

Supporting Information

Visible-Light-Induced Perfluoroalkylation Cyclization to Access Perfluoroalkylated Benzazepines and Benzoxepines by EDA Complexes

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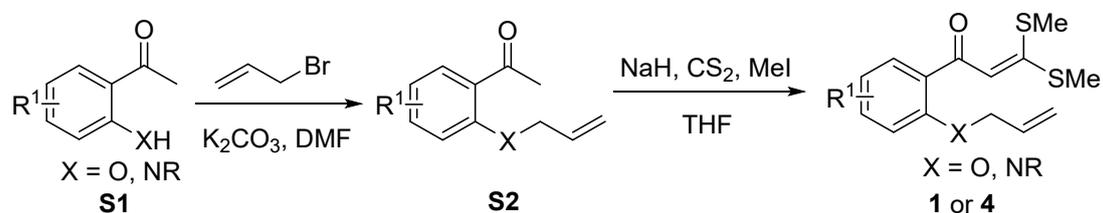
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General Information:

All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts and solvents were obtained from commercial suppliers. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Chemical shifts (δ) are given in ppm relative to CDCl_3 (7.26 ppm for ^1H and 77 ppm for ^{13}C) to internal TMS ($\delta = 0$ ppm) as internal standard. High-resolution mass spectra (HRMS) were obtained using ESI-TOF in positive mode. UV-Vis spectra were recorded in 1 cm path quartz cuvettes on a INESA L5S UV-VIS spectrophotometer. **2a-g** were commercially available reagents. Substrates **1** and **4** were prepared according to the related literature. [1]

General procedure for the synthesis of **1** or **4**



Step I: To a solution of **S1** (5 mmol, 1.0 equiv) in DMF (15 mL) was added K₂CO₃ (10 mmol, 2 equiv) and 3-bromoprop-1-ene (7.5 mmol, 1.5 equiv). The mixture was stirred at room temperature for 12 h. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue, which is purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10:1, v/v) to afford the corresponding product **S2**.

Step II: To a stirred suspension of NaH (8.0 mmol) in THF (8.0 mL) was added a solution of **S1** (2.0 mmol) in THF (2.0 mL) dropwise within 15 min at 0 °C. The reaction mixture was stirred for 20 min at 0 °C; then carbon disulfide (2.40 mmol) was added dropwise within 15 min at 0 °C. The reaction mixture was stirred for 30 min at 0 °C; then methyl iodide (4.40 mmol) was added dropwise during 15 min at 0 °C. The reaction mixture was then warmed to room temperature, and stirred for 5-6 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate) to afford the desired products **1** or **4**.

General procedure for synthesis of product **3** or **5**

Under an Ar atmosphere, **1** or **4** (0.1 mmol, 1.0 equiv.), **2** (0.2 mmol, 2.0 equiv.), K₂CO₃ (0.2 mmol, 2.0 equiv.) and CH₃CN (1 mL) were added to a Schlenk tube (10 mL). The reaction was stirred at room temperature for 12 h upon a 395nm LEDs irradiation. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate) to afford the desired products **3** or **5**.

The Gram-Scale Synthesis of Compound **3a**

Under an Ar atmosphere, **1a** (3 mmol, 1.30 g, 1.0 equiv.), **2a** (6 mmol, 2.08 g, 2.0 equiv.), K₂CO₃

(6 mmol, 0.83 g, 2.0 equiv.) and CH₃CN (30 mL) were added to a Schlenk tube (50 ml). The reaction was stirred at room temperature for 12 h upon a 395nm LEDs irradiation. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate) to afford the desired products **3a** (1.46 g) in 75% yield.

General Procedure for the Synthesis of 6

A round flask was equipped with a magnetic stir bar, **3a** (0.2 mmol, 130.2 mg, 1.0 equiv.), Hydrazine hydrate (20 mg, 0.4 mmol, 2 equiv) and EtOH (3 ml). The resulting mixture was reflux for 6 h. After the reaction was finished, the reaction mixture was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the desired product **6** in 93% (114.7 mg).

Trapping experiment with TEMPO

Under an Ar atmosphere, **1a** (0.1 mmol, 43.3 mg, 1.0 equiv.), **2a** (0.2 mmol, 69.2 mg, 2.0 equiv.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 equiv.), TEMPO (0.3 mmol, 46.8 mg, 3.0 equiv.) and CH₃CN (1 mL) were added to a Schlenk tube (10 ml). The reaction was stirred at room temperature for 12 h upon a 395nm LEDs irradiation. The reaction was completely inhibited, and no TEMPO-adducts were observed, with 94% of **1a** was recovered by column chromatography purification. The results indicate that the transformation proceeds through a radical pathway.

Light ON/OFF experiment

To a stub tube fitted with a magnetic stir bar was added **1a** (129.9 mg, 0.30 mmol), Perfluoroiodobutane (207.6 mg, 0.60 mmol), K₂CO₃ (69.7 mg, 0.6 mmol), and MeCN (3.0 mL, 0.1 M). Then the stub tube was evacuated and backfilled with nitrogen for three times. The reaction was designed to be irradiated under successive on/off LED irradiation conditions at every 2 h interval. As shown in Figure S1, when the reaction was irradiated with blue light, the yield increases significantly. In contrast, when the reaction was in the dark, no increase in yield was observed. The results demonstrate the importance of visible light irradiation in this reaction.

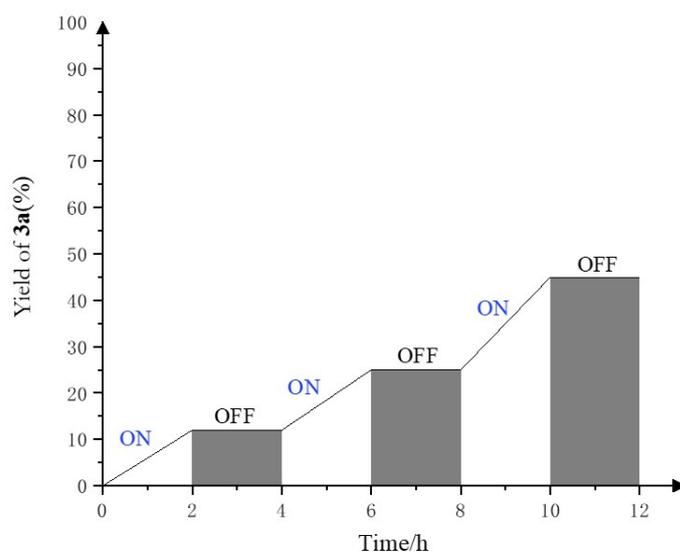


Figure S1. Light ON/OFF experiment for the model reaction.

UV-vis experiment

A UV-vis absorbance experiment has been carried out for confirming the formation of EDA complex. As shown in Figure S2, the black UV absorbance line came from IC_4F_9 solution, red one came from K_2CO_3 solution, and blue one came from the mixed solution of IC_4F_9 and K_2CO_3 . When IC_4F_9 and K_2CO_3 were mixed in MeCN (0.1 M), the UV absorption was red-shifted and shifted to the visible region obviously, accompanied by a gradual change of the solution from colourless to yellow, strongly suggesting that IC_4F_9 - K_2CO_3 EDA complex might indeed be formed in the mixed solution.

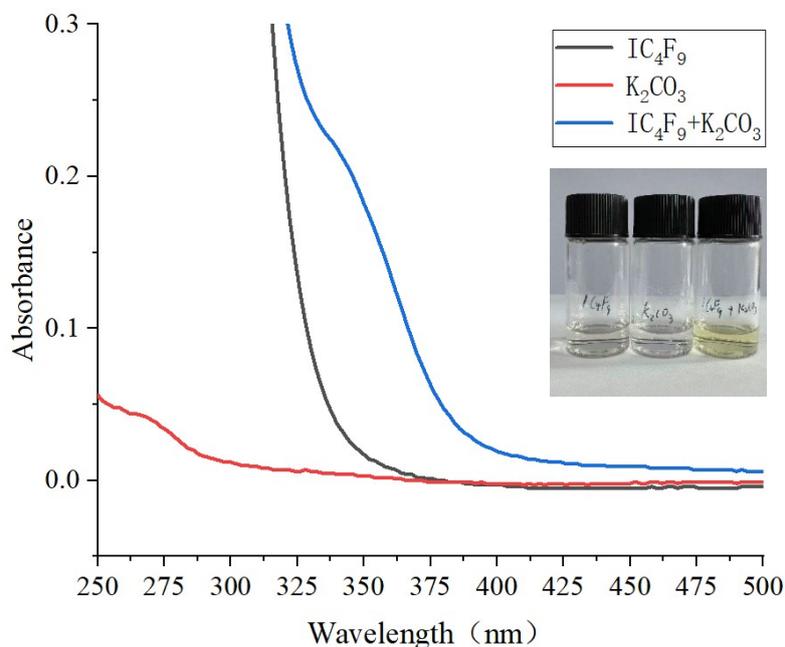
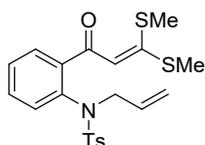


Figure S2. UV-vis absorption spectra.

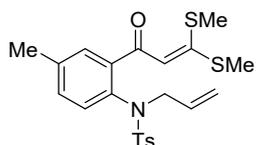
Reference:

[1] Wu, P.; Wang, L.; Wu, K.; Yu, Z. *Org. Lett.* **2015**, *17*, 868-871. (b) Wen, J.; Zhang, F.; Shi, W.; Lei, A. *Chem. Eur. J.* **2017**, *23*, 8814-8817. (c) Wang, Q.; Lou, J.; Wu, P.; Wu, K.; Yu, Z. *Adv. Synth. Catal.* **2019**, *359*, 2981-2998.

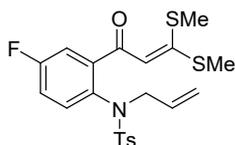
Characterization data of compounds



N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)phenyl)-4-methylbenzenesulfonamide (**1a**). White solid; mp: 112-113 °C; R_f = 0.40 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.65 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.38-7.28 (m, 4H), 6.84 (d, J = 7.6 Hz, 1H), 6.73 (s, 1H), 5.78-5.67 (m, 1H), 5.03-4.96 (m, 2H), 4.21 (d, J = 6.4 Hz, 1H), 2.55 (s, 6H), 2.45 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 187.3, 166.2, 143.5, 142.7, 136.8, 136.0, 132.3, 130.2, 129.7, 129.5, 129.2, 128.5, 127.9, 119.6, 113.5, 55.5, 21.5, 17.4, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_3\text{S}_3$ 434.0913; found 434.0915.

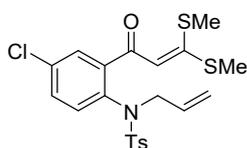


N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-4-methylphenyl)-4-methylbenzenesulfonamide (**1b**). White solid; mp: 114-115 °C; R_f = 0.45 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.65 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 1.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, J = 1.6 Hz, 1H), 6.75 (s, 1H), 6.70 (d, J = 8.0 Hz, 1H), 5.76-5.66 (m, 1H), 5.02-4.95 (m, 2H), 4.18 (d, J = 6.4 Hz, 2H), 2.55 (s, 3H), 2.54 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 187.5, 165.9, 143.4, 142.5, 138.6, 136.9, 133.3, 132.4, 130.9, 130.2, 129.5, 128.9, 127.9, 119.5, 113.7, 55.5, 21.5, 21.0, 17.4, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_3\text{S}_3$ 448.1069; found 448.1072.



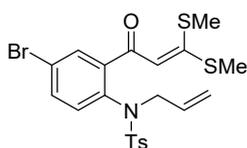
N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-4-fluorophenyl)-4-methylbenzenesulfonamide (**1c**).

White solid; mp: 117-118 °C; R_f = 0.45 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.63 (d, J = 8.4 Hz, 2H), 7.30-7.25 (m, 3H), 7.01-6.96 (m, 1H), 6.80 (dd, J = 8.8 Hz, J = 4.8 Hz, 1H), 6.68 (s, 1H), 5.76-5.66 (m, 1H), 5.05-4.96 (m, 2H), 4.18 (d, J = 5.2 Hz, 2H), 2.552 (s, 3H), 2.550 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.5, 167.7, 161.8 (d, J = 251.5 Hz), 144.8 (d, J = 7.0 Hz), 143.7, 136.5, 132.1, 131.8 (d, J = 3.3 Hz), 131.2 (d, J = 8.5 Hz), 129.6, 127.9, 119.9, 117.0 (d, J = 22.6 Hz), 116.4 (d, J = 23.6 Hz), 112.8, 55.6, 21.5, 17.4, 15.0 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -111.5 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{FNO}_3\text{S}_3$ 452.0819; found 452.0823.



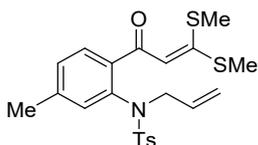
N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-4-chlorophenyl)-4-methylbenzenesulfonamide (**1d**).

White solid; mp: 120-121 °C; R_f = 0.45 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.63 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 2.4 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.27-7.25 (m, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.65 (s, 1H), 5.76-5.65 (m, 1H), 5.05-4.96 (m, 2H), 4.18 (d, J = 6.8 Hz, 2H), 2.551 (s, 3H), 2.547 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.5, 167.8, 144.2, 143.8, 136.4, 134.4, 134.4, 132.0, 130.7, 130.1, 129.6, 127.9, 120.0, 112.8, 55.5, 21.6, 17.4, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{ClNO}_3\text{S}_3$ 468.0523; found 468.0526.



N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-4-bromophenyl)-4-methylbenzenesulfonamide (**1e**).

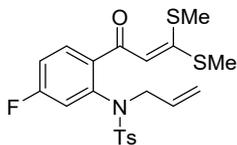
White solid; mp: 124-126 °C; R_f = 0.45 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.68 (d, J = 2.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.41 (dd, J = 8.4 Hz, J = 2.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 1H), 6.65 (s, 1H), 5.75-5.65 (m, 1H), 5.05-4.96 (m, 2H), 4.18 (d, J = 6.8 Hz, 2H), 2.550 (s, 3H), 2.547 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.3, 167.8, 144.4, 143.8, 136.3, 134.9, 133.1, 132.6, 131.9, 130.9, 129.6, 127.9, 122.5, 120.1, 112.8, 55.4, 21.5, 17.4, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{BrNO}_3\text{S}_3$ 512.0018; found 512.0024.



N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-5-methylphenyl)-4-methylbenzenesulfonamide (**1f**).

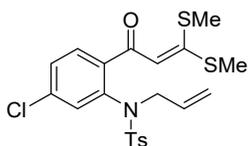
White solid; mp: 114-116 °C; R_f = 0.45 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.65 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 9.2 Hz, 2H), 7.16 (d, J = 7.6 Hz, J = 0.8 Hz, 1H), 6.71 (s, 1H), 6.65 (s, 1H), 5.79-5.69 (m, 1H), 5.03-4.97 (m, 2H), 4.20 (d,

$J = 6.8$ Hz, 2H), 2.53 (s, 6H), 2.44 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 187.1, 165.5, 143.5, 140.7, 139.6, 136.8, 136.0, 132.5, 129.9, 129.7, 129.4, 129.2, 128.0, 119.4, 113.7, 55.6, 21.5, 21.0, 17.3, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_3\text{S}_3$ 448.1069; found 448.1070.



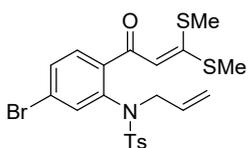
N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-5-fluorophenyl)-4-methylbenzenesulfonamide (**1g**).

White solid; mp: 112-113 °C; $R_f = 0.45$ (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.65$ (d, $J = 8.4$ Hz, 2H), 7.63-7.60 (m, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.10-7.05 (m, 1H), 6.74 (s, 1H), 6.52 (dd, $J = 9.2$ Hz, $J = 2.4$ Hz, 1H), 5.74-5.64 (m, 1H), 5.06-4.98 (m, 2H), 4.18 (d, $J = 6.4$ Hz, 2H), 2.56 (s, 3H), 2.55 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.9, 166.8, 162.8 (d, $J = 253.3$ Hz), 144.0, 138.9 (d, $J = 3.6$ Hz), 137.8 (d, $J = 9.4$ Hz), 136.2, 131.7, 131.6 (d, $J = 9.5$ Hz), 129.7, 127.9, 120.2, 116.1 (d, $J = 22.0$ Hz), 115.7 (d, $J = 21.1$ Hz), 113.2, 55.4, 21.6, 17.4, 15.0 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -108.8 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{FNO}_3\text{S}_3$ 452.0819; found 452.0824.



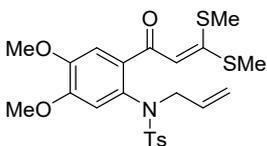
N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-5-chlorophenyl)-4-methylbenzenesulfonamide (**1h**).

White solid; mp: 114-115 °C; $R_f = 0.45$ (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.65$ (d, $J = 8.4$ Hz, 1H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.35-7.32 (m, 3H), 6.78 (d, $J = 2.0$ Hz, 1H), 6.73 (s, 1H), 5.74-5.64 (m, 1H), 5.06-4.97 (m, 2H), 4.17 (d, $J = 6.8$ Hz, 2H), 2.554 (s, 3H), 2.548 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.9, 167.3, 144.0, 141.1, 137.2, 136.1, 135.5, 131.7, 130.9, 129.7, 129.1, 128.8, 127.9, 120.2, 113.0, 55.4, 21.6, 17.4, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{ClNO}_3\text{S}_3$ 468.0523; found 468.0526.



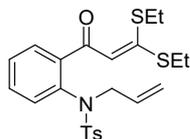
N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-5-bromophenyl)-4-methylbenzenesulfonamide (**1i**).

White solid; mp: 119-120 °C; $R_f = 0.45$ (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.65$ (d, $J = 8.4$ Hz, 1H), 7.51-7.46 (m, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 1.6$ Hz, 1H), 6.73 (s, 1H), 5.71-5.63 (m, 1H), 5.06-4.98 (m, 2H), 4.15 (d, $J = 5.6$ Hz, 2H), 2.554 (s, 3H), 2.548 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 186.0, 167.3, 144.0, 141.6, 137.3, 136.1, 132.0, 131.7, 131.7, 131.1, 129.7, 127.9, 123.5, 120.2, 113.1, 55.4, 21.6, 17.4, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{BrNO}_3\text{S}_3$ 512.0018; found 512.0023.

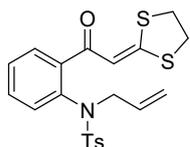


N-allyl-*N*-(2-(3,3-bis(methylthio)acryloyl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (**1j**).

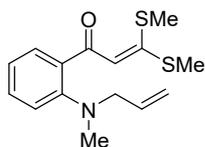
White solid; mp: 128-129 °C; R_f = 0.45 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.69 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.23 (s, 1H), 7.03 (s, 1H), 6.09 (s, 1H), 5.75-5.65 (m, 1H), 5.06-4.98 (m, 2H), 4.27 (s, 1H), 4.07 (s, 1H), 3.89 (s, 3H), 3.59 (s, 3H), 2.61 (s, 3H), 2.55 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.9, 165.9, 150.1, 148.6, 143.8, 136.6, 134.9, 131.9, 129.5, 129.3, 128.1, 119.9, 113.9, 112.4, 110.8, 55.9, 55.8, 55.7, 21.5, 17.6, 15.1 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_5\text{S}_3$ 494.1124; found 494.11127.



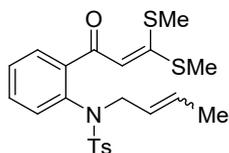
N-allyl-*N*-(2-(3,3-bis(ethylthio)acryloyl)phenyl)-4-methylbenzenesulfonamide (**1k**). White solid; mp: 125-126 °C; R_f = 0.45 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.64 (d, J = 7.6 Hz, 2H), 7.54 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.37-7.27 (m, 4H), 6.87 (d, J = 7.6 Hz, 1H), 6.68 (s, 1H), 5.81-5.71 (m, 1H), 5.03-4.97 (m, 2H), 4.23 (d, J = 6.8 Hz, 2H), 3.14-3.03 (m, 4H), 2.44 (s, 3H), 1.42-1.35 (m, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 187.3, 164.8, 143.5, 142.9, 136.8, 136.0, 132.5, 130.1, 129.6, 129.5, 128.5, 128.0, 119.5, 114.0, 55.6, 28.3, 25.6, 21.6, 13.8, 12.4 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_3\text{S}_3$ 462.1226; found 462.1229.



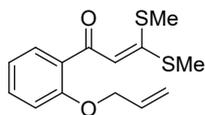
N-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-*N*-allyl-4-methylbenzenesulfonamide (**1l**). White solid; mp: 123-124 °C; R_f = 0.42 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.54 (d, J = 8.0 Hz, 3H), 7.36-7.34 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.02-7.00 (m, 1H), 6.92 (s, 1H), 5.95-5.85 (m, 1H), 5.08-5.03 (m, 2H), 4.28 (d, J = 6.8 Hz, 2H), 3.50-3.47 (m, 2H), 3.40-3.37 (m, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 187.5, 167.0, 143.3, 141.7, 136.3, 136.1, 133.0, 130.6, 130.4, 129.4, 129.2, 128.3, 127.9, 119.4, 112.2, 55.4, 38.9, 35.4, 21.6 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_3\text{S}_3$ 432.0756; found 432.0758.



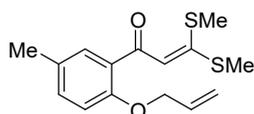
1-(2-(allyl(methyl)amino)phenyl)-3,3-bis(methylthio)prop-2-en-1-one (**1m**). White solid; mp: 112-113 °C; R_f = 0.45 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.55 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.35-7.31 (m, 1H), 7.00-6.96 (m, 2H), 6.89 (s, 1H), 5.84-5.74 (m, 1H), 5.20-5.14 (m, 2H), 3.60 (d, J = 6.4 Hz, 2H), 2.74 (s, 3H), 2.51 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 189.3, 162.3, 150.6, 134.2, 133.7, 131.0, 130.5, 121.0, 118.1, 118.0, 113.8, 60.4, 40.4, 17.0, 14.9 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{NOS}_2$ 294.0981; found 294.0982.



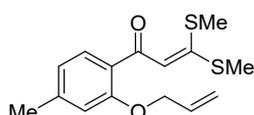
N-(2-(3,3-bis(methylthio)acryloyl)phenyl)-*N*-(but-2-en-1-yl)-4-methylbenzenesulfonamide (**1n**). White solid; mp: 114-115 °C; R_f = 0.46 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.65 (d, J = 8.0 Hz, 2H), 7.59 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.37-7.33 (m, 1H), 7.31-7.27 (m, 3H), 5.55-5.27 (m, 2H), 4.13 (s, 2H), 2.56 (s, 3H), 2.54 (s, 3H), 2.44 (s, 3H), 1.53 (d, J = 6.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 187.2, 165.8, 143.4, 142.7, 137.0, 136.1, 131.4, 130.2, 129.8, 129.5, 129.0, 128.4, 127.89, 124.7, 113.7, 54.9, 21.5, 17.7, 17.4, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_3\text{S}_3$ 448.1069; found 448.1072.



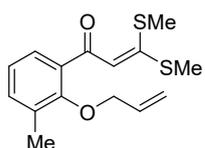
1-(2-(allyloxy)phenyl)-3,3-bis(methylthio)prop-2-en-1-one (**4a**). White solid; mp: 50-52 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.76 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.40-7.35 (m, 1H), 7.03-7.00 (m, 1H), 6.95 (s, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.11-6.01 (m, 1H), 5.45-5.39 (m, 1H), 5.31-5.27 (m, 1H), 4.58 (d, J = 5.2 Hz, 1H), 2.50 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.9, 163.4, 156.3, 132.8, 132.2, 131.0, 130.0, 121.0, 117.9, 114.9, 112.6, 69.2, 17.1, 14.9 ppm.



1-(2-(allyloxy)-5-methylphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**4b**). White solid; mp: 52-53 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.57 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 6.96 (s, 1H), 6.81 (d, J = 8.4 Hz, 1H), 6.09-6.00 (m, 1H), 5.40 (d, J = 13.2 Hz, 1H), 5.27 (d, J = 10.4 Hz, 1H), 4.55 (d, J = 5.2 Hz, 2H), 2.49 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.9, 163.2, 154.2, 132.9, 132.7, 131.3, 130.2, 129.6, 117.7, 114.9, 112.7, 69.3, 20.1, 17.1, 14.9 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{S}_2$ 295.0821; found 295.0823.

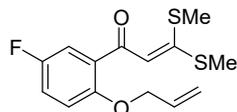


1-(2-(allyloxy)-4-methylphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**4c**). White solid; mp: 53-54 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.71 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.72 (s, 1H), 6.12-6.03 (m, 1H), 5.43 (d, J = 13.2 Hz, 1H), 5.30 (d, J = 10.4 Hz, 1H), 4.58 (d, J = 5.2 Hz, 2H), 2.51 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 185.7, 162.9, 156.5, 143.2, 132.9, 131.3, 127.2, 121.9, 118.0, 115.2, 113.3, 69.3, 21.7, 17.2, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{S}_2$ 295.0821; found 295.0823.

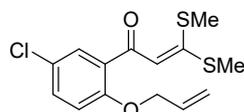


1-(2-(allyloxy)-3-methylphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**4d**). White solid; mp: 52-54 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.54 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.95 (s, 1H), 6.06-5.97 (m, 1H), 5.37 (d, J = 16.8 Hz, 1H), 5.23 (d, J = 10.4 Hz, 1H), 4.27 (d, J = 5.6 Hz, 2H), 2.53 (s, 3H), 2.48 (s, 3H), 2.31

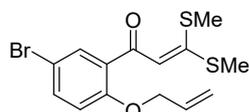
(s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 186.7, 164.6, 155.3, 134.3, 133.7, 133.6, 131.8, 128.4, 124.1, 117.6, 113.7, 75.4, 17.2, 16.2, 15.0 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{S}_2$ 295.0821; found 295.0825.



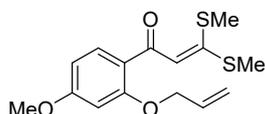
1-(2-(allyloxy)-5-fluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (4e). White solid; mp: 55-56 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.50 (dd, J = 8.8 Hz, J = 3.2 Hz, 1H), 7.09-7.05 (m, 1H), 6.96 (s, 1H), 6.87 (dd, J = 8.8 Hz, J = 4.0 Hz, 1H), 6.10-6.00 (m, 1H), 5.44-5.29 (m, 2H), 4.56 (d, J = 5.2 Hz, 2H), 2.52 (s, 3H), 2.47 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 184.2, 165.2, 158.3, 155.9, 152.6 (d, J = 1.9 Hz), 132.7, 131.2 (d, J = 6.1 Hz), 118.5 (d, J = 23.5 Hz), 118.3, 117.5, 117.2, 114.4 (d, J = 7.6 Hz), 114.2, 70.2, 17.2, 15.1 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -122.6 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{FO}_2\text{S}_2$ 299.0570; found 299.0574.



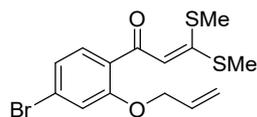
1-(2-(allyloxy)-5-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (4f). White solid; mp: 56-58 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.73 (d, J = 2.8 Hz, 1H), 7.31 (dd, J = 8.8 Hz, J = 2.8 Hz, 1H), 6.89 (s, 1H), 6.85 (d, J = 4.8 Hz, 1H), 6.09-6.00 (m, 1H), 5.42 (dd, J = 17.2 Hz, J = 1.2 Hz, 1H), 5.31 (dd, J = 10.4 Hz, J = 1.2 Hz, 1H), 4.57 (d, J = 5.2 Hz, 2H), 2.52 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 184.2, 165.3, 154.9, 132.4, 131.7, 131.3, 130.8, 126.3, 118.4, 114.2, 69.7, 17.2, 15.1 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{ClO}_2\text{S}_2$ 315.0275; found 315.0278.



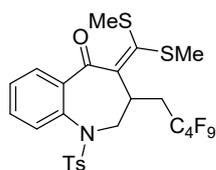
1-(2-(allyloxy)-5-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (4g). White solid; mp: 57-58 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.87 (d, J = 2.4 Hz, 1H), 7.45 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 6.88 (s, 1H), 6.80 (d, J = 8.8 Hz, 1H), 6.09-6.00 (m, 1H), 5.44-5.30 (m, 2H), 4.57 (d, J = 5.2 Hz, 1H), 2.52 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 184.1, 165.3, 155.3, 134.6, 133.7, 132.4, 131.7, 118.4, 114.6, 114.2, 113.6, 69.7, 17.3, 15.1 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{BrO}_2\text{S}_2$ 358.9770; found 358.9775.



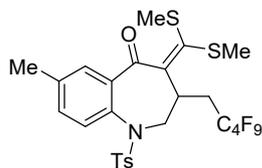
1-(2-(allyloxy)-4-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (4h). White solid; mp: 57-59 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.85 (d, J = 8.4 Hz, 1H), 7.03 (s, 1H), 6.56 (t, J = 7.6 Hz, 2H), 6.65 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 6.43 (d, J = 2.4 Hz, 1H), 6.13-6.03 (m, 1H), 5.44 (dd, J = 17.2 Hz, J = 1.2 Hz, 1H), 5.31 (dd, J = 10.4 Hz, J = 1.2 Hz, 1H), 4.57 (d, J = 5.6 Hz, 2H), 3.83 (s, 3H), 2.50 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 184.7, 163.3, 162.5, 158.1, 133.2, 132.7, 122.8, 118.4, 115.2, 105.4, 99.5, 69.4, 55.4, 17.2, 15.1 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3\text{S}_2$ 311.0770; found 311.0772.



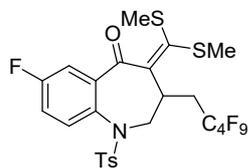
1-(2-(allyloxy)-4-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**4i**). White solid; mp: 57-59 °C; R_f = 0.35 (petroleum ether/ethyl acetate 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.66 (d, J = 8.4 Hz, 1H), 7.16 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.07 (d, J = 1.2 Hz, 1H), 6.90 (s, 1H), 6.10-6.01 (m, 1H), 5.44 (dd, J = 17.2 Hz, J = 1.2 Hz, 1H), 5.33 (dd, J = 10.4 Hz, J = 1.2 Hz, 1H), 4.59 (d, J = 5.2 Hz, 1H), 2.51 (s, 3H), 2.45 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 184.5, 164.8, 156.7, 132.5, 132.2, 128.8, 126.1, 124.3, 118.6, 116.0, 114.4, 69.7, 17.2, 15.1 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{BrO}_2\text{S}_2$ 358.9770; found 358.9974.



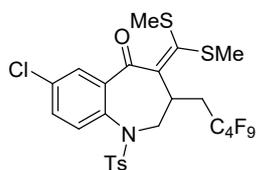
4-(bis(methylthio)methylene)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (**3a**). Yellow oil (54.7 mg, 84% yield); R_f = 0.49 (petroleum ether/ethyl acetate 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.96 (d, J = 6.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.44-7.40 (m, 1H), 7.34-7.27 (m, 4H), 4.77-4.70 (m, 1H), 4.65-4.59 (m, 1H), 3.31 (dd, J = 14.4 Hz, J = 10.0 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.35-2.20 (m, 1H), 2.18 (s, 3H), 2.11-1.95 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 193.8, 145.9, 144.1, 142.7, 140.3, 137.8, 133.3, 132.5, 130.2, 130.0, 127.1, 126.5, 124.6, 56.3 (d, J = 3.9 Hz), 38.5 (d, J = 2.4 Hz), 32.8 (t, J = 22.1 Hz), 21.6, 17.6, 16.5 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.99 – -81.05 (m, 3F), -110.39 – -110.19 (m, 1F), -114.78 – -114.59 (m, 1F), -124.20 – -124.35 (m, 2F), -125.81 – -125.97 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{23}\text{F}_9\text{NO}_3\text{S}_3$ 652.0691; found 652.0699.



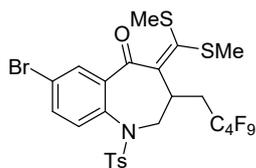
4-(bis(methylthio)methylene)-7-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (**3b**). Yellow oil (49.9 mg, 75% yield); R_f = 0.49 (petroleum ether/ethyl acetate 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.76 (d, J = 2.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.24-7.17 (m, 2H), 4.76-4.68 (m, 1H), 4.64-4.58 (m, 1H), 3.27 (dd, J = 14.4 Hz, J = 9.6 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.33-2.22 (m, 1H), 2.20 (s, 3H), 2.08-1.93 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 193.8, 145.8, 143.9, 140.8, 140.1, 138.0, 136.8, 134.2, 132.6, 130.3, 129.9, 127.0, 124.8, 56.4 (d, J = 4.0 Hz), 38.3, 33.0 (t, J = 34.4 Hz), 21.6, 20.7, 17.6, 16.5 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -81.00 – -81.06 (m, 3F), -110.57 – -111.33 (m, 1F), -113.74 – -114.53 (m, 1F), -124.22 – -124.36 (m, 2F), -125.83 – -125.96 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{25}\text{F}_9\text{NO}_3\text{S}_3$ 666.0847; found 666.0841.



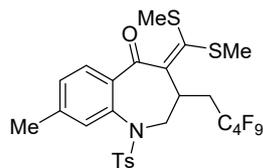
4-(bis(methylthio)methylene)-7-fluoro-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3c). Yellow oil (44.8 mg, 67% yield); R_f = 0.49 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.69 (d, J = 8.4 Hz, 2H), 7.62 (dd, J = 8.4 Hz, J = 3.2 Hz, 1H), 7.32-7.29 (m, 3H), 7.15-7.10 (m, 1H), 4.73-4.68 (m, 1H), 4.61 (dd, J = 14.4 Hz, J = 7.6 Hz, 1H), 3.31 (dd, J = 14.4 Hz, J = 8.8 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 2.34-2.18 (m, 1H), 2.22 (s, 3H), 2.08-1.92 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 192.1, 160.7 (d, J = 250.3 Hz), 144.4, 144.2, 138.3, 137.6, 135.0 (d, J = 6.7 Hz), 130.1, 127.4 (d, J = 8.0 Hz), 127.1, 120.4 (d, J = 23.2 Hz), 116.3 (d, J = 23.9 Hz), 56.4 (d, J = 3.7 Hz), 38.1, 33.0 (t, J = 21.2 Hz), 21.6, 17.7, 16.7 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -81.00 – -81.06 (m, 3F), -110.76 – -111.52 (m, 1F), -113.62 (s, 1F), -113.72 – -114.51 (m, 1F), -124.22 – -124.35 (m, 2F), -125.83 – -125.95 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{F}_{10}\text{NO}_3\text{S}_3$ 670.0597; found 670.0609.



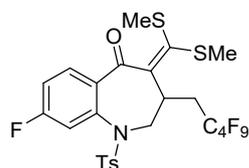
4-(bis(methylthio)methylene)-7-chloro-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3d). Yellow oil (52.1 mg, 76% yield); R_f = 0.49 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.90 (d, J = 2.4 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.37-7.30 (m, 4H), 4.73-4.59 (m, 2H), 3.27 (dd, J = 14.4 Hz, J = 9.6 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.36-2.21 (m, 1H), 2.18 (s, 3H), 2.11-1.95 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 192.6, 145.2, 144.4, 141.2, 141.0, 137.3, 133.6, 133.0, 132.4, 130.1, 129.7, 127.1, 126.0, 56.2 (d, J = 4.0 Hz), 38.5, 32.8 (t, J = 22.1 Hz), 21.6, 17.7, 16.4 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.99 – -81.05 (m, 3F), -110.20 – -111.00 (m, 1F), -113.79 – -114.59 (m, 1F), -124.18 – -124.28 (m, 2F), -125.81 – -125.94 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{ClF}_9\text{NO}_3\text{S}_3$ 686.0301; found 686.0308.



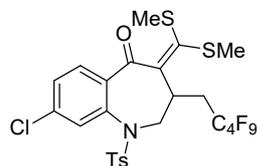
4-(bis(methylthio)methylene)-7-bromo-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3e). Yellow oil (58.2 mg, 80% yield); R_f = 0.49 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): δ = 8.05 (d, J = 2.4 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.50 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.72-4.58 (m, 2H), 3.26 (dd, J = 14.4 Hz, J = 9.6 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.36-2.24 (m, 1H), 2.18 (s, 3H), 2.11-1.96 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 192.6, 145.3, 144.4, 141.8, 140.8, 137.3, 135.9, 133.7, 132.7, 130.1, 127.1, 126.1, 119.9, 56.2 (d, J = 4.2 Hz), 38.5, 32.7 (t, J = 21.9 Hz), 21.6, 17.7, 16.3 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.98 – -81.04 (m, 3F), -110.11 – -110.90 (m, 1F), -113.79 – -114.59 (m, 1F), -124.16 – -124.27 (m, 2F), -125.80 – -125.93 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{BrF}_9\text{NO}_3\text{S}_3$ 729.9796; found 729.9800.



4-(bis(methylthio)methylene)-8-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (**3f**). Yellow oil (51.9 mg, 78% yield); R_f = 0.49 (petroleum ether/ethyl acetate 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.86 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.14-7.10 (m, 2H), 4.76-4.68 (m, 1H), 4.63-4.57 (m, 1H), 3.27 (dd, J = 14.8 Hz, J = 9.6 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H), 2.29-2.20 (m, 1H), 2.18 (s, 3H), 2.09-1.94 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 193.4, 146.0, 144.5, 144.0, 142.8, 140.2, 137.9, 130.1, 130.0, 129.9, 127.5, 127.1, 125.2, 56.3 (d, J = 3.8 Hz), 38.4, 32.9 (t, J = 22.3 Hz), 21.6 (d, J = 11.4 Hz), 17.6, 16.5 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.99 – -81.06 (m, 3F), -110.37 – -111.16 (m, 1F), -113.78 – -114.58 (m, 1F), -124.19 – -124.33 (m, 2F), -125.80 – -125.95 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{25}\text{F}_9\text{NO}_3\text{S}_3$ 666.0847; found 666.0852.

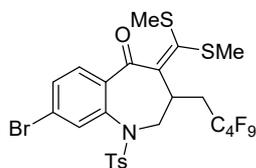


4-(bis(methylthio)methylene)-8-fluoro-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (**3g**). Yellow oil (59.5 mg, 89% yield); R_f = 0.49 (petroleum ether/ethyl acetate 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.97 (dd, J = 8.8 Hz, J = 6.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.10 (dd, J = 10.0 Hz, J = 2.4 Hz, 1H), 7.00-6.96 (m, 1H), 4.75-4.61 (m, 2H), 3.27 (dd, J = 13.6 Hz, J = 10.0 Hz, 1H), 2.47 (s, 3H), 2.38 (s, 3H), 2.37-2.28 (m, 1H), 2.16 (s, 3H), 2.13-1.98 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 192.9, 164.9 (d, J = 156.1 Hz), 146.1, 145.1 (d, J = 11.5 Hz), 144.6, 139.3, 137.1, 132.4 (d, J = 10.6 Hz), 130.2, 129.3, 128.4 (d, J = 3.9 Hz), 127.2, 113.7 (d, J = 22.1 Hz), 111.3 (d, J = 25.4 Hz), 56.2 (d, J = 4.3 Hz), 38.8, 32.6 (t, J = 22.1 Hz), 21.6, 17.6, 16.2 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.88 – -81.05 (m, 3F), -102.95 (s, 1F), -109.92 – -110.69 (m, 1F), -113.82 – -114.62 (m, 1F), -124.15 – -124.29 (m, 2F), -125.77 – -125.93 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{F}_{10}\text{NO}_3\text{S}_3$ 670.0597; found 670.0609.

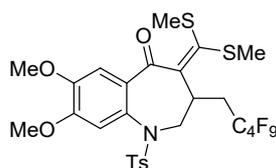


4-(bis(methylthio)methylene)-8-chloro-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (**3h**). Yellow oil (58.2 mg, 85% yield); R_f = 0.49 (petroleum ether/ethyl acetate 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.89 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 2.0 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.27-7.24 (m, 1H), 4.74-4.66 (m, 1H), 4.64-4.58 (m, 1H), 3.25 (dd, J = 14.8 Hz, J = 10.4 Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H), 2.36-2.25 (m, 1H), 2.17 (s, 3H), 2.12-1.97 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 193.0, 145.8, 144.5, 143.9, 140.0, 139.3, 137.1, 131.2, 130.5, 130.1, 127.2, 126.6, 124.4, 56.1 (d, J = 3.9 Hz), 38.6, 32.7

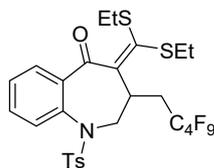
(t, $J = 22.0$ Hz), 21.6, 17.6, 16.3 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.85 – -81.05 (m, 3F), -110.05 – -110.84 (m, 1F), -113.79 – -114.60 (m, 1F), -124.13 – -124.29 (m, 2F), -125.78 – -125.94 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{ClF}_9\text{NO}_3\text{S}_3$ 686.0301; found 686.0307.



4-(bis(methylthio)methylene)-8-bromo-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3i). Yellow oil (60.5 mg, 83% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.80$ (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 2.0$ Hz, 1H), 7.42 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.74-4.66 (m, 1H), 4.63-4.57 (m, 1H), 3.24 (dd, $J = 14.8$ Hz, $J = 10.4$ Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H), 2.36-2.24 (m, 1H), 2.17 (s, 3H), 2.11-1.96 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 193.2, 145.7, 144.6, 143.8, 140.1, 137.1, 131.2, 130.9, 130.1, 129.6, 127.8, 127.4, 127.2, 56.1 (d, $J = 4.0$ Hz), 38.6, 32.7 (t, $J = 21.6$ Hz), 21.6, 17.6, 16.3 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.85 – -81.04 (m, 3F), -110.08 – -110.87 (m, 1F), -113.80 – -114.60 (m, 1F), -124.13 – -124.29 (m, 2F), -125.78 – -125.94 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{BrF}_9\text{NO}_3\text{S}_3$ 729.9796; found 729.9802.

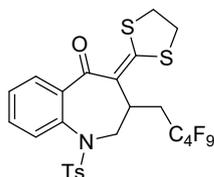


4-(bis(methylthio)methylene)-7,8-dimethoxy-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3j). Yellow oil (56.2 mg, 79% yield); $R_f = 0.35$ (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.73$ (d, $J = 8.0$ Hz, 2H), 7.45 (s, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.72 (s, 1H), 4.75-4.66 (m, 2H), 3.93 (s, 3H), 3.74 (s, 3H), 3.29 (dd, $J = 14.0$ Hz, $J = 8.4$ Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 2.36-2.24 (m, 1H), 2.22 (s, 3H), 2.08-1.95 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 192.1, 152.9, 147.8, 145.6, 144.0, 141.2, 138.2, 137.7, 130.0, 129.9, 127.2, 126.9, 125.8, 110.7, 108.0, 56.9, 56.1, 56.0, 38.3, 33.2 (t, $J = 22.1$ Hz), 21.5, 17.6, 16.5 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -81.00 – -81.06 (m, 3F), -110.60 – -111.36 (m, 1F), -113.71 – -114.51 (m, 1F), -124.18 – -124.32 (m, 2F), -125.82 – -125.94 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{27}\text{F}_{10}\text{NO}_5\text{S}_3$ 712.0902; found 712.0914.

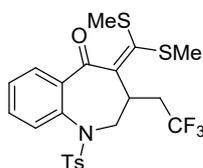


4-(bis(ethylthio)methylene)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3k). Yellow oil (48.9 mg, 72% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.93$ (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.40-7.35 (m, 3H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 1H), 4.84-4.76 (m, 1H), 4.62-4.56 (m, 1H), 3.27 (dd, $J = 14.8$ Hz, $J = 11.2$ Hz, 1H), 2.95-2.79 (m, 2H), 2.73-2.64 (m,

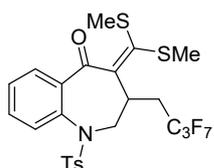
1H), 2.61-2.52 (m, 1H), 2.44 (s, 3H), 2.42-2.29 (m, 1H), 2.16-2.01 (m, 1H), 1.29 (t, $J = 1.9$ Hz, 3H), 0.92 (t, $J = 1.8$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 194.8, 148.5, 144.2, 143.3, 138.0, 135.3, 132.9, 131.8, 130.2, 130.1, 127.0, 125.6, 123.2, 56.0 (d, $J = 4.0$ Hz), 39.0 (d, $J = 2.4$ Hz), 32.7 (t, $J = 21.8$ Hz), 27.8, 27.5, 21.5, 15.1, 14.2 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -81.00 – -81.05 (m, 3F), -109.80 – -110.57 (m, 1F), -113.57 – -114.37 (m, 1F), -124.19 – -124.36 (m, 2F), -125.80 – -125.91 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{27}\text{F}_9\text{NO}_3\text{S}_3$ 680.1004; found 680.1008.



4-(1,3-dithiolan-2-ylidene)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (**3l**). Yellow oil (48.0 mg, 74% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.64$ -7.55 (m, 3H), 7.52-7.48 (m, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 4.62-4.56 (m, 1H), 3.75 (d, $J = 11.6$ Hz, 2H), 3.47-3.40 (m, 1H), 3.39-3.31 (m, 2H), 3.25-3.18 (m, 1H), 2.36 (s, 3H), 1.75-1.64 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 187.1, 143.2, 139.5, 136.3, 135.7, 133.0, 131.8, 129.9, 129.7, 129.6, 126.9, 121.9, 55.0, 39.3, 36.3, 35.8, 21.6 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -81.07 – -81.12 (m, 3F), -114.71 – -114.83 (m, 2F), -124.75 – -124.83 (m, 2F), -126.02 – -126.10 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{21}\text{F}_9\text{NO}_3\text{S}_3$ 650.0534; found 650.0541.

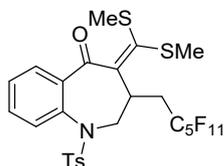


4-(bis(methylthio)methylene)-1-tosyl-3-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (**3m**). Yellow oil (22.0 mg, 44% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.95$ (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.43-7.39 (m, 1H), 7.34-7.28 (m, 4H), 4.65-4.54 (m, 2H), 3.29 (dd, $J = 13.6$ Hz, $J = 8.8$ Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.33-2.25 (m, 1H), 2.17 (s, 3H), 2.10-2.01 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 193.6, 145.6, 144.0, 142.6, 140.6, 137.8, 133.2, 132.7, 130.2, 130.0, 127.1, 126.5, 124.7, 55.9, 39.4, 36.1 (q, $J = 68.9$ Hz, $J = 38.1$ Hz), 21.6, 17.6, 16.6 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -63.9 ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{23}\text{F}_3\text{NO}_3\text{S}_3$ 502.0787; found 502.0791.

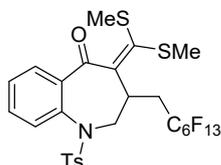


4-(bis(methylthio)methylene)-3-(2,2,3,3,4,4,4-heptafluorobutyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (**3n**). Yellow oil (42.1 mg, 70% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.96$ (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.44-7.39 (m, 1H), 7.35-7.28 (m, 4H), 4.77-4.69 (m, 1H), 4.64-4.58 (m, 1H), 3.30 (dd,

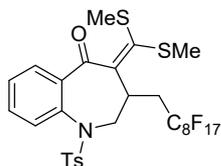
$J = 14.8$ Hz, $J = 9.6$ Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.35-2.20 (m, 1H), 2.18 (s, 3H), 2.10-1.94 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 193.9, 146.0, 144.1, 142.8, 140.3, 137.8, 133.2, 132.5, 130.2, 130.0, 127.1, 126.5, 124.6, 56.3 (d, $J = 3.9$ Hz), 38.5, 32.6 (t, $J = 22.3$ Hz), 21.6, 17.6, 16.5 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.30 – -80.36 (m, 3F), -110.01 – -110.82 (m, 1F), -114.57 – -115.38 (m, 1F), -127.54 – -127.70 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{23}\text{F}_7\text{NO}_3\text{S}_3$ 602.0723; found 602.0726.



4-(bis(methylthio)methylene)-1-tosyl-3-(2,2,3,3,4,4,5,5,6,6,6-undecafluorohexyl)-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3o). Yellow oil (50.5 mg, 72% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.96 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.44-7.39 (m, 1H), 7.34-7.28 (m, 4H), 4.77-4.70 (m, 1H), 4.62 (dd, $J = 13.6$ Hz, $J = 6.8$ Hz, 1H), 3.31 (dd, $J = 14.4$ Hz, $J = 9.6$ Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.36-2.23 (m, 1H), 2.18 (s, 3H), 2.11-1.95 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 193.9, 146.0, 144.1, 142.8, 140.3, 137.8, 133.3, 132.5, 130.2, 130.0, 127.1, 126.5, 124.6, 56.3 (d, $J = 3.9$ Hz), 38.5, 32.9 (t, $J = 22.0$ Hz), 21.6, 17.6, 16.5 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.77 – -80.82 (m, 3F), -110.17 – -110.98 (m, 1F), -113.57 – -114.37 (m, 1F), -122.46 – -122.59 (m, 2F), -123.49-123.60 (m, 2F), -126.21 – -126.32 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{23}\text{F}_{11}\text{NO}_3\text{S}_3$ 702.0659; found 702.0663.

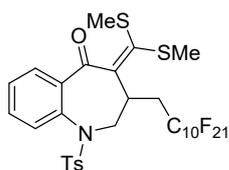


4-(bis(methylthio)methylene)-1-tosyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3p). Yellow oil (55.6 mg, 74% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.96 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.34-7.27 (m, 4H), 4.77-4.70 (m, 1H), 4.62 (dd, $J = 14.8$ Hz, $J = 6.8$ Hz, 1H), 3.30 (dd, $J = 14.8$ Hz, $J = 5.6$ Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.35-2.23 (m, 1H), 2.18 (s, 3H), 2.11-1.95 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 193.9, 145.9, 144.1, 142.8, 140.3, 137.8, 133.3, 132.5, 130.2, 130.0, 127.1, 126.5, 124.6, 56.3 (d, $J = 3.9$ Hz), 38.5, 32.9 (t, $J = 22.6$ Hz), 21.6, 17.6, 16.5 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.77 – -80.83 (m, 3F), -110.15 – -110.95 (m, 1F), -113.53 – -114.32 (m, 1F), -121.68 – -121.82 (m, 2F), -122.78 – -122.94 (m, 2F), -123.29 – -123.41 (m, 2F), -126.10 – -126.21 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{23}\text{F}_{13}\text{NO}_3\text{S}_3$ 752.0627; found 752.0632.

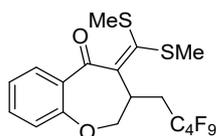


4-(bis(methylthio)methylene)-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluorononyl)-1-tosyl-

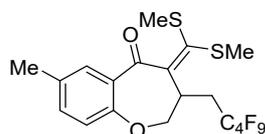
1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3q). Yellow oil (60.4 mg, 71% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.96$ (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.44-7.39 (m, 1H), 7.34-7.27 (m, 4H), 4.77-4.70 (m, 1H), 4.62 (dd, $J = 14.8$ Hz, $J = 7.2$ Hz, 1H), 3.30 (dd, $J = 14.8$ Hz, $J = 9.6$ Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.35-2.23 (m, 1H), 2.18 (s, 3H), 2.13-1.96 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 193.9, 146.0, 144.1, 142.8, 140.3, 137.8, 133.3, 132.5, 130.2, 130.0, 127.1, 126.5, 124.6, 56.4, 38.5, 32.9 (t, $J = 22.2$ Hz), 21.6, 17.6, 16.5 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.77 – -80.83 (m, 3F), -110.14 – -110.94 (m, 1F), -113.52 – -114.31 (m, 1F), -121.47 – -121.60 (m, 2F), -121.85 – -122.01 (m, 4F), -122.67 – -122.82 (m, 2F), -123.27 – -123.36 (m, 2F), -126.10 – -126.19 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{23}\text{F}_{17}\text{NO}_3\text{S}_3$ 852.0563; found 852.0567.



