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# Supporting Information

## Direct halosulfenylation of benzo[*b*]furans: a metal-free synthesis of 3-halo-2-thiobenzo[*b*]furans

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† These authors contributed equally.

# 1. Copies of $^{1}$H and $^{13}$CNMR spectra

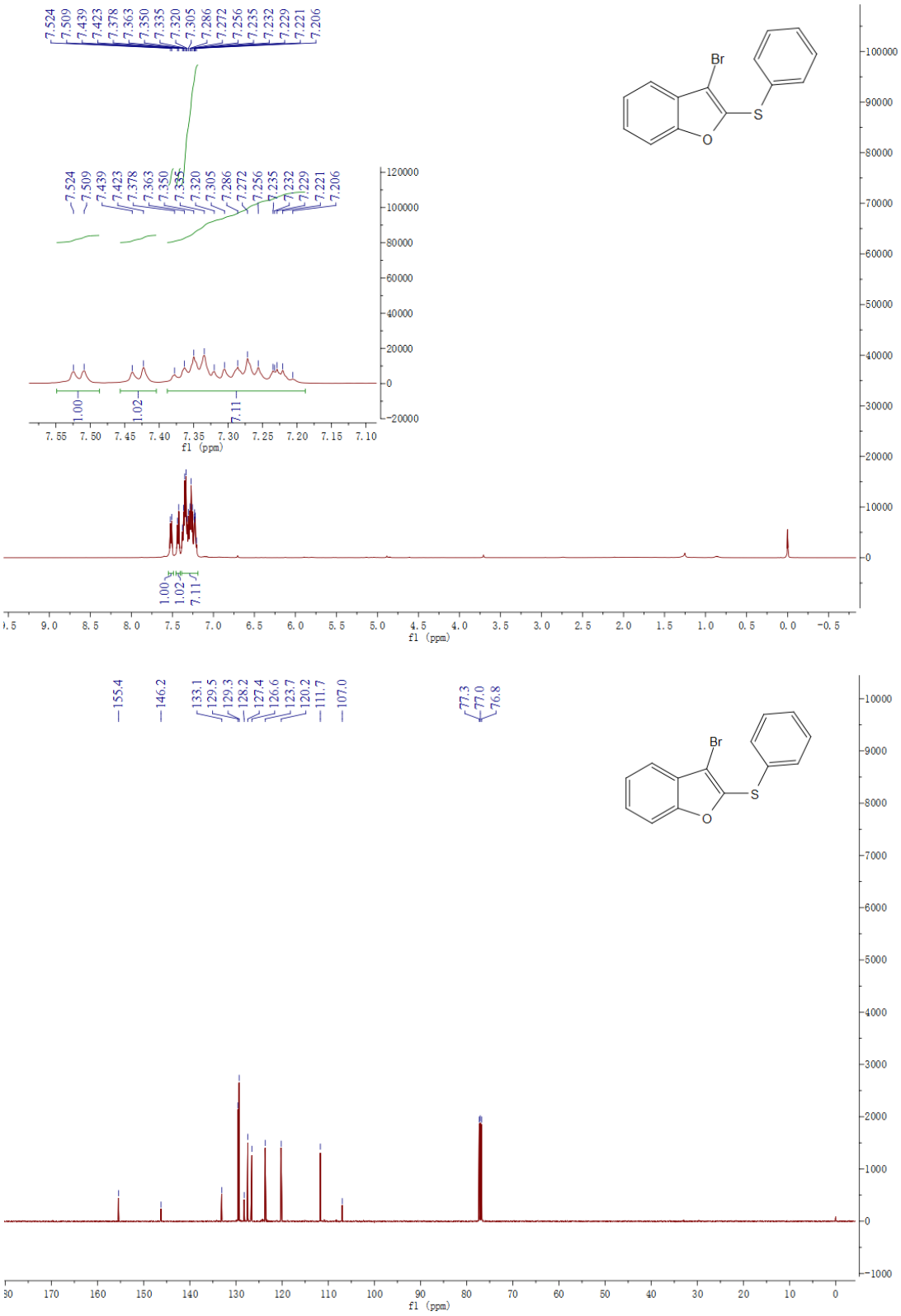


**Figure S1**. $^{1}$H NMR of **4a** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4a** (125 MHz, $CDCl_3$).

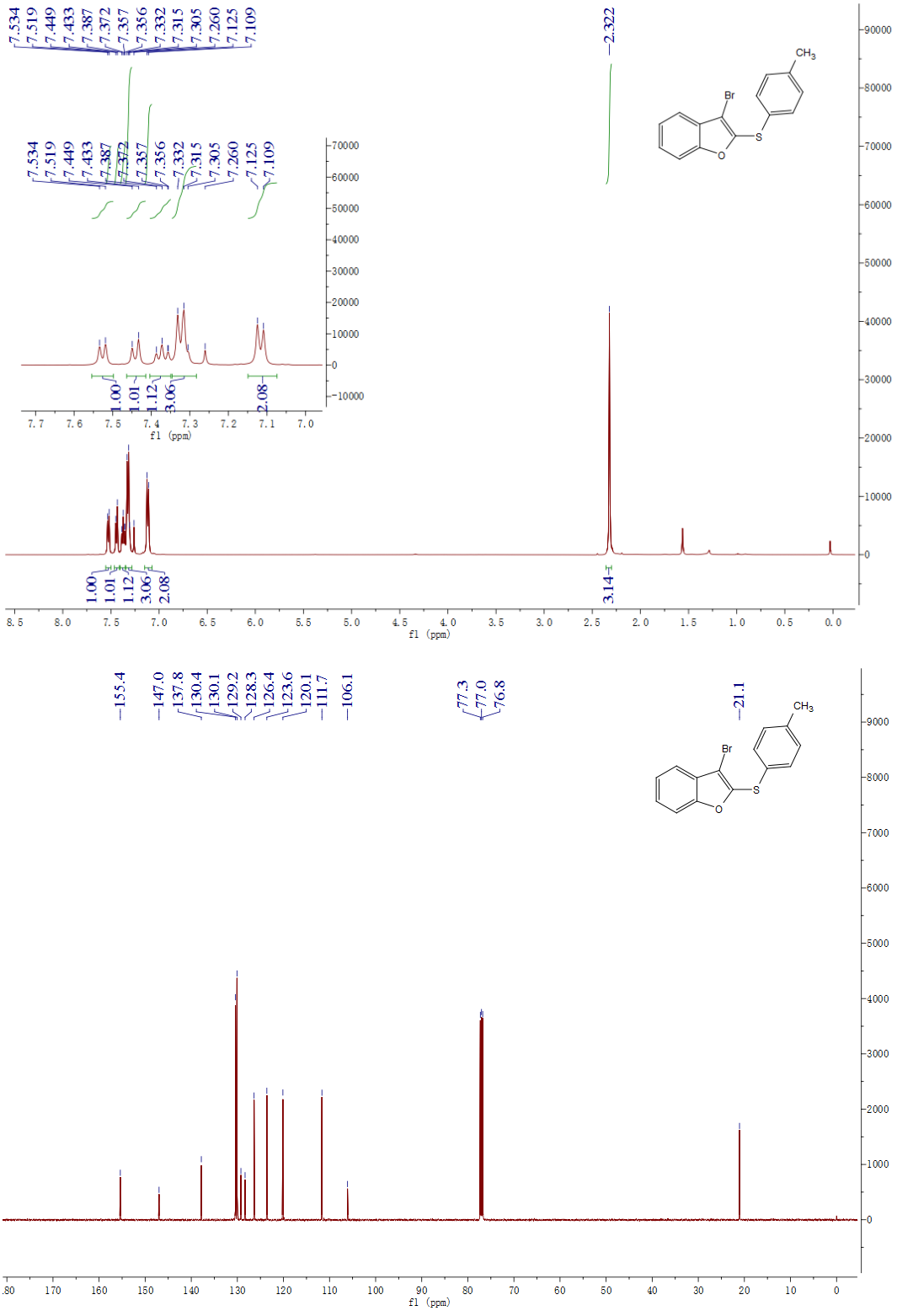


**Figure S2**. $^{1}$H NMR of **4b** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4b** (125 MHz, $CDCl_3$).

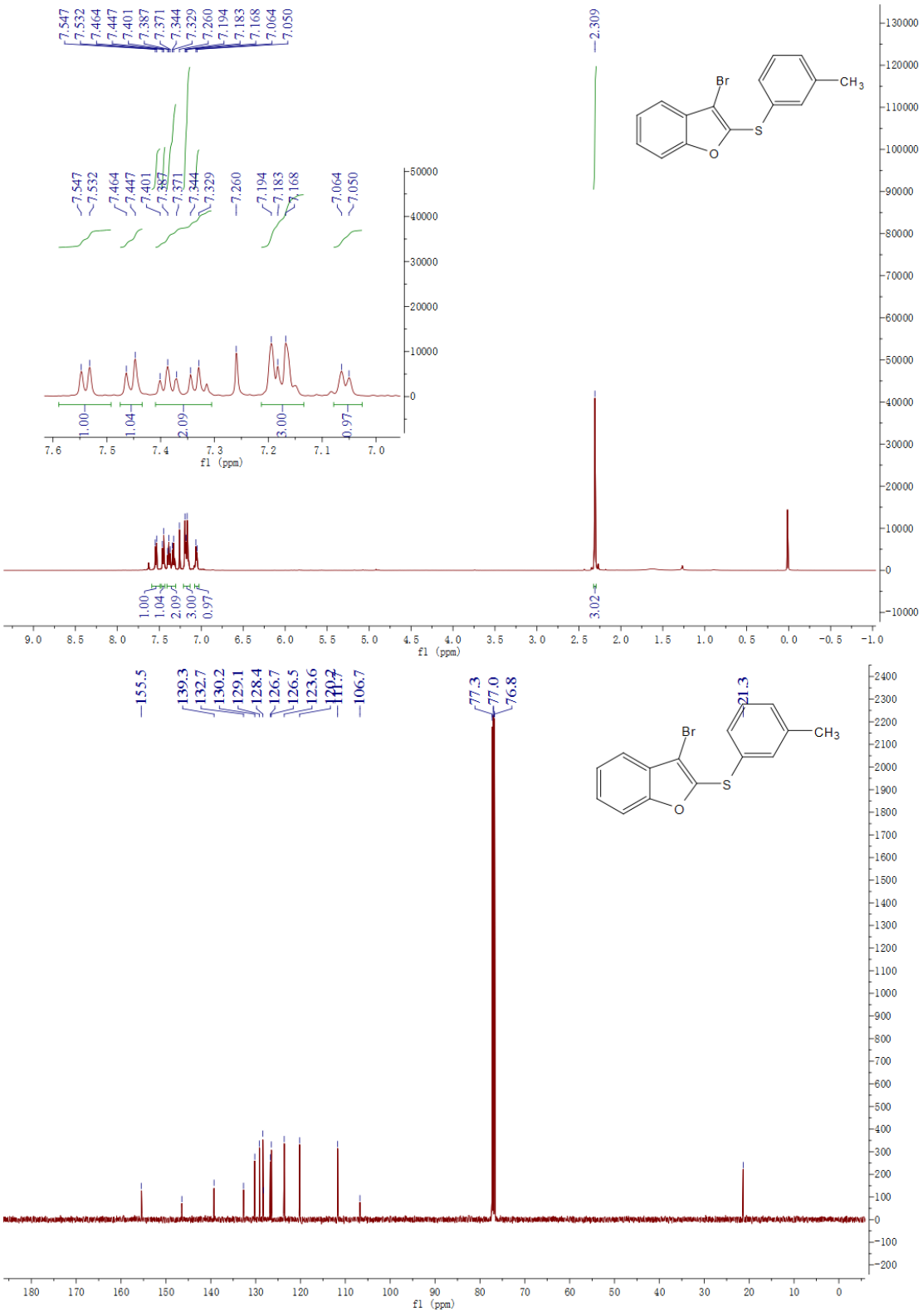


