Silver Salt Enabled H/D Exchange at β Position of Thiophene Rings: Synthesis of Fully Deuterated Thiophene Derivatives

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Supporting Information

General: General: NMR spectra were recorded at 23 ºC on a Varian VNMRS 300 MHz NMR spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts were determined relative to residual $CHCl_3$ (7.26 ppm) for proton, and to the $CDCl_3$ "triplet" at 77.23 ppm for carbon. GC-MS experiments were carried out using an Agilent GC/MS instrument consisting of a 6890N series GC and a 5973 Mass Selective Detector System. All yields reported refer to isolated yields unless otherwise indicated. All the reagents and solvents were purchased from commercial sources and used as received. The atom% deuterium incorporation was determined by both of GC-MS and ^1H NMR spectrum. Since the relative intensity was found to depend on the pulse delay, the pulse delay was adjusted to 120s to ensure complete relaxation occurred. The method to determine atom% deuterium incorporation using GC-MS is shown below.

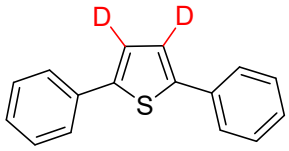
The incorporation of deuterium into each substrate was verified by GC-MS, observing a shift in the isotope distribution in the starting material (M) to show M+1 (d_1), M+2 (d_2), etc. Data processing was performed using the following formula:

Using compound **2aa** as example: isotope distribution (GC-MS): 2% d_0, 13% d_1, 85% d_2.

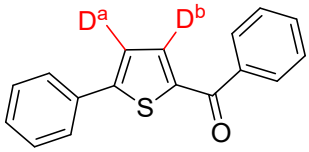
Atom% deuterium incorporation = [(%d_1 x 1) + (%d_2 x 2)] / 2

Atom% deuterium incorporation = [(13% x 1) + (85% x 2)] / 2 = 92%

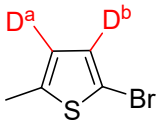
General Procedure for Ag_2CO_3 Catalyzed H/D Exchange: 2,5-diphenylthiophene (236 mg, 1 mmol), Ag_2CO_3 (138 mg, 0.5 mmol), D_2O (800 mg, 40 mmol), MePhos (182 mg, 0.5 mmol) were added to toluene (5 mL) in the air. The reaction was stirred at 100°C for 12 hours. Then the reaction was quenched with saturated NH_4Cl solution. The product was extracted with dichloromethane (3 x 20 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of solvents under vacuum, the crude product was purified via column chromatography.



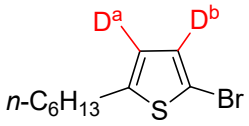
2aa[1]: Isolated yield: 219 mg (92%), white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.65 (m, 4 H), 7.41 (t, J = 7.5 Hz, 4 H), 7.33-7.26 (m, **2.15 residual H**)
HRMS (EI) m/z: calcd for $C_{16}H_{11}D_2S^+$- ([M^+H]-) 239.0863; Found 239.0859.
The level of deuterium incorporation was estimated: From ^{1}H NMR 92% (total: 0.92*2=1.84 D); From GC-MS: 1.84 D.



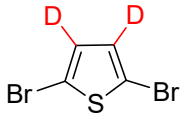
2ab: Isolated yield: 245 mg (92%), white solid.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.87-7.81 (m, 4 H), 7.69 (t, J = 7.4 Hz, 1 H), 7.59 (t, J = 7.5 Hz, **2.07 residual H**), 7.51 -7.42 (m, **3.02 residual H**).
^{13}C NMR (100 MHz, DMSO-d_6): 187.6, 152.5, 141.9, 137.9, 133.1, 133.0, 129.9, 129.3, 129.2, 126.6.
HRMS (EI) m/z: calcd for $C_{17}H_{10}D_2OSNa^+$- ([M^+Na]-) 289.0632; Found 289.0646
The level of deuterium incorporation was estimated: From ^{1}H NMR 93% (D^a) and 98% (D^b), (total: 0.93+0.98=1.91 D); From GC-MS: 1.94 D



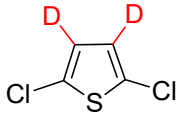
2ac: Isolated yield: 143 mg (80%), green solid.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.00 (s, **0.04 residual H**), 6.67 (s, **0.13 residual H**), 2.39 (s, 3 H).
^{13}C NMR (100 MHz, DMSO-d_6): 141.9, 129.2, 128.6, 126.7, 108.3, 15.9.
HRMS (EI) m/z: calcd for $C_5H_4D_2BrS^+$- ([M^+H]-) 178.9494; Found 178.9474
The level of deuterium incorporation was estimated: From ^{1}H NMR 87% (D^a) and 96% (D^b), (total: 0.96+0.87=1.83D); From GC-MS: 1.80 D



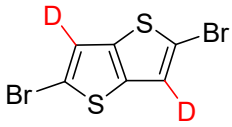
2ad: Isolated yield: 212 mg (87%), white solid.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.01(s, **0.03 residual H**), 6.69 (m, **0.35 residual H**), 2.73 (t, J = 7.6 Hz, 2 H), 1.56-1.54 (m, 2 H), 1.31-1.24 (m, 6 H), 0.87-0.83 (m, 3 H).
^{13}C NMR (100 MHz, $CDCl_3$): 147.8, 147.7, 125.8, 108.1, 31.4, 30.0, 29.9, 28.5, 22.5, 14.4.
HRMS (EI) m/z: calcd for $C_{10}H_{14}D_2BrS^+$- ([M^+H]-) 249.0276; Found 249.0265
The level of deuterium incorporation was estimated: From ^{1}H NMR 65% (D^a) and 97% (D^b) (total: 0.65+0.97=1.62 D); From GC-MS: 1.60 D



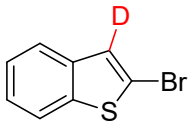
2ae: Isolated yield: 188 mg (78%), white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, **0.07 residual H**).
^{13}C NMR (100 MHz, $CDCl_3$): 130.2 (t, J = 26.6 Hz), 111.5.
HRMS (EI) m/z: calcd for $C_4D_2Br_2S^+$- ([M^+]-) 243.8349; Found 243.8342.
The level of deuterium incorporation was estimated: From ^{1}H NMR 97% (total: 0.97+0.97=1.94 D); From GC-MS: 1.90 D



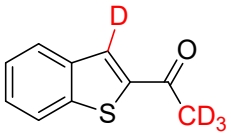
2af: Isolated yield: 108 mg (70%), white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (s, **0.05 residual H**).
^{13}C NMR (100 MHz, $CDCl_3$): 127.2 (t, J = 2.3 Hz), 126.5 (t, J = 26.9 Hz).
HRMS (EI) m/z: calcd for $C_4D_2Cl_2S^+$- ([M^+]-) 153.9380; Found 153.9374.
The level of deuterium incorporation was estimated: From ^{1}H NMR 97% (total: 0.97+0.98=1.95 D); From GC-MS: 1.92 D



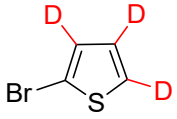
2ag: Isolated yield: 264 mg (88%), yellow solid.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, **0.09 residual H**).
^{13}C NMR (100 MHz, $CDCl_3$): 138.2, 121.8, 121.6 (t, J = 26.8 Hz), 113.6.
HRMS (EI) m/z: calcd for $C_6HD_2BrS_2^+$- ([M^+H]-) 300.8142; Found 300.8148.
The level of deuterium incorporation was estimated: From ^{1}H NMR 96%, (total: 0.96*2=1.92 D); From GC-MS: 1.88 D



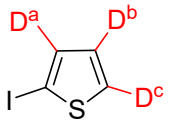
2ah: Isolated yield: 192 mg (90%), yellow solid.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.91-7.89 (m, 1 H), 7.78-7.74 (m, 1 H), 7.60 (s, **0.02 residual H**), 7.37-7.30 (m, 2 H).
^{13}C NMR (100 MHz, DMSO-d_6): 140.7, 139.8, 127.4, 125.6 (t, J = 25.9 Hz), 125.3, 123.5, 122.6, 116.2.
HRMS (EI) m/z: calcd for $C_8H_4DBrS^+$- ([M^+]-) 212.9358; Found 212.9352.
The level of deuterium incorporation was estimated: From ^{1}H NMR 98%, (total: 0.98 D); From GC-MS: 0.95 D



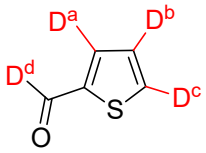
2ai: Isolated yield: 158 mg (88%), yellow solid.
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.35 (s, **0.06 residual H**), 8.04 (t, J = 7.5 Hz, 2 H), 7.56-7.45 (m, 2 H), 2.62 (s, **0.15 residual H**).
^{13}C NMR (100 MHz, DMSO-d_6): 193.3, 143.9, 142.1, 139.7, 131.7 (t, J = 23.3 Hz), 128.2, 126.8, 125.7, 123.8, 27.2.
HRMS (EI) m/z: calcd for $C_{10}H_4D_4OSNa^+$- ([M^+Na]-) 203.0439; Found 203.0426
The level of deuterium incorporation was estimated: From ^{1}H NMR 94%, 95%, 95% and 95%, (total: 0.94+0.95*3=3.79 D); From GC-MS: 3.68 D



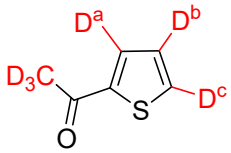
2ba[2]: Isolated yield: 93 mg (56%), colorless oil.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.57 (s, **0.05 residual H**), 7.21 (s, **0.05 residual H**), 6.97 (s, **0.04 residual H**).
HRMS (EI) m/z: calcd for $C_4HD_3BrS^+$- ([M^+H]-) 165.9405; Found 165.9418
The level of deuterium incorporation was estimated: From ^{1}H NMR: 95%, 95% and 96% (total: 0.95*2+0.96=2.86 D); From GC-MS: 2.91 D



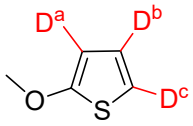
2bb[2]: Isolated yield: 145 mg (68%), colorless oil.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.64 (s, **0.05 residual H**), 7.33 (s, **0.05 residual H**), 6.87 (s, **0.09 residual H**).
HRMS (EI) m/z: calcd for $C_4HD_3IS^+$- ([M^+H]-) 213.9267; Found213.9281
The level of deuterium incorporation was estimated: From ^{1}H NMR: 95% (D^a), 95% (D^b) and 91% (D^c), (total: 0.95+0.95+0.91=2.81 D); From GC-MS: 2.85 D



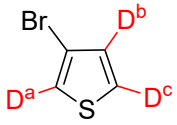
2bc: Isolated yield: 70 mg (60%), colorless oil.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.90 (s, **0.87 residual H**), 8.60 (s, **0.06 residual H**), 7.69 (s, **0.06 residual H**), 7.48 (s, **0.48 residual H**)
^{13}C NMR (100 MHz, DMSO-d_6): 187.0, 143.5, 139.6 (t, J = 29.2 Hz), 129.4 (t, J = 29.1 Hz), 125.4.
HRMS (EI) m/z: calcd for $C_5HD_4OS^+$- ([M^+H]-) 117.0307; Found 117.0304.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 94% (D^a), 52% (D^b), 94% (D^c) and 13% (D^d), (total: 0.94+0.52+0.94+0.13=2.53 D); From GC-MS: 2.49 D



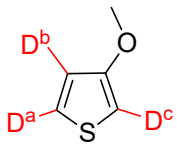
2bd: Isolated yield: 106 mg (80%), colorless oil.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, **0.16 residual H**), 7.64 (d, J = 2.3 Hz, **0.06 residual H**), 7.13 (d, J = 1.6 Hz, **0.35 residual H**), 2.54 (s, **0.15 residual H**).
^{13}C NMR (100 MHz, DMSO-d_6): 191.2, 144.6, 133.9 (t, J = 13.2 Hz), 132.7 (t, J = 14.0 Hz), 128.1 (t, J = 11.0 Hz), 25.3 (t, J = 15.2 Hz).
HRMS (EI) m/z: calcd for $C_6HD_6OS^+$- ([M^+H]-) 133.0589; Found 133.0600.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 84% (D^a), 65% (D^b) and 94% (D^c) and 95% (D), (total: 0.84+0.65+0.94+0.95*3=5.28 D); From GC-MS: 5.60 D



2be: Isolated yield: 80 mg (68%), colorless oil.
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.73 (s, **0.62 residual H**), 6.52 (s, **0.02 residual H**), 6.29 (s, **0.13 residual H**), 3.84 (s, 3 H).
^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 124.6 (t, J = 25.8 Hz), 111.8, 103.6 (t, J = 26.1 Hz), 60.4.
HRMS (EI) m/z: calcd for $C_5H_4D_3OS^+$- ([M^+H]-) 118.0400; Found 118.0387.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 87% (D^a), 38% (D^b) and 98% (D^c), (total: 0.87+0.38+0.98=2.23 D); From GC-MS: 2.40 D

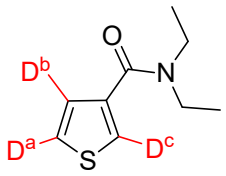


2bf: Isolated yield: 96 mg (60%), colorless oil.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, **0.04 residual H**), 7.23 (s, **0.09 residual H**), 7.02 (s, **0.04 residual H**).
^{13}C NMR (100 MHz, $CDCl_3$): 138.0, 129.1, 128.3, 125.4.
HRMS (EI) m/z: calcd for $C_4HD_3BrS^+$- ([M^+H]-) 165.9405; Found 165.9411.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 96% (D^a), 91% (D^b) and 96% (D^c), (total: 0.96+0.91+0.96=2.83 D); From GC-MS: 2.85 D

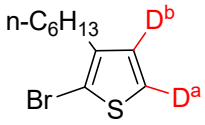


2bg: Isolated yield: 90 mg (68%), colorless oil.

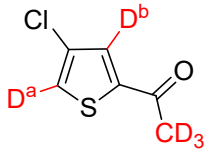
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.33 (s, **0.08 residual H**), 6.76 (s, **0.40 residual H**), 6.56 (s, **0.18 residual H**), 3.73 (s, 3 H).
^{13}C NMR (100 MHz, $CDCl_3$): 158.4, 124.5 (t, J = 27.2 Hz), 119.2, 96.6, 57.7.
HRMS (EI) m/z: calcd for $C_5H_4D_3OS^+$- ([M^+H]-) 118.0400; Found 118.0392.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 82% (D^a), 60% (D^b) and 92% (D^c), (total: 0.82+0.60+0.92=2.36 D); From GC-MS: 2.58 D



2bh: Isolated yield: 167 mg (90%), yellow oil.
^{1}H NMR (300 MHz, DMSO-d_6): δ 7.70 (s, **0.04 residual H**), 7.58 (s, **0.05 residual H**), 7.17 (s, **0.12 residual H**), 3.24 - 3.36 (m, 4 H), 1.10 (s, 6 H).
^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 137.3, 126.7, 125.5 (t, J = 28.1 Hz), 124.7 (t, J = 28.3 Hz), 43.2, 39.8, 14.5, 12.9.
HRMS (EI) m/z: calcd for $C_9H_{11}D_3NOS^+$- ([M^+H]-) 187.0979; Found 187.0974.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 96% (D^a), 87% (D^b) and 94% (D^c), (total: 0.96+0.87+0.94=2.77 D); From GC-MS: 2.76 D

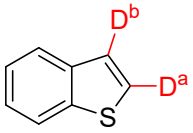


2bi: Isolated yield: 173 mg (70%), colorless oil.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.72 (s, **0.03 residual H**), 7.14 (s, **0.26 residual H**), 2.71 (t, J = 8.2 Hz, 2 H), 1.72 (t, J = 5.2 Hz, 2 H), 1.46 (s, 6 H), 1.05 (t, J = 9.4 Hz, 3 H).
^{13}C NMR (100 MHz, DMSO-d_6): 142.6, 129.3, 108.6, 95.6, 31.9, 30.0, 29.6, 29.2, 23.0, 14.8.
HRMS (EI) m/z: calcd for $C_{10}H_{14}D_2BrS^+$- ([M^+H]-) 249.0276; Found 249.0276.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 97% (D^a) and 74% (D^b), (total: 0.97+0.74=1.71 D); From GC-MS: 1.80 D.

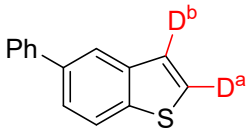


2bj: Isolated yield: 152 mg (92%), yellow oil.
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.02 (s, **0.06 residual H**), 7.99 (s, **0.06 residual H**), 2.51 – 2.53 (m, **0.03 residual H**).
^{13}C NMR (100 MHz, DMSO-d_6): 191.5, 144.9, 134.2, 125.2, 95.5, 27.0.

HRMS (EI) m/z: calcd for $C_6D_5ClOSNa^+$- ([M^+Na]-) 187.9956; Found 187.9955.
The level of deuterium incorporation was estimated: From ^1H NMR: 94% (D^a), 92% (D^b) and 99% (D), (total: 0.94+0.94+0.99*3=4.85 D); From GC-MS: 4.85 D.



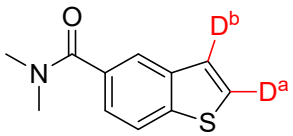
2bk: Isolated yield: 122 mg (90%), white solid.
^1H NMR (400 MHz, DMSO-d_6): δ 8.01-7.98 (m, 1 H), 7.87-7.90 (m, 1 H), 7.45 (s, **0.18 residual H**), 7.42-7.32 (m, **2.14 residual H**).
^{13}C NMR (100 MHz, DMSO-d_6): 140.1, 139.7, 127.7 (t, J = 28.1 Hz), 124.9, 124.5, 124.3, 123.3.
HRMS (EI) m/z: calcd for $C_8H_4D_2S^+Na^+$- ([M^+Na]-) 159.0213; Found 159.0208.
The level of deuterium incorporation was estimated: From ^1H NMR: 86% (D^a) and 82% (D^b), (total: 0.86+0.82=1.68 D); From GC-MS: 1.72 D.



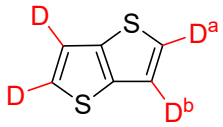
2bl: Isolated yield: 186 mg (88%), white solid.

^1H NMR (400 MHz, DMSO-d_6): δ 8.18 (d, J = 1.8 Hz, 1 H), 8.09 (d, J = 8.4 Hz, 1 H), 7.77-7.72 (m, 2 H), 7.70-7.65 (m, 1 H), 7.54-7.47 (m, **2.14 residual H**), 7.42 – 7.35 (m, **1.03 residual H**).

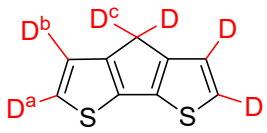
^{13}C NMR (100 MHz, DMSO-d_6): 140.6, 140.4, 138.6, 136.9, 136.8 (t, J = 28.1 Hz), 129.2, 127.5, 127.3, 123.7, 123.4, 121.9.
HRMS (EI) m/z: calcd for $C_{14}H_9D_2S^+$- ([M^+H]-) 213.0707; Found 213.0717.
The level of deuterium incorporation was estimated: From ^1H NMR: 97% (D^a) and 86% (D^b) (total: 0.97+0.86=1.83 D); From GC-MS: 1.84 D.



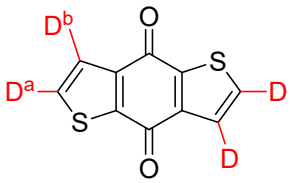
2bm: Isolated yield: 114 mg (55%), yellow oil.
^1H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, J = 8.3 Hz, 1 H), 7.93 (s, 1 H), 7.84 (s, **0.04 residual H**), 7.51 (s, **0.05 residual H**), 7.40-7.35 (m, 1 H), 2.97 (d, J = 26.5 Hz, 6 H).
^{13}C NMR (100 MHz, DMSO-d_6): 170.9, 140.6, 139.6, 133.3, 123.8, 123.7, 123.2, 122.9, 40.0.
HRMS (EI) m/z: calcd for $C_{11}H_{10}D_2NOS^+$- ([M^+H]-) 209.0760; Found 208.0756.
The level of deuterium incorporation was estimated: From ^1H NMR: 97% (D^a) and 96% (D^b), (total: 0.97+0.96=1.93 D); From GC-MS: 1.85 D



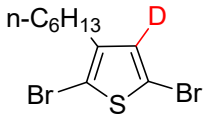
2bn: Isolated yield: 137 mg (95%), white solid.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, $CDCl_3$):δ 7.38 (s, **0.09 residual H**), 7.26 (s, **0.12 residual H**).
^{13}C NMR (100 MHz, $CDCl_3$): 139.9, 129.6, 128.8, 125.9.
HRMS (EI) m/z: calcd for $C_6D_4S_2^+Na^+$- ([M^+Na]-) 166.9898; Found 166.9895.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 94% (D^a) and 94% (D^b), (total: 0.94*2+0.94*2=3.76 D); From GC-MS: 3.76 D



2bo: Isolated yield: 156 mg (90%), yellow oil.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.43 (d, J = 4.9 Hz, **0.13 residual H**), 7.19 (s, **0.80 residual H**), 3.59 (s, **0.20 residual H**).
^{13}C NMR (100 MHz, $CDCl_3$): 149.7, 138.8, 124.6, 123.0, 29.7.
HRMS (EI) m/z: calcd for $C_9HD_6S_2^+$ - ([M^+H]-) 185.0360; Found 185.0356.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 94% (D^a), 60% (D^b) and 93% (D^c), (total: 0.94*2+0.60*2+0.93*2=4.94 D); From GC-MS: 5.04 D



2bp: Isolated yield: 202 mg (90%), yellow solid.
The percentage of deuteration was determined by using 1,4-dimethoxybenzene as internal standard in ^{1}H NMR spectroscopy experiment.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, **0.02 residual H**), 7.64 (s, **0.05 residual H**).
^{13}C NMR (100 MHz, $CDCl_3$): 174.7, 144.9, 142.9, 133.9, 126.7.
HRMS (EI) m/z: calcd for $C_{10}HD_4O_2S_2^+$- ([M^+H]-) 224.9977; Found 224.9958.
The level of deuterium incorporation was estimated: From ^{1}H NMR: 99% (D^a) and 97% (D^b), (total: 0.99*2+0.97*2=3.92 D); From GC-MS: 3.84 D