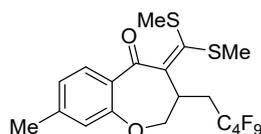
4-(bis(methylthio)methylene)-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-henicosafuoroundecyl)-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3r). Yellow oil (69.4 mg, 73% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.96$ (dd, $J = 8.0$ Hz, $J = 2.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.43-7.40 (m, 1H), 7.34-7.28 (m, 4H), 4.78-4.70 (m, 1H), 4.62 (dd, $J = 14.8$ Hz, $J = 6.8$ Hz, 1H), 3.31 (dd, $J = 14.8$ Hz, $J = 9.6$ Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.35-2.24 (m, 1H), 2.18 (s, 3H), 2.11-1.95 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 193.8, 146.0, 144.1, 142.8, 140.3, 137.9, 133.3, 132.6, 130.2, 130.0, 127.1, 126.5, 124.6, 56.3 (d, $J = 3.6$ Hz), 38.5, 32.9 (d, $J = 22.0$ Hz), 21.5, 17.6, 16.4 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.79 – -80.84 (m, 3F), -110.15 – -110.94 (m, 1F), -113.53 – -114.32 (m, 1F), -121.68 – -121.93 (m, 8F), -122.74 (s, 2F), -123.28 – -123.34 (m, 2F), -126.11 – -126.21 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{23}\text{F}_{21}\text{NO}_3\text{S}_3$ 952.0499; found 952.0507.



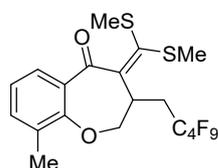
4-(bis(methylthio)methylene)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydrobenzo[b]oxepin-5(2H)-one (5a). Yellow oil (30.9 mg, 62% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.82$ (dd, $J = 8.0$ Hz, $J = 2.0$ Hz, 1H), 7.44-7.40 (m, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.01 (d, $J = 8.4$ Hz, 1H), 4.75-4.70 (m, 1H), 4.42-4.34 (m, 1H), 3.91 (t, $J = 12.0$ Hz, 1H), 2.46-2.31 (m, 1H), 2.35 (s, 3H), 2.24-2.08 (m, 1H), 2.17 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 194.1, 162.2, 147.9, 137.8, 134.0, 129.6, 127.4, 122.6, 119.7, 75.3 (d, $J = 5.2$ Hz), 39.2 (d, $J = 2.8$ Hz), 31.8 (t, $J = 22.5$ Hz), 17.7, 16.3 ppm. $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.97 – -81.04 (m, 3F), -109.19 – -110.00 (m, 1F), -114.52 – -115.32 (m, 1F), -124.13 – -124.31 (m, 2F), -125.76 – -125.92 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{16}\text{F}_9\text{O}_2\text{S}_2$ 499.0443; found 499.0457.



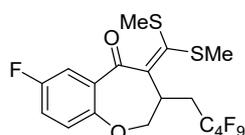
4-(bis(methylthio)methylene)-7-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydrobenzo[b]oxepin-5(2H)-one (5b). Yellow oil (28.2 mg, 55% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.62$ (s, 1H), 7.22 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 4.72-4.67 (m, 1H), 4.41-4.33 (m, 1H), 3.85 (t, $J = 12.0$ Hz, 1H), 2.45-2.29 (m, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.19 (s, 3H), 2.17-2.07 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 194.1, 160.3, 148.0, 137.7, 134.9, 132.2, 129.3, 127.1, 119.5, 75.4 (d, $J = 4.9$ Hz), 39.2 (d, $J = 2.6$ Hz), 31.8 (t, $J = 21.9$ Hz), 20.4, 17.7, 16.3 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -81.01 – -81.06 (m, 3F), -109.27 – -110.07 (m, 1F), -114.50 – -115.28 (m, 1F), -124.16 – -124.31 (m, 2F), -125.78 – -125.94 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_9\text{O}_2\text{S}_2$ 513.0599; found 513.0603.



4-(bis(methylthio)methylene)-8-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydrobenzo[b]oxepin-5(2H)-one (5c). Yellow oil (26.6 mg, 52% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.73$ (d, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 7.6$ Hz, 1H), 6.82 (s, 1H), 4.72-4.67 (m, 1H), 4.42-4.34 (m, 1H), 3.87 (t, $J = 12.0$ Hz, 1H), 2.53-2.29 (m, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.23-2.07 (m, 1H), 2.18 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 193.6, 162.4, 148.0, 145.4, 137.6, 129.5, 124.9, 123.8, 119.97, 75.3 (d, $J = 5.2$ Hz), 39.2 (d, $J = 2.8$ Hz), 31.8 (t, $J = 23.6$ Hz), 21.5, 17.7, 16.4 ppm. $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.97 – -81.04 (m, 3F), -109.20 – -109.99 (m, 1F), -114.52 – -115.33 (m, 1F), -124.15 – -124.29 (m, 2F), -125.76 – -125.92 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_9\text{O}_2\text{S}_2$ 513.0599; found 513.0615.

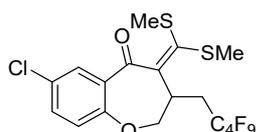


4-(bis(methylthio)methylene)-9-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydrobenzo[b]oxepin-5(2H)-one (5d). Yellow oil (33.3 mg, 65% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.66$ (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 7.29 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H), 7.00 (d, $J = 7.6$ Hz, 1H), 4.81-4.76 (m, 1H), 4.42-4.34 (m, 1H), 3.88 (t, $J = 12.0$ Hz, 1H), 2.47-2.32 (m, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H), 2.17-2.08 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 194.5, 160.6, 148.2, 137.1, 135.2, 128.6, 127.3, 122.1, 75.3 (d, $J = 5.3$ Hz), 39.4 (d, $J = 2.7$ Hz), 31.8 (t, $J = 22.4$ Hz), 17.7, 16.2, 16.0 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -81.04 – -81.09 (m, 3F), -109.05 – -109.86 (m, 1F), -114.56 – -115.35 (m, 1F), -124.18 – -124.31 (m, 2F), -125.79 – -125.95 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_9\text{O}_2\text{S}_2$ 513.0599; found 513.0607.

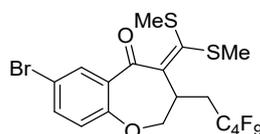


4-(bis(methylthio)methylene)-7-fluoro-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-

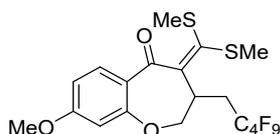
dihydrobenzo[b]oxepin-5(2H)-one (5e). Yellow oil (32.0 mg, 62% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.50$ (dd, $J = 8.4$ Hz, $J = 3.2$ Hz, 1H), 7.15-7.10 (m, 1H), 6.99 (dd, $J = 8.8$ Hz, $J = 4.4$ Hz, 1H), 4.74-4.68 (m, 1H), 4.42-4.34 (m, 1H), 3.87 (t, $J = 11.6$ Hz, 1H), 2.44-2.29 (m, 1H), 2.36 (s, 3H), 2.20 (s, 3H), 2.18-2.03 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 192.7, 158.3 (d, $J = 2.1$ Hz), 157.9 (d, $J = 244.3$ Hz), 146.9, 139.0, 128.3 (d, $J = 6.3$ Hz), 121.3 (d, $J = 7.6$ Hz), 121.1 (d, $J = 24.0$ Hz), 115.0 (d, $J = 24.2$ Hz), 75.7 (d, $J = 5.2$ Hz), 39.1 (d, $J = 2.7$ Hz), 31.8 (t, $J = 22.7$ Hz), 17.8, 16.4 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.99 – -81.06 (m, 3F), -109.32 – -110.13 (m, 1F), -114.48 – -115.27 (m, 1F), -120.32 (s, 1F), -124.17 – -124.30 (m, 2F), -125.77 – -125.93 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{15}\text{F}_{10}\text{O}_2\text{S}_2$ 517.0348; found 517.0352.



4-(bis(methylthio)methylene)-7-chloro-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydrobenzo[b]oxepin-5(2H)-one (5f). Yellow oil (25.5 mg, 48% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.78$ (d, $J = 2.4$ Hz, 1H), 7.35 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1H), 6.96 (d, $J = 8.8$ Hz, 1H), 4.73-4.68 (m, 1H), 4.39-4.32 (m, 1H), 3.90 (t, $J = 12.0$ Hz, 1H), 2.44-2.29 (m, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 2.19-2.03 (m, 1H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 192.6, 160.5, 146.8, 139.2, 133.7, 128.9, 128.4, 128.0, 121.3, 75.4 (d, $J = 5.1$ Hz), 39.0 (d, $J = 2.9$ Hz), 31.7 (t, $J = 22.2$ Hz), 17.8, 16.4 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.98 – -81.04 (m, 3F), -109.22 – -110.04 (m, 1F), -114.50 – -115.31 (m, 1F), -124.16 – -124.29 (m, 2F), -125.75 – -125.90 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{15}\text{ClF}_9\text{O}_2\text{S}_2$ 533.0053; found 533.0057.

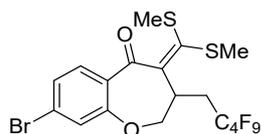


4-(bis(methylthio)methylene)-7-bromo-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydrobenzo[b]oxepin-5(2H)-one (5g). Yellow oil (30.5 mg, 53% yield); $R_f = 0.49$ (petroleum ether/ethyl acetate 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.92$ (d, $J = 2.4$ Hz, 1H), 7.49 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1H), 6.91 (d, $J = 8.8$ Hz, 1H), 4.73-4.68 (m, 1H), 4.39-4.31 (m, 1H), 3.91 (t, $J = 12.0$ Hz, 1H), 2.44-2.29 (m, 1H), 2.36 (s, 3H), 2.23-2.03 (m, 1H), 2.21 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 192.4, 160.9, 146.8, 139.3, 136.5, 131.9, 128.8, 121.6, 115.2, 75.3 (d, $J = 4.9$ Hz), 39.0 (d, $J = 2.9$ Hz), 31.71 (t, $J = 22.5$ Hz), 17.9, 16.4 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -80.98 – -81.04 (m, 3F), -109.24 – -110.01 (m, 1F), -114.52 – -115.31 (m, 1F), -124.16 – -124.30 (m, 2F), -125.74 – -125.91 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{15}\text{BrF}_9\text{O}_2\text{S}_2$ 576.9548; found 576.9553.

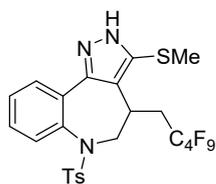


4-(bis(methylthio)methylene)-8-methoxy-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydrobenzo[b]oxepin-5(2H)-one (5h). Yellow oil (22.7 mg, 43% yield); $R_f = 0.49$ (petroleum

ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.81 (d, J = 8.8 Hz, 1H), 6.67 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 4.74-4.69 (m, 1H), 4.44-4.36 (m, 1H), 3.89 (t, J = 12.0 Hz, 1H), 3.93 (s, 3H), 2.45-2.30 (m, 1H), 2.35 (s, 3H), 2.19 (s, 3H), 2.17-2.07 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 192.4, 164.5, 164.5, 147.9, 137.5, 131.2, 120.7, 110.2, 103.7, 75.5 (d, J = 5.1 Hz), 55.6, 39.1 (d, J = 2.7 Hz), 31.9 (t, J = 22.2 Hz), 17.7, 16.4 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.98 – -81.04 (m, 3F), -109.15 – -109.95 (m, 1F), -114.53 – -115.33 (m, 1F), -124.14 – -124.29 (m, 2F), -125.76 – -125.92 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_9\text{O}_3\text{S}_2$ 529.0548; found 529.0551.



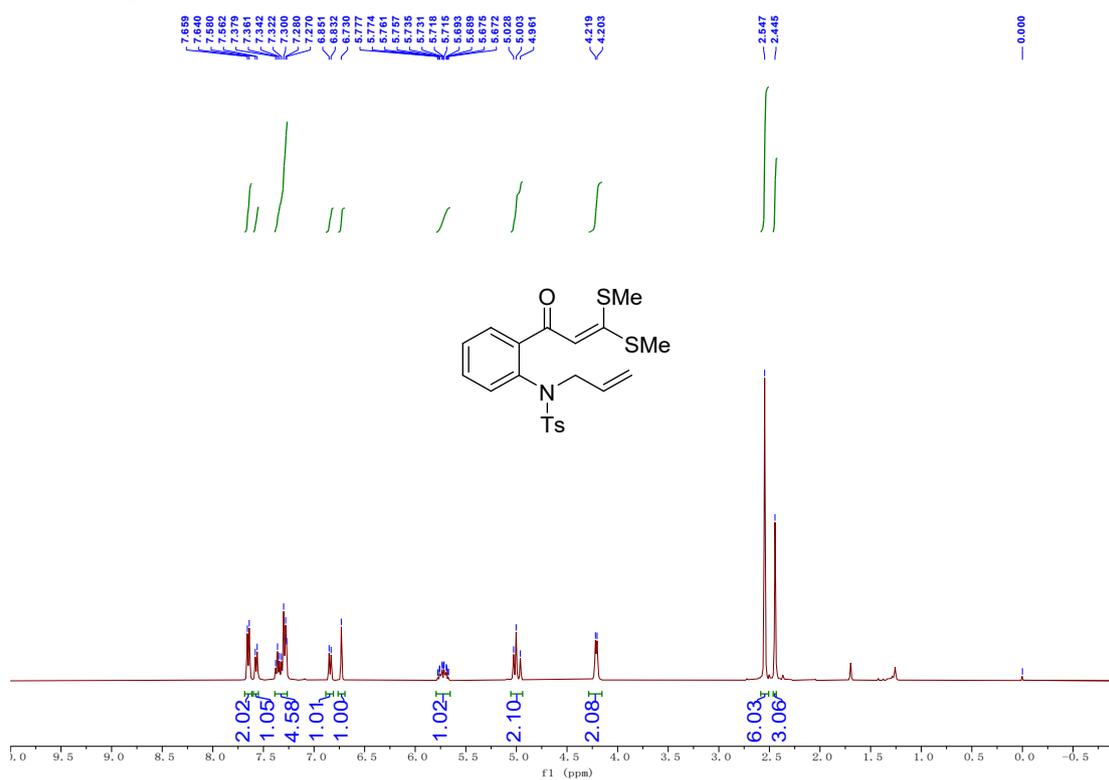
4-(bis(methylthio)methylene)-8-bromo-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydrobenzo[b]oxepin-5(2H)-one (5i). Yellow oil (37.4 mg, 65% yield); R_f = 0.49 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.68 (d, J = 8.4 Hz, 1H), 7.27-7.21 (m, 2H), 4.74-4.69 (m, 1H), 4.40-4.33 (m, 1H), 3.91 (t, J = 12.0 Hz, 1H), 2.45-2.30 (m, 1H), 2.35 (s, 3H), 2.19 (s, 3H), 2.17-2.08 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 193.0, 162.3, 147.1, 138.7, 130.7, 128.1, 126.3, 126.1, 122.9, 75.4 (d, J = 5.2 Hz), 39.0 (d, J = 2.8 Hz), 31.7 (t, J = 21.9 Hz), 17.8, 16.4 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ -80.97 – -81.04 (m, 3F), -109.14 – -109.95 (m, 1F), -114.54 – -115.33 (m, 1F), -124.14 – -124.28 (m, 2F), -125.76 – -125.92 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{15}\text{BrF}_9\text{O}_2\text{S}_2$ 576.9548; found 576.9551.



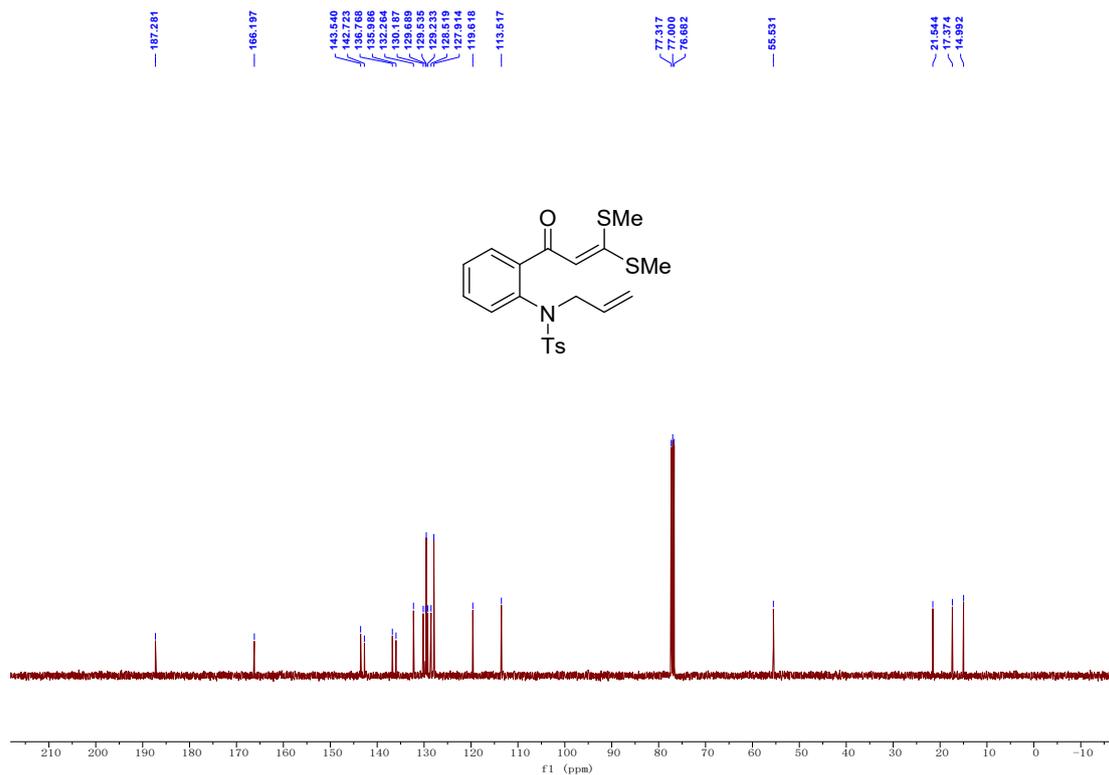
3-(methylthio)-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-6-tosyl-2,4,5,6-tetrahydrobenzo[b]pyrazolo[3,4-d]azepine (6). Yellow oil (57.4 mg, 93% yield); R_f = 0.49 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.64 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.54 (dd, J = 7.2 Hz, J = 2.0 Hz, 1H), 7.42-7.33 (m, 4H), 7.01 (d, J = 8.0 Hz, 2H), 4.88-4.82 (m, 1H), 3.74-3.66 (m, 1H), 3.28 (dd, J = 15.2 Hz, J = 11.2 Hz, 1H), 2.95-2.79 (m, 1H), 2.43 (s, 3H), 2.28 (s, 3H), 2.02-1.86 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3): δ 143.3, 139.5, 137.5, 130.0, 129.4, 129.0, 128.5, 127.9, 126.4, 125.9, 117.7, 55.0 (d, J = 5.5 Hz), 34.7 (d, J = 21.4 Hz), 29.3 (d, J = 3.1 Hz), 21.4, 15.8 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -80.97 – -81.04 (m, 3F), -108.73 – -109.52 (m, 1F), -114.34 – -115.13 (m, 1F), -124.44 – -124.63 (m, 2F), -125.77-125.92 (m, 2F) ppm. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{21}\text{F}_9\text{NO}_2\text{S}_2$ 618.0926; found 618.0941.

Copies of ^1H NMR, ^{13}C NMR, ^{19}F NMR

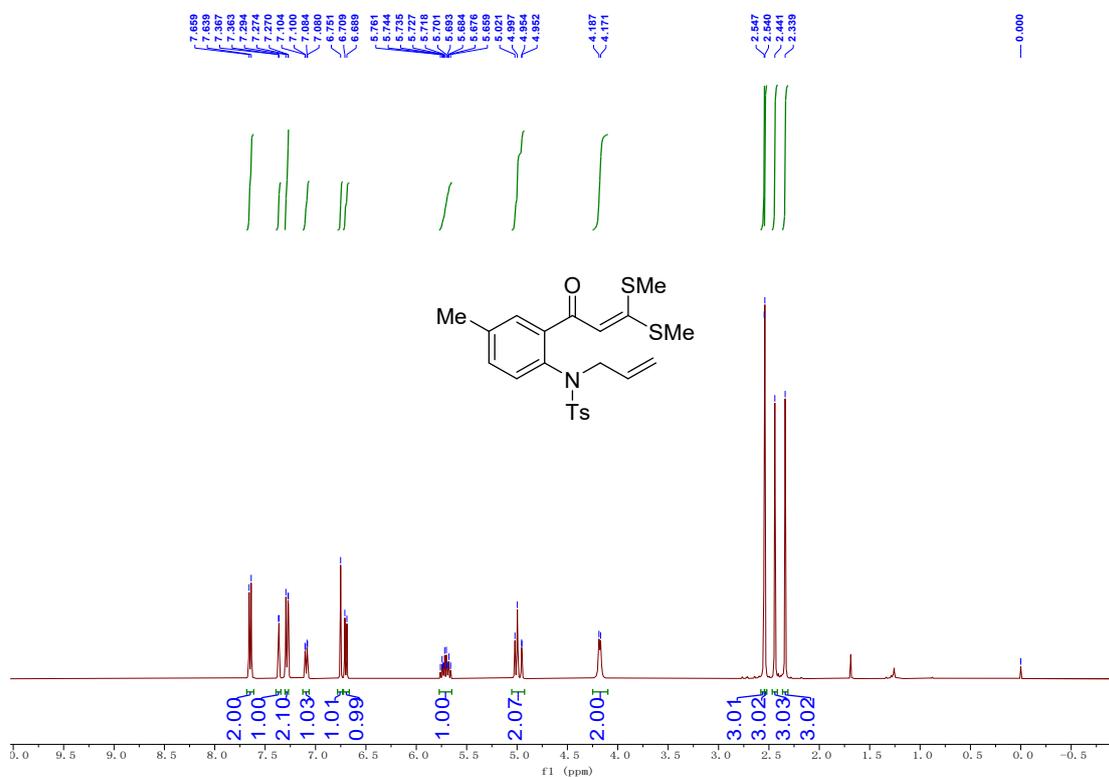
^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1a**



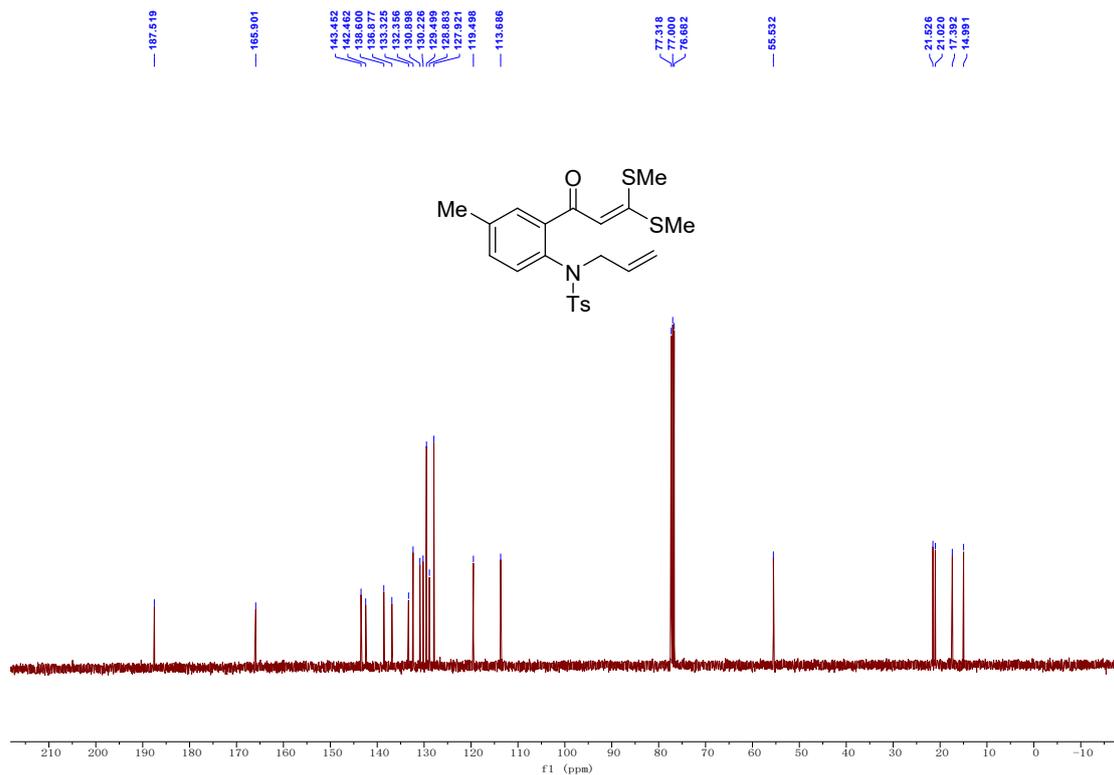
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298 K) of **1a**



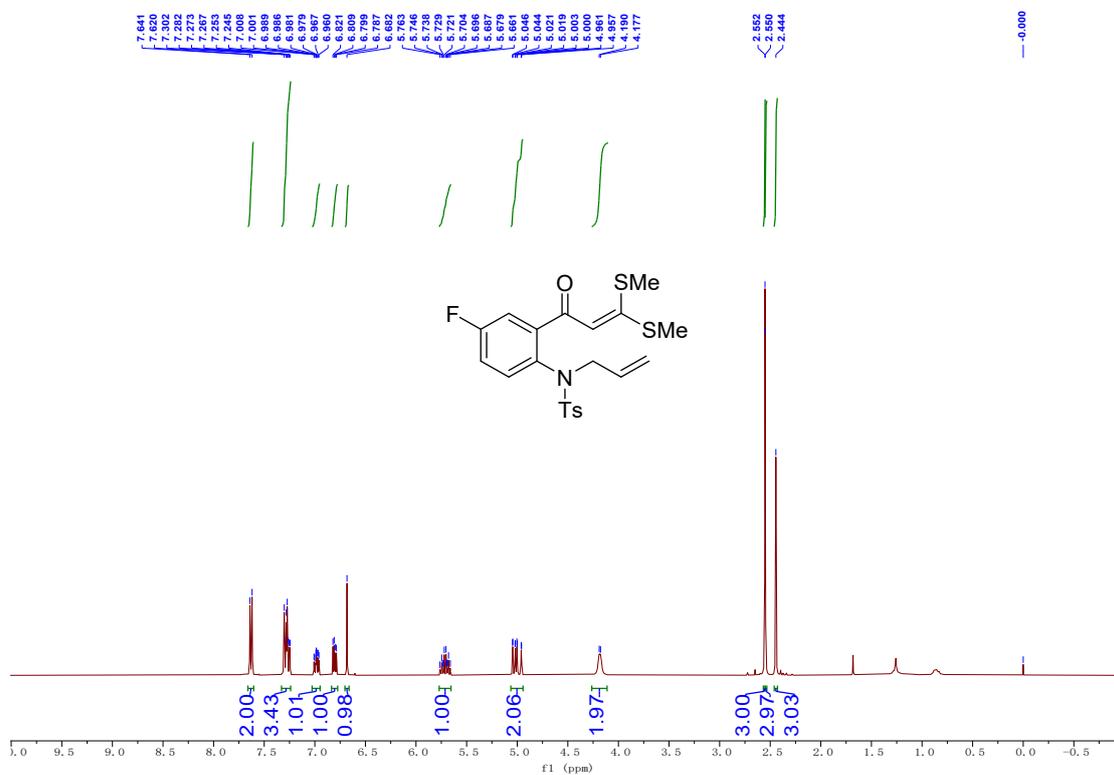
1H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1b**



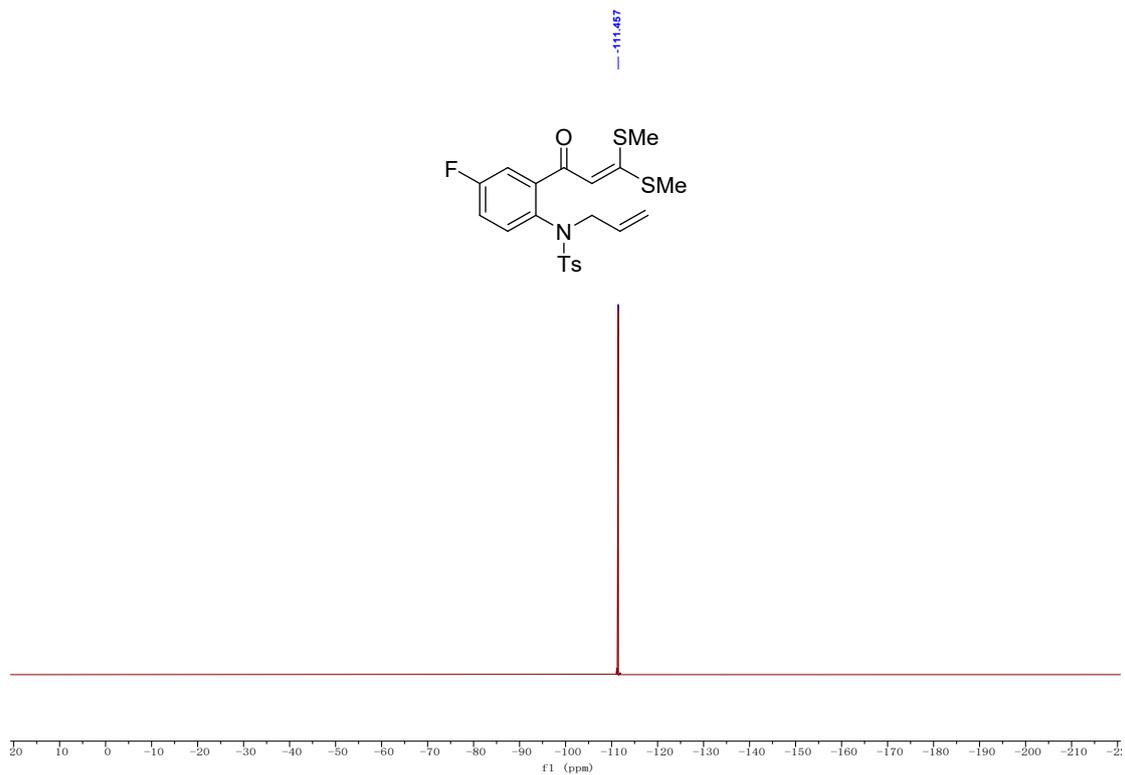
13C NMR spectrum (101 MHz, CDCl₃, 298 K) of **1b**



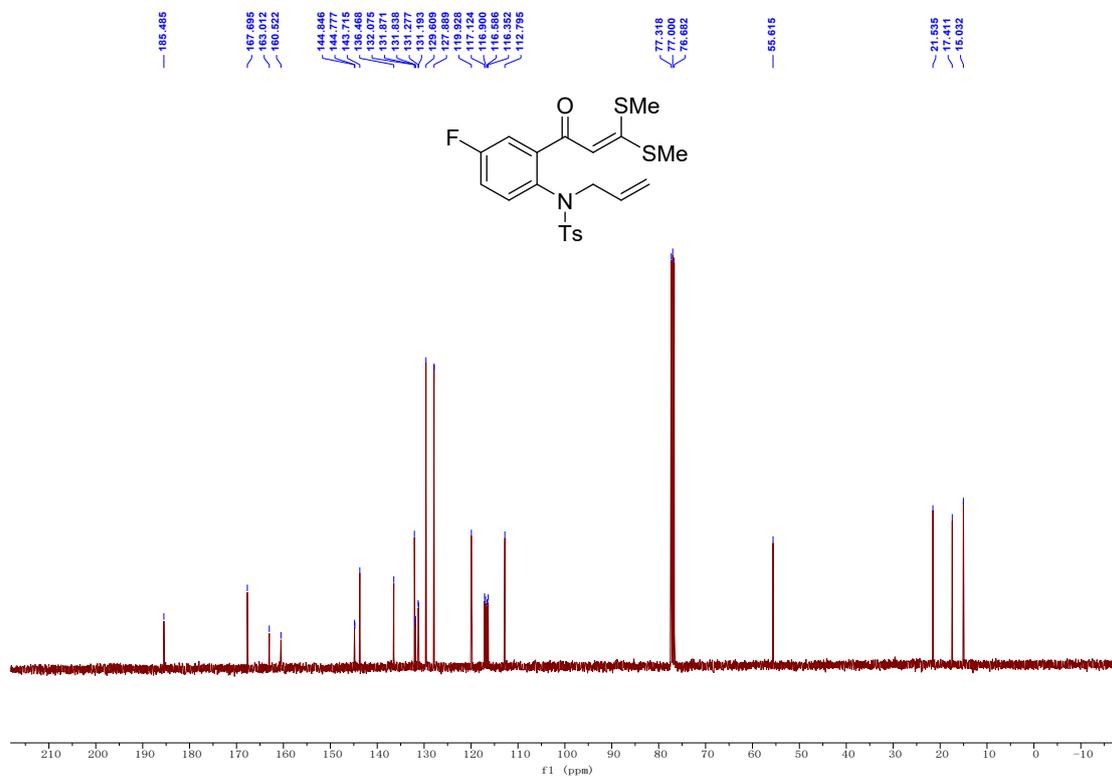
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1c**



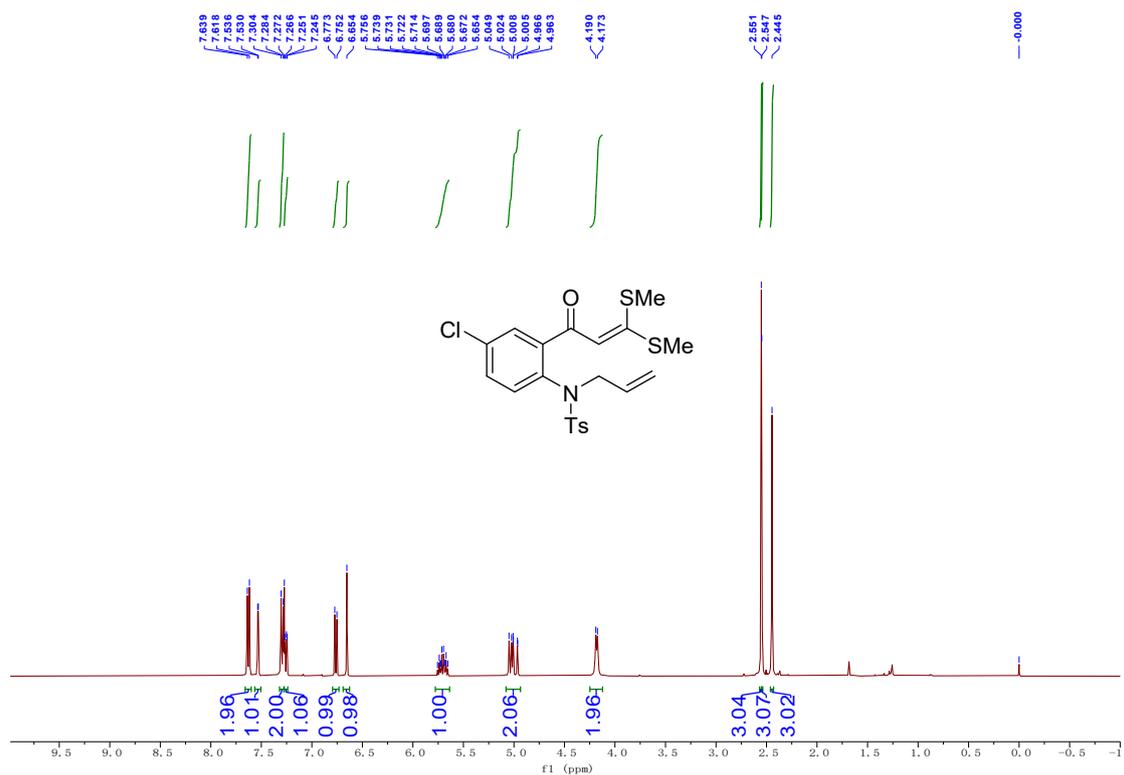
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **1c**



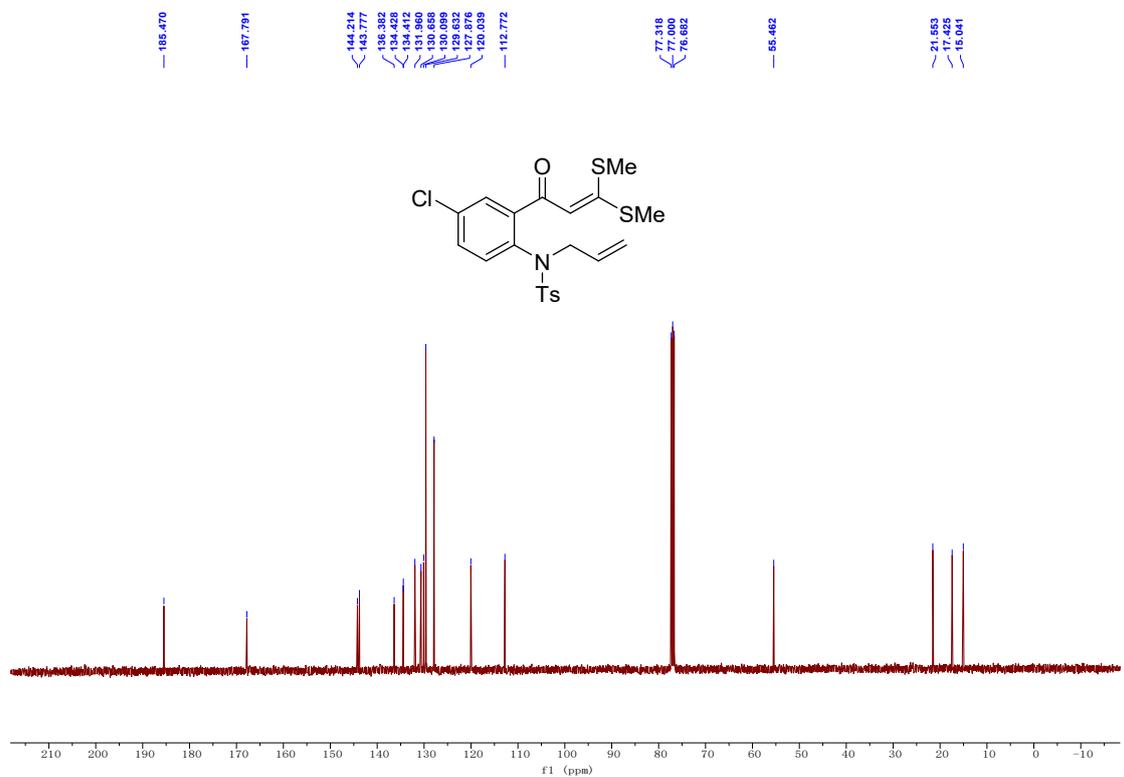
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298 K) of **1c**



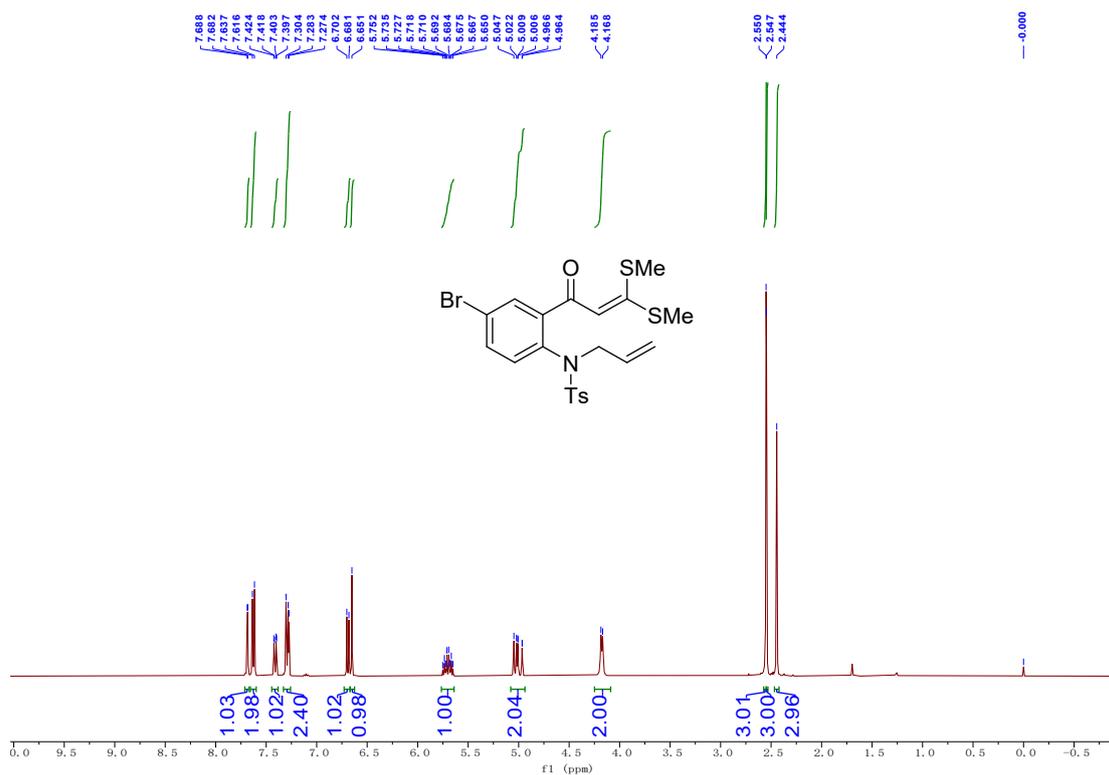
^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1d**



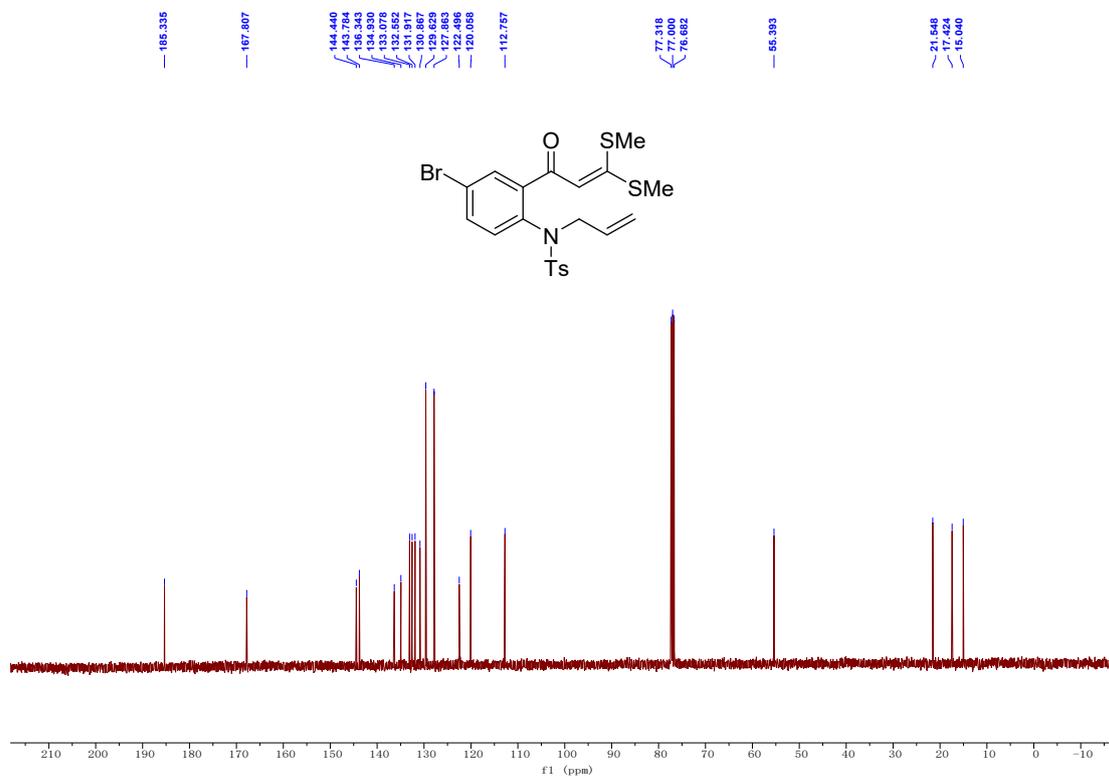
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **1d**



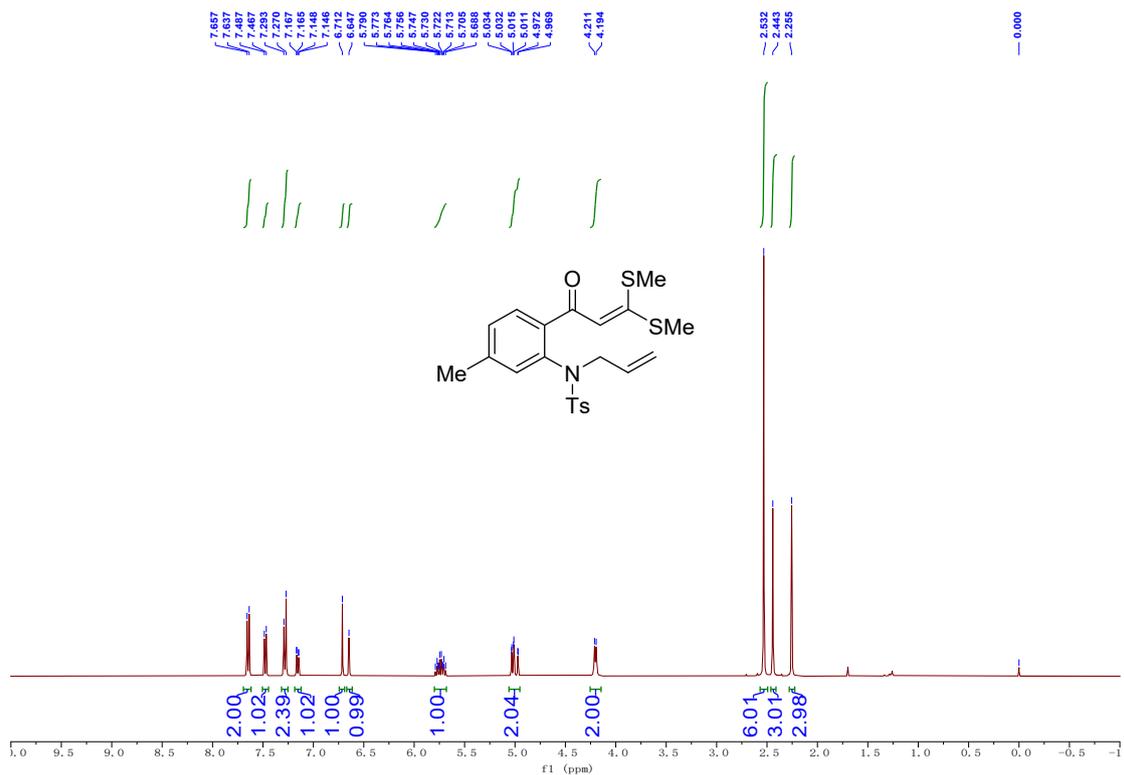
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1e**



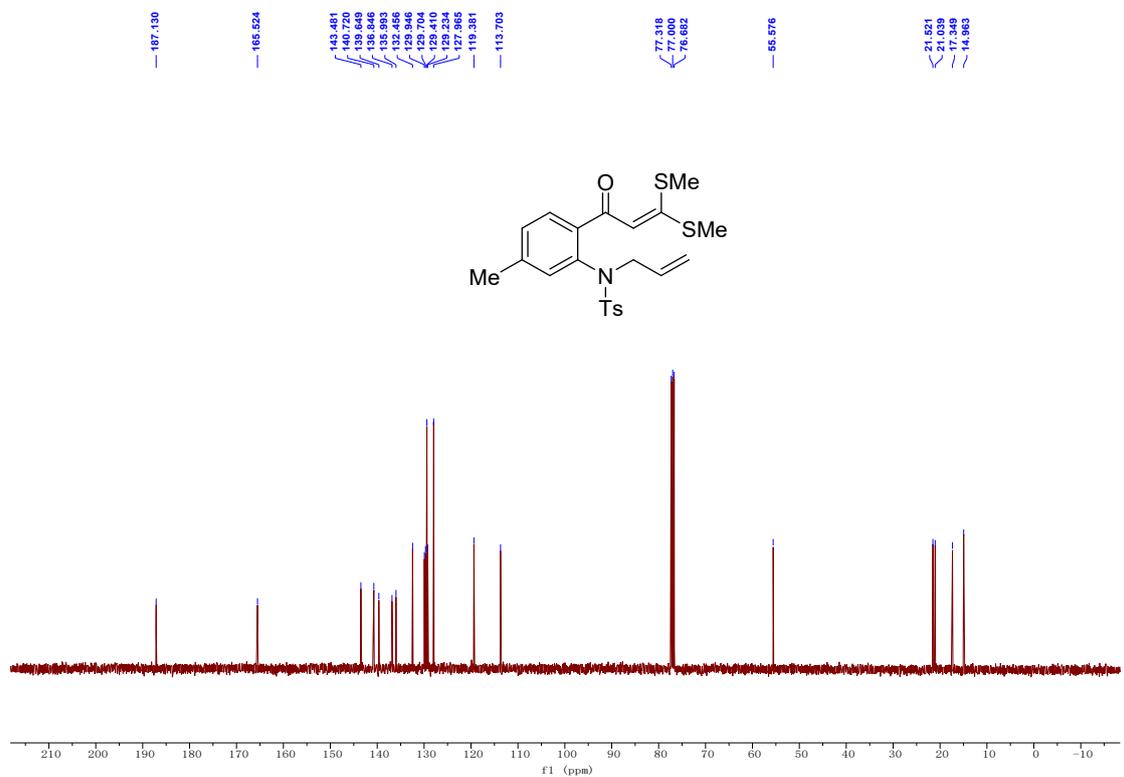
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 1e



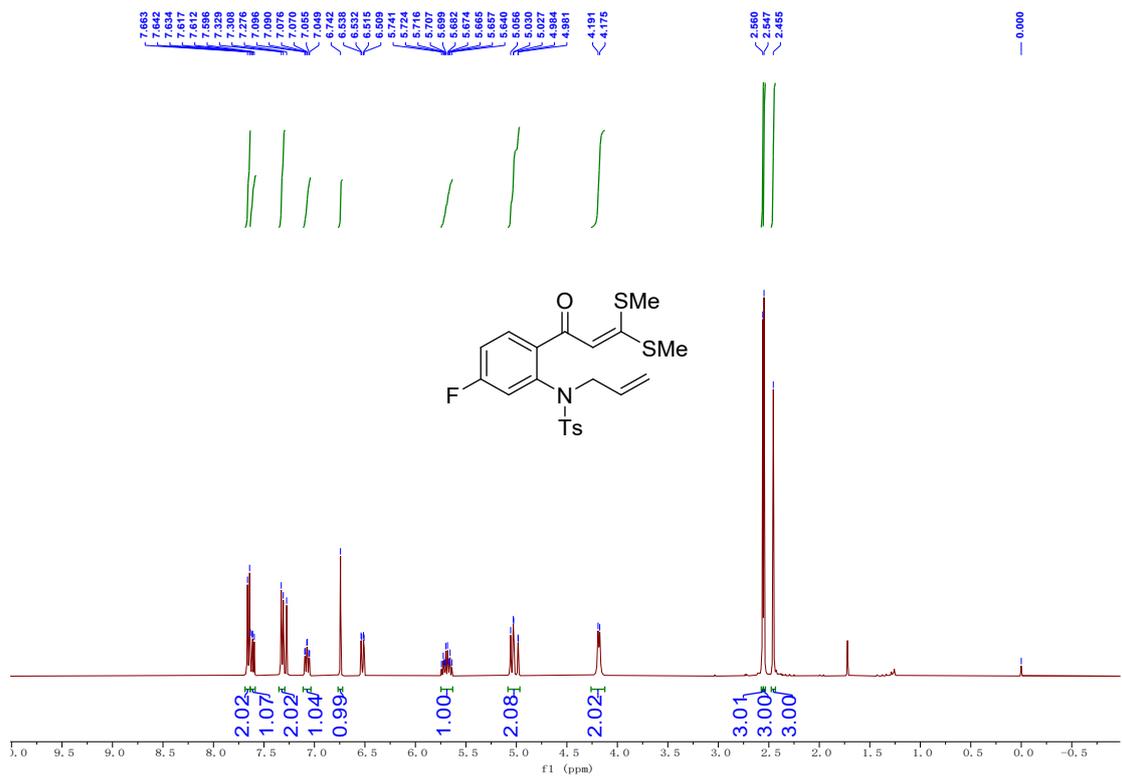
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 1f