**Figure S3**. $^{1}$H NMR of **4c** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4c** (125 MHz, $CDCl_3$).

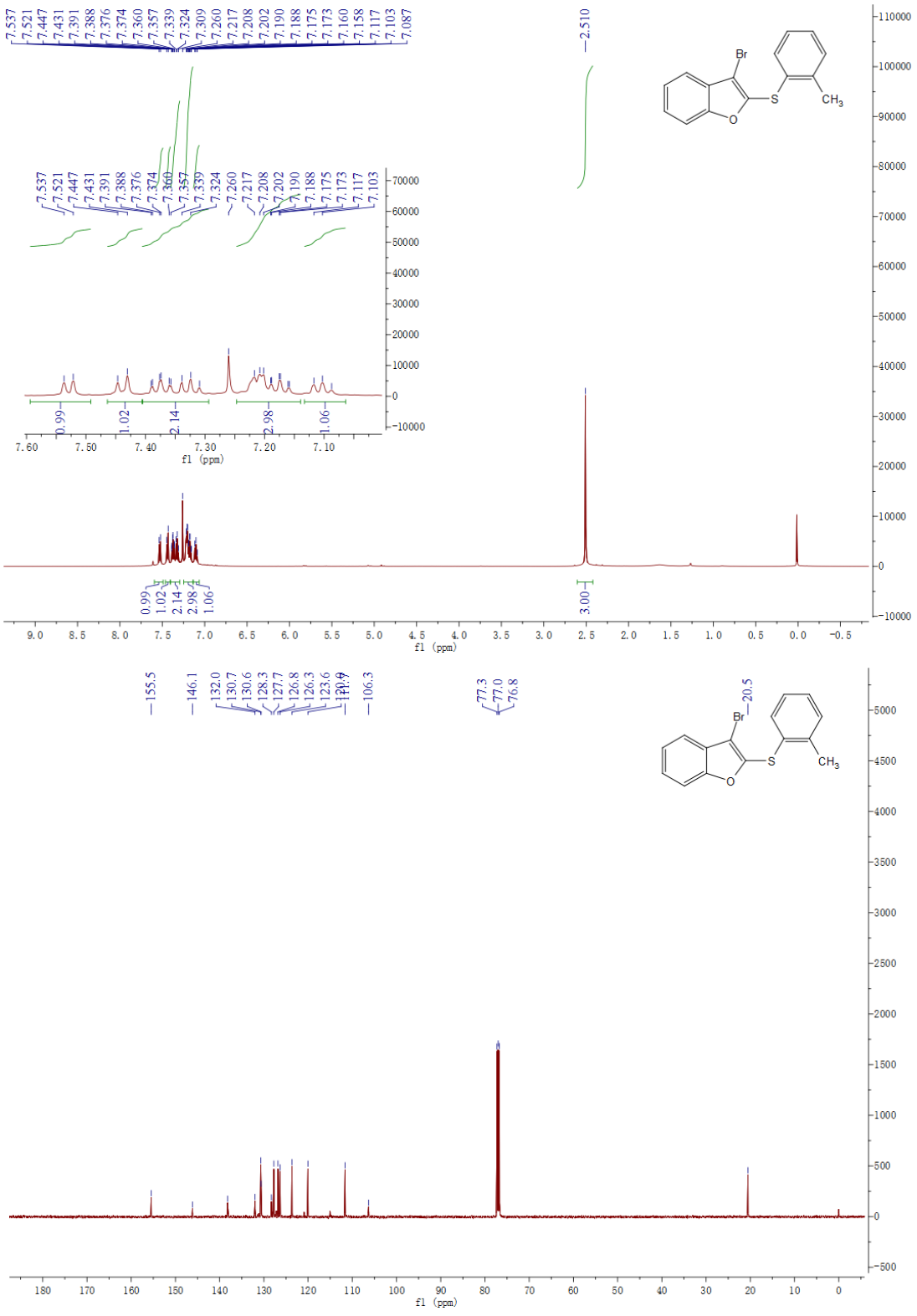


**Figure S4**. $^{1}$H NMR of **4d** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4d** (125 MHz, CDCl3).

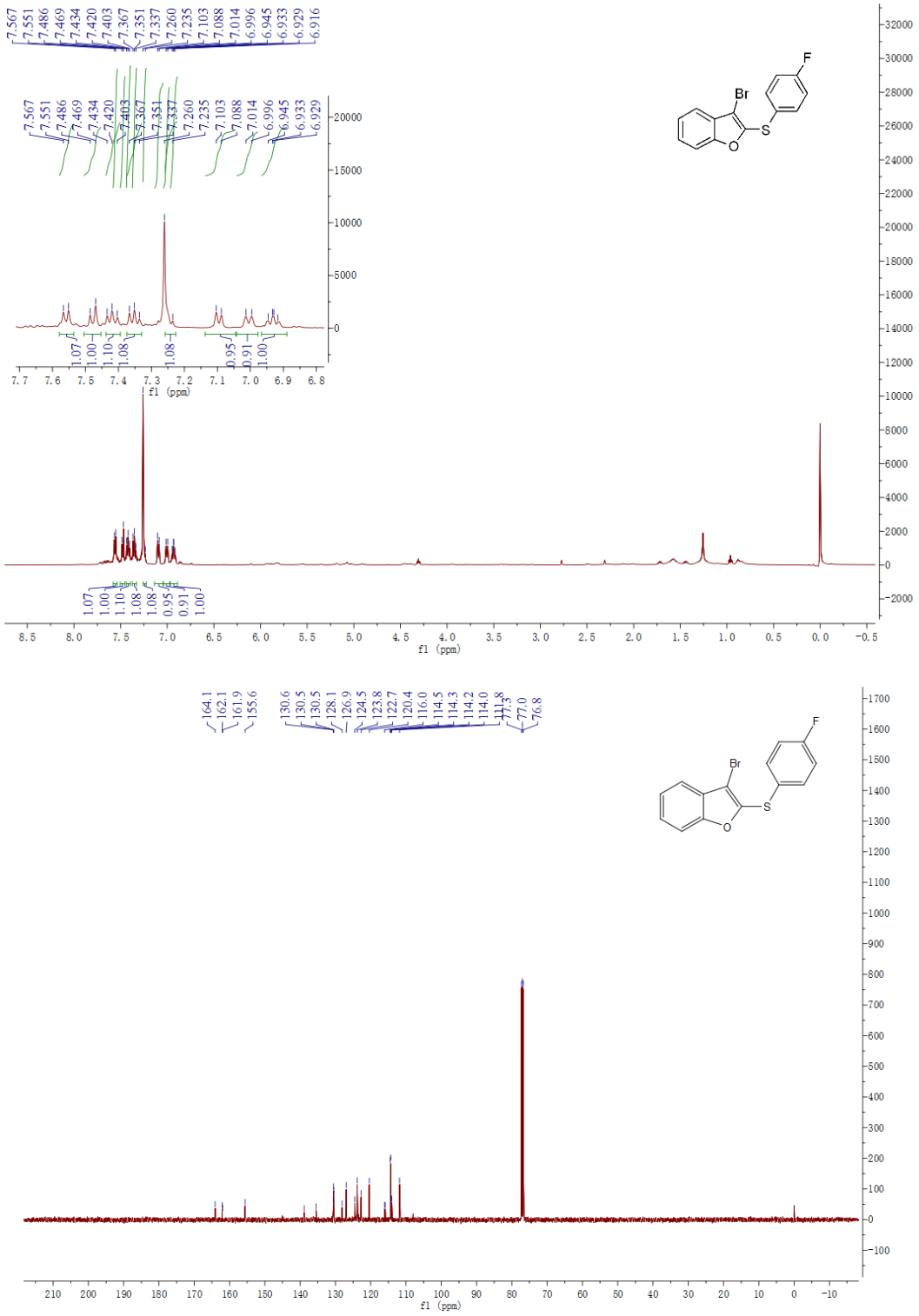


**Figure S5**. $^{1}$H NMR of **4e** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4e** (125 MHz, $CDCl_3$).

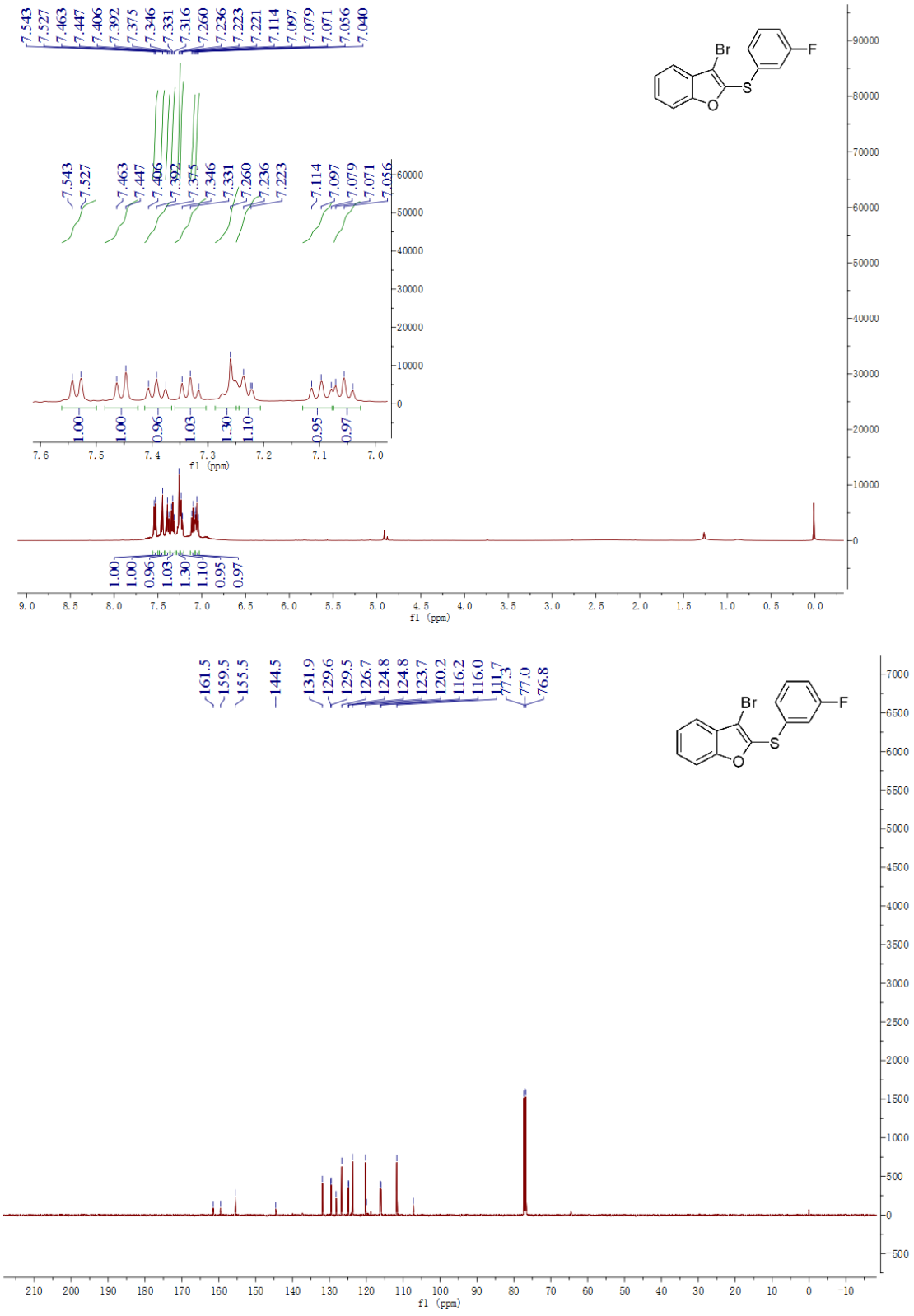


**Figure S6**. $^{1}$H NMR of **4f** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4f** (125 MHz, $CDCl_3$).

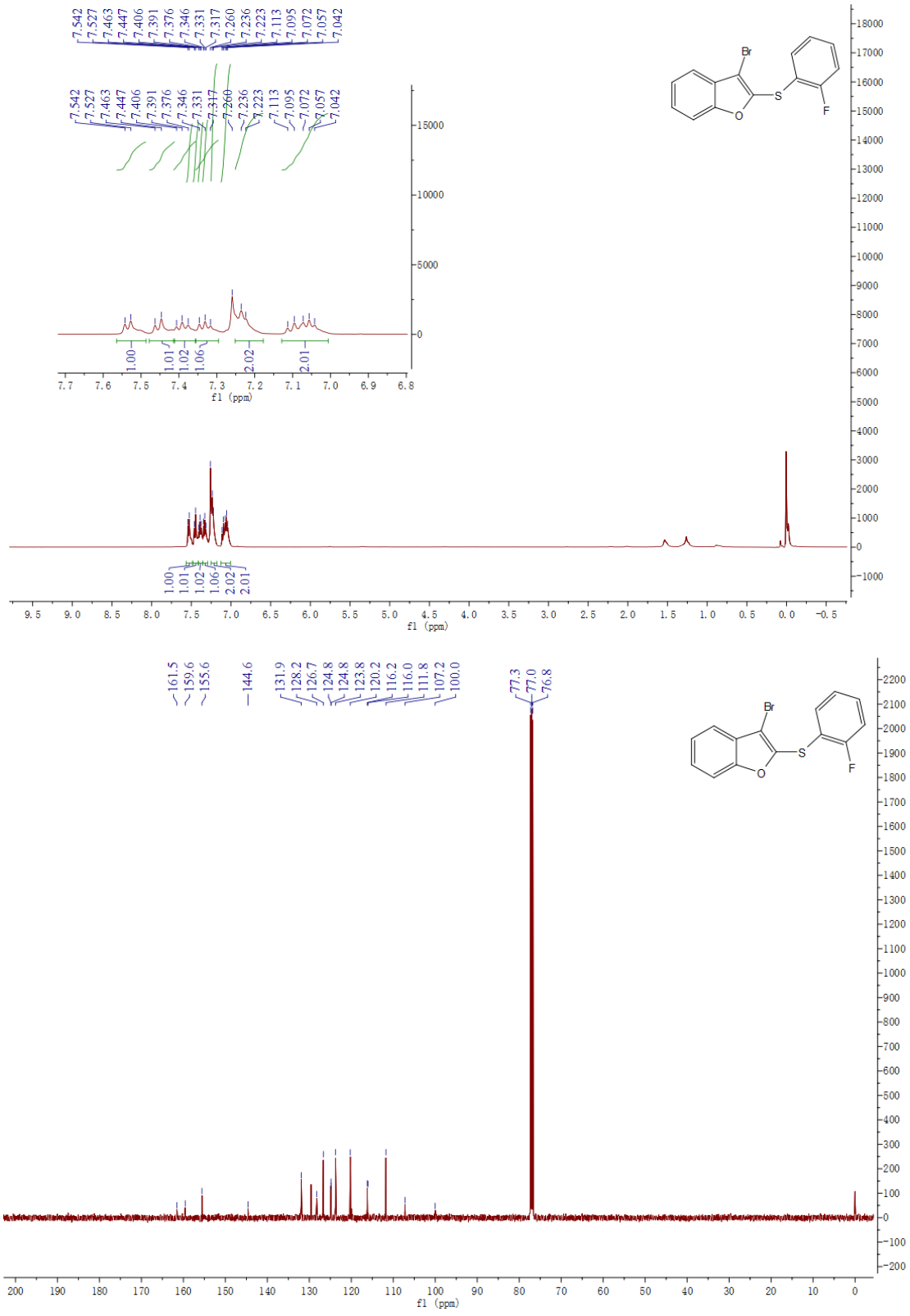


**Figure S7**. $^{1}H$ NMR of **4g** (500 MHz, $CDCl_3$) and $^{13}C$ NMR of **4g** (125 MHz, $CDCl_3$)

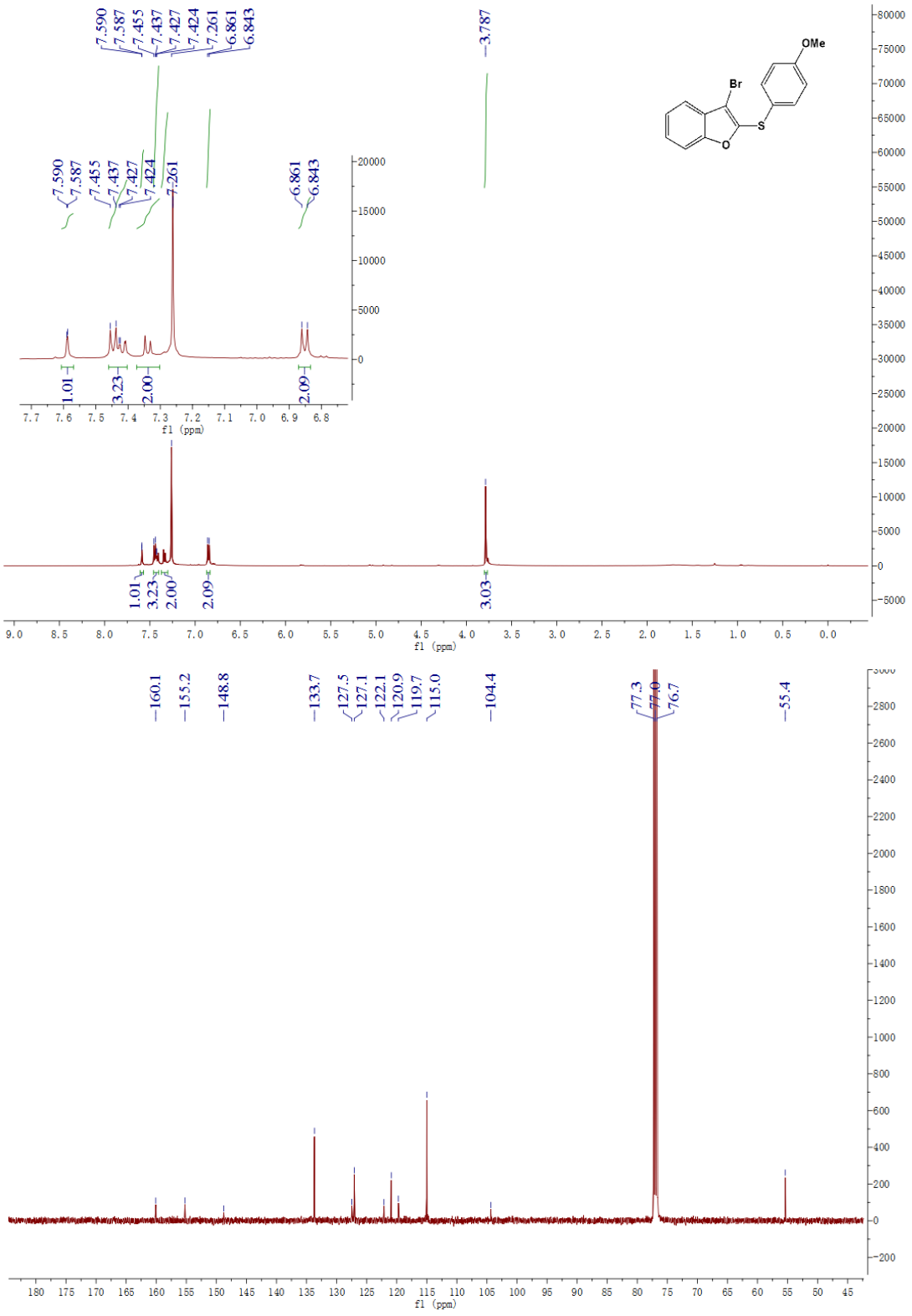


