, 164.4, 160.3, 132.6, 131.4, 128.2, 128.1, 123.2, 121.1, 105.1, 98.8, 93.2, 78.9, 67.8, 55.4, 35.3, 32.0, 27.7, 26.1. **HRMS** m/z (ESI) calcd for $C_{21}H_{23}O_3S$ $(M+H)^+$ 355.1362, found 355.1365.



45a

(8R,9S,13S,14S)-13-Methyl-3-(4-((phenylethynyl)thio)butoxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (45a): Following the general procedure A, compound **45a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Estrone (0.6 mmol, 162.2 mg), NaOH (1.2 mmol, 48.0 mg) in dry THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 2:1) as a white solid in 62% yield (85.3 mg). M.p. = 94-96 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.31 – 7.28 (m, 3H), 7.19 (d, J = 8.6 Hz, 1H), 6.72 (dd, J = 8.6, 2.7 Hz, 1H), 6.65 (d, J = 2.6 Hz, 1H), 4.00 (t, J = 6.0 Hz, 2H), 2.90 – 2.86 (m, 4H), 2.53 (dd, J = 19.0, 8.6 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.27 (dt, J = 10.6, 5.7 Hz, 1H), 2.21 – 2.12 (m, 1H), 2.11 – 1.95 (m, 7H), 1.63 – 1.48 (m, 6H), 0.91 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.9, 137.7, 132.0, 131.4, 128.2, 127.9, 126.3, 123.5, 114.5, 112.1, 93.1, 79.3, 67.1, 50.4, 47.9, 43.9, 38.3, 35.8, 35.4, 31.6, 29.6, 27.8, 26.5, 26.0, 25.9, 21.5, 13.8. **HRMS** m/z (ESI) calcd for $C_{30}H_{35}O_2S$ $(M+H)^+$ 459.2352, found 459.2349.



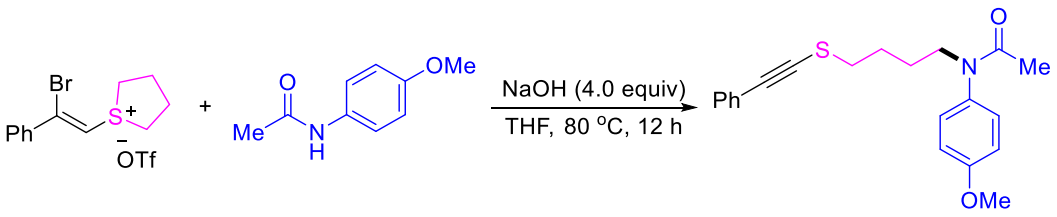
46a

(R)-2,5,7,8-Tetramethyl-6-(4-((phenylethynyl)thio)butoxy)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (46a): Following the general procedure A, compound **46a** was synthesized using *α*-bromostyrene sulfonium salt **1a** (0.3 mmol, 125.4 mg), Vitamin E (0.6 mmol, 258.4 mg) , NaOH (1.2 mmol, 48.0 mg) in dry THF (2.0 mL) at 100 ℃ for 12 h. The residue was purified through a silica gel flash column (PE/EA = 2:1) as a colorless oil in 61% yield (113.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.33 – 7.30 (m, 3H), 3.73 (t, *J* = 12.5 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.61 – 2.59 (m, 2H), 2.21 (s, 3H), 2.16 (s, 3H), 2.21 – 2.08 (m, 5H), 2.02 – 1.97 (m, 2H), 1.88 – 1.75 (m, 2H), 1.61 – 1.54 (m, 2H), 1.50 – 1.38 (m, 4H), 1.36 – 1.23 (m, 12H), 1.20 – 1.08 (m, 6H), 0.92 – 0.88 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2, 147.7, 131.4,

128.2, 127.9, 127.7, 125.7, 123.5, 122.8, 117.5, 93.1, 79.4, 74.7, 72.2, 40.1, 40.0, 39.4, 37.6, 37.4, 37.4, 37.3, 35.7, 32.8, 32.7, 31.3, 31.2, 29.0, 28.0, 26.4, 24.8, 24.4, 23.9, 22.7, 22.6, 21.0, 20.6, 19.7, 19.7, 19.6, 12.8, 11.9, 11.8. **HRMS** m/z (ESI) calcd for $C_{41}H_{63}O_2S$ $(M+H)^+$ 619.4543, found 619.4544.

5. Synthetic Application

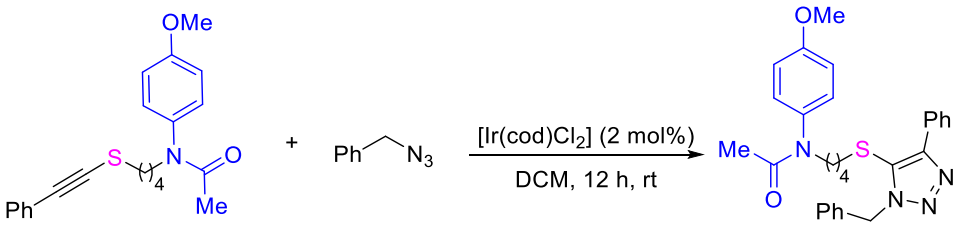
5.1 Scale-up Reaction



1, 5.0 mmol 3.0 (equiv) **36a**, 65% (1.15 g)

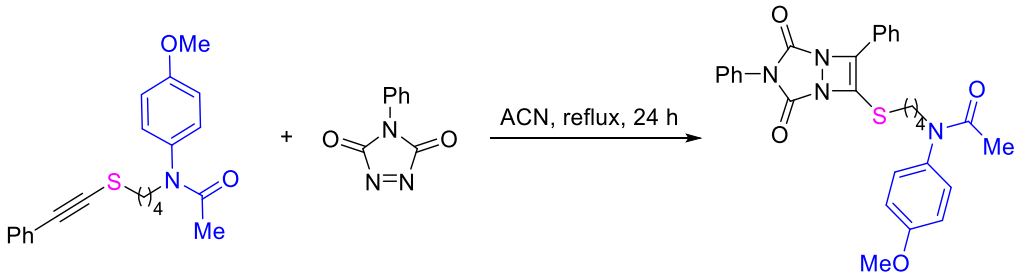
General procedure: To a solution of Methacetin (2.48 g, 15.0 mmol, 3.0 equiv) in THF (15 mL) was added α-bromostyrenesulfonium salt **1a** (2.10 g, 5.0 mmol, 1.0 equiv) and NaOH (800.0 mg, 20.0 mmol, 4.0 equiv). The reaction mixture was stirred at 80 ℃ for 12 h. The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA=4:1) to afford product **36a** (1.15g, 65%).

5.2 Product Derivatizations



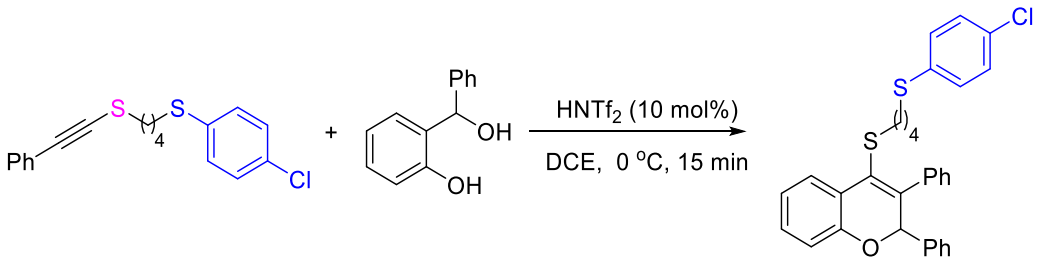
36a **47**, 75%

Following the relative literature [4]: General procedure for compound 47: Under an argon atmosphere, compound **36a** (70.7 mg, 0.2 mmol), (azidomethyl)benzene (39.9 mg, 0.30 mmol 1.5 equiv), [Ir(cod)Cl_2] (2.7 mg, 4.0 μmol, 2 mol%) and THF (2.0 mL) were added to a 10 mL schlenk tube at room temperature for 12 hours. The resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA = 4:1) to afford desired product **47** as a yellow oil in 75% yield (73.0 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 – 8.11 (m, 2H), 7.41 – 7.37 (m, 2H), 7.34 – 7.27 (m, 6H), 6.93 – 6.87 (m, 4H), 5.63 (s, 2H), 3.80 (s, 3H), 3.44 – 3.41 (m, 2H), 2.35 (t, J = 7.2 Hz, 2H), 1.75 (s, 3H), 1.33 – 1. 24 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.5, 158.9, 149.0, 135.4, 135.3, 130.6, 128.9, 128.7, 128.5, 128.3, 128.2, 127.6, 126.8, 125.3, 114.7, 55.4, 51.9, 47.9, 35.4, 26.4, 26.3, 22.6. **HRMS** m/z (ESI) calcd for $C_{28}H_{31}N_4O_2S$ $(M+H)^+$487.2162, found 487



36a **PTAD** **48**, 81%

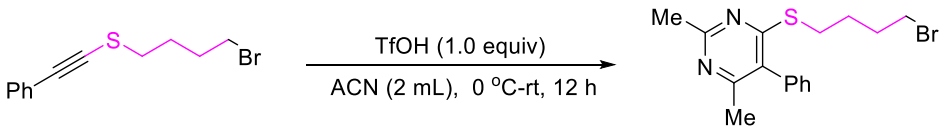
Following the relative literature [5]: General procedure for compound 48: A 10.0 mL dried schlenk tube with a stirring bar was added compound **36a** (70.7 mg, 0.2 mmol), 4-phenyl-1,2,4-triazoline-3,5-dione (**PTAD**) (45.5 mg, 0.26 mmol, 1.3 equiv) and ACN (2.0 mL). The reaction mixture was stirred at 60 °C for 24 h in air. The resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA = 3:1) to afford desired product **48** as a yellow oil in 81% yield (85.6 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.85 (m, 2H), 7.49 – 7.37 (m, 8H), 7.01 – 6.98 (m, 2H), 6.86 – 6.83 (m, 2H), 3.78 (s, 3H), 3.65 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H), 1.77 – 1.71 (m, 5H), 1.67 – 1.63 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.6, 158.8, 156.2, 155.0, 146.5, 135.5, 130.8, 129.9, 129.3, 129.0, 128.9, 128.7, 128.1, 126.2, 125.4, 125.4, 114.7, 55.4, 48.1, 34.5, 27.1, 26.5, 22.6. **HRMS** m/z (ESI) calcd for $C_{29}H_{29}N_4O_4S$ $(M+H)^+$ 529.1904, found 529.1905.



32a **49**, 82%

Following the relative literature [6]: General procedure for compound 49: A 10.0 mL dried Schlenk tube with a stirring bar was added compound **32a** (0.2 mmol, 66.4mg, 1.0 equiv), *o*-hydroxybenzyl alcohol (0.24 mmol, 40.5mg, 1.2 equiv) and DCE (4.0 mL). The $HNTf_2$ (0.2 M in DCE, 0.1 mL) was added reaction solution at 0 °C. Then, the progress of the reaction was monitored by TLC (the reaction typically took 15 mins). The resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA = 20:1) to afford desired product **49** as a colorless oil in 82% yield (84.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 1H), 7.33 – 7.25 (m, 7H), 7.20 – 7.10 (m, 8H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H),

6.05 (s, 1H), 2.67 (t, J = 6.7 Hz, 2H), 2.60 – 2.54 (m, 1H), 2.39 – 2.33 (m, 1H), 1.54 – 1.38 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 141.5, 138.4, 137.7, 135.1, 131.7, 130.3, 129.5, 129.3, 128.9, 128.5, 128.3, 128.0, 127.8, 126.5, 126.3, 122.5, 121.5, 117.0, 80.9, 33.3, 29.7, 28.0, 27.5. **HRMS** m/z (ESI) calcd for $C_{31}H_{28}ClOS_2$ $(M+H)^+$ 515.1265, found 515.1262.



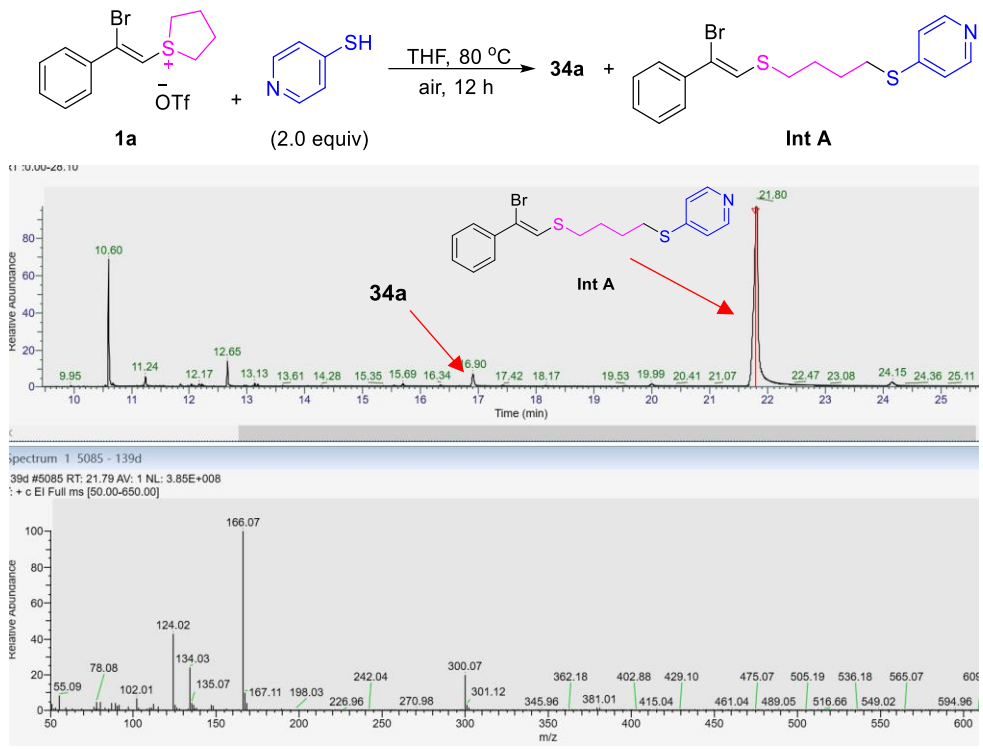
2a **50**, 60%

Following the relative literature [7]: General procedure for compound 50: Compound **2a** (0.2 mmol, 53.8 mg) and anhydrous ACN (2.0 mL) were added to a 10.0 mL dried schlenk tube at 0 ℃. The TfOH (0.2 mmol, 30.0 mg, 1.0 equiv) was added dropwise under air, then reaction mixture was stirred at 0 ℃ for 15 min before warming to rt for 12 h. The resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA = 20:1) to afford desired product **50** as a colorless oil in 60% yield (42.2 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 3H), 7.21 – 7.19 (m, 2H), 3.43 (t, J = 6.7 Hz, 2H), 3.13 (t, J = 7.2 Hz, 2H), 2.67 (s, 3H), 2.17 (s, 3H), 1.98 – 1.92 (m, 2H), 1.82 – 1.79 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.1, 165.3, 161.6, 135.2, 129.5, 128.9, 128.8, 128.4, 33.1, 31.7, 28.8, 27.8, 25.9, 22.3. **HRMS** m/z (ESI) calcd for $C_{16}H_{20}BrN_2S$ $(M+H)^+$ 351.0525, found 351.0525.

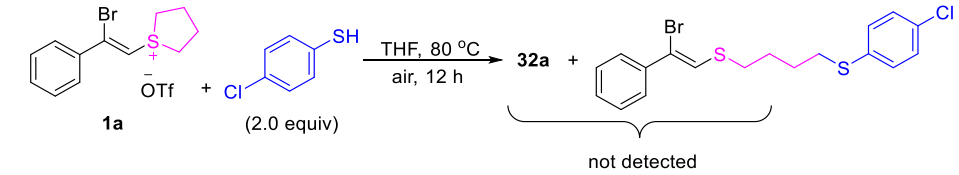
6. Mechanistic Studies

6.1 Control experiment

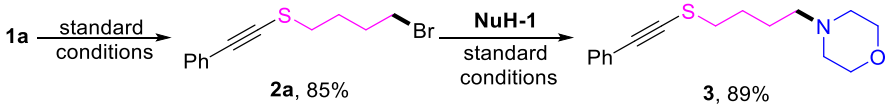
(a)



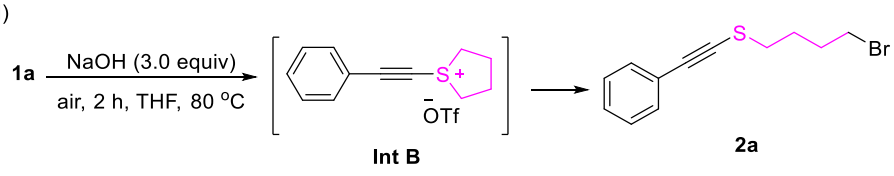
(b)

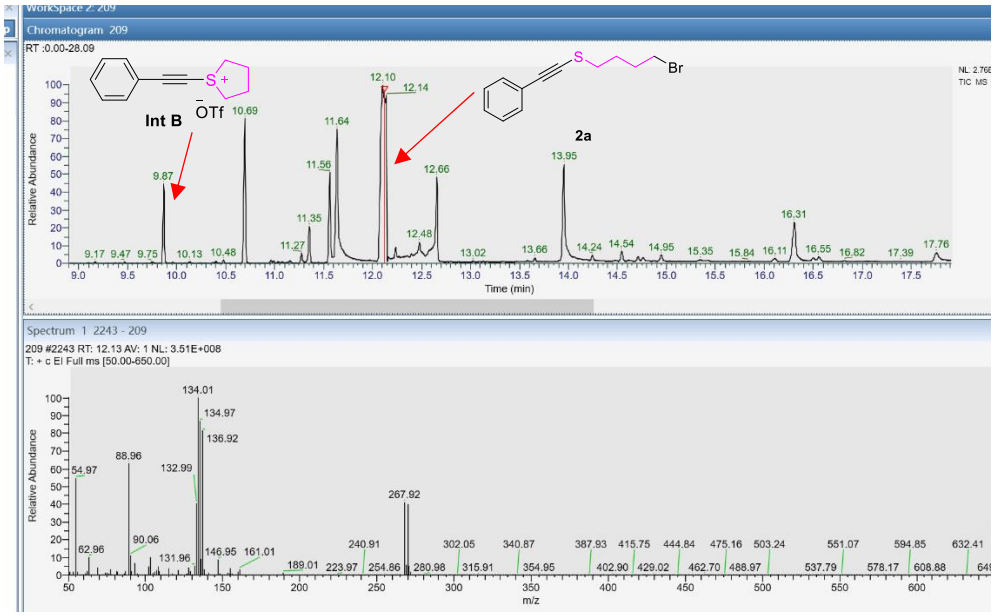


(c)

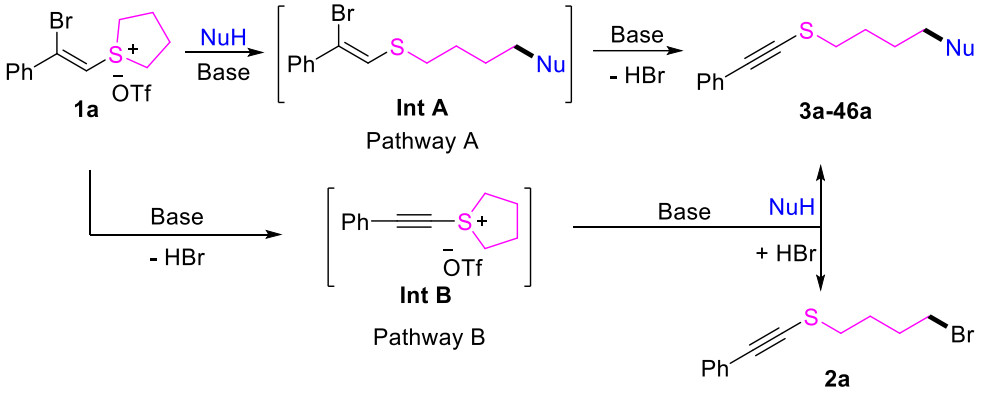


(d)





6.2 Proposed pathway



7. References

[1] H.-Z. Bu, H.-H. Li, W.-F. Luo, C. Luo, P.-C. Qian and L.-W. Ye, Synthesis of 2*H*-Chromenes via Unexpected [4 + 2] Annulation of Alkynyl Thioethers with o-Hydroxybenzyl Alcohols. *Org. Lett*., **2020**, *22*, 648−652.

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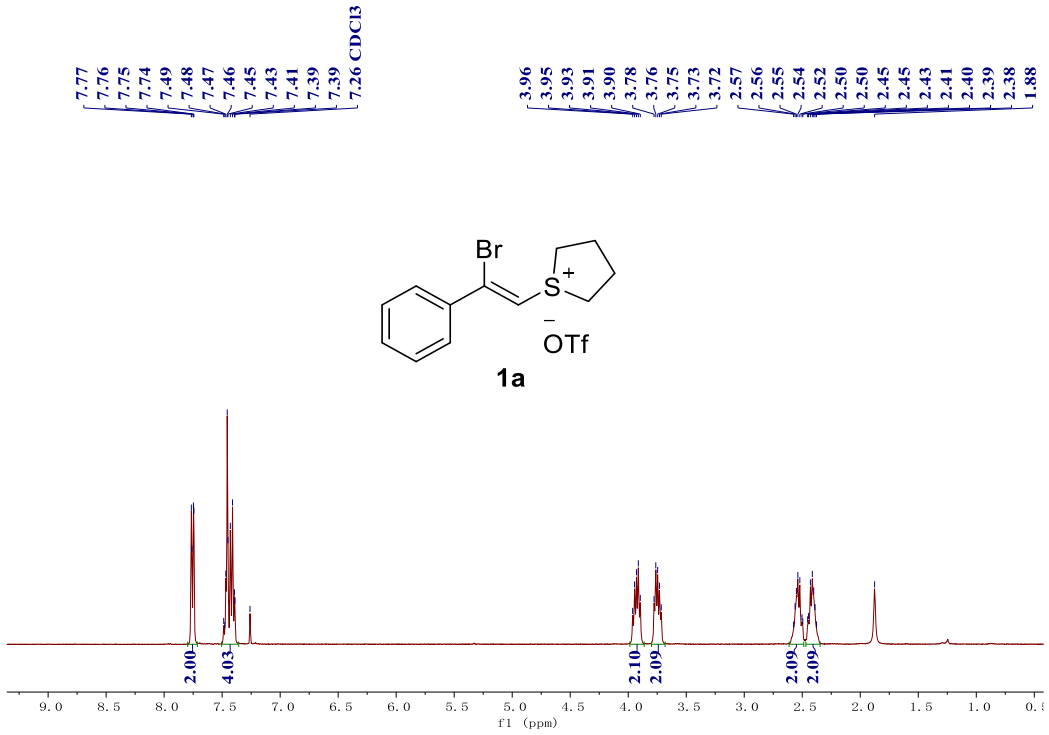
[6] H. Z. Bu, H. H. Li, W. F. Luo, C. Luo, P. C. Qian and L. W. Ye, Synthesis of 2H-Chromenes via Unexpected [4 + 2] Annulation of Alkynyl Thioethers with o-Hydroxybenzyl Alcohols. *Org. Lett.*, **2020**, *22*, 648−652.

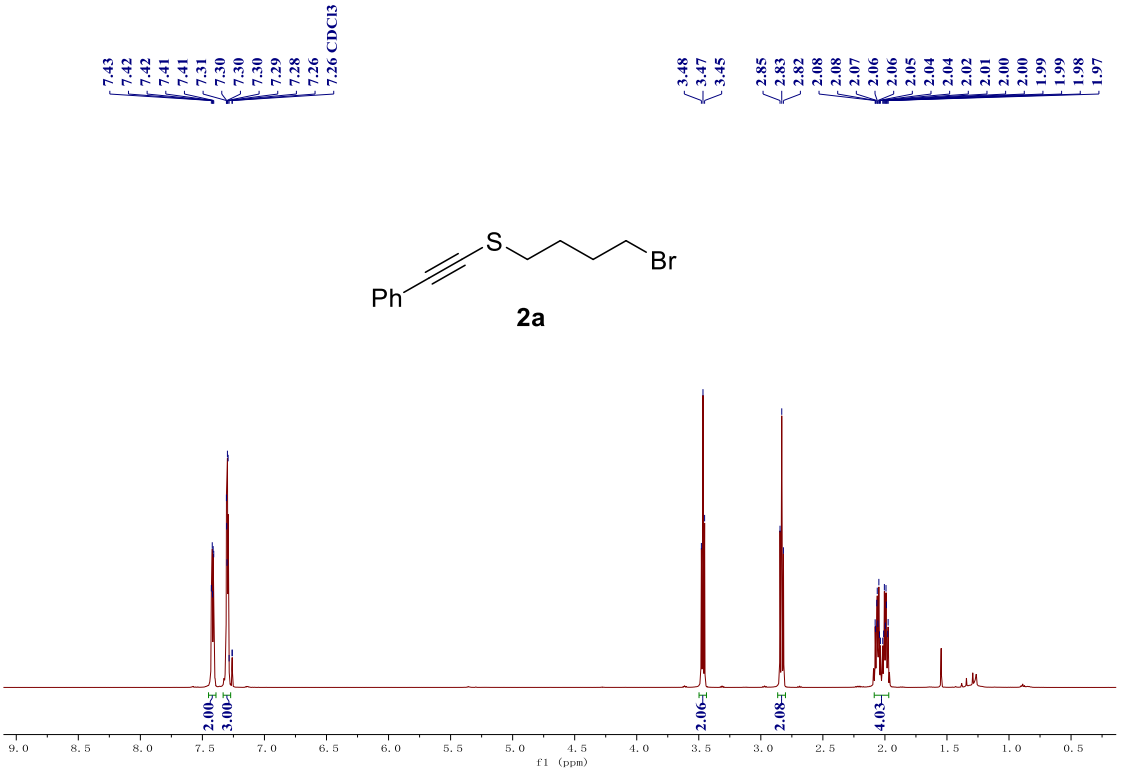
[7] L. G. Xie, S. Niyomchon, A. J. Mota, L. Gonzalez and N. Maulide, Metal-free intermolecular formal cycloadditions enable an orthogonal access to nitrogen heterocycles. *Nat. Commun.,* **2016**, *7*, 10914.

8. ^{1}H, ^{13}C, and ^{19}F NMR Spectra

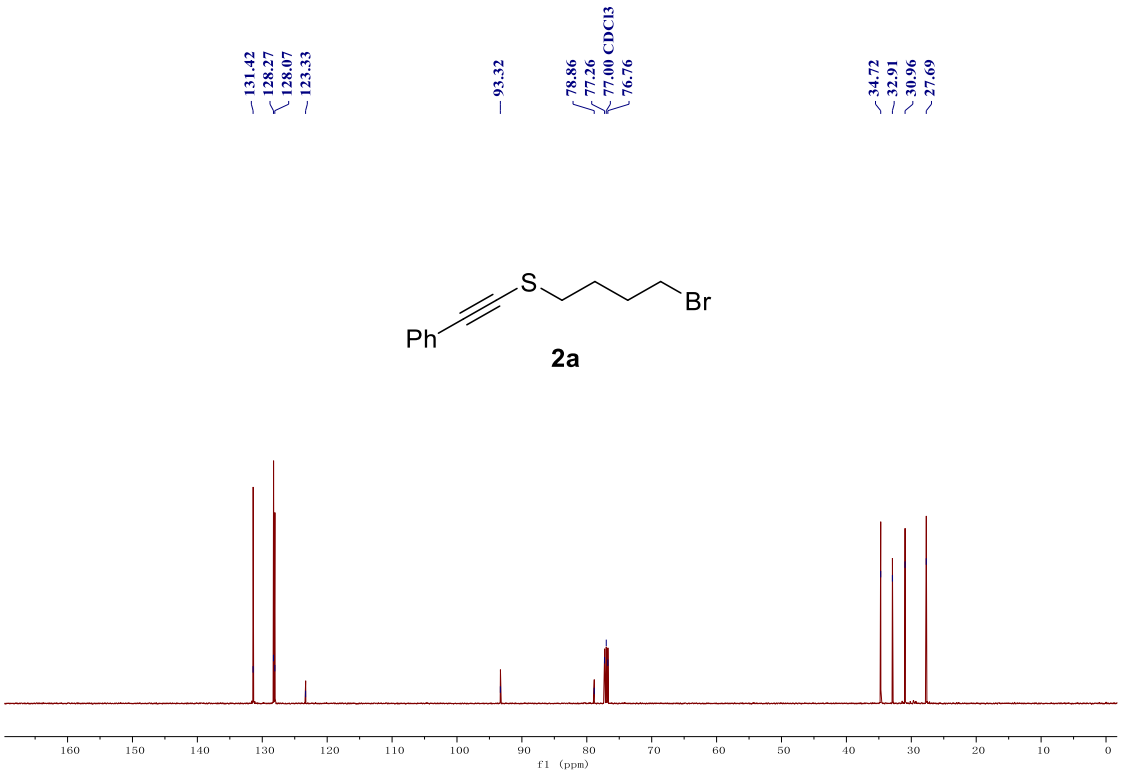
^{1}H NMR of 1a (400 MHz, $CDCl_3$)



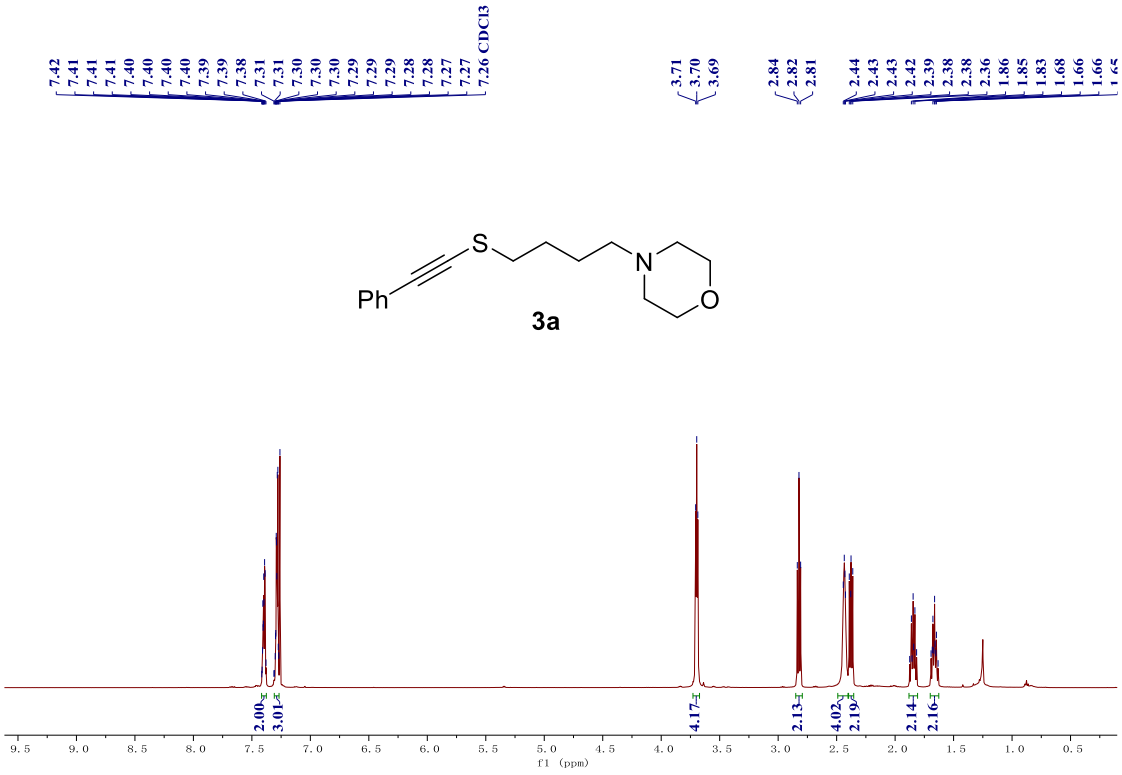
^{1}H NMR of 2a (500 MHz, $CDCl_3$**)**



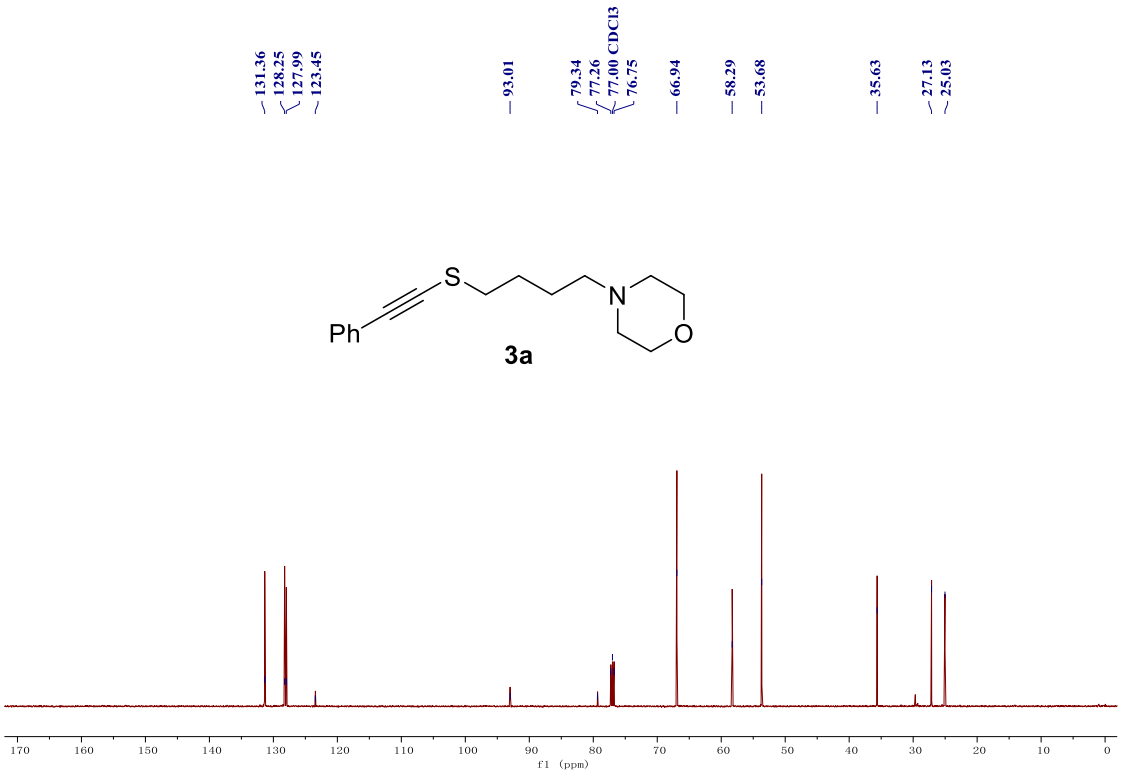
^{13}C NMR of 2a (126 MHz, $CDCl_3$**)**



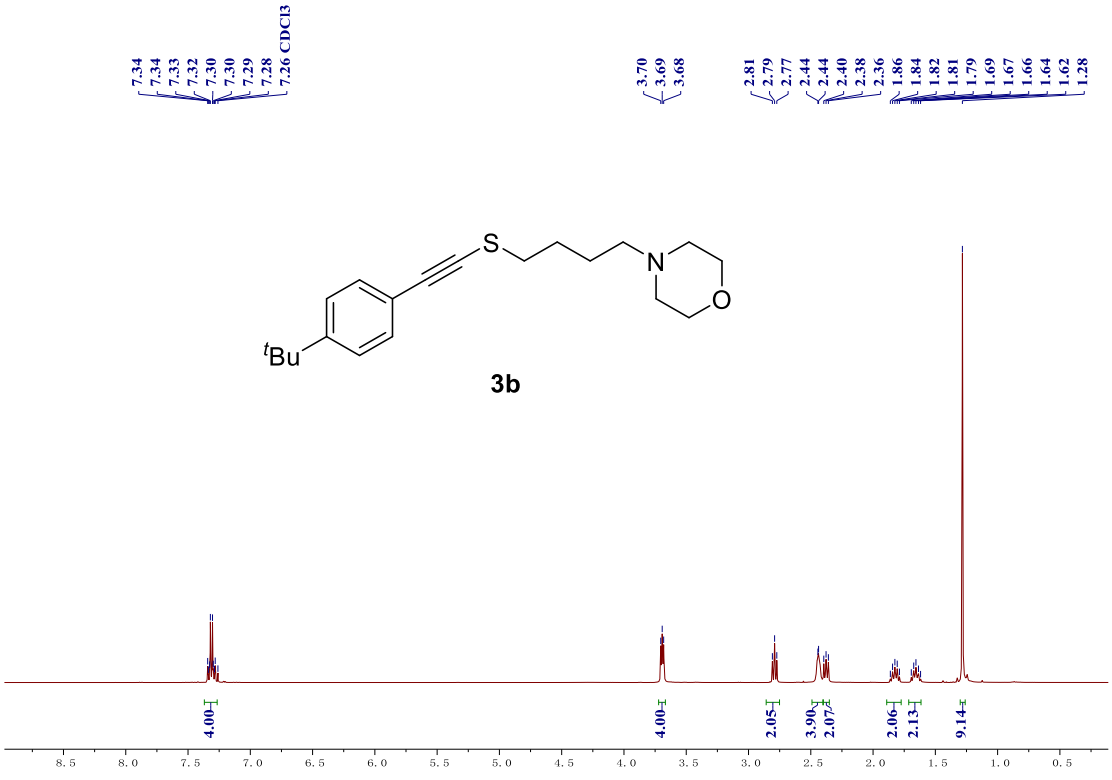
^{1}H NMR of 3a (500 MHz, $CDCl_3$**)**



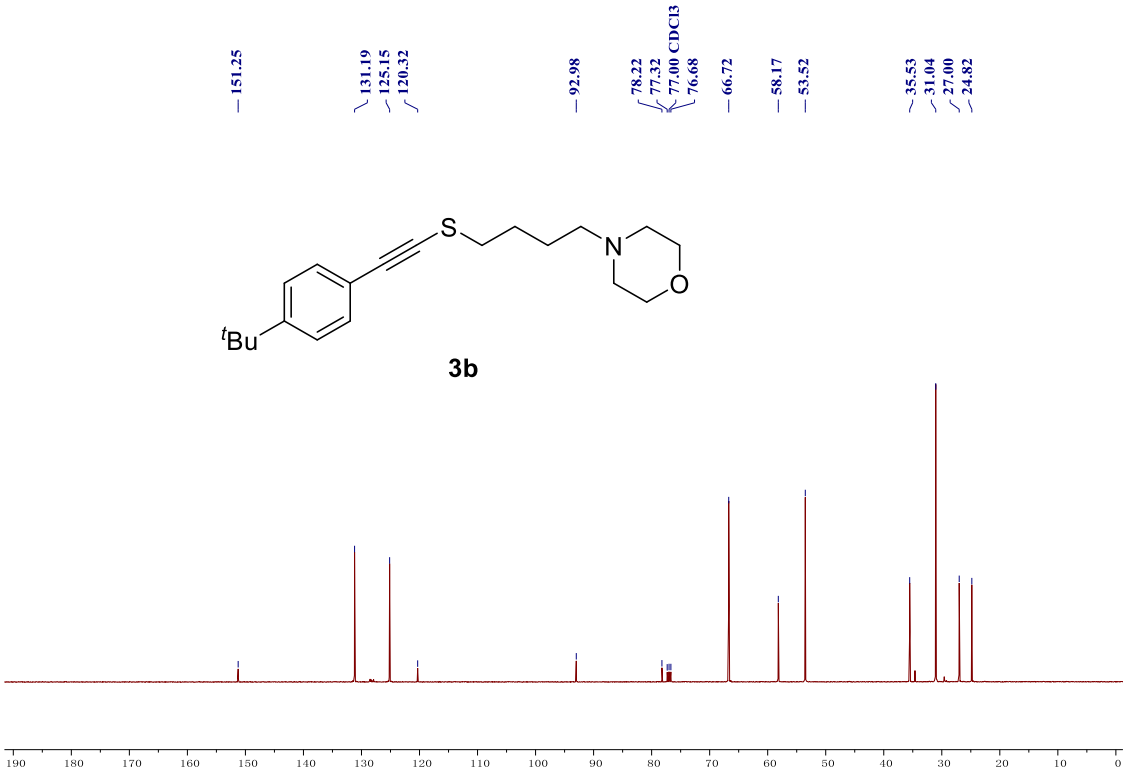
^{13}C NMR of 3a (126 MHz, $CDCl_3$**)**



