Convenient synthesis of thiolated 2,7-disubstituted tropones via double C–N bond cleavage of tropinone derivatives

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Supporting information

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General information

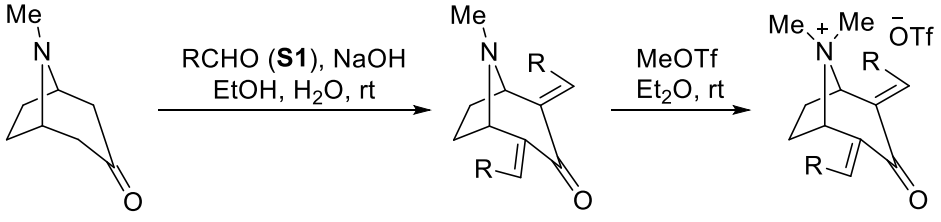
The ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker AC-500 FT spectrometer (500 MHz, 125 MHz, 471 MHz) and Bruker AC-400 FT spectrometer (400 MHz, 100 MHz, 376 MHz). The chemical shifts of ^{1}H NMR and ^{13}C NMR spectra were referenced internally with tetramethylsilane (δ H 0.00, δ C 0.0), or residual protio solvent signals $CDCl_3$ (δ C 77.2), DMSO-d_6 (δ C 49.5). The chemical shifts of ^{19}F NMR spectra were referenced to external trifluoroacetic acid. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). EI-mass or ESI-mass data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an EI or an ESI source and controlled by Xcalibur software. Melting points are uncorrected. X-ray crystallography analysis of single crystals was performed on a Rigaku SuperNova single crystal X-ray diffractometer.

Chemicals were purchased from the Adamas, Energy Chemical, Acros, Accela, Alfa Aesar, and TCI, and used as received.

Abbreviations: m-CPBA = 3-chloroperbenzoic acid, DBU = diazabicyclo[5.4.0]undec-7-ene, DCM = dichloromethane, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran, TMG = 1,1,3,3-Tetramethylguanidine, Ts = *p*-methylbenzenesulfonyl.

Preparation of 2,4-dialkylidenetropinone-derived quaternary ammonium salts

(1) Preparation of ammonium triflates **1a-l**, **1n**, and **1o**



tropinone **S2** **1a-l**, **1n**, **1o**

4-Formylphenyl 4-methylbenzenesulfonate (**S1g**) was prepared according to a literature procedure.[1]

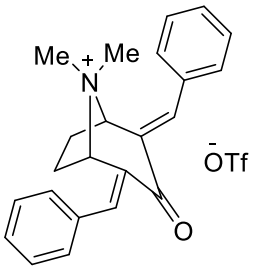
Condition A: To a solution of tropinone (696 mg, 5.0 mmol) in ethanol (20 mL) were added aldehyde **S1** (11.0 mmol, 2.2 equiv) and 5% sodium hydroxide solution (10 mL). The mixture was stirred at room temperature for 2-4 h, filtered, and washed twice with ethanol. The resulting solid crude product **S2** was directly used in the next reaction without further purification.

To a solution of crude product **S2** (5.0 mmol) in anhydrous ether (20 mL) was added methyl trifluoromethanesulfonate (903 mg, 0.62 mL, 5.5 mmol, 1.1 equiv). The mixture was stirred at room

temperature for 2 h, filtered, and washed twice with anhydrous ether to give ammonium triflates **1a**, **1d**, and **1h**.

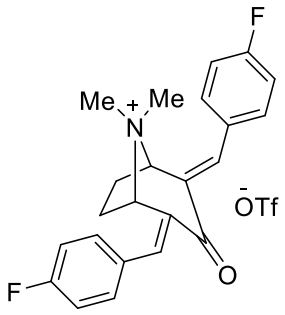
Condition B: Change from condition A by using tropinone (557 mg, 4.0 mmol) instead of tropinone (696 mg, 5.0 mmol) for the preparation of ammonium triflates **1b**, **1i**, **1j**, and **1o**.

Condition C: Change from condition A by using tropinone (418 mg, 3.0 mmol) instead of tropinone (696 mg, 5.0 mmol) for the preparation of ammonium triflates **1c**, **1e-g**, **1k**, **1l**, and **1n**.



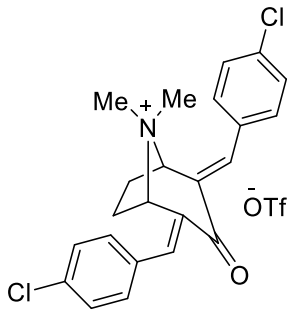
1a

(1*r*,5*s*)-2,4-Di((*E*)-benzylidene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1a**) was prepared according to condition A. Yellowish solid (2.09 g, 85% yield for two steps). m.p. 204 – 208 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.96 (s, 2H), 7.60 – 7.48 (m, 10H), 5.33 – 5.25 (m, 2H), 3.33 (s, 3H), 3.16 – 3.09 (m, 2H), 3.05 (s, 3H), 2.43 (dd, J = 14.5, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.1, 140.7, 132.8, 131.6, 130.9, 130.6, 129.2, 120.8 (q, $J_{C\text{-}F}$ = 320.3 Hz), 69.5, 50.0, 45.1, 28.0. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.77. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{23}H_{24}ON^+$ 330.1852; Found 330.1852.



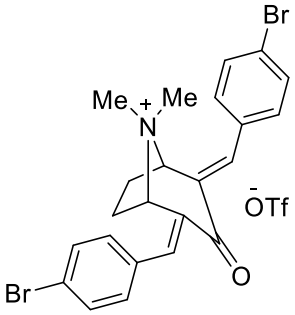
1b

(1*r*,5*s*)-2,4-Bis((*E*)-4-fluorobenzylidene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1b**) was prepared according to condition B. Yellowish solid (1.32 g, 64% yield for two steps). m.p. 249 – 252 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.93 (s, 2H), 7.63 – 7.56 (m, 4H), 7.41 – 7.35 (m, 4H), 5.28 (dd, J = 4.5, 2.5 Hz, 2H), 3.34 (s, 3H), 3.16 – 3.09 (m, 2H), 3.05 (s, 3H), 2.46 (dd, J = 14.5, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.0, 163.3 (d, $J_{C\text{-}F}$ = 248.8 Hz), 139.6, 133.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 131.4, 129.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 120.8 (q, $J_{C\text{-}F}$ = 320.1 Hz), 116.2 (d, $J_{C\text{-}F}$ = 21.6 Hz), 69.3, 50.0, 45.1, 27.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.77, -109.32. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{23}H_{22}ONF_2^+$ 366.1664; Found 366.1674.



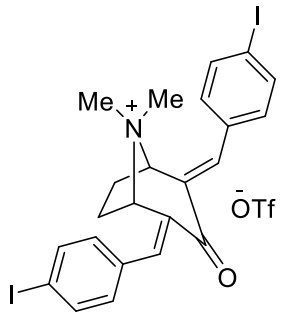
1c

(1*r*,5*s*)-2,4-Bis((*E*)-4-chlorobenzylidene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1c**) was prepared according to condition C. Yellowish solid (1.31 g, 79% yield for two steps). m.p. 247 – 253 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.94 (s, 2H), 7.61 (d, J = 8.5 Hz, 4H), 7.54 (d, J = 8.5 Hz, 4H), 5.28 – 5.20 (m, 2H), 3.29 (s, 3H), 3.11 – 3.04 (m, 2H), 3.01 (s, 3H), 2.44 (dd, J = 14.5, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.0, 139.5, 135.3, 132.5, 132.1, 131.6, 129.1, 120.7 (q, $J_{C\text{-}F}$ = 320.3 Hz), 69.2, 50.0, 45.1, 27.8. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.77. HRMS (ESI) m/z: $[M - OTf]^+$ Calcd for $C_{23}H_{22}ONCl_2^+$ 398.1073; Found 398.1068.



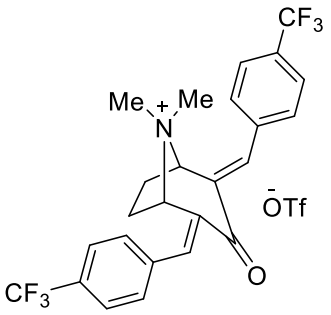
1d

(1*r*,5*s*)-2,4-Bis((*E*)-4-bromobenzylidene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1d**) was prepared according to condition A. Yellowish solid (2.84 g, 86% yield for two steps). m.p. 247 – 249 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.92 (s, 2H), 7.75 (d, J = 8.5 Hz, 4H), 7.46 (d, J = 8.5 Hz, 4H), 5.21 (dd, J = 4.5, 2.5 Hz, 2H), 3.27 (s, 3H), 3.07 – 3.02 (m, 2H), 3.00 (s, 3H), 2.44 (dd, J = 14.5, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.0, 139.6, 132.7, 132.2, 132.04, 131.98, 124.2, 120.7 (q, $J_{C\text{-}F}$ = 320.3 Hz), 69.2, 49.9, 45.1, 27.7. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.77. HRMS (ESI) m/z: $[M - OTf]^+$ Calcd for $C_{23}H_{22}ONBr_2^+$ 486.0063; Found 486.0059.



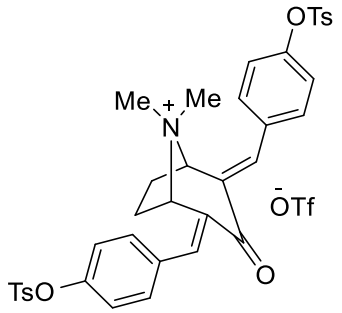
1e

(1*r*,5*s*)-2,4-Bis((*E*)-4-iodobenzylidene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1e**) was prepared according to condition C. Yellowish solid (1.83 g, 83% yield for two steps). m.p. 230 – 232 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, J = 8.4 Hz, 4H), 7.85 (s, 2H), 7.26 (d, J = 8.4 Hz, 4H), 5.21 (dd, J = 5.5, 3.0 Hz, 2H), 3.28 (s, 3H), 3.10 – 3.02 (m, 2H), 2.99 (s, 3H), 2.43 (dd, J = 17.5, 6.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.8, 139.9, 137.9, 132.4, 132.1, 132.0, 120.7 (q, $J_{C\text{-}F}$ = 320.3 Hz), 98.1, 69.2, 49.9, 45.1, 27.8. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.76. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{23}H_{22}ONI_2^+$ 581.9785; Found 581.9773.



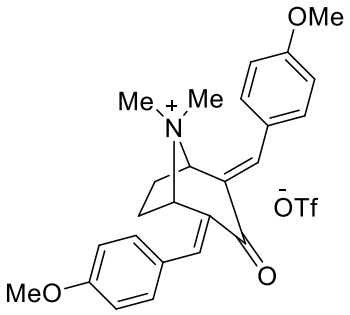
1f

(1*r*,5*s*)-8,8-Dimethyl-3-oxo-2,4-bis((*E*)-4-(trifluoromethyl)benzylidene)-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1f**) was prepared according to condition C. Yellow solid (1.14 g, 62% yield for two steps). m.p. 234 – 238 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (s, 2H), 7.88 (d, J = 8.0 Hz, 4H), 7.71 (d, J = 8.0 Hz, 4H), 5.32 – 5.21 (m, 2H), 3.31 (s, 3H), 3.19 – 3.09 (m, 2H), 3.05 (s, 3H), 2.57 (dd, J = 17.5, 6.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 181.0, 139.5, 136.8, 133.3, 131.3, 130.1 (q, $J_{C\text{-}F}$ = 31.9 Hz), 125.8 (q, $J_{C\text{-}F}$ = 3.9 Hz), 124.0 (q, $J_{C\text{-}F}$ = 270.6 Hz), 120.8 (q, $J_{C\text{-}F}$ = 320.1 Hz), 69.3, 50.0, 45.3, 27.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.42, -77.81. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{25}H_{22}ONF_6^+$ 466.1600; Found 466.1589.



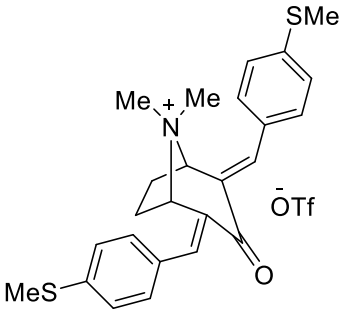
1g

(1*r*,5*s*)-8,8-Dimethyl-3-oxo-2,4-bis((*E*)-4-(tosyloxy)benzylidene)-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1g**) was prepared according to condition C. Yellow solid (1.08 g, 44% yield for two steps). m.p. 175 – 177 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.92 (s, 2H), 7.84 (d, J = 8.0 Hz, 4H), 7.58 (d, J = 8.0 Hz, 4H), 7.52 (d, J = 8.0 Hz, 4H), 7.25 (d, J = 8.0 Hz, 4H), 5.26 – 5.21 (m, 2H), 3.31 (s, 3H), 3.14 – 3.07 (m, 2H), 3.05 (s, 3H), 2.45 (s, 6H), 2.39 (dd, J = 14.5, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.0, 150.2, 146.2, 139.3, 132.9, 132.1, 131.9, 131.6, 130.5, 128.3, 122.7, 120.8 (q, $J_{C\text{-}F}$ = 320.1 Hz), 69.3, 50.1, 45.2, 27.8, 21.3. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.72. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{37}H_{36}ONS_2^+$ 670.1928; Found 670.1918.



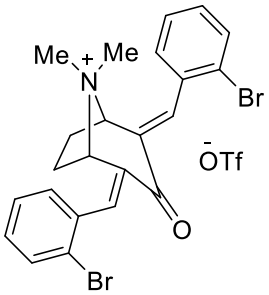
1h

(1*r*,5*s*)-2,4-Bis((*E*)-4-methoxybenzylidene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1h**) was prepared according to condition A. Yellow solid (1.54 g, 57% yield for two steps). m.p. 231 – 233 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (s, 2H), 7.50 (d, J = 8.8 Hz, 4H), 7.11 (d, J = 8.8 Hz, 4H), 5.28 (dd, J = 5.5, 2.5 Hz, 2H), 3.84 (s, 6H), 3.32 (s, 3H), 3.12 – 3.08 (m, 2H), 3.02 (s, 3H), 2.37 (dd, J = 17.5, 6.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.8, 161.3, 140.1, 133.1, 129.6, 125.3, 120.7 (q, $J_{C\text{-}F}$ = 320.3 Hz), 114.7, 69.4, 55.5, 50.0, 45.0, 27.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.77. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{25}H_{28}O_3N^+$ 390.2064; Found 390.2059.



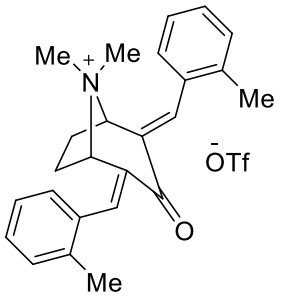
1i

(1*r*,5*s*)-8,8-Dimethyl-2,4-bis((*E*)-4-(methylthio)benzylidene)-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1i**) was prepared according to condition B. Yellow solid (1.57 g, 69% yield for two steps). m.p. 233 – 234 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.87 (s, 2H), 7.44 (d, J = 8.5 Hz, 4H), 7.39 (d, J = 8.5 Hz, 4H), 5.26 (dd, J = 4.5, 2.5 Hz, 2H), 3.30 (s, 3H), 3.12 – 3.04 (m, 2H), 3.01 (s, 3H), 2.54 (s, 6H), 2.39 (dd, J = 14.5, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 180.8, 142.6, 140.1, 131.4, 130.8, 128.9, 125.5, 120.7 (q, $J_{C\text{-}F}$ = 320.3 Hz), 69.4, 50.0, 45.0, 27.9, 14.1. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.77. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{25}H_{28}ONS_2^+$ 422.1607; Found 422.1597.



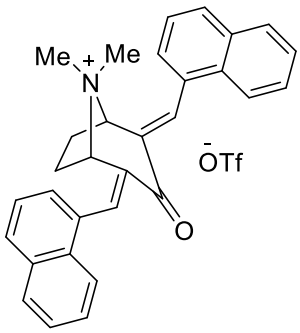
1j

(1*r*,5*s*)-2,4-Bis((*E*)-2-bromobenzylidene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1j**) was prepared according to condition B. Yellow solid (1.70 g, 67% yield for two steps). m.p. 200 – 202 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (s, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.2 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H), 5.10 – 5.01 (m, 2H), 3.28 (s, 3H), 3.09 (s, 3H), 3.06 – 2.97 (m, 2H), 2.50 (dd, J = 14.0, 5.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 181.3, 140.0, 133.1, 132.89, 132.85, 131.9, 131.0, 128.3, 124.6, 120.7 (q, $J_{C\text{-}F}$ = 320.1 Hz), 69.3, 49.8, 45.1, 27.7. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.77. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{23}H_{22}ONBr_2^+$ 486.0063; Found 486.0058.



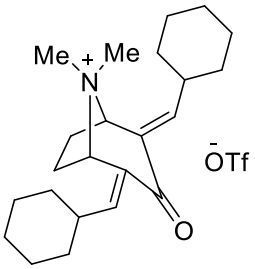
1k

(1*r*,5*s*)-8,8-Dimethyl-2,4-bis((*E*)-2-methylbenzylidene)-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1k**) was prepared according to condition C. Yellow solid (911 mg, 60% yield for two steps). m.p. 184 – 186 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.07 (s, 2H), 7.45 – 7.40 (m, 2H), 7.40 – 7.33 (m, 4H), 7.17 – 7.11 (m, 2H), 5.00 – 4.90 (m, 2H), 3.23 (s, 3H), 3.05 (s, 3H), 3.00 – 2.91 (m, 2H), 2.47 (dd, J = 14.5, 5.5 Hz, 2H), 2.35 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.7, 140.0, 138.4, 132.4, 132.2, 130.6, 130.2, 129.1, 126.3, 120.7 (q, $J_{C\text{-}F}$ = 320.1 Hz), 69.6, 49.8, 45.1, 27.9, 19.8. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.75. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{25}H_{28}ON^+$ 358.2165; Found 358.2161.



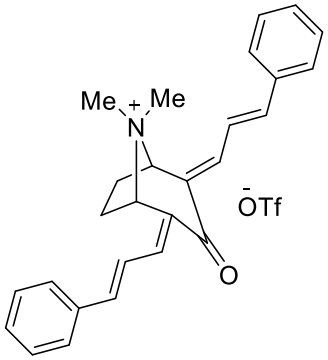
1l

(1*r*,5*s*)-8,8-Dimethyl-2,4-bis((*E*)-naphthalen-1-ylmethylene)-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1l**) was prepared according to condition C. Yellow solid (933 mg, 53% yield for two steps). m.p. 203 – 204 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.58 (s, 2H), 8.18 – 8.01 (m, 6H), 7.76 – 7.62 (m, 6H), 7.42 (d, J = 7.0 Hz, 2H), 5.13 – 5.01 (m, 2H), 3.18 (s, 3H), 3.08 (s, 3H), 3.05 – 2.97 (m, 2H), 2.66 – 2.55 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.7, 139.1, 133.9, 133.3, 131.5, 130.5, 130.1, 128.8, 128.0, 127.4, 126.9, 125.7, 124.4, 120.8 (q, $J_{C\text{-}F}$ = 320.3 Hz), 69.8, 49.7, 45.1, 27.9. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.69. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{31}H_{28}ON^+$ 430.2165; Found 430.2156.



1n

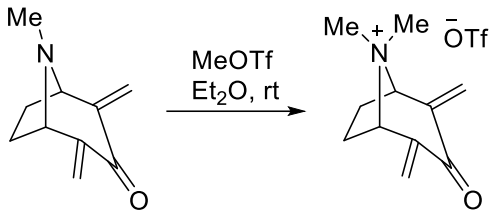
(1*r*,5*s*)-2,4-Bis((*E*)-cyclohexylmethylene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1n**) was prepared according to condition C. White solid (676 mg, 45% yield for two steps). m.p. 230 – 232 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.75 – 6.70 (m, 2H), 5.10 (dd, J = 4.5, 2.5 Hz, 2H), 3.30 (s, 3H), 2.98 (s, 3H), 2.81 – 2.73 (m, 2H), 2.55 – 2.45 (m, 2H), 2.43 (dd, J = 14.5, 5.5 Hz, 2H), 1.75 – 1.68 (m, 4H), 1.68 – 1.62 (m, 4H), 1.55 – 1.47 (m, 2H), 1.39 – 1.27 (m, 4H), 1.25 – 1.14 (m, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.8, 149.6, 131.5, 120.7 (q, $J_{C\text{-}F}$ = 320.3 Hz), 69.0, 49.6, 45.3, 35.8, 31.3, 31.0, 28.0, 25.2, 24.8, 24.6. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.78. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{23}H_{36}ON^+$ 342.2791; Found 342.2786.



1o

(1*r*,2*E*,4*E*,5*s*)-8,8-Dimethyl-3-oxo-2,4-bis((*E*)-3-phenylallylidene)-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1o**) was prepared according to condition B. Yellow solid (1.02 g, 48% yield for two steps). m.p. 183 – 187 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 – 7.71 (m, 4H), 7.58 – 7.54 (m, 2H), 7.47 – 7.39 (m, 8H), 7.36 – 7.31 (m, 2H), 5.57 – 5.53 (m, 2H), 3.41 (s, 3H), 3.09 (s, 3H), 2.92 – 2.85 (m, 2H), 2.02 (dd, J = 14.5, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.0, 145.6, 139.7, 135.9, 131.3, 130.0, 128.9, 128.1, 122.2, 120.8 (q, $J_{C\text{-}F}$ = 320.0 Hz), 69.5, 49.9, 45.6, 28.2. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.78. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{27}H_{28}ON^+$ 382.2165; Found 382.2173.

(2) Preparation of ammonium triflate **1m**

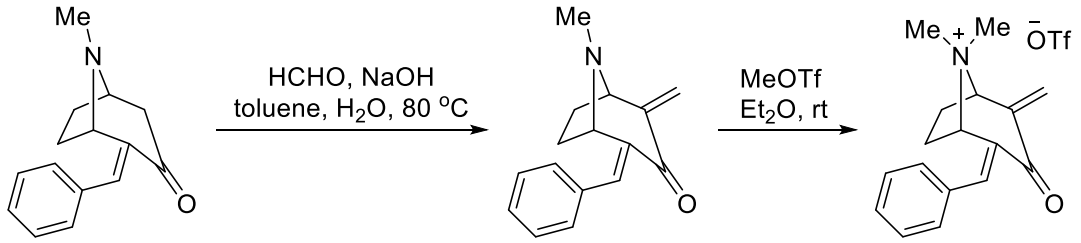


S2m **1m**

2,4-Dimethylidenetropinone **S2m** was prepared according to a literature procedure.[2]

To a solution of 2,4-dimethylidenetropinone **S2m** (196 mg, 1.2 mmol, 1.0 equiv) in anhydrous ether (10 mL) was added methyl trifluoromethanesulfonate (216 mg, 0.15 mL, 1.3 mmol, 1.1 equiv). The mixture was stirred at room temperature for 2 h, filtered, and washed twice with anhydrous ether to give (1*r*,5*s*)-8,8-dimethyl-2,4-dimethylene-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1m**) as a white solid (357 mg, 90% yield). m.p. 156 – 160 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.33 (s, 2H), 5.85 (s, 2H), 4.96 (dd, J = 4.5, 2.5 Hz, 2H), 3.25 (s, 3H), 3.06 (s, 3H), 2.80 – 2.67 (m, 2H), 2.07 (dd, J = 14.5, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 182.1, 140.3, 128.4, 120.7 (q, $J_{C\text{-}F}$ = 320.0 Hz), 73.6, 49.4, 45.8, 27.3. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.78. HRMS (ESI) m/z: [M - OTf]$^+$ Calcd for $C_{11}H_{16}ON^+$ 178.1226; Found 178.1223.

(3) Preparation of ammonium triflate **1p**



S3 **S2p** **1p**

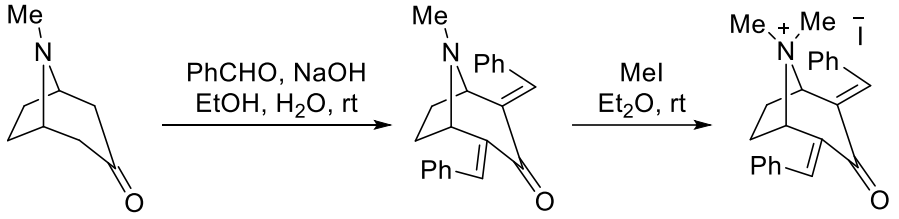
2-Benzylidenetropinone **S3** was prepared according to a literature procedure.[3]

To a solution of 2-benzylidenetropinone **S3** (455 mg, 2.0 mmol) in toluene (15 mL) were added paraformaldehyde (1.08 g, 12.0 mmol, 6.0 equiv) and 5% sodium hydroxide solution (25 mL). The mixture was heated at 80 °C for 5 h, and cooled to room temperature. The mixture was extracted twice with dichloromethane (20 mL), and the combined extracts were washed with saturated brine, and dried over anhydrous sodium sulfate. After the solvent was evaporated under reduced pressure, the residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 2/1) to give 2-methylene-4-phenylmethylene-3-tropinone (**S2p**) as a yellow oil (468 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.46 – 7.40 (m, 2H), 7.39 – 7.33 (m, 3H), 6.24 (d, J = 2.0 Hz, 1H), 5.32 (d, J = 2.0 Hz, 1H), 4.37 (d, J = 7.0 Hz, 1H), 3.95 (d, J = 7.0 Hz, 1H), 2.54 – 2.42 (m, 2H), 2.34 (s, 3H), 1.96 – 1.89 (m, 1H), 1.82 – 1.75 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 146.2, 138.5,

137.3, 135.1, 130.3, 129.0, 128.7, 121.8, 65.3, 60.9, 35.7, 30.5, 30.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}ON^+$ 240.1383; Found 240.1387.

To a solution of 2,4-dialkylidenetropinone **S2p** (479 mg, 2.0 mmol, 1.0 equiv) in anhydrous ether (10 mL) was added methyl trifluoromethanesulfonate (368 mg, 0.25 mL, 2.2 mmol, 1.1 equiv). The mixture was stirred at room temperature for 2 h, filtered, and washed twice with anhydrous ether to give (1*r*,5*s*)-2-(*E*)-benzylidene-8,8-dimethyl-4-methylene-3-oxo-8-azabicyclo[3.2.1]octan-8-ium trifluoromethanesulfonate (**1p**) as a yellow solid (651 mg, 86% yield). m.p. 172 – 175 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.91 (s, 1H), 7.60 – 7.48 (m, 5H), 6.40 (s, 1H), 5.87 (s, 1H), 5.27 (d, J = 6.5 Hz, 1H), 5.00 (d, J = 6.5 Hz, 1H), 3.30 (s, 3H), 3.06 (s, 3H), 3.02 – 2.94 (m, 1H), 2.93 – 2.83 (m, 1H), 2.39 – 2.29 (m, 1H), 2.22 – 2.11 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 181.6, 141.2, 140.3, 132.7, 131.6, 130.9, 130.6, 129.2, 127.9, 120.7 (q, $J_{C\text{-}F}$ = 320.1 Hz), 73.2, 69.7, 49.7, 45.5, 27.8, 27.6. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.73. HRMS (ESI) m/z: $[M - OTf]^+$ Calcd for $C_{17}H_{20}ON^+$ 254.1539; Found 254.1545.

(4) Preparation of ammonium triflate **1ab**

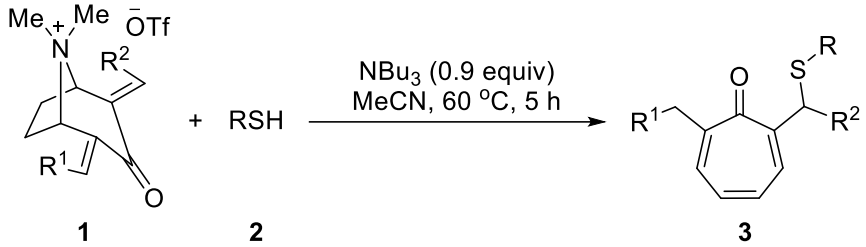


tropinone **S2a** **1ab**

To a solution of tropinone (418 mg, 3.0 mmol) in ethanol (15 mL) were added benzaldehyde (702 mg, 672 µL, 6.6 mmol, 2.2 equiv) and 5% sodium hydroxide solution (6.0 mL). The mixture was stirred at room temperature for 2 h, filtered, and washed twice with ethanol. The resulting solid crude product **S2a** was directly used in the next reaction without further purification.

To a solution of crude product **S2a** (3.0 mmol) in anhydrous ether (20 mL) was added methyl iodide (468 mg, 207 µL, 3.3 mmol, 1.1 equiv). The mixture was stirred at room temperature for 2 h, filtered, and washed twice with anhydrous ether to give (1*r*,5*s*)-2,4-di((*E*)-benzylidene)-8,8-dimethyl-3-oxo-8-azabicyclo[3.2.1]octan-8-ium iodide (**1ab**) as a yellowish solid (673 mg, 50% yield for two steps). m.p. 240 – 242 ℃.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (s, 2H), 7.60 – 7.52 (m, 10H), 5.27 (dd, J = 4.8, 2.8 Hz, 2H), 3.33 (s, 3H), 3.17 – 3.09 (m, 2H), 3.05 (s, 3H), 2.45 (dd, J = 14.4, 5.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 181.1, 140.6, 132.7, 131.6, 130.9, 130.5, 129.2, 69.3, 50.1, 45.1, 28.0. HRMS (ESI) m/z: $[M - I]^+$ Calcd for $C_{23}H_{24}ON^+$ 330.1852; Found 330.1854.

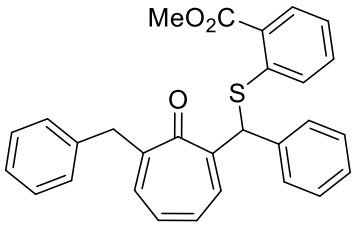
General procedure for the reaction of 2,4-dialkylidenetropinone-derived quaternary ammonium salts with thiols



1 **2** **3**

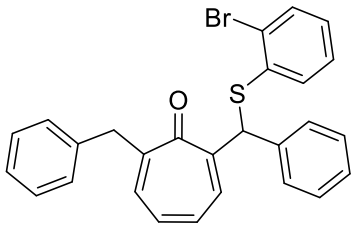
A mixture of 2,4-dialkylidenetropinone-derived quaternary ammonium salt **1** (0.20 mmol), thiol **2** (0.30 mmol), and tributylamine (33.4 mg, 43.0 μL, 0.18 mmol) in acetonitrile (1.2 mL) was heated in a sealed tube at 60 ℃ for 5 h, and cooled to room temperature. The mixture was directly purified by silica gel chromatography, using petroleum ether/ethyl acetate (5/1 ~ 25/1) as the eluent, to give tropone **3**.

Analytical data for the products (Schemes 2 and 3)



3a

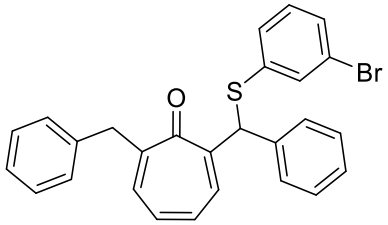
Methyl 2-(((6-benzyl-7-oxocyclohepta-1,3,5-trien-1-yl)(phenyl)methyl)thio)benzoate (**3a**). White solid (78.1 mg, 86% yield). m.p. 95 – 96 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.0, 1.5 Hz, 1H), 7.78 (dd, J = 8.0, 1.5 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.31 – 7.26 (m, 4H), 7.25 – 7.21 (m, 2H), 7.21 – 7.16 (m, 3H), 7.12 – 7.04 (m, 3H), 6.95 – 6.90 (m, 1H), 6.90 – 6.85 (m, 1H), 6.45 (s, 1H), 4.06 (d, J = 16.0 Hz, 1H), 4.01 (d, J = 16.0 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 167.0, 153.3, 150.3, 141.8, 139.3, 139.2, 136.0, 135.5, 133.3, 132.8, 132.1, 131.3, 129.5, 128.9, 128.8, 128.7, 127.6, 126.7, 126.5, 126.4, 124.1, 52.3, 50.6, 41.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{25}O_3S^+$ 453.1519; Found 453.1525.



3b

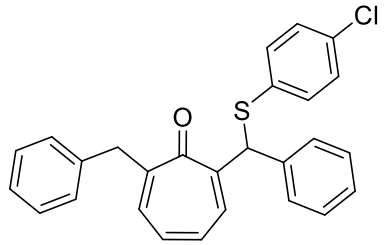
2-Benzyl-7-(((2-bromophenyl)thio)(phenyl)methyl)cyclohepta-2,4,6-trien-1-one (**3b**). Yellow oil (88.7 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 1H), 7.51 – 7.45 (m, 3H), 7.32 – 7.26 (m, 3H), 7.26 – 7.20 (m, 3H), 7.18 – 7.14 (m, 2H), 7.11 – 7.07 (m, 1H), 7.06 – 7.01 (m,

1H), 7.00 – 6.97 (m, 1H), 6.96 – 6.90 (m, 2H), 6.90 – 6.85 (m, 1H), 6.42 (s, 1H), 4.05 (d, *J* = 16.0 Hz, 1H), 3.99 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.7, 153.4, 149.8, 139.2, 138.9, 137.8, 135.7, 135.4, 133.4, 132.8, 132.0, 129.5, 128.8, 128.7, 128.1, 128.0, 127.8, 126.6, 126.5, 122.1, 51.8, 41.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}OBrNaS^+$ 495.0389; Found 495.0398.



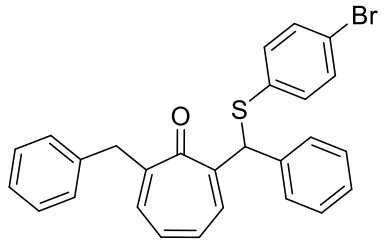
3c

2-Benzyl-7-(((3-bromophenyl)thio)(phenyl)methyl)cyclohepta-2,4,6-trien-1-one (**3c**). Yellow oil (90.5 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 1H), 7.49 – 7.44 (m, 2H), 7.38 (t, *J* = 2.0 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.26 – 7.20 (m, 4H), 7.18 – 7.12 (m, 3H), 7.08 – 7.04 (m, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.95 – 6.90 (m, 1H), 6.89 – 6.84 (m, 1H), 6.33 (s, 1H), 4.04 (d, *J* = 16.0 Hz, 1H), 3.99 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 153.5, 150.3, 139.4, 139.3, 138.6, 135.7, 135.4, 133.4, 131.85, 131.78, 130.3, 129.5, 129.4, 128.8, 128.7, 128.6, 127.68, 127.66, 126.5, 122.7, 52.9, 41.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}OBrS^+$ 473.0569; Found 473.0576.



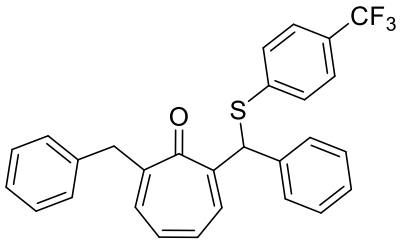
3d

2-Benzyl-7-(((4-chlorophenyl)thio)(phenyl)methyl)cyclohepta-2,4,6-trien-1-one (**3d**). Yellow oil (72.9 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.31 – 7.25 (m, 4H), 7.24 – 7.20 (m, 2H), 7.18 – 7.13 (m, 4H), 7.13 – 7.09 (m, 2H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.91 (t, *J* = 9.0 Hz, 1H), 6.85 (t, *J* = 9.0 Hz, 1H), 6.29 (s, 1H), 4.03 (d, *J* = 16.0 Hz, 1H), 3.97 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 153.4, 150.5, 139.6, 139.2, 135.7, 135.3, 134.6, 133.3, 132.6, 131.8, 131.1, 129.5, 129.1, 128.74, 128.67, 128.6, 127.6, 126.5, 53.3, 41.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}OClS^+$ 429.1074; Found 429.1081.



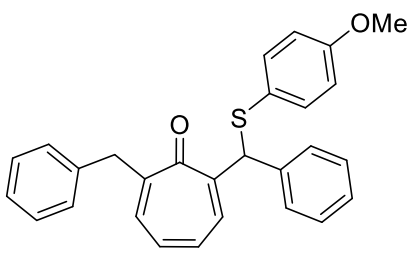
3e

2-Benzyl-7-(((4-bromophenyl)thio)(phenyl)methyl)cyclohepta-2,4,6-trien-1-one (**3e**). Yellow oil (75.9 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 1H), 7.48 – 7.43 (m, 2H), 7.30 – 7.24 (m, 5H), 7.24 – 7.18 (m, 3H), 7.16 – 7.13 (m, 2H), 7.10 – 7.03 (m, 3H), 6.92 – 6.86 (m, 1H), 6.85 – 6.80 (m, 1H), 6.30 (s, 1H), 4.03 (d, J = 16.0 Hz, 1H), 3.97 (d, J = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.5, 153.4, 150.4, 139.5, 139.2, 135.6, 135.3, 133.3, 131.9, 131.8, 131.1, 129.4, 128.7, 128.6, 128.5, 127.6, 126.5, 120.4, 53.0, 41.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}OBrS^+$ 473.0569; Found 473.0575.



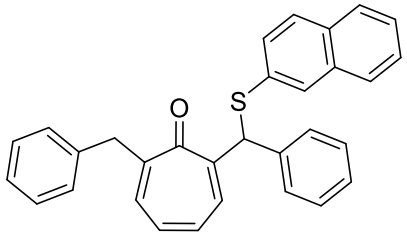
3f

2-Benzyl-7-(phenyl((4-(trifluoromethyl)phenyl)thio)methyl)cyclohepta-2,4,6-trien-1-one (**3f**). Yellow oil (87.3 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.0, 1.5 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.24 (m, 5H), 7.24 – 7.20 (m, 3H), 7.19 – 7.14 (m, 2H), 7.10 (dd, J = 8.0, 1.5 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.89 – 6.84 (m, 1H), 6.43 (s, 1H), 4.08 (d, J = 16.0 Hz, 1H), 3.98 (d, J = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.5, 153.5, 150.1, 141.8, 139.1, 139.0, 135.7, 135.4, 133.5, 131.9, 129.5, 128.9, 128.7, 128.5, 127.8, 127.7 (q, J_{C-F} = 32.4 Hz), 127.6, 126.6, 125.7 (q, J_{C-F} = 3.8 Hz), 124.2 (q, J_{C-F} = 270.1 Hz), 51.8, 41.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.35. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{22}OF_3S^+$ 463.1338; Found 463.1343.



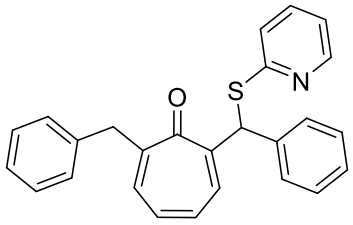
3g

2-Benzyl-7-(((4-methoxyphenyl)thio)(phenyl)methyl)cyclohepta-2,4,6-trien-1-one (**3g**). Yellow oil (38.7 mg, 46% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 9.0 Hz, 1H), 7.46 (d, J = 7.5 Hz, 2H), 7.29 – 7.24 (m, 6H), 7.20 (t, J = 7.0 Hz, 2H), 7.13 (d, J = 7.5 Hz, 2H), 7.01 (d, J = 9.0 Hz, 1H), 6.94 (t, J = 9.5 Hz, 1H), 6.84 (t, J = 9.5 Hz, 1H), 6.73 – 6.70 (m, 2H), 6.15 (s, 1H), 3.99 (d, J = 16.5 Hz, 1H), 3.95 (d, J = 16.5 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.8, 159.3, 153.3, 151.3, 140.4, 139.4, 135.7, 135.1, 133.8, 133.0, 131.9, 129.6, 128.67, 128.66, 128.6, 127.3, 126.5, 126.1, 114.6, 55.4, 55.1, 41.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}O_2S^+$ 425.1570; Found 425.1576.



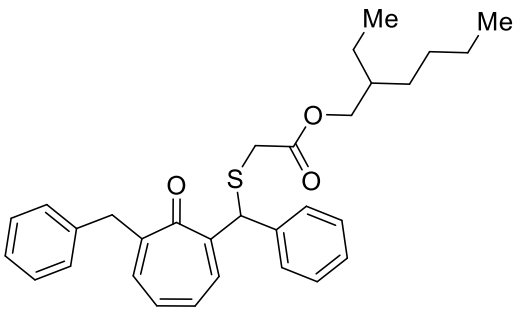
3h

2-Benzyl-7-((naphthalen-2-ylthio)(phenyl)methyl)cyclohepta-2,4,6-trien-1-one (**3h**). Yellow oil (35.6 mg, 40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H), 7.74 – 7.70 (m, 1H), 7.66 – 7.61 (m, 2H), 7.60 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 7.42 – 7.36 (m, 3H), 7.28 (t, J = 7.5 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.15 – 7.09 (m, 2H), 7.05 – 7.00 (m, 1H), 6.92 (t, J = 9.5 Hz, 1H), 6.83 (t, J = 9.5 Hz, 1H), 6.48 (s, 1H), 4.01 (d, J = 16.0 Hz, 1H), 3.96 (d, J = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.8, 153.4, 150.8, 139.9, 139.4, 135.7, 135.3, 133.8, 133.6, 133.2, 132.0, 131.9, 129.6, 128.75, 128.68, 128.5, 127.9, 127.7, 127.6, 127.5, 127.4, 126.51, 126.49, 125.9, 53.0, 41.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{24}ONaS^+$ 467.1440; Found 467.1447.



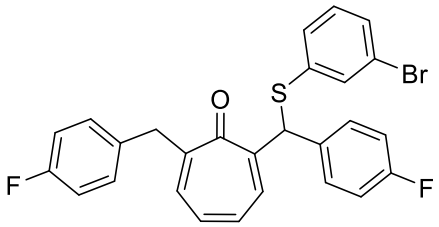
3i

2-Benzyl-7-(phenyl(pyridin-2-ylthio)methyl)cyclohepta-2,4,6-trien-1-one (**3i**). Yellow oil (20.7 mg, 26% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.26 (m, 1H), 7.83 – 7.78 (m, 1H), 7.53 – 7.49 (m, 2H), 7.42 – 7.37 (m, 1H), 7.30 – 7.25 (m, 4H), 7.24 – 7.16 (m, 4H), 7.11 – 7.03 (m, 2H), 6.95 – 6.90 (m, 2H), 6.89 – 6.83 (m, 1H), 6.74 (s, 1H), 4.10 (d, J = 16.0 Hz, 1H), 3.98 (d, J = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.9, 158.7, 153.3, 151.4, 149.4, 139.7, 139.5, 136.3, 135.2, 135.1, 133.1, 131.9, 129.6, 128.7, 128.6, 128.5, 127.3, 126.5, 121.6, 119.8, 50.7, 41.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}ONS^+$ 396.1417; Found 396.1421.



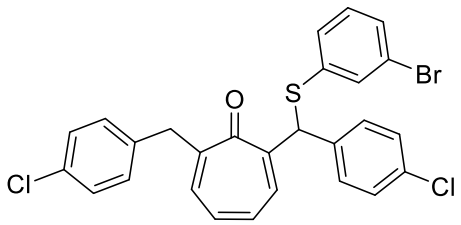
3j

2-Ethylhexyl 2-(((6-benzyl-7-oxocyclohepta-1,3,5-trien-1-yl)(phenyl)methyl)thio)acetate (**3j**). Yellow oil (47.9 mg, 49% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 1H), 7.49 – 7.44 (m, 2H), 7.32 – 7.15 (m, 8H), 7.03 (dd, J = 8.5, 1.0 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.90 – 6.85 (m, 1H), 5.96 (s, 1H), 4.00 (s, 2H), 3.98 – 3.89 (m, 2H), 3.24 (d, J = 14.5 Hz, 1H), 3.18 (d, J = 14.5 Hz, 1H), 1.58 – 1.50 (m, 1H), 1.36 – 1.28 (m, 4H), 1.27 – 1.24 (m, 4H), 0.91 – 0.84 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 170.1, 153.6, 150.7, 139.8, 139.3, 135.3, 135.0, 133.1, 131.8, 129.6, 128.7, 128.64, 128.62, 127.5, 126.5, 68.0, 51.2, 41.2, 38.68, 38.67, 35.0, 30.3, 28.98, 28.96, 23.7, 23.1, 14.2, 11.1, 11.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{37}O_3S^+$ 489.2458; Found 489.2461.



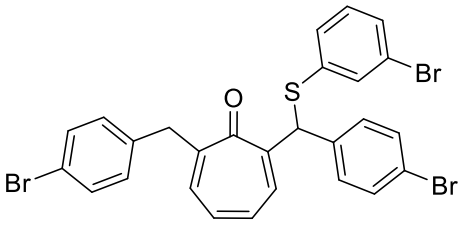
3k

2-(((3-Bromophenyl)thio)(4-fluorophenyl)methyl)-7-(4-fluorobenzyl)cyclohepta-2,4,6-trien-1-one (**3k**). Yellow oil (73.2 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 1H), 7.42 – 7.35 (m, 3H), 7.25 – 7.21 (m, 1H), 7.13 – 7.07 (m, 4H), 7.00 (t, J = 8.0 Hz, 1H), 6.98 – 6.92 (m, 5H), 6.91 – 6.87 (m, 1H), 6.25 (s, 1H), 3.96 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.4, 162.9 (d, $J_{C\text{-}F}$ = 62.6 Hz), 160.9 (d, $J_{C\text{-}F}$ = 60.3 Hz), 153.1, 150.1, 138.2, 135.5, 135.3, 135.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 134.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 133.4, 131.9 (d, $J_{C\text{-}F}$ = 5.0 Hz), 130.8 (d, $J_{C\text{-}F}$ = 7.8 Hz), 130.3, 130.2 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.6, 127.8, 122.7, 115.7, 115.5 (d, $J_{C\text{-}F}$ = 5.5 Hz), 115.3, 52.4, 40.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.43, -116.51. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{20}OBrF_2S^+$ 509.0381; Found 509.0388.



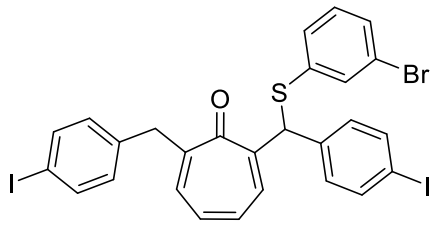
3l

2-(((3-Bromophenyl)thio)(4-chlorophenyl)methyl)-7-(4-chlorobenzyl)cyclohepta-2,4,6-trien-1-one (**3l**). Yellow oil (61.0 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 1H), 7.38 – 7.33 (m, 3H), 7.27 – 7.20 (m, 5H), 7.14 – 7.06 (m, 4H), 7.02 (t, J = 8.0 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.94 – 6.89 (m, 1H), 6.21 (s, 1H), 3.95 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.3, 152.9, 150.0, 138.0, 137.9, 137.6, 135.6, 135.5, 133.6, 133.5, 132.4, 132.1, 132.0, 130.7, 130.4, 129.9, 129.8, 128.9, 128.7, 127.9, 122.8, 52.6, 41.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{20}OBrCl_2S^+$ 540.9790; Found 540.9795.



3m

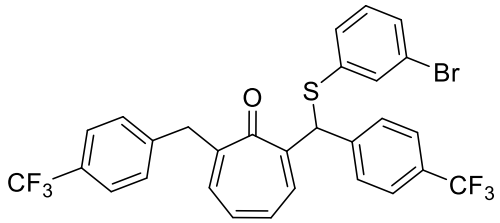
2-(4-Bromobenzyl)-7-((4-bromophenyl)((3-bromophenyl)thio)methyl)cyclohepta-2,4,6-trien-1-one (**3m**). Yellow oil (101.5 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 1H), 7.42 – 7.33 (m, 5H), 7.32 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.13 – 7.09 (m, 2H), 7.04 – 6.99 (m, 3H), 6.98 – 6.93 (m, 1H), 6.93 – 6.88 (m, 1H), 6.19 (s, 1H), 3.95 (d, J = 16.5 Hz, 1H), 3.91 (d, J = 16.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2, 152.7, 150.0, 138.4, 138.1, 137.9, 135.6, 135.5, 133.5, 132.1, 132.0, 131.8, 131.7, 131.0, 130.4, 130.2, 129.8, 127.9, 122.8, 121.7, 120.4, 52.6, 41.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{20}OBr_3S^+$ 628.8780; Found 628.8778.



3n

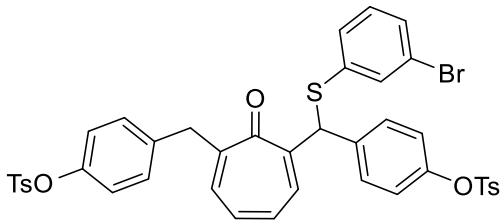
2-(((3-Bromophenyl)thio)(4-iodophenyl)methyl)-7-(4-iodobenzyl)cyclohepta-2,4,6-trien-1-one (**3n**). Yellow oil (94.8 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.52 (m, 5H), 7.35 (t, J = 2.0 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.20 – 7.15 (m, 2H), 7.13 – 7.09 (m, 2H), 7.02 (t, J = 7.5 Hz, 1H),

6.99 – 6.94 (m, 1H), 6.94 – 6.88 (m, 3H), 6.18 (s, 1H), 3.94 (d, *J* = 16.5 Hz, 1H), 3.91 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2, 152.7, 149.9, 139.1, 138.8, 137.9, 137.8, 137.7, 135.7, 135.6, 133.5, 132.1, 131.9, 131.4, 130.5, 130.4, 129.7, 127.8, 122.8, 93.5, 91.9, 52.7, 41.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{20}OBrI_2S^+$ 724.8502; Found 724.8500.



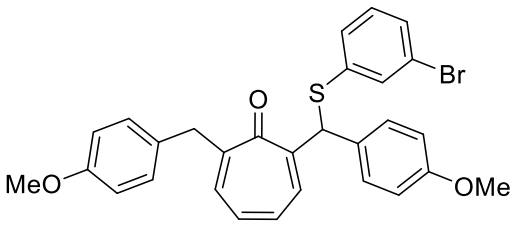
3o

2-(((3-Bromophenyl)thio)(4-(trifluoromethyl)phenyl)methyl)-7-(4-(trifluoromethyl)benzyl)cyclohepta-2,4,6-trien-1-one (**3o**). Yellow oil (92.2 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 1H), 7.58 – 7.52 (m, 4H), 7.52 – 7.48 (m, 2H), 7.38 (t, *J* = 2.0 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.21 – 7.17 (m, 1H), 7.15 – 7.11 (m, 1H), 7.05 – 6.94 (m, 3H), 6.27 (s, 1H), 4.07 (d, *J* = 16.5 Hz, 1H). 4.03 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.1, 152.4, 149.9, 143.5, 143.3, 137.6, 136.00, 135.95, 133.7, 132.3, 132.2, 130.5, 130.0, 129.8 (q, J_{C-F} = 32.3 Hz), 129.5, 128.9, 128.8 (q, J_{C-F} = 32.1 Hz), 128.1, 125.7 (q, J_{C-F} = 3.8 Hz), 125.5 (q, J_{C-F} = 3.8 Hz), 124.3 (q, J_{C-F} = 270.4 Hz), 124.1 (q, J_{C-F} = 270.4 Hz), 122.8, 53.1, 41.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.33, -62.49. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{20}OBrF_6S^+$ 609.0317; Found 609.0320.



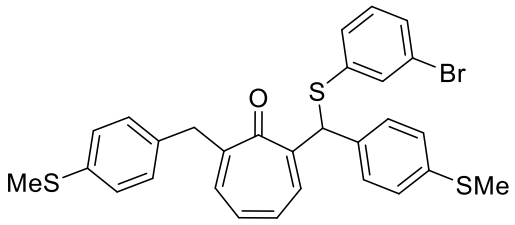
3p

4-((6-(((3-Bromophenyl)thio)(4-(tosyloxy)phenyl)methyl)-7-oxocyclohepta-1,3,5-trien-1-yl)methyl)phenyl 4-methylbenzenesulfonate (**3p**). Yellow oil (84.0 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.63 – 7.60 (m, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.24 (m, 6H), 7.12 – 7.06 (m, 4H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.95 – 6.92 (m, 1H), 6.92 – 6.87 (m, 4H), 6.19 (s, 1H), 3.98 (d, *J* = 15.5 Hz, 1H), 3.90 (d, *J* = 15.5 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2, 152.7, 150.1, 148.9, 148.2, 145.6, 145.4, 138.4, 138.2, 137.9, 135.9, 135.8, 133.6, 132.5, 132.4, 132.2, 132.1, 130.5, 130.4, 129.89, 129.86, 129.80, 129.78, 128.54, 128.52, 128.1, 122.7, 122.6, 122.5, 52.4, 40.9, 21.85, 21.83. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{34}O_7BrS_3^+$ 813.0645; Found 813.0639.



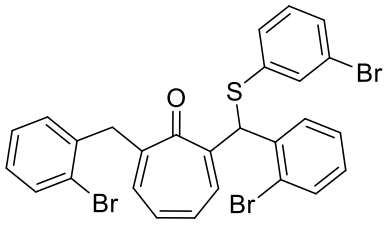
3q

2-(((3-Bromophenyl)thio)(4-methoxyphenyl)methyl)-7-(4-methoxybenzyl)cyclohepta-2,4,6-trien-1-one (**3q**). Yellow oil (59.3 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 1H), 7.39 – 7.34 (m, 3H), 7.24 – 7.20 (m, 1H), 7.14 – 7.10 (m, 1H), 7.09 – 7.03 (m, 3H), 7.00 (t, J = 8.0 Hz, 1H), 6.95 – 6.90 (m, 1H), 6.89 – 6.84 (m, 1H), 6.83 – 6.78 (m, 4H), 6.28 (s, 1H), 3.94 (s, 2H), 3.77 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.7, 159.0, 158.3, 153.8, 150.3, 138.8, 135.4, 135.1, 133.3, 131.7, 131.6, 131.20, 131.17, 130.5, 130.3, 129.7, 129.3, 127.5, 122.7, 114.12, 114.06, 55.3, 52.2, 40.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{26}O_3BrS^+$ 533.0781; Found 533.0776.



3r

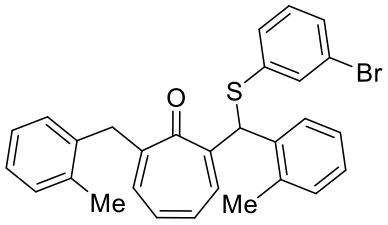
2-(((3-Bromophenyl)thio)(4-(methylthio)phenyl)methyl)-7-(4-(methylthio)benzyl)cyclohepta-2,4,6-trien-1-one (**3r**). Red oil (63.1 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 1H), 7.38 – 7.34 (m, 3H), 7.25 – 7.21 (m, 1H), 7.18 – 7.14 (m, 4H), 7.13 – 7.06 (m, 4H), 7.01 (t, J = 8.0 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.91 – 6.86 (m, 1H), 6.26 (s, 1H), 3.96 (s, 2H), 2.46 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.4, 153.3, 150.1, 138.4, 138.0, 136.3, 136.0, 135.9, 135.5, 135.3, 133.4, 131.9, 131.7, 130.3, 129.9, 129.4, 129.0, 127.6, 127.0, 126.5, 122.7, 52.5, 40.9, 16.1, 15.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{26}OBrS_3^+$ 565.0324; Found 565.0325.



3s

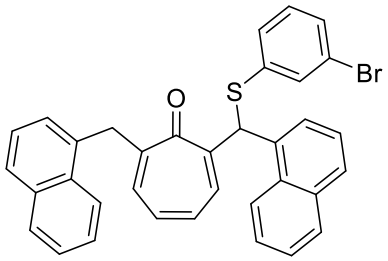
2-(2-Bromobenzyl)-7-((2-bromophenyl)((3-bromophenyl)thio)methyl)cyclohepta-2,4,6-trien-1-one (**3s**). Yellow oil (102 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, J = 7.5, 2.0 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.46 (t, J = 2.0 Hz, 1H), 7.40 (dd, J = 7.5, 2.0 Hz, 1H), 7.31 (t, J = 7.5 Hz,

1H), 7.28 – 7.22 (m, 4H), 7.17 – 7.05 (m, 3H), 6.95 – 6.86 (m, 3H), 6.51 (s, 1H), 4.23 (d, *J* = 17.0 Hz, 1H), 4.14 (d, *J* = 17.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.1, 151.5, 148.6, 138.70, 138.69, 138.6, 135.9, 134.7, 133.6, 133.5, 133.1, 132.1, 131.70, 131.66, 130.5, 130.1, 129.7, 129.4, 128.5, 127.71, 127.65, 127.6, 125.6, 125.5, 122.8, 54.0, 41.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{20}OBr_3S^+$ 628.8780; Found 628.8788.



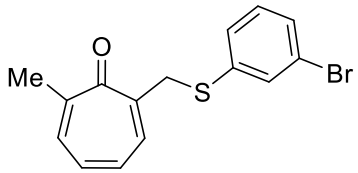
3t

2-(((3-Bromophenyl)thio)(o-tolyl)methyl)-7-(2-methylbenzyl)cyclohepta-2,4,6-trien-1-one (**3t**). Yellow oil (62.0 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 1H), 7.52 – 7.48 (m, 1H), 7.39 (t, *J* = 2.0 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.19 – 7.12 (m, 7H), 7.07 – 7.01 (m, 2H), 6.94 – 6.88 (m, 1H), 6.85 – 6.77 (m, 2H), 6.45 (s, 1H), 4.02 (d, *J* = 17.5 Hz, 1H), 3.98 (d, *J* = 17.5 Hz, 1H), 2.40 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 152.5, 149.0, 139.1, 137.3, 137.2, 137.11, 137.05, 135.8, 134.3, 133.3, 131.5, 131.2, 130.9, 130.6, 130.5, 130.3, 129.3, 127.77, 127.75, 127.1, 127.0, 126.3, 126.2, 122.7, 50.4, 38.5, 19.6, 19.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{26}OBrS^+$ 501.0882; Found 501.0891.



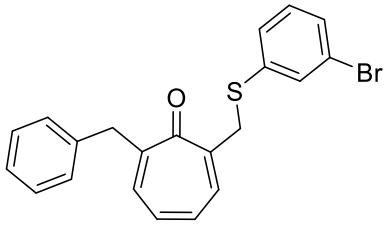
3u

2-(((3-Bromophenyl)thio)(naphthalen-1-yl)methyl)-7-(naphthalen-1-ylmethyl)cyclohepta-2,4,6-trien-1-one (**3u**). Yellow oil (58.0 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.0 Hz, 1H), 8.07 – 8.04 (m, 1H), 7.89 – 7.85 (m, 2H), 7.81 (t, *J* = 8.5 Hz, 2H), 7.76 – 7.73 (m, 1H), 7.53 – 7.48 (m, 4H), 7.48 – 7.44 (m, 2H), 7.42 – 7.35 (m, 3H), 7.29 – 7.24 (m, 2H), 7.24 – 7.23 (m, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.77 – 6.72 (m, 1H), 6.70 – 6.65 (m, 1H), 4.62 (d, *J* = 18.5 Hz, 1H), 4.52 (d, *J* = 18.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.1, 153.1, 150.0, 139.1, 136.0, 135.4, 135.3, 135.2, 134.2, 134.1, 133.6, 132.3, 131.9, 131.7, 131.5, 130.4, 129.5, 129.0, 128.83, 128.78, 128.4, 127.8, 127.6, 127.0, 126.6, 126.4, 126.1, 125.9, 125.8, 125.5, 124.5, 123.6, 122.7, 50.1, 38.1. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{26}OBrS^+$ 573.0882; Found 573.0873.



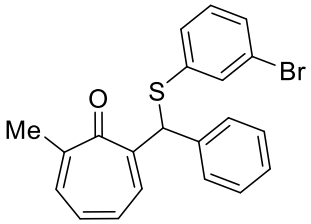
3v

2-(((3-Bromophenyl)thio)methyl)-7-methylcyclohepta-2,4,6-trien-1-one (**3v**). Yellow oil (40.4 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, J = 1.5 Hz, 1H), 7.38 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.11 (t, J = 8.0 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.89 – 6.83 (m, 1H), 4.14 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.2, 151.0, 146.6, 138.7, 135.2, 135.1, 133.5, 133.0, 131.5, 130.3, 129.7, 129.0, 122.7, 39.5, 23.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}OBrS^+$ 320.9943; Found 320.9951.



3w

2-Benzyl-7-(((3-bromophenyl)thio)methyl)cyclohepta-2,4,6-trien-1-one (**3w**). Yellow oil (44.3 mg, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (t, J = 1.5 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.26 – 7.16 (m, 5H), 7.15 – 7.12 (m, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.91 – 6.85 (m, 1H), 6.84 – 6.78 (m, 1H), 4.13 (s, 2H), 4.04 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.7, 153.1, 147.4, 139.3, 138.6, 135.5, 135.1, 133.3, 133.0, 131.8, 130.3, 129.7, 129.6, 129.0, 128.7, 126.5, 122.7, 41.4, 39.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{17}OBrNaS^+$ 419.0076; Found 419.0079.



