Supporting Information *for*

Copper-Mediated One-Pot Synthesis of 2,2-Difluoro-1,3-Benzoxathioles from *o*-Bromophenols and Trifluoromethanethiolate

Mengjia Zhang, Shouxiong Chen, and Zhiqiang Weng*

State Key Laboratory of Photocatalysis on Energy and Environment College of Chemistry, Fuzhou University, Fuzhou, 350108, China

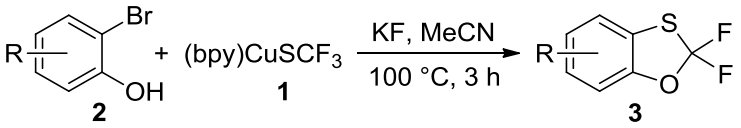
E-mail: zweng@fzu.edu.cn

Table of Contents

General information

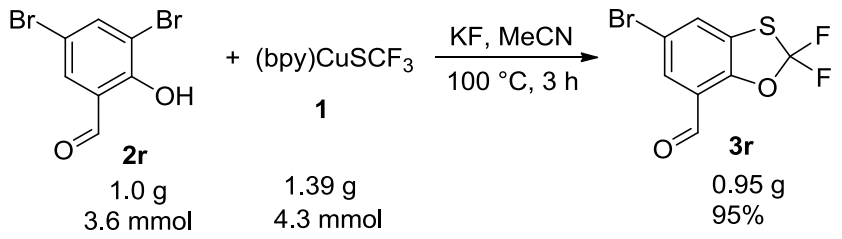
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR (chloroform δ 7.26) and ^{13}C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on Waters GCT-TOF. (bpy)$CuSCF_3$ (**1**),[1,2] $CsSCF_3$,[3] (8*R*,13*S*,14*S*)-2-bromo-3-hydroxy-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (**2ai**),[4] and 4-methoxy-2-((trifluoromethyl)thio)phenol (**3f′**)[5] were prepared according to the published procedures. Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

General procedure of copper-mediated synthesis of 2,2-difluoro-1,3-benzoxathioles



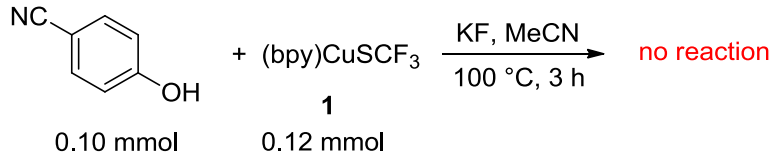
In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar were added [(bpy)$CuSCF_3$] (**1**) (116 mg, 0.36 mmol, 1.2 equiv), *o*-bromophenol (0.30 mmol, 1.0 equiv), KF (0.30 mmol, 1.0 equiv) and CH_3CN (2.50 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 3 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was diluted with *n*-pentane (20 × 3 mL), washed with saturated brine (30 mL), and water (20 mL), dried over $MgSO_4$, and filtered. The residue obtained was purified by column chromatography on silica gel with *n*-pentane/ dichloromethane or *n*-pentane/ diethyl ether.

Procedure for synthesis of 5-bromo-2,2-difluorobenzo[*d*][1,3]oxathiole-7-carbaldehyde (3r) in a 3.6 mmol scale reaction.



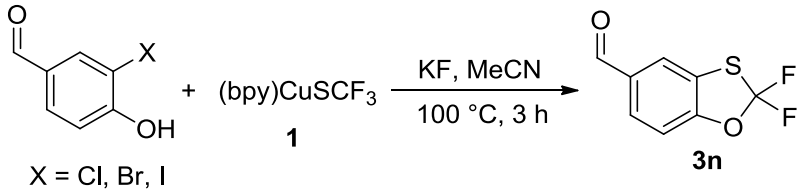
In a glove box filled with nitrogen, to an oven-dried 100 mL pressure tube equipped with a stir bar were added [(bpy)CuSCF$_3$] (**1**) (1.39 g, 4.3 mmol, 1.2 equiv), 3,5-dibromo-2-hydroxybenzaldehyde (1.0 g, 3.60 mmol, 1.0 equiv), KF (209 mg, 3.6 mmol, 1.0 equiv), and CH_3CN (25.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 3 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was diluted with *n*-pentane (50 × 3 mL), washed with saturated brine (30 mL), and water (20 mL), dried over $MgSO_4$, and filtered. The residue obtained was purified by column chromatography on silica gel with *n*-pentane/ diethyl ether to give 0.95 g of product **3r** (95% yield).

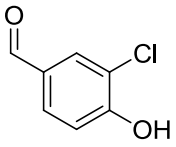
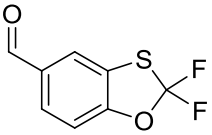
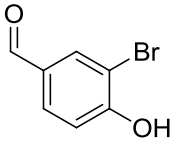
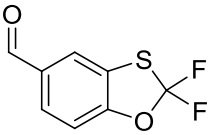
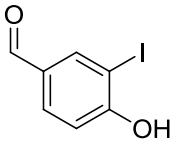
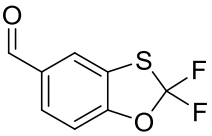
Procedure for reaction of 4-hydroxybenzonitrile with [(bpy)CuSCF$_3$] (1).



In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar were added [(bpy)CuSCF$_3$] (**1**) (38 mg, 0.12 mmol, 1.2 equiv), 4-hydroxybenzonitrile (12 mg, 0.10 mmol), KF (5.8 mg, 0.10 mmol, 1.0 equiv) and CH_3CN (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 3 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was filtered through a layer of Celite. The mixture solution was analyzed by GC/MS and ^{19}F NMR spectroscopy. No product was detected.

The effects of the halides for the reaction



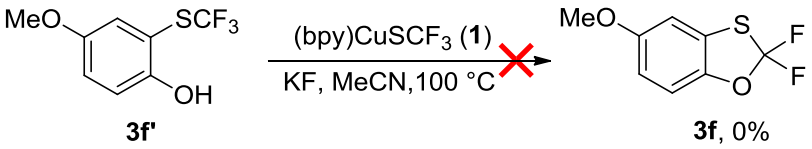
entry	*o*-halophenols	product	yield (%)
1	 **2n-1**	 **3n**	5% [a]
2	 **2n**	 **3n**	99% [b]
3	 **2n-3**	 **3n**	100% [a]

[a] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard. [b] Isolated yield

The effects of the halides were investigated with *o*-halophenol substrates **2n-1**, **2n**, and **2n-3** (entries 1–3); 3-bromo-4-hydroxybenzaldehyde (**2n**) and 4-hydroxy-3-iodobenzaldehyde (**2n-3**) were readily converted into **3n** in excellent yields (99% and 100%, respectively), while 3-chloro-4-hydroxybenzaldehyde (**2n-1**) was only difluoromethylenated in 5% yield (^{19}F NMR).

Mechanism exploratory experiment

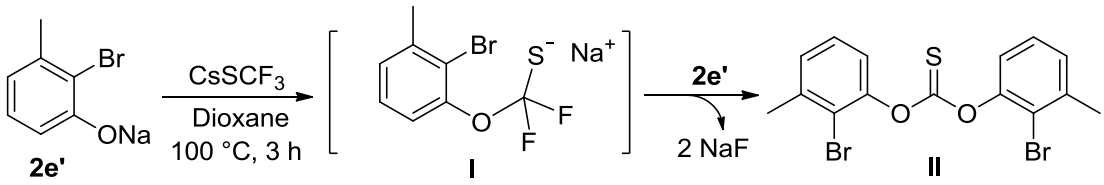
Procedure for the attempted transformation of 4-methoxy-2-((trifluoromethyl)thio)phenol 3f′ to 2,2-difluoro-1,3-benzoxathiole product 3f



3f' **3f**, 0%

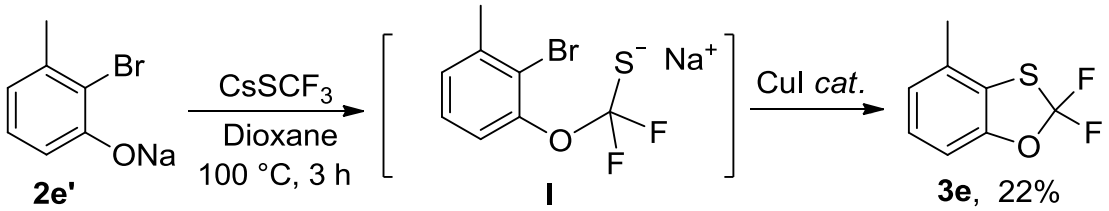
In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added compound **3f′** (22.4 mg, 0.10 mmol), [(bpy)$CuSCF_3$] (**1**) (38.8 mg, 0.12 mmol, 1.2 equiv), KF (7.1 mg, 0.12 mmol, 1.2 equiv), MeCN (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 3 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was filtered through a layer of Celite. No 2,2-difluoro-5-methoxybenzo[*d*][1,3]oxathiole (**3f**) was detected by ^{19}F NMR spectroscopy.

Procedure for the attempted isolation of *O*,*O*-bis(2-bromo-3-methylphenyl) carbonothioate II



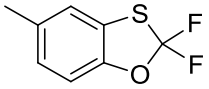
In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added sodium 2-bromo-3-methylphenoxide **2e′** (63 mg, 0.30 mmol), $CsSCF_3$ (85 mg, 0.36 mmol, 1.2 equiv), and dioxane (2.5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 3 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was filtered through a layer of Celite. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with *n*-pentane/diethyl ether to give 35 mg of product *O*,*O*-bis(2-bromo-3-methylphenyl) carbonothioate **II** (56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 2.52 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9 (s), 150.8 (s), 140.5 (s), 128.9 (s), 127.8 (s), 121.1 (s), 118.6 (s), 23.1 (s). HR-MS (ESI) m/z: calcd. for $C_{15}H_{12}O_2Br_2S$: $[M+H]^+$: 416.8977; found: 416.8969.

Procedure for the attempted transformation of intermediate I to 2,2-difluoro-1,3-benzoxathiole product 3e under copper-catalyzed conditions



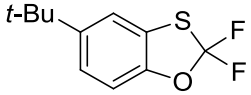
In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added sodium 2-bromo-3-methylphenoxide **2e′** (63 mg, 0.30 mmol), $CsSCF_3$ (85 mg, 0.36 mmol, 1.2 equiv), and dioxane (2.5 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 3 h. The reaction mixture was cooled to room temperature, and was added CuI (5.7 mg, 0.01 mmol, 0.10 equiv), phen (11.8 mg, 0.06 mol, 0.20 equiv), The reaction mixture was further stirred at 100 °C for 3 h. The tube was removed from the oil bath and cooled to room temperature, and then 10 μL (trifluoromethoxy)benzene was added as an internal standard. The resulting mixture was filtered through a layer of Celite. The filtrate was analyzed by ^{19}F NMR and GC-MS. The yield of the 2,2-difluoro-4-methylbenzo[*d*][1,3]oxathiole **3e** was calculated to be 22%.

Data for compounds 3



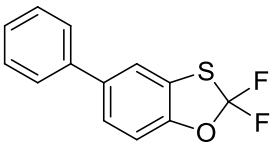
2,2-Difluoro-5-methylbenzo[*d*][1,3]oxathiole (**3a**)

Following the general procedure and workup, **3a** was isolated as a pale yellow oil in 78% yield (44 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 1H), 7.03 – 6.92 (m, 2H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.8 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5 (s), 138.9 (t, *J* = 284.5 Hz), 134.2 (s), 127.2 (s), 122.1 (s), 121.9 (s), 110.7 (s), 20.9 (s). IR (KBr): ν 2926, 1763, 1598, 1482, 1243, 1149, 1131, 1099, 1072, 1033, 902, 805, 716, 649, 554, 503 cm^{-1}. GC-MS m/z 188 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_6OF_2S$: 188.0107; found: 188.0102.



5-(*tert*-Butyl)-2,2-difluorobenzo[*d*][1,3]oxathiole (**3b**)

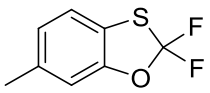
Following the general procedure and workup, **3b** was isolated as a yellow oil in 75% yield (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 1.30 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.8 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9 (s), 147.3 (s), 139.0 (t, *J* = 285.0 Hz), 123.7 (s), 121.9 (s), 118.6 (s), 110.5 (s), 34.7 (s), 31.4 (s). IR (KBr): ν 2964, 1597, 1489, 1364, 1259, 1240, 1149, 1120, 1078, 1033, 907, 871, 814, 717, 605, 438 cm^{-1}. GC-MS m/z 230 (M^+). HR-MS (EI) m/z: calcd. for $C_{11}H_{12}OF_2S$: 230.0577; found: 230.0585.



2,2-Difluoro-5-phenylbenzo[*d*][1,3]oxathiole (**3c**)

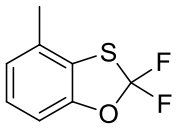
Following the general procedure and workup, **3c** was isolated as a yellow oil in 77% yield (58 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.51 – 7.44 (m,

3H), 7.43 – 7.38 (m, 2H), 7.16 (d, J = 8.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.5 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9 (t, J = 1.3 Hz), 139.8 (s), 139.0 (t, J = 285.6 Hz), 138.3 (s), 129.0 (s), 127.7 (s), 127.0 (s), 125.7 (s), 123.0 (s), 120.3 (t, J = 1.4 Hz), 111.3 (s). IR (KBr): ν 3031, 2919, 1598, 1467, 1400, 1237, 1145, 1106, 1069, 1031, 904, 818, 757, 714, 696, 677, 592, 526 cm^{-1}. GC-MS m/z 251 (M^+). HR-MS (EI) m/z: calcd. for $C_{13}H_8OF_2S$: 250.0264; found: 250.0271.



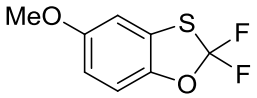
2,2-Difluoro-6-methylbenzo[*d*][1,3]oxathiole (**3d**)

Following the general procedure and workup, **3d** was obtained as a yellow oil in 59% yield (33 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 7.9 Hz, 1H), 6.99 – 6.88 (m, 2H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 (t, J = 1.3 Hz), 139.1 (t, J = 284.9 Hz), 137.2 (s), 125.1 (s), 121.2 (t, J = 1.3 Hz), 118.8 (s), 111.9 (s), 21.2 (s). IR (KBr): ν 2919, 2849, 1463, 1157, 1109, 905, 731, 650, 422 cm^{-1}. GC-MS m/z 188 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_6OF_2S$: 188.0107; found: 188.0110.



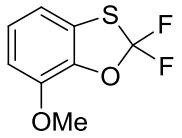
2,2-Difluoro-4-methylbenzo[*d*][1,3]oxathiole (**3e**)

Following the general procedure and workup, **3e** was obtained as a yellow oil in 61% yield (34 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, J = 7.9 Hz, 1H), 6.99 – 6.90 (m, 2H), 2.30 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.1 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3 (t, J = 1.2 Hz), 138.7 (t, J = 284.6 Hz), 131.8 (t, J = 1.1 Hz), 126.5 (s), 125.0 (s), 122.3 (s), 108.4 (s), 20.4 (s). IR (KBr): ν 2925, 2854, 2015, 1611, 1581, 1459, 1263, 1250, 1153, 1126, 1077, 1015, 907, 766, 704, 475, 440 cm^{-1}; GC-MS m/z 188 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_6OF_2S$: 188.0107; found: 188.0105.



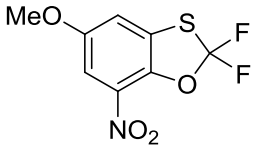
2,2-Difluoro-5-methoxybenzo[*d*][1,3]oxathiole (**3f**)

Following the general procedure and workup, **3f** was obtained as a yellow oil in 73% yield (45 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.9 Hz, 1H), 6.83 – 6.78 (m, 1H), 6.72 (dd, *J* = 8.9, 1.4 Hz, 1H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.8 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (s), 143.8 (s), 138.9 (t, *J* = 284.9 Hz), 123.1 (s), 111.9 (s), 111.4 (s), 107.4 (s), 55.9 (s). IR (KBr): ν 2939, 2838, 1760, 1593, 1482, 1442, 1219, 1151, 1103, 1070, 1035, 901, 830, 798, 717, 634, 580 cm^{-1}. GC-MS m/z 204 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_6O_2F_2S$: 204.0057; found: 204.0054.



2,2-Difluoro-7-methoxybenzo[*d*][1,3]oxathiole (**3g**)

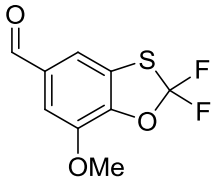
Following the general procedure and workup, **3g** was obtained as a yellow oil in 99% yield (61 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, *J* = 8.1 Hz, 1H), 6.85 – 6.74 (m, 2H), 3.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.0 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9 (s), 139.1 (t, *J* = 286.2 Hz), 138.1 (s), 124.8 (s), 123.2 (s), 113.5 (s), 110.3 (s), 56.3 (s). IR (KBr): ν 2942, 2842, 1609, 1487, 1322, 1282, 1240, 1140, 1083, 1030, 874, 802, 756, 708, 644, 572, 507 cm^{-1}. GC-MS m/z 204 (M^+). HR-MS (EI): m/z: calcd. for $C_8H_6O_2F_2S$: 204.0057; found: 204.0056.



2,2-Difluoro-5-methoxy-7-nitrobenzo[*d*][1,3]oxathiole (**3h**)

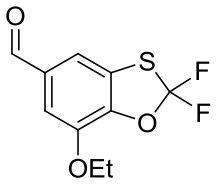
Following the general procedure and workup, **3h** was obtained as a pale yellow solid

in 99% yield (74 mg). Mp: 103-105 °C. ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.6 Hz, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.0 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (s), 138.9 (t, *J* = 289.1 Hz), 137.1 (t, *J* = 2.0 Hz), 133.7 (s), 127.2 (s), 114.4 (t, *J* = 1.6 Hz), 106.3 (s), 56.4 (s). IR (KBr): ν 3109, 2922, 2848, 1618, 1534, 1480, 1441, 1349, 1291, 1242, 1209, 1129, 1106, 1067, 1037, 928, 862, 763 cm^{-1}. GC-MS m/z 249 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_5NO_4F_2S$: 248.9907; found: 248.9903.



2,2-difluoro-7-methoxybenzo[*d*][1,3]oxathiole-5-carbaldehyde (**3i**)

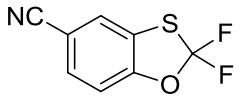
Following the general procedure and workup, **3i** was obtained as a pale yellow solid in 99% yield (69 mg). Mp: 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.40 (s, 1H), 7.34 (s, 1H), 4.00 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -28.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7 (s), 145.4 (s), 142.1 (t, *J* = 1.0 Hz), 139.1 (t, *J* = 288.8 Hz), 133.8 (s), 124.2 (s), 116.6 (t, *J* = 1.3 Hz), 110.2 (s), 56.5 (s). IR(KBr): ν 3095, 2924, 2866, 1697, 1606, 1486, 1302, 1260, 1082, 1032, 842, 722, 686, 637, 574, 520 cm^{-1}. GC-MS m/z 232 (M^+). HR-MS (EI) m/z: calcd. for $C_9H_6O_3F_2S$: 232.0006; found: 232.0012.



7-Ethoxy-2,2-difluorobenzo[*d*][1,3]oxathiole-5-carbaldehyde (**3j**)

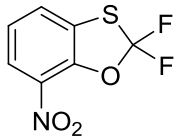
Following the general procedure and workup, **3j** was obtained as a pale yellow solid in 99% yield (73 mg). Mp: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.38 (s, 1H), 7.33 (s, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 1.51 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR

(376 MHz, $CDCl_3$) δ -28.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7 (s), 144.7 (s), 142.3 (s), 139.1 (t, *J* = 288.5 Hz), 133.8 (s), 124.3 (s), 116.3 (t, *J* = 1.3 Hz), 111.2 (s), 65.3 (s), 14.6 (s). IR (KBr): ν 2986, 1694, 1606, 1476, 1434, 1387, 1298, 1235, 1156, 1122, 1070, 915, 846, 825, 718, 650, 580, 546 cm^{-1}. GC-MS m/z 246 (M^+). HR-MS (EI) m/z: calcd. for $C_{10}H_8O_3F_2S$: 246.0162; found: 246.0160.



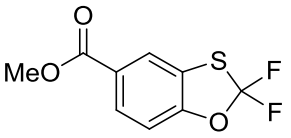
2,2-Difluorobenzo[*d*][1,3]oxathiole-5-carbonitrile (**3k**)

Following the general procedure and workup, **3k** was obtained as a pale yellow solid in 81% yield (48 mg). Mp: 108-110 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.8 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9 (s), 138.6 (t, *J* = 288.7 Hz), 131.5 (s), 125.3 (s), 124.5 (s), 117.5 (s), 111.9 (s), 108.8 (s). IR (KBr): ν 3110, 3045, 2234, 1884, 1588, 1473, 1402, 1254, 1118, 1096, 1073, 1034, 906, 885, 815, 731, 592, 479 cm^{-1}. GC-MS m/z 199 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_3NOF_2S$: 198.9903; found: 198.9906.



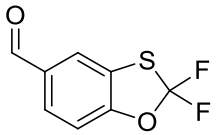
2,2-Difluoro-7-nitrobenzo[*d*][1,3]oxathiole (**3l**)

Following the general procedure and workup, **3l** was obtained as a pale yellow solid in 99% yield (65 mg). Mp: 137-140 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.3 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.32 (t, *J* = 8.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.3 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5 (t, *J* = 2.0 Hz), 139.1 (t, *J* = 289.7 Hz), 134.0 (s), 127.1 (t, *J* = 1.6 Hz), 126.4 (s), 124.4 (s), 122.7 (s). IR (KBr): ν 1604, 1533, 1460, 1347, 1319, 1250, 1136, 1056, 889, 796, 759, 728, 649, 603, 577, 455 cm^{-1}. GC-MS m/z 219 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_3NO_3F_2S$: 218.9802; found: 218.9811.



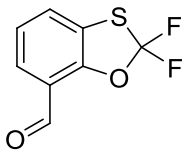
Methyl 2,2-difluorobenzo[*d*][1,3]oxathiole-5-carboxylate (**3m**)

Following the general procedure and workup, **3m** was obtained as a pale yellow solid in 99 % yield (69 mg). Mp: 79-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.0 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (s), 152.3 (t, *J* = 1.2 Hz), 138.9 (t, *J* = 287.1 Hz), 129.0 (s), 126.9 (s), 123.3 (t, *J* = 1.5 Hz), 123.0 (s), 110.9 (s), 52.4 (s). IR (KBr): ν 2955, 1718, 1595, 1282, 1256, 1139, 1078, 1031, 974, 760, 737, 714, 702, 622, 454 cm^{-1}. GC-MS m/z 232 (M^+). HR-MS (EI) m/z: calcd. for $C_9H_6O_3F_2S$: 232.0006; found: 232.0003.



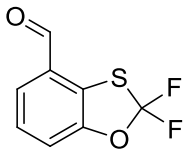
2,2-Difluorobenzo[*d*][1,3]oxathiole-5-carbaldehyde (**3n**)

Following the general procedure and workup, **3n** was obtained as a pale yellow solid in 99% yield (60 mg). Mp: 56-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.82 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6 (s), 153.3 (s), 138.8 (t, *J* = 287.9 Hz), 133.4 (s), 130.1 (s), 124.3 (s), 122.4 (s), 111.5 (s). IR (KBr): ν 2849, 1693, 1586, 1477, 1421, 1389, 1249, 1142, 1081, 1029, 904, 818, 736, 693, 616, 556 cm^{-1}. GC-MS m/z 202 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_4O_2F_2S$: 201.9900; found: 201.9892.



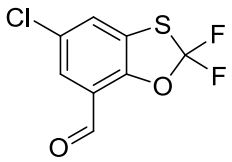
2,2-Difluorobenzo[*d*][1,3]oxathiole-7-carbaldehyde (**3o**)

Following the general procedure and workup, **3o** was obtained as a pale yellow solid in 99% yield (60 mg). Mp: 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.8 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6 (s), 150.3 (t, *J* = 1.4 Hz), 139.5 (t, *J* = 288.3 Hz), 127.0 (t, *J* = 1.5 Hz), 125.5 (s), 124.6 (s), 124.2 (t, *J* = 0.7 Hz), 120.7 (s). IR (KBr): ν 3093, 2922, 2856, 1688, 1607, 1571, 1442, 1393, 1257, 1126, 1079, 1057, 978, 878, 782, 735, 716, 504 cm^{-1}. GC-MS m/z 202 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_4O_2F_2S$: 201.9900; found: 201.9896.



2,2-Difluorobenzo[*d*][1,3]oxathiole-4-carbaldehyde (**3p**)

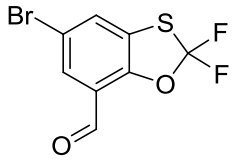
Following the general procedure and workup, **3p** was obtained as a pale yellow solid in 64% yield (39 mg). Mp: 66-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -31.4 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1 (s), 150.7 (t, *J* = 1.4 Hz), 139.9 (t, *J* = 287.3 Hz), 129.8 (s), 128.1 (s), 126.8 (s), 123.3 (s), 115.8 (s). IR (KBr): ν 2859, 1680, 1574, 1443, 1388, 1331, 1261, 1225, 1129, 1082, 1010, 904, 775, 727, 675, 649, 536 cm^{-1}. GC-MS m/z 202 (M^+). HR-MS (EI) m/z calcd. for $C_8H_4O_2F_2S$: 201.9900; found: 201.9905.



5-Chloro-2,2-difluorobenzo[*d*][1,3]oxathiole-7-carbaldehyde (**3q**)

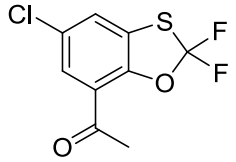
Following the general procedure and workup, **3q** was obtained as a pale yellow solid in 99% yield (70 mg). Mp: 95-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.66 (s, 1H), 7.45 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.7 (s, 2F). ^{13}C NMR (101

MHz, $CDCl_3$) δ 185.2 (s), 149.0 (s), 139.4 (t, *J* = 289.9 Hz), 130.5 (s), 126.6 (s), 126.0 (s), 125.0 (s), 121.0 (s). IR (KBr): ν 1698, 1547, 1448, 1393, 1311, 1216, 1161, 1067, 904, 727, 649, 620, 520, 463 cm^{-1}. GC-MS m/z 236 (M^+). HR-MS (EI) m/z calcd. for $C_8H_3O_2F_2SCl$: 235.9510; found: 235.9520.



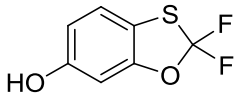
5-Bromo-2,2-difluorobenzo[*d*][1,3]oxathiole-7-carbaldehyde (**3r**)

Following the general procedure and workup, **3r** was obtained as a pale yellow solid in 99% yield (84 mg). Mp: 98-101 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.83 (s, 1H), 7.61 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.6 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.2 (s), 149.4 (t, *J* = 1.4 Hz), 139.3 (t, *J* = 290.0 Hz), 129.3 (t, *J* = 1.6 Hz), 128.0 (s), 126.3 (s), 121.3 (s), 117.3 (s). IR (KBr): ν 2986, 1694, 1606, 1476, 1387, 1298, 1235, 1156, 1122, 1070, 915, 846, 825, 718, 650, 580, 546 cm^{-1}. GC-MS m/z 281 (M^+). HR-MS (EI): m/z calcd. for $C_8H_3O_2F_2SBr$: 279.9005; found: 279.9009.



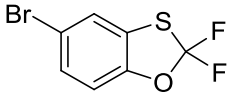
1-(5-Chloro-2,2-difluorobenzo[*d*][1,3]oxathiol-7-yl)ethanone (**3s**)

Following the general procedure and workup, **3s** was obtained as a pale yellow solid in 99% yield (75 mg). Mp: 126-128 °C. ^1HNMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.2 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 2.69 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4 (s), 146.6 (t, *J* = 1.4 Hz), 138.6 (t, *J* = 288.3 Hz), 130.1 (s), 127.0 (s), 125.7 (t, *J* = 0.8 Hz), 125.3 (t, *J* = 1.6 Hz), 123.0 (s), 30.7 (s). IR (KBr): ν 3080, 1686, 1593, 1569, 1430, 1364, 1313, 1253, 1230, 1157, 1091, 1057, 977, 881, 785, 716, 599, 470 cm^{-1}. GC-MS m/z 250 (M^+). HR-MS (EI) m/z calcd. For: $C_9H_5O_2F_2SCl$: 249.9667; found: 249.9664.



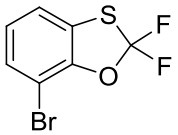
2,2-Difluorobenzo[*d*][1,3]oxathiol-6-ol (**3t**)

Following the general procedure and workup, **3t** was obtained as a pale yellow solid in 72% yield (41 mg). Mp: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 1H), 7.06 – 6.98 (m, 2H), -O*H* was not detected. ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.6 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8 (s), 149.6 (s), 139.2 (t, *J* = 287.1 Hz), 121.9 (s), 121.1 (s), 118.0 (s), 106.2 (s). IR (KBr): ν 2928, 1594, 1474, 1280, 1158, 1125, 1100, 1030, 902, 722, 649, 427 cm^{-1}. GC-MS: m/z 190 (M^+). HR-MS (EI): m/z calcd. for $C_7H_4O_2F_2S$: 189.9900; found: 189.9899.



5-Bromo-2,2-difluorobenzo[*d*][1,3]oxathiole (**3u**)

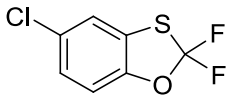
Following the general procedure and workup, **3u** was obtained as a pale yellow oil in 99% yield (75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 1.7 Hz, 1H), 7.33 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.2 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4 (s), 138.7 (t, *J* = 286.8 Hz), 129.6 (s), 124.4 (s), 124.3 (s), 116.5 (s), 112.5 (s). IR (KBr): ν 2921, 1773, 1557, 1462, 1393, 1239, 1148, 1111, 1072, 1056, 1031, 859, 804, 749, 711, 617, 550, 527, 452 cm^{-1}. GC-MS m/z 252 (M^+). HR-MS (EI) m/z calcd. for: $C_7H_3OF_2SBr$: 251.9056; found: 251.9065.



7-Bromo-2,2-difluorobenzo[*d*][1,3]oxathiole (**3v**)

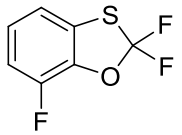
Following the general procedure and workup, **3v** was obtained as a pale yellow oil in 90% yield (68 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.0 (s, 2F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9 (s), 137.8 (t, *J* = 287.6 Hz), 132.1 (s), 130.1 (s), 125.3 (s), 120.5 (s), 104.2 (s). IR (KBr): ν 2919, 1591, 1459, 1436, 1307, 1244, 1139, 1124, 1073, 1039, 877, 781, 759, 701, 649, 596, 511 cm^{-1}. GC-MS m/z 252 (M^+). HR-MS (EI) m/z calcd. for $C_7H_3OF_2SBr$: 251.9056; found: 251.9064.



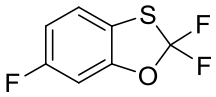
5-Chloro-2,2-difluorobenzo[*d*][1,3]oxathiole (**3w**)

Following the general procedure and workup, **3w** was obtained as a pale yellow oil in 75% yield (47 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.2 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0 (t, *J* = 1.3 Hz), 138.8 (t, *J* = 286.8 Hz), 129.6 (s), 126.7 (s), 124.0 (s), 121.5 (s), 112.0 (s). IR (KBr): ν 2926, 1594, 1465, 1242, 1157, 1124, 1073, 1034, 903, 808, 771, 715, 650, 555, 466 cm^{-1}. GC-MS m/z 208 (M^+). HR-MS (EI): m/z calcd. for $C_7H_3OF_2SCl$: 207.9561; found: 207.9568.



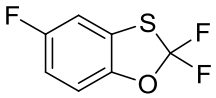
2,2,7-Trifluorobenzo[*d*][1,3]oxathiole (**3x**)

Following the general procedure and workup, **3x** was obtained as a pale yellow oil in 91% yield (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 1H), 7.06 – 6.99 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.9 (s, 2F), -133.4 (dd, *J* = 9.5, 4.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5 (s), 146.0 (s), 139.1 (t, *J* = 288.3 Hz), 136.8 (d, *J* = 12.5 Hz), 124.9 (d, *J* = 6.4 Hz), 116.9 (d, *J* = 3.9 Hz), 114.3 (d, *J* = 17.1 Hz). IR (KBr): ν 2926, 1618, 1483, 1454, 1269, 1145, 1072, 908, 764, 714, 701, 650, 514 cm^{-1}. GC-MS m/z 192 (M^+). HR-MS (EI): m/z calcd. for: $C_7H_3OF_3S$: 191.9857; found: 191.9852.



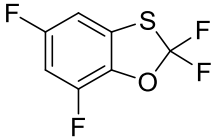
2,2,6-Trifluorobenzo[*d*][1,3]oxathiole (**3y**)

Following the general procedure and workup, **3y** was obtained as a pale yellow oil in 83% yield (48 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 1H), 6.96 – 6.83 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.2 (s, 2F), -113.5 (td, *J* = 8.5, 5.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (d, *J* = 246.0 Hz), 149.6 (d, *J* = 12.8 Hz), 139.4 (t, *J* = 286.8 Hz), 122.0 (d, *J* = 9.4 Hz), 117.4 (d, *J* = 3.5 Hz), 111.6 (d, *J* = 23.3 Hz), 100.4 (d, *J* = 28.3 Hz). IR (KBr): ν 2924, 1614, 1600, 1479, 1434, 1280, 1162, 1143, 1126, 1101, 1080, 1036, 967, 907, 846, 801, 733, 699, 597, 491 cm^{-1}. GC-MS m/z 192 (M^+). HR-MS (EI): m/z calcd. for $C_7H_3OF_3S$: 191.9857; found: 191.9863.



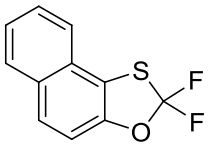
2,2,5-Trifluorobenzo[*d*][1,3]oxathiole (**3z**)

Following the general procedure and workup, **3z** was obtained as a pale yellow oil in 56% yield (32 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 6.96 (m, 2H), 6.91 (td, *J* = 8.7, 2.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.1 (s, 2F), -117.5 (td, *J* = 8.0, 4.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 (dt, *J* = 243.8, 1.0 Hz), 145.6 (dd, *J* = 4.0, 1.5 Hz), 138.9 (t, *J* = 286.1 Hz), 123.6 (d, *J* = 10.5 Hz), 113.3 (d, *J* = 24.5 Hz), 111.8 (d, *J* = 8.8 Hz), 109.2 (dt, *J* = 28.4, 1.6 Hz). IR (KBr): ν 2922, 2852, 1613, 1597, 1476, 1311, 1248, 1157, 1090, 1031, 914, 836, 806, 717, 599, 504 cm^{-1}. GC-MS m/z 192 (M^+). HR-MS (EI): m/z calcd. for $C_7H_3OF_3S$: 191.9857; found: 191.9858.



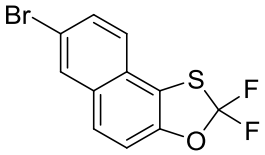
2,2,5,7-Tetrafluorobenzo[*d*][1,3]oxathiole (**3aa**)

Following the general procedure and workup, **3aa** was obtained as a pale yellow oil in 92% yield (58 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 – 6.68 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.7 (s, 2F), -113.9 (dd, *J* = 7.9, 2.5 Hz, 1F), -129.2 (dd, *J* = 9.9, 2.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (dd, *J* = 247.0, 9.5 Hz), 146.7 (dd, *J* = 254.2, 12.8 Hz), 139.0 (t, *J* = 289.1 Hz), 133.4 (d, *J* = 13.2 Hz), 126.2 – 124.0 (m), 104.6 (dd, *J* = 28.8, 3.4 Hz), 102.8 (dd, *J* = 27.7, 20.9 Hz). IR (KBr): ν 2920, 1630, 1607, 1485, 1439, 1302, 1231, 1161, 1117, 1073, 992, 903, 842, 725, 695, 656, 600, 536, 504, 441 cm^{-1}. GC-MS m/z 210 (M^+). HR-MS (EI) m/z calcd. for $C_7H_2OF_4S$: 209.9762; found: 209.9761.



2,2-Difluoronaphtho[1,2-*d*][1,3]oxathiole (**3ab**)

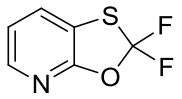
Following the general procedure and workup, **3ab** was obtained as a pale yellow oil in 59% yield (40 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.53 – 7.44 (m, 2H), 7.32 (d, *J* = 8.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -28.7 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2 (t, *J* = 1.1 Hz), 139.7 (t, *J* = 286.2 Hz), 130.6 (s), 129.0 (s), 127.6 (s), 127.5 (s), 127.2 (t, *J* = 1.0 Hz), 125.4 (s), 123.9 (s), 116.3 (s), 111.6 (s). IR (KBr): ν 3061, 2925, 1628, 1596, 1514, 1459, 1369, 1344, 1251, 1159, 1142, 1085, 1024, 969, 903, 800, 762, 738, 679, 524, 493 cm^{-1}. GC-MS m/z 224 (M^+). HR-MS (EI) m/z calcd. for $C_{11}H_6OF_2S$: 224.0107; found: 224.0109.



7-Bromo-2,2-difluoronaphtho[1,2-*d*][1,3]oxathiole (**3ac**)

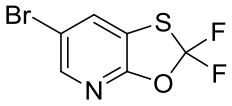
Following the general procedure and workup, **3ac** was obtained as a pale yellow solid in 85% yield (77 mg). Mp: 117-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H),

7.72 – 7.49 (m, 2H), 7.34 – 7.24 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -28.4 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4 (t, *J* = 1.1 Hz), 139.5 (t, *J* = 287.1 Hz), 131.6 (s), 130.9 (s), 130.8 (s), 126.5 (s), 125.6 (t, *J* = 1.0 Hz), 125.4 (s), 119.2 (s), 116.3 7(s), 112.6 (s). IR (KBr): ν 3071, 2924, 2863, 1679, 1570, 1444, 1392, 1309, 1216, 1161, 1066, 905, 724, 649, 619, 574 cm^{-1}. GC-MS m/z 301 (M^+). HR-MS (EI) m/z calcd. for $C_{11}H_5OF_2SBr$: 301.9213; found: 301.9217.



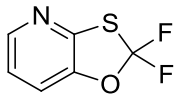
2,2-Difluoro-[1,3]oxathiolo[5,4-*b*]pyridine (**3ad**)

Following the general procedure and workup, **3ad** was obtained as a pale yellow oil in 79% yield (41 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 5.0 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.13 (dd, *J* = 7.6, 5.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -31.1 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (t, *J* = 2.6 Hz), 144.9 (s), 135.2 (t, *J* = 286.3 Hz), 130.6 (t, *J* = 1.6 Hz), 120.6 (s), 117.7 (s). IR (KBr): ν 2917, 2849, 1590, 1571, 1411, 1252, 1136, 1101, 1017, 902, 785, 741, 727, 701, 642, 587, 501 cm^{-1}. GC-MS: m/z 175 (M^+). HR-MS (EI) m/z calcd. for $C_6H_3NOF_2S$: 174.9903; found: 174.9904.



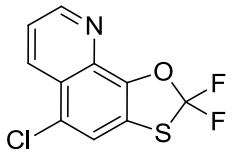
6-Bromo-2,2-difluoro-[1,3]oxathiolo[5,4-*b*]pyridine (**3ae**)

Following the general procedure and workup, **3ae** was obtained as a pale yellow oil in 98% yield (75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.0 Hz, 1H), 7.77 – 7.74 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.5 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5 (t, *J* = 2.8 Hz), 145.5 (s), 135.1 (t, *J* = 288.2 Hz), 132.9 (t, *J* = 1.7 Hz), 119.6 (s), 115.6 (s). IR (KBr): ν 2932, 1736, 1604, 1469, 1454, 1431, 1406, 1374, 1262, 1207, 1147, 1081, 1039, 905, 798, 730, 648, 584, 487 cm^{-1}. GC-MS m/z 254 (M^+). HR-MS (EI) m/z calcd. for $C_6H_2NOF_2SBr$: 252.9009; found: 252.9012.



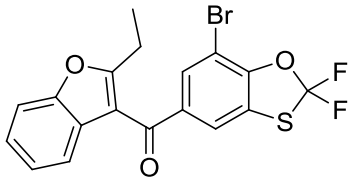
2,2-Difluoro-[1,3]oxathiolo[4,5-*b*]pyridine (**3af**)

Following the general procedure and workup, **3af** was obtained as a pale yellow oil in 62% yield (33 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 4.6 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.14 (dd, *J* = 8.1, 5.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -28.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0 (s), 145.2 (t, *J* = 1.0 Hz), 144.9 (s), 136.9 (t, *J* = 287.1 Hz), 121.4 (s), 117.0 (s). IR (KBr): ν 2918, 1598, 1410, 1297, 1271, 1200, 1135, 1110, 1076, 1041, 788, 727, 699, 547, 495 cm^{-1}. GC-MS m/z 175 (M^+). HR-MS (EI) m/z calcd. for $C_6H_3NOF_2S$: 174.9903; found: 174.9909.



5-Chloro-2,2-difluoro-[1,3]oxathiolo[4,5-*h*]quinoline (**3ag**)

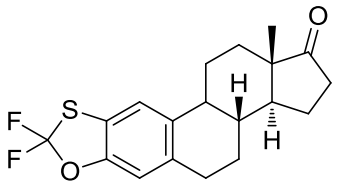
Following the general procedure and workup, **3ag** was obtained as a pale yellow solid in 85% yield (63 mg). Mp: 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 4.0 Hz, 1H), 8.55 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.50 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -27.6 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1 (s), 142.6 (t, *J* = 1.1 Hz), 139.4 (t, *J* = 289.2 Hz), 135.3 (s), 133.5 (s), 127.1 (s), 125.1 (s), 122.1 (s), 121.0 (s), 119.2 (t, *J* = 1.4 Hz). IR (KBr): ν 2980, 1615, 1494, 1455, 1349, 1158, 1077, 903, 722, 648, 502 cm^{-1}. GC-MS m/z 258 (M^+). HR-MS (EI) m/z calcd. for $C_{10}H_4NOF_2SCl$: 258.9670; found: 258.9674.



(7-Bromo-2,2-difluorobenzo[*d*][1,3]oxathiol-5-yl)(2-ethylbenzofuran-3-yl)methanone

(**3ah**)

Following the general procedure and workup, **3ah** was obtained as a pale yellow solid in 99% yield (121 mg). Mp: 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.73 (s, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 2.96 (q, *J* = 7.5 Hz, 2H), 1.40 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.2 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1 (s), 167.0 (s), 153.7 (s), 149.6 (t, *J* = 1.5 Hz), 137.9 (t, *J* = 289.7 Hz), 136.9 (s), 131.9 (s), 126.4 (s), 124.8 (s), 124.0 (s), 123.9 (s), 121.5 (t, *J* = 1.4 Hz), 121.0 (s), 115.1 (s), 111.3 (s), 104.1 (s), 22.0 (s), 12.3 (s). IR (KBr): ν 2978, 1648, 1573, 1452, 1281, 1257, 1150, 1090, 1043, 907, 871, 749, 731, 709, 649, 557 cm^{-1}. HR-MS (EI) m/z calcd. for $C_{18}H_{11}O_3F_2SBr$: 423.9580; found: 423.9585.

