Supporting Information *for*

Copper-catalyzed synthesis of 2,2-difluoro-1,3-benzoxathioles(selenoles) and their insecticidal activities: the selenium effect

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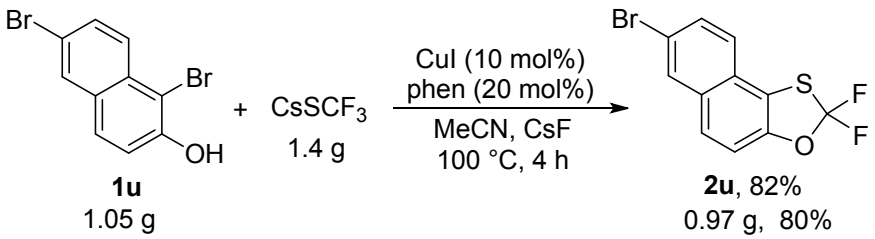
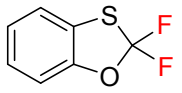
Procedure for gram scale reaction for synthesis of 7-bromo-2,2-difluoronaphtho[1,2-*d*][1,3]oxathiole (2u)



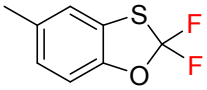
In a glove box filled with nitrogen, to an oven-dried 100 mL pressure tube equipped with a stir bar were added $CsSCF_3$ (1.25 g, 5.2 mmol, 1.5 equiv), 1,6-dibromo-2-naphtho **1u** (1.05 g, 3.45 mmol), CsF (524 mg, 3.45 mmol, 1.0 equiv), CuI (66 mg, 0.35 mmol, 10 mol%), phen (125 mg, 0.69 mmol, 20 mol%), and CH_3CN (15 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 4 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was neutralized by sodium bicarbonate aqueous solution, 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 0.97 g of product **2u** (80% yield).

Data for compounds 2



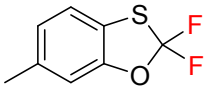
2,2-Difluorobenzo[*d*][1,3]oxathiole (**2a**)

Obtained as a pale yellow oil in 60% yield (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 2H), 7.17 – 7.07 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.6 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4 (s), 138.8 (t, J = 285.0 Hz), 126.7 (s), 124.4 (s), 122.3 (s), 121.6 (s), 111.2 (s). IR (KBr): ν 2926, 1579, 1466, 1235, 1146, 1107, 1073, 1036, 1014, 905, 881, 735, 699, 650, 495 cm^{-1}. GC-MS m/z 174 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_4OF_2S$: 173.9951; found: 173.9952.



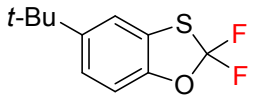
2,2-Difluoro-5-methylbenzo[*d*][1,3]oxathiole (**2b**)[1]

Obtained as a pale yellow oil in 65% yield (61 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.99 – 6.90 (m, 2H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5 (s), 138.9 (t, J = 285.7 Hz), 134.2 (s), 127.2 (s), 122.1 (s), 121.9 (s), 110.7 (s), 20.9 (s). GC-MS m/z 188 (M^+).



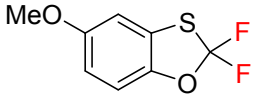
2,2-Difluoro-6-methylbenzo[*d*][1,3]oxathiole (**2c**)[1]

Obtained as a pale yellow oil in 69% yield (65 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 7.9 Hz, 1H), 6.95 (d, J = 7.9 Hz, 1H), 6.93 (s, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -30.8 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 (t, J = 1.2 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). GC-MS m/z 188 (M^+).



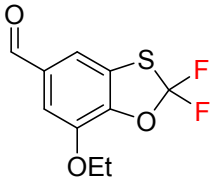
5-(*tert*-Butyl)-2,2-difluorobenzo[*d*][1,3]oxathiole (**2d**)[1]

Obtained as a pale yellow oil in 80% yield (92 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.19 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 8.5 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), 34.8 (s), 31.4 (s). GC-MS m/z 230 (M^+).



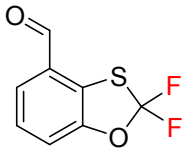
2,2-Difluoro-5-methoxybenzo[d][1,3]oxathiole (**2e**)[1]

Obtained as a pale yellow oil in 76% yield (88 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 8.9 Hz, 1H), 6.80 (s, 1H), 6.72 (d, J = 8.9 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). GC-MS m/z 204 (M^+).



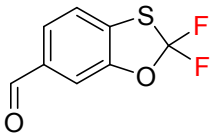
7-Ethoxy-2,2-difluorobenzo[*d*][1,3]oxathiole-5-carbaldehyde (**2f**)[1]

Obtained as a white solid in 91% yield (112 mg). ^{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). GC-MS m/z 246 (M^+).



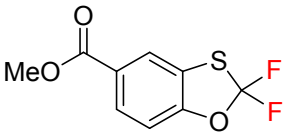
2,2-Difluorobenzo[*d*][1,3]oxathiole-4-carbaldehyde (**2g**)[1]

Obtained as a white solid in 85% yield (112 mg). ^{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). GC-MS m/z 202 (M^+).



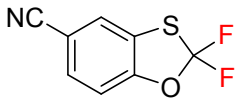
2,2-Difluorobenzo[*d*][1,3]oxathiole-6-carbaldehyde (**2h**)[1]

Obtained as a white solid in 62% yield (63 mg). ^{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). GC-MS m/z 202 (M^+).



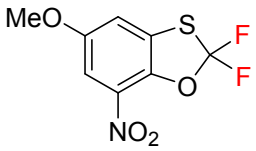
Methyl 2,2-difluorobenzo[*d*][1,3]oxathiole-5-carboxylate (**2i**)[1]

Obtained as a white solid in 99% yield (115 mg). ^{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). GC-MS m/z 232 (M^+).



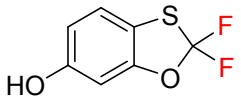
2,2-Difluorobenzo[*d*][1,3]oxathiole-5-carbonitrile (**2j**)[1]

Obtained as a white solid in 99% yield (99 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 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), 108.7 (s). GC-MS m/z 199 (M^+).



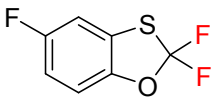
2,2-Difluoro-5-methoxy-7-nitrobenzo[*d*][1,3]oxathiole (**2k**)[1]

Obtained as a white solid in 35% yield (44 mg). ^{1}H NMR (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), 139.0 (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). GC-MS m/z 249 (M^+).



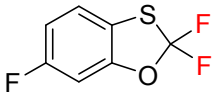
2,2-Difluorobenzo[*d*][1,3]oxathiol-6-ol (**2l**)[1]

Obtained as a white solid in 95% yield (91 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 1H), 7.06 – 6.97 (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), 139.3 (t, J = 287.1 Hz), 121.9 (s), 121.1 (s), 118.0 (s), 106.2 (s). GC-MS m/z 190 (M^+).



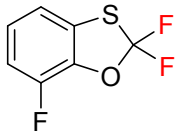
2,2,5-Trifluorobenzo[*d*][1,3]oxathiole (**2m**)[1]

Obtained as a pale yellow oil in 80% yield (77 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 6.95 (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 (dt, *J* = 2.8, 1.5 Hz), 138.9 (t, *J* = 286.1 Hz), 123.7 (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). GC-MS m/z 192 (M^+).



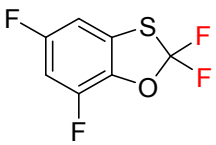
2,2,6-Trifluorobenzo[*d*][1,3]oxathiole (**2n**)[1]

Obtained as a pale yellow oil in 77% yield (74 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 1H), 6.98 – 6.80 (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). GC-MS m/z 192 (M^+).



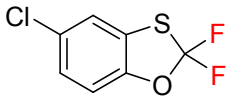
2,2,7-Trifluorobenzo[*d*][1,3]oxathiole (**2o**)[1]

Obtained as a pale yellow oil in 82% yield (79 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.06 (m, 1H), 7.06 – 6.96 (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). GC-MS m/z 192 (M^+).



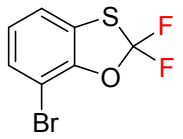
2,2,5,7-Tetrafluorobenzo[*d*][1,3]oxathiole (**2p**)[1]

Obtained as a pale yellow oil in 75% yield (79 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 – 6.64 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.7 (s, 2F), -113.7 – -114.1 (m, 1F), -129.2 (d, *J* = 9.7 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 (dd, *J* = 12.9, 1.8 Hz), 125.4 (dd, *J* = 12.0, 2.7 Hz), 104.6 (dd, *J* = 28.1, 4.2 Hz), 102.8 (dd, *J* = 27.7, 20.9 Hz). GC-MS m/z 210 (M^+).



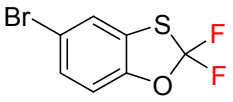
5-Chloro-2,2-difluorobenzo[*d*][1,3]oxathiole (**2q**)[1]

Obtained as a pale yellow oil in 71% yield (74 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). GC-MS m/z 208 (M^+).



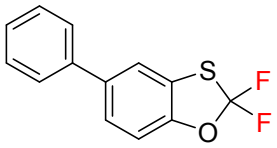
7-Bromo-2,2-difluorobenzo[*d*][1,3]oxathiole (**2r**)[1]

Obtained as a pale yellow oil in 94% yield (119 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 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), 130.1 (s), 125.3 (s), 123.3 (s), 120.5 (s), 104.2 (s). GC-MS m/z 252 (M^+).



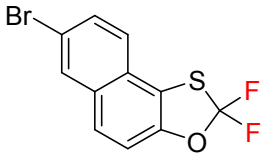
5-Bromo-2,2-difluorobenzo[*d*][1,3]oxathiole (**2s**)[1]

Obtained as a pale yellow oil in 91% yield (115 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), 129.7 (s), 124.4 (s), 124.3 (s), 116.5 (s), 112.5 (s). GC-MS m/z 252 (M^+).



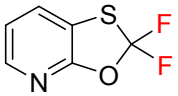
2,2-Difluoro-5-phenylbenzo[*d*][1,3]oxathiole (**2t**)[1]

Obtained a pale yellow oil in 65% yield (81 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.51 – 7.44 (m, 3H), 7.43 – 7.36 (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), 138.2 (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). GC-MS m/z 251 (M^+).



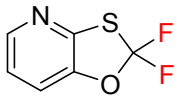
7-Bromo-2,2-difluoronaphtho[1,2-*d*][1,3]oxathiole (**2u**)[1]

Obtained as a white solid in 82% yield (124 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.65 – 7.55 (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), 116.7 (s), 112.6 (s). GC-MS m/z 303 (M^+).



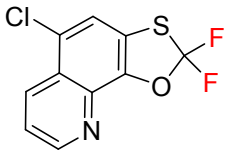
2,2-Difluoro-[1,3]oxathiolo[5,4-*b*]pyridine (**2v**)[1]

Obtained as pale yellow oil in 82% yield (72 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). GC-MS: m/z 175 (M^+).



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

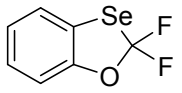
Obtained as pale yellow oil in 89% yield (77 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 4.6 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.14 (dd, J = 8.1, 5.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -28.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0 (s), 145.2 (t, J = 1.0 Hz), 144.9 (s), 136.9 (t, J = 287.1 Hz), 121.4 (s), 117.0 (s). GC-MS: m/z 175 (M^+).



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

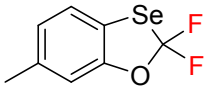
Obtained as white solid in 65% yield (84 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 4.0 Hz, 1H), 8.55 (d, J = 8.6 Hz, 1H), 7.60 – 7.49 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -27.6 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1 (s), 142.6 (t, J = 1.1 Hz), 139.4 (t, J = 289.2 Hz), 135.3 (s), 133.5 (s), 127.1 (s), 125.1 (s), 122.1 (s), 121.0 (s), 119.2 (t, J = 1.4 Hz). GC-MS m/z 258 (M^+).

Data for compounds 3.



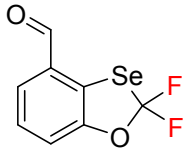
2,2-Difluorobenzo[*d*][1,3]oxaselenole (**3a**)

Obtained as a pale yellow oil in 57% yield (63 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.17 – 7.06 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -26.3 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (t, *J* = 2.2 Hz), 133.3 (t, *J* = 303.7 Hz), 127.3 (s), 125.2 (t, *J* = 1.1 Hz), 124.6 (s), 120.5 (s), 112.1 (s). IR (KBr): ν 3090, 1580, 1463, 1451, 1301, 1233, 1137, 1088, 1030, 1008, 878, 742, 670, 615 cm^{-1}. GC-MS m/z 222 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_4OF_2{}^{74}Se$: 215.9455; found: 215.9448.



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

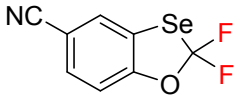
Obtained as a pale white solid in 58% yield (68 mg). M.p. 43–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.9 Hz, 1H), 6.99 – 6.89 (m, 2H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -26.5 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0 (t, *J* = 1.7 Hz), 137.9 (s), 133.4 (t, *J* = 303.6 Hz), 125.4 (s), 124.8 (s), 116.6 (s), 112.8 (s), 21.2 (s). IR (KBr): ν 2925, 1577, 1479, 1253, 1138, 1082, 1024, 904, 801, 729, 695, 649, 569, 427 cm^{-1}. GC-MS m/z 236 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_6OF_2{}^{74}Se$: 229.9611; found: 229.9608.



2,2-Difluorobenzo[*d*][1,3]oxaselenole-4-carbaldehyde (**3g**)

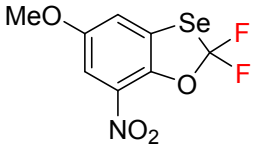
Obtained as a white solid in 85% yield (106 mg). M.p. 80–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -28.5 (s, 2F). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 190.3 (s), 152.5 (t, J = 2.8 Hz), 135.0 (t, J = 306.3 Hz), 132.0 (s), 128.5 (s), 127.5 (s), 122.1 (s), 116.7 (s). IR (KBr): ν 3020, 1673, 1572, 1438, 1379, 1325, 1258, 1135, 1072, 1010, 904, 819, 727, 698, 650, 491 cm^{-1}. GC-MS m/z 251 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_4O_2F_2{}^{74}Se$: 243.9404; found: 243.9412.



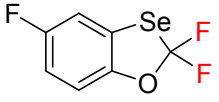
2,2-Difluorobenzo[*d*][1,3]oxaselenole-5-carbonitrile (**3j**)

Obtained as a white solid in 67% yield (83 mg). M.p. 132–135 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 8.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -29.6 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4 (t, J = 2.3 Hz), 133.2 (t, J = 306.9 Hz), 132.0 (s), 129.0 (t, J = 1.4 Hz), 122.4 (s), 117.6 (s), 112.7 (s), 108.9 (s). IR (KBr): ν 3106, 2230, 1974, 1479, 1469, 1250, 1109, 1075, 1032, 903, 871, 726, 649, 585, 489 cm^{-1}. GC-MS m/z 247 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_3NOF_2{}^{74}Se$: 240.9407; found: 240.9405.



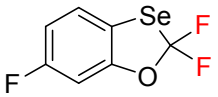
2,2-Difluoro-5-methoxy-7-nitrobenzo[*d*][1,3]oxaselenole (**3k**)

Obtained as a white solid in 64% yield (95 mg). M.p. 160–163 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 1H), 7.48 (s, 1H), 3.83 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -28.0 (s, 2F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.8 (s), 137.8 (t, J = 2.9 Hz), 134.5 (t, J = 305.3 Hz), 134.4 (s), 126.9 (s), 119.1 (s), 107.7 (s), 56.8 (s). IR (KBr): ν 2250, 2125, 1661, 1534, 1470, 1354, 1230, 1052, 1023, 1004 cm^{-1}. GC-MS m/z 297 (M^+). HR-MS (EI) m/z: calcd. for $C_8H_5NO_4F_2{}^{74}Se$: 290.9411; found: 290.9402.



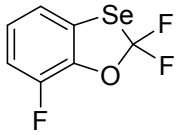
2,2,5-Trifluorobenzo[*d*][1,3]oxaselenole (**3m**)

Obtained as a pale yellow oil in 60% yield (72 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.01 (m, 2H), 6.94 (t, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -25.8 (s, 2F), -117.6 (d, *J* = 2.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2 (d, *J* = 244.8 Hz), 147.2 (d, *J* = 2.3 Hz), 133.4 (t, *J* = 304.5 Hz), 121.6 (d, *J* = 9.5 Hz), 114.1 (d, *J* = 24.4 Hz), 112.6 (d, *J* = 3.3 Hz), 112.4 (d, *J* = 22.5 Hz). IR (KBr): ν 2927, 1593, 1473, 1304, 1248, 1145, 1076, 1024, 903, 828, 807, 726, 650, 523, 439 cm^{-1}. GC-MS m/z 240 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_3OF_3{}^{74}Se$: 233.9361; found: 233.9367.



2,2,6-Trifluorobenzo[*d*][1,3]oxaselenole (**3n**)

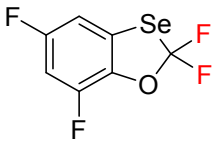
Obtained as a pale yellow oil in 74% yield (88 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 1H), 6.94 – 6.84 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -25.8 (s, 2F), -113.4 (dd, *J* = 14.2, 8.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.0 Hz), 151.1 (dt, *J* = 12.6, 2.3 Hz), 133.6 (t, *J* = 305.3 Hz), 125.5 (d, *J* = 9.2 Hz), 115.0 (d, *J* = 3.5 Hz), 111.9 (d, *J* = 22.8 Hz), 101.1 (d, *J* = 27.8 Hz). IR (KBr): ν 3050, 1597, 1475, 1428, 1277, 1141, 1113, 1079, 1026, 967, 905, 846, 800, 786, 731, 696, 586, 435 cm^{-1}. GC-MS m/z 240 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_3OF_3{}^{74}Se$: 233.9361; found: 233.9365.



2,2,7-Trifluorobenzo[*d*][1,3]oxaselenole (**3o**)

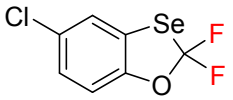
Obtained as a pale yellow oil in 96% yield (115 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 6.63 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -25.6 (s, 2F), -131.7 (d, *J* = 8.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0 (d, *J* = 252.5 Hz), 138.4 (dt, *J* = 4.8, 2.0 Hz), 133.6 (td, *J* = 306.9, 1.3 Hz), 125.1 (d, *J* = 6.2 Hz), 122.7 (s), 120.3 (d, *J* = 4.0 Hz), 114.7 (d, *J* = 17.2 Hz). IR (KBr): ν 2950, 1614, 1480, 1450, 1270, 1182,

1139, 1064, 905, 884, 765, 730, 700, 650, 613, 515 cm^{-1}. GC-MS m/z 240 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_3OF_3{}^{74}Se$: 233.9361; found: 233.9366.



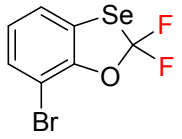
2,2,5,7-Tetrafluorobenzo[*d*][1,3]oxaselenole (**3p**)

Obtained a pale yellow oil in 99% yield (127 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.75 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -25.4 (s, 2F), -114.2 (t, J = 6.5 Hz, 1F), -127.7 (d, J = 9.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (dd, J = 247.9, 9.3 Hz), 147.4 (dd, J = 255.0, 12.4 Hz), 135.1 (ddd, J = 12.0, 6.5, 2.7 Hz), 133.5 (td, J = 307.6, 1.1 Hz), 123.2 (d, J = 10.8 Hz), 107.6 (ddt, J = 27.0, 4.1, 1.2 Hz), 103.3 (dd, J = 27.6, 21.0 Hz). IR (KBr): ν 3100, 2970, 1622, 1609, 1477, 1435, 1225, 1143, 1115, 1057, 989, 904, 826, 727, 693, 599, 526 cm^{-1}. GC-MS m/z 259 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_2OF_4{}^{74}Se$: 251.9267; found: 251.9265.



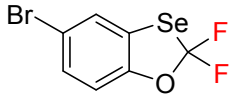
5-Chloro-2,2-difluorobenzo[*d*][1,3]oxaselenole (**3q**)

Obtained as a pale yellow oil in 81% yield (103 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.21 (d, J = 8.6 Hz, 1H), 7.03 (d, J = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -25.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 (s), 133.3 (t, J = 305.1 Hz), 129.7 (s), 127.4 (s), 124.9 (s), 122.0 (s), 112.8 (s). IR (KBr): ν 2925, 1591, 1459, 1239, 1143, 1101, 1068, 1029, 904, 861, 809, 729, 692, 650, 546, 471 cm^{-1}. GC-MS m/z 256 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_3OF_2Cl^{74}Se$: 249.9065; found: 249.9069.



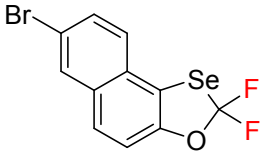
7-Bromo-2,2-difluorobenzo[*d*][1,3]oxaselenole (**3r**)

Obtained as a pale yellow oil in 99% yield (148 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -25.7 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2 (t, *J* = 2.5 Hz), 132.1 (t, *J* = 305.9 Hz), 130.9 (s), 125.6 (s), 124.1 (s), 121.2 (s), 105.2 (s). IR (KBr): ν 3106, 1582, 1455, 1433, 1244, 1139, 1099, 1036, 903, 876, 759, 748, 699, 649, 590, 442 cm^{-1}. GC-MS m/z 300 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_3OF_2Br^{74}Se$: 293.8560; found: 293.8567.



5-Bromo-2,2-difluorobenzo[*d*][1,3]oxaselenole (**3s**)

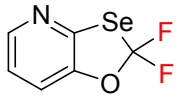
Obtained as a pale yellow oil in 91% yield (136 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.35 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -25.8 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9 (t, *J* = 2.3 Hz), 133.2 (t, *J* = 305.2 Hz), 130.3 (s), 127.7 (t, *J* = 1.2 Hz), 122.5 (s), 116.8 (t, *J* = 1.1 Hz), 113.3 (s). IR (KBr): ν 3050, 1573, 1457, 1236, 1139, 1061, 1026, 903, 806, 722, 688, 609, 541, 515 cm^{-1}. GC-MS m/z 300 (M^+). HR-MS (EI) m/z: calcd. for $C_7H_3OF_2Br^{74}Se$: 293.8560; found: 293.8571.



7-Bromo-2,2-difluoronaphtho[1,2-*d*][1,3]oxaselenole (**3u**)

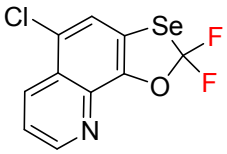
Obtained as a white solid in 60% yield (105 mg). M.p. 66–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.74 – 7.58 (m, 2H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -24.2 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0 (t, *J* = 2.0 Hz), 133.8 (t, *J* = 305.5 Hz), 131.7 (s), 131.0 (s), 130.9 (s), 128.2 (s), 127.2 (s), 119.1 (s), 116.2 (s), 113.4 (s). IR (KBr): ν 2825, 1583, 1565, 1497, 1343, 1263, 1242, 1127, 1066, 1001, 951, 904, 878, 796, 678, 649, 503, 459 cm^{-1}. GC-MS

m/z 350 (M^+). HR-MS (EI) m/z: calcd. for $C_{11}H_5OF_2{}^{74}SeBr$: 343.8717; found: 343.8720.



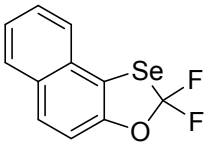
2,2-Difluoro-[1,3]oxaselenolo[4,5-*b*]pyridine (**3w**)

Obtained as a pale yellow oil in 74% yield (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.24 – 7.13 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -24.7 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3 (s), 146.6 (s), 145.5 (s), 132.5 (t, J = 305.4 Hz), 121.9 (s), 117.7 (s). IR (KBr): ν 3025, 1588, 1406, 1286, 1199, 1099, 1026, 904, 790, 721, 705, 670, 649, 538 cm^{-1}. GC-MS m/z 223 (M^+). HR-MS (EI) m/z: calcd. for $C_6H_3NOF_2{}^{74}Se$: 216.9407; found: 216.9411.



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

Obtained as a white solid in 52% yield (80 mg). M.p. 119–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 3.8 Hz, 1H), 8.49 (d, J = 8.6 Hz, 1H), 7.60 – 7.46 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -23.2 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9 (s), 144.0 (t, J = 2.0 Hz), 135.8 (s), 134.0 (t, J = 307.3 Hz), 133.4 (s), 127.0 (s), 125.4 (s), 122.1 (s), 119.1 (s). IR (KBr): ν 2842, 1608, 1582, 1490, 1453, 1351, 1294, 1144, 1023, 1004, 821, 757, 622 cm^{-1}. GC-MS m/z 307 (M^+). HR-MS (EI) m/z: calcd. for $C_{10}H_4NOF_2Cl{}^{74}Se$: 300.9174; found: 300.9179.



2,2-difluoronaphtho[1,2-d][1,3]oxaselenole (**3y**)

Obtained as a pale yellow oil in 40% yield (55 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -24.4 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7 (s), 133.9 (t, *J* = 304.9 Hz), 130.7 (s), 129.7 (s), 128.9 (s), 128.2 (s), 127.7 (s), 125.7 (s), 125.4 (s), 115.8 (s), 112.5 (s). IR (KBr): ν 3058, 1626, 1592, 1512, 1458, 1366, 1244, 1138, 1074, 1025, 903, 802, 761, 725, 650, 516, 452 cm^{-1}. GC-MS m/z 272 (M^+). HR-MS (EI) m/z: calcd. for $C_{11}H_6OF_2{}^{74}Se$: 265.9611; found: 265.9619.

The procedure for the insecticidal assay

Each of the test compounds was first dissolved in 5 mL of mixture of acetone and methanol (1:1 by volume), and then 5 mL of water containing 0.1% Tween 80 was added to generate a 10 mL stock solution of 600 mg/L concentration.

The cabbage leaves were cut into small circular pieces (ϕ = 30 mm), and placed on the glass Petri dishes (ϕ = 60 mm) layered with filter papers that had been wet with sterilized distilled water. The cabbage leaves were prayed with the aforementioned solutions using a Airbrush sprayer (dosage 0.5 mL). After they were air dried, the third-instar insects were introduced to the cabbage leaves. They were kept in a special room for normal cultivation (temperature: 23-25 °C; RH: 40-60%, L/D: 13 h/11 h). Assessments were made after 72 h by the number of killed and size of live insects relative to that in the negative control, and evaluations were based on a percentage scale of 0-100, in which 100 was total kill and 0 was no activity. To compare their activities, the commercial products abamectin and imidacloprid was tested at the concentration of 10 mg/L under the same conditions.

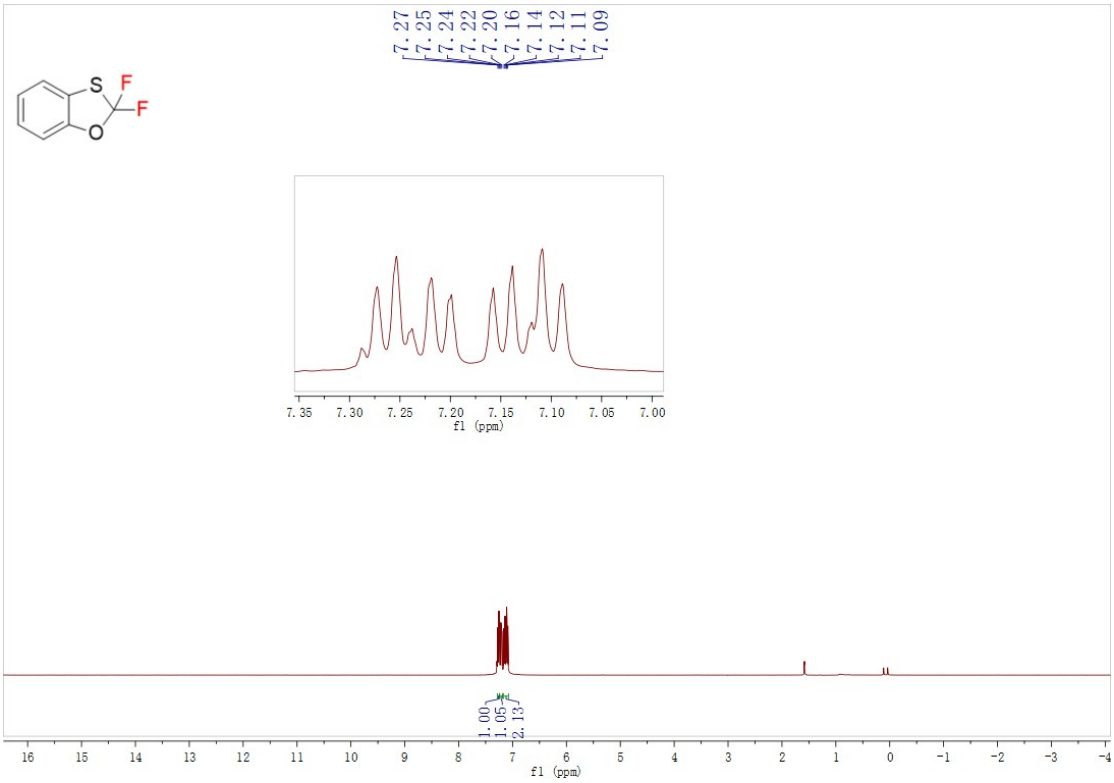
For the insecticidal activities against leucania separate, the corn leaf disks (2 mm × 5 mm) were used instead of the cabbage leaves.

References:

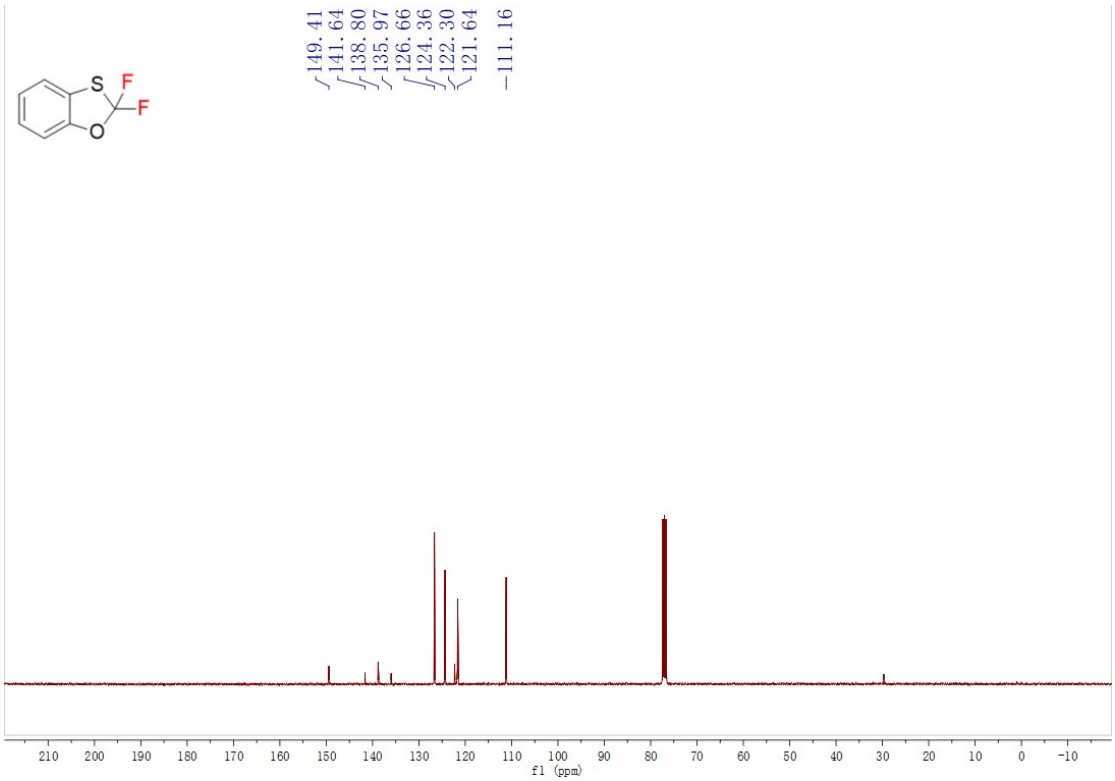
(1) Zhang, M.; Chen, S.; Weng, Z. *Org. Lett.* **2018**, *20*, 481.

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

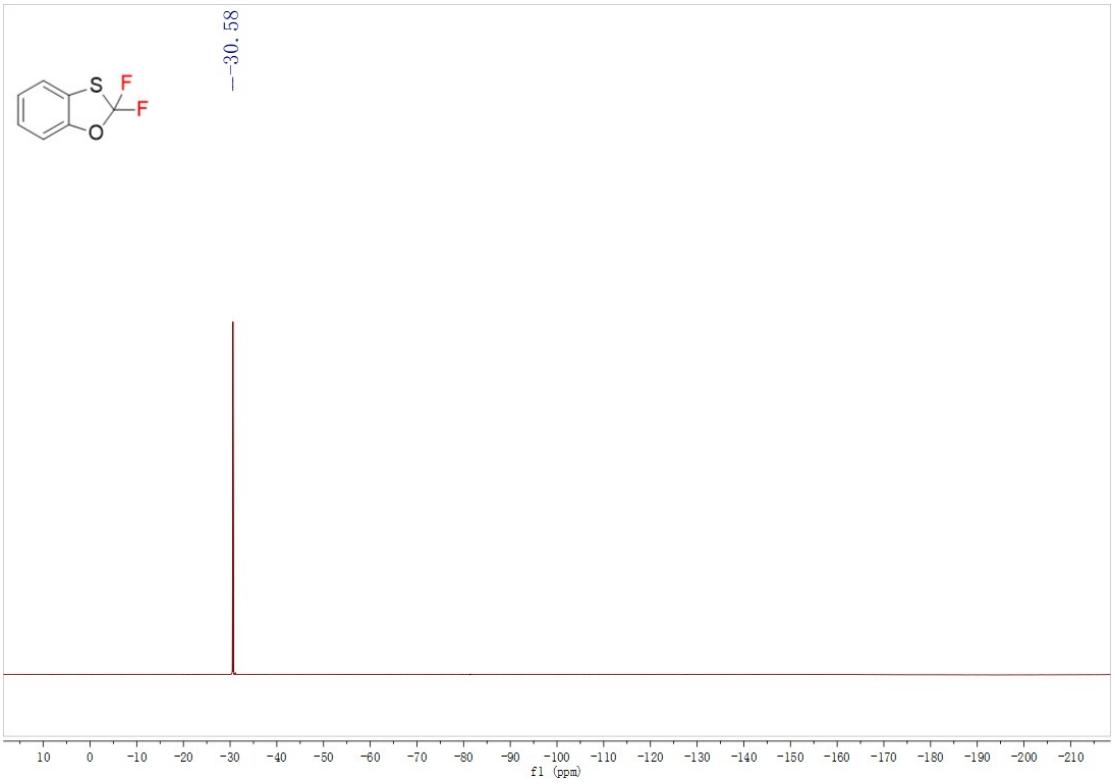
^{1}H NMR spectrum of **2a** in $CDCl_3$



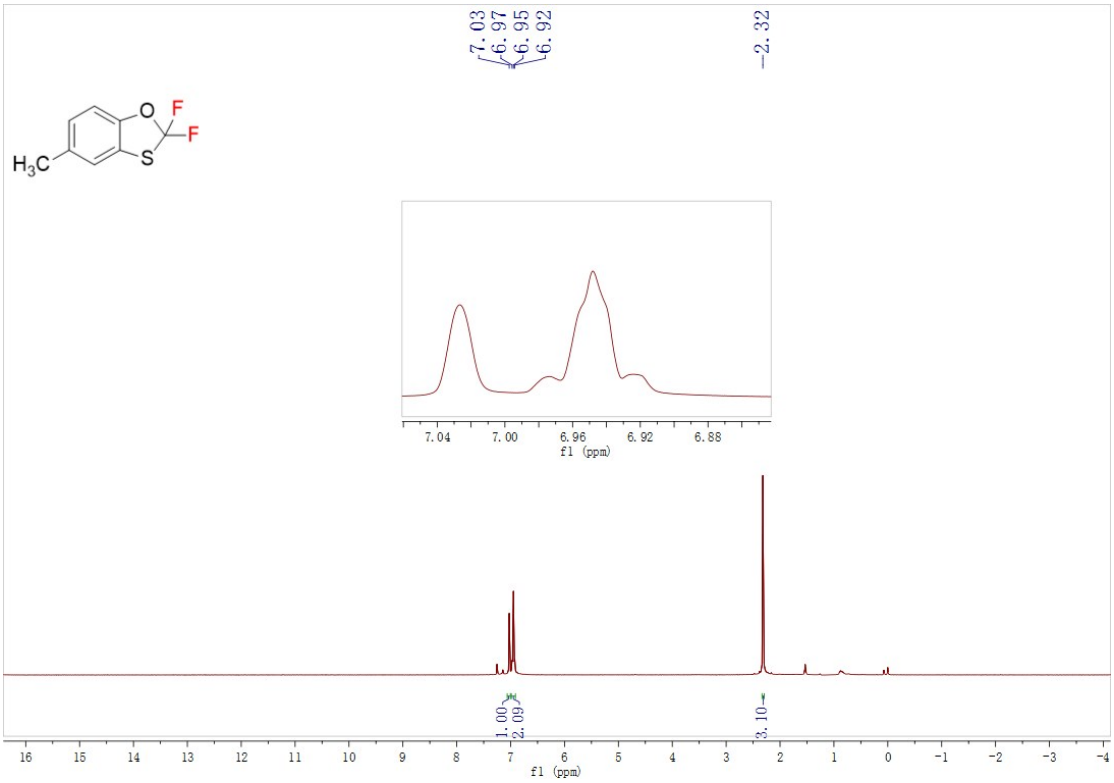
^{13}C NMR spectrum of **2a** in $CDCl_3$



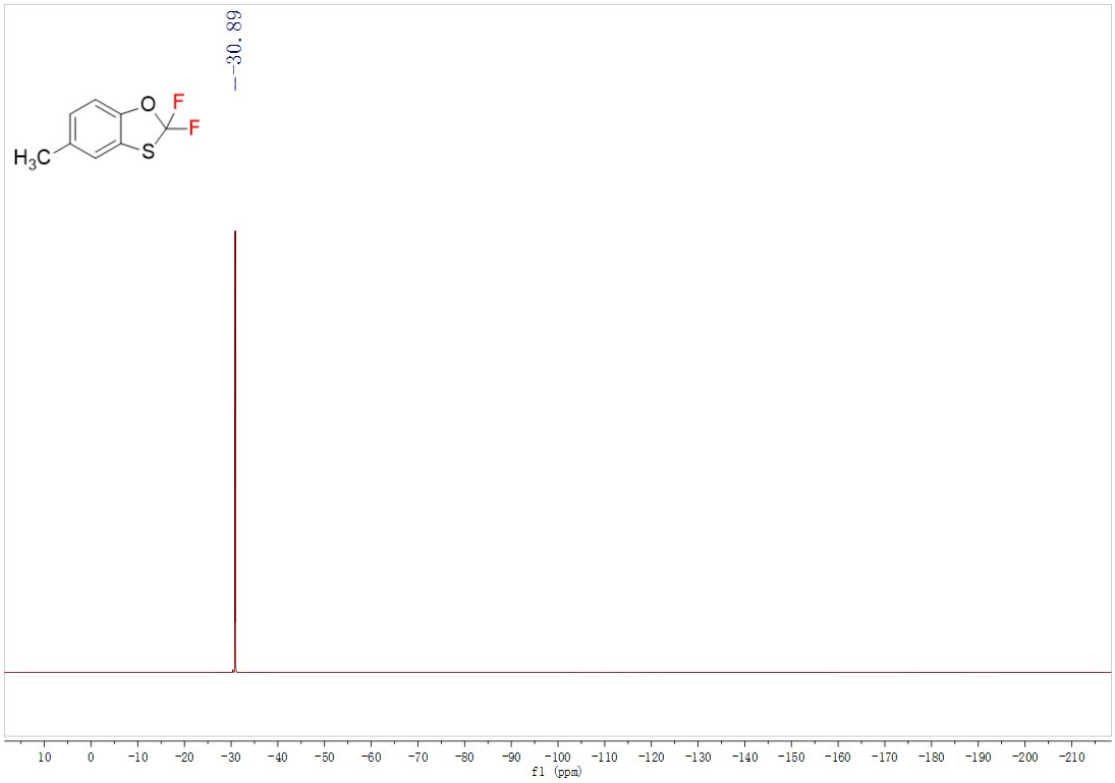
^{19}F NMR spectrum of **2a** in $CDCl_3$



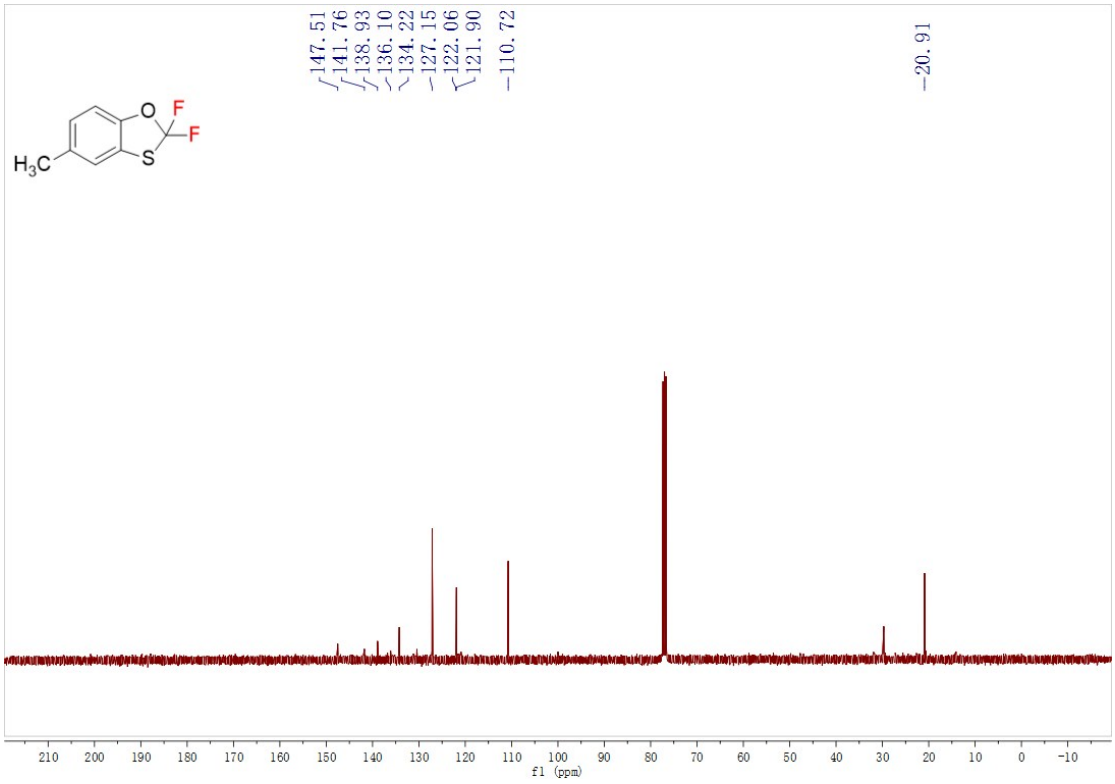
^{1}H NMR spectrum of **2b** in $CDCl_3$



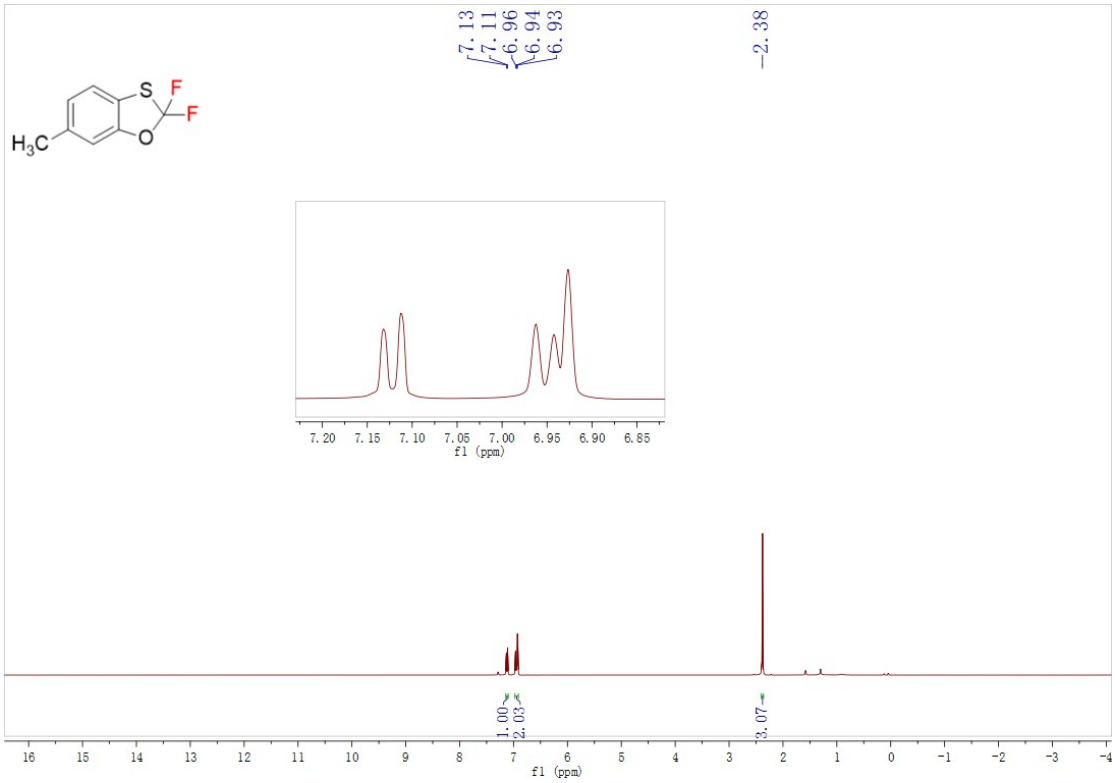
^{19}F NMR spectrum of **2b** in $CDCl_3$