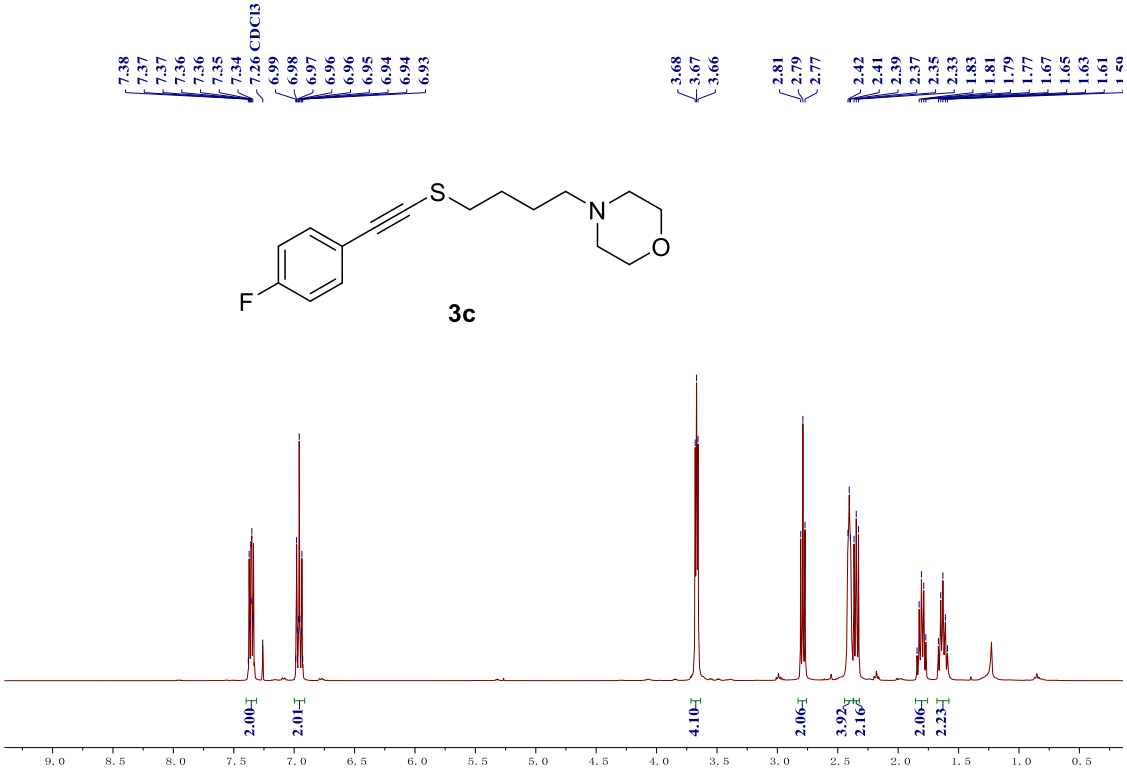
^{1}H NMR of 3b (400 MHz, $CDCl_3$**)**



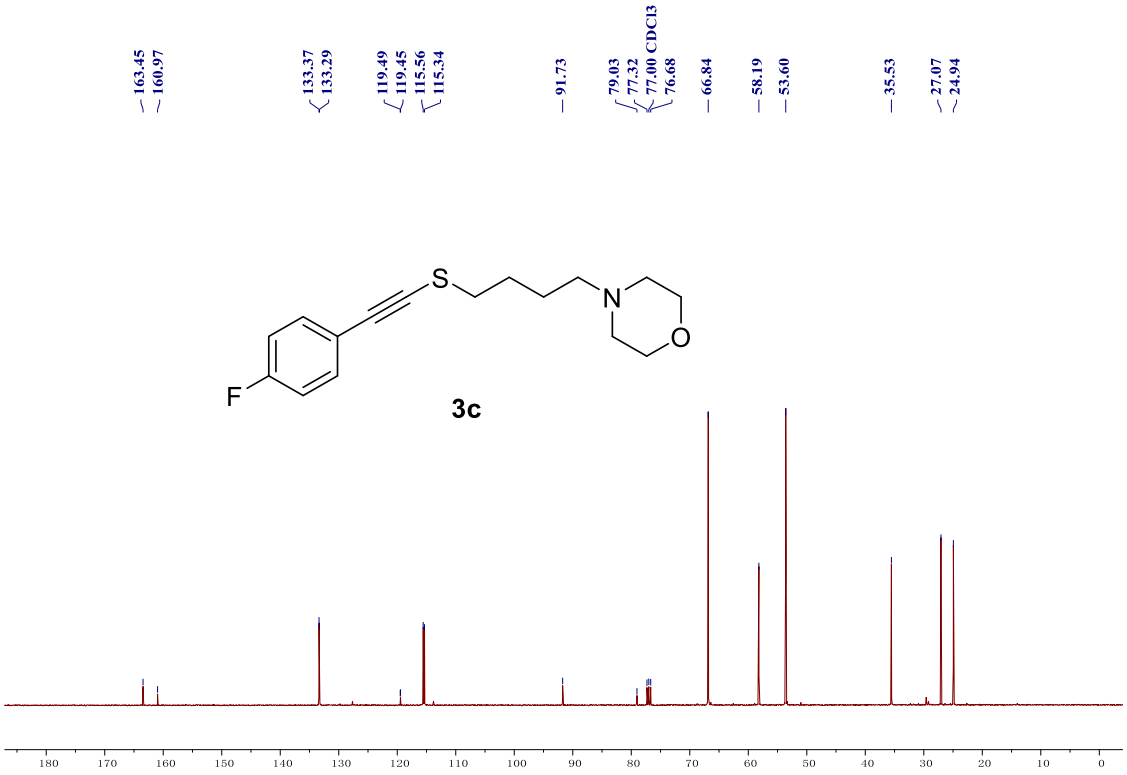
^{13}C NMR of 3b (101 MHz, $CDCl_3$**)**



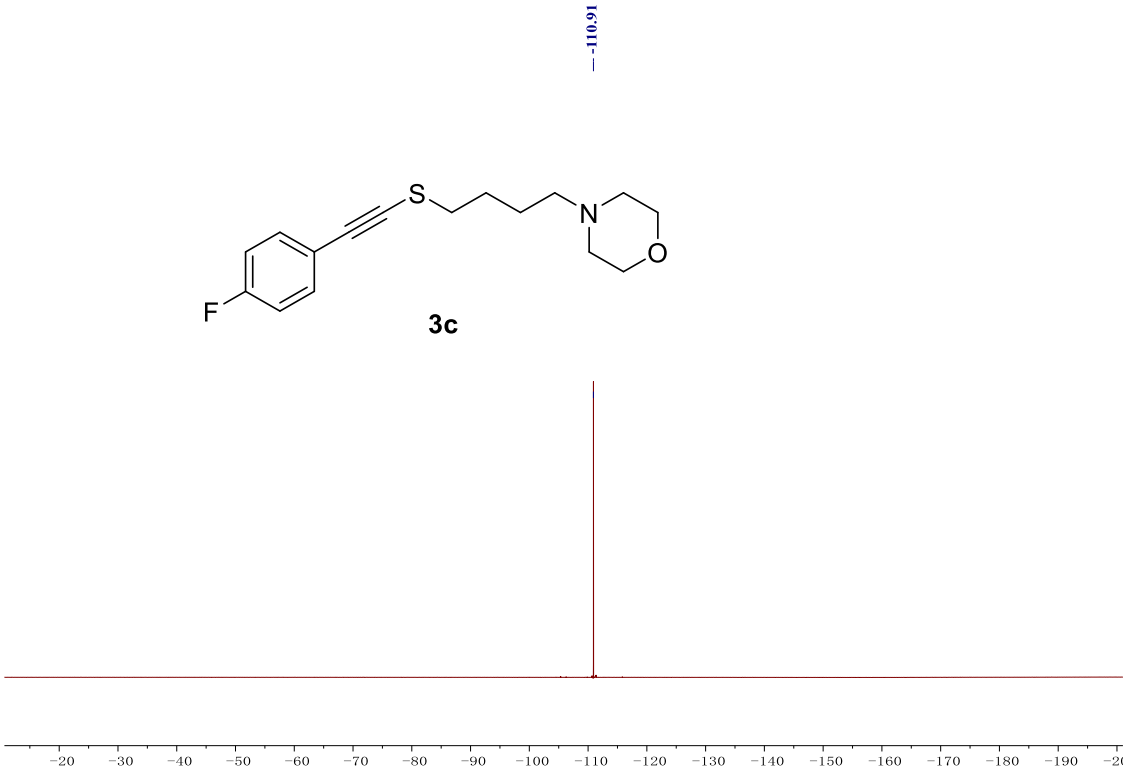
^{1}H NMR of 3c (400 MHz, $CDCl_3$**)**



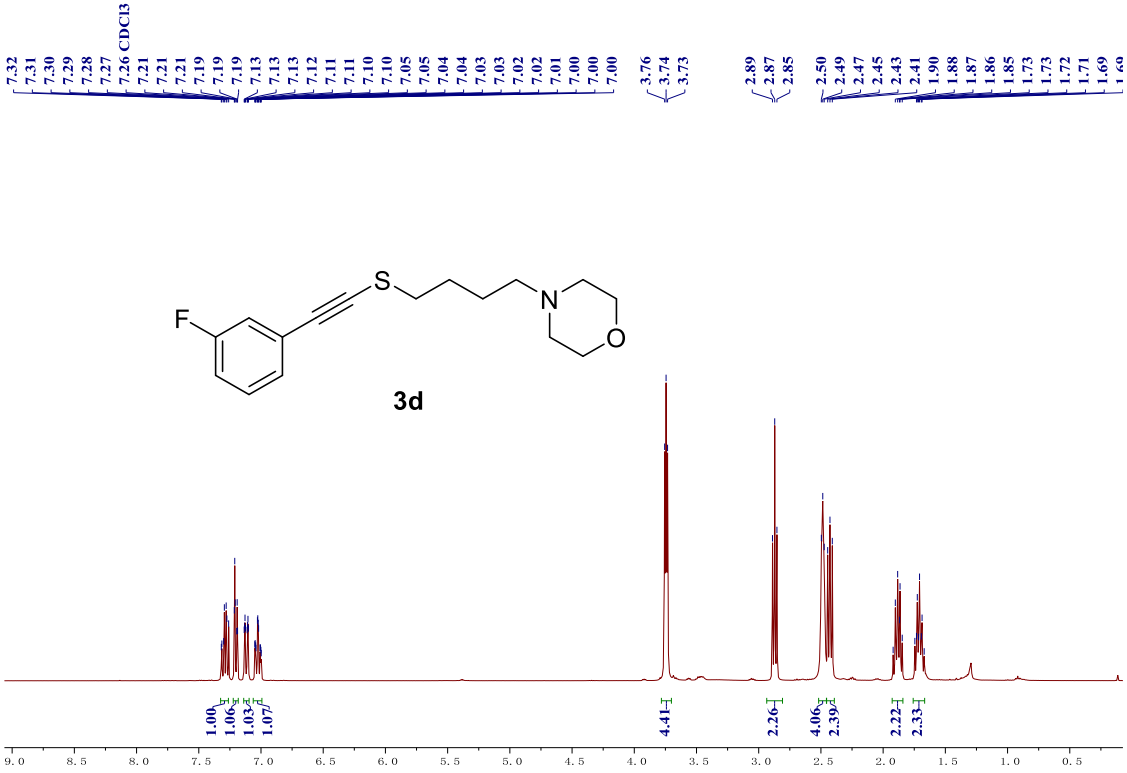
^{13}C NMR of 3c (101 MHz, $CDCl_3$**)**



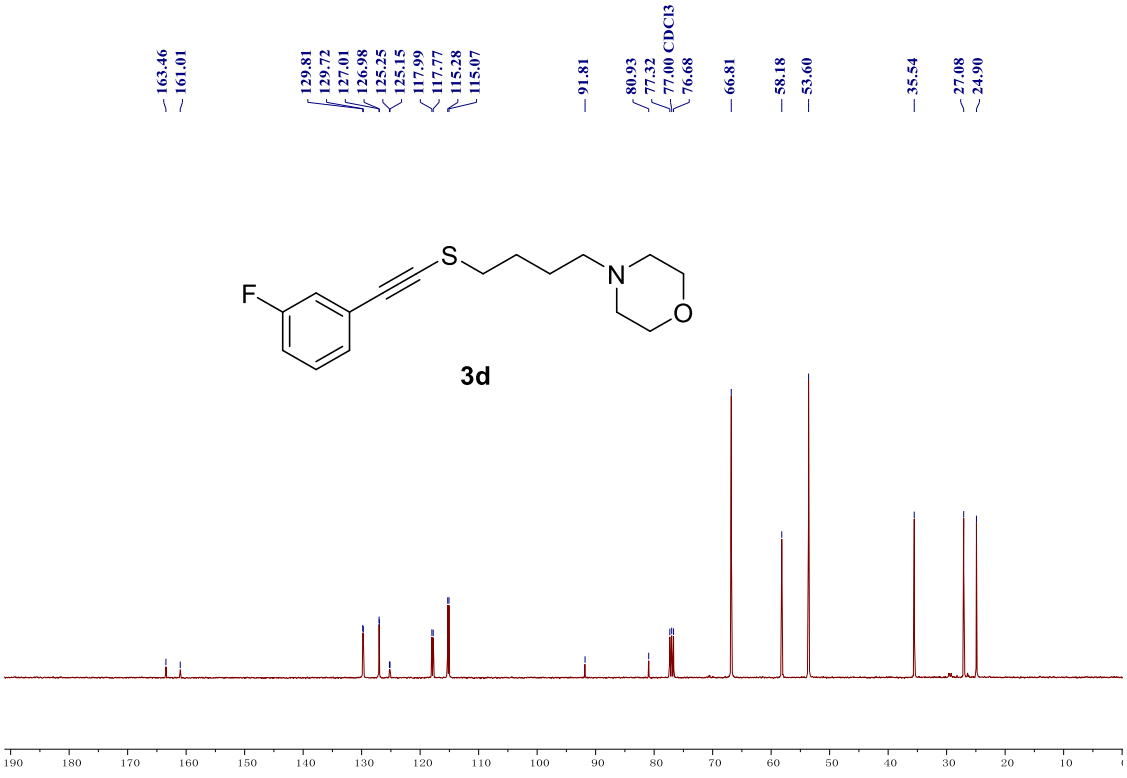
^{19}F NMR of 3c (376 MHz, $CDCl_3$)



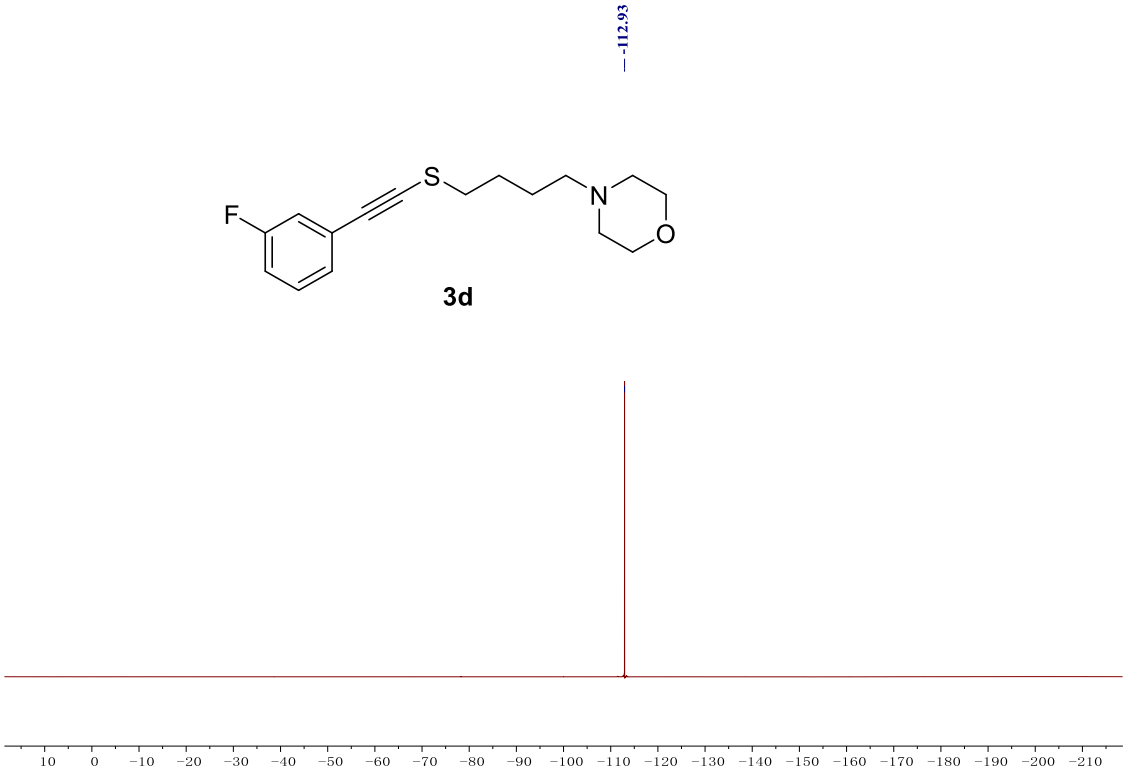
^{1}H NMR of 3d (400 MHz, $CDCl_3$)



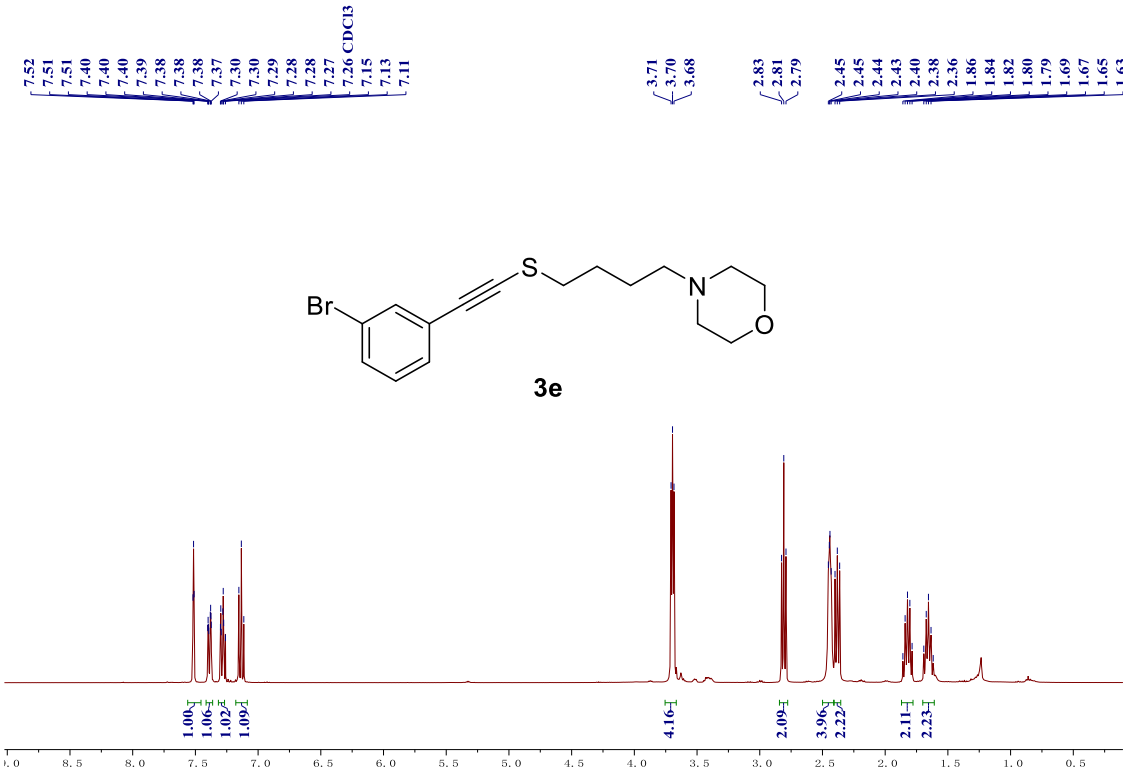
^{13}C NMR of 3d (101 MHz, $CDCl_3$**)**



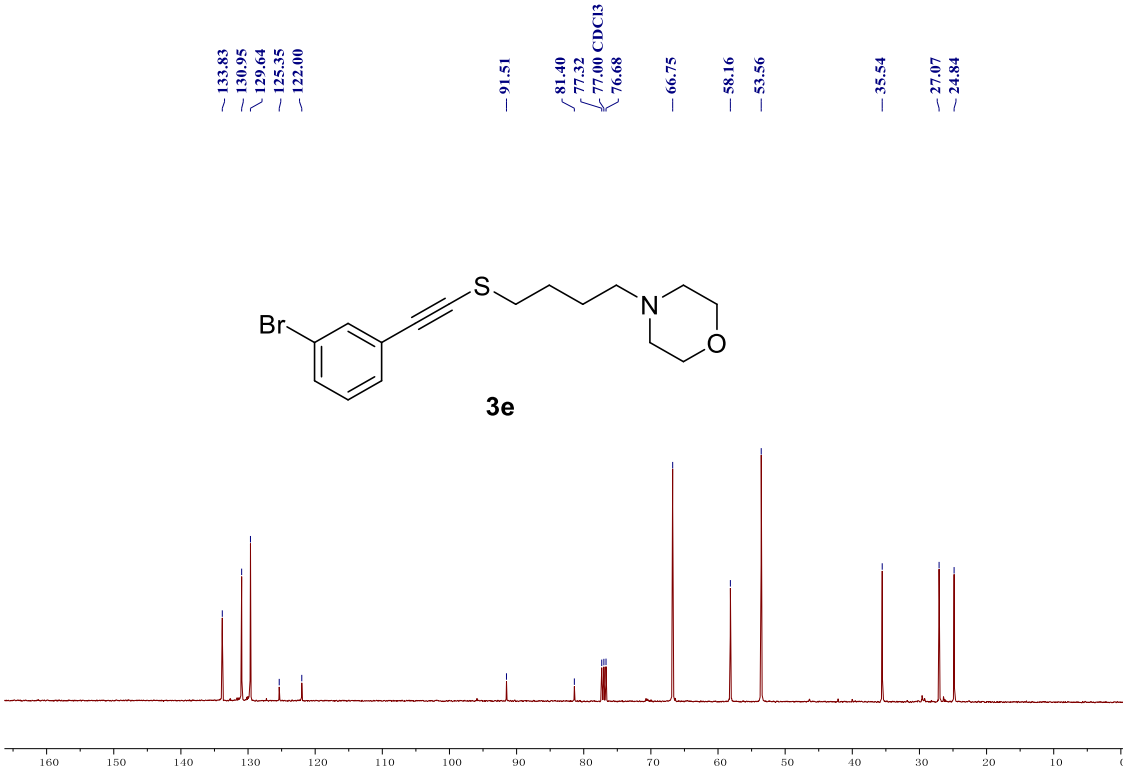
^{19}F NMR of 3d (376 MHz, $CDCl_3$)



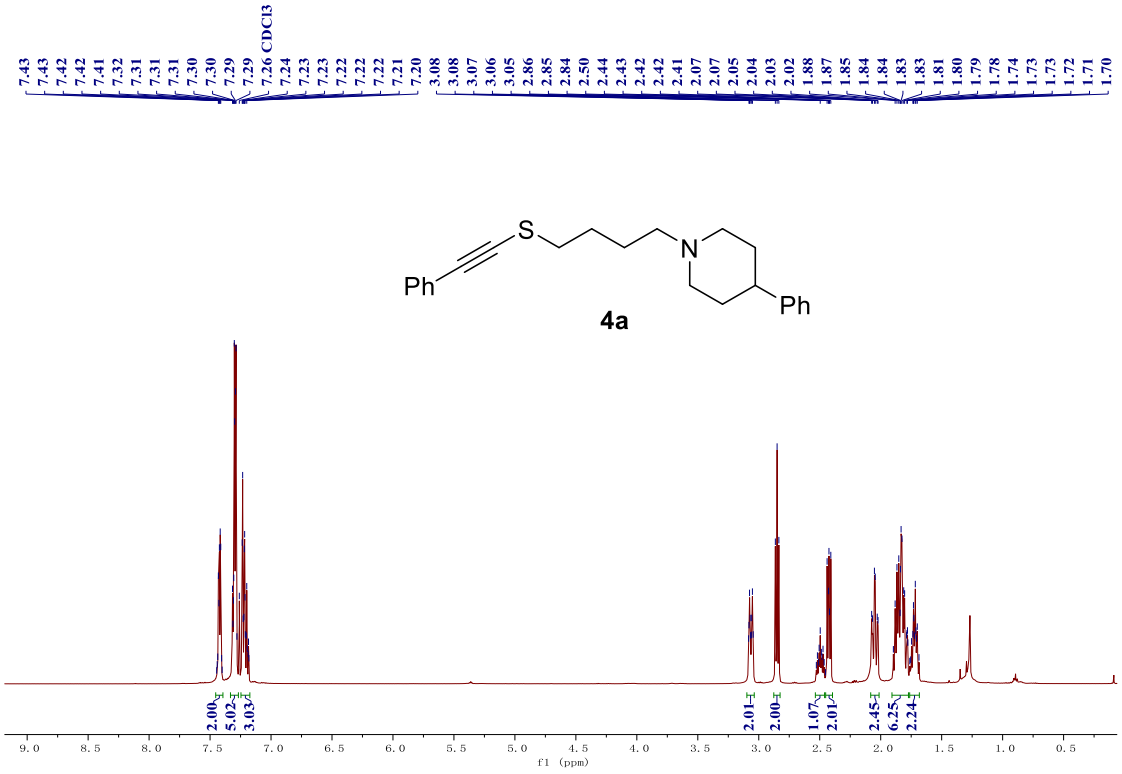
^{1}H NMR of 3e (400 MHz, $CDCl_3$)



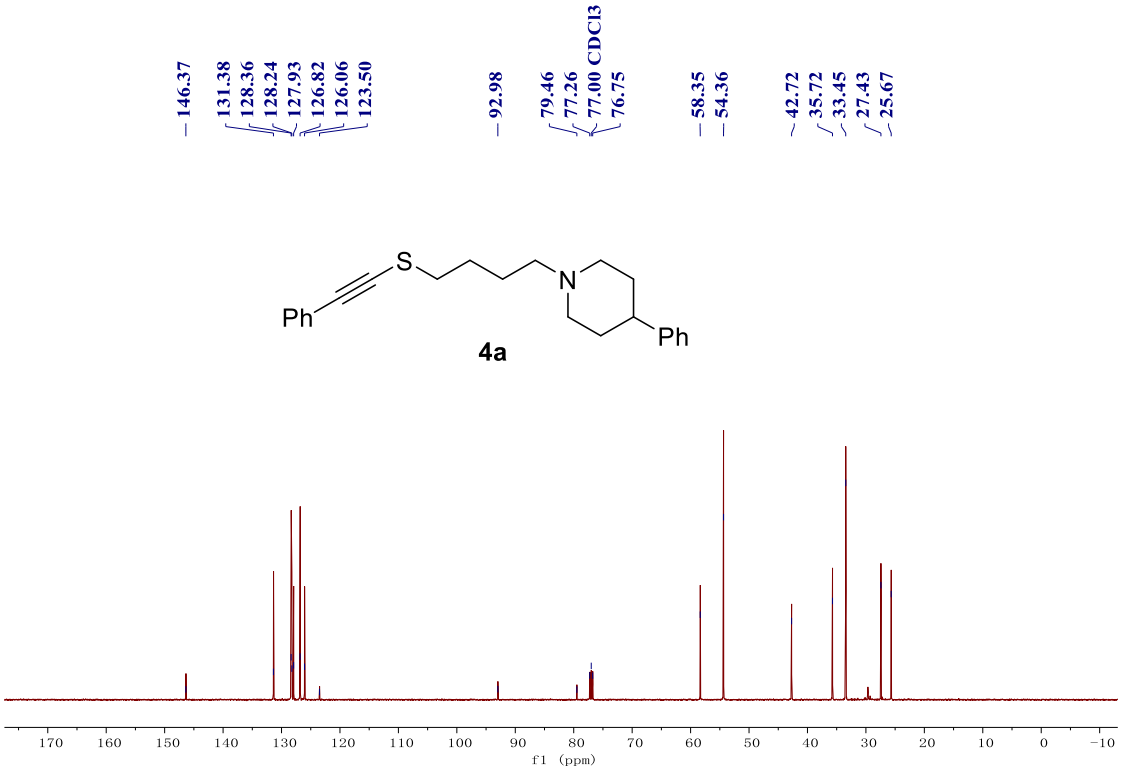
^{13}C NMR of 3e (101 MHz, $CDCl_3$**)**



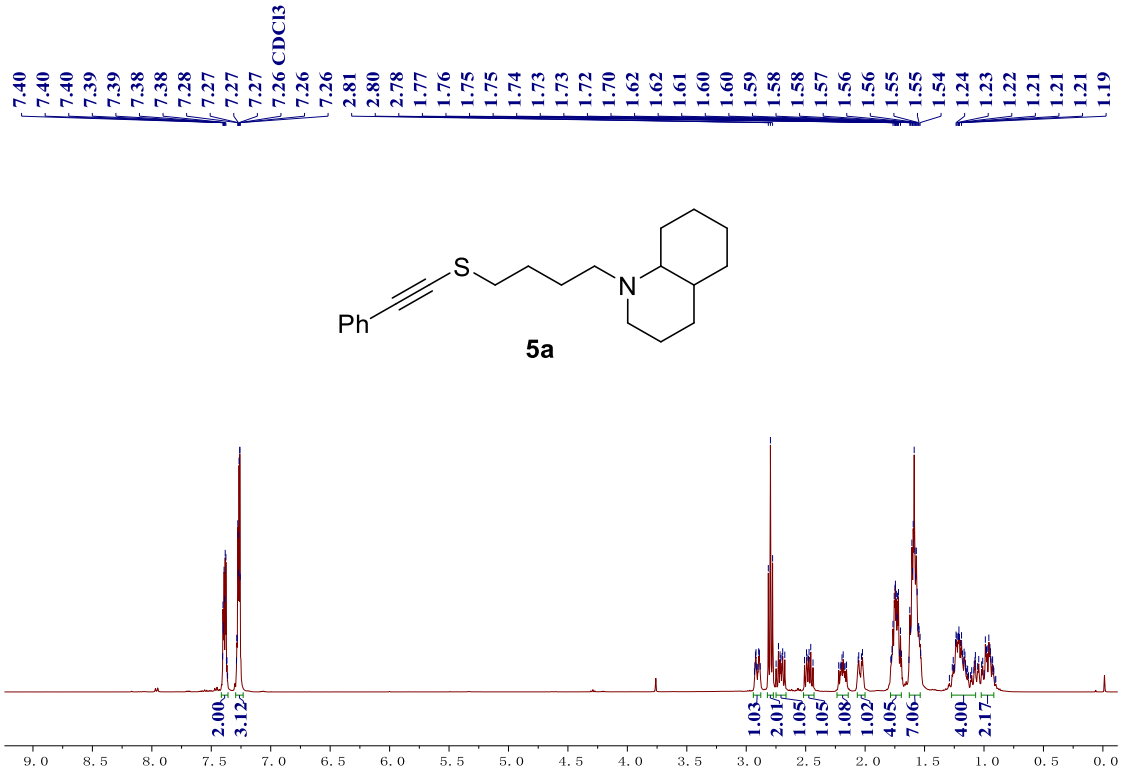
^{1}H NMR of 4a (500 MHz, $CDCl_3$**)**



^{13}C NMR of 4a (126 MHz, $CDCl_3$**)**



^{1}H NMR of 5a (400 MHz, $CDCl_3$**)**



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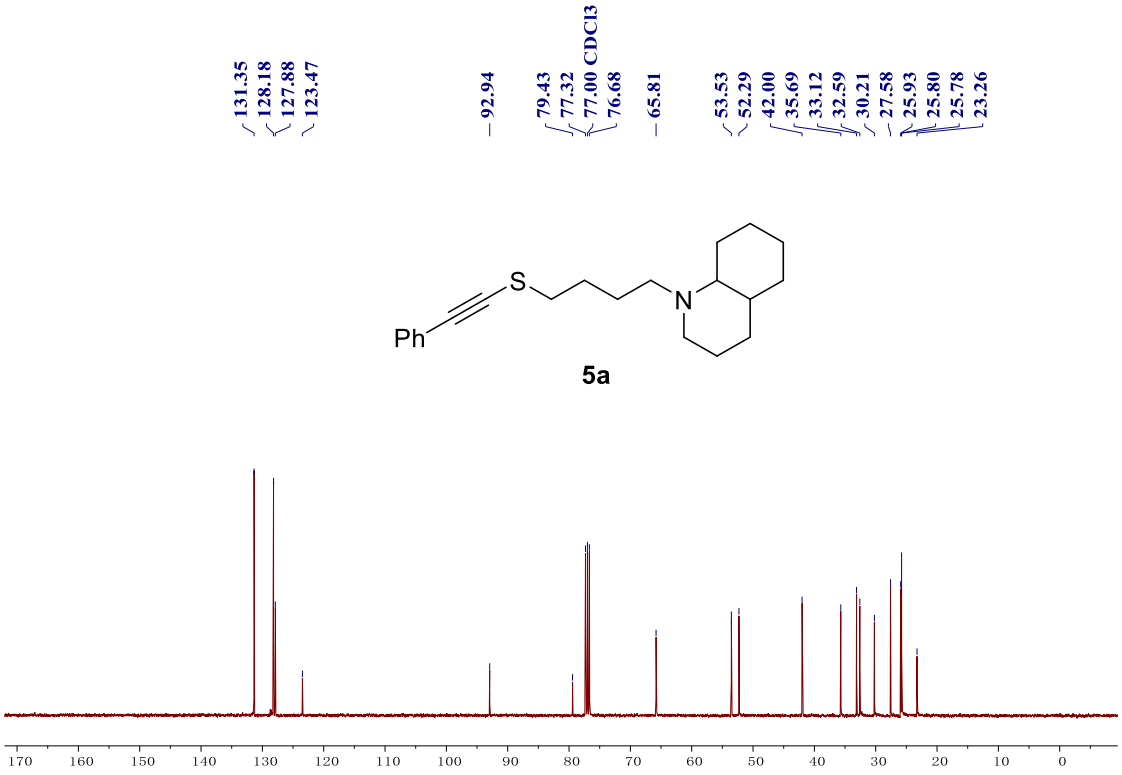
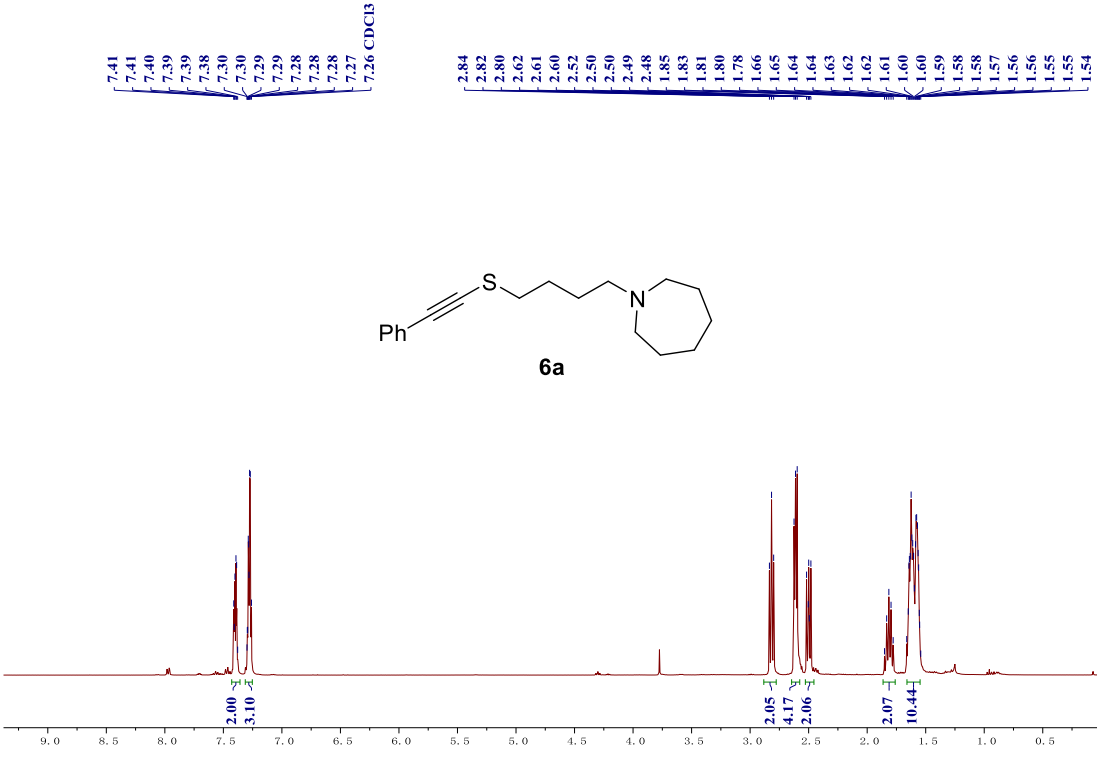


^{1}H NMR of 6a (400 MHz, $CDCl_3$**)**



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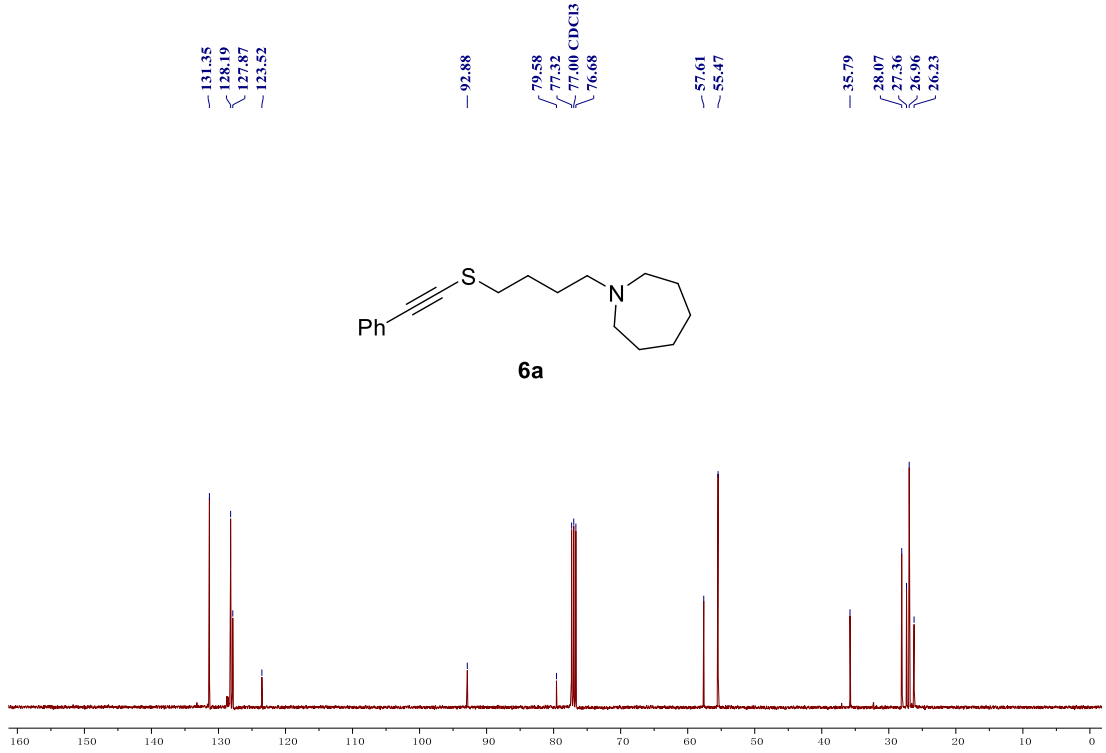
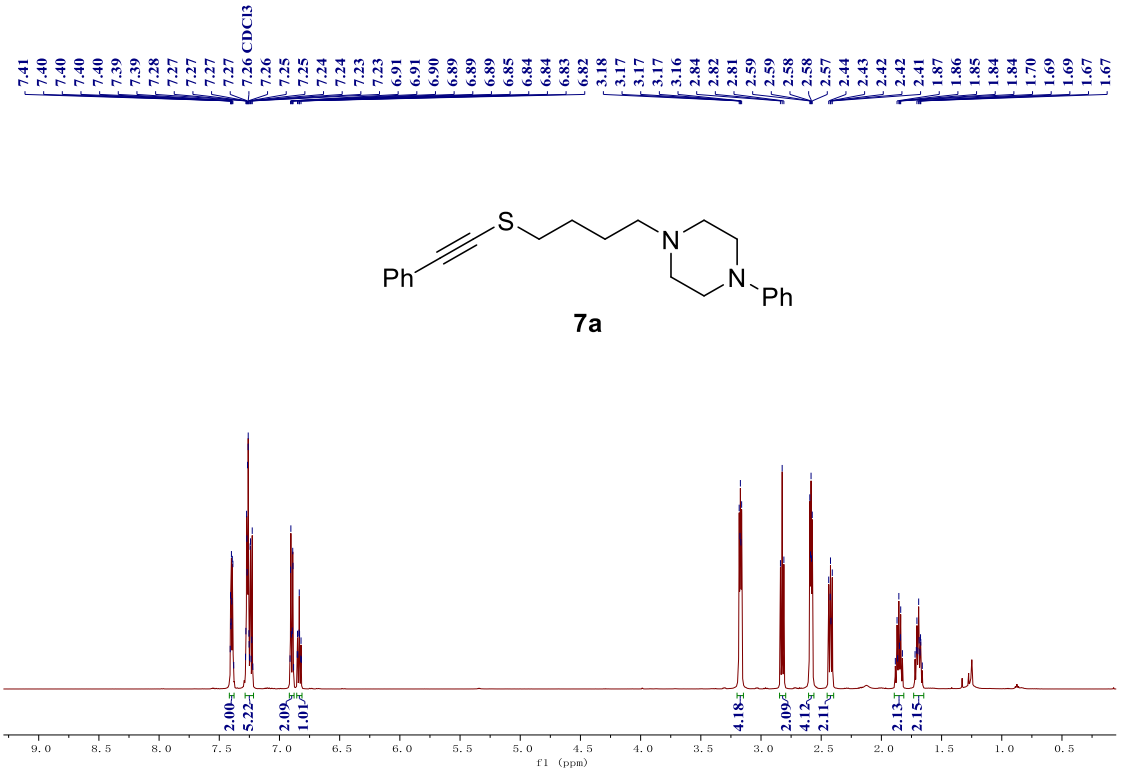
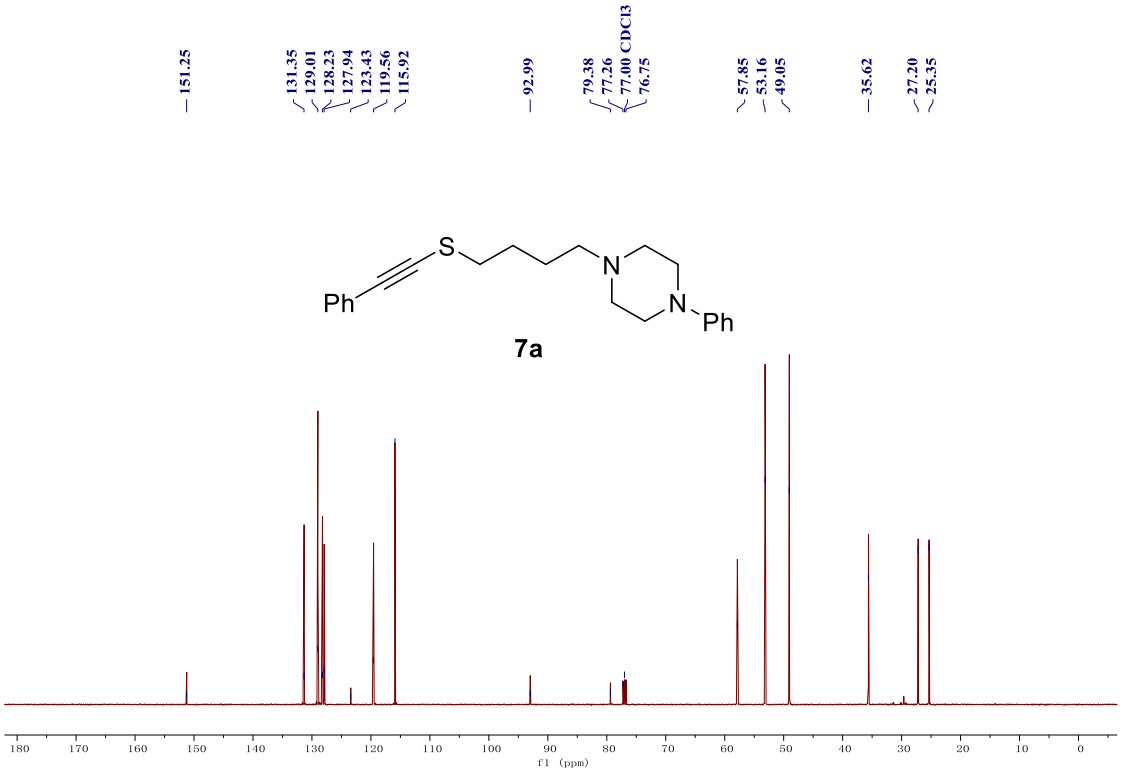