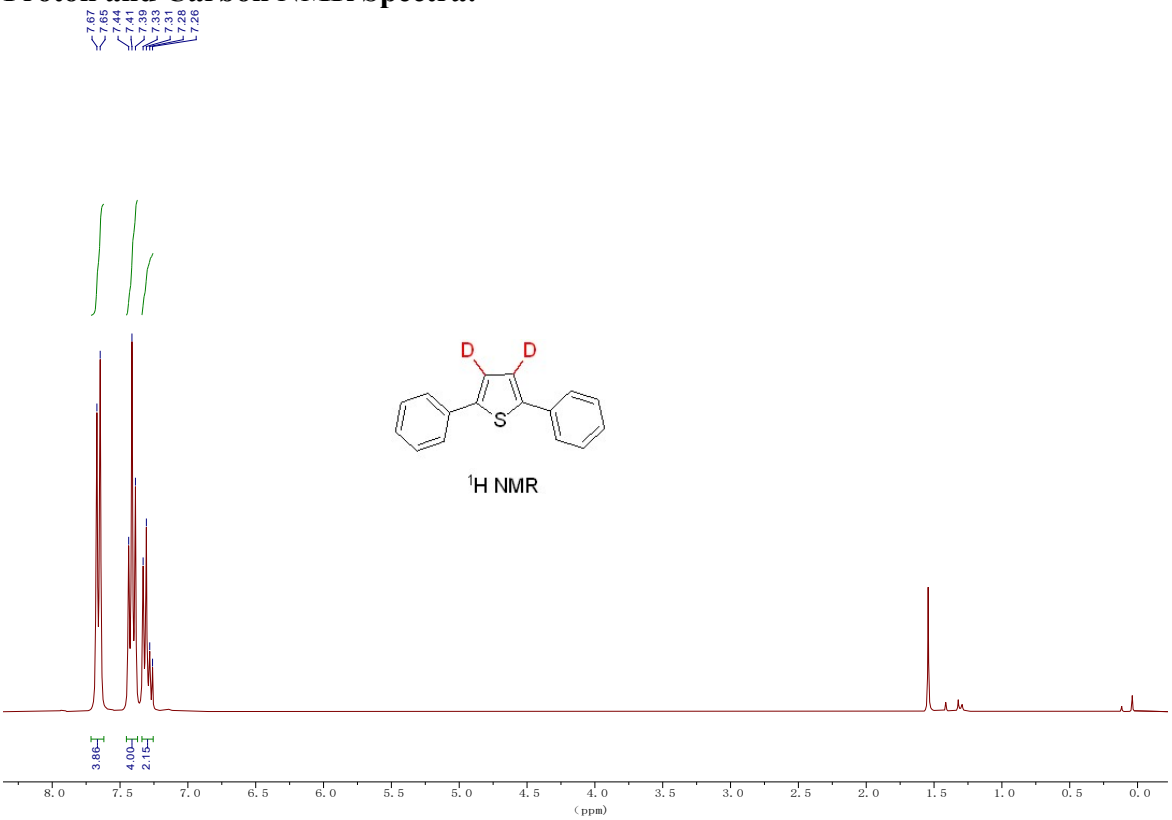


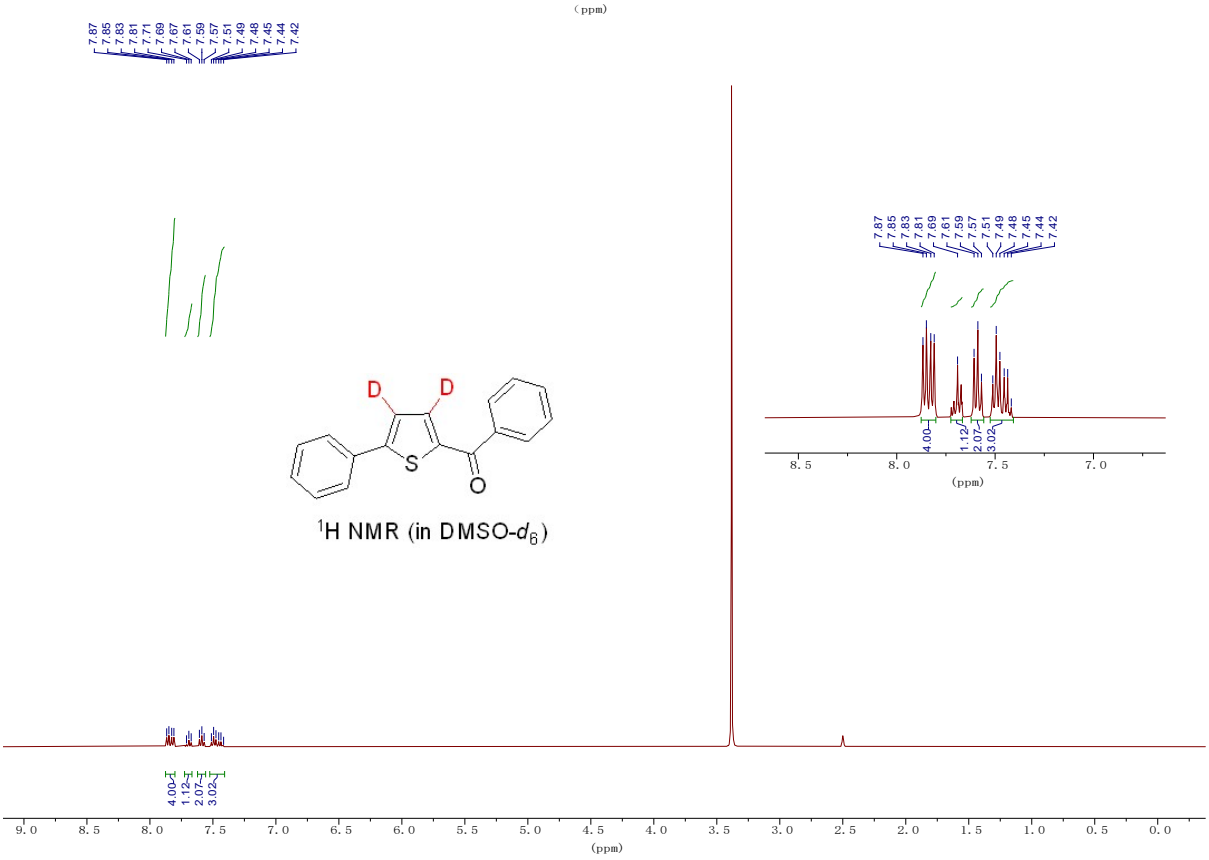
3a[3]: Isolated yield: 310 mg (95%), colorless oil .
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (s, **0.03 residual H**), 2.50 (s, 2 H), 1.52 (s, 2 H), 1.30 (s, 6 H), 0.89 (s, 3 H).
^{13}C NMR (100 MHz, $CDCl_3$): 143.6, 110.2, 108.1, 100.0, 31.4, 29.4, 29.3, 28.6, 22.5, 14.5.
Deuterium incorporation expected at δ 6.78
HRMS (EI) m/z: calcd for $C_{10}H_{14}DBr_2S^+$- ([M^+H]-) 327.9304; Found 327.9308
The level of deuterium incorporation was estimated: From ^{1}H NMR: 97%, (total: 0.97 D); From GC-MS: 0.98 D

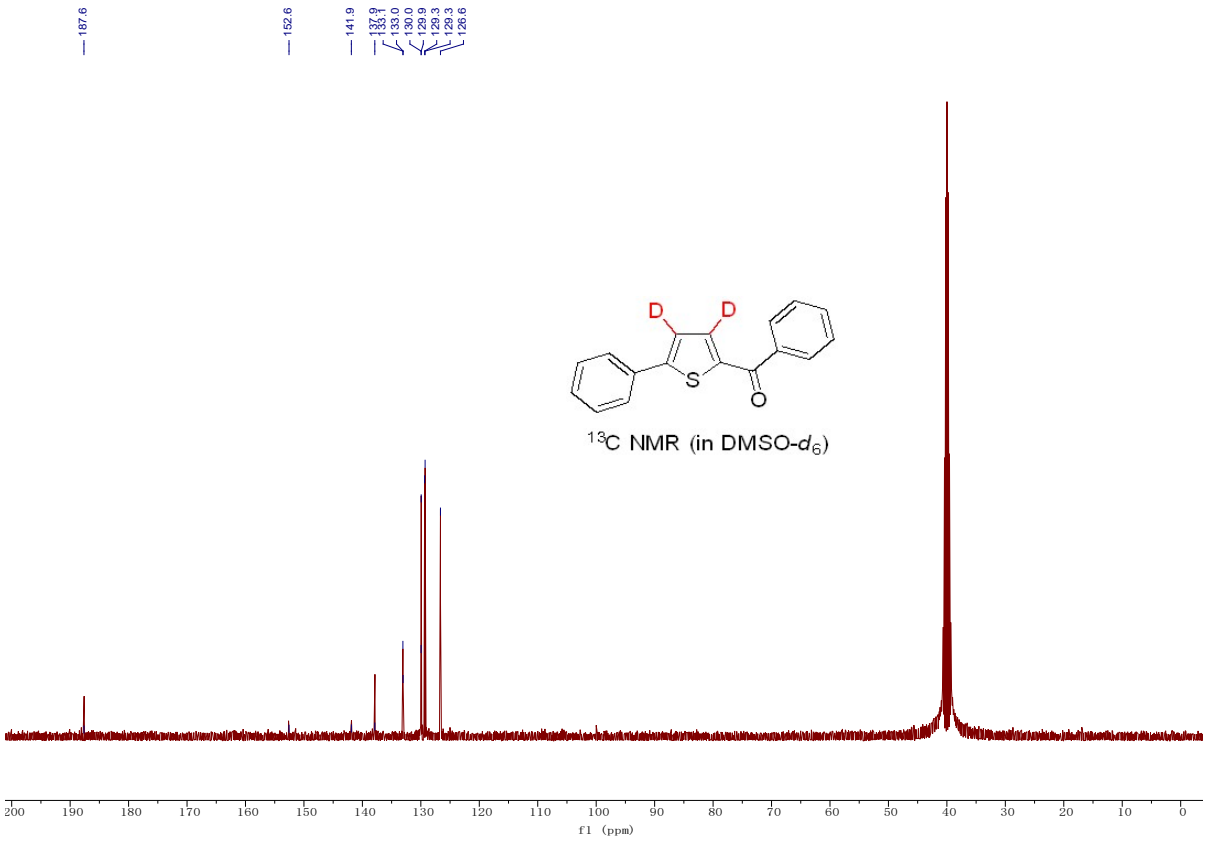
Reference:

1. Zhang, G.; Hong, Y.; Hong C.; Bian, C.; Liu, C.; Lei A. *Org. Lett.* **2014**, *16*, 6156−6159.
2. Zhang, Y. Preparation of deuterated C-glycoside derivatives for treating diabetes, CAN 165:365596, 2016, 08, 24.
3. Shao, M.; Keum, J.; Chen, J.; He, Y.; Chen, W.; Browning, J. F.; Jakowski, J.; Sumpter, B. G.; Ivanov, I. N.; Ma, Y. Z.; Rouleau, C. M.; Smith, S. C.; Geohegan, D. B.; Hong, K.; Xiao, K. Nature Commun. 2014, 1-13.

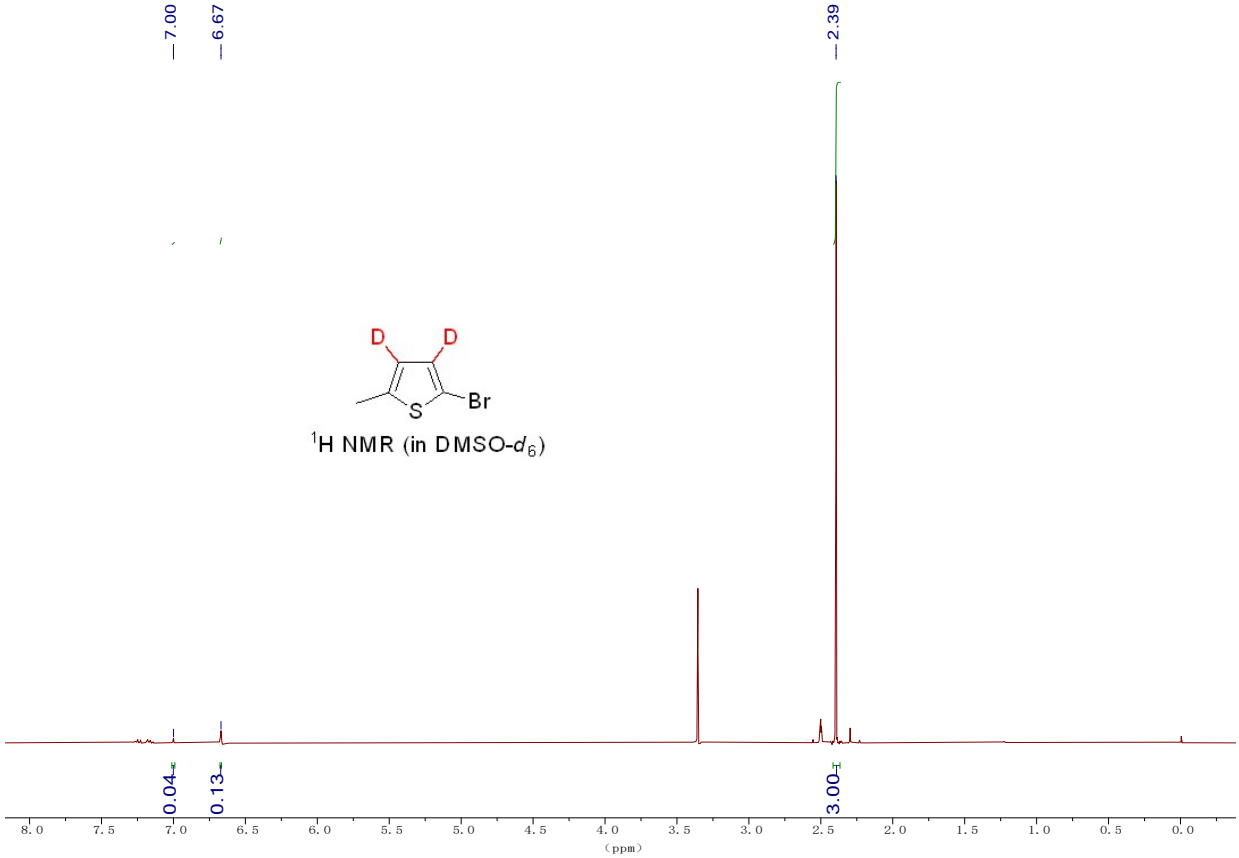
Proton and Carbon NMR Spectra:



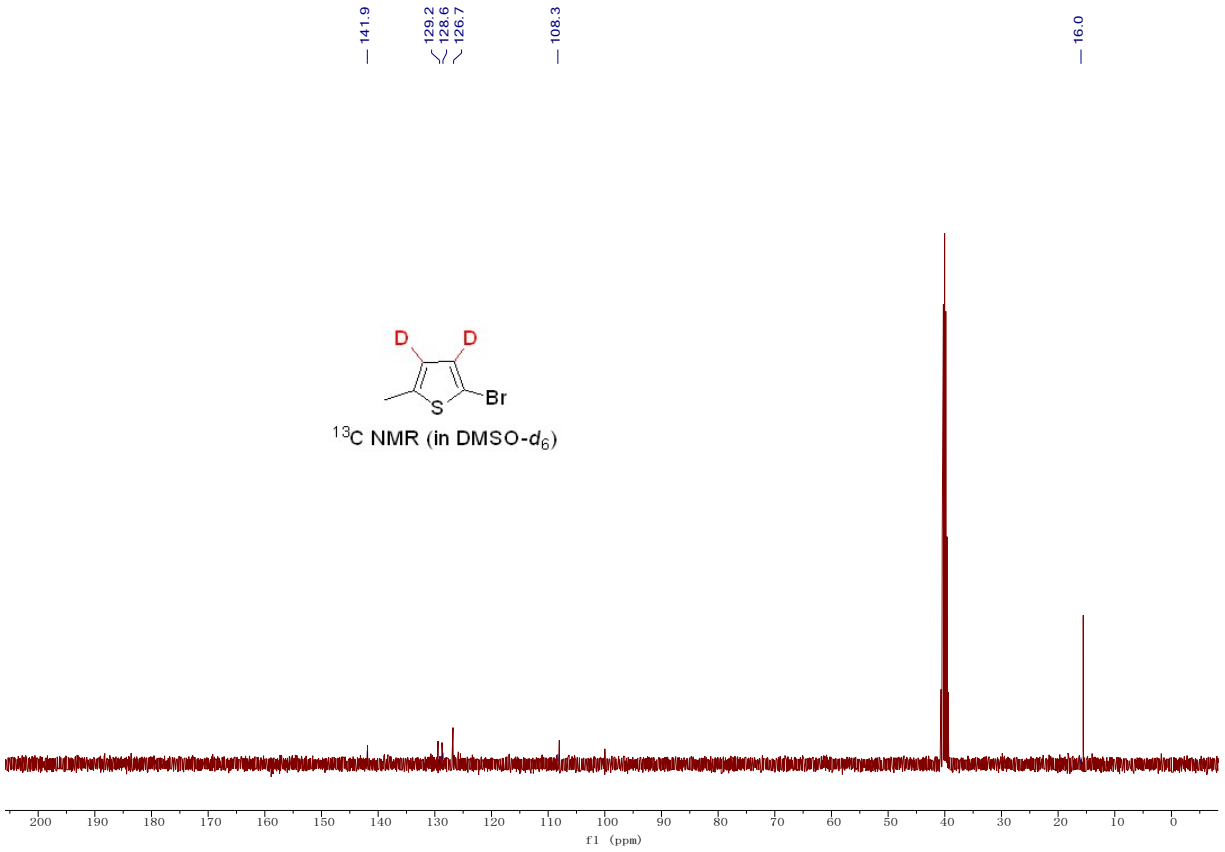


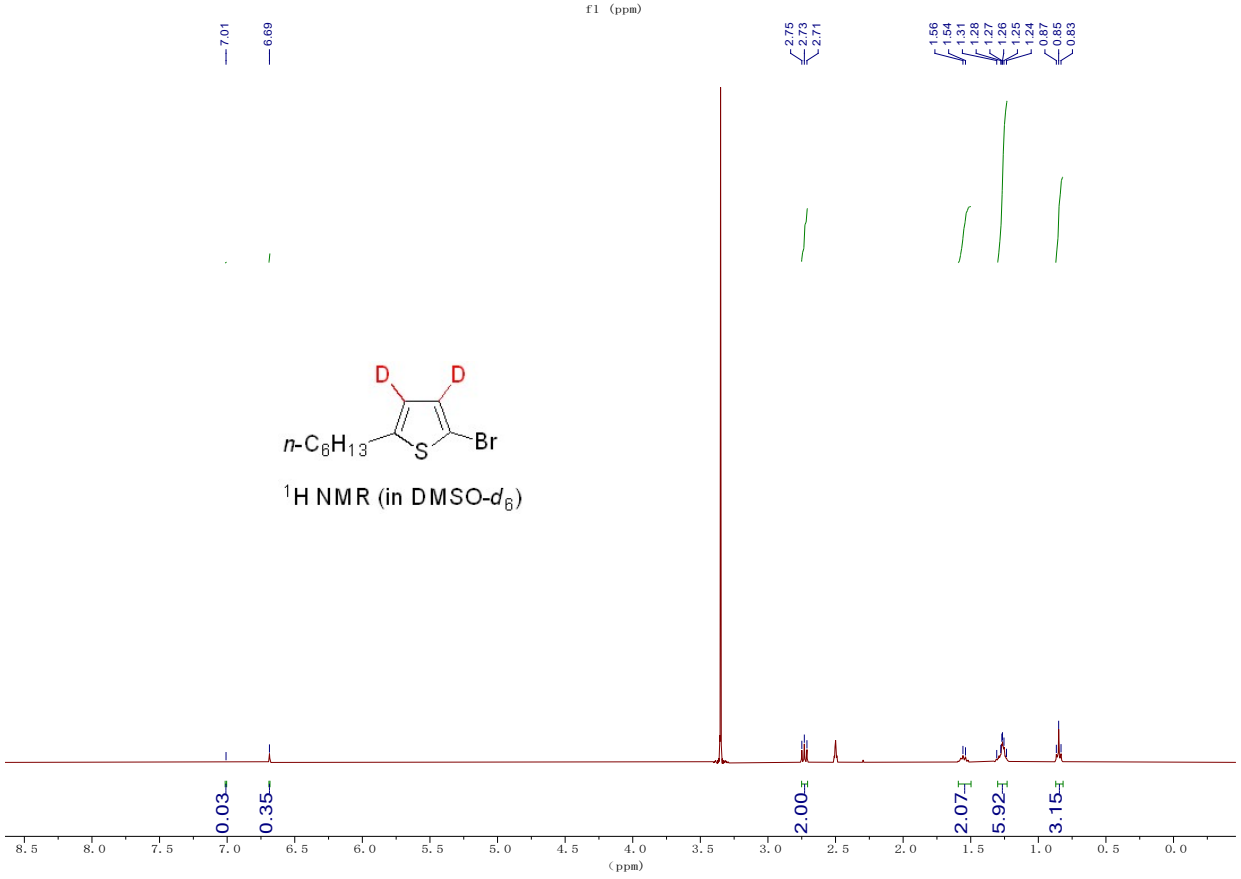


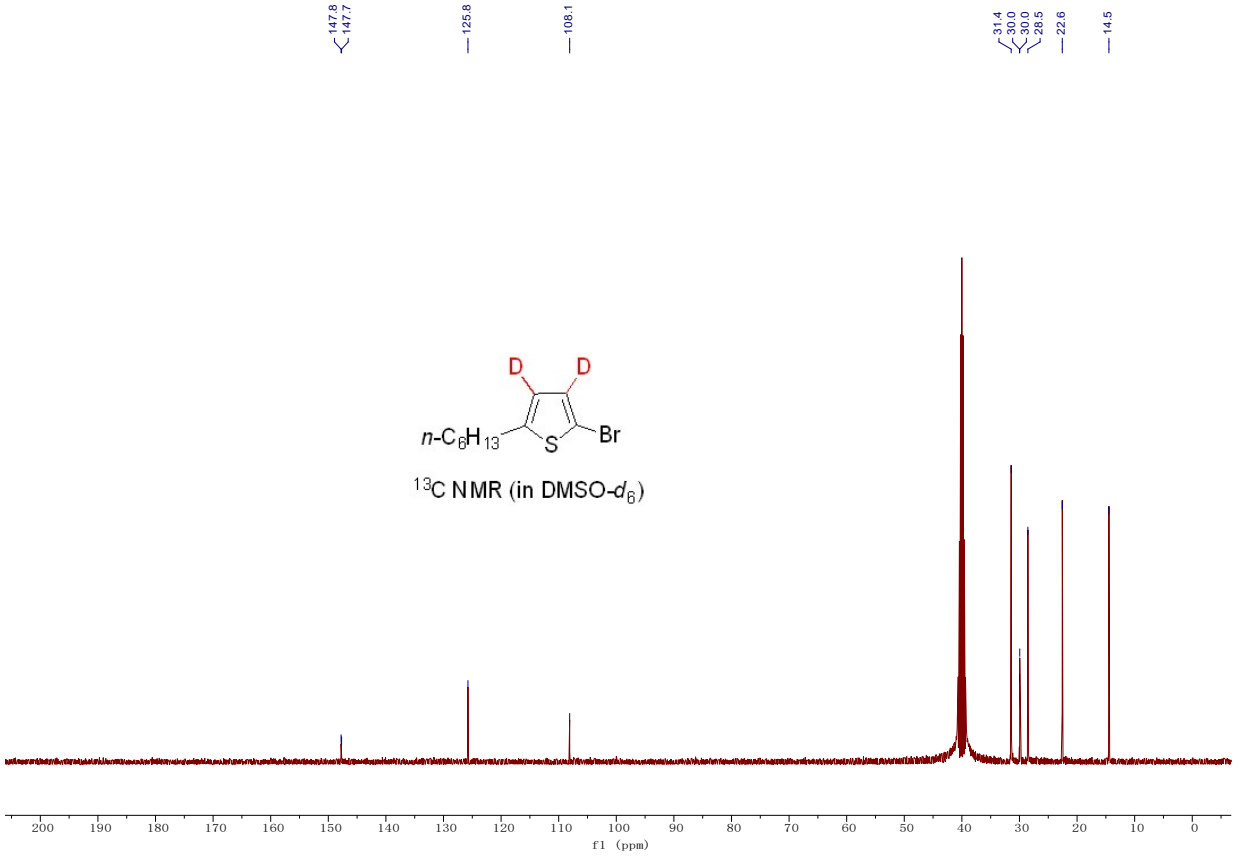
^{13}C NMR (in DMSO-d_6)

