Supplementary Information

Construction of Sulfur-substituted Methylenecyclobutanes via Thioaromatization of [1.1.1]Propellane with Sulfenamides

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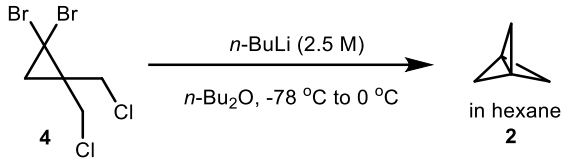
1. General information

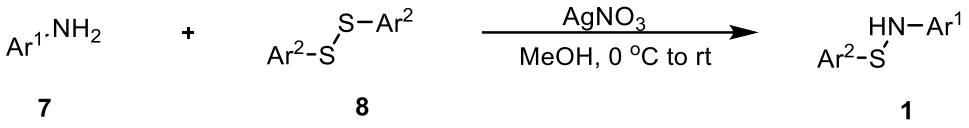
Commercially available reagents and solvents were used without any purification. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm). Melting points were determined using a Büchi B-540 capillary melting point apparatus. ^{1}H NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometers. ^{13}C NMR spectra were recorded using a Bruker Advance III 100 MHz spectrometers. ^{19}F NMR spectra were recorded using a Bruker Advance III 376 MHz spectrometers. Chemical shifts of ^{1}H NMR were reported relative to the solvent signal ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). Chemical shifts of ^{13}C NMR were reported relative to the solvent signal ($CDCl_3$: δ = 77.00 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were recorded on Waters SYNAPT G2-S spectrometer. UV/vis studies were measured in a 1 cm quartz cuvette using a Shimadzu 2550 UV spectrophotometer. Column chromatography was performed on silica gel (300-400 mesh). The silica gel were purchased from Leyan.com and energy-chemical.com.

2. Typical procedure for preparation of [1.1.1]propellane[1]



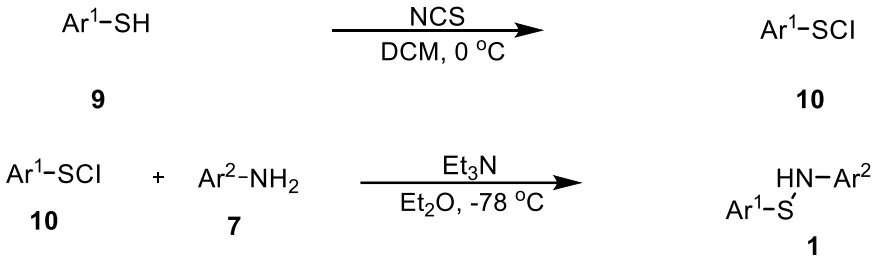
n-BuLi (32 mL, 80 mmol, 2.0 eq, 2.5 M in hexane) was added dropwise to the solution of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (**4**) (40 mmol, 1.0 eq) in anhydrous dibutyl ether (40 mL) under argon atmosphere at -78 °C for 1 h. After an additional 2 h, the mixture was stirred at 0 °C for 2 h. The mixture was distilled under vacuum to afford **2**: liquid in hexane. The concentration can be measured by ^{1}H-NMR with 1,3,5-trimethoxybenzene as an internal standard (typically concentrations are 0.2 – 1.0 M).

3. Typical procedure A for preparation of sulfenamides (1a-1o, 1s-1u, 1w-1x, and 1q)[2]



To an ice-cooled solution of silver nitrate (3.0 mmol, 1.0 eq), disulfide **8** (3.0 mmol, 1.0 eq) in methanol (20 mL) was added aniline **7** (9.0 mmol, 3.0 eq) at 0 °C. Then the reaction mixture was allowed to warm to 25 °C and stirred for 12 h. After the reaction was complete as determined by TLC, the silver mercaptide was filtered and the filtrate was removed under reduced pressure. It was added with H_2O (10 mL) at room temperature, and then extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4 filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether : ethyl acetate = 100:1) to afford the product **1**. The ^{1}H NMR data of substrates **1a-1c**, [3] **1h-1j**, [3] **1ac,** [3]and **1g**[2] are in accordance with the literature values.

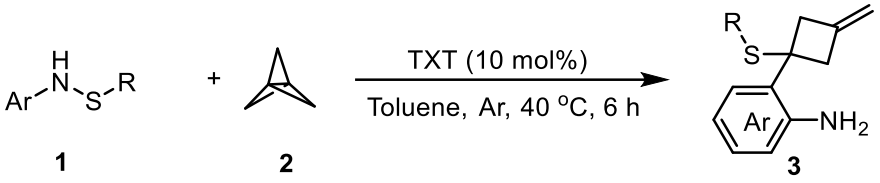
4. Typical procedure B for preparation of sulfenamides (1p, 1r, and 1v)[4]



To an ice-cooled solution of NCS (6.2 mmol, 1.5 eq) in dry dichloromethane (5 mL) was added phenylthiophenol **9** (5 mmol, 1.0 eq) under argon atmosphere. After stirring for 1 h, the mixture was diluted with *n*-hexane (5 mL). Then the mixture was filtered and the filtrate was removed under reduced pressure to afford the crude product **10**, which was used in the next step without further purification. Benzene sulfenyl chloride **10** (5 mmol, 1.0 eq) was dissolved in dry diethyl ether (5 mL) under argon atmosphere and this solution was added dropwise 15 min to a mixture of aniline **7** (7.5 mmol, 1.5 eq) and Et_3N (15.0 mmol, 2.0 eq) in dry diethyl ether (5 mL) at -78 °C. After the reaction mixture stirred at this temperature for an additional 30 min, 25 mL of *n*-pentane was added and the reaction mixture was allowed to warm to 0 °C. After the filtration, the filtrate was washed with water (10 mL) and then extracted with ethyl acetate (30 mL ×3). The combined organic layer

was washed with brine and dried over Na_2SO_4 filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether: ethyl acetate = 200:1) to afford the product **1**.

5. Typical procedure for preparation of 3

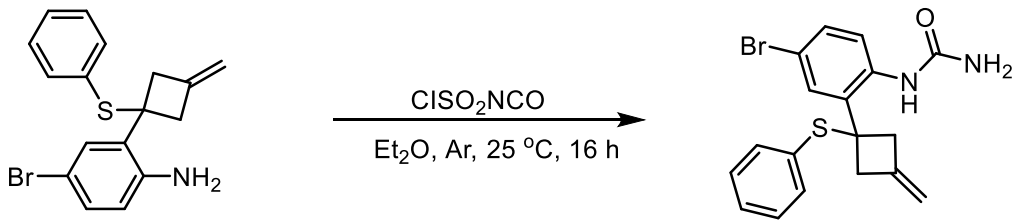


1 **2** **3**

An oven-dried 10 mL reaction tube equipped with a magnetic stir bar was charged with TXT (0.02 mmol, 10 mol%) and **1** (0.2 mmol, 1.0 eq). Toluene (2 mL) and **2** (0.6 mmol, 3.0 eq) was added to the mixture sequentially under argon atmosphere. The resulting mixture was then stirred at 40 °C for 6 -24 h. After the reaction was completed as monitored by TLC, the reaction mixture was quenched with H_2O (10 mL) and then extracted with ethyl acetate (10 mL ×3). The combined organic layer was washed brine, dried over Na_2SO_4 filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether: ethyl acetate = 200:1) to afford the product **3**.

6. Product derivatization

6.1 Preparation of 1-(4-bromo-2-(3-methylene-1-(phenylthio)cyclobutyl)phenyl) urea 4[5]

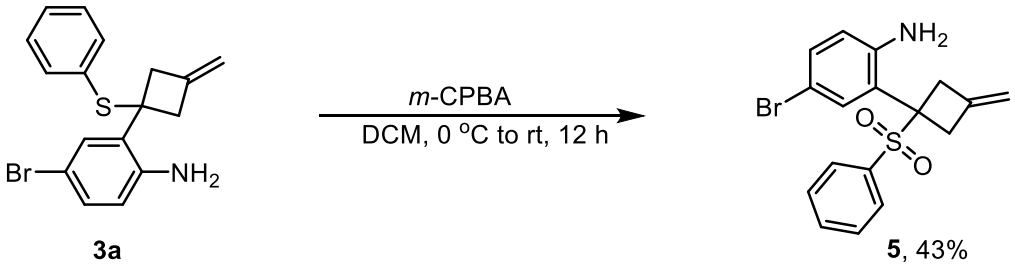


3a **4**, 66%

To an solution of **3a** (69.0 mg, 0.2 mmol) in ether (2.5 mL) was added chlorosulfonyl isocyanate (33.7 mg, 0.2 mmol). The reaction mixture was stirred at 25 °C for 16 h. After the reaction was complete as determined by TLC, the reaction mixture was quenched with brine (10 mL) and then extracted with ethyl acetate (10 mL ×3). The organic layer was dried over Na_2SO_4 filtered, and

then concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1 to 1:1) to afford the product **4** (51.4 mg, 66%) as a white solid. M.p.:203.5-204.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (d, J = 8.6 Hz, 1H), 7.42 – 7.33 (m, 1H), 7.31 (dd, J = 8.8, 2.4 Hz, 1H), 7.28 – 7.19 (m, 2H), 7.03 (d, J = 7.4 Hz, 2H), 6.96 (br, 1H), 6.53 (br, 2H), 6.32 (d, J = 2.4 Hz, 1H), 5.01 – 4.90 (m, 2H), 3.33 – 3.12 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.7, 141.9, 136.8, 136.0, 135.6, 131.3, 129.8, 129.7, 129.4, 128.7, 127.0, 114.1, 107.9, 51.2, 44.5. HRMS (ESI) m/z: calcd for $C_{18}H_{18}BrN_2OS$ $[M+H]^+$ 389.0318, found: 389.0306.

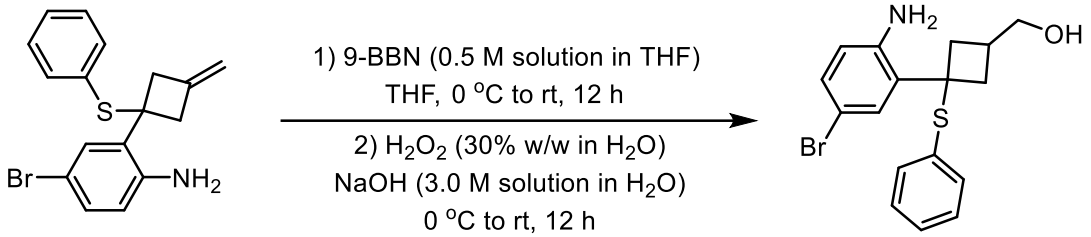
6.2 Preparation of 4-bromo-2-(3-methylene-1-(phenylsulfonyl)cyclobutyl)aniline 5[6]



3a **5**, 43%

To a solution of **3a** (38.3 mg, 0.1 mmol) in DCM (1 mL), *m*-CPBA (104.4 mg, 0.3 mmol) was added at 0 ºC, and stirred at room temperature for 12 h. After the reaction was complete as determined by TLC, the reaction mixture was quenched with water (10 mL) and then extracted with DCM (10 mL ×3). The combined organic layers was washed with saturated Na_2SO_3 solution (15 mL) followed by saturated $NaHCO_3$ solution (15 mL), dried over Na_2SO_4 filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether : ethyl acetate = 20:1) to afford the product **5** (16.2 mg, 43%) as a white solid; M.p.:136.8 - 137.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 2.0 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.44 (dd, J = 8.6, 2.0 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 5.77 (d, J = 8.6 Hz, 1H), 5.06-4.93 (m, 2H), 4.27 – 4.04 (m, 2H), 3.94 – 3.76 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 141.9, 140.2, 135.1, 134.1, 133.5, 132.3, 130.8, 130.1, 128.5, 108.1, 107.0, 67.1, 43.4. HRMS (ESI) m/z: calcd for $C_{17}H_{17}BrNO_2S$ $[M+H]^+$ 378.0158, found: 378.0140.

6.3 Preparation of (3-(2-amino-5-bromophenyl)-3-(phenylthio)cyclobutyl)methanol 6[7]

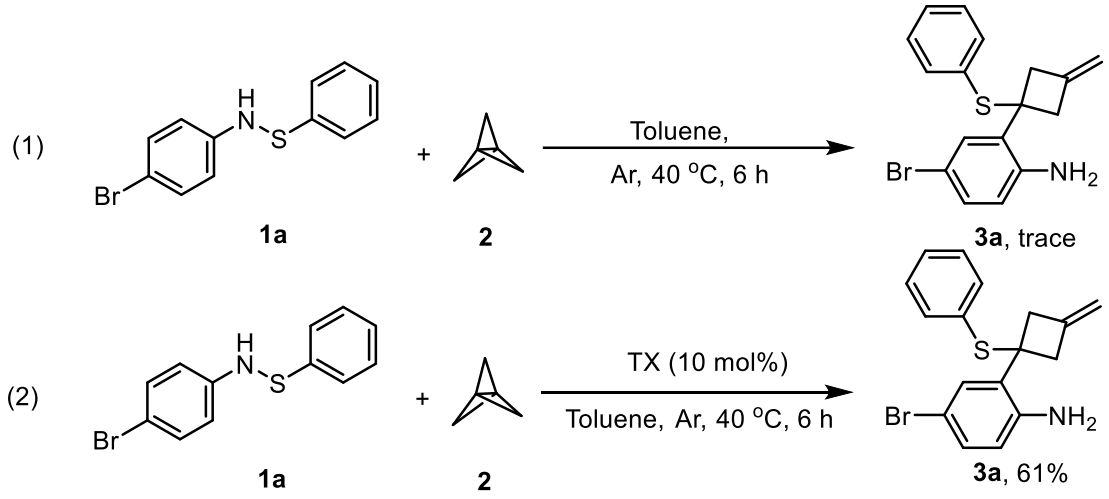


3a **6**, 44%

To a solution of **3a** (68.7 mg, 0.2 mmol) in THF (2 mL), 9-BBN (73.3 mg, 0.3 mmol) was added slowly dropwise at 0 ºC, and stirred at room temperature for 12 h. The reaction mixture was cooled to 0 ºC, and H_2O (24 uL), 30% H_2O_2 (80 uL) and 3 N NaOH (80 uL) were added successively. After the reaction was complete as determined by TLC, the reaction mixture was quenched with 10 H_2O (10 mL) and then extracted with ethyl acetate (10 mL ×3). The combined organic layers was washed with brine, dried over Na_2SO_4 filtered, and then concentrated under reduced pressure.. The residue was purified by flash column chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford the product **6** (32.0 mg, 44%, *dr* = 2.5:1) as a white solid. M.p.:152.1 - 152.8 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 – 7.29 (m, 1H), 7.29 – 7.20 (m, 2H), 7.18 – 7.09 (m, 2H), 7.08 – 7.00 (m, 1H), 6.72 – 6.58 (m, 1.73H) 6.21 (d, *J* = 2.4 Hz, 0.27H), 5.02 (br, 1.46H), 4.89 (br, 0.54H), 4.57 – 4.47 (m, 1H), 3.47 – 3.42 (m, 1.46H), 3.31 – 3.28 (m, 0.56H), 2.79 – 2.68 (m, 1.46H), 2.66 – 2.54 (m, 0.54H), 2.47 – 2.43 (m, 0.27H), 2.33 – 2.20 (m, 2H), 2.15 – 2.04 (m, 0.73H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.0, 144.4, 136.0, 135.5, 132.19, 132.17, 130.1, 129.8, 129.4, 129.0, 128.8, 128.6, 128.5, 127.9, 118.0, 117.4, 106.6, 106.2, 65.0, 63.7, 52.6, 51.9, 36.1, 31.7, 31.1, 26.1. HRMS (ESI) m/z: calcd for $C_{17}H_{18}BrNNaOS$ $[M+Na]^+$ 386.0185, found: 386.0189.

7. Mechanistic experiments

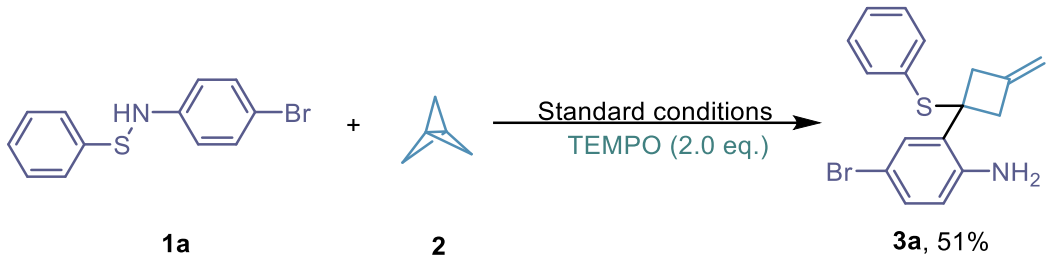
7.1 Control experiments



Reaction 1: An oven-dried 10 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (55.3 mg, 0.2 mmol). Toluene (2 mL) and **2** (0.76 mL, 0.80 M, 0.6 mmol) was added to the mixture sequentially under argon atmosphere. The resulting mixture was then stirred at 40 °C for 6 h. After the reaction was completed as monitored by TLC, the reaction mixture was quenched with H_2O (10 mL) and then extracted with ethyl acetate (10 mL ×3). The combined organic layers was washed brine and dried over Na_2SO_4 filtered, and then concentrated under reduced pressure. The reaction solution was detected by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard and only trace amount of product **3a** was detected.

Reaction 2: An oven-dried 10 mL reaction tube equipped with a magnetic stir bar was charged with **1a** (56.0 mg, 0.2 mmol) and TXT (4.2 mg, 10 mol%). Toluene (2 mL) and **2** (0.76 mL, 0.80 M, 0.6 mmol) was added to the mixture sequentially under argon atmosphere. The resulting mixture was then stirred at 40 °C for 6 h. After the reaction was completed as monitored by TLC, the reaction mixture was quenched with H_2O (10 mL) and then extracted with ethyl acetate (10 mL ×3), washed brine and dried over Na_2SO_4 filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether : ethyl acetate = 150:1) to afford the product **3a** (42.1 mg, 61%) as a white solid.

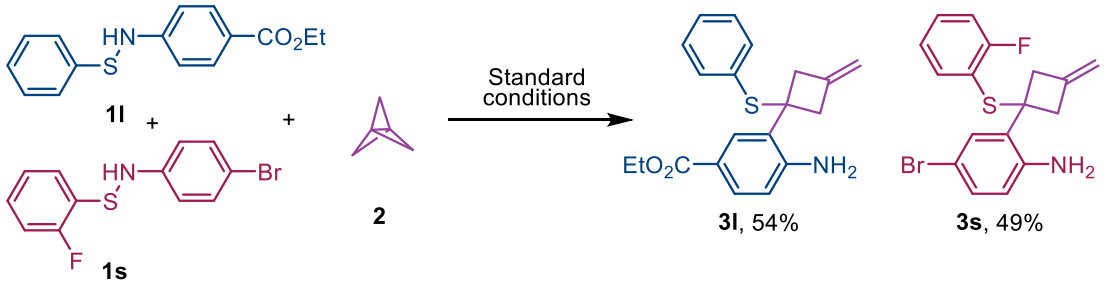
7.2 Radical trapping experiment



1a **2** **3a**, 51%

An oven-dried 10 mL reaction tube equipped with a magnetic stir bar was charged with TXT (4.7 mg, 10 mol%), **TEMPO** (63.2 mg, 0.4 mmol) and **1** (56.2 mg, 0.2 mmol). Toluene (2 mL) and **2** (0.86 mL, 0.71 M, 0.6 mmol) was added to the mixture sequentially under argon atmosphere. The resulting mixture was then stirred at 40 °C for 6 h. After the reaction was completed as monitored by TLC, the reaction mixture was quenched with H_2O (10 mL) and then extracted with ethyl acetate (10 mL ×3), washed brine and dried over Na_2SO_4 filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether: ethyl acetate = 150:1) to afford the product **3a** (35.6 mg, 51%) as a white solid.

7.3 Cross-experiment



An oven-dried 10 mL reaction tube equipped with a magnetic stir bar was charged with TXT (4.4 mg, 10 mol%), **1l** (54.8 mg, 0.2 mmol) and **1s** (57.3 mg, 0.2 mmol). Toluene (2 mL) and **2** (0.88 mL, 0.68 M, 0.6 mmol) was added to the mixture sequentially under argon atmosphere. The resulting mixture was then stirred at 40 °C for 6 h. After the reaction was completed as monitored by TLC, the reaction mixture was quenched with H_2O (10 mL) and then extracted with ethyl acetate (10 mL ×3), washed brine and dried over Na_2SO_4 filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate =150： 1 to 40： 1) to afford the product **3l** (36.7 mg, 54%) as a white solid and **3s** (34.5 mg, 49%) as a white solid.

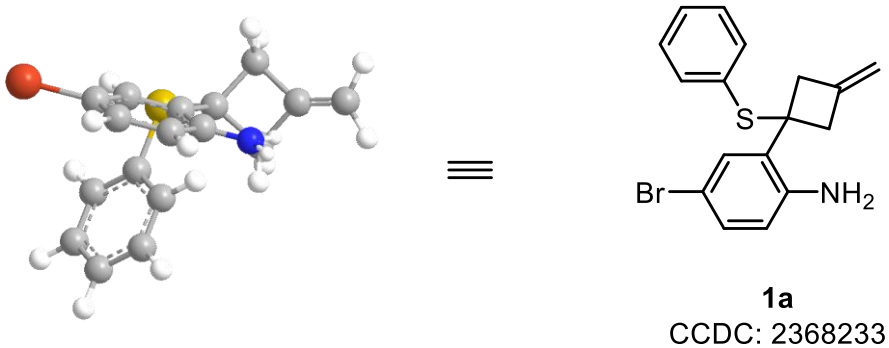
7.4 Exploring the role of hydrogen protons

1y **2** **3y**, n.r.

An oven-dried 10 mL reaction tube equipped with a magnetic stir bar was charged with TXT (4.3 mg, 10 mol%) and **1y** (43.9 mg, 0.2 mmol). Toluene (2 mL) and **2** (0.78 mL, 0.78 M, 0.6 mmol) was added to the mixture sequentially under argon atmosphere. After being stirred for 6 h at 40 ºC, no product was detected by TLC analysis.

8. X-ray crystallographic data

The data of **1a** was collected by a Bruker APEX-II CCD equipped with a Mo radiation source (K = 1.34139 Å) at 170.0 K. CCDC 2368233 (**1a**) contains the crystallographic data for this paper.



1a
CCDC: 2368233

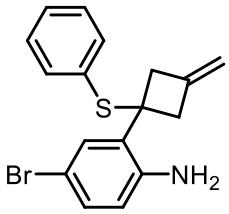
Table 1 Crystal data and structure refinement for 3a.

Identification code	240625_HJ_3_150_0m
Empirical formula	$C_{17}H_{16}BrNS$
Formula weight	346.28
Temperature/K	170.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.4027(4)
b/Å	12.8347(5)
c/Å	13.5644(5)
α/°	90
β/°	108.2640(10)
γ/°	90

Volume/Å^3	1554.50(11)
Z	4
ρ_{calc}g/cm^3	1.480
μ/mm^{-1}	3.146
F(000)	704.0
Crystal size/mm^3	0.06 × 0.04 × 0.04
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.46 to 121.596
Index ranges	-11 ≤ h ≤ 12, -16 ≤ k ≤ 16, -17 ≤ l ≤ 16
Reflections collected	14153
Independent reflections	3532 [R_{int} = 0.0404, R_{sigma} = 0.0486]
Data/restraints/parameters	3532/0/182
Goodness-of-fit on F^2	1.104
Final R indexes [I>=2σ (I)]	R_1 = 0.0348, wR_2 = 0.0819
Final R indexes [all data]	R_1 = 0.0371, wR_2 = 0.0831
Largest diff. peak/hole / e Å^{-3}	0.59/-0.43

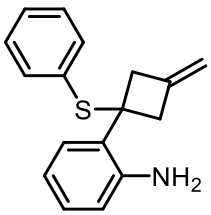
9. Characterization of products

4-bromo-2-(3-methylene-1-(phenylthio)cyclobutyl)aniline (3a)



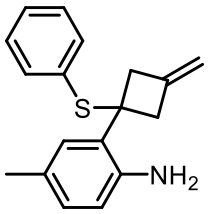
Eluent in chromatography: petroleum ether/ethyl acetate =150:1, **3a** was isolated as a white solid (42.1 mg, 61%); M.p.: 113.6-114.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 1H), 7.23 – 7.15 (m, 2H), 7.14 – 7.02 (m, 3H), 6.58 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 5.01 – 4.92 (m, 2H), 3.39 – 3.27 (m, 2H), 3.32 (br, 2H), 3.17 – 3.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 141.9, 136.0, 132.0, 130.7, 130.6, 130.4, 129.2, 128.5, 118.3, 109.7, 108.2, 51.7, 44.6; HRMS (ESI) m/z: calcd for $C_{17}H_{17}BrNS$ $[M+H]^+$ 346.0260, found: 346.0258.

2-(3-methylene-1-(phenylthio)cyclobutyl)aniline （3b）



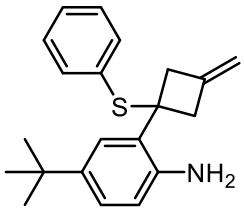
Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3b** was isolated as a white solid (28.4 mg, 52%); M.p.: 52.7-53.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 – 7.25 (m, 1H), 7.24 – 7.15 (m, 2H), 7.13 – 7.04 (m, 2H), 6.99 – 6.88 (m, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.44 – 6.38 (m, 1H), 6.38 – 6.31 (m, 1H), 4.90-4.84 (m, 2H), 4.82 (br, 2H), 3.30 – 3.21 (m, 2H), 3.19 – 3.08 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.5, 142.9, 135.4, 132.5, 128.7, 128.5, 127.9, 127.6, 125.9, 115.9, 115.6, 107.5, 51.9, 44.4; HRMS (ESI) m/z: calcd for $C_{17}H_{18}NS$ $[M+H]^+$ 268.1154, found: 268.1165.

4-methyl-2-(3-methylene-1-(phenylthio)cyclobutyl)aniline (3c)



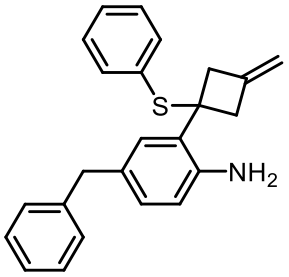
Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3c** was isolated as a white solid (19.5 mg, 40%); M.p.: 51.3-52.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.19 – 7.11 (m, 2H), 7.11 – 7.04 (m, 2H), 6.88 – 6.80 (m, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.20 (d, J = 2.0 Hz, 1H), 4.97 – 4.91 (m, 2H), 3.43 – 3.33 (m, 2H), 3.18 – 3.08 (m, 2H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.5, 136.2, 132.5, 128.8, 128.7, 128.54, 128.47, 128.2, 127.1, 117.1, 107.7, 52.2, 44.7, 20.3; HRMS (ESI) m/z: calcd for $C_{18}H_{20}NS$ $[M+H]^+$ 282.1311, found: 282.1329.

4-(*tert*-butyl)-2-(3-methylene-1-(phenylthio)cyclobutyl)aniline (3d)



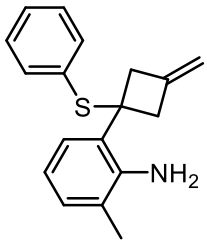
Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3d** was isolated as a white solid (33.4 mg, 52%); M.p.: 116.6-117.5 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31 – 7.23 (m, 1H), 7.20 – 7.10 (m, 2H), 7.05 – 6.98 (m, 2H), 6.94 (dd, J = 8.4, 2.4 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.19 (d, J = 2.4 Hz, 1H), 4.94 – 4.85 (m, 2H), 4.58 (br, 2H), 3.31 – 3.22 (m, 2H), 3.19 – 3.09 (m, 2H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.0, 142.7, 137.4, 135.6, 132.6, 128.6, 128.4, 125.5, 124.39, 124.35, 115.7, 107.6, 52.4, 44.5, 33.3, 31.3; HRMS (ESI) m/z: calcd for $C_{21}H_{26}NS$ $[M+H]^+$ 324.1781, found: 324.1772.

4-Benzyl-2-(3-methylene-1-(phenylthio)cyclobutyl)aniline (3e)



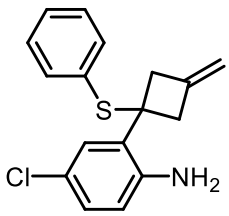
Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3e** was isolated as a colorless liquid (39.6 mg, 55%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 – 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.10 (m, 3H), 7.09 – 7.02 (m, 2H), 7.01 – 6.91 (m, 2H), 6.78 (dd, J = 8.0, 2.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.32 (d, J = 2.0 Hz, 1H), 4.90 – 4.84 (m, 2H), 4.70 (br, 2H), 3.61 (s, 2H), 3.30 – 3.20 (m, 2H), 3.17 – 3.07 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.6, 142.9, 142.0, 135.1, 132.6, 128.50, 128.48, 128.4, 128.3, 128.2, 127.9, 126.0, 125.6, 116.2, 107.6, 51.8, 44.5, 40.3; HRMS (ESI) m/z: calcd for $C_{24}H_{24}NS$ $[M+H]^+$ 358.1624, found: 358.1625.

2-methyl-6-(3-methylene-1-(phenylthio)cyclobutyl)aniline (3f).



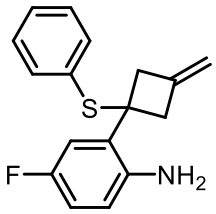
Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3f** was isolated as a white solid (24.8 mg, 44%); M.p.:51.4-52.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 1H), 7.18 – 7.11 (m, 2H), 7.10 – 7.01 (m, 2H), 6.96 (d, J = 8.2 Hz, 1H), 6.51 – 6.42 (m, 1H), 6.32 (d, J = 7.6 Hz, 1H), 4.99 – 4.89 (m, 2H), 3.93 (br, 2H), 3.44 – 3.30 (m, 2H), 3.21 – 3.06 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.4, 136.1, 132.5, 129.3, 128.7, 128.2, 127.5, 126.2, 122.9, 117.0, 107.7, 52.3, 44.9, 17.6; HRMS (ESI) m/z: calcd for $C_{18}H_{20}NS$ $[M+H]^+$ 282.1311, found: 282.1315.