^{1}H NMR of 7a (500 MHz, $CDCl_3$**)**



^{13}C NMR of 7a (126 MHz, $CDCl_3$**)**



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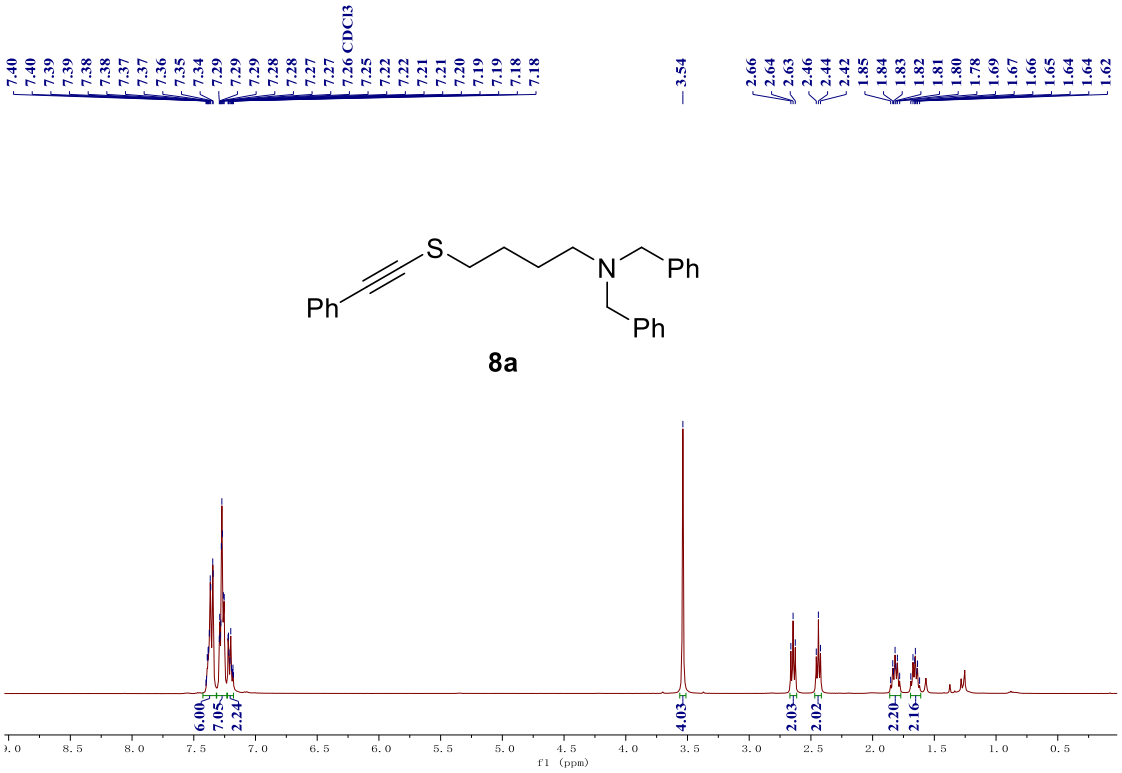

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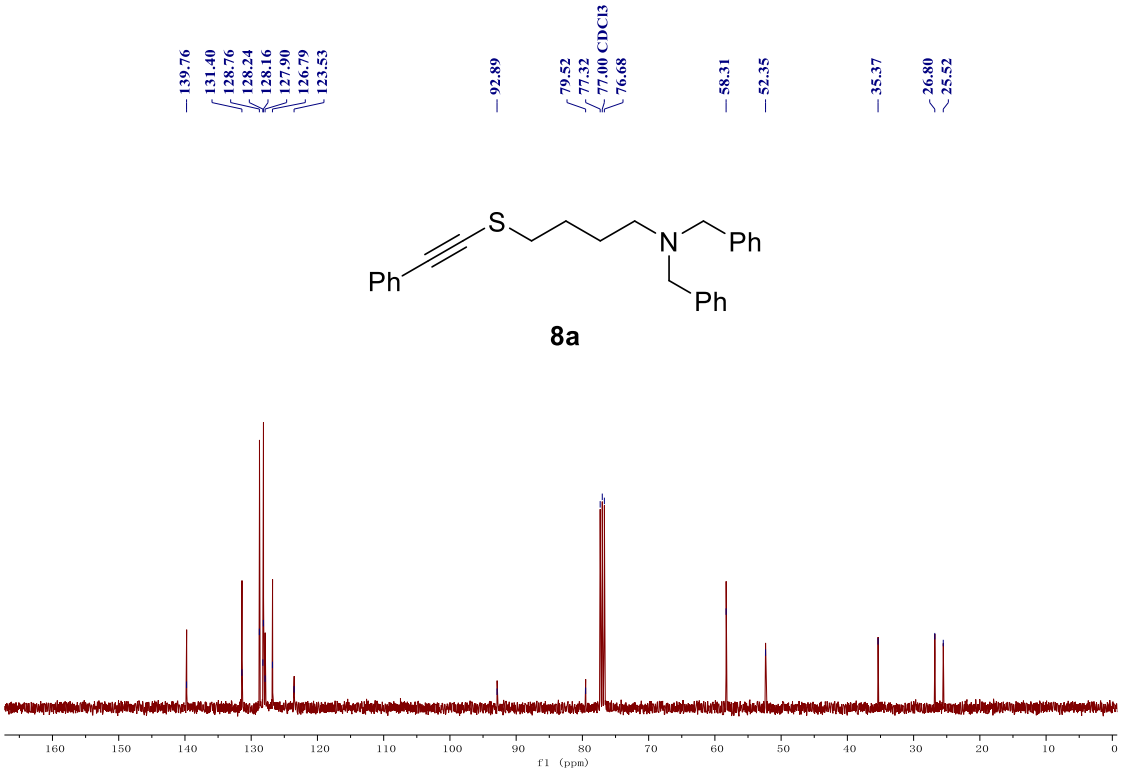

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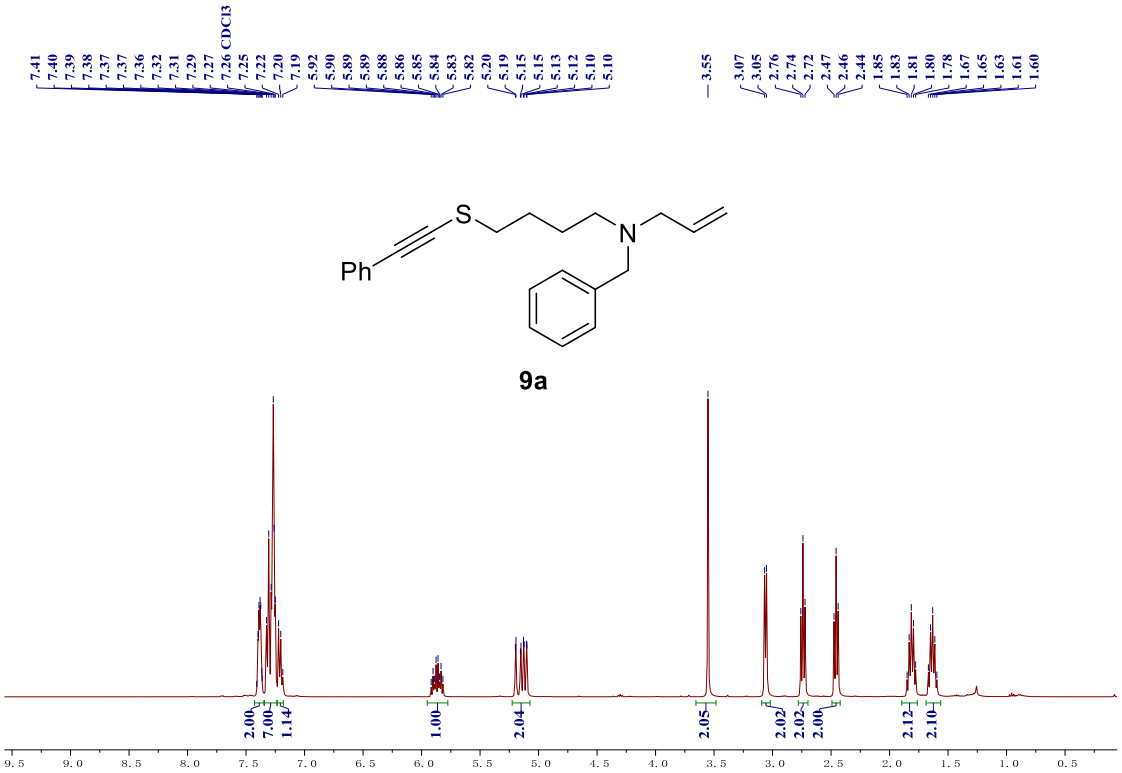

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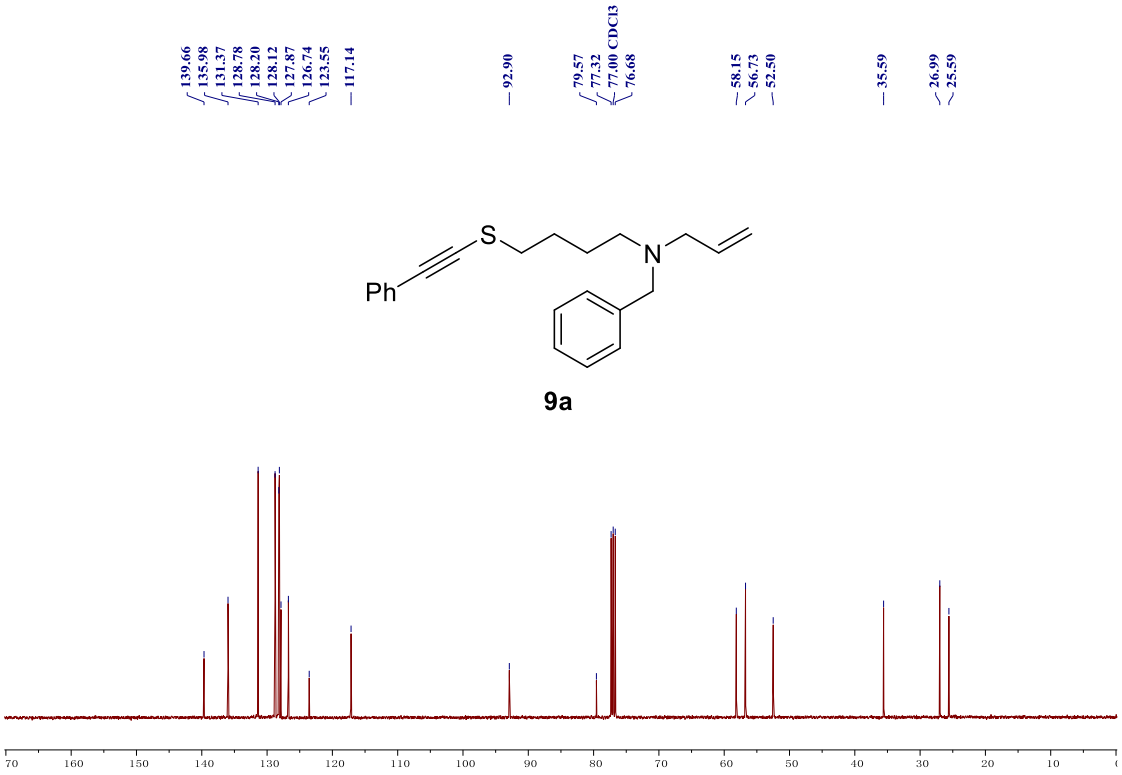
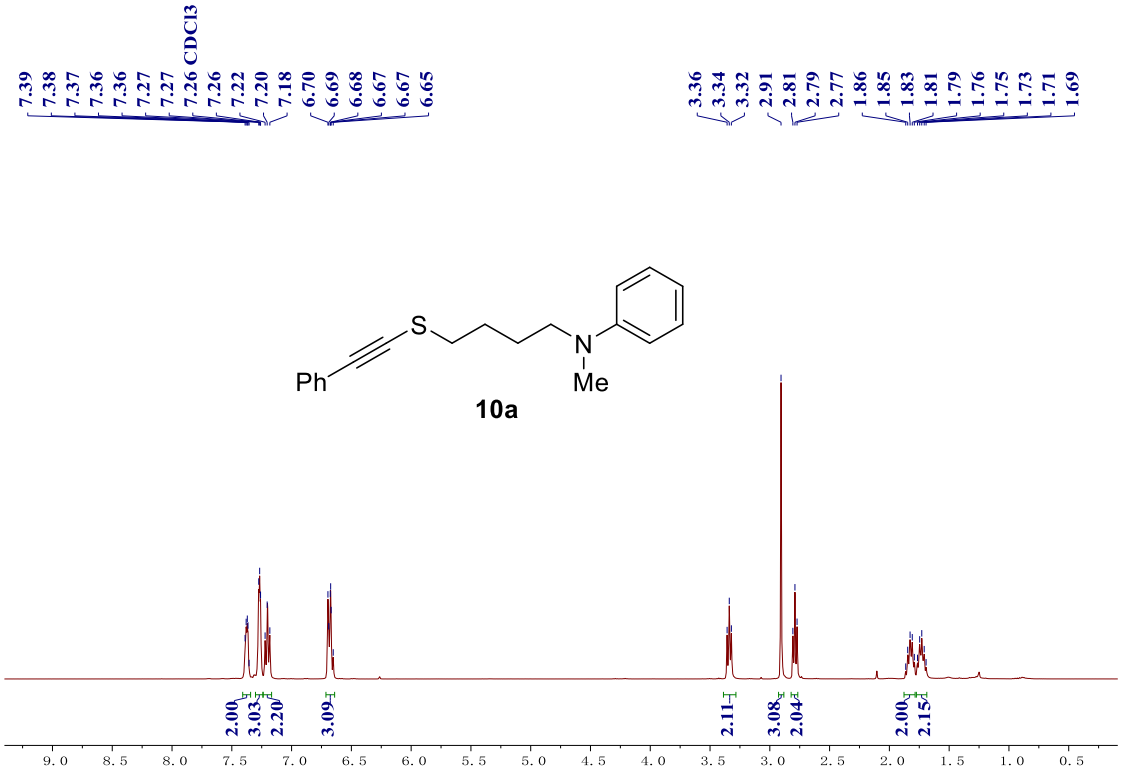
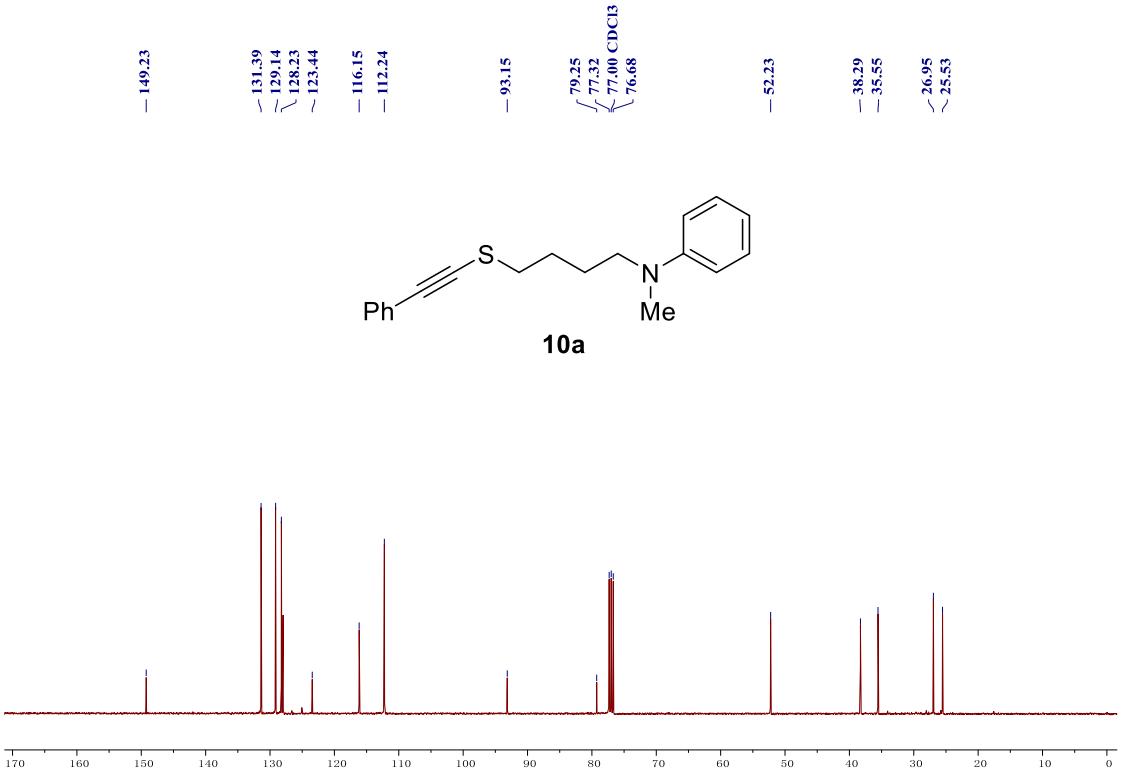


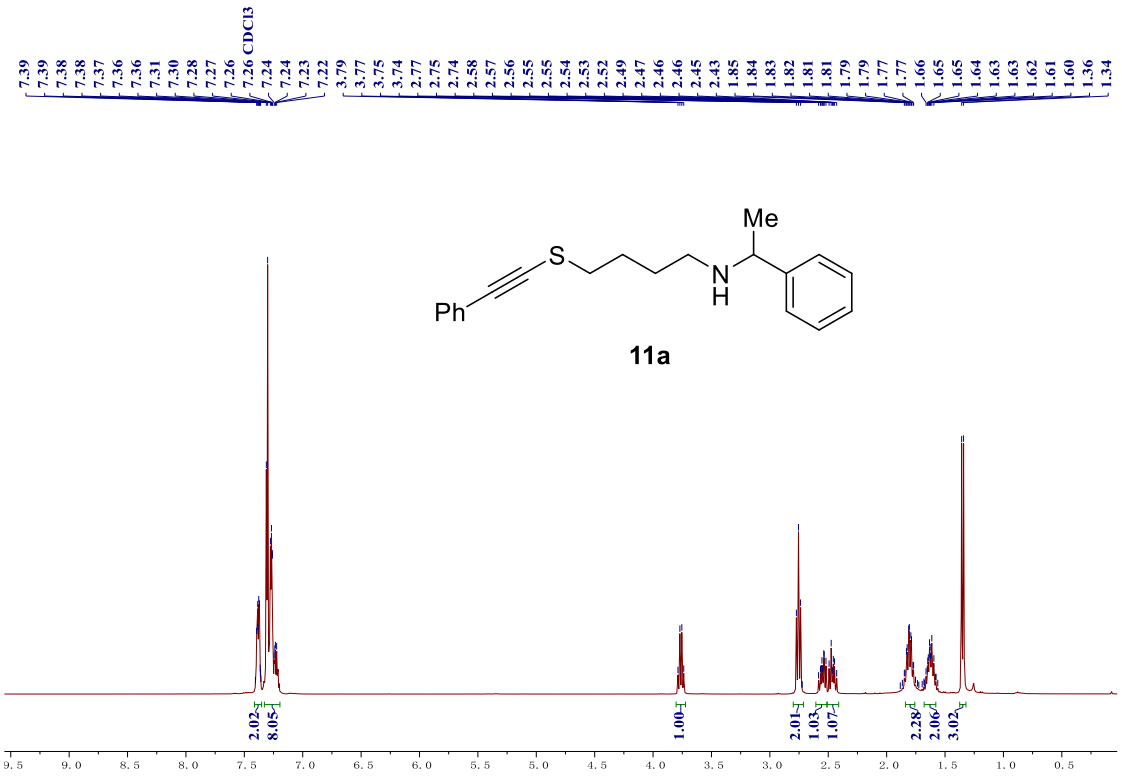
^{1}H NMR of 10a (400 MHz, $CDCl_3$)



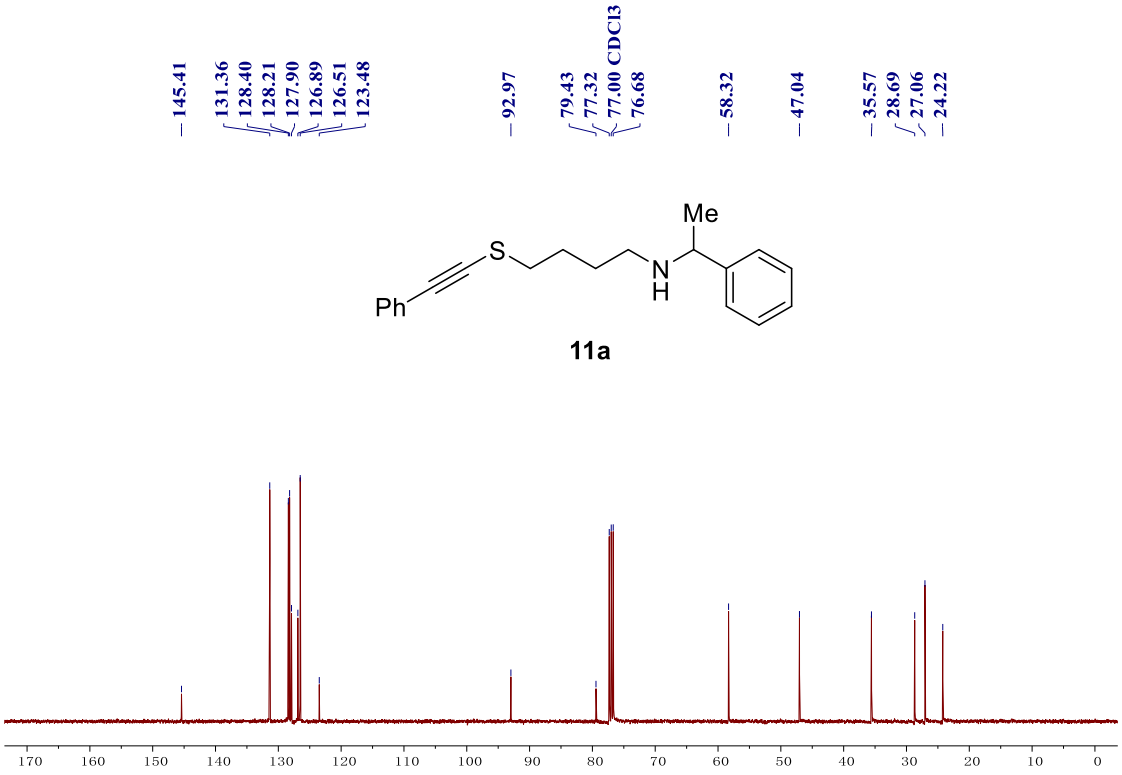
^{13}C NMR of 10a (101 MHz, $CDCl_3$**)**



^{1}H NMR of 11a (400 MHz, $CDCl_3$**)**



^{13}C NMR of 11a (101 MHz, $CDCl_3$**)**



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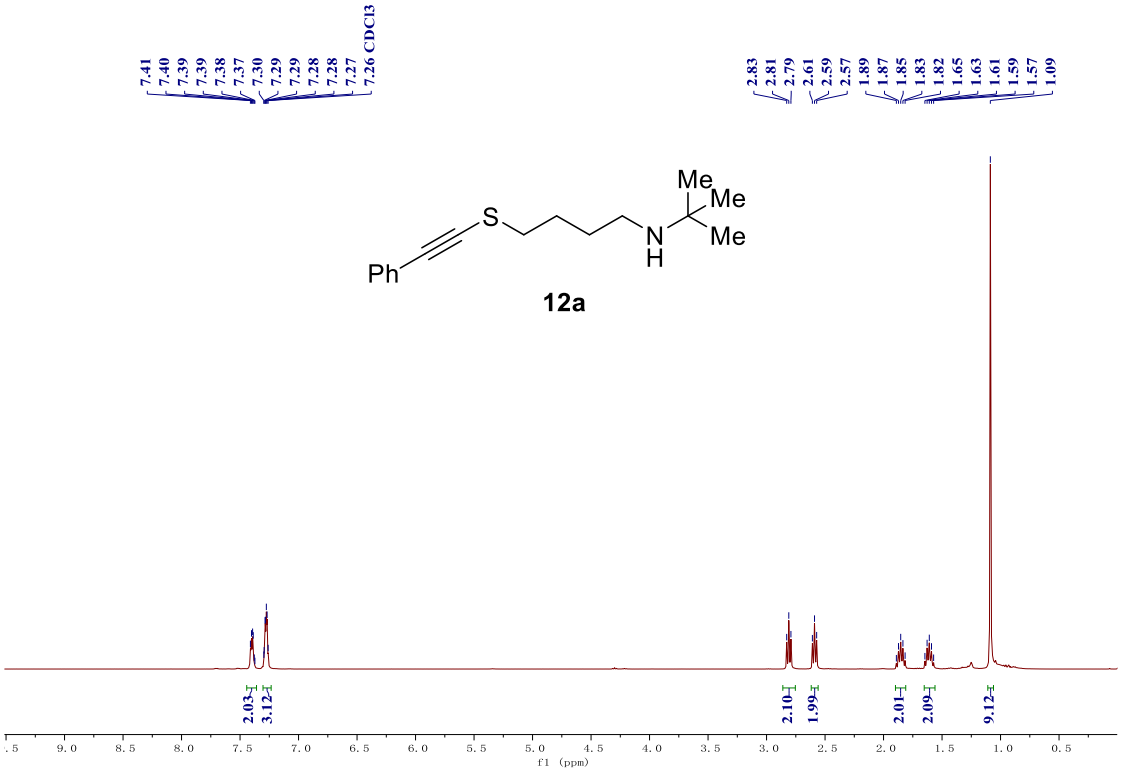
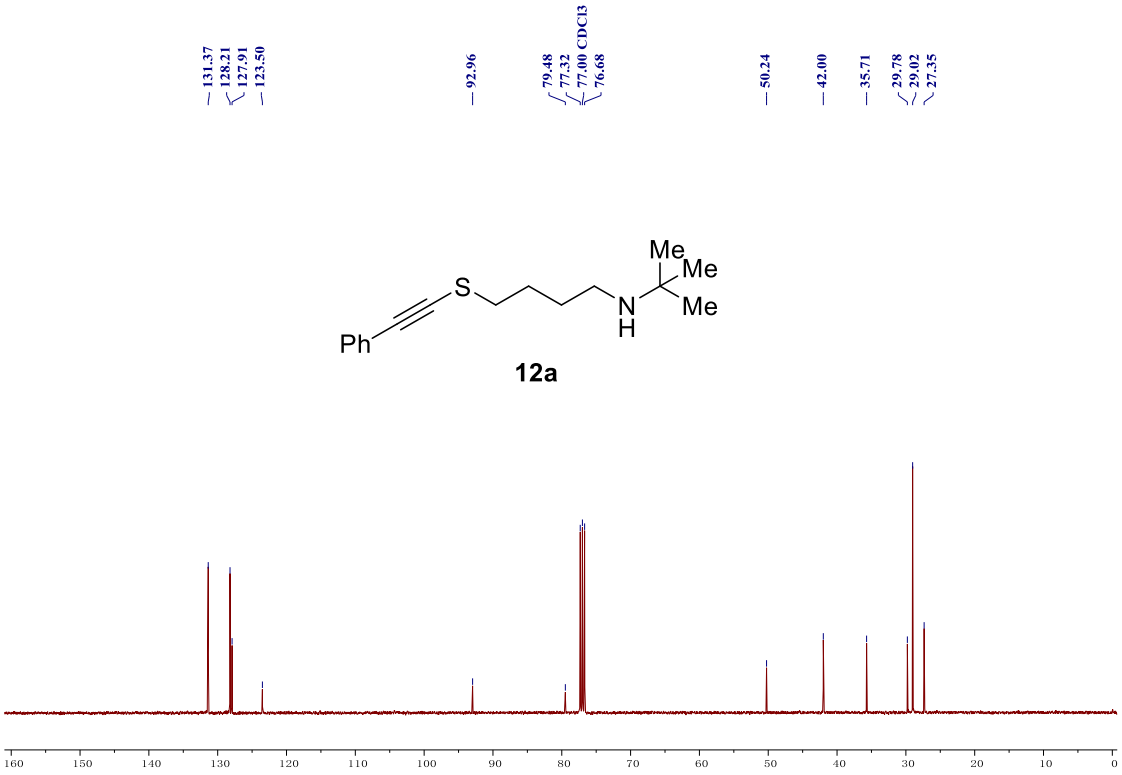
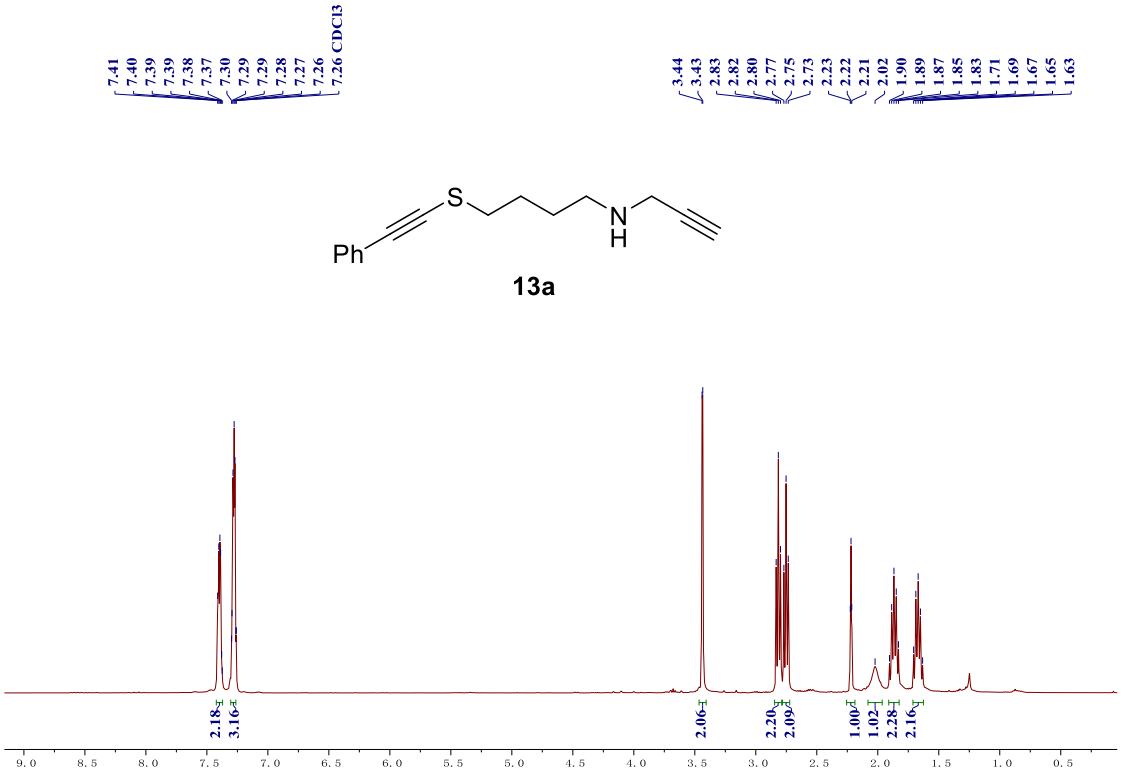


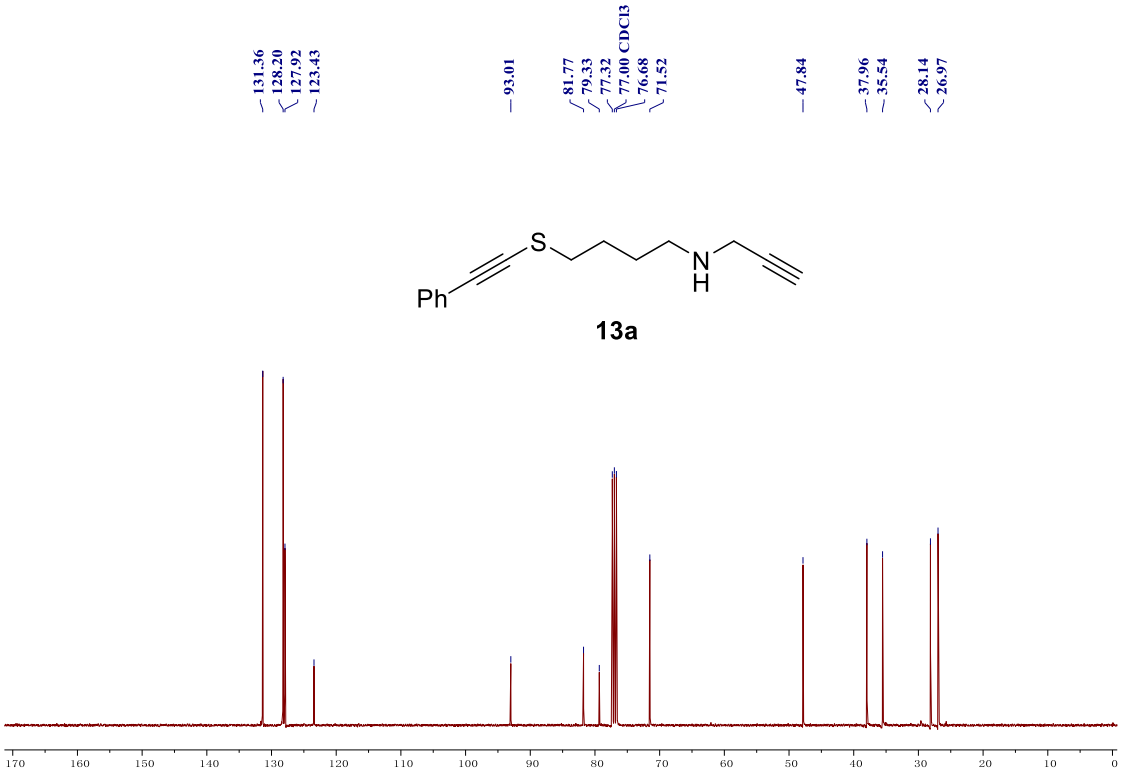
^{13}C NMR of 12a (101 MHz, $CDCl_3$**)**



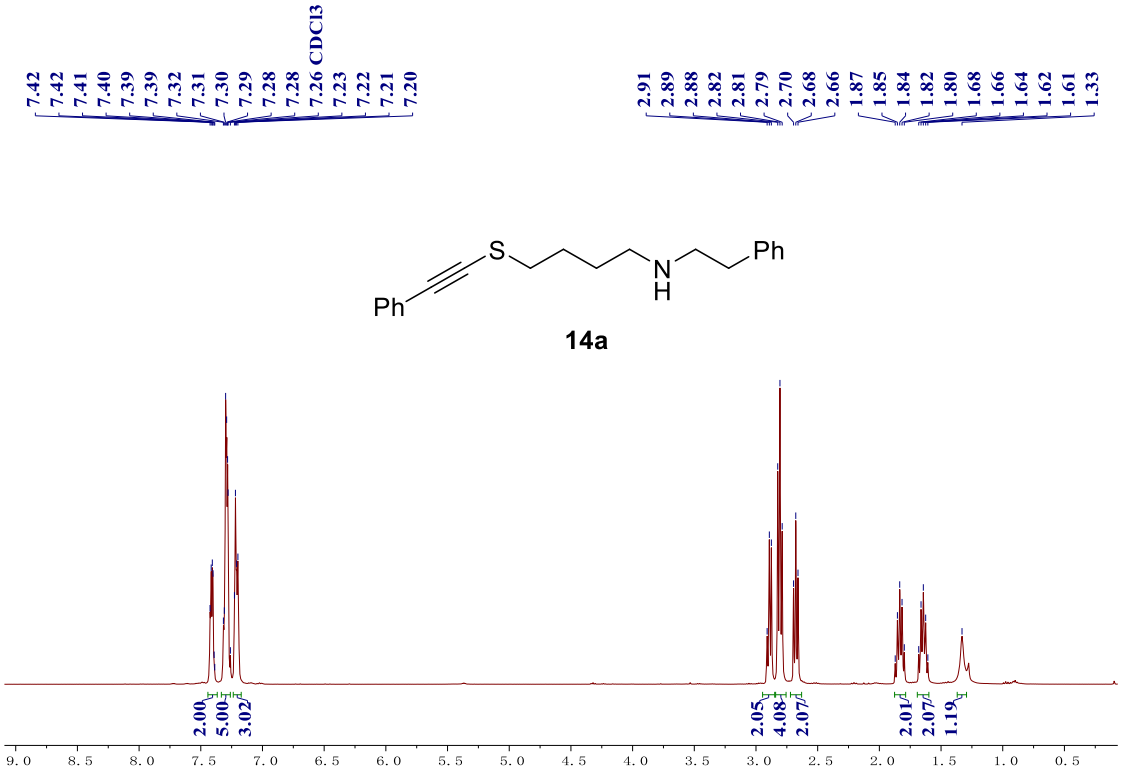
^{1}H NMR of 13a (400 MHz, $CDCl_3$**)**