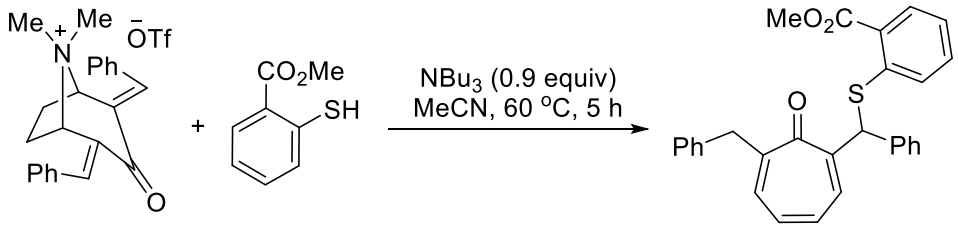
3w'

2-(((3-Bromophenyl)thio)(phenyl)methyl)-7-methylcyclohepta-2,4,6-trien-1-one (**3w'**). Yellow oil (20.9 mg, 26% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.0, 1.5 Hz, 1H), 7.49 (dd, J = 8.0, 1.5 Hz, 2H), 7.40 (t, J = 1.5 Hz, 1H), 7.35 (dt, J = 8.0, 1.5 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.27 – 7.22 (m, 2H), 7.18 (dt, J = 8.0, 1.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 7.00 – 6.90 (m, 2H), 6.33 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.8, 151.6, 149.7, 139.5, 138.6, 136.0, 135.1, 133.6,

131.9, 131.7, 130.3, 129.5, 128.8, 128.6, 127.8, 127.7, 122.7, 52.9, 24.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{17}OBrNaS^+$ 419.0076; Found 419.0079.

Scale-up reaction and synthetic transformations (Scheme 4)

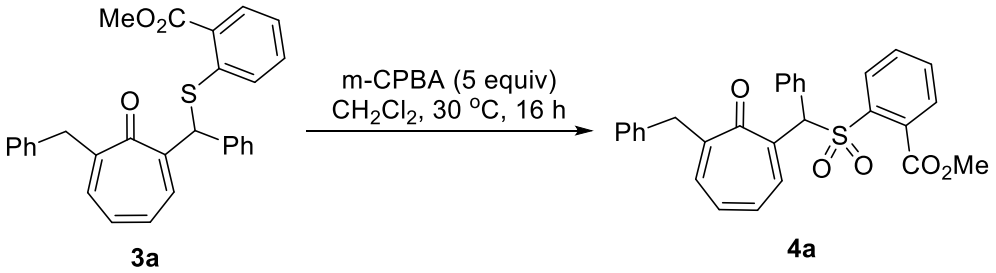
(1) Scale-up reaction



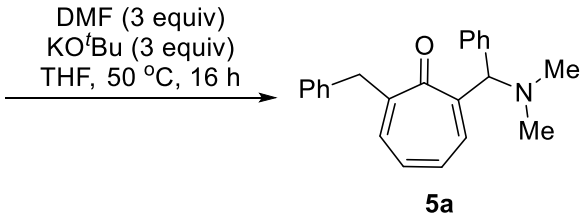
1a, 2.4 mmol **2a** **3a**, 870 mg, 80%

A mixture of 2,4-dibenzylidenetropinone-derived quaternary ammonium salt **1a** (1.15 mg, 2.4 mmol), methyl thiosalicylate (**2a**) (606 mg, 370 μL, 3.6 mmol), and tributylamine (445 mg, 516 μL, 2.16 mmol) in acetonitrile (1.2 mL) was heated in a sealed tube at 60 ℃ (oil bath) for 5 h, and cooled to room temperature. The mixture was concentrated under reduced pressure and purified by silica gel chromatography, using petroleum ether /ethyl acetate (5/1) as the eluent, to give tropone **3a** as a white solid (870 mg, 80% yield).

(2) Synthetic transformations



3a **4a**



5a

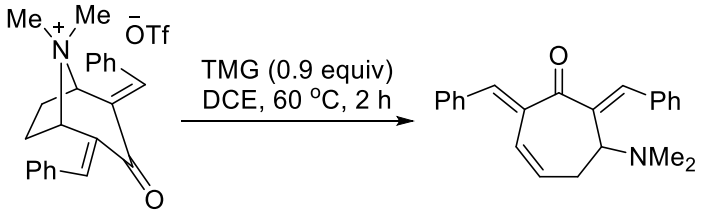
A suspension of *m*-chloroperoxybenzoic acid (86.1 mg, 0.50 mmol) and tropone **3a** (45.3 mg, 0.10 mmol) in dichloromethane (1.5 mL) was stirred at 30 ℃ for 16 h, and were added dichloromethane (5.0 mL) and saturated aqueous sodium bicarbonate (2.0 mL). The mixture was separated, and the aqueous layer was extracted twice with dichloromethane (5.0 mL). The organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue

was purified by silica gel chromatography, using petroleum ether and ethyl acetate (2:1) as the eluent, to give methyl 2-(((6-benzyl-7-oxocyclohepta-1,3,5-trien-1-yl)(phenyl)methyl)sulfonyl)benzoate (**4a**) as a yellow solid (42.2 mg, 87% yield). m.p. 124 – 127 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.45 (m, 1H), 7.66 (dd, J = 7.5, 1.5 Hz, 1H), 7.57 (td, J = 7.5, 1.5 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.37 (dd, J = 7.5, 1.5 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.27 – 7.26 (m, 1H), 7.26 – 7.25 (m, 2H), 7.25 – 7.23 (m, 1H), 7.22 – 7.18 (m, 2H), 7.14 – 7.11 (m, 2H), 7.11 – 7.04 (m, 2H), 7.00 – 6.96 (m, 1H), 3.95 (d, J = 16.0 Hz, 1H), 3.85 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2, 167.6, 153.8, 143.2, 139.0, 137.1, 136.8, 135.6, 134.4, 133.7, 133.6, 132.8, 131.9, 131.8, 130.6, 130.1, 129.8, 129.5, 128.9, 128.71, 128.66, 126.6, 68.6, 53.5, 41.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{24}O_5NaS^+$ 507.1237; Found 507.1240.

A suspension of KO^{t}Bu (33.7 mg, 0.30 mmol) and *N*,*N*-dimethylformamide (21.9 mg, 23.0 μL, 0.30 mmol) in tetrahydrofuran (1.0 mL) was stirred at room temperature for 15 min, and was added sulfone **4a** (48.4 mg, 0.10 mmol). The mixture was heated at 50 ℃ (oil bath) for 16 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (1:1) as the eluent, to give 2-(6-benzyl-7-oxocyclohepta-1,3,5-trien-1-yl)-*N*,*N*-dimethyl-2-phenylacetamide (**5a**) as a yellow oil (16.8 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 1H), 7.50 – 7.46 (m, 2H), 7.28 – 7.23 (m, 4H), 7.22 – 7.16 (m, 2H), 7.15 – 7.11 (m, 2H), 7.08 – 6.99 (m, 2H), 6.87 – 6.82 (m, 1H), 4.77 (s, 1H), 4.02 (d, J = 16.5 Hz, 1H), 3.93 (d, J = 16.5 Hz, 1H), 2.18 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.3, 153.4, 139.6, 134.9, 134.2, 132.6, 132.5, 129.6, 128.7, 128.6, 128.4, 127.2, 126.4, 71.7, 44.7, 41.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}ON^+$ 333.1852; Found 333.1851.

Mechanistic studies (Scheme 5)

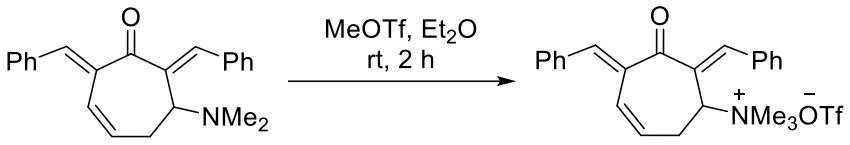
(a) Control experiments



1a **6a**

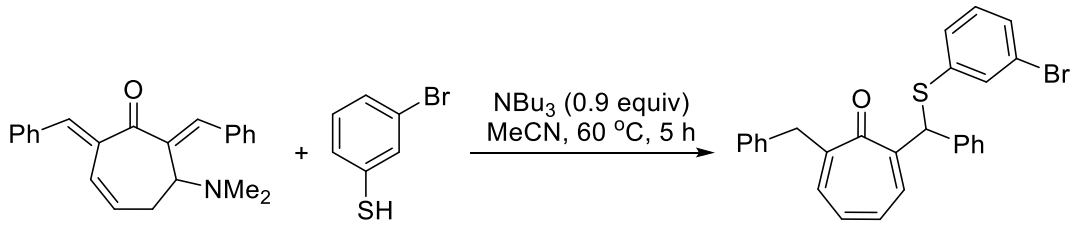
A mixture of 2,4-dibenzylidenetropinone-derived quaternary ammonium salt **1a** (192 mg, 0.40 mmol) and 1,1,3,3-tetramethylguanidine (41.5 mg, 45.4 μL, 0.36 mmol) in 1,2-dichloroethane (2.0 mL) was heated in a sealed tube at 60 ℃ (oil bath) for 2 h, and cooled to room temperature. The mixture was directly purified by silica gel chromatography, using petroleum ether/ethyl acetate (7/1) as the eluent, to give 2,7-di((*E*)-benzylidene)-6-(dimethylamino)cyclohept-3-en-1-one (**6a**) as a yellow oil (78.1 mg, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 3H), 7.41 – 7.35 (m, 7H),

7.34 – 7.28 (m, 2H), 6.45 – 6.37 (m, 1H), 5.75 (dt, *J* = 12.5, 4.5 Hz, 1H), 3.60 (t, *J* = 4.0 Hz, 1H), 2.94 – 2.86 (m, 1H), 2.66 – 2.59 (m, 1H), 2.18 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 145.8, 137.5, 136.5, 136.3, 135.8, 135.4, 130.6, 129.5, 128.6, 128.30, 128.26, 128.2, 126.8, 124.7, 61.2, 43.0, 33.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}ON^+$ 330.1852; Found 330.1859.



6a **7a**

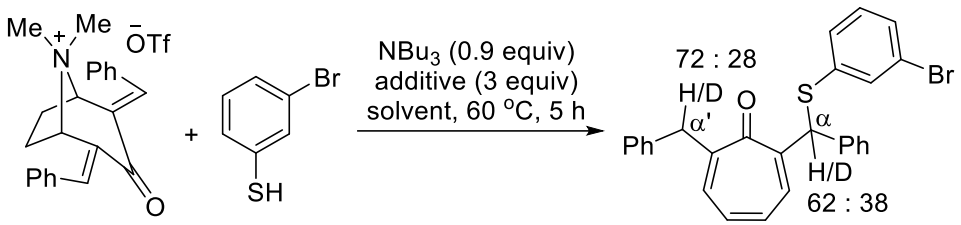
A mixture of aminated trienone **6a** (65.6 mg, 0.20 mmol) and methyl trifluoromethanesulfonate (36.1 mg, 24.9 μL, 0.22 mmol) in diethyl ether (2.0 mL) was stirred in a sealed tube at room temperature for 2 h. The mixture was filtered, washed twice with anhydrous ether, and gave 5,7-di((*E*)-benzylidene)-*N*,*N*,*N*-trimethyl-6-oxocyclohept-3-en-1-aminium triflate **7a** as a white solid (61.3 mg, 62% yield). m.p. 125 – 128 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.80 (s, 1H), 7.67 – 7.63 (m, 2H), 7.53 – 7.49 (m, 3H), 7.49 – 7.45 (m, 2H), 7.45 – 7.42 (m, 1H), 7.42 – 7.38 (m, 2H), 7.24 (s, 1H), 6.77 (d, *J* = 10.5 Hz, 1H), 6.38 – 6.32 (m, 1H), 5.33 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.95 – 2.88 (m, 2H), 2.91 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 195.7, 141.4, 139.4, 137.9, 134.2, 133.92, 133.91, 131.6, 131.0, 130.6, 129.2, 129.0, 128.92, 128.87, 127.9, 120.7 (q, J_{C-F} = 320.3 Hz), 70.1, 50.9, 24.2. ^{19}F NMR (471 MHz, DMSO-d_6) δ -77.76. HRMS (ESI) m/z: $[M - OTf]^+$ Calcd for $C_{24}H_{26}ON^+$ 344.2009; Found 344.2009.



6a **2c** **3c**

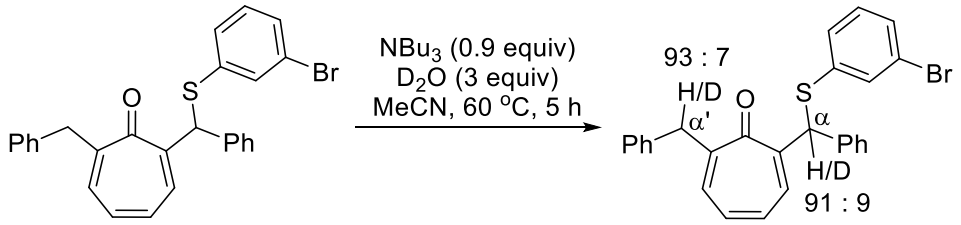
A mixture of aminated trienone **6a** (65.6 mg, 0.20 mmol), 3-bromothiophenol (**2c**) (56.7 mg, 32.0 μL, 0.30 mmol), and tributylamine (33.4 mg, 43.0 μL, 0.18 mmol) in acetonitrile (1.2 mL) was heated in a sealed tube at 60 °C (oil bath) for 5 h, and cooled to room temperature. The mixture was directly purified by silica gel chromatography, using petroleum ether/ethyl acetate (20/1) as the eluent, to give tropone **3c** as a yellow oil (58.0 mg, 61% yield).

(b) Deuterium-labelling experiments



1a **2c** **3c/3c-D**

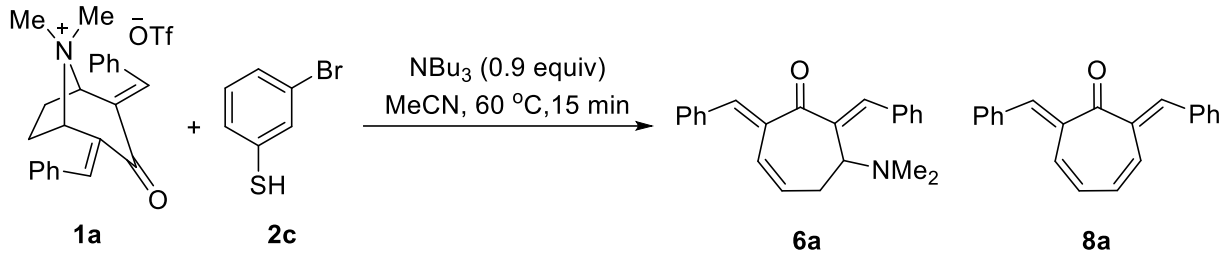
A mixture of 2,4-dibenzylidenetropinone-derived quaternary ammonium salt **1a** (95.8 mg, 0.20 mmol), 3-bromothiophenol (**2c**) (56.7 mg, 32.0 μL, 0.30 mmol), D_2O (12.0 mg, 12.0 μL, 0.60 mmol), and tributylamine (33.4 mg, 43.0 μL, 0.18 mmol) in acetonitrile (1.2 mL) was heated in a sealed tube at 60 ℃ (oil bath) for 5 h, and cooled to room temperature. The mixture was directly purified by silica gel chromatography, using petroleum ether/ethyl acetate (20/1) as the eluent, to give tropone **3c/3c-D** as a yellow oil (74.1 mg, 78% yield) with 38% and 28% deuteration rates at the α- and α'-benzylic positions according to ^{1}H NMR spectroscopic analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.5, 2.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.40 – 7.37 (m, 1H), 7.32 – 7.23 (m, 5H), 7.23 – 7.19 (m, 2H), 7.16 (d, J = 7.5 Hz, 2H), 7.13 (dd, J = 7.5, 1.5 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.95 – 6.89 (m, 1H), 6.89 – 6.83 (m, 1H), 6.33 (s, 0.62H), 4.06 – 3.96 (m, 1.44H).



3c **3c/3c-D**

A mixture of tropone **3c** (94.7 mg, 0.20 mmol), D_2O (12.0 mg, 12.0 μL, 0.60 mmol), and tributylamine (33.4 mg, 43.0 μL, 0.18 mmol) in acetonitrile (1.2 mL) was heated in a sealed tube at 60 ℃ (oil bath) for 5 h, and cooled to room temperature. The mixture was directly purified by silica gel chromatography, using petroleum ether/ethyl acetate (20/1) as the eluent, to give tropone **3c/3c-D** as a yellow oil with 9% and 7% deuteration rates at the α- and α'-benzylic positions according to ^{1}H NMR spectroscopic analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 8.5, 1.0 Hz, 1H), 7.46 (dd, J = 7.5, 1.5 Hz, 2H), 7.31 – 7.20 (m, 9H), 7.18 – 7.14 (m, 2H), 7.11 – 7.05 (m, 3H), 6.96 – 6.90 (m, 1H), 6.89 – 6.83 (m, 1H), 6.30 (s, 0.91H), 4.07 – 3.94 (m, 1.86H).

ESI-MS analysis of the reaction mixture (Scheme 6)



1a **2c** **6a** **8a**

A mixture of 2,4-dibenzylidenetropinone-derived quaternary ammonium salt **1a** (95.8 mg, 0.20 mmol), 3-bromothiophenol (**2c**) (56.7 mg, 32.0 μL, 0.30 mmol), and tributylamine (33.4 mg, 43.0 μL, 0.18 mmol) in acetonitrile (1.2 mL) was heated in a sealed tube at 60 ℃ (oil bath) for 15 min, and cooled to room temperature. The mixture was subjected to electron spray ionization-mass spectrometric analysis. We tentatively assigned the following two intermediates:

Intermediate **6a**: HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{23}H_{23}NO^+$ 329.1774; Found 329.1782.

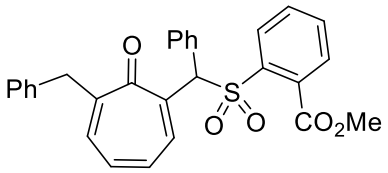
Intermediate **8a**: HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}O^+$ 285.1274; Found 285.1277.

References

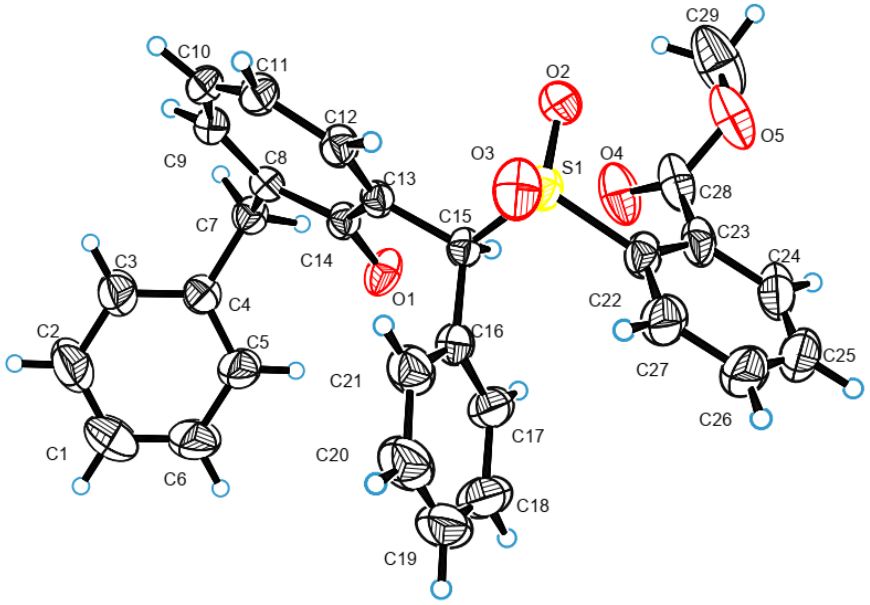
1. T. Rerkrachaneekorn, T. Tankam, M. Sukwattanasinitt and S. Wacharasindhu, *Tetrahedron Lett.*, 2021, **70**, 153017.
2. A. B. Shapiro and A. M. Belostotskii, *Russ. Chem. Bull.*, 1989, **38**, 593.
3. G. Zheng, L. P. Dwoskin and P. A. Crooks, *Synth. Commun.*, 2004, **34**, 1931.

Crystallographic data

The crystal of compound **4a** was obtained by leaving alone its solution in chloroform and methanol at room temperature in the open air for one week. The crystal data of compound **4a** have been deposited in CCDC with number 2260119.



4a



Molecular structure of compound **4a** was obtained by single-crystal X-ray diffraction studies with the ellipsoid contour at 35% probability levels.

Table 1 Crystal data and structure refinement for HL-DER-M_auto.

Identification code	HL-DER-M_auto
Empirical formula	$C_{29}H_{24}O_5S$
Formula weight	484.54
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.2396(3)
b/Å	7.38829(13)
c/Å	27.2180(5)
α/°	90
β/°	92.5426(19)
γ/°	90
Volume/Å^3	2458.90(8)
Z	4
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	1.482
F(000)	1016.0

Crystal size/mm^3	0.25 × 0.22 × 0.21
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.796 to 145.684
Index ranges	-14 ≤ h ≤ 15, -8 ≤ k ≤ 6, -30 ≤ l ≤ 33
Reflections collected	8851
Independent reflections	4740 [R_{int} = 0.0263, R_{sigma} = 0.0334]
Data/restraints/parameters	4740/0/318
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.1144
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1250
Largest diff. peak/hole / e Å^{-3}	0.21/-0.27

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for HL-DER-M_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	7531.2(4)	5528.5(6)	3600.1(2)	49.69(15)
O2	8679.4(12)	5548(2)	3514.5(5)	62.6(4)
O1	7996.7(13)	7672.6(17)	5066.3(5)	62.0(4)
O3	6925.6(15)	3919(2)	3483.9(6)	71.0(4)
O5	9318.8(18)	9293(3)	2993.8(6)	91.5(6)
O4	8825.6(18)	9554(3)	3772.7(6)	87.7(6)
C13	7942.9(14)	5007(2)	4609.3(6)	41.0(4)
C8	8899.6(14)	5337(2)	5482.4(7)	44.0(4)
C12	8073.1(16)	3210(2)	4529.0(7)	48.3(4)
C15	7351.1(14)	6222(2)	4229.6(6)	43.3(4)
C14	8266.4(14)	6063(2)	5052.7(6)	42.9(4)
C7	9133.5(16)	6686(3)	5889.1(7)	51.5(4)
C16	6151.1(16)	6540(3)	4317.2(7)	52.3(4)
C10	9132.4(17)	2037(3)	5262.3(8)	55.1(5)
C4	8201.7(17)	6819(3)	6237.0(7)	54.7(5)
C11	8591.9(17)	1851(2)	4823.7(8)	54.0(5)

Atom	*x*	*y*	*z*	U(eq)
C9	9279.5(16)	3619(3)	5551.2(7)	50.7(4)
C22	6899.3(18)	7316(3)	3255.8(7)	53.9(5)
C23	7473(2)	8875(3)	3145.2(7)	61.8(5)
C28	8597(2)	9259(3)	3349.5(8)	71.2(7)
C27	5831(2)	7066(4)	3081.6(9)	72.9(6)
C21	5418.1(19)	5120(4)	4327.1(10)	71.7(6)
C17	5784(2)	8293(4)	4377.8(9)	69.5(6)
C5	7429(2)	8179(4)	6195.2(10)	77.0(7)
C24	6950(3)	10172(4)	2847.2(9)	87.3(9)
C3	8121(3)	5596(4)	6611.5(10)	84.5(8)
C26	5331(3)	8394(5)	2792.8(10)	97.7(10)
C25	5892(3)	9925(5)	2674.9(11)	104.6(12)
C20	4318(2)	5450(6)	4386.8(12)	97.2(10)
C19	3958(2)	7189(6)	4446.4(12)	104.2(12)
C18	4679(2)	8599(5)	4448.8(11)	94.4(10)
C1	6508(3)	7027(6)	6880.3(14)	117.1(12)
C2	7271(3)	5699(5)	6932.4(13)	116.9(13)
C6	6590(3)	8277(5)	6517.5(13)	106.0(11)
C29	10415(3)	9737(6)	3149.5(14)	131.6(16)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for HL-DER-M_auto. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	65.9(3)	43.9(2)	39.1(2)	-1.44(18)	0.54(19)	1.9(2)
O2	68.3(9)	74.3(9)	45.8(8)	0.8(7)	8.3(6)	12.8(7)
O1	94.6(11)	37.6(7)	52.7(8)	-1.7(6)	-10.3(7)	9.2(6)
O3	105.2(12)	49.6(8)	57.4(9)	-7.5(7)	-7.3(8)	-11.7(8)
O5	125.3(16)	101.5(13)	49.1(9)	-8.1(9)	21.1(9)	-50.1(12)
O4	132.2(16)	88.3(12)	42.9(9)	-9.2(8)	6.8(9)	-30.7(11)
C13	45.7(8)	37.2(8)	40.5(9)	2.9(7)	6.6(7)	-1.2(7)
C8	43.8(9)	47.0(9)	41.5(9)	1.3(7)	6.1(7)	0.6(7)
C12	60.6(11)	38.9(8)	45.6(10)	-0.2(7)	5.9(8)	-0.5(8)
C15	52.4(9)	38.4(8)	39.1(9)	1.2(7)	1.3(7)	-0.9(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	51.0(9)	36.7(8)	41.2(9)	2.3(7)	4.7(7)	0.3(7)
C7	55.1(10)	53.1(10)	46.1(10)	-1.1(8)	-1.2(8)	0.4(8)
C16	53.4(10)	62.1(11)	41.1(10)	4.3(8)	-0.3(8)	4.3(9)
C10	66.9(12)	42.1(9)	57.2(12)	9.0(8)	13.1(9)	13.7(8)
C4	63.9(12)	57.2(11)	42.9(10)	-7.0(8)	0.1(8)	2.8(9)
C11	70.7(12)	35.0(8)	57.1(12)	0.8(8)	13.0(9)	5.3(8)
C9	54.4(10)	52.3(10)	45.7(10)	6.8(8)	5.8(8)	7.7(8)
C22	73.4(13)	53.8(10)	34.2(9)	-0.8(8)	-1.2(8)	7.1(9)
C23	100.6(17)	51.8(11)	33.6(9)	-0.1(8)	9.5(10)	5.4(11)
C28	121(2)	50.4(11)	42.8(11)	-1.5(9)	15.2(12)	-20.7(12)
C27	78.5(15)	87.0(16)	52.3(13)	-1.8(11)	-7.0(11)	11.2(13)
C21	59.4(12)	86.6(15)	69.3(15)	8.7(13)	4.8(11)	-10.1(12)
C17	68.4(14)	77.4(14)	62.5(14)	-0.9(11)	1.2(11)	20.2(11)
C5	82.8(16)	86.1(16)	62.5(14)	0.1(12)	7.1(12)	26.0(13)
C24	149(3)	64.1(14)	50.3(14)	13.0(11)	21.0(16)	24.3(16)
C3	112(2)	77.4(16)	65.9(15)	11.1(13)	25.9(14)	18.2(15)
C26	97(2)	137(3)	57.4(15)	7.5(17)	-7.5(14)	46(2)
C25	144(3)	113(2)	57.7(16)	21.5(16)	14.5(18)	66(2)
C20	58.1(15)	146(3)	88(2)	15(2)	6.7(13)	-16.8(17)
C19	55.2(15)	177(4)	81(2)	15(2)	9.4(13)	19(2)
C18	80.0(18)	123(2)	79.6(19)	-3.0(17)	0.2(14)	45.2(19)
C1	120(3)	144(3)	92(2)	-4(2)	54(2)	23(2)
C2	160(3)	109(2)	87(2)	21.6(19)	64(2)	17(2)
C6	102(2)	134(3)	85(2)	-4(2)	26.1(17)	48(2)
C29	136(3)	179(4)	80(2)	-7(2)	18(2)	-89(3)

Table 4 Bond Lengths for HL-DER-M_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.4348(16)	C10	C11	1.346(3)
S1	O3	1.4292(15)	C10	C9	1.416(3)
S1	C15	1.8112(18)	C4	C5	1.381(3)
S1	C22	1.776(2)	C4	C3	1.369(3)
O1	C14	1.235(2)	C22	C23	1.389(3)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O5	C28	1.339(3)	C22	C27	1.384(3)
O5	C29	1.427(4)	C23	C28	1.488(4)
O4	C28	1.193(3)	C23	C24	1.393(3)
C13	C12	1.356(2)	C27	C26	1.383(4)
C13	C15	1.527(2)	C21	C20	1.385(4)
C13	C14	1.477(2)	C17	C18	1.393(4)
C8	C14	1.475(2)	C5	C6	1.382(4)
C8	C7	1.508(3)	C24	C25	1.369(5)
C8	C9	1.361(3)	C3	C2	1.390(4)
C12	C11	1.417(3)	C26	C25	1.368(5)
C15	C16	1.517(3)	C20	C19	1.371(5)
C7	C4	1.517(3)	C19	C18	1.365(5)
C16	C21	1.381(3)	C1	C2	1.357(5)
C16	C17	1.384(3)	C1	C6	1.359(5)

Table 5 Bond Angles for HL-DER-M_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	C15	108.18(9)	C3	C4	C5	118.0(2)
O2	S1	C22	108.26(10)	C10	C11	C12	128.32(18)
O3	S1	O2	118.33(10)	C8	C9	C10	131.21(18)
O3	S1	C15	111.18(9)	C23	C22	S1	121.20(17)
O3	S1	C22	106.99(10)	C27	C22	S1	117.66(17)
C22	S1	C15	102.72(8)	C27	C22	C23	121.1(2)
C28	O5	C29	115.5(2)	C22	C23	C28	123.06(19)
C12	C13	C15	121.48(17)	C22	C23	C24	118.2(3)
C12	C13	C14	128.32(17)	C24	C23	C28	118.7(2)
C14	C13	C15	110.13(14)	O5	C28	C23	111.2(2)
C14	C8	C7	114.66(15)	O4	C28	O5	124.1(3)
C9	C8	C14	127.77(17)	O4	C28	C23	124.7(2)
C9	C8	C7	117.57(17)	C26	C27	C22	119.2(3)
C13	C12	C11	130.92(19)	C16	C21	C20	120.3(3)
C13	C15	S1	113.56(12)	C16	C17	C18	119.4(3)
C16	C15	S1	110.60(12)	C4	C5	C6	120.7(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	C15	C13	114.71(15)	C25	C24	C23	120.7(3)
O1	C14	C13	118.10(16)	C4	C3	C2	120.8(3)
O1	C14	C8	117.29(16)	C25	C26	C27	120.4(3)
C8	C14	C13	124.61(15)	C26	C25	C24	120.4(3)
C8	C7	C4	112.17(16)	C19	C20	C21	119.9(3)
C21	C16	C15	121.34(19)	C18	C19	C20	120.4(3)
C21	C16	C17	119.6(2)	C19	C18	C17	120.4(3)
C17	C16	C15	119.04(19)	C2	C1	C6	119.6(3)
C11	C10	C9	128.48(17)	C1	C2	C3	120.3(3)
C5	C4	C7	121.8(2)	C1	C6	C5	120.4(3)
C3	C4	C7	120.2(2)				

Table 6 Torsion Angles for HL-DER-M_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C15	C16	C21	70.0(2)	C7	C8	C9	C10	174.82(19)
S1	C15	C16	C17	-108.58(19)	C7	C4	C5	C6	-179.7(3)
S1	C22	C23	C28	-7.1(3)	C7	C4	C3	C2	-179.9(3)
S1	C22	C23	C24	175.94(17)	C16	C21	C20	C19	-1.3(5)
S1	C22	C27	C26	-177.0(2)	C16	C17	C18	C19	-1.6(4)
O2	S1	C15	C13	-59.09(14)	C4	C5	C6	C1	-0.4(5)
O2	S1	C15	C16	170.29(13)	C4	C3	C2	C1	-0.4(6)
O2	S1	C22	C23	-28.39(19)	C11	C10	C9	C8	2.7(4)
O2	S1	C22	C27	148.60(17)	C9	C8	C14	O1	179.67(19)
O3	S1	C15	C13	72.43(15)	C9	C8	C14	C13	-0.8(3)
O3	S1	C15	C16	-58.19(15)	C9	C8	C7	C4	-94.3(2)
O3	S1	C22	C23	-156.96(16)	C9	C10	C11	C12	3.1(4)
O3	S1	C22	C27	20.0(2)	C22	S1	C15	C13	-173.44(13)
C13	C12	C11	C10	-2.6(4)	C22	S1	C15	C16	55.94(15)
C13	C15	C16	C21	-60.0(2)	C22	C23	C28	O5	115.0(2)
C13	C15	C16	C17	121.4(2)	C22	C23	C28	O4	-67.0(3)
C8	C7	C4	C5	-98.4(2)	C22	C23	C24	C25	1.0(4)
C8	C7	C4	C3	83.0(3)	C22	C27	C26	C25	0.9(4)
C12	C13	C15	S1	-32.6(2)	C23	C22	C27	C26	0.0(3)

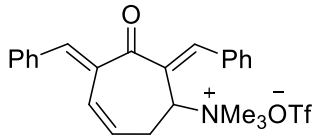
A	B	C	D	Angle/°	A	B	C	D	Angle/°
C12	C13	C15	C16	95.9(2)	C23	C24	C25	C26	0.0(4)
C12	C13	C14	O1	-174.46(19)	C28	C23	C24	C25	-176.1(2)
C12	C13	C14	C8	6.0(3)	C27	C22	C23	C28	176.0(2)
C15	S1	C22	C23	85.89(17)	C27	C22	C23	C24	-1.0(3)
C15	S1	C22	C27	-97.11(18)	C27	C26	C25	C24	-0.9(5)
C15	C13	C12	C11	179.53(19)	C21	C16	C17	C18	0.1(3)
C15	C13	C14	O1	2.6(2)	C21	C20	C19	C18	-0.2(5)
C15	C13	C14	C8	-176.92(16)	C17	C16	C21	C20	1.4(4)
C15	C16	C21	C20	-177.2(2)	C5	C4	C3	C2	1.5(5)
C15	C16	C17	C18	178.7(2)	C24	C23	C28	O5	-68.0(3)
C14	C13	C12	C11	-3.7(3)	C24	C23	C28	O4	109.9(3)
C14	C13	C15	S1	150.06(12)	C3	C4	C5	C6	-1.1(4)
C14	C13	C15	C16	-81.40(18)	C20	C19	C18	C17	1.7(5)
C14	C8	C7	C4	85.3(2)	C2	C1	C6	C5	1.5(7)
C14	C8	C9	C10	-4.7(3)	C6	C1	C2	C3	-1.2(7)
C7	C8	C14	O1	0.2(2)	C29	O5	C28	O4	-0.8(4)
C7	C8	C14	C13	179.71(16)	C29	O5	C28	C23	177.2(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for HL-DER-M_auto.

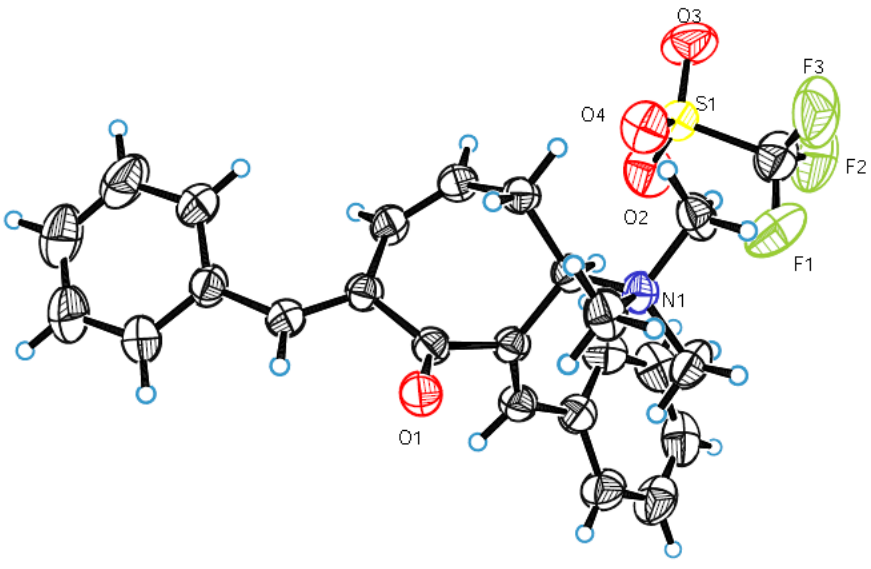
Atom	*x*	*y*	*z*	U(eq)
H12	7771	2799	4230	58
H15	7702	7411	4263	52
H7A	9259	7867	5746	62
H7B	9796	6332	6073	62
H10	9451	989	5393	66
H11	8554	682	4698	65
H9	9711	3457	5838	61
H27	5453	6017	3158	88
H21	5664	3937	4293	86
H17	6270	9259	4371	83
H5	7475	9039	5947	92
H24	7323	11218	2764	105

Atom	*x*	*y*	*z*	U(eq)
H3	8642	4685	6652	101
H26	4610	8247	2678	117
H25	5553	10802	2477	126
H20	3824	4493	4386	117
H19	3219	7410	4486	125
H18	4430	9772	4498	113
H1	5933	7080	7092	140
H2	7224	4855	7184	140
H6	6079	9205	6486	127
H29A	10889	9548	2882	197
H29B	10644	8979	3421	197
H29C	10450	10983	3249	197

The crystal of compound **7a** was obtained by leaving alone its solution in chloroform and hexane at room temperature in the open air for two days. The crystal data of compound **7a** have been deposited in CCDC with number 2260124.



7a



Molecular structure of compound **7a** was obtained by single-crystal X-ray diffraction studies with the ellipsoid contour at 35% probability levels.

Table 1 Crystal data and structure refinement for hl-1_autored.

Identification code	hl-1_autored
Empirical formula	$C_{25}H_{26}F_3NO_4S$
Formula weight	493.53
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.2016(2)
b/Å	16.5260(2)
c/Å	11.22516(19)
α/°	90
β/°	103.2304(16)
γ/°	90
Volume/Å^3	2745.15(7)
Z	4
ρ_{calc}g/cm^3	1.194
μ/mm^{-1}	1.474
F(000)	1032.0
Crystal size/mm^3	0.22 × 0.15 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.02 to 145.978
Index ranges	-17 ≤ h ≤ 18, -12 ≤ k ≤ 20, -13 ≤ l ≤ 12
Reflections collected	10398
Independent reflections	5335 [R_{int} = 0.0190, R_{sigma} = 0.0263]
Data/restraints/parameters	5335/0/311
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.1484
Final R indexes [all data]	R_1 = 0.0568, wR_2 = 0.1555
Largest diff. peak/hole / e Å^{-3}	0.36/-0.25

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for hl-1_autored. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	-828.4(3)	3358.0(3)	2897.9(5)	59.65(18)
O1	3931.0(9)	5321.3(8)	4829.1(14)	64.4(4)
N1	1440.2(10)	5693.0(9)	3304.5(14)	50.4(4)
O4	-248.9(12)	3916.3(11)	3657.2(17)	85.7(5)
C6	1708.4(11)	4825.5(10)	3785.0(16)	46.2(4)
C2	3536.0(12)	4123.2(11)	5771.7(17)	49.3(4)
O2	-382.4(15)	2748.6(11)	2367(2)	100.6(6)
C7	2654.7(12)	4607.6(10)	3677.6(16)	47.1(4)
C5	1633.7(12)	4718.8(11)	5106.1(17)	51.6(4)
C3	2753.9(13)	3613.3(11)	5816.0(19)	56.0(4)
C1	3416.6(12)	4752.6(10)	4791.2(17)	49.0(4)
F1	-726.3(19)	4310.7(14)	1090(2)	139.9(8)
C4	1901.8(13)	3869.4(12)	5510.2(19)	57.3(5)
C15	4386.2(13)	4022.1(12)	6438.3(17)	54.3(4)
O3	-1557.9(15)	3074.2(16)	3367(2)	114.7(8)
C8	2888.4(13)	4224.4(12)	2743.1(18)	56.5(4)
F2	-1902.2(18)	3559.4(19)	760.1(19)	159.5(10)
C9	2328.8(14)	3902.6(12)	1598.3(19)	58.5(5)
C23	498.9(13)	5875.5(13)	3443(2)	65.5(5)
F3	-1814(2)	4565.3(16)	1958(2)	161.9(11)
C22	2065.6(14)	6330.6(11)	3977(2)	64.8(5)
C16	4753.3(14)	3437.2(13)	7391.5(18)	59.7(5)
C24	1439.4(19)	5744.3(15)	1974(2)	74.9(6)
C14	2623.5(19)	4007.4(17)	522(2)	78.4(7)
C11	1038.5(19)	3175.2(16)	441(3)	84.0(7)
C17	4250.6(18)	3040.7(17)	8106(2)	78.2(7)
C12	1327(2)	3287.8(18)	-610(3)	90.2(8)
C13	2115(2)	3705(2)	-573(2)	95.0(9)
C21	5678.6(17)	3281.7(19)	7618(2)	86.4(8)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for hl-1_autored. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C25	-1350(2)	3971(2)	1599(3)	93.7(8)
C18	4657(3)	2489(2)	8985(3)	105.6(10)
C19	5566(3)	2322(2)	9154(3)	118.5(12)
C20	6076(2)	2716(2)	8484(3)	116.0(12)
C10	1533.9(17)	3470.7(13)	1545(2)	72.0(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for hl-1_autored. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	66.2(3)	51.0(3)	59.2(3)	-5.6(2)	9.0(2)	-8.2(2)
O1	55.0(7)	57.9(8)	77.2(9)	15.1(7)	8.6(6)	-10.2(6)
N1	53.9(8)	42.3(7)	53.4(8)	3.7(6)	9.2(6)	3.2(6)
O4	90.8(11)	75.5(10)	82.7(11)	-18.5(9)	3.4(9)	-20.5(9)
C6	49.2(9)	37.9(8)	51.2(9)	1.3(7)	11.1(7)	0.6(7)
C2	51.5(9)	45.3(9)	52.0(9)	3.7(7)	13.8(7)	1.9(7)
O2	124.6(16)	63.7(10)	113.2(15)	-16.2(10)	26.9(12)	15.5(10)
C7	50.5(9)	42.1(8)	49.8(9)	5.6(7)	14.0(7)	0.8(7)
C5	51.3(9)	50.5(9)	56.4(10)	4.9(8)	19.2(8)	2.3(7)
C3	59.8(10)	43.0(9)	64.5(11)	12.4(8)	13.0(9)	-2.1(8)
C1	46.9(9)	46.0(9)	55.2(10)	5.4(7)	13.8(7)	0.8(7)
F1	201(2)	123.7(16)	104.2(14)	35.8(12)	54.5(15)	-11.7(16)
C4	55.6(10)	52.0(10)	65.9(12)	12.7(9)	16.8(9)	-7.7(8)
C15	54.1(10)	56.2(10)	53.0(10)	5.2(8)	13.4(8)	-0.8(8)
O3	103.7(14)	143.7(19)	103.2(15)	11.5(14)	37.3(12)	-46.1(14)
C8	56.3(10)	57.5(10)	58.3(11)	3.3(8)	18.8(8)	4.8(8)
F2	166(2)	191(2)	86.6(13)	-6.7(14)	-42.6(13)	0.7(18)
C9	66.4(11)	53.6(10)	57.8(11)	-1.9(8)	18.9(9)	13.5(9)
C23	51.3(10)	54.8(11)	88.0(15)	7.3(10)	11.0(10)	8.7(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for hl-1_autored. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F3	192(2)	137.8(18)	145.0(19)	23.3(16)	17.0(17)	91.1(19)
C22	62.5(11)	42.1(9)	84.3(14)	5.5(9)	5.7(10)	-3.5(8)
C16	62.9(11)	61.1(11)	52.9(10)	7.8(9)	8.6(9)	5.5(9)
C24	103.2(17)	66.6(13)	54.1(12)	15.4(10)	16.1(11)	16.9(12)
C14	88.9(16)	87.9(16)	63.4(13)	-2.1(12)	28.1(12)	10.7(13)
C11	83.1(16)	66.1(13)	98.0(19)	-26.5(13)	11.0(14)	8.0(12)
C17	78.3(15)	87.8(16)	68.5(14)	24.5(12)	16.7(11)	0.9(12)
C12	99(2)	84.0(17)	76.2(17)	-19.7(14)	-3.9(14)	28.7(15)
C13	124(2)	105(2)	56.7(13)	-3.7(14)	22.5(14)	32.0(19)
C21	64.9(13)	113(2)	77.2(15)	23.1(15)	7.9(11)	15.6(13)
C25	109(2)	90.8(19)	77.4(17)	0.4(15)	12.6(16)	11.1(17)
C18	135(3)	97(2)	80.5(18)	37.7(16)	13.9(18)	-7.9(19)
C19	130(3)	105(2)	105(2)	44(2)	-4(2)	31(2)
C20	94(2)	140(3)	105(2)	36(2)	2.9(18)	44(2)
C10	84.4(15)	56.6(11)	78.5(15)	-15.3(10)	25.8(12)	1.6(11)

Table 4 Bond Lengths for hl-1_autored.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O4	1.4179(16)	F1	C25	1.337(4)
S1	O2	1.4188(19)	C15	C16	1.455(3)
S1	O3	1.4124(19)	C8	C9	1.469(3)
S1	C25	1.804(3)	F2	C25	1.301(4)
O1	C1	1.217(2)	C9	C14	1.392(3)
N1	C6	1.553(2)	C9	C10	1.393(3)
N1	C23	1.505(2)	F3	C25	1.323(4)
N1	C22	1.502(2)	C16	C17	1.392(3)
N1	C24	1.496(3)	C16	C21	1.395(3)
C6	C7	1.514(2)	C14	C13	1.387(4)
C6	C5	1.523(3)	C11	C12	1.362(4)

Table 4 Bond Lengths for hl-1_autored.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C2	C3	1.467(3)	C11	C10	1.383(3)
C2	C1	1.495(2)	C17	C18	1.380(4)
C2	C15	1.347(3)	C12	C13	1.374(4)
C7	C1	1.516(3)	C21	C20	1.384(4)
C7	C8	1.341(3)	C18	C19	1.379(5)
C5	C4	1.503(3)	C19	C20	1.362(5)
C3	C4	1.331(3)			

Table 5 Bond Angles for hl-1_autored.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	S1	O2	115.05(13)	C3	C4	C5	123.76(17)
O4	S1	C25	102.59(13)	C2	C15	C16	130.43(18)
O2	S1	C25	102.93(14)	C7	C8	C9	130.64(18)
O3	S1	O4	115.13(13)	C14	C9	C8	118.5(2)
O3	S1	O2	114.35(15)	C14	C9	C10	118.3(2)
O3	S1	C25	104.51(16)	C10	C9	C8	123.12(19)
C23	N1	C6	109.24(14)	C17	C16	C15	124.6(2)
C22	N1	C6	112.80(13)	C17	C16	C21	118.2(2)
C22	N1	C23	108.38(16)	C21	C16	C15	117.2(2)
C24	N1	C6	109.83(14)	C13	C14	C9	119.9(3)
C24	N1	C23	107.94(17)	C12	C11	C10	120.7(3)
C24	N1	C22	108.53(17)	C18	C17	C16	120.5(3)
C7	C6	N1	111.75(13)	C11	C12	C13	119.5(3)
C7	C6	C5	109.50(14)	C12	C13	C14	120.9(3)
C5	C6	N1	111.89(14)	C20	C21	C16	120.8(3)
C3	C2	C1	117.50(16)	F1	C25	S1	110.9(2)
C15	C2	C3	126.26(17)	F2	C25	S1	112.5(2)
C15	C2	C1	115.76(16)	F2	C25	F1	108.3(3)
C6	C7	C1	117.21(15)	F2	C25	F3	108.0(3)
C8	C7	C6	126.95(17)	F3	C25	S1	109.7(2)

Table 5 Bond Angles for hl-1_autored.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	C7	C1	115.49(16)	F3	C25	F1	107.4(3)
C4	C5	C6	109.06(16)	C19	C18	C17	120.1(3)
C4	C3	C2	123.84(17)	C20	C19	C18	120.5(3)
O1	C1	C2	122.87(17)	C19	C20	C21	119.9(3)
O1	C1	C7	120.96(16)	C11	C10	C9	120.6(2)
C2	C1	C7	115.98(15)				

Table 6 Torsion Angles for hl-1_autored.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C6	C7	C1	94.25(17)	C15	C2	C1	C7	150.20(17)
N1	C6	C7	C8	-92.9(2)	C15	C16	C17	C18	179.5(3)
N1	C6	C5	C4	179.99(14)	C15	C16	C21	C20	-178.1(3)
O4	S1	C25	F1	56.9(2)	O3	S1	C25	F1	177.4(2)
O4	S1	C25	F2	178.3(2)	O3	S1	C25	F2	-61.2(3)
O4	S1	C25	F3	-61.5(3)	O3	S1	C25	F3	59.0(3)
C6	C7	C1	O1	-104.7(2)	C8	C7	C1	O1	81.6(2)
C6	C7	C1	C2	80.21(19)	C8	C7	C1	C2	-93.5(2)
C6	C7	C8	C9	-0.9(3)	C8	C9	C14	C13	179.5(2)
C6	C5	C4	C3	76.9(3)	C8	C9	C10	C11	-179.4(2)
C2	C3	C4	C5	-1.4(3)	C9	C14	C13	C12	-1.2(4)
C2	C15	C16	C17	-23.9(4)	C23	N1	C6	C7	-179.63(15)
C2	C15	C16	C21	157.7(2)	C23	N1	C6	C5	-56.43(19)
O2	S1	C25	F1	-62.9(2)	C22	N1	C6	C7	-59.0(2)
O2	S1	C25	F2	58.6(3)	C22	N1	C6	C5	64.2(2)
O2	S1	C25	F3	178.7(2)	C16	C17	C18	C19	-0.5(5)
C7	C6	C5	C4	-55.55(19)	C16	C21	C20	C19	-2.1(6)
C7	C8	C9	C14	139.2(2)	C24	N1	C6	C7	62.2(2)
C7	C8	C9	C10	-43.3(3)	C24	N1	C6	C5	-174.64(17)
C5	C6	C7	C1	-30.3(2)	C14	C9	C10	C11	-1.9(3)
C5	C6	C7	C8	142.60(18)	C11	C12	C13	C14	0.5(4)

Table 6 Torsion Angles for hl-1_autored.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	C2	C1	O1	162.56(19)	C17	C16	C21	C20	3.5(4)
C3	C2	C1	C7	-22.4(2)	C17	C18	C19	C20	2.0(6)
C3	C2	C15	C16	-3.4(3)	C12	C11	C10	C9	1.2(4)
C1	C2	C3	C4	-33.4(3)	C21	C16	C17	C18	-2.2(4)
C1	C2	C15	C16	-175.3(2)	C18	C19	C20	C21	-0.7(6)
C1	C7	C8	C9	172.08(19)	C10	C9	C14	C13	1.9(4)
C15	C2	C3	C4	154.9(2)	C10	C11	C12	C13	-0.5(4)
C15	C2	C1	O1	-24.8(3)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for hl-1_autored.

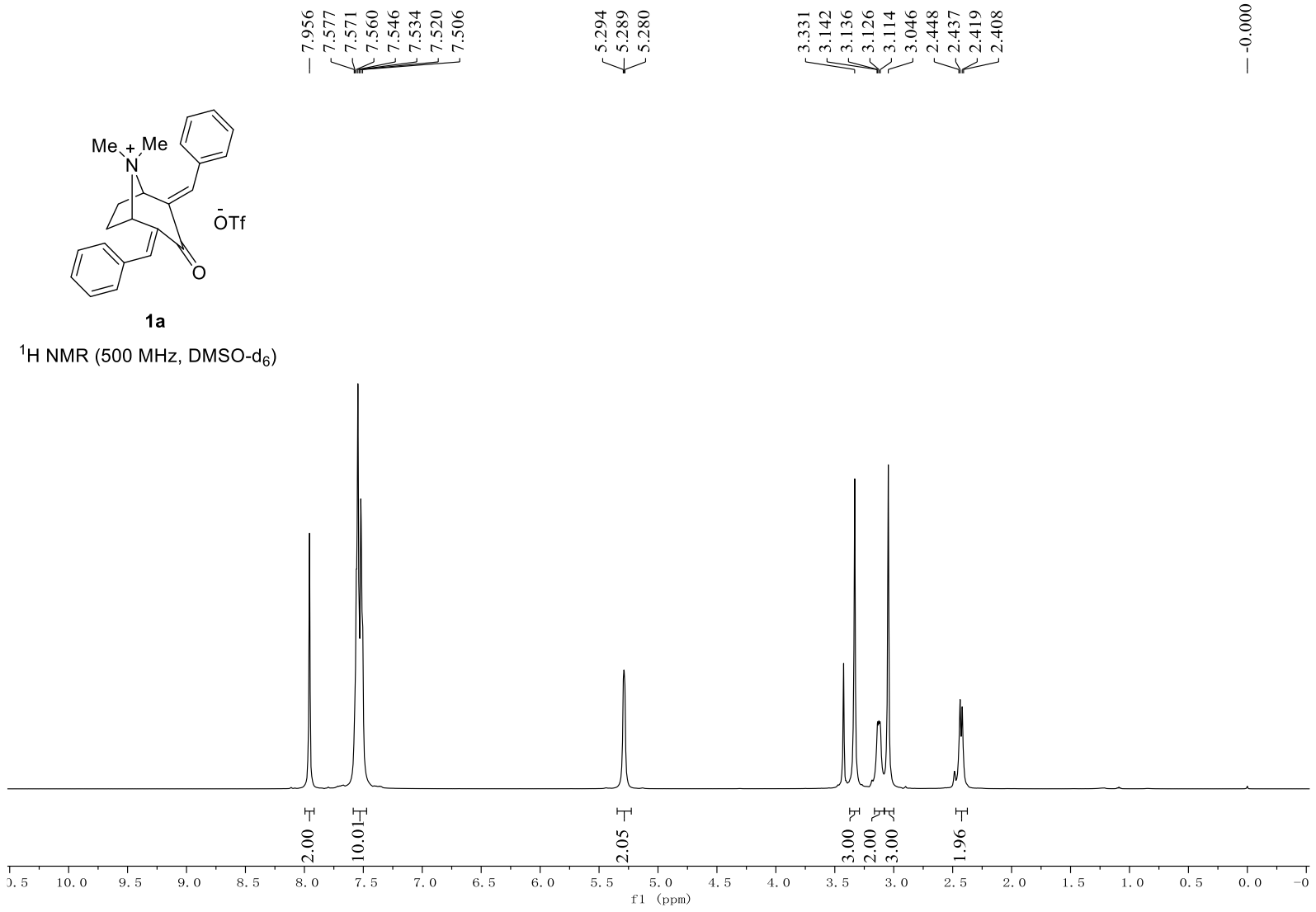
Atom	*x*	*y*	*z*	U(eq)
H6	1288	4445	3279	55
H5A	2027	5102	5628	62
H5B	1018	4821	5170	62
H3	2860	3080	6073	67
H4	1446	3502	5549	69
H15	4806	4385	6261	65
H8	3507	4150	2835	68
H23A	101	5444	3090	98
H23B	294	6373	3031	98
H23C	501	5925	4295	98
H22A	2046	6326	4826	97
H22B	1879	6852	3633	97
H22C	2671	6222	3901	97
H24A	2040	5652	1866	112
H24B	1239	6272	1670	112
H24C	1039	5342	1531	112
H14	3161	4280	538	94
H11	503	2897	416	101
H17	3636	3148	7991	94

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for hl-1_autored.

Atom	*x*	*y*	*z*	U(eq)
H12	993	3084	-1348	108
H13	2309	3786	-1291	114
H21	6033	3562	7182	104
H18	4317	2230	9463	127
H19	5833	1937	9729	142
H20	6690	2604	8609	139
H10	1334	3380	2257	86

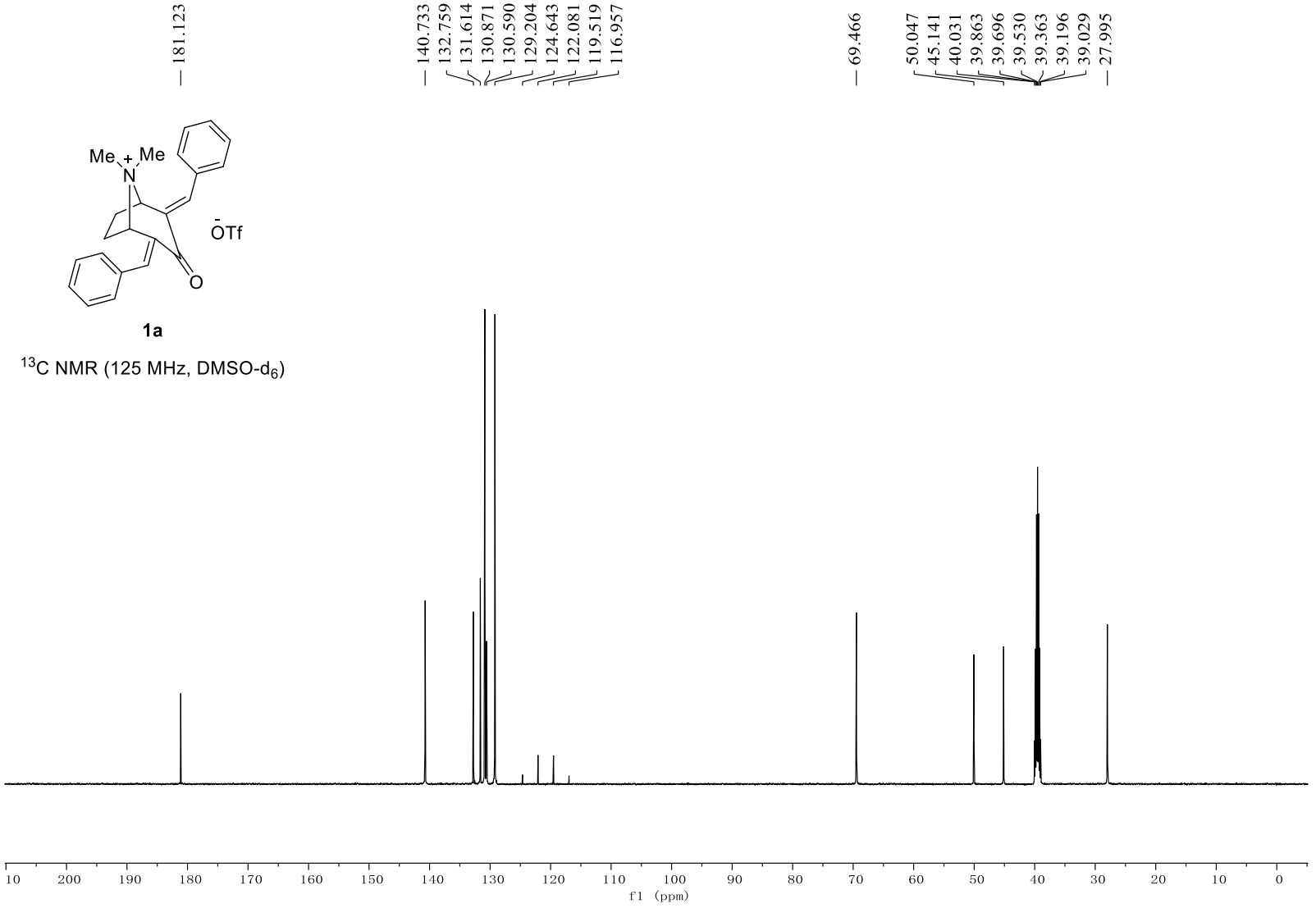
Table 8 Solvent masks information for hl-1_autored.

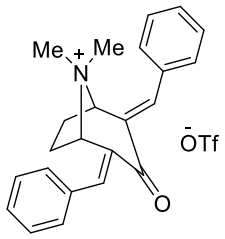
Number	X	Y	Z	Volume	Electron count	Content
1	0.500	0.500	1.000	202.8	45.5	?
2	0.500	1.000	0.500	202.8	45.5	?



1a

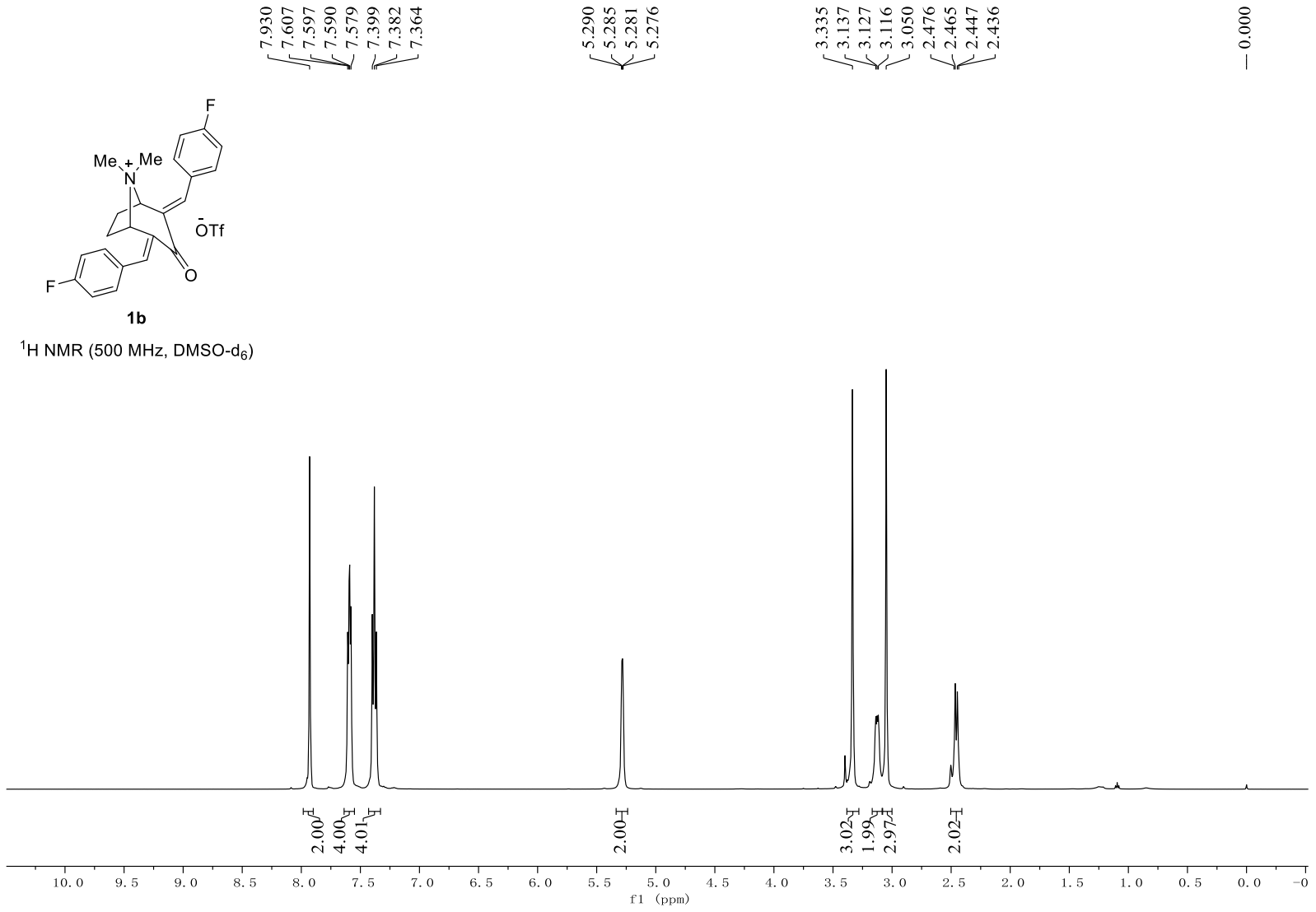
^{1}H NMR (500 MHz, DMSO-d_6)

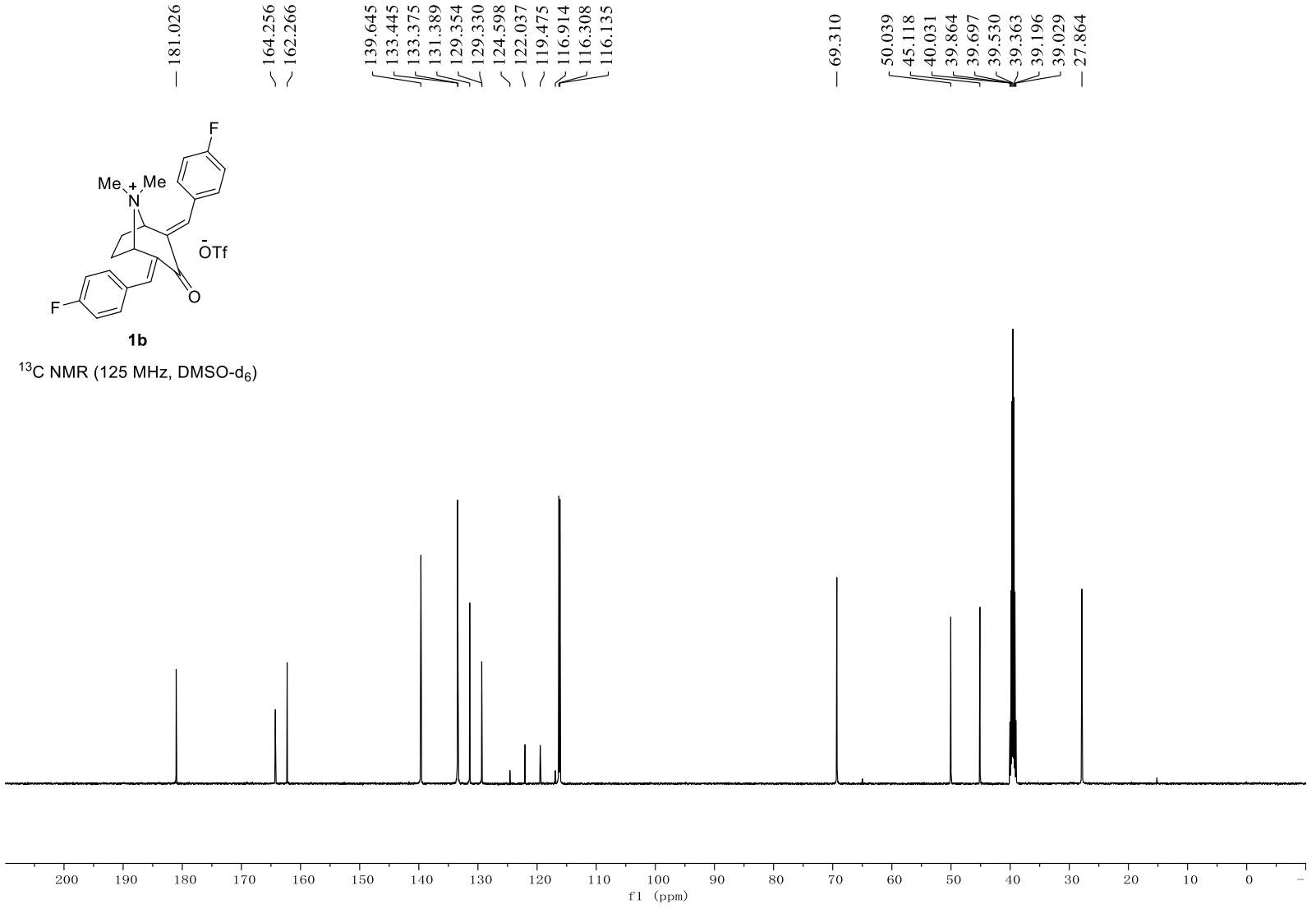

181.123
140.733
132.759
131.614
130.871
130.590
129.204
124.643
122.081
119.519
116.957
69.466
50.047
45.141
40.031
39.863
39.696
39.530
39.363
39.196
39.029
27.995
Me
N
Me
OTf
O
1a
13C NMR (125 MHz, DMSO-d6)
f1 (ppm)

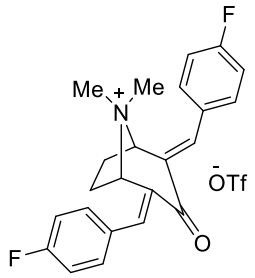


1a

^{19}F NMR (471 MHz, DMSO-d_6)

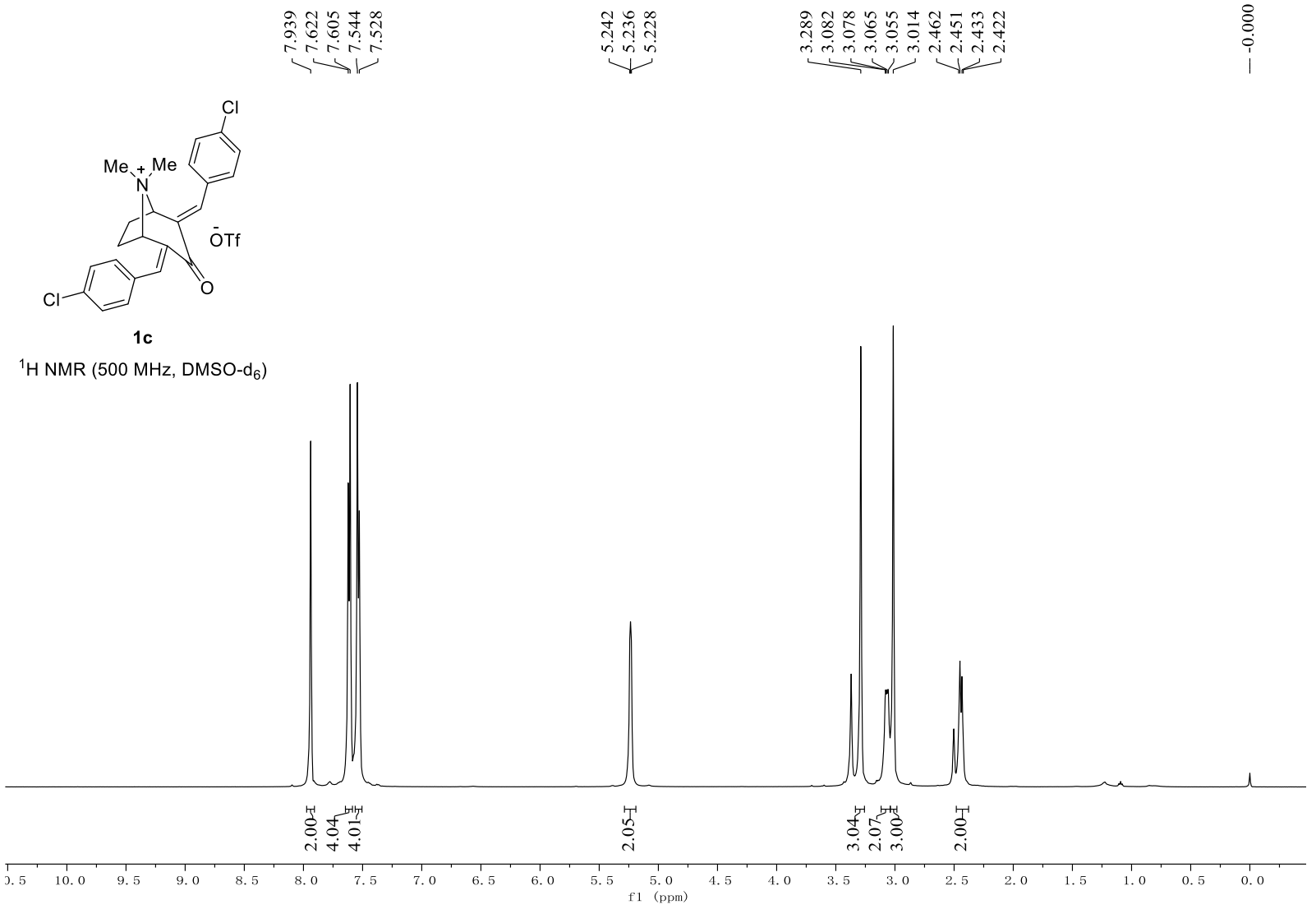

7.930
7.607
7.597
7.590
7.579
7.399
7.382
7.364
5.290
5.285
5.281
5.276
3.335
3.137
3.127
3.116
3.050
2.476
2.465
2.447
2.436
0.000
F
Me
N
Me
OTf
O
F
1b
1H NMR (500 MHz, DMSO-d6)
2.00
4.00
4.01
2.00
3.02
1.99
2.97
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

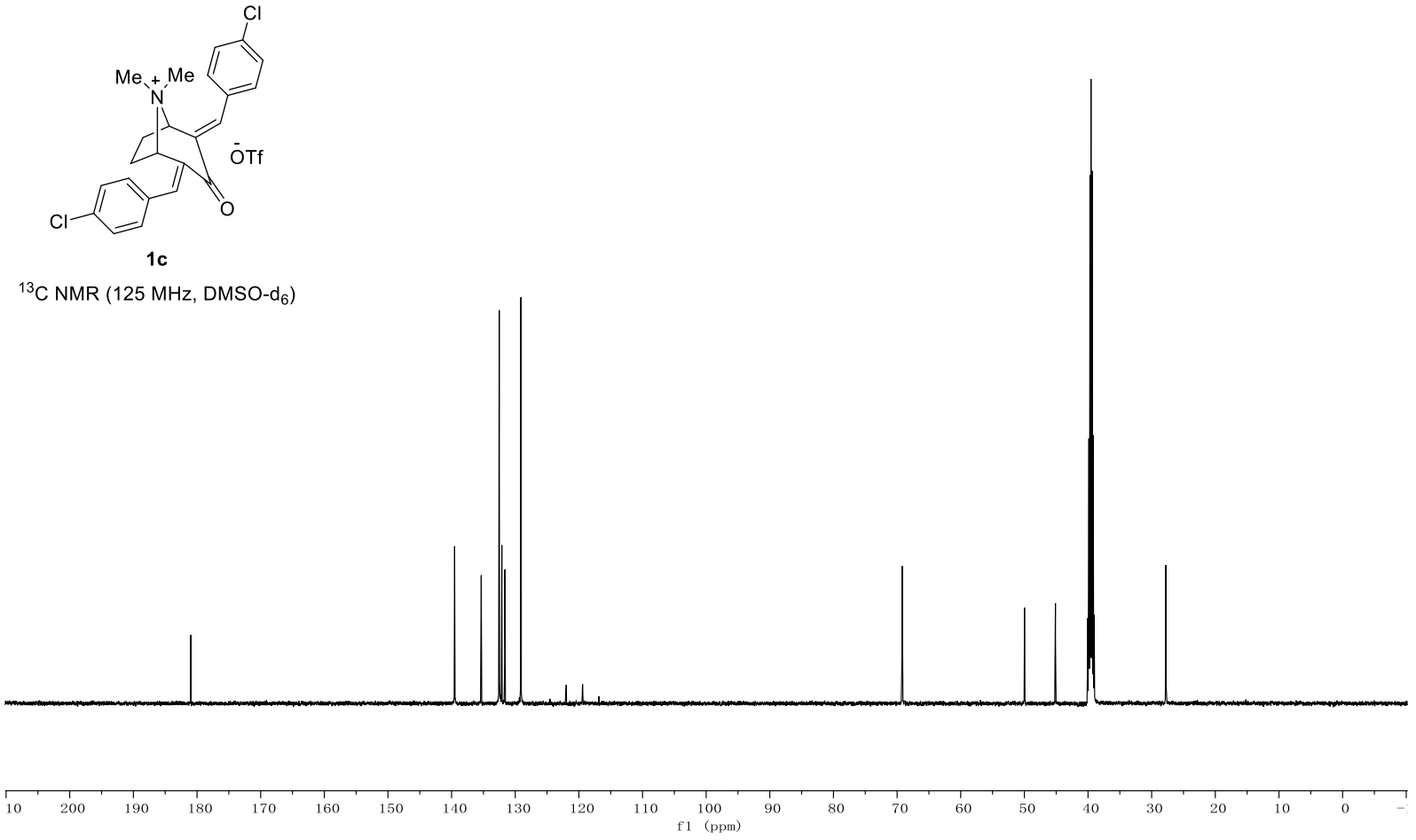

181.026
164.256
162.266
139.645
133.445
133.375
131.389
129.354
129.330
124.598
122.037
119.475
116.914
116.308
116.135
69.310
50.039
45.118
40.031
39.864
39.697
39.530
39.363
39.196
39.029
27.864
F
Me
N
+
Me
OTf
O
F
1b
13C NMR (125 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

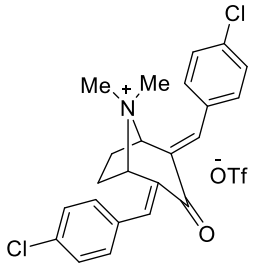


1b

^{19}F NMR (471 MHz, DMSO-d_6)

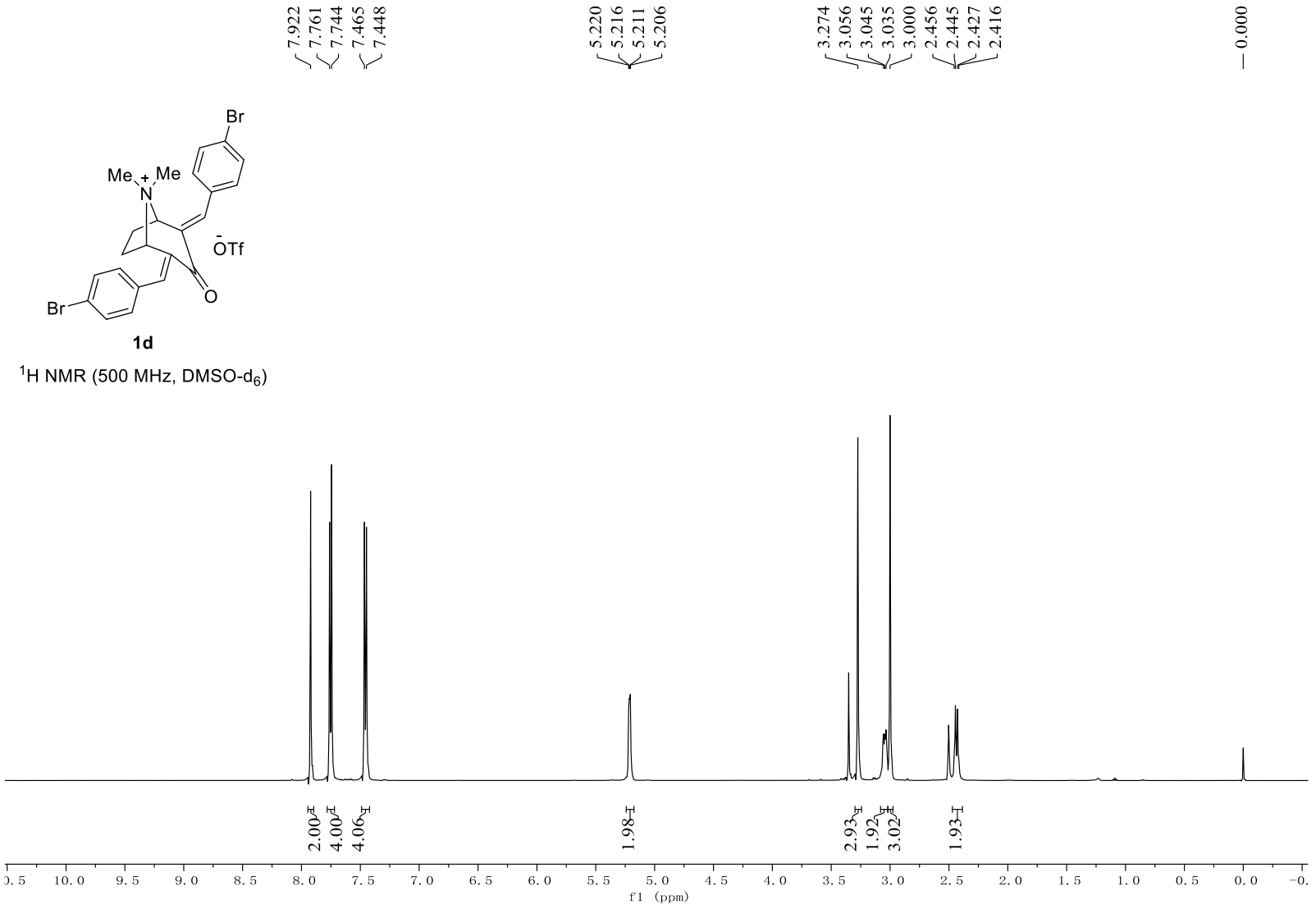

7.939
7.622
7.605
7.544
7.528
5.242
5.236
5.228
3.289
3.082
3.078
3.065
3.055
3.014
2.462
2.451
2.433
2.422
-0.000
Cl
Me
N
Me
OTf
O
Cl
1c
1H NMR (500 MHz, DMSO-d6)
2.00
4.04
4.01
2.05
3.04
2.07
3.00
2.00
f1 (ppm)

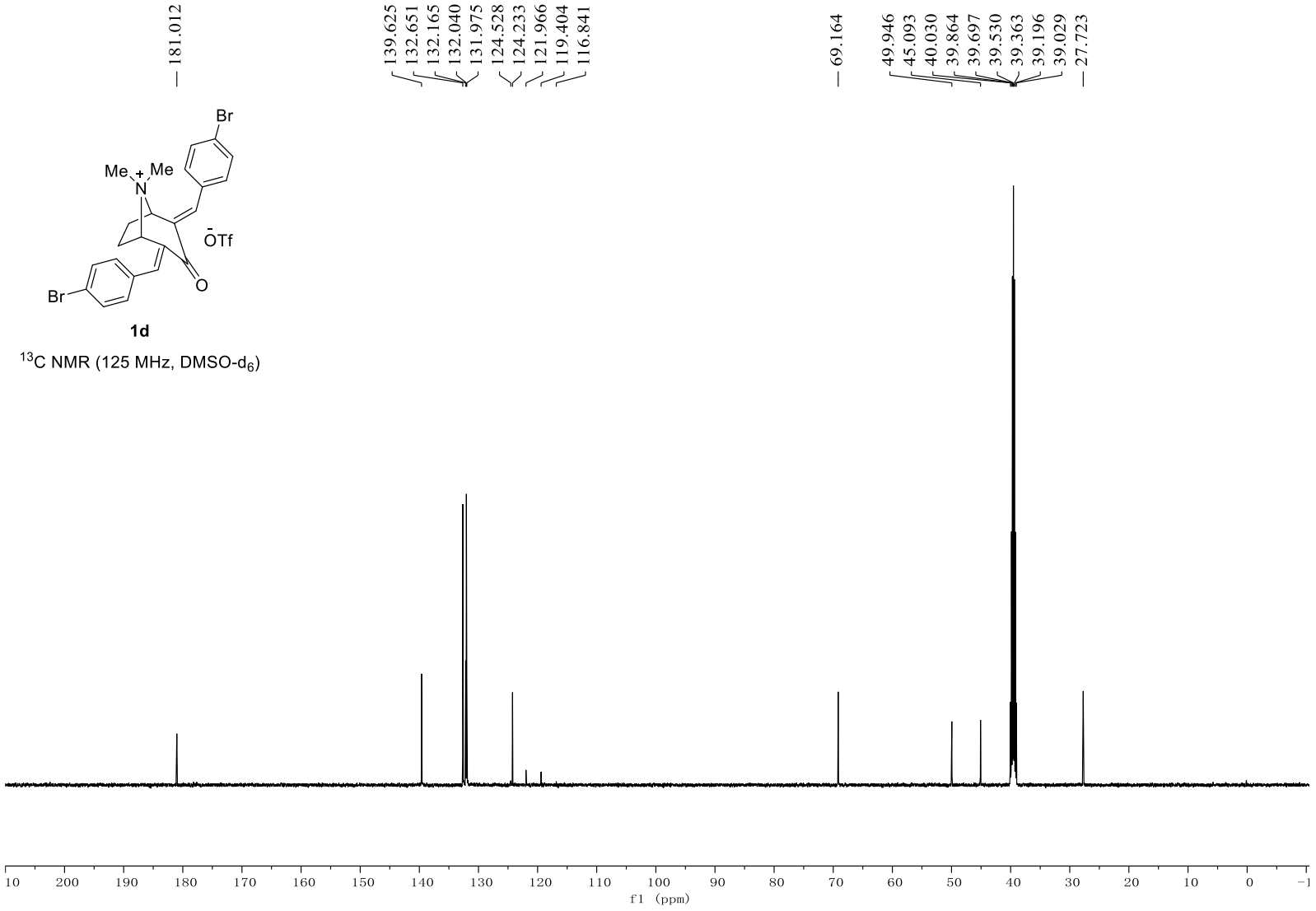

180.987
139.527
135.345
132.517
132.108
131.636
129.118
124.546
121.983
119.421
116.858
69.195
49.978
45.118
40.031
39.863
39.696
39.530
39.363
39.196
39.029
27.763
Cl
Me
N
Me
OTf
O
Cl
1c
13C NMR (125 MHz, DMSO-d6)
f1 (ppm)



1c

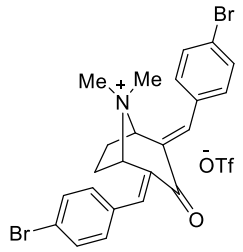
^{19}F NMR (471 MHz, DMSO-d_6)


7.922
7.761
7.744
7.465
7.448
5.220
5.216
5.211
5.206
3.274
3.056
3.045
3.035
3.000
2.456
2.445
2.427
2.416
0.000
Br
Me
N
Me
OTf
O
Br
1d
1H NMR (500 MHz, DMSO-d6)
2.00
4.00
4.06
1.98
2.93
1.92
3.02
1.93
f1 (ppm)



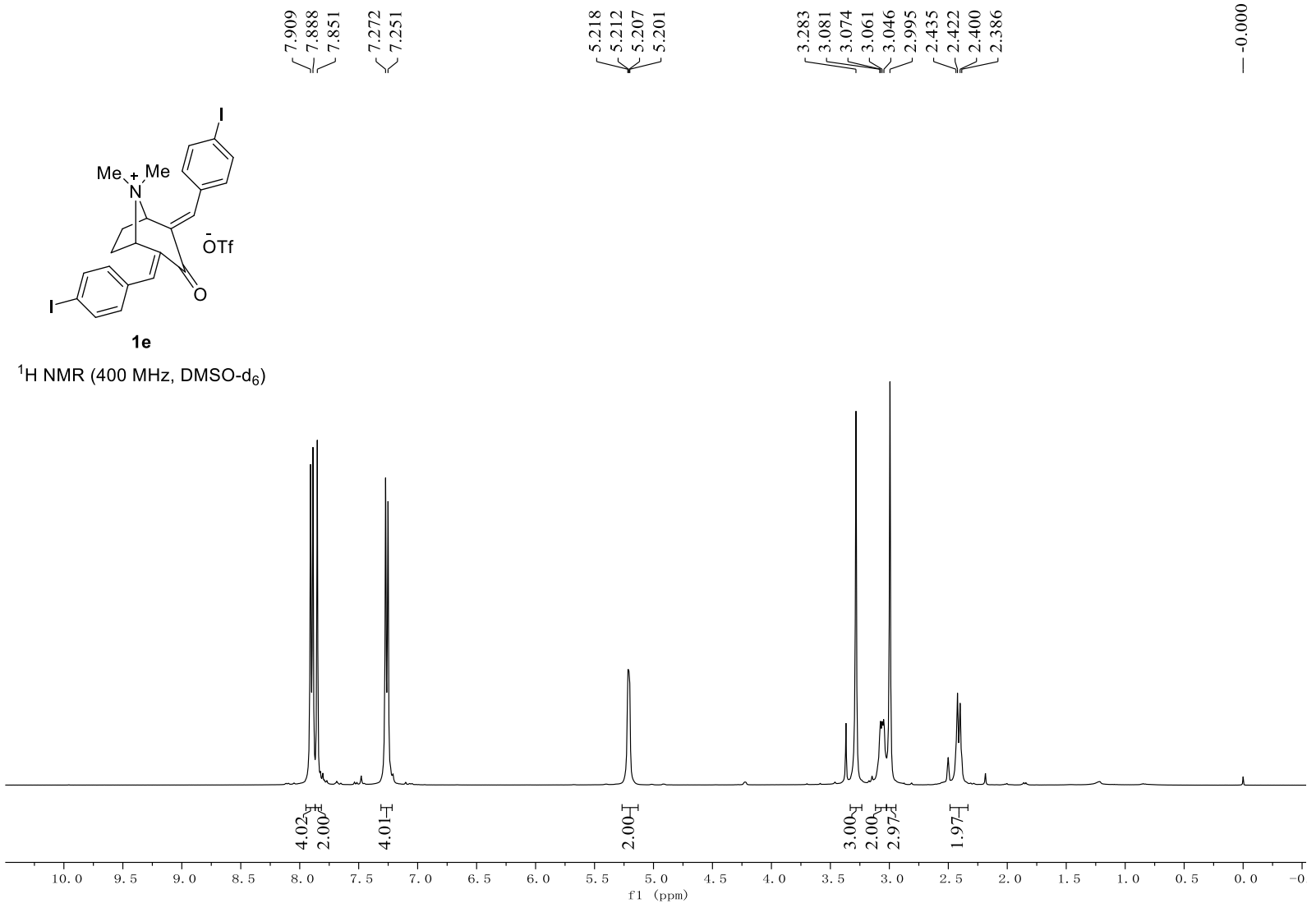
1d

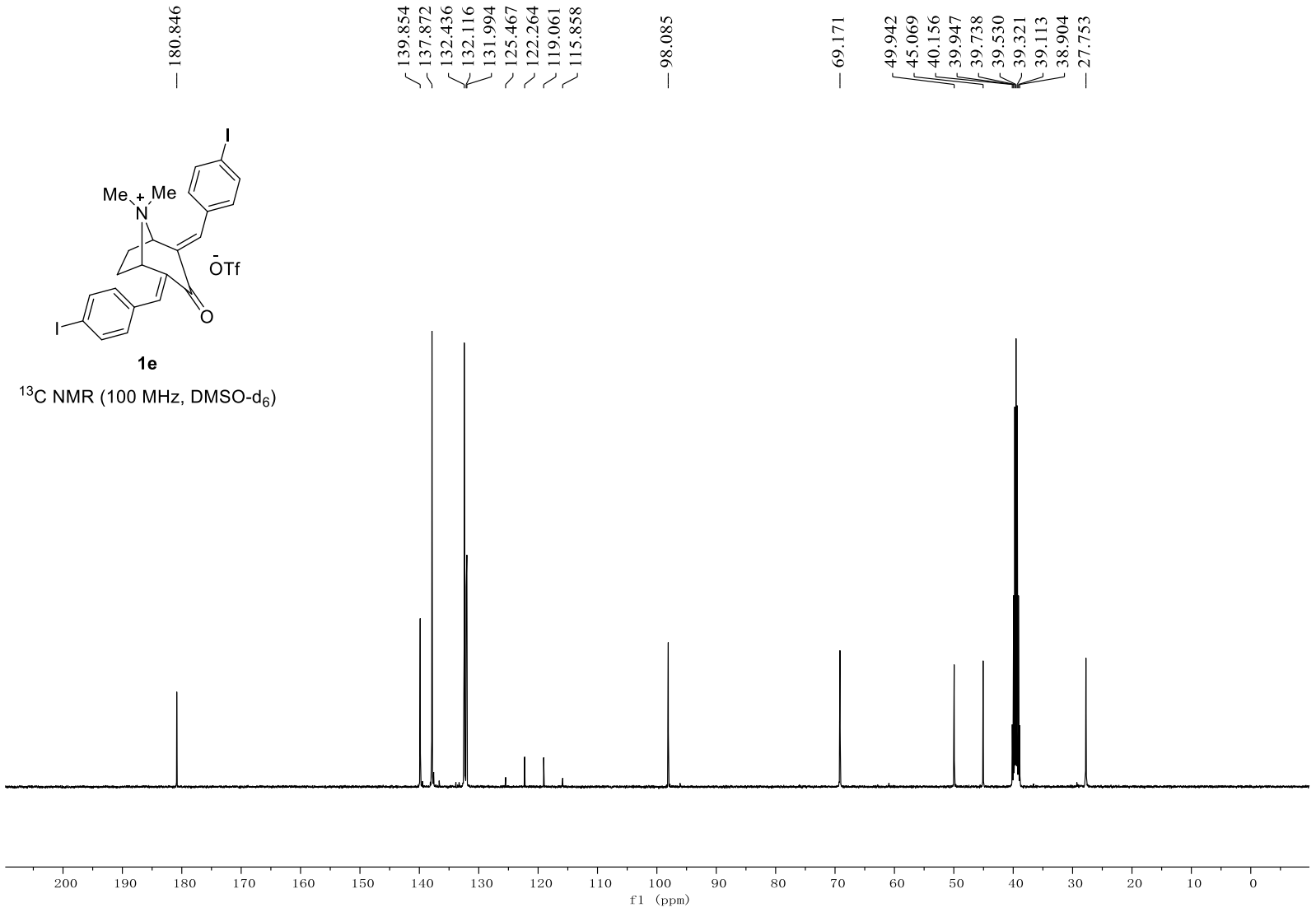
^{13}C NMR (125 MHz, DMSO-d_6)

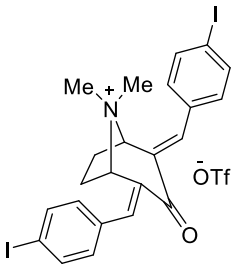


1d

^{19}F NMR (471 MHz, DMSO-d_6)

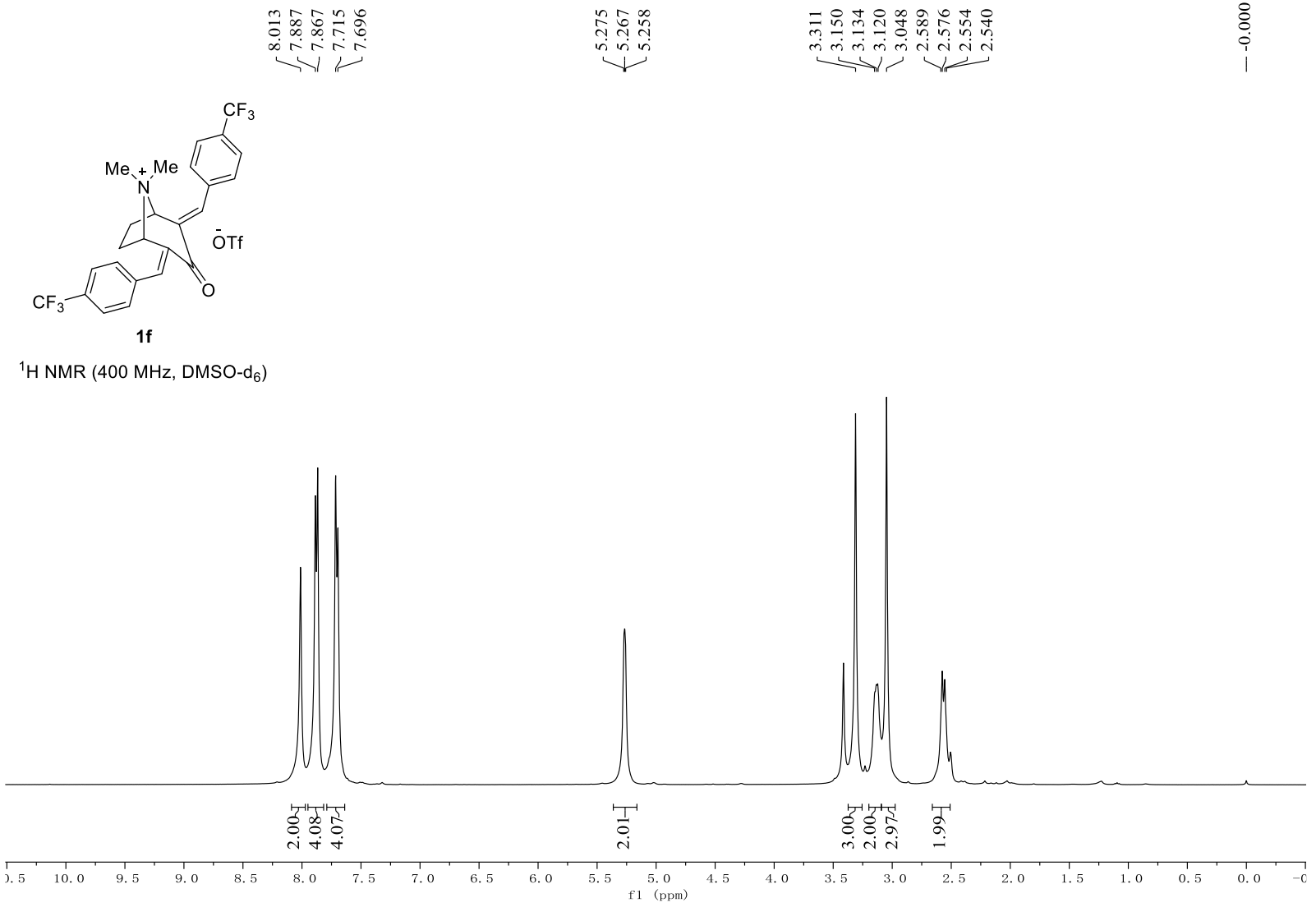

7.909
7.888
7.851
7.272
7.251
5.218
5.212
5.207
5.201
3.283
3.081
3.074
3.061
3.046
2.995
2.435
2.422
2.400
2.386
-0.000
I
Me
N
Me
OTf
O
I
1e
1H NMR (400 MHz, DMSO-d6)
4.02
2.00
4.01
2.00
3.00
2.00
2.97
1.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

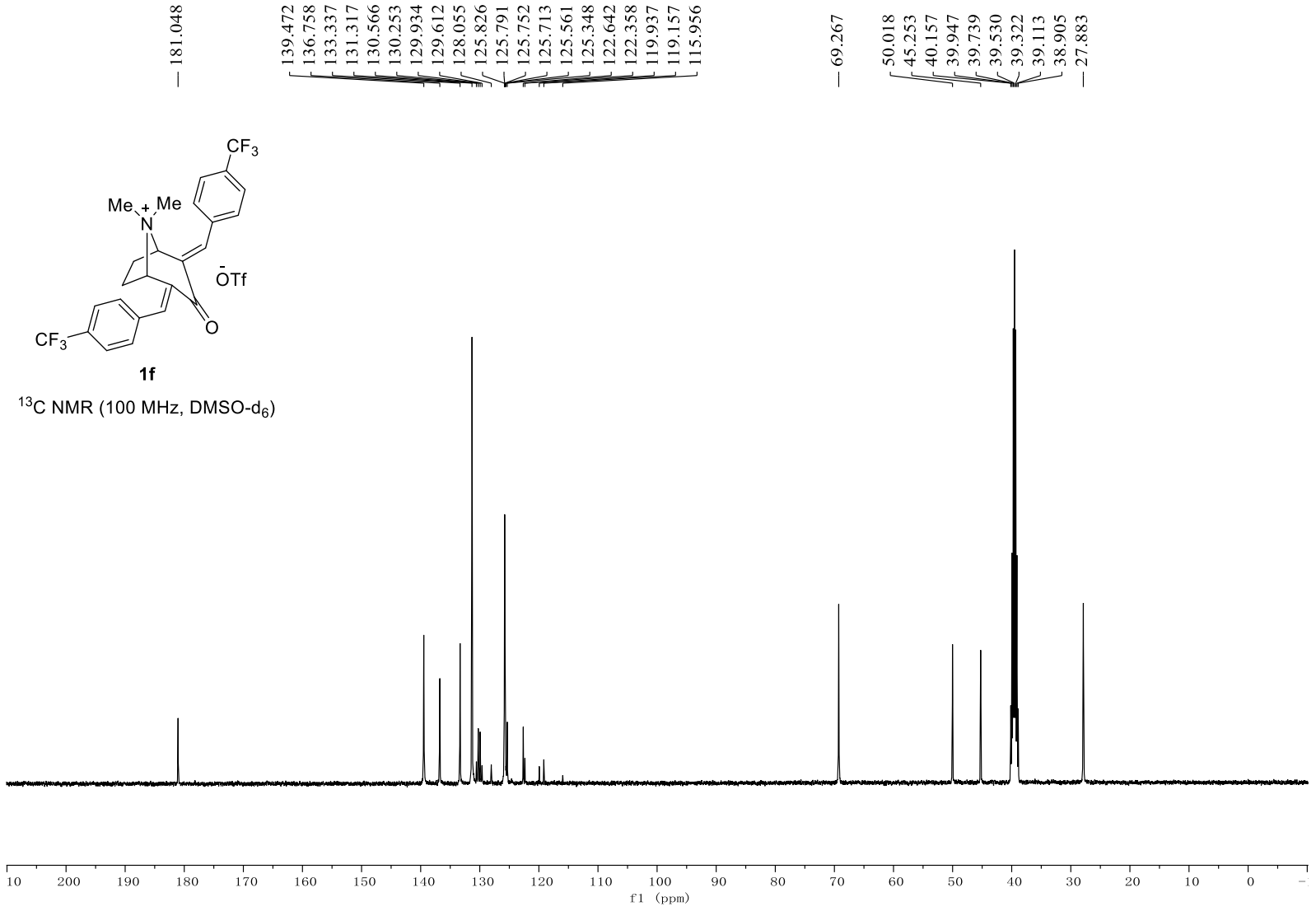

180.846
139.854
137.872
132.436
132.116
131.994
125.467
122.264
119.061
115.858
98.085
69.171
49.942
45.069
40.156
39.947
39.738
39.530
39.321
39.113
38.904
27.753
I
Me
N
Me
OTf
O
I
1e
13C NMR (100 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

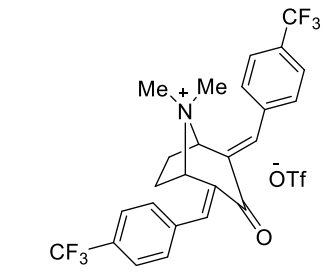


1e

^{19}F NMR (376 MHz, DMSO-d_6)

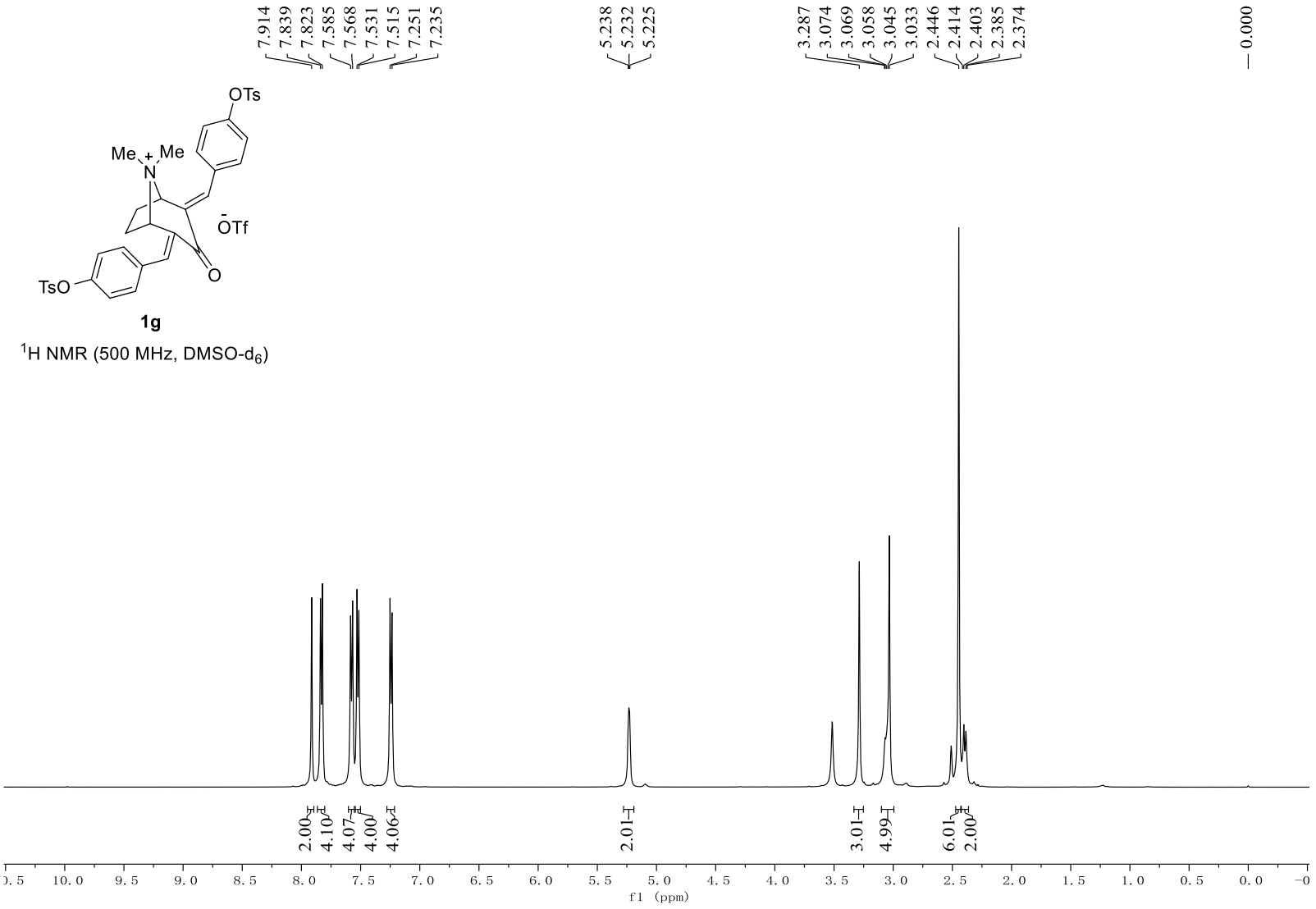

8.013
7.887
7.867
7.715
7.696
5.275
5.267
5.258
3.311
3.150
3.134
3.120
3.048
2.589
2.576
2.554
2.540
-0.000
CF3
Me
N
Me
OTf
O
CF3
1f
1H NMR (400 MHz, DMSO-d6)
2.00
4.08
4.07
2.01
3.00
2.00
2.97
1.99
f1 (ppm)

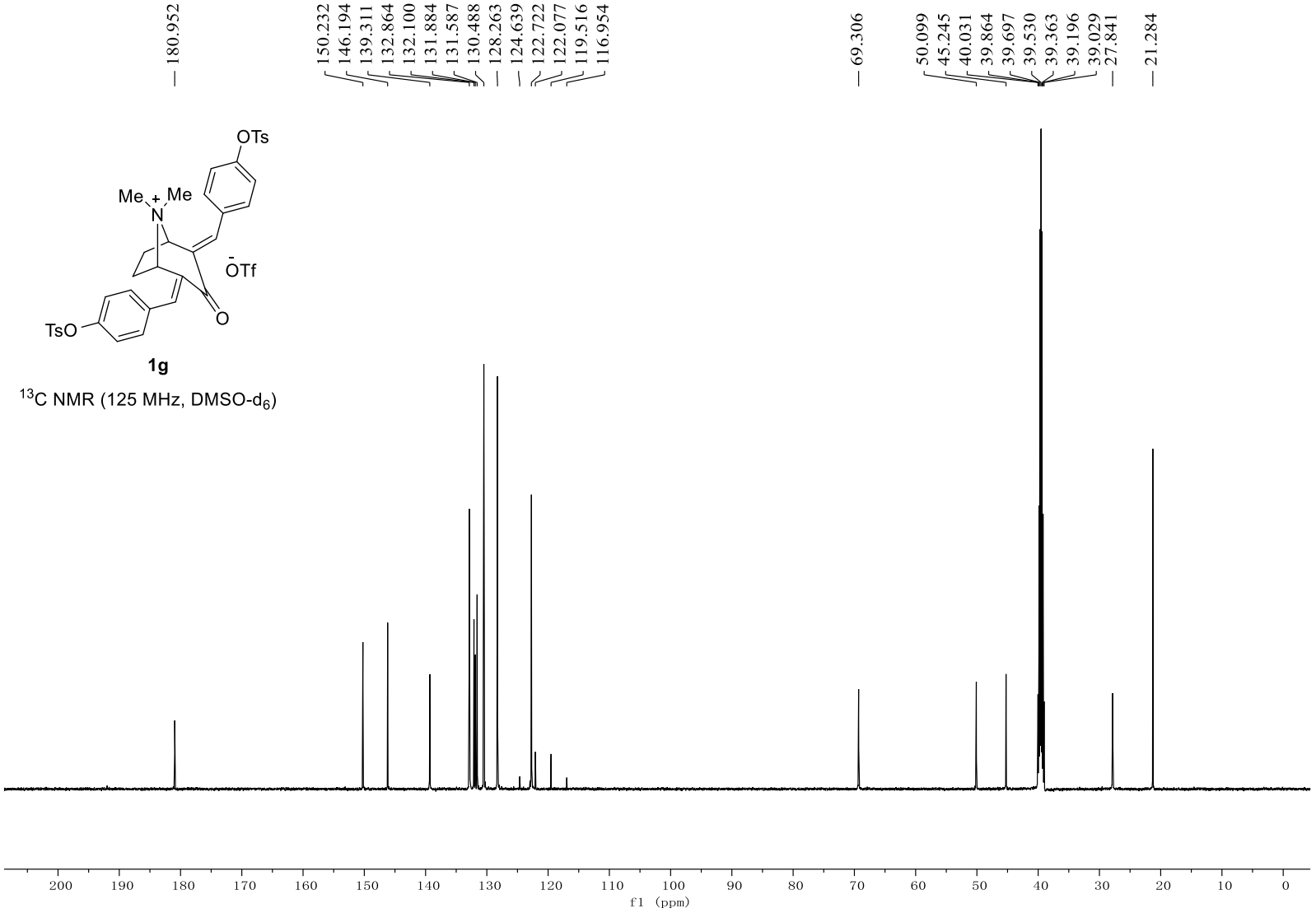

181.048
139.472
136.758
133.337
131.317
130.566
130.253
129.934
129.612
128.055
125.826
125.791
125.752
125.713
125.561
125.348
122.642
122.358
119.937
119.157
115.956
69.267
50.018
45.253
40.157
39.947
39.739
39.530
39.322
39.113
38.905
27.883
CF3
Me
N
Me
OTf
O
CF3
1f
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)

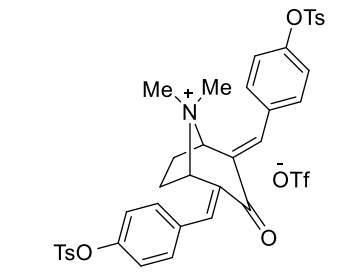


1f

^{19}F NMR (376 MHz, DMSO-d_6)

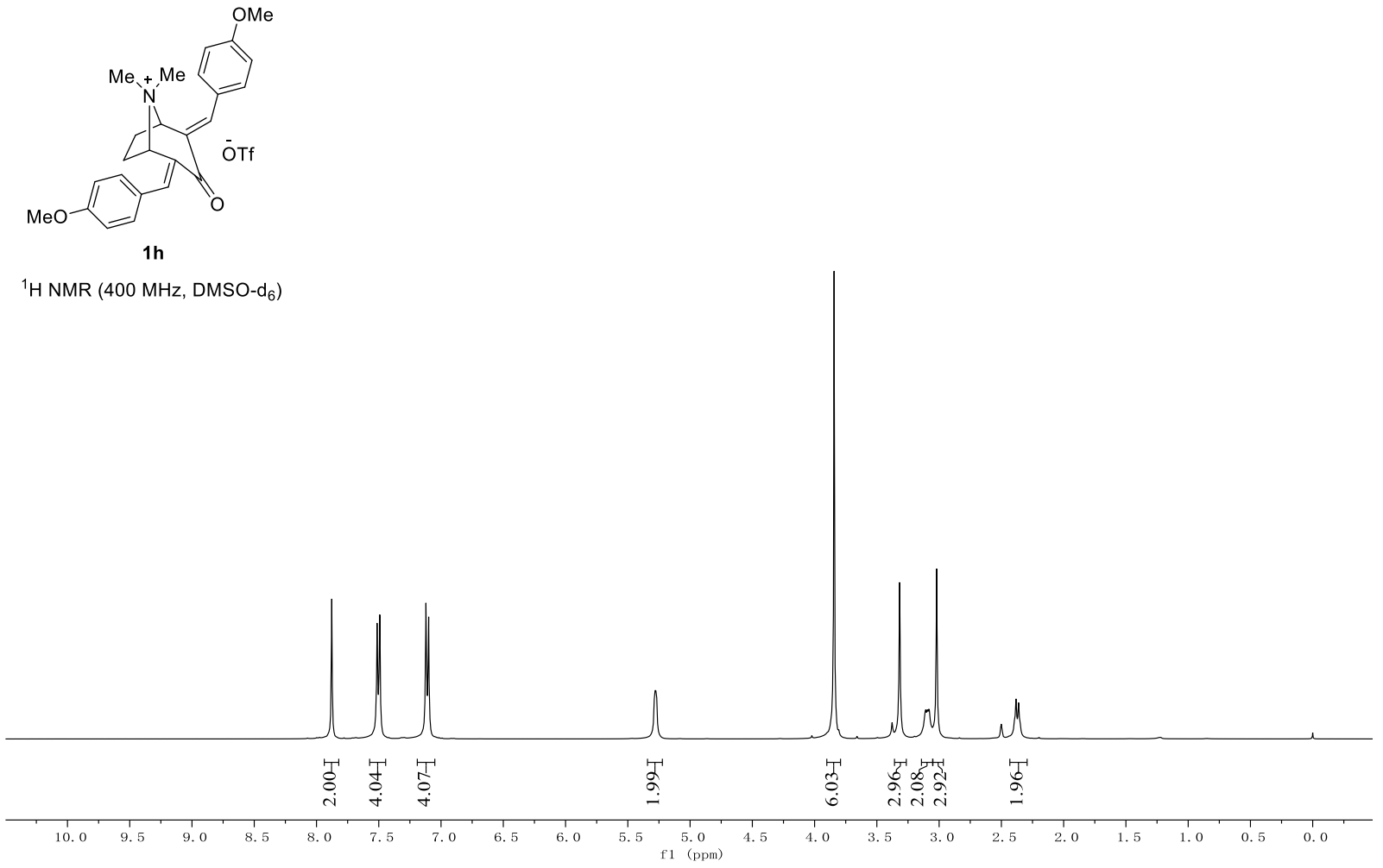

7.914
7.839
7.823
7.585
7.568
7.531
7.515
7.251
7.235
5.238
5.232
5.225
3.287
3.074
3.069
3.058
3.045
3.033
2.446
2.414
2.403
2.385
2.374
0.000
OTs
Me
Me
N
OTf
O
TsO
1g
1H NMR (500 MHz, DMSO-d6)
2.00
4.10
4.07
4.00
4.06
2.01
3.01
4.99
6.01
2.00
f1 (ppm)

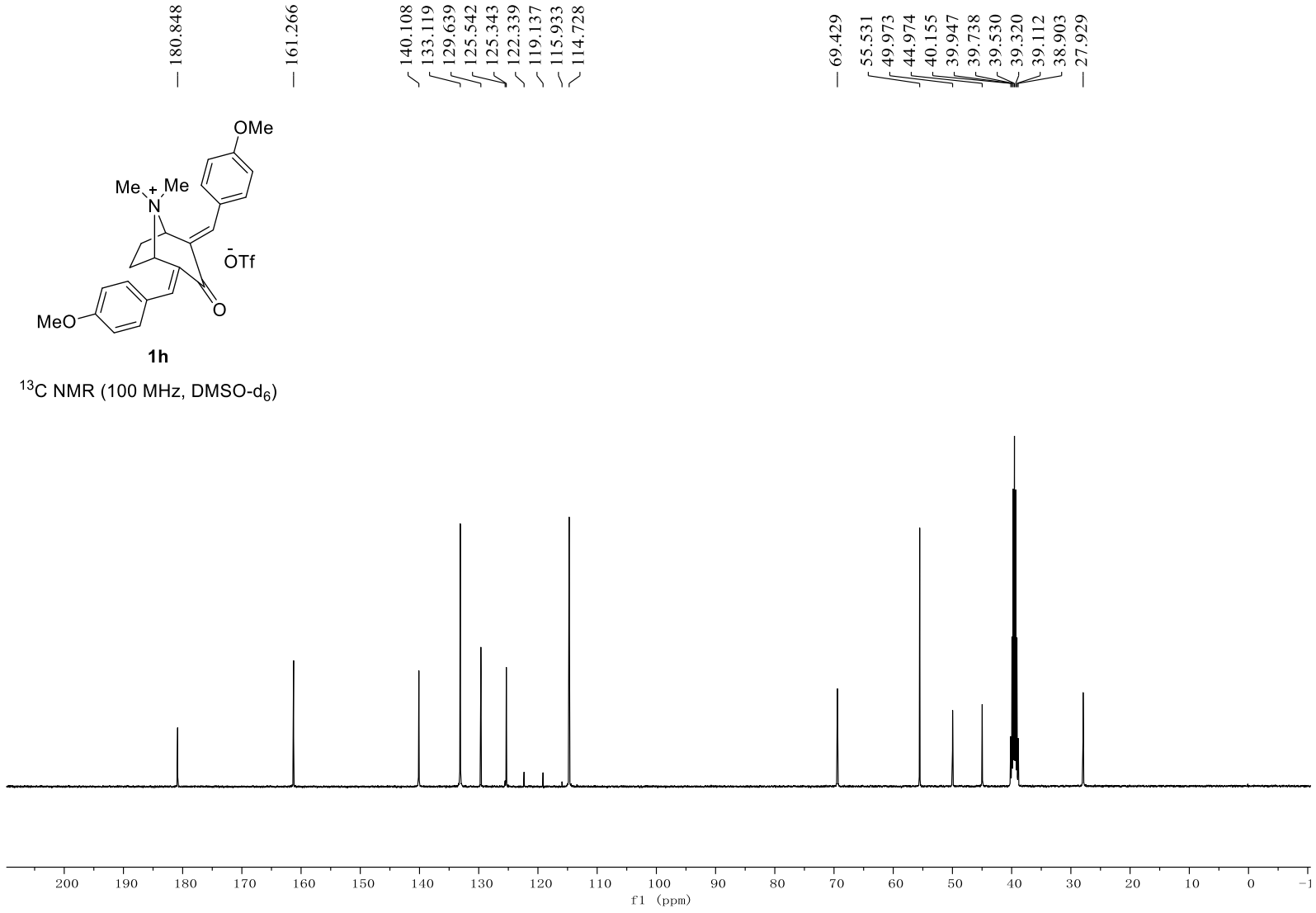

180.952
150.232
146.194
139.311
132.864
132.100
131.884
131.587
130.488
128.263
124.639
122.722
122.077
119.516
116.954
69.306
50.099
45.245
40.031
39.864
39.697
39.530
39.363
39.196
39.029
27.841
21.284
OTs
Me
N
Me
OTf
O
TsO
1g
13C NMR (125 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

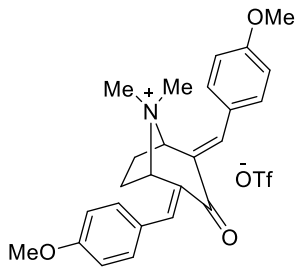


1g

^{19}F NMR (471 MHz, DMSO-d_6)

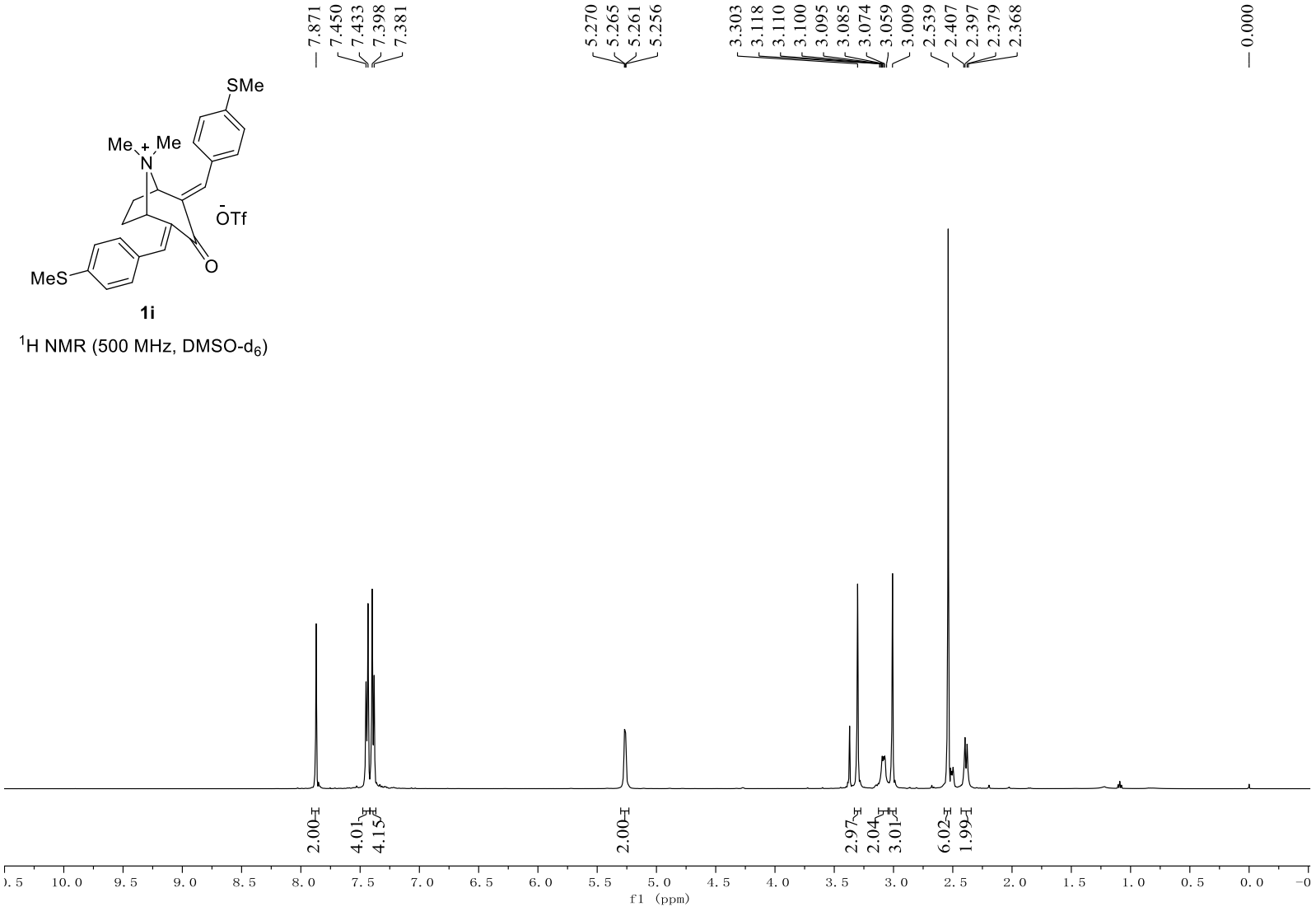

7.877
7.514
7.492
7.121
7.099
5.286
5.281
5.275
5.268
3.844
3.317
3.116
3.108
3.095
3.083
3.020
2.396
2.383
2.361
2.347
-0.000
OMe
Me
N
Me
OTf
O
MeO
1h
1H NMR (400 MHz, DMSO-d6)
2.00
4.04
4.07
1.99
6.03
2.96
2.08
2.92
1.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


180.848
161.266
140.108
133.119
129.639
125.542
125.343
122.339
119.137
115.933
114.728
69.429
55.531
49.973
44.974
40.155
39.947
39.738
39.530
39.320
39.112
38.903
27.929
OMe
Me
N
Me
OTf
O
MeO
1h
13C NMR (100 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



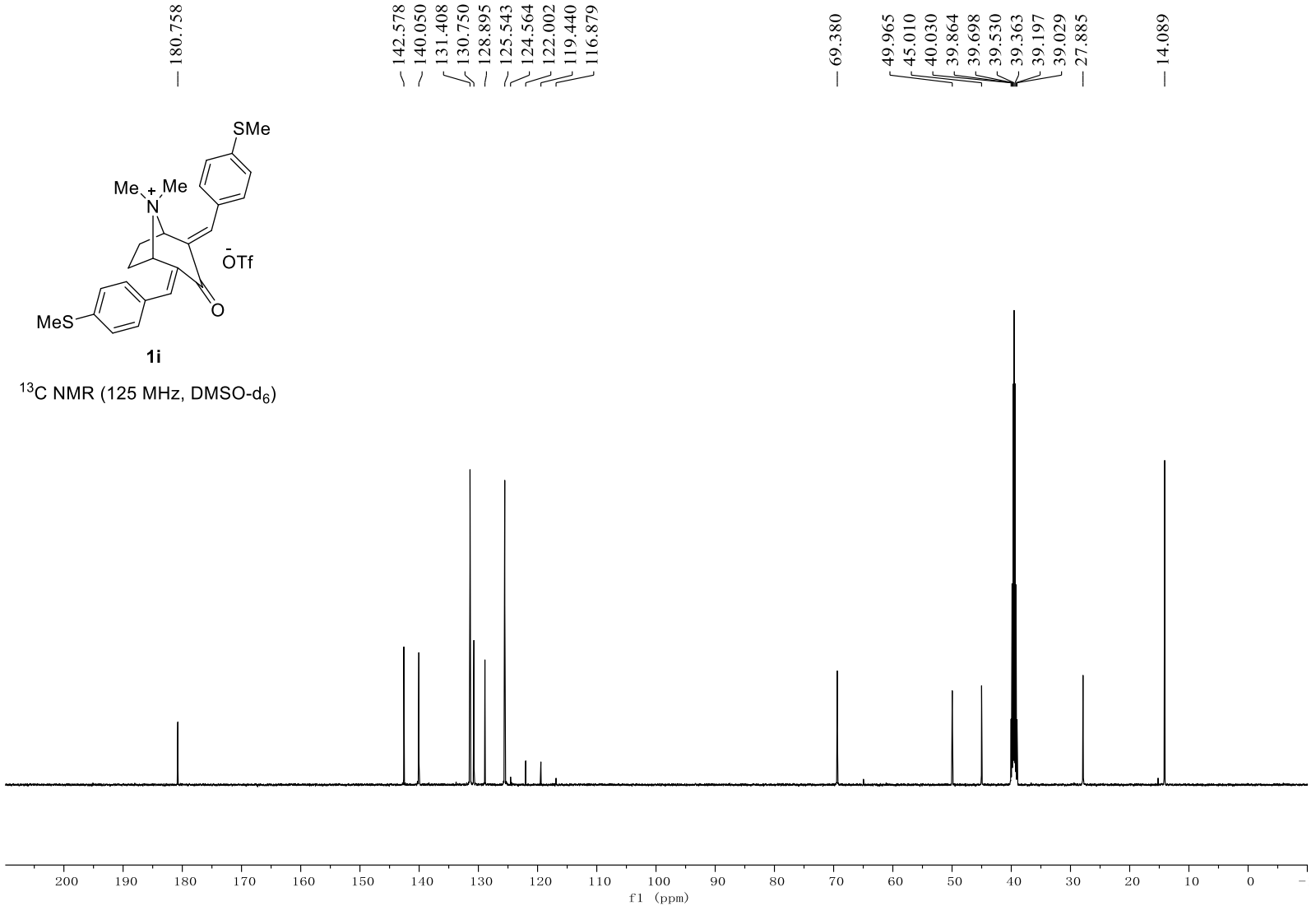
1h

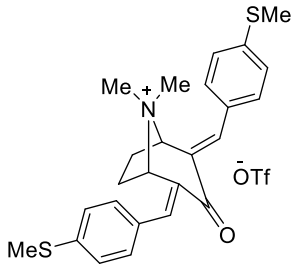
^{19}F NMR (376 MHz, DMSO-d_6)



1i

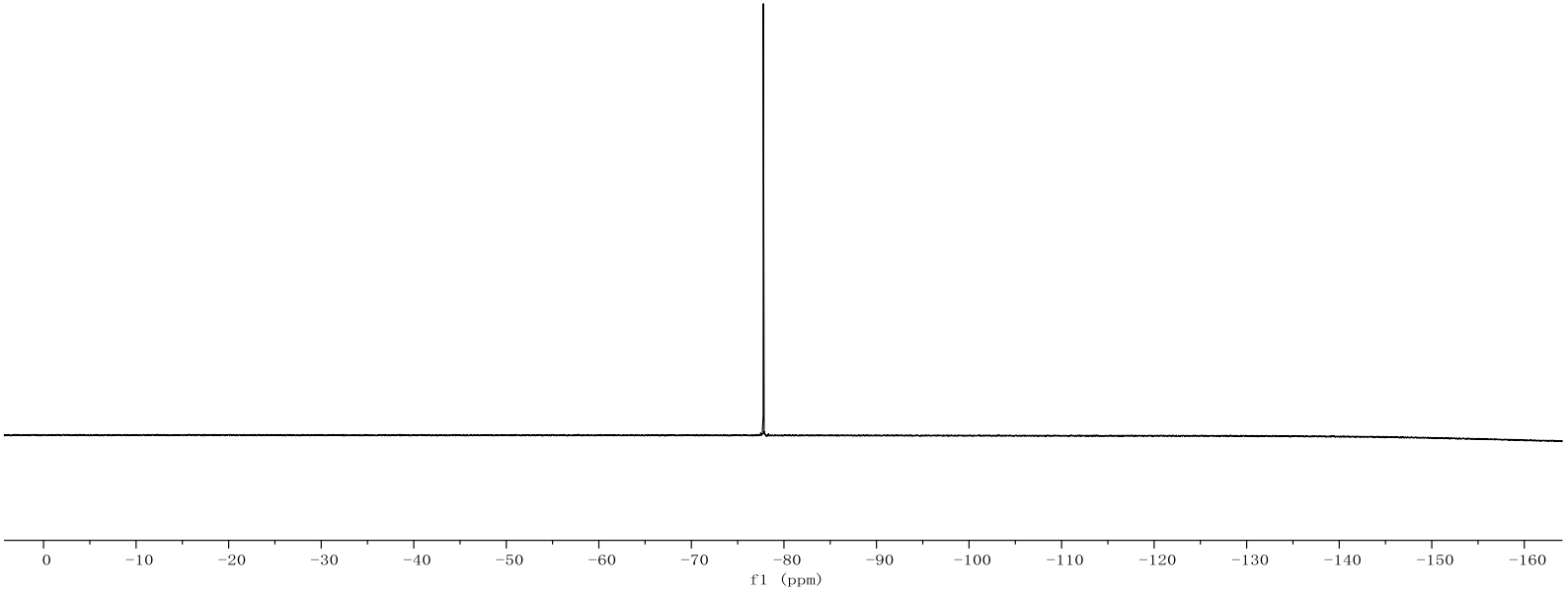
^{1}H NMR (500 MHz, DMSO-d_6)

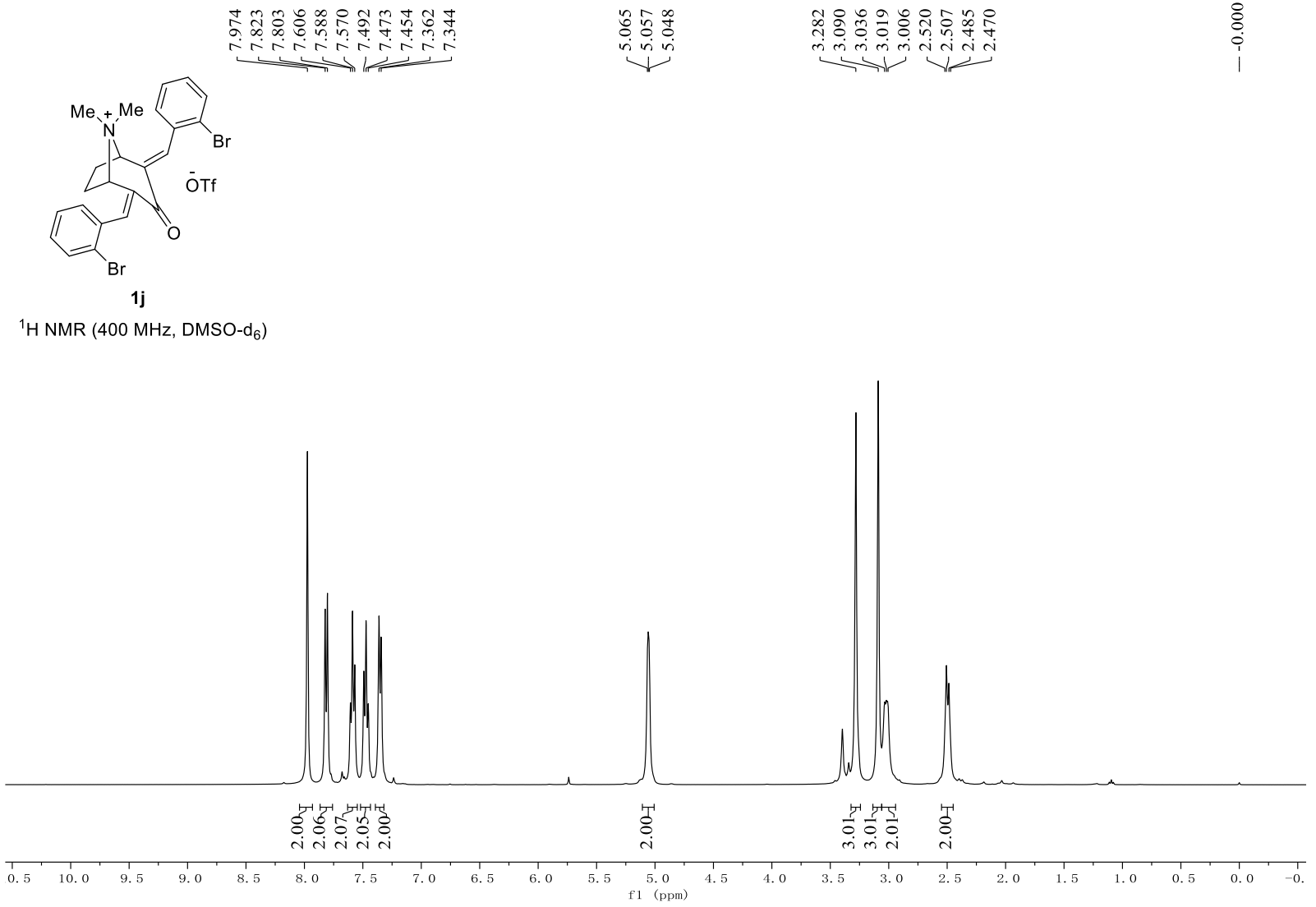

180.758
142.578
140.050
131.408
130.750
128.895
125.543
124.564
122.002
119.440
116.879
69.380
49.965
45.010
40.030
39.864
39.698
39.530
39.363
39.197
39.029
27.885
14.089
SMe
Me
N
Me
OTf
O
MeS
1i
13C NMR (125 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1i

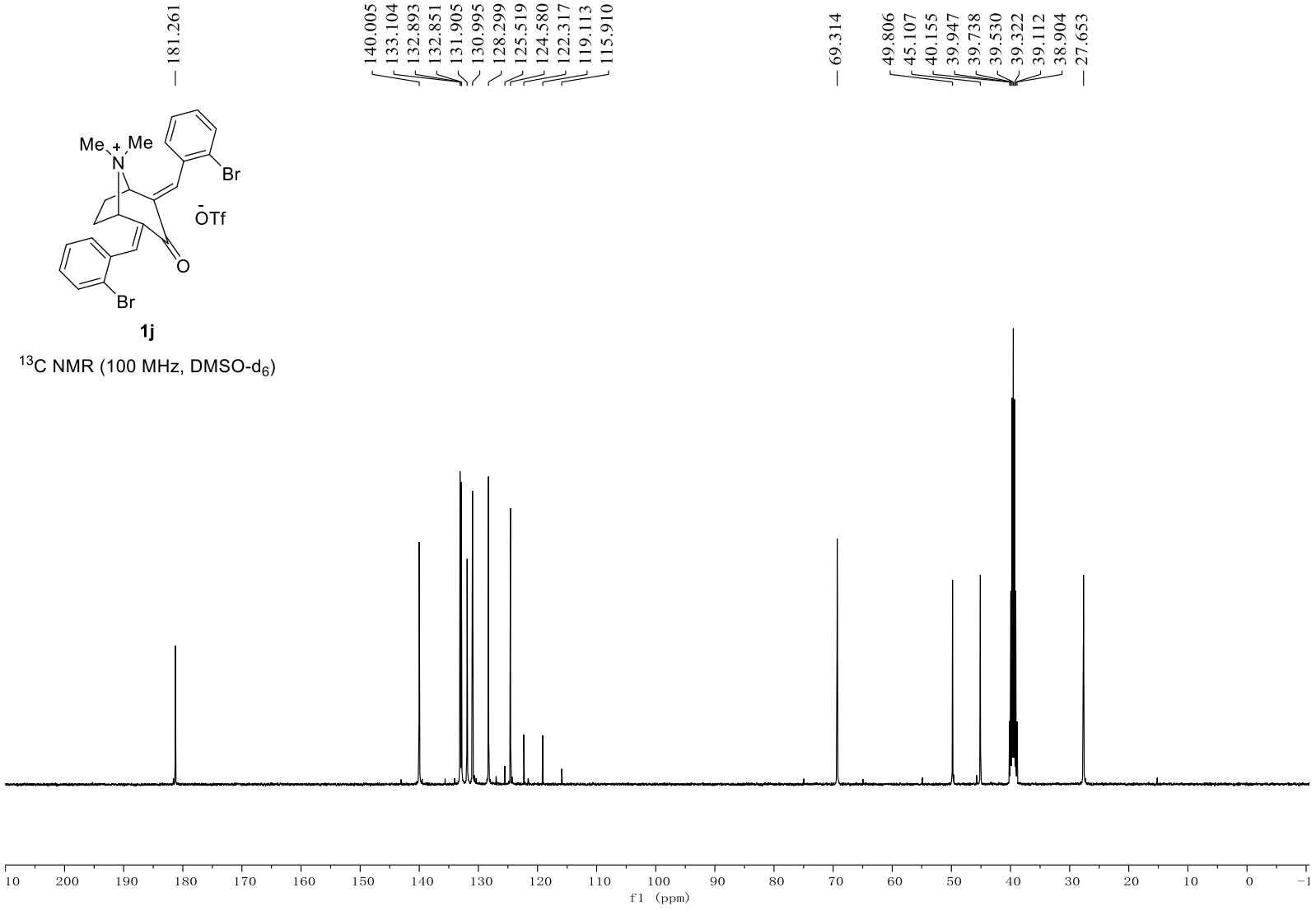
^{19}F NMR (376 MHz, DMSO-d_6)

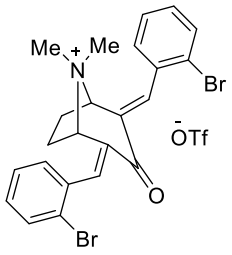




1j

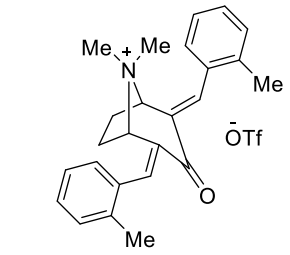
^{1}H NMR (400 MHz, DMSO-d_6)


181.261
140.005
133.104
132.893
132.851
131.905
130.995
128.299
125.519
124.580
122.317
119.113
115.910
69.314
49.806
45.107
40.155
39.947
39.738
39.530
39.322
39.112
38.904
27.653
Me
N
Me
Br
OTf
O
Br
1j
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)



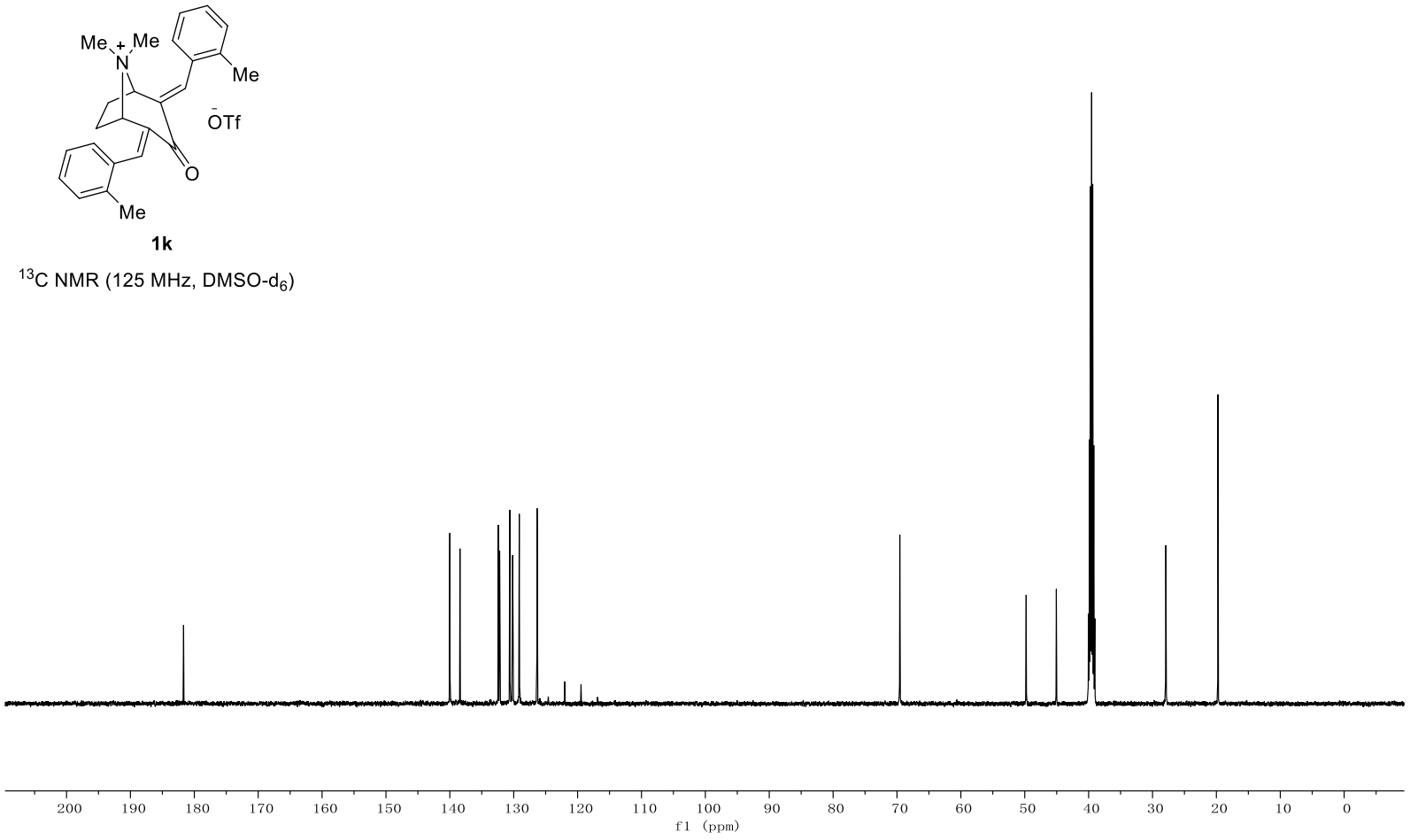
1j

^{19}F NMR (376 MHz, DMSO-d_6)



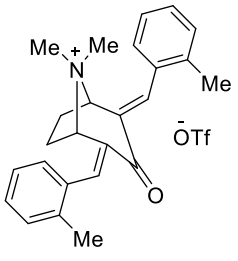
1k

^{1}H NMR (500 MHz, DMSO-d_6)



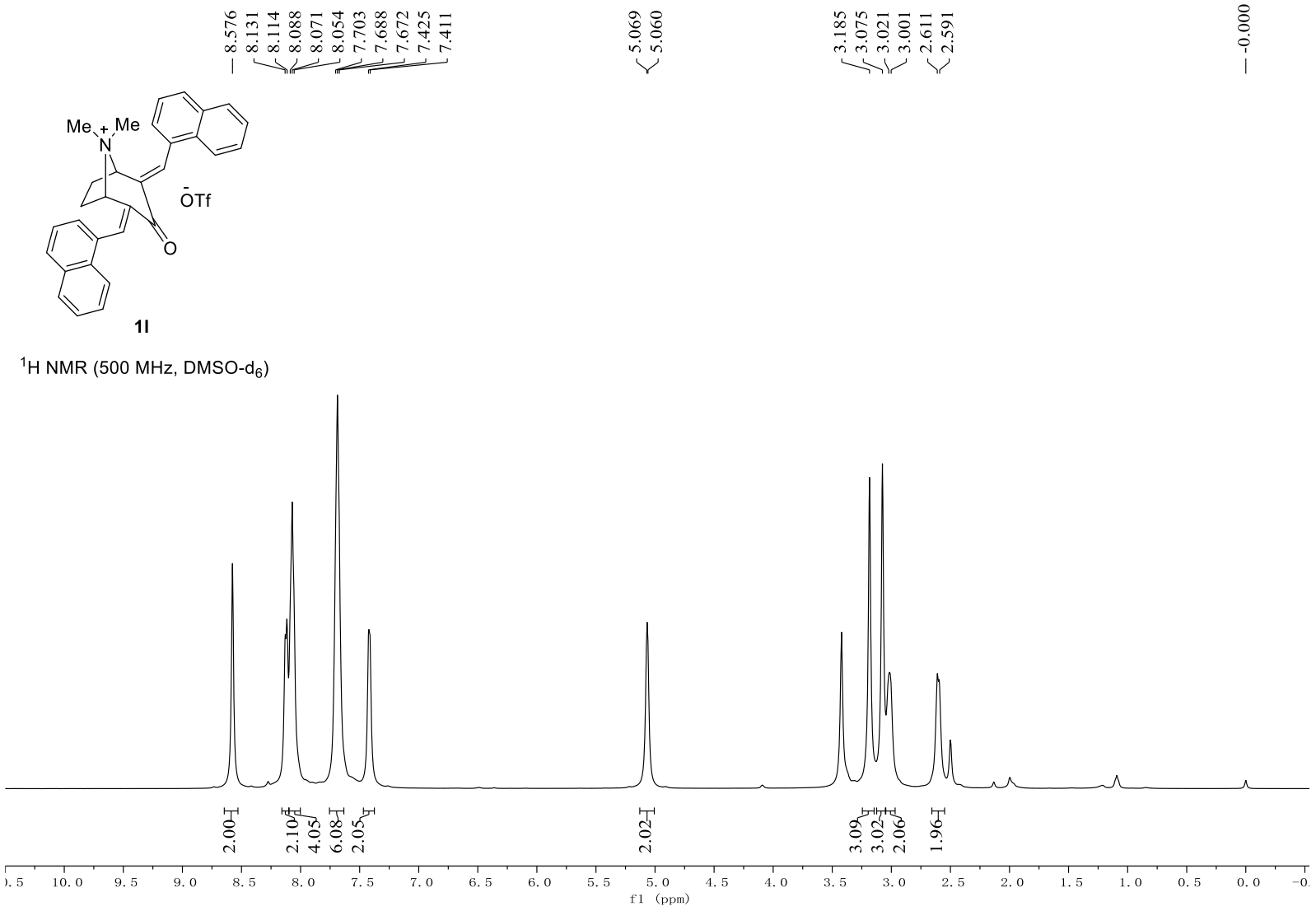
1k

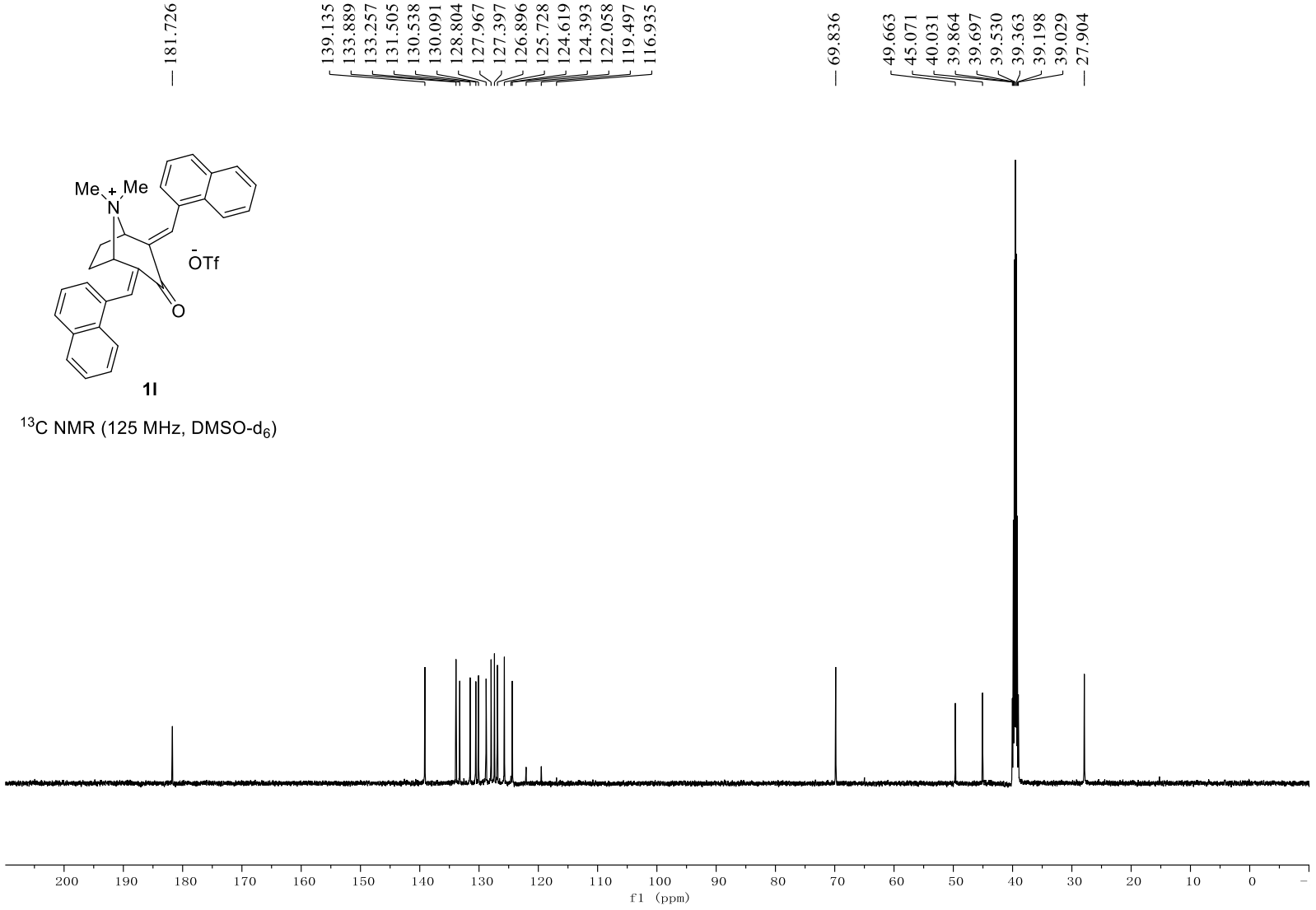
^{13}C NMR (125 MHz, DMSO-d_6)



1k

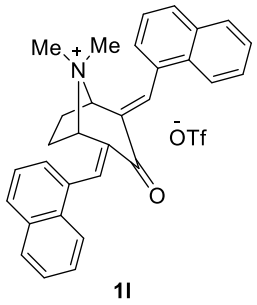
^{19}F NMR (471 MHz, DMSO-d_6)


8.576
8.131
8.114
8.088
8.071
8.054
7.703
7.688
7.672
7.425
7.411
5.069
5.060
3.185
3.075
3.021
3.001
2.611
2.591
-0.000
Me
N
Me
OTf
O
1I
1H NMR (500 MHz, DMSO-d6)
2.00
2.10
4.05
6.08
2.05
2.02
3.09
3.02
2.06
1.96
f1 (ppm)



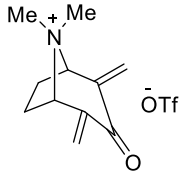
1l

^{13}C NMR (125 MHz, DMSO-d_6)



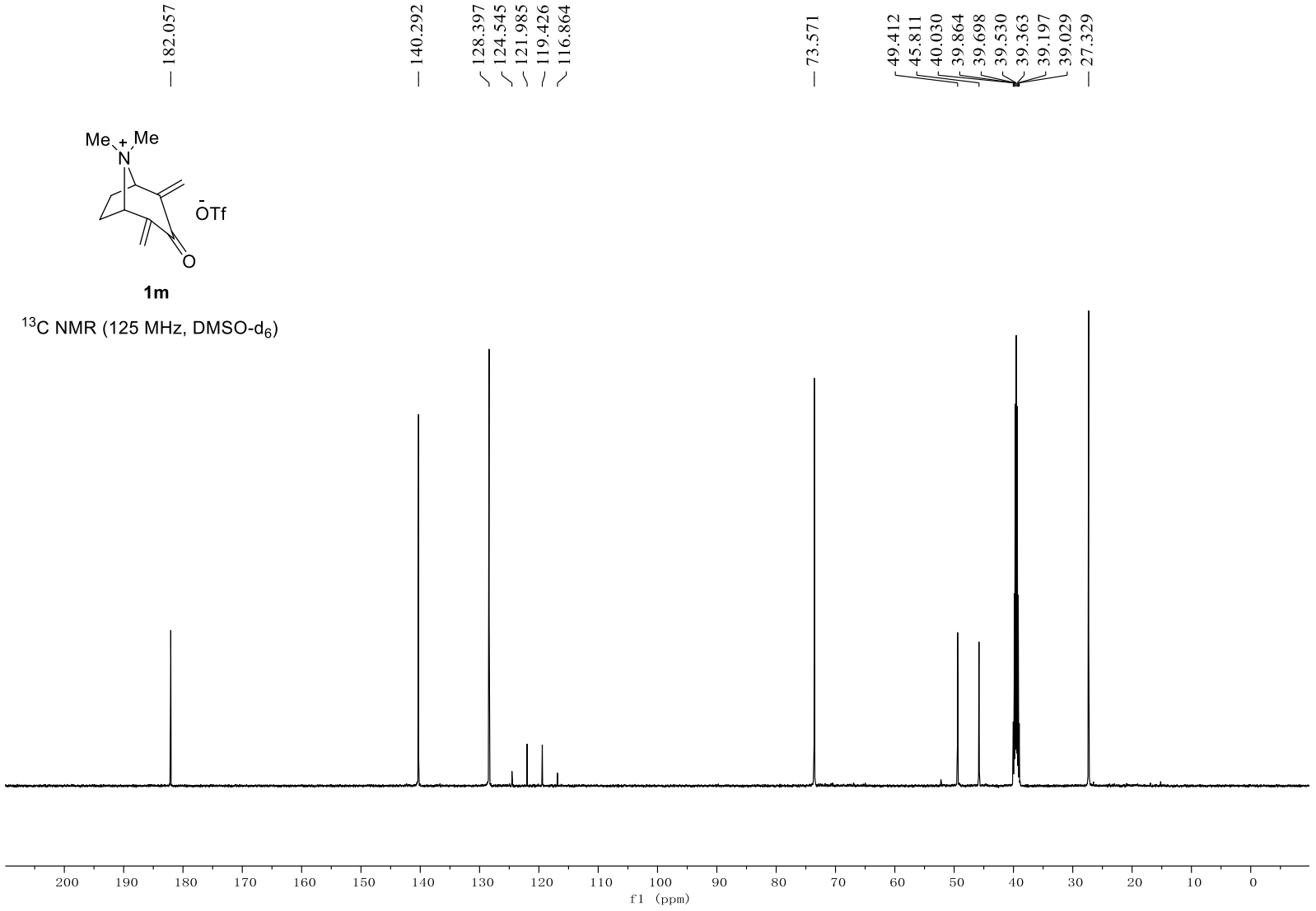
1l

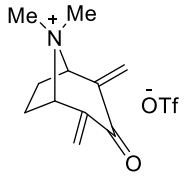
^{19}F NMR (470 MHz, DMSO-d_6)



1m

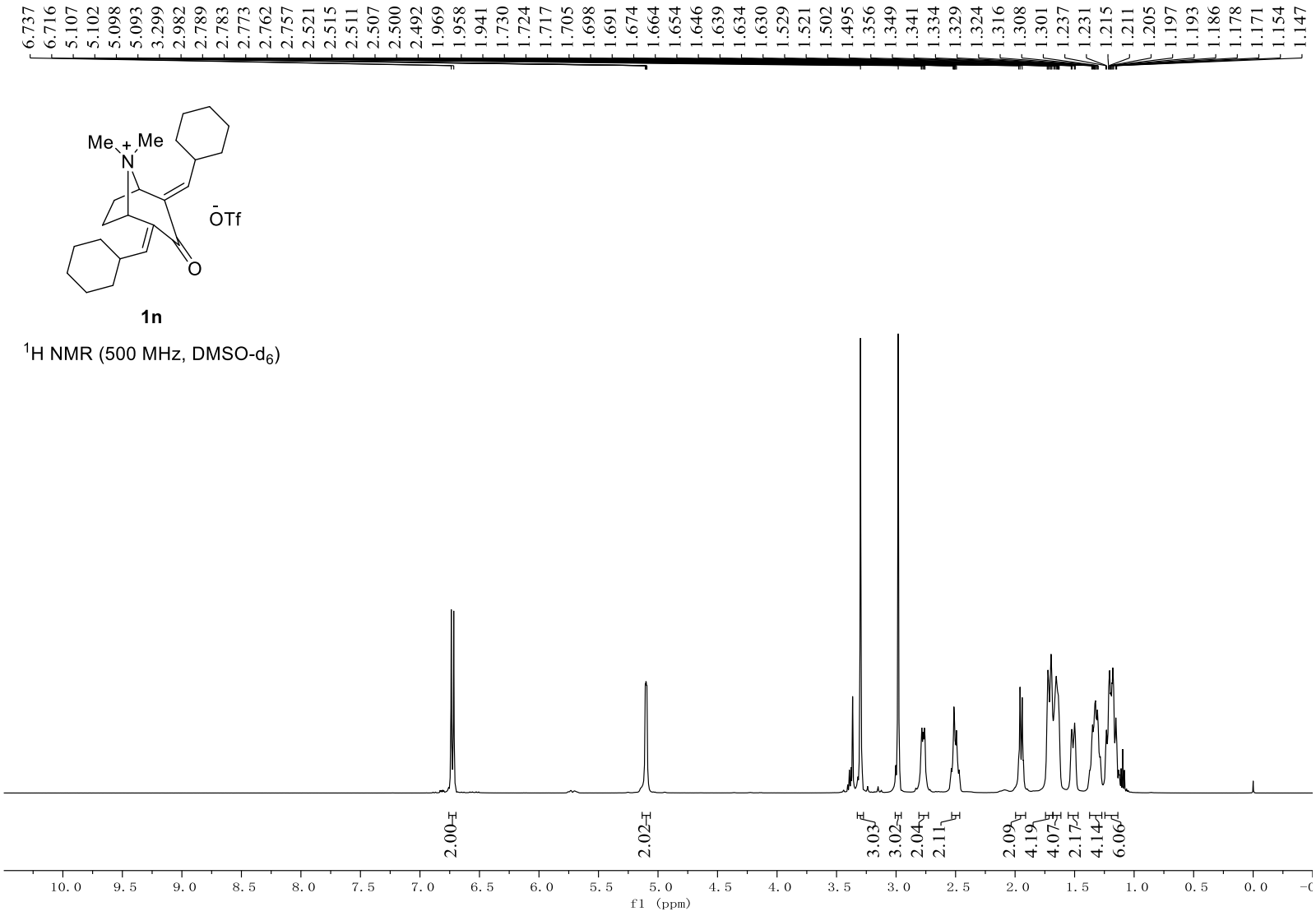
^{1}H NMR (500 MHz, DMSO-d_6)

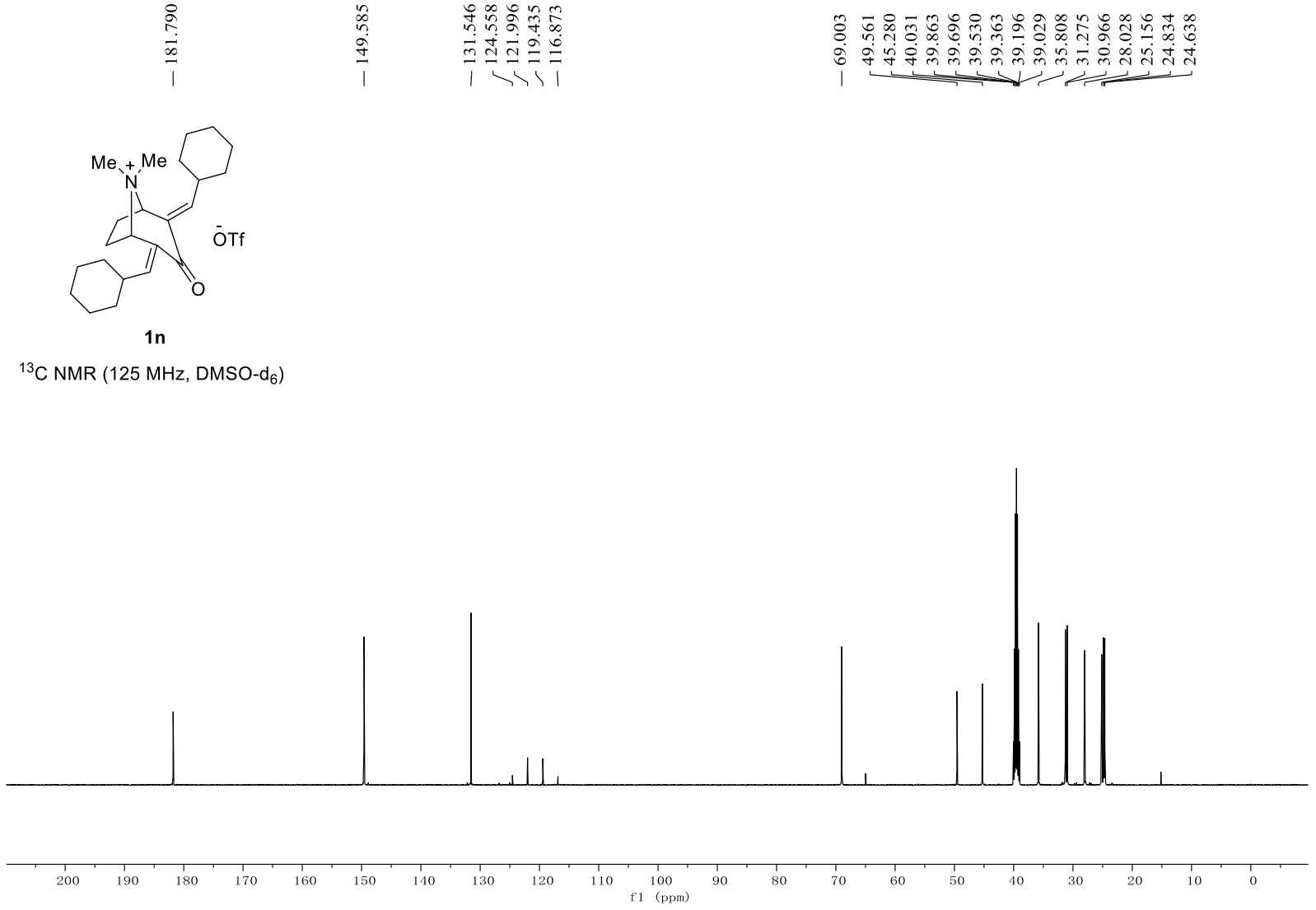

182.057
140.292
128.397
124.545
121.985
119.426
116.864
73.571
49.412
45.811
40.030
39.864
39.698
39.530
39.363
39.197
39.029
27.329
Me
N
Me
OTf
O
1m
13C NMR (125 MHz, DMSO-d6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



1m

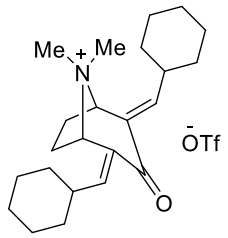
^{19}F NMR (471 MHz, DMSO-d_6)


6.737
6.716
5.107
5.102
5.098
5.093
3.299
2.982
2.789
2.783
2.773
2.762
2.757
2.521
2.515
2.511
2.507
2.500
2.492
1.969
1.958
1.941
1.730
1.724
1.717
1.705
1.698
1.691
1.674
1.664
1.654
1.646
1.639
1.634
1.630
1.529
1.521
1.502
1.495
1.356
1.349
1.341
1.334
1.329
1.324
1.316
1.308
1.301
1.237
1.231
1.215
1.211
1.205
1.197
1.193
1.186
1.178
1.171
1.154
1.147
Me
N
Me
OTf
O
1n
1H NMR (500 MHz, DMSO-d6)
2.00
2.02
3.03
3.02
2.04
2.11
2.09
4.19
4.07
2.17
4.14
6.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



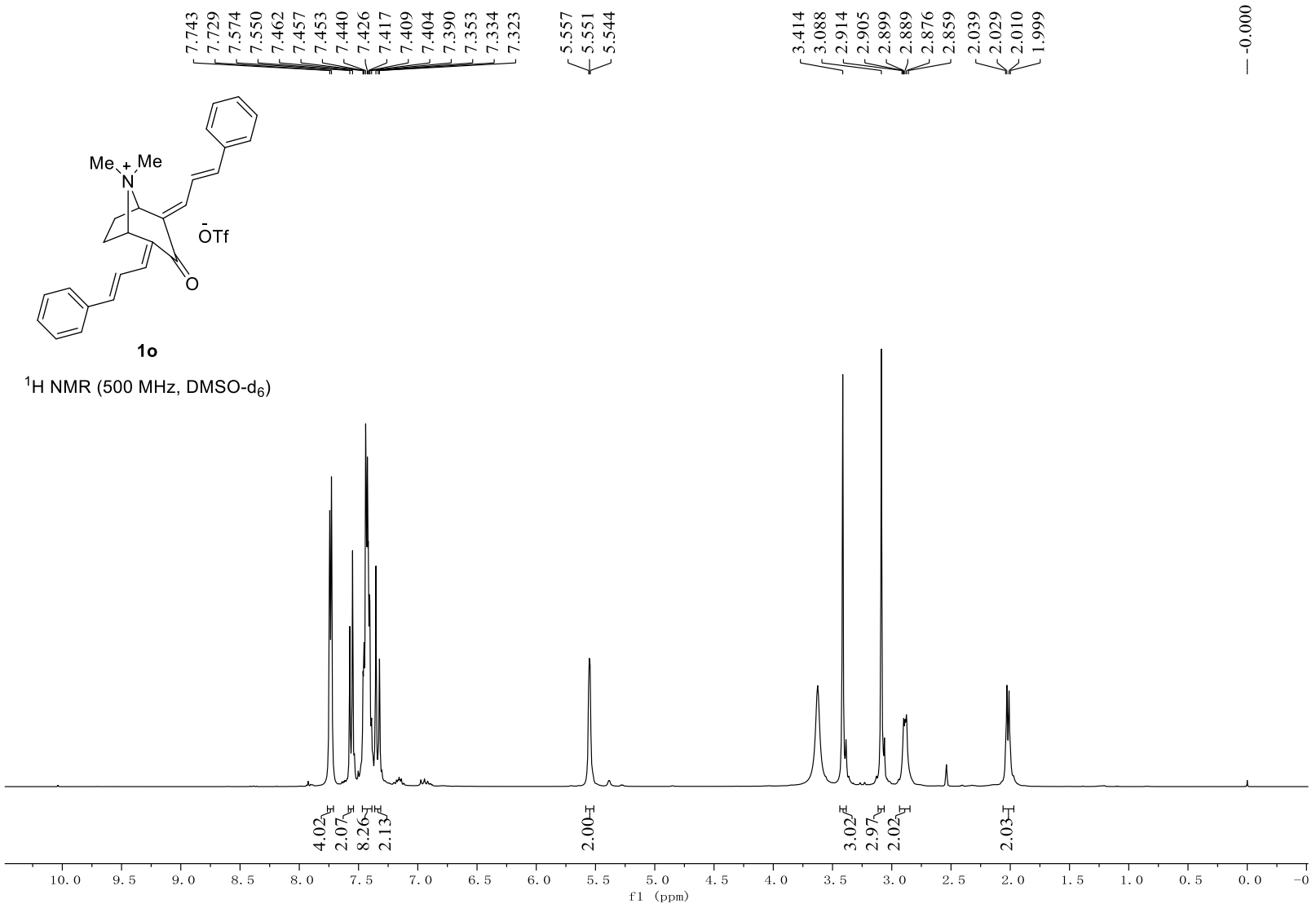
1n

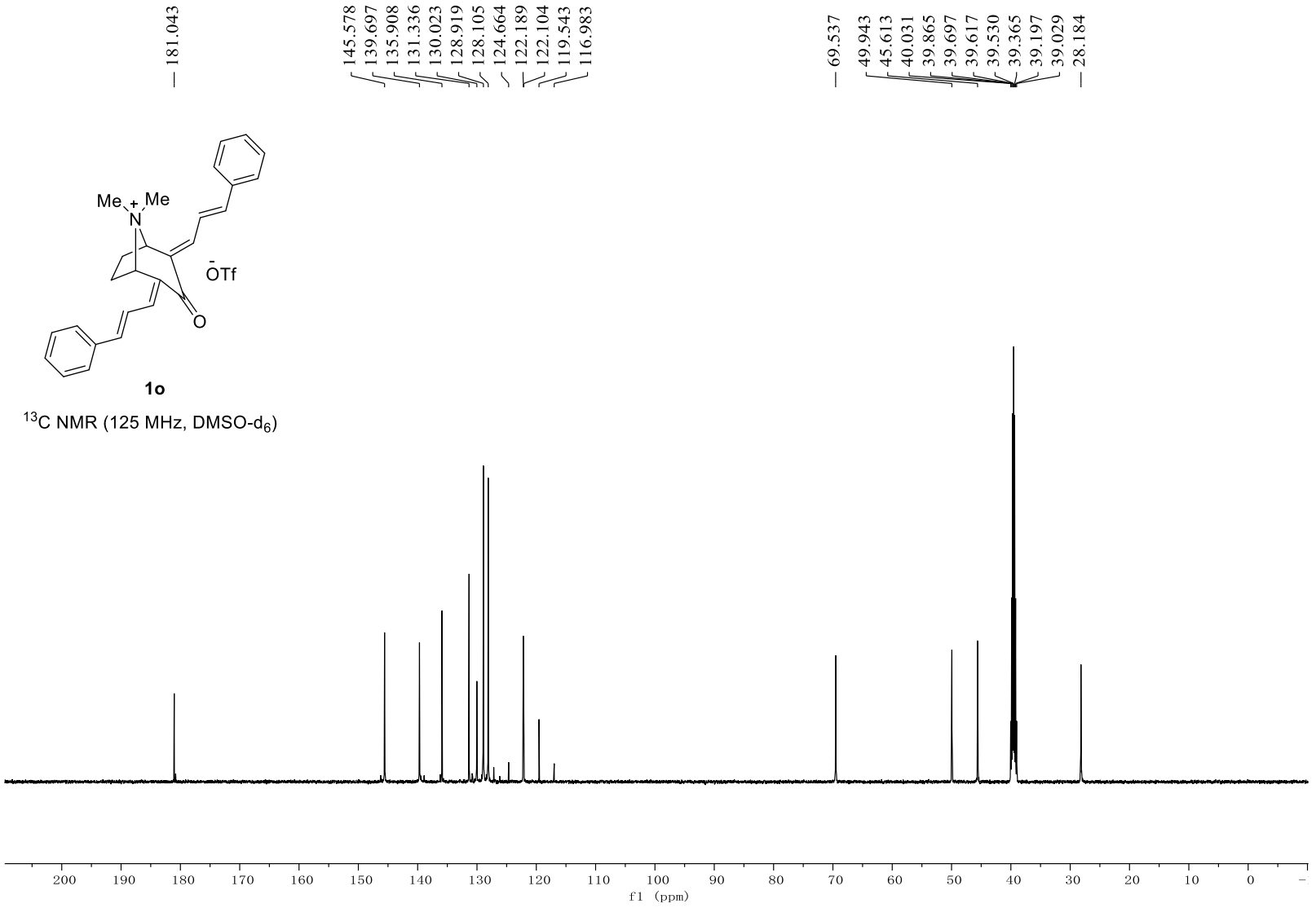
^{13}C NMR (125 MHz, DMSO-d_6)

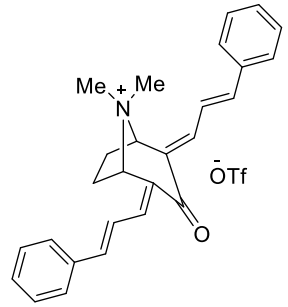


1n

^{19}F NMR (471 MHz, DMSO-d_6)

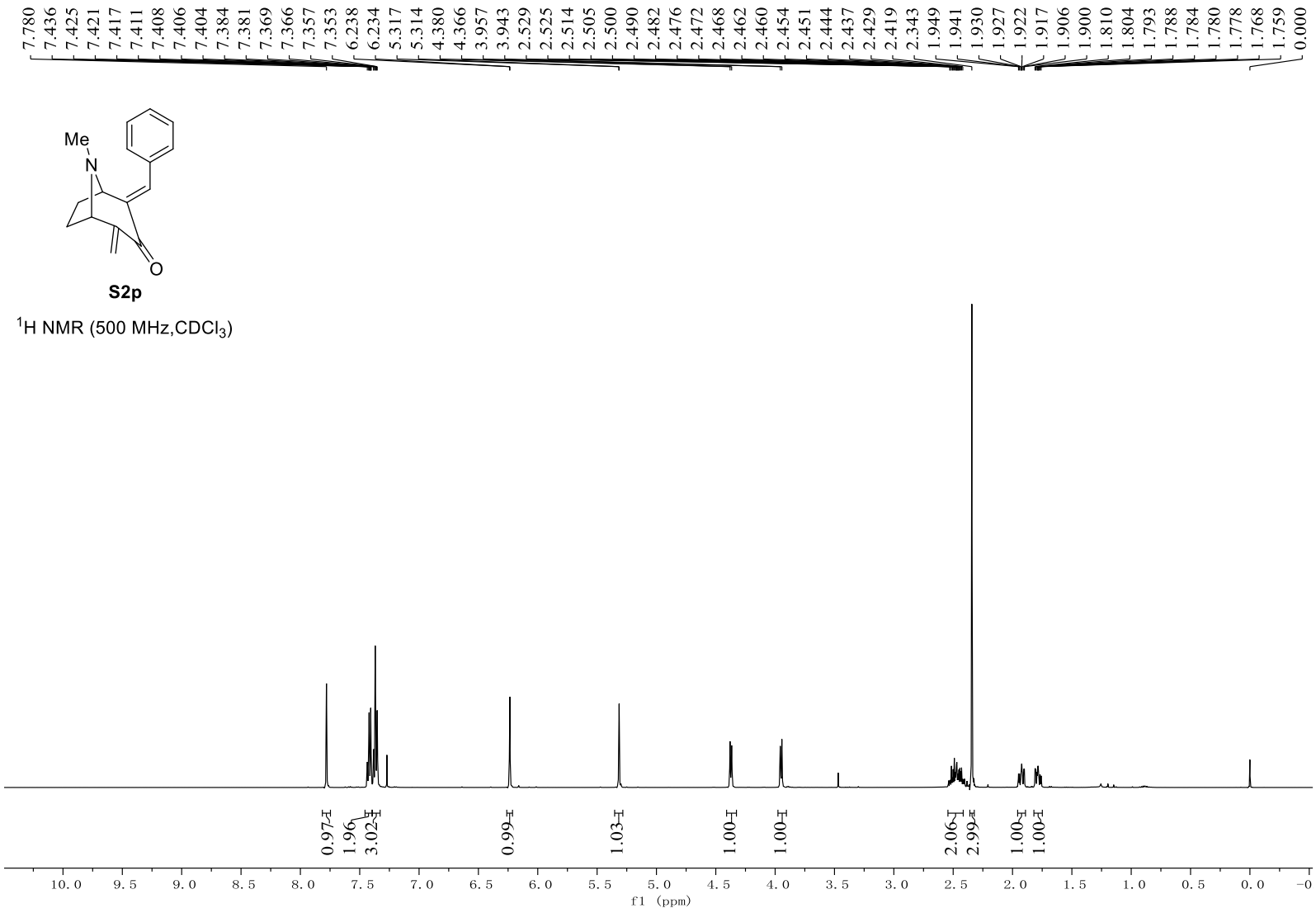

7.743
7.729
7.574
7.550
7.462
7.457
7.453
7.440
7.426
7.417
7.409
7.404
7.390
7.353
7.334
7.323
5.557
5.551
5.544
3.414
3.088
2.914
2.905
2.899
2.889
2.876
2.859
2.039
2.029
2.010
1.999
-0.000
Me
N
Me
OTf
O
1o
1H NMR (500 MHz, DMSO-d6)
4.02
2.07
8.26
2.13
2.00
3.02
2.97
2.02
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

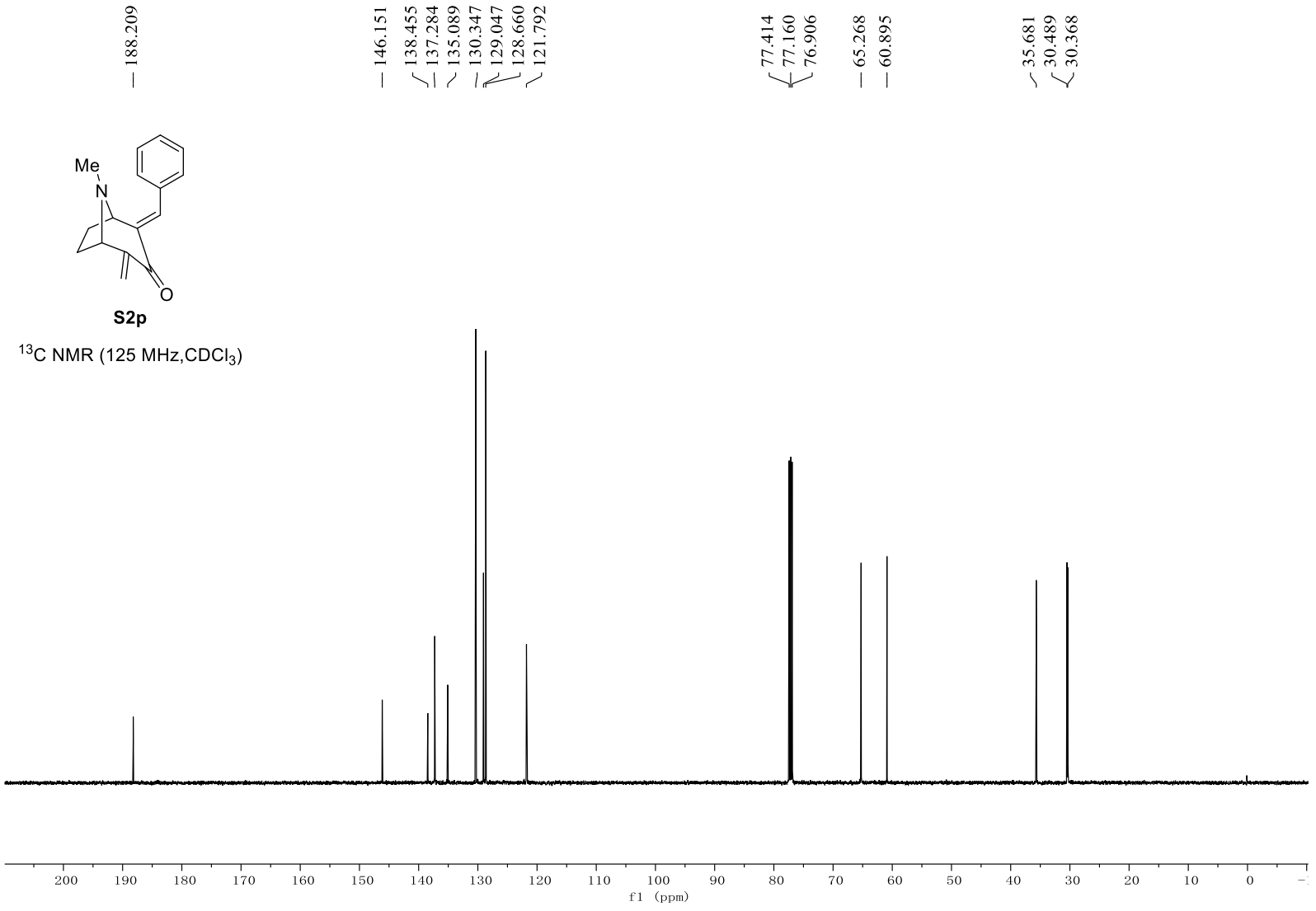

181.043
145.578
139.697
135.908
131.336
130.023
128.919
128.105
124.664
122.189
122.104
119.543
116.983
69.537
49.943
45.613
40.031
39.865
39.697
39.617
39.530
39.365
39.197
39.029
28.184
Me
N
Me
OTf
O
1o
13C NMR (125 MHz, DMSO-d6)
f1 (ppm)

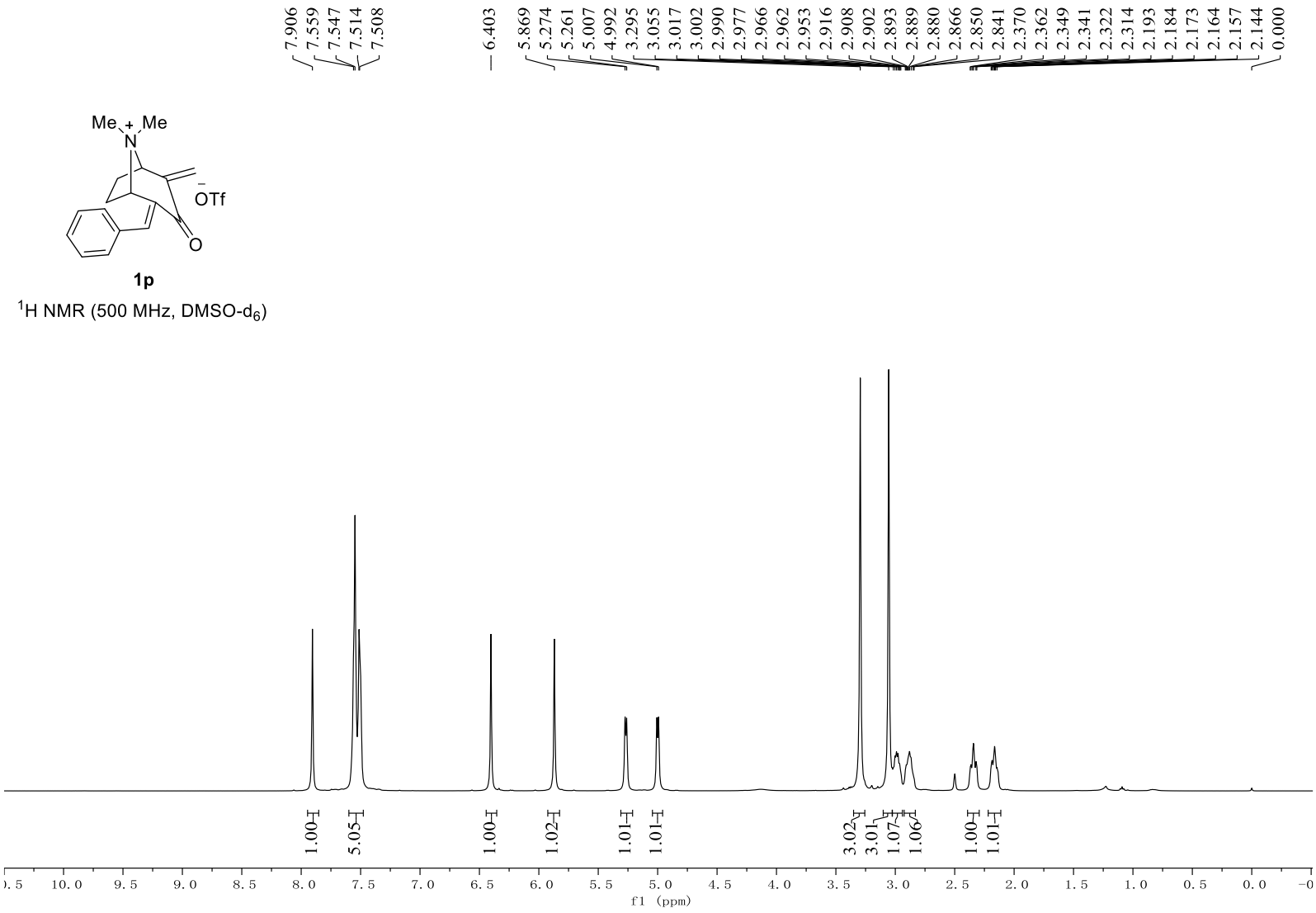


1o

^{19}F NMR (471 MHz, DMSO-d_6)

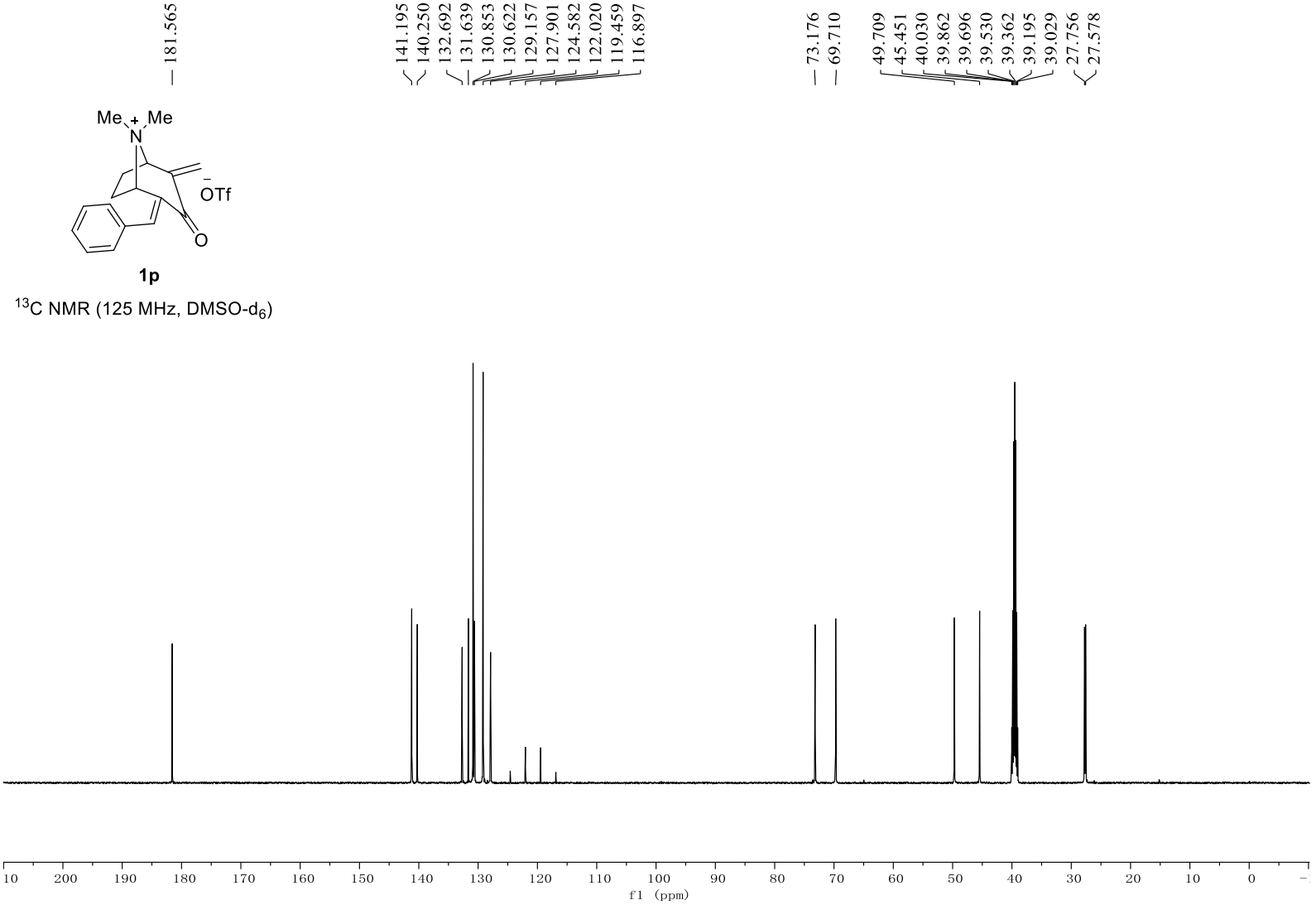

7.780
7.436
7.425
7.421
7.417
7.411
7.408
7.406
7.404
7.384
7.381
7.369
7.366
7.357
7.353
6.238
6.234
5.317
5.314
4.380
4.366
3.957
3.943
2.529
2.525
2.514
2.505
2.500
2.490
2.482
2.476
2.472
2.468
2.462
2.460
2.454
2.451
2.444
2.437
2.429
2.419
2.343
1.949
1.941
1.930
1.927
1.922
1.917
1.906
1.900
1.810
1.804
1.793
1.788
1.784
1.780
1.778
1.768
1.759
0.000
Me
N
O
S2p
1H NMR (500 MHz,CDCl3)
0.97
1.96
3.02
0.99
1.03
1.00
1.00
2.06
2.99
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


188.209
146.151
138.455
137.284
135.089
130.347
129.047
128.660
121.792
77.414
77.160
76.906
65.268
60.895
35.681
30.489
30.368
Me
N
O
S2p
13C NMR (125 MHz,CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



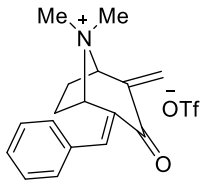
1p

^{1}H NMR (500 MHz, DMSO-d_6)



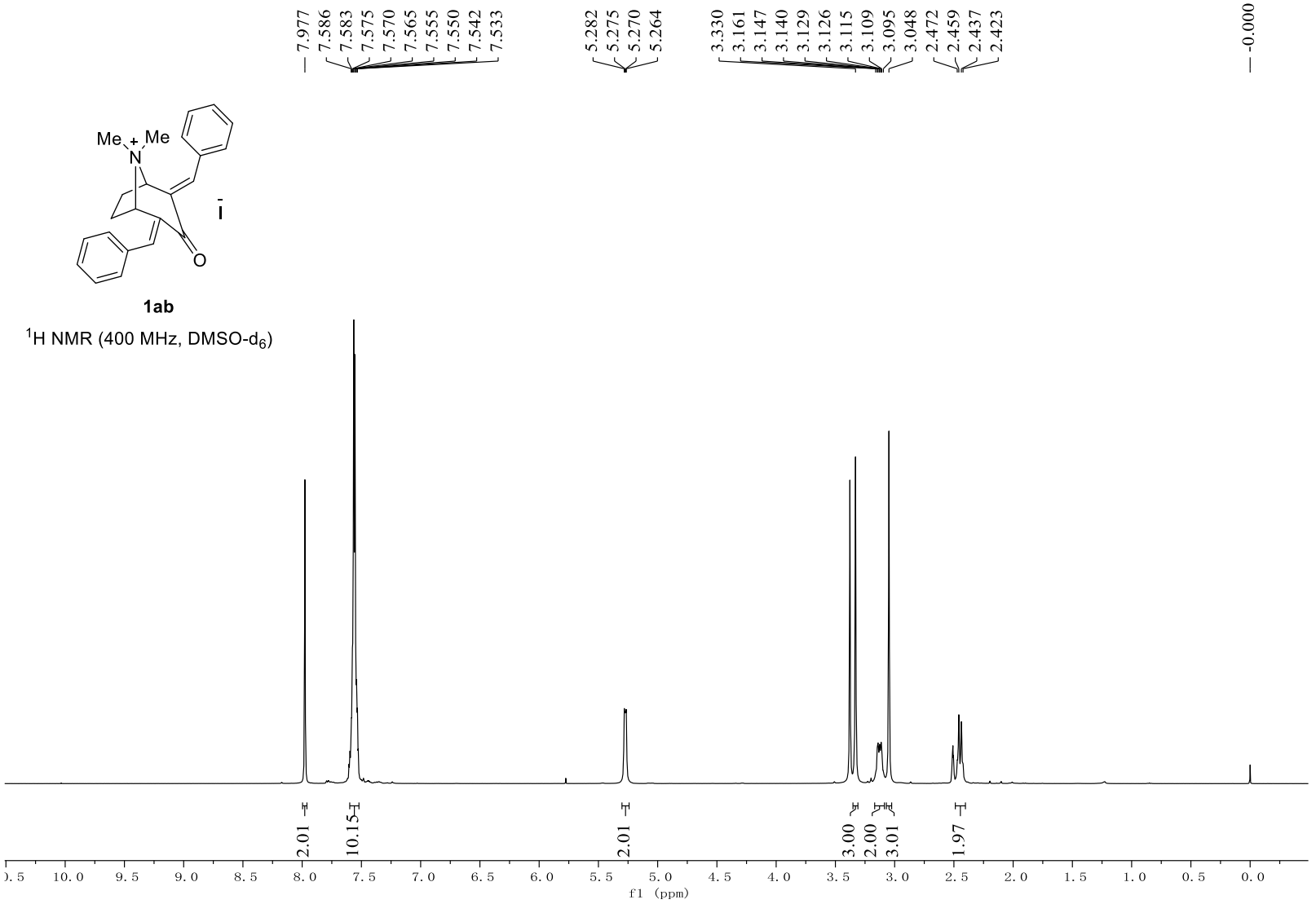
1p

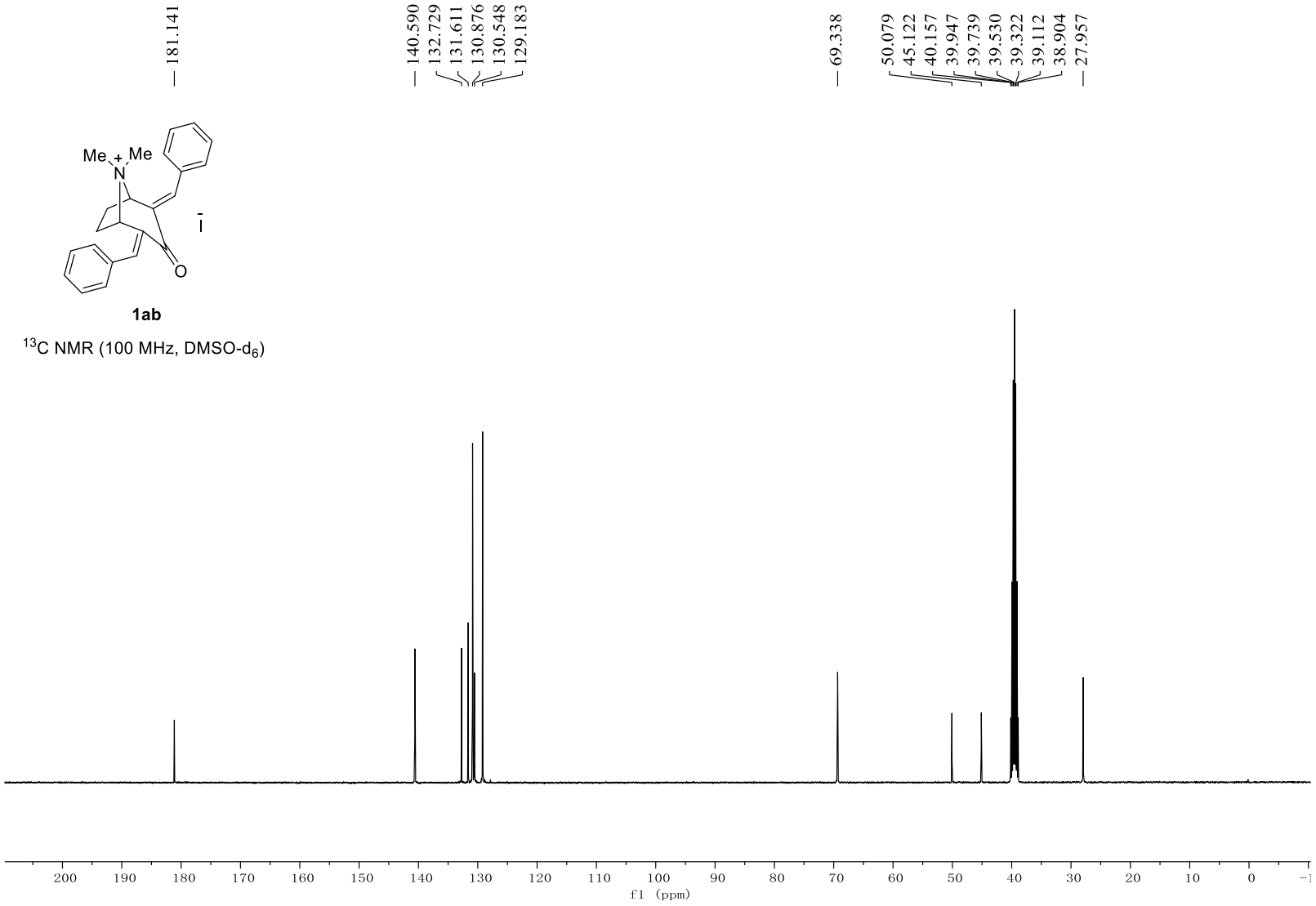
^{13}C NMR (125 MHz, DMSO-d_6)

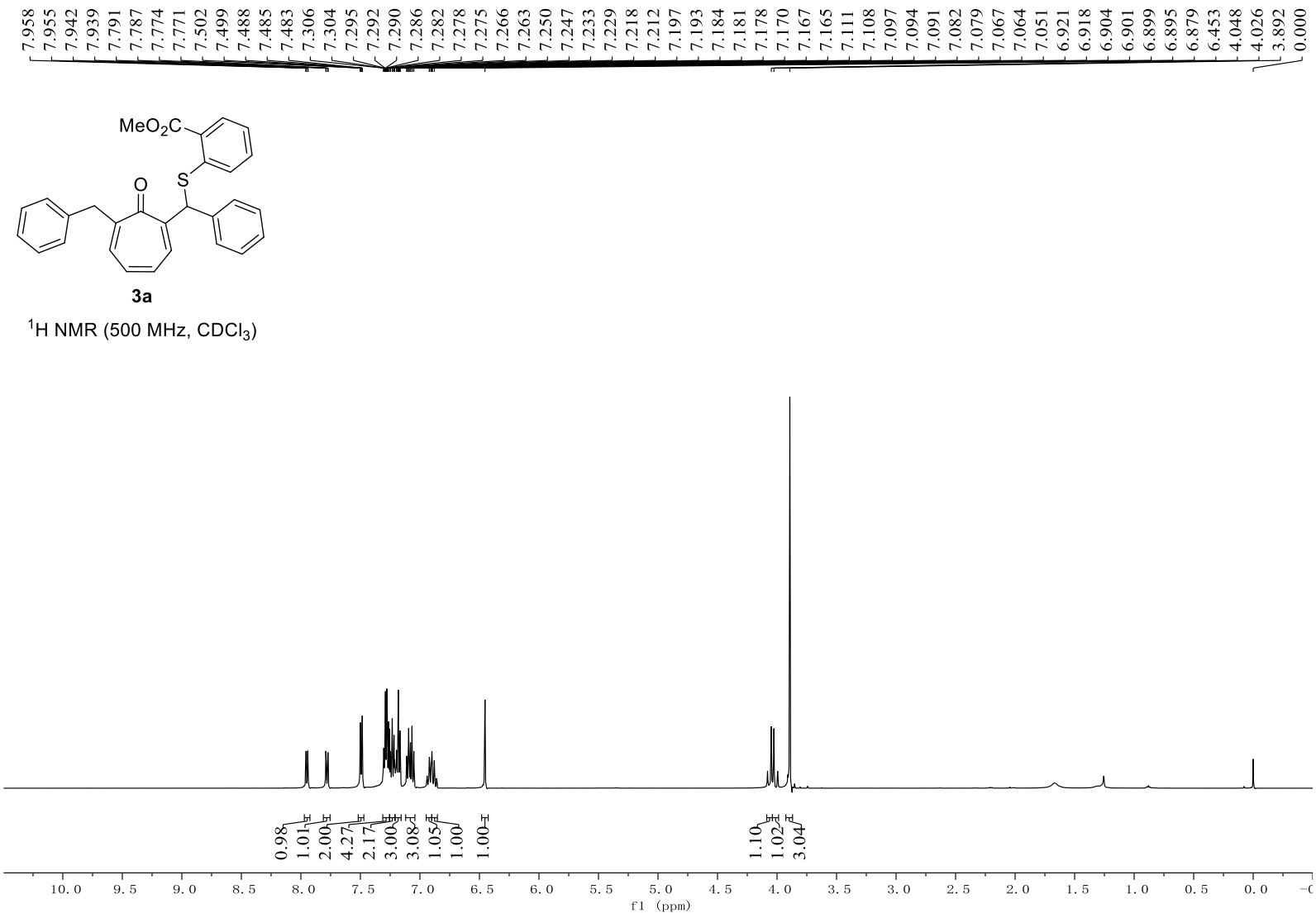


1p

^{19}F NMR (470 MHz, DMSO-d_6)

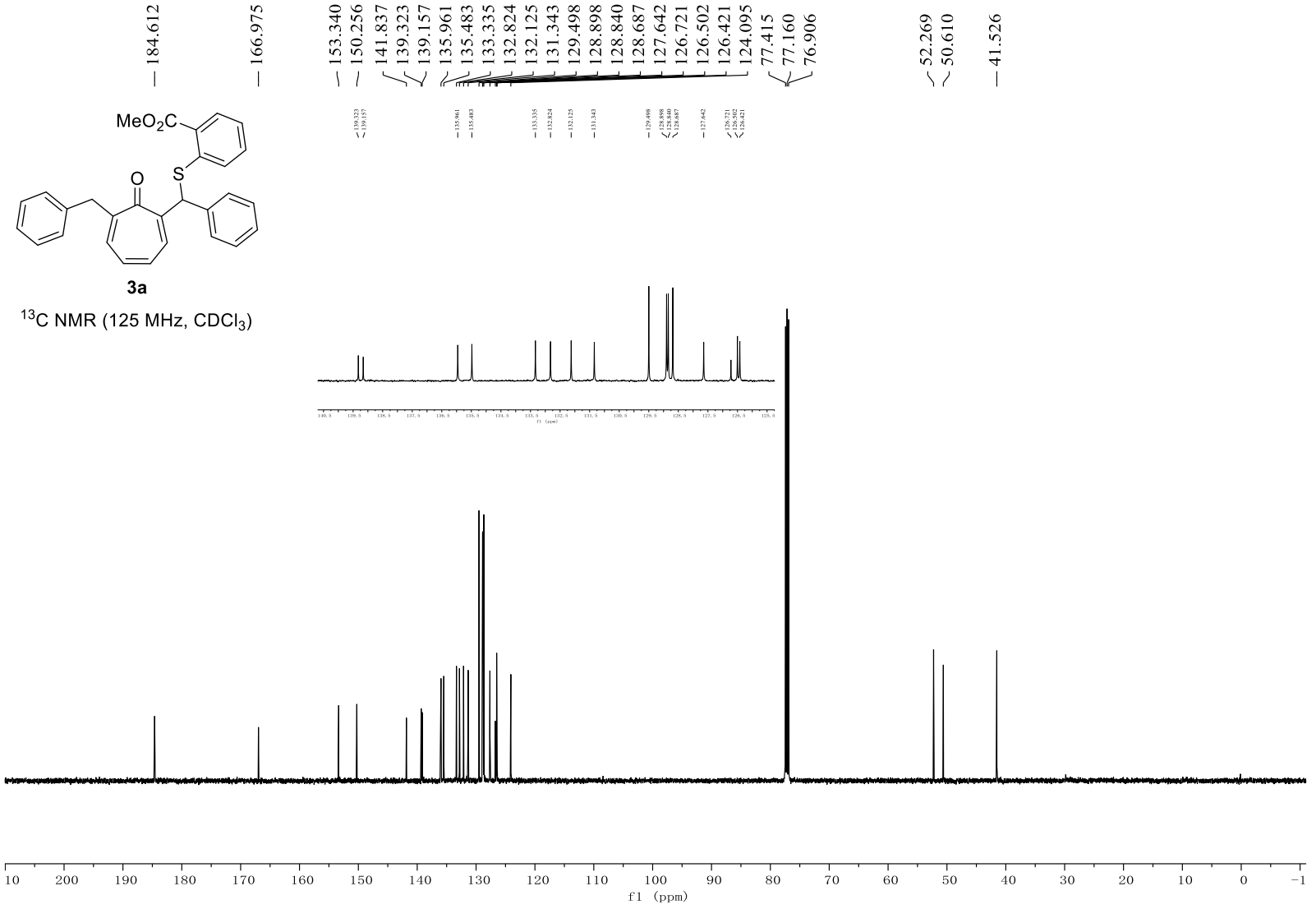

7.977
7.586
7.583
7.575
7.570
7.565
7.555
7.550
7.542
7.533
5.282
5.275
5.270
5.264
3.330
3.161
3.147
3.140
3.129
3.126
3.115
3.109
3.095
3.048
2.472
2.459
2.437
2.423
-0.000
Me
N
Me
I
O
1ab
1H NMR (400 MHz, DMSO-d6)
2.01
10.15
2.01
3.00
2.00
3.01
1.97
f1 (ppm)

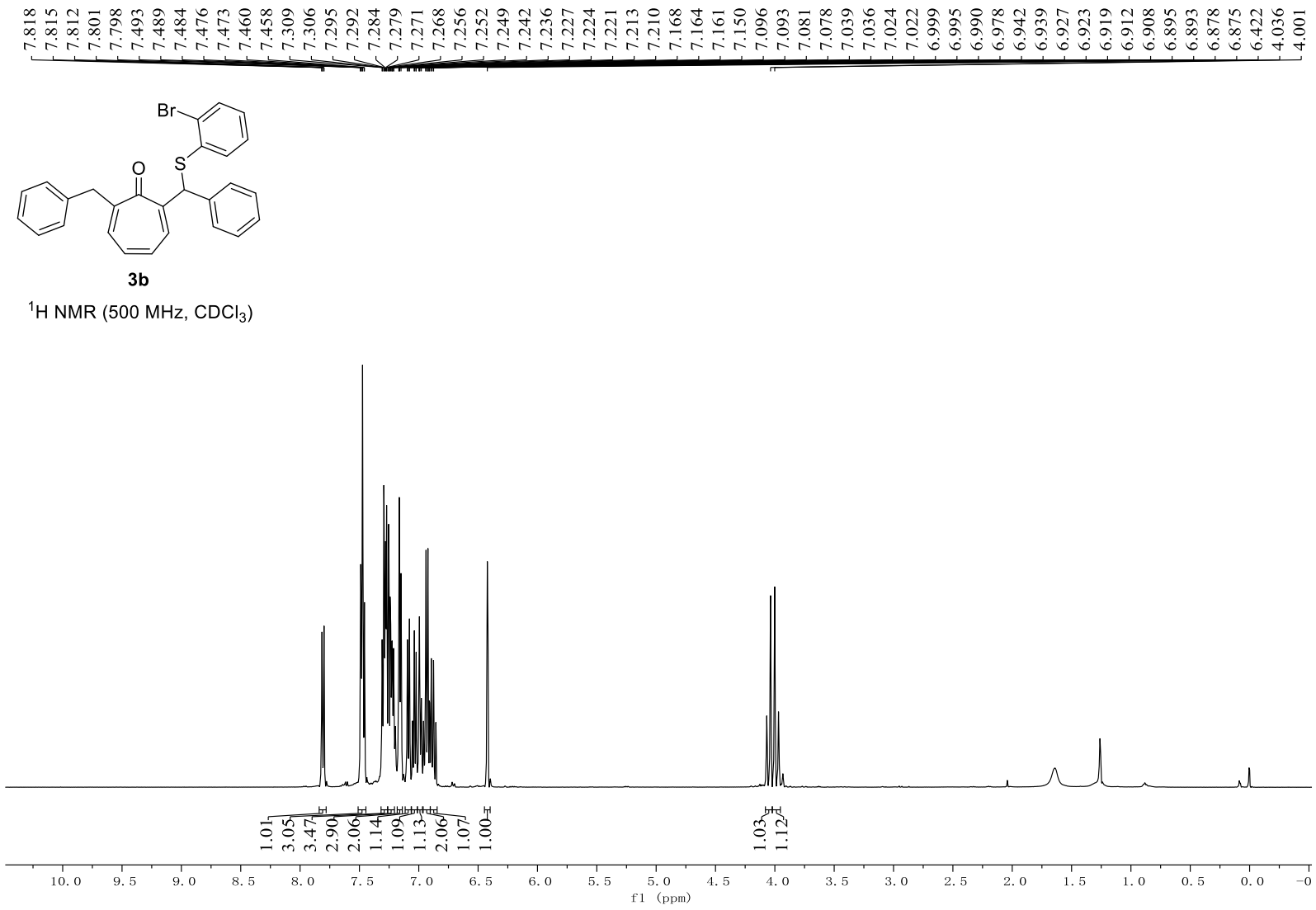

181.141
140.590
132.729
131.611
130.876
130.548
129.183
69.338
50.079
45.122
40.157
39.947
39.739
39.530
39.322
39.112
38.904
27.957
Me
Me
N
O
I
1ab
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)



3a

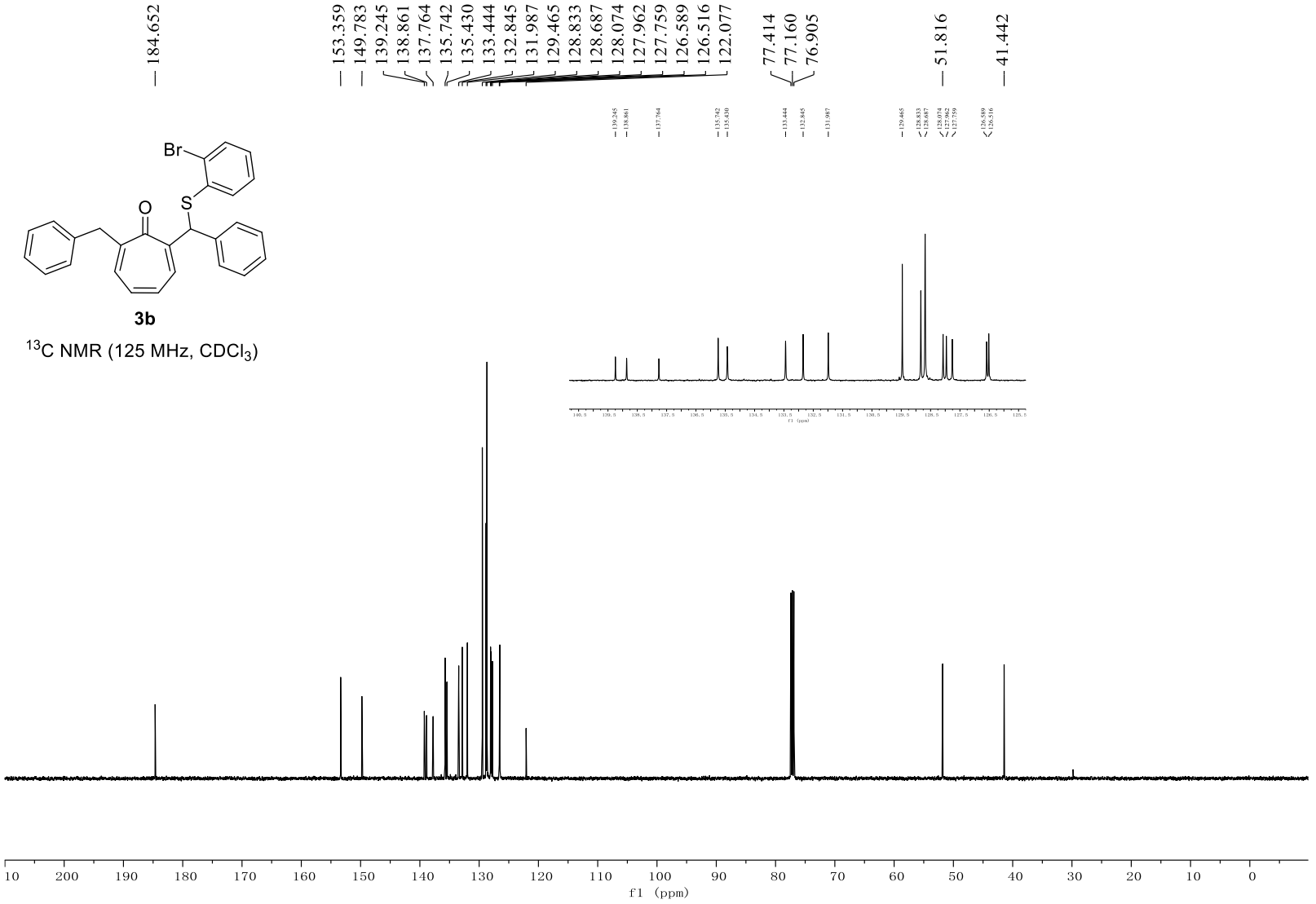
^{1}H NMR (500 MHz, $CDCl_3$)


184.612
166.975
153.340
150.256
141.837
139.323
139.157
135.961
135.483
133.335
132.824
132.125
131.343
129.498
128.898
128.840
128.687
127.642
126.721
126.502
126.421
124.095
77.415
77.160
76.906
52.269
50.610
41.526
MeO2C
O
S
3a
13C NMR (125 MHz, CDCl3)
f1 (ppm)



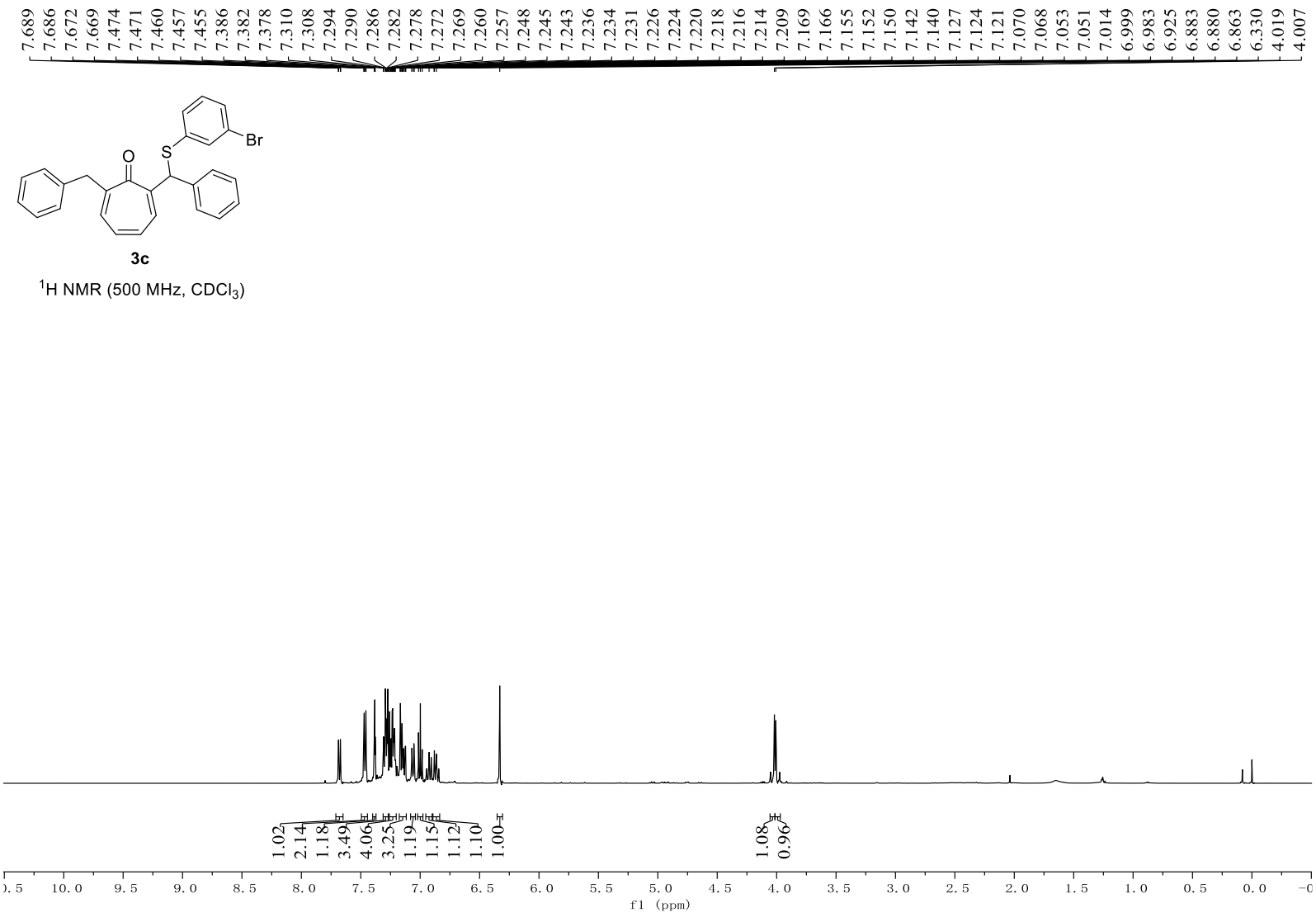
3b

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



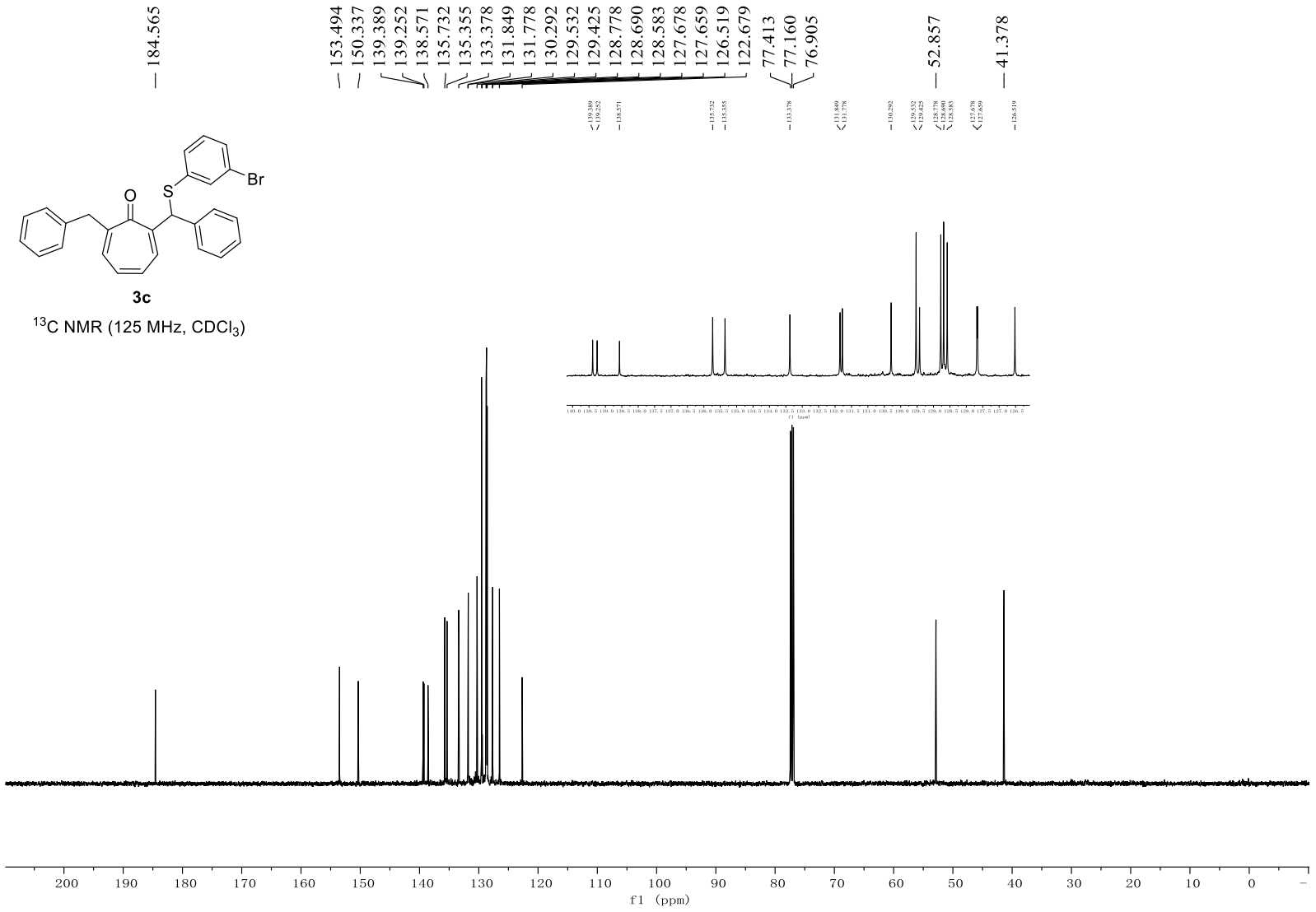
3b

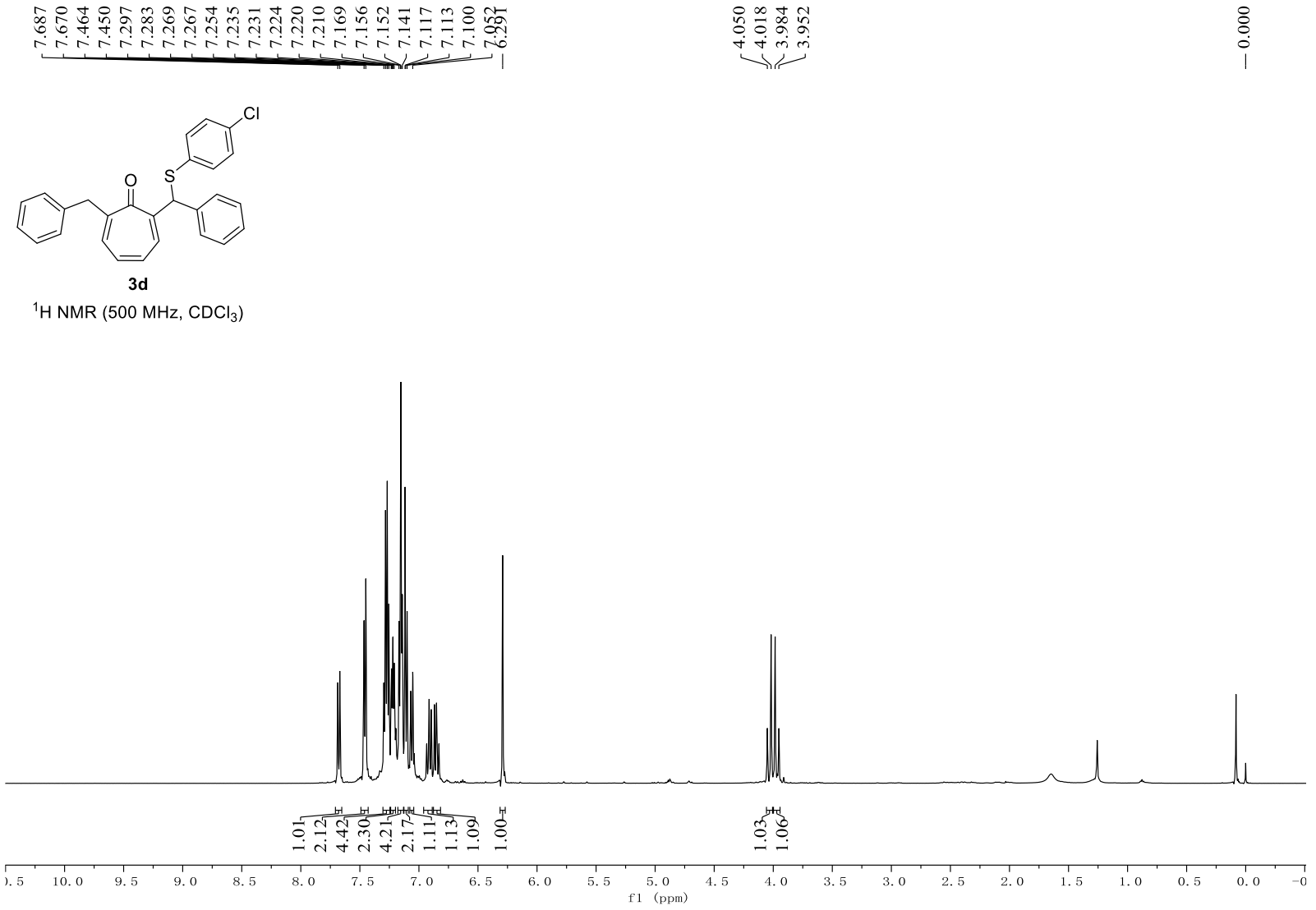
^{13}C NMR (125 MHz, $CDCl_3$)



3c

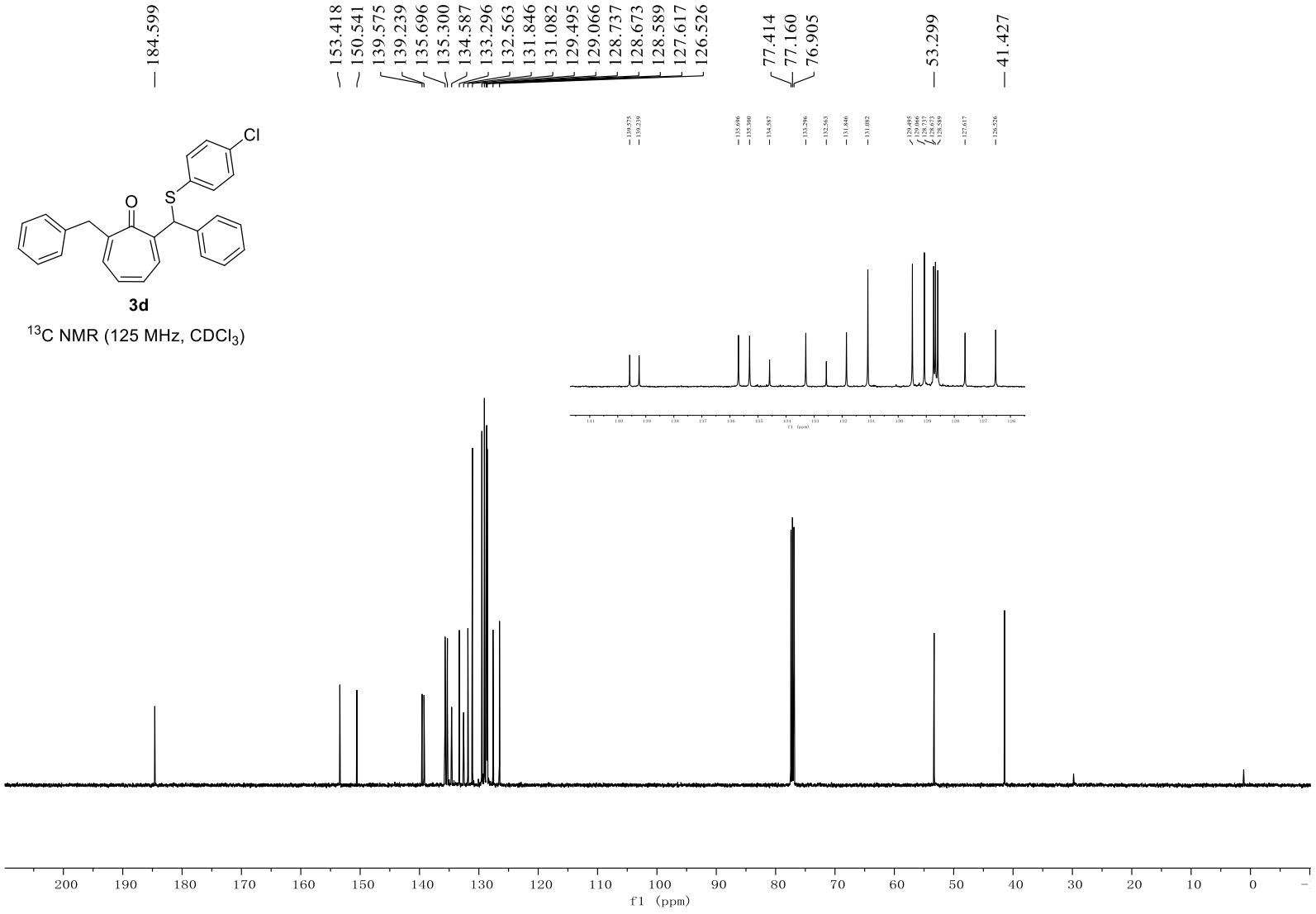
^{1}H NMR (500 MHz, $CDCl_3$)

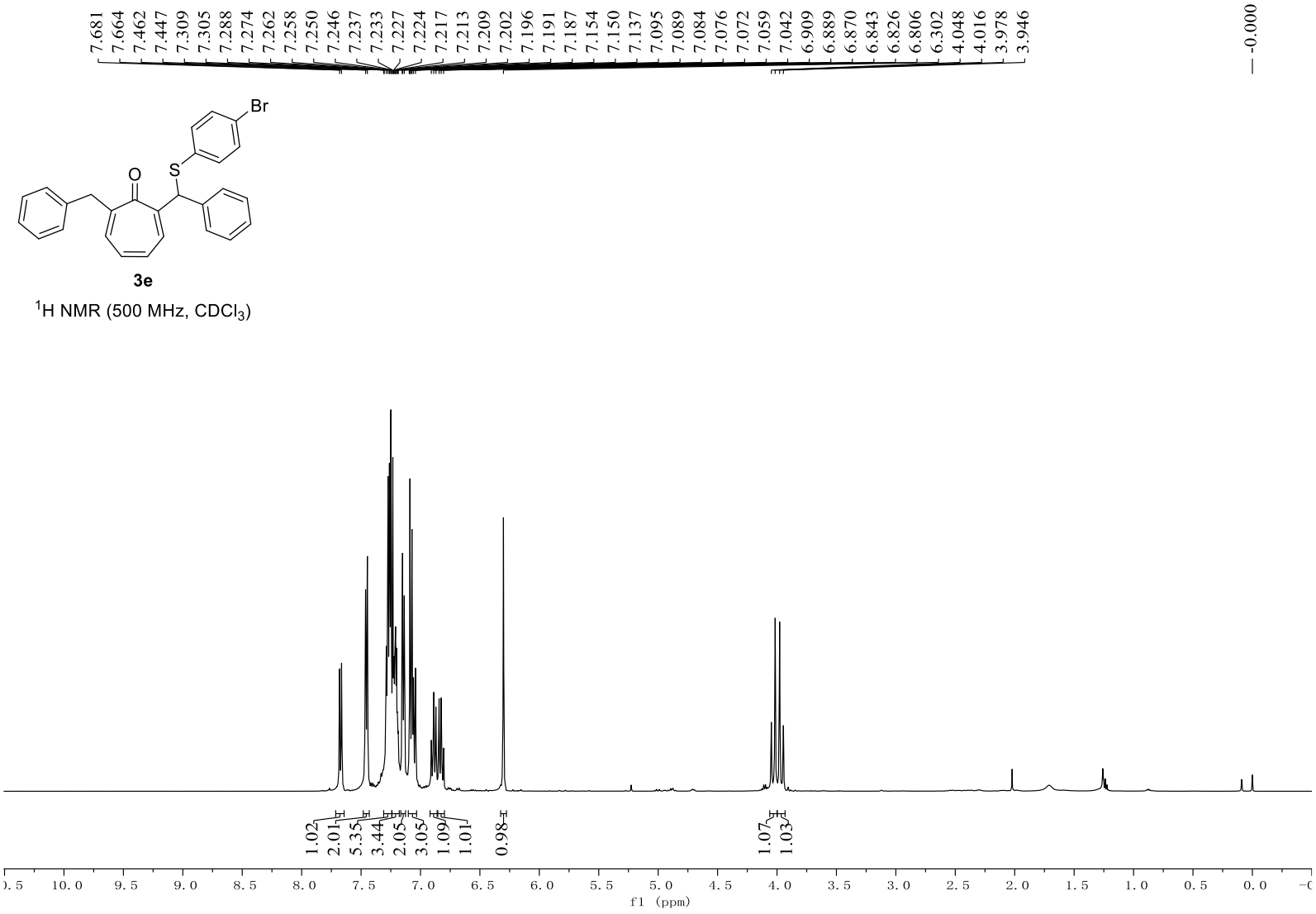

184.565
153.494
150.337
139.389
139.252
138.571
135.732
135.355
133.378
131.849
131.778
130.292
129.532
129.425
128.778
128.690
128.583
127.678
127.659
126.519
122.679
77.413
77.160
76.905
52.857
41.378
Br
S
O
3c
13C NMR (125 MHz, CDCl3)
f1 (ppm)



3d

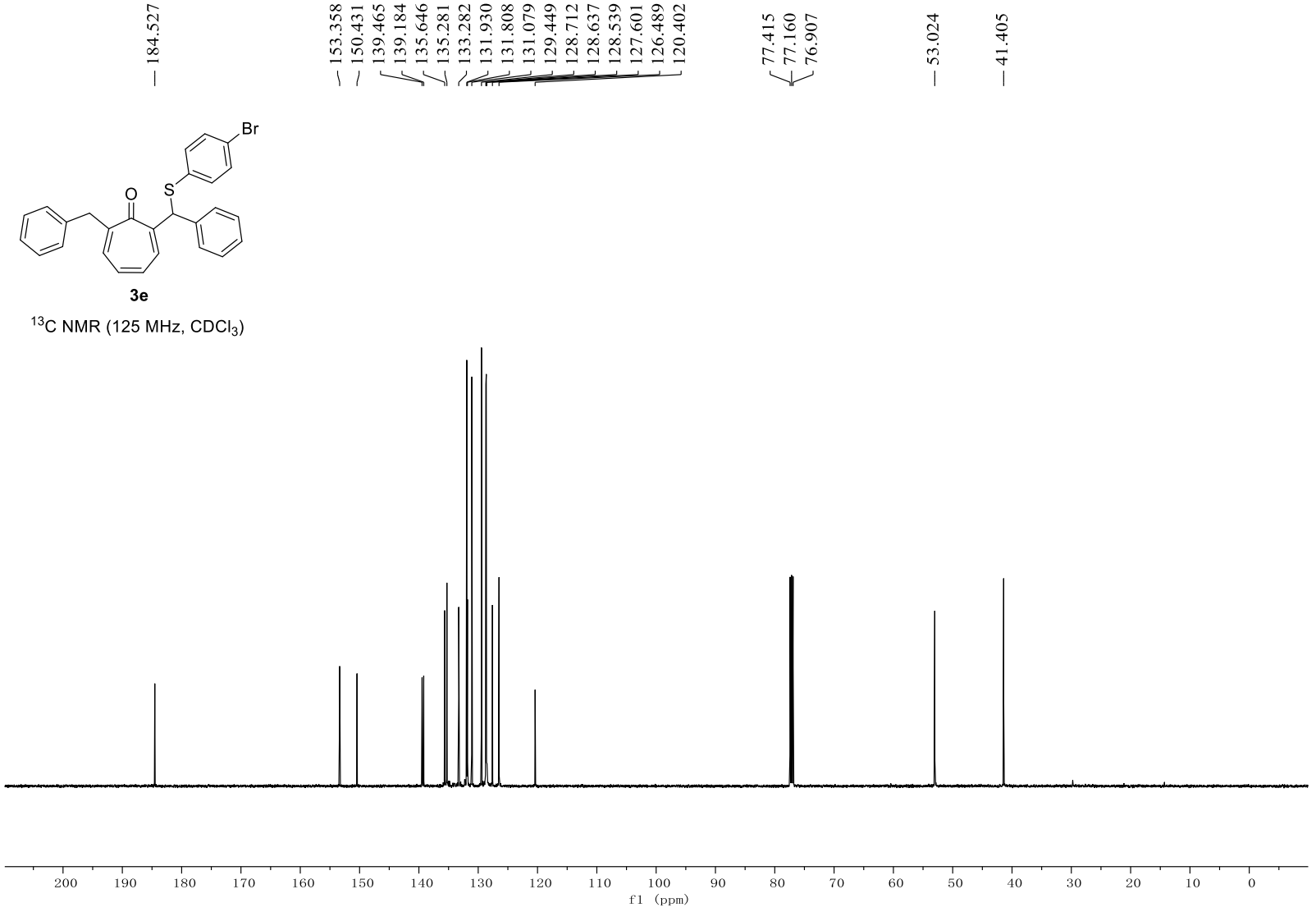
^{1}H NMR (500 MHz, $CDCl_3$)

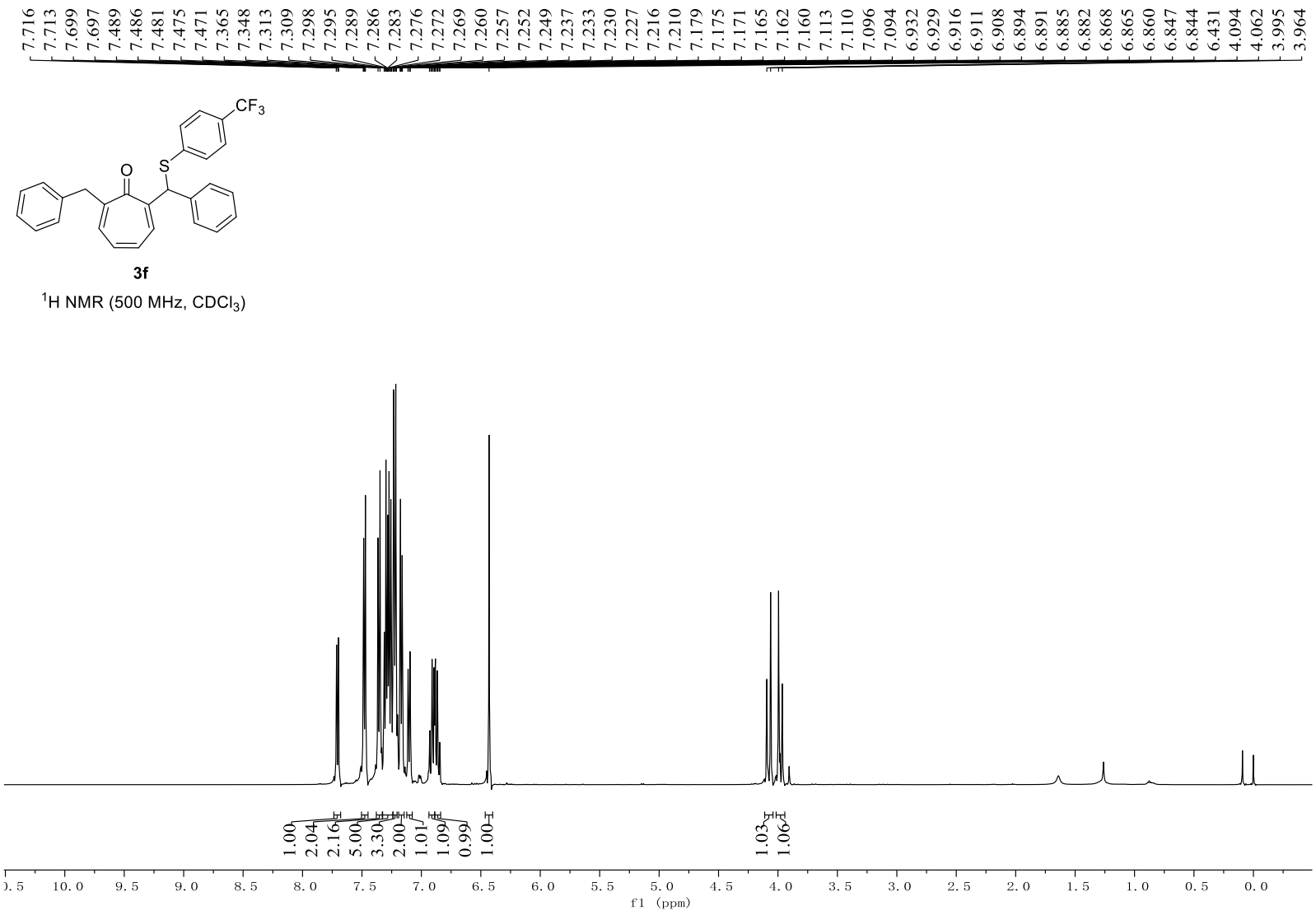

184.599
153.418
150.541
139.575
139.239
135.696
135.300
134.587
133.296
132.563
131.846
131.082
129.495
129.066
128.737
128.673
128.589
127.617
126.526
77.414
77.160
76.905
53.299
41.427
Cl
O
S
3d
13C NMR (125 MHz, CDCl3)
f1 (ppm)



3e

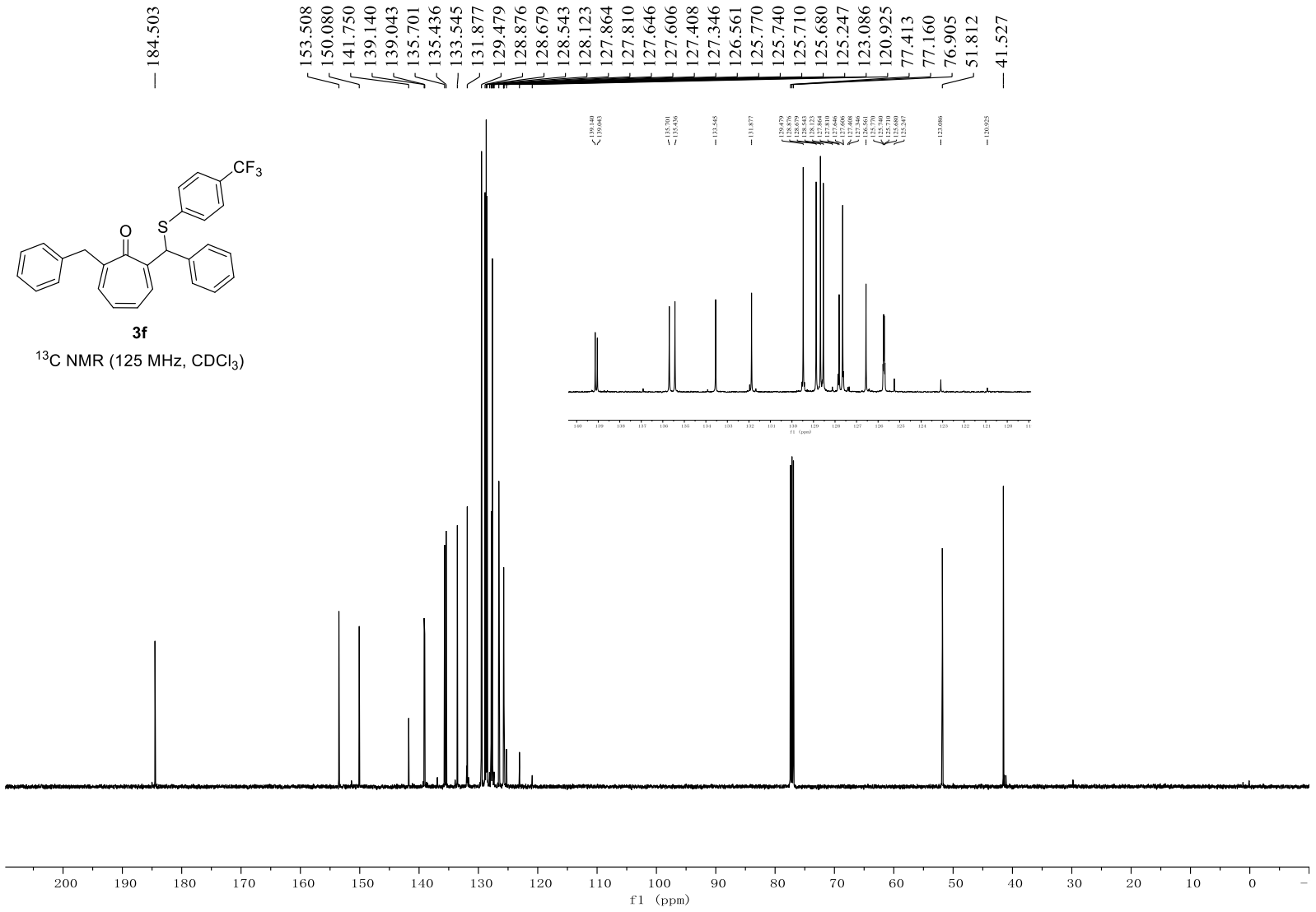
^{1}H NMR (500 MHz, $CDCl_3$)