4-chloro-2-(3-methylene-1-(phenylthio)cyclobutyl)aniline (3g)



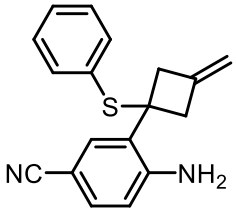
Eluent in chromatography: petroleum ether/ethyl acetate = 150:1, **3g** was isolated as a white solid (35.8 mg, 58%); M.p.: 107.8-108.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 1H), 7.23 – 7.14 (m, 2H), 7.12 – 7.05 (m, 2H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.33 (d, *J* = 2.4 Hz, 1H), 5.00 – 4.93 (m, 2H), 3.53 (br, 2H), 3.38 – 3.28 (m, 2H), 3.17 – 3.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 142.0, 136.0, 132.0, 129.9, 129.1, 128.5, 127.9, 127.7, 122.5, 117.8, 108.2, 51.7, 44.6; HRMS (ESI) m/z: calcd for $C_{17}H_{17}CINS$ $[M+H]^+$ 302.0765, found: 302.0752.

4-fluoro-2-(3-methylene-1-(phenylthio)cyclobutyl)aniline (3h)



Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3h** was isolated as a colorless liquid (32.5 mg, 57%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 – 7.27 (m, 1H), 7.26 – 7.17 (m, 2H), 7.13 – 7.04 (m, 2H), 6.82 – 6.74 (m, 1H), 6.73 – 6.66 (m, 1H), 6.16 (dd, *J* = 10.4, 2.8 Hz, 1H), 4.94 – 4.83 (m, 2H), 4.72 (br, 2H), 3.31 – 3.21 (m, 2H), 3.18 – 3.09 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.8 (d, *J* = 231.5 Hz), 142.5, 141.9 (d, *J* = 1.7 Hz), 135.5, 132.1, 129.0, 128.6, 127.4 (d, *J* = 6.2 Hz), 116.7 (d, *J* = 7.6 Hz), 114.04 (d, *J* = 48.4 Hz), 114.03 (d, *J* = 3.9 Hz), 107.7, 51.7, 44.3; ^{19}F NMR (376 MHz, DMSO-d_6) δ -129.29; HRMS (ESI) m/z: calcd for $C_{17}H_{17}FNS$ $[M+H]^+$ 286.1060, found: 286.1068.

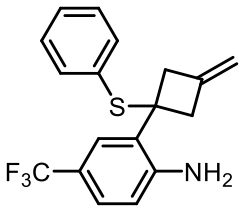
4-amino-3-(3-methylene-1-(phenylthio)cyclobutyl)benzonitrile (3i)



Eluent in chromatography: petroleum ether/ethyl acetate = 40:1, **3i** was isolated as a colorless liquid (29.6 mg, 50%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 – 7.28 (m, 2H), 7.27 – 7.18 (m, 2H), 7.11 – 7.01 (m, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 2.0 Hz, 1H), 5.83 (br, 2H), 4.94 – 4.85 (m, 2H), 3.29 – 3.14 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.5, 142.3, 135.6, 132.1, 131.9, 131.8, 129.1, 128.6, 125.6, 120.3, 115.5, 107.8, 95.5, 51.3, 44.1; HRMS (ESI) m/z: calcd for

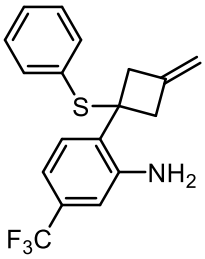
$C_{18}H_{17}N_2S$ $[M+H]^+$ 293.1107, found: 293.1118.

2-(3-methylene-1-(phenylthio)cyclobutyl)-4-(trifluoromethyl)aniline (3j)



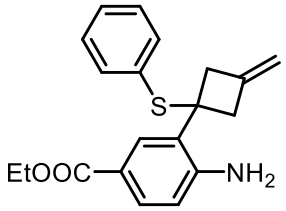
Eluent in chromatography: petroleum ether/ethyl acetate = 100:1, **3j** was isolated as a white solid (33.7 mg, 50%); M.p.: 113.6-114.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 – 7.26 (m, 1H), 7.26 – 7.11 (m, 3H), 7.04 (d, J = 7.4 Hz, 2H), 6.81 (d, J = 8.0 Hz, 1H), 6.37 (d, J = 2.0 Hz, 1H), 5.49 (br, 2H), 4.99 – 4.82 (m, 2H), 3.30 – 3.12 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.6, 142.3, 135.8, 132.1, 129.0, 128.5, 125.2, 125.1 (q, J = 270.2 Hz), 124.8 (q, J = 3.8 Hz), 124.7 (q, J = 4.2 Hz), 115.2, 114.9 (q, J = 31.8 Hz), 107.8, 51.6, 44.1; ^{19}F NMR (376 MHz, DMSO-d_6) δ -54.45; HRMS (ESI) m/z: calcd for $C_{18}H_{17}F_3NS$ $[M+H]^+$ 336.1028, found: 336.1049.

2-(3-methylene-1-(phenylthio)cyclobutyl)-5-(trifluoromethyl)aniline (3k).



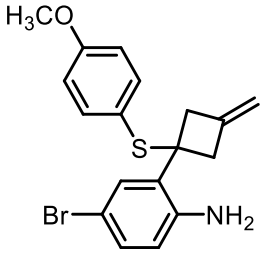
Eluent in chromatography: petroleum ether/ethyl acetate = 100:1, **3k** was isolated as a white solid (33.5 mg, 50%); M.p.:113.6-114.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.33 (m, 3H), 7.30 – 7.22 (m, 2H), 7.20 – 7.13 (m, 1H), 7.04 (dd, J = 8.2, 1.4 Hz, 1H), 6.87 (dd, J = 7.8, 1.4 Hz, 1H), 5.17 (br, 2H), 4.74 – 4.48 (m, 2H), 3.58 – 3.38 (m, 2H), 3.31 – 3.16 (m, 2H);^{13}C NMR (100 MHz, DMSO-d_6) δ 147.9, 142.3 (q, J = 2.1 Hz),136.9, 131.3, 129.5, 128.6, 127.9, 127.2 (q, J = 29.5 Hz), 124.5 (q, J = 272.0 Hz), 124.0, 120.7, 115.8 (q, J = 6.9 Hz).106.0, 51.7, 47.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -52.84; HRMS (ESI) m/z: calcd for $C_{19}H_{17}F_3NO_2S$ $[M+HCOO]^-$ 380.0937, found: 380.0932.

ethyl 4-amino-3-(3-methylene-1-(phenylthio)cyclobutyl)benzoate (3l)



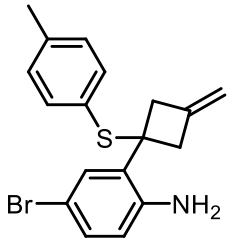
Eluent in chromatography: petroleum ether/ethyl acetate = 40:1, **3l** was isolated as a white solid (34.9 mg, 52%); M.p.: 86.5-87.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55 (dd, J = 8.4, 2.0 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.23 – 7.15 (m, 2H), 7.11 – 7.05 (m, 2H), 6.92 (d, J = 2.0 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 5.65 (br, 2H), 4.93– 4.84 (m, 2H), 4.12 (q, J = 7.2 Hz, 2H), 3.25– 3.18 (m, 4H), 1.19 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7, 149.9, 142.4, 135.7, 132.2, 129.5, 128.9, 128.5, 124.7, 115.8, 114.8, 107.8, 59.5, 51.5, 44.2, 14.3; HRMS (ESI) m/z: calcd for $C_{20}H_{22}NO_2S$ $[M+H]^+$ 340.1366, found: 340.1368.

4-bromo-2-(1-((4-methoxyphenyl)thio)-3-methylenecyclobutyl)aniline (3m)



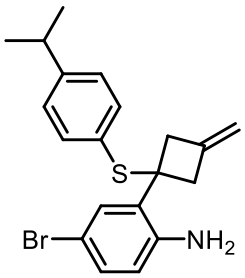
Eluent in chromatography: petroleum ether/ethyl acetate = 150:1, **3m** was isolated as a white solid (44.0 mg, 58%); M.p.: 83.0-83.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.07 (dd, J = 8.4, 2.4 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.82 – 6.75 (m, 2H), 6.67 (d, J = 8.6 Hz, 1H), 6.31 (d, J = 2.4 Hz, 1H), 4.95 (br, 2H), 4.90 – 4.82 (m, 2H), 3.72 (s, 3H), 3.24 – 3.14 (m, 2H), 3.13 – 3.05 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.2, 144.7, 142.5, 137.7, 130.1, 129.8, 128.4, 122.7, 117.6, 114.1, 107.6, 106.4, 55.2, 51.5, 43.9; HRMS (ESI) m/z: calcd for $C_{18}H_{19}BrNOS$ $[M+H]^+$ 376.0365, found: 376.0365.

4-bromo-2-(3-methylene-1-(p-tolylthio)cyclobutyl)aniline (3n)



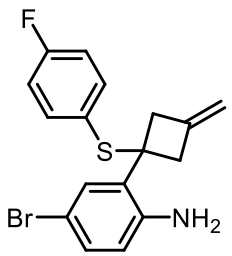
Eluent in chromatography: petroleum ether/ethyl acetate = 150:1, **3n** was isolated as a white solid (39.6 mg, 55%); M.p.: 99.4-100.6°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.10 – 7.01 (m, 3H), 7.00 – 6.92 (m, 2H), 6.66 (d, J = 8.4 Hz, 1H), 6.34 (d, J = 2.4 Hz, 1H), 4.97 (br, 2H), 4.90 – 4.83 (m, 2H), 3.25 – 3.16 (m, 2H), 3.15 – 3.06 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.7, 142.5, 138.8, 135.8, 130.2, 129.8, 129.2, 128.6, 128.3, 117.7, 107.7, 106.4, 51.5, 44.1, 20.8; HRMS (ESI) m/z: calcd for $C_{18}H_{19}BrNS$ $[M+H]^+$ 360.0417, found: 360.0403.

4-bromo-2-(1-((4-isopropylphenyl)thio)-3-methylenecyclobutyl)aniline (3o)



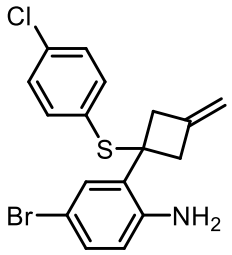
Eluent in chromatography: petroleum ether/ethyl acetate = 150:1, **3o** was isolated as a colorless liquid (35.7 mg, 46%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.11 – 7.06 (m, 2H), 7.05 (dd, J = 8.8, 2.4 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.66 (d, J = 8.4 Hz, 1H), 6.22 (d, J = 2.4 Hz, 1H), 4.95 (br, 2H), 4.90 – 4.85 (m, 2H), 3.26 – 3.17 (m, 2H), 3.16 – 3.06 (m, 2H), 2.87 – 2.77 (m, 1H), 1.15 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.6, 144.7, 142.5, 135.9, 130.1, 129.8, 129.0, 128.2, 126.5, 117.6, 107.6, 106.3, 51.7, 44.2, 33.2, 23.7; HRMS (ESI) m/z: calcd for $C_{20}H_{23}BrNS$ $[M+H]^+$ 388.0729, found: 388.0723.

4-bromo-2-(1-((4-fluorophenyl)thio)-3-methylenecyclobutyl)aniline (3p)



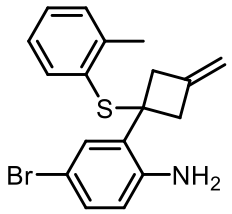
Eluent in chromatography: petroleum ether/ethyl acetate = 150:1, **3p** was isolated as a white solid (34.1 mg, 48%); M.p.: 72.3-73.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.17 – 7.00 (m, 5H), 6.67 (d, J = 8.4 Hz, 1H), 6.31 (d, J = 2.4 Hz, 1H), 4.99 (br, 2H), 4.93 – 4.82 (m, 2H), 3.28 – 3.18 (m, 2H), 3.18 – 3.07 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.8 (d, J = 246.9 Hz), 144.7, 142.3, 138.3 (d, J = 8.6 Hz), 130.3, 129.8, 127.83, 127.80, 117.6, 115.6 (d, J = 21.8 Hz), 107.7, 106.2, 52.8, 44.1; ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.19; HRMS (ESI) m/z: calcd for $C_{17}H_{16}BrFNS$ $[M+H]^+$ 366.0145, found: 366.0146.

4-bromo-2-(1-((4-chlorophenyl)thio)-3-methylenecyclobutyl)aniline (3q)



Eluent in chromatography: petroleum ether/ethyl acetate = 80:1, **3q** was isolated as a white solid (39.2 mg, 52%); M.p.: 99.0-100.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.32 – 7.25 (m, 2H), 7.11 – 7.03 (m, 3H), 6.66 (d, J = 8.6 Hz, 1H), 6.36 (d, J = 2.4 Hz, 1H), 5.00 (br, 2H), 4.91 – 4.84 (m, 2H), 3.29 – 3.20 (m, 2H), 3.19 – 3.09 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.7, 142.2, 137.4, 134.3, 131.1, 130.4, 129.8, 128.6, 127.7, 117.7, 107.8, 106.3, 52.0, 44.3; HRMS (ESI) m/z: calcd for $C_{17}H_{16}BrClNS$ $[M+H]^+$ 379.9870, found: 379.9875.

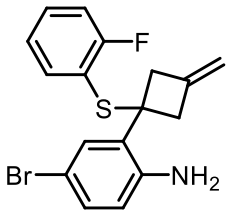
4-bromo-2-(3-methylene-1-(o-tolylthio)cyclobutyl)aniline (3r)



Eluent in chromatography: petroleum ether/ethyl acetate = 150:1, **3r** was isolated as a white solid (41.1 mg, 57%); M.p.: 95.3-96.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.25 – 7.20 (m, 1H), 7.19 – 7.15 (m, 1H), 7.14 – 7.03 (m, 3H), 6.63 (d, J = 8.4 Hz, 1H), 6.31 (d, J = 2.4 Hz, 1H), 4.99 (br, 2H), 4.94 – 4.88 (m, 2H), 3.25 – 3.17 (m, 2H), 3.16 – 3.09 (m, 2H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.8, 142.8, 142.7, 136.7, 131.4, 130.2, 130.1, 129.6, 129.1, 128.5, 125.9, 117.5, 107.6, 106.3, 52.0, 44.2, 20.2; HRMS (ESI) m/z: calcd for $C_{18}H_{19}BrNS$ $[M+H]^+$ 360.0416, found:

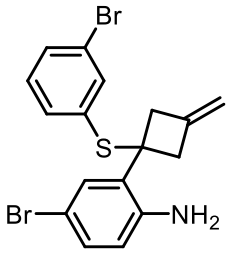
360.0439.

4-bromo-2-(1-((2-fluorophenyl)thio)-3-methylenecyclobutyl)aniline (3s)



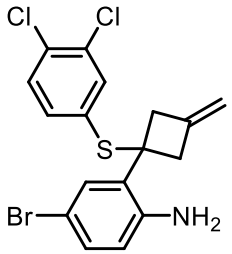
Eluent in chromatography: petroleum ether/ethyl acetate = 150:1, **3s** was isolated as a white solid (37.4 mg, 51%); M.p.:96.7-97.9 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46 – 7.35 (m, 1H), 7.22 – 7.09 (m, 2H), 7.10 – 6.98 (m, 2H), 6.64 (d, J = 8.0 Hz, 1H), 6.43 (d, J = 2.4 Hz, 1H), 5.02 (br, 2H), 4.91-4.82 (m, 2H), 3.32 – 3.24 (m, 2H), 3.24 – 3.14 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.1 (d, J = 245.1 Hz), 145.0, 142.1, 138.4, 131.9 (d, J = 8.3 Hz), 130.4, 129.4, 127.6, 124.5 (d, J = 3.7 Hz), 118.7 (d, J = 18.7 Hz), 117.7, 115.7 (d, J = 23.6 Hz), 107.6, 106.3, 52.4, 44.6; ^{19}F NMR (376 MHz, DMSO-d_6) δ -106.92; HRMS (ESI) m/z: calcd for $C_{17}H_{16}BrFNS$ $[M+H]^+$ 364.0165, found: 364.0187.

4-bromo-2-(1-((3-bromophenyl)thio)-3-methylenecyclobutyl)aniline (3t)



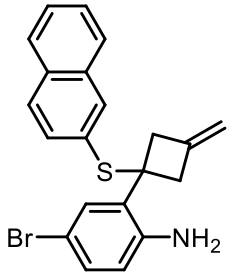
Eluent in chromatography: petroleum ether/ethyl acetate = 100:1, **3t** was isolated as a white solid (42.5 mg, 50%); M.p.:78.8-79.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 – 7.47 (m, 1H), 7.28 – 7.15 (m, 2H), 7.14 – 7.02 (m, 2H), 6.68 (d, J = 8.6 Hz, 1H), 6.40 (d, J = 2.4 Hz, 1H), 5.02 (br, 2H), 4.94 – 4.83 (m, 2H), 3.30 – 3.21 (m, 2H), 3.20 – 3.06 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.7, 142.1, 137.6, 134.5, 134.4, 131.8, 130.5, 130.4, 129.9, 127.5, 121.3, 117.7, 107.9, 106.3, 52.1, 44.2; HRMS (ESI) m/z: calcd for $C_{17}H_{16}Br_2NS$ $[M+H]^+$ 425.9345, found: 425.9333.

4-bromo-2-(1-((3,4-dichlorophenyl)thio)-3-methylenecyclobutyl)aniline (3u)



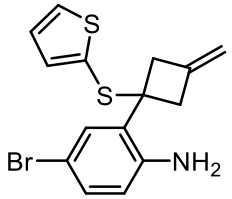
Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3u** was isolated as a white solid (38.1 mg, 47%); M.p.:107.8-108.9 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (d, J = 8.2 Hz, 1H), 7.15 (dd, J = 8.4, 2.0 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.68 (d, J = 8.6 Hz, 1H), 6.41 (d, J = 2.4 Hz, 1H), 5.04 (br, 2H), 4.93 – 4.84 (m, 2H), 3.31 – 3.23 (m, 2H), 3.22 – 3.11 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.7, 142.0, 136.8, 135.5, 133.0, 132.2, 130.9, 130.6, 130.4, 129.9, 127.2, 117.7, 107.9, 106.2, 52.5, 44.3; HRMS (ESI) m/z: calcd for $C_{18}H_{15}BrCI_2NO_2S$ $[M+HCOO]^-$ 457.9389, found: 457.9349.

4-bromo-2-(3-methylene-1-(naphthalen-2-ylthio)cyclobutyl)aniline (3v)



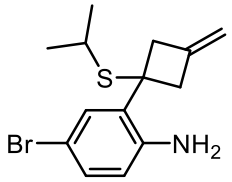
Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3v** was isolated as a white solid (41.3 mg, 52%); M.p.:99.2-100.2 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 – 7.84 (m, 1H), 7.84 – 7.78 (m, 1H), 7.78 – 7.69 (m, 2H), 7.57 – 7.47 (m, 2H), 7.13 – 6.99 (m, 2H), 6.70 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 2.4 Hz, 1H), 5.06 (br, 2H), 4.95-4.81 (m, 2H), 3.31 – 3.15 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.8, 142.4, 135.1, 132.8, 132.6, 132.1, 130.3, 129.9, 129.7, 128.1, 127.72, 127.69, 127.5, 126.9, 126.5, 117.7, 107.8, 106.3, 51.8, 44.3; HRMS (ESI) m/z: calcd for $C_{21}H_{19}BrNS$ $[M+H]^+$ 396.0416, found: 396.0405.

4-bromo-2-(3-methylene-1-(thiophen-2-ylthio)cyclobutyl)aniline (3w).



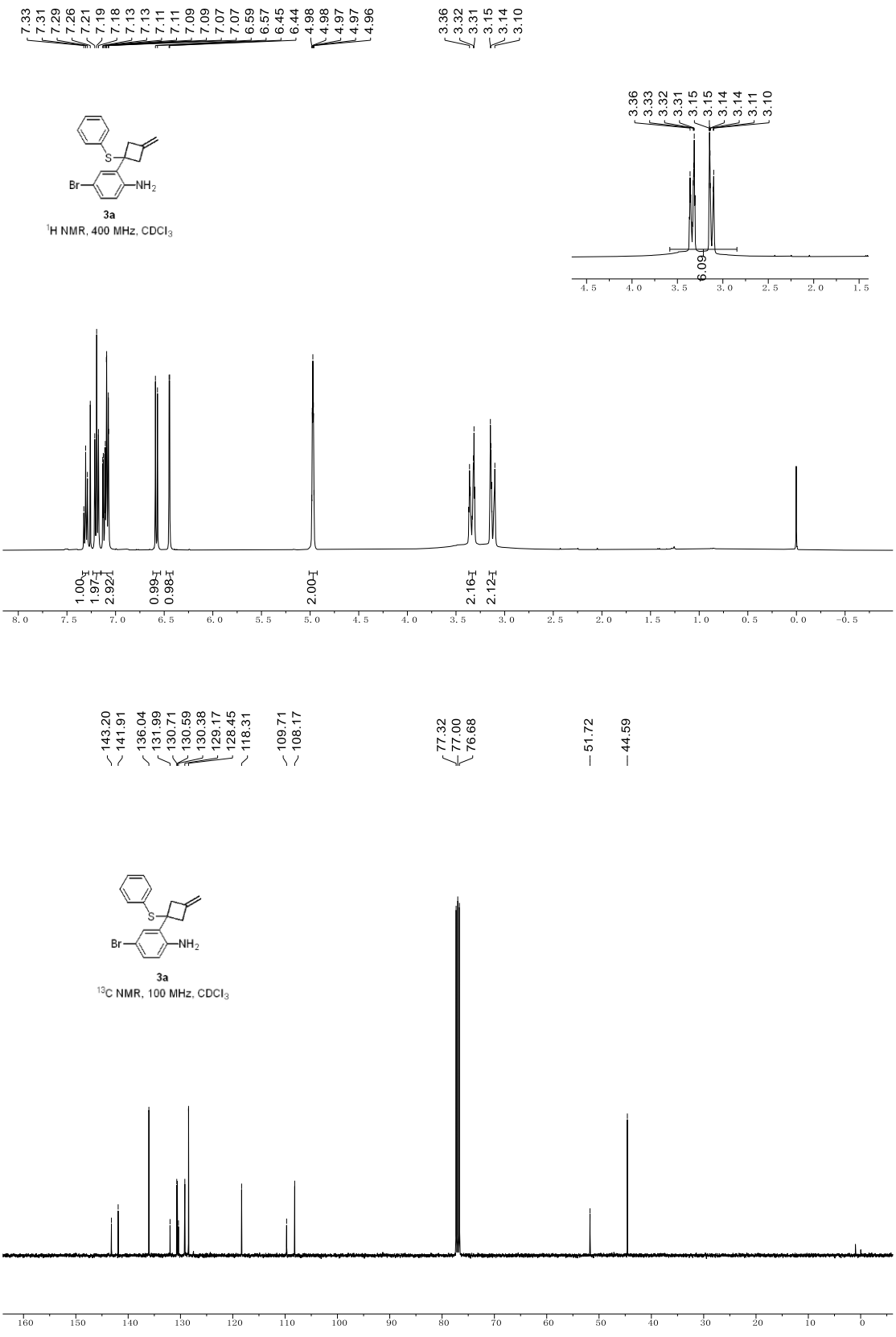
Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3w** was isolated as a white solid (34.1 mg, 48%); M.p.:124.5-129.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.13 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.95 – 6.89 (m, 1H), 6.84 – 6.78 (m, 1H), 6.62 – 6.50 (m, 2H), 5.07 – 4.88 (m, 2H), 3.90 (br, 2H), 3.43 – 3.31 (m, 2H), 3.24 – 3.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 141.4, 136.6, 131.3, 130.8, 130.7, 130.6, 129.6, 127.4, 118.3, 109.7, 108.4, 53.1, 44.3; HRMS (ESI) m/z: calcd for $C_{15}H_{13}BrNS_2$ $[M-H]^-$ 349.9678, found: 349.9681.

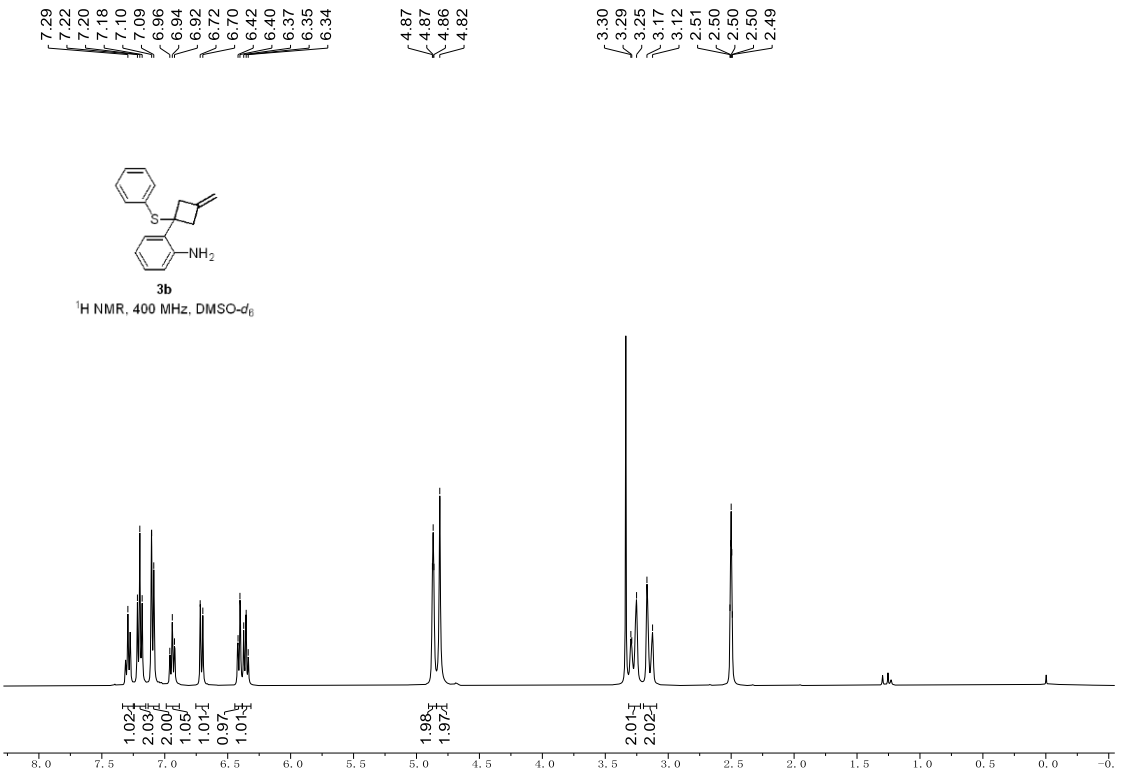
4-bromo-2-(1-(isopropylthio)-3-methylenecyclobutyl)aniline (3x)



Eluent in chromatography: petroleum ether/ethyl acetate = 200:1, **3x** was isolated as a white solid (32.7 mg, 50%); M.p.:132.3-137.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.08 (m, 2H), 6.61 – 6.48 (m, 1H), 5.01 – 4.82 (m, 2H), 4.00 (br, 2H), 3.57 – 3.29 (m, 2H), 3.19 – 2.93 (m, 2H), 2.53 – 2.39 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.4, 130.7, 130.0, 129.8, 118.4, 109.6, 107.8, 48.2, 46.1, 35.7, 24.1; HRMS (ESI) m/z: calcd for $C_{14}H_{19}BrNNaS$ $[M+Na]^+$ 334.0236, found: 334.0222.

