Regio- and stereoselectively oxidative conversion of alkynes to sulfenylated α,β-unsaturated carbonyls

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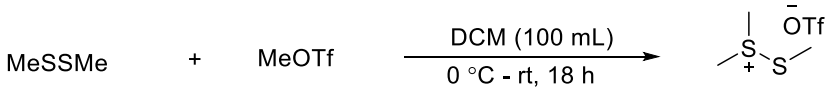
Contents

1 General Information

All reactions involving air or moisture sensitive reagents were carried out in flame dried glass ware under argon atmosphere using standard Schlenk techniques. Solvents were either freshly distilled or obtained in extra-dry grade from commercial sources, and store over molecular sieve (3 Å). Diethyl ether (Et_2O) was distilled over sodium/benzophenone and stored over activated molecular sieve (3 Å). Dichloromethane (CH_2Cl_2) was refluxed over CaH_2 and used as freshly distilled. Otherwise noted, commercially available chemicals were purchased from Energy Chemical. Column chromatography was performed with silica gel (300−400 mesh). Merck silica gel 60 F254 plates were used for thin layer chromatography (TLC). Visualisation was accomplished under UV light (254/366 nm) and by staining with $KMnO_4$ staining dip. The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^1H), 101 MHz (^{13}C), 376 MHz (^{19}F) and 162 MHz (^{31}P) in $CDCl_3$ with tetramethylsilane as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm). Splitting patterns were designated as s, singlet; d, doublet; t; dd, doublet of doublets; m, multiplet. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer. The single-crystal diffraction analysis was collected on Bruker APEX Duo II equipment CCD area detector at 296 K.

2 General Procedures

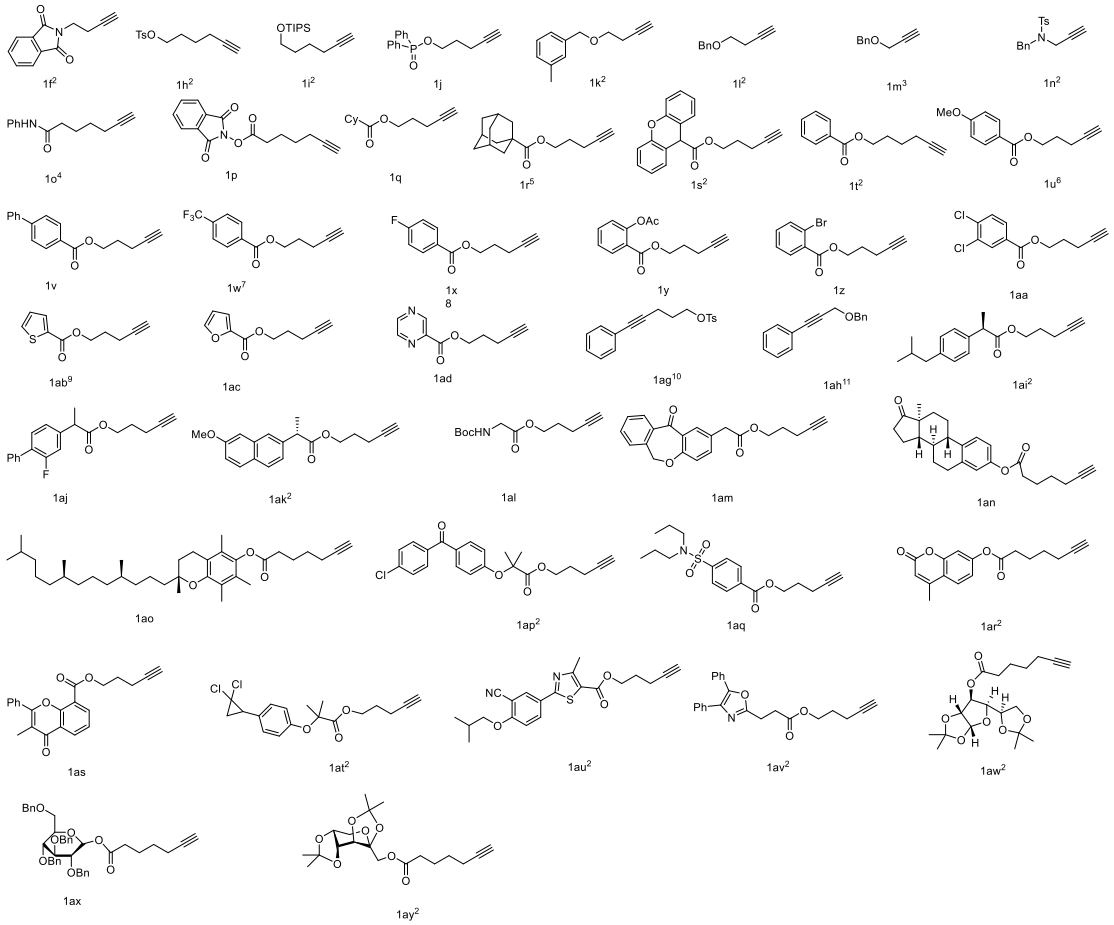
2-1: Preparation of dimethyl(methylthio)sulfonium trifluoromethanesulfonate (DMTSM)



At 0 °C (ice bath), to a solution of methyl trifluoromethanesulfonate (0.12 mol, 13.58 mL, 1.2 equiv)

in CH_2Cl_2 (100 mL), Me_2S_2 (0.1 mol, 8.85 mL, 1.0 equiv) was added dropwise in 30 min. The mixture was stirred for 1 h at that temperature, following by 18 h at room temperature.[1] Upon completion, the white solid was collected by filtration and washed with fresh distilled Et_2O under nitrogen atmosphere, affording dimethyl(methylthio)sulfonium trifluoromethanesulfonate as a white solid (23.13 g, 90% yield).

2-2: The alkynes shown below were synthesized according to the published procedure[2-11]



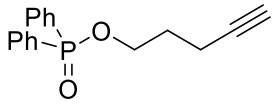
2-3: General procedure for preparation of sulfenylated α,β-unsaturated aldehydes

Under a nitrogen atmosphere, a 25 mL Schlenk-type tube equipped with a magnetic stir bar was charged with DMTSM (0.45 mmol, 115.0 mg, 1.5 equiv), the corresponding alkynes (0.3 mmol, 1.0 equiv), dichloromethane (2 mL) and dimethyl sulfoxide (2 mL) at 0 ºC. The reaction mixture was

then warmed to ambient temperature (23 °C) and stirred for 12 h, before being quenched with brine. The mixture was extracted with CH_2Cl_2 (10 mL X 3), and the combined organic layer were washed with water and brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was then purified by column chromatography.

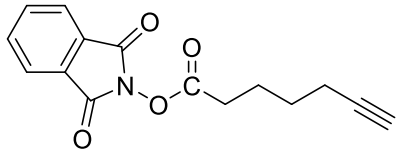
3 Synthesis and characterization

Pent-4-yn-1-yl diphenylphosphinate (1j)



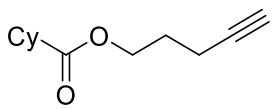
To a stirred solution of diphenylphosphinyl chloride (708 mg, 3.0 mmol, 1.0 equiv) in 20 mL of Et_2O, Et_3N (333 mg, 3.3 mmol, 1.1 equiv) and pent-4-yn-1-ol (252 mg, 3.0 mmol, 1.0 equiv) were added at 0 ºC under nitrogen atmosphere. The solution was stirred at room temperature for 6 h, before the removal of the solvent under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1j** (724 mg, 85% yield) as a white solid, R_f = 0.2 (10% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.77 (m, 4H), 7.51–7.40 (m, 6H), 4.11 (q, *J* = 6.2 Hz, 2H), 2.36–2.32 (m, 2H), 1.95–1.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 10.1 Hz), 131.2 (d, *J* = 137.0 Hz), 128.4 (d, *J* = 13.1 Hz), 82.8, 69.1, 63.2 (d, *J* = 5.8 Hz), 29.3 (d, *J* = 6.8 Hz), 14.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}O_2P$ 285.1039; Found 285.1031.

Pent-4-yn-1-yl 1,3-dioxoisoindoline-2-carboxylate (1p)



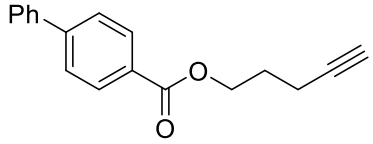
Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with 6-heptynoic acid (378 mg, 3.0 mmol, 1.0 equiv), *N*,*N'*-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), 2-hydroxyisoindoline-1,3-dione (442 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1p** (569 mg, 72% yield) as a white solid, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 2H), 7.81–7.74 (m, 2H), 2.72–2.69 (m, 2H), 2.29–2.25 (m, 2H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.96–1.88 (m, 2H), 1.72–1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 161.9, 134.7, 128.8, 123.9, 83.5, 68.9, 30.4, 27.3, 23.6, 18.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}NO_4$ 272.0917; Found 272.0919.

Pent-4-yn-1-yl cyclohexanecarboxylate (1q)



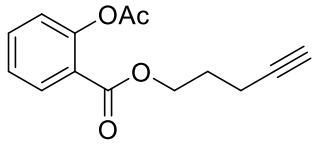
Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with cyclohexanecarboxylic acid (384 mg, 3.0 mmol, 1.0 equiv), *N*,*N'*-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1q** (477 mg, 82% yield) as a colourless oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (t, *J* = 6.3 Hz, 2H), 2.28–2.21 (m, 3H), 1.93 (t, *J* = 2.6 Hz, 1H), 1.86–1.77 (m, 4H), 1.72–1.68 (m, 2H), 1.43–1.34 (m, 2H), 1.28–1.14 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 82.9, 68.8, 62.4, 55.6, 43.0, 34.8, 28.9, 27.5, 25.6, 25.3, 15.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}O_2$ 195.1380; Found 195.1376.

Pent-4-yn-1-yl [1,1'-biphenyl]-4-carboxylate (1v)



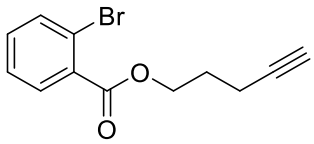
Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with [1,1'-biphenyl]-4-carboxylic acid (594 mg, 3.0 mmol, 1.0 equiv), *N*,*N'*-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1v** (633 mg, 80% yield) as a colourless oil, R_f = 0.2 (3% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.70–7.64 (m, 4H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 4.49 (t, *J* = 6.3 Hz, 2H), 2.62–2.42 (m, 2H), 2.09–2.02 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 145.5, 139.8, 130.0, 128.8, 128.0, 127.1, 126.9, 82.9, 69.1, 63.3, 27.6, 15.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}O_2$ 265.1223; Found 265.1223.

Pent-4-yn-1-yl 2-acetoxybenzoate (1y)



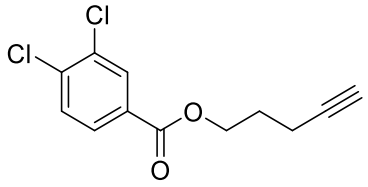
Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with 2-acetoxybenzoic acid (540 mg, 3.0 mmol, 1.0 equiv), *N*,*N'*-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1y** (649 mg, 88% yield) as a colourless oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55–7.51 (m, 1H), 7.31–7.26 (m, 1H), 7.08 (dd, *J* = 8.1, 0.8 Hz, 1H), 4.36 (t, *J* = 6.3 Hz, 2H), 2.35–2.31 (m, 5H), 2.00–1.92 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 164.1, 150.5, 133.7, 131.5, 125.8, 123.7, 123.0, 82.7, 69.2, 63.4, 27.4, 20.9, 15.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}O_4Na$ 269.0784; Found 269.0783.

Pent-4-yn-1-yl 2-bromobenzoate (1z)



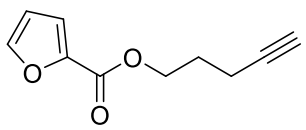
Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with 2-bromobenzoic acid (597 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1z** (588 mg, 74% yield) as a colourless oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.38–7.30 (m, 2H), 4.44 (t, *J* = 6.2 Hz, 2H), 2.42–2.38 (m, 2H), 2.03– 1.97 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 134.3, 132.5, 132.2, 131.3, 127.1, 121.5, 82.9, 69.2, 64.1, 27.4, 15.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}BrO_2$ 267.0015; Found 267.0016.

Pent-4-yn-1-yl 2,4,6-trichlorobenzoate (1aa)



Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with 2,4,6-trichlorobenzoic acid (669 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1aa** (693 mg, 80% yield) as a white solid, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.9 Hz, 1H), 7.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52–7.49 (m, 1H), 4.43 (t, *J* = 6.3 Hz, 2H), 2.39–2.35 (m, 2H), 2.02–1.96 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 137.5, 132.8, 131.4, 130.5, 129.9, 128.6, 82.8, 69.2, 64.1, 27.5, 15.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}Cl_2O_2$ 257.0131; Found 257.0126.

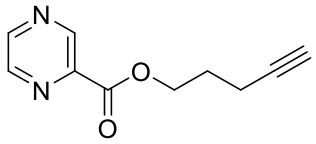
Pent-4-yn-1-yl furan-2-carboxylate (1ac)



Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with furan-2-carboxylic acid (336 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1ac** (453 mg, 85% yield) as a yellow oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 0.8 Hz, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 6.47 (dd, *J* = 3.5, 1.7 Hz, 1H),

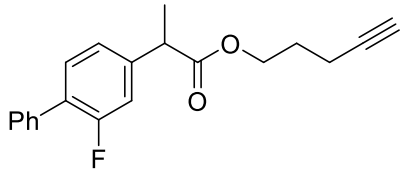
4.37 (t, *J* = 6.3 Hz, 2H), 2.34–2.30 (m, 2H), 1.97–1.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 146.2, 144.5, 117.8, 111.7, 82.8, 69.1, 63.3, 27.5, 15.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}O_3$ 179.0703; Found 179.0698.

Pent-4-yn-1-yl pyrazine-2-carboxylate (1ad)



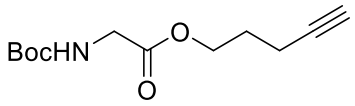
Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with pyrazine-2-carboxylic acid (372 mg, 3.0 mmol, 1.0 equiv), *N*,*N'*-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1ad** (456 mg, 80% yield) as a yellow oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.73–8.69 (m, 2H), 4.51 (t, *J* = 6.4 Hz, 2H), 2.36–2.32 (m, 2H), 2.04–1.09 (m, 2H), 1.95 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 147.6, 146.1, 144.3, 143.2, 82.5, 69.3, 64.7, 27.3, 15.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O_2$ 191.0815; Found 191.0812.

pent-4-yn-1-yl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (1aj)



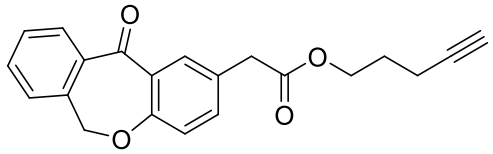
Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (732 mg, 3.0 mmol, 1.0 equiv), *N*,*N'*-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1aj** (558 mg, 60% yield) as a yellow oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (m, 2H), 7.47–7.36 (m, 4H), 7.19–7.14 (m, 2H), 4.23 (t, *J* = 6.3 Hz, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 2.25–2.21 (m, 2H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.89–1.82 (m, 2H), 1.56 (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 (d, *J* = 1.1 Hz), 130.7 (d, *J* = 4.0 Hz), 128.9, 128.8, 128.3, 127.6, 123.4 (d, *J* = 3.3 Hz), 115.1 (d, *J* = 23.7 Hz), 82.8, 69.0, 63.4, 44.9, 27.3, 18.2, 15.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}FO_2$ 311.1442; Found 311.1442.

Pent-4-yn-1-yl (tert-butoxycarbonyl)glycinate (1al)



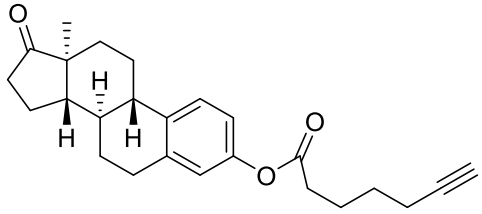
Under nitrogen atmosphere, a 50 mL flamed dried round bottom flask was charged with (*tert*-butoxycarbonyl)glycine (525 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1al** (404 mg, 56% yield) as a white solid, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (br, 1H), 4.26 (t, *J* = 6.3 Hz, 2H), 3.91 (d, *J* = 5.5 Hz, 2H), 2.31–2.27 (d, *J* = 16.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.191–1.84 (m 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 155.6, 82.7, 80.0, 69.1, 63.7, 42.3, 28.2, 27.3, 15.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{20}NO_4$ 242.1387; Found 242.1389.

Pent-4-yn-1-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (1am）



Under nitrogen atmosphere, a 50 mL flamed dried round bottom flask was charged with 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetic acid (804 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1am** (601 mg, 60% yield) as a white solid, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.2 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.60–7.56 (m, 1H), 7.51–7.43 (m, 2H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 5.20 (s, 2H), 4.23 (t, *J* = 6.3 Hz, 2H), 3.67 (s, 2H), 2.28 (d, *J* = 16.6 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.88 (d, *J* = 26.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 171.3, 160.4, 140.4, 136.3, 135.5, 132.7, 132.4, 129.4, 129.2, 127.8, 127.7, 125.1, 121.0, 82.9, 73.6, 69.0, 63.4, 40.1, 27.4, 15.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}O_4$ 335.1278; Found 335.1278.

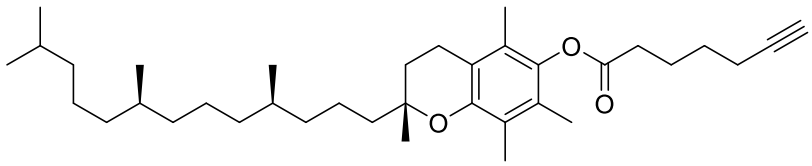
(8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl hept-6-ynoate (1an）



Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with 6-heptynoic acid (378 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol,

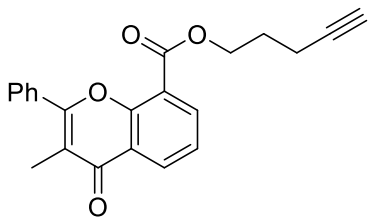
1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), (8R,9S,13S,14S)-3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (972 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1an** (816 mg, 72% yield) as a white solid, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 1H), 6.85–6.80 (m, 2H), 2.91–2.89 (m, 2H), 2.60–2.38 (m, 4H), 2.28–2.24 (m, 3H), 2.16–1.83 (m, 7H), 1.69–1.39 (m, 8H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 172.1, 148.5, 137.9, 137.3, 126.3, 121.5, 118.7, 68.7, 50.3, 47.9, 44.1, 37.9, 35.8, 33.8, 31.5, 29.3, 27.7, 26.3, 25.7, 23.9, 21.5, 18.1, 13.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{31}O_3$ 379.2268; Found 379.2269.

(R)-2,5,7,8-Tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl hept-6-ynoate (1ao)



Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with 6-heptynoic acid (378 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-ol (1.50 g, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1ao** (968 mg, 60% yield) as a yellow oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65–2.57 (m, 4H), 2.29–2.25 (m, 2H), 2.08 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.94–1.64 (m, 8H), 1.57–1.47 (m, 3H), 1.40–1.23 (m, 12H), 1.18–1.04 (m, 8H), 0.87–0.83 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 149.3, 140.4, 126.6, 124.8, 123.0, 117.3, 100.0, 83.8, 75.0, 68.7, 55.7, 39.3, 37.4 (2C), 37.3, 34.9, 33.6, 32.8, 32.7, 28.0, 25.4, 24.8, 24.7, 24.4, 24.2, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 18.2, 13.0, 12.1, 11.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{36}H_{59}O_3$ 539.4459; Found 539.4462.

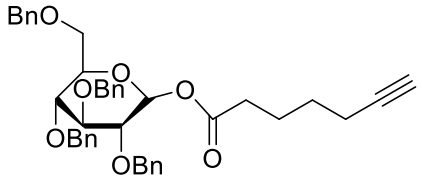
Pent-4-yn-1-yl 3-methyl-4-oxo-2-phenyl-4H-chromene-8-carboxylate (1as)



Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with 3-methyl-4-oxo-2-phenyl-4H-chromene-8-carboxylic acid (840 mg, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified

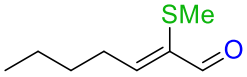
by flash column chromatography on silica gel to give the product **1as** (747 mg, 72% yield) as a white solid, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.25 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.76–7.73 (m, 2H), 7.55–7.48 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 1H), 4.43 (t, *J* = 6.3 Hz, 2H), 2.22–2.18 (m, 5H), 1.96–1.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 164.3, 161.0, 154.3, 136.1, 132.9, 130.7, 130.4, 129.1, 128.4, 123.9, 123.1, 120.4, 117.6, 82.8, 69.1, 63.9, 27.4, 15.1, 11.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}O_4Na$ 369.1097; Found 369.1083.

(2R,3S,4R,5S,6S)-3,4,5-Tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl hept-6-ynoate (1ax)



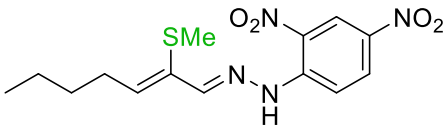
Under nitrogen atmosphere, a 100 mL flamed dried round bottom flask was charged with (2S,3S,4R,5S,6S)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-ol (1.62 g, 3.0 mmol, 1.0 equiv), *N*,*N*′-dicyclohexylcarbodiimide (743 mg, 3.6 mmol, 1.2 equiv), DMAP (73 mg, 0.6 mmol, 20 mol%), pent-4-yn-1-ol (302 mg, 3.6 mmol, 1.2 equiv) and DCM (30 mL, 0.1 M). The reaction mixture was then stirred at 23 °C for 18 hours and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **1ax** (1.17 g, 60% yield) as a white solid, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 18H), 7.18–7.16 (m, 2H), 6.43 (d, *J* = 3.4 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.89–4.84 (m, 2H), 4.74–4.62 (m, 3H), 4.54–4.50 (m, 2H), 3.98–3.88 (m, 2H), 3.79–3.66 (m, 4H), 2.46–2,42 (m, 2H), 2,21–2.17 (m, 2H), 1.95–1.96 (m, 1H), 1.83–1.75 (m, 2H), 1.63–1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 138.6, 138.0, 137.7, 137.6, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 89.9, 83.8, 81.6, 78.9, 76.8, 75.6, 75.3, 73.5, 73.1, 72.9, 68.7, 68.0, 33.7, 27.5, 23.9, 18.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{41}H_{44}O_7Na$ 671.2979; Found 671.2979.

(Z)-2-(Methylthio)hept-2-enal (2a)



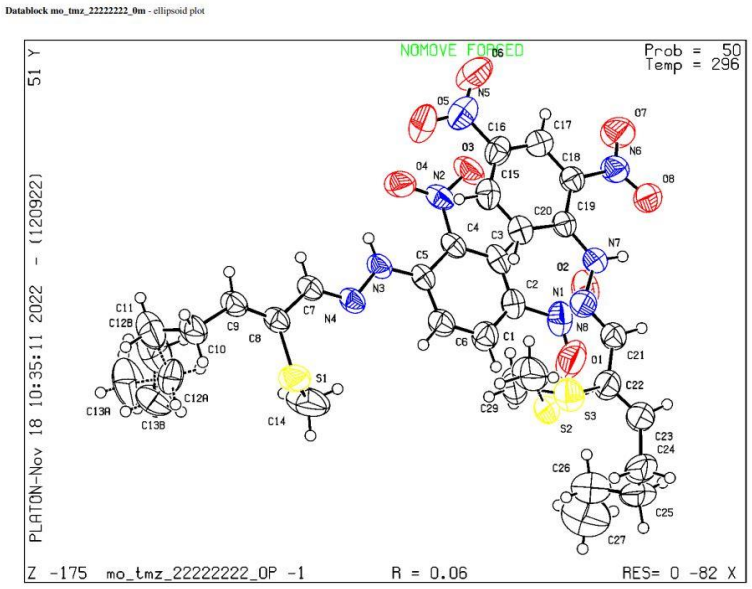
Following the general procedure, hept-1-yne **1a** (28.8 mg, 0.3 mmol) was used to give the product **2a** (31.2 mg, 66% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 2.58 (dd, *J* = 14.8, 7.4 Hz, 2H), 2.29 (s, 3H), 1.53–1.45 (m, 2H), 1.42–1.34 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 159.8, 139.3, 30.3, 22.4, 15.8, 13.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_{15}OS$ 159.0838; Found 159.0843.

(E)-1-(2,4-Dinitrophenyl)-2-((Z)-2-(methylthio)hept-2-en-1-ylidene)hydrazine (S-2a)



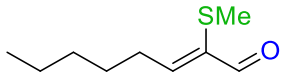
To a solution of (2,4-dinitrophenyl)hydrazine (3 mmol) and **2a** (3 mmol) in ethanol (10 mL) was added a few drops of AcOH. The mixture was stirred and heated (oil bath) to reflux for 6 h. The precipitated hydrazone was filtered, washed with ethanol and dried over Na_2SO_4. The pure hydrazone was obtained after recrystallization from ethanol. The product **S-2a** was obtained as a red solid (0.96 g, 95%), R_f = 0.25 (10% EA in PE). Single crystals suitable for X-ray analysis were obtained by recrystallization from a solution of the title compound in dichloromethane and n-hexane (CCDC Number 2220571). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 9.12 (d, *J* = 2.5 Hz, 1H), 8.33 (dd, *J* = 9.6, 2.5 Hz, 1H), 7.99 (d, *J* = 9.6 Hz, 1H), 7.79 (s, 1H), 6.45 (t, *J* = 7.5 Hz, 1H), 2.58 (q, *J* = 7.3 Hz, 2H), 2.38 (s, 3H), 1.50–1.35 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.6, 144.9, 138.1, 132.2, 130.1, 129.2, 123.5, 116.6, 30.9, 30.2, 22.4, 16.9, 13.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}N_4O_4S$ 339.1122; Found 339.1121.

ORTEP drawing of S-2a (50% thermal ellipsoids)**:**



Crystallographic Description: The single-crystal diffraction analysis was collected on Bruker APEX Duo II equipment CCD area detector at 296 K. The X-ray generator was operated at 50 kV and 35 mA using Mo Kα (λ = 0.71073 Å) radiation. Data integration was performed using SAINT. Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using SADABS. Those structures were solved with the ShelXT1 structure solution program using Intrinsic Phasing and refined with the ShelXL-20182 refinement package using Least Squares minimization on Olex-23 software. All the solvent molecules which are highly disordered and not able to be modeled were treated by the SQUEEZE routine in PLATON. The topological analyses were performed with TOPOS4.

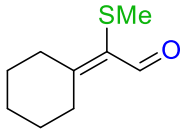
(Z)-2-(Methylthio)oct-2-enal (2b)



Following the general procedure, oct-1-yne **1b** (33.0 mg, 0.3 mmol) was used to give the product **2b** (35.0 mg, 68% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ

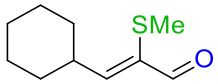
9.40 (s, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 2.57 (q *J* = 7.4 Hz, 2H), 2.28 (s, 3H), 1.54–1.47 (m, 2H), 1.34–1.30 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 159.8, 139.3, 31.4, 30.6, 27.9, 22.3, 15.8, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{17}OS$ 173.0995; Found 173.0991.

2-Cyclohexylidene-2-(methylthio)acetaldehyde (2c)



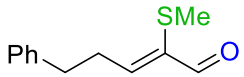
Following the general procedure, ethynylcyclohexane **1c** (32.4 mg, 0.3 mmol) was used to give the product **2c** (23.4 mg, 46% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 2.84–2.78 (m, 4H), 2.18 (s, 3H), 1.73–1.65 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 170.6, 130.7, 35.6, 31.2, 28.8, 28.5, 26.3, 17.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{15}OS$ 171.0838; Found 171.0835.

(Z)-3-Cyclohexyl-2-(methylthio)acrylaldehyde (2d)



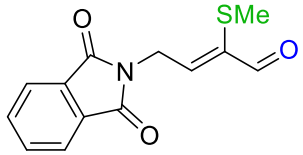
Following the general procedure, prop-2-yn-1-ylcyclohexane **1d** (36.6 mg, 0.3 mmol) was used to give the product **2d** (42.0 mg, Z:E = 10 :1, 76% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 6.74 (d, *J* = 9.4 Hz, 1H), 2.98–2.88 (m, 1H), 2.31 (s, 3H), 1.79–1.71 (m, 4H), 1.42–1.16 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 148.9, 137.9, 40.9, 24.0, 18.2, 17.2, 13.8, 13.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{17}OS$ 185.0995; Found 185.0988.

(Z)-2-(Methylthio)-5-phenylpent-2-enal (2e)



Following the general procedure, pent-4-yn-1-ylbenzene **1e** (43.2mg, 0.3 mmol) was used to give the product **2e** (38.3 mg, 62% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.33–7.29 (m, 2H), 7.24–7.21 (m, 3H), 6.93 (t, *J* = 7.1 Hz, 1H), 2.96–2.91 (m, 2H), 2.87–2.83 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 157.9, 140.2, 140.0, 128.5, 128.3, 126.3, 34.2, 32.0, 15.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}OS$ 207.0838; Found 207.0839.

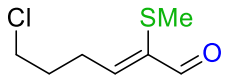
(Z)-4-(1,3-Dioxoisoindolin-2-yl)-2-(methylthio)but-2-enal (2f)



Following the general procedure, 2-(but-3-yn-1-yl)isoindoline-1,3-dione **1f** (35.7 mg, 0.3 mmol) was used to give the product **2f** (50.1 mg, Z:E = 7:1, 64% yield) as a white solid, R_f = 0.2 (20% EA

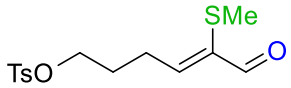
in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.84–7.81 (m, 2H), 7.78–7.74 (m, 2H), 7.16 (t, *J* = 5.6 Hz, 1H), 5.18 (d, *J* = 5.6 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 163.4, 148.0, 141.3, 134.7, 128.5, 123.7, 75.0, 15.4. HRMS (ESI) m/z: $[M + K]^+$ Calcd for $C_{13}H_{11}NO_3SK$ 300.0091; Found 300.0099.

(Z)-6-Chloro-2-(methylthio)hex-2-enal (2g)



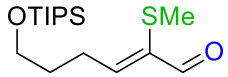
Following the general procedure, 6-chlorohex-1-yne **1g** (33.9 mg, 0.3 mmol) was used to give the product **2g** (32.6 mg, Z:E > 20:1, 61% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 3.58 (t, *J* = 6.5 Hz, 2H), 2.75 (dd, *J* = 14.9, 7.4 Hz, 2H), 2.31 (s, 3H), 2.03–1.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 156.5, 140.5, 44.0, 31.0, 28.0, 15.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_7H_{11}ClOSNa$ 201.0111; Found 201.0107.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 4-methylbenzenesulfonate (2h)



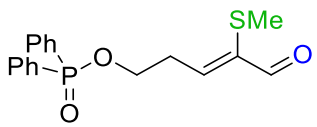
Following the general procedure, pent-4-yn-1-yl 4-methylbenzenesulfonate **1h** (71.4 mg, 0.3 mmol) was used to give the product **2h** (52.2 mg, Z:E > 20:1, 58% yield) as a white solid, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 4.07 (t, *J* = 6.2 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 2.28 (s, 3H), 1.91–1.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 156.0, 144.9, 140.4, 132.7, 129.9, 127.8, 69.3, 27.5, 26.6, 21.6, 15.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_4S_2Na$ 337.0539; Found 337.0549.

(Z)-2-(Methylthio)-6-((triisopropylsilyl)oxy)hex-2-enal (2i)



Following the general procedure, triisopropyl(pent-4-yn-1-yloxy)silane **1i** (72.0 mg, 0.3 mmol) was used to give the product **2i** (43.6 mg, 46% yield) as a yellow oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 3.75 (t, *J* = 6.1 Hz, 2H), 2.69 (q, *J* = 7.4 Hz, 2H), 2.30 (s, 3H), 1.79–1.72 (m, 2H), 1.15–1.05 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 159.7, 139.3, 62.7, 31.6, 27.6, 18.0, 15.8, 11.9, 11.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{32}O_2SSiNa$ 339.1784; Found 339.1796.

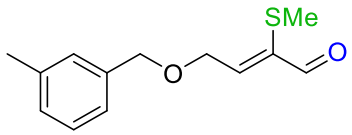
(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl diphenylphosphinate (2j)



Following the general procedure, pent-4-yn-1-yl diphenylphosphinate **1j** (85.2 mg, 0.3 mmol) was used to give the product **2j** (49.8 mg, 48% yield) as a yellow oil, R_f = 0.2 (10% EA in PE). ^{1}H NMR

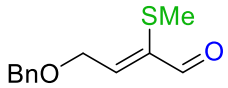
(400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.81–7.75 (m, 4H), 7.54–7.49 (m, 2H), 7.46–7.41 (m, 4H), 6.94 (t, *J* = 7.0 Hz, 1H), 4.19 (q, *J* = 6.4 Hz, 2H), 2.98 (q, *J* = 6.4 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.44, 153.23, 132.35 (d, *J* = 2.8 Hz), 131.49 (d, *J* = 10.3 Hz), 141.46, 130.10, 128.56 (d, *J* = 13.2 Hz), 62.62 (d, *J* = 5.8 Hz), 31.77 (d, *J* = 6.5 Hz), 15.57. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}O_3PS$ 347.0865; Found 347.0851.

(Z)-4-((4-Methylbenzyl)oxy)-2-(methylthio)but-2-enal (2k)



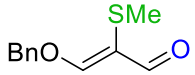
Following the general procedure, 1-((but-3-yn-1-yloxy)methyl)-4-methylbenzene **1k** (52.2 mg, 0.3 mmol) was used to give the product **2k** (51.0 mg, 72% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^1H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17–7.12 (m, 3H), 7.00 (t, *J* = 5.3 Hz, 1H), 4.56 (s, 2H), 4.51 (d, *J* = 5.3 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 153.9, 138.8, 138.2, 137.2, 128.7, 128.6, 128.4, 125.0, 73.3, 67.8, 21.3, 15.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_2SNa$ 259.0763; Found 259.0761.

(Z)-4-(Benzyloxy)-2-(methylthio)but-2-enal (2l)



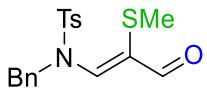
Following the general procedure, ((but-3-yn-1-yloxy)methyl)benzene **1l** (48.0 mg, 0.3 mmol) was used to give the product **2l** (44.0 mg, 66% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^1H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.37–7.30 (m, 5H), 6.99 (t, *J* = 5.3 Hz, 1H), 4.60 (s, 2H), 4.51 (d, *J* = 5.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 153.8, 138.8, 137.3, 128.5, 128.0, 127.9, 73.3, 67.8, 15.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}O_2S$ 223.0787; Found 223.0795.

(Z)-3-(Benzyloxy)-2-(methylthio)acrylaldehyde (2m)



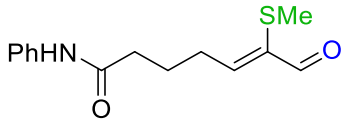
Following the general procedure, ((prop-2-yn-1-yloxy)methyl)benzene **1m** (43.8 mg, 0.3 mmol) was used to give the product **2m** (34.3 mg, 55% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.44 (s, 1H), 7.42–7.35 (m, 5H), 5.23 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 169.3, 134.7, 129.1, 128.9, 127.8, 118.2, 77.2, 15.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}O_2S$ 209.0631; Found 209.0638.

(Z)-N-benzyl-4-methyl-N-(2-(methylthio)-3-oxoprop-1-en-1-yl)benzenesulfonamide (2n)



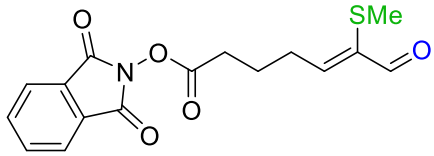
Following the general procedure, N-benzyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide **1n** (89.7 mg, 0.3 mmol) was used to give the product **2n** (32.5 mg, 30% yield) as a yellow oil, R_f = 0.2 (10% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.14 (s, 1H), 7.66–7.64 (m, 2H), 7.317.20 (m, 5H), 7.14–7.12 (m, 2H), 5.46 (s, 2H), 2.43 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 149.6, 145.5, 135.6, 134.6, 130.2, 128.4, 127.4, 127.3, 126.5, 115.8, 49.8, 21.6, 17.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}NO_3S_2$ 362.0879; Found 362.0880.

(Z)-6-(Methylthio)-7-oxo-N-phenylhept-5-enamide (2o)



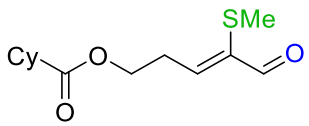
Following the general procedure, N-phenylhept-6-ynamide **1o** (60.3 mg, 0.3 mmol) was used to give the product **2o** (40.2 mg, 51% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.94 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.30 (dd, *J* = 11.6, 4.1 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 2.66 (q, *J* = 7.4 Hz, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.29 (s, 3H), 1.99–1.92 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 170.6, 158.2, 139.9, 137.8, 128.8, 124.2, 119.9, 36.5, 29.9, 23.9, 15.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}NO_2S$ 264.1053; Found 264.1560.

(Z)-7-(1,3-Dioxoisoindolin-2-yl)-2-(methylthio)-7-oxohept-2-enal (2p)



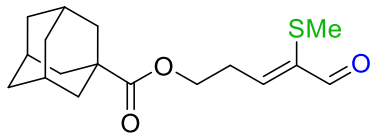
Following the general procedure, 1,3-dioxoisoindolin-2-yl hept-6-ynoate **1p** (81.3 mg, 0.3 mmol) was used to give the product **2p** (65.1 mg, 68% yield) as a white solid, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.87–7.84 (m, 2H), 7.79–7.76 (m, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 2.76–2.70 (m, 4H), 2.30 (s, 3H), 2.04–1.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 168.9, 161.7, 156.2, 156.2, 140.6, 134.8, 128.7, 123.9, 30.3, 29.4, 23.1, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_5S$ 334.0744; Found 334.0744.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl cyclohexanecarboxylate (2q)



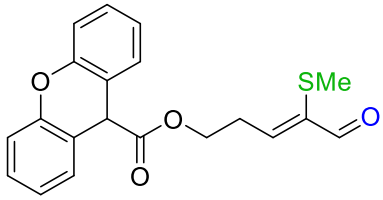
Following the general procedure, pent-4-yn-1-yl cyclohexanecarboxylate **1q** (58.2 mg, 0.3 mmol) was used to give the product **2q** (42.2 mg, 55% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 6.89 (t, *J* = 7.1 Hz, 1H), 4.23 (t, *J* = 6.3 Hz, 2H), 2.91 (q, *J* = 6.4 Hz, 2H), 2.31 (s, 3H), 2.31–2.25 (m, 1H), 1.89–1.85 (m, 2H), 1.74–1.71 (m, 2H), 1.64–1.62 (m, 1H), 1.45–1.36 (m, 2H), 1.32–1.18 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 175.9, 153.6, 141.3, 61.7, 43.0, 30.2, 28.9, 25.6, 25.3, 15.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{21}O_3S$ 257.1206; Found 257.1207.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl-adamantane-1-carboxylate (2r)



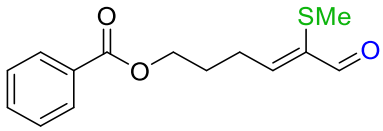
Following the general procedure, pent-4-yn-1-yl-adamantane-1-carboxylate **1r** (73.8 mg, 0.3 mmol) was used to give the product **2r** (51.7 mg, 56% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 6.88 (t, *J* = 7.1 Hz, 1H), 4.21 (t, *J* = 6.3 Hz, 2H), 2.91 (dd, *J* = 13.4, 6.3 Hz, 2H), 2.30 (s, 3H), 1.98 (s, 3H), 1.84–1.85 (m, 6H), 1.72–1.64 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 177.4, 153.7, 141.3, 61.6, 40.6, 38.7, 36.3, 30.2, 27.8, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{25}O_3S$ 309.1519; Found 309.1518.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 9H-xanthene-9-carboxylate (2s)



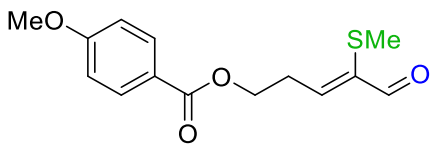
Following the general procedure, pent-4-yn-1-yl 9H-xanthene-9-carboxylate **1s** (87.6 mg, 0.3 mmol) was used to give the product **2s** (64.8 mg, 61% yield) as a white solid, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.34–7.29 (m, 4H), 7.16–7.14 (m, 2H), 7.11–7.07 (m, 2H), 6.50 (t, *J* = 7.0 Hz, 1H), 5.01 (s, 1H), 4.22 (t, *J* = 6.1 Hz, 2H), 2.81 (q, *J* = 6.2 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 171.4, 153.2, 151.2, 141.1, 129.2, 128.8, 123.3, 118.1, 116.9, 62.9, 45.5, 29.7, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}O_4S$ 355.0999; Found 355.0993.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl benzoate (2t)



Following the general procedure, hex-5-yn-1-yl benzoate **1t** (60.6 mg, 0.3 mmol) was used to give the product **2t** (46.7 mg, 59% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 8.04–8.00 (m, 2H), 7.57–7.53 (m, 1H), 7.45–7.41 (m, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 4.37 (t, *J* = 6.3 Hz, 2H), 2.76 (q, *J* = 7.4 Hz, 2H), 2.28 (s, 3H), 2.04–1.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 166.4, 157.2, 140.1, 133.0, 129.9, 129.4, 128.3, 63.9, 27.4, 27.3, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}O_3S$ 265.0893; Found 265.0902.

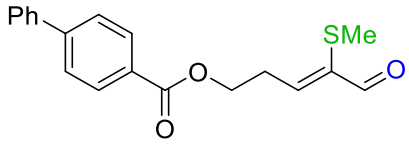
(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 3-methoxybenzoate (2u)



Following the general procedure, pent-4-yn-1-yl 4-methoxybenzoate **1u** (65.4 mg, 0.3 mmol) was

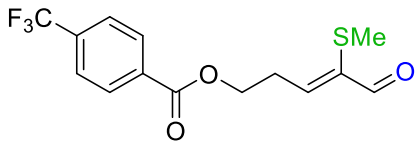
used to give the product **2u** (58.0 mg, Z:E > 20:1, 69% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.96–7.94 (m, 2H), 6.98 (t, *J* = 7.1 Hz, 1H), 6.91–6.87 (m, 2H), 4.44 (t, *J* = 6.3 Hz, 2H), 3.83 (s, 3H), 3.03 (dd, *J* = 13.4, 6.4 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 166.0, 163.4, 153.5, 141.4, 131.5, 122.0, 113.6, 62.2, 55.3, 30.2, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}O_4S$ 281.0842; Found 281.0840.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl [1,1'-biphenyl]-3-carboxylate (2v)



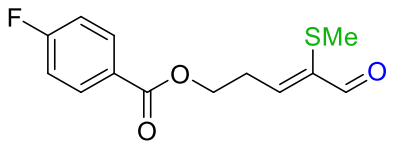
Following the general procedure, pent-4-yn-1-yl [1,1'-biphenyl]-4-carboxylate **1v** (79.2 mg, 0.3 mmol) was used to give the product **2v** (54.8 mg, Z:E > 20:1, 56% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.11–8.07 (m, 2H), 7.67–7.61 (m, 4H), 7.48–7.44 (m, 2H), 7.41–7.37 (m, 1H), 7.01 (t, *J* = 7.1 Hz, 1H), 4.52 (t, *J* = 6.3 Hz, 2H), 3.09 (q, *J* = 6.4 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 166.2, 153.2, 145.8, 141.5, 139.7, 130.0, 128.9, 128.4, 128.1, 127.2, 127.0, 62.6, 30.2, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}O_3S$ 327.1049; Found 327.1051.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 3-(trifluoromethyl)benzoate (2w)



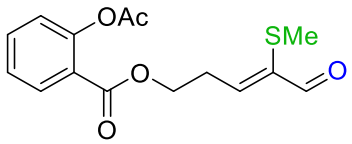
Following the general procedure, pent-4-yn-1-yl 4-(trifluoromethyl)benzoate **1w** (76.8 mg, 0.3 mmol) was used to give the product **2w** (49.6 mg, 52% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.14–8.12 (m, 2H), 7.89–7.71 (m, 2H), 6.97 (t, *J* = 7.2 Hz, 1H), 4.53 (t, *J* = 6.3 Hz, 2H), 3.08 (q, *J* = 6.4 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 165.2, 152.5, 141.8, 134.6 (q, *J* = 32.7 Hz), 132.9, 130.0, 125.4 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), , 63.1, 30.1, 15.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}F_3O_3S$ 319.0610; Found 319.0610.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 3-fluorobenzoate (2x)



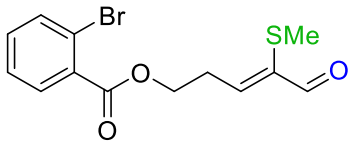
Following the general procedure, pent-4-yn-1-yl 4-fluorobenzoate **1x** (61.8 mg, 0.3 mmol) was used to give the product **2x** (52.3 mg, 65% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.08–8.03 (m, 2H), 7.16–7.10 (s, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 4.51 (t, *J* = 6.3 Hz, 2H), 3.08 (q, *J* = 6.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 165.8 (d, *J* = 254.4 Hz), 165.4, 152.9, 141.7, 132.1 (d, *J* = 9.4 Hz), 126.0 (d, *J* = 3.0 Hz), 115.6 (d, *J* = 22.0 Hz), 62.7, 30.2, 15.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.1. HRMS (ESI) m/z: $[M + K]^+$ Calcd for $C_{13}H_{13}FO_3SK$ 307.0201; Found 307.0202.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 2-acetoxybenzoate (2y)



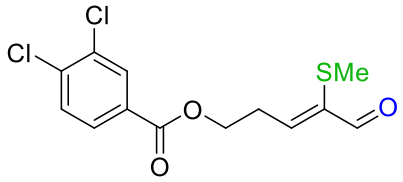
Following the general procedure, pent-4-yn-1-yl 2-acetoxybenzoate **1y** (73.8mg, 0.3 mmol) was used to give the product **2y** (61.9 mg, 67% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.98 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.58–7.54 (m, 1H), 7.32–7.28 (m, 1H), 7.09 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.94 (t, *J* = 7.1 Hz, 1H), 4.43 (t, *J* = 6.3 Hz, 2H), 3.02 (dd, *J* = 13.3, 6.5 Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 169.5, 164.1, 152.9, 150.7, 141.5, 134.1, 131.5, 126.0, 123.7, 122.7, 62.6, 30.0, 21.0, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}O_5S$ 309.0791; Found 309.0785.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 2-bromobenzoate (2z)



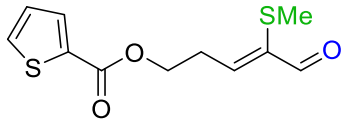
Following the general procedure, pent-4-yn-1-yl 2-bromobenzoate **1z** (79.5 mg, 0.3 mmol) was used to give the product **2z** (53.9 mg, 55% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.76 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.38–7.30 (m, 2H), 7.00 (t, *J* = 7.1 Hz, 1H), 4.51 (t, *J* = 6.2 Hz, 2H), 3.06 (d, *J* = 6.4 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 165.9, 153.2, 141.5, 134.3, 132.7, 131.7, 131.3, 127.2, 121.6, 63.2, 30.0, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}BrO_3S$ 328.9842; Found 328.9841.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 2,4,6-trichlorobenzoate (2aa)



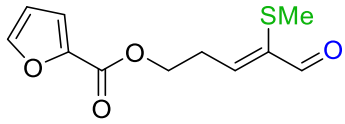
Following the general procedure, pent-4-yn-1-yl 2,4,6-trichlorobenzoate **1aa** (86.7 mg, 0.3 mmol) was used to give the product **2aa** (56.9 mg, 54% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.10 (d, *J* = 2.0 Hz, 1H), 7.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 4.51 (t, *J* = 6.3 Hz, 2H), 3.08 (q, *J* =6.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 164.5, 152.3, 141.8, 137.8, 132.9, 131.4, 130.5, 129.5, 128.6, 63.2, 30.0, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}Cl_2O_3S$ 318.9957; Found 318.9946.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl thiophene-2-carboxylate (2ab)



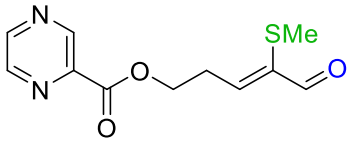
Following the general procedure, pent-4-yn-1-yl thiophene-2-carboxylate **1ab** (58.2 mg, 0.3 mmol) was used to give the product **2ab** (53.8 mg, Z:E > 20:1, 70% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.79 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.56 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.09 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 4.46 (t, *J* = 6.3 Hz, 2H), 3.04 (q, *J* = 6.4 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 161.9, 153.1, 141.6, 133.7, 133.1, 132.7, 127.8, 62.7, 30.2, 15.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{12}O_3S_2Na$ 279.0120; Found 279.0121.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl furan-2-carboxylate (2ac)



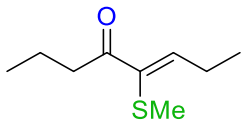
Following the general procedure, pent-4-yn-1-yl furan-2-carboxylate **1ac** (53.4 mg, 0.3 mmol) was used to give the product **2ac** (40.3 mg, 56% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.57–7.56 (m, 1H), 7.17 (d, *J* = 2.8 Hz, 1H), 6.95 (t, *J* = 7.1 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.46 (t, *J* = 6.3 Hz, 2H), 3.03 (q, *J* = 6.4 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 158.4, 152.9, 146.5, 144.1, 141.6, 118.3, 111.9, 62.4, 30.1, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}O_4S$ 241.0529; Found 241.0529.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl pyrazine-2-carboxylate (2ad)



Following the general procedure, pent-4-yn-1-yl pyrazine-2-carboxylate **1ad** (57.0 mg, 0.3 mmol) was used to give the product **2ad** (45.4 mg, 60% yield) as a yellow oil, R_f = 0.2 (10% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 9.27 (d, *J* = 1.4 Hz, 1H), 8.75 (d, *J* = 2.4 Hz, 1H), 8.71–8.69 (m, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 4.60 (t, *J* = 6.4 Hz, 2H), 3.09 (q, *J* = 6.4 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 163.7, 152.0, 147.8, 146.2, 144.4, 142.9, 141.8, 63.7, 29.9, 15.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2O_3S$ 253.0641; Found 253.0637.

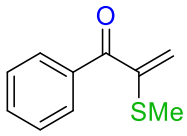
(Z)-5-(Methylthio)oct-5-en-4-one (2ae)



Following the general procedure, oct-4-yne **1ae** (33.0 mg, 0.3 mmol) was used to give the product **2ae** (42.8 mg, 83% yield) as a yellow oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (t, *J* = 7.2 Hz, 1H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.52–2.44 (m, 2H), 2.17 (s, 3H), 1.69–1.60 (m,

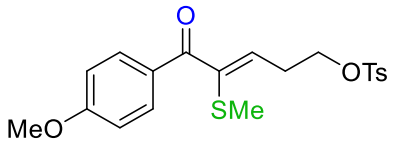
2H), 1.08 (t, *J* = 7.6 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 148.9, 137.9, 40.9, 24.0, 18.2, 17.2, 13.8, 13.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{17}OS$ 173.0995; Found 173.0990.

2-(Methylthio)-1-phenylprop-2-en-1-one (2af)



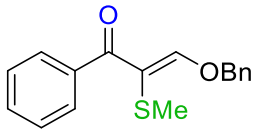
Following the general procedure, prop-1-yn-1-ylbenzene **1af** (34.8 mg, 0.3 mmol) was used to give the product **2af** (29.9 mg, 56% yield) as a yellow oil, R_f = 0.2 (2% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.83 (s, 1H), 5.63 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 146.7, 136.5, 132.7, 129.6, 128.3, 118.6, 14.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}OS$ 179.0525; Found 179.0524.

(Z)-4-(Methylthio)-5-oxo-5-phenylpent-3-en-1-yl 4-methylbenzenesulfonate (2ag)



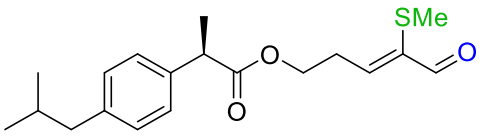
Following the general procedure, 5-phenylpent-4-yn-1-yl 4-methylbenzenesulfonate **1ag** (94.2 mg, 0.3 mmol) was used to give the product **2ag** (49.6 mg, 44% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2H), 7.73–7.71 (m, 2H), 7.33–7.31 (m, 2H), 6.94–6.92 (m, 2H), 5.69 (t, *J* = 7.6 Hz, 1H), 3.98 (t, *J* = 6.4 Hz, 2H), 3.88 (s, 3H), 2.44 (s, 3H), 2.33 (q, *J* = 6.4 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 164.4, 144.8, 138.2, 132.8, 132.2, 129.8, 128.1, 127.8, 123.8, 114.0, 69.1, 55.6, 29.7, 21.6, 15.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}O_5S_2Na$ 429.0801; Found 429.0799.

(Z)-3-(Benzyloxy)-2-(methylthio)-1-phenylprop-2-en-1-one (2ah)



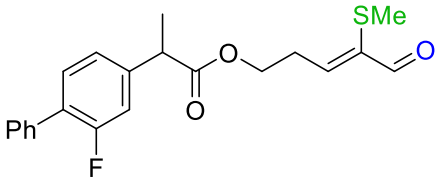
Following the general procedure, (3-(benzyloxy)prop-1-yn-1-yl)benzene **1ah** (66.6 mg, 0.3 mmol) was used to give the product **2ah** (42.6 mg, Z:E = 10:1, 50% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (m, 2H), 7.52–7.48 (m, 1H), 7.40–7.32 (m, 8H), 5.12 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1, 163.5, 138.9, 135.2, 131.5, 128.9, 128.8 (2C), 128.1, 127.7, 116.3, 76.5, 16.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_2S$ 285.0944; Found 285.0943.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl (R)-2-(4-isobutylphenyl)propanoate (2ai)



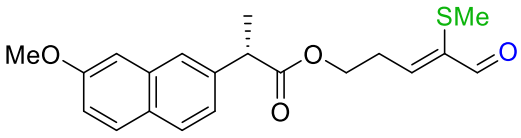
Following the general procedure, pent-4-yn-1-yl (R)-2-(4-isobutylphenyl)propanoate **1ai** (81.6 mg, 0.3 mmol) was used to give the product **2ai** (57.1 mg, 57% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.19–7.17 (m, 2H), 7.09–7.07 (m, 2H), 6.68 (t, *J* = 7.1 Hz, 1H), 4.29–4.18 (m, 2H), 3.69 (q, *J* = 7.1 Hz, 1H), 2.89–2.83 (m, 2H), 2.43 (d, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 1.88–1.78 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 174.5, 153.5, 141.2, 140.7, 137.4, 129.3, 127.1, 62.2, 45.0, 44.9, 30.1, 30.0, 22.3, 18.2, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{27}O_3S$ 335.1675; Found 335.1665.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (2aj)



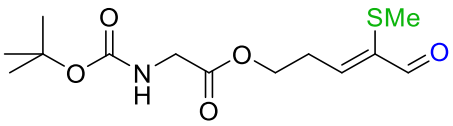
Following the general procedure, pent-4-yn-1-yl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate **1aj** (93.0 mg, 0.3 mmol) was used to give the product **2aj** (50.2 mg, 45% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.54–7.52 (m, 2H), 7.46–7.34 (m, 4H), 7.15–7.09 (m, 2H), 6.77 (t, *J* = 7.1 Hz, 1H), 4.28 (t, *J* = 6.3 Hz, 2H), 3.76 (q, *J* = 7.1 Hz, 1H), 2.94–2.88 (m, 2H), 2.29 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 173.8, 159.6 (d, *J* = 248.5 Hz), 152.9, 141.5, 141.4 (d, *J* = 7.7 Hz), 135.2, 130.8 (d, *J* = 3.9 Hz), 128.9 (d, *J* = 2.9 Hz), 128.4, 127.91 (d, *J* = 13.5 Hz), 127.7, 123.5 (d, *J* = 3.4 Hz), 115.2 (d, *J* = 23.7 Hz), 62.5, 44.9, 30.0, 18.2, 15.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}FO_3S$ 373.1268; Found 373.1273.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl (S)-2-(7-methoxynaphthalen-2-yl)propanoate (2ak)



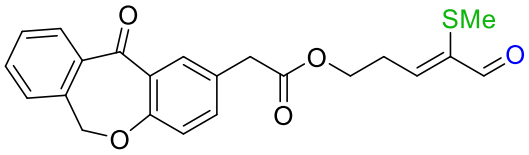
Following the general procedure, pent-4-yn-1-yl (S)-2-(7-methoxynaphthalen-2-yl)propanoate **1ak** (88.8 mg, 0.3 mmol) was used to give the product **2ak** (67.7 mg, 63% yield) as a yellow oil, R_f = 0.2 (4% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.69– 7.65 (m, 3H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.16–7.10 (m, 2H), 6.62 (t, *J* = 7.1 Hz, 1H), 4.29–4.19 (m, 2H), 3.91 (s, 3H), 3.85 (q, *J* = 7.1 Hz, 1H), 2.87–2.81 (m, 2H), 2.22 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 174.4, 157.6, 153.3, 141.2, 135.3, 133.6, 129.1, 128.8, 127.1, 126.0, 125.9, 119.1, 105.5, 62.3, 55.3, 45.3, 30.0, 18.1, 15.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O_4S$ 359.1312; Found 359.1306

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl (tert-butoxycarbonyl)glycinate (2al)



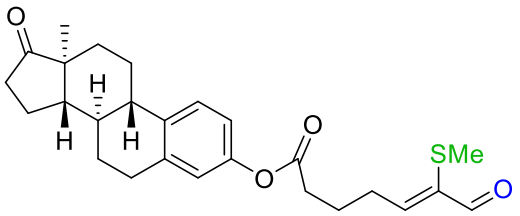
Following the general procedure, pent-4-yn-1-yl (tert-butoxycarbonyl)glycinate **1al** (72.3 mg, 0.3 mmol) was used to give the product **2al** (50.0 mg, 55% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 6.88 (t, *J* = 7.1 Hz, 1H), 5.02 (br, 1H), 4.32 (t, *J* = 6.3 Hz, 2H), 3.91 (d, *J* = 5.6 Hz, 2H), 2.93 (q, *J* = 6.5 Hz, 2H), 2.32 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 170.3, 155.6, 152.5, 141.7, 80.1, 62.9, 42.3, 29.9, 28.2, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{24}NO_5S$ 318.1370; Found 318.1369.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (2am)



Following the general procedure, pent-4-yn-1-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate **1am** (100.2 mg, 0.3 mmol) was used to give the product **2a**m(54.6 mg, 46% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, *d*^{6}-DMSO) δ 9.41 (s, 1H), 7.98 (d, *J* = 2.2 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 1H), 7.68–7.64 (m, 1H), 7.57–7.51 (m, 2H), 7.47 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.12 (t, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 5.28 (s, 2H), 4.25 (t, *J* = 6.2 Hz, 2H), 3.73 (s, 2H), 2.85 (dd, *J* = 13.1, 6.4 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, *d*^{6}-DMSO) δ 191.2, 190.1, 171.1, 159.9, 155.1, 140.1, 139.9, 136.9, 135.9, 133.1, 131.8, 129.2, 128.8, 128.3, 128.0, 124.5, 120.7, 72.7, 62.3, 40.1, 29.9, 15.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}O_5S$ 397.1104; Found 397.1104.

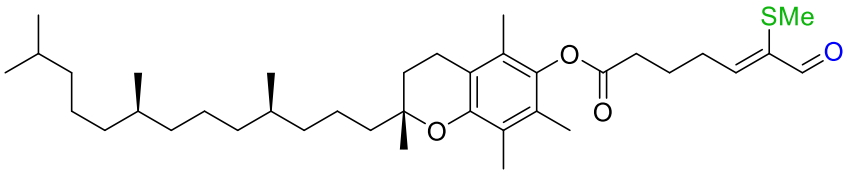
(8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (Z)-6-(methylthio)-7-oxohept-5-enoate (2an)



Following the general procedure, (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl hept-6-ynoate **1an** (113.4 mg, 0.3 mmol) was used to give the product **2an** (42.2 mg, 32% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.85–6.79 (m, 2H), 2.90–2.88 (m, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.61 (t, *J* = 7.3 Hz, 2H), 2.53–2.46 (m, 1H), 2.42–2.36 (m, 1H), 2.32 (s, 3H), 2.16–1.92 (m, 7H), 1.65–1.43 (m, 6H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.7, 190.6, 171.7, 157.1, 148.3, 140.3, 138.0, 137.4, 126.4, 121.4, 118.6, 50.3, 47.8,

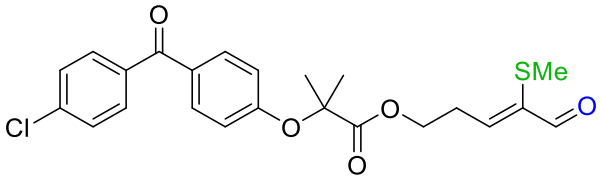
44.0, 37.9, 35.8, 33.5, 31.4, 29.7, 29.3, 26.2, 25.6, 23.4, 21.5, 15.7, 13.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{33}O_4S$ 441.2094; Found 441.2091.

(R)-2,5,7,8-Tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl (Z)-6-(methylthio)-7-oxohept-5-enoate (2ao)



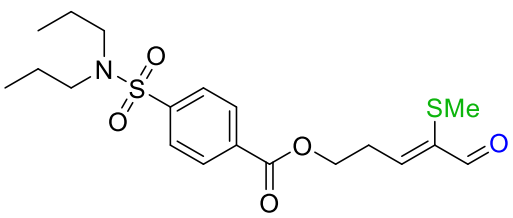
Following the general procedure, (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl hept-6-ynoate **1ao** (161.4 mg, Z:E > 20:1, 0.3 mmol) was used to give the product **2ao** (81.0 mg, 45% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 2.78–2.66 (m, 4H), 2.59 (t, *J* = 6.7 Hz, 2H), 2.34 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.82–1.76 (m, 2H), 1.56–1.49 (m, 4H), 1.43–1.24 (m, 12H), 1.21–1.03 (m, 7H), 0.88–0.84 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 171.5, 157.2, 149.4, 140.3, 126.5, 124.7, 123.0, 117.3, 75.0, 39.3, 37.4 (2C), 37.2, 33.4, 32.7, 32.6, 30.0, 27.9, 24.7, 24.4, 23.6, 22.7, 22.6, 20.9, 20.5, 19.7, 19.6, 15.7, 13.0, 12.1, 11.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{61}O_4S$ 601.4285; Found 601.4293.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (2ap)



Following the general procedure, pent-4-yn-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate **1ap** (115.2 mg, 0.3 mmol) was used to give the product **2ap** (70.0 mg, Z:E = 15:1, 53% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.73–7.67 (m, 4H), 7.45–7.42 (m, 2H), 6.83–6.80 (m, 2H), 6.61 (t, *J* = 7.1 Hz, 1H), 4.32 (t, *J* = 6.3 Hz, 2H), 2.87 (dd, *J* = 13.3, 6.3 Hz, 2H), 2.27 (s, 3H), 1.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 190.1, 173.6, 159.4, 152.1, 141.5, 138.3, 136.2, 132.0, 131.1, 130.3, 128.5, 116.9, 79.2, 63.3, 29.7, 25.3, 15.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{23}ClO_5SNa$ 469.0847; Found 469.0855.