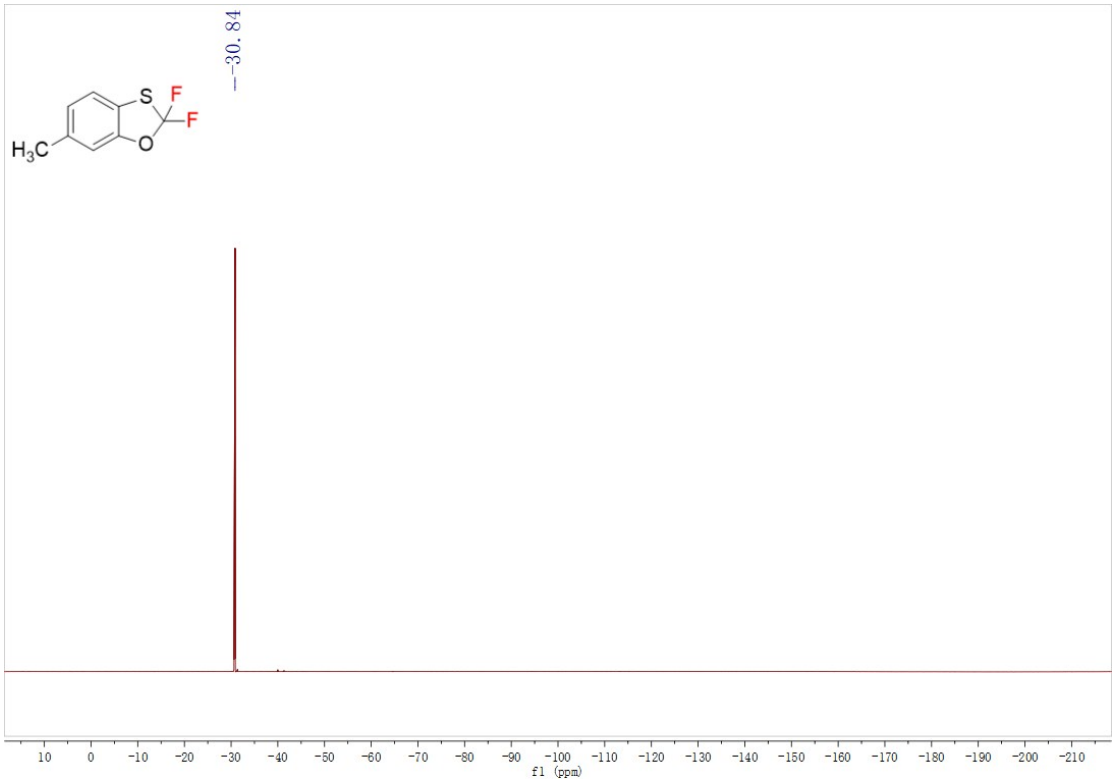
^{13}C NMR spectrum of **2b** in $CDCl_3$



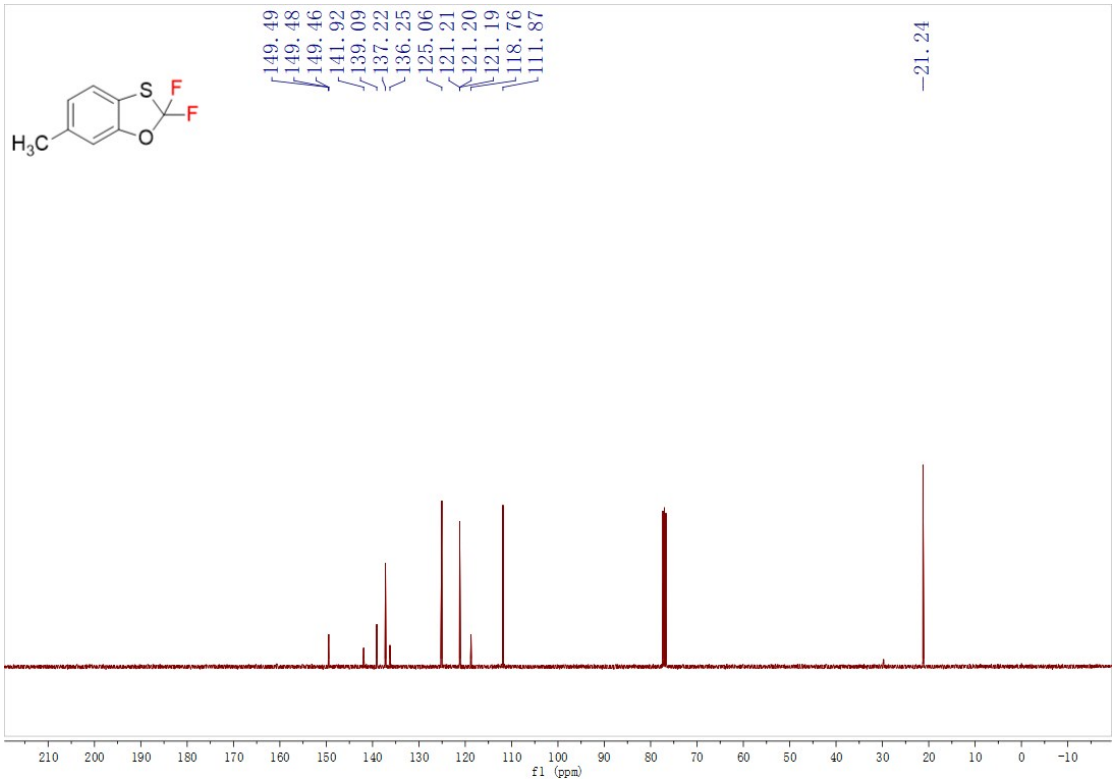
^{1}H NMR spectrum of **2c** in $CDCl_3$



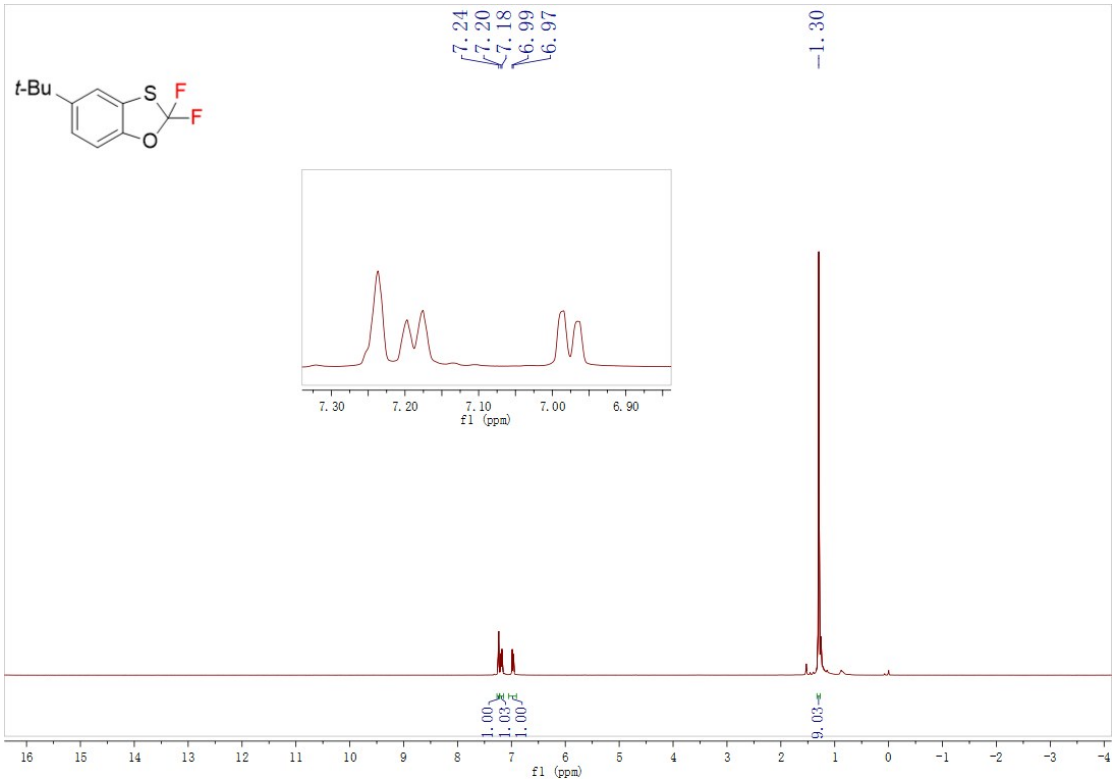
^{19}F NMR spectrum of **2c** in $CDCl_3$



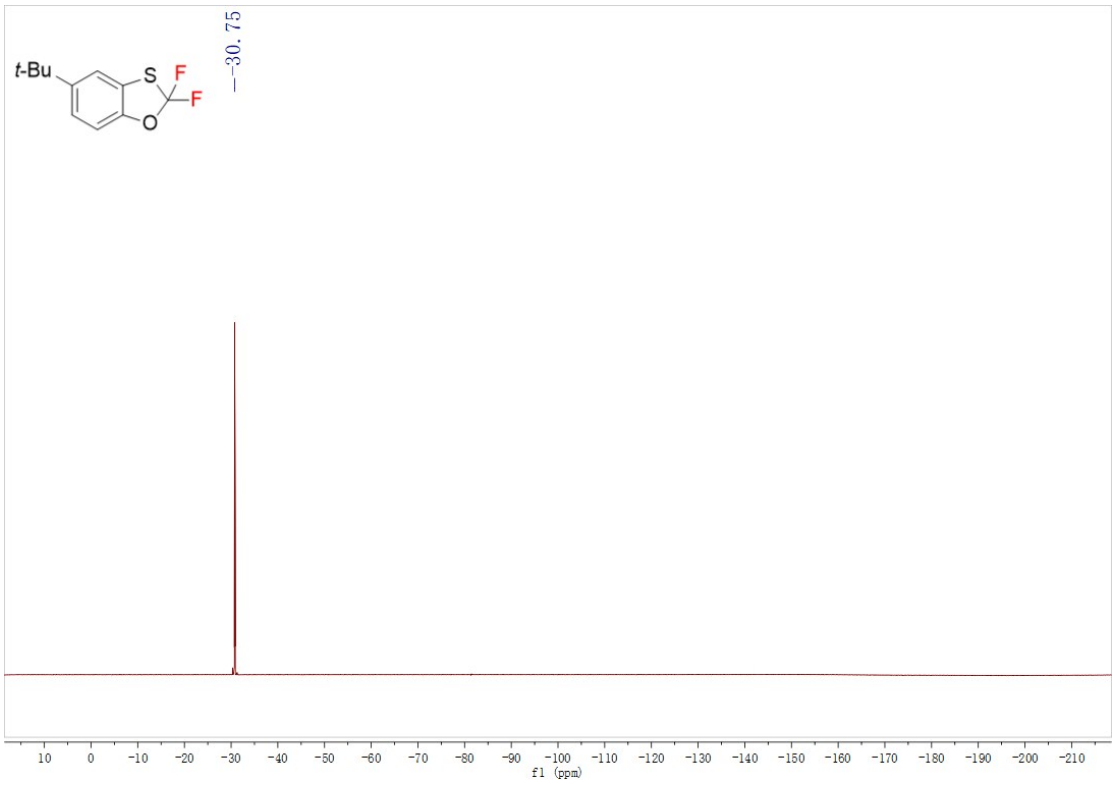
^{13}C NMR spectrum of **2c** in $CDCl_3$



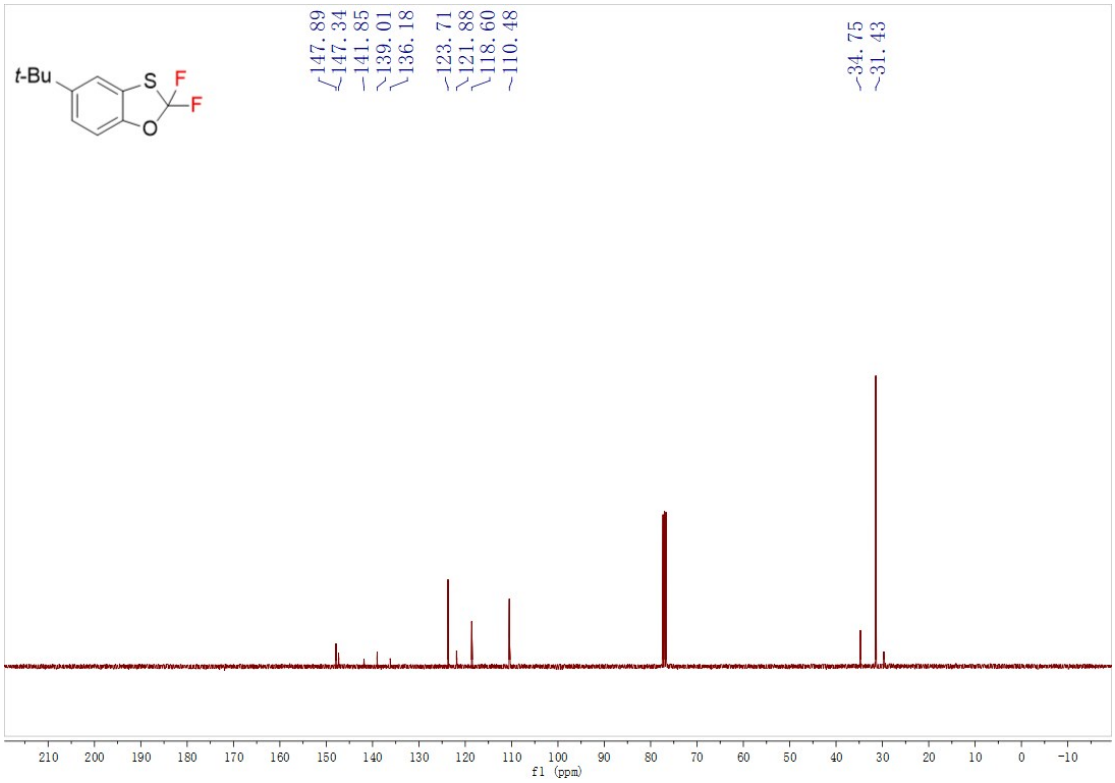
^{1}H NMR spectrum of **2d** in $CDCl_3$



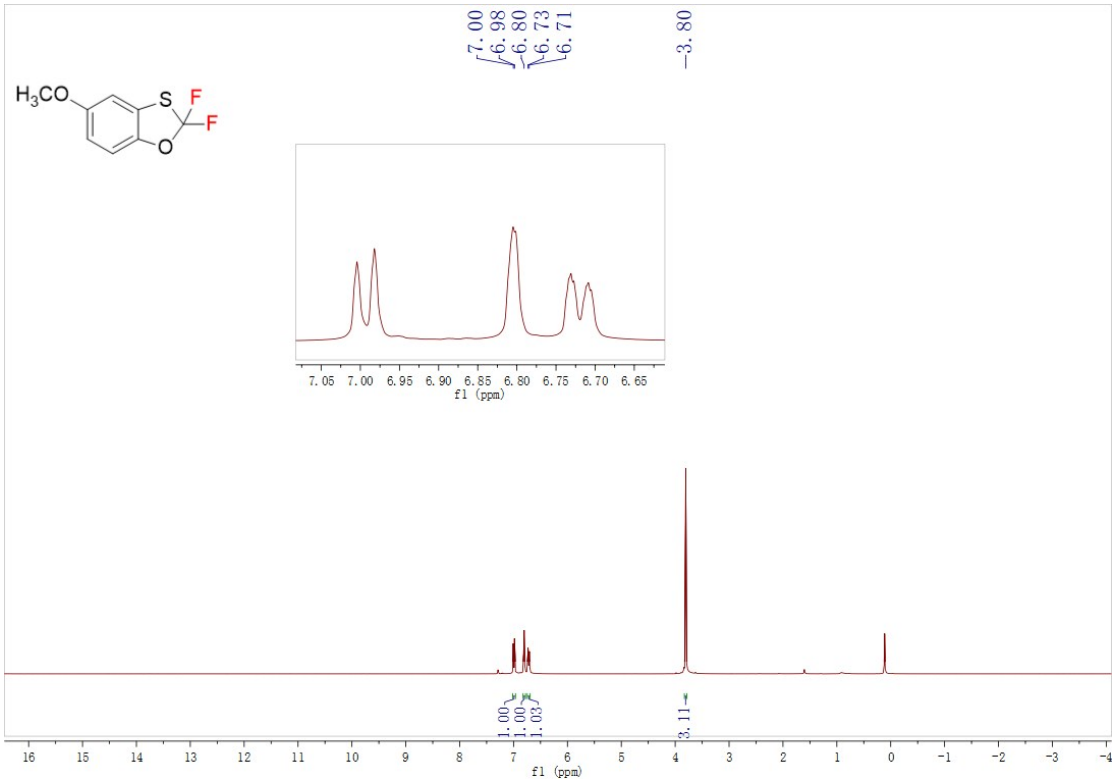
^{19}F NMR spectrum of **2d** in $CDCl_3$



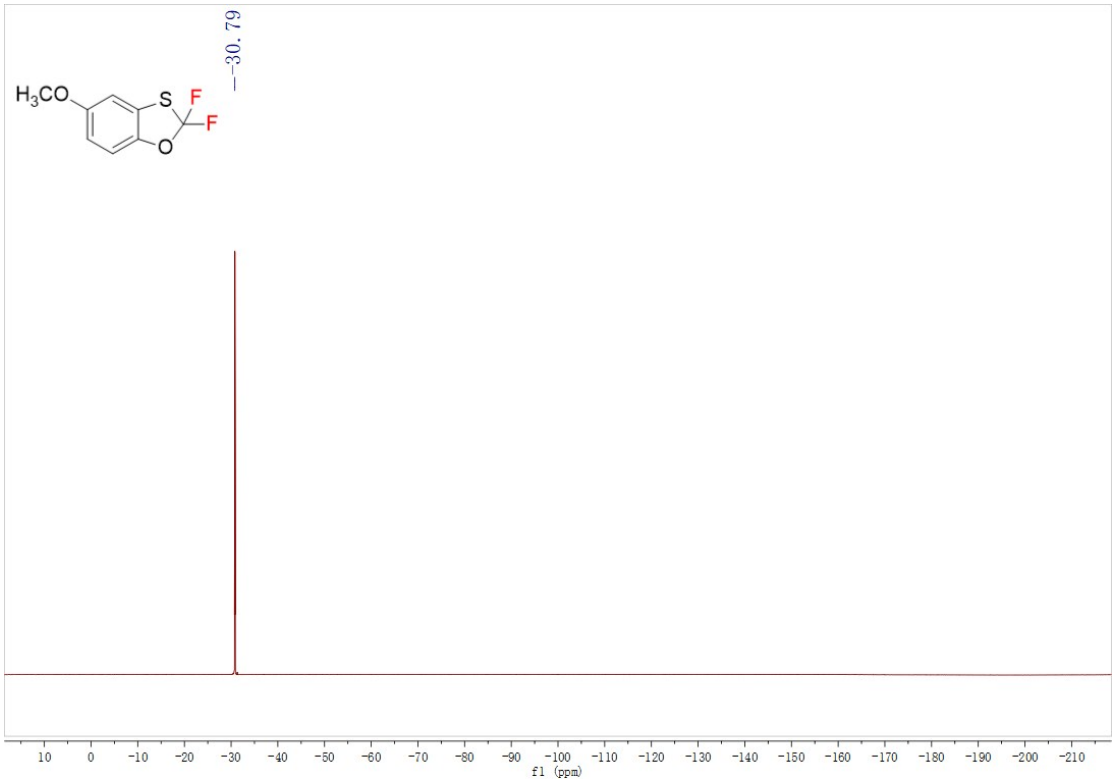
^{13}C NMR spectrum of **2d** in $CDCl_3$



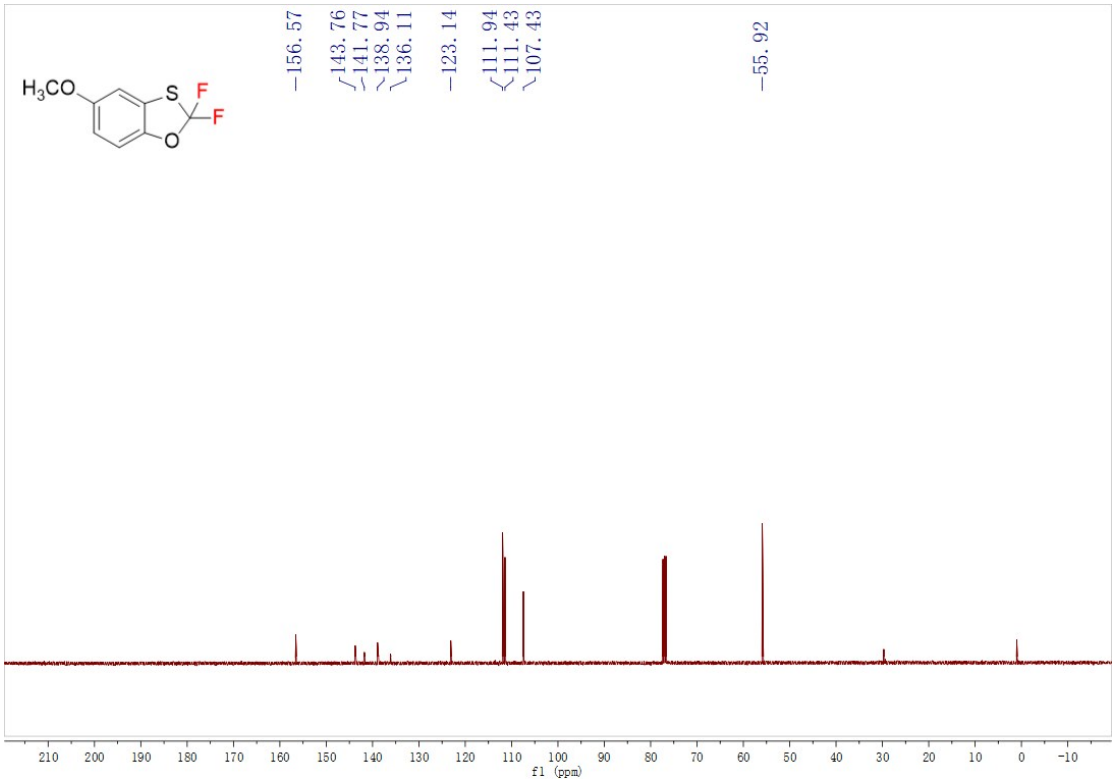
^{1}H NMR spectrum of **2e** in $CDCl_3$



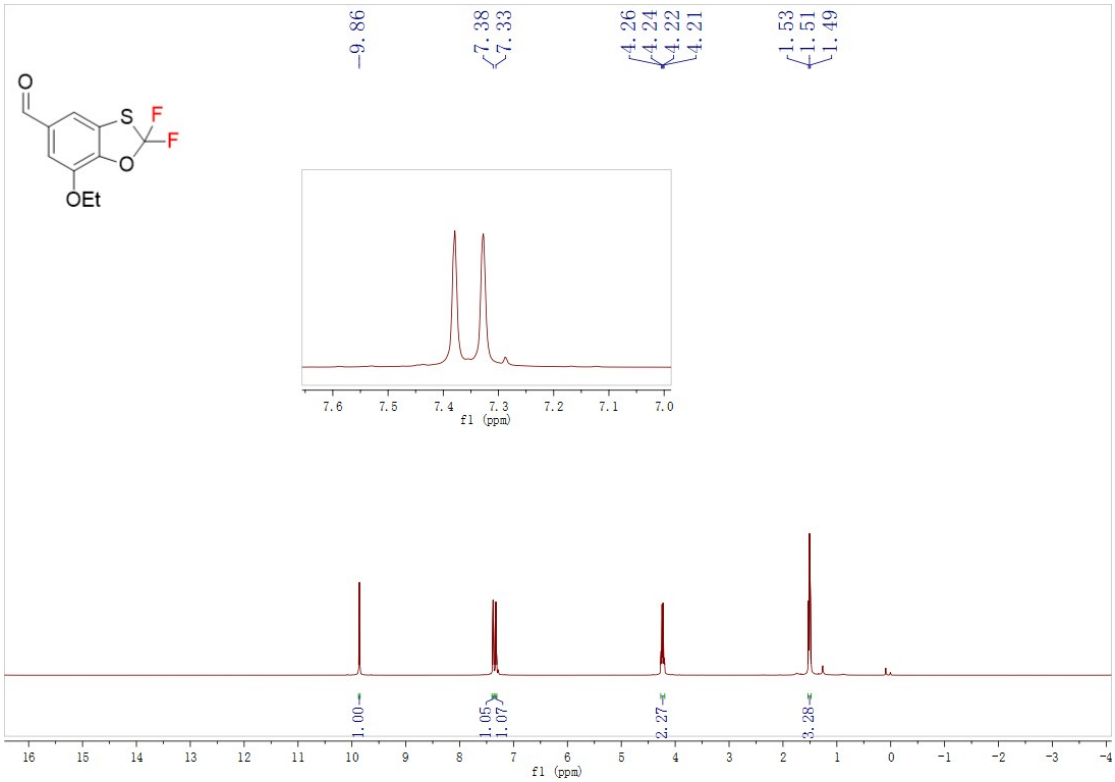
^{19}F NMR spectrum of **2e** in $CDCl_3$



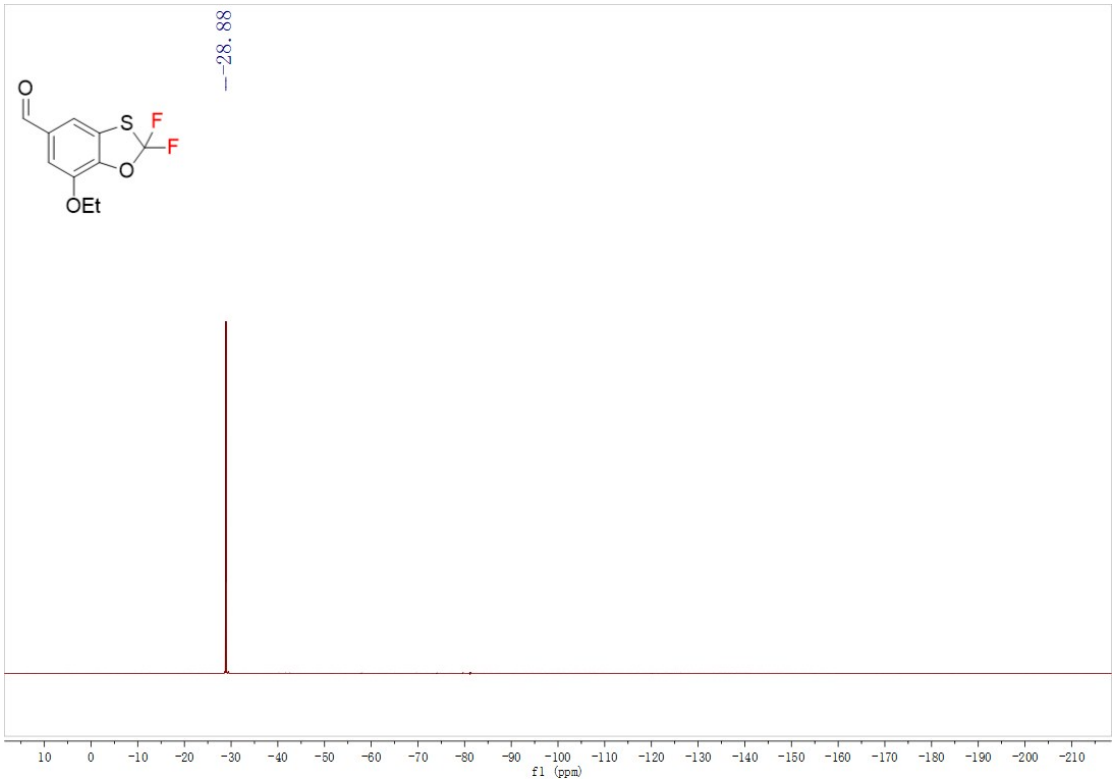
^{13}C NMR spectrum of **2e** in $CDCl_3$



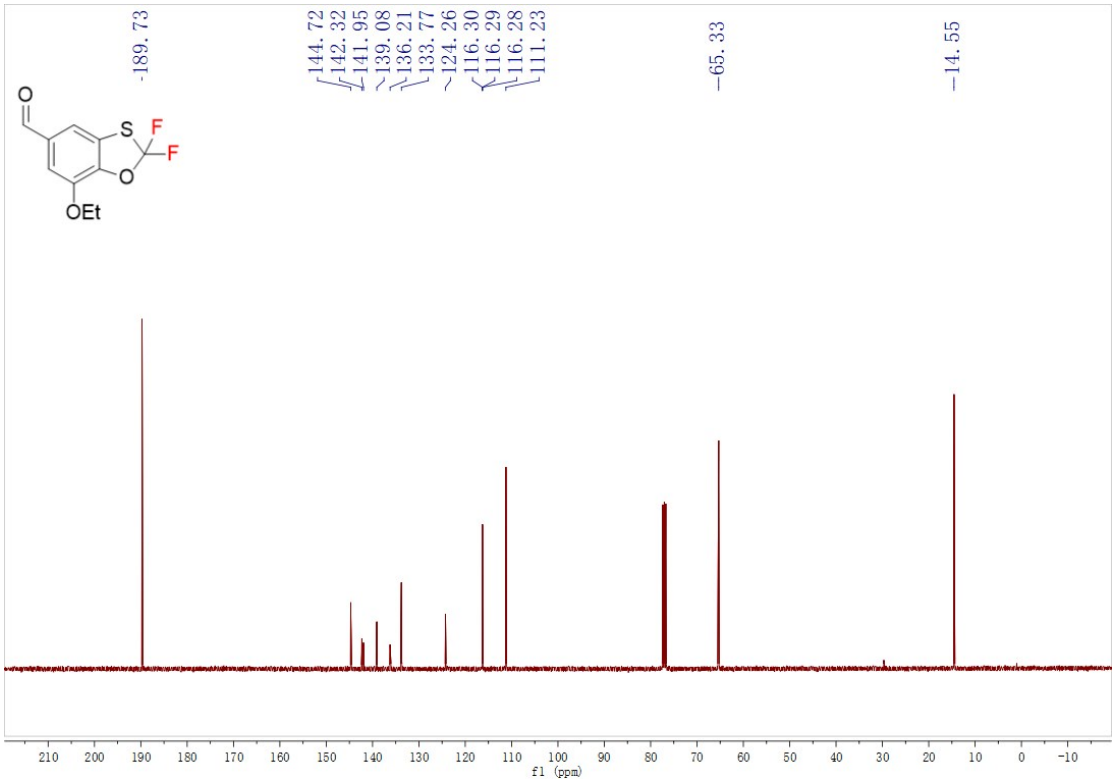
^{1}H NMR spectrum of **2f** in $CDCl_3$



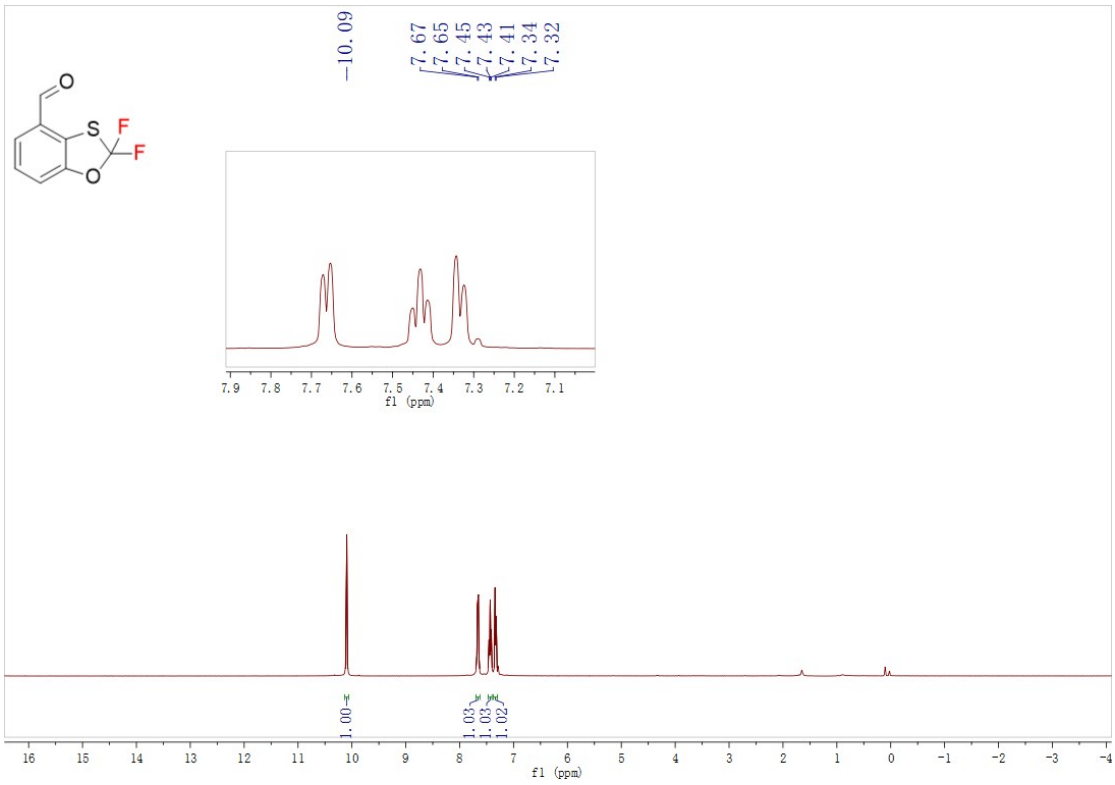
^{19}F NMR spectrum of **2f** in $CDCl_3$



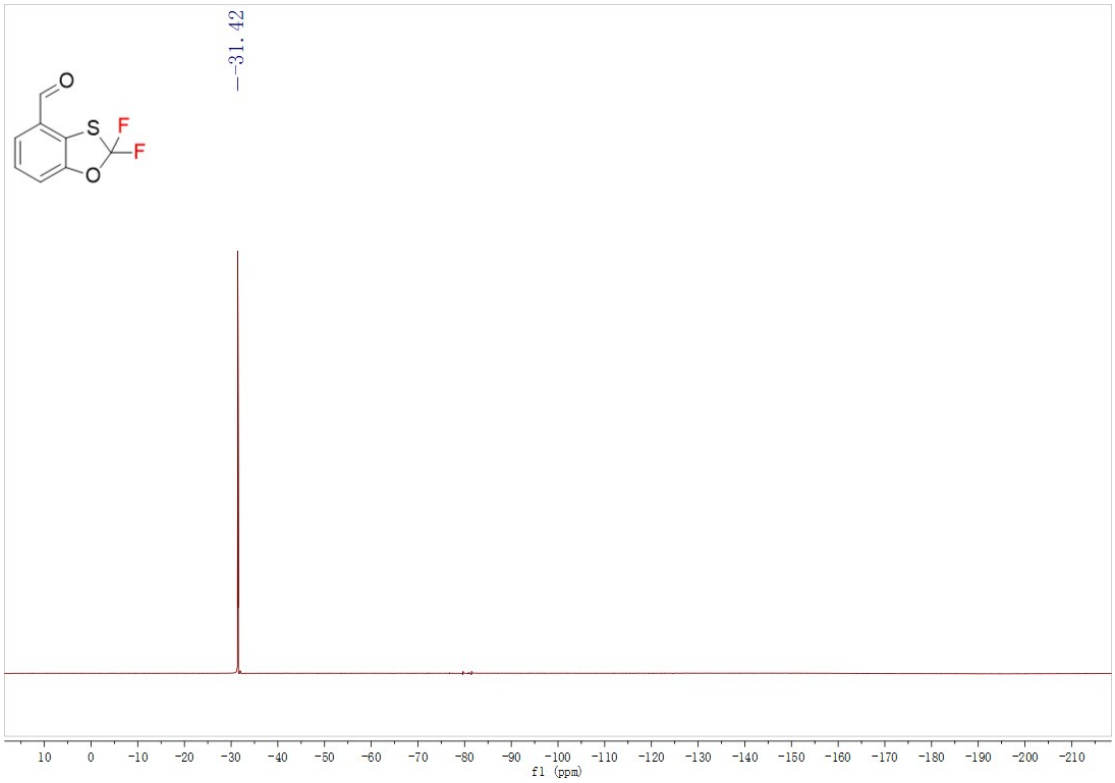
^{13}C NMR spectrum of **2f** in $CDCl_3$



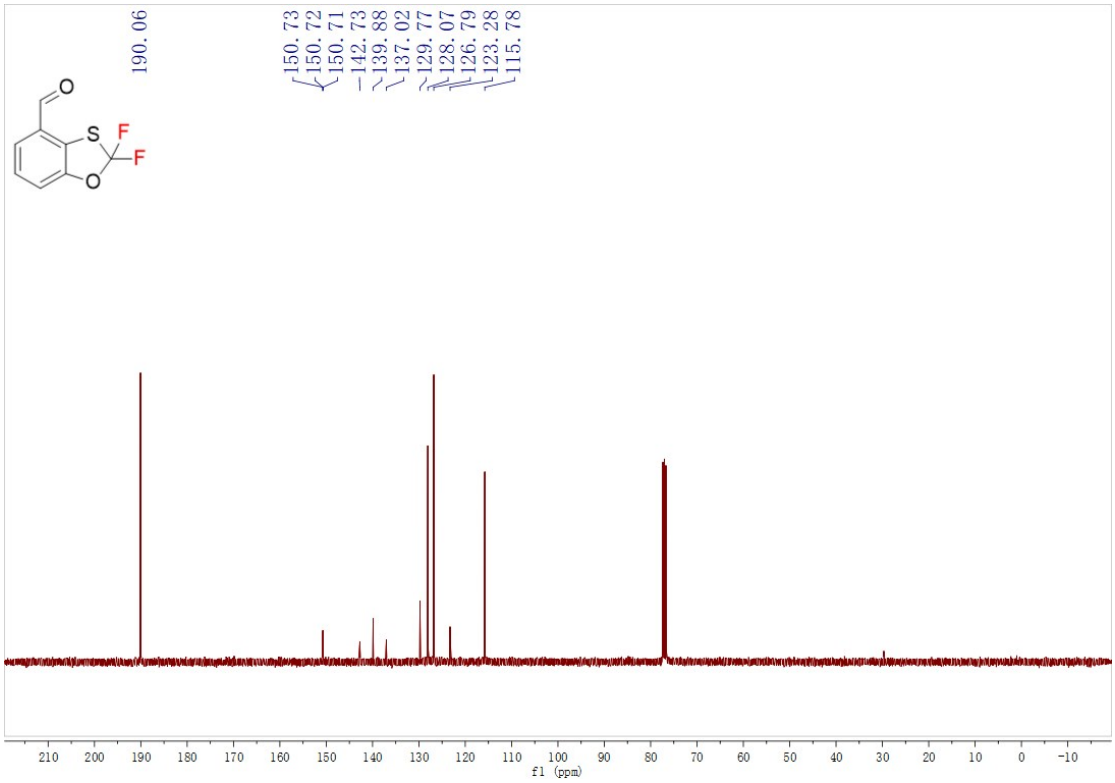
^{1}H NMR spectrum of **2g** in $CDCl_3$



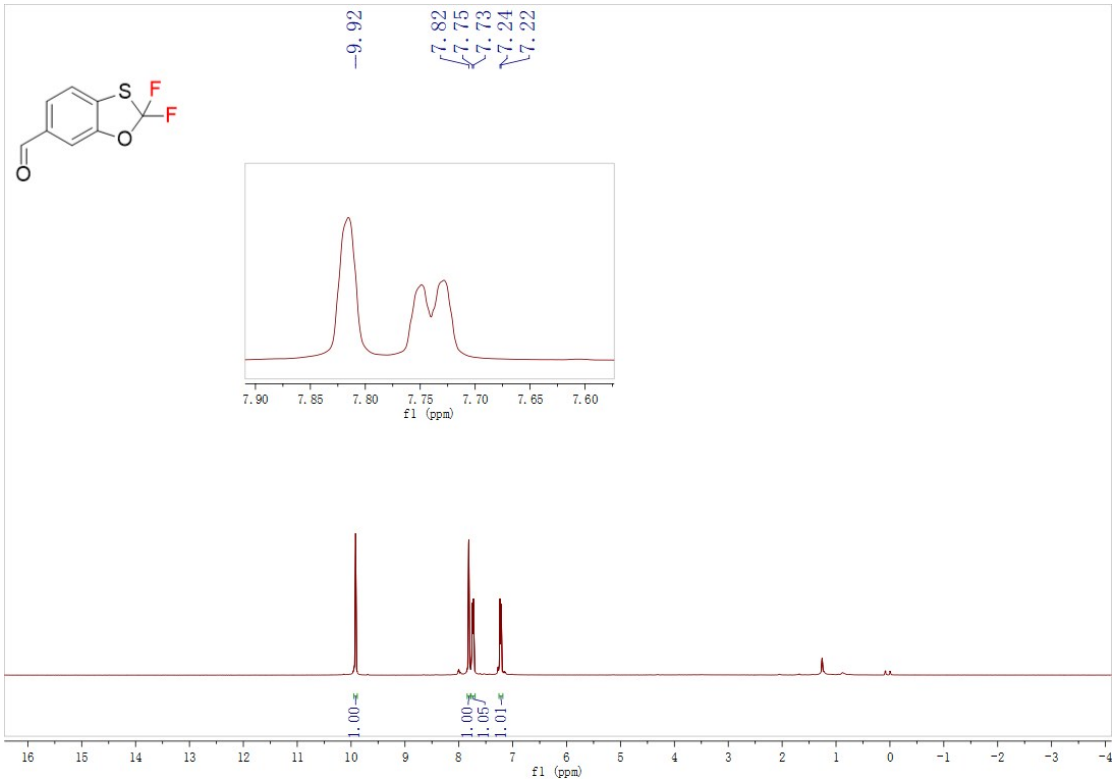
^{19}F NMR spectrum of **2g** in $CDCl_3$



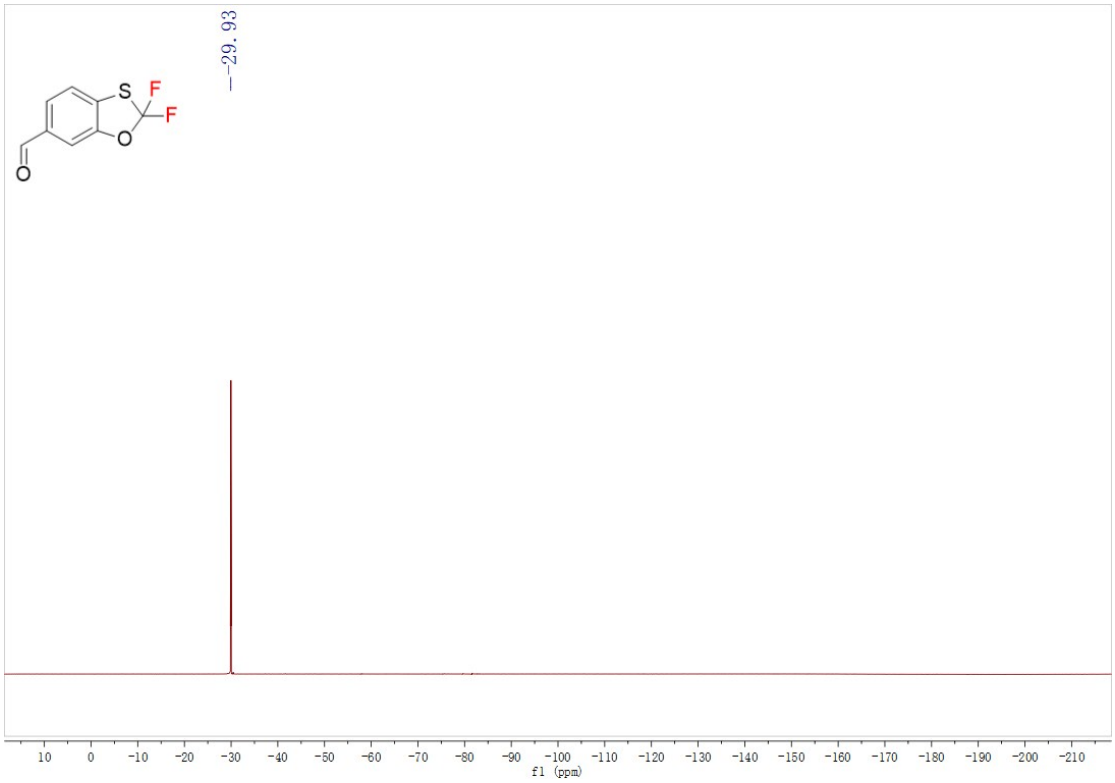
^{13}C NMR spectrum of **2g** in $CDCl_3$