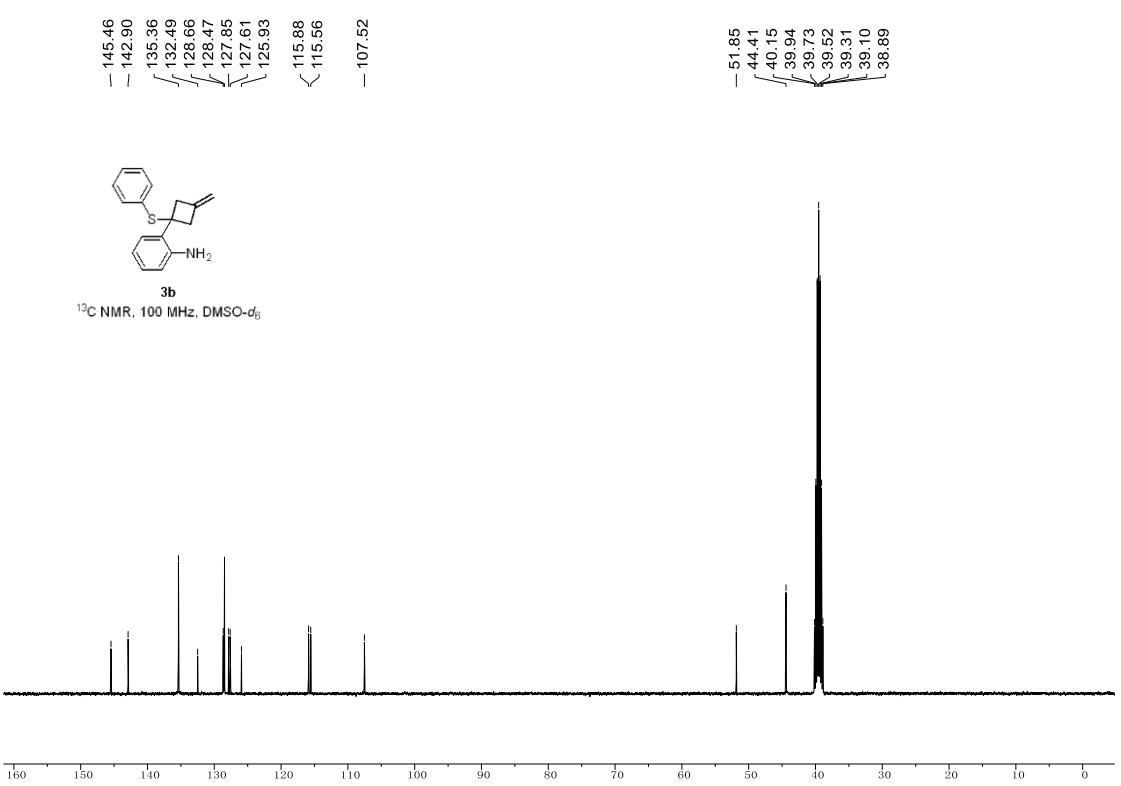
10. Copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of products





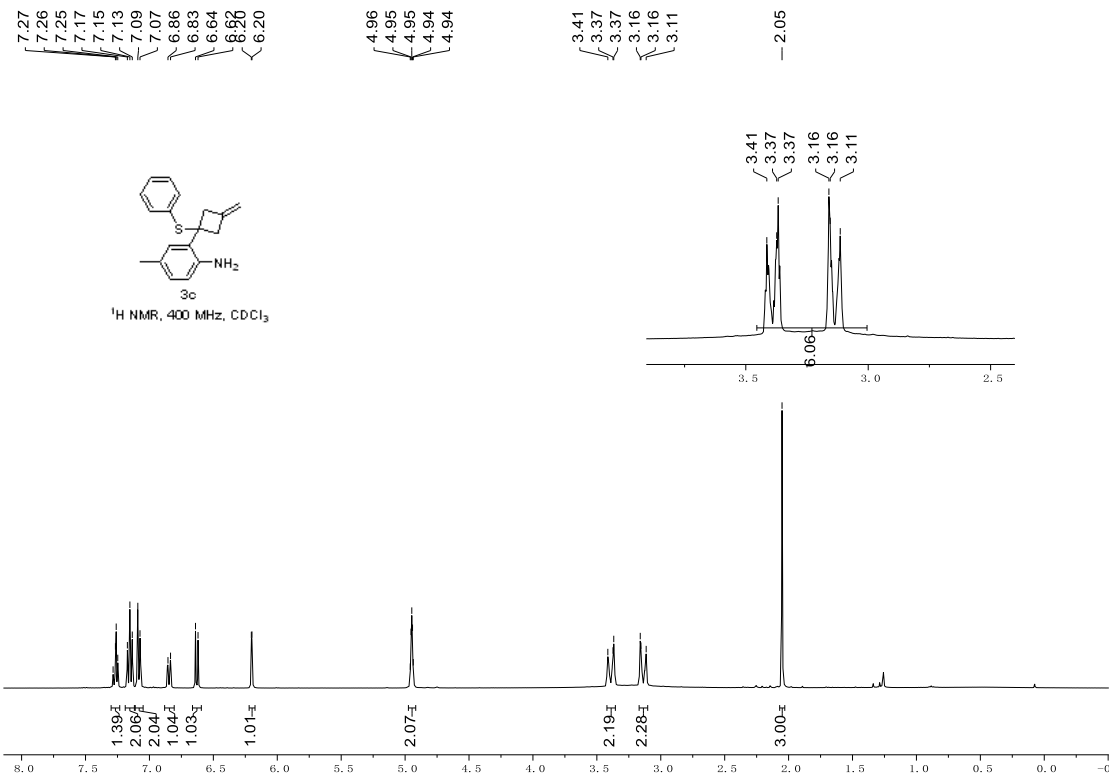
3b

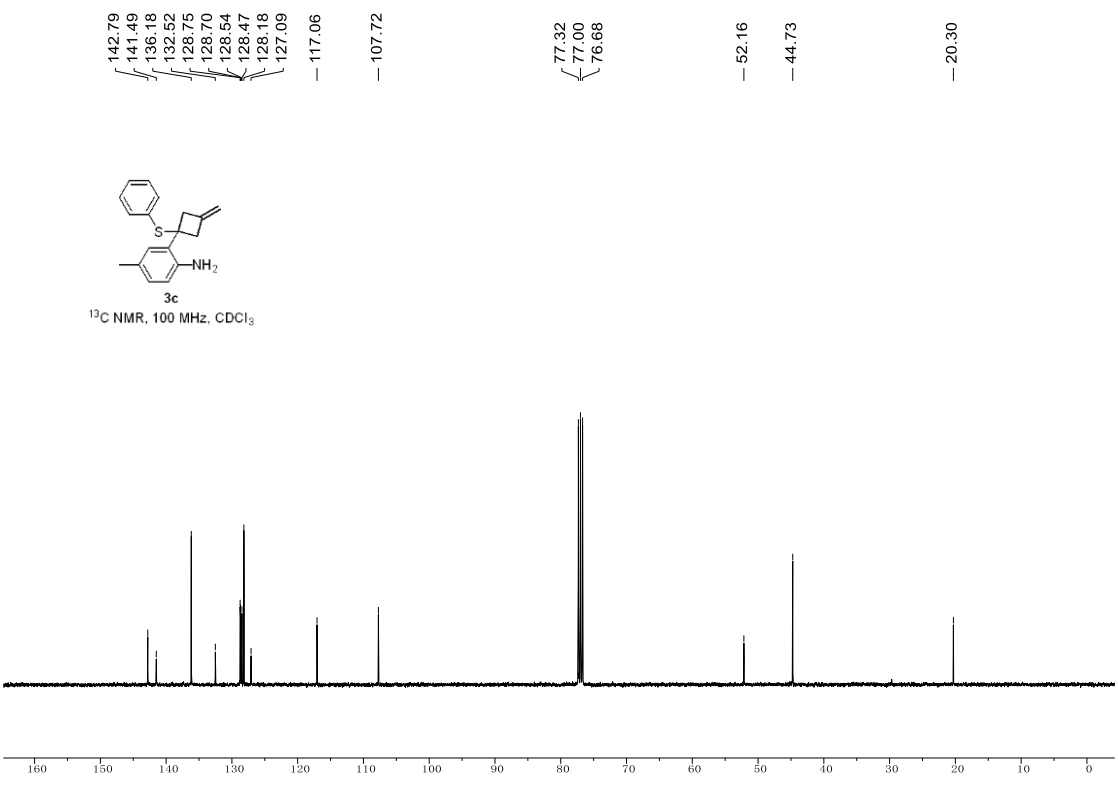
^{1}H NMR, 400 MHz, DMSO-d_6

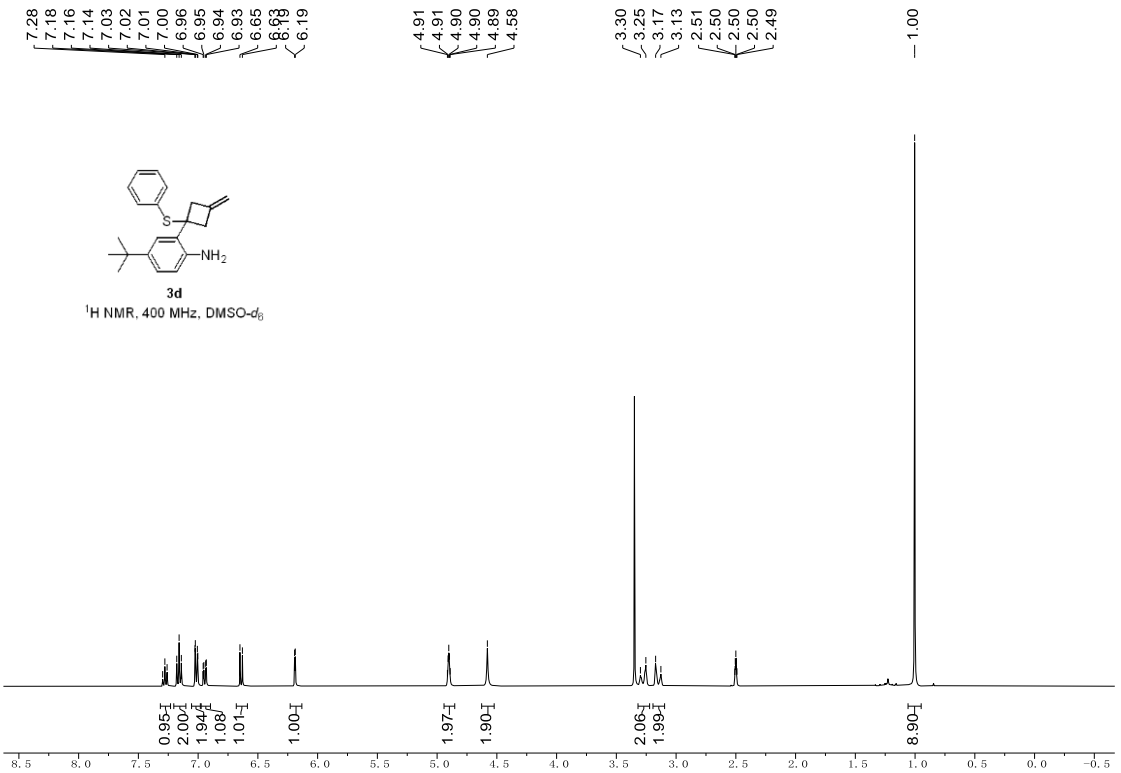


3b

^{13}C NMR, 100 MHz, DMSO-d_6

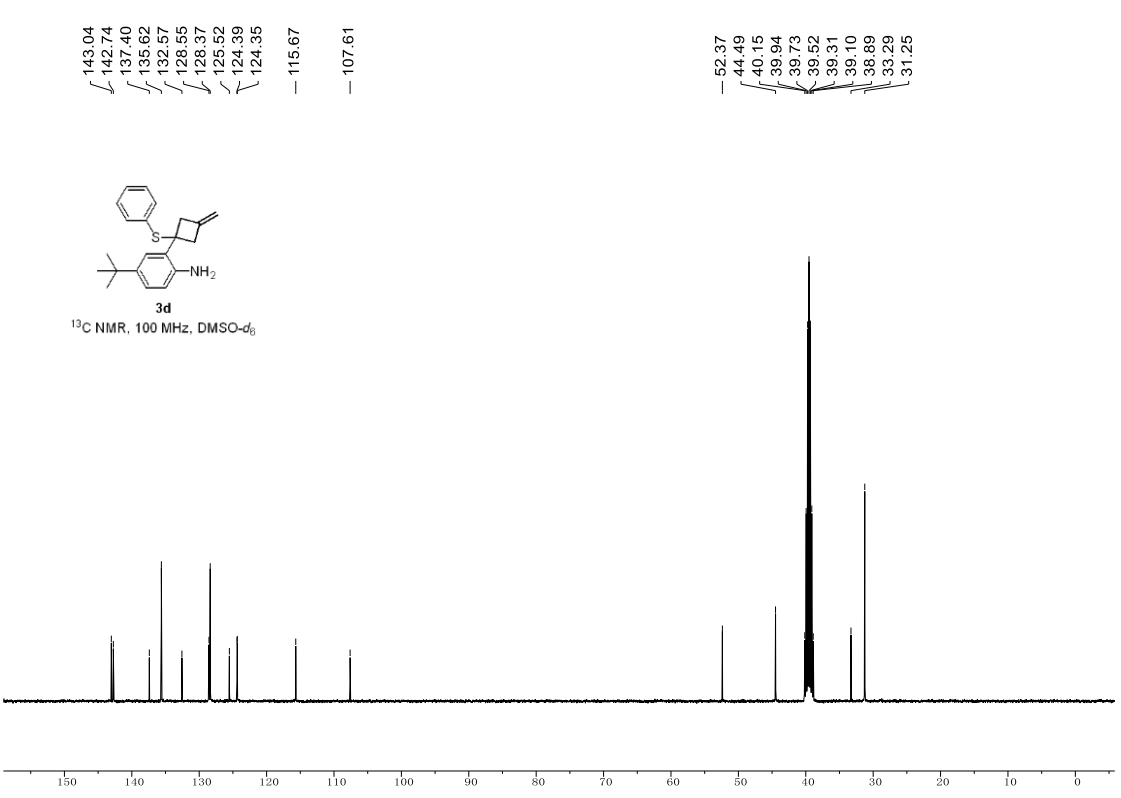

7.27
7.26
7.25
7.17
7.15
7.13
7.09
7.07
6.86
6.83
6.64
6.20
4.96
4.95
4.95
4.94
4.94
3.41
3.37
3.37
3.16
3.16
3.11
2.05
S
NH2
3c
1H NMR, 400 MHz, CDCl3
6.06
1.39
2.06
2.04
1.04
1.03
1.01
2.07
2.19
2.28
3.00


142.79
141.49
136.18
132.52
128.75
128.70
128.54
128.47
128.18
127.09
117.06
107.72
77.32
77.00
76.68
52.16
44.73
20.30
S
NH2
3c
13C NMR, 100 MHz, CDCl3



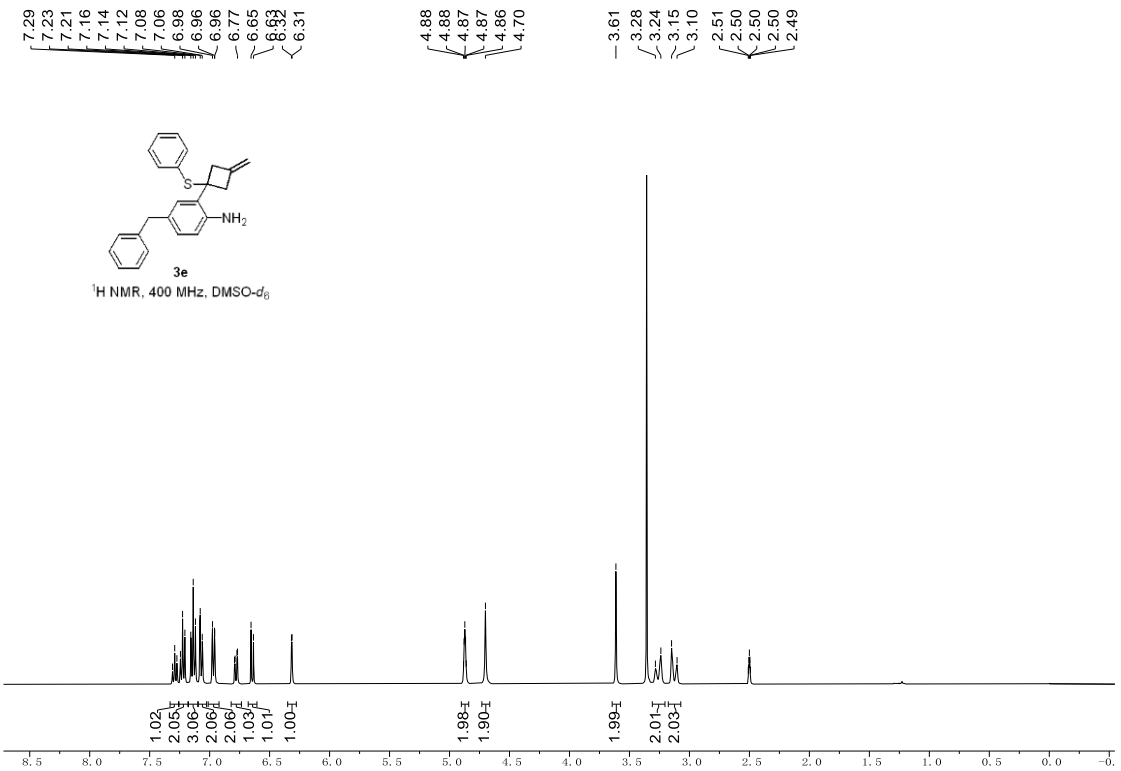
3d

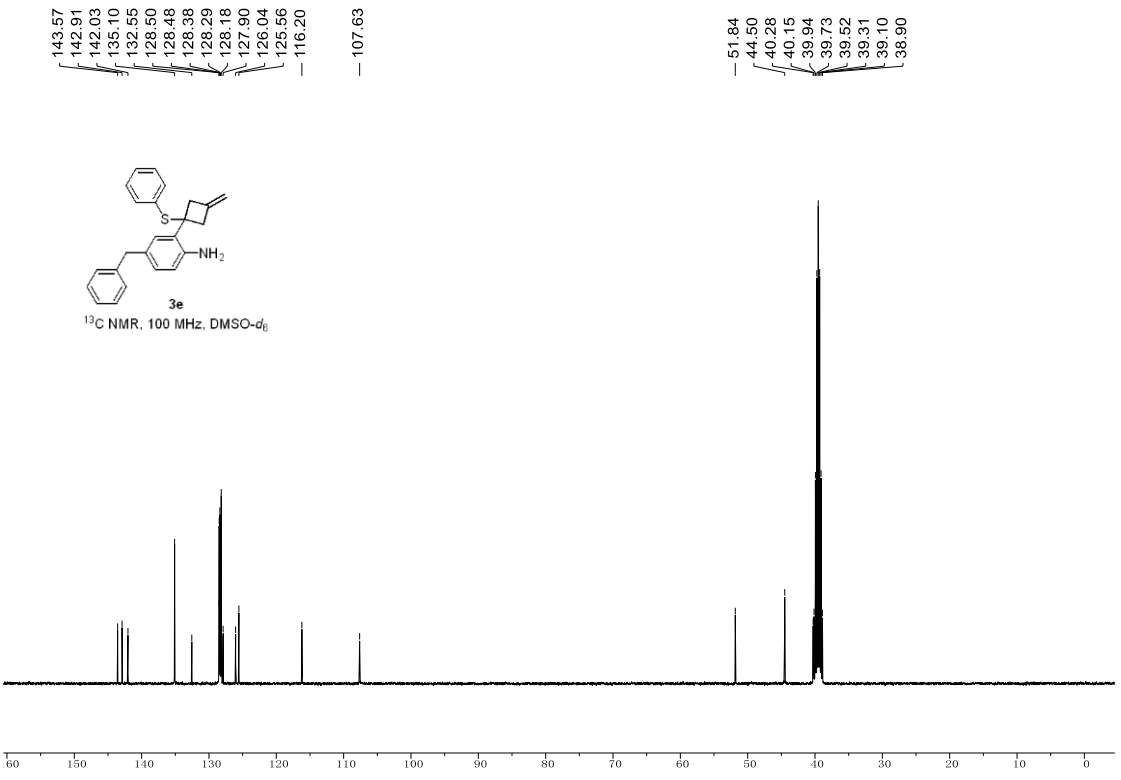
^{1}H NMR, 400 MHz, DMSO-d_6

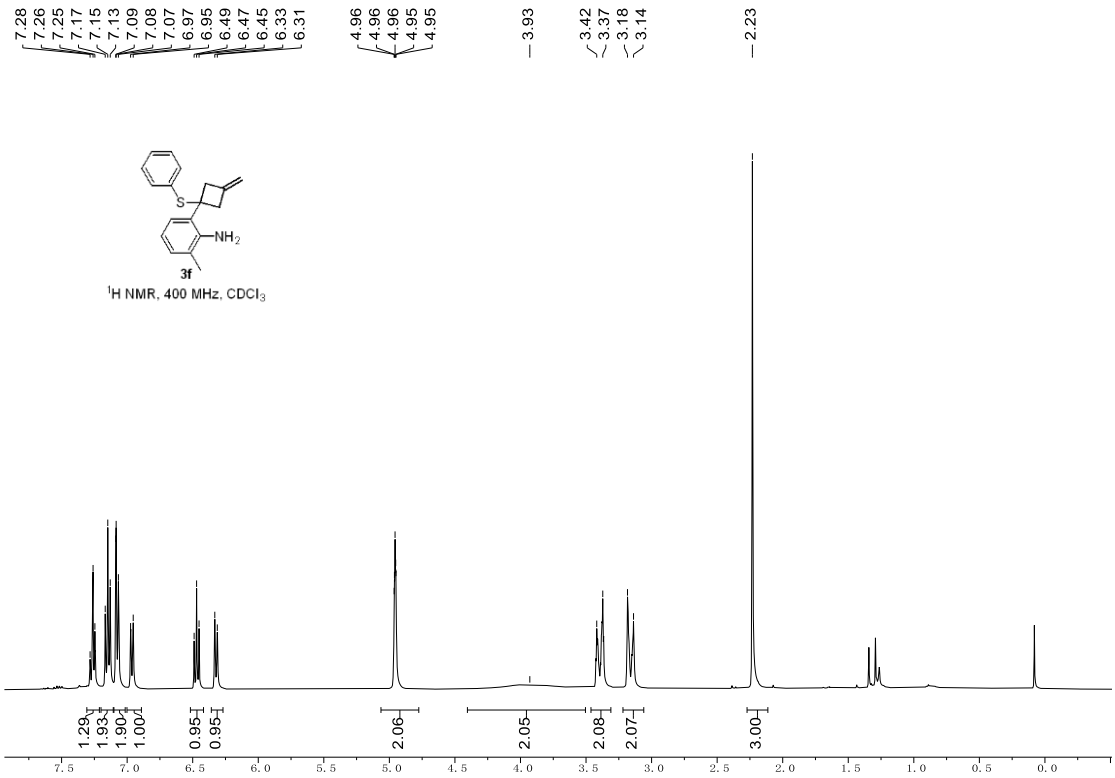


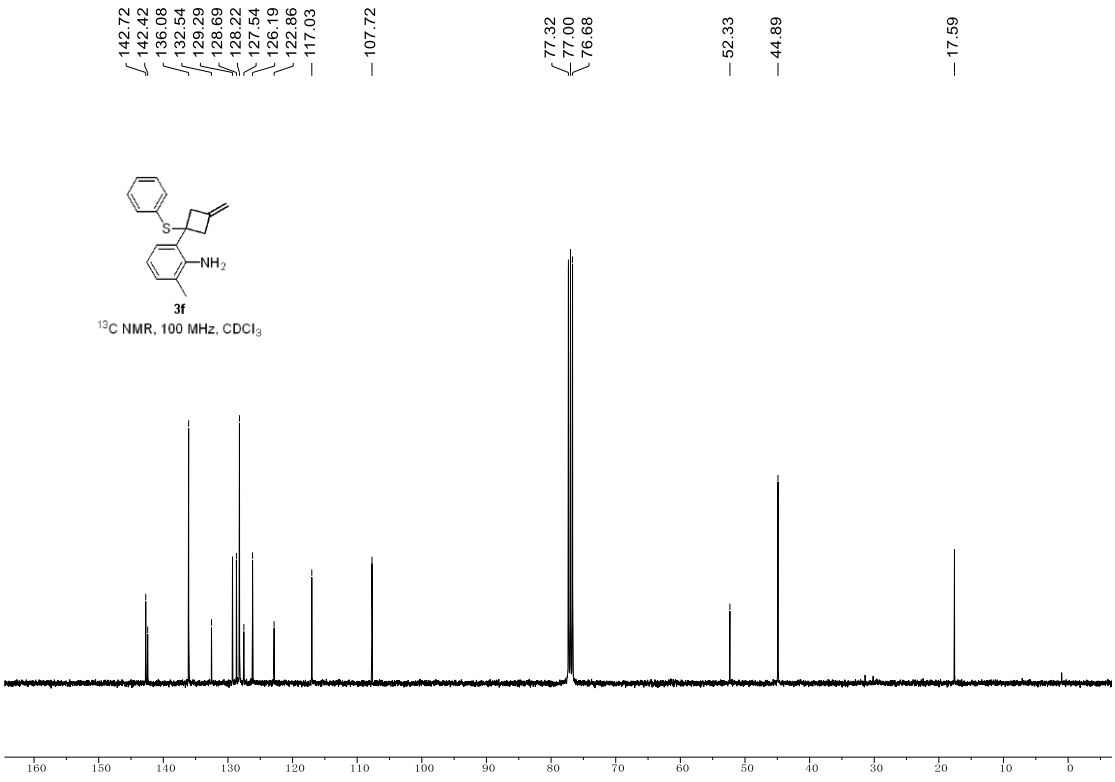
3d

^{13}C NMR, 100 MHz, DMSO-d_6


7.29
7.23
7.21
7.16
7.14
7.12
7.08
7.06
6.98
6.96
6.96
6.77
6.65
6.63
6.32
6.31
4.88
4.88
4.87
4.87
4.86
4.70
3.61
3.28
3.24
3.15
3.10
2.51
2.50
2.50
2.50
2.49
S
NH2
3e
1H NMR, 400 MHz, DMSO-d6
1.02
2.05
3.06
2.06
2.06
1.03
1.01
1.00
1.98
1.90
1.99
2.01
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


143.57
142.91
142.03
135.10
132.55
128.50
128.48
128.38
128.29
128.18
127.90
126.04
125.56
116.20
107.63
51.84
44.50
40.28
40.15
39.94
39.73
39.52
39.31
39.10
38.90
S
NH2
3e
13C NMR, 100 MHz, DMSO-d6
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.28
7.26
7.25
7.17
7.15
7.13
7.09
7.08
7.07
6.97
6.95
6.49
6.47
6.45
6.33
6.31
4.96
4.96
4.96
4.95
4.95
3.93
3.42
3.37
3.18
3.14
2.23
NH2
3f
1H NMR, 400 MHz, CDCl3
1.29
1.93
1.90
1.00
0.95
0.95
2.06
2.05
2.08
2.07
3.00


142.72
142.42
136.08
132.54
129.29
128.69
128.22
127.54
126.19
122.86
117.03
107.72
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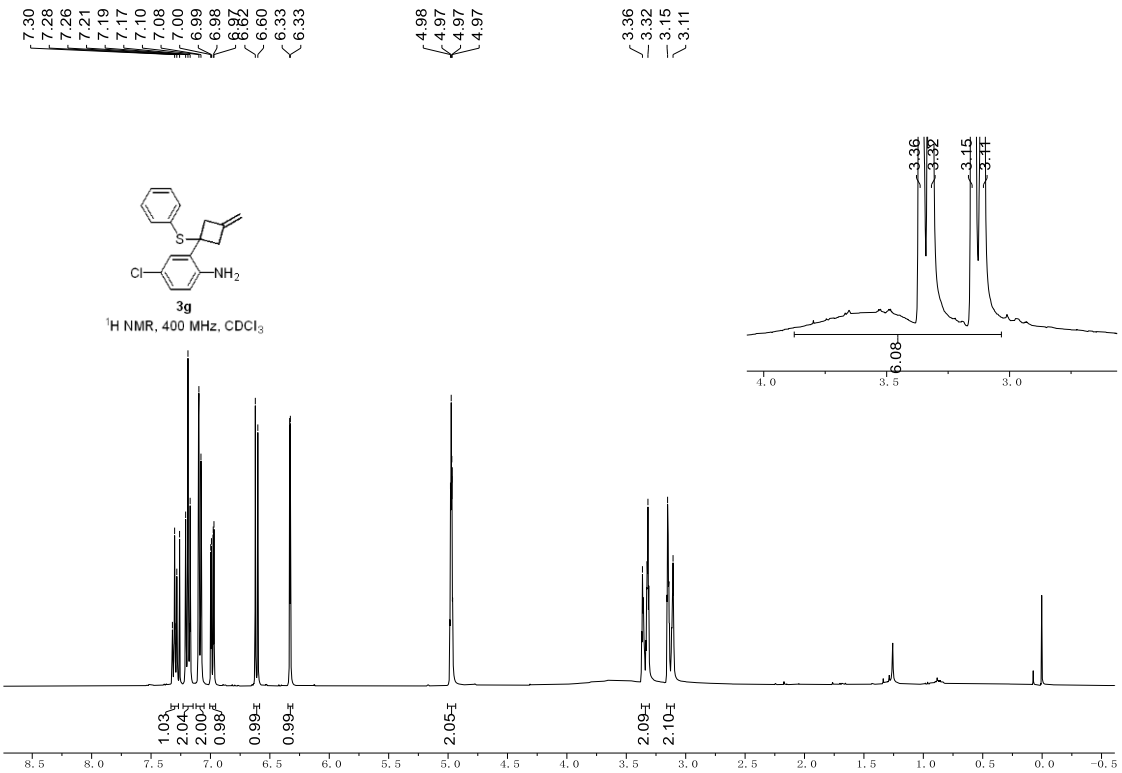
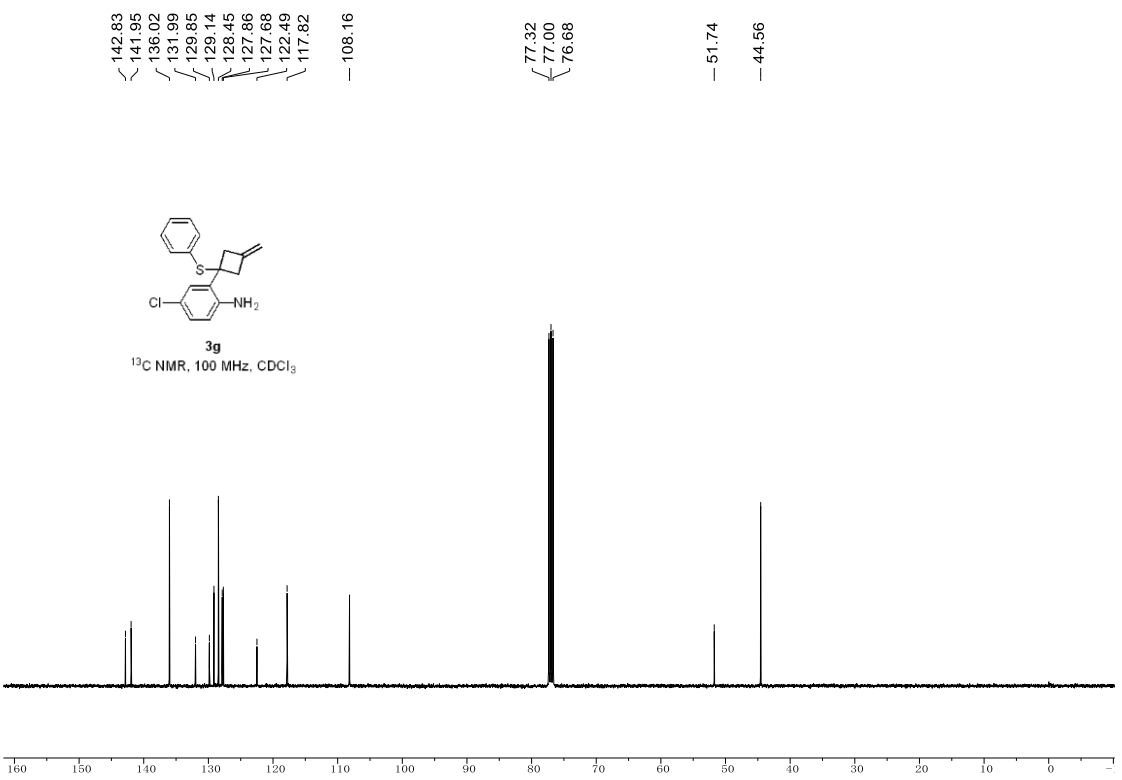
76.68
52.33
44.89
17.59
NH2
3f
13C NMR, 100 MHz, CDCl3


7.30
7.28
7.26
7.21
7.19
7.17
7.10
7.08
7.00
6.99
6.98
6.97
6.82
6.60
6.33
6.33
4.98
4.97
4.97
4.97
3.36
3.32
3.15
3.11
3g
1H NMR, 400 MHz, CDCl3
6.08
1.03
2.04
2.00
0.98
0.99
0.99
2.05
2.09
2.10