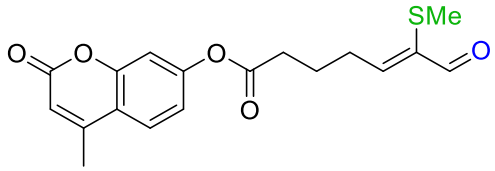
(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (2aq)



Following the general procedure, pent-4-yn-1-yl 4-(N,N-dipropylsulfamoyl)benzoate **1aq** (105.3

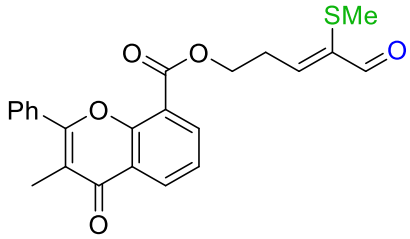
mg, 0.3 mmol) was used to give the product **2aq** (59.4 mg, 48% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, *d*^{6}-DMSO) δ 9.47 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 7.1 Hz, 1H), 4.50 (t, *J* = 6.1 Hz, 2H), 3.06–2.99 (m, 6H), 2.22 (s, 3H), 1.50–1.40 (m, 4H), 0.79 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, *d*^{6}-DMSO) δ 191.5, 164.7, 155.0, 143.7, 140.4, 133.0, 130.3, 127.3, 63.5, 49.6, 30.0, 21.6, 15.2, 11.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{19}H_{28}NO_5S_2$ 414.1403; Found 414.1402.

4-Methyl-2-oxo-2H-chromen-7-yl (Z)-6-(methylthio)-7-oxohept-5-enoate (2ar)



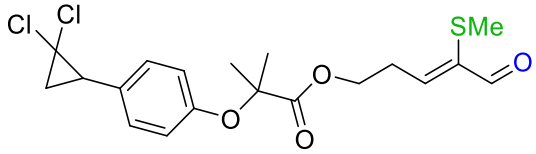
Following the general procedure, 4-methyl-2-oxo-2H-chromen-7-yl hept-6-ynoate **1ar** (85.2 mg, 0.3 mmol) was used to give the product **2ar** (60.2 mg, 58% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.15–7.10 (m, 1H), 7.06 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.26 (d, *J* = 1.0 Hz, 1H), 2.76–2.65 (m, 5H), 2.42 (d, *J* = 1.1 Hz, 3H), 2.32 (s, 3H), 2.03–1.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 170.7, 160.4, 156.7, 154.1, 152.8, 151.9, 140.5, 125.4, 117.9, 117.8, 114.5, 110.3, 33.4, 29.6, 23.2, 18.7, 15.7. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{18}H_{19}O_5S$ 347.0948; Found 347.0947.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 3-methyl-4-oxo-2-phenyl-4H-chromene-8-carboxylate (2as)



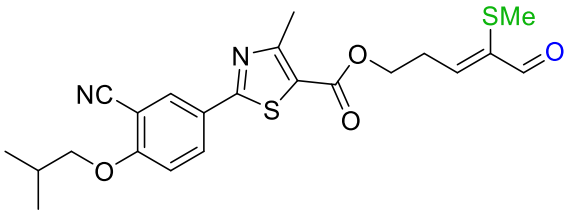
Following the general procedure, pent-4-yn-1-yl 3-methyl-4-oxo-2-phenyl-4H-chromene-8-carboxylate **1at** (103.8 mg, 0.3 mmol) was used to give the product **2as** (45.3 mg, 37% yield) as a yellow oil, R_f = 0.2 (20 % EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.47 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.26 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.77–7.74 (m, 2H), 7.55–7.50 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 1H), 6.79 (t, *J* = 7.1 Hz, 1H), 4.52 (t, *J* = 6.3 Hz, 2H), 3.01 (q, *J* = 6.5 Hz, 2H), 2.27 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 178.1, 164.2, 160.9, 154.4, 152.6, 141.4, 136.3, 132.9, 131.1, 130.6, 129.2, 128.5, 124.0, 123.3, 120.0, 117.7, 63.1, 30.0, 15.6, 11.7. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{23}H_{20}O_5SNa$ 431.0924; Found 431.0924.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (2at)



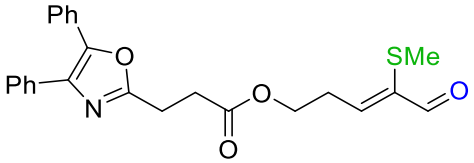
Following the general procedure, pent-4-yn-1-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate **1at** (106.2 mg, 0.3 mmol) was used to give the product **2at** (36.2 mg, 29% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.11–7.09 (m, 2H), 6.79–6.76 (m, 2H), 6.57 (t, *J* = 7.0 Hz, 1H), 4.30 (t, *J* = 6.2 Hz, 2H), 2.89–2.79 (m, 3H), 2.28 (s, 3H), 1.94 (t, *J* = 7.6 Hz, 1H), 1.76 (dd, *J* = 8.2, 7.6 Hz, 1H), 1.61 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 174.1, 154.9, 152.8, 141.3, 129.7, 128.0, 117.9, 78.9, 63.1, 60.8, 34.7, 29.8, 25.8, 25.4, 25.4, 15.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}Cl_2O_4SNa$ 439.0508; Found 439.0510.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (2au)



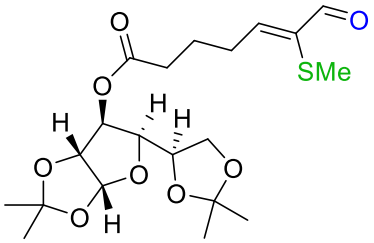
Following the general procedure, pent-4-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate **1au** (114.6 mg, 0.3 mmol) was used to give the product **2au** (61.2 mg, Z:E = 10:1，48% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.14–8.13 (m, 1H), 8.06–8.03 (m, 1H), 7.00–6.93 (m, 2H), 4.46 (t, *J* = 6.3 Hz, 2H), 3.88 (d, *J* = 6.5 Hz, 2H), 3.04 (t, *J* = 6.4 Hz, 2H), 2.73 (s, 3H), 2.32 (s, 3H), 2.24 – 2.13 (m, 1H), 1.07 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 167.4, 162.4, 161.7, 161.6, 152.6, 141.7, 132.5, 132.0, 125.7, 121.0, 115.3, 112.5, 102.8, 75.6, 62.8, 30.1, 28.0, 19.0, 17.5, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}N_2O_4S_2$ 445.1250; Found 445.1251.

(Z)-4-(Methylthio)-5-oxopent-3-en-1-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (2av)



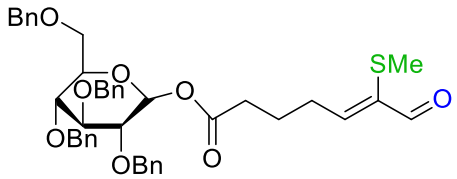
Following the general procedure, pent-4-yn-1-yl 3-(4,5-diphenyloxazol-2-yl)propanoate **1av** (107.7 mg, 0.3 mmol) was used to give the product **2av** (66.9 mg, Z:E > 20:1, 53% yield) as a yellow oil, R_f = 0.2 (10% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.62–7.60 (m, 2H), 7.57–7.54 (m, 2H), 7.37–7.30 (m, 6H), 6.87 (t, *J* = 7.1 Hz, 1H), 4.29 (t, *J* = 6.3 Hz, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.94–2.89 (m, 4H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 171.8, 161.5, 153.1, 145.3, 141.4, 135.0, 132.2, 128.8, 128.6, 128.5, 128.4, 128.0, 127.7, 126.3, 62.4, 30.9, 30.0, 23.3, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}NO_4S$ 422.1421; Found 422.1421.

(3aR,5R,6S,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (Z)-6-(methylthio)-7-oxohept-5-enoate (2aw)



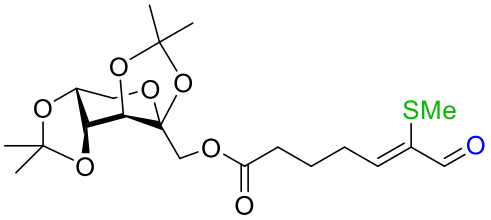
Following the general procedure, (3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl hept-6-ynoate **1aw** (110.4 mg, 0.3 mmol) was used to give the product **2aw** (74.8 mg, 58% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 5.85 (d, *J* = 3.7 Hz, 1H), 5.24 (d, *J* = 2.1 Hz, 1H), 4.46 (d, *J* = 3.7 Hz, 1H), 4.18–4.14 (m, 2H), 4.07–3.97 (m, 2H), 2.65–2.59 (m, 2H), 2.42–2.42 (m, 2H), 2.28 (s, 3H), 1.89–1.80 (m, 2H), 1.49 (s, 3H), 1.37 (s, 3H), 1.27 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 171.4, 156.8, 140.2, 112.2, 109.3, 104.9, 83.2, 79.7, 76.1, 72.3, 67.2, 33.4, 29.7, 26.8, 26.6, 26.1, 25.2, 23.3, 15.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{31}O_8S$ 431.1734; Found 431.1725.

(2R,3S,4R,5S,6S)-3,4,5-Tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl (Z)-6-(methylthio)-7-oxohept-5-enoate (2ax)



Following the general procedure, (2R,3S,4R,5S,6S)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl hept-6-ynoate **1ax** (194.4 mg, 0.3 mmol) was used to give the product **2ax** (59.6 mg, 28% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.35–7.26 (m, 18H), 7.16–7.13 (m, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 3.5 Hz, 1H), 4.98–4.95 (m, 1H), 4.86–4.82 (m, 2H), 4.72–4.60 (m, 3H), 4.52–4.48 (m, 2H), 3.96–3.86 (m, 2H), 3.77–3.64 (m, 4H), 2.66–2.60 (m, 2H), 2.48–2.44 (m, 2H), 2.29 (s, 3H), 1.91–1.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 171.3, 157.2, 140.2, 138.5, 137.9, 137.7, 137.5, 128.4 (3C), 128.1, 128.0, 127.9 (2C), 127.8 (2C), 127.7, 127.6, 90.1, 81.6, 78.8, 76.8, 75.6, 75.3, 73.5, 73.2, 72.9, 68.0, 33.6, 29.7, 23.4, 15.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{47}O_8S$ 711.2986; Found 711.2915.

((3aS,5aR,8aR,8bS)-2,2,7,7-Tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl (Z)-6-(methylthio)-7-oxohept-5-enoate (2ay)



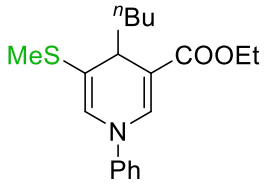
Following the general procedure, ((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl hept-6-ynoate **1ay** (110.4 mg, 0.3 mmol) was

used to give the product **2ay** (83.8 mg, Z:E > 20:1, 65% yield) as a yellow oil, R_f = 0.2 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 6.85 (t, *J* = 7.3 Hz, 1H), 4.56 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.24 (d, *J* = 2.5 Hz, 1H), 4.19 (d, *J* = 7.9 Hz, 1H), 4.00 (d, *J* = 11.7 Hz, 1H), 3.85 (dd, *J* = 13.0, 1.6 Hz, 1H), 3.71 (d, *J* = 13.0 Hz, 1H), 2.60 (q, *J* = 7.4 Hz, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.26 (s, 3H), 1.83 (q, *J* = 7.5 Hz, 2H), 1.49 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 172.0, 157.2, 140.1, 109.0, 108.6, 101.3, 70.6, 70.4, 69.9, 65.3, 61.1, 33.2, 29.7, 26.3, 25.8, 25.1, 23.9, 23.2, 15.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{30}O_8SNa$ 453.1554; Found 453.1550.

Procedure for synthesis of 2a on 6 mmol scale:

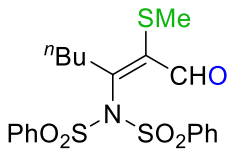
Under a nitrogen atmosphere, a 250 mL Schlenk-type tube equipped with a magnetic stir bar was charged with DMTSM (2.33 g, 9.0 mmol, 1.5 equiv), the corresponding hept-1-yne (576 mg, 6.0 mmol, 1.0 equiv) and dichloromethane (40.0 mL) and dimethyl sulfoxide (40.0 mL) at 0 ºC (ice bath). The reaction mixture was then warmed to ambient temperature (23 °C) and stirred for 12 h, before being quenched with aqueous NaCl. The mixture was extracted with CH_2Cl_2 (10 mL X 3), and the combined organic layer were washed with water and brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. After purification by column chromatography on silica gel give the product **2a** (645.1 mg, 67%) as a yellow oil, R_f = 0.2 (2% EA in PE).

Ethyl 4-butyl-5-(methylthio)-1-phenyl-1,4-dihydropyridine-3-carboxylate (3)[12]



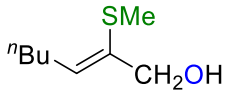
Ethyl propiolate (0.6 mmol, 58.8 mg, 2.0 equiv), **2a** (47.4 mg, 0.3 mmol, 1.0 equiv), aniline (0.36 mmol, 33.5 mg, 1.2 equiv), $Cu(OTf)_2$ (0.015 mmol, 5.4 mg, 5 mol%) and in THF (0.1 M) added to a Schlenk tube under a nitrogen atmosphere. Then the mixture was stirred at 60 °C (oil bath) under argon atmosphere with TLC monitoring until the complete consumption of **2a.** The resulting reaction mixture was cooled to ambient temperature and then quenched with aqueous saturated NH_4Cl, the organic layer was then extracted with EtOAc (5 mL X 3), washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated in vacuum to give the crude product. After purification by column chromatography on silica gel give the product **3** (51.6 mg, 52%) as a yellow oil, R_f = 0.4 (9% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 1.1 Hz, 1H), 7.40–7.36 (m, 2H), 7.19–7.15 (m, 3H), 6.46 (d, *J* = 1.1 Hz, 1H), 4.28–4.14 (m, 2H), 3.68 (t, *J* = 4.4 Hz, 1H), 2.28 (s, 3H), 1.67–1.55 (m, 2H), 1.31–1.27 (m, 7H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 143.5, 137.1, 129.6, 124.9, 124.5, 119.6, 118.0, 103.9, 59.8, 36.4, 34.2, 26.7, 22.9, 16.0, 14.4, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{26}NO_2S$ 332.1679; Found 332.1686

(E)-N-(2-(Methylthio)-1-oxohept-2-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (4)[13]



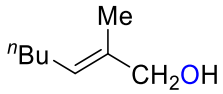
To a solution of **2a** (47.4 mg, 0.3 mmol, 1.0 equiv) in EtOAc (0.1 M) was added N-fluorobis(benzenesulfonyl)imide (113.4 mg, 0.36 mmol, 1.2 equiv) in seal tube under a nitrogen atmosphere and heated at 80 °C with an oil bath for the 12 h. The resulting reaction mixture was cooled to ambient temperature and then quenched with aqueous saturated NH_4Cl, the organic layer was then extracted with EtOAc (5 mL X 3), washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated in vacuum to give the crude product. After purification by column chromatography on silica gel give the product **4** (76.1 mg, 56%) as a yellow solid, R_f = 0.4 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.05–8.03 (m, 4H), 7.74–7.79 (,, 2H), 7.61–7.57 (m, 4H), 2.64–2.60 (m, 2H), 2.29 (s, 3H), 1.62–1.54 (m, 2H), 1.31–1.22 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.6, 151.7, 144.7, 137.9, 134.8, 129.3, 129.0, 38.2, 29.6, 23.0, 16.4, 13.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}NO_5S_3$ 453.0859; Found 453.0861.

(Z)-2-(Methylthio)hept-2-en-1-ol(Z)-2-(methylthio)hept-2-en-1-ol (S-5)[14]



A solution of **2a** (47.4 mg, 0.3 mmol, 1.0 equiv) in MeOH (0.1 M) was added $NaBH_4$ (22.2 mg, 0.6 mmol, 2.0 equiv) at 0 ºC (ice bath), then the reaction mixture was then warmed to ambient temperature and stirred for 12 h. The resulting reaction mixture was cooled to ambient temperature and then quenched with aqueous saturated NH_4Cl, the organic layer was then extracted with EtOAc (5 mL X 3), washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated in vacuum to give the crude product. After purification by column chromatography on silica gel give the product **S-5** (45.6 mg, 95%) as a yellow solid, R_f = 0.4 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (t, *J* = 7.1 Hz, 1H), 4.19 (s, 2H), 2.28–2.23 (m, 5H), 1.85 (s, 1H), 1.37–1.32 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 133.5, 65.6, 31.2, 28.8, 22.3, 14.8, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_{17}OS$ 161.0995; Found 161.0995.

(E)-2-Methylhept-2-en-1-ol (5)[15]

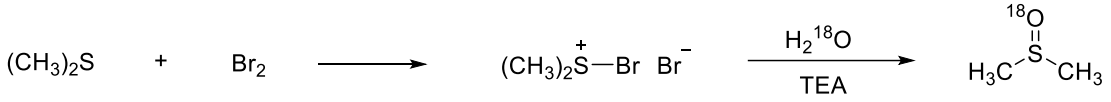


To a solution of **S-6** (48.0 mg, 0.3 mmol, 1.0 equiv) in THF (0.1 M) was successively added $Pd_2(dba)_3$ (2.75 mg, 0.03 mmol, 0.1 equiv) and CH_3MgBr (1.0 mL, 3.0 M in 2-methyl-THF, 3.0 mmol, 10.0 equiv) in seal tube under a nitrogen atmosphere and heated at 80 °C (oil bath) for the 12 h. The resulting reaction mixture was cooled to ambient temperature and then quenched with aqueous saturated NH_4Cl, the organic layer was then extracted with EtOAc (5 mL X 3), washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated in vacuum to give the crude product. After purification by column chromatography on silica gel give the product **5** (27.6 mg, 72%) as a colourless liquid, R_f = 0.4 (20% EA in PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (t, *J* = 7.2 Hz, 1H), 3.97 (s, 2H), 2.02–2.00 (m, 2H), 1.73 (br, 1H), 1.64 (s, 3H), 1.33–1.30 (m, 4H), 0.88 (t, *J*

= 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 126.5, 68.9, 31.6, 27.2, 22.3, 13.9, 13.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{16}ONa$ 151.1093 Found 151.1095.

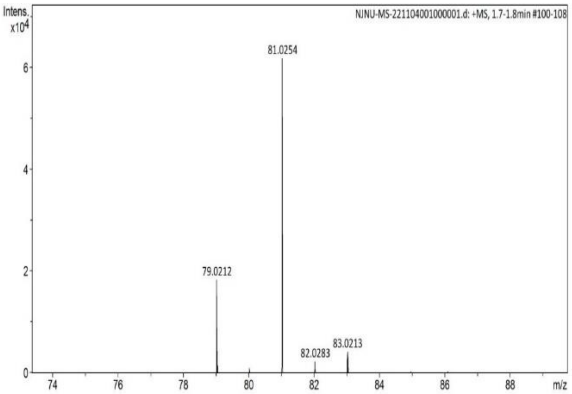
Control Experiments

Method for preparation of ^{18}O labeled DMSO[16]



Step I: Bromine (5.6 mL, 110 mmol, 1.0 equiv) was added dropwise over 40 min to a vigorously stirred, ice-cooled solution of dimethyl sulfide (9.8 mL, 110 mmol, 1.0 equiv) in carbon tetrachloride (90 mL).The resulting yellowish precipitate were removed by filtration and washed with cold chloroform. The residue was dried under reduced pressure at room temperature to give (bromodimethyl)sulfonium bromide (17.4 g, 72%) as a yellow solid.

Step II : (bromodimethyl)sulfonium bromide (2.5 g, 11.2 mmol, 1.0 equiv) was added portionwise over 15 min to a vigorously stirred solution of triethylamine (3.15 mL, 22.5 mmol, 2.0 equiv) and ^{18}O-labeled water (97 atom% ^{18}O) (0.10 mL, 5.5 mmol) in tetrahydrofuran (7.0 mL). The temperature of the reaction was maintained below 50 ℃ by occasional cooling with ice. The precipitate of triethylamine hydrobromide was removed by centrifugation and washed twice with ether. The combined yellow supernatant and washings were dried on high vacuum pressure pump at room temperature (15 mm) to remove the solvent and purification by column chromatography on silica gel give the ^{18}O-labeled DMSO as a yellow liquid, R_f = 0.4 (20% EA in PE).



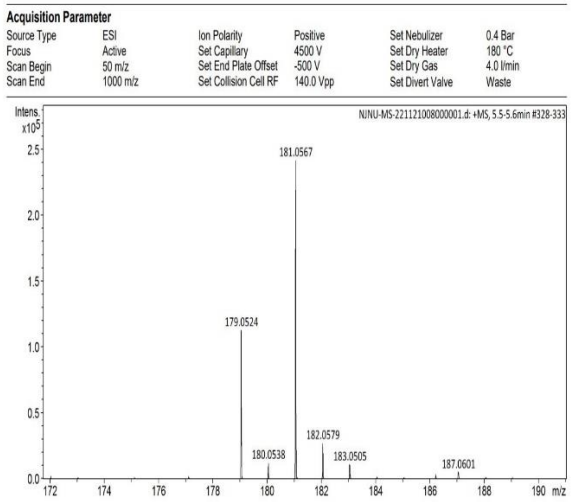
#	m/z	Res.	S/N	I	I %	FWHM
1	79.0212	10445	675.9	18335	9.6	0.0076
2	81.0254	8370	2222.1	61767	32.4	0.0097
3	83.0213	8485	146.9	4178	2.2	0.0098
4	101.0036	10505	604.4	19618	10.3	0.0096
5	103.0080	8809	1371.8	45166	23.7	0.0117
6	119.0874	11603	266.1	9494	5.0	0.0103
7	126.0138	9508	94.8	3459	1.8	0.0133
8	127.0167	11825	125.9	4609	2.4	0.0107
9	148.0137	12232	215.7	8233	4.3	0.0121
10	149.0161	8952	183.4	7012	3.7	0.0166
11	274.2747	13603	4411.0	190891	100.0	0.0202
12	275.2753	11101	622.0	26928	14.1	0.0248
13	282.2755	11994	81.8	3536	1.9	0.0235
14	284.2948	12278	103.3	4458	2.3	0.0232
15	302.3032	11050	154.5	6580	3.4	0.0274
16	318.2995	13473	3375.5	141884	74.3	0.0236
17	319.3024	12512	541.9	22733	11.9	0.0255
18	335.2409	12820	102.8	4186	2.2	0.0262
19	338.3414	12424	517.8	21011	11.0	0.0272
20	339.3446	15556	153.8	6226	3.3	0.0218
21	340.2580	14194	603.4	24394	12.8	0.0240
22	340.7584	12435	210.1	8499	4.5	0.0274
23	362.3281	11713	807.0	31438	16.5	0.0309
24	363.3286	12968	193.2	7510	3.9	0.0280
25	384.3092	13089	114.7	4335	2.3	0.0294
26	406.3534	13653	237.1	8665	4.5	0.0298
27	415.2146	13589	525.3	18973	9.9	0.0306
28	416.2198	12015	135.1	4870	2.6	0.0346
29	437.1947	13430	252.2	8721	4.6	0.0326
30	453.3490	14226	104.6	3529	1.8	0.0319

HRMS (ESI^+): exact mass calculated for $[M + H^+]$ (C_2H_7OS) requires m/z 79.0212, found m/z 79.0212. Exact mass calculated for $[M + H]$ ($C_2H_7{}^{18}OS$) requires m/z 81.0225, found m/z 81.0254. The ^{18}O content was determined by HRMS at 77%.

Procedure for preparation of ^{18}O-2af

Under a nitrogen atmosphere, a 25 mL Schlenk-type tube equipped with a magnetic stir bar was charged with DMTSM (0.45 mmol, 115.0 mg, 1.5 equiv), the corresponding alkynes (0.3 mmol, 1.0 equiv) and dichloromethane (2 mL) and ^{18}O-dimethyl sulfoxide (2 mL) at 0 ºC (ice bath). The reaction mixture was then warmed to ambient temperature (23 °C) and stirred for 12 h, before being quenched with aqueous NaCl. The mixture was extracted with CH_2Cl_2 (5 mL X 3), and the combined

organic layer were washed with water and brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. After purification by column chromatography on silica gel give the product **^{18}O-2af** (24.5 mg, 46%) as a yellow liquid, R_f = 0.4 (20% EA in PE).

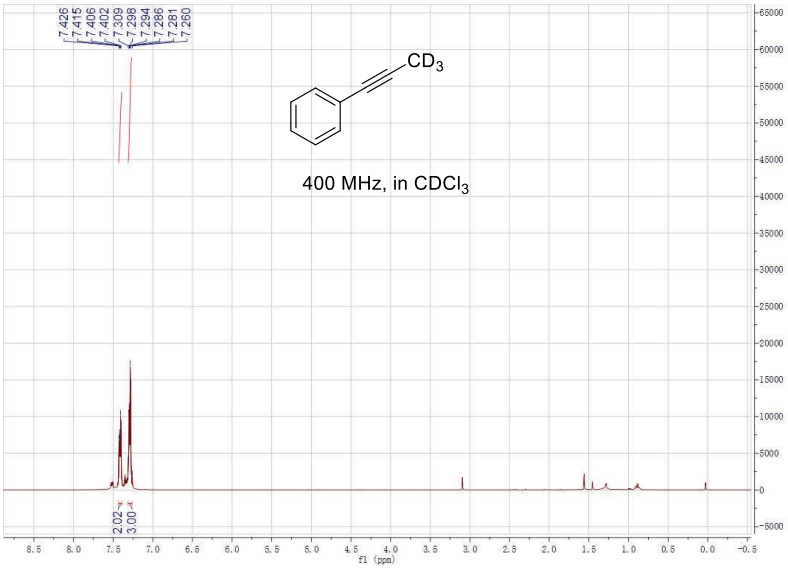


#	m/z	Res.	S/N	I	I %	FWHM
1	151.0568	8634	635.7	29063	12.0	0.0175
2	179.0524	10916	2136.2	112540	46.6	0.0164
3	180.0538	9301	227.9	12079	5.0	0.0194
4	181.0567	11086	4523.2	241441	100.0	0.0163
5	182.0579	10871	504.8	27116	11.2	0.0167
6	183.0505	9107	203.3	10958	4.5	0.0201
7	201.0318	12476	662.0	38997	16.2	0.0161
8	203.0377	10179	1190.3	70749	29.3	0.0199
9	205.0666	9668	262.7	15773	6.5	0.0212
10	207.0702	9883	445.3	26989	11.2	0.0210
11	221.0471	11705	213.8	13840	5.7	0.0189
12	274.2735	11672	904.2	64982	26.9	0.0235
13	282.2778	14481	212.0	15258	6.3	0.0195
14	283.1000	12071	200.6	14448	6.0	0.0235
15	284.2958	10786	294.4	21157	8.8	0.0264
16	302.3047	11343	166.3	11825	4.9	0.0267
17	309.0949	10014	162.9	11480	4.8	0.0309
18	311.0983	11636	731.0	51306	21.2	0.0267
19	312.3278	10748	158.0	11077	4.6	0.0291
20	313.1025	12543	893.2	62582	25.9	0.0250
21	318.2991	12185	319.0	22117	9.2	0.0261
22	331.2836	12361	164.5	11099	4.6	0.0268
23	338.3434	13117	382.7	25368	10.5	0.0258
24	340.2592	13292	293.0	19354	8.0	0.0256
25	357.0992	11605	258.3	16183	6.7	0.0308
26	359.1040	11353	823.0	51235	21.2	0.0316
27	360.1040	12520	234.2	14518	6.0	0.0288
28	361.1074	13719	1190.3	73587	30.5	0.0263
29	362.1116	11653	224.9	13880	5.7	0.0311
30	383.0927	11190	188.1	10913	4.5	0.0342

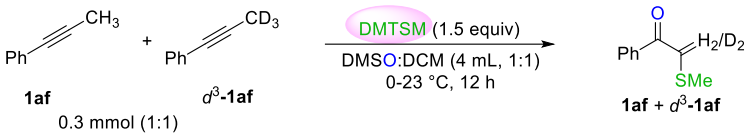
HRMS (ESI$^+$): exact mass calculated for $[M + H^+]$ ($C_{10}H_{11}OS$) requires m/z 179.0525, found m/z 179.0524. Exact mass calculated for $[M + H^+]$ ($C_{10}H_{11}{}^{18}OS$) requires m/z 181.0568, found m/z 181.0567. The **^{18}O-2af** was determined by HRMS at $\frac{241441}{112540+241441} = 68\%$

Method for preparation of *d*^{3}-prop-1-yn-1-ylbenzene[17]

To a flame-dried round-bottom flask under nitrogen was added phenylacetylene (0.5 mL, 4.6 mmol, 1 equiv) followed by THF (30 mL, 0.15 M). The flask was placed in an ice/water bath. n-Butyllithium (4 mL, 2.5 M in hexanes, 10 mmol, 2 equiv) was added slowly and the reaction was allowed to stir for 1 hour. *d*^{3}-iodomethane (3 mL, 9.6 mmol, 2.1 equiv) was added at -20 ºC and the reaction was allowed to stir at room temperature for 1 hour. The reaction was quenched with a saturated solution of NH_4Cl and extracted with DCM (5 mL X 3). The organic layers were combined and dried over $MgSO_4$, and the solvent removed under pressure. After purification by column chromatography on silica gel give the product ***d*^{3}-1af** (492 mg, 90%) as a yellow liquid, R_f = 0.7 (1% EA in PE).



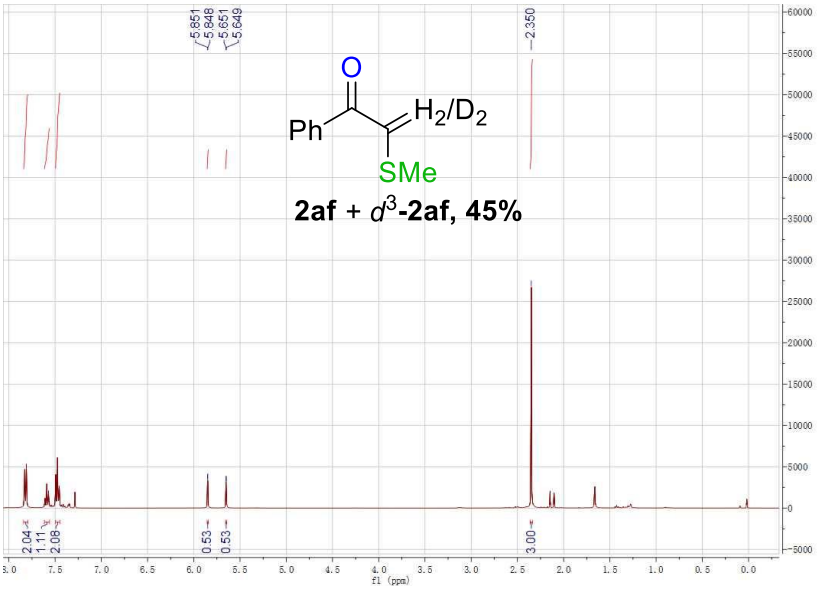
Method for KIE experience

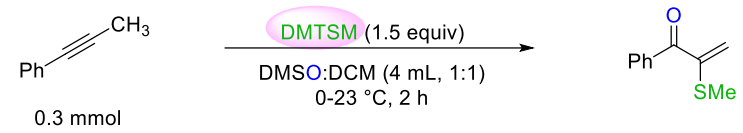


1af + ***d*³-1af**

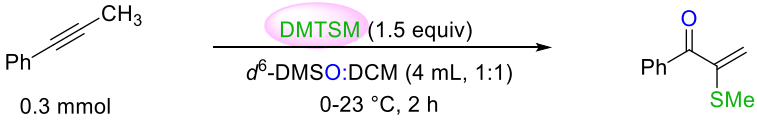
0.3 mmol (1:1)

A reaction flask (25 mL) was charged with DMTSM (115 mg, 0.45 mmol, 1.5 equiv), **1af** (17.4 mg, 0.15 mmol), ***d*³-1af** (17.8 mg, 0.15 mmol), then the DCM (2 mL) and DMSO (2 mL) was added at 0 ºC. The reaction mixture was then warmed to ambient temperature (23 ℃) and stirred for 6 h, before being quenched with aqueous NaCl. The mixture was extracted with CH_2Cl_2 (10 mL X 3), and the combined organic layer were washed with water and brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure. After purification by column chromatography on silica gel give the product **2af + *d*³-2af** (22.4 mg, 45%) as a colourless oil, R_f = 0.4 (2% EA in PE). KIE value (k_H/k_D = 1.13) was determined on the basis of ^{1}H NMR analysis.



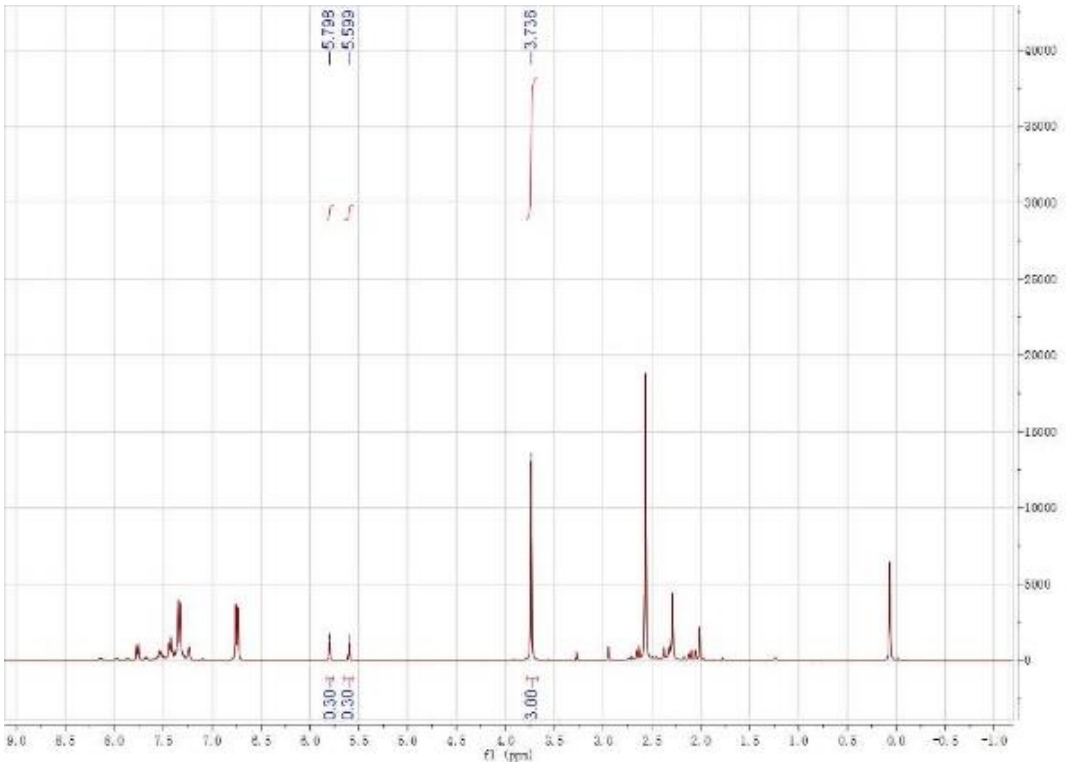


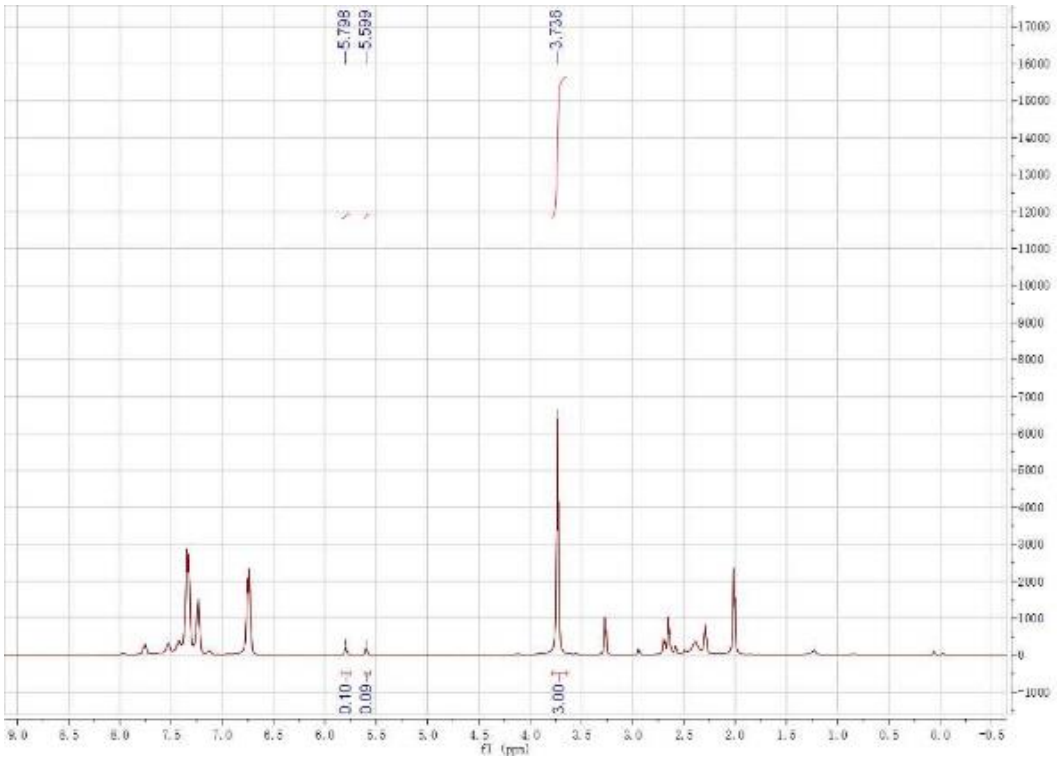
A reaction flask (25 mL) was charged with DMTSM (115 mg, 0.45 mmol, 1.5 equiv), **1af** (17.4 mg, 0.15 mmol), then the DCM (2 mL) and DMSO (2 mL) was added at 0 ºC (ice bath). The reaction mixture was then warmed to ambient temperature and stirred for 2 h, before being quenched with aqueous NaCl. The mixture was extracted with CH_2Cl_2 (10 mL X 3), and the combined organic layer were washed with water and brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure, then added anisole (0.3 mmol) into the crude reaction solution for quantitative analysis.



A reaction flask (25 mL) was charged with DMTSM (115 mg, 0.45 mmol, 1.5 equiv), **1af** (17.4 mg, 0.15 mmol), then the DCM (2 mL) and d^6-DMSO (2 mL) was added at 0 ºC. The reaction mixture was then warmed to ambient temperature and stirred for 2 h, before being quenched with aqueous NaCl. The mixture was extracted with CH_2Cl_2 (10 mL X 3), and the combined organic layer were washed with water and brine, dried over Na_2SO_4, filtrated and concentrated under reduced pressure, then added anisole (0.3 mmol) into the crude reaction solution for quantitative analysis.

KIE value (k_H/k_D = 3.0) was determined on the basis of ^{1}H NMR analysis.





4 Reference

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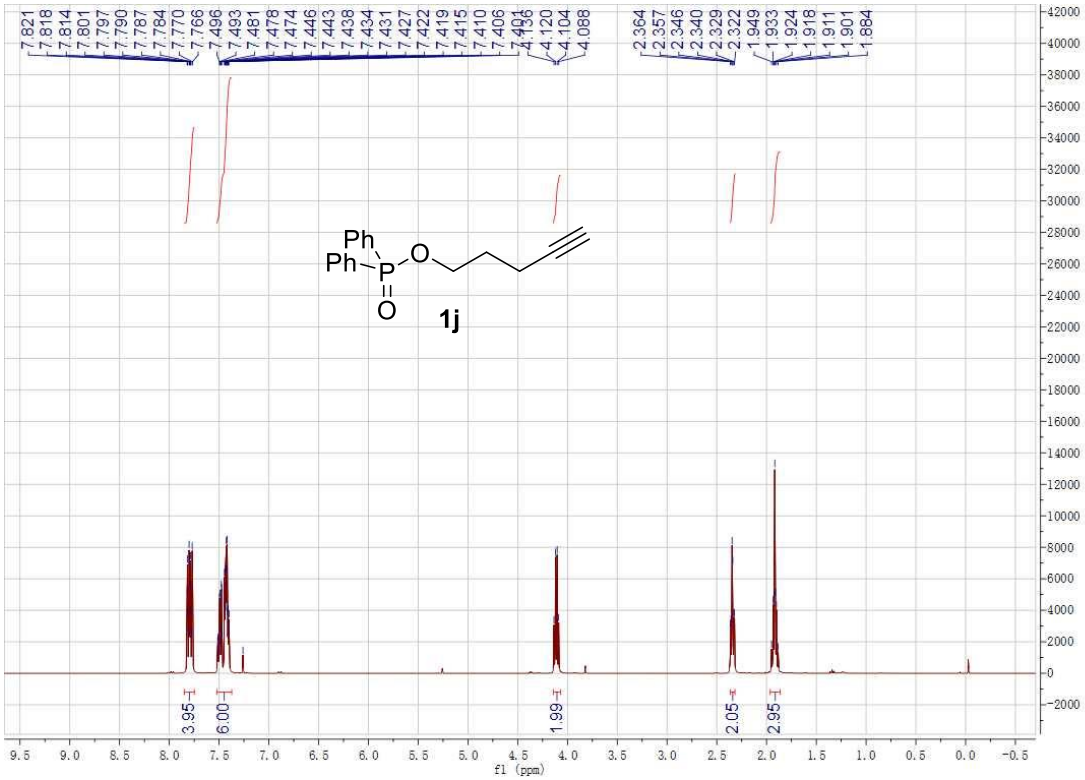
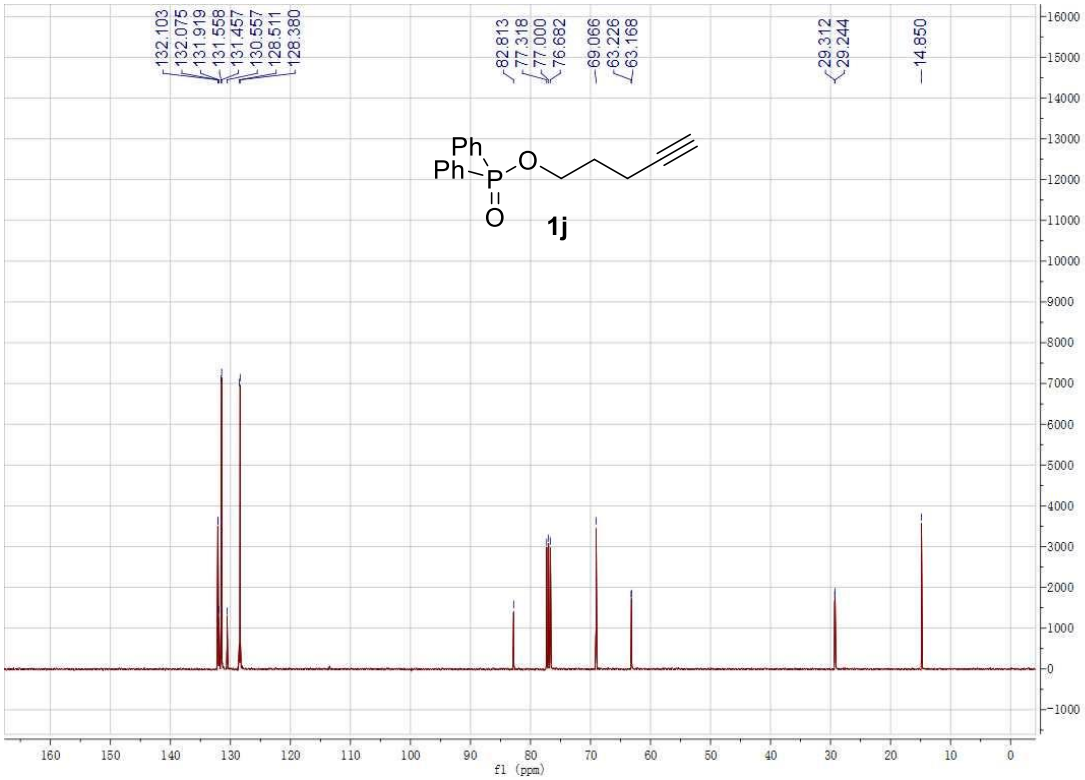
5 NMR Spectra

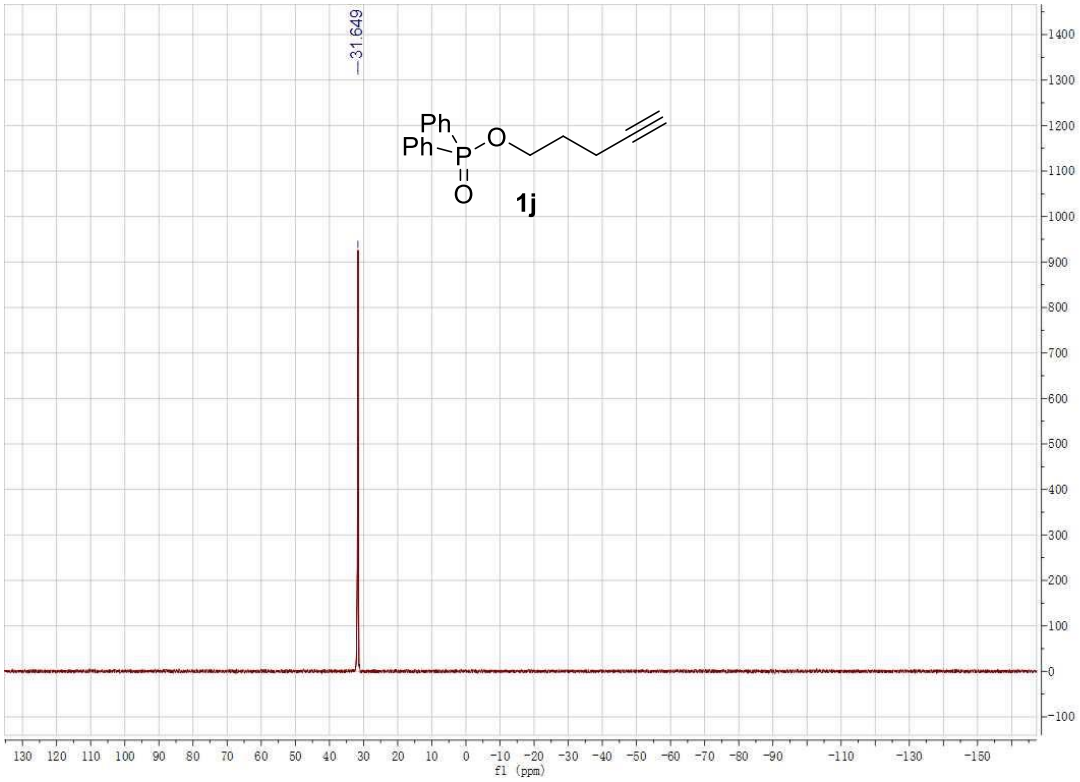
^{1}H NMR spectrum of 1j in $CDCl_3$, 400 MHz



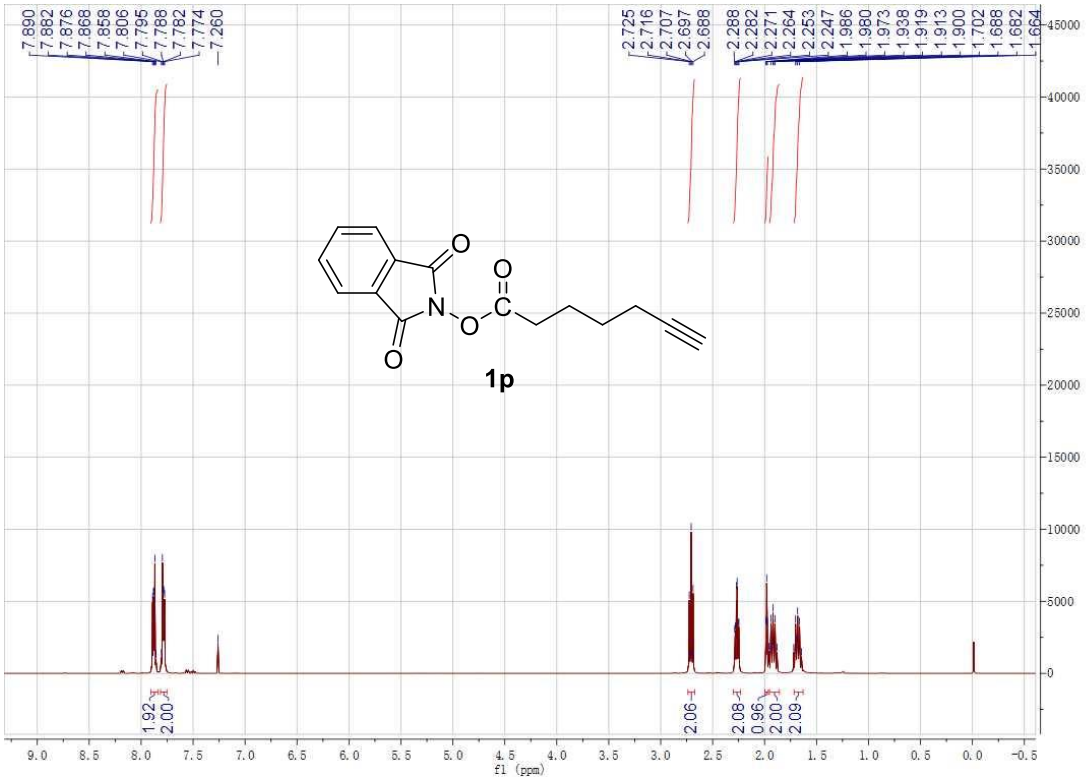
^{13}C NMR spectrum of 1j in $CDCl_3$, 101 MHz



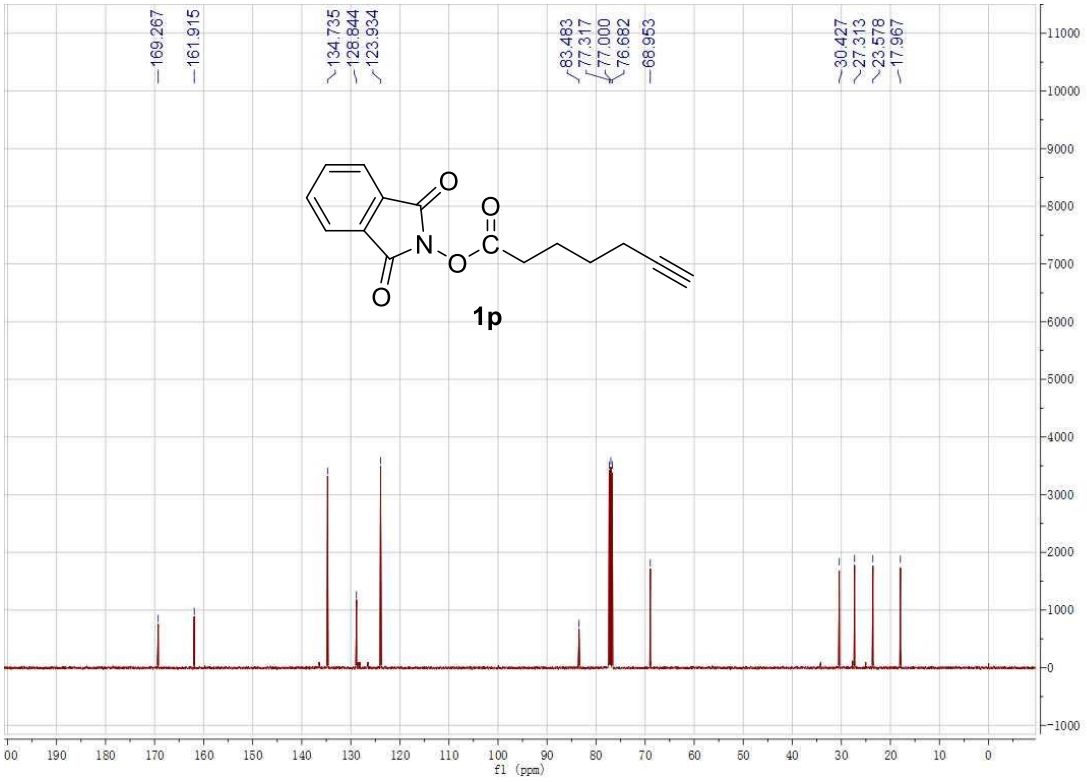
^{31}P NMR spectrum of 1j in $CDCl_3$, 162 MHz



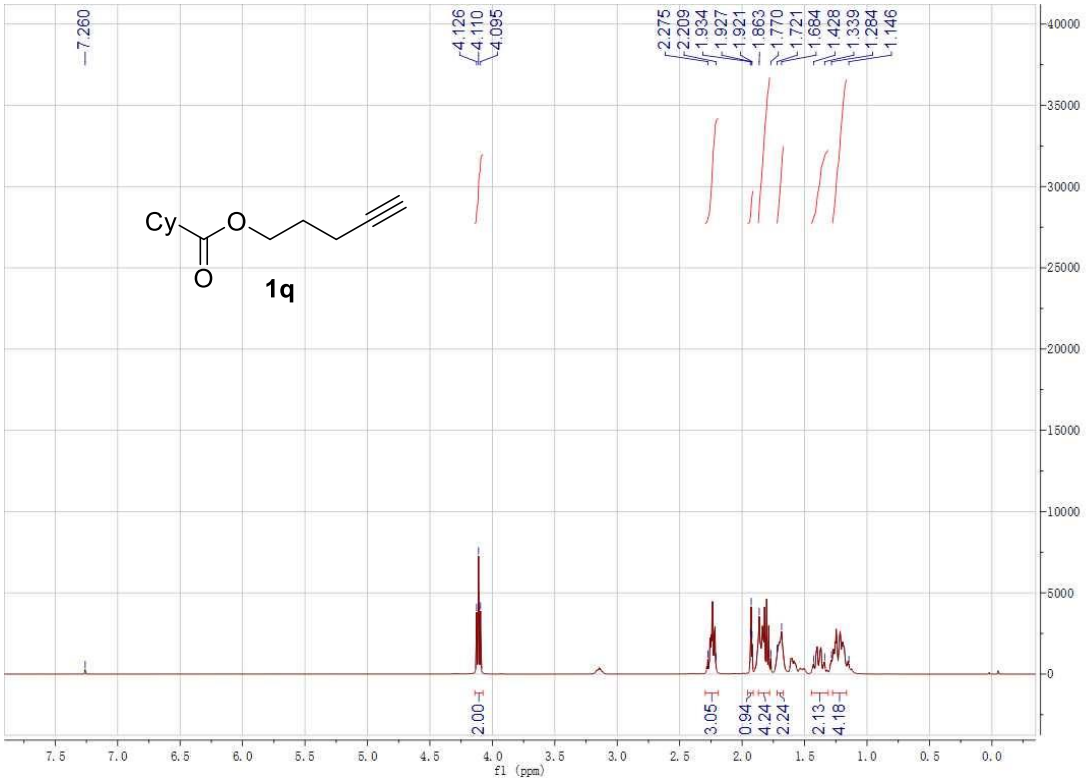
^{1}H NMR spectrum of 1p in $CDCl_3$, 400 MHz



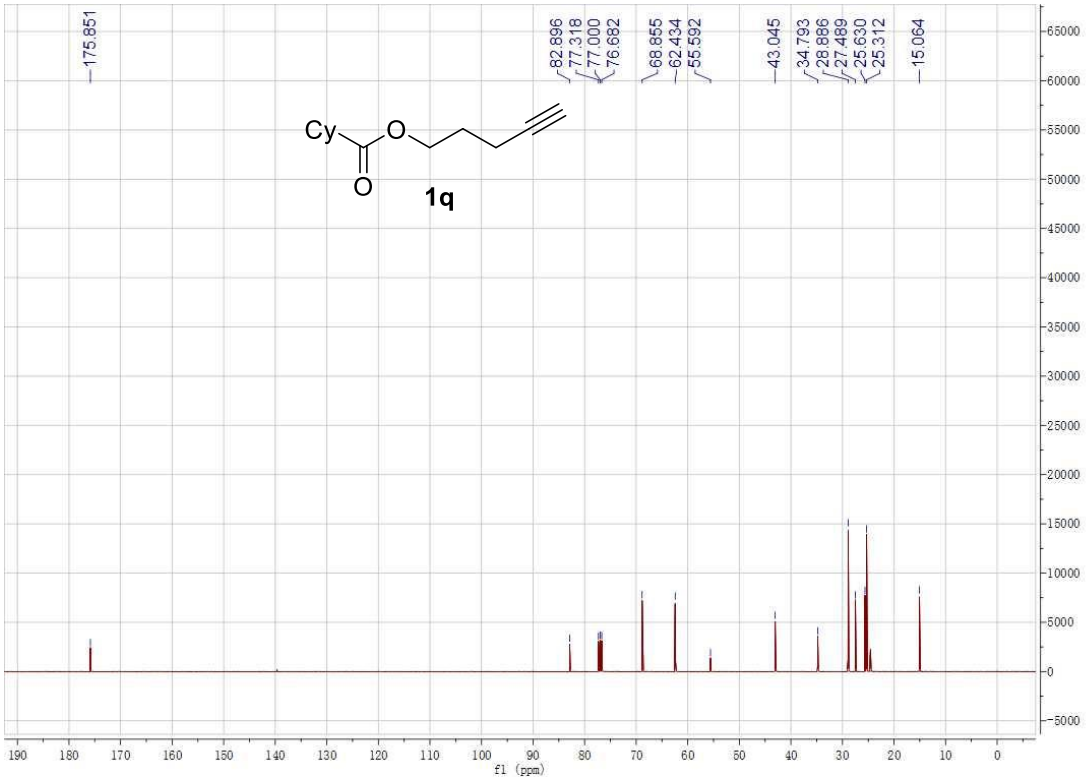
^{13}C NMR spectrum of 1p in $CDCl_3$, 101 MHz



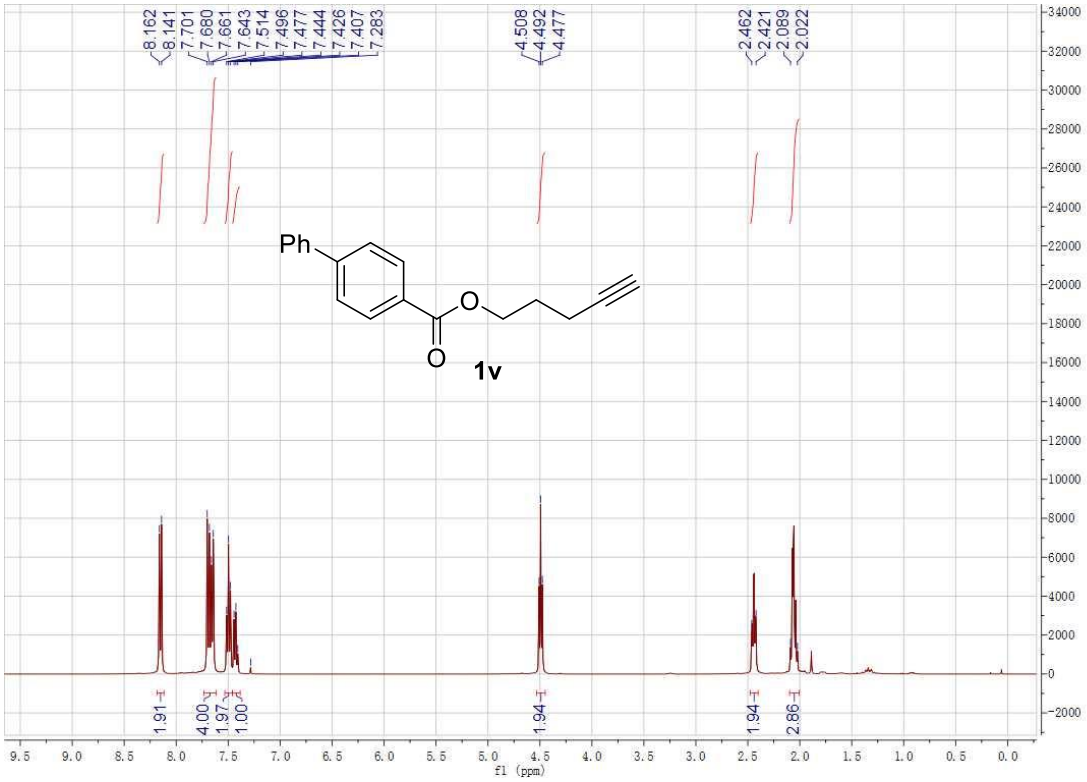
^{1}H NMR spectrum of 1q in $CDCl_3$, 400 MHz



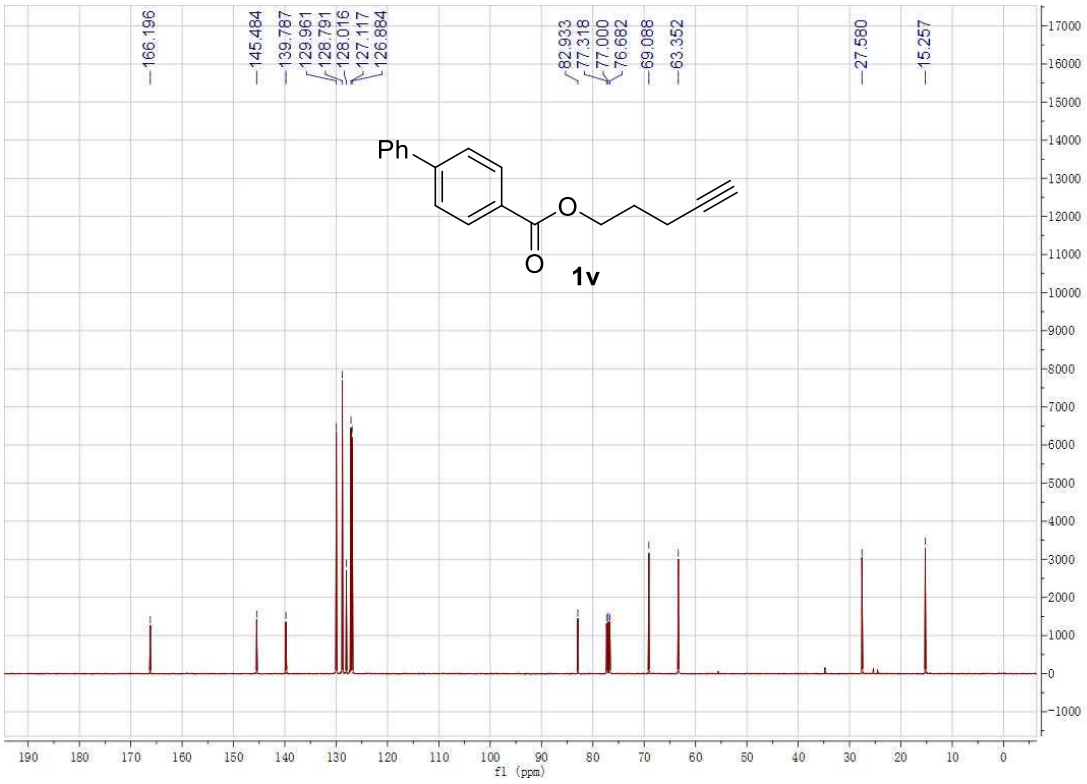
^{13}C NMR spectrum of 1q in $CDCl_3$, 101 MHz