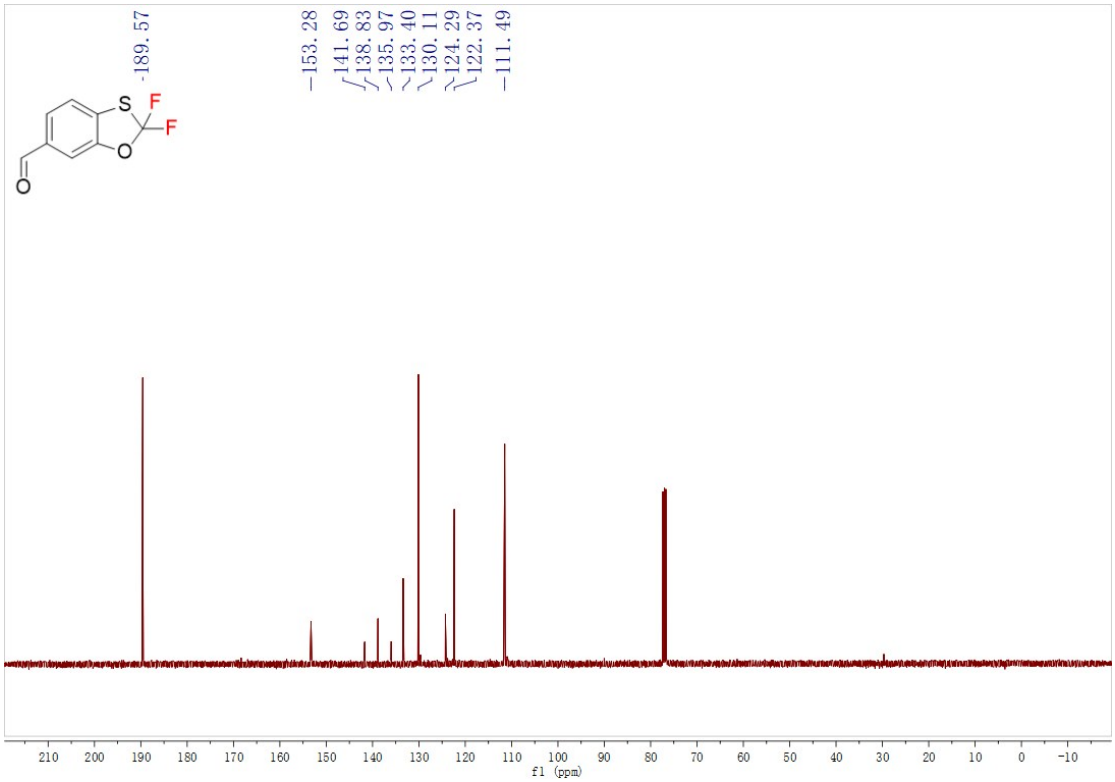
^{1}H NMR spectrum of **2h** in $CDCl_3$



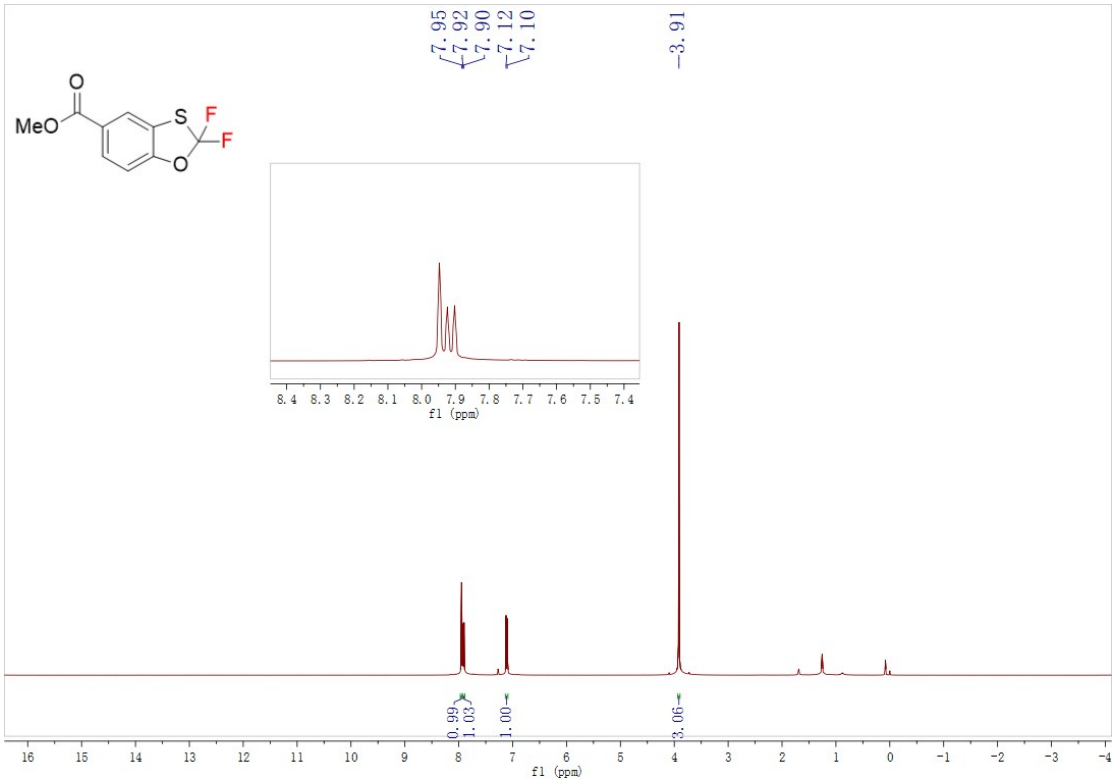
^{19}F NMR spectrum of **2h** in $CDCl_3$



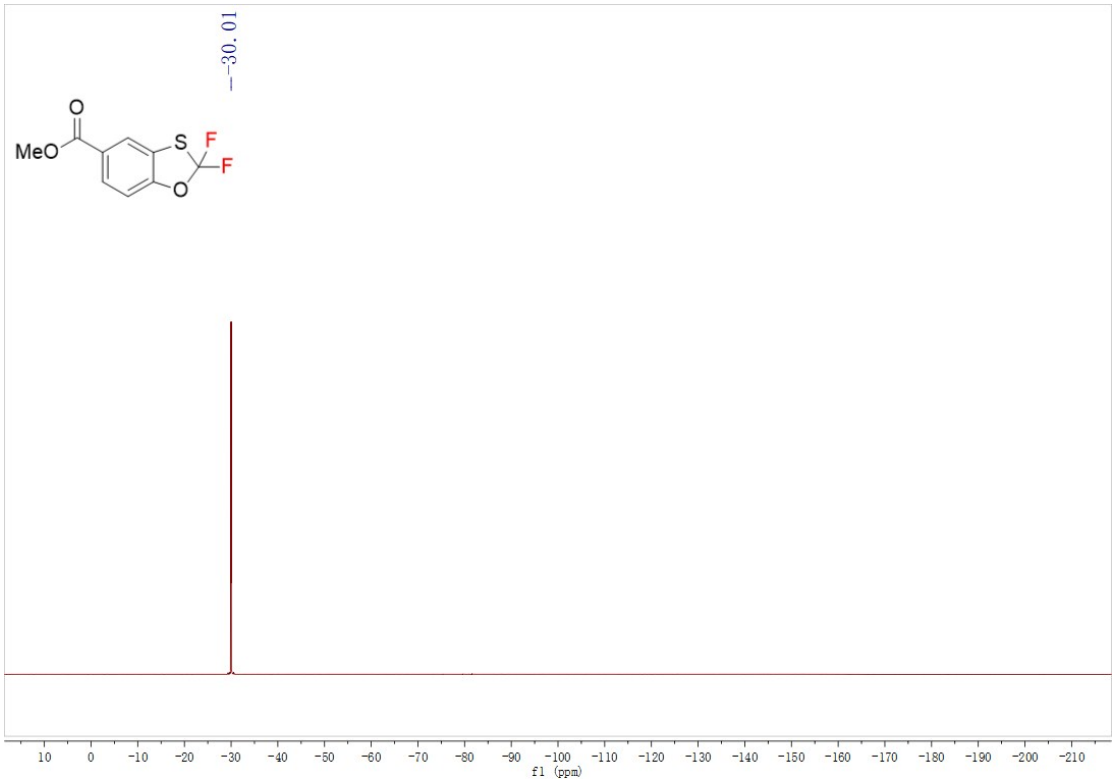
^{13}C NMR spectrum of **2h** in $CDCl_3$



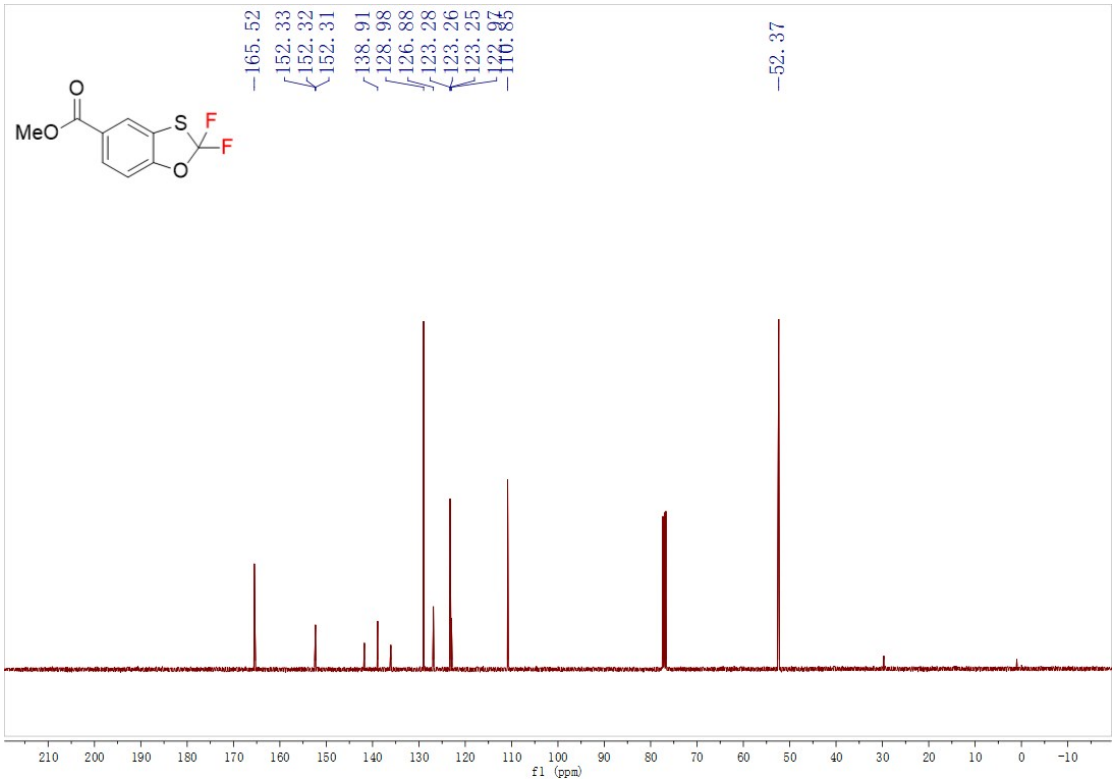
^{1}H NMR spectrum of **2i** in $CDCl_3$



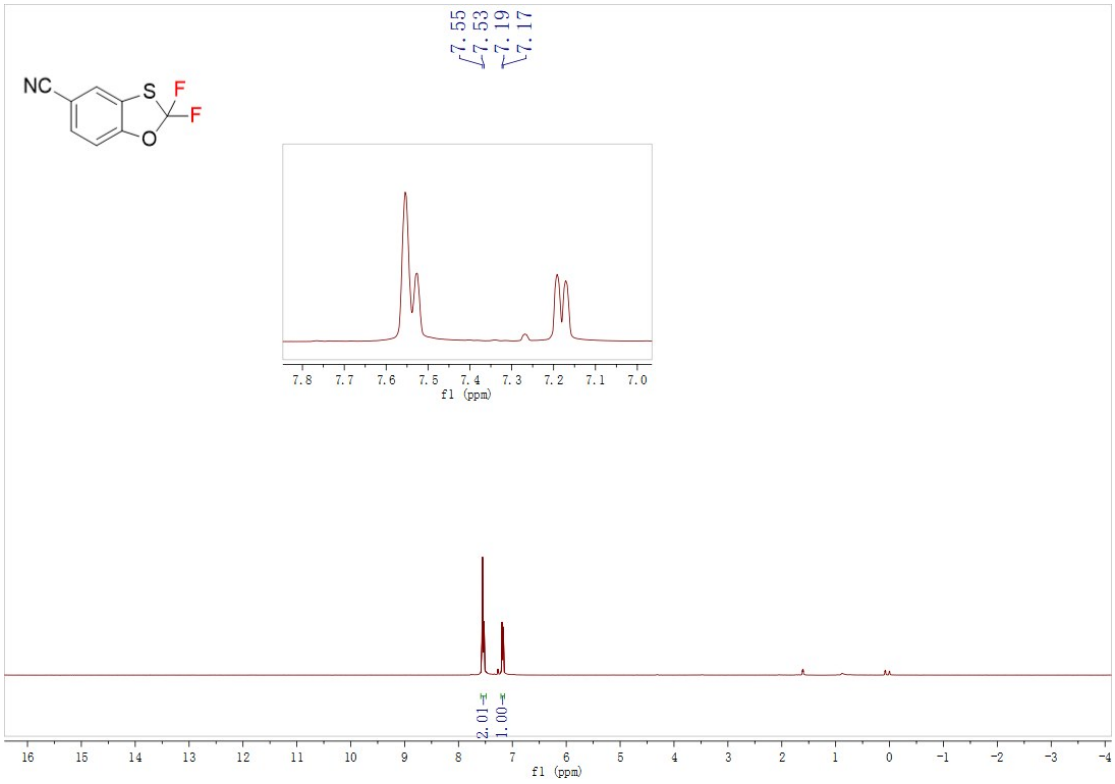
^{19}F NMR spectrum of **2i** in $CDCl_3$



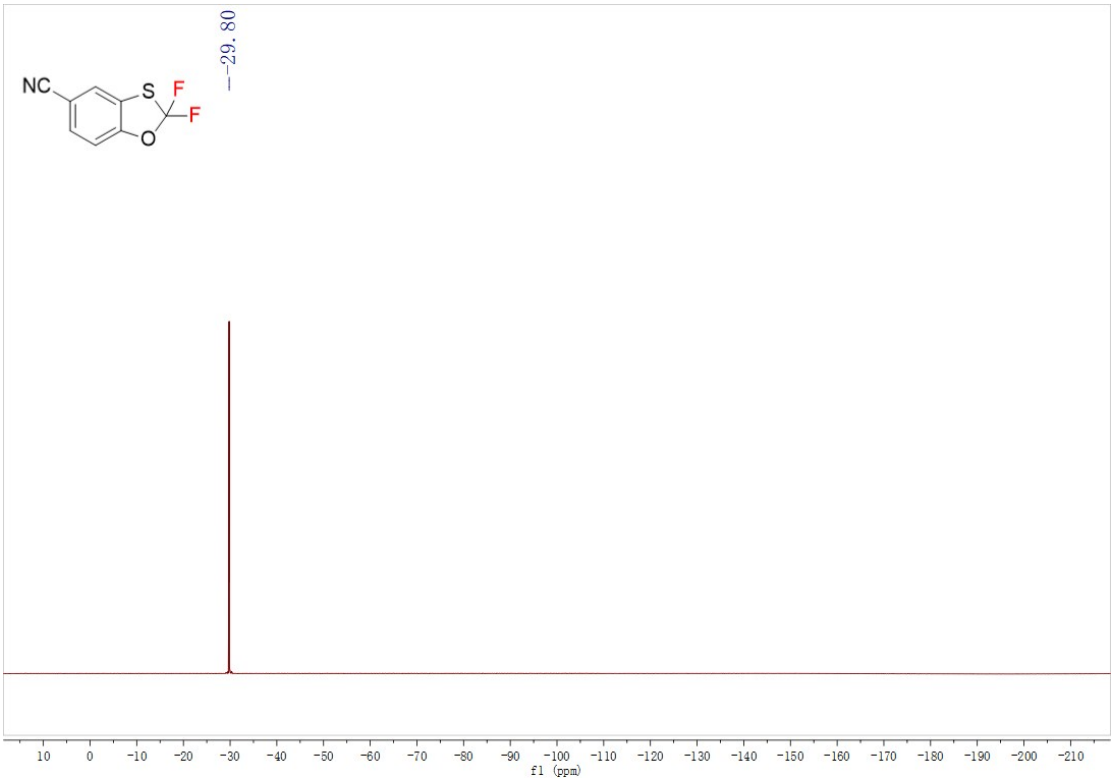
^{13}C NMR spectrum of **2i** in $CDCl_3$



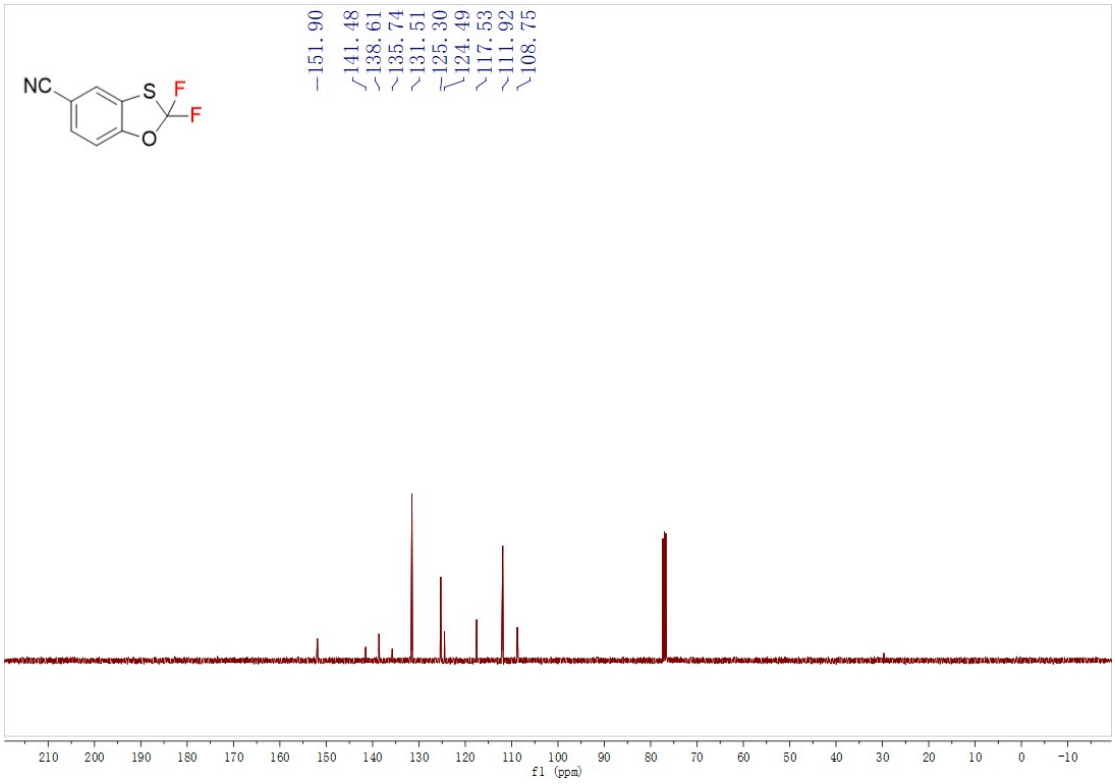
^{1}H NMR spectrum of **2j** in $CDCl_3$



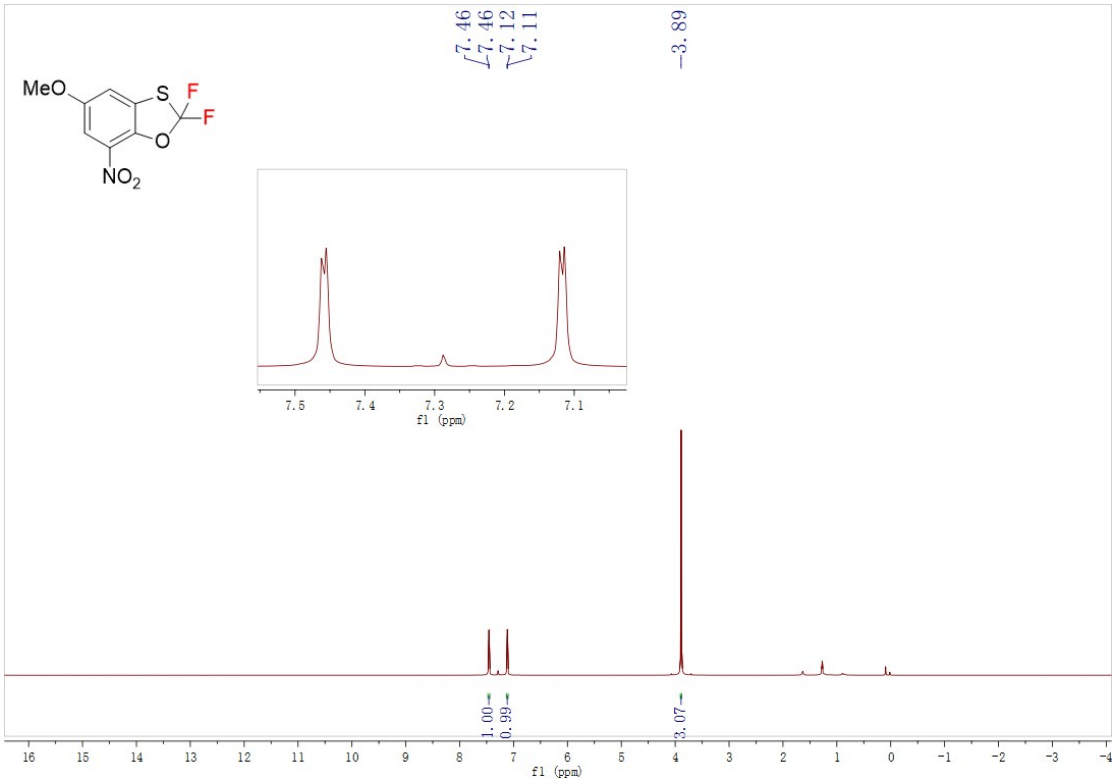
^{19}F NMR spectrum of **2j** in $CDCl_3$



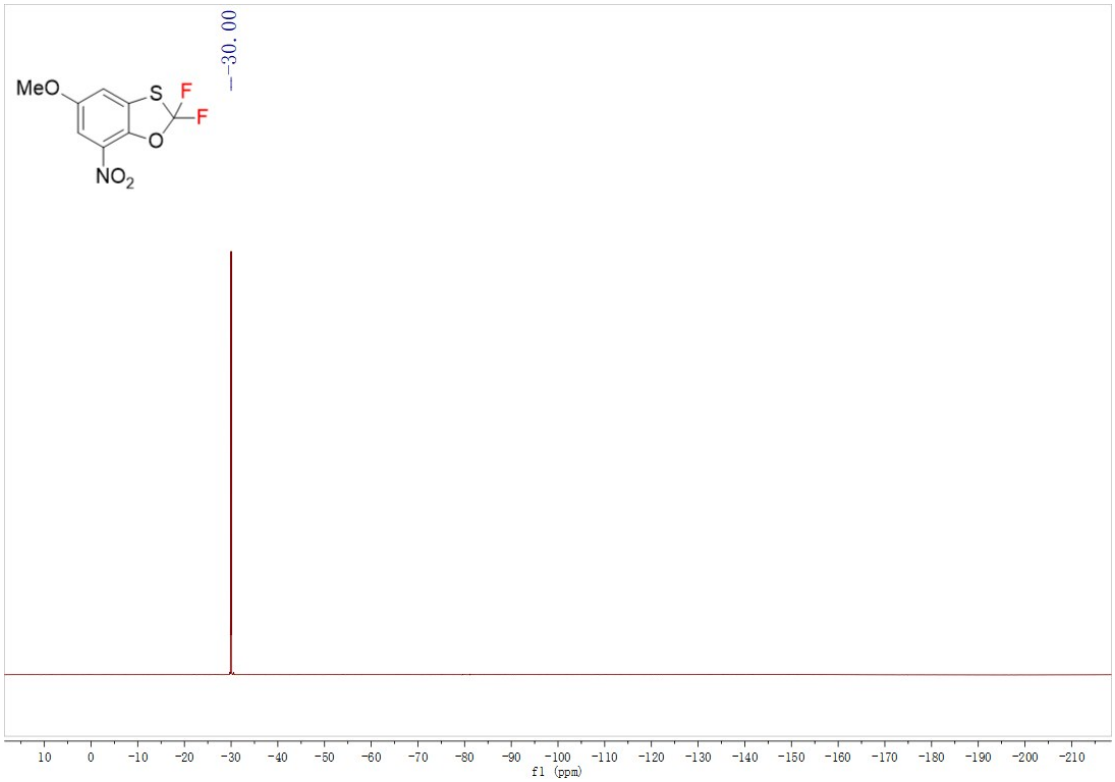
^{13}C NMR spectrum of **2j** in $CDCl_3$



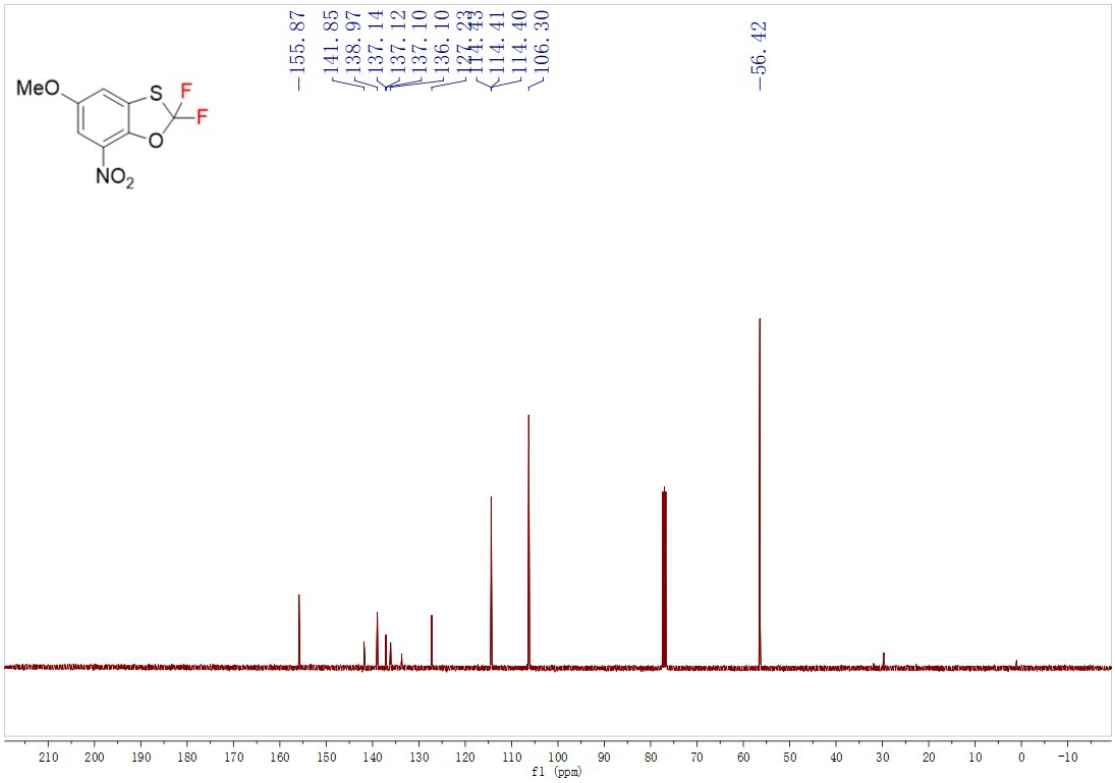
^{1}H NMR spectrum of **2k** in $CDCl_3$



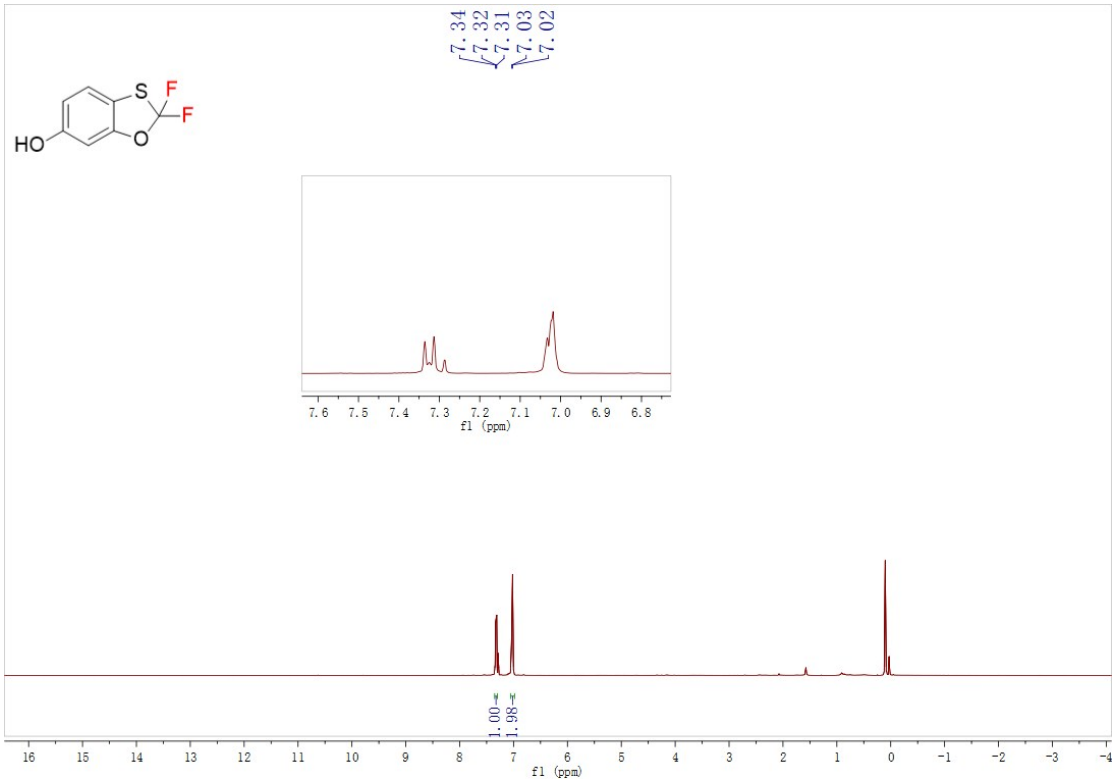
^{19}F NMR spectrum of **2k** in $CDCl_3$



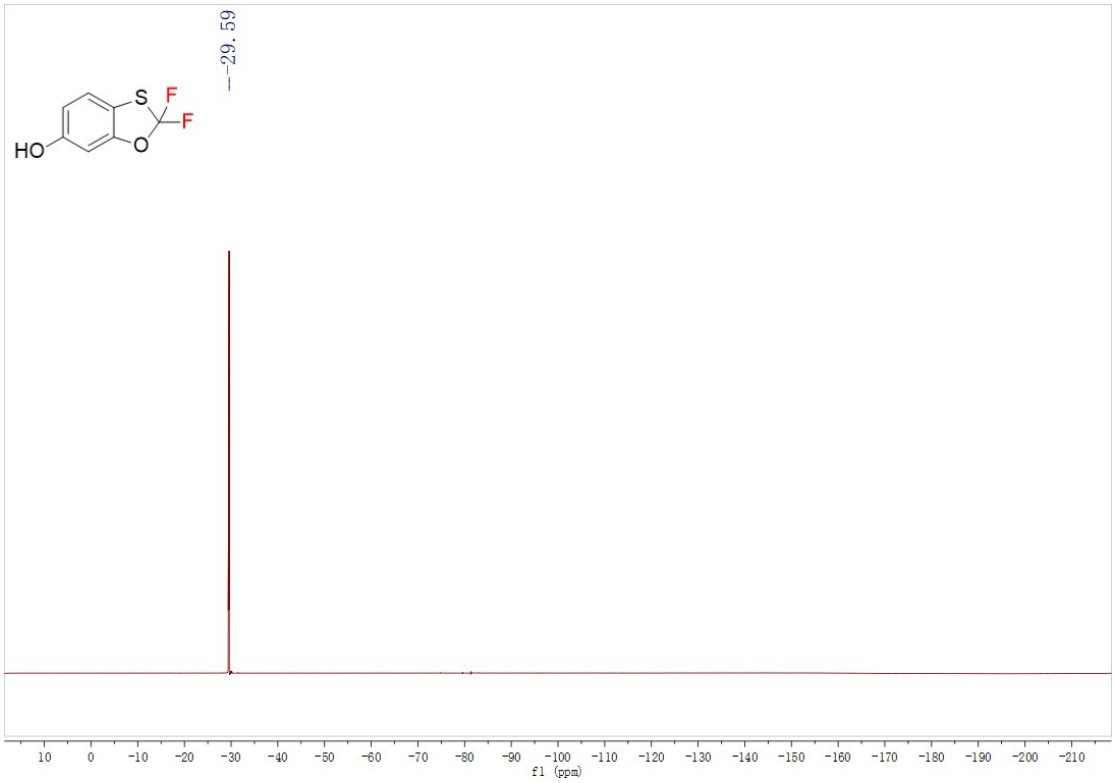
^{13}C NMR spectrum of **2k** in $CDCl_3$



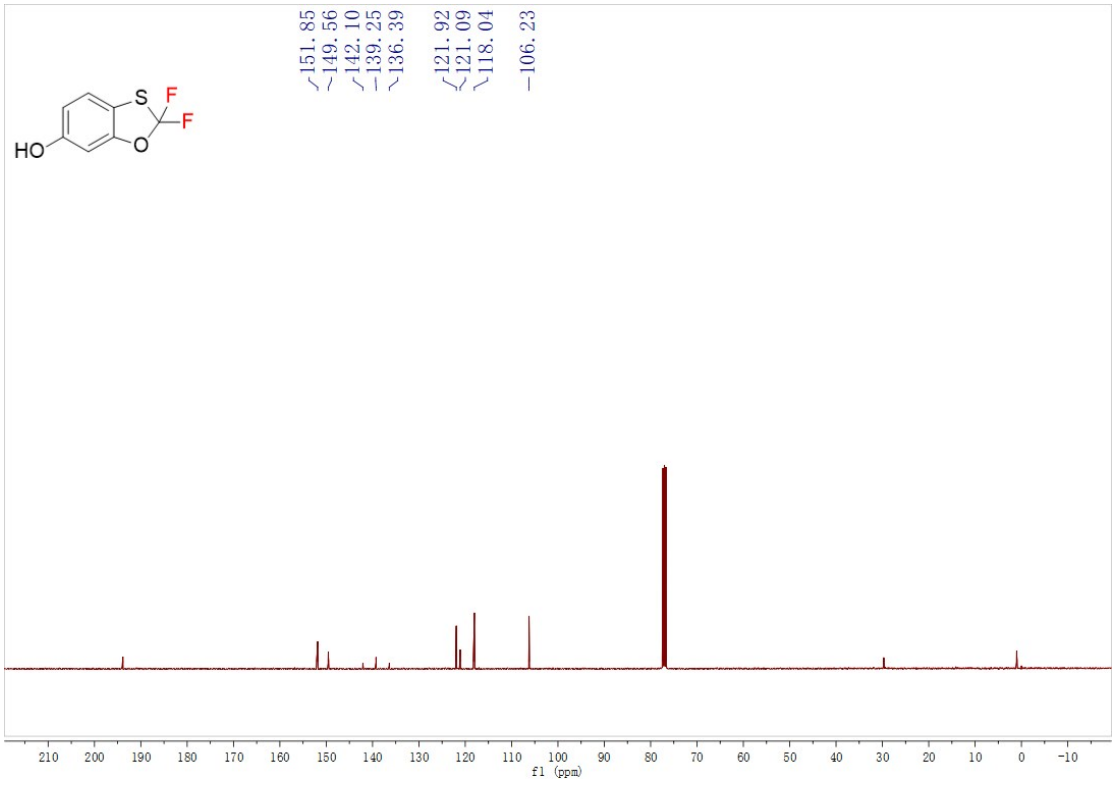
^{1}H NMR spectrum of **2l** in $CDCl_3$



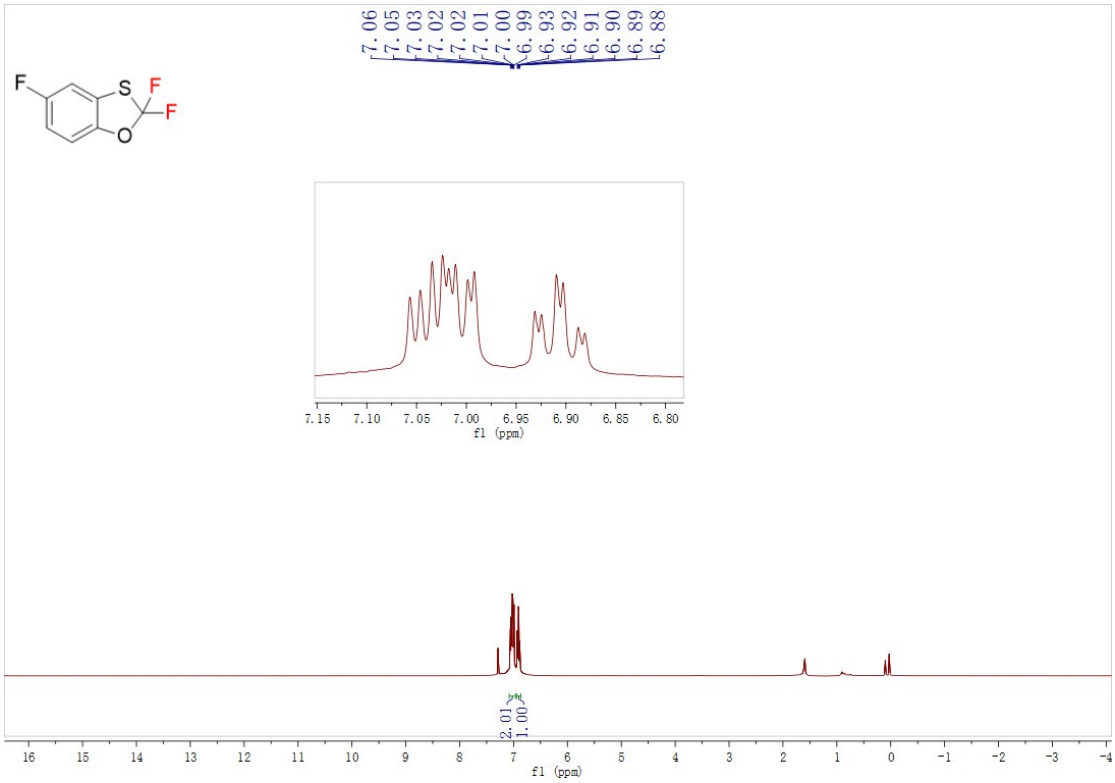
^{19}F NMR spectrum of **2l** in $CDCl_3$



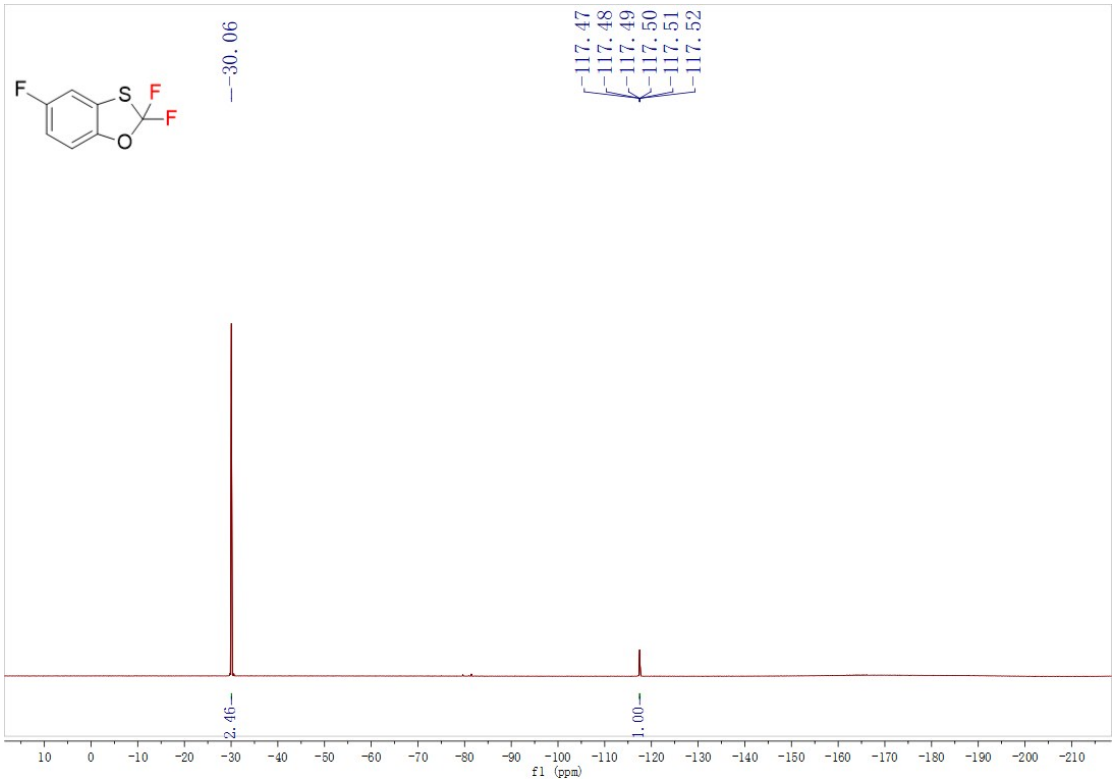
^{13}C NMR spectrum of **2l** in $CDCl_3$



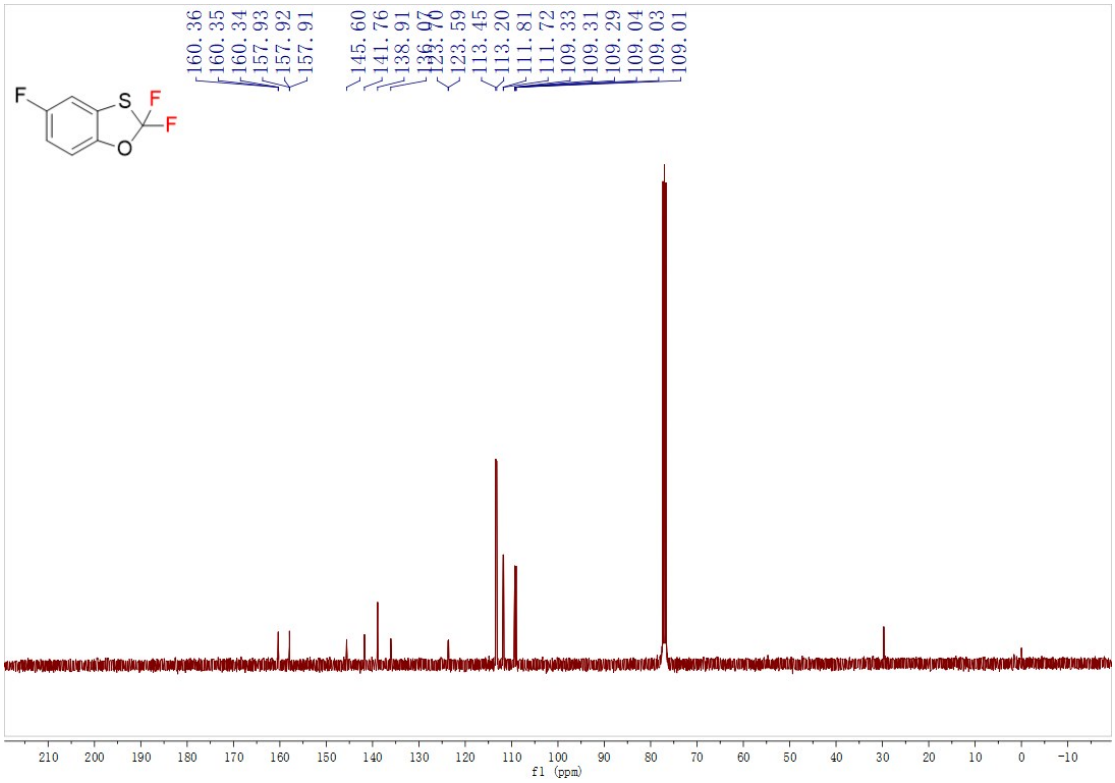
^{1}H NMR spectrum of **2m** in $CDCl_3$