**Figure S8**. $^{1}$H NMR of **4h** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4h** (125 MHz, $CDCl_3$).

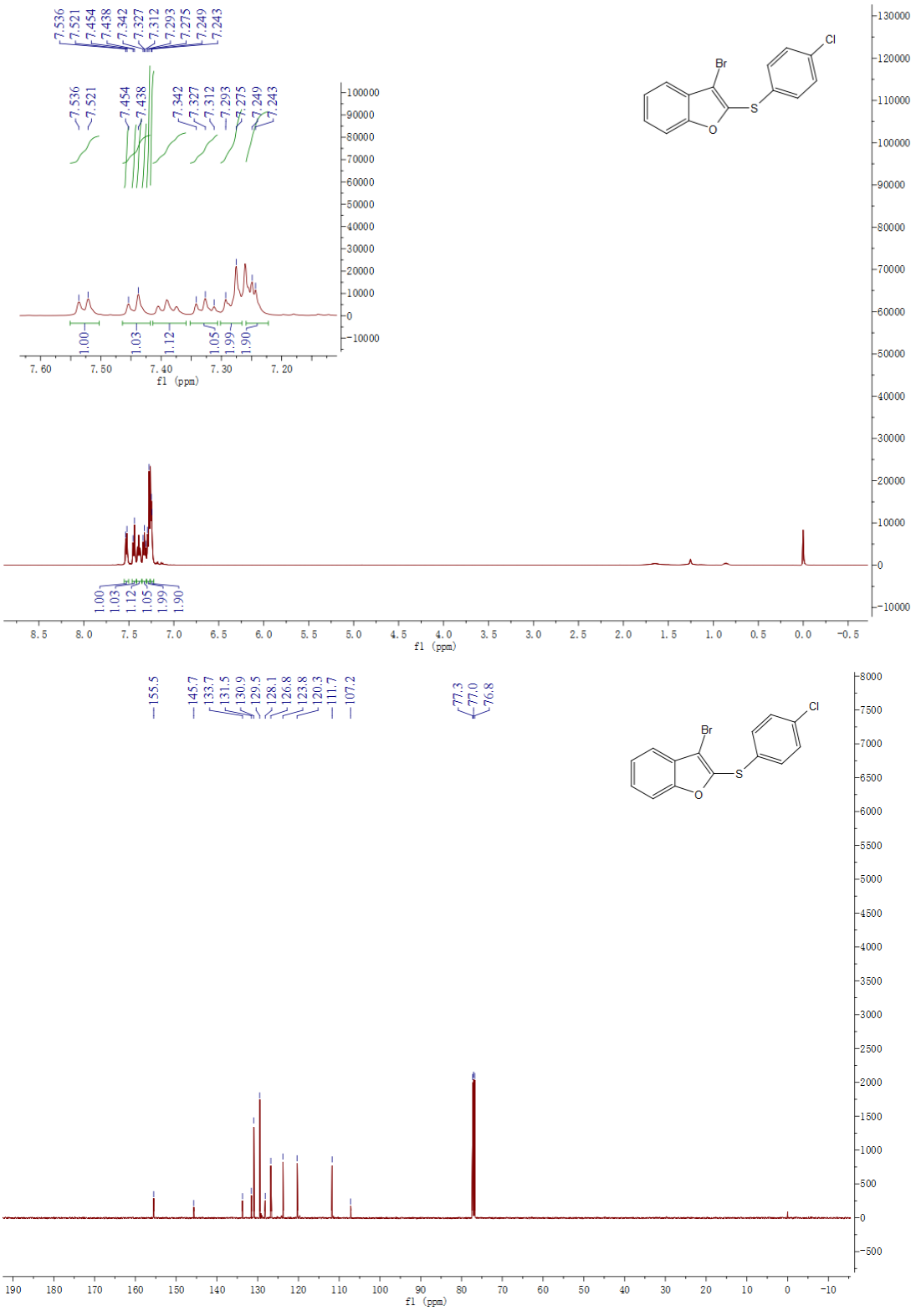


**Figure S9**. $^{1}$H NMR of **4i** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4i** (125 MHz, $CDCl_3$).

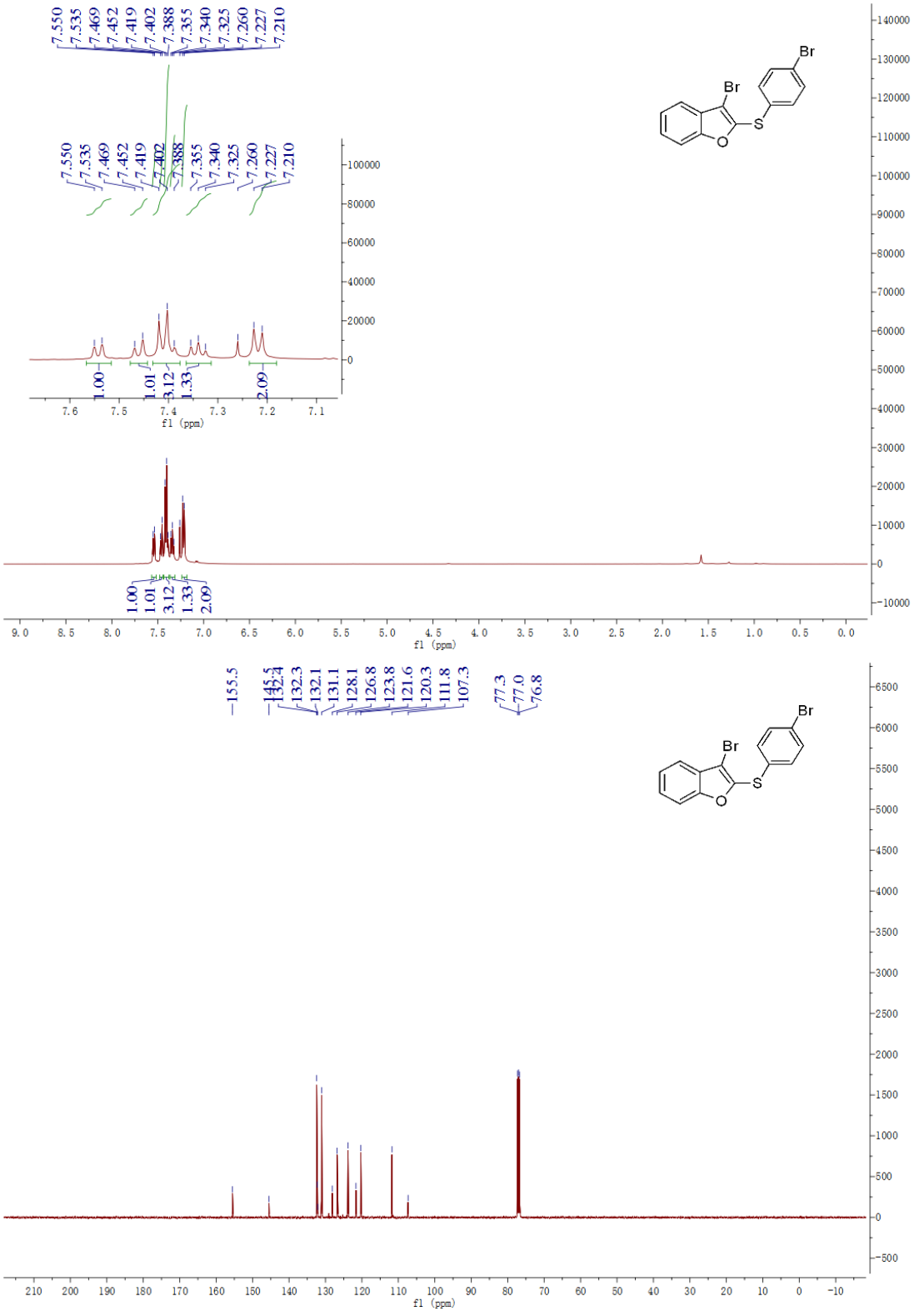


**Figure S10**. $^{1}$H NMR of **4j** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4j** (125 MHz, $CDCl_3$).

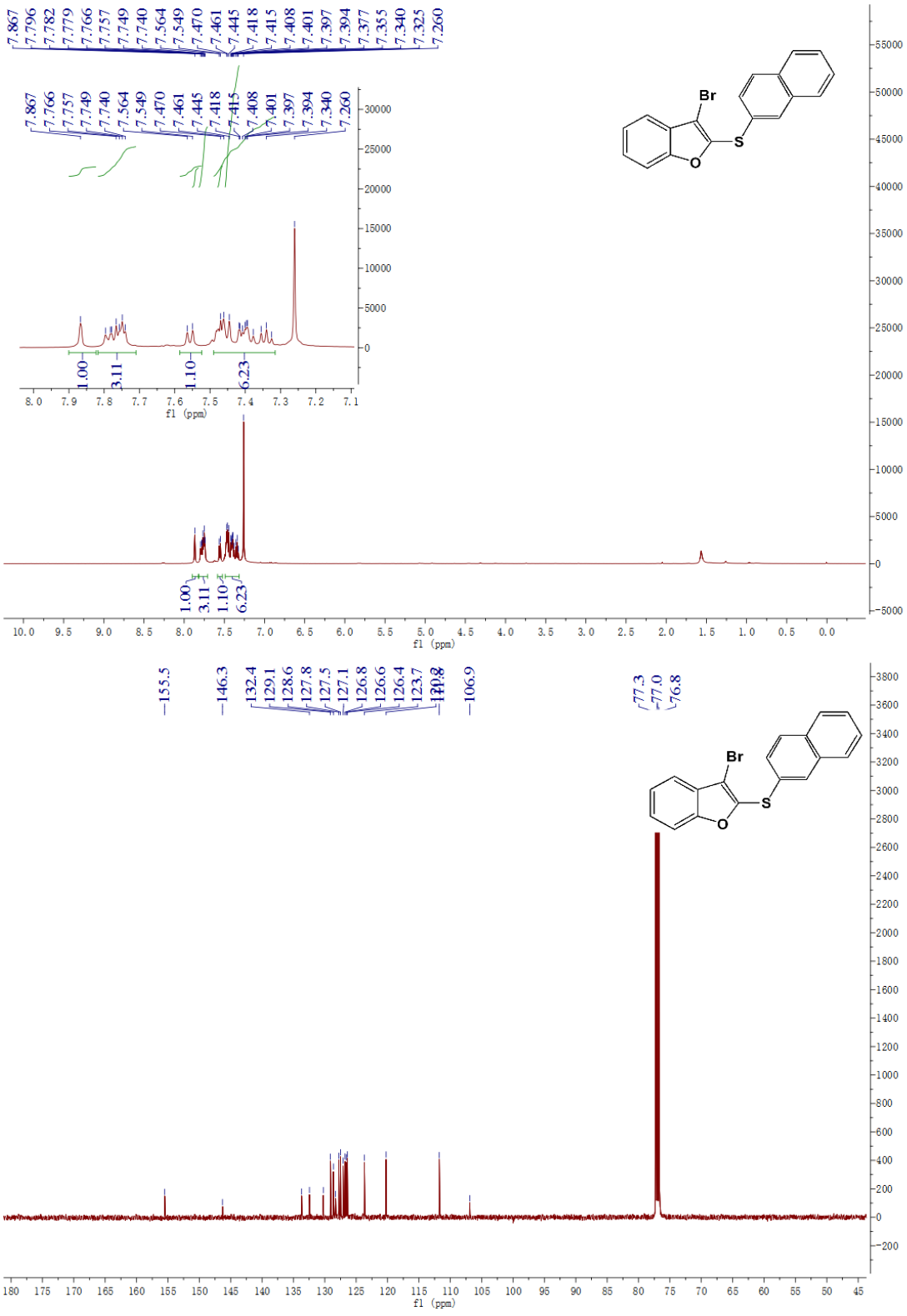


**Figure S11**. $^{1}$H NMR of **4k** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4k** (125 MHz, $CDCl_3$).

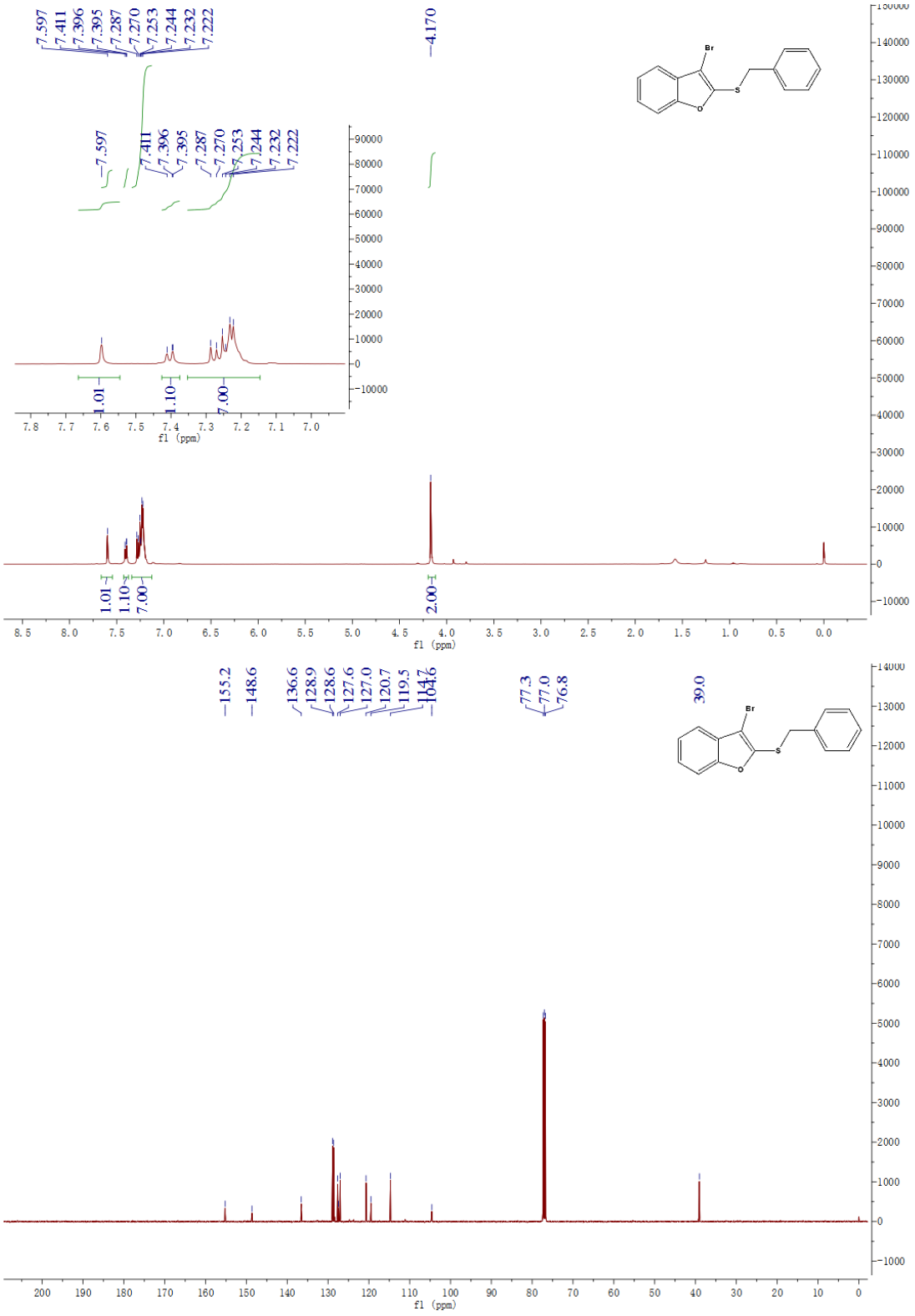