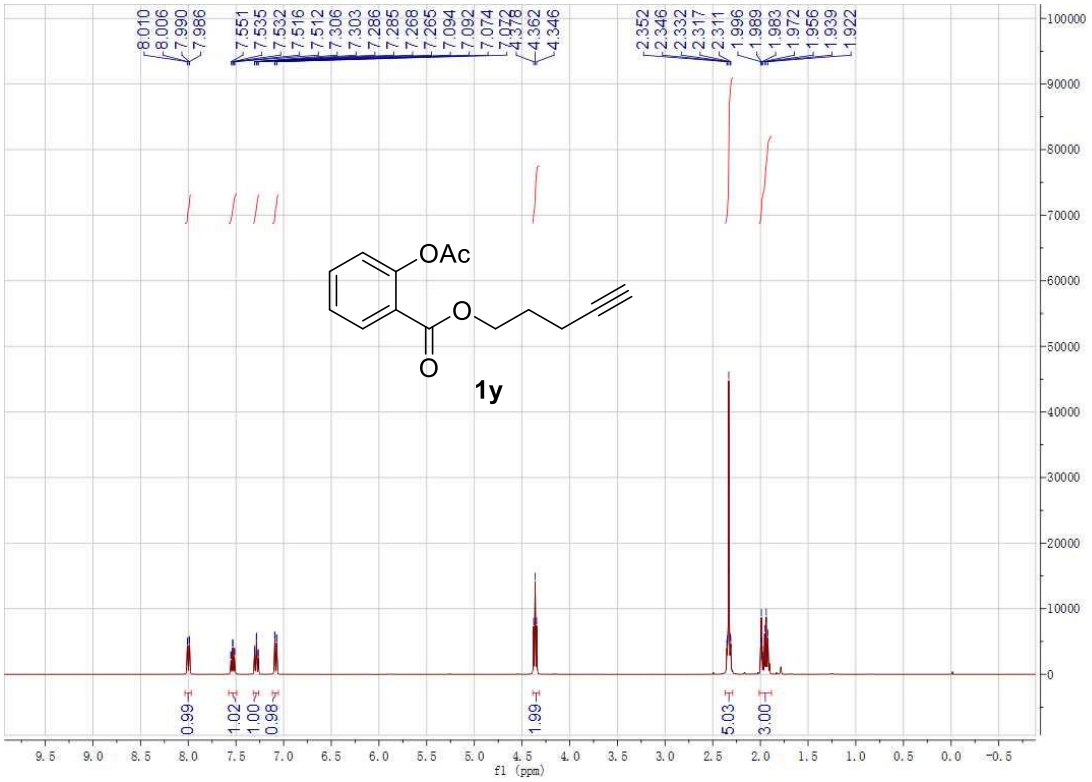
^{1}H NMR spectrum of 1v in $CDCl_3$, 400 MHz



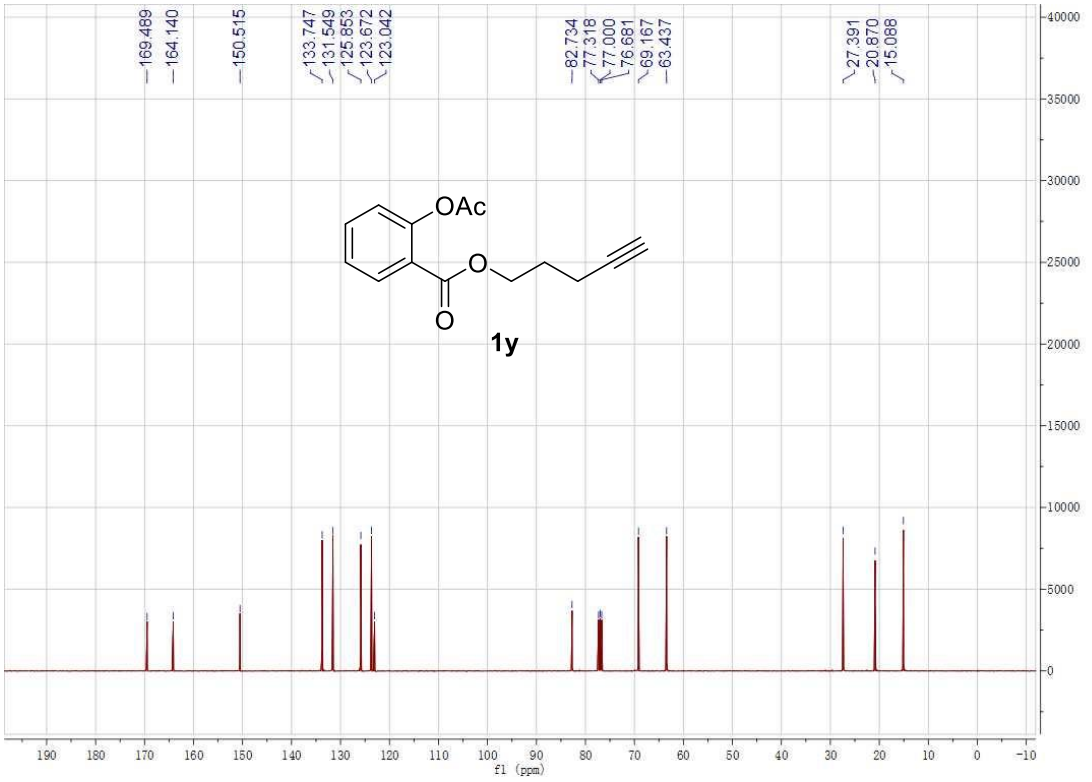
^{13}C NMR spectrum of 1v in $CDCl_3$, 101 MHz



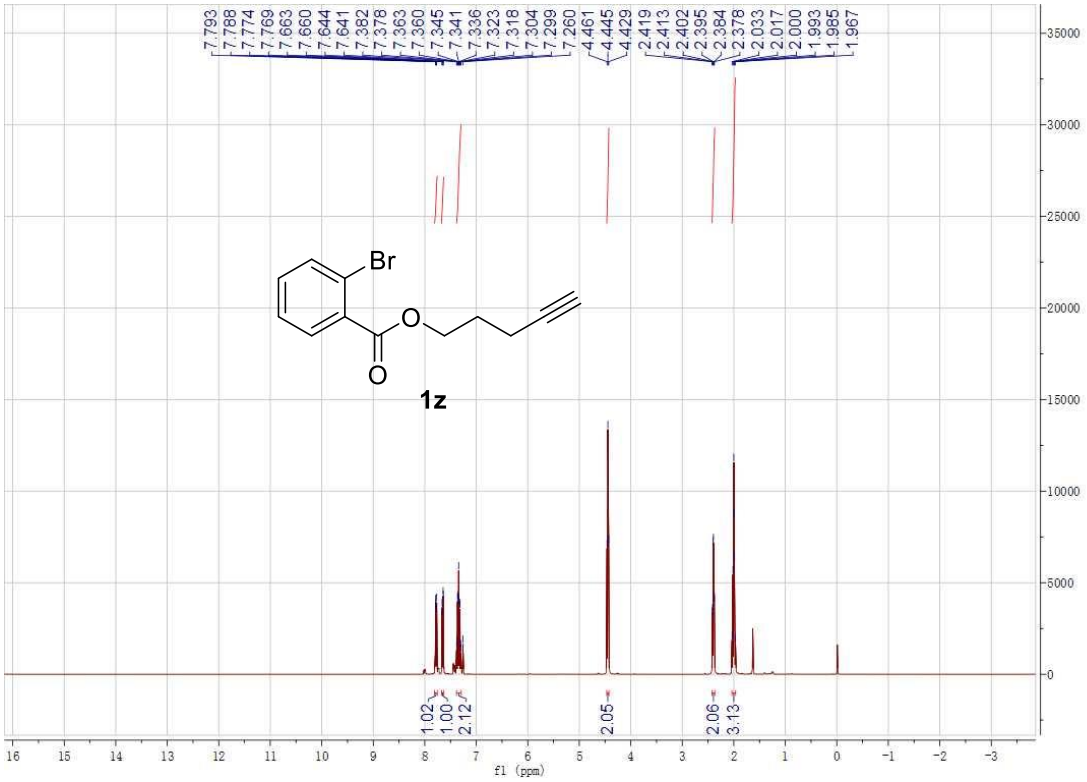
^{1}H NMR spectrum of 1y in $CDCl_3$, 400 MHz



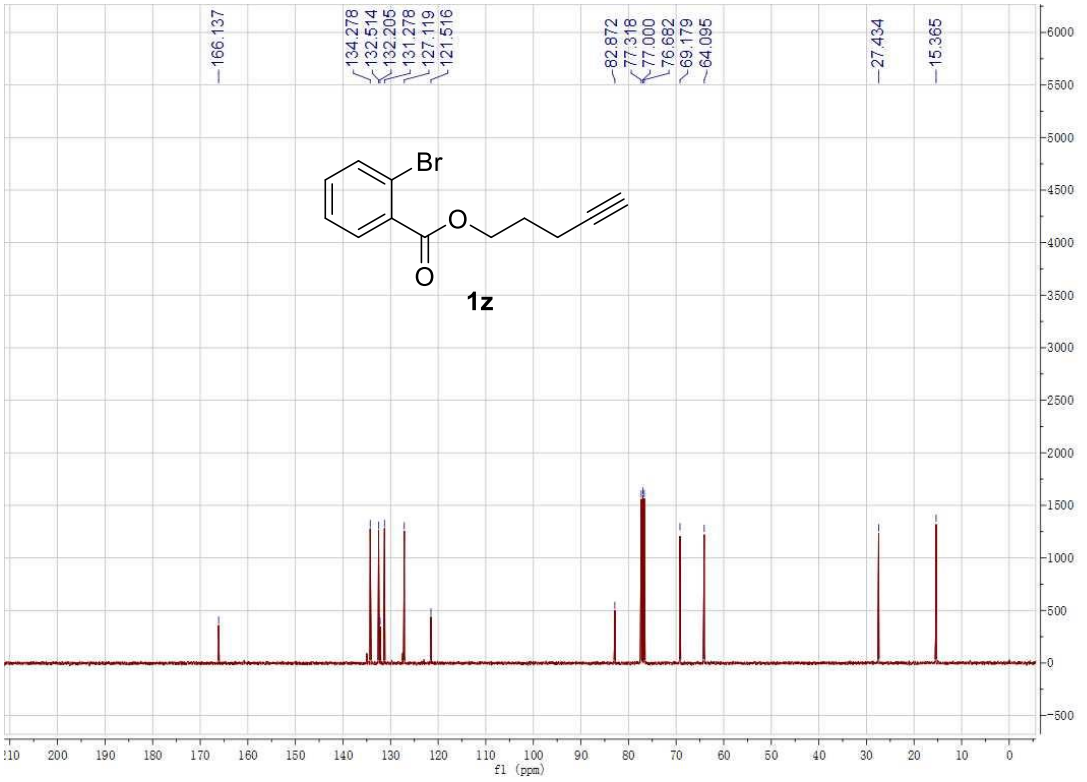
^{13}C NMR spectrum of 1y in $CDCl_3$, 101 MHz



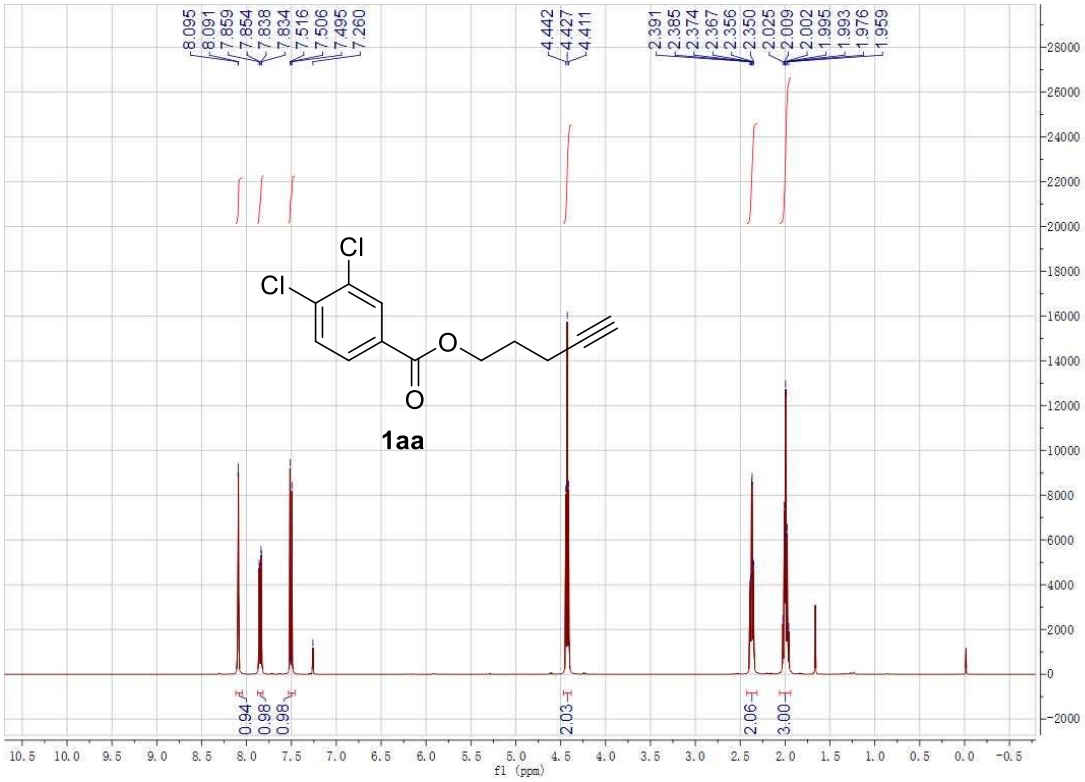
^{1}H NMR spectrum of 1z in $CDCl_3$, 400 MHz



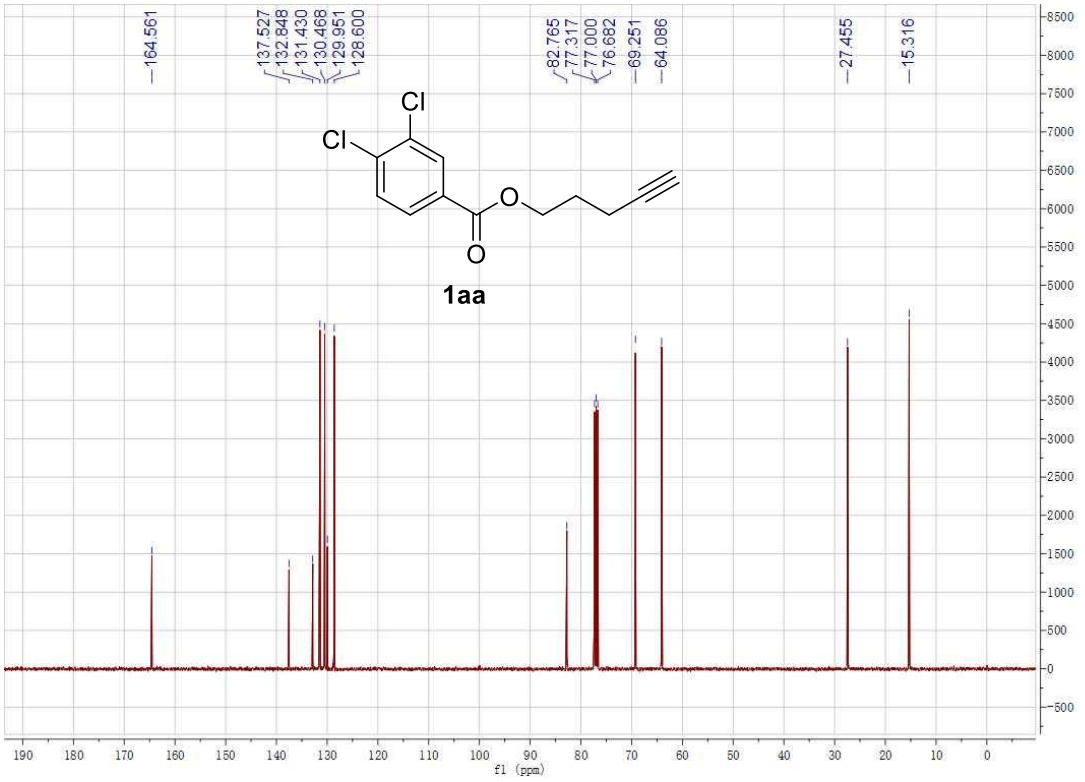
^{13}C NMR spectrum of 1z in $CDCl_3$, 101 MHz



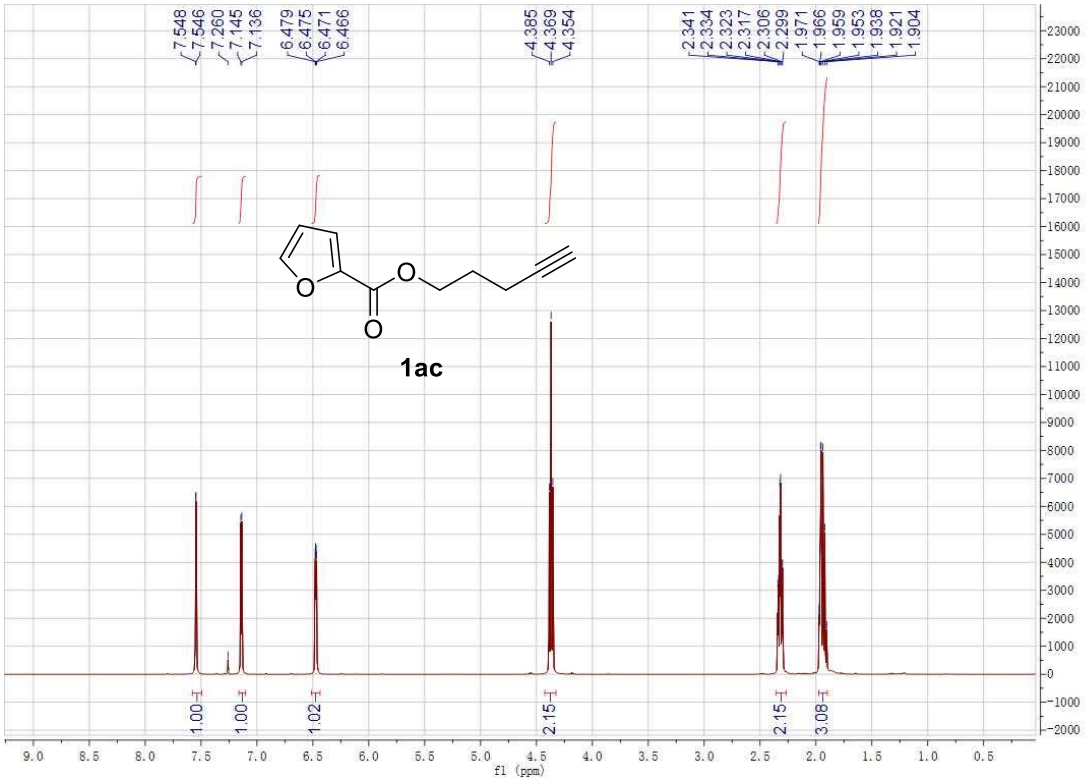
^{1}H NMR spectrum of 1aa in $CDCl_3$, 400 MHz



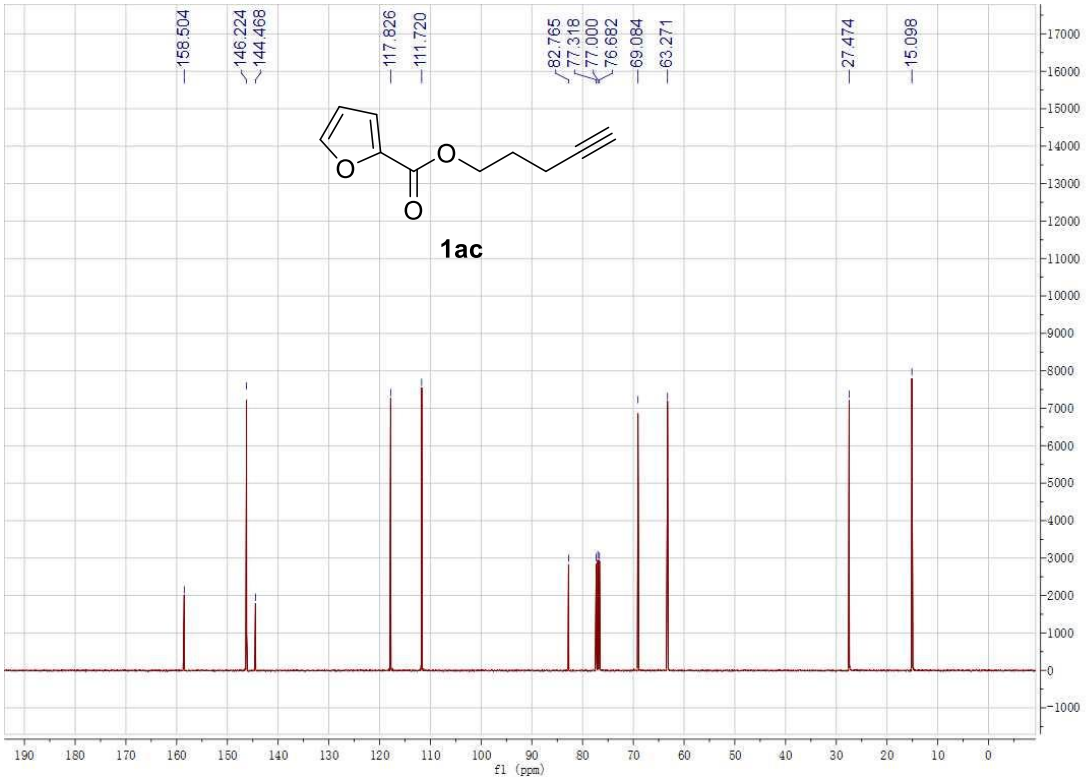
^{13}C NMR spectrum of 1aa in $CDCl_3$, 101 MHz



^{1}H NMR spectrum of 1ac in $CDCl_3$, 400 MHz



^{13}C NMR spectrum of 1ac in $CDCl_3$, 101 MHz



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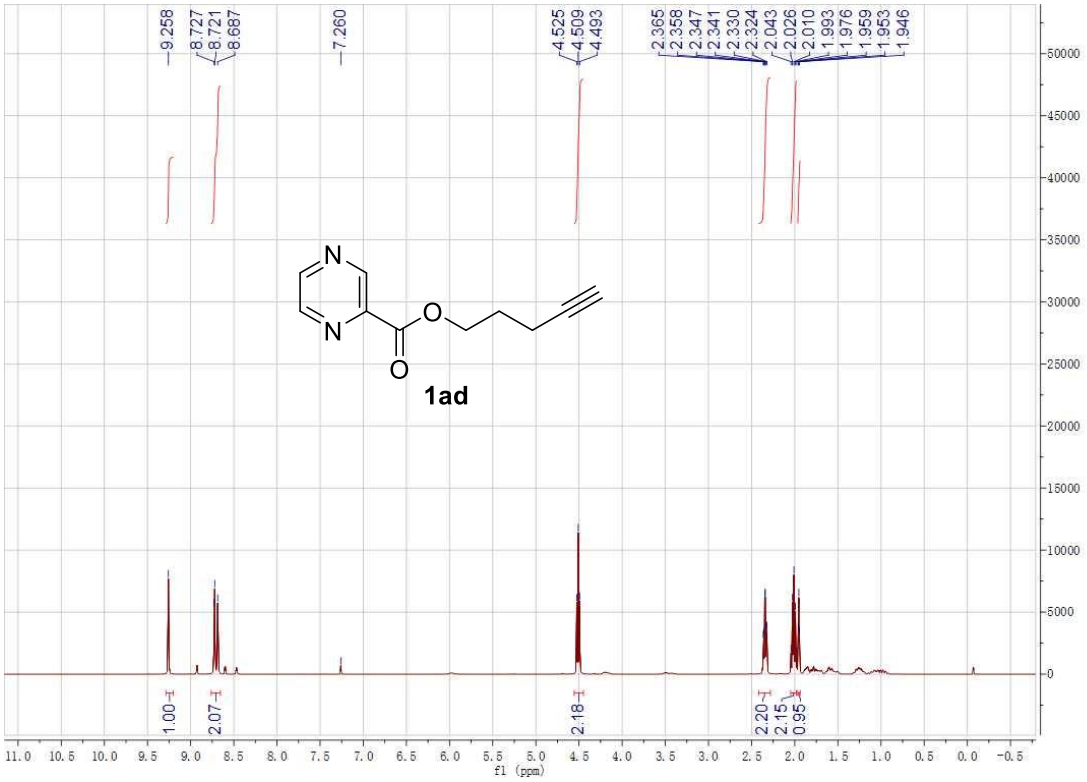
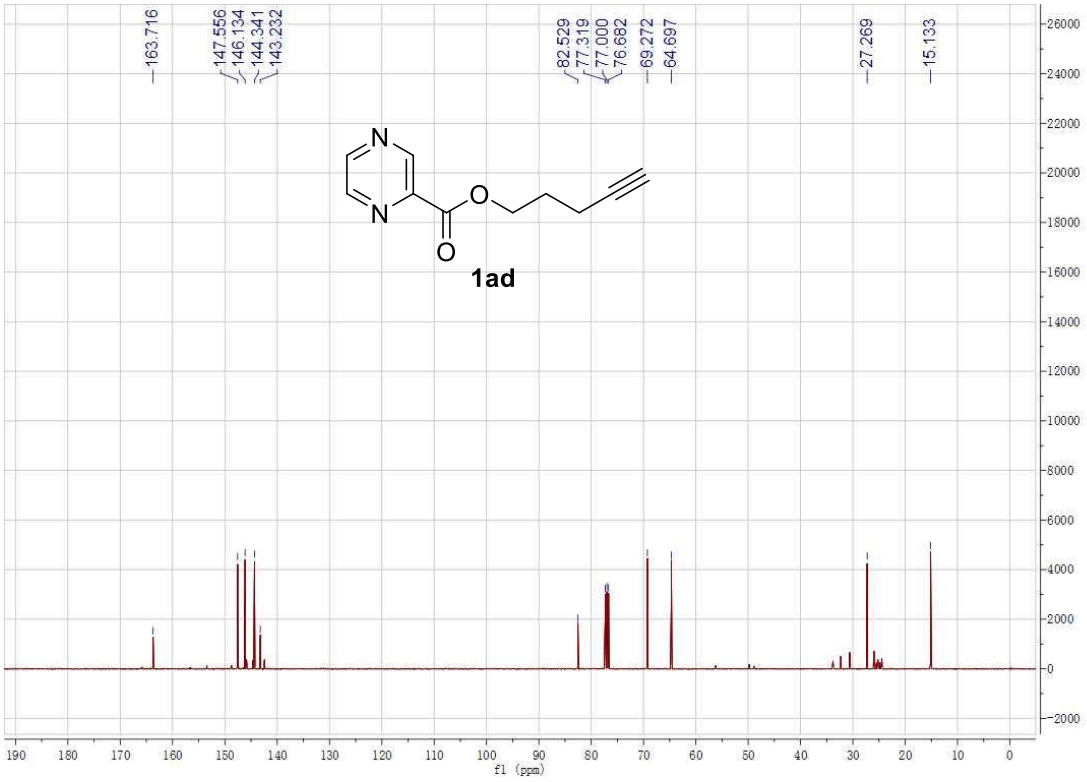
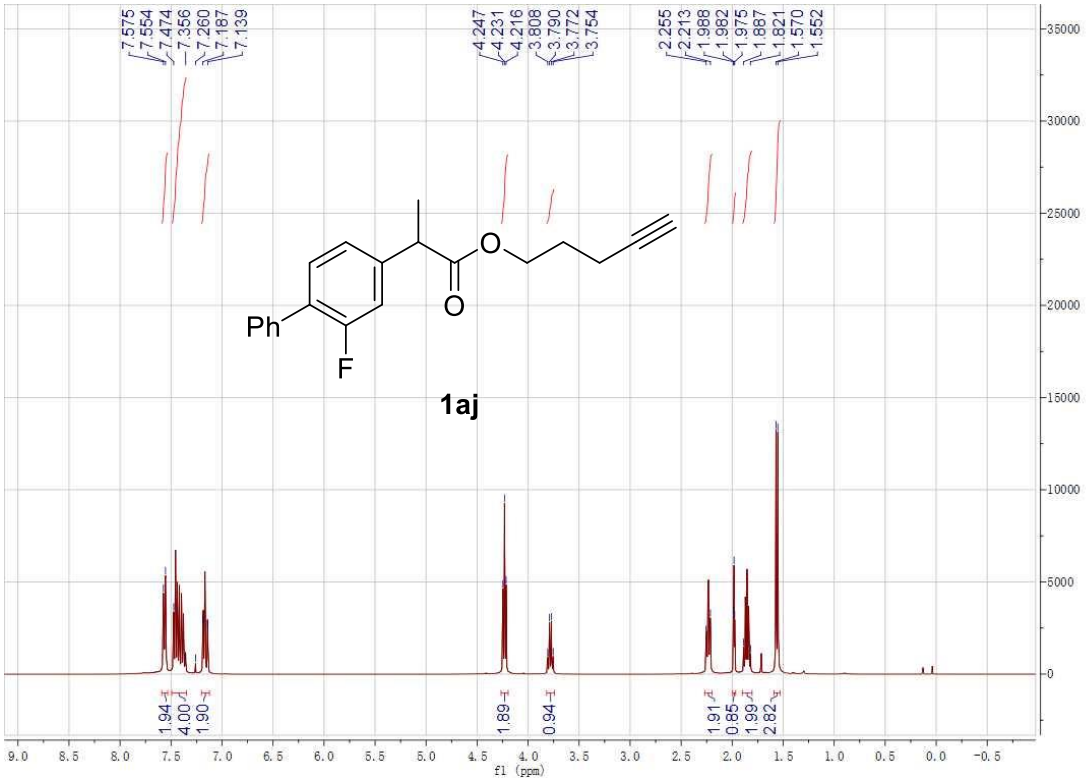


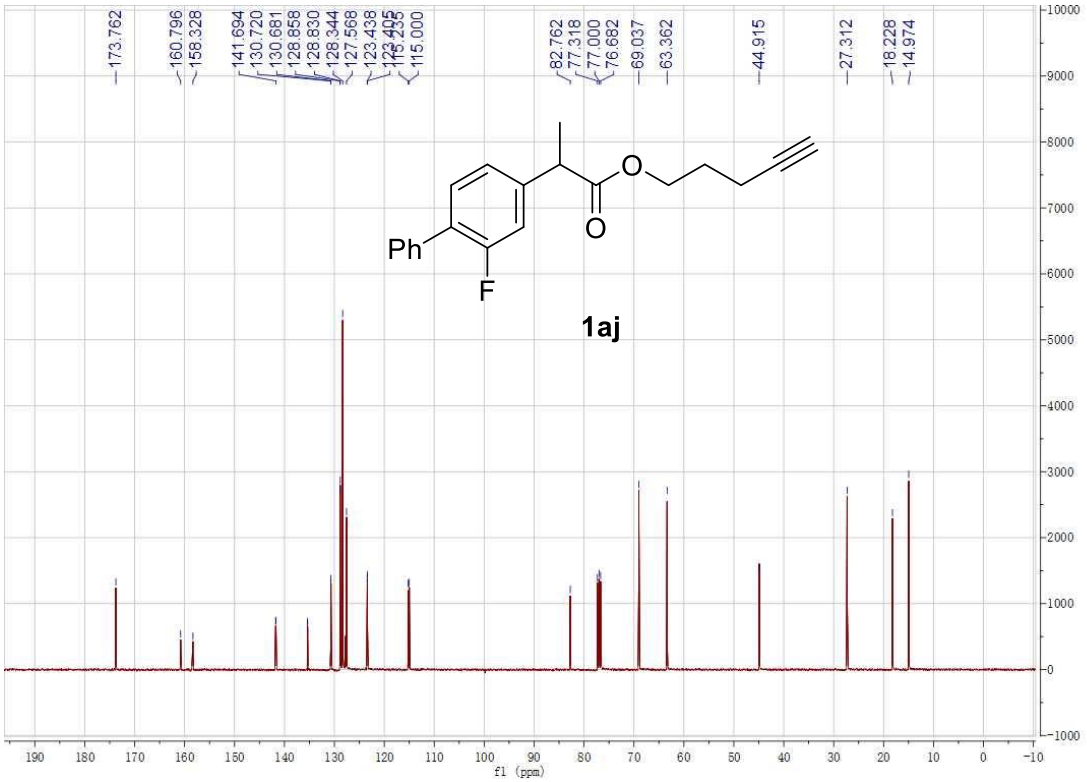
^{13}C NMR spectrum of 1ad in $CDCl_3$, 101 MHz



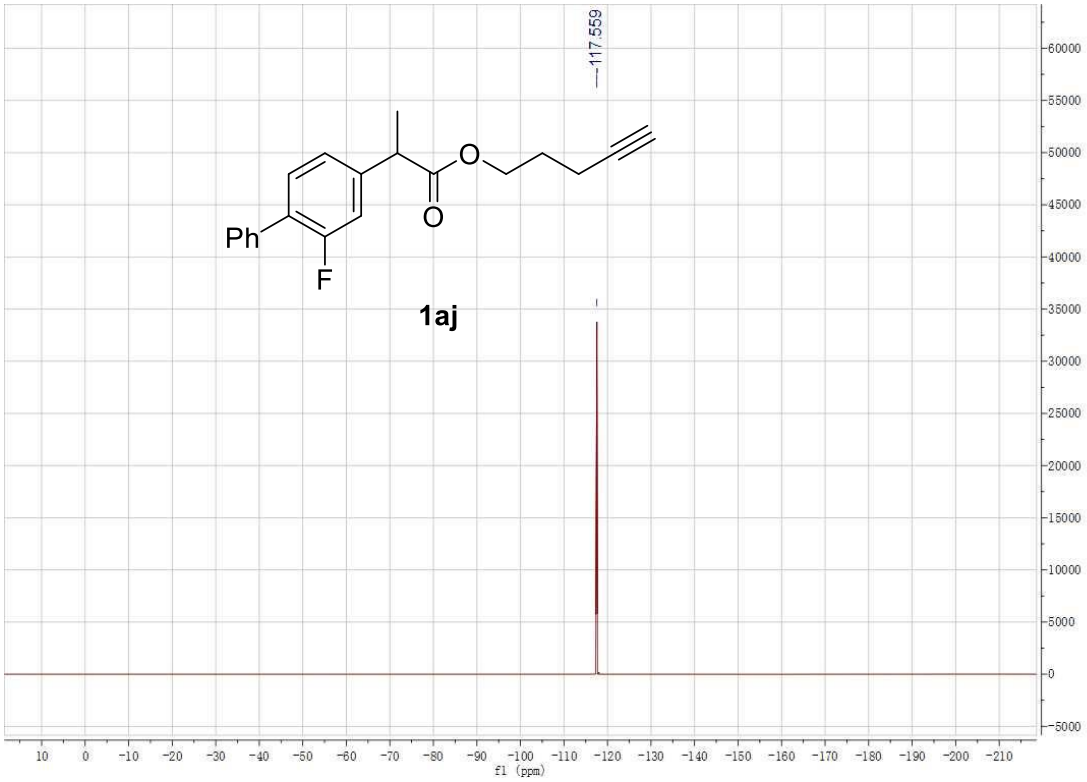
^{1}H NMR spectrum of 1aj in $CDCl_3$, 400 MHz



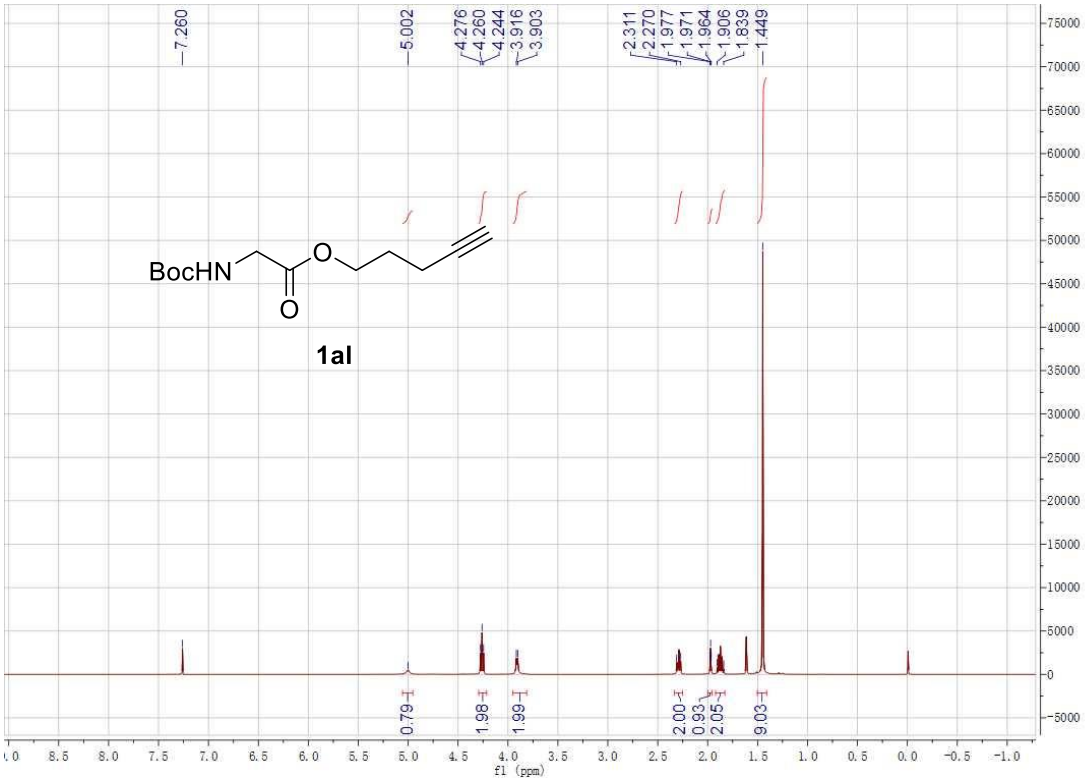
^{13}C NMR spectrum of 1aj in $CDCl_3$, 101 MHz



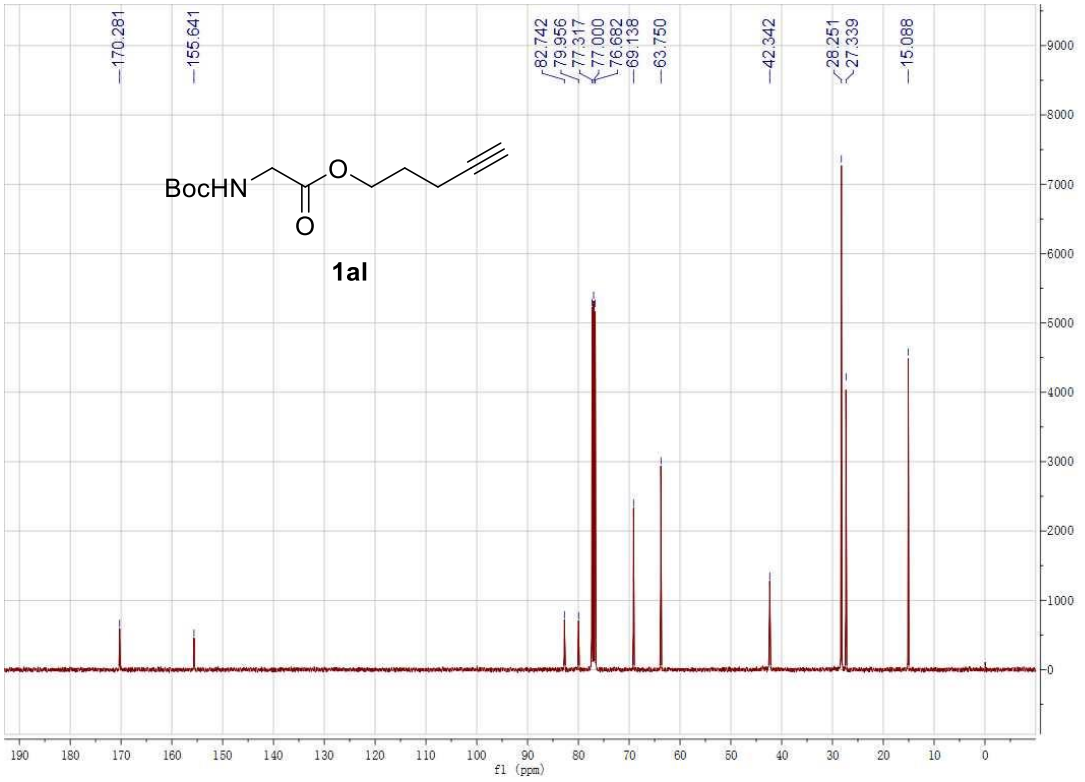
^{19}F NMR spectrum of 1aj in $CDCl_3$, 376 MHz



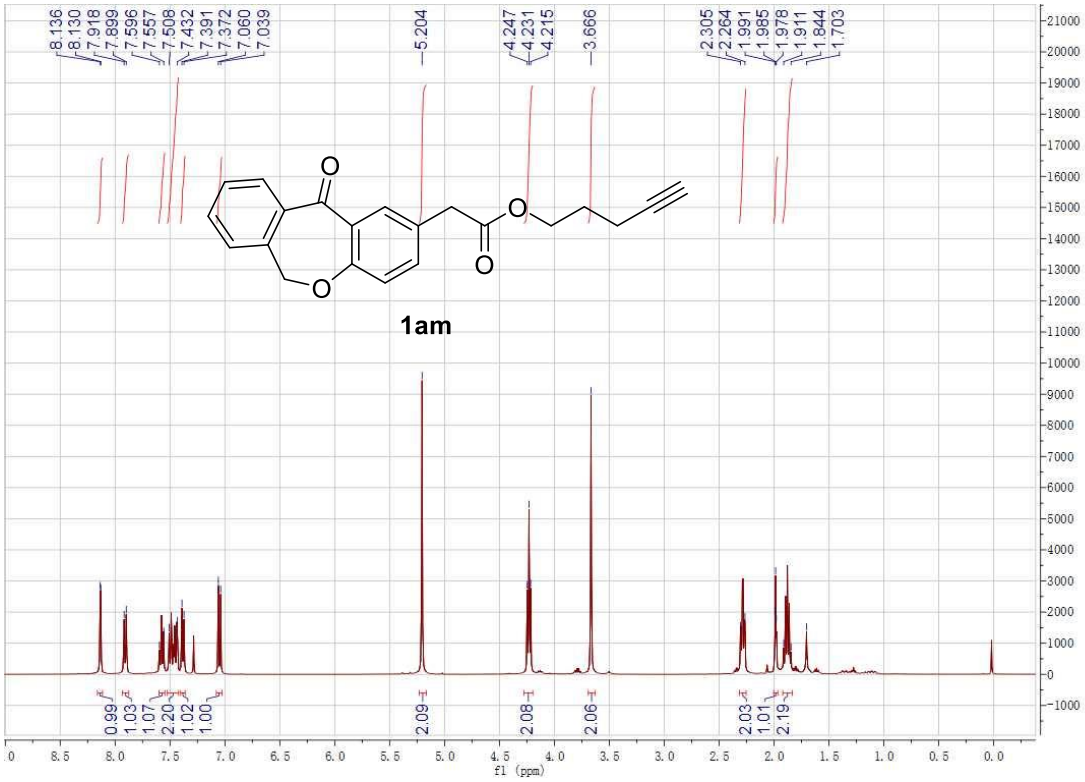
^{1}H NMR spectrum of 1al in $CDCl_3$, 400 MHz



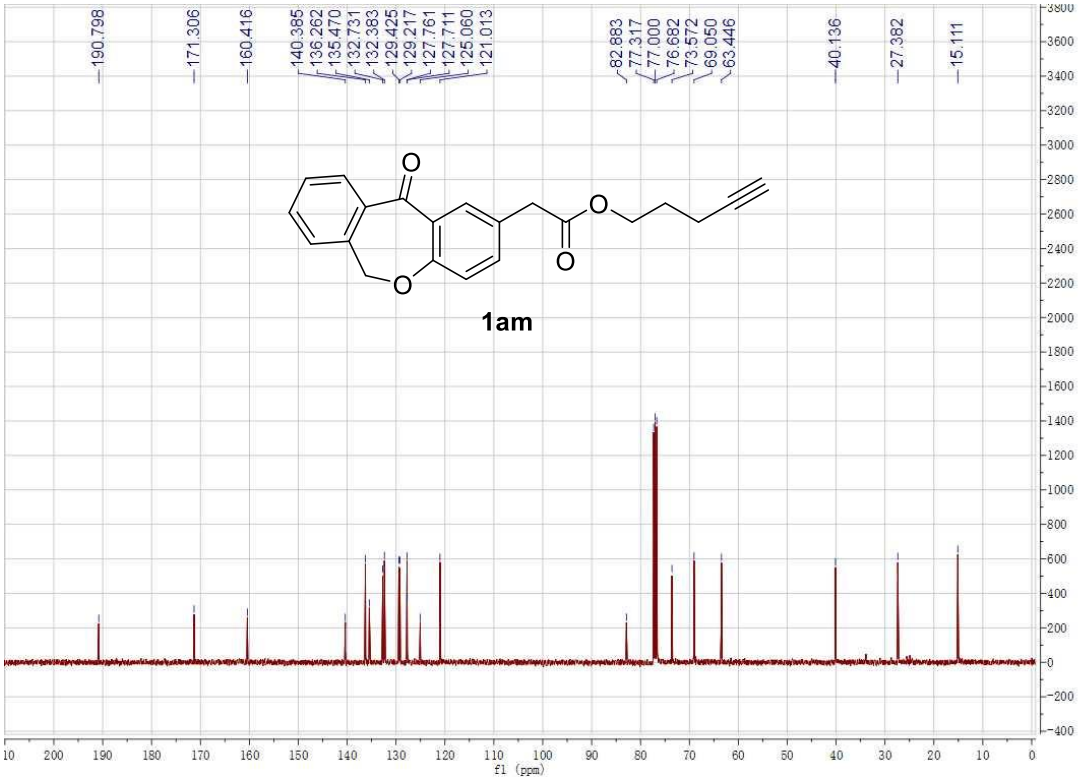
^{13}C NMR spectrum of 1al in $CDCl_3$, 101 MHz



^{1}H NMR spectrum of 1am in $CDCl_3$, 400 MHz



^{13}C NMR spectrum of 1am in $CDCl_3$, 101 MHz



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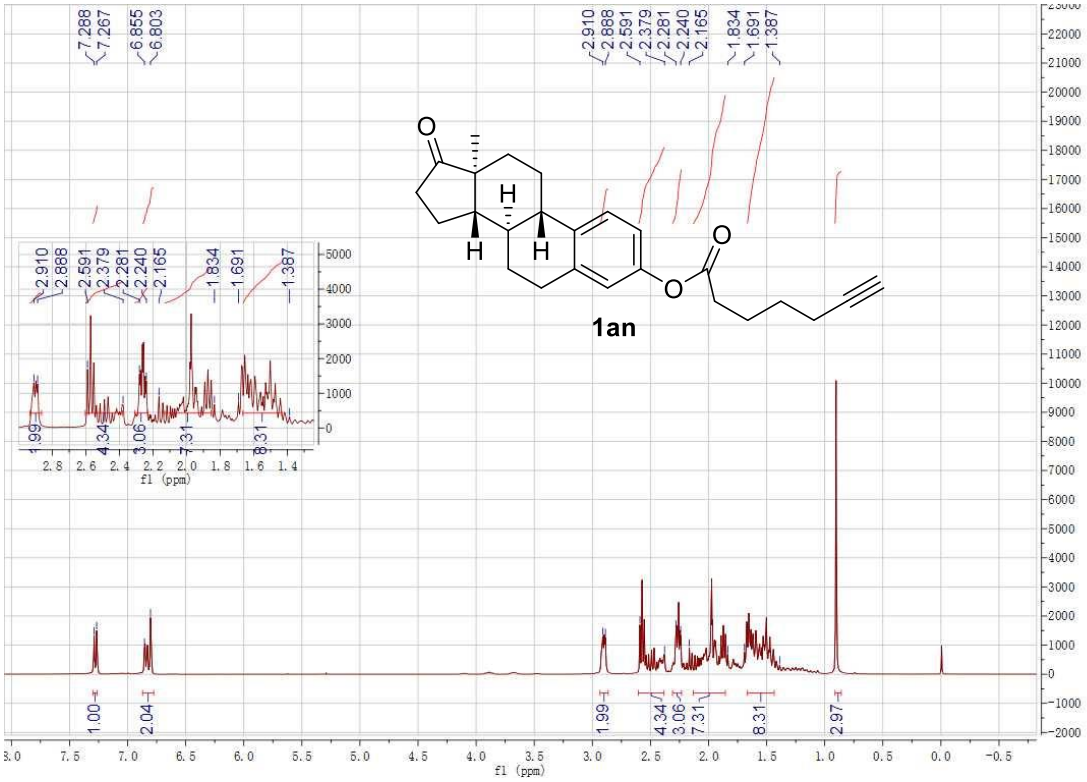

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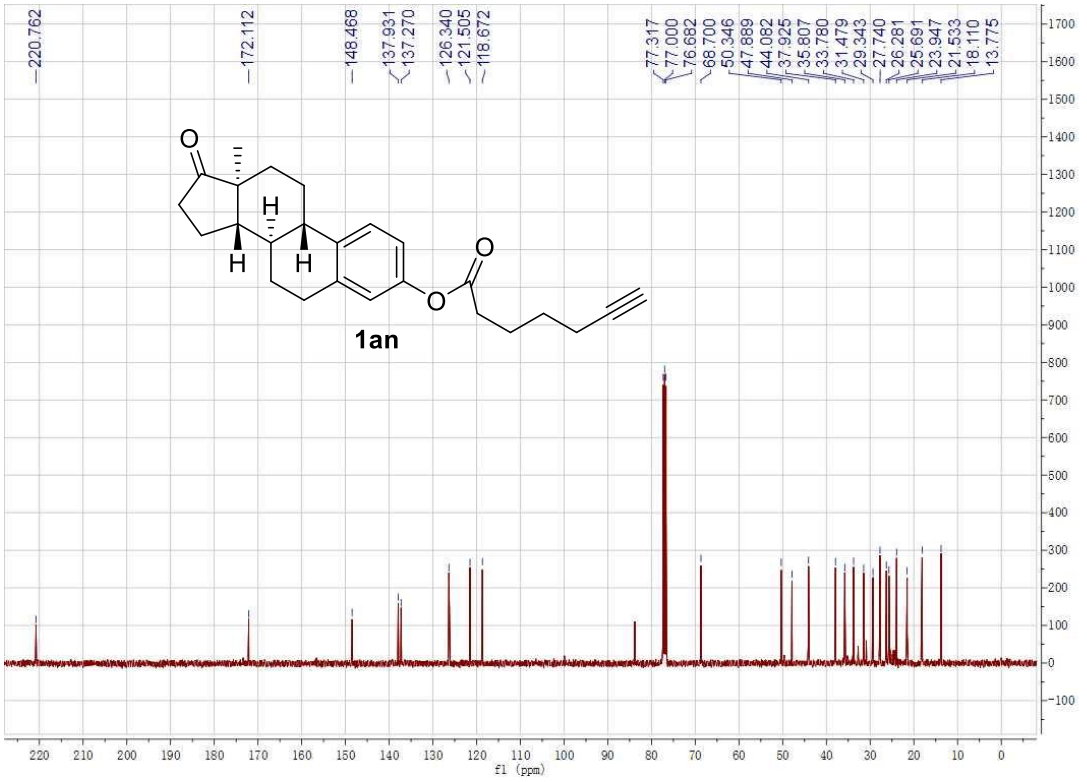

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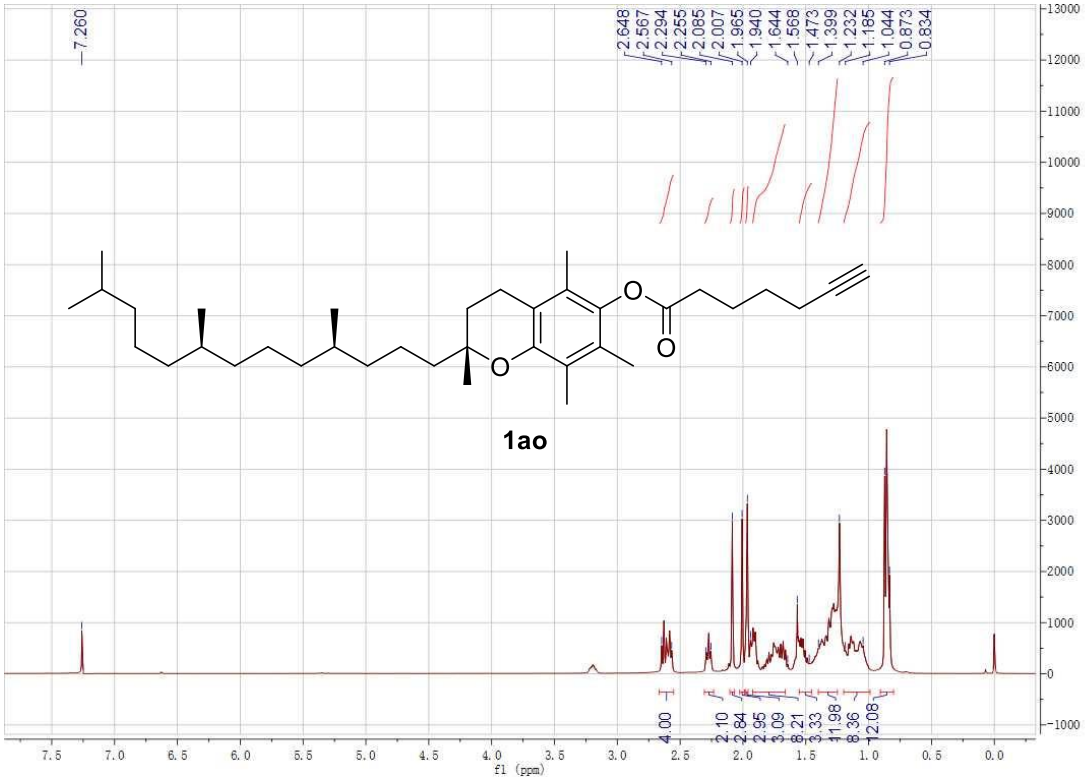
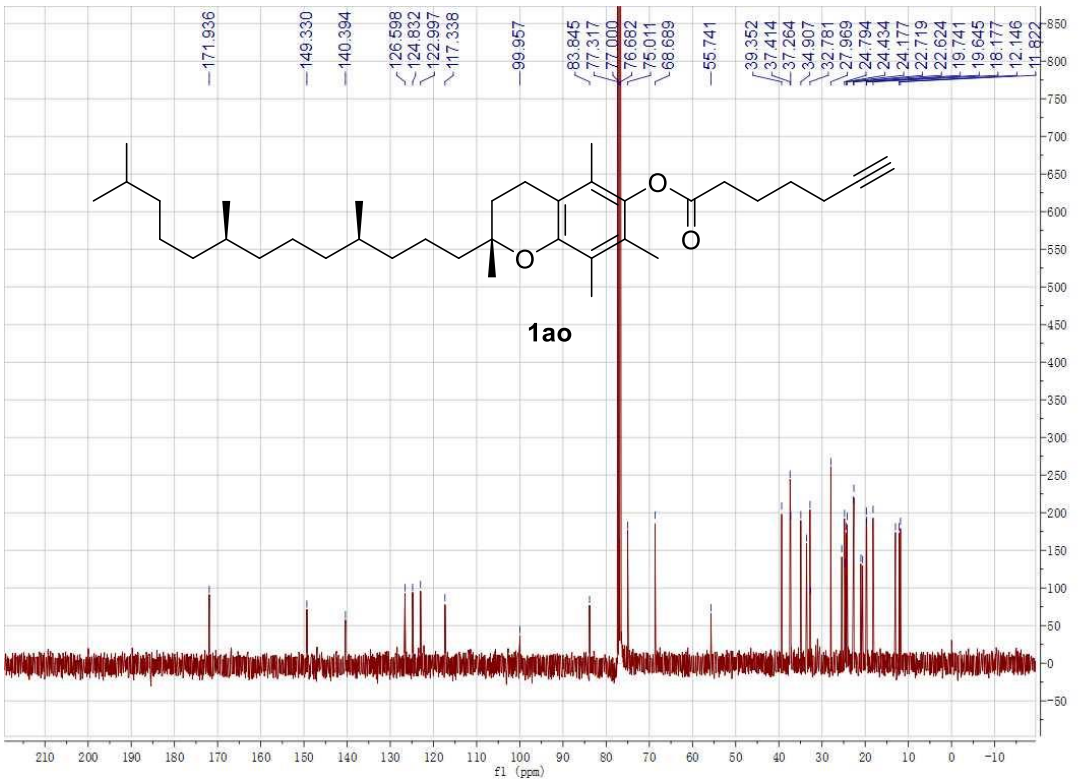


^{13}C NMR spectrum of 1ao in $CDCl_3$, 101 MHz



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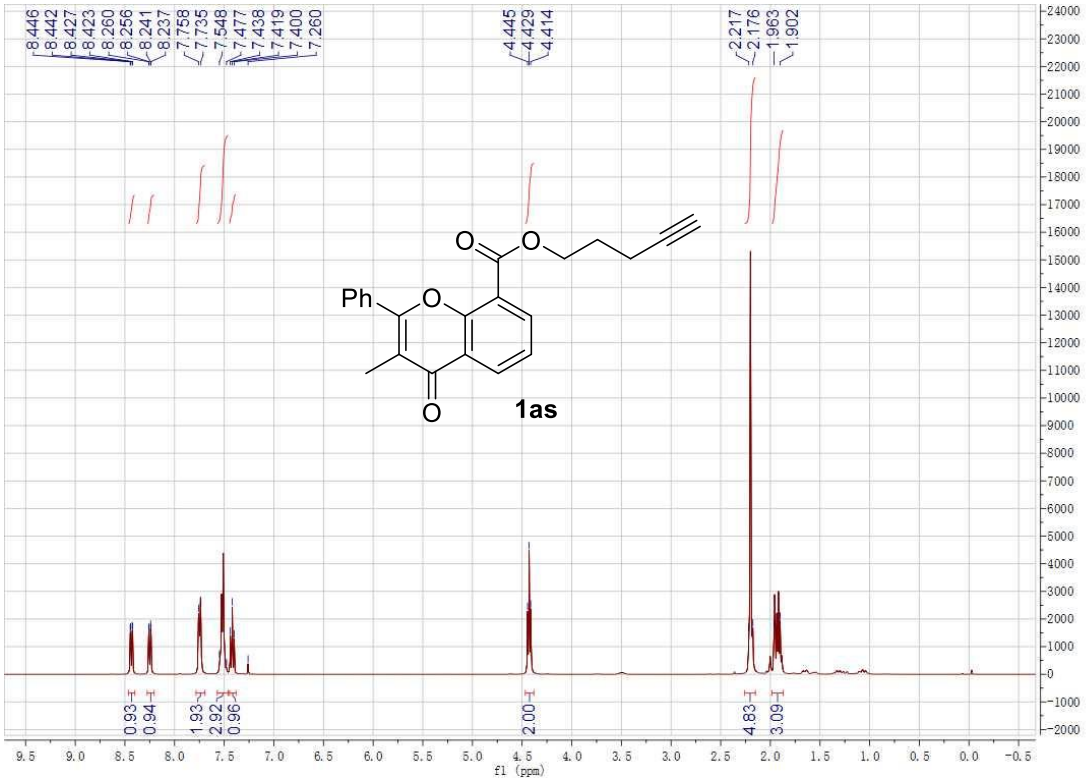

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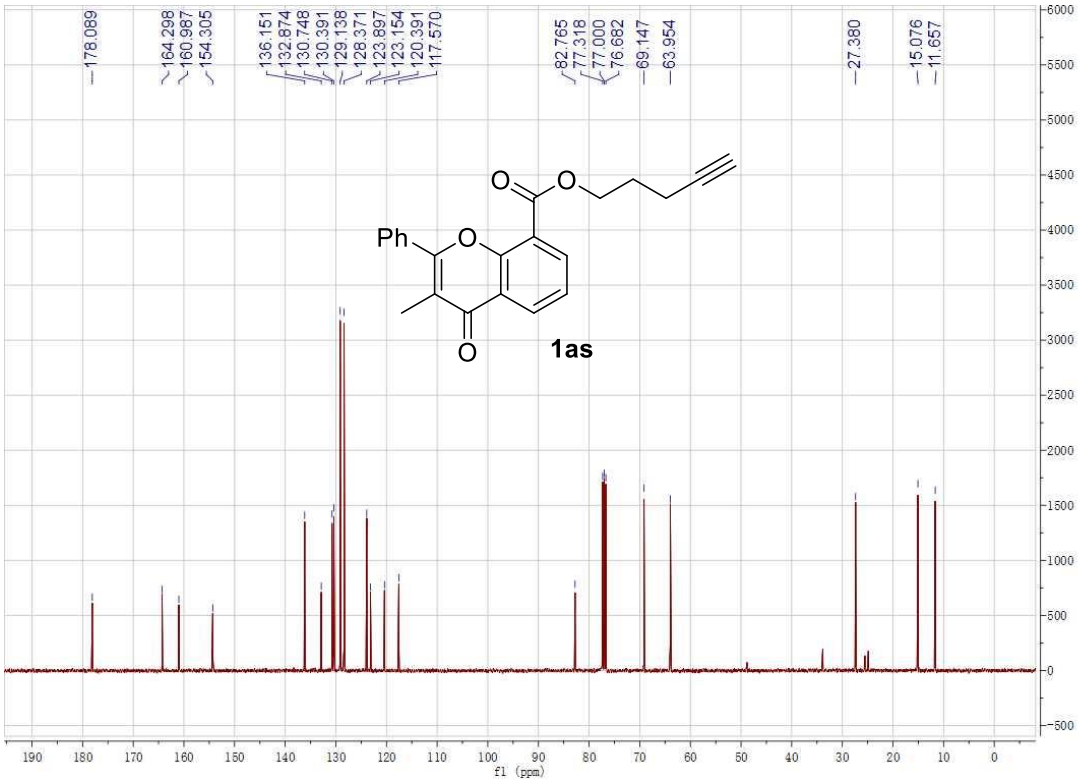

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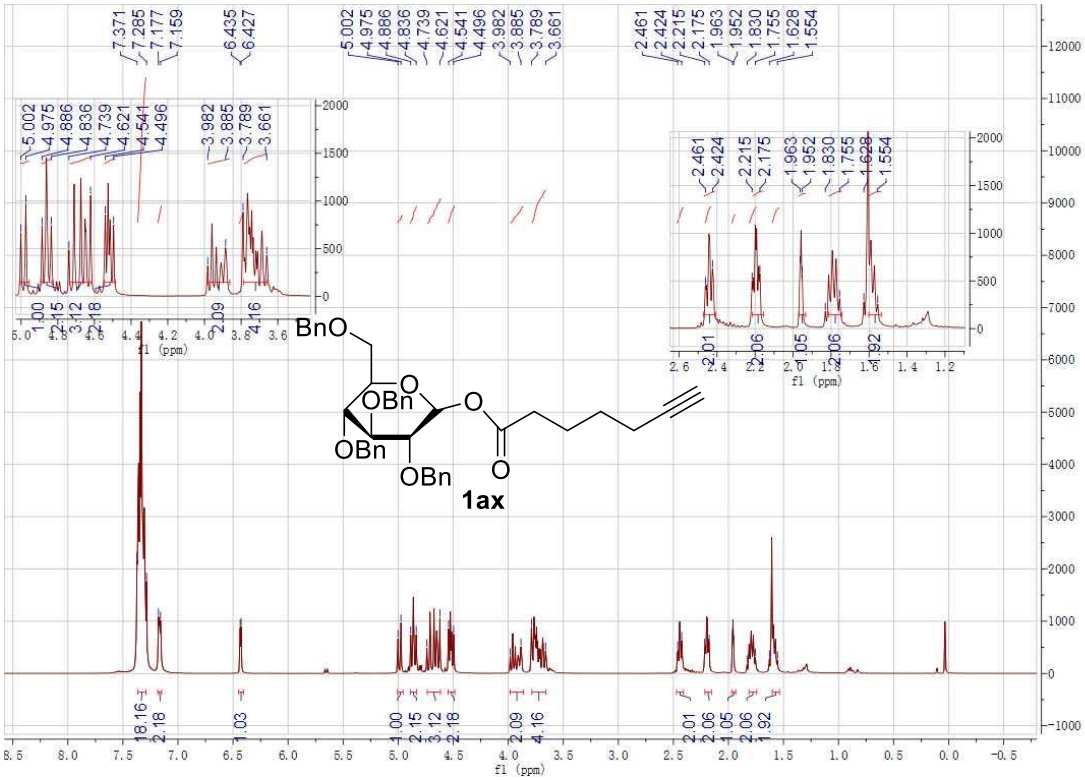