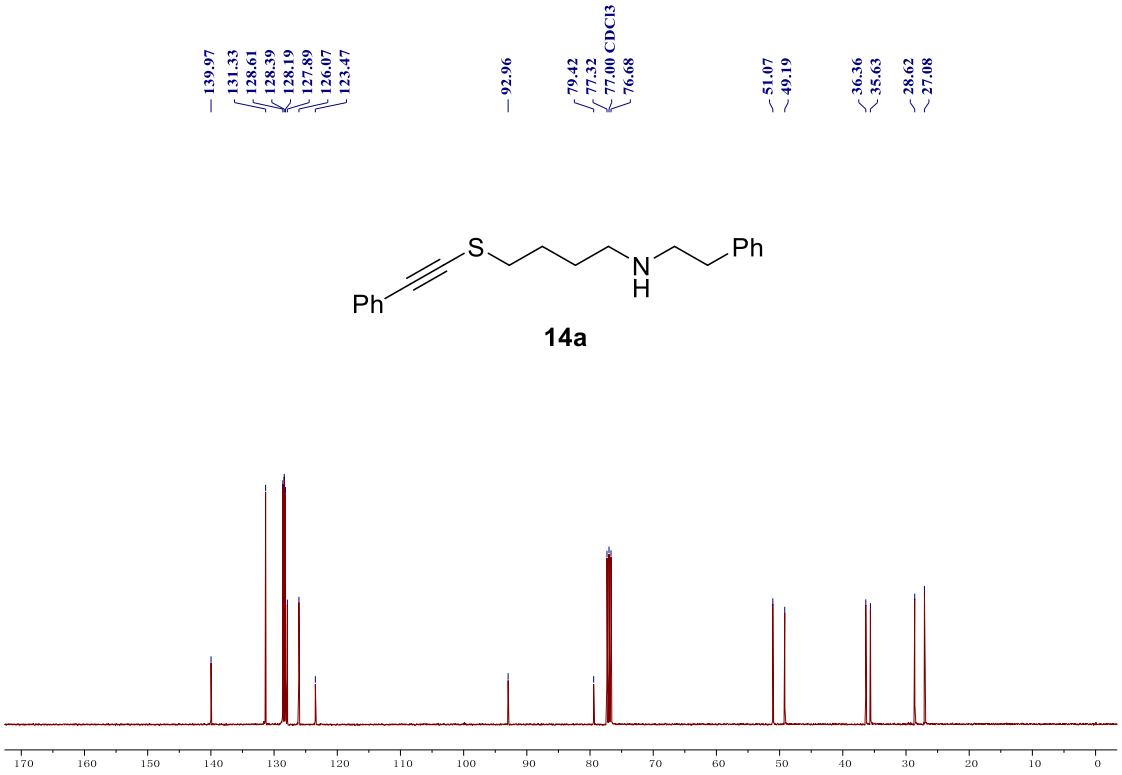
^{13}C NMR of 13a (101 MHz, $CDCl_3$**)**



^{1}H NMR of 14a (400 MHz, $CDCl_3$**)**

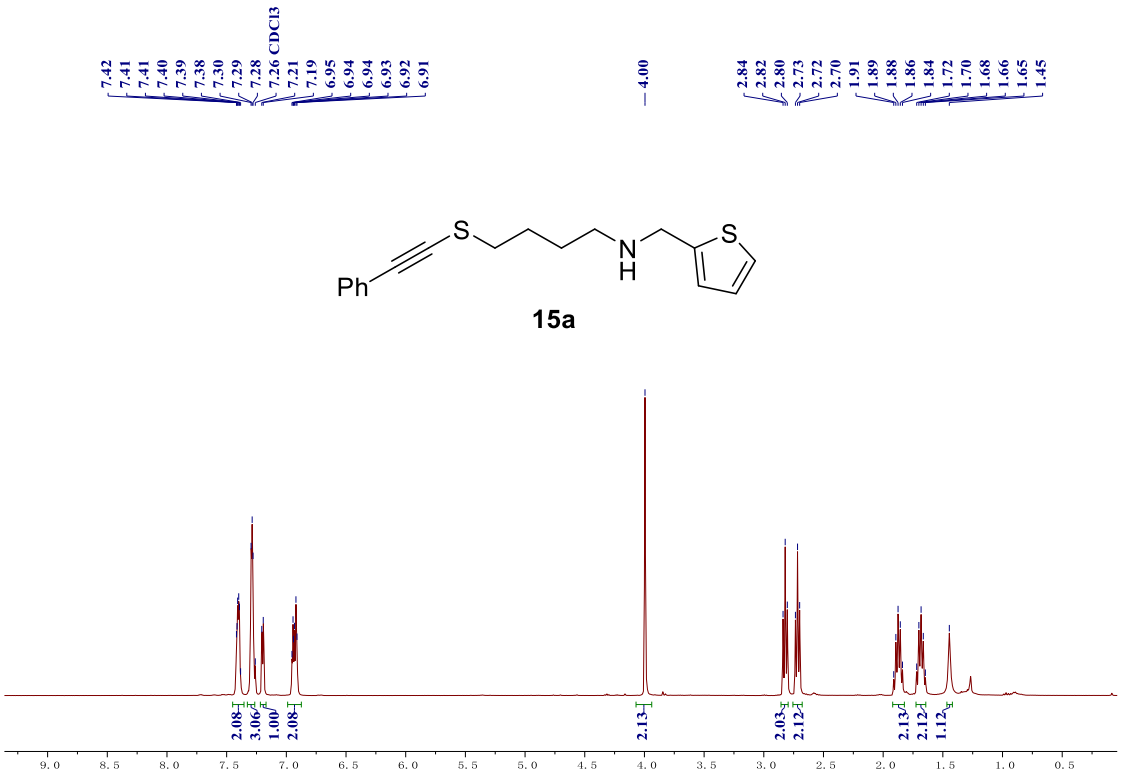


^{13}C NMR of 14a (101 MHz, $CDCl_3$**)**



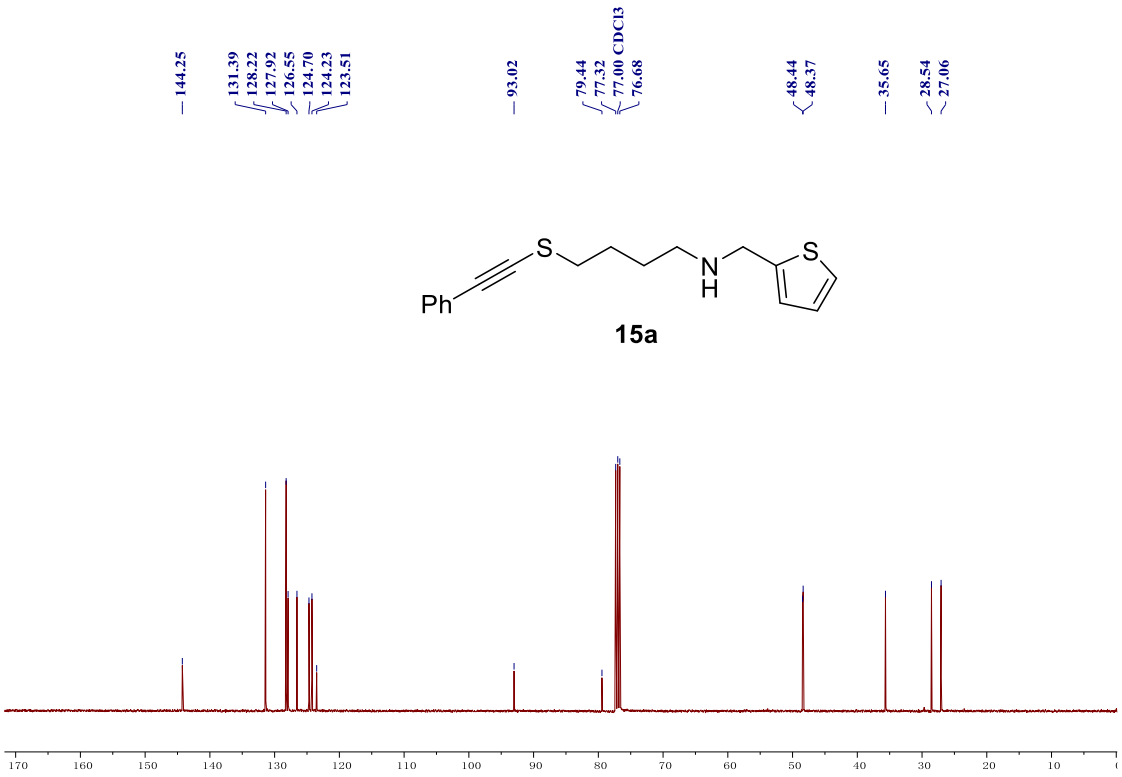
14a

^{1}H NMR of 15a (400 MHz, $CDCl_3$**)**

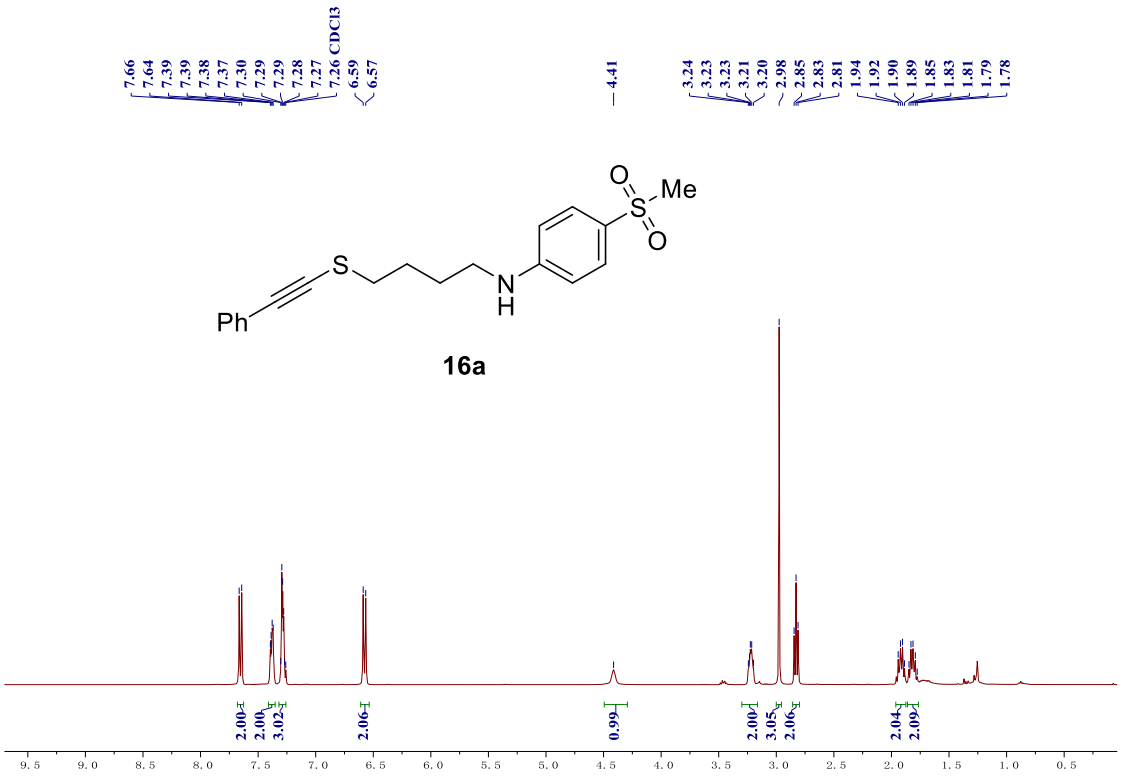


15a

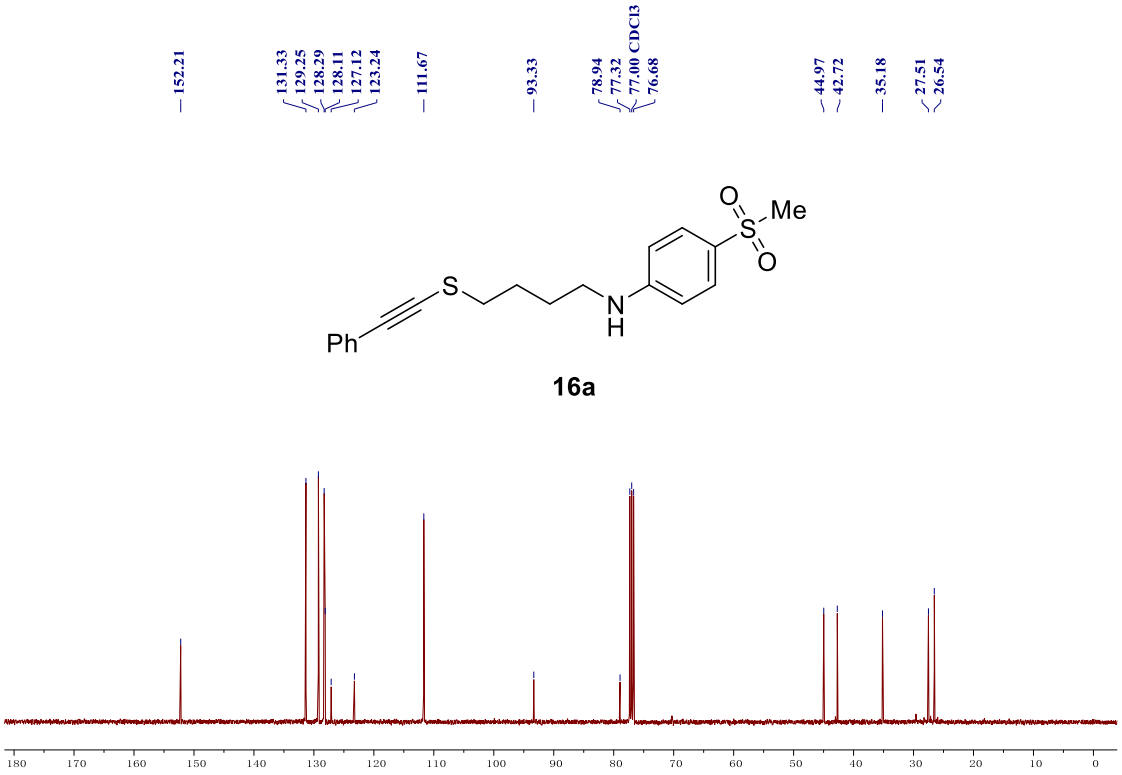
^{13}C NMR of 15a (101 MHz, $CDCl_3$**)**



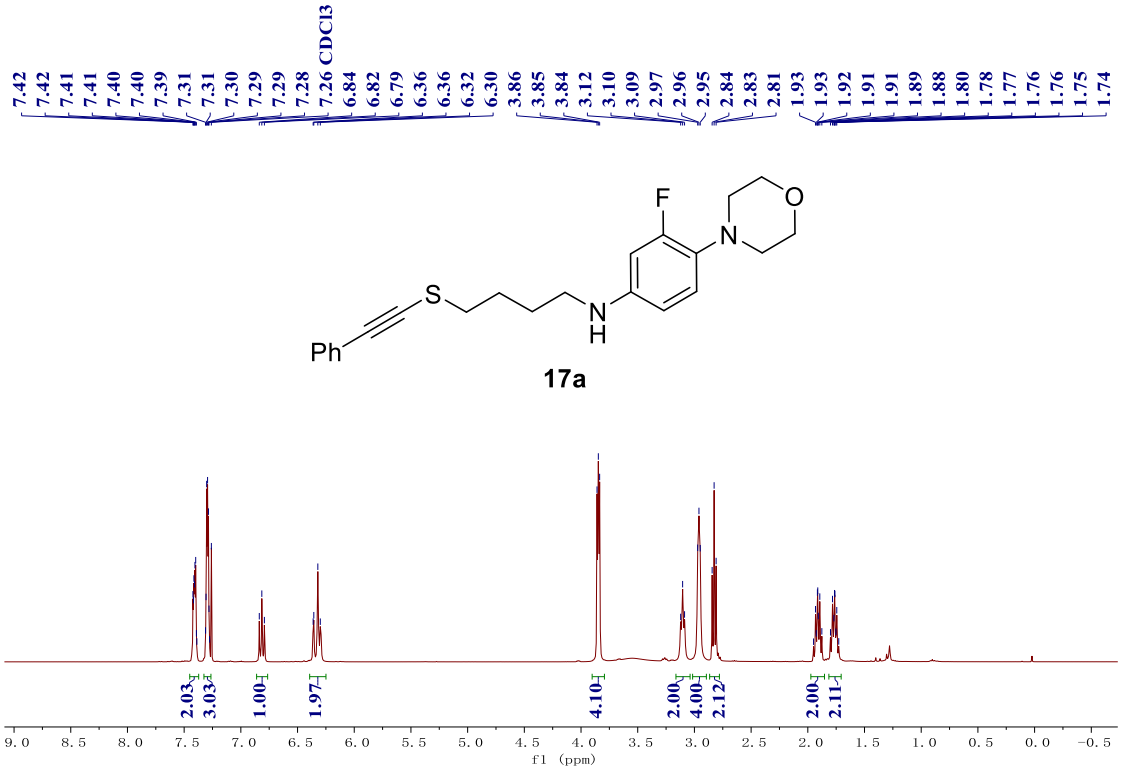
^{1}H NMR of 16a (400 MHz, $CDCl_3$**)**



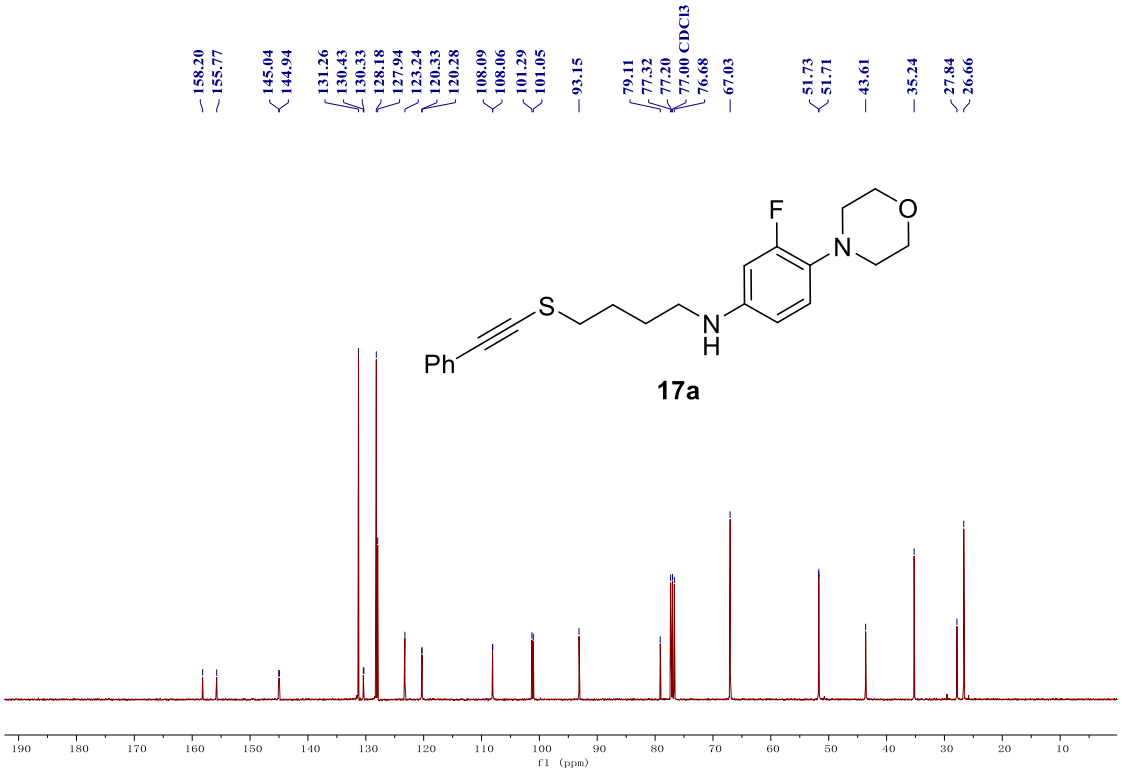
^{13}C NMR of 16a (101 MHz, $CDCl_3$**)**



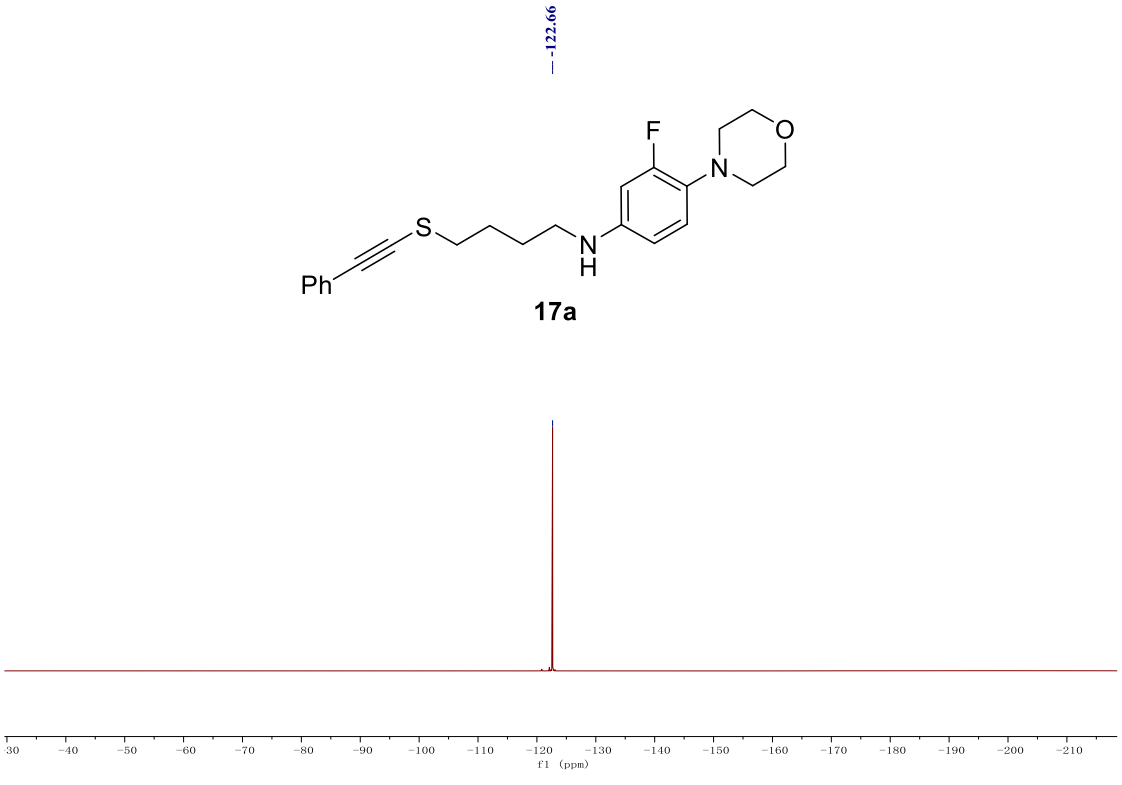
^{1}H NMR of 17a (400 MHz, $CDCl_3$**)**



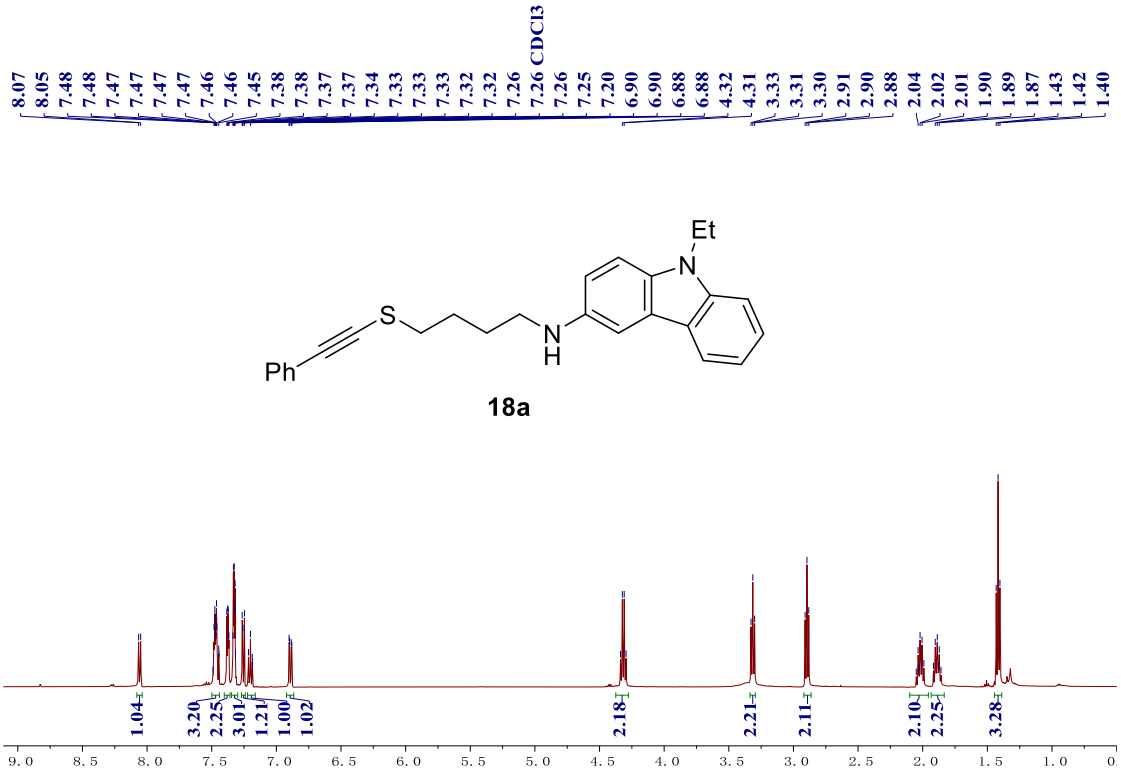
^{13}C NMR of 17a (101 MHz, $CDCl_3$**)**



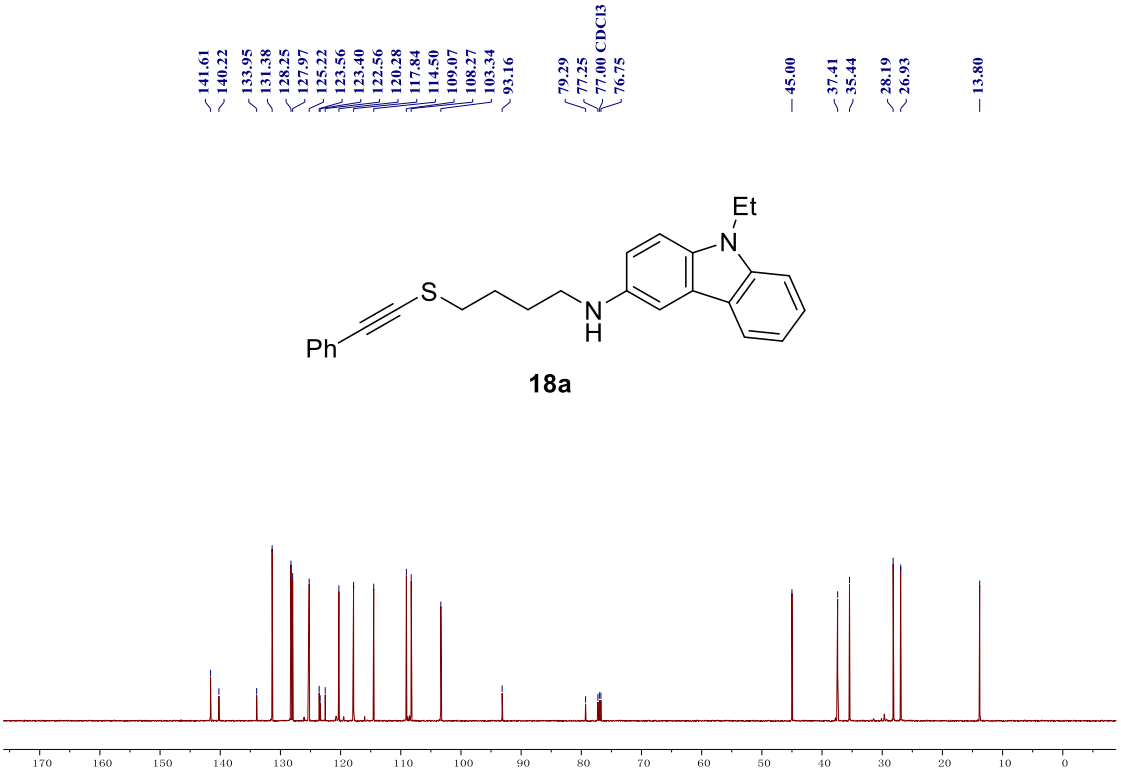
^{19}F NMR of 17a (376 MHz, $CDCl_3$**)**



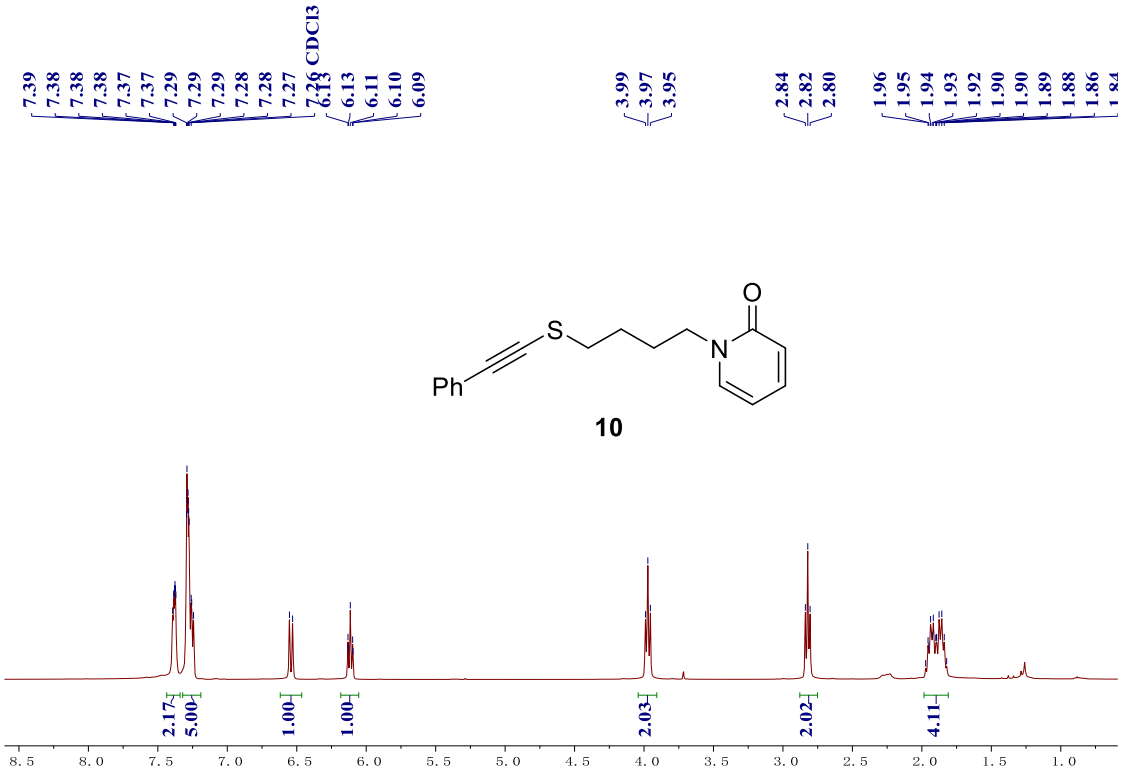
^{1}H NMR of 18a (500 MHz, $CDCl_3$**)**



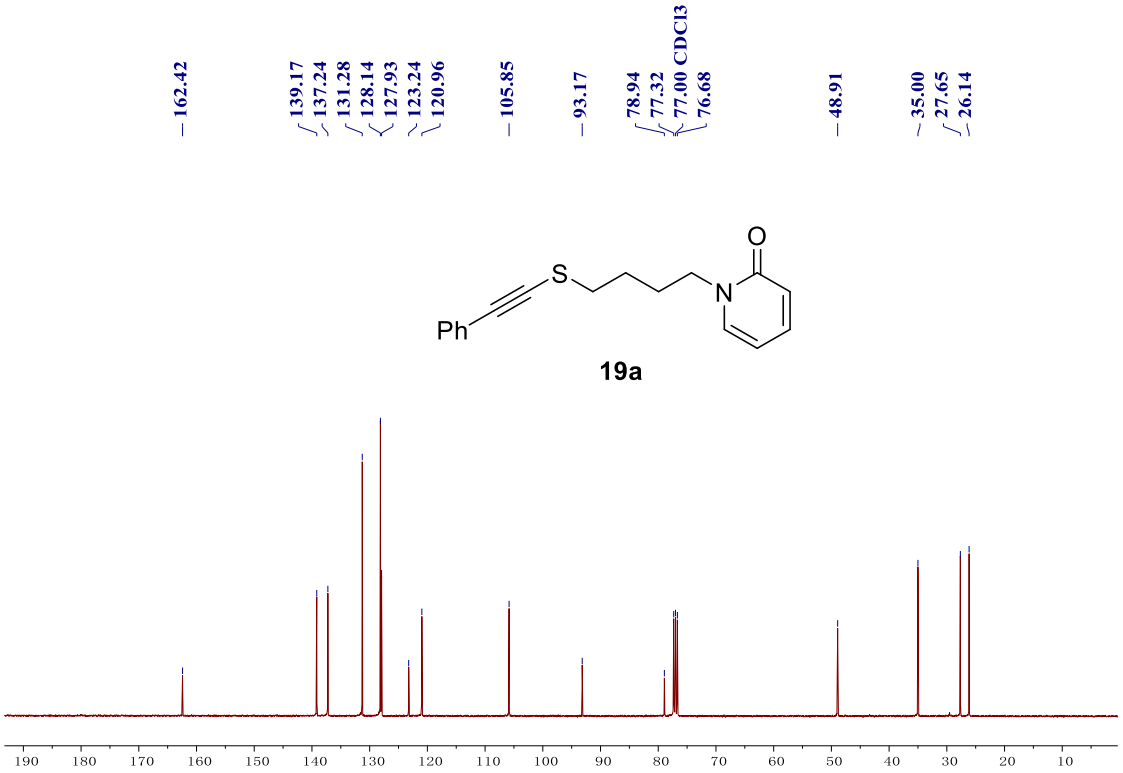
^{13}C NMR of 18a (126 MHz, $CDCl_3$**)**



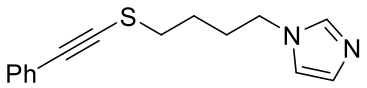
^{1}H NMR of 19a (400 MHz, $CDCl_3$**)**



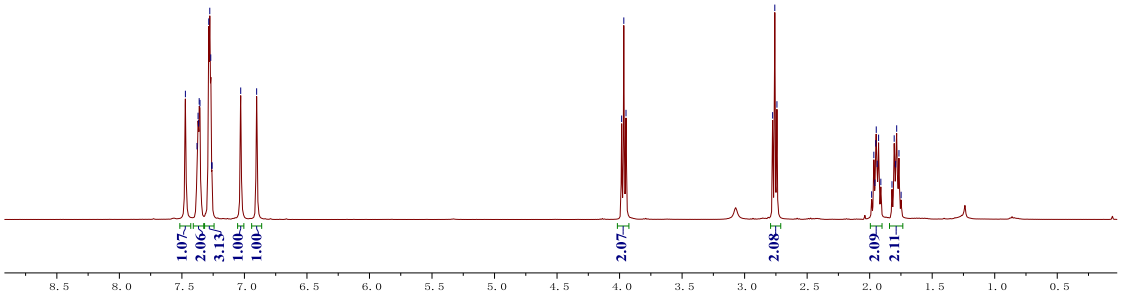
^{13}C NMR of 19a (101 MHz, $CDCl_3$**)**



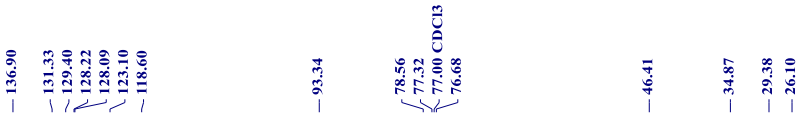
^{1}H NMR of 20a (400 MHz, $CDCl_3$**)**

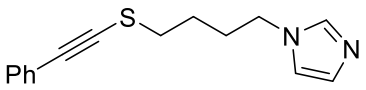


20a

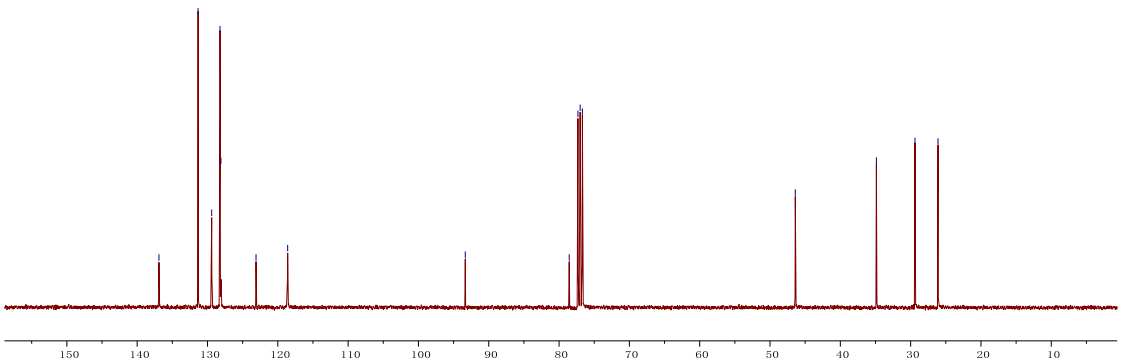


^{13}C NMR of 20a (101 MHz, $CDCl_3$**)**

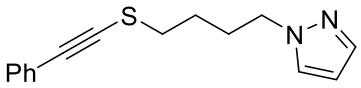




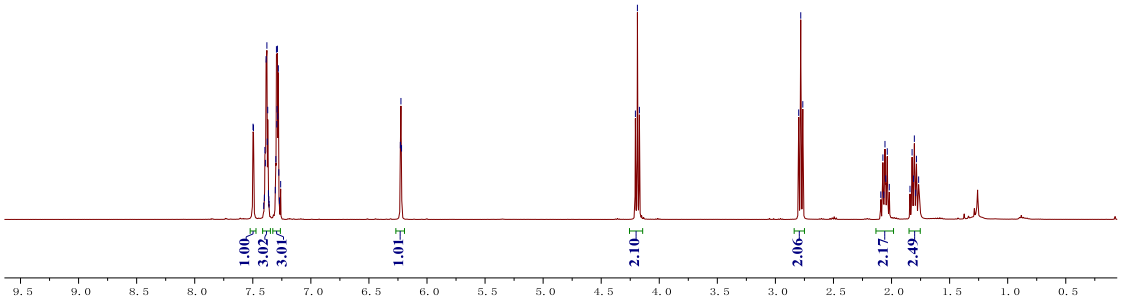
20a



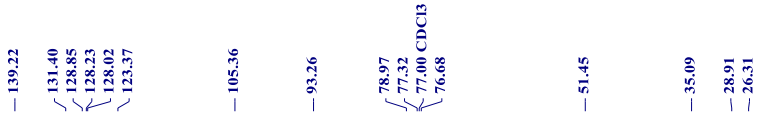
^{1}H NMR of 21a (400 MHz, $CDCl_3$**)**