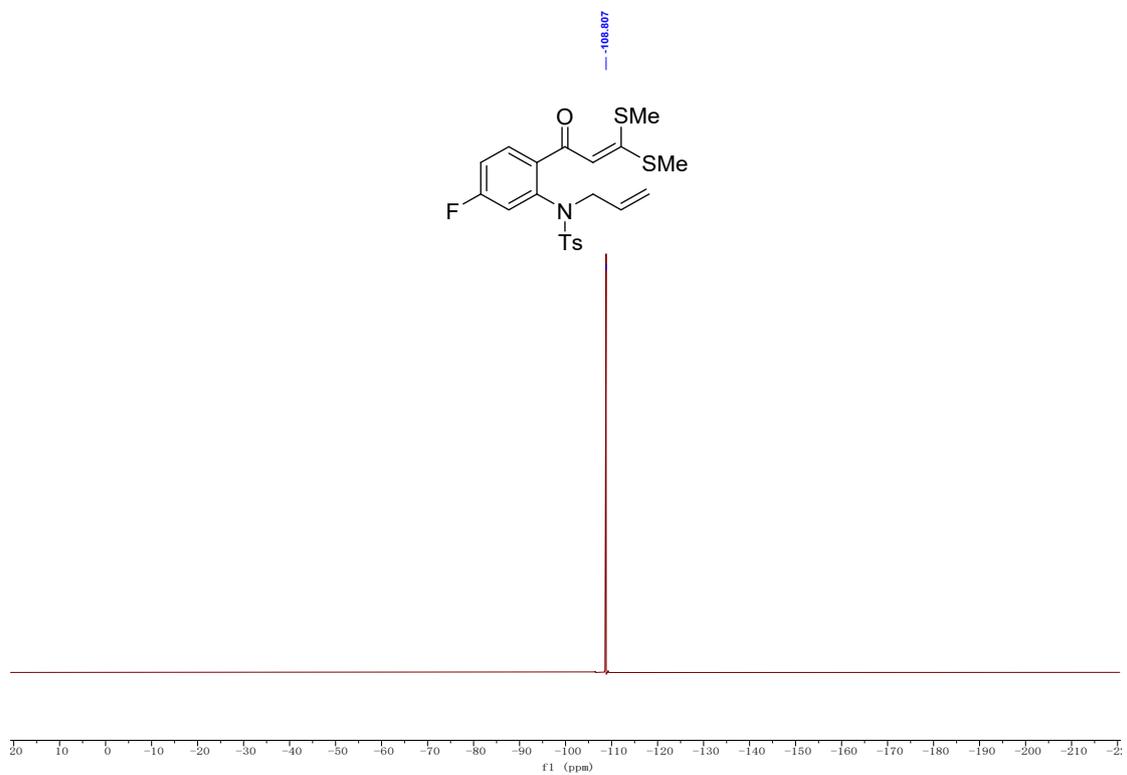
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **1f**



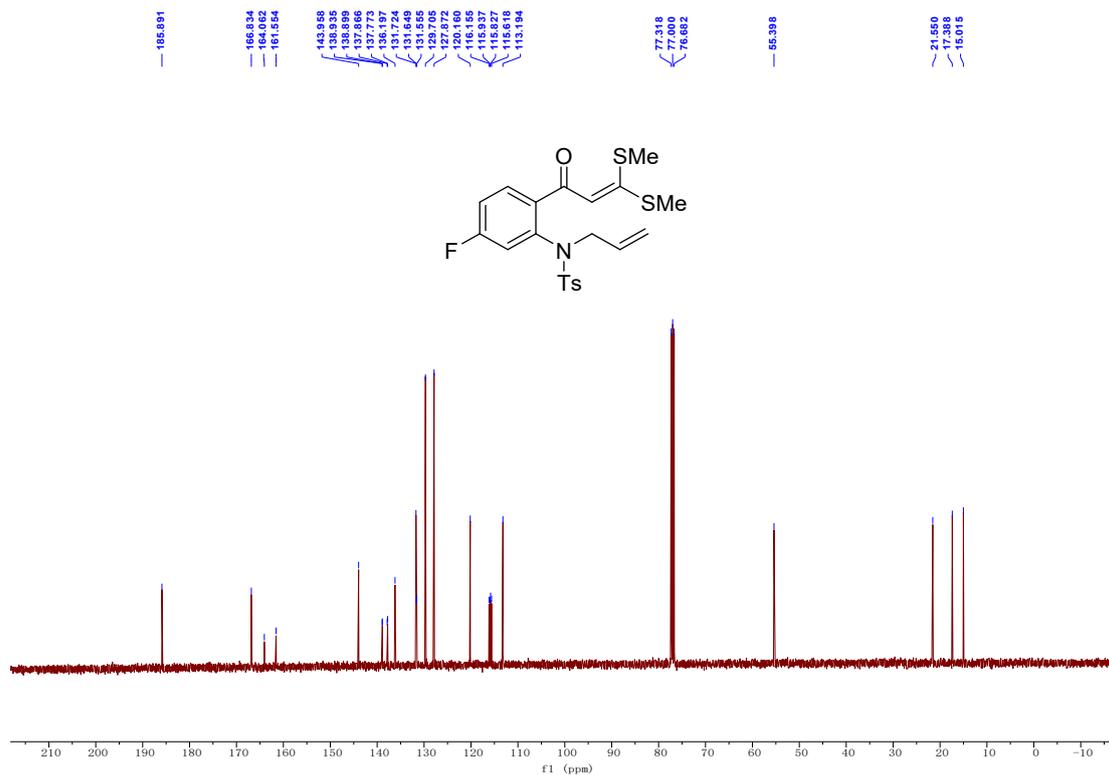
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1g**



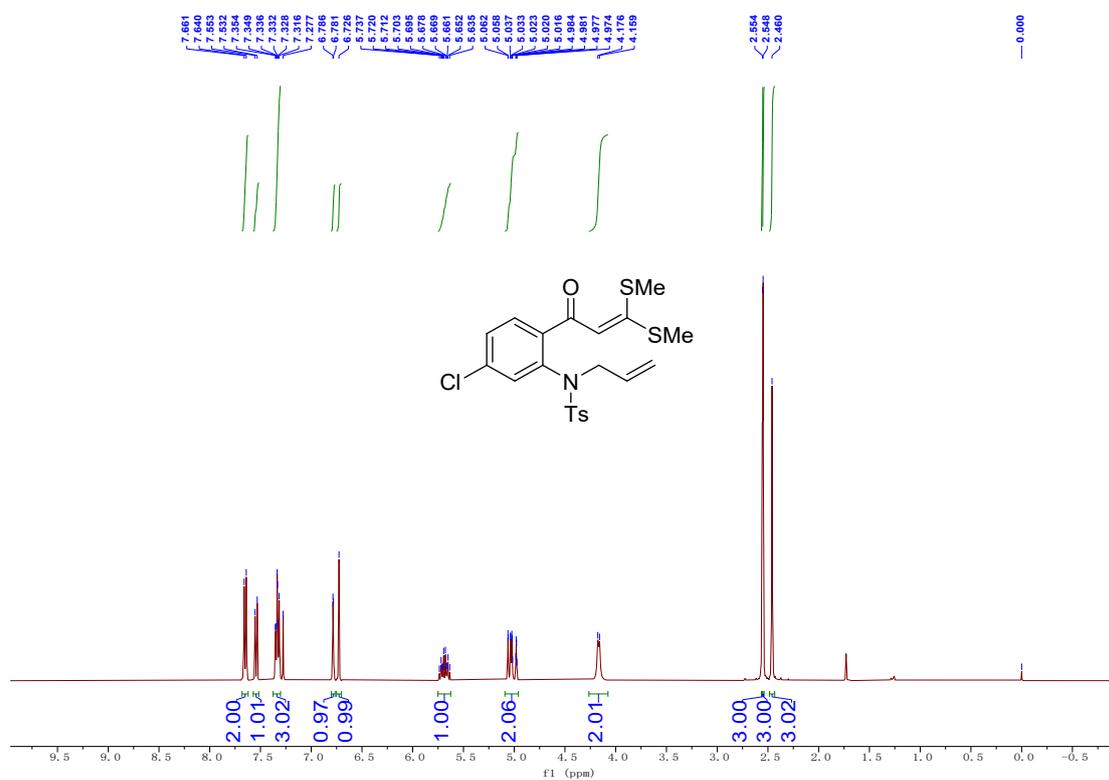
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **1g**



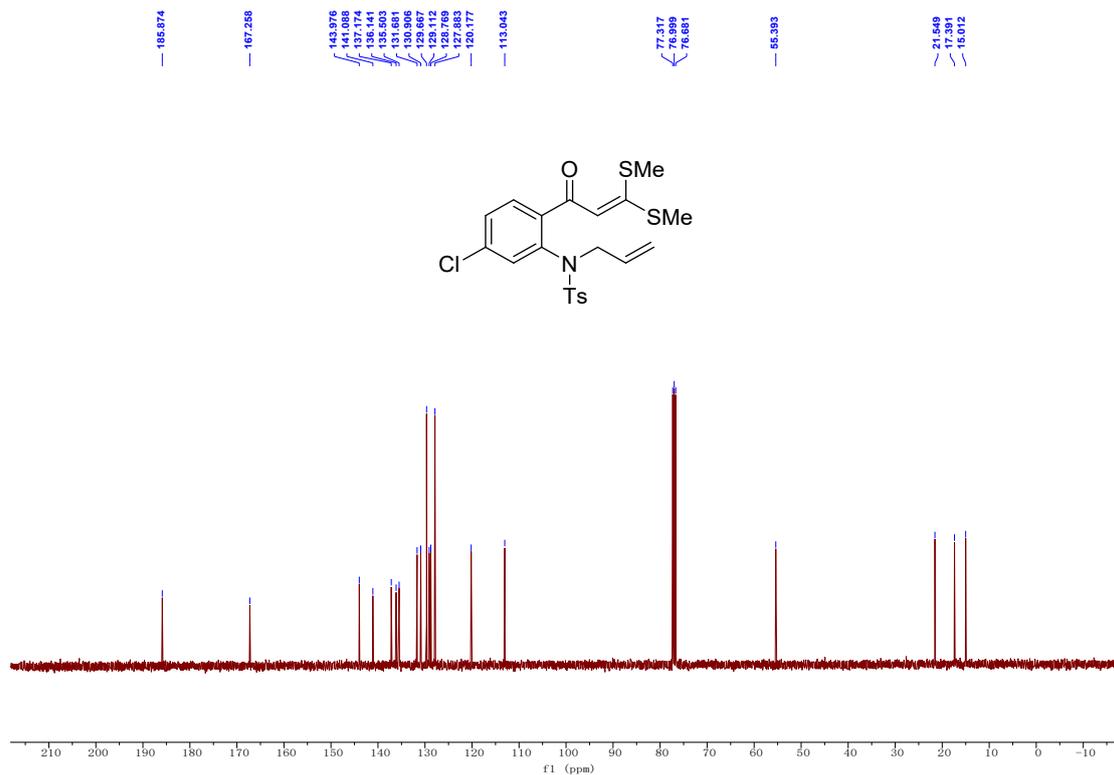
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **1g**



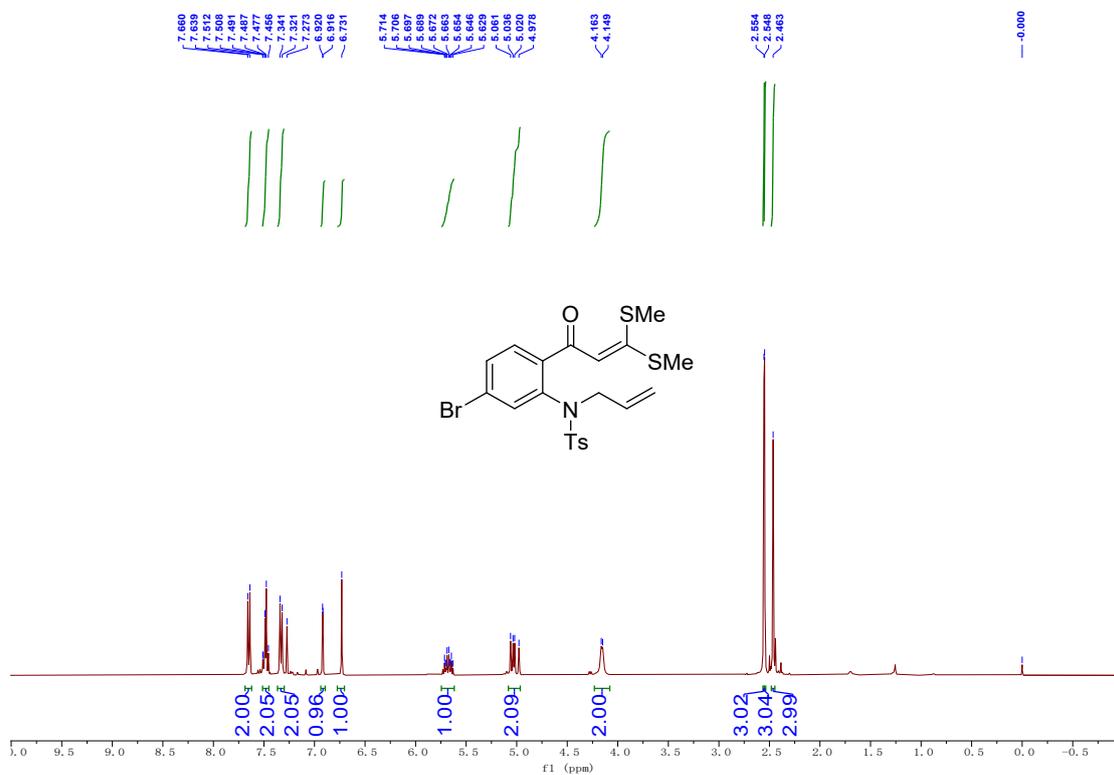
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1h**



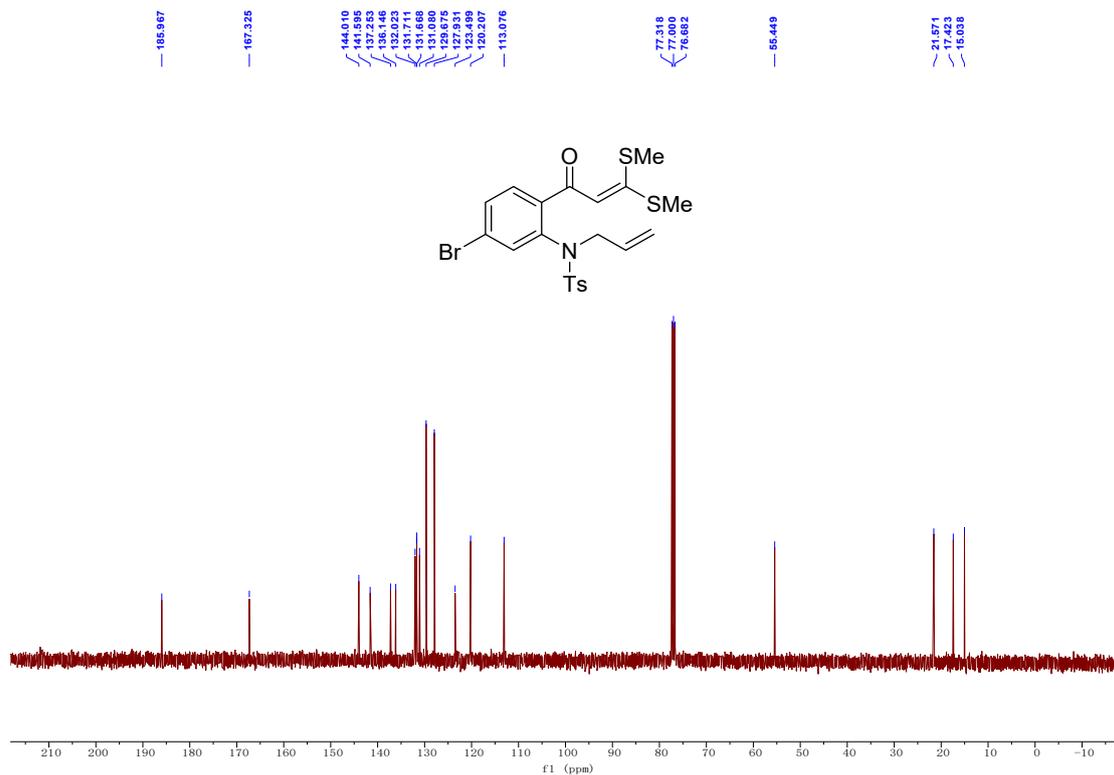
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **1h**



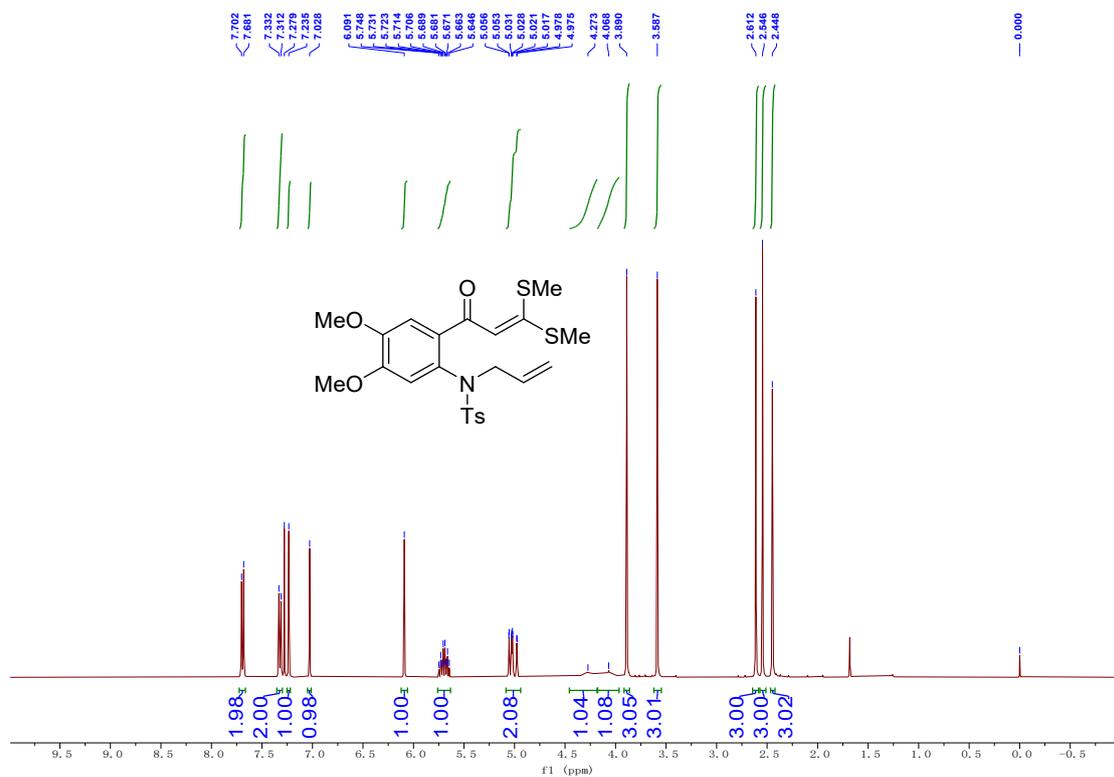
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1i**



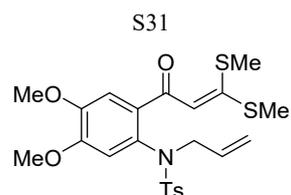
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **4i**

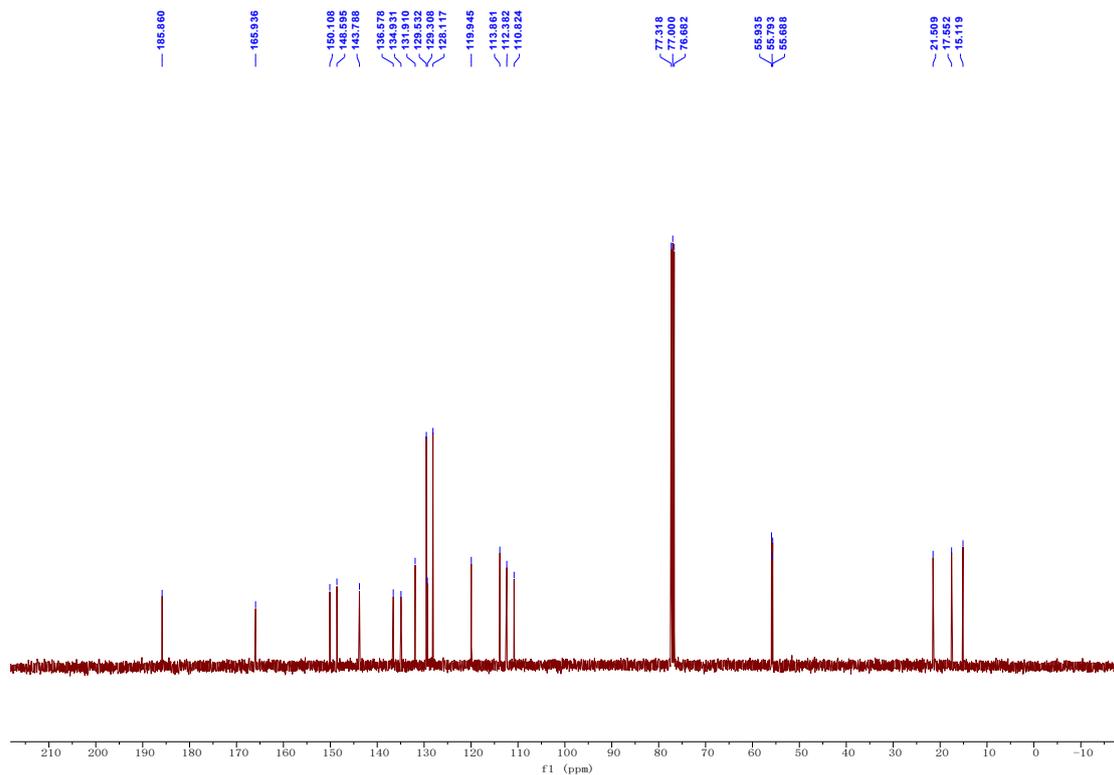


¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1j**

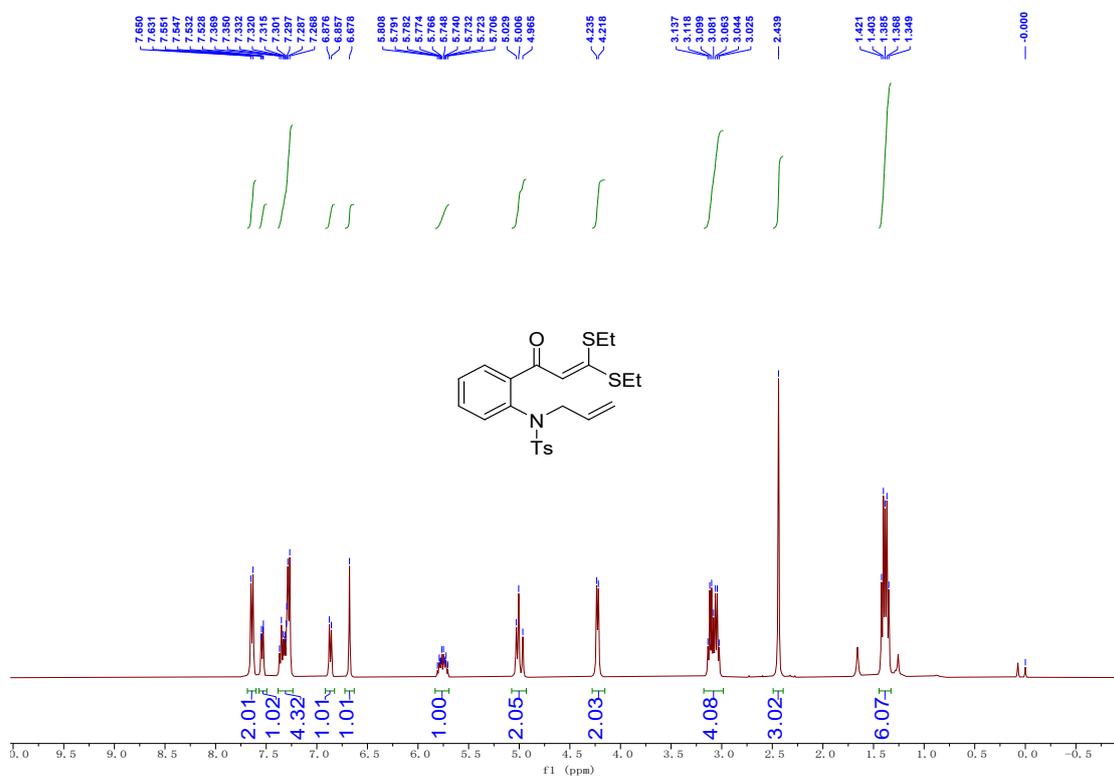


¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **1j**

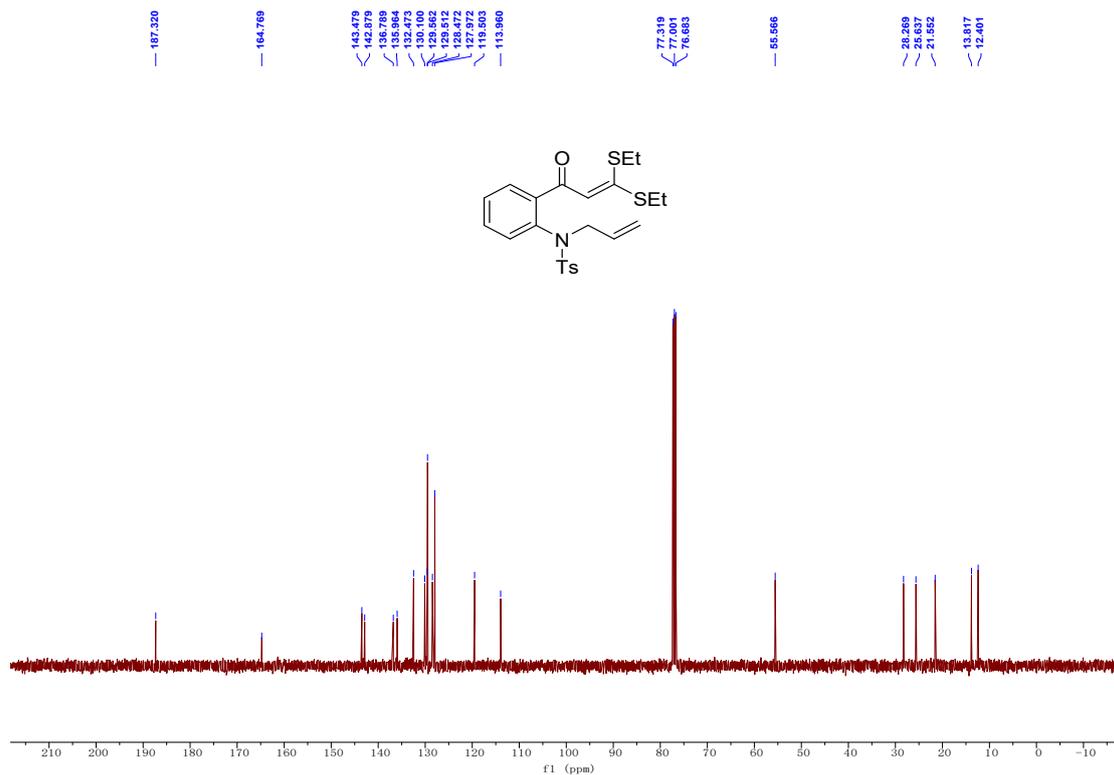




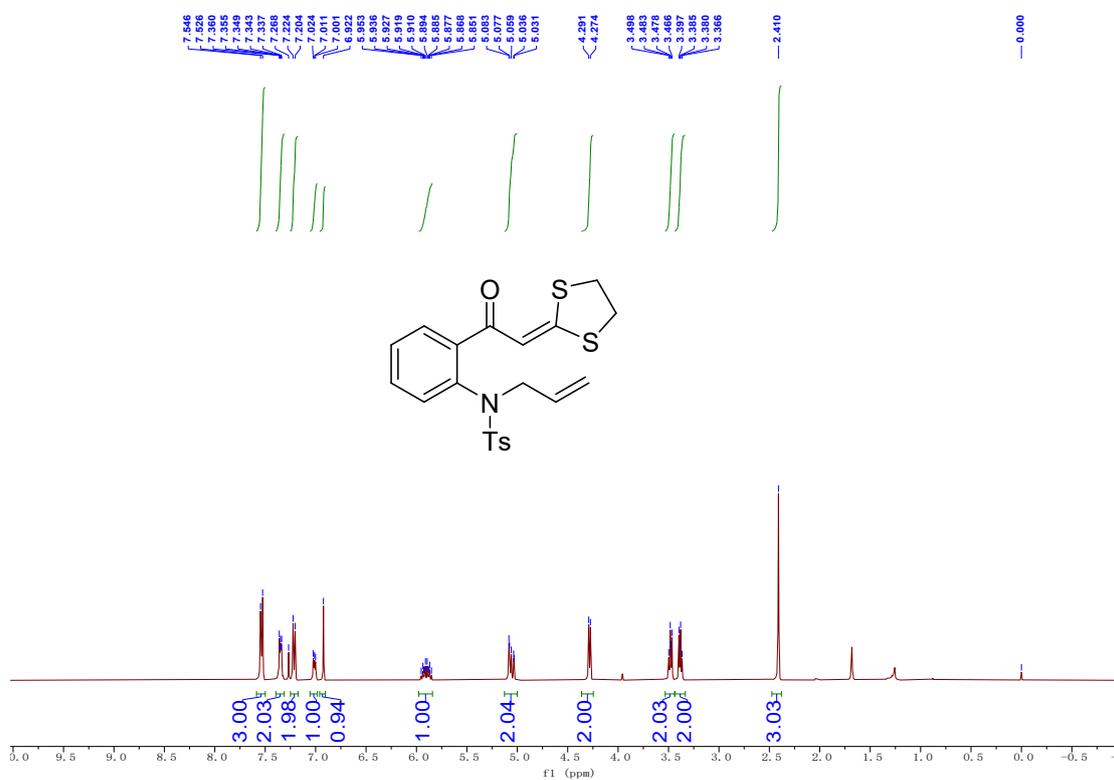
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1k**



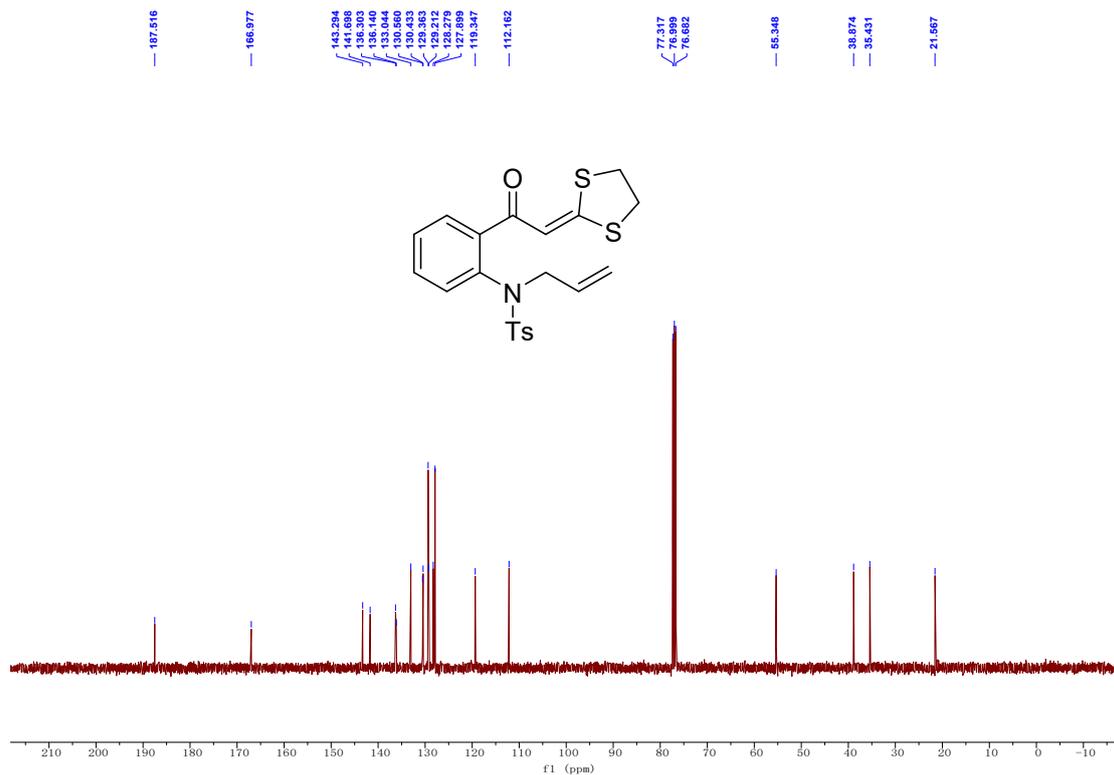
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **1k**



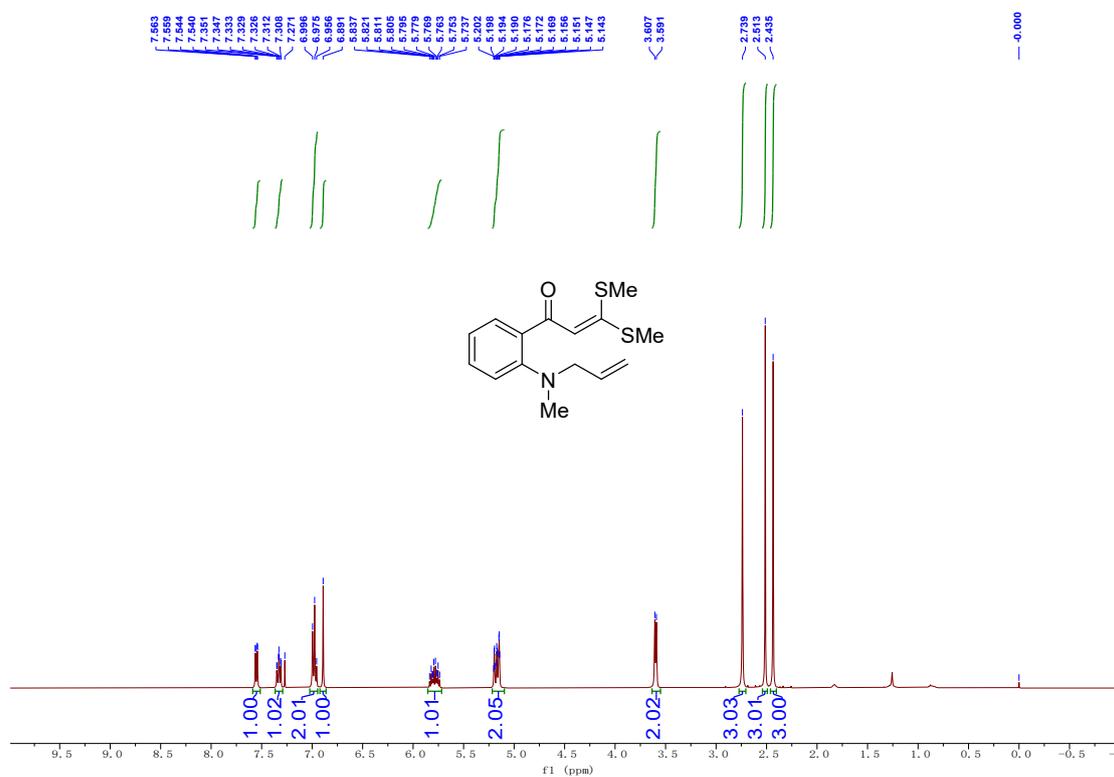
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **11**



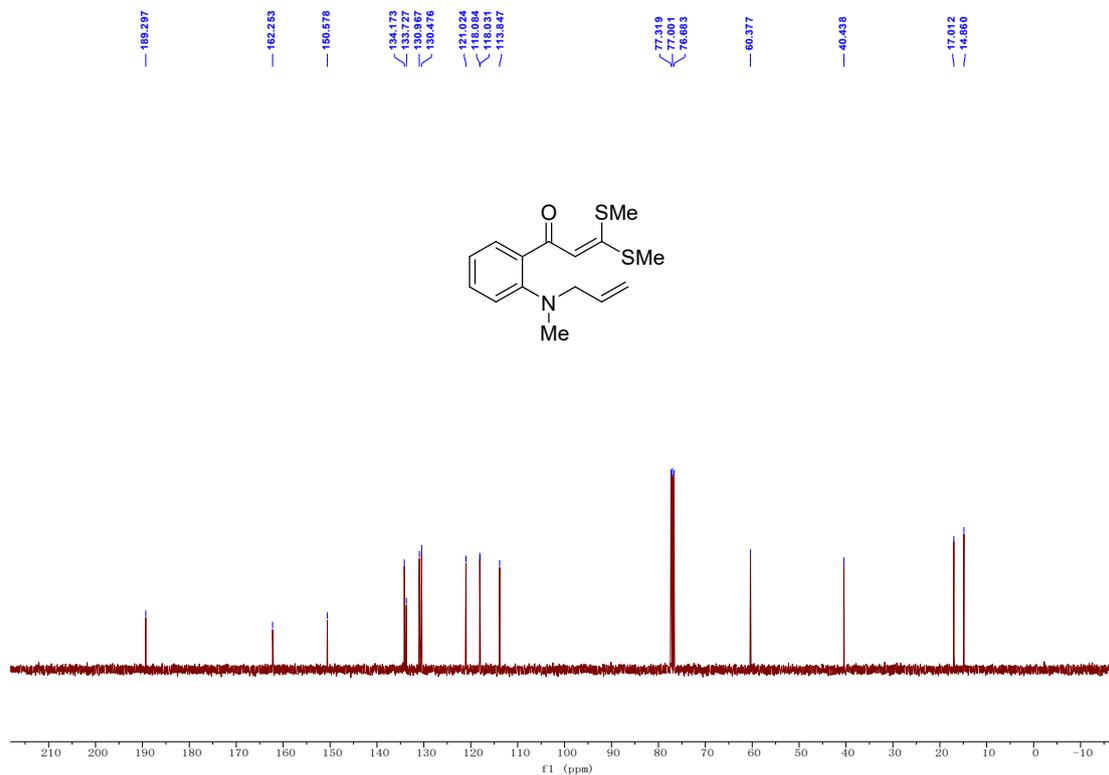
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **11**



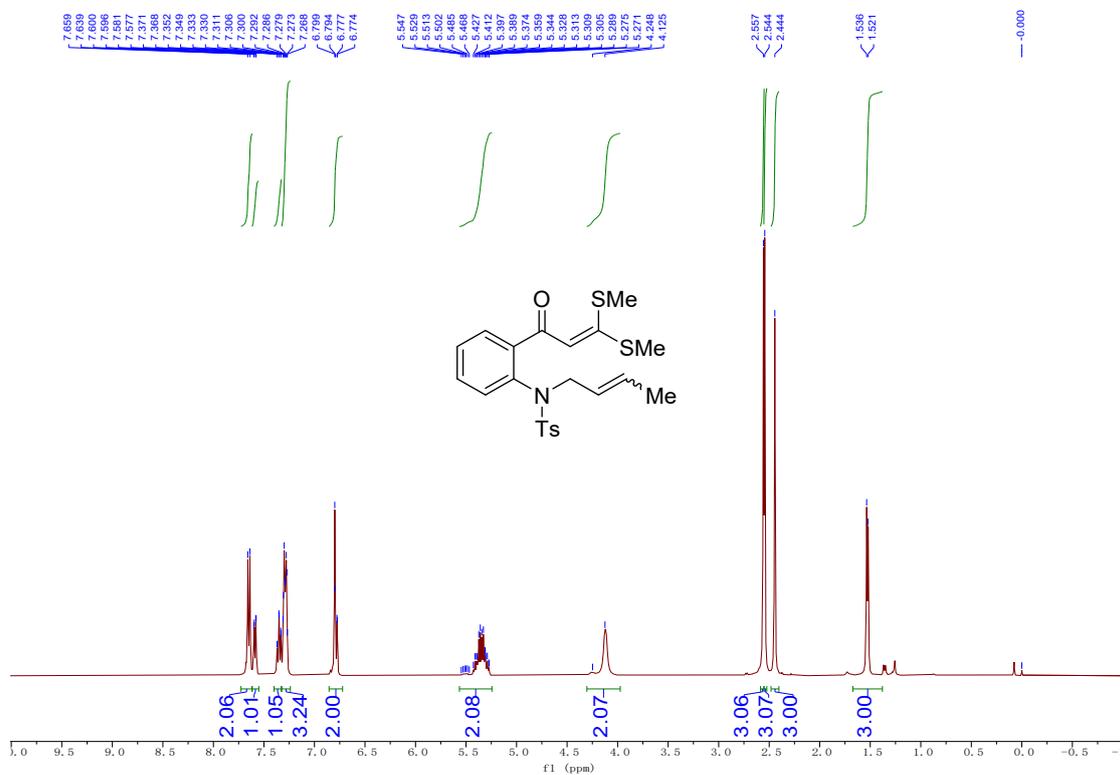
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1m**



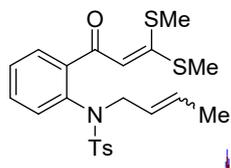
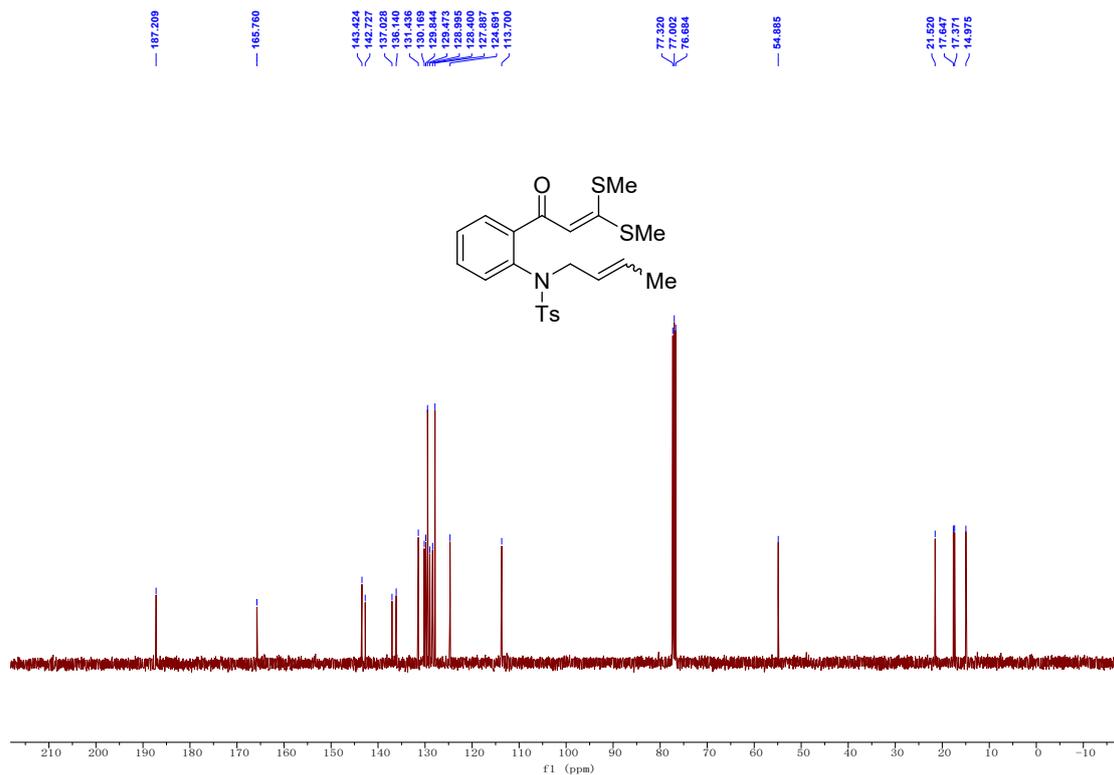
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **1m**



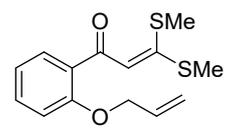
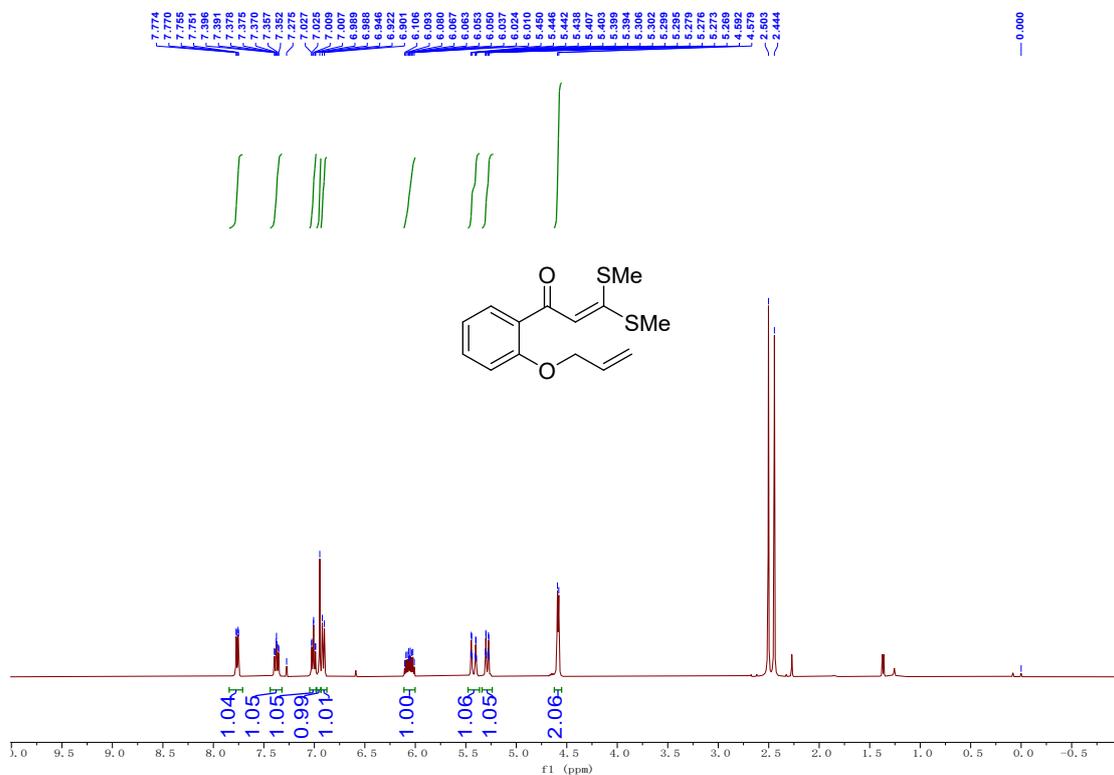
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **1n**



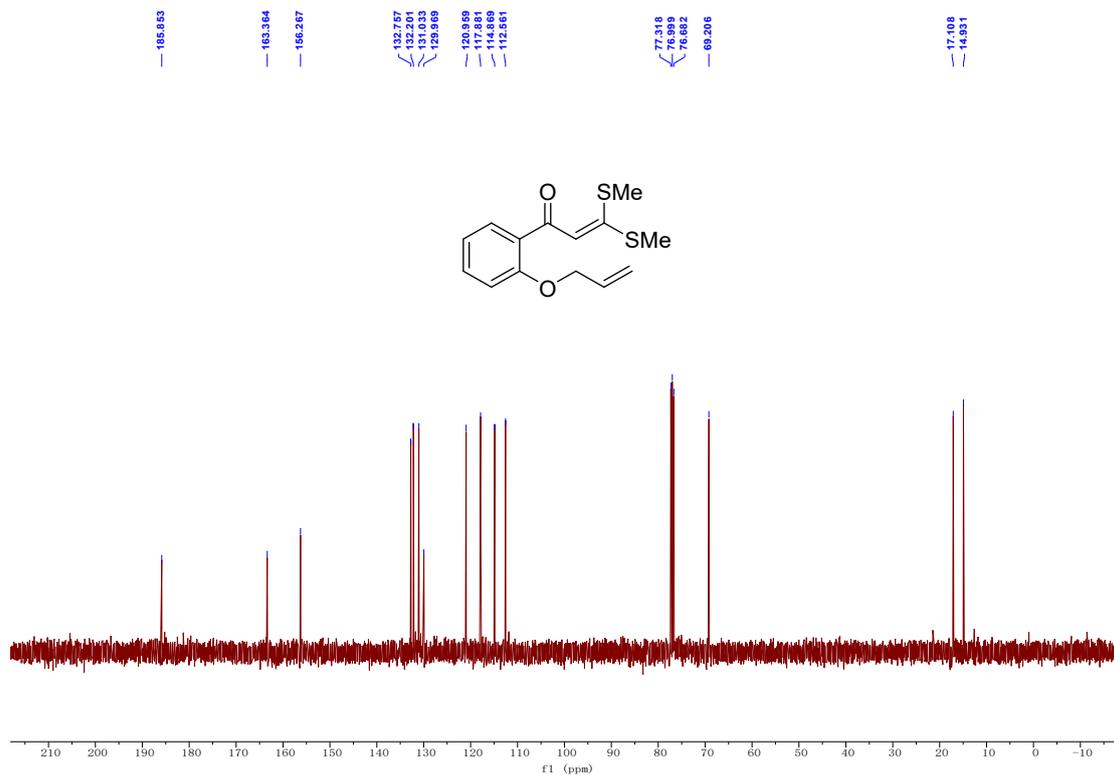
¹³C NMR spectrum (400 MHz, CDCl₃, 298 K) of **1n**



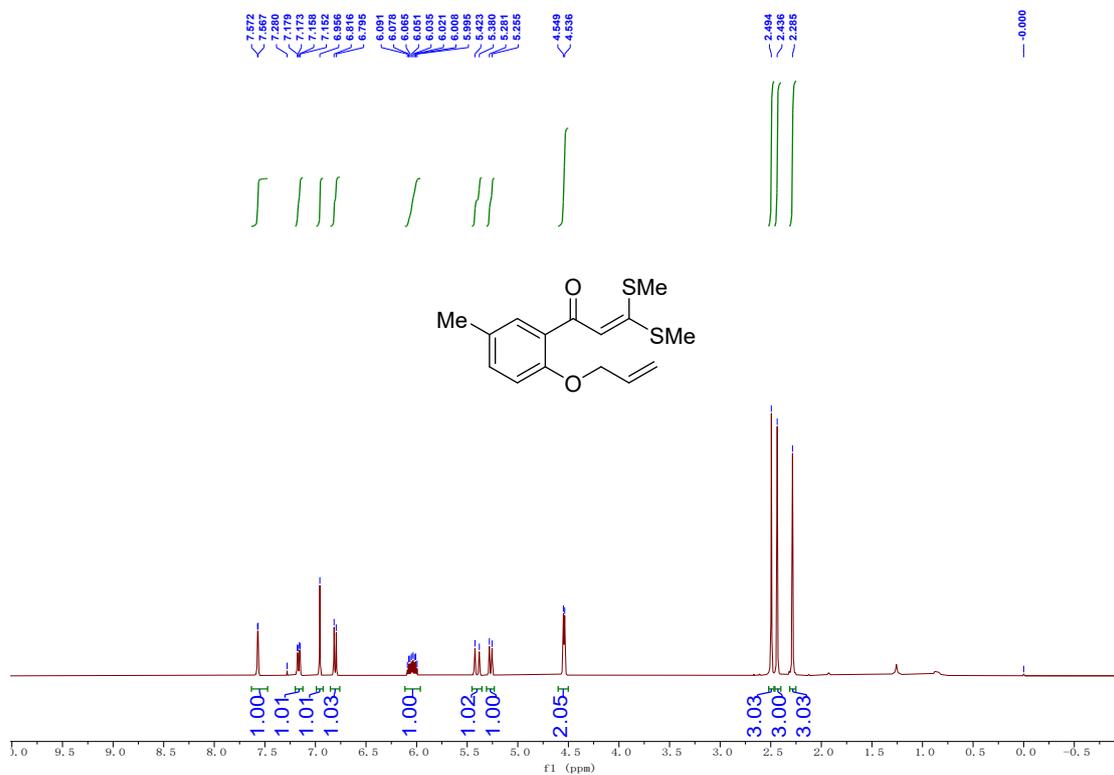
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **4a**