142.83
141.95
136.02
131.99
129.85
129.14
128.45
127.86
127.68
122.49
117.82
108.16
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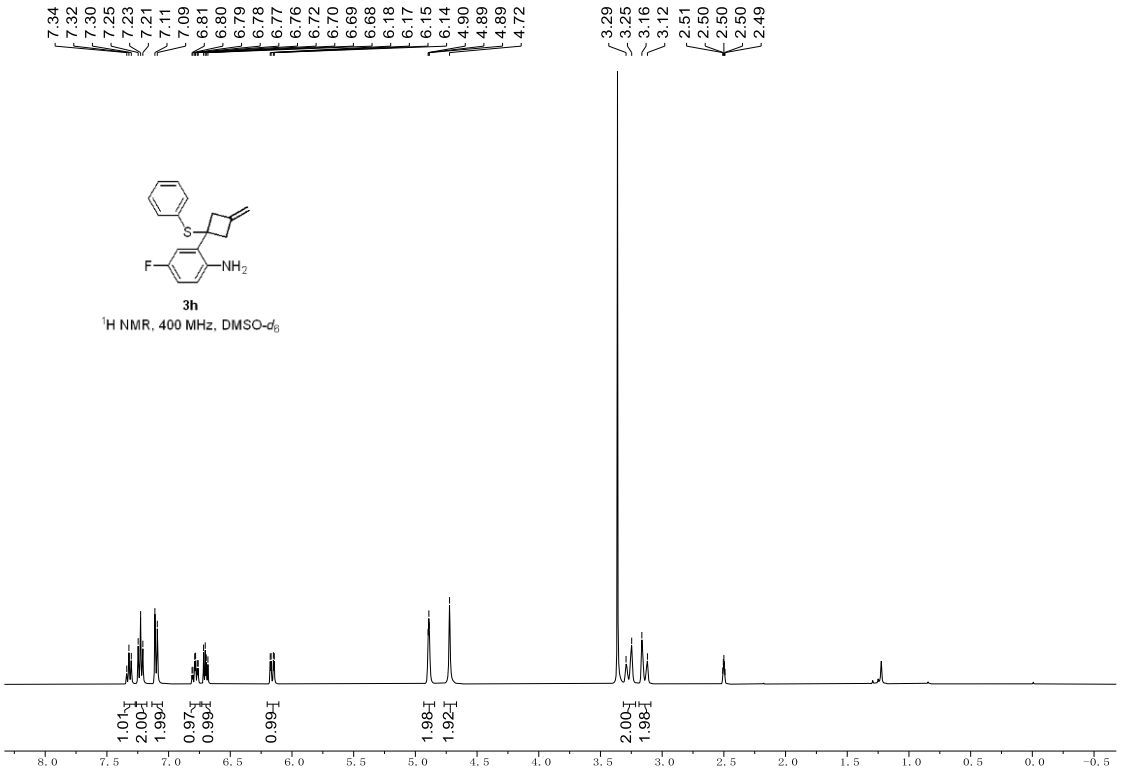
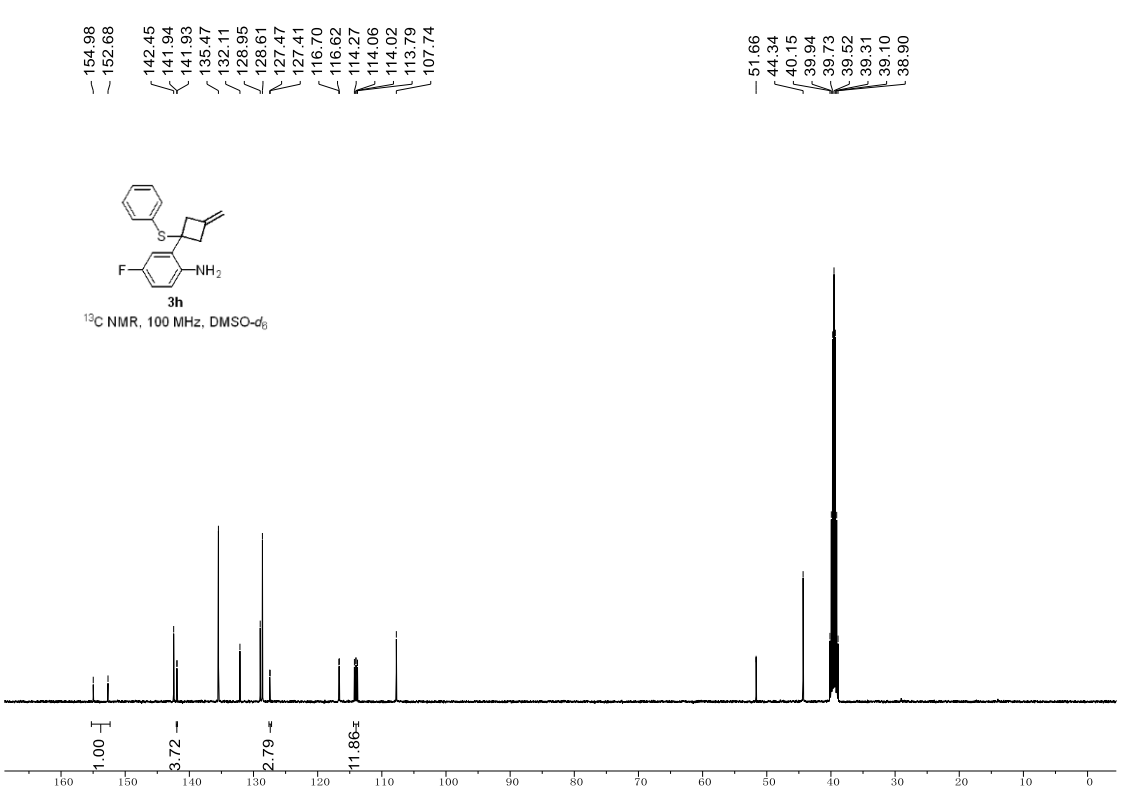
51.74
44.56
3g
13C NMR, 100 MHz, CDCl3



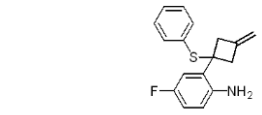
3h

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



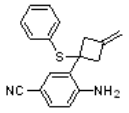
3h

^{13}C NMR, 100 MHz, DMSO-d_6



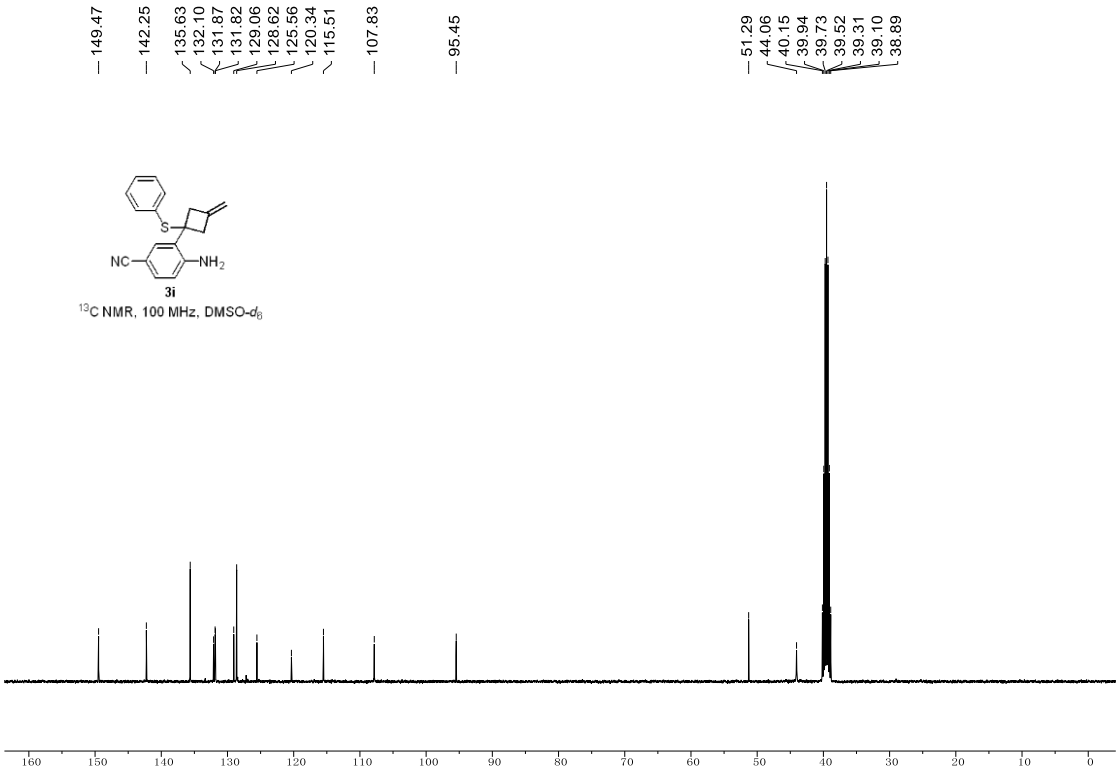
3h

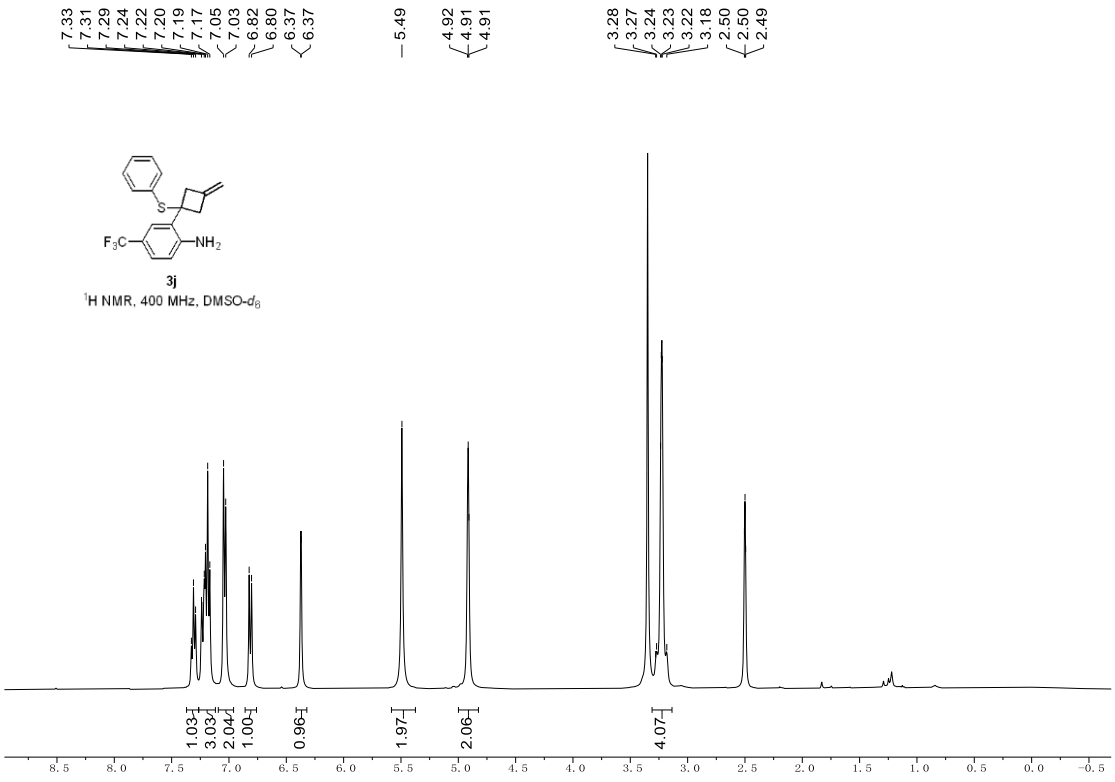
^{19}F NMR, 376MHz, DMSO-d_6

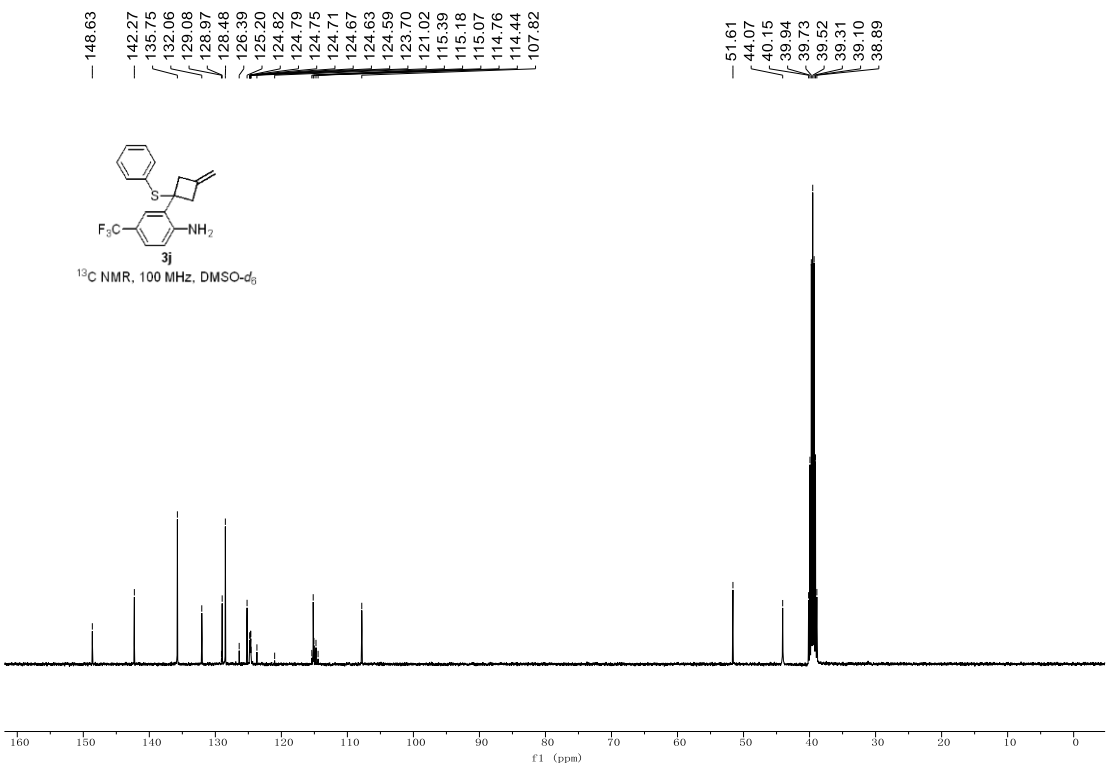


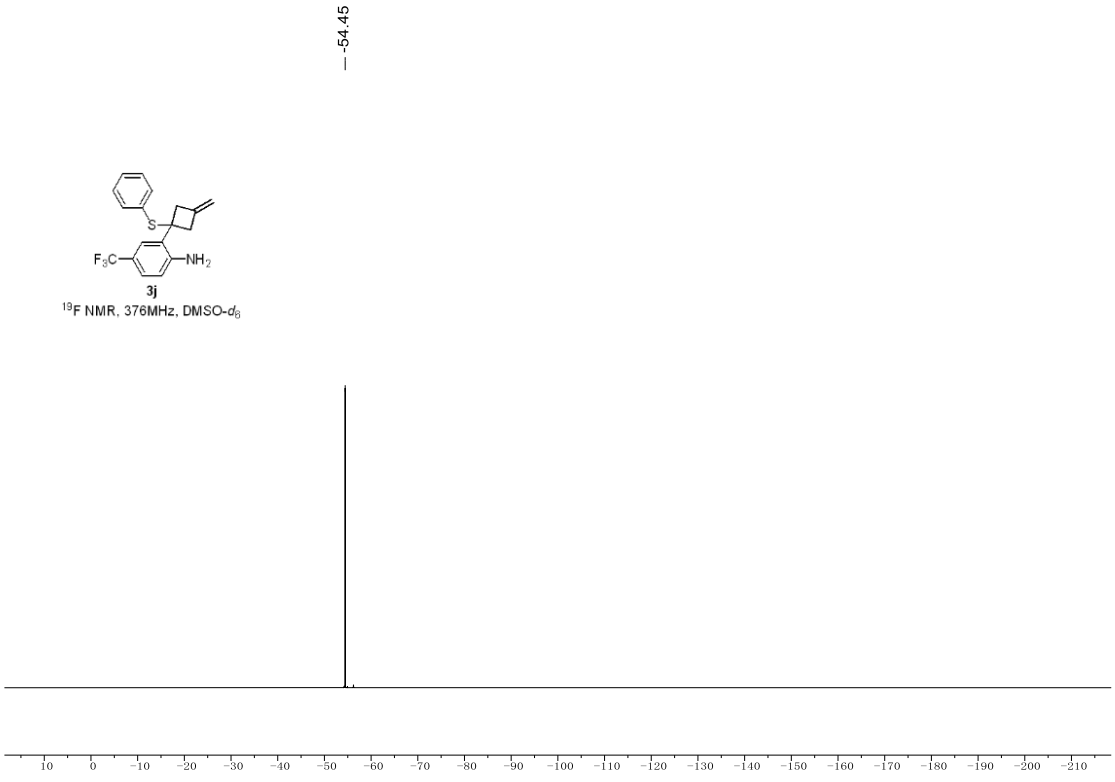
3i

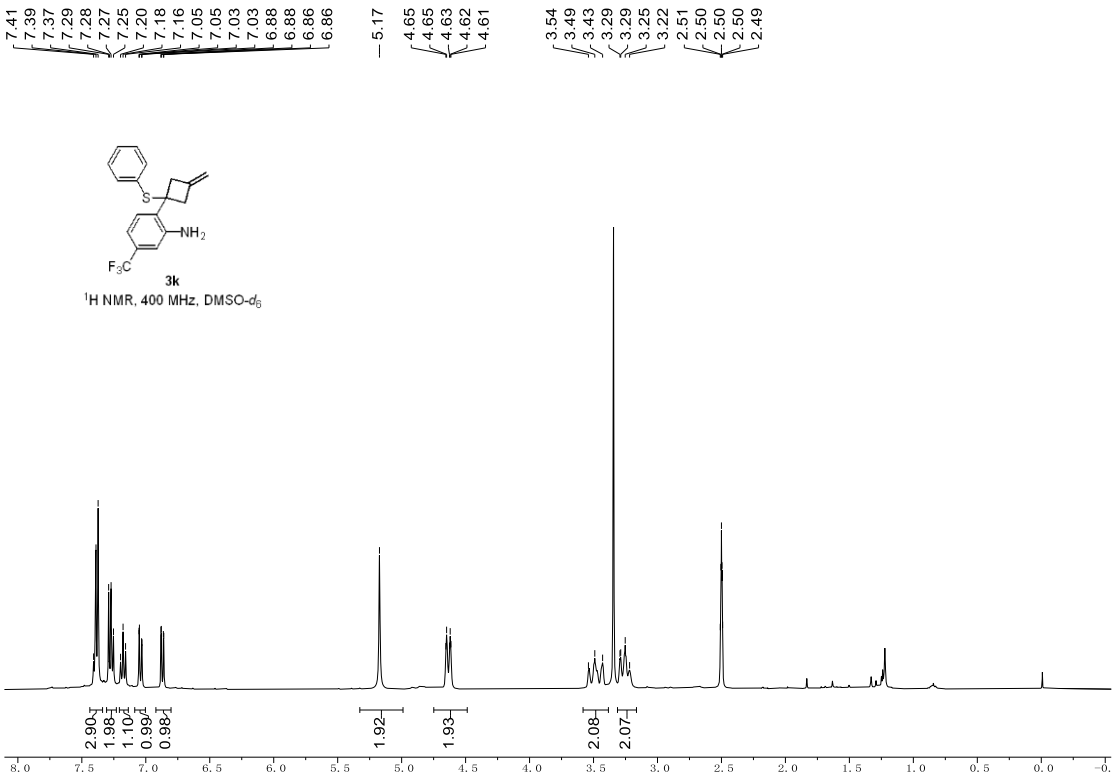
^{1}H NMR, 400 MHz, DMSO-d_6

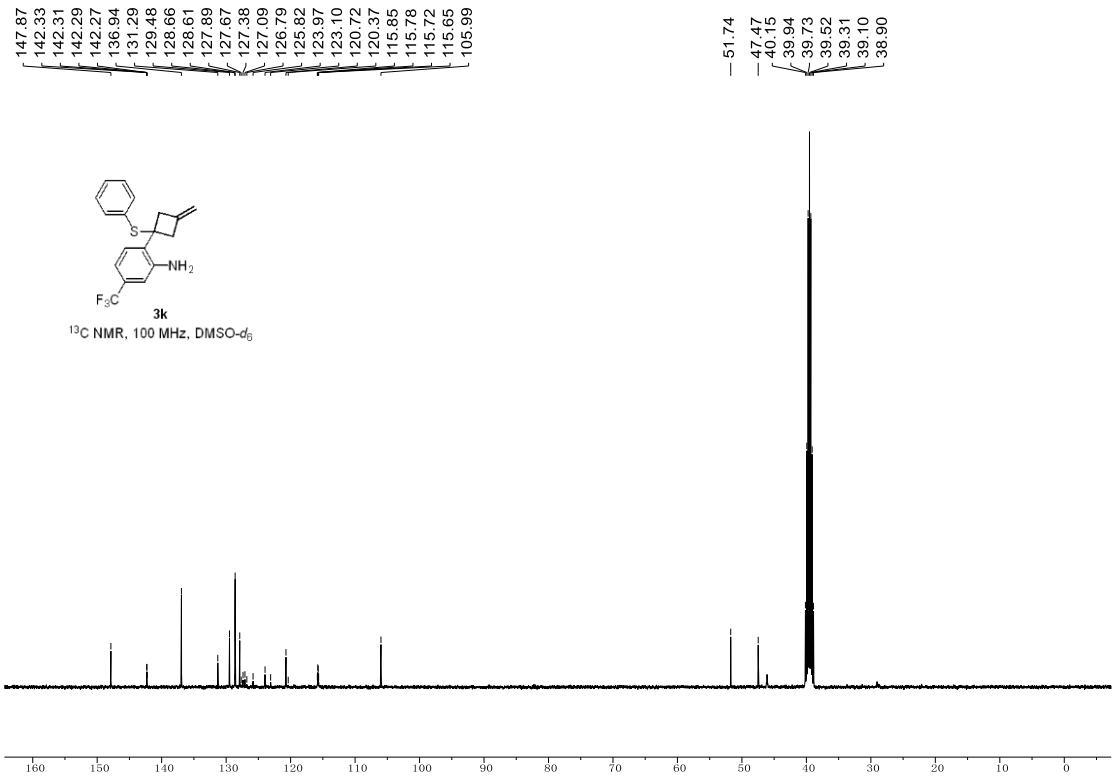

149.47
142.25
135.63
132.10
131.87
131.82
129.06
128.62
125.56
120.34
115.51
107.83
95.45
51.29
44.06
40.15
39.94
39.73
39.52
39.31
39.10
38.89
S
NC
NH2
3i
13C NMR, 100 MHz, DMSO-d6


7.33
7.31
7.29
7.24
7.22
7.20
7.19
7.17
7.05
7.03
6.82
6.80
6.37
6.37
5.49
4.92
4.91
4.91
3.28
3.27
3.24
3.23
3.22
3.18
2.50
2.50
2.49
S
F3C
NH2
3j
1H NMR, 400 MHz, DMSO-d6
1.03
3.03
2.04
1.00
0.96
1.97
2.06
4.07


148.63
142.27
135.75
132.06
129.08
128.97
128.48
126.39
125.20
124.82
124.79
124.75
124.71
124.67
124.63
124.59
123.70
121.02
115.39
115.18
115.07
114.76
114.44
107.82
51.61
44.07
40.15
39.94
39.73
39.52
39.31
39.10
38.89
S
F3C
NH2
3j
13C NMR, 100 MHz, DMSO-d6
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-54.45
S
F3C
NH2
3j
19F NMR, 376MHz, DMSO-d6
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210


7.41
7.39
7.37
7.29
7.28
7.27
7.25
7.20
7.18
7.16
7.05
7.05
7.03
7.03
6.88
6.88
6.86
6.86
5.17
4.65
4.65
4.63
4.62
4.61
3.54
3.49
3.43
3.29
3.29
3.25
3.22
2.51
2.50
2.50
2.50
2.49
S
NH2
F3C
3k
1H NMR, 400 MHz, DMSO-d6
2.90
1.98
1.10
0.99
0.98
1.92
1.93
2.08
2.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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142.33
142.31
142.29
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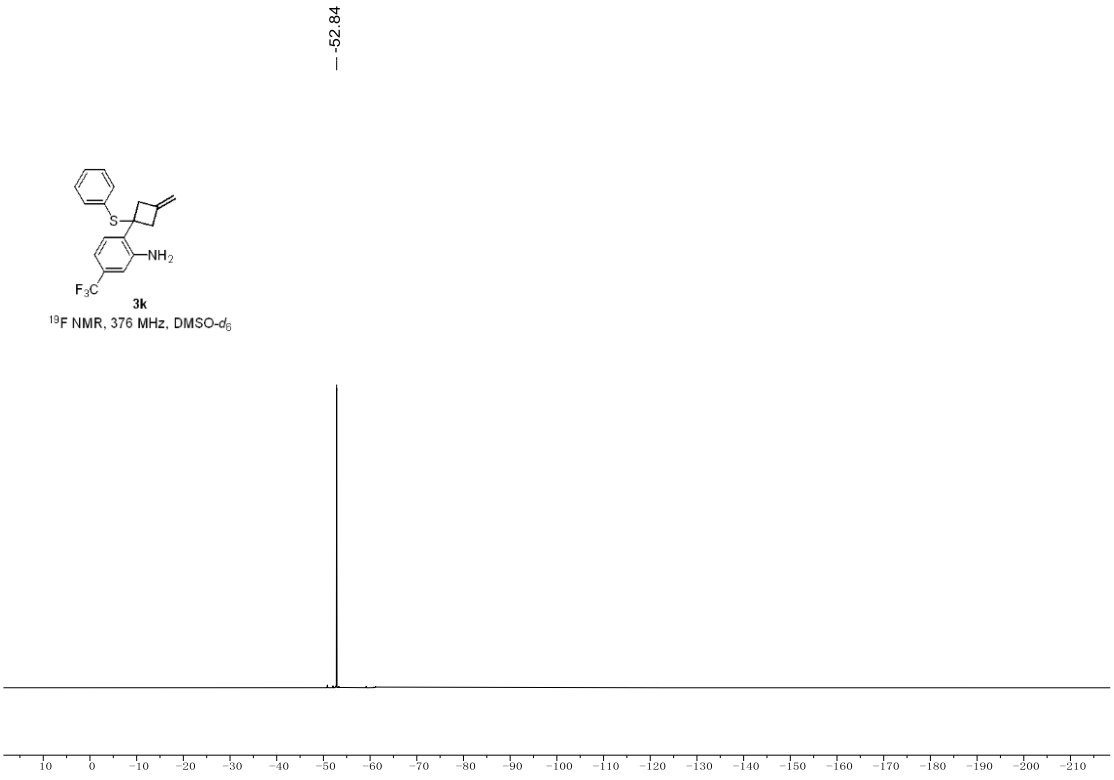
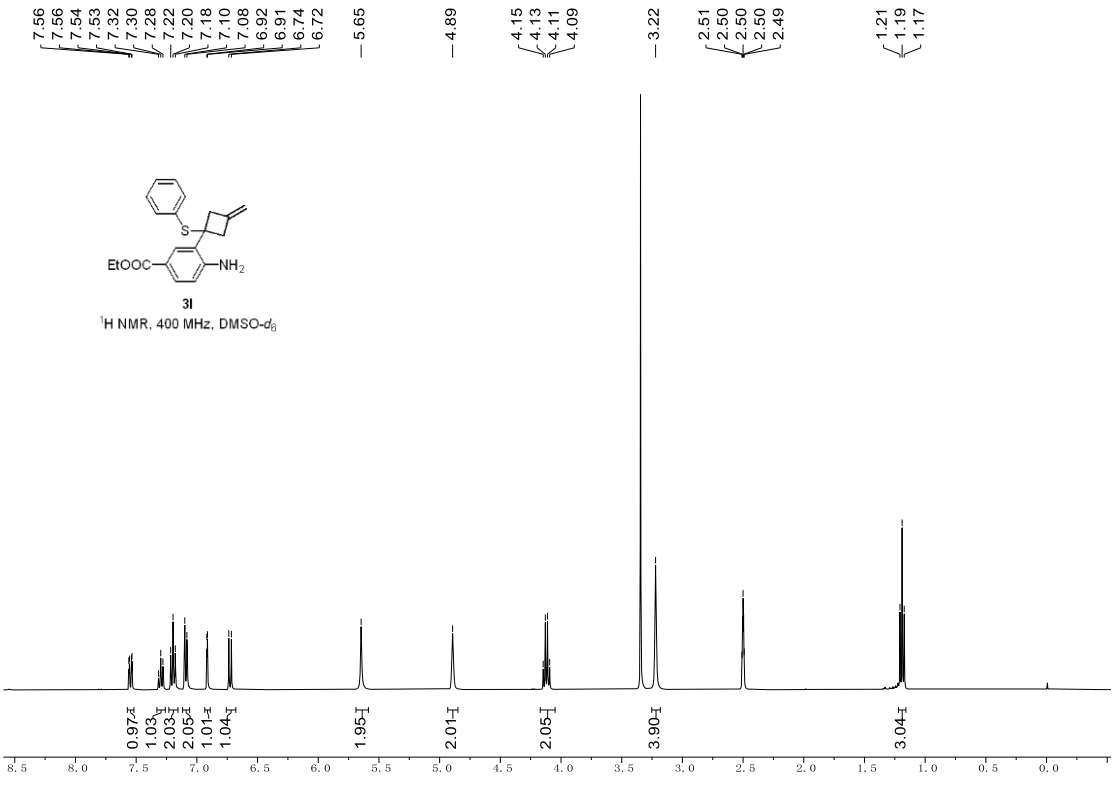
136.94
131.29
129.48
128.66
128.61
127.89
127.67
127.38
127.09
126.79
125.82
123.97
123.10
120.72
120.37
115.85
115.78
115.72
115.65
105.99
51.74
47.47
40.15
39.94
39.73
39.52
39.31
39.10
38.90
S
NH2
F3C
3k
13C NMR, 100 MHz, DMSO-d6
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