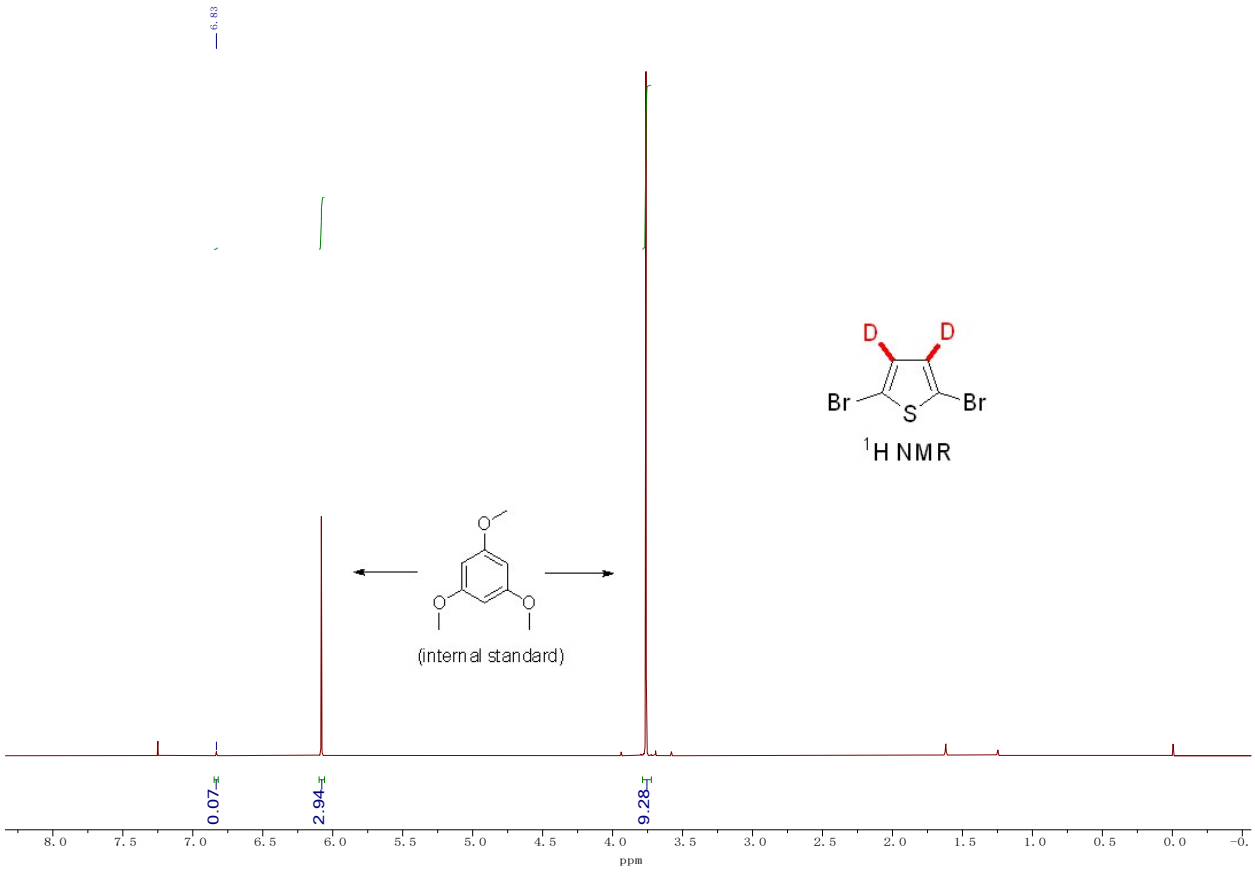


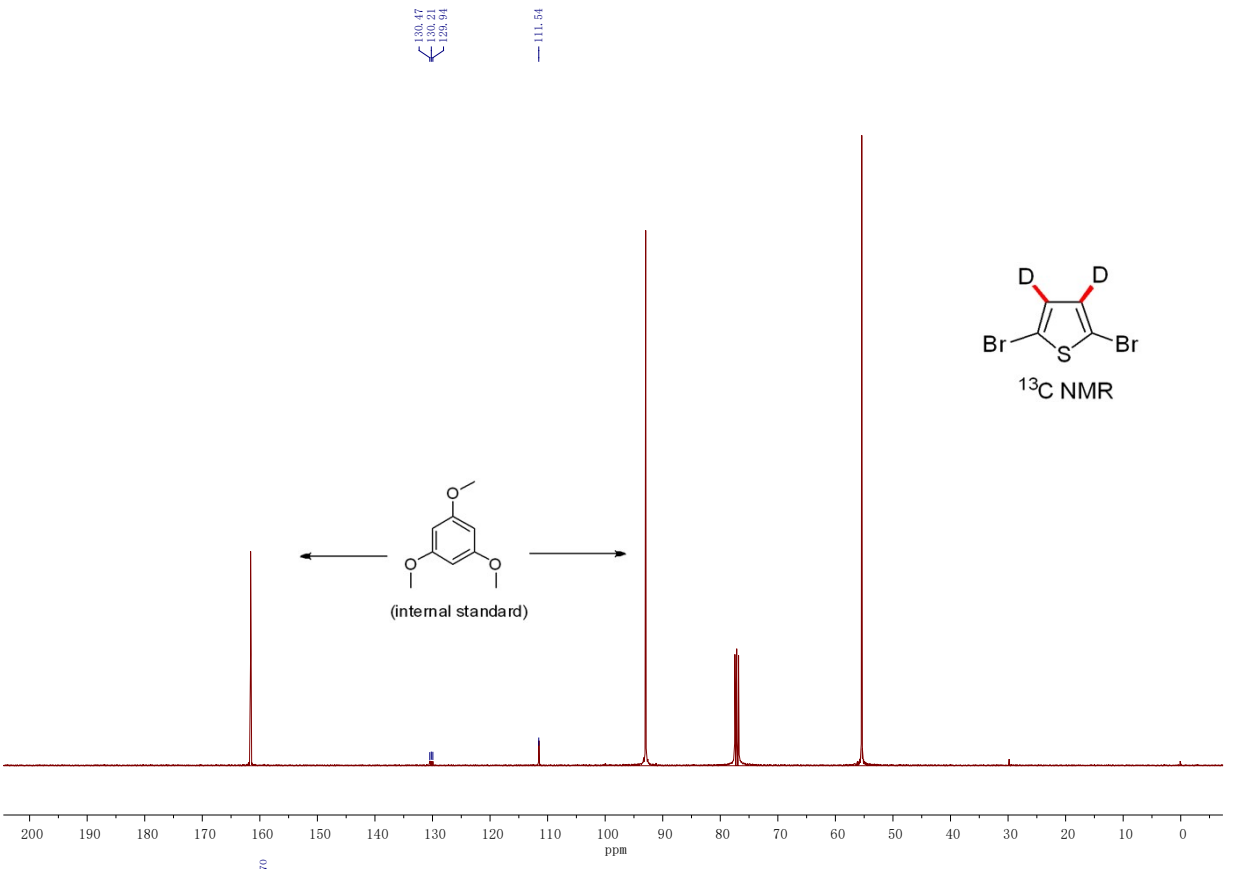
^{1}H NMR (in DMSO-d_6)

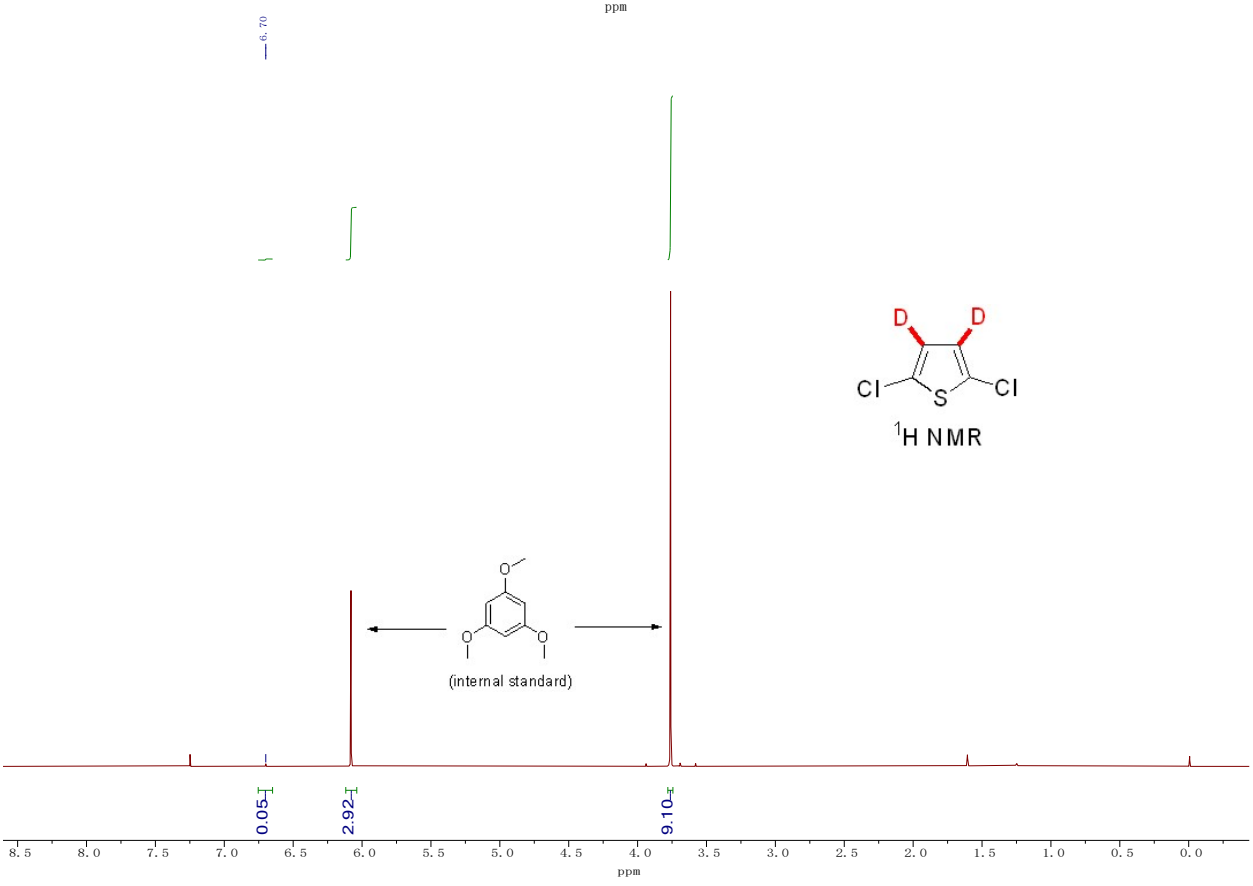

141.9
129.2
128.6
126.7
108.3
16.0
D
D
Br
S
^{13}C NMR (in DMSO-d_6)
f1 (ppm)

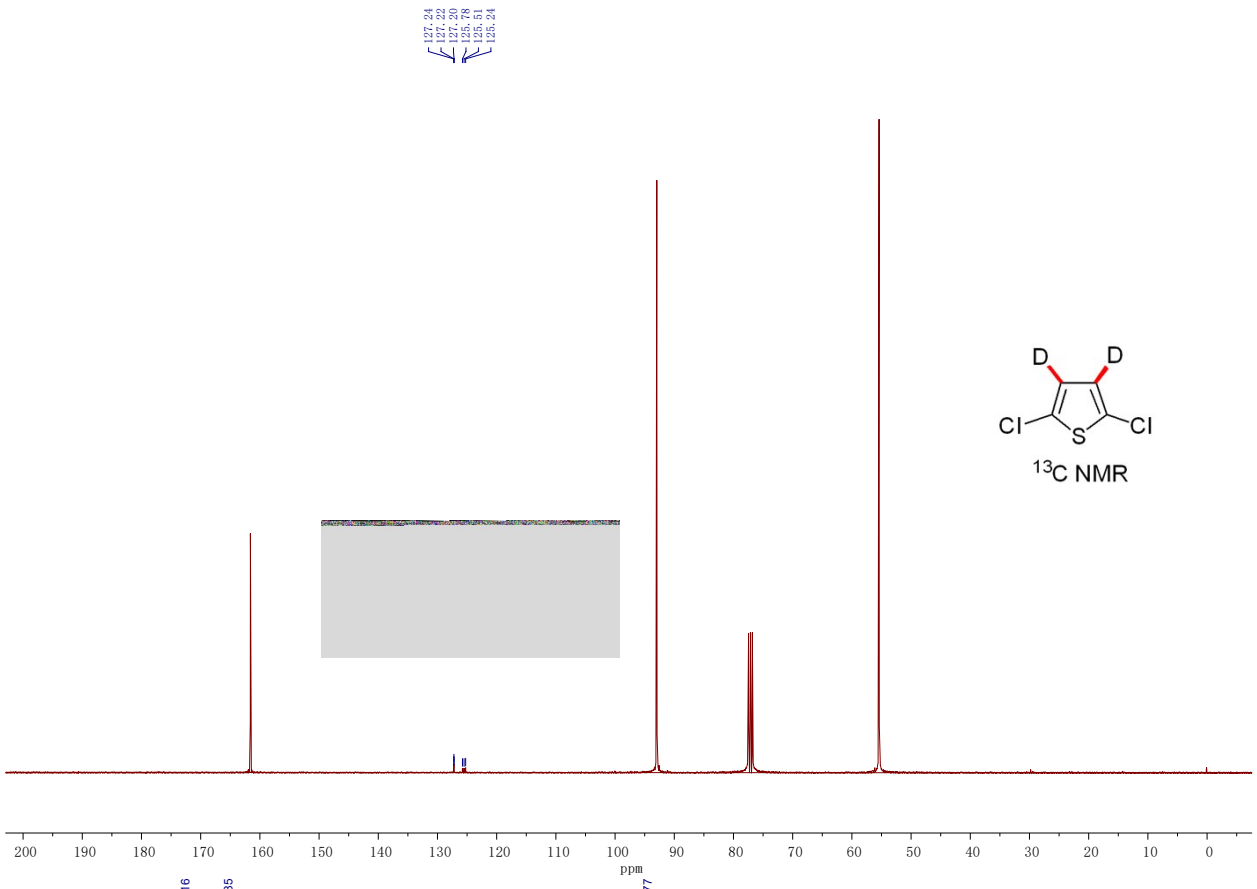

7.01
6.69
2.75
2.73
2.71
1.56
1.54
1.31
1.28
1.27
1.26
1.25
1.24
0.87
0.85
0.83
D
D
n-C_6H_{13}
Br
S
^{1}H NMR (in DMSO-d_6)
0.03
0.35
2.00
2.07
5.92
3.15
(ppm)

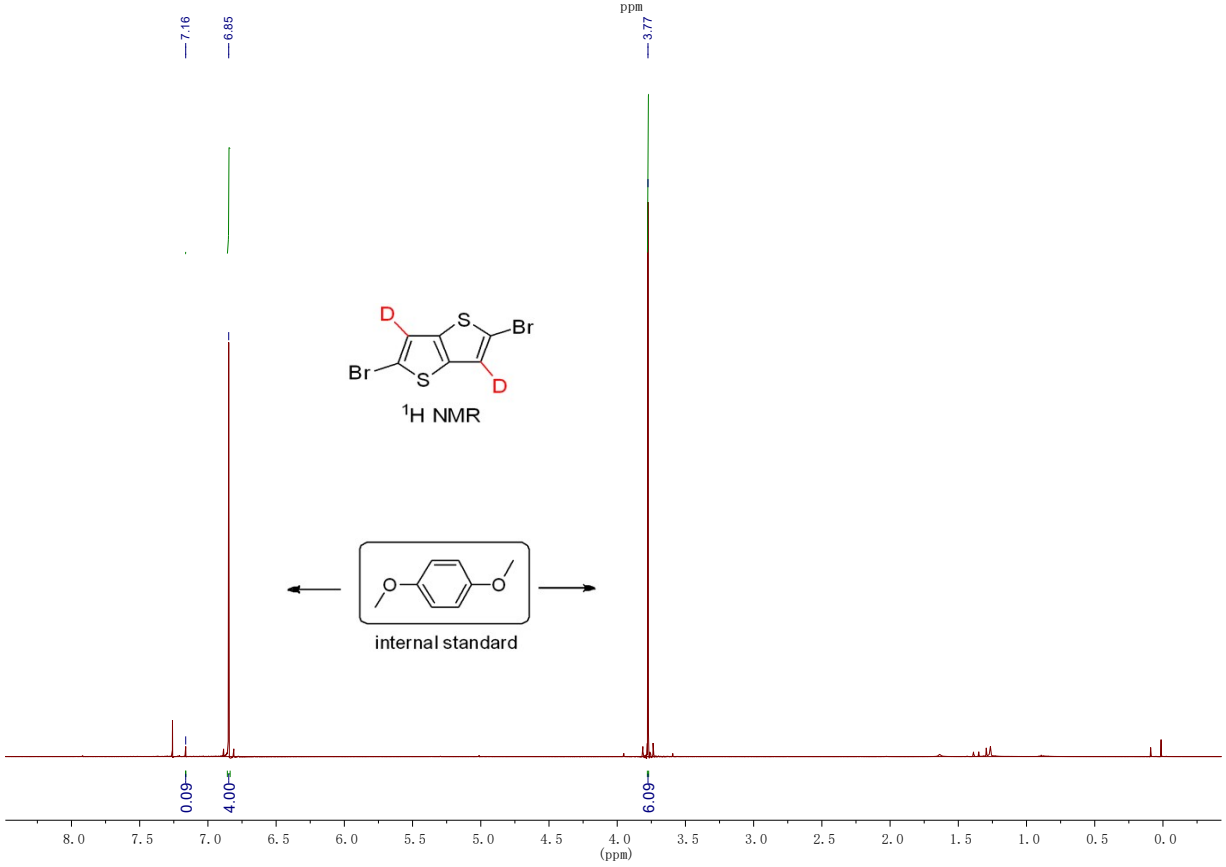

147.8
147.7
125.8
108.1
31.4
30.0
30.0
28.5
22.6
14.5
D
D
n-C6H13
S
Br
13C NMR (in DMSO-d6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

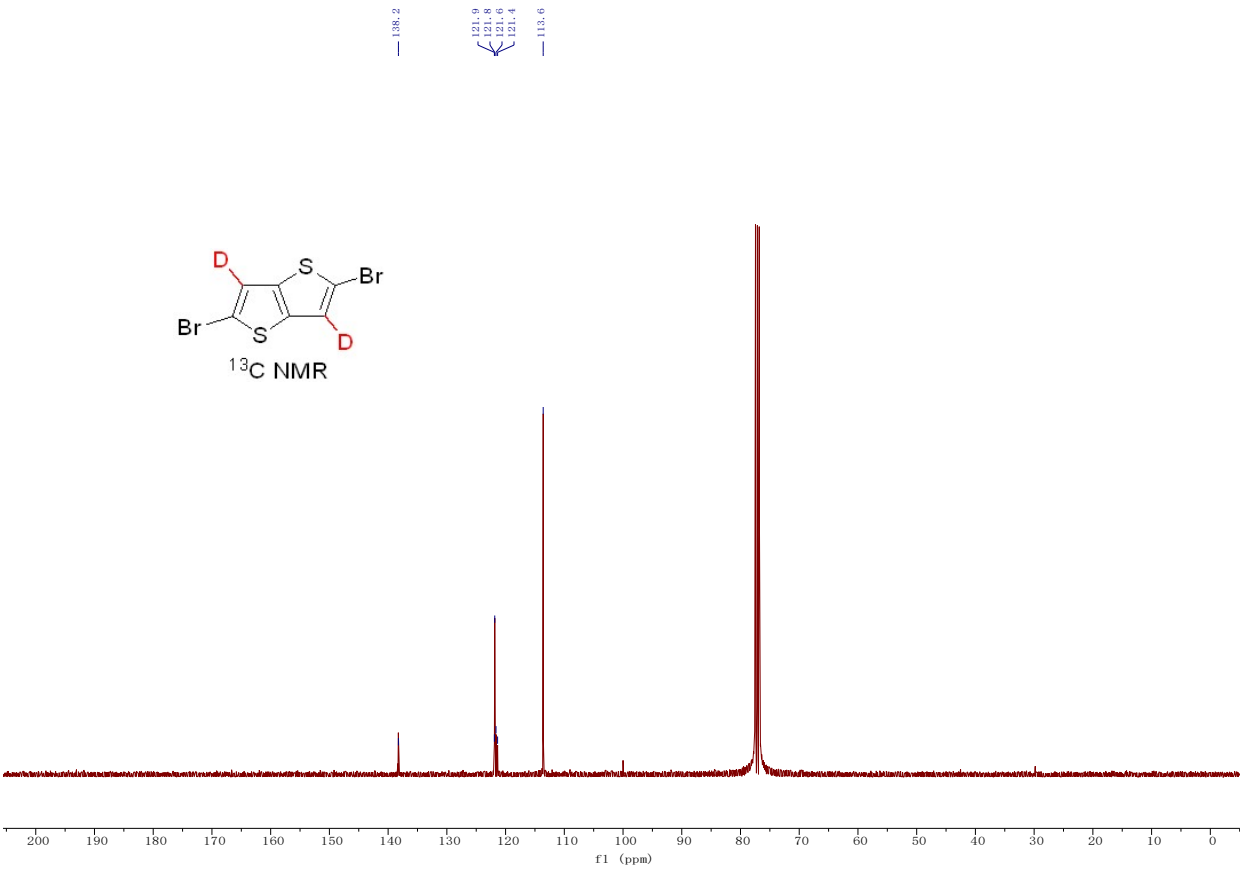

6.83
D
D
Br
S
Br
1H NMR
(internal standard)
0.07
2.94
9.28
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
ppm

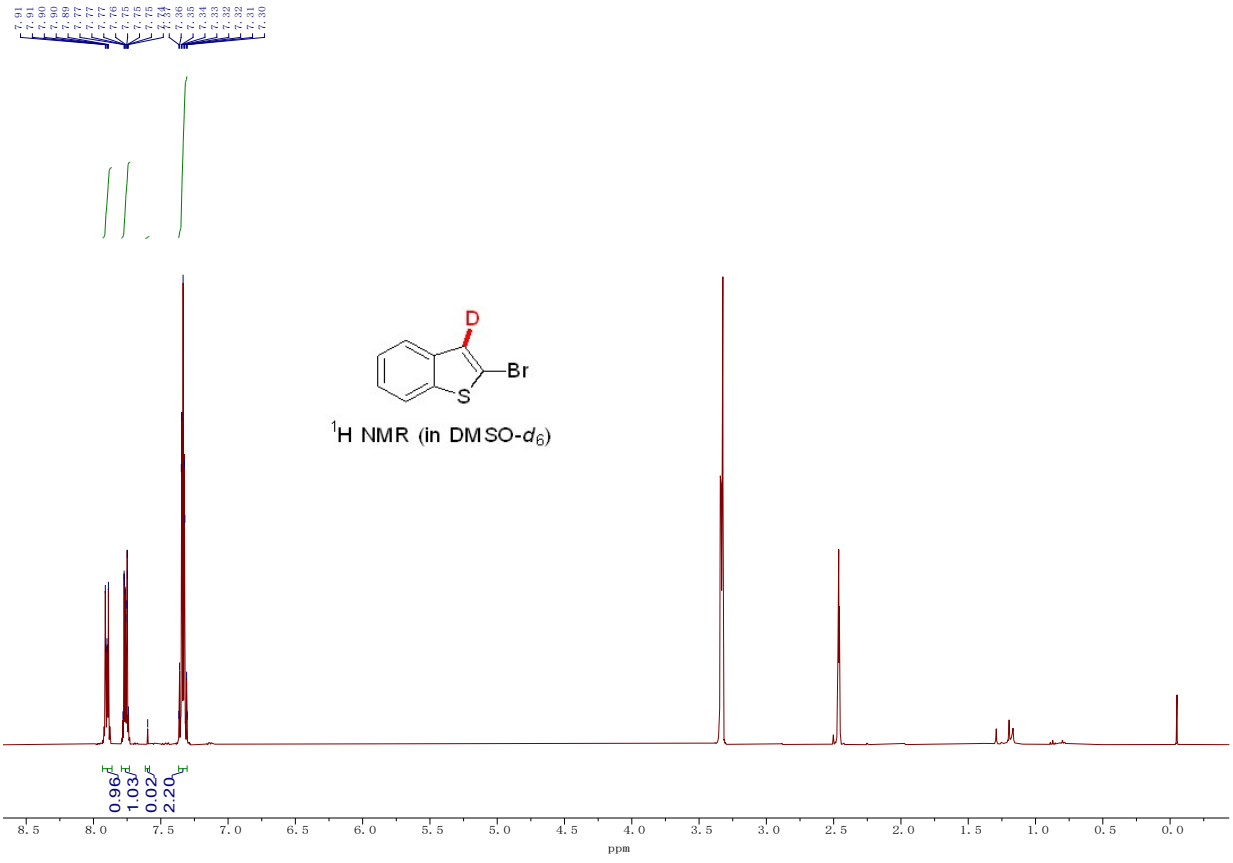

130.47
130.21
129.94
111.54
D
D
Br
S
Br
^{13}C NMR
O
O
O
(internal standard)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