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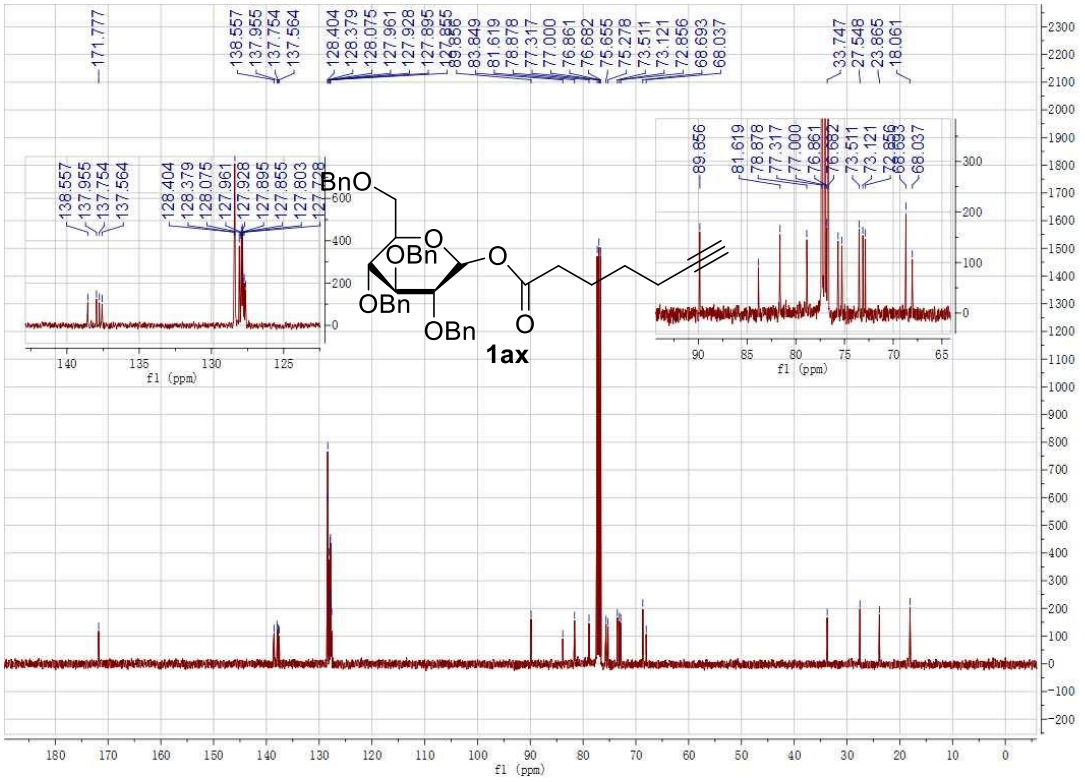

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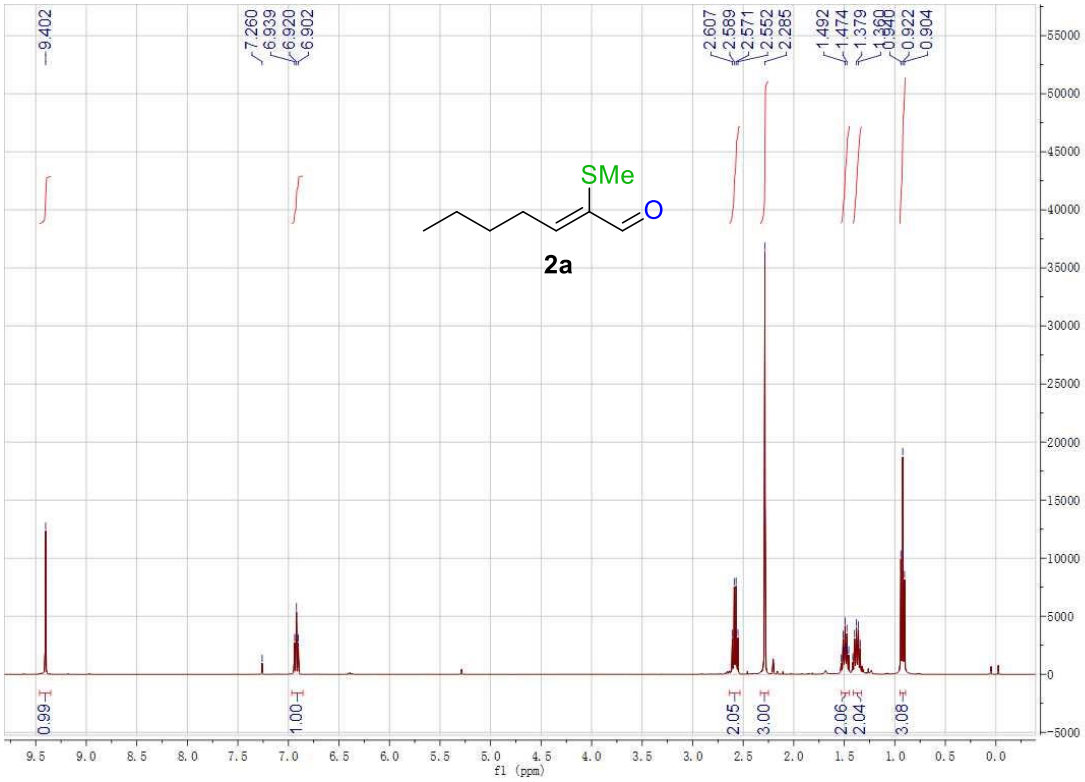

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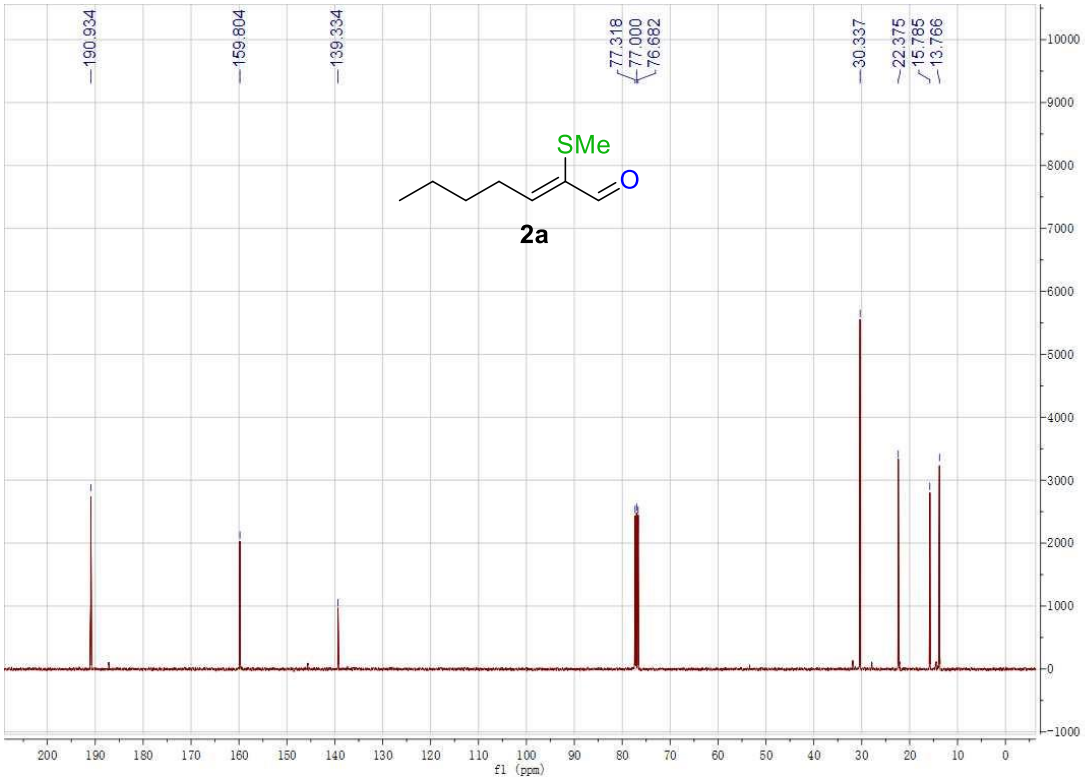
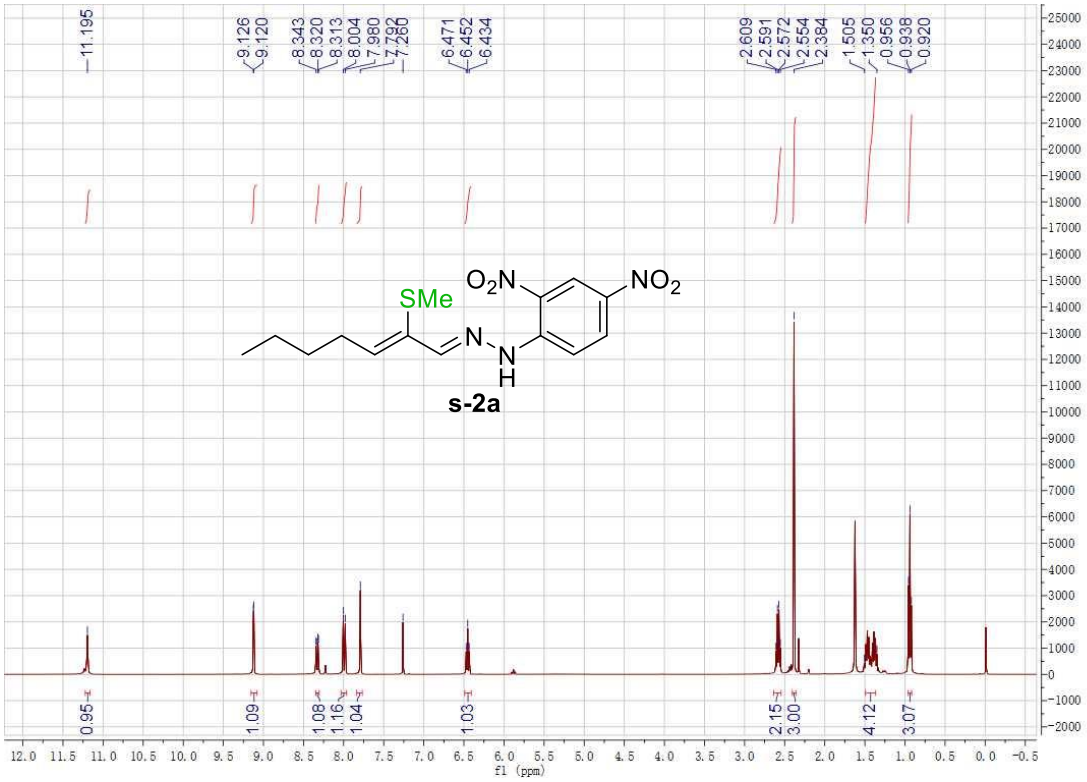


^{1}H NMR spectrum of s-2a in $CDCl_3$, 400 MHz



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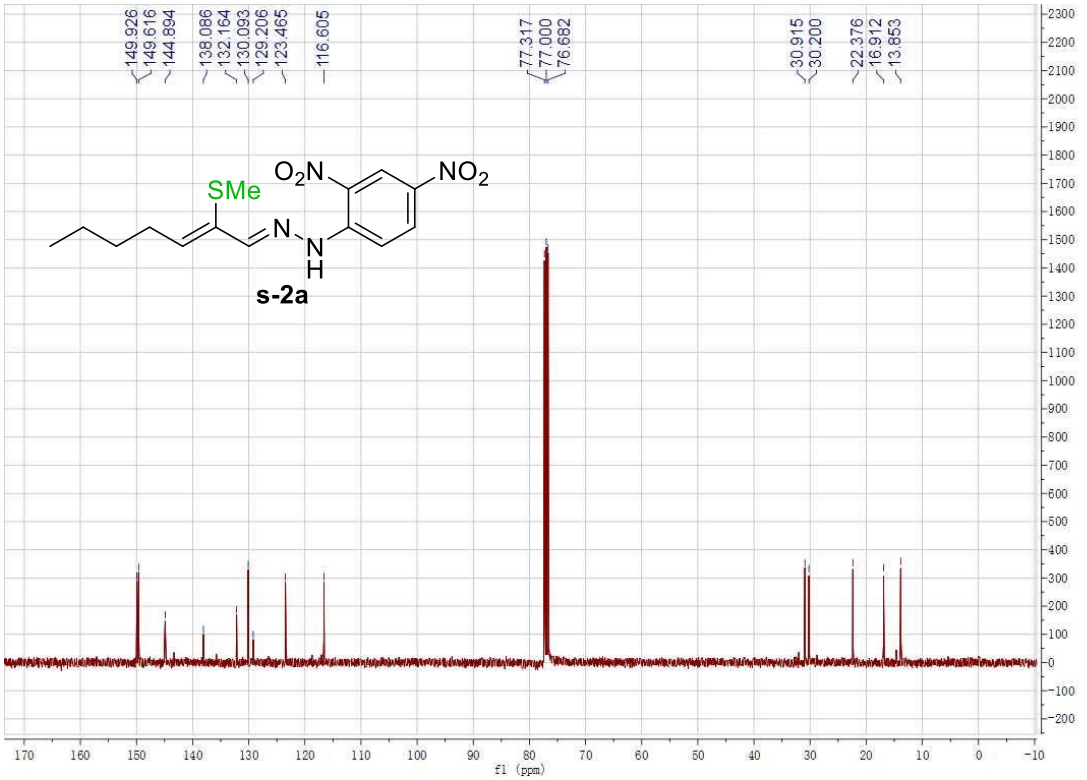
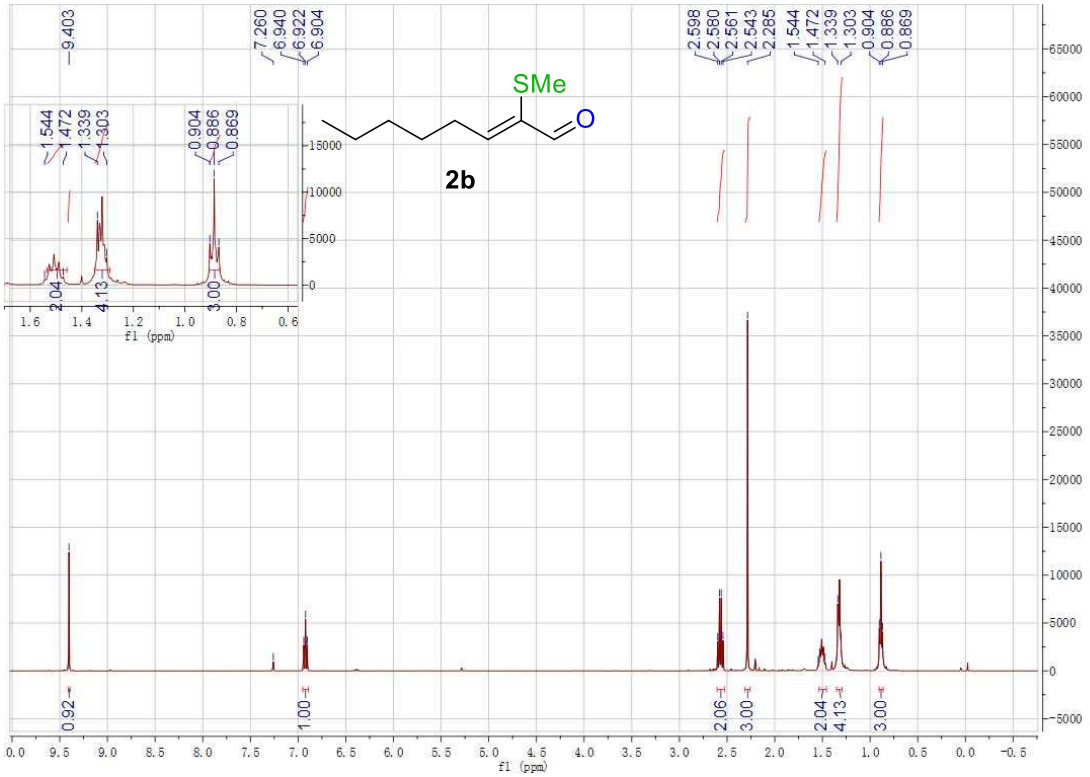


^{1}H NMR spectrum of 2b in $CDCl_3$, 400 MHz



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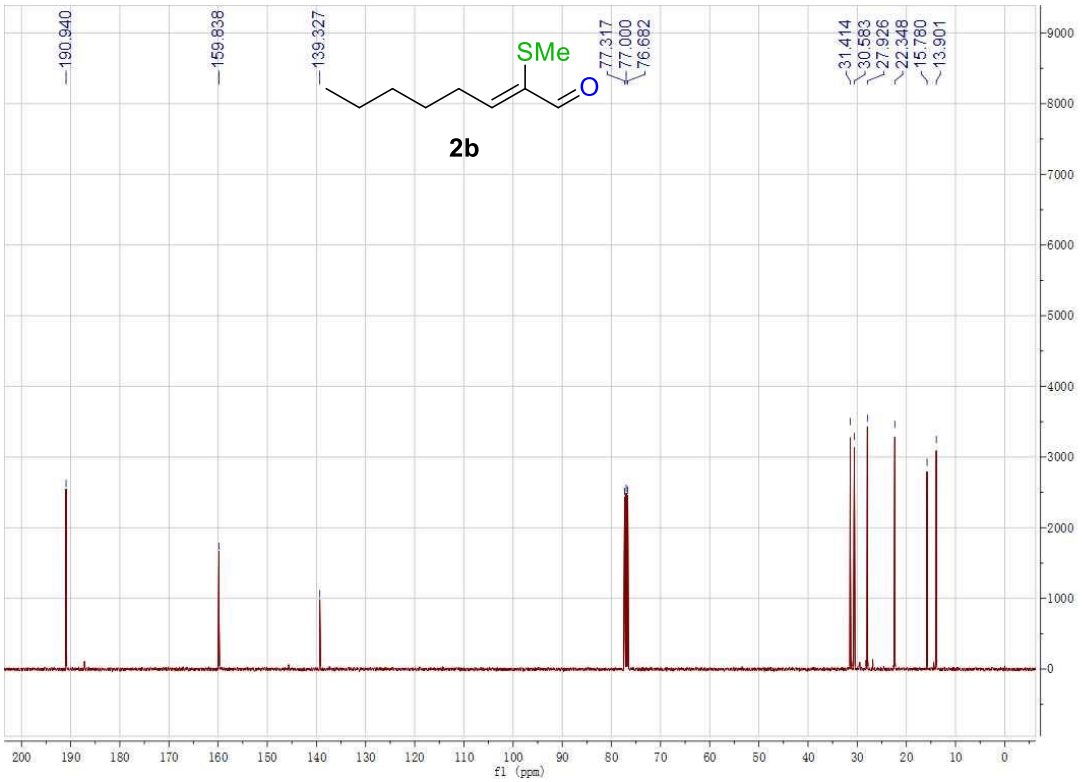

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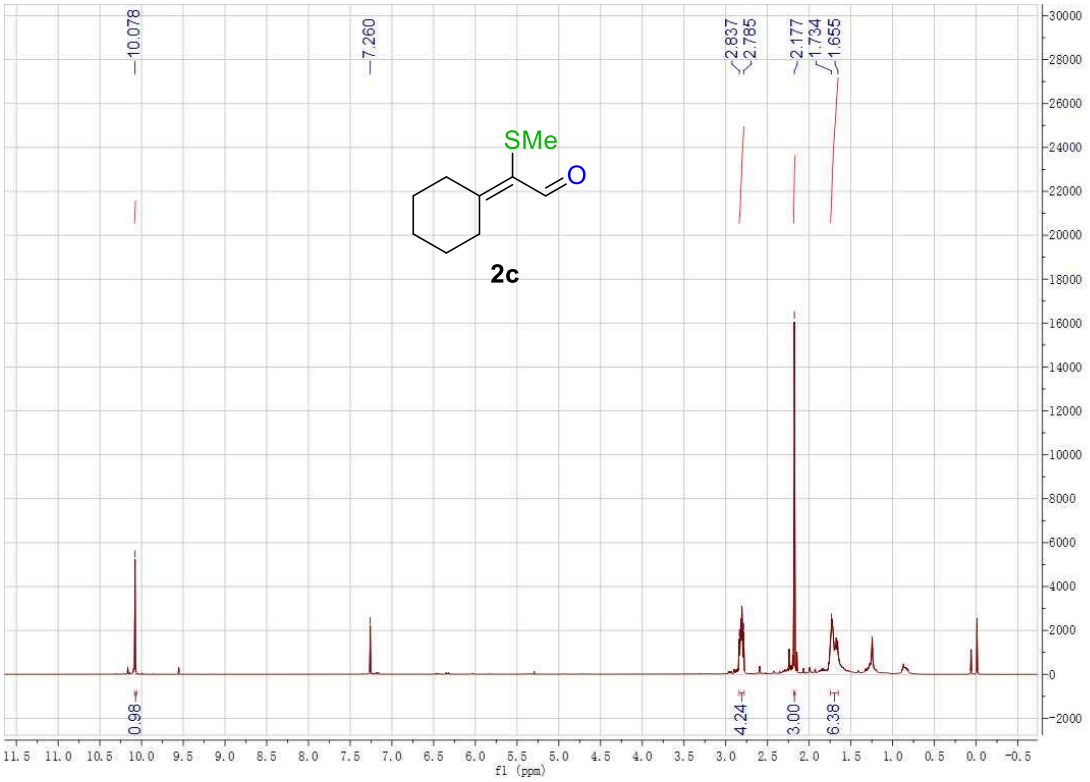

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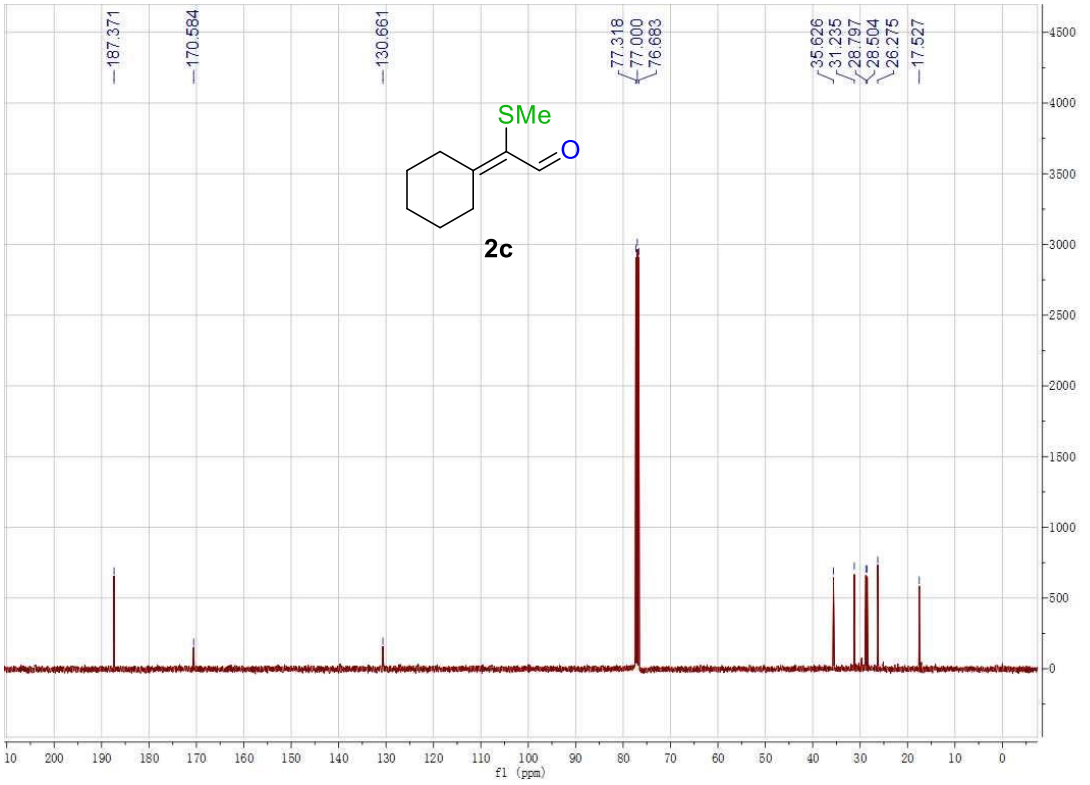

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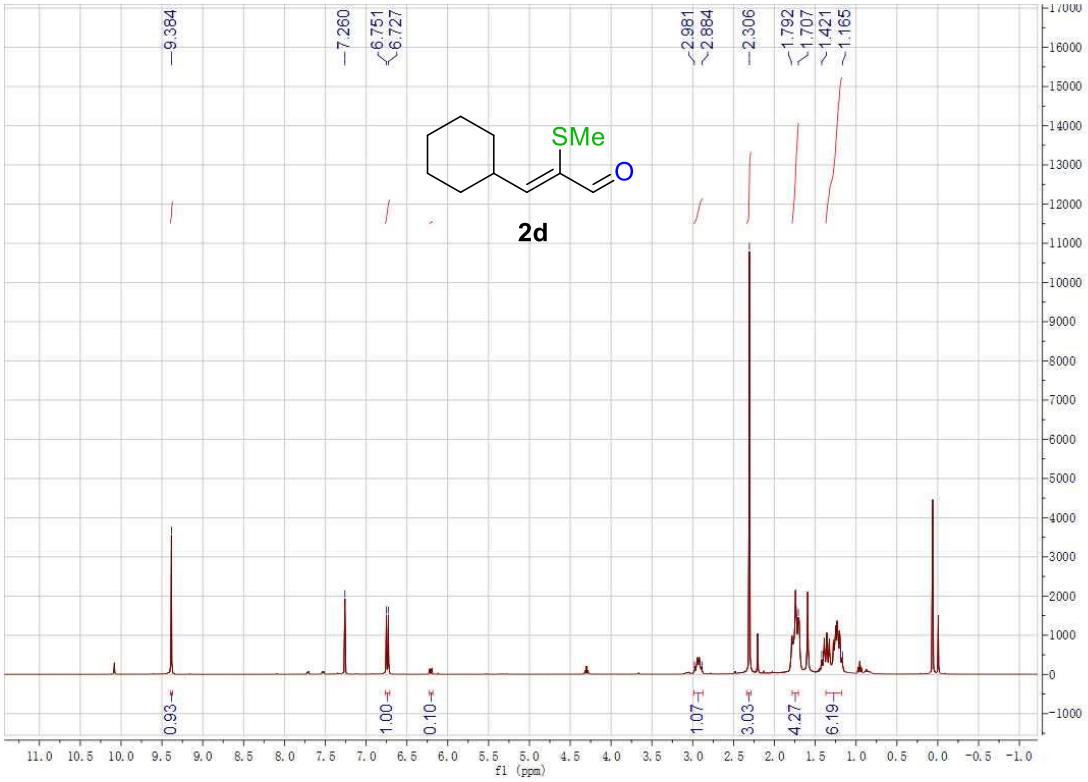

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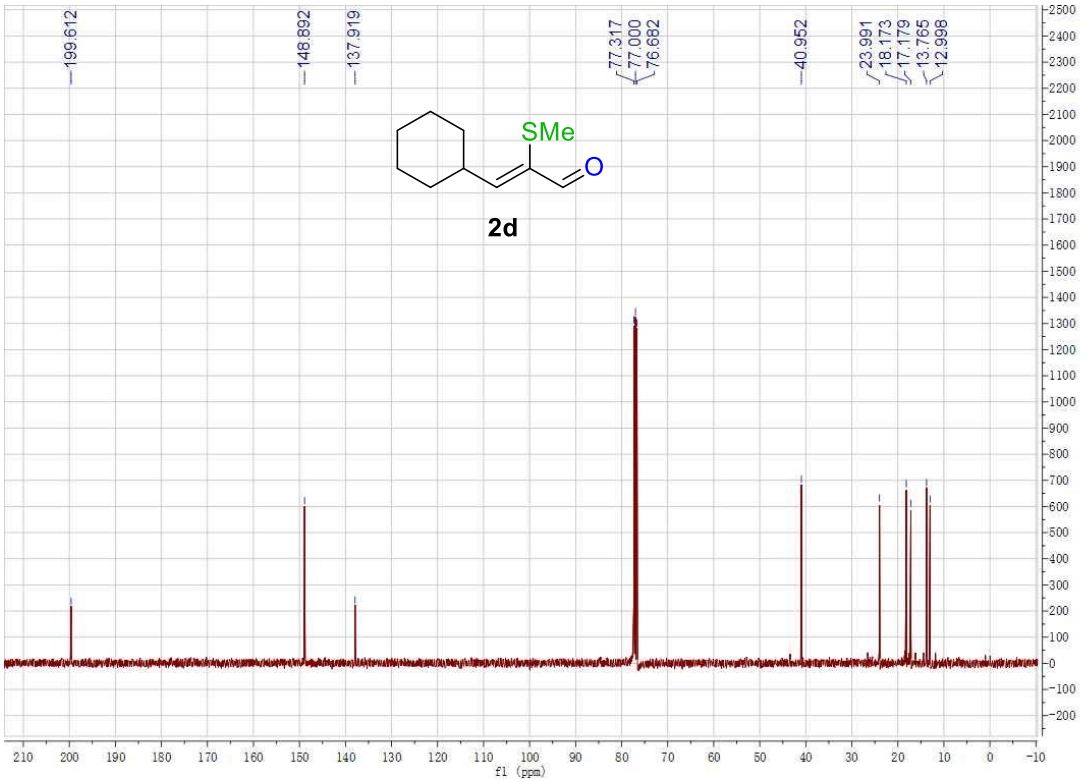

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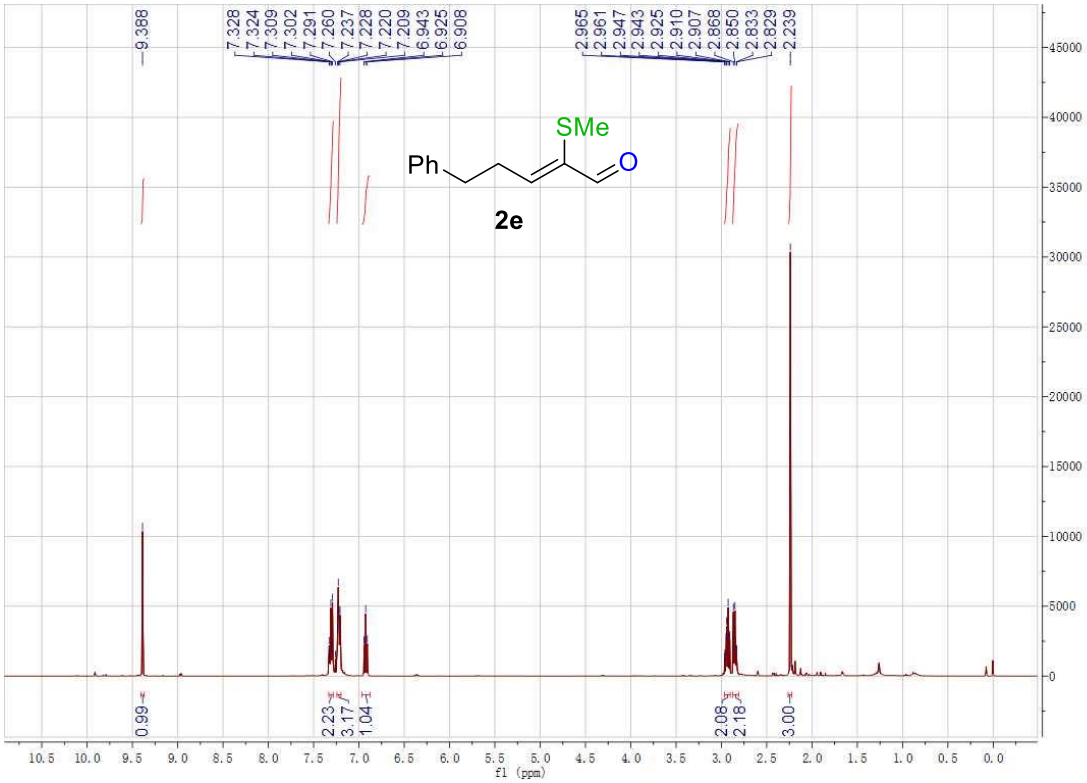
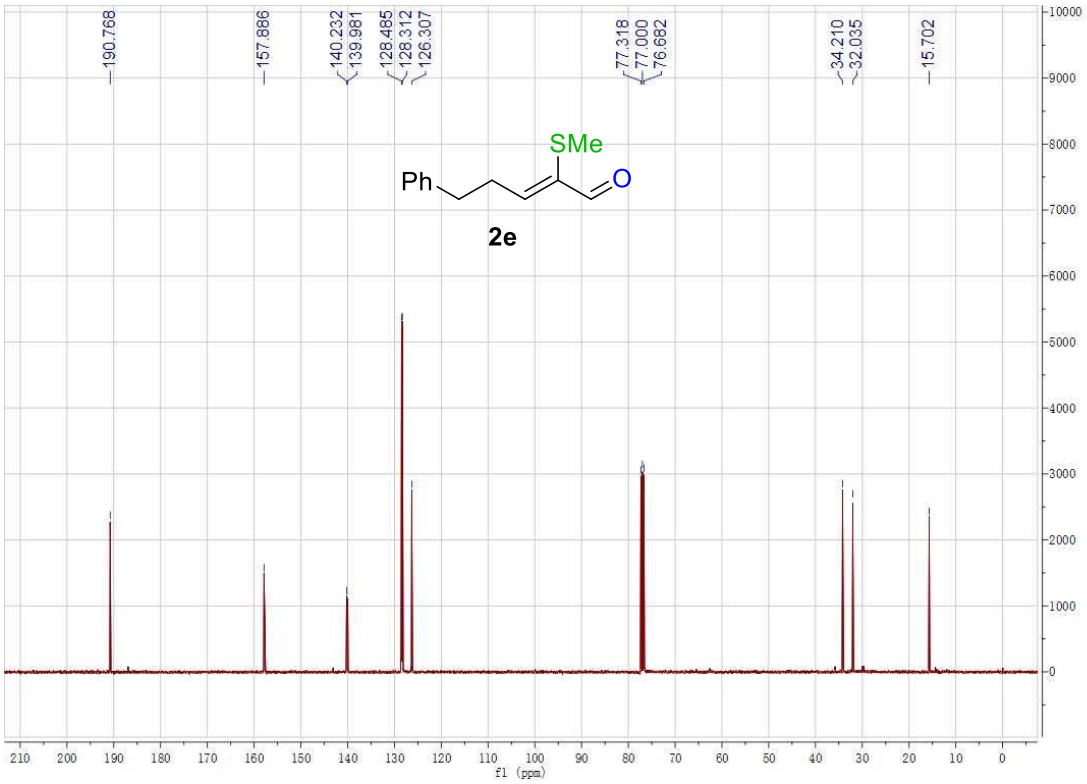
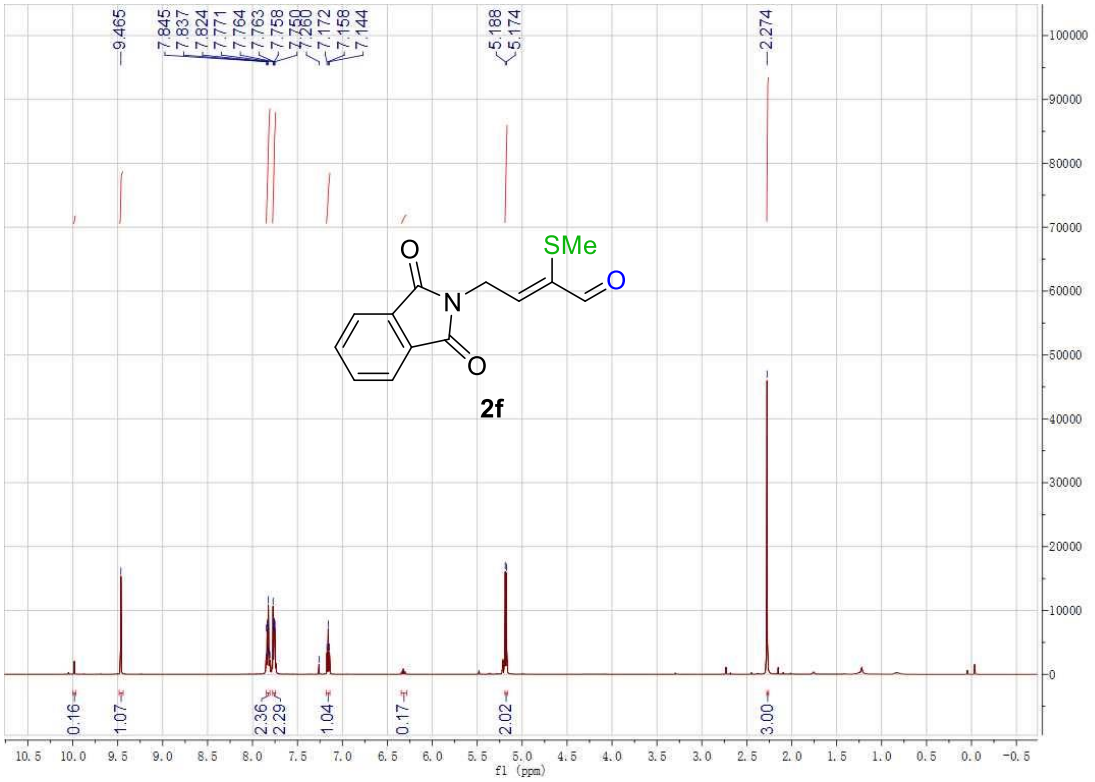


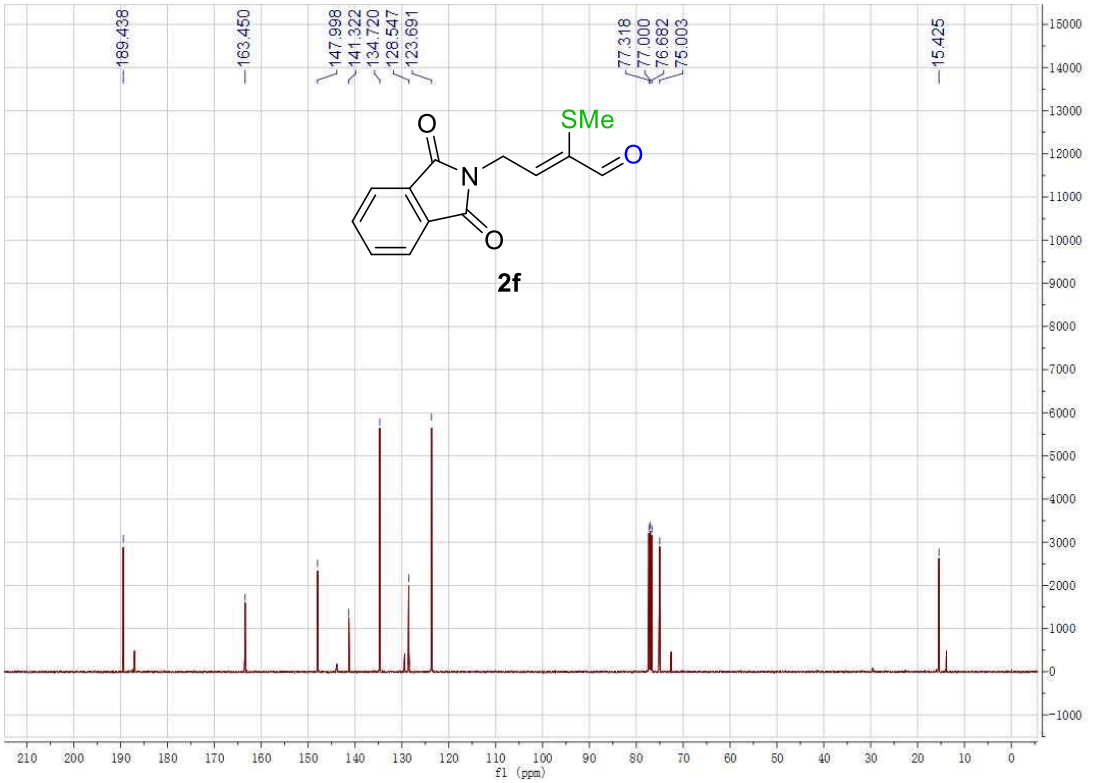
^{13}C NMR spectrum of 2e in $CDCl_3$, 101 MHz



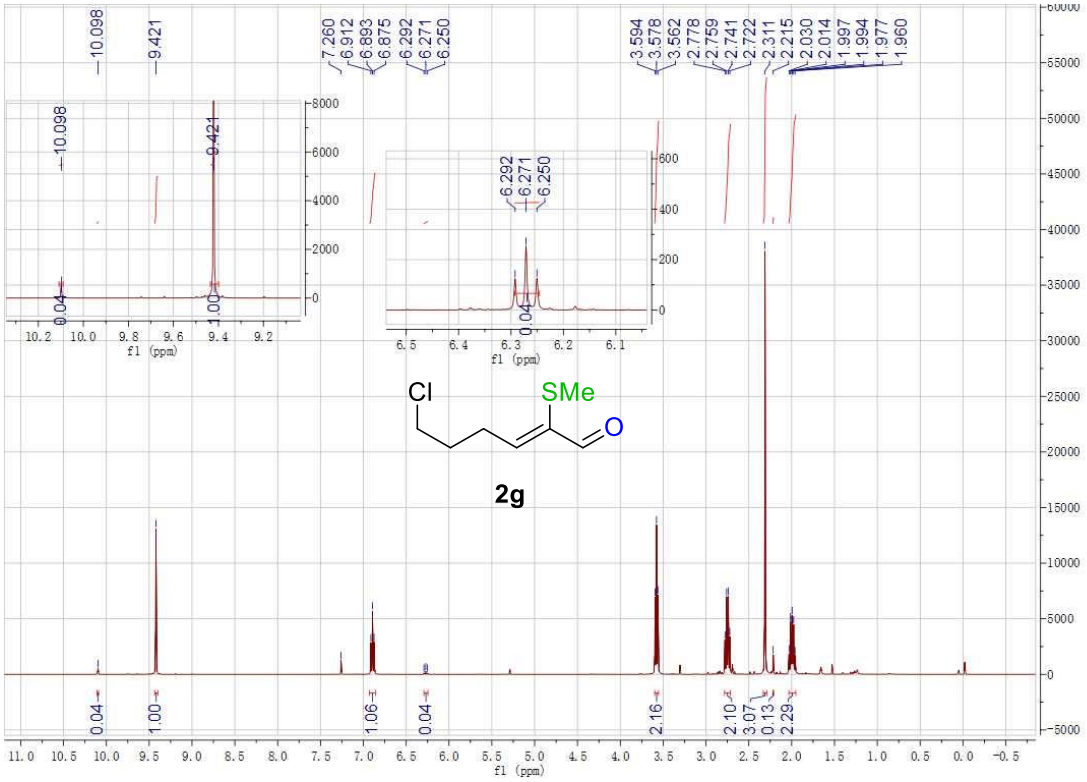
^{1}H NMR spectrum of 2f in $CDCl_3$, 400 MHz



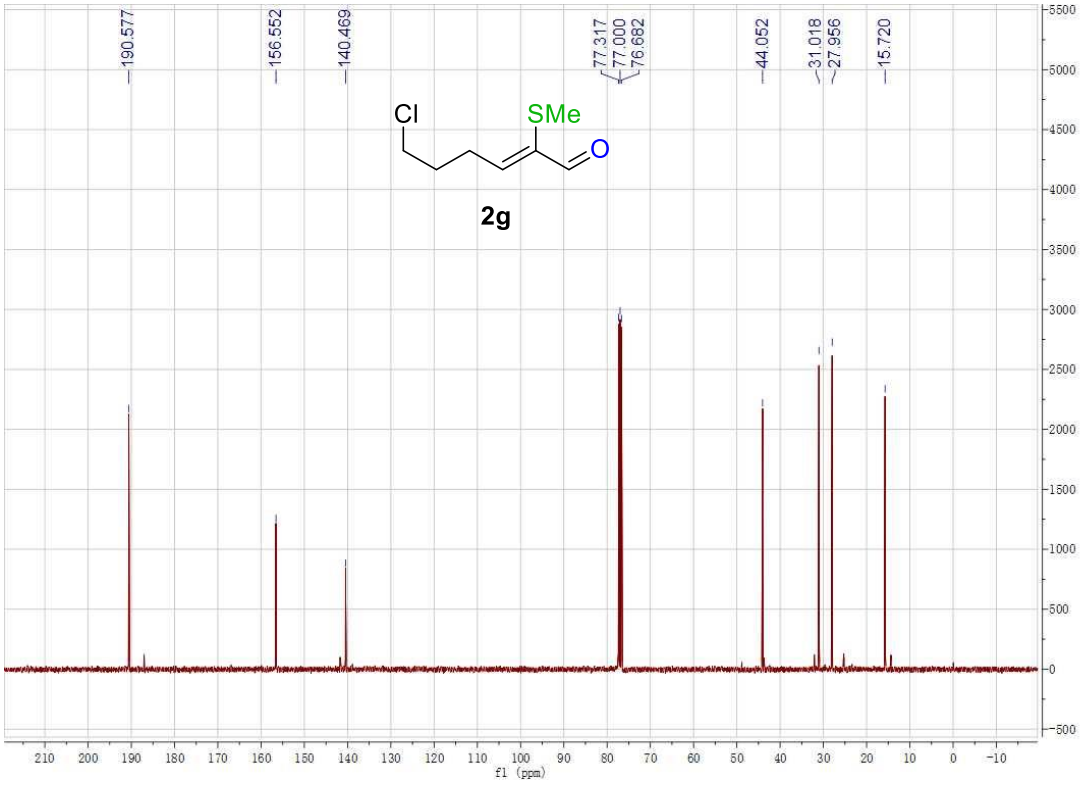
^{13}C NMR spectrum of 2f in $CDCl_3$, 101 MHz



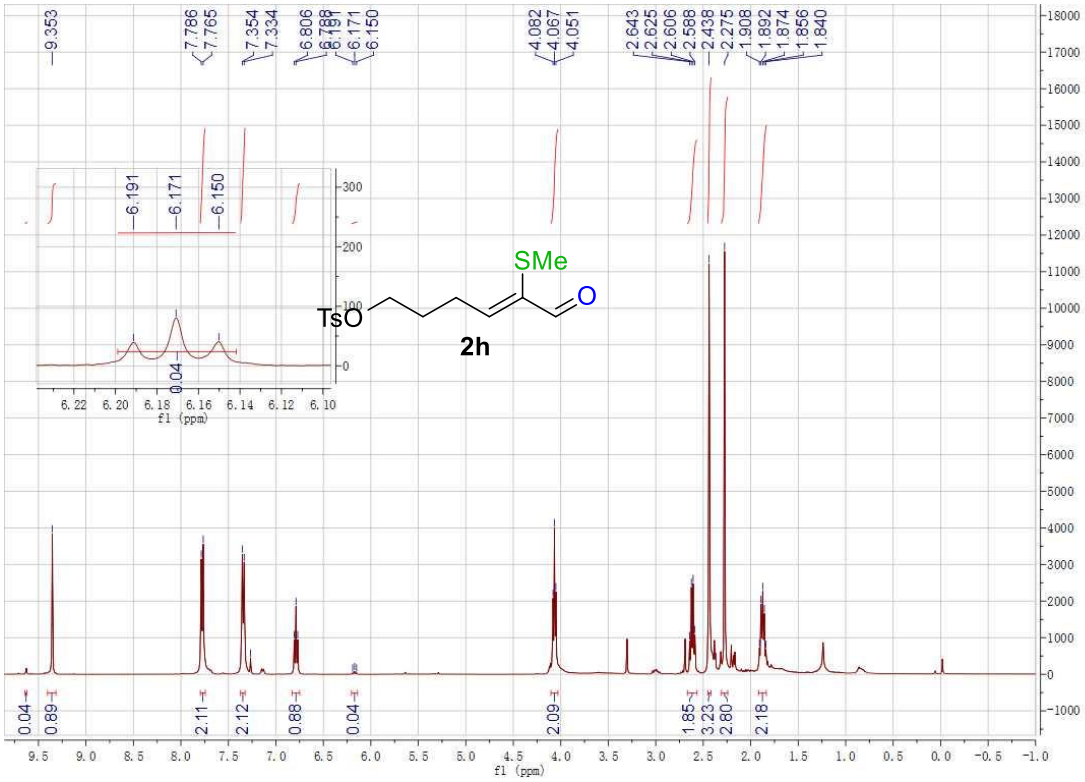
^{1}H NMR spectrum of 2g in $CDCl_3$, 400 MHz



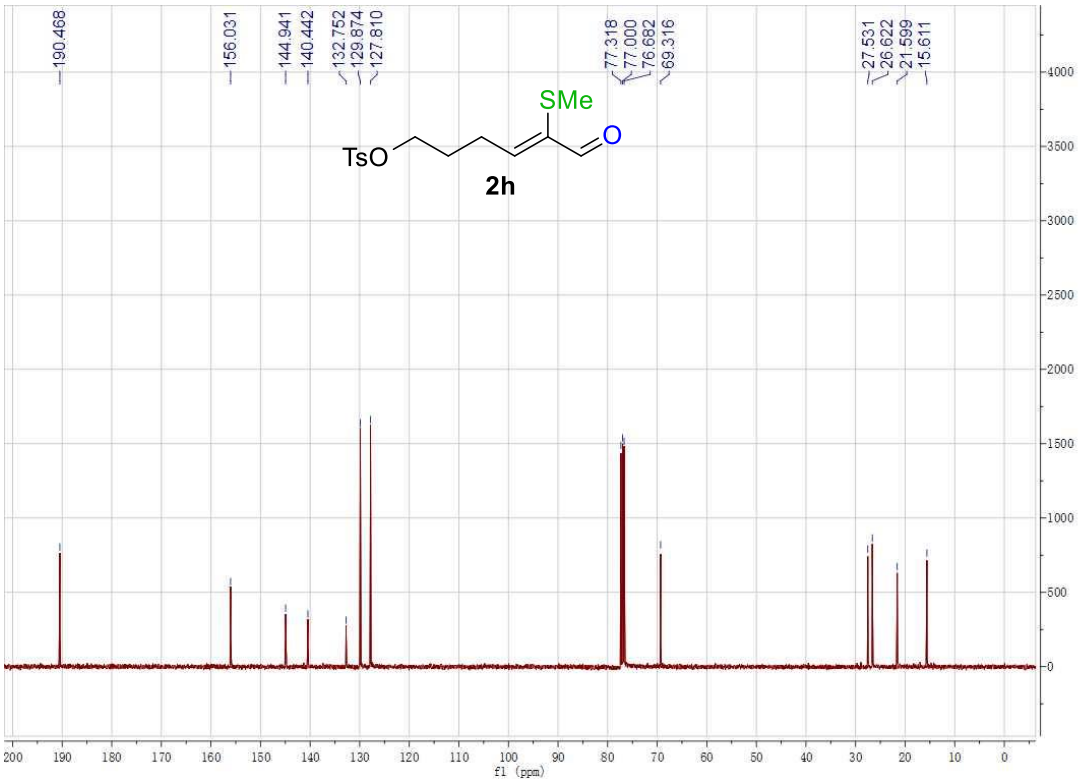
^{13}C NMR spectrum of 2g in $CDCl_3$, 101 MHz



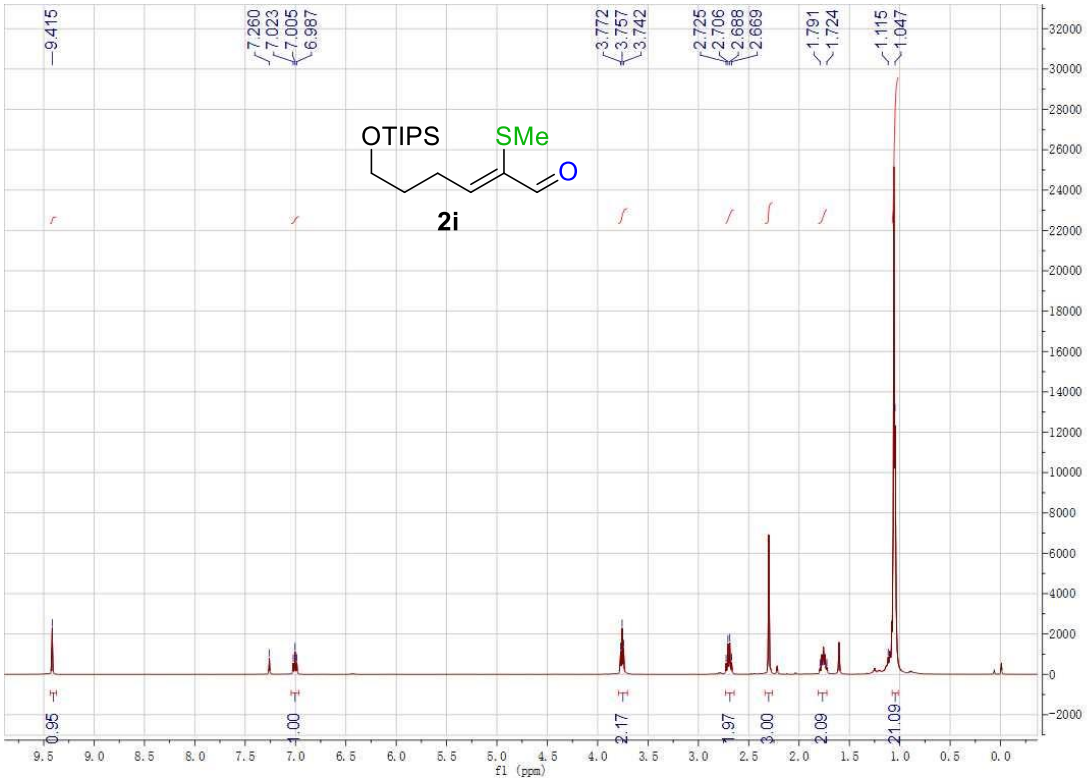
^{1}H NMR spectrum of 2h in $CDCl_3$, 400 MHz



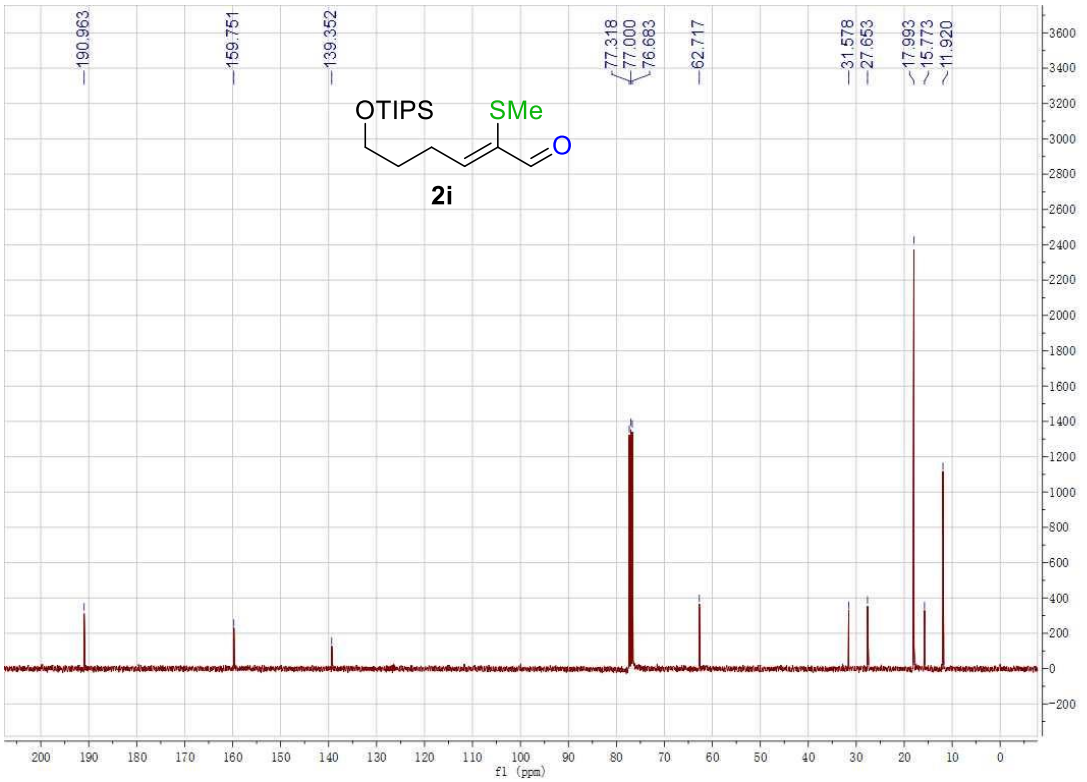
^{13}C NMR spectrum of 2h in $CDCl_3$, 101 MHz



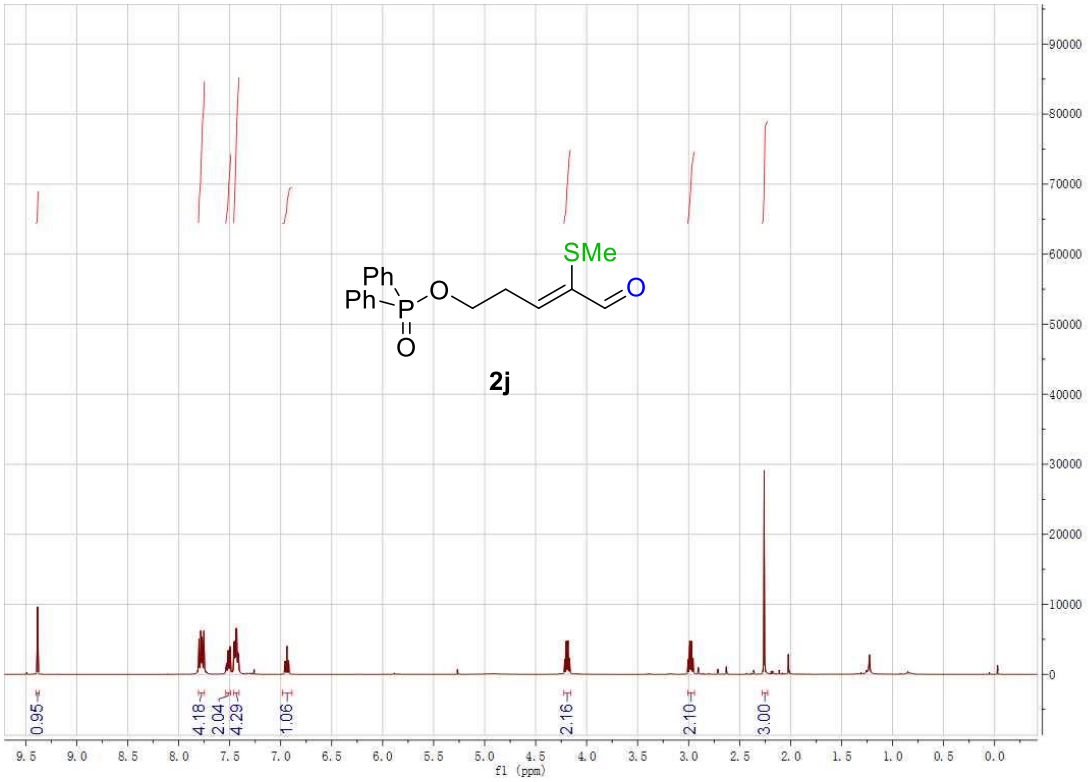
^{1}H NMR spectrum of 2i in $CDCl_3$, 400 MHz



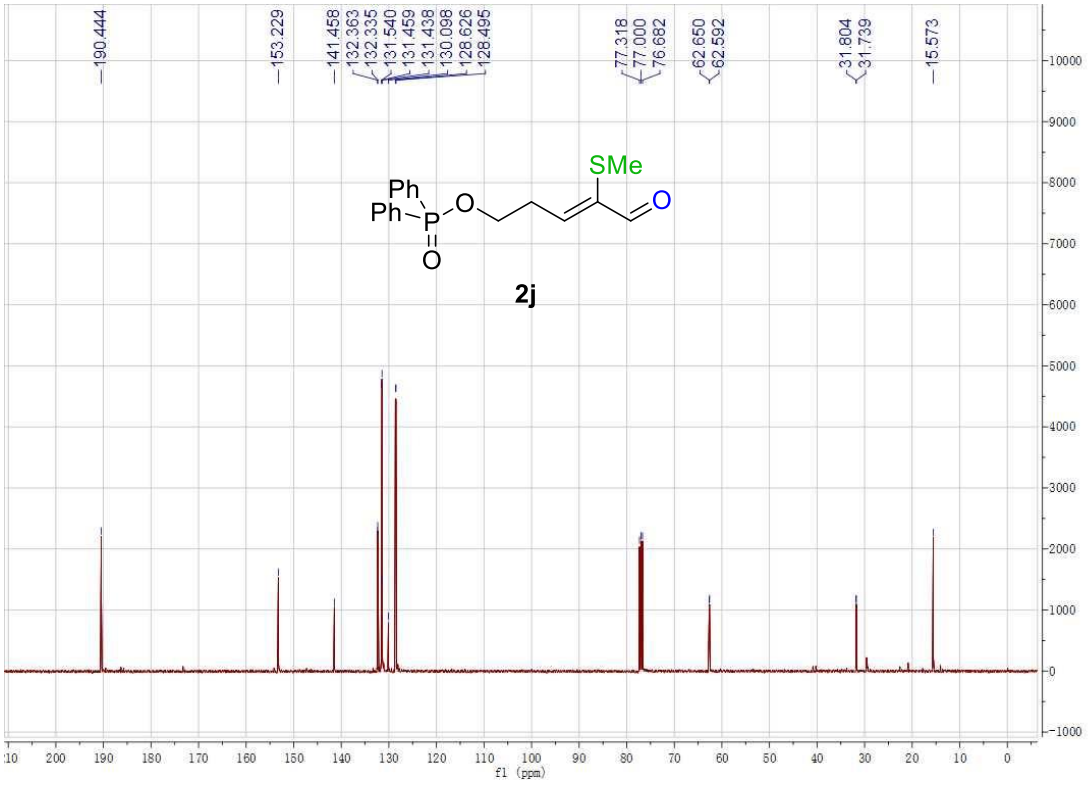
^{13}C NMR spectrum of 2i in $CDCl_3$, 101 MHz



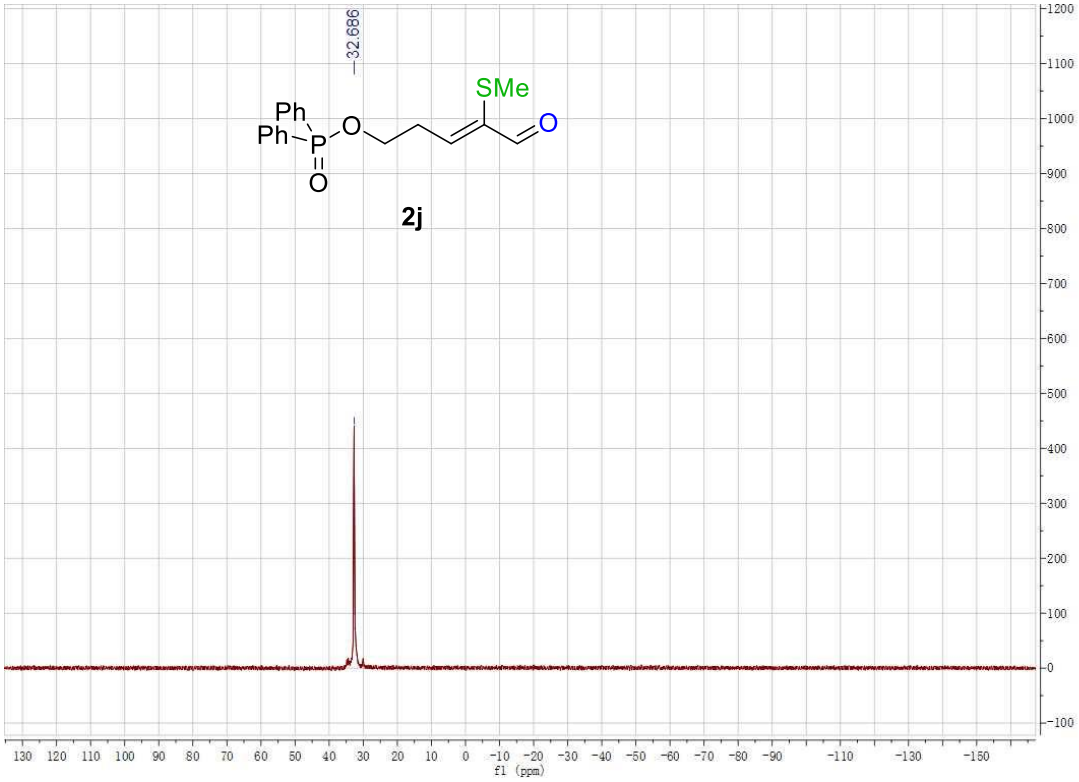
^{1}H NMR spectrum of 2j in $CDCl_3$, 400 MHz