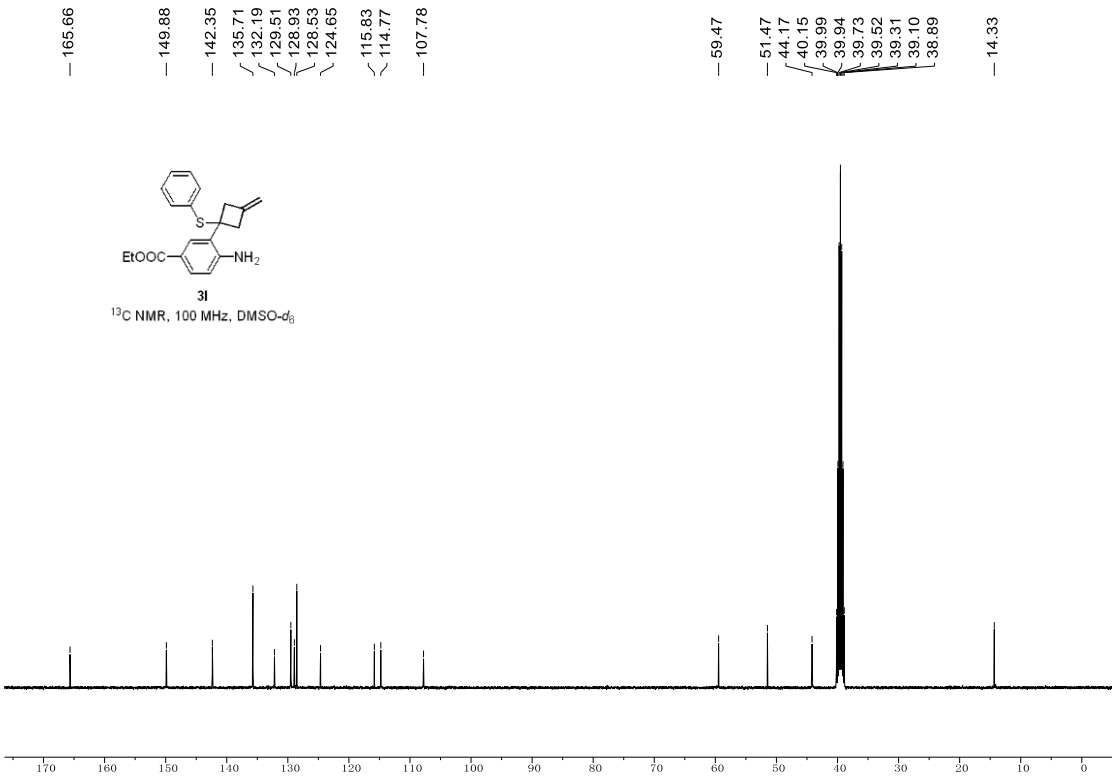
3k

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



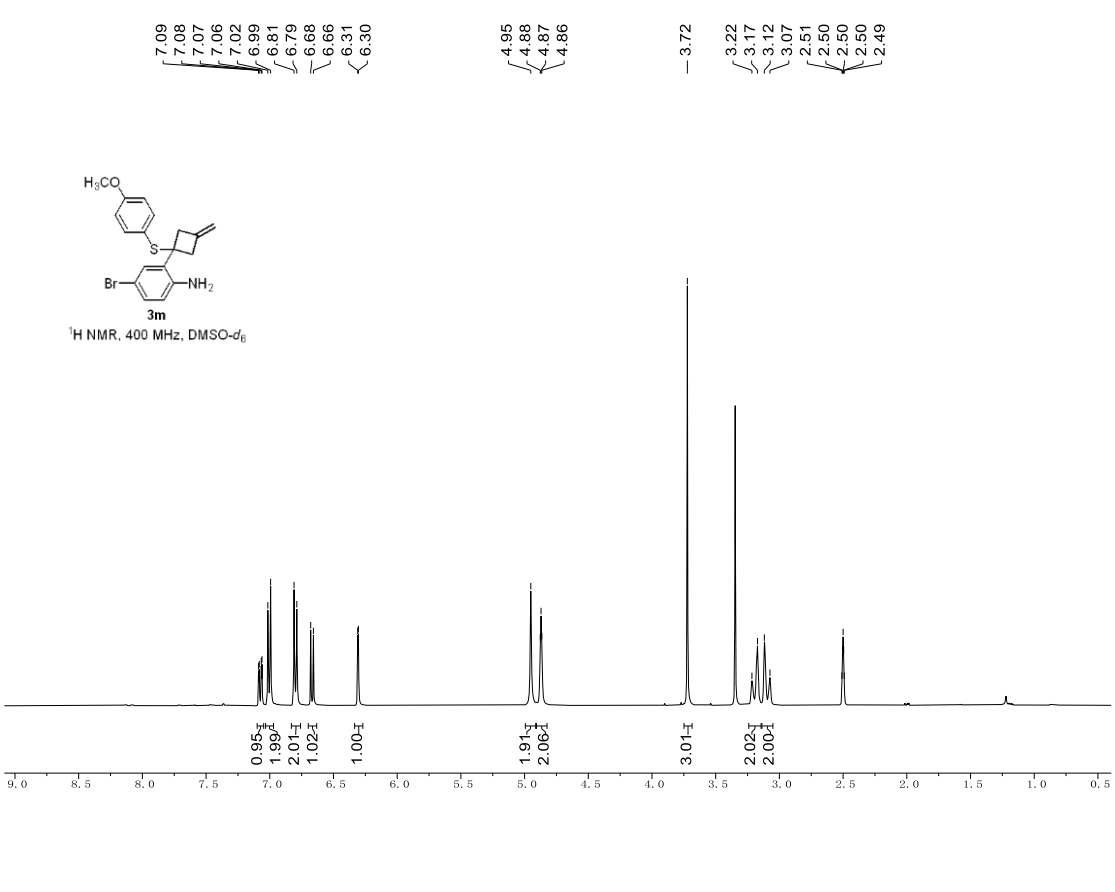
3l

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



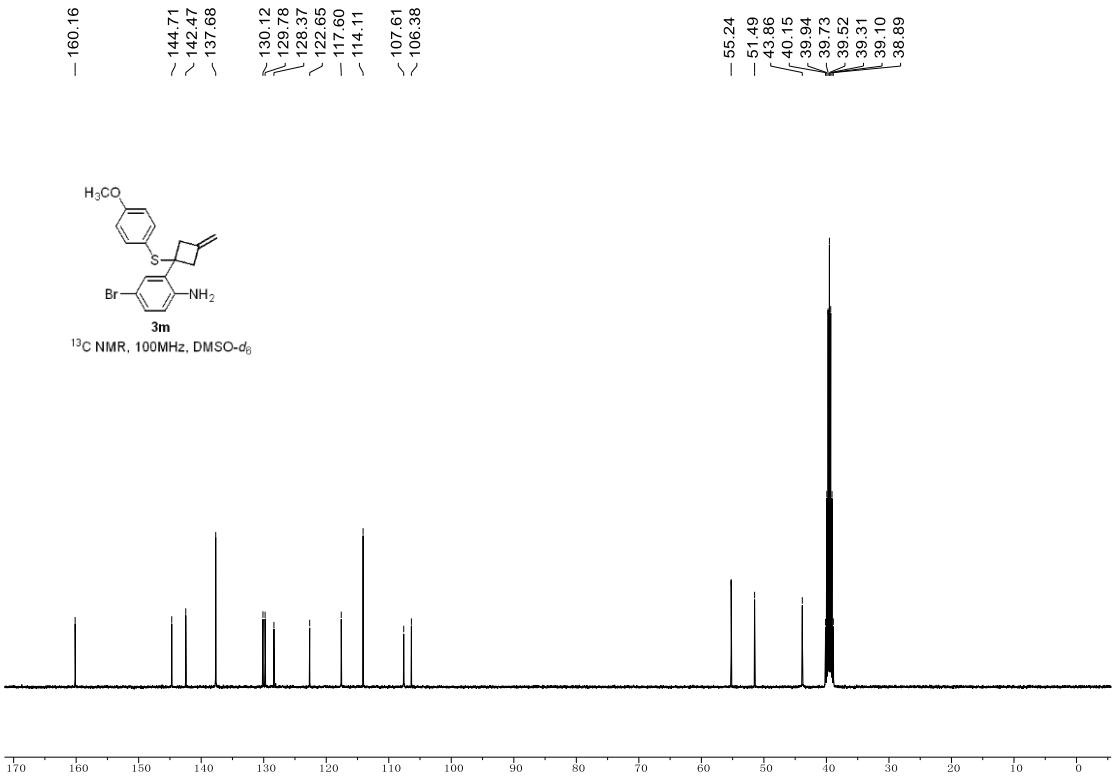
3l

^{13}C NMR, 100 MHz, DMSO-d_6



3m

^{1}H NMR, 400 MHz, DMSO-d_6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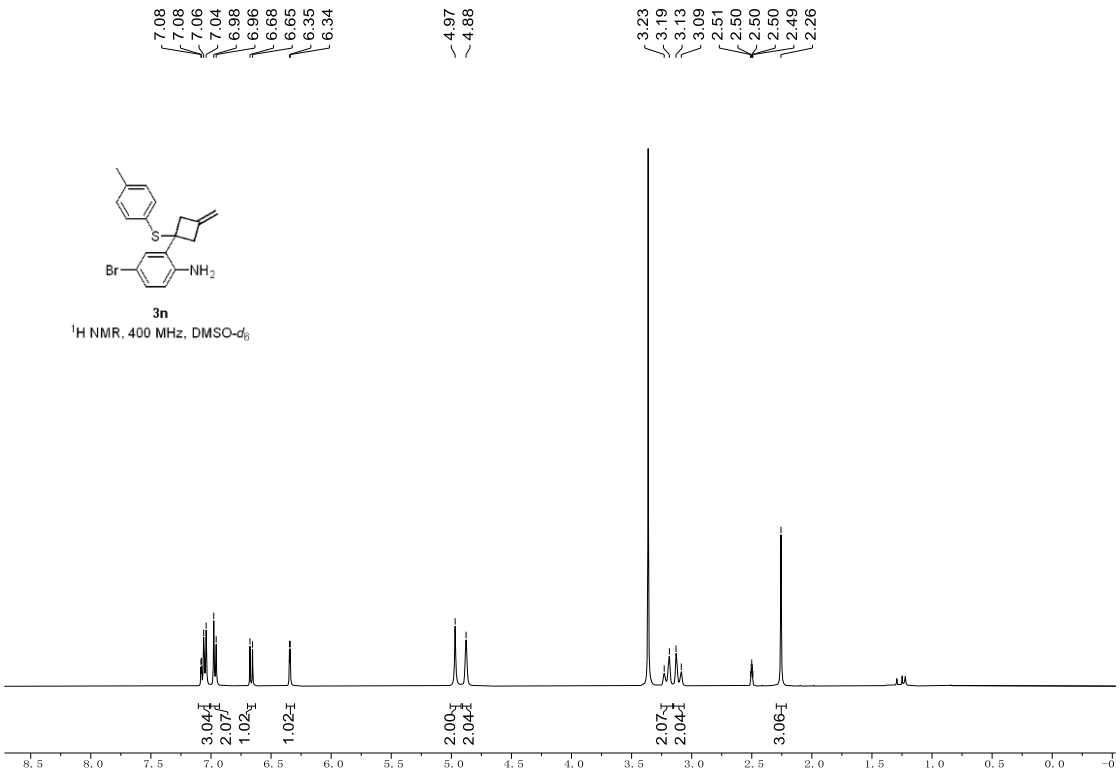
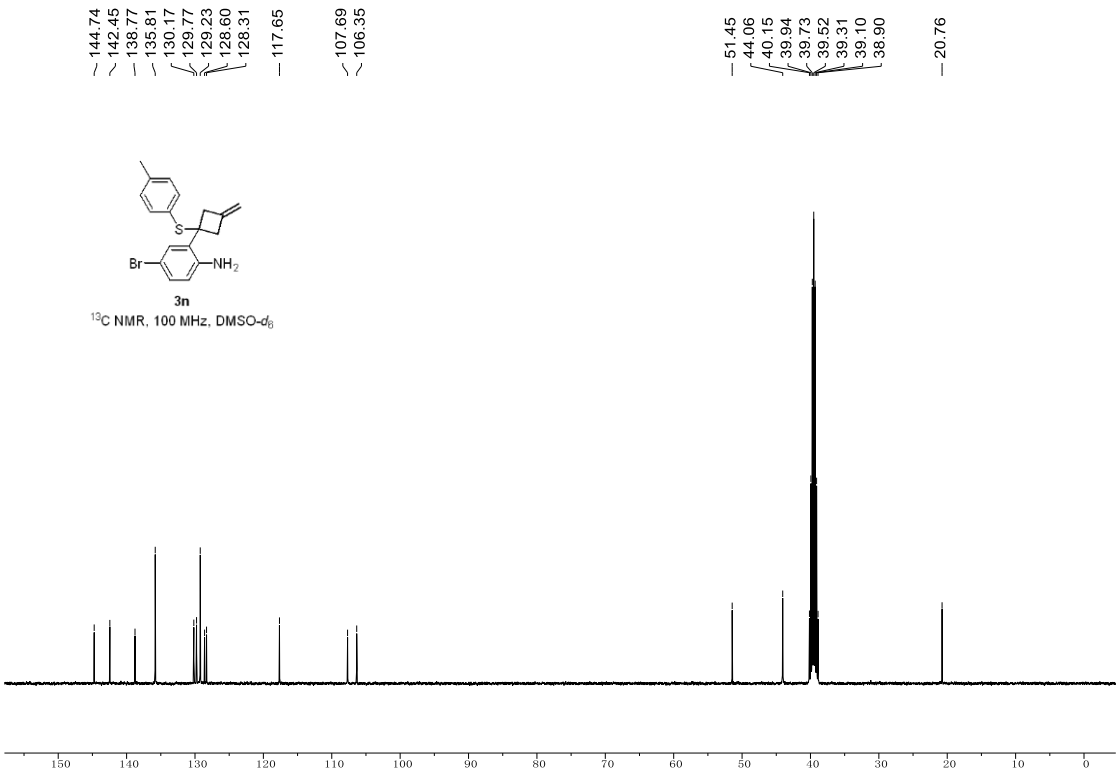
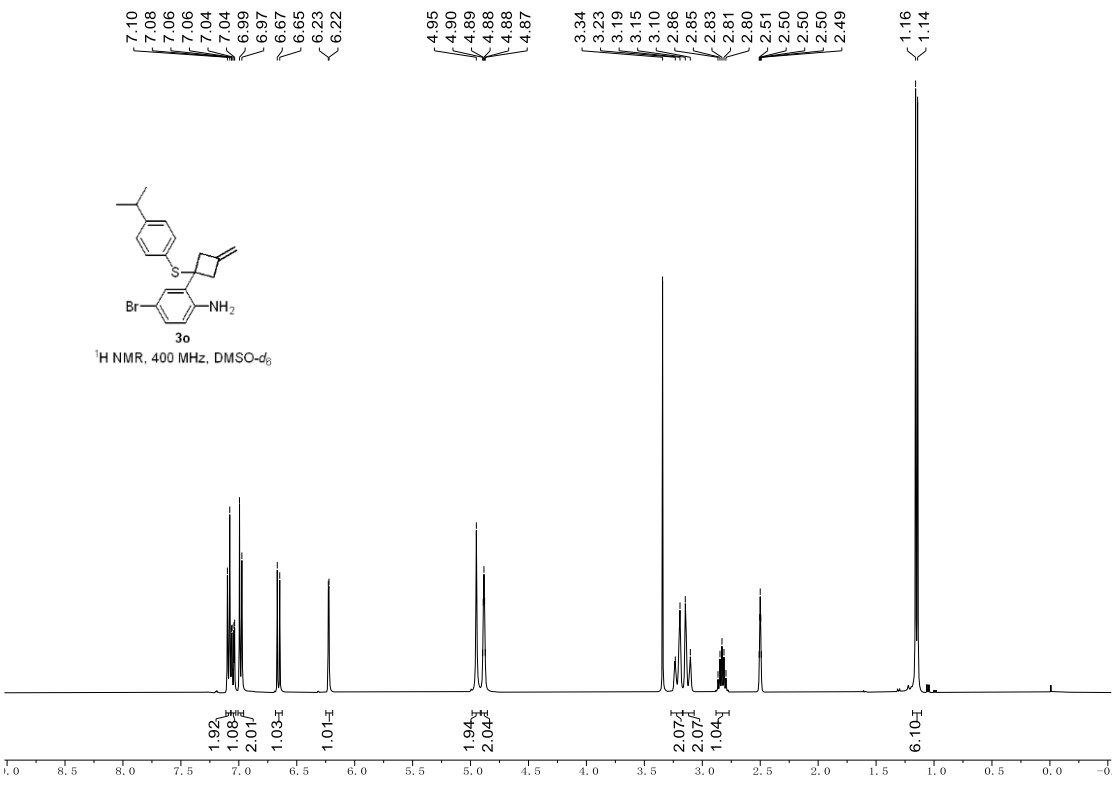
144.71
142.47
137.68
130.12
129.78
128.37
122.65
117.60
114.11
107.61
106.38
55.24
51.49
43.86
40.15
39.94
39.73
39.52
39.31
39.10
38.89
H3CO
S
Br
NH2
3m
13C NMR, 100MHz, DMSO-d6


7.08
7.08
7.06
7.04
6.98
6.96
6.68
6.65
6.35
6.34
4.97
4.88
3.23
3.19
3.13
3.09
2.51
2.50
2.50
2.50
2.49
2.26
S
Br
NH2
3n
1H NMR, 400 MHz, DMSO-d6
3.04
2.07
1.02
1.02
2.00
2.04
2.07
2.04
3.06