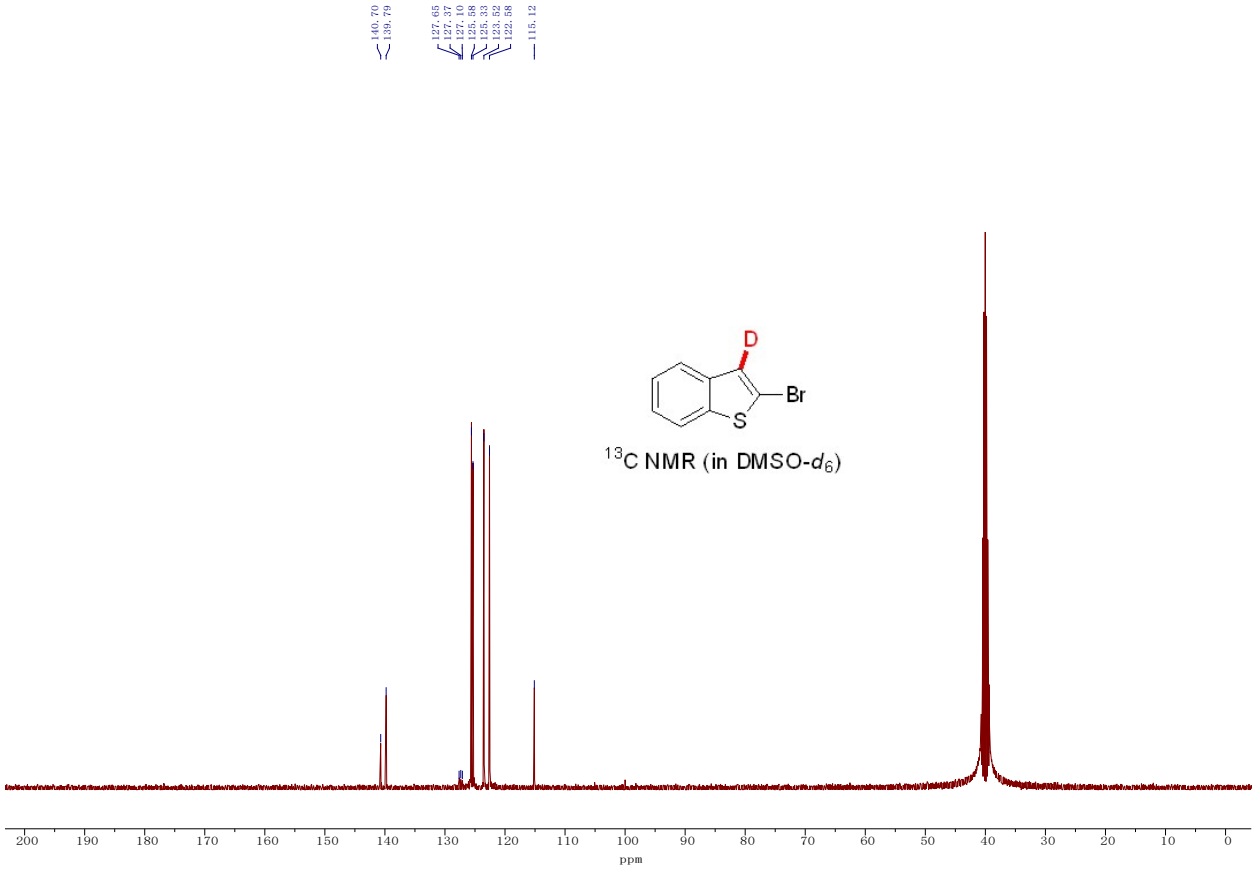

6.70
D
D
Cl
S
Cl
^{1}H NMR
O
O
O
(internal standard)
0.05
2.92
9.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

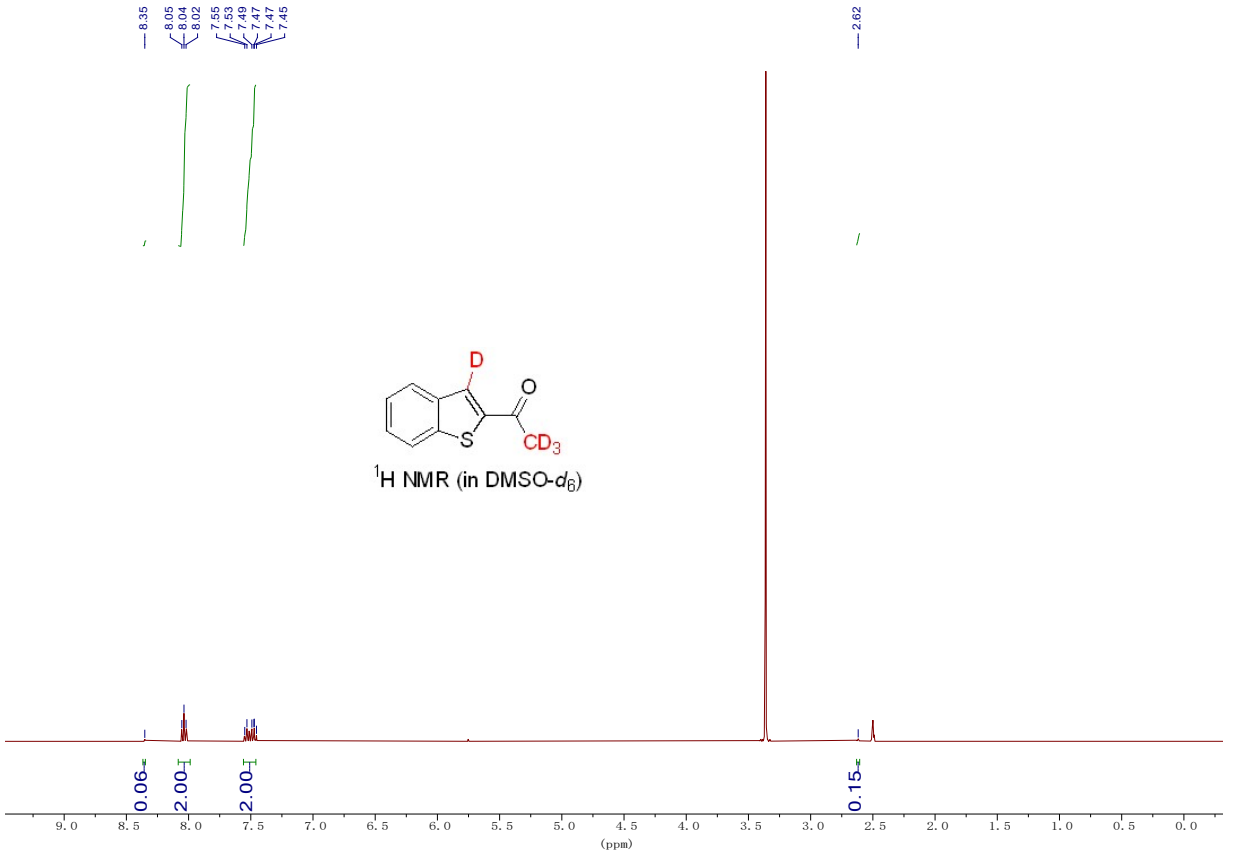

127.24
127.22
127.20
125.78
125.51
125.24
D
D
Cl
Cl
S
13C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

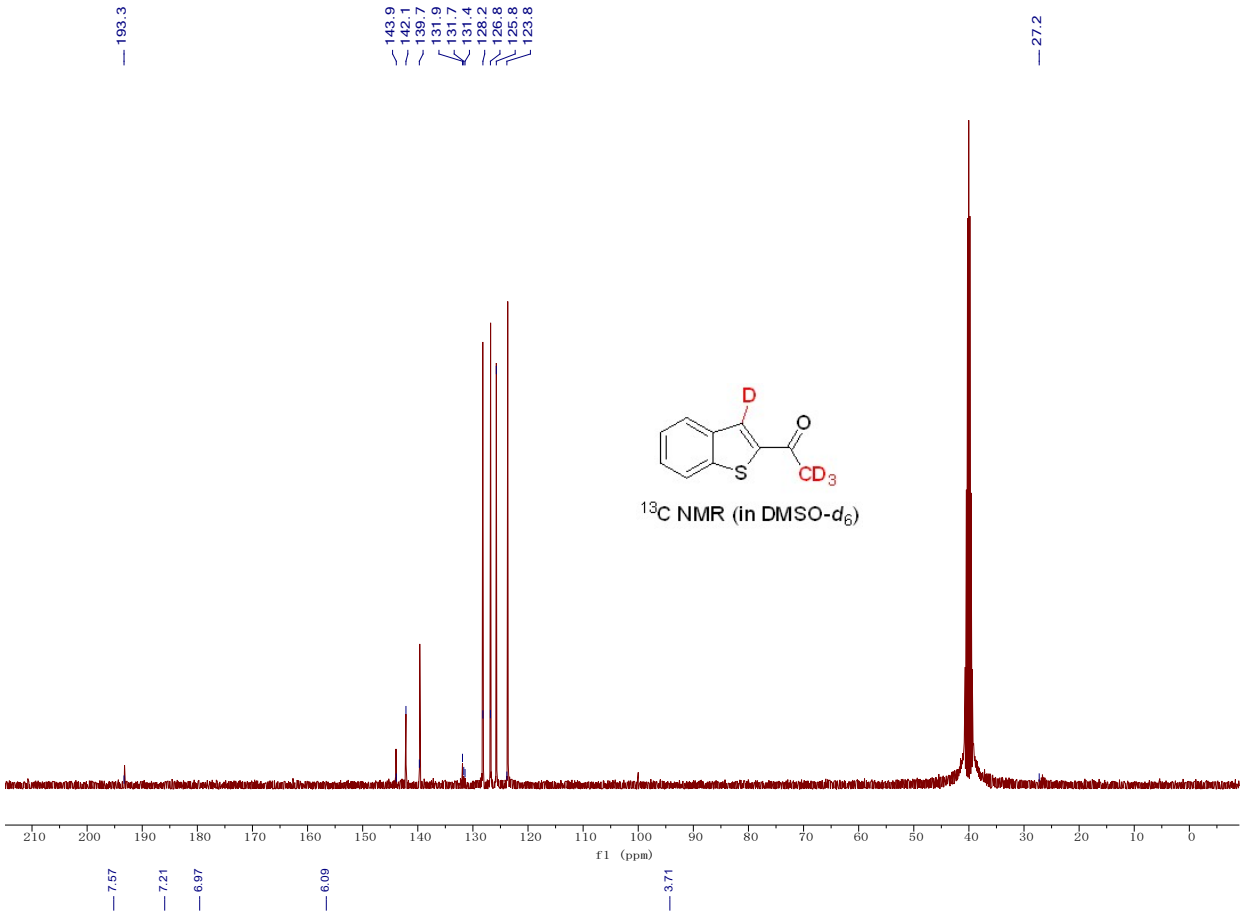

7.16
6.85
3.77
D
S
Br
Br
S
D
1H NMR
internal standard
0.09
4.00
6.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

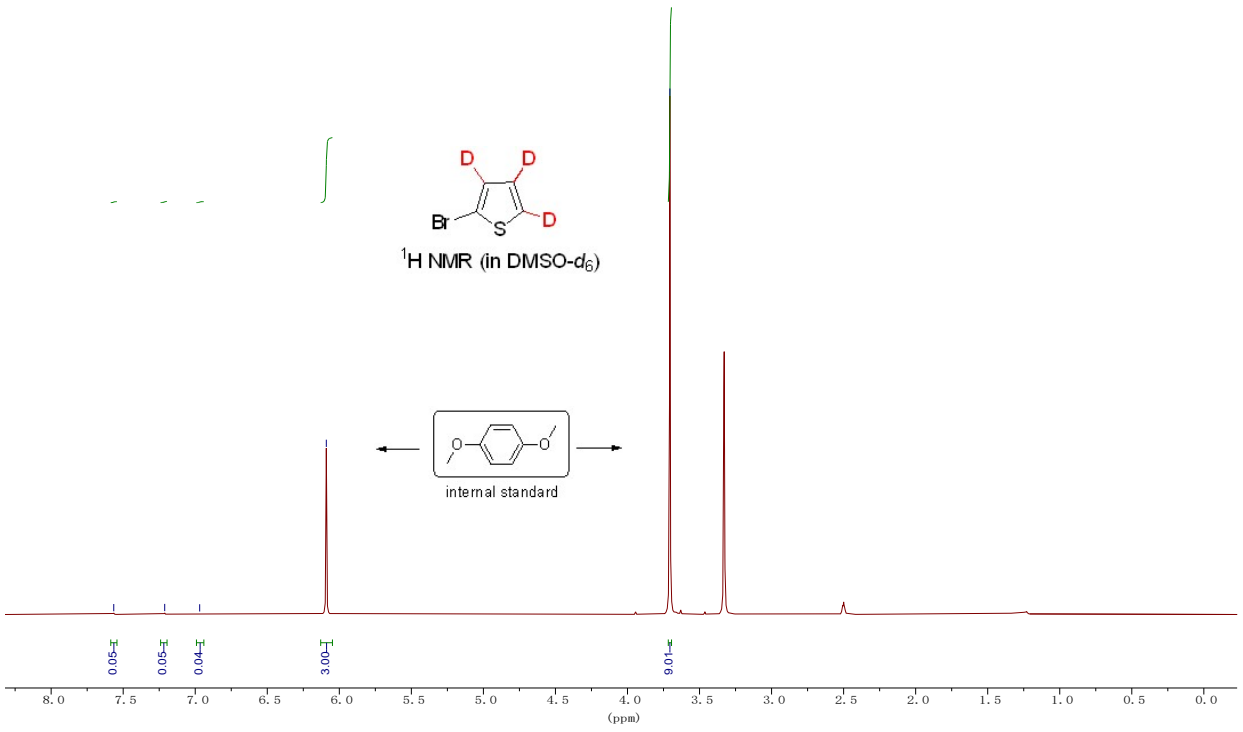

138.2
121.9
121.8
121.6
121.4
113.6
D
S
Br
Br
S
D
13C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

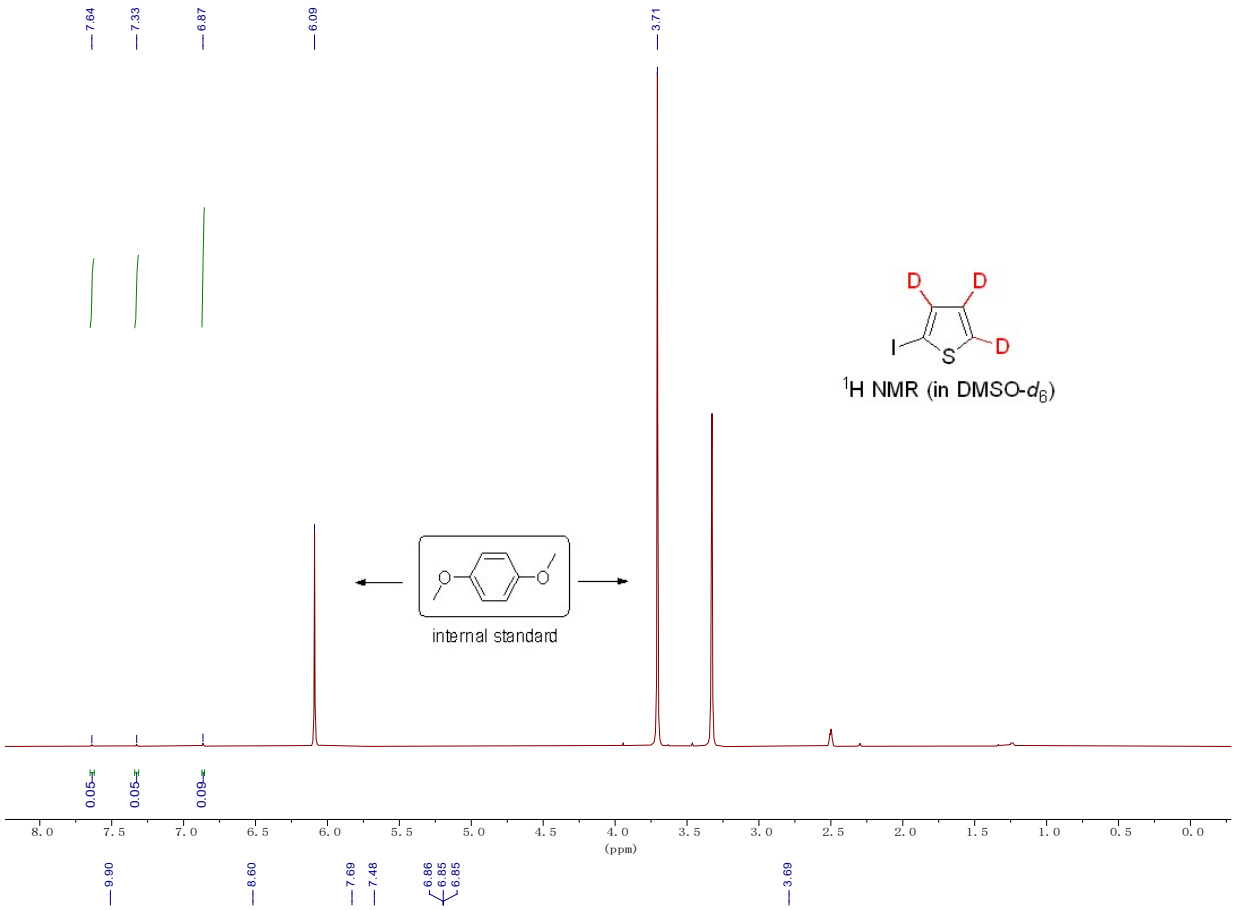

7.91
7.91
7.90
7.90
7.89
7.77
7.77
7.77
7.76
7.75
7.75
7.75
7.74
7.74
7.36
7.35
7.34
7.34
7.32
7.32
7.31
7.30
D
Br
S
1H NMR (in DMSO-d6)
0.96
1.03
0.02
2.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

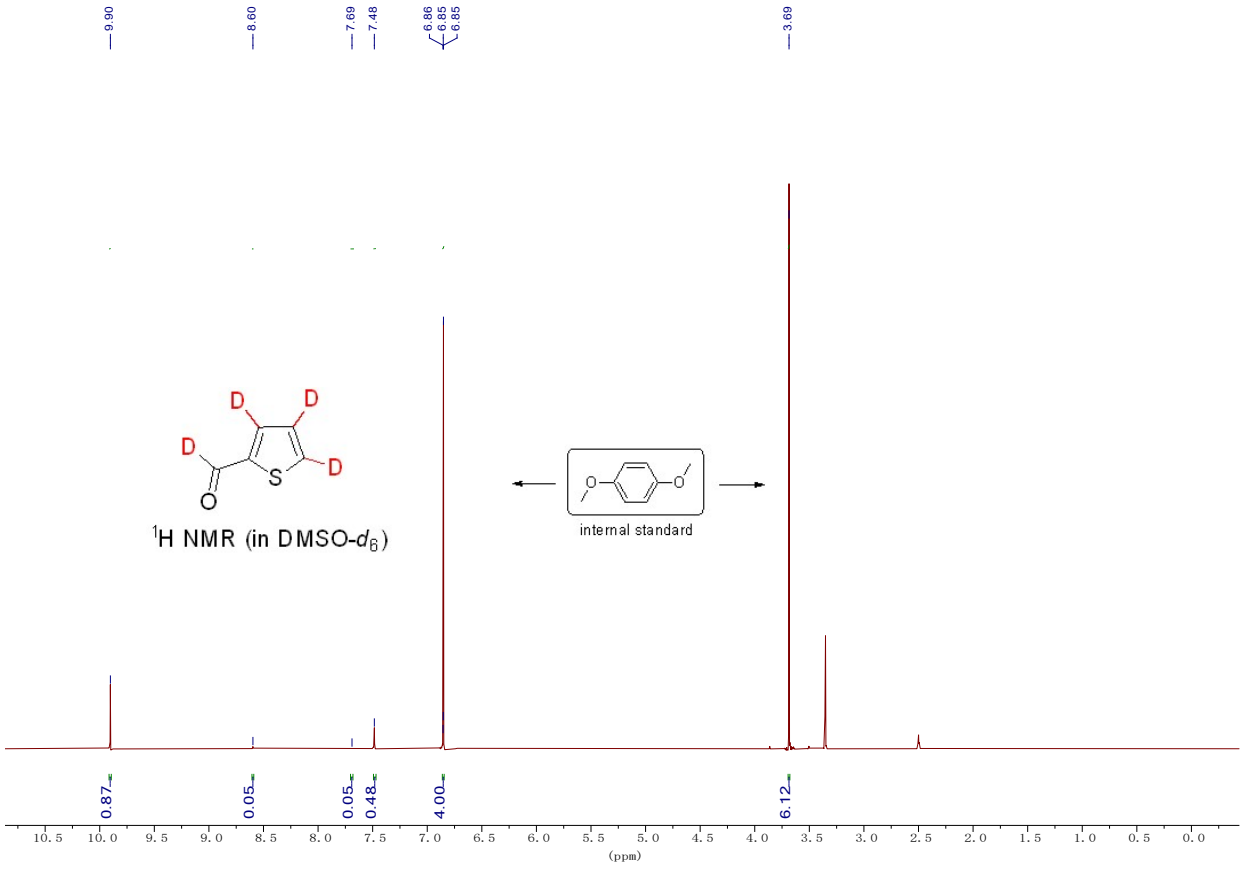

140.70
139.79
127.65
127.37
127.10
125.98
125.33
123.62
122.58
115.12
D
Br
S
^{13}C NMR (in DMSO-d_6)
ppm

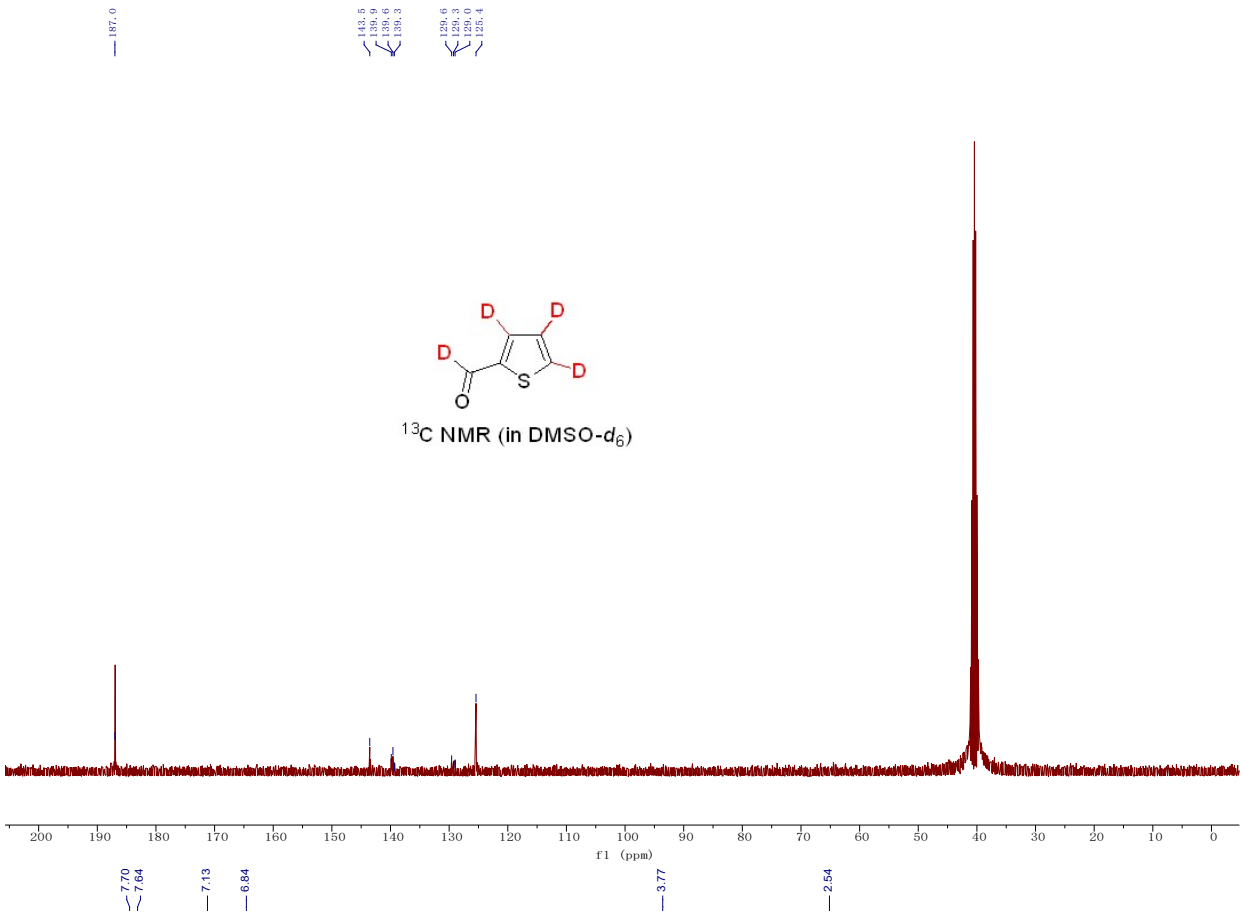

8.35
8.05
8.04
8.02
7.55
7.53
7.49
7.47
7.47
7.45
2.62
D
O
S
CD_3
^{1}H NMR (in DMSO-d_6)
0.06
2.00
2.00
0.15
(ppm)