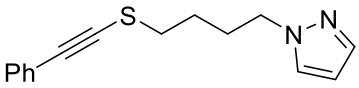


21a

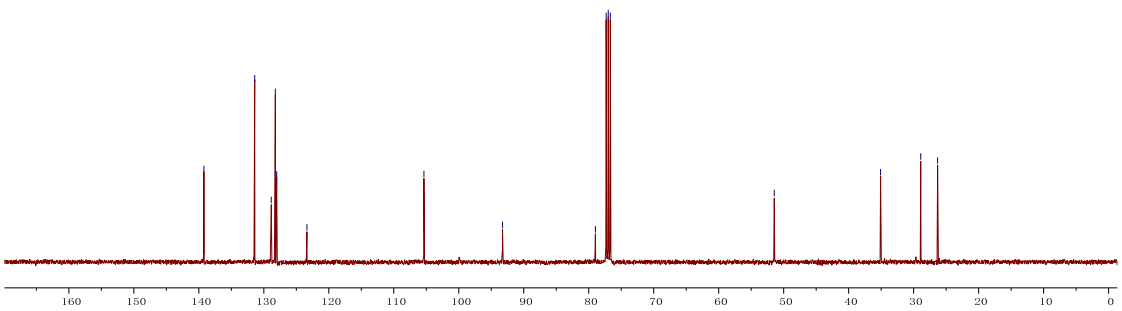


^{13}C NMR of 21a (101 MHz, $CDCl_3$**)**

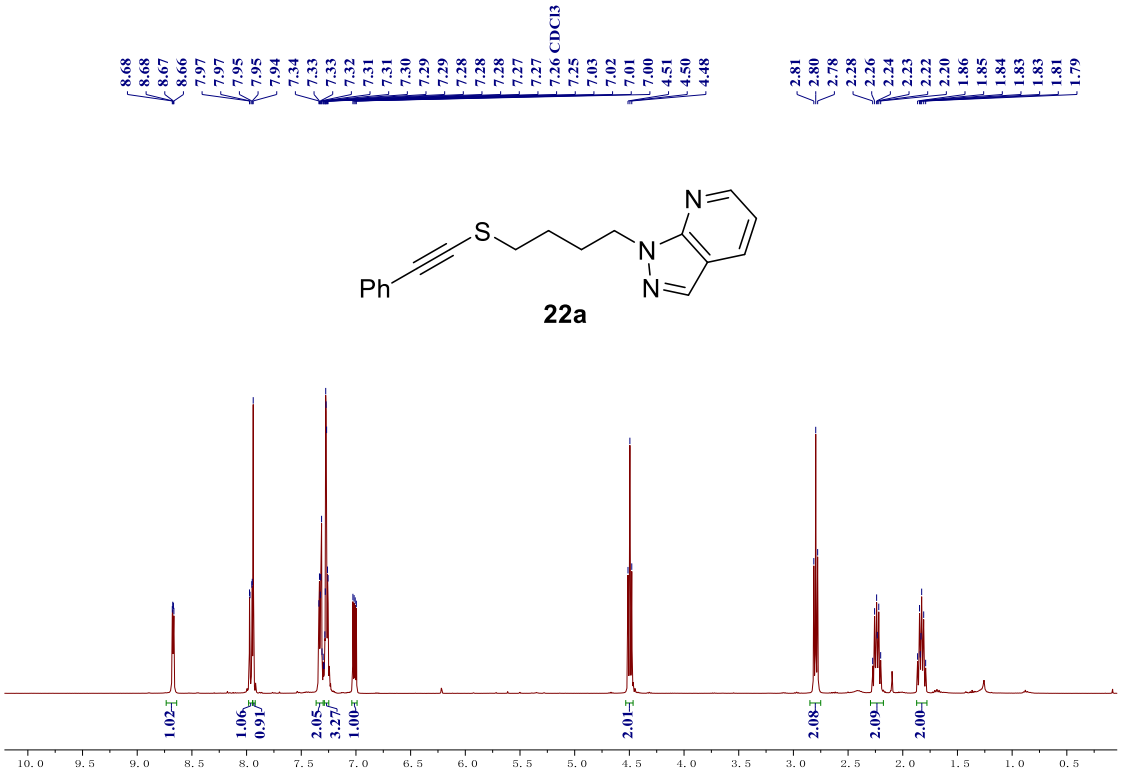




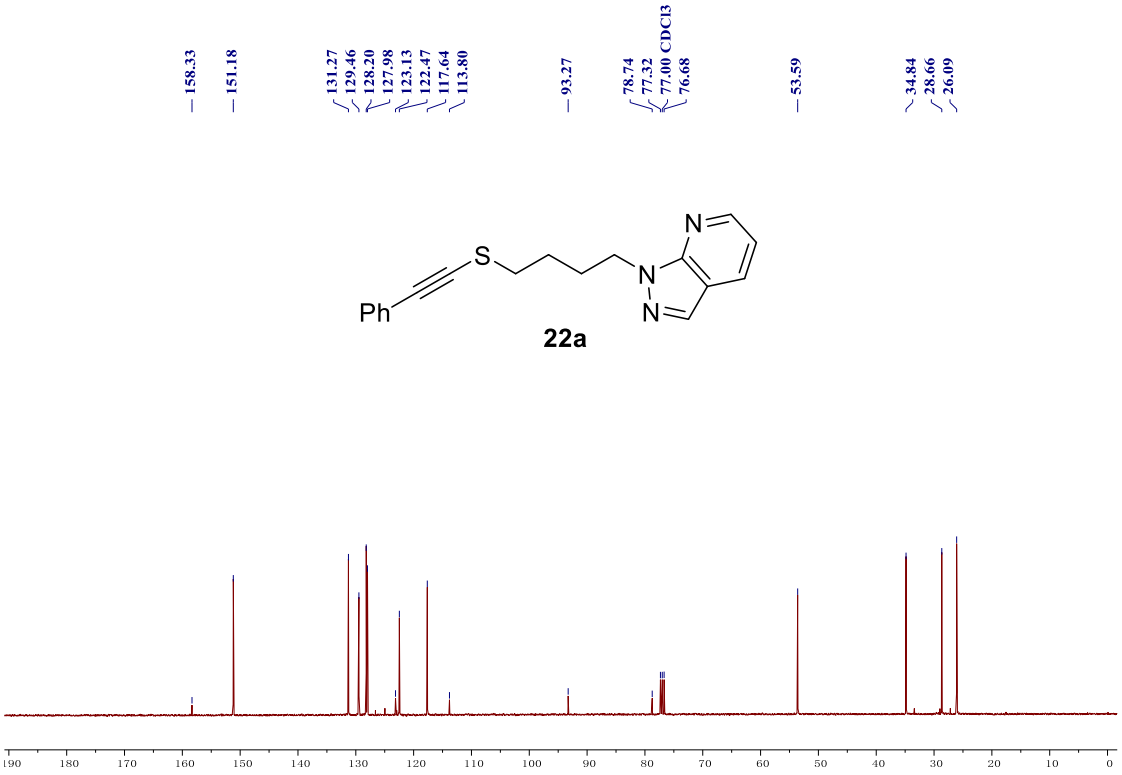
21a



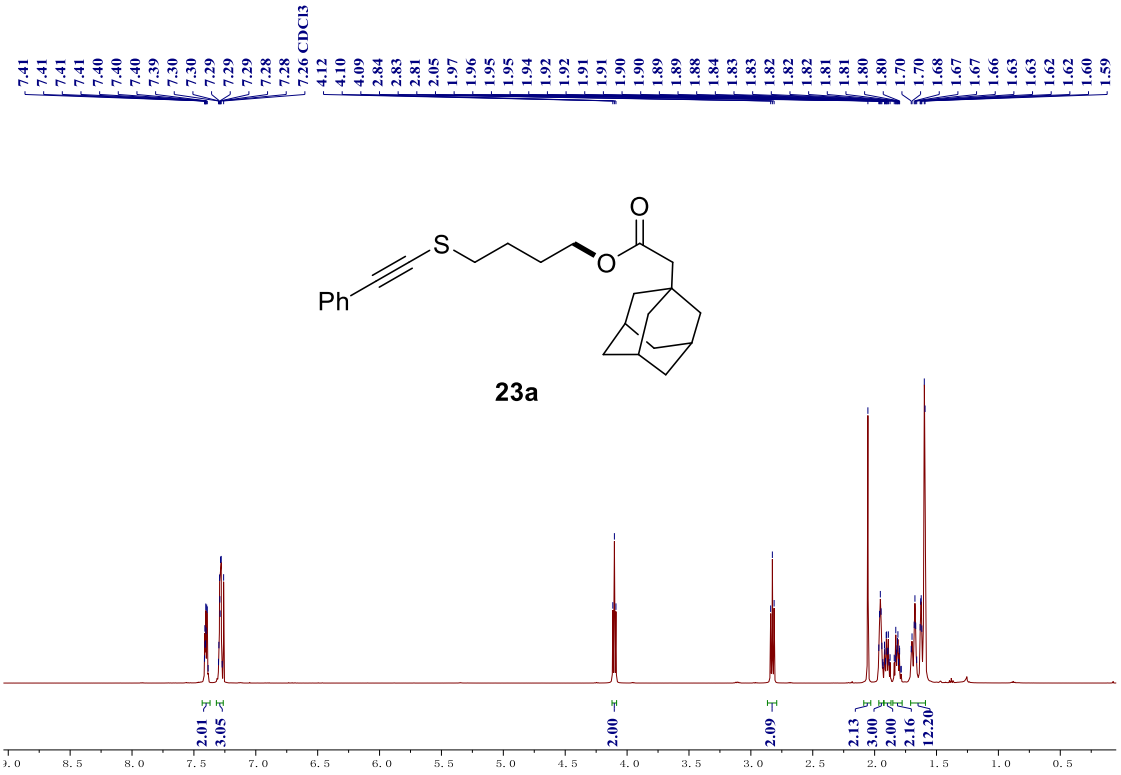
^{1}H NMR of 22a (400 MHz, $CDCl_3$**)**



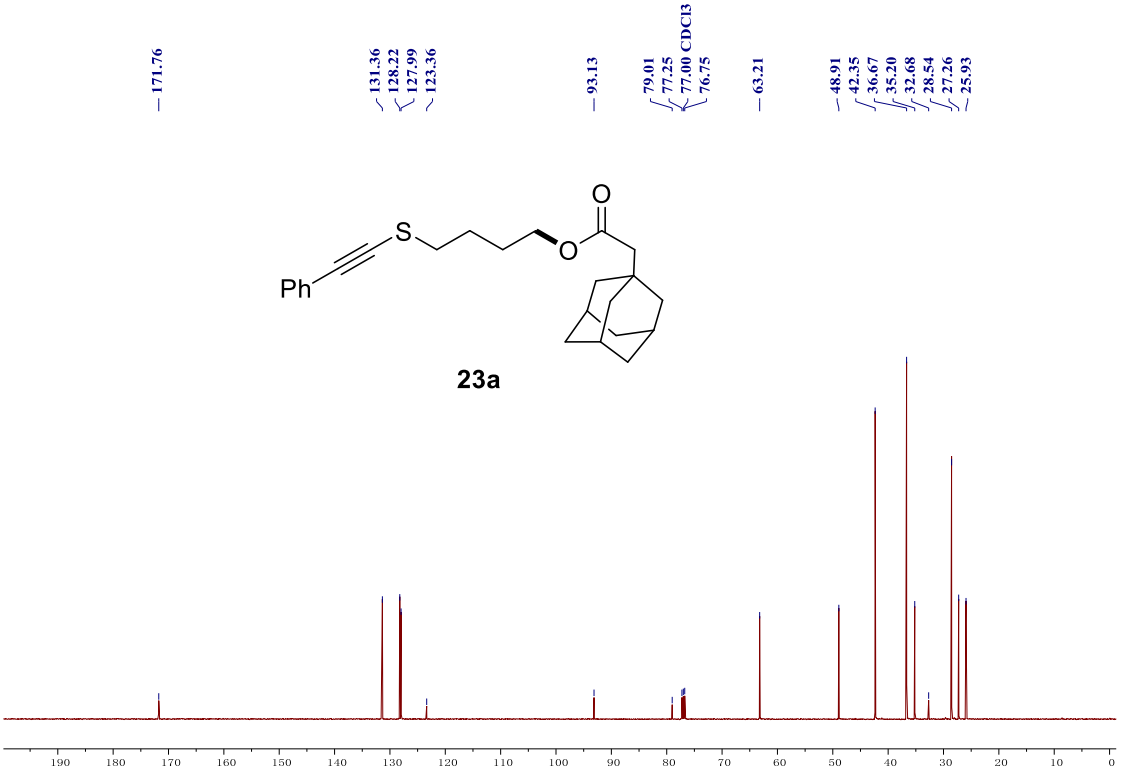
^{13}C NMR of 22a (101 MHz, $CDCl_3$**)**



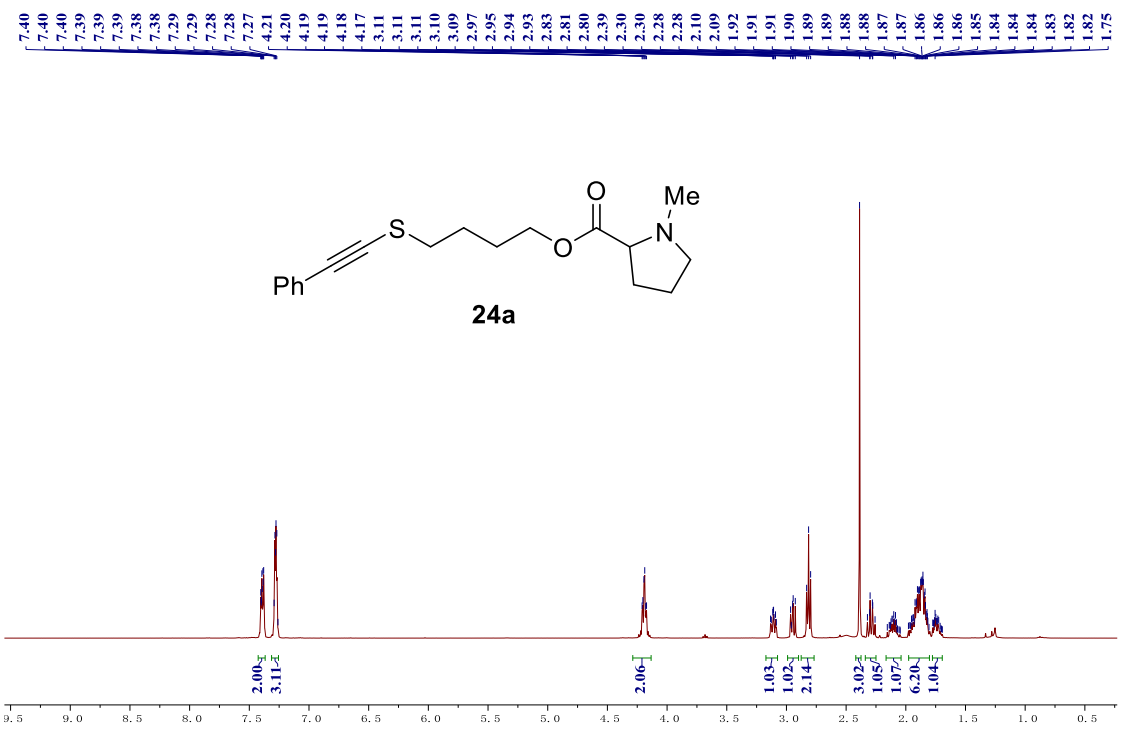
^{1}H NMR of 23a (500 MHz, $CDCl_3$**)**



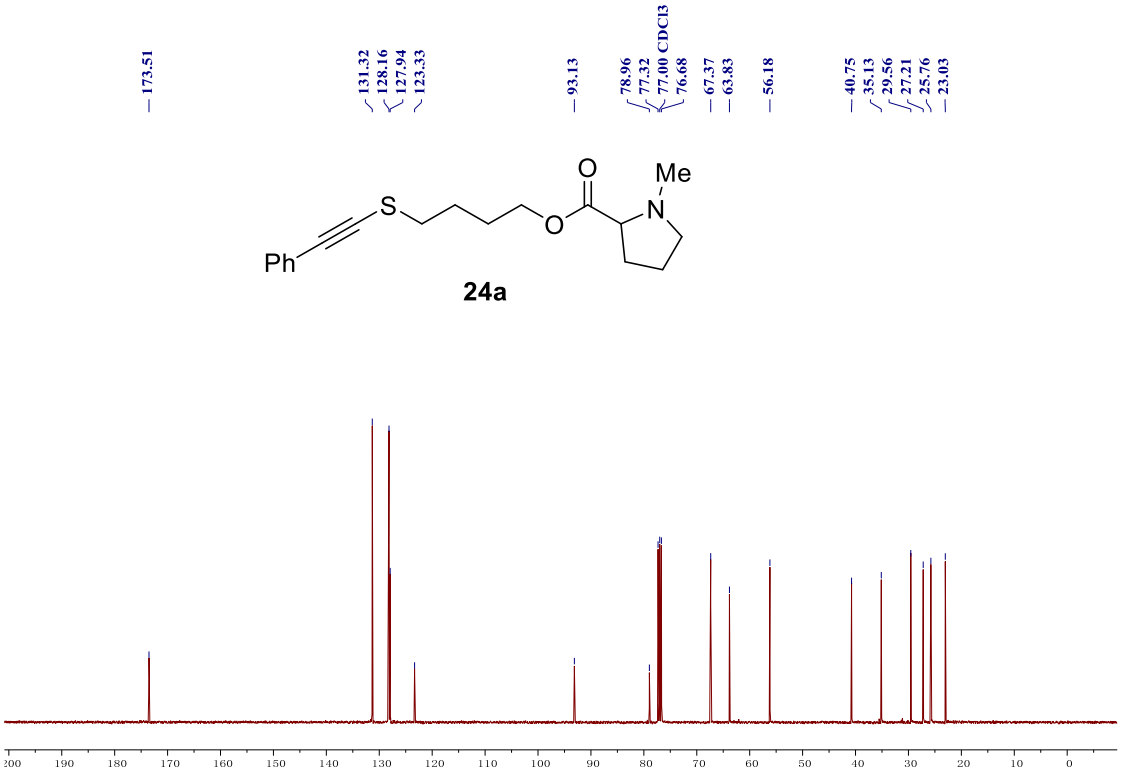
^{13}C NMR of 23a (126 MHz, $CDCl_3$**)**



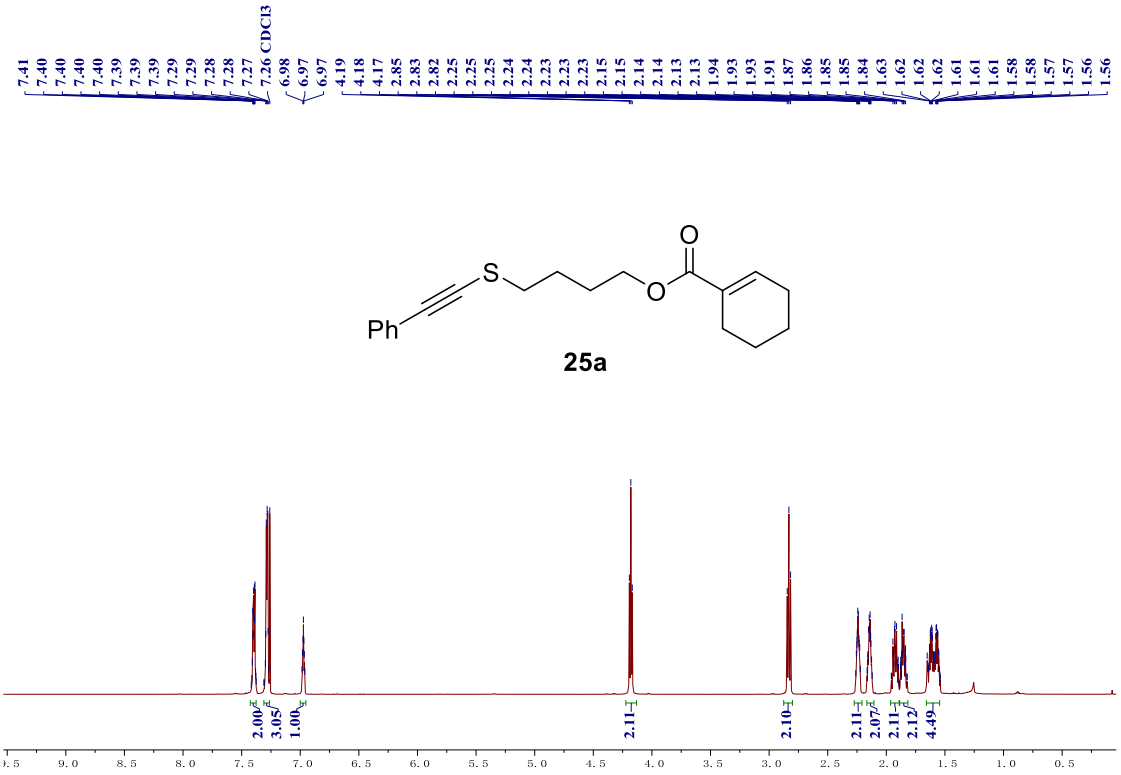
^{1}H NMR of 24a (400 MHz, $CDCl_3$**)**



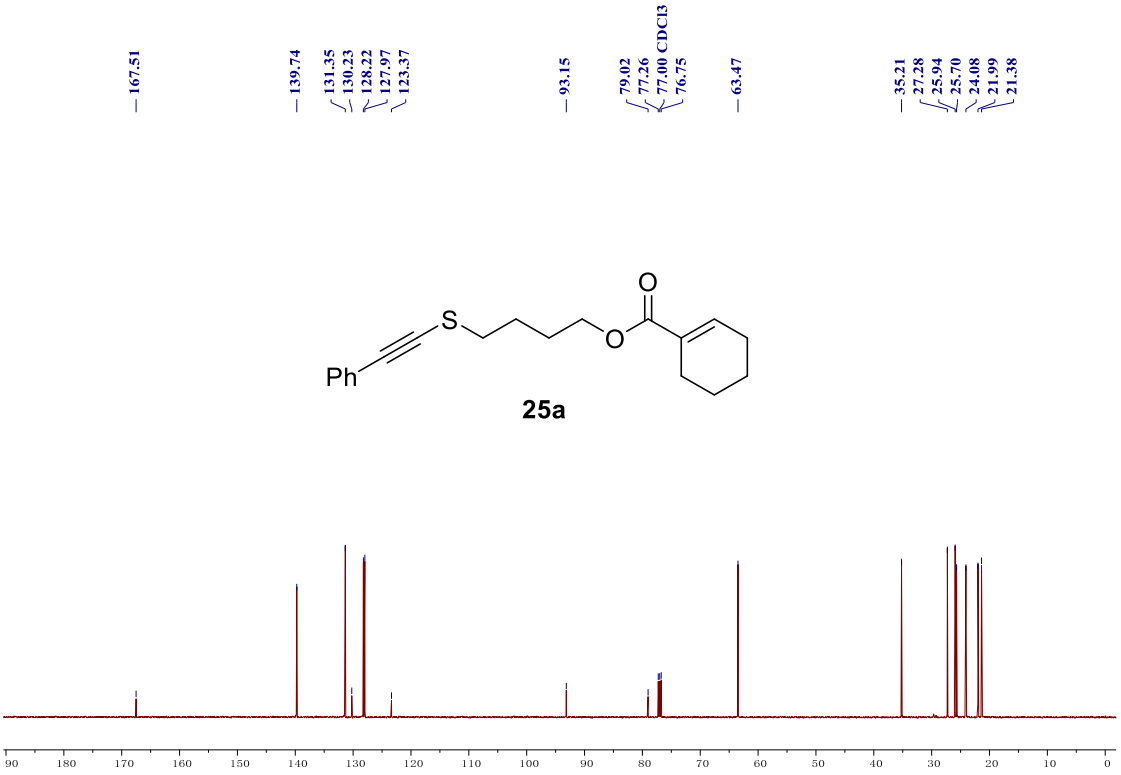
^{13}C NMR of 24a (101 MHz, $CDCl_3$**)**



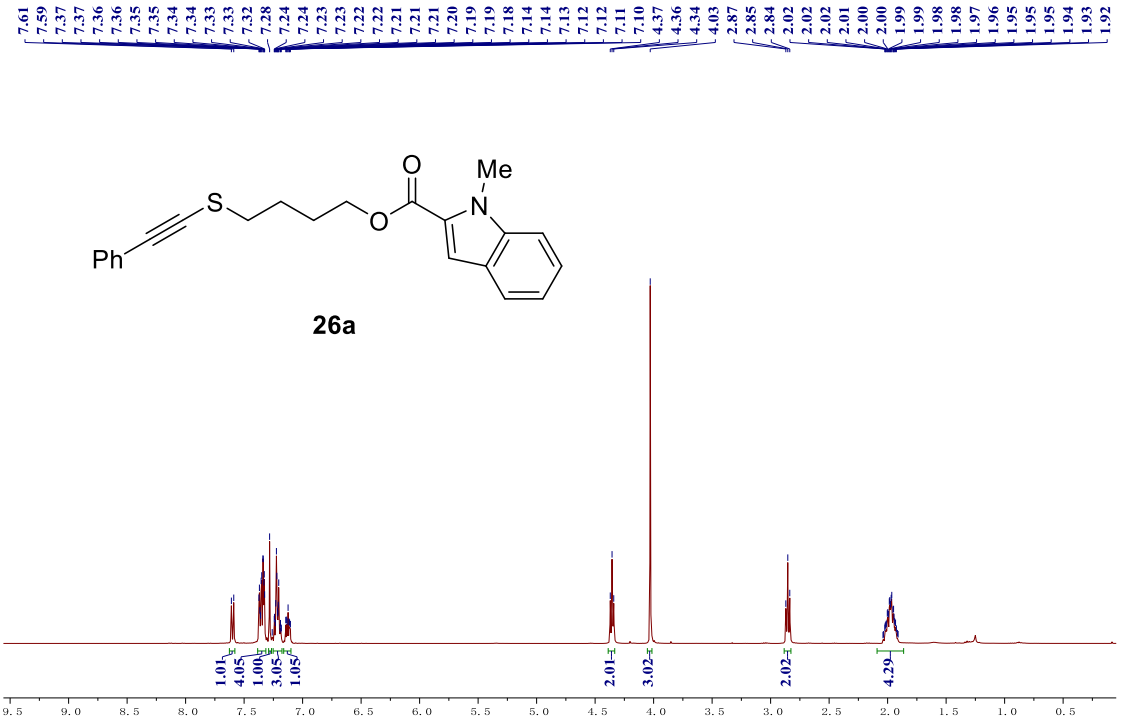
^{1}H NMR of 25a (500 MHz, $CDCl_3$**)**



^{13}C NMR of 25a (126 MHz, $CDCl_3$**)**

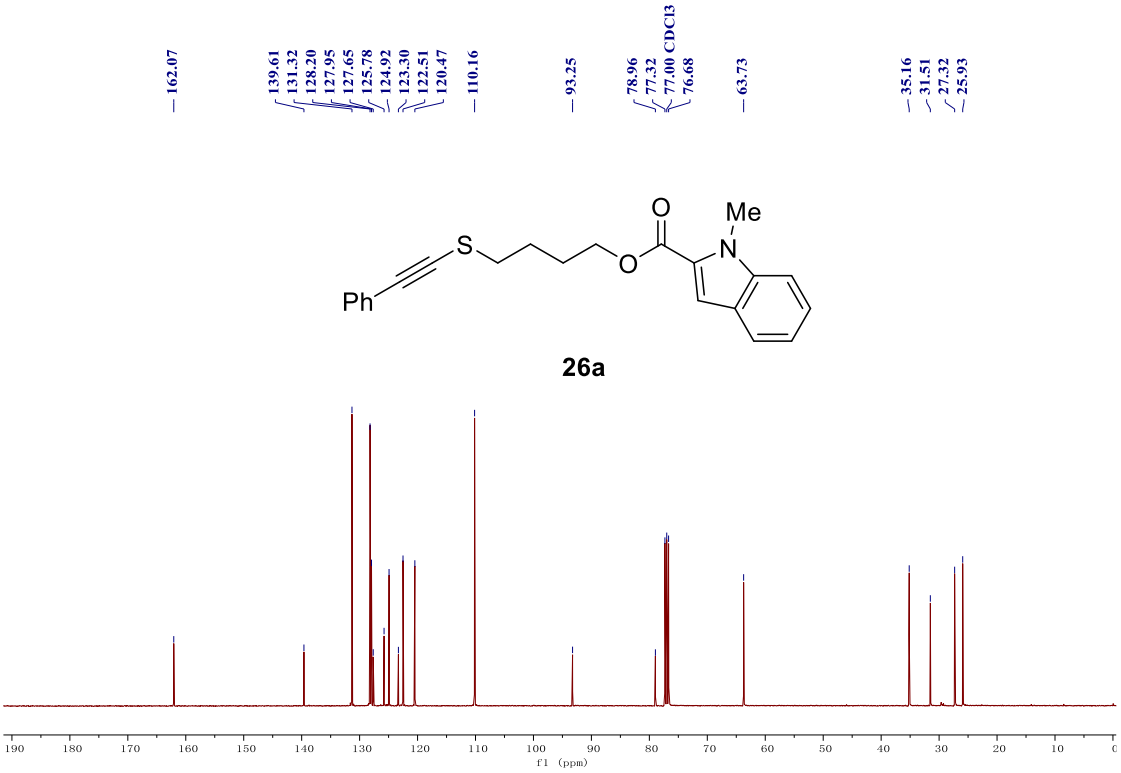


^{1}H NMR of 26a (400 MHz, $CDCl_3$**)**



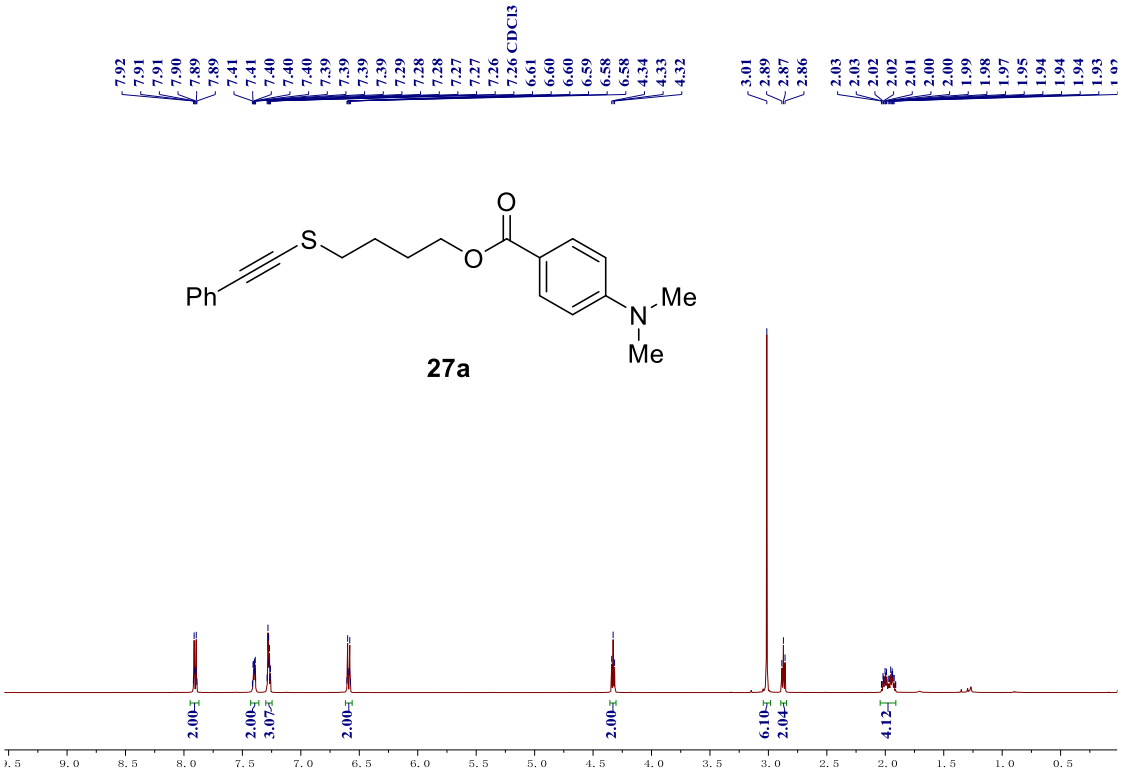
26a

^{13}C NMR of 26a (101 MHz, $CDCl_3$**)**

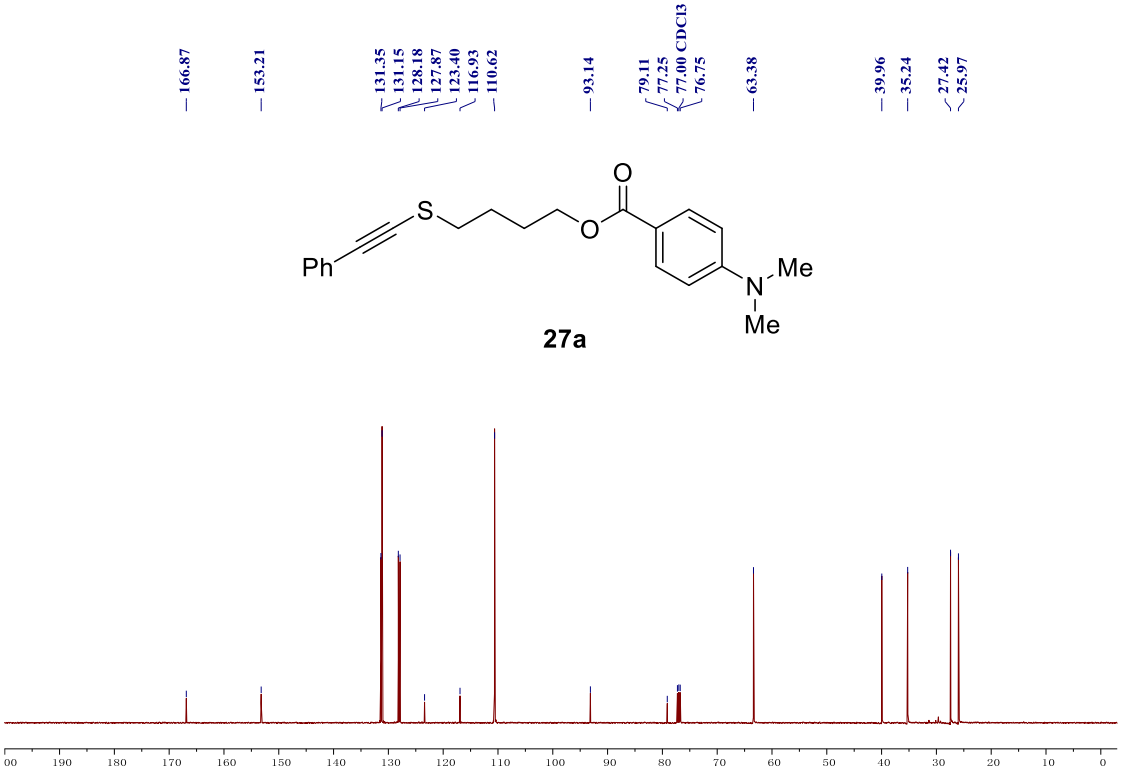


26a

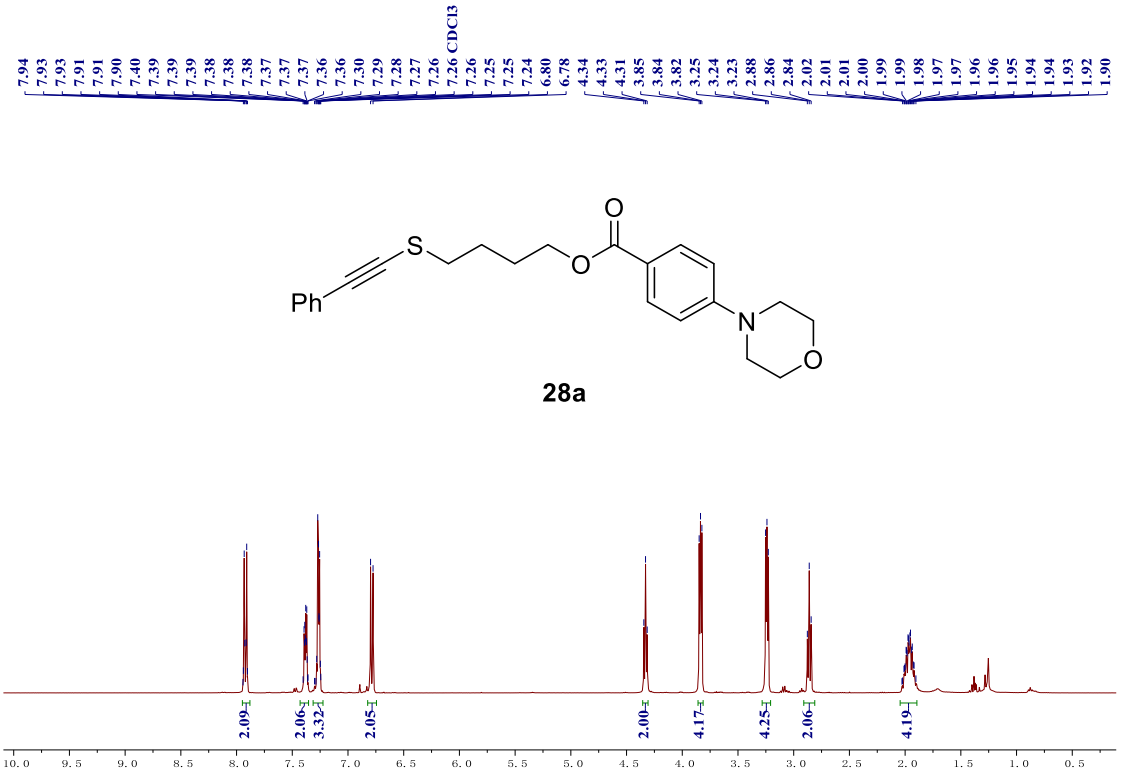
^{1}H NMR of 27a (500 MHz, $CDCl_3$**)**



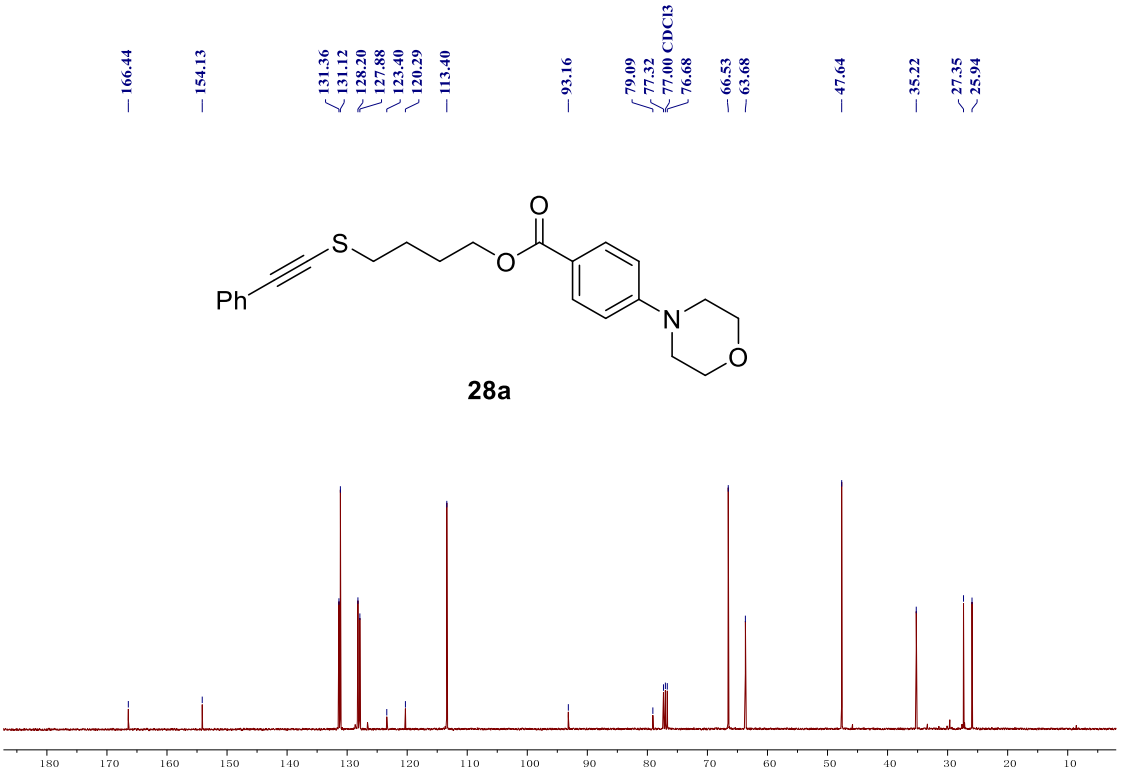
^{13}C NMR of 27a (126 MHz, $CDCl_3$**)**



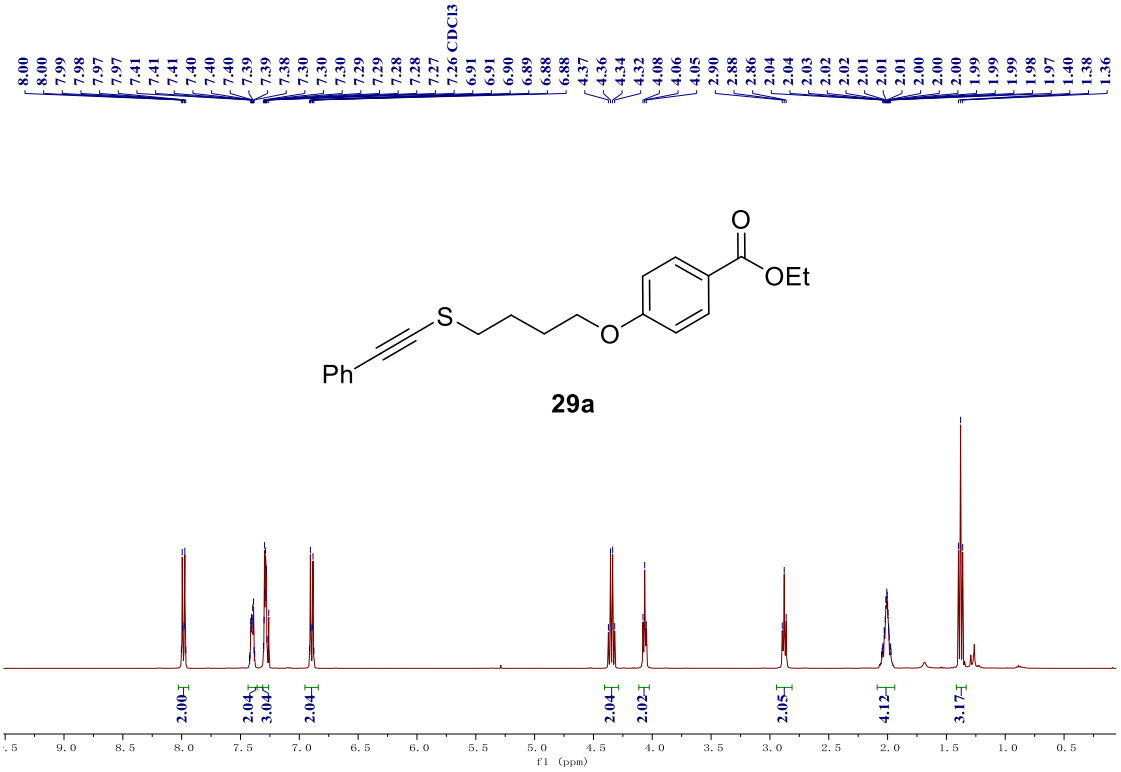
^{1}H NMR of 28a (400 MHz, $CDCl_3$**)**