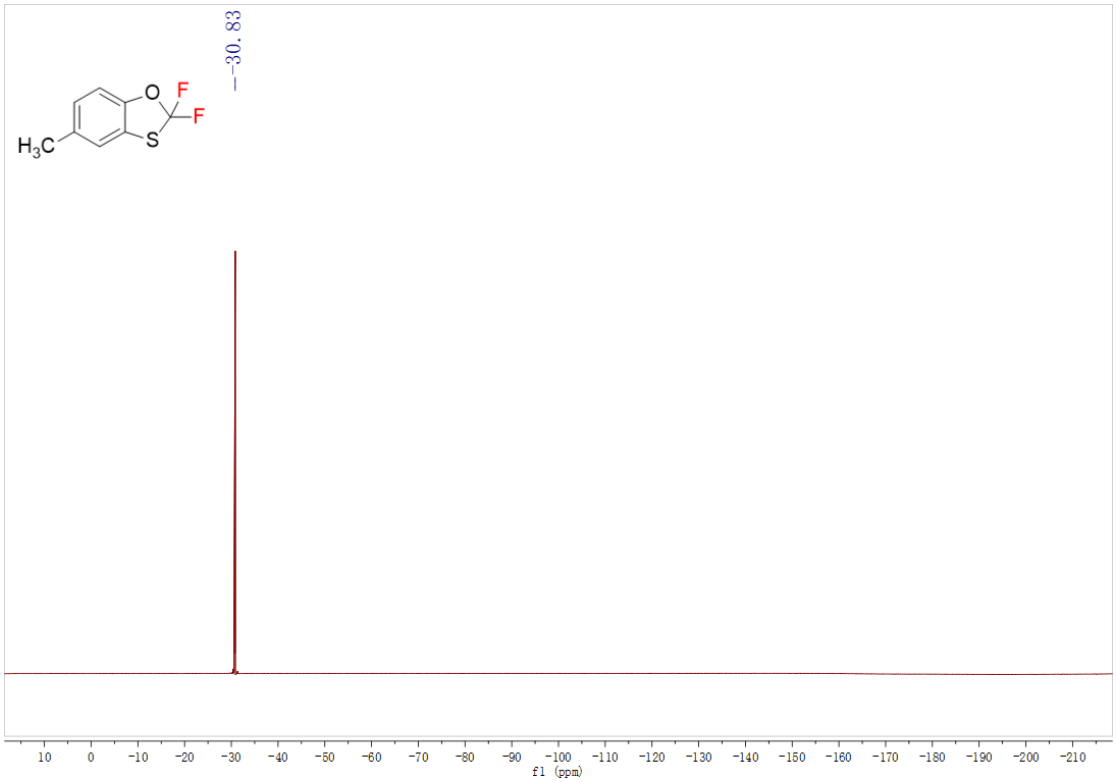


(3a*S*,3b*R*,12a*S*)-8,8-difluoro-12a-methyl-2,3,3a,3b,4,5,10b,11,12,12a-decahydro-1*H*-cyclopenta[7,8]phenanthro[3,2-*d*][1,3]oxathiol-1-one (**3ai**)

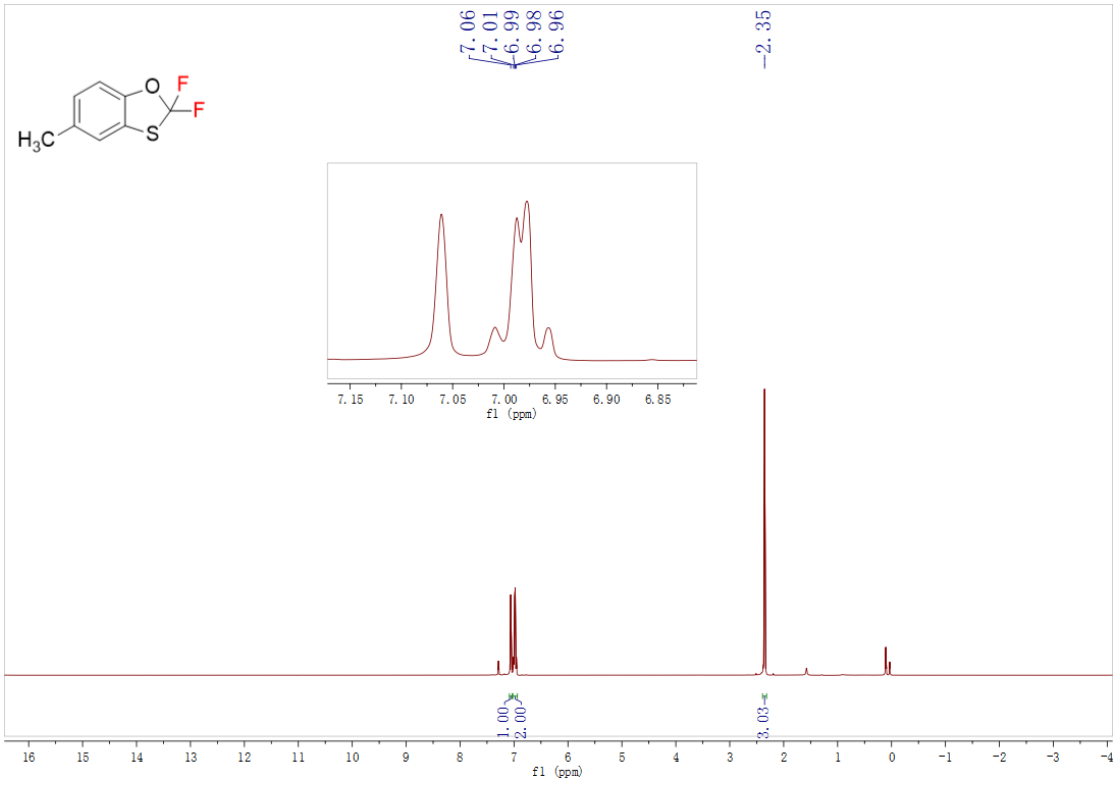
Following the general procedure and workup, **3ai** was obtained as a pale yellow oil in 50% yield (53 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 2.78 – 1.91 (m, 9H), 1.74 – 1.40 (m, 6H), 0.93 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.9 (d, *J* = 46.1 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3 (t, *J* = 1.1 Hz), 139.1 (t, *J* = 285.5 Hz), 136.0 (s), 130.3 (t, *J* = 1.1 Hz), 123.6 (s), 121.9 (s), 108.2 (s), 50.3 (s), 47.8 (s), 44.4 (s), 43.9 (s), 37.9 (s), 35.8 (s), 31.5 (s), 28.6 (s), 26.0 (s), 25.9 (s), 21.6 (s), 13.8 (s). IR (KBr): ν 3045, 1580, 1560, 1431, 1374, 1255, 1232, 1153, 1118, 1088, 1036, 898, 771, 732, 624, 555, 458 cm^{-1}. HR-MS (EI) m/z calcd. for $C_{19}H_{20}O_2F_2S$: 350.1152; found: 350.1151.

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

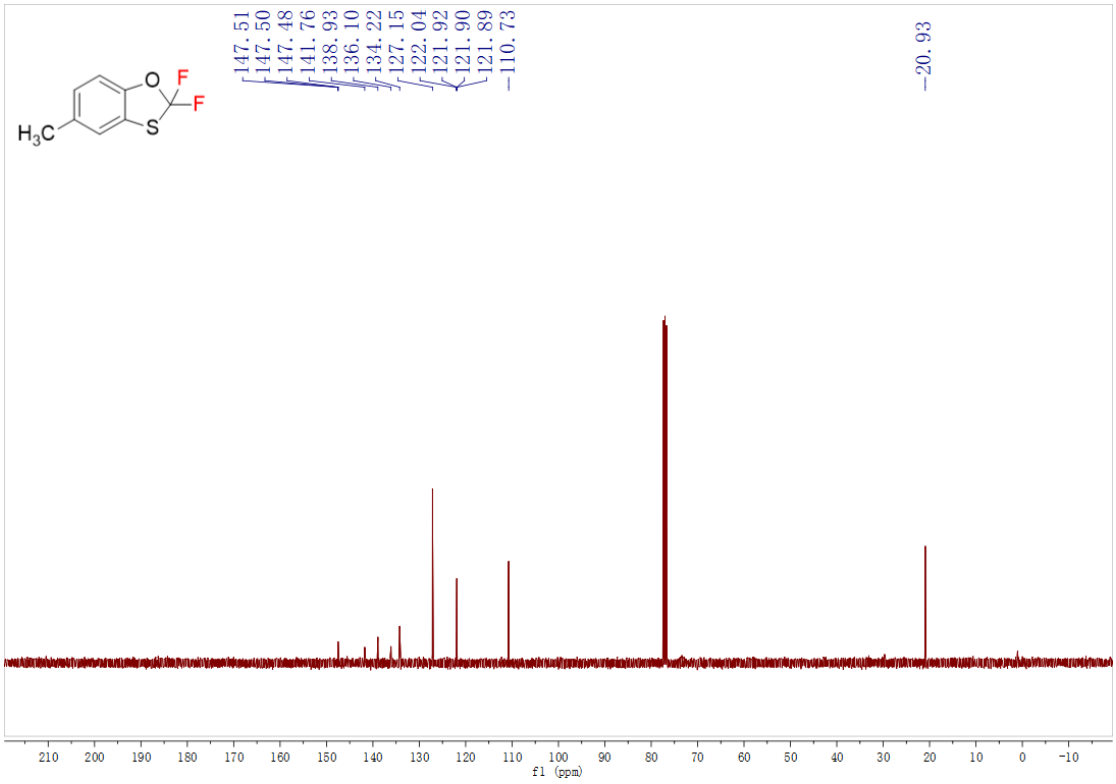
^{19}F NMR spectrum of **3a** in $CDCl_3$



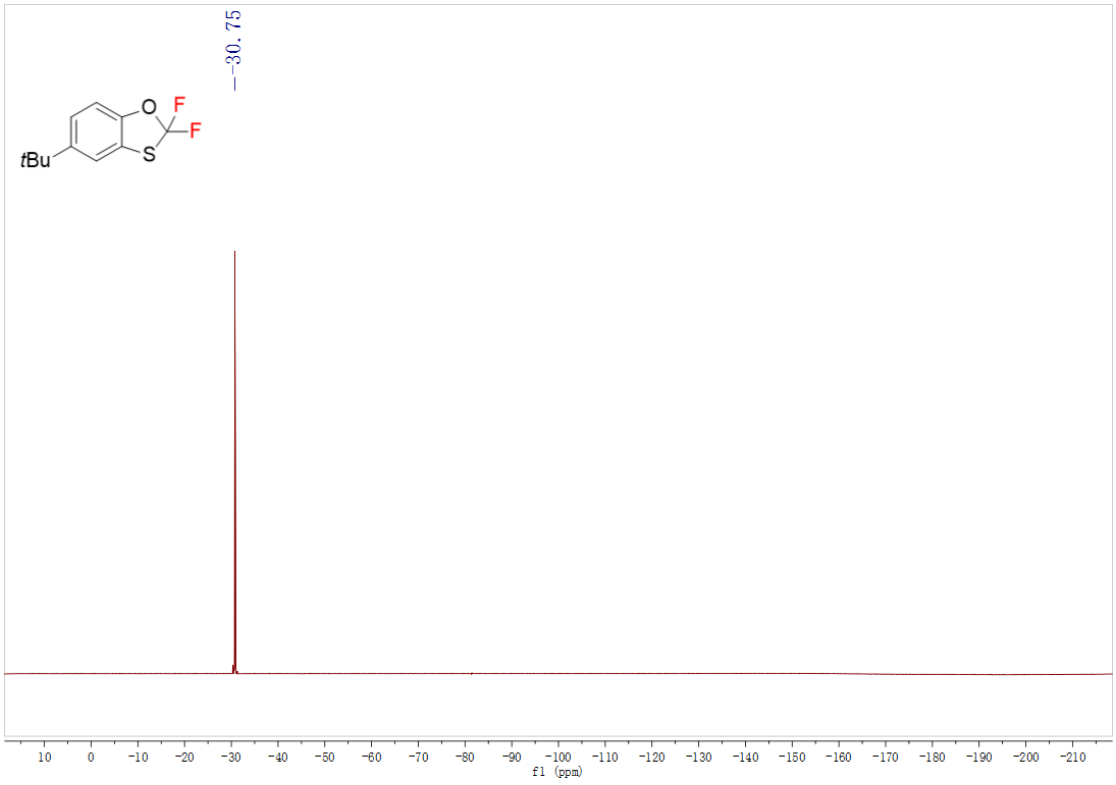
^{1}H NMR spectrum of **3a** in $CDCl_3$



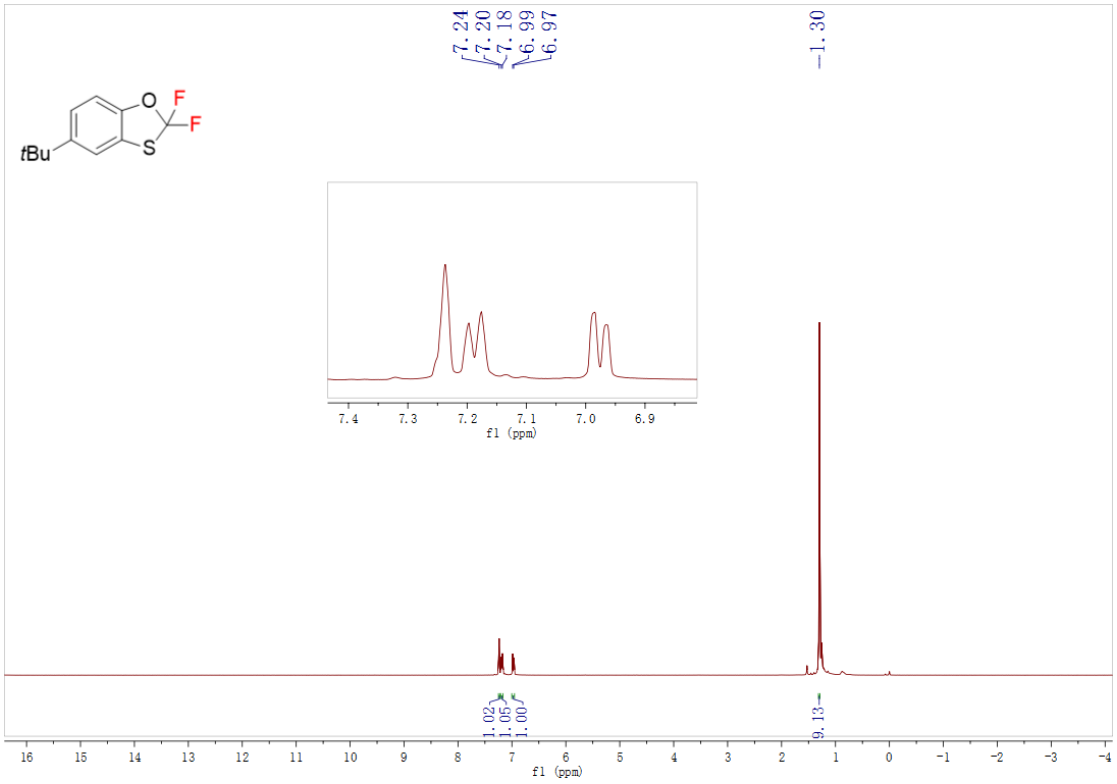
^{13}C NMR spectrum of **3a** in $CDCl_3$



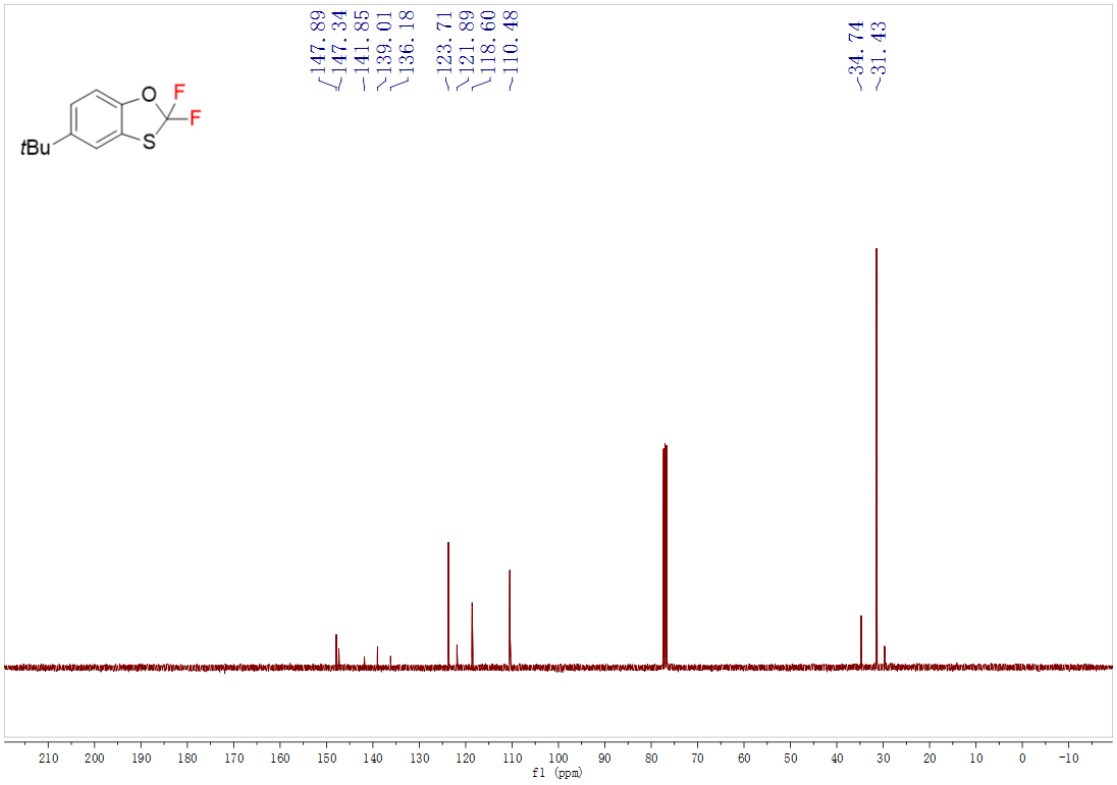
^{19}F NMR spectrum of **3b** in $CDCl_3$



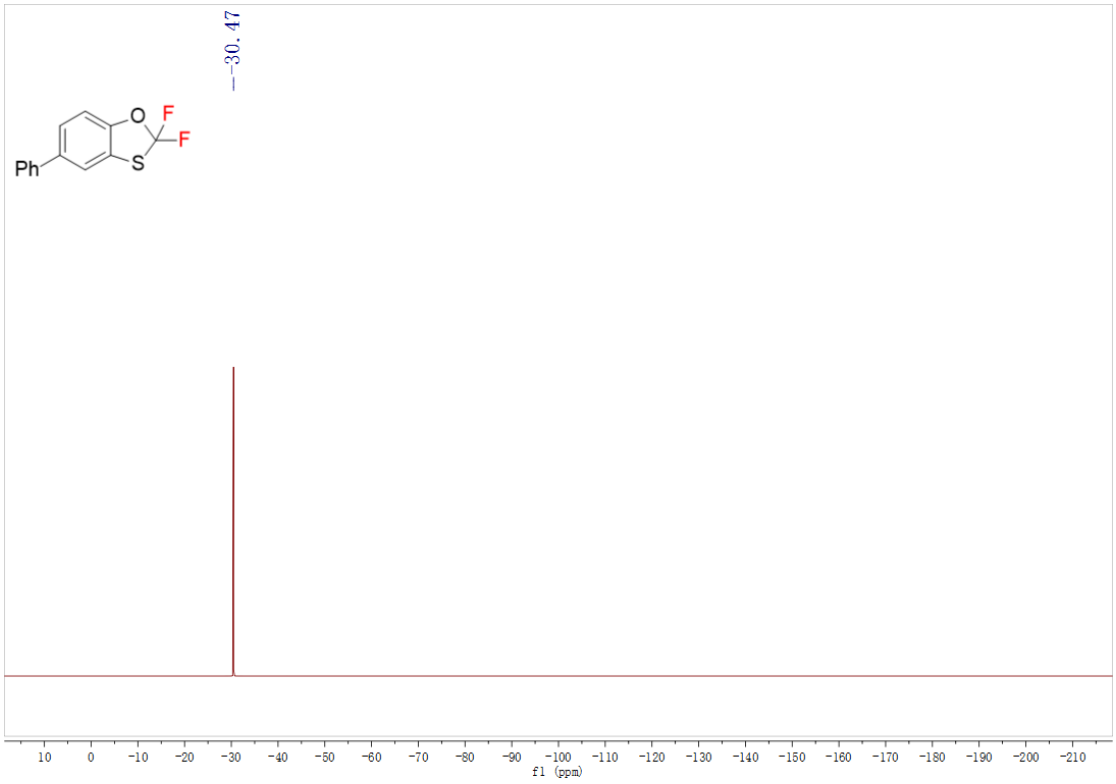
^{1}H NMR spectrum of **3b** in $CDCl_3$



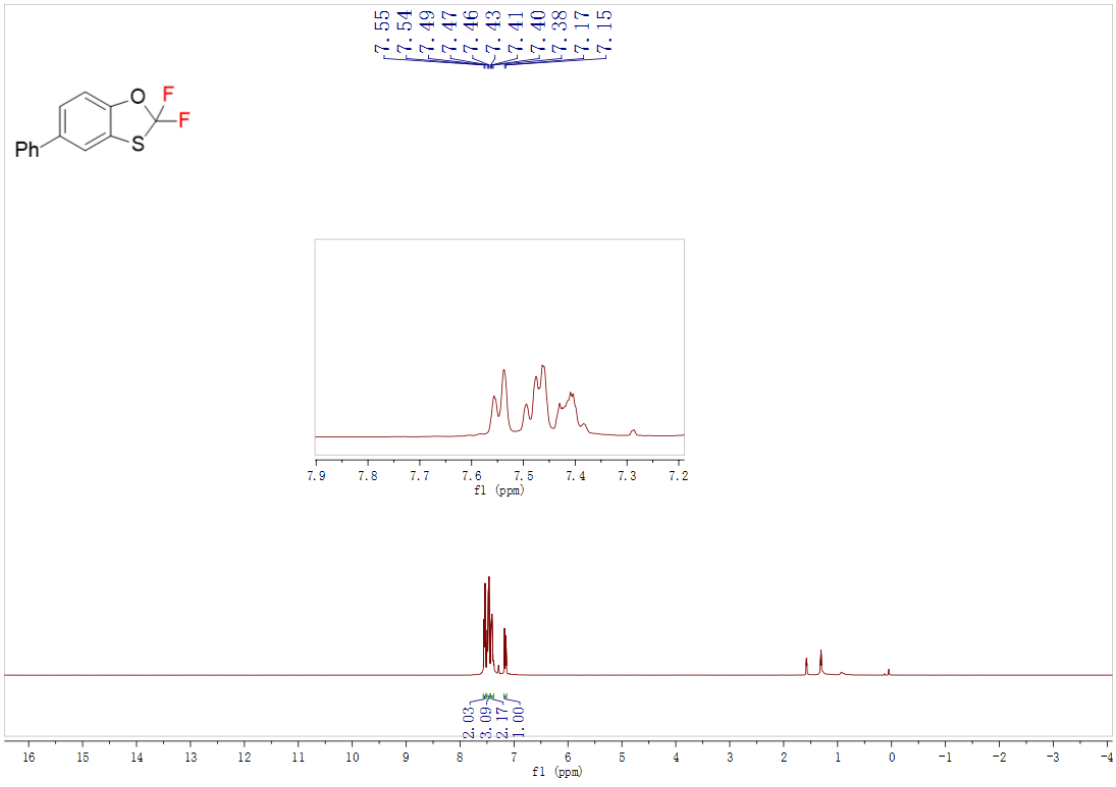
^{13}C NMR spectrum of **3b** in $CDCl_3$



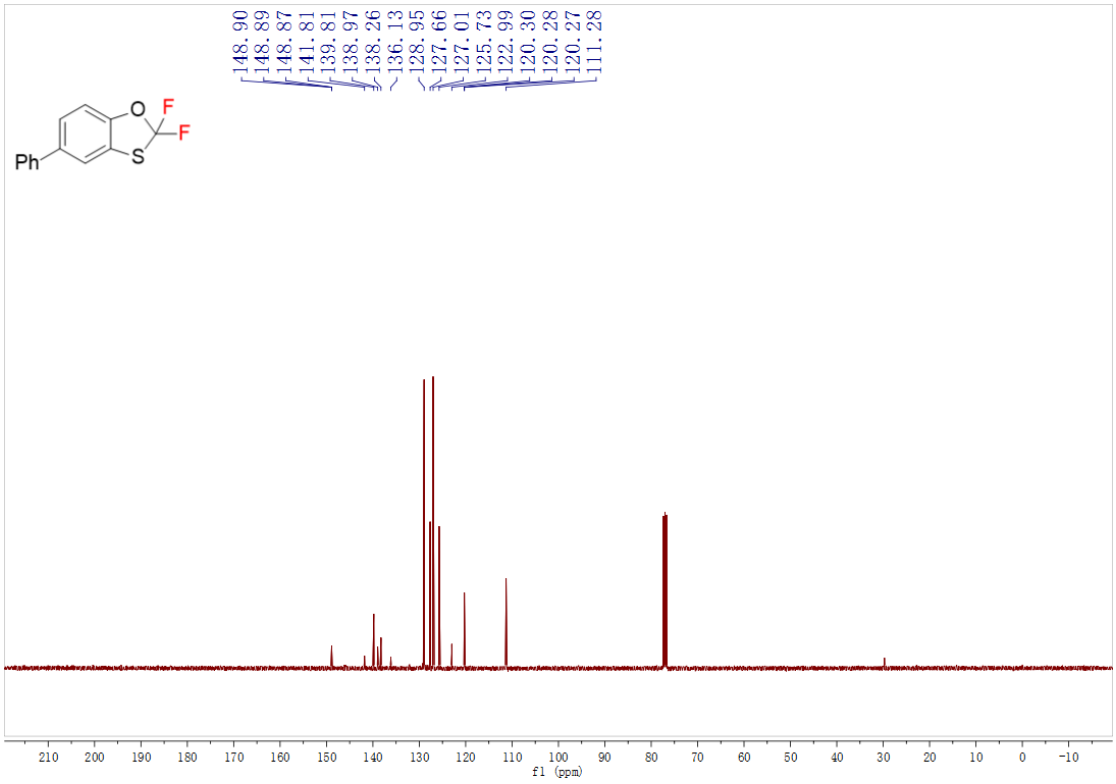
^{19}F NMR spectrum of **3c** in $CDCl_3$



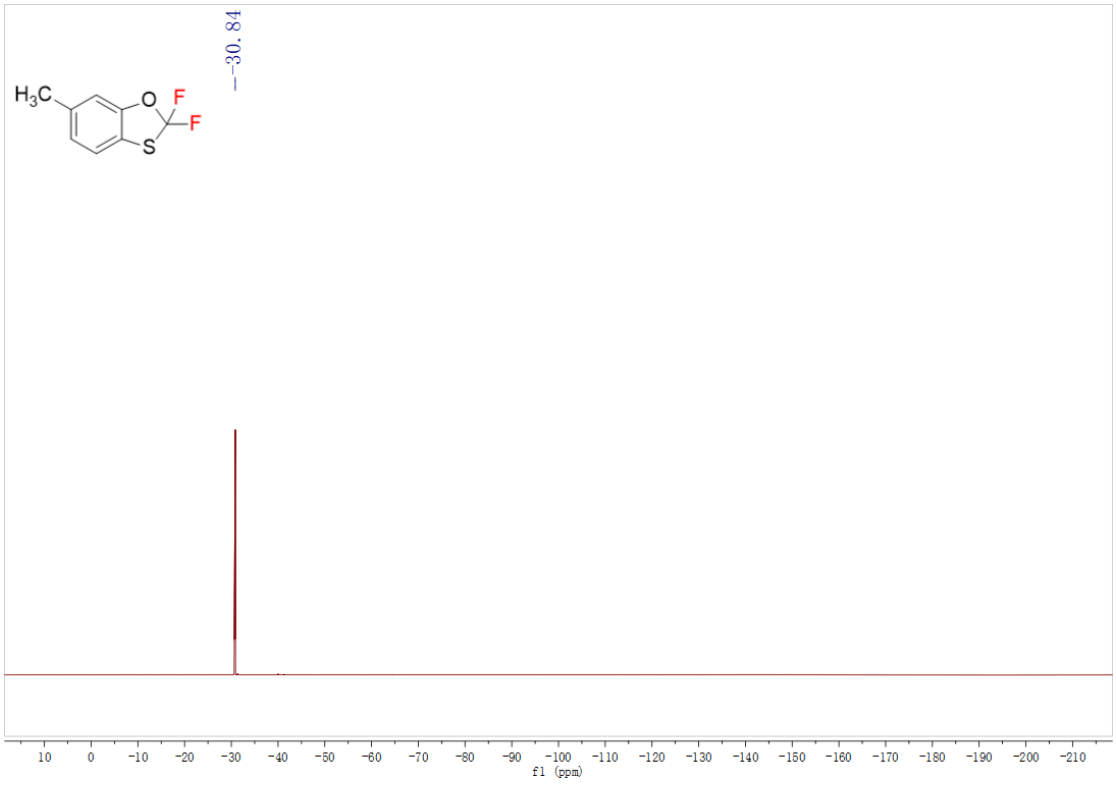
^{1}H NMR spectrum of **3c** in $CDCl_3$



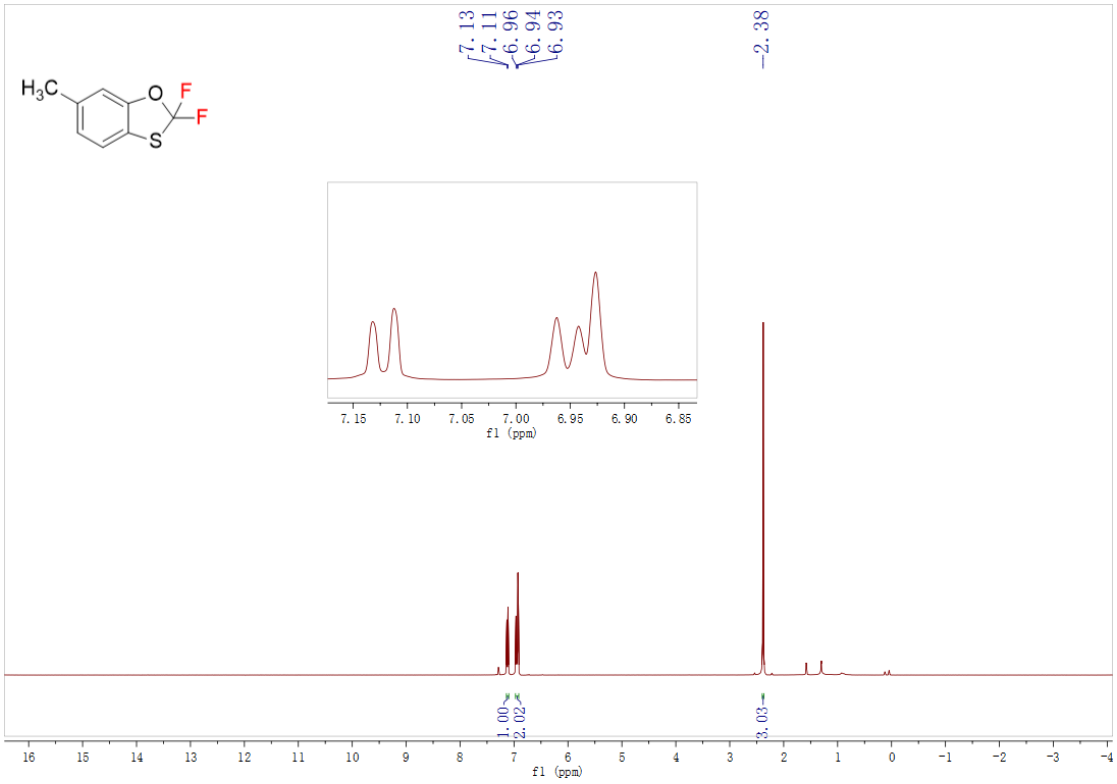
^{13}C NMR spectrum of **3c** in $CDCl_3$



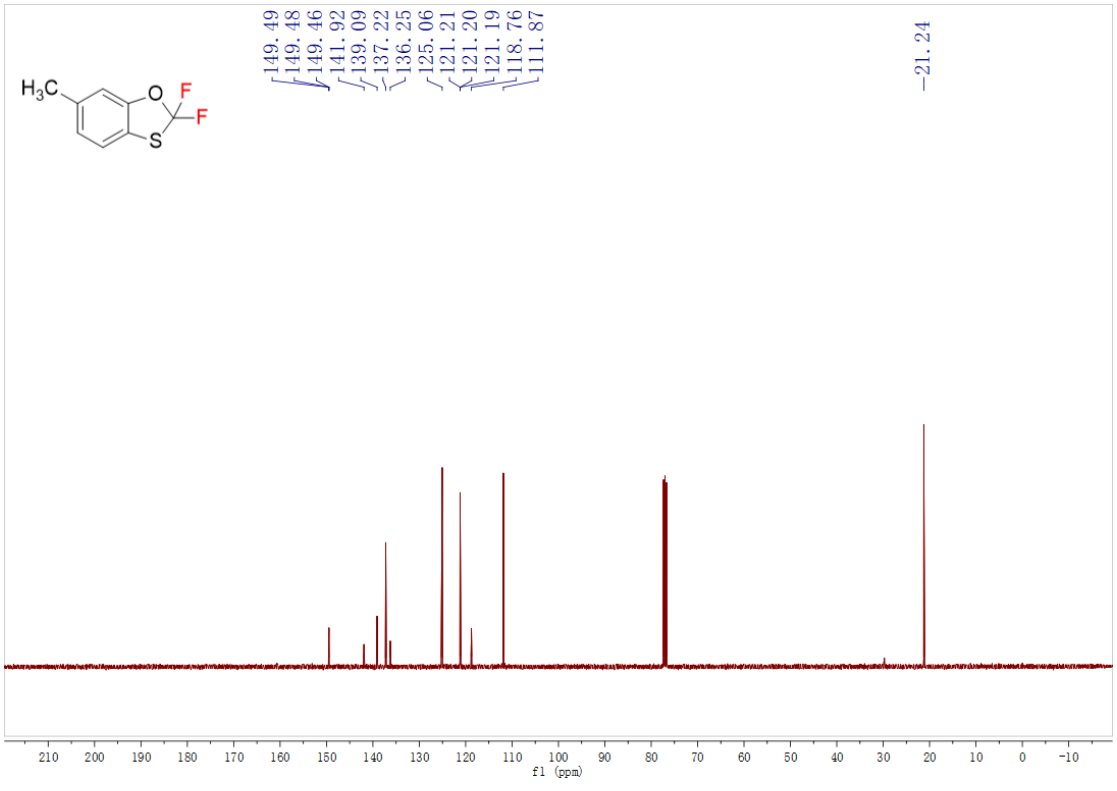
^{19}F NMR spectrum of **3d** in $CDCl_3$



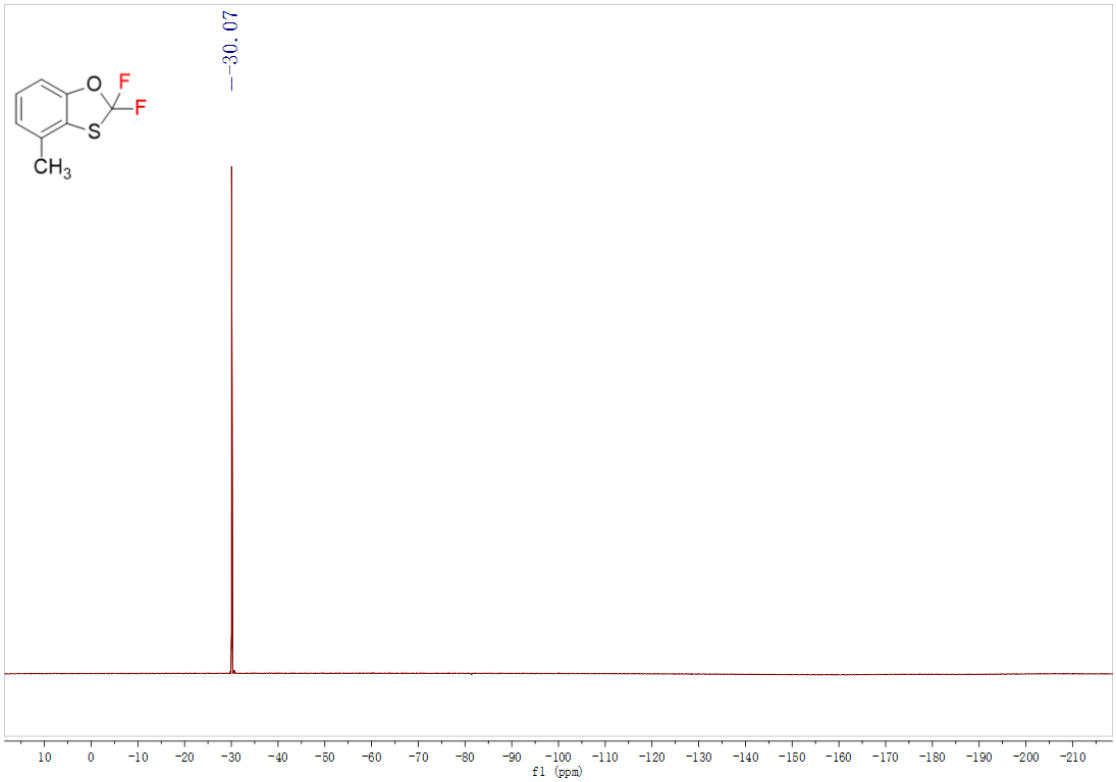
^{1}H NMR spectrum of **3d** in $CDCl_3$



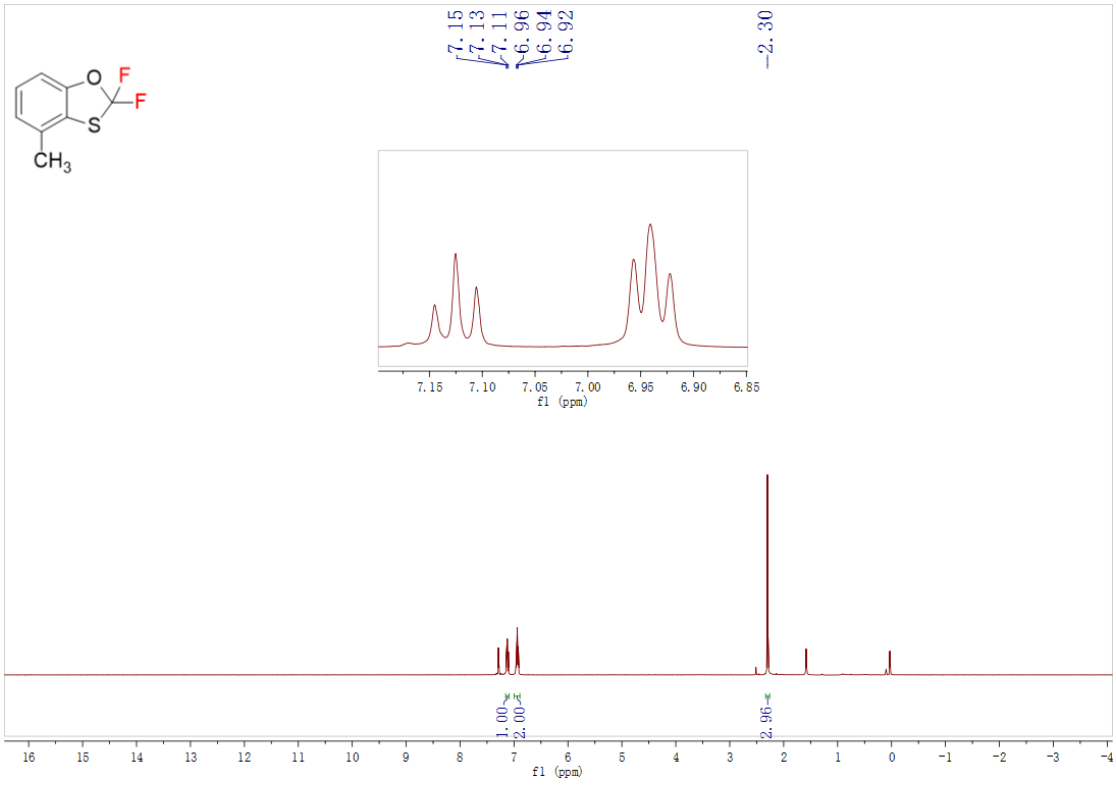
^{13}C NMR spectrum of **3d** in $CDCl_3$



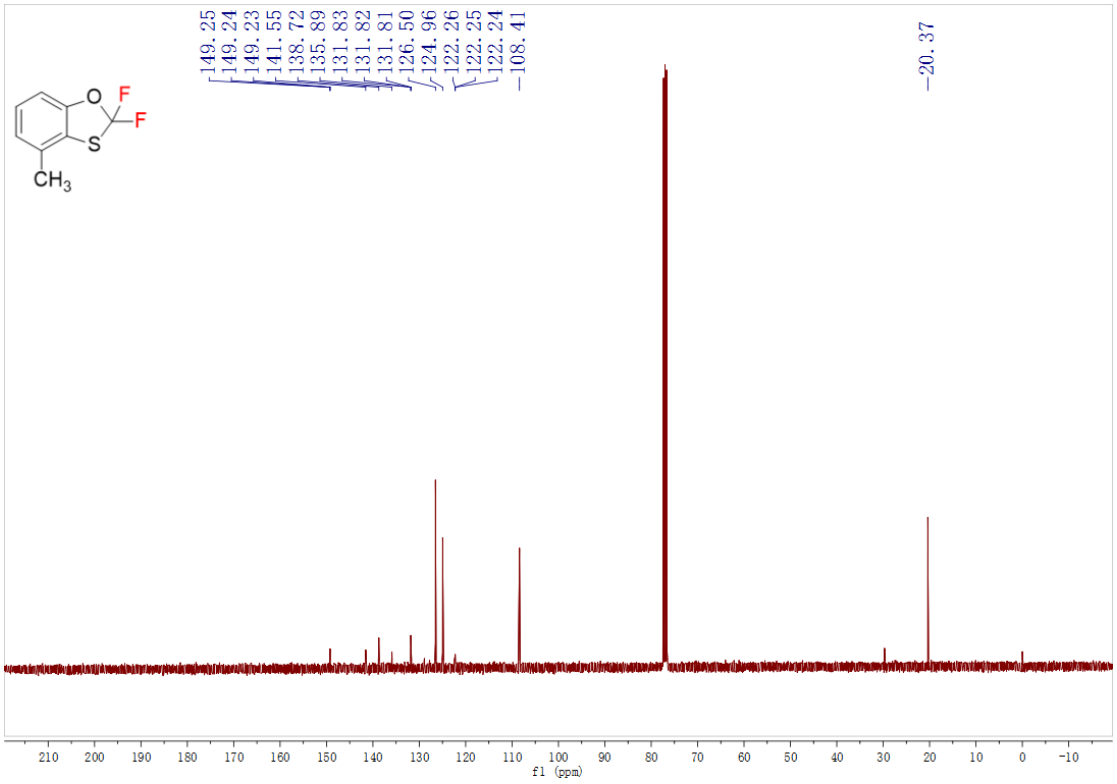
^{19}F NMR spectrum of **3e** in $CDCl_3$



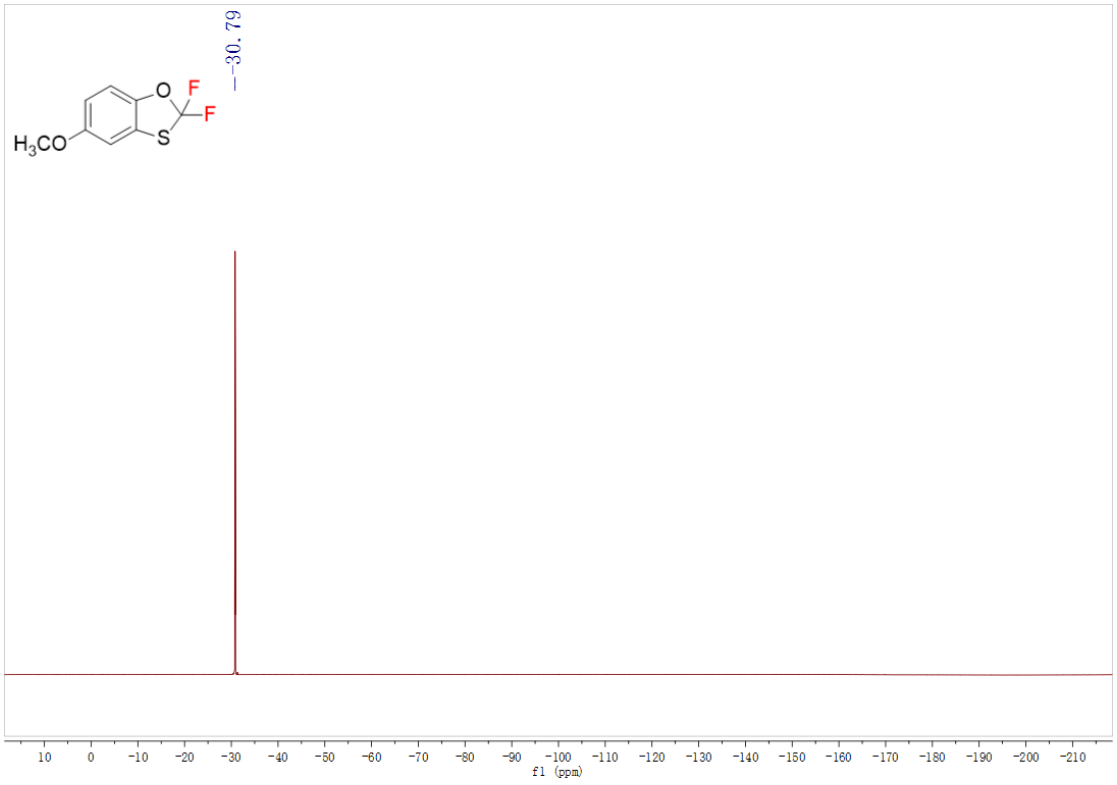
^{1}H NMR spectrum of **3e** in $CDCl_3$



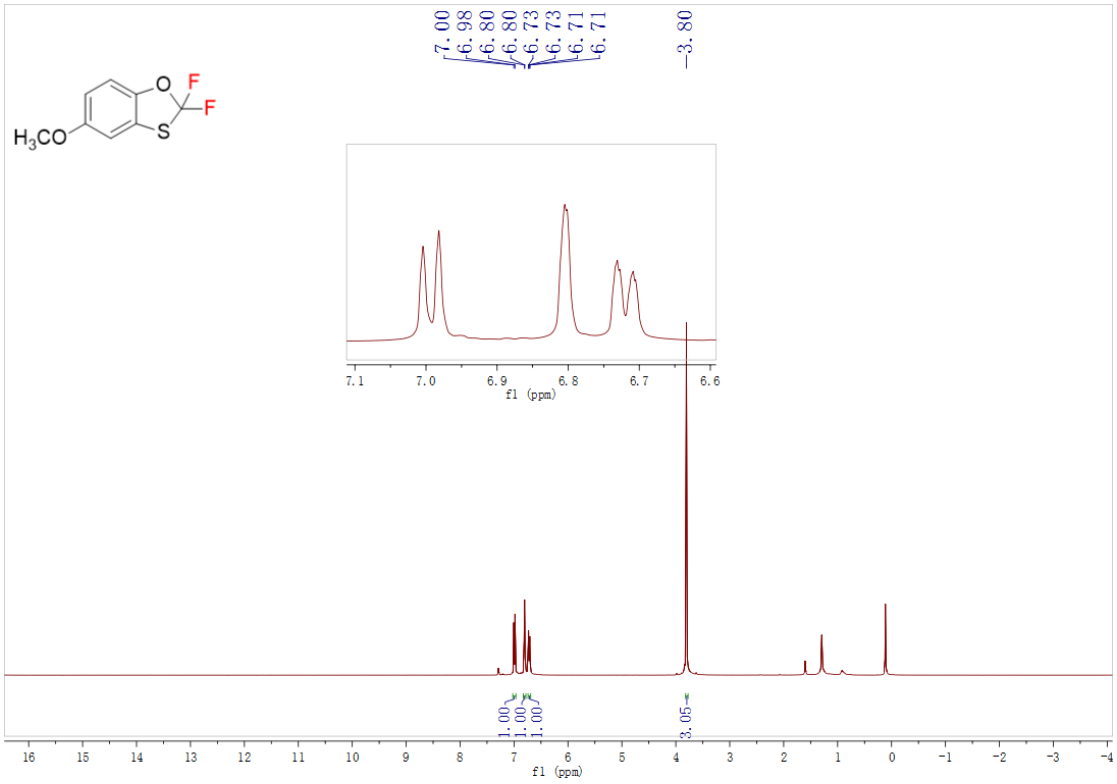
^{13}C NMR spectrum of **3e** in $CDCl_3$



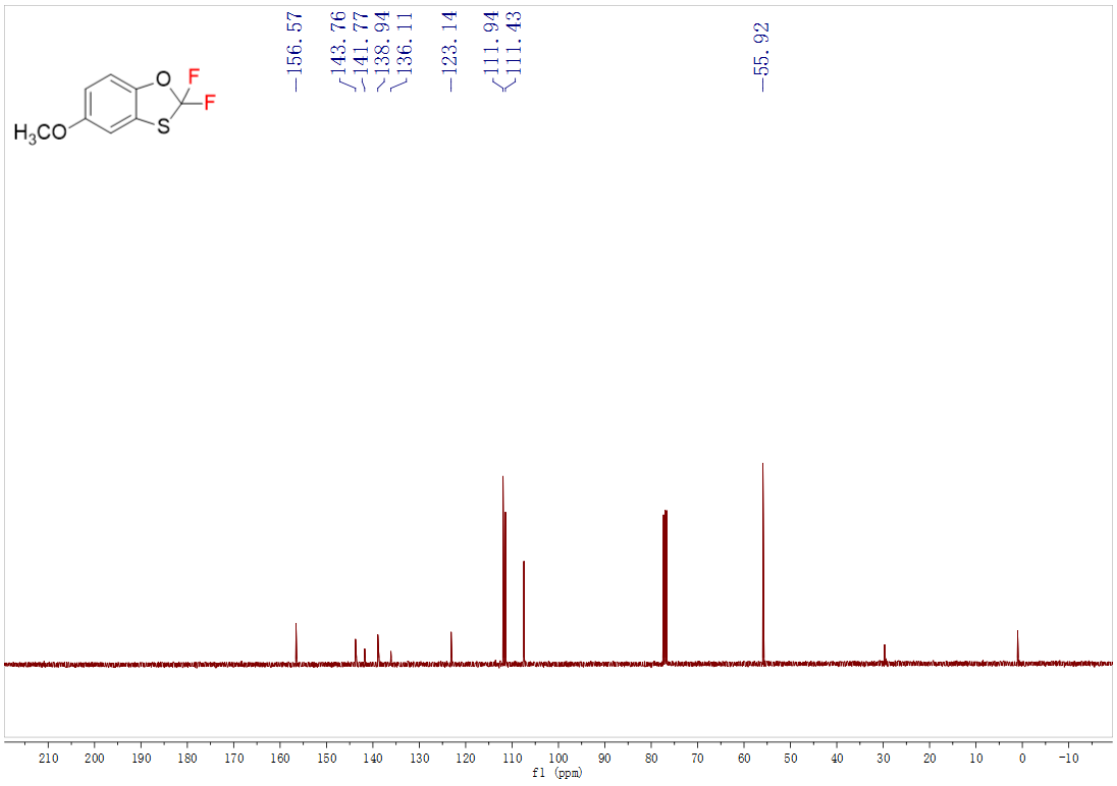
^{19}F NMR spectrum of **3f** in $CDCl_3$



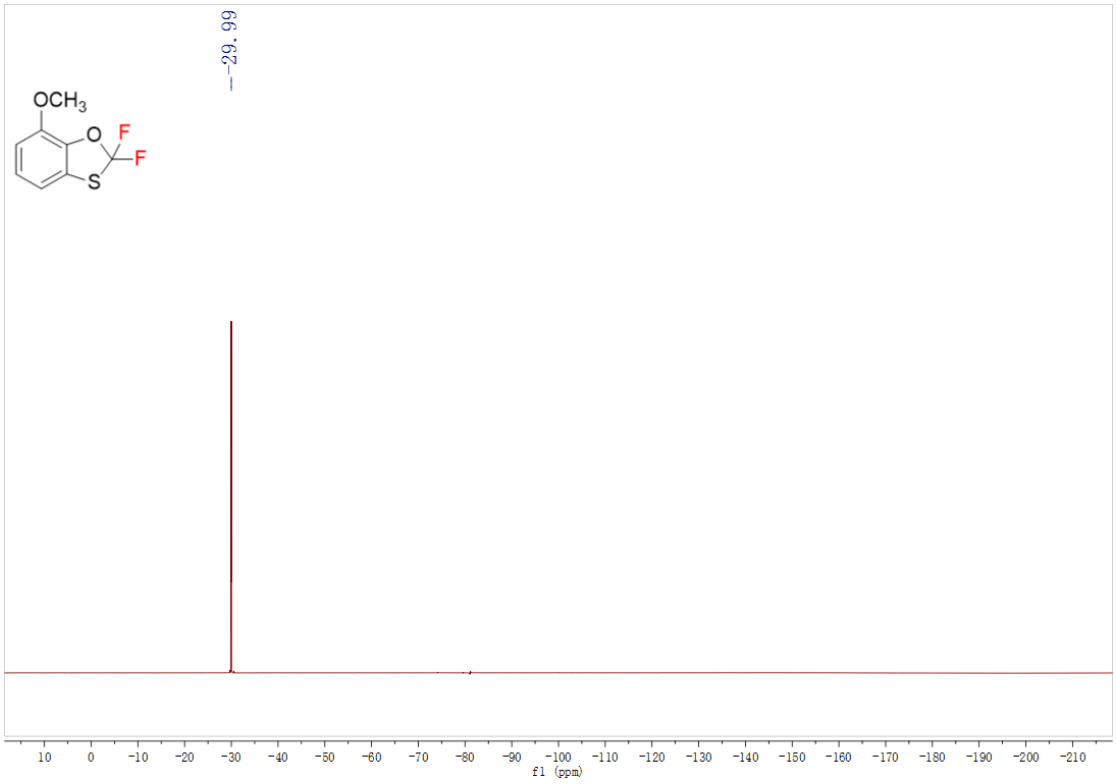
^{1}H NMR spectrum of **3f** in $CDCl_3$



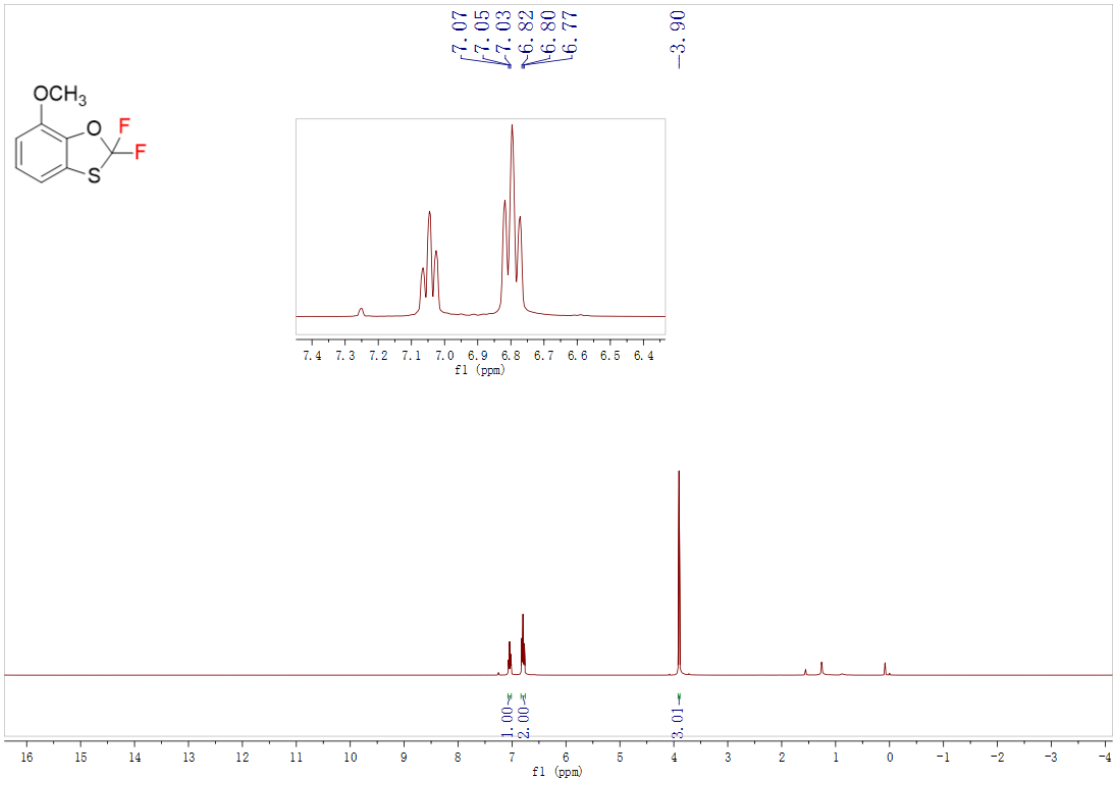
^{13}C NMR spectrum of **3f** in $CDCl_3$



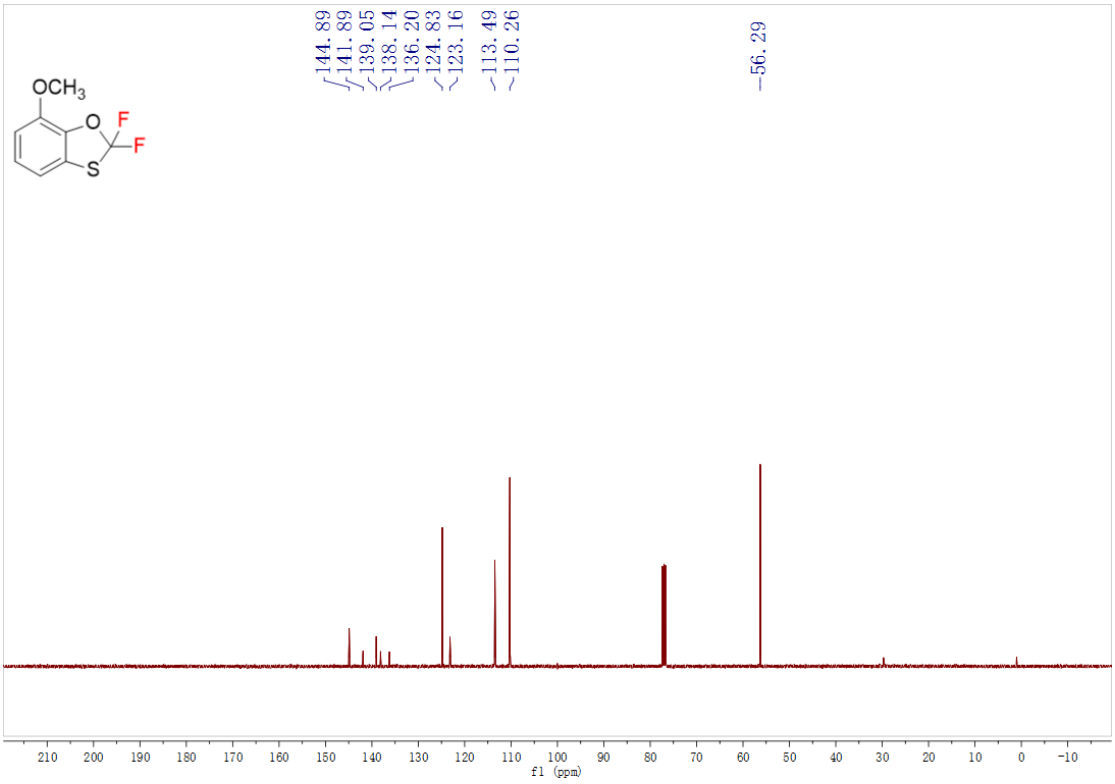
^{19}F NMR spectrum of **3g** in $CDCl_3$



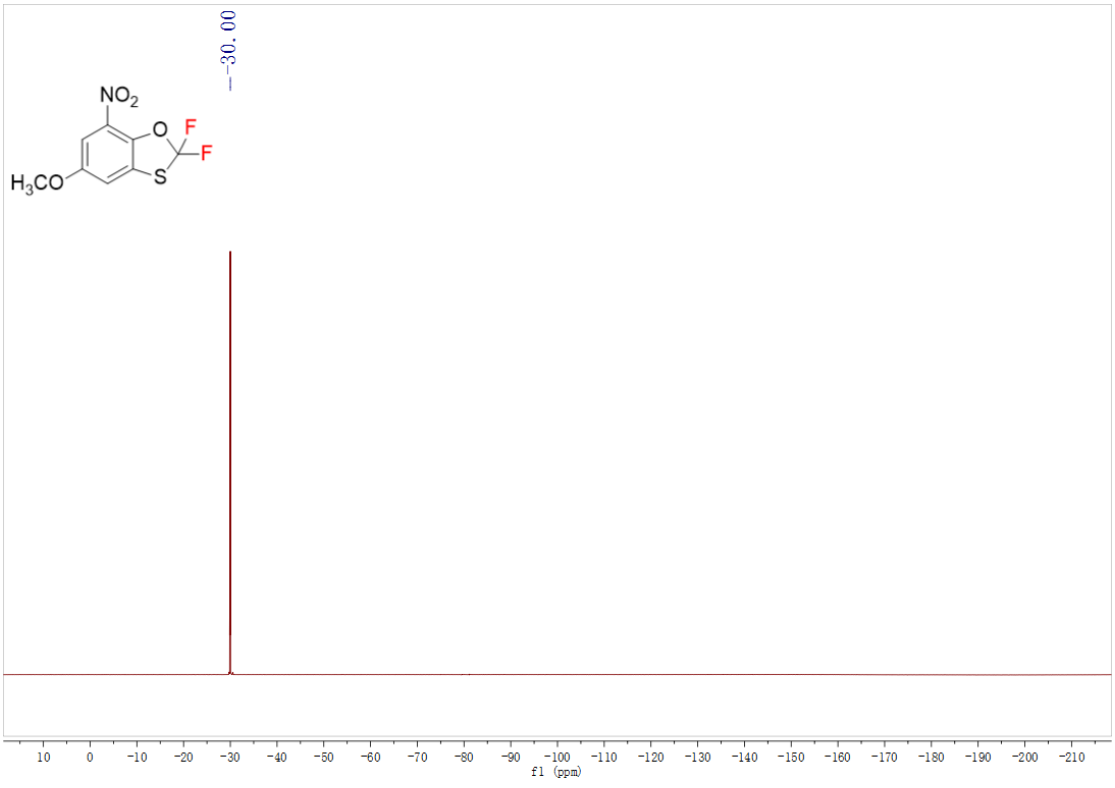
^{1}H NMR spectrum of **3g** in $CDCl_3$



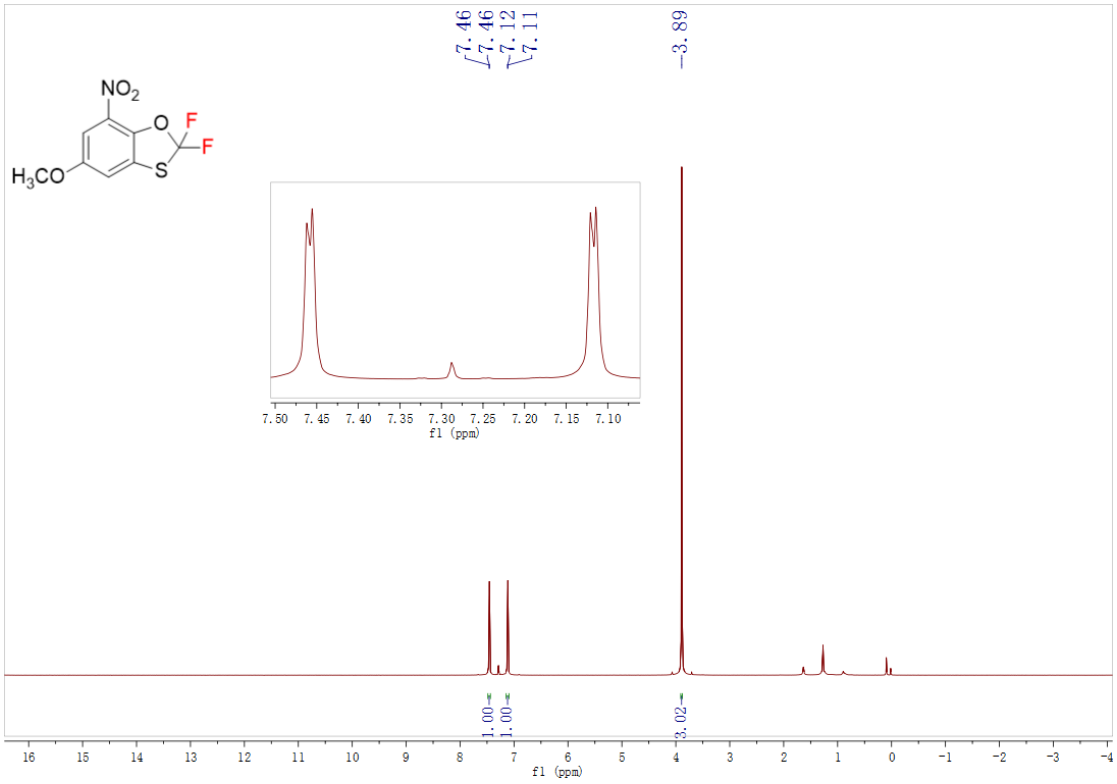
^{13}C NMR spectrum of **3g** in $CDCl_3$



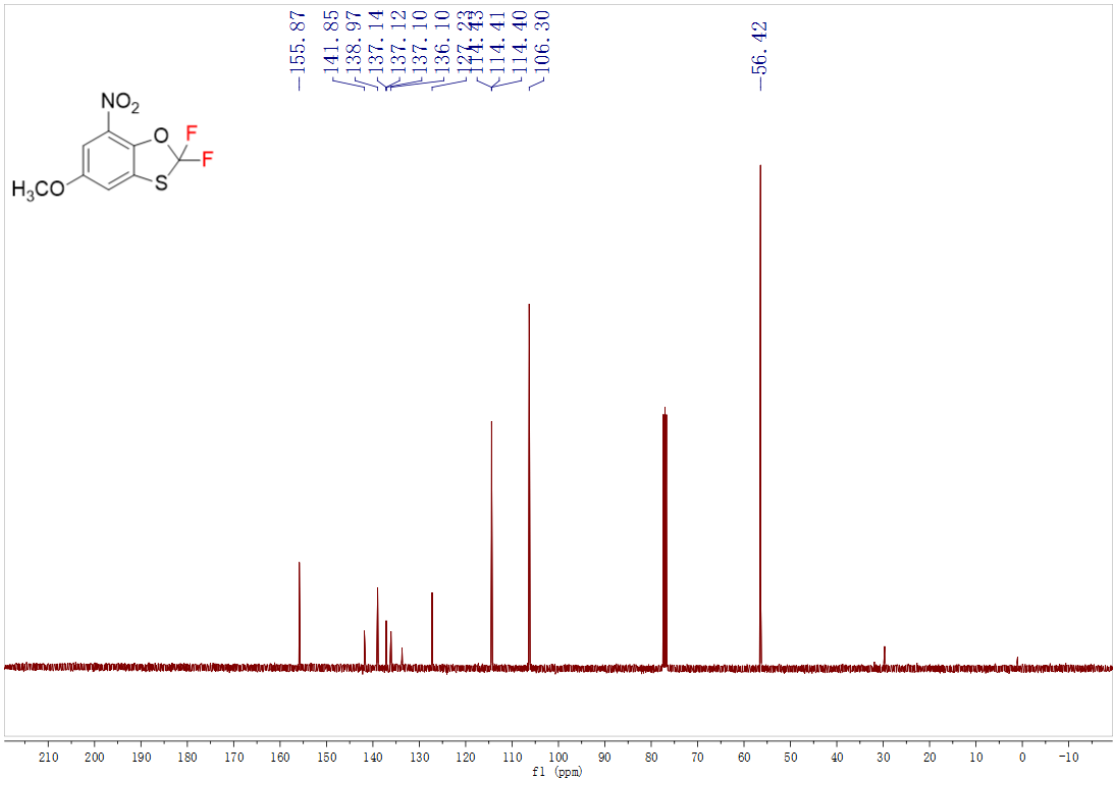
^{19}F NMR spectrum of **3h** in $CDCl_3$



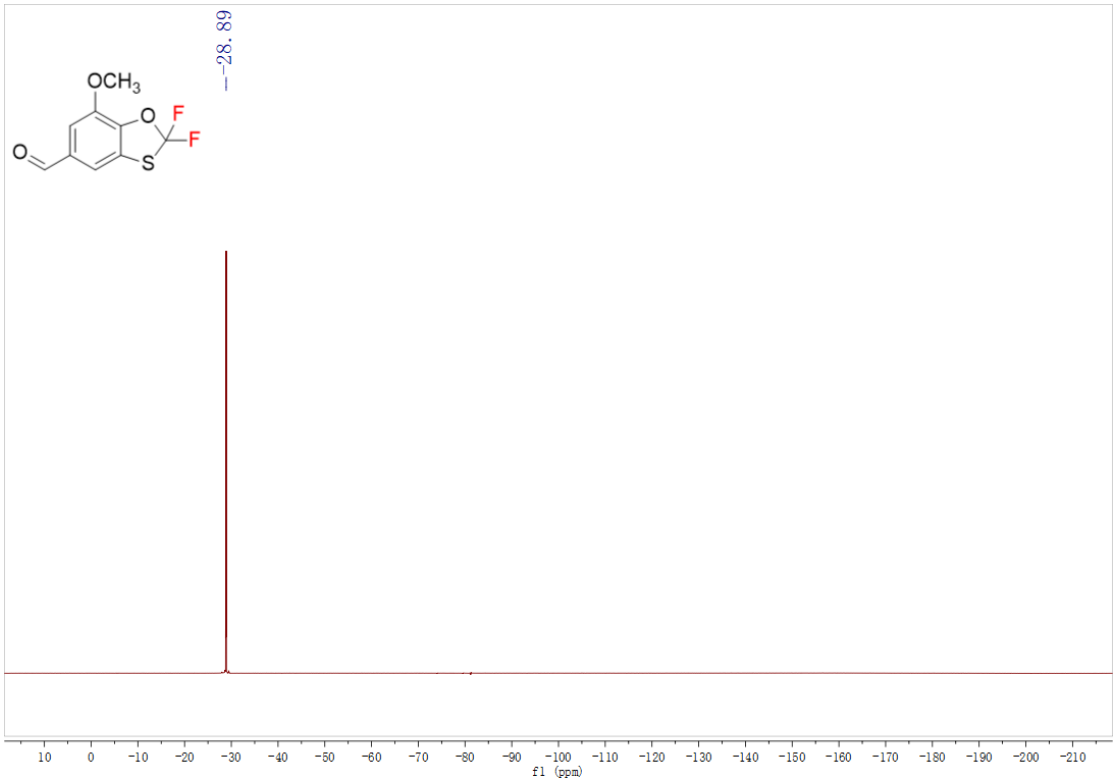
^{1}H NMR spectrum of **3h** in $CDCl_3$



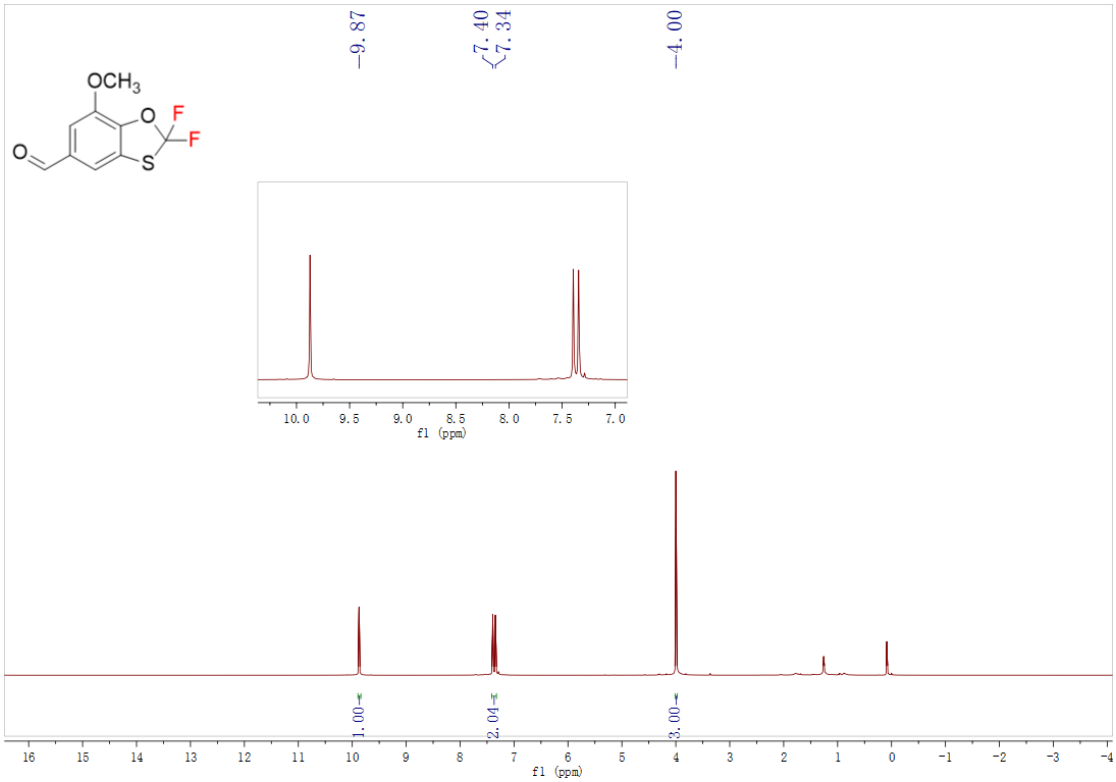
^{13}C NMR spectrum of **3h** in $CDCl_3$



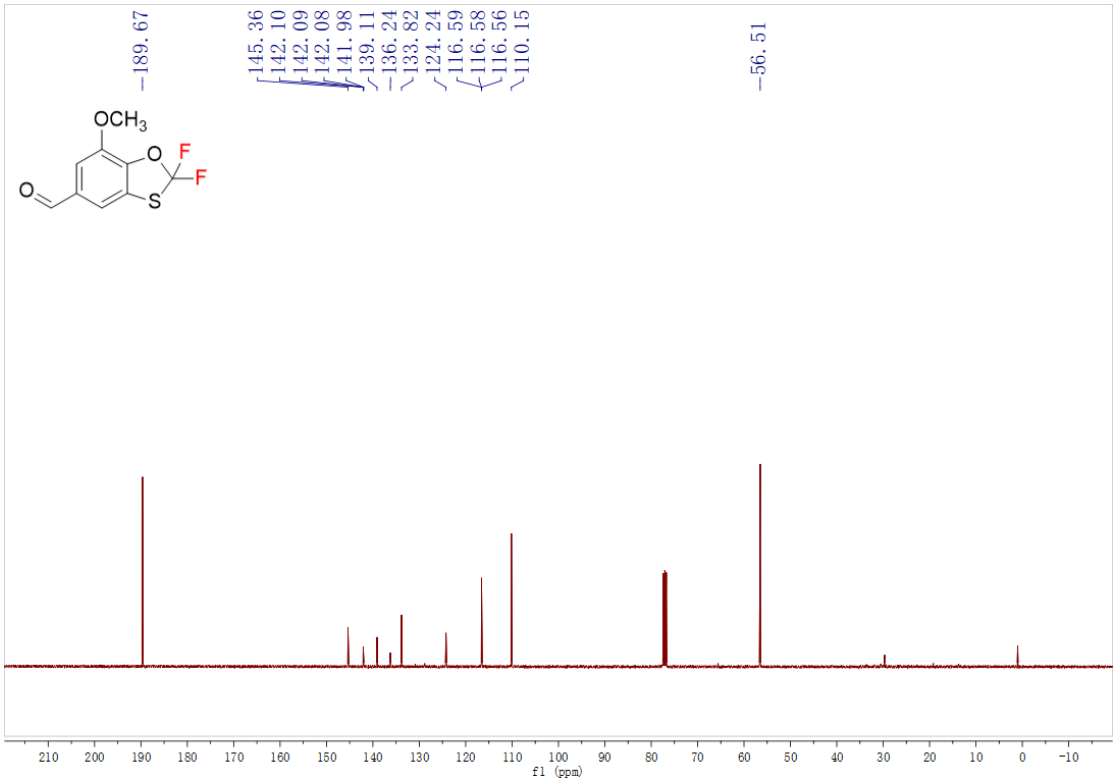
^{19}F NMR spectrum of **3i** in $CDCl_3$



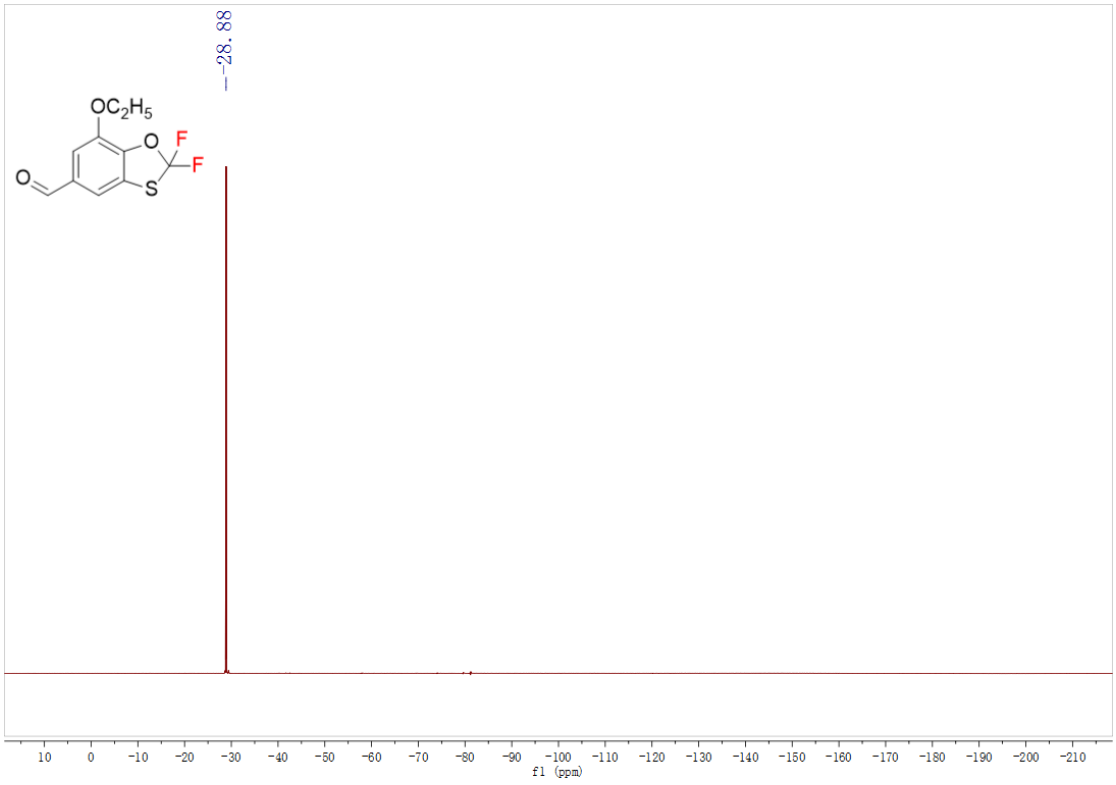
^{1}H NMR spectrum of **3i** in $CDCl_3$



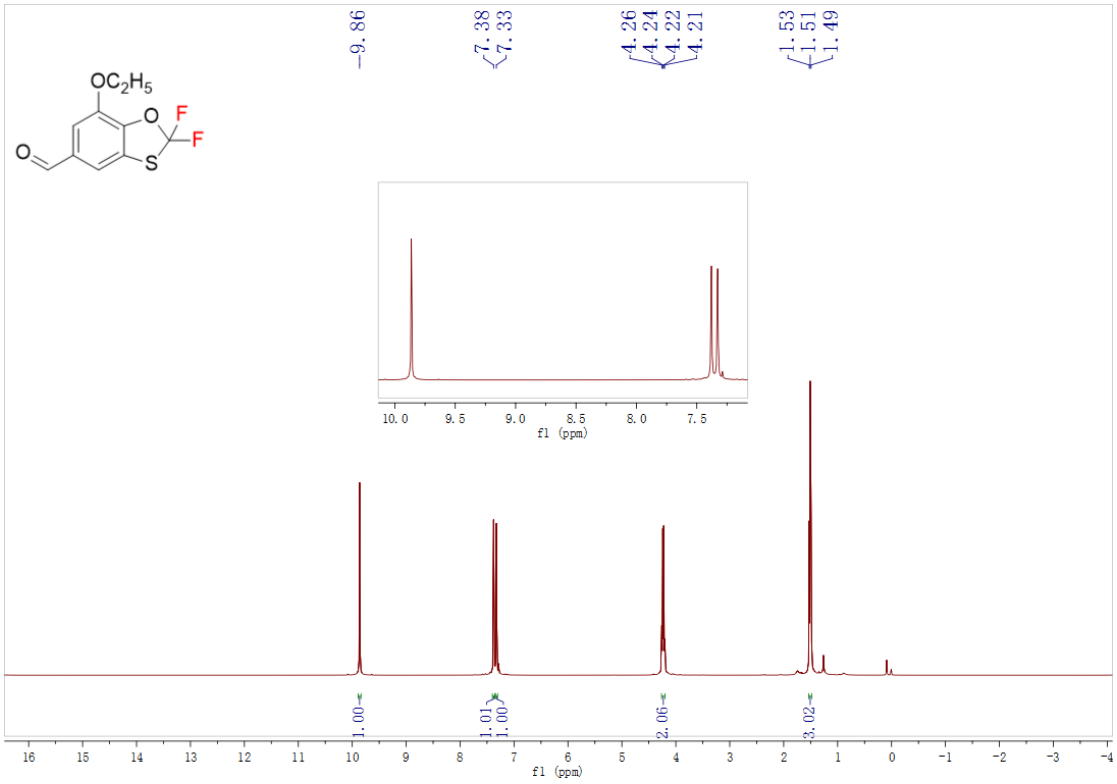
^{13}C NMR spectrum of **3i** in $CDCl_3$



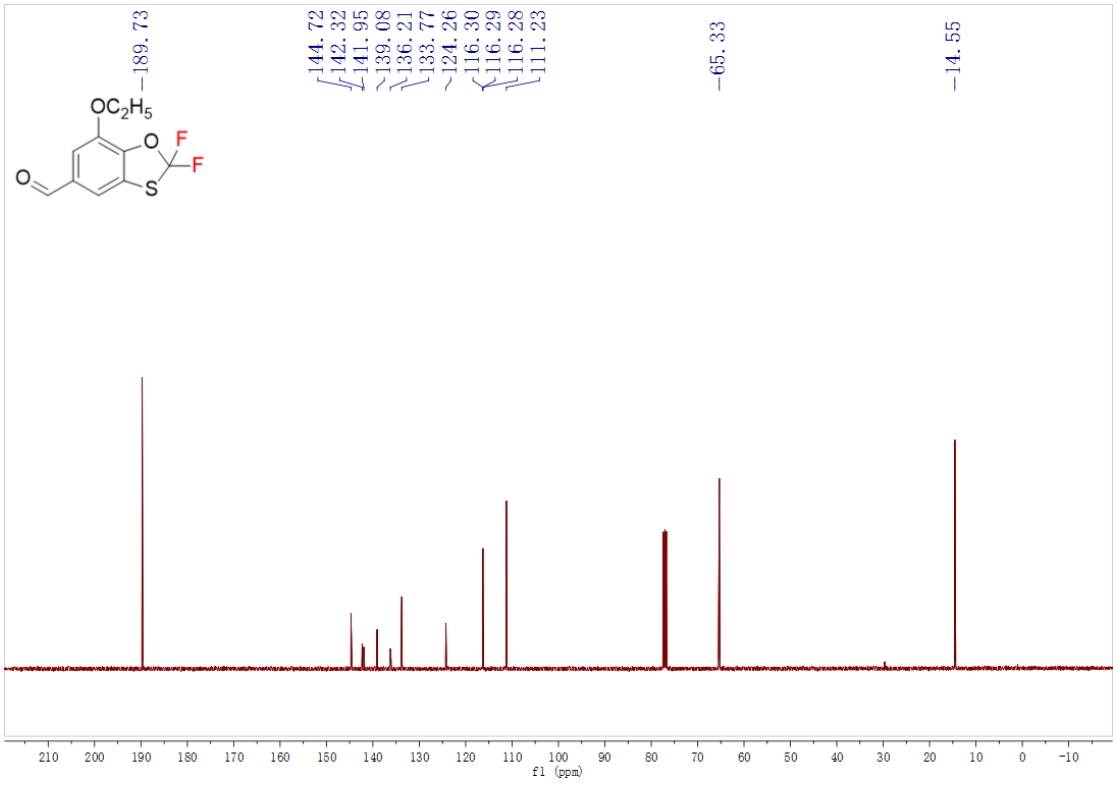
^{19}F NMR spectrum of **3j** in $CDCl_3$



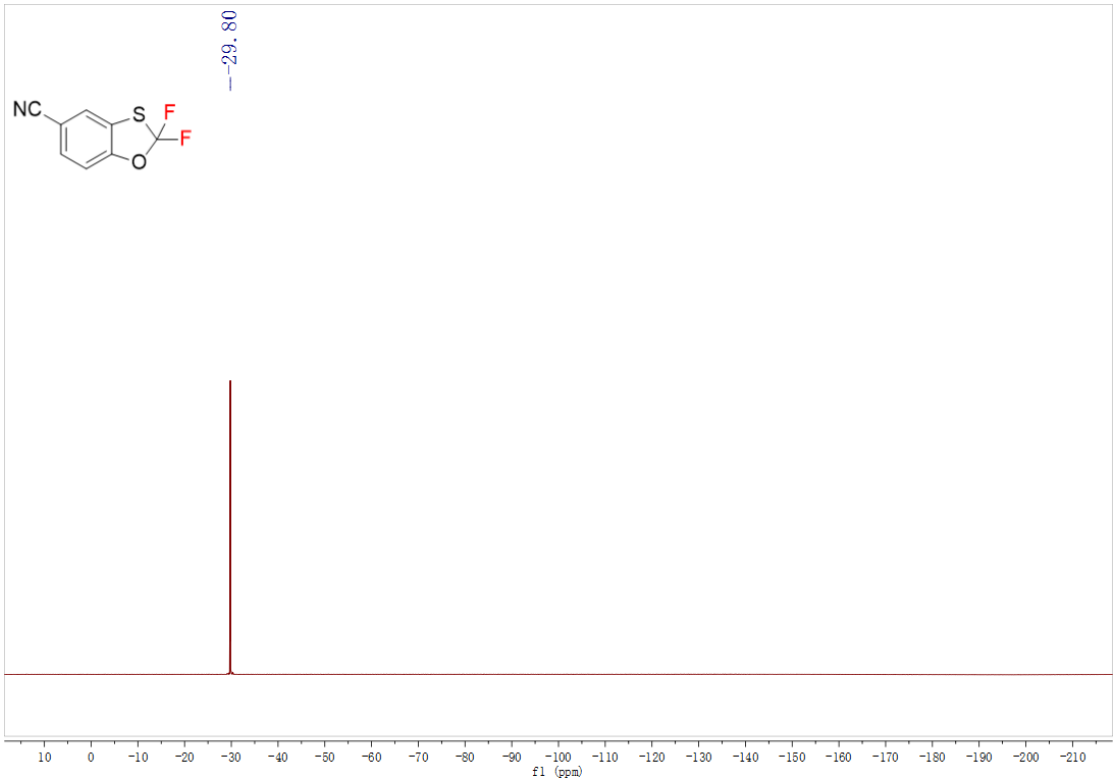
^{1}H NMR spectrum of **3j** in $CDCl_3$



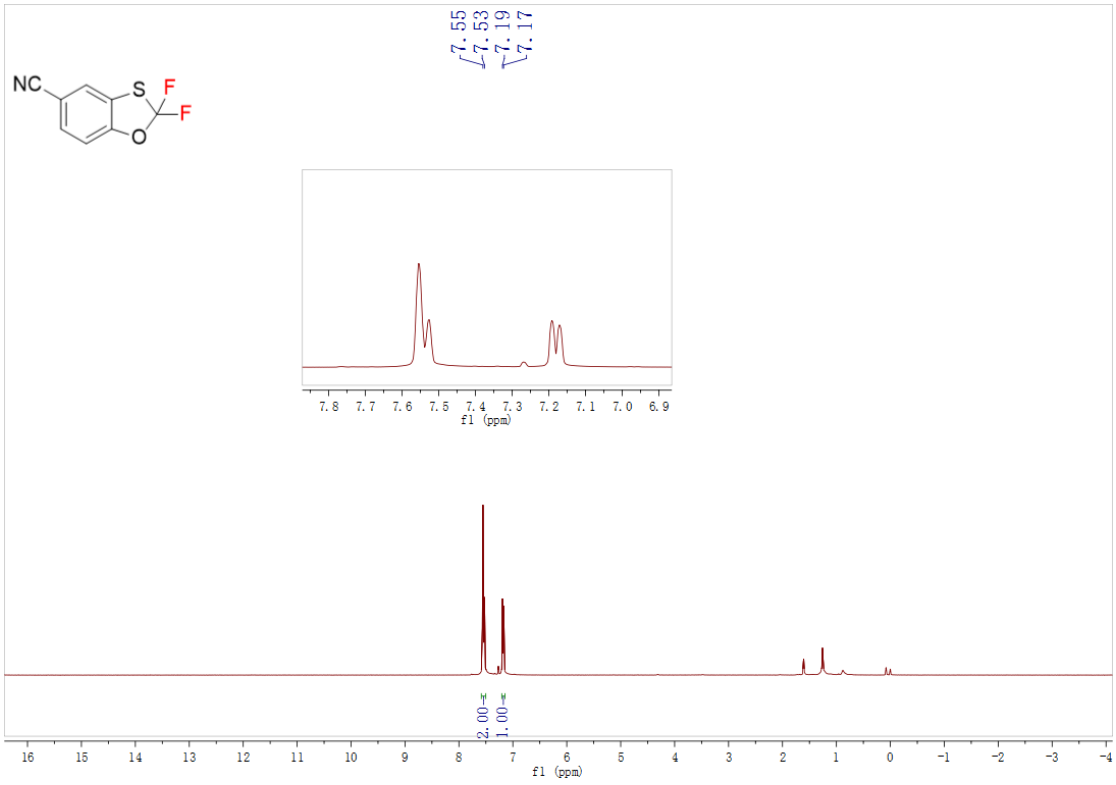
^{13}C NMR spectrum of **3j** in $CDCl_3$



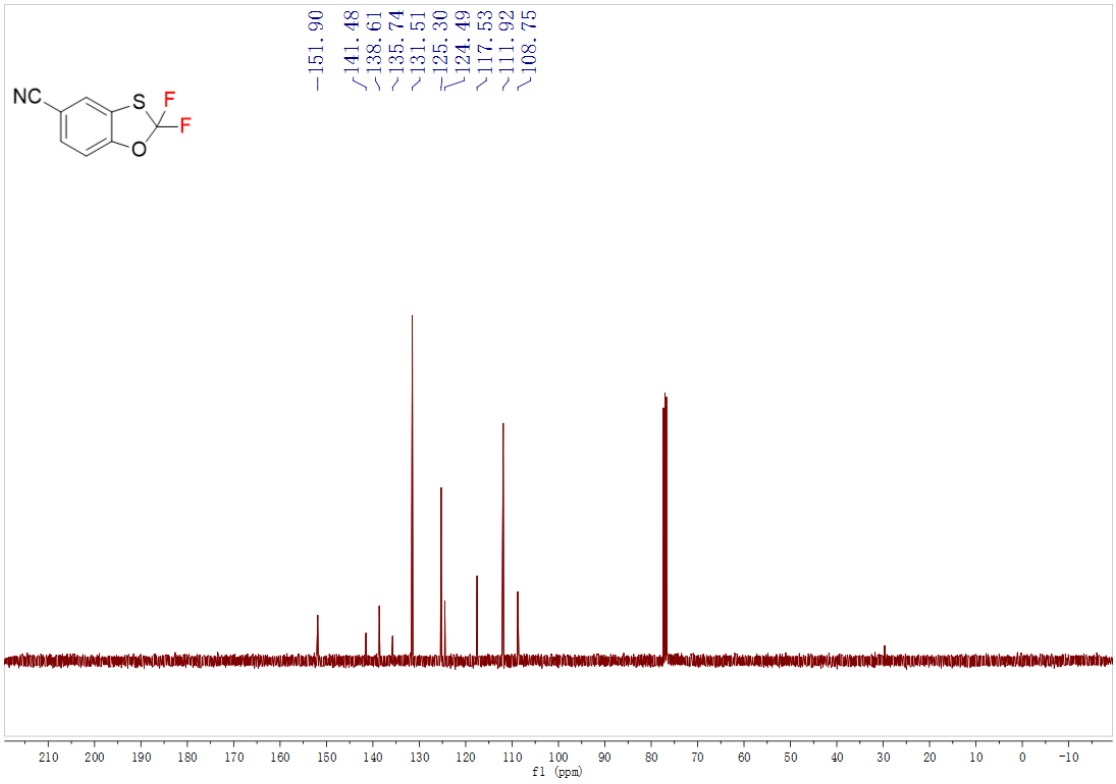
^{19}F NMR spectrum of **3k** in $CDCl_3$



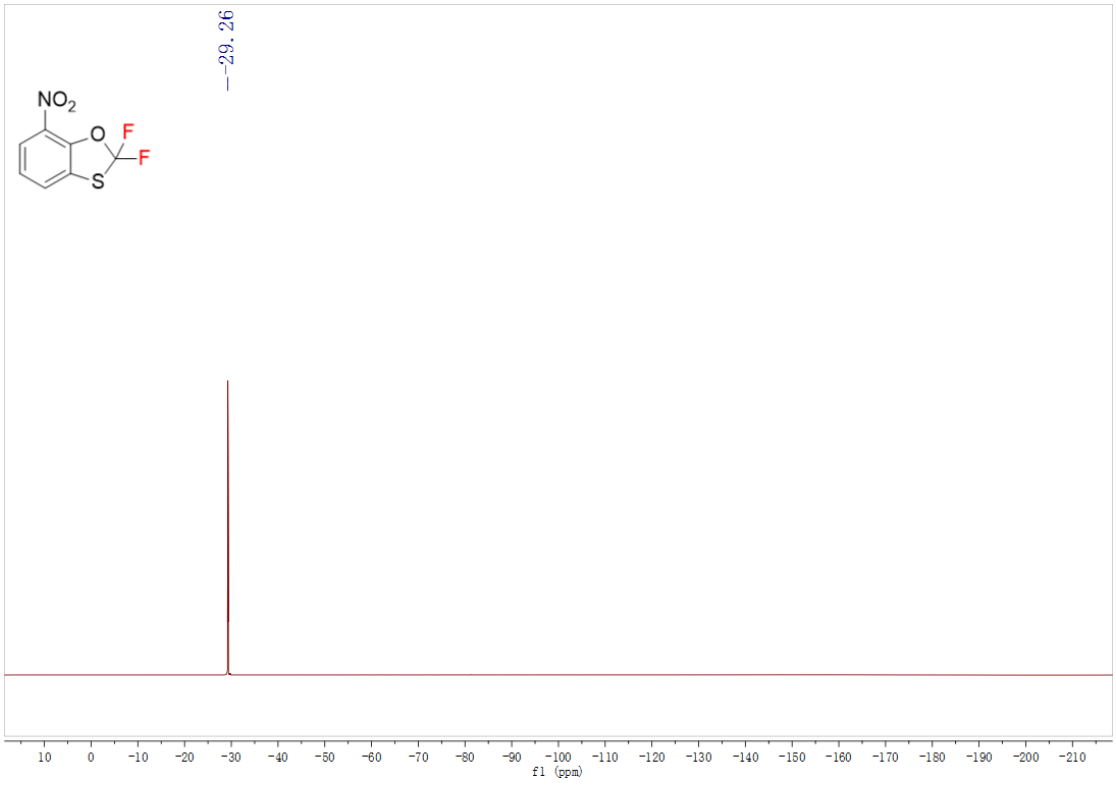
^{1}H NMR spectrum of **3k** in $CDCl_3$



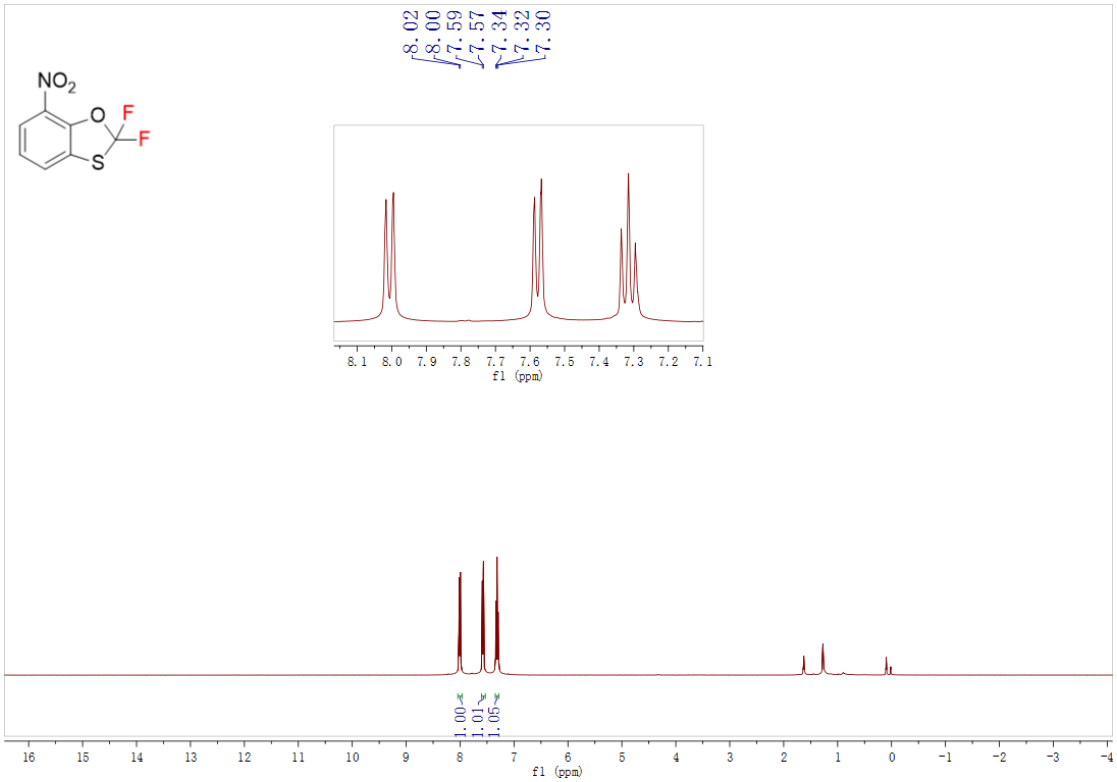
^{13}C NMR spectrum of **3k** in $CDCl_3$



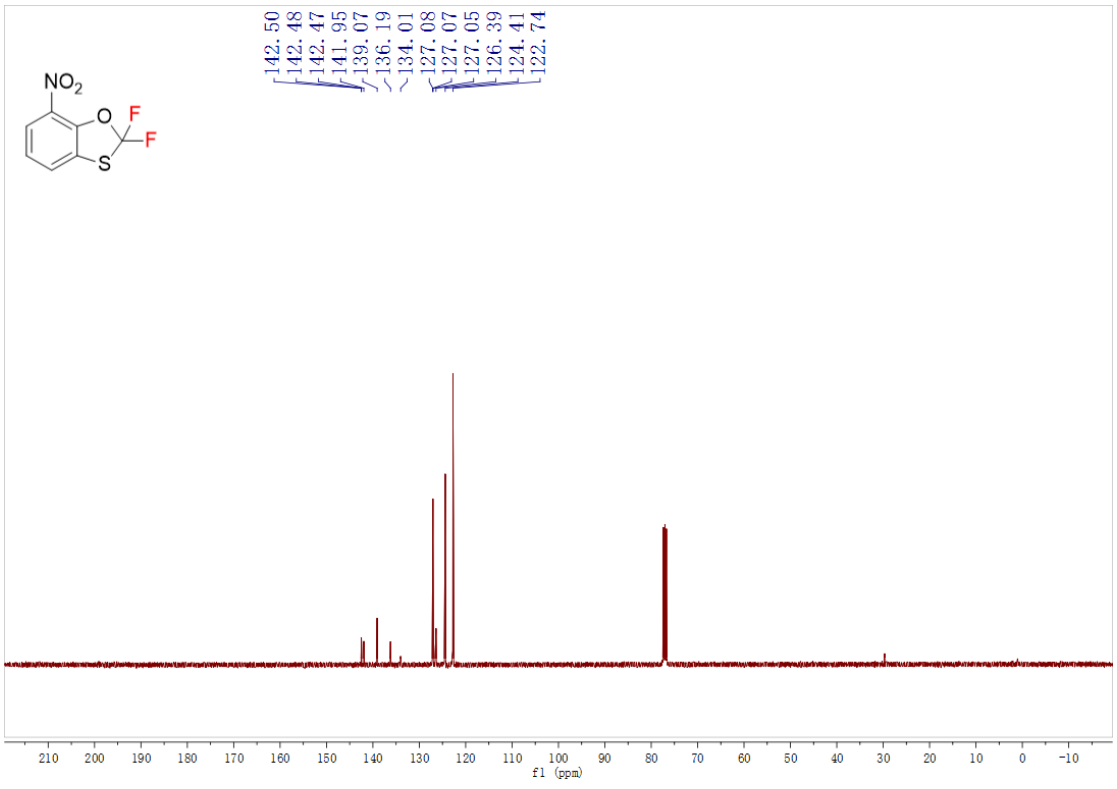
^{19}F NMR spectrum of **3l** in $CDCl_3$



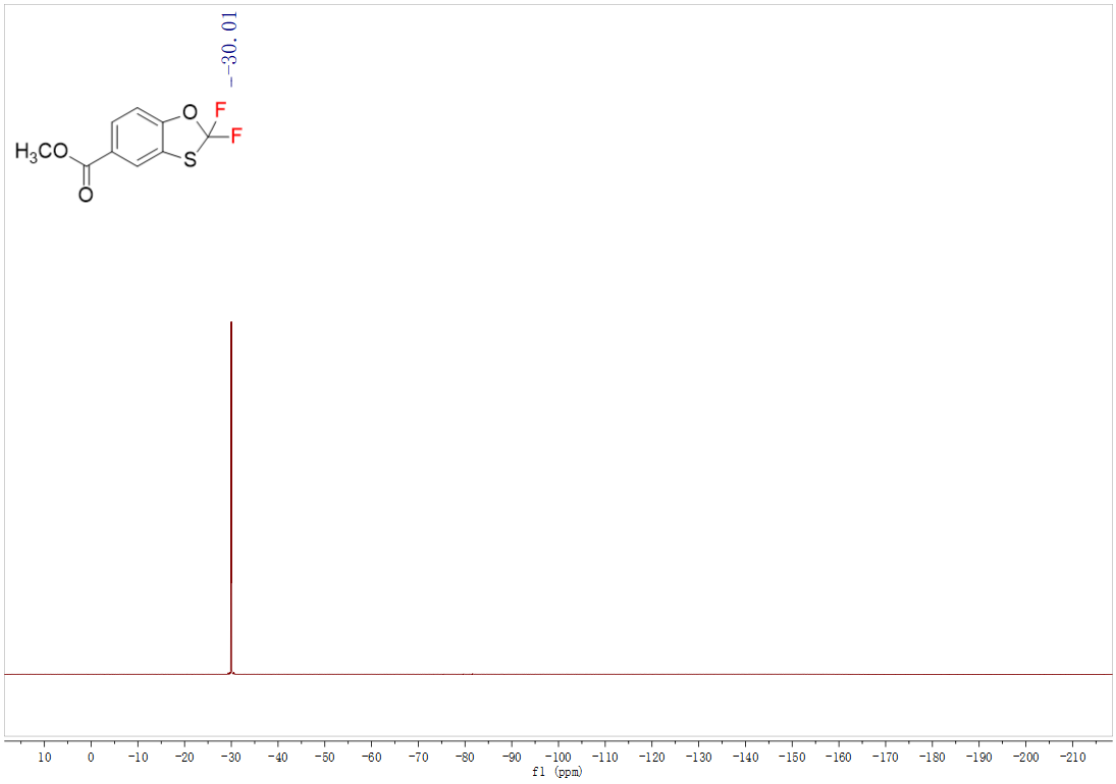
^{1}H NMR spectrum of **3l** in $CDCl_3$



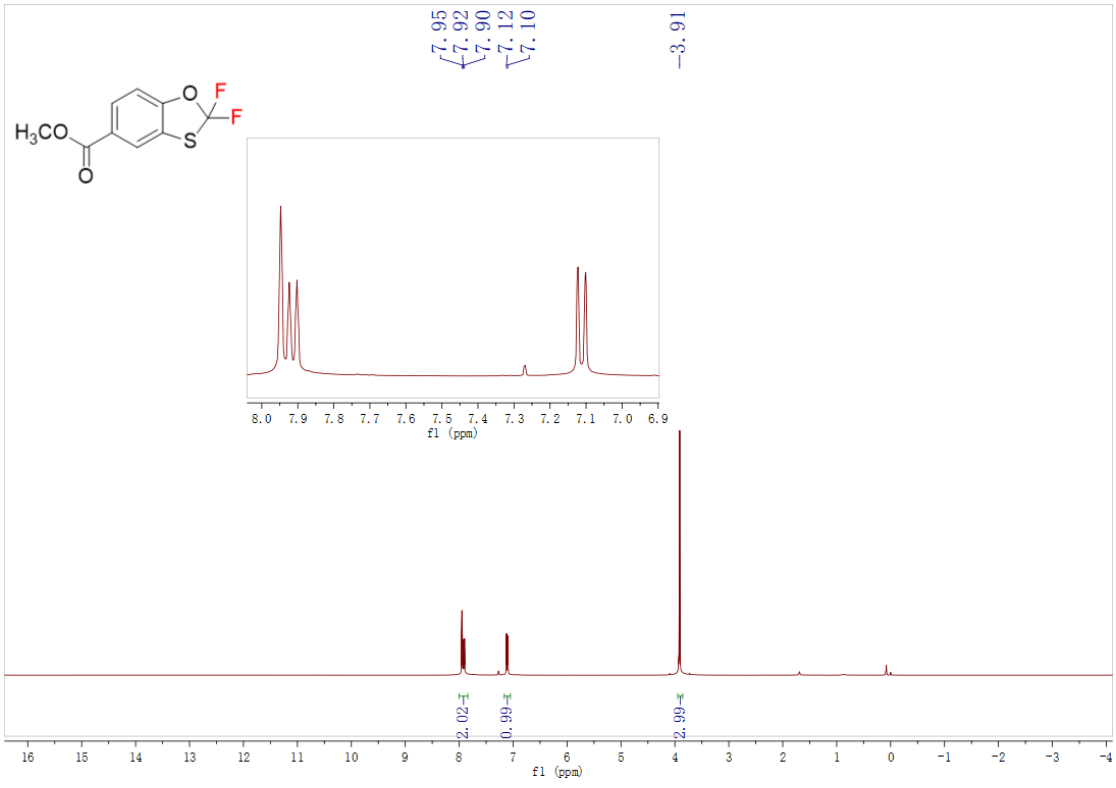
^{13}C NMR spectrum of **3l** in $CDCl_3$



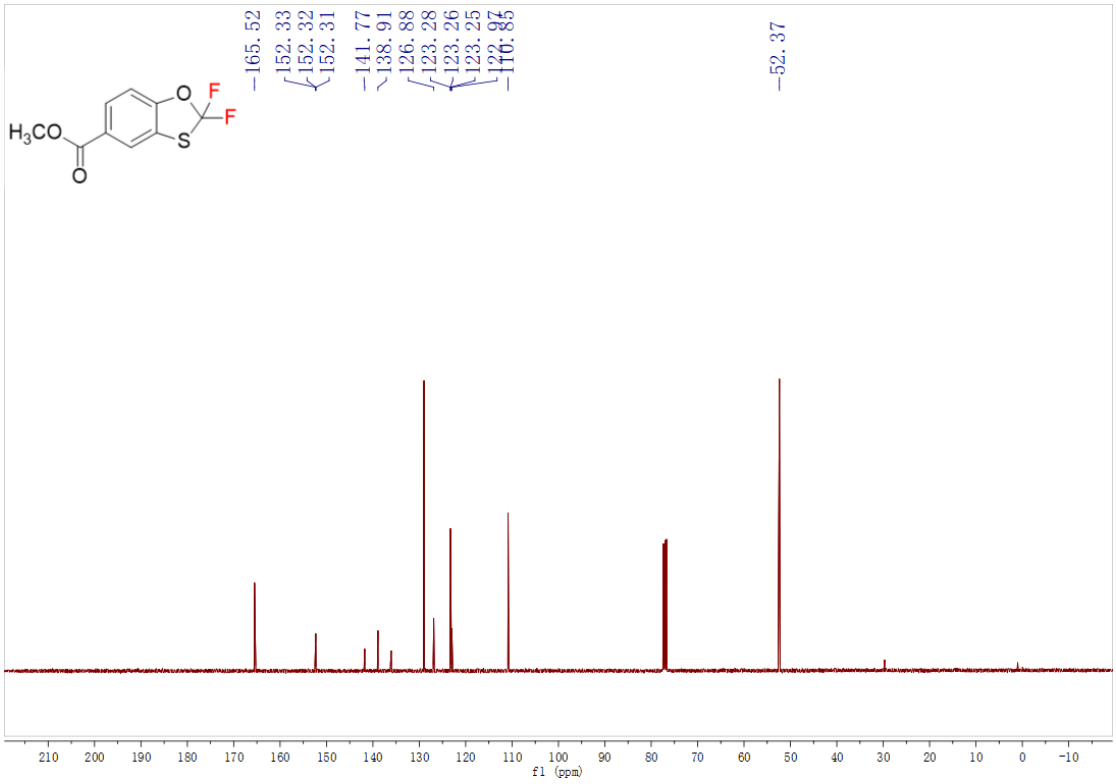
^{19}F NMR spectrum of **3m** in $CDCl_3$



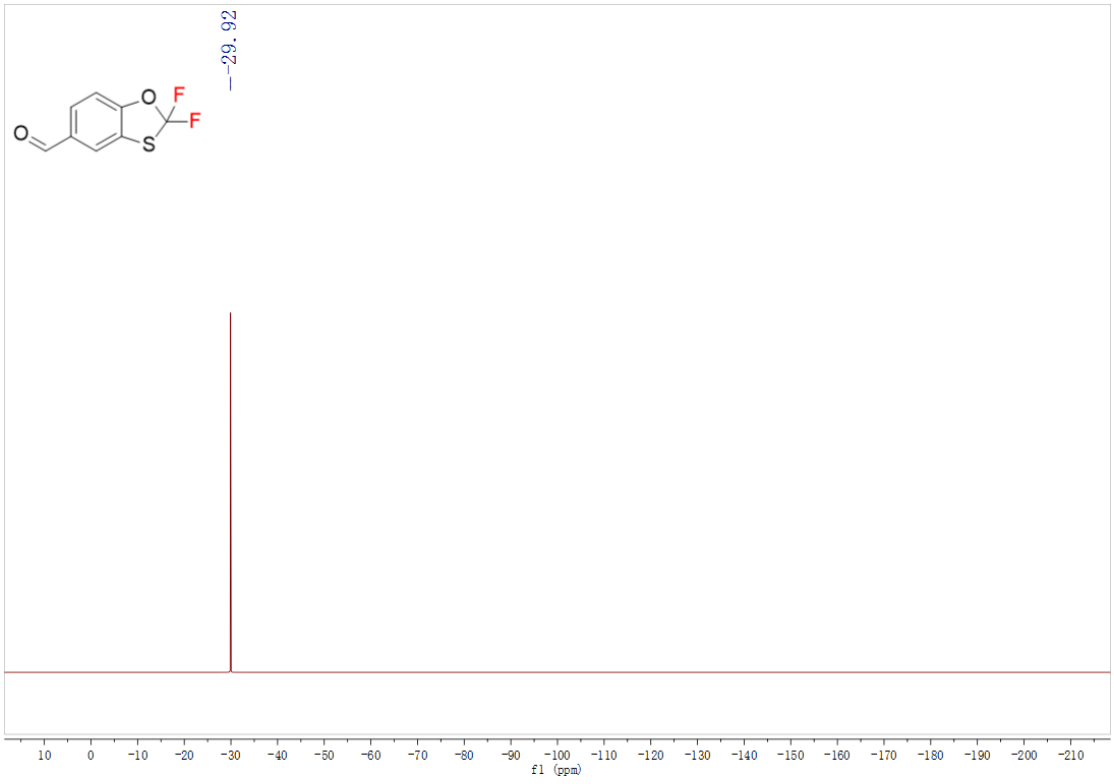
^{1}H NMR spectrum of **3m** in $CDCl_3$



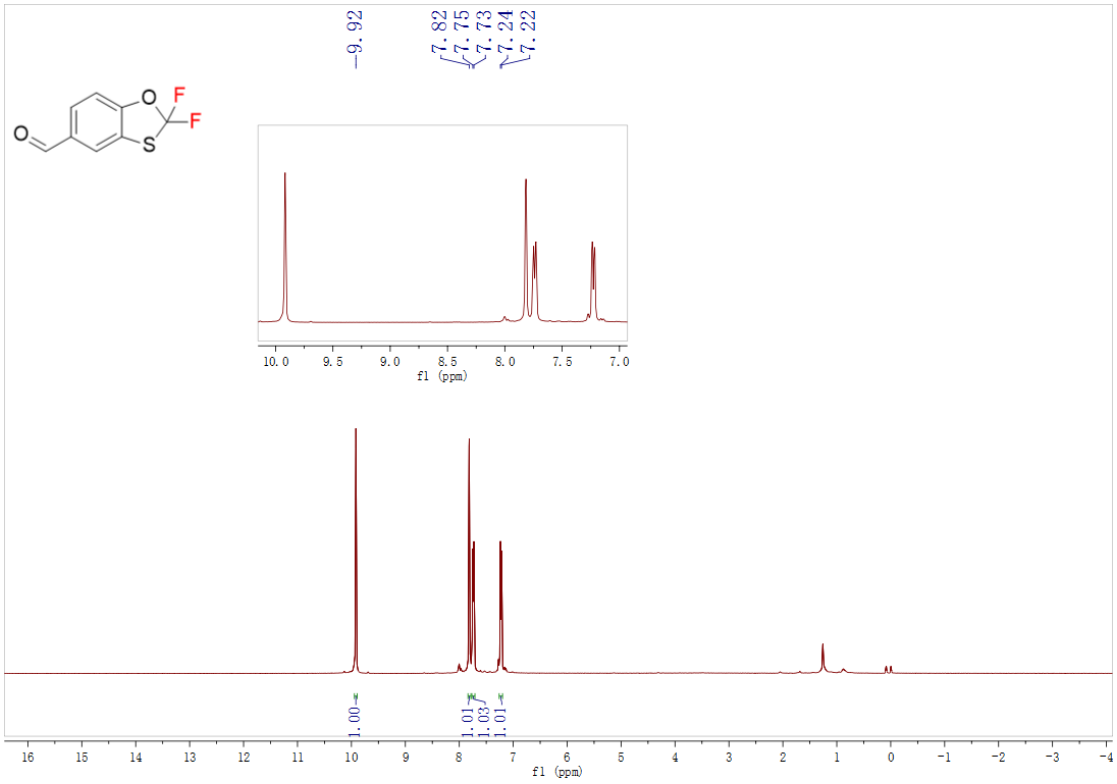
^{13}C NMR spectrum of **3m** in $CDCl_3$



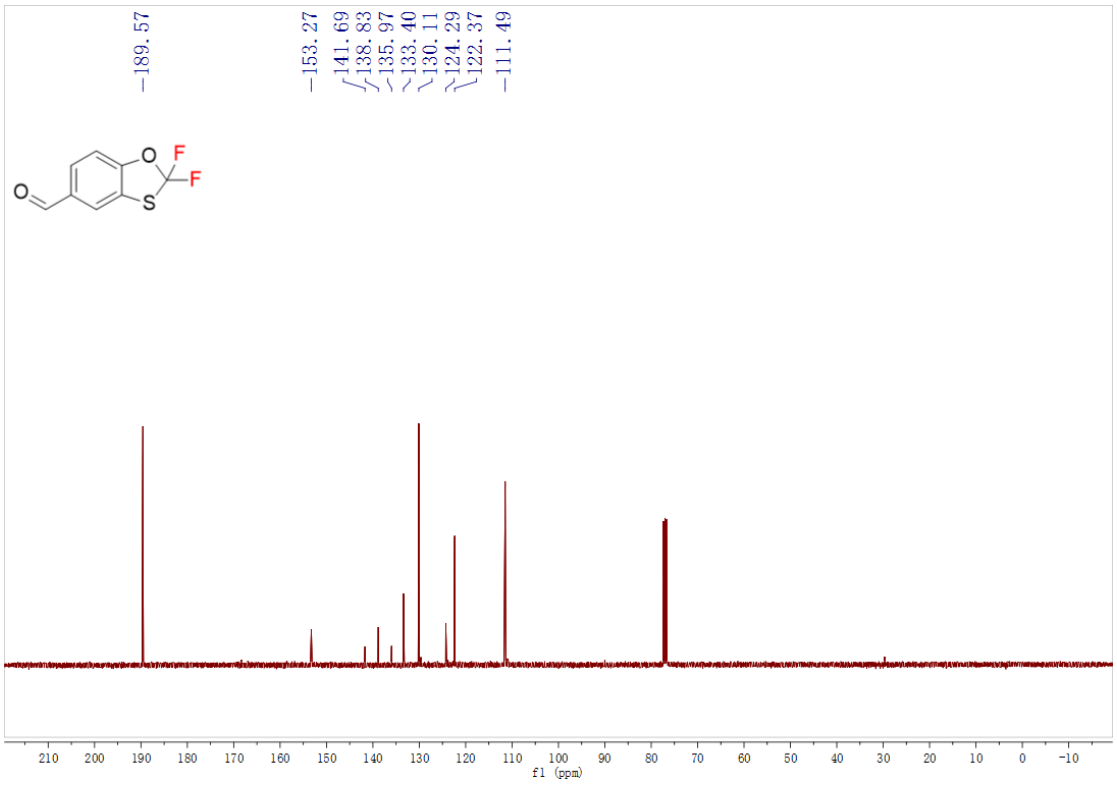
^{19}F NMR spectrum of **3n** in $CDCl_3$



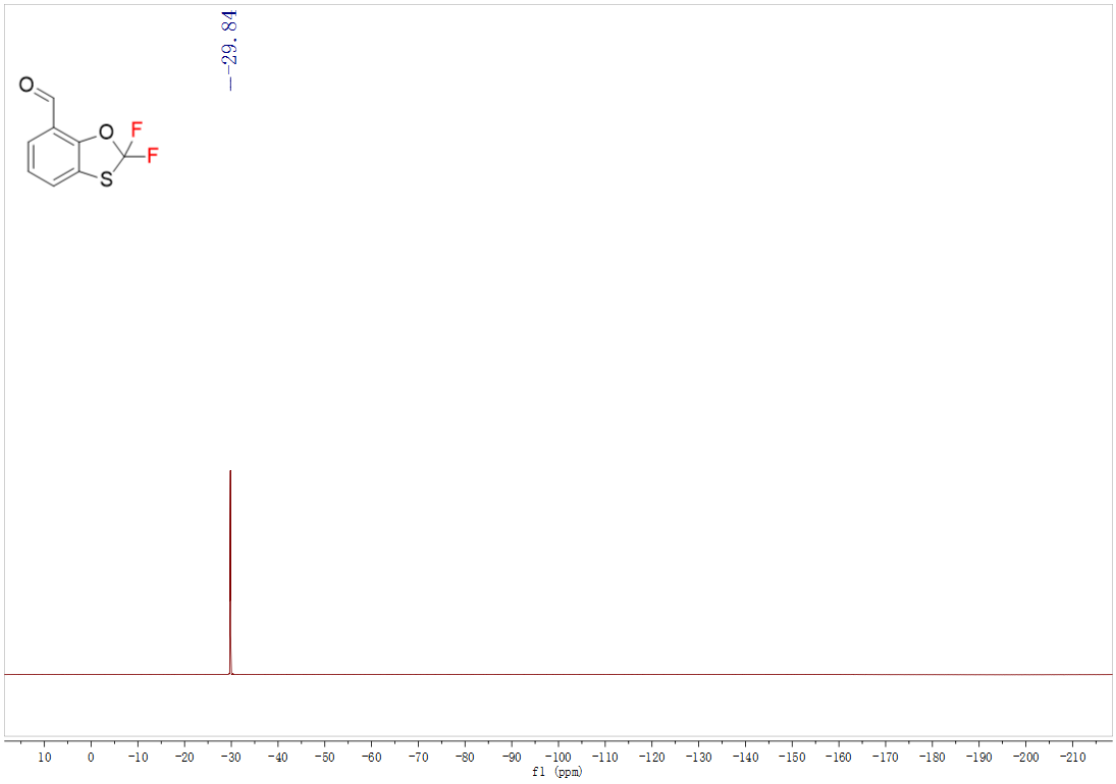
^{1}H NMR spectrum of **3n** in $CDCl_3$



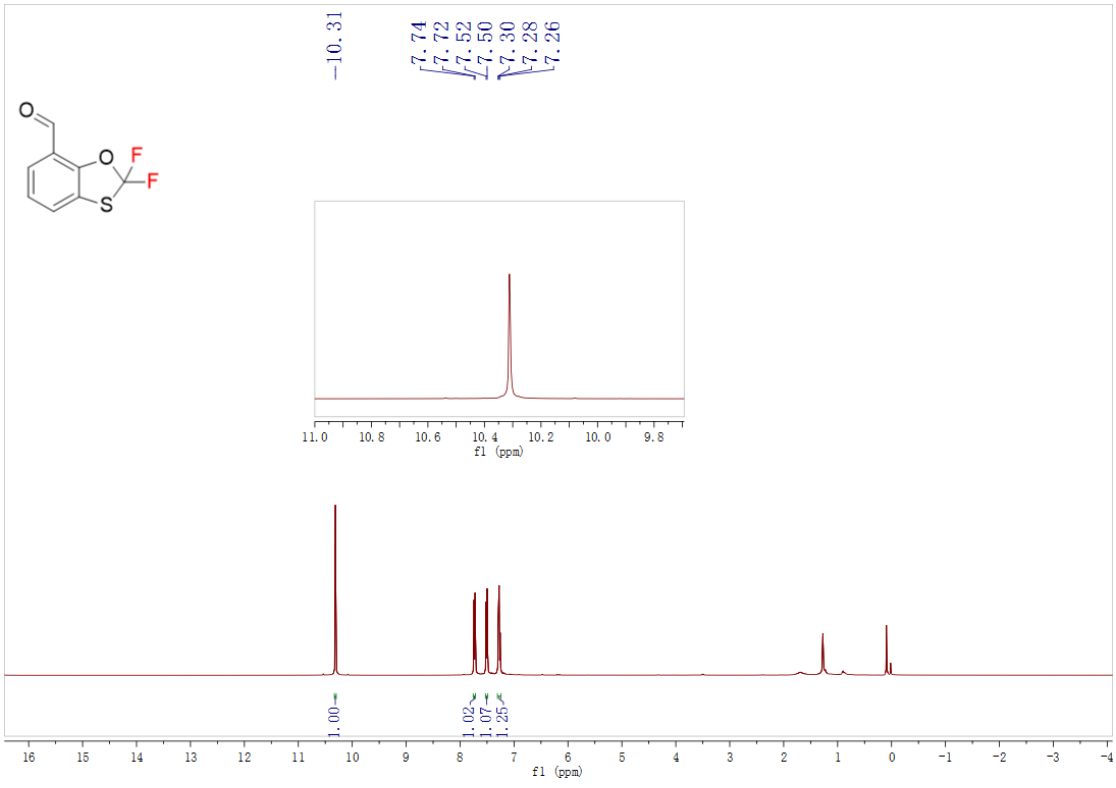
^{13}C NMR spectrum of **3n** in $CDCl_3$



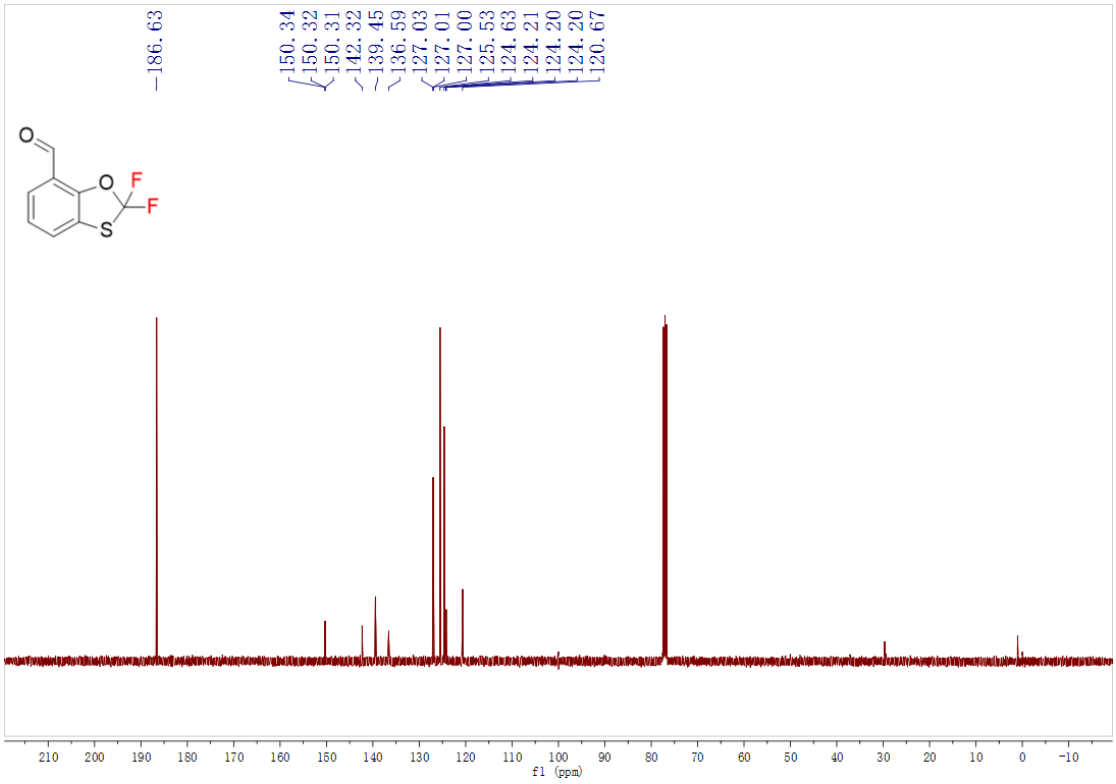
^{19}F NMR spectrum of **3o** in $CDCl_3$



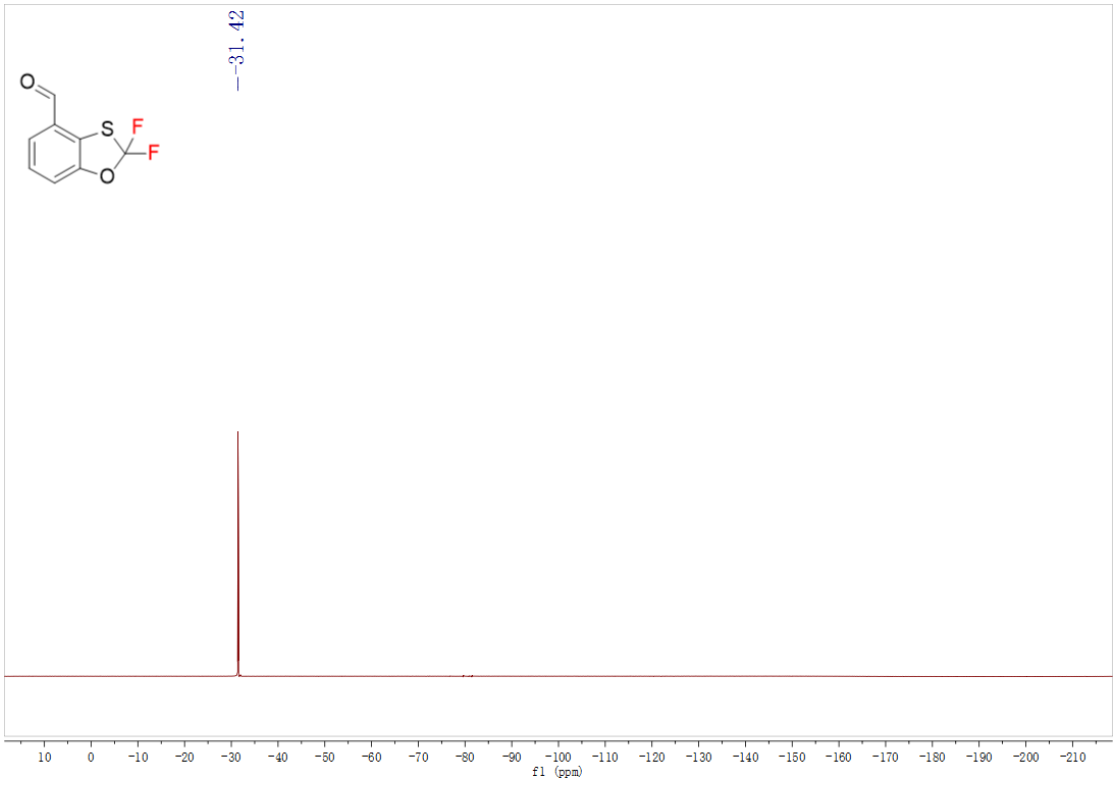
^{1}H NMR spectrum of **3o** in $CDCl_3$



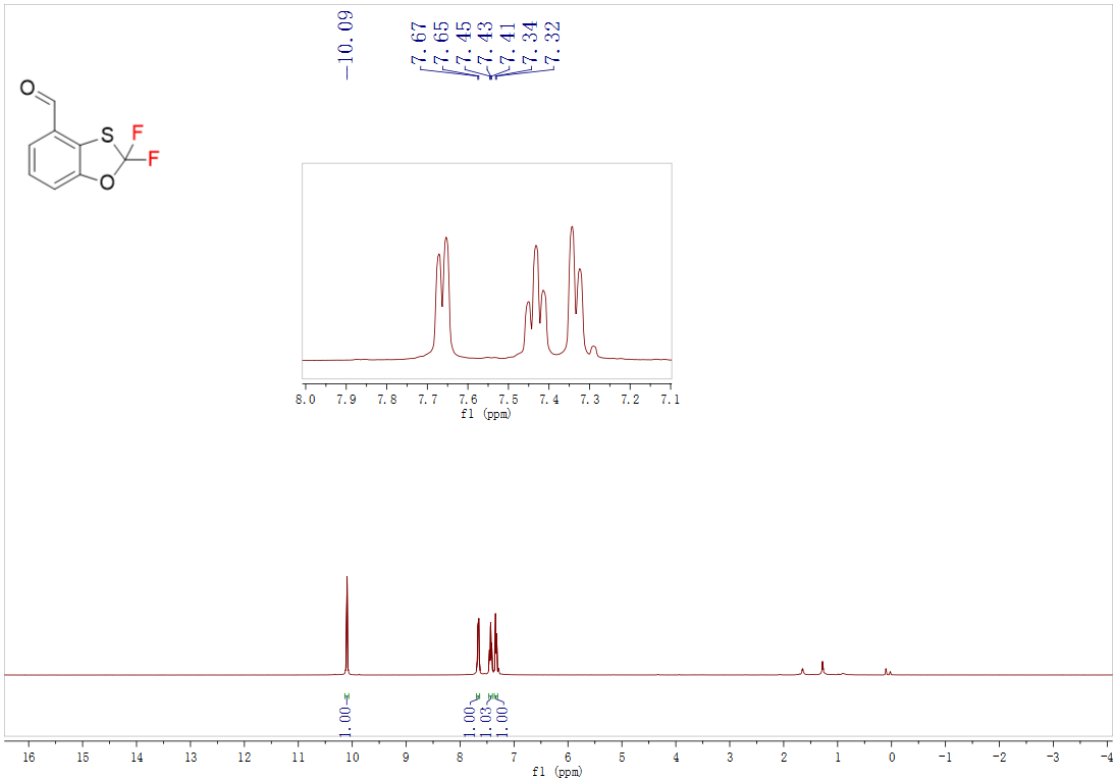
^{13}C NMR spectrum of **3o** in $CDCl_3$



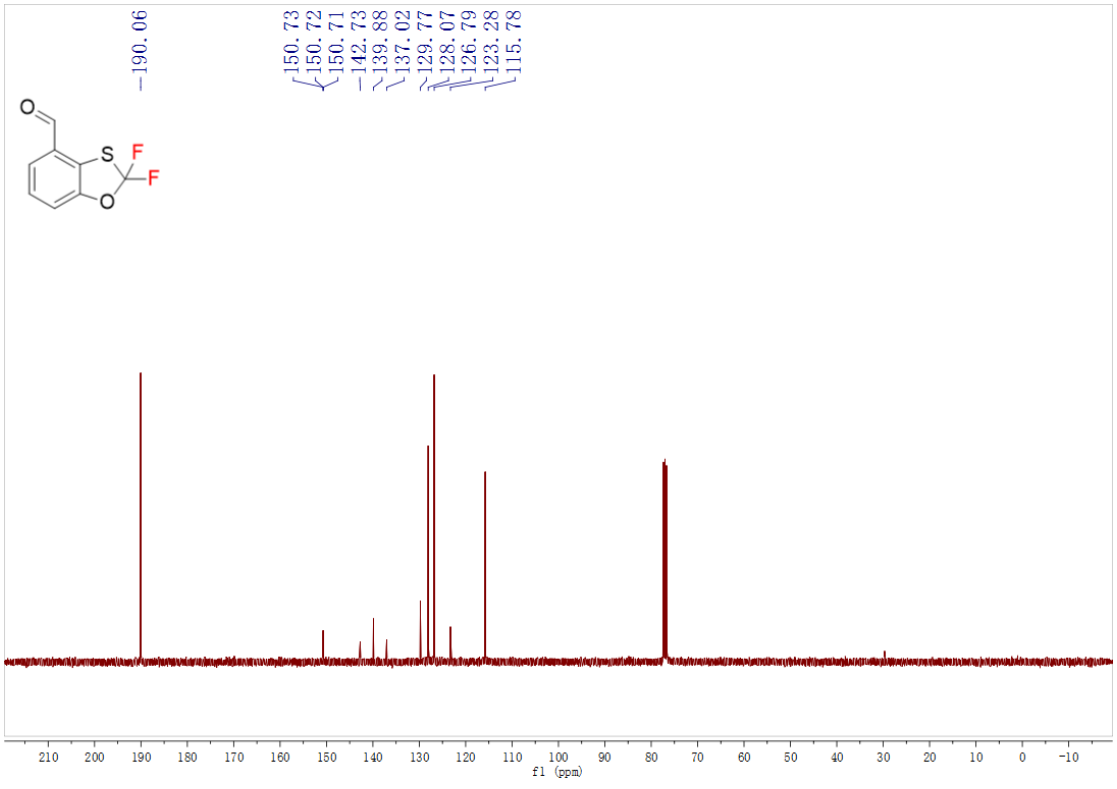
^{19}F NMR spectrum of **3p** in $CDCl_3$



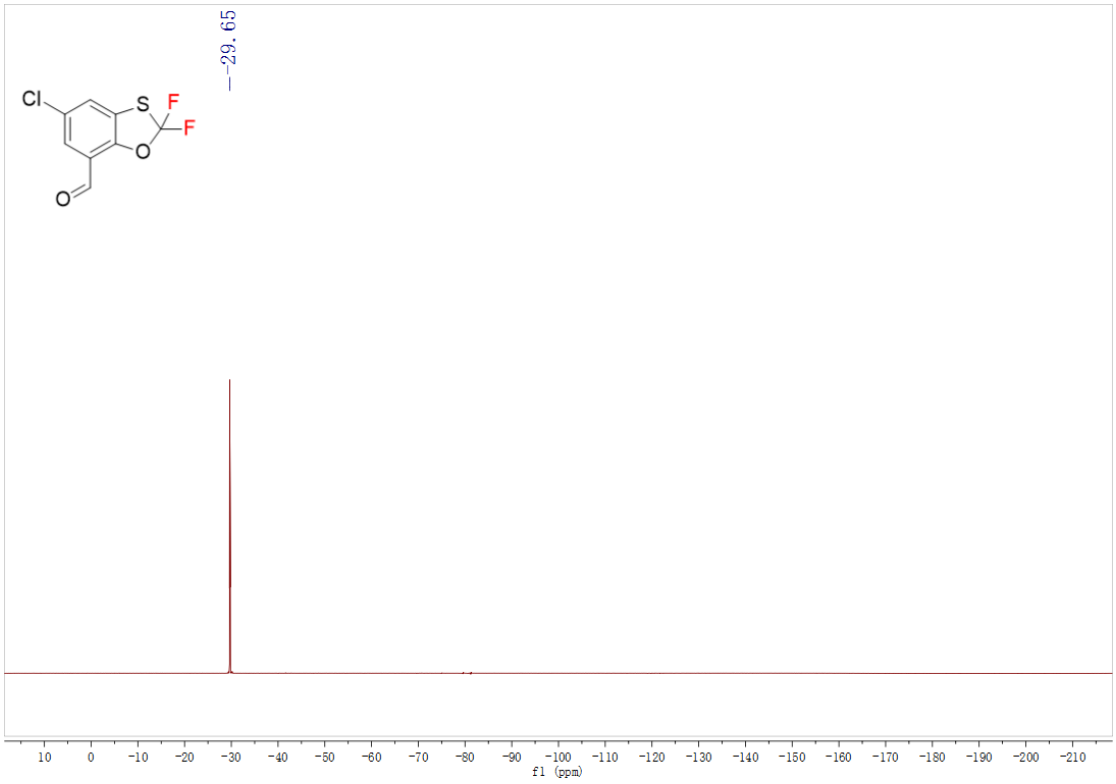
^{1}H NMR spectrum of **3p** in $CDCl_3$



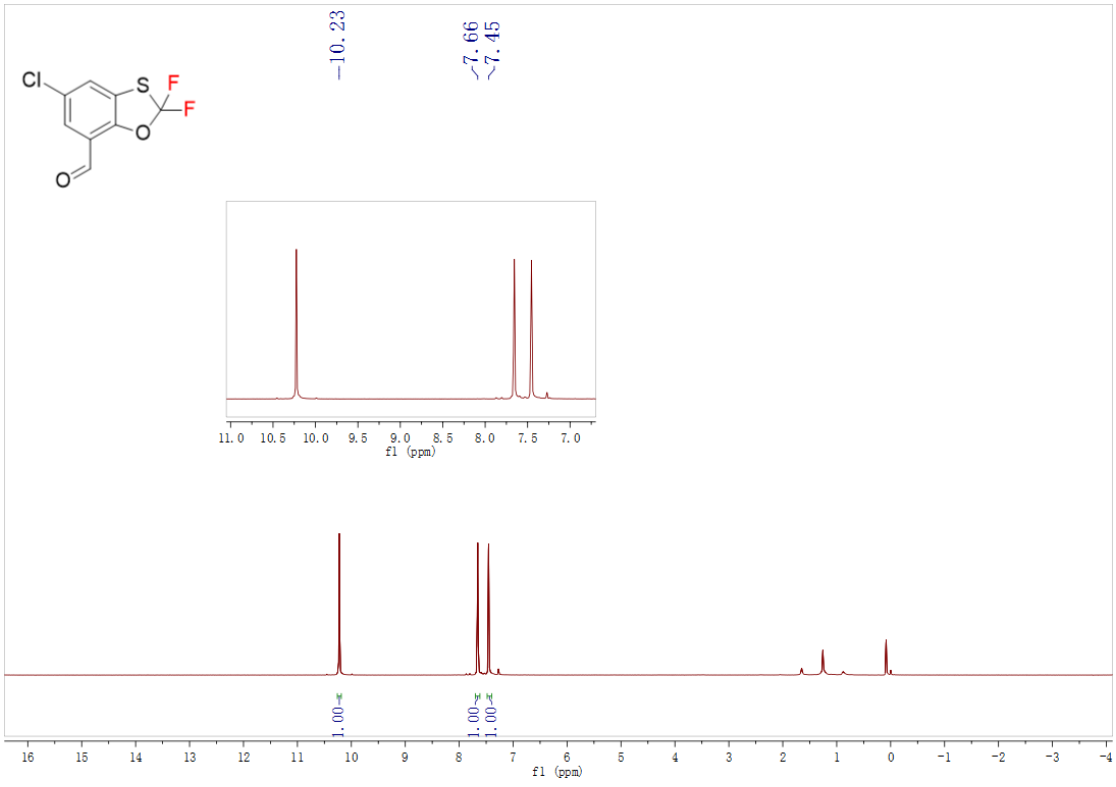
^{13}C NMR spectrum of **3p** in $CDCl_3$



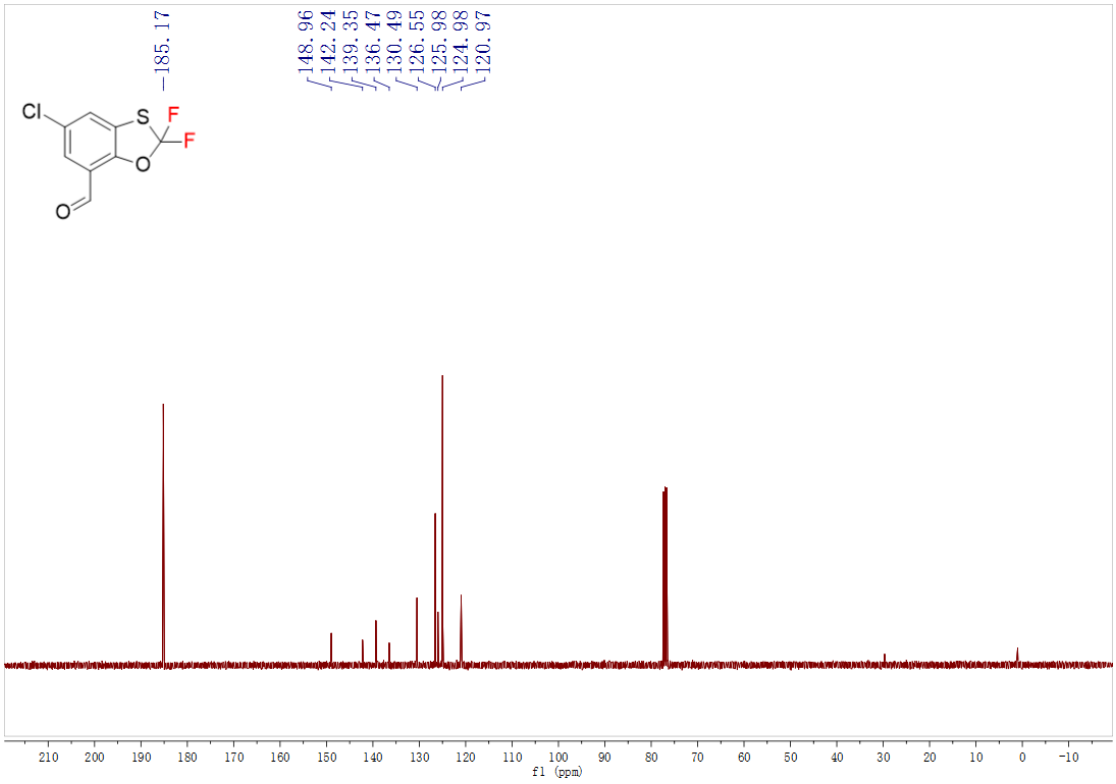
^{19}F NMR spectrum of **3q** in $CDCl_3$



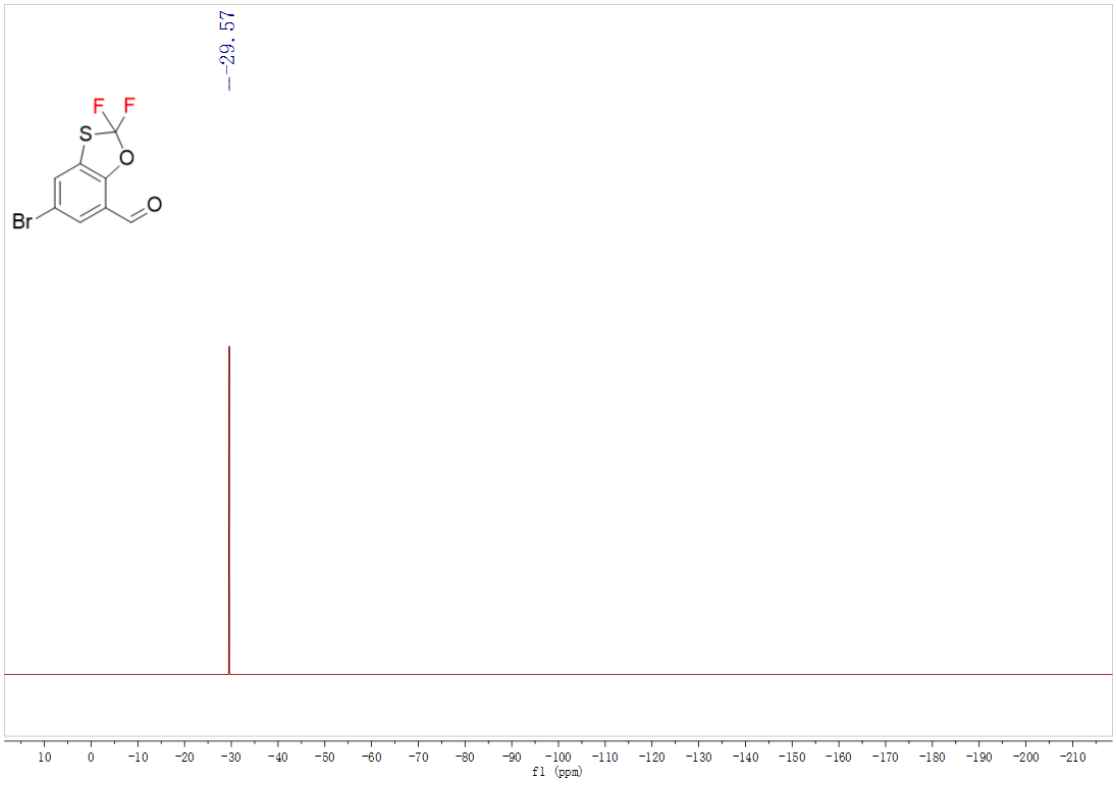
^{1}H NMR spectrum of **3q** in $CDCl_3$



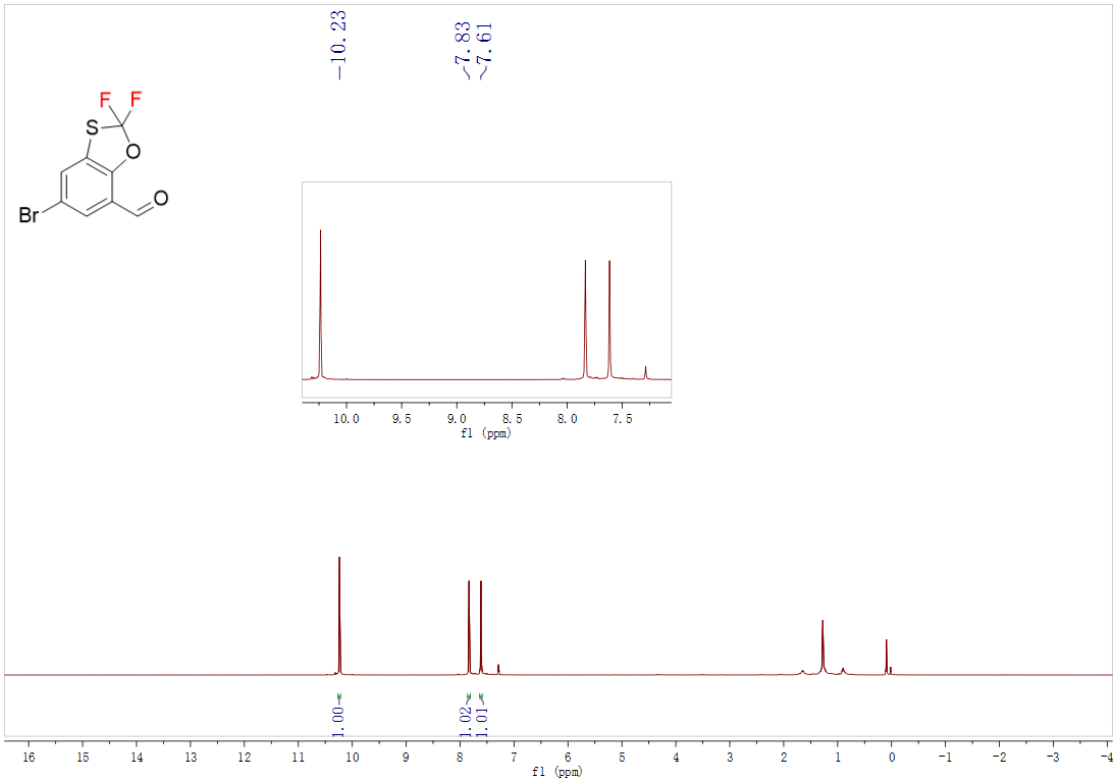
^{13}C NMR spectrum of **3q** in $CDCl_3$



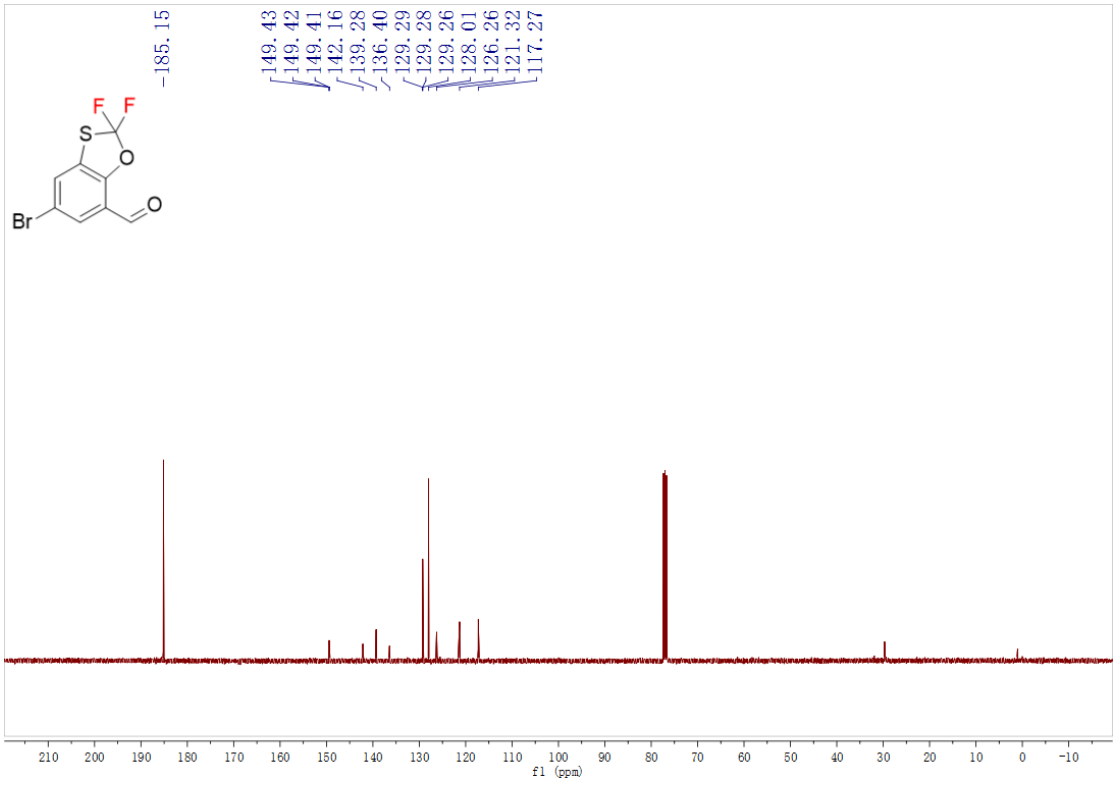
^{19}F NMR spectrum of **3r** in $CDCl_3$



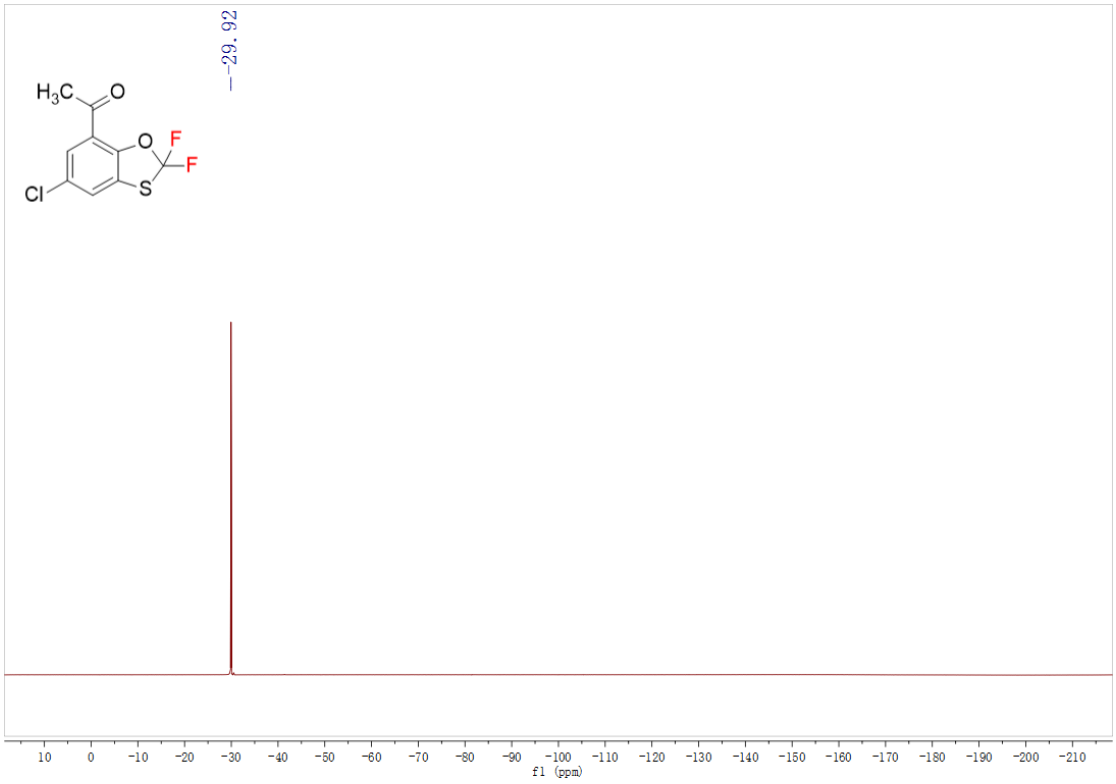
^{1}H NMR spectrum of **3r** in $CDCl_3$



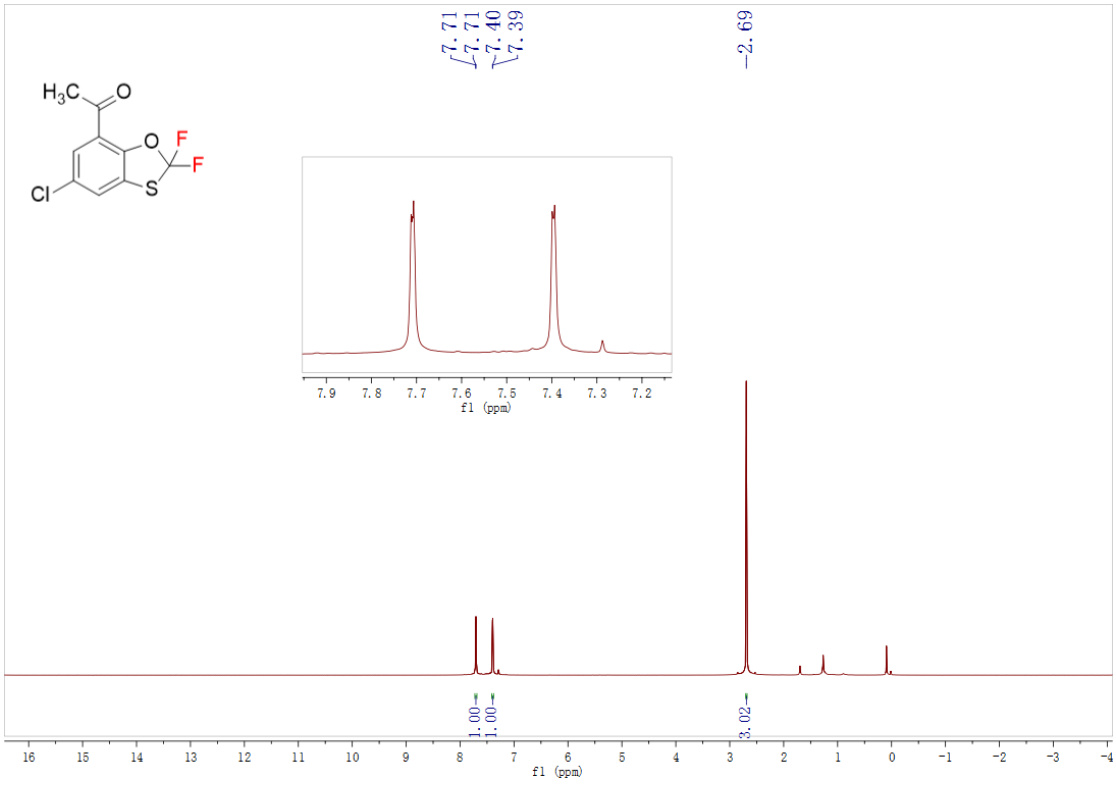
^{13}C NMR spectrum of **3r** in $CDCl_3$



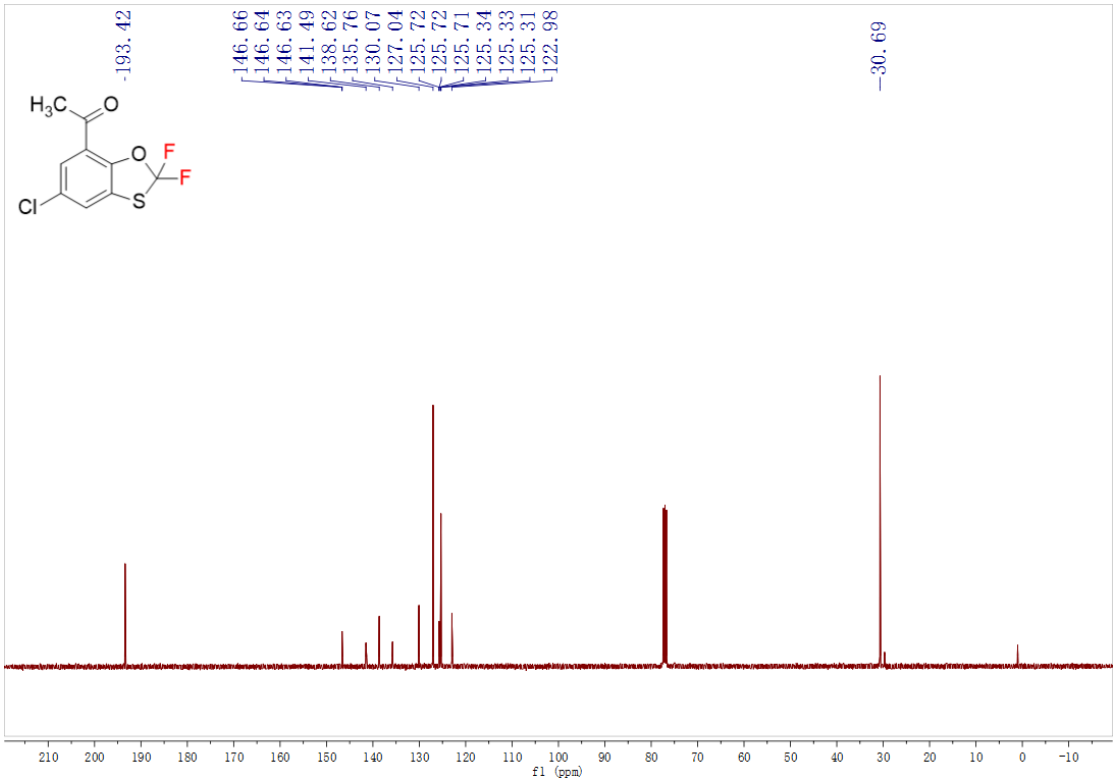
^{19}F NMR spectrum of **3s** in $CDCl_3$



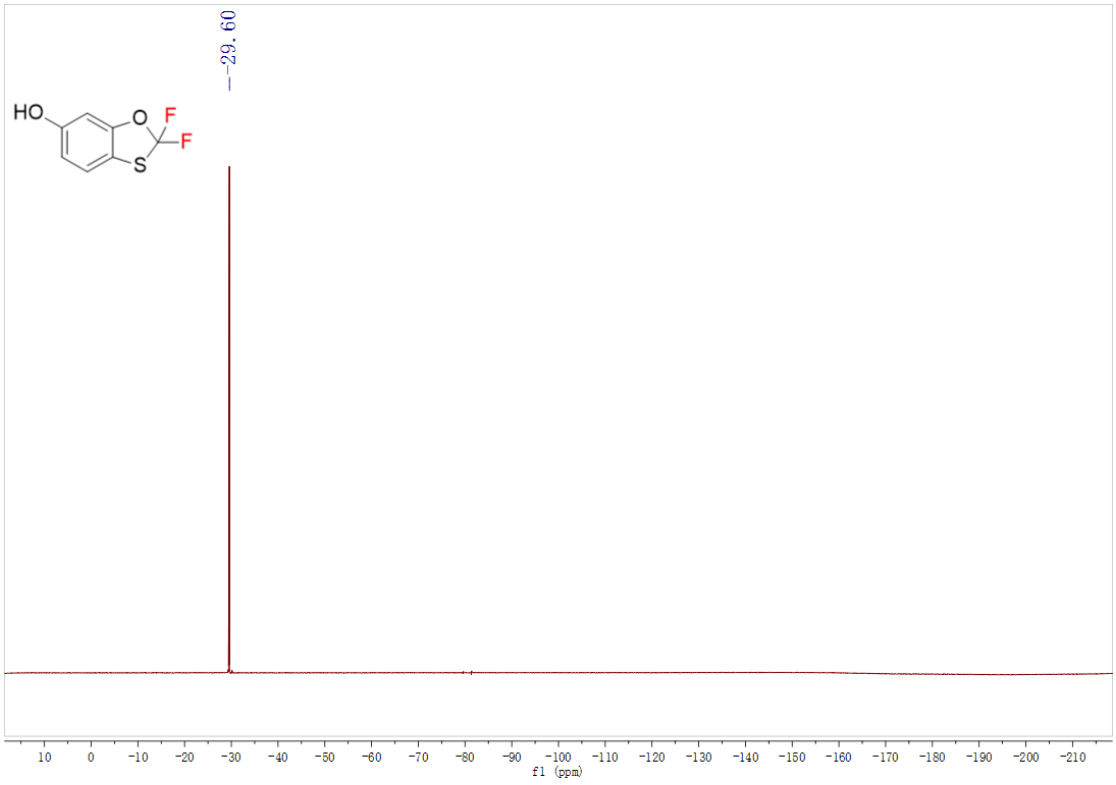
^{1}H NMR spectrum of **3s** in $CDCl_3$



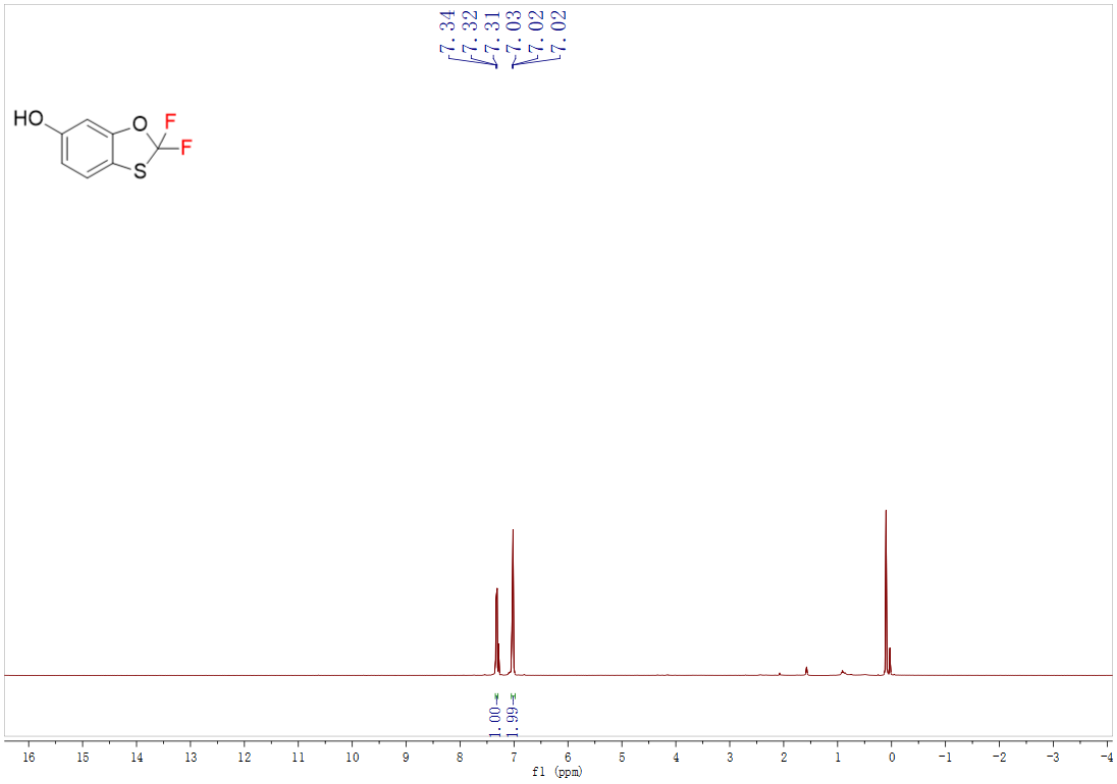
^{13}C NMR spectrum of **3s** in $CDCl_3$



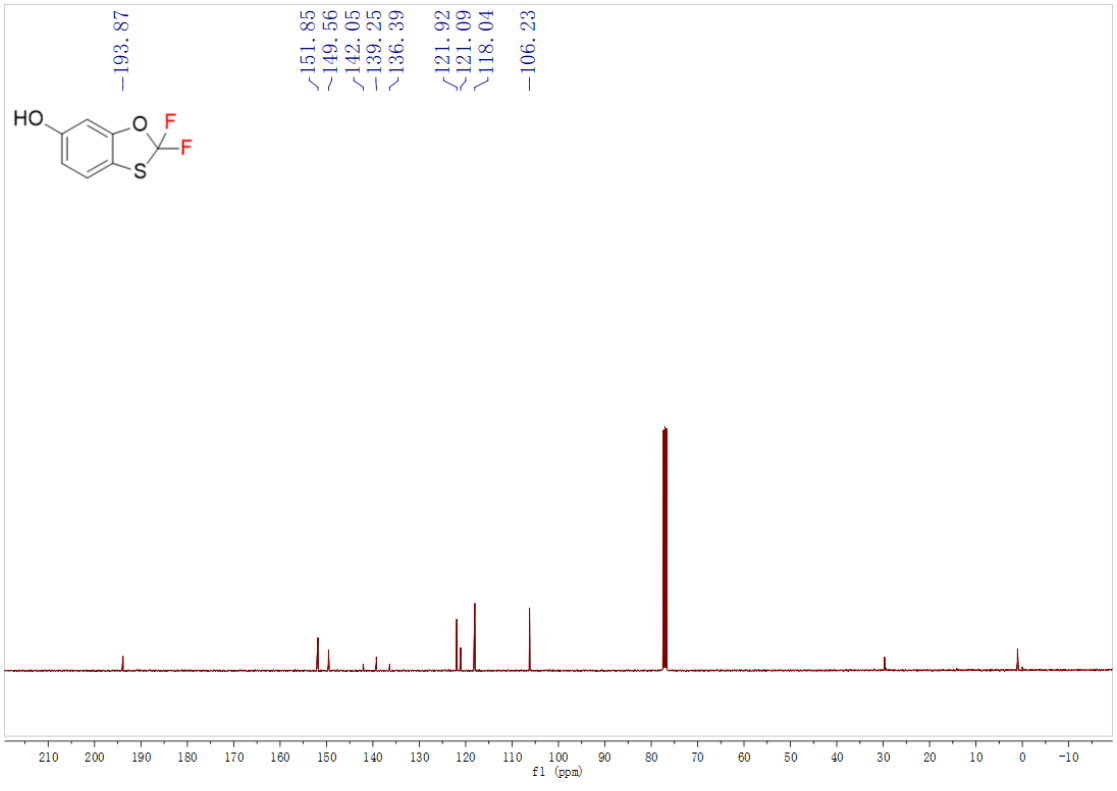
^{19}F NMR spectrum of **3t** in $CDCl_3$



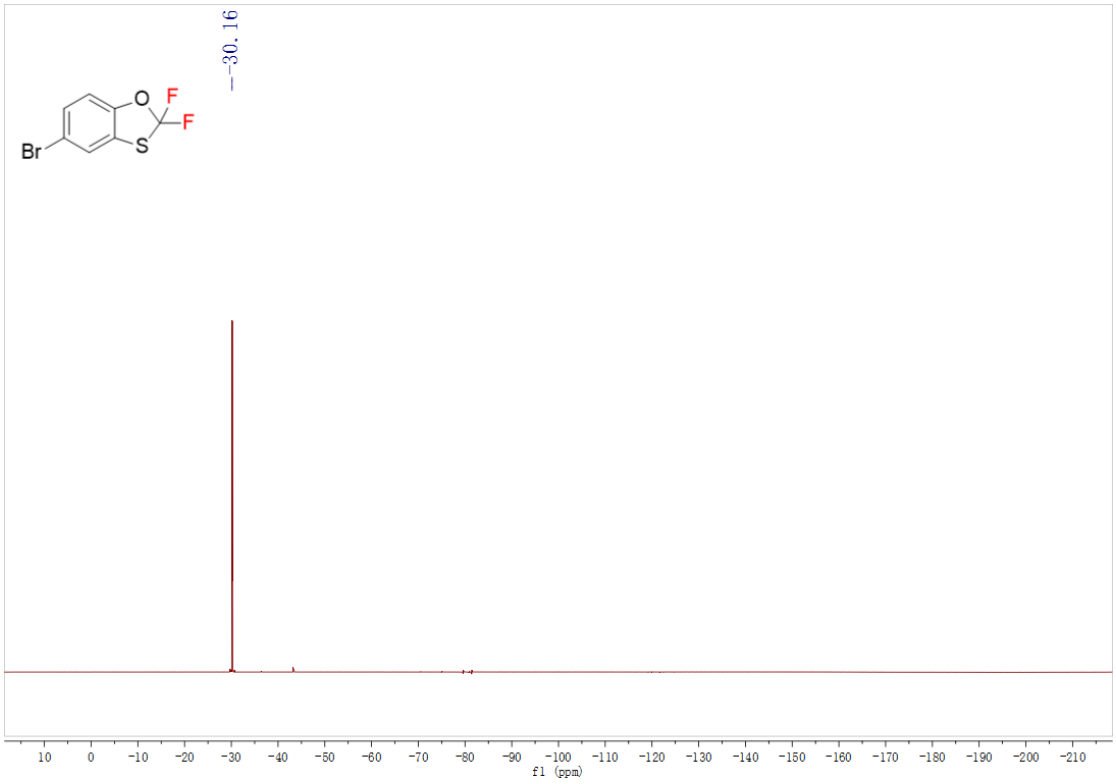
^{1}H NMR spectrum of **3t** in $CDCl_3$



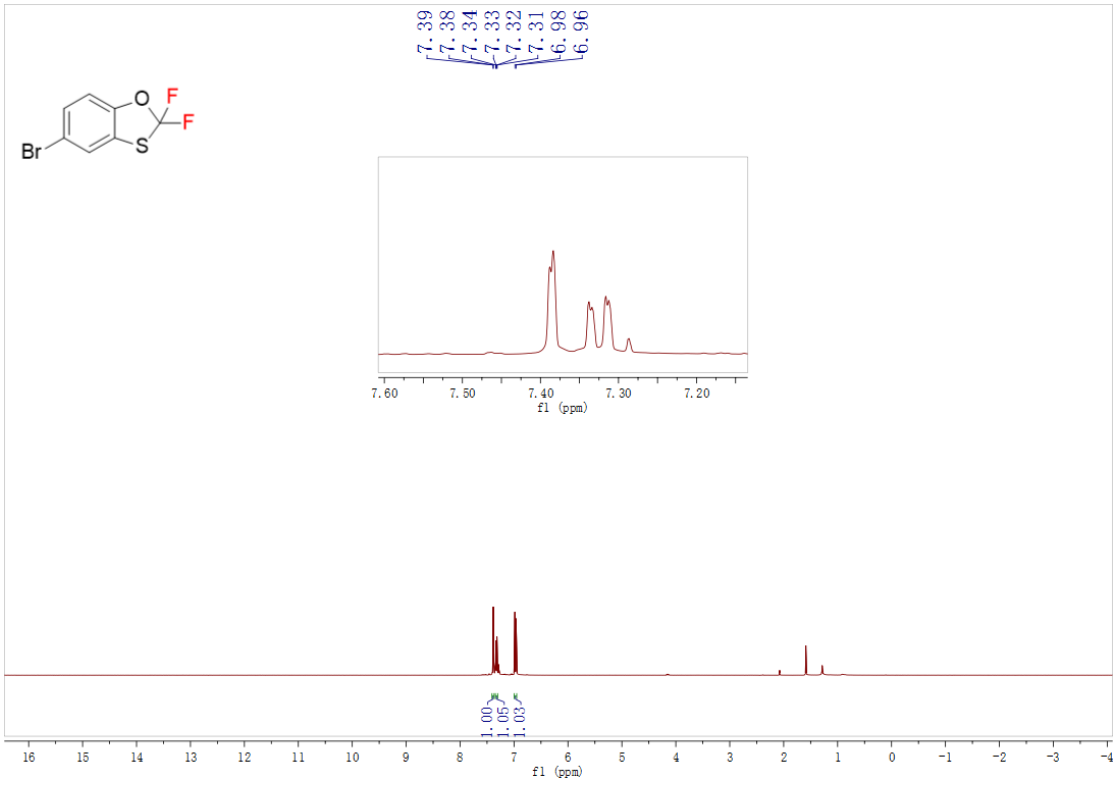
^{13}C NMR spectrum of **3t** in $CDCl_3$



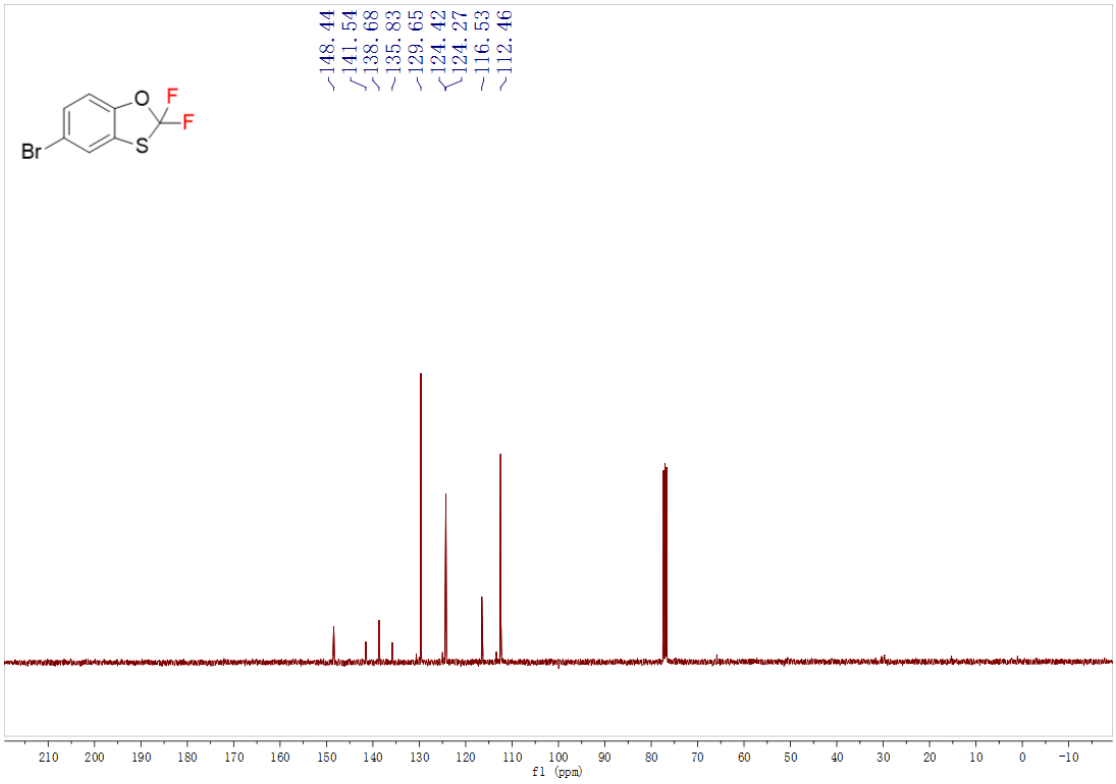
^{19}F NMR spectrum of **3u** in $CDCl_3$



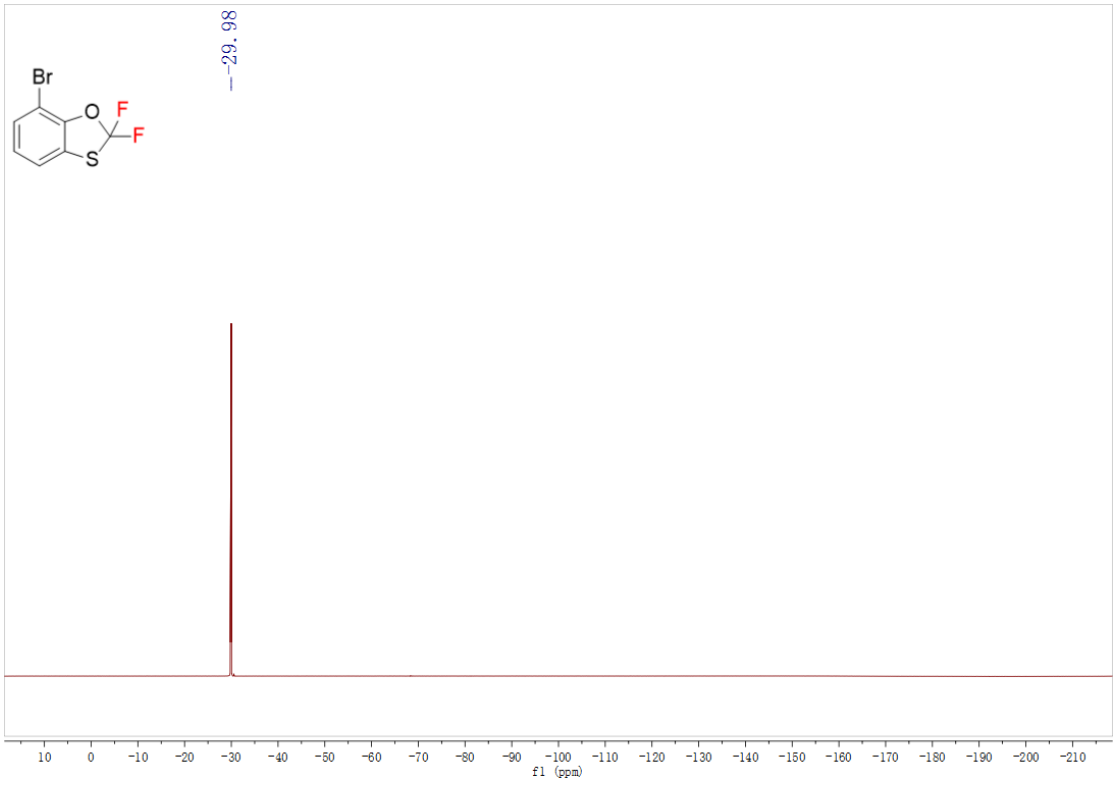
^{1}H NMR spectrum of **3u** in $CDCl_3$



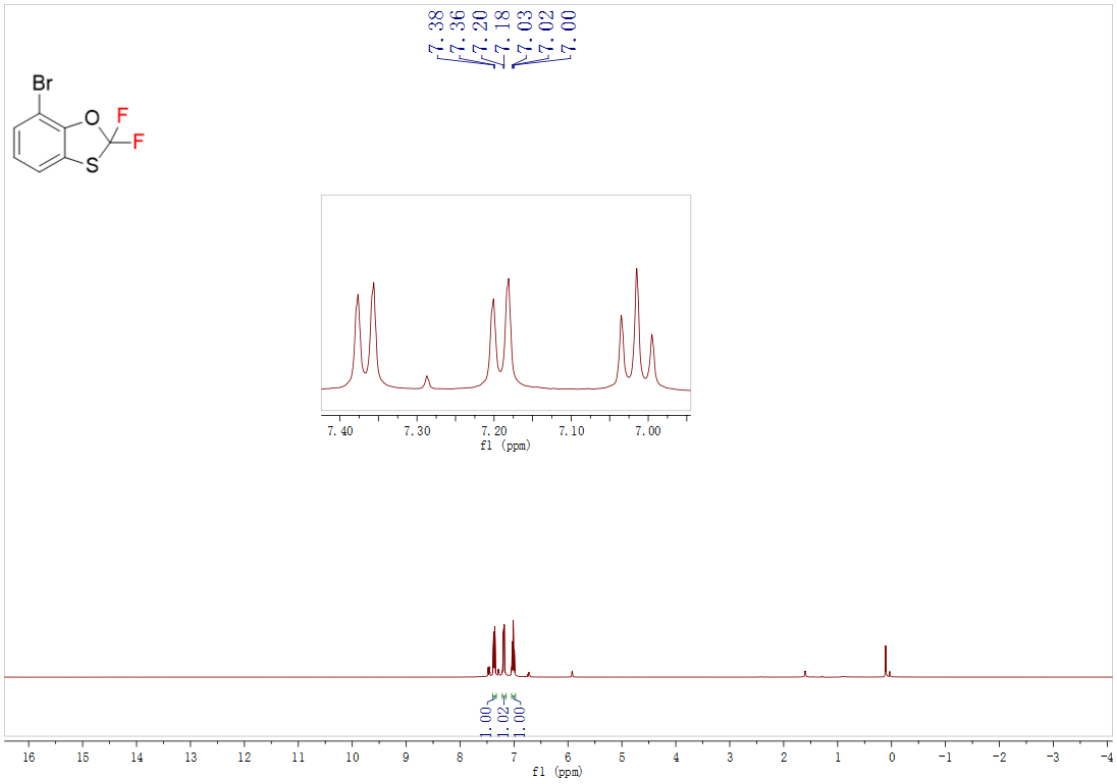
^{13}C NMR spectrum of **3u** in $CDCl_3$



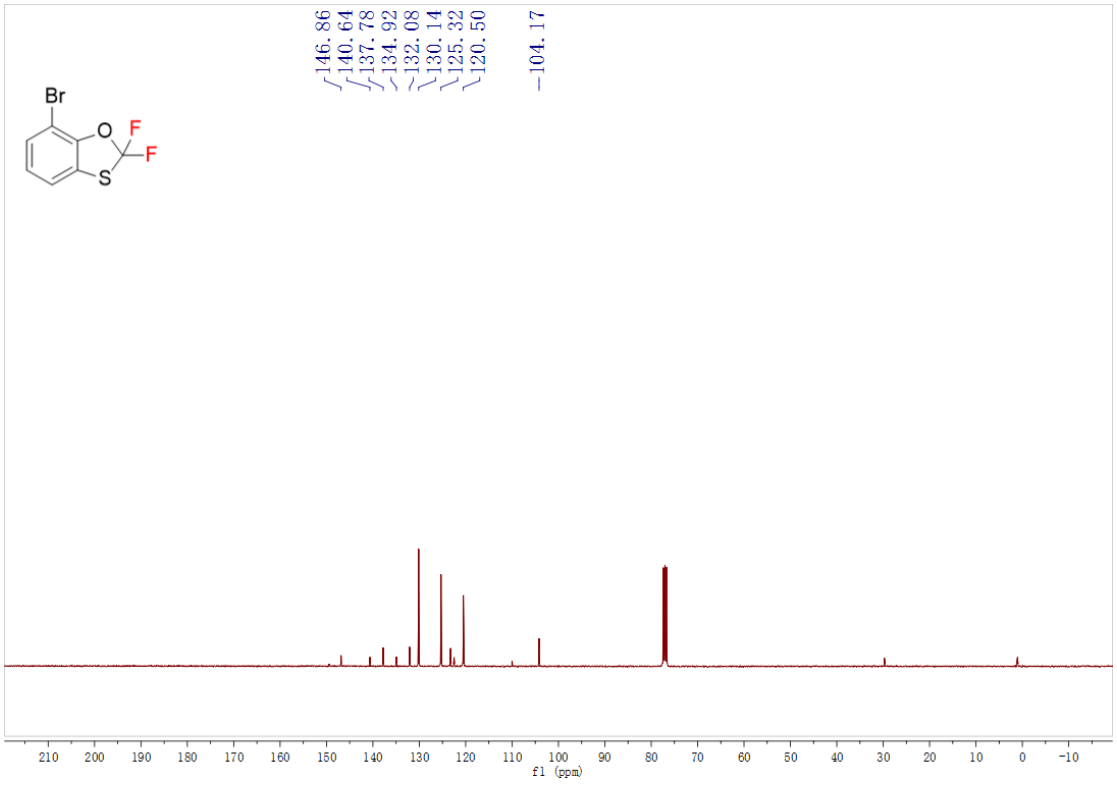
^{19}F NMR spectrum of **3v** in $CDCl_3$



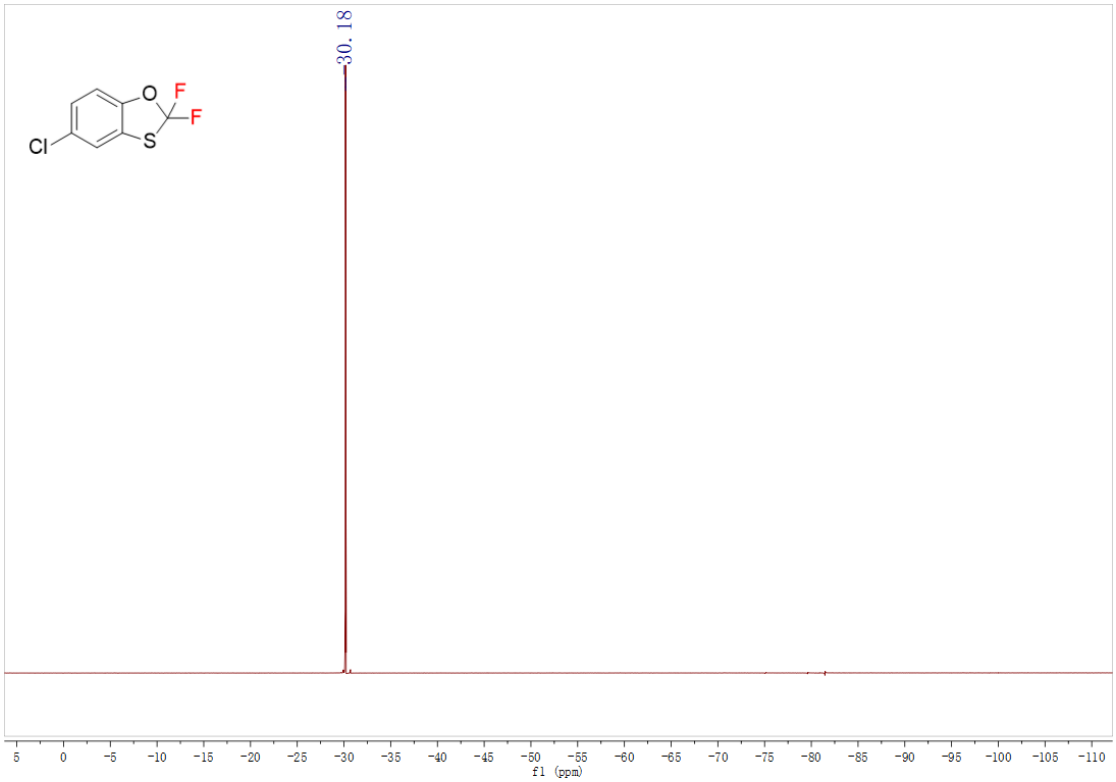
^{1}H NMR spectrum of **3v** in $CDCl_3$



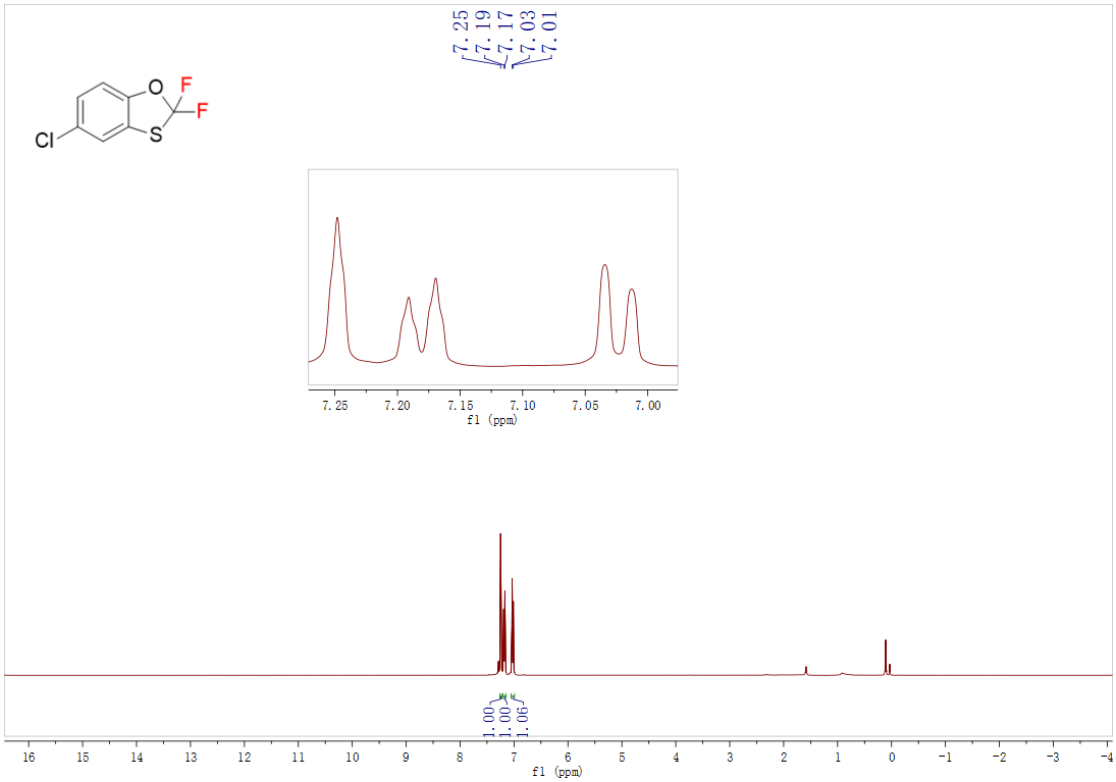
^{13}C NMR spectrum of **3v** in $CDCl_3$



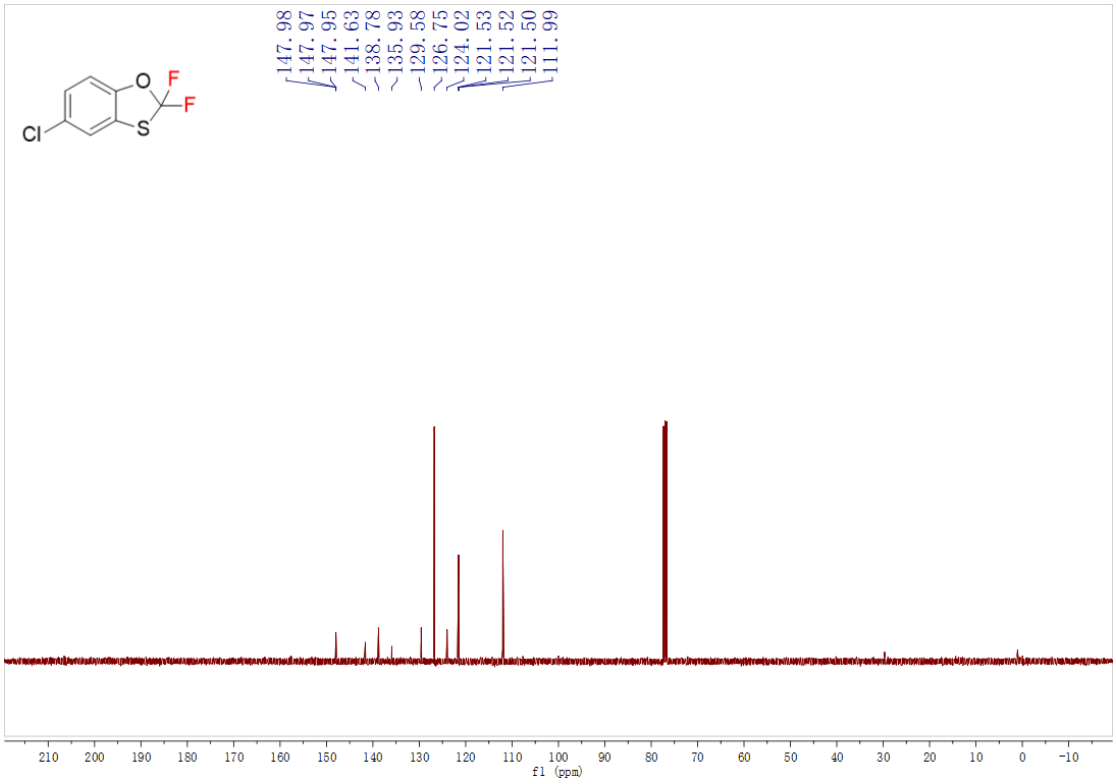
^{19}F NMR spectrum of **3w** in $CDCl_3$



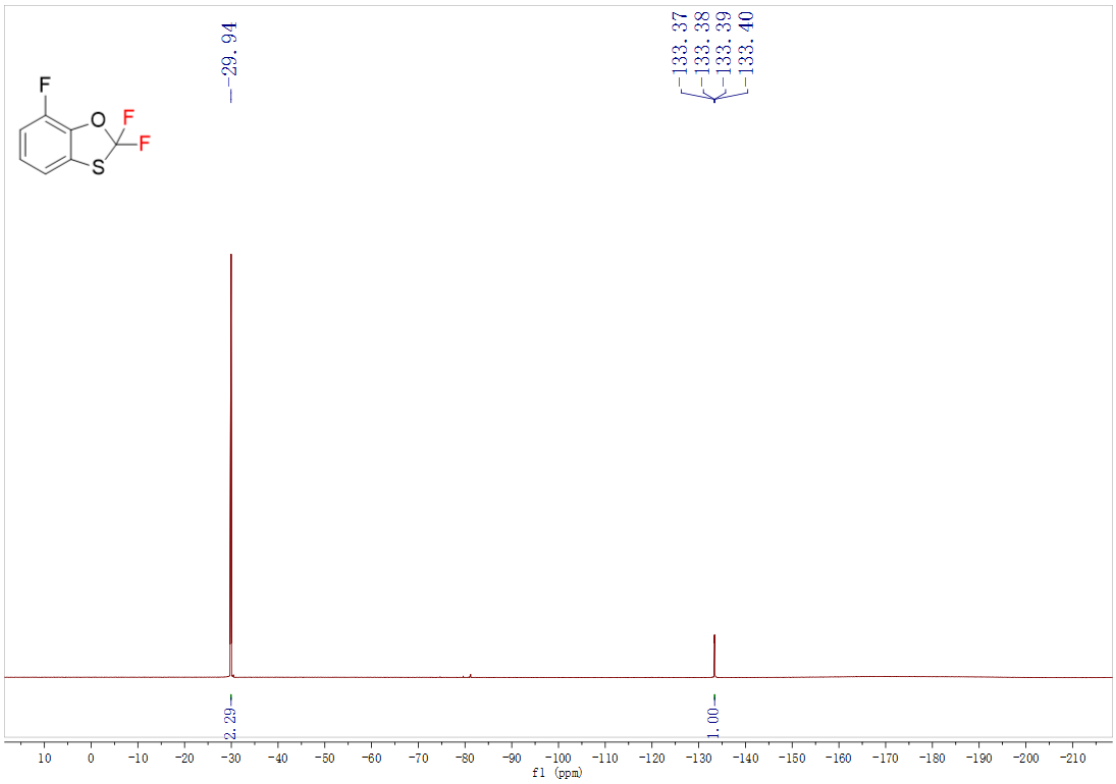
^{1}H NMR spectrum of **3w** in $CDCl_3$



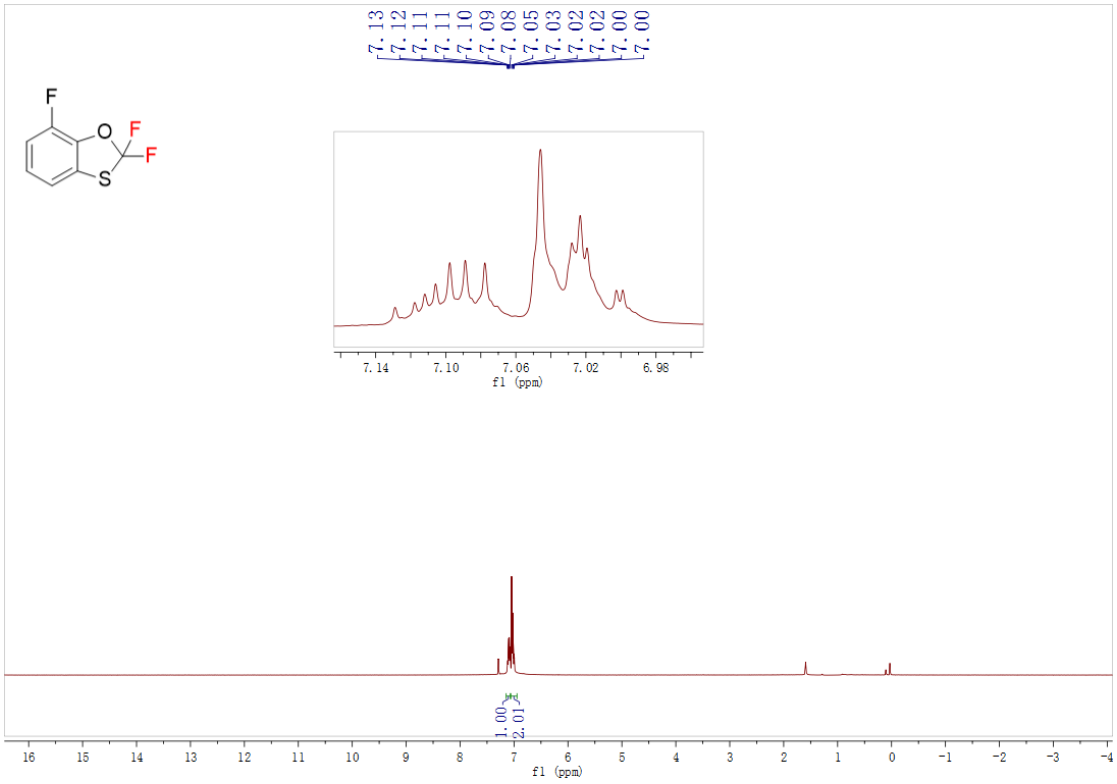
^{13}C NMR spectrum of **3w** in $CDCl_3$



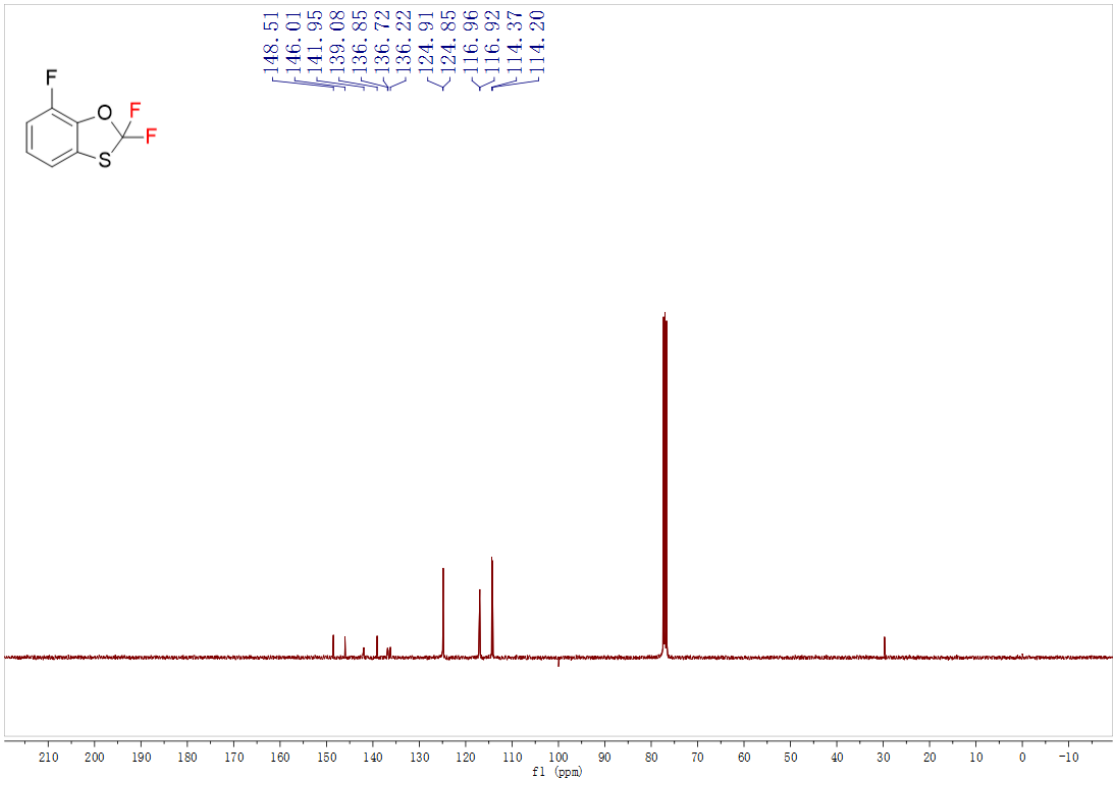
^{19}F NMR spectrum of **3x** in $CDCl_3$



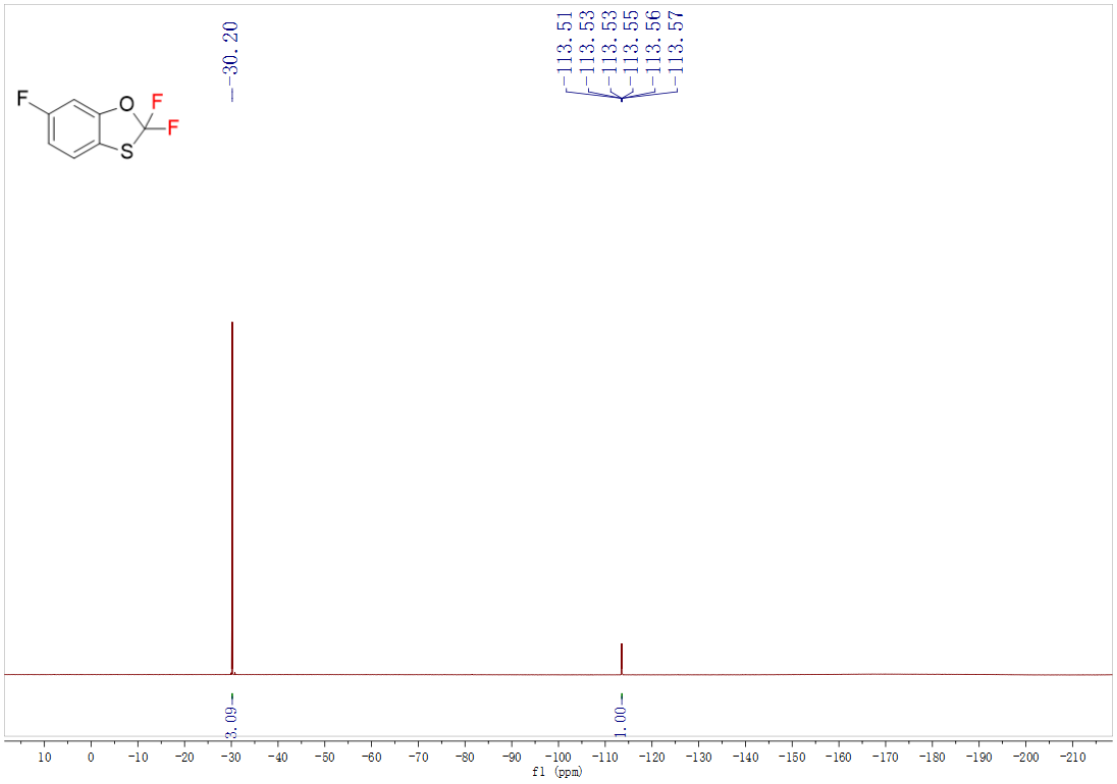
^{1}H NMR spectrum of **3x** in $CDCl_3$



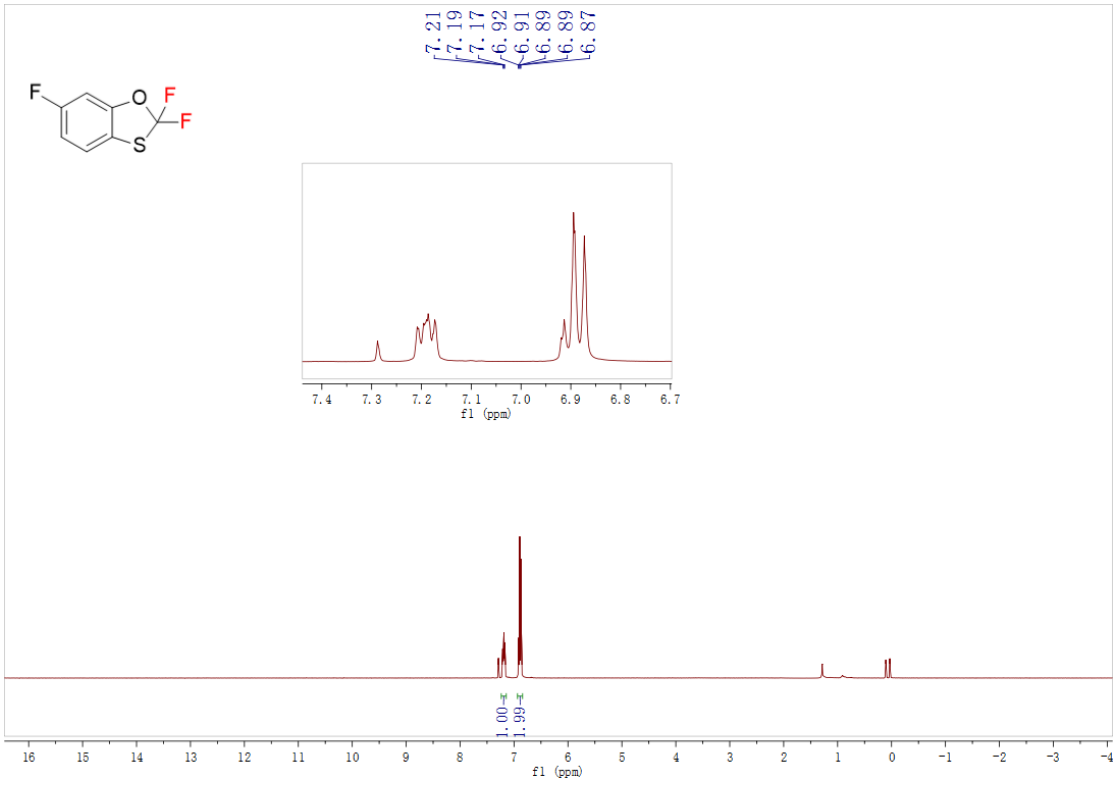
^{13}C NMR spectrum of **3x** in $CDCl_3$



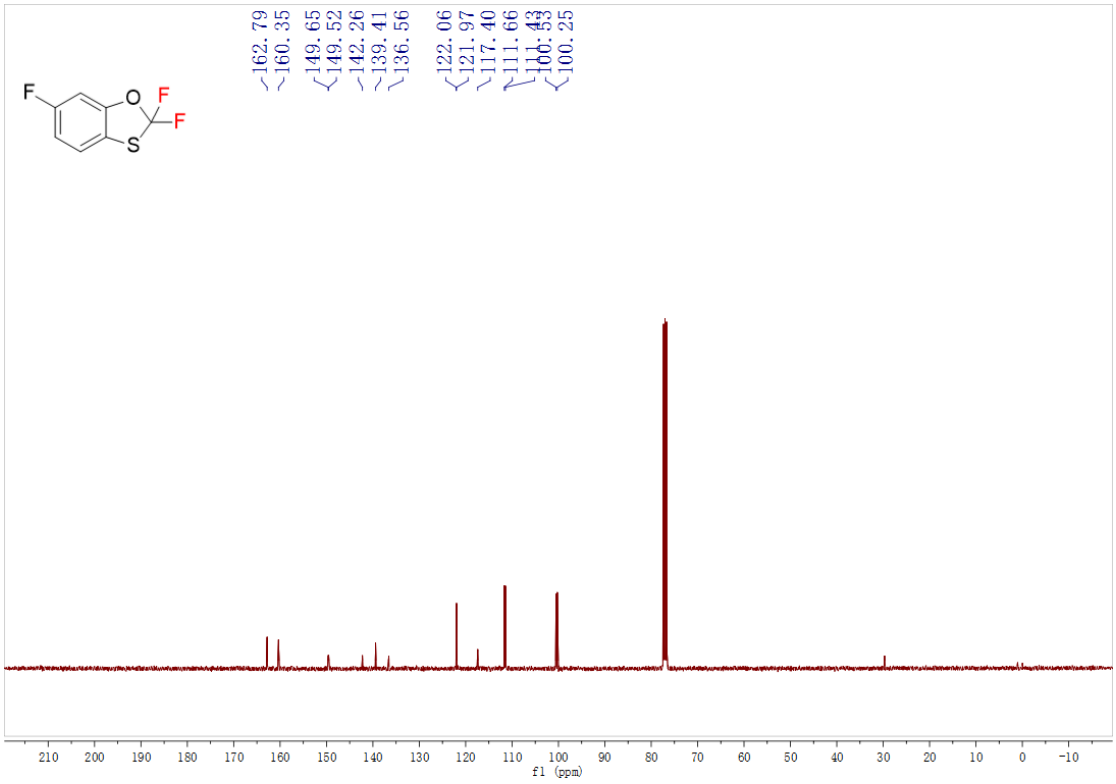
^{19}F NMR spectrum of **3y** in $CDCl_3$



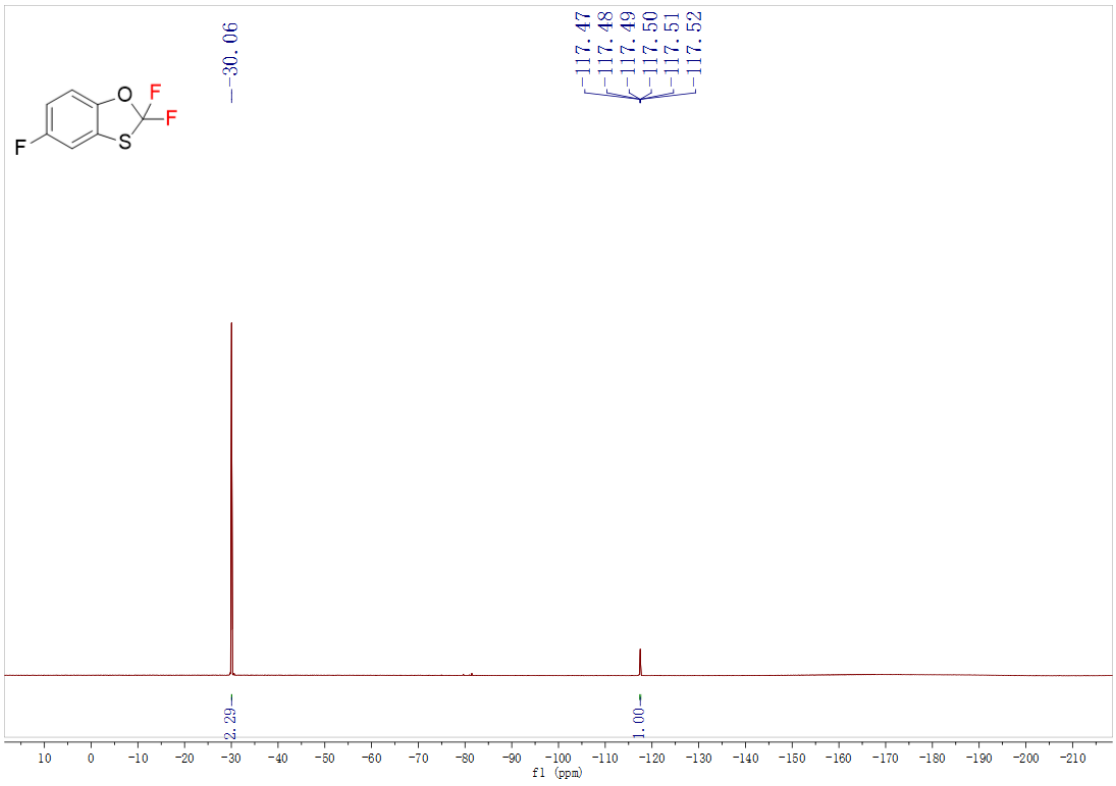
^{1}H NMR spectrum of **3y** in $CDCl_3$



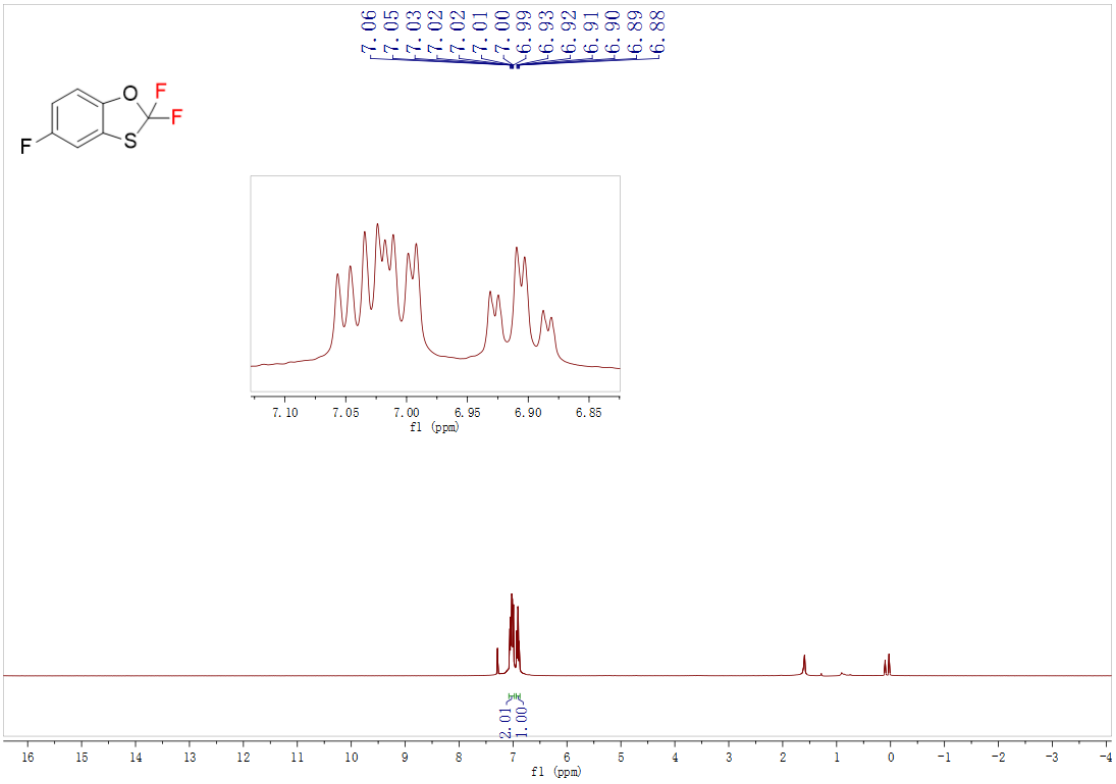
^{13}C NMR spectrum of **3y** in $CDCl_3$



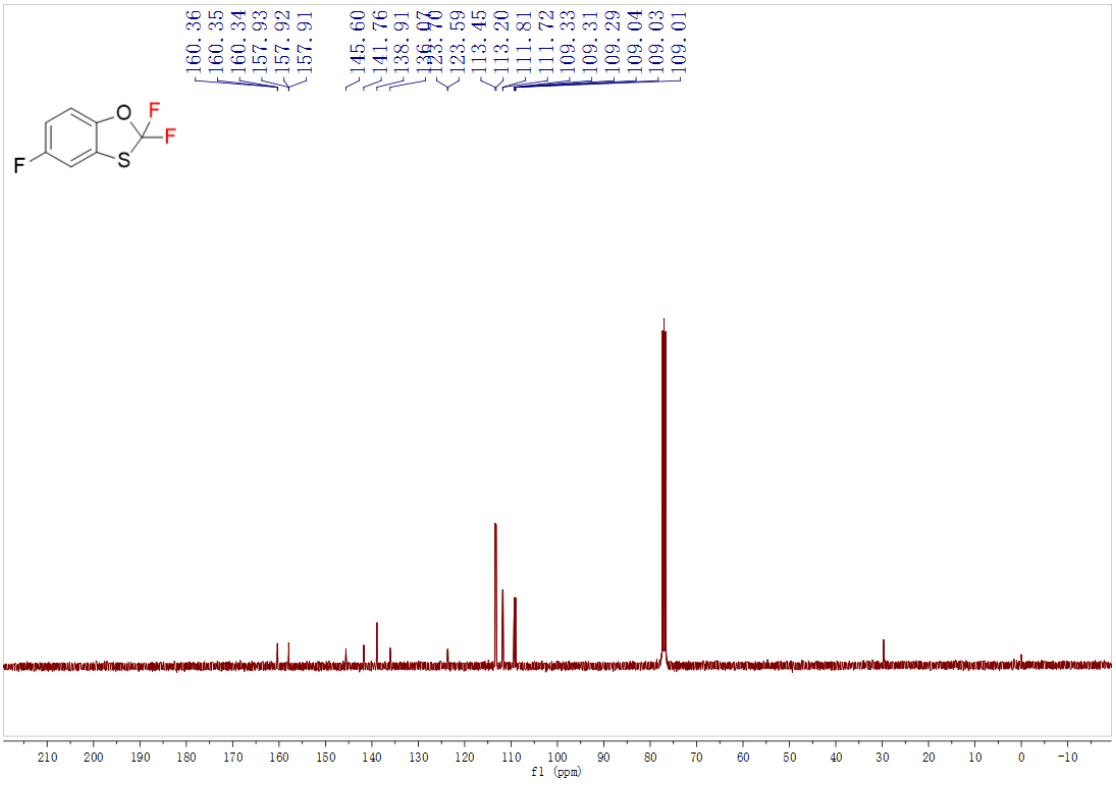
^{19}F NMR spectrum of **3z** in $CDCl_3$



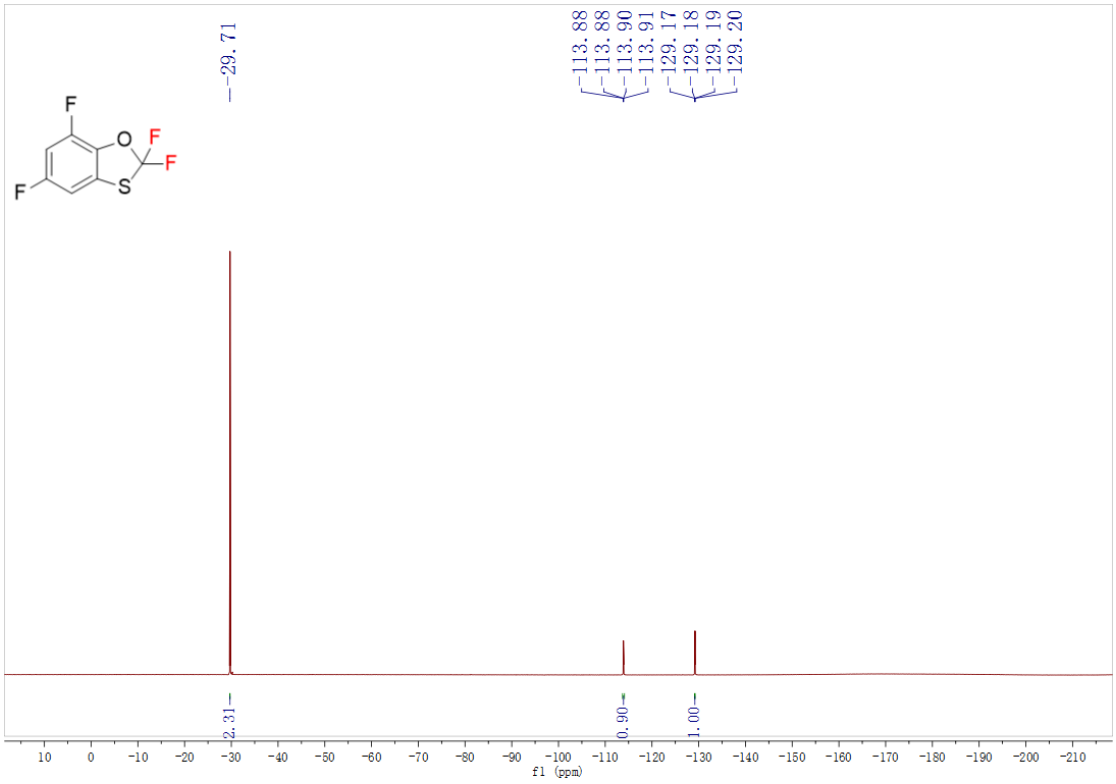
^{1}H NMR spectrum of **3z** in $CDCl_3$



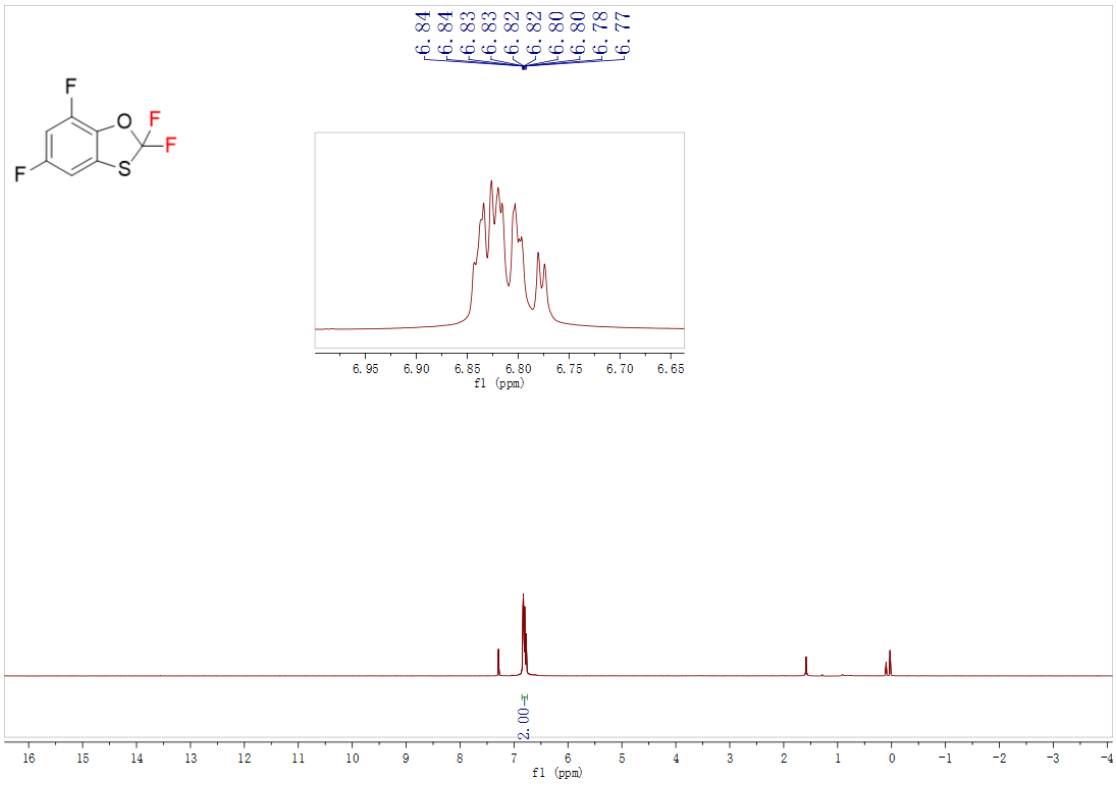
^{13}C NMR spectrum of **3z** in $CDCl_3$



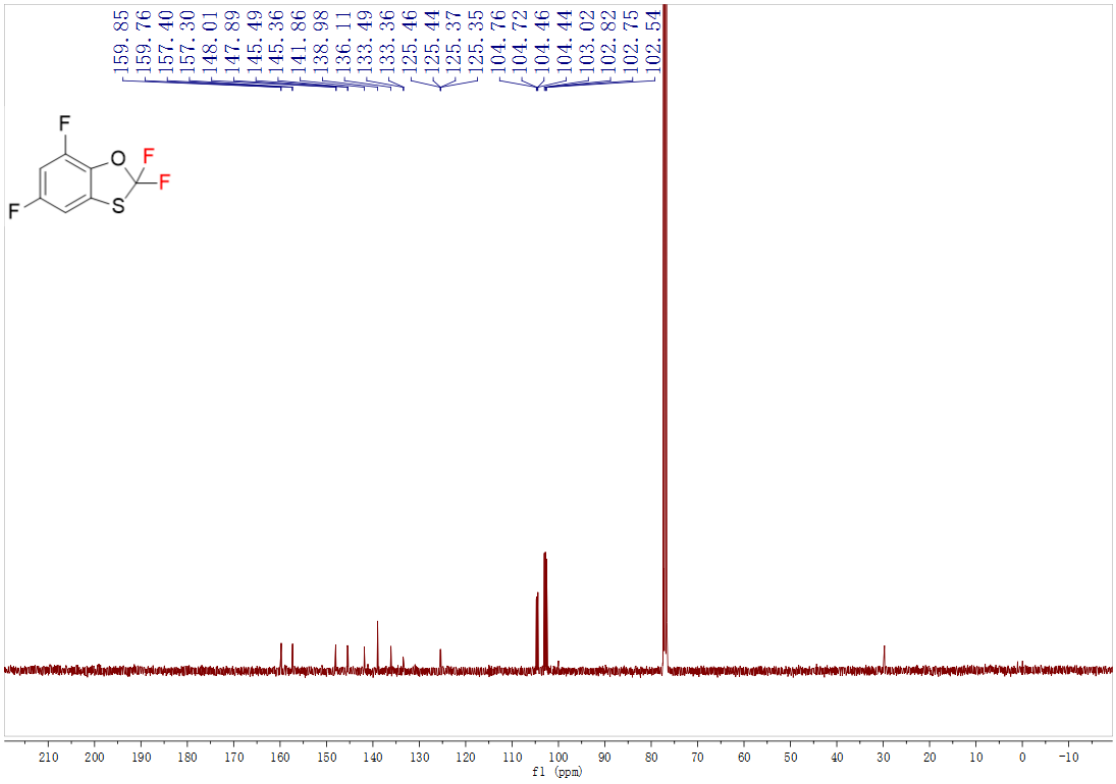
^{19}F NMR spectrum of **3aa** in $CDCl_3$



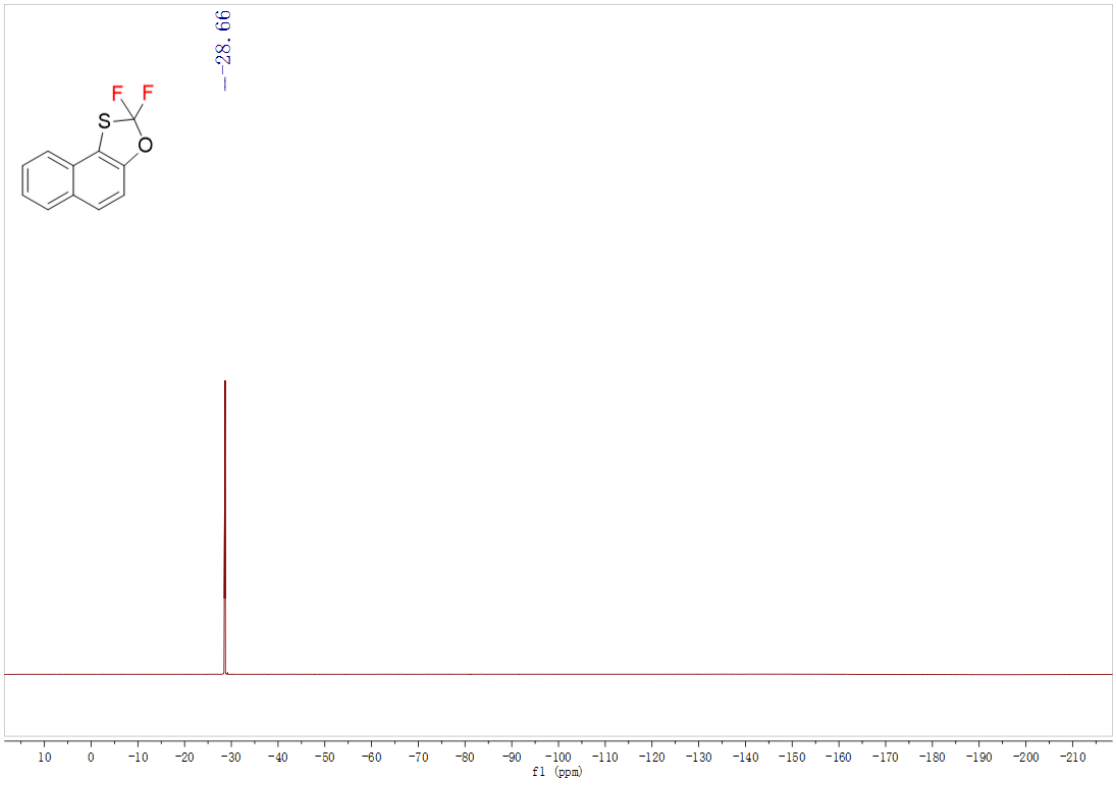
^{1}H NMR spectrum of **3aa** in $CDCl_3$



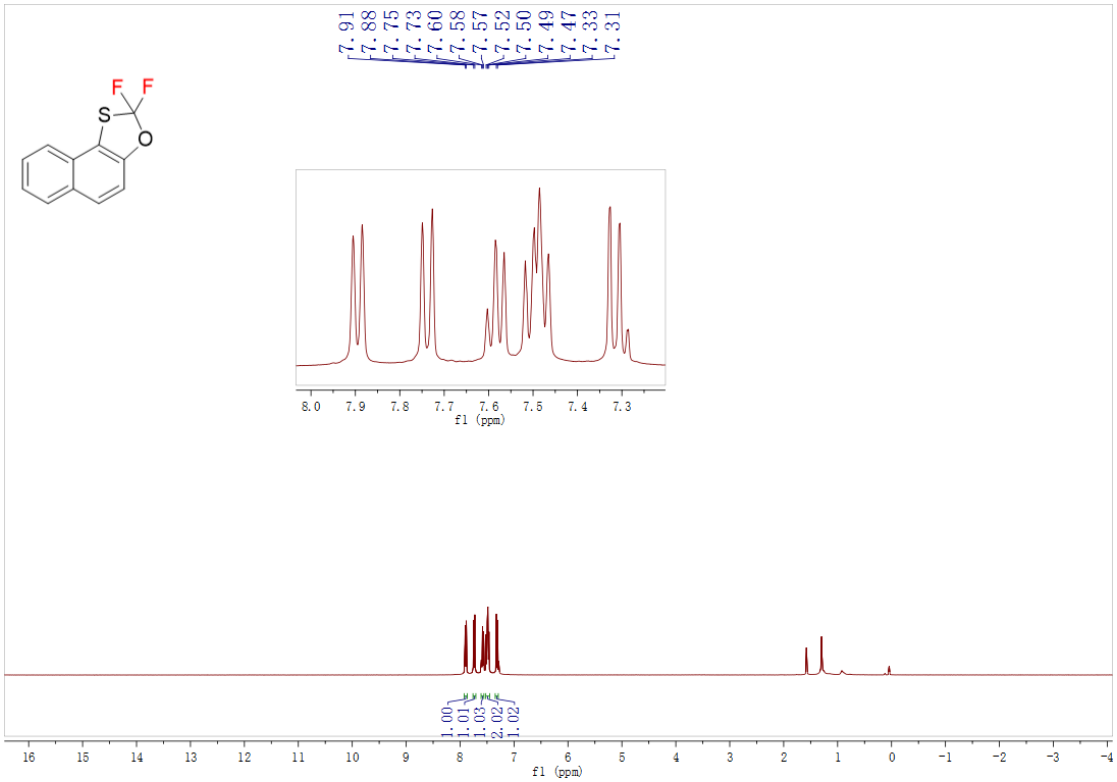
^{13}C NMR spectrum of **3aa** in $CDCl_3$



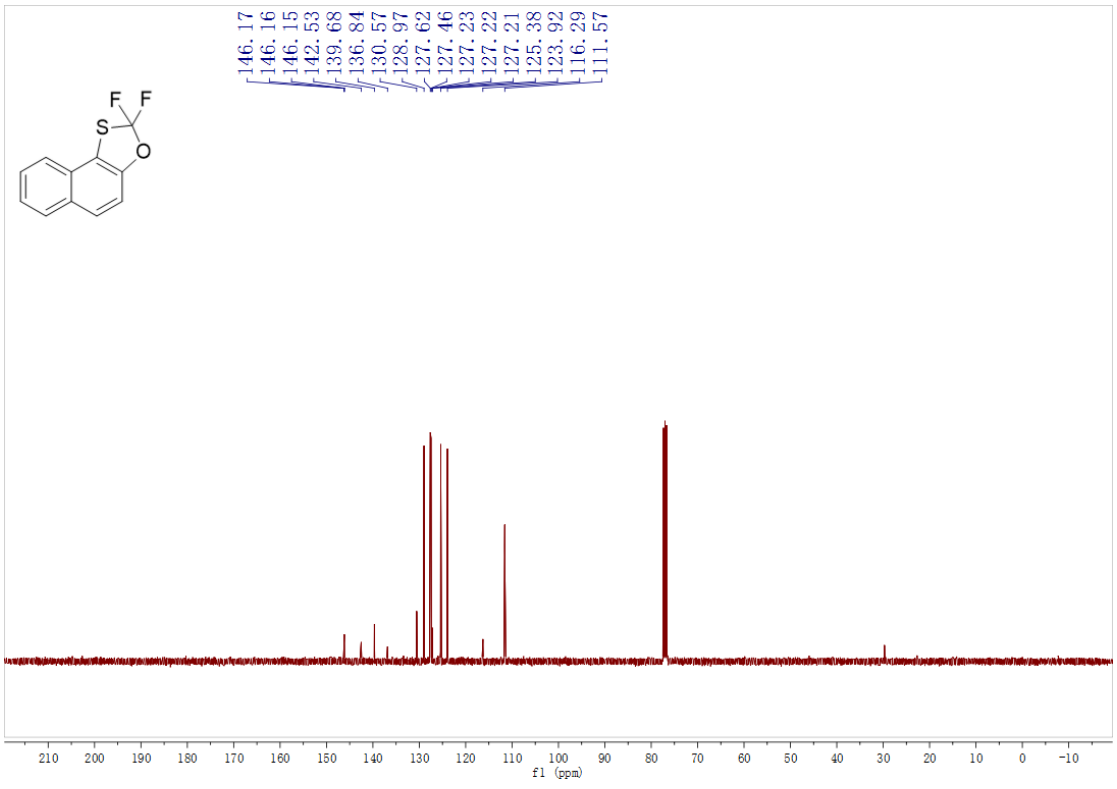
^{19}F NMR spectrum of **3ab** in $CDCl_3$



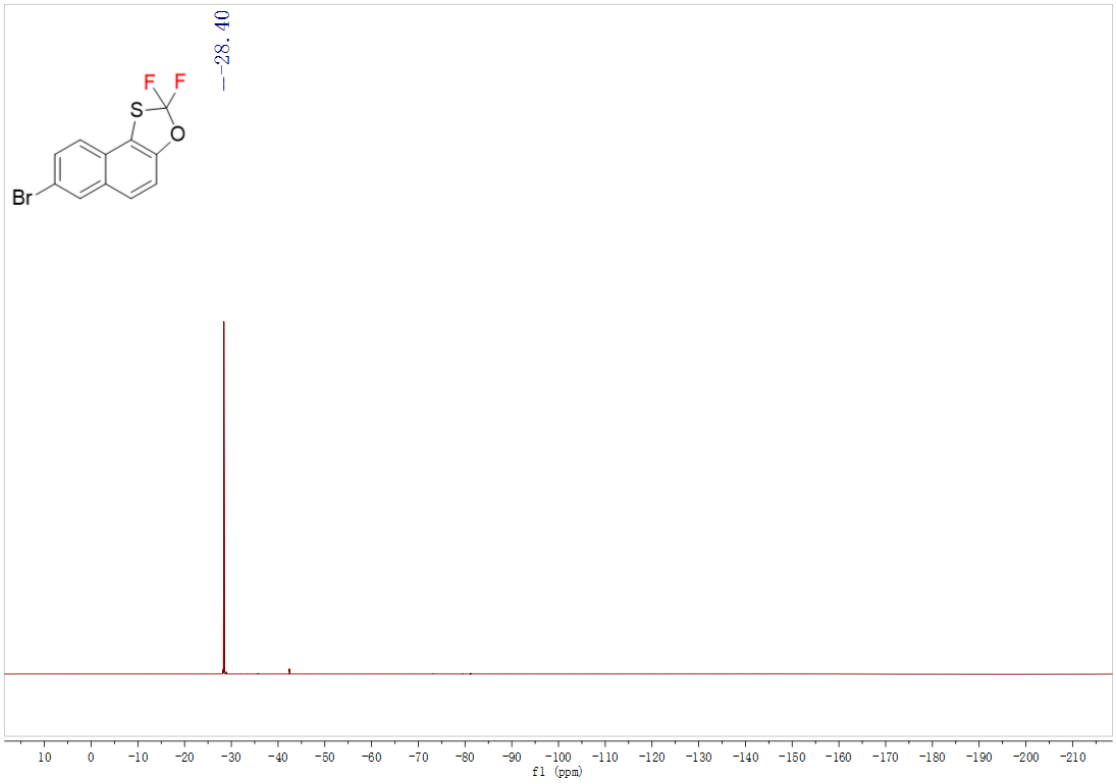
^{1}H NMR spectrum of **3ab** in $CDCl_3$



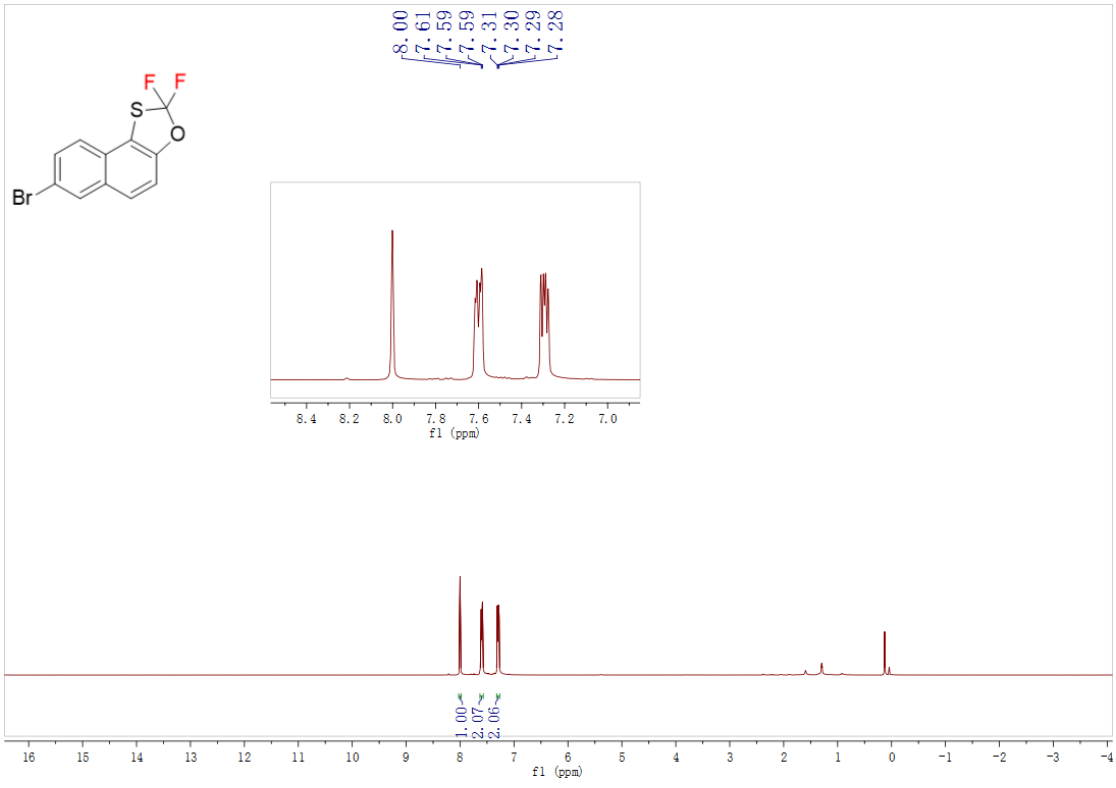
^{13}C NMR spectrum of **3ab** in $CDCl_3$



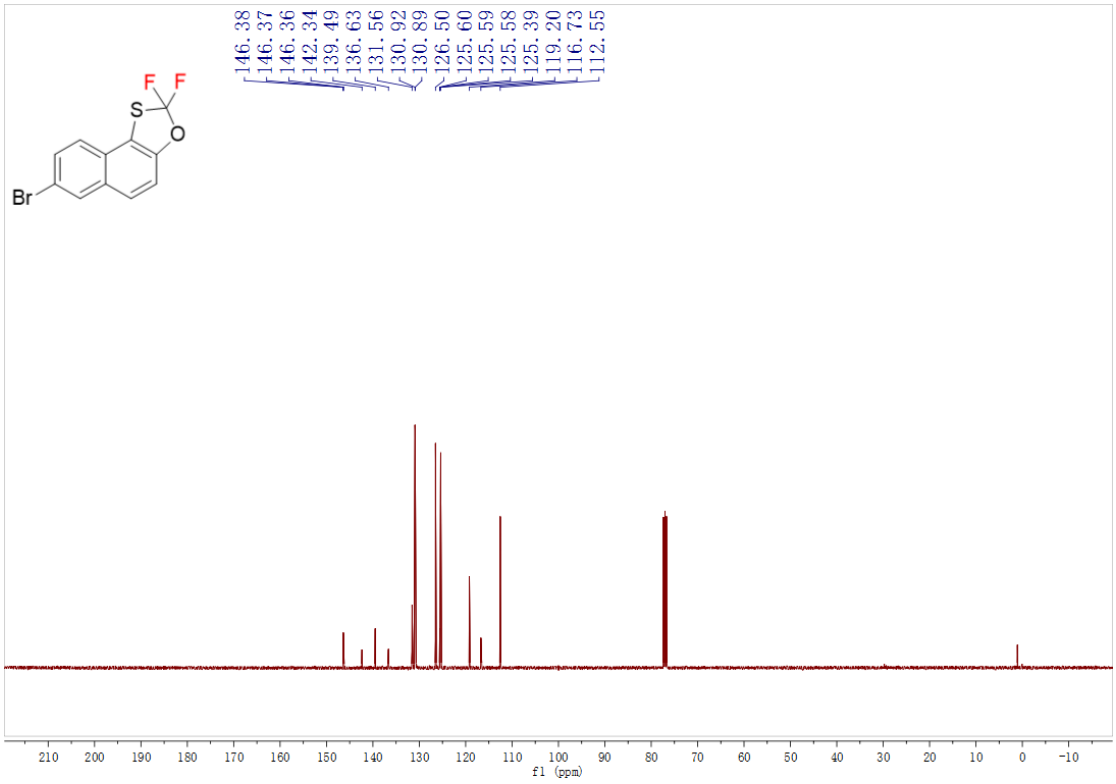
^{19}F NMR spectrum of **3ac** in $CDCl_3$



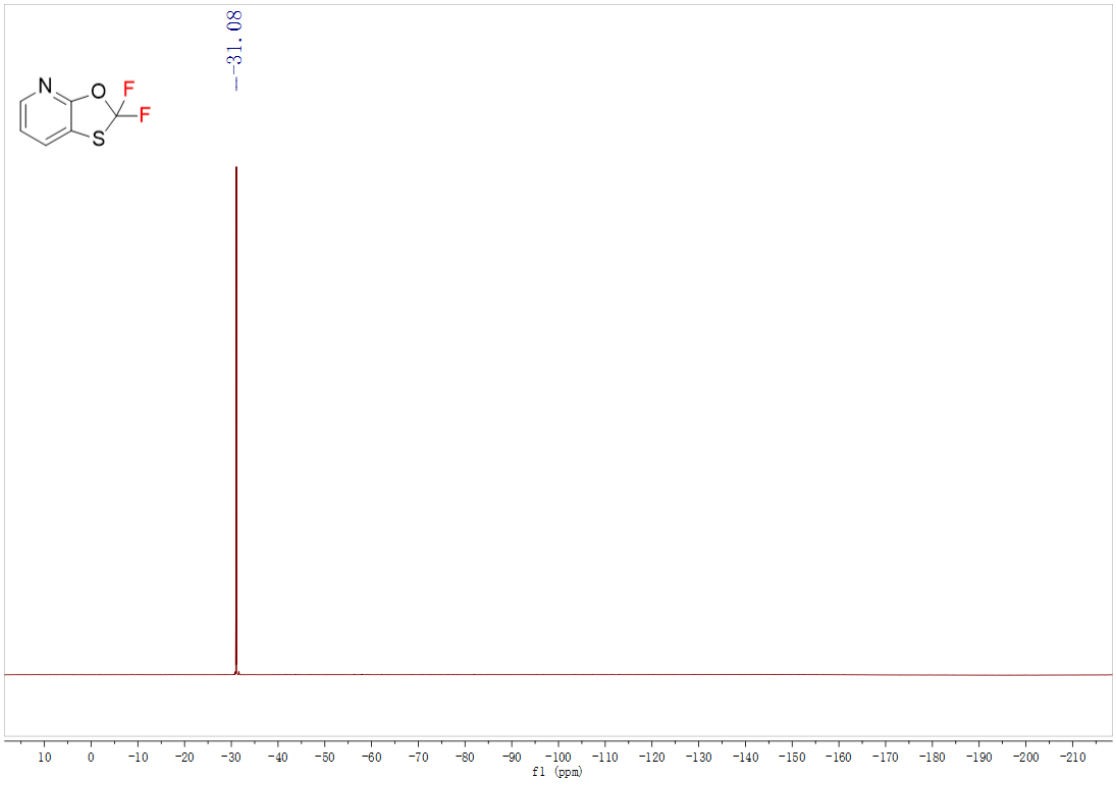
^{1}H NMR spectrum of **3ac** in $CDCl_3$



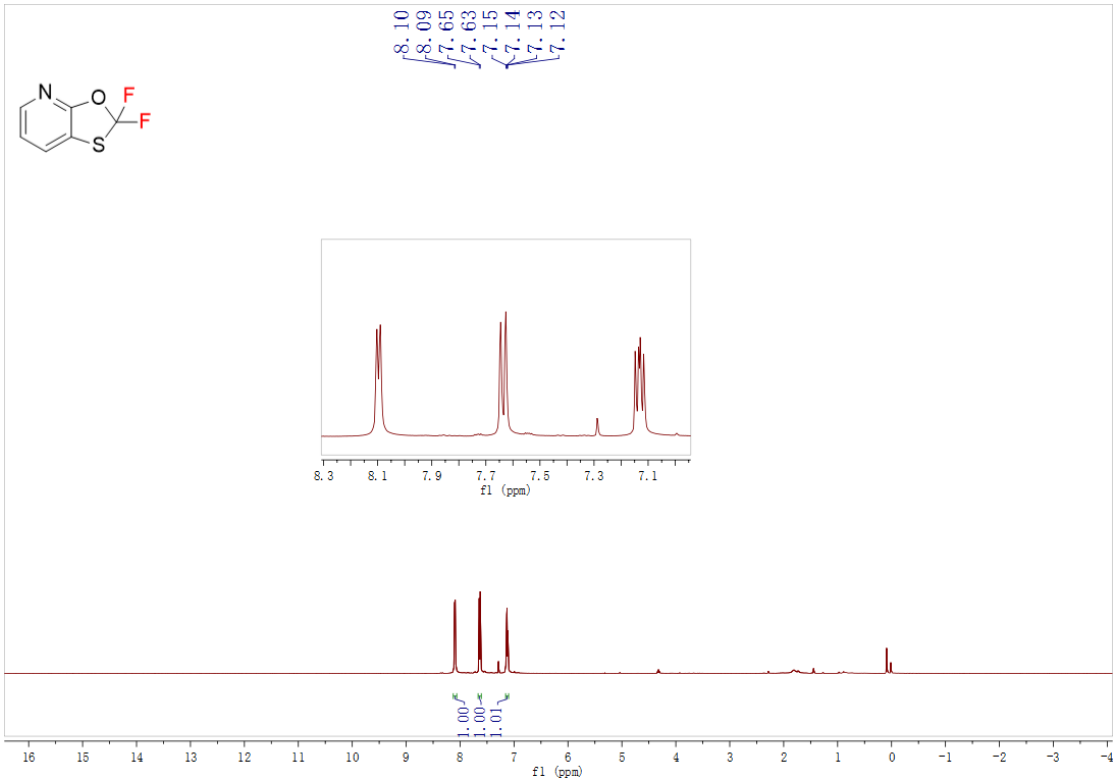
^{13}C NMR spectrum of **3ac** in $CDCl_3$



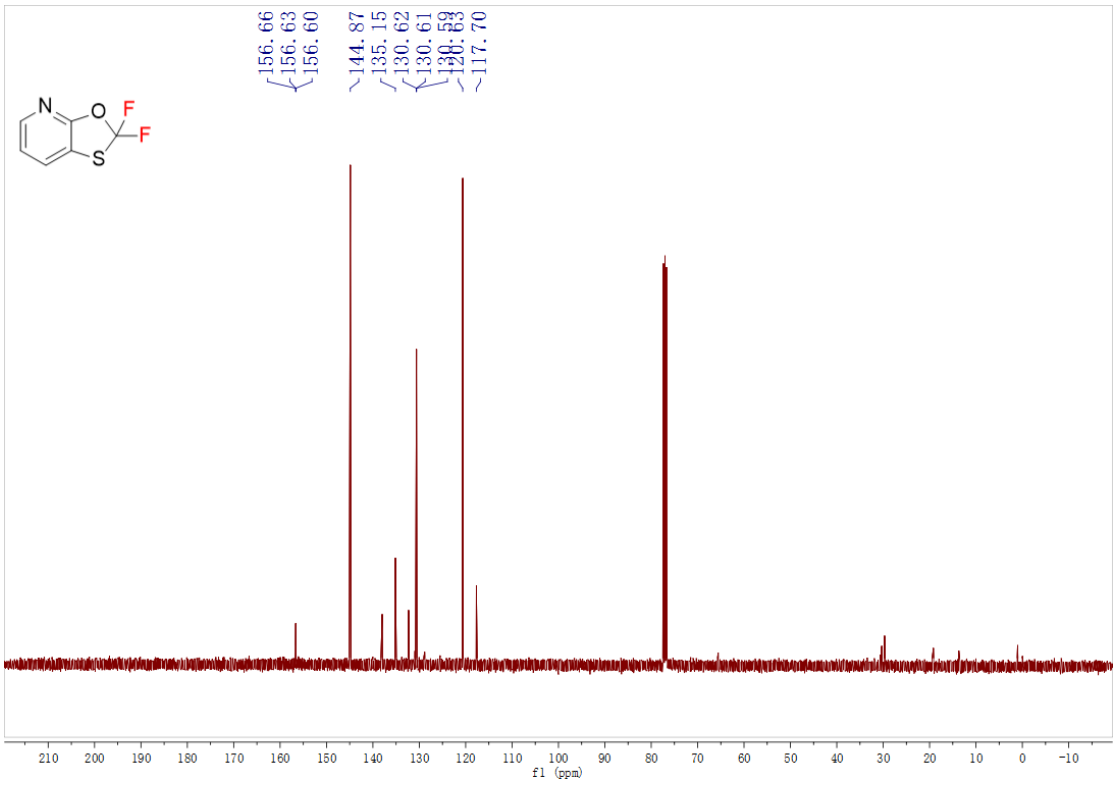
^{19}F NMR spectrum of **3ad** in $CDCl_3$



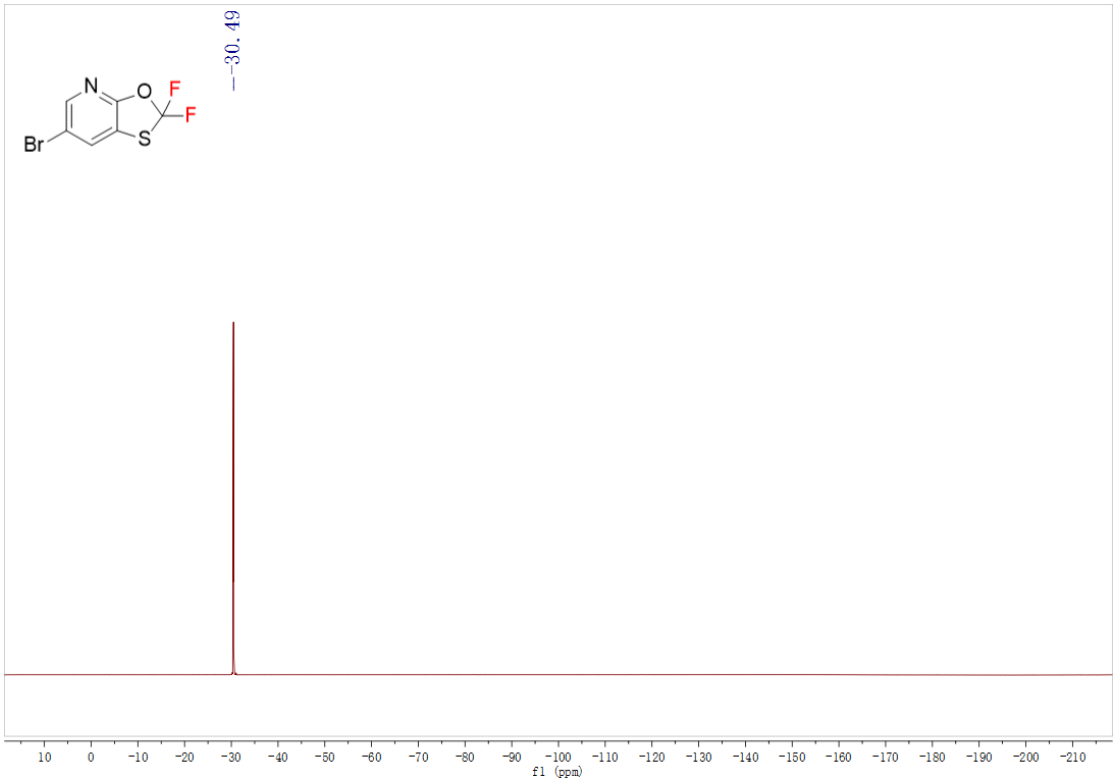
^{1}H NMR spectrum of **3ad** in $CDCl_3$



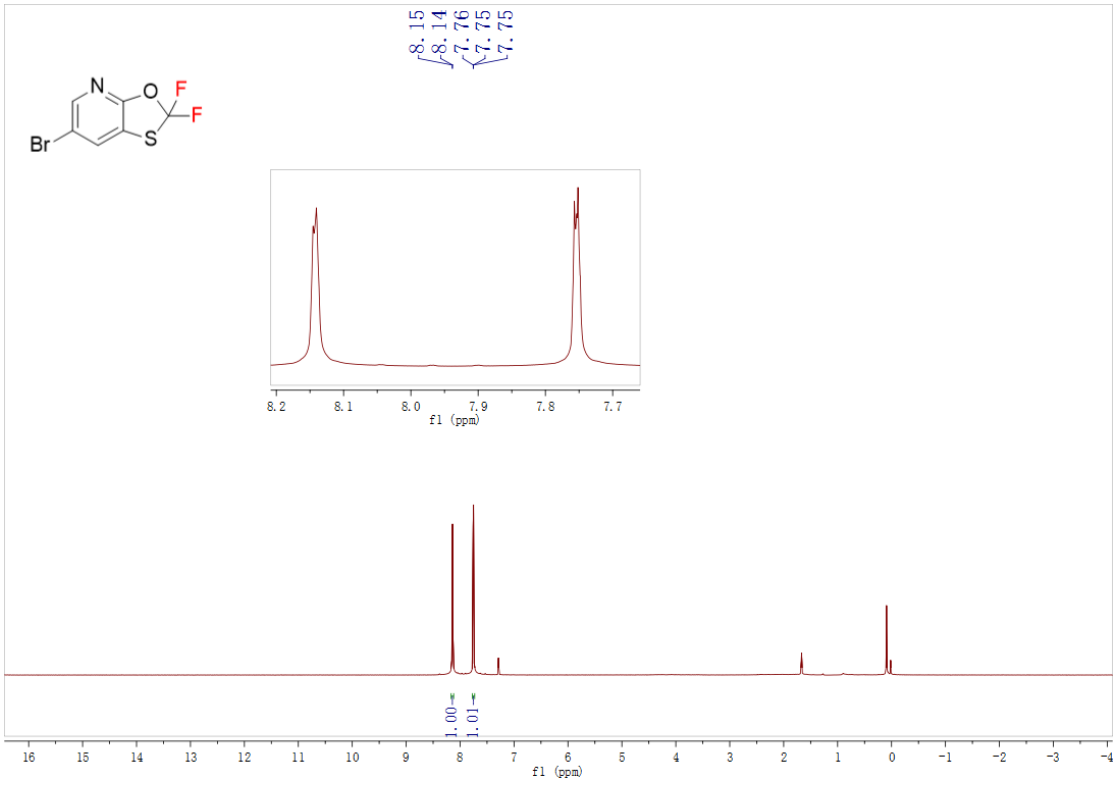
^{13}C NMR spectrum of **3ad** in $CDCl_3$



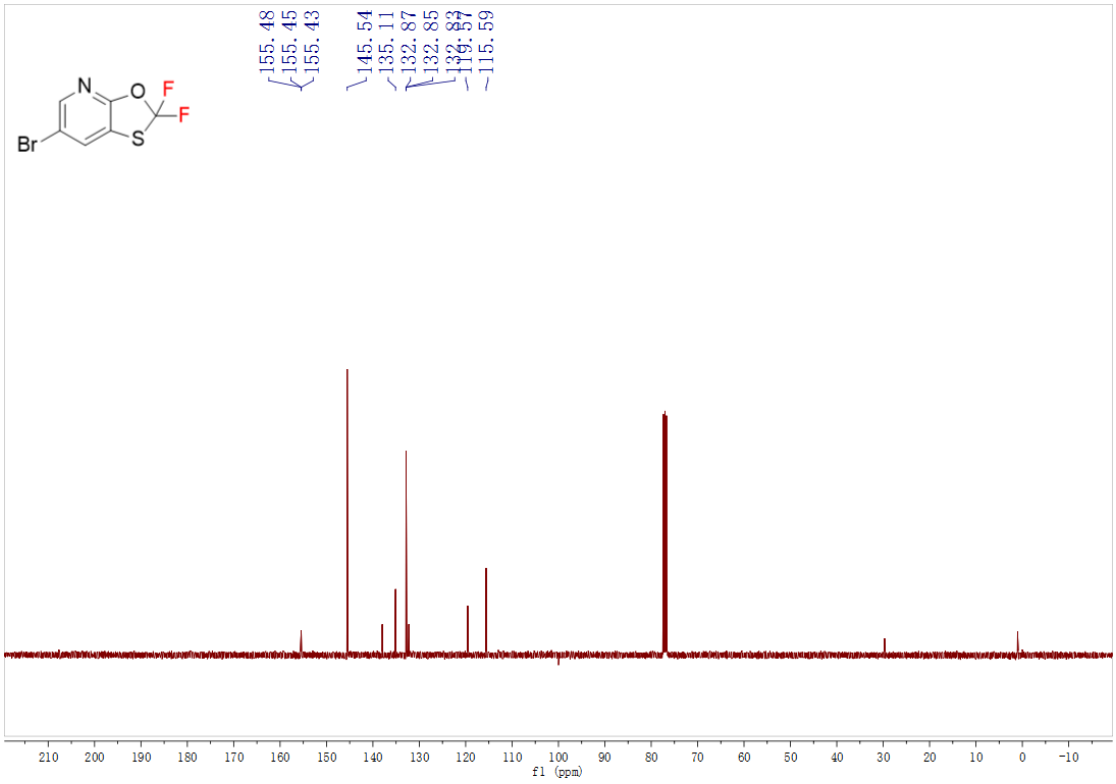
^{19}F NMR spectrum of **3ae** in $CDCl_3$



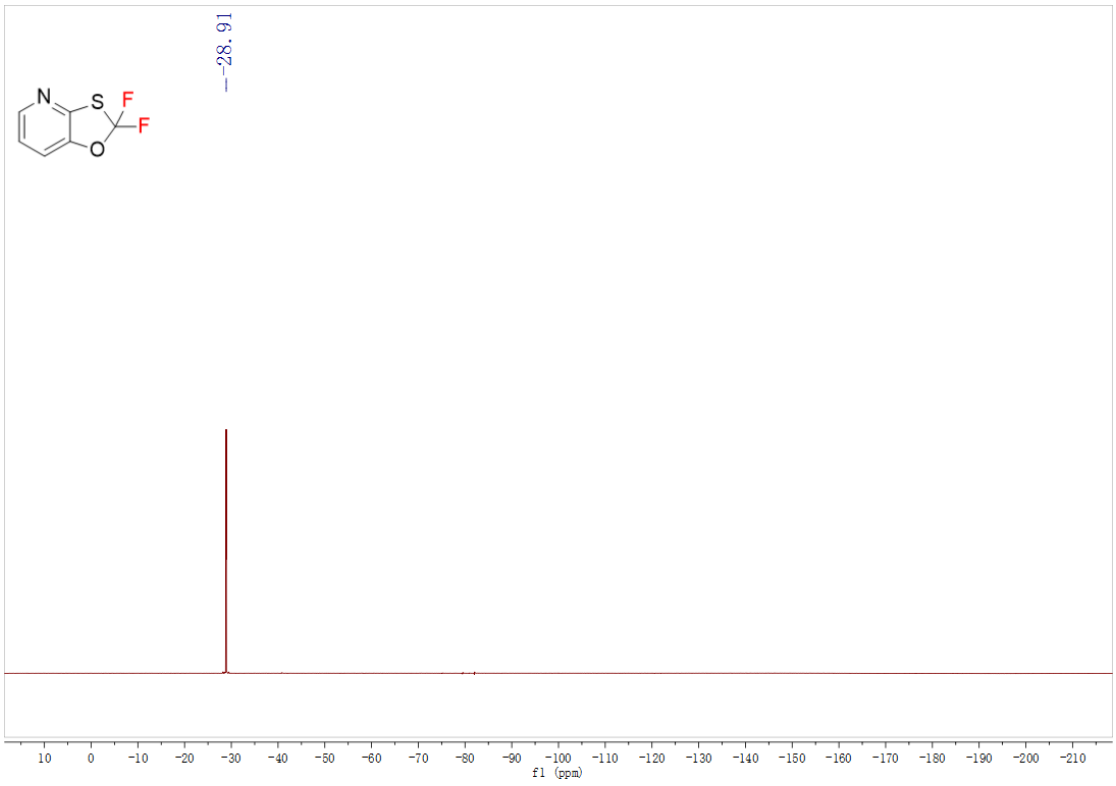
^{1}H NMR spectrum of **3ae** in $CDCl_3$



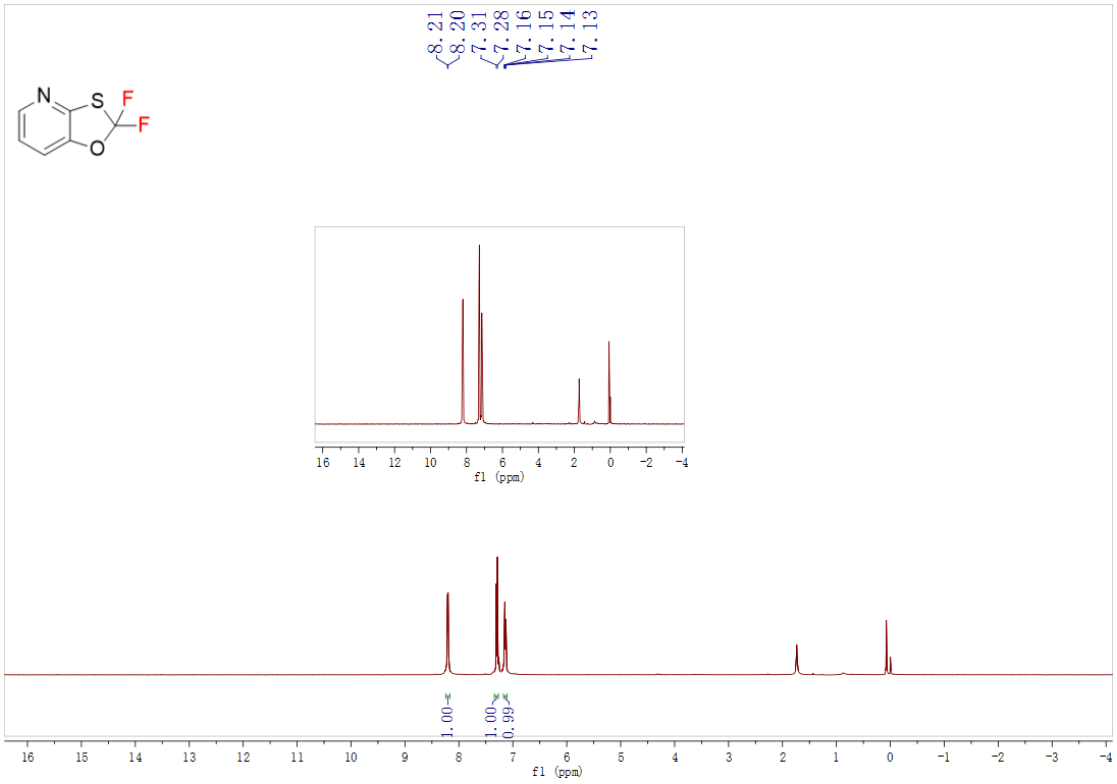
^{13}C NMR spectrum of **3ae** in $CDCl_3$



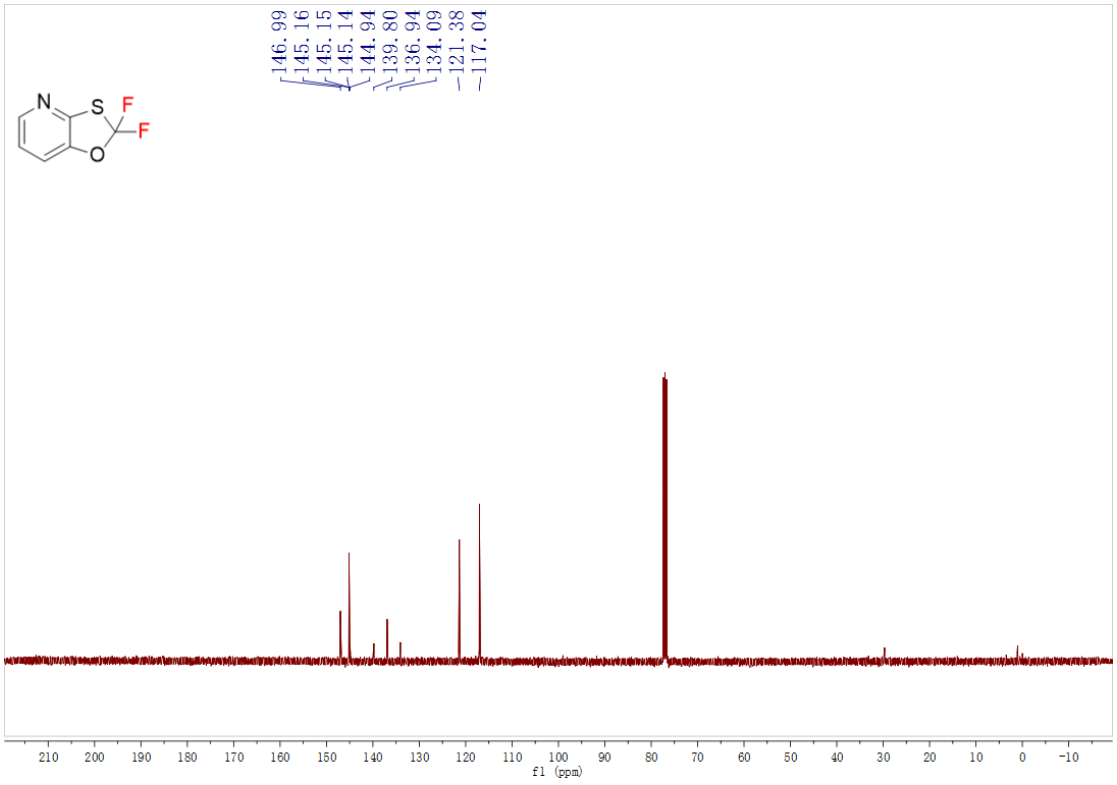
^{19}F NMR spectrum of **3af** in $CDCl_3$



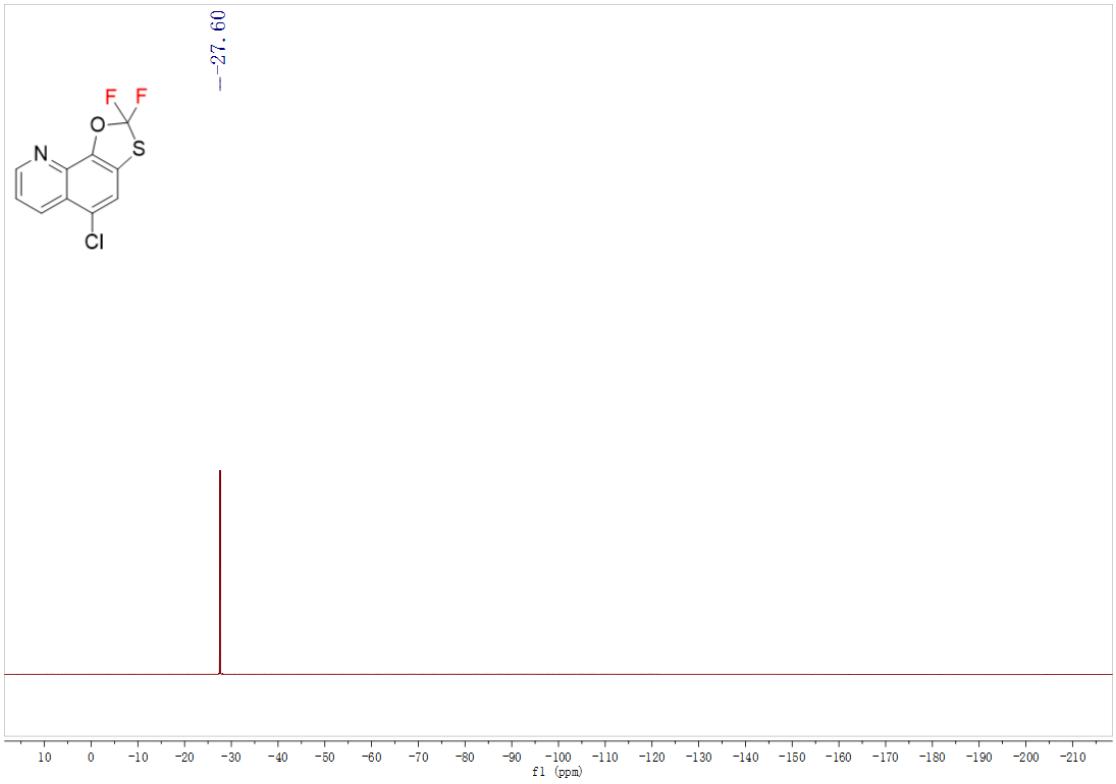
^{1}H NMR spectrum of **3af** in $CDCl_3$



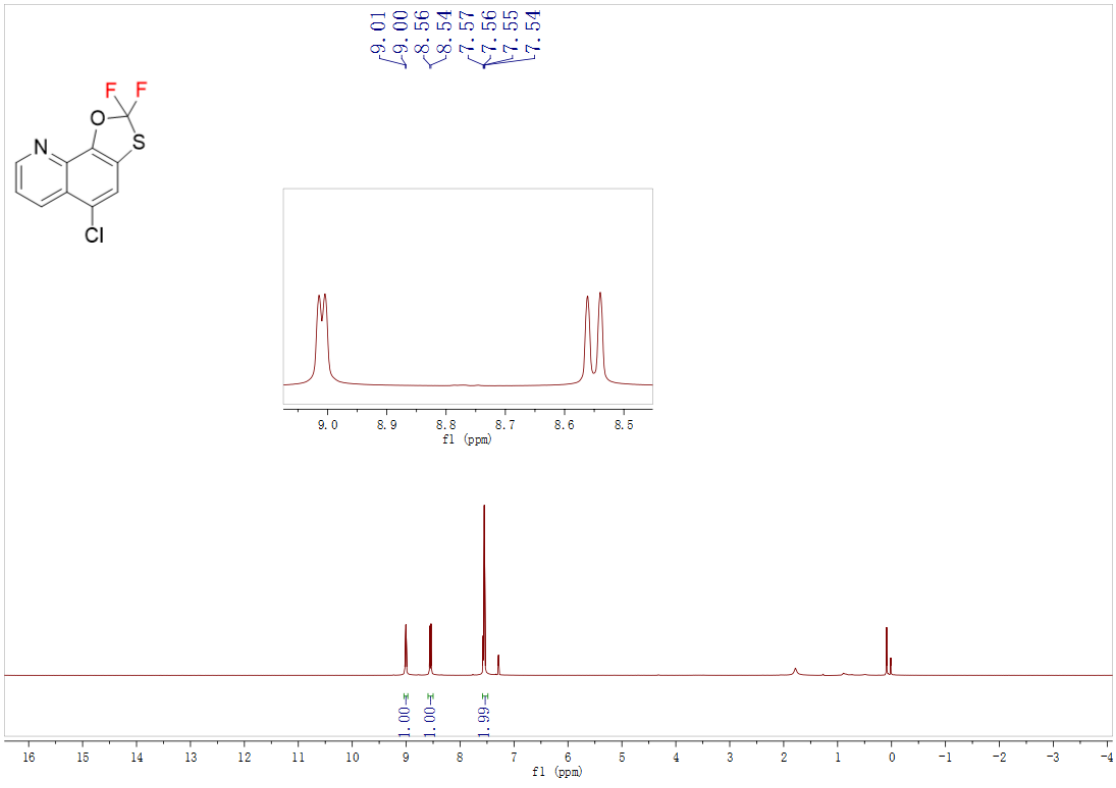
^{13}C NMR spectrum of **3af** in $CDCl_3$



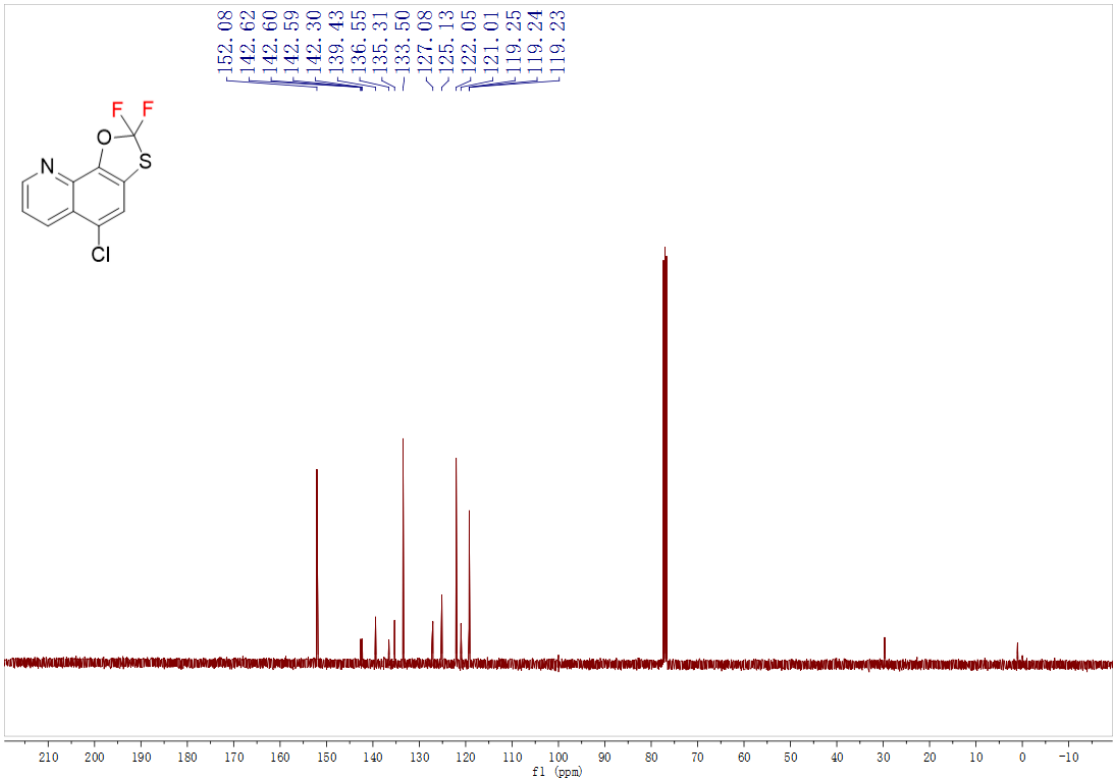
^{19}F NMR spectrum of **3ag** in $CDCl_3$



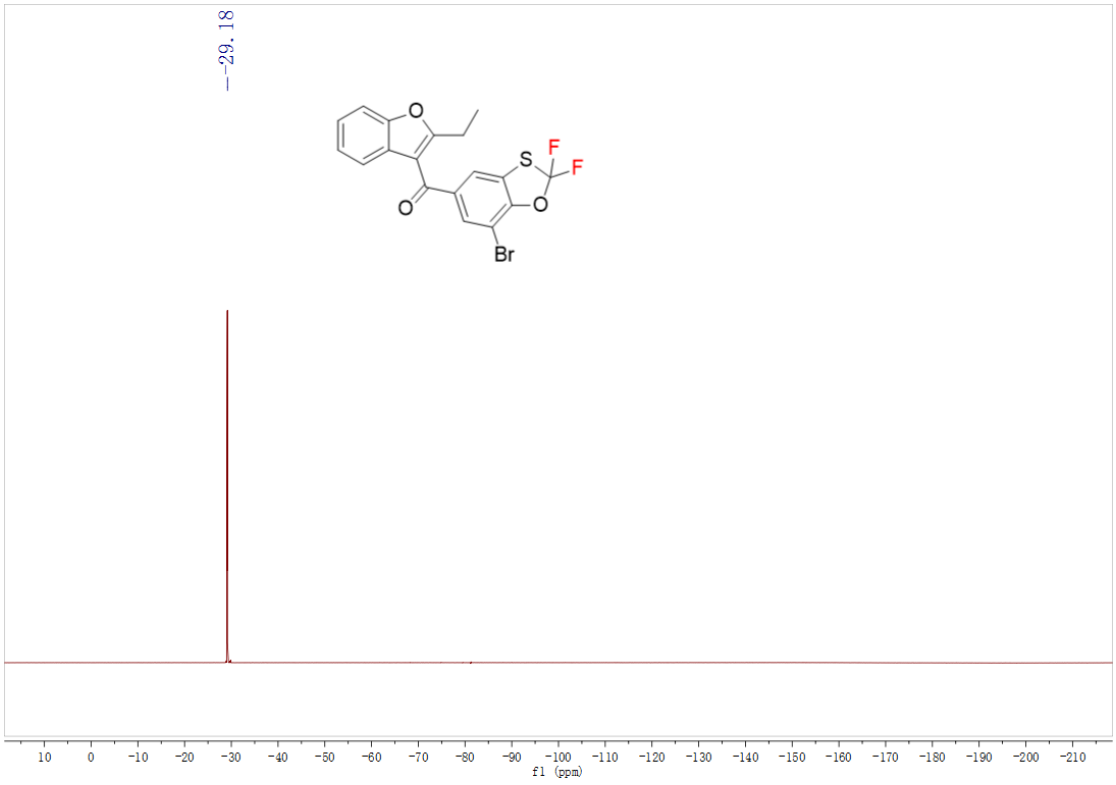
^{1}H NMR spectrum of **3ag** in $CDCl_3$



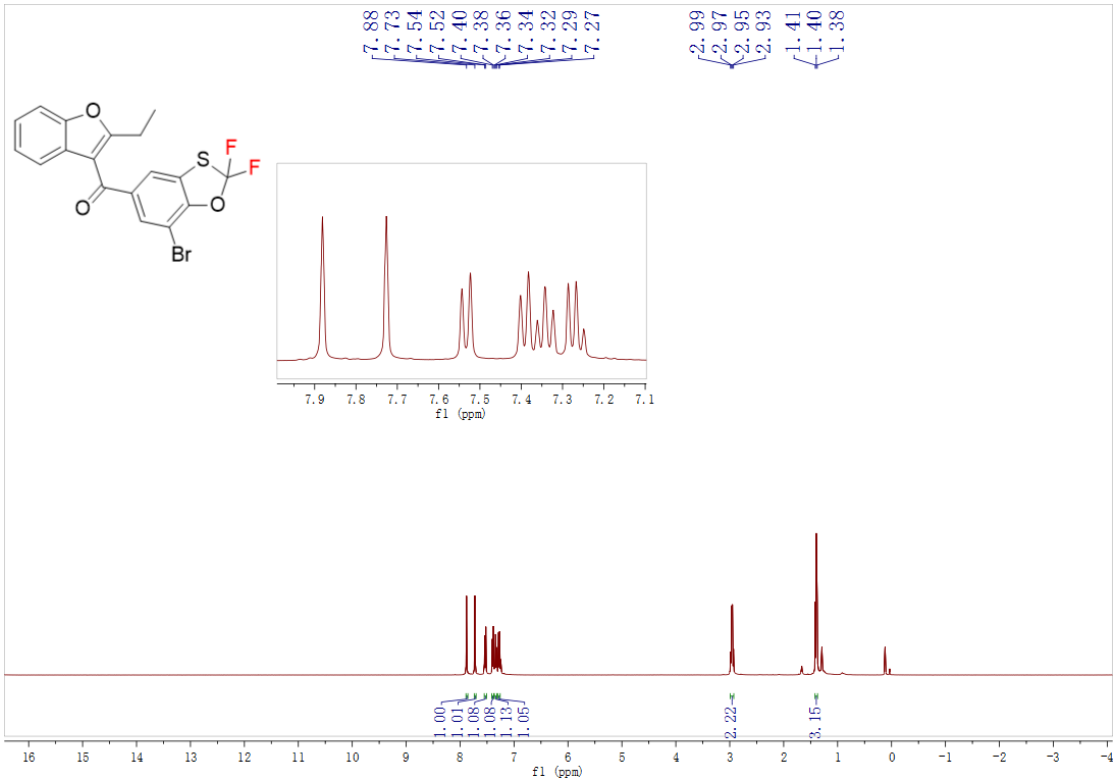
^{13}C NMR spectrum of **3ag** in $CDCl_3$



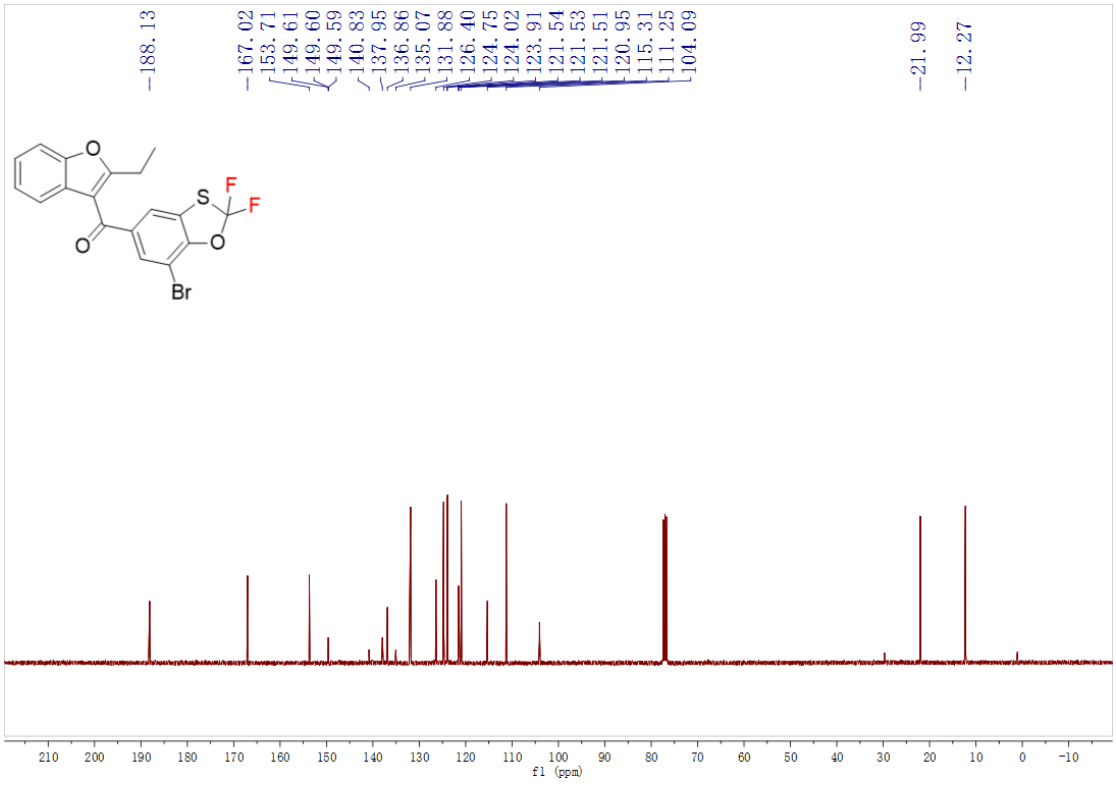
^{19}F NMR spectrum of **3ah** in $CDCl_3$



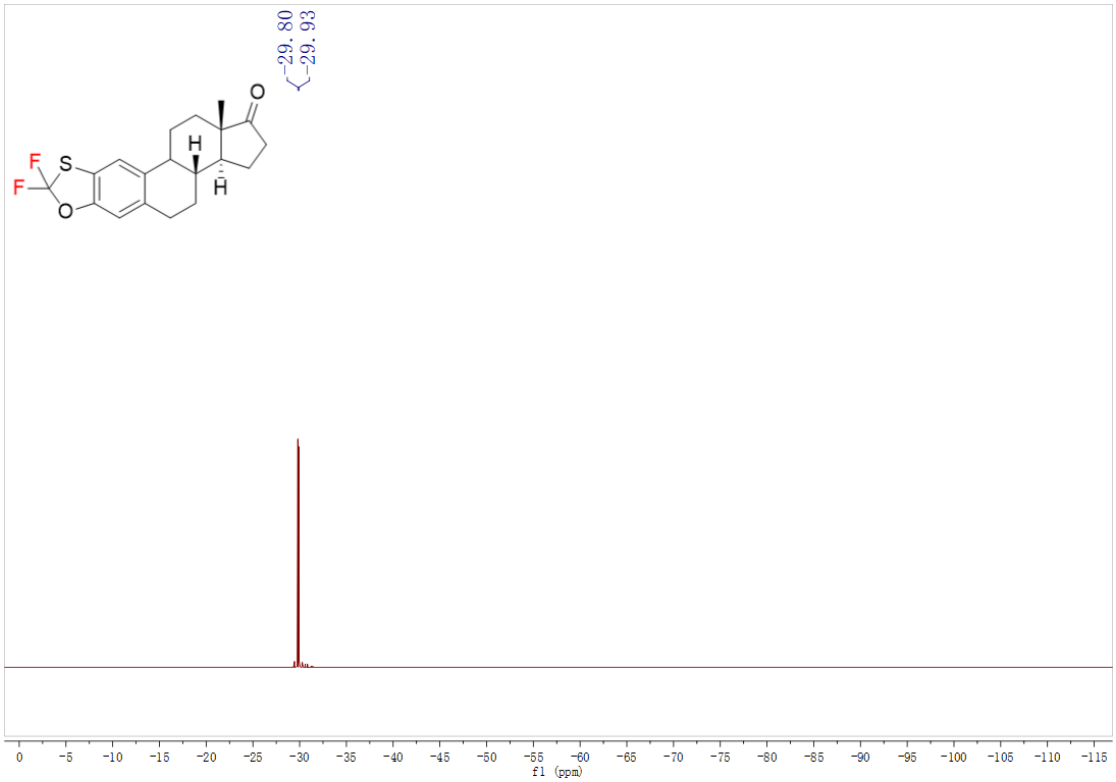
^{1}H NMR spectrum of **3ah** in $CDCl_3$



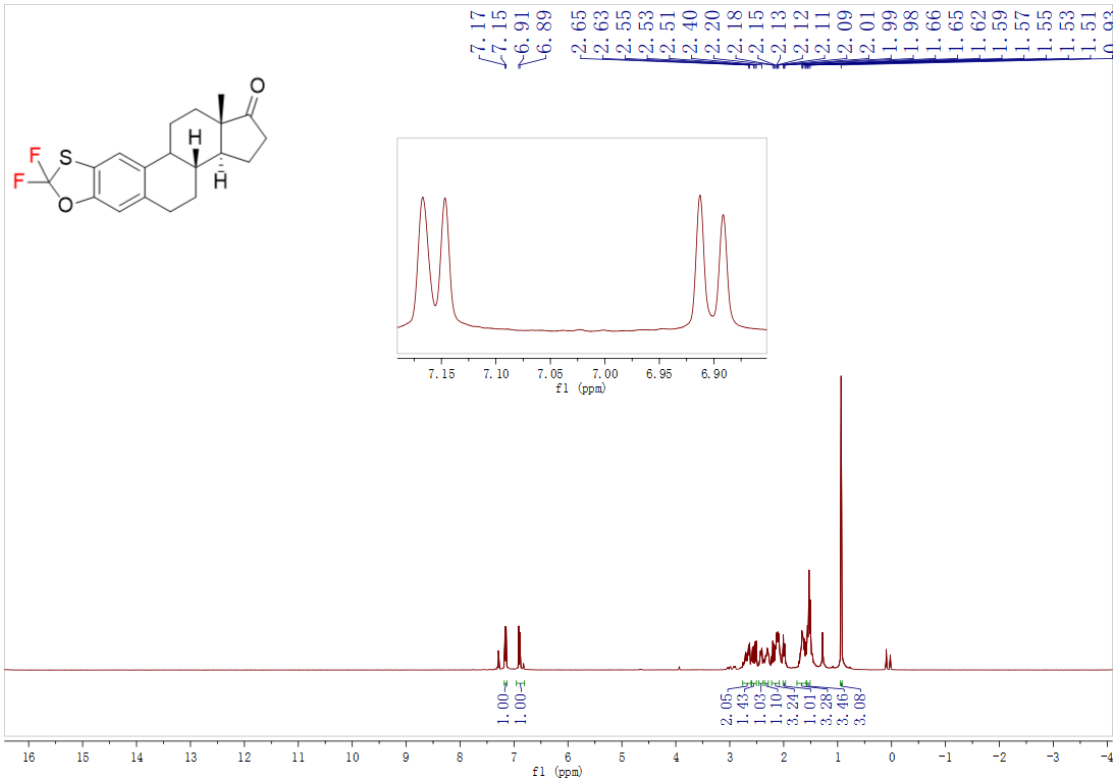
^{13}C NMR spectrum of **3ah** in $CDCl_3$



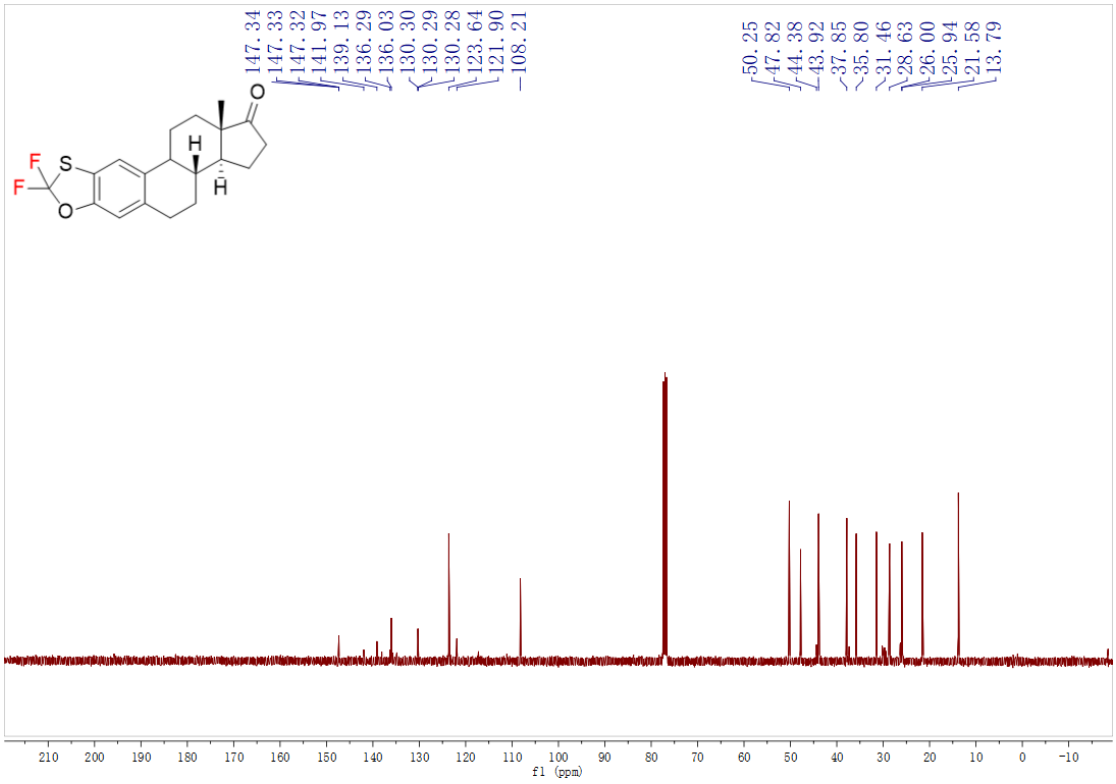
^{19}F NMR spectrum of **3ai** in $CDCl_3$



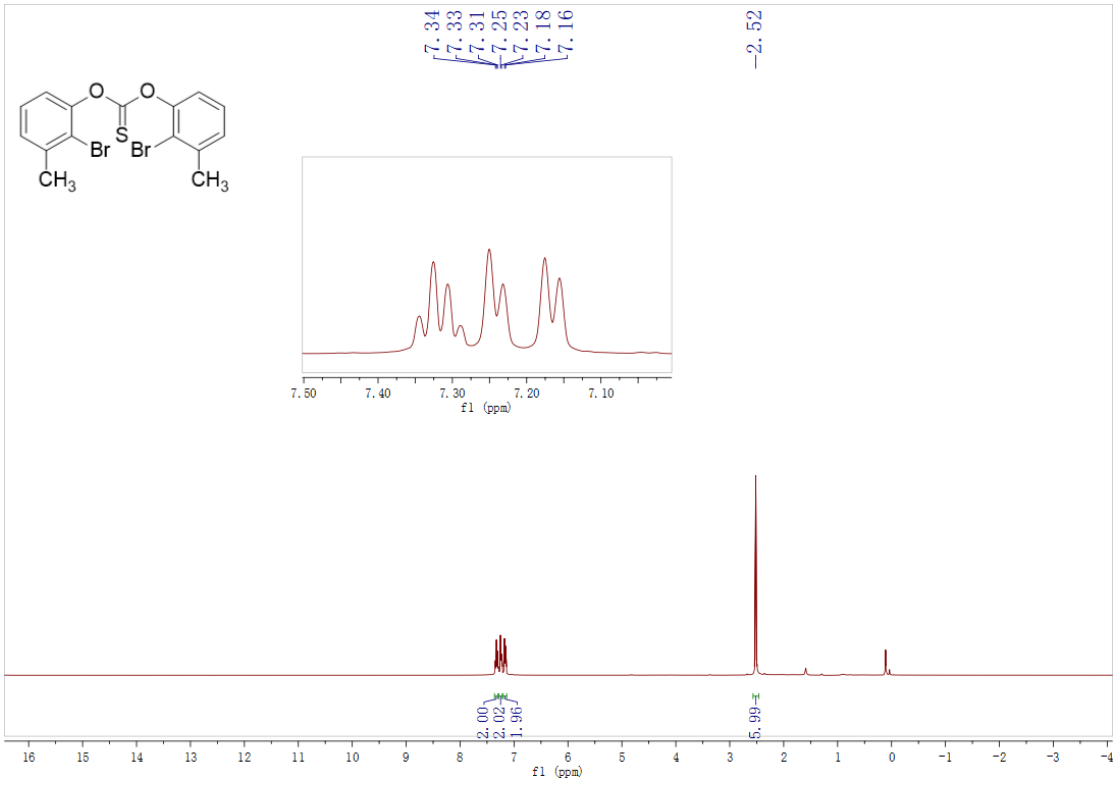
^{1}H NMR spectrum of **3ai** in $CDCl_3$



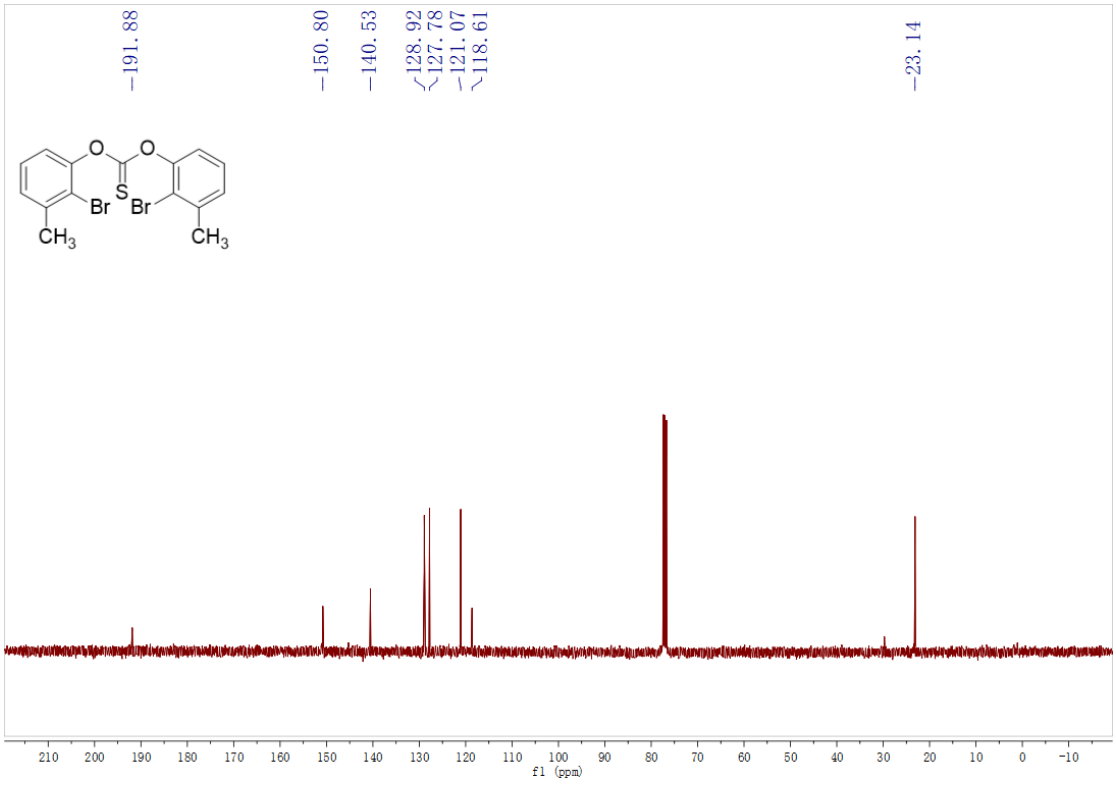
^{13}C NMR spectrum of **3ai** in $CDCl_3$



^{1}H NMR spectrum of **II** in $CDCl_3$



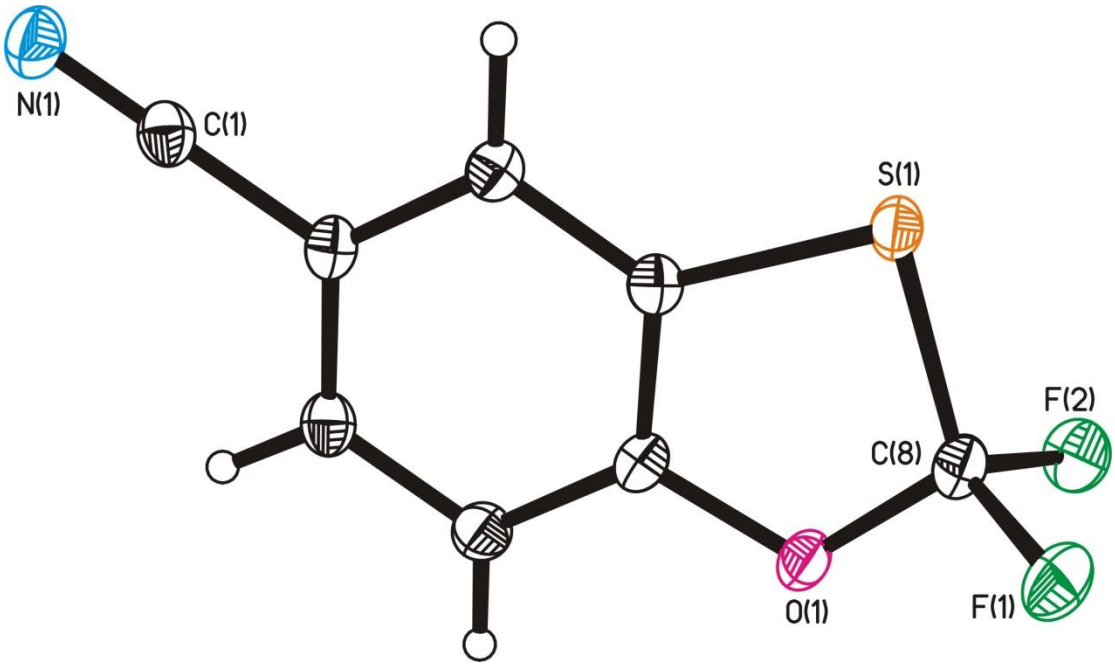
^{13}C NMR spectrum of **II** in $CDCl_3$



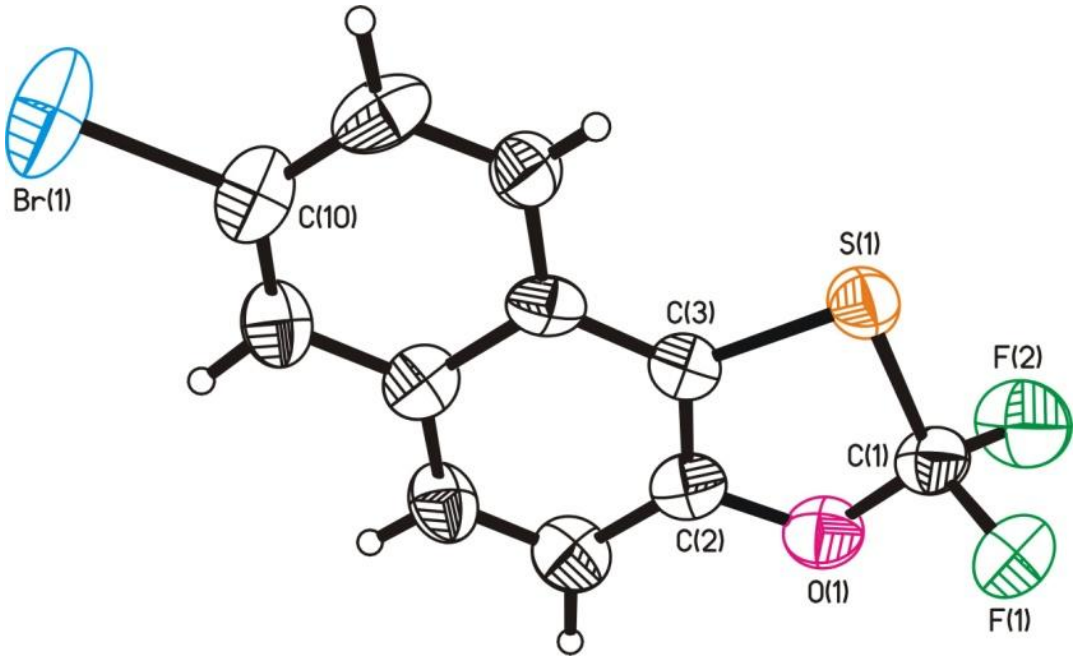
Crystal structure analyses.

The suitable crystals of **3k** (CCDC1584864) and **3ac** (CCDC1564419) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ºC, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the **SMART** suite of programs and for absorption effects with SADABS.[6] Structure solution and refinement were carried out with the SHELXTL suite of programs.[6] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

ORTEP diagrams



ORTEP diagram of compound **3k.** Thermal ellipsoids are drawn at 40% probability.



ORTEP diagram of compound **3ac.** Thermal ellipsoids are drawn at 40% probability.

Refenences:

(1) Weng, Z.; He, W.; Chen, C.; Lee, R.; Tan, D.; Lai, Z.; Kong, D.; Yuan, Y.; Huang, K.-W. *Angew. Chem. Int. Ed.* **2013**, *52*, 1548.

(2) Zhang, Y.; Gan, K.; Weng, Z. *Org. Process Res. Dev.* **2016**, *20*, 799.

(3) Tyrra, W.; Naumann, D.; Hoge, B.; Yagupolskii, Y. L. *J. Fluorine Chem.* **2003**, *119*, 101.

(4) Chen, A. Y.; Lee, A. J.; Jiang, X.-R.; Zhu, B. T. *J. Med. Chem.* **2007**, *50*, 5372.

(5) Xu, C.; Ma, B.; Shen, Q. *Angew. Chem. Int. Ed.* **2014**, *53*, 9316.

(6) SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.