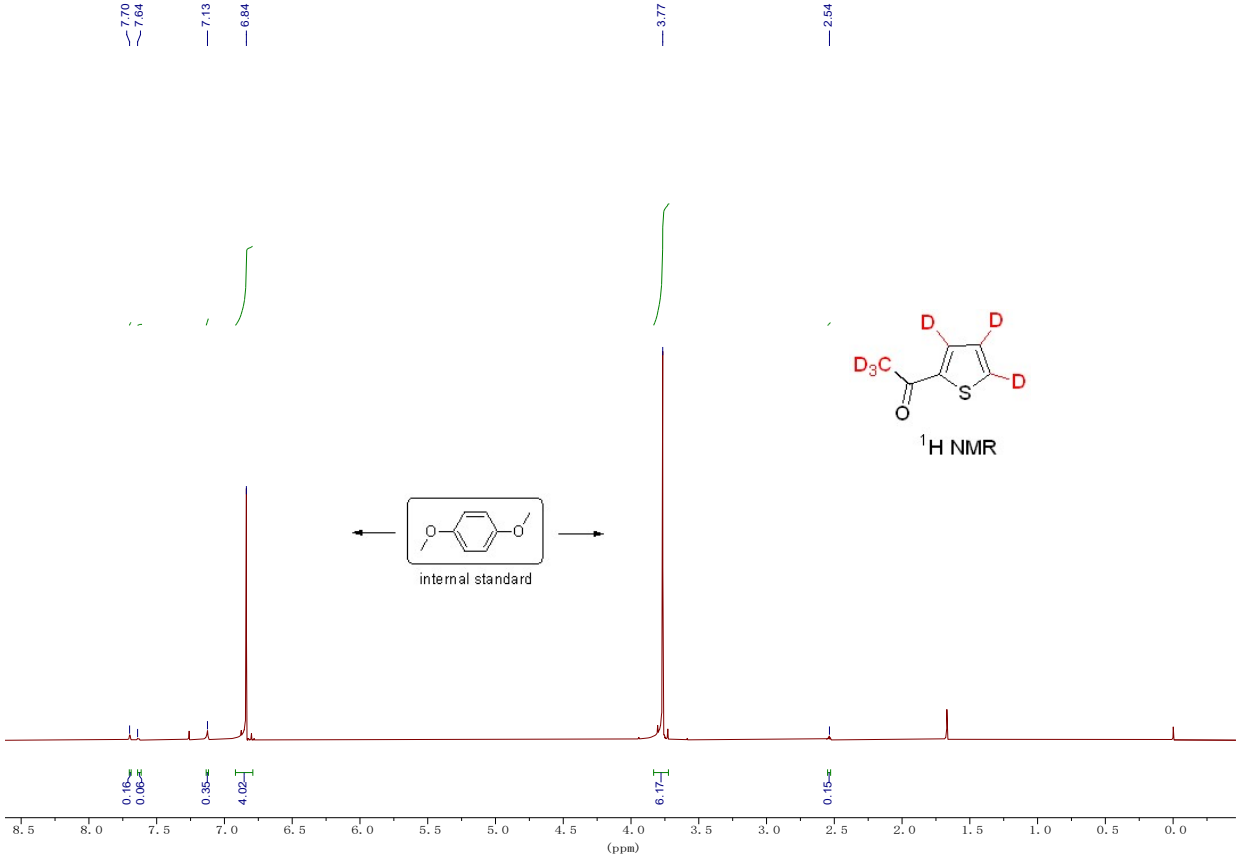

193.3
143.9
142.1
139.7
131.9
131.7
131.4
128.2
126.8
125.8
123.8
27.2
D
O
S
CD3
13C NMR (in DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

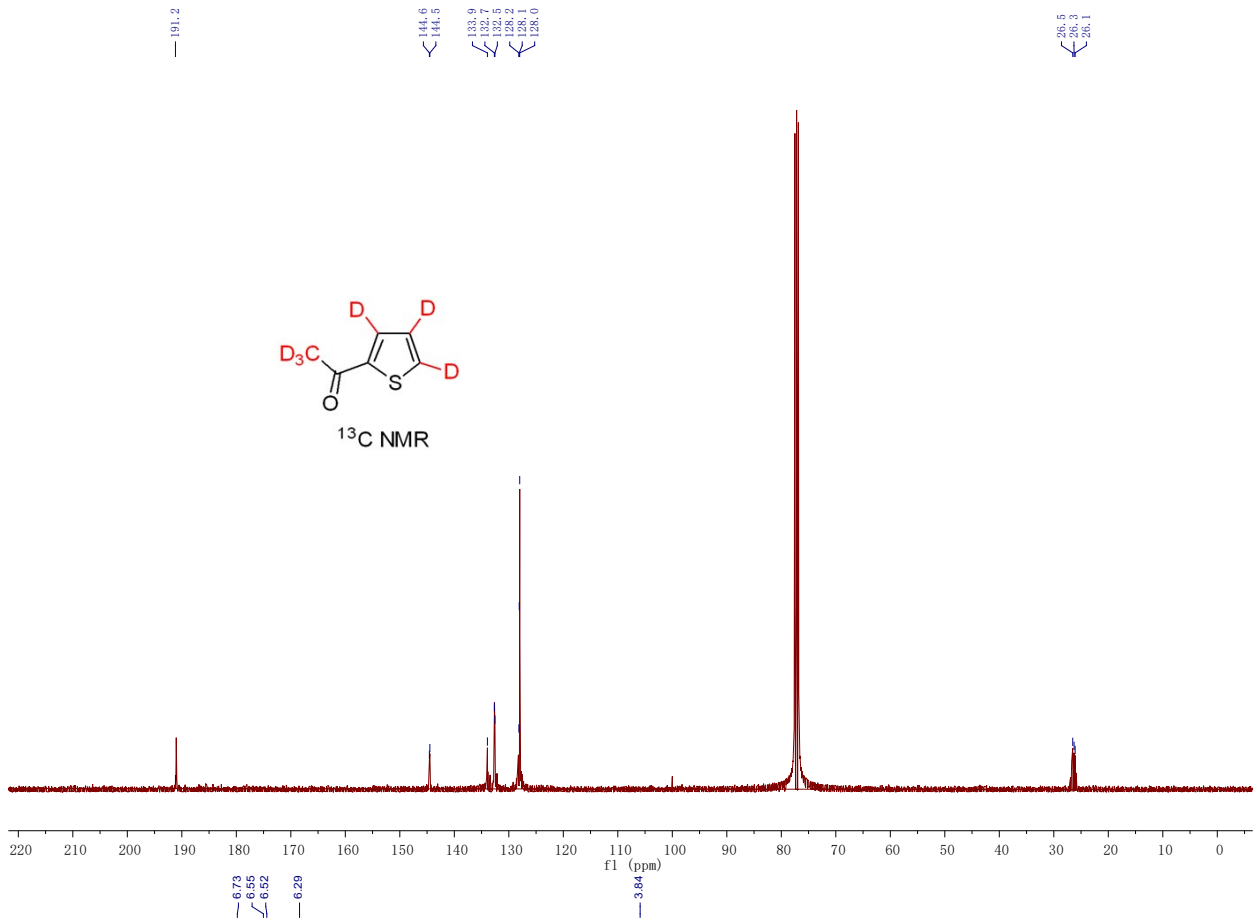

7.57
7.21
6.97
6.09
3.71
D
D
Br
S
D
1H NMR (in DMSO-d6)
O
O
internal standard
0.05
0.05
0.04
3.00
9.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

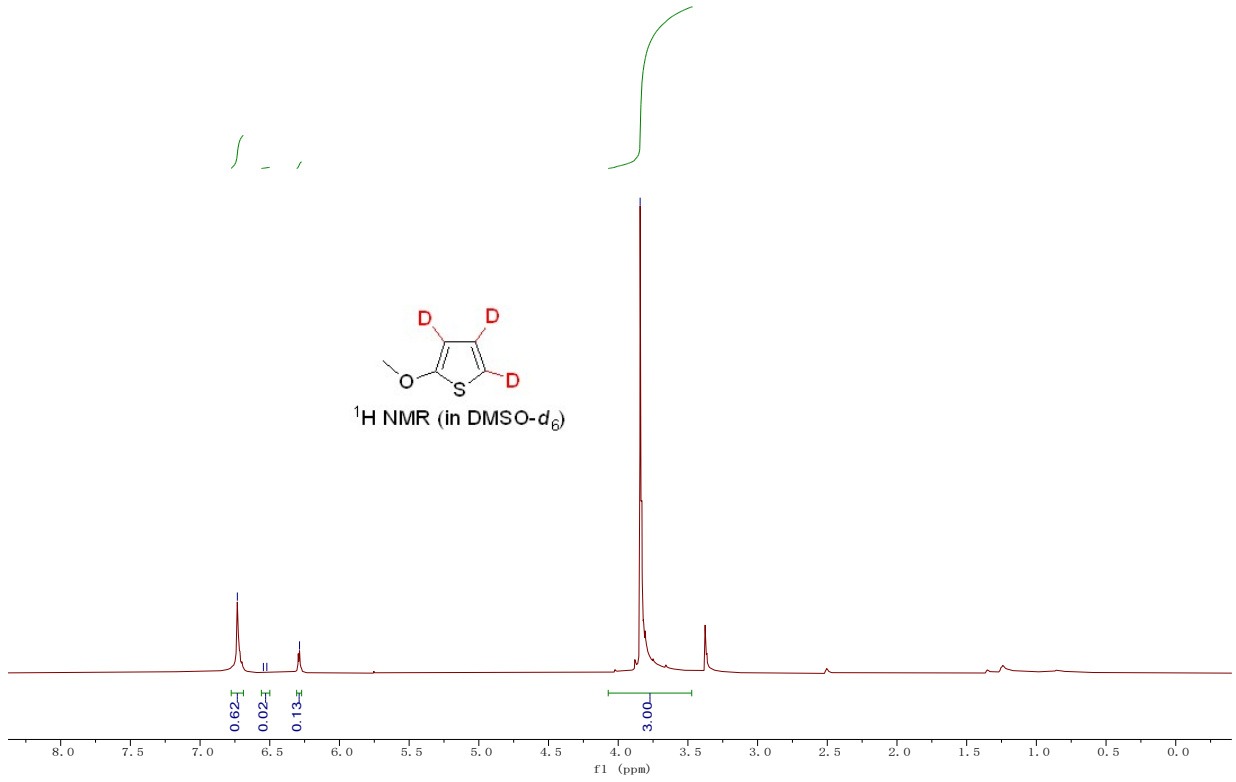

7.64
7.33
6.87
6.09
3.71
D
D
I
S
D
^{1}H NMR (in DMSO-d_6)
internal standard
0.05
0.05
0.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

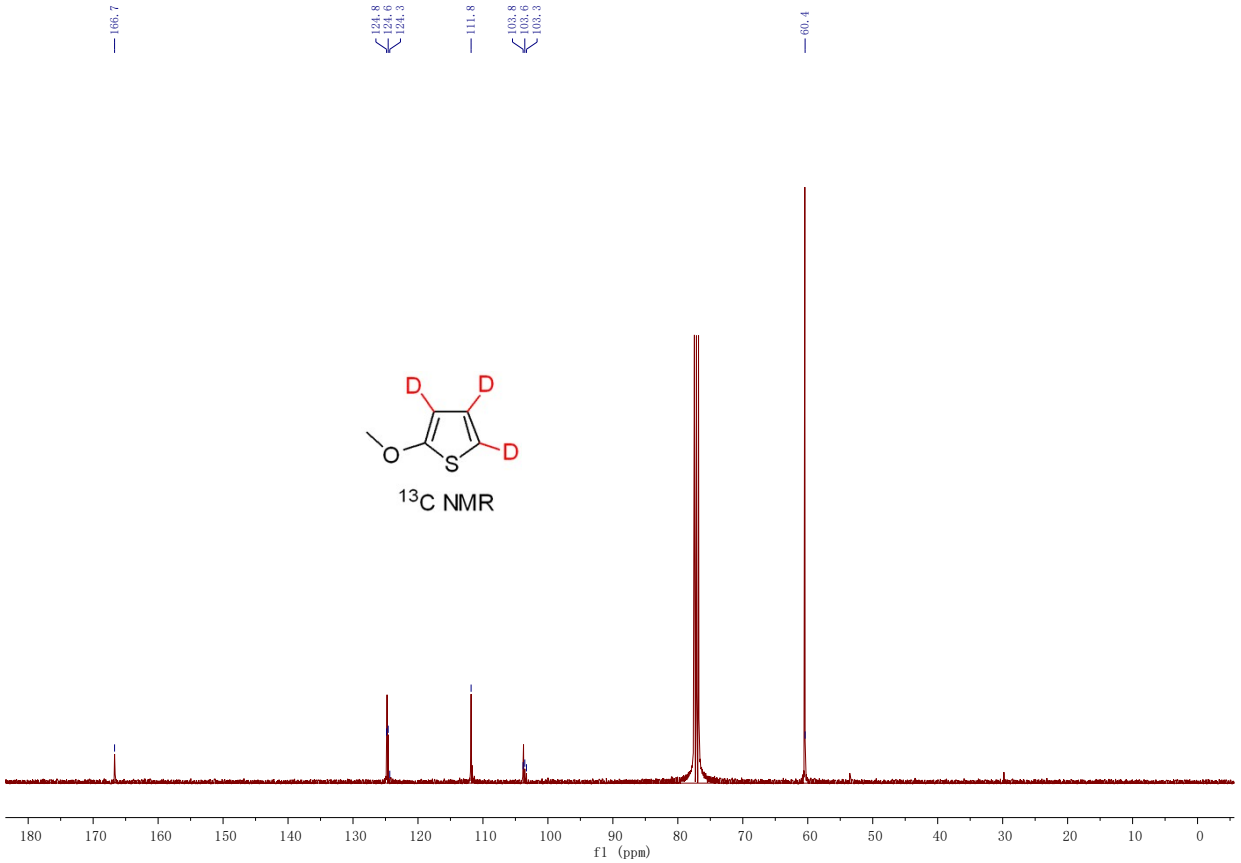

9.90
8.60
7.69
7.48
6.86
6.85
6.85
3.69
D
D
D
D
S
O
^{1}H NMR (in DMSO-d_6)
internal standard
0.87
0.05
0.05
0.48
4.00
6.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

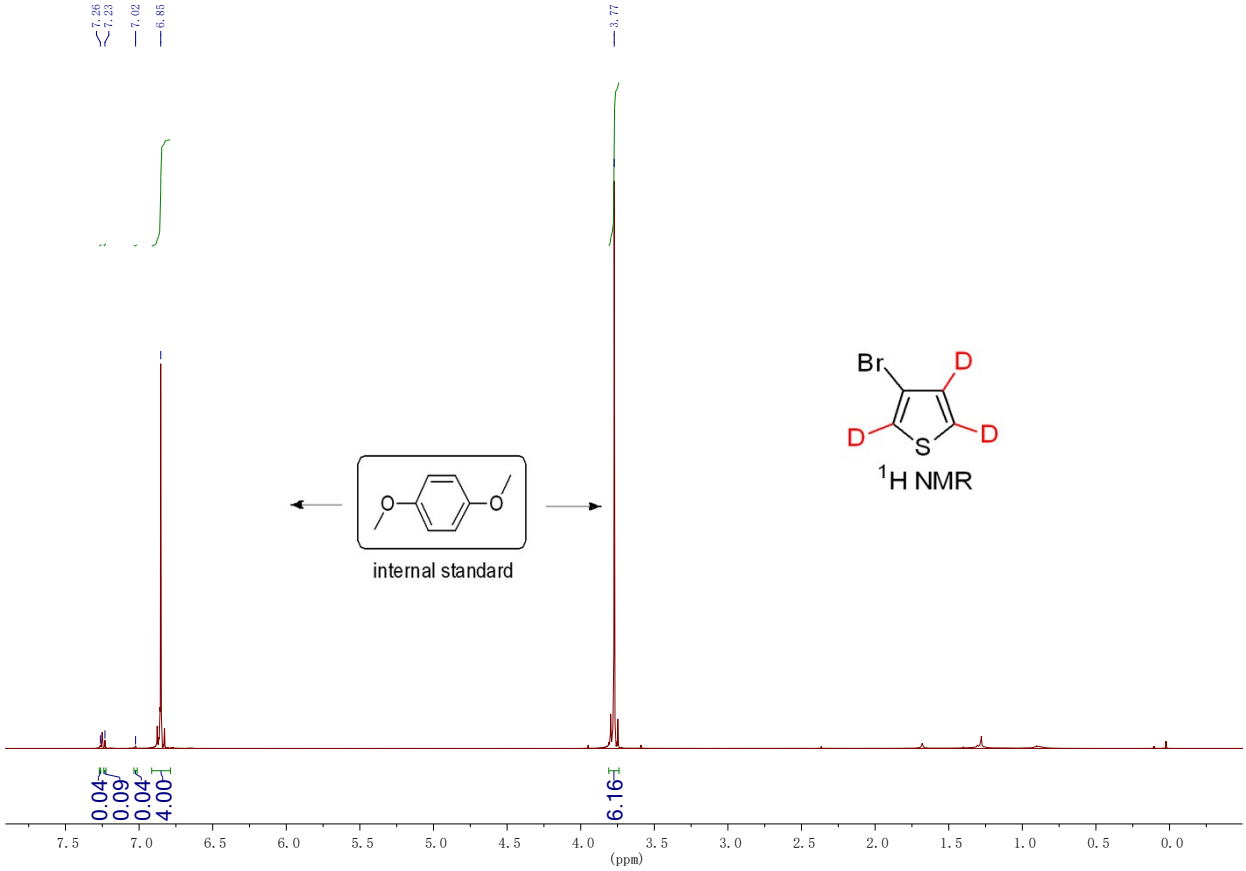

187.0
143.5
139.9
139.6
139.3
129.6
129.3
129.0
125.4
D
D
D
D
S
O
^{13}C NMR (in DMSO-d_6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

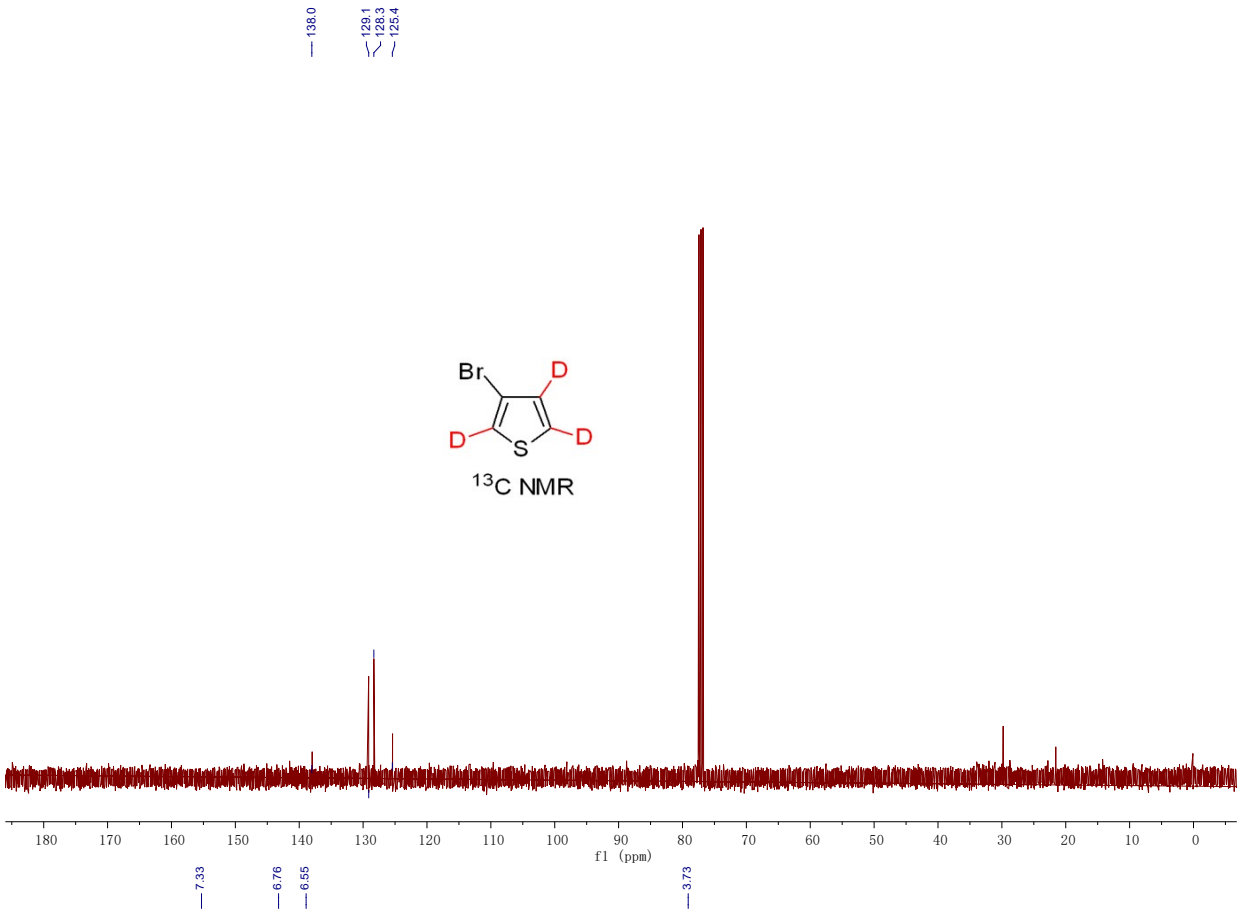

7.70
7.64
7.13
6.84
3.77
2.54
D
D
D_3C
D
S
O
^{1}H NMR
O
O
internal standard
0.16
0.06
0.35
4.02
6.17
0.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

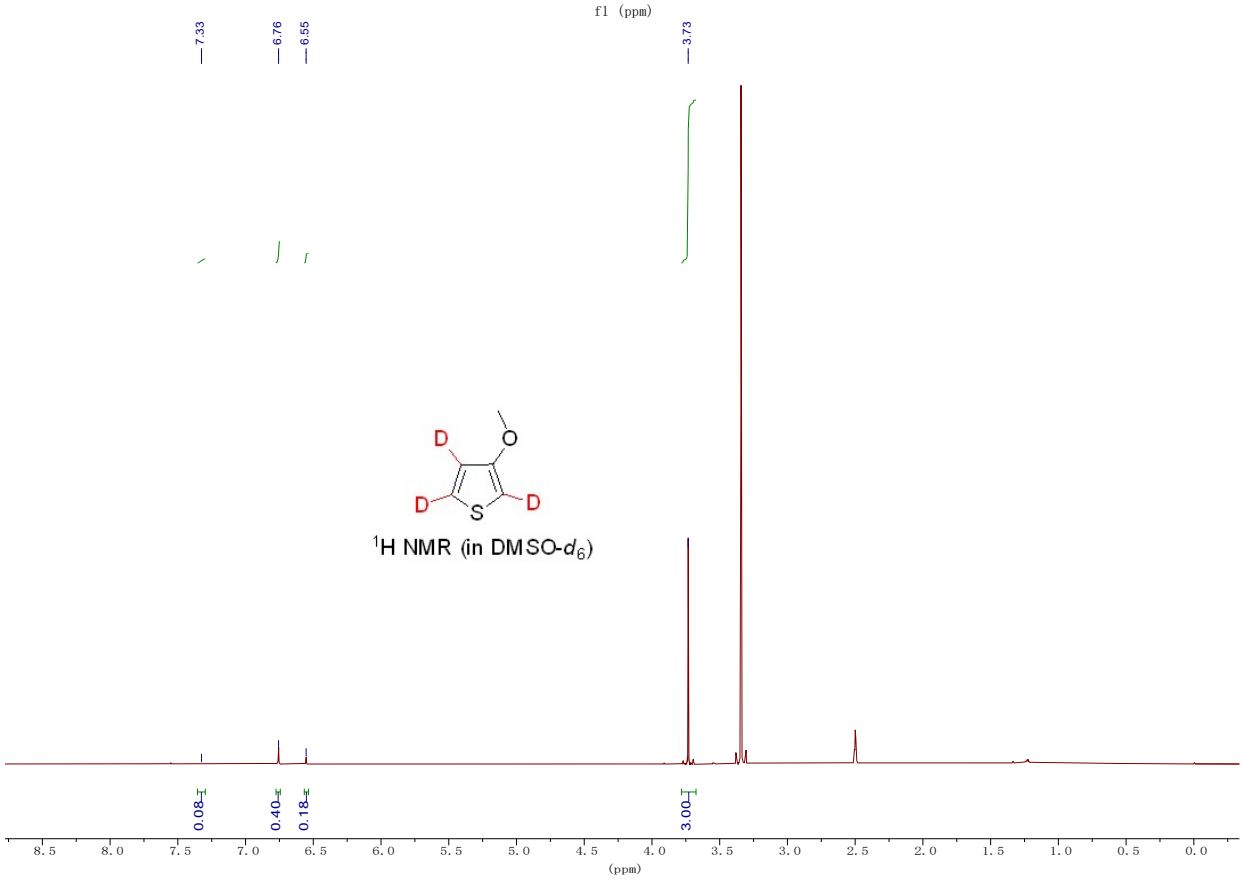

191.2
144.6
144.5
133.9
132.7
132.5
128.2
128.1
128.0
26.5
26.3
26.1
D
D
D3C
S
D
O
13C NMR
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