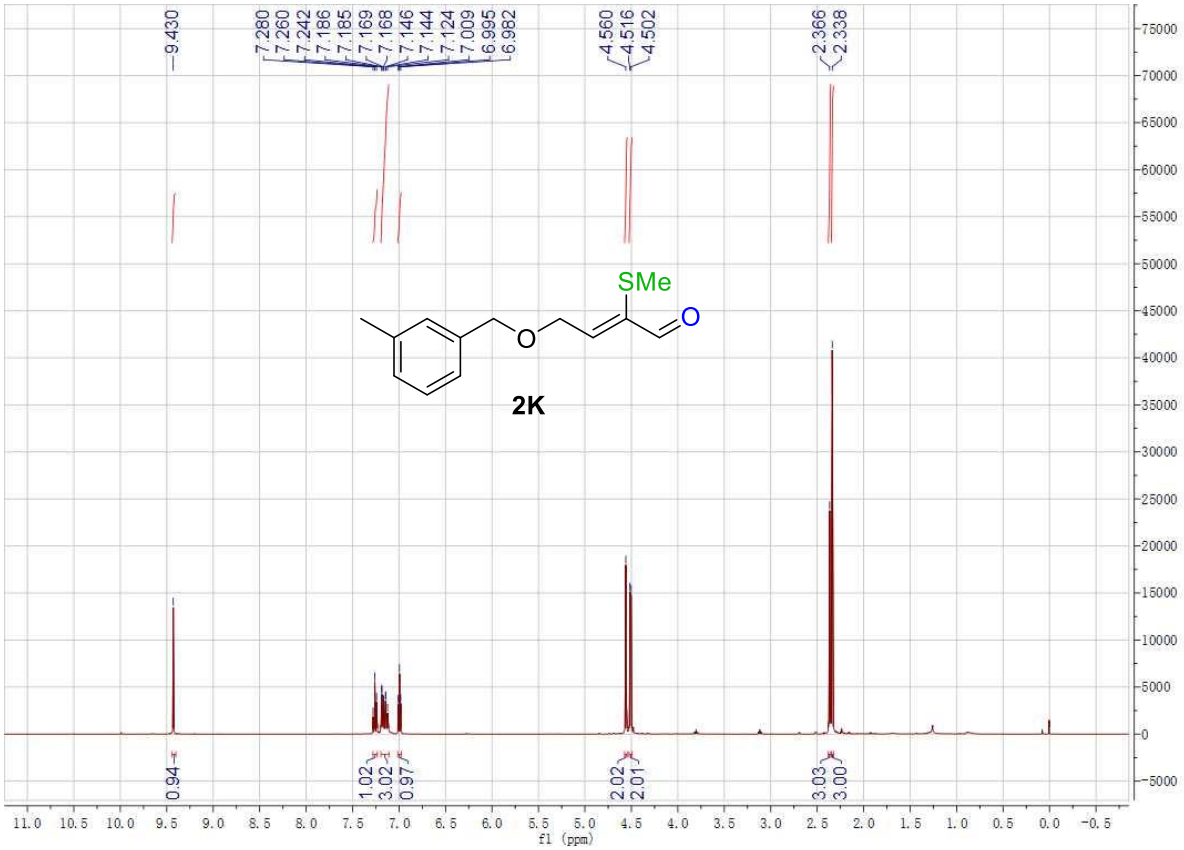
^{13}C NMR spectrum of 2j in $CDCl_3$, 101 MHz



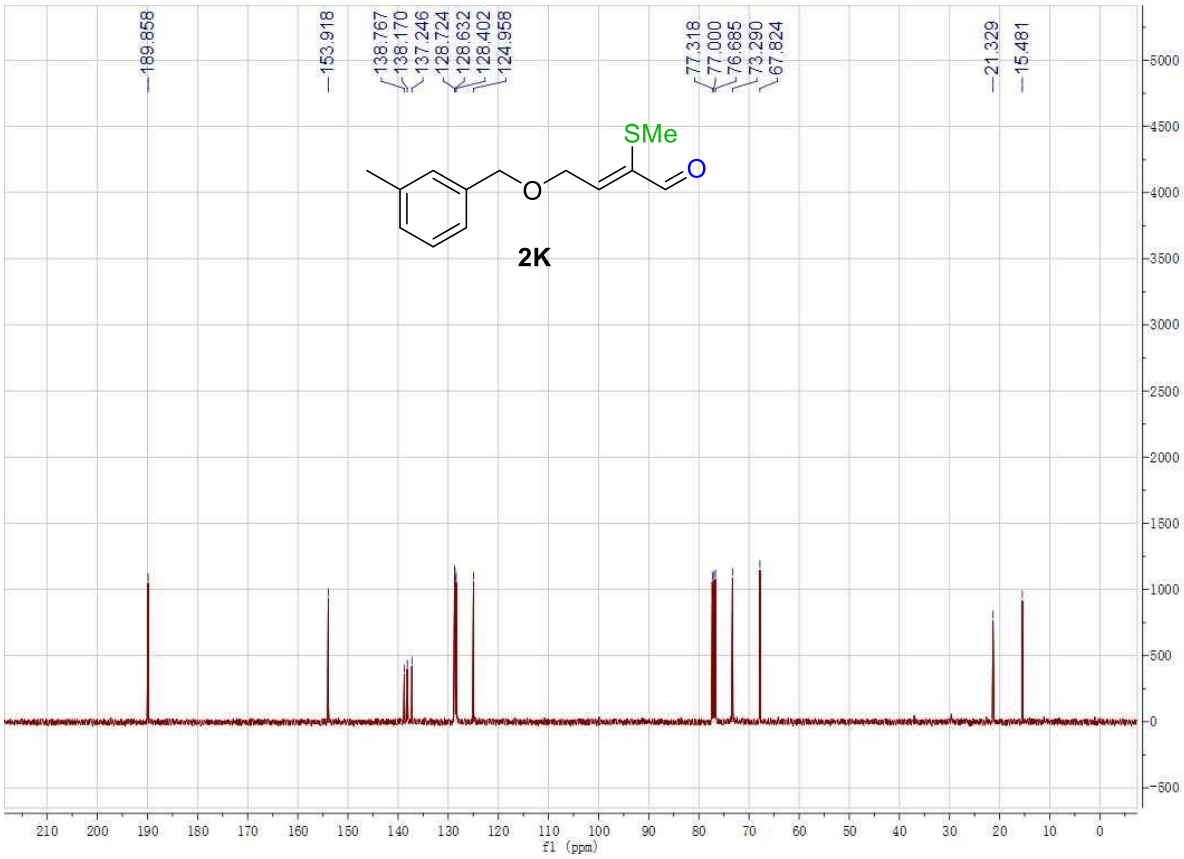
^{31}P NMR spectrum of 2j in $CDCl_3$, 162 MHz



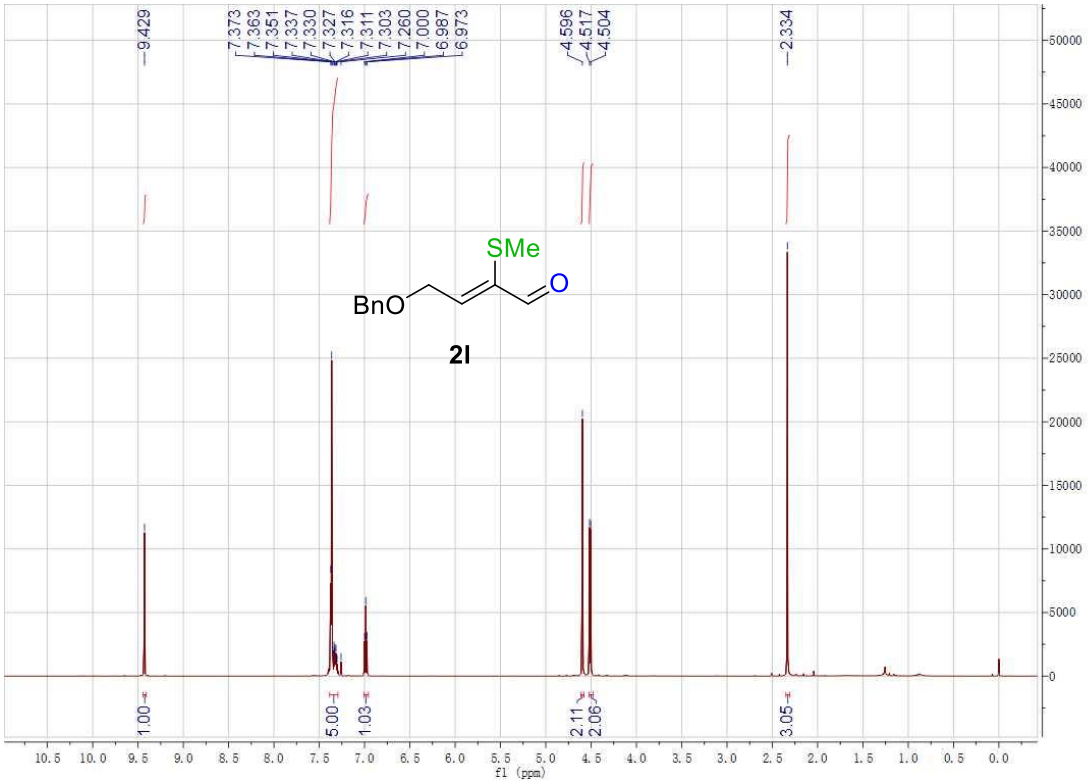
^{1}H NMR spectrum of 2k in $CDCl_3$, 400 MHz



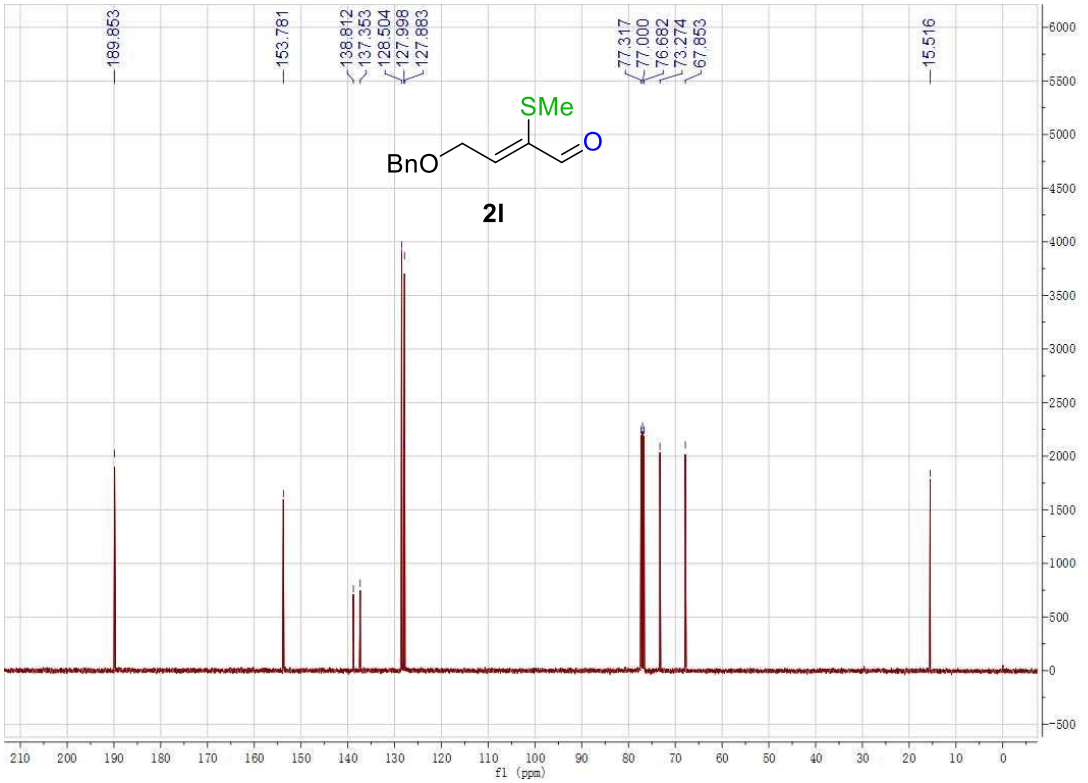
^{13}C NMR spectrum of 2k in $CDCl_3$, 101 MHz



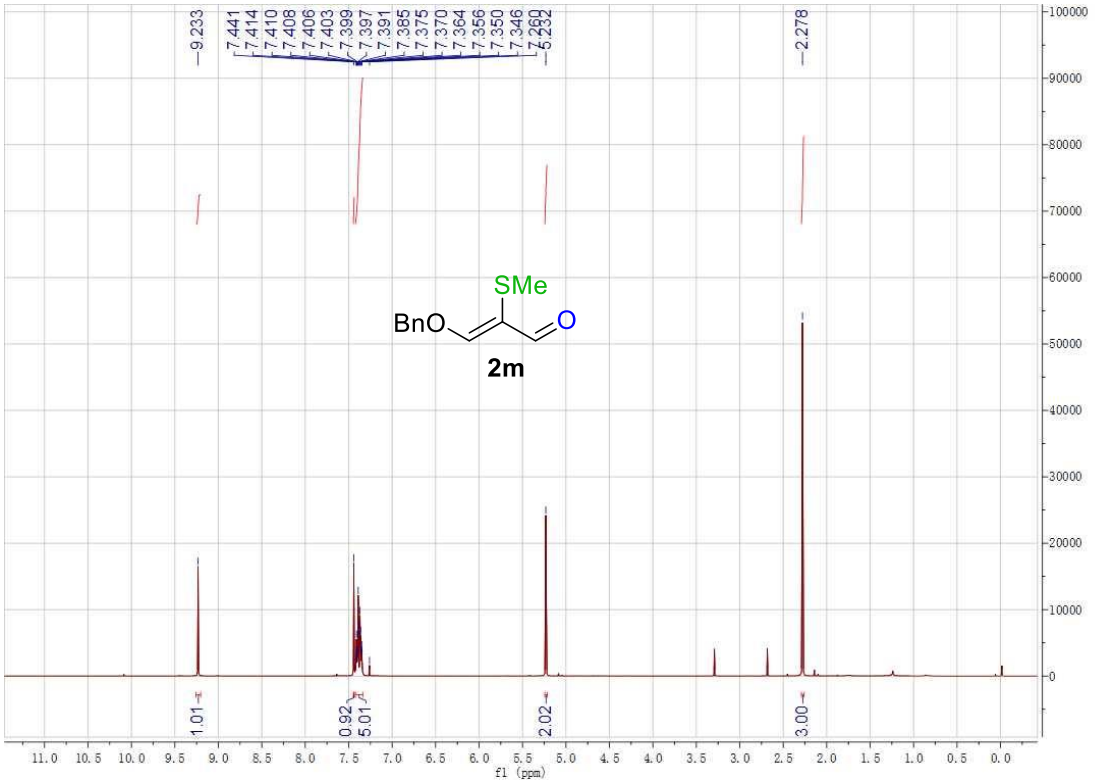
^{1}H NMR spectrum of 2l in $CDCl_3$, 400 MHz



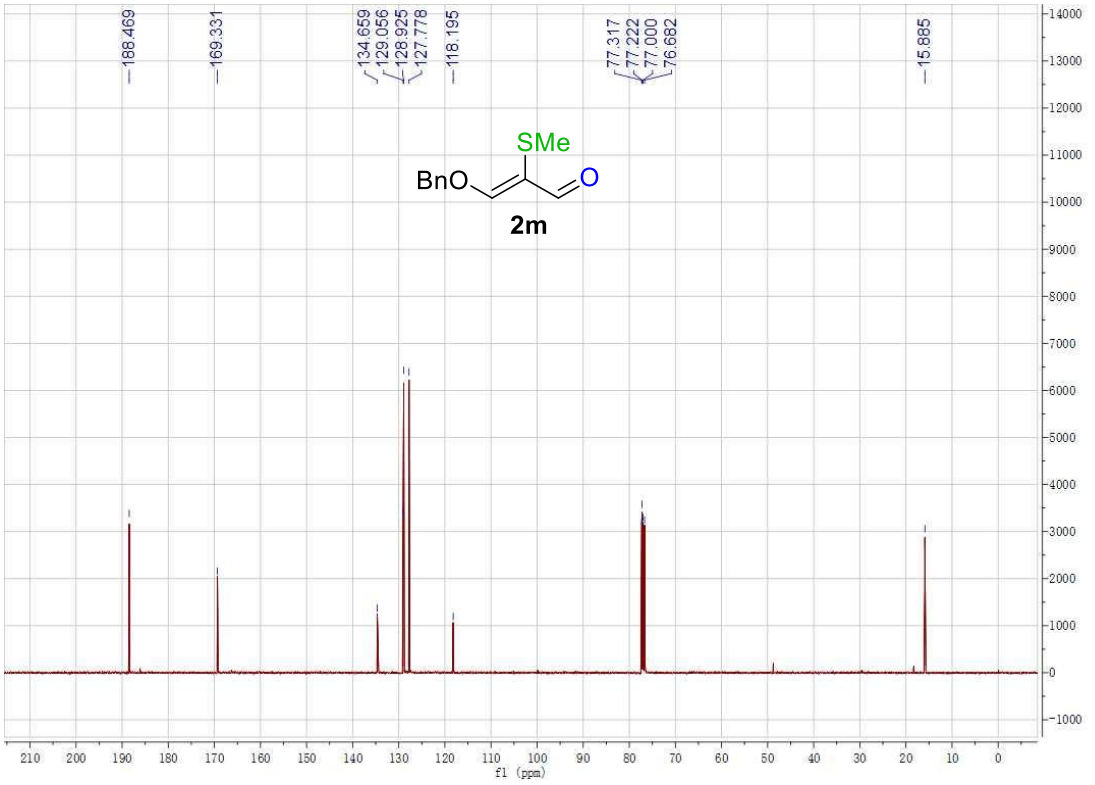
^{13}C NMR spectrum of 2l in $CDCl_3$, 101 MHz



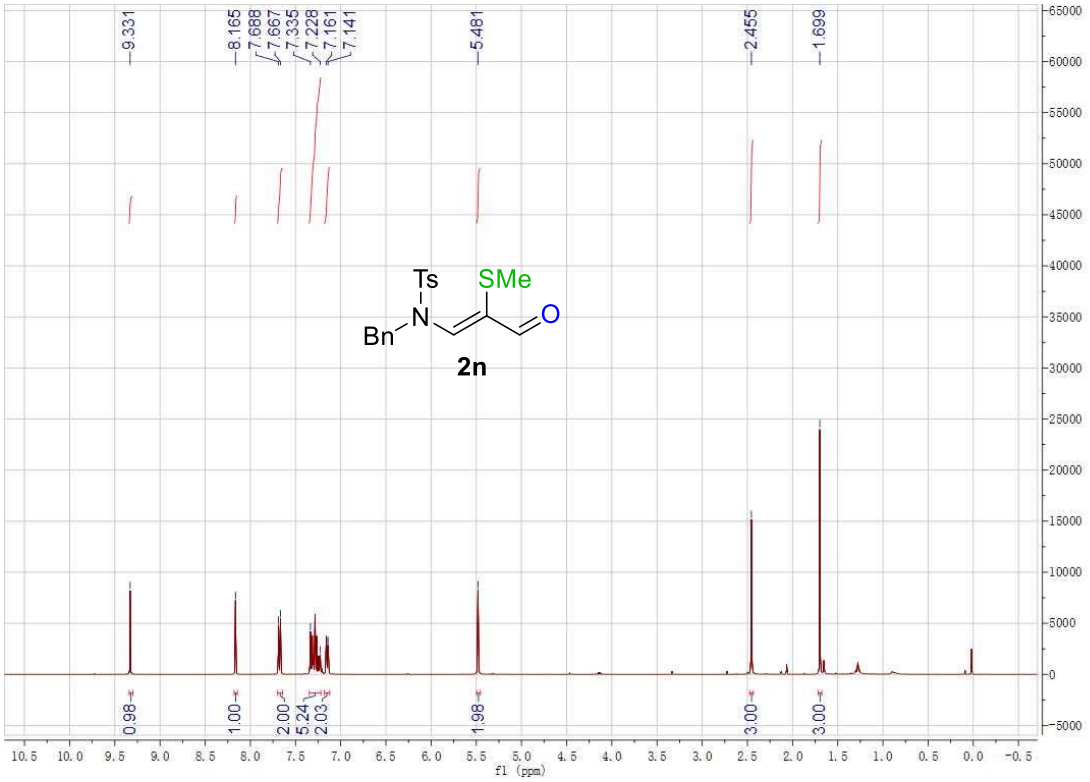
^{1}H NMR spectrum of 2m in $CDCl_3$, 400 MHz



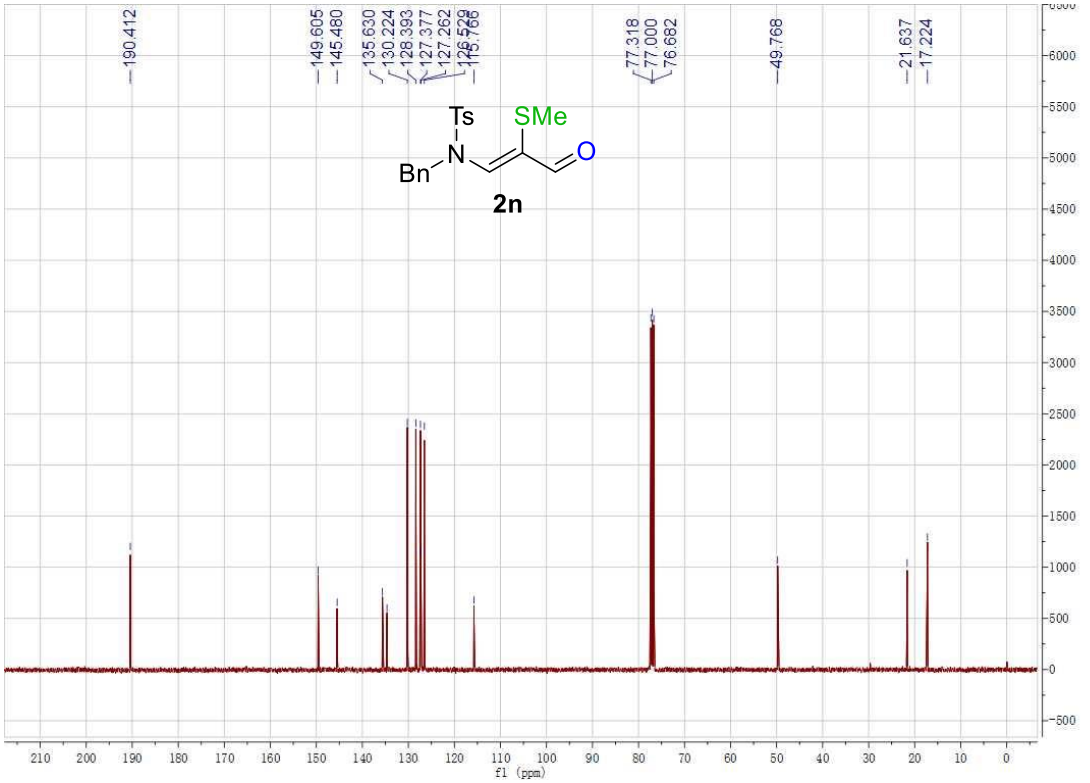
^{13}C NMR spectrum of 2m in $CDCl_3$, 101 MHz



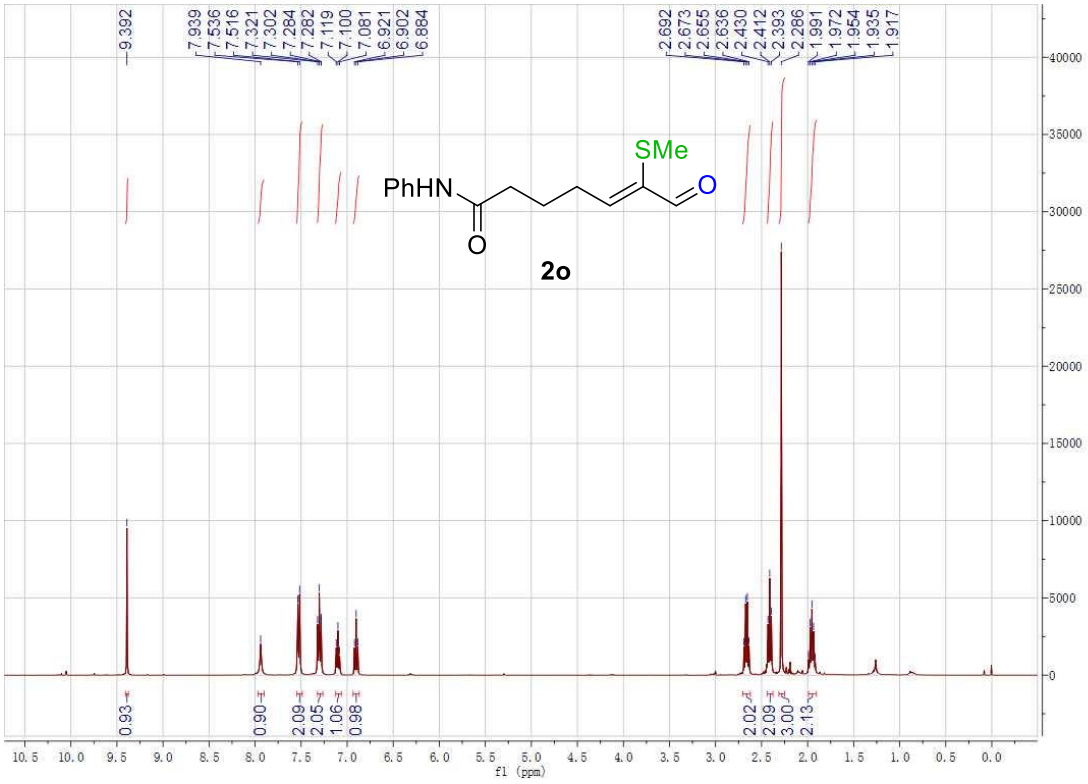
^{1}H NMR spectrum of 2n in $CDCl_3$, 400 MHz



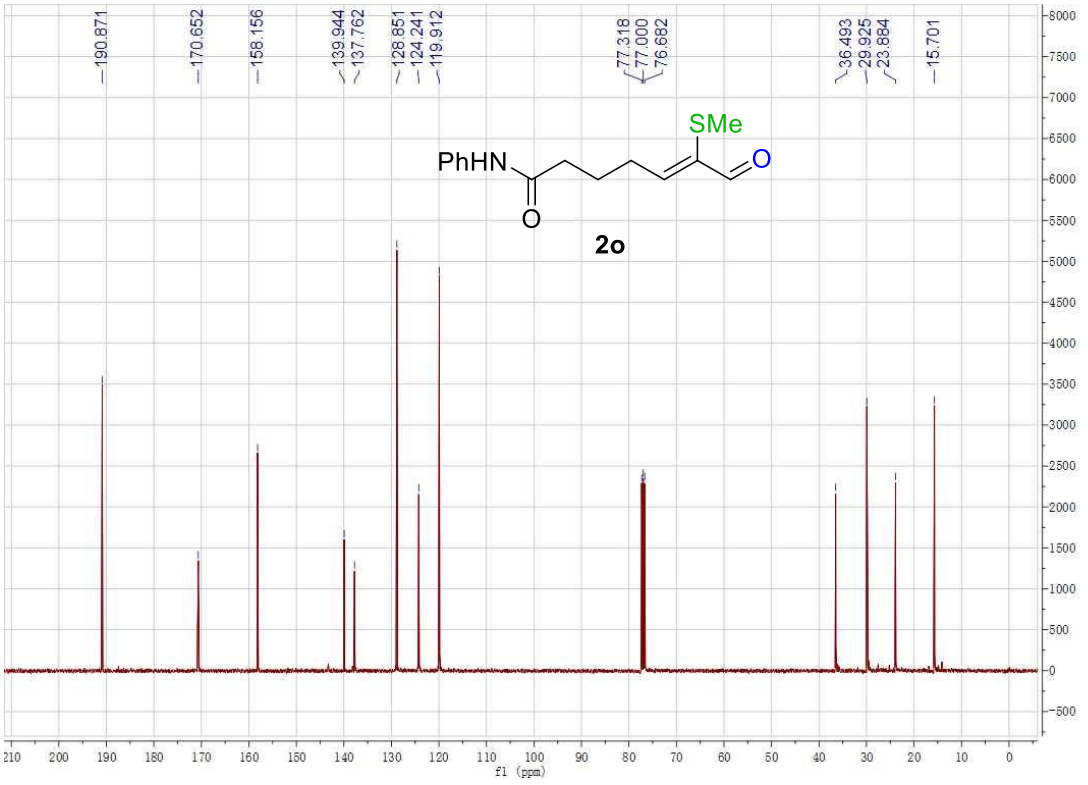
^{13}C NMR spectrum of 2n in $CDCl_3$, 101 MHz



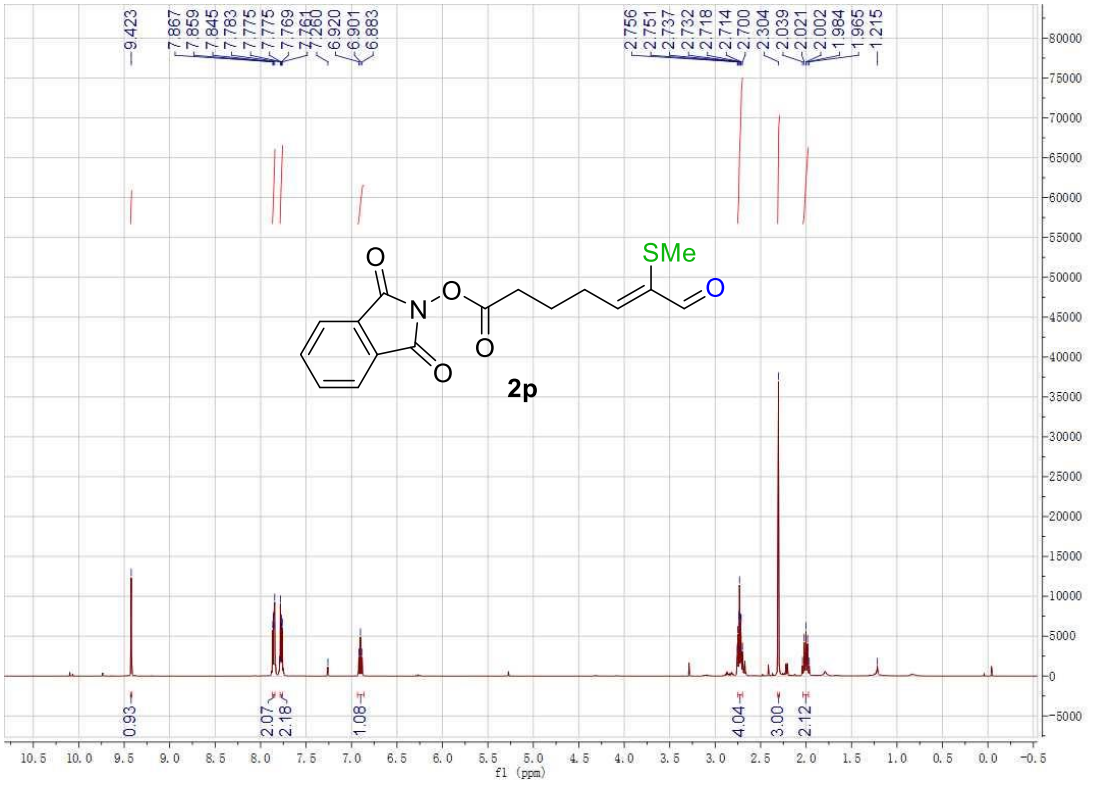
^{1}H NMR spectrum of 2o in $CDCl_3$, 400 MHz



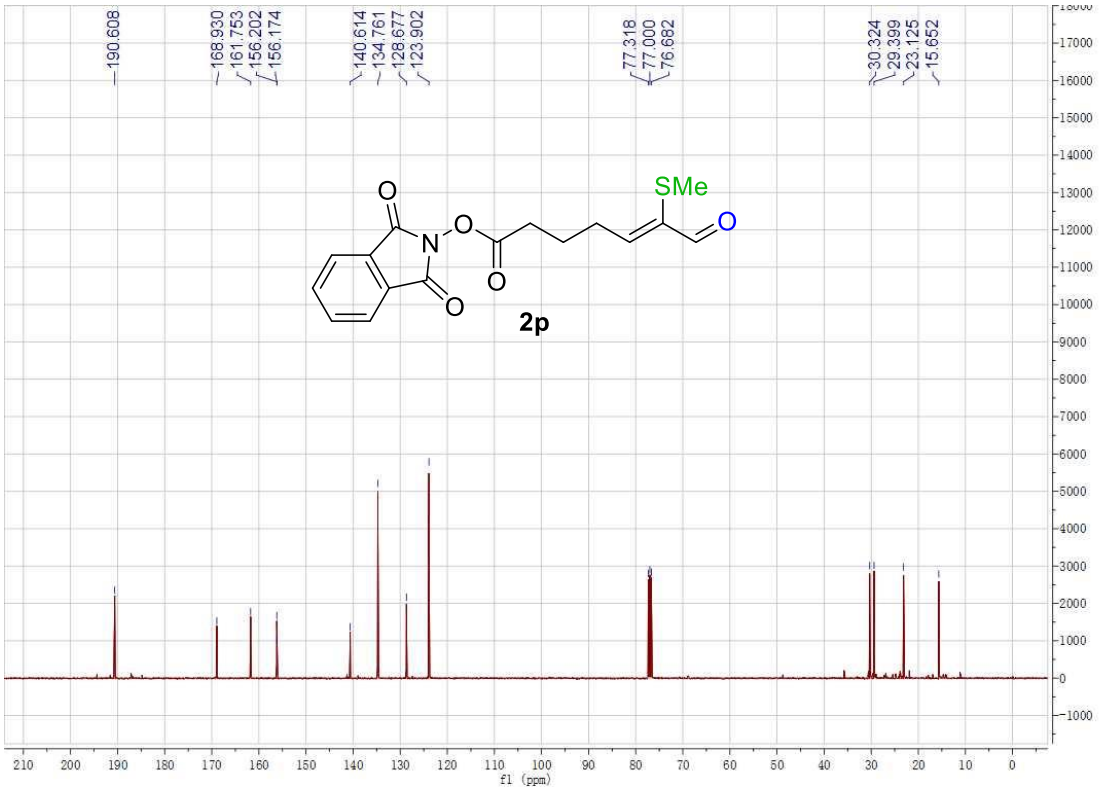
^{13}C NMR spectrum of 2o in $CDCl_3$, 101 MHz



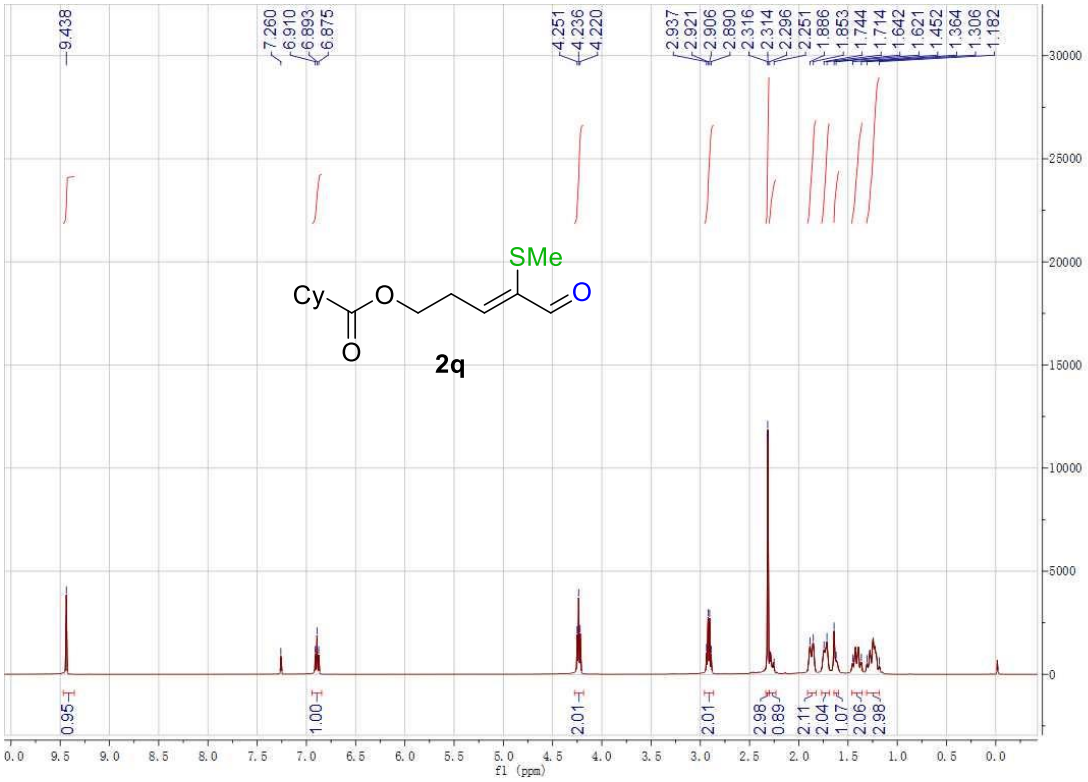
^{1}H NMR spectrum of 2p in $CDCl_3$, 400 MHz



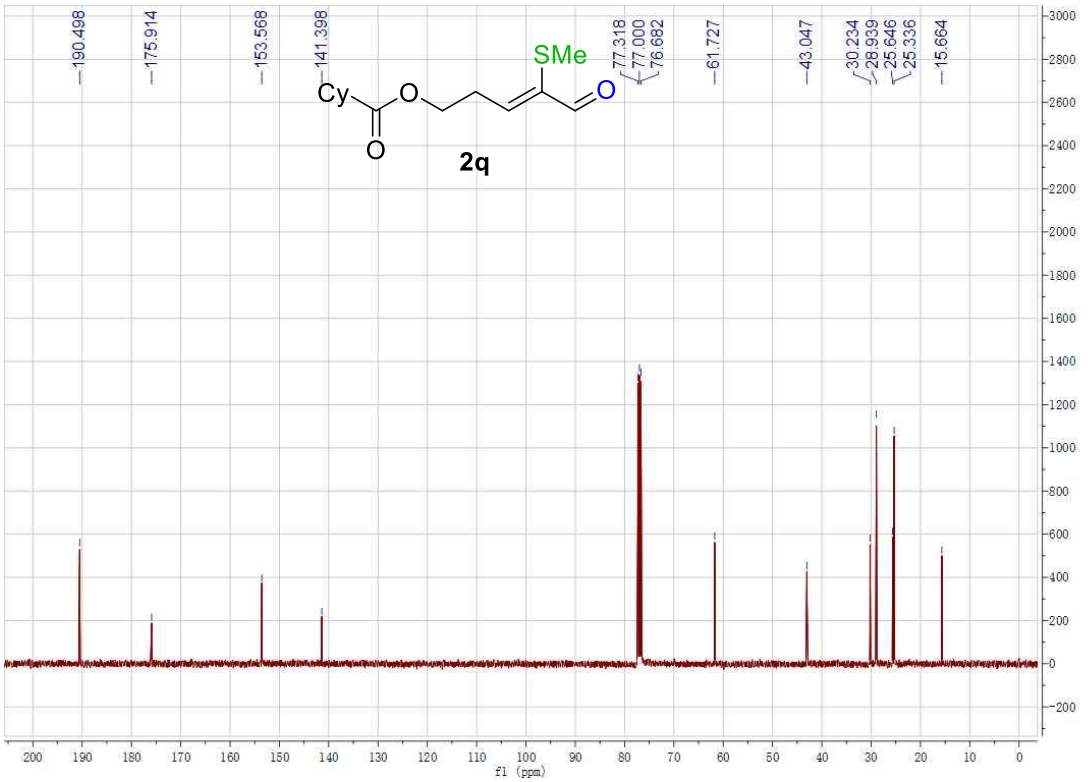
^{13}C NMR spectrum of 2p in $CDCl_3$, 101 MHz



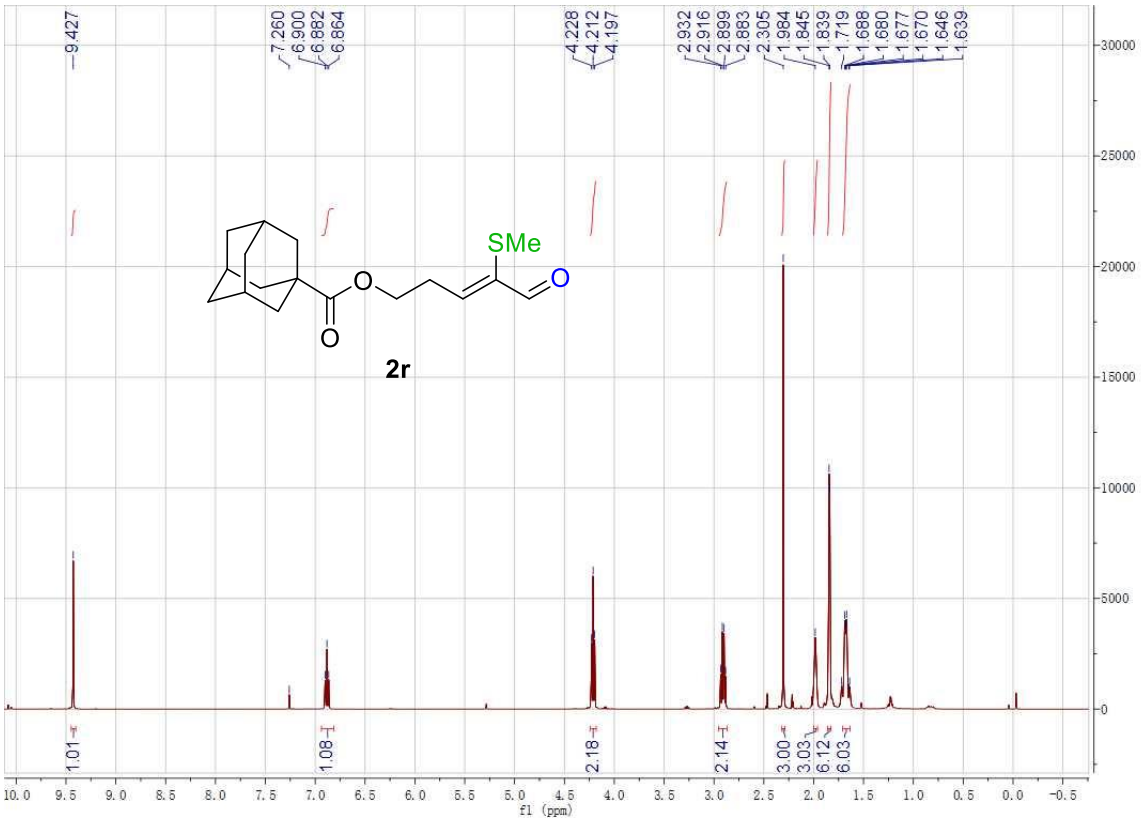
^{1}H NMR spectrum of 2q in $CDCl_3$, 400 MHz



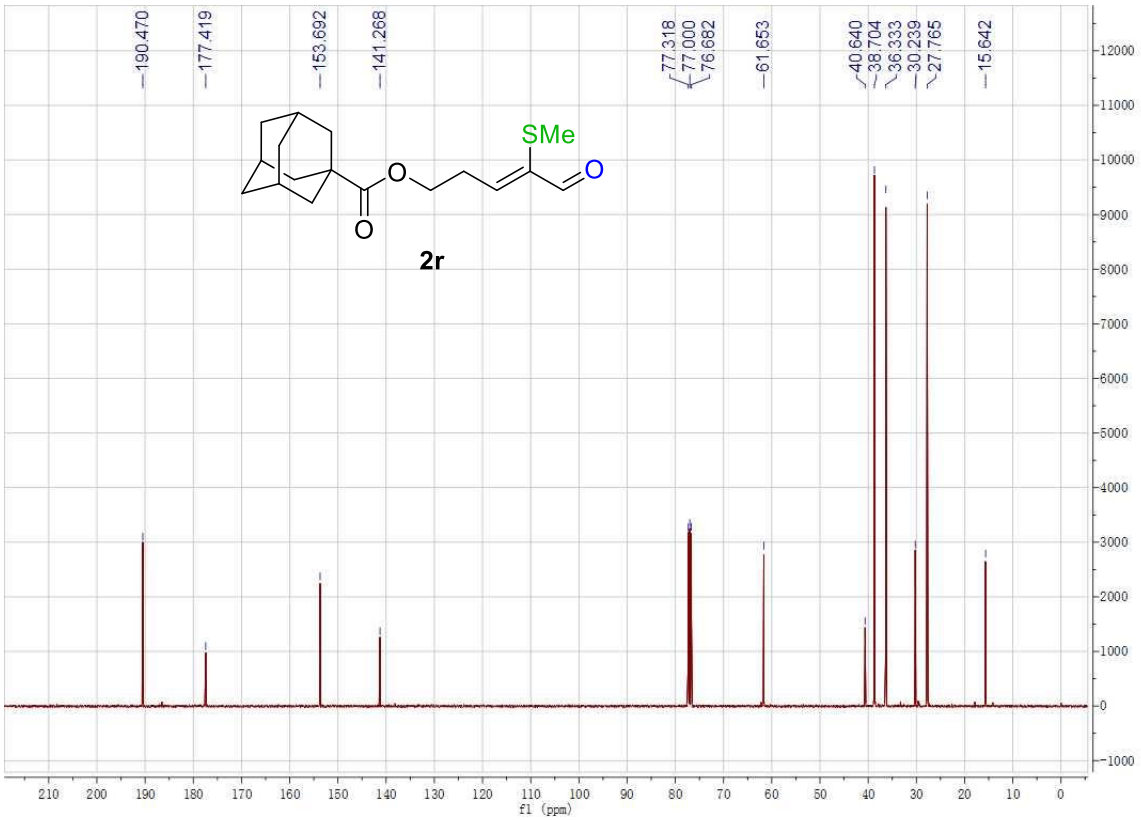
^{13}C NMR spectrum of 2q in $CDCl_3$, 101 MHz



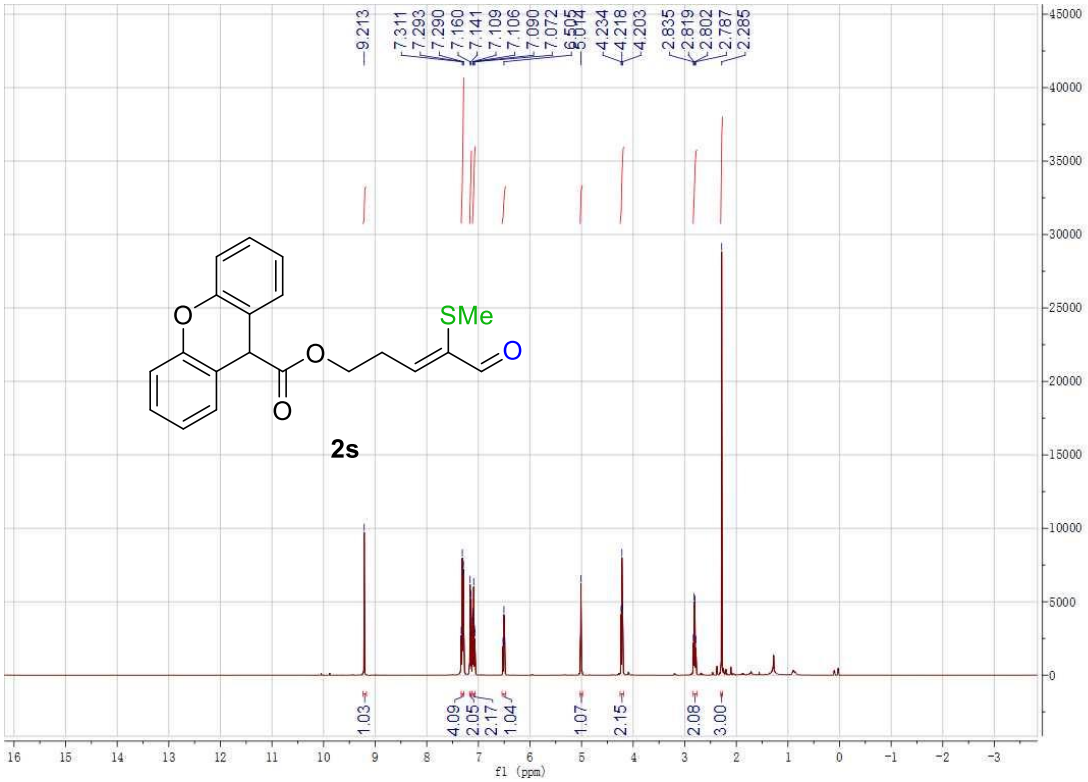
^{1}H NMR spectrum of 2r in $CDCl_3$, 400 MHz



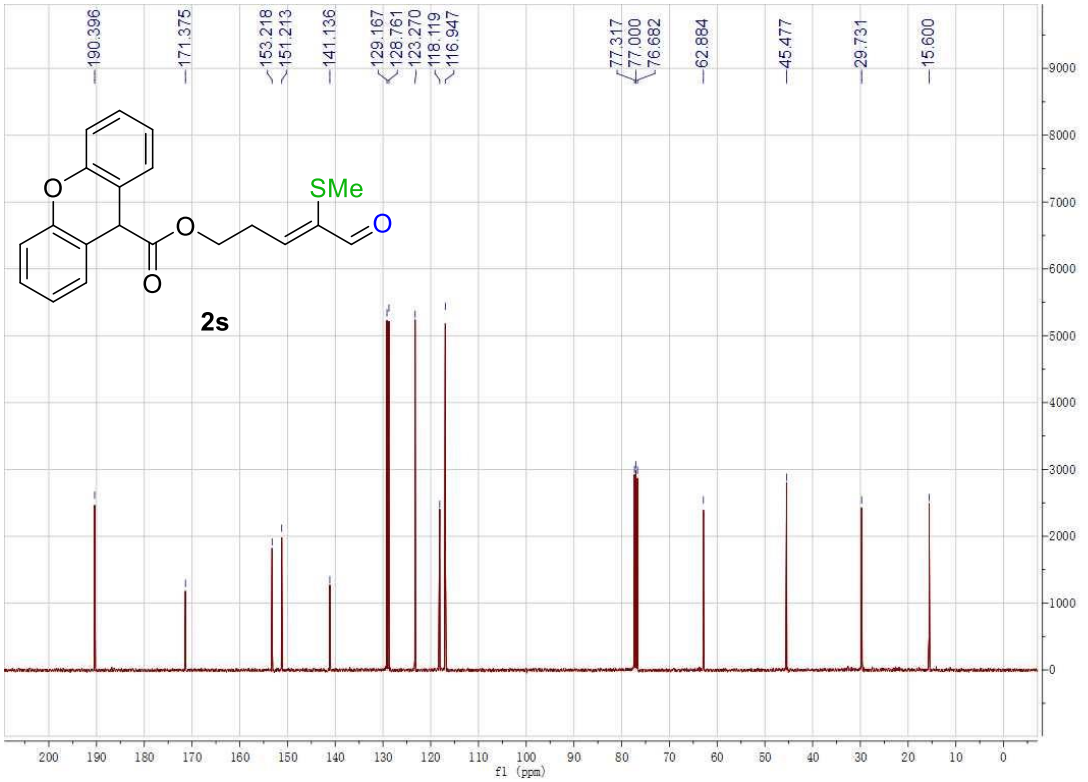
^{13}C NMR spectrum of 2r in $CDCl_3$, 101 MHz



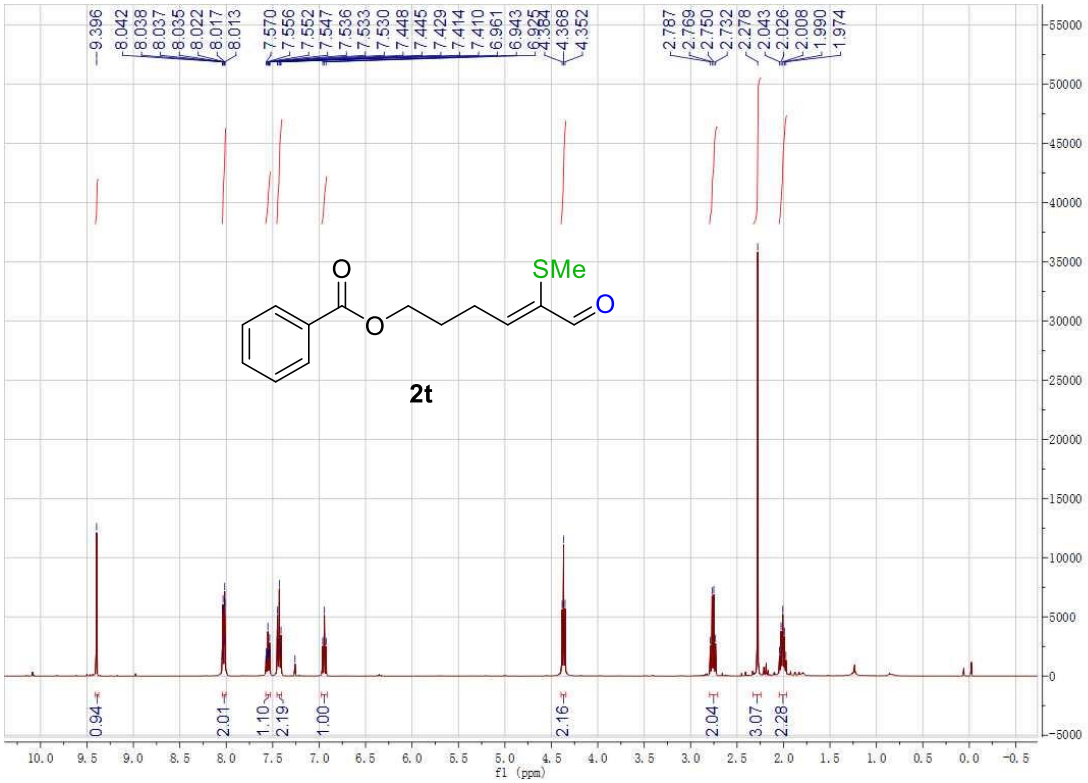
^{1}H NMR spectrum of 2s in $CDCl_3$, 400 MHz



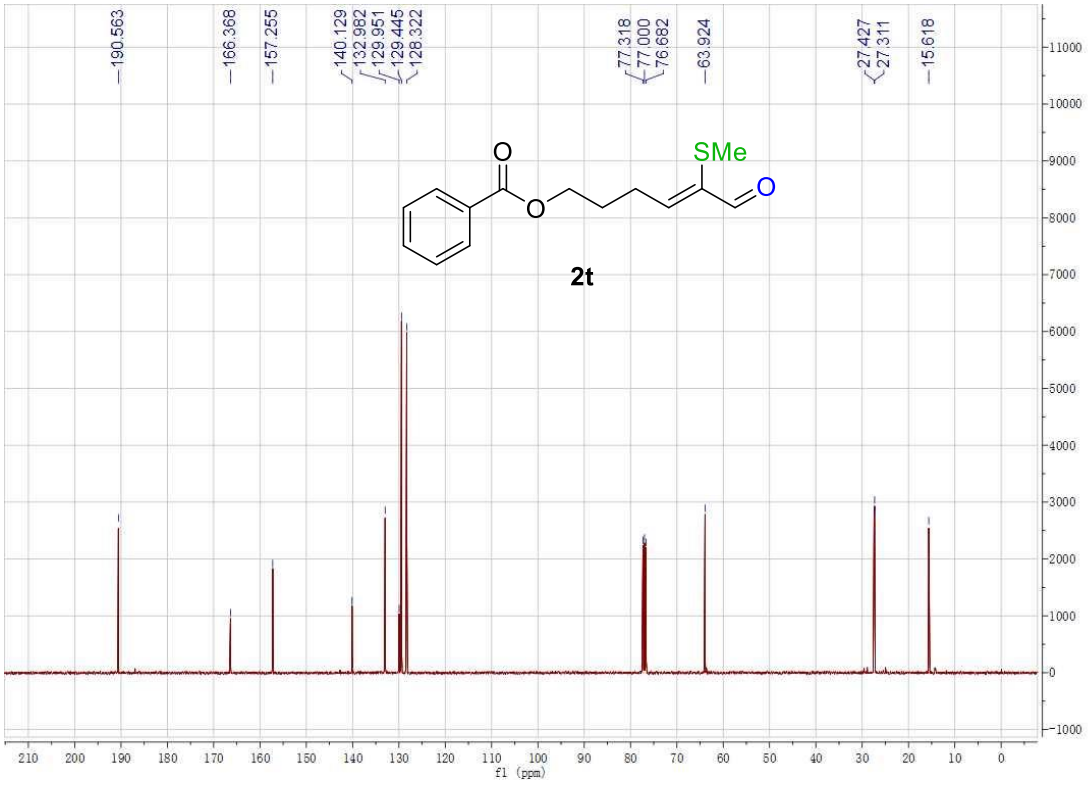
^{13}C NMR spectrum of 2s in $CDCl_3$, 101 MHz



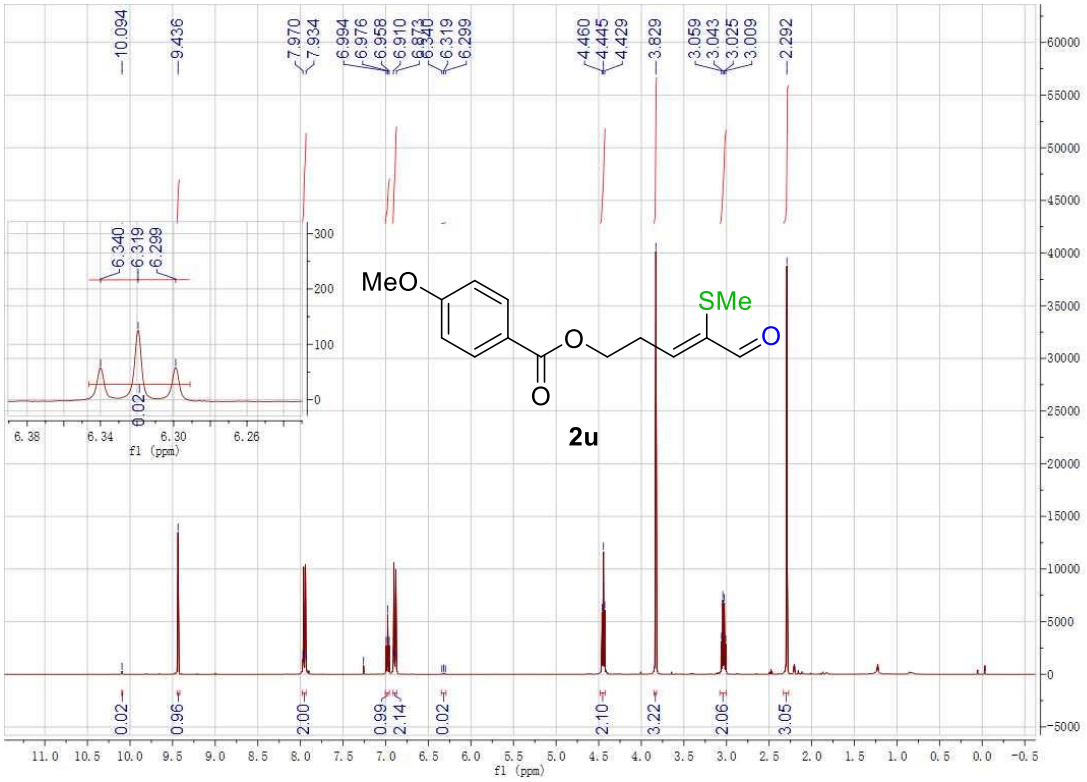
^{1}H NMR spectrum of 2t in $CDCl_3$, 400 MHz



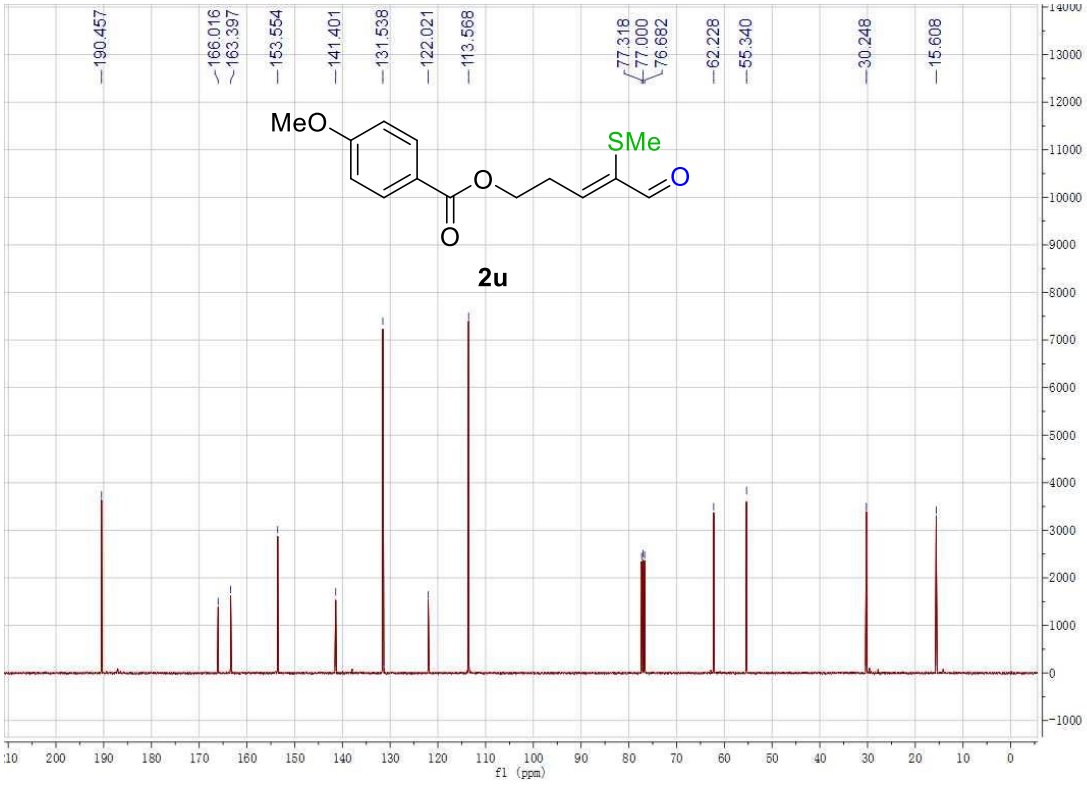
^{13}C NMR spectrum of 2t in $CDCl_3$, 101 MHz