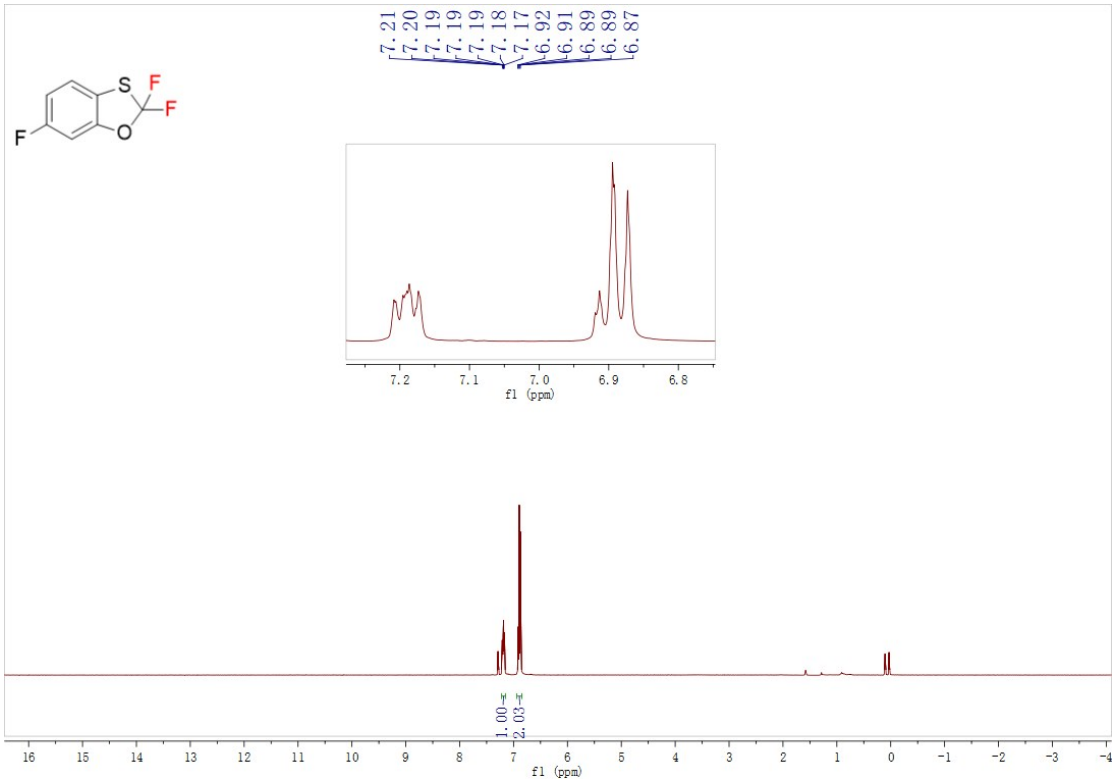
^{19}F NMR spectrum of **2m** in $CDCl_3$



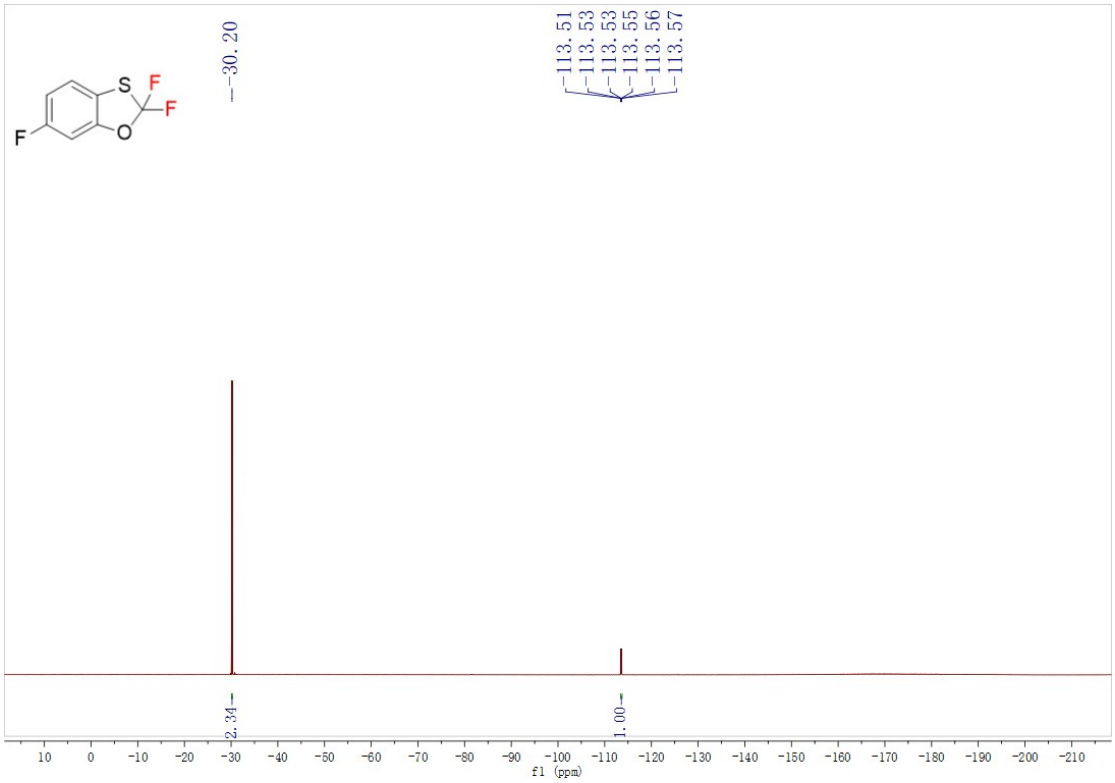
^{13}C NMR spectrum of **2m** in $CDCl_3$



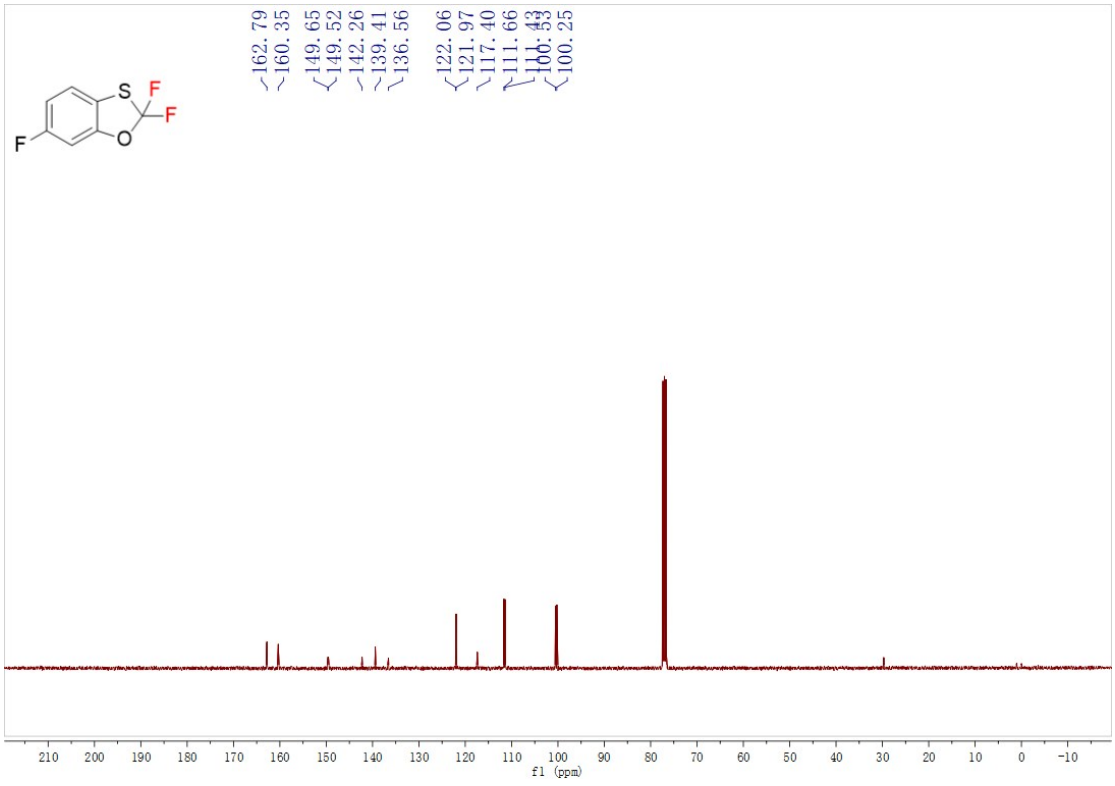
^{1}H NMR spectrum of **2n** in $CDCl_3$



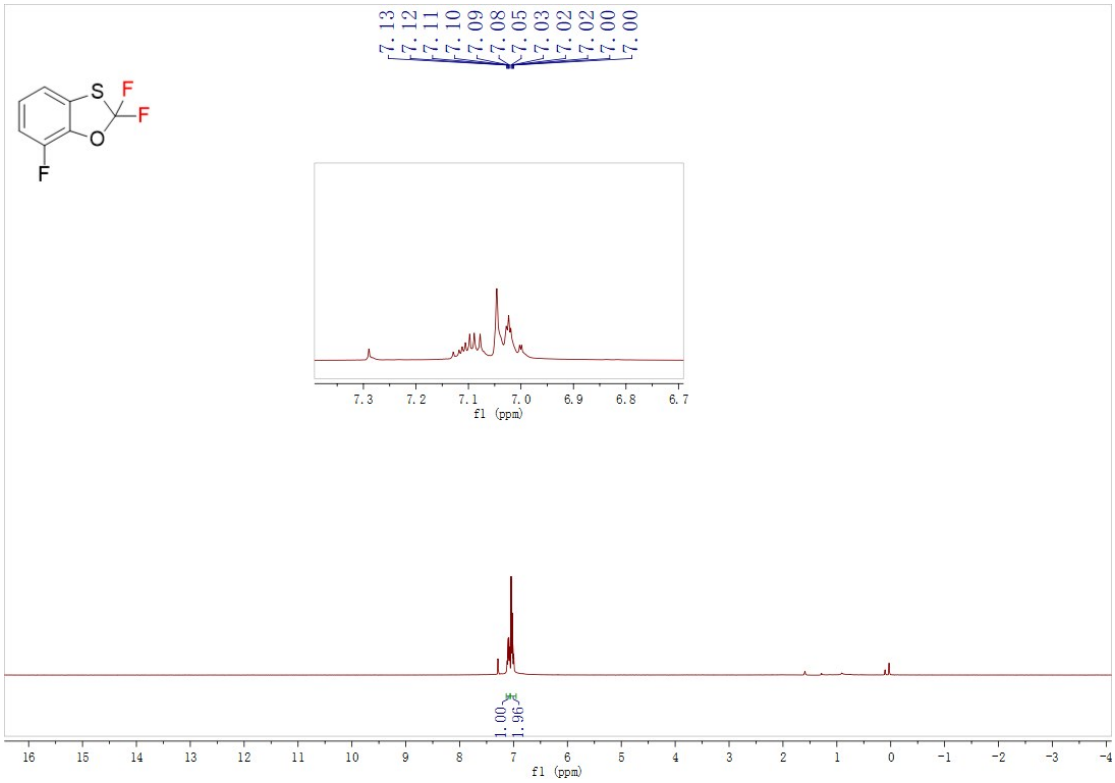
^{19}F NMR spectrum of **2n** in $CDCl_3$



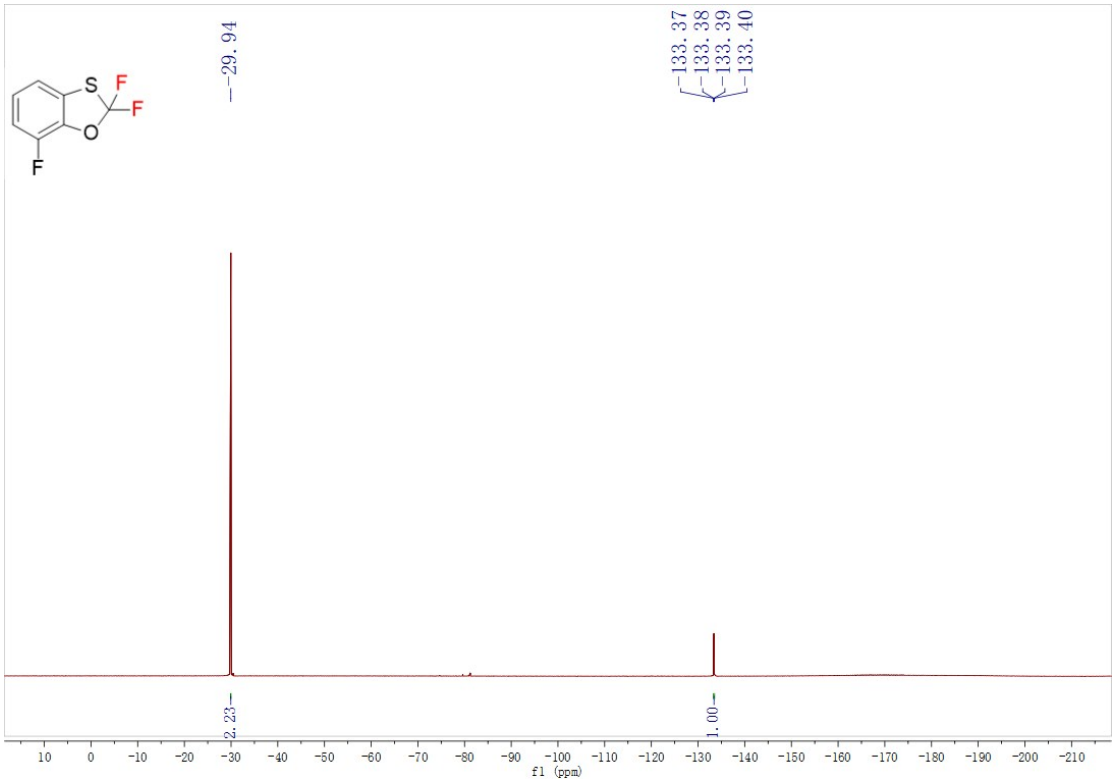
^{13}C NMR spectrum of **2n** in $CDCl_3$



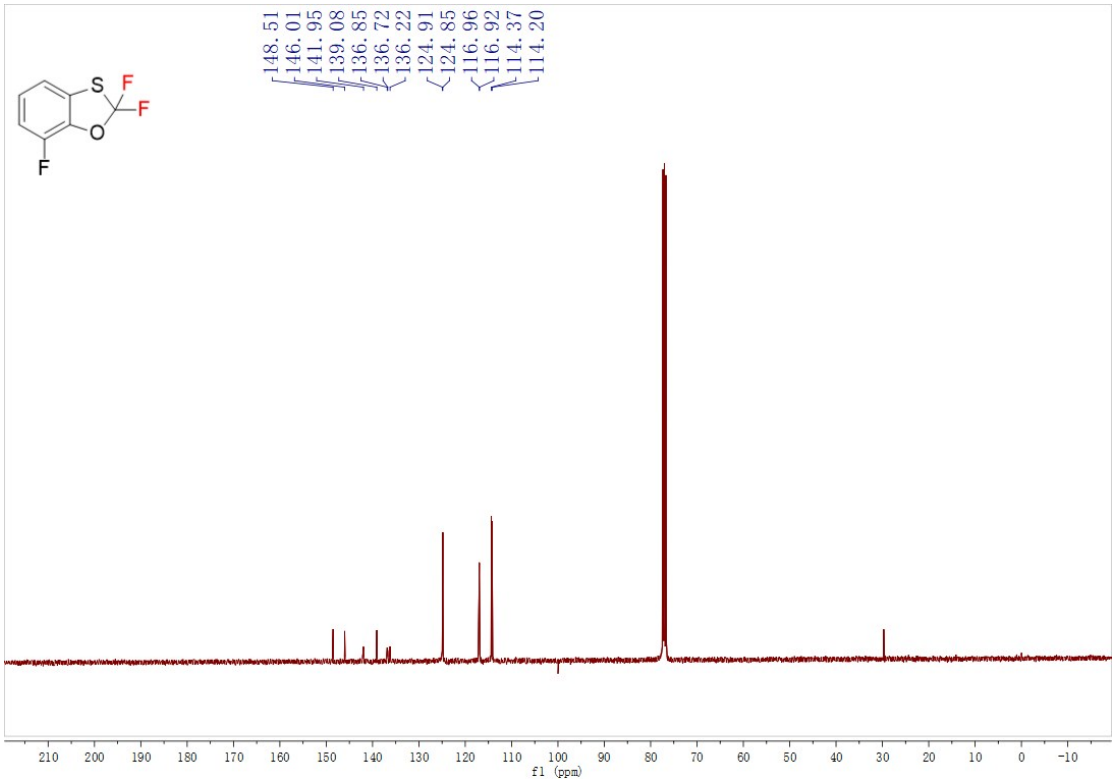
^{1}H NMR spectrum of **2o** in $CDCl_3$



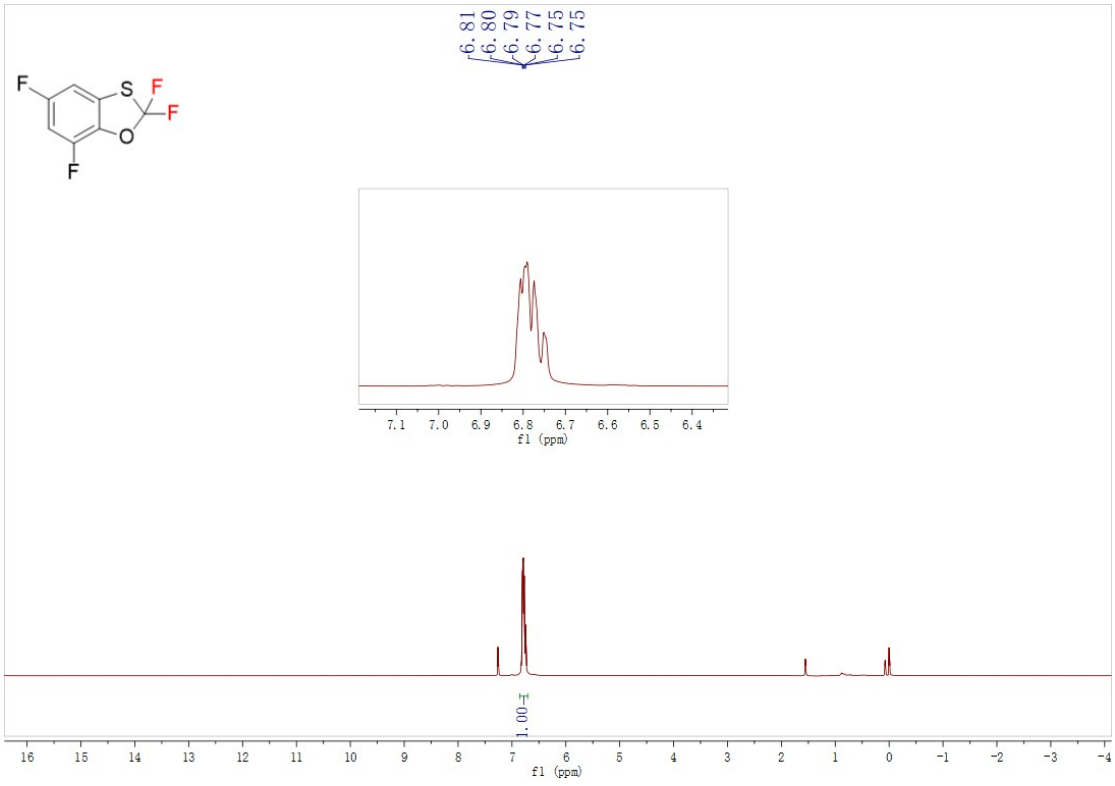
^{19}F NMR spectrum of **2o** in $CDCl_3$



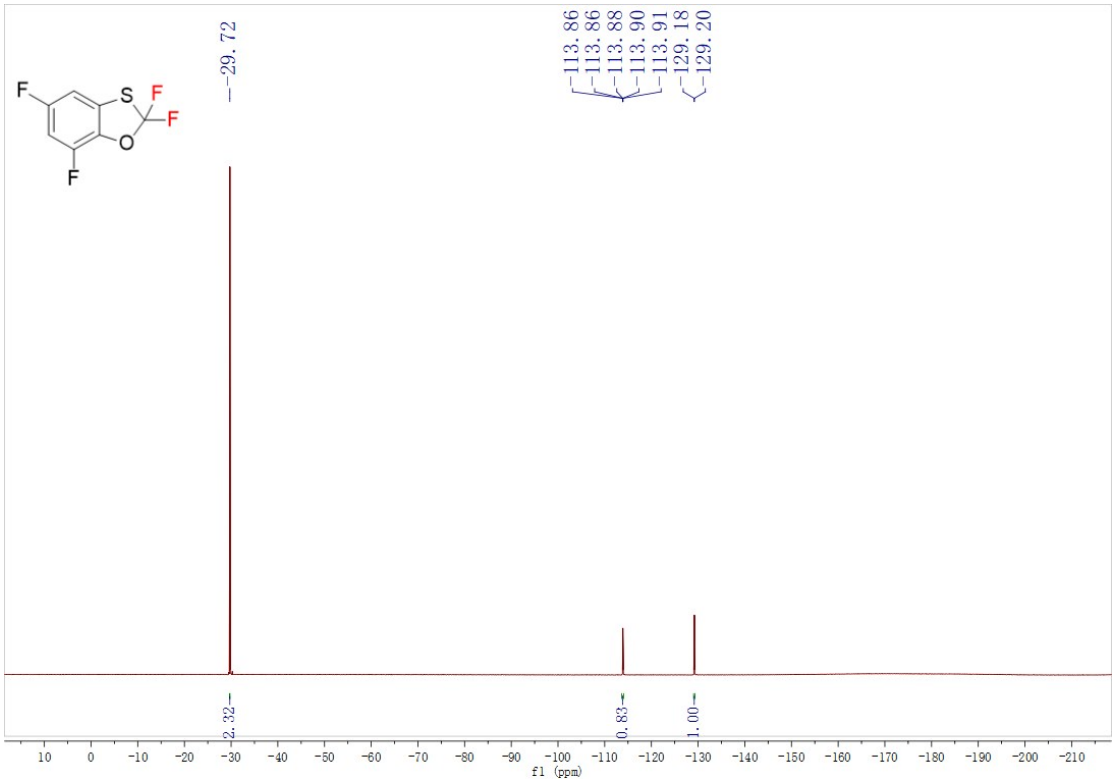
^{13}C NMR spectrum of **2o** in $CDCl_3$



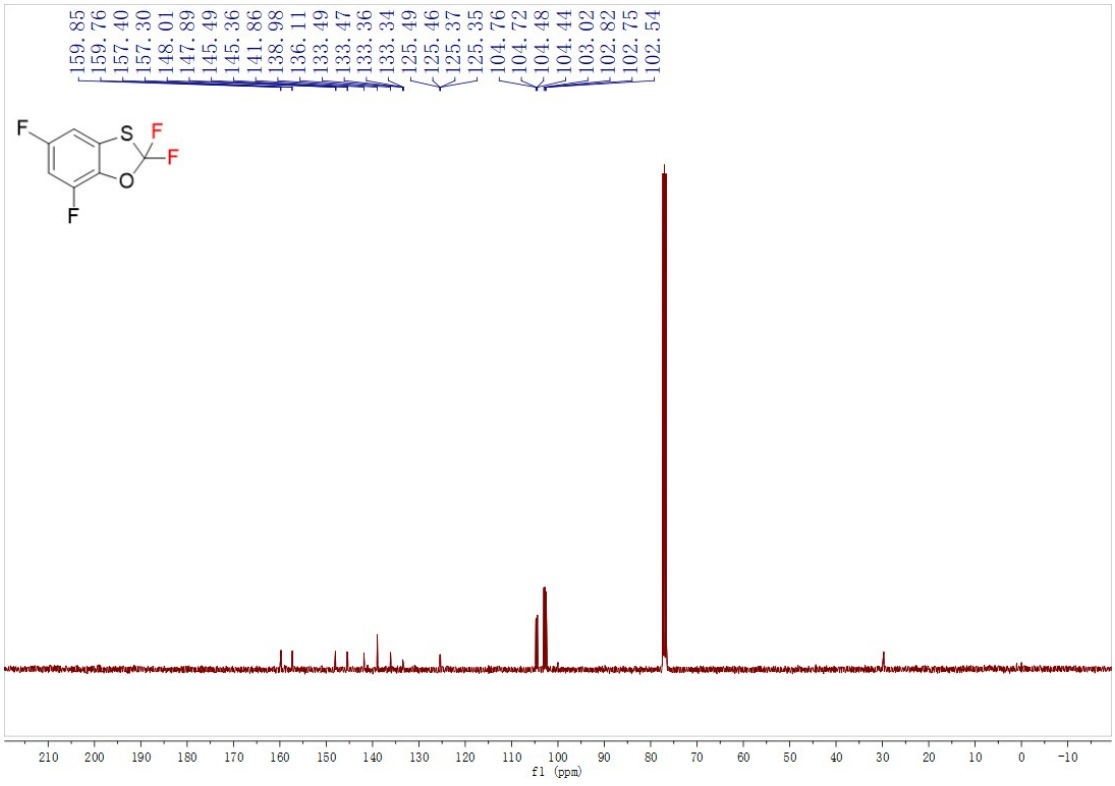
^{1}H NMR spectrum of **2p** in $CDCl_3$



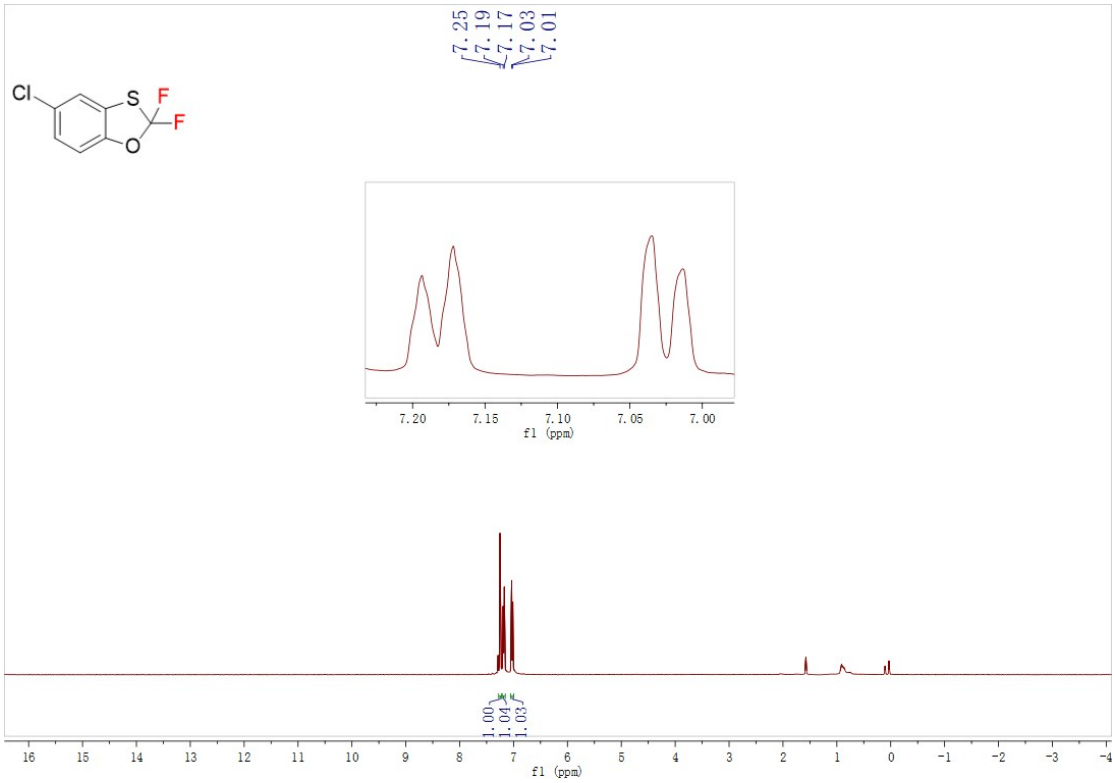
^{19}F NMR spectrum of **2p** in $CDCl_3$



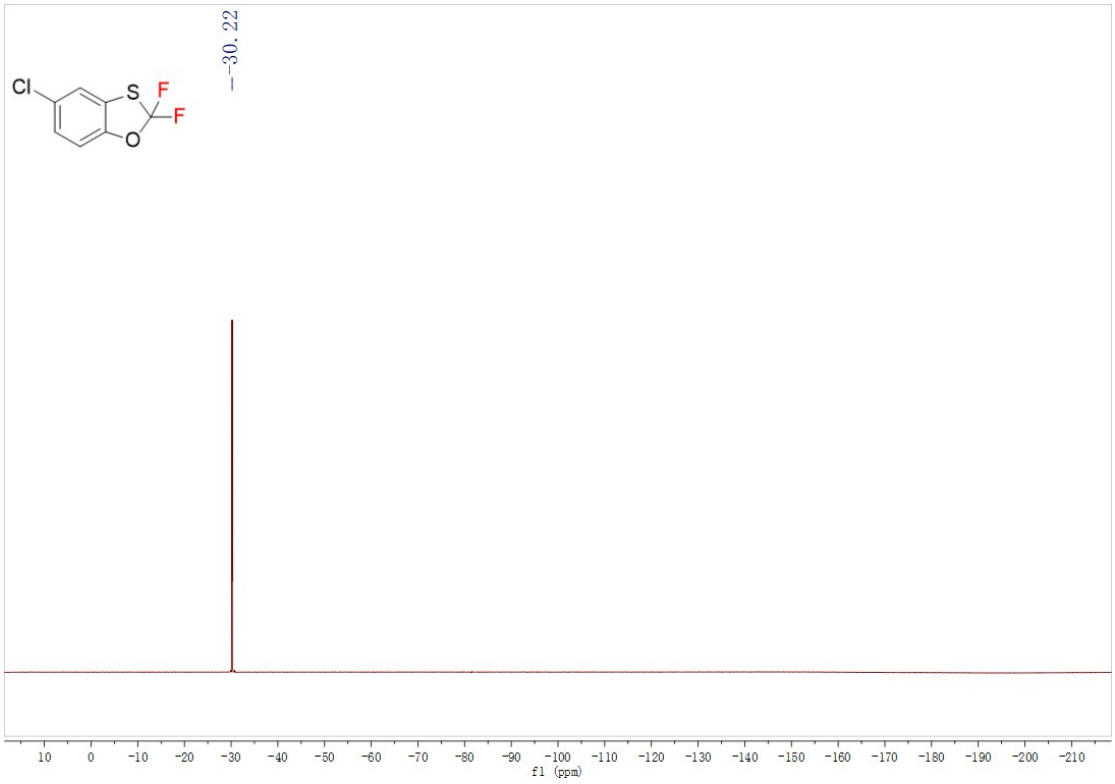
^{13}C NMR spectrum of **2p** in $CDCl_3$



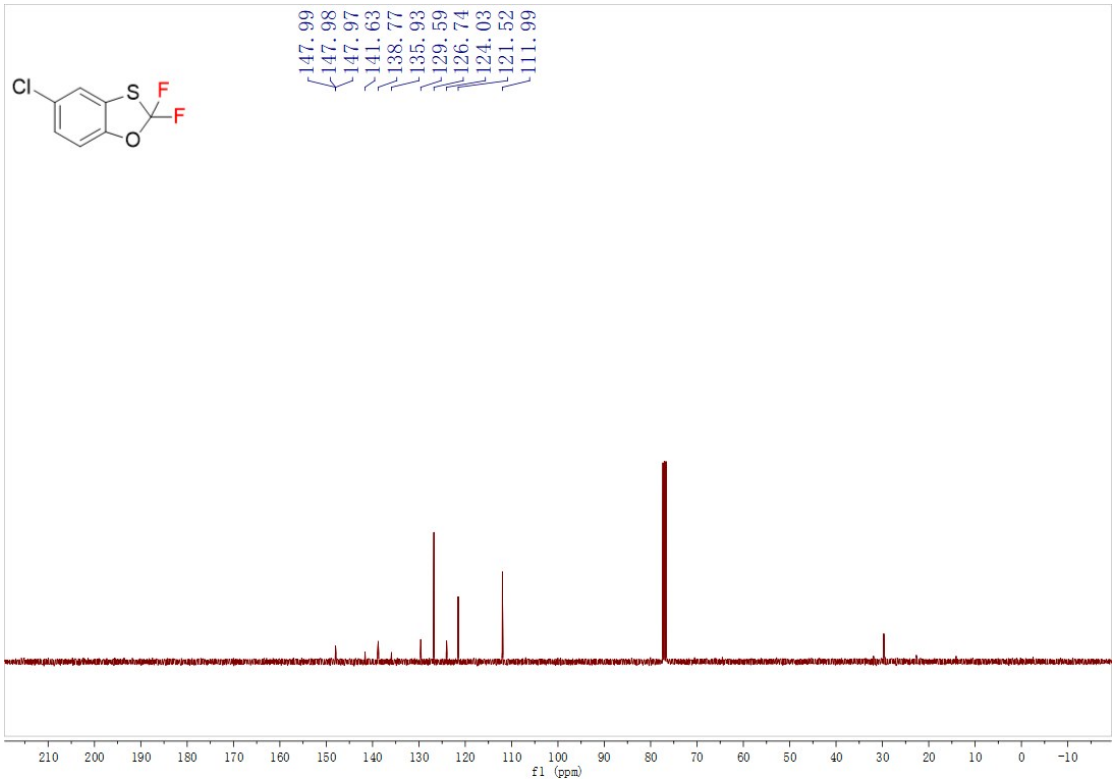
^{1}H NMR spectrum of **2q** in $CDCl_3$



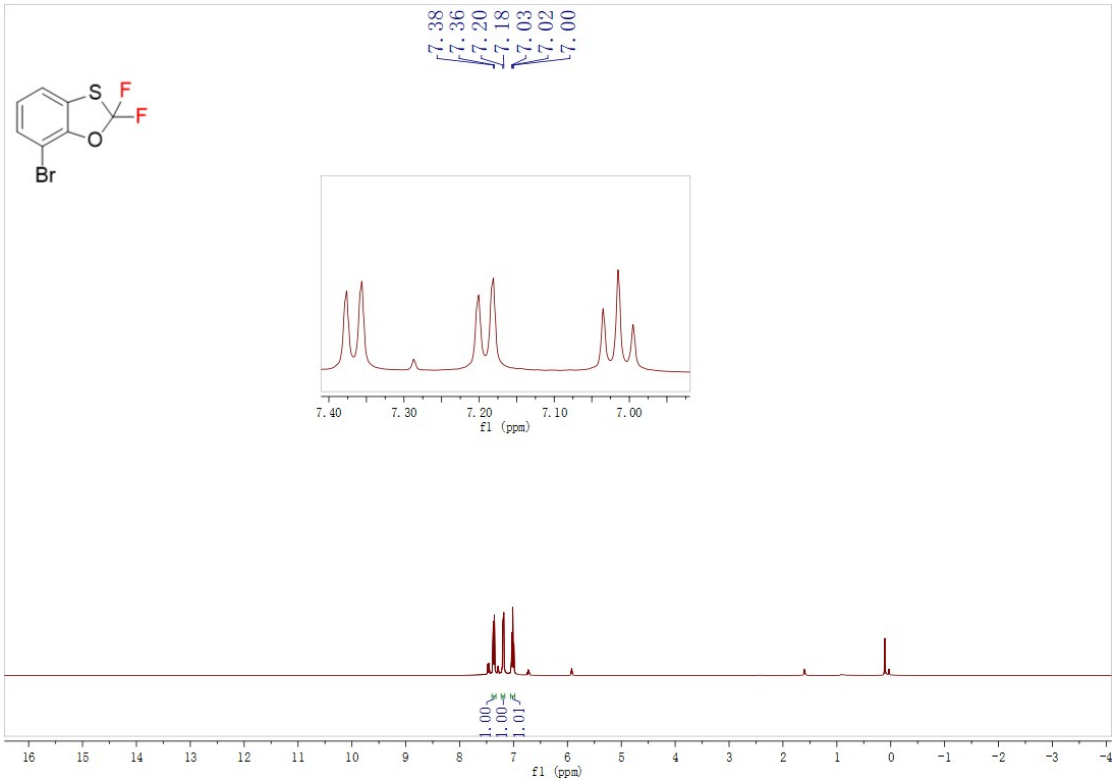
^{19}F NMR spectrum of **2q** in $CDCl_3$



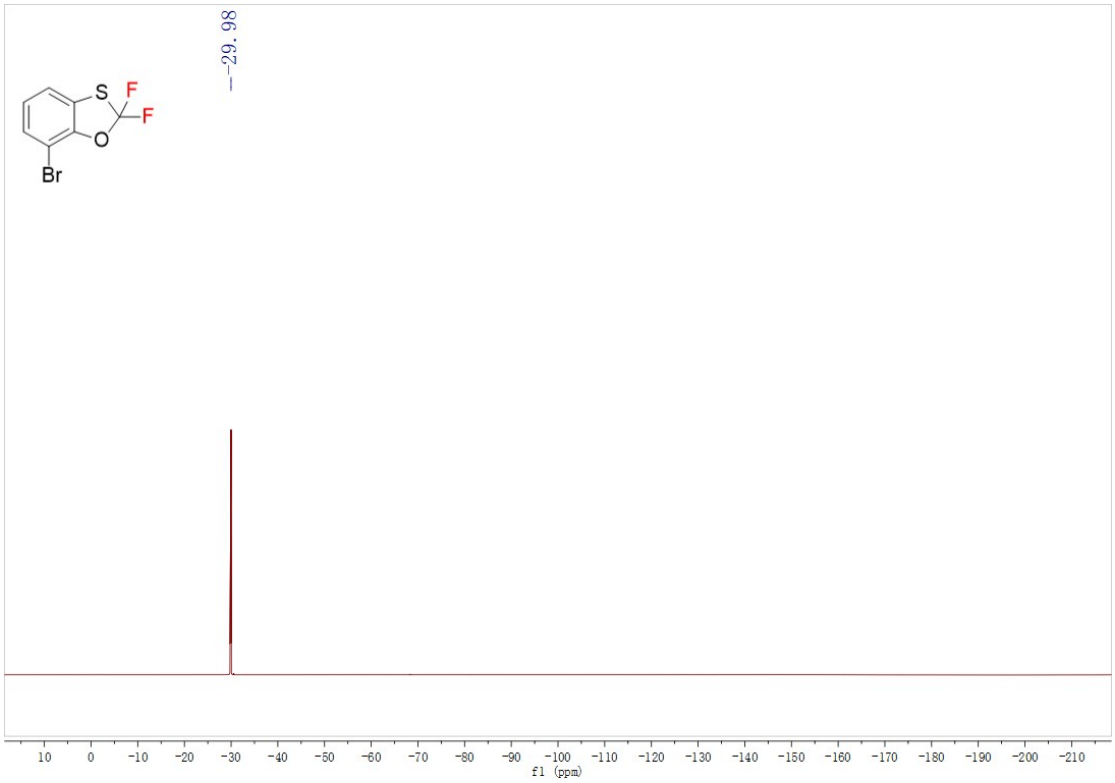
^{13}C NMR spectrum of **2q** in $CDCl_3$



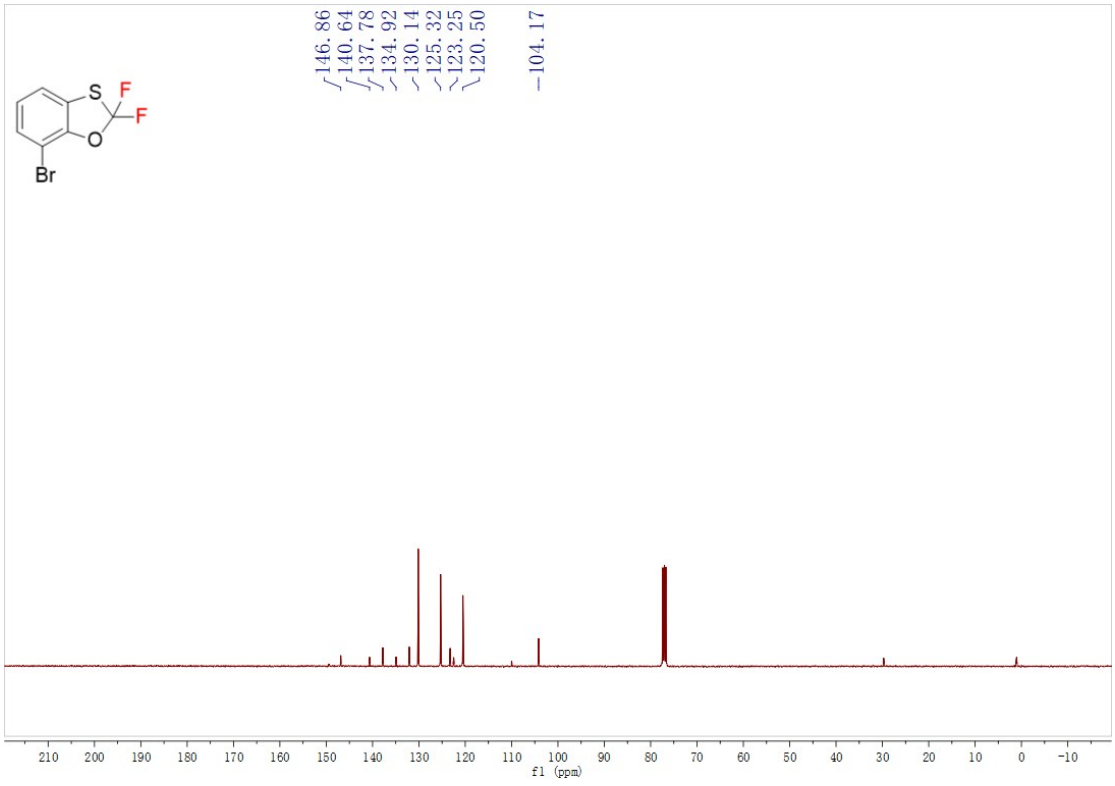
^{1}H NMR spectrum of **2r** in $CDCl_3$



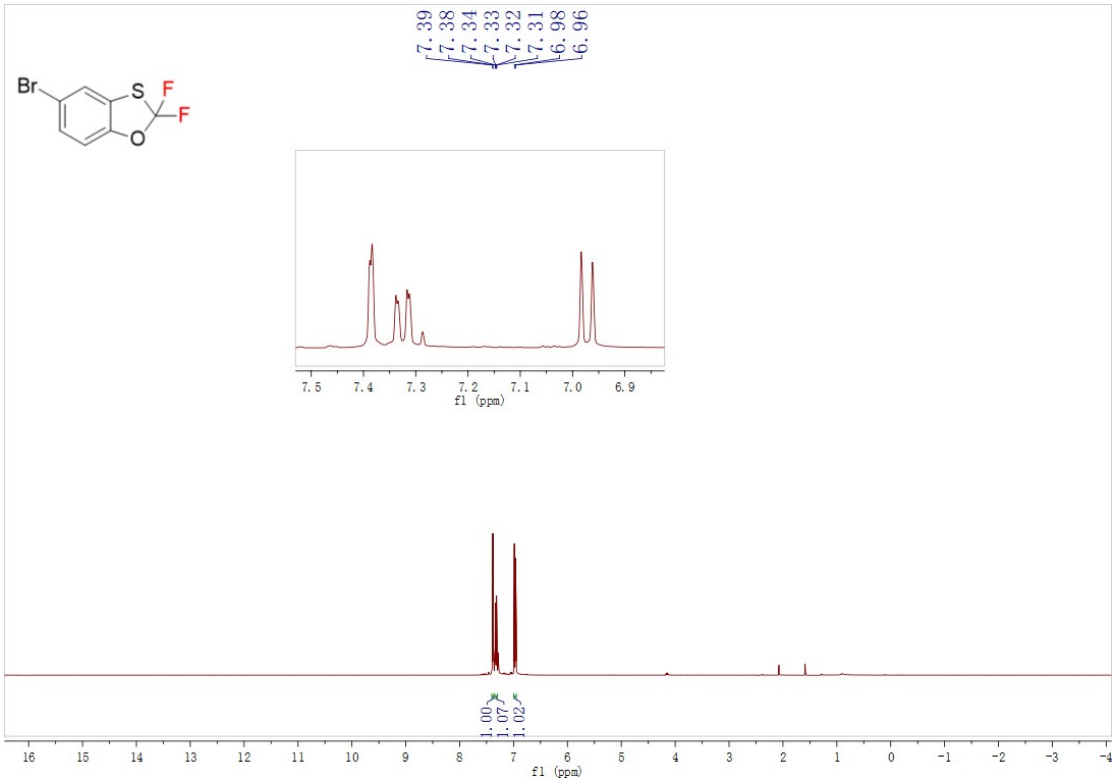
^{19}F NMR spectrum of **2r** in $CDCl_3$