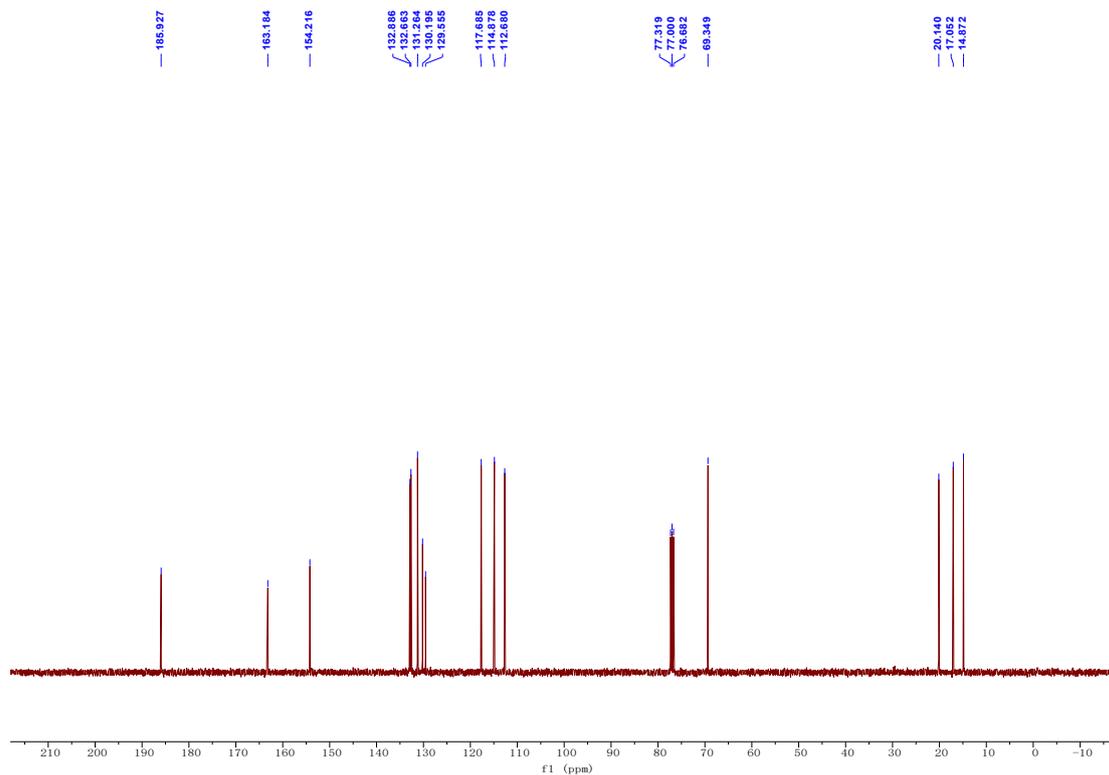
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **4a**



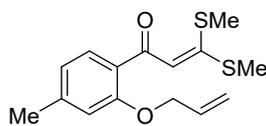
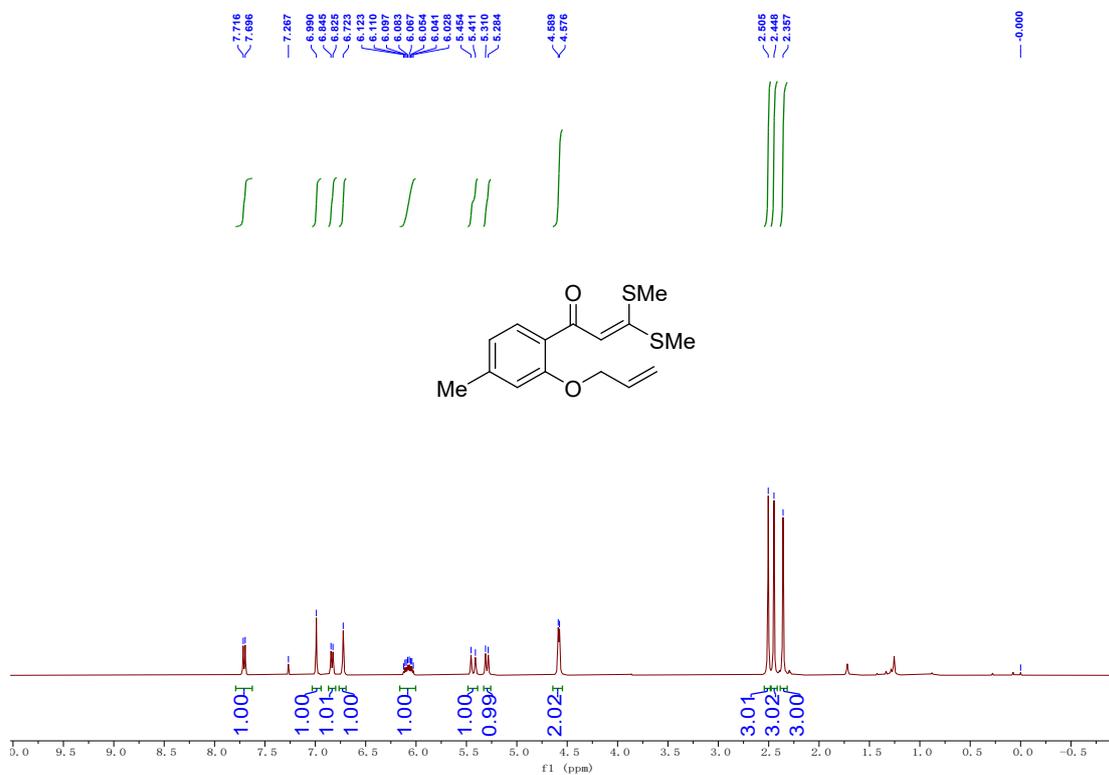
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **4b**



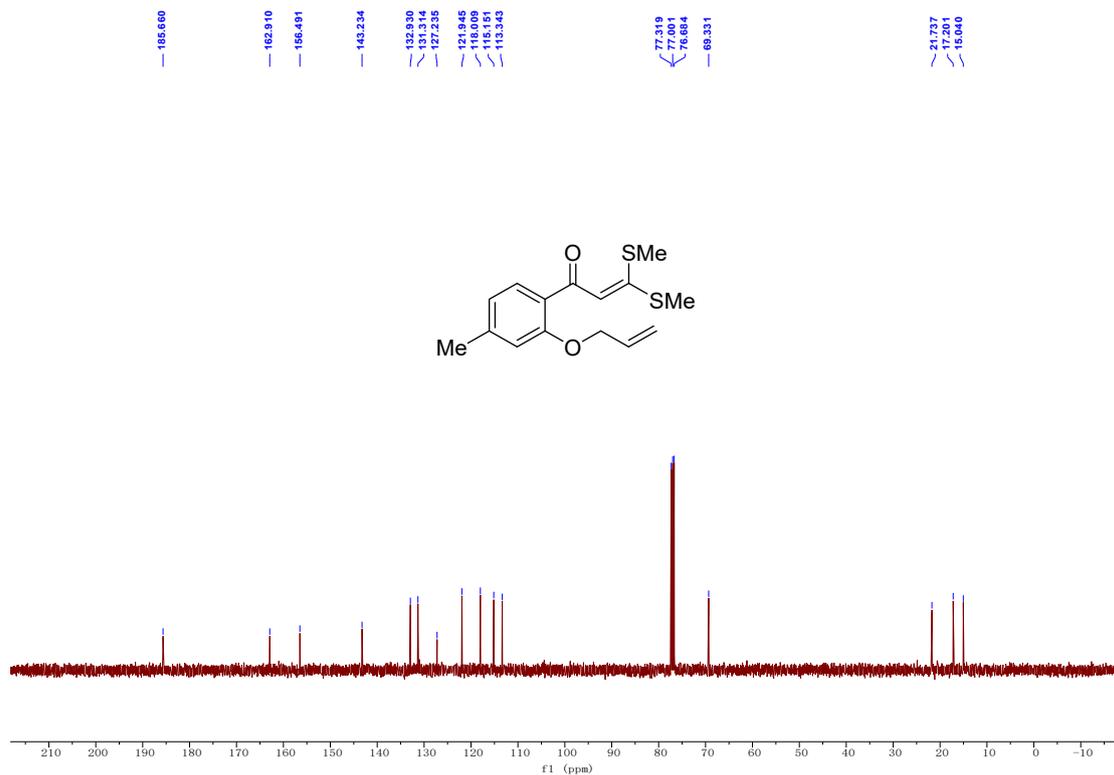
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **4b**



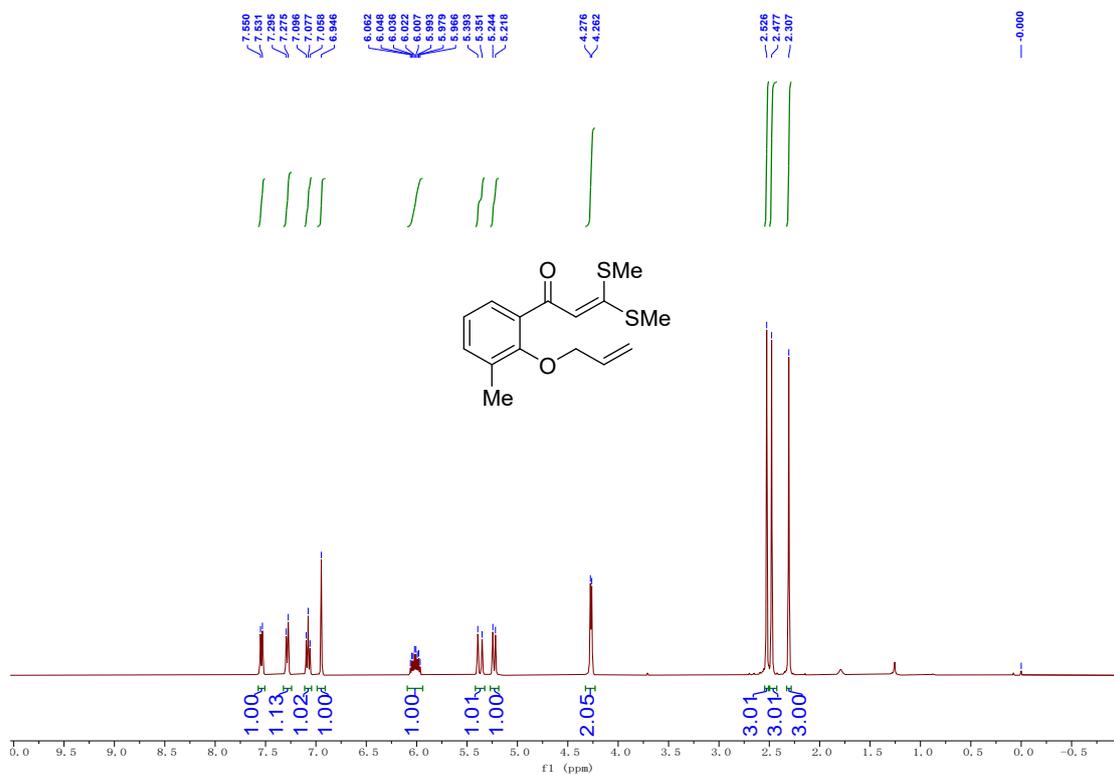
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **4c**



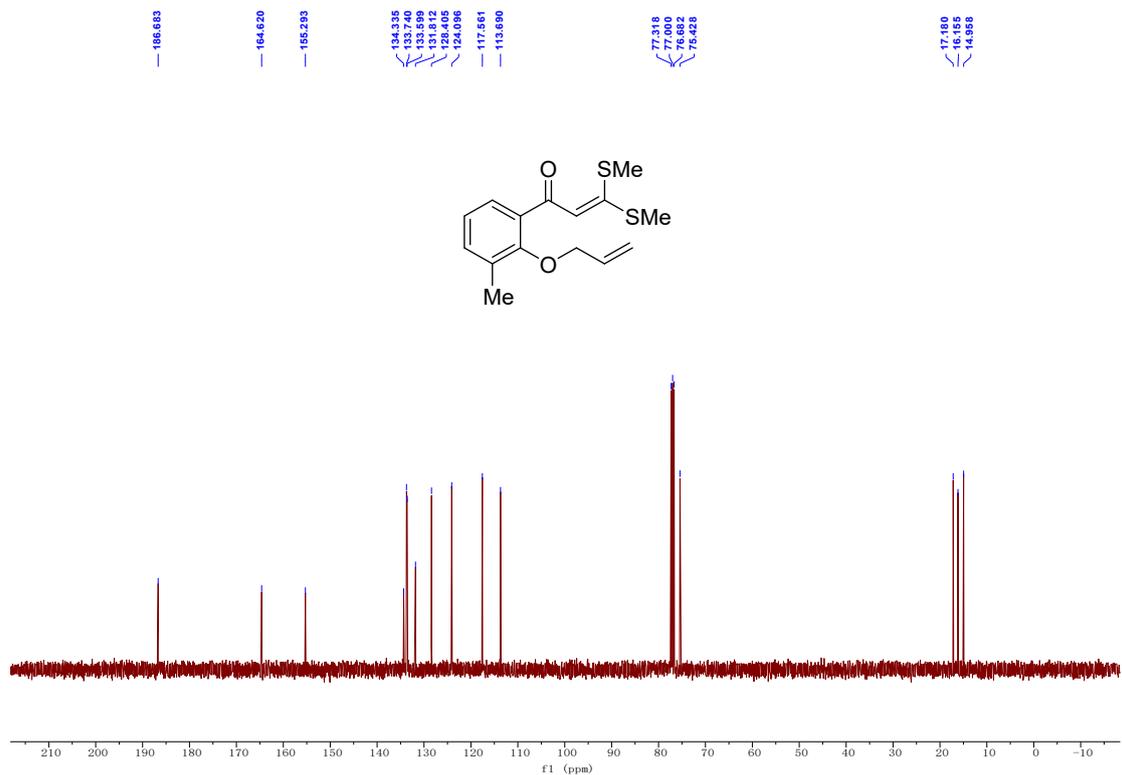
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **4c**



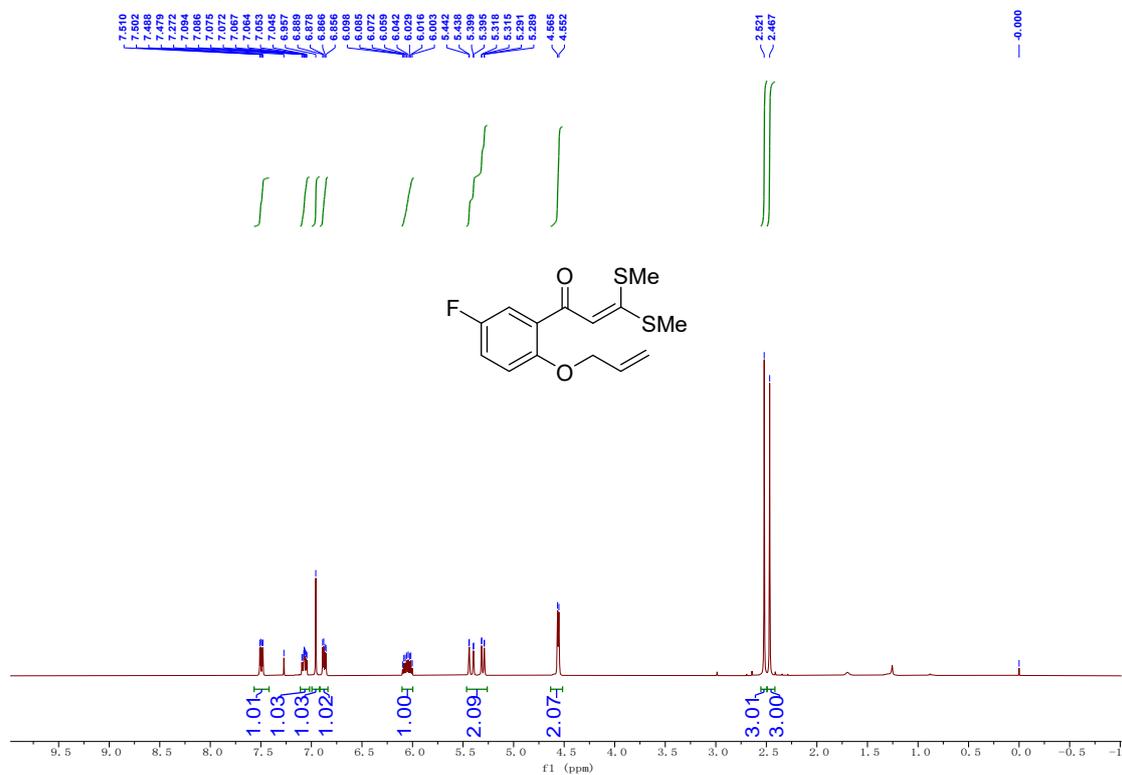
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **4d**



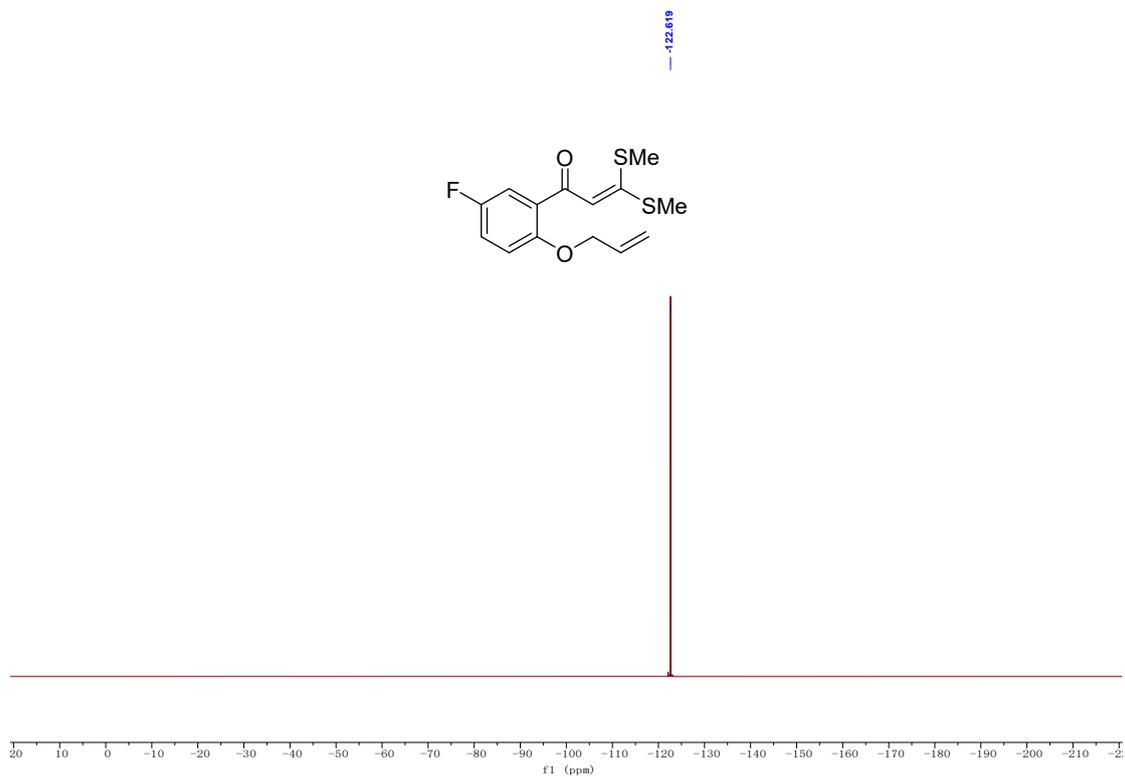
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **4d**



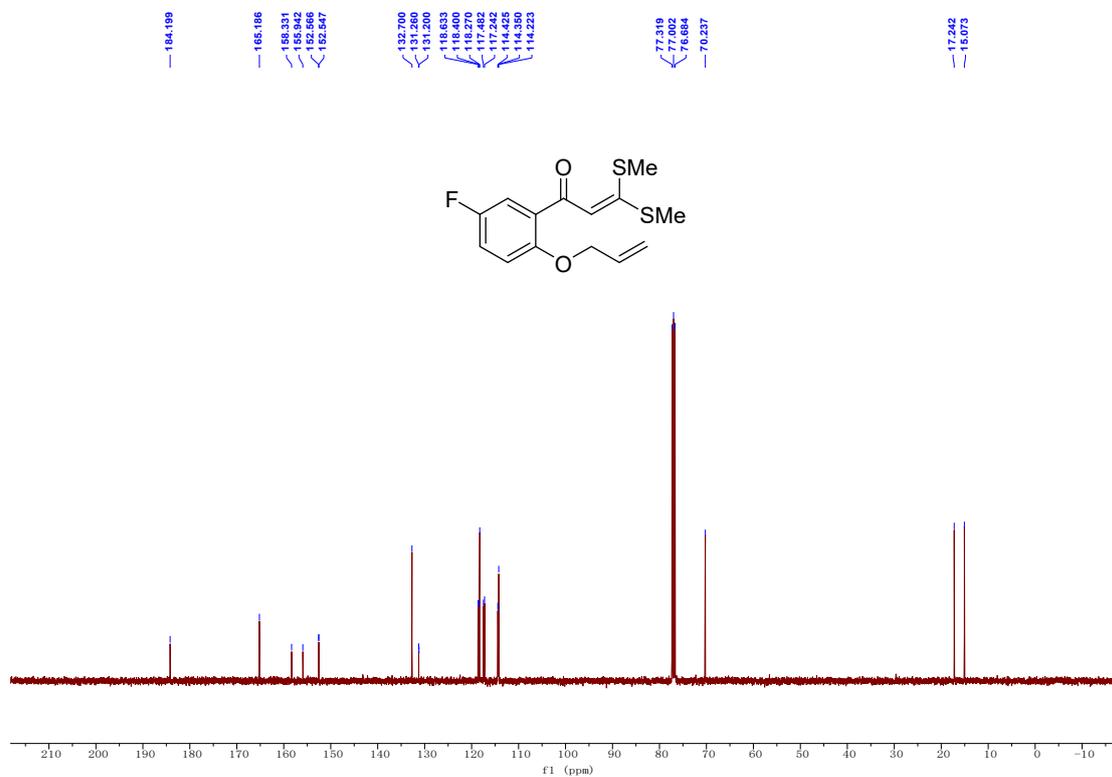
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 4e



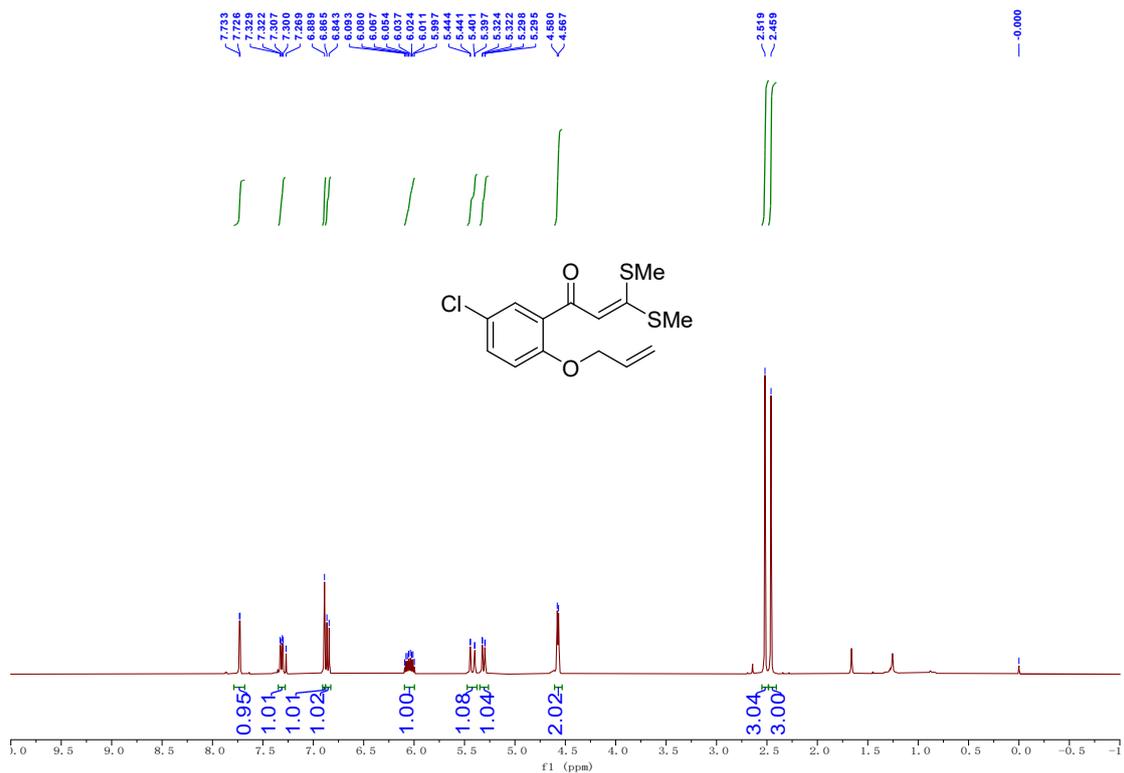
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 4e



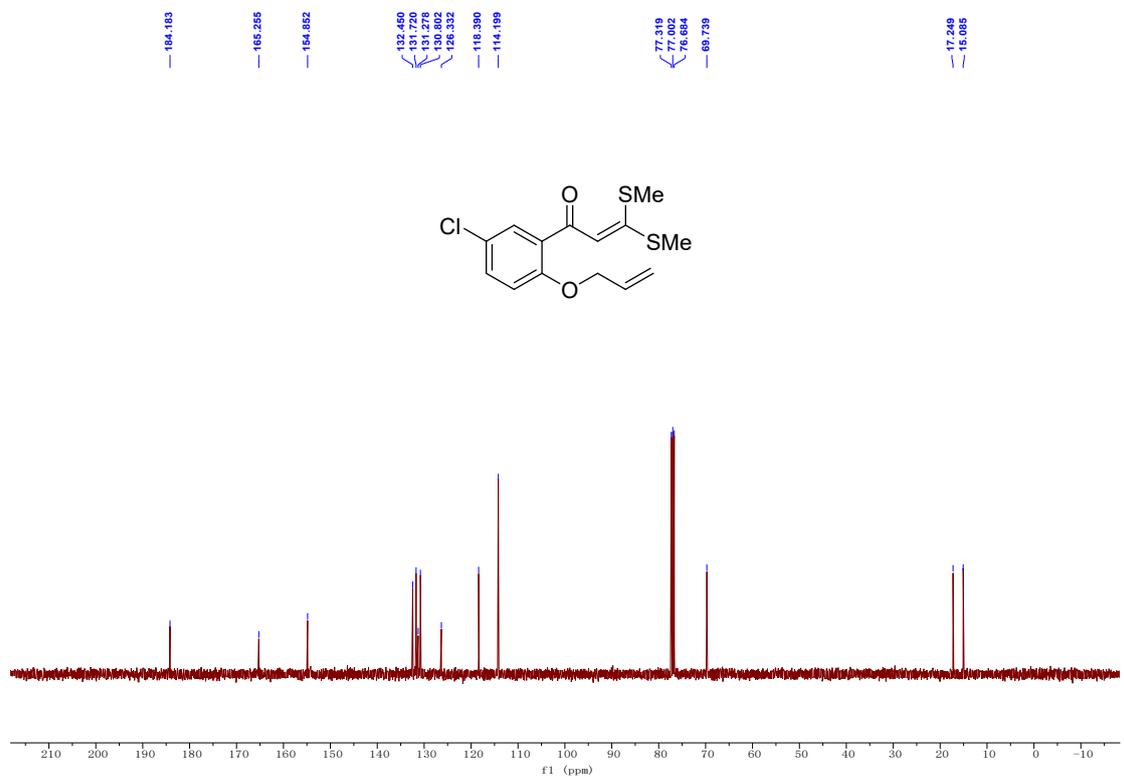
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 4e



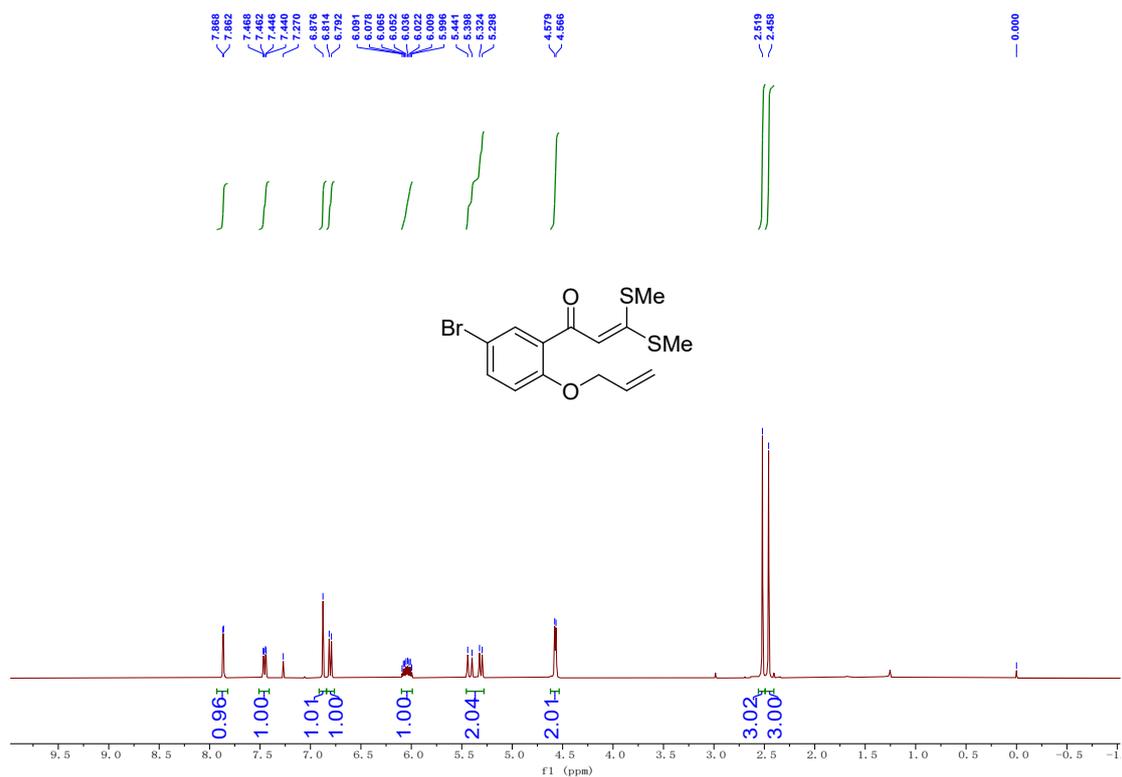
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 4f



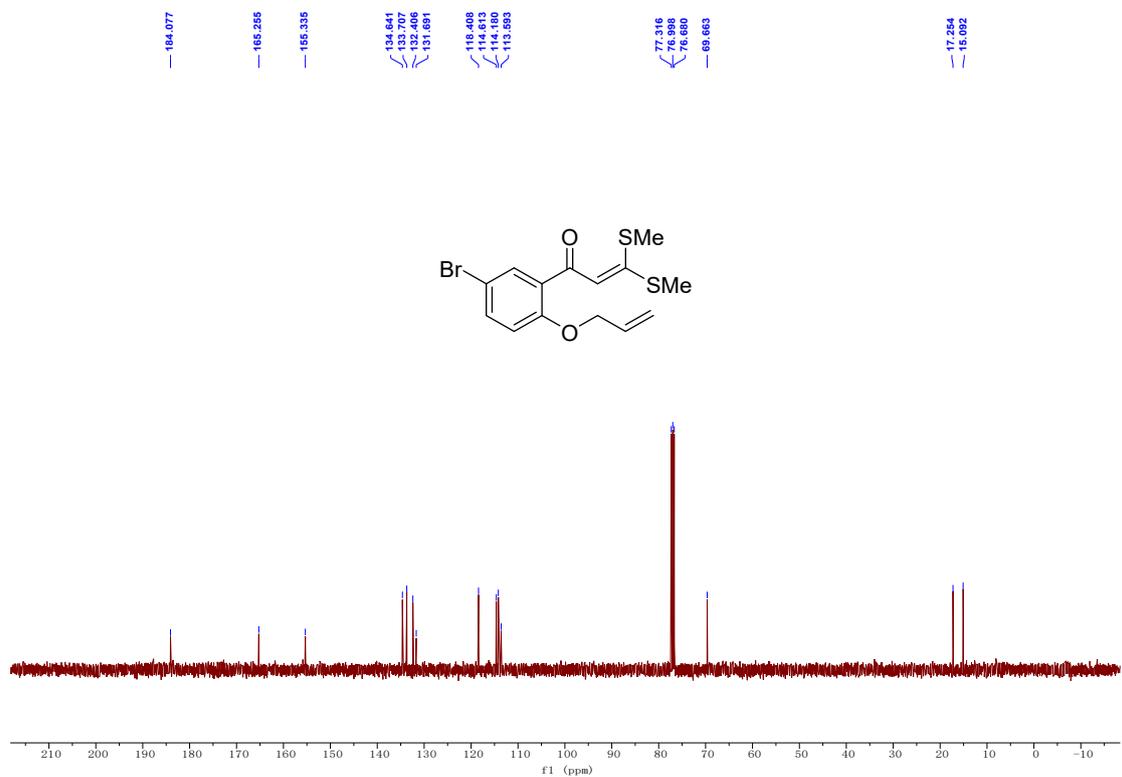
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 4f



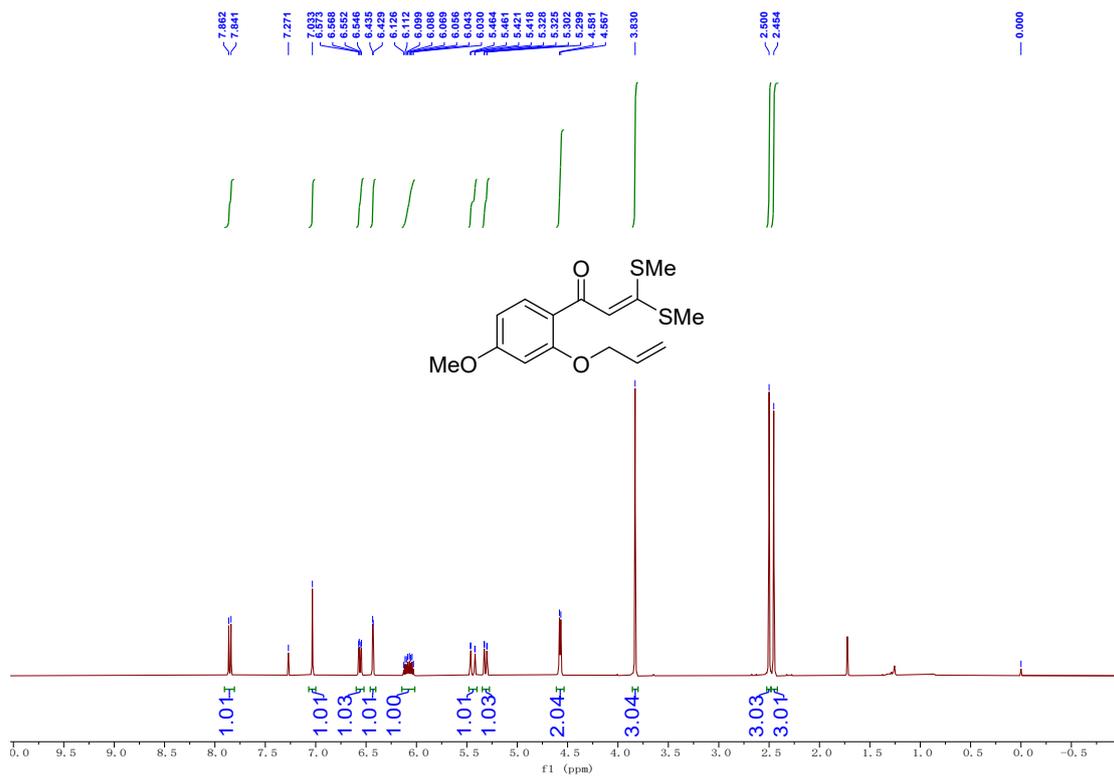
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 4g



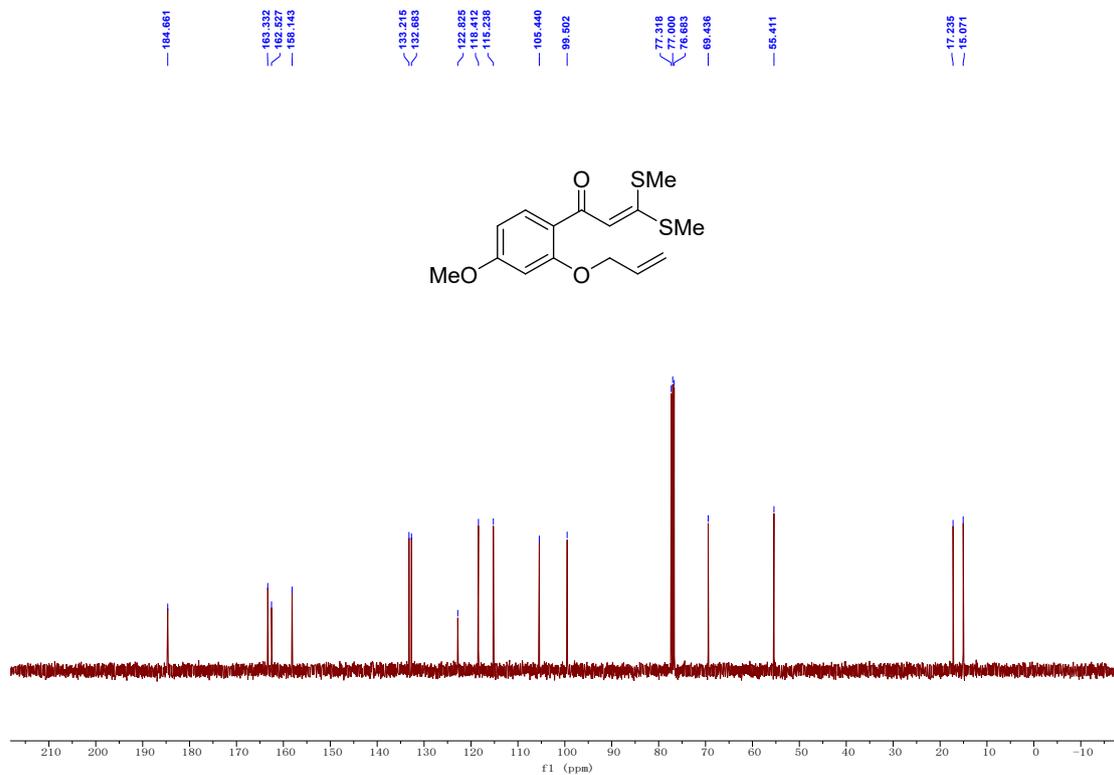
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 4g



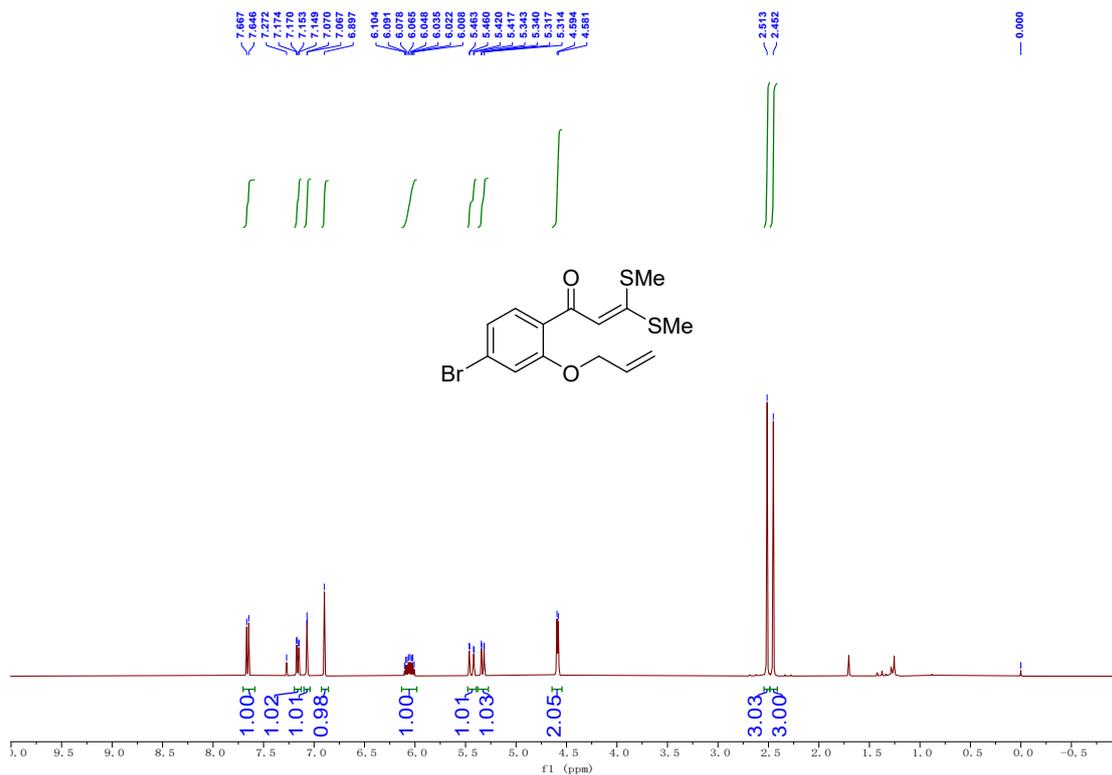
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 4h



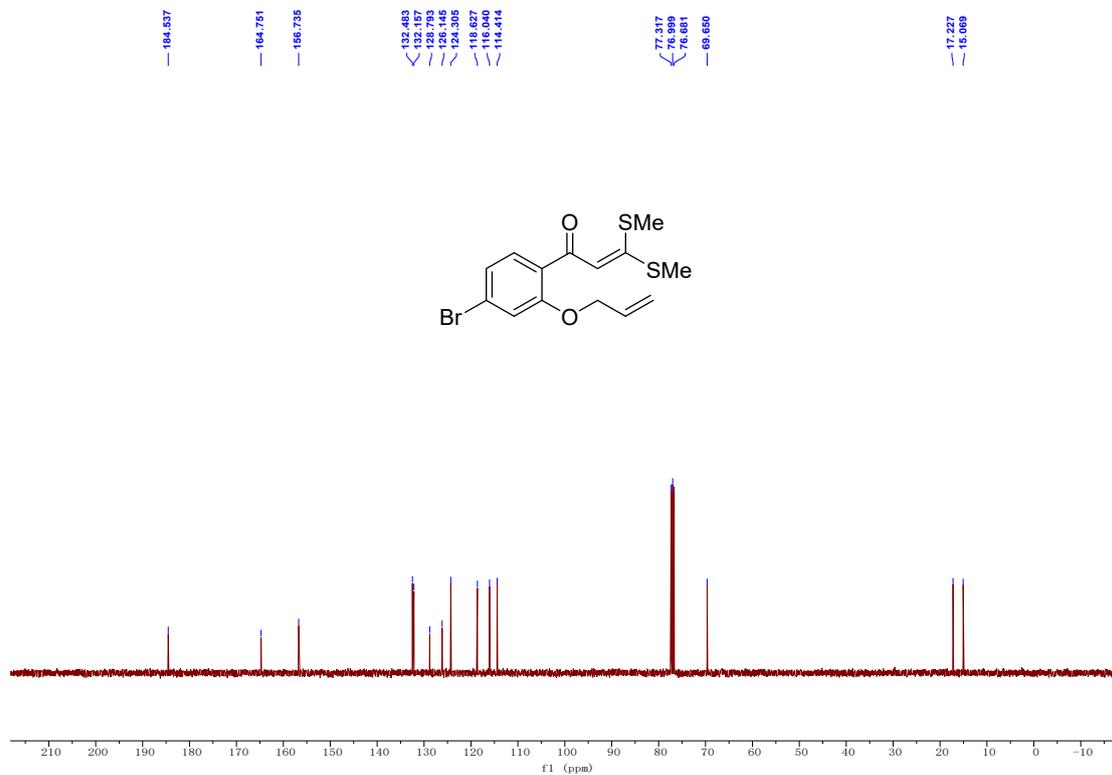
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 4h



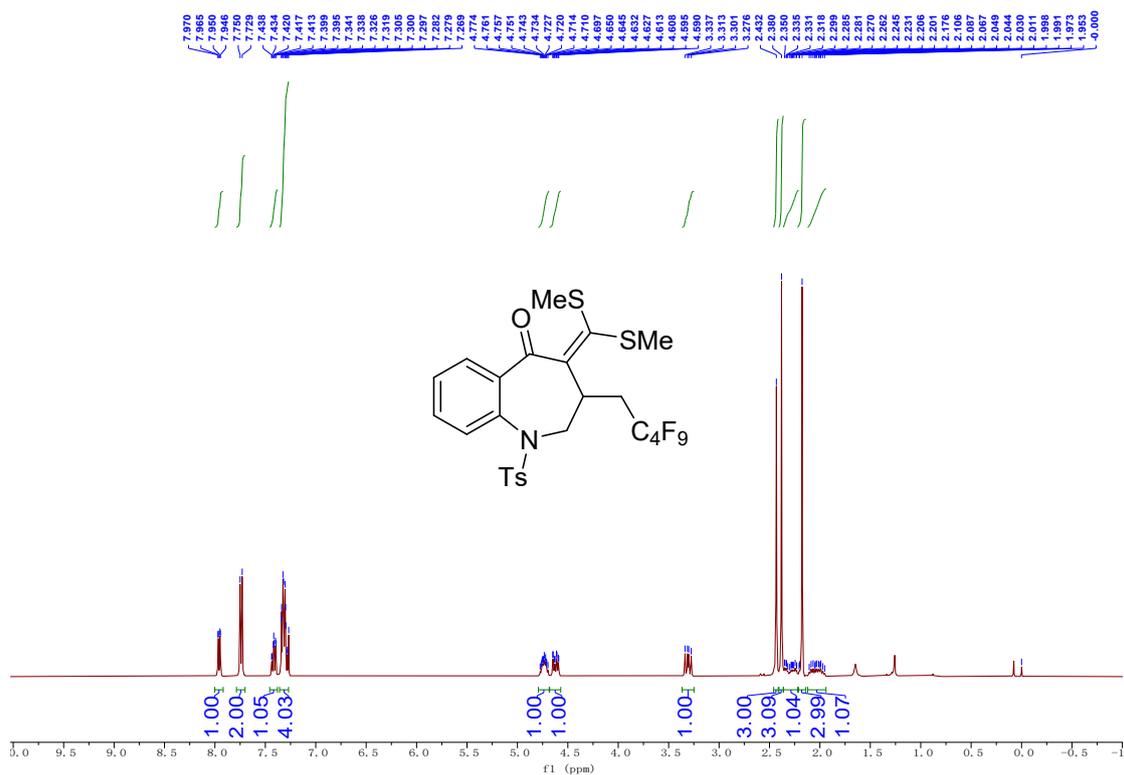
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 4i



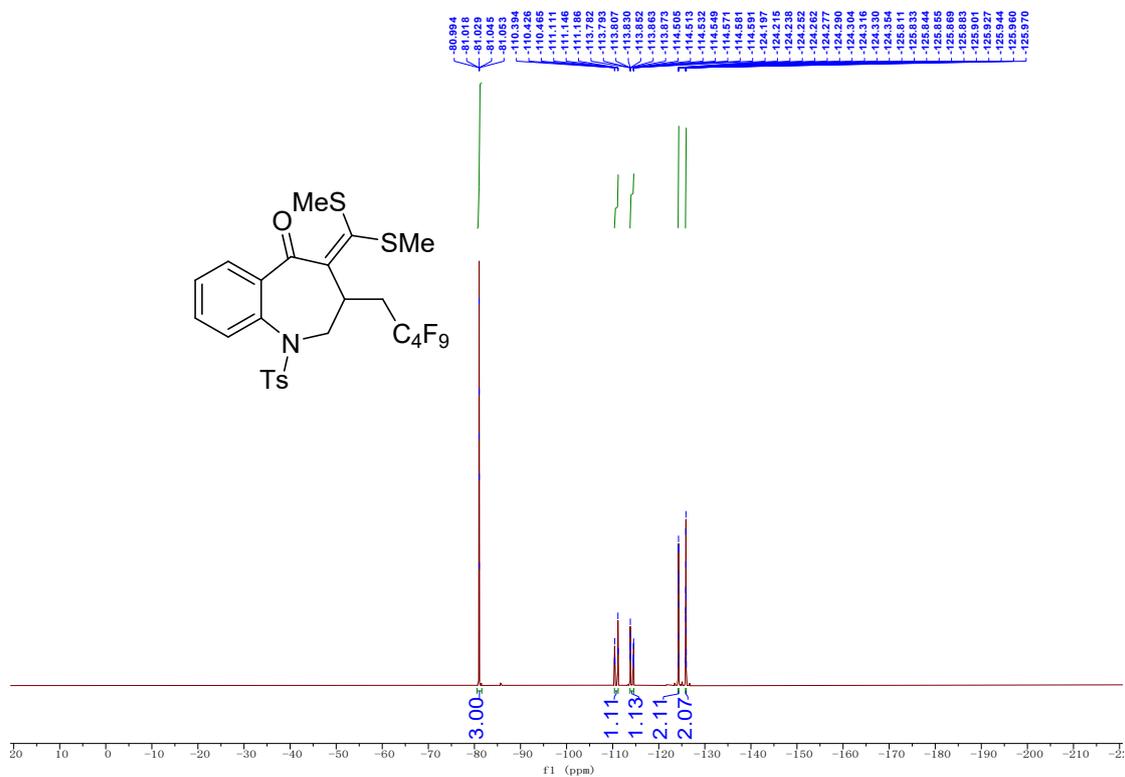
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 4i



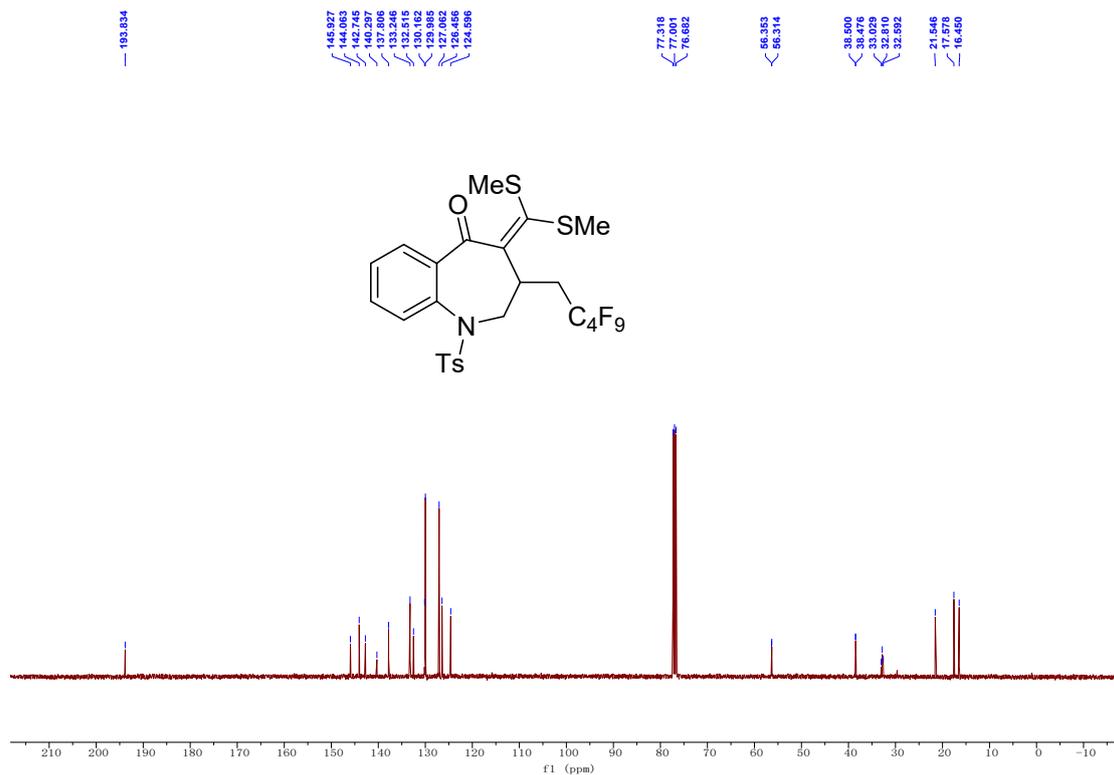
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 3a