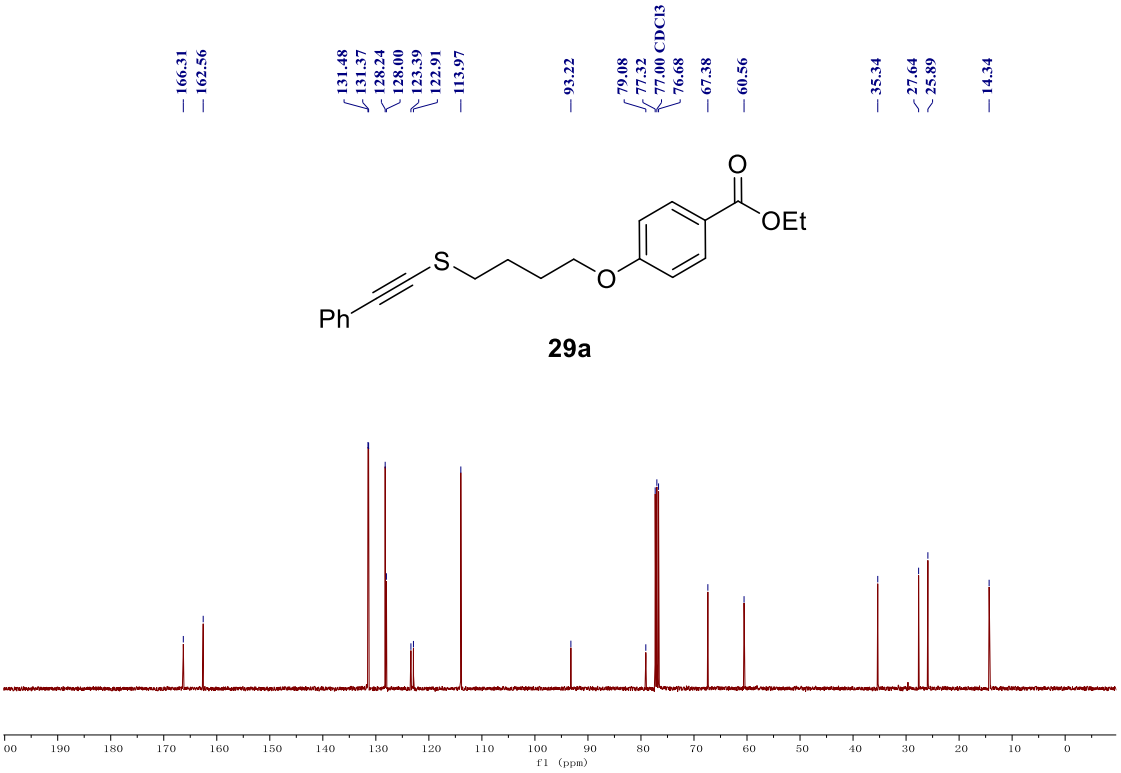
^{13}C NMR of 28a (101 MHz, $CDCl_3$**)**



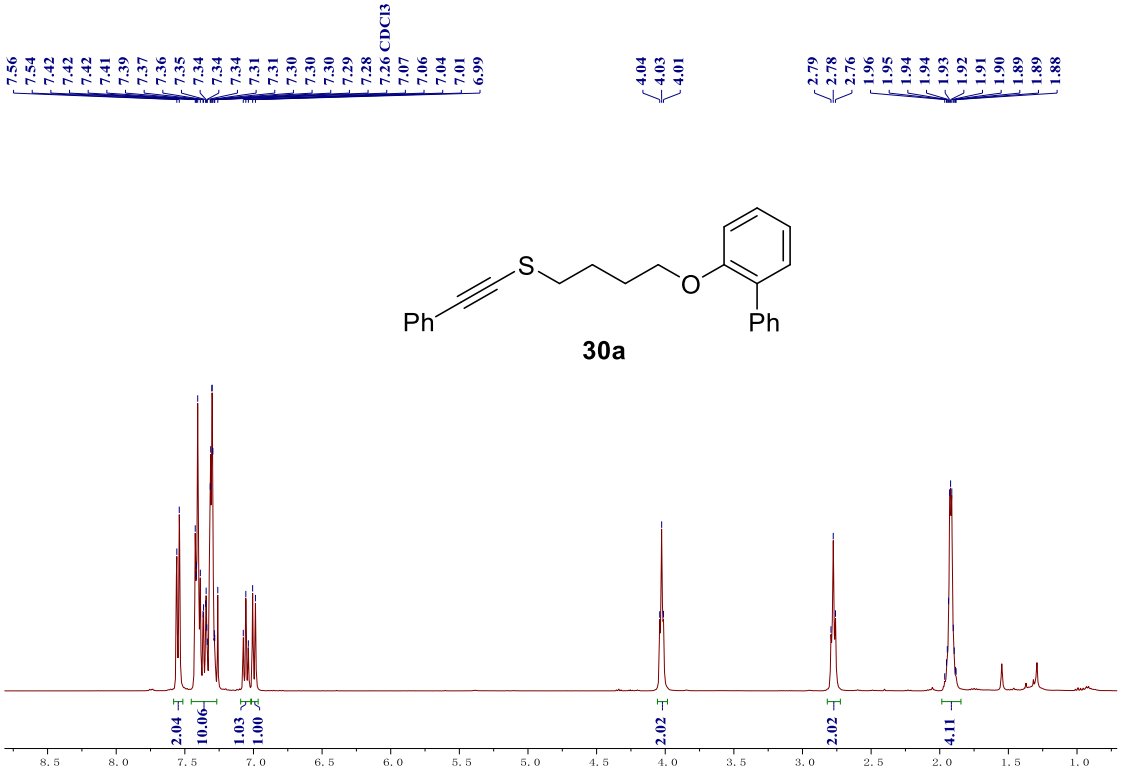
^{1}H NMR of 29a (400 MHz, $CDCl_3$**)**



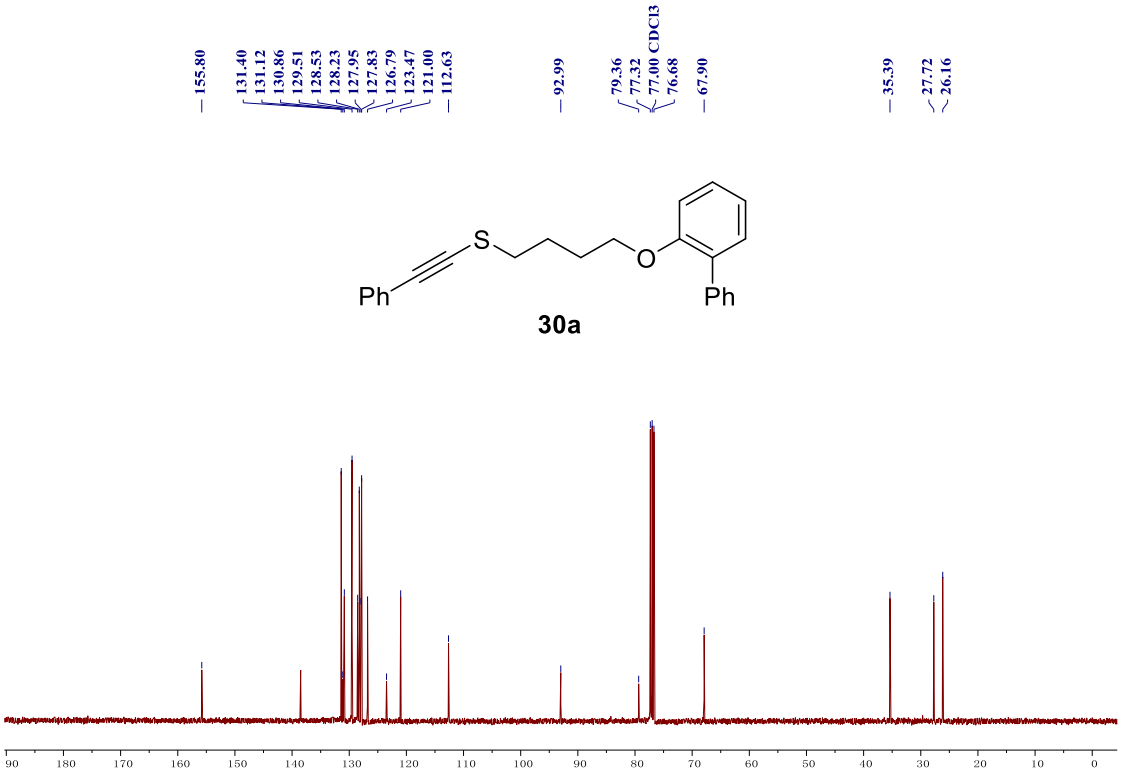
^{13}C NMR of 29a (101 MHz, $CDCl_3$**)**



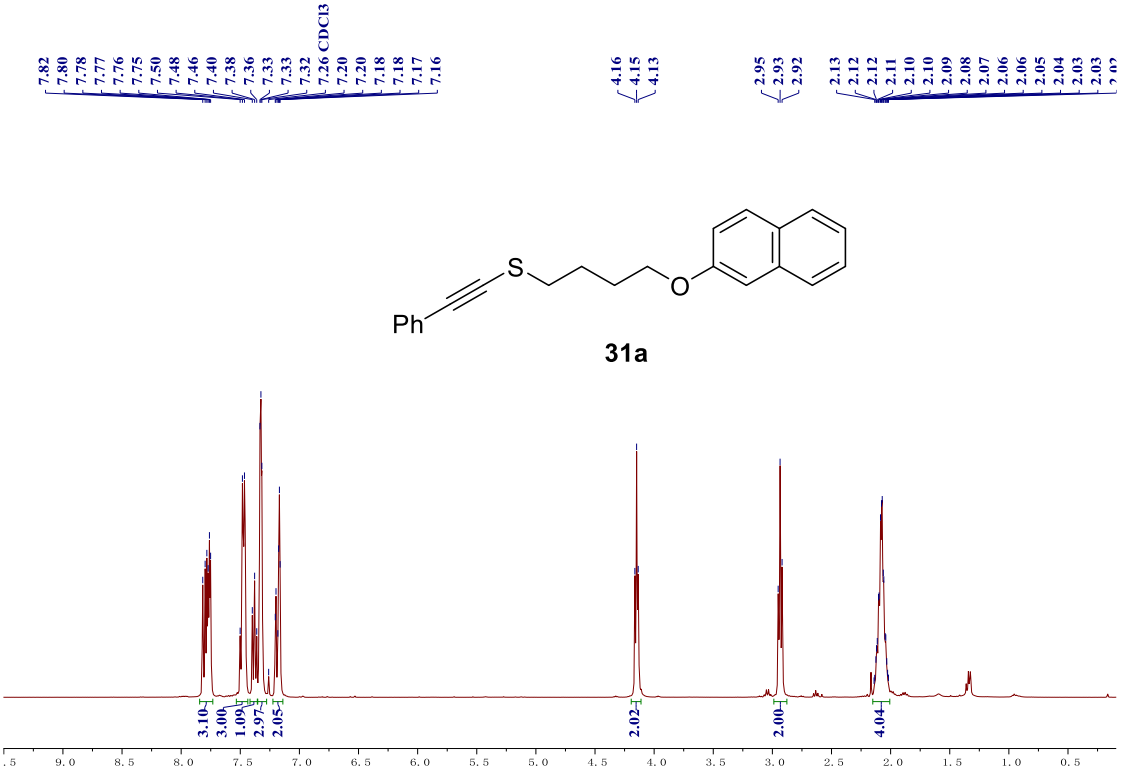
^{1}H NMR of 30a (400 MHz, $CDCl_3$**)**



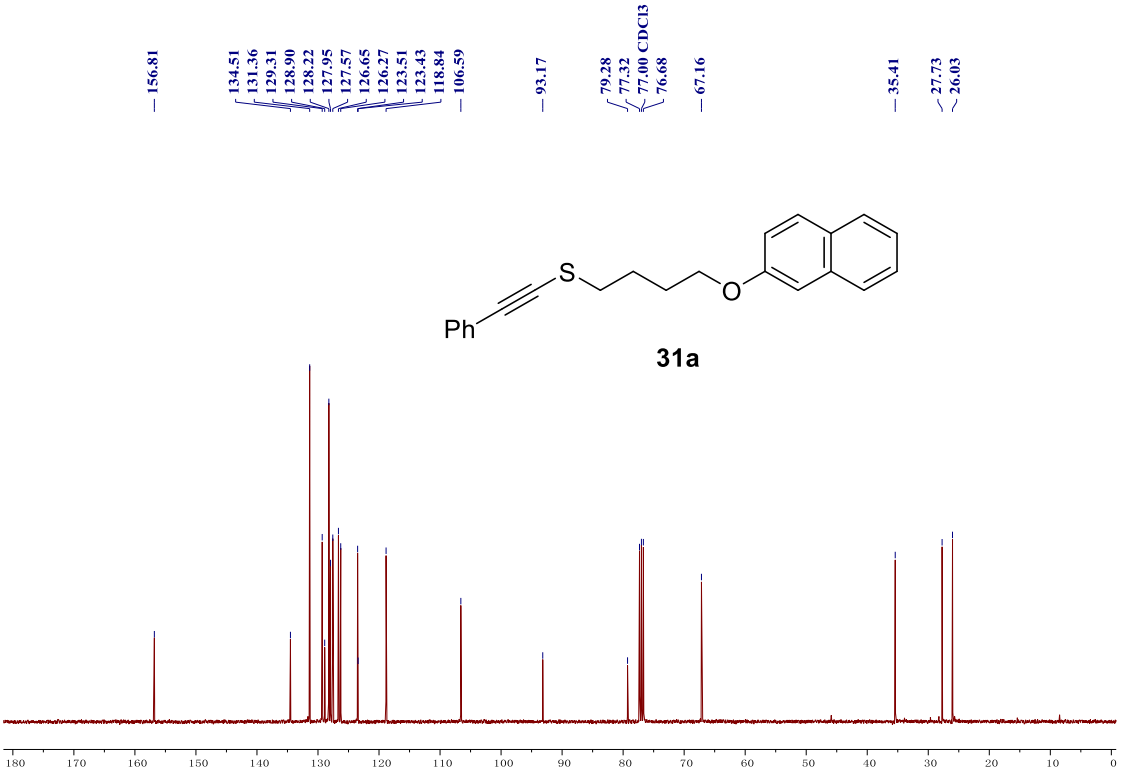
^{13}C NMR of 30a (101 MHz, $CDCl_3$**)**



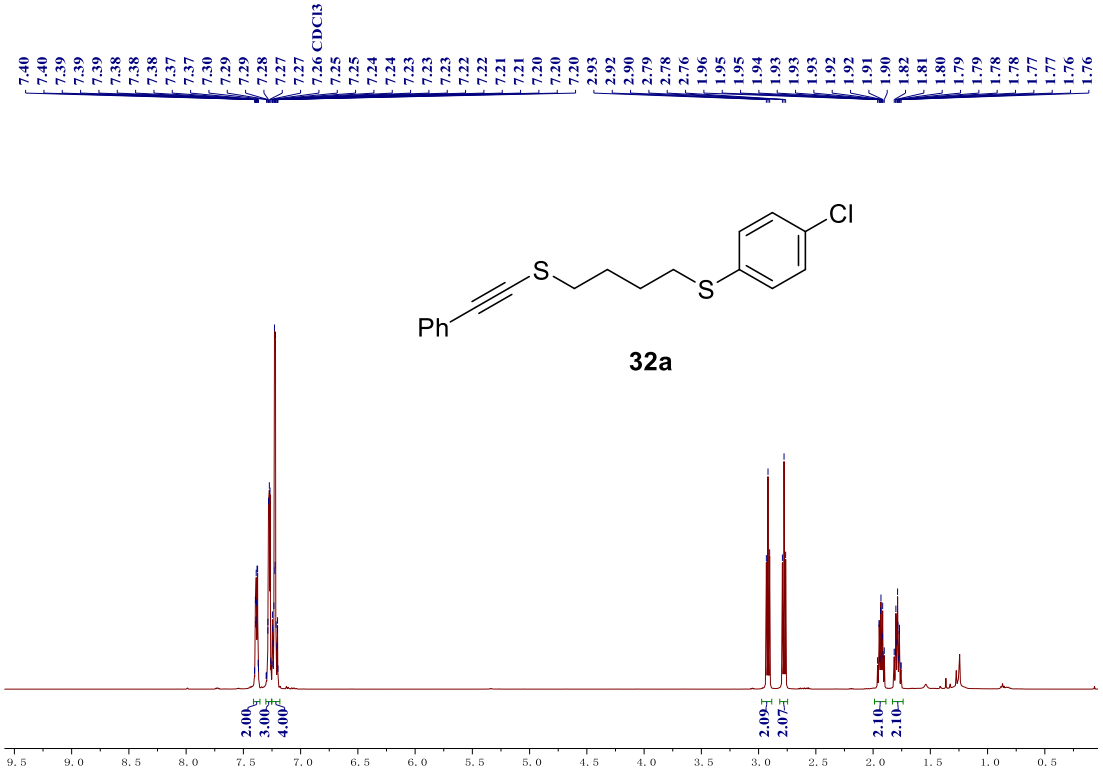
^{1}H NMR of 31a (400 MHz, $CDCl_3$**)**



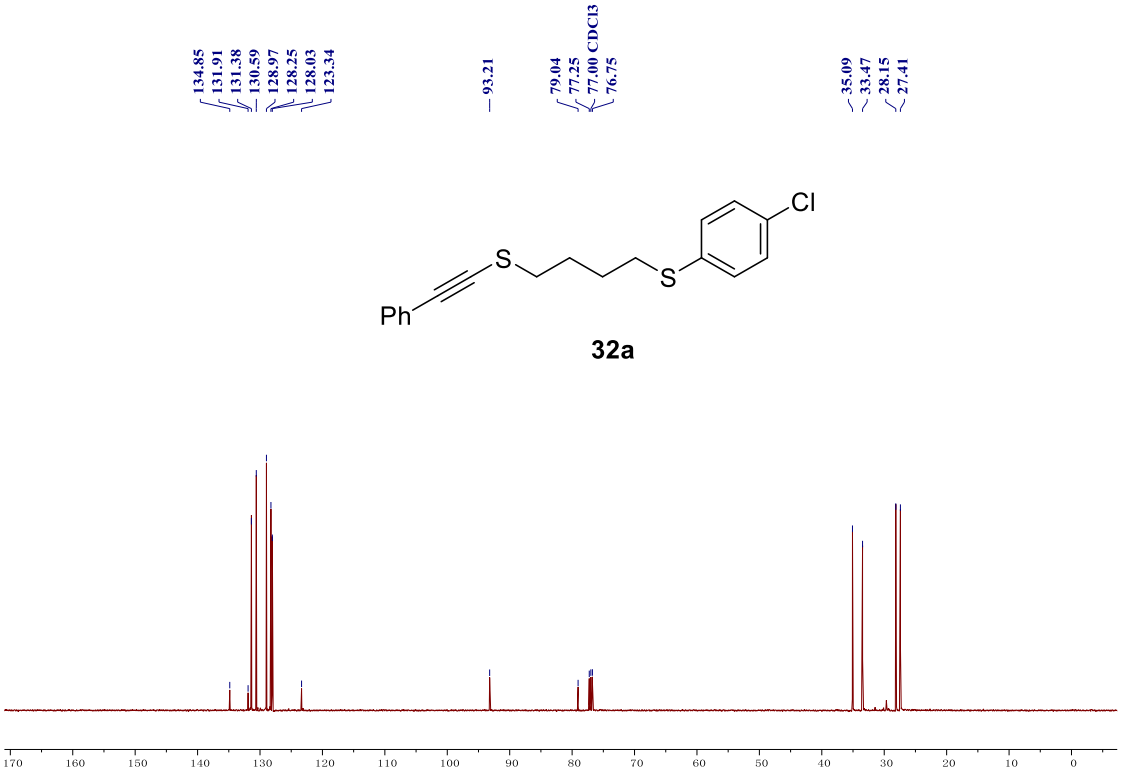
^{13}C NMR of 31a (101 MHz, $CDCl_3$**)**



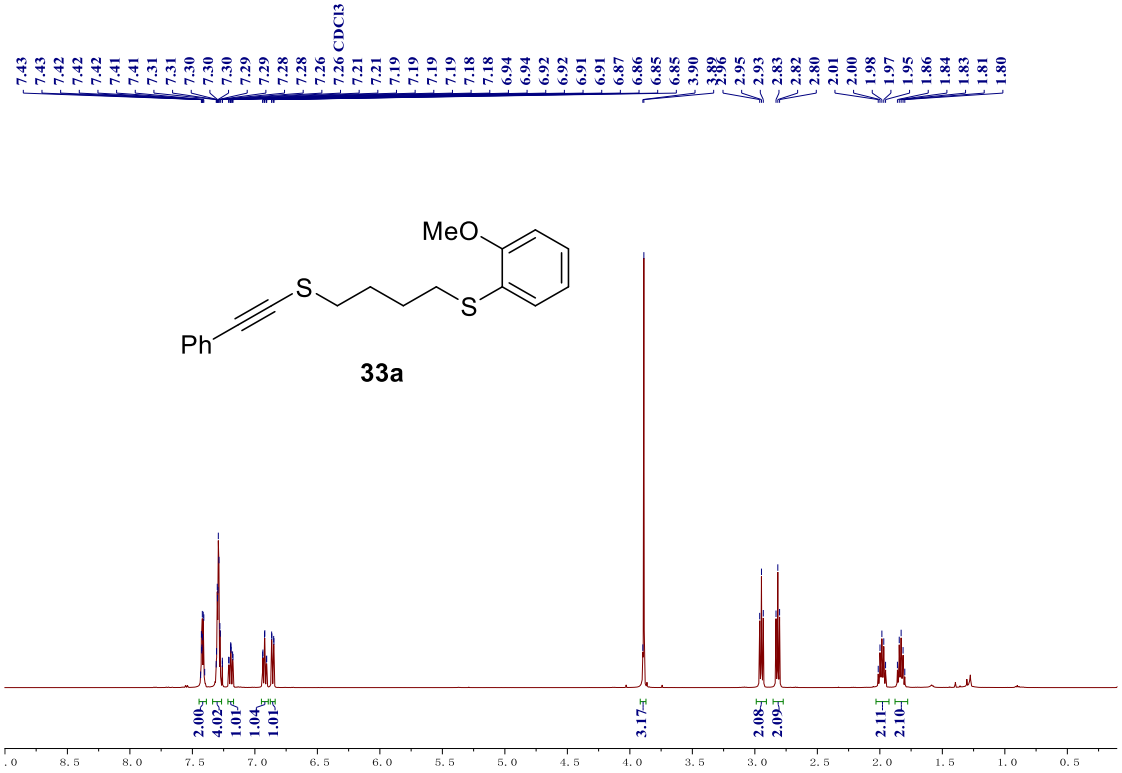
^{1}H NMR of 32a (500 MHz, $CDCl_3$**)**



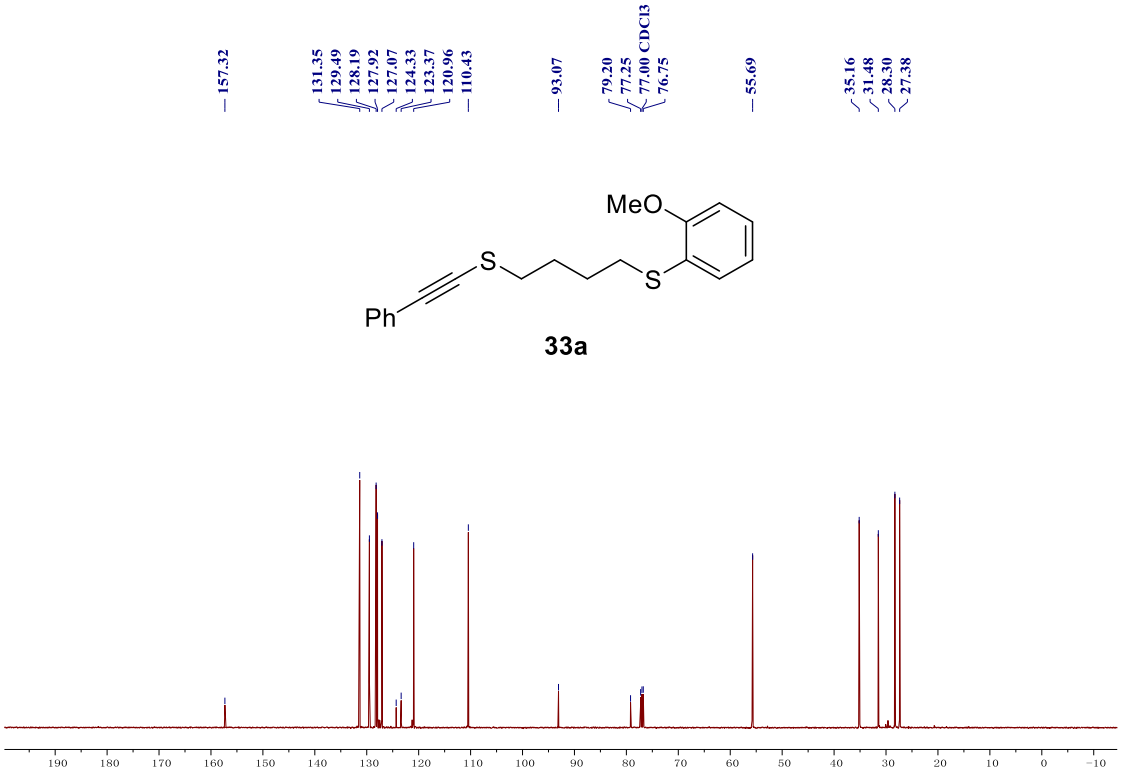
^{13}C NMR of 32a (101 MHz, $CDCl_3$**)**



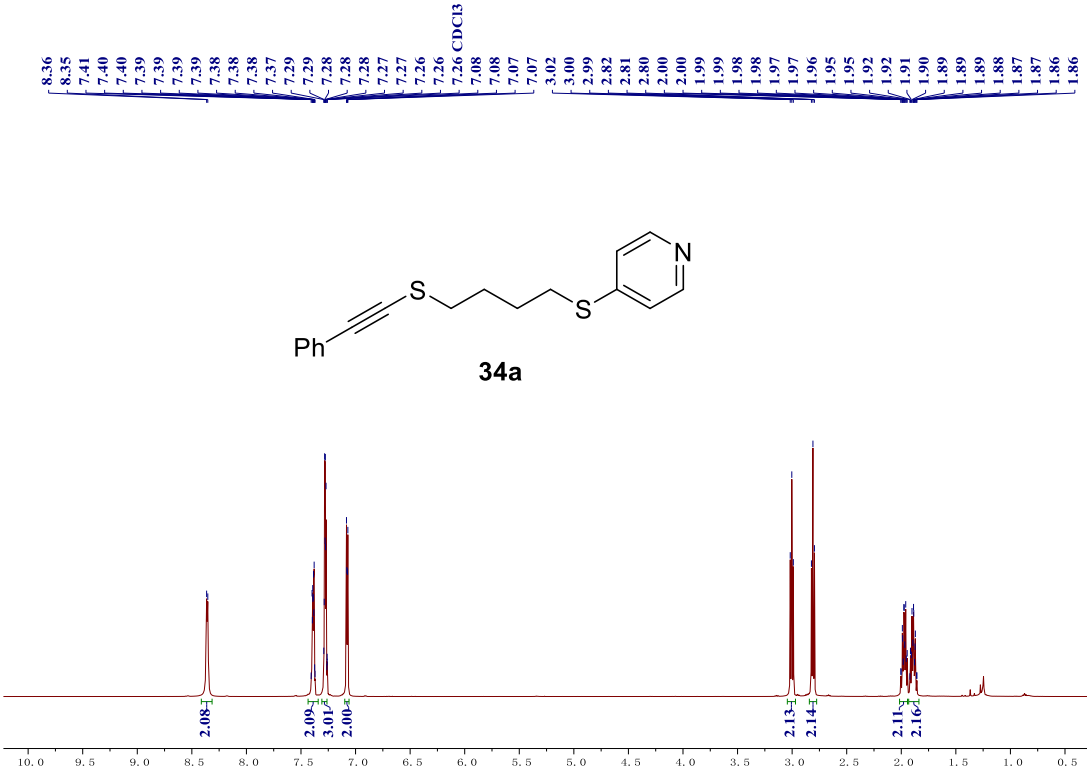
^{1}H NMR of 33a (500 MHz, $CDCl_3$**)**



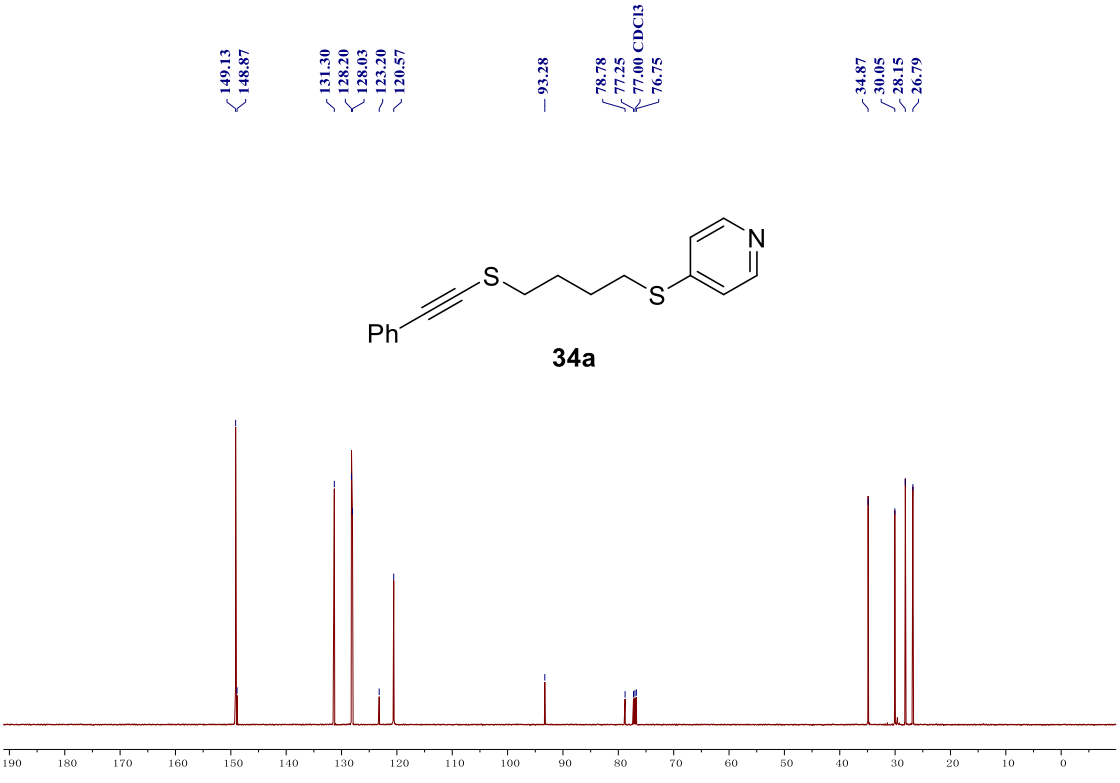
^{13}C NMR of 33a (126 MHz, $CDCl_3$**)**



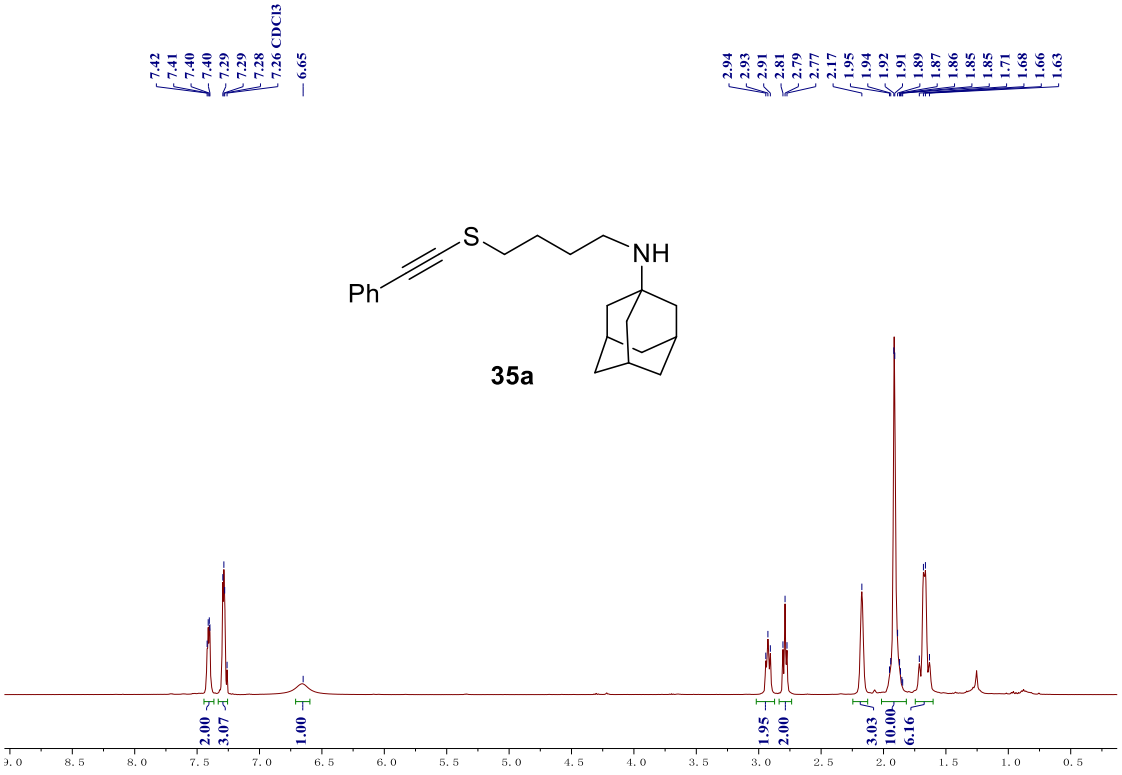
^{1}H NMR of 34a (500 MHz, $CDCl_3$**)**



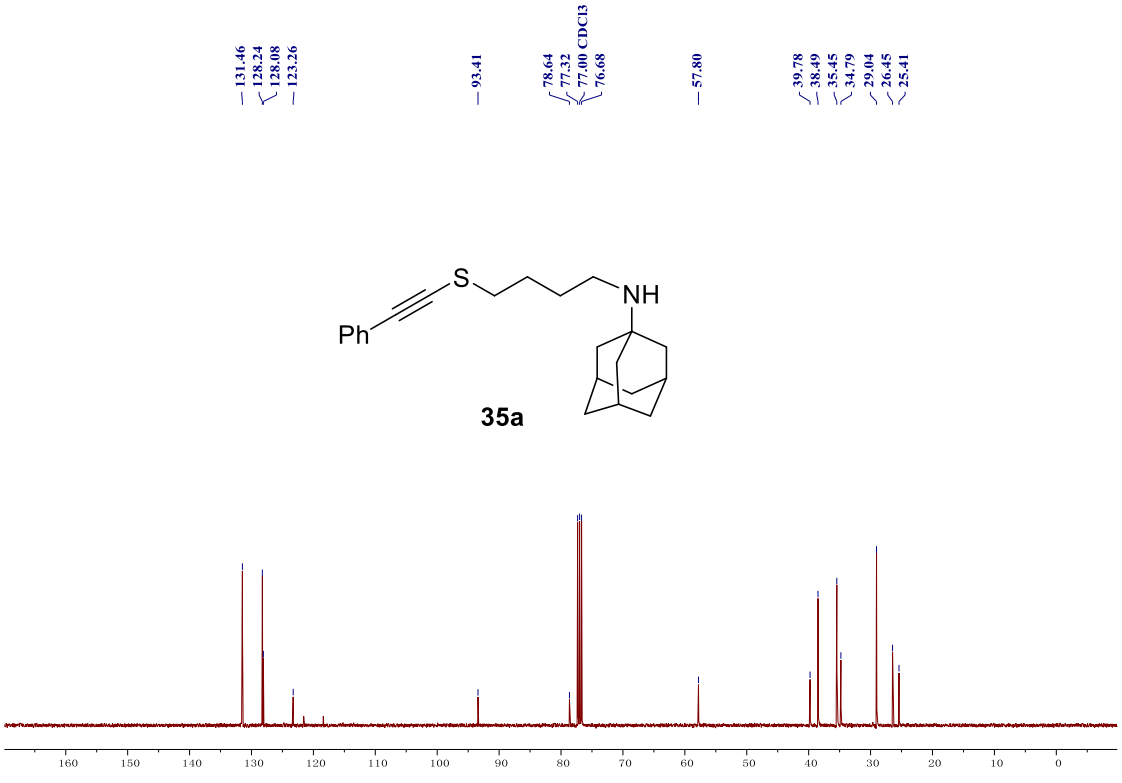
^{13}C NMR of 34a (126 MHz, $CDCl_3$**)**



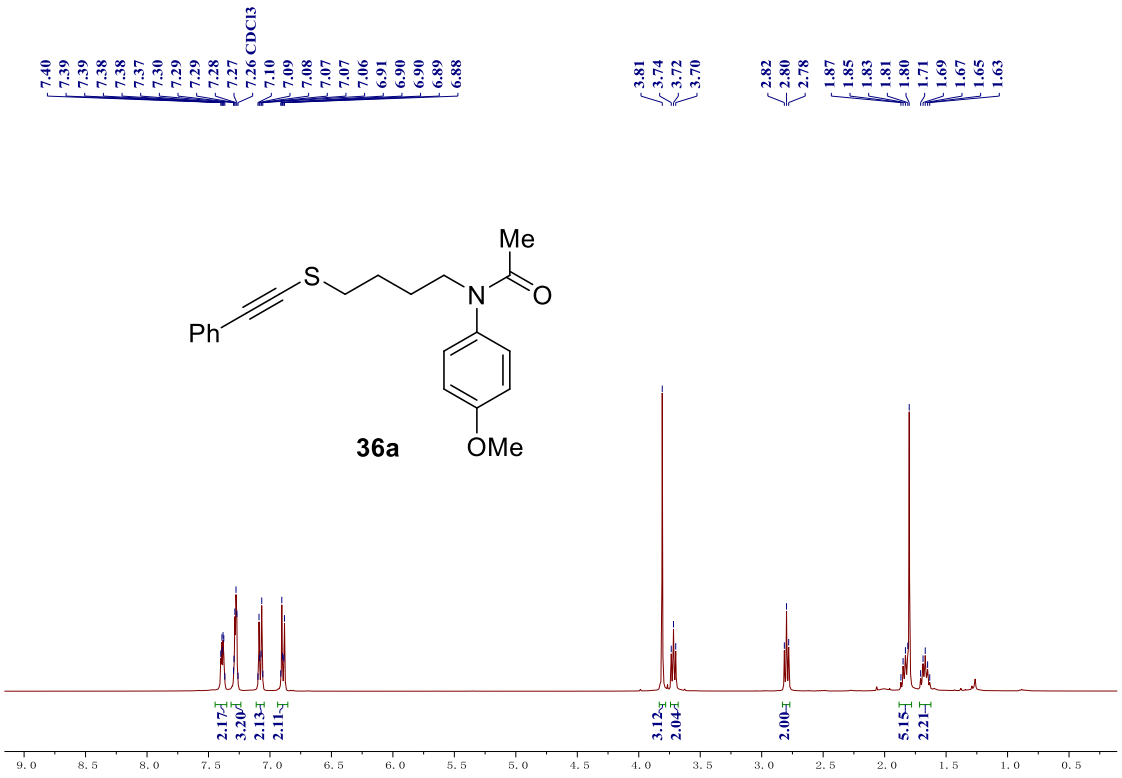
^{1}H NMR of 35a (400 MHz, $CDCl_3$**)**