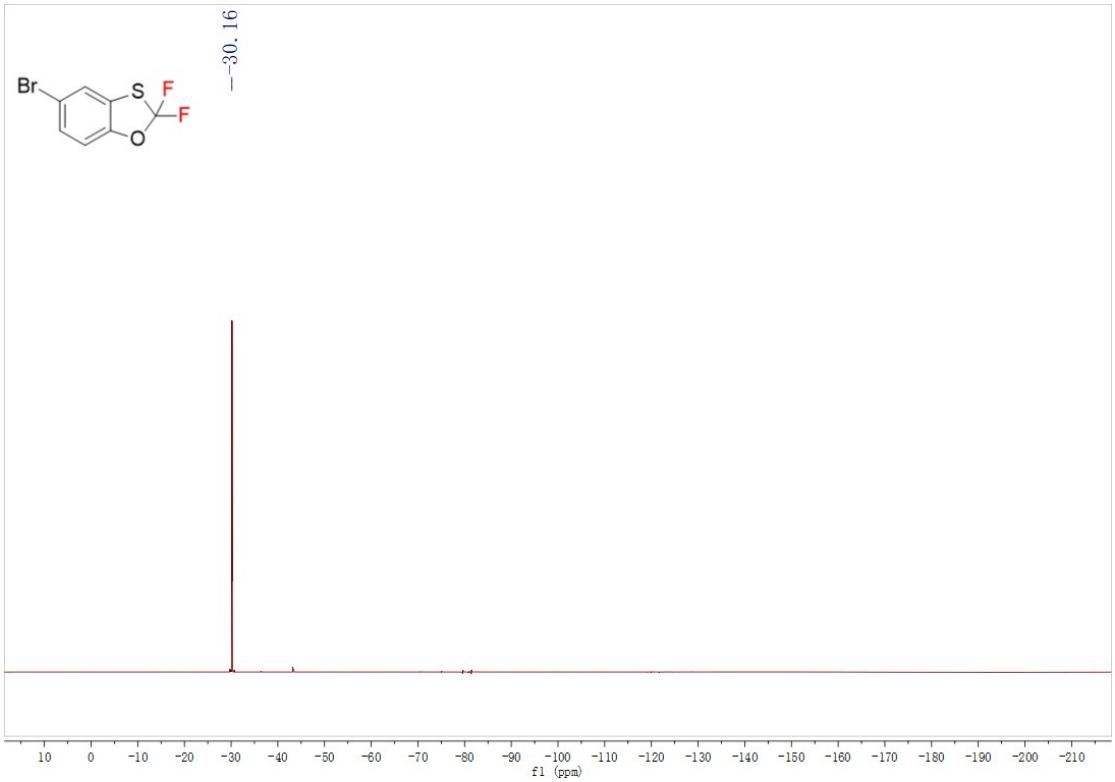
^{13}C NMR spectrum of **2r** in $CDCl_3$



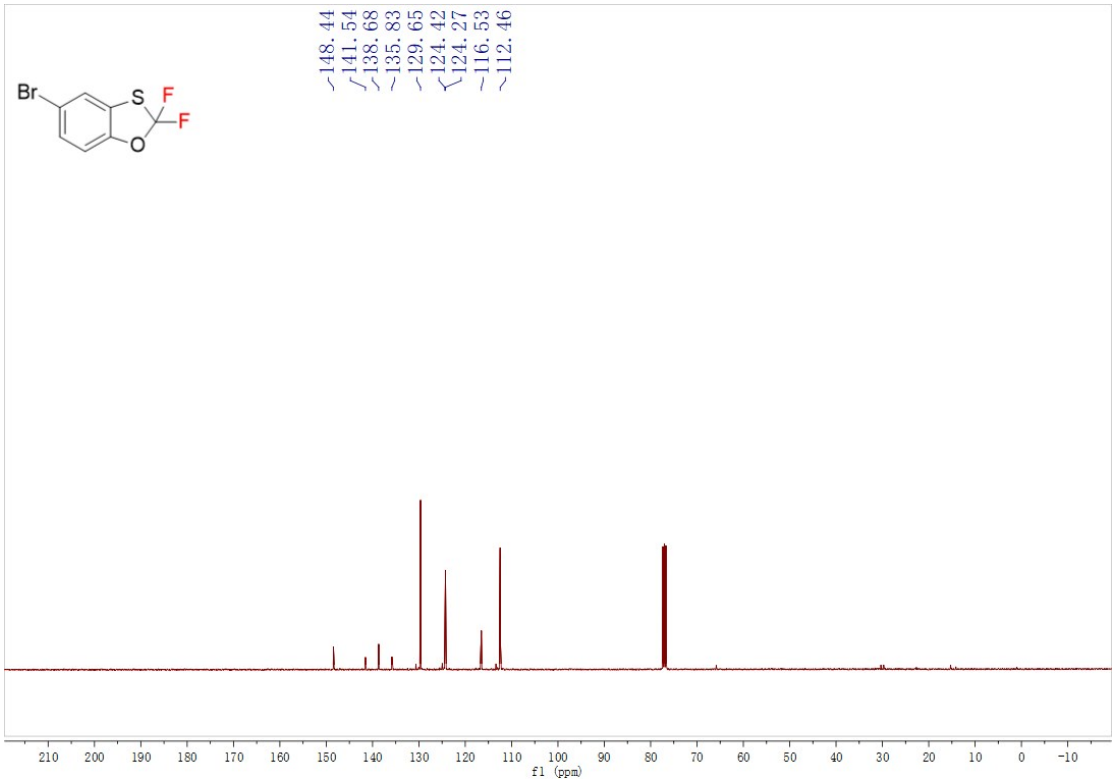
^{1}H NMR spectrum of **2s** in $CDCl_3$



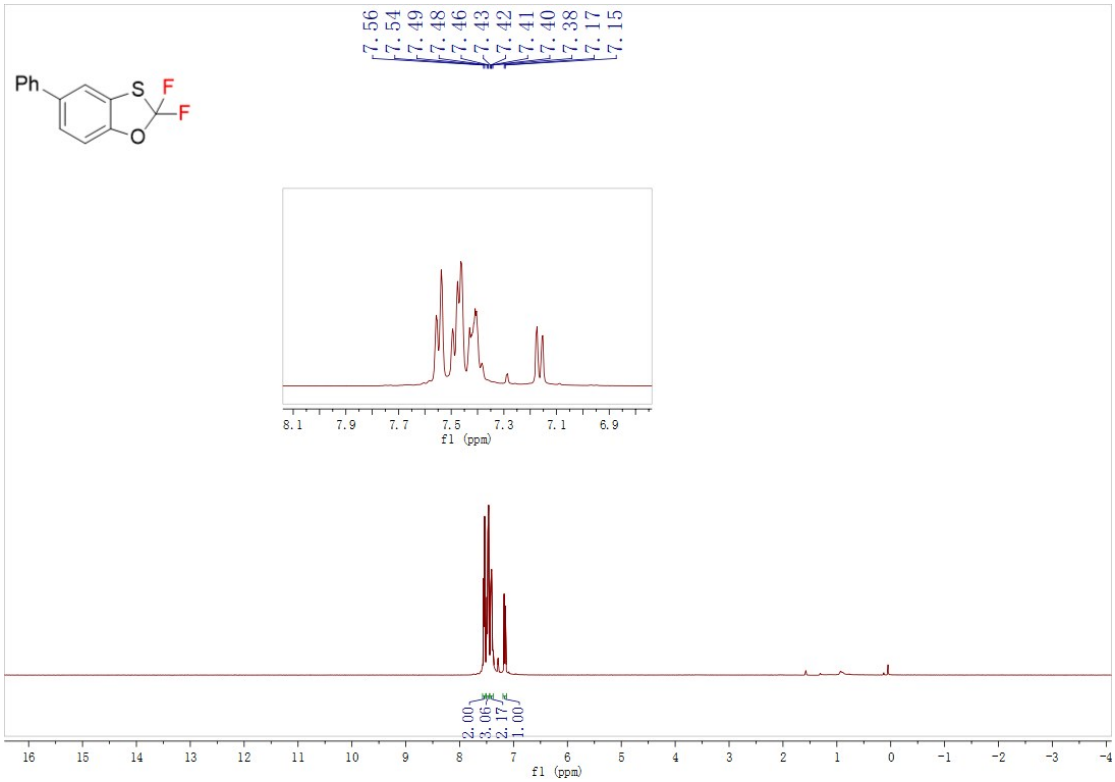
^{19}F NMR spectrum of **2s** in $CDCl_3$



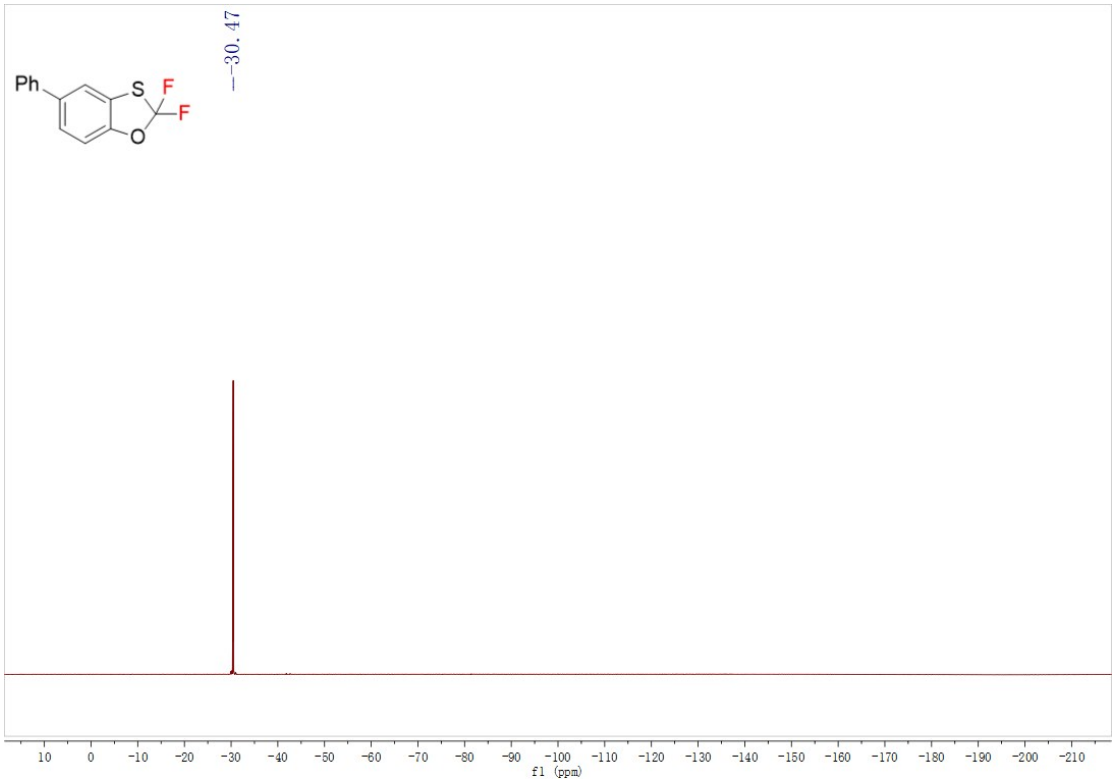
^{13}C NMR spectrum of **2s** in $CDCl_3$



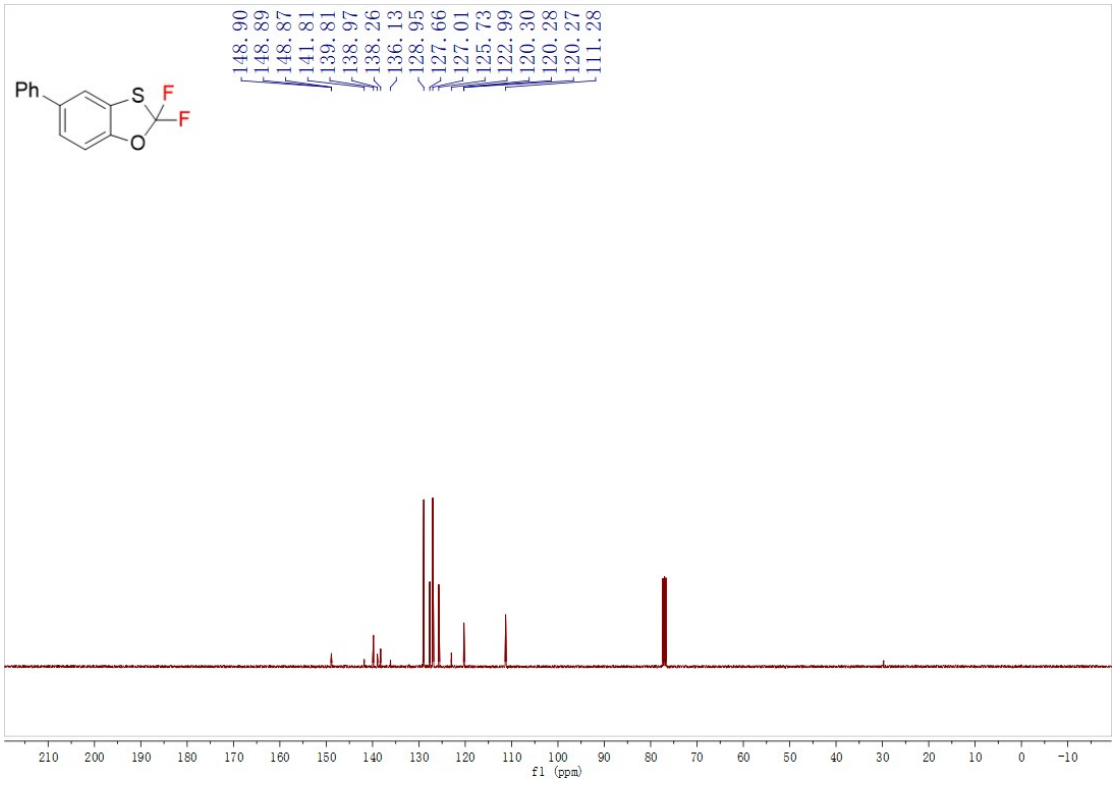
^{1}H NMR spectrum of **2t** in $CDCl_3$



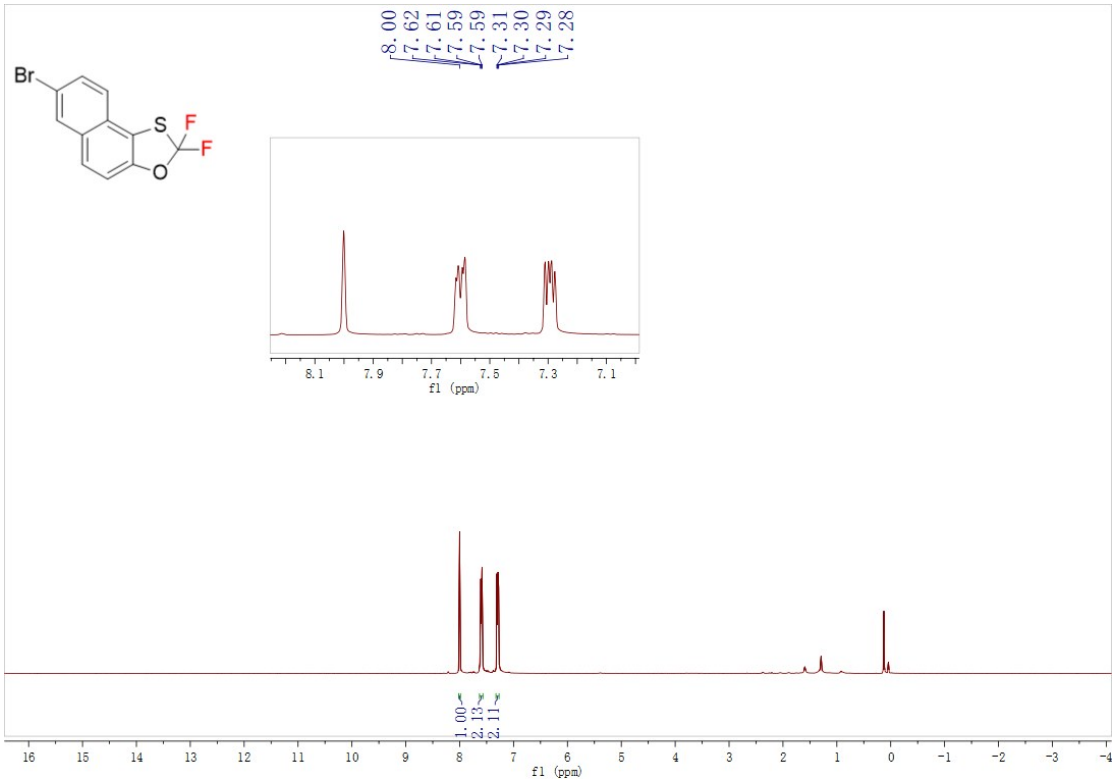
^{19}F NMR spectrum of **2t** in $CDCl_3$



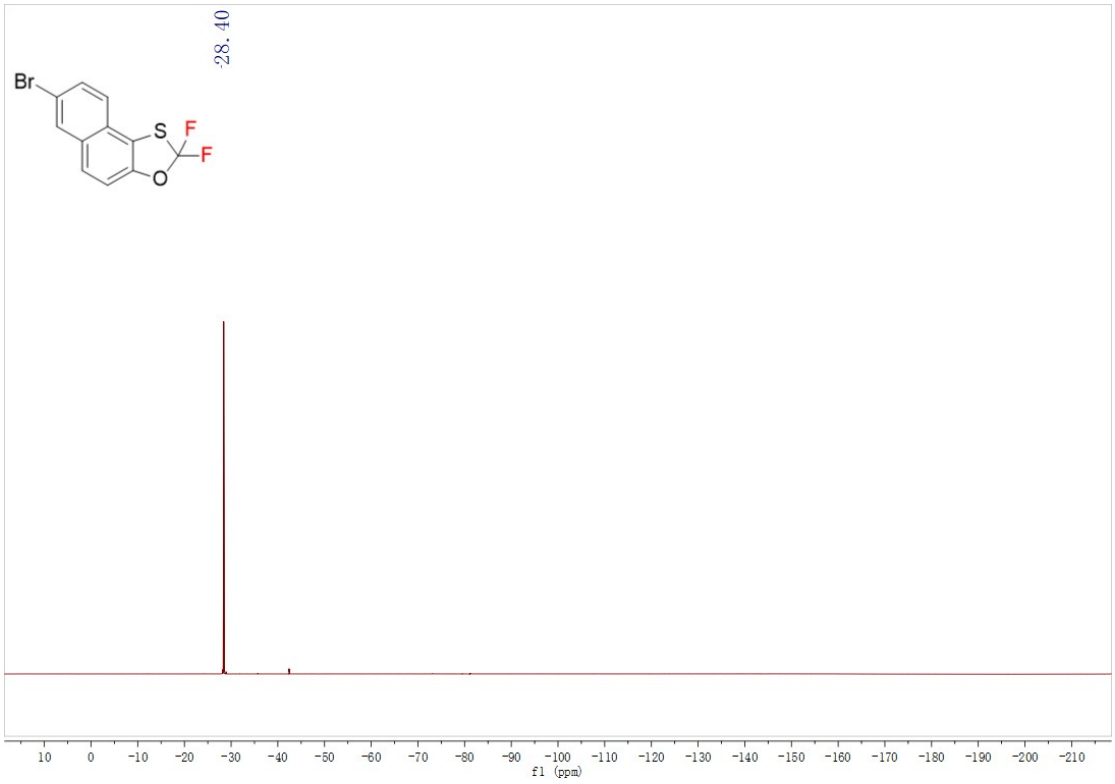
^{13}C NMR spectrum of **2t** in $CDCl_3$



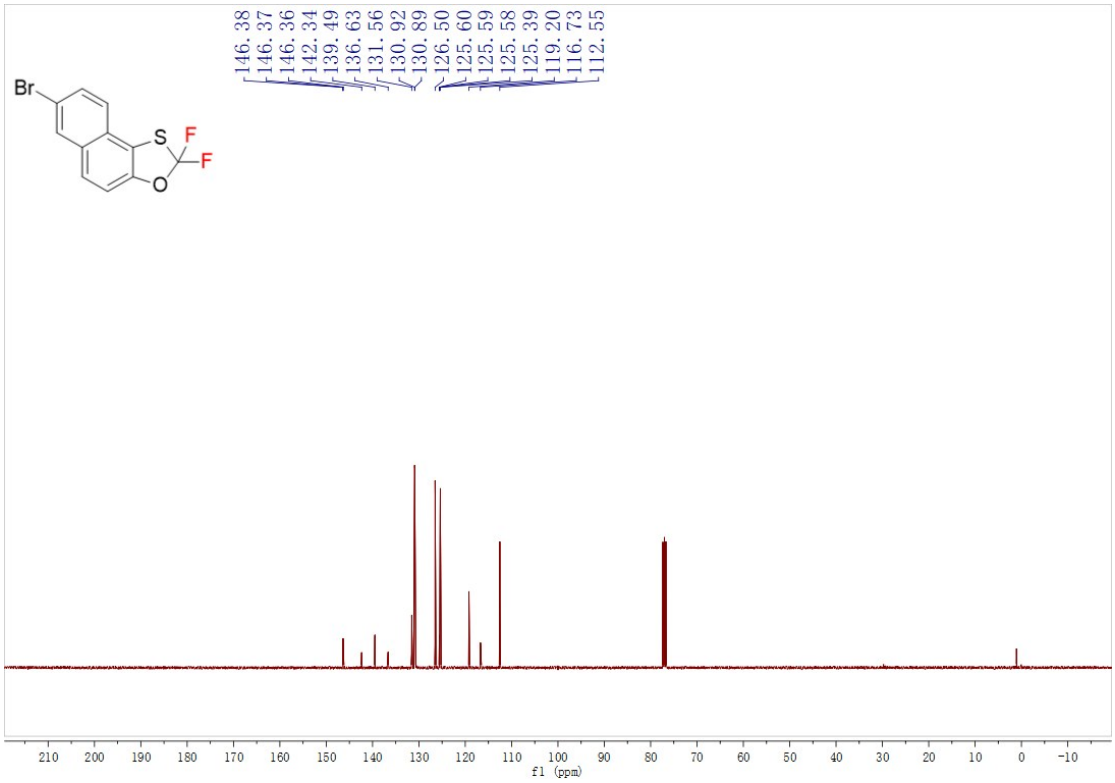
^{1}H NMR spectrum of **2u** in $CDCl_3$



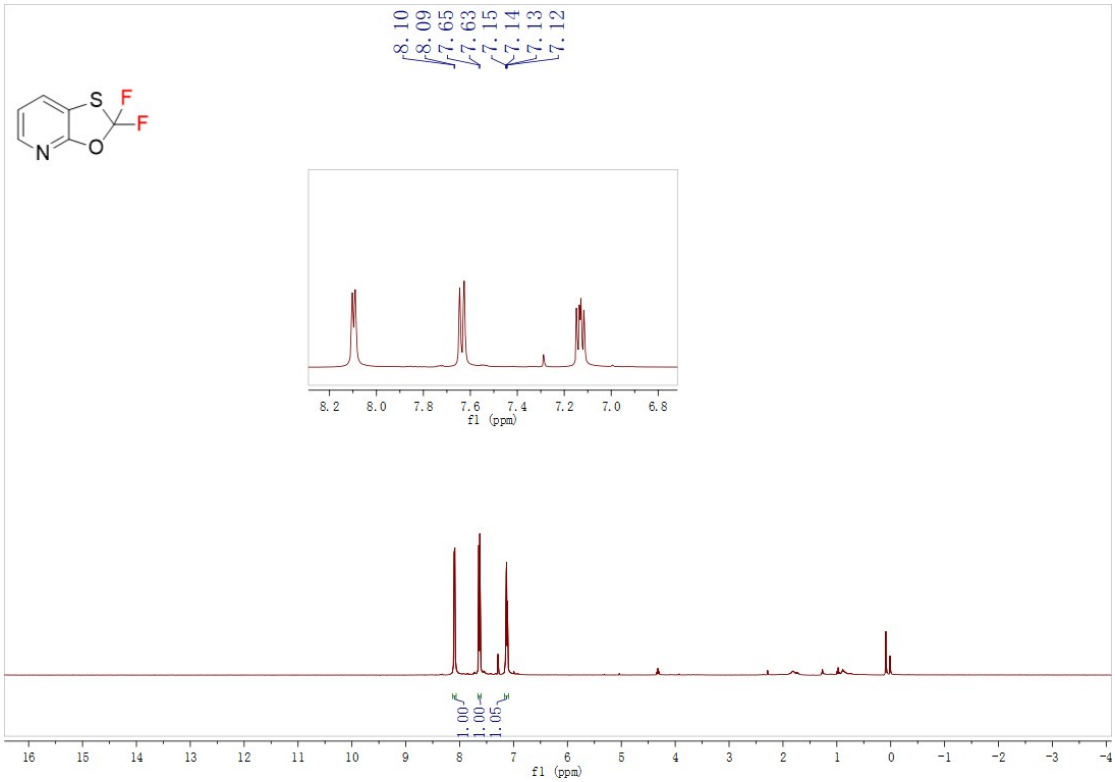
^{19}F NMR spectrum of **2u** in $CDCl_3$



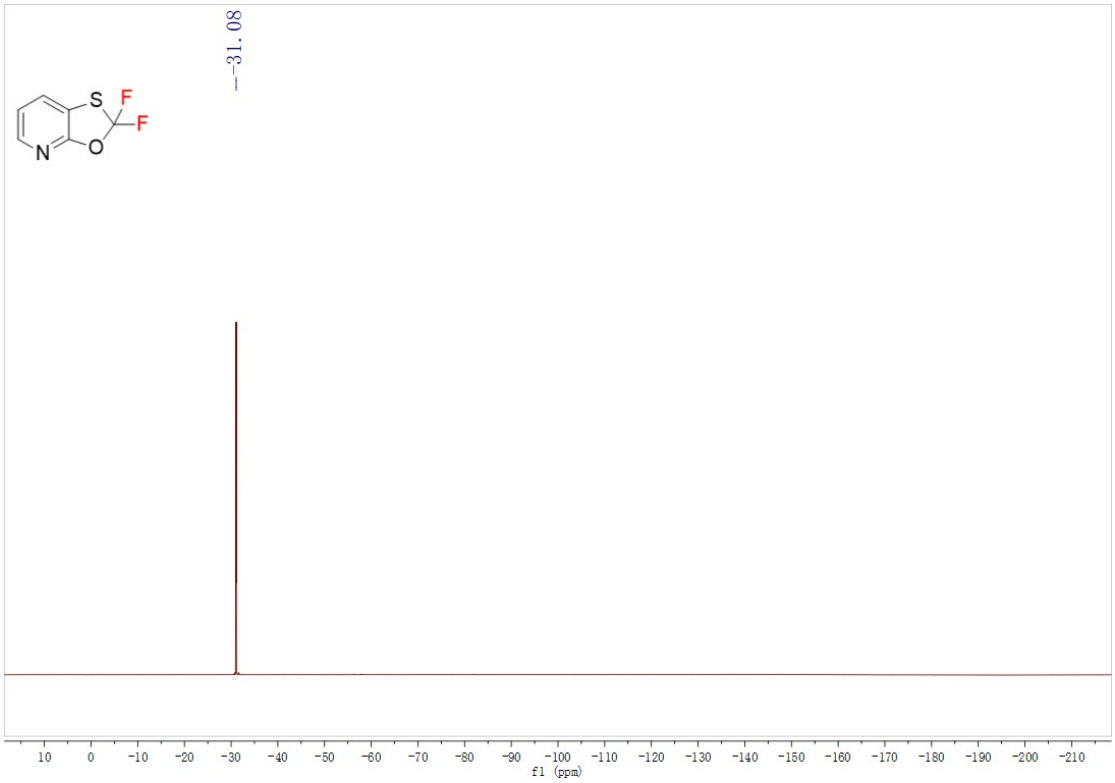
^{13}C NMR spectrum of **2u** in $CDCl_3$



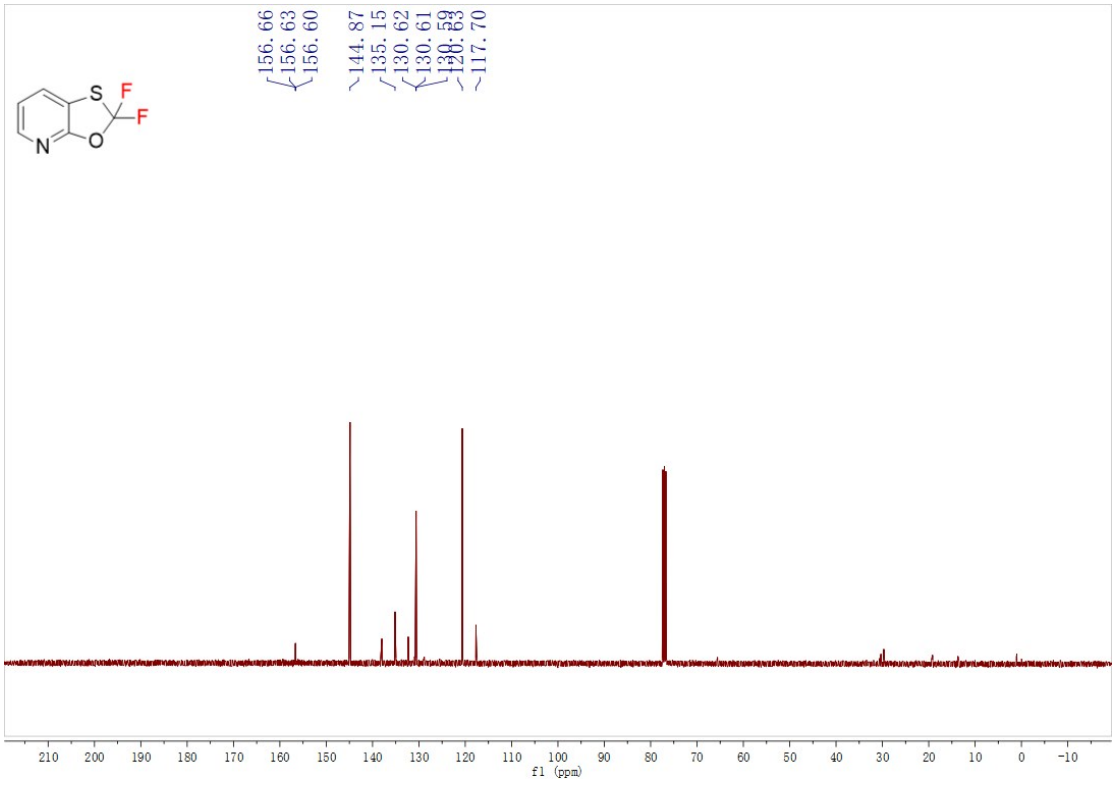
^{1}H NMR spectrum of **2v** in $CDCl_3$



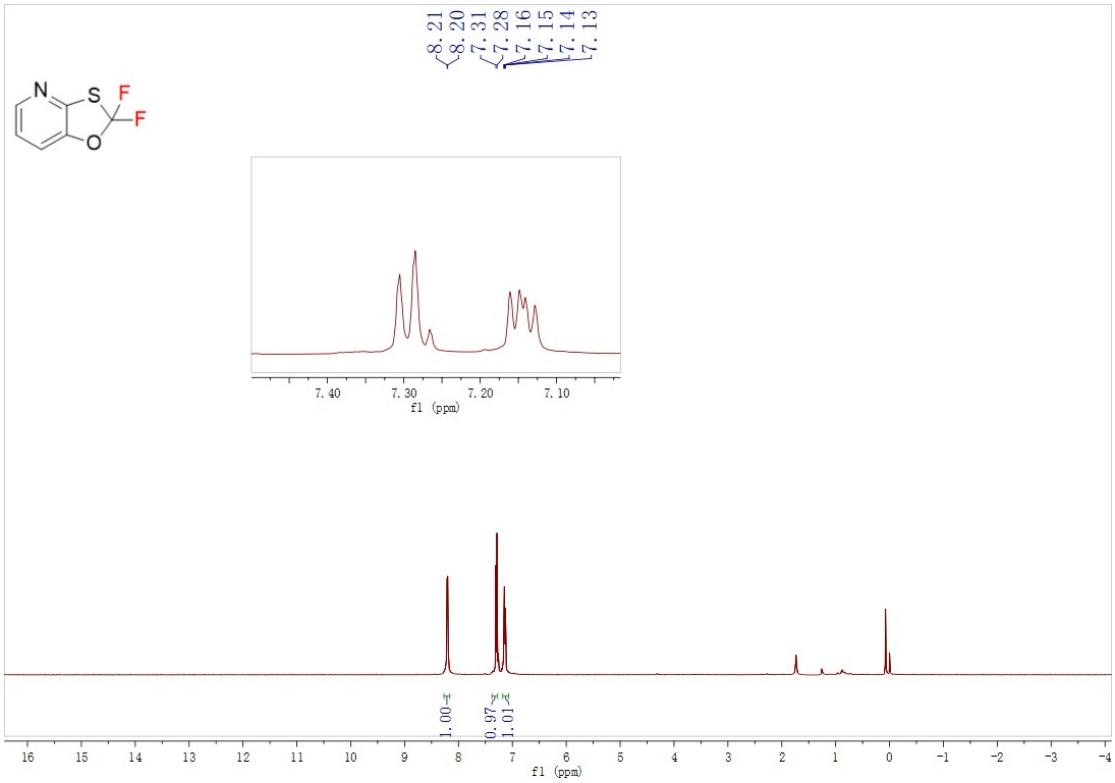
^{19}F NMR spectrum of **2v** in $CDCl_3$



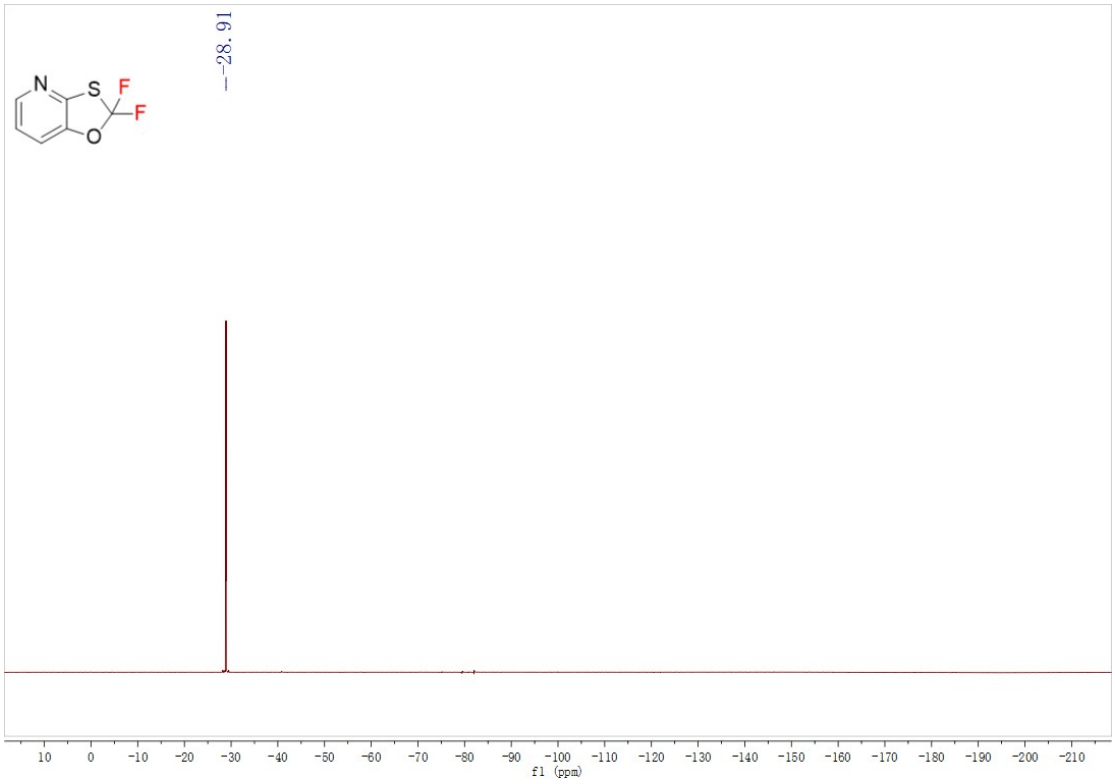
^{13}C NMR spectrum of **2v**in $CDCl_3$



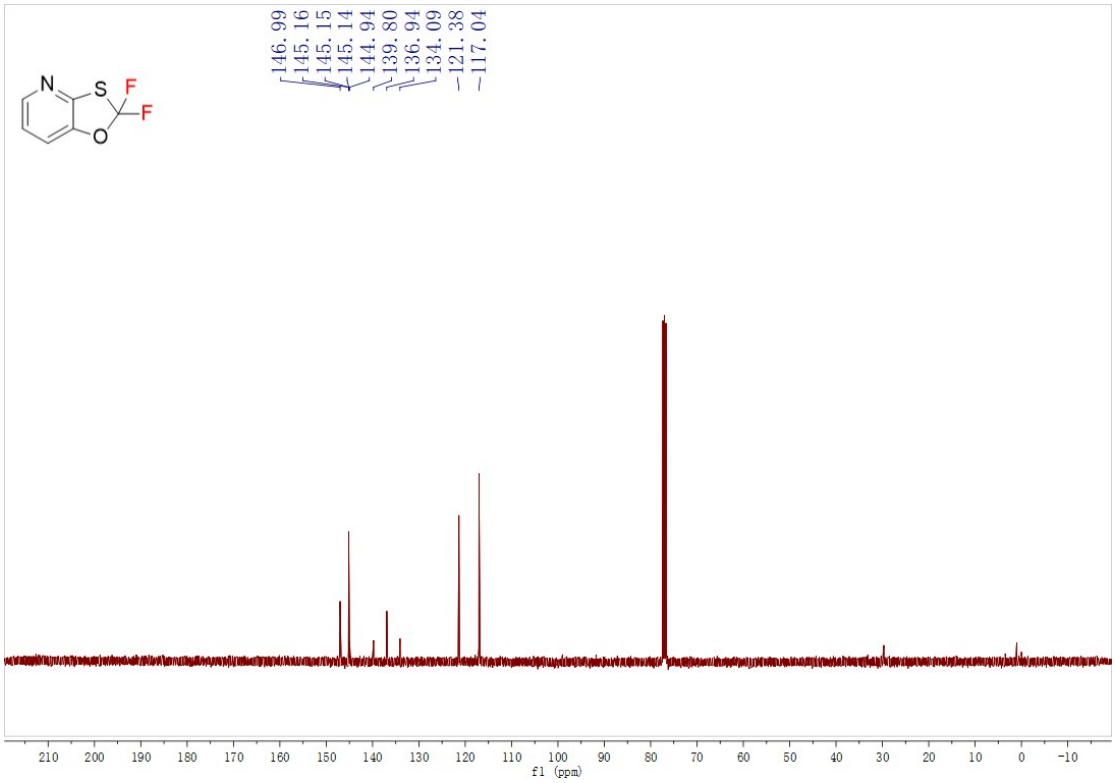
^{1}H NMR spectrum of **2w** in $CDCl_3$



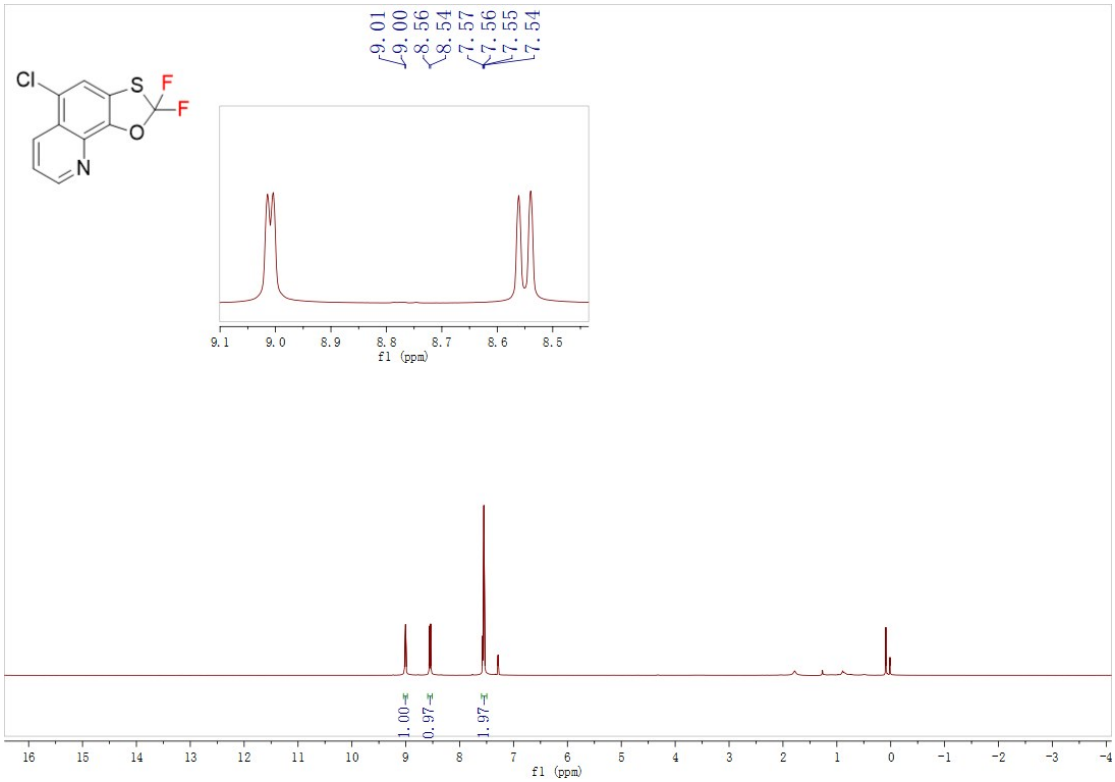
^{19}F NMR spectrum of **2w** in $CDCl_3$



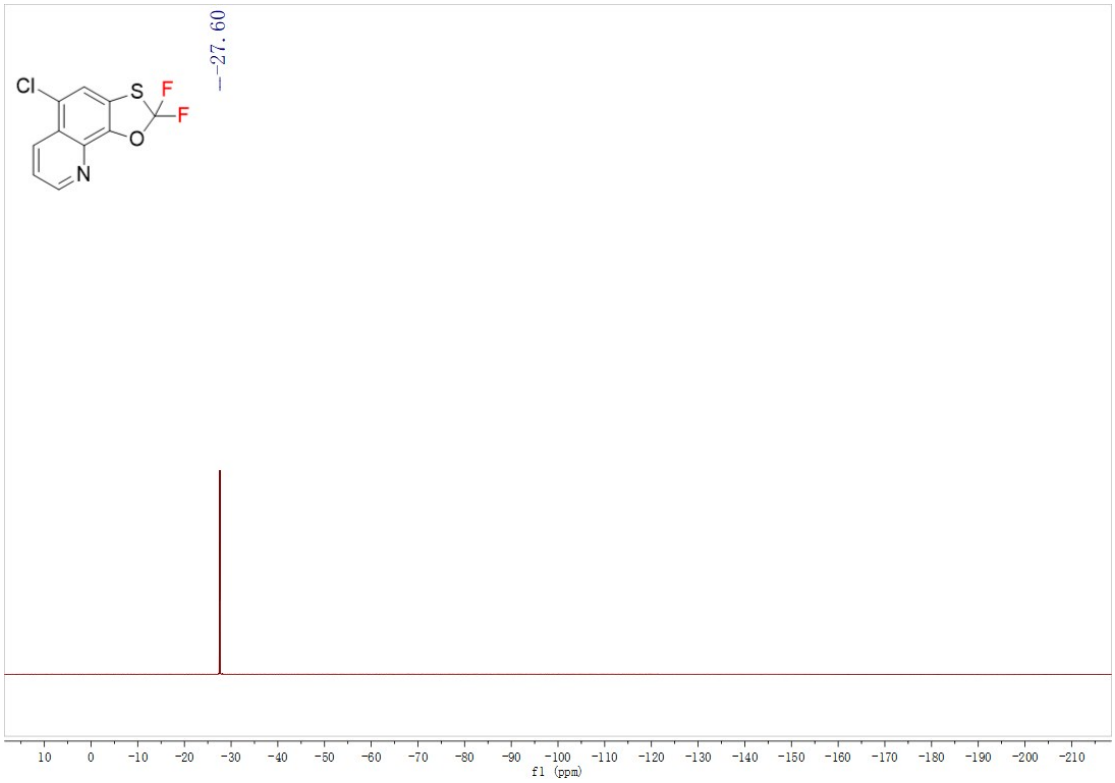
^{13}C NMR spectrum of **2w** in $CDCl_3$