**Figure S12**. $^{1}$H NMR of **4l** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4l** (125 MHz, $CDCl_3$).

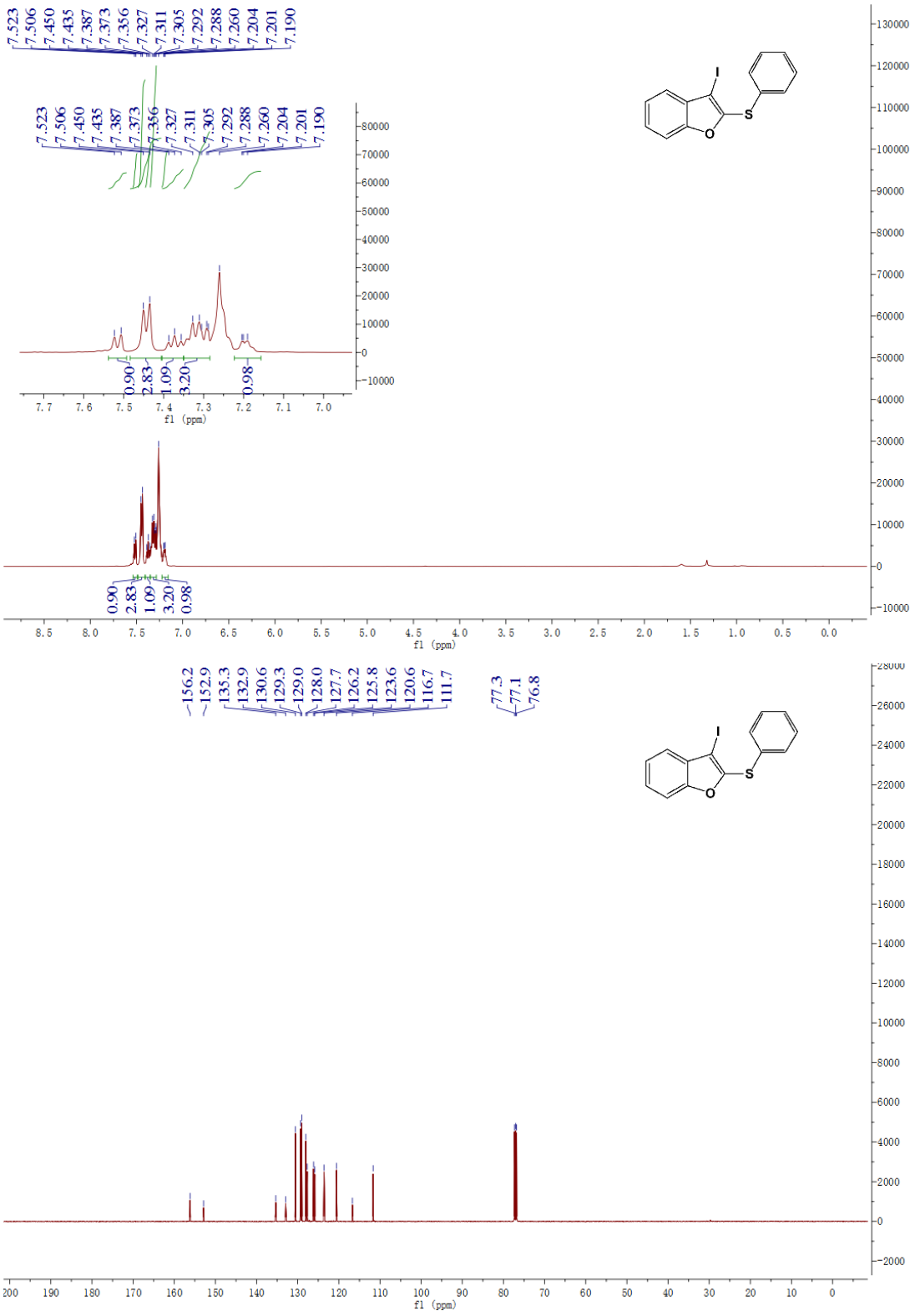


**Figure S13**. $^{1}H$ NMR of **4m** (500 MHz, $CDCl_3$) and $^{13}C$ NMR of **4m** (125 MHz, $CDCl_3$).

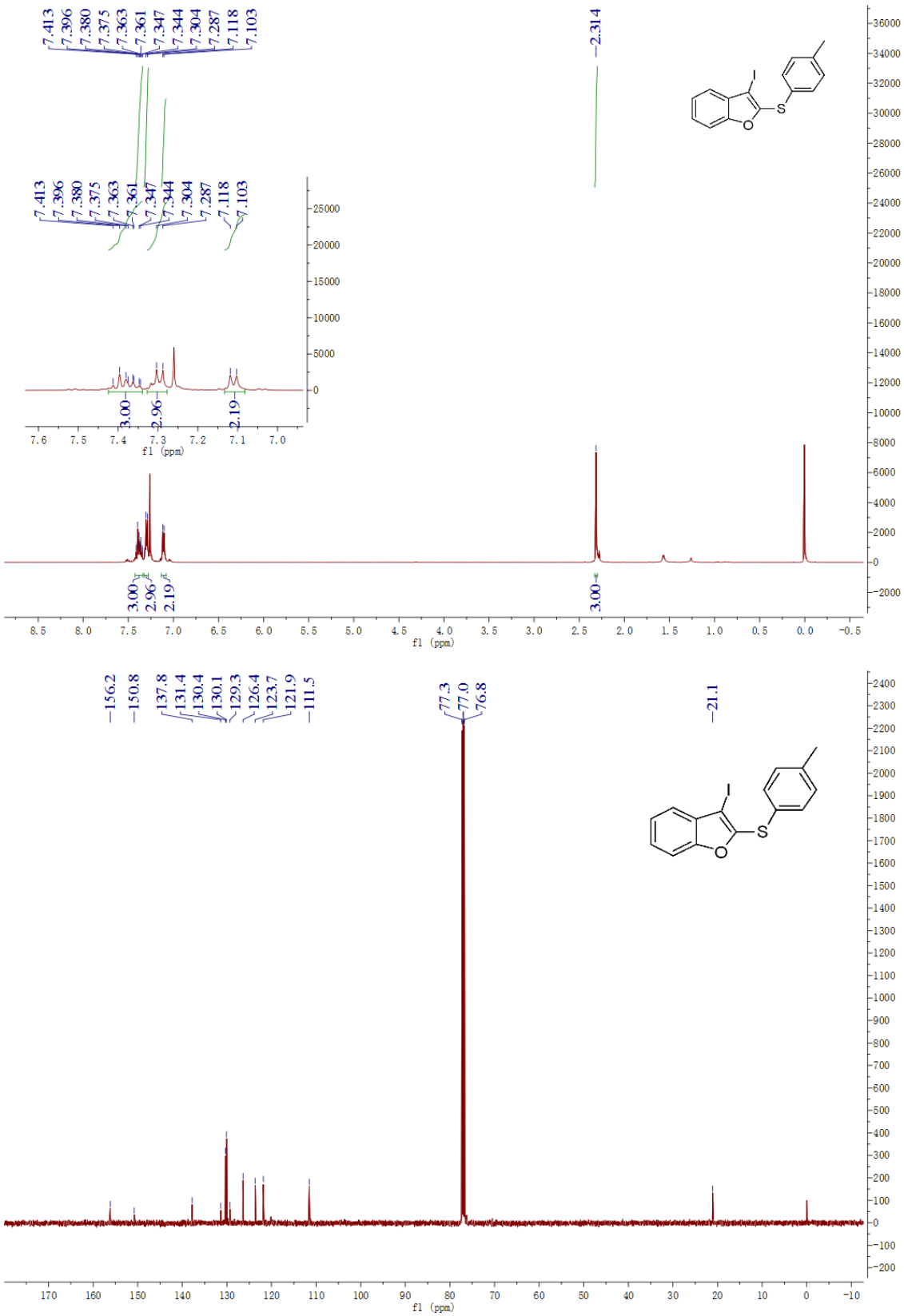


**Figure S14**. $^{1}$H NMR of **4n** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4n** (125 MHz, $CDCl_3$).

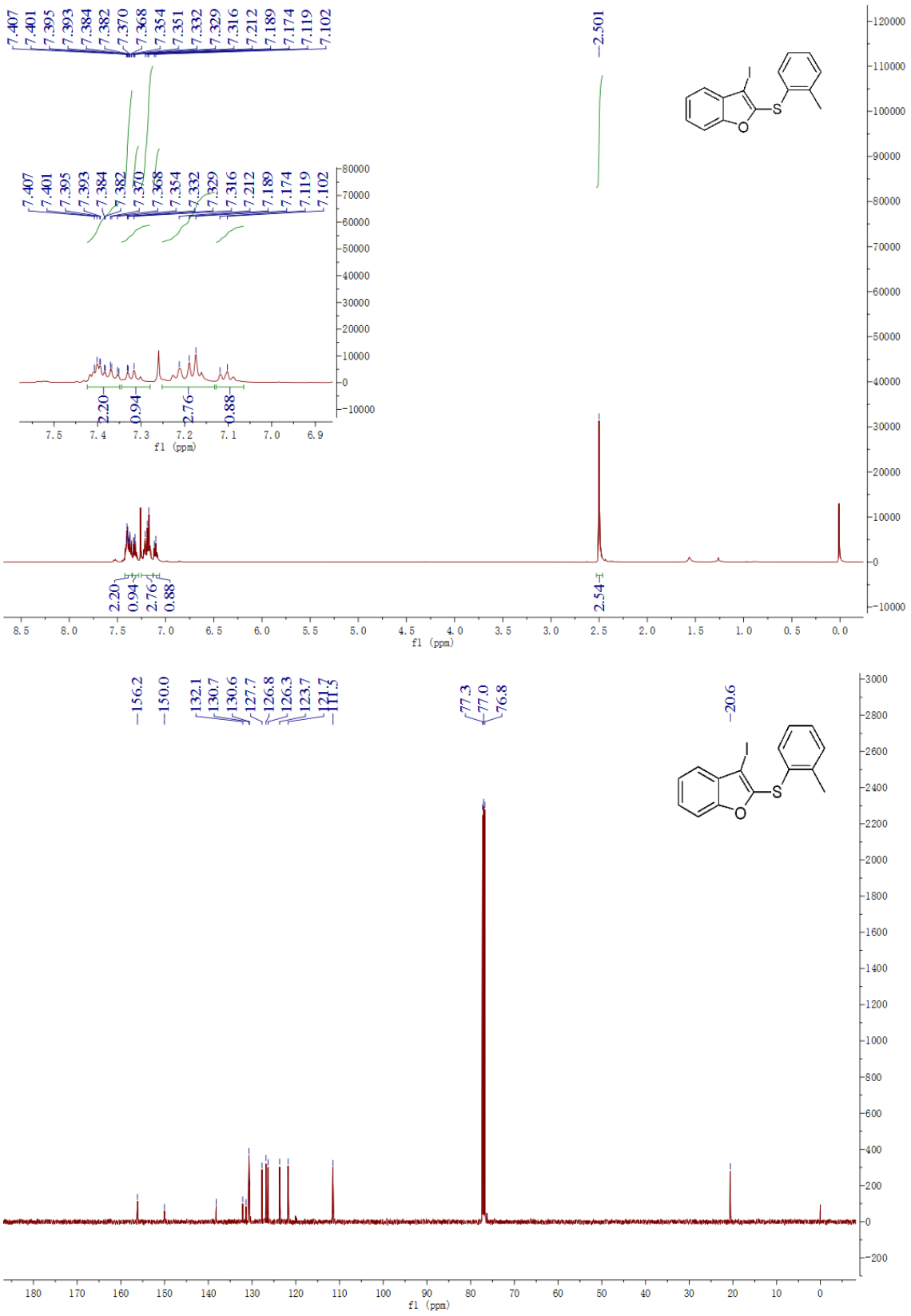


**Figure S15**. $^{1}H$ NMR of **4o** (500 MHz, $CDCl_3$) and $^{13}C$ NMR of **4o** (125 MHz, $CDCl_3$)

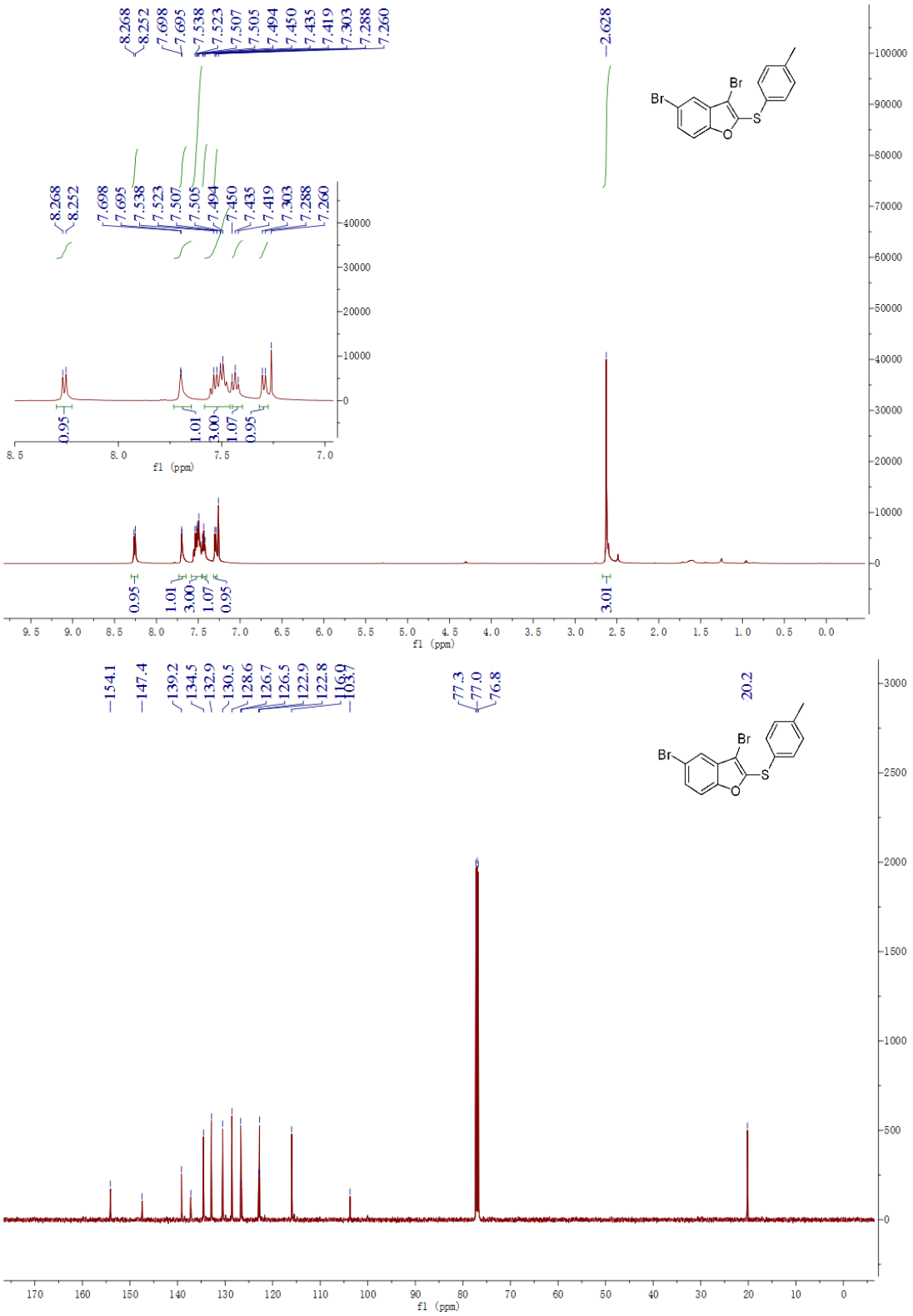


**Figure S16**. $^{1}$H NMR of **4p** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4p** (125 MHz, $CDCl_3$)

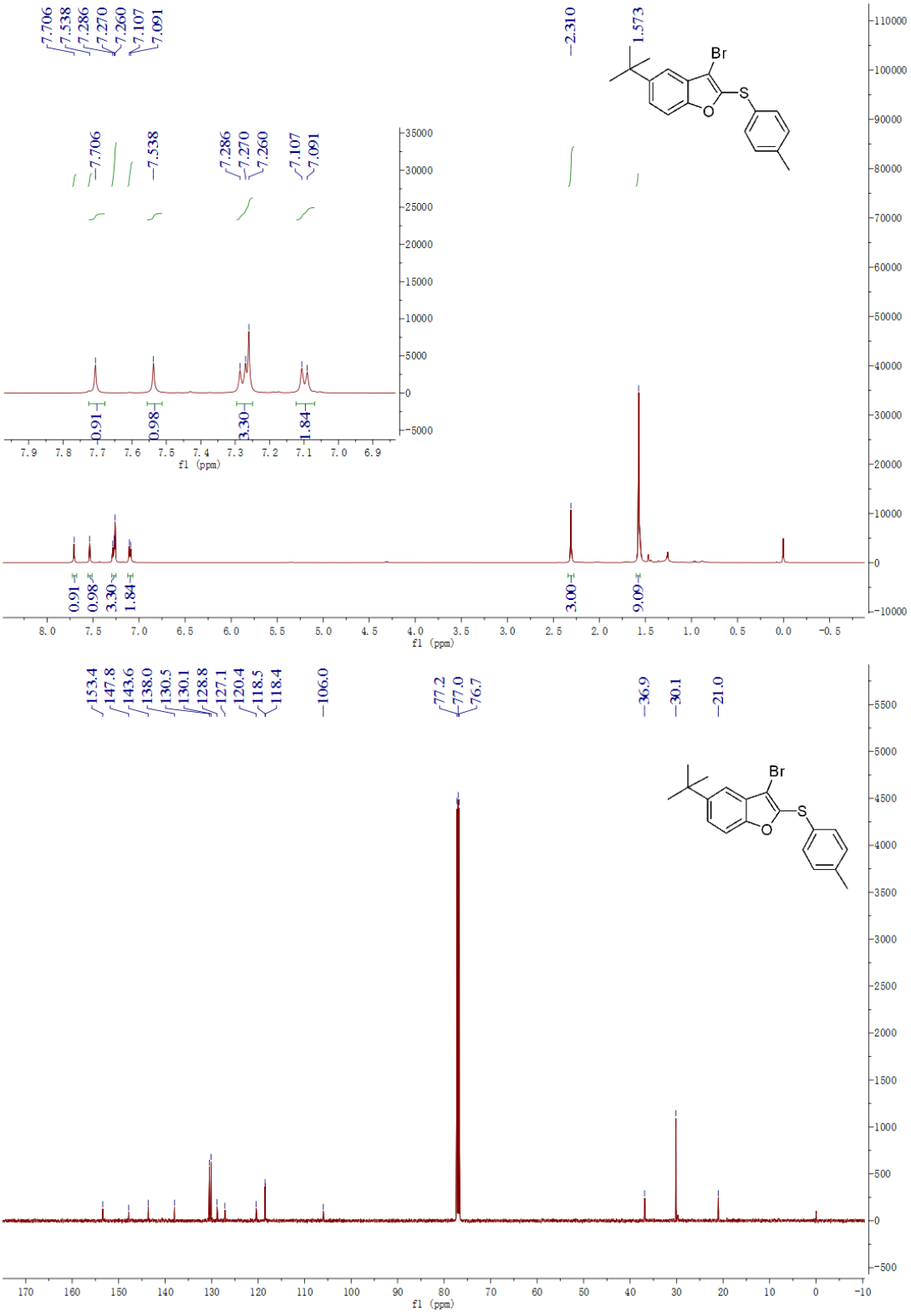


**Figure S17**. $^{1}$H NMR of **4q** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4q** (125 MHz, $CDCl_3$)

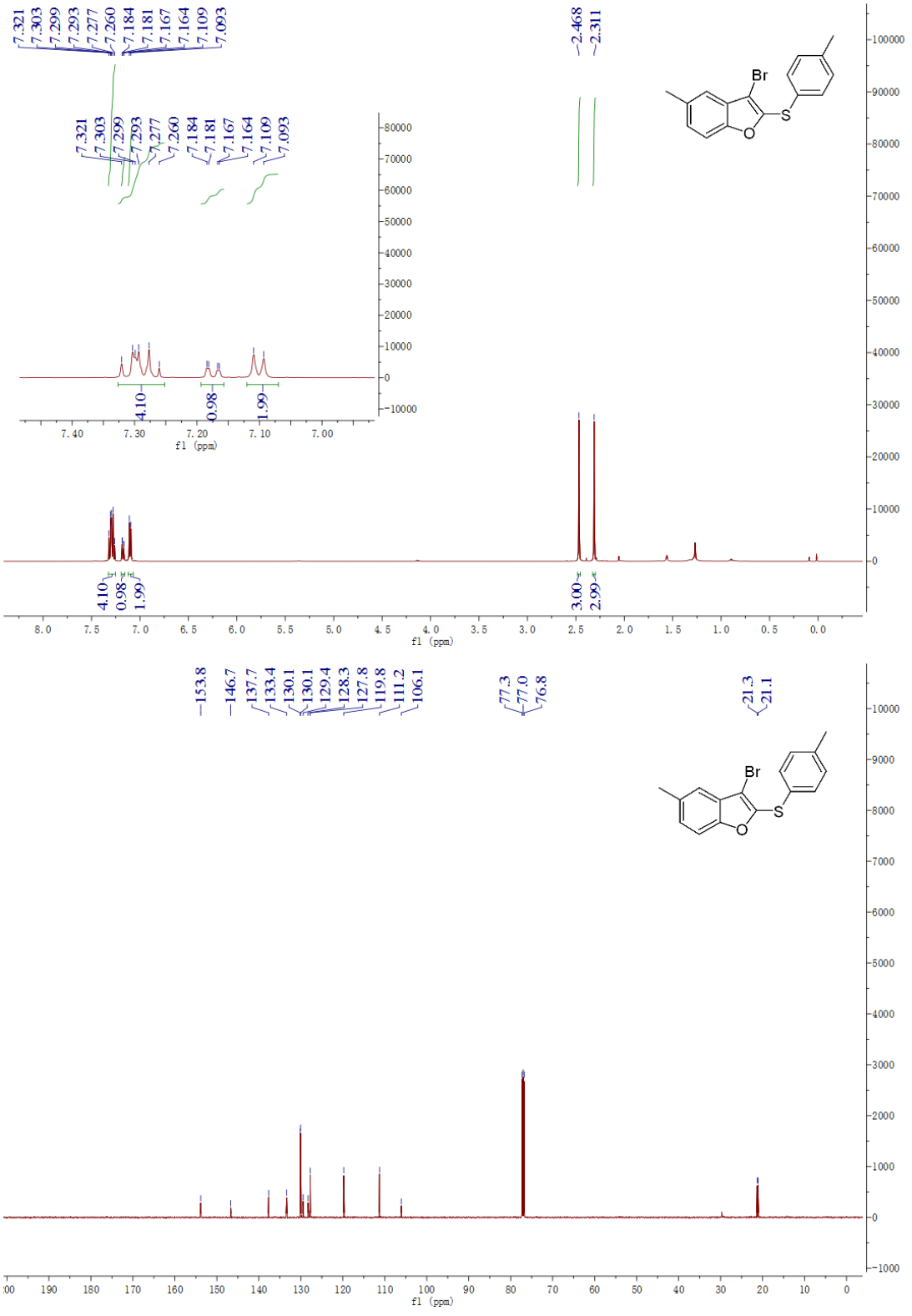


**Figure S18**. $^{1}$H NMR of **4r** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4r** (125 MHz, $CDCl_3$)

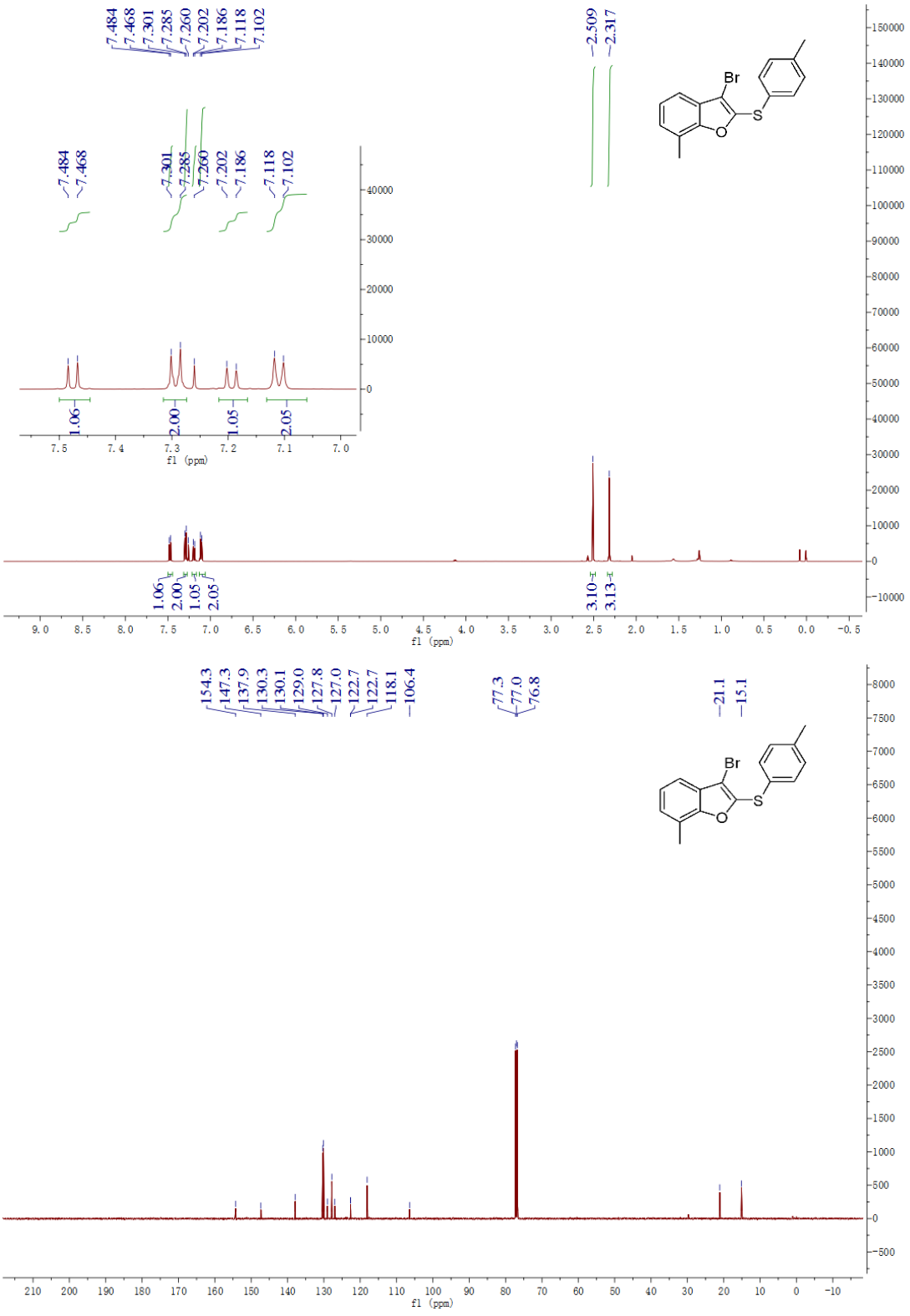


**Figure S19**. $^{1}$H NMR of **4s** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **4s** (125 MHz, $CDCl_3$)

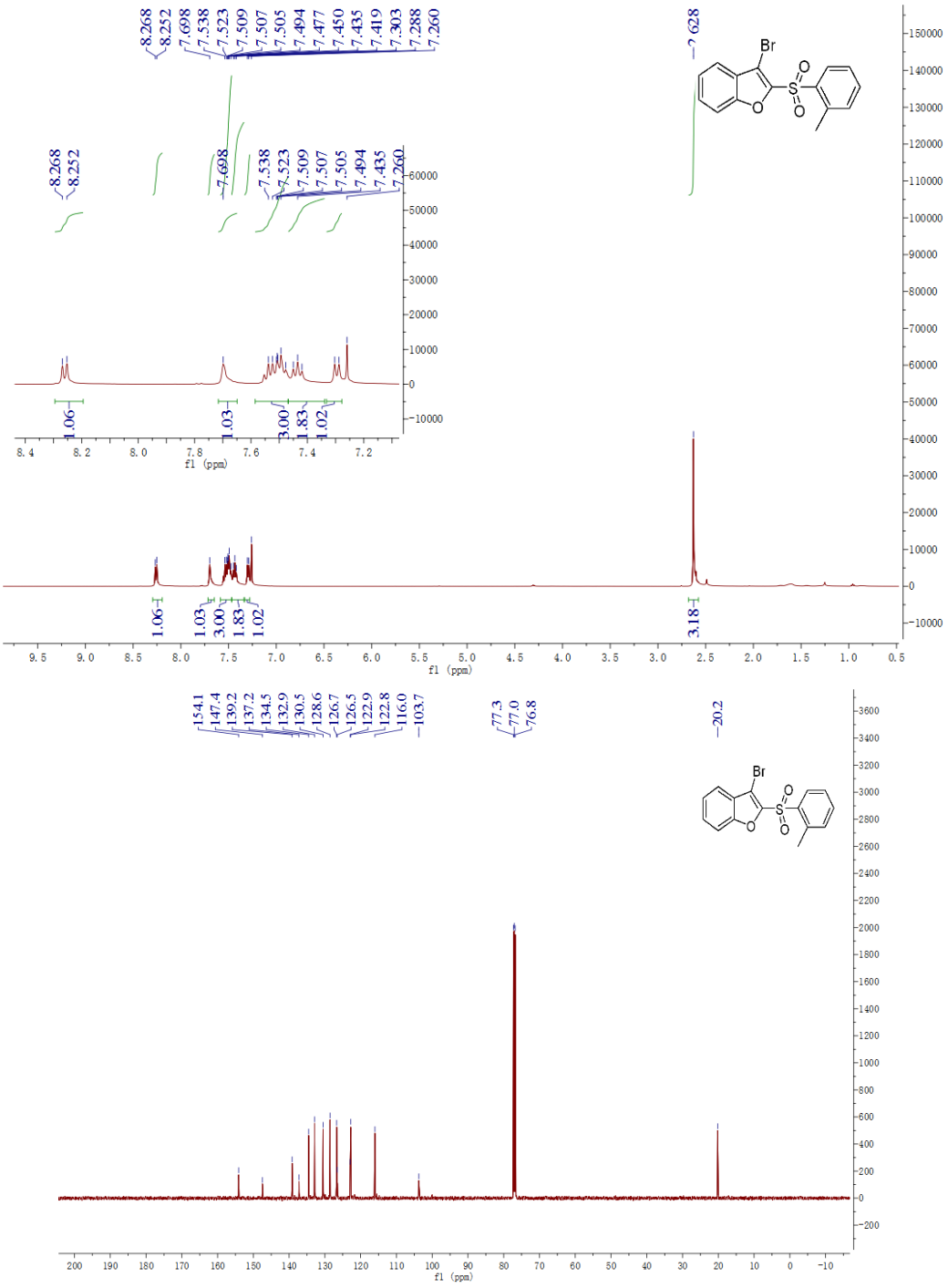


**Figure S20**. $^{1}H$ NMR of **5a** (500 MHz, $CDCl_3$) and $^{13}C$ NMR of **5a** (125 MHz, $CDCl_3$).

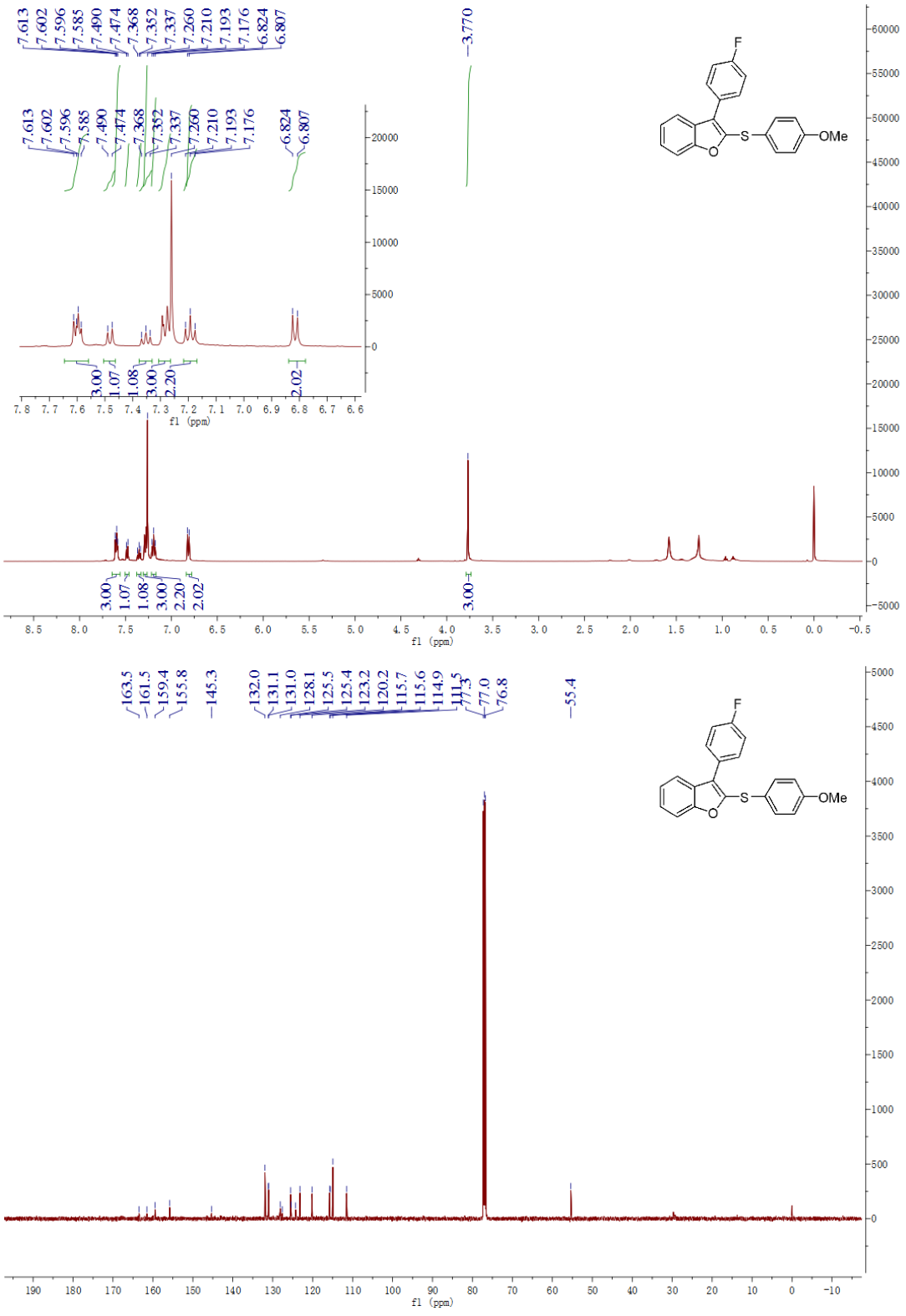


**Figure S21**. $^{1}$H NMR of **I** (500 MHz, CDCl3) and $^{13}$C NMR of **I** (125 MHz, CDCl3).

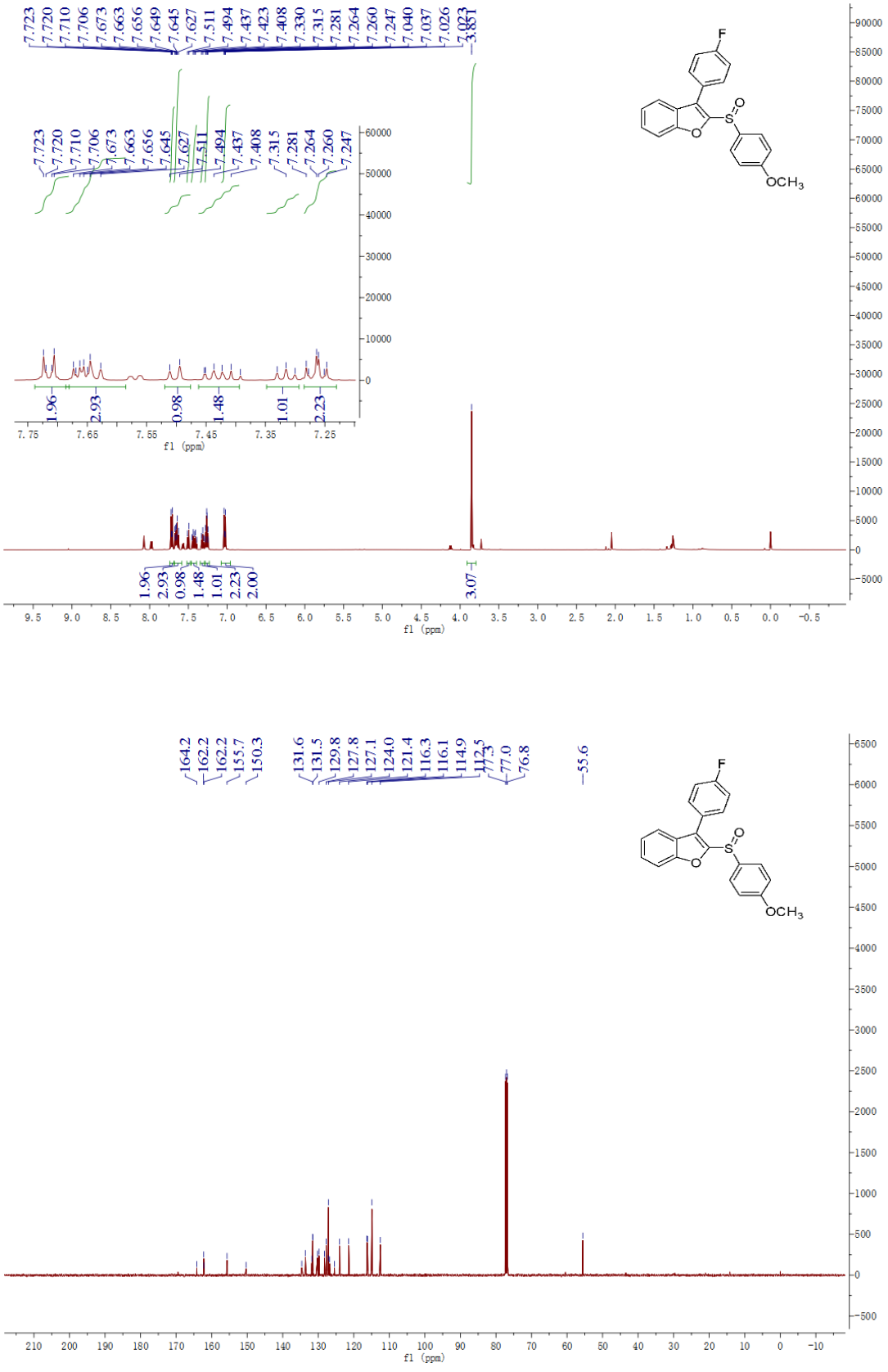


**Figure S22**. $^{1}$H NMR of **7a** (500 MHz, $CDCl_3$) and $^{13}$C NMR of **7a** (125 MHz, $CDCl_3$).

## 2. X-ray Crystallographic Data for Product 5a

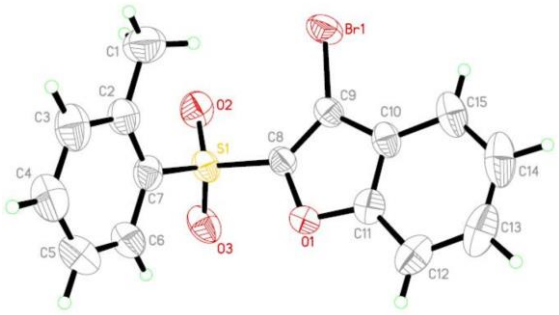


**Figure S23** X-ray crystal structure of **5a**

Table 1. Crystal data and structure refinement for mo_20110714A_0m.

| | |
|---|---|
| Identification code | mo_20110714a_0m |
| Empirical formula | C15 H11 Br O3 S |
| Formula weight | 351.21 |
| Temperature | 298(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P -1 |
| Unit cell dimensions | a = 7.7178(7) A alpha = 84.587(2) deg. |
| | b = 9.2215(9) A beta = 86.687(3) deg. |
| | c = 9.9594(10) A gamma = 78.032(3) deg. |
| Volume | 689.78(12) A^3 |
| Z, Calculated density | 2, 1.691 Mg/m^3 |
| Absorption coefficient | 3.134 mm^-1 |
| F(000) | 352 |
| Crystal size | 0.23 x 0.15 x 0.11 mm |
| Theta range for data collection | 2.06 to 25.50 deg. |
| Limiting indices | -7<=h<=9, -11<=k<=11, -12<=l<=12 |
| Reflections collected / unique | 5705 / 2509 [R(int) = 0.0240] |
| Completeness to theta = 25.50 | 98.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7243 and 0.5326 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2509 / 0 / 182 |
| Goodness-of-fit on F^2 | 1.034 |
| Final R indices [I>2sigma(I)] | R1 = 0.0394, wR2 = 0.1266 |
| R indices (all data) | R1 = 0.0496, wR2 = 0.1643 |
| Largest diff. peak and hole | 0.680 and -0.532 e.A^-3 |

Table 2. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mo_20110714A_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 4431(1) | 4128(1) | 3588(1) | 53(1) |
| S(1) | 2868(1) | 8225(1) | 2619(1) | 39(1) |
| O(1) | 2158(4) | 6968(3) | 500(3) | 41(1) |
| O(2) | 3830(4) | 7726(4) | 3809(3) | 54(1) |
| O(3) | 3433(4) | 9302(3) | 1670(4) | 56(1) |
| C(1) | 526(8) | 7093(7) | 5092(6) | 68(1) |
| C(2) | -301(6) | 8317(5) | 4105(4) | 45(1) |
| C(3) | -2111(7) | 8921(6) | 4285(6) | 59(1) |
| C(4) | -2997(8) | 10036(6) | 3386(6) | 63(1) |
| C(5) | -2054(7) | 10596(6) | 2287(6) | 59(1) |
| C(6) | -291(6) | 10023(5) | 2098(5) | 50(1) |
| C(7) | 564(6) | 8895(5) | 3010(4) | 43(1) |
| C(8) | 2855(5) | 6652(4) | 1761(4) | 37(1) |
| C(9) | 3397(5) | 5148(4) | 2059(4) | 37(1) |
| C(10) | 2997(5) | 4463(5) | 908(4) | 41(1) |
| C(11) | 2259(5) | 5612(5) | -2(4) | 40(1) |
| C(12) | 1687(7) | 5416(7) | -1257(5) | 58(1) |
| C(13) | 1921(7) | 3965(8) | -1554(6) | 66(2) |
| C(14) | 2719(8) | 2761(7) | -660(7) | 70(2) |
| C(15) | 3240(6) | 2986(5) | 584(6) | 54(1) |

Table 3. Bond lengths [A] and angles [deg] for mo_20110714A_0m.

| | |
|---|---|
| Br(1)-C(9) | 1.843(4) |
| S(1)-O(3) | 1.423(3) |
| S(1)-O(2) | 1.423(4) |
| S(1)-C(8) | 1.754(4) |
| S(1)-C(7) | 1.791(5) |
| O(1)-C(8) | 1.376(5) |
| O(1)-C(11) | 1.376(5) |
| C(1)-C(2) | 1.488(7) |
| C(1)-H(1A) | 0.9600 |
| C(1)-H(1B) | 0.9600 |
| C(1)-H(1C) | 0.9600 |
| C(2)-C(7) | 1.369(6) |
| C(2)-C(3) | 1.401(7) |
| C(3)-C(4) | 1.390(8) |
| C(3)-H(3) | 0.9300 |
| C(4)-C(5) | 1.397(8) |
| C(4)-H(4) | 0.9300 |
| C(5)-C(6) | 1.363(7) |
| C(5)-H(5) | 0.9300 |
| C(6)-C(7) | 1.396(7) |
| C(6)-H(6) | 0.9300 |
| C(8)-C(9) | 1.372(6) |
| C(9)-C(10) | 1.438(6) |
| C(10)-C(11) | 1.377(6) |
| C(10)-C(15) | 1.401(6) |
| C(11)-C(12) | 1.389(6) |
| C(12)-C(13) | 1.371(8) |
| C(12)-H(12) | 0.9300 |
| C(13)-C(14) | 1.414(10) |
| C(13)-H(13) | 0.9300 |
| C(14)-C(15) | 1.371(8) |
| C(14)-H(14) | 0.9300 |
| C(15)-H(15) | 0.9300 |

| | |
|---|---|
| O(3)-S(1)-O(2) | 119.6(2) |
| O(3)-S(1)-C(8) | 107.3(2) |
| O(2)-S(1)-C(8) | 107.2(2) |
| O(3)-S(1)-C(7) | 107.2(2) |
| O(2)-S(1)-C(7) | 111.4(2) |
| C(8)-S(1)-C(7) | 102.73(19) |

| | |
|---|---|
| C(8)-O(1)-C(11) | 105.6(3) |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| C(7)-C(2)-C(3) | 116.7(5) |
| C(7)-C(2)-C(1) | 125.1(4) |
| C(3)-C(2)-C(1) | 118.2(5) |
| C(4)-C(3)-C(2) | 121.8(5) |
| C(4)-C(3)-H(3) | 119.1 |
| C(2)-C(3)-H(3) | 119.1 |
| C(3)-C(4)-C(5) | 119.3(5) |
| C(3)-C(4)-H(4) | 120.3 |
| C(5)-C(4)-H(4) | 120.3 |
| C(6)-C(5)-C(4) | 119.6(5) |
| C(6)-C(5)-H(5) | 120.2 |
| C(4)-C(5)-H(5) | 120.2 |
| C(5)-C(6)-C(7) | 119.9(5) |
| C(5)-C(6)-H(6) | 120.1 |
| C(7)-C(6)-H(6) | 120.1 |
| C(2)-C(7)-C(6) | 122.6(4) |
| C(2)-C(7)-S(1) | 122.3(4) |
| C(6)-C(7)-S(1) | 115.0(3) |
| C(9)-C(8)-O(1) | 111.5(3) |
| C(9)-C(8)-S(1) | 134.3(3) |
| O(1)-C(8)-S(1) | 114.3(3) |
| C(8)-C(9)-C(10) | 105.8(4) |
| C(8)-C(9)-Br(1) | 129.4(3) |
| C(10)-C(9)-Br(1) | 124.7(3) |
| C(11)-C(10)-C(15) | 120.2(4) |
| C(11)-C(10)-C(9) | 106.0(4) |
| C(15)-C(10)-C(9) | 133.8(4) |
| O(1)-C(11)-C(10) | 111.1(3) |
| O(1)-C(11)-C(12) | 124.8(4) |
| C(10)-C(11)-C(12) | 124.1(4) |
| C(13)-C(12)-C(11) | 115.0(5) |
| C(13)-C(12)-H(12) | 122.5 |
| C(11)-C(12)-H(12) | 122.5 |
| C(12)-C(13)-C(14) | 122.4(5) |
| C(12)-C(13)-H(13) | 118.8 |
| C(14)-C(13)-H(13) | 118.8 |
| C(15)-C(14)-C(13) | 121.3(5) |

| | |
|---|---|
| C(15)-C(14)-H(14) | 119.3 |
| C(13)-C(14)-H(14) | 119.3 |
| C(14)-C(15)-C(10) | 117.0(5) |
| C(14)-C(15)-H(15) | 121.5 |
| C(10)-C(15)-H(15) | 121.5 |

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mo_20110714A_0m. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Br(1) | 58(1) | 41(1) | 56(1) | 9(1) | -14(1) | -1(1) |
| S(1) | 39(1) | 31(1) | 50(1) | -7(1) | -1(1) | -9(1) |
| O(1) | 48(2) | 34(1) | 38(1) | 1(1) | -4(1) | -4(1) |
| O(2) | 54(2) | 56(2) | 56(2) | -14(2) | -17(2) | -12(2) |
| O(3) | 49(2) | 37(2) | 83(2) | -2(2) | 10(2) | -15(1) |
| C(1) | 68(3) | 74(4) | 57(3) | 7(3) | -3(3) | -7(3) |
| C(2) | 45(2) | 40(2) | 50(2) | -9(2) | -2(2) | -11(2) |
| C(3) | 45(3) | 54(3) | 77(3) | -18(2) | 6(2) | -10(2) |
| C(4) | 55(3) | 49(3) | 84(4) | -12(3) | 6(3) | -7(2) |
| C(5) | 53(3) | 44(2) | 76(3) | 3(2) | -12(2) | -5(2) |
| C(6) | 52(3) | 38(2) | 59(3) | -3(2) | -2(2) | -7(2) |
| C(7) | 48(2) | 37(2) | 47(2) | -12(2) | 1(2) | -14(2) |
| C(8) | 38(2) | 32(2) | 40(2) | -3(2) | -4(2) | -3(2) |
| C(9) | 31(2) | 33(2) | 44(2) | -2(2) | -2(2) | -6(2) |
| C(10) | 34(2) | 36(2) | 52(2) | -9(2) | 4(2) | -7(2) |
| C(11) | 28(2) | 47(2) | 46(2) | -10(2) | 1(2) | -9(2) |
| C(12) | 61(3) | 74(3) | 43(2) | -13(2) | -1(2) | -21(3) |
| C(13) | 51(3) | 92(4) | 64(3) | -41(3) | 6(2) | -24(3) |
| C(14) | 63(3) | 63(3) | 94(4) | -44(3) | 13(3) | -25(3) |
| C(15) | 41(2) | 41(2) | 82(3) | -20(2) | 8(2) | -12(2) |

Table 5. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for mo_20110714A_0m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 1225 | 6300 | 4617 | 102 |
| H(1B) | -385 | 6727 | 5637 | 102 |
| H(1C) | 1271 | 7461 | 5661 | 102 |
| H(3) | -2738 | 8566 | 5026 | 70 |
| H(4) | -4205 | 10406 | 3514 | 76 |
| H(5) | -2626 | 11355 | 1687 | 70 |
| H(6) | 342 | 10383 | 1362 | 60 |
| H(12) | 1184 | 6211 | -1851 | 69 |
| H(13) | 1540 | 3765 | -2374 | 79 |
| H(14) | 2895 | 1798 | -921 | 84 |
| H(15) | 3732 | 2195 | 1185 | 64 |

Table 6. Torsion angles [deg] for mo_20110714A_0m.

| | |
|---|---|
| C(7)-C(2)-C(3)-C(4) | 1.0(7) |
| C(1)-C(2)-C(3)-C(4) | -178.1(5) |
| C(2)-C(3)-C(4)-C(5) | -1.4(8) |
| C(3)-C(4)-C(5)-C(6) | 1.2(8) |
| C(4)-C(5)-C(6)-C(7) | -0.7(7) |
| C(3)-C(2)-C(7)-C(6) | -0.5(6) |
| C(1)-C(2)-C(7)-C(6) | 178.5(5) |
| C(3)-C(2)-C(7)-S(1) | -178.9(3) |
| C(1)-C(2)-C(7)-S(1) | 0.1(6) |
| C(5)-C(6)-C(7)-C(2) | 0.4(7) |
| C(5)-C(6)-C(7)-S(1) | 178.9(4) |
| O(3)-S(1)-C(7)-C(2) | -164.6(3) |
| O(2)-S(1)-C(7)-C(2) | -32.0(4) |
| C(8)-S(1)-C(7)-C(2) | 82.5(4) |
| O(3)-S(1)-C(7)-C(6) | 16.8(4) |
| O(2)-S(1)-C(7)-C(6) | 149.5(3) |
| C(8)-S(1)-C(7)-C(6) | -96.0(3) |
| C(11)-O(1)-C(8)-C(9) | 0.4(4) |
| C(11)-O(1)-C(8)-S(1) | -179.9(3) |
| O(3)-S(1)-C(8)-C(9) | 136.8(4) |
| O(2)-S(1)-C(8)-C(9) | 7.1(5) |
| C(7)-S(1)-C(8)-C(9) | -110.4(5) |
| O(3)-S(1)-C(8)-O(1) | -42.8(3) |
| O(2)-S(1)-C(8)-O(1) | -172.5(3) |
| C(7)-S(1)-C(8)-O(1) | 70.0(3) |
| O(1)-C(8)-C(9)-C(10) | -0.6(5) |
| S(1)-C(8)-C(9)-C(10) | 179.7(3) |
| O(1)-C(8)-C(9)-Br(1) | 179.4(3) |
| S(1)-C(8)-C(9)-Br(1) | -0.2(7) |
| C(8)-C(9)-C(10)-C(11) | 0.6(4) |
| Br(1)-C(9)-C(10)-C(11) | -179.5(3) |
| C(8)-C(9)-C(10)-C(15) | 179.2(4) |
| Br(1)-C(9)-C(10)-C(15) | -0.9(7) |
| C(8)-O(1)-C(11)-C(10) | 0.0(4) |
| C(8)-O(1)-C(11)-C(12) | 179.7(4) |
| C(15)-C(10)-C(11)-O(1) | -179.2(4) |
| C(9)-C(10)-C(11)-O(1) | -0.4(4) |
| C(15)-C(10)-C(11)-C(12) | 1.1(6) |
| C(9)-C(10)-C(11)-C(12) | 179.9(4) |
| O(1)-C(11)-C(12)-C(13) | 179.8(4) |

| | |
|---|---|
| C(10)-C(11)-C(12)-C(13) | -0.5(7) |
| C(11)-C(12)-C(13)-C(14) | -1.3(7) |
| C(12)-C(13)-C(14)-C(15) | 2.7(8) |
| C(13)-C(14)-C(15)-C(10) | -2.0(7) |
| C(11)-C(10)-C(15)-C(14) | 0.2(6) |
| C(9)-C(10)-C(15)-C(14) | -178.2(5) |

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_20110714A_0m [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|