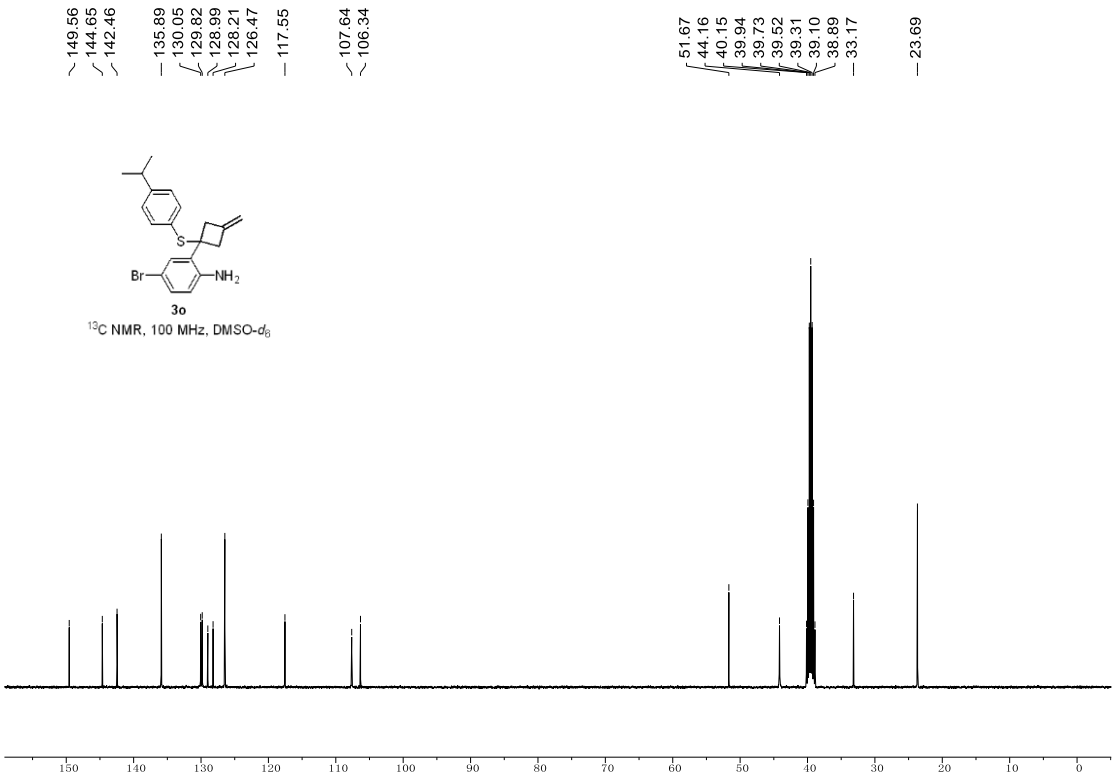
3n

^{13}C NMR, 100 MHz, DMSO-d_6



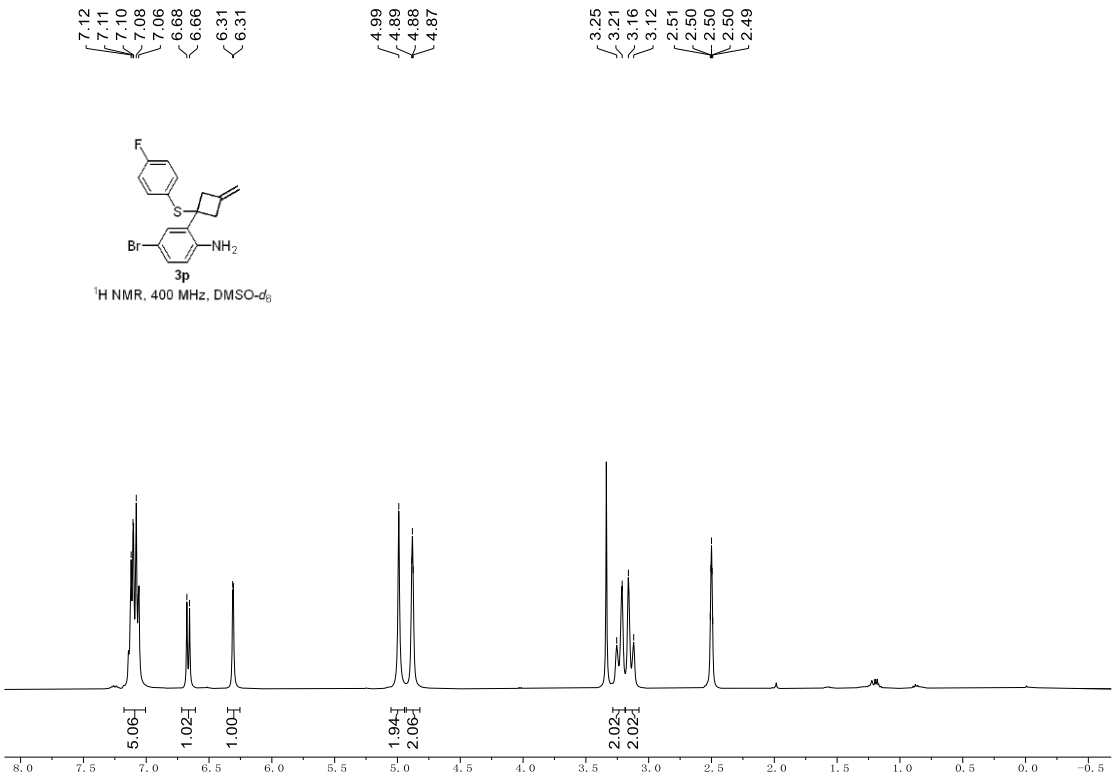
3o

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



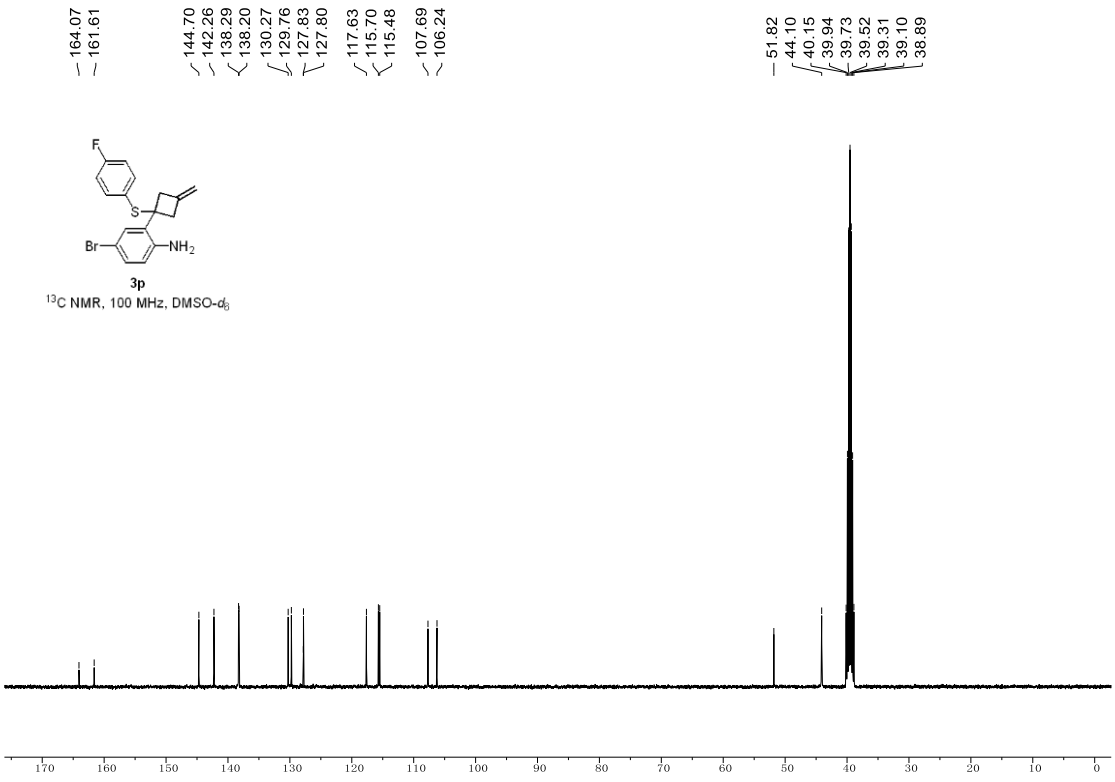
3o

^{13}C NMR, 100 MHz, DMSO-d_6



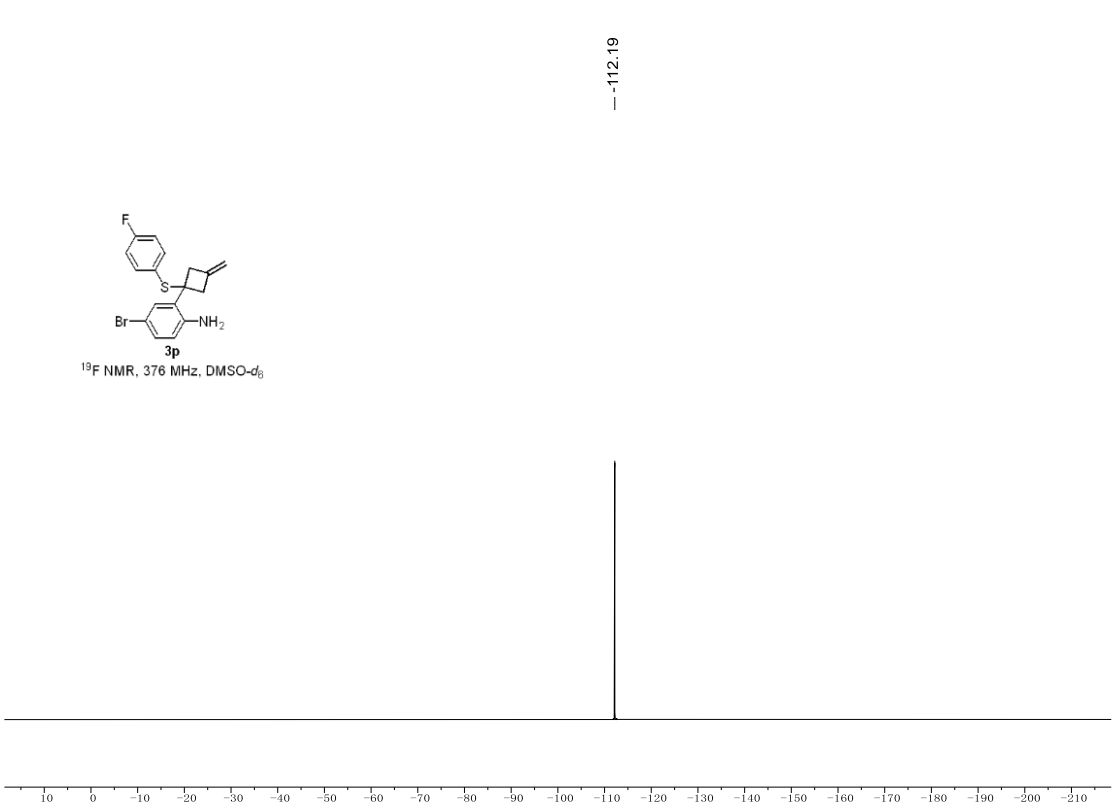
3p

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



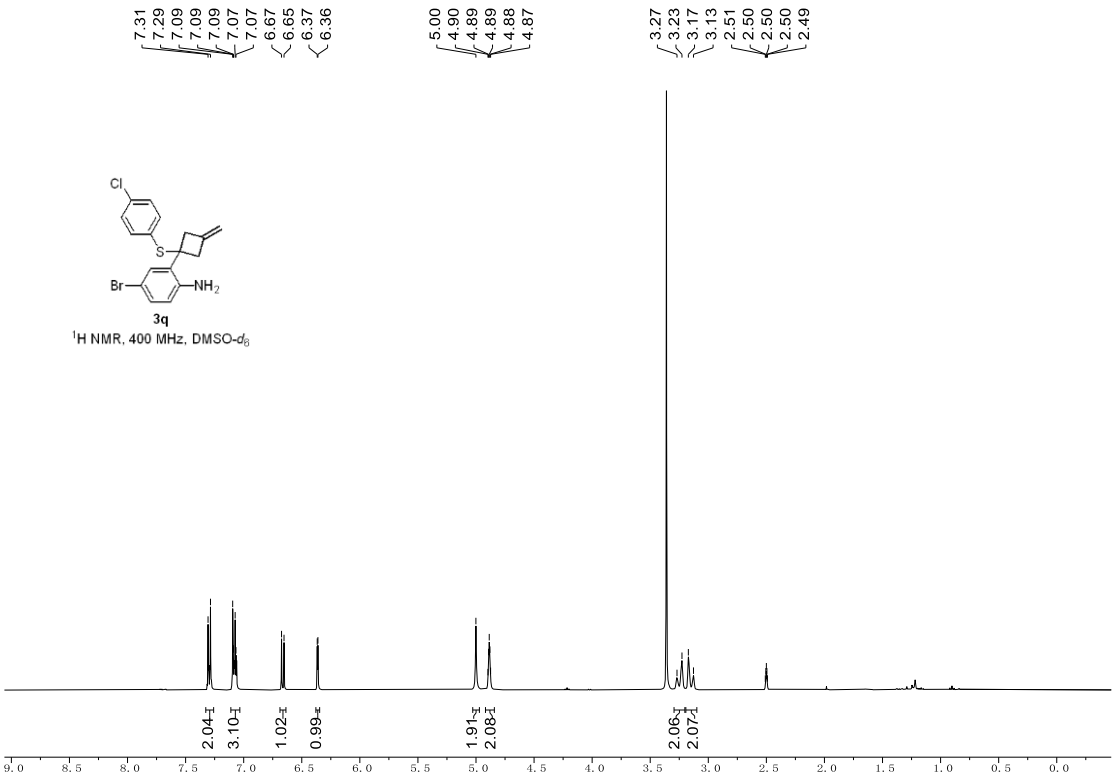
3p

^{13}C NMR, 100 MHz, DMSO-d_6



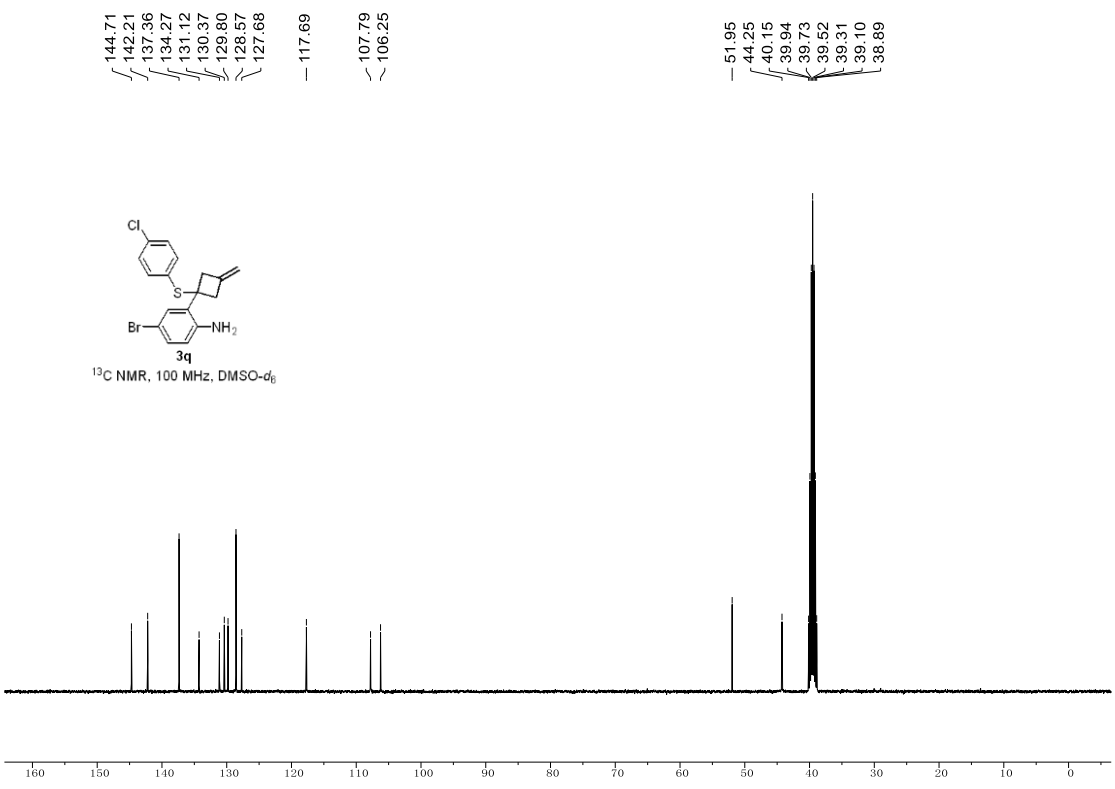
3p

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



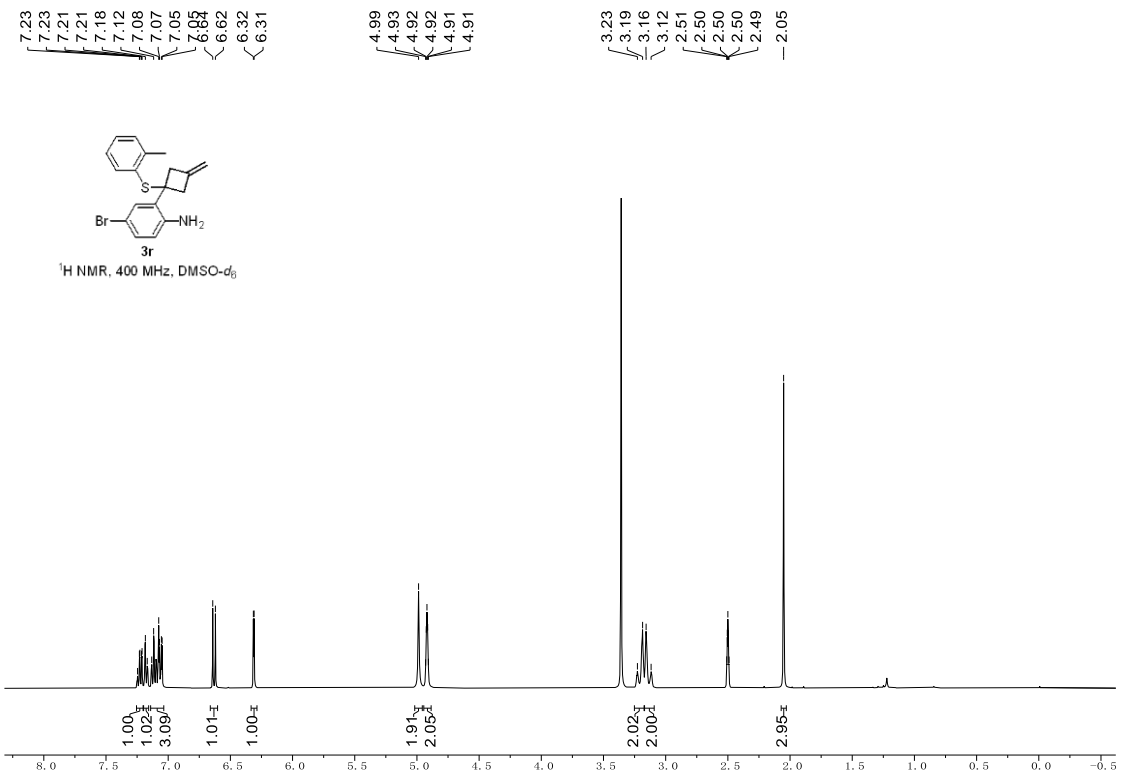
3q

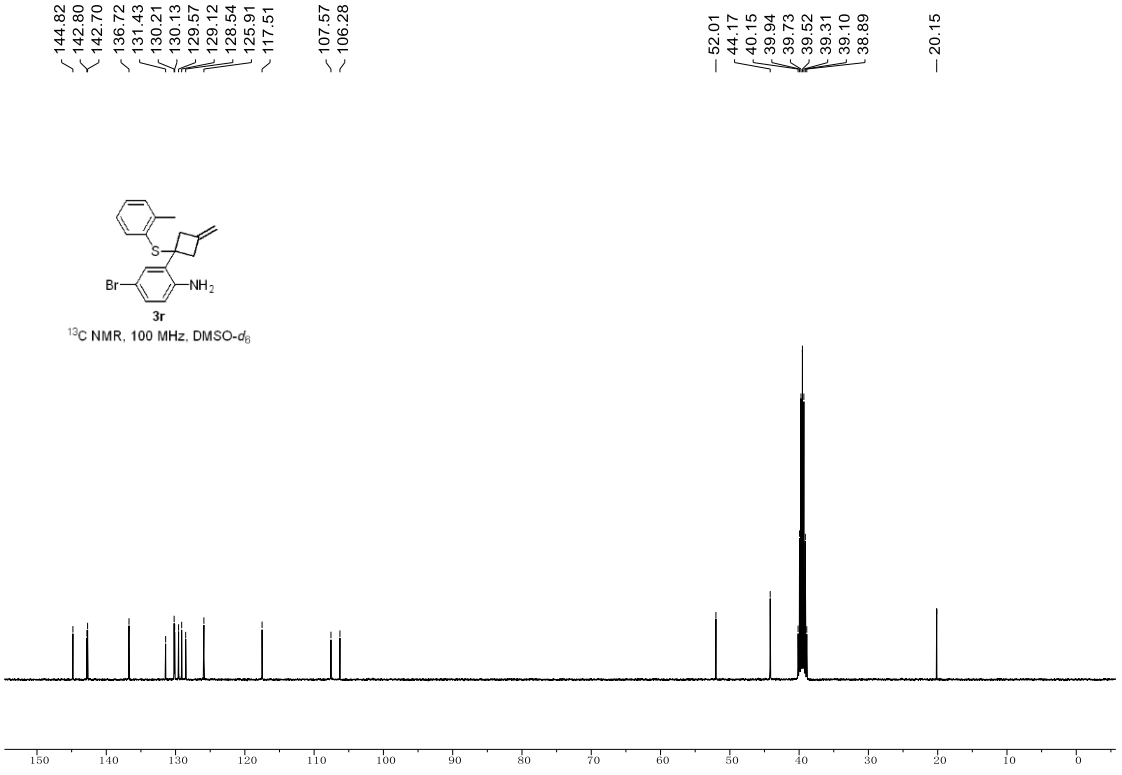
^{1}H NMR, 400 MHz, DMSO-d_6

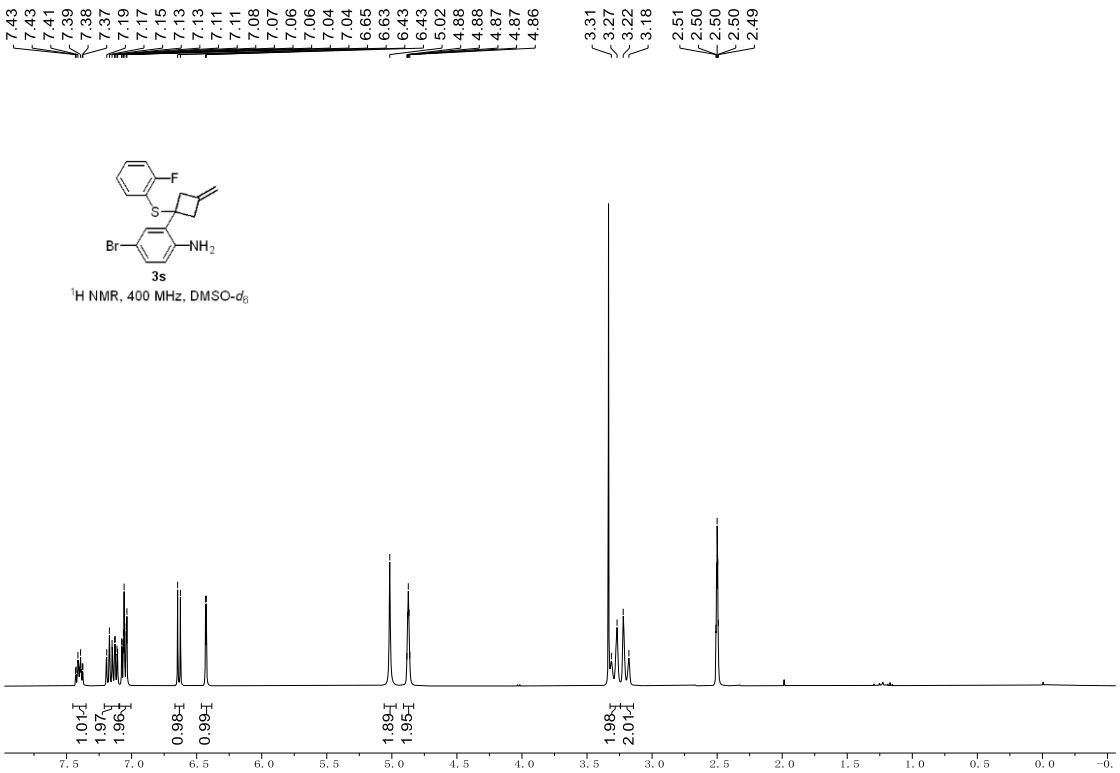


3q

^{13}C NMR, 100 MHz, DMSO-d_6


7.23
7.23
7.21
7.21
7.18
7.12
7.08
7.07
7.05
7.05
6.84
6.62
6.32
6.31
4.99
4.93
4.92
4.92
4.91
4.91
3.23
3.19
3.16
3.12
2.51
2.50
2.50
2.50
2.49
2.05
Br
NH2
3r
1H NMR, 400 MHz, DMSO-d6
1.00
1.02
3.09
1.01
1.00
1.91
2.05
2.02
2.00
2.95


144.82
142.80
142.70
136.72
131.43
130.21
130.13
129.57
129.12
128.54
125.91
117.51
107.57
106.28
52.01
44.17
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.15
Br
NH2
3r
13C NMR, 100 MHz, DMSO-d6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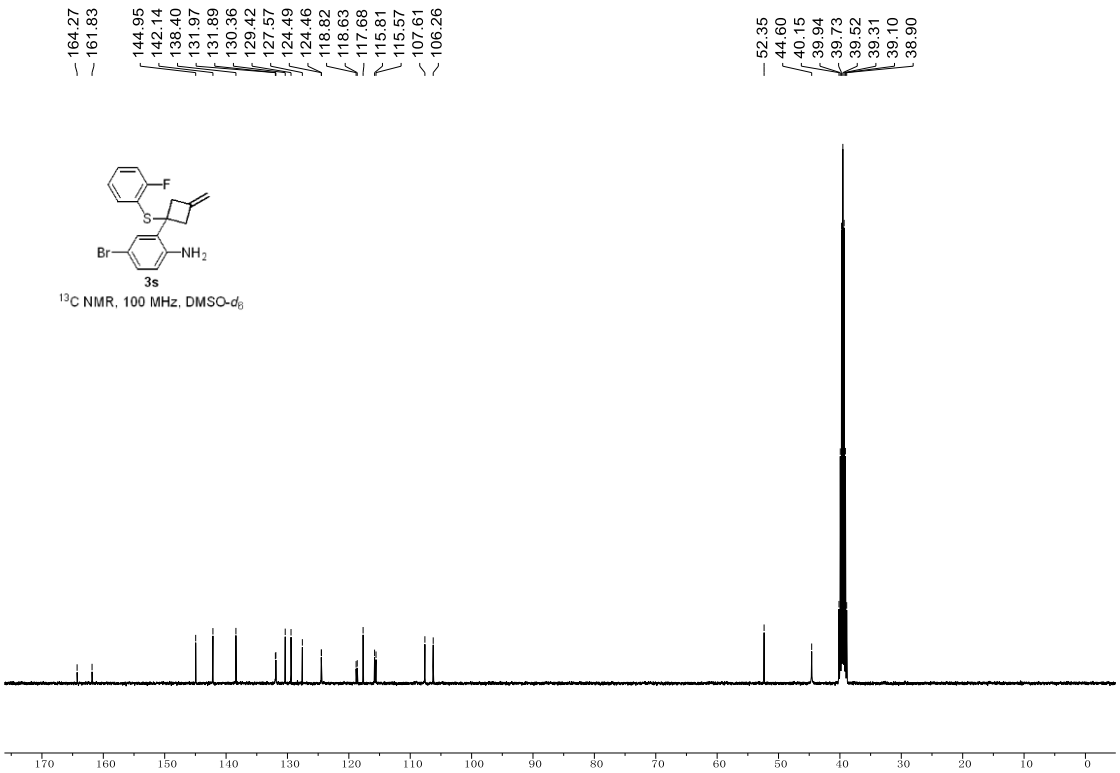
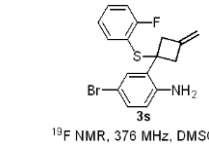
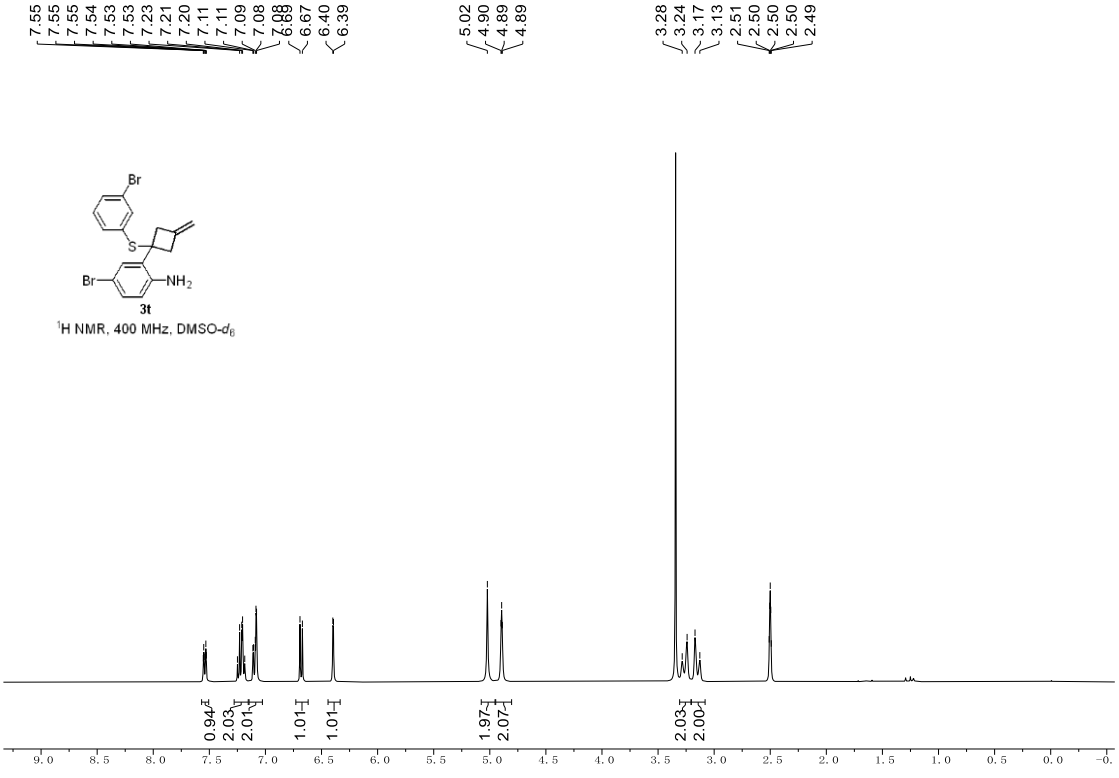
7.43
7.41
7.39
7.38
7.37
7.19
7.17
7.15
7.13
7.13
7.11
7.11
7.08
7.07
7.06
7.06
7.04
7.04
6.65
6.63
6.43
6.43
5.02
4.88
4.88
4.87
4.87
4.86
3.31
3.27
3.22
3.18
2.51
2.50
2.50
2.50
2.49
F
S
Br
NH2
3s
1H NMR, 400 MHz, DMSO-d6
1.01
1.97
1.96
0.98
0.99
1.89
1.95
1.98
2.01


164.27
161.83
144.95
142.14
138.40
131.97
131.89
130.36
129.42
127.57
124.49
124.46
118.82
118.63
117.68
115.81
115.57
107.61
106.26
52.35
44.60
40.15
39.94
39.73
39.52
39.31
39.10
38.90
F
S
Br
NH2
3s
13C NMR, 100 MHz, DMSO-d6