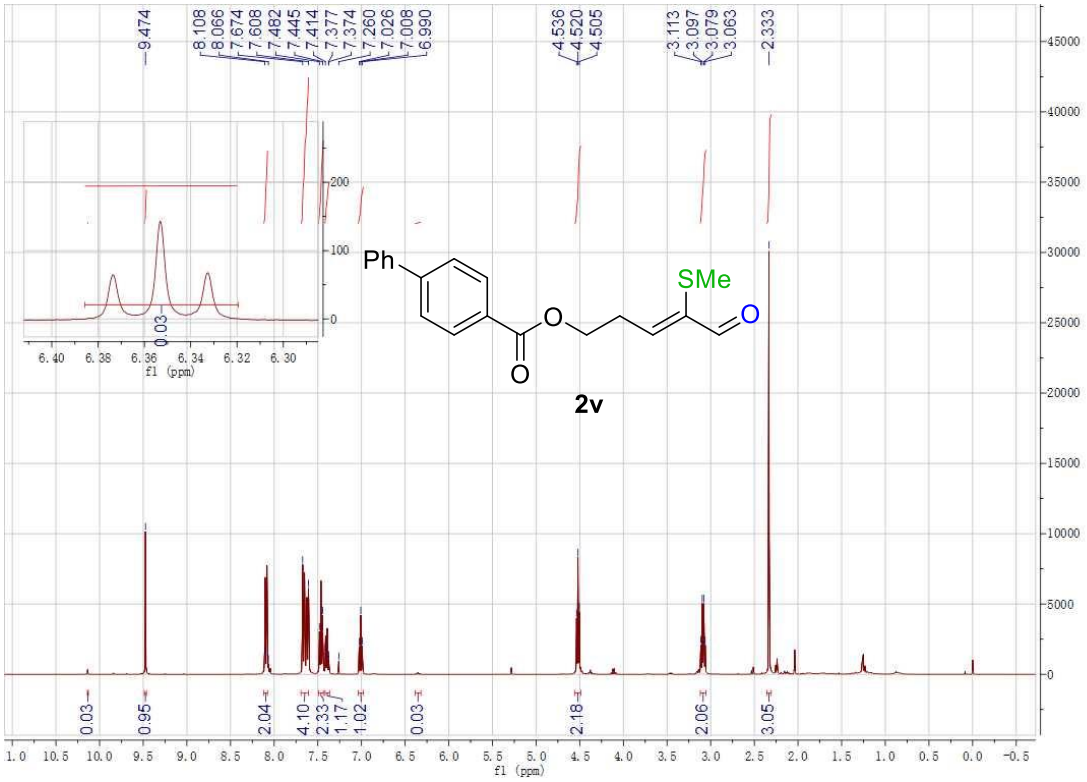
^{1}H NMR spectrum of u in $CDCl_3$, 400 MHz



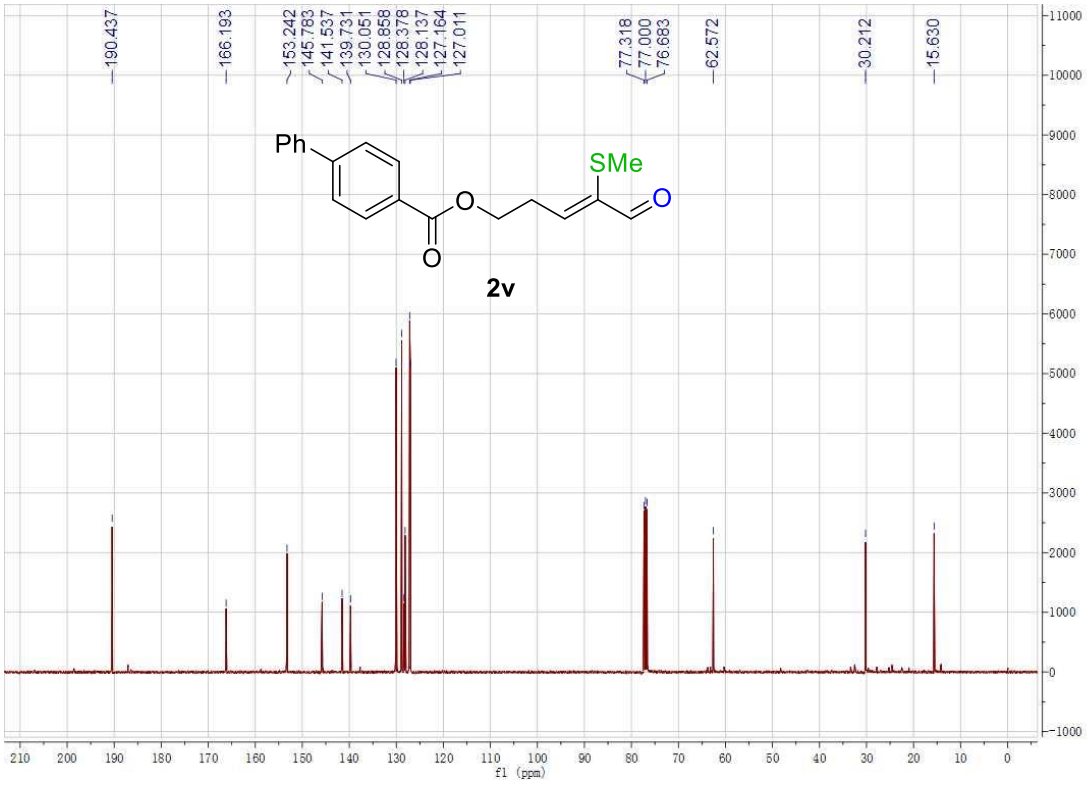
^{13}C NMR spectrum of 2u in $CDCl_3$, 101 MHz



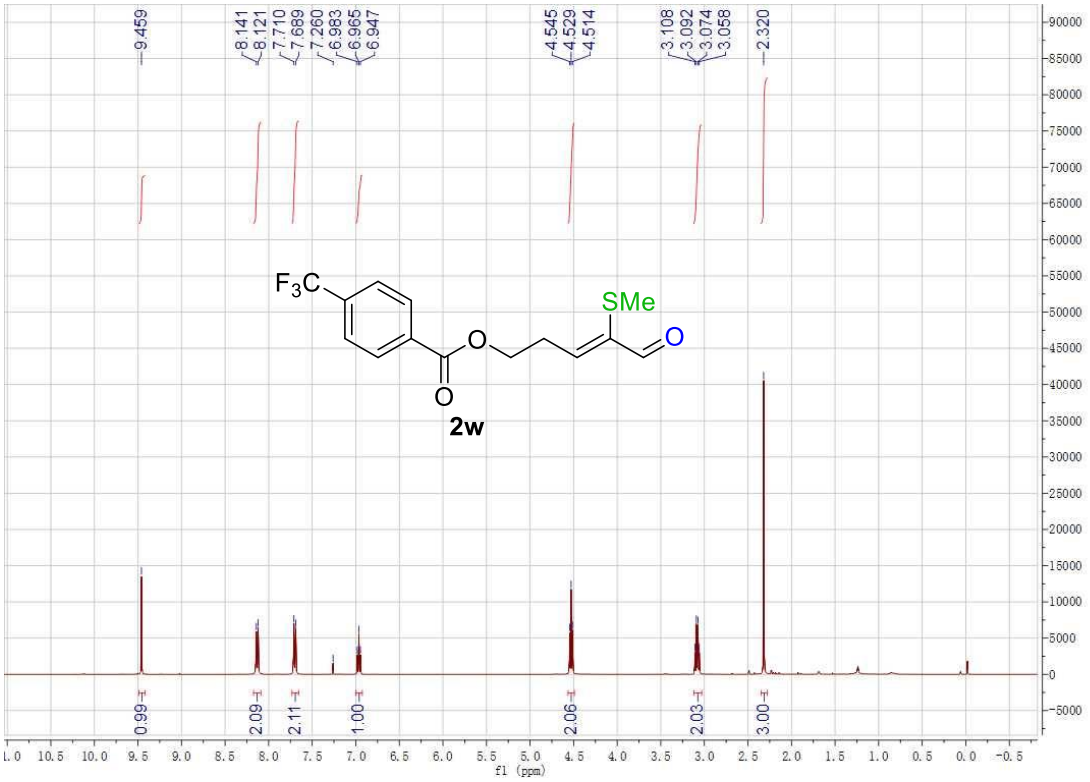
^{1}H NMR spectrum of 2v in $CDCl_3$, 400 MHz



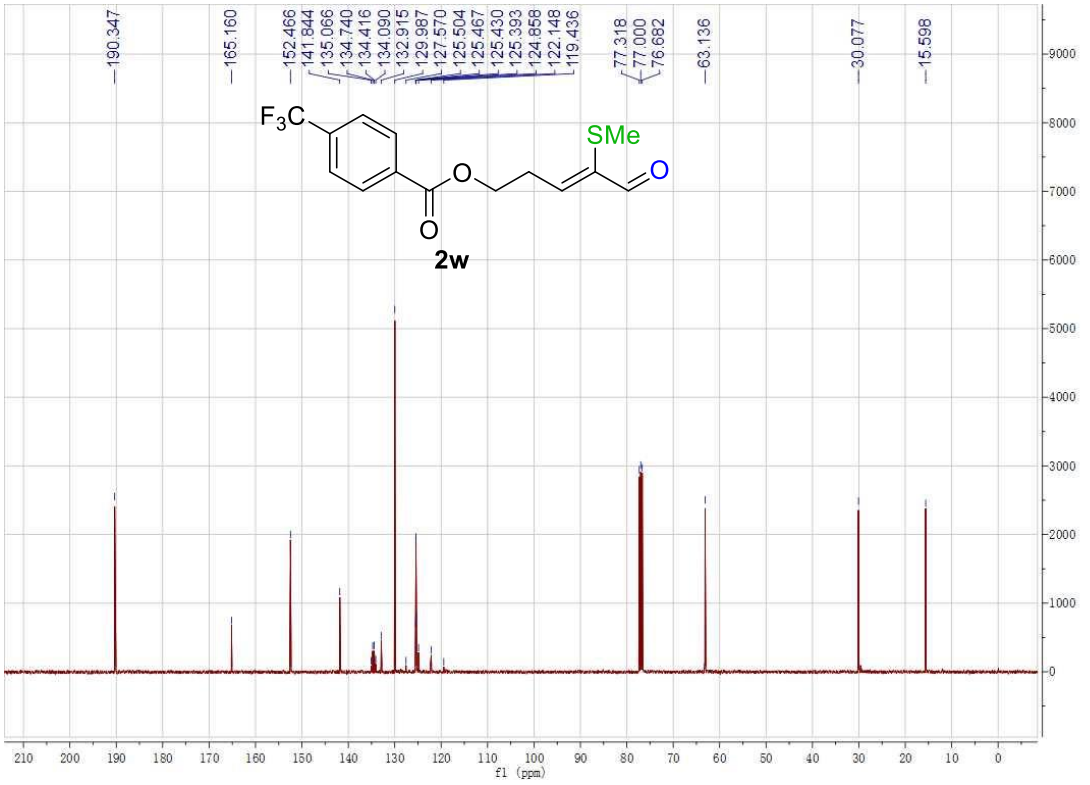
^{13}C NMR spectrum of 2v in $CDCl_3$, 101 MHz



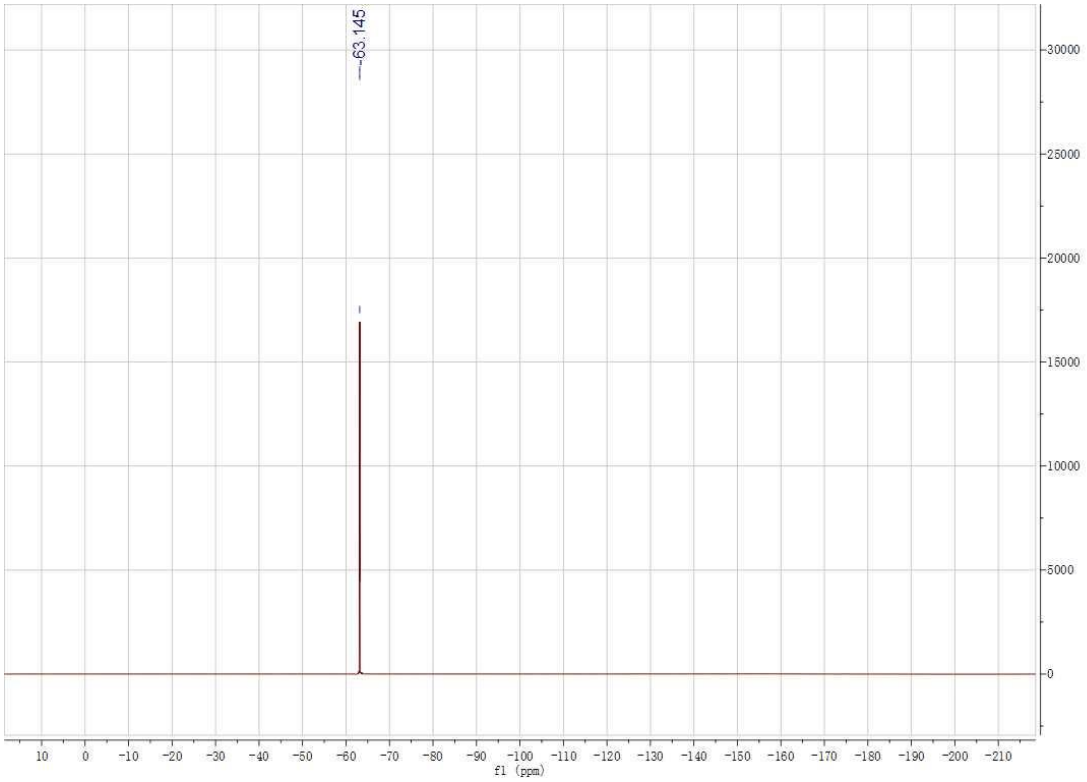
^{1}H NMR spectrum of 2w in $CDCl_3$, 400 MHz



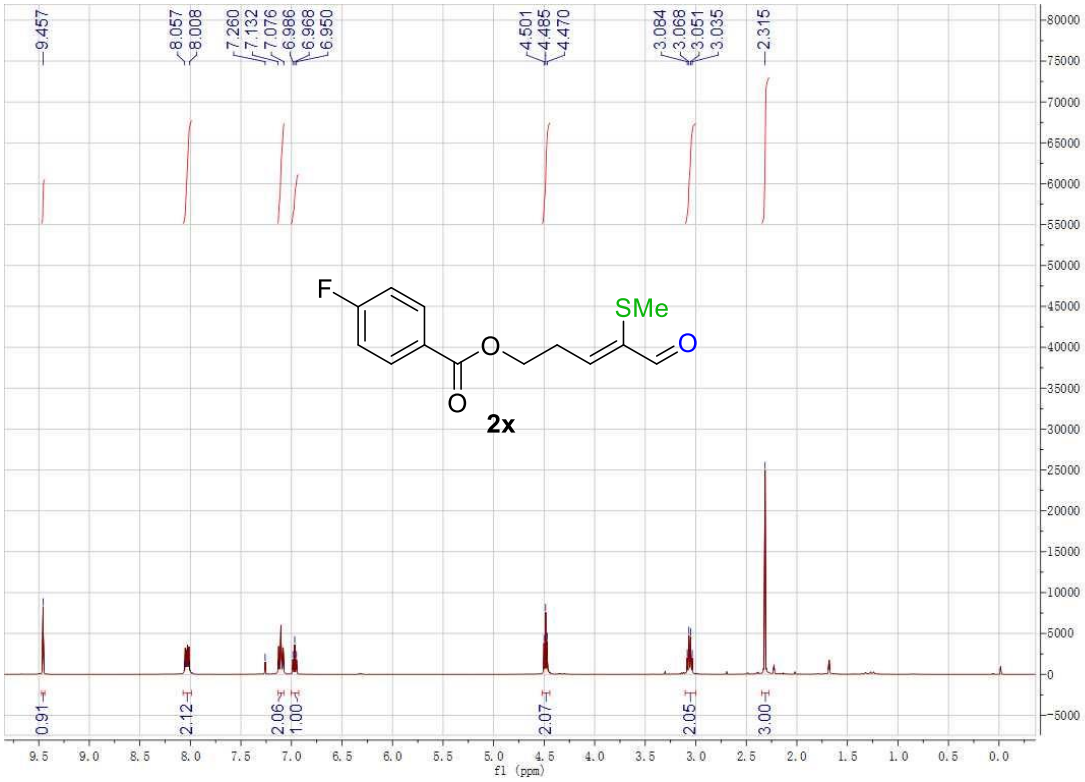
^{13}C NMR spectrum of 2w in $CDCl_3$, 101 MHz



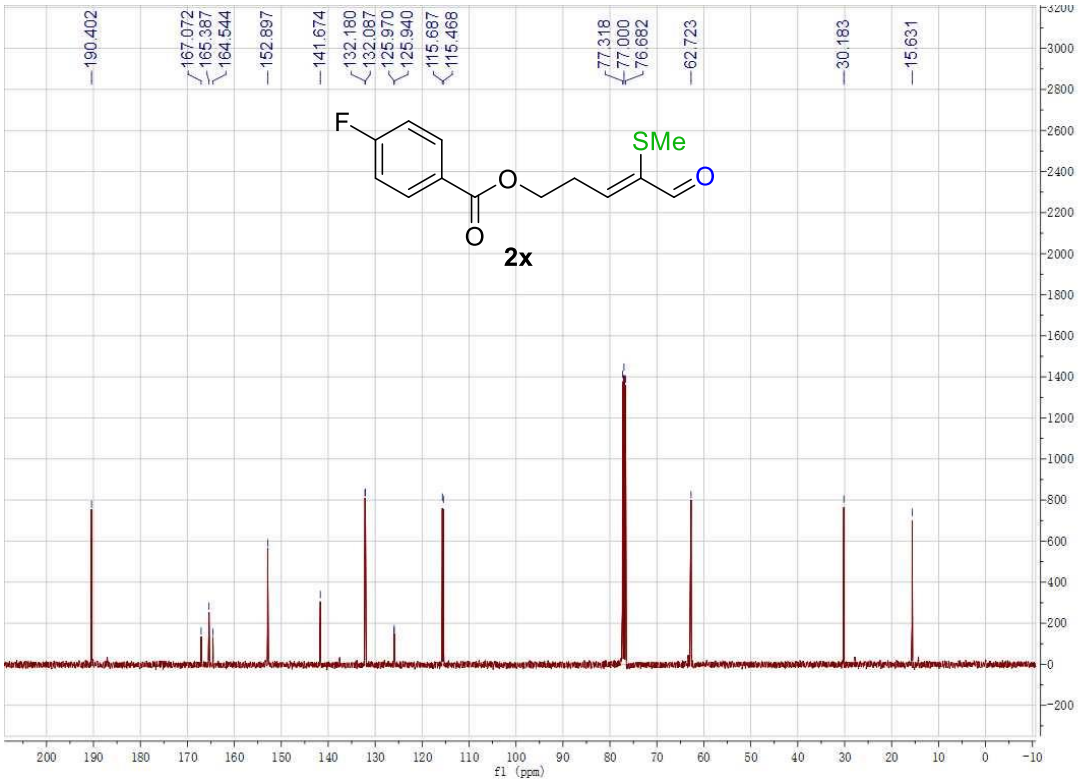
^{19}F NMR spectrum of 2w in $CDCl_3$, 376 MHz



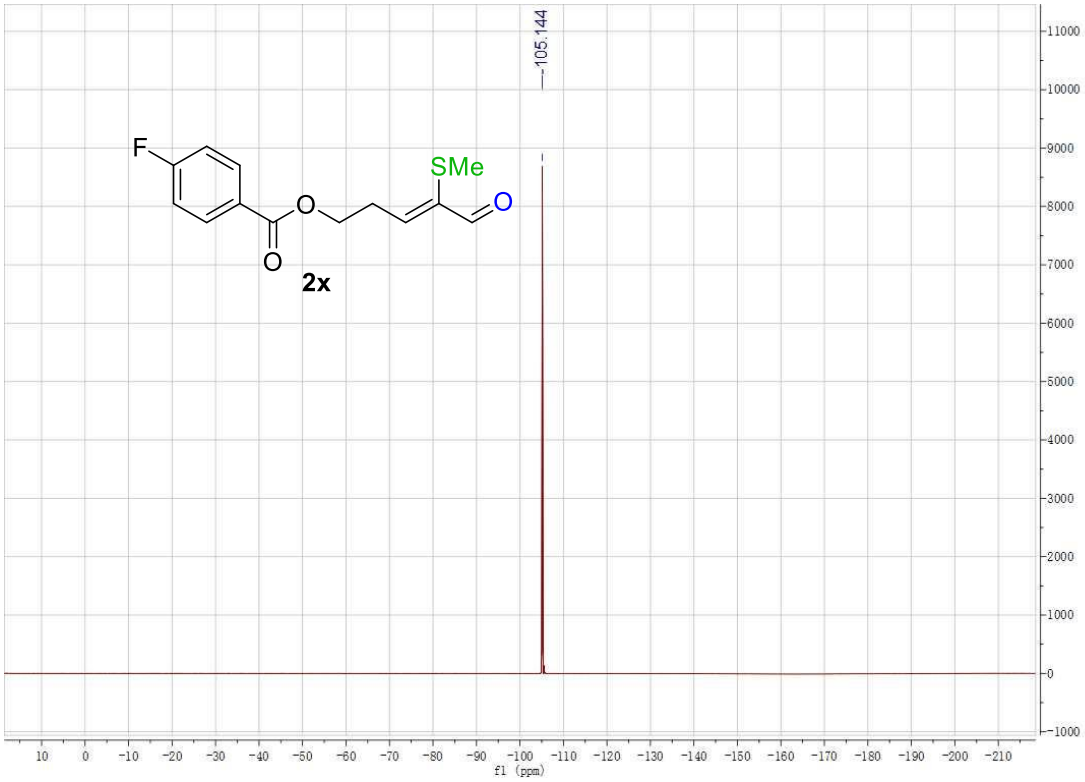
^{1}H NMR spectrum of 2x in $CDCl_3$, 400 MHz



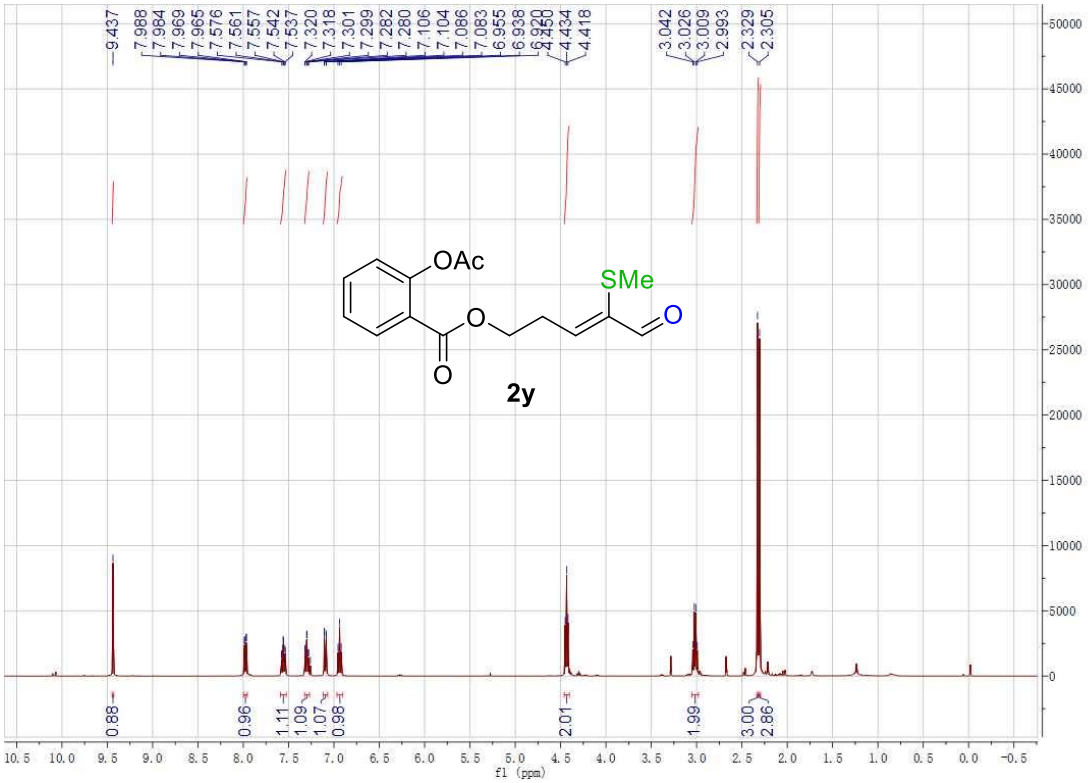
^{13}C NMR spectrum of 2x in $CDCl_3$, 101 MHz



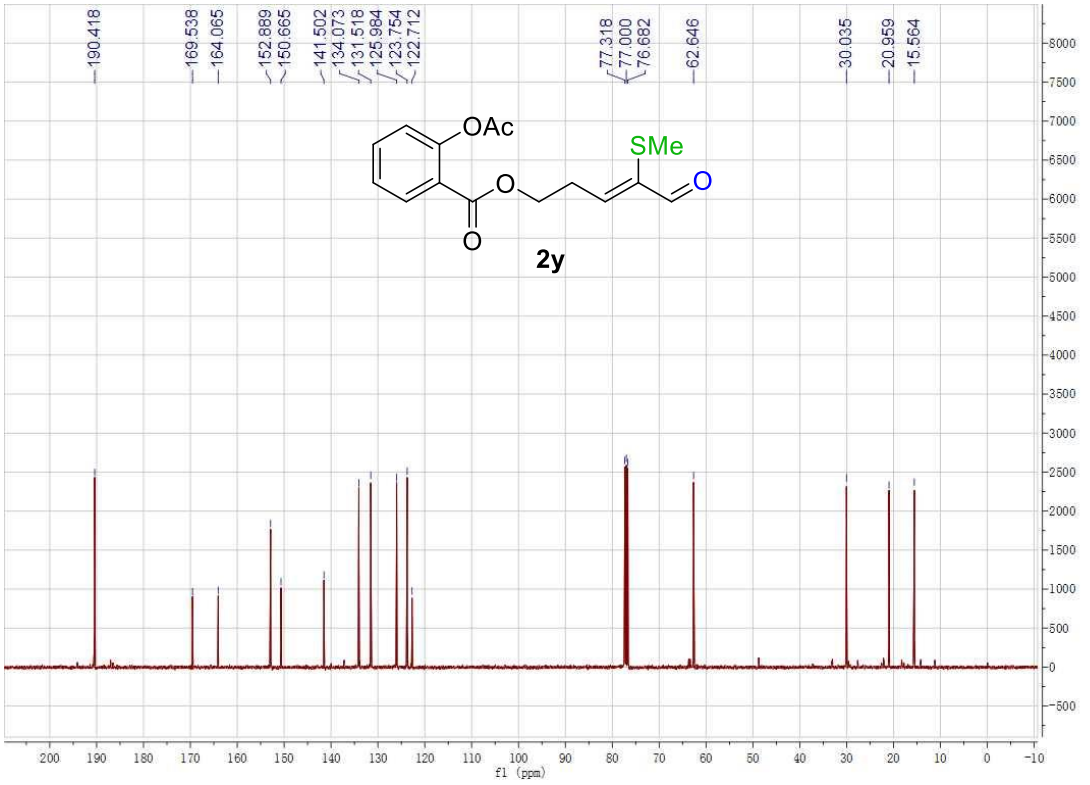
^{19}F NMR spectrum of 2x in $CDCl_3$, 376 MHz



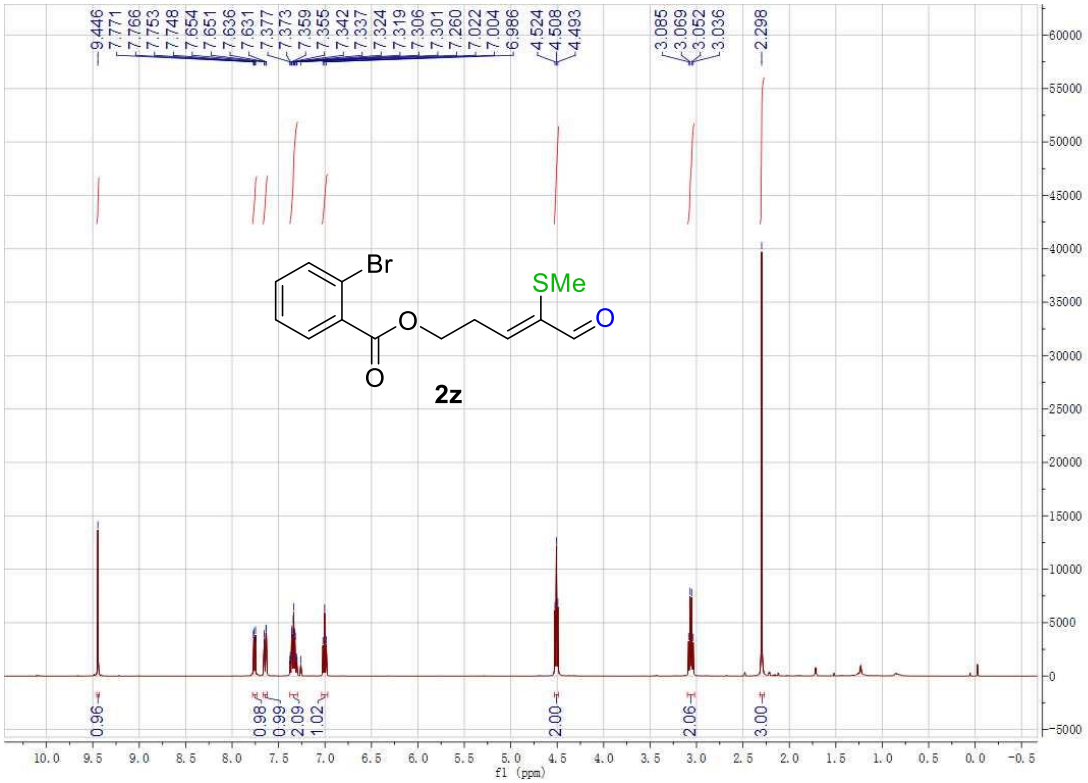
^{1}H NMR spectrum of 2y in $CDCl_3$, 400 MHz



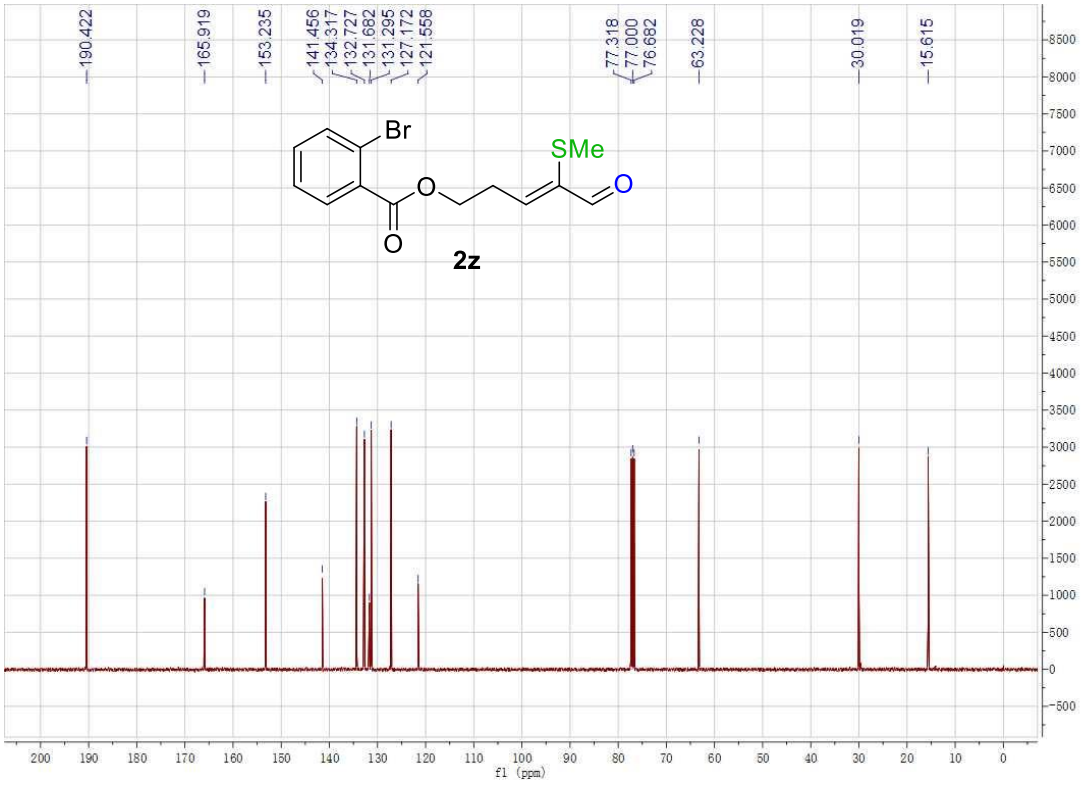
^{13}C NMR spectrum of 2y in $CDCl_3$, 101 MHz



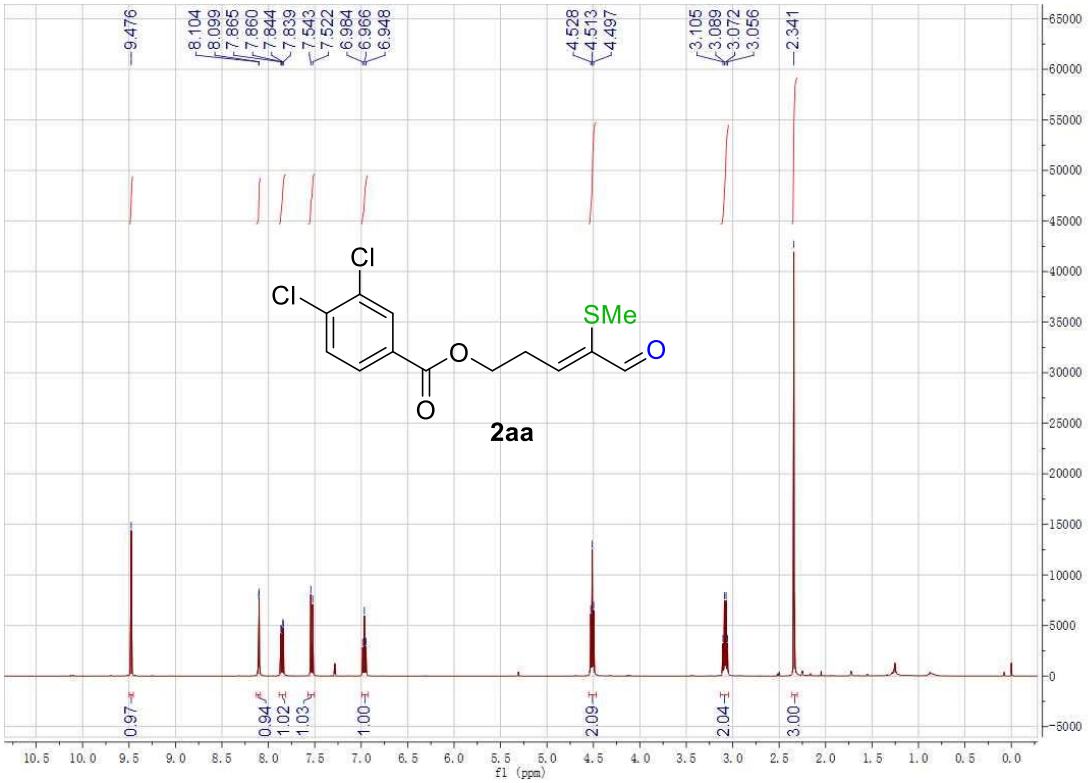
^{1}H NMR spectrum of 2z in $CDCl_3$, 400 MHz



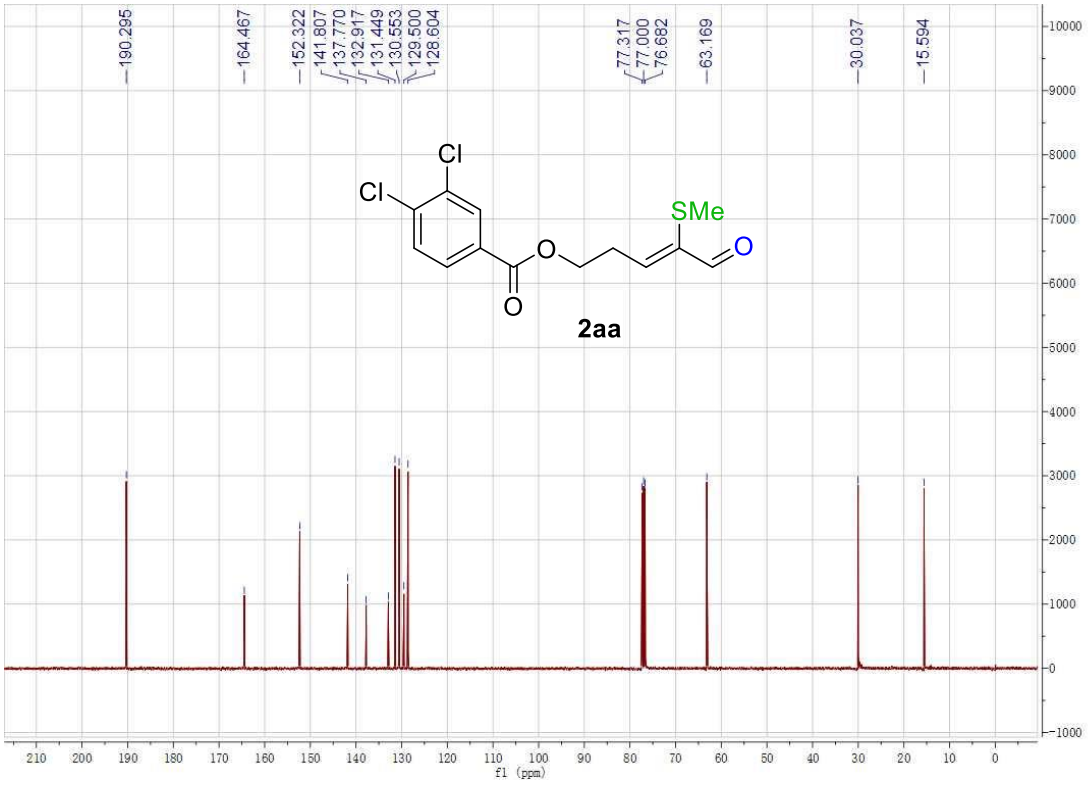
^{13}C NMR spectrum of 2z in $CDCl_3$, 101 MHz



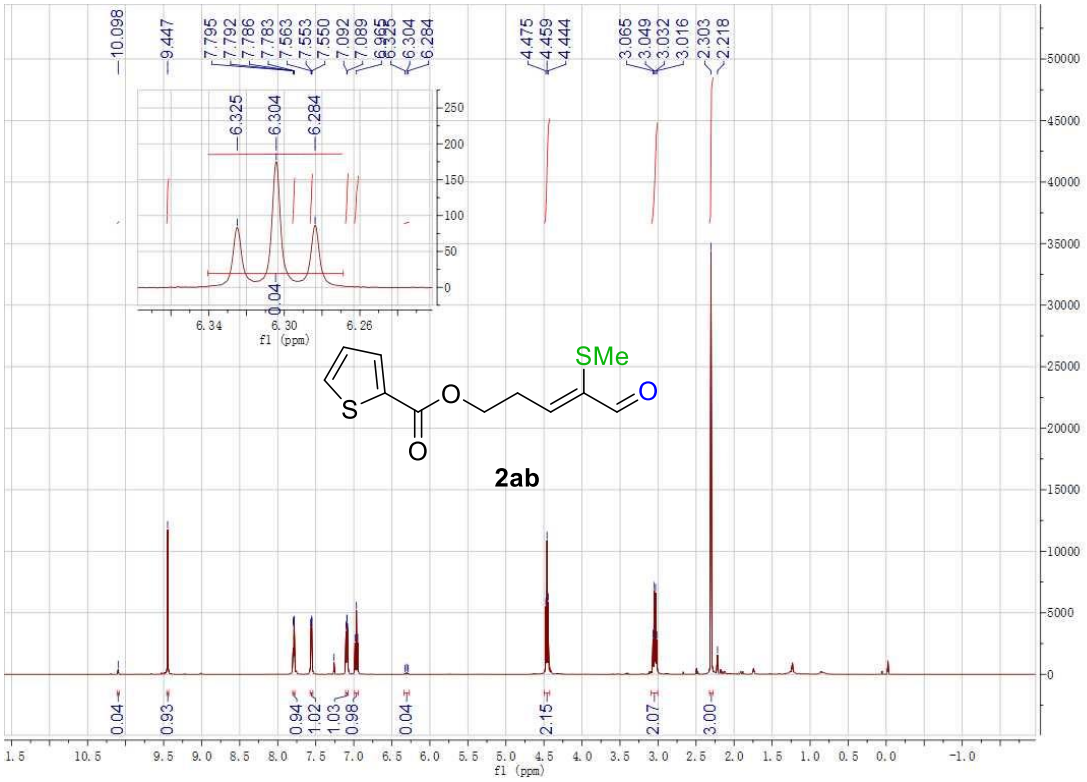
^{1}H NMR spectrum of 2aa in $CDCl_3$, 400 MHz



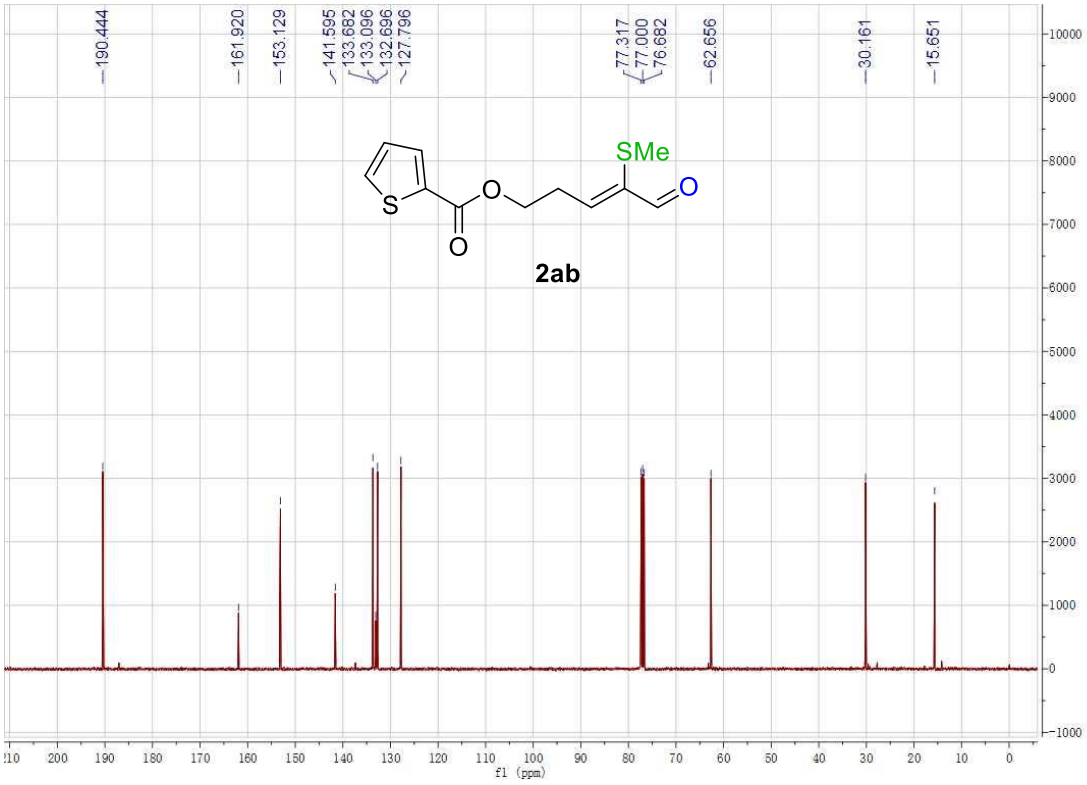
^{13}C NMR spectrum of 2aa in $CDCl_3$, 101 MHz



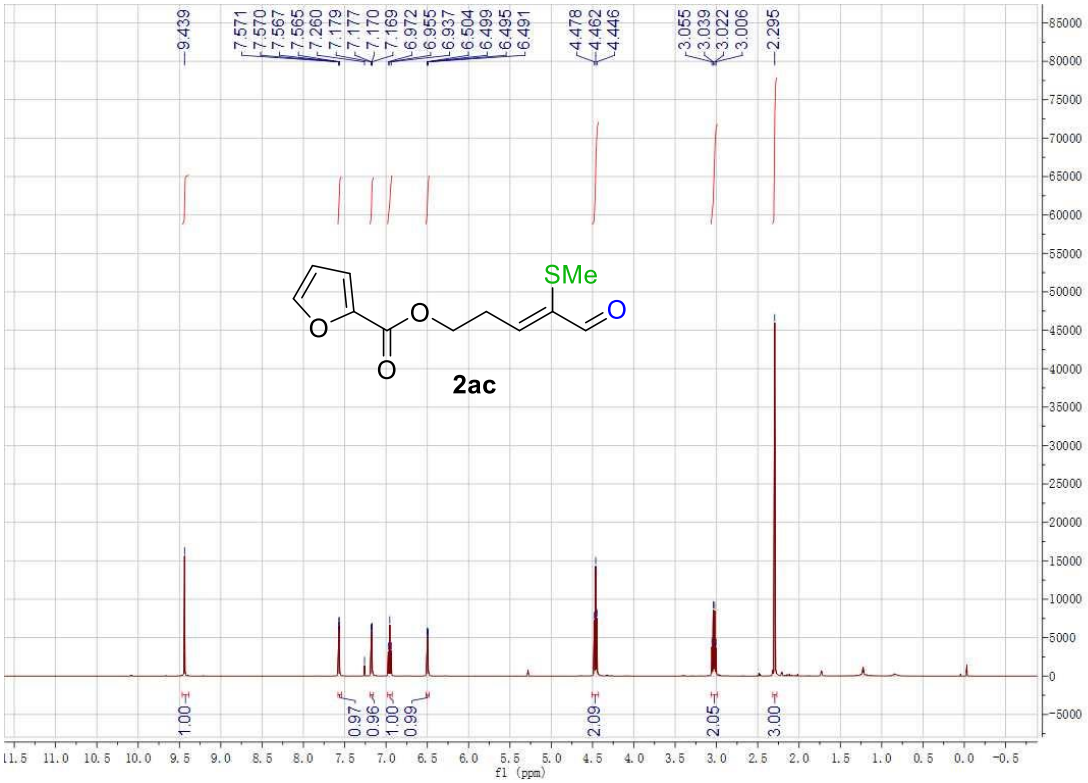
^{1}H NMR spectrum of 2ab in $CDCl_3$, 400 MHz



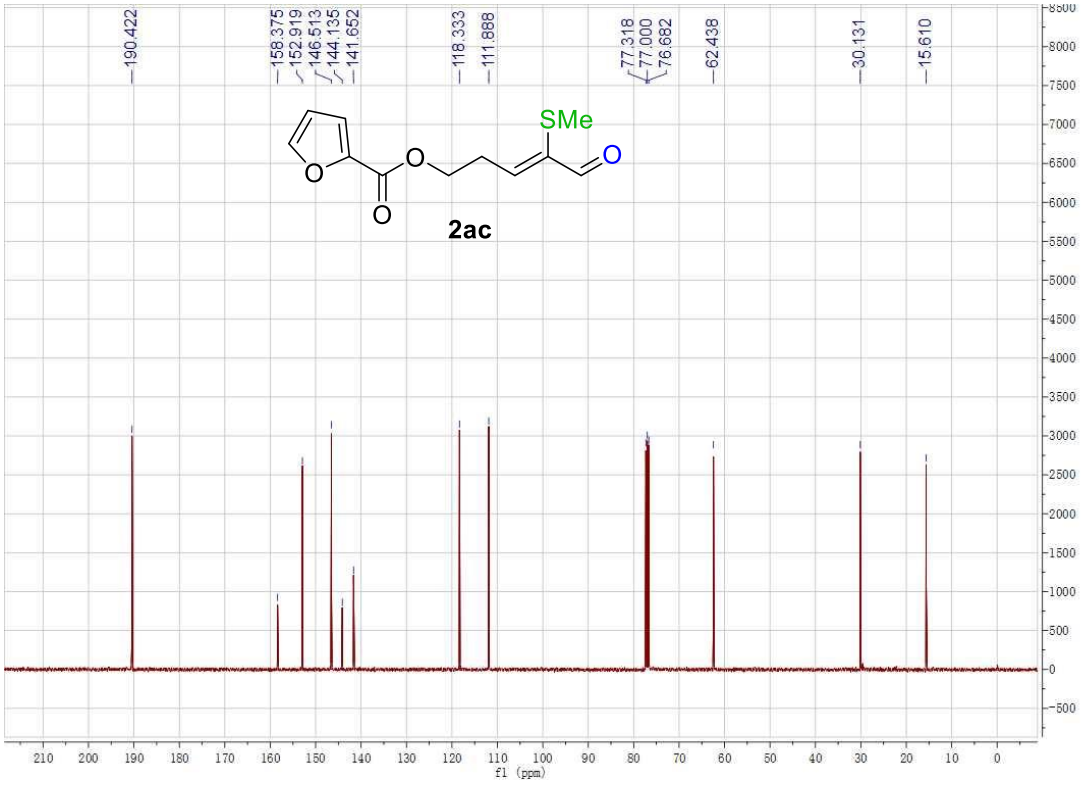
^{13}C NMR spectrum of 2ab in $CDCl_3$, 101 MHz



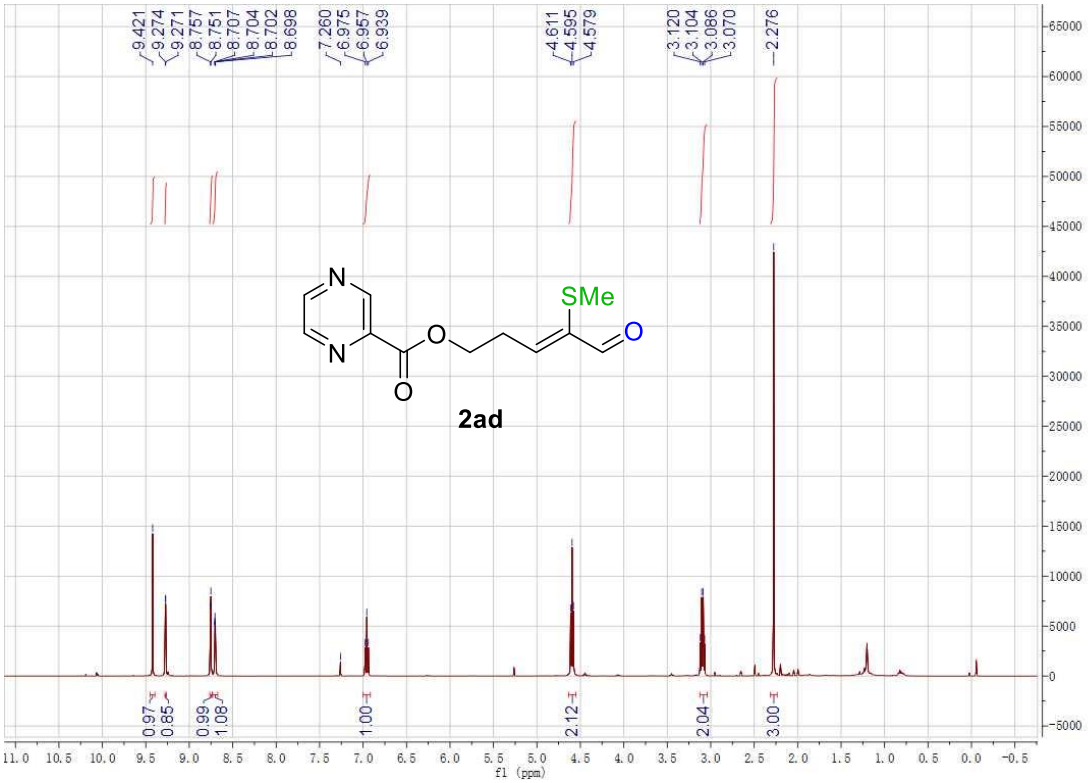
^{1}H NMR spectrum of 2ac in $CDCl_3$, 400 MHz



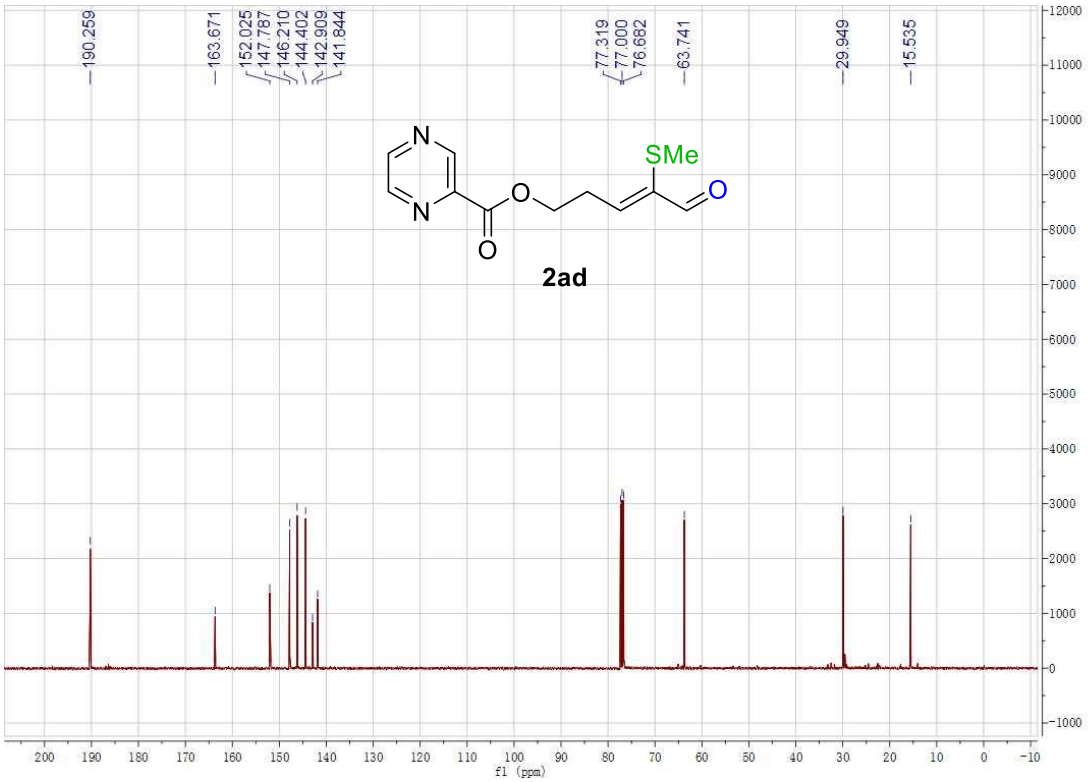
^{13}C NMR spectrum of 2ac in $CDCl_3$, 101 MHz



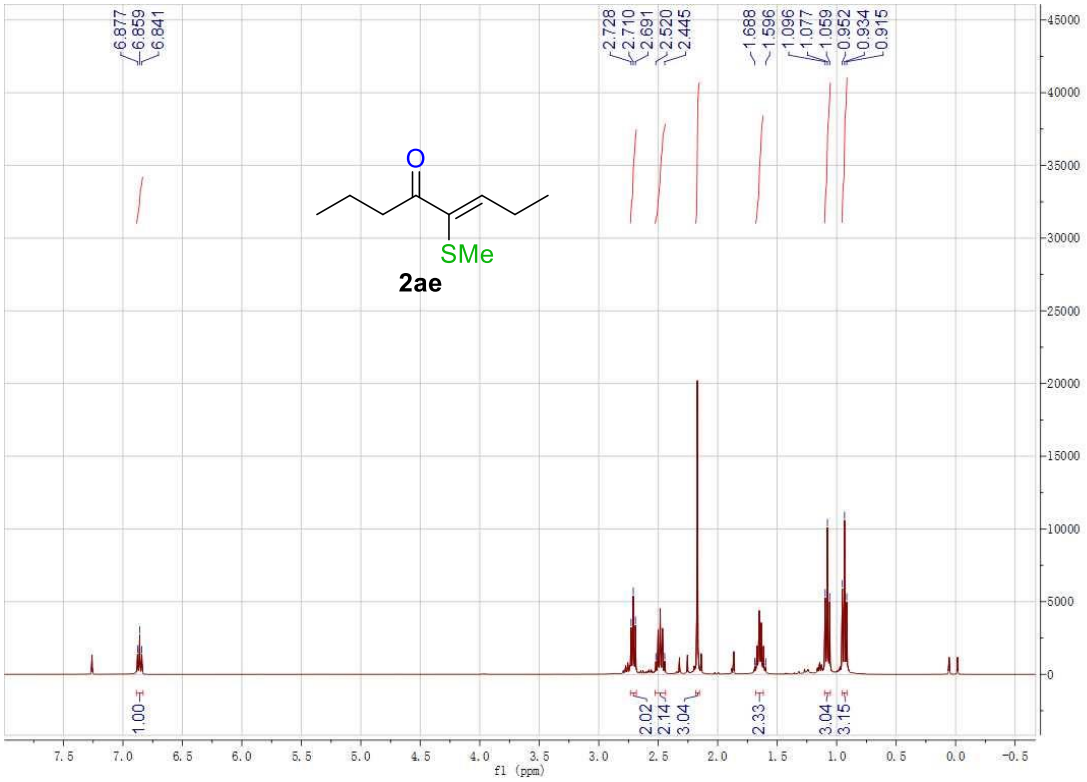
^{1}H NMR spectrum of 2ad in $CDCl_3$, 400 MHz



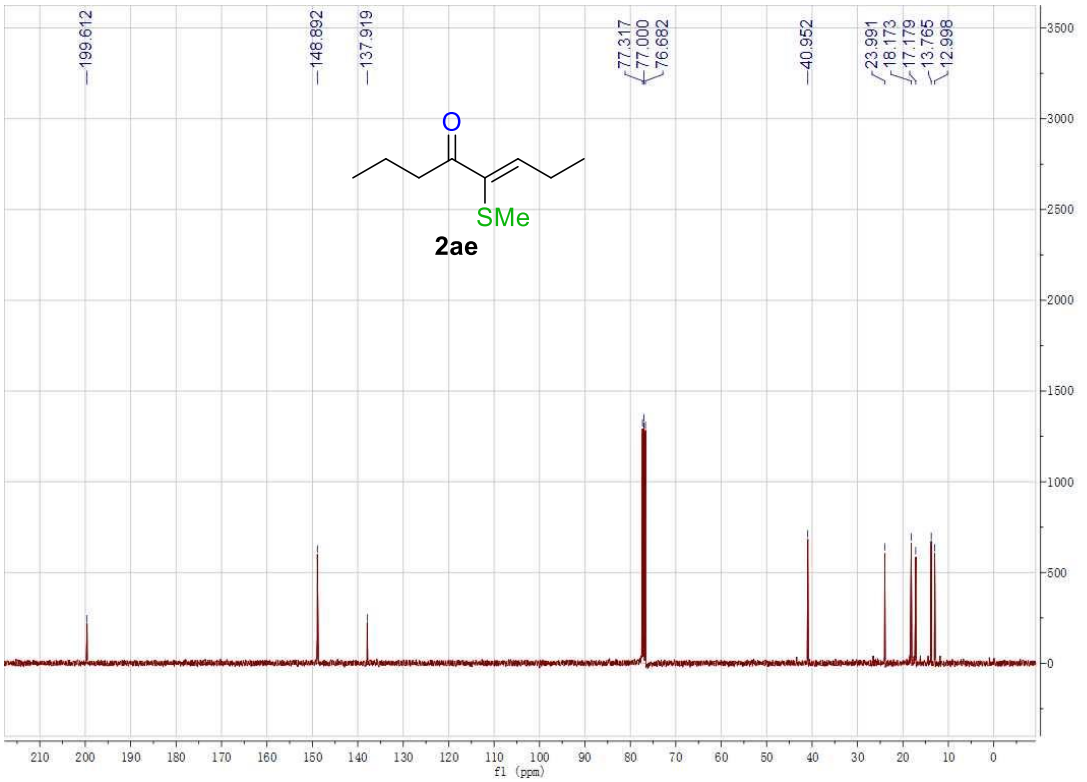
^{13}C NMR spectrum of 2ad in $CDCl_3$, 101 MHz



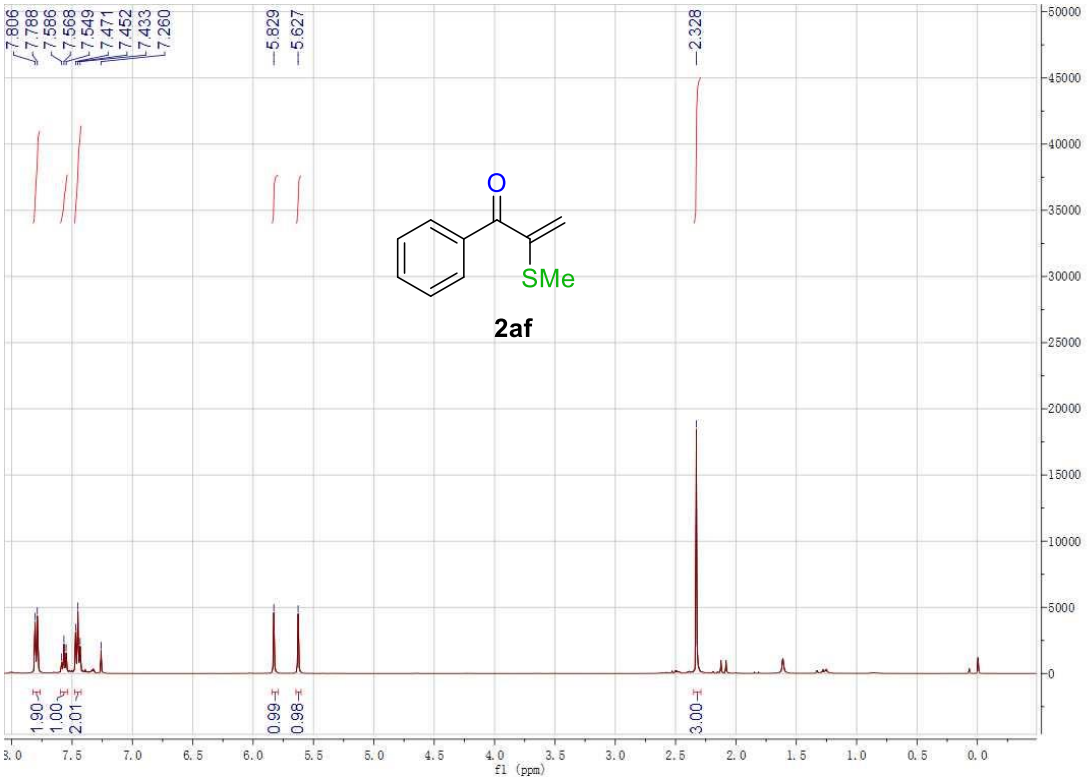
^{1}H NMR spectrum of 2ae in $CDCl_3$, 400 MHz



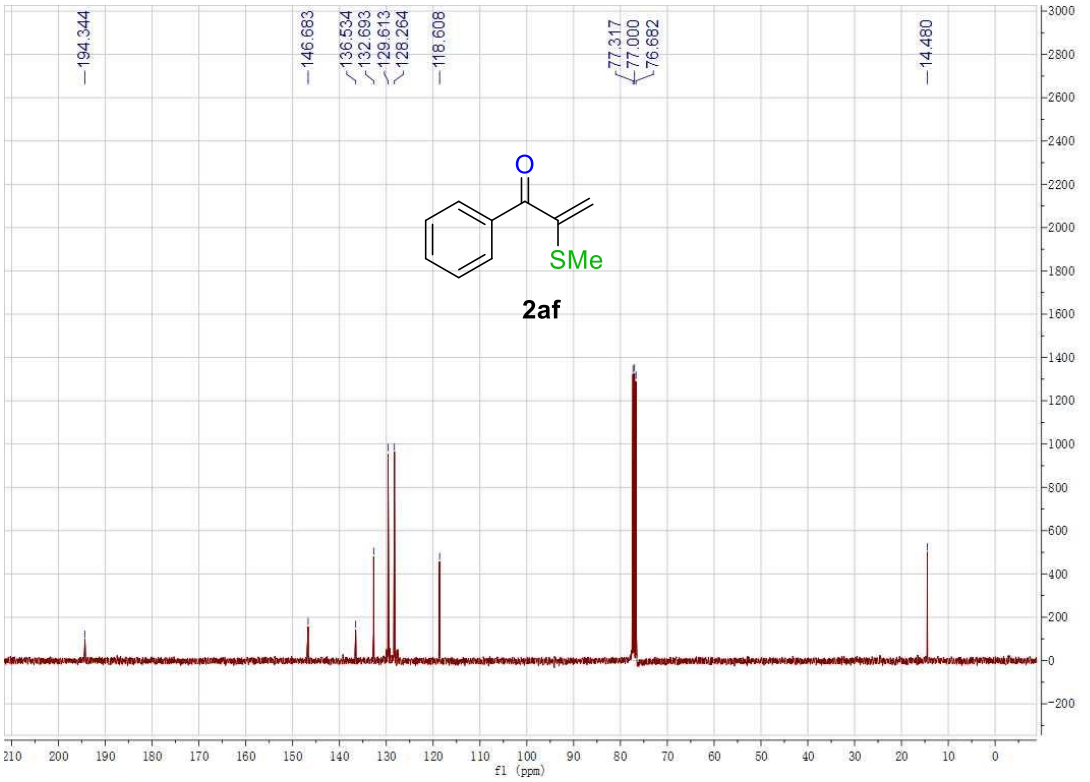
^{13}C NMR spectrum of 2ae in $CDCl_3$, 101 MHz



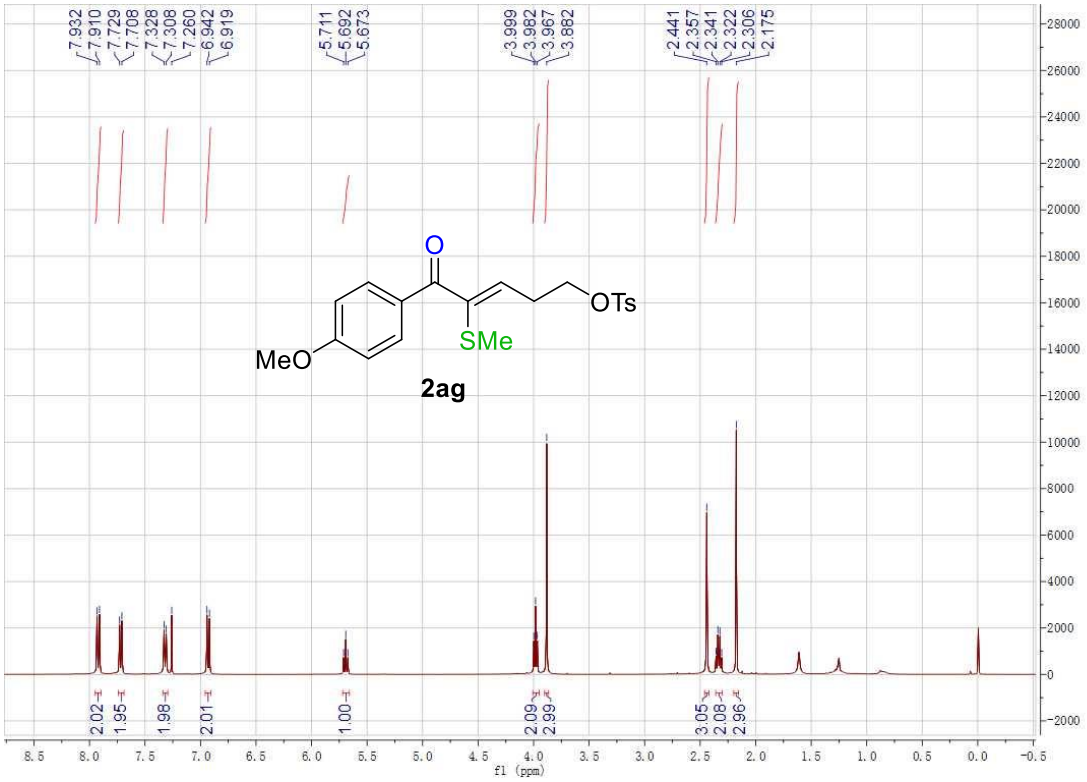
^{1}H NMR spectrum of 2af in $CDCl_3$, 400 MHz



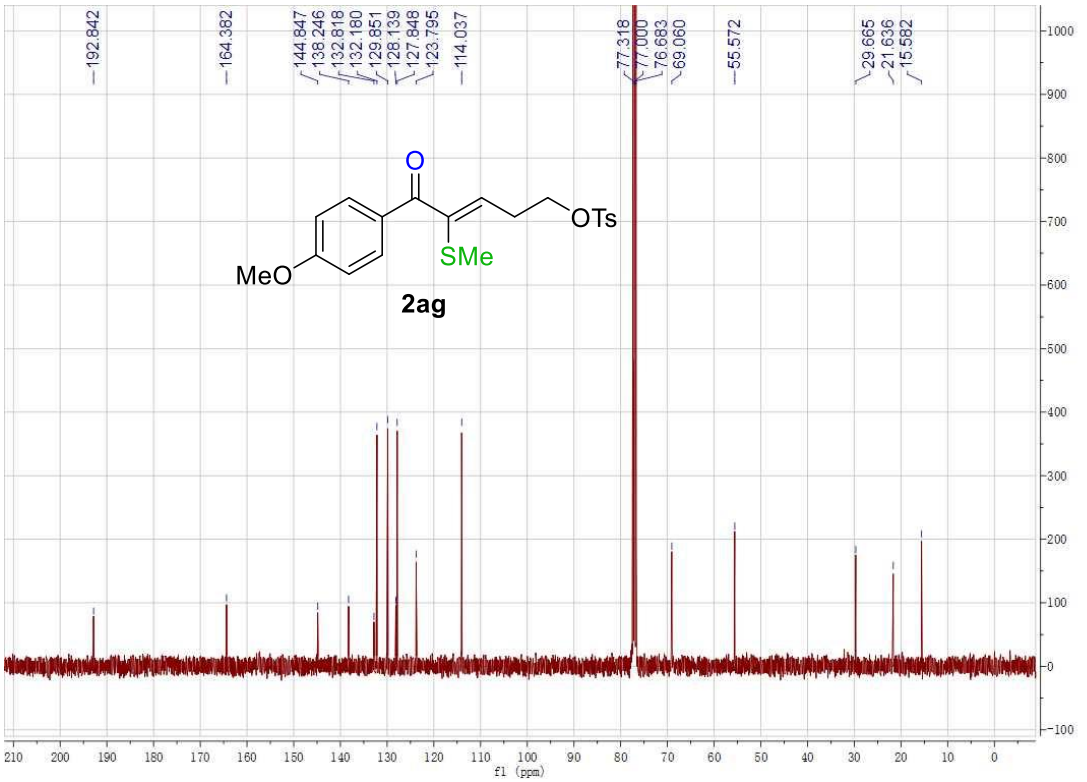
^{13}C NMR spectrum of 2af in $CDCl_3$, 101 MHz



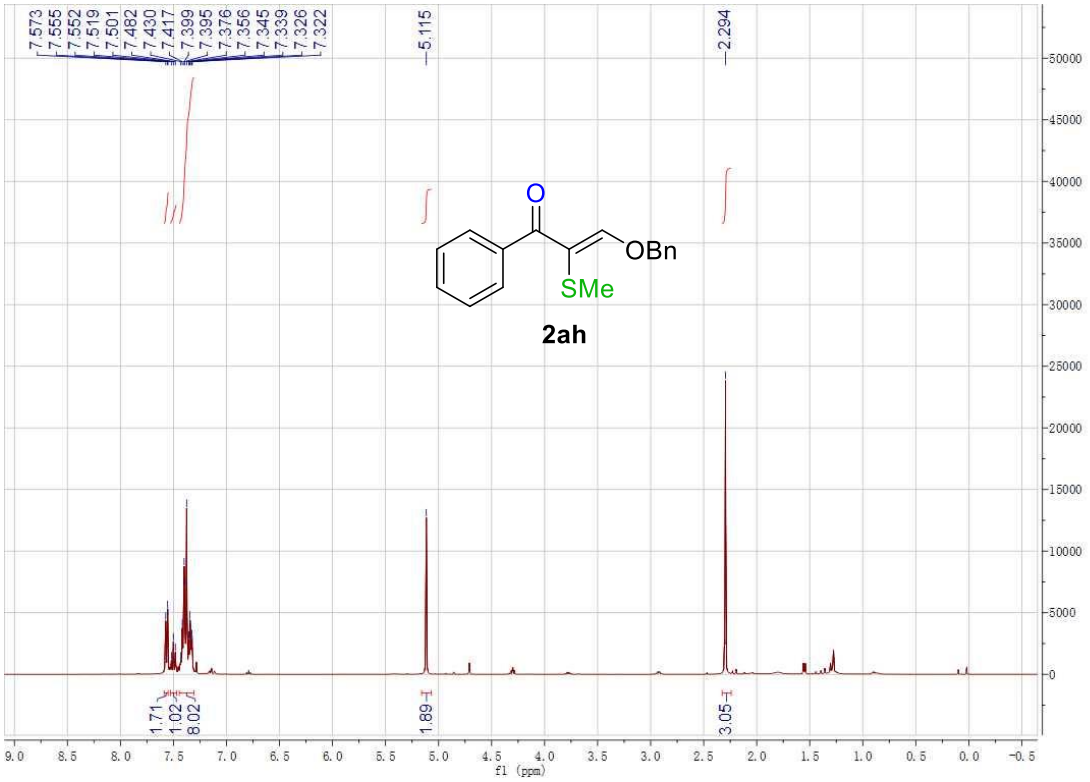
^{1}H NMR spectrum of 2ag in $CDCl_3$, 400 MHz



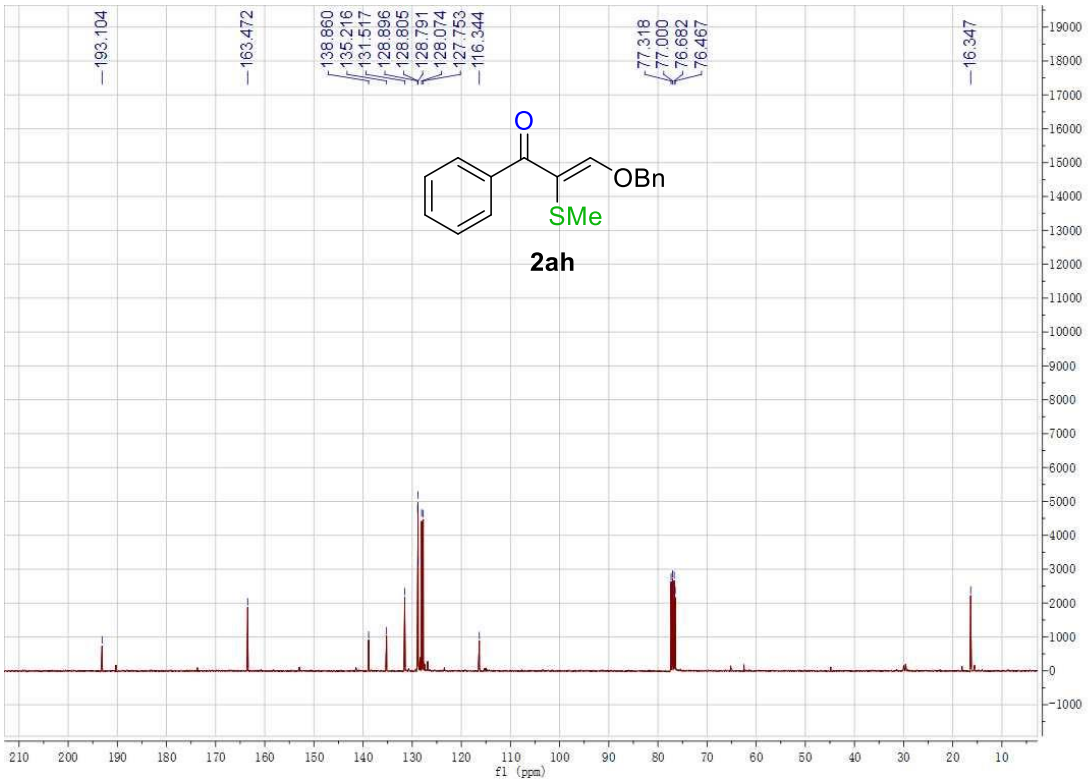
^{13}C NMR spectrum of 2ag in $CDCl_3$, 101 MHz



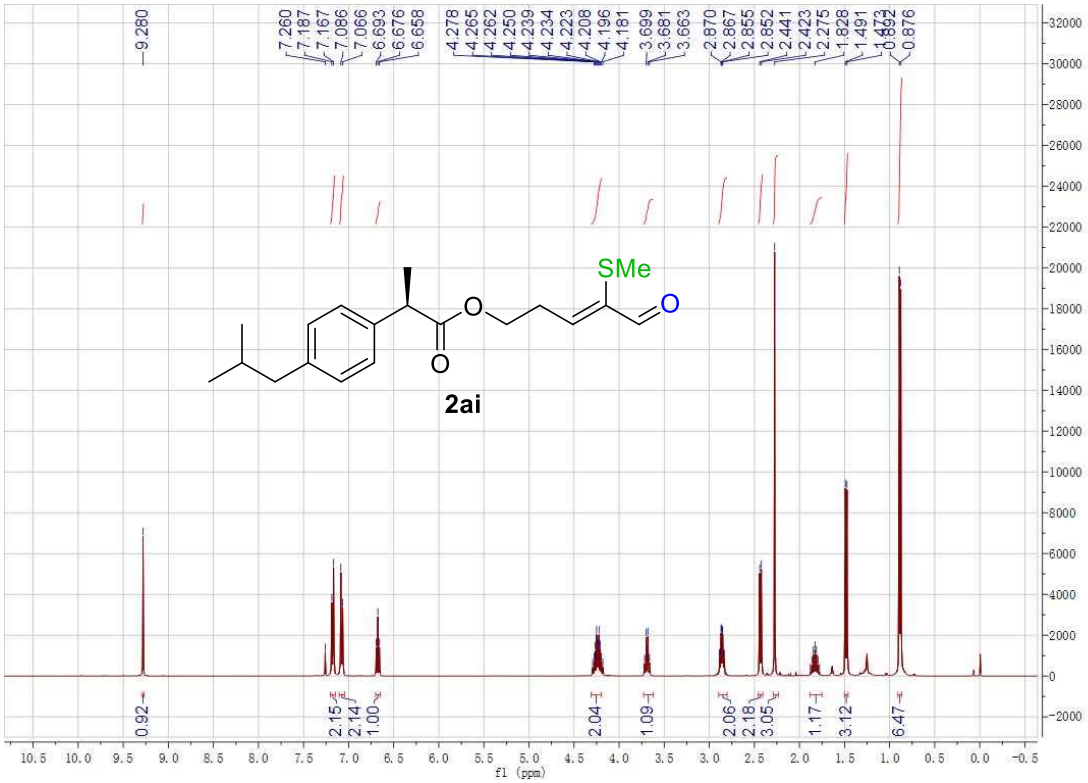
^{1}H NMR spectrum of 2ah in $CDCl_3$, 400 MHz



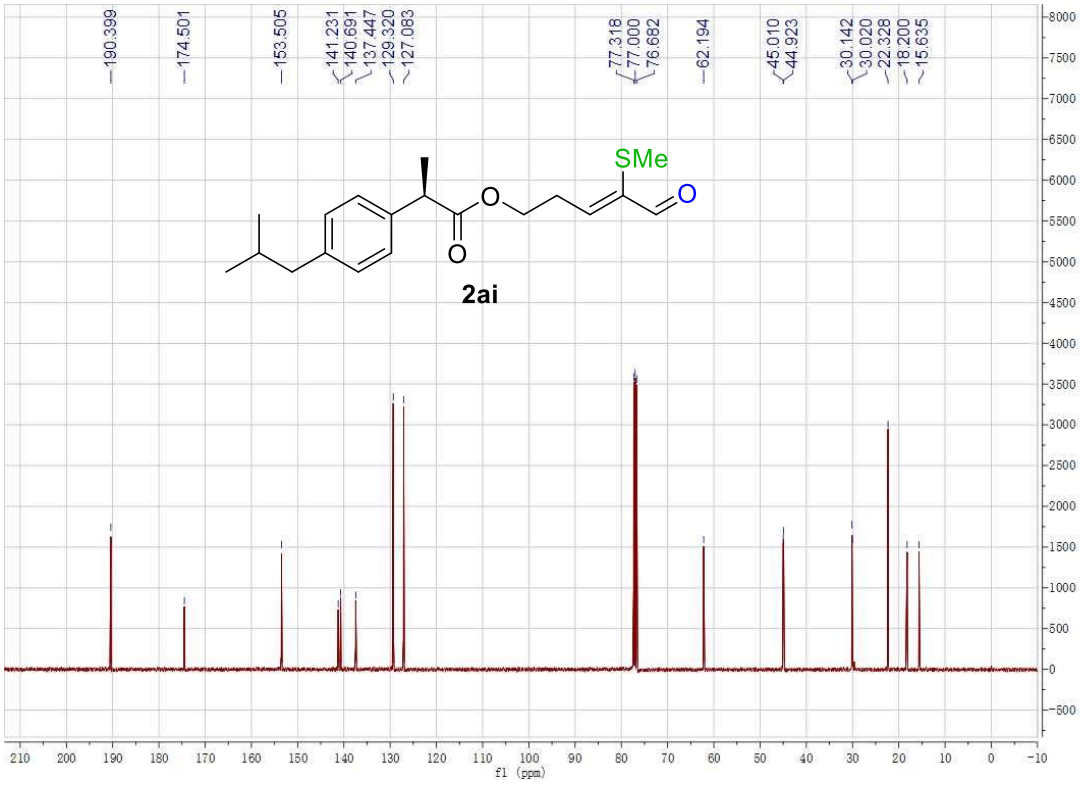
^{13}C NMR spectrum of 2ah in $CDCl_3$, 101 MHz



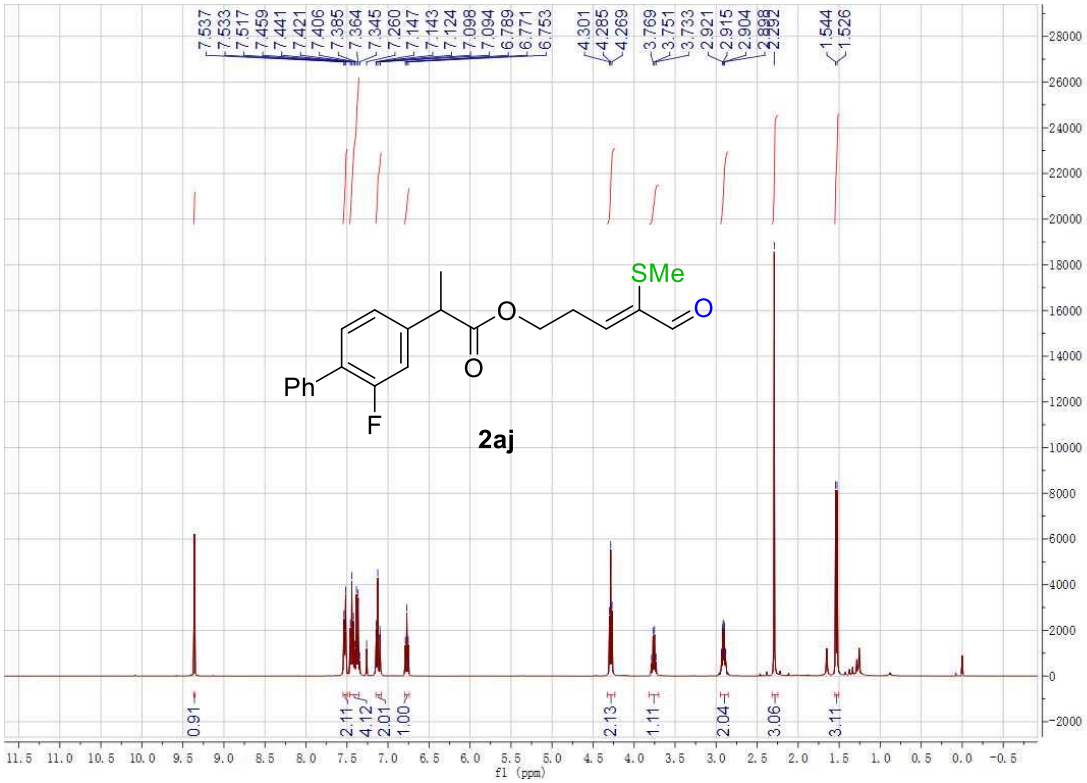
^{1}H NMR spectrum of 2ai in $CDCl_3$, 400 MHz



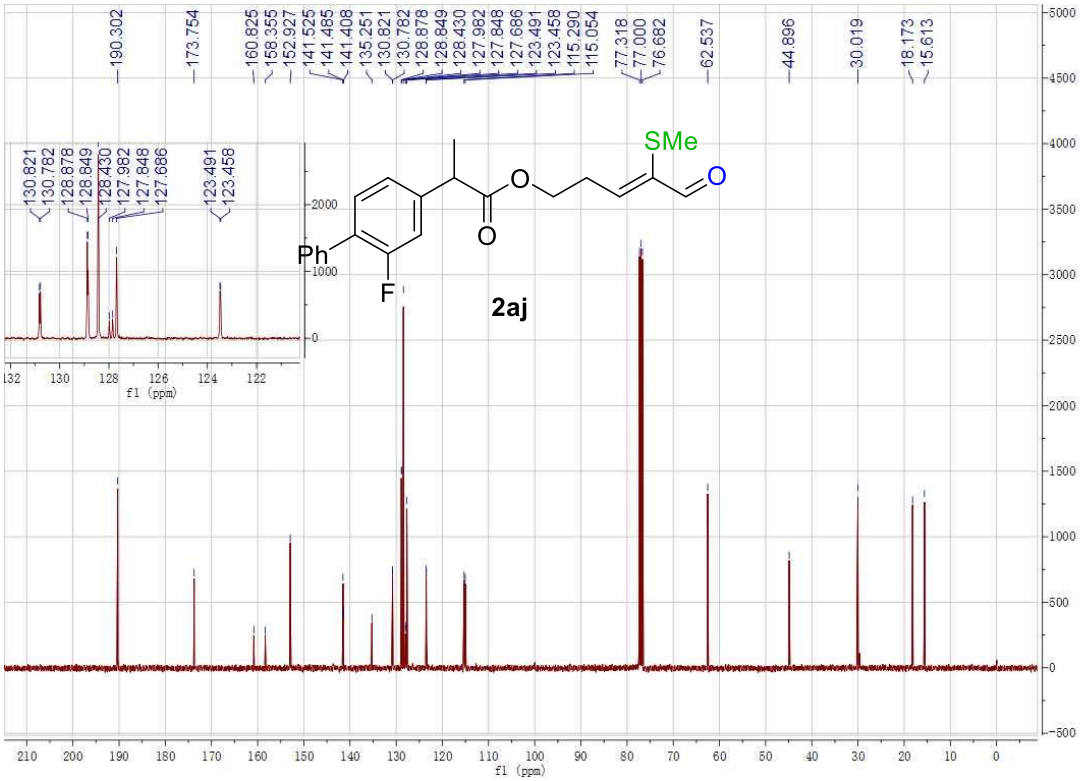
^{13}C NMR spectrum of 2ai in $CDCl_3$, 101 MHz



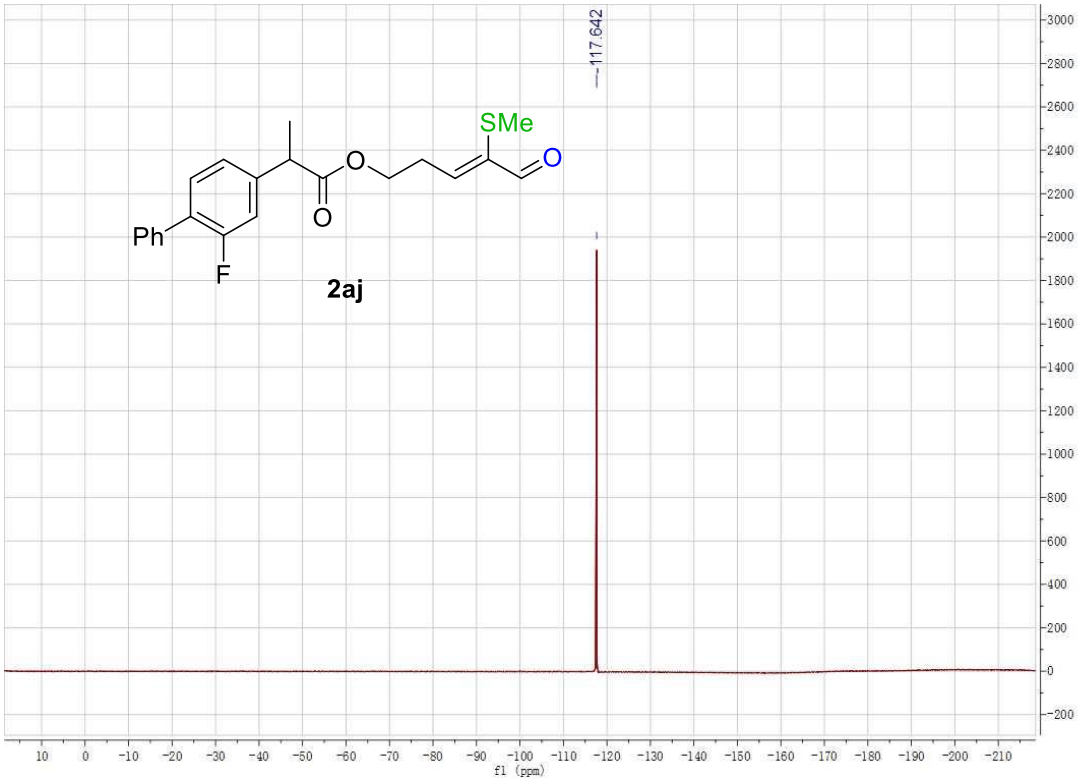
^{1}H NMR spectrum of 2aj in $CDCl_3$, 400 MHz



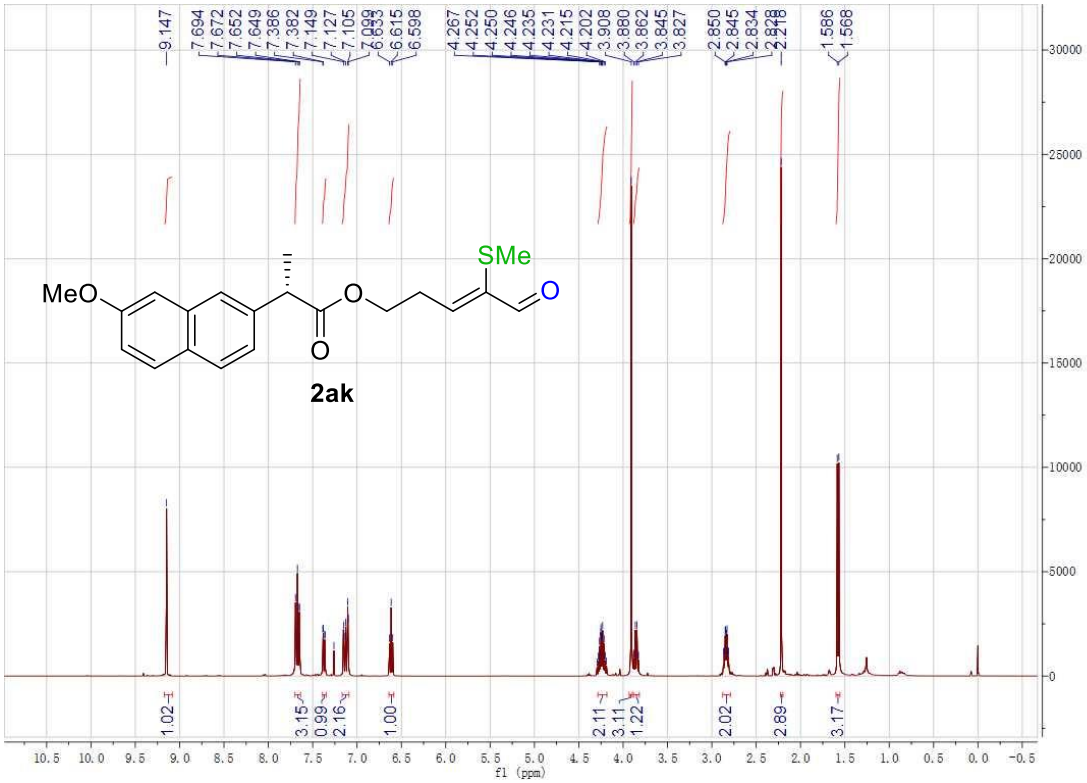
^{13}C NMR spectrum of 2aj in $CDCl_3$, 101 MHz



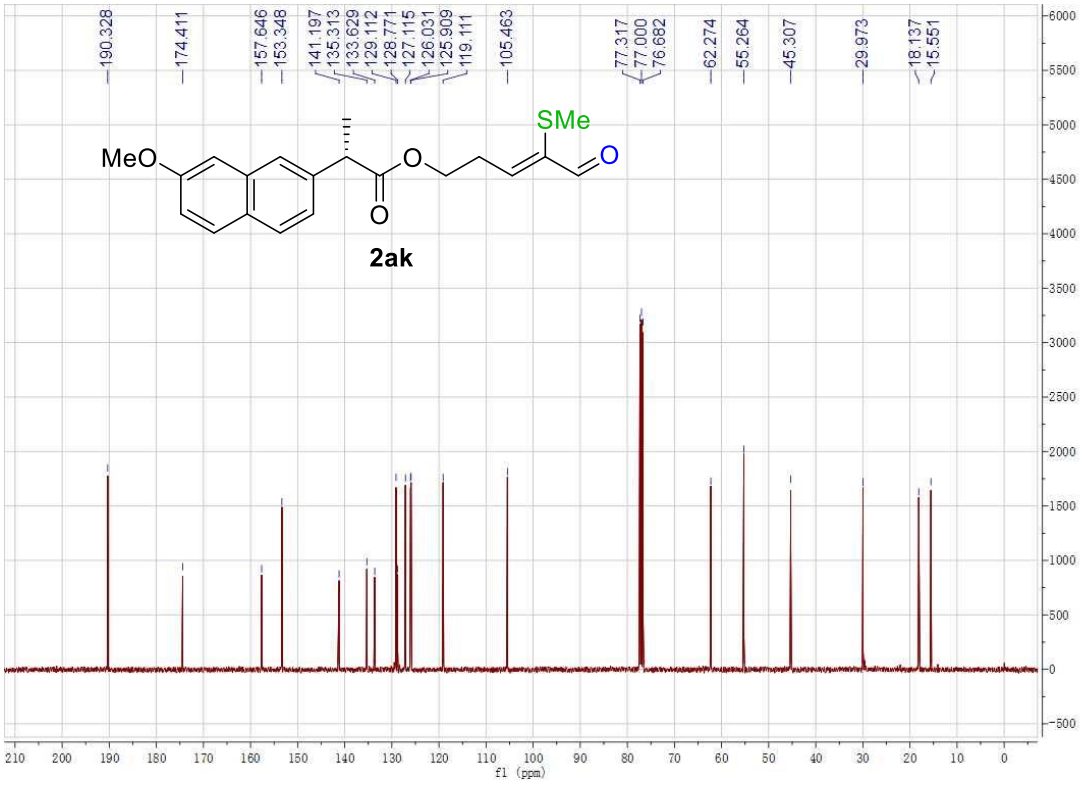
^{19}F NMR spectrum of 2aj in $CDCl_3$, 376 MHz



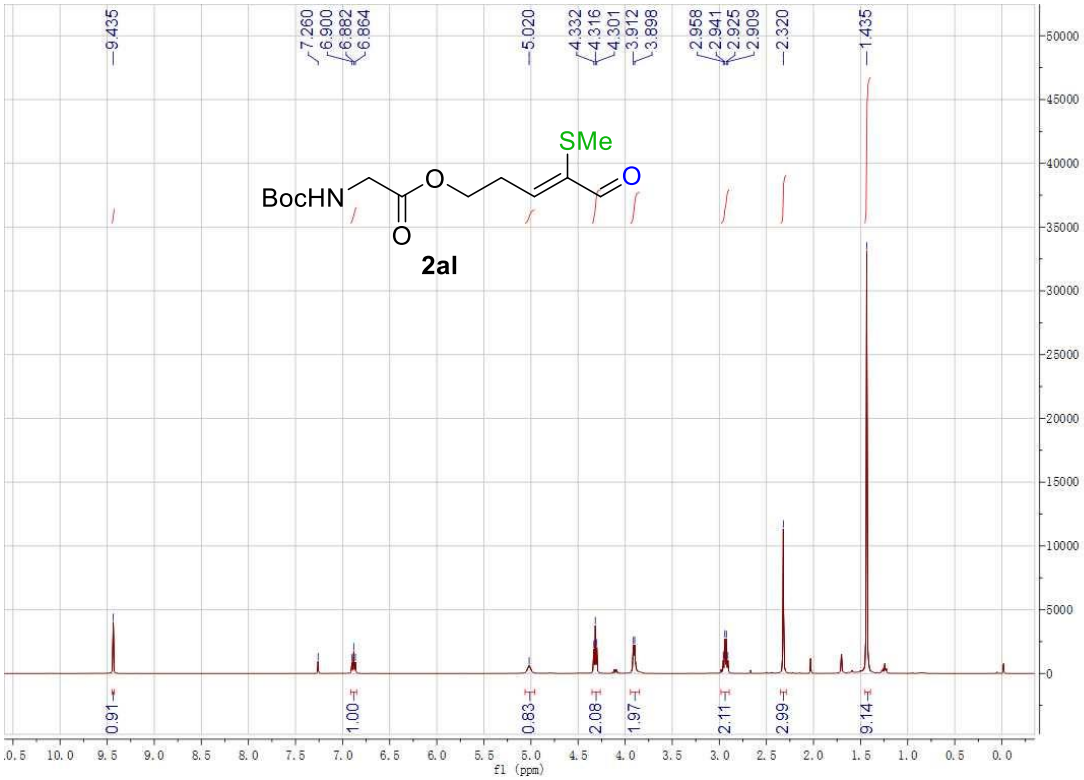
^{1}H NMR spectrum of 2ak in $CDCl_3$, 400 MHz



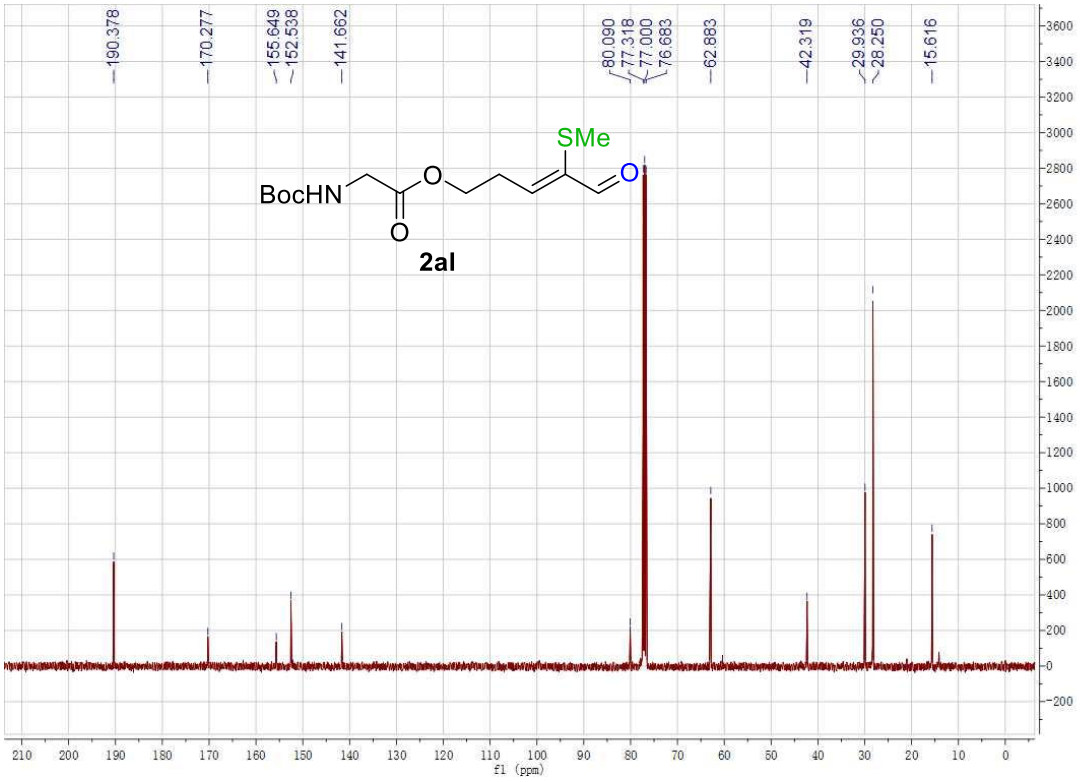
^{13}C NMR spectrum of 2ak in $CDCl_3$, 101 MHz



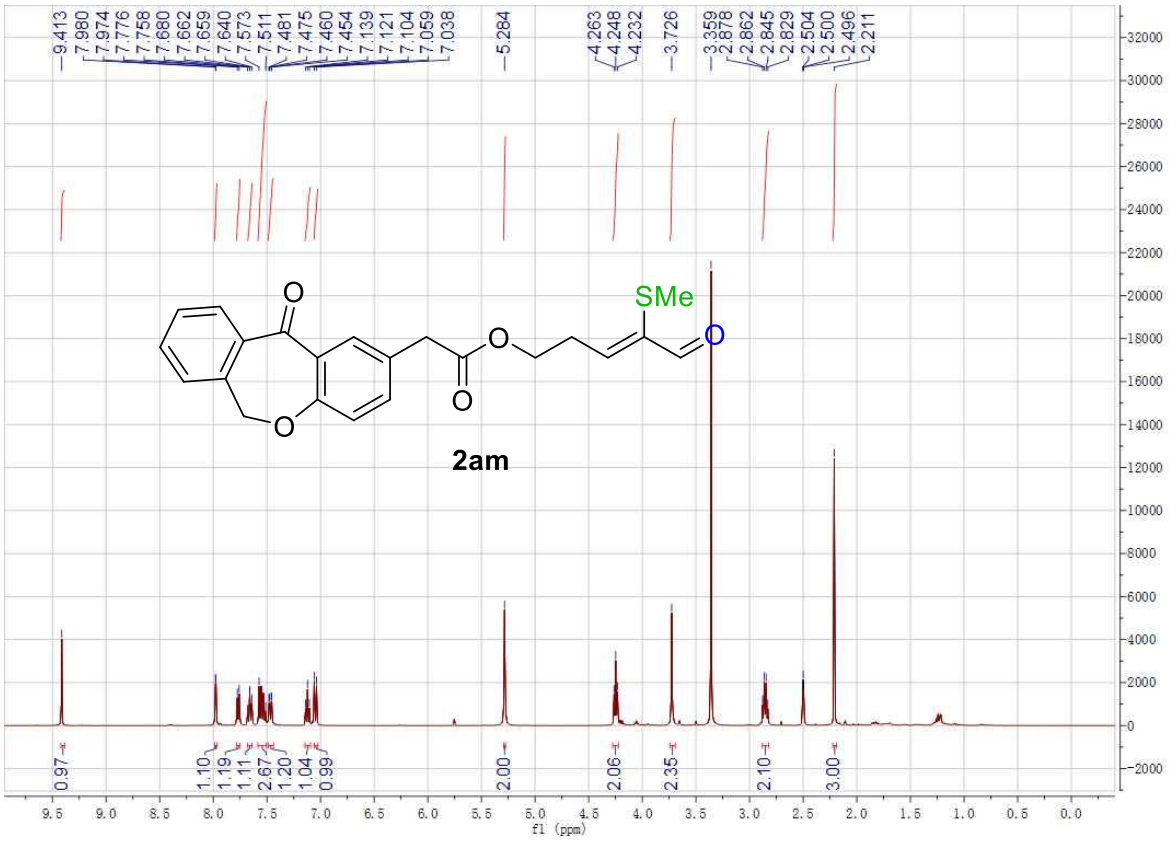
^{1}H NMR spectrum of 2al in $CDCl_3$, 400 MHz



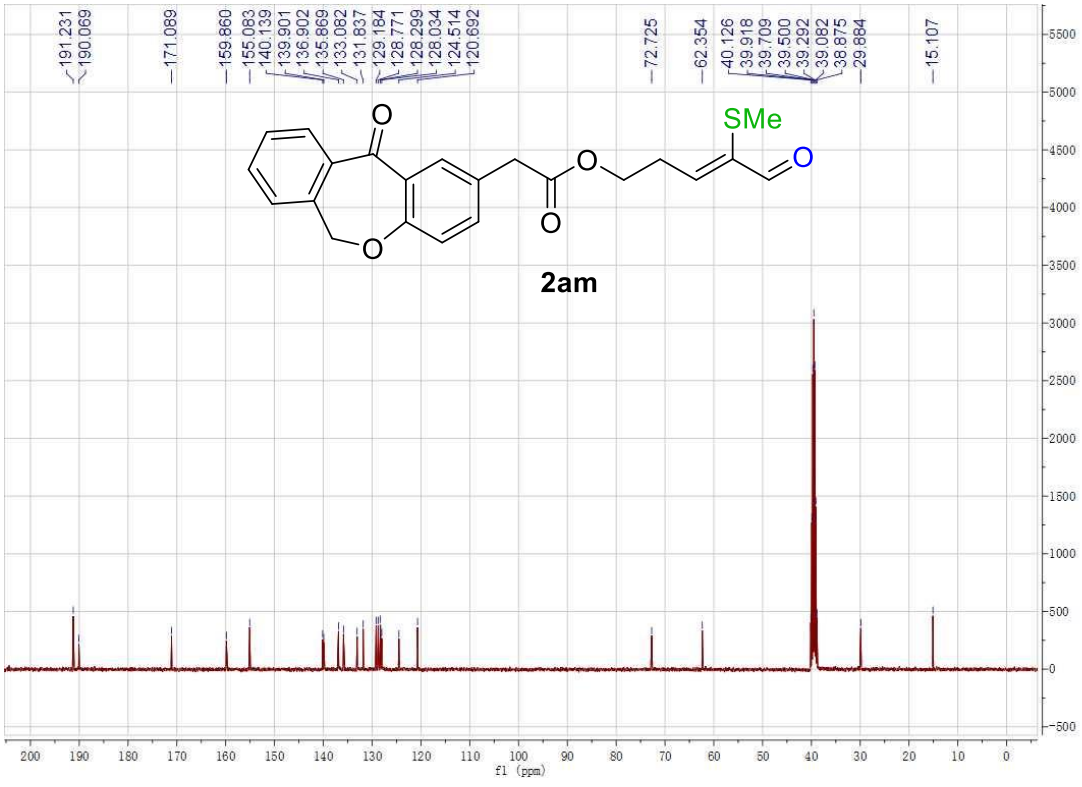
^{13}C NMR spectrum of 2al in $CDCl_3$, 101 MHz



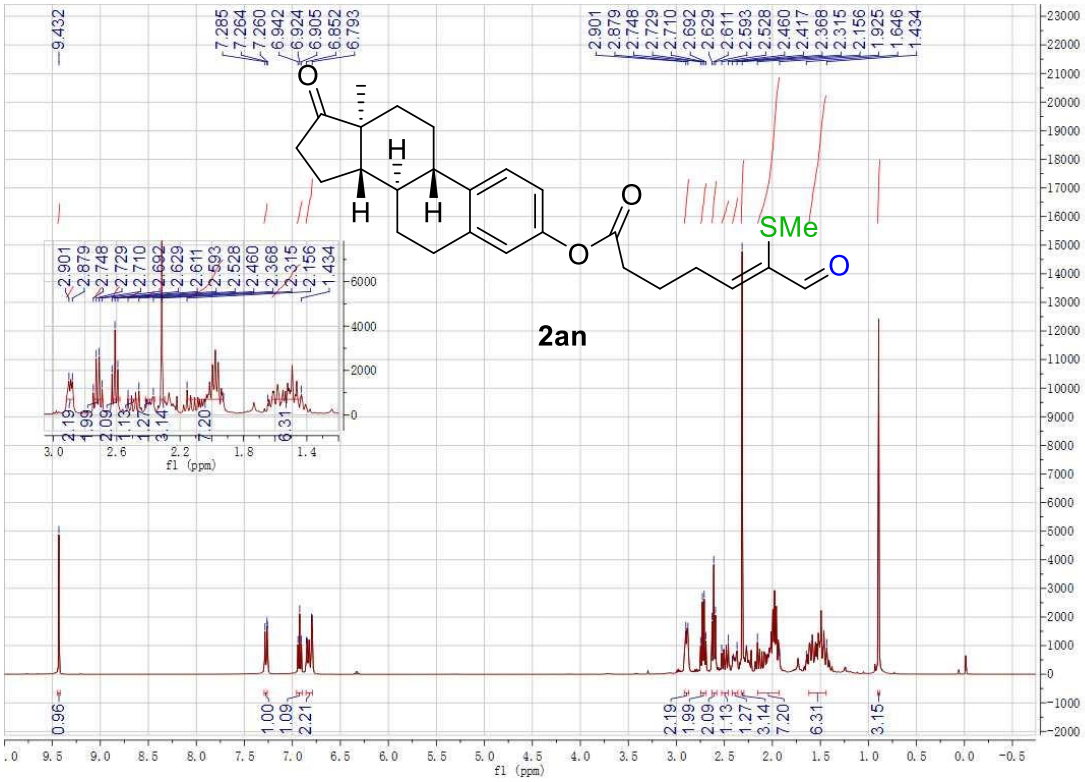
^{1}H NMR spectrum of 2am in d^{6}-DMSO, 400 MHz



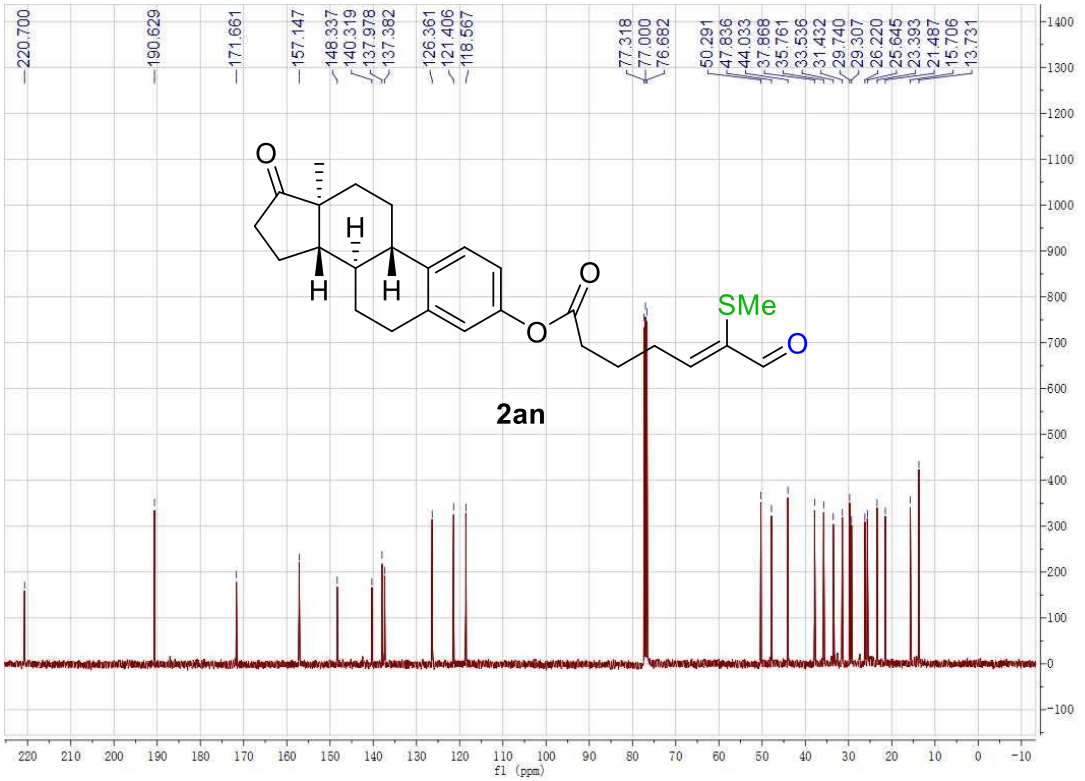
^{13}C NMR spectrum of 2am in d^{6}-DMSO, 101 MHz



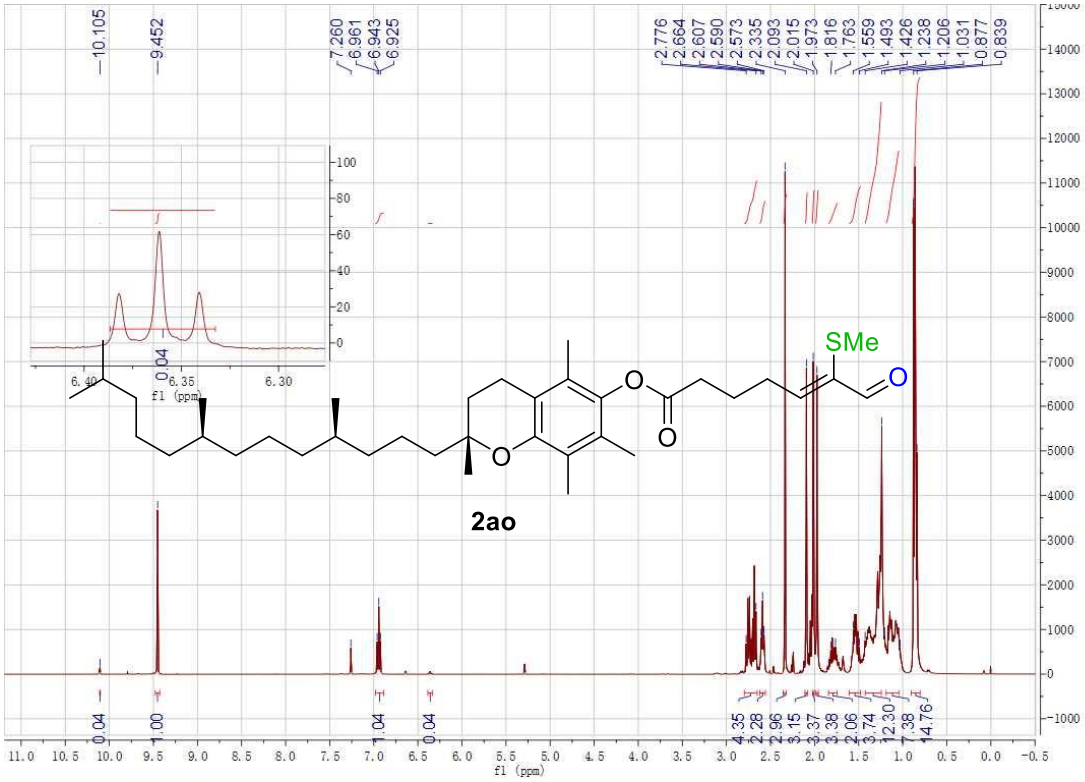
^{1}H NMR spectrum of 2an in $CDCl_3$, 400 MHz



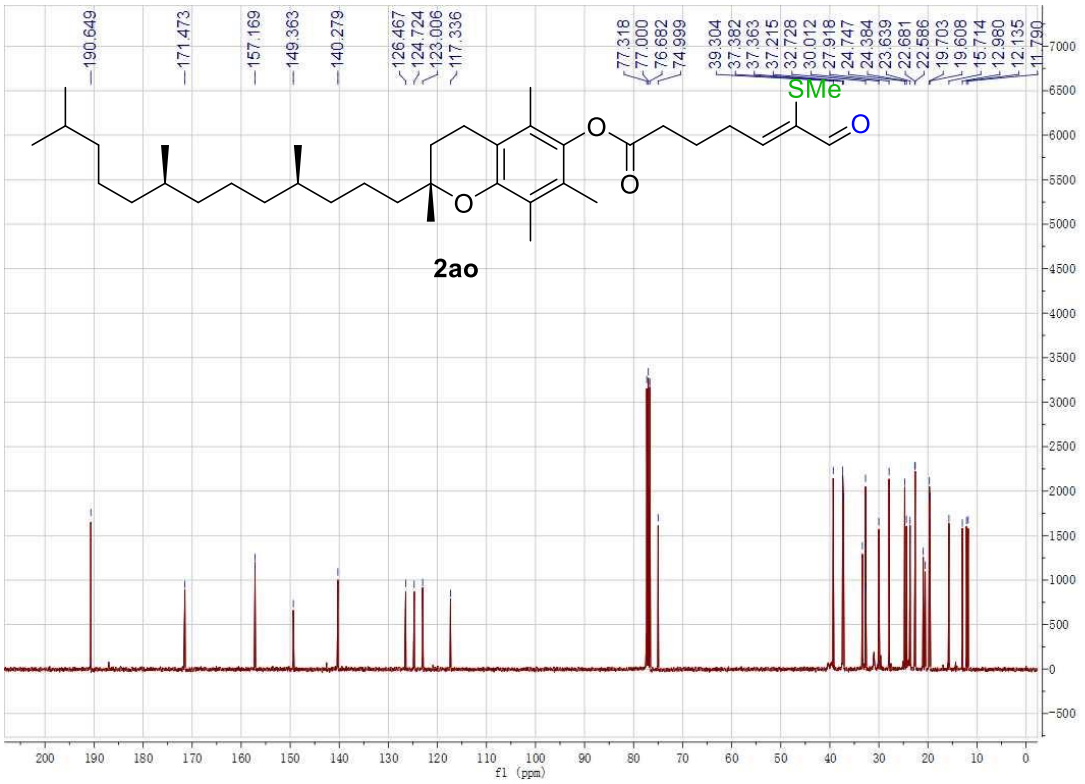
^{13}C NMR spectrum of 2an in $CDCl_3$, 101 MHz



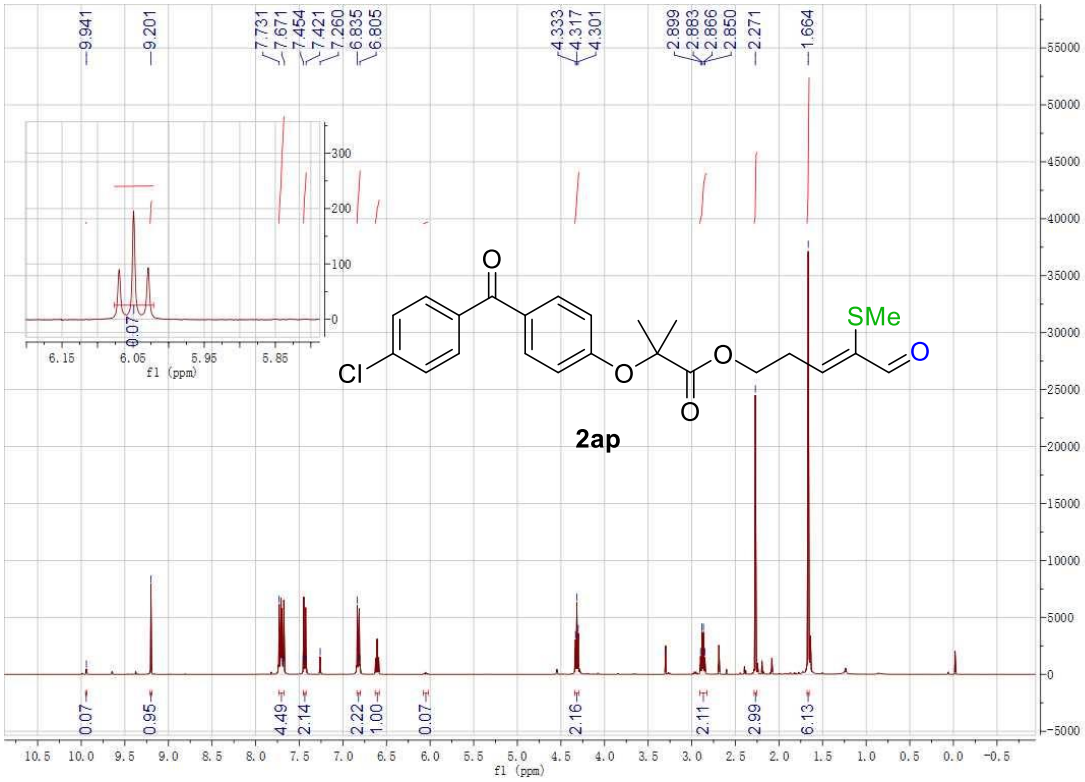
^{1}H NMR spectrum of 2ao in $CDCl_3$, 400 MHz



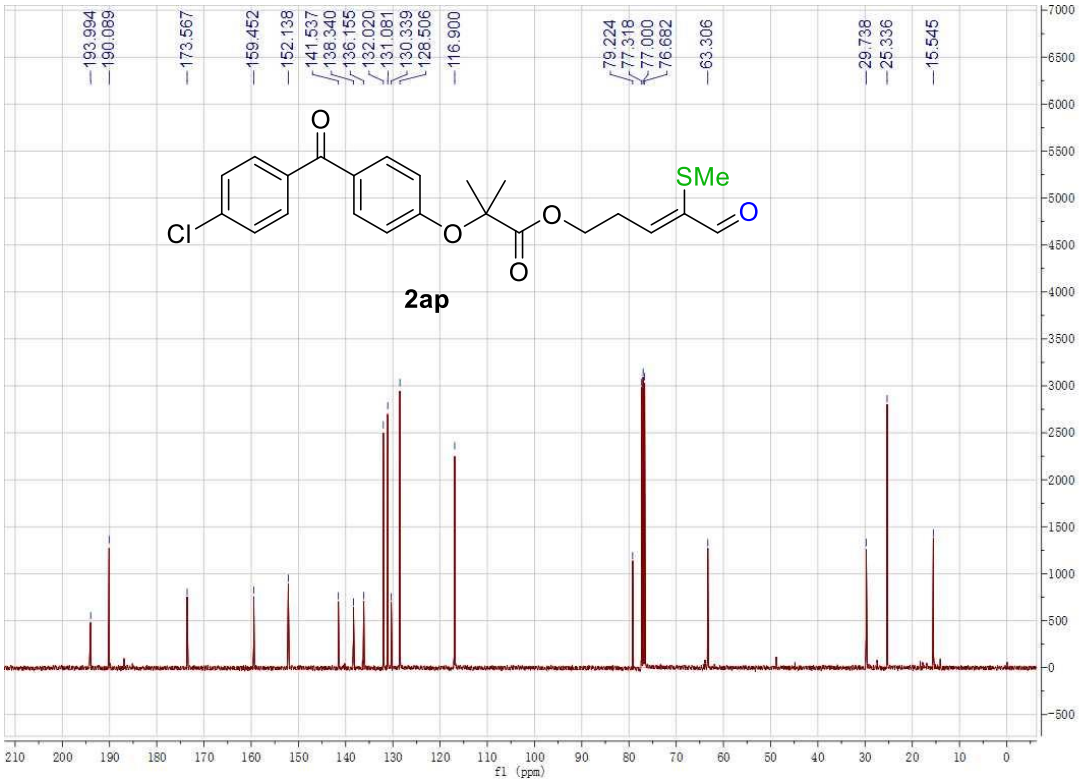
^{13}C NMR spectrum of 2ao in $CDCl_3$, 101 MHz



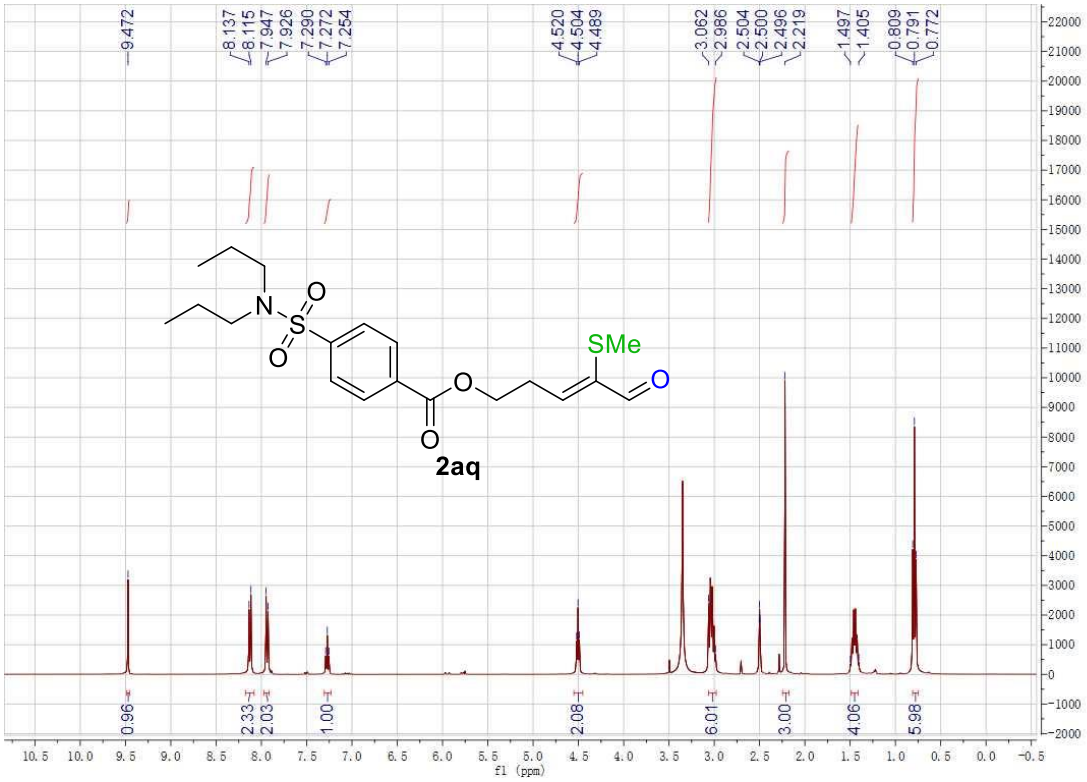
^{1}H NMR spectrum of 2ap in $CDCl_3$, 400 MHz



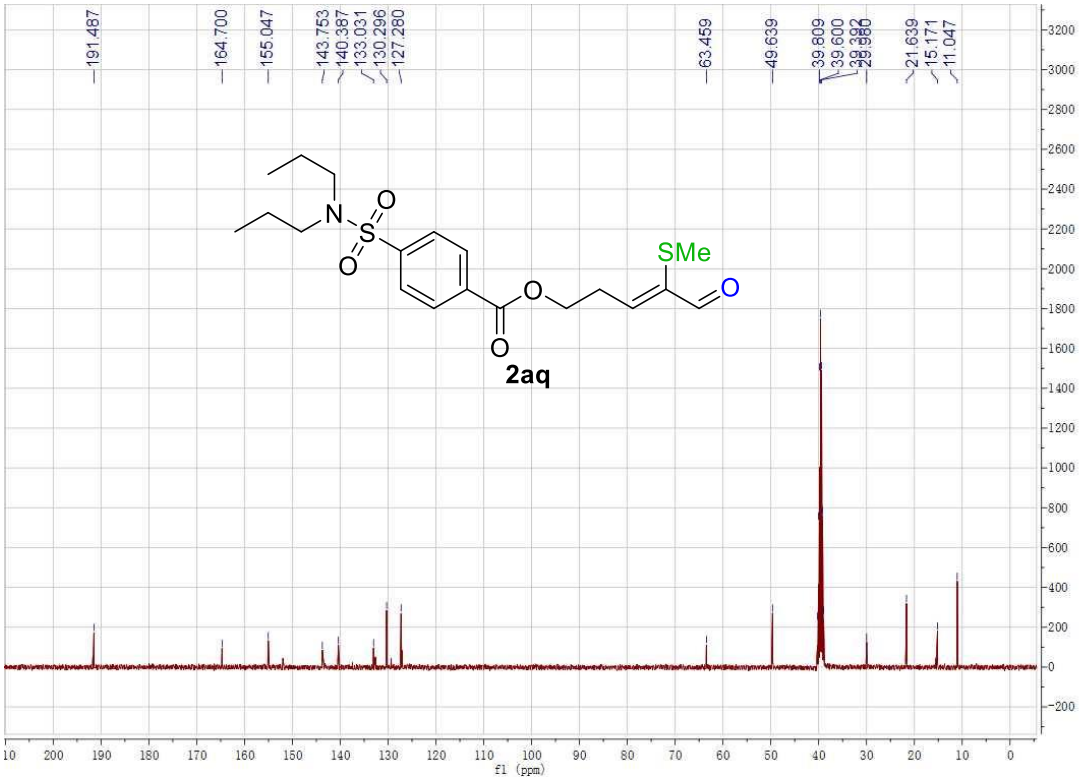
^{13}C NMR spectrum of 2ap in $CDCl_3$, 101 MHz