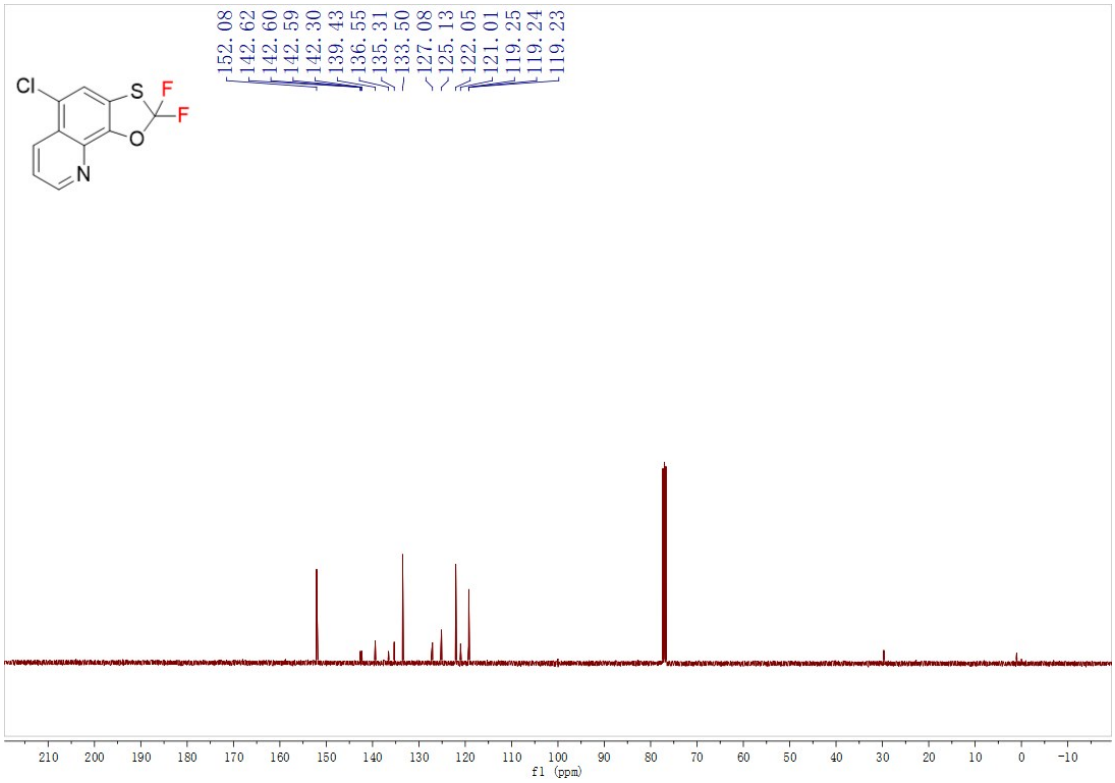
^{1}H NMR spectrum of **2x** in $CDCl_3$



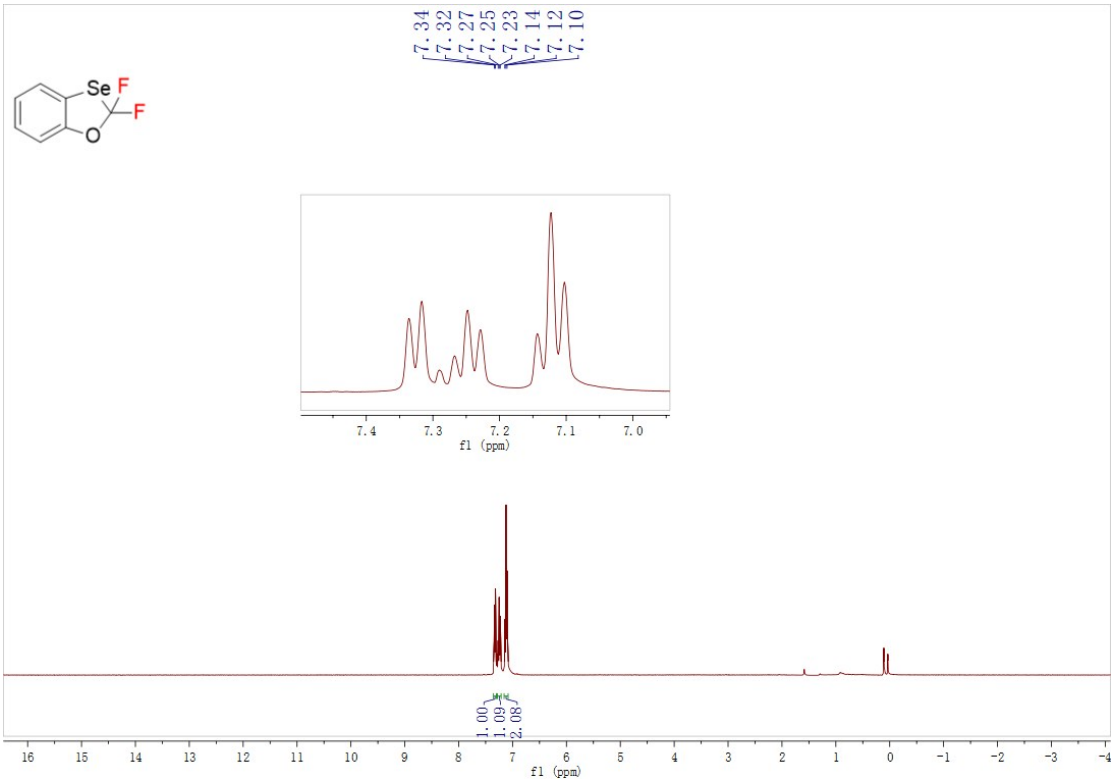
^{19}F NMR spectrum of **2x** in $CDCl_3$



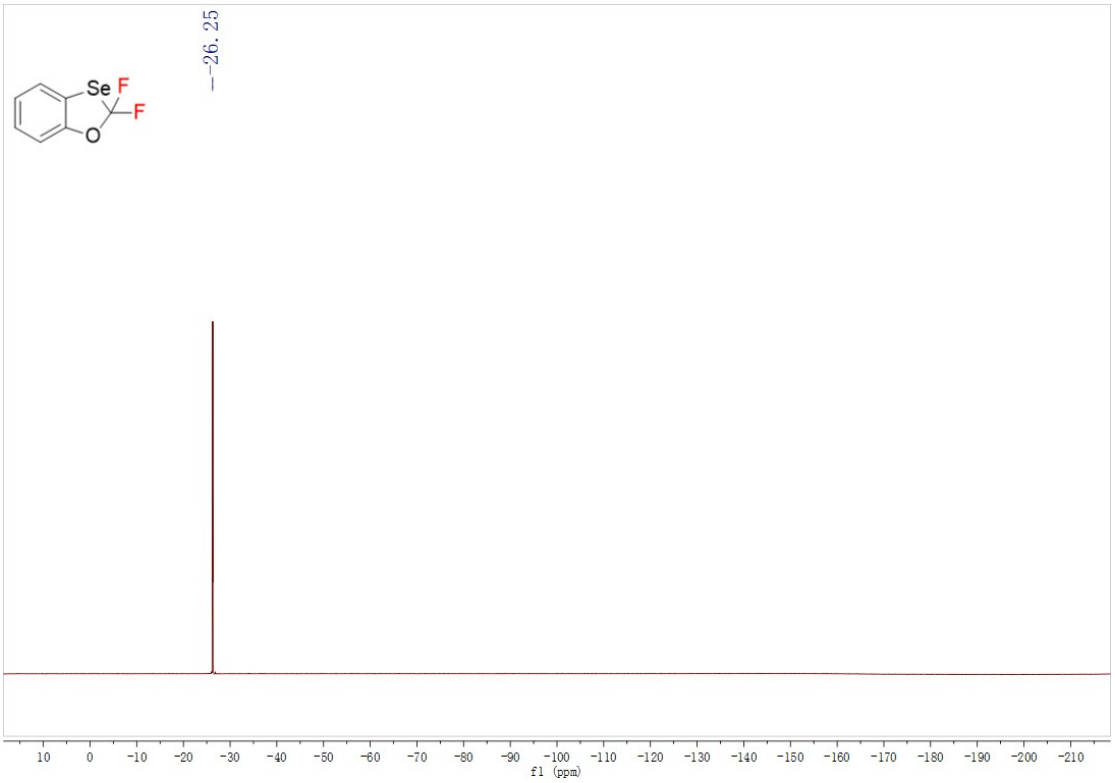
^{13}C NMR spectrum of **2x** in $CDCl_3$



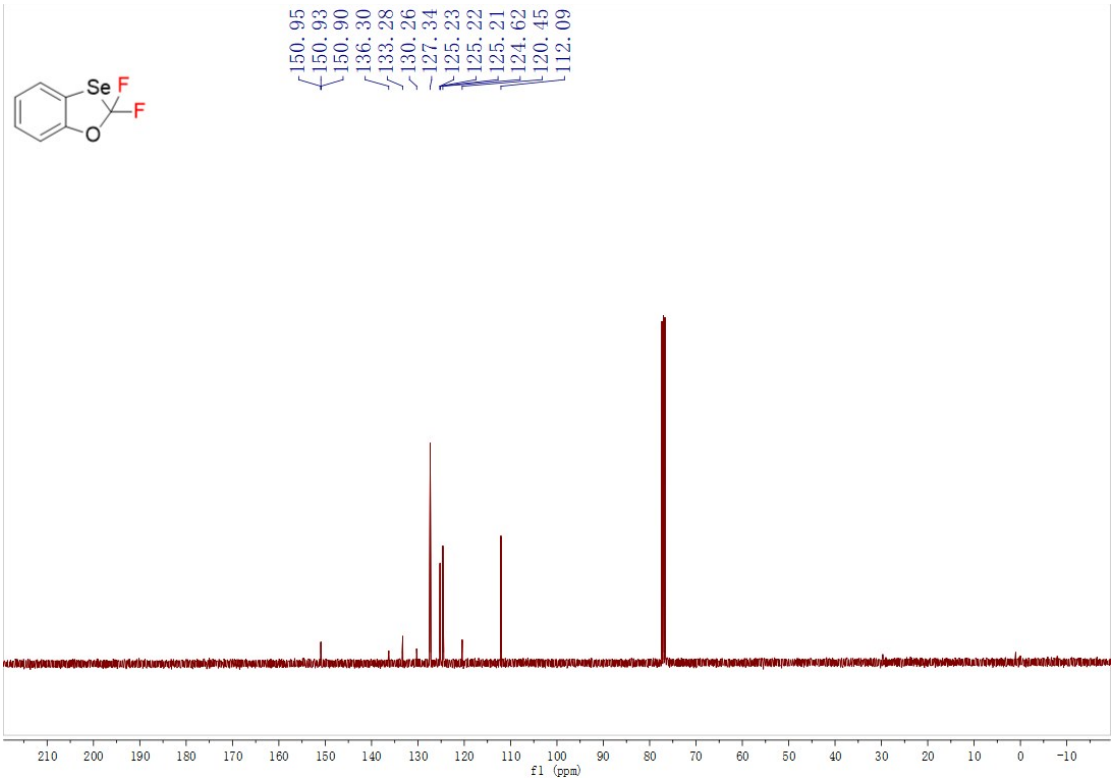
^{1}H NMR spectrum of **3a** in $CDCl_3$



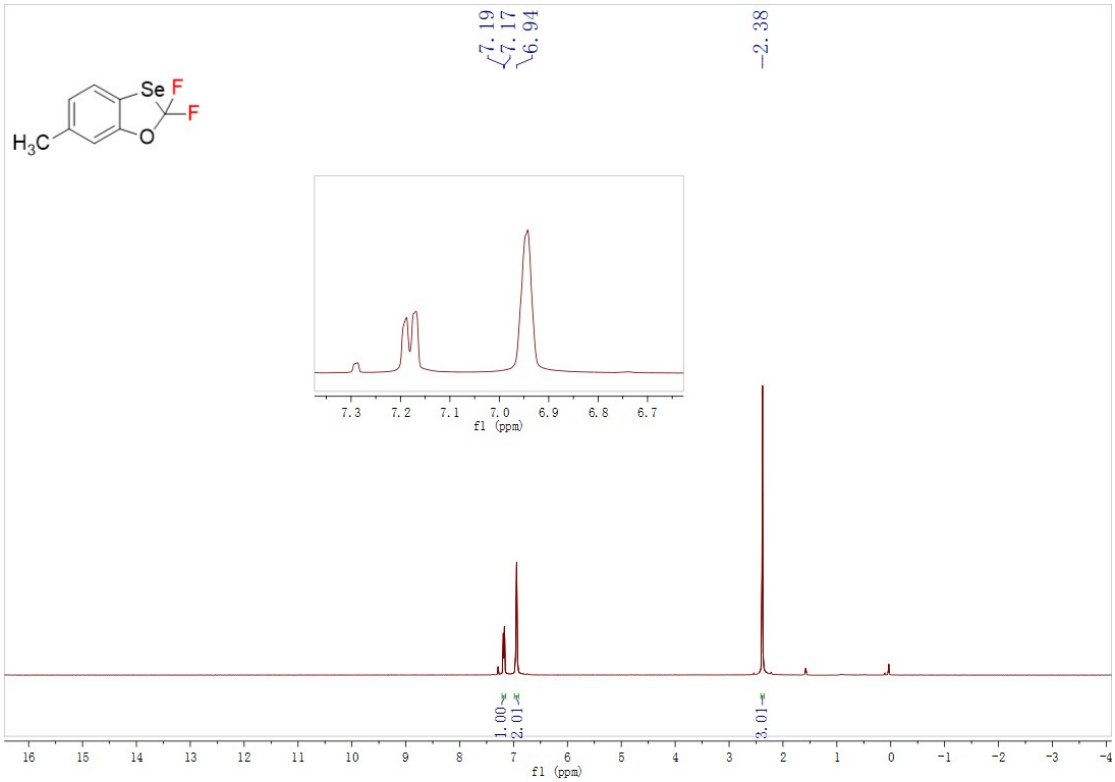
^{19}F NMR spectrum of **3a** in $CDCl_3$



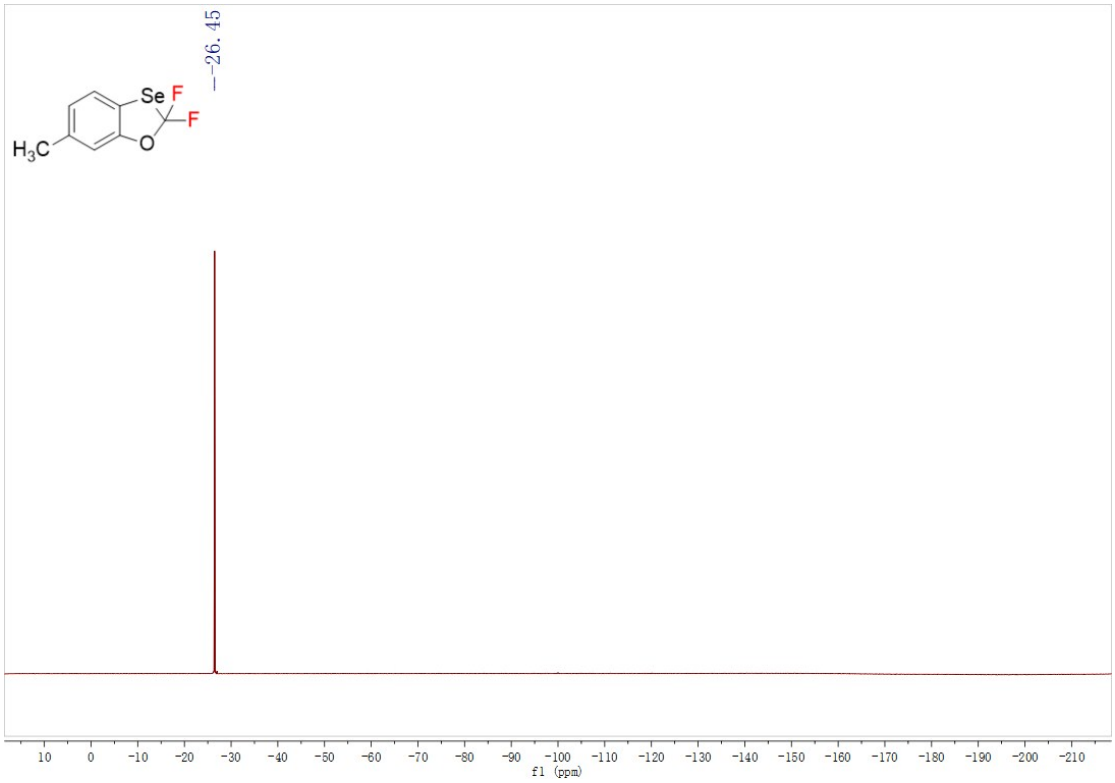
^{13}C NMR spectrum of **3a** in $CDCl_3$



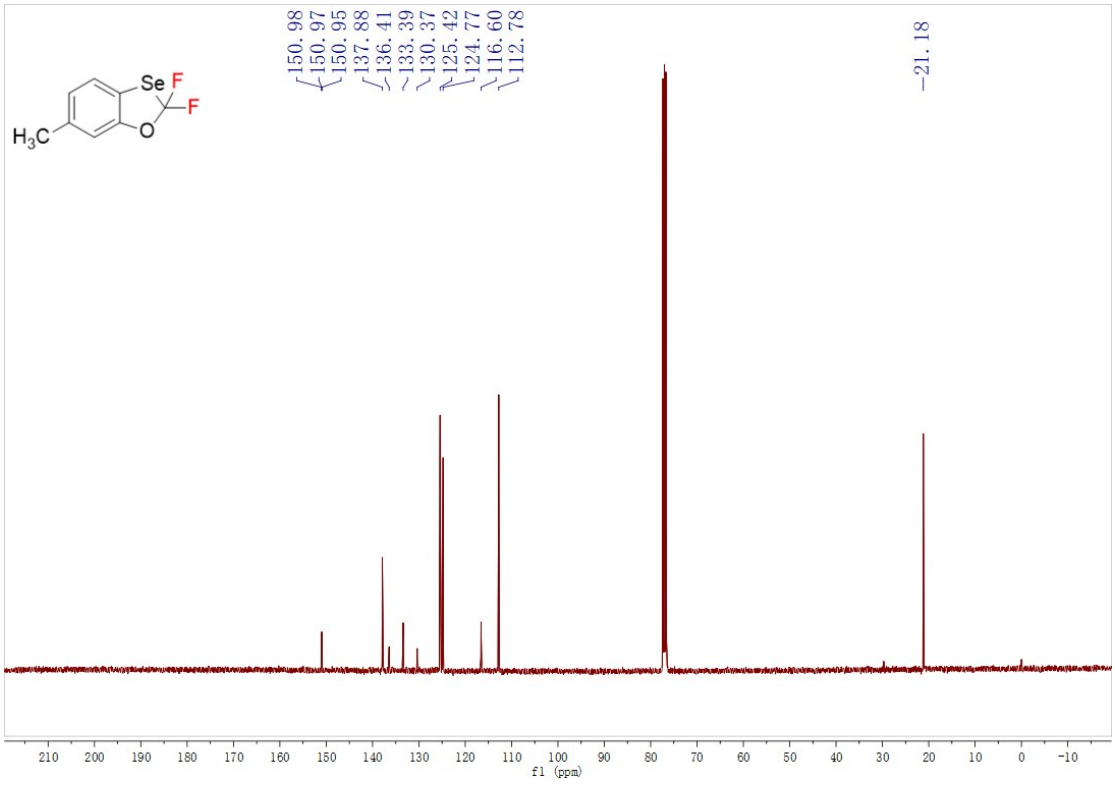
^{1}H NMR spectrum of **3c** in $CDCl_3$



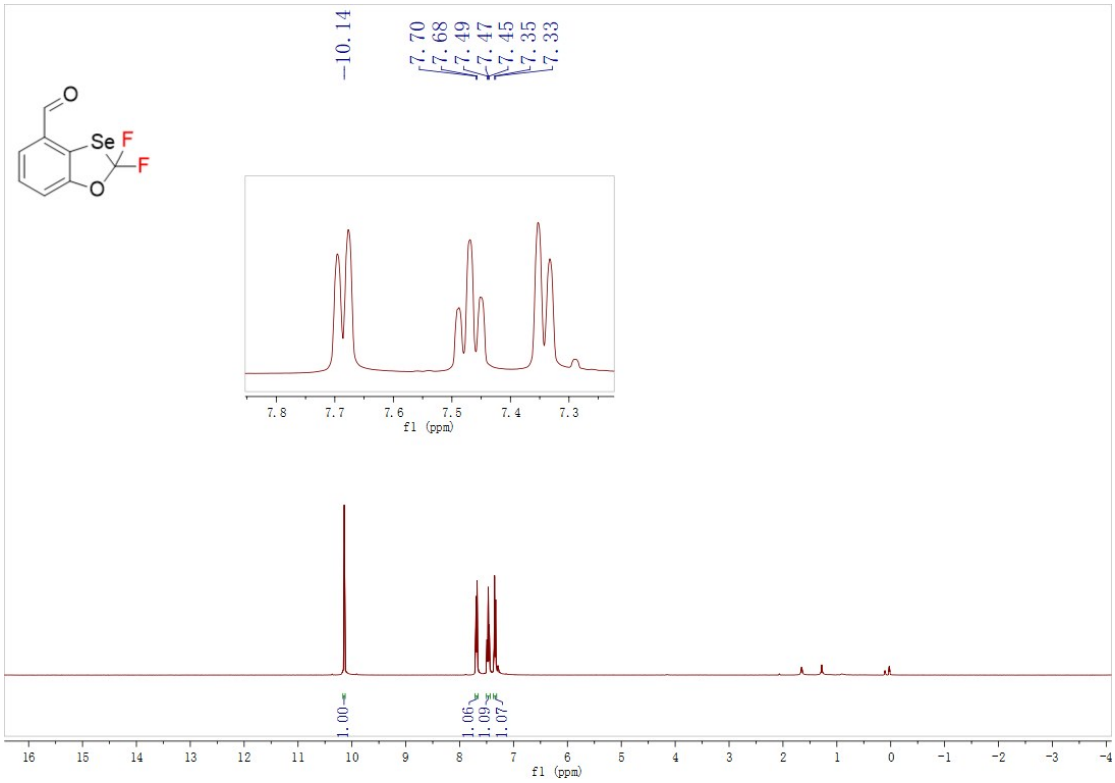
^{19}F NMR spectrum of **3c** in $CDCl_3$



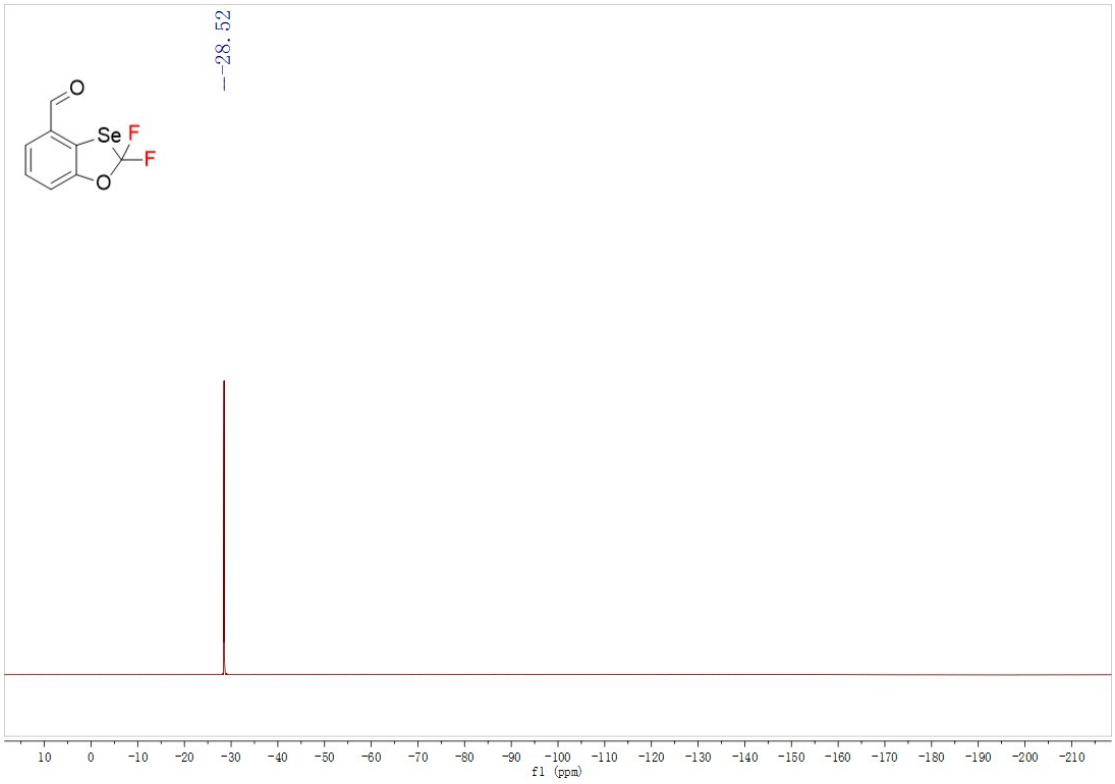
^{13}C NMR spectrum of **3c** in $CDCl_3$



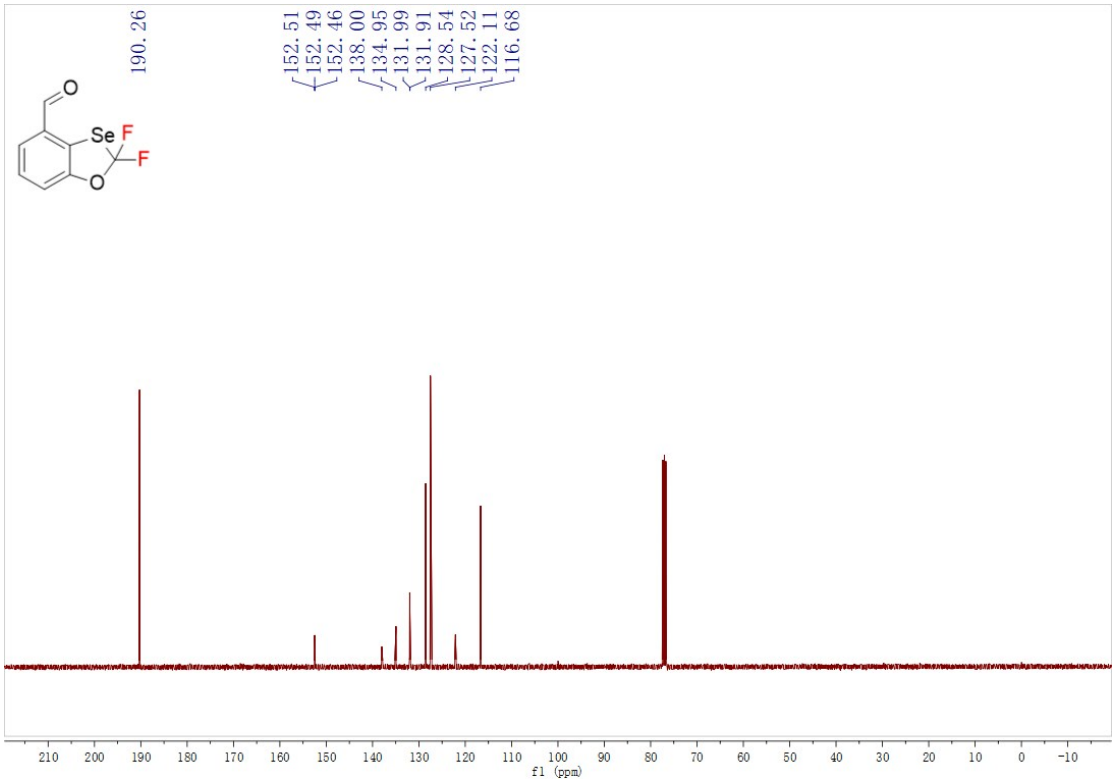
^{1}H NMR spectrum of **3g** in $CDCl_3$



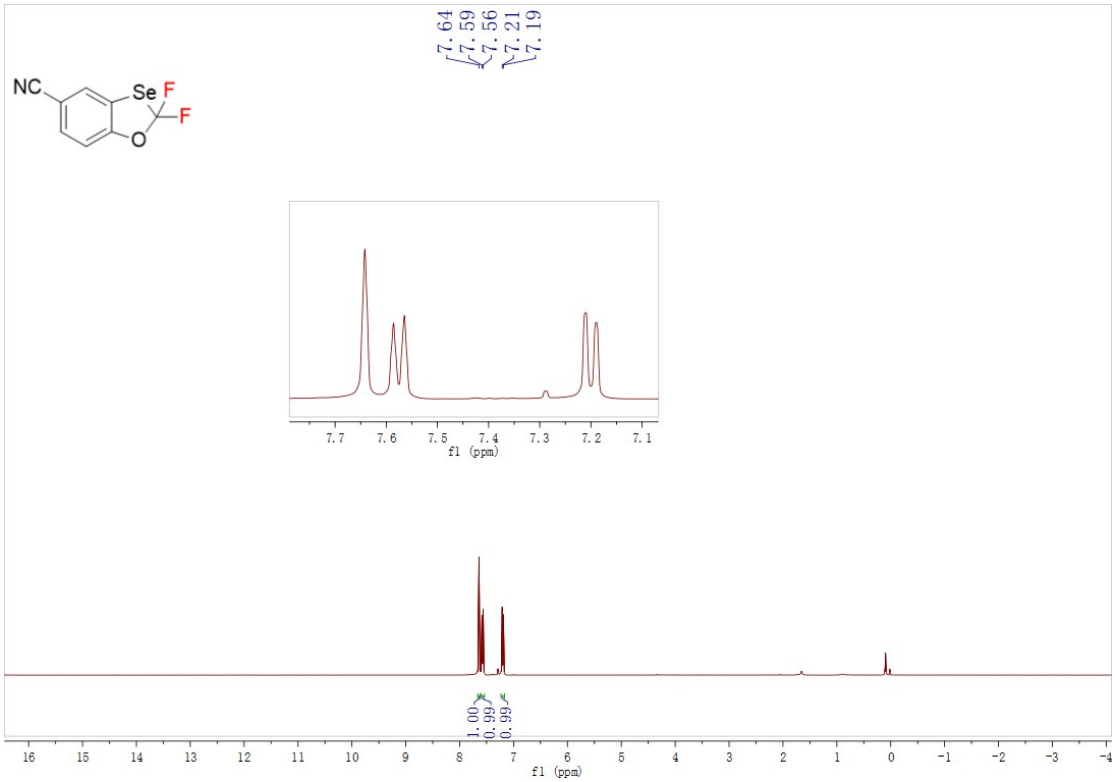
^{19}F NMR spectrum of **3g** in $CDCl_3$



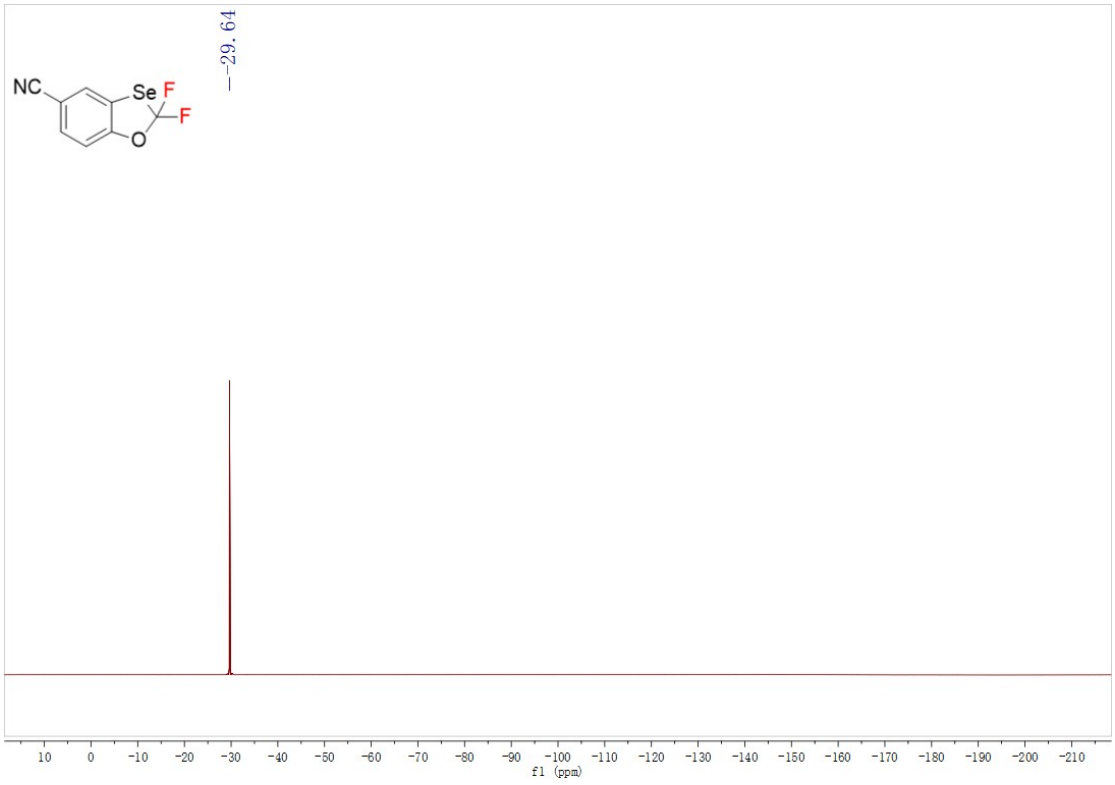
^{13}C NMR spectrum of **3g** in $CDCl_3$



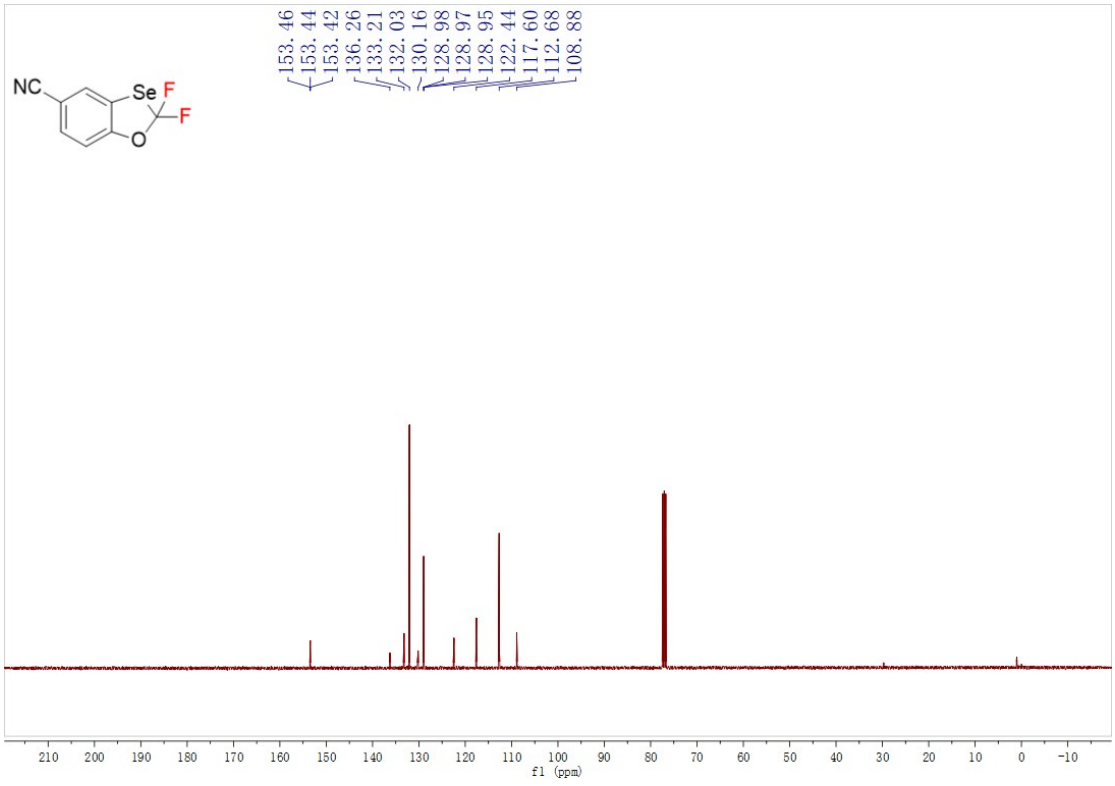
^{1}H NMR spectrum of **3j** in $CDCl_3$



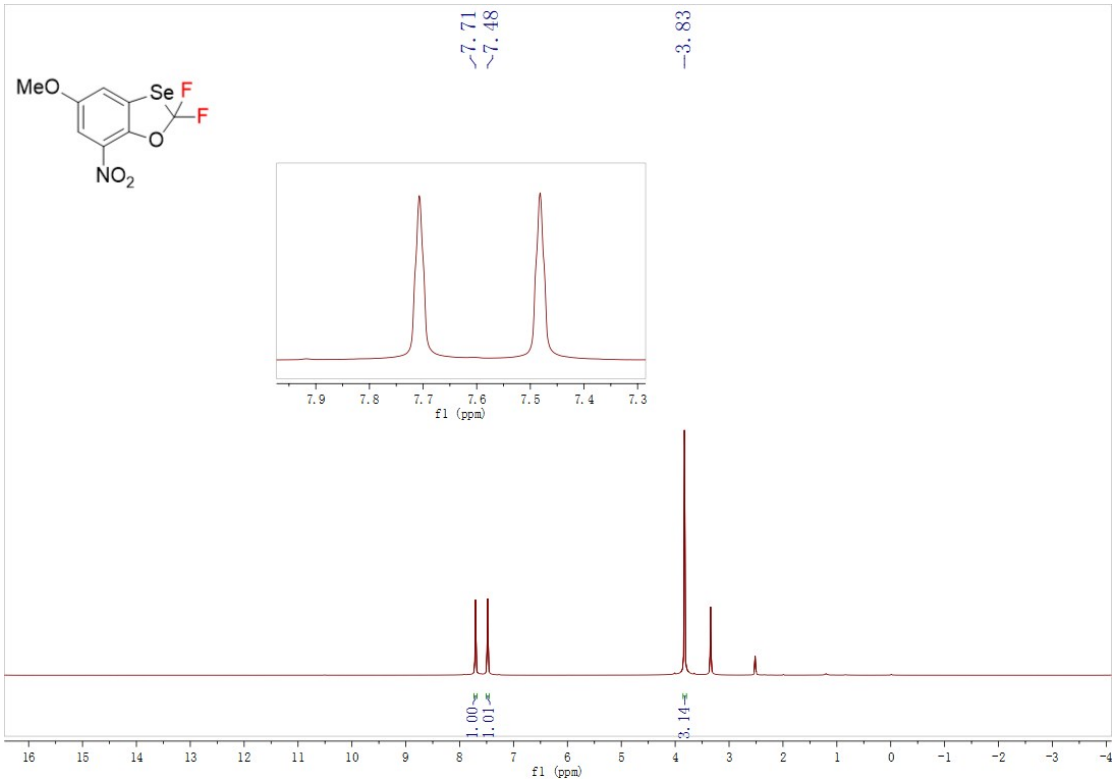
^{19}F NMR spectrum of **3j** in $CDCl_3$



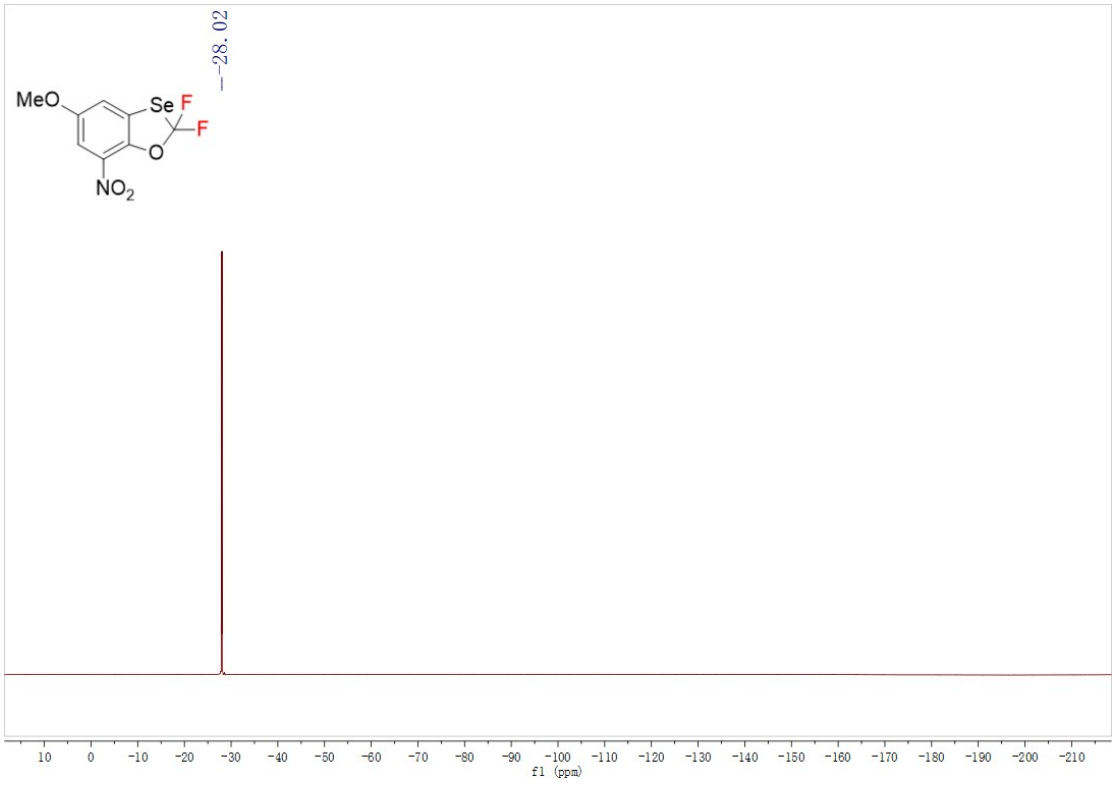
^{13}C NMR spectrum of **3j** in $CDCl_3$



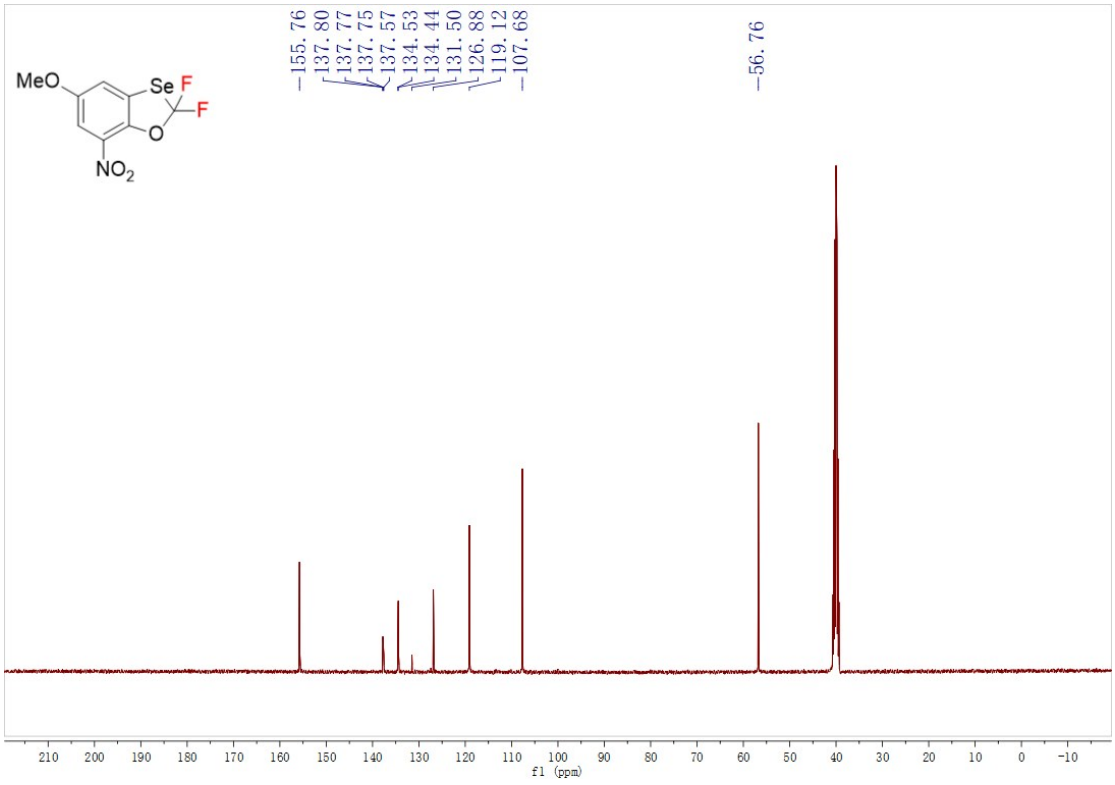
[1]H NMR spectrum of **3k** in DMSO-d_6



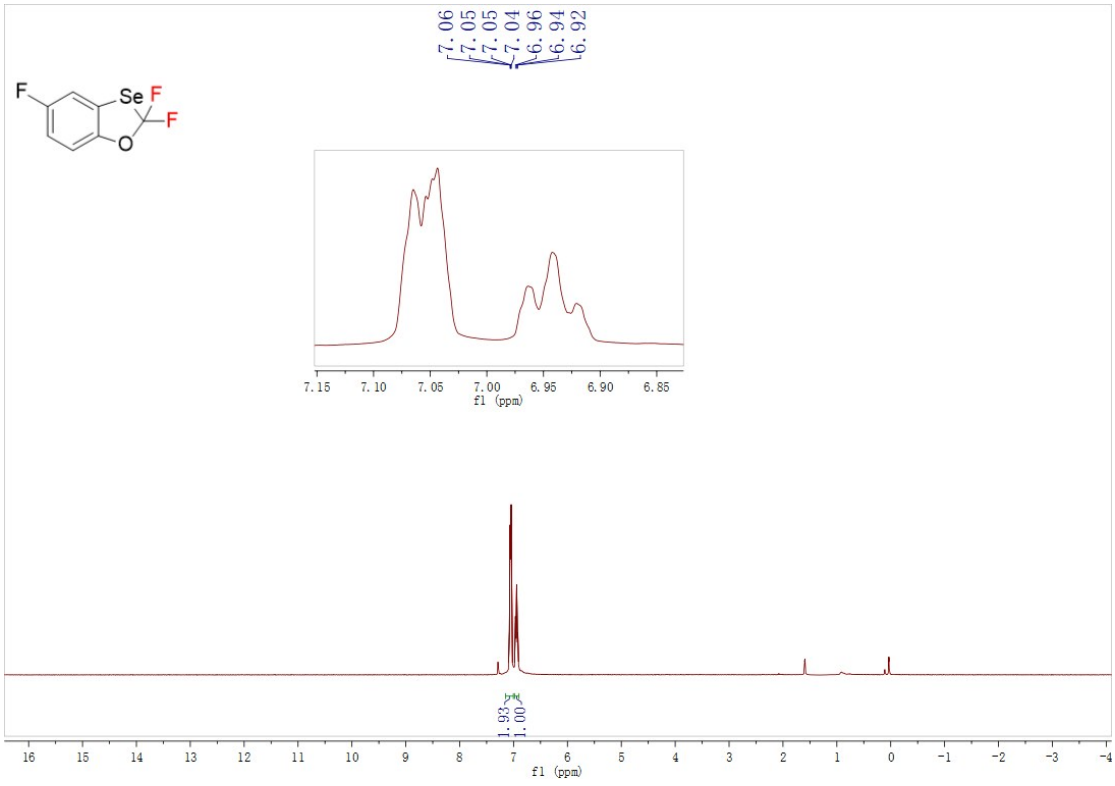
[19]F NMR spectrum of **3k** in DMSO-d_6



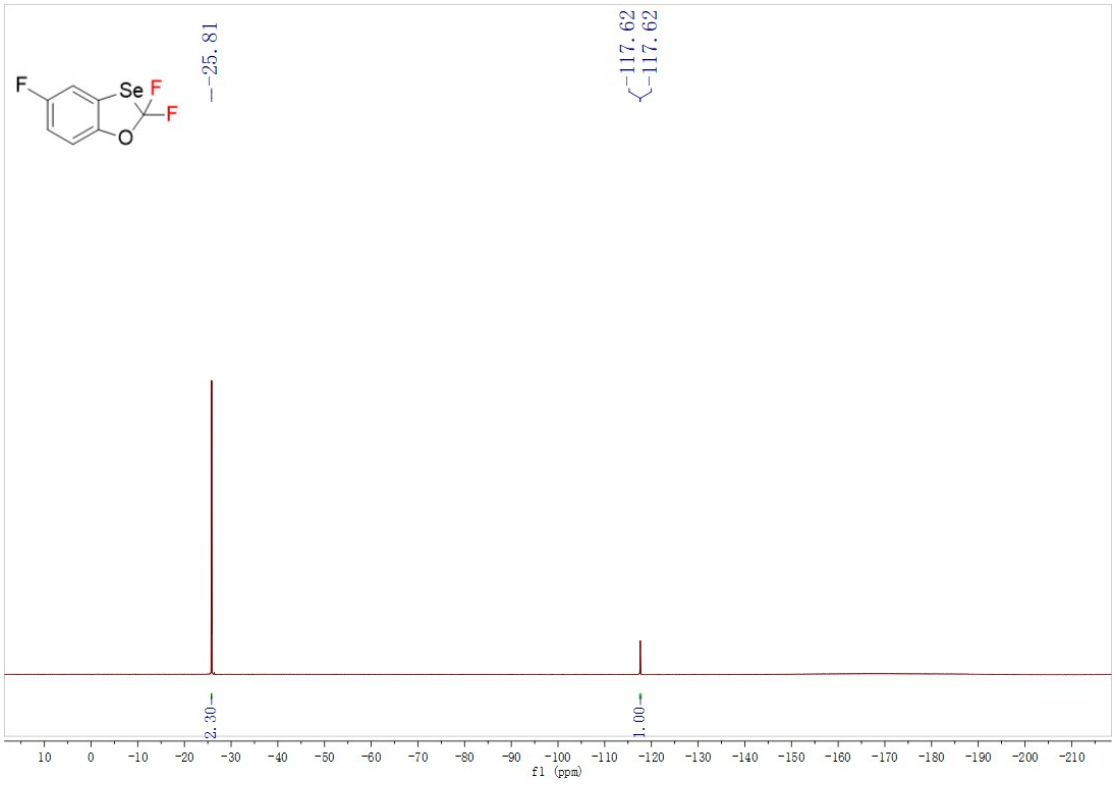
^{13}C NMR spectrum of **3k** in DMSO-d_6



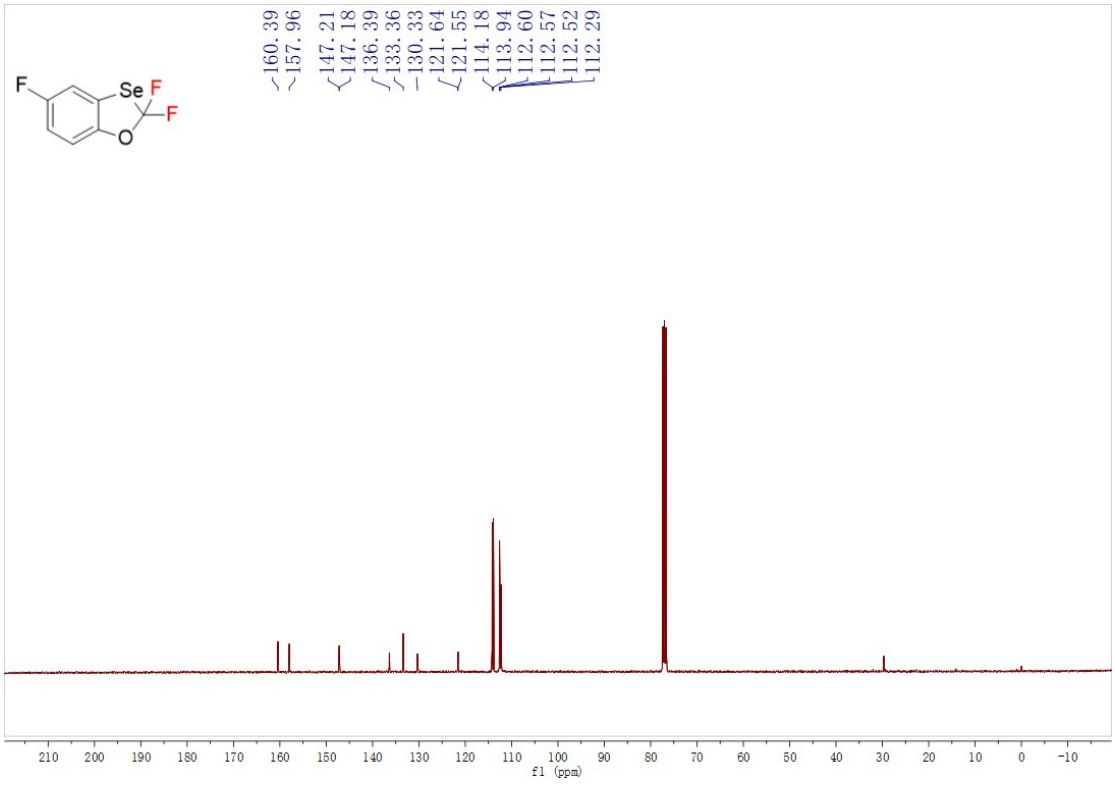
^{1}H NMR spectrum of **3m** in $CDCl_3$



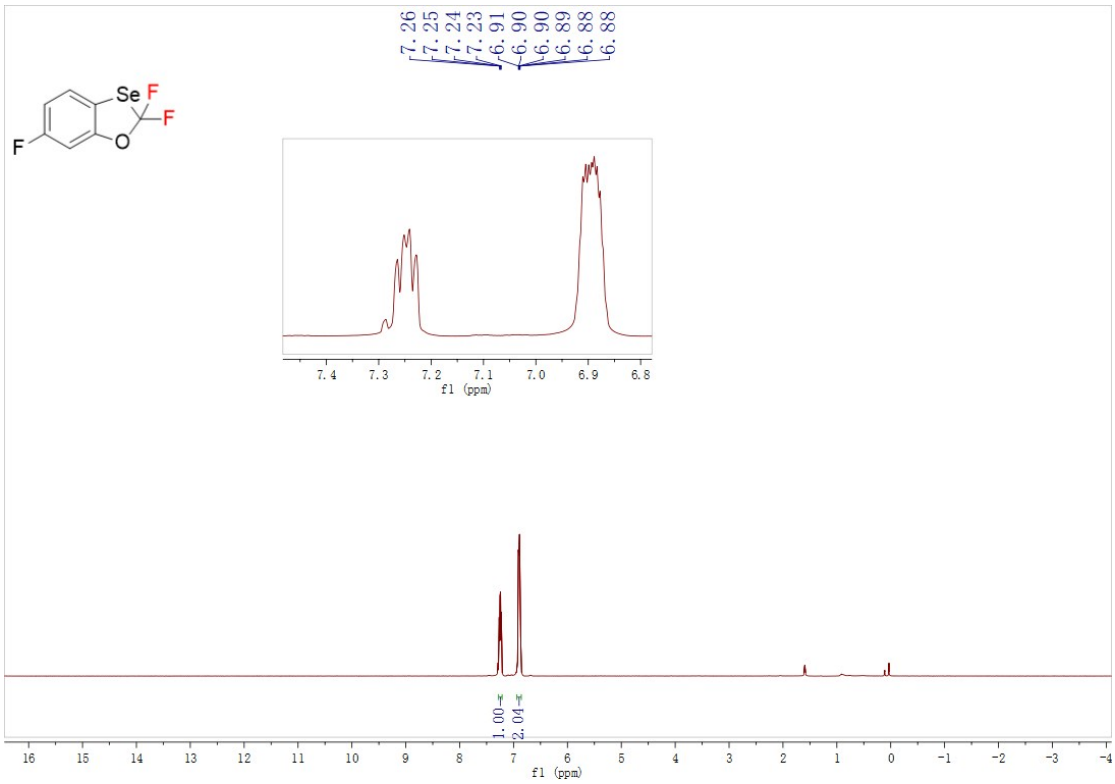
^{19}F NMR spectrum of **3m** in $CDCl_3$



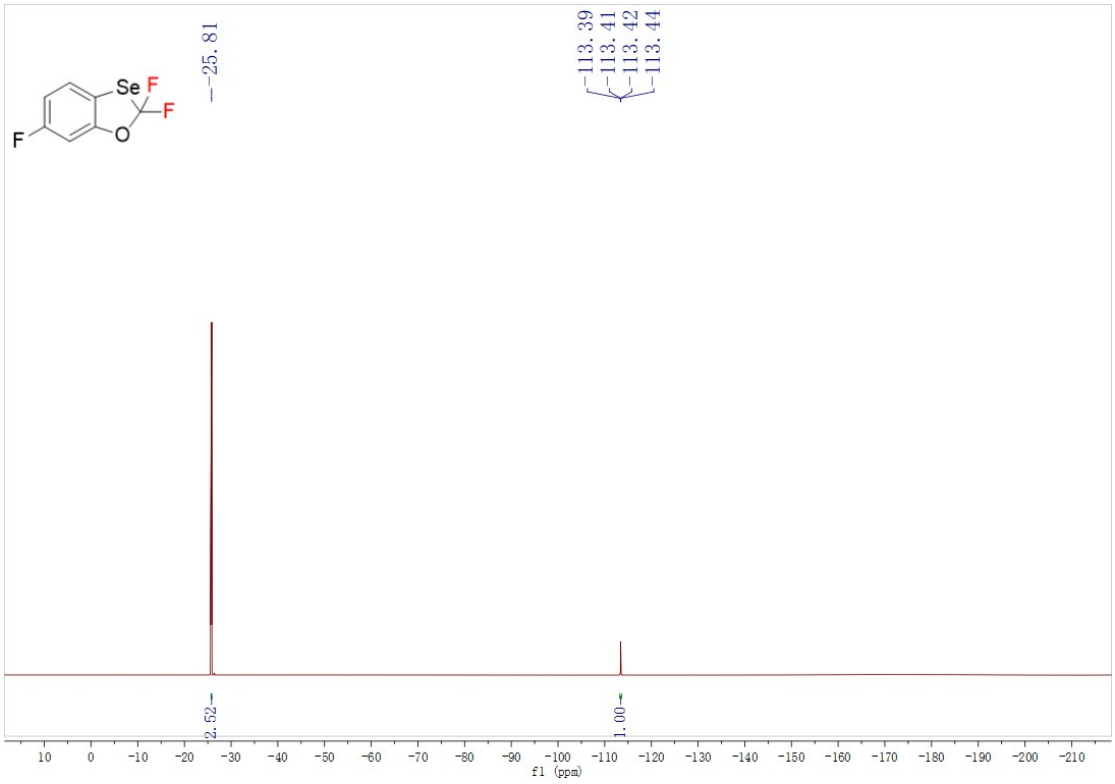
^{13}C NMR spectrum of **3m** in $CDCl_3$



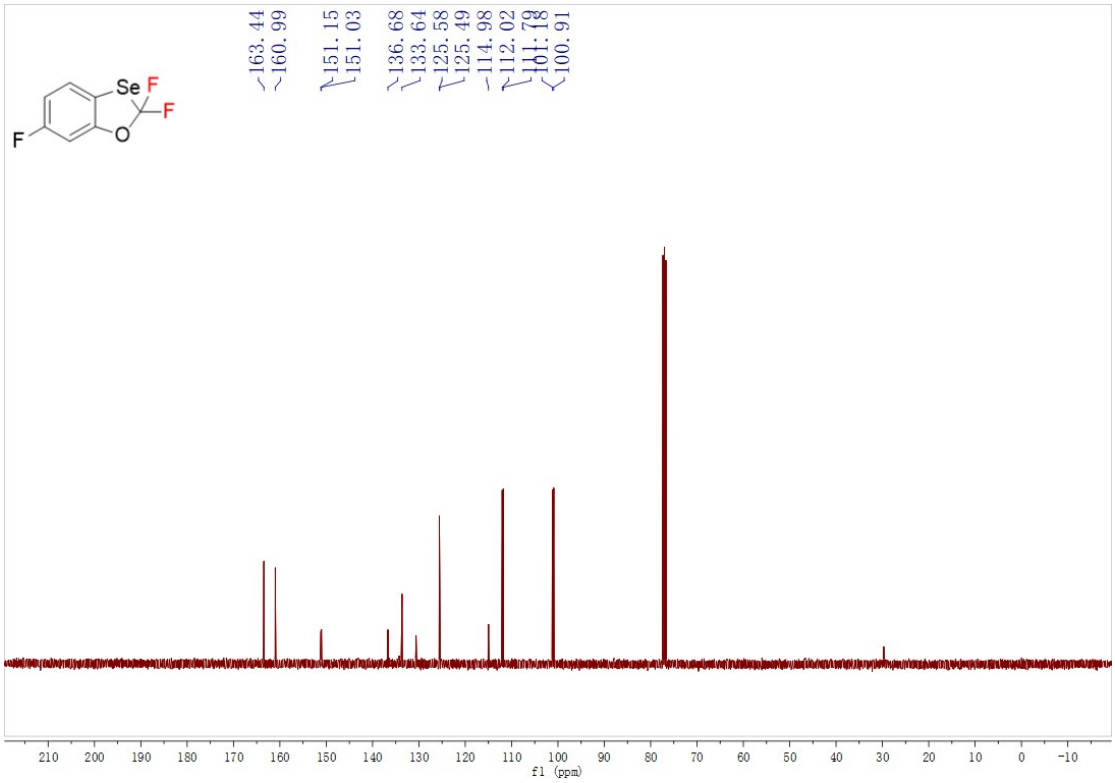
^{1}H NMR spectrum of **3n** in $CDCl_3$



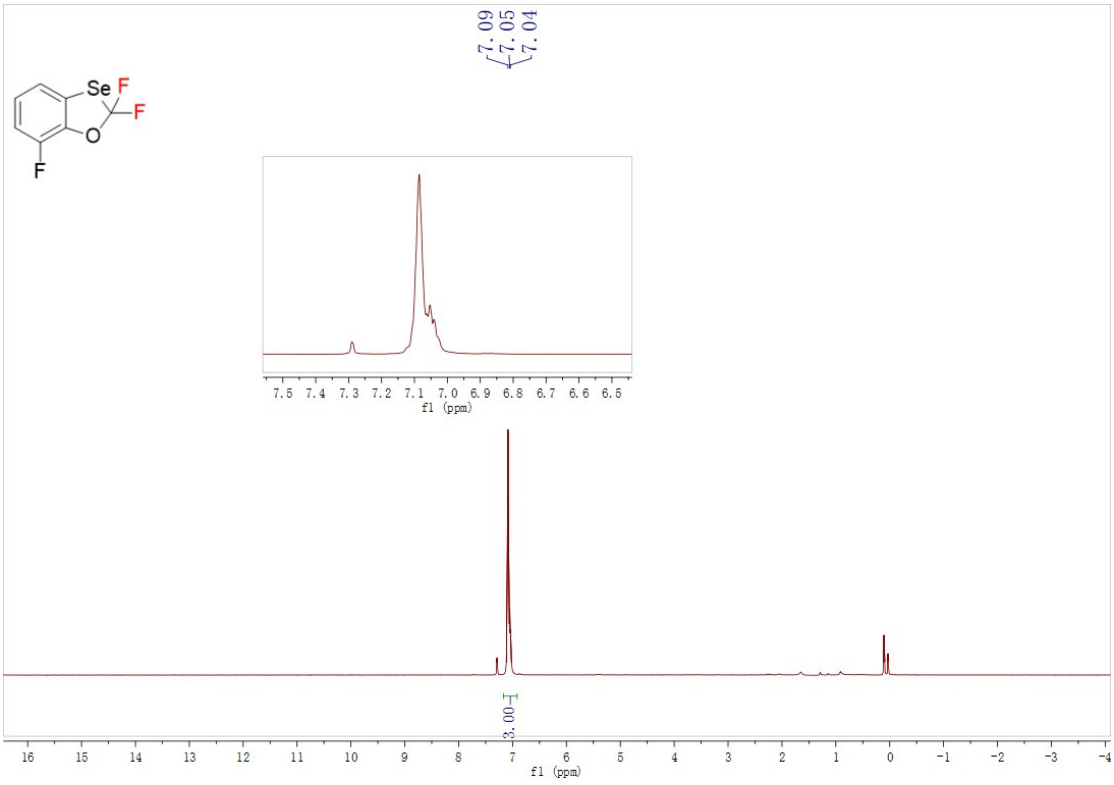
^{19}F NMR spectrum of **3n** in $CDCl_3$



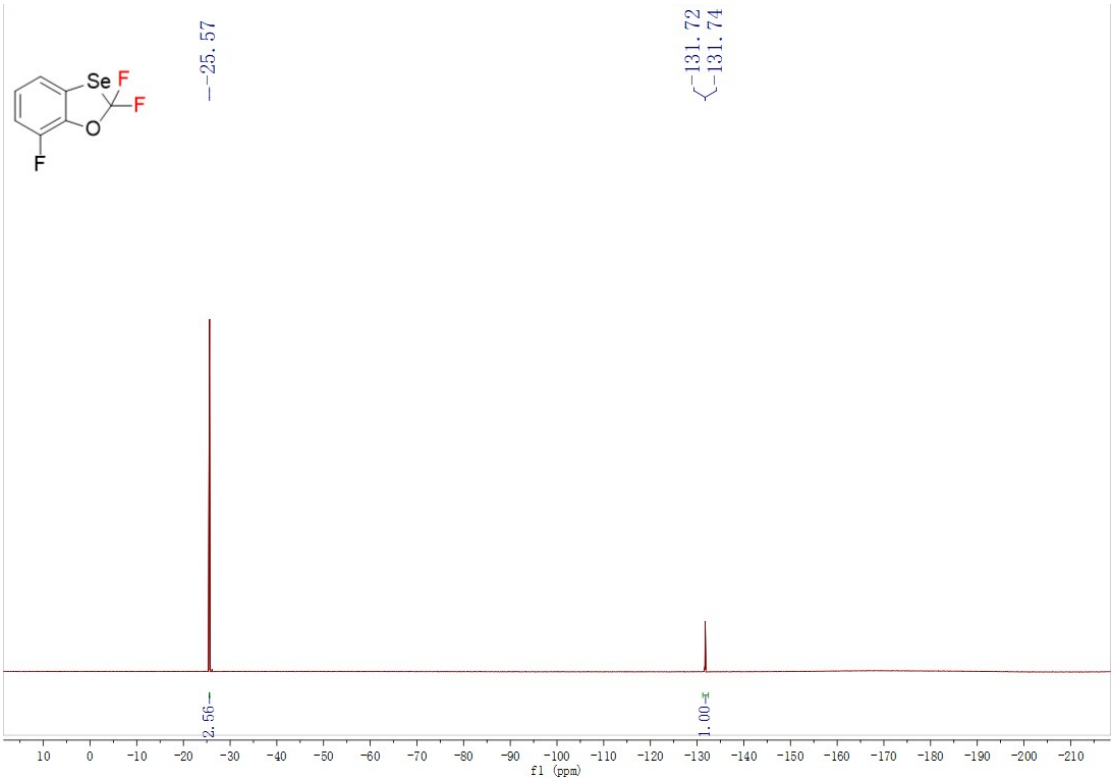
^{13}C NMR spectrum of **3n** in $CDCl_3$



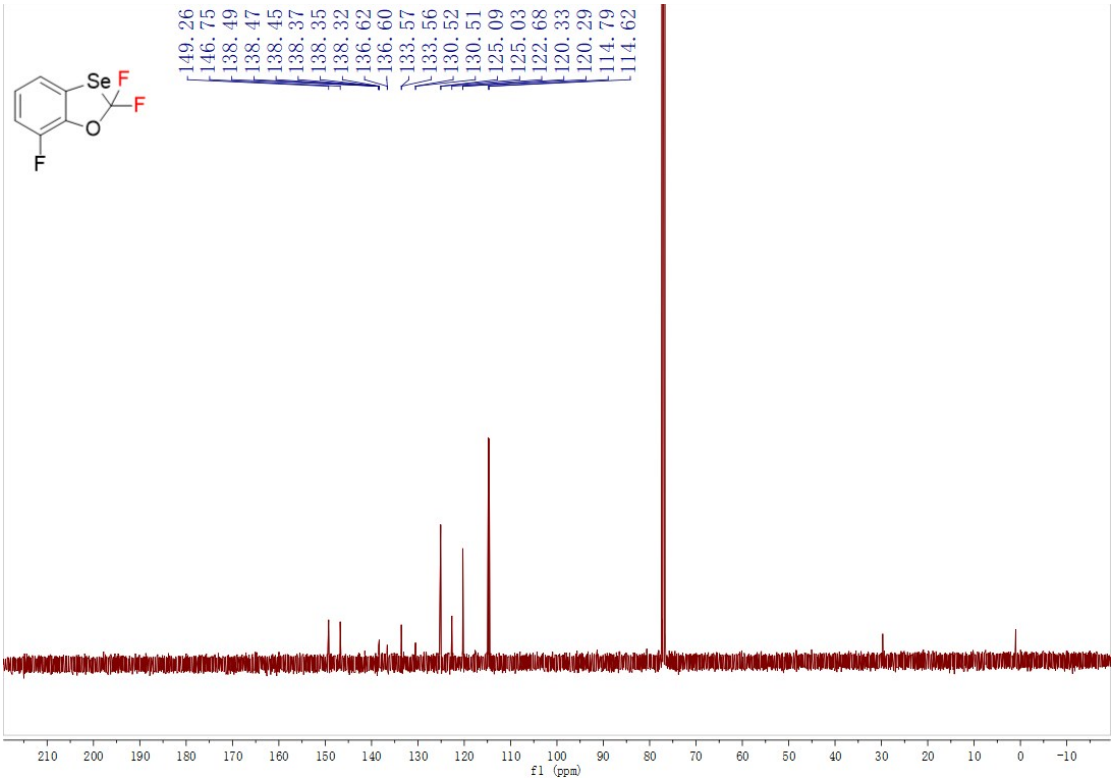
^{1}H NMR spectrum of **3o** in $CDCl_3$



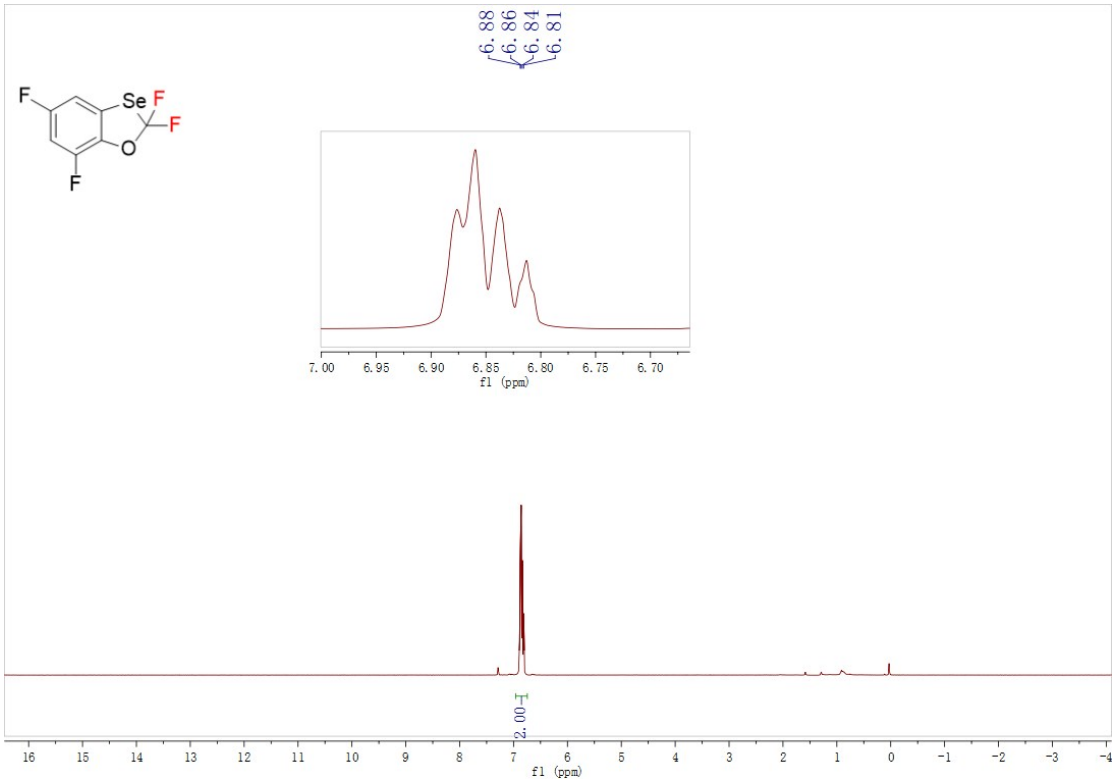
^{19}F NMR spectrum of **3o** in $CDCl_3$



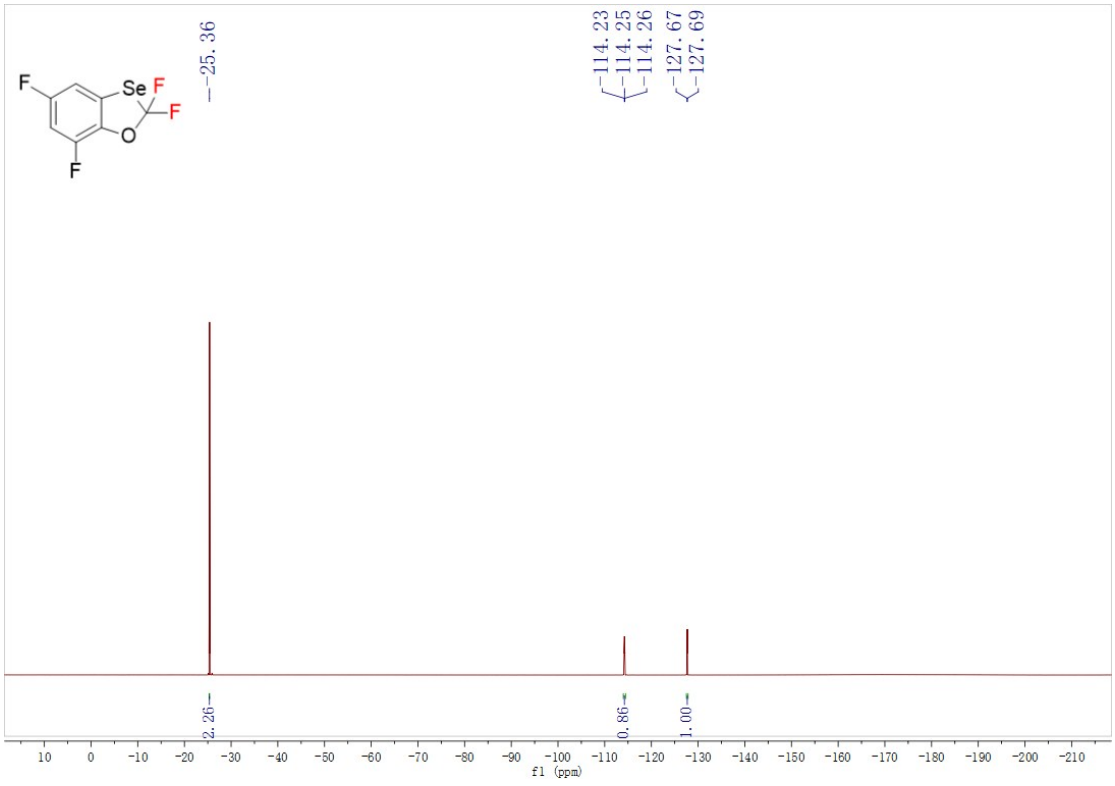
^{13}C NMR spectrum of **3o** in $CDCl_3$



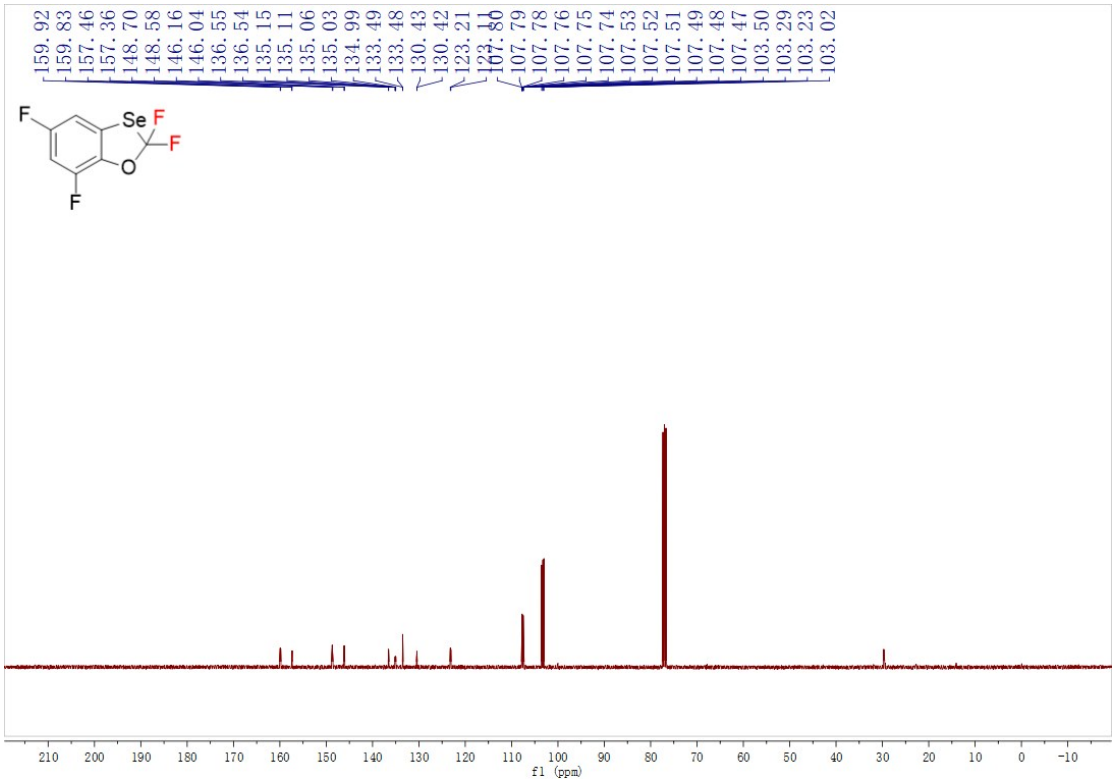
^{1}H NMR spectrum of **3p** in $CDCl_3$



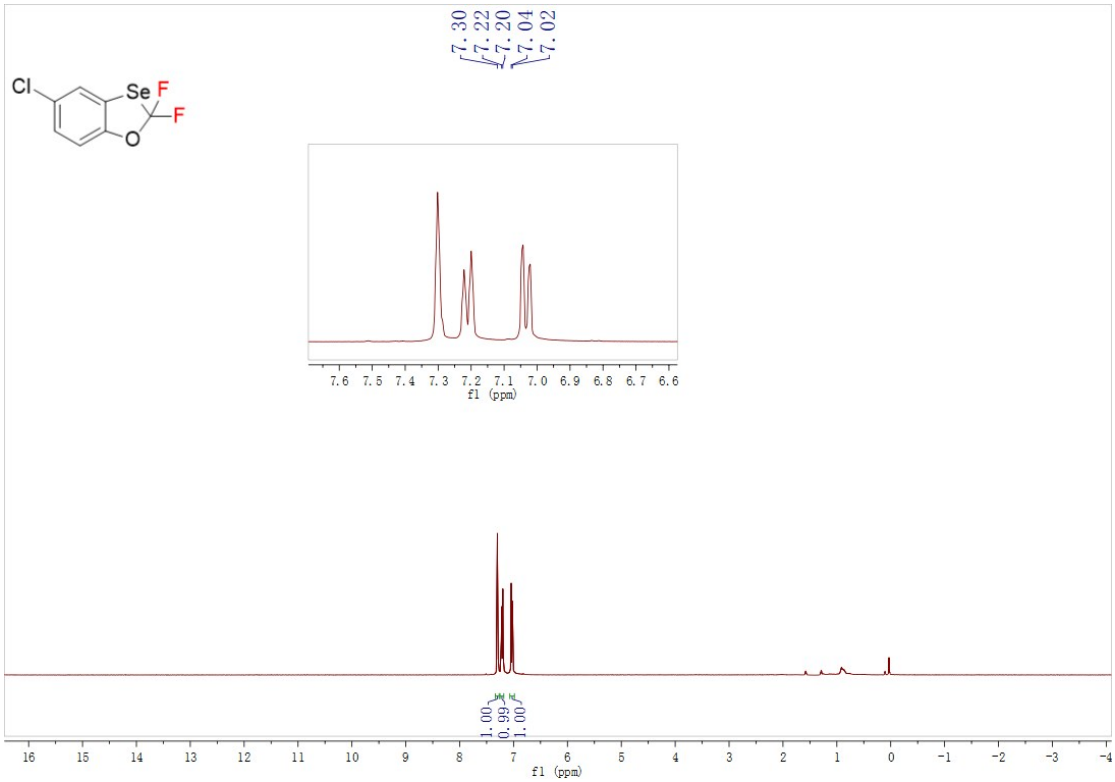
^{19}F NMR spectrum of **3p** in $CDCl_3$



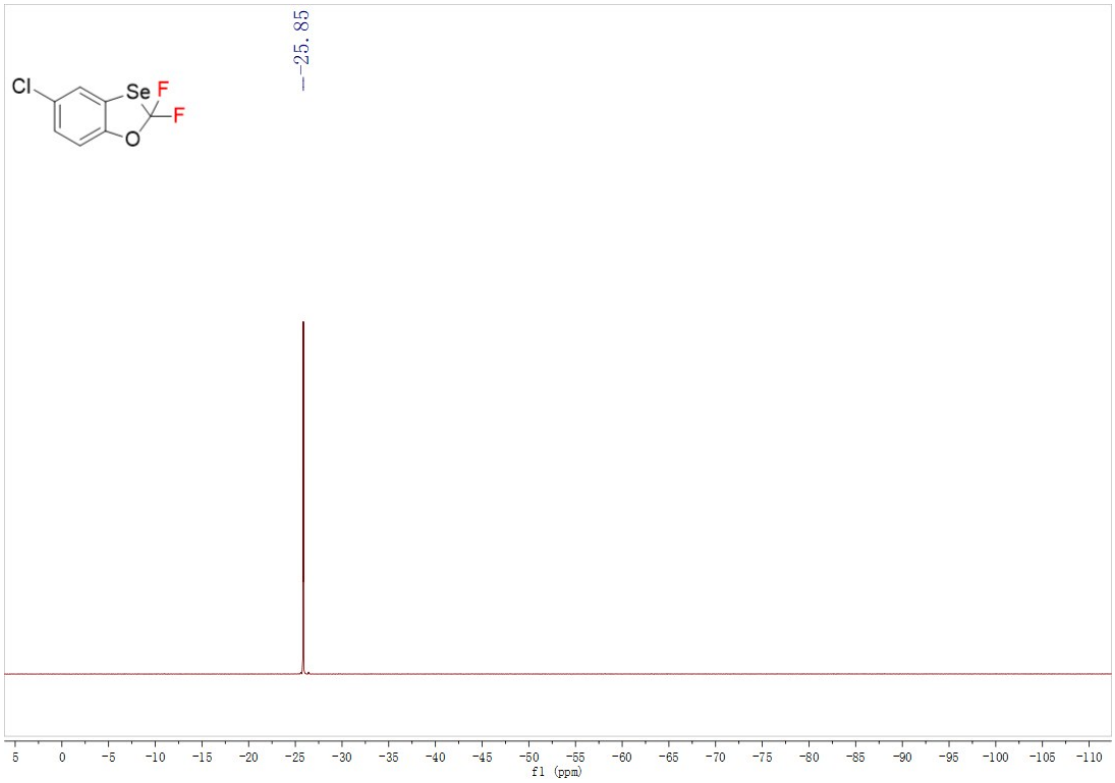
^{13}C NMR spectrum of **3p** in $CDCl_3$



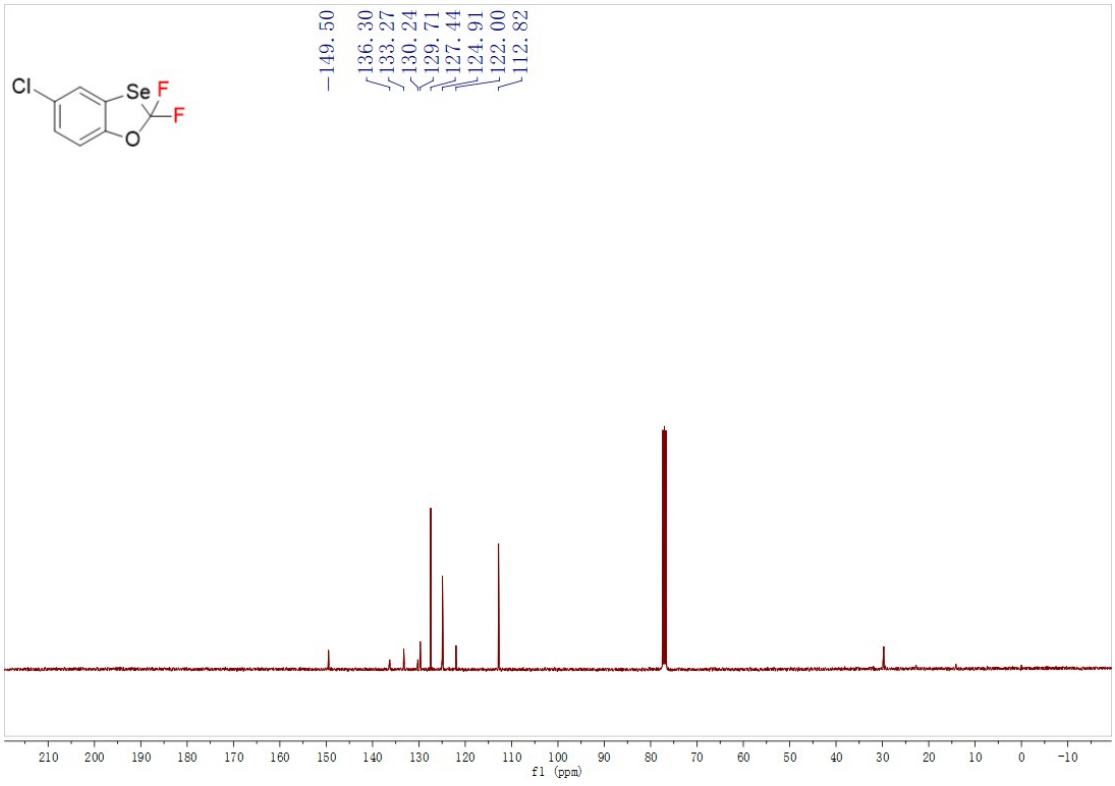
^{1}H NMR spectrum of **3q** in $CDCl_3$



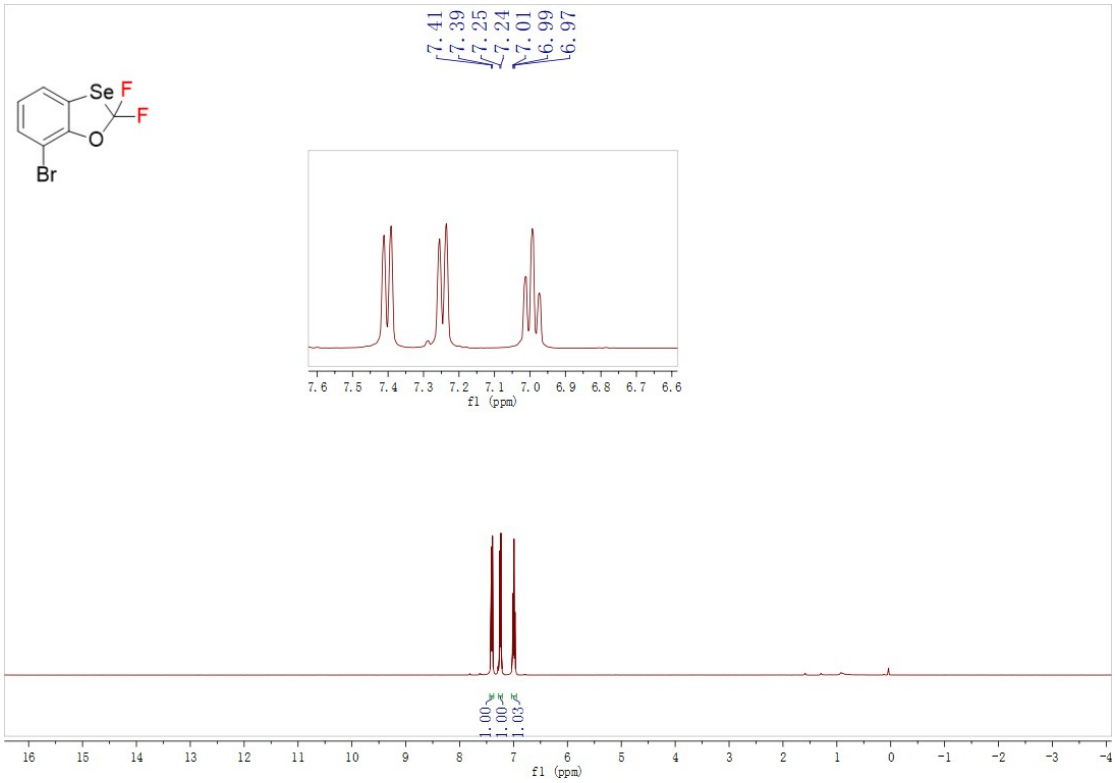
^{19}F NMR spectrum of **3q** in $CDCl_3$



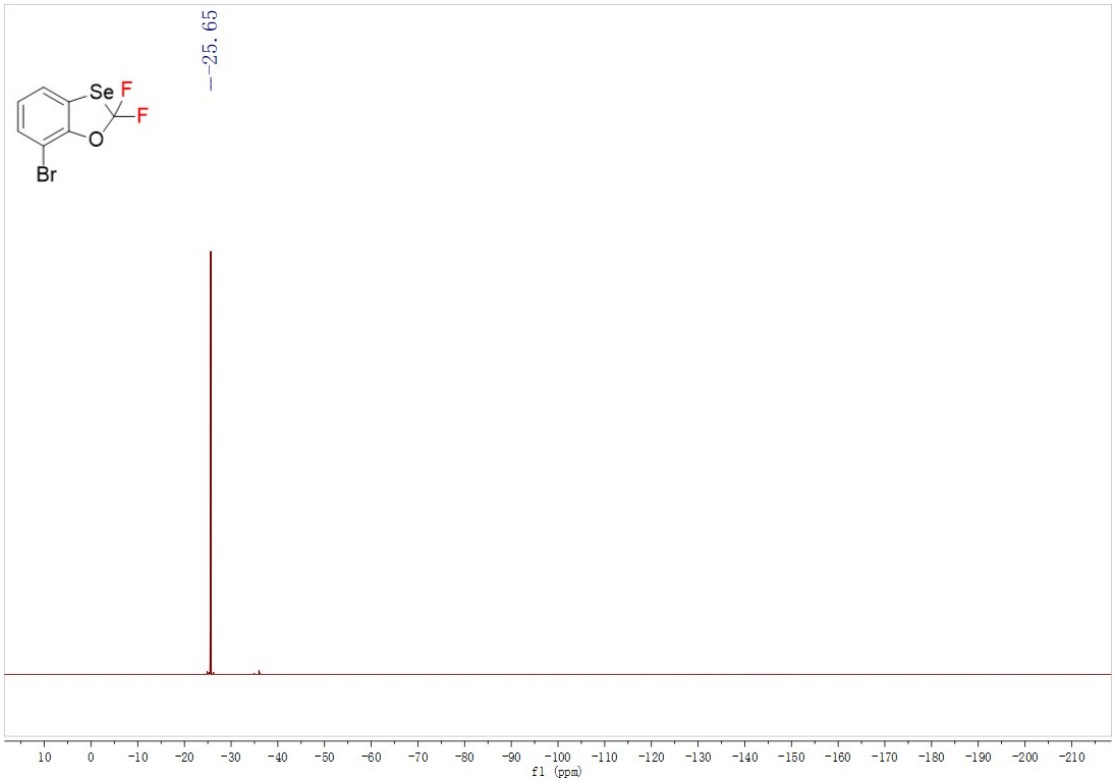
^{13}C NMR spectrum of **3q** in $CDCl_3$



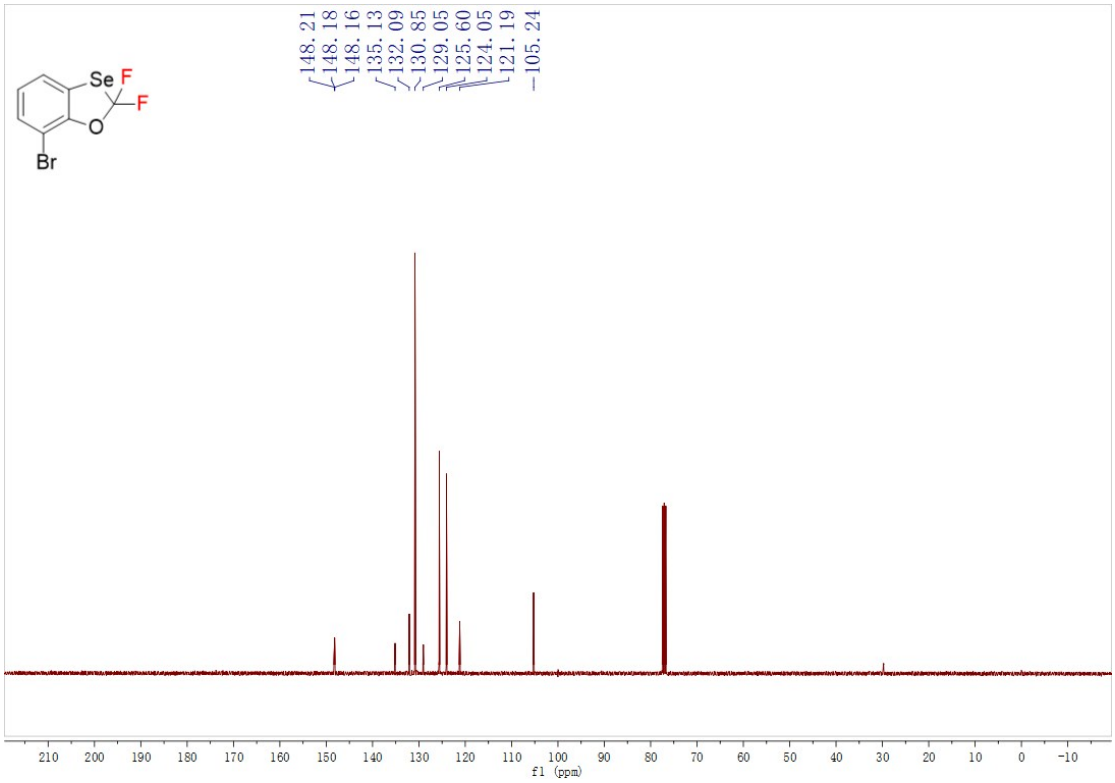
^{1}H NMR spectrum of **3r** in $CDCl_3$



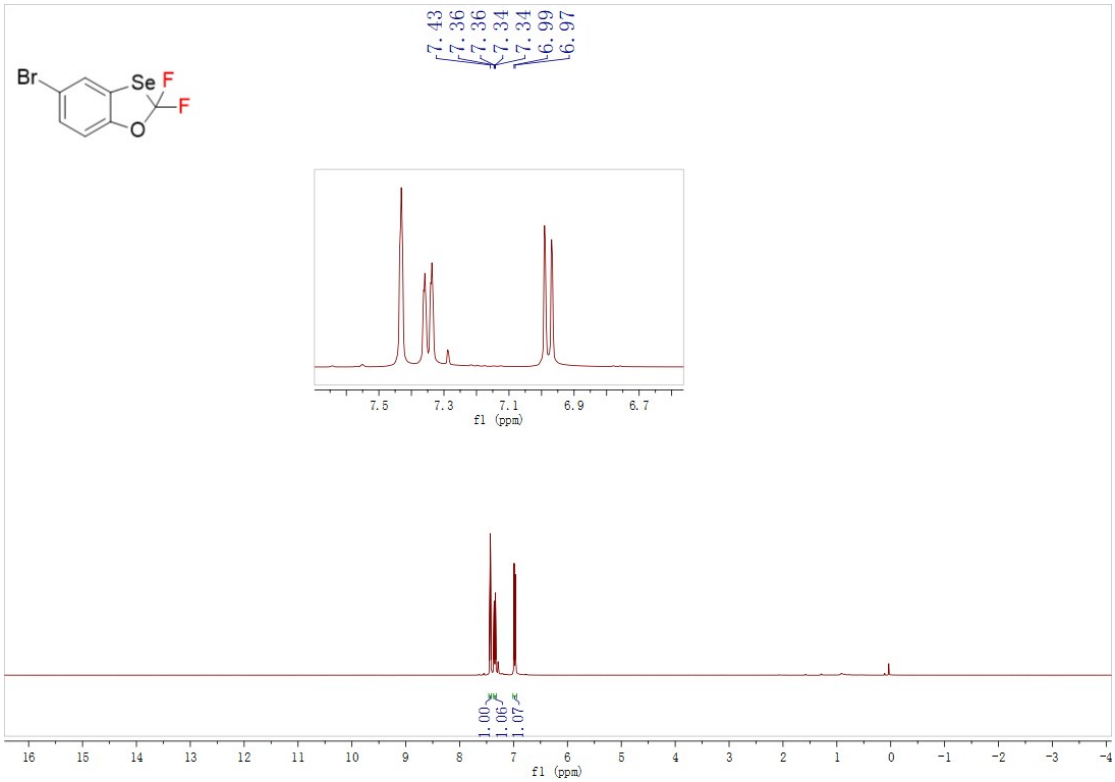
^{19}F NMR spectrum of **3r** in $CDCl_3$



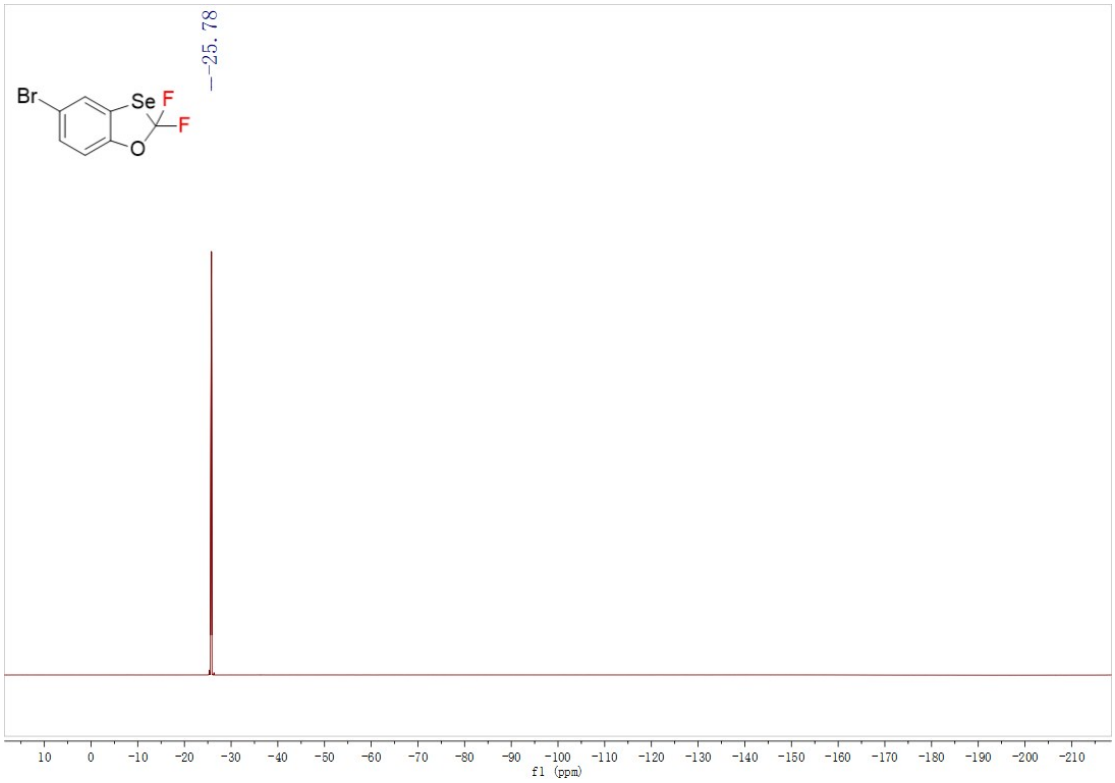
^{13}C NMR spectrum of **3r** in $CDCl_3$



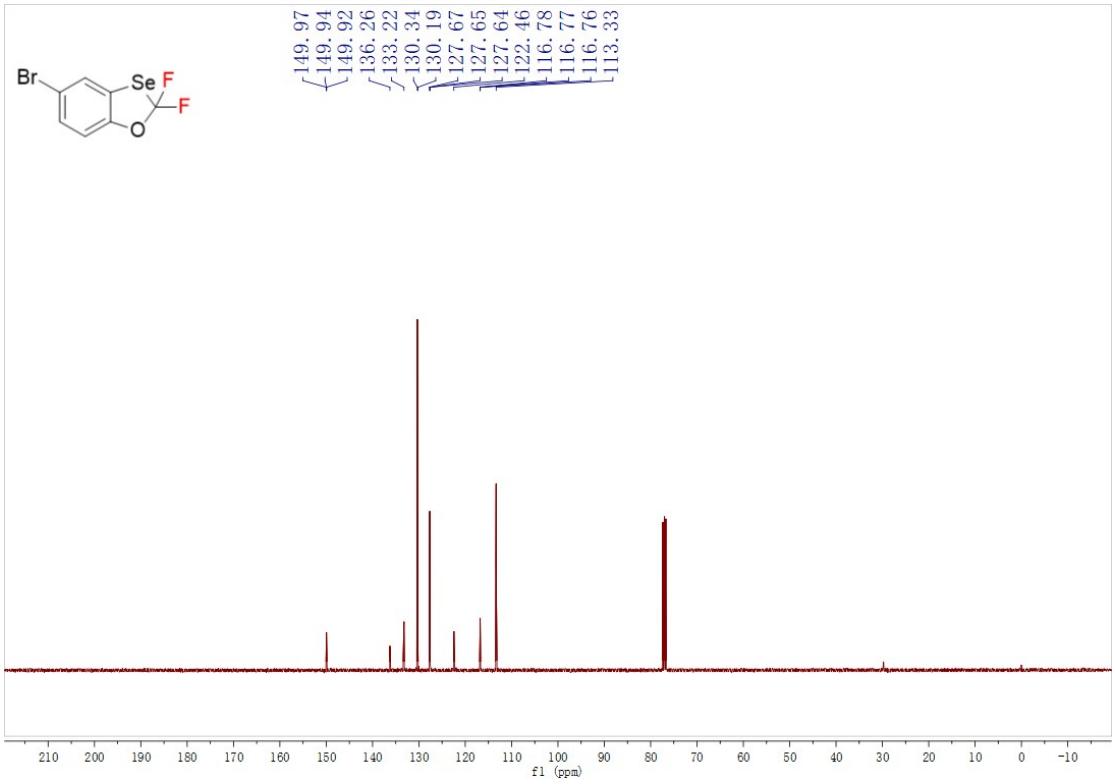
^{1}H NMR spectrum of **3s** in $CDCl_3$



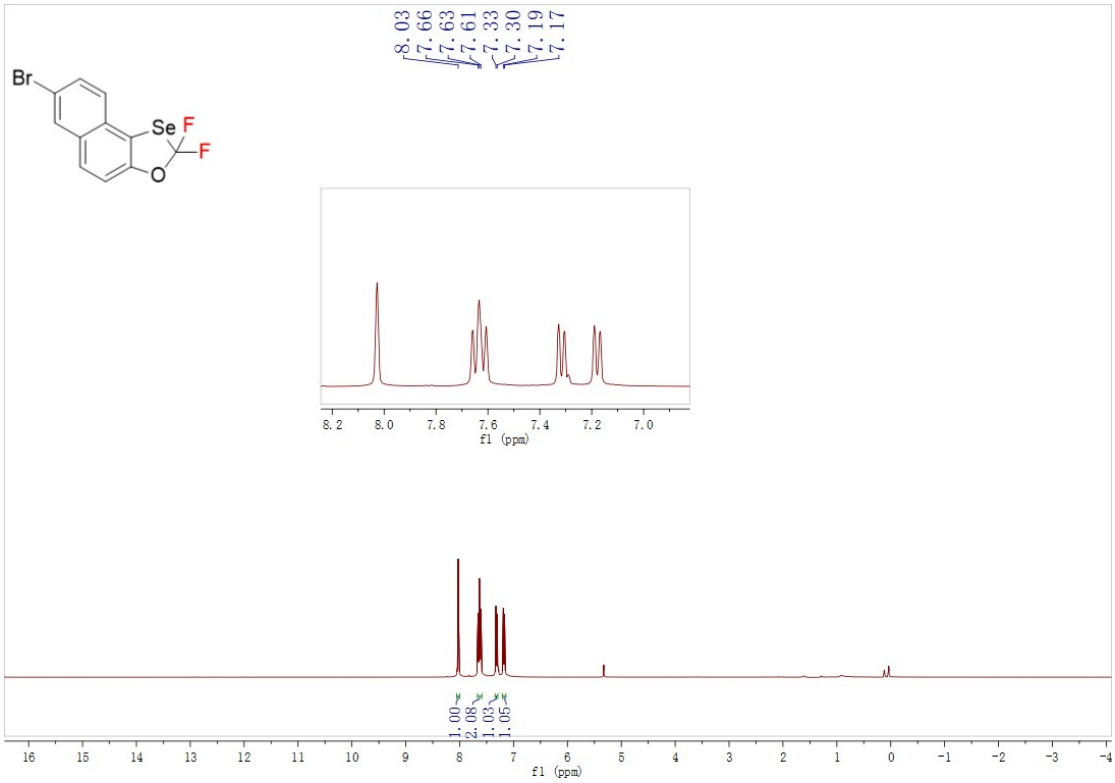
^{19}F NMR spectrum of **3s** in $CDCl_3$



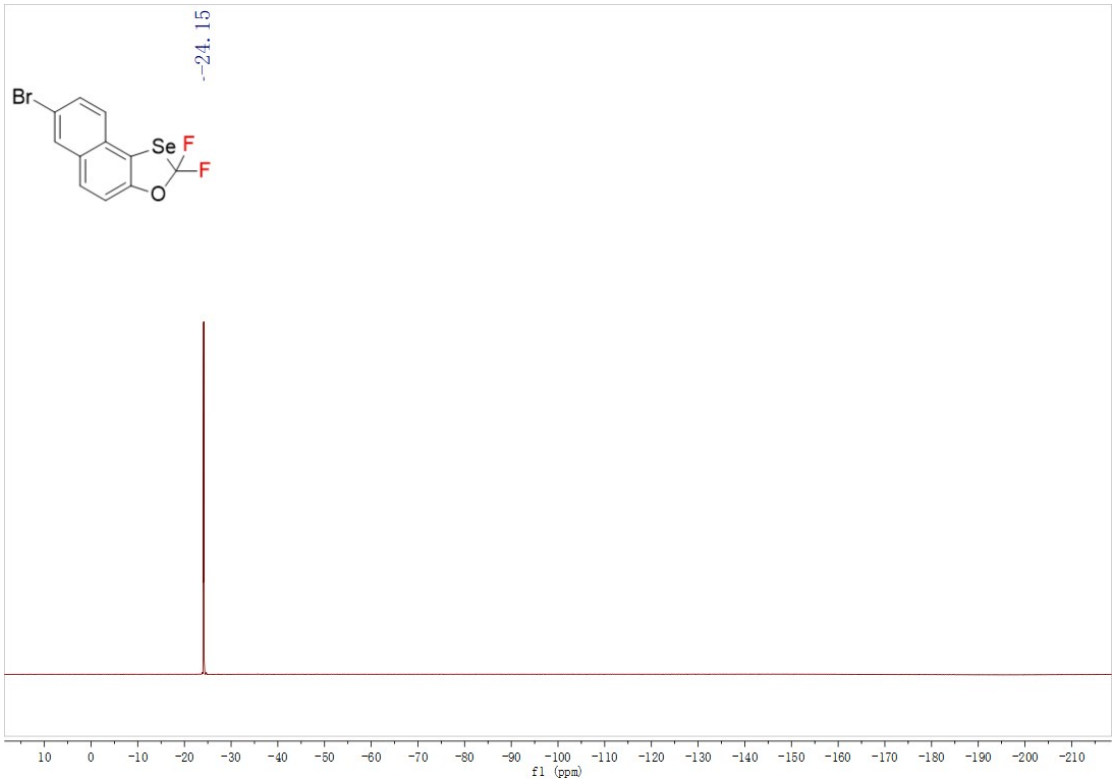
^{13}C NMR spectrum of **3s** in $CDCl_3$



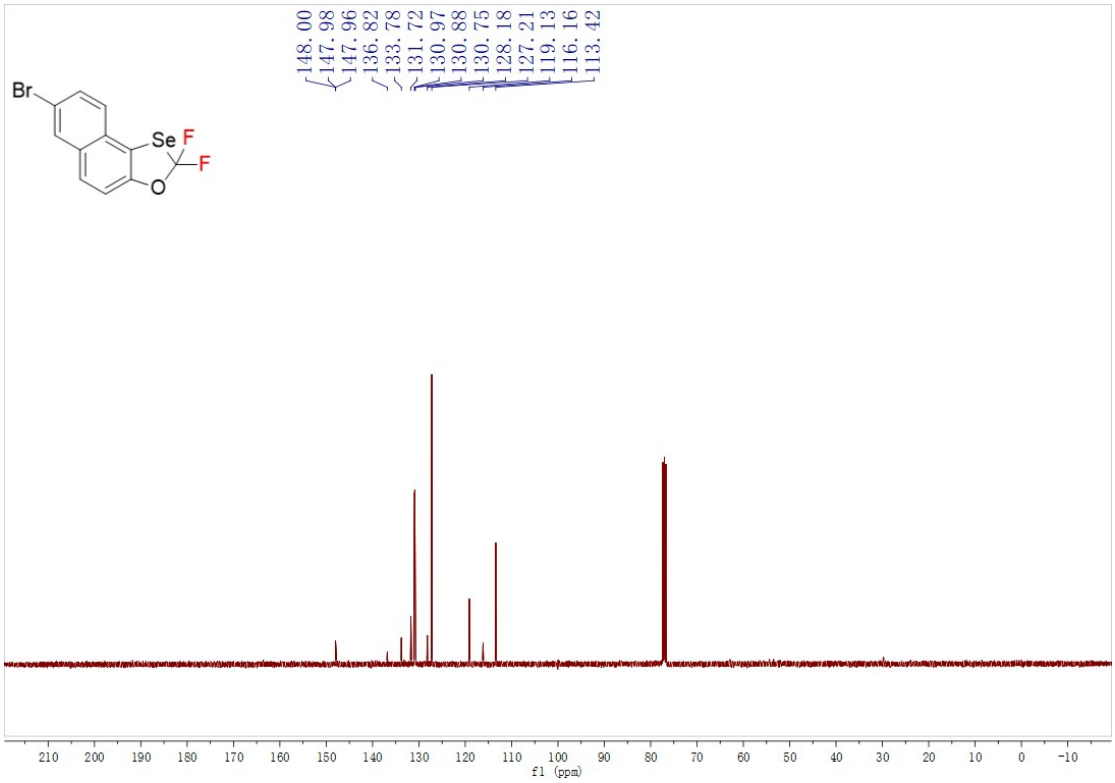
^{1}H NMR spectrum of **3u** in $CDCl_3$



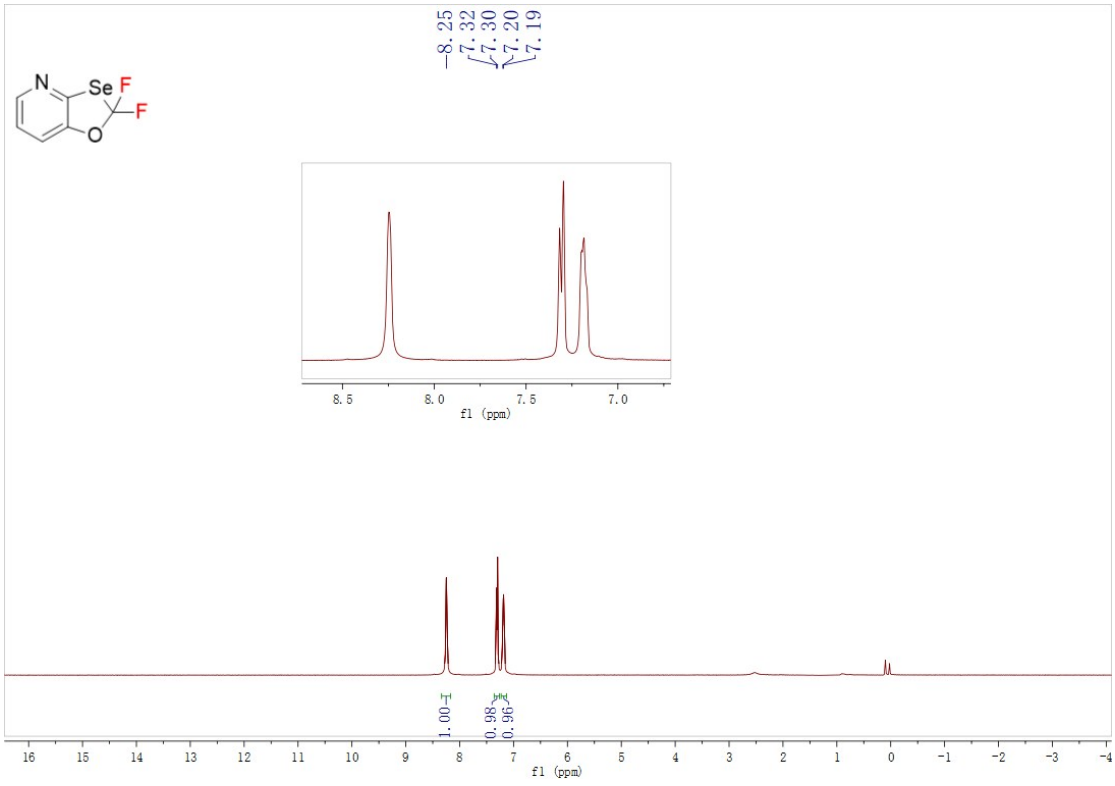
^{19}F NMR spectrum of **3u** in $CDCl_3$



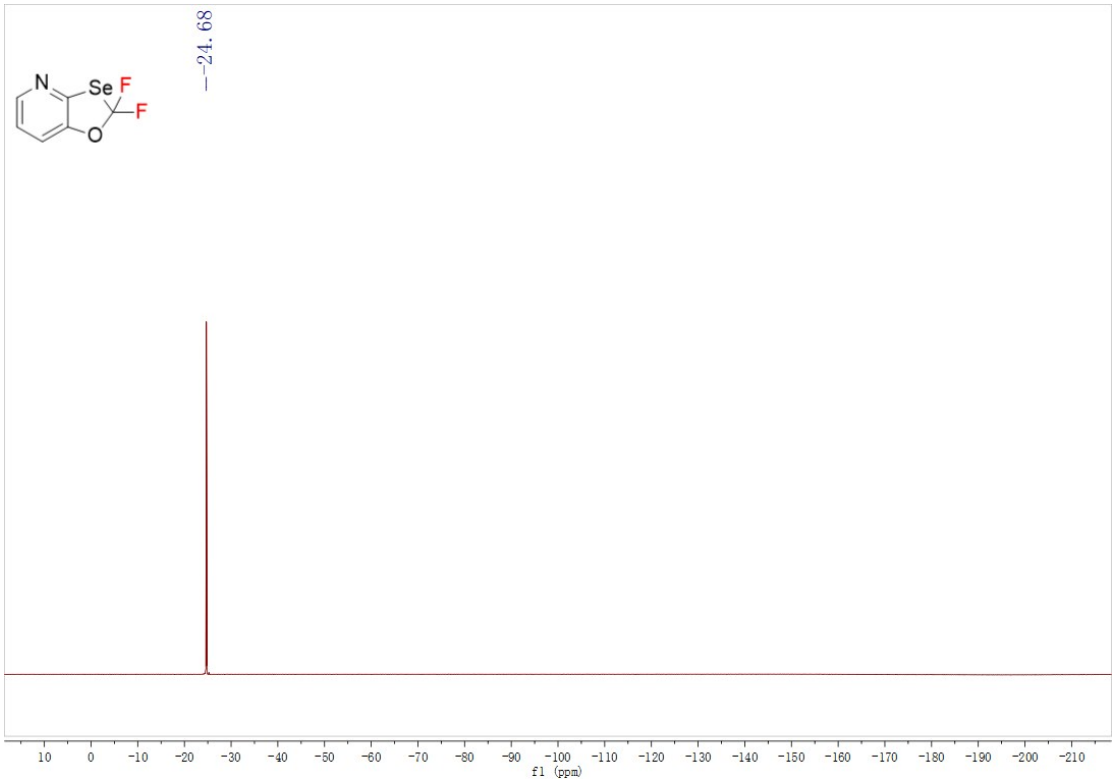
^{13}C NMR spectrum of **3u** in $CDCl_3$



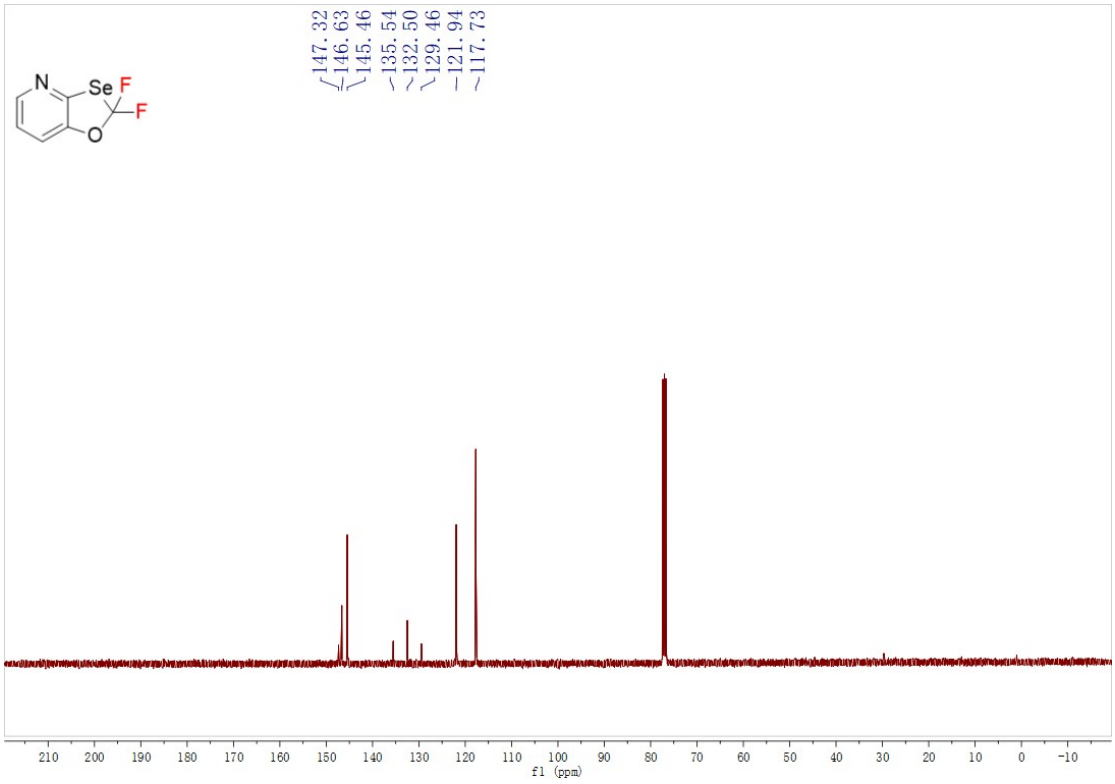
^{1}H NMR spectrum of **3w** in $CDCl_3$



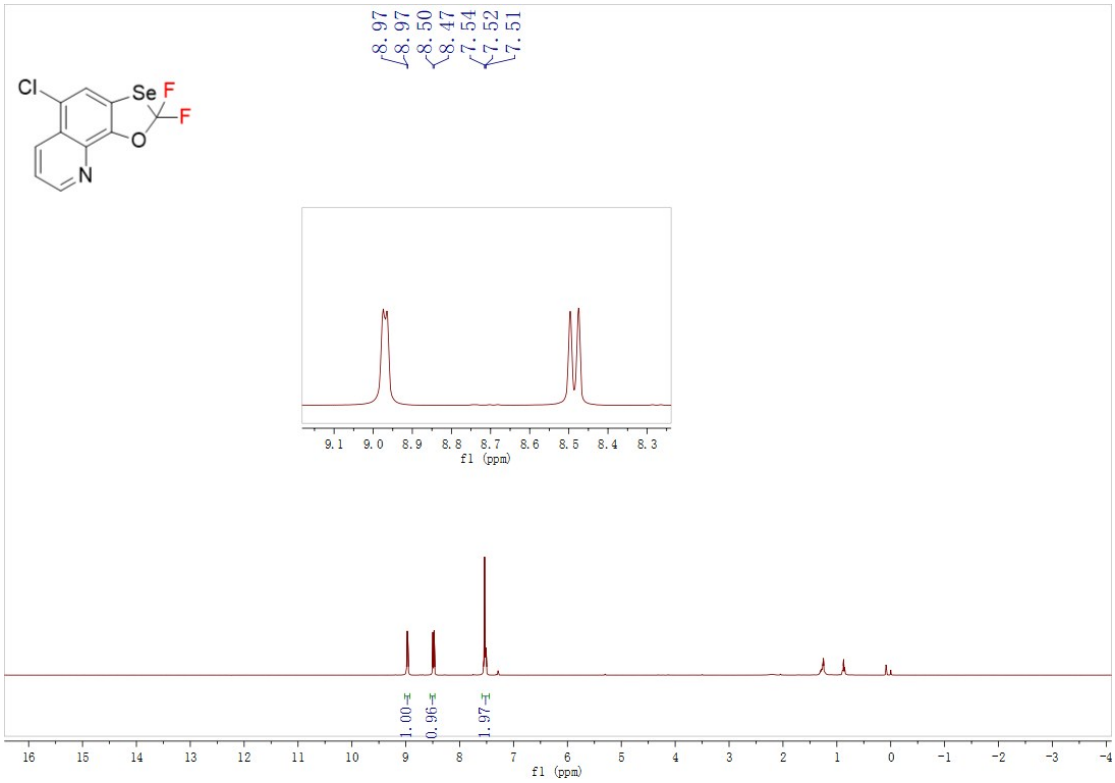
^{19}F NMR spectrum of **3w** in $CDCl_3$



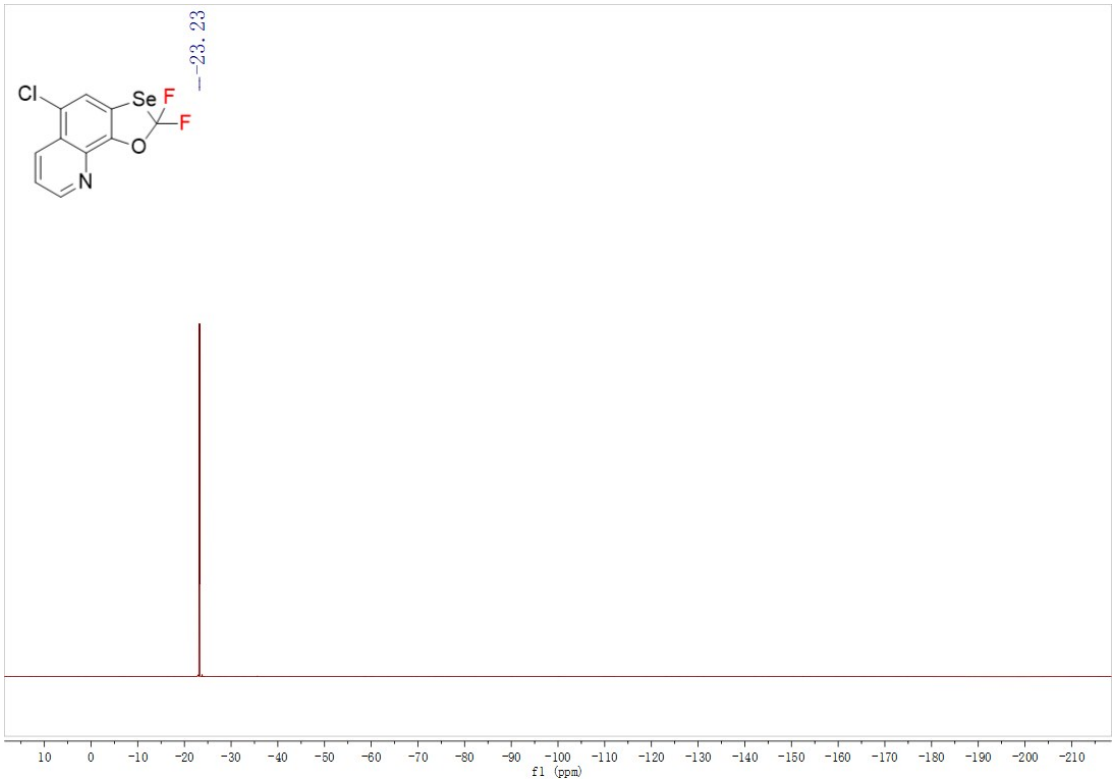
^{13}C NMR spectrum of **3w** in $CDCl_3$



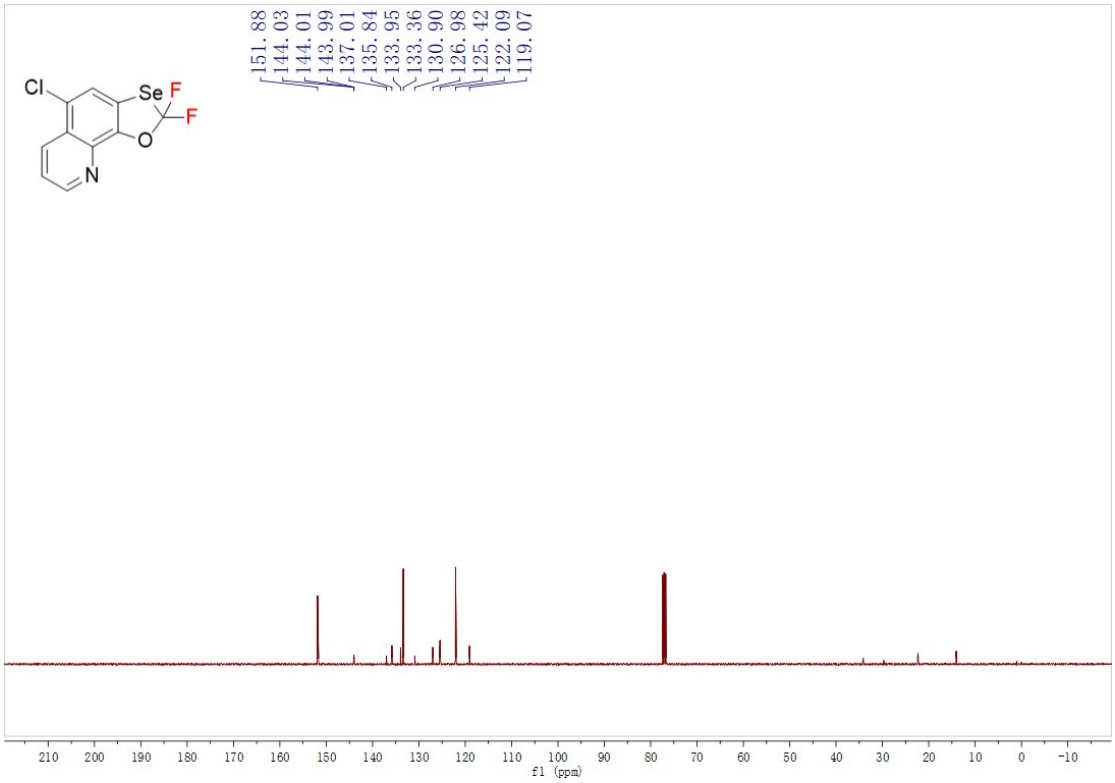
^{1}H NMR spectrum of **3x** in $CDCl_3$



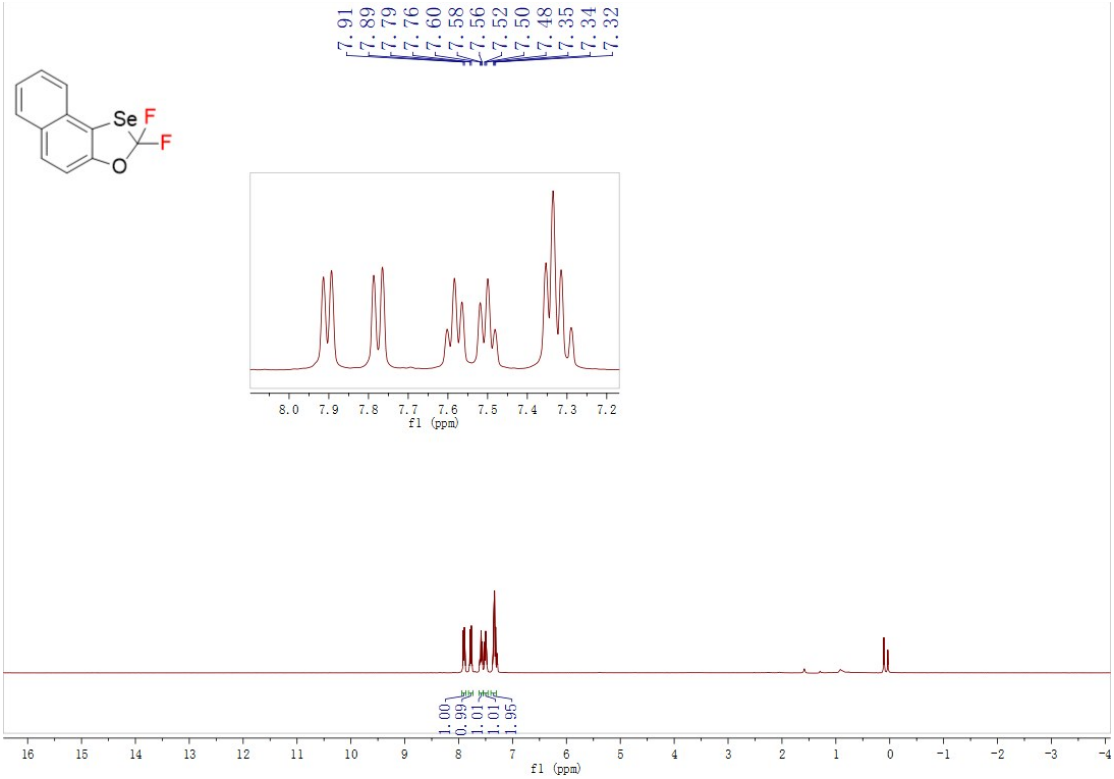
^{19}F NMR spectrum of **3x** in $CDCl_3$



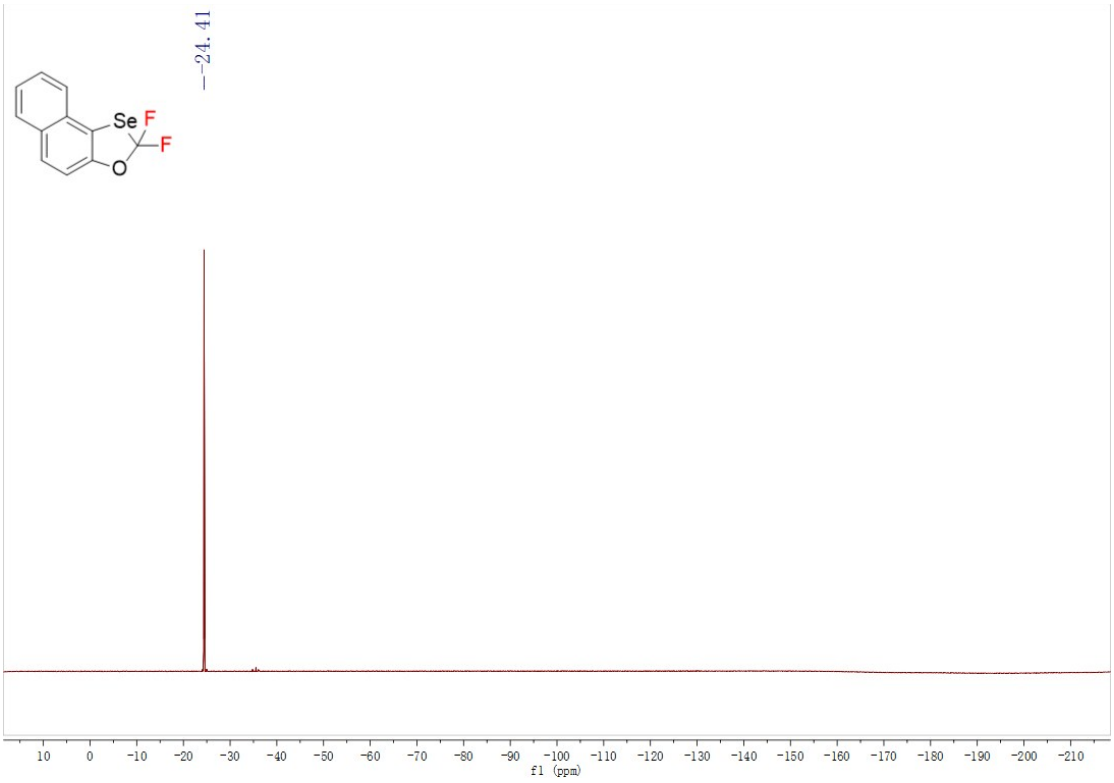
^{13}C NMR spectrum of **3x** in $CDCl_3$



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



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



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