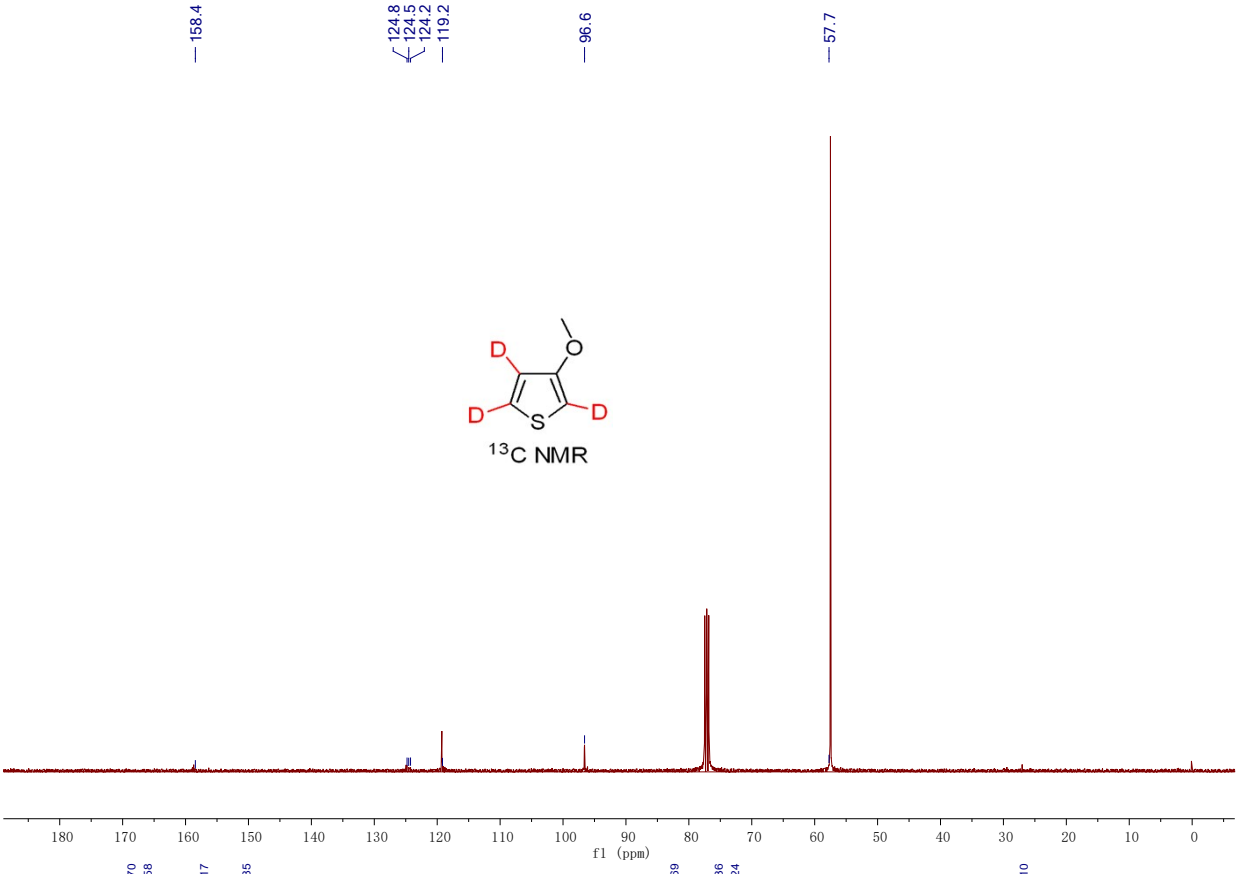

6.73
6.55
6.52
6.29
3.84
D
D
O
S
D
1H NMR (in DMSO-d6)
0.62
0.02
0.13
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

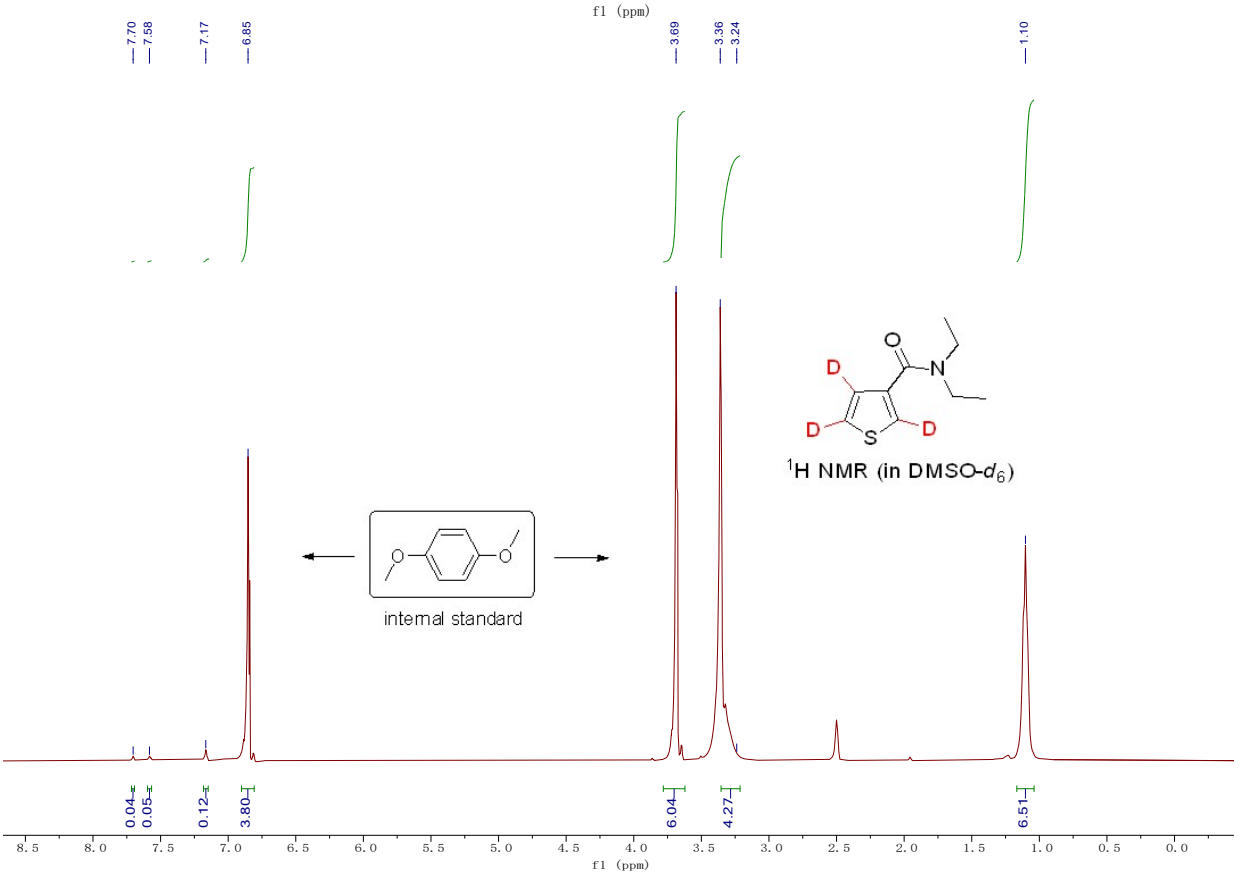

166.7
124.8
124.6
124.3
111.8
103.8
103.6
103.3
60.4
D
D
D
O
S
^{13}C NMR
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

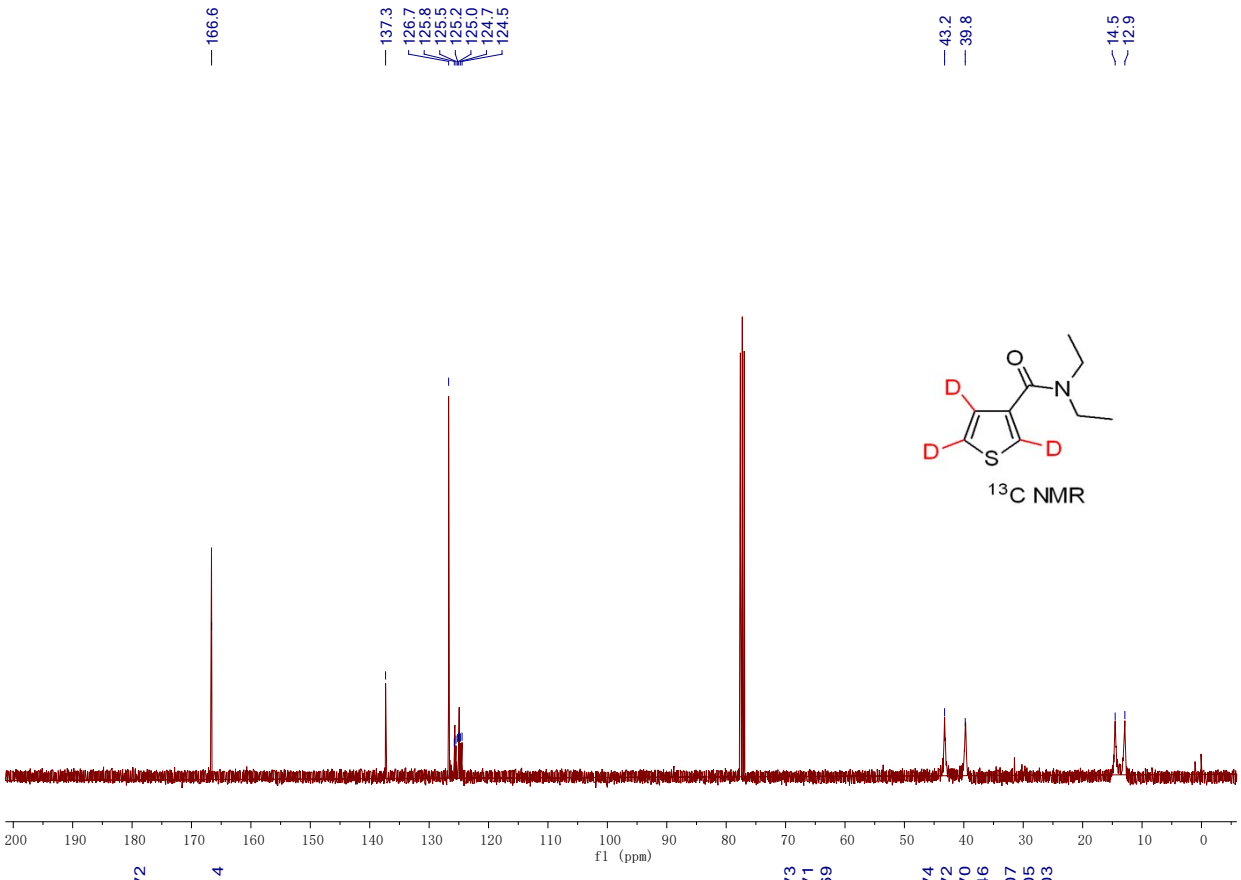

7.26
7.23
7.02
6.85
3.77
Br
D
D
D
S
^{1}H NMR
O
O
internal standard
0.04
0.09
0.04
4.00
6.16
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

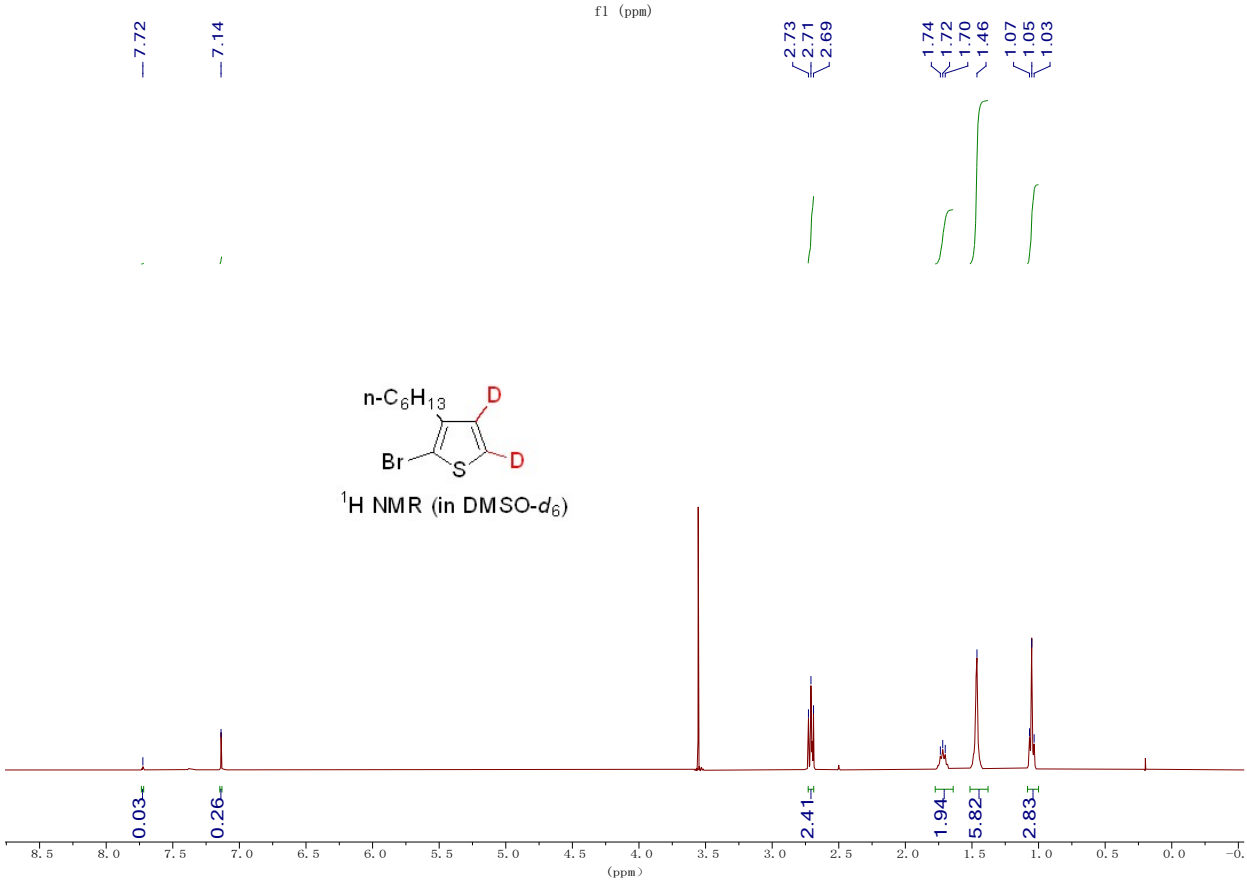

138.0
129.1
128.3
125.4
Br
D
D
D
S
13C NMR
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

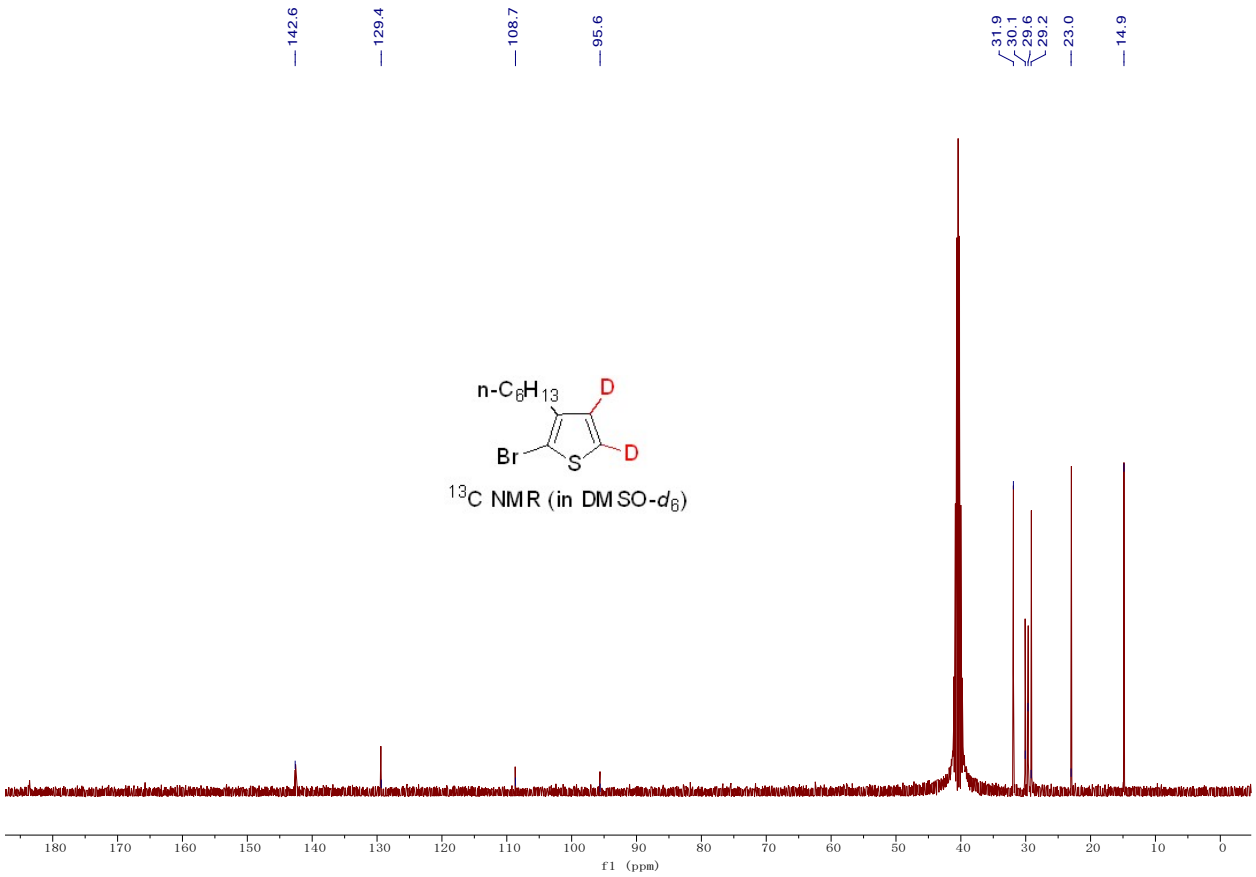

7.33
6.76
6.55
3.73
D
O
D
D
S
1H NMR (in DMSO-d6)
0.08
0.40
0.18
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

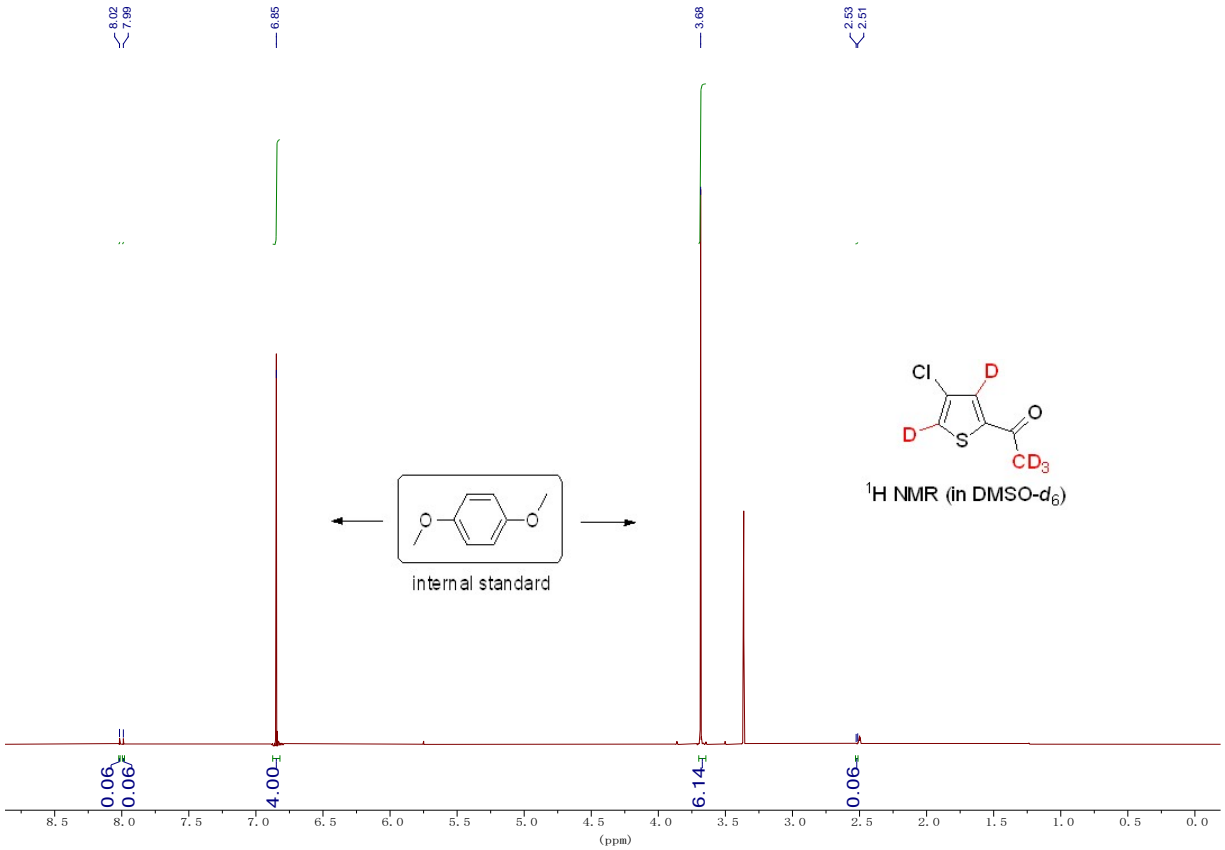

158.4
124.8
124.5
124.2
119.2
96.6
57.7
D
O
D
D
S
13C NMR
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

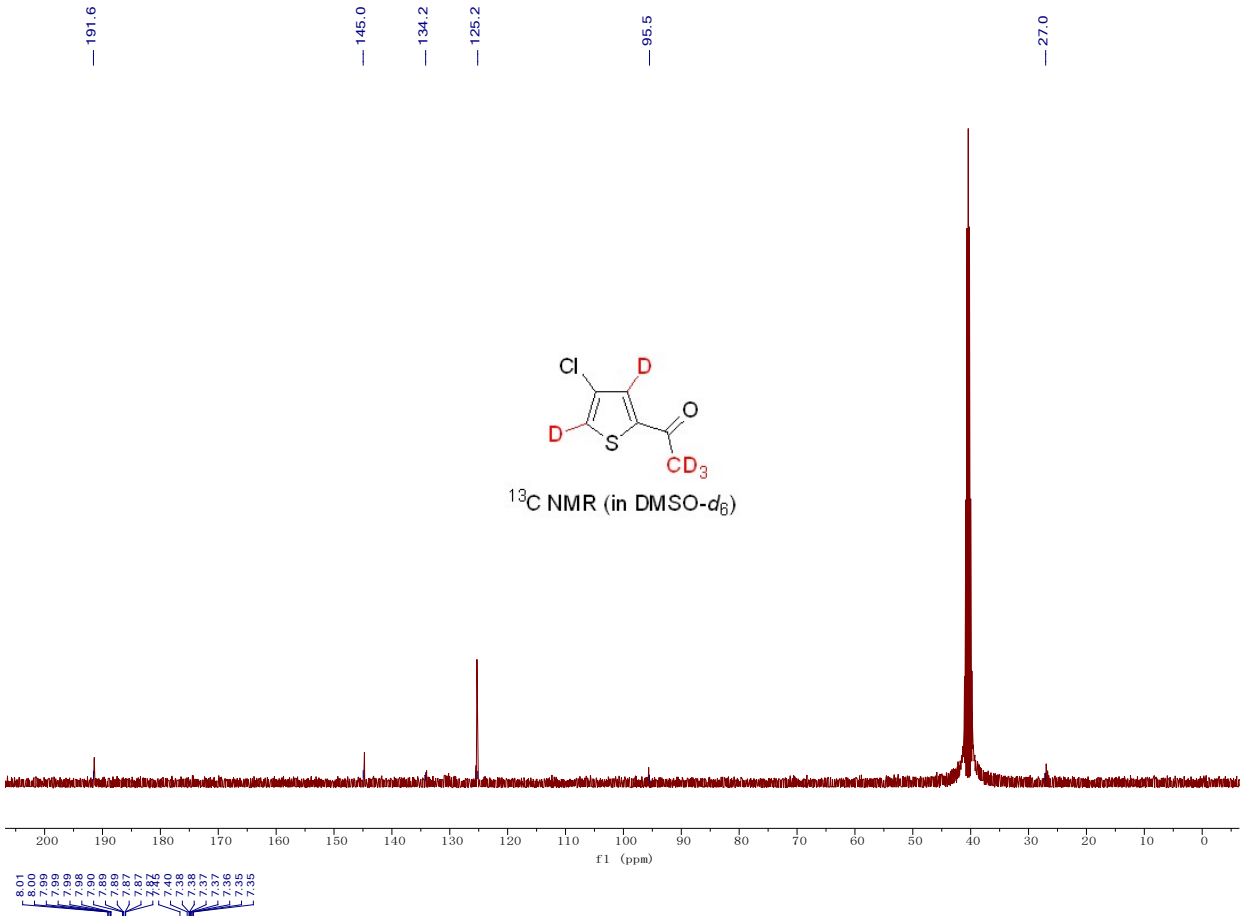

7.70
7.58
7.17
6.85
3.69
3.36
3.24
1.10
O
N
D
D
D
S
1H NMR (in DMSO-d6)
O
O
internal standard
0.04
0.05
0.12
3.80
6.04
4.27
6.51
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