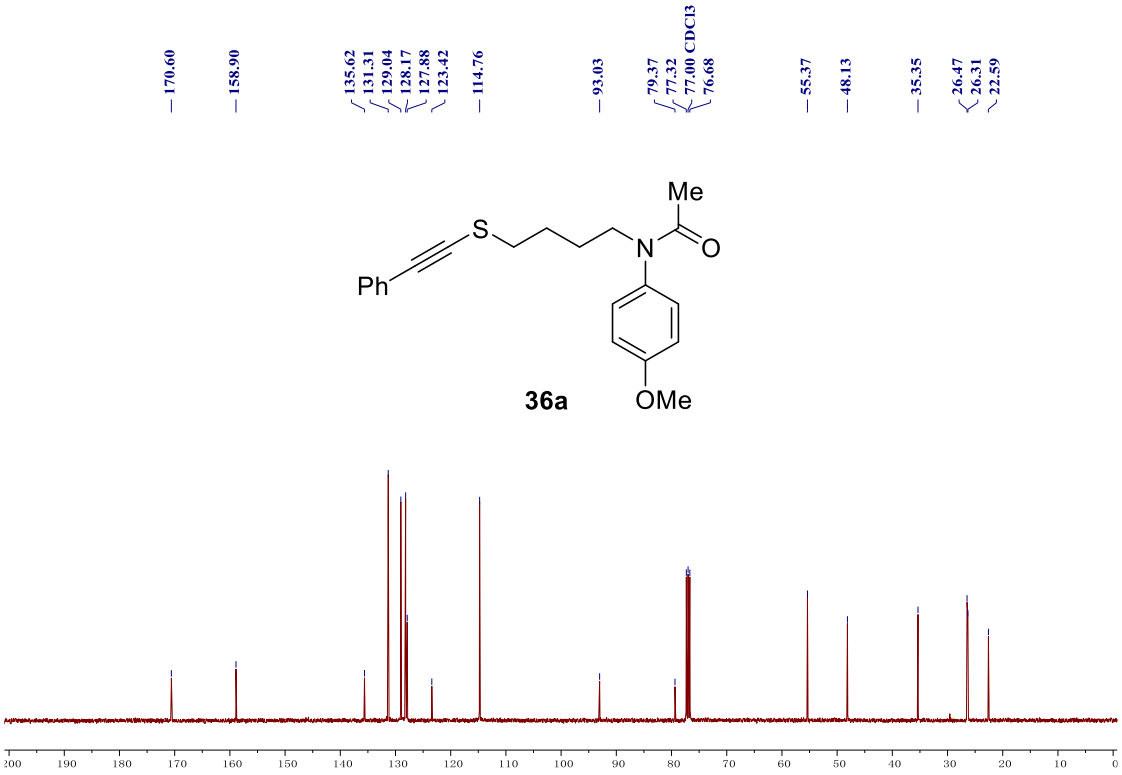
^{13}C NMR of 35a (101 MHz, $CDCl_3$**)**



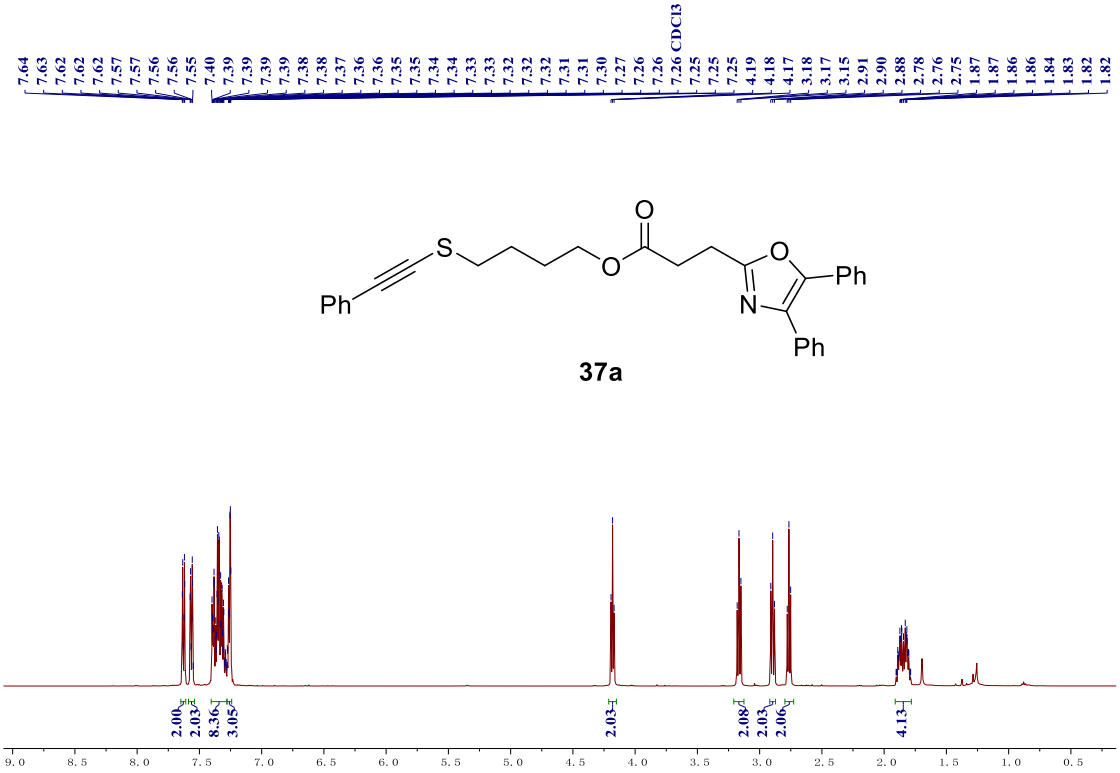
^{1}H NMR of 36a (400 MHz, $CDCl_3$**)**



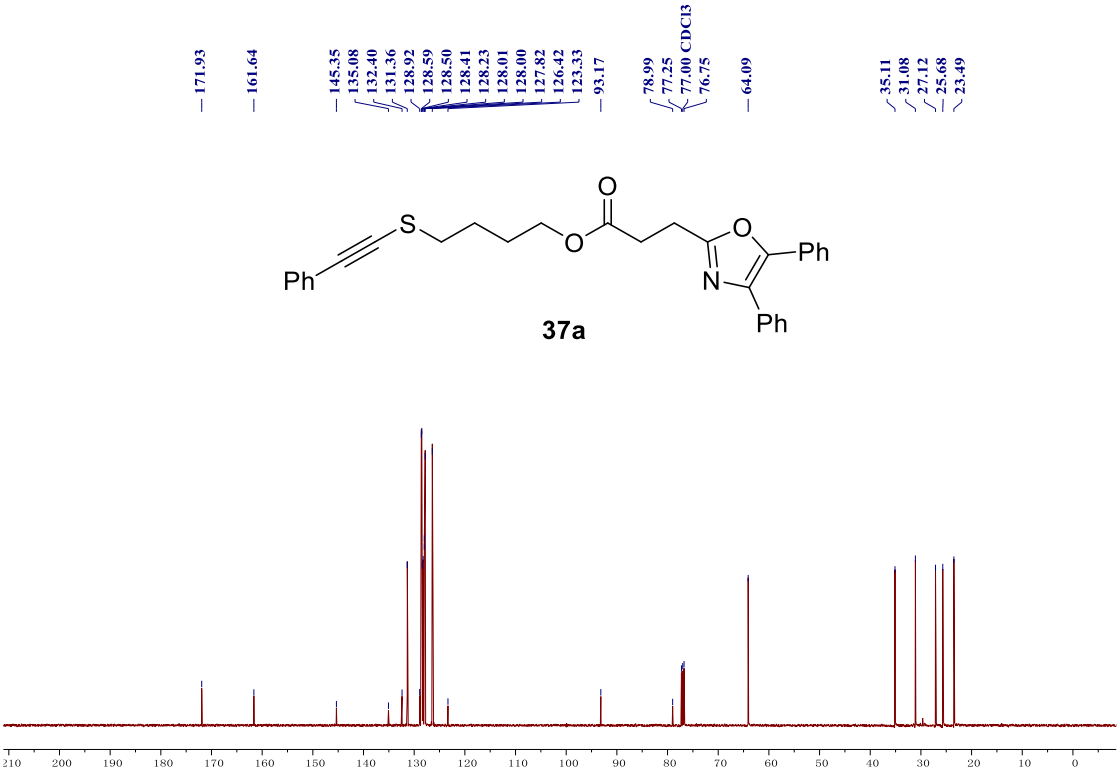
^{13}C NMR of 36a (101 MHz, $CDCl_3$**)**



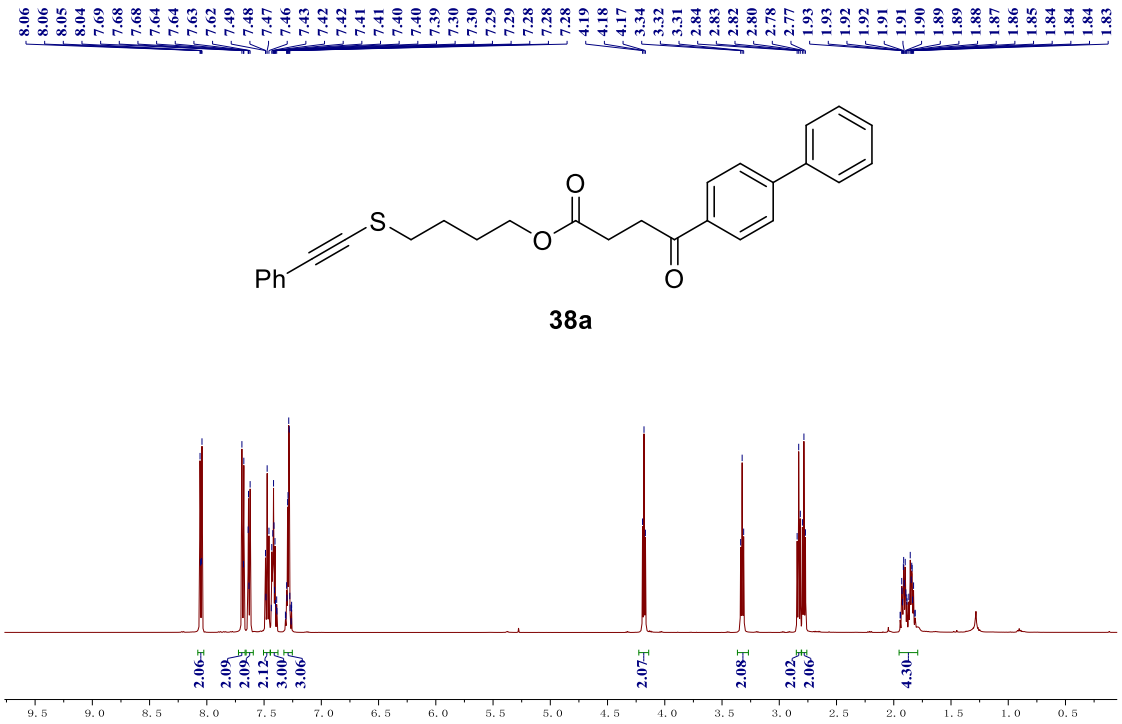
^{1}H NMR of 37a (500 MHz, $CDCl_3$**)**



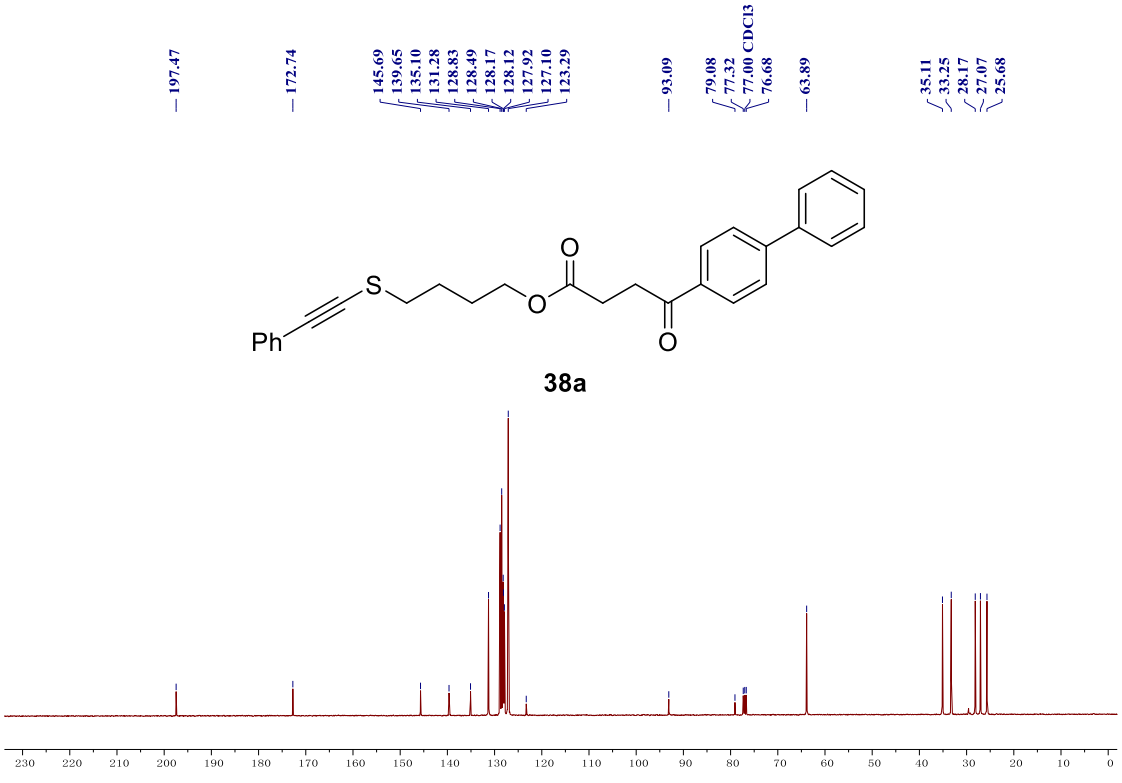
^{13}C NMR of 37a (126 MHz, $CDCl_3$**)**



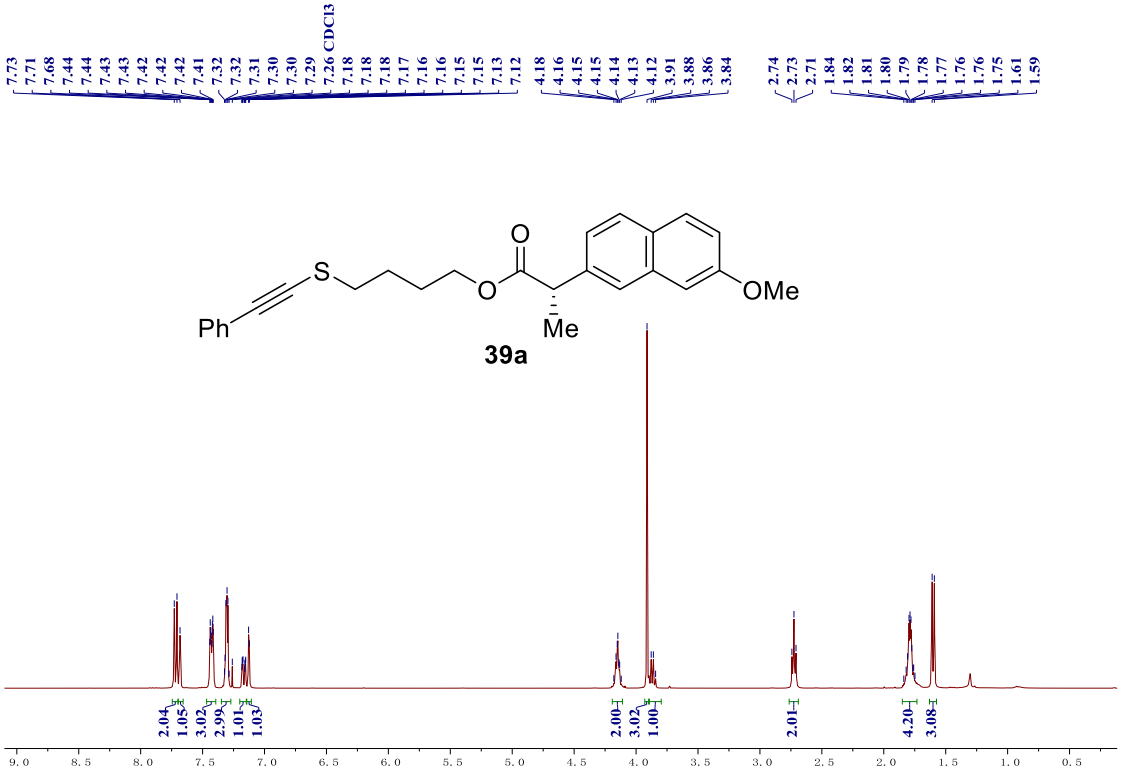
^{1}H NMR of 38a (500 MHz, $CDCl_3$**)**



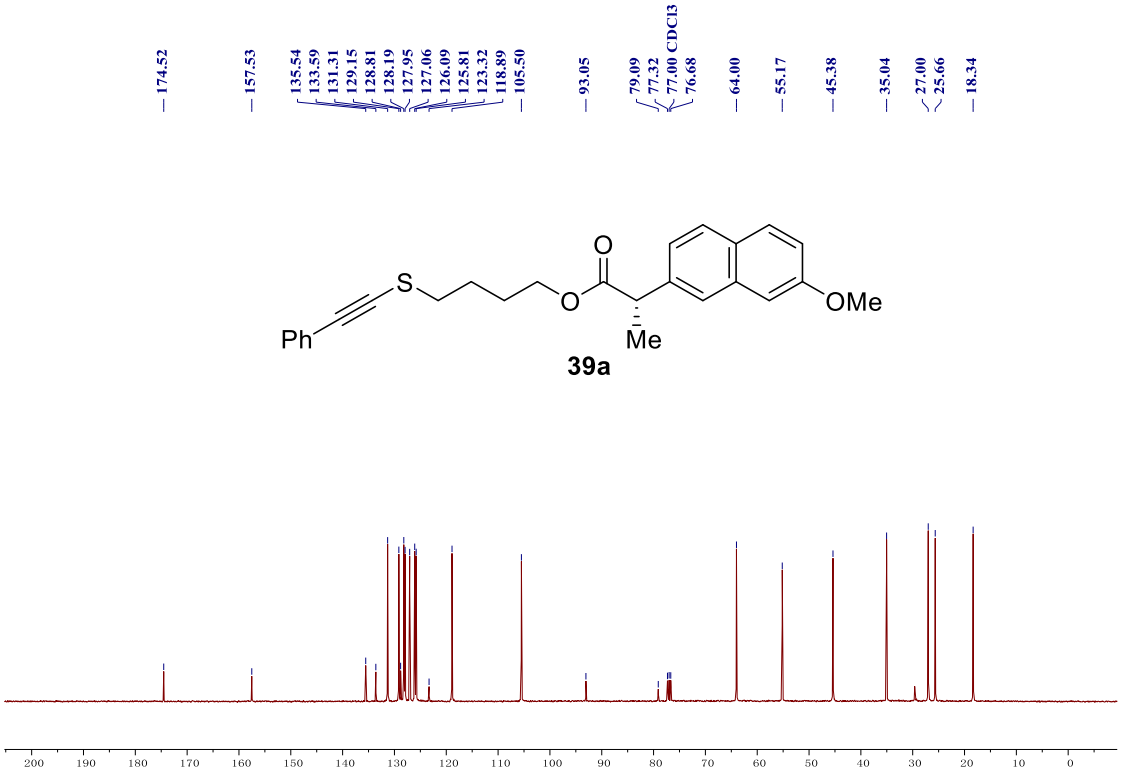
^{13}C NMR of 38a (126 MHz, $CDCl_3$**)**



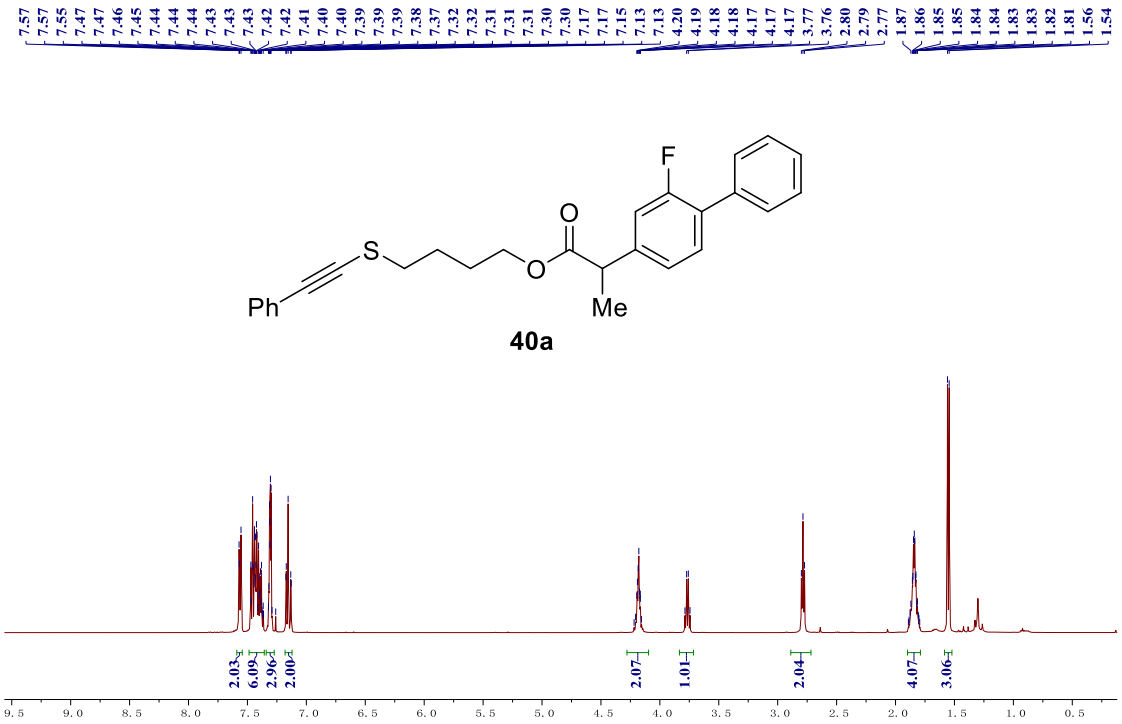
^{1}H NMR of 39a (400 MHz, $CDCl_3$)



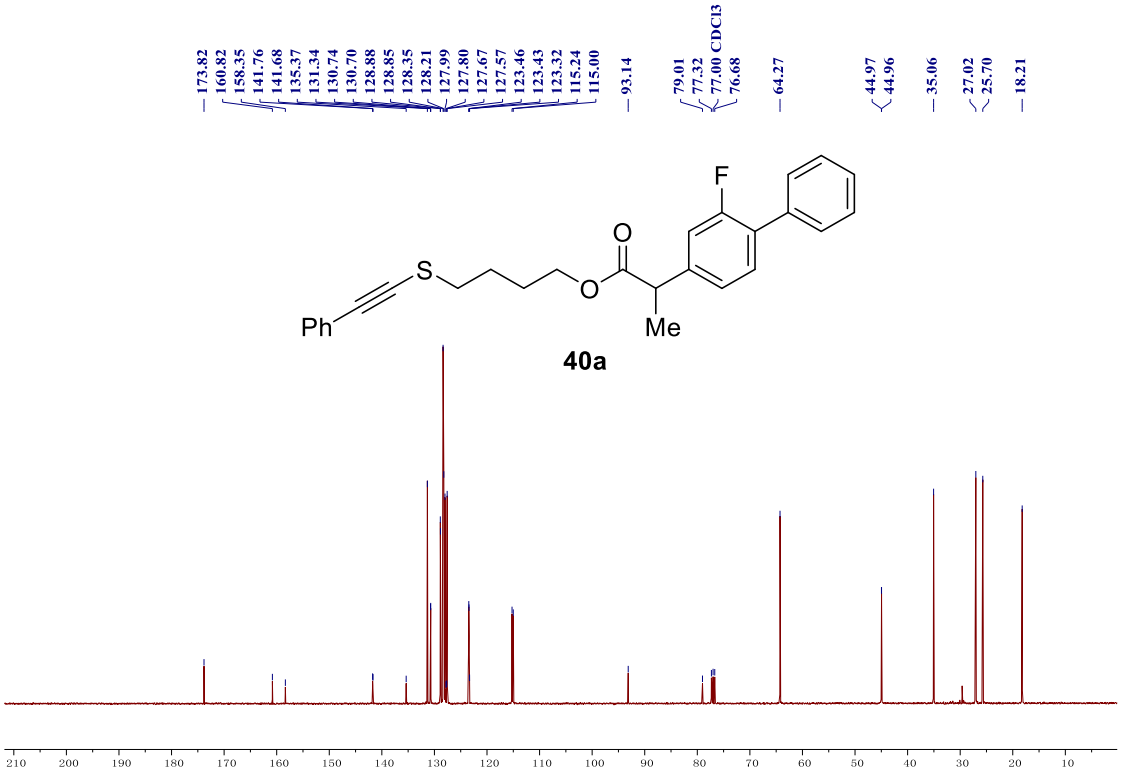
^{13}C NMR of 39a (101 MHz, $CDCl_3$)



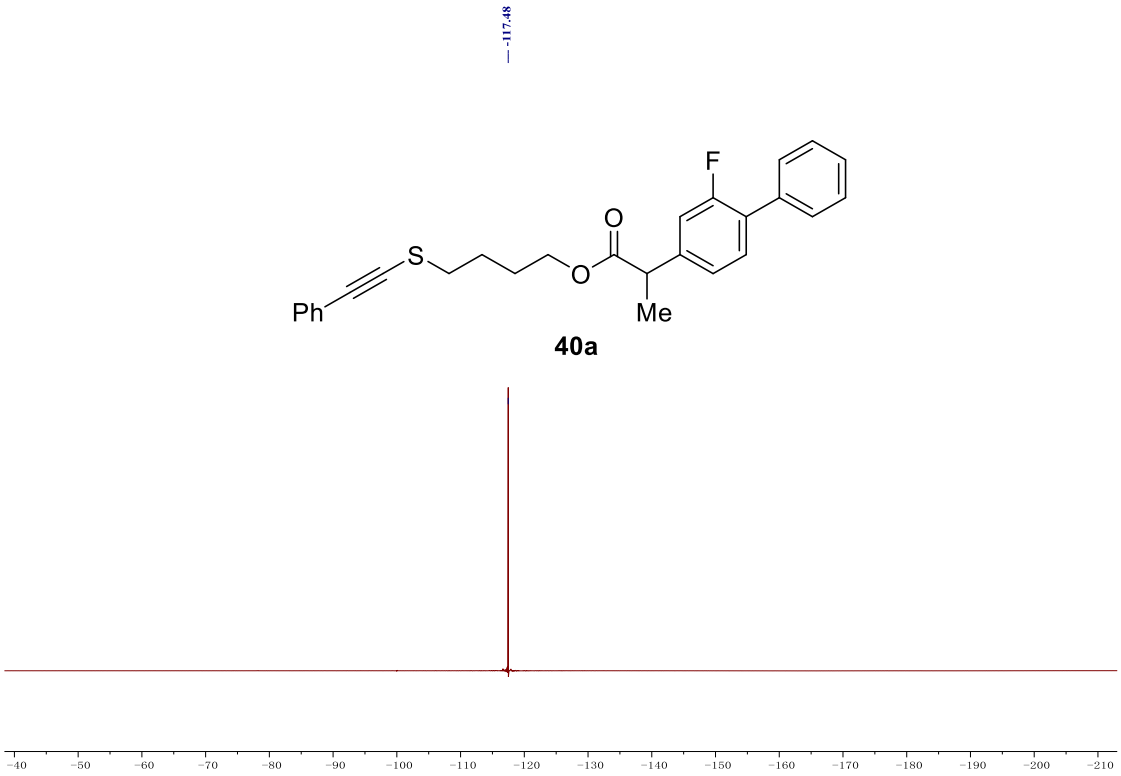
^{1}H NMR of 40a (500 MHz, $CDCl_3$**)**



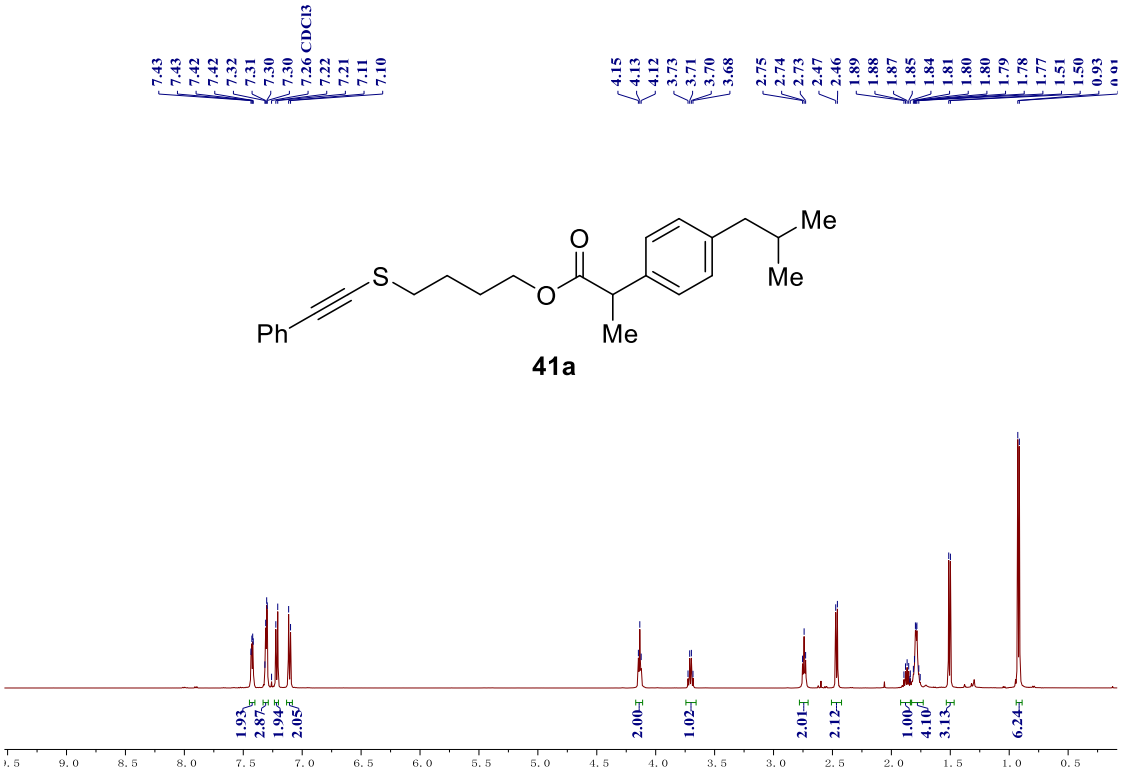
^{13}C NMR of 40a (126 MHz, $CDCl_3$**)**



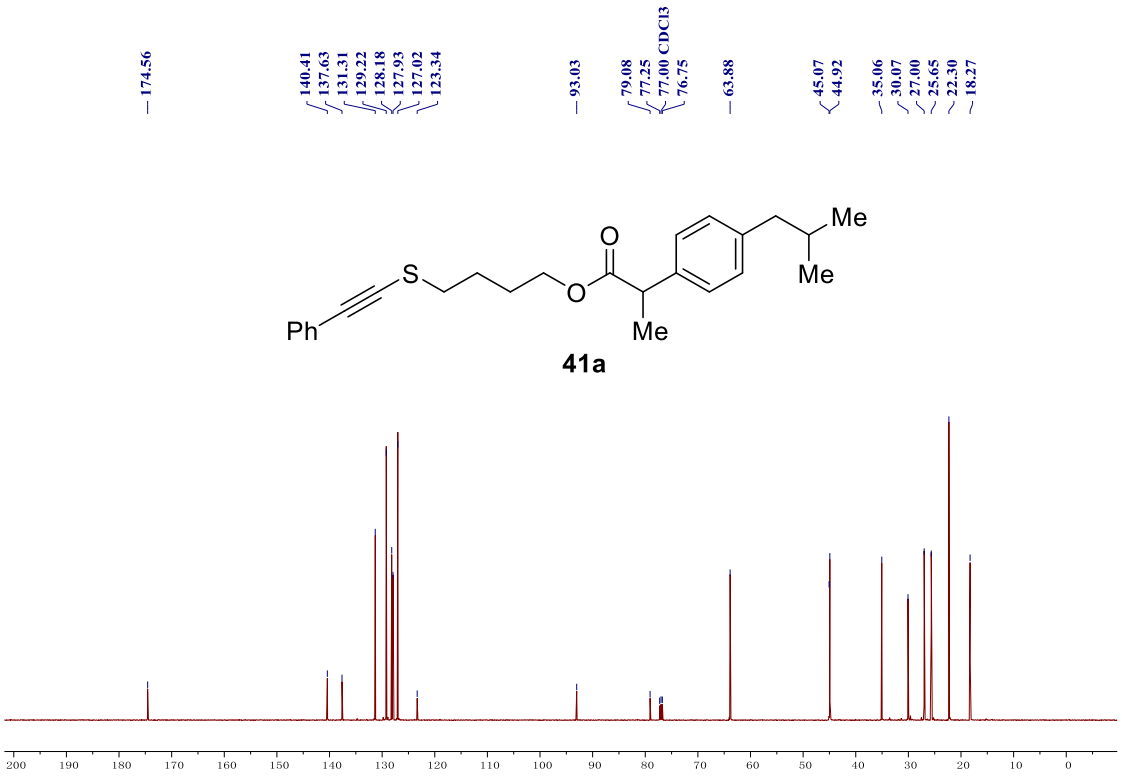
^{19}F NMR of 40a (376 MHz, $CDCl_3$**)**



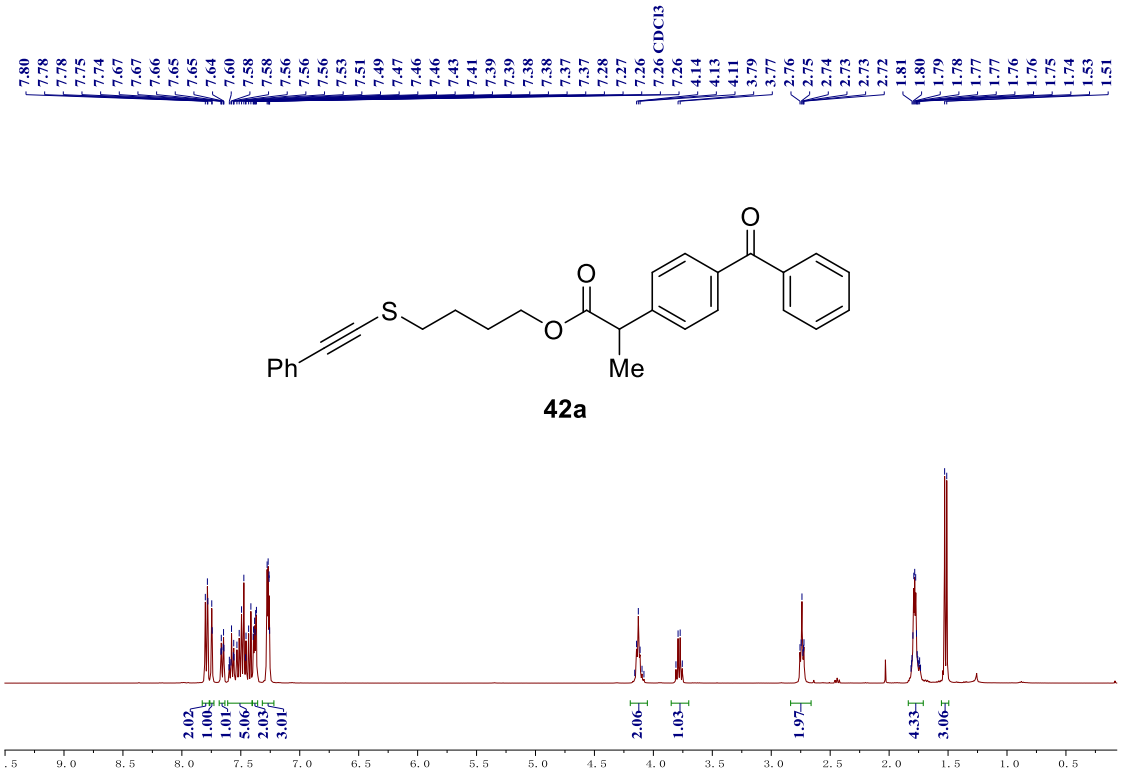
^{1}H NMR of 41a (500 MHz, $CDCl_3$**)**



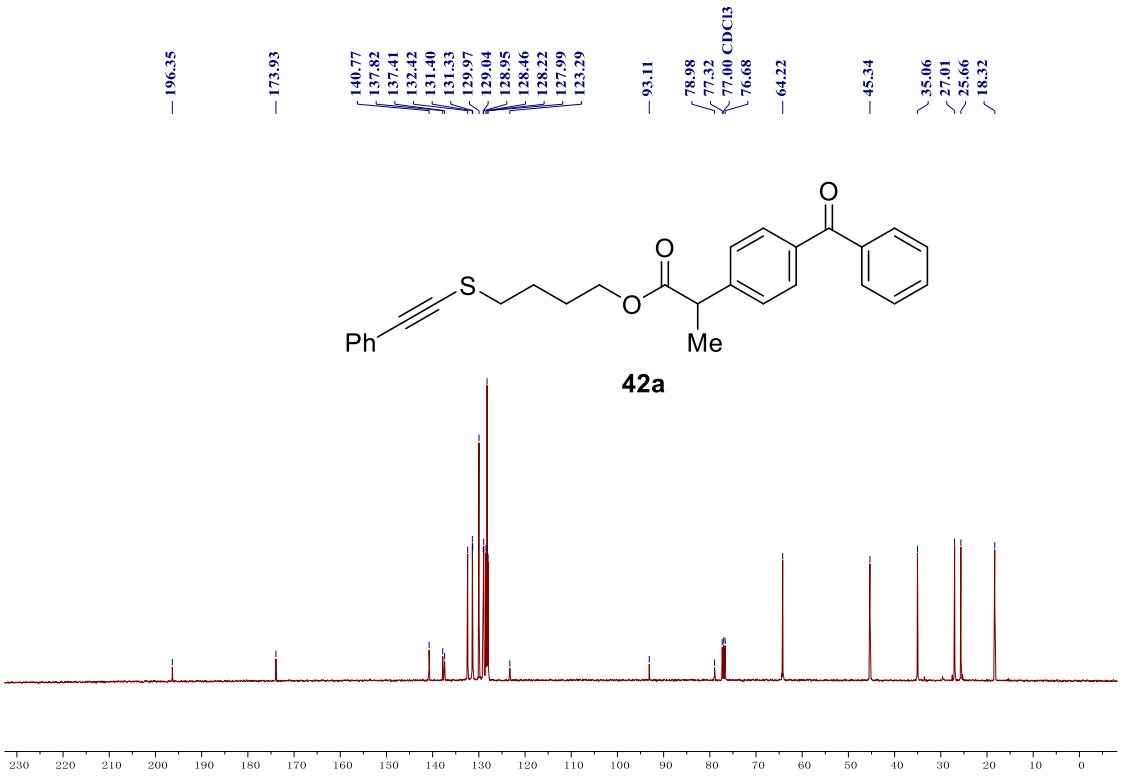
^{13}C NMR of 41a (126 MHz, $CDCl_3$**)**



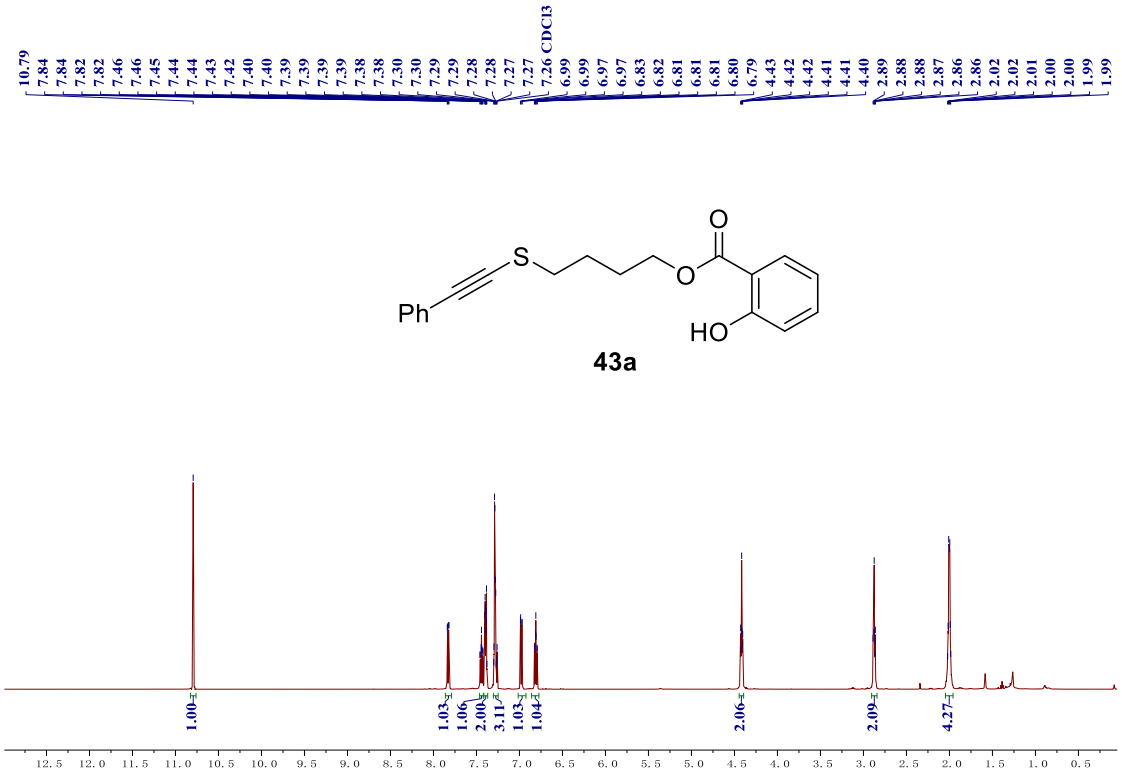
^{1}H NMR of 42a (400 MHz, $CDCl_3$**)**