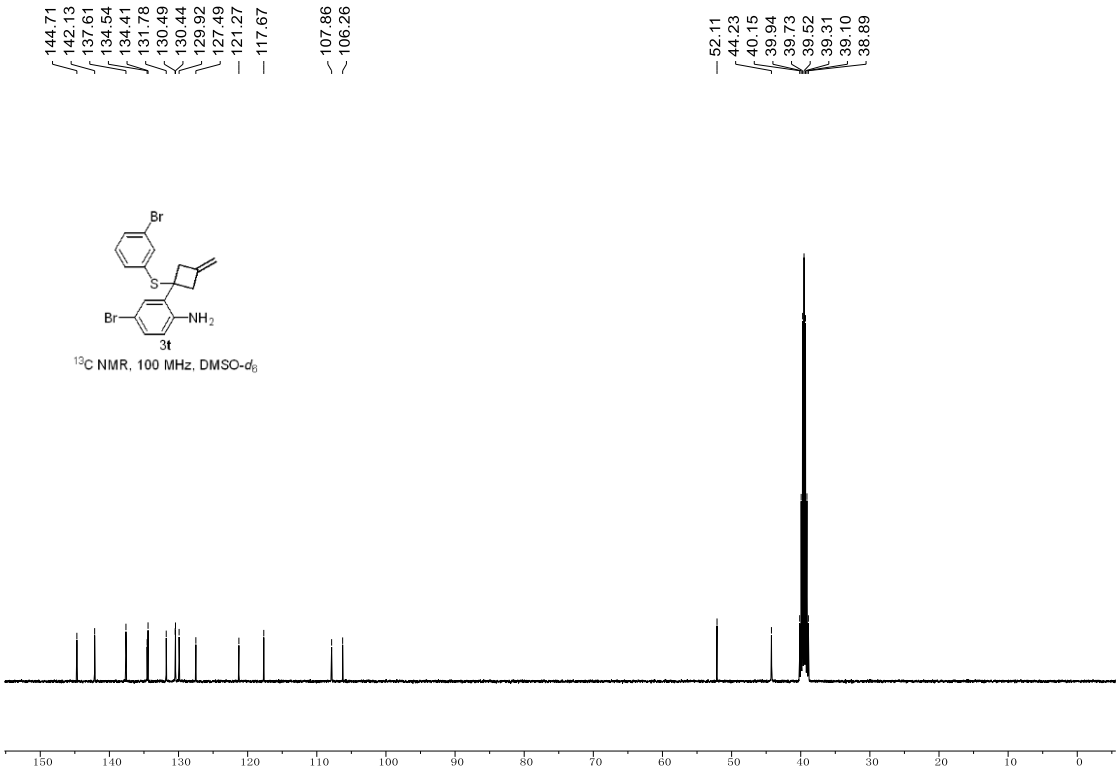
3s

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



3t

^{1}H NMR, 400 MHz, DMSO-d_6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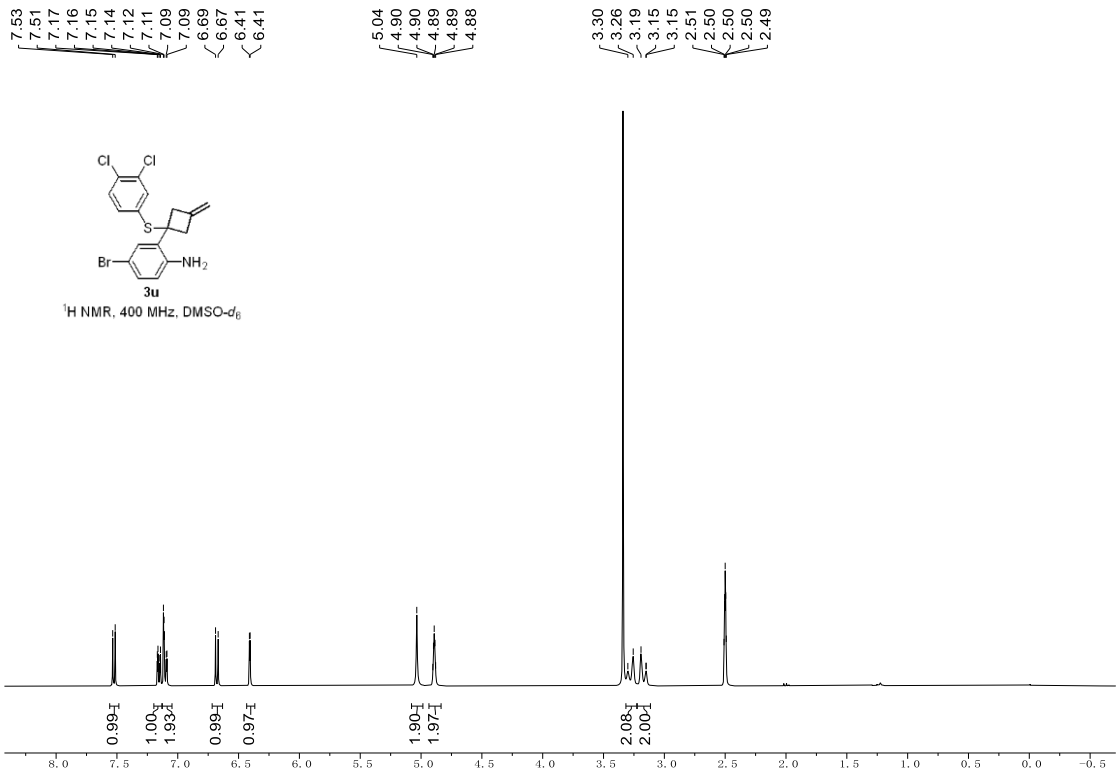
137.61
134.54
134.41
131.78
130.49
130.44
129.92
127.49
121.27
117.67
107.86
106.26
52.11
44.23
40.15
39.94
39.73
39.52
39.31
39.10
38.89
Br
S
Br
NH2
3t
13C NMR, 100 MHz, DMSO-d6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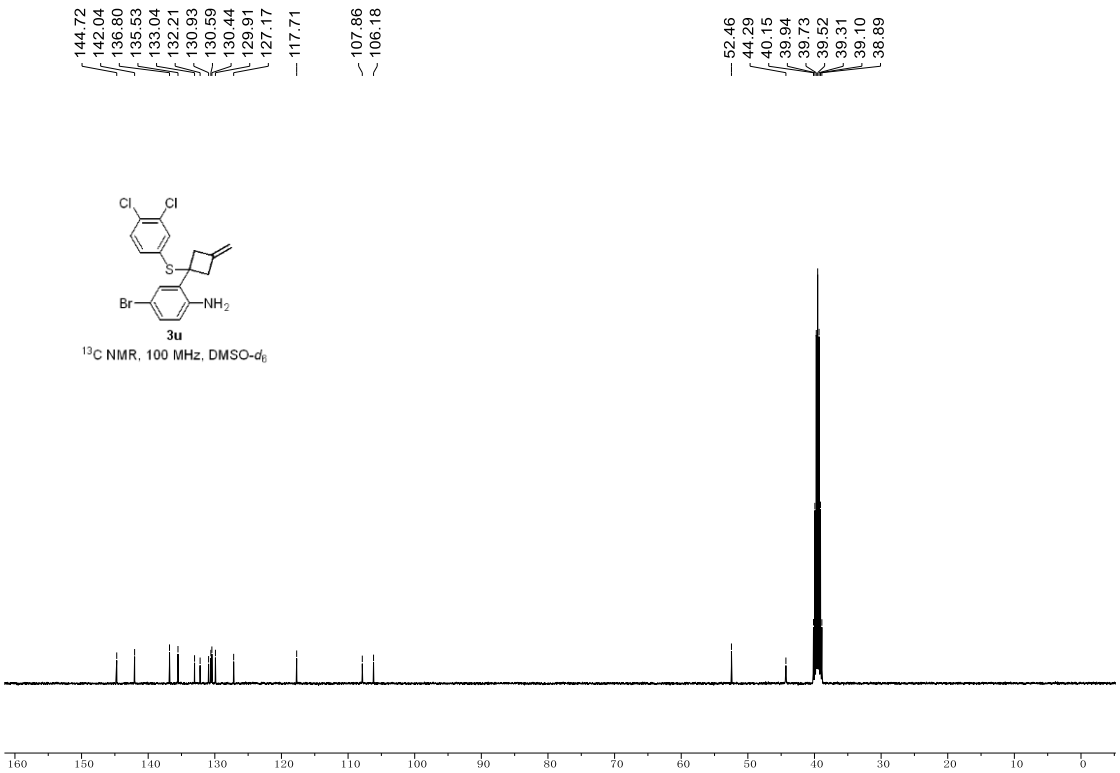
7.51
7.17
7.16
7.15
7.14
7.12
7.11
7.09
7.09
6.69
6.67
6.41
6.41
5.04
4.90
4.90
4.89
4.89
4.88
3.30
3.26
3.19
3.15
3.15
2.51
2.50
2.50
2.50
2.49
Cl
Cl
S
Br
NH2
3u
1H NMR, 400 MHz, DMSO-d6
0.99
1.00
1.93
0.99
0.97
1.90
1.97
2.08
2.00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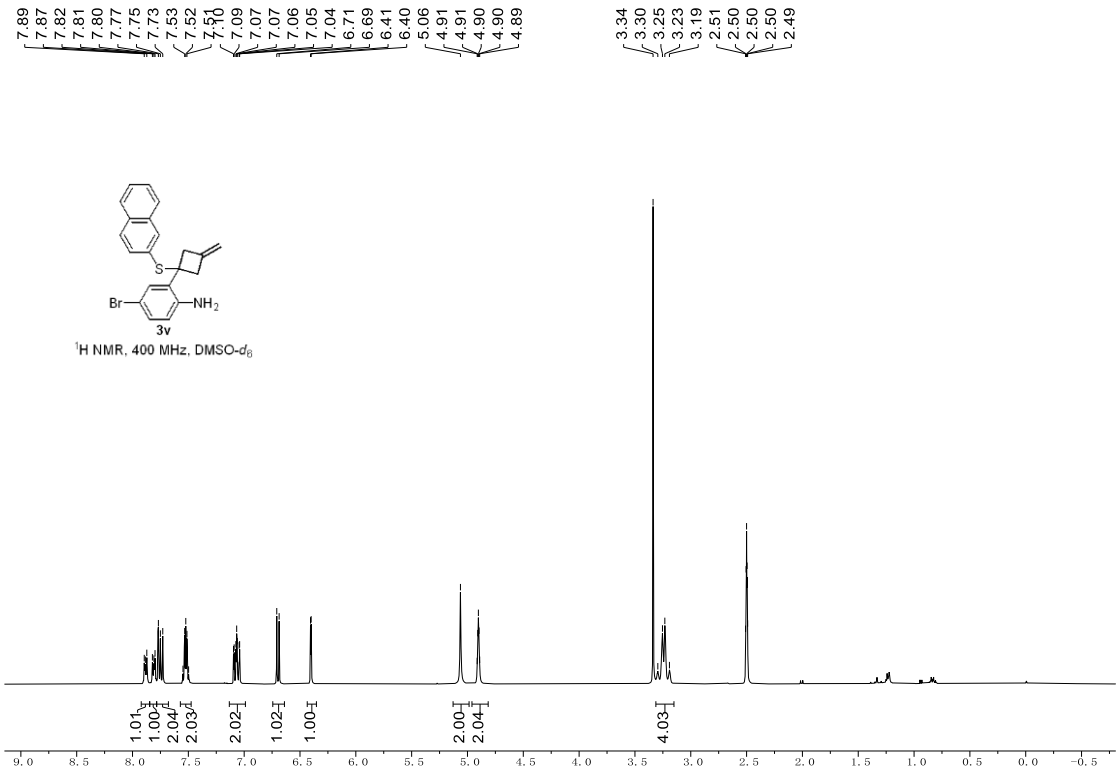
135.53
133.04
132.21
130.93
130.59
130.44
129.91
127.17
117.71
107.86
106.18
52.46
44.29
40.15
39.94
39.73
39.52
39.31
39.10
38.89
Cl
Cl
S
Br
NH2
3u
13C NMR, 100 MHz, DMSO-d6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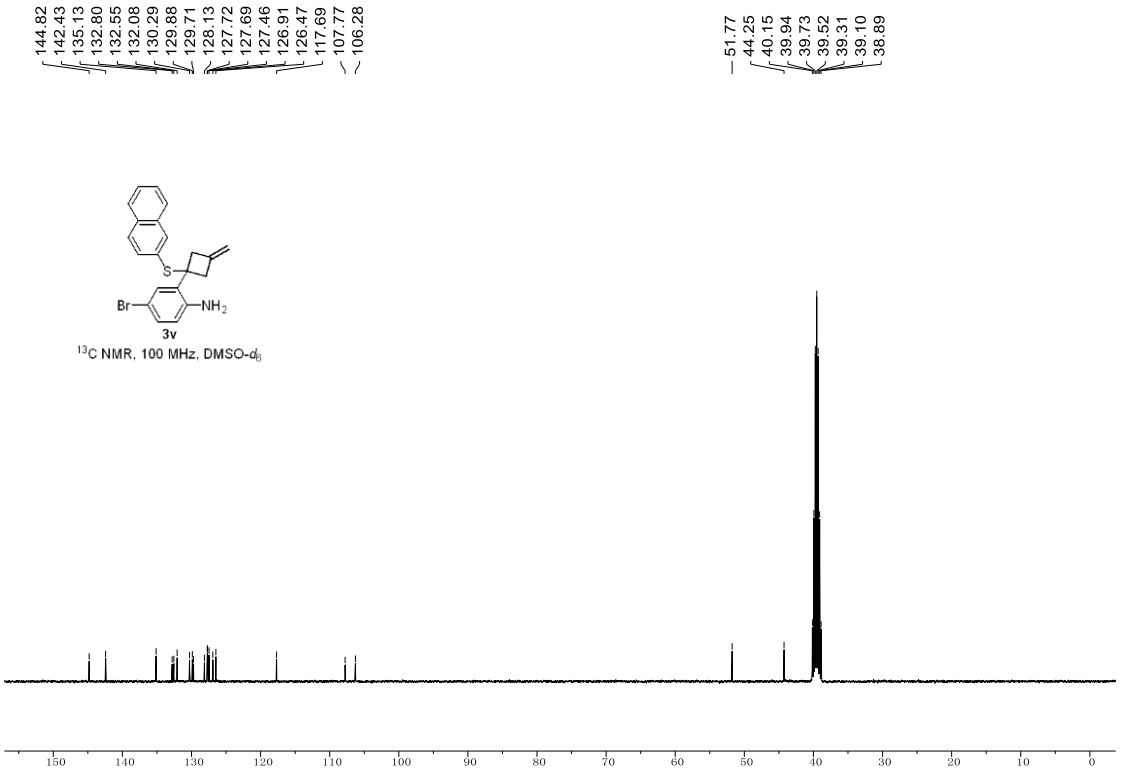
7.77
7.75
7.73
7.53
7.52
7.51
7.10
7.09
7.07
7.07
7.06
7.05
7.04
6.71
6.69
6.41
6.40
5.06
4.91
4.91
4.90
4.90
4.89
3.34
3.30
3.25
3.23
3.19
2.51
2.50
2.50
2.50
2.49
S
Br
NH2
3v
1H NMR, 400 MHz, DMSO-d6
1.01
1.00
2.04
2.03
2.02
1.02
1.00
2.00
2.04
4.03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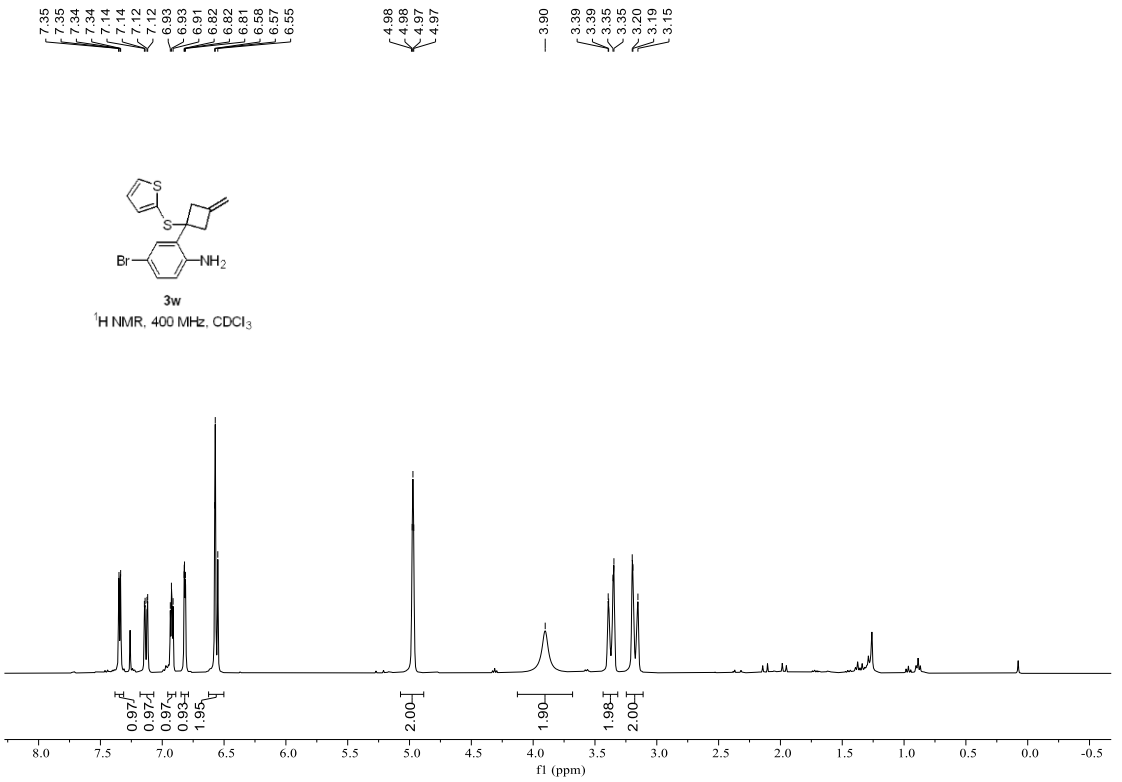
142.43
135.13
132.80
132.55
132.08
130.29
129.88
129.71
128.13
127.72
127.69
127.46
126.91
126.47
117.69
107.77
106.28
51.77
44.25
40.15
39.94
39.73
39.52
39.31
39.10
38.89
Br
NH2
3v
13C NMR, 100 MHz, DMSO-d6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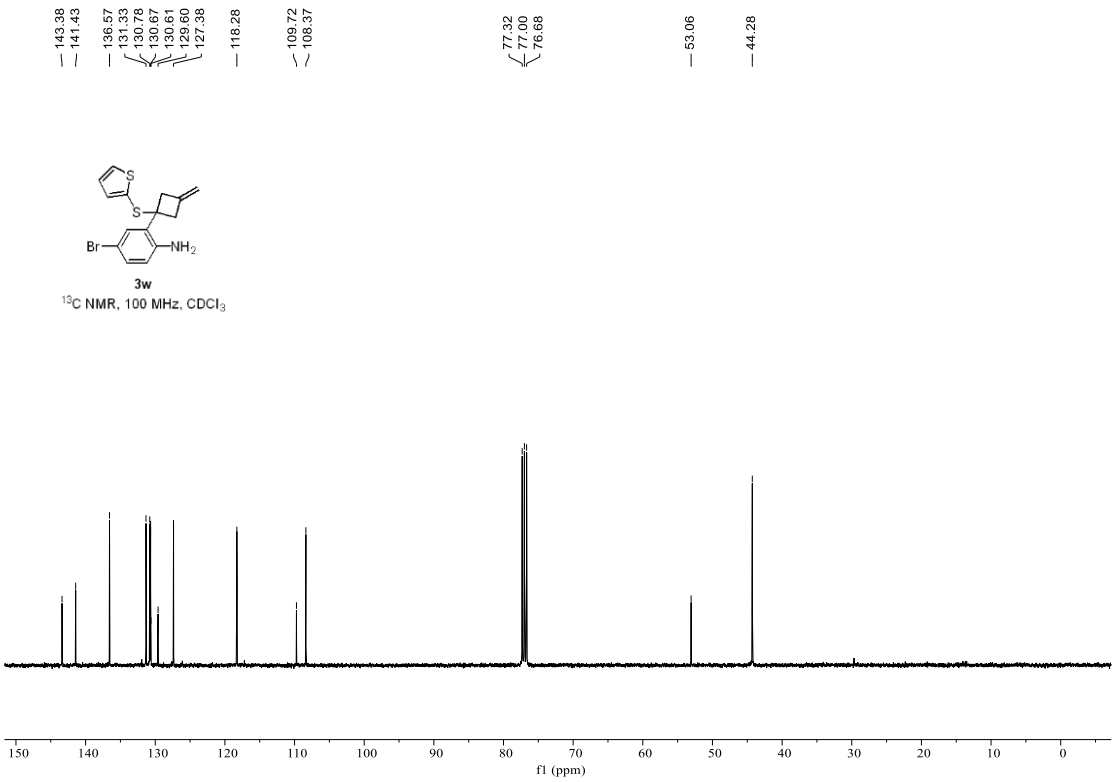
7.35
7.34
7.34
7.14
7.14
7.12
7.12
6.93
6.93
6.91
6.91
6.82
6.82
6.81
6.58
6.57
6.55
4.98
4.98
4.97
4.97
3.90
3.39
3.39
3.35
3.35
3.20
3.19
3.15
Br
NH2
3w
1H NMR, 400 MHz, CDCl3
0.97
0.97
0.97
0.93
1.95
2.00
1.90
1.98
2.00
f1 (ppm)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136.57
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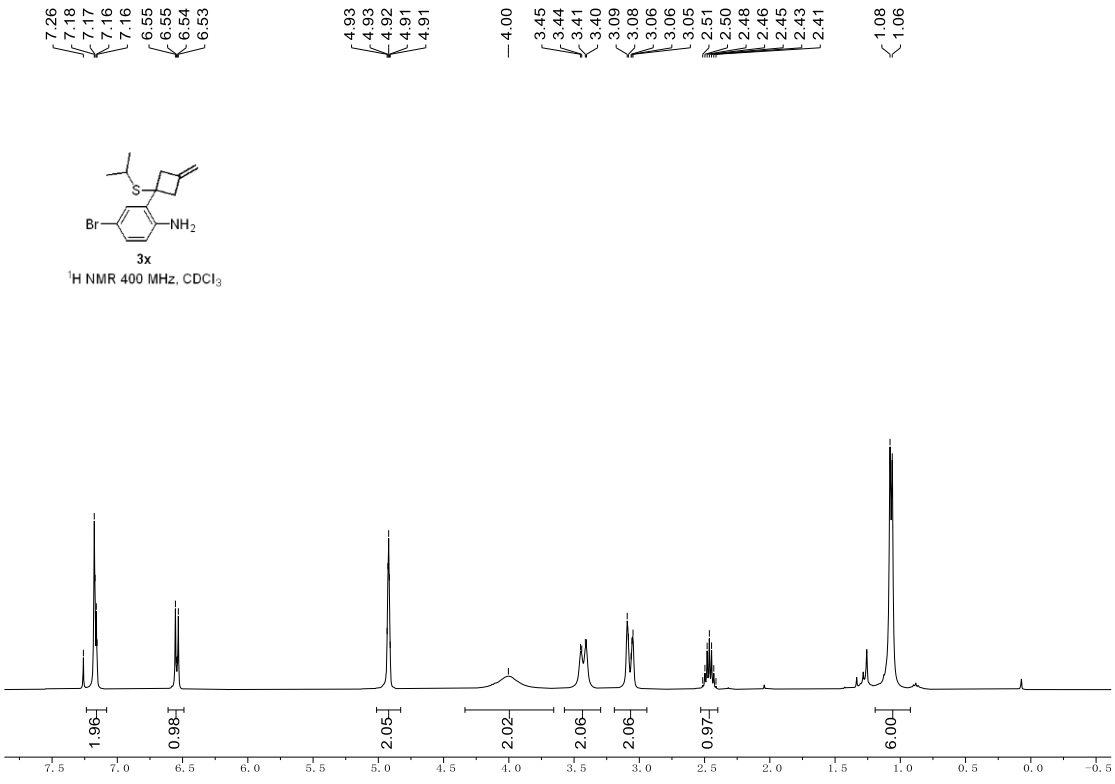
130.78
130.67
130.61
129.60
127.38
118.28
109.72
108.37
77.32
77.00
76.68
53.06
44.28
Br
NH2
3w
13C NMR, 100 MHz, CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.18
7.17
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7.16
6.55
6.55
6.54
6.53
4.93
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4.92
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4.91
4.00
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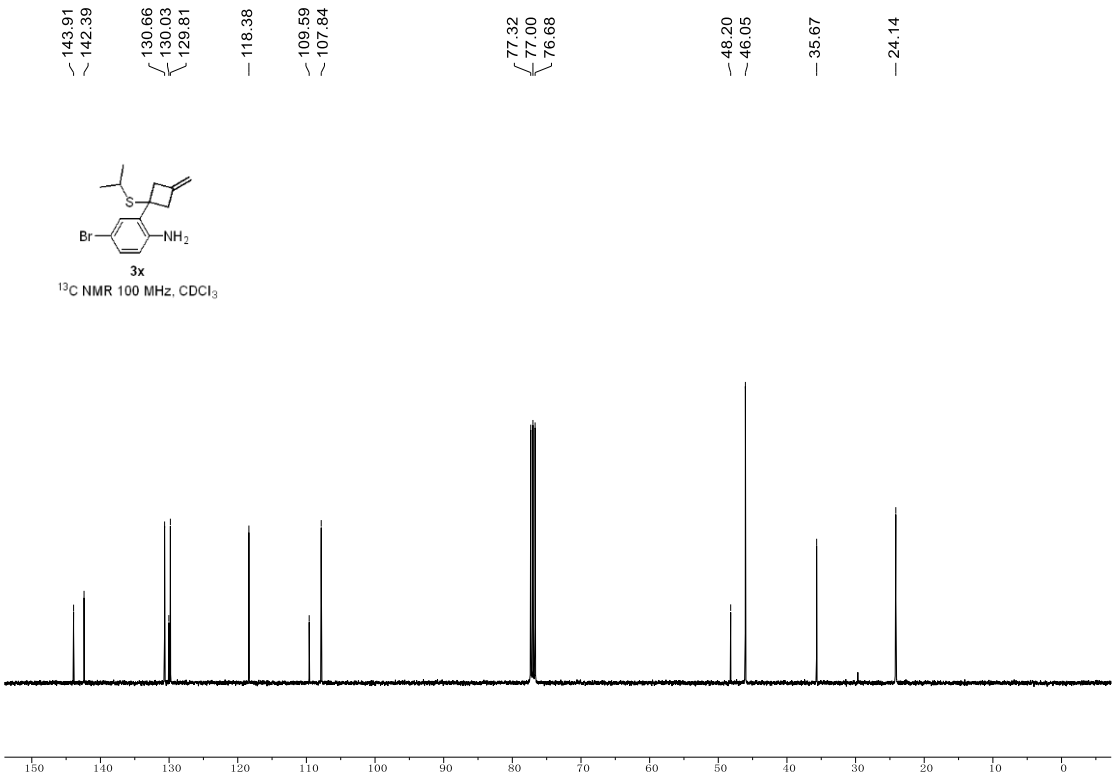
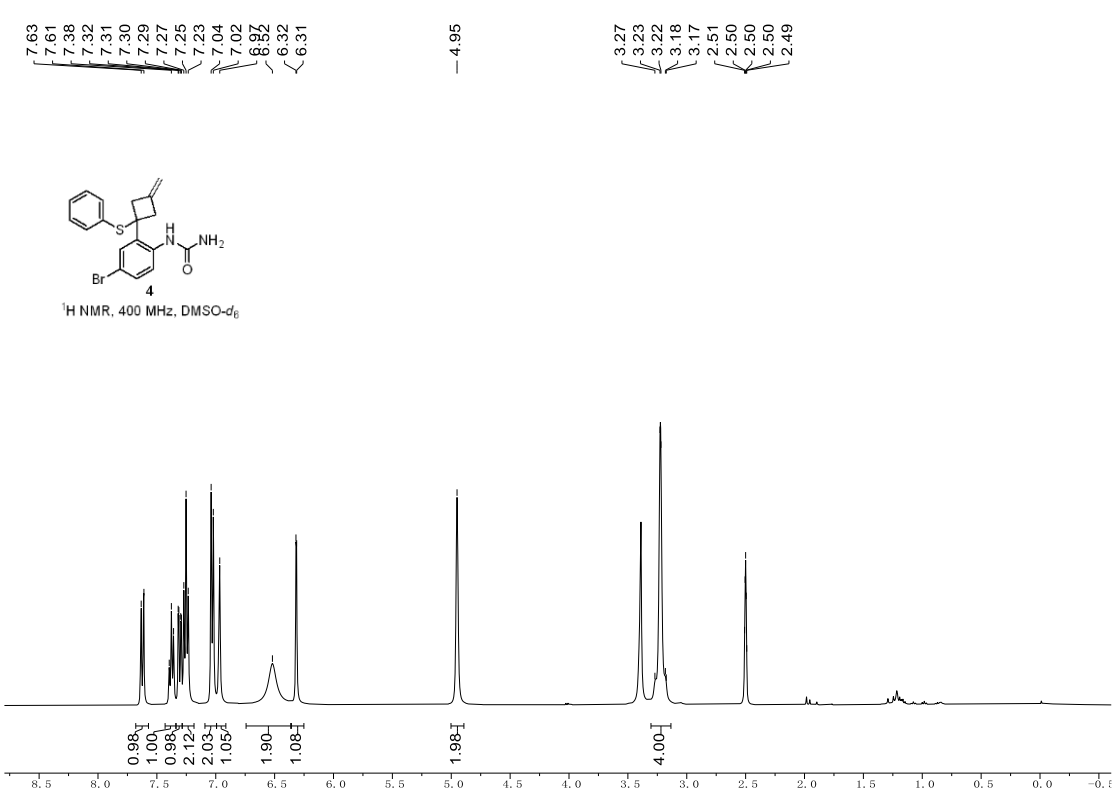
3.05
2.51
2.50
2.48
2.46
2.45
2.43
2.41
1.08
1.06
Br
NH2
3x
1H NMR 400 MHz, CDCl3
1.96
0.98
2.05
2.02
2.06
2.06
0.97
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5


143.91
142.39
130.66
130.03
129.81
118.38
109.59
107.84
77.32
77.00
76.68
48.20
46.05
35.67
24.14
Br
NH2
3x
13C NMR 100 MHz, CDCl3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7.61
7.38
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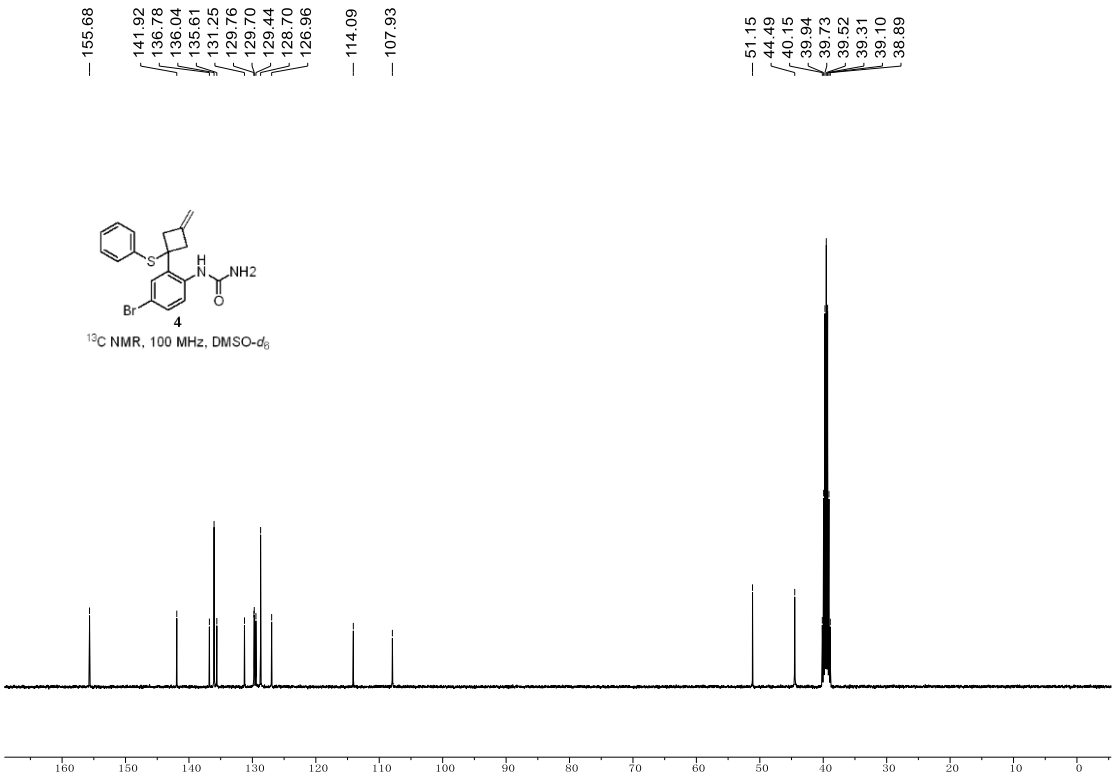
7.31
7.30
7.29
7.27
7.25
7.23
7.04
7.02
6.32
6.31
4.95
3.27
3.23
3.22
3.18
3.17
2.51
2.50
2.50
2.50
2.49
Br
NH2
4
1H NMR, 400 MHz, DMSO-d6
0.98
1.00
0.96
2.12
2.03
1.05
1.90
1.08
1.98
4.00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136.78
136.04
135.61
131.25
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129.70
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128.70
126.96
114.09
107.93
51.15
44.49
40.15
39.94
39.73
39.52
39.31
39.10
38.89
S
N
H
NH2
O
Br
4
13C NMR, 100 MHz, DMSO-d6
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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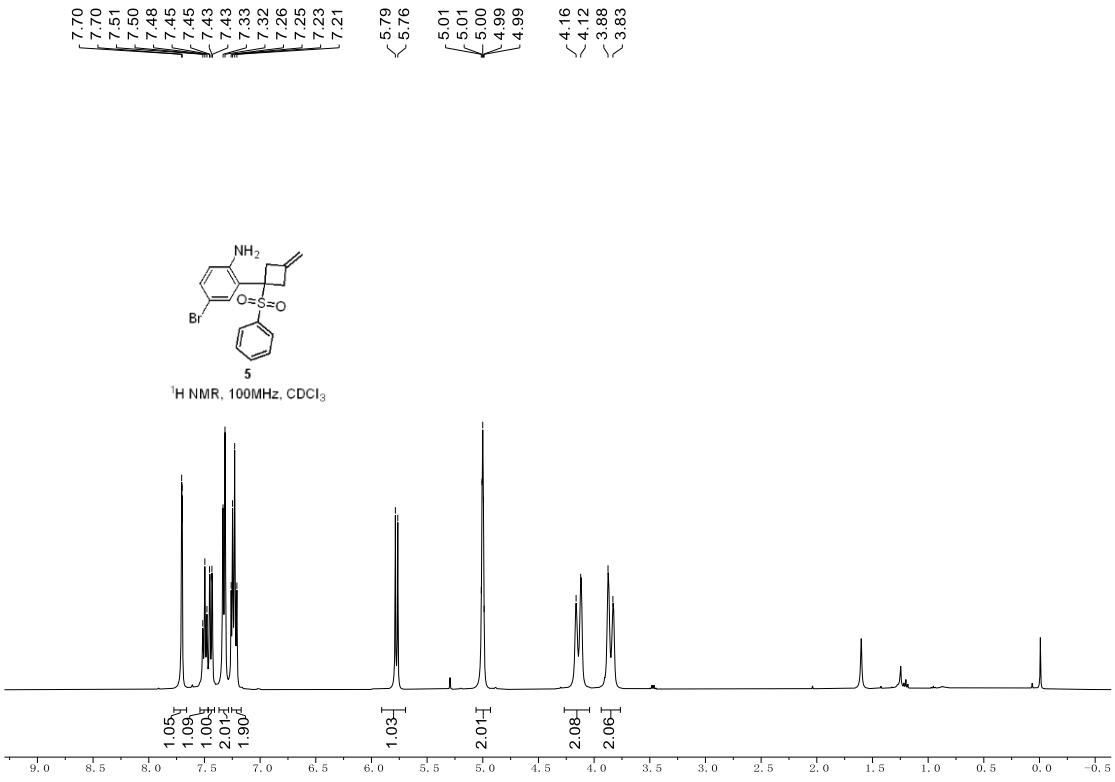
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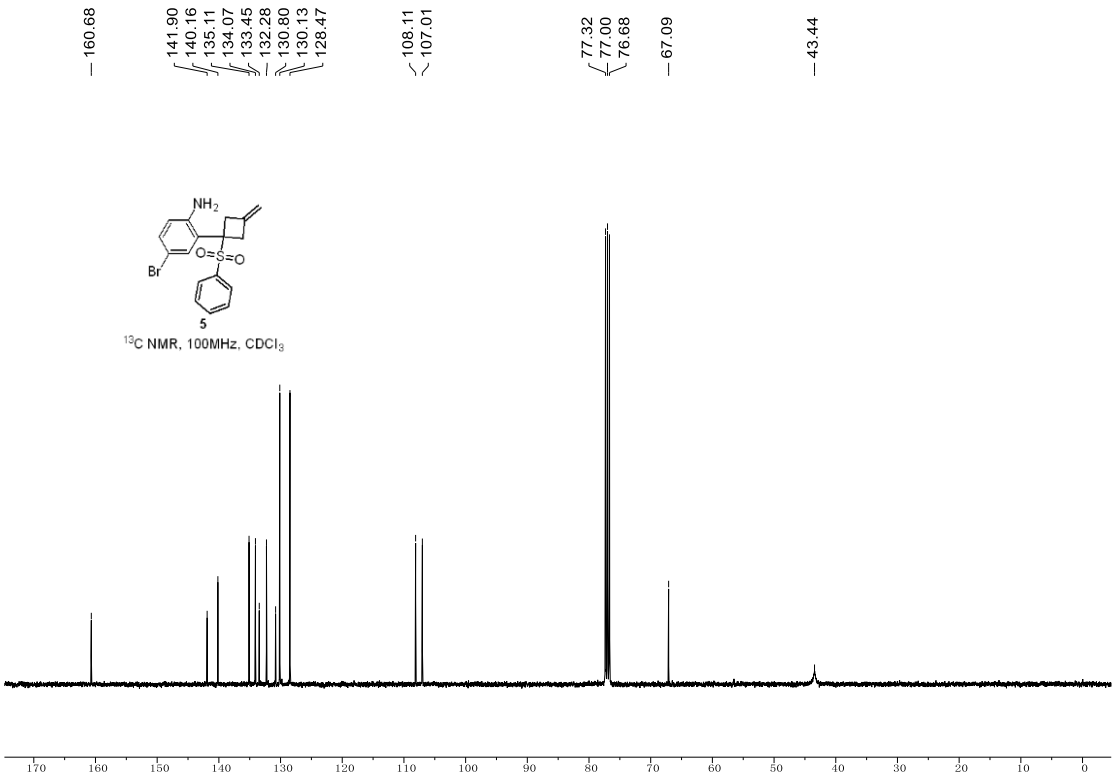
7.70
7.51
7.50
7.48
7.45
7.45
7.43
7.43
7.33
7.32
7.26
7.25
7.23
7.21
5.79
5.76
5.01
5.01
5.00
4.99
4.99
4.16
4.12
3.88
3.83
NH2
O
S
O
Br
5
1H NMR, 100MHz, CDCl3
1.05
1.09
1.00
2.01
1.90
1.03
2.01
2.08
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5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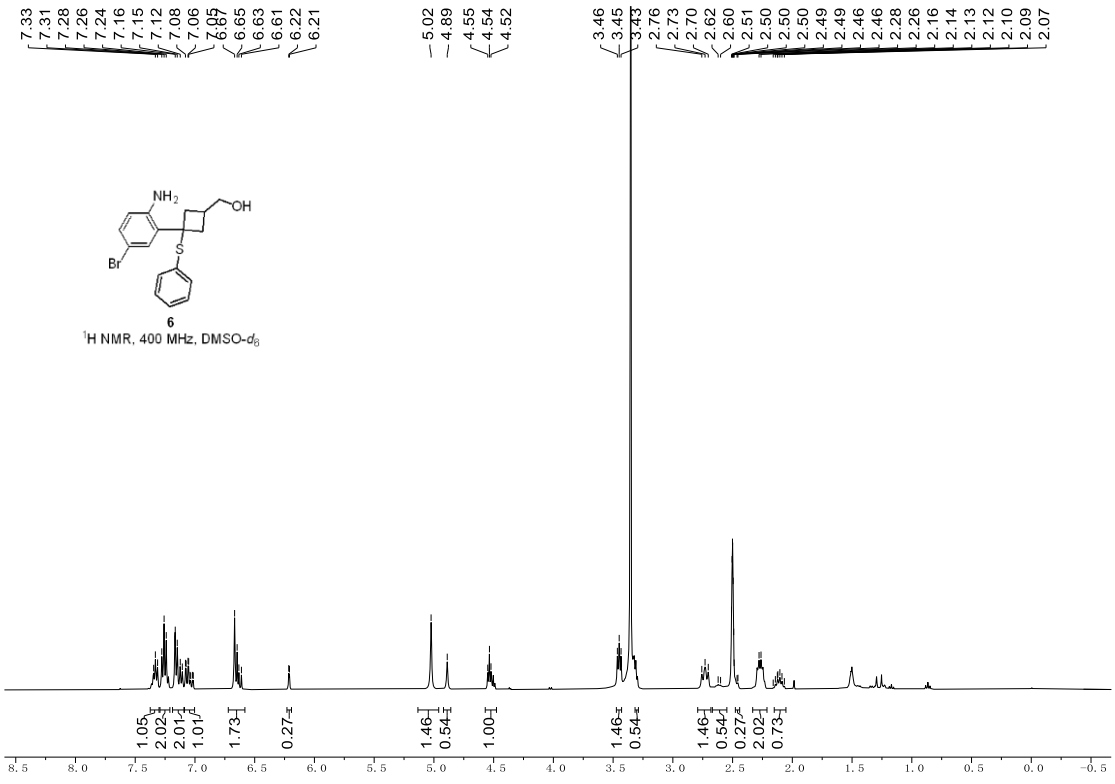
141.90
140.16
135.11
134.07
133.45
132.28
130.80
130.13
128.47
108.11
107.01
77.32
77.00
76.68
67.09
43.44
NH2
Br
O=S=O
5
13C NMR, 100MHz, CDCl3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7.16
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7.12
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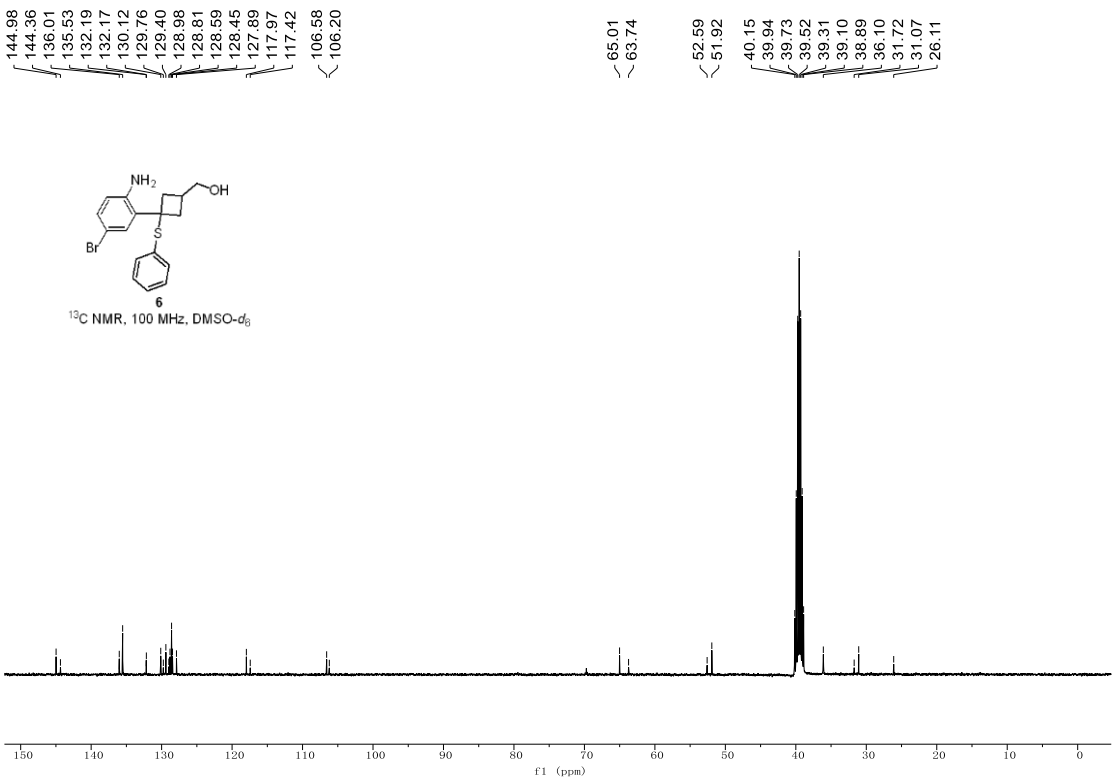
7.06
6.65
6.63
6.61
6.22
6.21
5.02
4.89
4.55
4.54
4.52
3.46
3.45
3.43
2.76
2.73
2.70
2.62
2.60
2.51
2.50
2.49
2.46
2.28
2.26
2.16
2.14
2.13
2.12
2.10
2.09
2.07
NH2
OH
Br
S
6
1H NMR, 400 MHz, DMSO-d6
1.05
2.02
2.01
1.01
1.73
0.27
1.46
0.54
1.00
1.46
0.54
1.46
0.54
0.27
2.02
0.73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144.36
136.01
135.53
132.19
132.17
130.12
129.76
129.40
128.98
128.81
128.59
128.45
127.89
117.97
117.42
106.58
106.20
65.01
63.74
52.59
51.92
40.15
39.94
39.73
39.52
39.31
39.10
38.89
36.10
31.72
31.07
26.11
NH2
OH
Br
S
6
13C NMR, 100 MHz, DMSO-d6
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