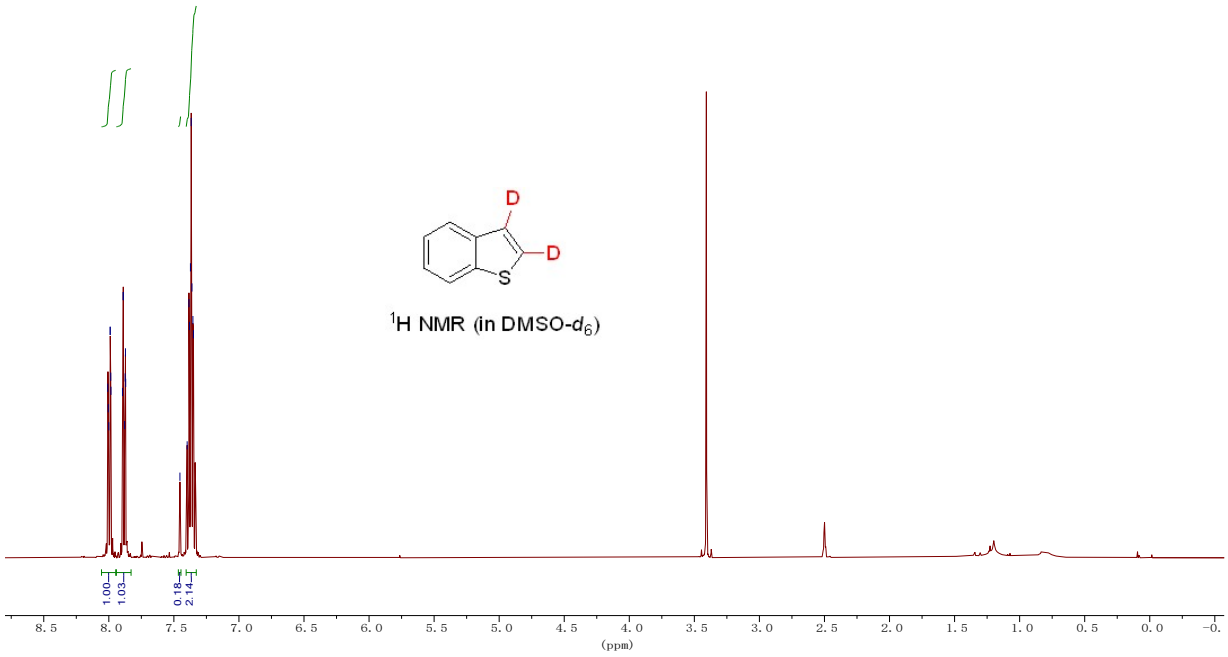

166.6
137.3
126.7
125.8
125.5
125.2
125.0
124.7
124.5
43.2
39.8
14.5
12.9
O
N
D
D
D
S
13C NMR
f1 (ppm)

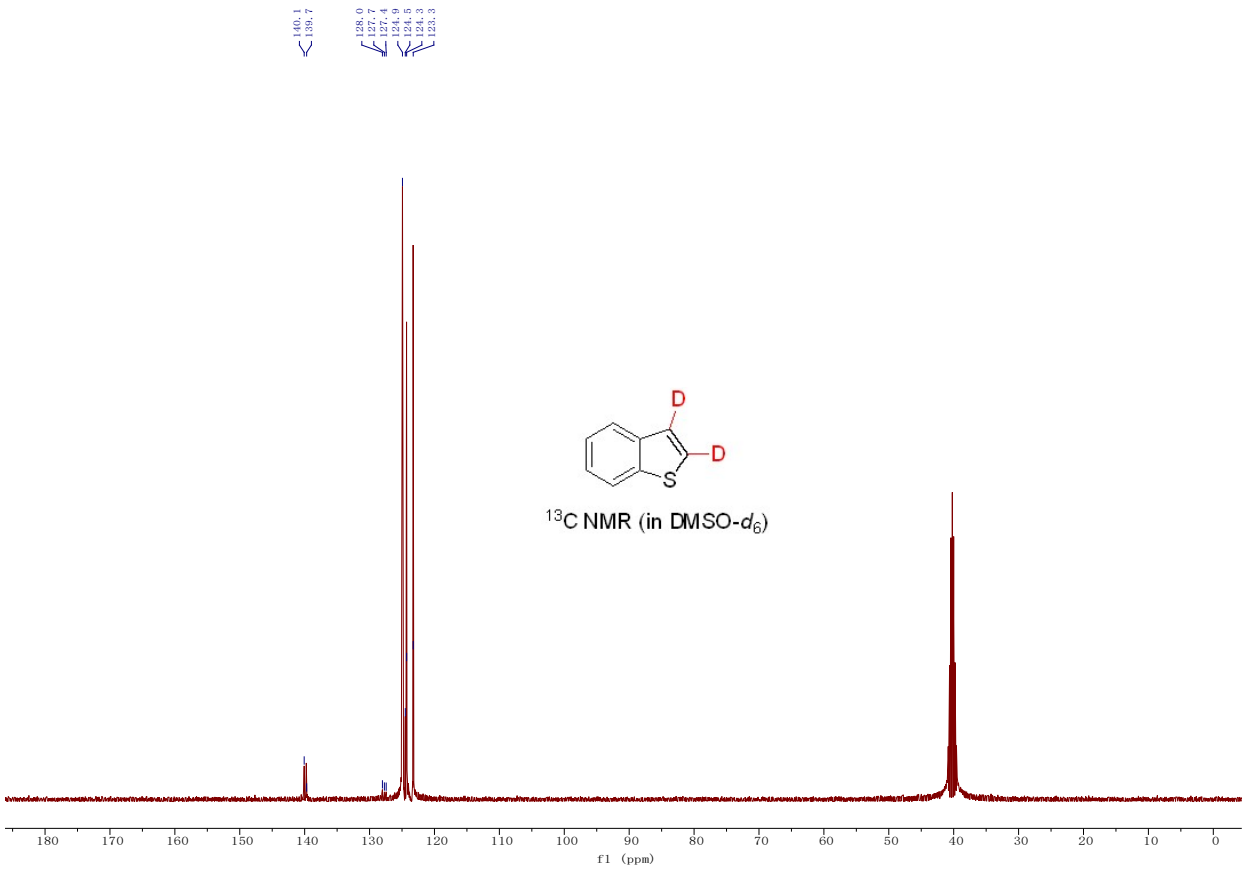

7.72
7.14
2.73
2.71
2.69
1.74
1.72
1.70
1.46
1.07
1.05
1.03
n-C6H13
D
Br
S
D
1H NMR (in DMSO-d6)
0.03
0.26
2.41
1.94
5.82
2.83
(ppm)


142.6
129.4
108.7
95.6
31.9
30.1
29.6
29.2
23.0
14.9
n-C6H13
D
Br
S
D
13C NMR (in DMSO-d6)
f1 (ppm)

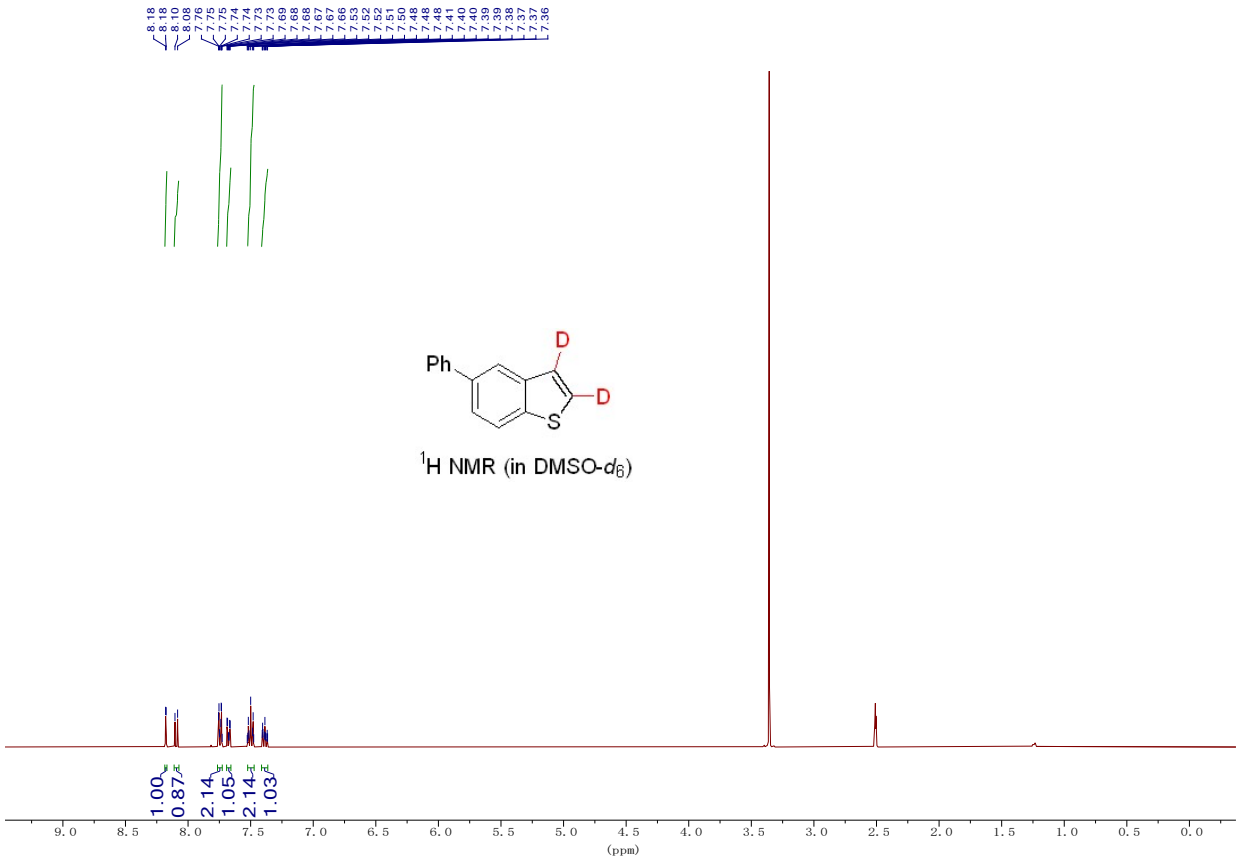

8.02
7.99
6.85
3.68
2.53
2.51
Cl
D
D
S
O
CD3
1H NMR (in DMSO-d6)
internal standard
0.06
0.06
4.00
6.14
0.06
(ppm)


191.6
145.0
134.2
125.2
95.5
27.0
Cl
D
O
D
S
CD3
13C NMR (in DMSO-d6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
8.01
8.00
7.99
7.99
7.99
7.98
7.98
7.89
7.89
7.87
7.87
7.42
7.40
7.38
7.38
7.37
7.36
7.35

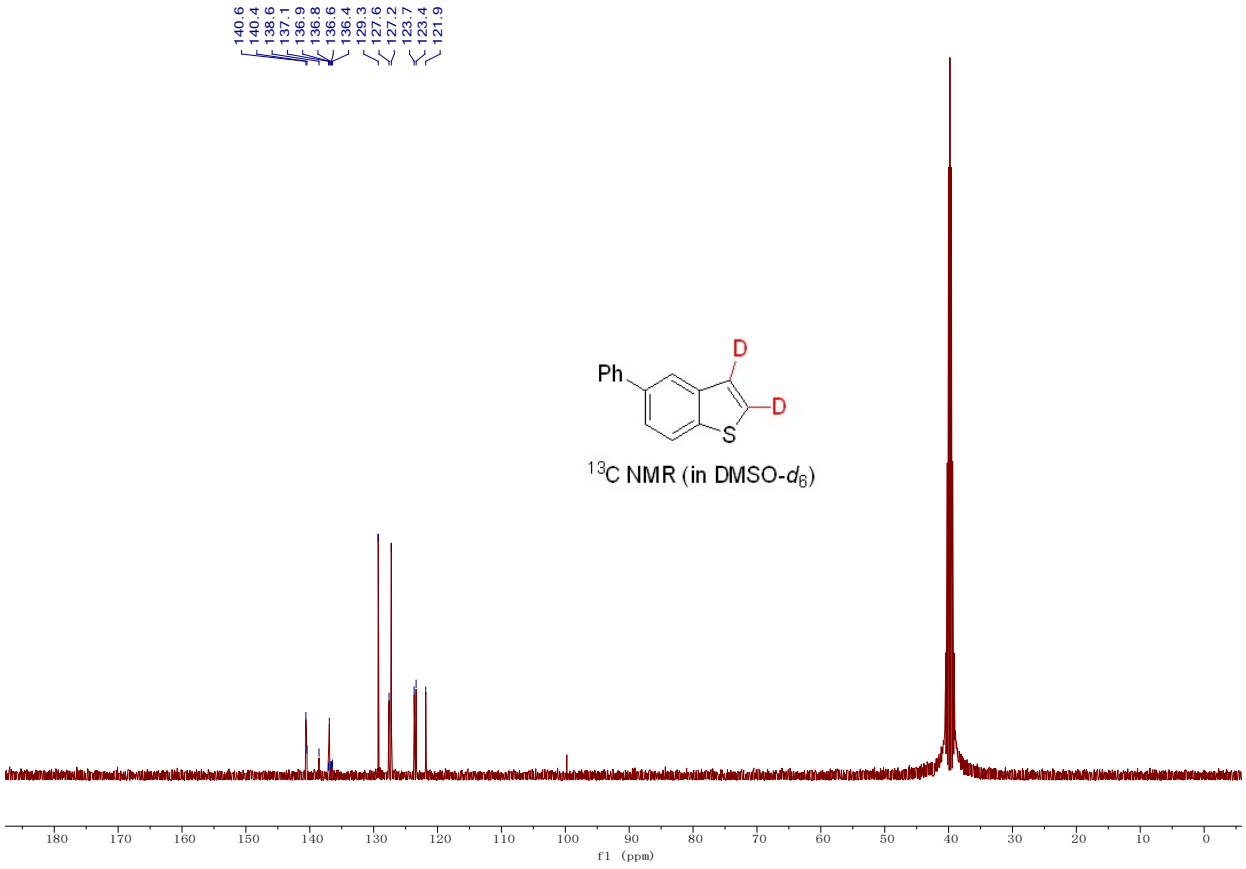

D
D
S
1H NMR (in DMSO-d6)
1.00
1.03
0.18
2.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
(ppm)



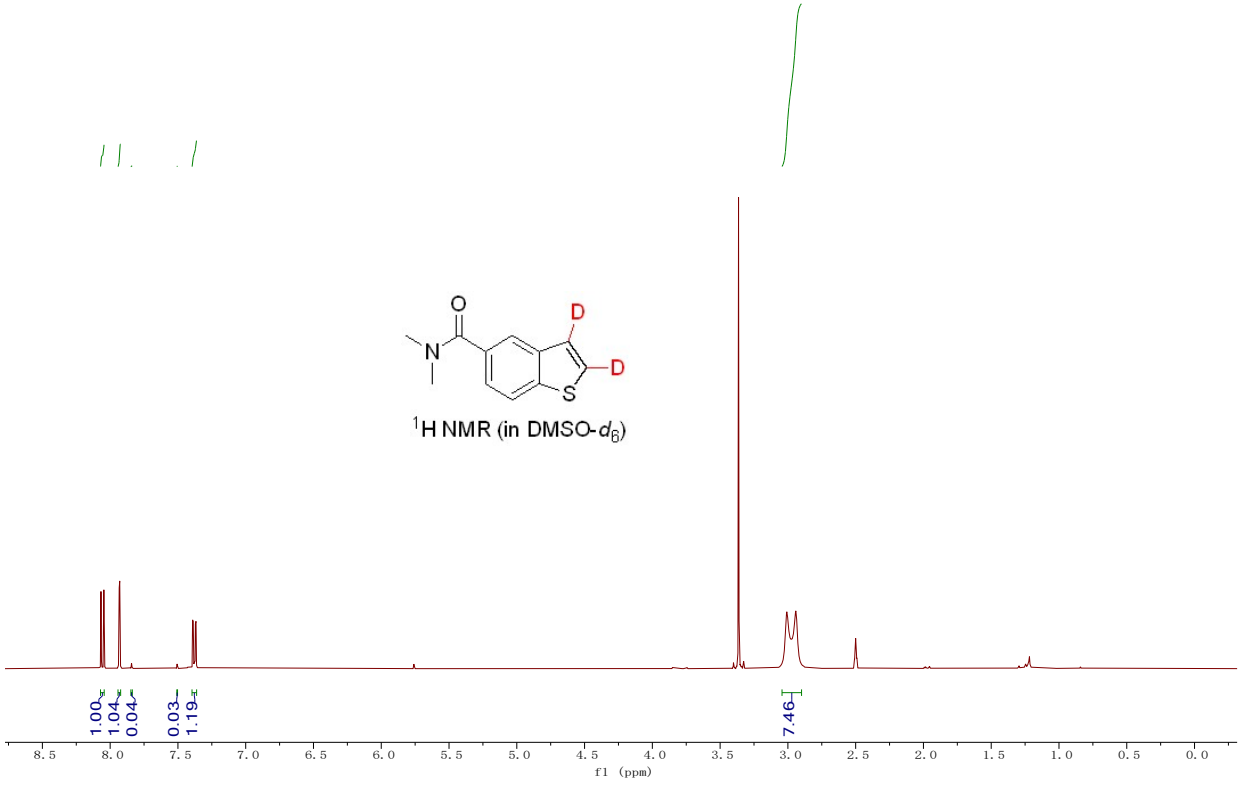
^{13}C NMR (in DMSO-d_6)



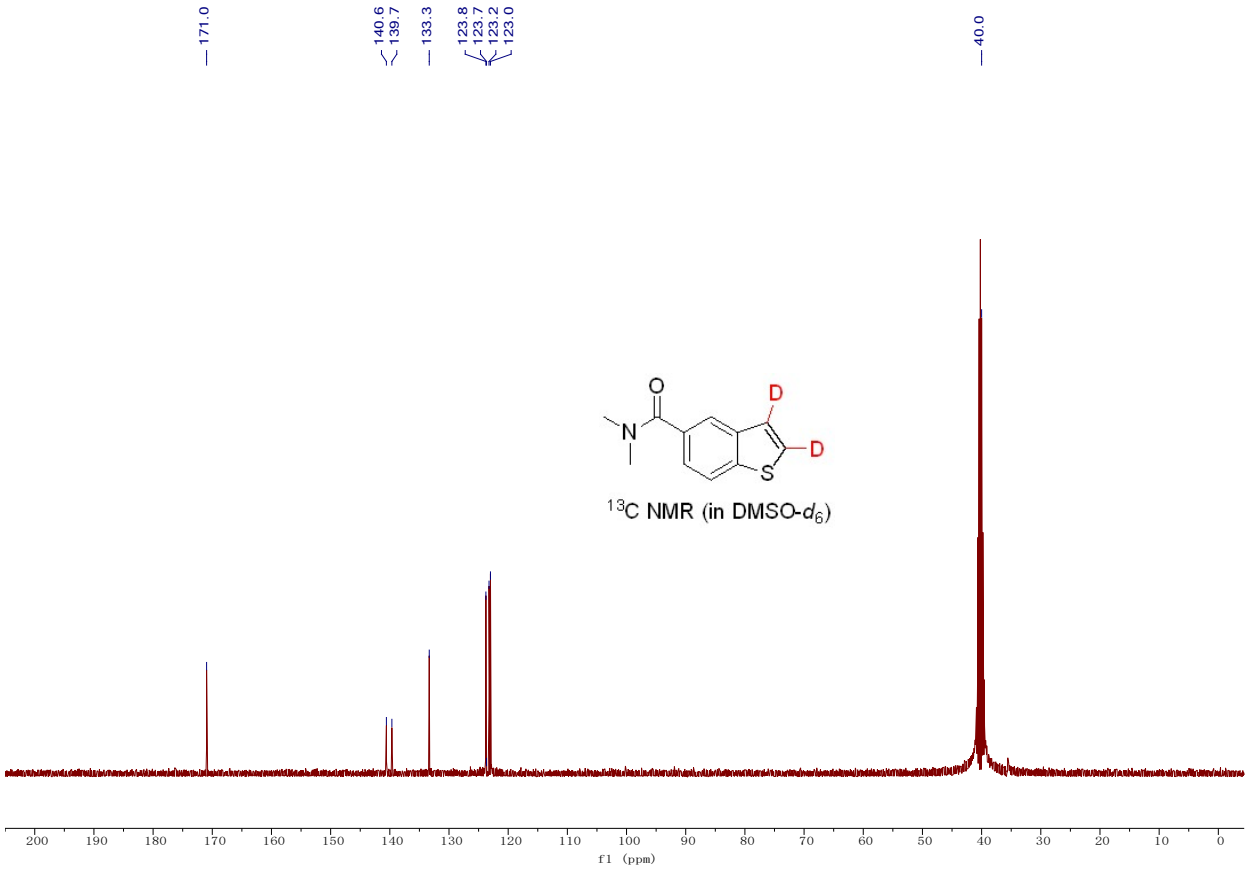
^{1}H NMR (in DMSO-d_6)