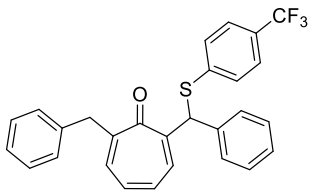

184.527
153.358
150.431
139.465
139.184
135.646
135.281
133.282
131.930
131.808
131.079
129.449
128.712
128.637
128.539
127.601
126.489
120.402
77.415
77.160
76.907
53.024
41.405
Br
S
O
3e
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3f

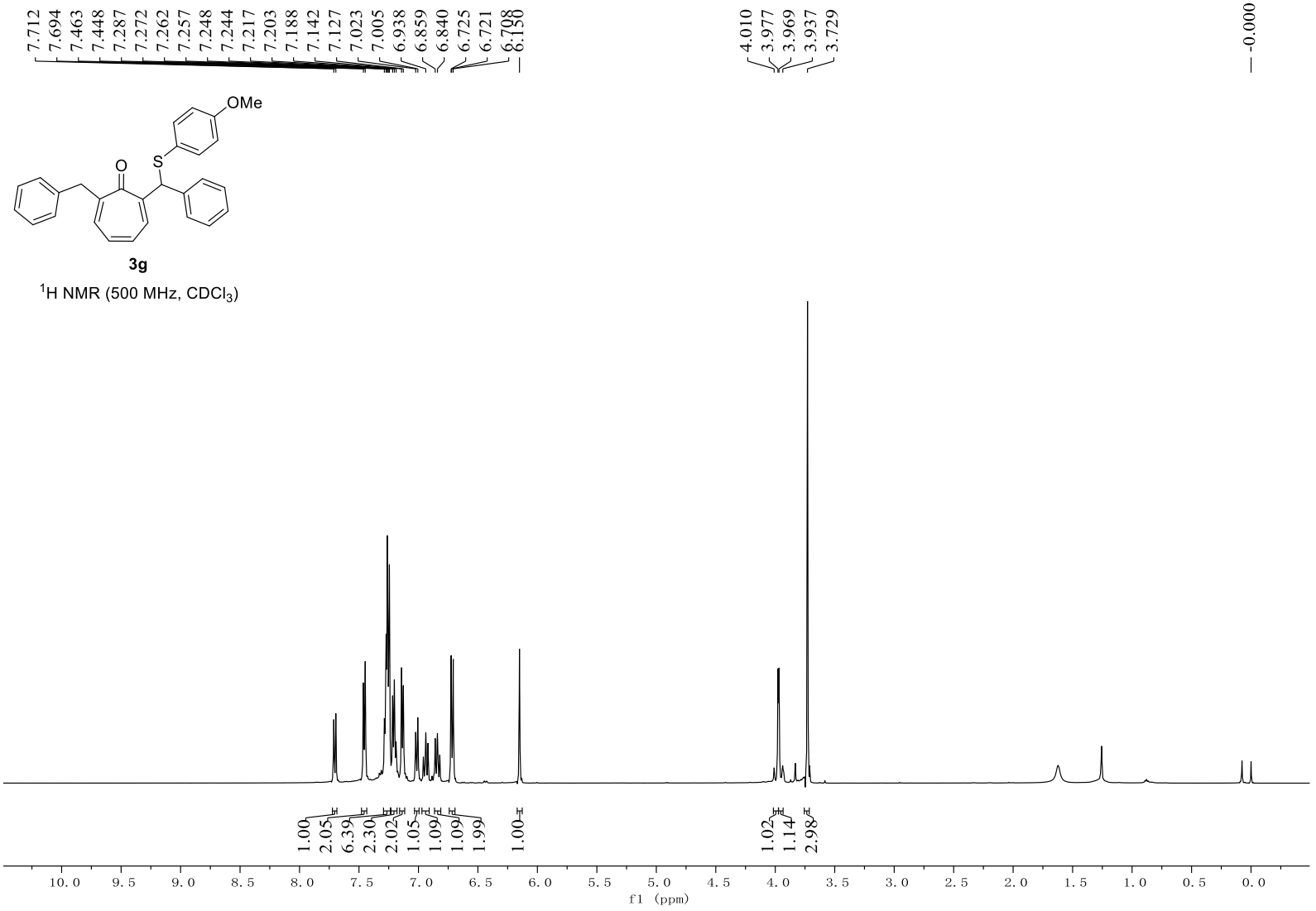
^{1}H NMR (500 MHz, $CDCl_3$)

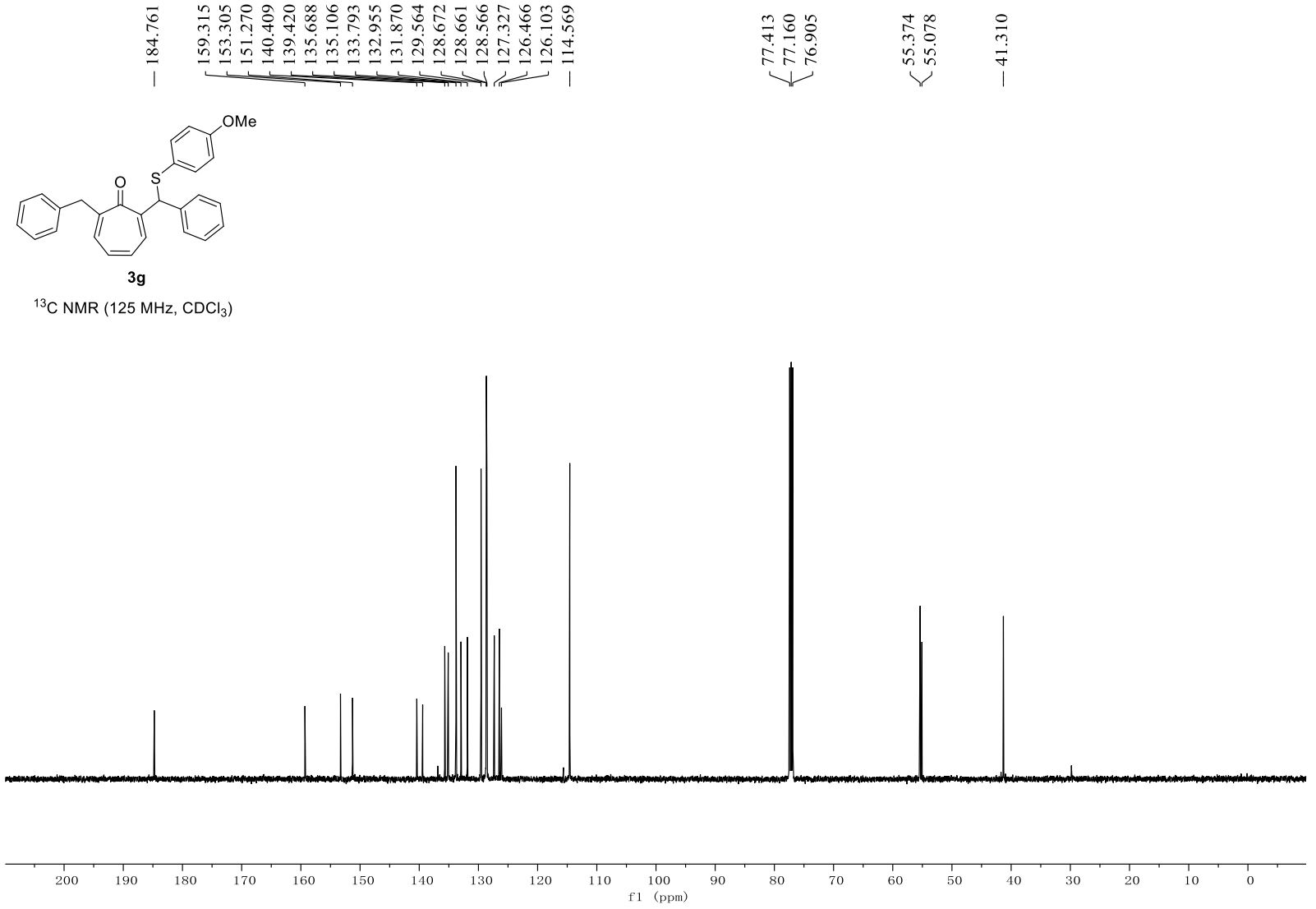

184.503
153.508
150.080
141.750
139.140
139.043
135.701
135.436
133.545
131.877
129.479
128.876
128.679
128.543
128.123
127.864
127.810
127.646
127.606
127.408
127.346
126.561
125.770
125.740
125.710
125.680
125.247
123.086
120.925
77.413
77.160
76.905
51.812
41.527
O
S
CF3
3f
13C NMR (125 MHz, CDCl3)
f1 (ppm)

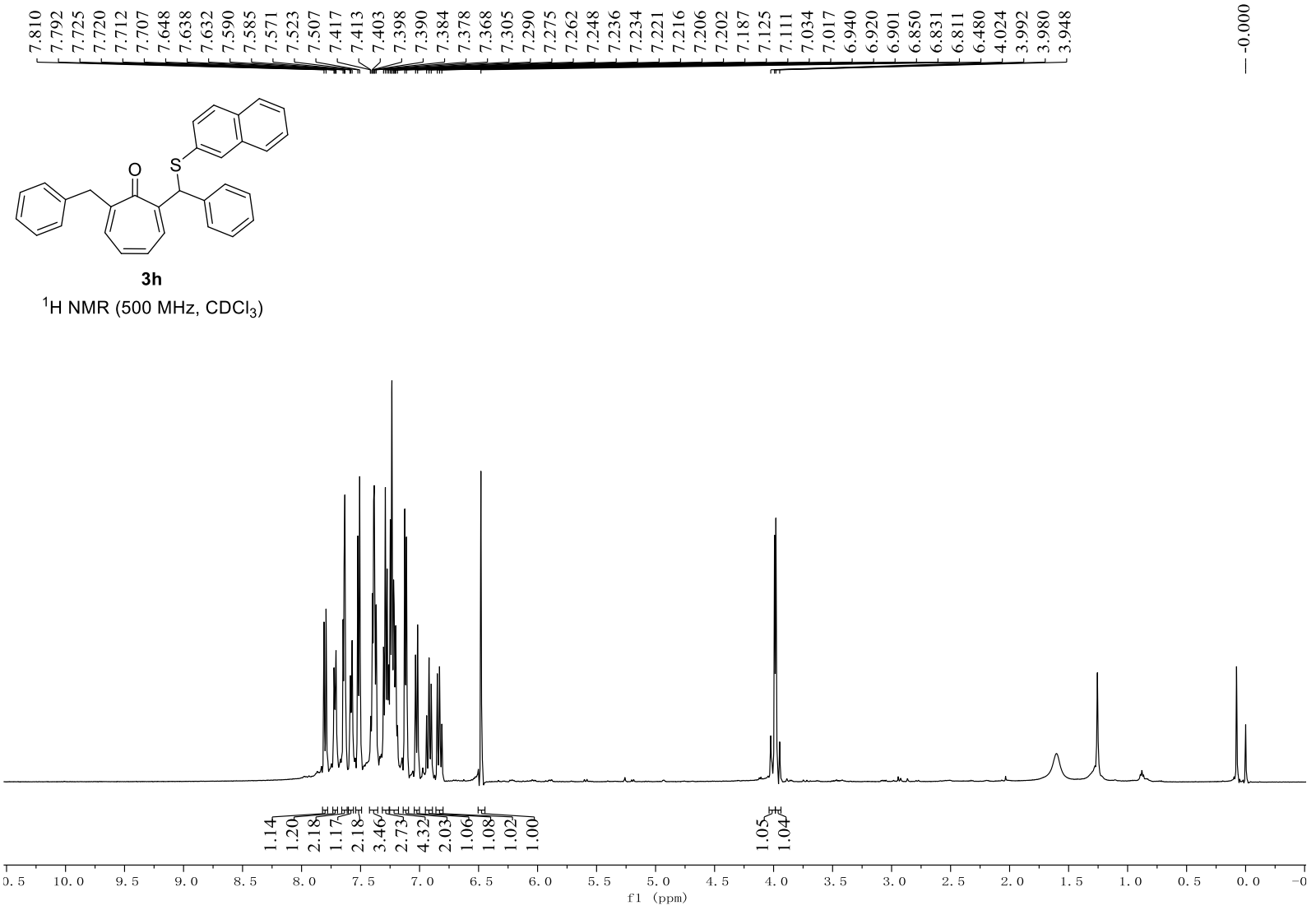


3f

^{19}F NMR (471 MHz, $CDCl_3$)

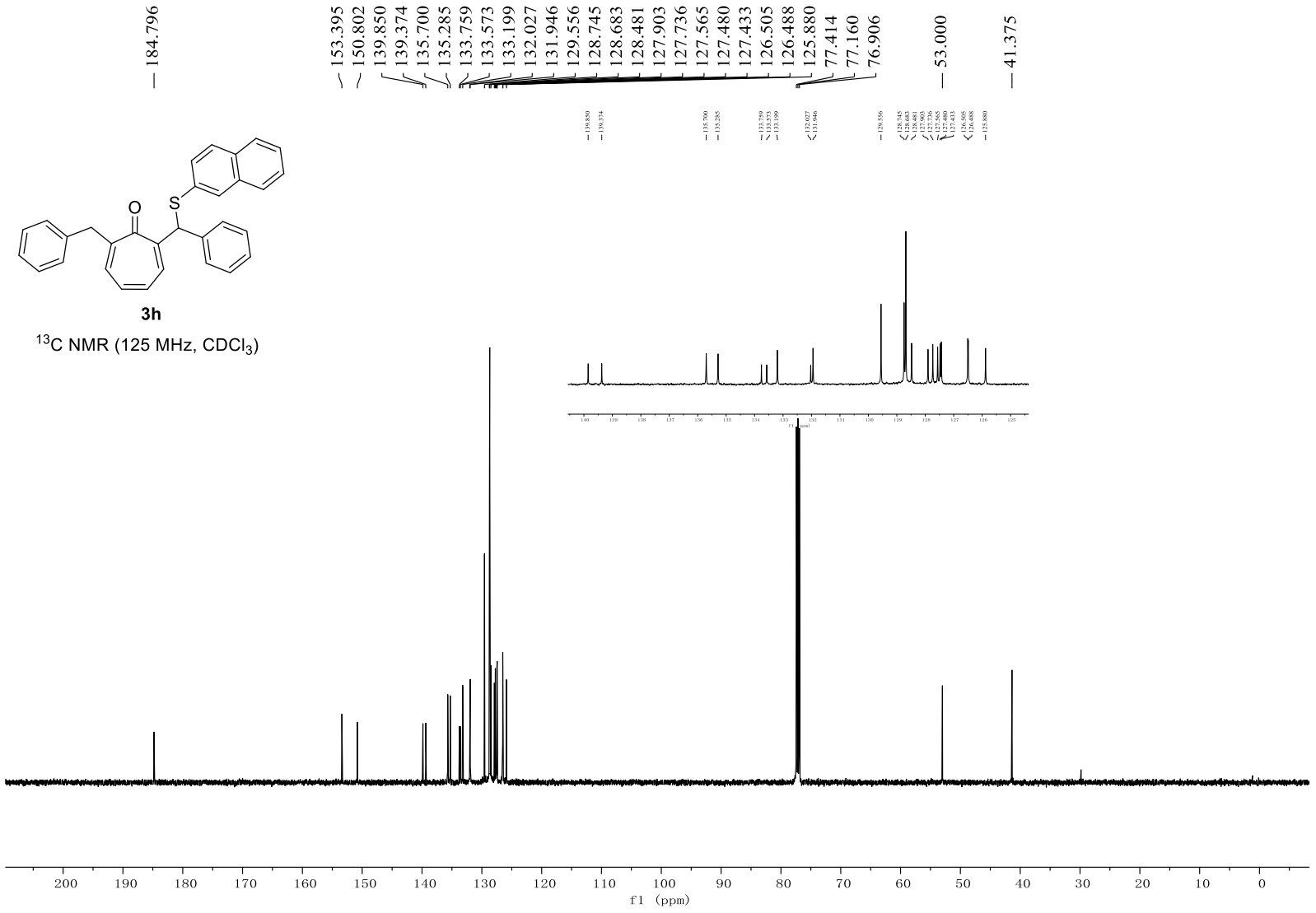

7.712
7.694
7.463
7.448
7.287
7.272
7.262
7.257
7.248
7.244
7.217
7.203
7.188
7.142
7.127
7.023
7.005
6.938
6.859
6.840
6.725
6.721
6.708
6.150
4.010
3.977
3.969
3.937
3.729
-0.000
OMe
S
O
3g
1H NMR (500 MHz, CDCl3)
1.00
2.05
6.39
2.30
2.02
1.05
1.09
1.09
1.99
1.00
1.02
1.14
2.98
f1 (ppm)

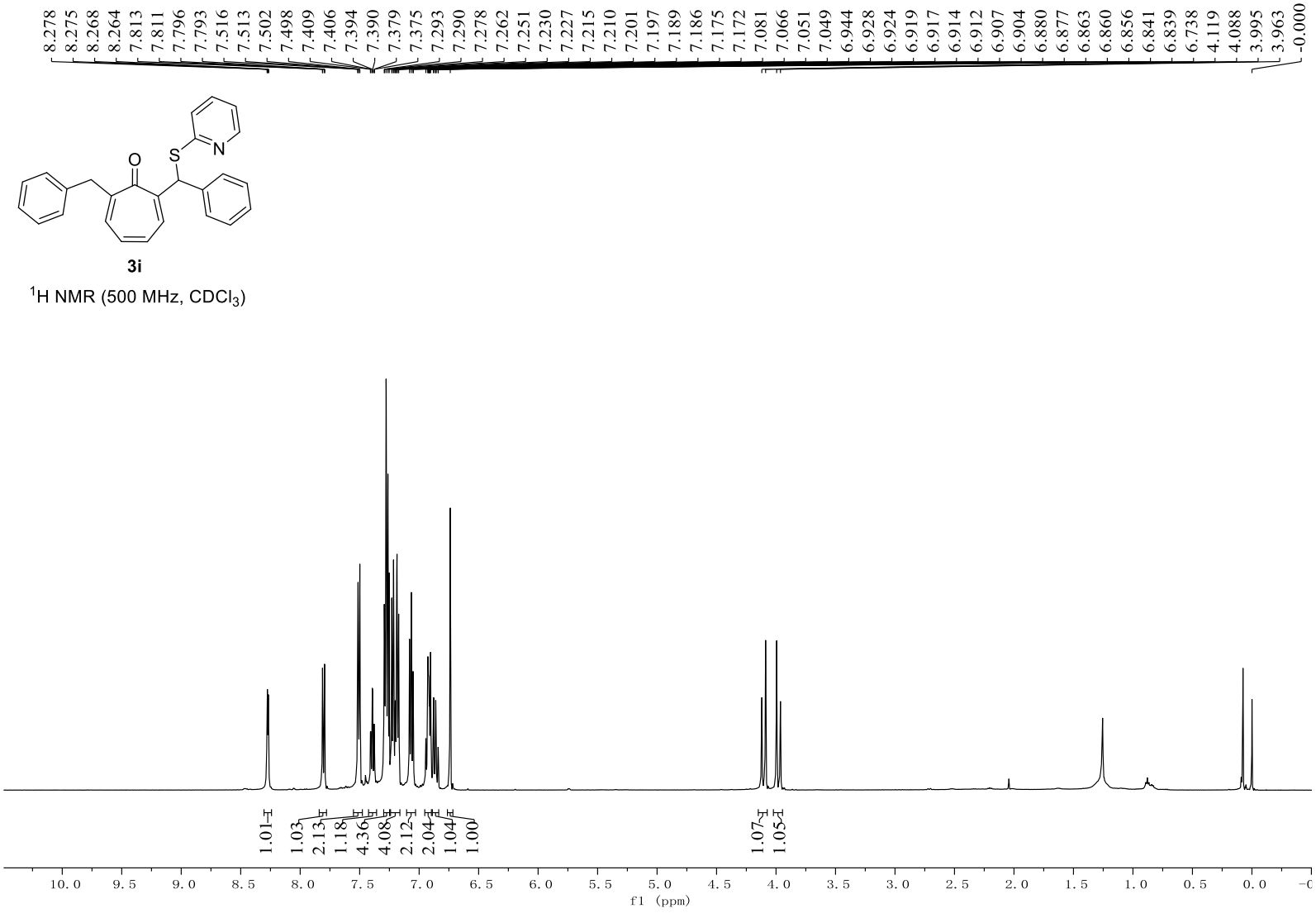

184.761
159.315
153.305
151.270
140.409
139.420
135.688
135.106
133.793
132.955
131.870
129.564
128.672
128.661
128.566
127.327
126.466
126.103
114.569
77.413
77.160
76.905
55.374
55.078
41.310
OMe
S
O
3g
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3h

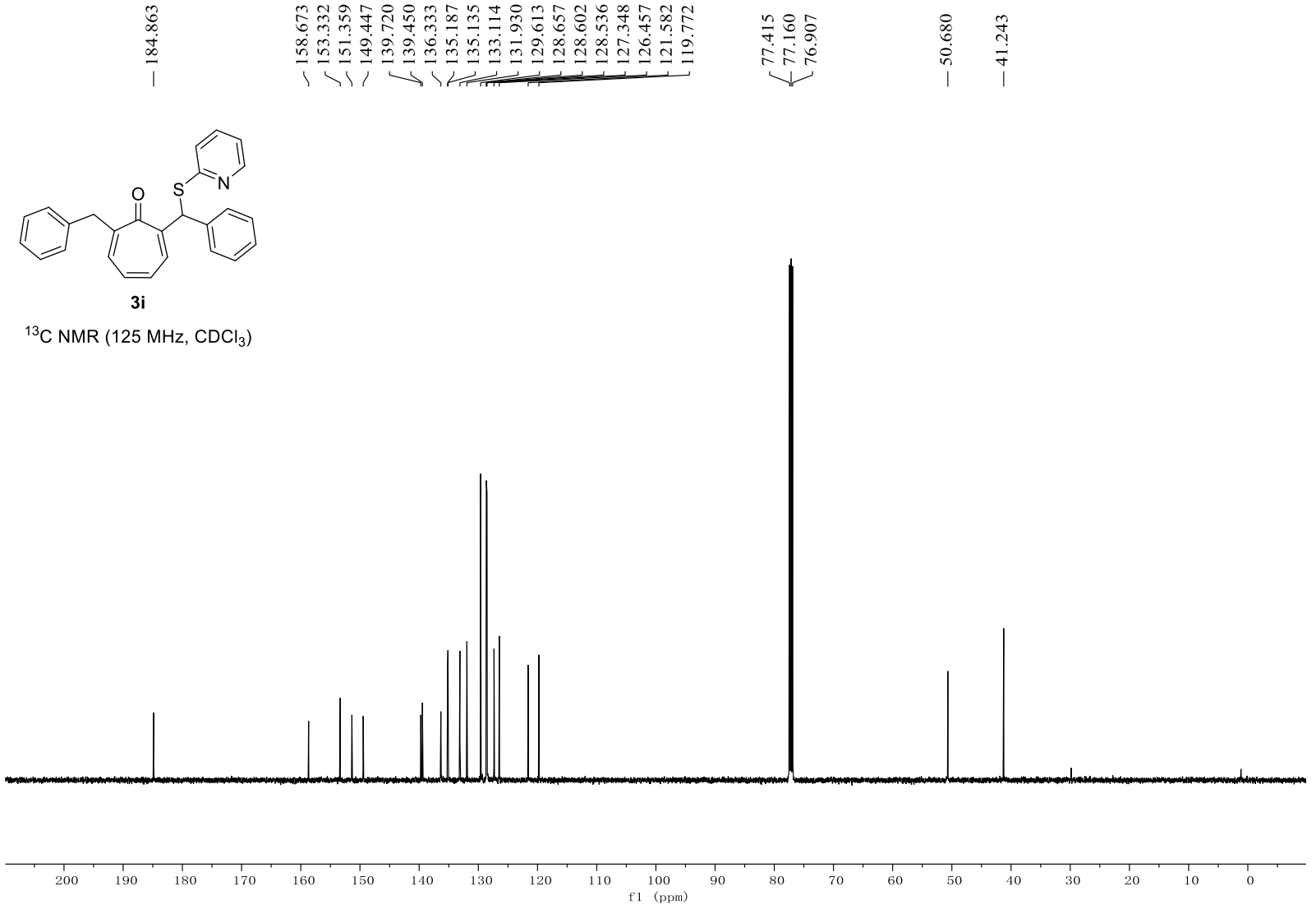
^{1}H NMR (500 MHz, $CDCl_3$)

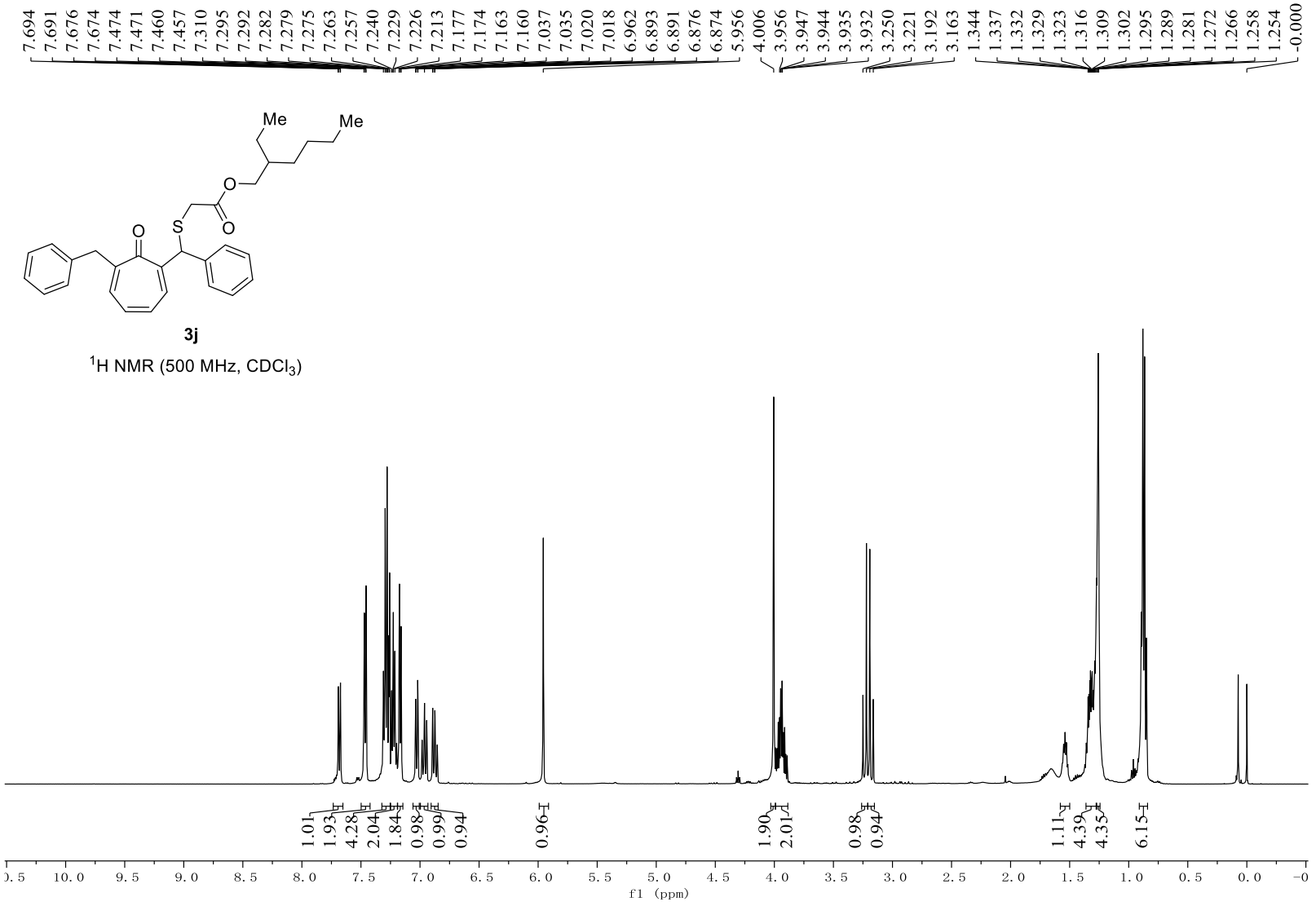

184.796
153.395
150.802
139.850
139.374
135.700
135.285
133.759
133.573
133.199
132.027
131.946
129.556
128.745
128.683
128.481
127.903
127.736
127.565
127.480
127.433
126.505
126.488
125.880
77.414
77.160
76.906
53.000
41.375
O
S
3h
13C NMR (125 MHz, CDCl3)
f1 (ppm)

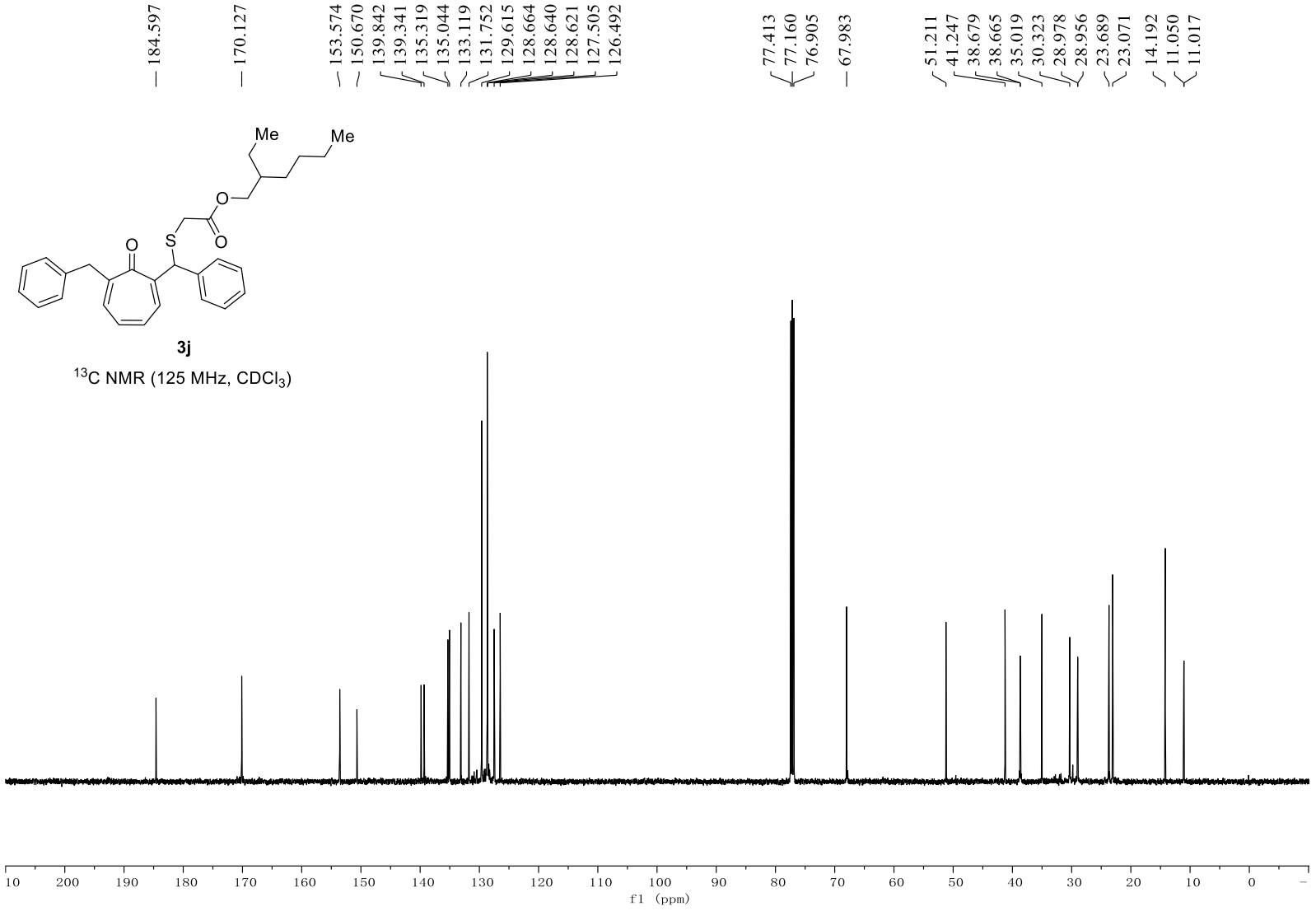


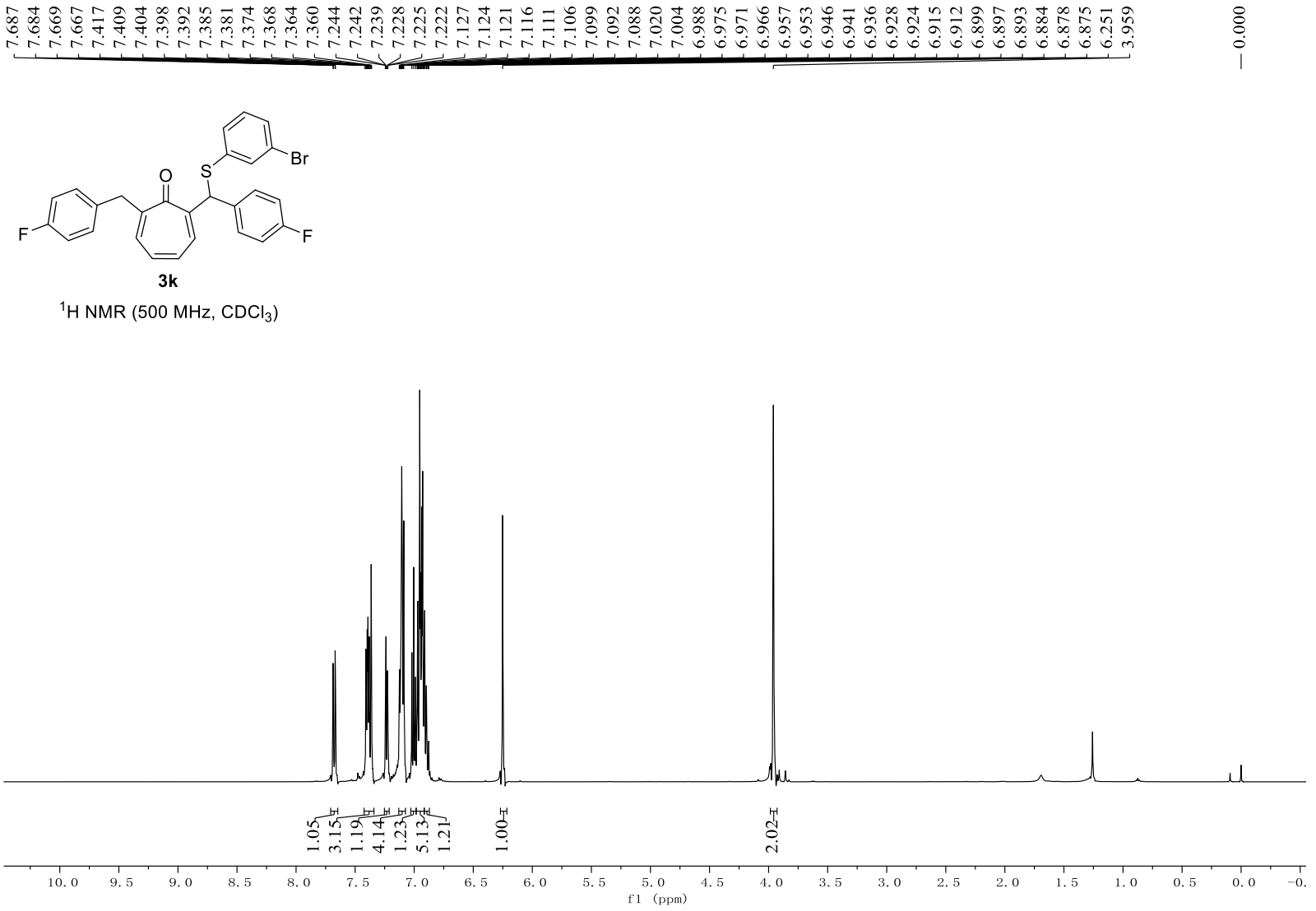
3i

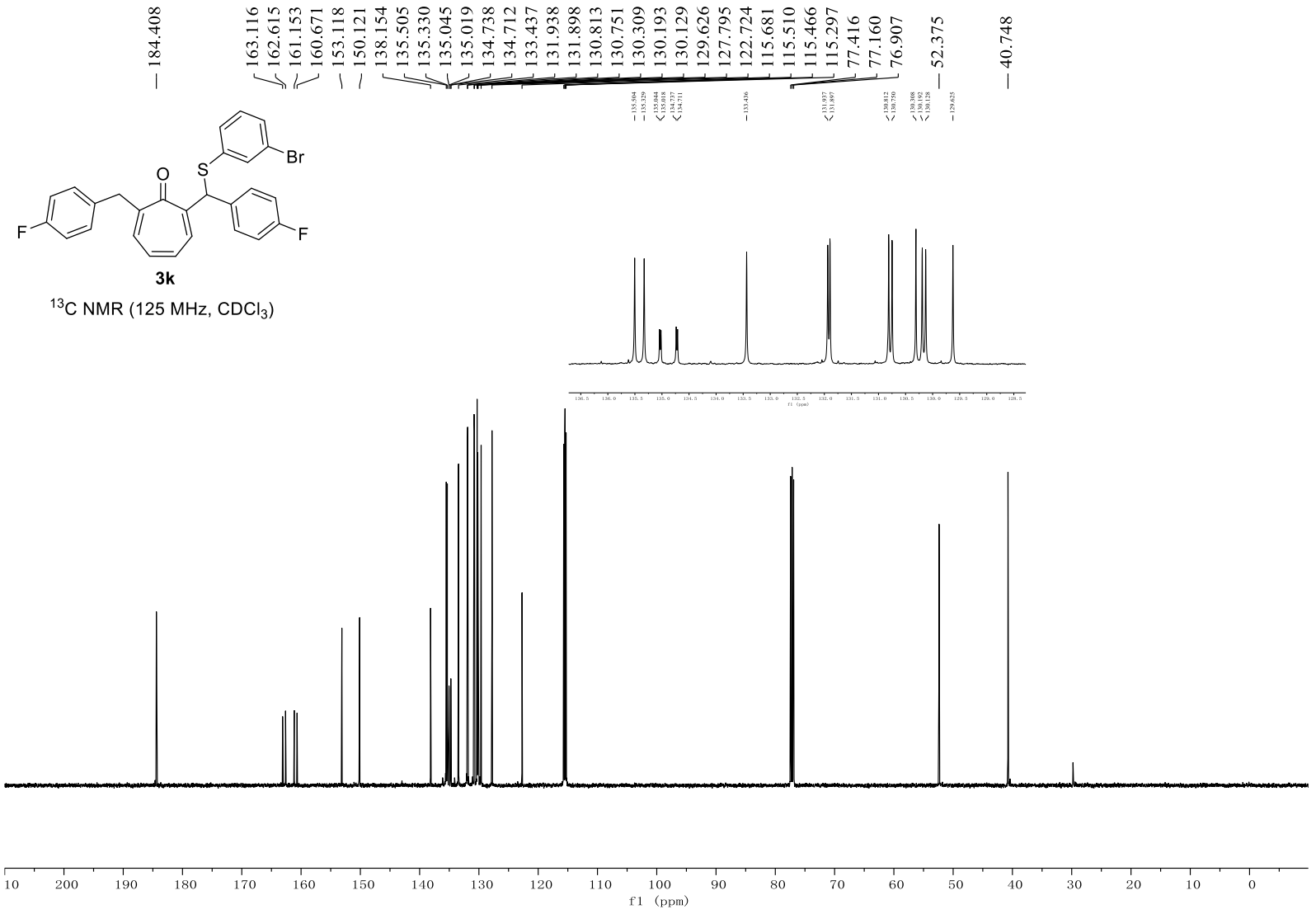
^{1}H NMR (500 MHz, $CDCl_3$)

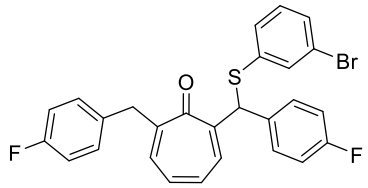

184.863
158.673
153.332
151.359
149.447
139.720
139.450
136.333
135.187
135.135
133.114
131.930
129.613
128.657
128.602
128.536
127.348
126.457
121.582
119.772
77.415
77.160
76.907
50.680
41.243
O
S
N
3i
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.694
7.691
7.676
7.674
7.474
7.471
7.460
7.457
7.310
7.295
7.292
7.282
7.279
7.275
7.263
7.257
7.240
7.229
7.226
7.213
7.177
7.174
7.163
7.160
7.037
7.035
7.020
7.018
6.962
6.893
6.891
6.876
6.874
5.956
4.006
3.956
3.947
3.944
3.935
3.932
3.250
3.221
3.192
3.163
1.344
1.337
1.332
1.329
1.323
1.316
1.309
1.302
1.295
1.289
1.281
1.272
1.266
1.258
1.254
-0.000
Me
Me
O
O
S
O
3j
1H NMR (500 MHz, CDCl3)
1.01
1.93
4.28
2.04
1.84
0.98
0.99
0.94
0.96
1.90
2.01
0.98
0.94
1.11
4.39
4.35
6.15
f1 (ppm)


184.597
170.127
153.574
150.670
139.842
139.341
135.319
135.044
133.119
131.752
129.615
128.664
128.640
128.621
127.505
126.492
77.413
77.160
76.905
67.983
51.211
41.247
38.679
38.665
35.019
30.323
28.978
28.956
23.689
23.071
14.192
11.050
11.017
Me
Me
O
O
S
O
O
3j
13C NMR (125 MHz, CDCl3)
f1 (ppm)

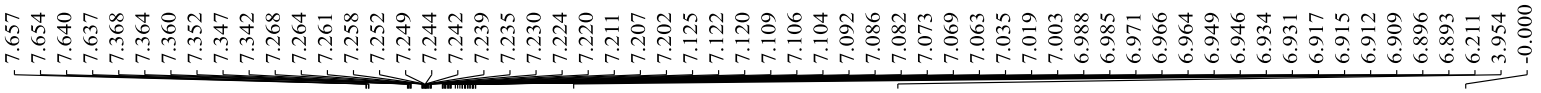

7.687
7.684
7.669
7.667
7.417
7.409
7.404
7.398
7.392
7.385
7.381
7.374
7.368
7.364
7.360
7.244
7.242
7.239
7.228
7.225
7.222
7.127
7.124
7.121
7.116
7.111
7.106
7.099
7.092
7.088
7.020
7.004
6.988
6.975
6.971
6.966
6.957
6.953
6.946
6.941
6.936
6.928
6.924
6.915
6.912
6.899
6.897
6.893
6.884
6.878
6.875
6.251
3.959
0.000
O
S
Br
F
F
3k
1H NMR (500 MHz, CDCl3)
1.05
3.15
1.19
4.14
1.23
5.13
1.21
1.00
2.02
f1 (ppm)

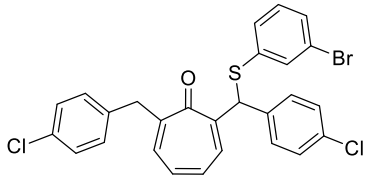

184.408
163.116
162.615
161.153
160.671
153.118
150.121
138.154
135.505
135.330
135.045
135.019
134.738
134.712
133.437
131.938
131.898
130.813
130.751
130.309
130.193
130.129
129.626
127.795
122.724
115.681
115.510
115.466
115.297
77.416
77.160
76.907
52.375
40.748
Br
S
O
F
F
3k
13C NMR (125 MHz, CDCl3)
f1 (ppm)



3k

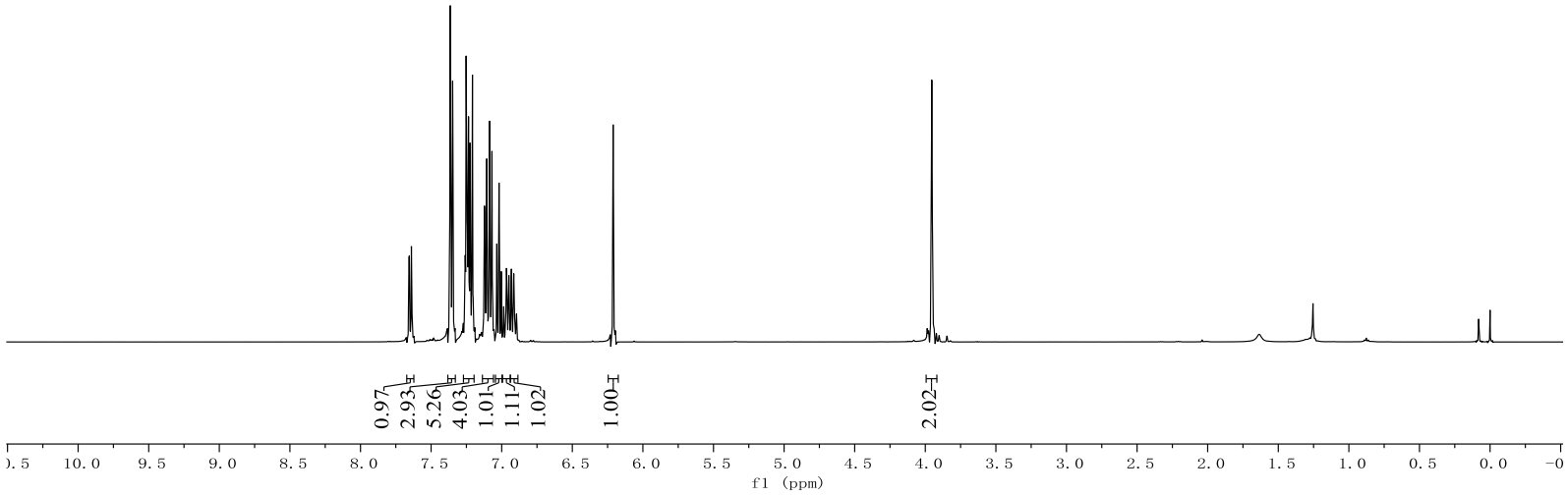
^{19}F NMR (470 MHz, $CDCl_3$)

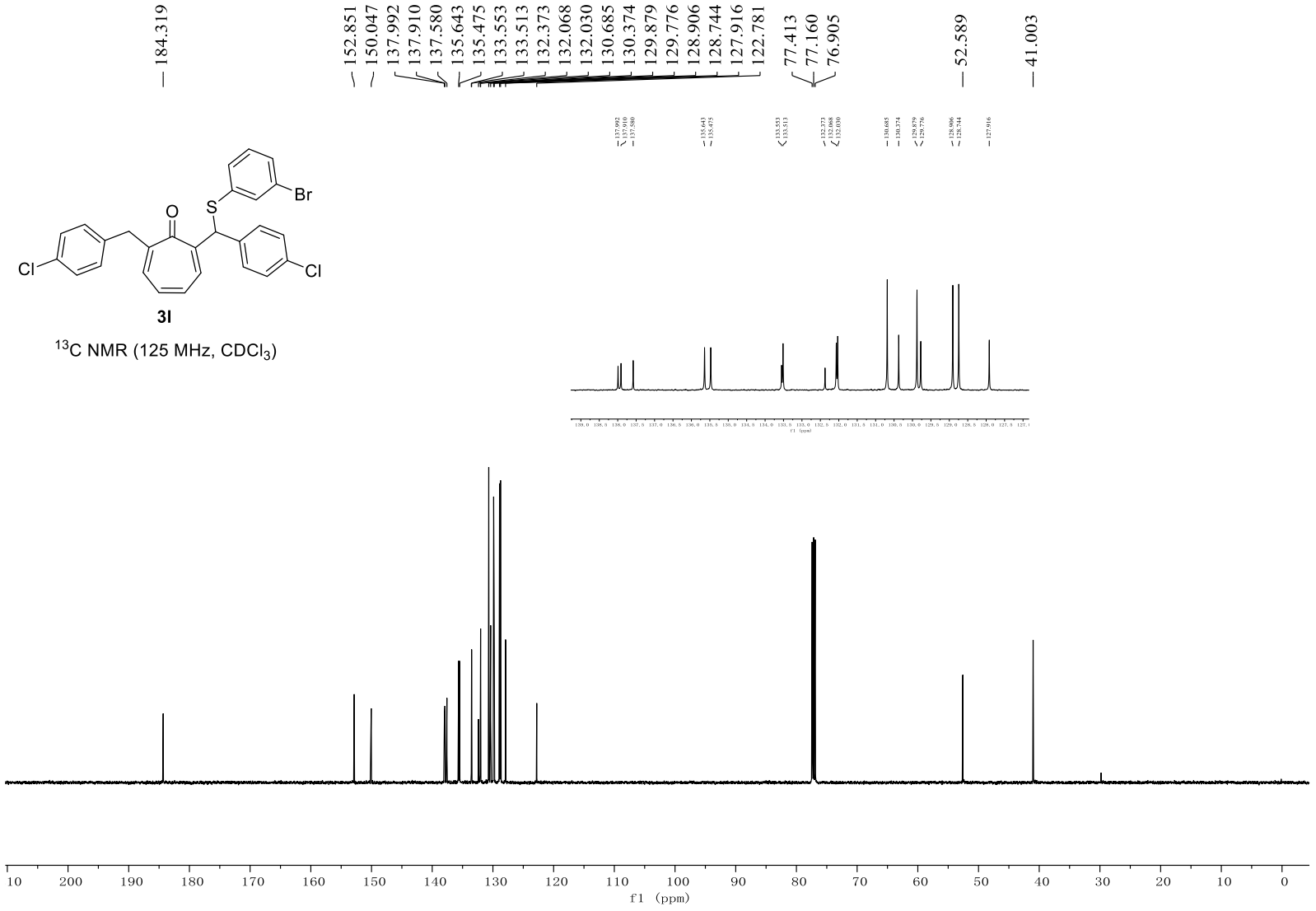


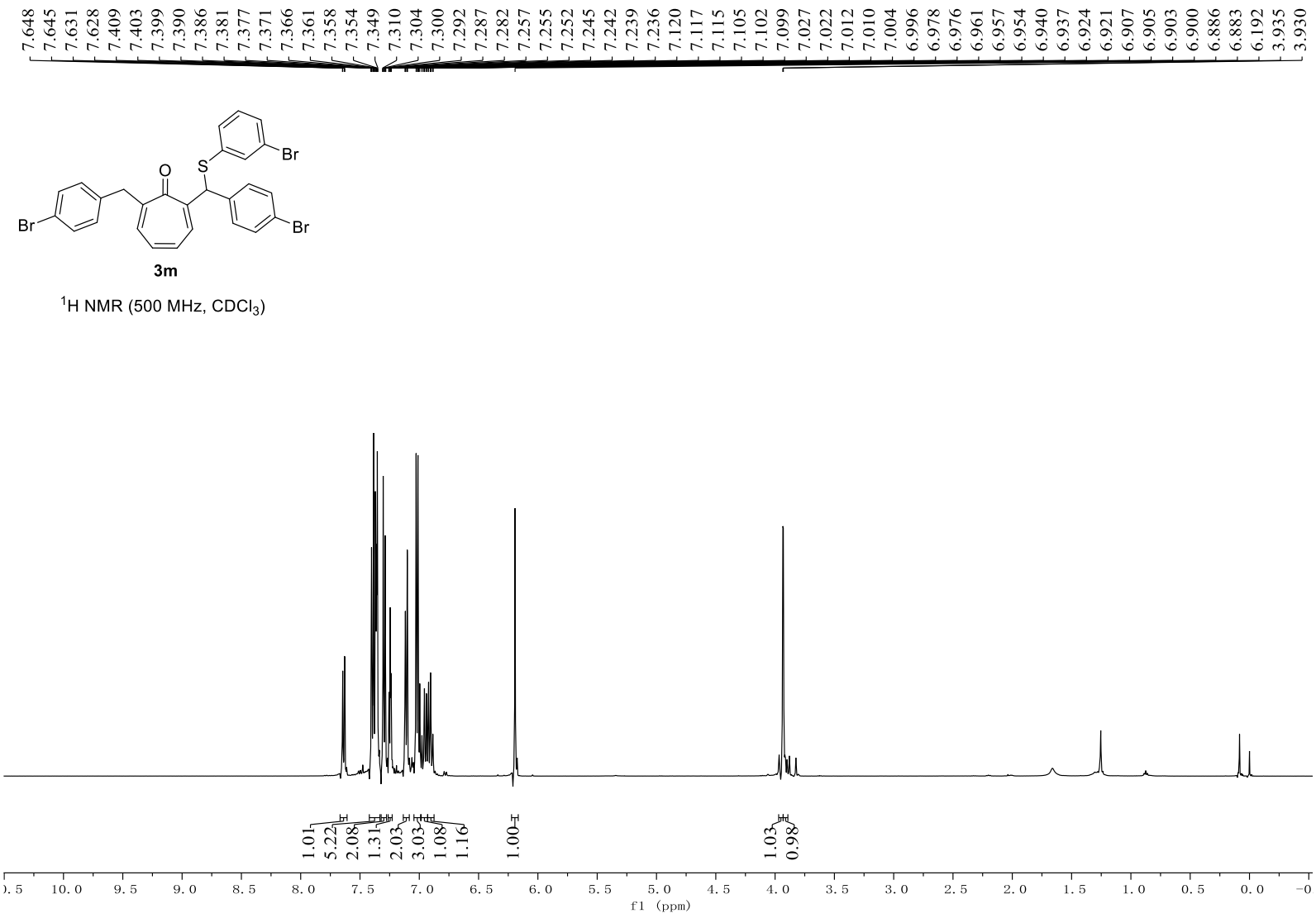


3l

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

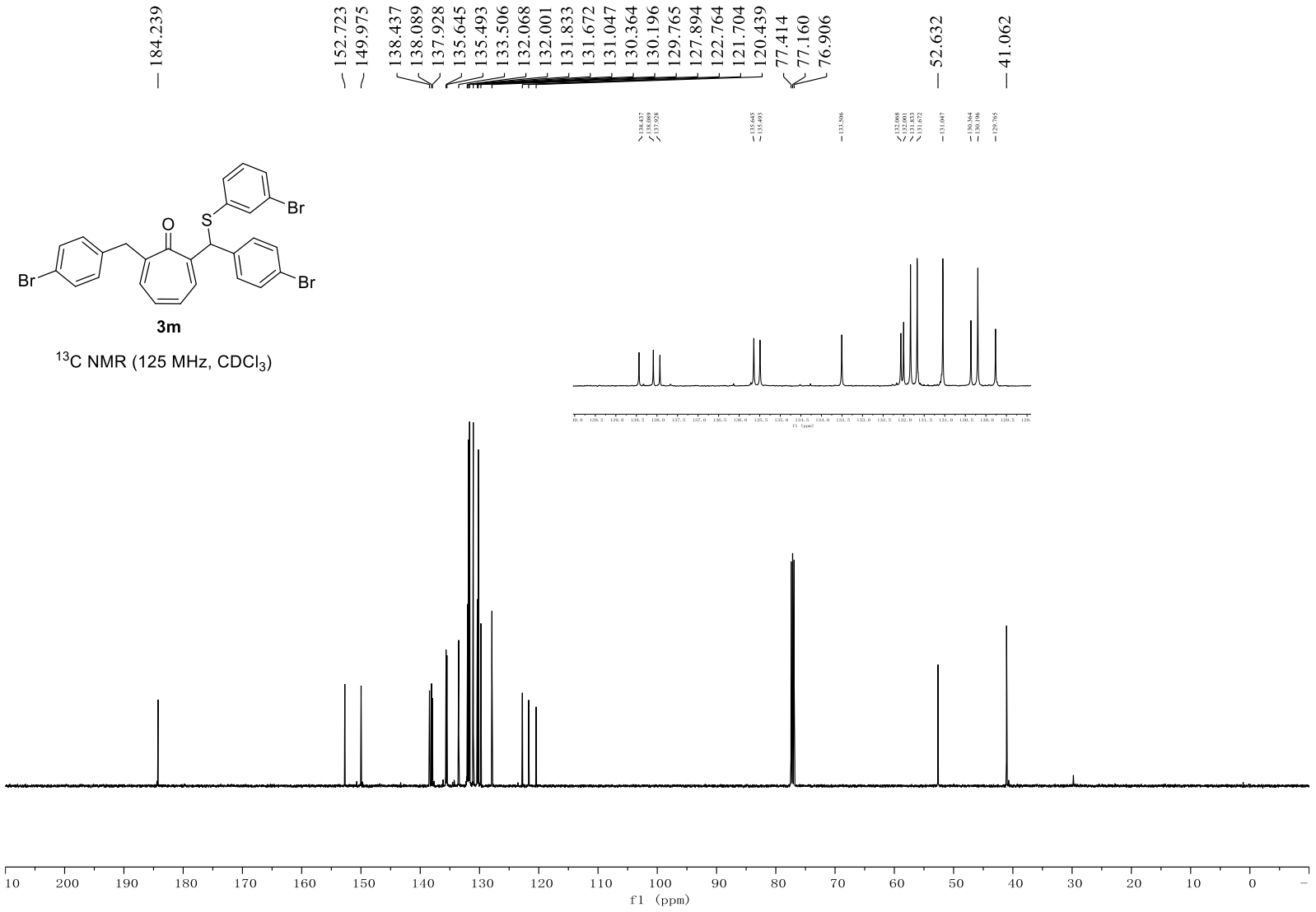


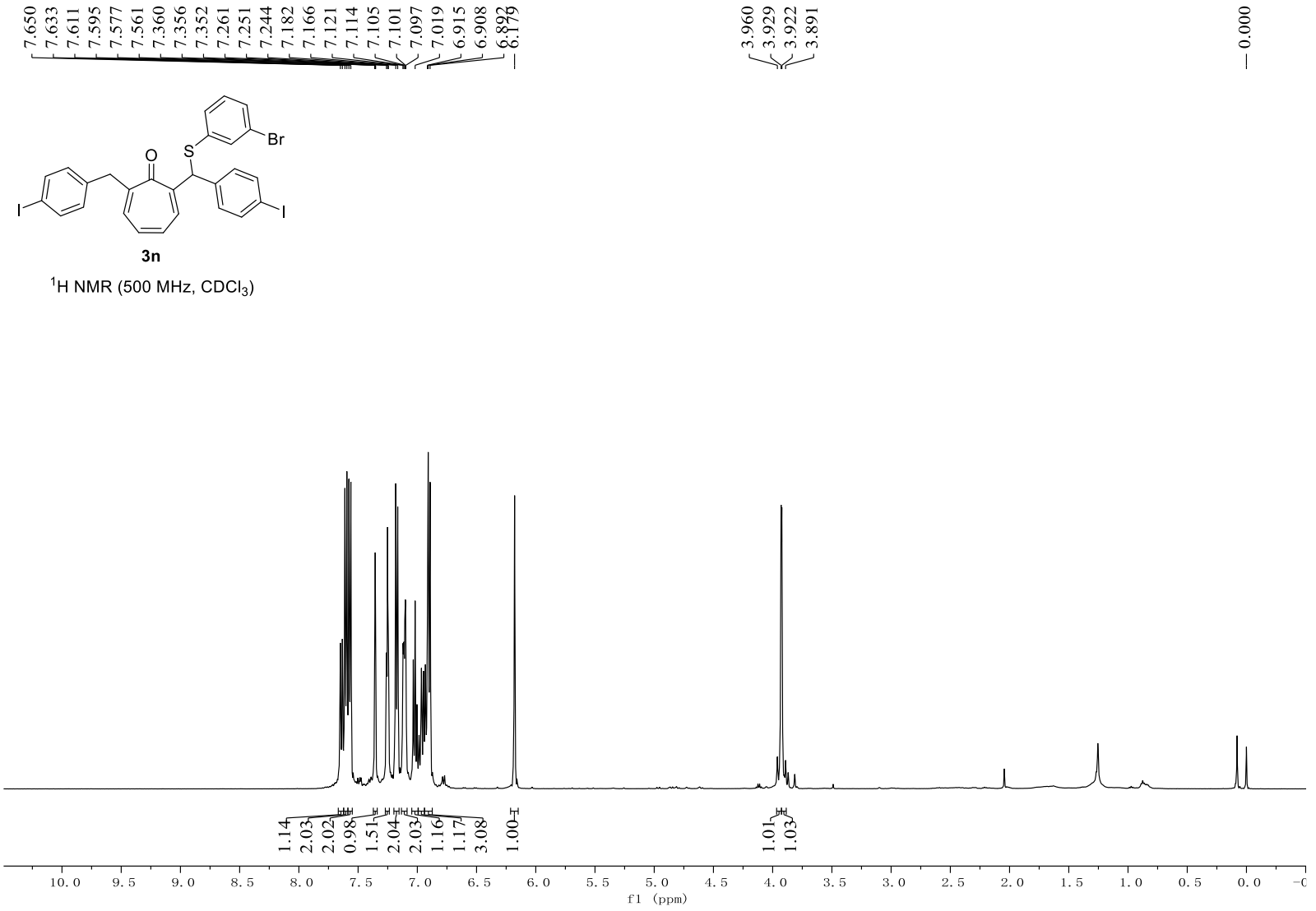

184.319
152.851
150.047
137.992
137.910
137.580
135.643
135.475
133.553
133.513
132.373
132.068
132.030
130.685
130.374
129.879
129.776
128.906
128.744
127.916
122.781
77.413
77.160
76.905
52.589
41.003
Br
S
O
Cl
Cl
3l
13C NMR (125 MHz, CDCl3)
f1 (ppm)



3m

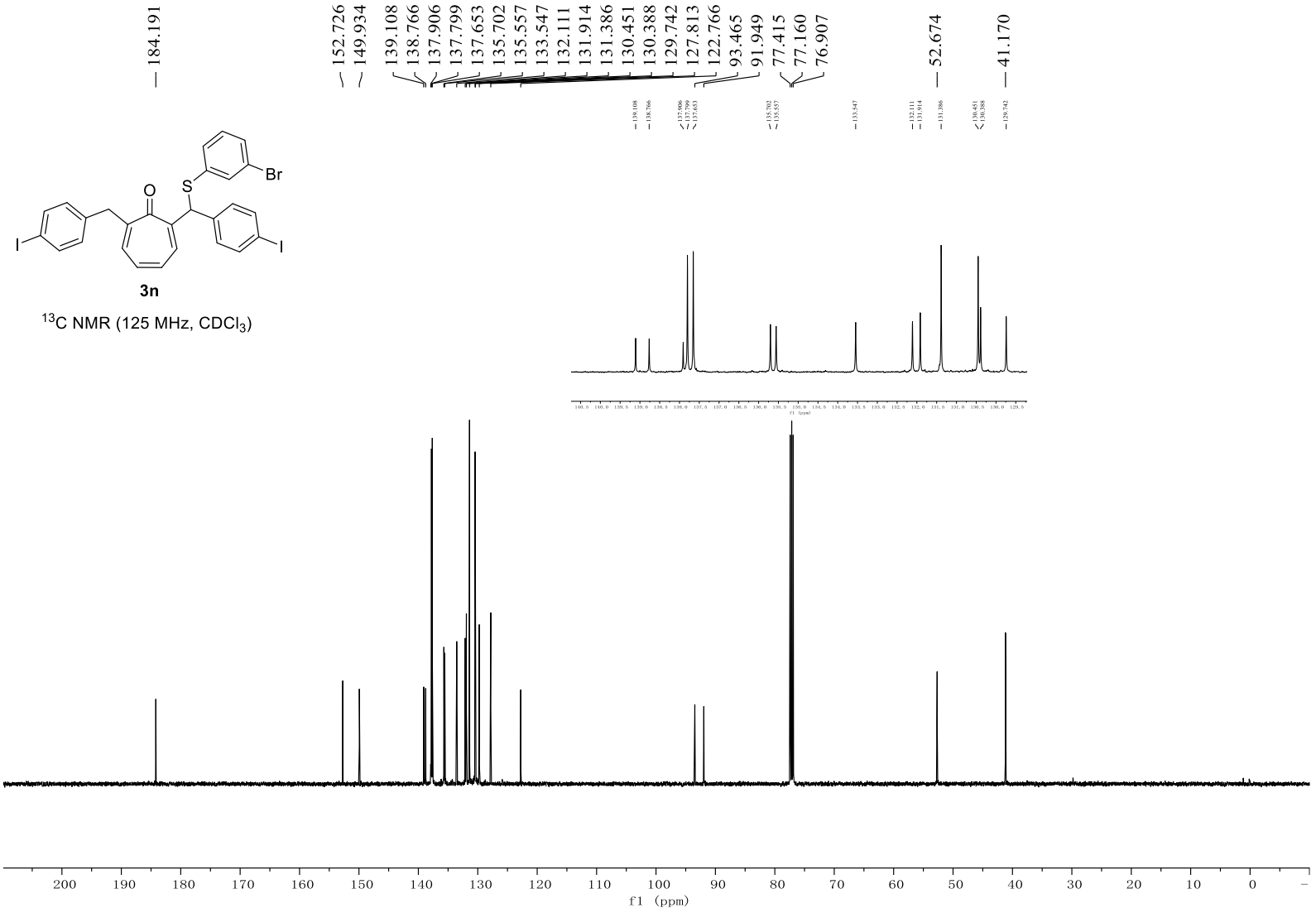
^{1}H NMR (500 MHz, $CDCl_3$)

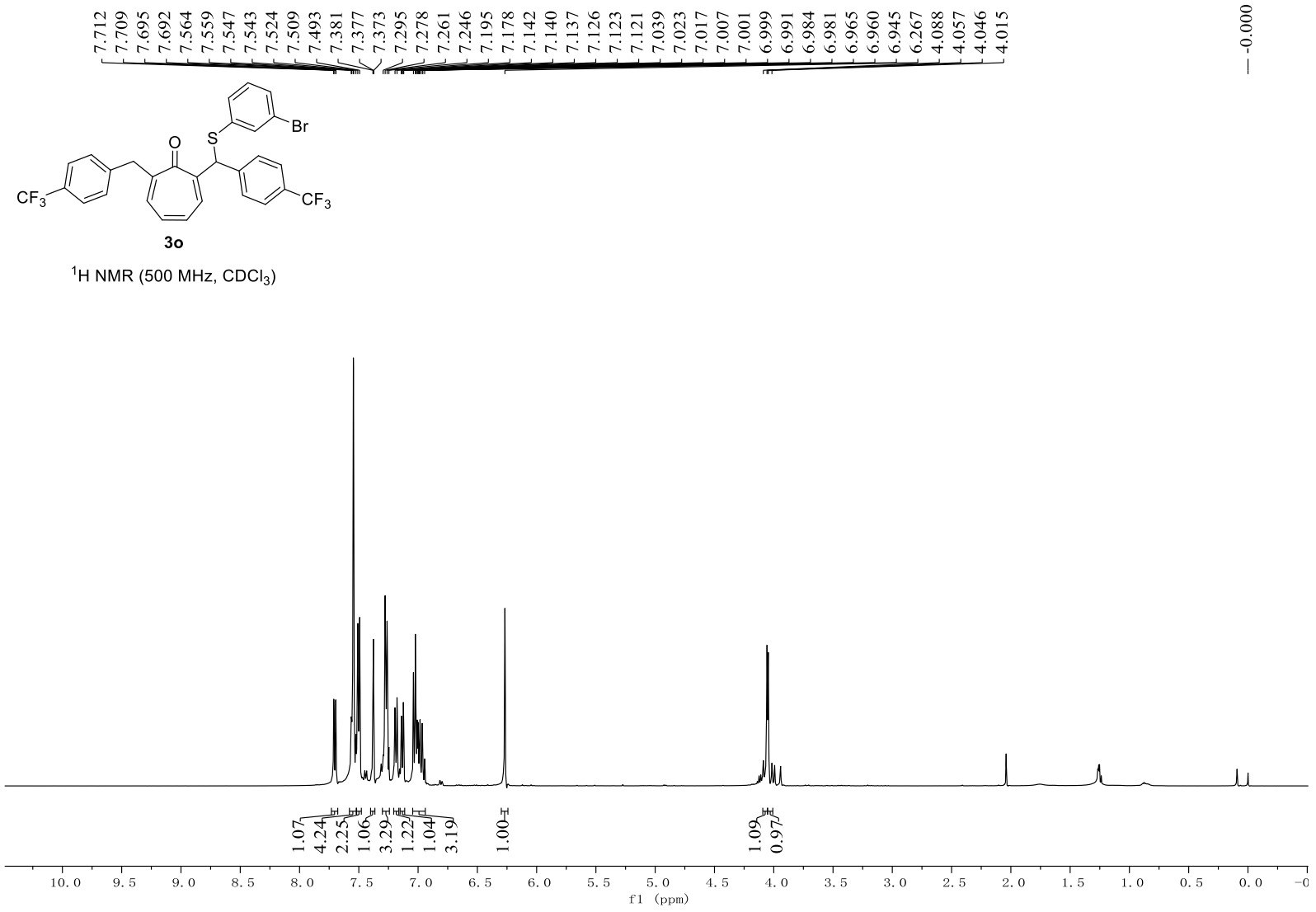

184.239
152.723
149.975
138.437
138.089
137.928
135.645
135.493
133.506
132.068
132.001
131.833
131.672
131.047
130.364
130.196
129.765
127.894
122.764
121.704
120.439
77.414
77.160
76.906
52.632
41.062
O
S
Br
Br
Br
3m
13C NMR (125 MHz, CDCl3)
f1 (ppm)

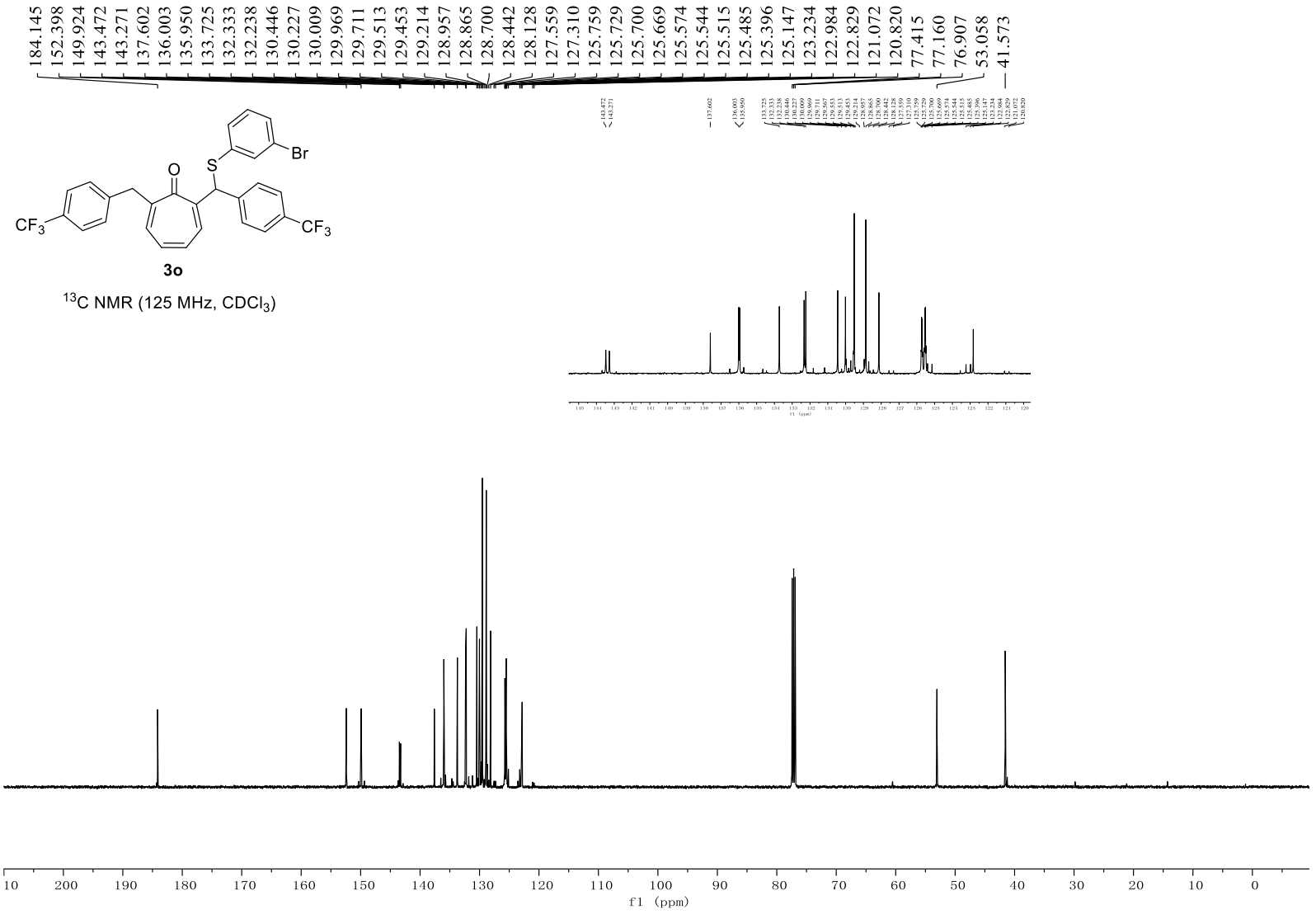


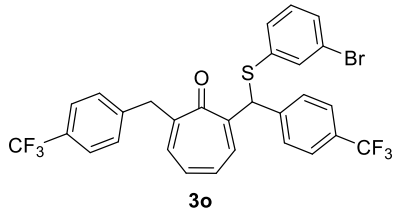
3n

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


184.191
152.726
149.934
139.108
138.766
137.906
137.799
137.653
135.702
135.557
133.547
132.111
131.914
131.386
130.451
130.388
129.742
127.813
122.766
93.465
91.949
77.415
77.160
76.907
52.674
41.170
Br
S
O
I
I
3n
13C NMR (125 MHz, CDCl3)
f1 (ppm)

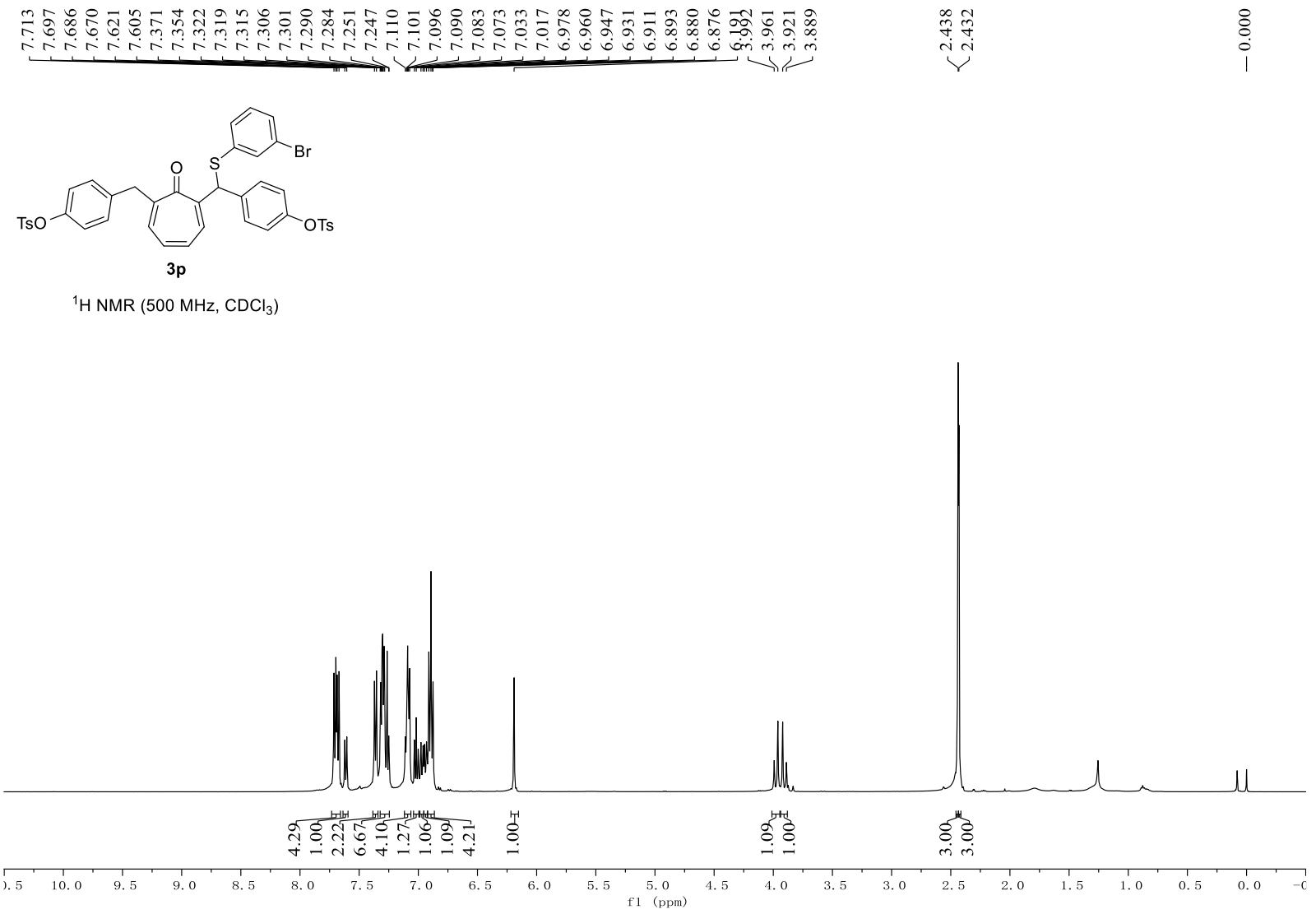

7.712
7.709
7.695
7.692
7.564
7.559
7.547
7.543
7.524
7.509
7.493
7.381
7.377
7.373
7.295
7.278
7.261
7.246
7.195
7.178
7.142
7.140
7.137
7.126
7.123
7.121
7.039
7.023
7.017
7.007
7.001
6.999
6.991
6.984
6.981
6.965
6.960
6.945
6.267
4.088
4.057
4.046
4.015
-0.000
Br
S
O
CF3
CF3
3o
1H NMR (500 MHz, CDCl3)
1.07
4.24
2.25
1.06
3.29
1.22
1.04
3.19
1.00
1.09
0.97
f1 (ppm)


184.145
152.398
149.924
143.472
143.271
137.602
136.003
135.950
133.725
132.333
132.238
130.446
130.227
130.009
129.969
129.711
129.513
129.453
129.214
128.957
128.865
128.700
128.442
128.128
127.559
127.310
125.759
125.729
125.700
125.669
125.574
125.544
125.515
125.485
125.396
125.147
123.234
122.984
122.829
121.072
120.820
77.415
77.160
76.907
53.058
41.573
Br
S
O
CF3
CF3
3o
13C NMR (125 MHz, CDCl3)
f1 (ppm)



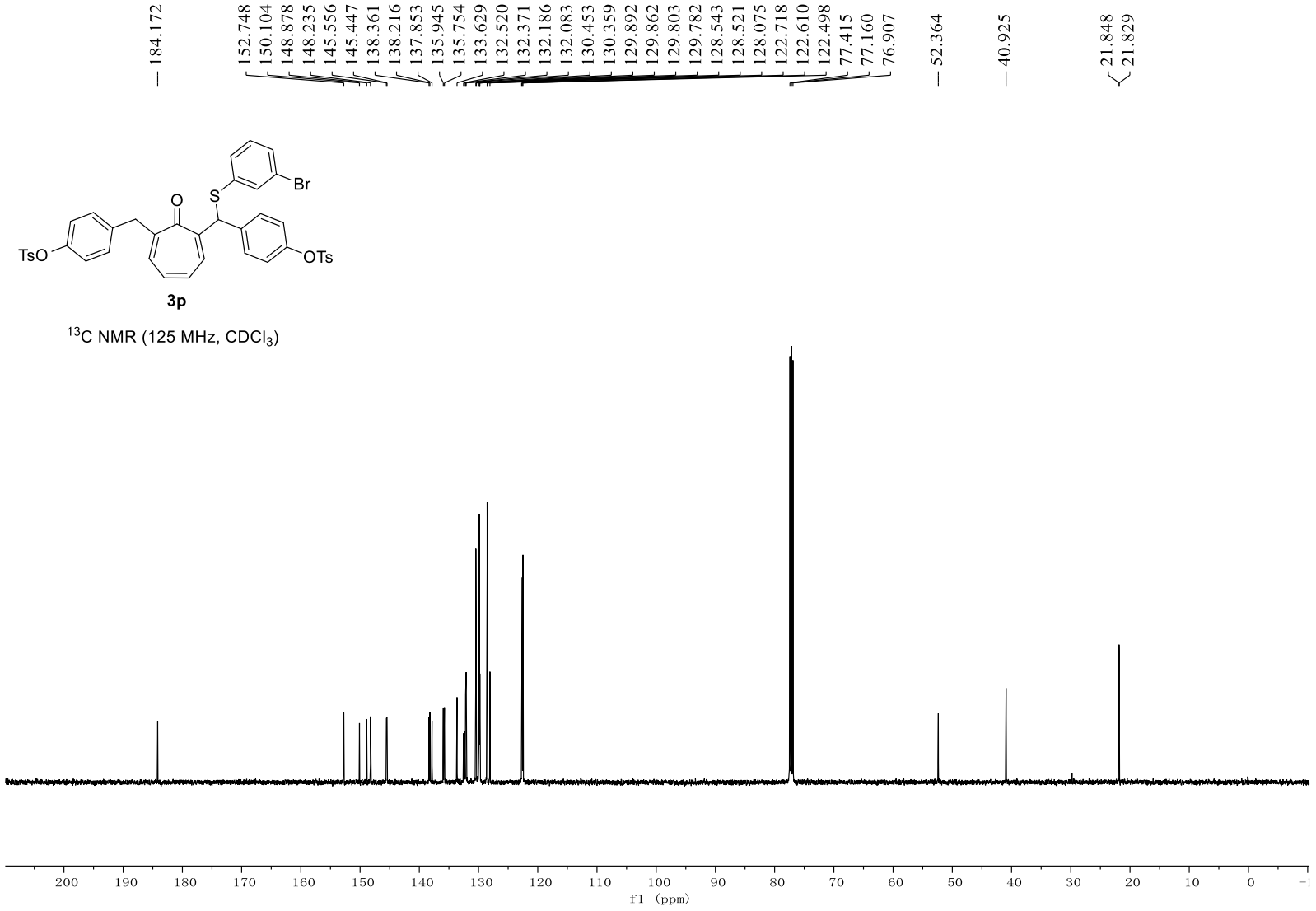
3o

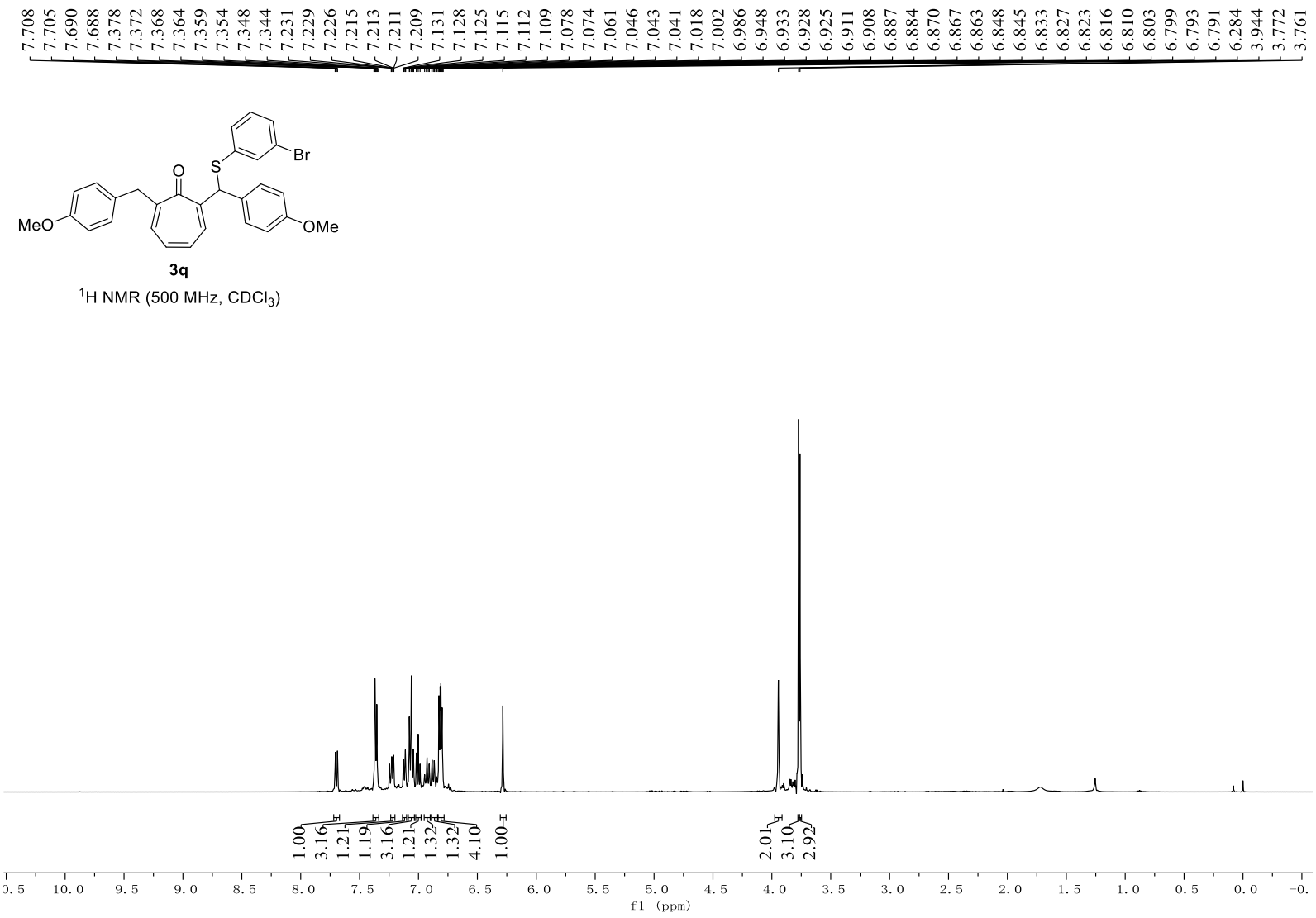
^{19}F NMR (471 MHz, $CDCl_3$)



3p

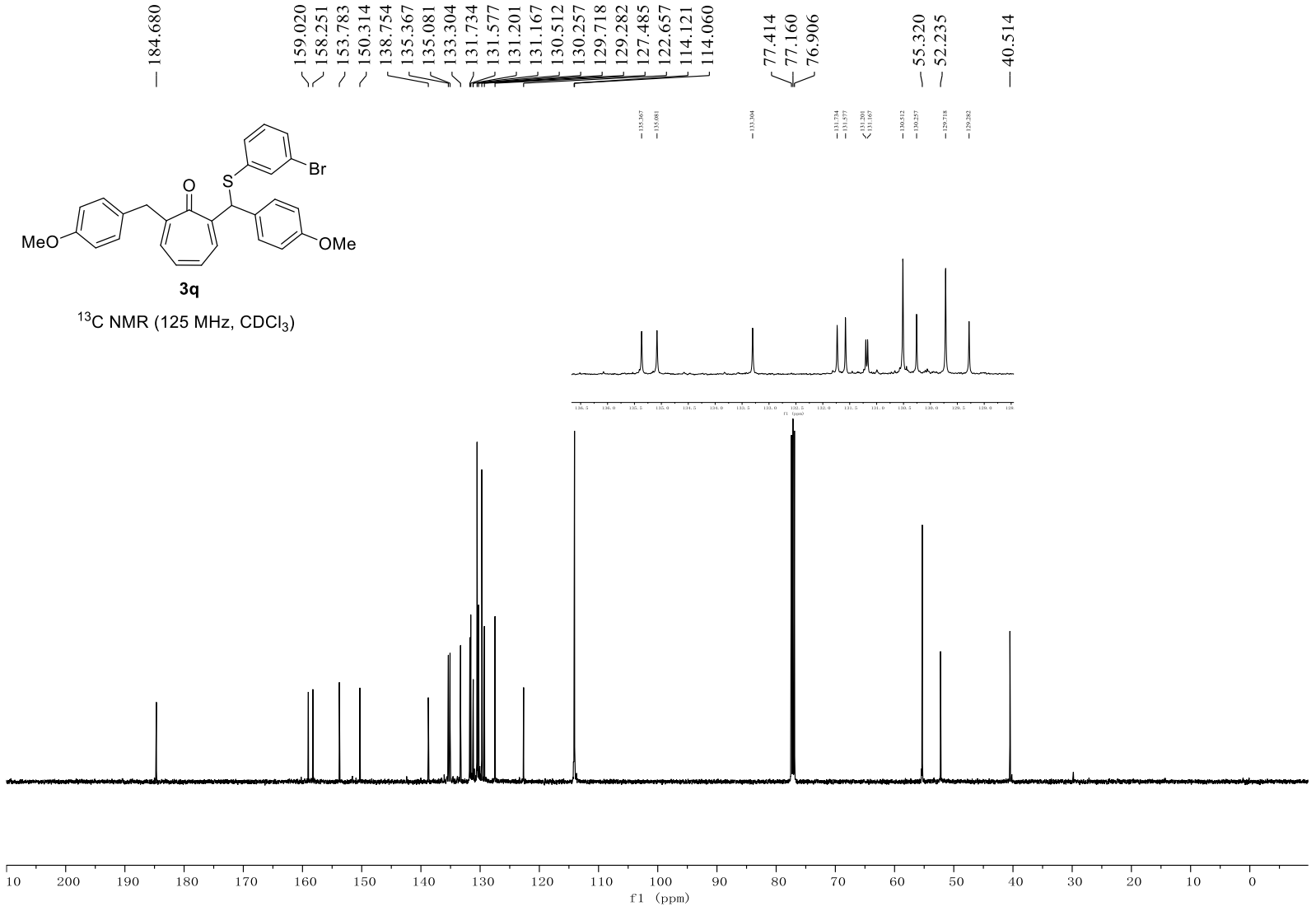
^{1}H NMR (500 MHz, $CDCl_3$)

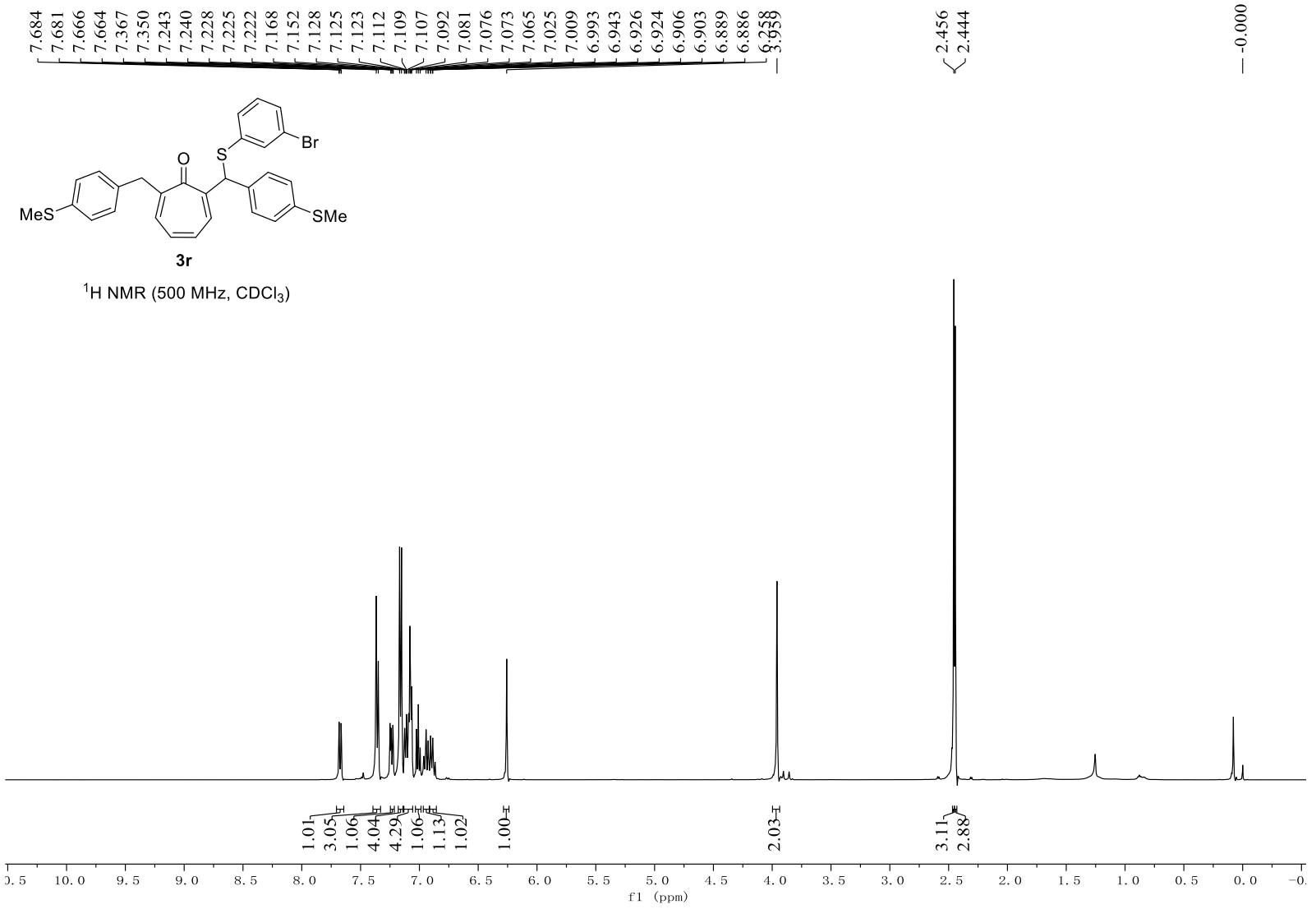

184.172
152.748
150.104
148.878
148.235
145.556
145.447
138.361
138.216
137.853
135.945
135.754
133.629
132.520
132.371
132.186
132.083
130.453
130.359
129.892
129.862
129.803
129.782
128.543
128.521
128.075
122.718
122.610
122.498
77.415
77.160
76.907
52.364
40.925
21.848
21.829
Br
S
O
TsO
OTs
3p
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

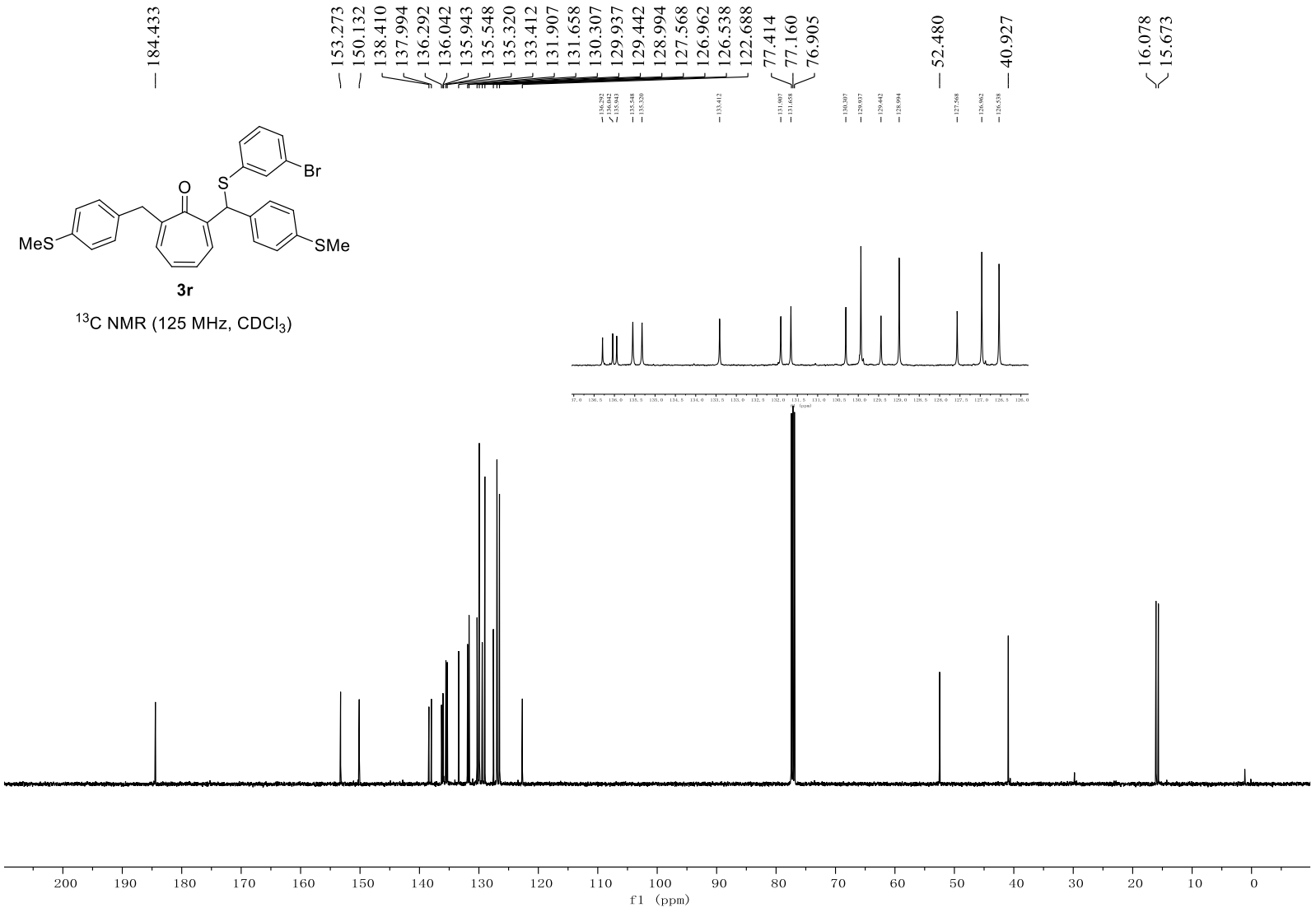


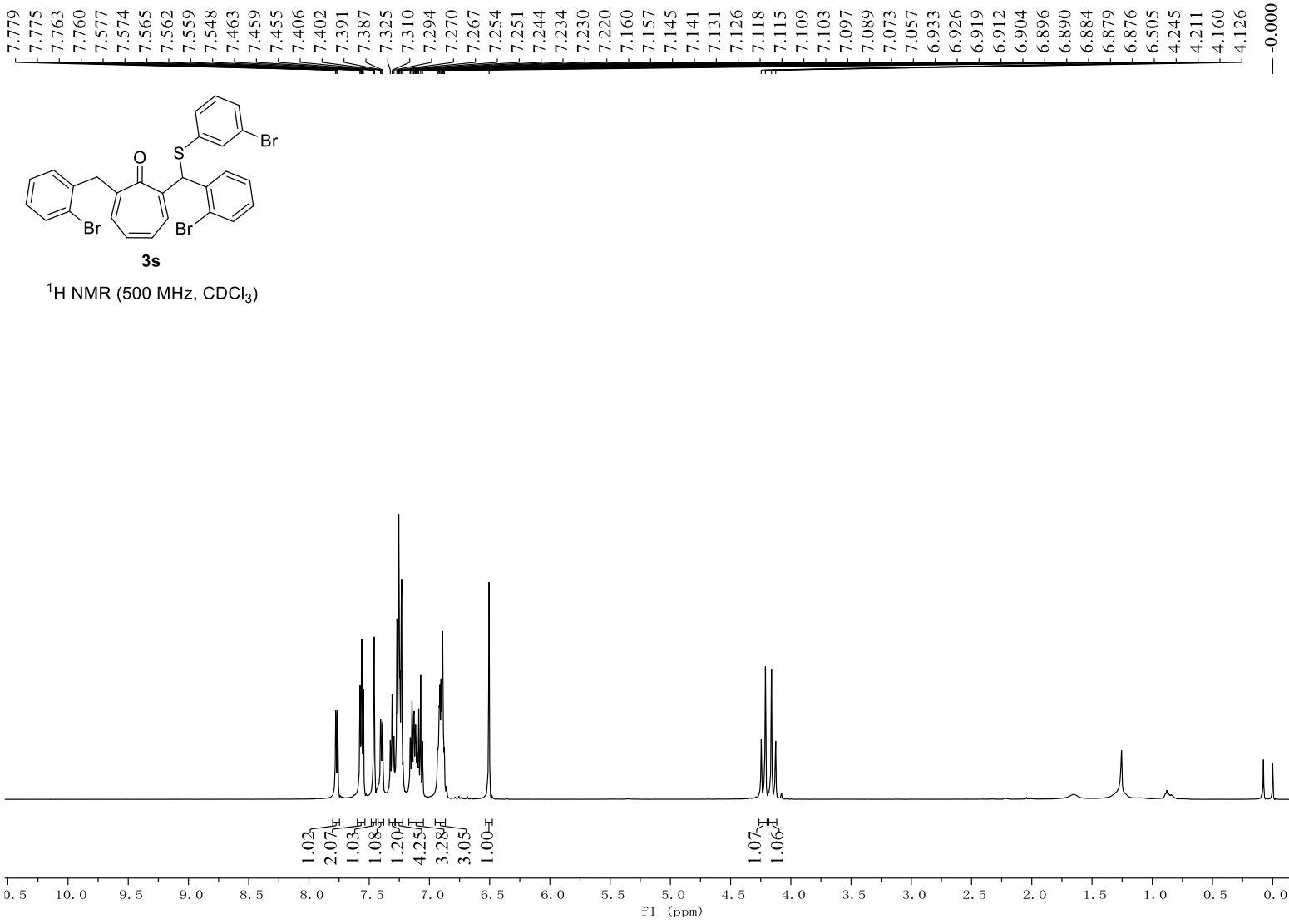
3q

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


184.680
159.020
158.251
153.783
150.314
138.754
135.367
135.081
133.304
131.734
131.577
131.201
131.167
130.512
130.257
129.718
129.282
127.485
122.657
114.121
114.060
77.414
77.160
76.906
55.320
52.235
40.514
Br
S
O
MeO
OMe
3q
13C NMR (125 MHz, CDCl3)
f1 (ppm)

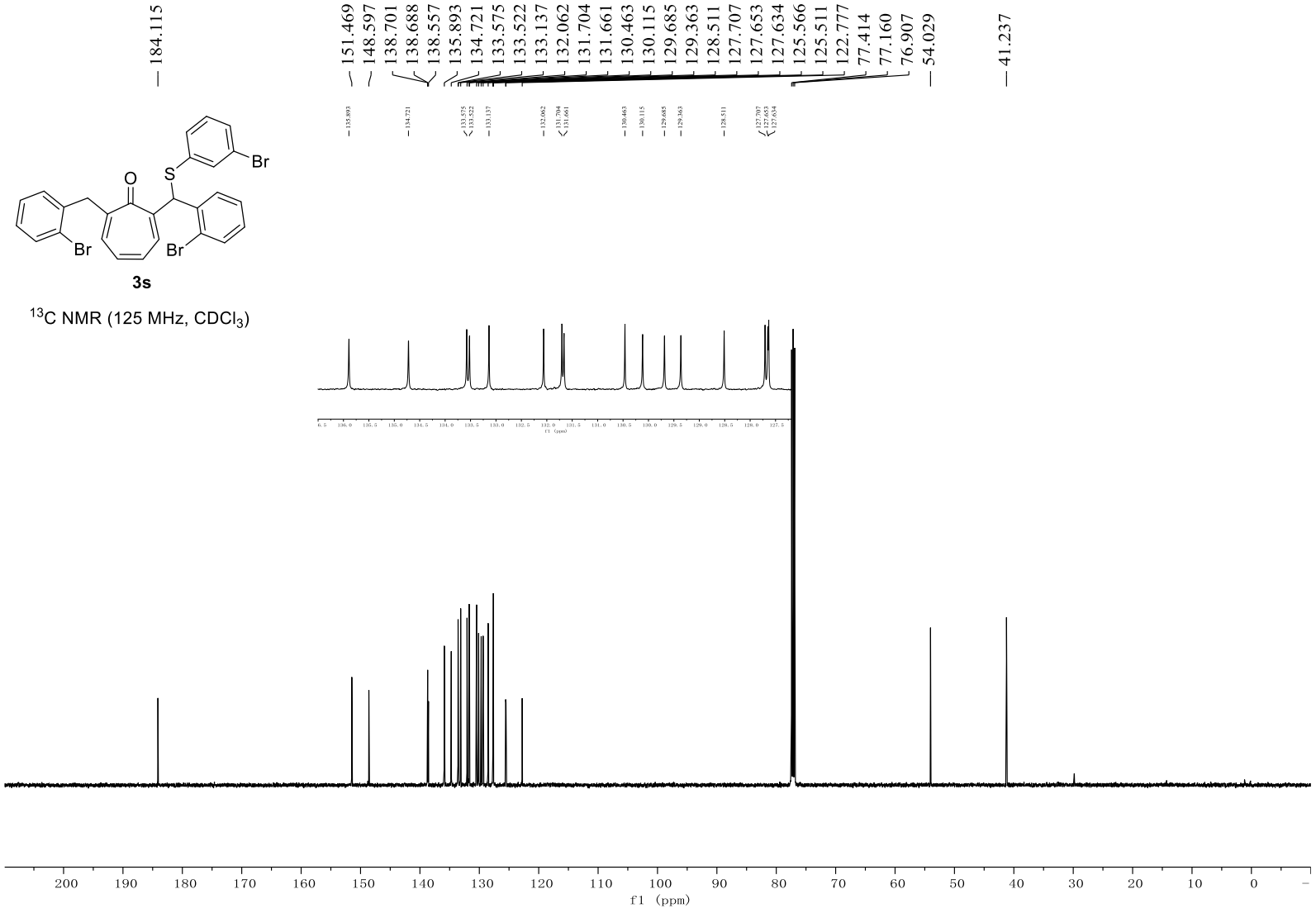

7.684
7.681
7.666
7.664
7.367
7.350
7.243
7.240
7.228
7.225
7.222
7.168
7.152
7.128
7.125
7.123
7.112
7.109
7.107
7.092
7.081
7.076
7.073
7.065
7.025
7.009
6.993
6.943
6.926
6.924
6.906
6.903
6.889
6.886
6.258
3.958
2.456
2.444
-0.000
Br
S
O
MeS
SMe
3r
1H NMR (500 MHz, CDCl3)
1.01
3.05
1.06
4.04
4.29
1.06
1.13
1.02
1.00
2.03
3.11
2.88
f1 (ppm)

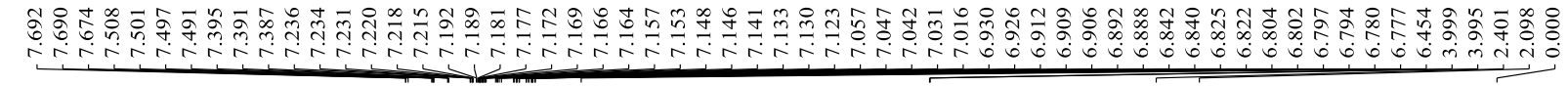

184.433
153.273
150.132
138.410
137.994
136.292
136.042
135.943
135.548
135.320
133.412
131.907
131.658
130.307
129.937
129.442
128.994
127.568
126.962
126.538
122.688
77.414
77.160
76.905
52.480
40.927
16.078
15.673
Br
S
O
MeS
SMe
3r
13C NMR (125 MHz, CDCl3)
f1 (ppm)

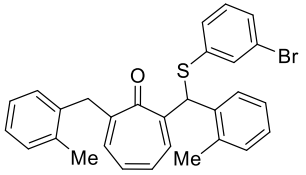


3s

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

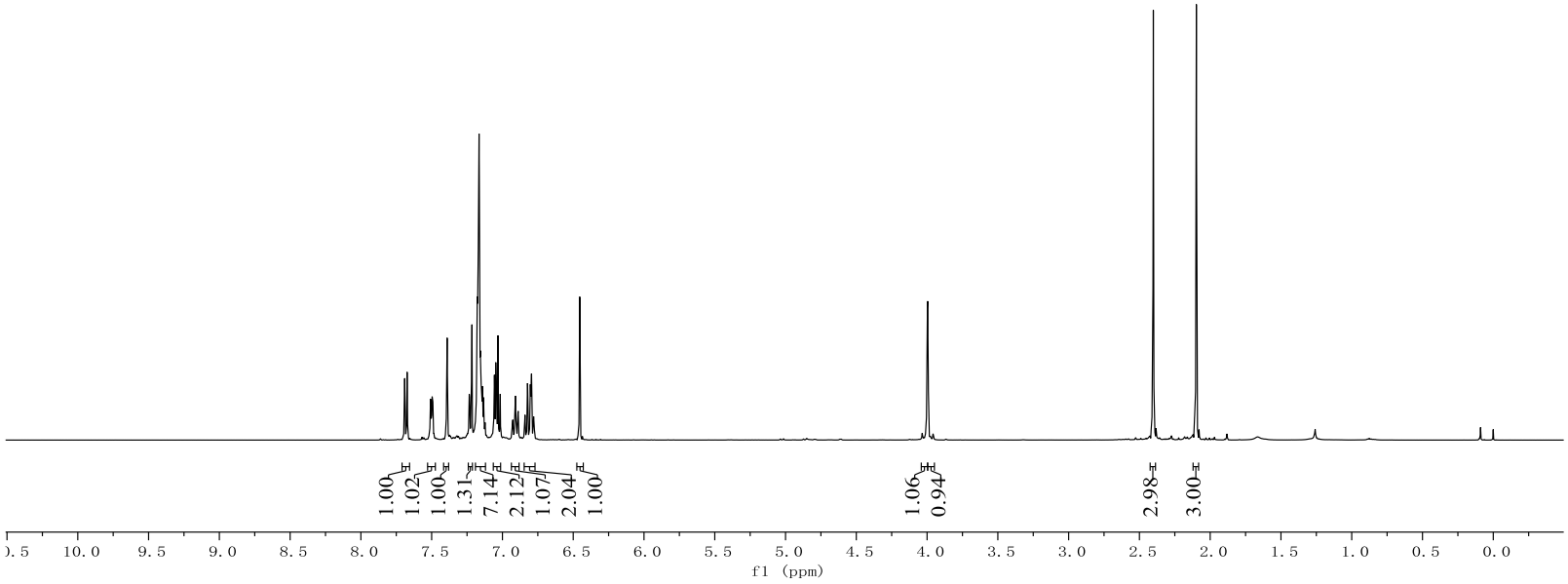

184.115
151.469
148.597
138.701
138.688
138.557
135.893
134.721
133.575
133.522
133.137
132.062
131.704
131.661
130.463
130.115
129.685
129.363
128.511
127.707
127.653
127.634
125.566
125.511
122.777
77.414
77.160
76.907
54.029
41.237
O
S
Br
Br
Br
3s
^{13}C NMR (125 MHz, CDCl$_3$)
f1 (ppm)

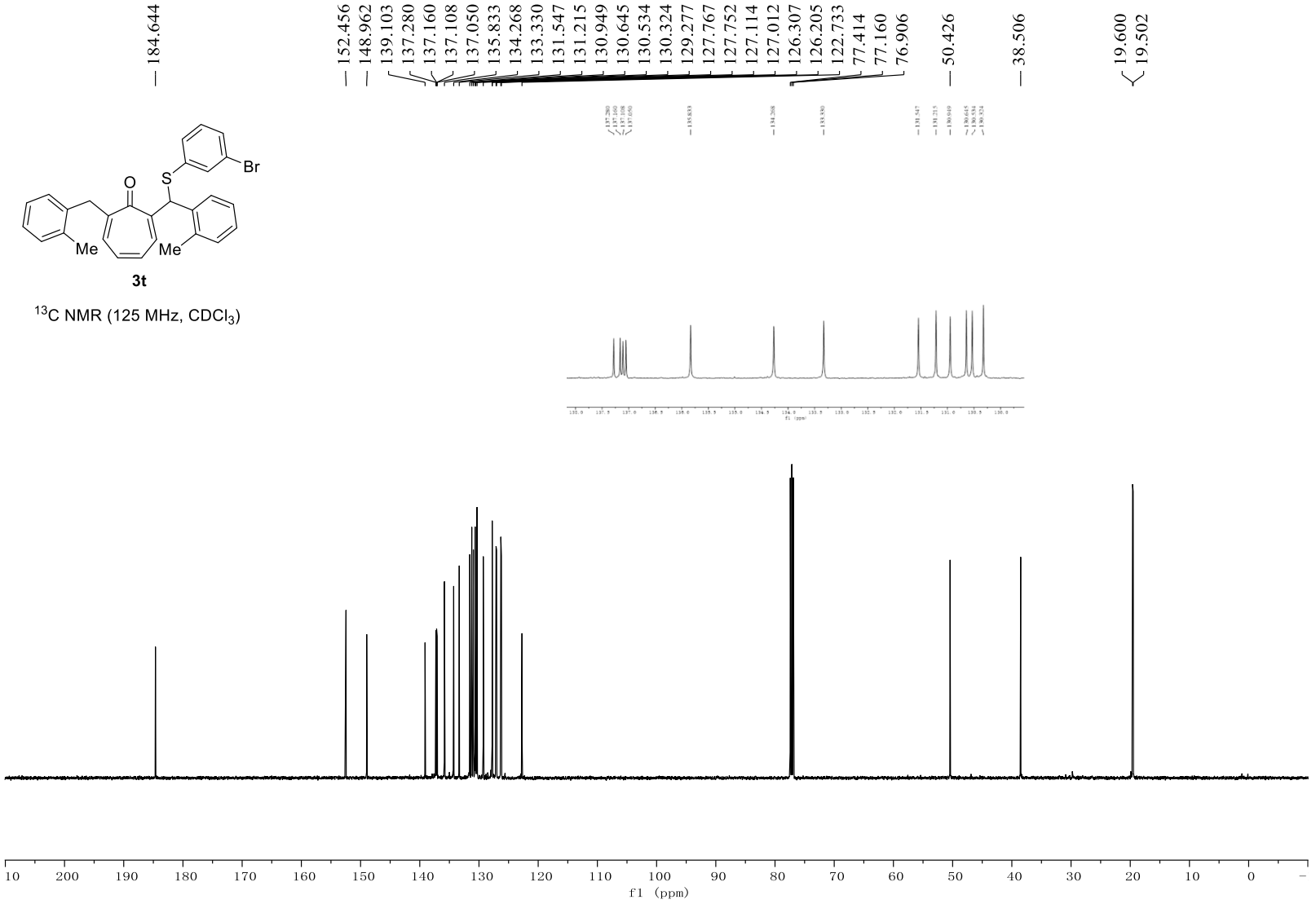


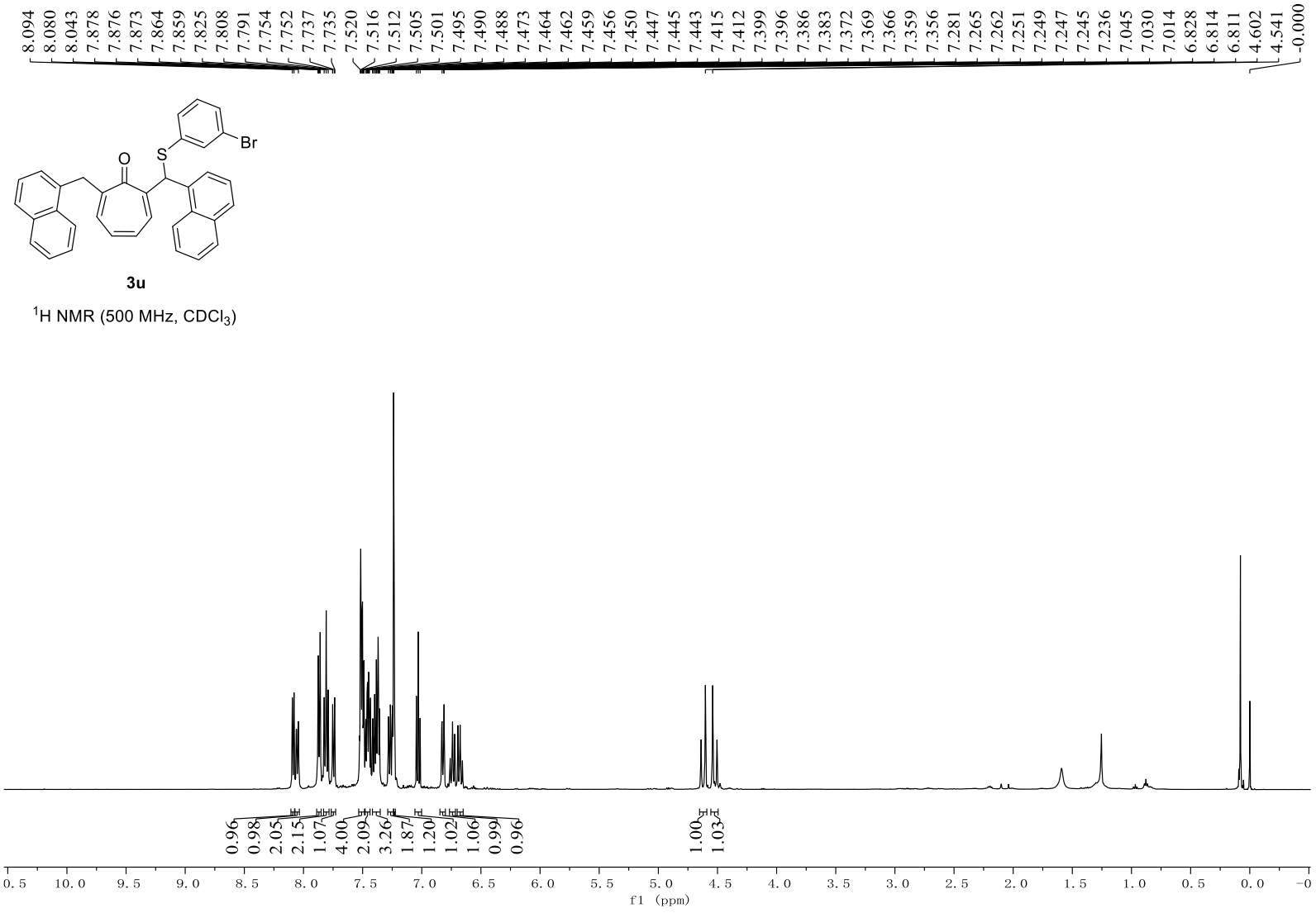


3t

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

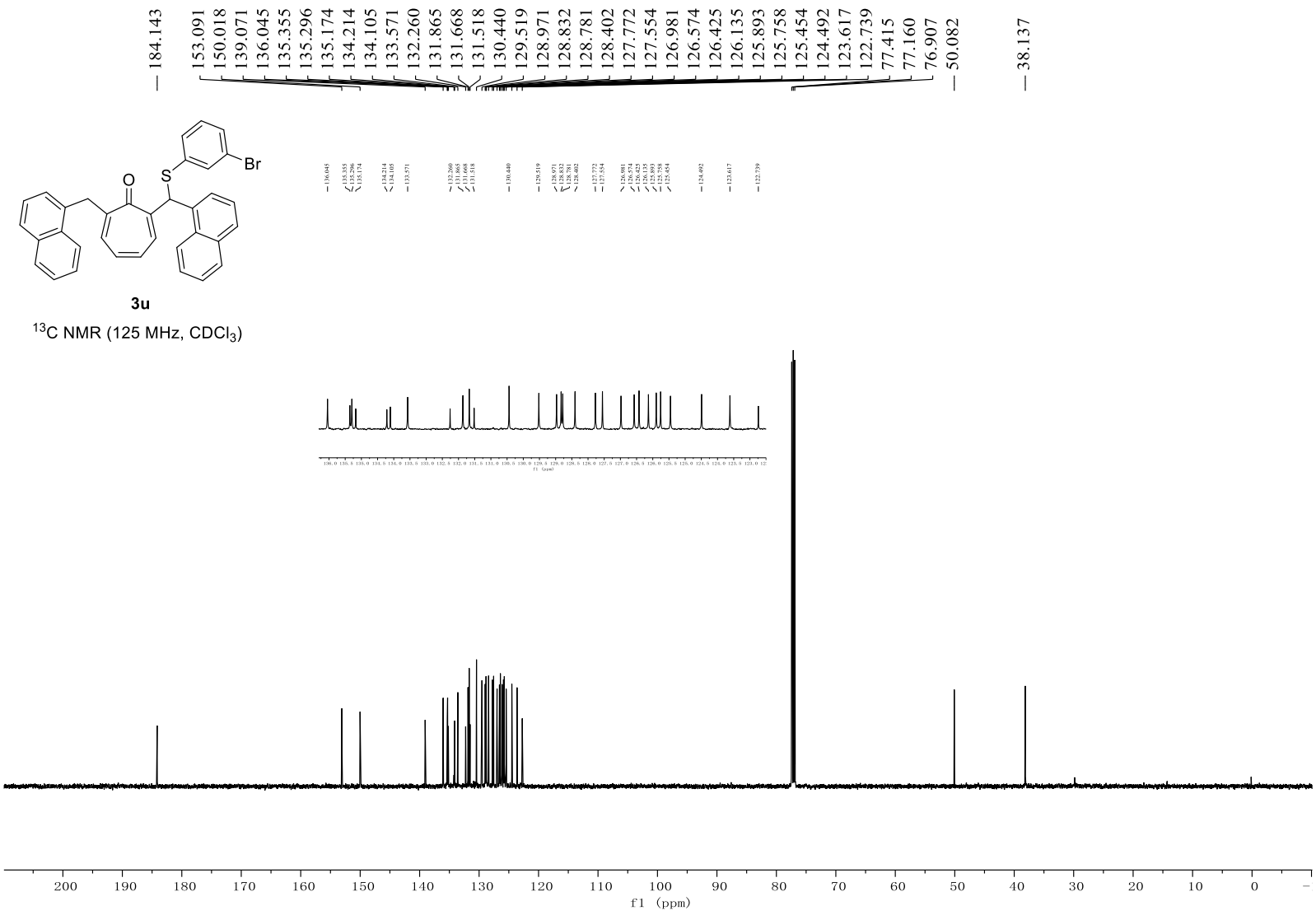


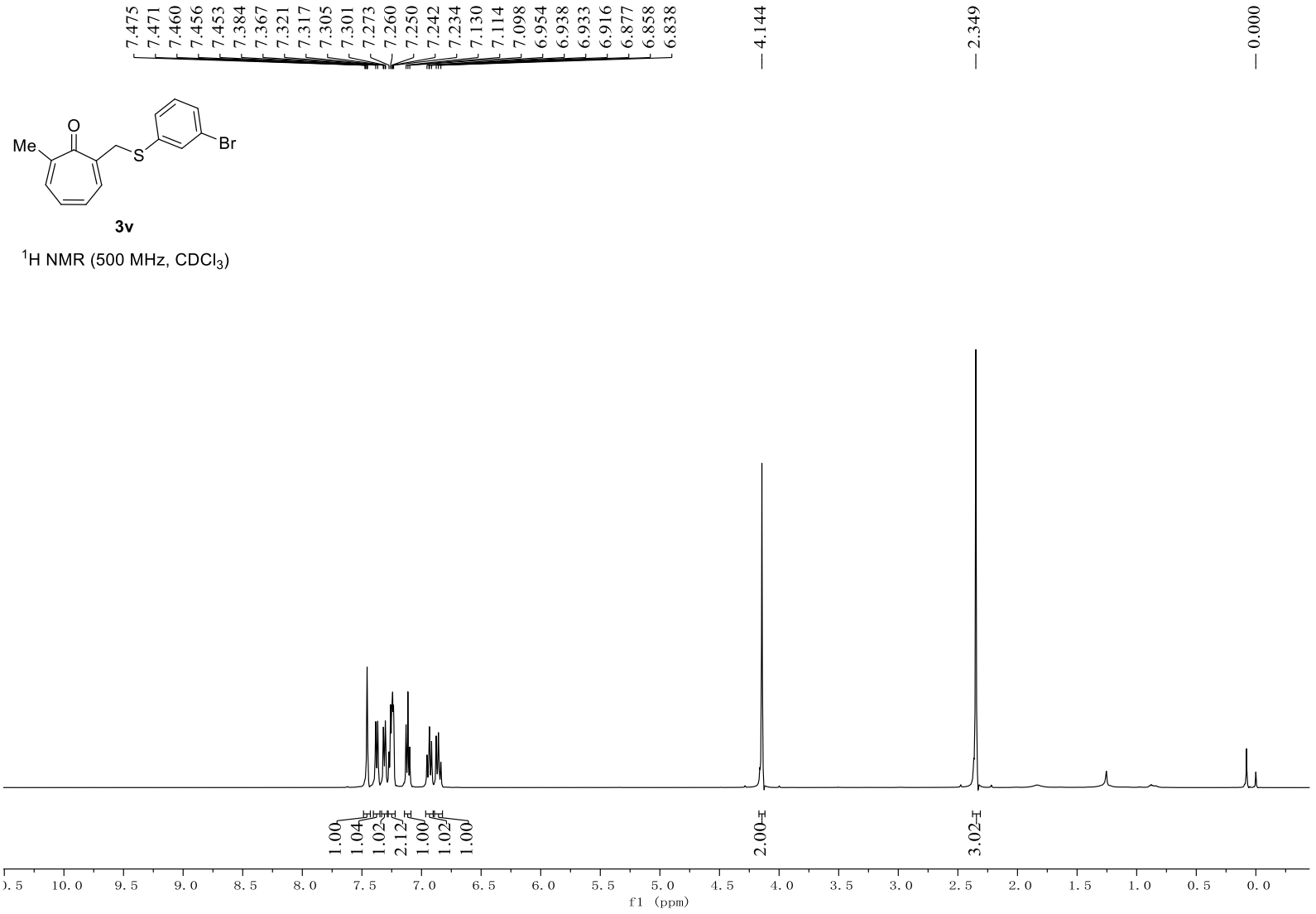

184.644
152.456
148.962
139.103
137.280
137.160
137.108
137.050
135.833
134.268
133.330
131.547
131.215
130.949
130.645
130.534
130.324
129.277
127.767
127.752
127.114
127.012
126.307
126.205
122.733
77.414
77.160
76.906
50.426
38.506
19.600
19.502
Br
S
O
Me
Me
3t
13C NMR (125 MHz, CDCl3)
f1 (ppm)



3u

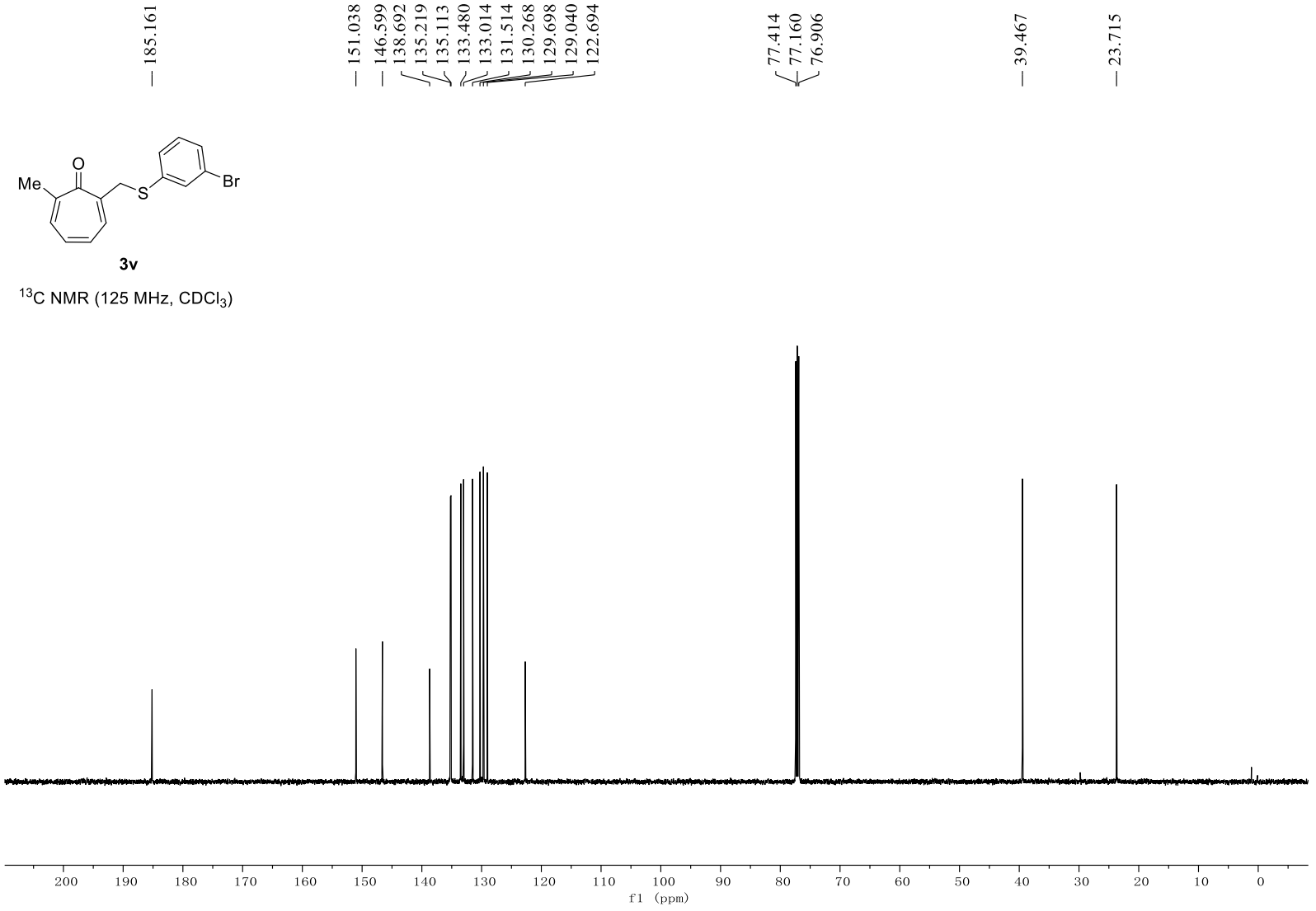
^{1}H NMR (500 MHz, $CDCl_3$)

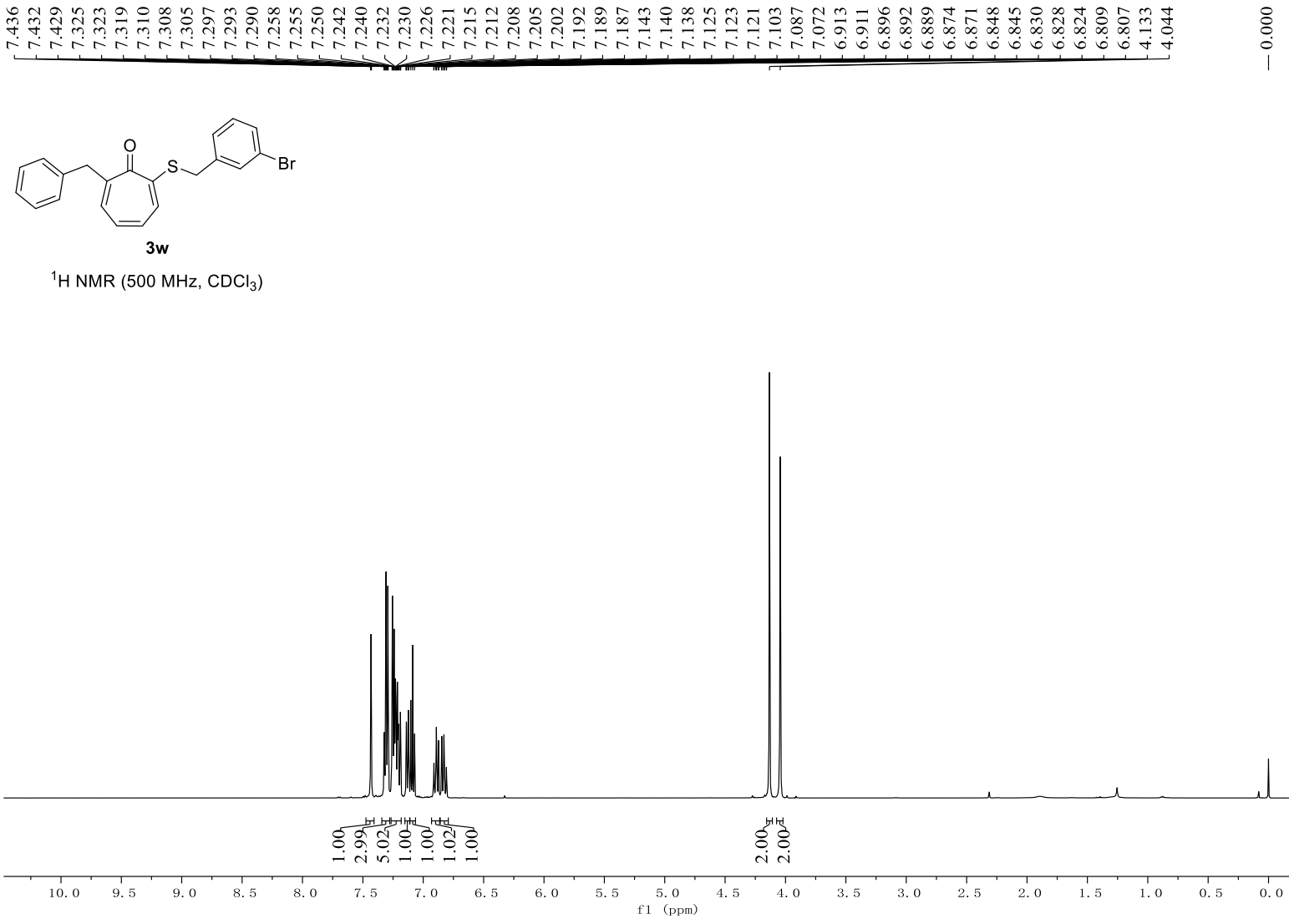

184.143
153.091
150.018
139.071
136.045
135.355
135.296
135.174
134.214
134.105
133.571
132.260
131.865
131.668
131.518
130.440
129.519
128.971
128.832
128.781
128.402
127.772
127.554
126.981
126.574
126.425
126.135
125.893
125.758
125.454
124.492
123.617
122.739
77.415
77.160
76.907
50.082
38.137
O
S
Br
3u
13C NMR (125 MHz, CDCl3)
f1 (ppm)



3v

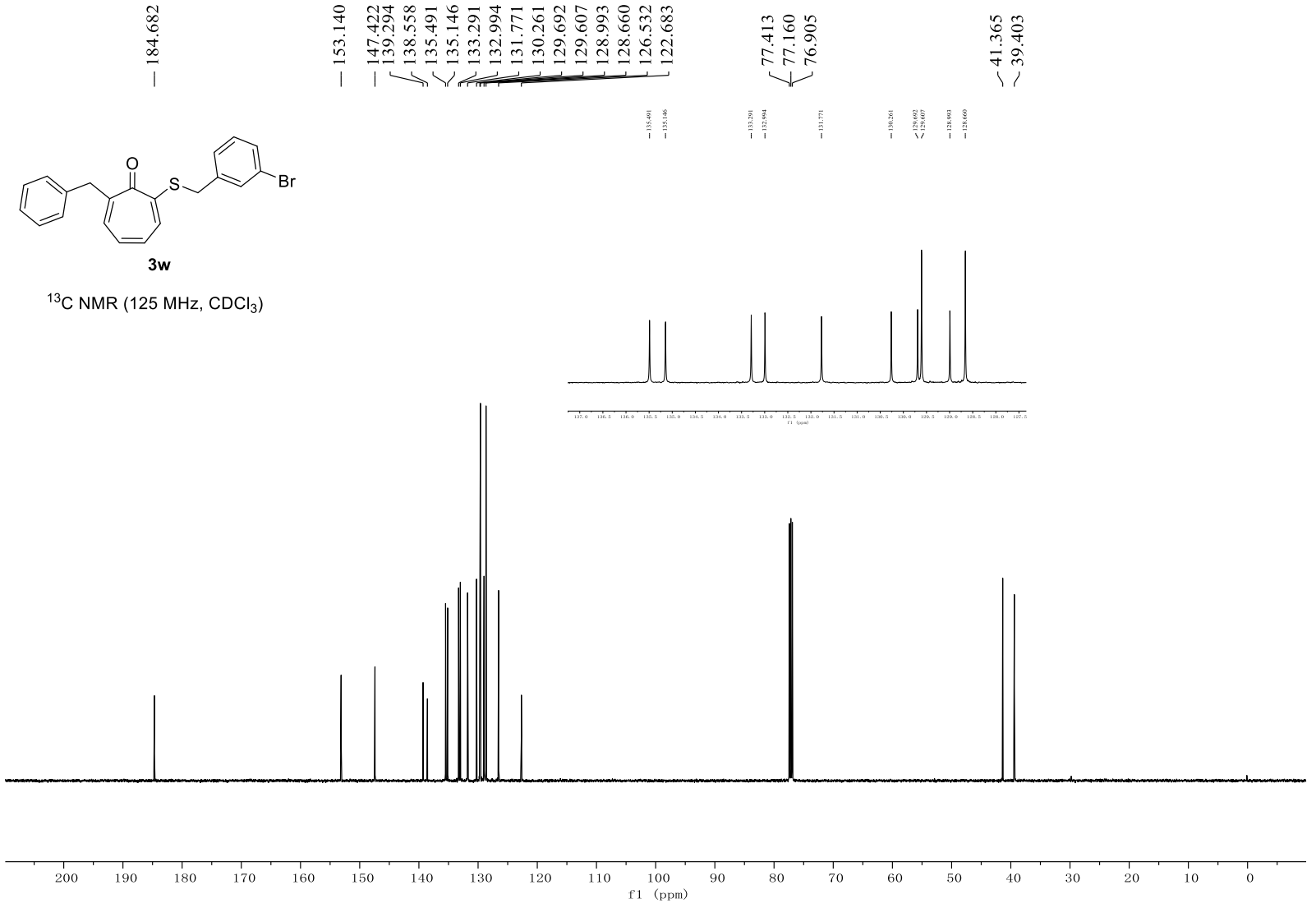
^{1}H NMR (500 MHz, $CDCl_3$)

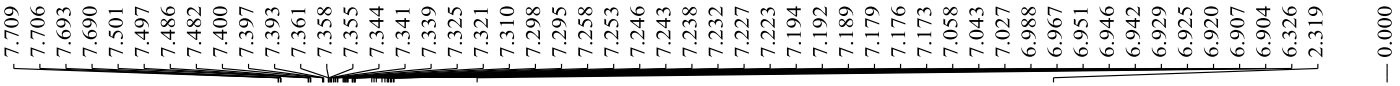

185.161
151.038
146.599
138.692
135.219
135.113
133.480
133.014
131.514
130.268
129.698
129.040
122.694
77.414
77.160
76.906
39.467
23.715
O
Me
S
Br
3v
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

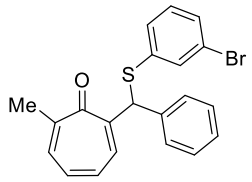


3w

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

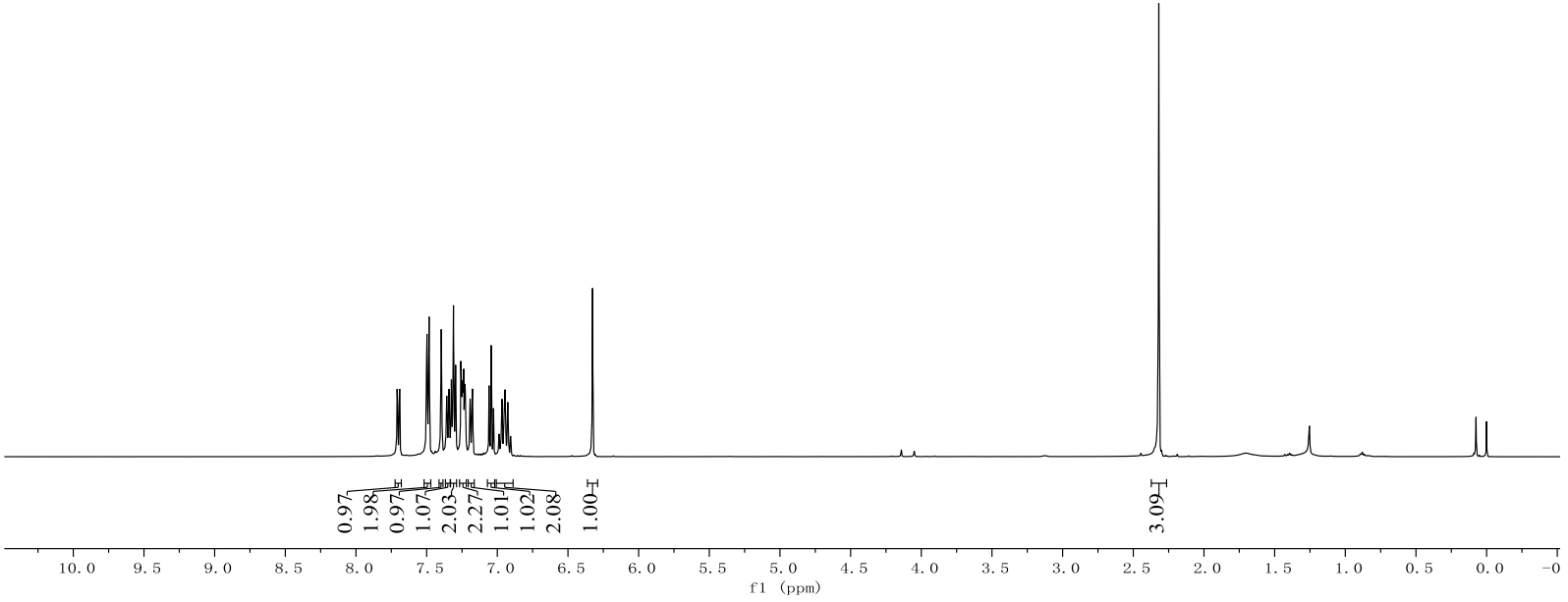

184.682
153.140
147.422
139.294
138.558
135.491
135.146
133.291
132.994
131.771
130.261
129.692
129.607
128.993
128.660
126.532
122.683
77.413
77.160
76.905
41.365
39.403
O
S
Br
3w
13C NMR (125 MHz, CDCl3)
f1 (ppm)

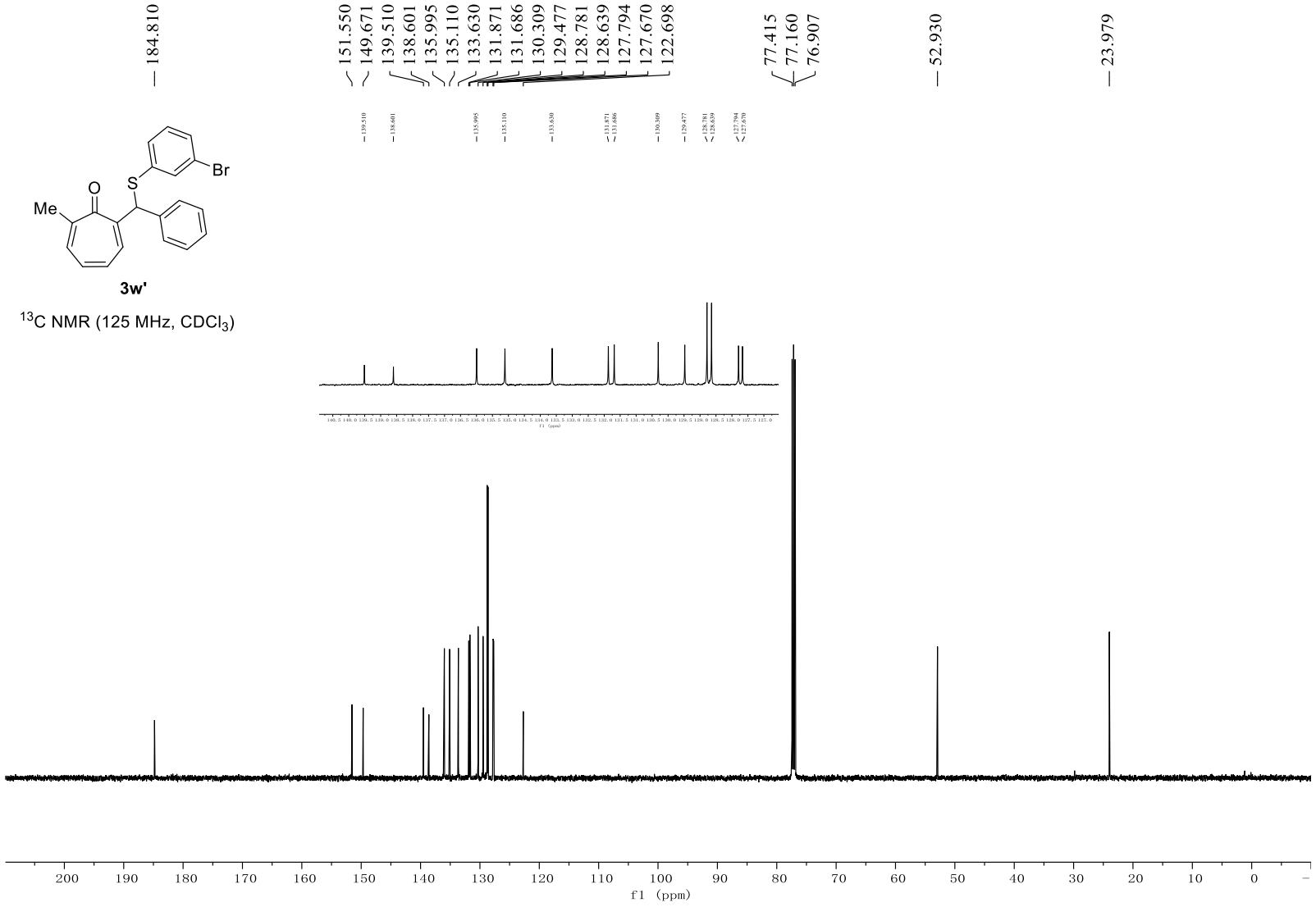


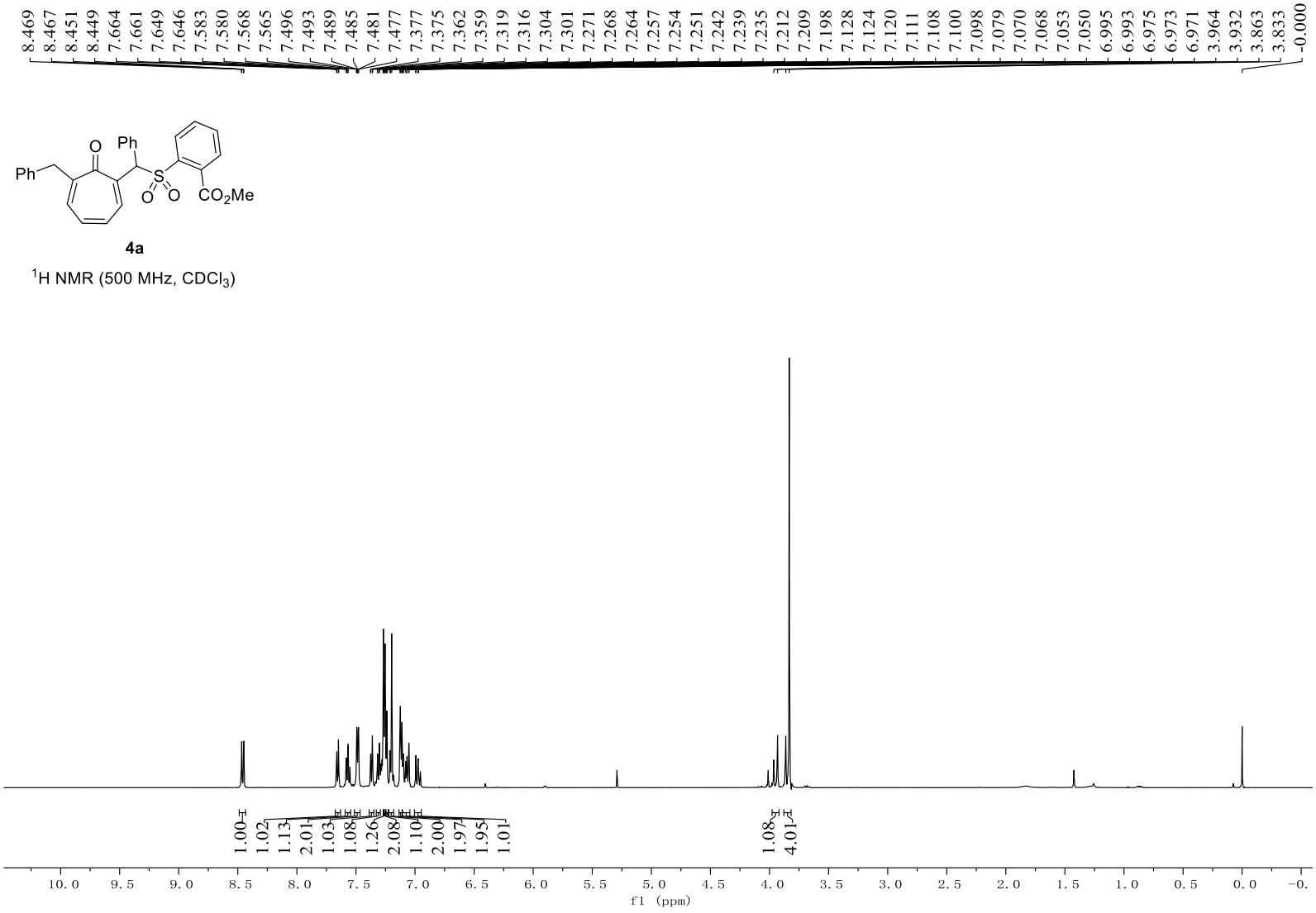


3w'

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

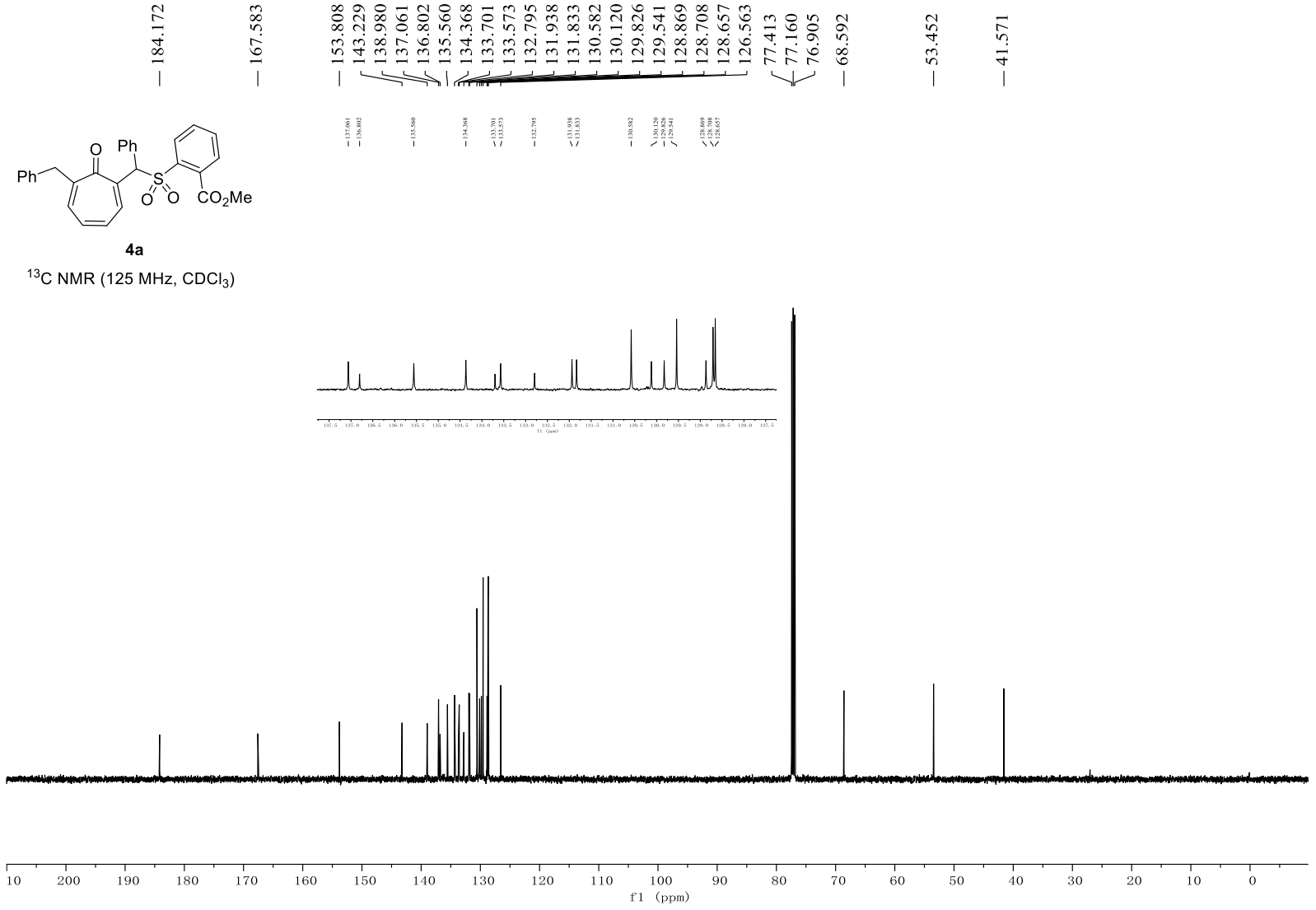



184.810
151.550
149.671
139.510
138.601
135.995
135.110
133.630
131.871
131.686
130.309
129.477
128.781
128.639
127.794
127.670
122.698
77.415
77.160
76.907
52.930
23.979
O
S
Br
Me
3w'
13C NMR (125 MHz, CDCl3)
f1 (ppm)



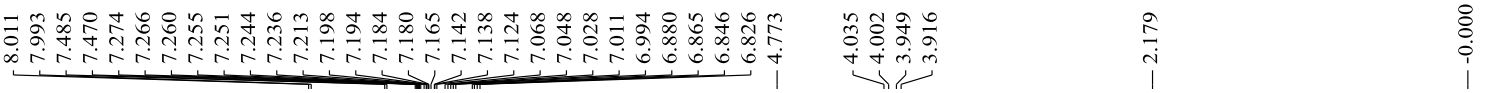
4a

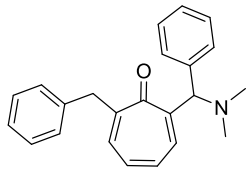
^{1}H NMR (500 MHz, $CDCl_3$)



4a

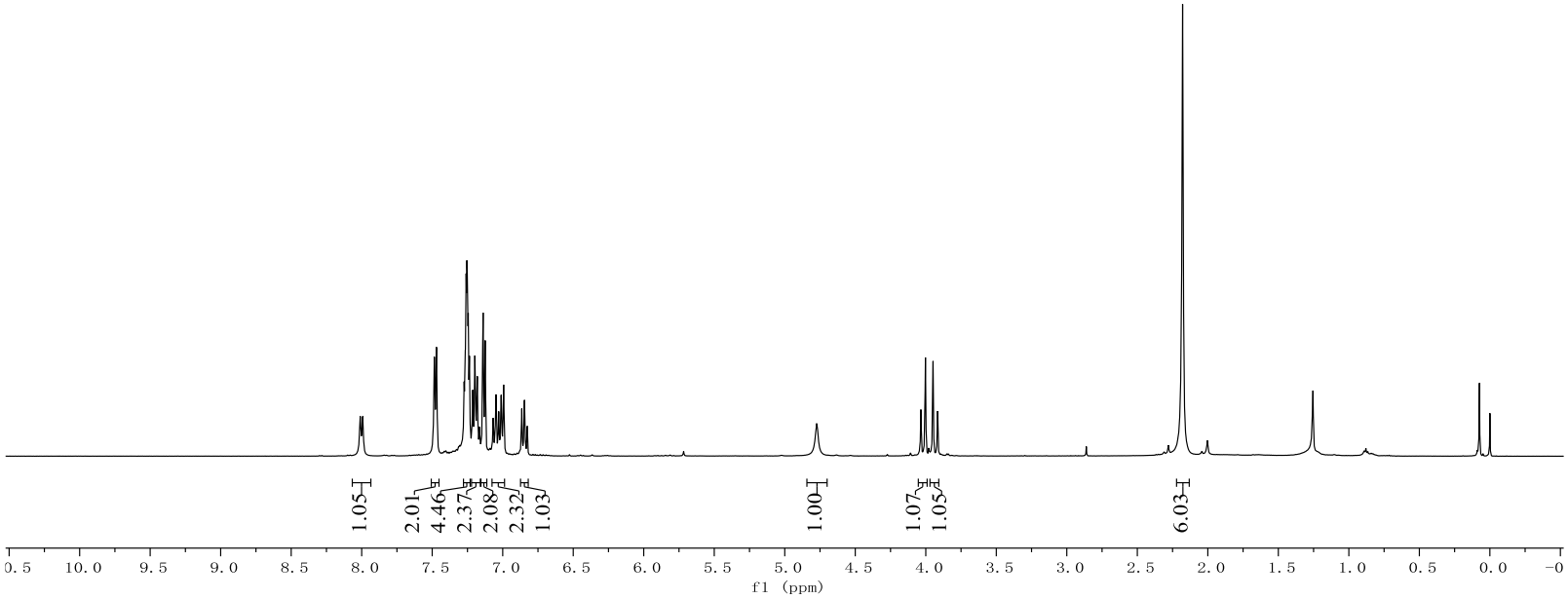
^{13}C NMR (125 MHz, $CDCl_3$)

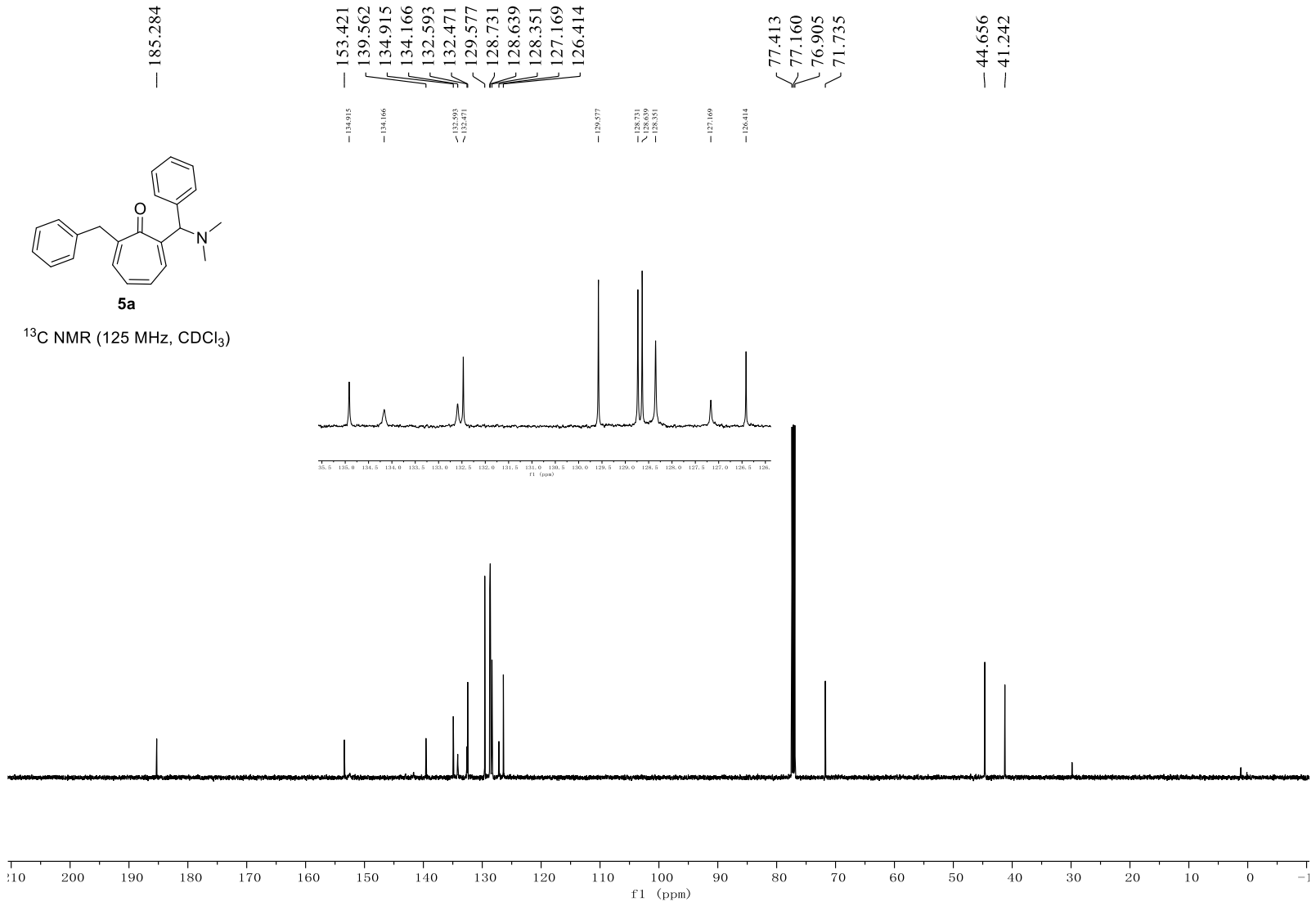




5a

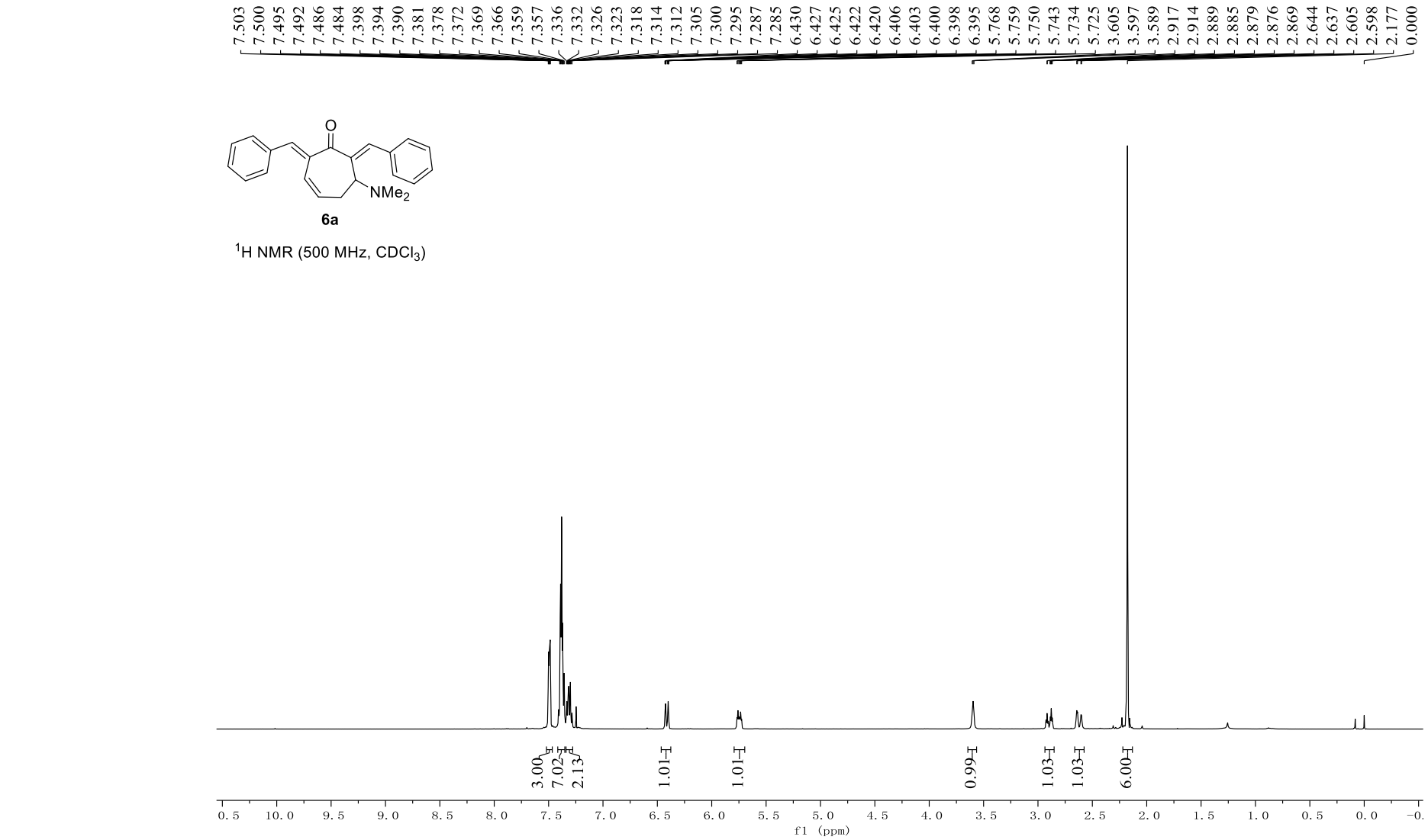
^{1}H NMR (500 MHz, $CDCl_3$)

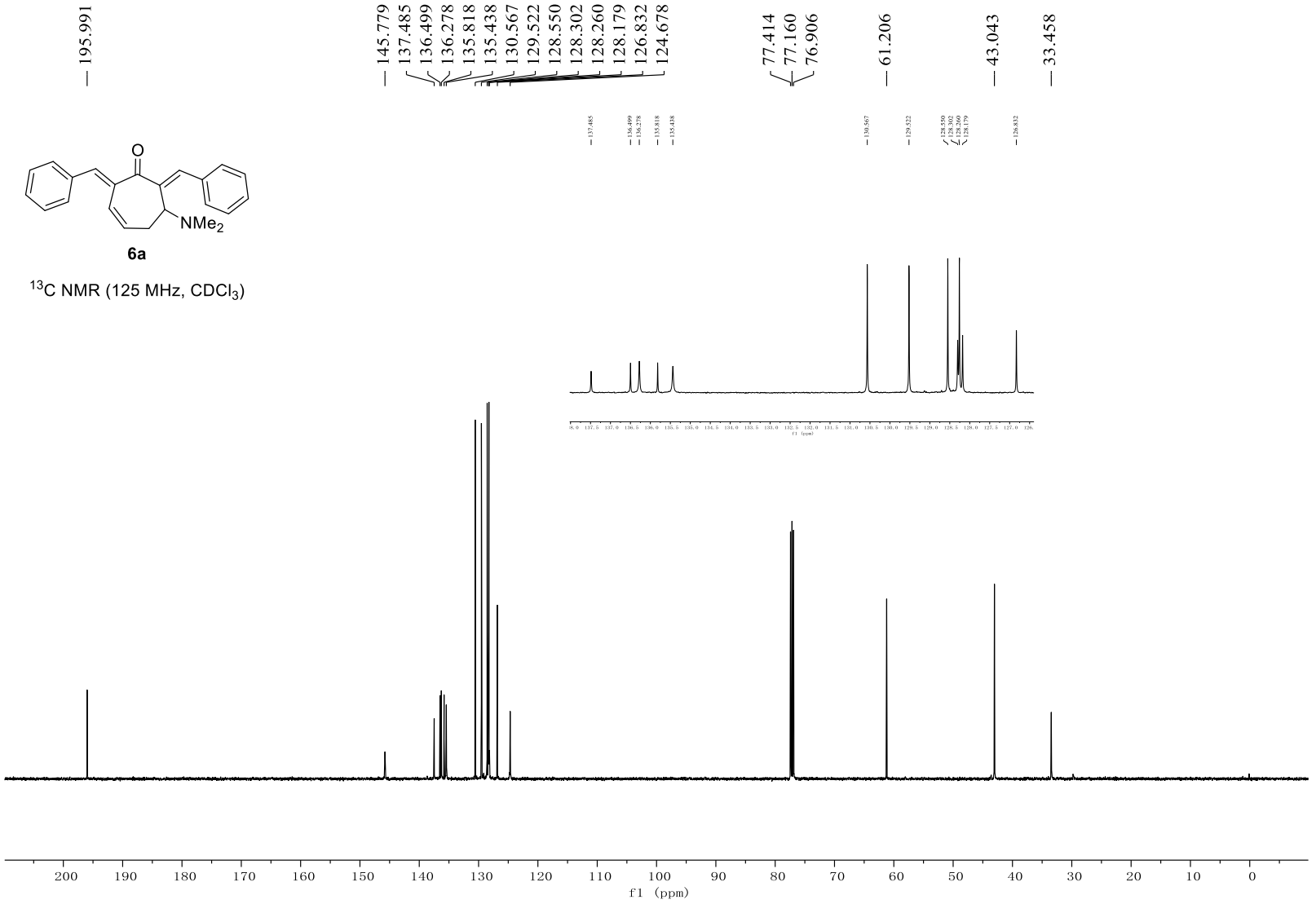


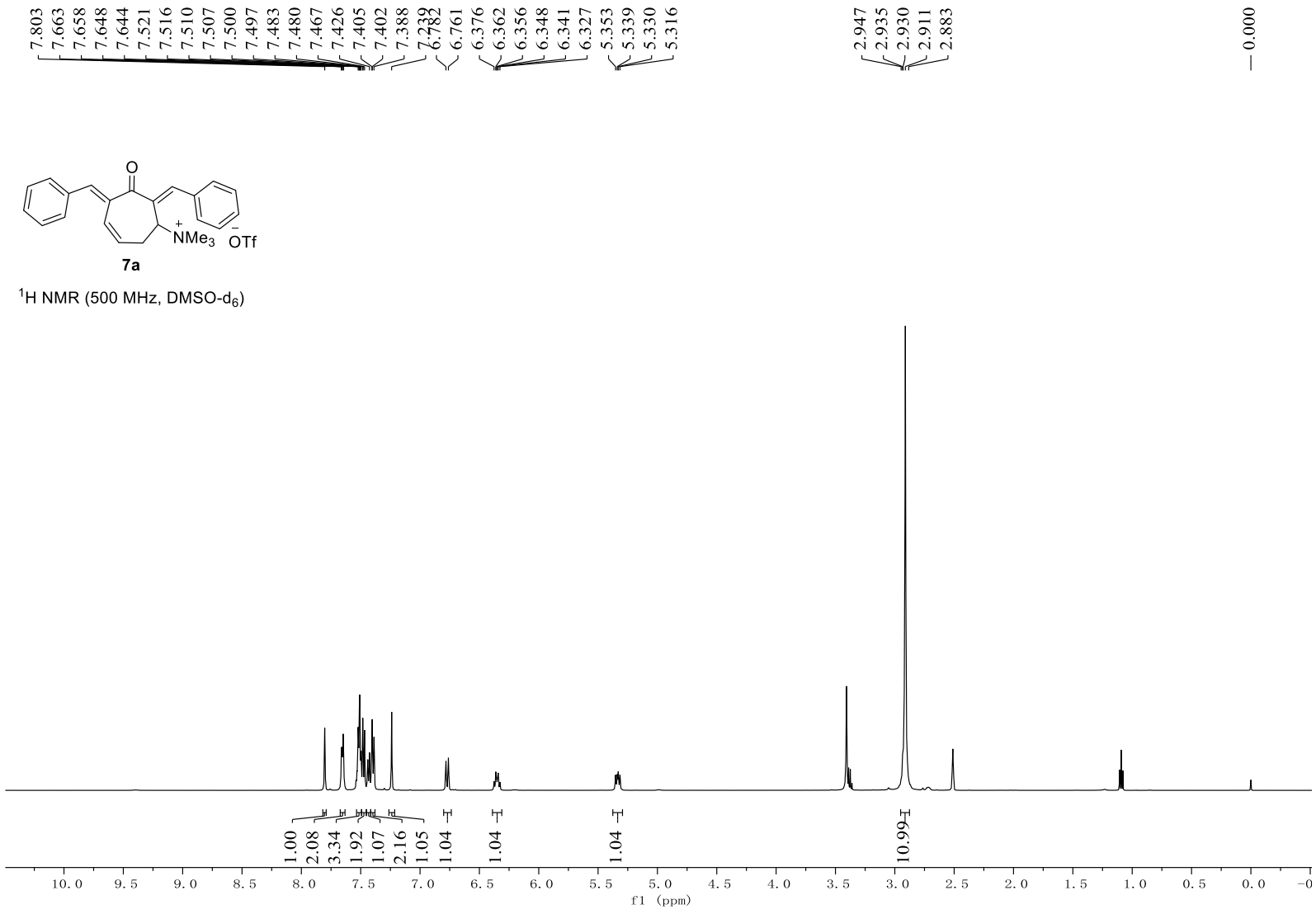


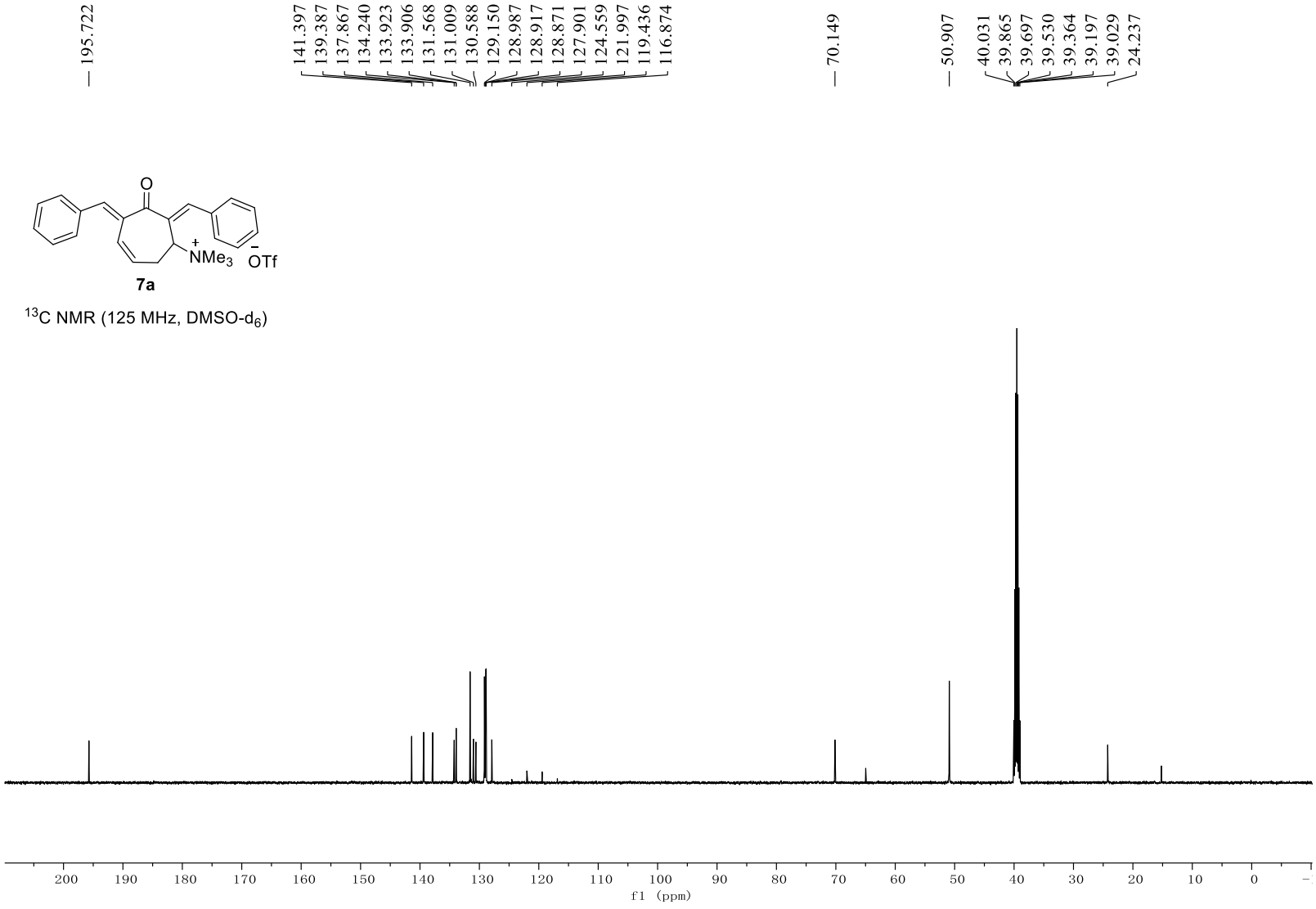
5a

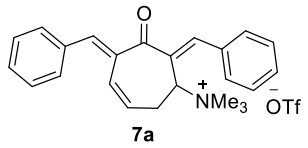
^{13}C NMR (125 MHz, $CDCl_3$)


7.503
7.500
7.495
7.492
7.486
7.484
7.398
7.394
7.390
7.381
7.378
7.372
7.369
7.366
7.359
7.357
7.336
7.332
7.326
7.323
7.318
7.314
7.312
7.305
7.300
7.295
7.287
7.285
6.430
6.427
6.425
6.422
6.420
6.406
6.403
6.400
6.398
6.395
5.768
5.759
5.750
5.743
5.734
5.725
3.605
3.597
3.589
2.917
2.914
2.889
2.885
2.879
2.876
2.869
2.644
2.637
2.605
2.598
2.177
0.000
O
NMe2
6a
1H NMR (500 MHz, CDCl3)
3.00
7.02
2.13
1.01
1.01
0.99
1.03
1.03
6.00
f1 (ppm)


195.991
145.779
137.485
136.499
136.278
135.818
135.438
130.567
129.522
128.550
128.302
128.260
128.179
126.832
124.678
77.414
77.160
76.906
61.206
43.043
33.458
O
NMe2
6a
13C NMR (125 MHz, CDCl3)
f1 (ppm)

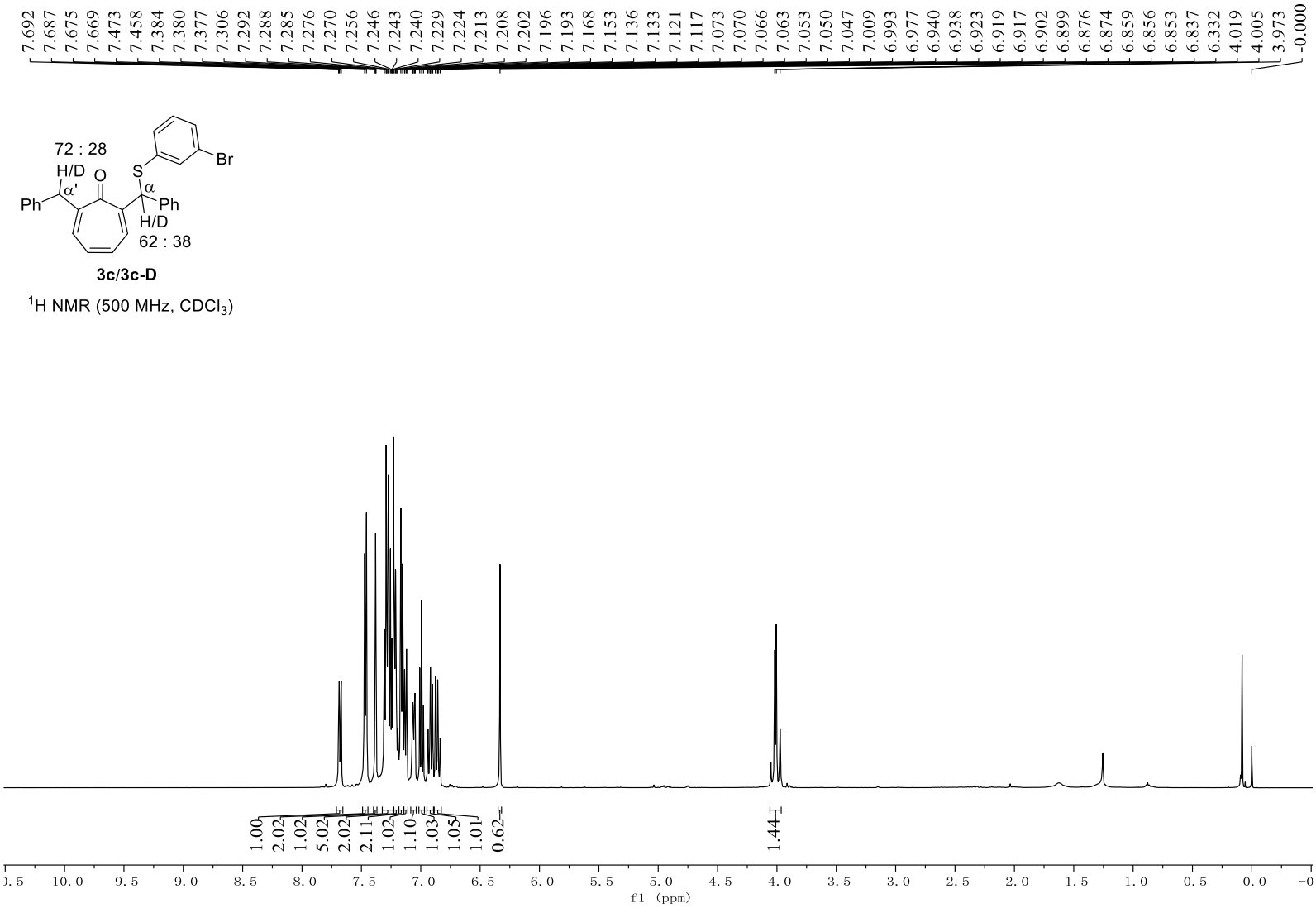

7.803
7.663
7.658
7.648
7.644
7.521
7.516
7.510
7.507
7.500
7.497
7.483
7.480
7.467
7.426
7.405
7.402
7.388
7.239
6.782
6.761
6.376
6.362
6.356
6.348
6.341
6.327
5.353
5.339
5.330
5.316
2.947
2.935
2.930
2.911
2.883
0.000
O
NMe3
OTf
7a
1H NMR (500 MHz, DMSO-d6)
1.00
2.08
3.34
1.92
1.07
2.16
1.05
1.04
1.04
1.04
10.99
f1 (ppm)


195.722
141.397
139.387
137.867
134.240
133.923
133.906
131.568
131.009
130.588
129.150
128.987
128.917
128.871
127.901
124.559
121.997
119.436
116.874
70.149
50.907
40.031
39.865
39.697
39.530
39.364
39.197
39.029
24.237
O
NMe3
OTf
7a
13C NMR (125 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



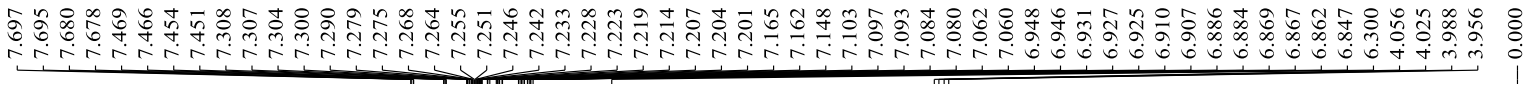
7a

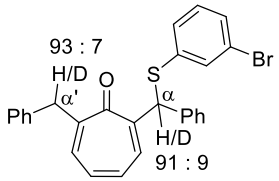
^{19}F NMR (471 MHz, DMSO-d_6)



3c/3c-D

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





3c/3c-D

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