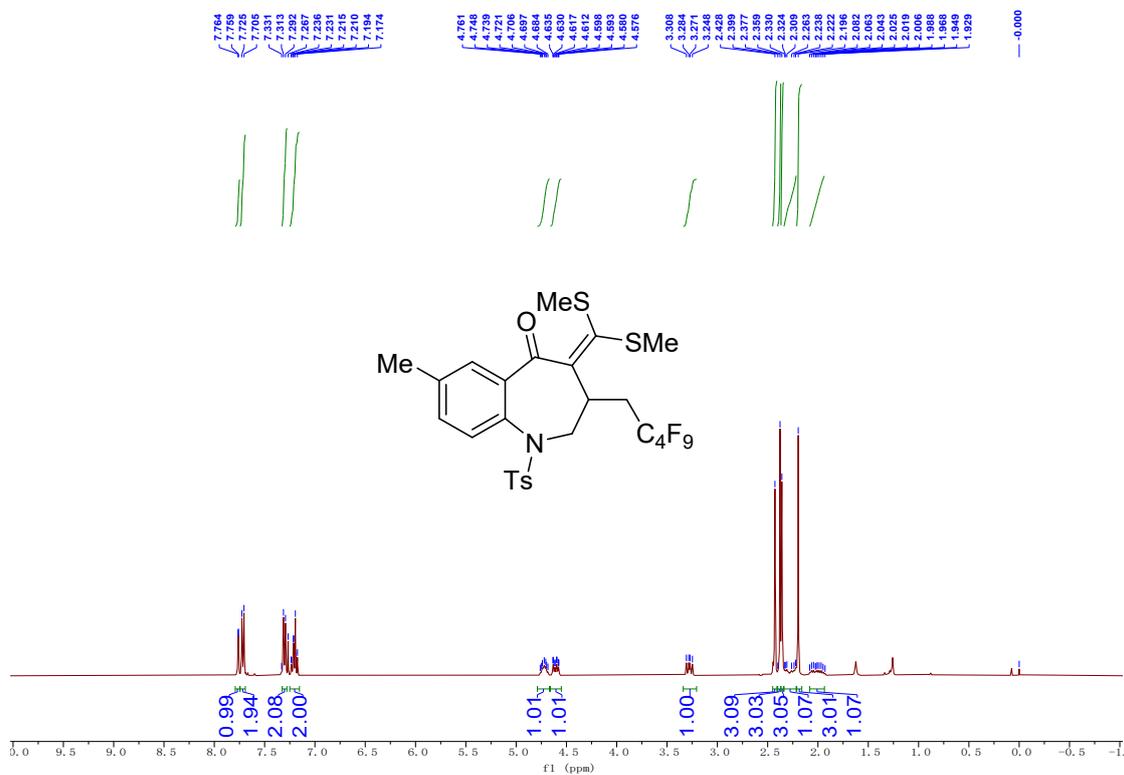
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3a**



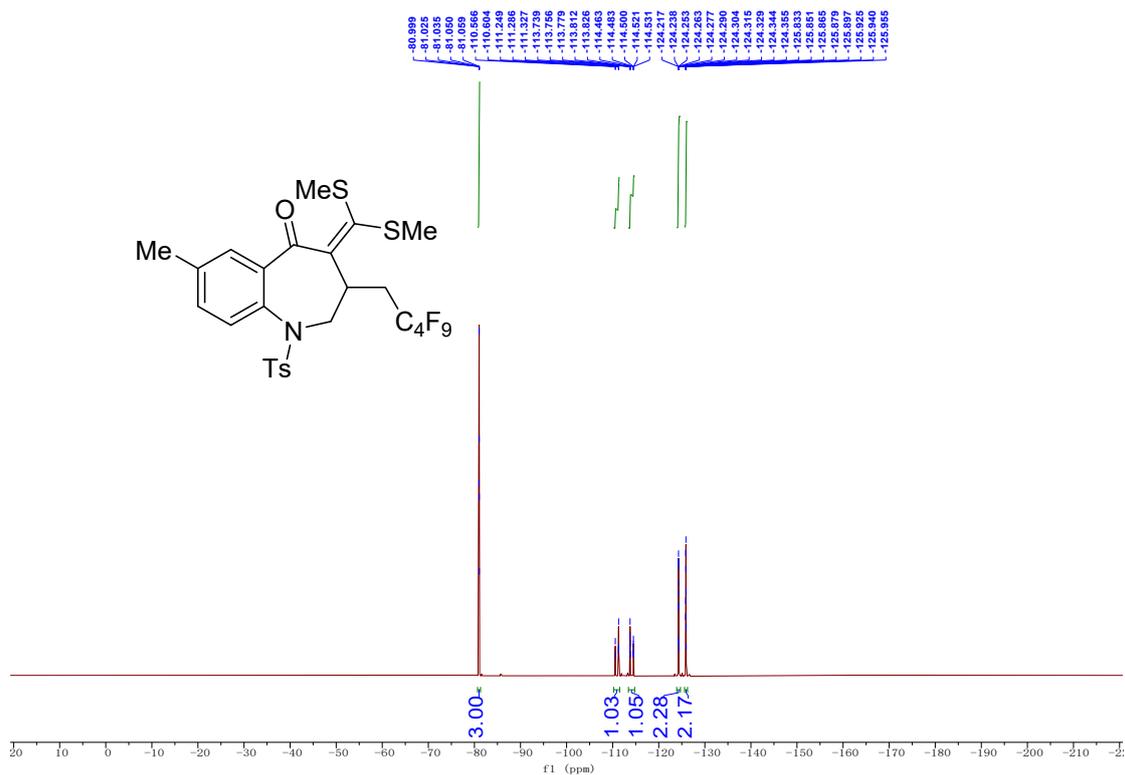
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3a**



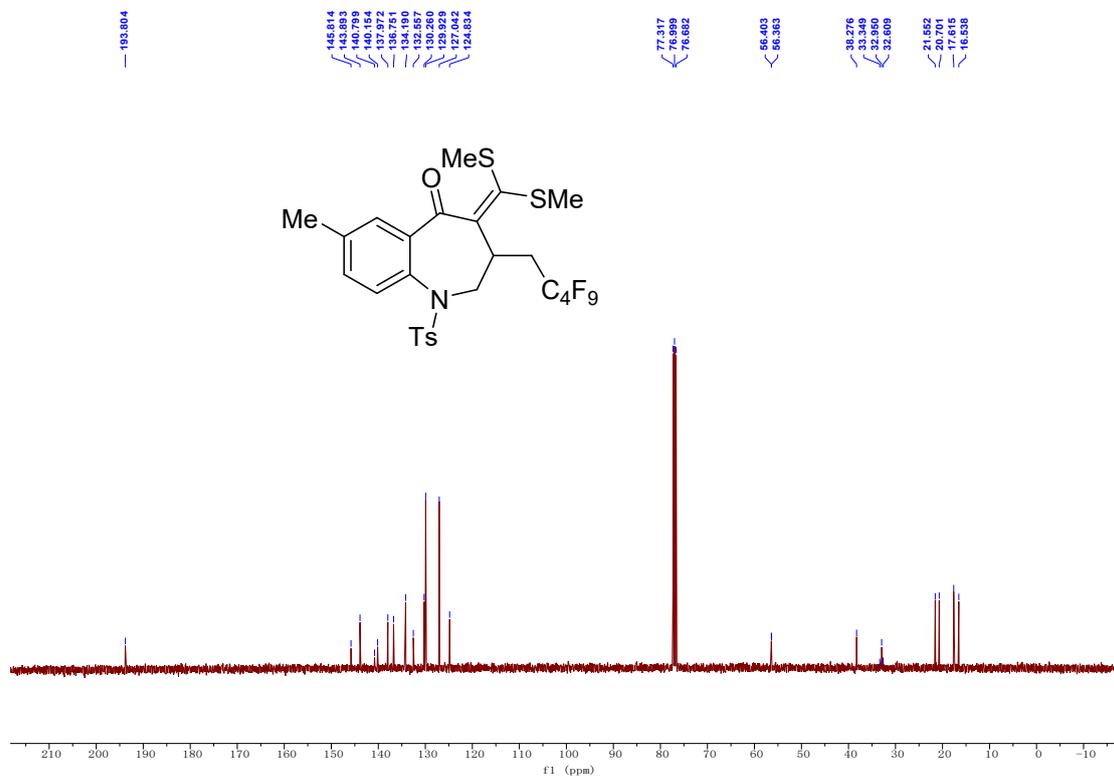
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3b**



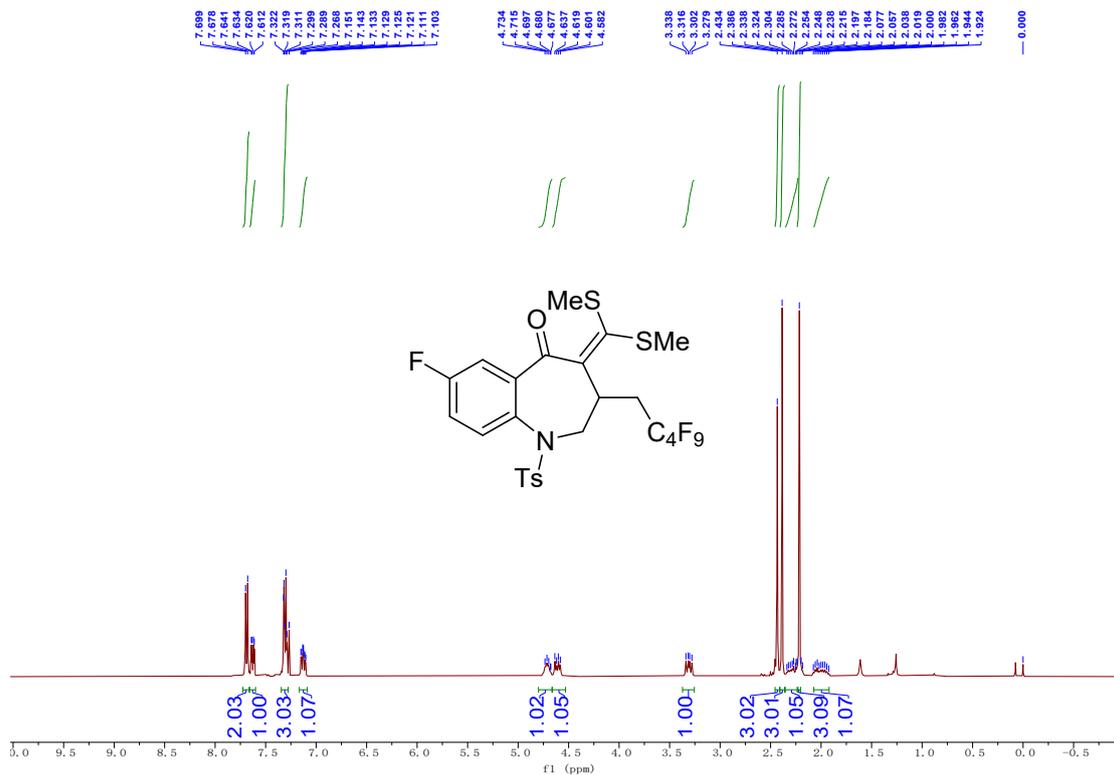
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3b**



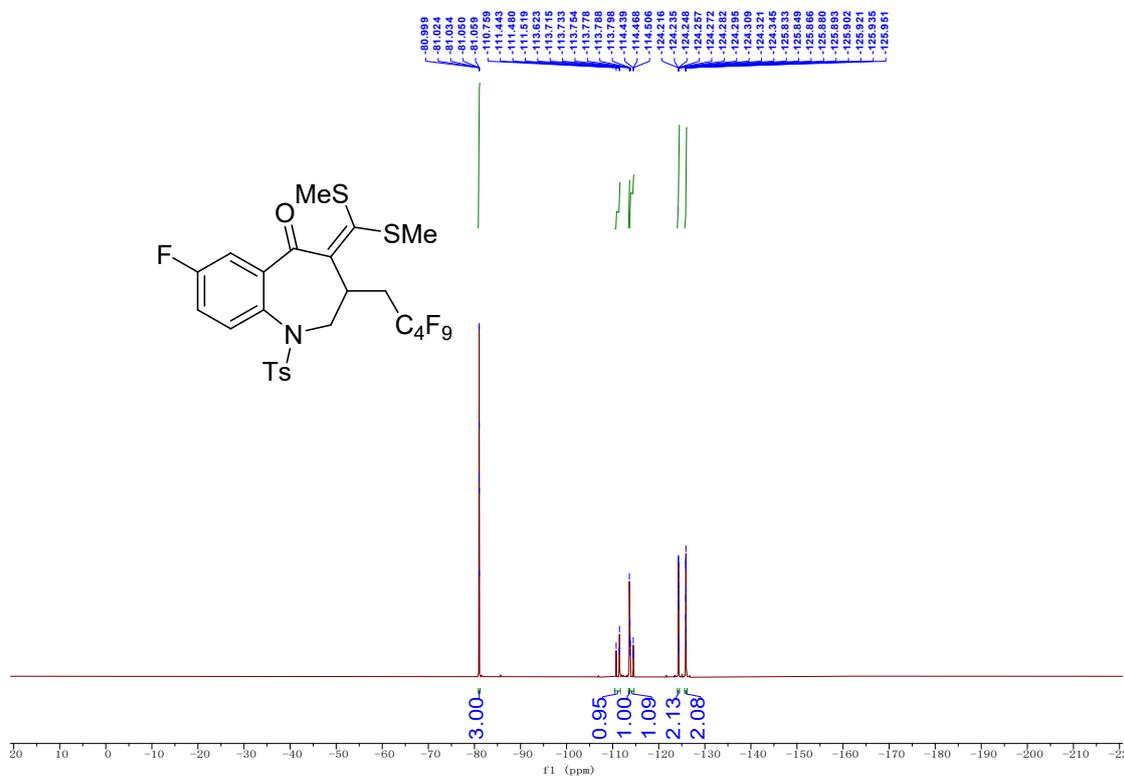
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3b**



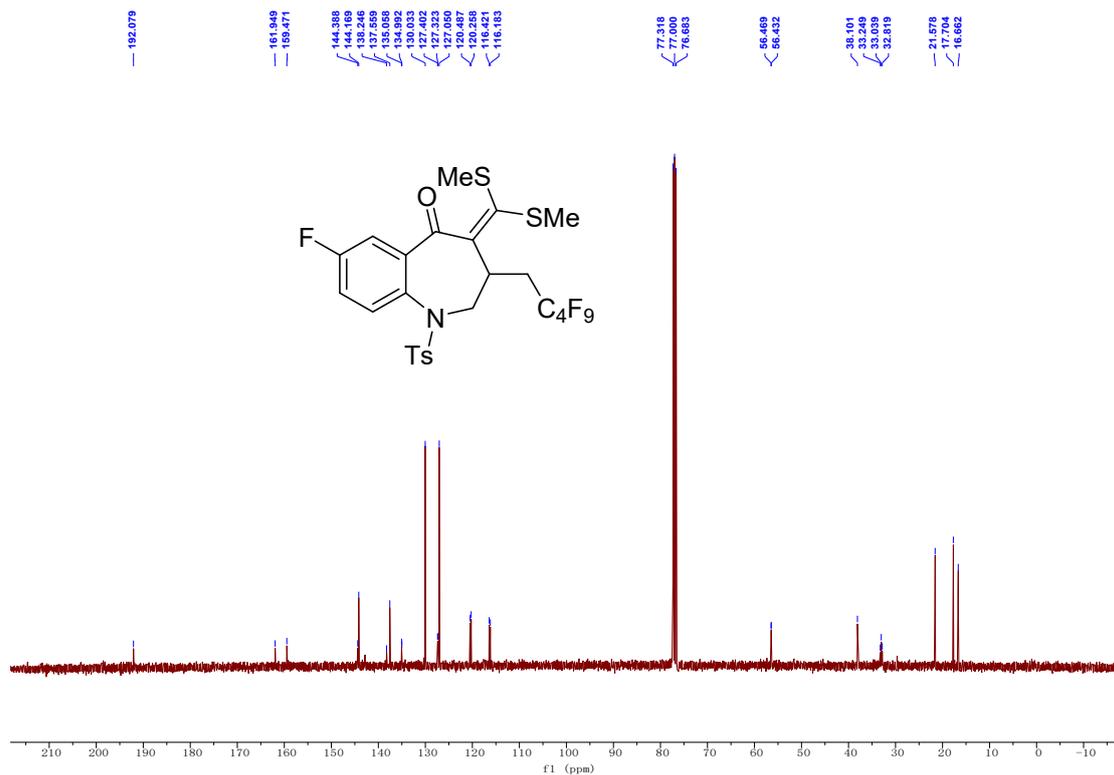
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3c**



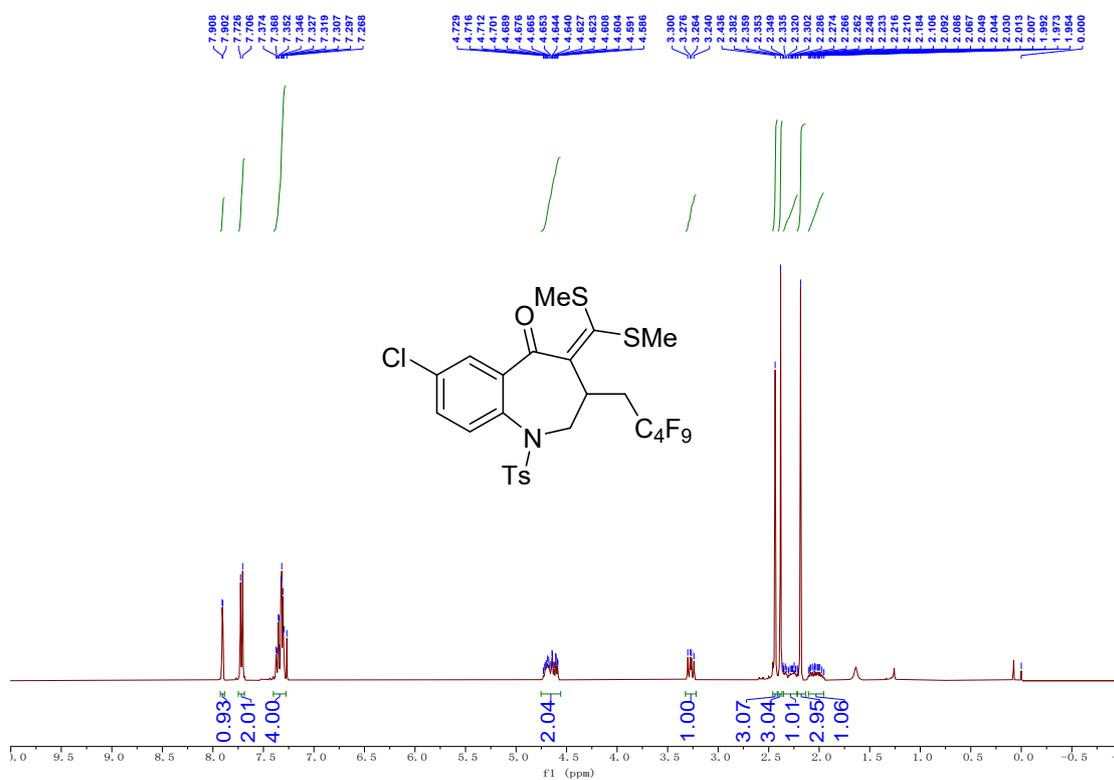
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 3c



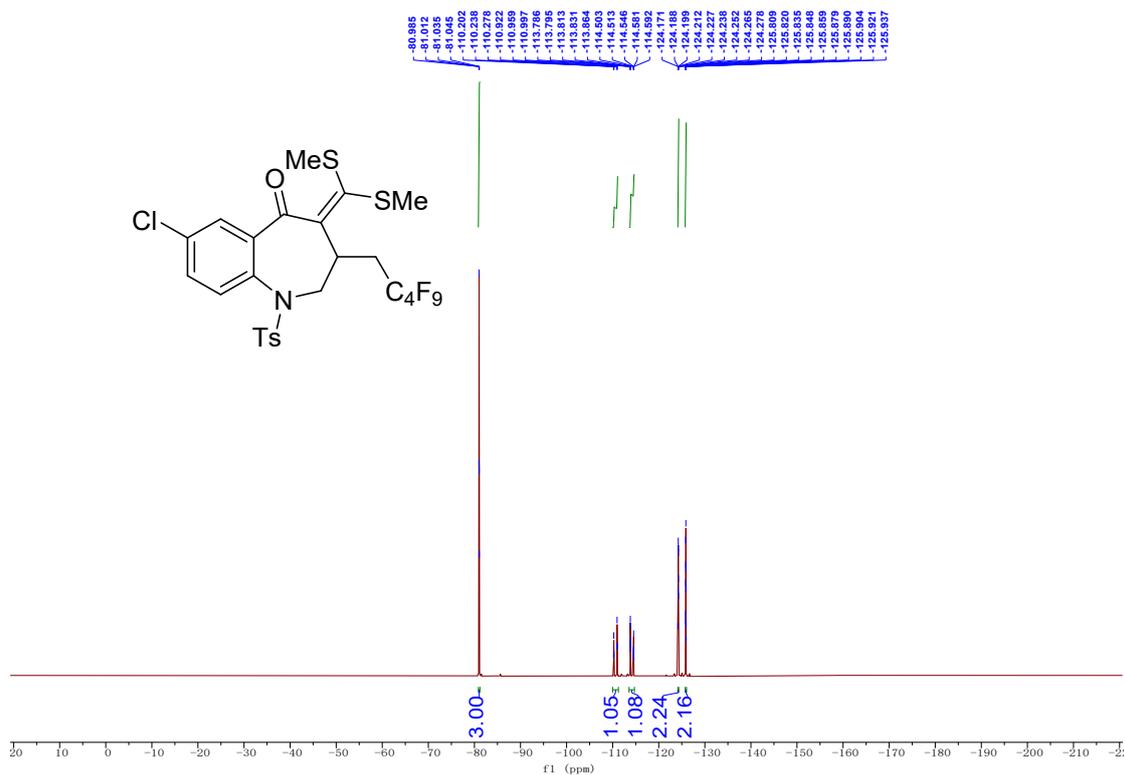
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 3c



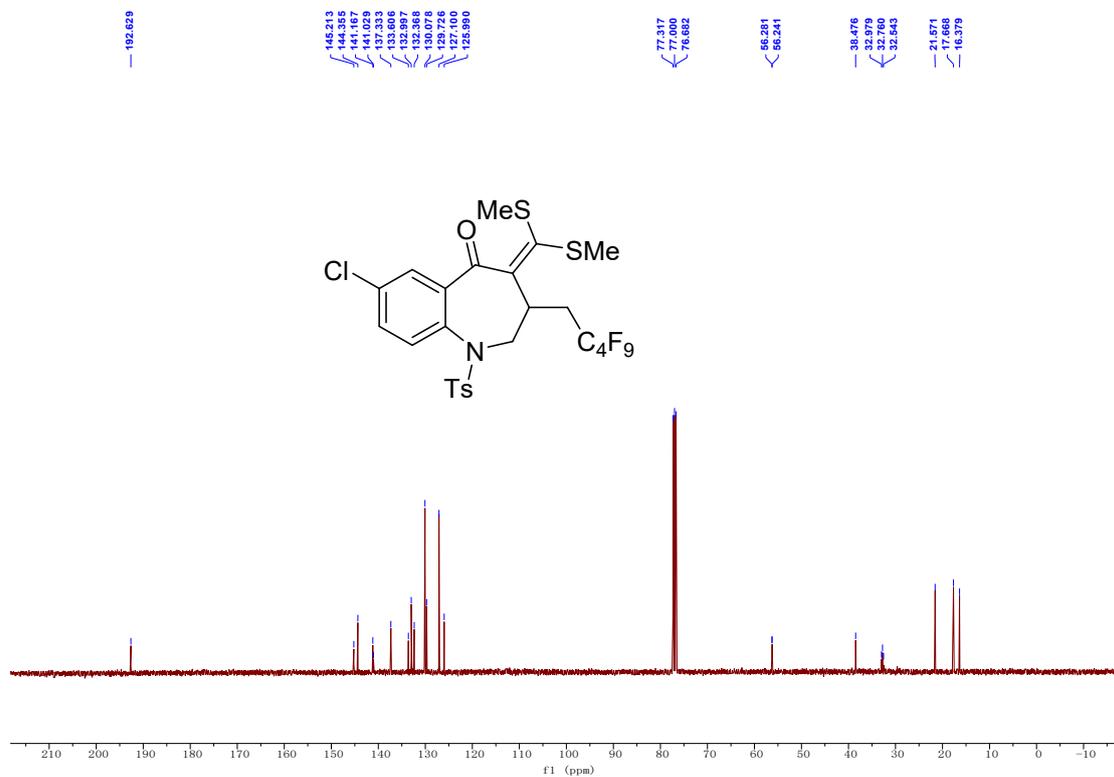
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3d**



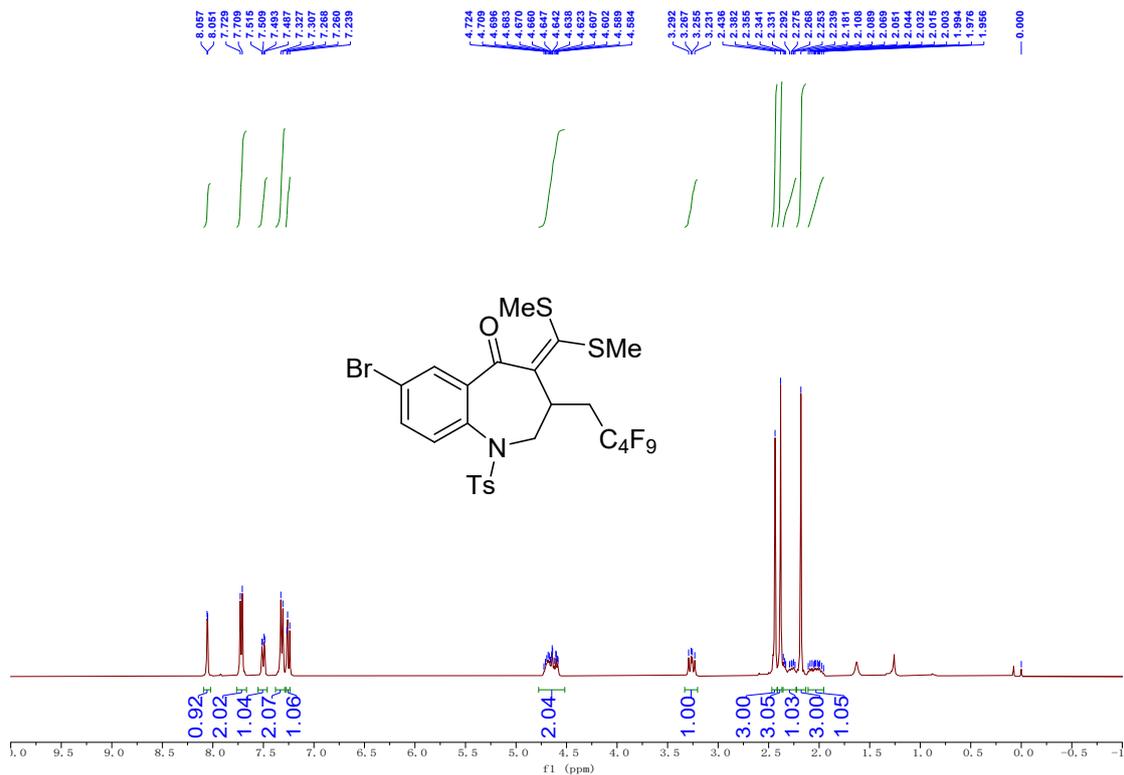
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3d**



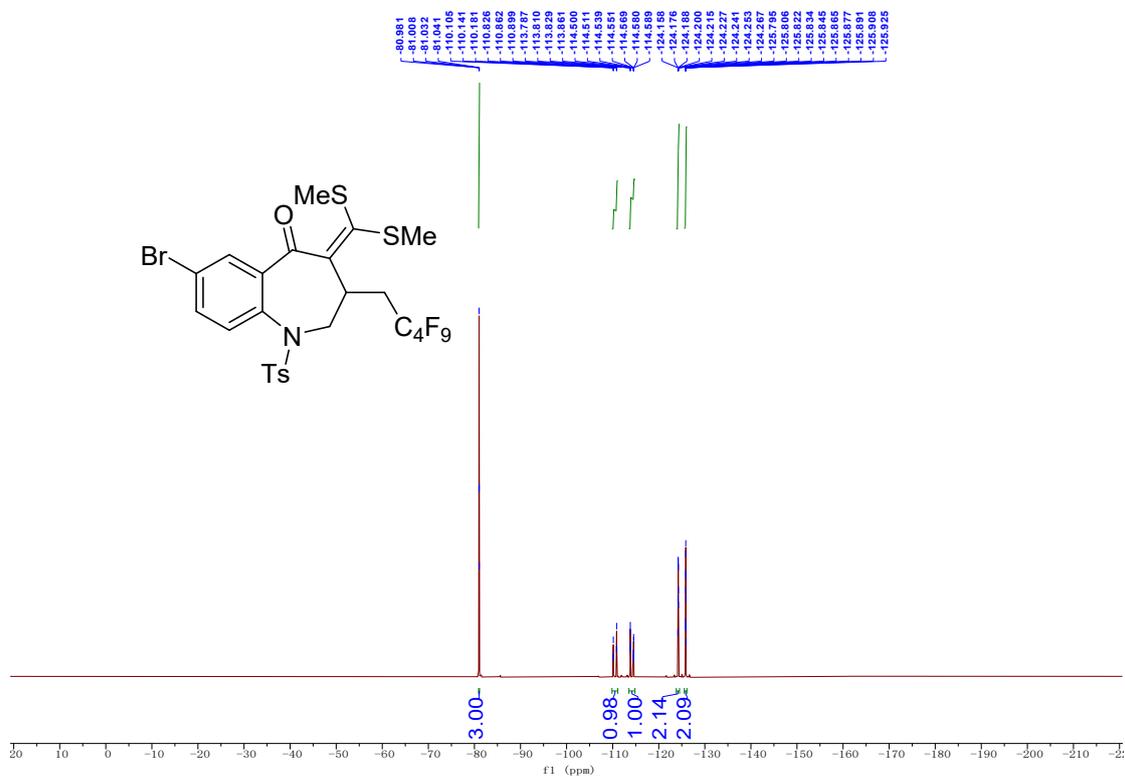
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3d**



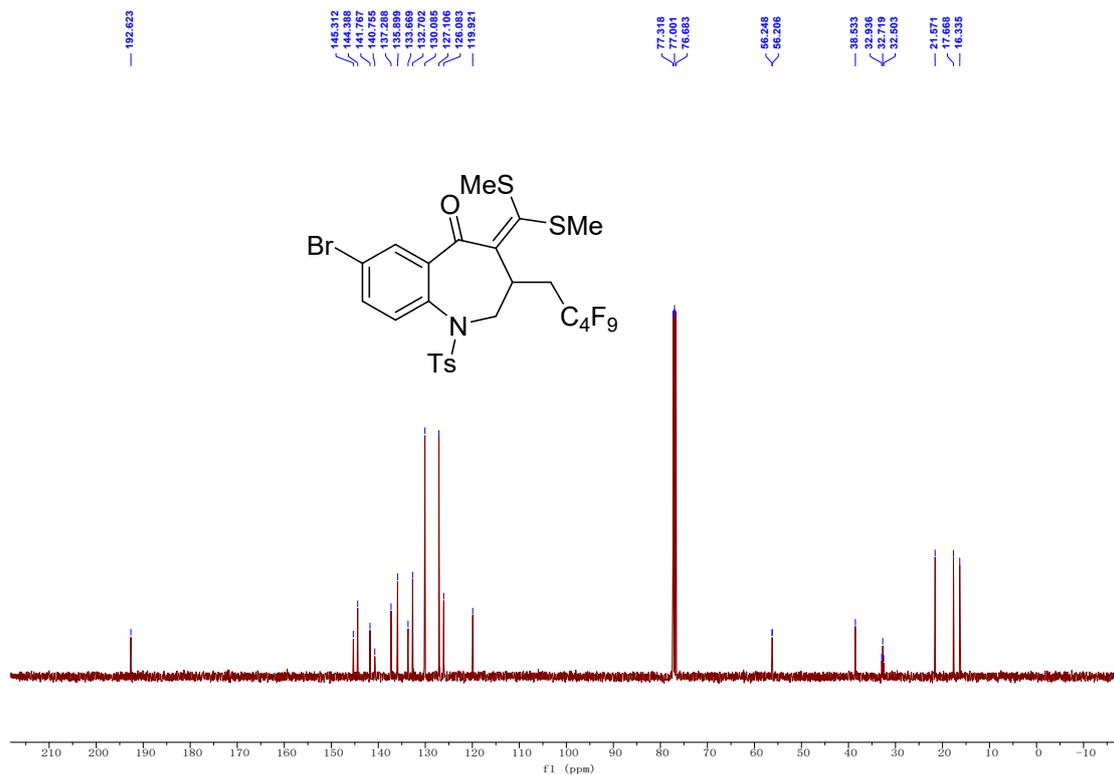
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3e**



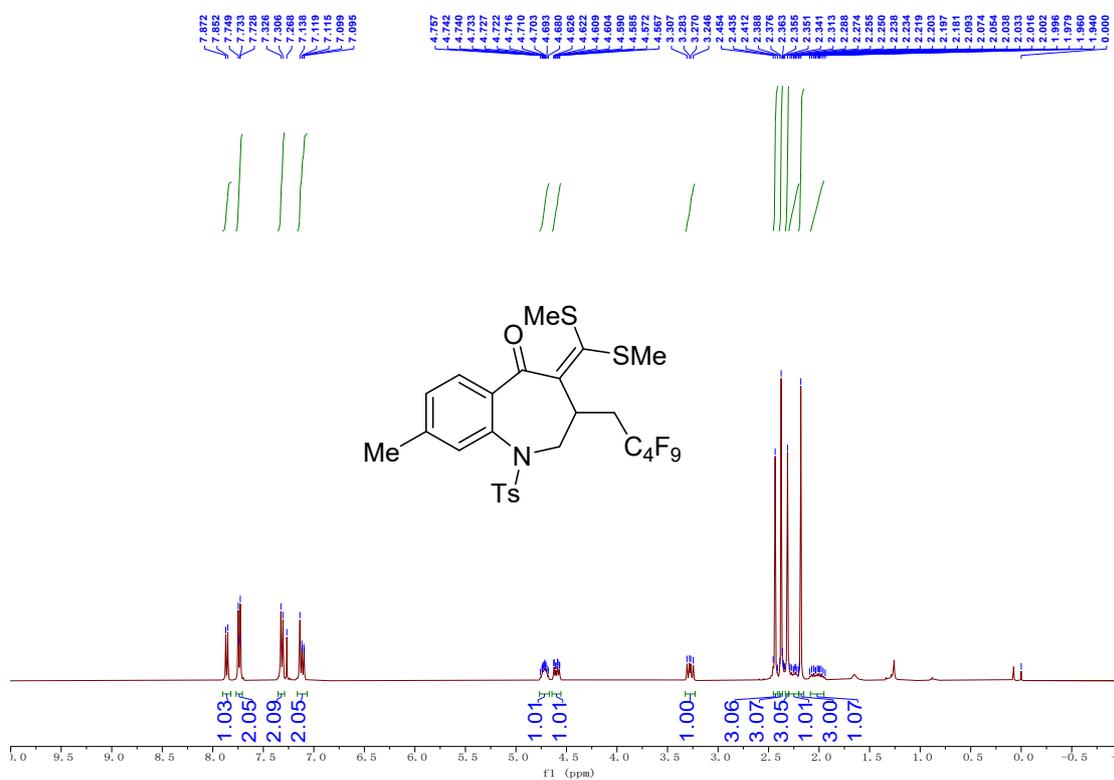
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 3e



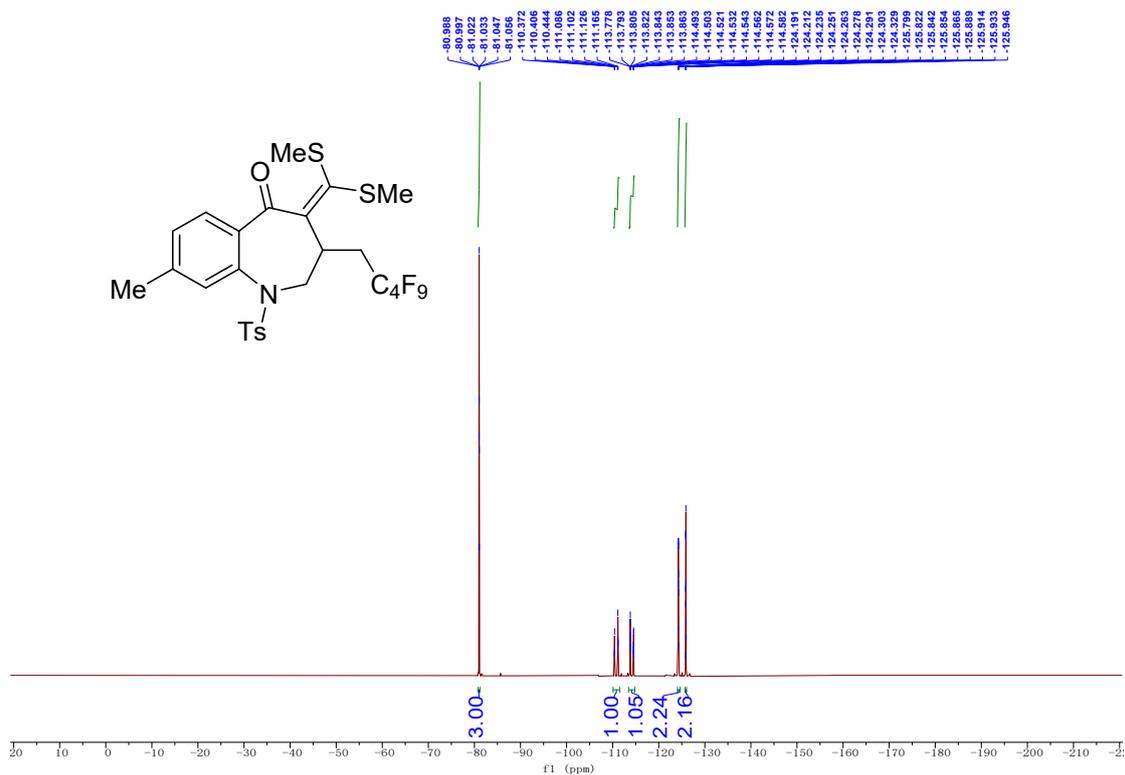
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 3e

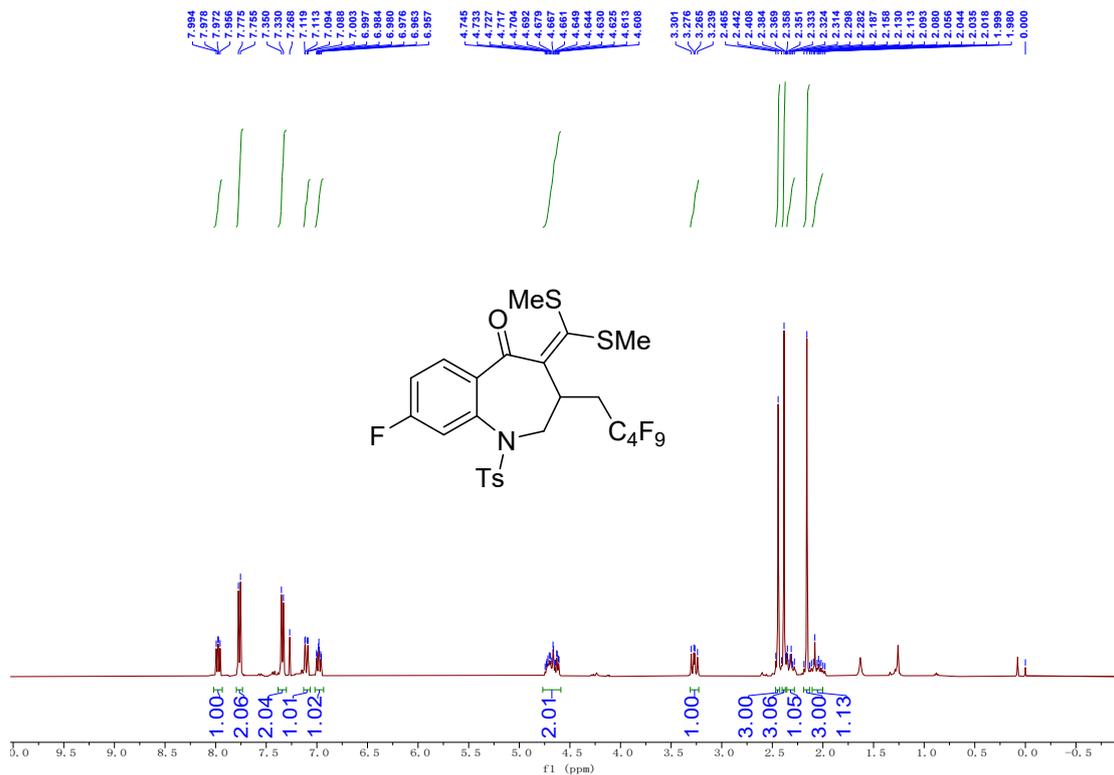


¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3f**

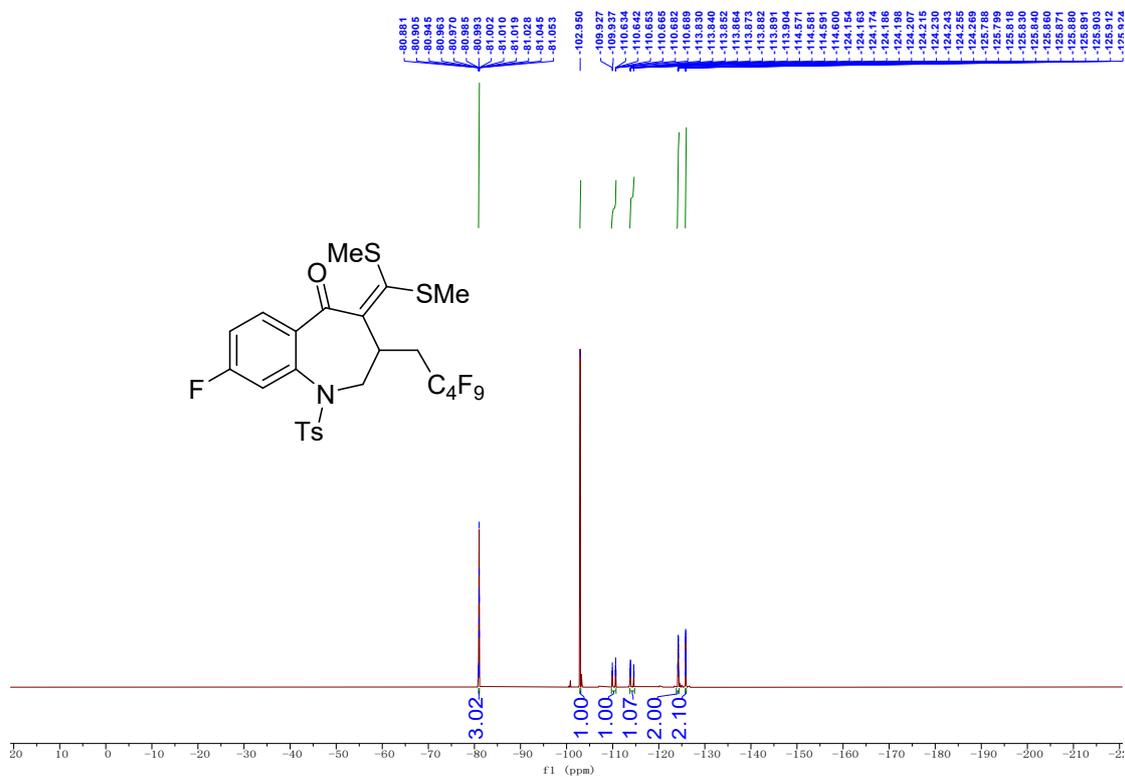


¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3f**

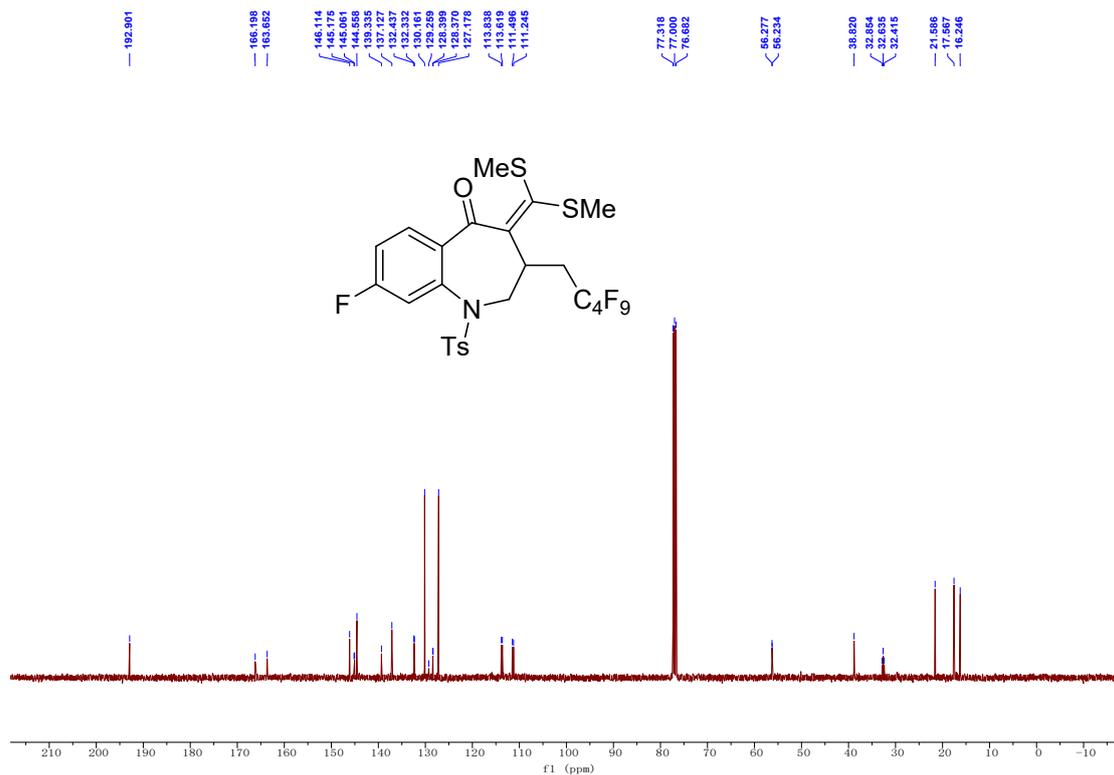




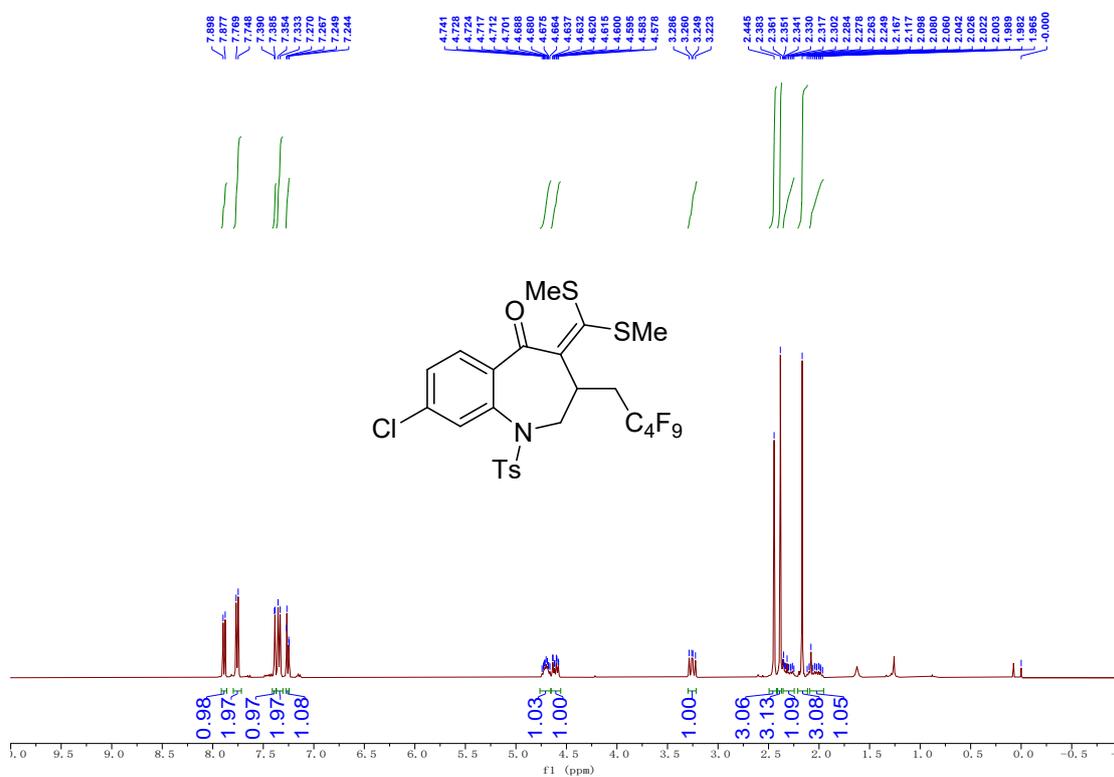
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3g**



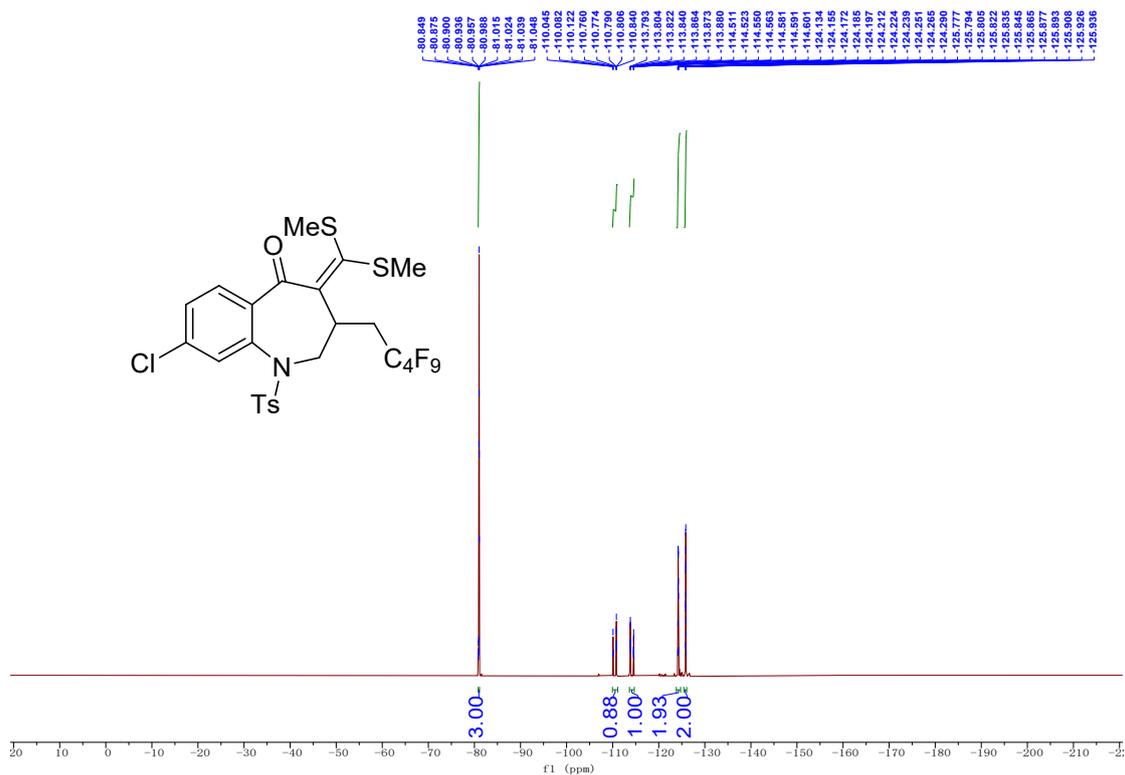
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3g**



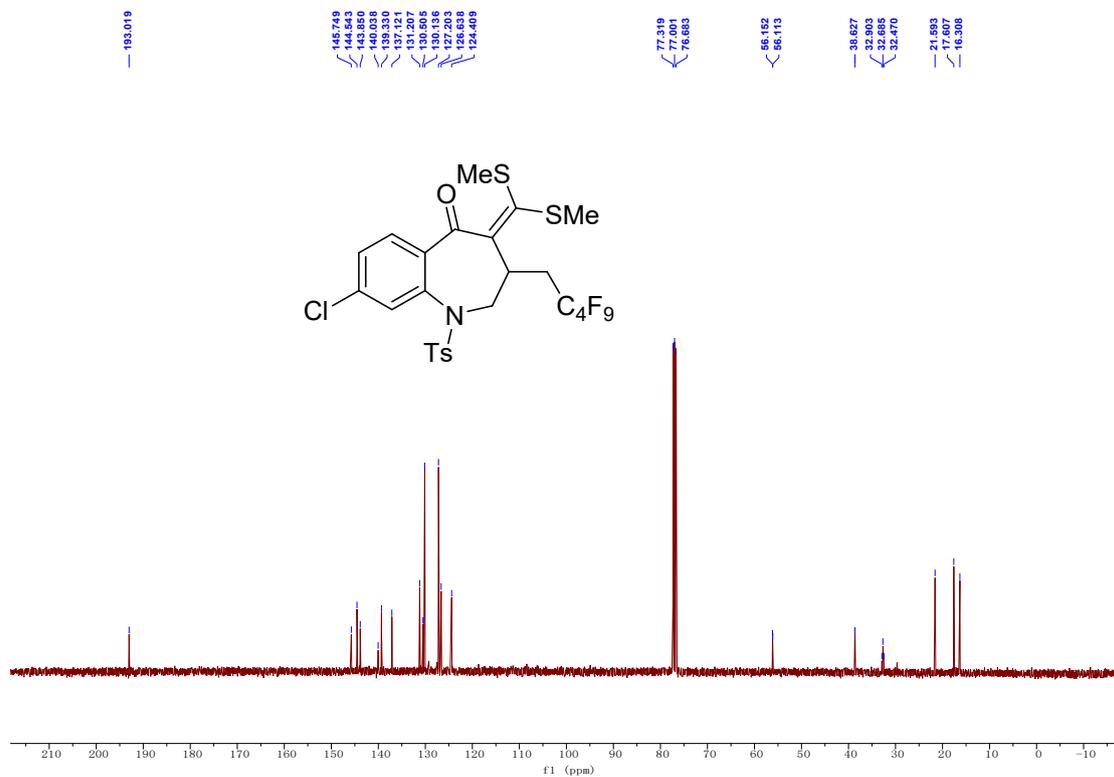
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3h**



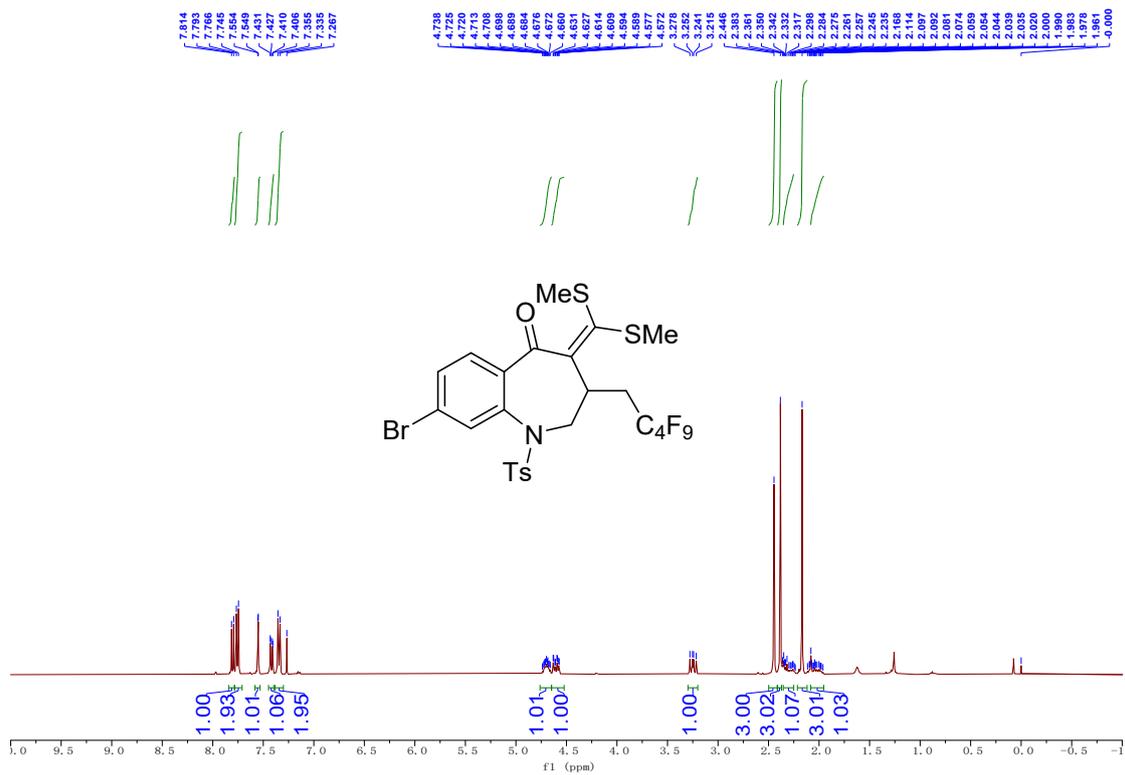
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3h**



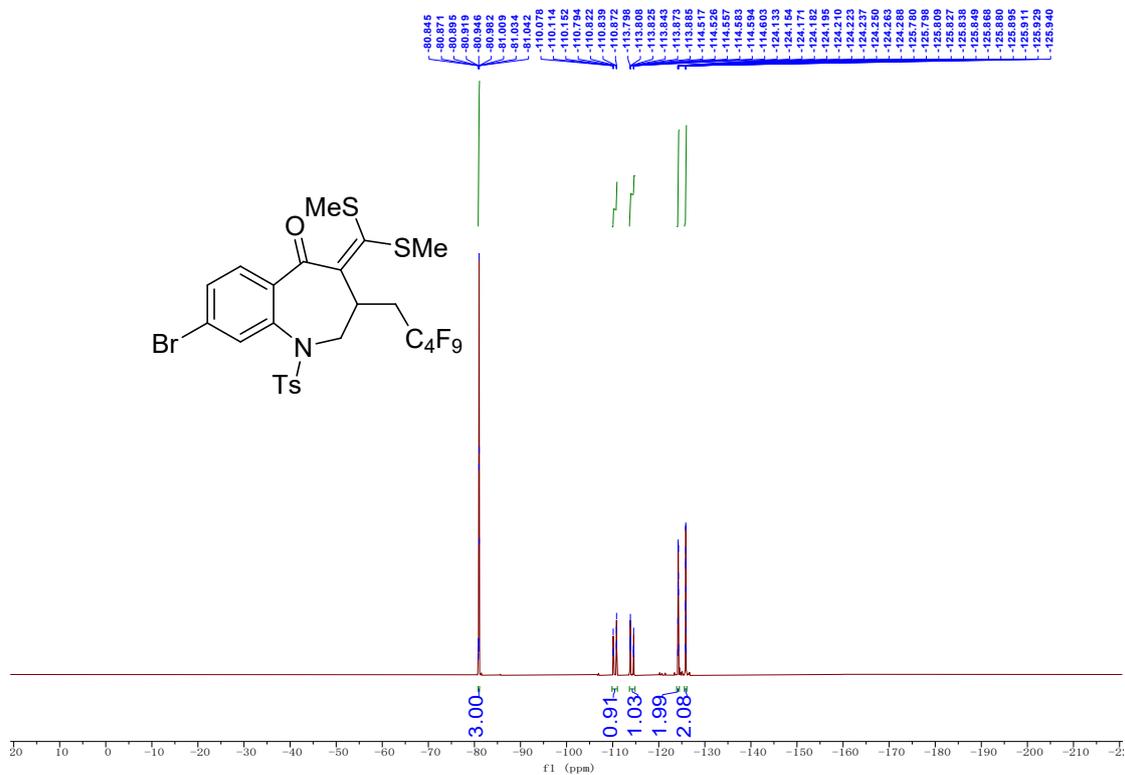
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3h**



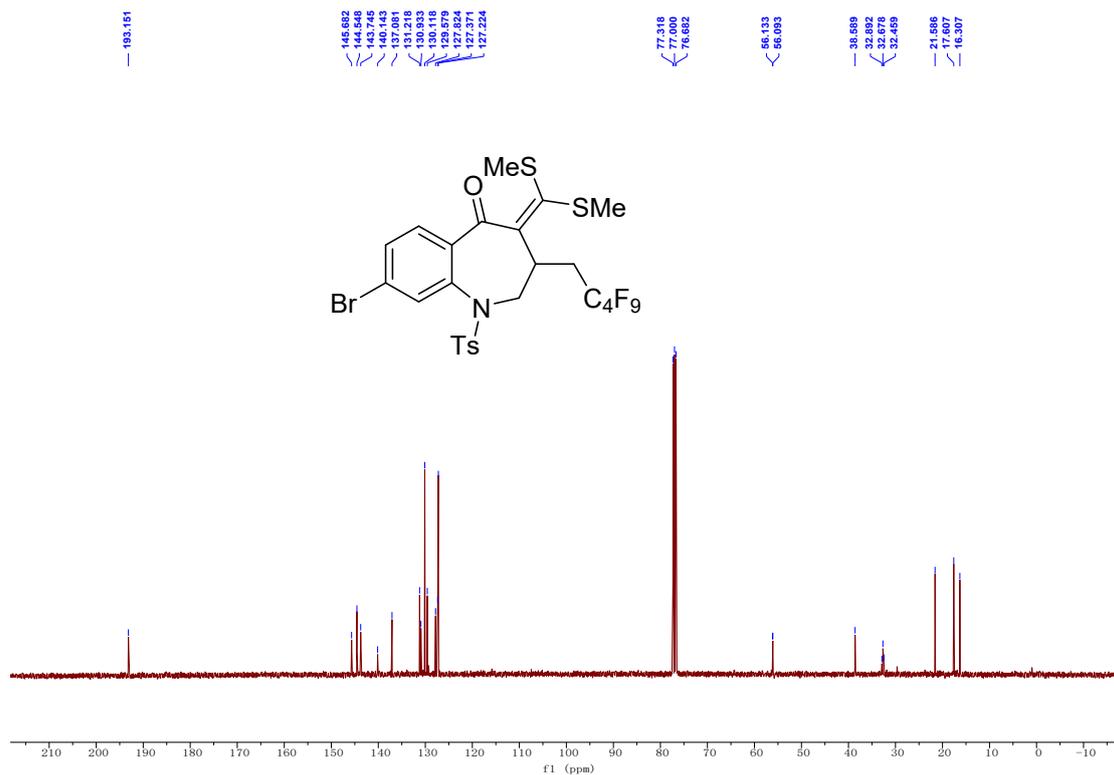
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3i**



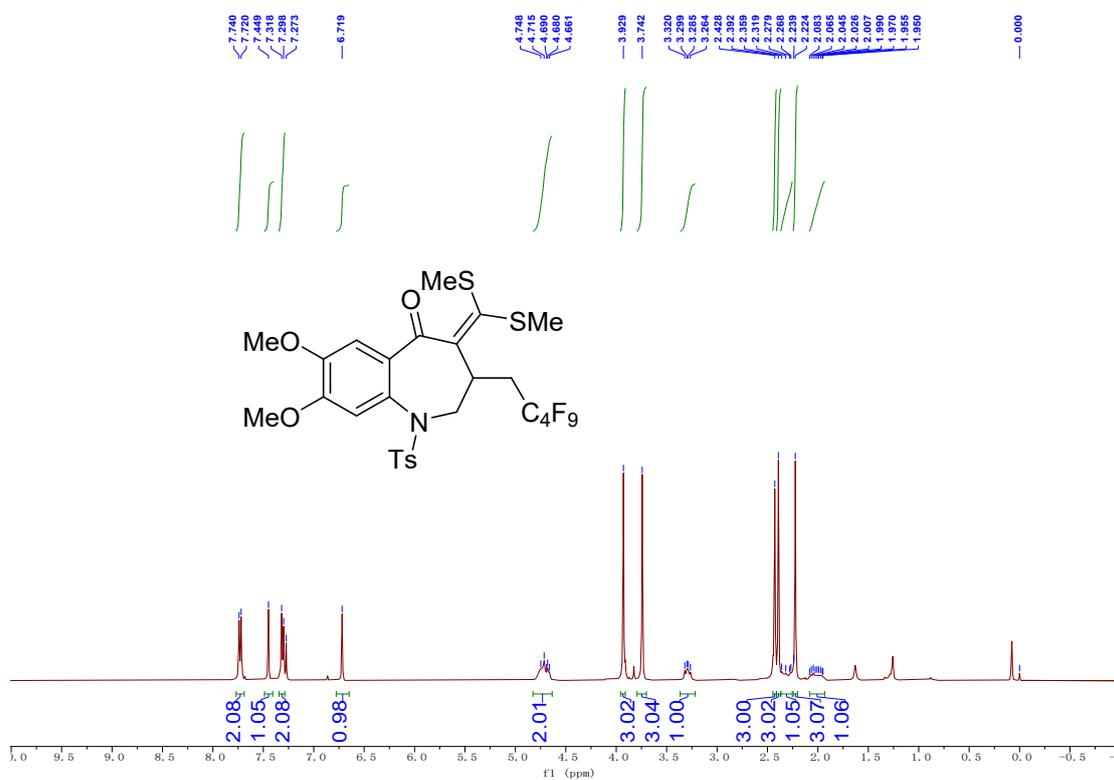
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3i**



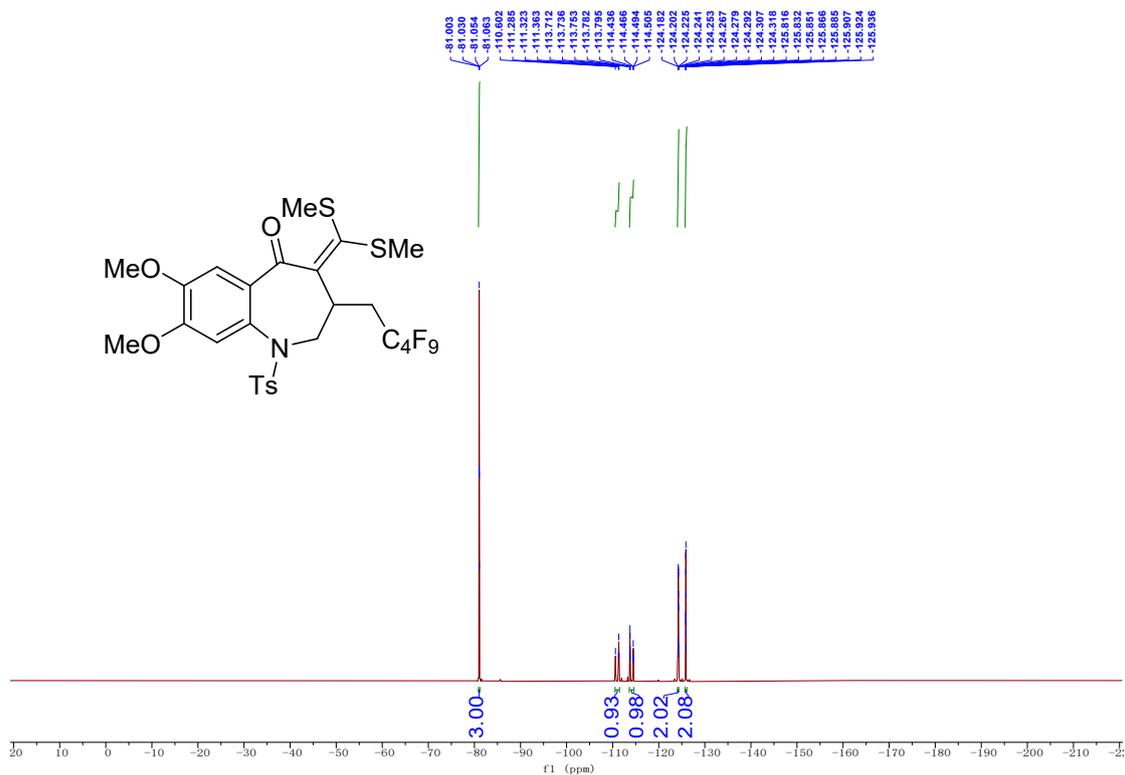
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3i**



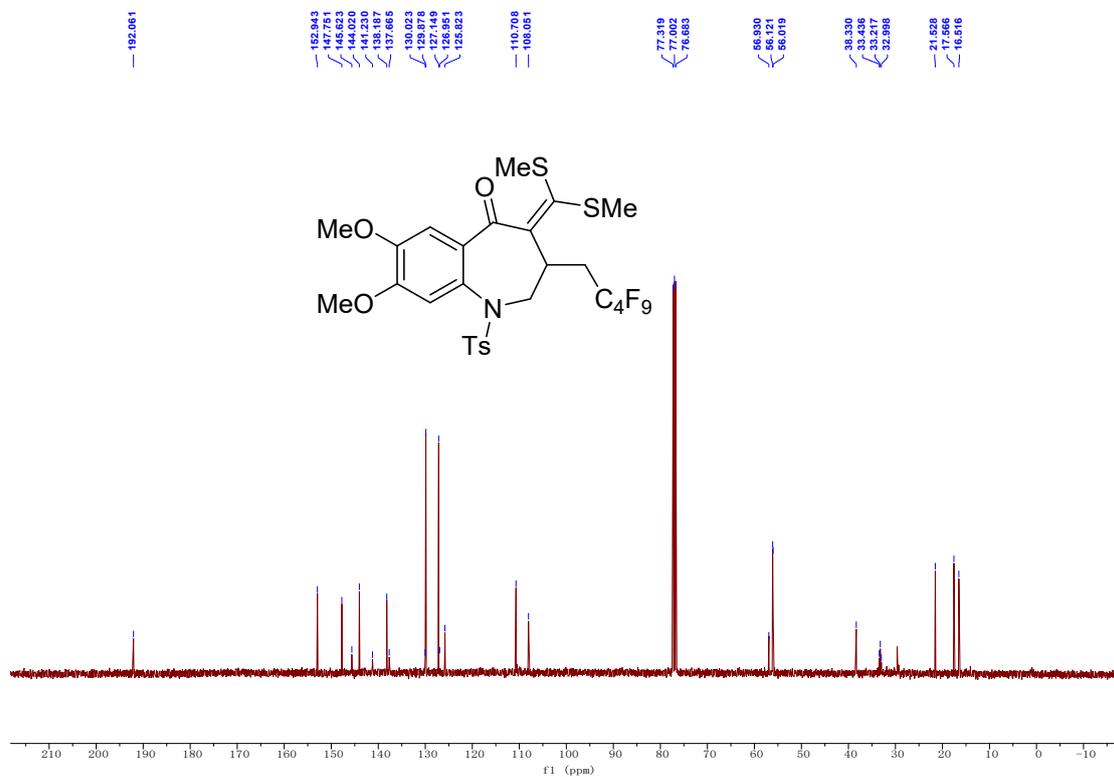
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 3j



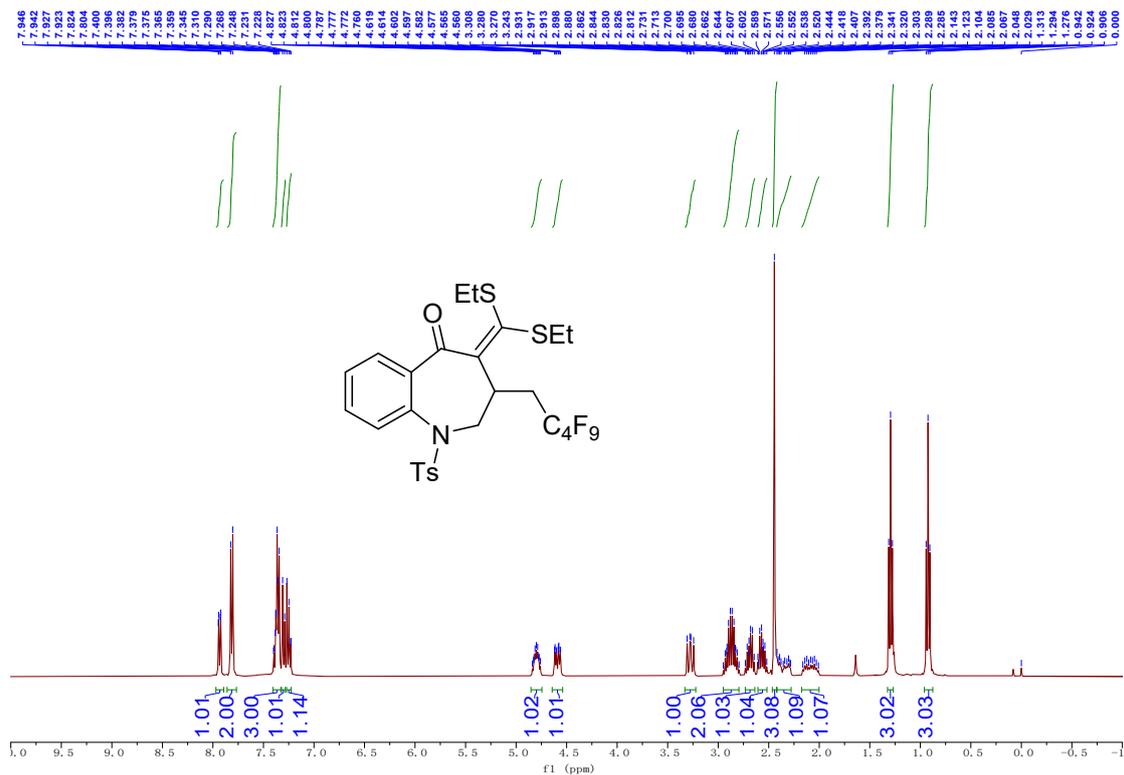
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 3j



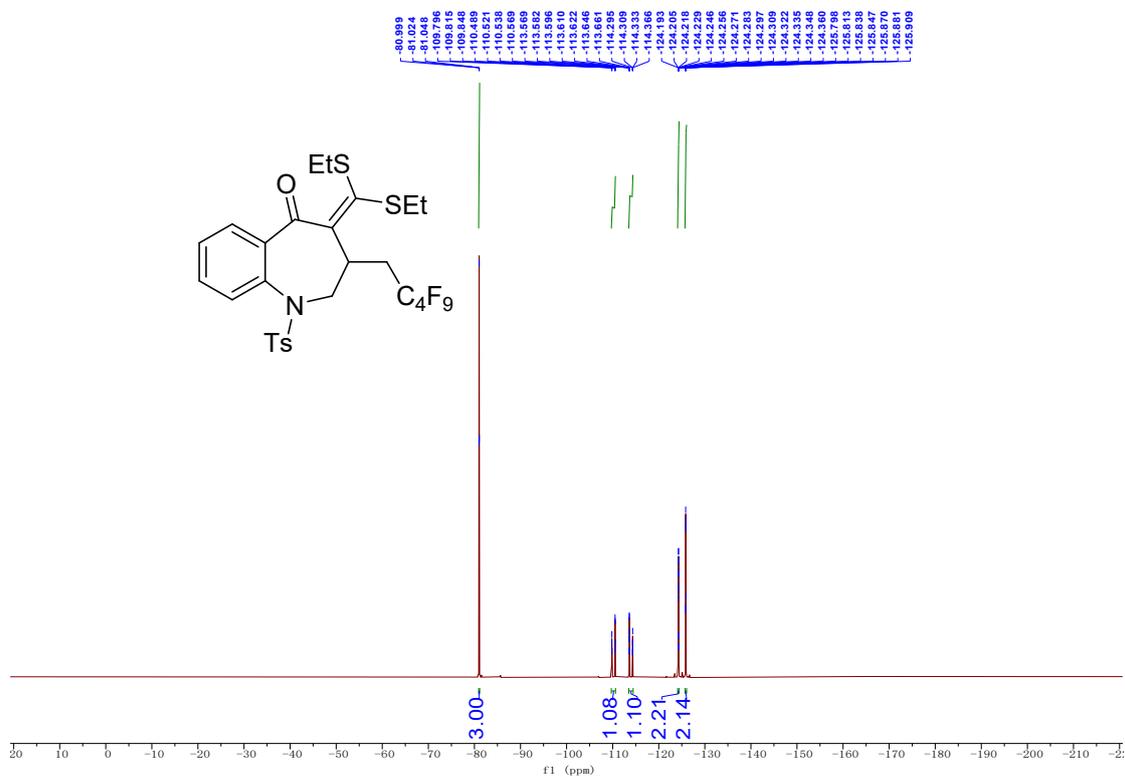
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3j**



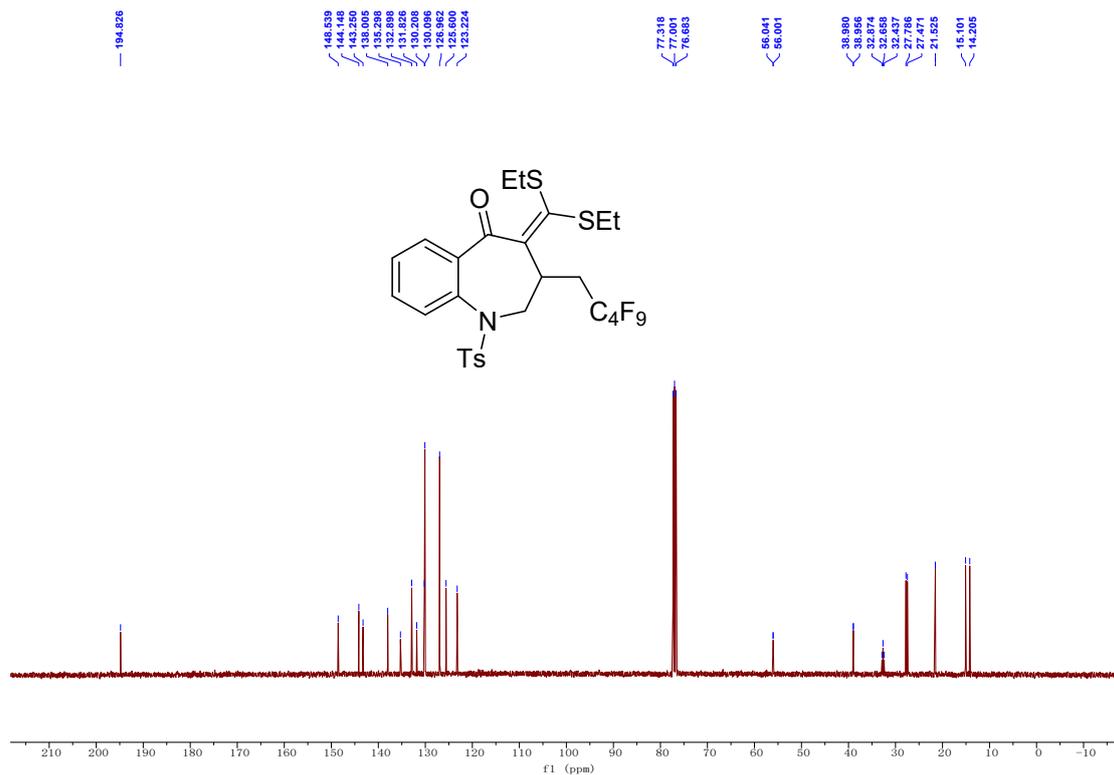
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3k**



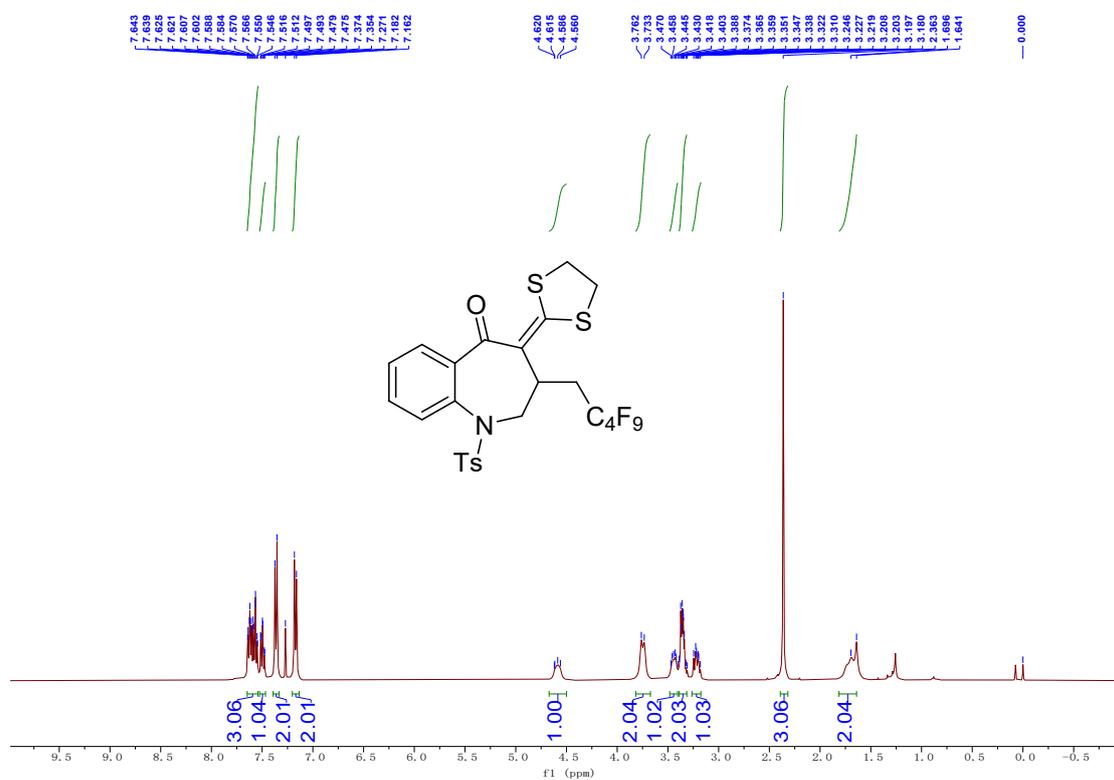
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3k**



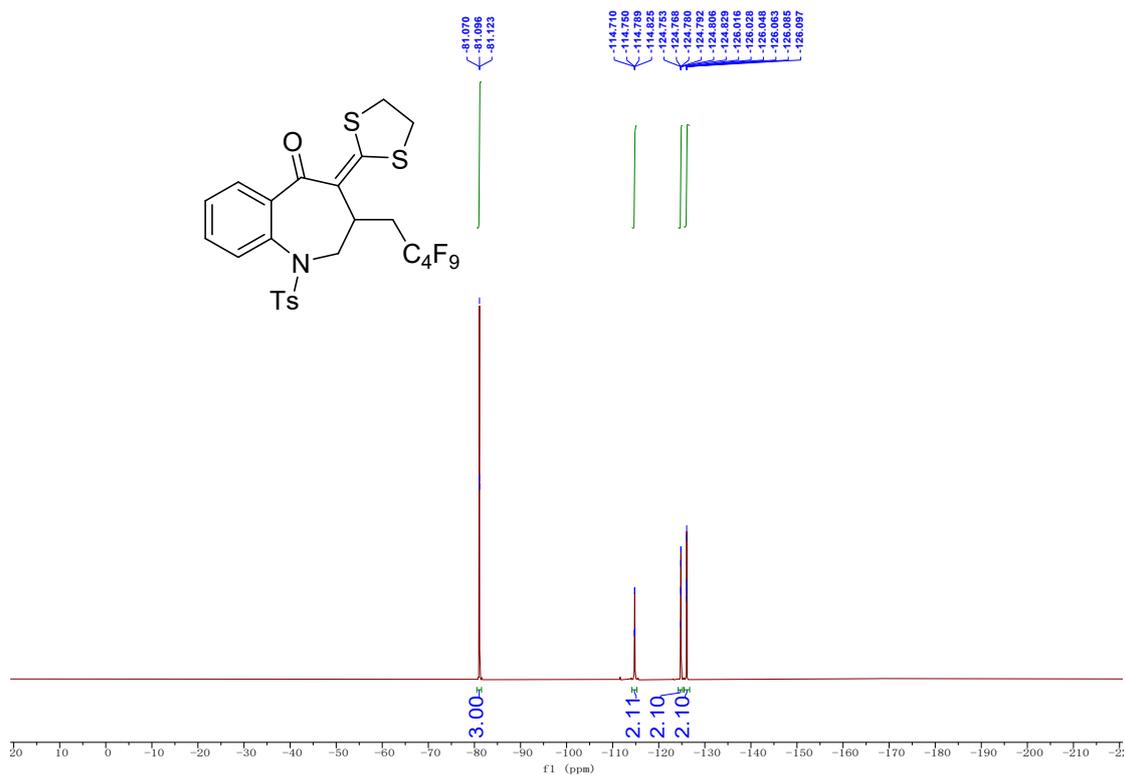
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3k**



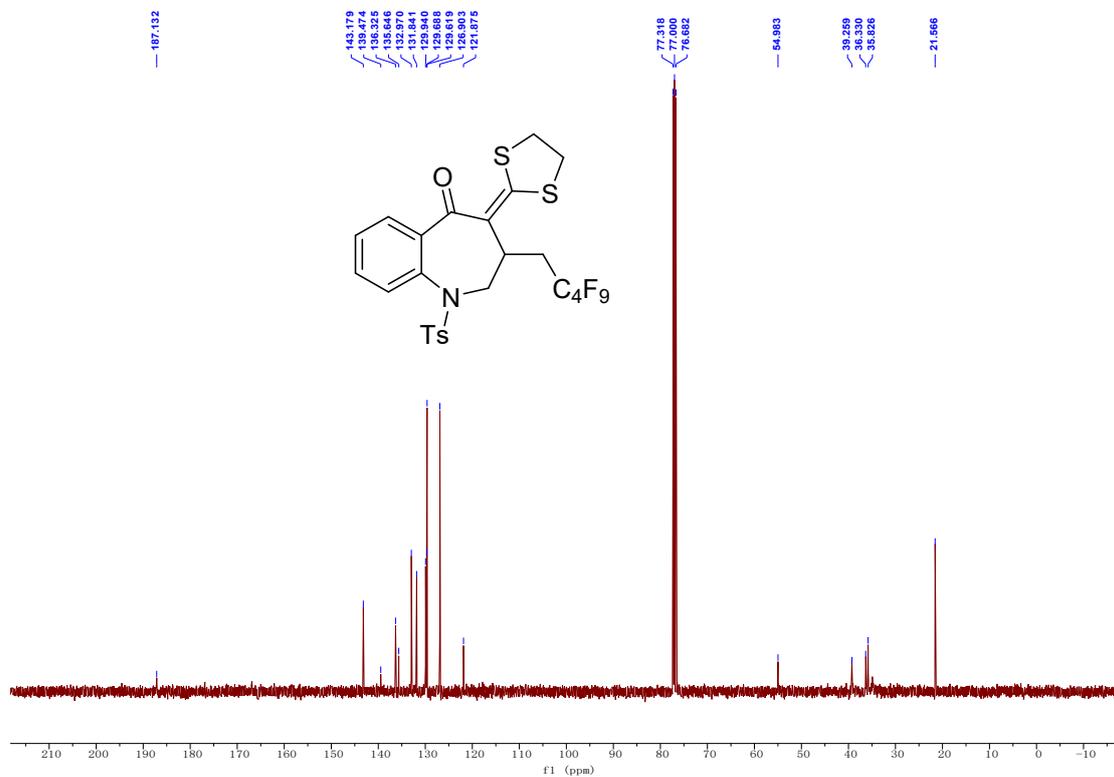
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 31



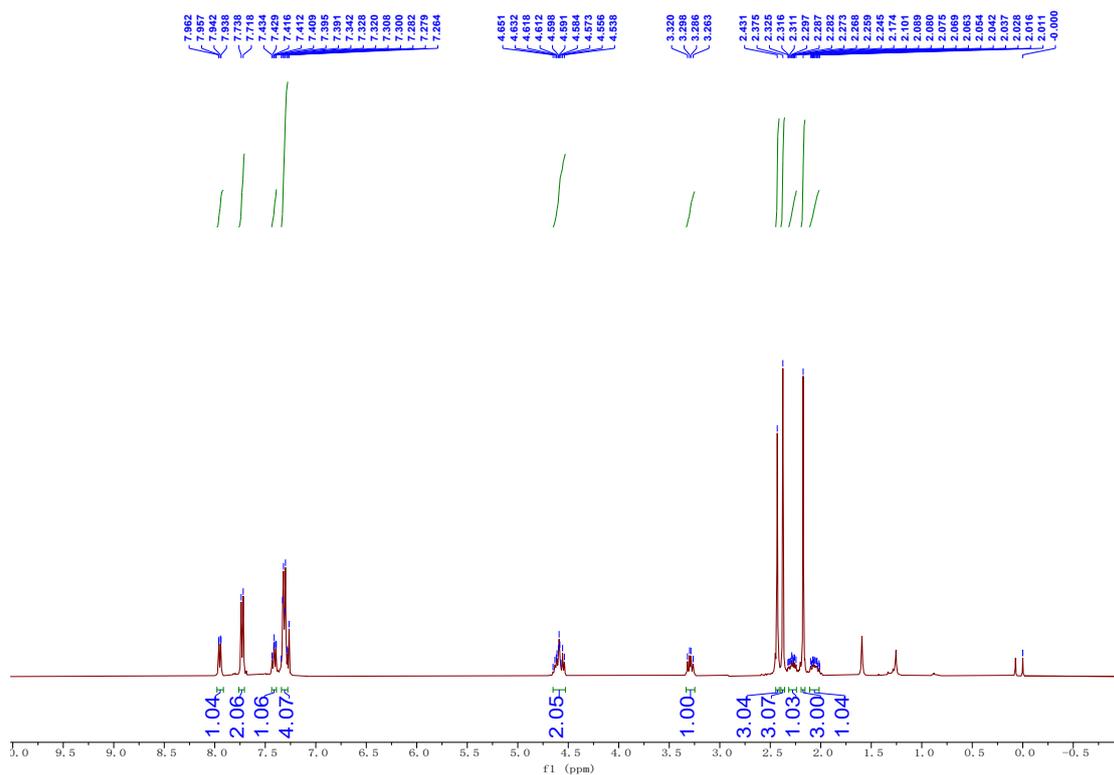
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 31



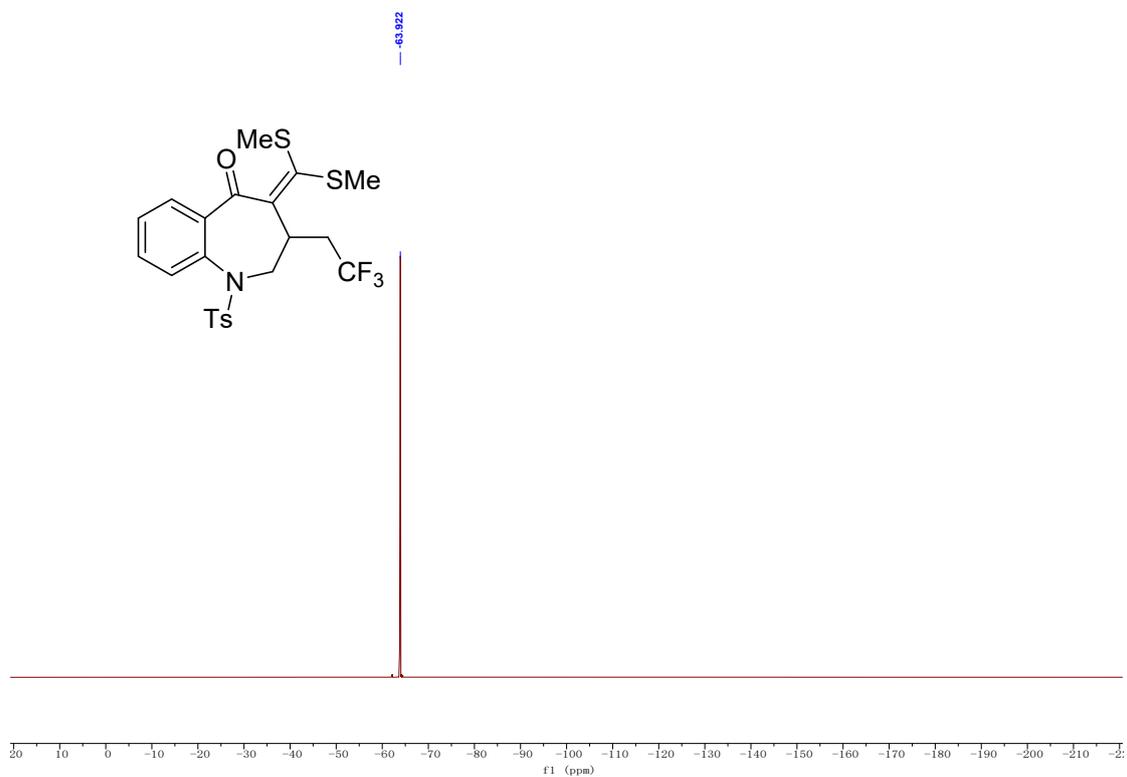
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 3l



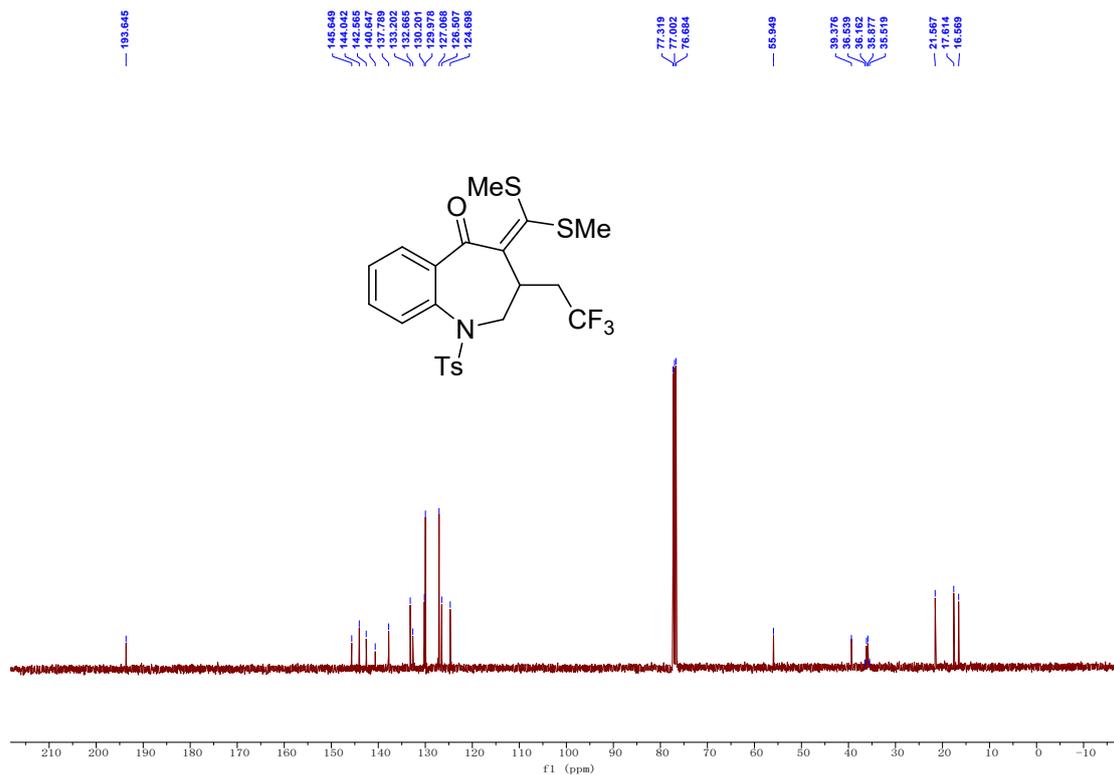
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 3m



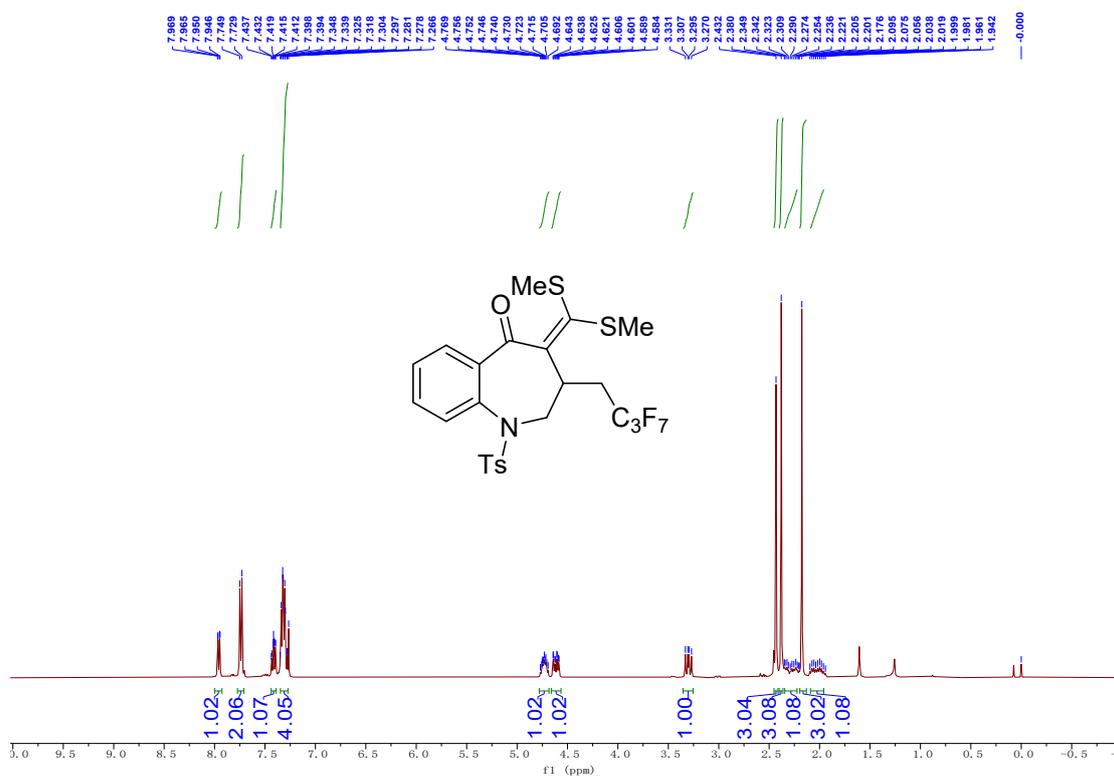
^{19}F NMR spectrum (376 MHz, CDCl_3 , 298 K) of **3m**



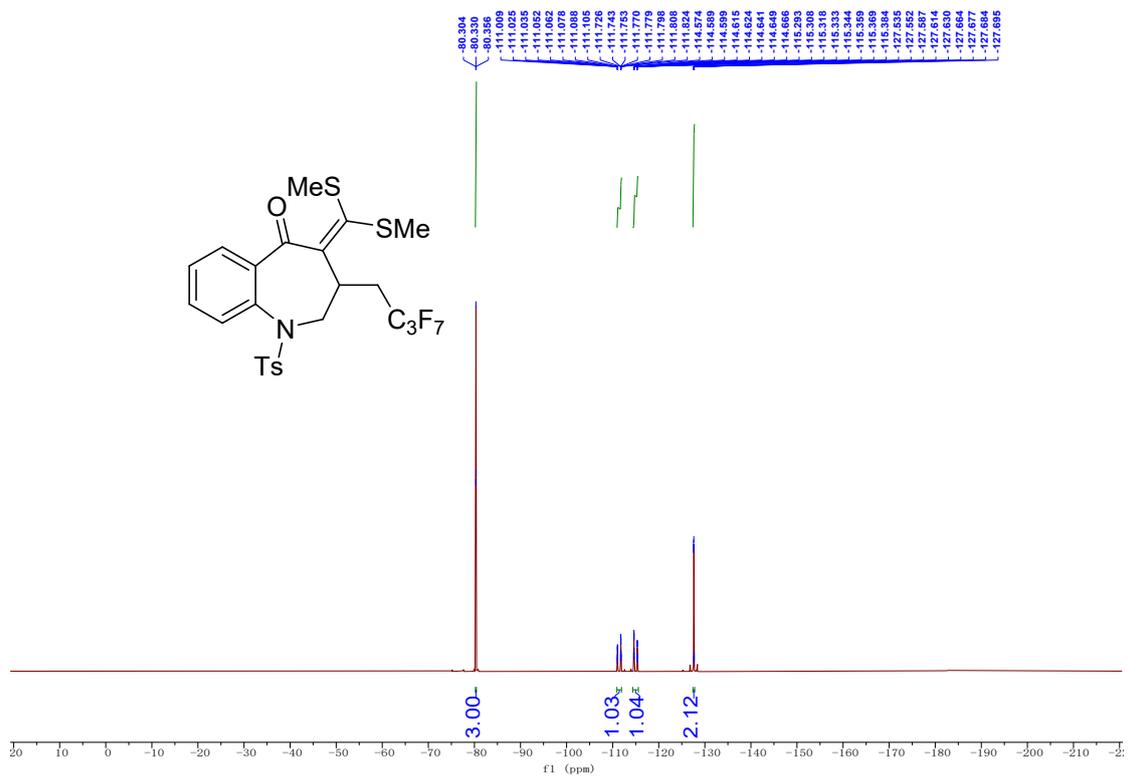
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298 K) of **3m**



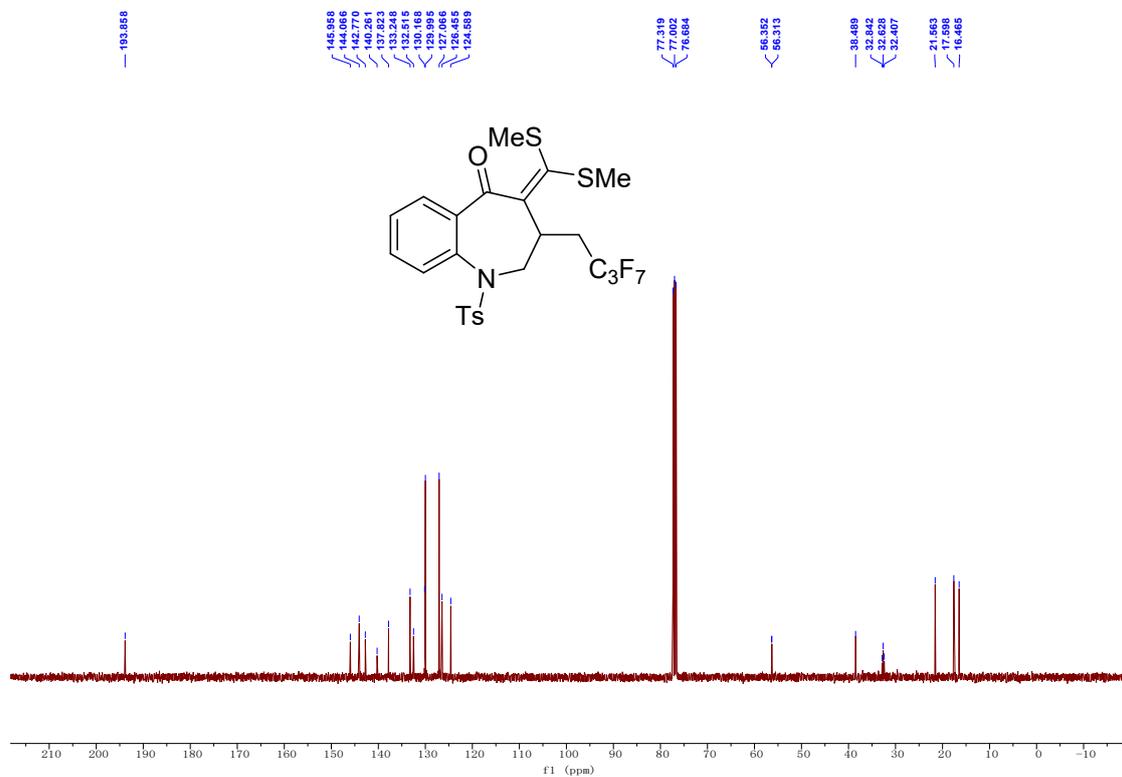
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3n**



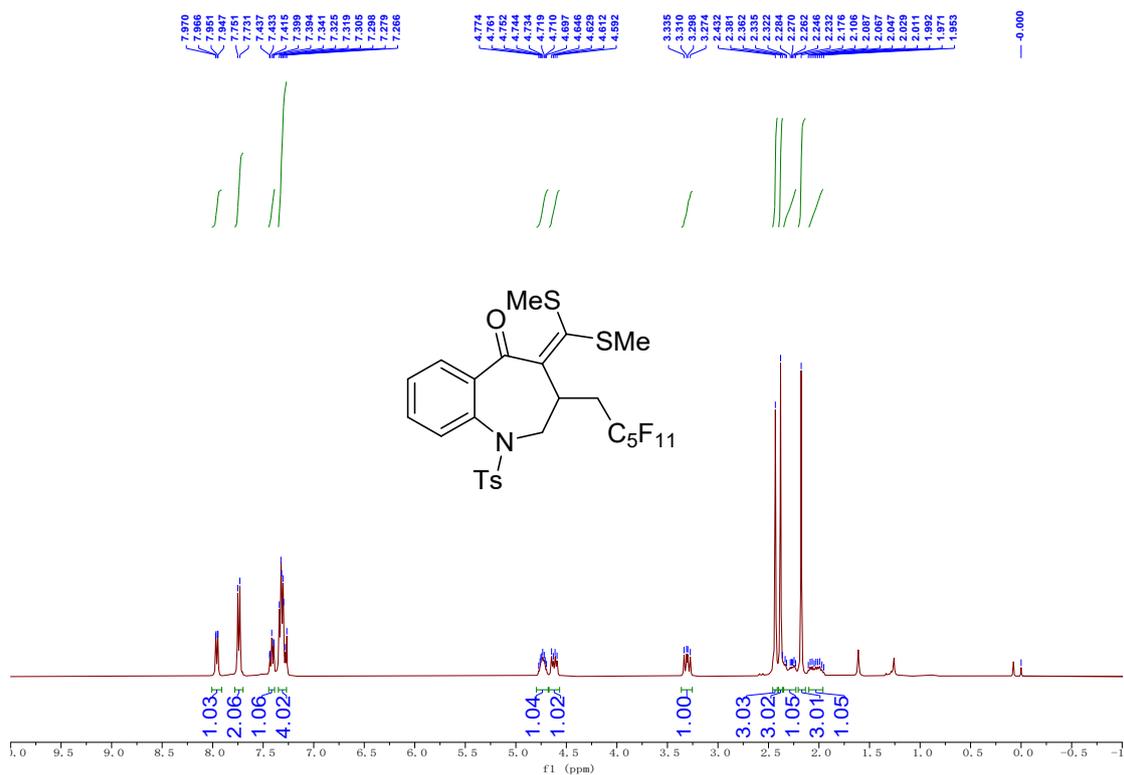
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3n**



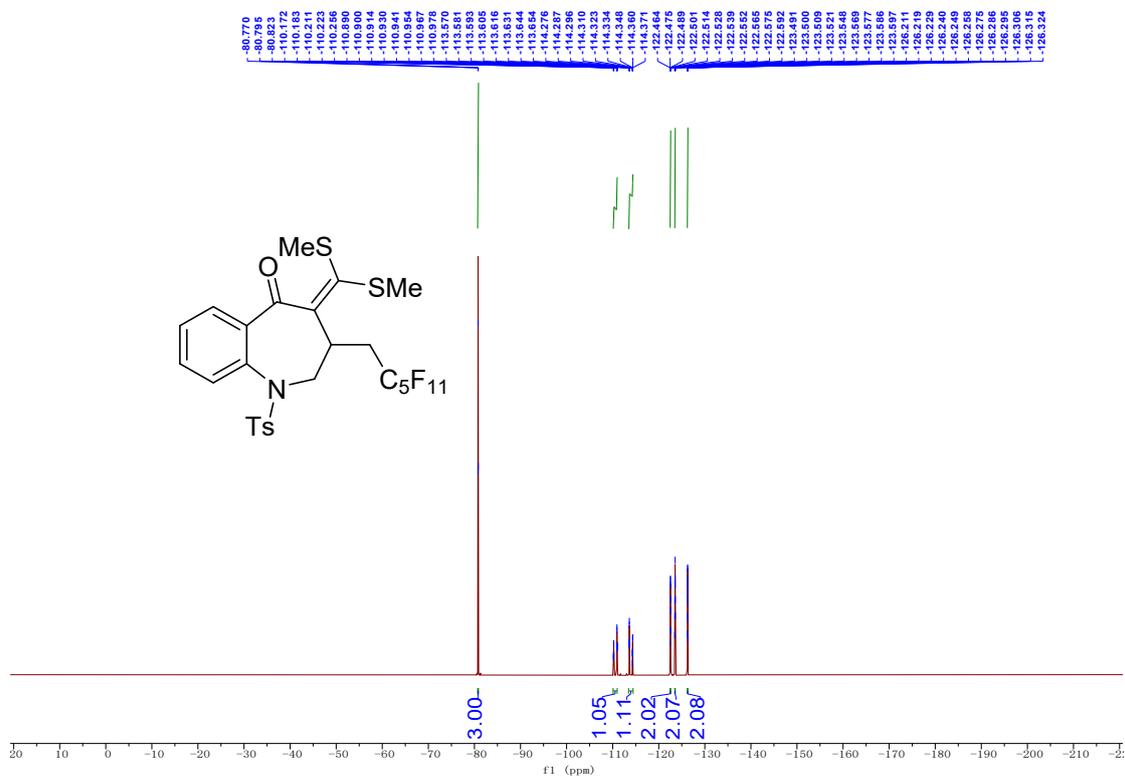
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3n**



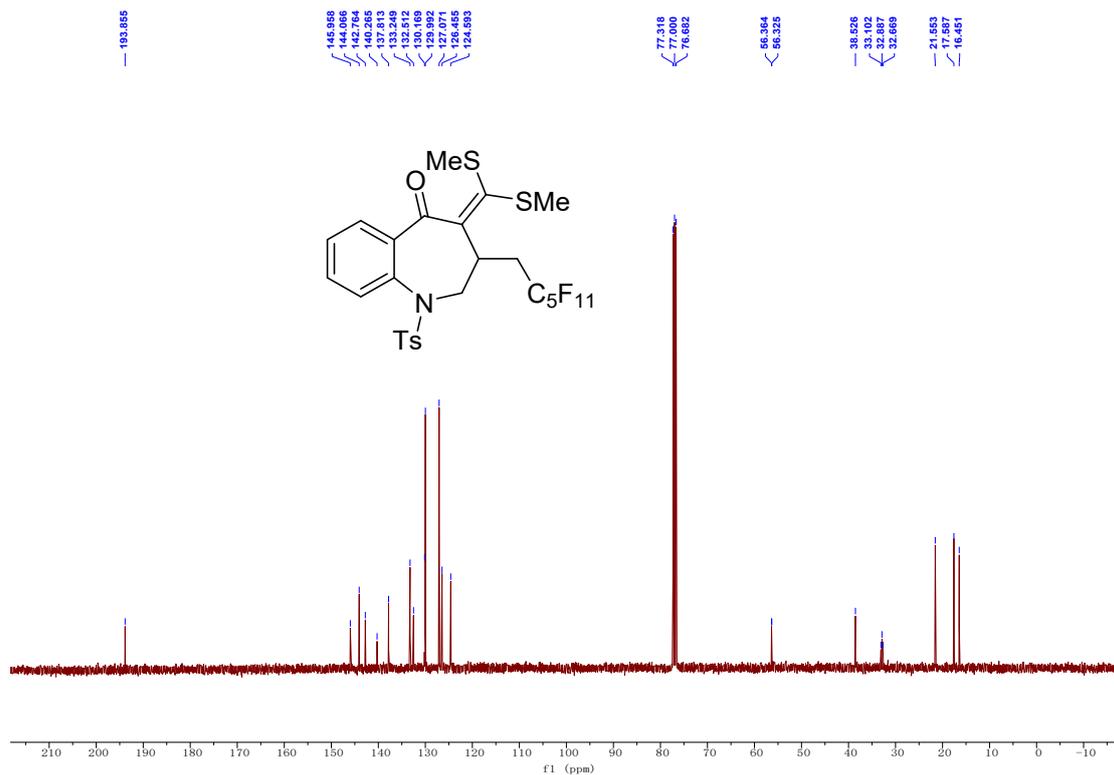
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3o**



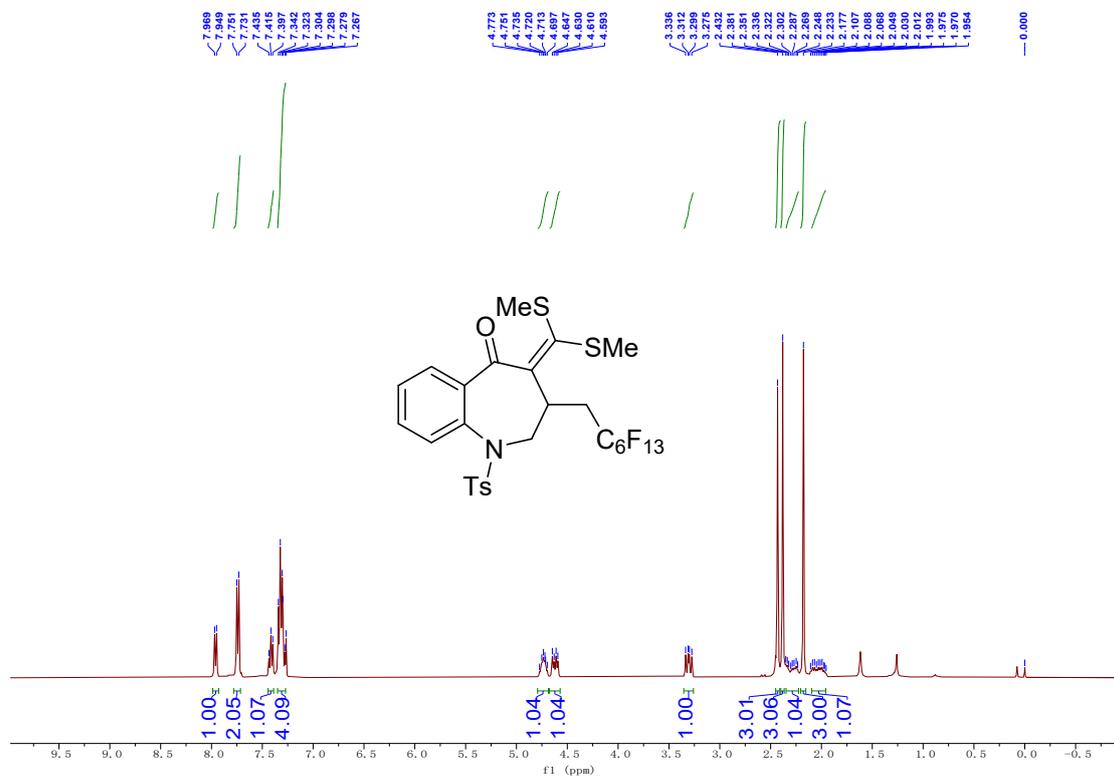
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **30**



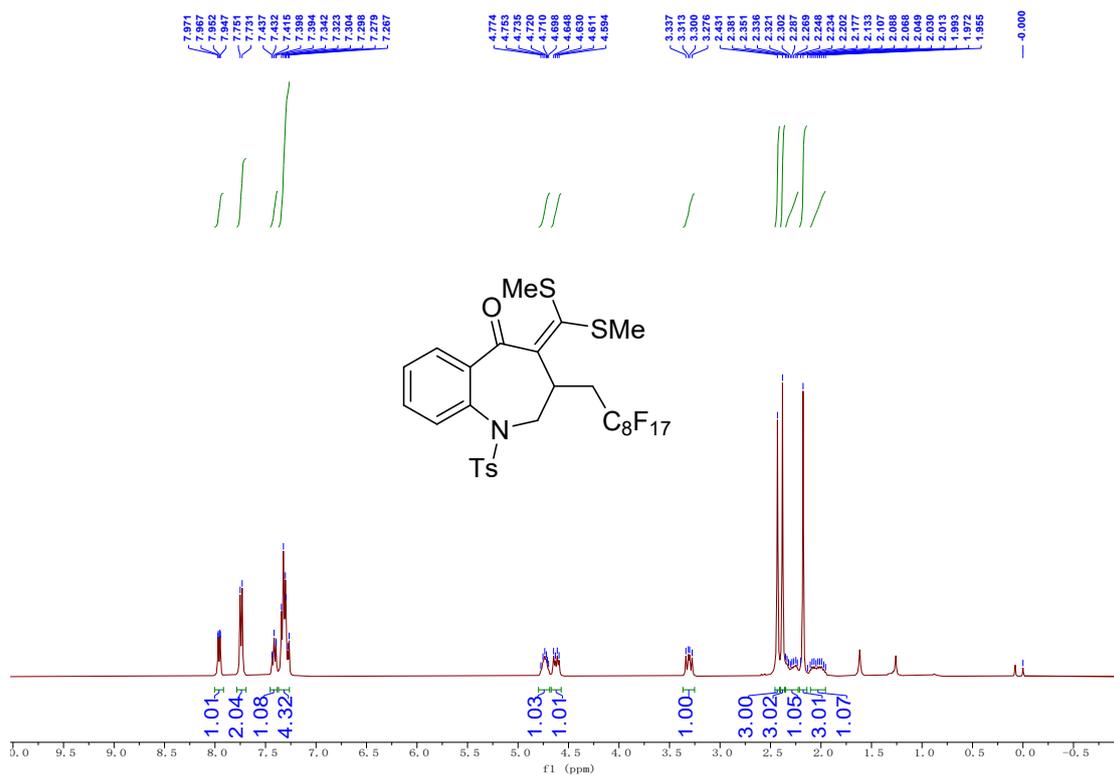
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **30**



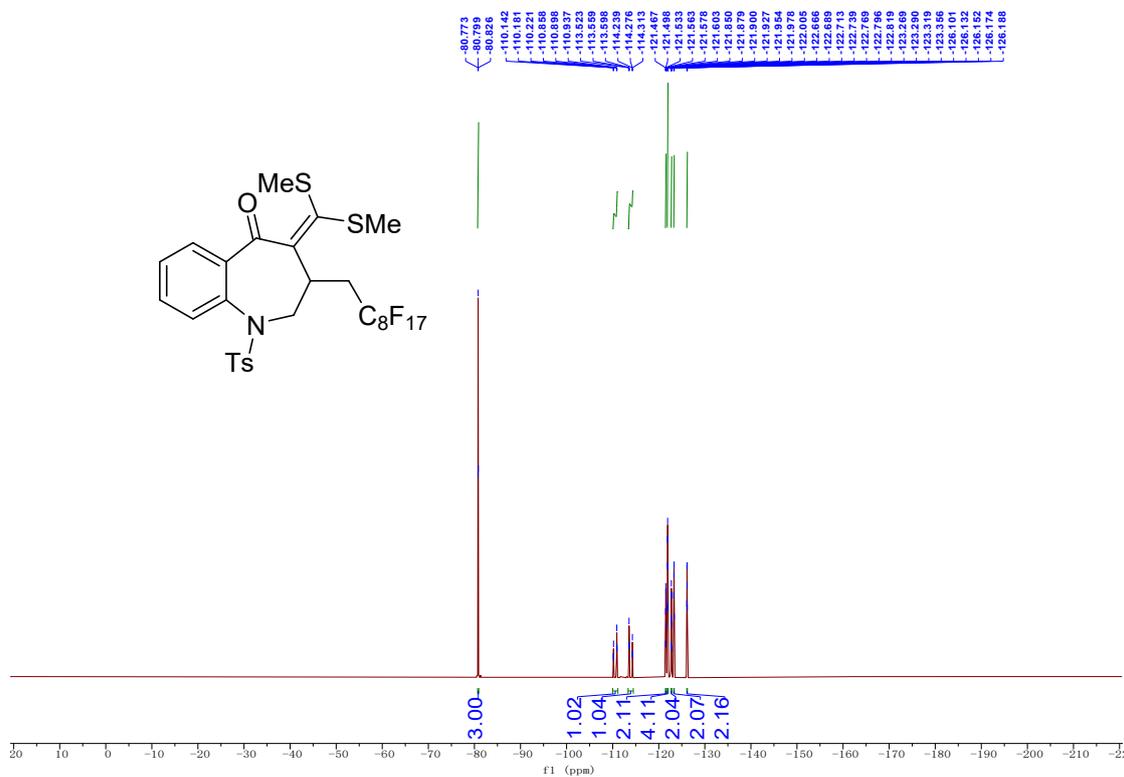
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 3p



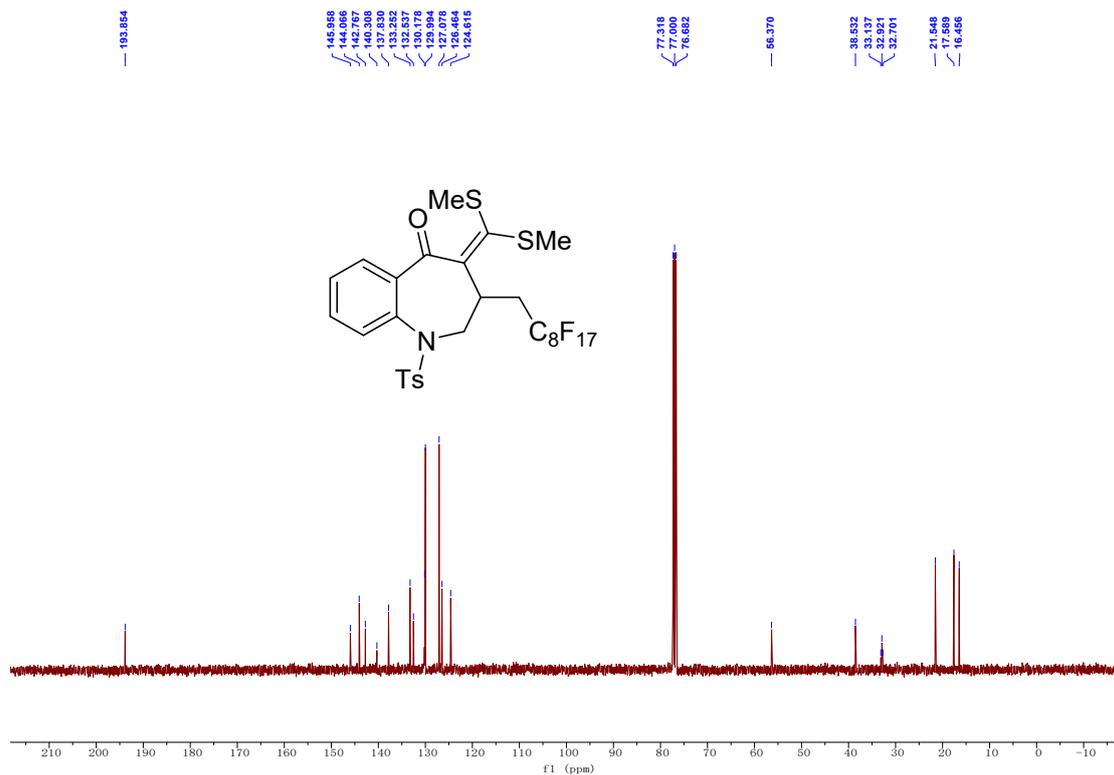
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 3p



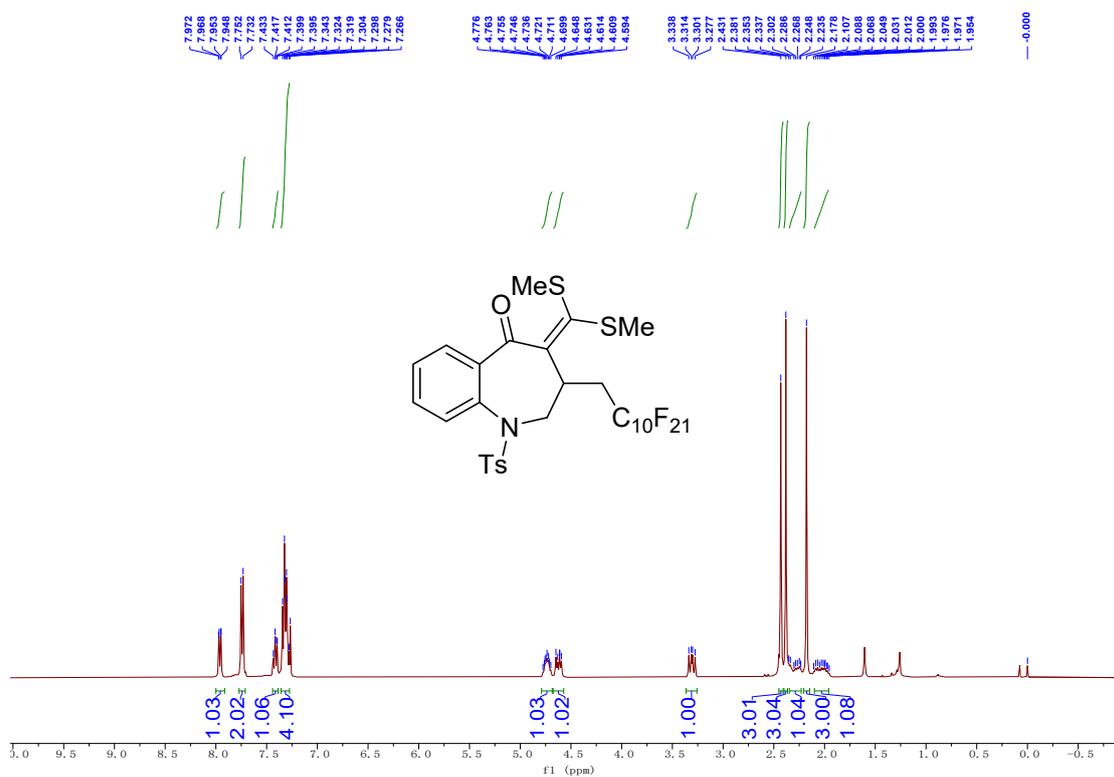
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3q**



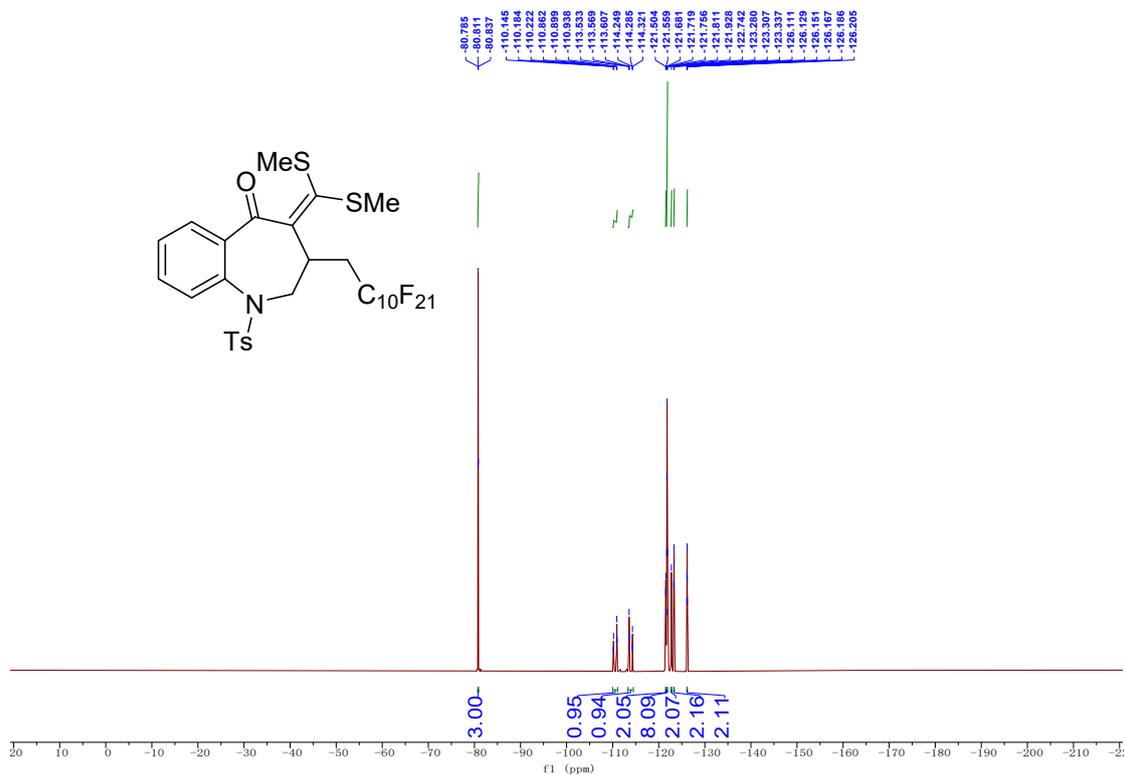
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3q**



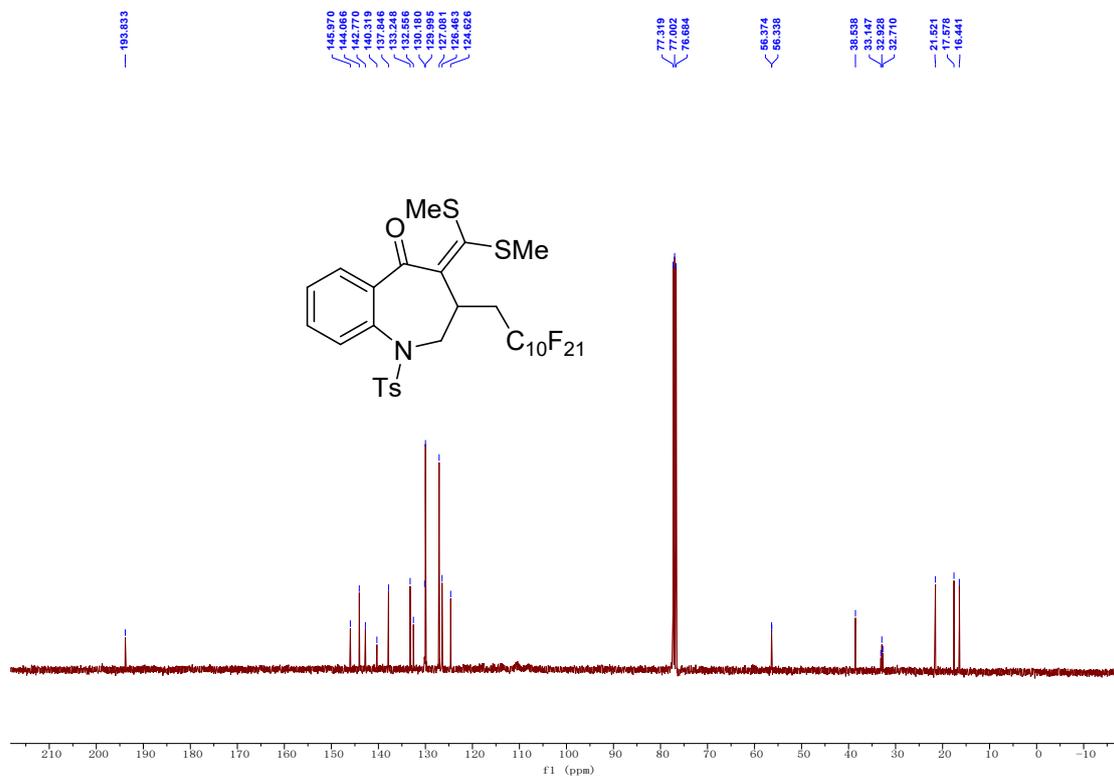
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3r**



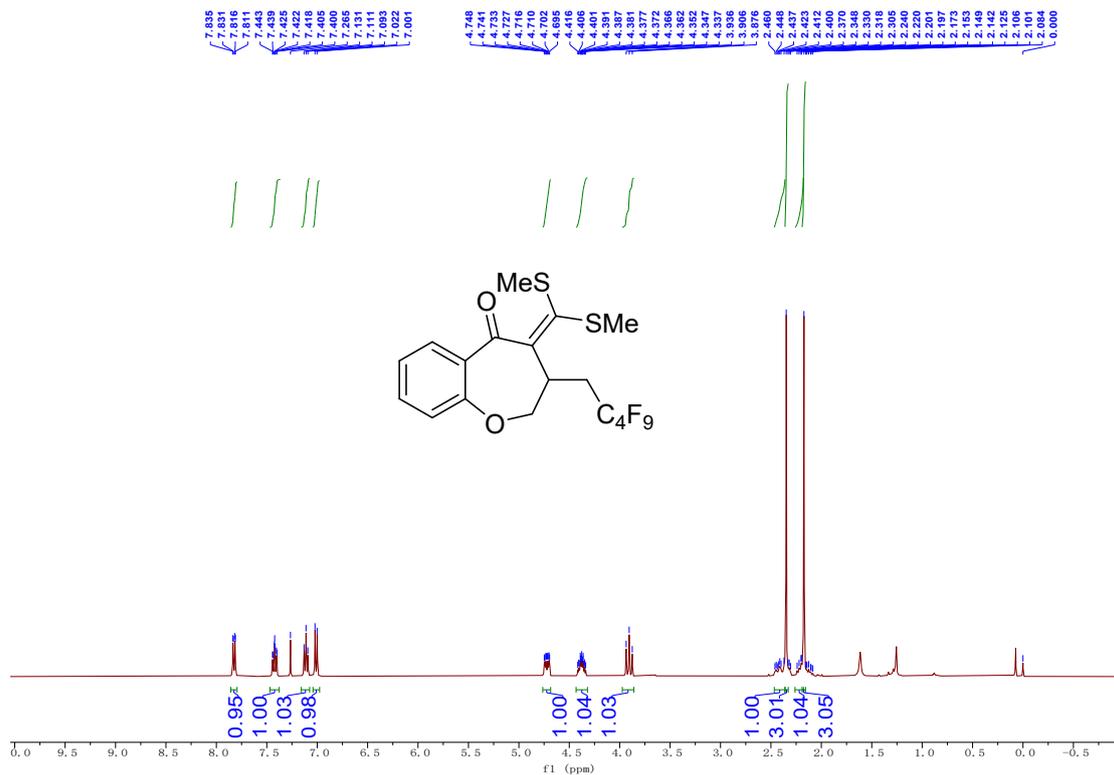
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **3r**



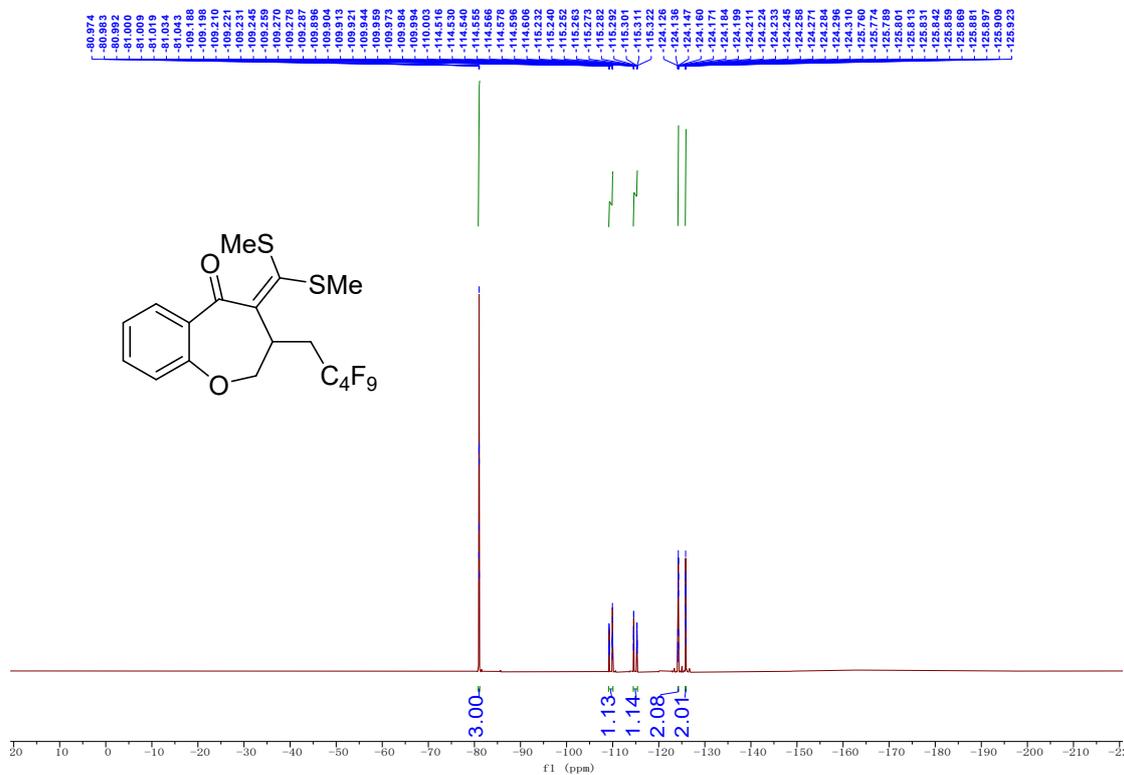
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **3r**



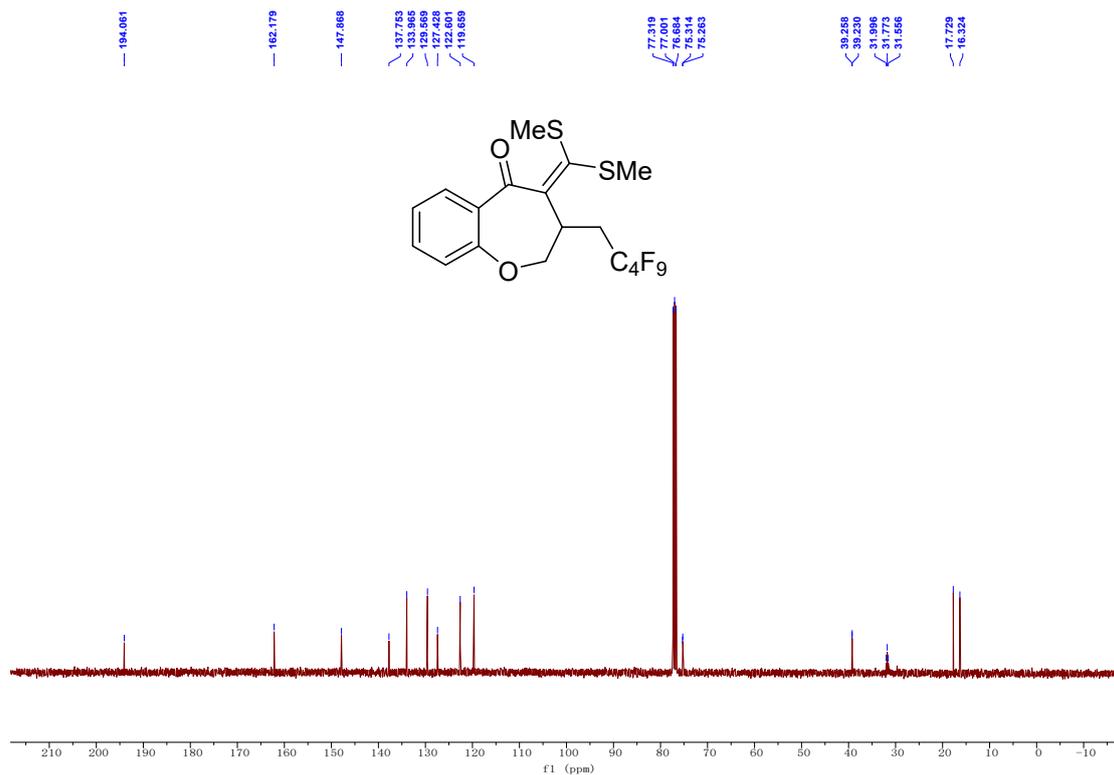
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **5a**



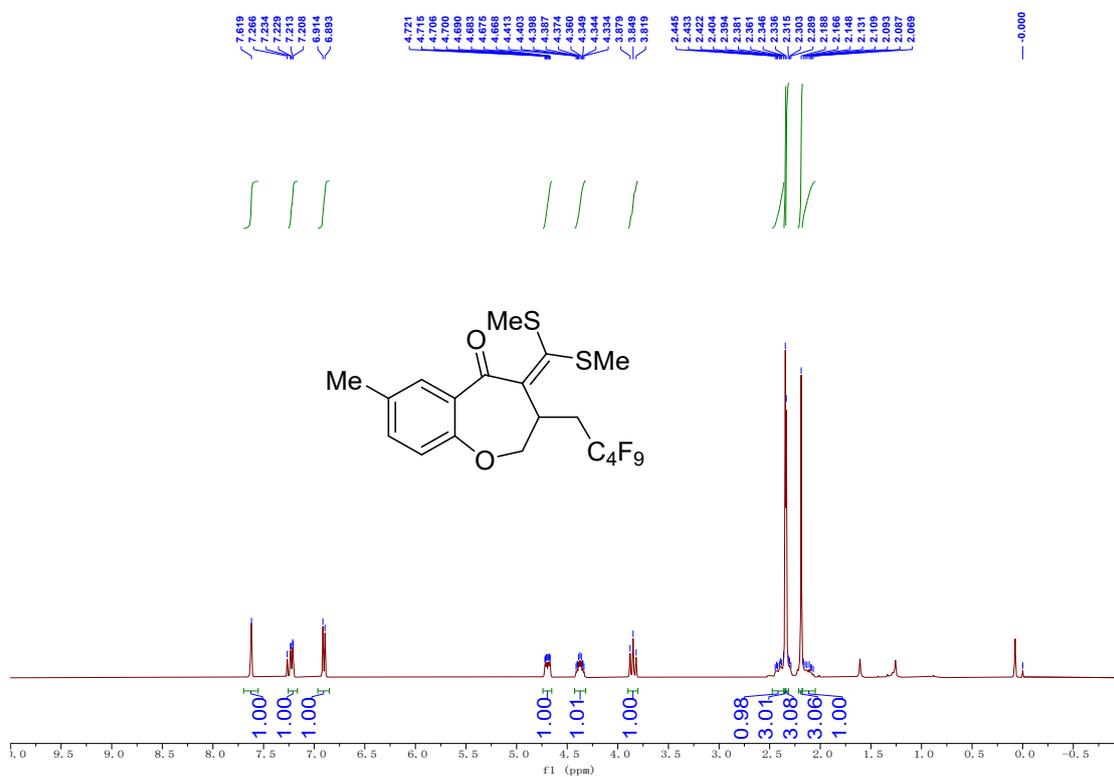
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 5a



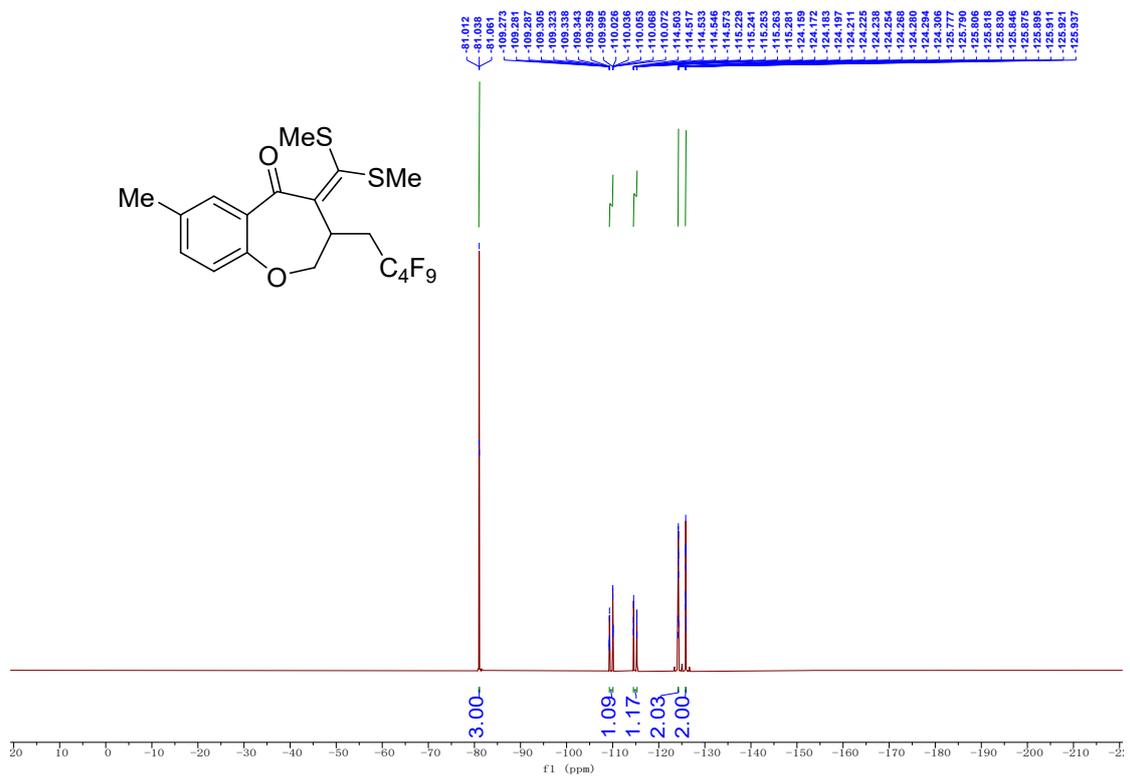
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 5a



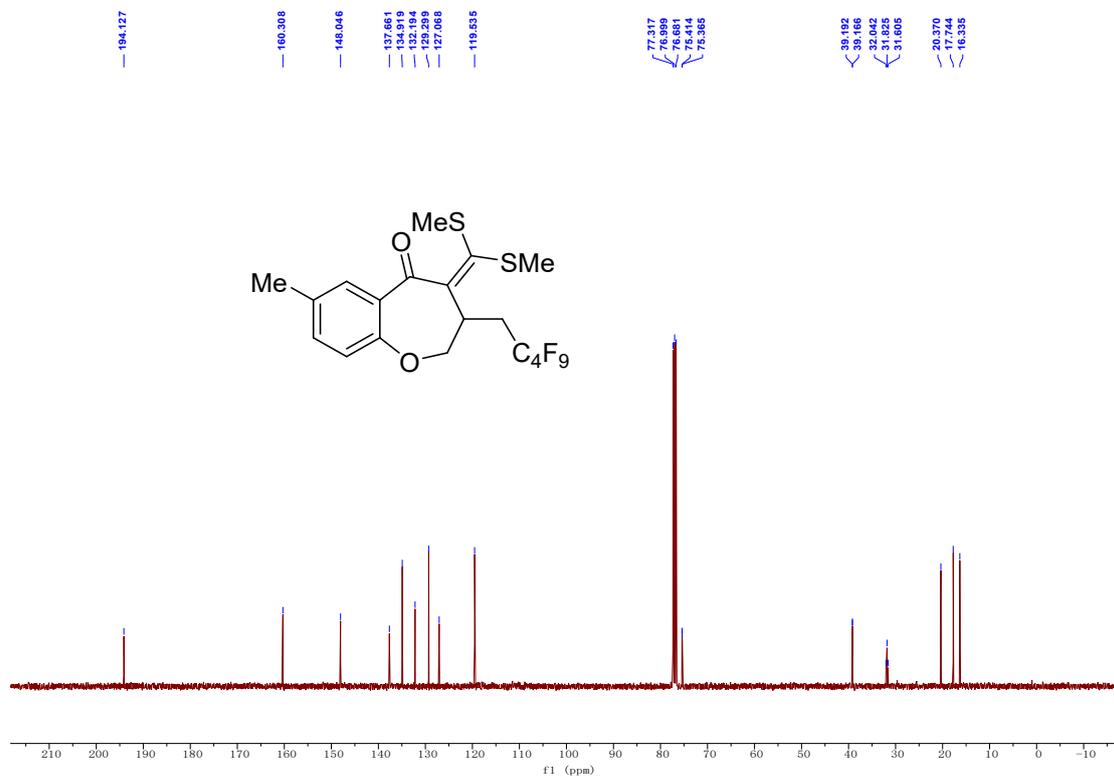
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5b



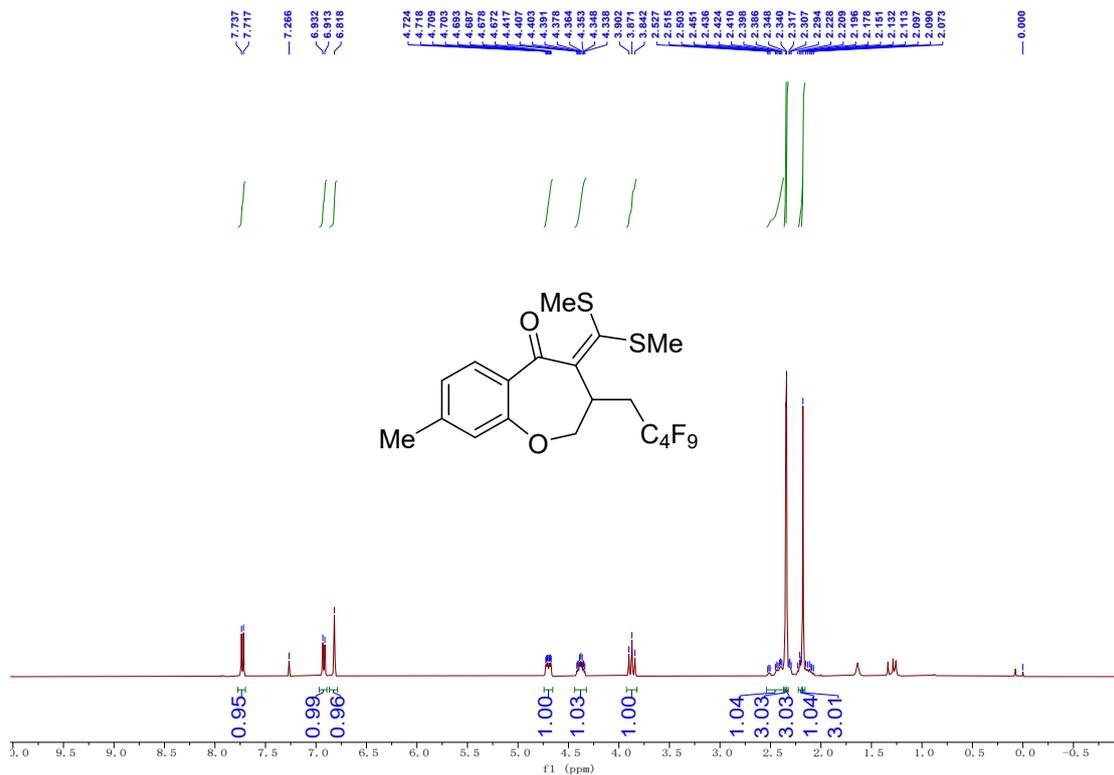
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 5b



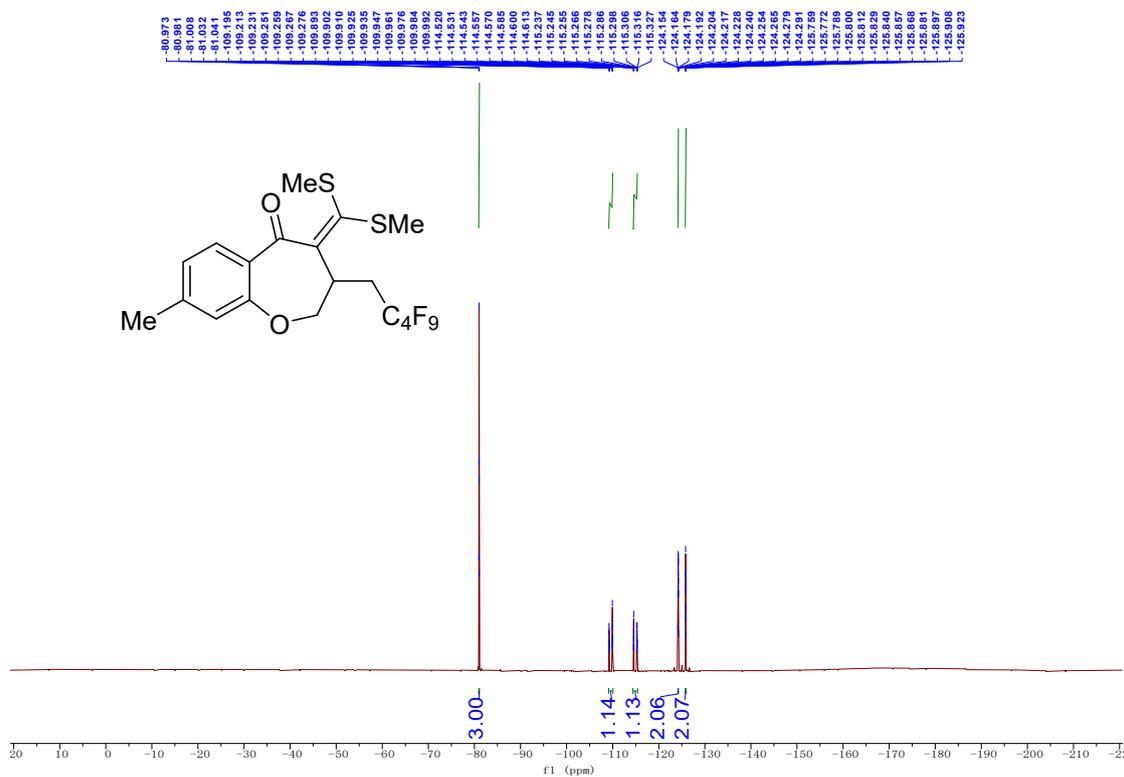
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **5b**