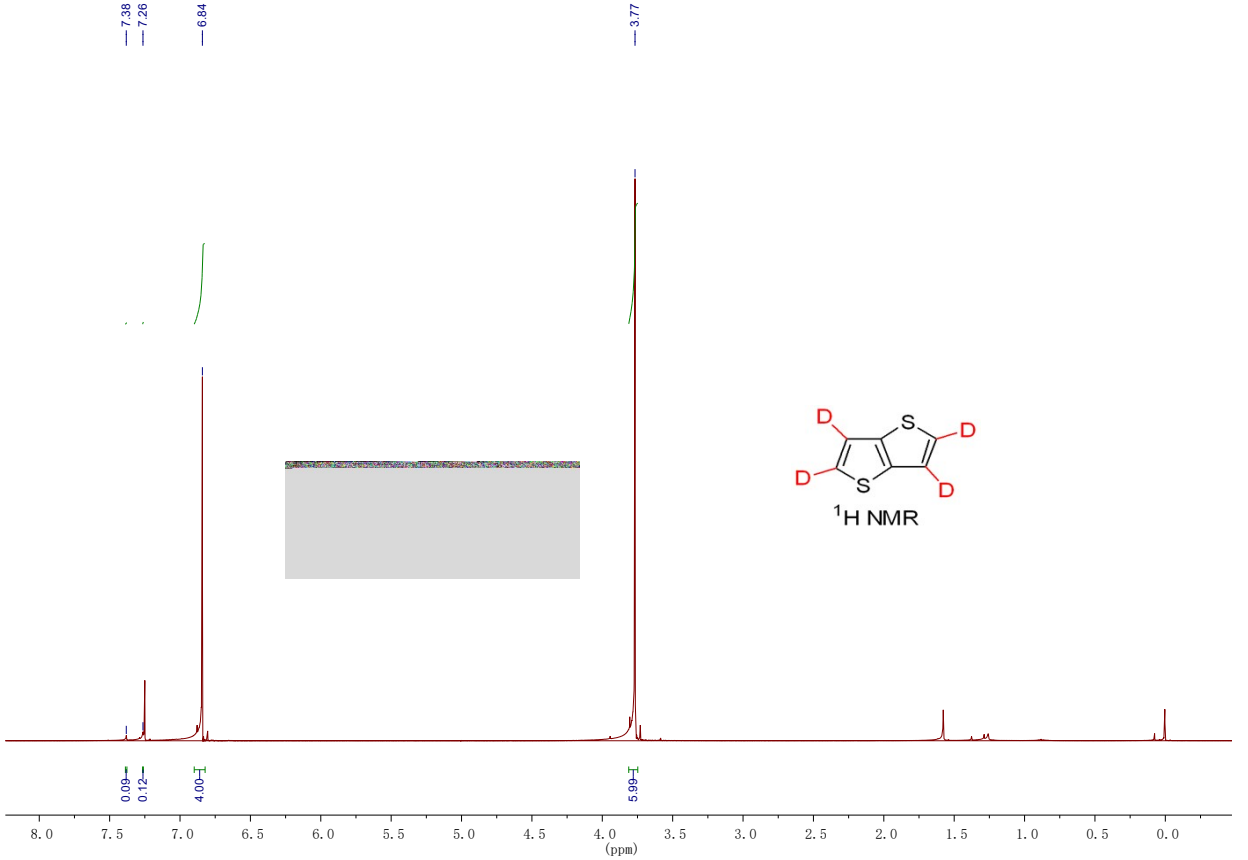


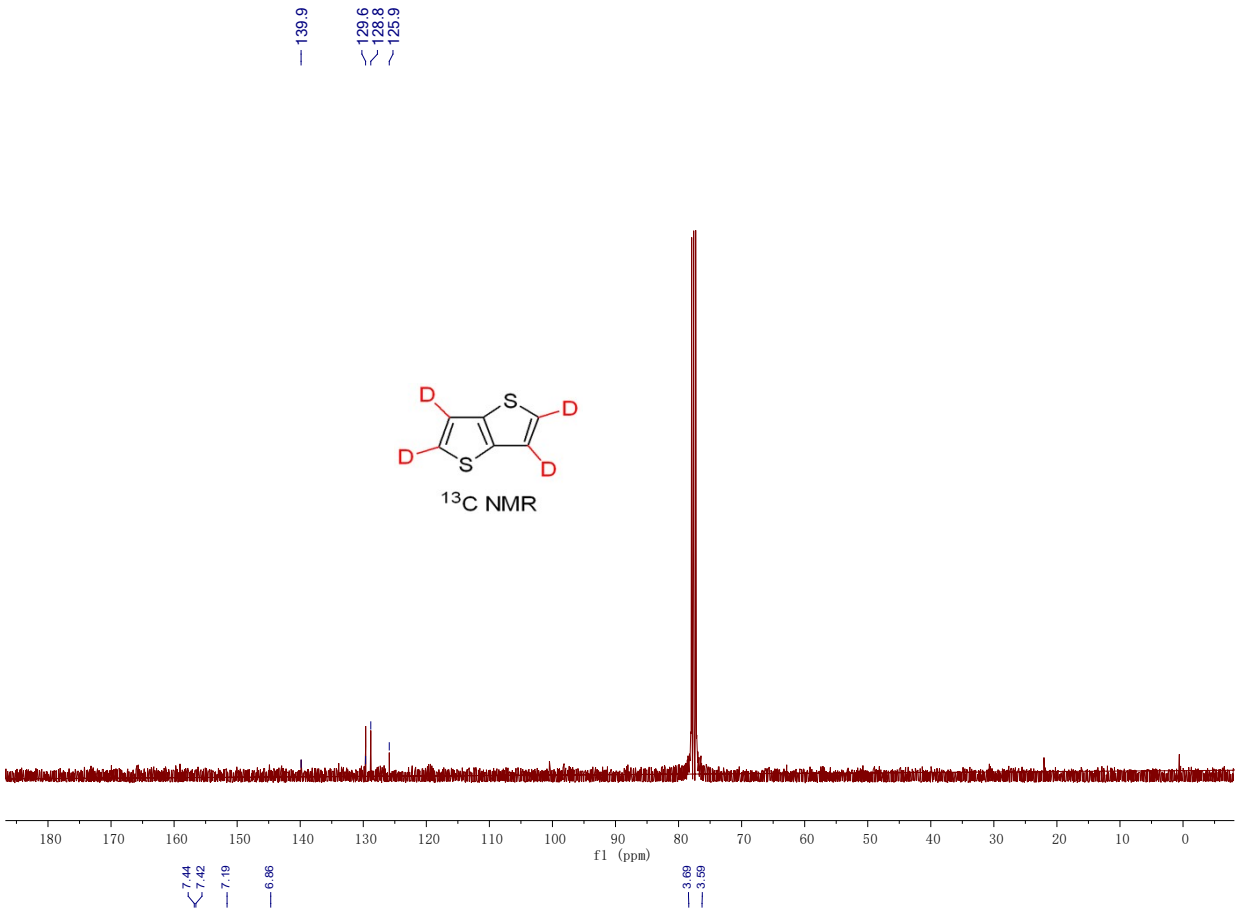
^{13}C NMR (in DMSO-d_6)

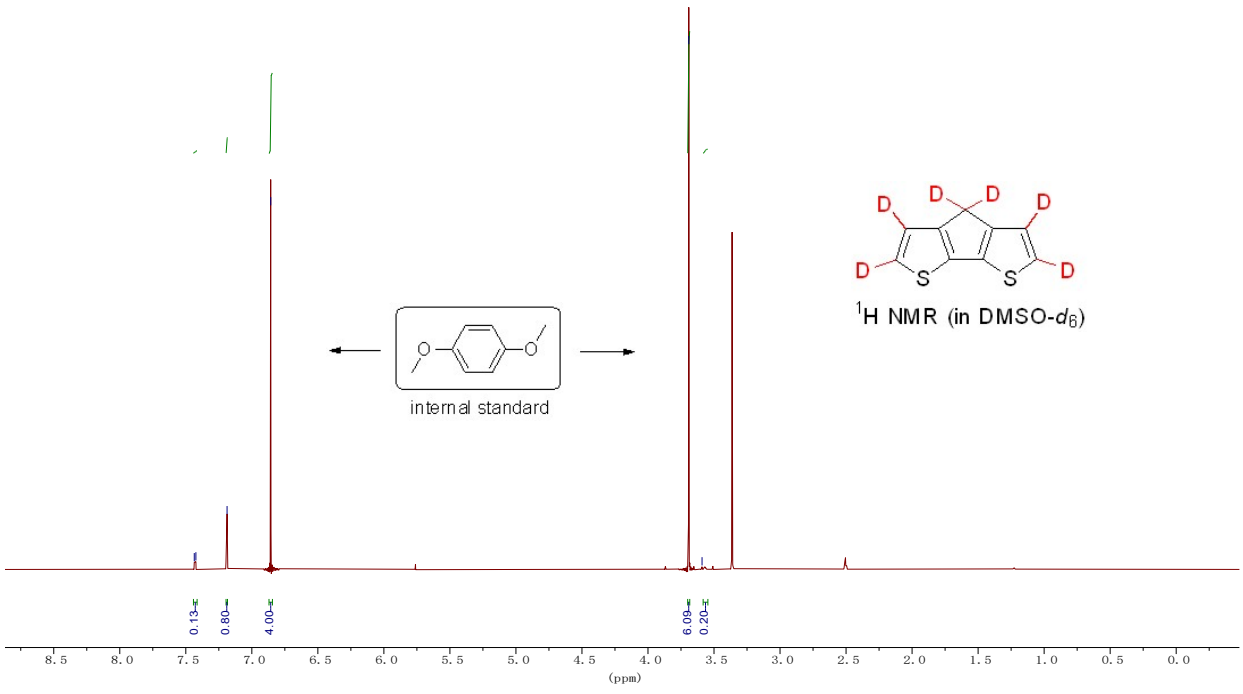


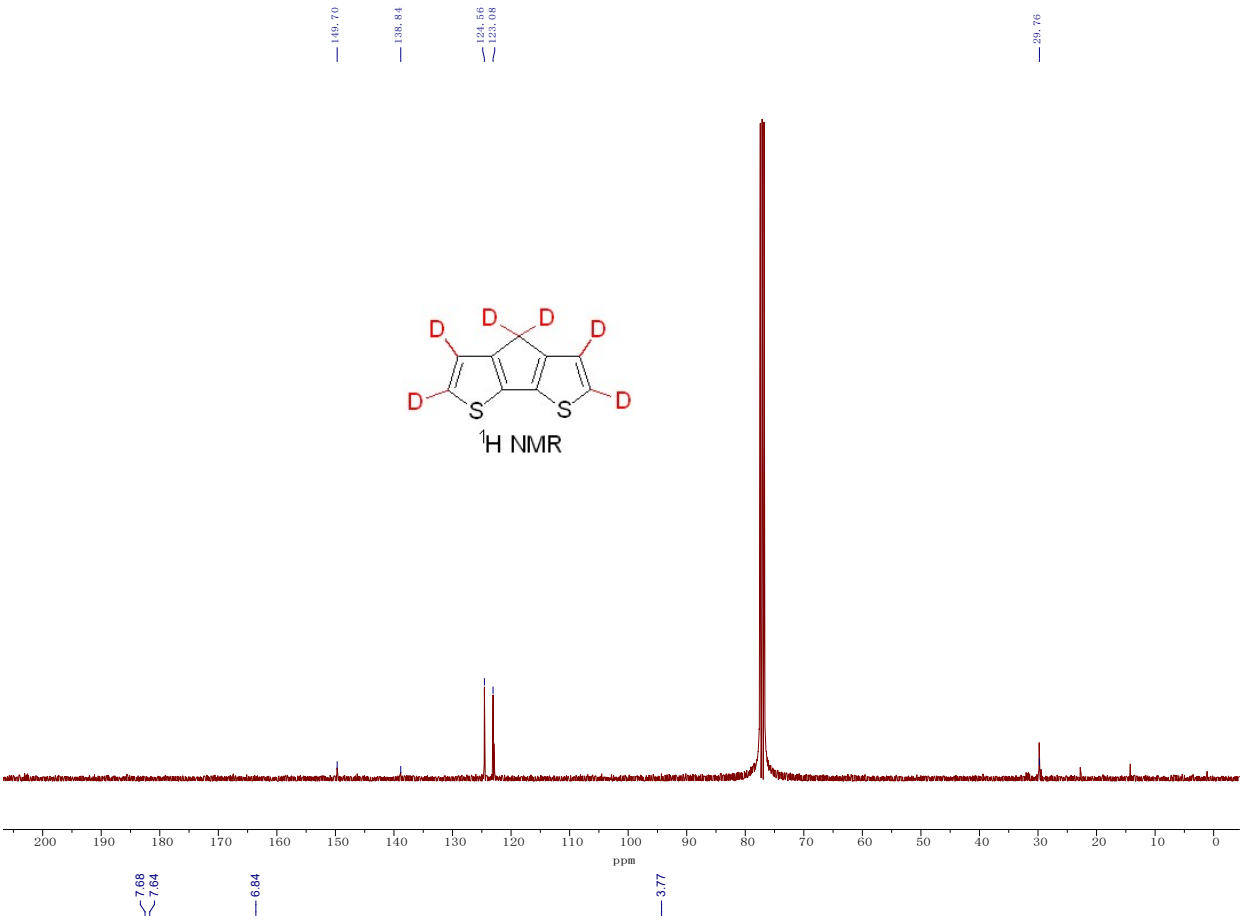
^{1}H NMR (in DMSO-d_6)

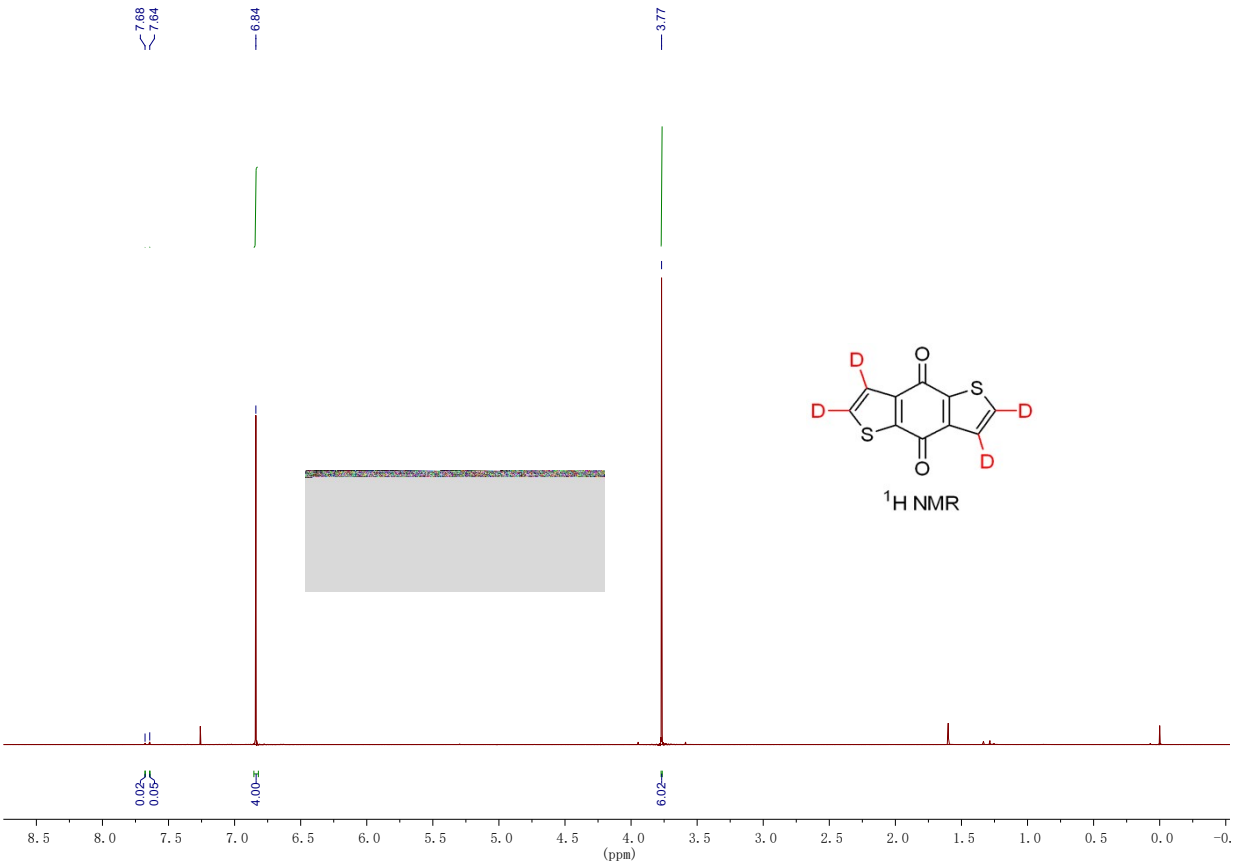

171.0
140.6
139.7
133.3
123.8
123.7
123.2
123.0
40.0
O
N
D
D
S
^{13}C NMR (in DMSO-d_6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

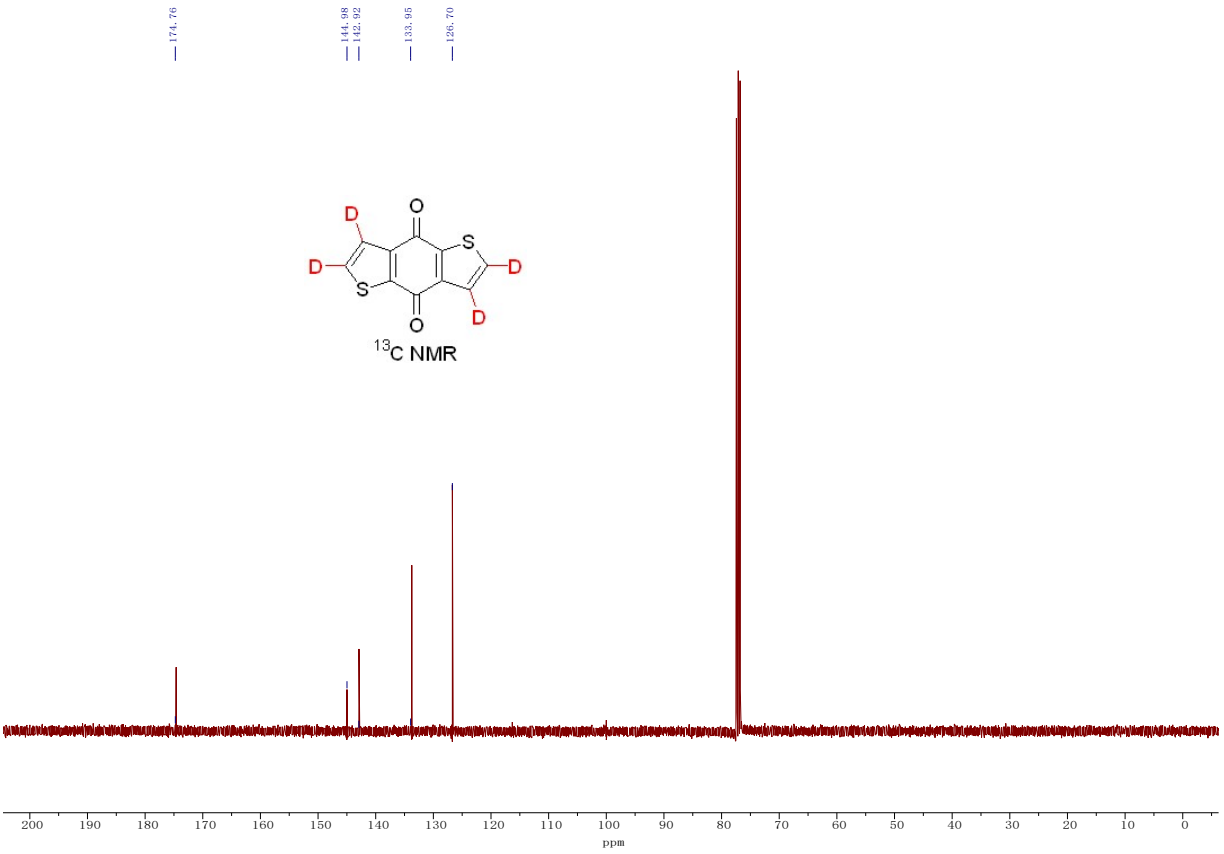

7.38
7.26
6.84
3.77
D
S
D
D
D
S
^{1}H NMR
0.09
0.12
4.00
5.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

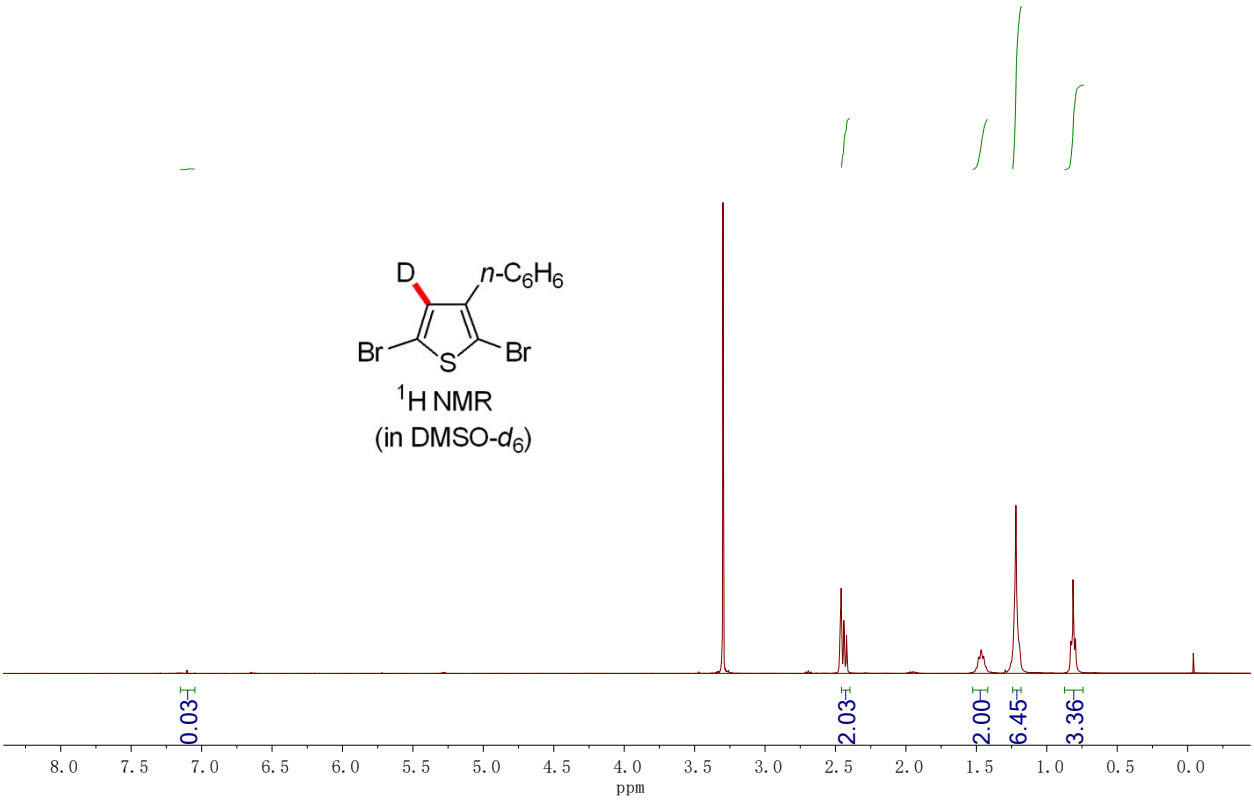

139.9
129.6
128.8
125.9
D
S
D
D
S
D
13C NMR
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
7.44
7.42
7.19
6.86
3.69
3.59

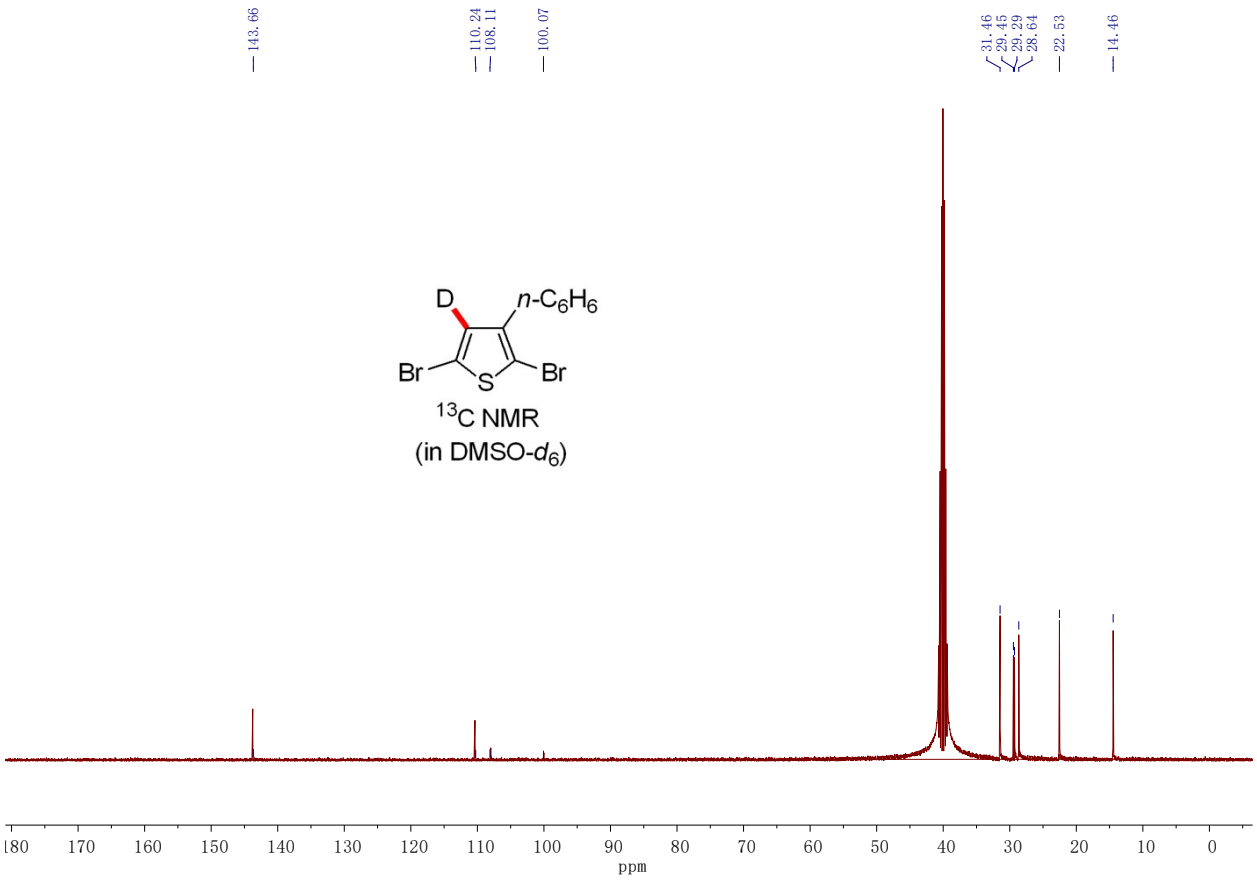

D
D
D
D
D
S
S
D
1H NMR (in DMSO-d6)
O
O
internal standard
0.13
0.80
4.00
6.09
0.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


149.70
138.84
124.56
123.08
29.76
D
D
D
D
D
D
S
S
^{1}H NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.68
7.64
6.84
3.77
D
D
O
S
S
D
D
O
^{1}H NMR
0.02
0.05
4.00
6.02
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.
(ppm)


174.76
144.98
142.92
133.95
126.70
D
O
S
D
D
S
D
O
^{13}C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


D
n-C6H6
Br
S
Br
^{1}H NMR
(in DMSO-d_6)
0.03
2.03
2.00
6.45
3.36
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
ppm


143.66
110.24
108.11
100.07
31.46
29.45
29.29
28.64
22.53
14.46
D
n-C6H6
Br
S
Br
13C NMR
(in DMSO-d6)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm