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Supporting Information

Visible Light-Induced Generation of Alkenyl Radicals from Alkenyl Sulfonium Salts: Direct Synthesis of 11-Alkenyl-Substituted Dibenzodiazepines

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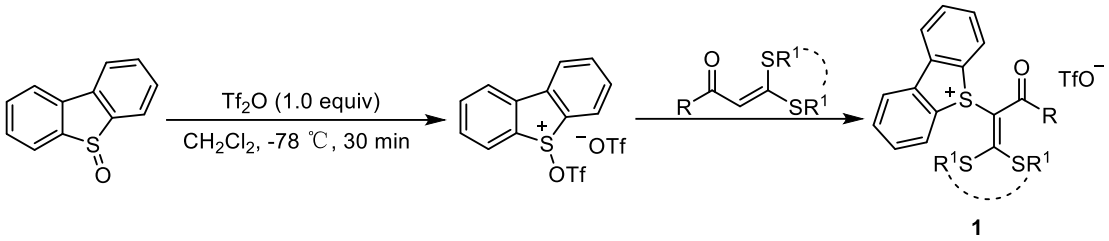
I. General Information:

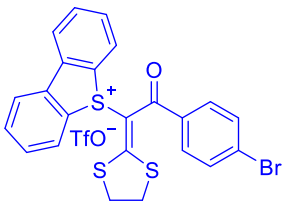
All reagents were purchased and used as received from their respective suppliers unless otherwise noted. *o*-isocyanodiaryl amines **2** were synthesized according to known literature procedure.[1] Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 500 MHz and 600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 565 MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound **3at** was glued on glass fiber, respectively. Data were collected at 293 K on a Bruker SMART APEX II CCD diffractometer using graphite-monochromated Mo Kradiation (λ = 0.71073Å) and IP technique in the range $2.19° < \theta < 27.48°$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. Stern-Volmer fluorescence quenching experiments were taken at ambient temperature using Fluorescence spectrophotometer. Blue LEDs (15 W, λ = 465 nm) was purchased from Sigma-Aldrich (SynLED parallel photoreactor Z742680). Quartz tube (10 mL) was used as the irradiation vessel.

II. Synthetic Substrates and Analytical Data of Compounds of 1:



The alkenyl sulfonium triflates salts were prepared according to the reported literature procedures.[2,3,4] A typical procedure for the synthesis of alkenyl sulfonium triflates salts (**1**)-synthesis of **1**: A solution of dibenzo[b,d]thiophene 5-oxide (4.00 g, 20 mmol) in CH_2Cl_2 (200 mL) was cooled to -78 °C under a N_2 atmosphere, and Tf_2O (1.1 equiv) was then added dropwise. The reaction mixture was stirred at -78 °C for 30 min, followed by addition of α-oxo ketene dithioacetal (6.02 g, 20 mmol), and allowed to warm up to ambient temperature. Stirring was continued for 12 h at ambient temperature. After α-oxo ketene dithioacetal was completely consumed by TLC, the reaction mixture was quenched with water and extracted with water and brine. The organic layer is dried ($NaSO_4$), filtered, and concentrated. Further purification is usually necessary and can optionally be done by means of flash chromatography with silica gel column chromatography (eluent: CH_2Cl_2/methanol = 20:1, v/v), affording **1** as yellow solids.

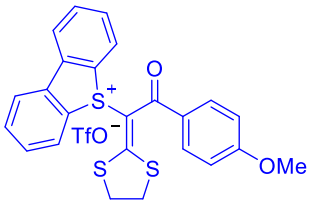
5-(2-(4-Bromophenyl)-1-(1,3-dithiolan-2-ylidene)-2-oxoethyl)-5*H*-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1a):



Yellow solid (7.86 g, 62%); m.p. 66.4-67.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 2H), 7.42 (s, 2H), 7.39 (s, 2H), 3.86 (s, 2H), 3.73 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.57, 186.21, 139.01, 134.93, 134.07, 132.23, 131.47, 130.35, 129.16, 128.59, 127.29, 123.80, 121.02 (q, *J* = 321.18 Hz),

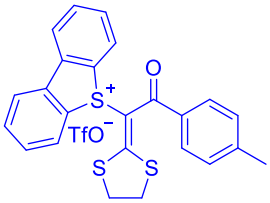
100.18, 42.02, 39.44; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -77.90 (s, 3F); **HRMS** (ESI) m/z calculated $C_{23}H_{16}BrOS_3^+$ $[M]^+$ 482.9541, found 482.9544.

5-(1-(1,3-Dithiolan-2-ylidene)-2-(4-methoxyphenyl)-2-oxoethyl)-5*H*-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1b):



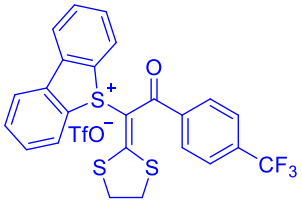
Yellow solid (6.67 g, 57%); m.p. 156.8-157.4 ℃; **^{1}H NMR** (600 MHz, CD_3CN) δ 8.13 (d, *J* = 8.2 Hz, 4H), 7.84 (t, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.9 Hz, 2H), 7.48 (s, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 3.83 (s, 3H), 3.75 (s, 2H), 3.68 (s, 2H); **^{13}C NMR** (151 MHz, CD_3CN) δ 187.49, 186.56, 164.81, 139.96, 134.57, 131.98, 131.70, 130.08, 129.06, 127.58, 124.57, 121.79 (q, *J* = 321.03 Hz), 117.92, 114.78, 100.80, 56.13, 42.16, 40.12; **^{19}F NMR** (565 MHz, CD_3CN) δ -79.02 (s, 3F)**;** **HRMS** (ESI) m/z calculated $C_{24}H_{19}O_2S_3^+$ $[M]^+$ 435.0542, found 435.0545.

5-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(p-tolyl)ethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1c):



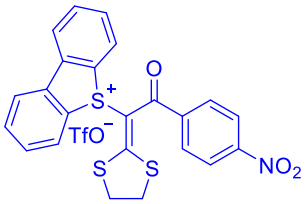
Yellow solid (6.14 g, 54%); m.p. 186.4-187.3 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.90 (s, 2H), 3.70 (s, 2H), 2.36 (s, 3H).; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 187.96, 186.91, 145.02, 139.09, 134.00, 133.33, 131.36, 129.78, 129.15, 127.13, 123.86, 121.05 (q, *J* = 321.48 Hz), 100.53, 41.90, 39.42, 21.77; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -77.94 (s, 3F); **HRMS** (ESI) m/z calculated $C_{24}H_{19}OS_3^+$ $[M]^+$ 419.0593, found 419.0599.

5-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1d):



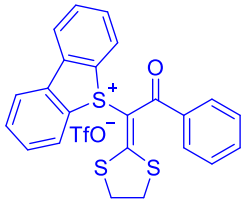
Yellow solid (8.36 g, 67%); m.p. 65.8-66.5 °C; **^{1}H NMR** (500 MHz, CD_3CN) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.93 (s, 2H), 7.77 (t, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.45 (s, 4H), 3.90 (s, 2H), 3.78 (s, 2H); **^{13}C NMR** (151 MHz, CD_3CN) δ 192.73, 186.16, 139.54, 138.76, 134.16, 133.53 (q, *J* = 32.7 Hz), 131.57, 128.94, 128.41, 127.27, 125.53, 123.79, 123.31 (q, *J* = 272.86 Hz), 121.01 (q, *J* = 321.18 Hz), 99.37, 41.93, 39.31; **^{19}F NMR** (565 MHz, CD_3CN) δ -63.19 (s, 3F), -77.97 (s, 3F); **HRMS** (ESI) m/z calculated $C_{24}H_{16}F_3OS_3^+$ $[M]^+$ 473.0310, found 473.0302.

5-(1-(1,3-Dithiolan-2-ylidene)-2-(4-nitrophenyl)-2-oxoethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1e):



Yellow solid (5.50 g, 46%); m.p. 78.7-79.5 °C; **^{1}H NMR** (600 MHz, CD_3CN) δ 8.13 (d, *J* = 8.1 Hz, 2H), 7.95 (s, 3H), 7.80 (t, *J* = 7.7 Hz, 3H), 7.71 (t, *J* = 7.7 Hz, 2H), 7.00 (s, 2H), 3.79 (s, 4H); **^{13}C NMR** (151 MHz, CD_3CN) δ 197.77, 187.89, 150.99, 144.04, 140.73, 136.06, 133.30, 130.21, 129.07, 125.87, 125.19, 123.03 (q, *J* = 318.00 Hz), 121.01, 119.32, 100.41, 43.44, 41.21; **^{19}F NMR** (565 MHz, CD_3CN) δ -78.81 (s, 3F)**; HRMS** (ESI) m/z calculated $C_{23}H_{16}NO_3S_3^+$ $[M]^+$ 450.0287, found 450.0296.

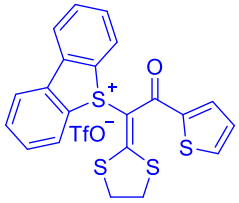
5-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethane -sulfonate (1f):



Yellow solid (4.33 g, 39%); m.p. 63.7-64.6 °C; **^{1}H NMR** (600 MHz, CD_3CN) δ 8.12 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.83 (t, *J* = 7.6 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 2H), 7.49 (s, 1H), 7.27

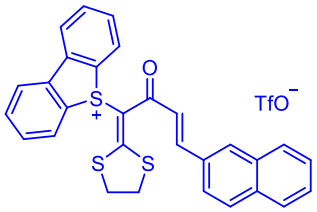
(s, 4H), 3.69 (s, 4H); **^{13}C NMR** (151 MHz, CD_3CN) δ 191.84, 188.43, 139.90, 137.13, 134.63, 133.38, 131.80, 129.72, 129.28, 128.54, 127.55, 124.65, 121.49 (q, *J* = 320.12 Hz), 118.12, 100.24, 41.98, 39.98; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -79.19 (s, 3F); **HRMS** (ESI) m/z calculated $C_{23}H_{17}OS_3^+$ $[M]^+$ 405.0436, found 405.0443.

5-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(thiophen-2-yl)ethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1g):



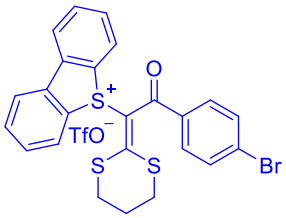
Yellow solid (5.73 g, 51%); m.p. 149.8-150.8 ℃; **^{1}H NMR** (600 MHz, CD_3CN) δ 8.14 (d, *J* = 7.8 Hz, 2H), 8.11 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 2H), 7.78 (s, 1H), 7.65 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 4.4 Hz, 1H), 3.74 (s, 2H), 3.67 (s, 2H); **^{13}C NMR** (151 MHz, CD_3CN) δ 187.59, 178.98, 140.90, 139.74, 137.53, 136.71, 134.64, 131.67, 129.46, 129.23, 127.64, 124.59, 121.68 (q, *J* = 321.18 Hz), 117.96, 99.05, 41.84, 40.26; **^{19}F NMR** (565 MHz, CD_3CN) δ -78.71 (s, 3F); **HRMS** (ESI) m/z calculated $C_{21}H_{15}OS_4^+$ $[M]^+$ 411.0000, found 411.0006.

(E)-5-(1-(1,3-dithiolan-2-ylidene)-4-(naphthalen-2-yl)-2-oxobut-3-en-1-yl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1h):



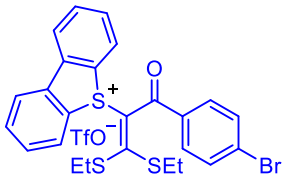
Yellow solid (7.19 g, 57%); m.p. 104.4-105.3 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97-7.85 (m, 2H), 7.71-7.62 (m, 3H), 7.50-7.44 (m, 6H), 7.35-7.29 (m, 3H), 7.19-7.12 (m, 3H), 3.54-3.37 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 182.47, 178.88, 146.95, 140.33, 136.00, 135.87, 135.75, 134.66, 133.14, 132.98, 132.60, 132.09, 130.41, 130.34, 129.56, 129.43, 128.99, 128.92, 128.70, 126.01, 125.68, 122.86, 122.96 (q, *J* = 321.63 Hz), 119.15, 100.86, 89.96, 42.29, 40.68; **HRMS** (ESI) m/z calculated $C_{29}H_{21}OS_3^+$ $[M]^+$ 481.0749, found 481.0757.

5-(2-(4-Bromophenyl)-1-(1,3-dithian-2-ylidene)-2-oxoethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1i):



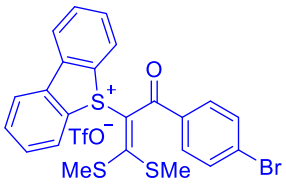
Yellow solid (8.29 g, 64%); m.p. 76.7-77.3 °C; **^{1}H NMR** (500 MHz, CD_3CN) δ 8.15 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 7.9 Hz, 2H), 7.78 (t, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 3.39 (q, *J* = 7.6 Hz, 1H), 3.06 (q, J = 7.5 Hz, 1H), 1.55 (t, J = 7.1 Hz, 2H), 1.11 (t, J = 7.5 Hz, 2H); **^{13}C NMR** (151 MHz, CD_3CN) δ 185.34, 168.58, 140.30, 134.96, 132.63, 131.84, 131.00, 130.14, 130.01, 128.74, 124.57, 121.71 (q, *J* = 321.18 Hz), 119.13, 117.90, 32.04, 31.90, 14.51; **^{19}F NMR** (565 MHz, CD_3CN) δ -78.97 (s, 3F); **HRMS** (ESI) m/z calculated $C_{24}H_{18}BrOS_3^+$ $[M]^+$ 496.9698, found 496.9693.

5-(3-(4-Bromophenyl)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1j):



Yellow solid (7.30 g, 55%); m.p. 63.8-64.2 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.49-7.45 (m, 4H), 3.42 (q, *J* = 7.1 Hz, 2H), 2.96 (q, *J* = 7.0, 6.5 Hz, 2H), 1.53 (t, *J* = 6.0 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 184.47 , 166.42 , 139.54 , 134.91 , 134.30 , 132.40 , 131.17 , 131.04 , 130.47 , 129.53 , 128.36 , 126.77 , 123.90, 122.69 , 120.98 (q, *J* = 321.63 Hz), 119.45 , 31.85 , 31.50 , 14.43 , 14.23; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -77.87 (s, 3F); **HRMS** (ESI) m/z calculated $C_{25}H_{22}BrOS_3^+$ $[M]^+$ 513.0011, found 513.0008.

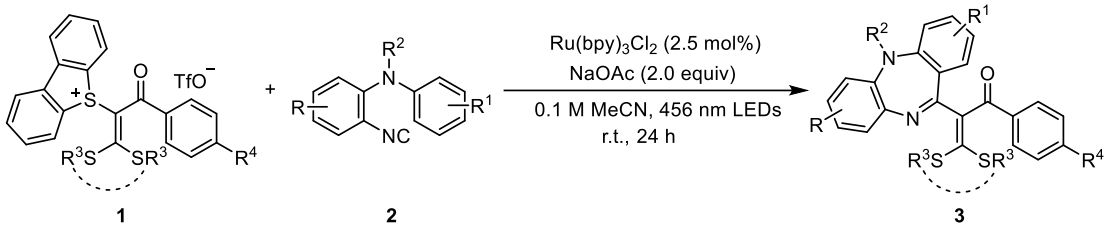
5-(3-(4-Bromophenyl)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (1k):



Yellow solid (6.99 g, 55%); m.p. 63.8-64.2 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 8.8 Hz, 3H), 7.39 (t, *J* = 8.8 Hz, 3H), 2.81 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 184.44, 169.82, 139.42, 134.99, 134.25, 132.38, 131.13, 130.97, 130.37, 129.51, 128.25, 123.89, 121.03 (q, *J* = 321.18 Hz), 117.03, 19.48, 18.89; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -77.85 (s, 3F); **HRMS** (ESI) m/z calculated $C_{23}H_{18}OS_3^+$ $[M]^+$ 484.9698, found 484.9695.

III. Synthetic Procedures and Analytical Data of Compounds of 3:

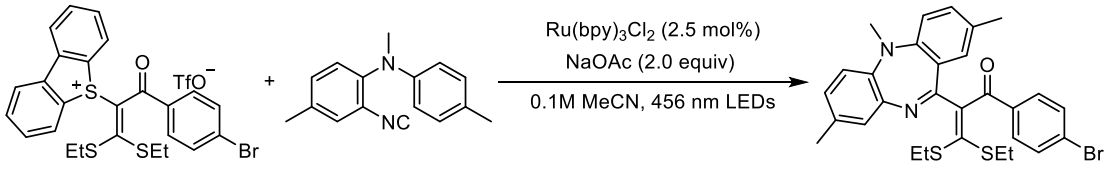
1. A general synthesis of compound 3:



1 2 3

A sealed tube equipped with a magnetic stir bar was charged with alkenysulfonium salts **1** (0.3 mmol, 1.5 equiv), *o*-isocyanodiaryl amine **2** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.005 mmol, 2.5 mol%), NaOAc (0.4 mmol, 2.0 equiv) and dry CH_3CN (2.0 mL) were added. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs. After the complete conversion of the *o*-isocyanodiaryl amine **2** (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (EtOAc/petroleum ether) to give the product **3** as yellow solid.

2. A gram-scale synthesis of compound 3jz:



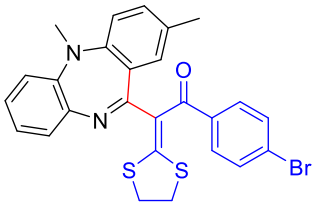
1j,3.98 g
6 mmol

2z,0.95 g
4 mmol

3jz, 1.76 g (78%)

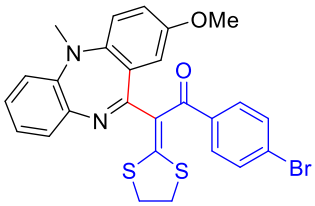
An oven-dried vial equipped with a magnetic stir bar was charged with α-oxo ketene dithioacetal **1j** (6 mmol, 3.98 g), *o*-isocyanodiaryl amine **2z** (4 mmol, 0.95 g), $Ru(bpy)_3Cl_2$ (0.094 mmol, 0.06 g), NaOAc (8 mmol, 0.66 g) and dry CH_3CN (4.0 mL) were added. Subsequently, the reaction mixture was stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs for 48 h. After the reaction was complete, the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:10, V/V) to give the product **3jz** (1.76 g, 78%) as a yellow solid.

1-(4-Bromophenyl)-2-(2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3aa):



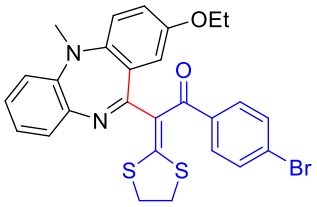
Yellow solid (93.8 mg, 90%); m.p. 271.0-271.9 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.33 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.73 (s, 1H), 6.41 (d, *J* = 8.2 Hz, 1H), 3.55-3.31 (m, 4H), 2.93 (s, 3H), 2.10 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.38, 171.21, 169.07, 154.20, 146.87, 142.30, 139.07, 132.55, 132.40, 130.50, 130.25, 129.36, 129.28, 126.78, 126.60, 126.52, 125.05, 123.92, 117.83, 116.41, 37.78, 36.75, 36.34, 20.35; **HRMS** (ESI) m/z calculated $C_{26}H_{22}BrOS_2^+$ $[M + H]^+$ 521.0351, found 521.0351.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(2-methoxy-5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one) (3ab):



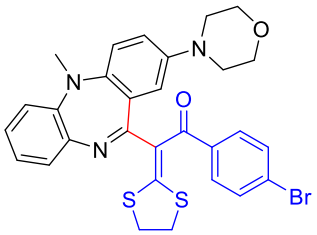
Yellow solid (97.8 mg, 91%); m.p. 228.2-229.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 6.1 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.58 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.40 (s, 1H), 6.39 (d, *J* = 6.6 Hz, 1H), 3.55 (s, 3H), 3.48-3.24 (m, 4H), 2.85 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.48, 155.46, 149.76, 147.11, 142.16, 138.92, 131.08, 130.54, 129.51, 126.83, 126.64, 126.21, 125.23, 123.89, 117.79, 117.64, 117.50, 113.57, 55.79, 37.71, 36.81, 36.40; **HRMS** (ESI) m/z calculated $C_{26}H_{22}BrO_2S_2$ $[M + H]^+$ 537.0301, found 537.0294.

1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(2-ethoxy-5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3ac):



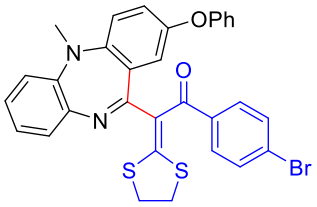
Yellow solid (98.2 mg, 89%); m.p. 180.3-181.0 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 6.4 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.64 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.46 (d, *J* = 2.9 Hz, 1H), 6.45 (d, *J* = 10.7 Hz, 1H), 3.87-3.76 (m, 2H), 3.54-3.29 (m, 4H), 2.92 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.42, 171.11, 168.36, 154.78, 149.64, 147.13, 142.18, 138.93, 131.08, 130.54, 129.52, 126.82, 126.64, 126.25, 125.22, 123.85, 118.40, 117.64, 117.47, 114.35, 64.06, 37.73, 36.79, 36.40, 14.71; **HRMS** (ESI) m/z calculated $C_{27}H_{24}BrN_2O_2S_2$ $[M + H]^+$ 551.0457, found 551.0462.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(5-methyl-2-morpholino-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3ad):



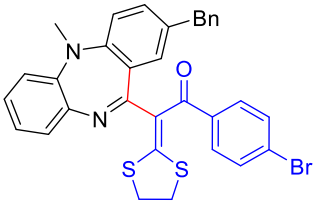
Yellow solid (98.4 mg, 83%); m.p. 241.2-242.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.35 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.27 (d, *J* = 6.1 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.65 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.46 (d, *J* = 2.9 Hz, 1H), 6.44 (d, *J* = 8.8 Hz, 1H), 3.80-3.75 (m, 4H), 3.54-3.32 (m, 4H), 2.95-2.91 (m, 2H), 2.92 (s, 3H), 2.86-2.82 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.95, 170.59, 168.38, 149.69, 147.49, 147.10, 142.20, 138.78, 130.92, 130.53, 129.53, 126.71, 126.62, 126.32, 125.37, 123.84, 119.82, 117.61, 117.20, 116.81, 66.78, 50.08, 37.53, 36.91, 36.29; **HRMS** (ESI) m/z calculated $C_{29}H_{27}BrN_3O_3S_2^+$ $[M + H]^+$ 592.0723, found 592.0722.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(5-methyl-2-phenoxy-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3ae):



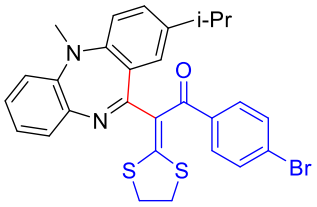
Yellow solid (104.3 mg, 87%); m.p. 180.5-181.4 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.19 (t, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.70 (dd, *J* = 7.6, 3.6 Hz, 3H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.44 (d, *J* = 8.7 Hz, 1H), 3.45-3.18 (m, 4H), 2.89 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.58, 172.11, 168.14, 157.69, 152.25, 152.00, 146.66, 142.12, 138.97, 131.69, 130.61, 129.67, 129.64, 127.04, 126.79, 125.97, 125.34, 124.13, 123.11, 122.82, 120.33, 117.91, 117.78, 117.56, 37.85, 36.70, 36.59; **HRMS** (ESI) m/z calculated $C_{31}H_{24}BrN_2O_2S_2^+$ $[M + H]^+$ 599.0457, found 599.0459.

2-(2-benzyl-5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3af):



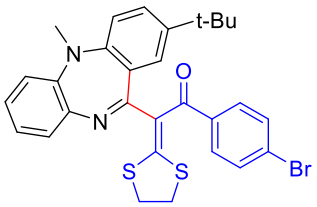
Yellow solid (105.2 mg, 88%); m.p. 106.7-107.7 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 1H), 7.34-7.26 (m, 4H), 7.21-7.18 (m, 3H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.10-7.02 (m, 3H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.84 (d, 1H), 6.80 (s, 1H), 6.43 (d, *J* = 8.3 Hz, 1H), 3.71 (s, 2H), 3.54-3.31 (m, 4H), 2.93 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.32, 171.10, 168.78, 154.76, 146.70, 142.30, 140.87, 138.88, 135.97, 132.20, 130.47, 130.40, 129.47, 129.33, 128.62, 128.51, 126.77, 126.63, 126.43, 126.22, 125.12, 123.99, 117.88, 116.81, 40.94, 37.67, 36.80, 36.38; **HRMS** (ESI) m/z calculated $C_{32}H_{26}BrN_2OS_2^+$ $[M +H]^+$ 597.0664, found 597.0668.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(2-isopropyl-5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3ag):



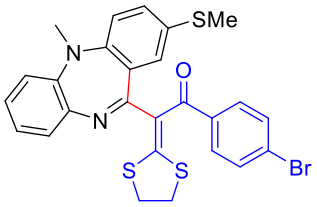
Yellow solid (103.3 mg, 94%); m.p. 232.8-233.6 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 2.2 Hz, 1H), 6.36 (d, *J* = 8.3 Hz, 1H), 3.48-3.26 (m, 4H), 2.88 (s, 3H), 2.63-2.57 (m, 1H), δ 1.02 (d, *J* = 4.8 Hz, 3H), 1.01 (d, *J* = 4.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.63, 170.90, 169.07, 154.53, 146.91, 143.57, 142.35, 138.89, 130.41, 130.22, 129.62, 129.38, 127.26, 126.71, 126.57, 125.18, 123.94, 117.90, 116.45, 37.63, 36.83, 36.38, 33.21, 24.17, 23.64; **HRMS** (ESI) m/z calculated $C_{28}H_{26}BrN_2OS_2^+$ $[M+H]^+$ 549.0664, found 549.0662.

71-(4-Bromophenyl)-2-(2-(tert-butyl)-5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3ah):



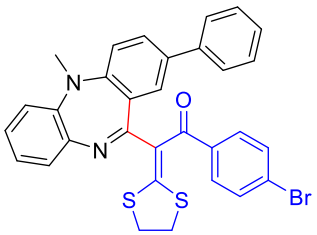
Yellow solid (96.9 mg, 86%); m.p. 242.5-242.7 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 9.1 Hz, 2H), 7.11-7.08 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 2.3 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.42 (d, *J* = 8.5 Hz, 1H), 3.54-3.33 (m, 4H), 2.95 (s, 3H), 1.16 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.76, 170.45, 169.06, 154.29, 146.86, 145.70, 142.45, 138.80, 130.39, 129.91, 129.41, 128.49, 126.62, 126.57, 126.53, 126.37, 125.26, 123.93, 117.88, 116.06, 37.51, 36.88, 36.33, 34.02, 31.17; **HRMS** (ESI) m/z calculated $C_{29}H_{28}BrN_2OS_2^+$ $[M+H]^+$ 563.0821, found 563.0829.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(5-methyl-2-(methylthio)-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3ai):



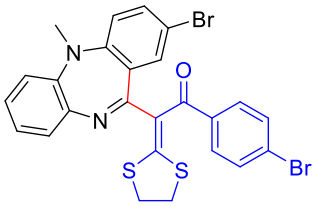
Yellow solid (90.8 mg, 82%); m.p. 255.6-256.2 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.07-7.01 (m, 2H), 6.86 (s, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 8.5 Hz, 1H), 3.56-3.331 (m, 4H), 2.94 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.33, 171.64, 168.27, 154.60, 146.42, 142.21, 139.05, 132.39, 131.54, 131.06, 130.58, 129.33, 128.64, 126.88, 126.70, 126.19, 125.17, 124.17, 118.00, 117.06, 37.75, 36.79, 36.39, 17.34; **HRMS** (ESI) m/z calculated $C_{26}H_{21}BrN_2OS_3^+$ [M + H]$^+$ 553.0072, found 553.0070.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(5-methyl-2-phenyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3aj):



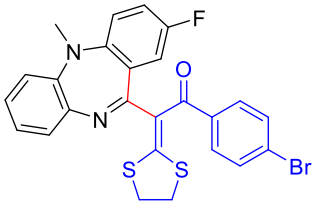
Yellow solid (102.7 mg, 88%); m.p. 295.7-296.2 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.39-7.33 (m, 5H), 7.31-7.25 (m, 4H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 3.56-3.32 (m, 4H), 3.00 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.72, 171.37, 168.85, 156.05, 146.49, 142.42, 139.85, 139.18, 136.21, 130.72, 130.56, 130.35, 129.26, 128.86, 127.88, 127.24, 126.83, 126.71, 126.49, 125.12, 124.19, 118.14, 116.84, 37.71, 36.81, 36.47; **HRMS** (ESI) m/z calculated $C_{31}H_{24}BrN_2OS_2^+$ [M + H]$^+$ 583.0508, found 583.0497.

2-(2-Bromo-5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3ak):



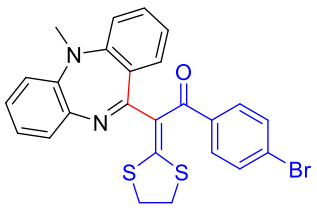
Yellow solid (73.9 mg, 63%); m.p. 256.4-257.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.34 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.17 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 8.7 Hz, 1H), 3.57-3.31 (m, 4H), 2.92 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.00, 172.70, 167.45, 155.56, 146.00, 142.05, 139.22, 134.38, 132.21, 131.49, 130.66, 129.28, 127.08, 126.77, 125.87, 125.07, 124.39, 118.17, 118.11, 115.78, 37.89, 36.76, 36.45; **HRMS** (ESI) m/z calculated $C_{25}H_{19}Br_2N_2OS_2^+$ $[M + H]^+$ 584.9300, found 584.9295.

11-(Difluoro(phenylthio)methyl)-5-ethyl-2-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine (3al):



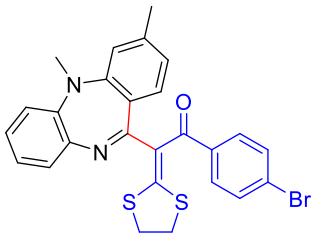
Yellow solid (59.9 mg, 57%); m.p. 194.7-195.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.82-6.78 (m, 1H), 6.65 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.49-6.46 (m, 1H), 3.57-3.31 (m, 4H), 2.93 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.92, 172.33, 167.55, 158.57 (d, *J* = 244.62 Hz), 152.26 (d, *J* = 2.4 Hz), 146.46, 142.04, 138.99, 131.66 (d, *J* = 6.4 Hz), 130.63, 129.47, 127.11, 126.80, 125.85, 125.23, 124.22, 118.27 (d, *J* = 22.5 Hz), 117.91, 117.77 (d, *J* = 7.8 Hz), 115.39 (d, *J* = 23.3 Hz), 37.89, 36.74, 36.57; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -119.97 (m, 1F); **HRMS** (ESI) m/z calculated $C_{25}H_{19}BrFN_2OS_2^+$ $[M + H]^+$ 525.0101, found 525.0094.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3am):



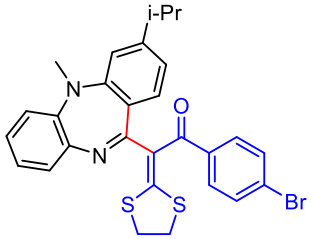
Yellow solid (71.0 mg, 70%); m.p. 224.5-225.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.12-7.02 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 3.54-3.28 (m, 4H), 2.94 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.30, 171.28, 169.29, 156.64, 146.65, 142.36, 138.95, 131.86, 130.50, 129.39, 129.22, 126.86, 126.69, 126.56, 125.10, 124.09, 122.98, 118.11, 116.59, 37.84, 36.72, 36.40; **HRMS** (ESI) m/z calculated $C_{25}H_{20}BrN_2OS_2^+$ $[M + H]^+$ 507.0195, found 507.0196.

1-(4-Bromophenyl)-2-(3,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3an):



Yellow oil (65.7 mg, 63%); m.p. 217.3-217.9 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.30 (s, 1H), 3.53-3.27 (m, 4H), 2.94 (s, 3H), 2.13 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.21, 170.92, 169.29, 156.63, 146.72, 142.55, 142.51, 138.94, 130.38, 129.47, 129.15, 127.76, 126.73, 126.67, 126.62, 125.08, 124.01, 123.69, 118.03, 117.34, 37.82, 36.69, 36.39, 21.38; **HRMS** (ESI) m/z calculated $C_{26}H_{22}BrN_2OS_2^+$ $[M + H]^+$ 521.0351, found 521.0352.

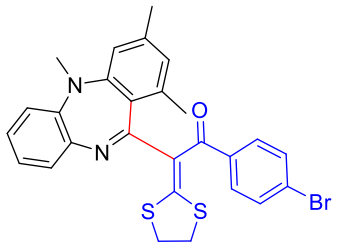
1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(3-isopropyl-5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3ao):



Yellow solid (62.6 mg, 57%); m.p. 224.5-225.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* =

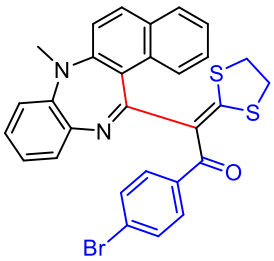
7.7 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 7.4 Hz, 1H), 6.28 (s, 1H), 3.54-3.28 (m, 4H), 2.97 (s, 3H), 2.71-2.63 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.58, 171.23, 169.32, 157.10, 153.22, 146.78, 142.73, 139.17, 130.34, 129.43, 129.20, 128.08, 126.78, 126.59, 126.56, 124.72, 124.03, 120.83, 118.24, 114.45, 37.79, 36.69, 36.40, 34.21, 23.86, 23.32; **HRMS** (ESI) m/z calculated $C_{28}H_{26}BrN_2OS_2^+$ $[M + H]^+$ 549.0664, found 549.0669.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(1,3,5-trimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3ap):



Yellow solid (87.8 mg, 82%); m.p. 242.5-243.5 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.05-7.01 (m, 2H), 6.87-6.80 (m, 2H), 6.84-6.83 (m, 1H), 6.45 (s, 1H), 6.03 (s, 1H), 3.53-3.26 (m, 4H), 2.85 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.88, 169.45, 168.93, 159.18, 146.75, 143.02, 141.03, 138.84, 137.28, 130.33, 128.78, 128.03, 127.04, 126.44, 126.00, 125.62, 124.99, 123.98, 118.01, 114.04, 37.55, 36.74, 36.34, 21.12, 20.19; **HRMS** (ESI) m/z calculated $C_{27}H_{24}BrN_2OS_2^+$ $[M + H]^+$ 535.0508, found 535.0497.

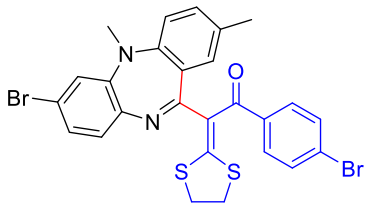
1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(5-methyl-5H-benzo[b]naphtho[2,3-e][1,4]diazepin-12-yl)ethan-1-one (3aq):



Yellow solid (105.9 mg, 95%); m.p. 256.4-257.5 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.40-7.35 (m, 2H), 7.28-7.24 (m, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.06-7.04 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.89-6.86 (m, 1H), 6.66 (d, *J* = 9.0 Hz, 1H),

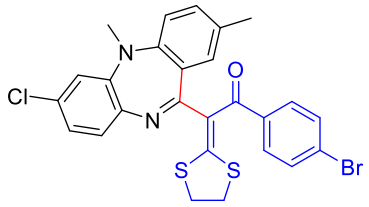
3.54-3.36 (m, 4H), 3.07 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.81, 169.50, 168.17, 157.32, 147.50, 143.41, 139.08, 132.08, 131.34, 130.37, 130.34, 128.42, 128.37, 127.63, 127.25, 126.03, 125.67, 125.20, 124.72, 124.58, 124.36, 123.20, 118.16, 115.66, 37.39, 37.04, 36.34; **HRMS** (ESI) m/z calculated $C_{29}H_{22}BrN_2OS_2^+$ $[M + H]^+$ 557.0351, found 557.0346.

2-(7-Bromo-2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3ar):



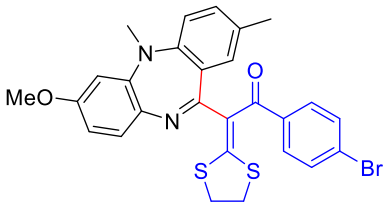
Yellow solid (109.3 mg, 91%); m.p. 268.4-269.1 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.17-7.12 (m, 2H), 6.95 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 3.55-3.29 (m, 4H), 2.89 (s, 3H), 2.10 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.38, 171.63, 169.28, 153.37, 147.80, 141.31, 139.05, 133.11, 132.60, 130.54, 130.14, 129.33, 129.31, 127.67, 126.94, 126.23, 125.15, 121.23, 120.40, 116.66, 37.77, 36.78, 36.41, 20.35; **HRMS** (ESI) m/z calculated $C_{26}H_{21}Br_2N_2OS_2^+$ $[M\ ]^+$ 598.9457, found 598.9459.

1-(4-Bromophenyl)-2-(7-chloro-2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3as):



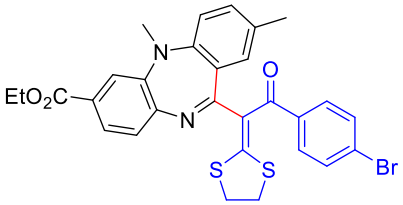
Yellow solid (96.7 mg, 87%); m.p. 258.2-258.8 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.1 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.91 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 6.72 (d, *J* = 2.1 Hz, 1H), 6.41 (d, *J* = 8.2 Hz, 1H), 3.56-3.30 (m, 4H), 2.90 (s, 3H), 2.11 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.41, 171.58, 169.21, 153.33, 147.61, 140.82, 139.05, 133.11, 132.58, 132.49, 130.54, 130.16, 129.32, 127.36, 126.24, 125.15, 123.97, 118.32, 116.64, 37.77, 36.77, 36.39, 20.35; **HRMS** (ESI) m/z calculated $C_{26}H_{21}BrClN_2OS_2^+$ $[M + H]^+$ 554.9962, found 554.9938.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(7-methoxy-2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3at):



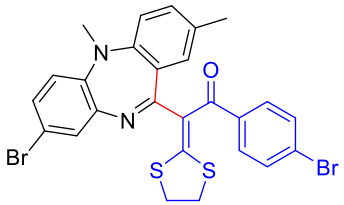
Yellow solid (88.2 mg, 80%); m.p. 266.5-267.7 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.24-7.14 (m, 3H), 6.82 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.64 (d, *J* = 2.1 Hz, 1H), 6.52 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.34 (dd, *J* = 5.5, 2.8 Hz, 2H), 3.70 (s, 3H), 3.49-3.23 (m, 4H), 2.84 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.32, 170.59, 167.37, 159.34, 153.28, 147.79, 139.11, 135.77, 132.75, 132.22, 130.47, 130.41, 129.41, 129.12, 127.51, 126.60, 124.99, 116.57, 108.26, 104.79, 55.49, 37.79, 36.74, 36.44, 20.36; **HRMS** (ESI) m/z calculated $C_{27}H_{24}BrN_2O_2S_2^+$ $[M + H]^+$ 551.0457, found 551.0457.

Ethyl 11-(2-(4-bromophenyl)-1-(1,3-dithiolan-2-ylidene)-2-oxoethyl)-2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepine-7-carboxylate (3au):



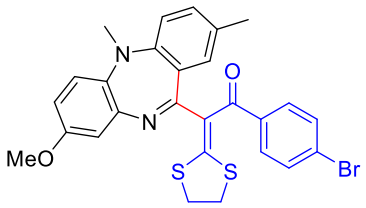
Yellow solid (109.2 mg, 92%); m.p. 190.6-191.4 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.1 Hz, 1H), 7.77 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.90 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 6.41 (d, *J* = 8.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.57-3.33 (m, 4H), 2.96 (s, 3H), 2.11 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.43, 172.00, 169.57, 166.20, 153.11, 151.29, 141.86, 139.15, 133.11, 132.54, 130.54, 130.27, 129.35, 129.30, 128.14, 128.03, 126.13, 126.01, 125.11, 117.53, 116.82, 60.78, 37.73, 36.86, 36.53, 20.33, 14.40; **HRMS** (ESI) m/z calculated $C_{29}H_{26}BrN_2O_3S_2^+$ $[M + H]^+$ 593.0563, found 593.0561.

2-(8-Bromo-2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3av):



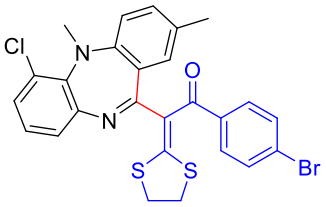
Yellow solid (93.7 mg, 78%); m.p. 281.1-282.2 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.11 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 1H), 6.31 (d, *J* = 8.3 Hz, 1H), 3.49-3.26 (m, 4H), 2.82 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.47, 172.04, 169.96, 153.71, 146.11, 143.62, 139.05, 132.94, 132.62, 130.53, 130.13, 129.38, 129.28, 129.15, 129.03, 126.10, 125.15, 119.12, 116.49, 116.47, 37.75, 36.80, 36.35, 20.35; **HRMS** (ESI) m/z calculated $C_{26}H_{21}Br_2N_2OS_2^+$ $[M + H]^+$ 598.9457, found 598.9455.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(8-methoxy-2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3aw):



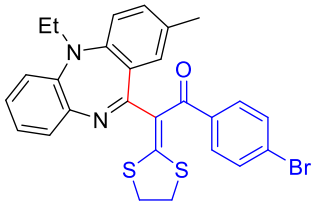
Yellow solid (90.4 mg, 82%); m.p. 227.4-227.9 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.81 (dd, *J* = 9.1, 2.4 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 1H), 6.66 (s, 1H), 6.60 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.32 (d, *J* = 8.2 Hz, 1H), 3.70 (s, 3H), 3.49-3.26 (m, 4H), 2.83 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.43, 171.11, 169.48, 156.24, 154.67, 143.12, 140.18, 139.00, 132.41, 130.46, 130.12, 129.37, 129.31, 126.60, 125.01, 118.17, 116.03, 112.43, 111.21, 55.66, 37.76, 36.76, 36.37, 20.33; **HRMS** (ESI) m/z calculated $C_{27}H_{24}BrN_2O_2S_2^+$ $[M + H]^+$ 551.0457, found 551.0464.

1-(4-Bromophenyl)-2-(6-chloro-2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3ax):



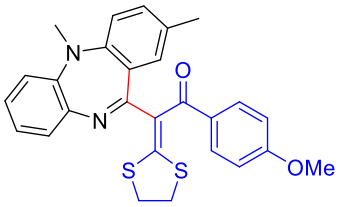
Yellow solid (92.3 mg, 83%); m.p. 232.4-233.1 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.26 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.13 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.02 (t, *J* = 7.9 Hz, 1H), 6.97 (dd, 1H), 6.80 (d, *J* = 2.1 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 3.55-3.33 (m, 4H), 3.21 (s, 3H), 2.14 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.67, 171.38, 168.91, 153.76, 147.67, 140.94, 139.19, 133.49, 132.98, 130.97, 130.64, 129.93, 129.75, 129.22, 128.61, 126.64, 125.64, 125.40, 124.92, 120.88, 39.23, 37.71, 36.82, 20.57; **HRMS** (ESI) m/z calculated $C_{26}H_{21}BrClN_2OS_2^+$ $[M + H]^+$ 554.9962, found 554.9954.

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(5-ethyl-2-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)ethan-1-one (3ay):



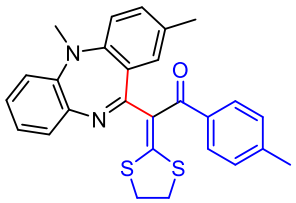
Yellow solid (92.1 mg, 86%); m.p. 205.8-206.7 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 3.67-3.61 (m, 1H), 3.55-3.31 (m, 4H), 2.98-2.91 (m, 1H), 2.11 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.78, 154.34, 143.99, 139.21, 132.67, 130.51, 129.29, 126.65, 126.45, 125.23, 123.94, 118.90, 117.33, 41.95, 37.73, 36.80, 20.40, 13.19; **HRMS** (ESI) m/z calculated $C_{27}H_{24}BrN_2OS_2^+$ $[M + H]^+$ 535.0508, found 535.0516.

2-(2,5-Dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)-1-(4-methoxyphenyl)ethan-1-one (3ba):



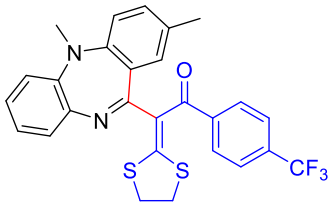
Yellow solid (74.7 mg, 79%); m.p. 226.3-227.1 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 2H), 7.35 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.08 (td, *J* = 7.6, 1.7 Hz, 1H), 7.02 (td, *J* = 7.5, 1.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 2.1 Hz, 1H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H), 3.75-3.31 (m, 4H), 2.97 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.48, 171.15, 168.25, 155.46, 149.76, 147.11, 142.16, 138.92, 131.08, 130.54, 129.51, 126.83, 126.64, 126.21, 125.23, 123.89, 117.79, 117.64, 117.50, 113.57, 55.79, 37.71, 36.81, 36.40; **HRMS** (ESI) m/z calculated $C_{27}H_{25}N_2O_2S_2^+$ $[M + H]^+$ 473.1352, found 473.1342.

2-(2,5-Dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)-1-(p-tolyl)ethan-1-one (3ca):



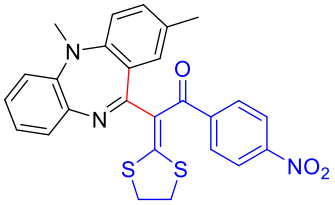
Yellow solid (66.7 mg, 73%); m.p. 180.4-181.2 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.34 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.75 (s, 1H), 6.37 (d, *J* = 8.2 Hz, 1H), 3.52-3.31 (m, 4H), 2.91 (s, 3H), 2.26 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.45, 169.50, 169.24, 154.08, 146.96, 142.41, 140.94, 137.52, 132.43, 132.10, 130.39, 129.30, 128.12, 127.97, 126.99, 126.62, 126.54, 123.79, 117.67, 116.33, 37.62, 36.73, 36.26, 21.52, 20.34; **HRMS** (ESI) m/z calculated $C_{27}H_{25}N_2OS_2^+$ $[M + H]^+$ 457.1403, found 457.1402.

2-(2,5-Dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3da):



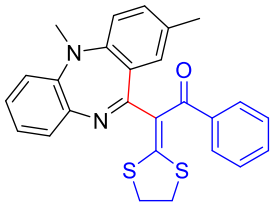
Yellow solid (77.6 mg, 76%); m.p. 219.7-220.2 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.11-7.07 (m, 1H), 7.04-7.01 (m, 1H), 6.85 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.82 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.72 (d, *J* = 2.1 Hz, 1H), 6.31 (d, *J* = 8.3 Hz, 1H), 3.57-3.34 (m, 4H), 2.84 (s, 3H), 2.11 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.23, 172.30, 169.03, 154.29, 146.79, 143.38, 142.27, 132.55, 132.48, 131.66 (q, *J* = 32.3 Hz), 130.13, 129.40, 127.84, 126.87, 126.57, 126.40, 124.24 (q, *J* = 3.6 Hz), 123.96, 123.85 (q, *J* = 273.3 Hz), 117.89, 116.28, 37.90, 36.74, 36.10, 20.32; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.87 (s, 3F); **HRMS** (ESI) m/z calculated $C_{27}H_{22}F_3N_2OS_2^+$ $[M + H]^+$ 511.0020, found 511.0010.

2-(2,5-Dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)-1-(4-nitrophenyl)ethan-1-one (3ea):



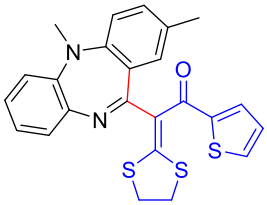
Yellow solid (51.7 mg, 53%); m.p. 255.6-256.0 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.32 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.12-7.09 (m, 1H), 7.05-7.02 (m, 1H), 6.86 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.72 (d, *J* = 2.1 Hz, 1H), 6.31 (d, *J* = 8.3 Hz, 1H), 3.60-3.35 (m, 4H), 2.87 (s, 3H), 2.11 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.10, 173.72, 168.59, 154.29, 148.40, 146.66, 145.59, 142.19, 132.74, 132.64, 130.17, 129.51, 128.48, 127.01, 126.56, 126.18, 124.09, 122.49, 117.96, 116.39, 37.97, 36.80, 36.39, 20.32; **HRMS** (ESI) m/z calculated $C_{26}H_{22}N_3O_3S_2^+$ $[M + H]^+$ 488.1097, found 488.1093.

2-(2,5-Dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (3fa):



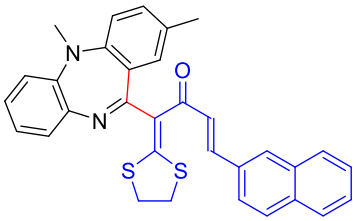
Yellow solid (62.0 mg, 70%); m.p. 190.2-191.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.09-7.06 (m, 1H), 7.03-7.00 (m, 1H), 6.83 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 2.1 Hz, 1H), 6.34 (d, *J* = 8.2 Hz, 1H), 3.53-3.32 (m, 4H), 2.90 (s, 3H), 2.10 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.62, 170.43, 169.23, 154.19, 146.98, 142.39, 140.20, 132.44, 132.15, 130.49, 130.31, 129.35, 127.85, 127.32, 126.84, 126.61, 126.59, 123.82, 117.750, 116.38, 37.70, 36.74, 36.28, 20.35; **HRMS** (ESI) m/z calculated $C_{26}H_{23}N_2OS_2^+$ $[M + H]^+$ 443.1246, found 443.1244.

2-(2,5-Dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithiolan-2-ylidene)-1-(thiophen-2-yl)ethan-1-one (3ga):



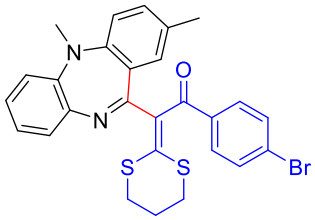
Yellow solid (75.4 mg, 84%); m.p. 235.1-236.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 3.9 Hz, 1H), 7.40-7.34 (m, 2H), 7.15-7.11 (m, 1H), 7.06-7.03 (m, 1H), 6.96 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.87-6.84 (m, 2H), 6.61 (d, *J* = 8.2 Hz, 1H), 3.48-3.33 (m, 4H), 3.12 (s, 3H), 2.11 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 183.04, 169.83, 168.80, 153.89, 146.90, 145.29, 142.23, 132.97, 132.61, 132.47, 131.92, 130.29, 129.31, 126.95, 126.82, 126.77, 126.14, 123.98, 117.75, 116.96, 37.79, 36.73, 36.48, 20.47; **HRMS** (ESI) m/z calculated $C_{24}H_{21}N_2OS_3^+$ $[M + H]^+$ 449.0811, found 449.0818.

(E)-1-(2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-1-(1,3-dithiolan-2-ylidene)-4-(naphthalen-2-yl)but-3-en-2-one (3ha):



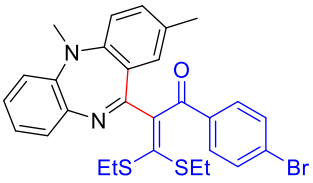
Yellow solid (41.5 mg, 40%); m.p. 219.8-220.0 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.79 (m, 3H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 15.6 Hz, 1H), 7.53-7.47 (m, 3H), 7.39 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.24-7.18 (m, 1H), 7.17 (d, *J* = 15.6 Hz, 1H), 7.13 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.13-7.08 (m, 1H), 7.03 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 3.59-3.35 (m, 4H), 3.34 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 185.22, 168.93, 154.08, 146.87, 141.48, 134.00, 133.35, 133.32, 133.04, 132.98, 130.22, 130.04, 129.69, 128.43, 128.29, 127.71, 127.09, 127.00, 126.96, 126.58, 125.66, 124.14, 123.84, 117.65, 117.05, 38.40, 37.11, 36.40, 20.53; **HRMS** (ESI) m/z calculated $C_{32}H_{27}N_2OS_2^+$ $[M + H]^+$ 519.1559, found 519.1564.

1-(4-Bromophenyl)-2-(2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-(1,3-dithian-2-ylidene)ethan-1-one (3ia):



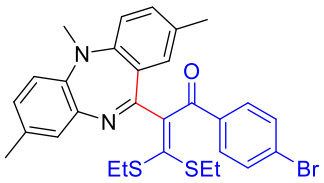
Yellow solid (81.4 mg, 76%); m.p. 201.8-201.5 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.34 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.12-7.09 (m, 1H), 7.05-7.03 (m, 1H), 6.92 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.84 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.76 (d, *J* = 2.1 Hz, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 3.30-3.21 (m, 2H), 2.88 (s, 3H), 2.86-2.79 (m, 2H), 2.39-2.31 (m, 2H), 2.14 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.43, 168.36, 167.37, 154.44, 147.08, 142.60, 138.57, 135.45, 132.50, 132.41, 130.59, 129.84, 129.64, 126.82, 126.61, 125.54, 123.92, 117.90, 116.33, 36.34, 30.14, 29.68, 25.12, 20.37; **HRMS** (ESI) m/z calculated $C_{27}H_{24}BrN_2OS_2^+$ $[M + H]^+$ 535.0508, found 535.0498.

1-(4-Bromophenyl)-2-(2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-3,3-bis(ethylthio)prop-2-en-1-one (3ja):



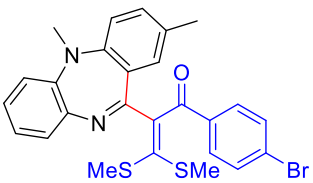
Yellow solid (75.0 mg, 68%); m.p. 187.5-188.2 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.25 (s, 1H) 7.12 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.09-7.05 (m, 1H), 6.94-6.90 (m, 2H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 3.17 (s, 3H), 2.72-2.62 (m, 4H), 2.24 (s, 3H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.76, 167.86, 155.20, 146.84, 146.21, 143.00, 142.12, 136.98, 132.71, 131.93, 131.62, 131.36, 130.01, 129.88, 128.16, 127.56, 127.07, 123.69, 117.50, 116.79, 36.82, 28.72, 28.08, 20.57, 14.79, 14.59; **HRMS** (ESI) m/z calculated $C_{28}H_{28}BrN_2OS_2^+$ $[M + H]^+$ 551.0821, found 551.0813.

1-(4-bromophenyl)-3,3-bis(ethylthio)-2-(2,5,8-trimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)prop-2-en-1-one (3jw):



Yellow solid (89.4 mg, 79%); m.p. 182.9-183.6 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.25 (s, 1H), 7.10 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.88 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.88-6.87 (m, 3H), 3.14 (s, 3H), 2.72-2.64 (m, 4H), 2.24 (s, 3H), 2.16 (s, 3H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.84, 167.90, 155.40, 146.29, 144.34, 142.90, 141.81, 137.06, 133.25, 132.55, 131.87, 131.61, 131.37, 129.93, 129.89, 128.42, 127.70, 127.52, 117.18, 116.57, 36.77, 28.71, 28.08, 20.57, 20.35, 14.80, 14.59; **HRMS** (ESI) m/z calculated $C_{29}H_{30}BrN_2OS_2^+$ $[M + H]^+$ 565.0977, found 565.0975.

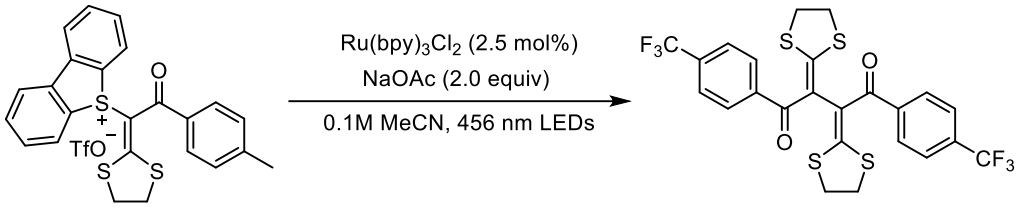
1-(4-Bromophenyl)-2-(2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-3,3-bis(methylthio)prop-2-en-1-one (3ka):



Yellow solid (76.4 mg, 73%); m.p. 194.6-195.7 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.16 (s, 1H), 7.11-7.06 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 3.12 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.16, 167.90, 155.13, 147.43, 146.81, 144.34, 142.10, 136.91, 132.60, 132.16, 131.44, 131.15, 129.75, 129.66, 127.97, 127.49, 127.15, 123.77, 117.54, 116.89, 36.78, 20.57, 17.74, 16.98; **HRMS** (ESI) m/z calculated $C_{26}H_{24}BrN_2OS_2^+$ $[M + H]^+$ 523.0508, found 523.0510.

IV. Control Experiments for Mechanistic Studies:

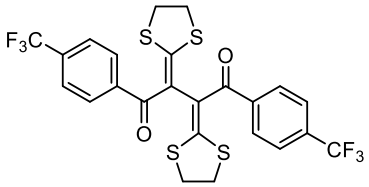
1. Identify Intermediates of Reactions Experiments:



1d **8**, isolated yield: 22%

A sealed tube equipped with a magnetic stir bar was charged with the alkenysulfonium salts **1d** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.005 mmol, 2.5 mol%), NaOAc (0.4 mmol, 2.0 equiv) and dry CH_3CN (2.0 mL) were added. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs. After the complete conversion of the alkenysulfonium salt **1d** (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the product **8**.

2,3-Di(1,3-dithiolan-2-ylidene)-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (8):



Yellow solid (12.7 mg, 22%); m.p. 48.6-49.6 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.92-2.85 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.65, 181.57, 174.32, 141.90, 138.87, 135.03 (q, *J* = 32.7 Hz), 132.54 (q, *J* = 32.7 Hz), 129.46, 129.16, 125.71 (q, *J* = 3.6 Hz), 124.85 (q, *J* = 3.6 Hz), 123.77 (q, *J* = 273.31 Hz), 123.53 (q, *J* = 273.31 Hz), 111.59, 96.81, 92.28, 41.05, 35.77, 35.59, 35.40; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.85, -63.09; **HRMS** (ESI) m/z calculated $C_{24}H_{17}F_6O_2S_4^+$ $[M + H]^+$ 579.0010, found 579.0012.

2. Stern-Volmer Quenching Experiments:

Emission intensities were recorded using a spectrofluorimeter. All $Ru(bpy)_3Cl_2$

solutions were excited at 460 nm and the emission intensity at 600 nm was observed. First, the emission spectrum of a 5×10^{-5} M solution of $Ru(bpy)_3Cl_2$ in MeCN was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.

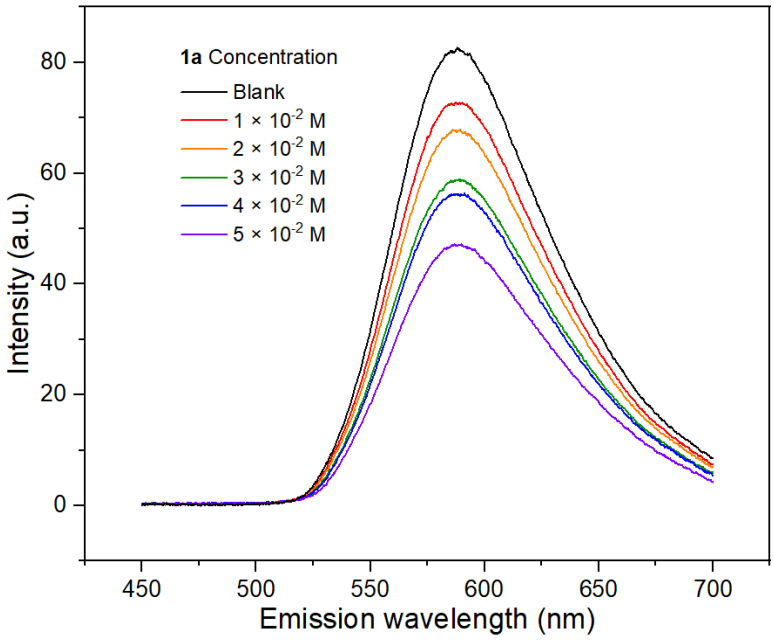


Figure 1. $Ru(bpy)_3Cl_2$ Emission Quenching by Alkenysulfonium Salt **1a**

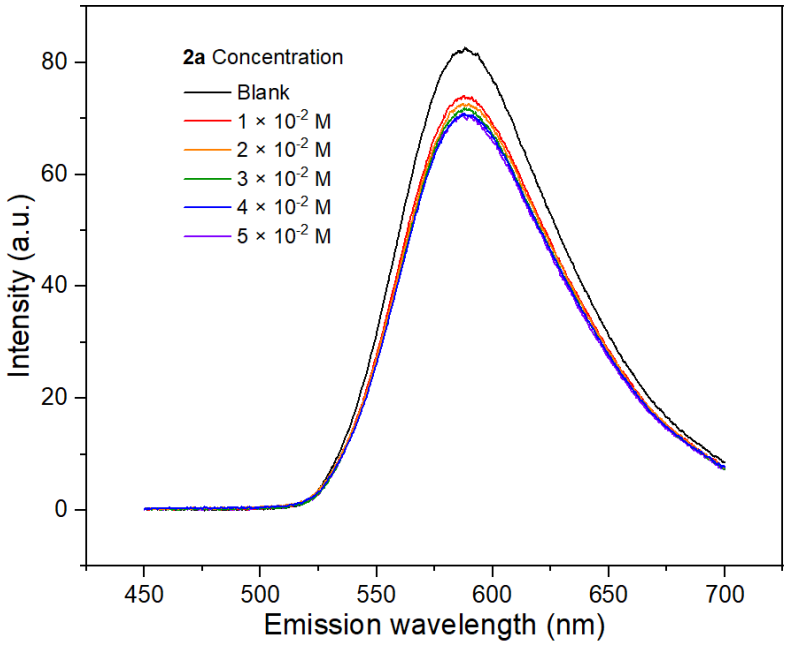


Figure 2. $Ru(bpy)_3Cl_2$ Emission Quenching by *o*-Isocyanodiaryl Amine **2a**

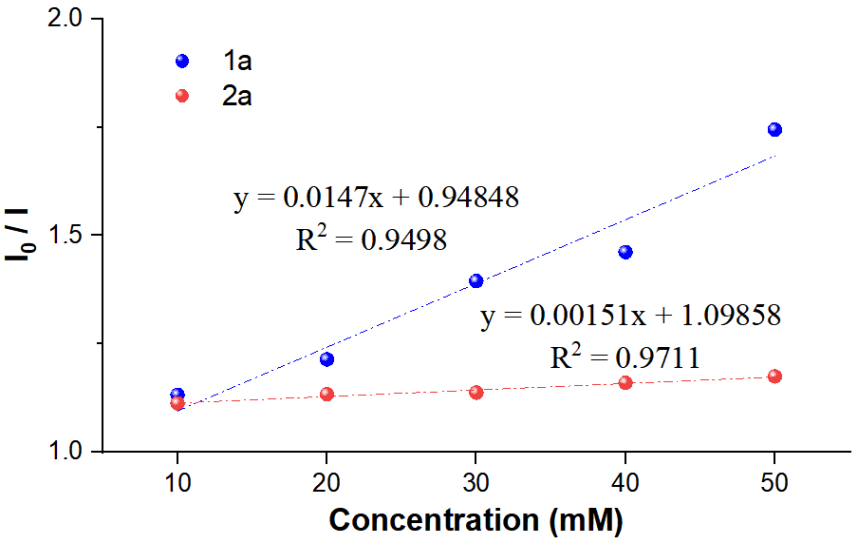


Figure 3. $Ru(bpy)_3Cl_2$ Emission Quenching Studies

3.Cyclic Voltammetry Experiments:

For the electrochemical measurements, a three-electrode system connected to an electrochemical station was used: A reference electrode, Ag/AgCl in 0.1 M KCl; A glassy carbon electrode as the working electrode; and a Pt wire as the counter electrode. All electrochemical measurements were performed in degassed MeCN under dry N_2 atmosphere. CV spectra of **1a** is reported at 3 mM in 0.1 M NBu_4PF_6 in degassed MeCN with scan rate 50 mV/s.

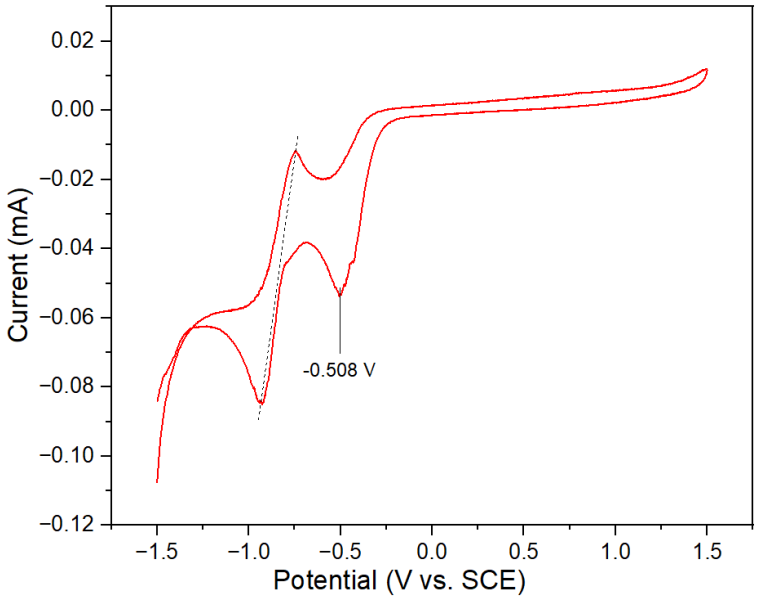
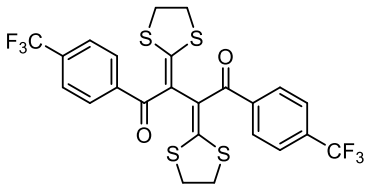


Figure 4. Cyclic Voltammetry (CV) Experiments

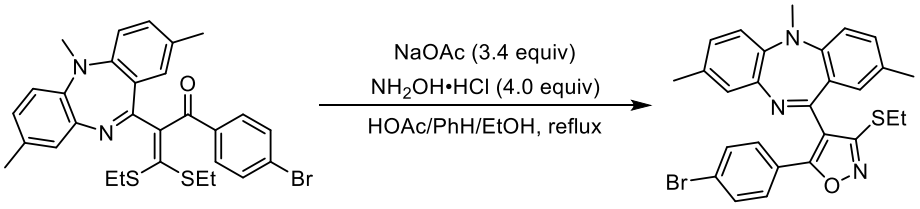
2,3-Di(1,3-dithiolan-2-ylidene)-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (8):



Yellow solid (12.7 mg, 22%); m.p. 48.6-49.6 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.89 (tt, *J* = 6.3, 3.8 Hz, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.65, 181.57, 174.32, 141.90, 138.87, 135.03 (q, *J* = 32.7 Hz), 132.54 (q, *J* = 32.7 Hz), 129.46, 129.16, 125.71 (q, *J* = 3.6 Hz), 124.85 (q, *J* = 3.6 Hz), 123.77 (q, *J* = 273.31 Hz), 123.53 (q, *J* = 273.31 Hz), 111.59, 96.81, 92.28, 41.05, 35.77, 35.59, 35.40; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.85, -63.09; **HRMS** (ESI) m/z calculated $C_{24}H_{17}F_6O_2S_4^+$ $[M + H]^+$ 579.0010, found 579.0012.

V. Applications of 11-Alkenyl-Substituted Dibenzodiazepines 3:

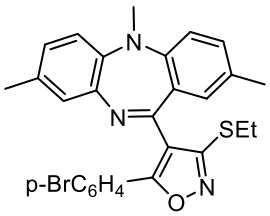
1. Construction of Substituted Isoxazoles:



3jz **4**

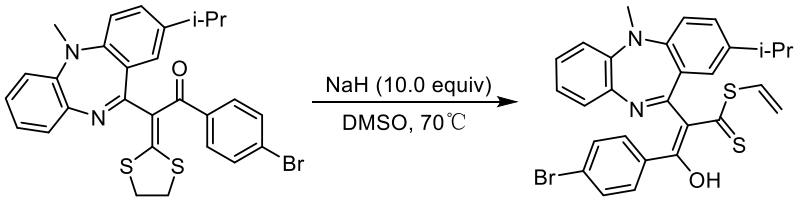
To a stirred solution of the dibenzodiazepine **3jz** (0.57 g, 1 mmol) in benzene (10 mL) + AcOH (10 mL), asolution of NaOAc (0.28 g, 3.4 mmol) and NH_2OH•HCl (0.28 g, 4 mmol) in H_2O (1 mL) is added. The mixture is made homogenous by the addition of EtOH (5 mL) and refluxed for 8-10 h. It is then evaporated to dryness under reduced pressure, and extracted with CH_2Cl_2. The CH_2Cl_2 layer is washed with H_2O, dried by Na_2SO_4, and evaporated to give a residue. The residue was purified by silica column chromatography to give the isoxazole **4**.

5-(4-Bromophenyl)-3-(ethylthio)-4-(2,5,8-trimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)isoxazole (4):



White solid (290.3 mg, 56% yield); m.p. 194.7-195.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.56 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 3.21-3.17 (m, 2H), 2.92 (s, 3H), 2.31 (s, 3H), 2.13 (s, 3H), 1.39 (t, *J* = 7.4 Hz, 3H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.63, 163.33, 160.38, 150.66, 145.79, 137.76, 136.75, 132.49, 132.08, 131.80, 129.68, 128.10, 127.15, 126.10, 126.04, 124.94, 119.65, 118.88, 118.41, 112.33, 41.00, 25.30, 21.15, 20.40, 13.77; **HRMS** (ESI) m/z calculated $C_{27}H_{25}BrN_3OS^+$ 518.0896; Found 518.0901.

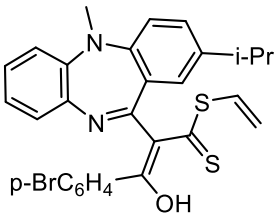
2. Synthesis of Thiothioester 5:



3ag **5**

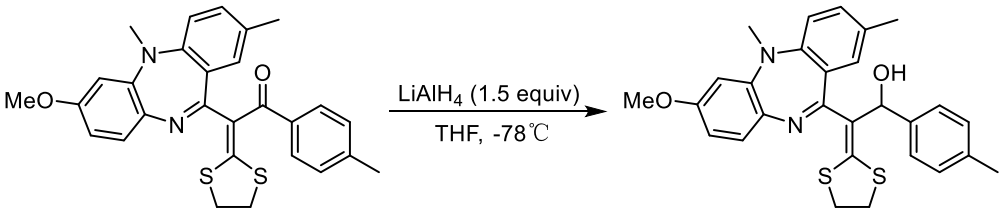
NaH (60% suspension in mineral oil, 0.08 g, 2 mmol) was suspended in DMSO (2 mL), the mixture was stirred at 70°C for 1 h, and the dibenzodiazepine **3ag** (0.2 mmol) was added. The reaction mixture was stirred at this temperature for 30-45 min, then poured into cold water, made neutral with 1 M HCl, and extracted with CH_2Cl_2. The combined organic layer was washed with H_2O, dried (Na_2SO_4), and evaporated to give a residue. This residue was purified by silica column chromatography to give the **5**.

Vinyl(Z)-3-(4-bromophenyl)-3-hydroxy-2-(2-isopropyl-5-methyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)prop-2-enedithioate (5):



Red solid (104.4 mg, 95% yield); m.p. 156.8-157.6 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 16.19 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 9.9 Hz, 2H), 7.23 (d, *J* = 10.0 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 2H), 7.06 (td, *J* = 7.6, 1.3 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 5.60 (d, *J* = 10.0 Hz, 1H), 5.57 (d, *J* = 17.1 Hz, 1H), 3.06 (s, 3H), 2.74-2.67 (m, *J* = 6.9 Hz, 1H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.60, 194.89, 164.27, 153.34, 150.29, 144.63, 138.43, 131.21, 131.14, 130.86, 130.77, 130.52, 129.91, 127.52, 127.26, 126.91, 124.29, 123.65, 120.87, 118.76, 118.19, 117.31, 36.35, 33.18, 23.75, 23.25; **HRMS** (ESI) m/z calculated $C_{28}H_{26}BrN_2OS_2^+$ 549.0664; Found 549.0667.

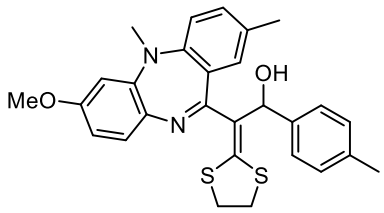
3. Alcohols Obtained via Reduction Reactions:



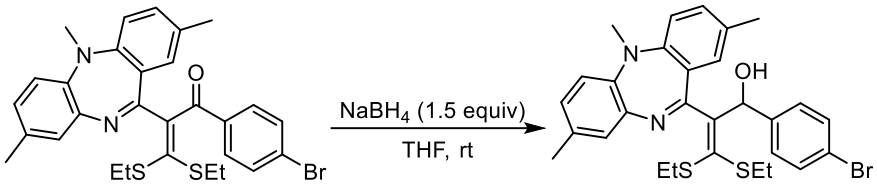
3ct **6a**

A 25 mL Schlenk flask was charged with the dibenzodiazepine **3ct** (0.10 g, 0.2 mmol), THF (5 mL) and a stir bar under N_2 at -78℃, then a solution of $LiAlH_4$ (0.3 mL, 1 M in THF, 0.3 mmol) was added. The mixture was stirred at -78℃ for 1 h，and then was stirred at room temperature for 0.5 h. Then the resulting mixture was quenched by saturated NH_4Cl aqueous solution, extracted with, dried with anhydrous Na_2SO_4, concentrated in vacuo, and purified by silica column chromatography to give the **6a**.

2-(1,3-Dithiolan-2-ylidene)-2-(7-methoxy-2,5-dimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-1-(p-tolyl)ethan-1-ol (6a):



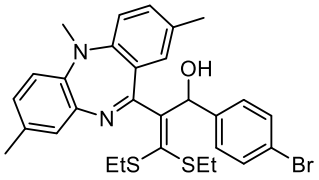
Yellow solid (89.9 mg, 92% yield); m.p. 216.6-217.4 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.38 (s, 1H), 7.12 (d, *J* = 5.7 Hz, 2H), 7.11 (d, *J* = 6.3 Hz, 1H), 7.07 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.59 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.45 (d, *J* = 2.6 Hz, 1H), 6.16 (d, *J* = 2.1 Hz, 1H), 6.00 (s, 1H), 3.76 (s, 3H), 3.44-3.32 (m, 2H), 3.24 (dd, *J* = 6.7, 4.5 Hz, 2H), 3.18 (s, 3H), 2.28 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.46, 159.40, 153.78, 148.63, 147.41, 141.33, 136.33, 134.11, 133.43, 132.13, 130.73, 129.02, 128.78, 128.32, 127.90, 125.22, 116.93, 108.26, 104.42, 79.20, 55.51, 39.11, 37.22, 36.72, 21.08, 20.50; **HRMS** (ESI) m/z calculated $C_{28}H_{29}N_2O_2S_2^+$ 489.1665, Found 489.1672.



3jz **6b**

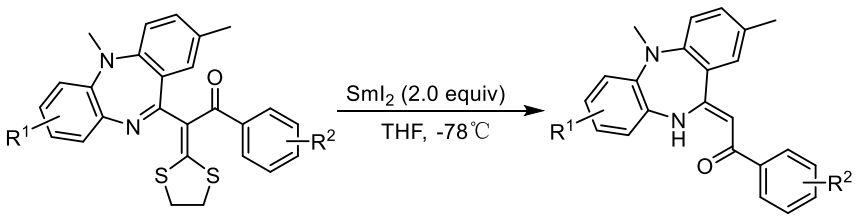
A 25 mL flask was charged with dibenzodiazepine **3jz** (0.57 g, 1 mmol), EtOH (10 mL) and a stir bar under room temperature, then 0.72 g $NaBH_4$ (0.06g, 1.5 mmol) was added and the mixture was refluxed for 1 h. The contents were poured into cold saturated aqueous solution of NH_4Cl. The mixture was extracted with CH_2Cl_2, dried and concentrated. The residue was purified by flash silica column chromatography to give the product **6b**.

1-(4-Bromophenyl)-3,3-bis(ethylthio)-2-(2,5,8-trimethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl) prop-2-en-1-ol (6b):



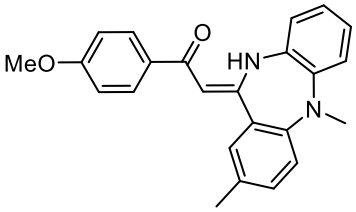
Yellow solid (482.5 mg, 85% yield); m.p. 103.3-104.2 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.44-7.41 (m, 4H), 7.05 (s, 1H), 6.97 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.95 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.73-6.71 (m, 2H), 5.53-5.45 (m, 1H), 3.17 (s, 3H), 3.08-3.02 (m, 1H), 2.79-2.73 (m, 1H), 2.50-2.41 (m, 2H), 2.29 (s, 3H), 1.89 (s, 3H), 1.36 (t, *J* = 7.3 Hz, 3H), 0.65 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.81, 155.44, 146.73, 145.27, 142.96, 140.26, 139.84, 133.48, 132.30, 131.62, 131.47, 131.16, 128.45, 128.17, 127.93, 127.81, 120.82, 117.48, 116.63, 75.10, 36.73, 28.52, 27.88, 20.52, 20.16, 15.11, 14.13; **HRMS** (ESI) m/z calculated $C_{29}H_{32}BrN_2OS_2^+$ 567.1134; Found 567.1128.

4. Selective Reductive Removal of 1,3-Dithiolanes:



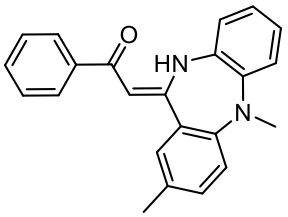
To the 10 mL THF solution of compound **3** (0.2 mmol), under N_2 and at -78℃, was dropwise added a commercial solution of 0.1 M SmI_2 in THF until the resulting solution was permanently blue (4.0 mL, 0.4 mmol). The reaction mixture was stirred for 30 min at room temperature, and then a 0.5 M solution of NH_3 in EtOH (8 mL) was added and the mixture was stirred for 20 min. Finally H_2O was added, and the mixture was saturated with Na_2SO_4. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), and the organic phase, dried with anhydrous Na_2SO_4, was evaporated under reduced pressure. The crude was purified by flash chromatography to give the **7**.

(Z)-2-(2,5-Dimethyl-5,10-dihydro-11H-dibenzo[b,e][1,4]diazepin-11-ylidene)-1-(4-methoxyphenyl)ethan-1-one (7a):



Orange solid (55.5 mg, 75% yield); m.p. 56.5-57.1 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.62 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 2.1 Hz, 1H), 7.22 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.10-7.07 (m, 2H), 7.03 (d, *J* = 7.5 Hz, 1H), 7.02-6.99 (m, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.06 (s, 1H), 3.87 (s, 3H), 3.29 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.18, 162.62, 162.01, 151.92, 146.91, 133.35, 133.29, 133.07, 132.55, 130.13, 129.04, 128.38, 125.14, 123.96, 122.37, 118.28, 117.67, 113.55, 93.44, 55.39, 37.64, 20.61; **HRMS** (ESI) m/z calculated $C_{24}H_{23}N_2O_2^+$ 371.1754; Found 371.1763.

(Z)-2-(2,5-Dimethyl-5,10-dihydro-11H-dibenzo[b,e][1,4]diazepin-11-ylidene)-1-phenylethan-1-one (7b):



Orange solid (42.2 mg, 62% yield); m.p. 68.5-69.3 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.70 (s, 1H), 7.97 (d, *J* = 6.5 Hz, 2H), 7.49-7.43 (m, 3H), 7.36 (s, 1H), 7.23 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.11-7.09 (m, 2H), 7.04 (d, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 8.3 Hz, 2H), 6.10 (s, 1H), 3.30 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.03, 163.23, 152.03, 147.09, 140.42, 133.41, 133.15, 132.71, 130.94, 130.17, 128.33, 128.21, 127.14, 125.38, 124.00, 122.48, 118.34, 117.72, 93.85, 37.63, 20.61; **HRMS** (ESI) m/z calculated $C_{23}H_{21}N_2O^+$ 341.1648; Found 341.1655.

IV. ORTEP Drawing of Compound 3at:

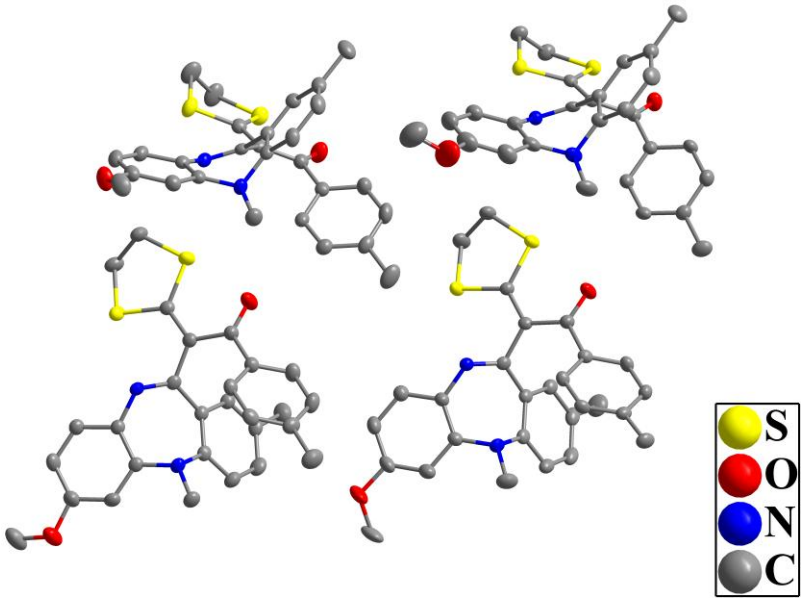


Figure 5. The ORTEP drawing of crystal 3at (The ellipsoid contour percent probability level is 50%).

Method of Crystallization: The compounds **3at** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

References:

1. (a) S. Yuan, X. Liu, Z. Huang, S. Gui, Y. Diao, Y.-Y. Peng and Q. Ding, Tetrabutylammonium Chloride-Induced Cascade Radical Addition/ Cyclization of O-Isocyanodiaryl Amines: A Novel Protocol for the Synthesis of 11-Trifluoromethylated Dibenzodiazepines, *J. Org. Chem.*, 2022, **87**, 16542−16549. (b) X. Liu, S. Yuan, Y. Liu, M. Ni, J. Xu, S. Gui, Y.-Y. Peng and Q. Ding, Mn(III)-Mediated Radical Addition/Cyclization of Isocyanides with Aryl Boronic Acids/Diarylphosphine Oxides: Access to 11-Functionalized Dibenzodiazepines, *J. Org. Chem.*, 2023, **88**, 198−210. (c) Y. Liu, W. Gao, S. Yuan, M. Ni, T. Hao, C. Zeng, X. Xu, Y. Fu, Y. Peng and Q. Ding, One-pot synthesis of 11-sulfenyl dibenzodiazepines via tandem sulfenylation/ cyclization of o-isocyanodiaryl amines and diaryl disulfides, *Org. Biomol. Chem.*, 2023, **21**, 4257–4263. (d) S. Yuan, Y. Liu, M. Ni, T. Hao, Y. Peng and Q. Ding, $Fe(acac)_2$/TBHP-promoted synthesis of 11-functionalized dibenzodiazepines via alkoxycarbonylation and carboxamidation of o-isocyanodiaryl amines, *Chem. Commun.*, 2022, **58**, 10985–10988.
2. (a) X.-C. Xu, D. N. Wu, Y. X. Liang, M. Yang, H. Y. Yuan and Y.-L. Zhao, Visible Light-Induced Coupling Cyclization Reaction of α-Diazosulfonium Triflates with α-Oxocarboxylic Acids or Alkynes, *J. Org. Chem.*, **2022**, *87*, 16604–16616. (b) X. Li, C. Golz, M. Alcarazo, α-Diazo Sulfonium Triflates: Synthesis, Structure, and Application to the Synthesis of 1-(Dialkylamino)-1,2,3-triazoles, *Angew. Chem. Int. Ed.*, 2021, **60**, 6943−6948.
3. M. Šiauciulis, N. Ahlsten, A. P. Pulis and D. J. Procter, Transition-Metal-Free Cross-Coupling of Benzothiophenes and Styrenes in a Stereoselective Synthesis of Substituted (*E,Z*)-1,3-Dienes *Angew. Chem. Int. Ed*., 2019, **58**, 8779−8783.
4. L. Zhu, H. Yu, Q. Guo, Q. Chen, Z. Xu and R. Wang, C–H Bonds Phosphorylation of Ketene Dithioacetals, *Org. Lett.,* 2015, **17**, 1978–1981.

V. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Compounds 1 and 3-7:

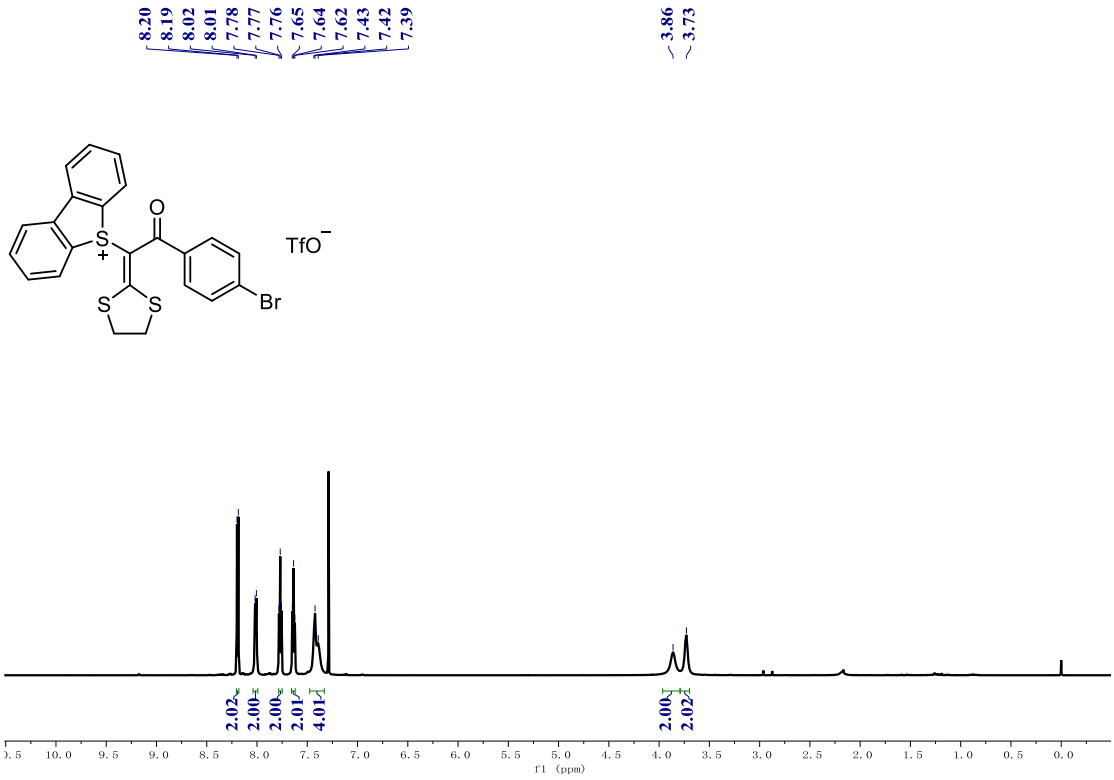


Figure 6. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **1a**

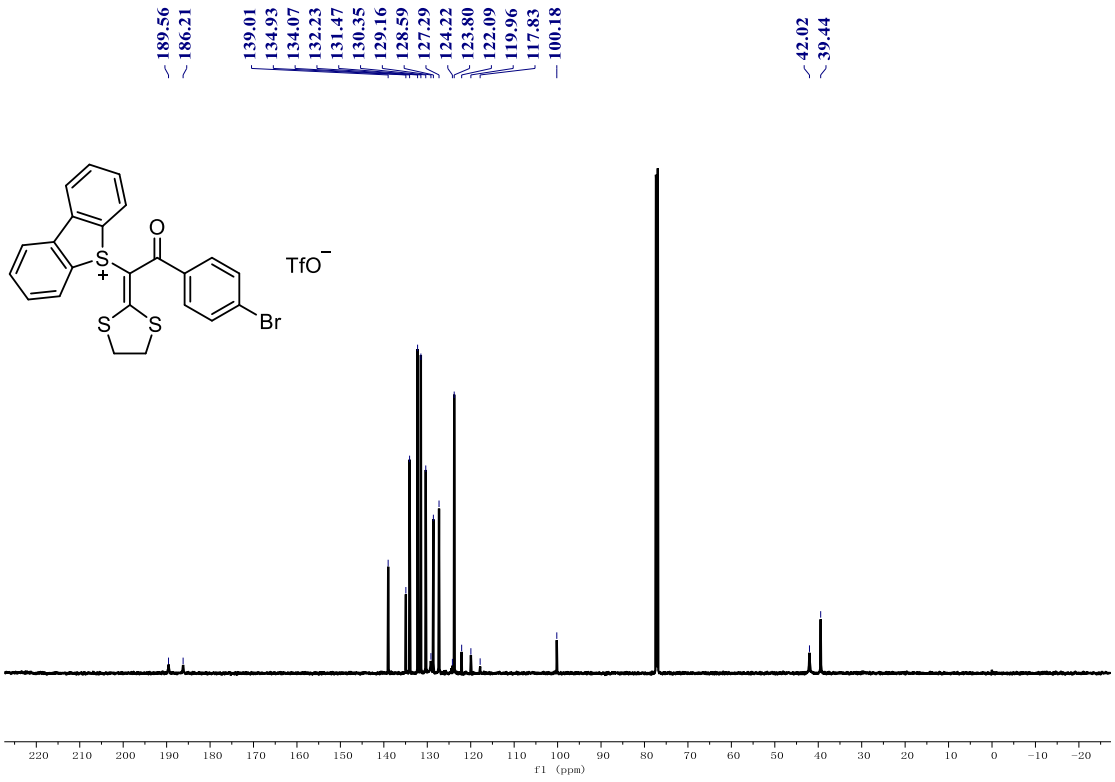


Figure 7. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **1a**

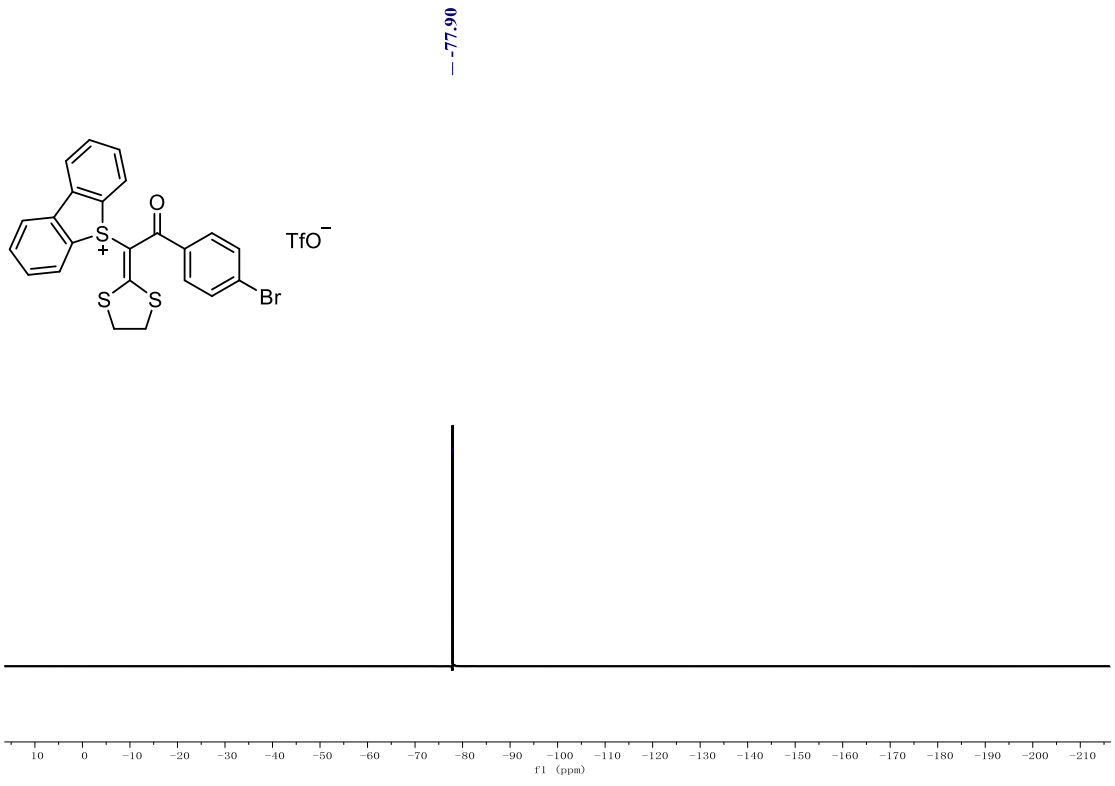


Figure 8. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **1a**

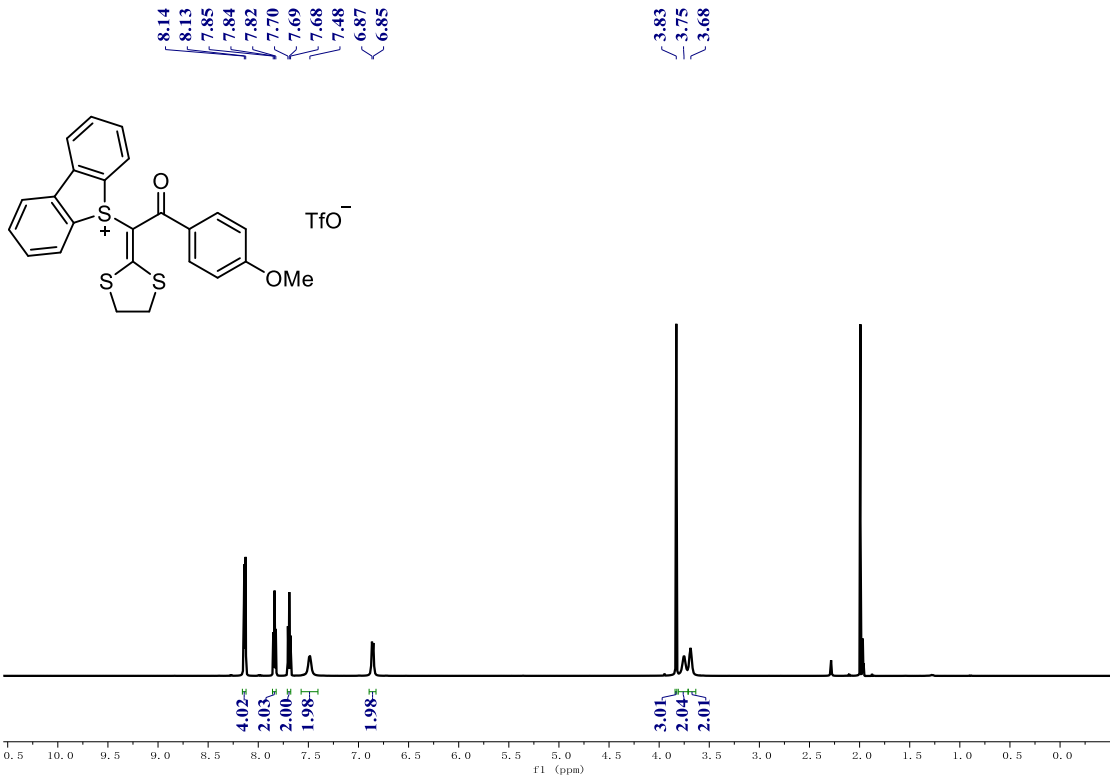


Figure 9. ^{1}H NMR (600 MHz, CD_3CN) spectra of compound **1b**

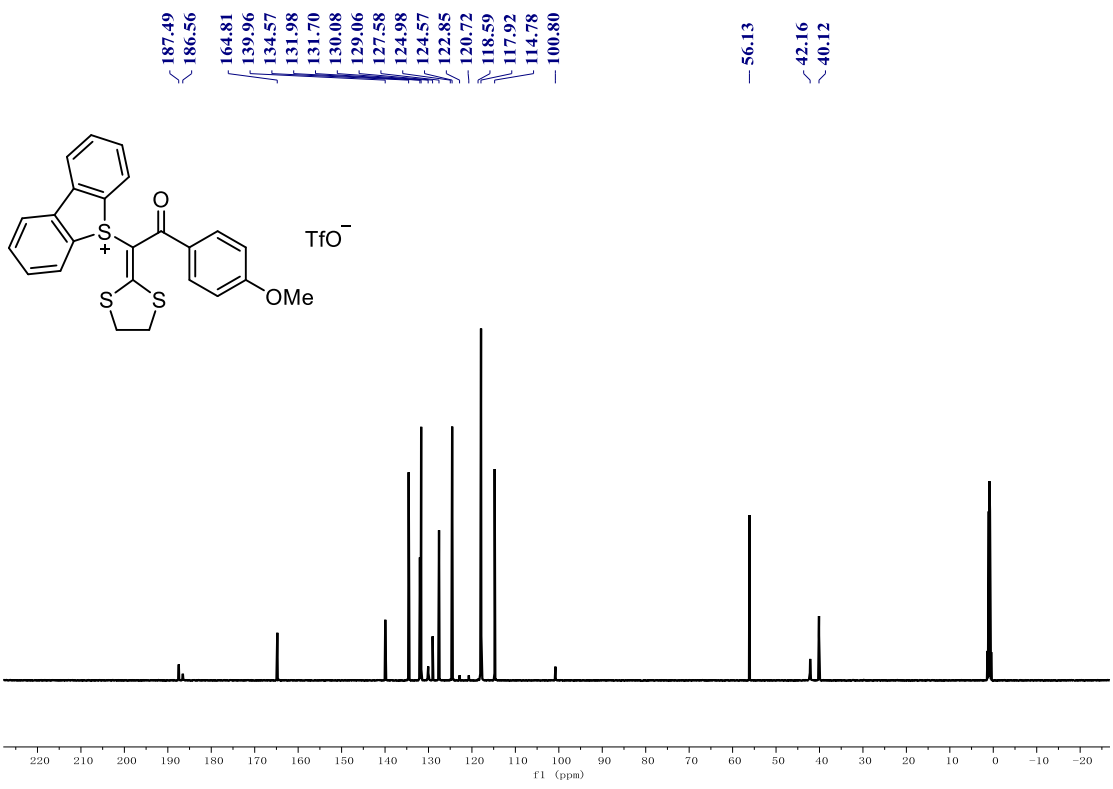


Figure 10. ^{13}C NMR (151 MHz, CD_3CN) spectra of compound **1b**

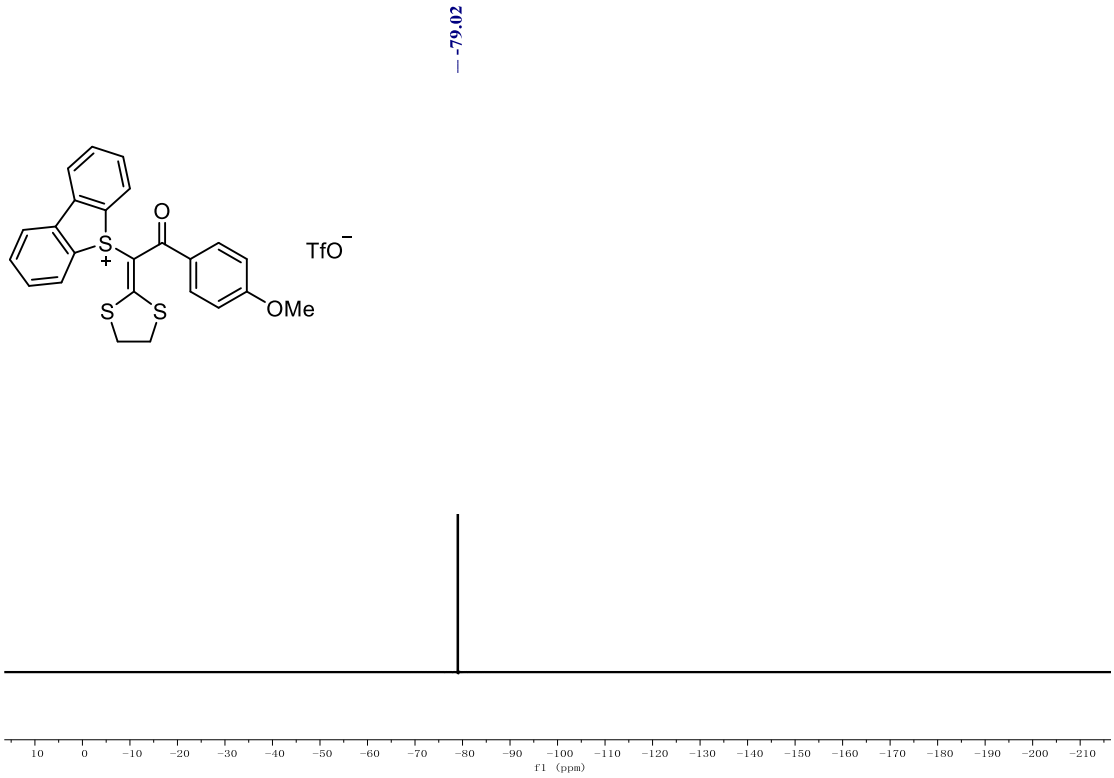


Figure 11. ^{19}F NMR (565 MHz, CD_3CN) spectra of compound **1b**

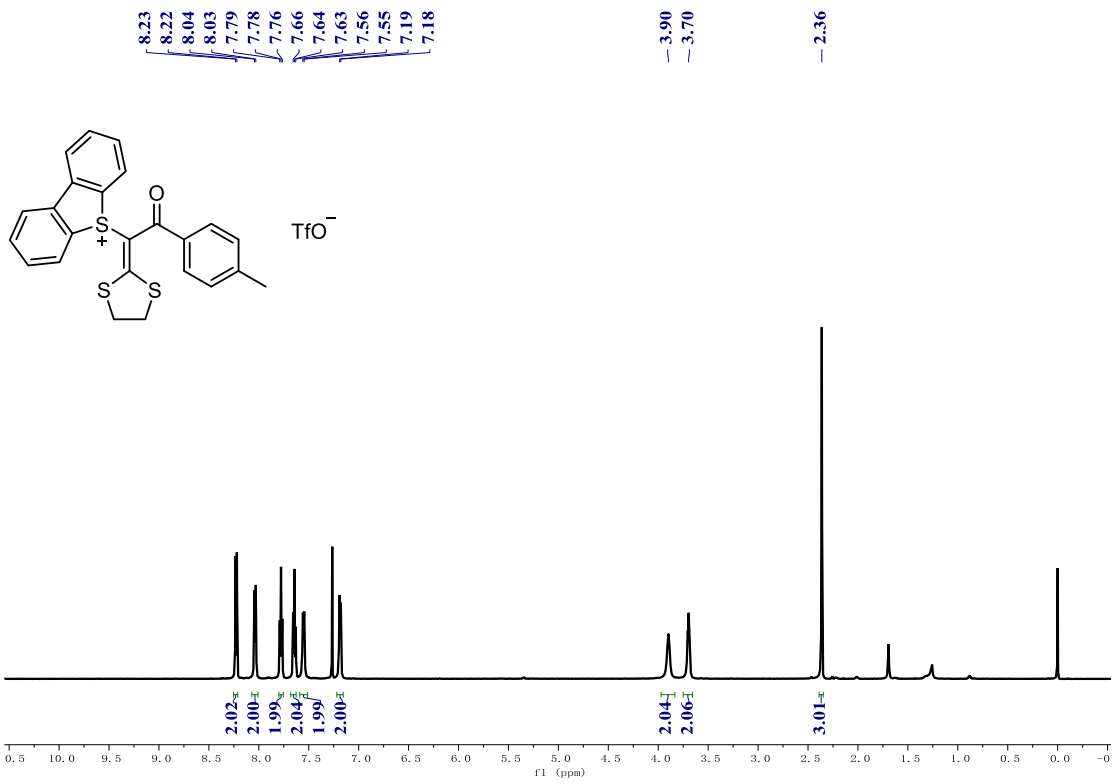


Figure 12. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **1c**

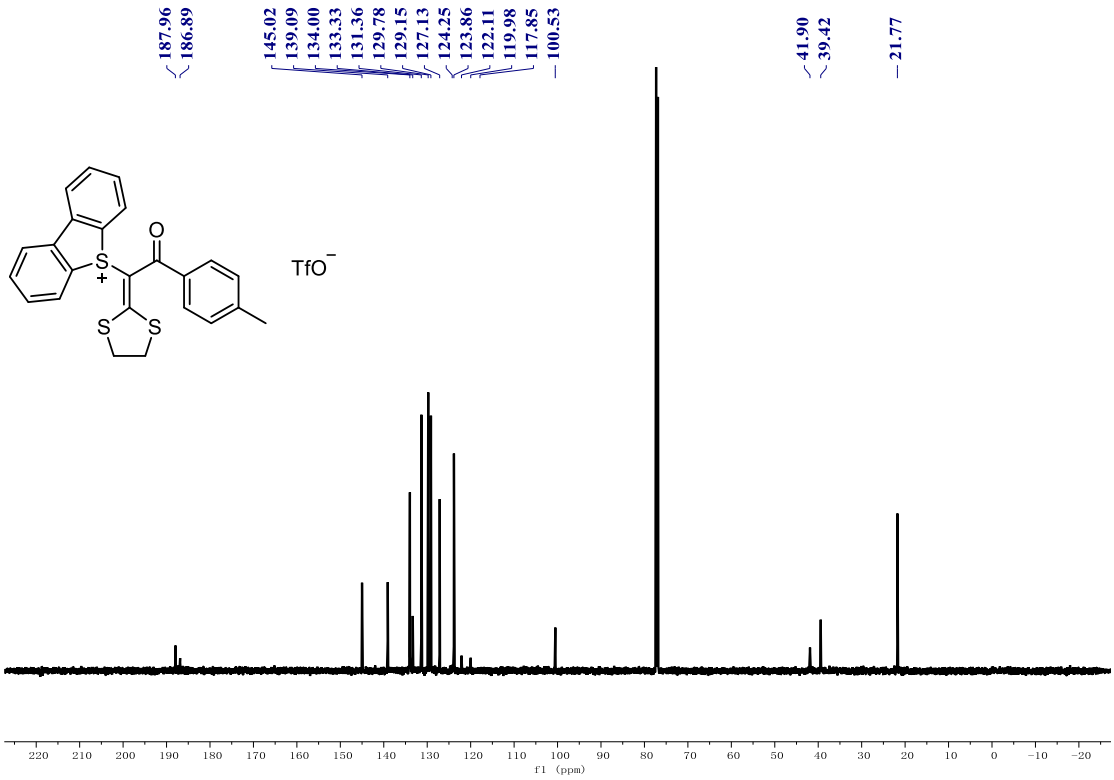


Figure 13. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **1c**

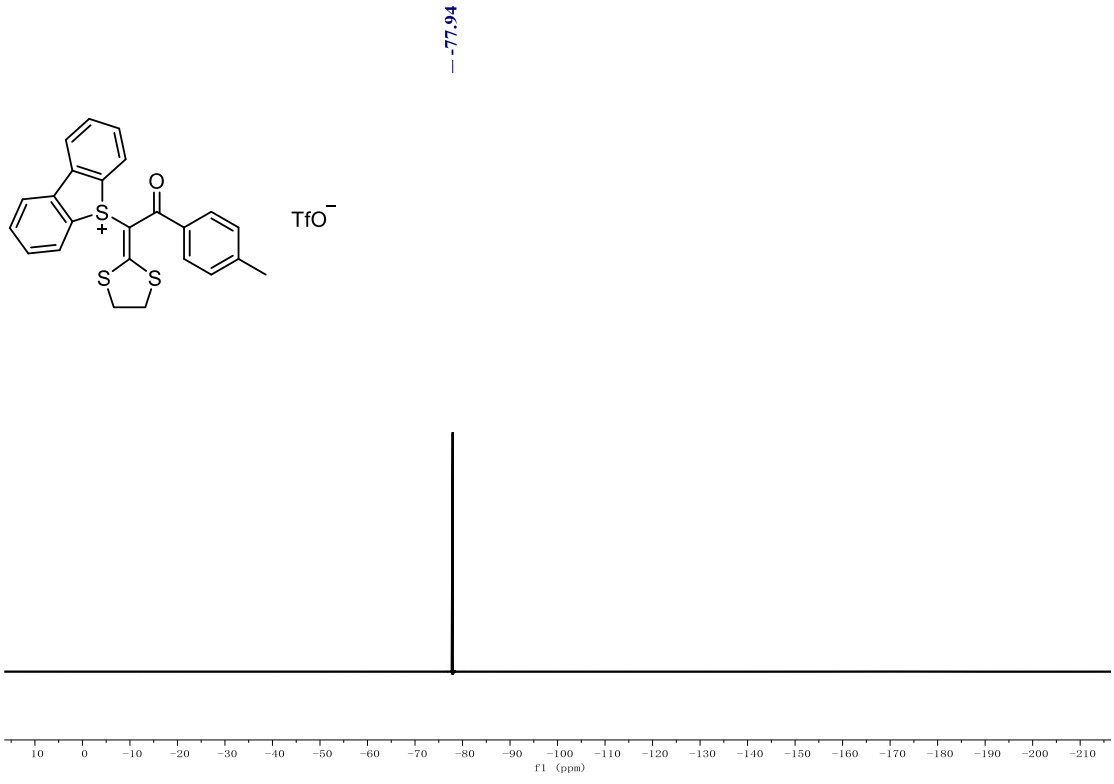


Figure 14. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **1c**

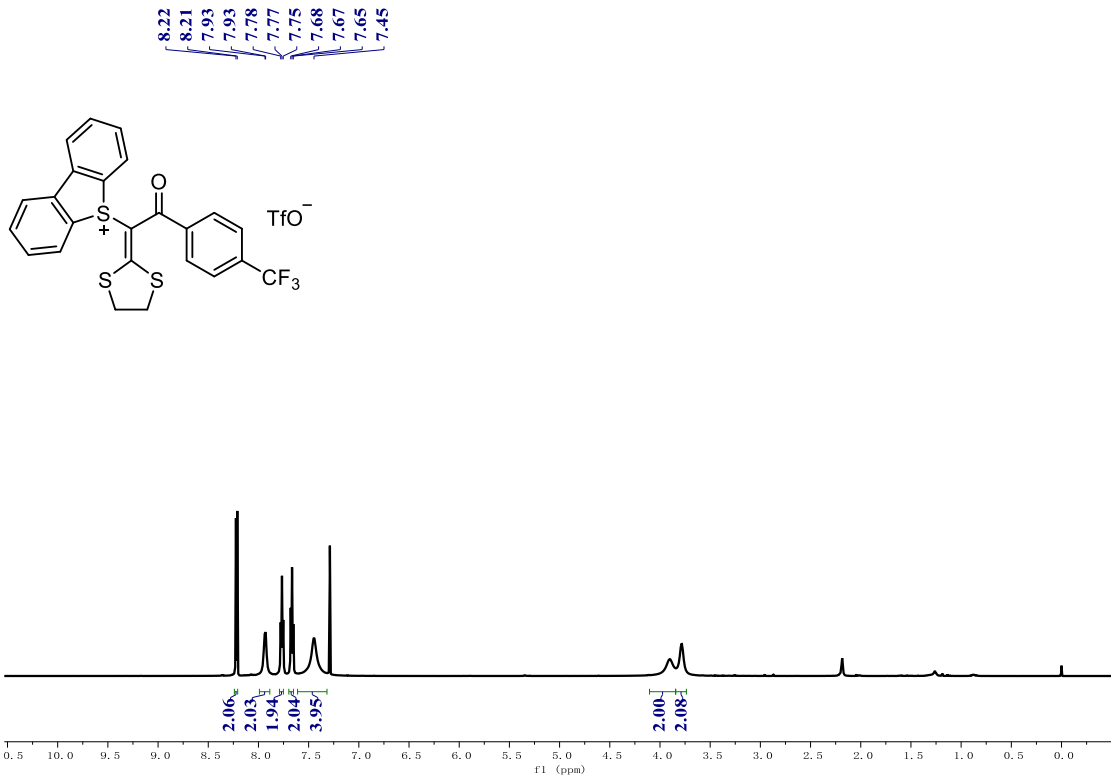


Figure 15. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **1d**

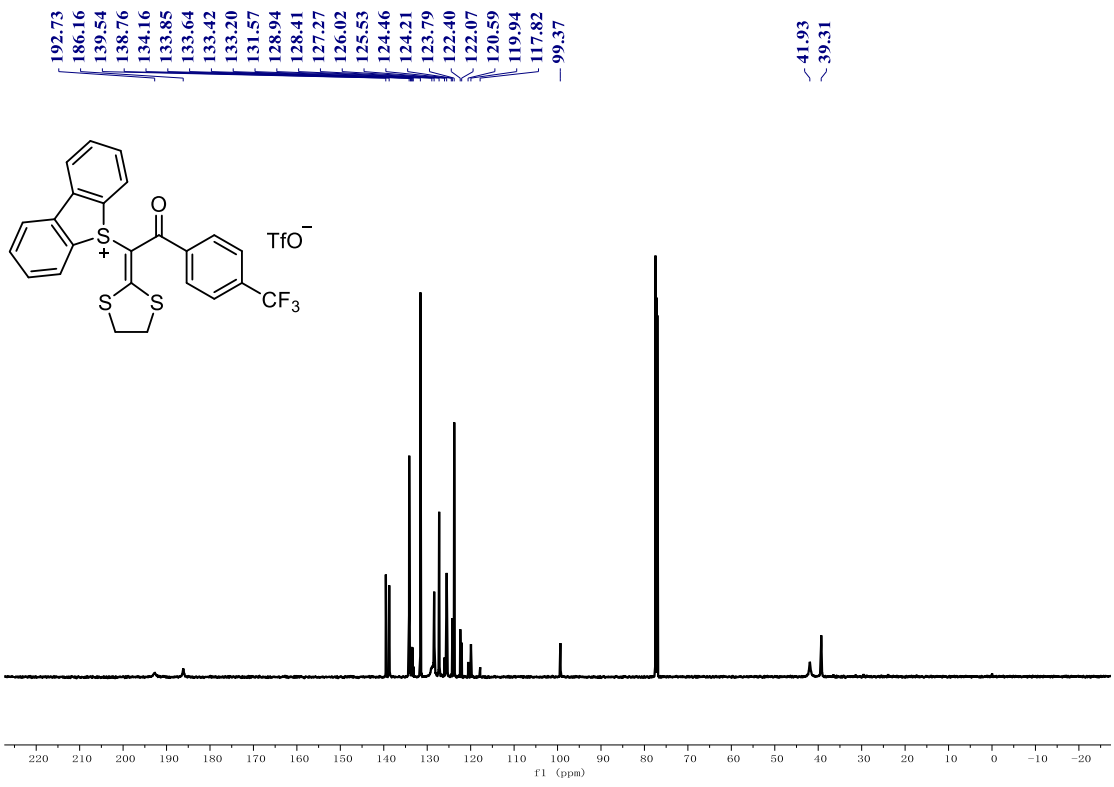


Figure 16. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **1d**

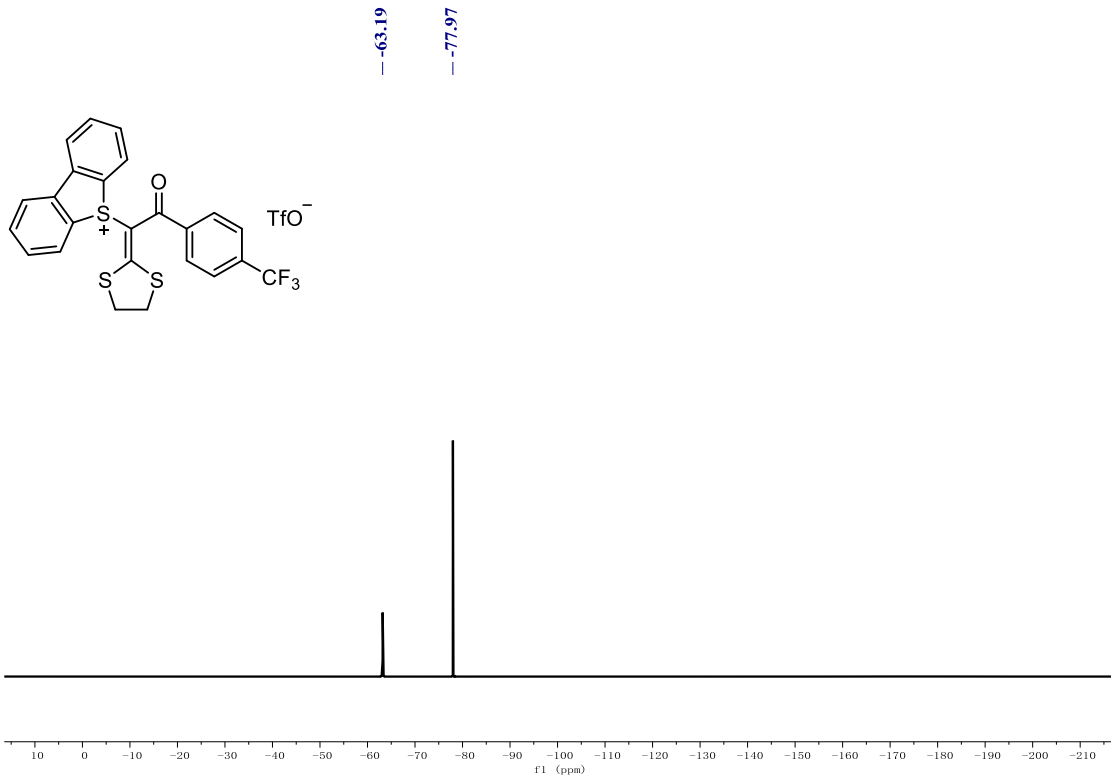


Figure 17. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **1d**

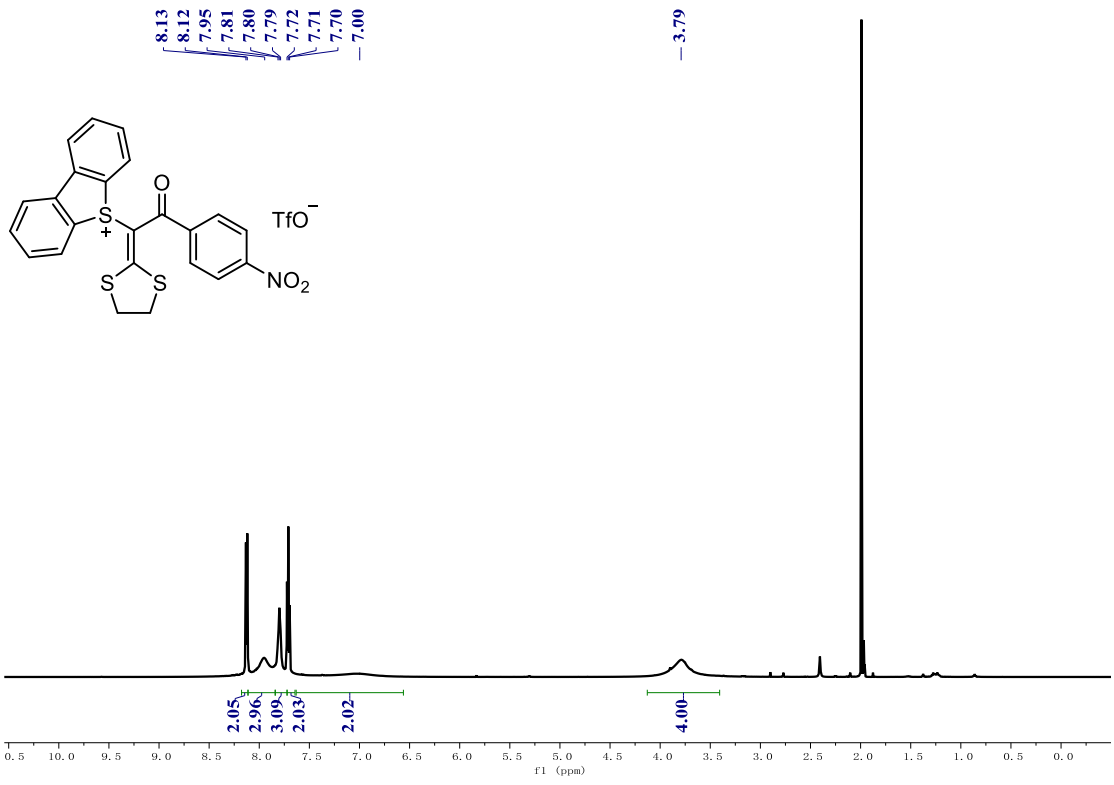


Figure 18. ^{1}H NMR (600 MHz, CD_3CN) spectra of compound **1e**

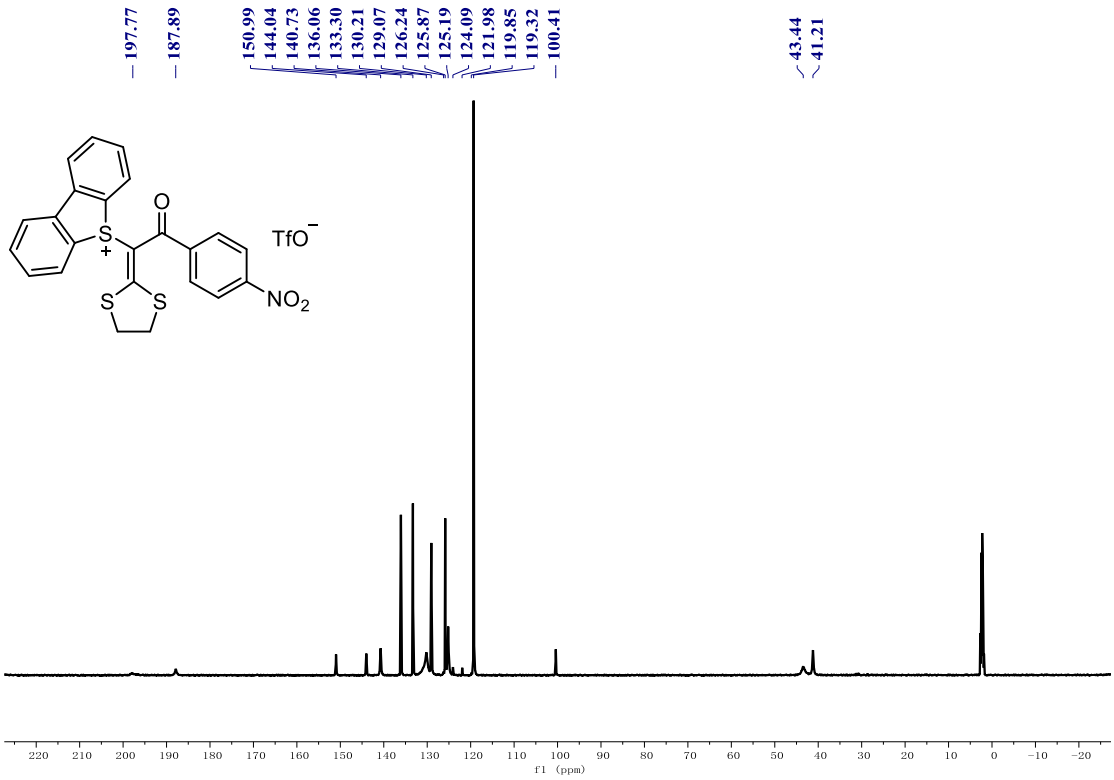


Figure 19. ^{13}C NMR (151 MHz, CD_3CN) spectra of compound **1e**

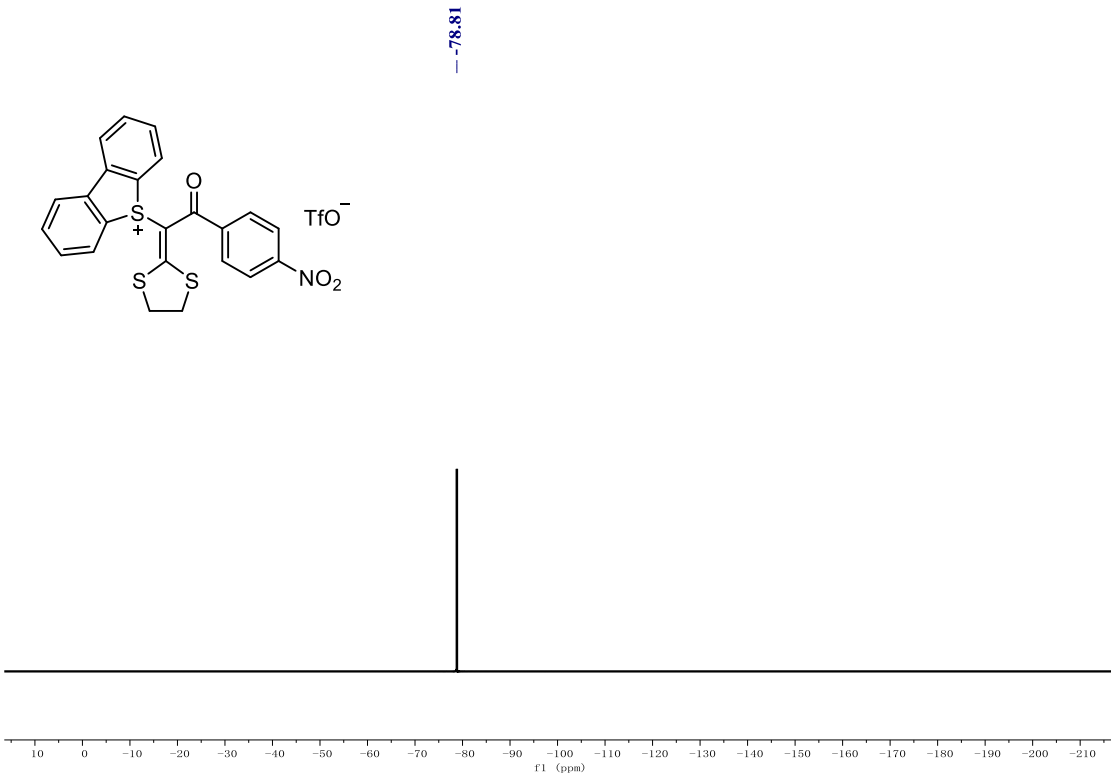


Figure 20. ^{19}F NMR (565 MHz, CD_3CN) spectra of compound **1e**

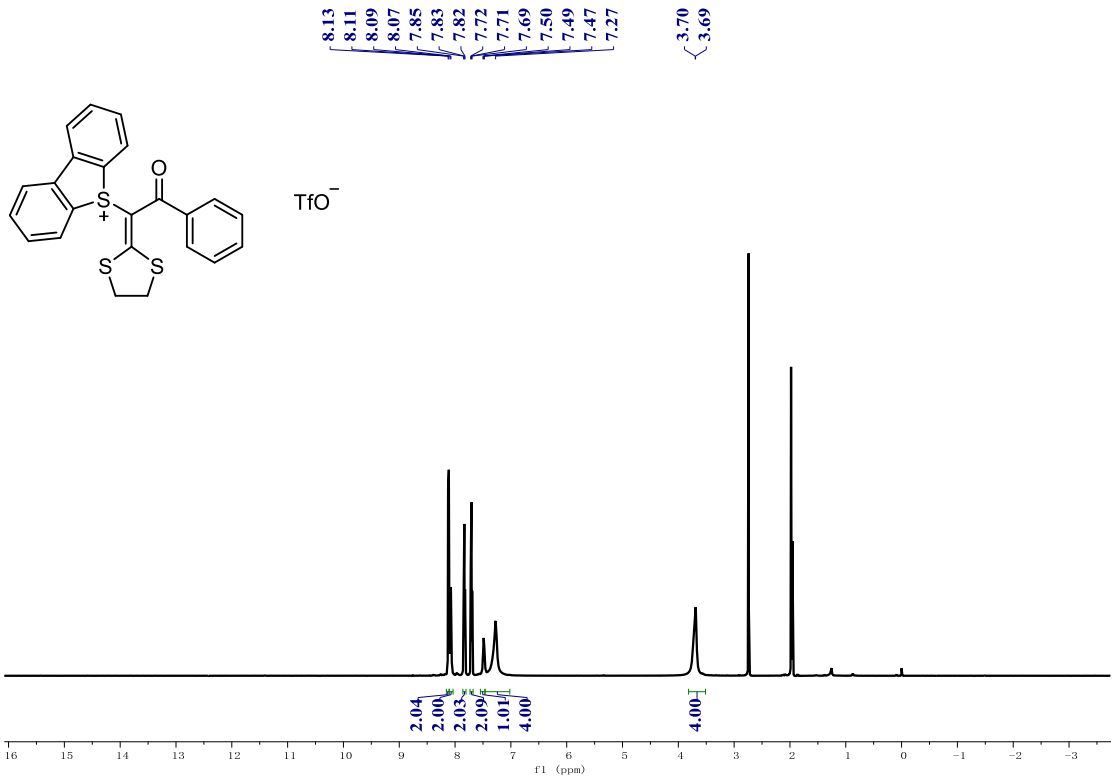


Figure 21. ^{1}H NMR (600 MHz, CD_3CN) spectra of compound **1f**

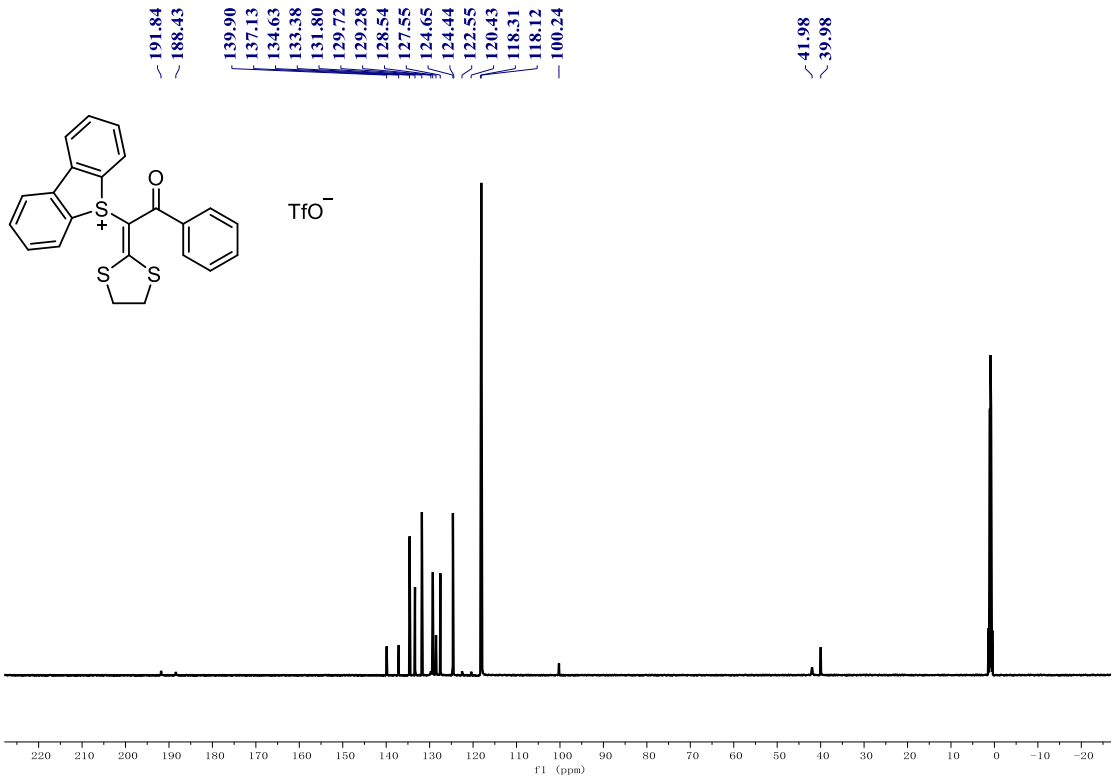


Figure 22. ^{13}C NMR (151 MHz, CD_3CN) spectra of compound **1f**

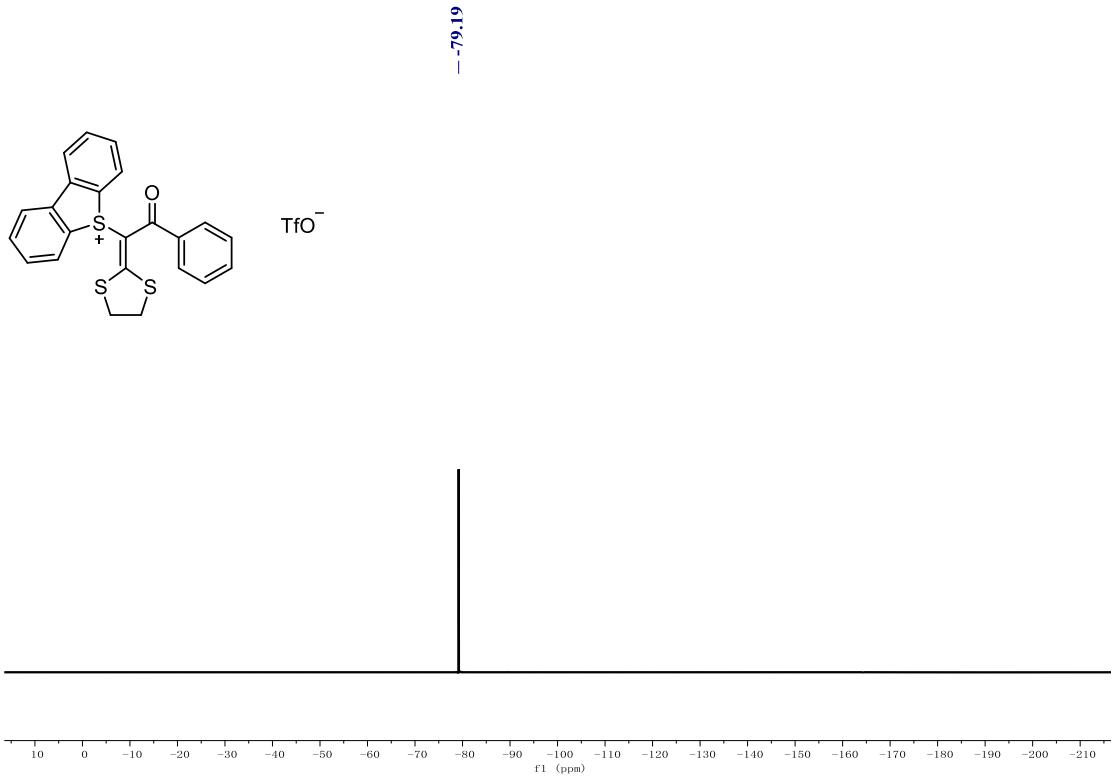


Figure 23. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **1f**

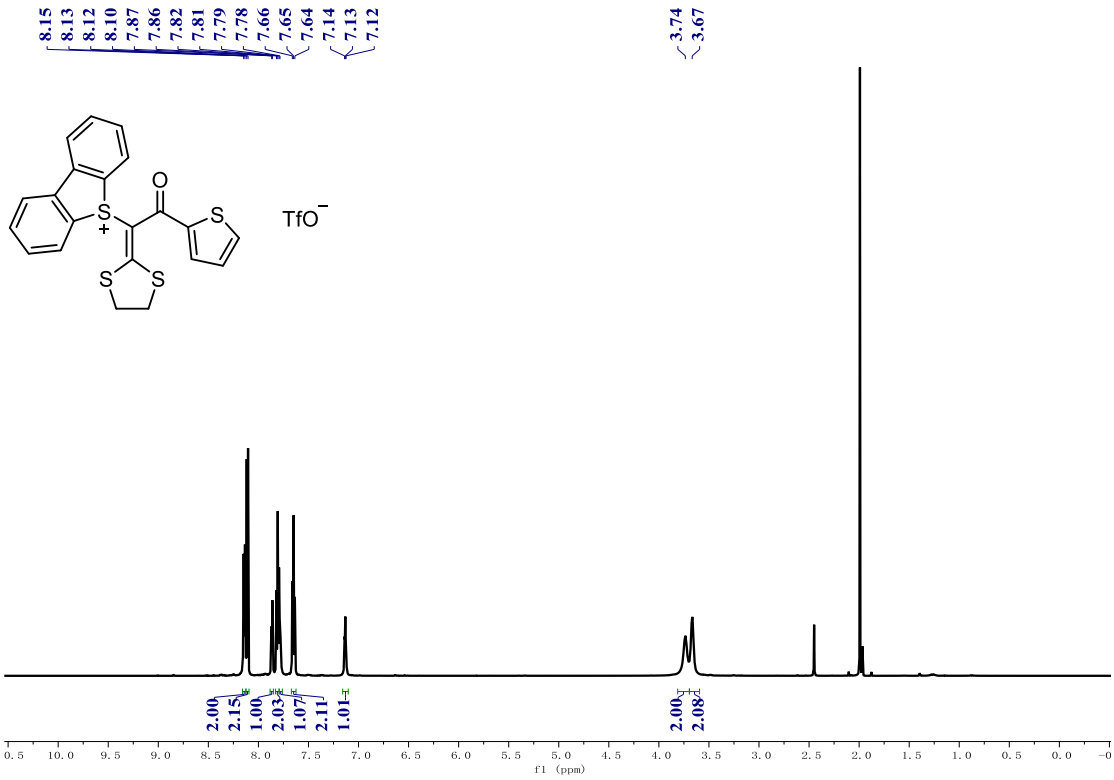


Figure 24. ^{1}H NMR (600 MHz, CD_3CN) spectra of compound **1g**

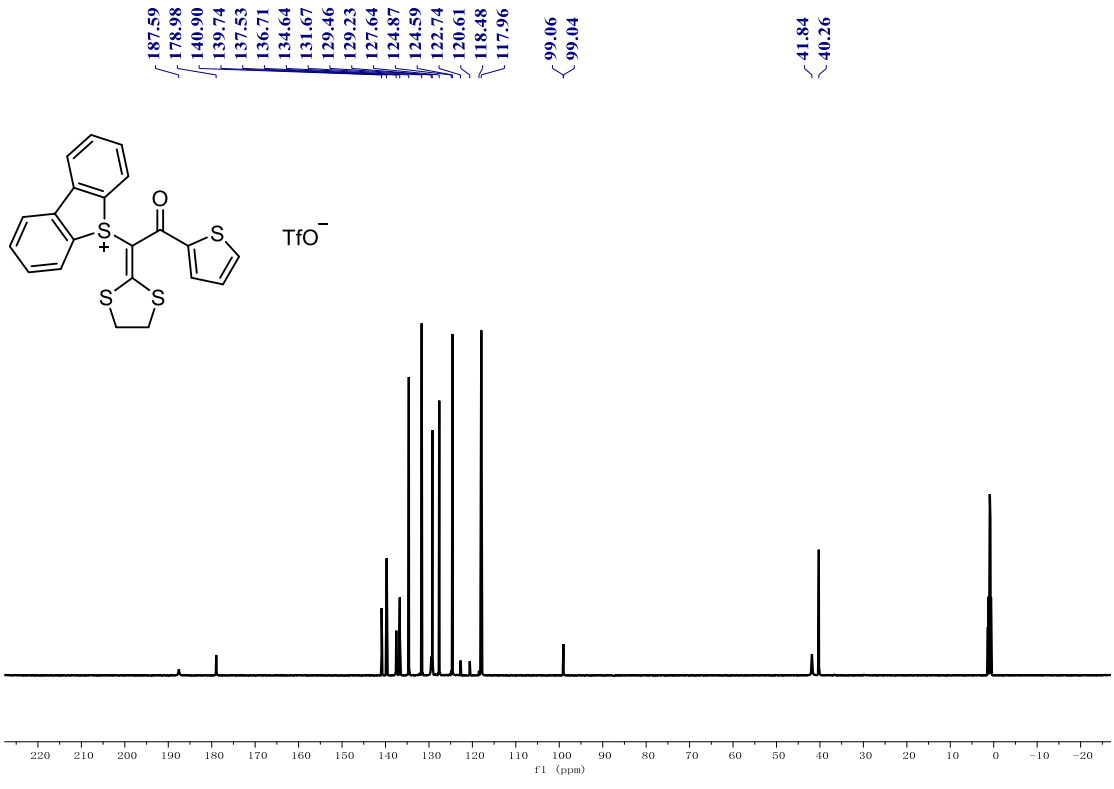


Figure 25. ^{13}C NMR (151 MHz, CD_3CN) spectra of compound **1g**

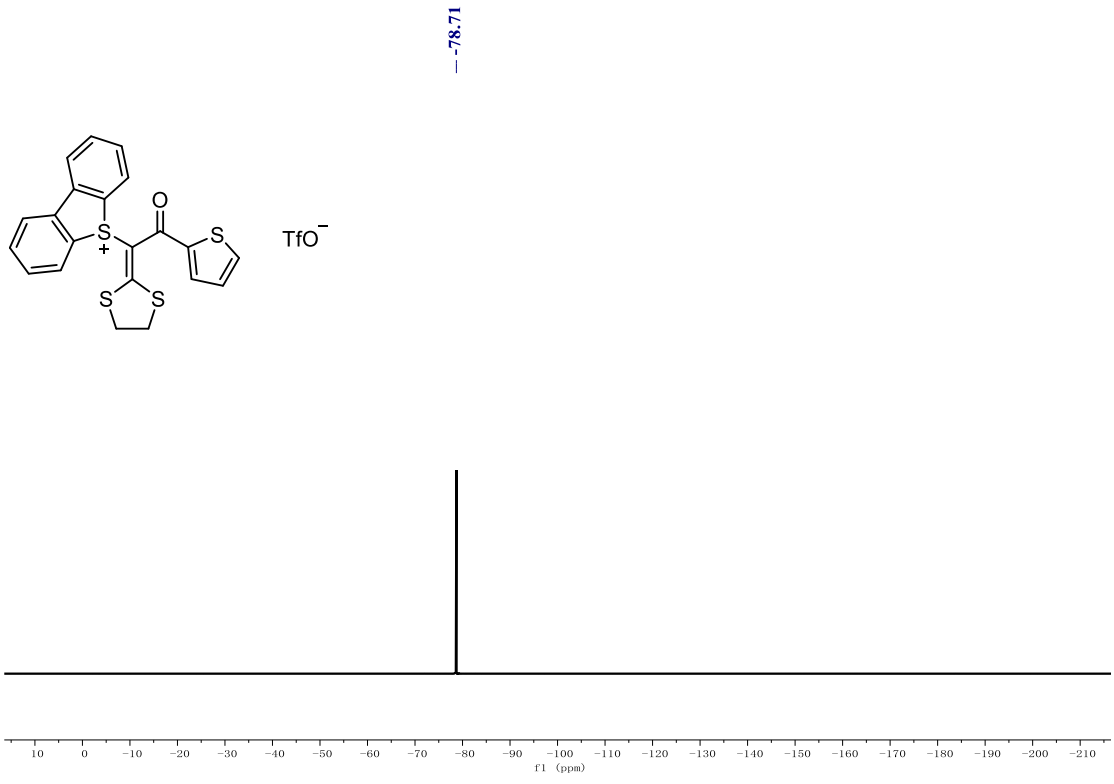


Figure 26. ^{19}F NMR (565 MHz, CD_3CN) spectra of compound **1g**

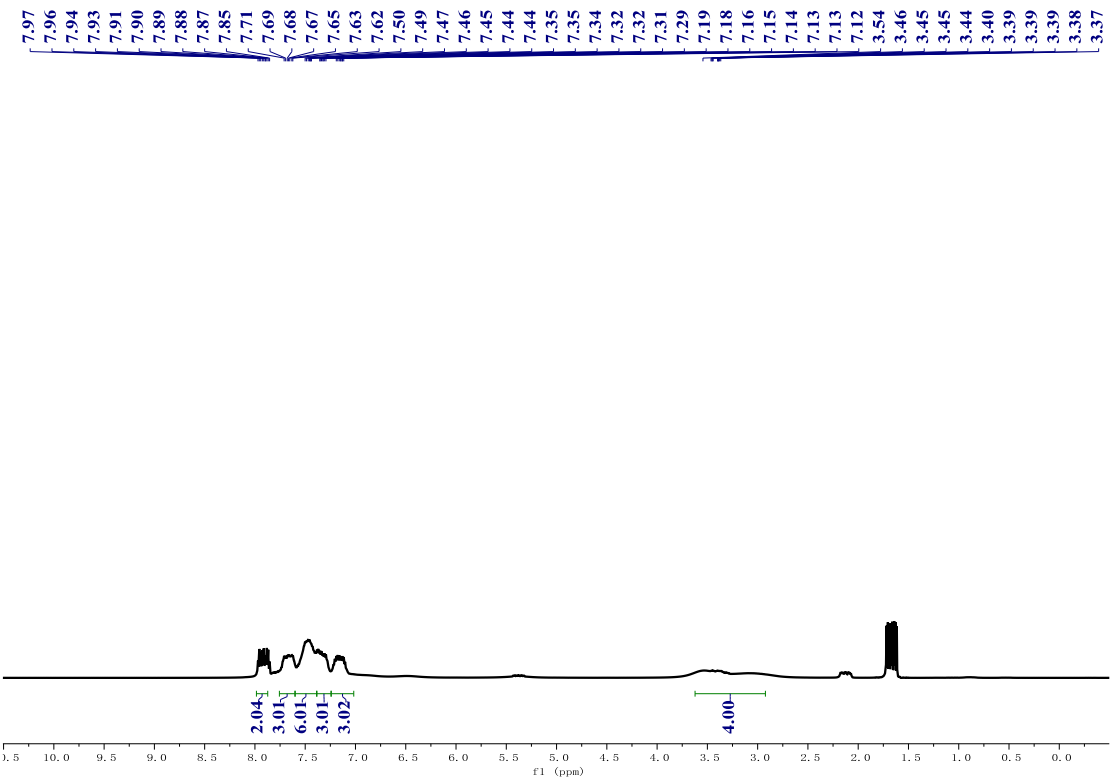


Figure 27. ^{1}H NMR (600 MHz, CD_3CN) spectra of compound **1h**

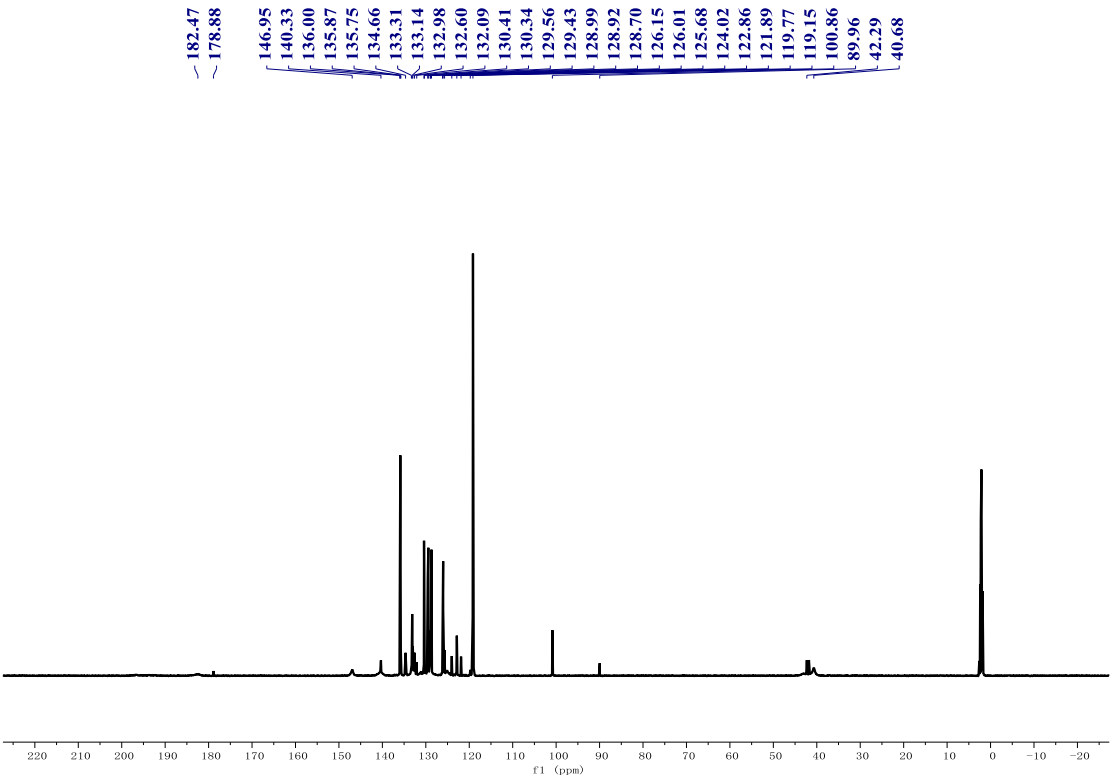


Figure 28. ^{13}C NMR (151 MHz, CD_3CN) spectra of compound **1h**

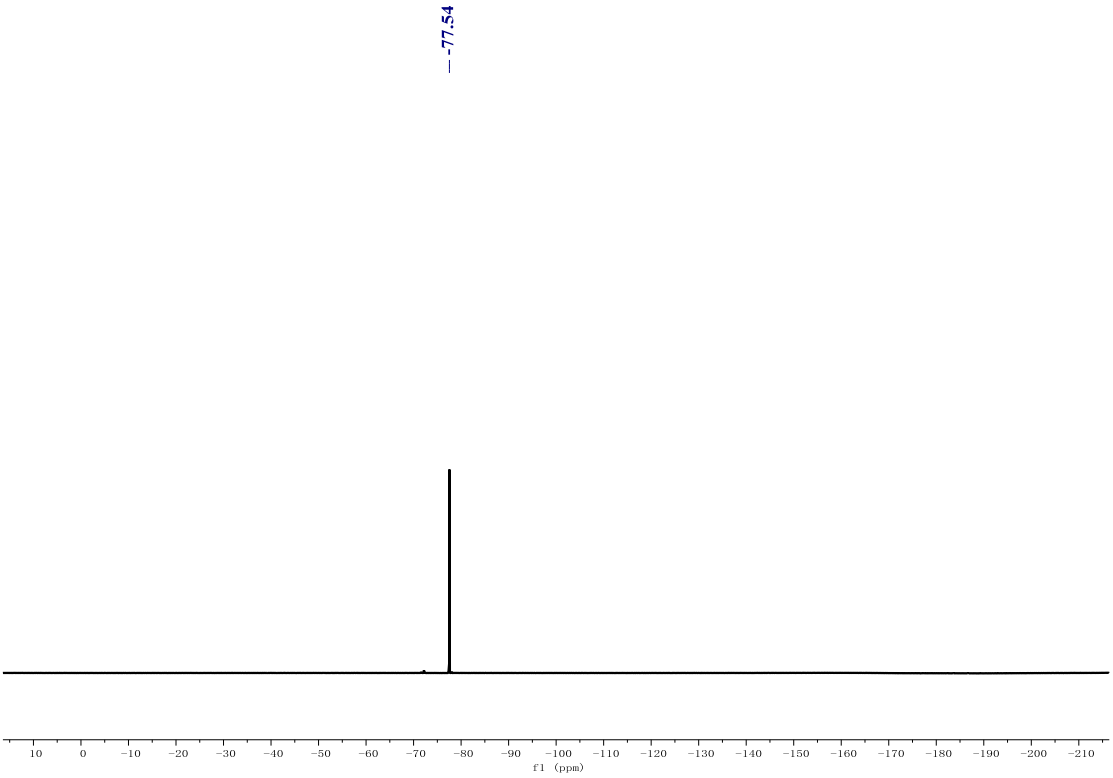


Figure 29. ^{19}F NMR (565 MHz, CD_3CN) spectra of compound **1h**

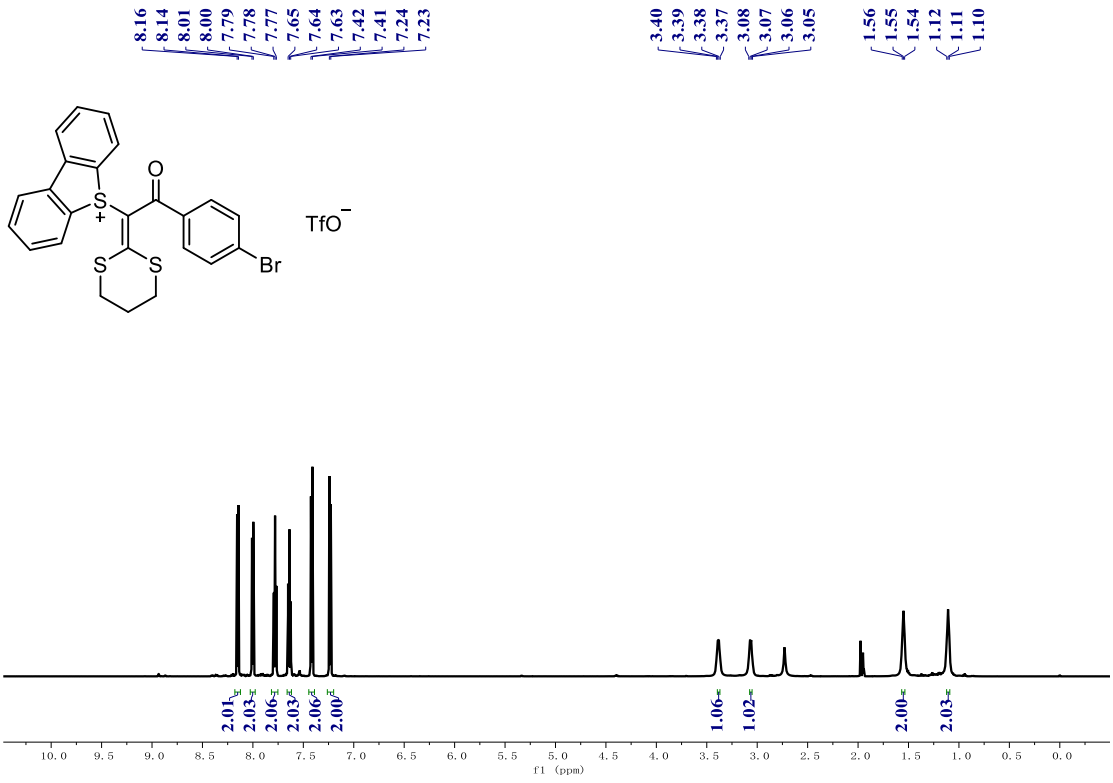


Figure 30. ^{1}H NMR (600 MHz, CD_3CN) spectra of compound **1i**

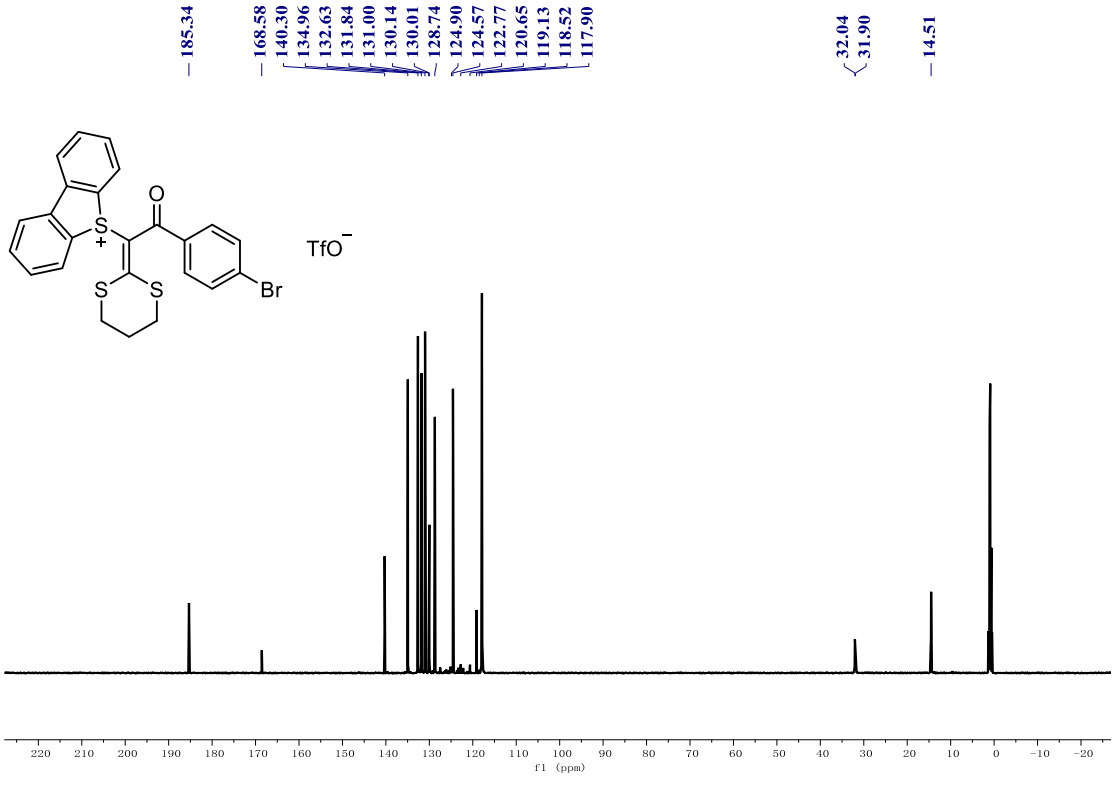


Figure 31. ^{13}C NMR (151 MHz, CD_3CN) spectra of compound **1i**

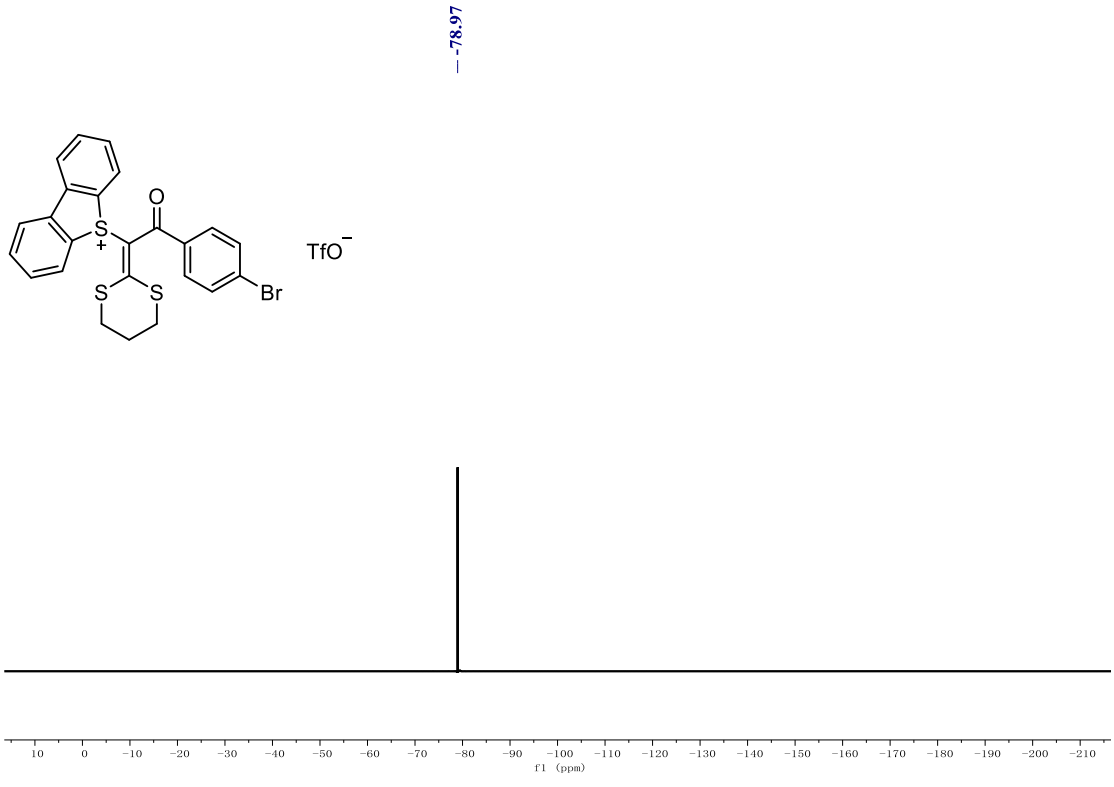


Figure 32. ^{19}F NMR (565 MHz, CD_3CN) spectra of compound **1i**

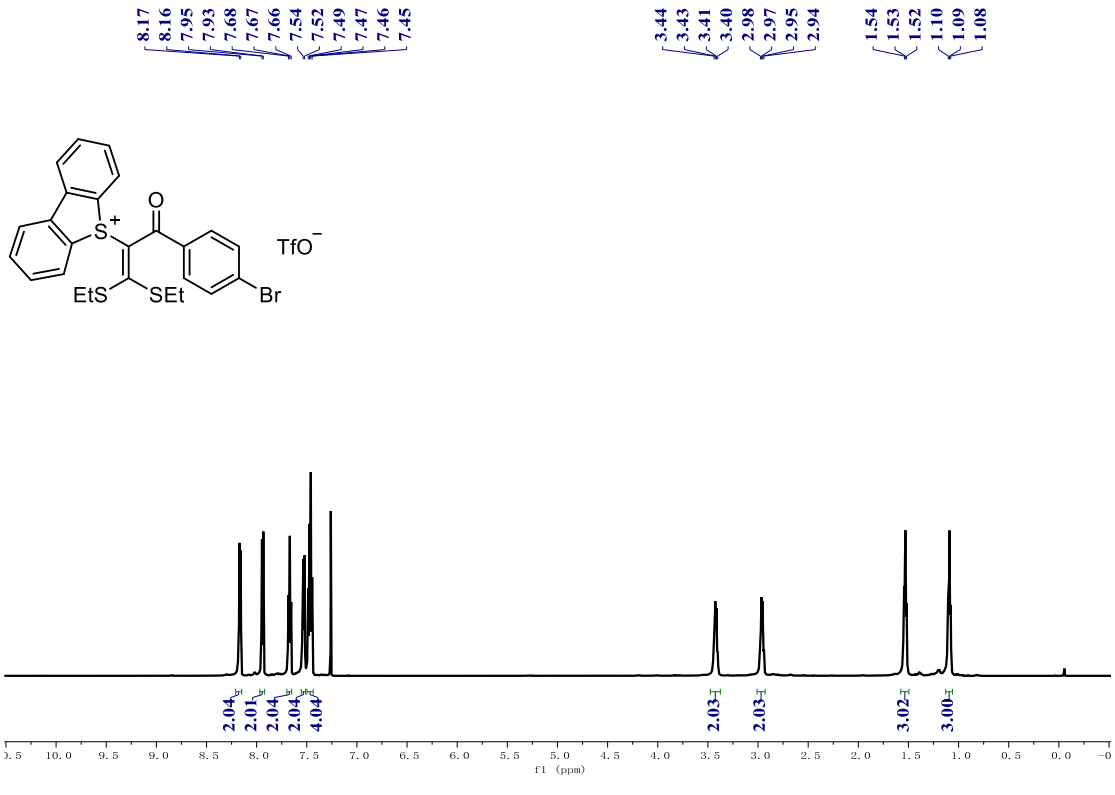


Figure 33. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **1j**

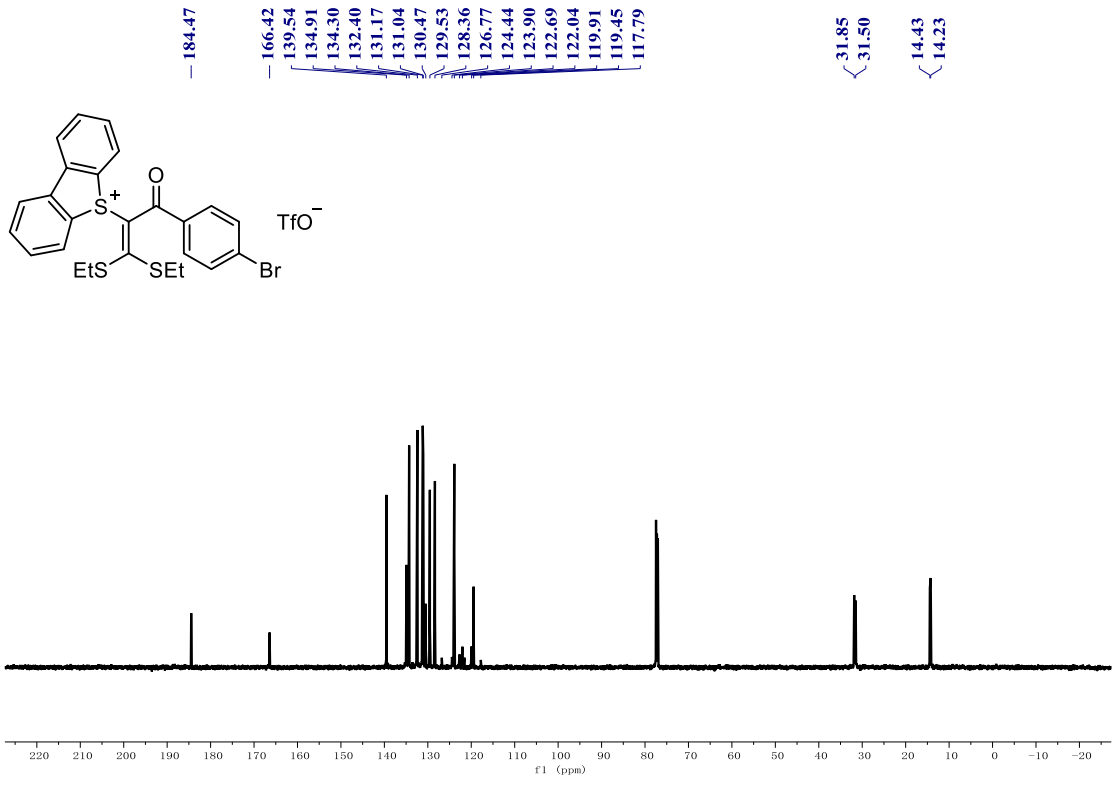


Figure 34. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **1j**

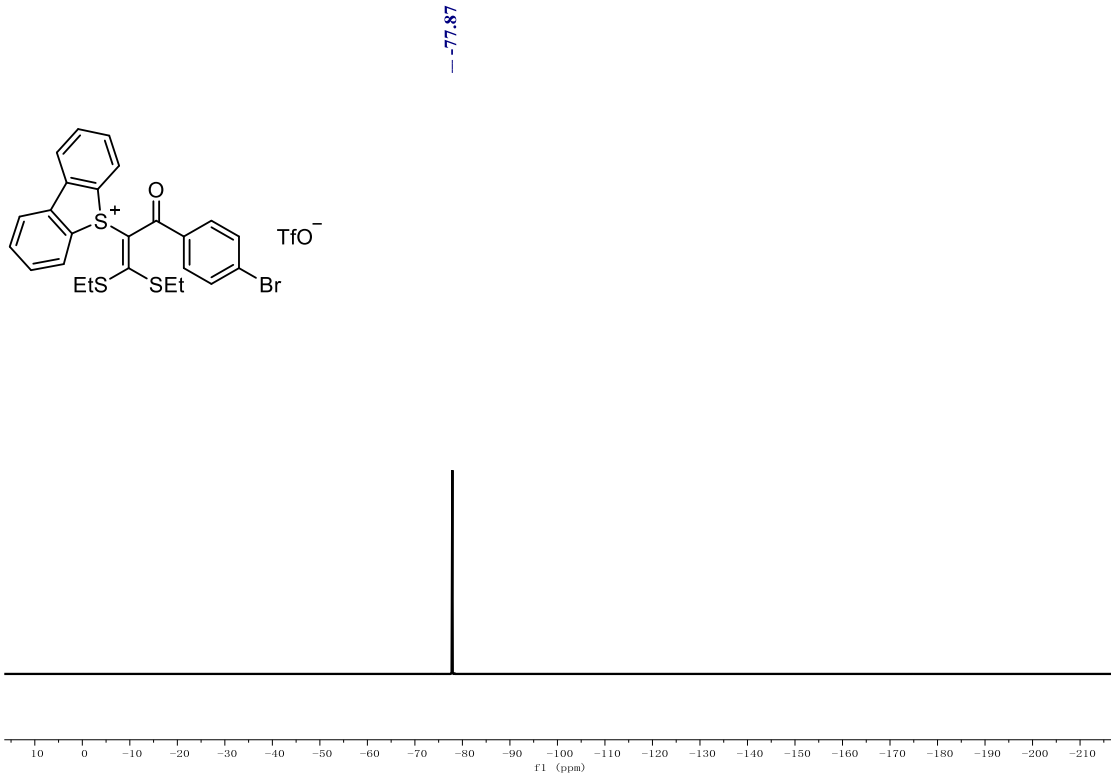


Figure 35. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **1j**

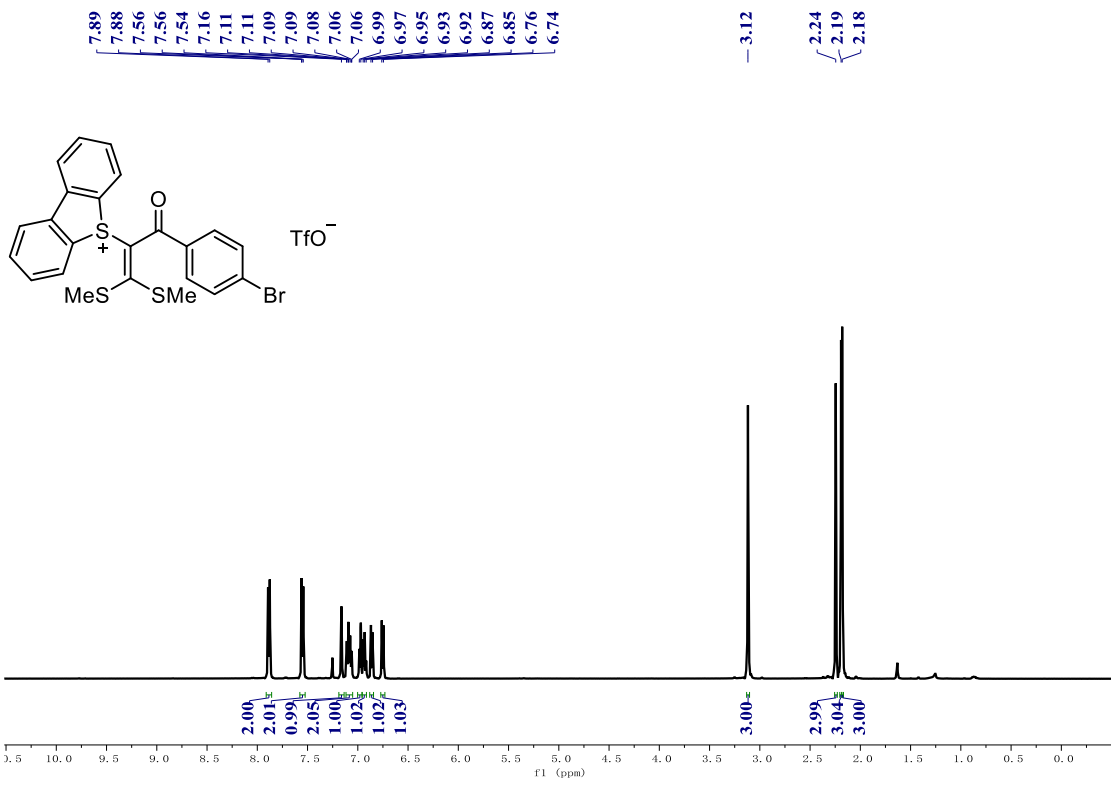


Figure 36. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **1i**

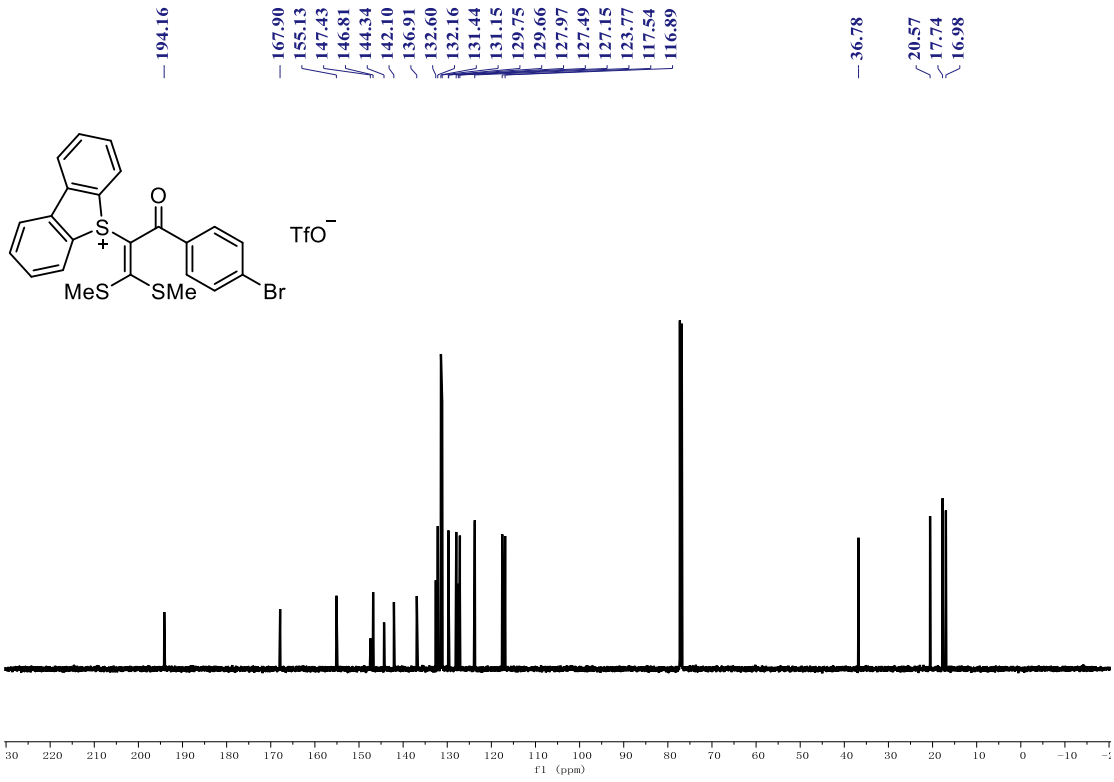


Figure 37. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **1i**

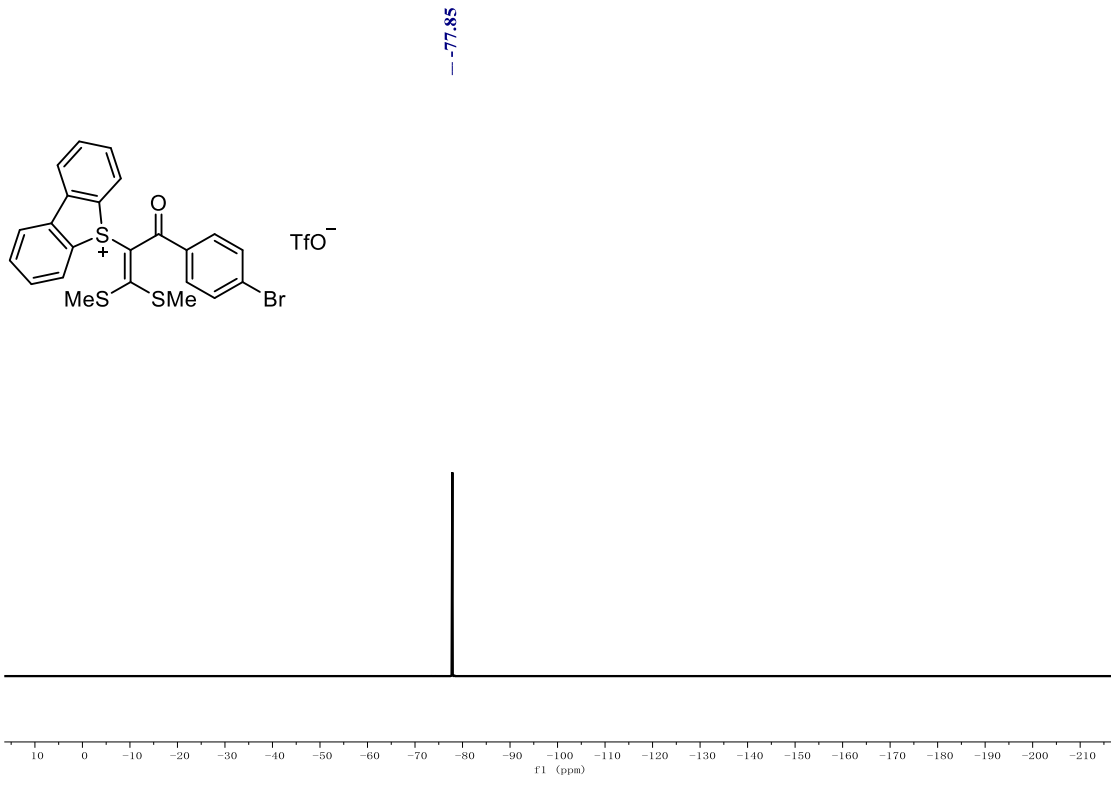


Figure 38. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **1i**

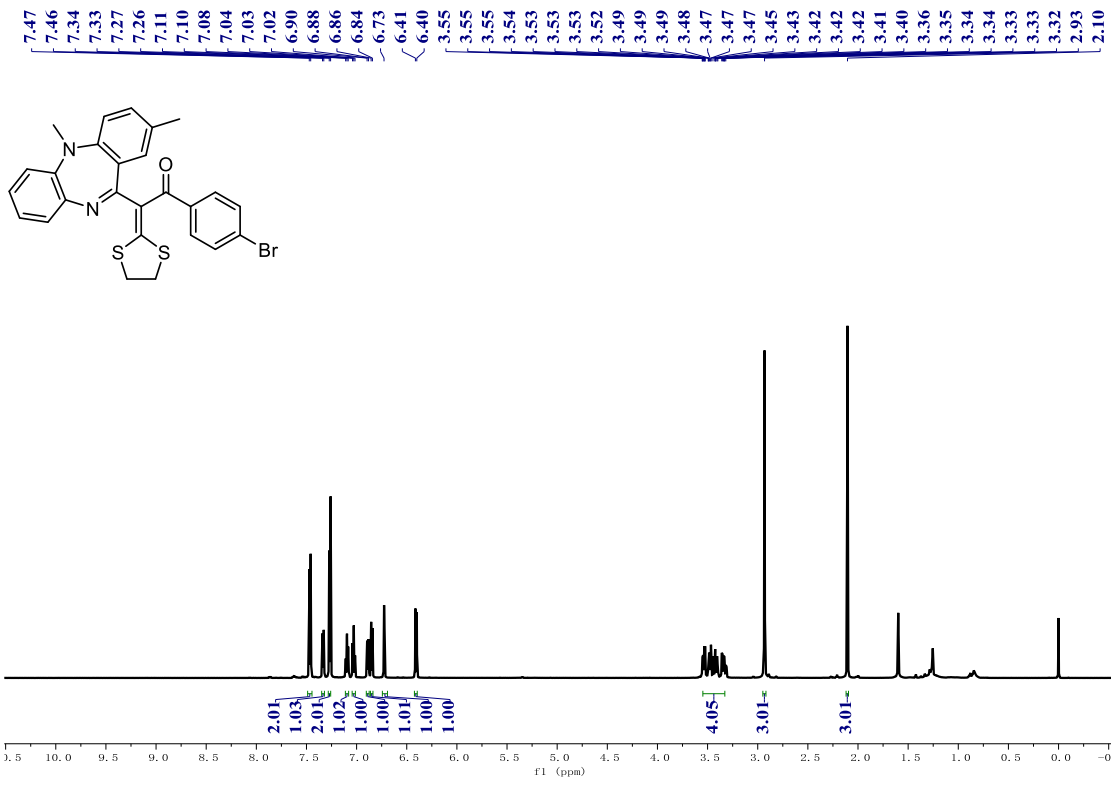


Figure 39. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3aa**

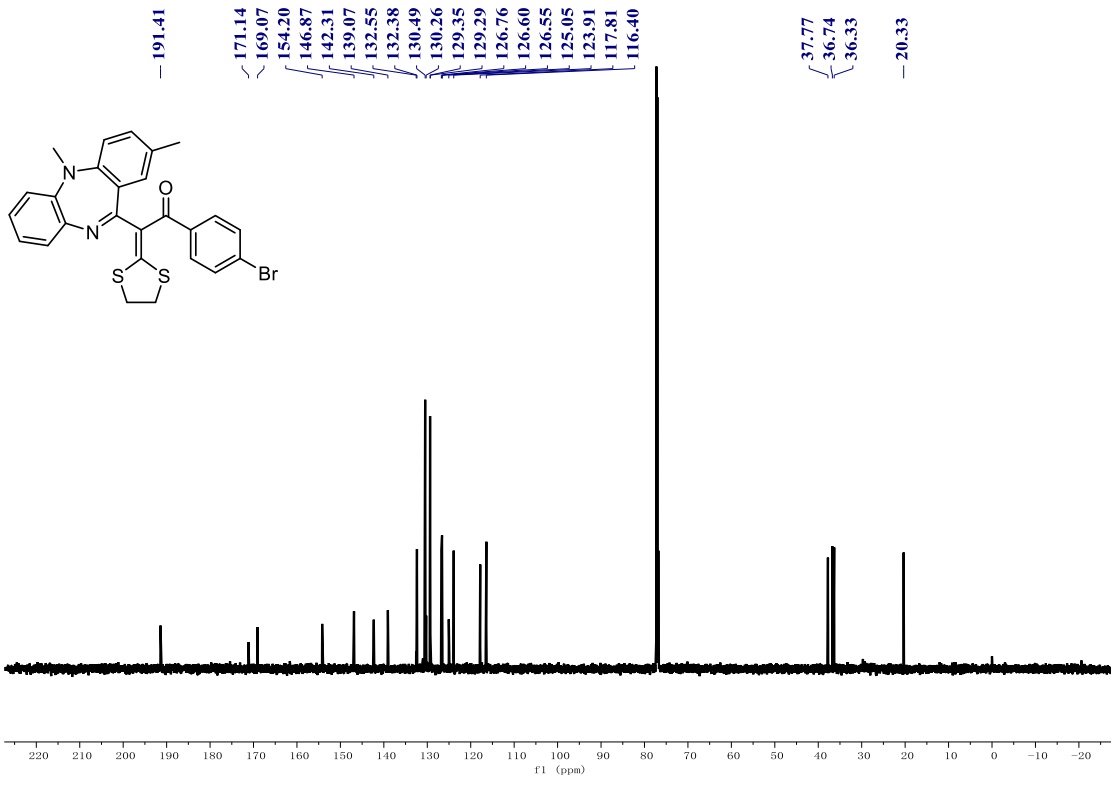


Figure 40. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3aa**

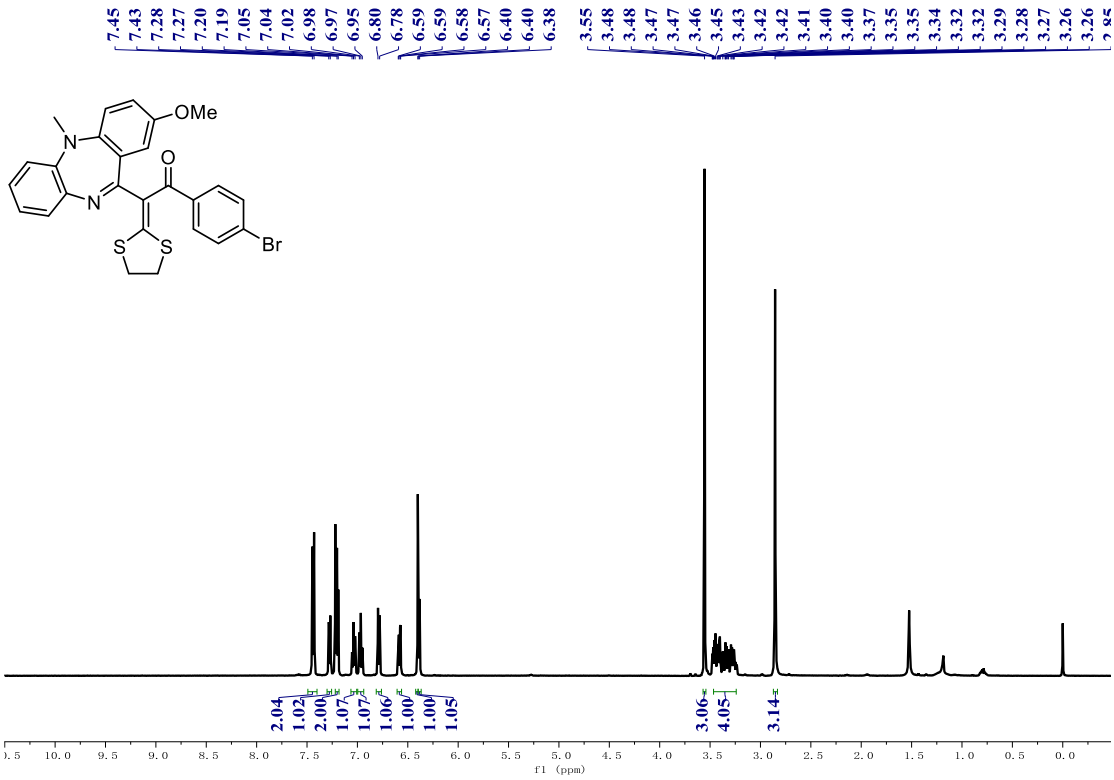


Figure 41. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ab**

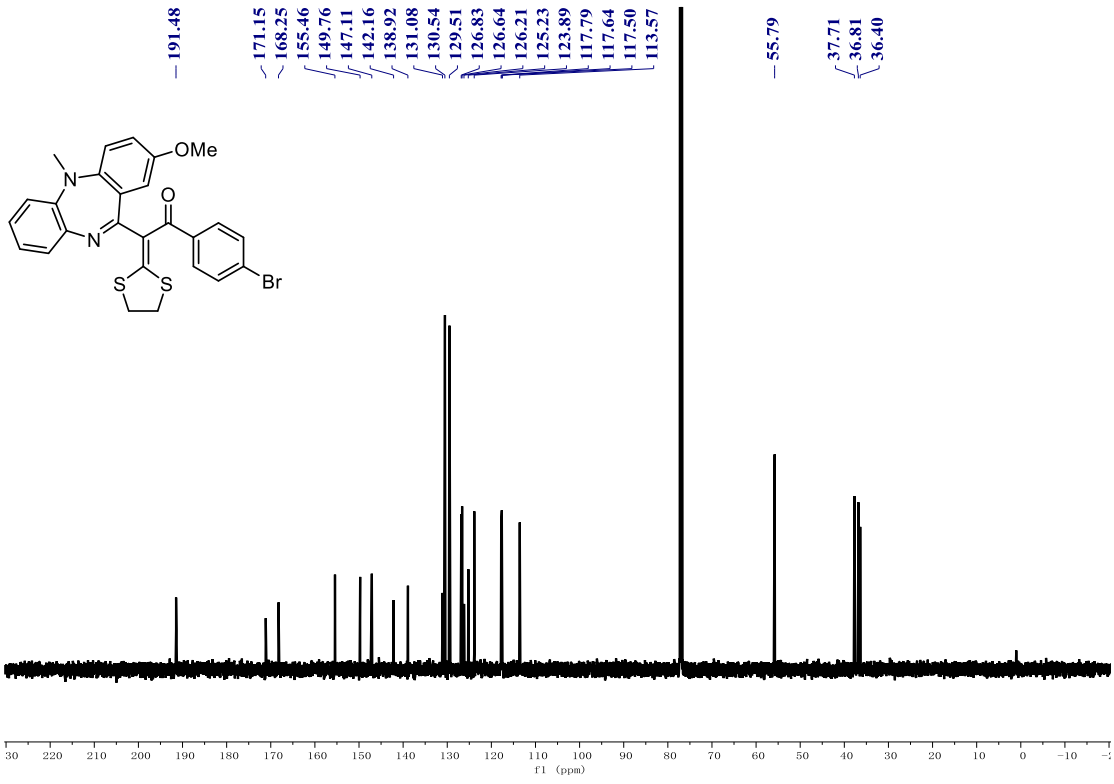


Figure 42. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ab**

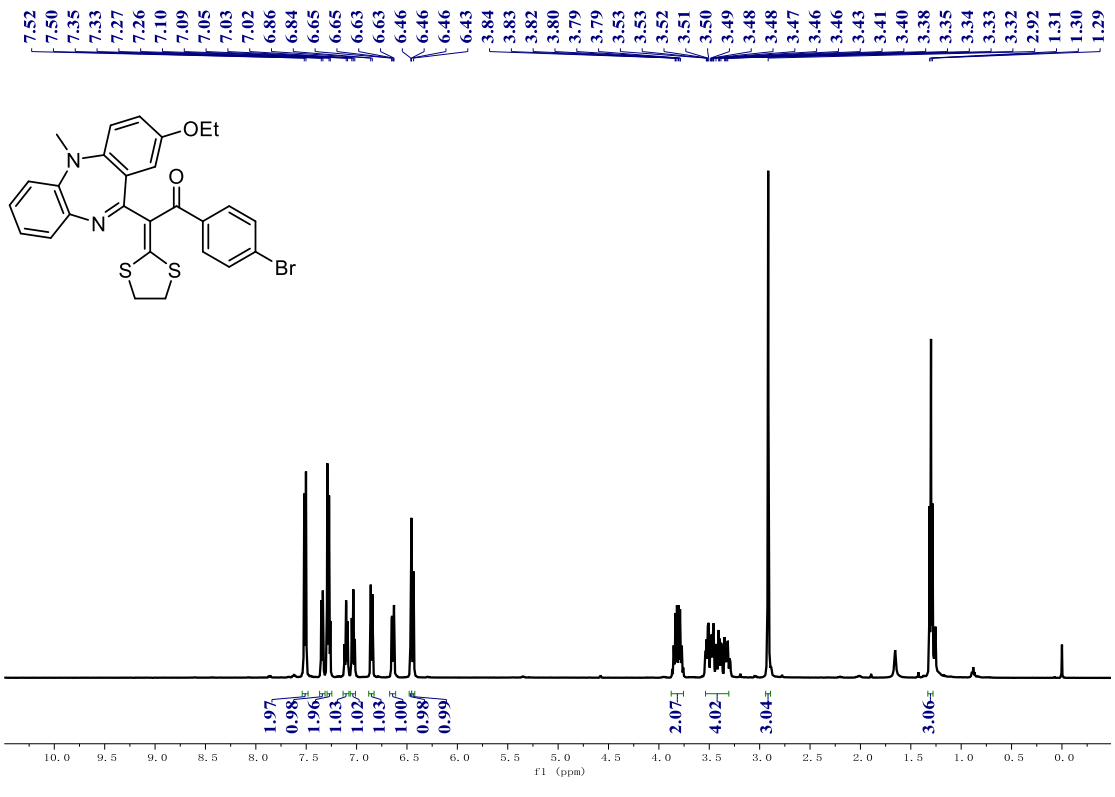


Figure 43. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ac**

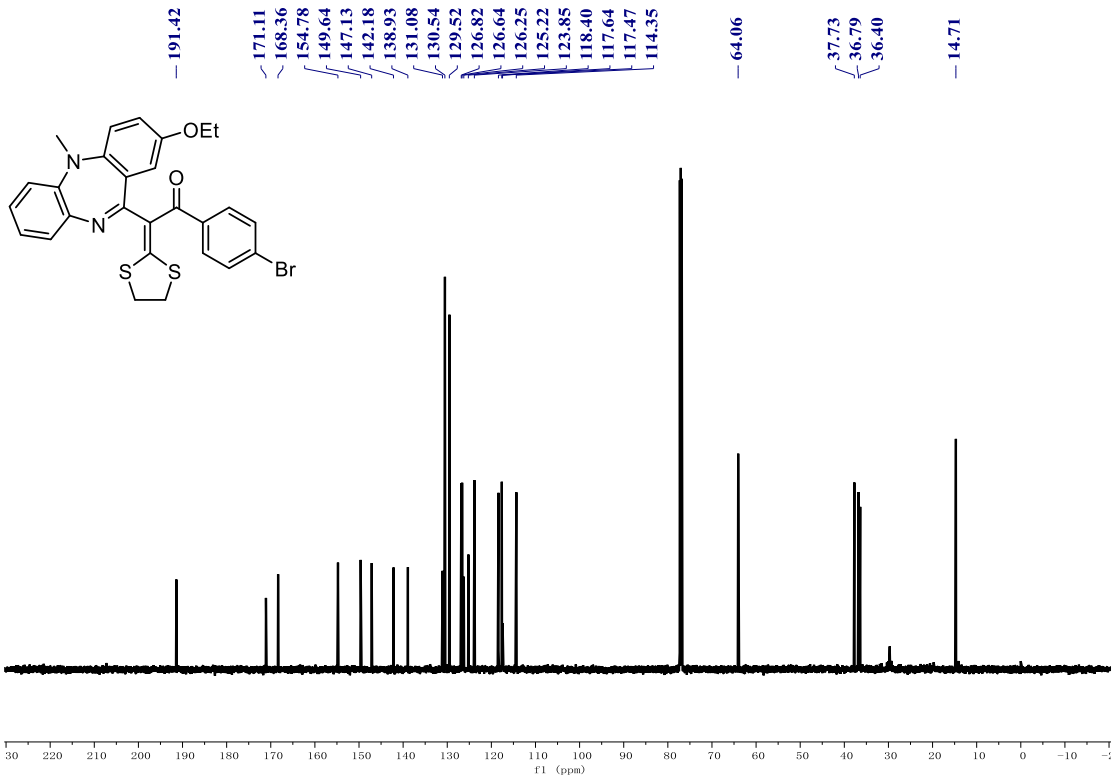


Figure 44. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ac**

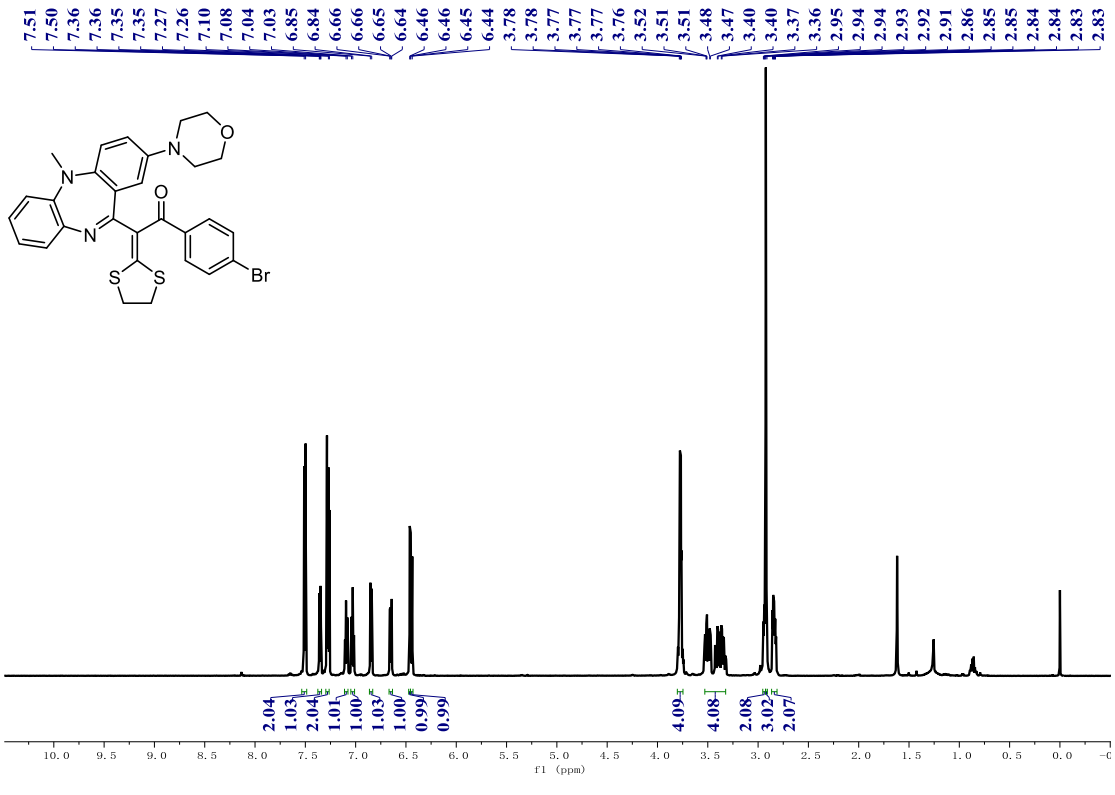


Figure 45. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ad**

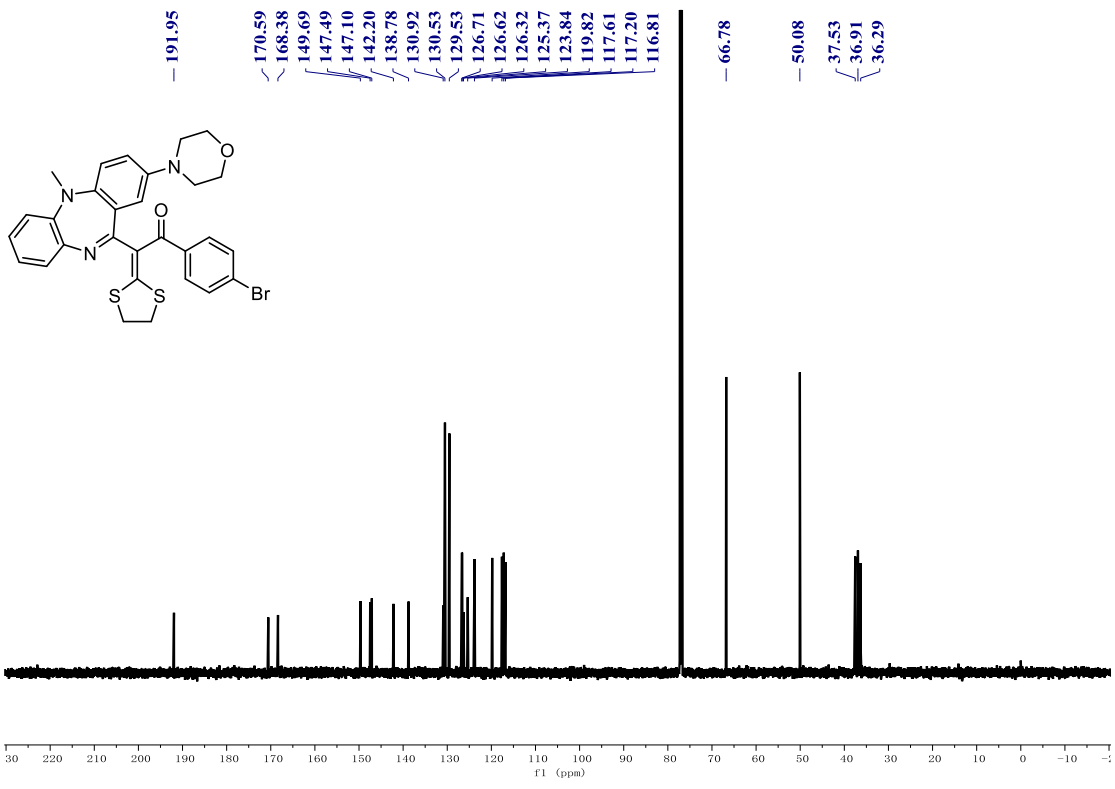


Figure 46. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ad**

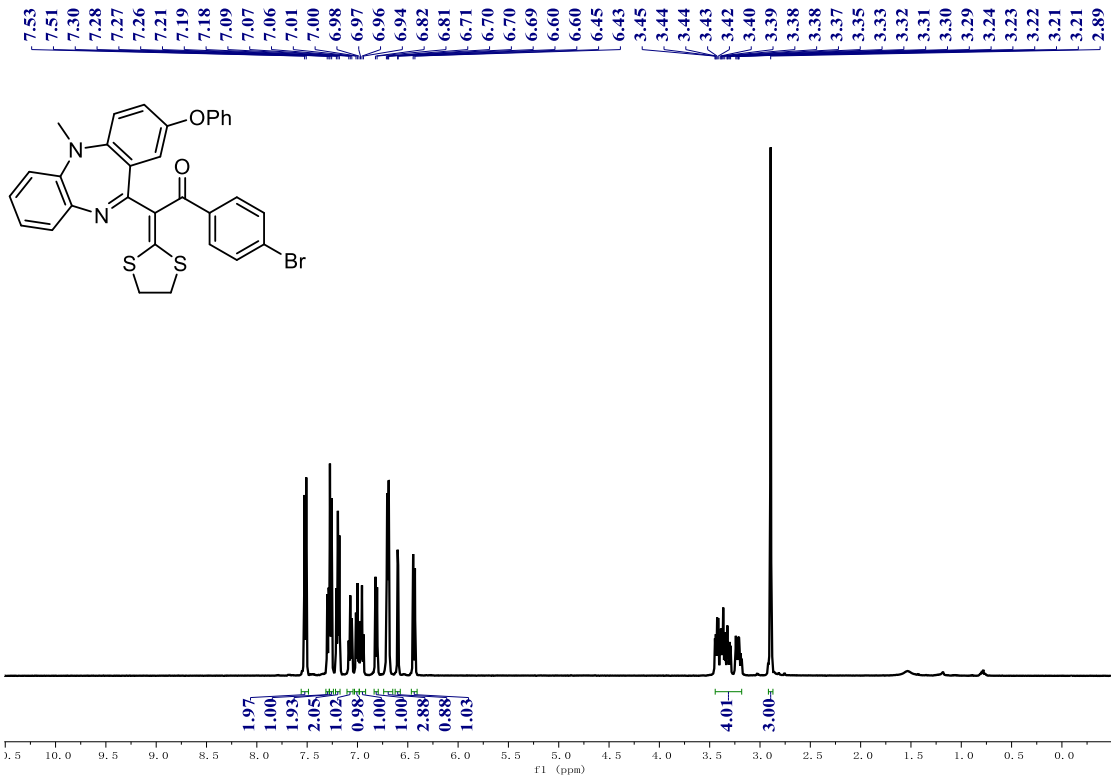


Figure 47. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ae**

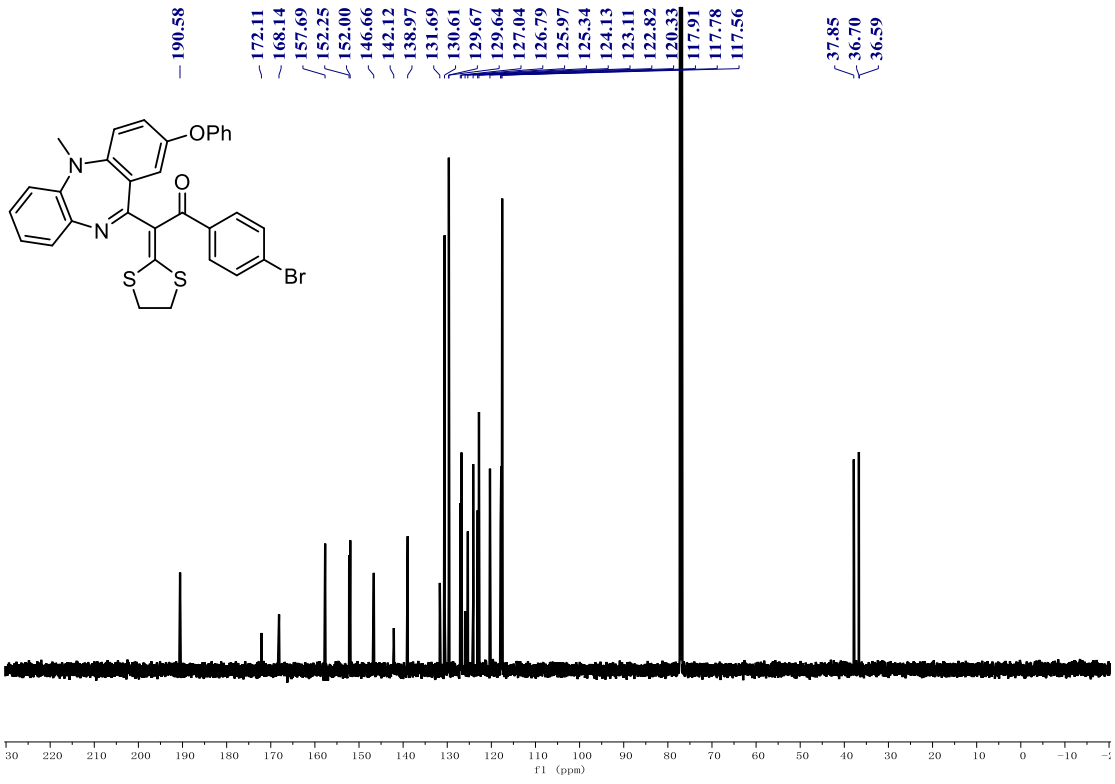


Figure 48. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ae**

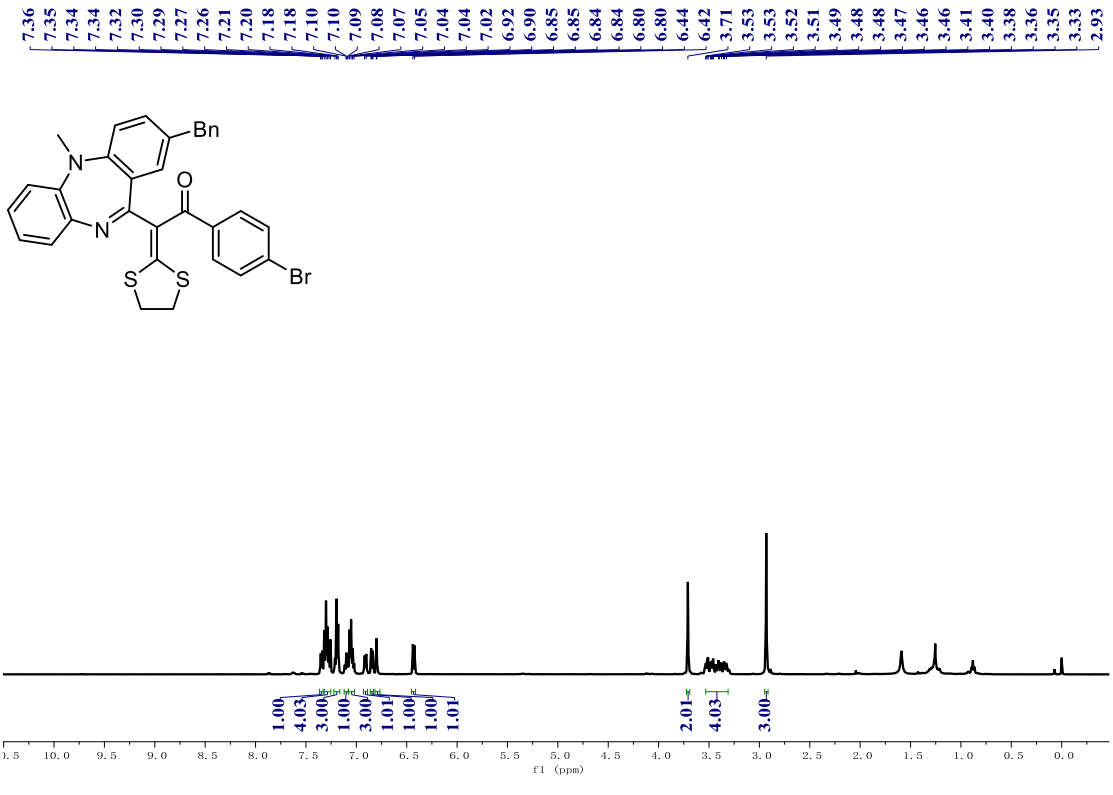


Figure 49. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3af**

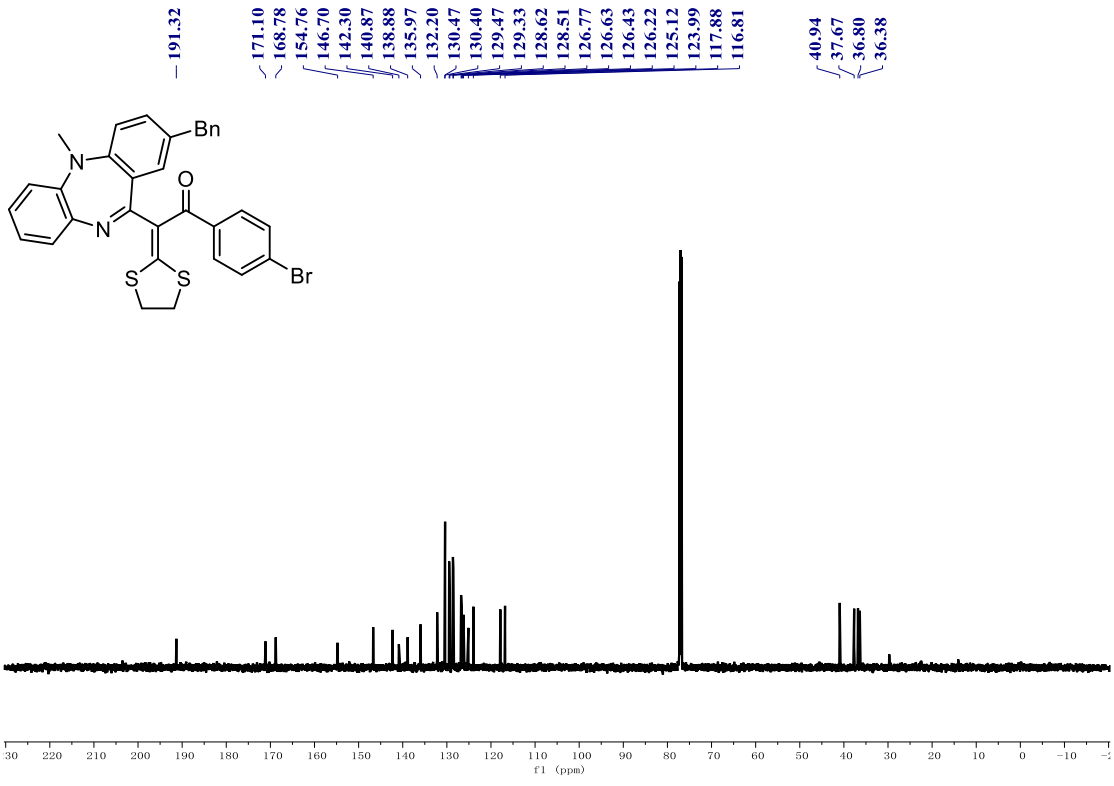


Figure 50. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3af**

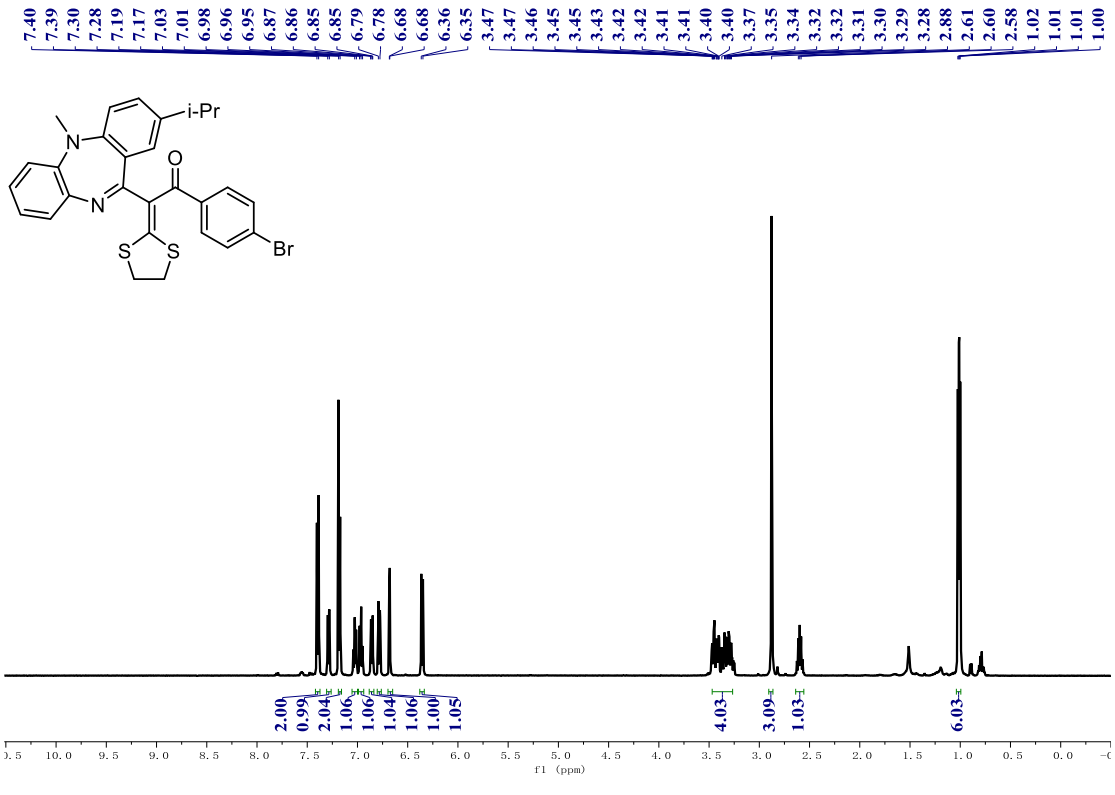


Figure 51. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ag**

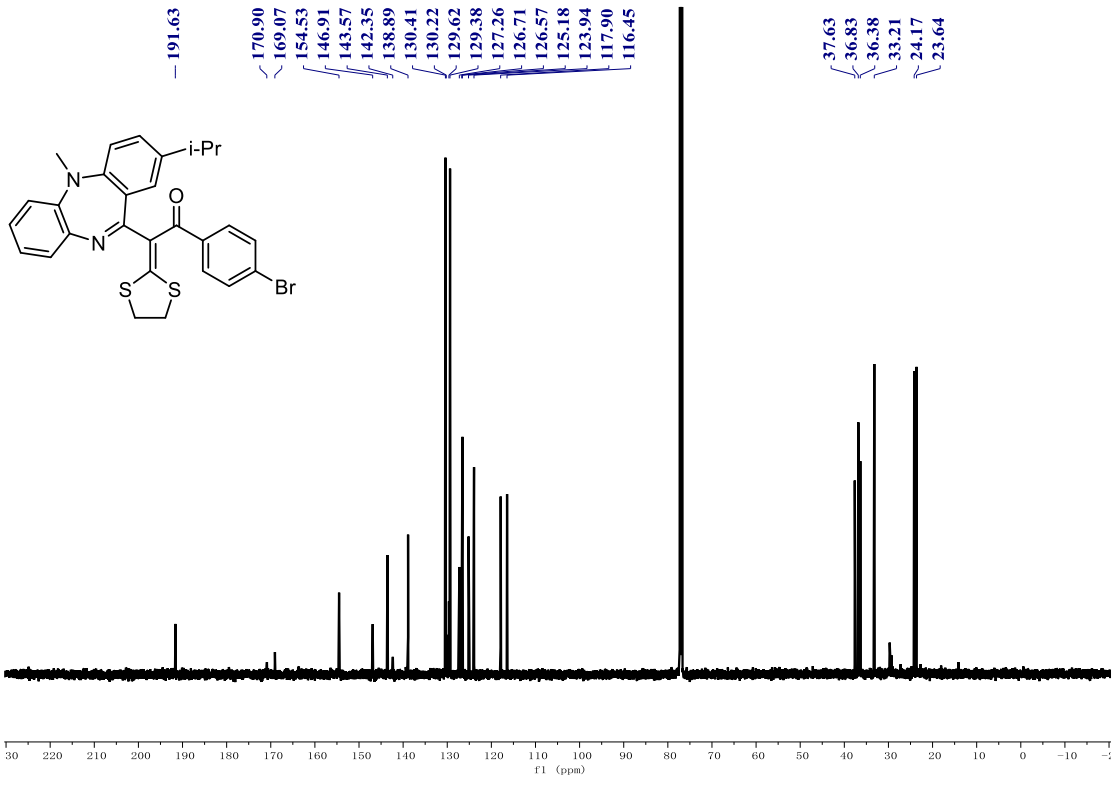


Figure 52. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ag**

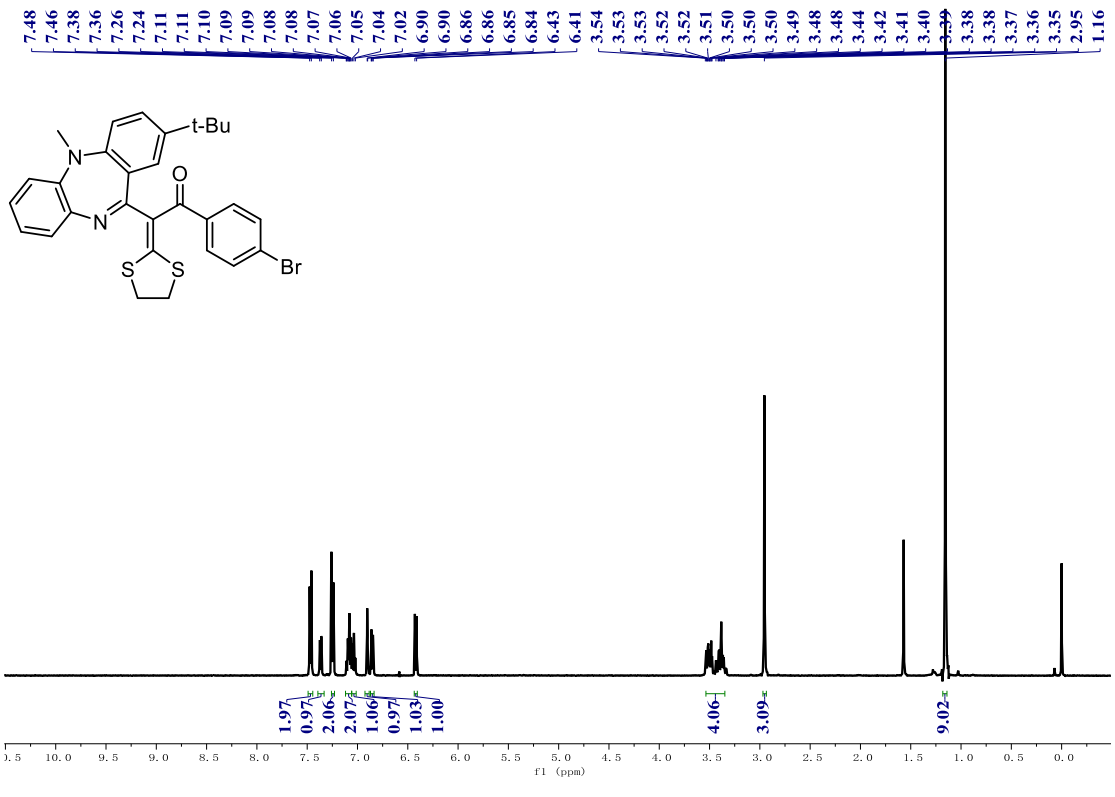


Figure 53. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ah**

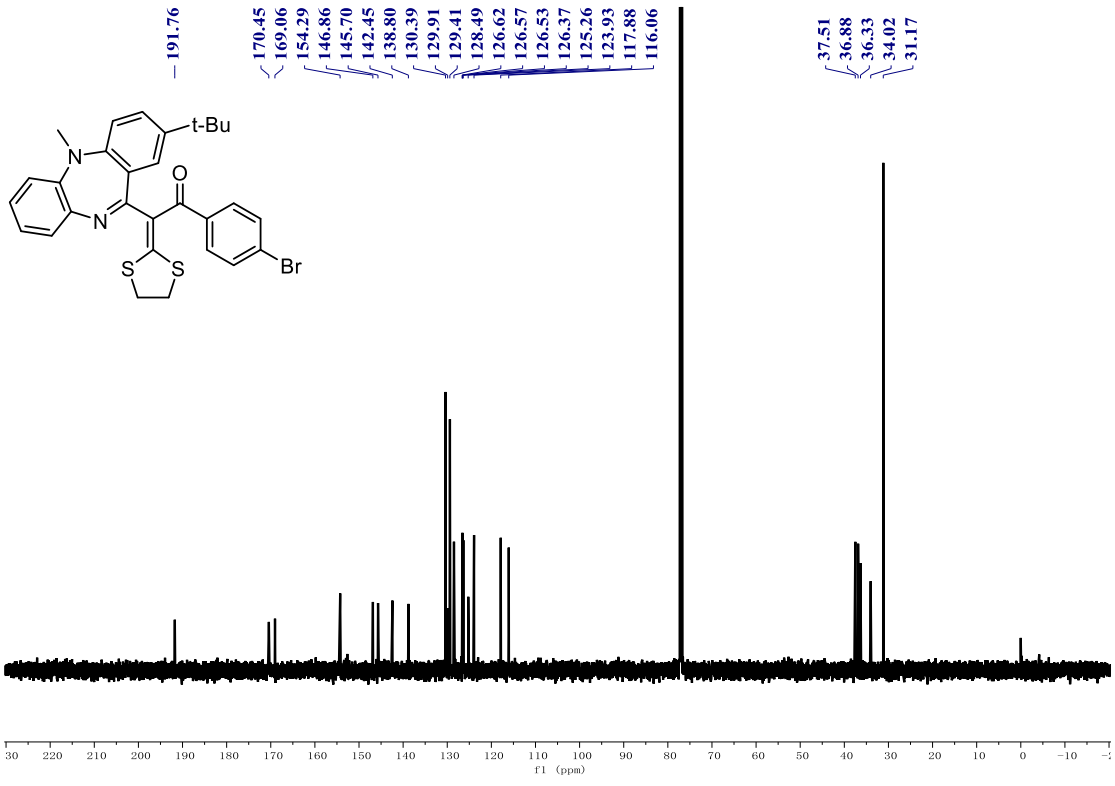


Figure 54. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ah**

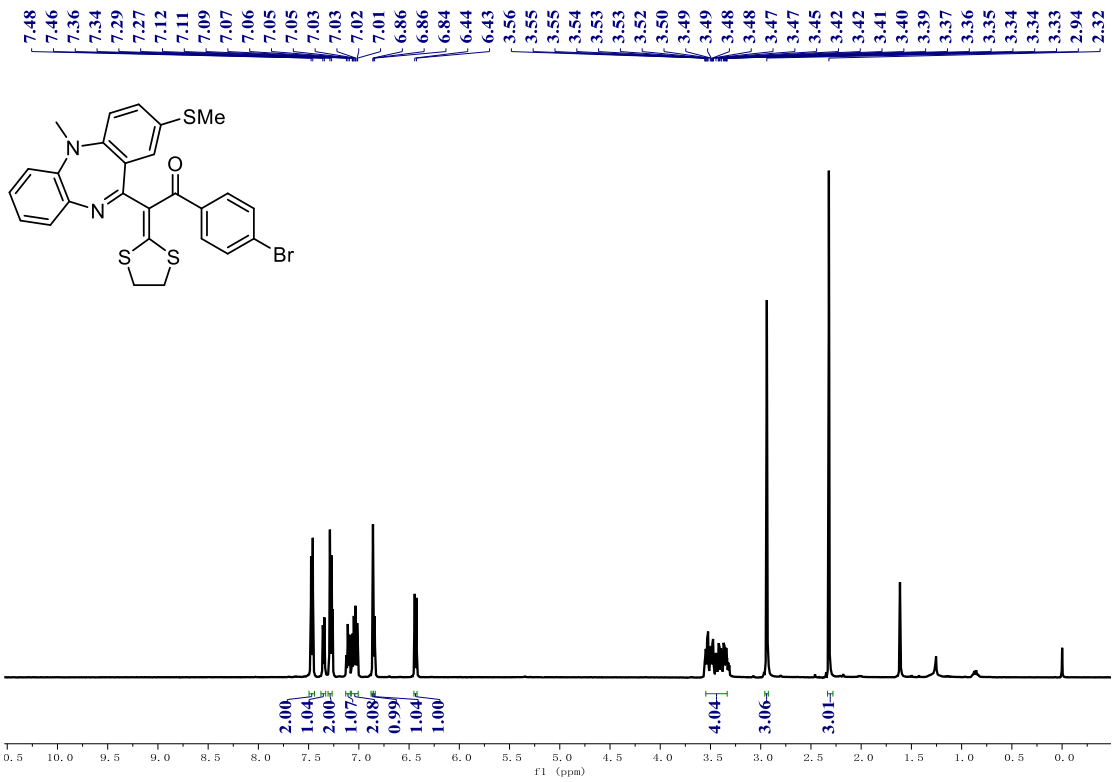


Figure 55. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ai**

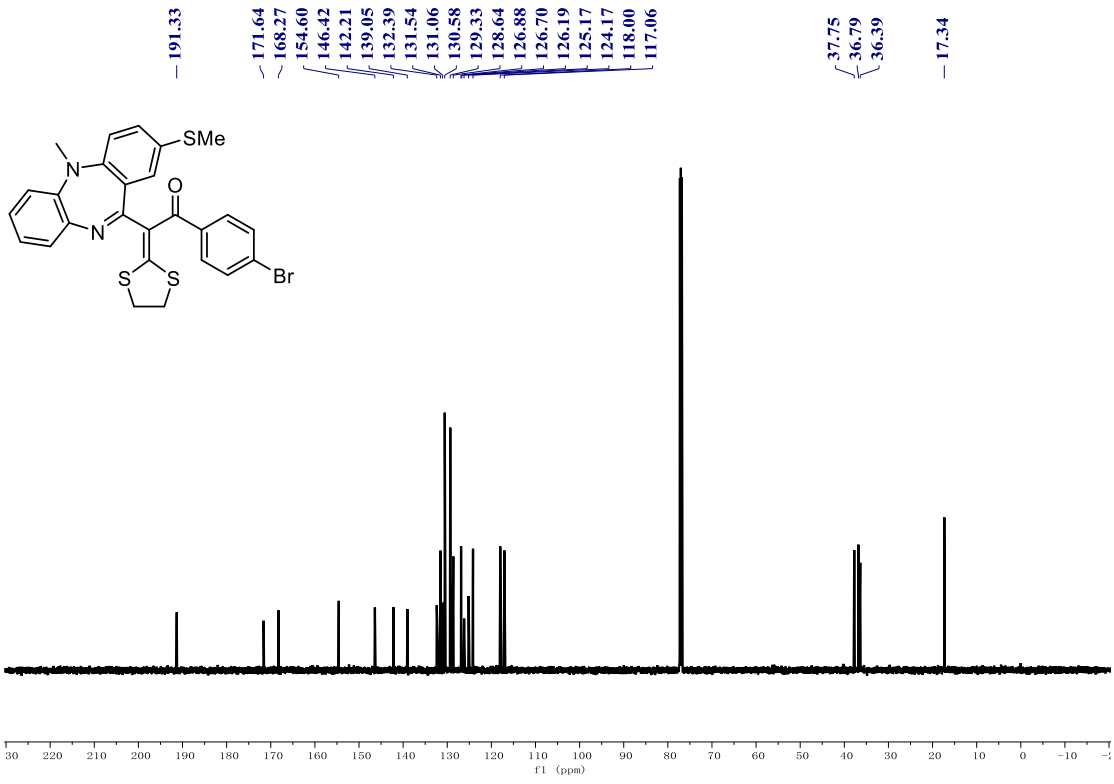


Figure 56. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ai**

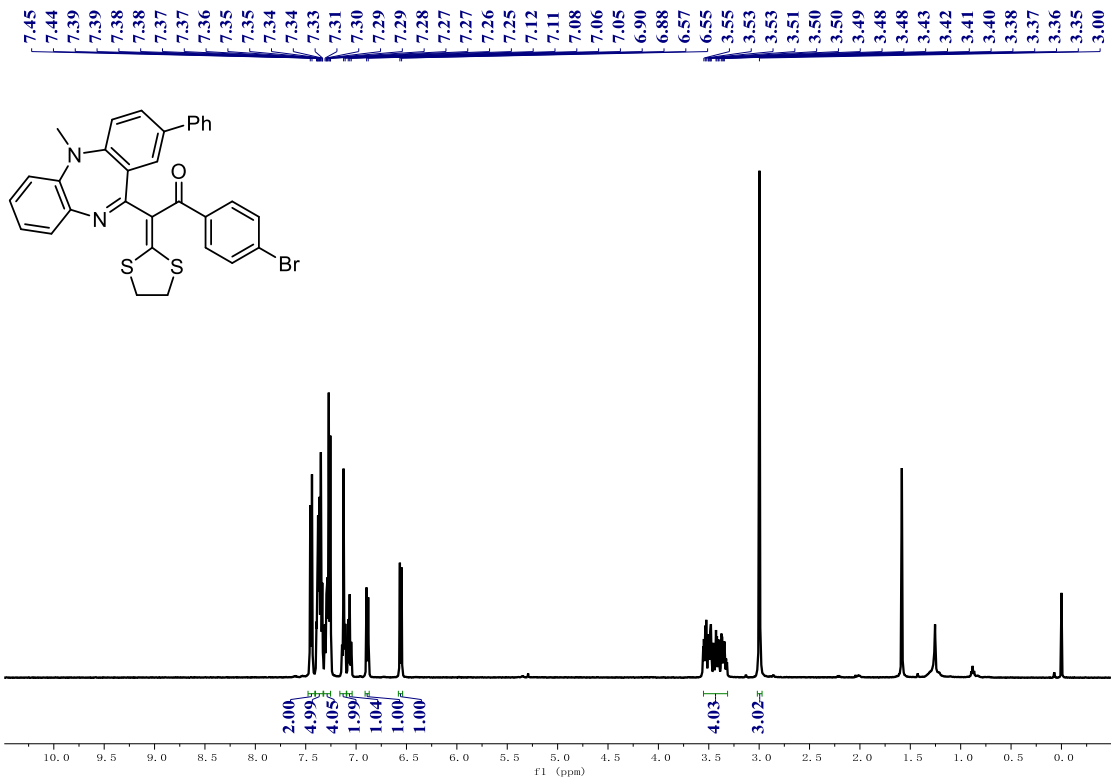


Figure 57. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3aj**

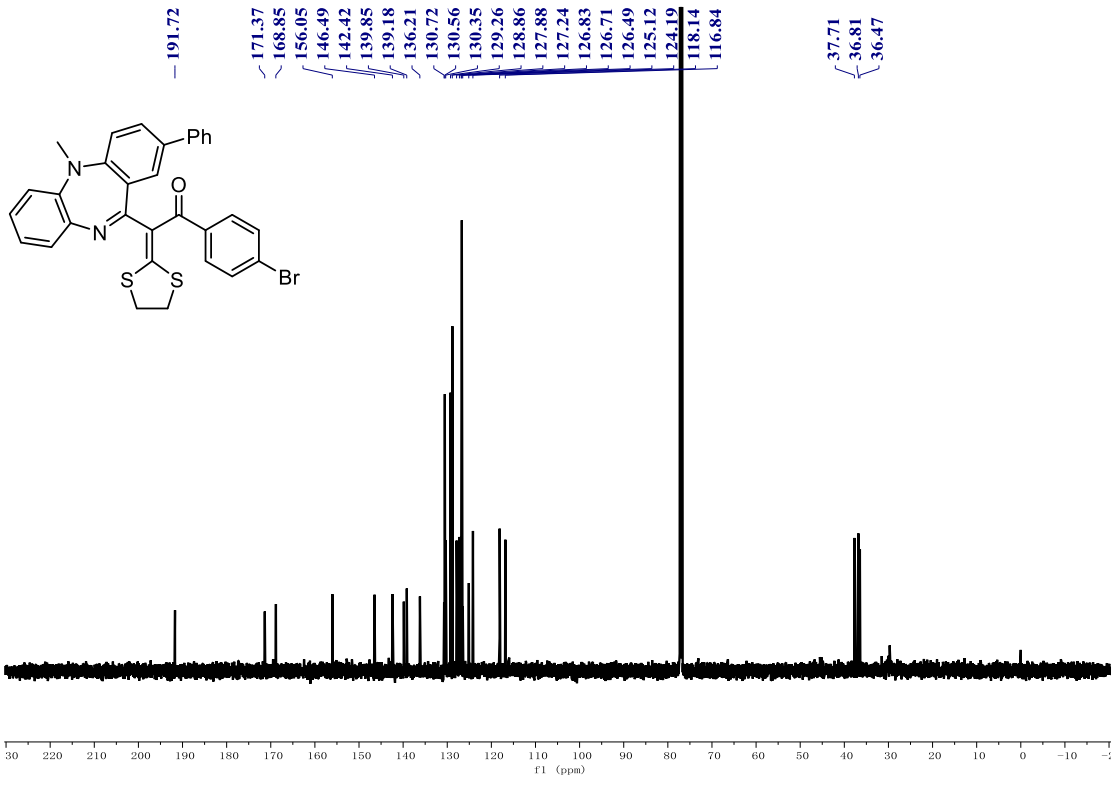


Figure 58. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3aj**

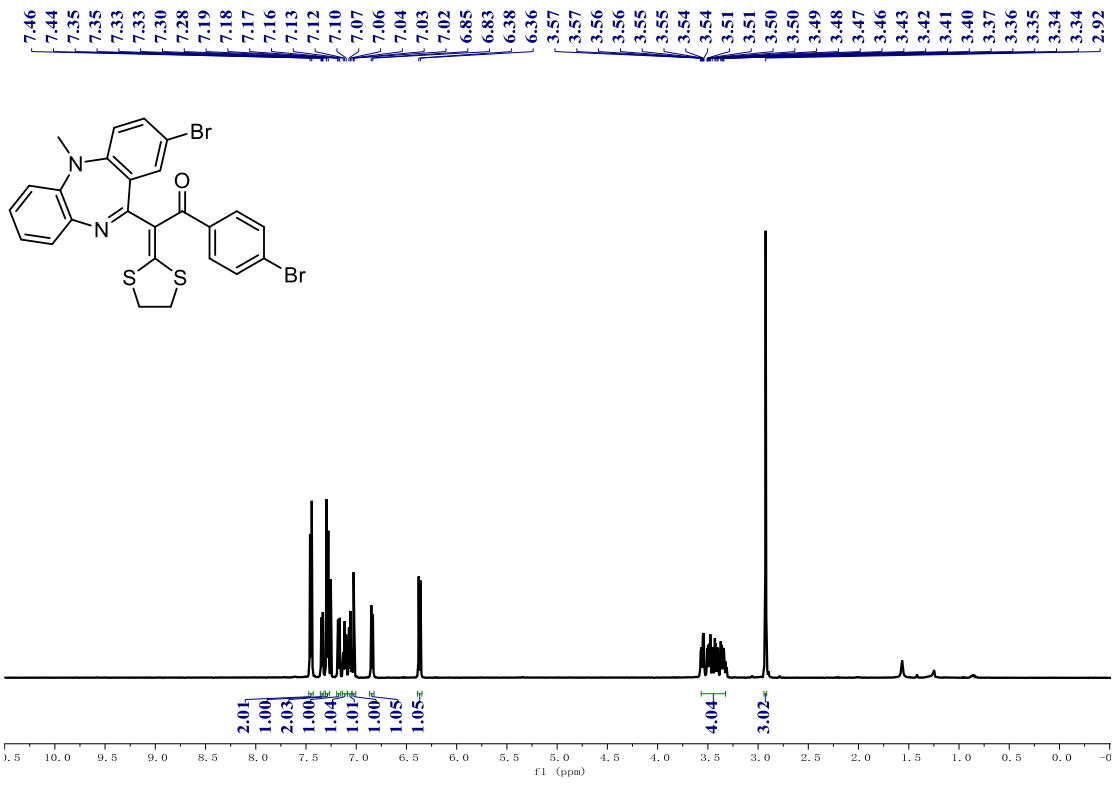


Figure 59. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ak**

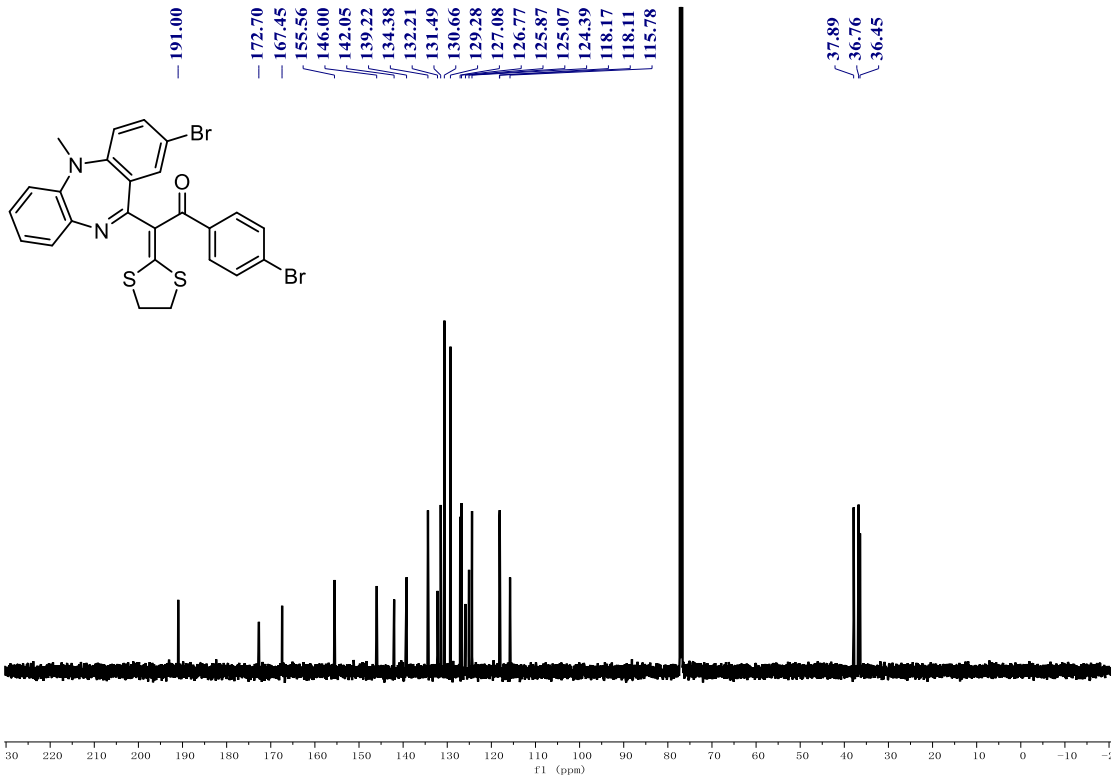


Figure 60. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ak**

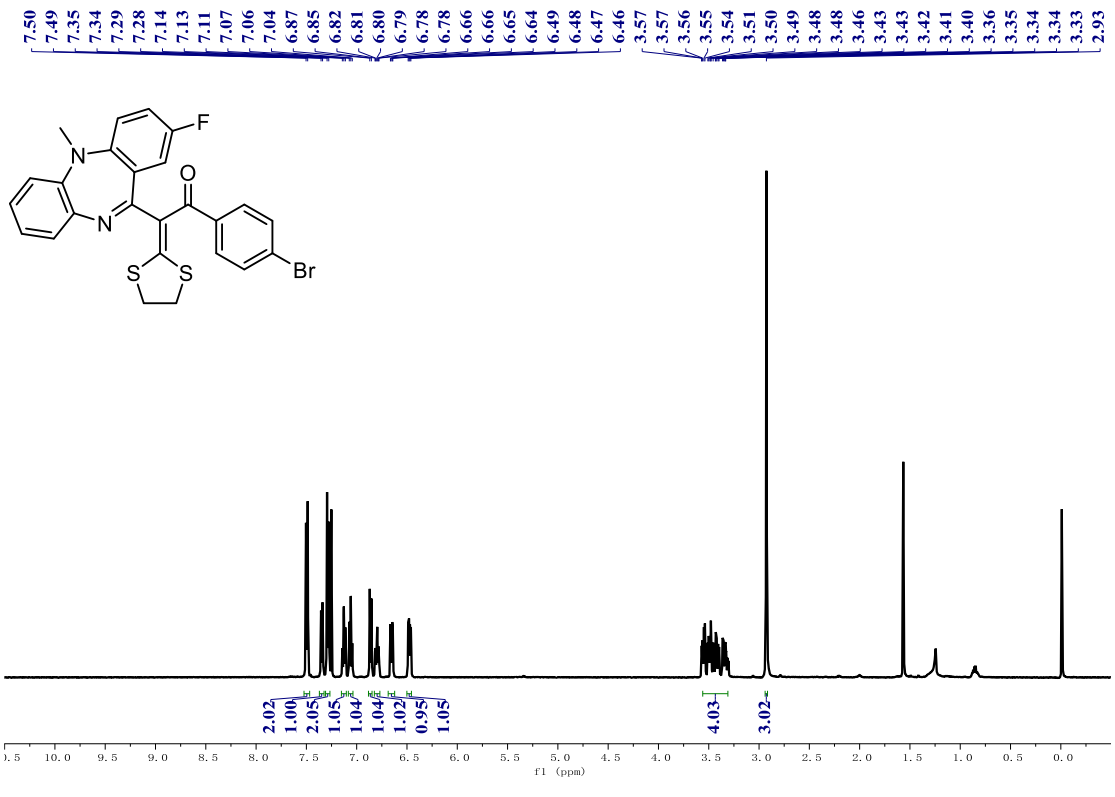


Figure 61. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3al**

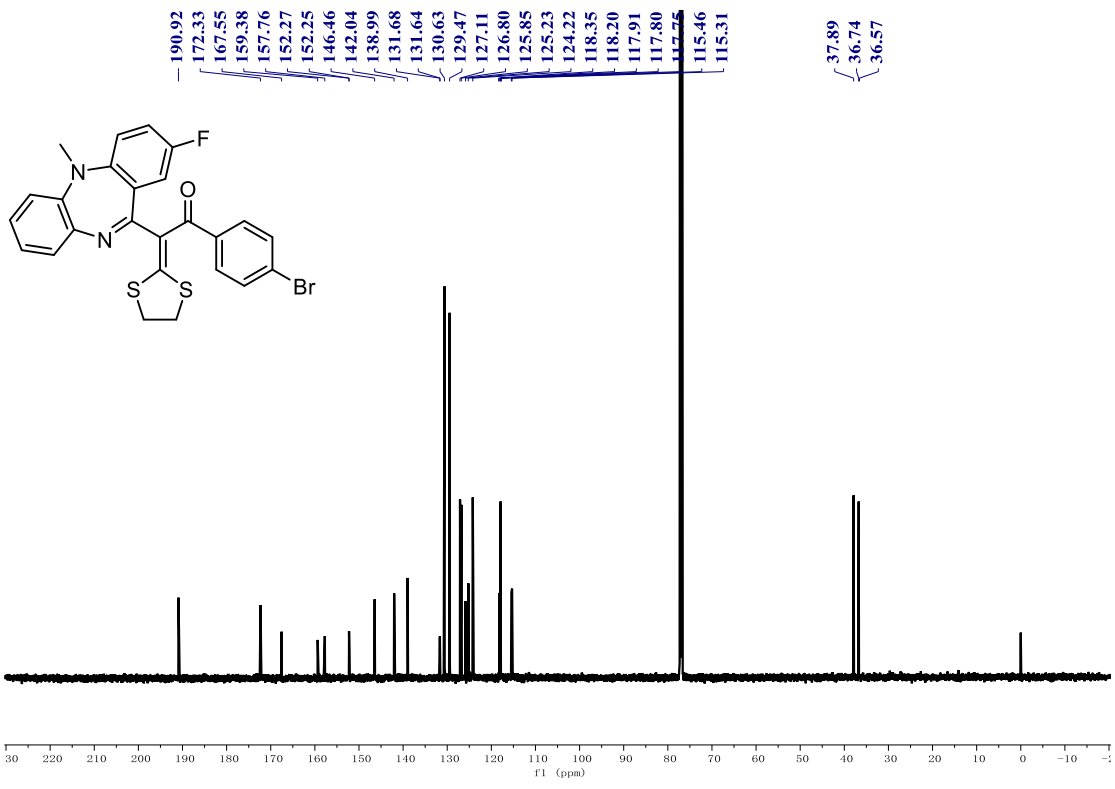


Figure 62. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3al**

Figure 63. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **3al**

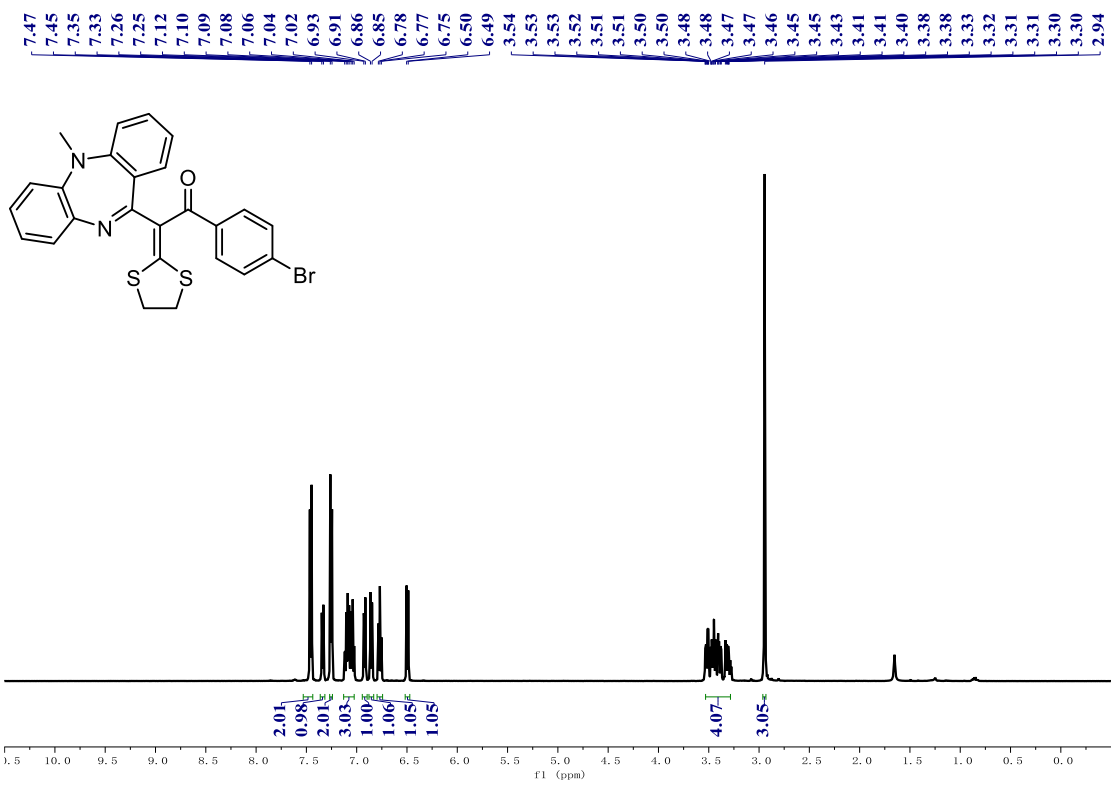


Figure 64. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3am**

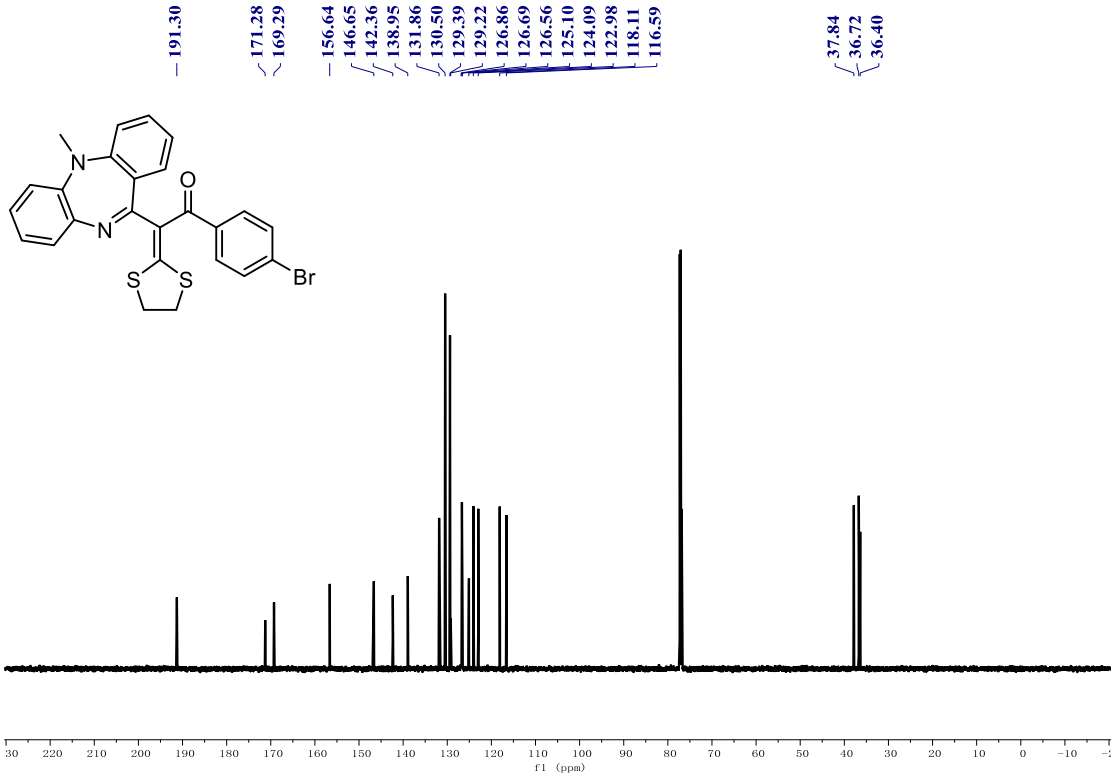


Figure 65. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3am**

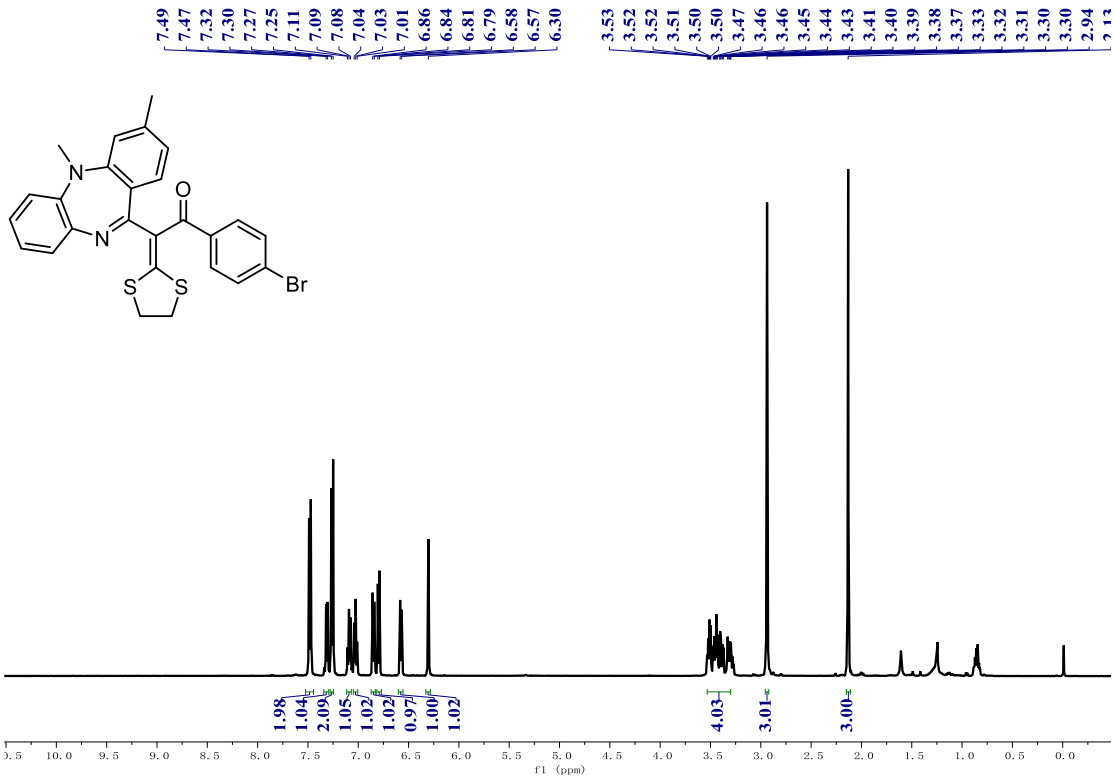


Figure 66. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3an**

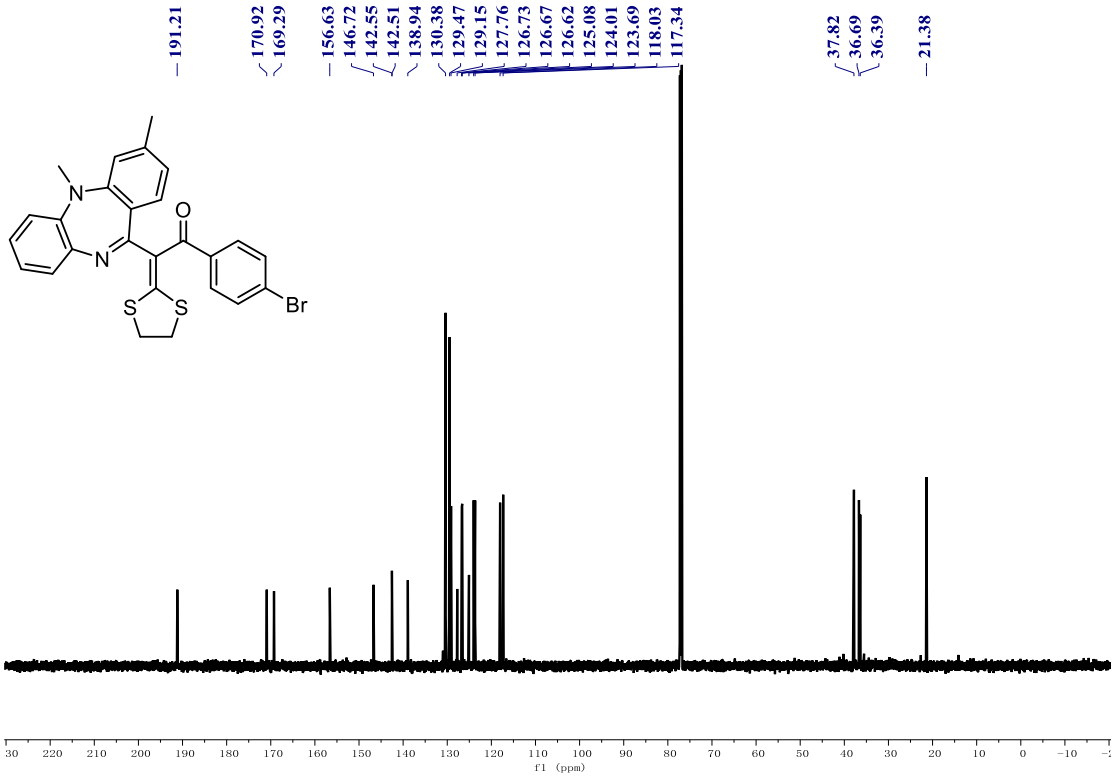


Figure 67. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3an**

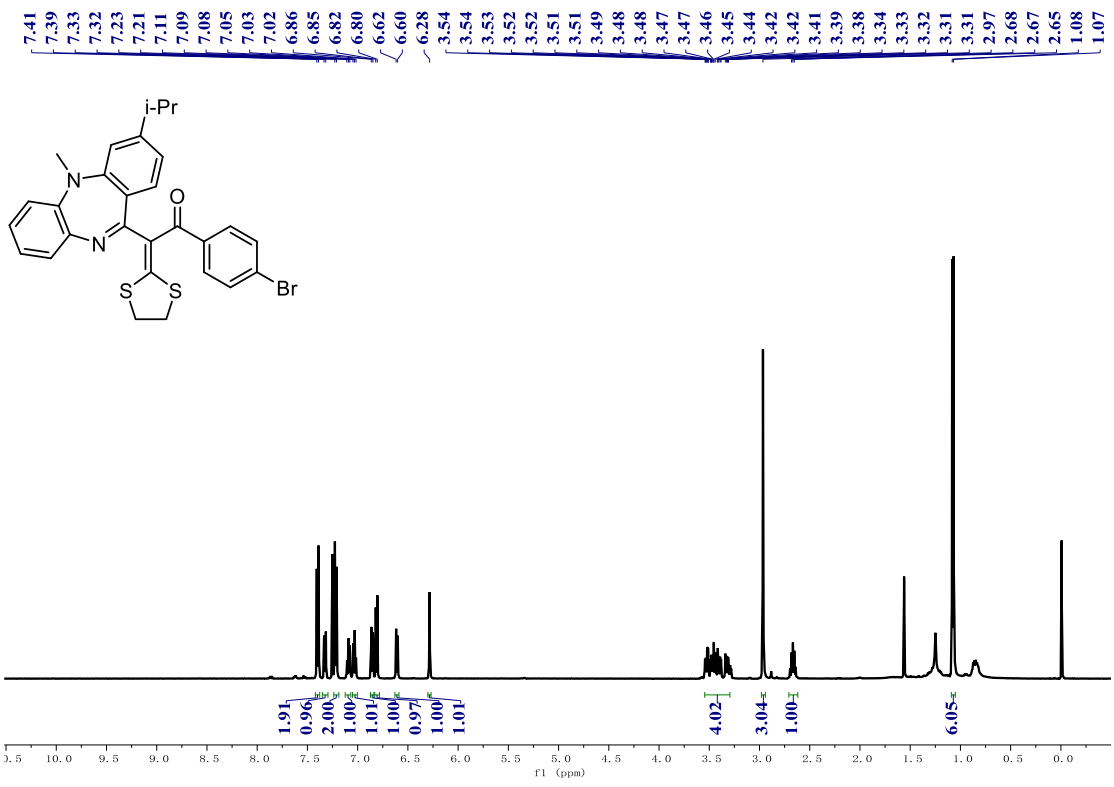


Figure 68. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ao**

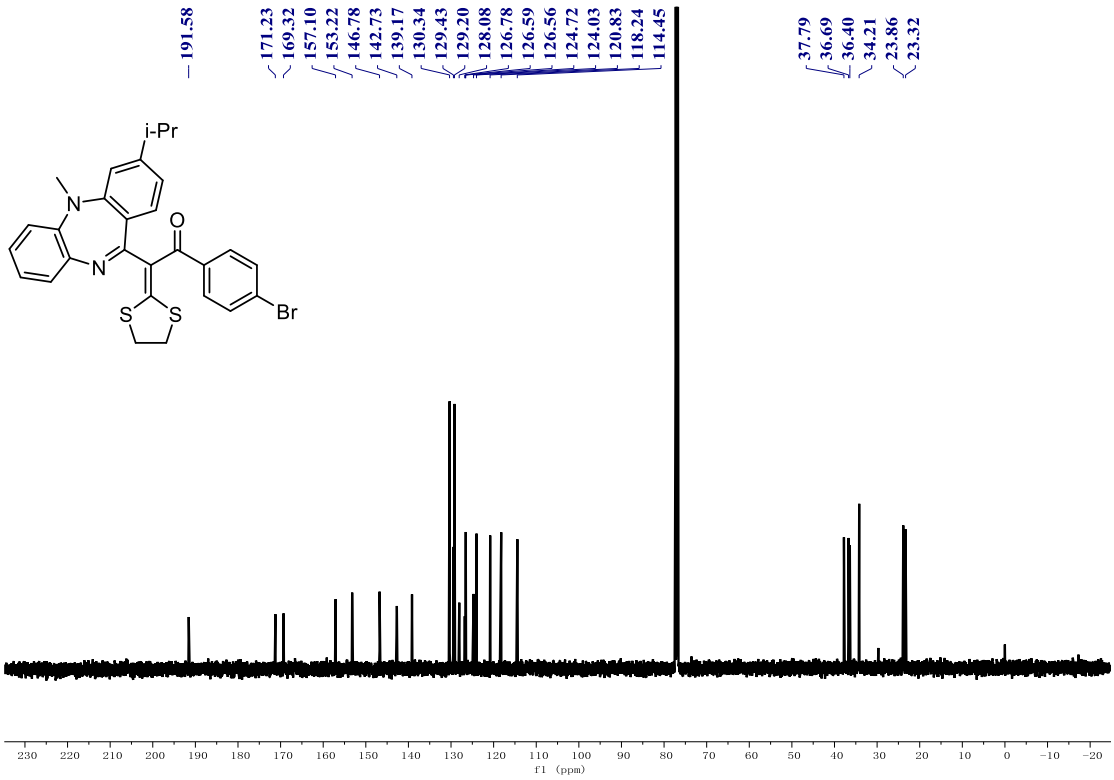


Figure 69. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ao**

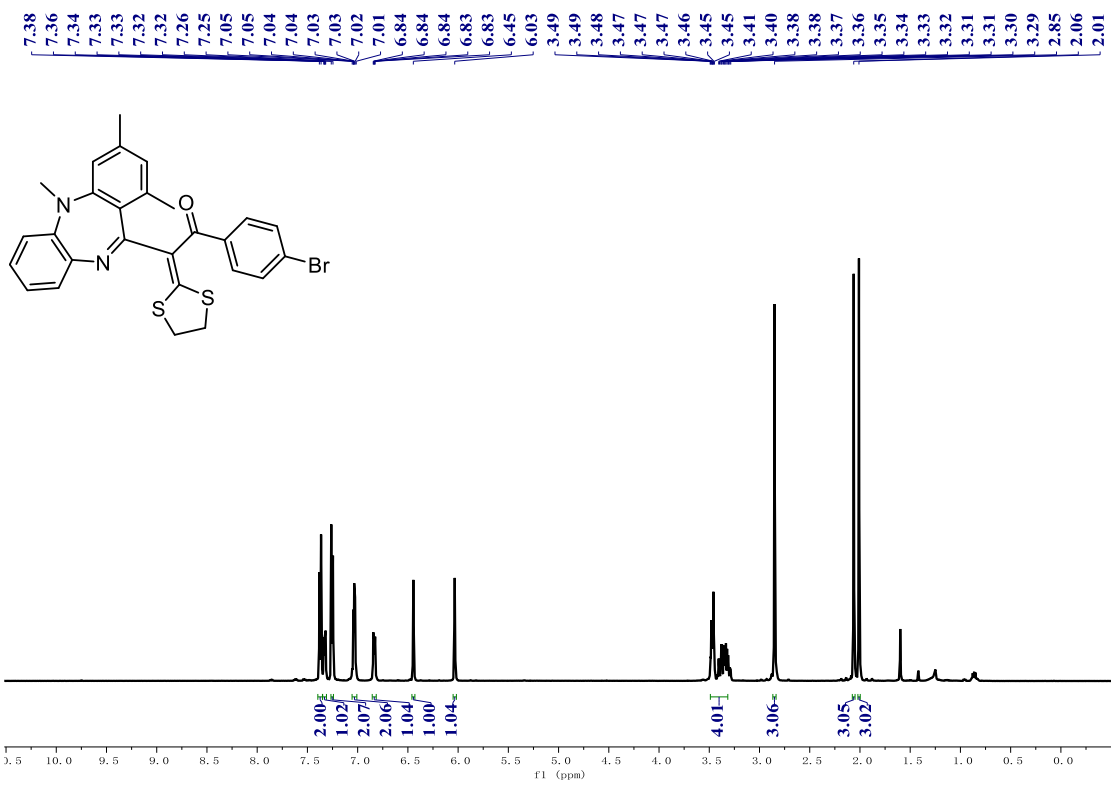


Figure 70. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ap**

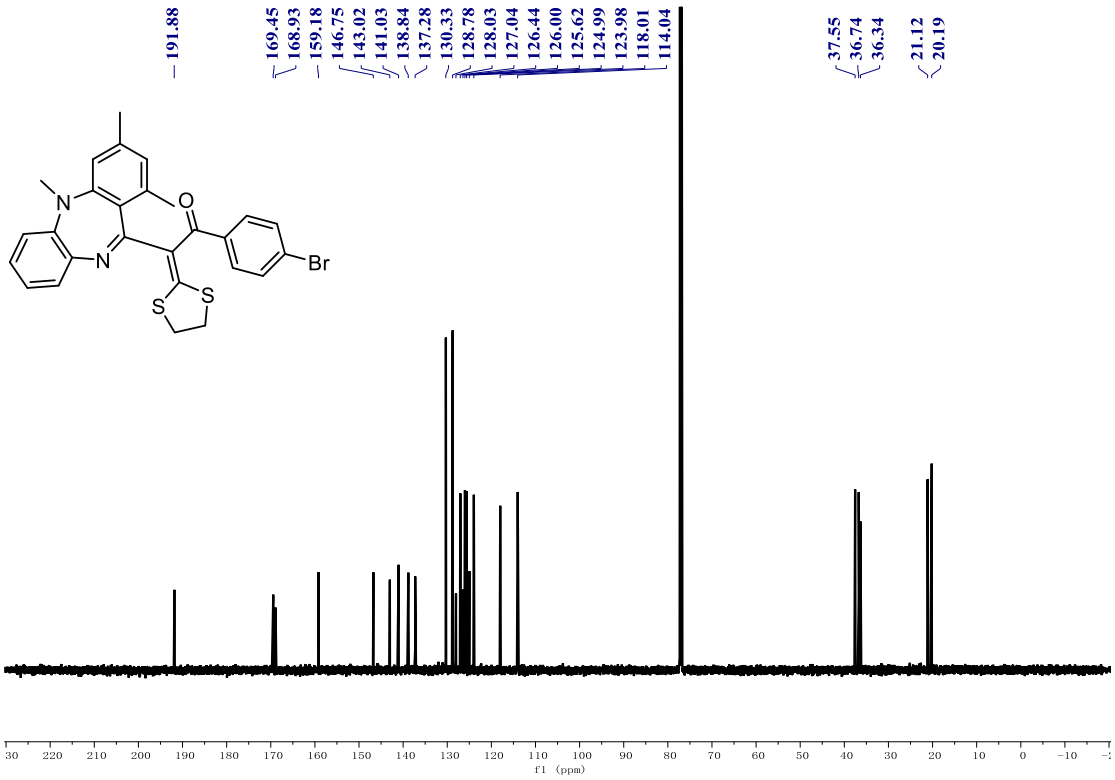


Figure 71. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ap**

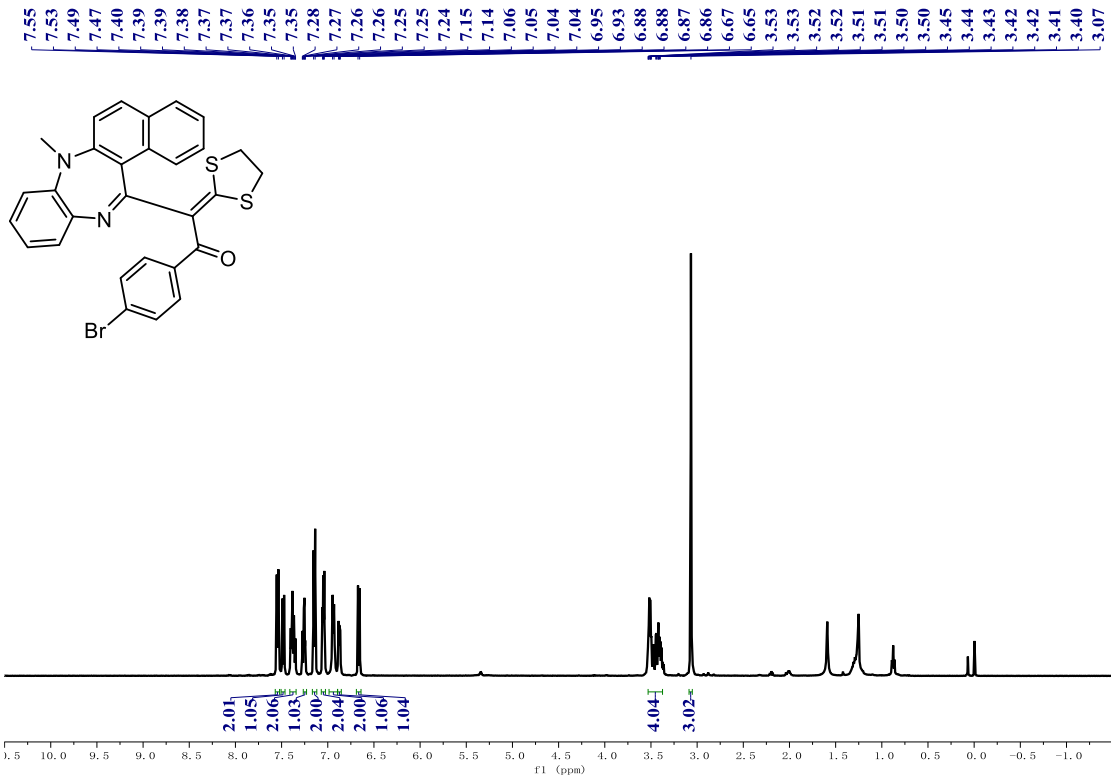


Figure 72. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3aq**

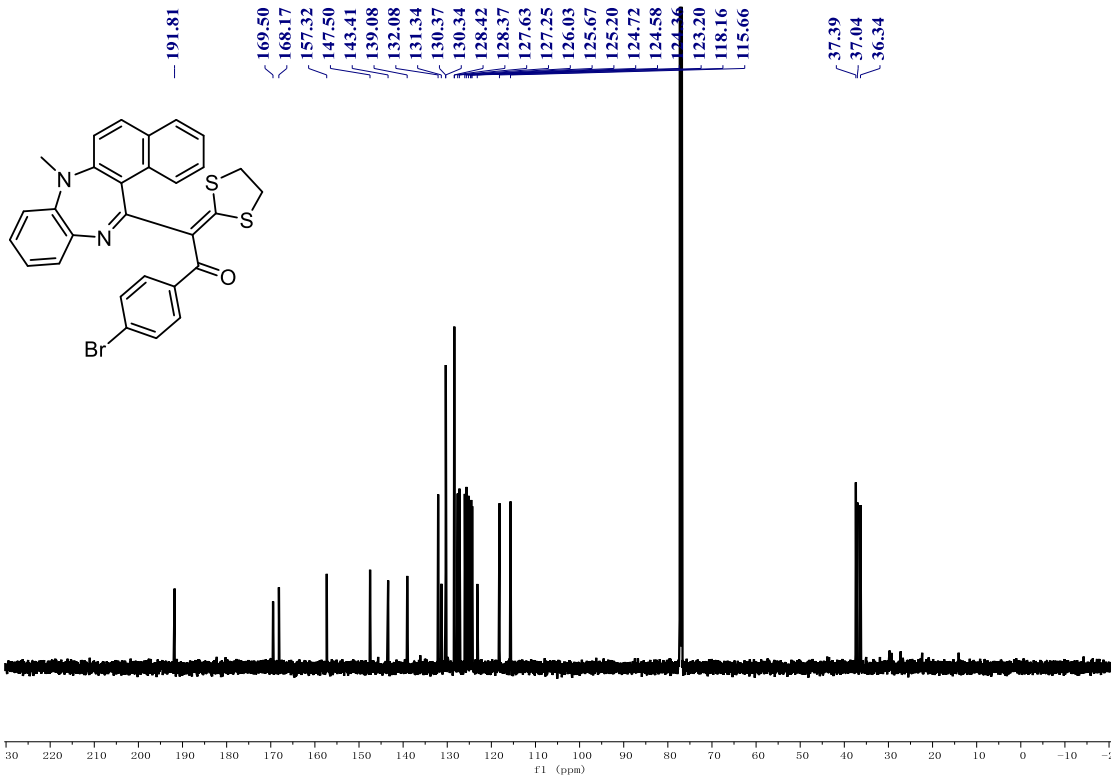


Figure 73. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3aq**

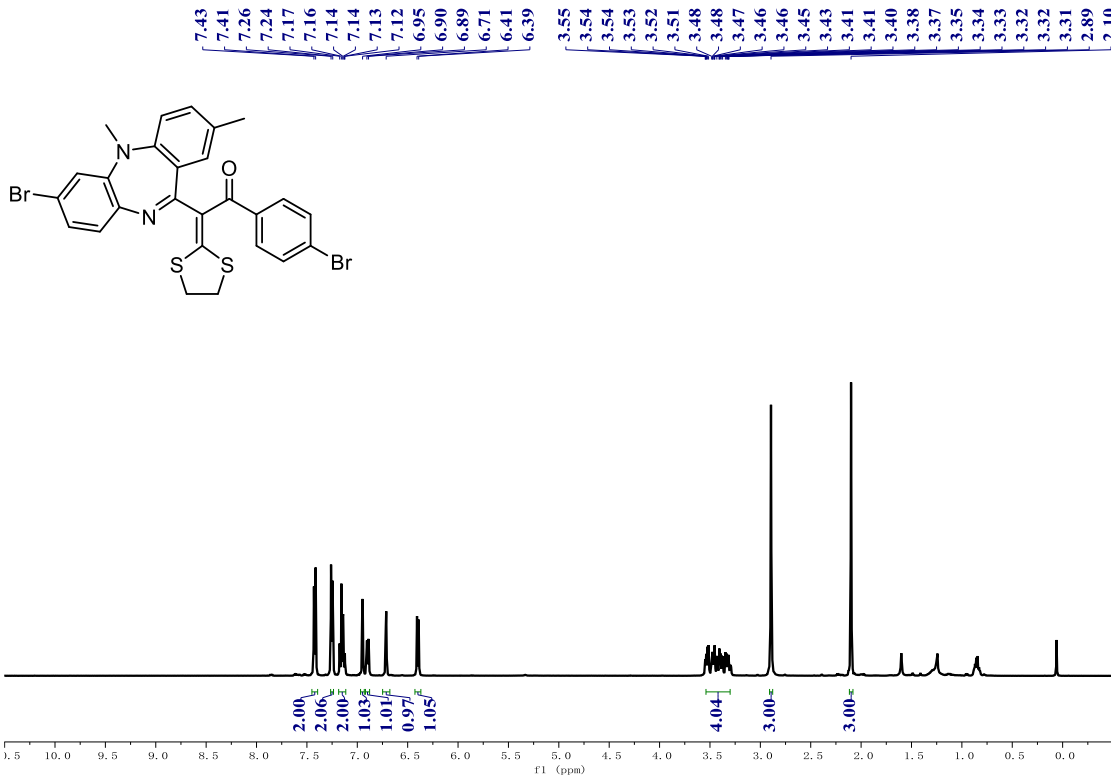


Figure 74. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ar**

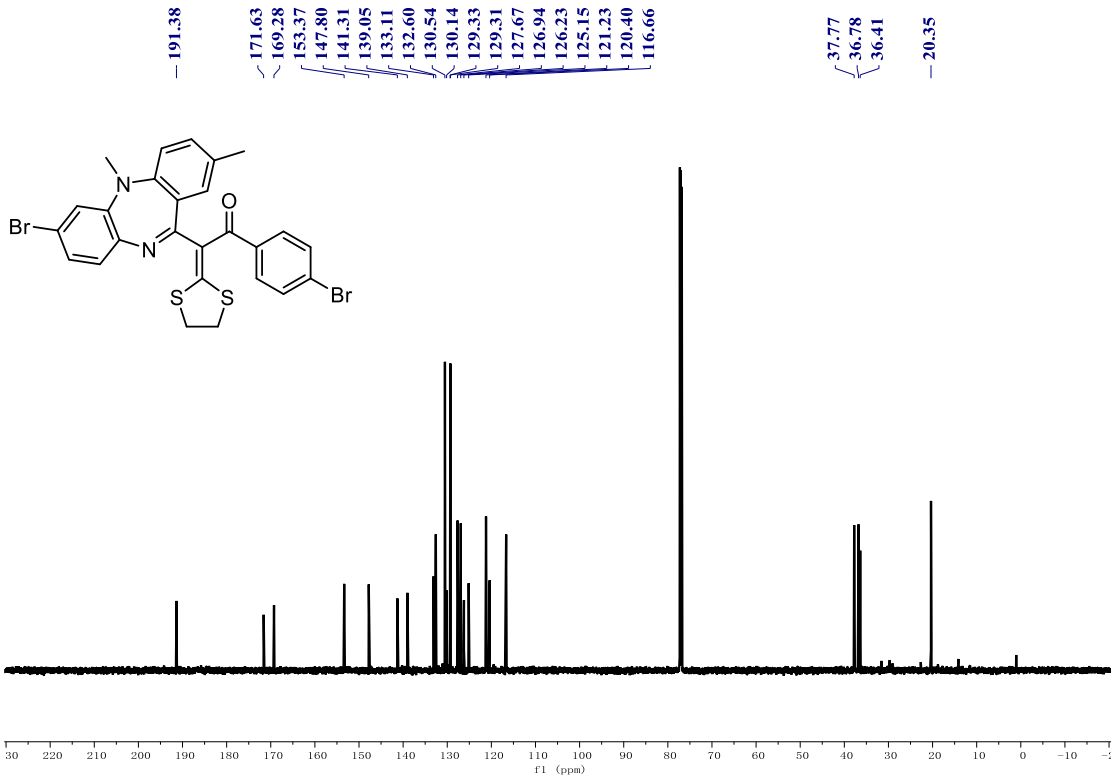


Figure 75. ^{13}C NMR (600 MHz, $CDCl_3$) spectra of compound **3ar**

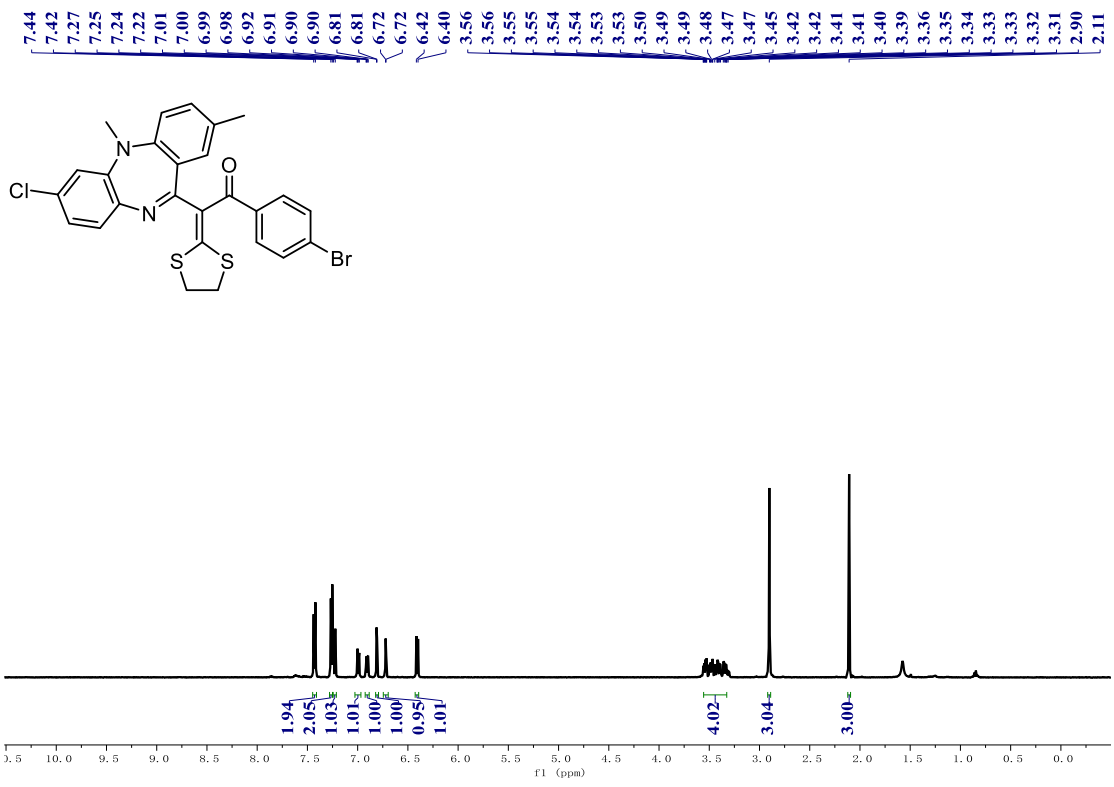


Figure 76. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3as**

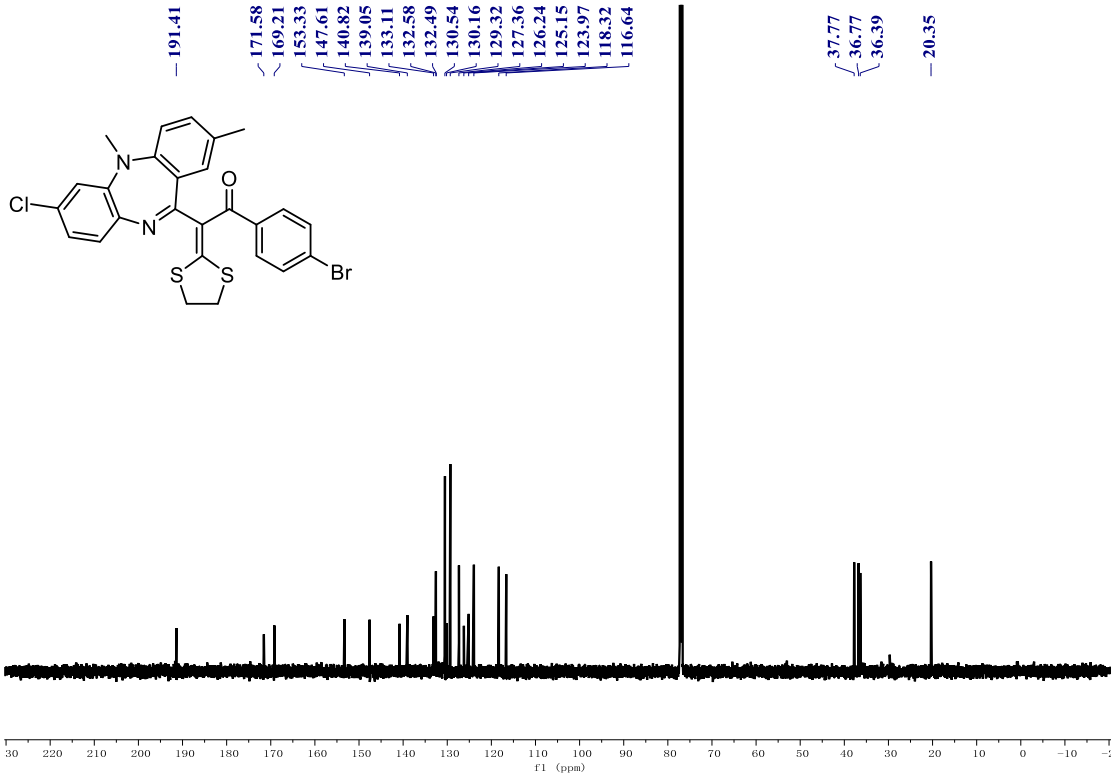


Figure 77. ^{13}C NMR (600 MHz, $CDCl_3$) spectra of compound **3as**

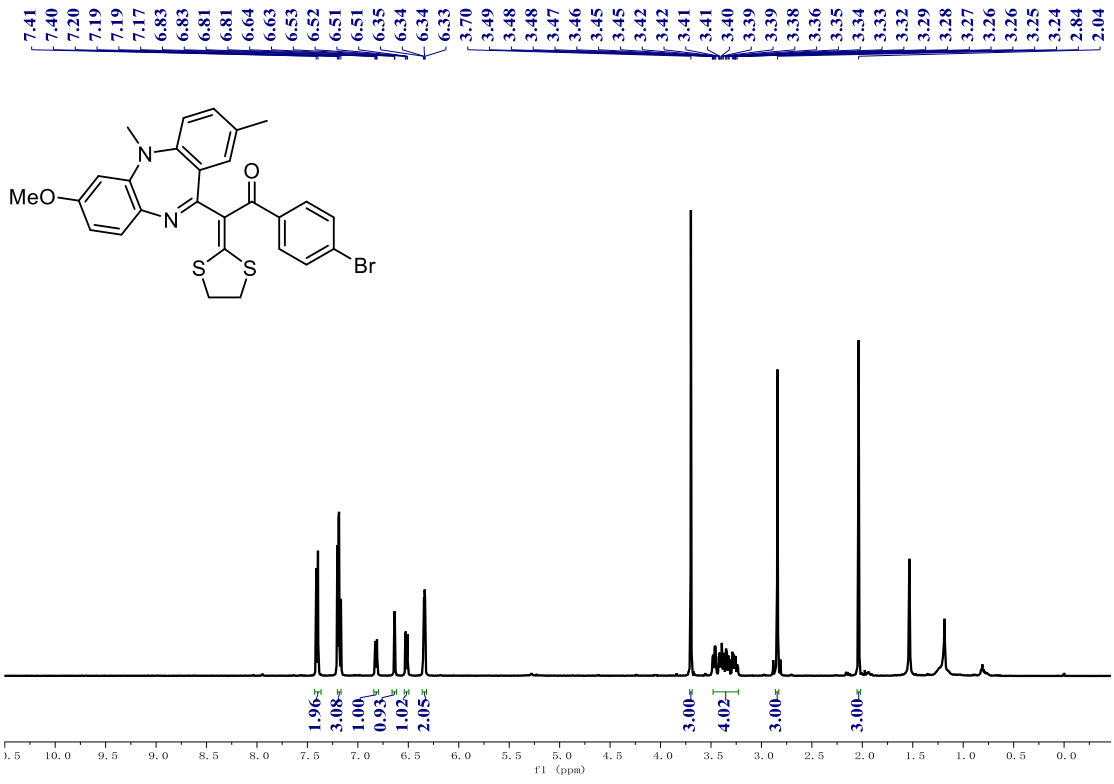


Figure 78. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3at**

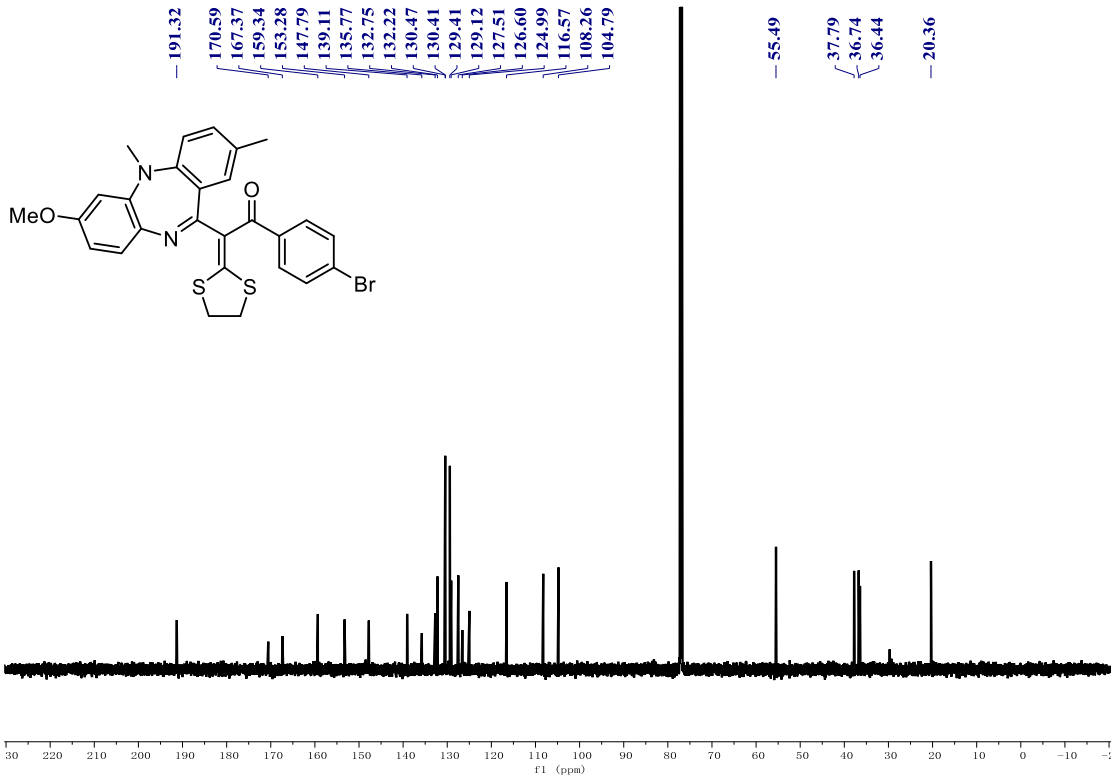


Figure 79. ^{13}C NMR (600 MHz, $CDCl_3$) spectra of compound **3at**

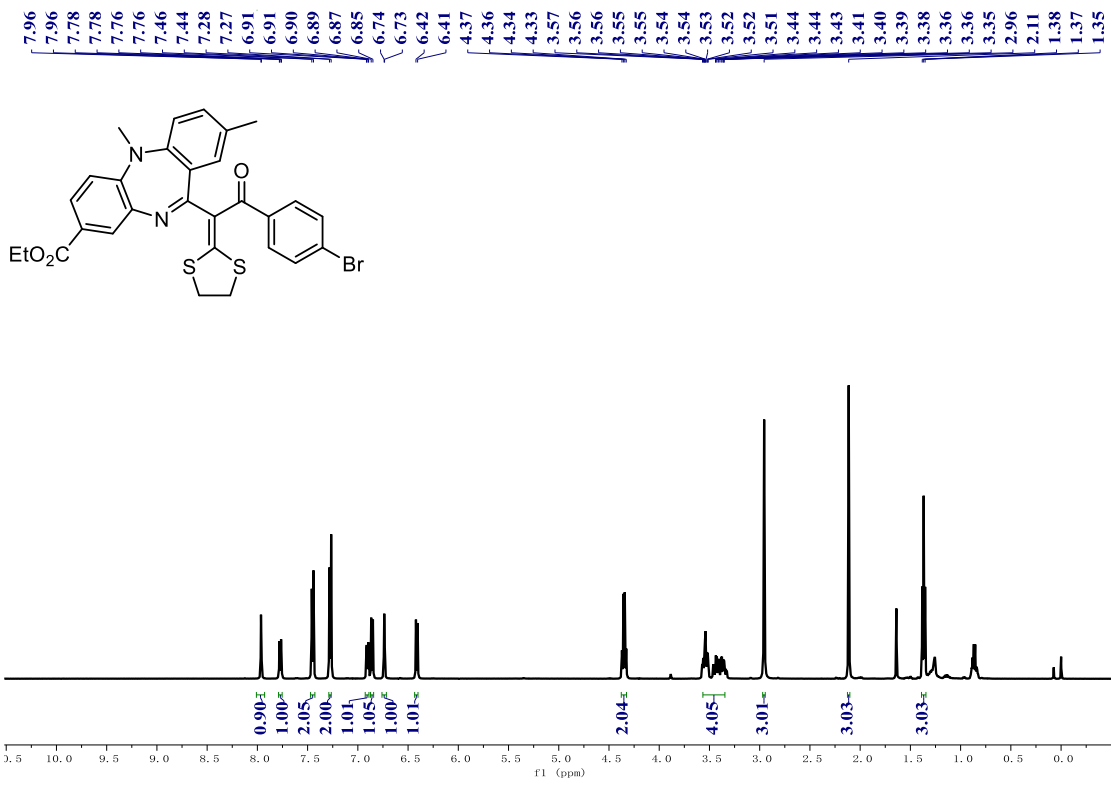


Figure 80. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3au**

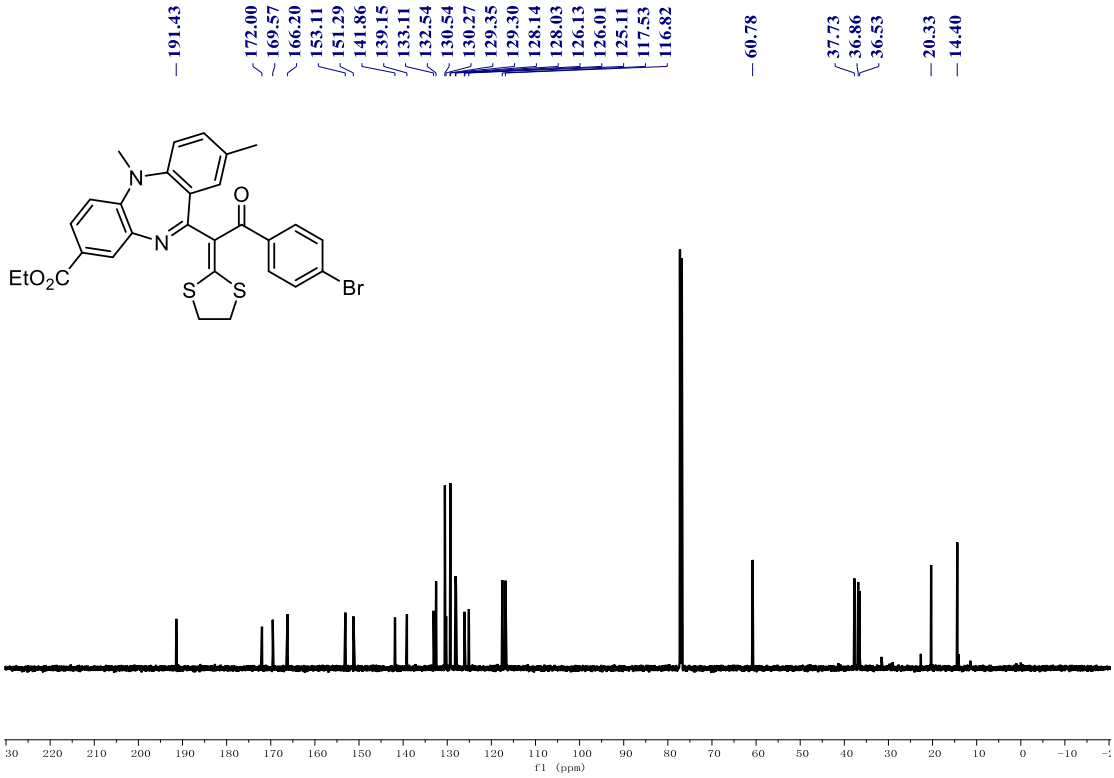


Figure 81. ^{13}C NMR (600 MHz, $CDCl_3$) spectra of compound **3au**

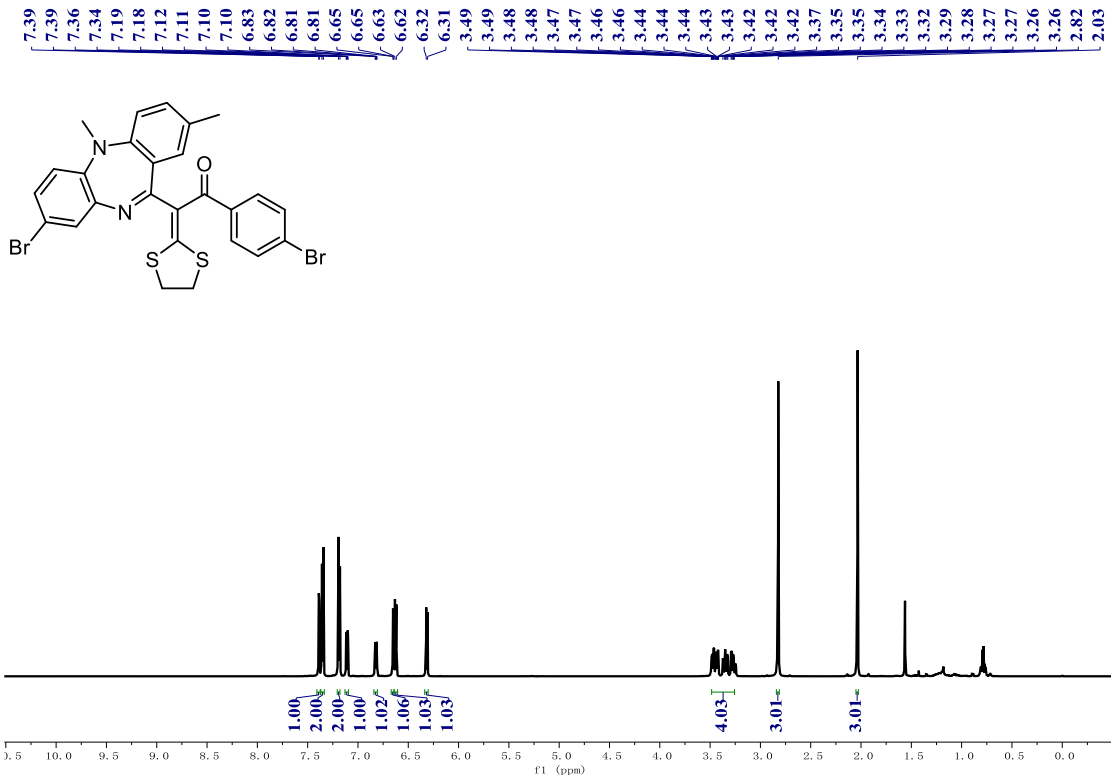


Figure 82. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3av**

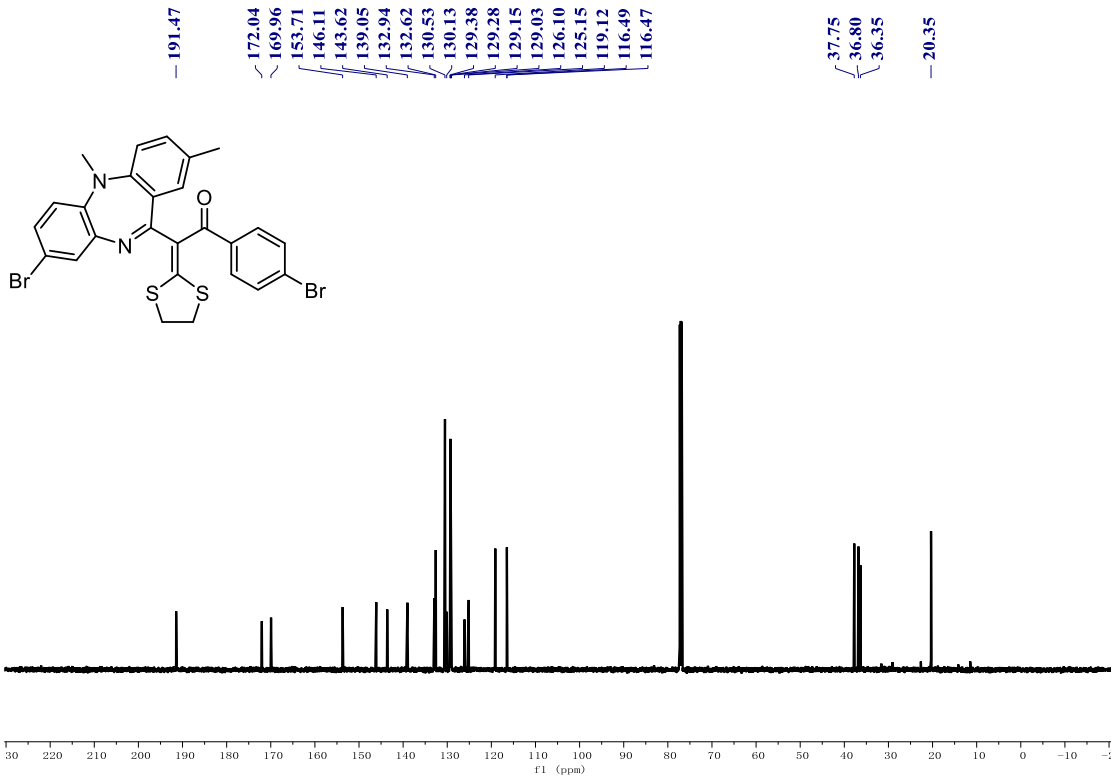


Figure 83. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3av**

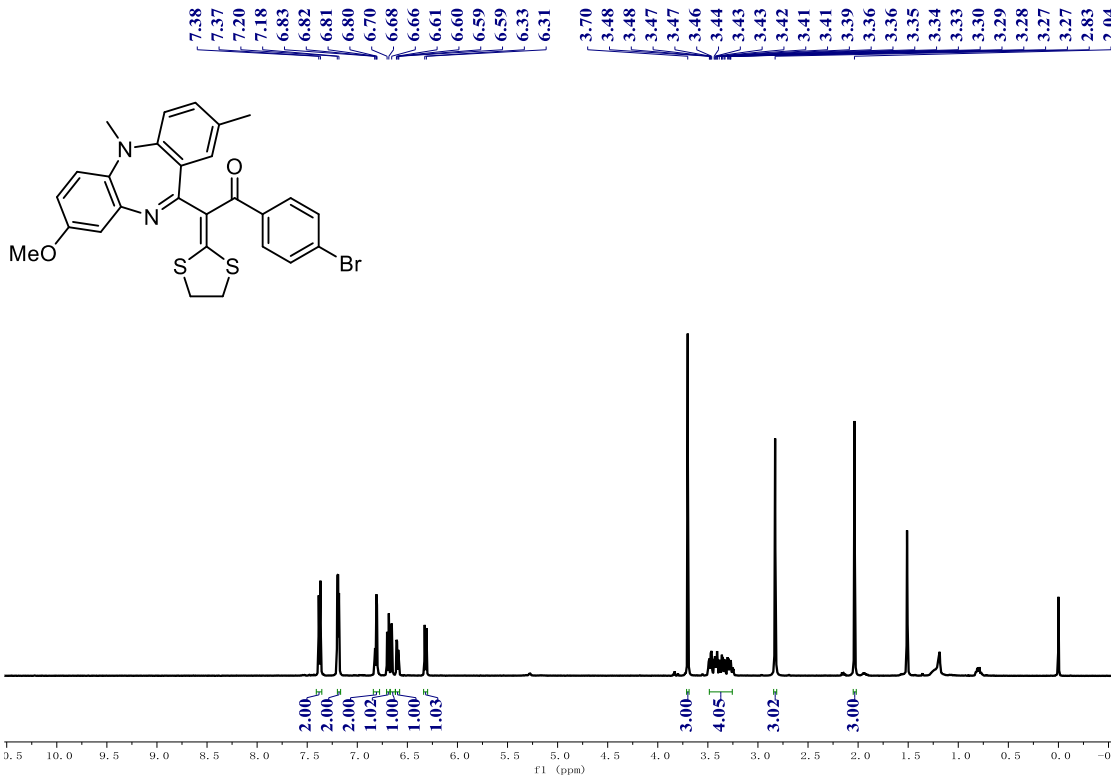


Figure 84. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3aw**

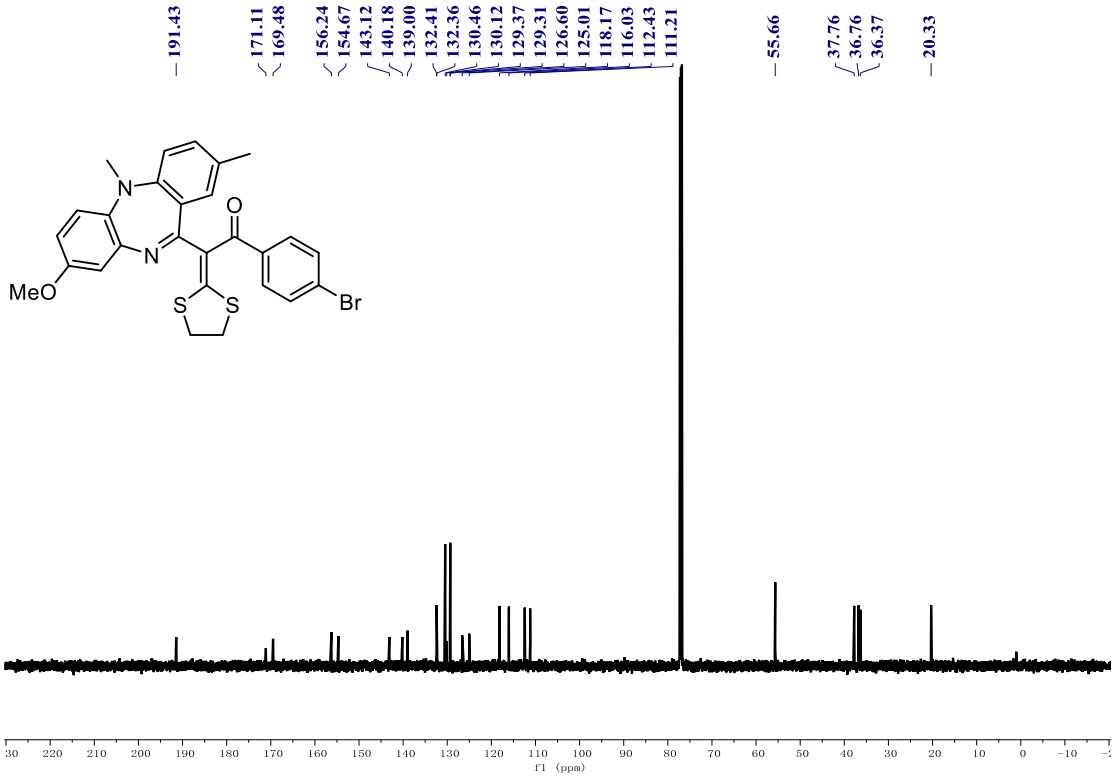


Figure 85. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3aw**

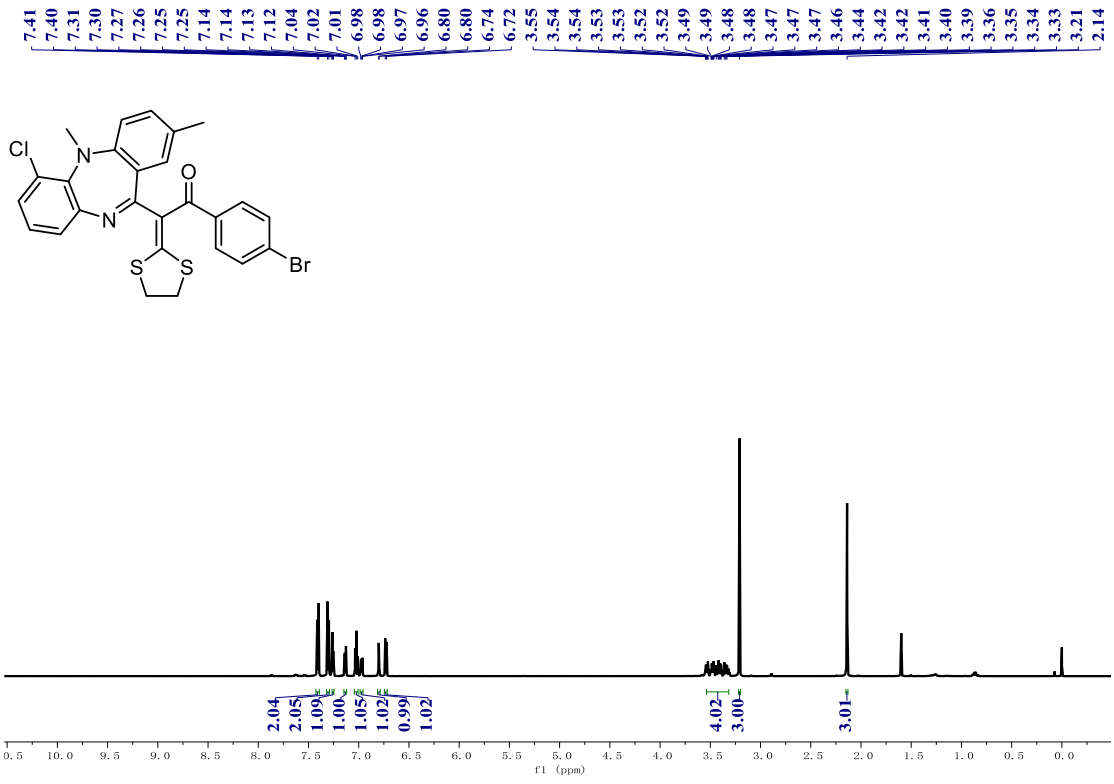


Figure 86. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ax**

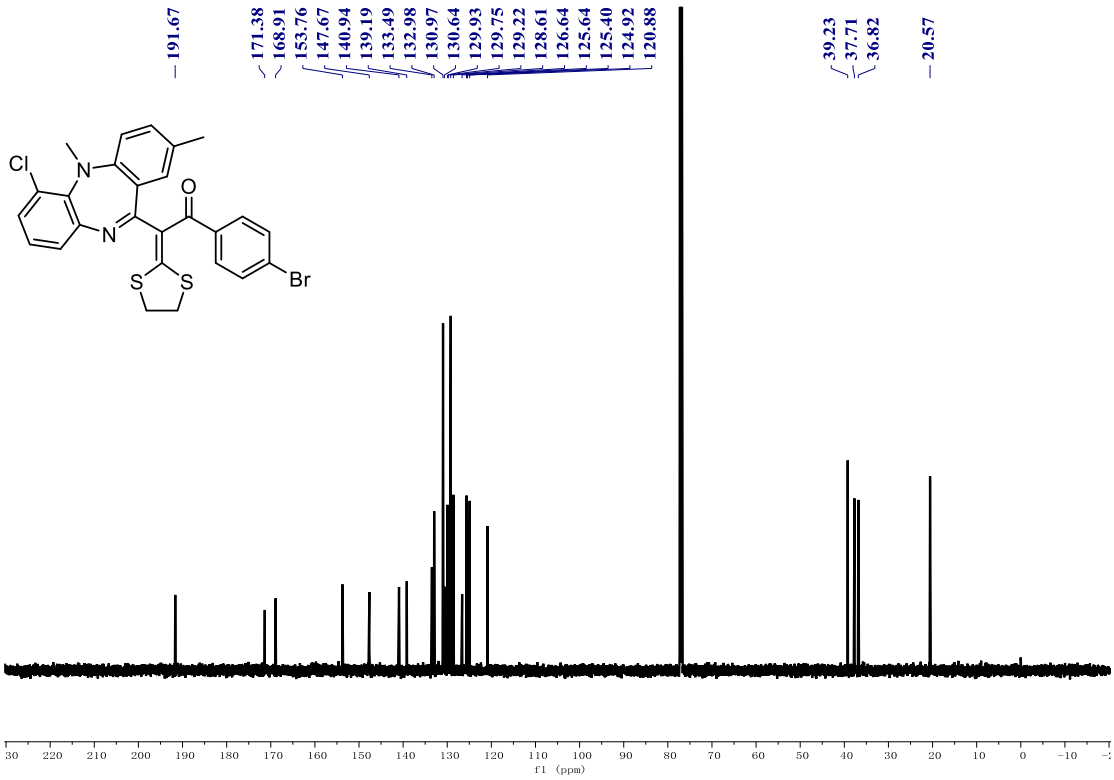


Figure 87. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ax**

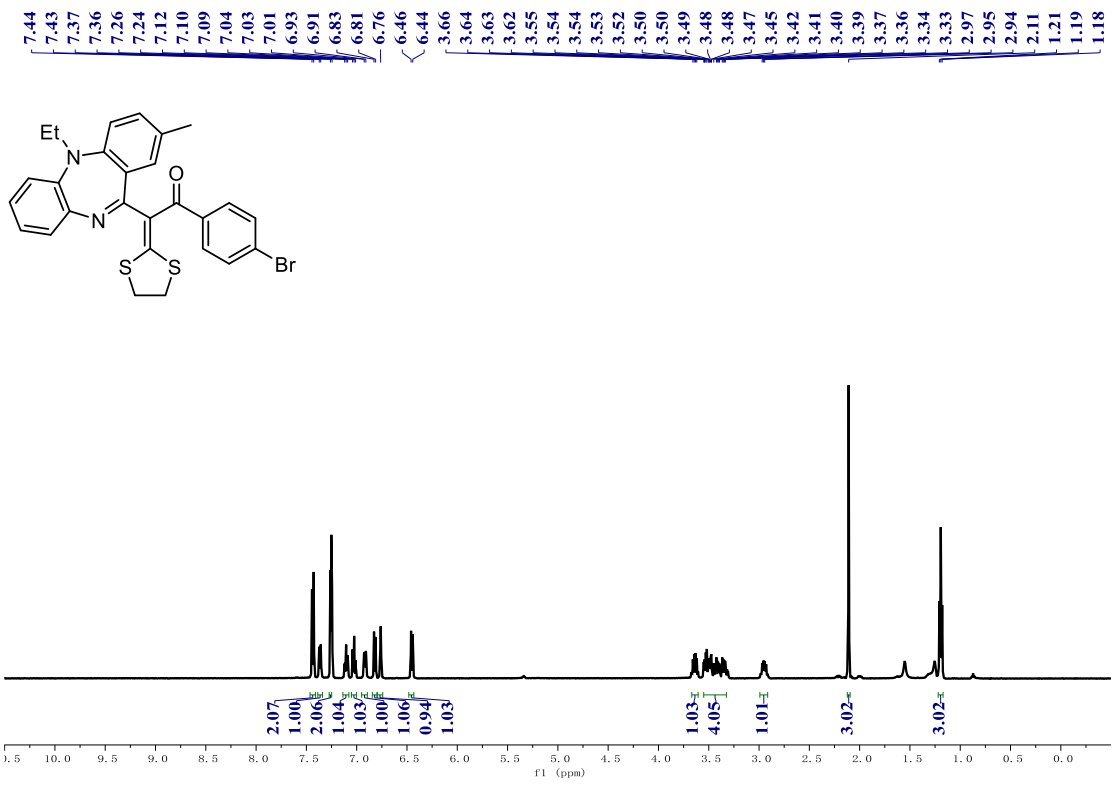


Figure 88. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ay**

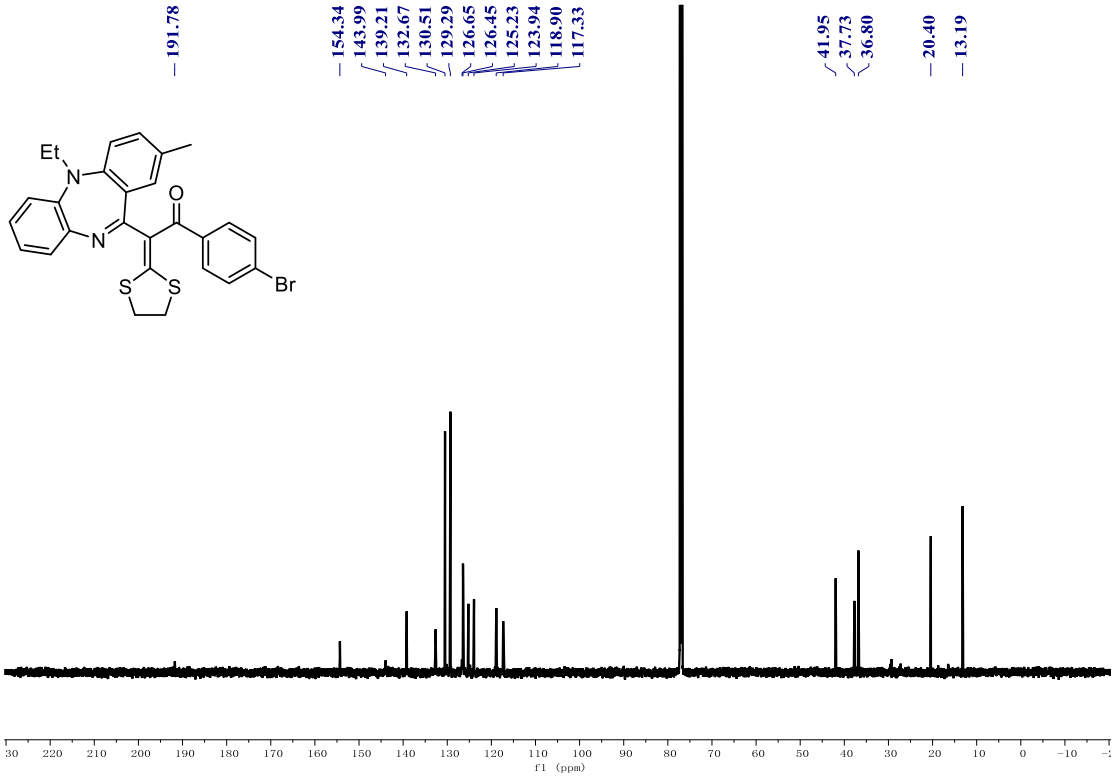


Figure 89. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ay**

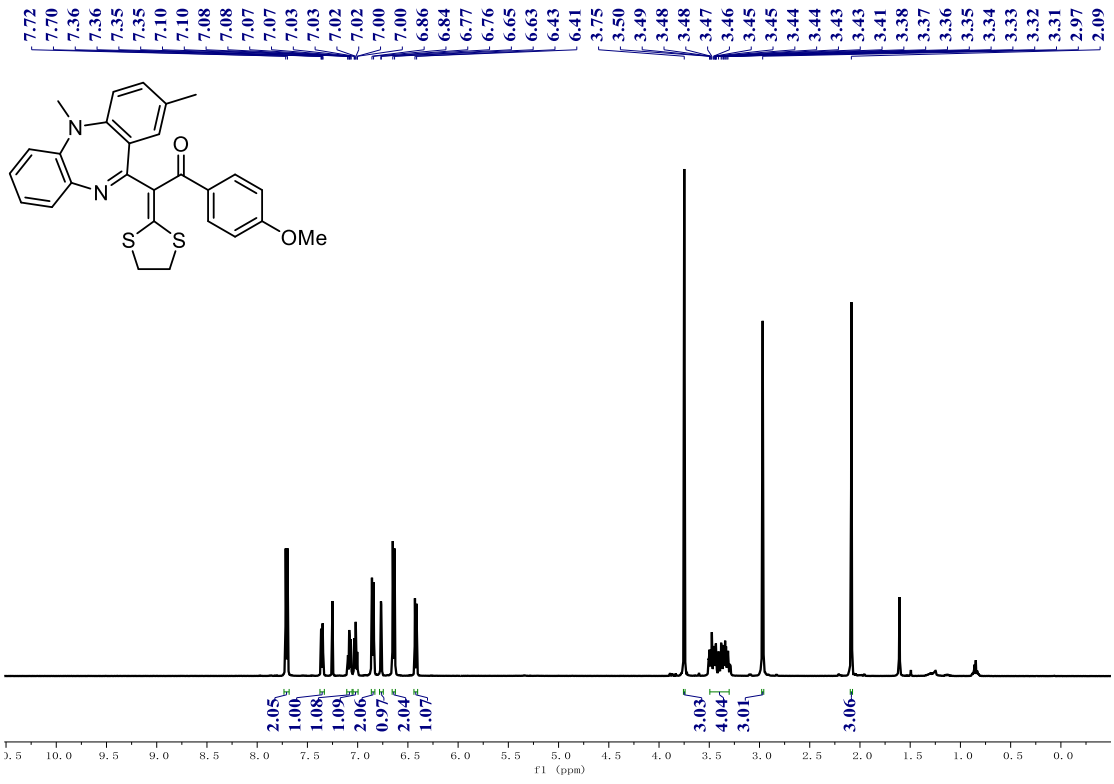


Figure 90. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ba**

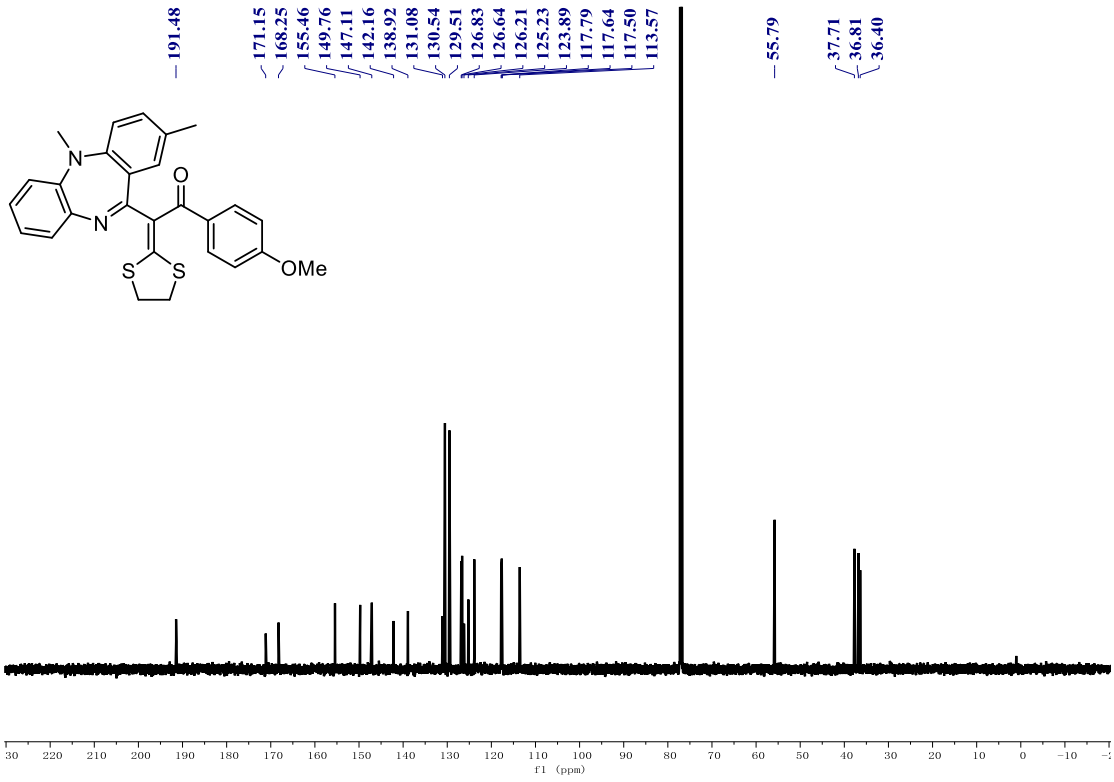


Figure 91. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ba**

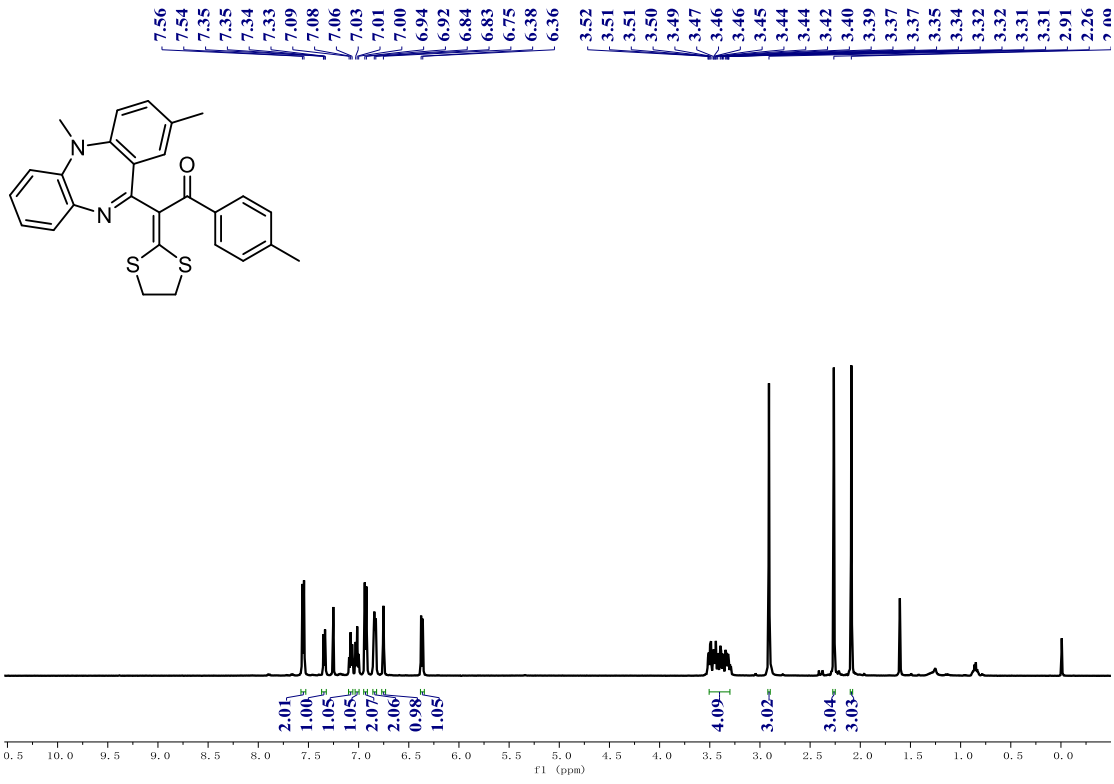


Figure 92. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ca**

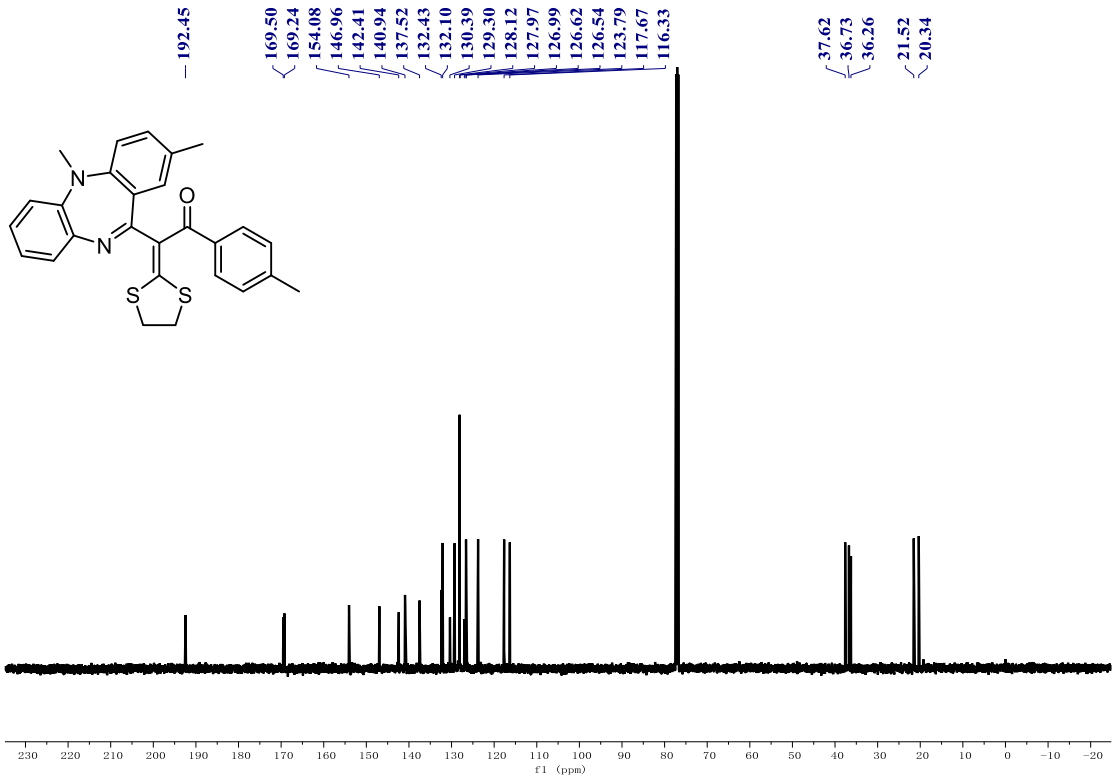


Figure 93. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ca**

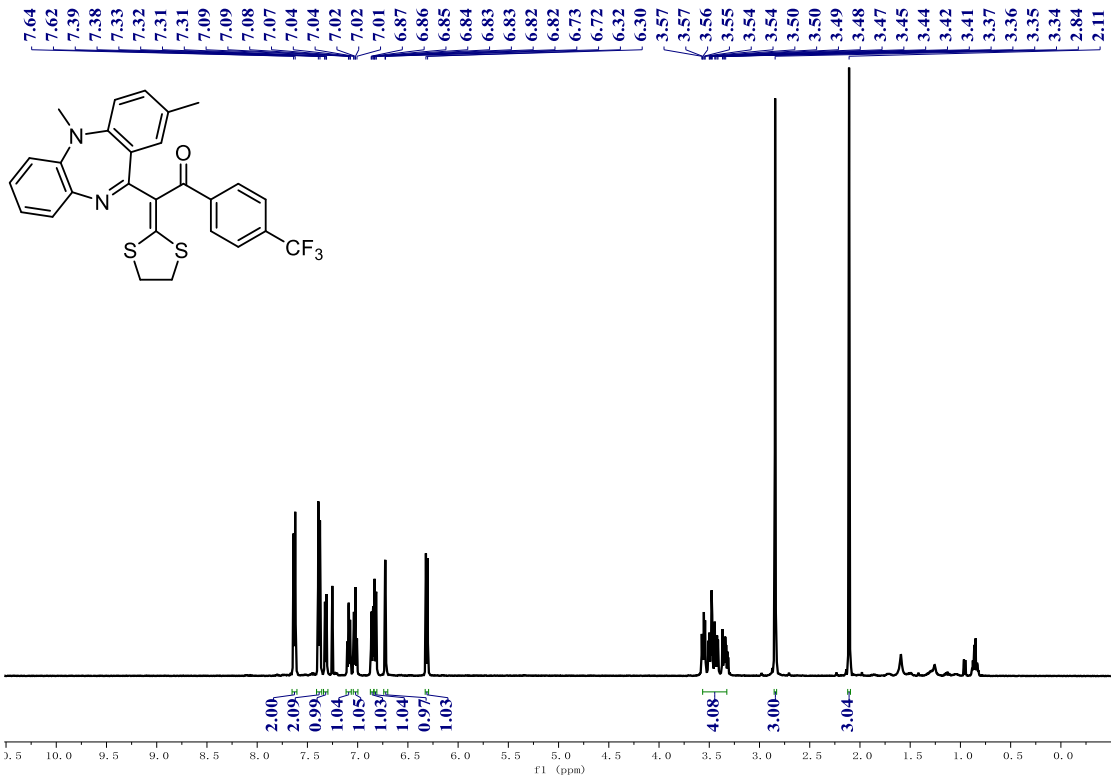


Figure 94. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3da**

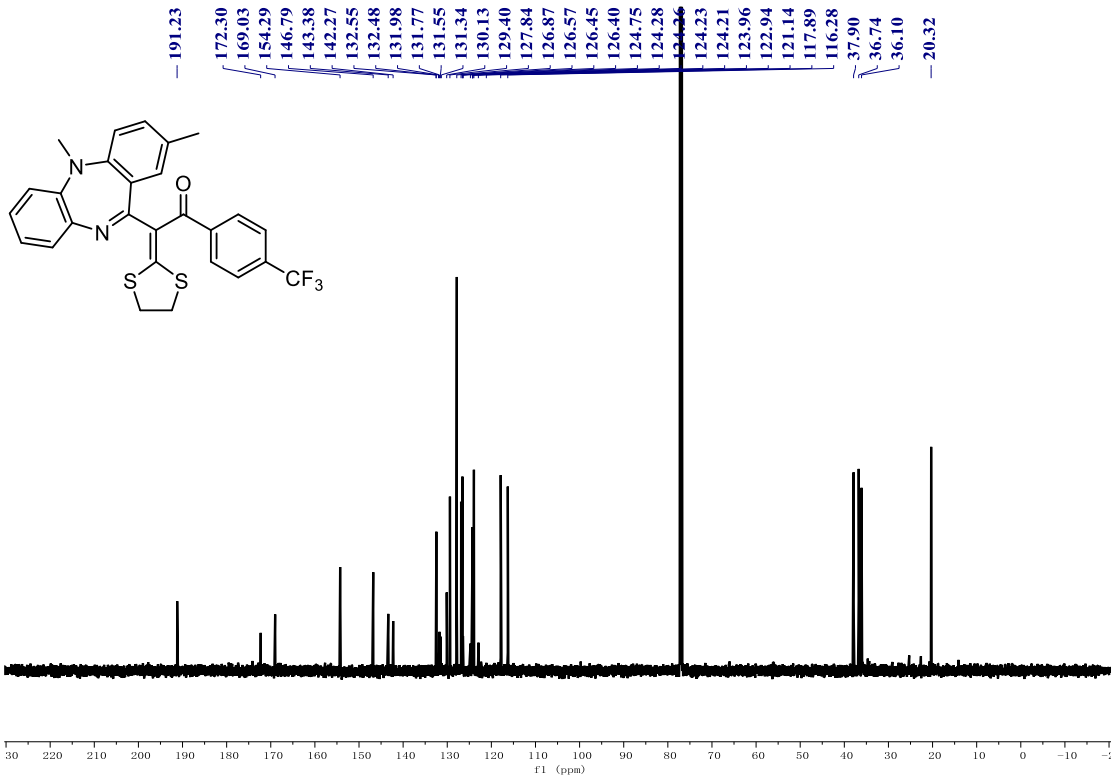


Figure 95. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3da**

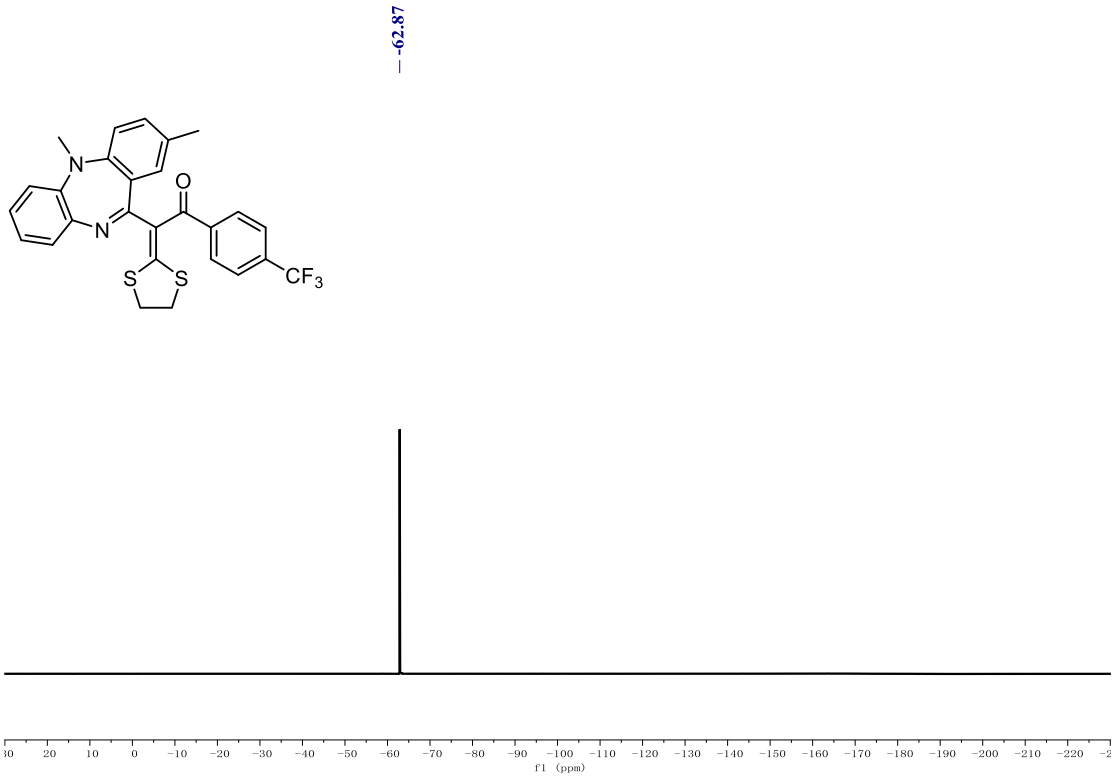


Figure 96. ^{19}C NMR (565 MHz, $CDCl_3$) spectra of compound **3da**

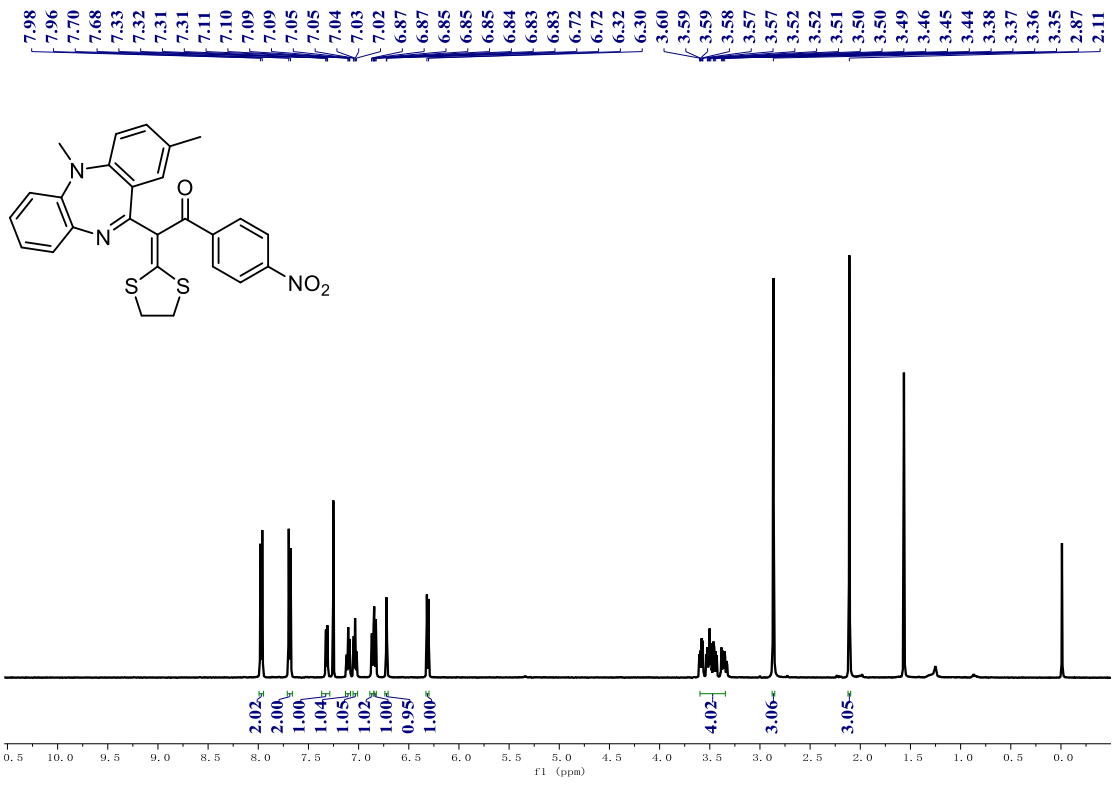


Figure 97. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ea**

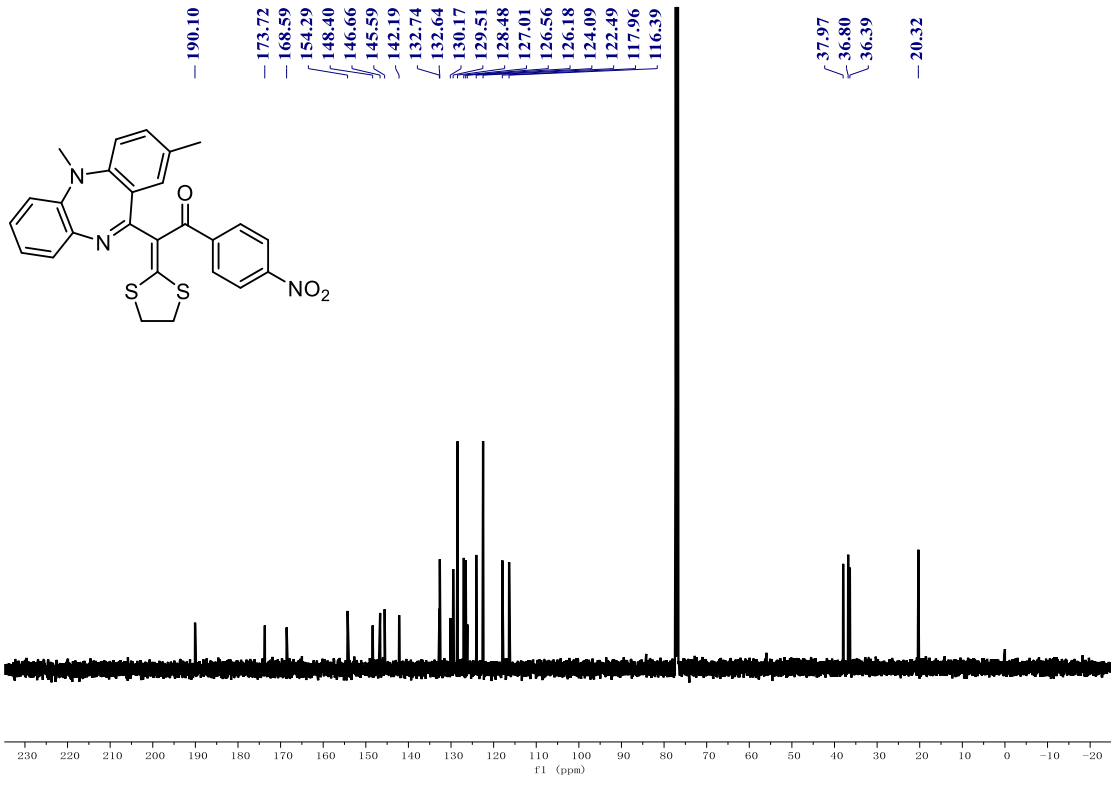


Figure 98. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ea**

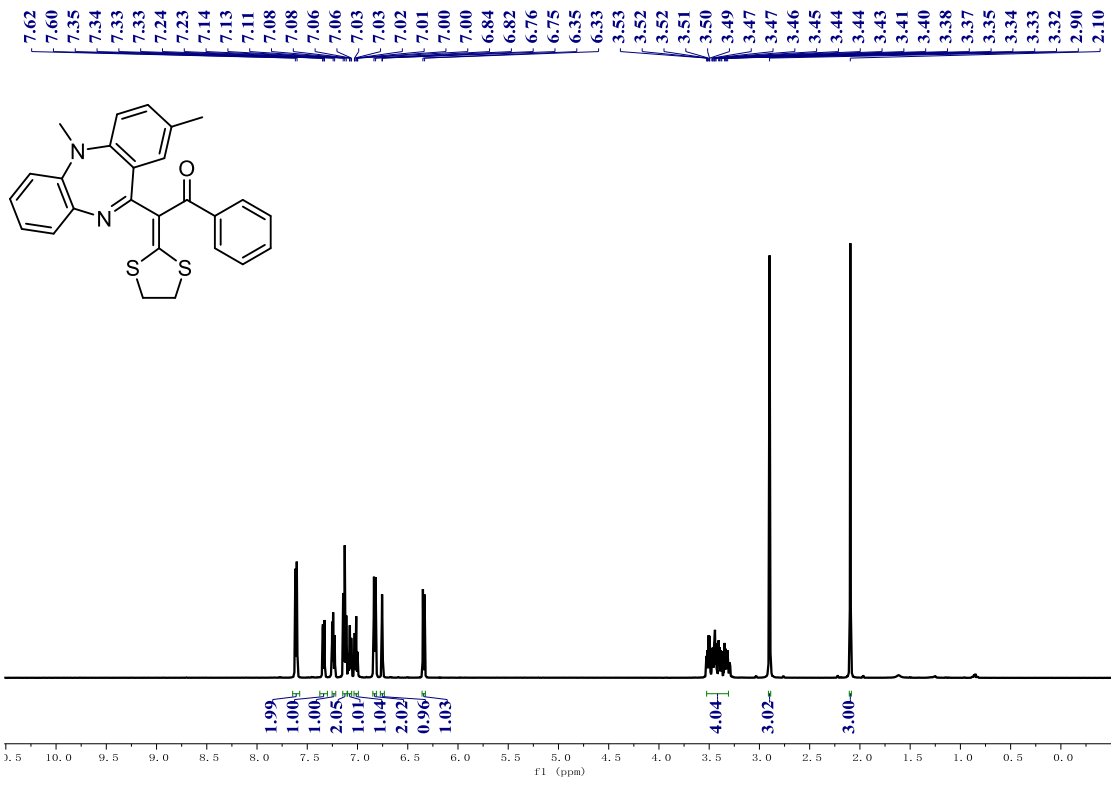


Figure 99. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3fa**

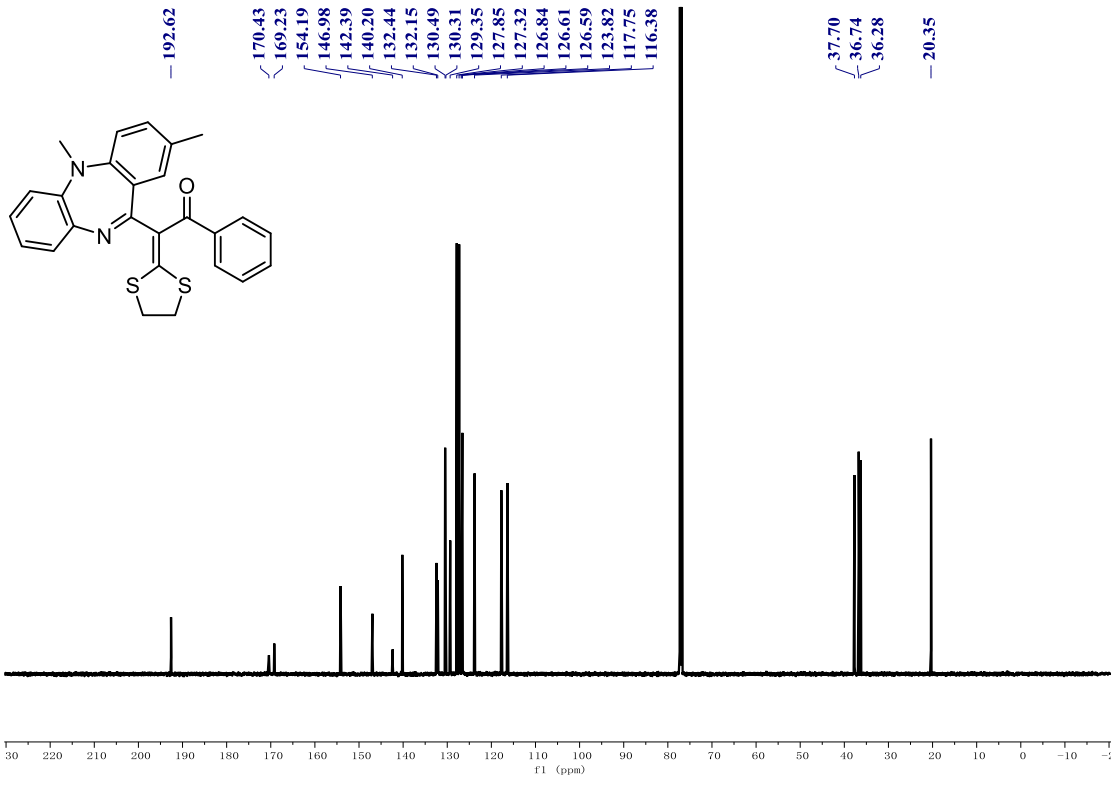


Figure 100. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3fa**

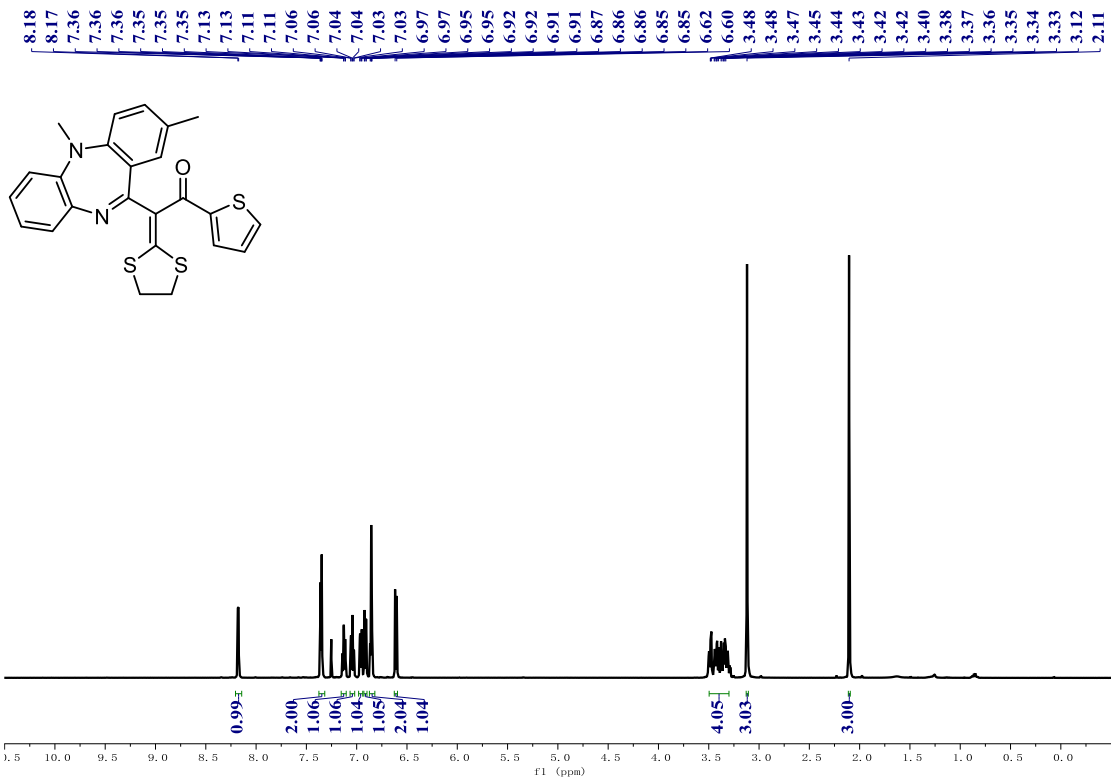


Figure 101. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ga**

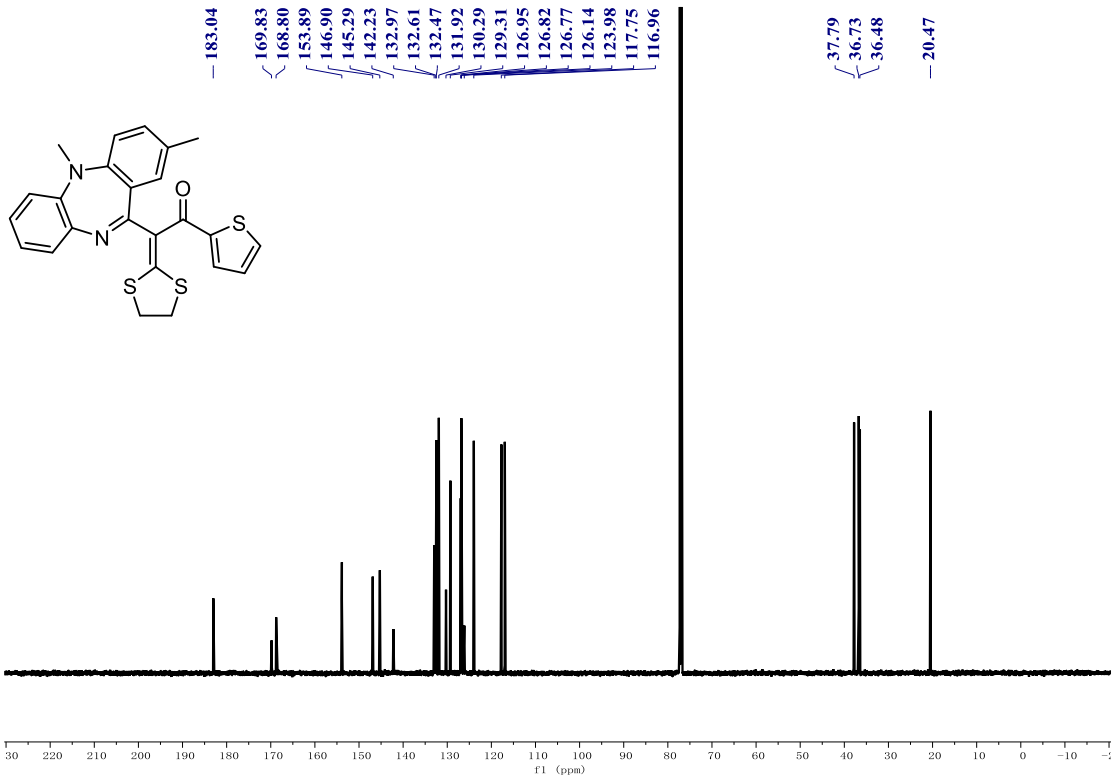


Figure 102. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ga**

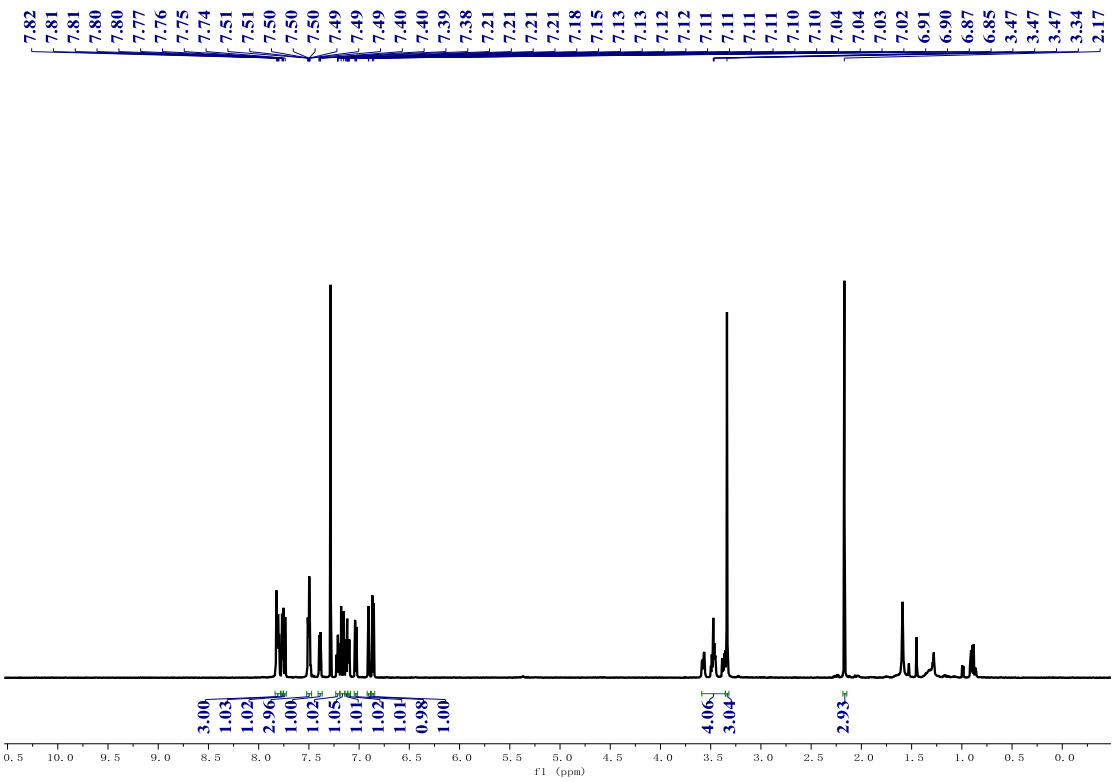


Figure 103. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ha**

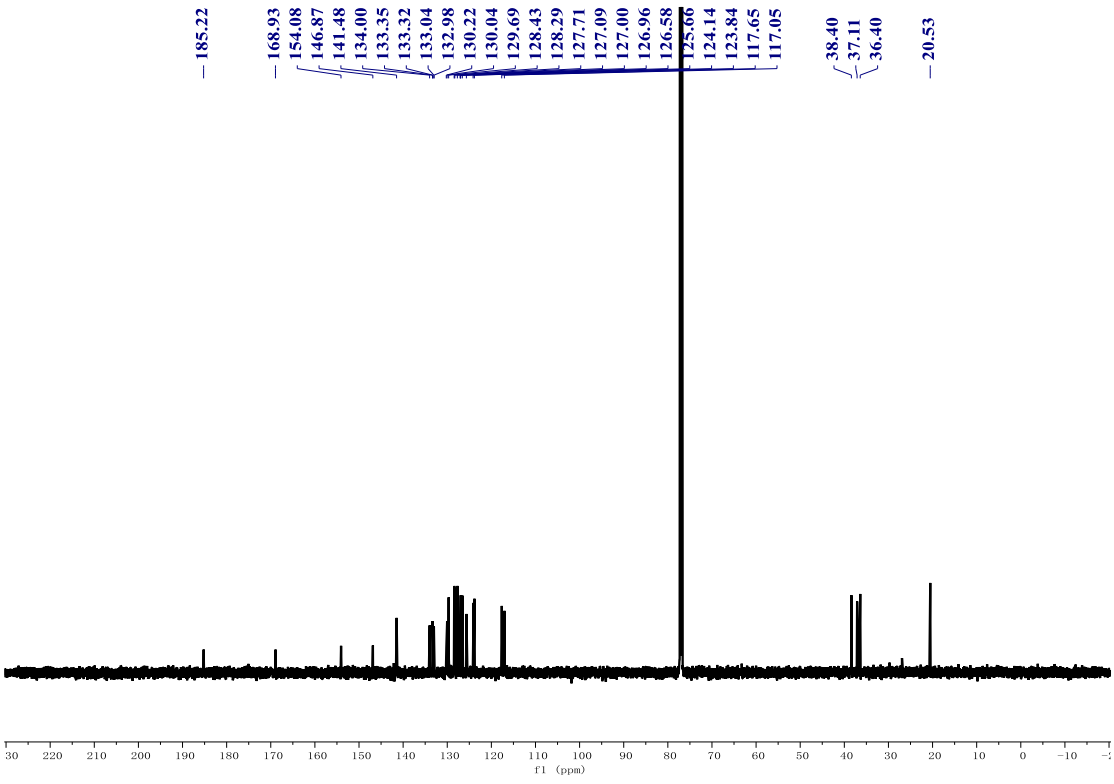


Figure 104. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ha**

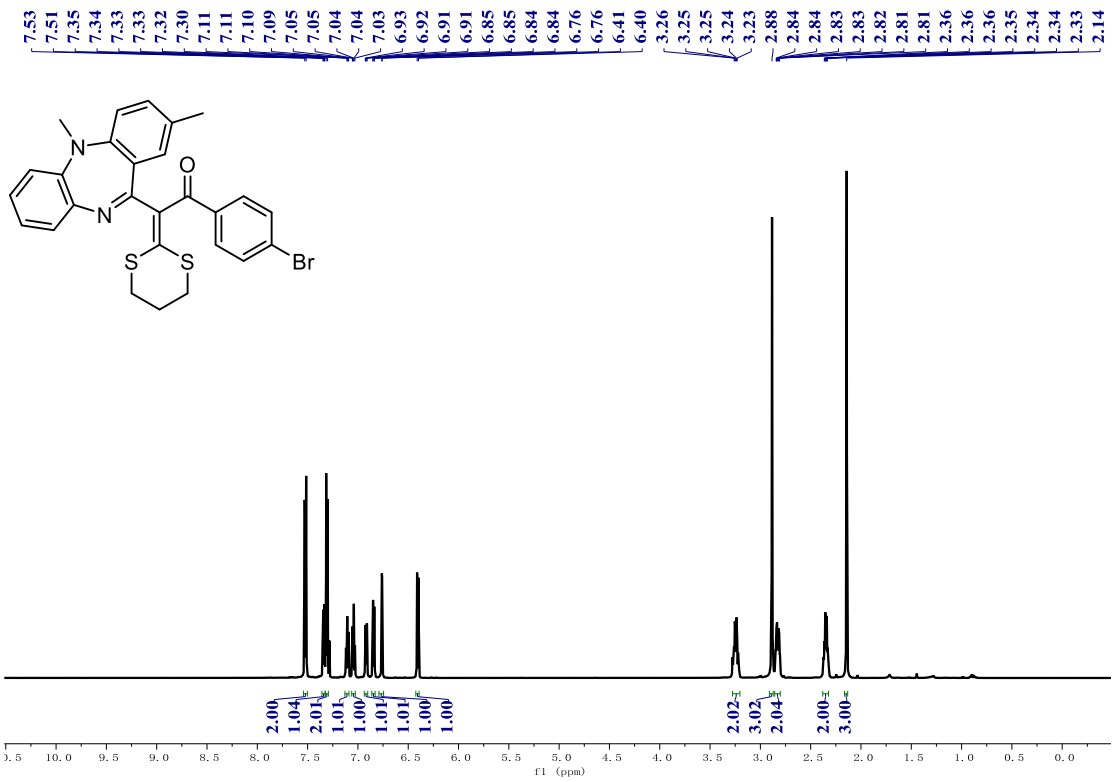


Figure 105. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ia**

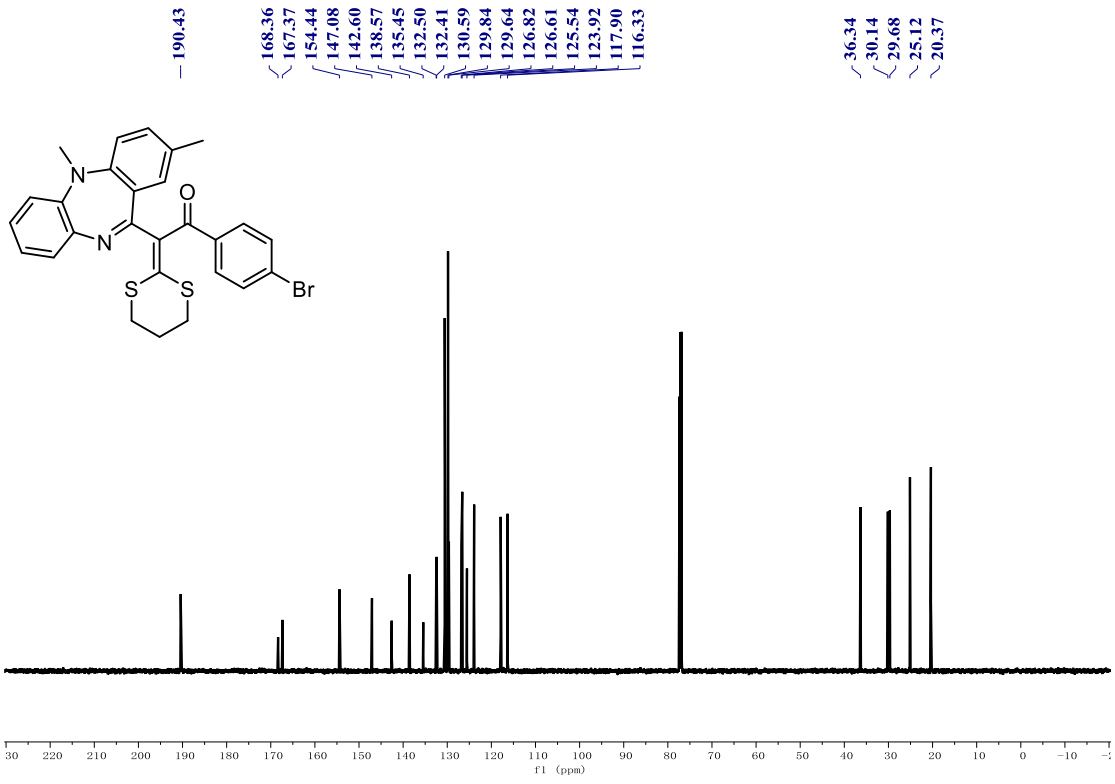


Figure 106. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ia**

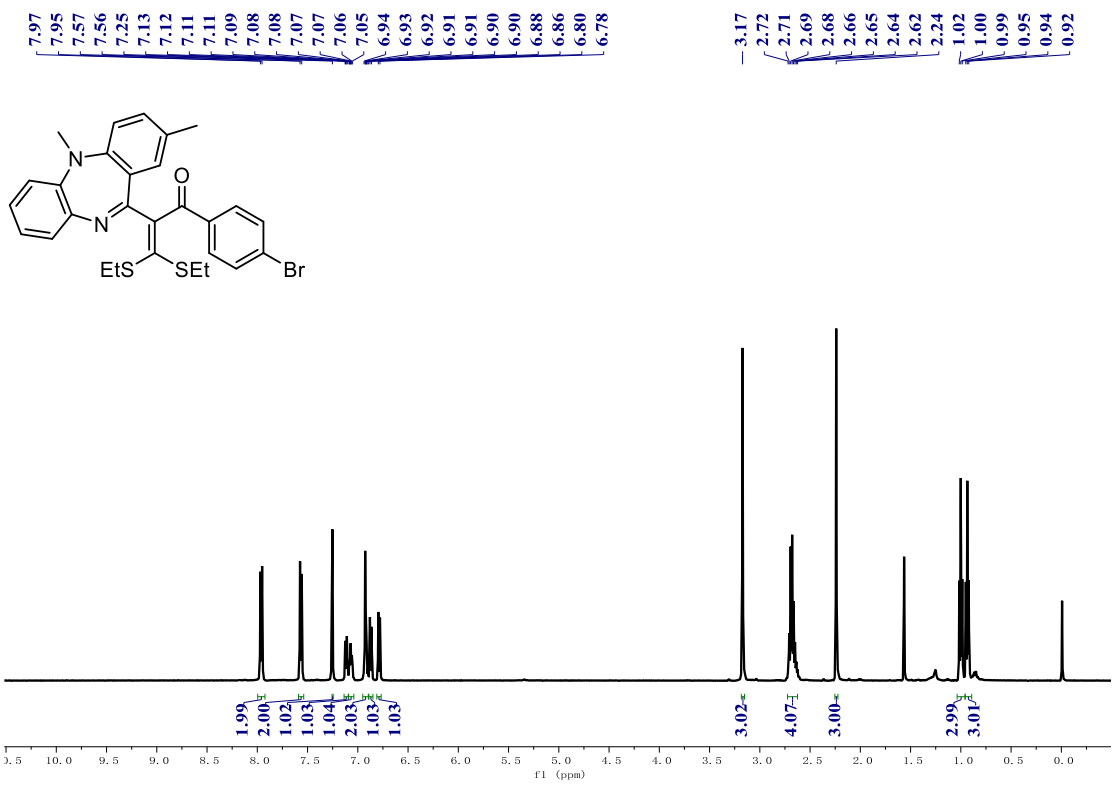


Figure 107. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ja**

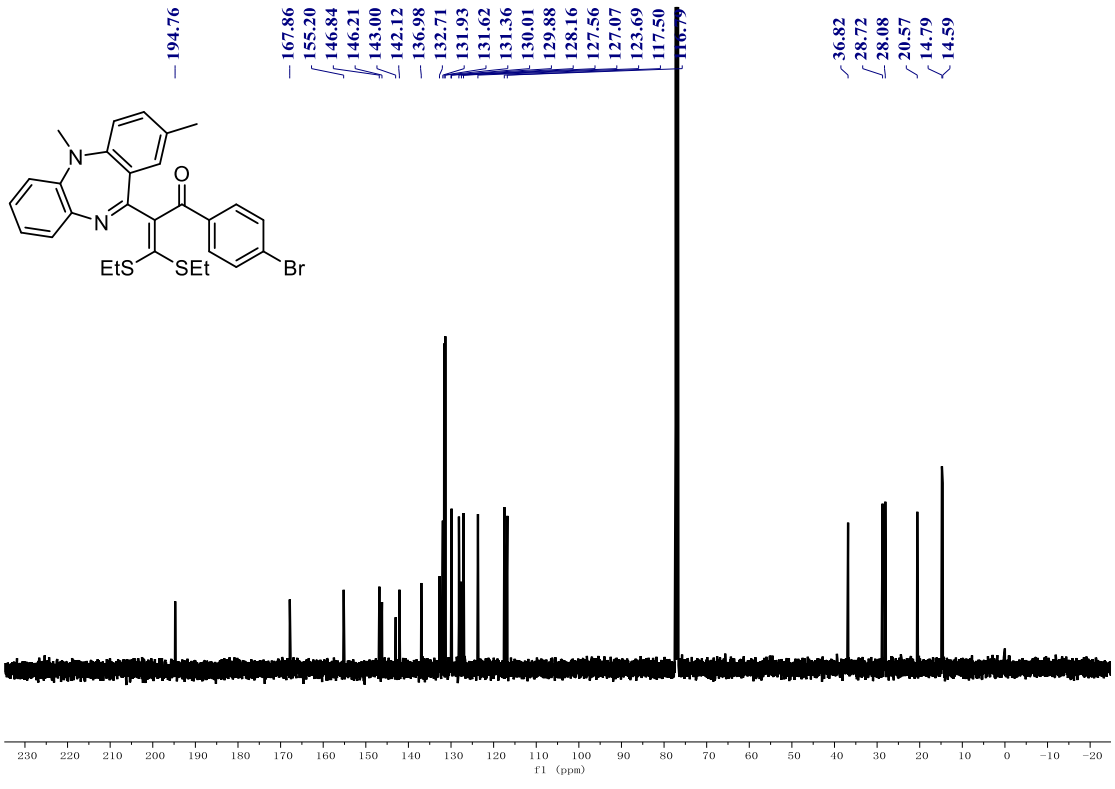


Figure 108. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ja**

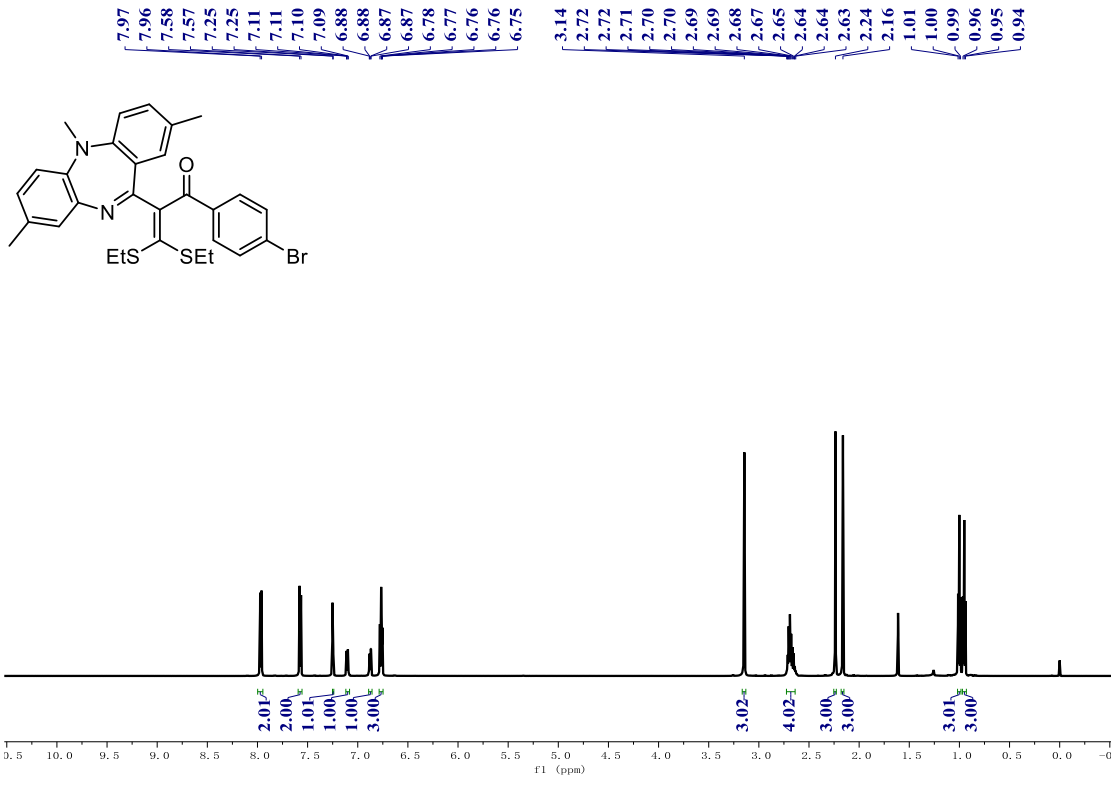


Figure 109. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3jw**

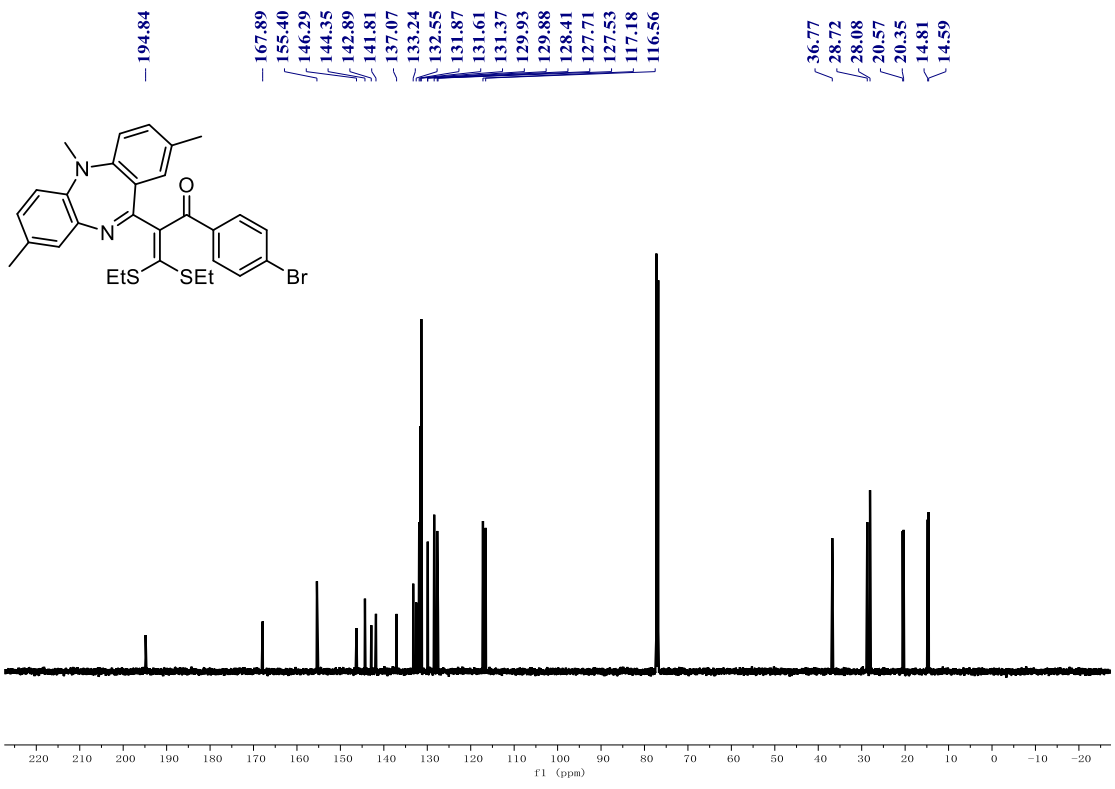


Figure 110. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3jw**

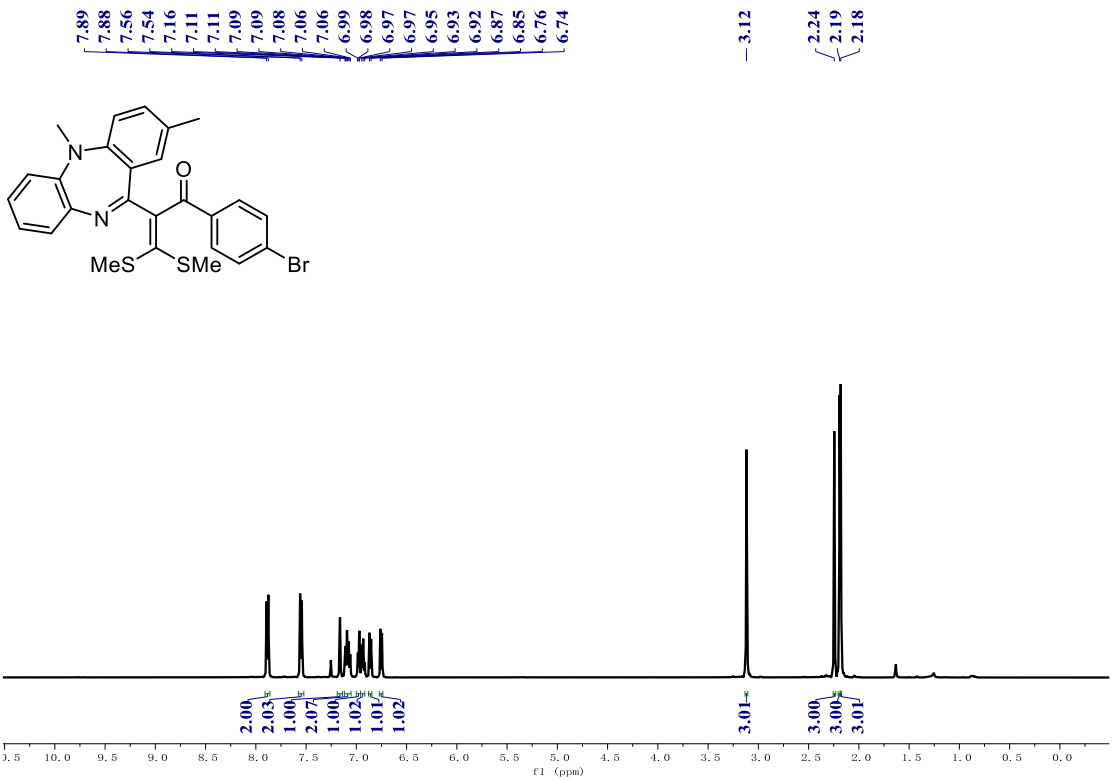


Figure 111. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ka**

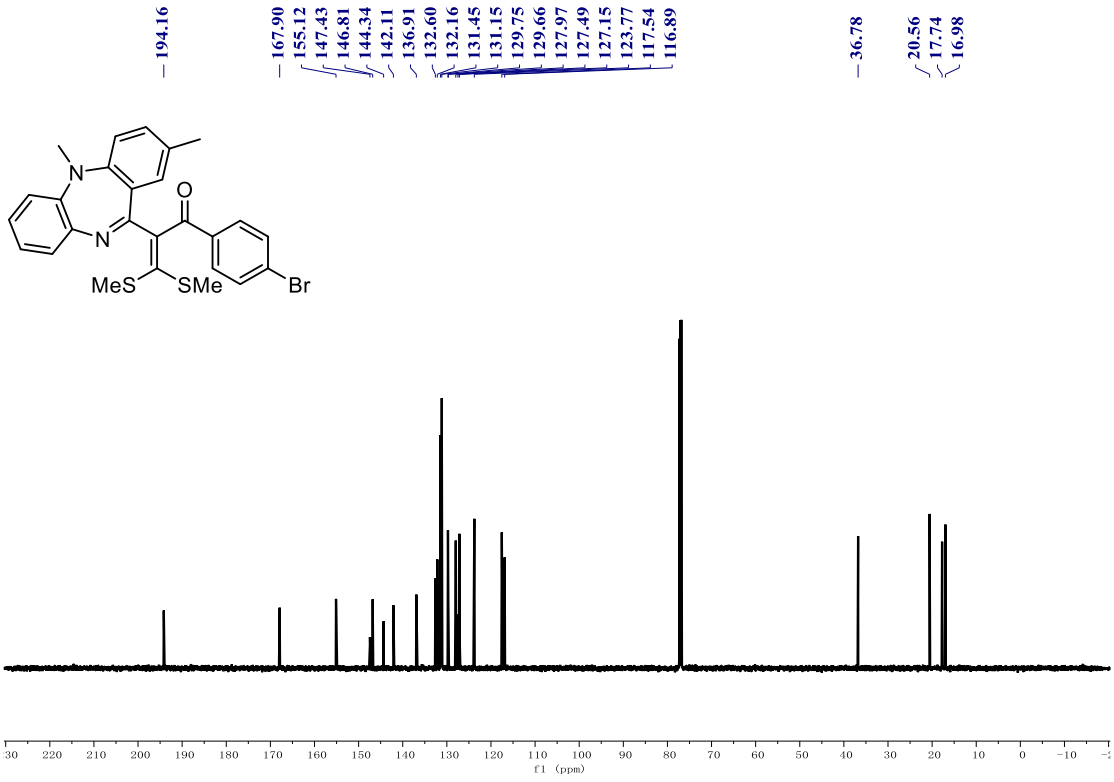


Figure 112. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ka**

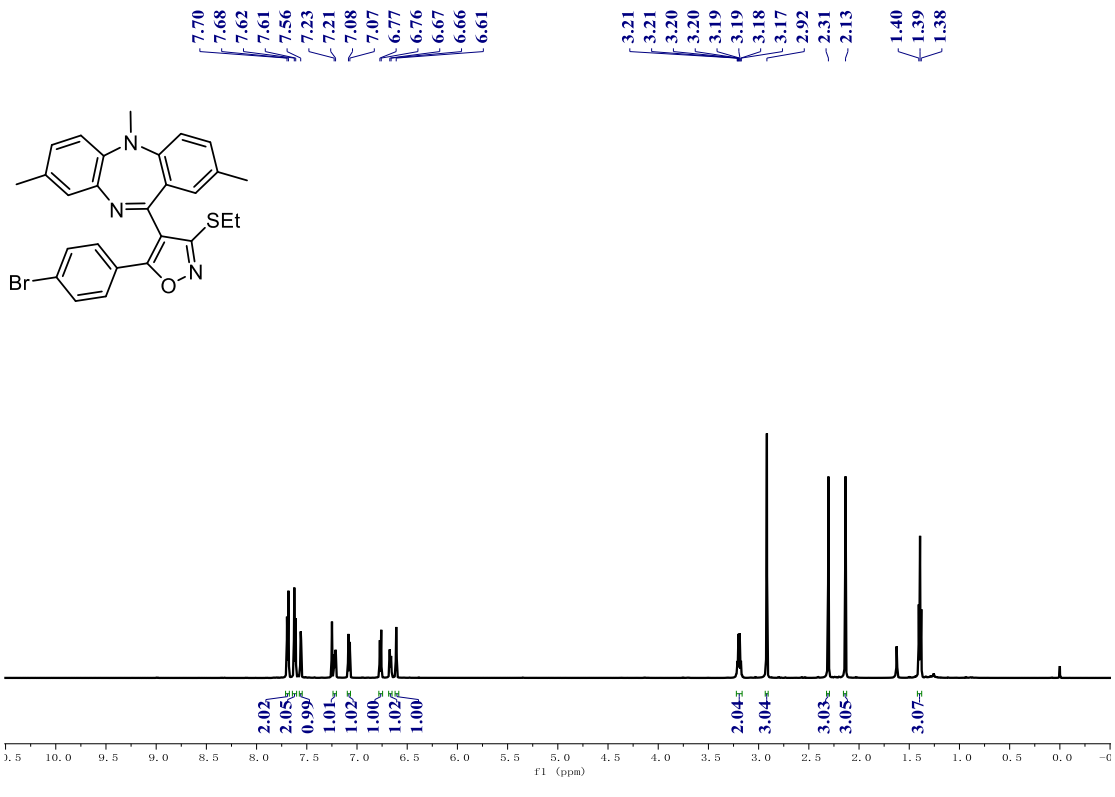


Figure 113. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4**

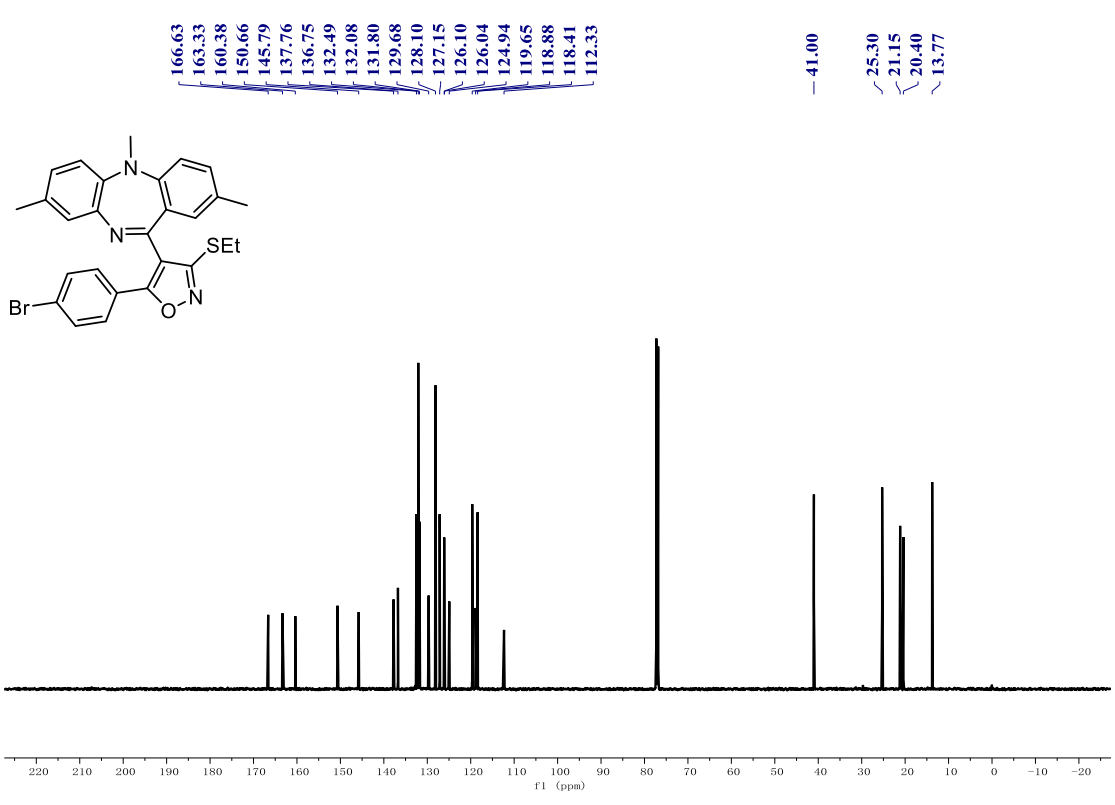


Figure 114. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4**

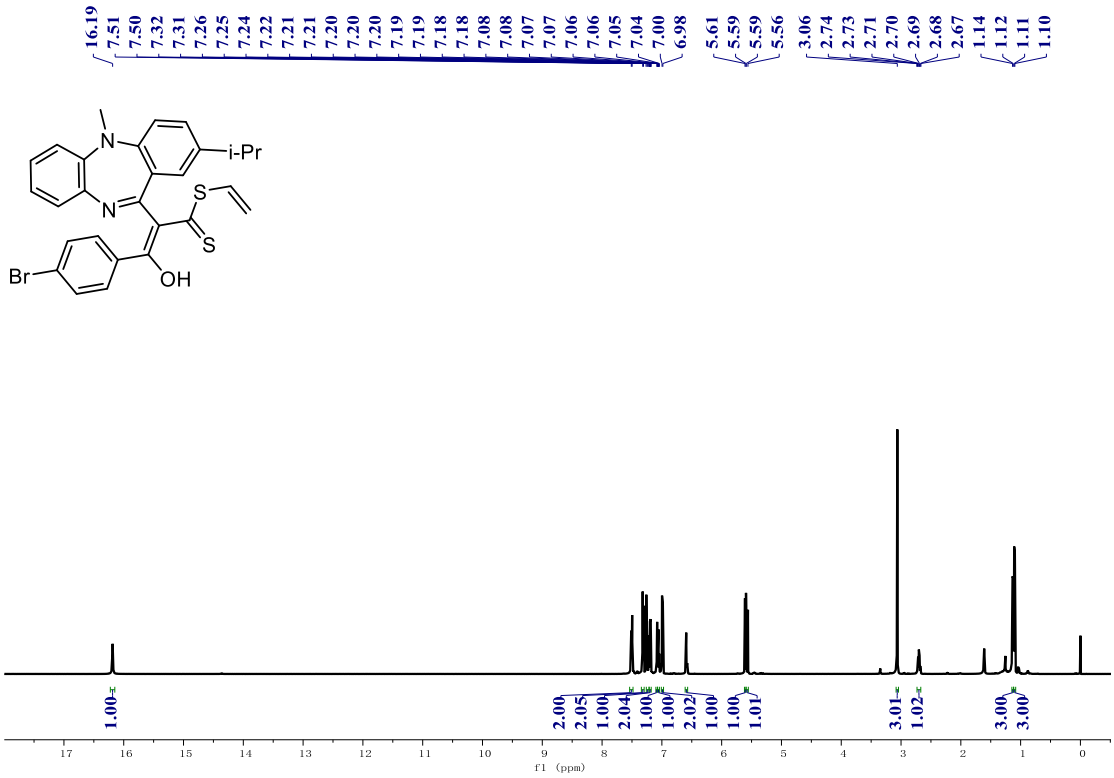


Figure 115. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **5**

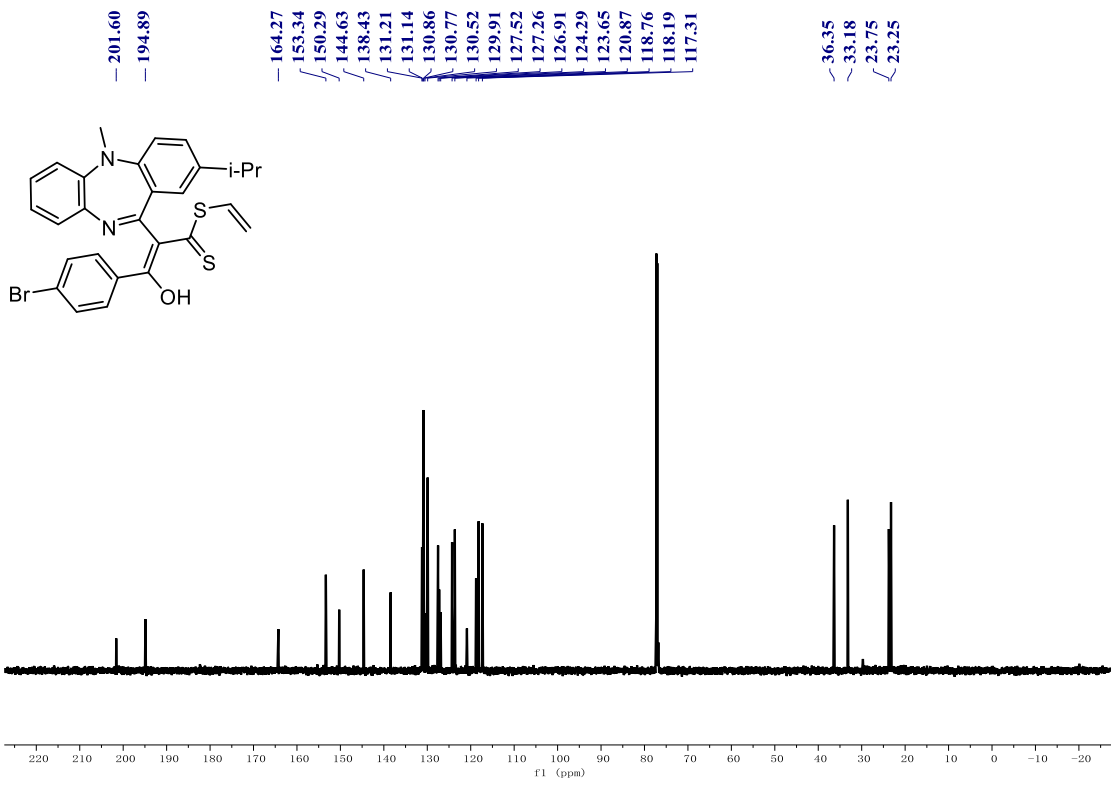


Figure 116. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **5**

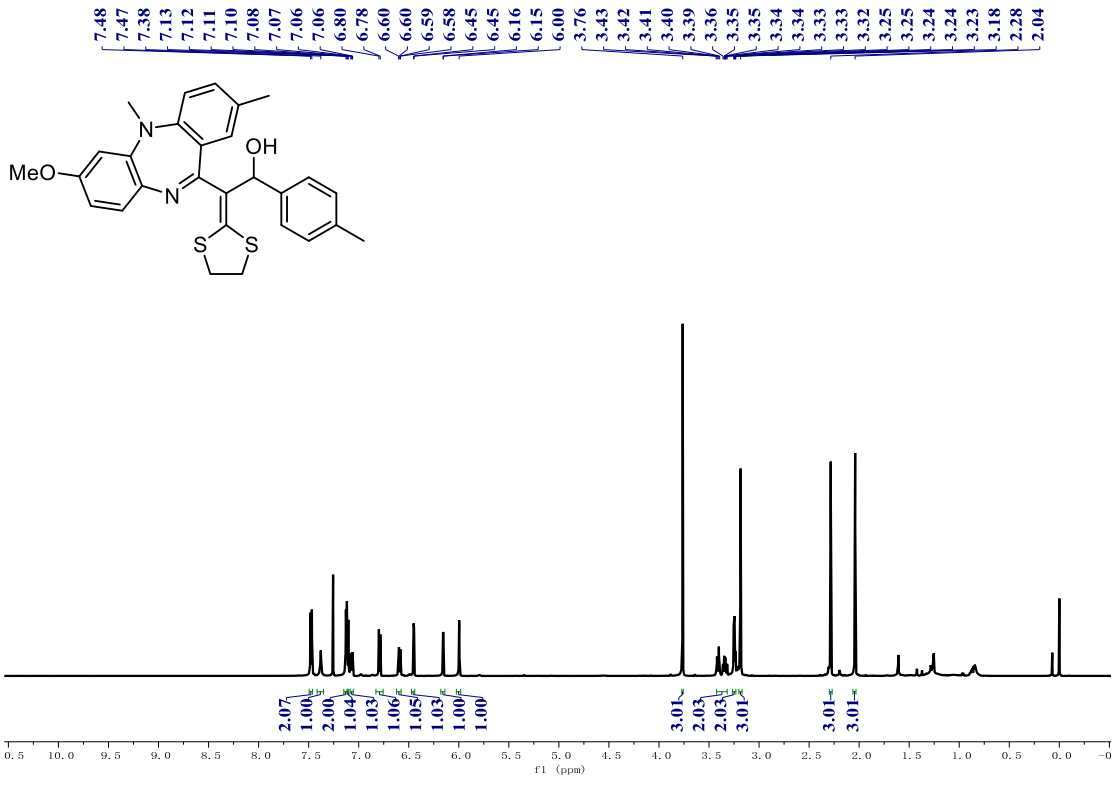


Figure 117. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **6a**

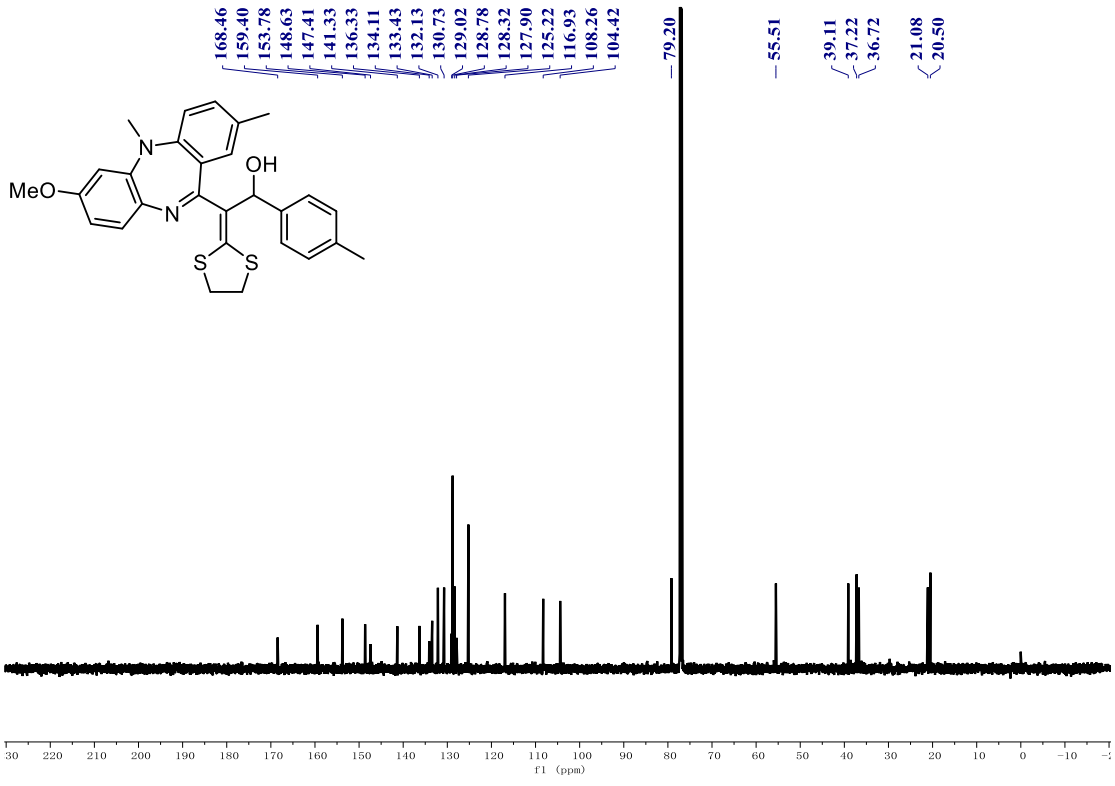


Figure 118. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **6a**

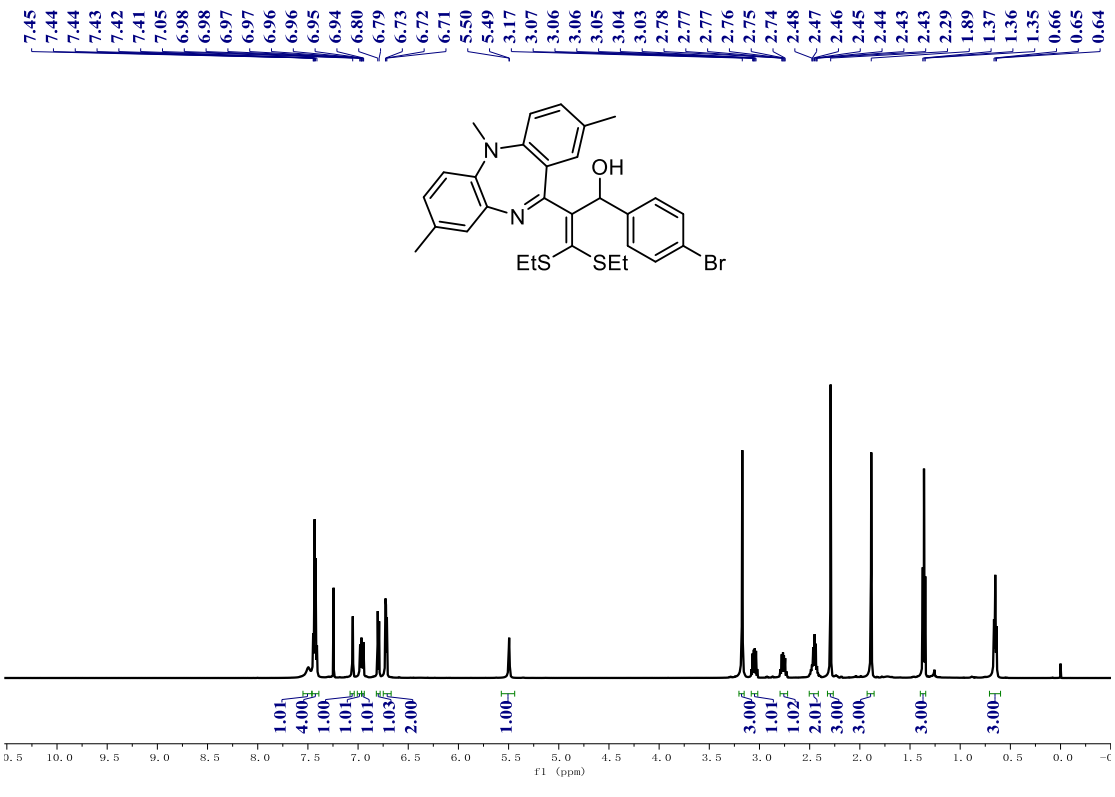


Figure 119. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **6b**

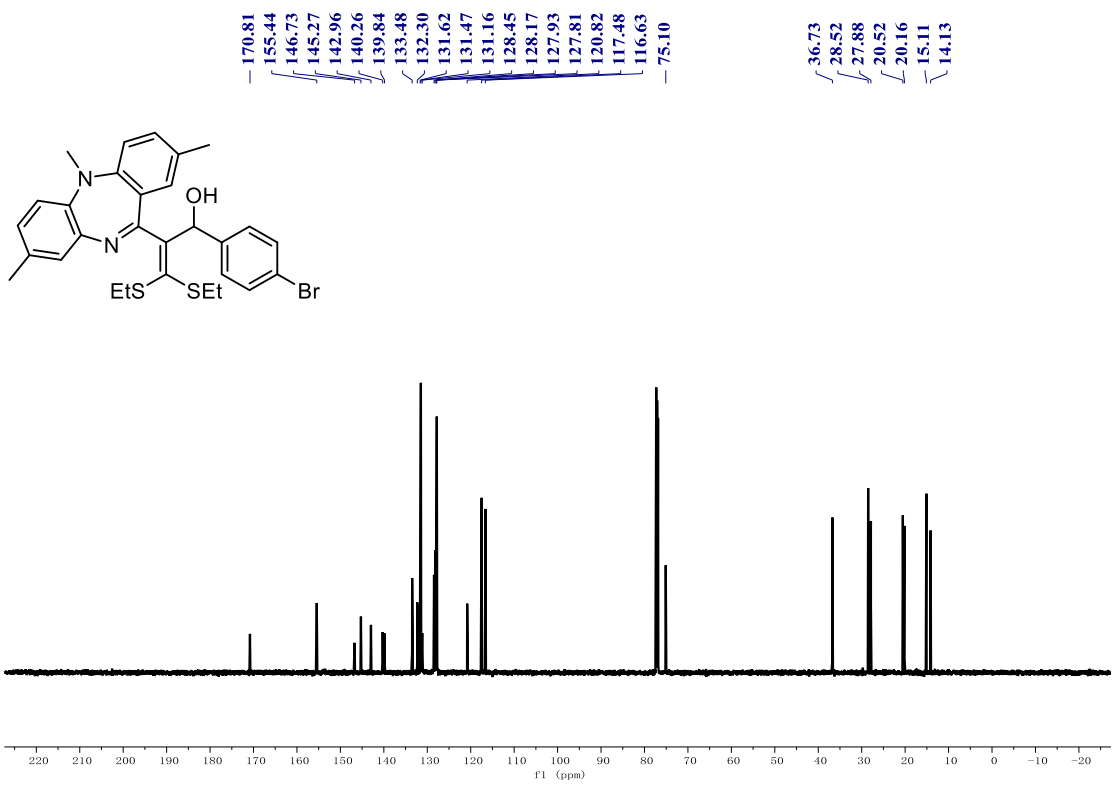


Figure 120. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **6b**

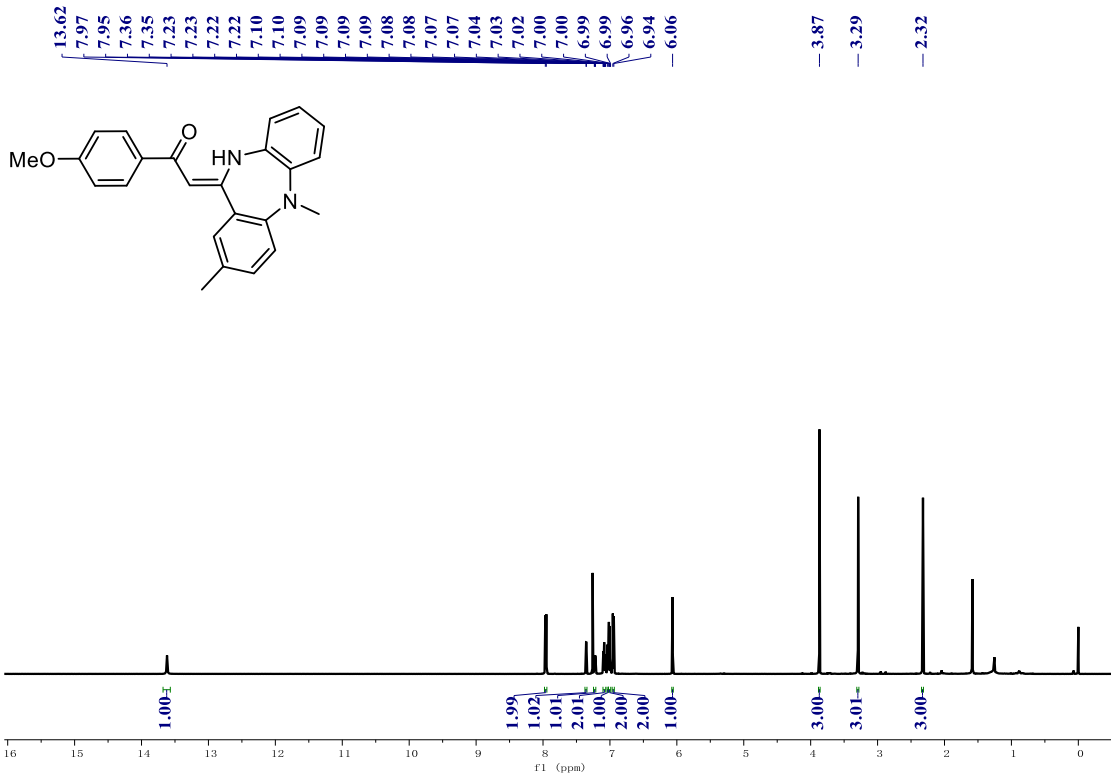


Figure 121. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **7a**

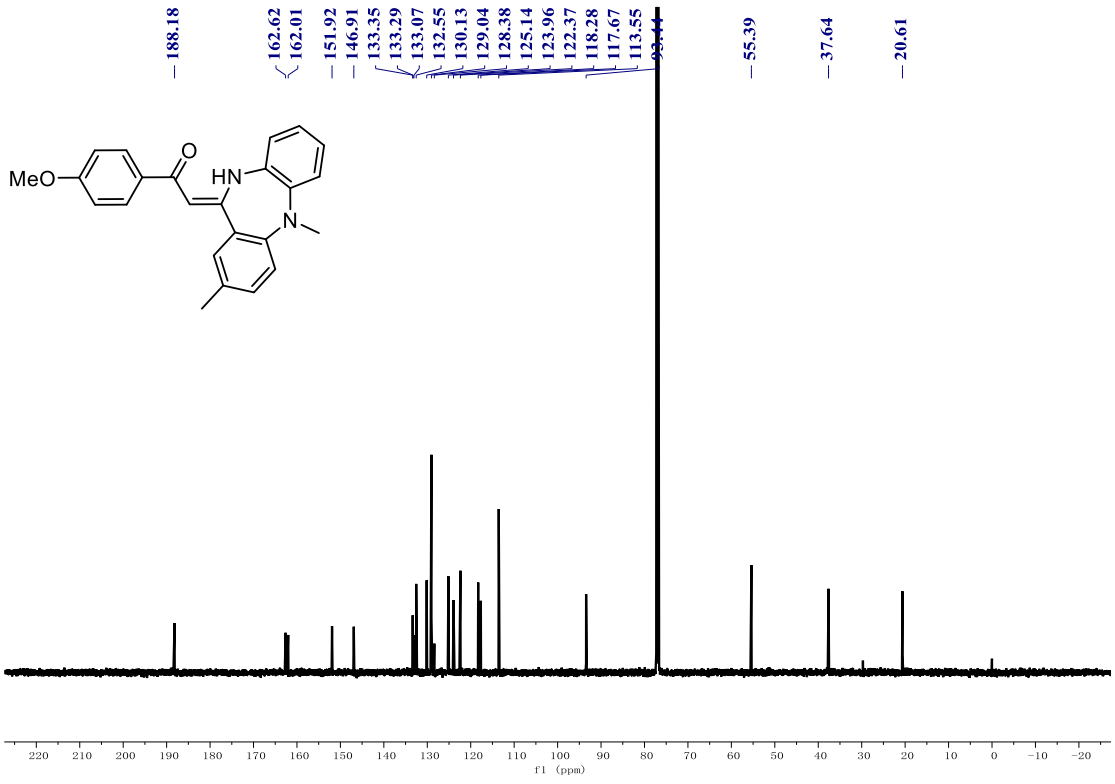


Figure 122. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **7a**

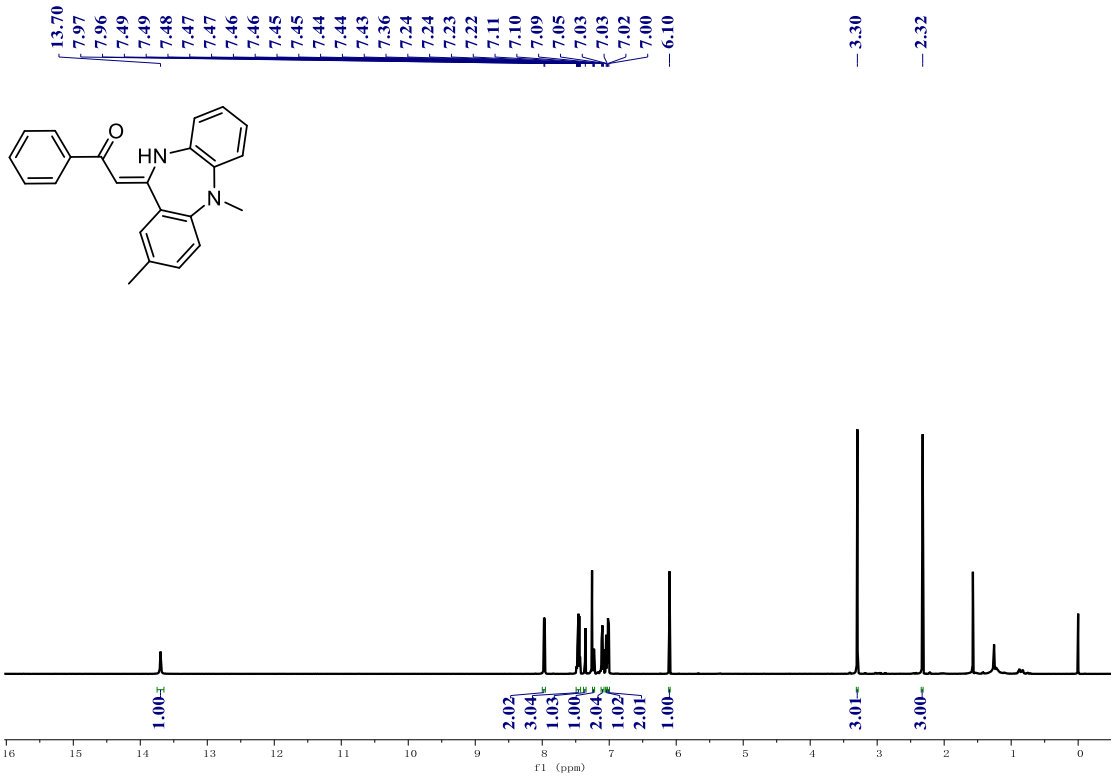


Figure 123. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **7b**

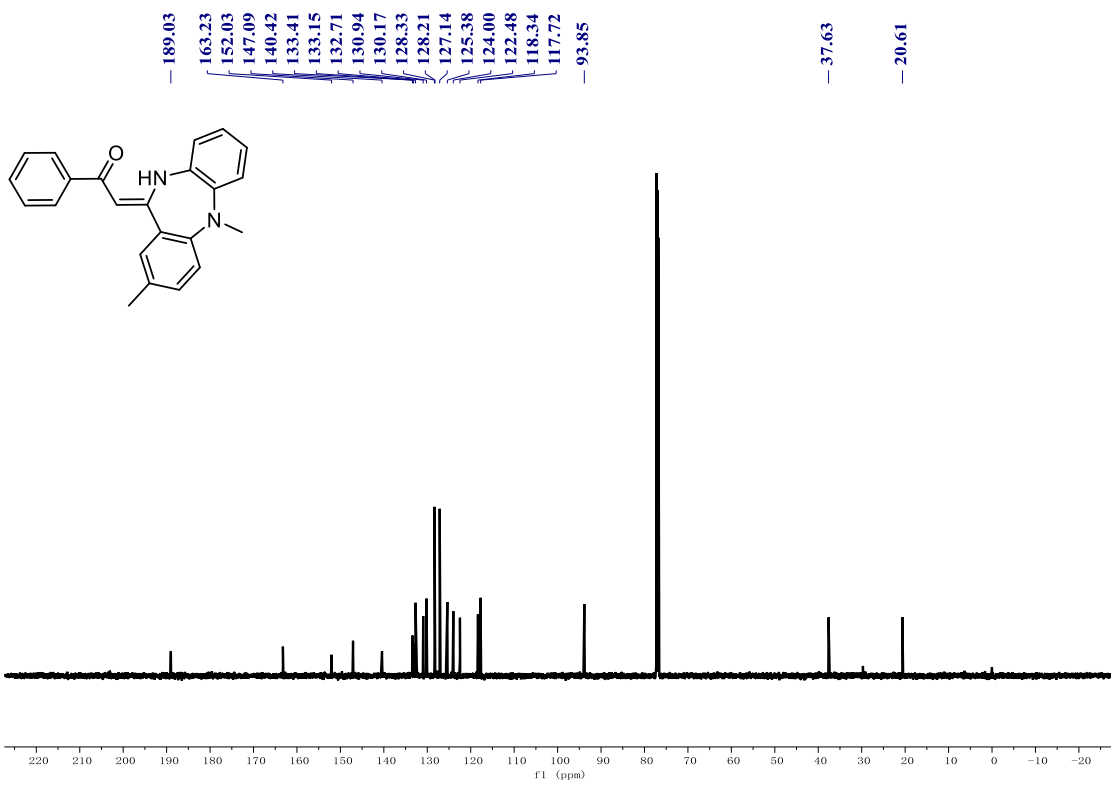


Figure 124. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **7b**

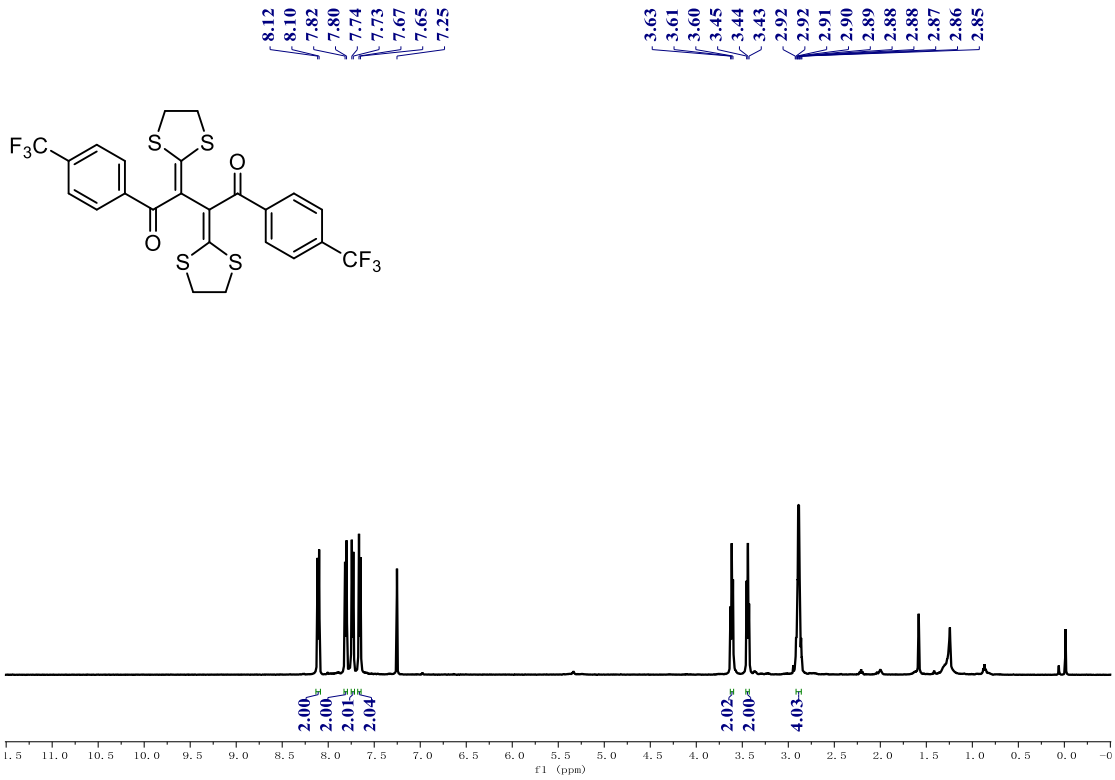


Figure 125. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **8**

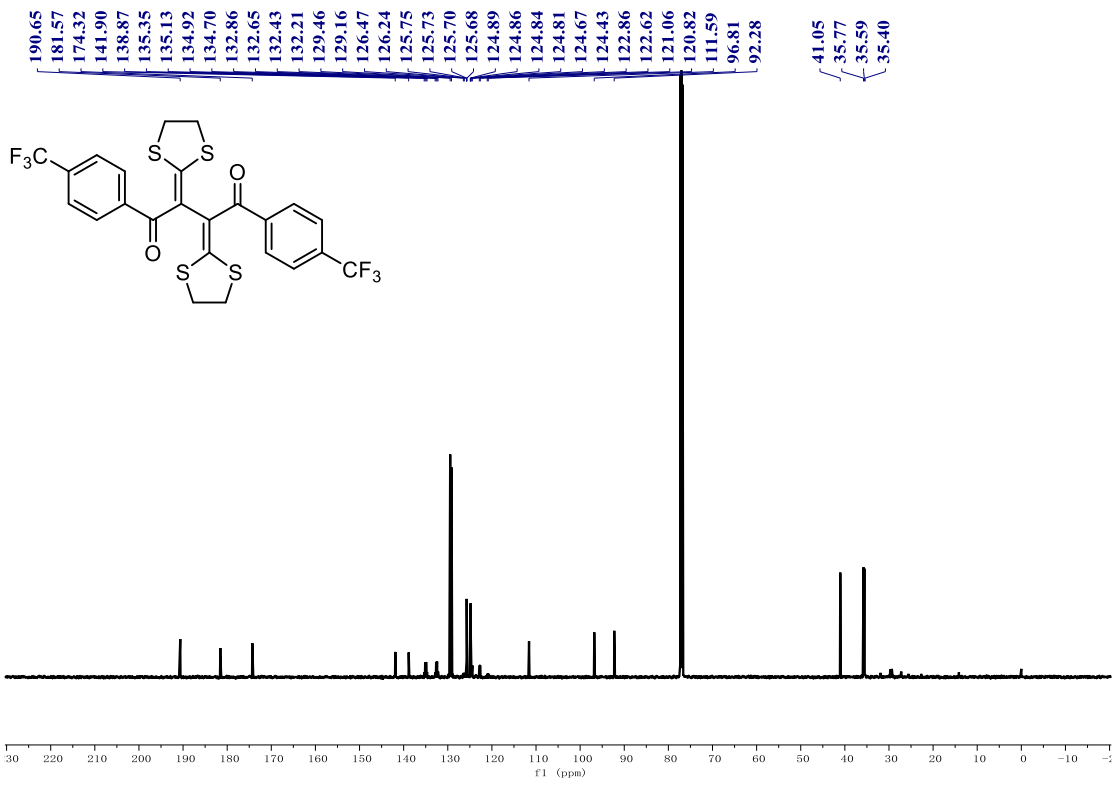


Figure 126. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8**

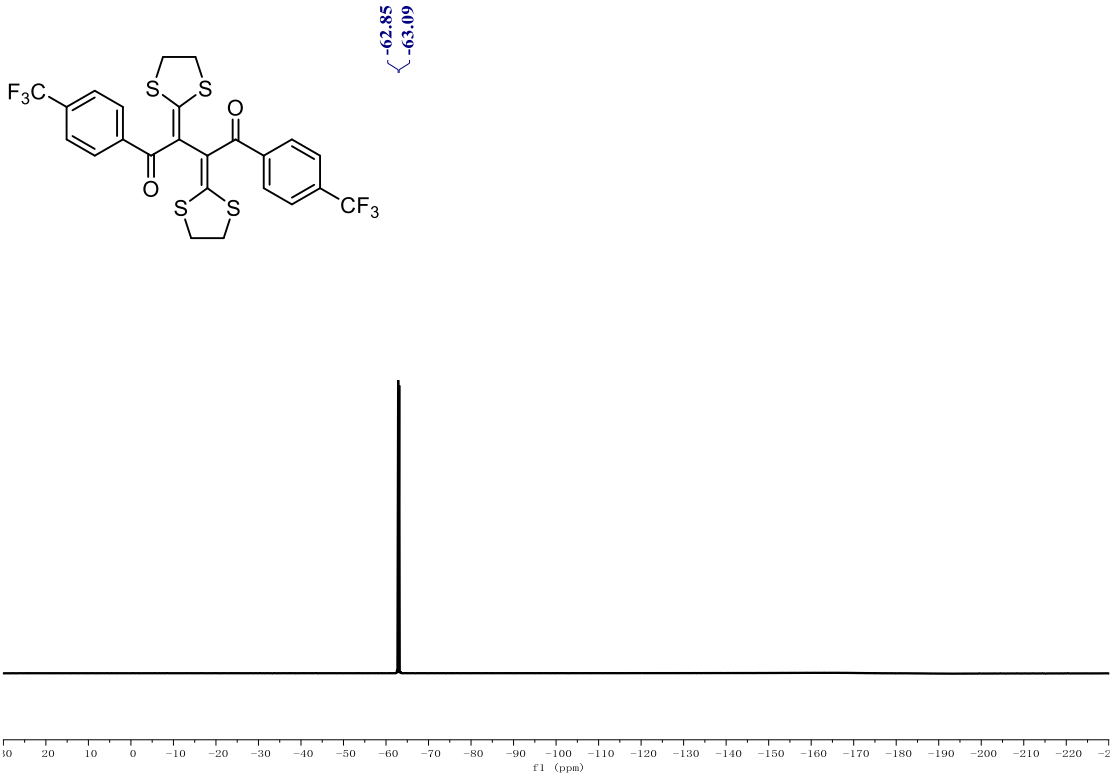


Figure 127. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **8**