11. Calculational details

All computations were conducted using Density Functional Theory (DFT) with the Gaussian 09 software package.[8] Geometry optimizations for all intermediates and transition states were carried out at the ωb97xd-D3(BJ) level of theory. All calculations were performed in the gas phase using basis set of def2svp[9]. Vibrational frequency calculations were carried out at the same level to confirm the nature of each stationary point (either a local minimum or a transition state) and to obtain thermal corrections for free energy calculations. To improve energetic accuracy, solvation single-point energies were refined using the ωb97xd-D3(BJ)-def2tzvp level of theory in solvent of toluene with IEFPCM[10] continuous solvent model. In order to compensate for the overestimation of the entropic, a correction factor which consists on 1/2 of the entropy correction was applied.[11] The calculated 3D optimized structures are displayed utilizing CYLview visualization program.[12]

Table S1. The calculated energies of stationary points (in Hartree/Particle).

Structure	E_{ele}	H_{corr}	G_{corr}	H_{sol}	0.5TS	G_{sol}
1a	-3490.464376	0.205368	0.147666	-3490.259008	0.028851	-3490.287859
2a	-194.014397	0.098809	0.067676	-193.915588	0.015567	-193.931155
TS1A	-3684.436599	0.302439	0.229772	-3684.134160	0.036334	-3684.170493
INT1A	-3684.485318	0.304885	0.236590	-3684.180433	0.034148	-3684.214581
TS2A	-3684.479608	0.302430	0.233676	-3684.177178	0.034377	-3684.211555
INT2A	-3684.528102	0.304730	0.239771	-3684.223372	0.032480	-3684.255852
TXT	-973.648175	0.185608	0.136784	-973.462567	0.024412	-973.486979
TS3A-TXT	-4658.153006	0.487884	0.395709	-4657.665122	0.046088	-4657.711209
INT3A-TXT	-4658.239942	0.495670	0.404608	-4657.744272	0.045531	-4657.789803
TS4A-TXT	-4658.182144	0.490339	0.398525	-4657.691805	0.045907	-4657.737712
TS3B	-3684.452442	0.299268	0.231607	-3684.153174	0.033831	-3684.187005
3a	-3684.587891	0.306458	0.239160	-3684.281433	0.033649	-3684.315082

Note: E_{ele} (electronic energies in solvent), H_{corr} (the thermal correction to enthalpy in gas), G_{corr} (the thermal correction to Gibbs free energy in gas), H_{sol} (sum of electronic and thermal enthalpies in solvent), 0.5TS (half the gas phase entropy), and G_{sol} (sum of electronic and thermal free energies

in solvent).

Cartesian coordinates (unit: angstrom)

1a

C	-0.14676200	1.21896800	0.27658600
C	-0.40485800	0.34019800	-0.78301600
C	-1.65967800	-0.24497100	-0.92324700
C	-2.66908100	0.03321000	-0.00464500
C	-2.42489900	0.90263100	1.05694500
C	-1.17294600	1.49110800	1.19419000
H	0.38430800	0.11445100	-1.50174100
H	-1.84746700	-0.92849000	-1.75282200
H	-3.21260500	1.12587600	1.77813800
H	-0.99053100	2.17748700	2.02511100
Br	-4.37295300	-0.76931800	-0.19687300
N	1.10102700	1.81680300	0.45860300
H	1.23440900	2.36176200	1.30110700
S	2.39195000	1.73429400	-0.60480800
C	3.22874500	0.22458000	-0.14647800
C	4.39925700	-0.08699900	-0.84741900
C	2.76081000	-0.63383100	0.84918600
C	5.09527100	-1.25525100	-0.54847000
H	4.76894500	0.58544600	-1.62659000
C	3.46504800	-1.80218500	1.13910300
H	1.84535000	-0.39277400	1.39214400
C	4.63131800	-2.11815300	0.44501200
H	6.00993400	-1.49172200	-1.09661500
H	3.09210600	-2.47302300	1.91623000
H	5.17714300	-3.03502600	0.67581800

2a

C	0.00025500	-0.00024500	-0.77350000
C	-0.30792700	1.26024600	-0.00006200
H	0.44748500	2.05110300	-0.00018800
H	-1.34327800	1.61296700	0.00023600
C	1.24595300	-0.36371800	-0.00008400
H	1.55514800	-1.41281700	-0.00028400
H	2.06869900	0.35680600	-0.00007400
C	-0.93851000	-0.89631000	-0.00007400
H	-2.00082800	-0.63659700	-0.00030900
H	-0.72824500	-1.96963400	0.00026700
C	0.00039900	-0.00027800	0.77377900

TS1A

C	0.86301700	-0.56736300	-0.64507700
C	1.54808200	-1.57586400	0.05406300
C	2.89545500	-1.43767000	0.36449000
C	3.58246900	-0.28729500	-0.02108200
C	2.91789900	0.72124600	-0.71388300
C	1.56727200	0.58506200	-1.02093100
H	1.01343900	-2.48090400	0.35166300
H	3.41338800	-2.23135300	0.90571100
H	3.45203100	1.62455200	-1.01308500
H	1.04880600	1.38183100	-1.55693900
Br	5.41995300	-0.09600000	0.39984700
S	-1.46884400	0.32548900	-1.74177600
C	-1.99753100	1.47822700	-0.48623300
C	-2.94696300	2.43762400	-0.85595700
C	-1.52647900	1.43460200	0.82716800
C	-3.42328200	3.34427000	0.08809700

H	-3.31936300	2.47383200	-1.88377800
C	-2.00740900	2.34878900	1.76374800
H	-0.78978300	0.68341600	1.11612500
C	-2.95677100	3.30345000	1.40241100
H	-4.16579100	4.08877100	-0.20750300
H	-1.63048000	2.31177600	2.78844200
H	-3.32923800	4.01635100	2.14064400
C	-4.28659400	-2.39270200	-0.86189400
H	-4.16035700	-3.36080700	-1.35982600
H	-4.90638200	-1.69207400	-1.44336800
C	-4.46521600	-3.31900600	1.49985200
H	-4.30795100	-3.11435600	2.56202500
H	-4.57679900	-4.36193300	1.19193100
C	-3.97842700	-0.94434400	0.73310900
H	-4.57779600	-0.17324900	0.22271600
H	-3.56851000	-0.58779700	1.68459200
C	-3.09347200	-1.76037400	-0.18296000
C	-4.58719000	-2.31384400	0.60979400
H	-1.02432000	-1.49737600	-0.46604100
N	-0.48527200	-0.75105200	-0.92683200

INT1A

C	0.03304800	-0.32745900	1.78603000
C	-1.05578000	0.56275500	1.85103600
C	-2.24337000	0.31285300	1.16961500
C	-2.35416100	-0.83728800	0.39361000
C	-1.30423600	-1.75905300	0.33601400
C	-0.12797200	-1.50415700	1.02578800
H	-0.95943600	1.48246400	2.43432200
H	-3.06492700	1.02892900	1.21493500

H	-1.41017700	-2.67154100	-0.25304700
H	0.69627600	-2.21673900	0.97592900
Br	-3.94333800	-1.16207000	-0.58433300
N	1.28237800	-0.01912400	2.31024400
H	1.17944900	0.68106400	3.04690300
C	2.91604400	-0.11837800	0.00861800
C	3.21940500	0.08078000	-1.33971200
C	3.29833400	-1.29248900	0.65933000
C	3.87565300	-0.92225900	-2.04999700
H	2.94801500	1.01765000	-1.82751500
C	3.96162500	-2.28434000	-0.06047200
H	3.04479300	-1.42007000	1.71176600
C	4.24471300	-2.10630600	-1.41398500
H	4.10197200	-0.77129500	-3.10738300
H	4.25521100	-3.20707300	0.44430200
H	4.75961400	-2.89028400	-1.97327400
S	2.15287900	1.22498000	0.92447500
C	1.11464500	1.92339500	-0.11293200
C	0.40600800	3.26514900	0.03611900
C	0.16504300	1.44161500	-1.20434500
H	0.98326700	4.13128400	-0.33381100
H	-0.00122200	3.52132900	1.02798200
H	0.61527400	1.37841300	-2.21099900
H	-0.39300300	0.50995700	-1.02067500
C	-0.61438100	2.72527600	-0.95909000
C	-1.79457800	3.16342500	-1.38070200
H	-2.40017200	2.57275900	-2.07303500
H	-2.20103200	4.11869200	-1.03759200

TS2A

C	-0.72208700	2.41206100	-0.34440800
C	-2.15088800	0.40563300	-1.01271400
C	-2.69303200	0.40458900	0.22692300
C	-2.26372200	1.34424300	1.24695700
C	-1.33162600	2.28672800	0.98205100
H	-2.49830000	-0.29761500	-1.77083300
H	-2.72658600	1.28438000	2.23412700
H	-1.04600900	3.01061200	1.75036400
Br	-4.04912500	-0.83109100	0.68539900
C	0.37091100	-0.97270800	0.10387800
C	0.54663900	-1.07490600	-2.06969700
H	-0.37241200	-0.66776400	0.85769900
H	1.27761700	-1.32378200	0.62461200
H	-0.03772200	-0.85550400	-2.97642900
H	1.53478100	-1.46003600	-2.37594500
C	-0.08848900	-1.92560600	-0.98417400
C	-0.86985300	-2.99914100	-0.99285000
H	-1.12983600	-3.50190300	-1.92806700
H	-1.28379400	-3.40447600	-0.06620500
C	-1.03660600	1.28219900	-1.31006200
H	-0.83944000	1.52538900	-2.35774100
C	0.68962600	0.01943300	-1.00816100
S	2.08080100	1.22436700	-0.97929500
C	3.23887800	0.28948300	0.01022200
C	4.11599200	-0.61805500	-0.59344900
C	3.28843800	0.47995600	1.39541400
C	5.01844400	-1.34223500	0.18421300
H	4.08690700	-0.75143700	-1.67703000
C	4.19233400	-0.24507500	2.16995200
H	2.60633300	1.19559500	1.85917400

C	5.05637100	-1.15849100	1.56611700
H	5.69799700	-2.05159300	-0.29312600
H	4.22363100	-0.09368800	3.25115500
H	5.76302600	-1.72712400	2.17433300
N	0.09834000	3.30489200	-0.72622300
H	0.31401700	3.95435500	0.03595200

INT2A

C	0.88669600	1.97710200	-0.83697000
C	1.52275000	-0.27824300	0.04238900
C	2.71766600	-0.14930200	-0.55117900
C	2.98585100	0.91607900	-1.51570200
C	2.10187200	1.91781200	-1.67358600
H	1.34899400	-1.08643900	0.75300900
H	3.92680300	0.89959800	-2.06920000
H	2.31761200	2.75652900	-2.34099500
Br	4.13555500	-1.34473700	-0.17286400
C	-1.06551000	-0.54912700	1.47685700
C	-0.31230800	1.41544200	2.01573900
H	-0.75064000	-1.50855200	1.03869600
H	-2.13394800	-0.63020200	1.72412900
H	0.62368500	1.98996400	1.98923000
H	-1.10390400	2.04886200	2.44231800
C	-0.26921400	0.03136700	2.62426100
C	0.35116100	-0.50108600	3.67166300
H	0.93913600	0.11713900	4.35496800
H	0.29358800	-1.57314200	3.87868500
C	0.37782200	0.63079300	-0.34477600
H	-0.05915100	0.15626900	-1.24992600
C	-0.76731800	0.75336200	0.67858800

S	-2.24418000	1.53910000	-0.11430800
C	-3.24826300	0.10749600	-0.46967600
C	-2.89053300	-0.79715600	-1.47720800
C	-4.43929200	-0.09842000	0.23637900
C	-3.68874100	-1.90638500	-1.74719300
H	-1.98372300	-0.62429200	-2.06059000
C	-5.24999200	-1.19632300	-0.05131000
H	-4.72201400	0.60935700	1.01860700
C	-4.87212900	-2.10715700	-1.03639600
H	-3.39273000	-2.61010100	-2.52827500
H	-6.17924100	-1.34364600	0.50350000
H	-5.50326300	-2.97105900	-1.25579200
N	0.28382200	3.04997600	-0.51462000
H	0.71135100	3.86256600	-0.96813200

TXT

C	-3.79366600	-0.62174900	0.00013000
C	-2.64075100	-1.39003600	0.00007500
C	-1.37829800	-0.77233200	-0.00002700
C	-1.28476800	0.62833400	-0.00005000
C	-2.47002800	1.38496000	0.00001400
C	-3.71236500	0.77633000	0.00010100
C	1.28476800	0.62833400	-0.00004100
C	1.37829800	-0.77233200	-0.00002500
C	2.64075100	-1.39003600	0.00005600
H	2.70805400	-2.48063000	0.00007000
C	3.79366600	-0.62174900	0.00012000
C	3.71236500	0.77633000	0.00011400
C	2.47002800	1.38496000	0.00002800
H	-4.76764400	-1.11564900	0.00021100

H	-2.70805400	-2.48063000	0.00011300
H	-2.36420600	2.47107500	-0.00001300
H	-4.62171300	1.38003500	0.00014900
H	4.76764400	-1.11564900	0.00019100
H	4.62171400	1.38003500	0.00016800
H	2.36420600	2.47107500	0.00000900
C	0.00000000	1.38248900	-0.00014400
O	0.00000000	2.59893700	-0.00008700
S	0.00000000	-1.85388600	-0.00014400

TS3A-TXT

C	-0.90621900	0.57189700	1.17842200
C	0.08236300	2.52607500	-0.02753200
C	-1.04409400	3.25508800	0.20049800
C	-2.12365600	2.70232900	0.95407500
C	-2.05013900	1.42609300	1.42065300
H	0.92551600	2.96403600	-0.56660800
H	-3.00941700	3.31042900	1.14770900
H	-2.86819300	0.98722800	1.99425900
Br	-1.20019100	5.02671600	-0.44944700
C	2.59860200	1.64060900	1.30218400
C	2.00684500	-0.41410400	1.62727700
H	2.02328600	2.30074800	1.97218100
H	3.27511100	2.25689500	0.69287500
H	1.25639400	-0.44889600	2.43163400
H	2.20841500	-1.43927000	1.28305800
C	3.17730200	0.45267000	2.03278000
C	4.31993300	0.22181100	2.66708400
H	4.55464300	-0.76807400	3.06623600
H	5.06573200	1.01047600	2.79375600

C	0.19291700	1.14928400	0.39850600
C	1.63975600	0.65840200	0.55327500
S	2.24104300	0.25170800	-1.15757800
C	3.93998400	-0.21139500	-0.88848900
C	4.95830400	0.74366800	-0.96930500
C	4.26517000	-1.54440600	-0.61343500
C	6.28014300	0.38001100	-0.72264900
H	4.70623100	1.77669400	-1.21745300
C	5.58719800	-1.90583300	-0.36652000
H	3.47156500	-2.29408300	-0.58319700
C	6.59421600	-0.94207900	-0.40979400
H	7.06905100	1.13327600	-0.77509900
H	5.83207000	-2.94600900	-0.14082300
H	7.63054400	-1.22450400	-0.21195800
C	0.09593300	-5.12243200	-0.31521200
C	-1.15896700	-4.86657400	0.21863200
C	-1.75179900	-3.60552800	0.05668100
C	-1.07030700	-2.59856200	-0.64749000
C	0.19655000	-2.87962900	-1.18749900
C	0.77736800	-4.12735900	-1.02476700
C	-3.04154500	-0.97453300	-0.58580000
C	-3.87499200	-1.85713000	0.12502200
C	-5.21741800	-1.52463600	0.34387900
H	-5.86004300	-2.21039300	0.90072800
C	-5.73238500	-0.33300700	-0.15185400
C	-4.91899000	0.54005100	-0.87802700
C	-3.58588100	0.21946700	-1.08643300
H	0.54533200	-6.10885200	-0.18272500
H	-1.69319300	-5.64701100	0.76544200
H	0.71494700	-2.07888400	-1.71775900

H	1.75950100	-4.33240000	-1.45538800
H	-6.78274000	-0.08999000	0.02194600
H	-5.32630000	1.47071800	-1.27680500
H	-2.92904000	0.88542000	-1.64726900
C	-1.61415400	-1.23913600	-0.79515300
S	-3.31505500	-3.36824500	0.80762200
N	-1.04289200	-0.70607100	1.45334100
H	-0.17969700	-1.21436500	1.26319700
O	-0.90481800	-0.36415000	-1.39571000
H	-0.39226700	0.44535400	-0.68979300

INT3A-TXT

C	0.74072800	0.34759900	-0.25770200
C	2.95232300	-0.28499800	0.51300100
C	3.51946400	0.77934300	-0.17397700
C	2.70928500	1.62888400	-0.92147900
C	1.34152100	1.40206000	-0.96849500
H	3.59629800	-0.96398600	1.07483500
H	3.14271900	2.45935400	-1.48065800
H	0.72625200	2.04109800	-1.59529400
Br	5.39073800	1.06239700	-0.10420600
C	1.74965200	-2.08554300	2.59746800
C	-0.29430400	-1.70678100	1.99005900
H	2.17541600	-1.18065400	3.05949500
H	2.51230900	-2.87930200	2.59876200
H	-0.58010100	-0.67467900	2.24816700
H	-1.15608000	-2.20575900	1.51934300
C	0.37803600	-2.41051600	3.14330900
C	-0.05804800	-3.13151300	4.16855600
H	-1.12697500	-3.28162600	4.33995300

H	0.63899700	-3.60043900	4.86771800
C	1.57345300	-0.51710300	0.49610200
C	1.07150100	-1.73548000	1.23462900
S	1.25956600	-3.26932600	0.20268000
C	0.32147700	-2.82907100	-1.24468900
C	-1.02663700	-3.19422900	-1.35251800
C	0.93037500	-2.11414500	-2.28250600
C	-1.76341300	-2.82924600	-2.47725000
H	-1.49255500	-3.76569200	-0.54685600
C	0.18941200	-1.74512500	-3.40422700
H	1.98248700	-1.83729200	-2.19486500
C	-1.15801600	-2.09991900	-3.50191700
H	-2.81527500	-3.11135600	-2.55170900
H	0.66899500	-1.18331200	-4.20880300
H	-1.73467500	-1.81675800	-4.38583900
C	-5.23813200	-1.03602800	0.46878600
C	-4.45984300	-0.31673500	1.37100700
C	-3.33521100	0.38164300	0.92140800
C	-2.97479700	0.34130100	-0.43359200
C	-3.79540100	-0.33696600	-1.33330500
C	-4.91899600	-1.02943100	-0.88875900
C	-1.59404900	2.40284000	-0.33940800
C	-1.84404900	2.63395300	1.01909100
C	-1.70075500	3.91593600	1.55891000
H	-1.90109800	4.08037300	2.61985900
C	-1.33840400	4.97835400	0.73841400
C	-1.15757100	4.76989100	-0.62857900
C	-1.29394900	3.49160000	-1.16052500
H	-6.11637400	-1.57780900	0.82579000
H	-4.73627900	-0.27191100	2.42679200

H	-3.53326600	-0.31908400	-2.39151400
H	-5.54768800	-1.56473000	-1.60319300
H	-1.22555300	5.97702200	1.16520600
H	-0.90517000	5.60601200	-1.28368300
H	-1.15038100	3.31205500	-2.22628100
C	-1.65239100	0.97401900	-0.88261600
S	-2.40785400	1.33898500	2.08673400
N	-0.62724500	0.12953600	-0.31108900
H	-0.94761200	-0.79459300	-0.06351900
O	-1.55351400	1.03644200	-2.28187700
H	-1.19837400	0.18878700	-2.57965400

TS4A-TXT

C	-0.68301600	0.10638300	0.53505200
C	-2.61218000	-0.73959900	-0.63382500
C	-3.40219000	0.24764000	-0.06069400
C	-2.85062300	1.16557000	0.82984200
C	-1.49933100	1.07550900	1.12890100
H	-3.06985100	-1.46873200	-1.30400600
H	-3.46906100	1.93322500	1.29587000
H	-1.06276200	1.76660400	1.84840600
Br	-5.24399100	0.33120000	-0.48069600
C	-0.89377700	-2.40098000	-2.43661100
C	0.96235600	-1.75153000	-1.53744200
H	-1.34960500	-1.55560300	-2.97639400
H	-1.54136900	-3.28502700	-2.53970800
H	1.10791400	-0.69198300	-1.78988700
H	1.81832700	-2.09991000	-0.94001900
C	0.57609700	-2.54433300	-2.76058000
C	1.26065500	-3.19908500	-3.68937300

H	2.35361000	-3.19788800	-3.68760700
H	0.75278500	-3.76054000	-4.47752300
C	-1.24184000	-0.82844600	-0.35926700
C	-0.48101200	-1.97261000	-0.99256600
S	-0.62149500	-3.51123500	0.03306800
C	0.18956900	-2.98656100	1.52723400
C	1.57793200	-3.12089600	1.66375200
C	-0.55261100	-2.39666000	2.55656500
C	2.22106700	-2.61545200	2.79163600
H	2.14824800	-3.61538100	0.87440400
C	0.09444300	-1.90146000	3.68704000
H	-1.63454100	-2.30041800	2.44659800
C	1.48126600	-1.99632600	3.79890900
H	3.30544600	-2.70148700	2.88359800
H	-0.48640400	-1.42364700	4.47863200
H	1.98843300	-1.58047100	4.67104600
C	4.74247600	0.08506200	-1.95906200
C	3.61485400	0.78709300	-2.37506600
C	2.67403400	1.21368800	-1.43248700
C	2.86220000	0.93406500	-0.07293200
C	4.01299100	0.25670000	0.33302800
C	4.94836500	-0.17431900	-0.60292900
C	1.15008400	2.61543300	0.68384500
C	0.78555300	3.00218500	-0.61026100
C	0.07911000	4.19211000	-0.81679200
H	-0.20290900	4.48648200	-1.83016700
C	-0.23492300	5.00648100	0.26598100
C	0.17980800	4.65673000	1.55319600
C	0.87265800	3.46832200	1.75441400
H	5.47330400	-0.24658100	-2.69963000

H	3.46164200	1.00884100	-3.43358900
H	4.13150500	0.07944400	1.40376400
H	5.84227000	-0.71000900	-0.27695600
H	-0.78288100	5.93619300	0.09860400
H	-0.04061300	5.31317200	2.39742400
H	1.20667500	3.14317500	2.74191300
C	1.82122100	1.29083500	0.97010100
S	1.20998700	2.02082800	-2.01798600
N	0.68783500	0.06793700	0.92260500
H	1.16596800	-0.75102600	0.55077700
O	2.14277600	1.05461500	2.23847600
H	1.11921700	0.21028500	2.04378200

TS3B

C	0.09141400	2.34187600	-0.72671200
C	-1.56563500	1.97139600	0.63422900
H	1.02423600	2.53007000	-0.16968000
H	0.30701600	2.39390900	-1.80504400
H	-1.25259700	2.05761100	1.68568700
H	-2.63749400	1.72887900	0.61679000
C	-1.07722500	3.13977400	-0.19522600
C	-1.55505400	4.35296200	-0.44465600
H	-2.47447900	4.70832400	0.02792700
H	-1.04572100	5.03000100	-1.13528600
S	-1.47640400	0.30291500	-1.63813100
C	-2.62503000	-0.78386300	-0.82296400
C	-2.22671400	-2.06021800	-0.40596200
C	-3.94479700	-0.36966900	-0.60769800
C	-3.13163700	-2.89891900	0.24202400
H	-1.20290300	-2.38912400	-0.59163300

C	-4.84904800	-1.21414700	0.03454700
H	-4.25685100	0.61815900	-0.95409300
C	-4.44193900	-2.47659600	0.46463800
H	-2.81169600	-3.89044500	0.56947900
H	-5.87721300	-0.88404800	0.19817900
H	-5.15034800	-3.13660500	0.97004400
C	0.56449200	0.21798000	1.95480300
C	1.37419600	-0.44547400	-0.25769800
C	1.87324100	0.60007600	2.38286100
C	2.63668600	-0.35880900	0.25824100
H	1.21057400	-0.74628700	-1.29596800
C	2.89017400	0.23995700	1.53910700
H	2.06864000	1.00920800	3.37577800
H	3.92826500	0.38169300	1.84845300
Br	4.13593000	-0.92003900	-0.76067000
C	0.25585700	0.01185700	0.53234100
H	-0.79869100	-0.56531800	1.32553400
C	-0.61403600	1.05604200	-0.18809300
N	-0.48956500	-0.21397300	2.60442000
H	-0.66854600	0.06113300	3.57375400

3a

C	-3.60342100	1.42439000	-0.09936100
C	-2.59332200	2.37370100	-0.01554000
C	-1.24419000	2.00373100	0.10468500
C	-0.92330100	0.62723200	0.18268400
C	-1.94464200	-0.31713500	0.06339300
C	-3.27290200	0.07236300	-0.07457000
H	-4.64379200	1.73749600	-0.19874800
H	-2.85104700	3.43509700	-0.05770700

H	-1.70044000	-1.38015300	0.08346500
Br	-4.62933600	-1.24109600	-0.22744600
N	-0.25247100	2.96759200	0.19068100
H	0.62523400	2.70565900	-0.25027600
H	-0.54501900	3.90041200	-0.07169800
C	0.50765900	0.18392400	0.37836100
C	1.30503800	0.81435200	1.56652300
C	0.76946600	-1.21551700	1.00880600
H	0.61441700	1.22628800	2.31944100
H	2.06206200	1.57648300	1.33687700
H	-0.10384900	-1.56870700	1.57978400
H	1.10227300	-2.01934700	0.33715900
C	1.79888700	-0.57181000	1.90999400
C	2.82547500	-1.03569400	2.61213400
H	3.03748000	-2.10660300	2.66458300
H	3.49506400	-0.35924700	3.14929700
S	1.30677300	0.40964600	-1.28760000
C	3.00517900	-0.03779600	-0.97801600
C	3.93645500	0.92253200	-0.56885600
C	3.41907600	-1.36122100	-1.16529200
C	5.25325200	0.55407300	-0.30284600
H	3.62334100	1.96261800	-0.45683500
C	4.73652300	-1.72741300	-0.90032400
H	2.69895600	-2.10242400	-1.51780600
C	5.65217700	-0.77293700	-0.45916700
H	5.97240000	1.30770100	0.02483800
H	5.04961600	-2.76412200	-1.04121300
H	6.68455600	-1.06090900	-0.24937300

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