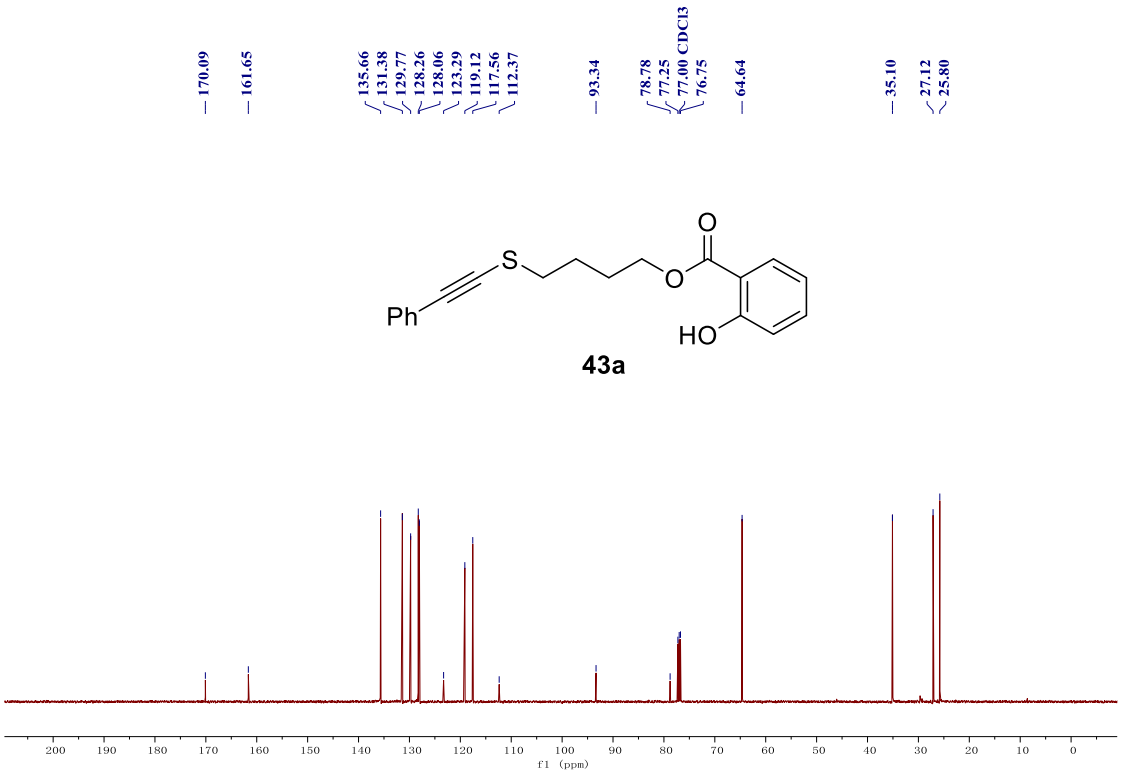
^{13}C NMR of 42a (101 MHz, $CDCl_3$**)**



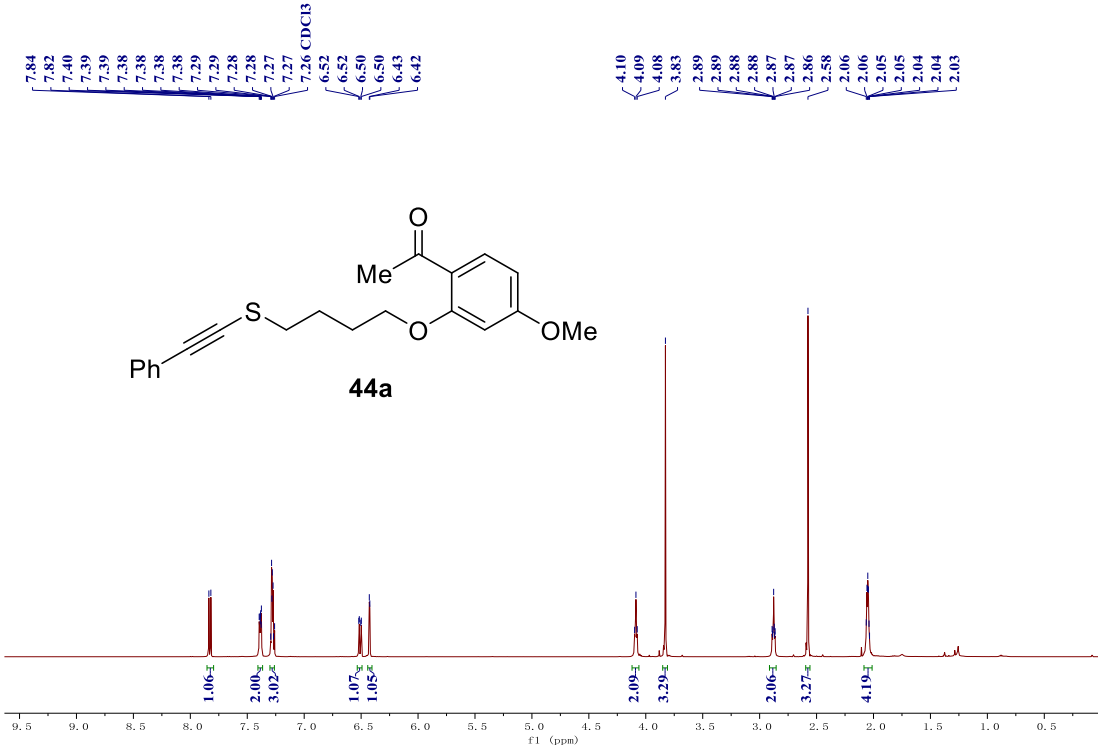
^{1}H NMR of 43a (500 MHz, $CDCl_3$**)**



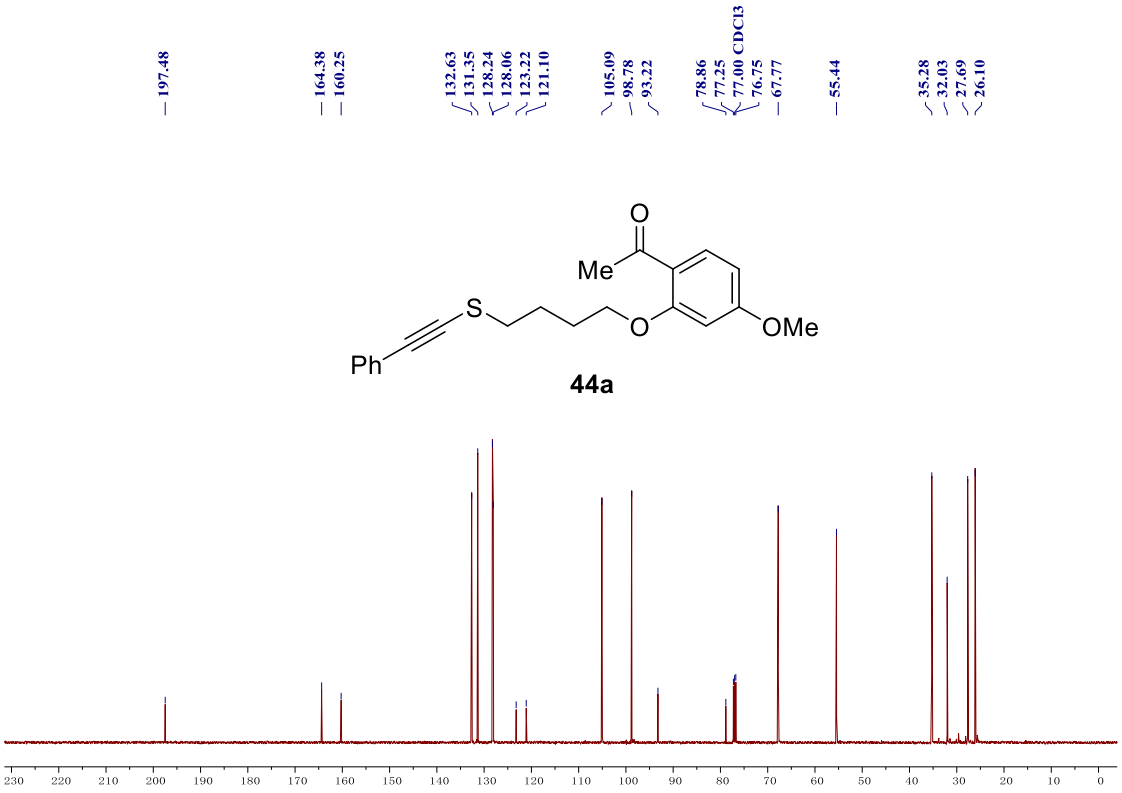
^{13}C NMR of 43a (126 MHz, $CDCl_3$**)**



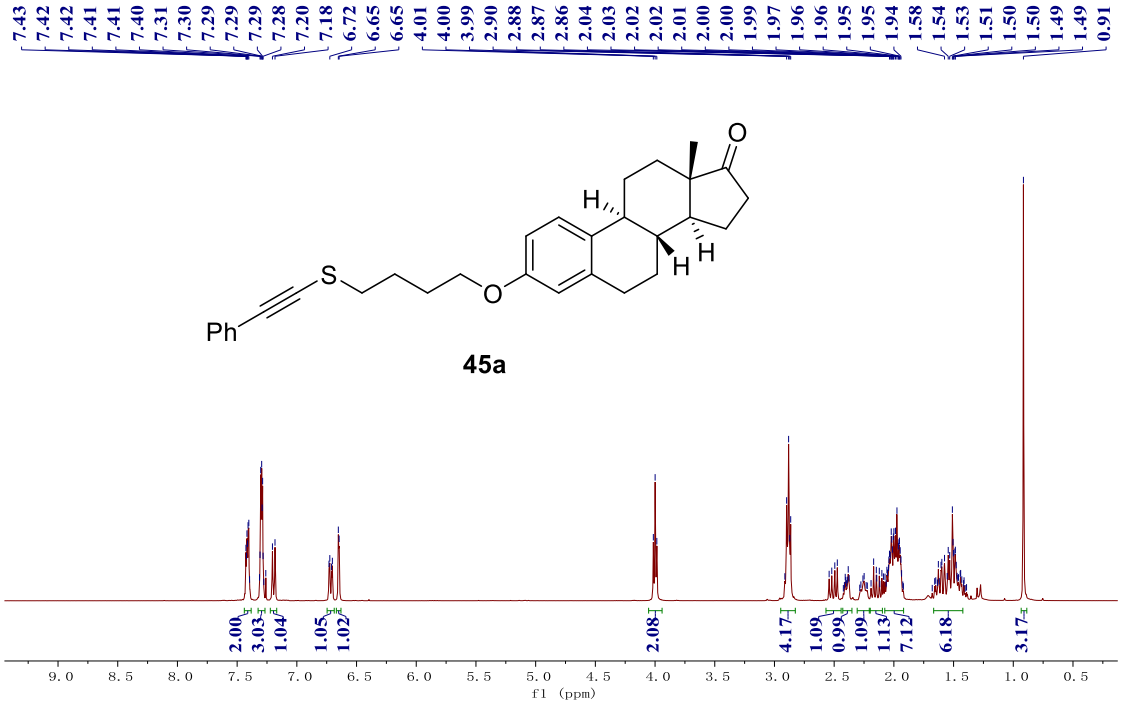
^{1}H NMR of 44a (500 MHz, $CDCl_3$**)**



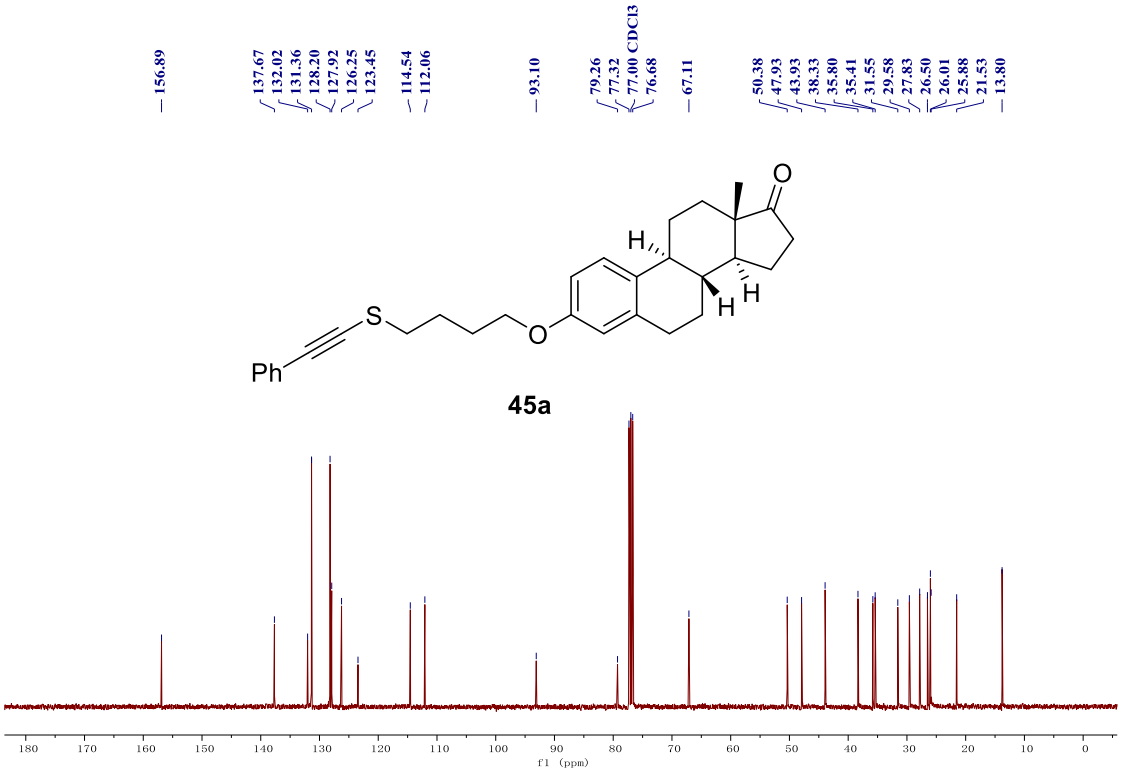
^{13}C NMR of 44a (126 MHz, $CDCl_3$**)**



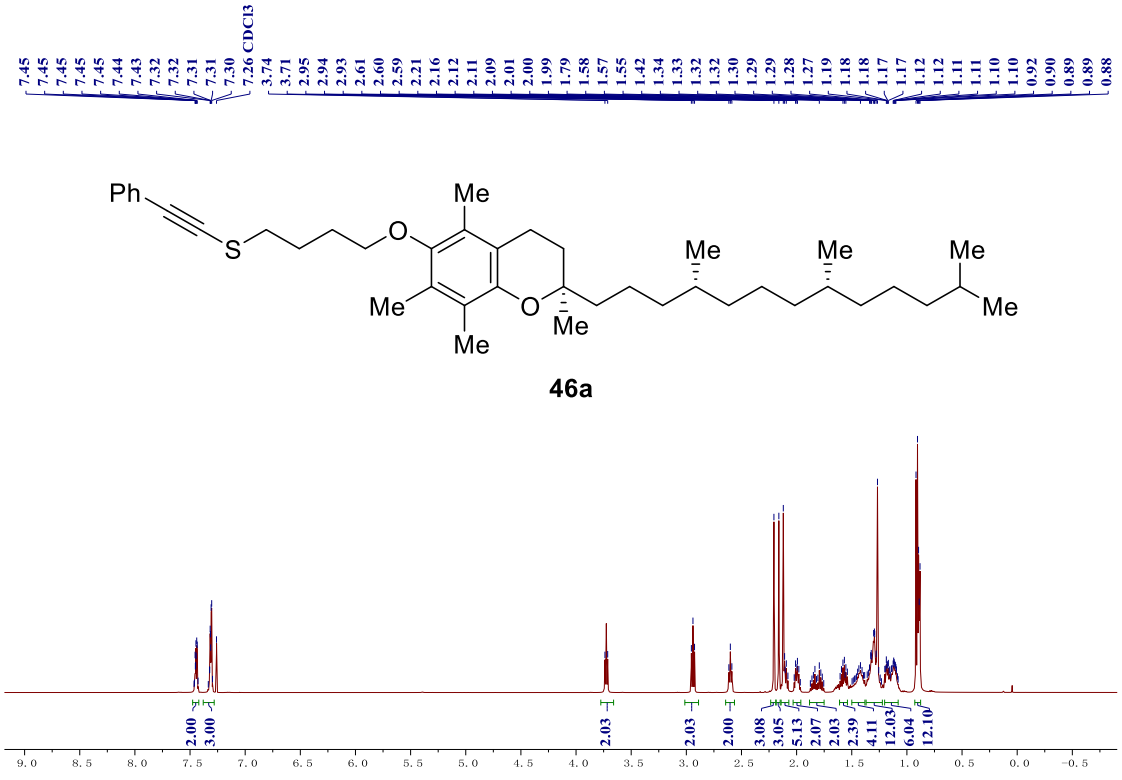
^{1}H NMR of 45a (400 MHz, $CDCl_3$**)**



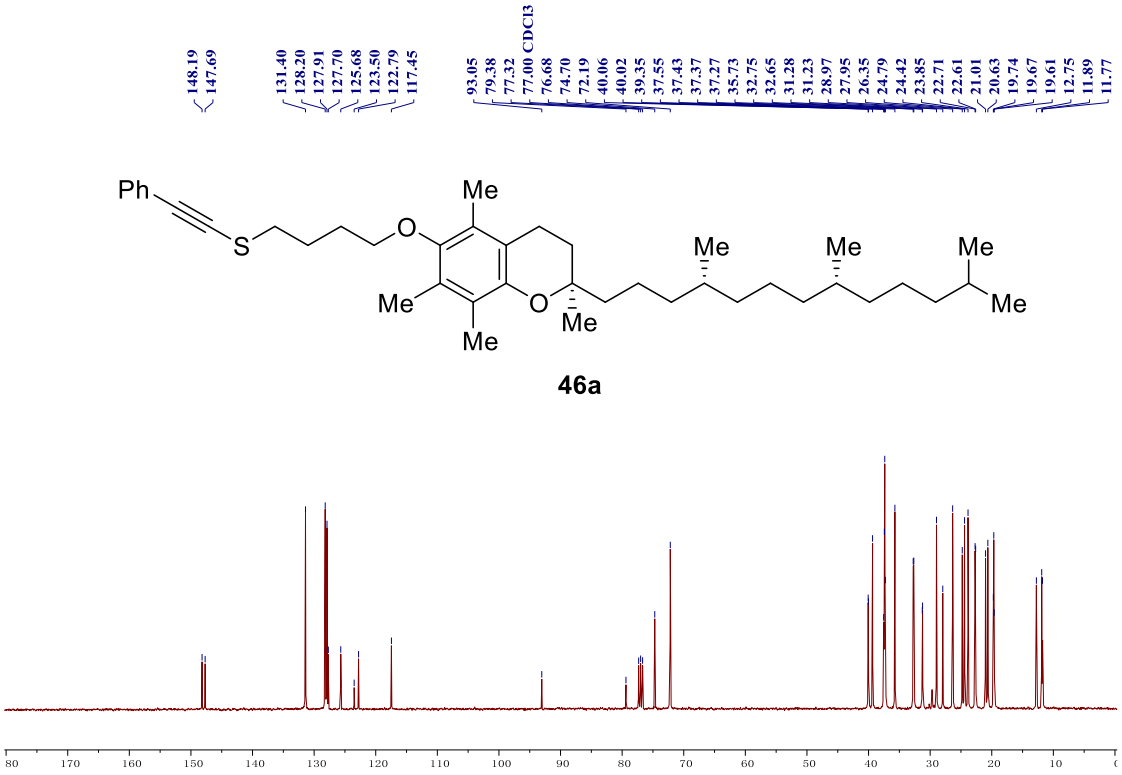
^{13}C NMR of 45a (101 MHz, $CDCl_3$**)**



^{1}H NMR of 46a (500 MHz, $CDCl_3$**)**

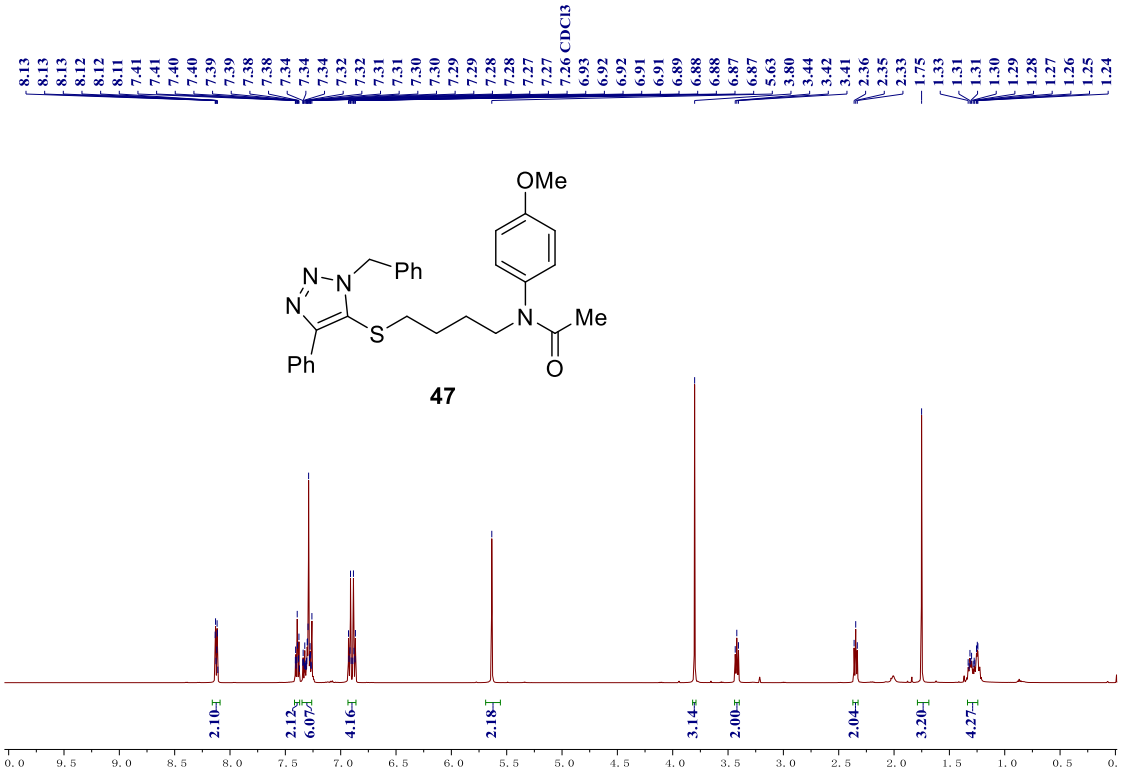


^{13}C NMR of 46a (101 MHz, $CDCl_3$**)**



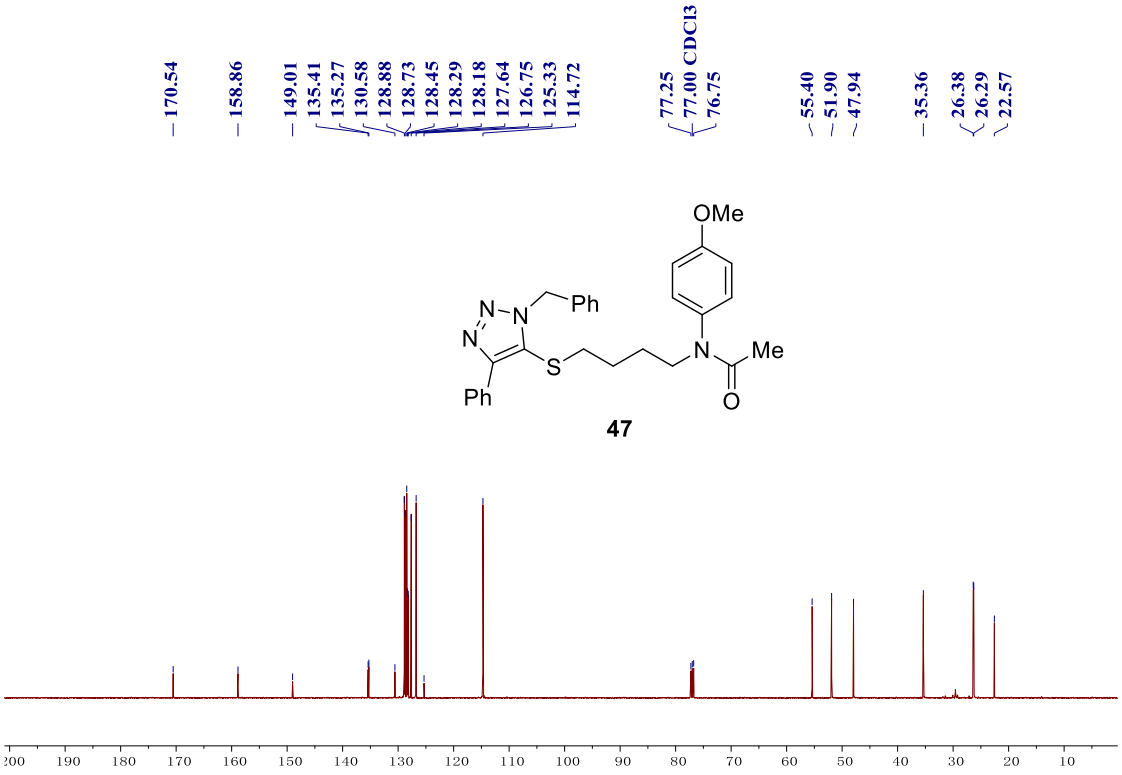
46a

^{1}H NMR of 47 (500 MHz, $CDCl_3$**)**

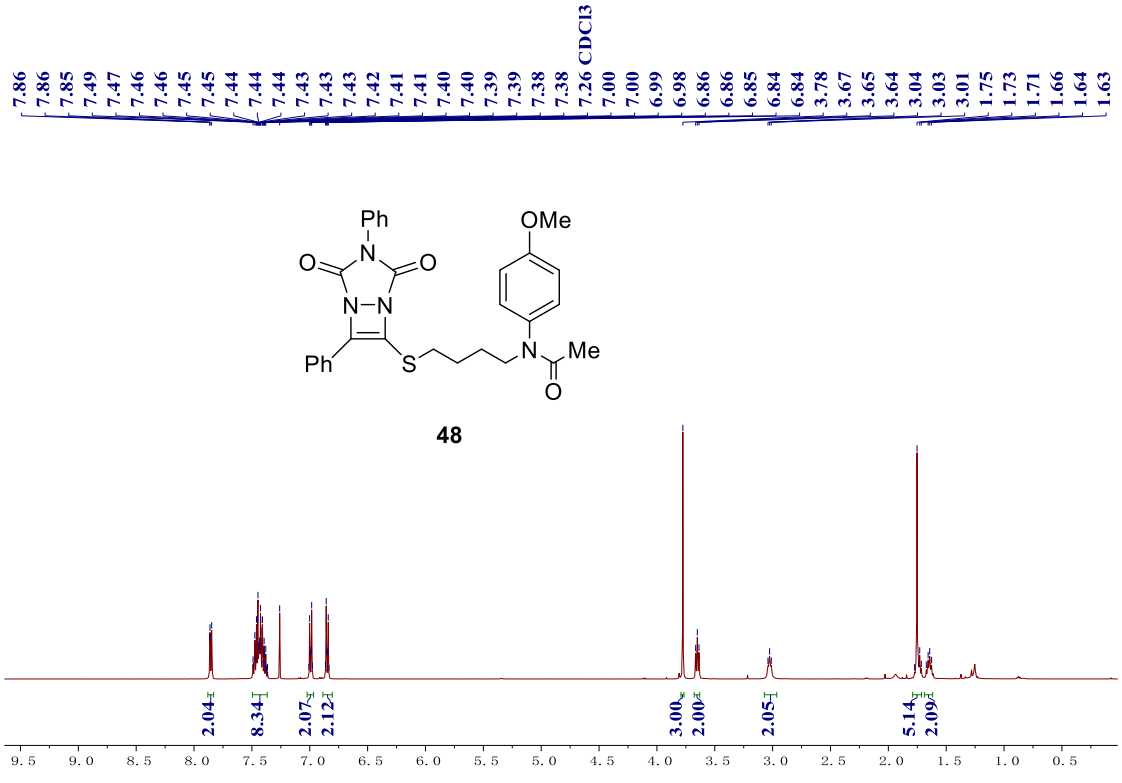


47

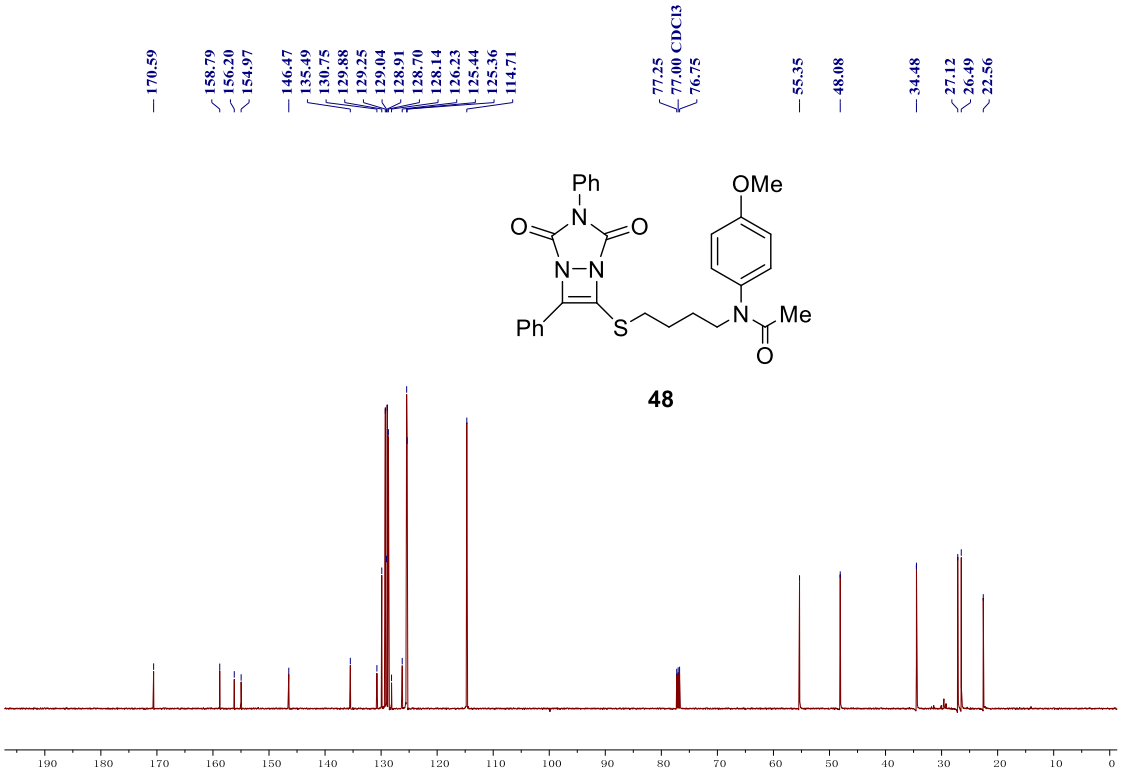
^{13}C NMR of 47 (126 MHz, $CDCl_3$**)**



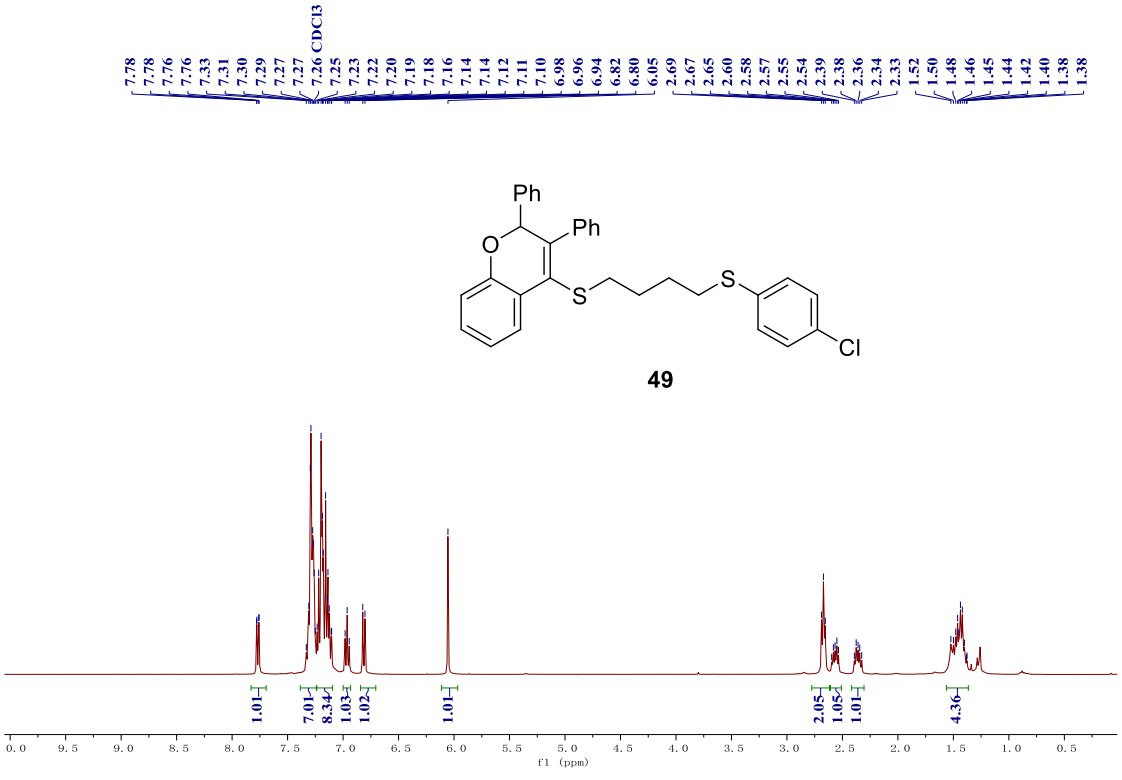
^{1}H NMR of 48 (500 MHz, $CDCl_3$**)**



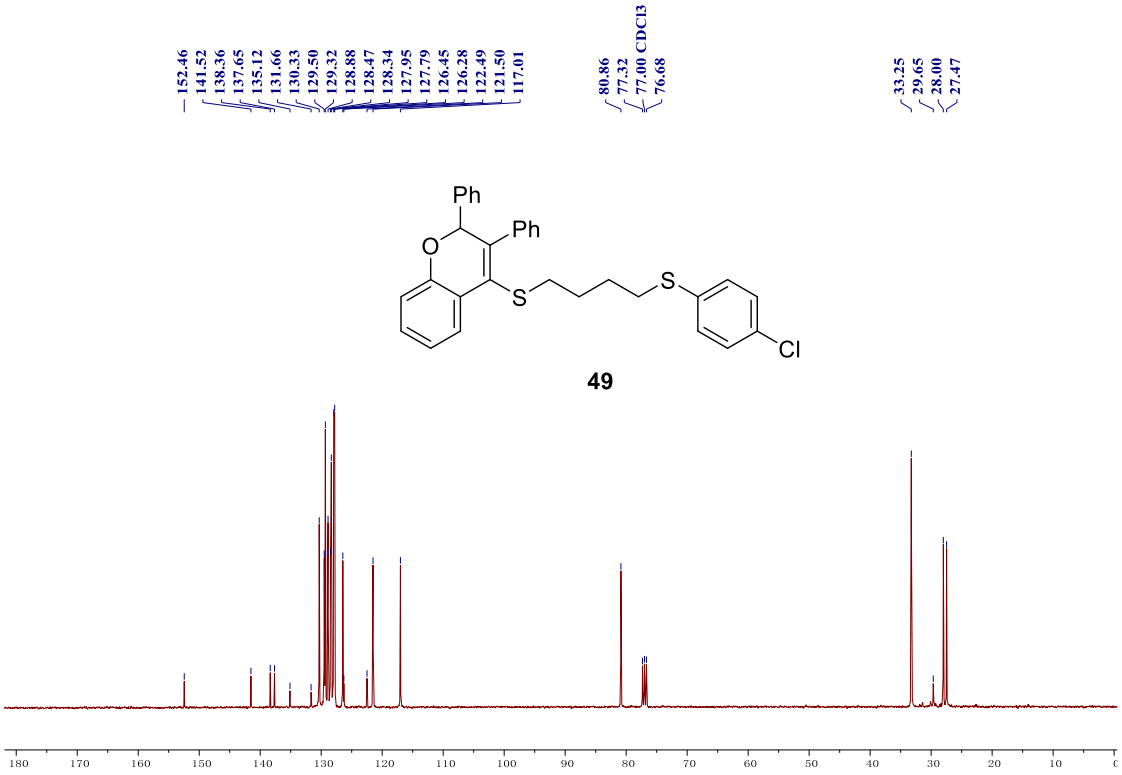
^{13}C NMR of 48 (126 MHz, $CDCl_3$**)**



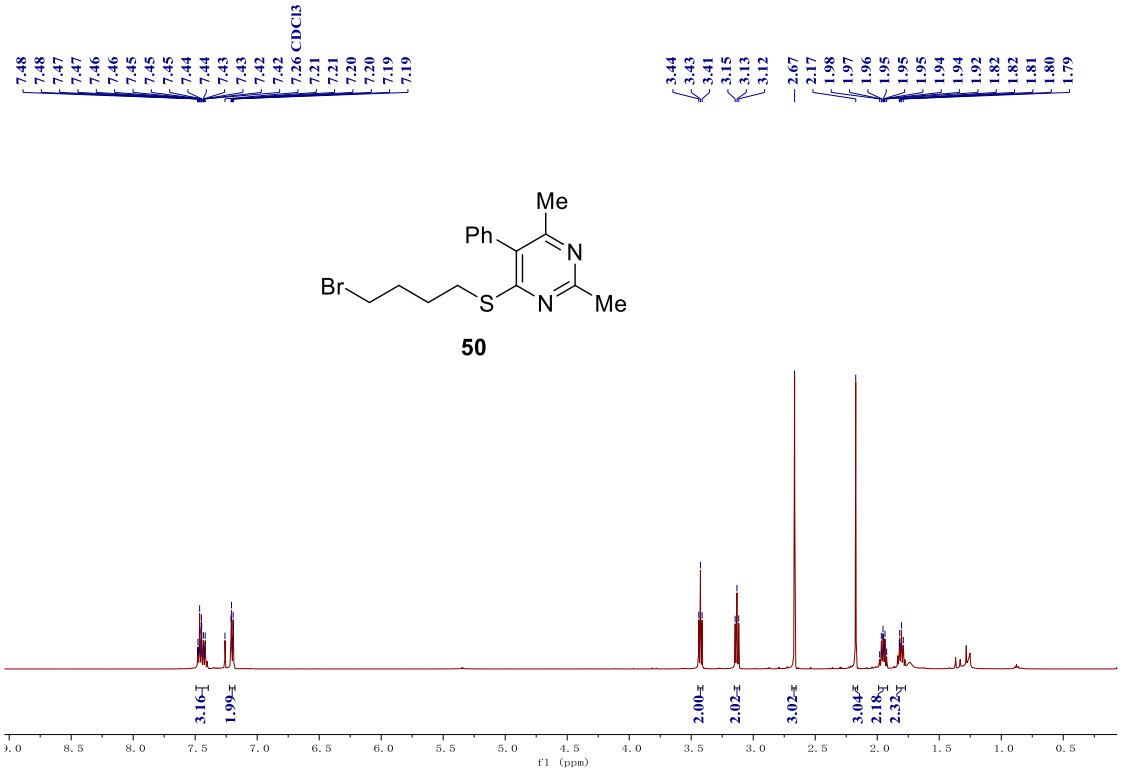
^{1}H NMR of 49 (400 MHz, $CDCl_3$**)**



^{13}C NMR of 49 (101 MHz, $CDCl_3$**)**



^{1}H NMR of 50 (500 MHz, $CDCl_3$**)**



^{13}C NMR of 50 (126 MHz, $CDCl_3$**)**