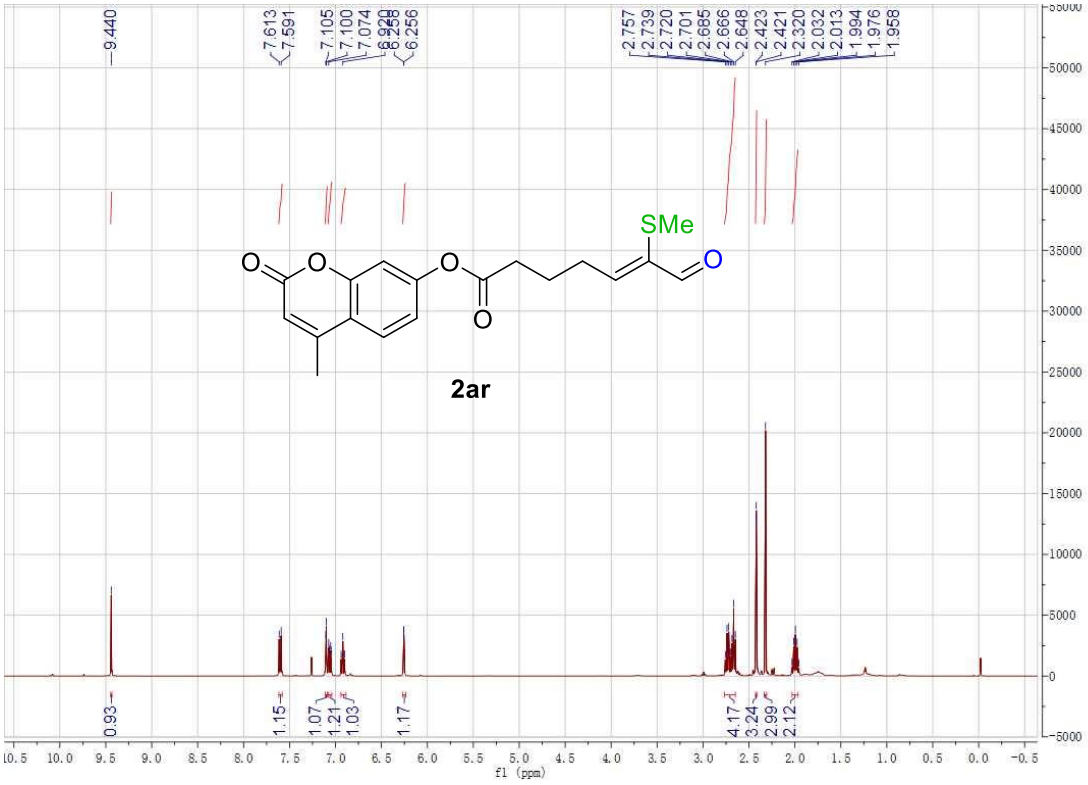
^{1}H NMR spectrum of 2aq in *d*^{6}-DMSO, 400 MHz



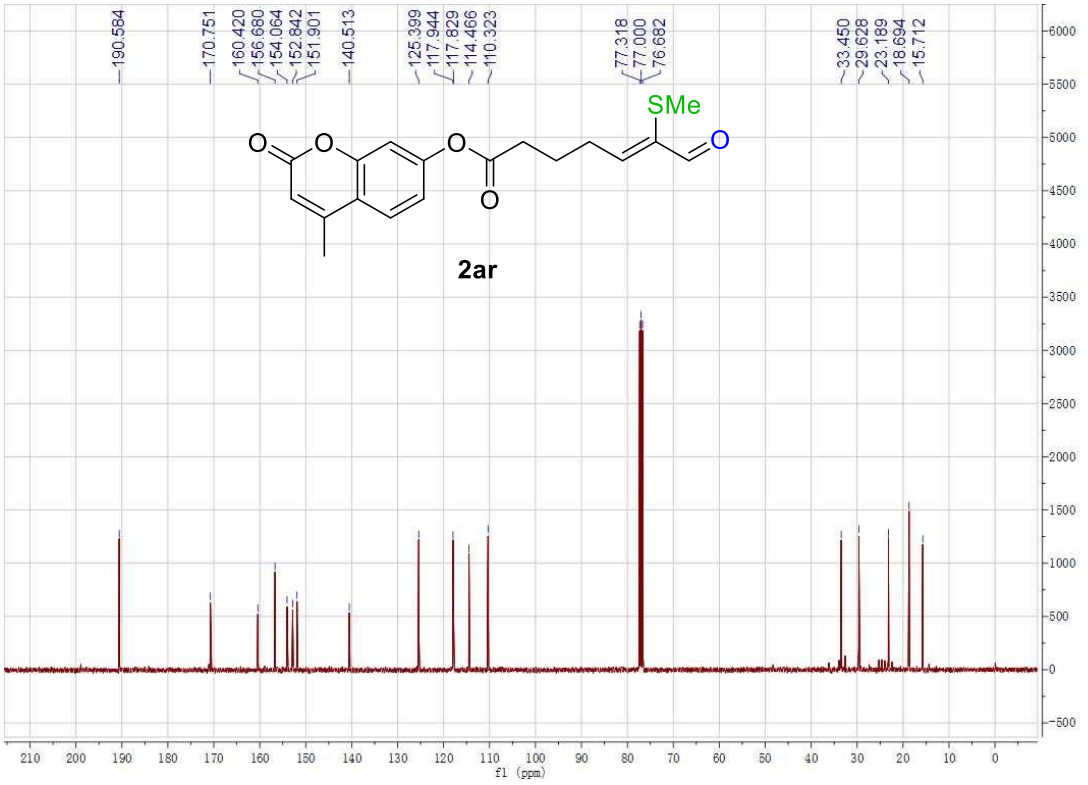
^{13}C NMR spectrum of 2aq in *d*^{6}-DMSO, 101 MHz



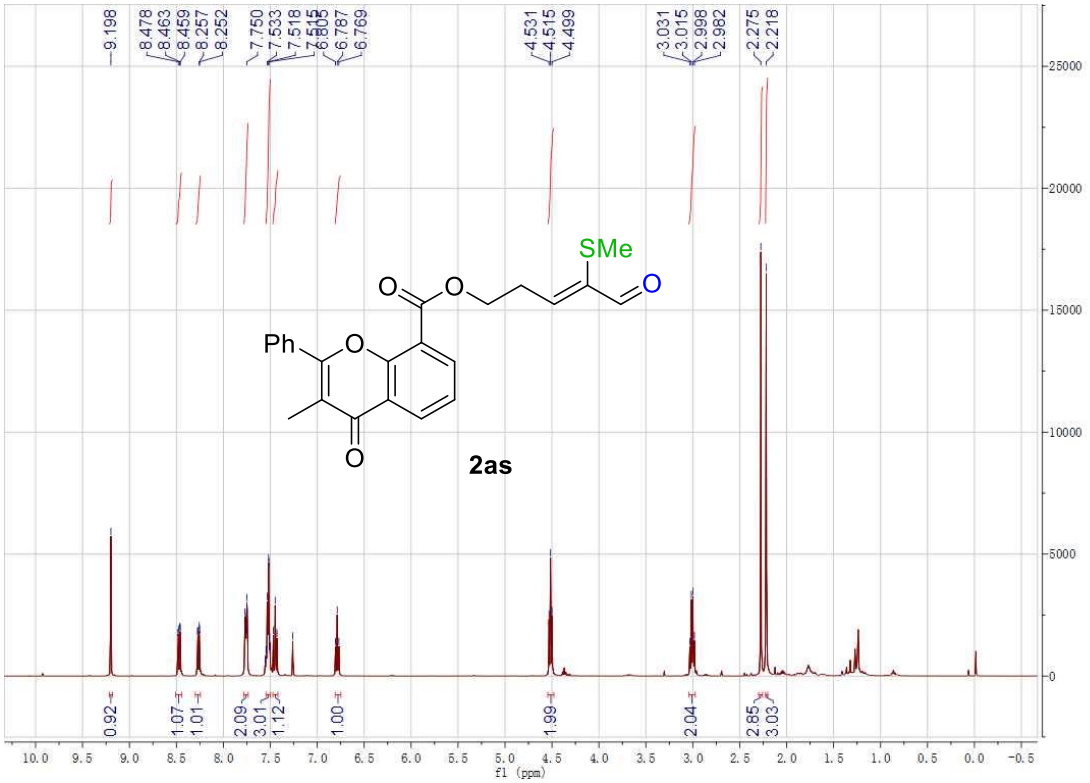
^{1}H NMR spectrum of 2ar in $CDCl_3$, 400 MHz



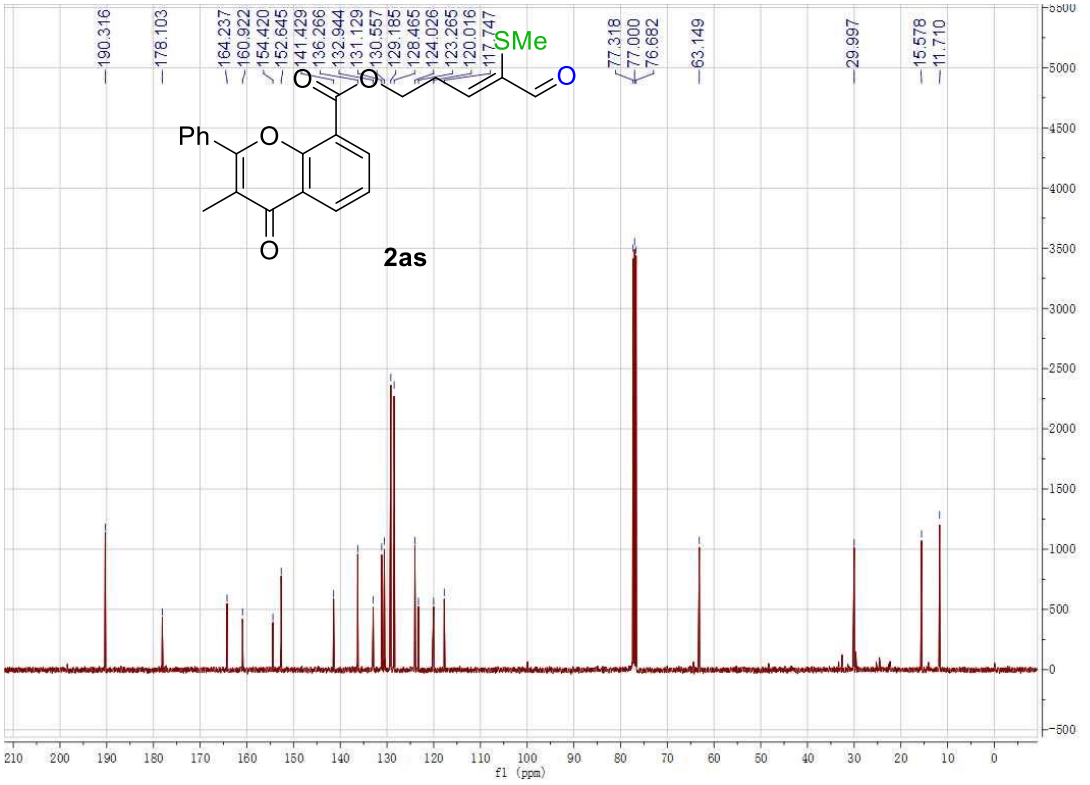
^{13}C NMR spectrum of 2ar in $CDCl_3$, 101 MHz



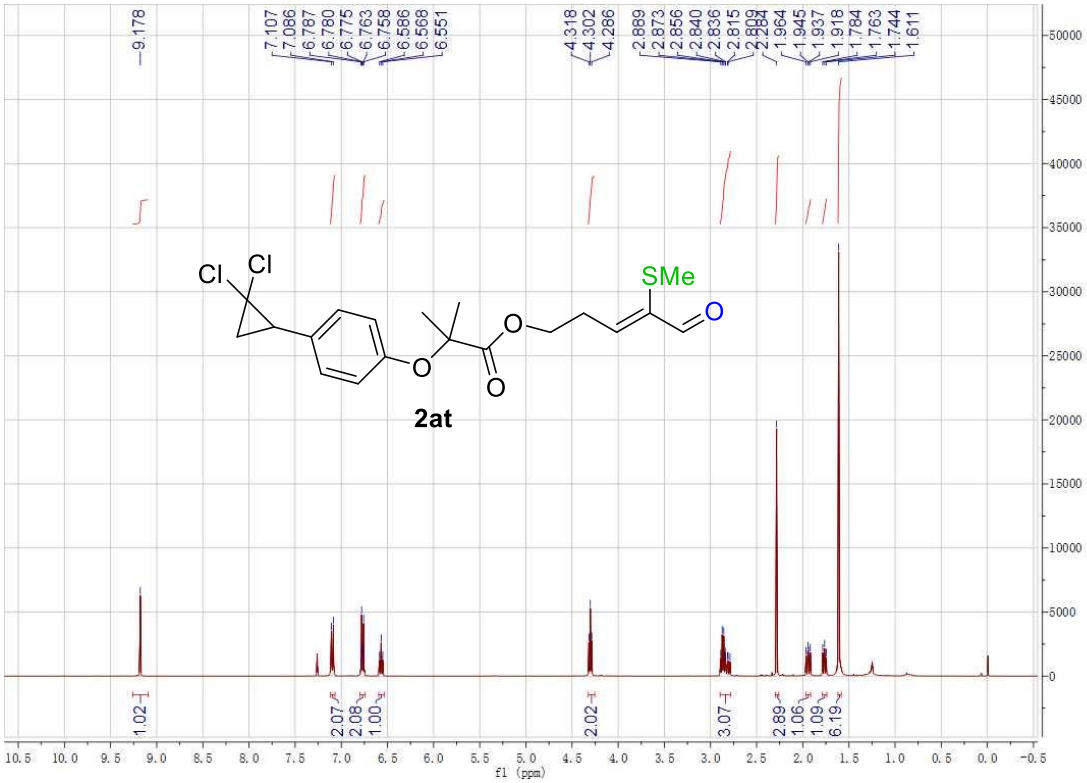
^{1}H NMR spectrum of 2as in $CDCl_3$, 400 MHz



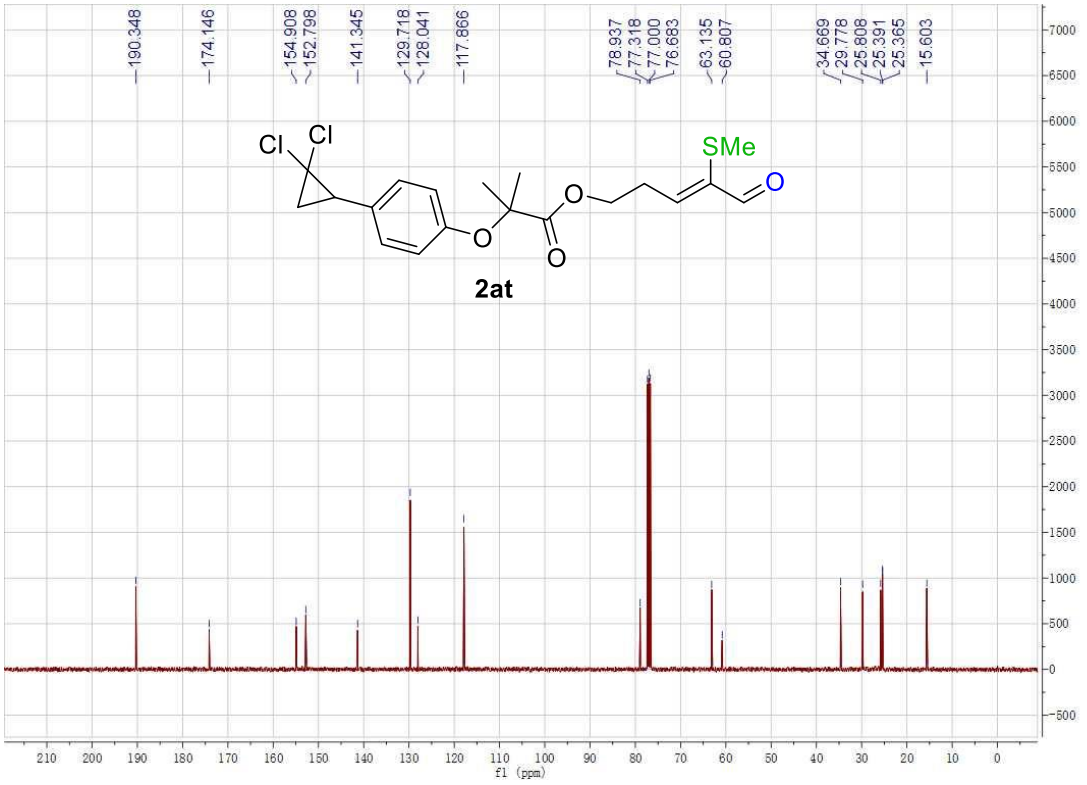
^{13}C NMR spectrum of 2as in $CDCl_3$, 101 MHz



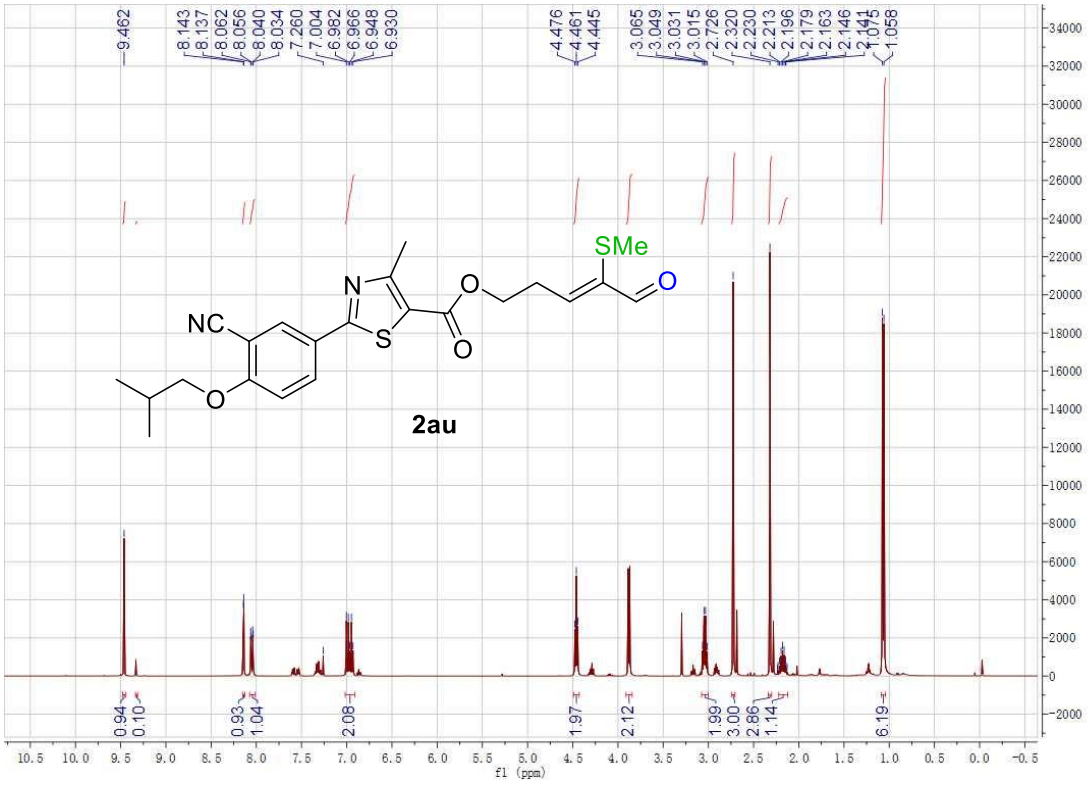
^{1}H NMR spectrum of 2at in $CDCl_3$, 400 MHz



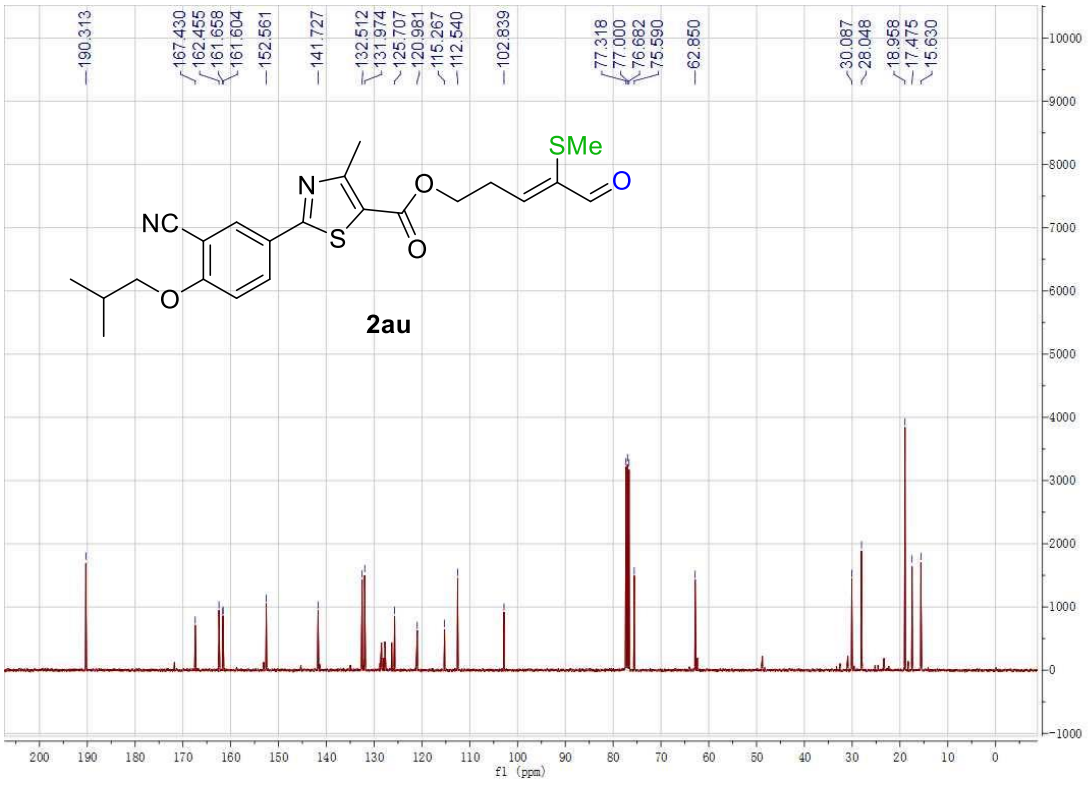
^{13}C NMR spectrum of 2at in $CDCl_3$, 101 MHz



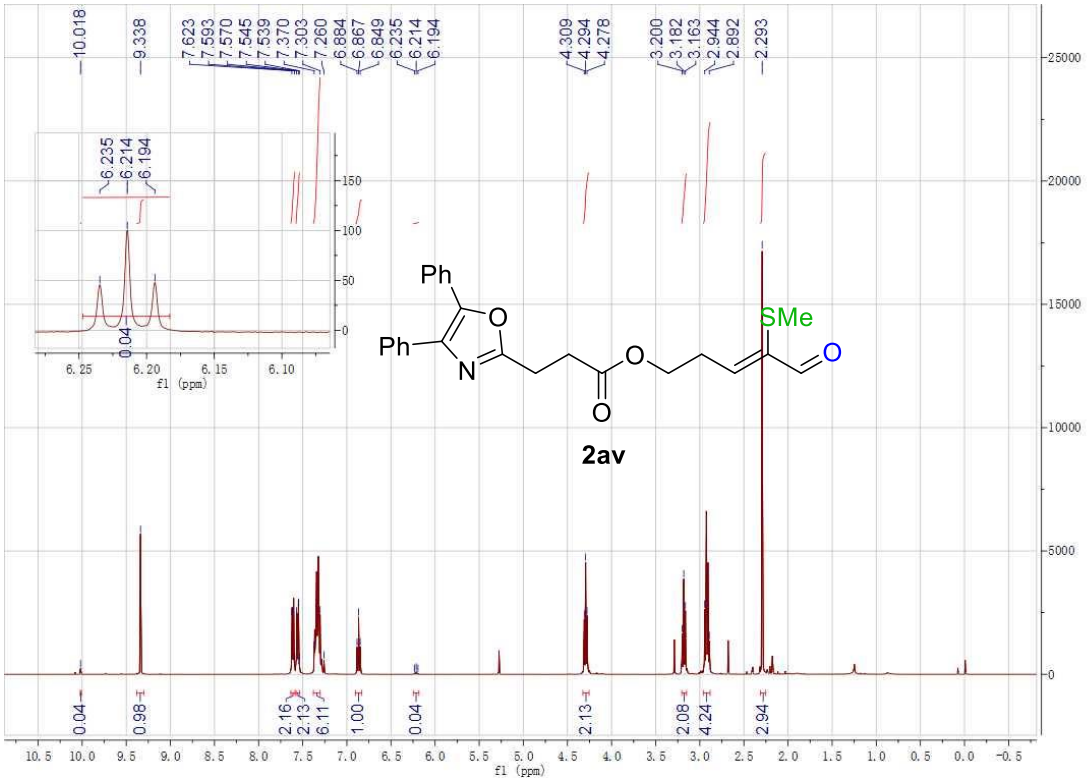
^{1}H NMR spectrum of 2au in $CDCl_3$, 400 MHz



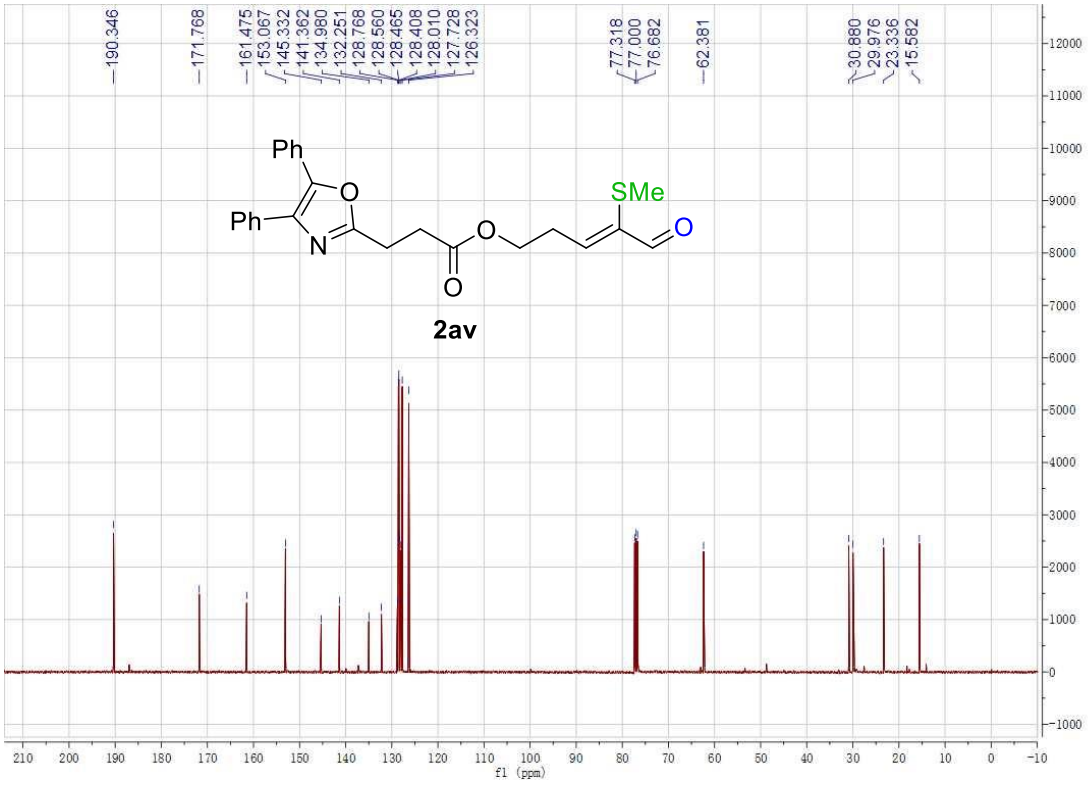
^{13}C NMR spectrum of 2au in $CDCl_3$, 101 MHz



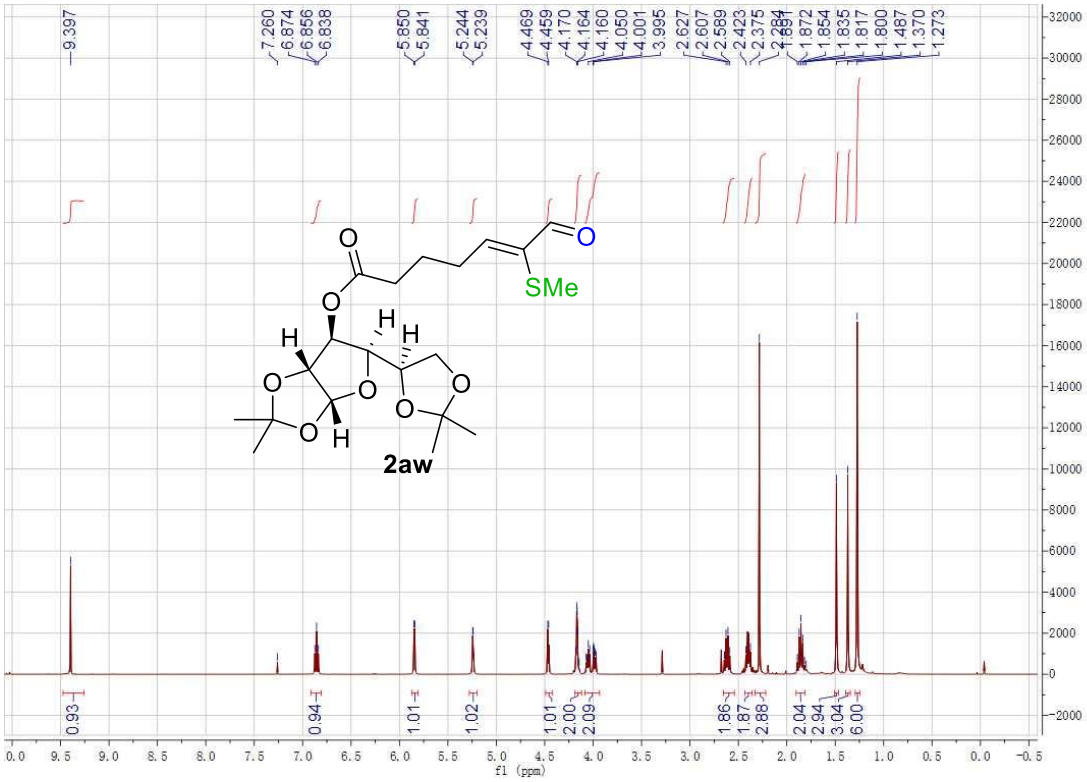
^{1}H NMR spectrum of 2av in $CDCl_3$, 400 MHz



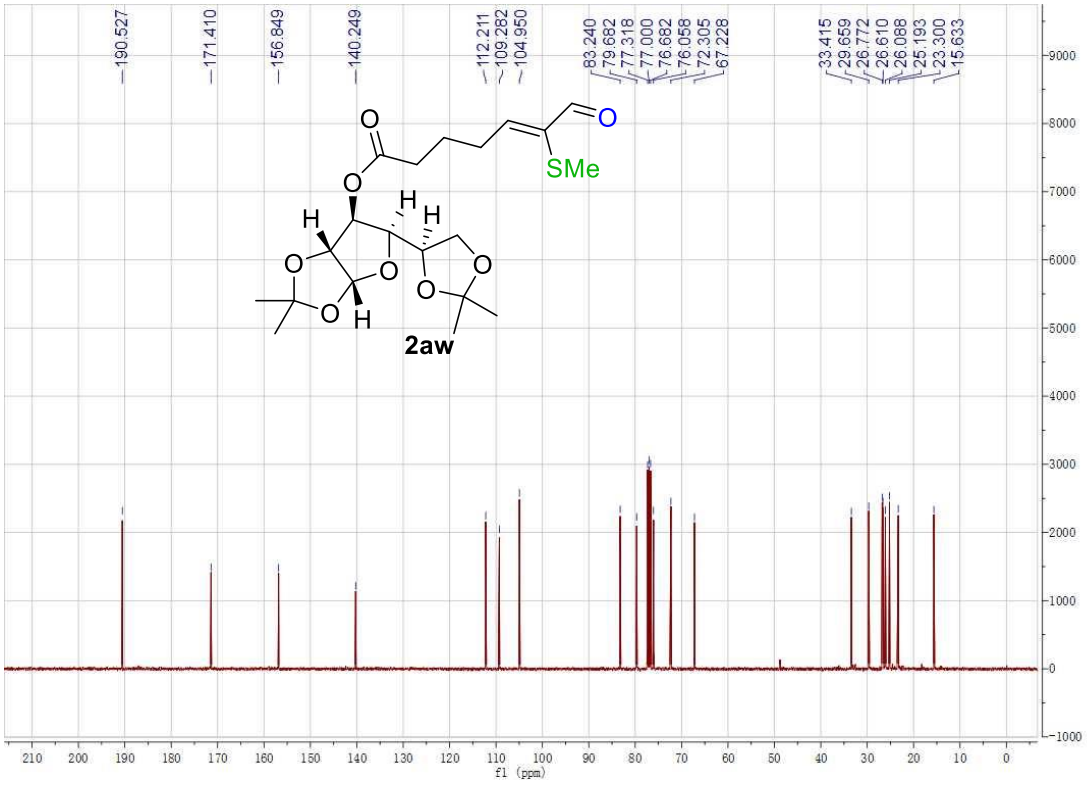
^{13}C NMR spectrum of 2av in $CDCl_3$, 101 MHz



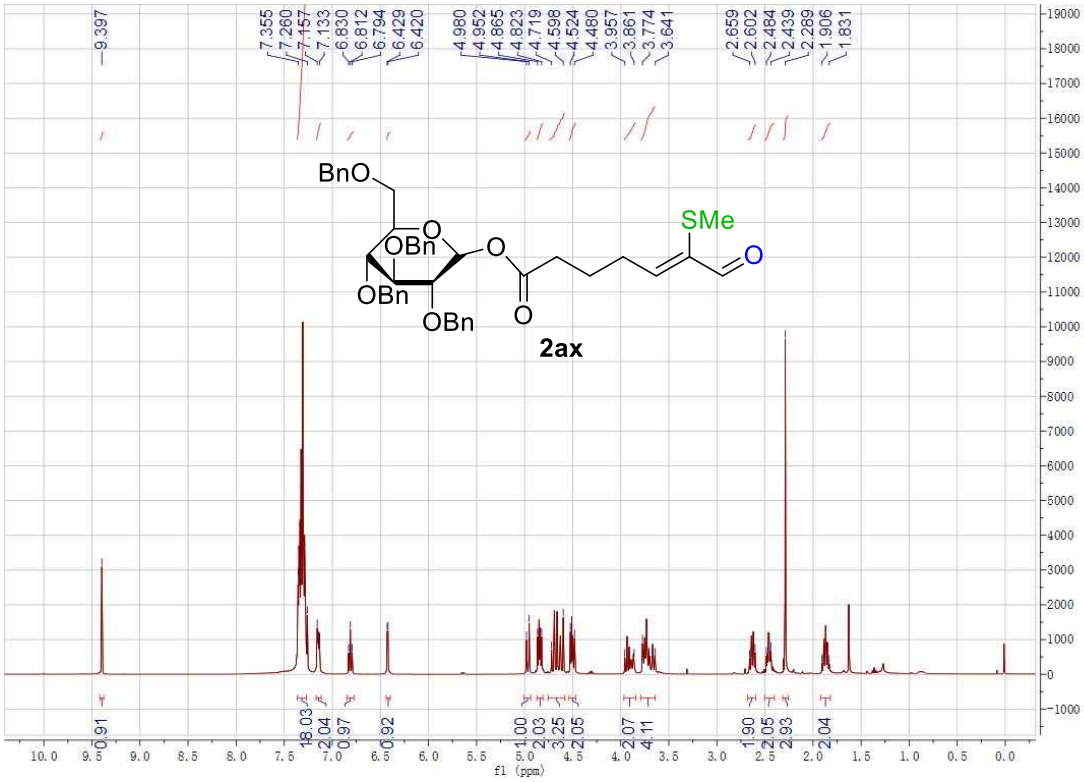
^{1}H NMR spectrum of 2aw in $CDCl_3$, 400 MHz



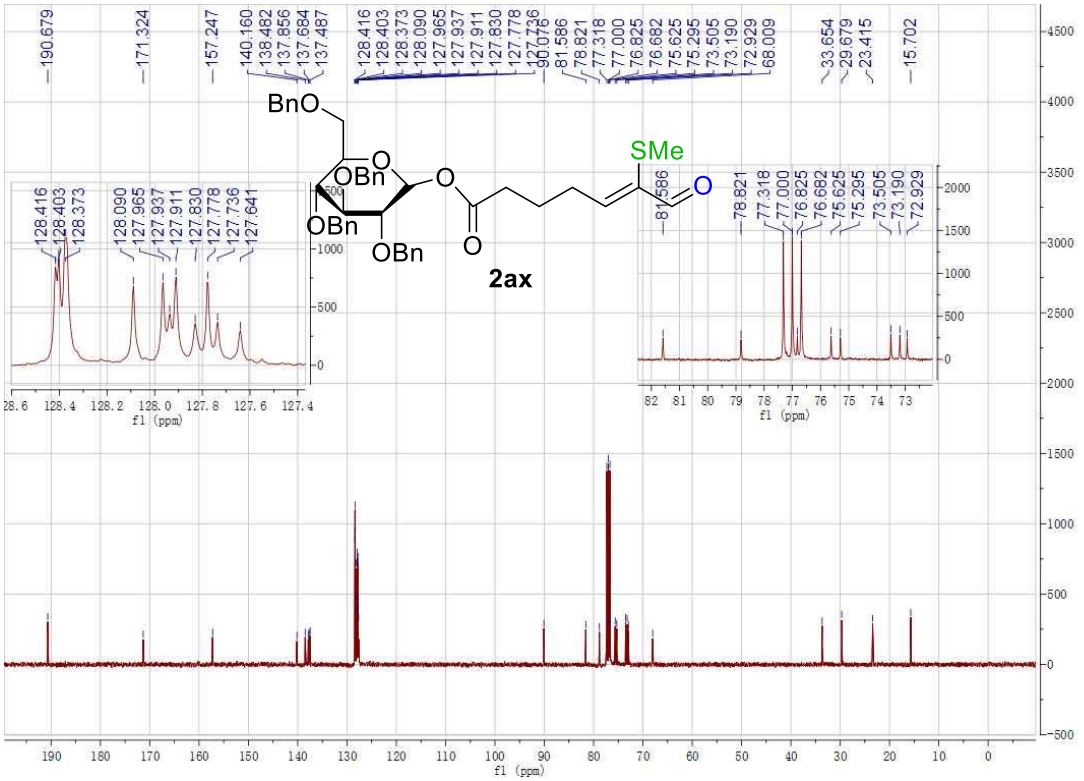
^{13}C NMR spectrum of 2aw in $CDCl_3$, 101 MHz



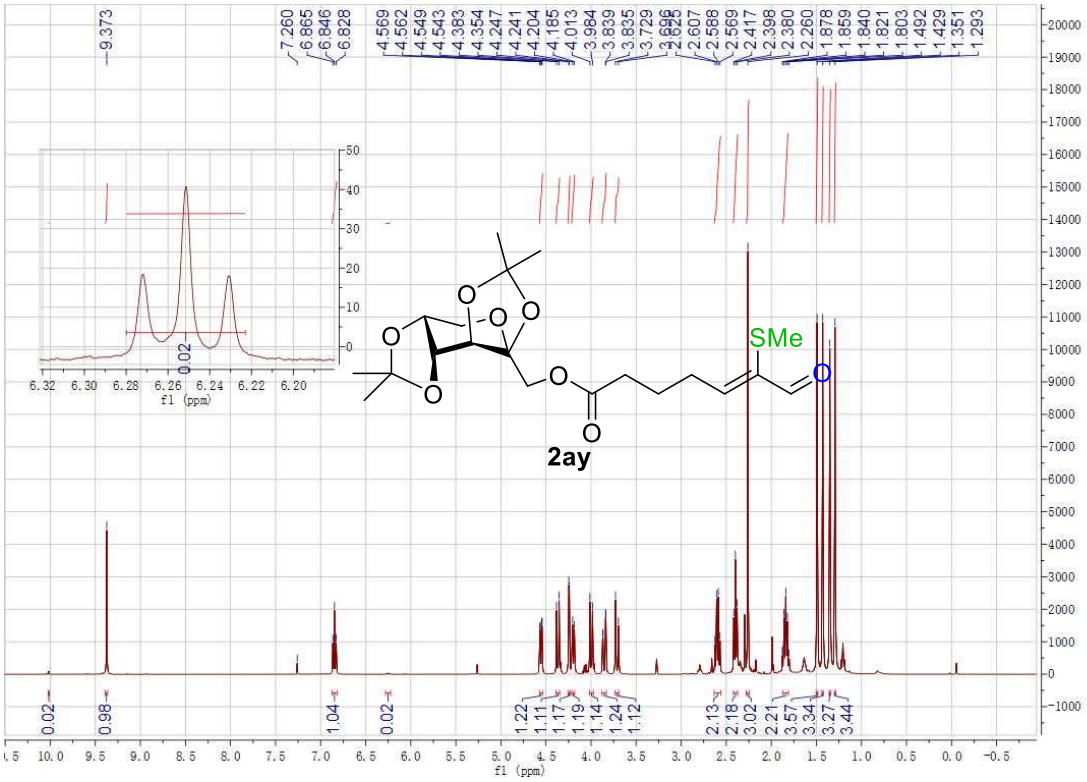
^{1}H NMR spectrum of 2ax in $CDCl_3$, 400 MHz



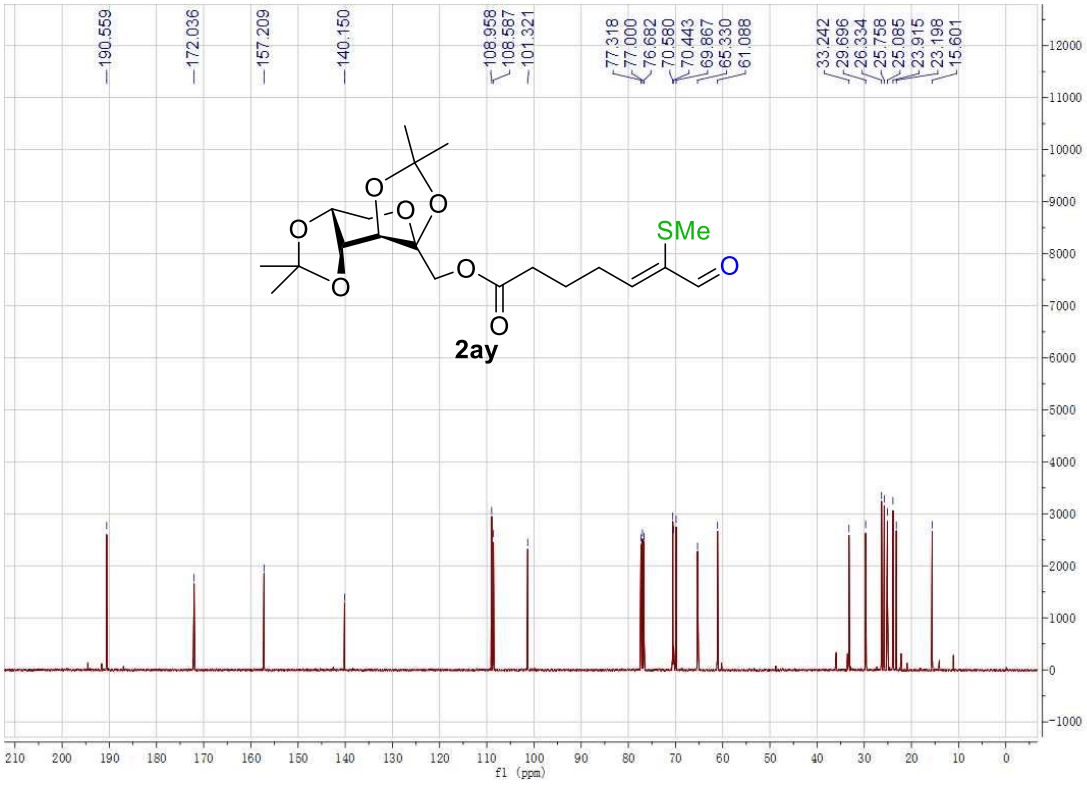
^{13}C NMR spectrum of 2ax in $CDCl_3$, 101 MHz



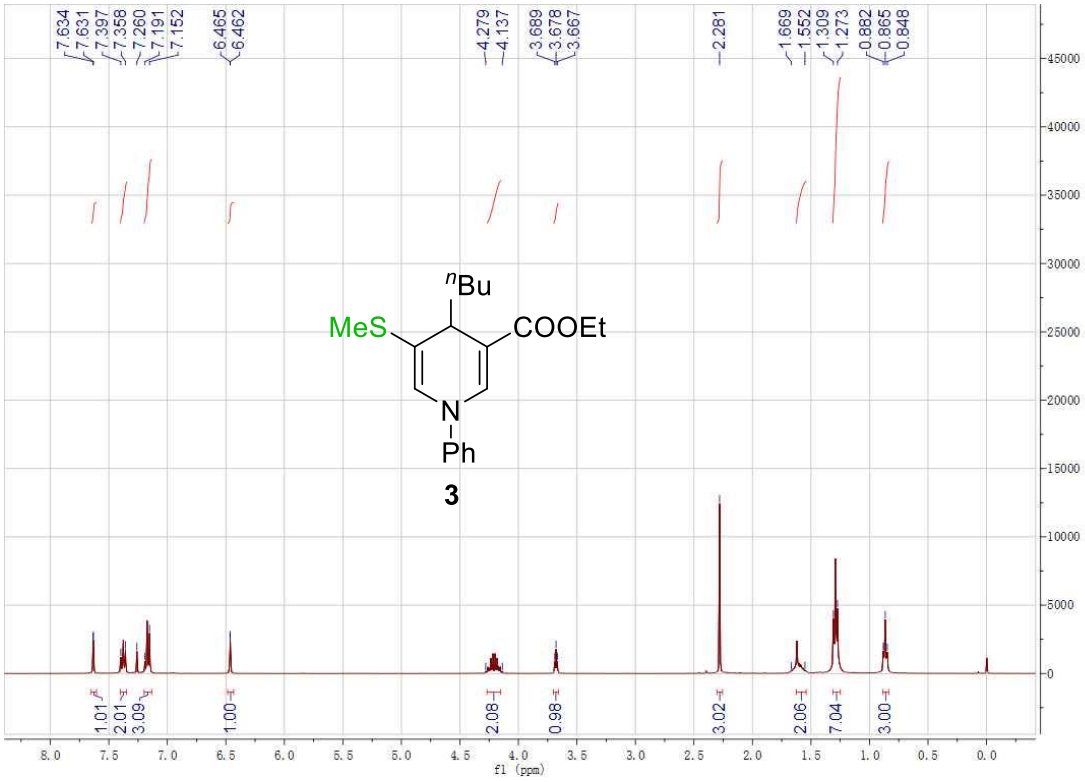
^{1}H NMR spectrum of 2ay in $CDCl_3$, 400 MHz



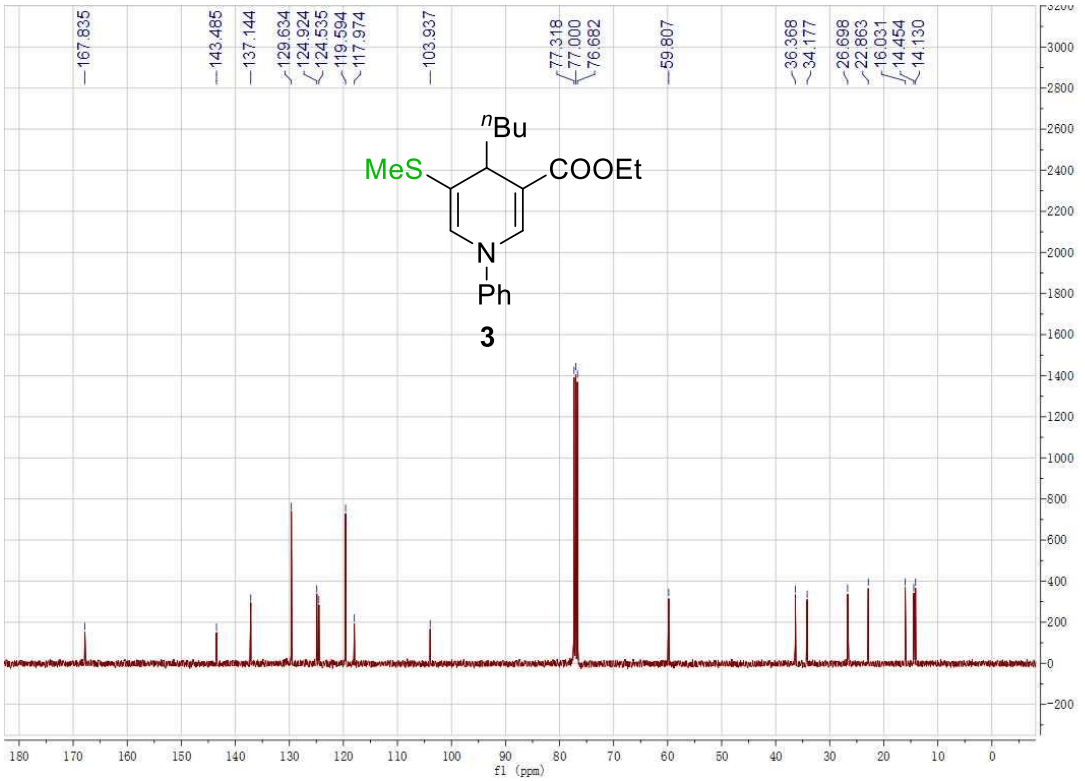
^{13}C NMR spectrum of 2ay in $CDCl_3$, 101 MHz



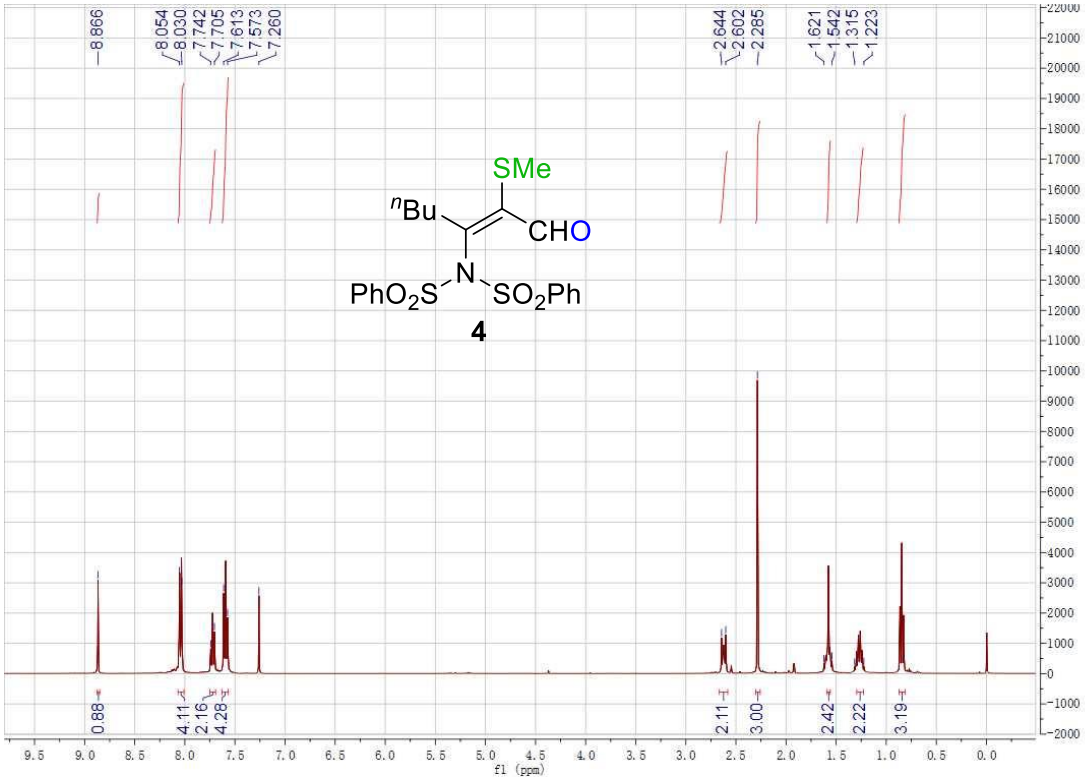
^{1}H NMR spectrum of 3 in $CDCl_3$, 400 MHz



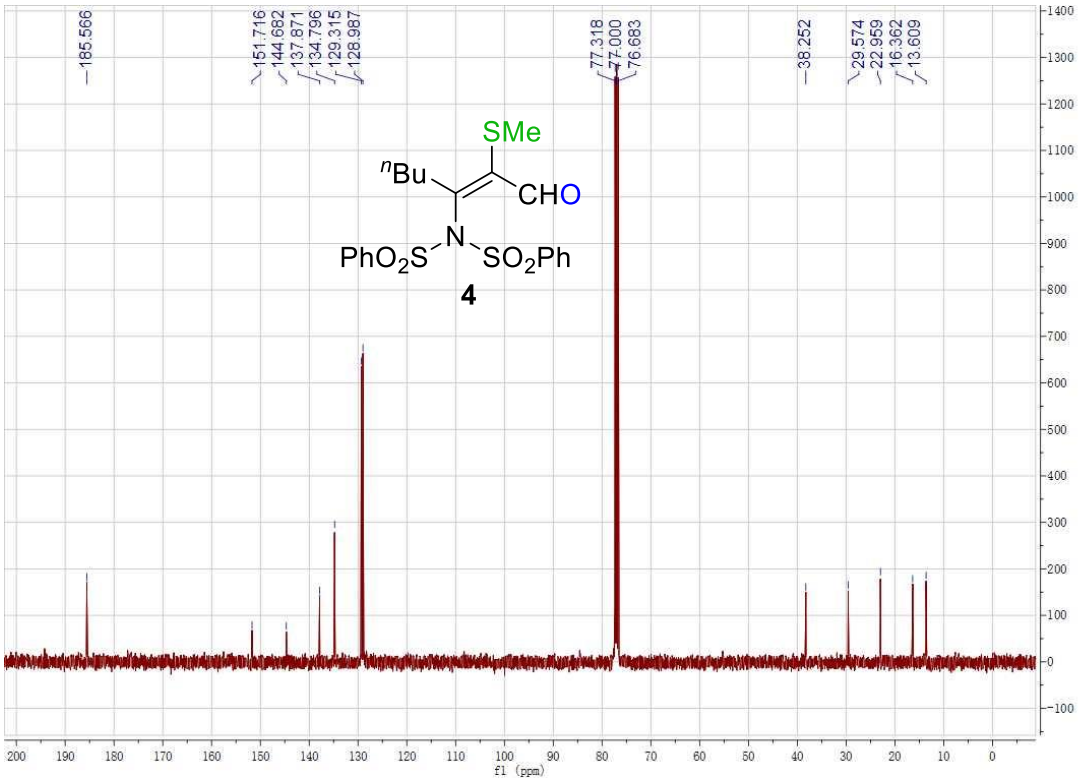
^{13}C NMR spectrum of 3 in $CDCl_3$, 101 MHz



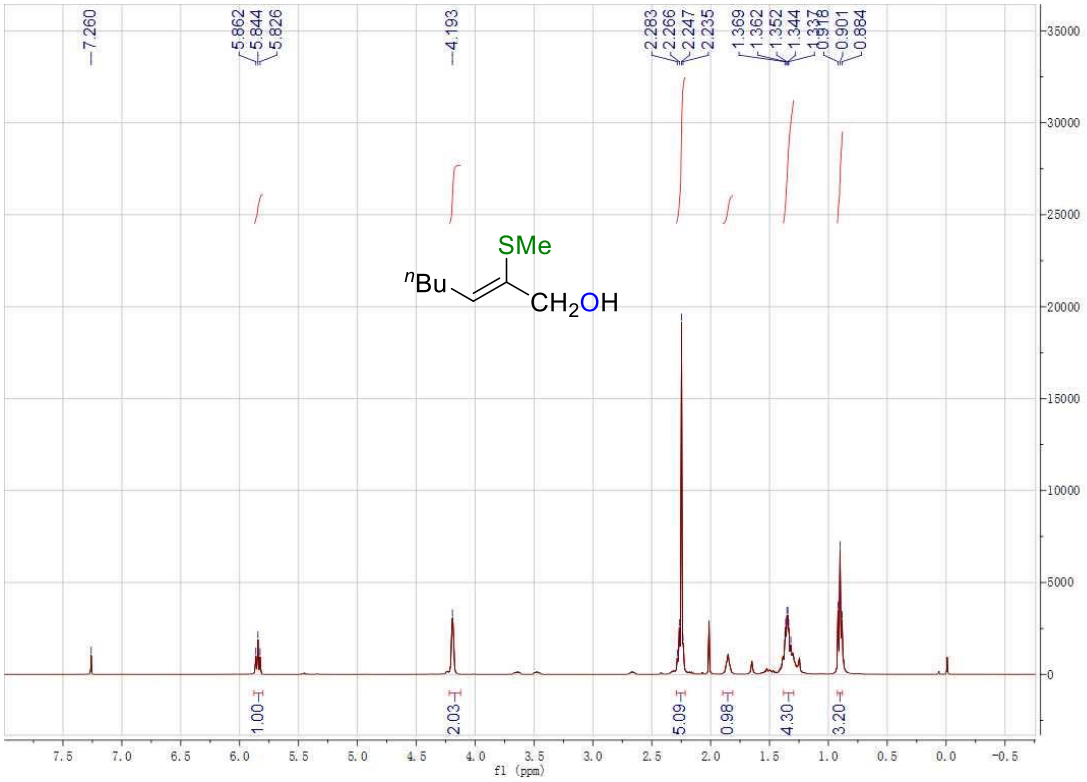
^{1}H NMR spectrum of 4 in $CDCl_3$, 400 MHz



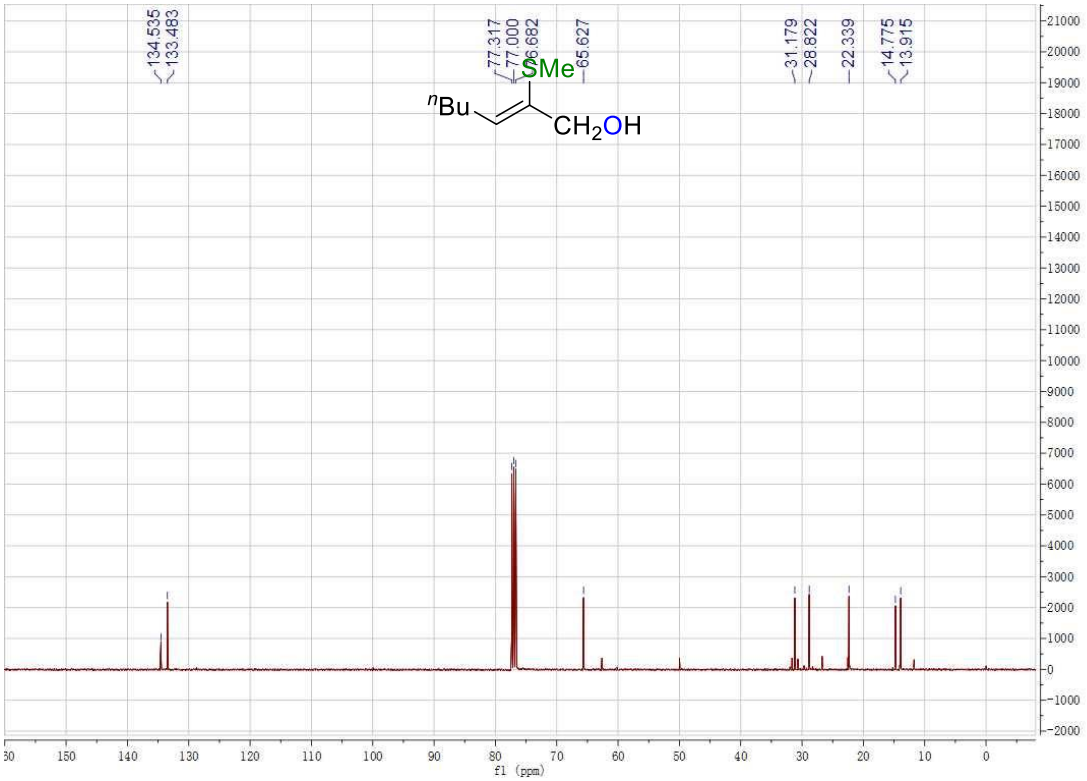
^{13}C NMR spectrum of 4 in $CDCl_3$, 101 MHz



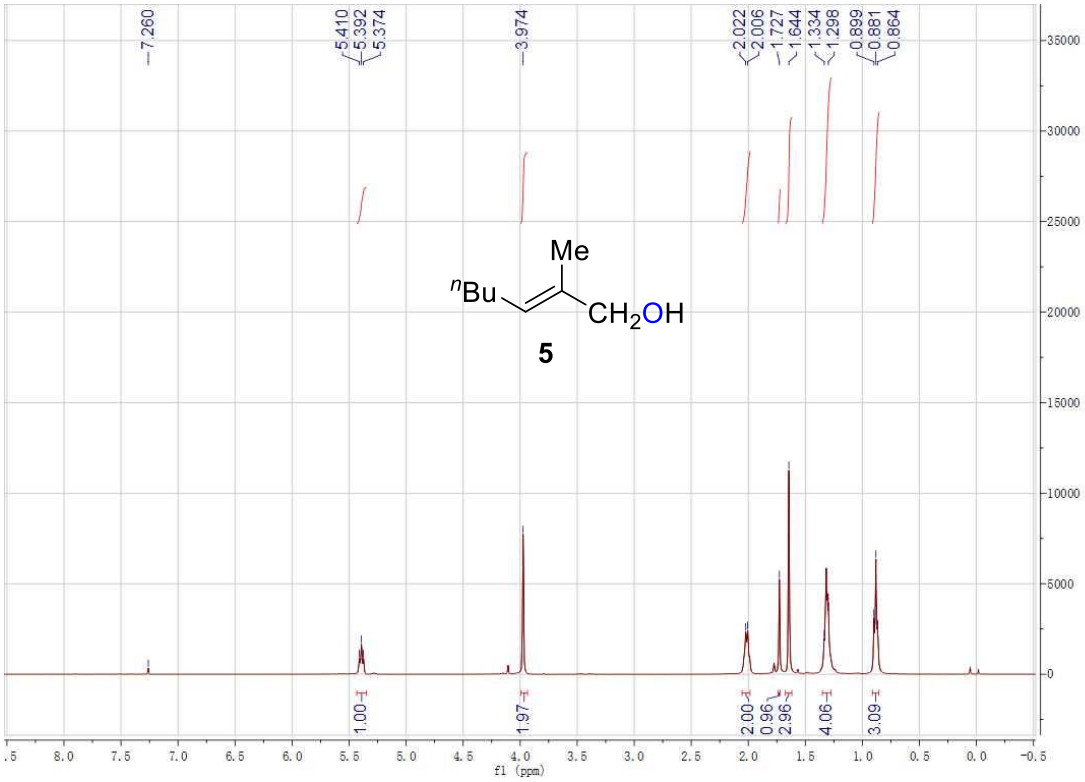
^{1}H NMR spectrum of s-5 in $CDCl_3$, 400 MHz



^{13}C NMR spectrum of s-5 in $CDCl_3$, 101 MHz



^{1}H NMR spectrum of 5 in $CDCl_3$, 400 MHz



^{13}C NMR spectrum of 5 in $CDCl_3$, 101 MHz