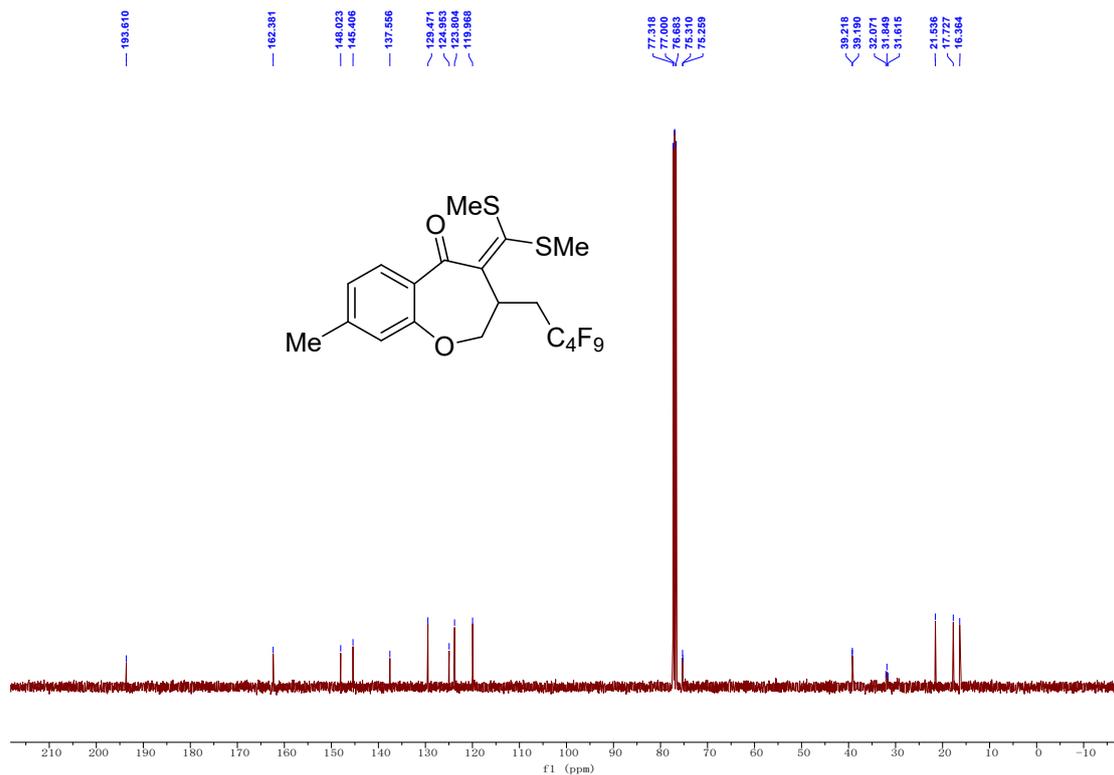
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **5c**



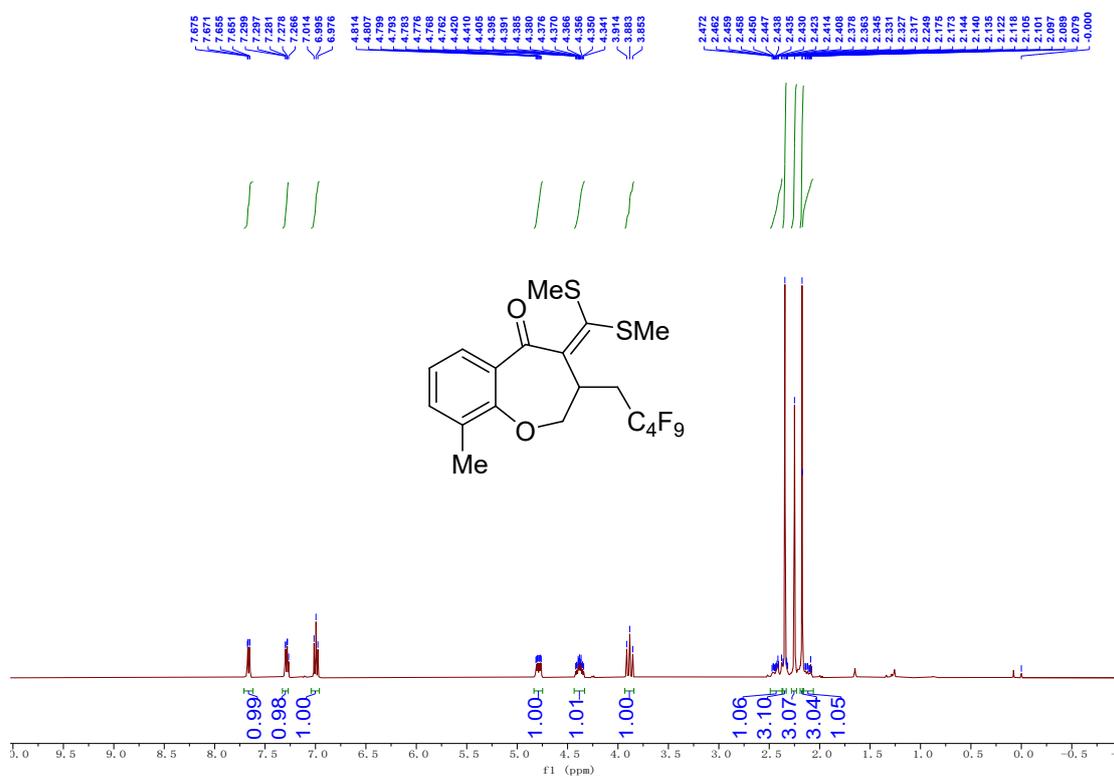
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **5c**



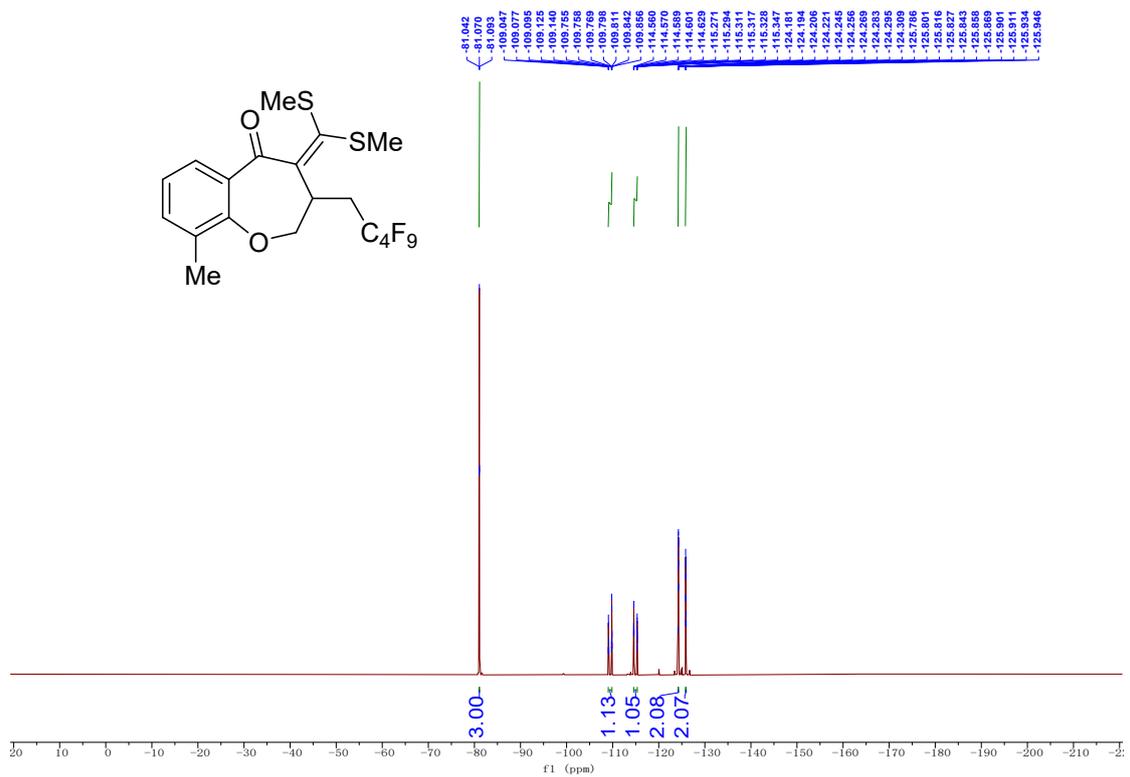
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **5c**



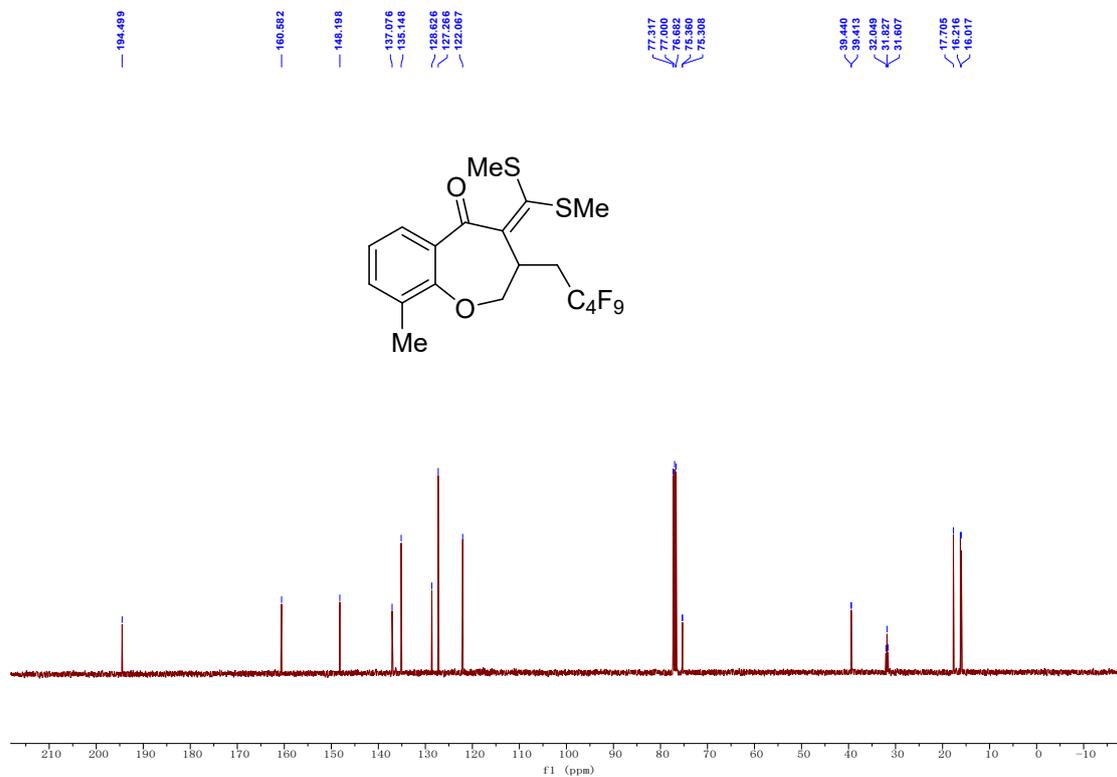
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **5d**



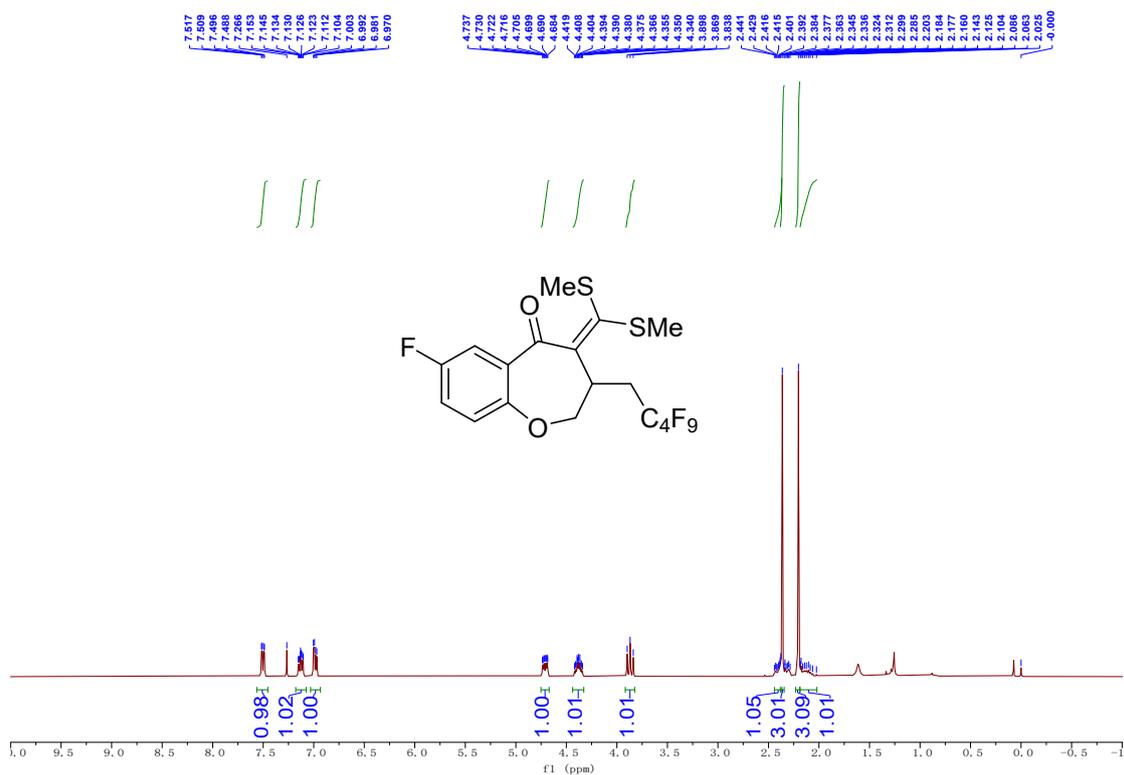
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **5d**



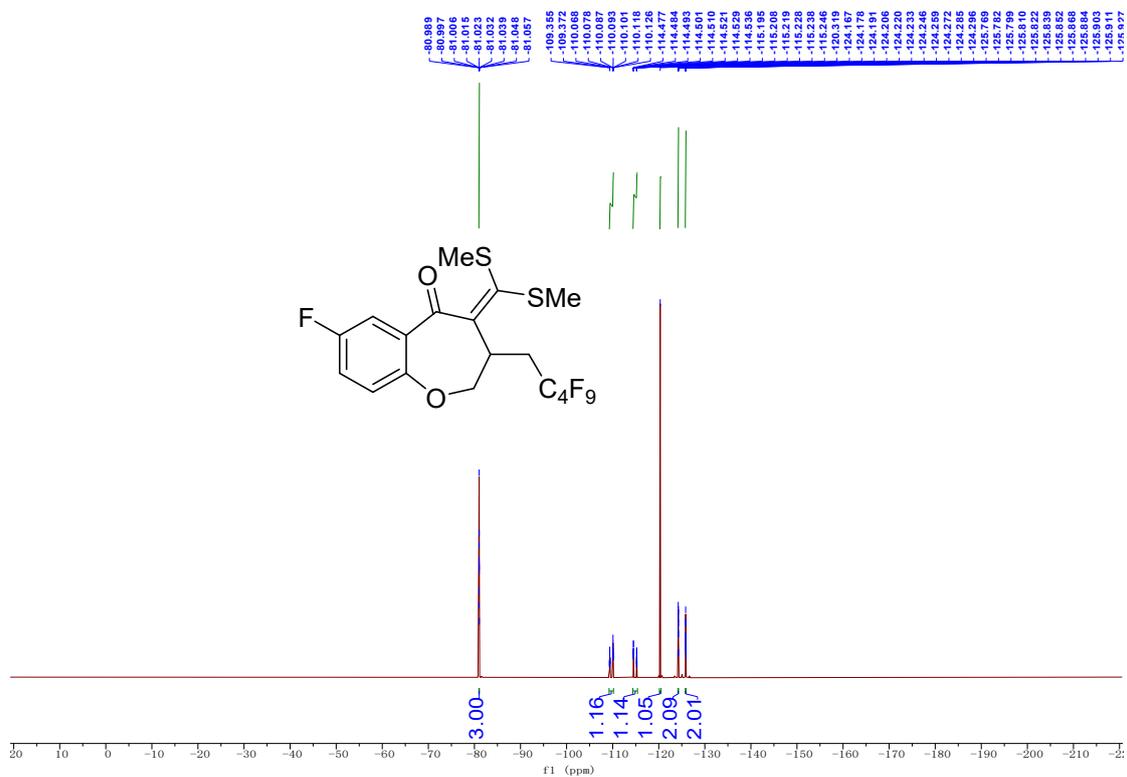
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 5d



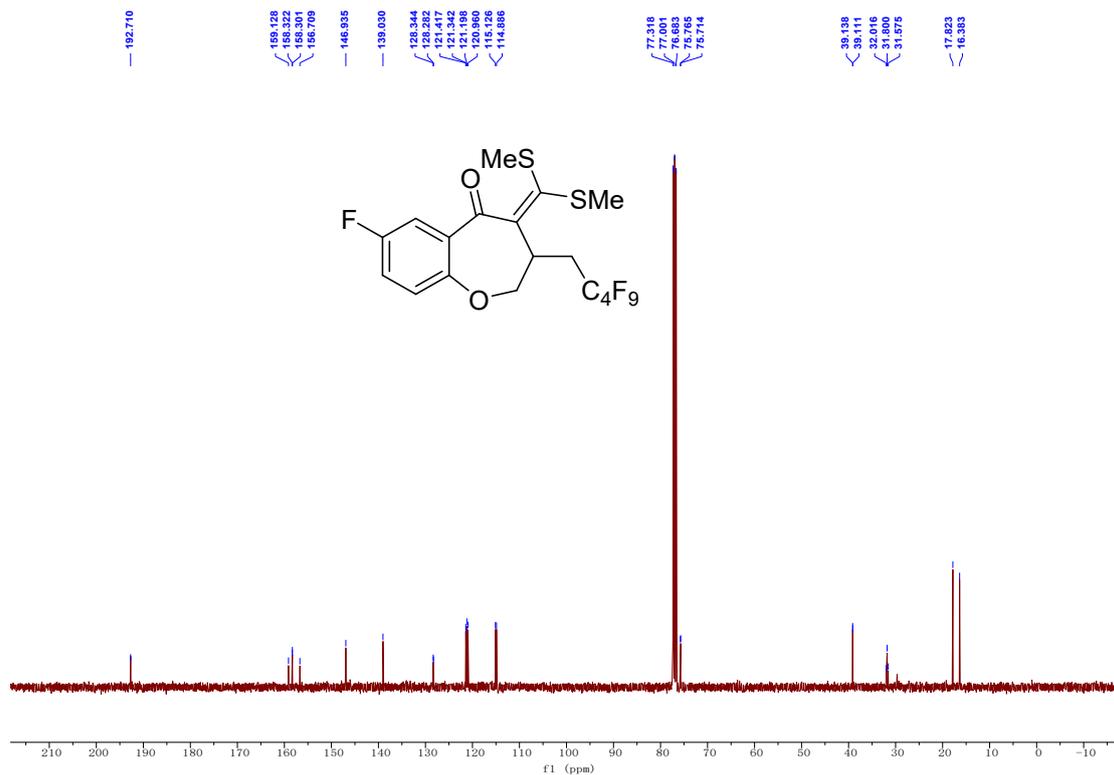
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5e



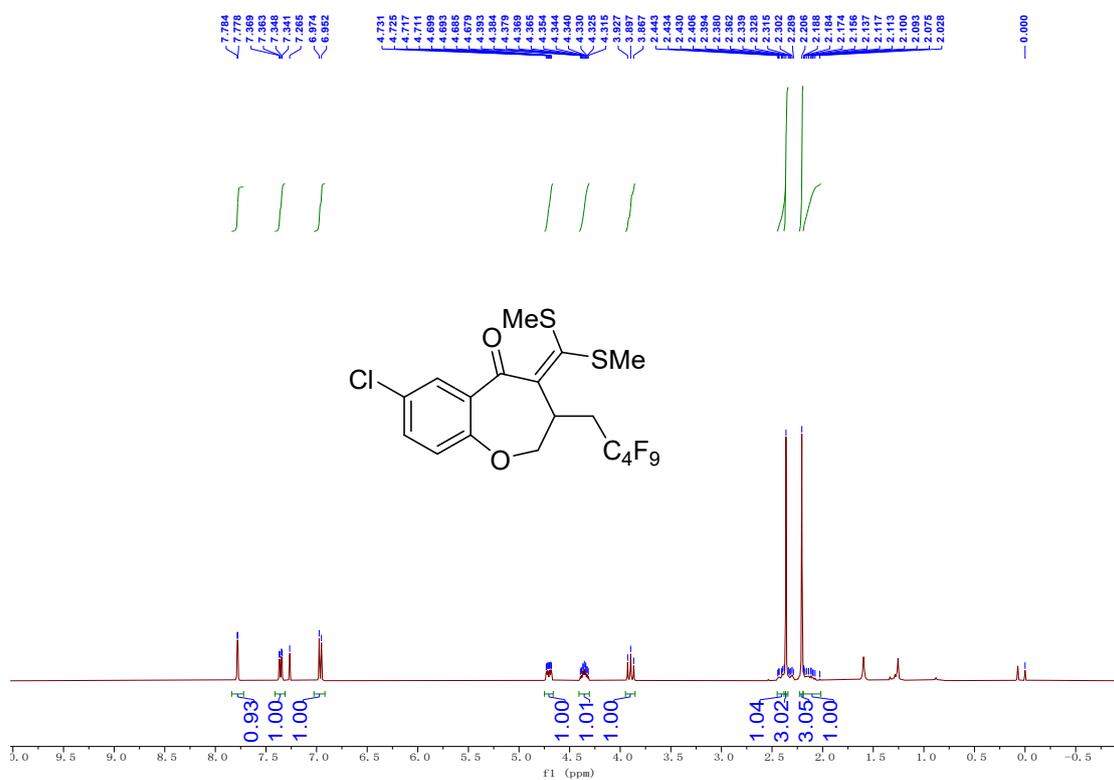
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 5e



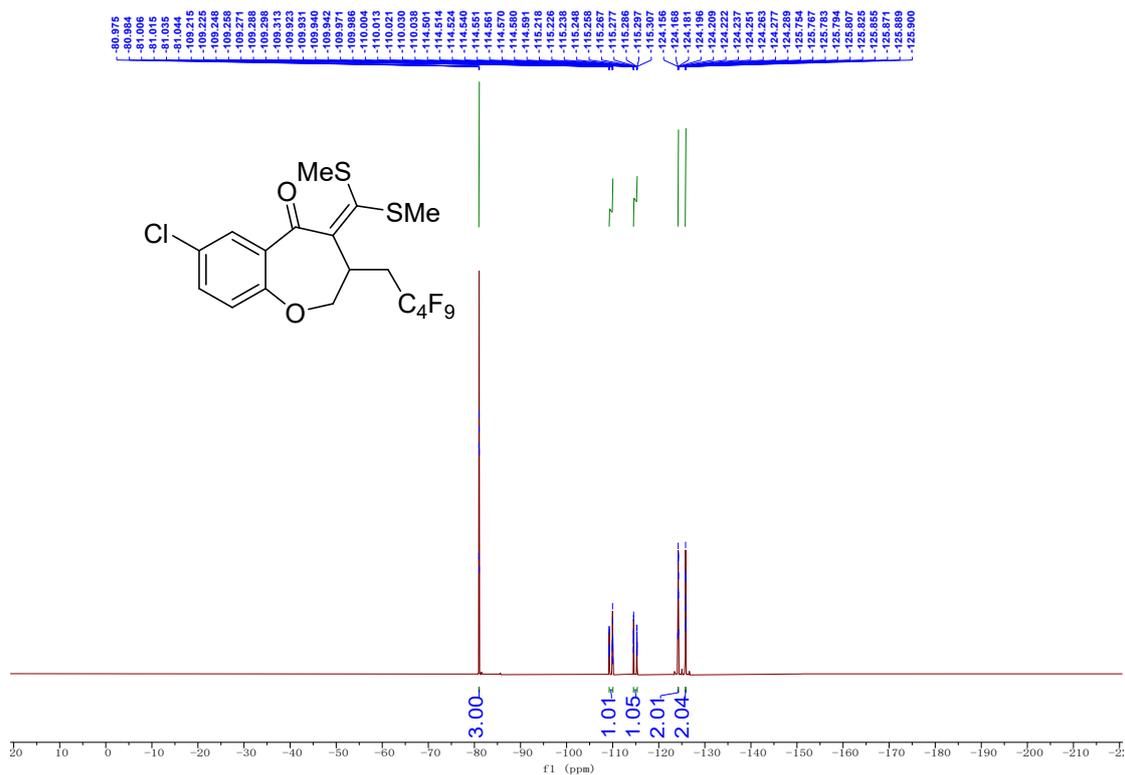
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 5e



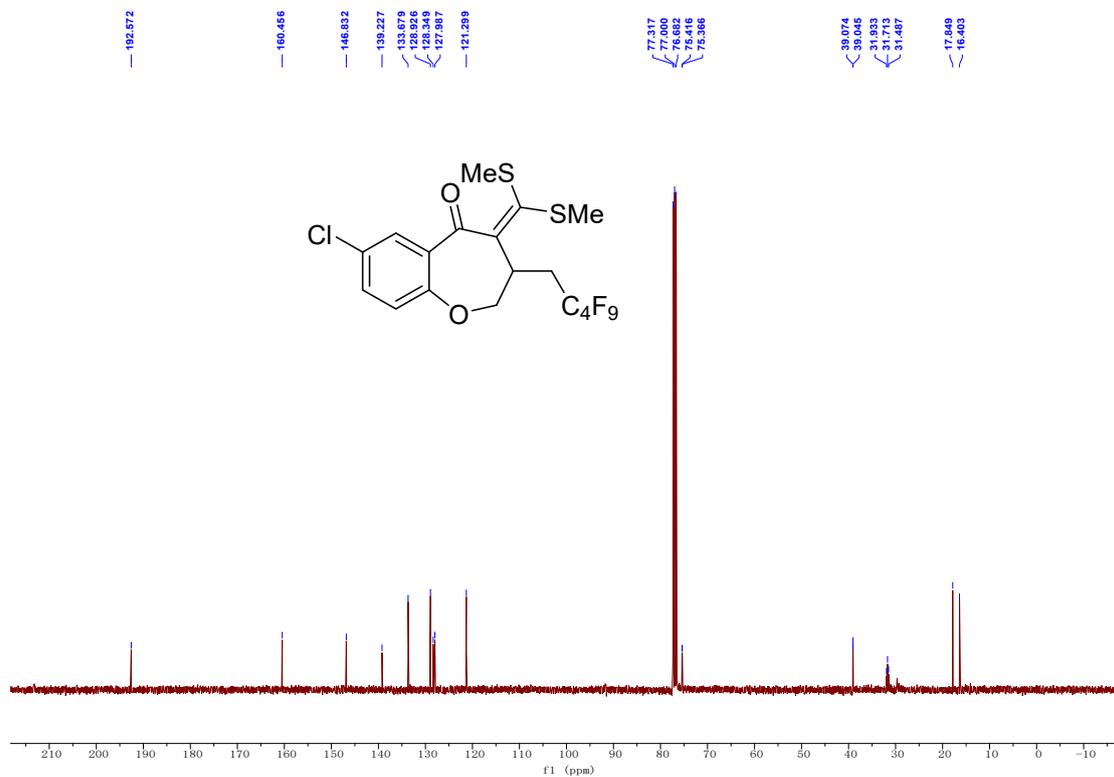
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5f



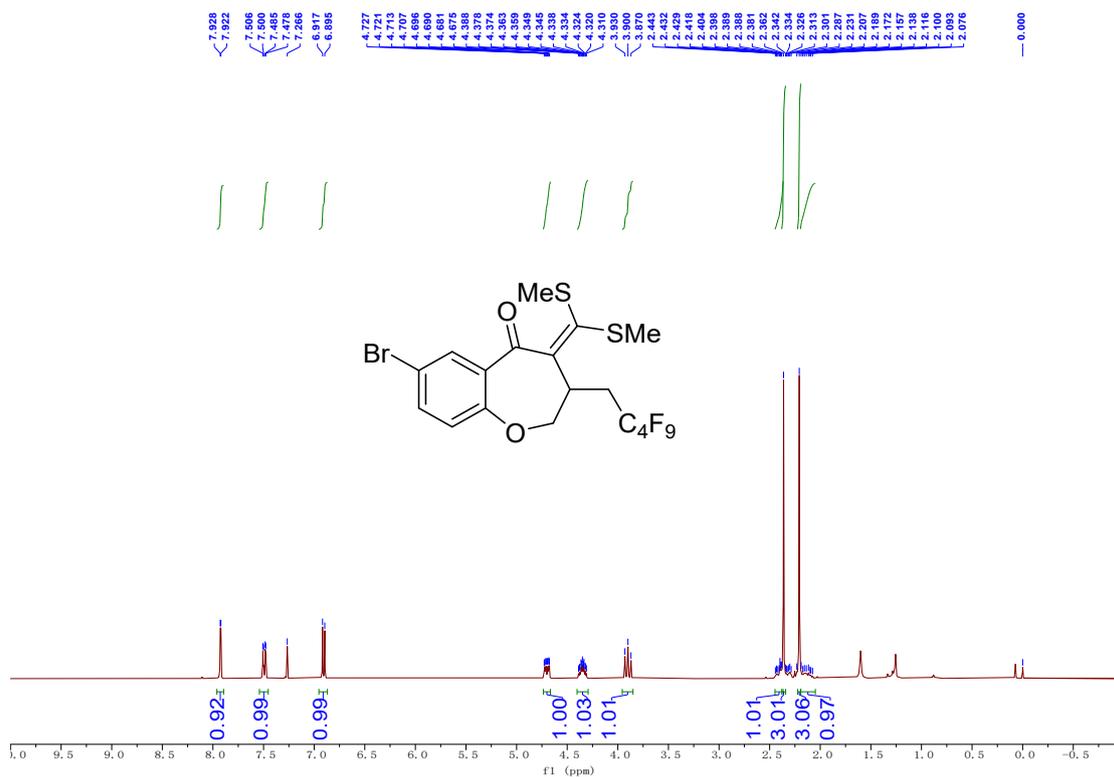
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 5f



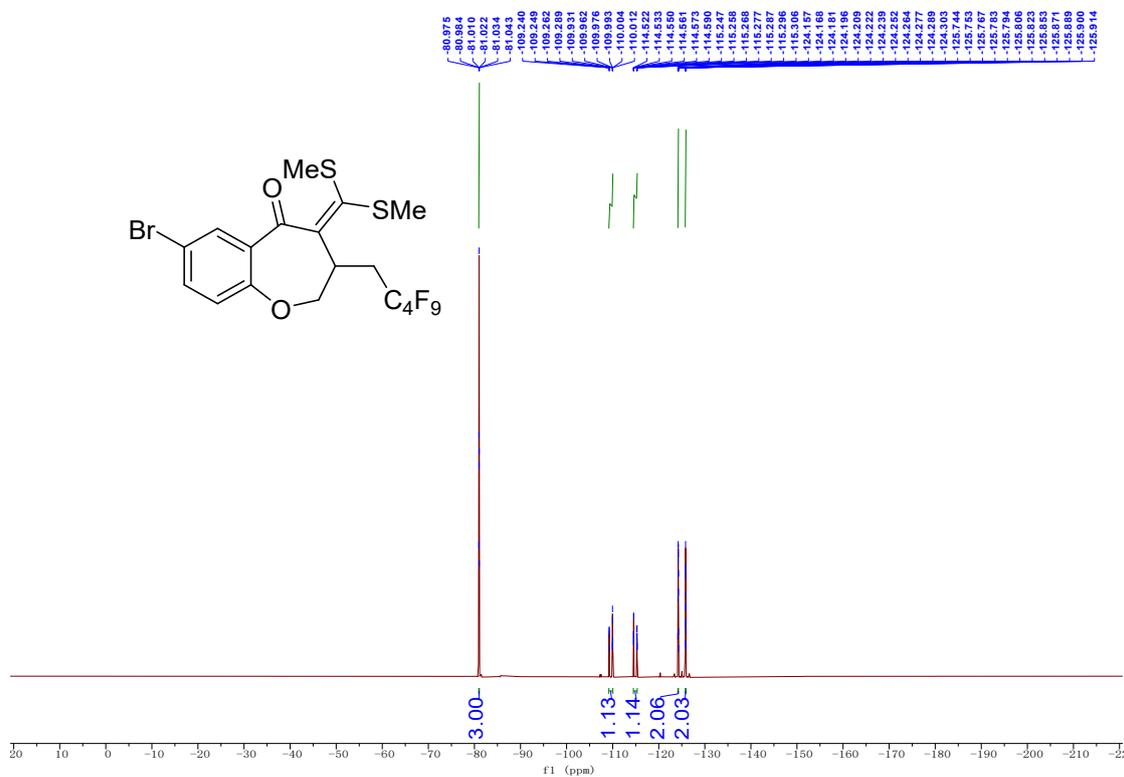
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **5f**



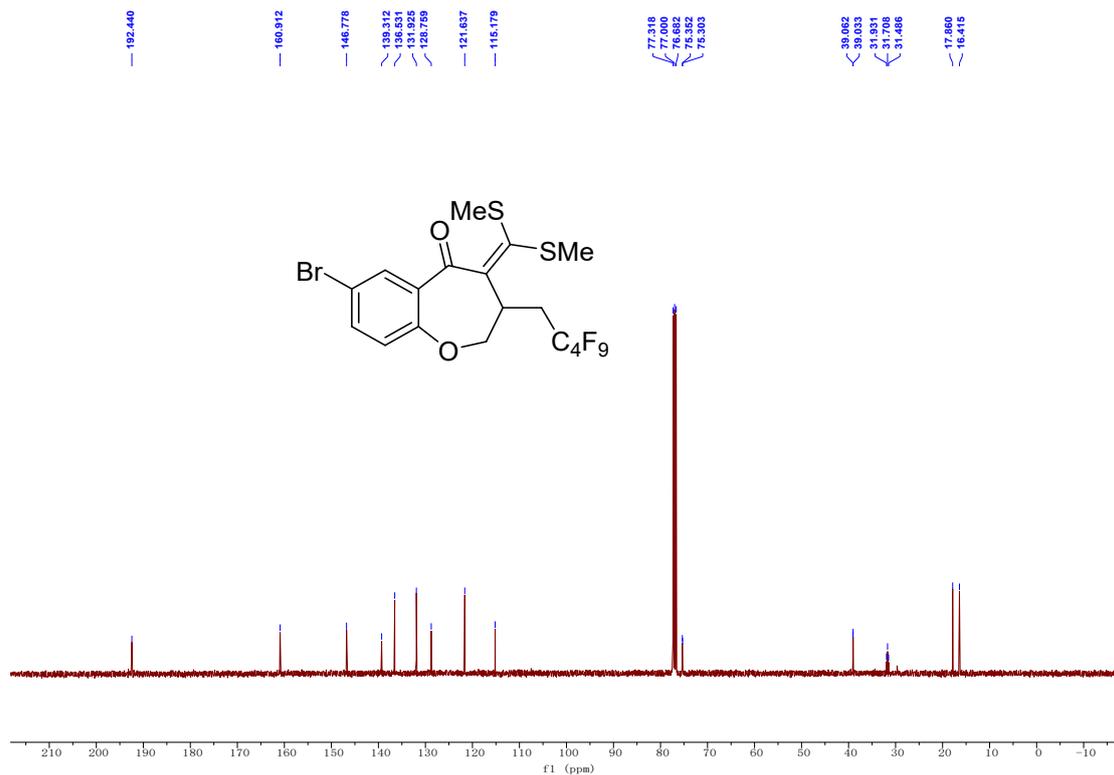
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **5g**



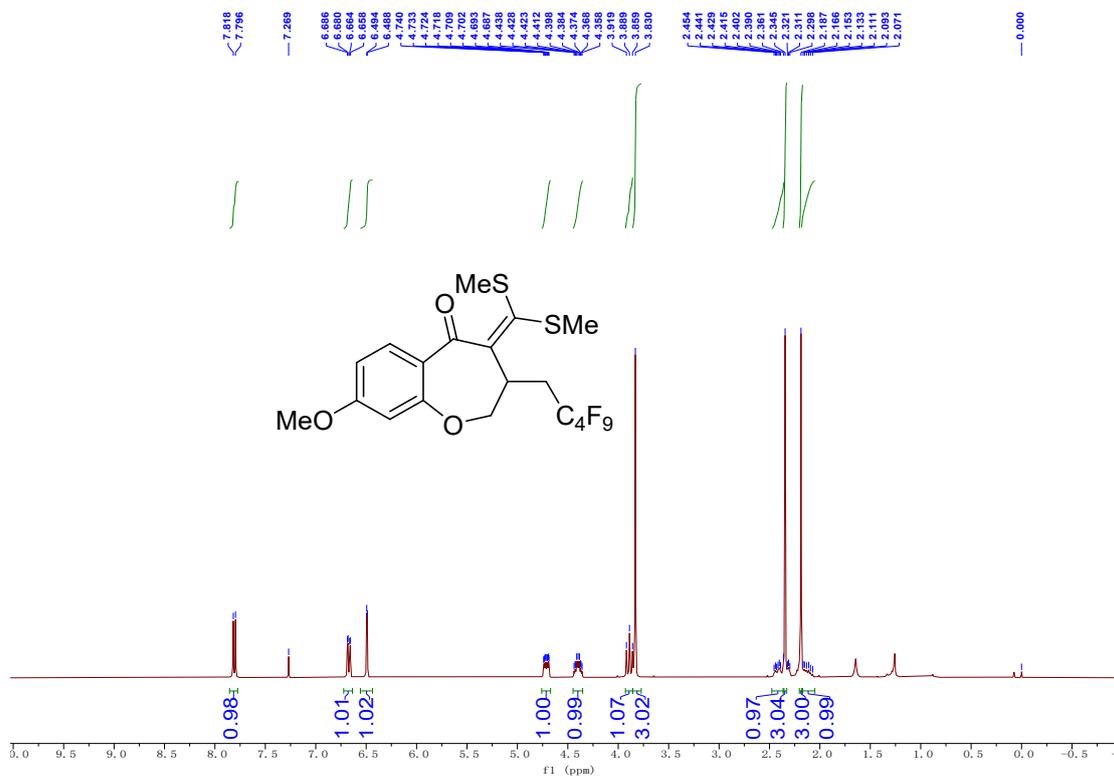
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of **5g**



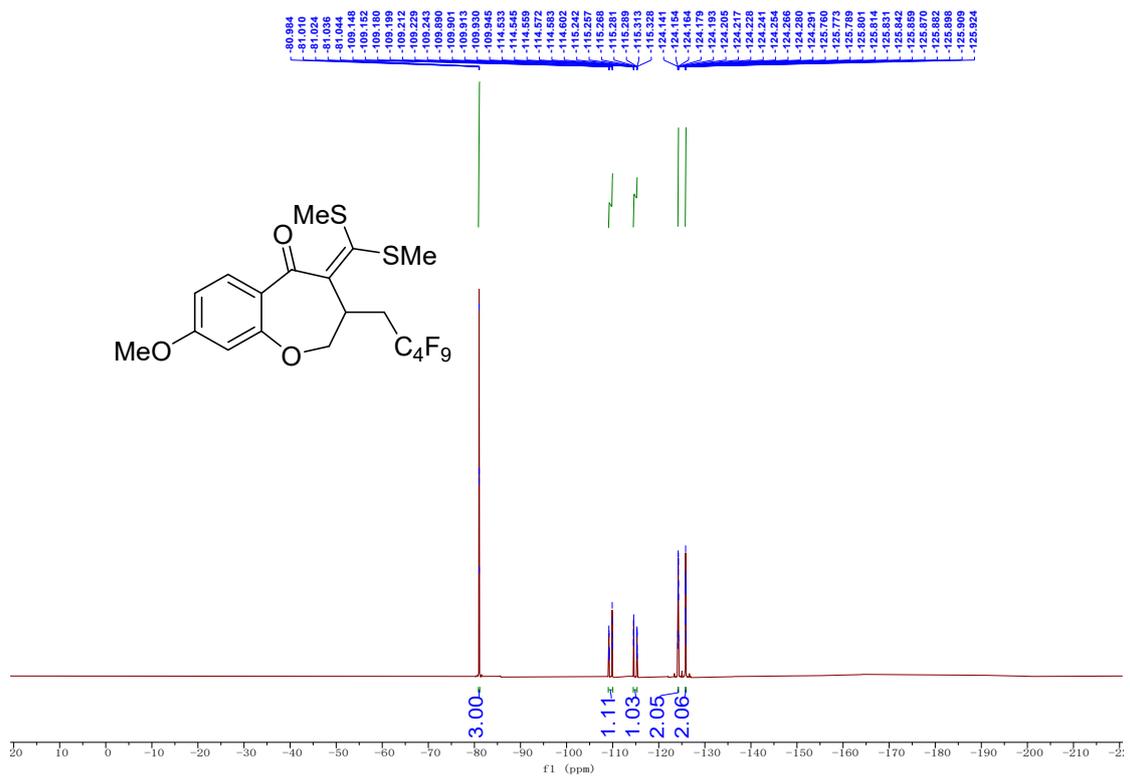
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **5g**



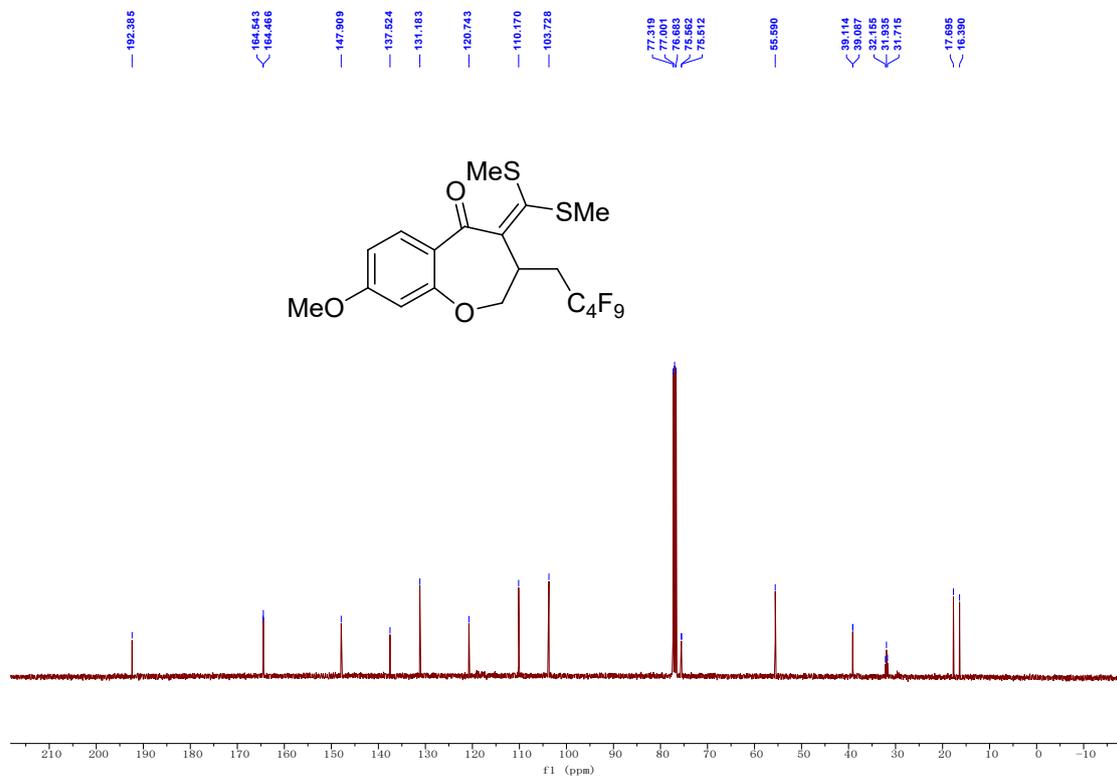
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5h



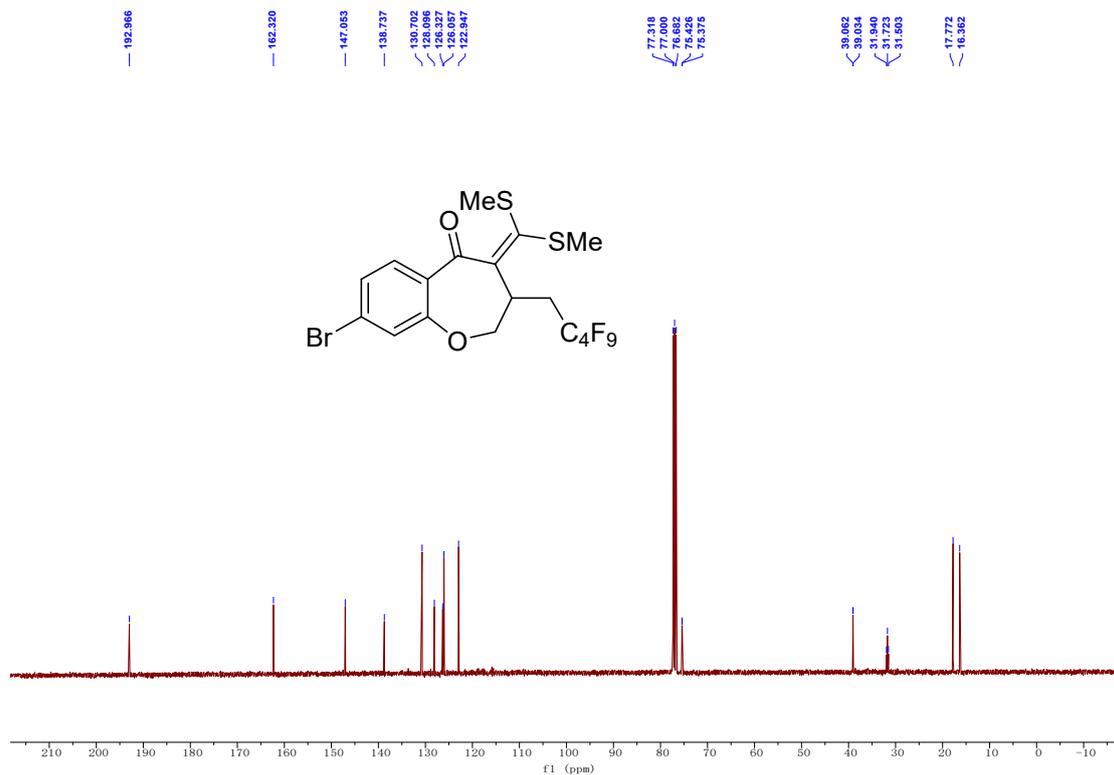
¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 5h



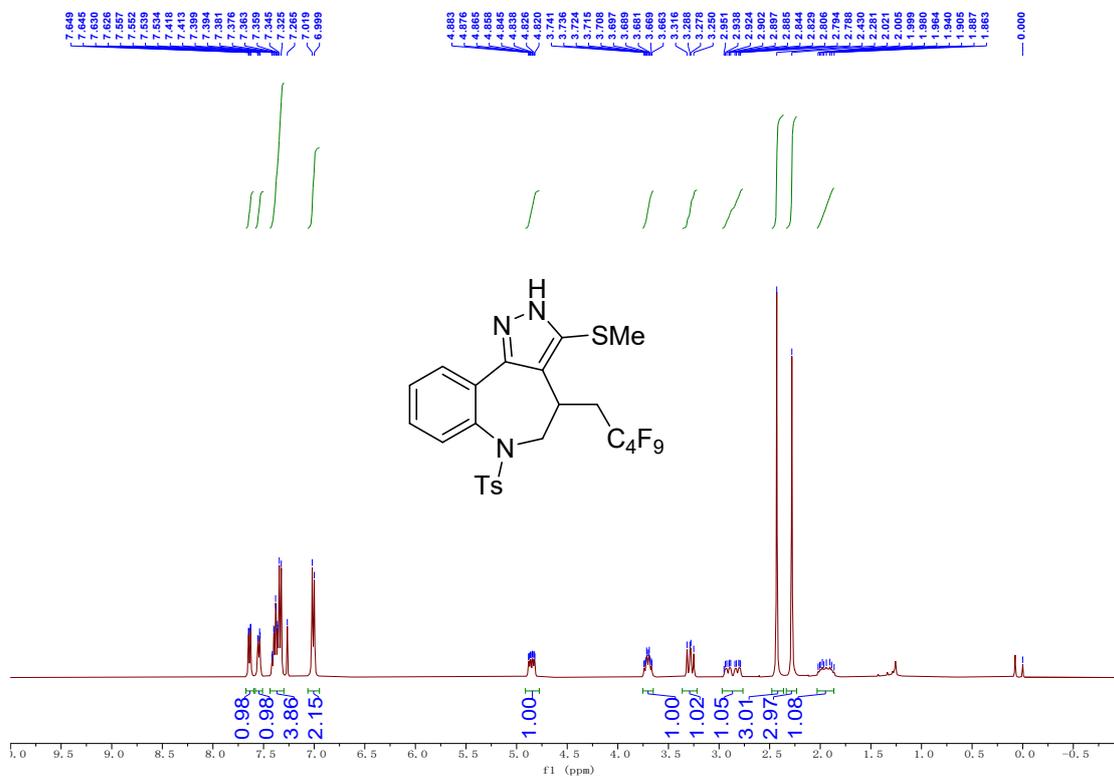
¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 5h



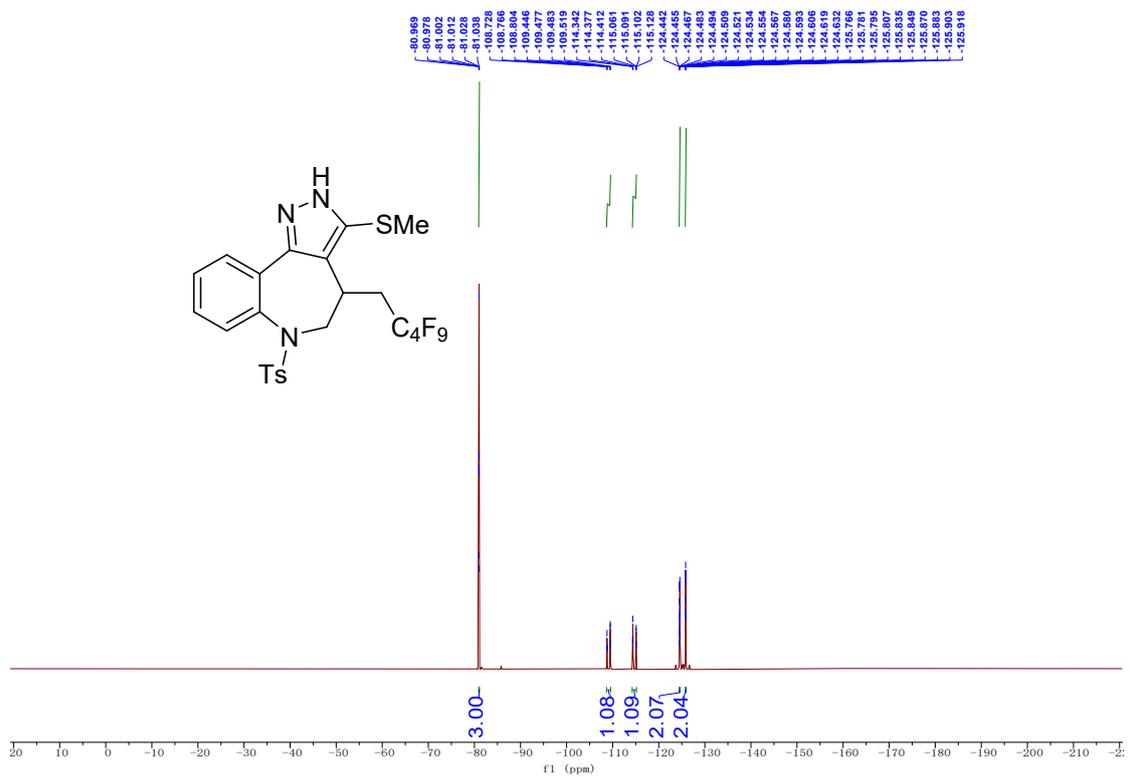
¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5i



¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 6



¹⁹F NMR spectrum (376 MHz, CDCl₃, 298 K) of 6



¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of **6**

