Oxy-polybrominated diphenyl ethers from the Indonesian marine sponge, *Lamellodysidea herbacea:* X-ray, SAR, and computational studies

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Figure S1. ^{1}H NMR spectrum of **1** (Me$_2$CO-d_6, 500 MHz)
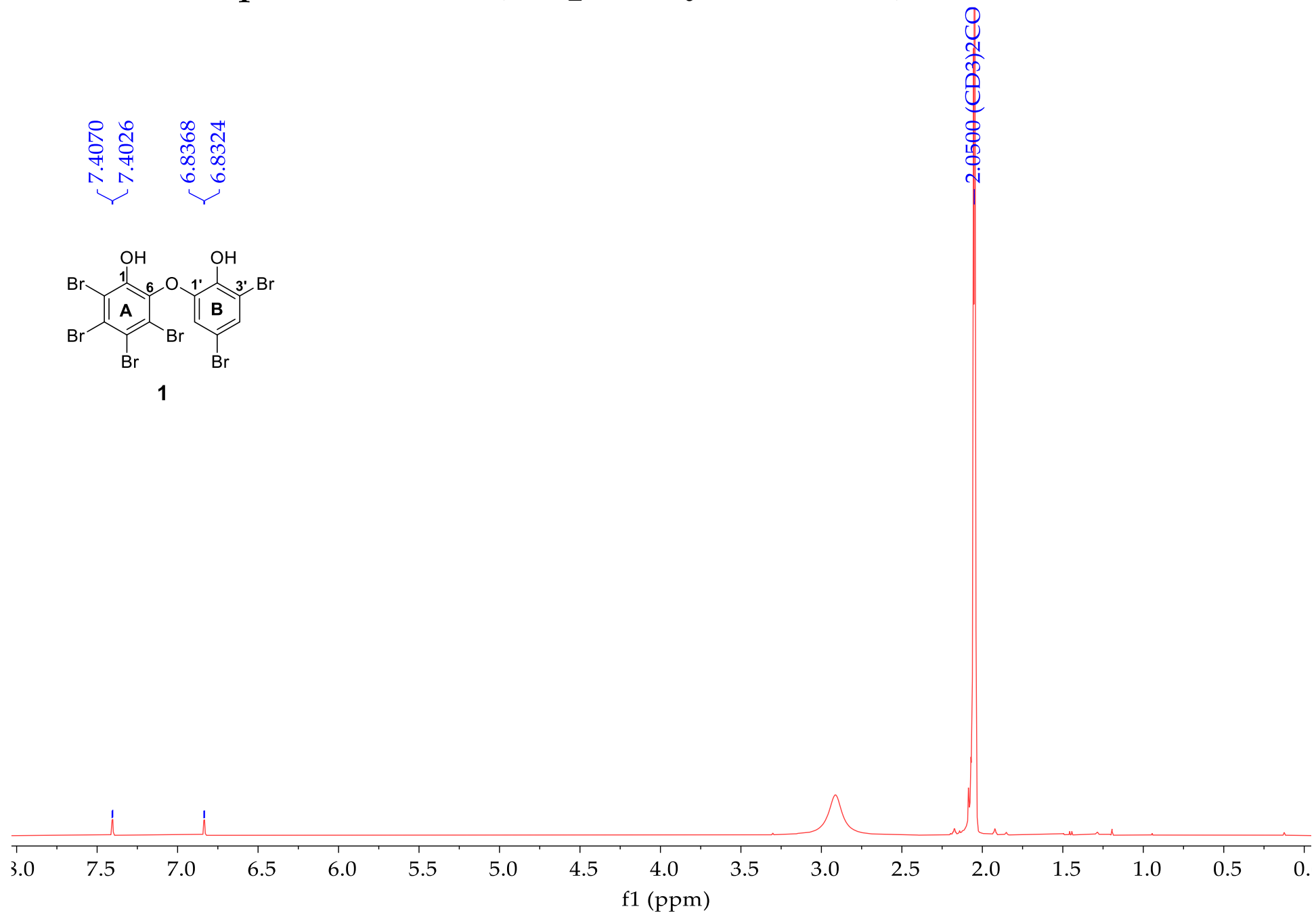
Figure S2. ^{1}H NMR spectrum of **1** (CD$_3$OD, 500 MHz)
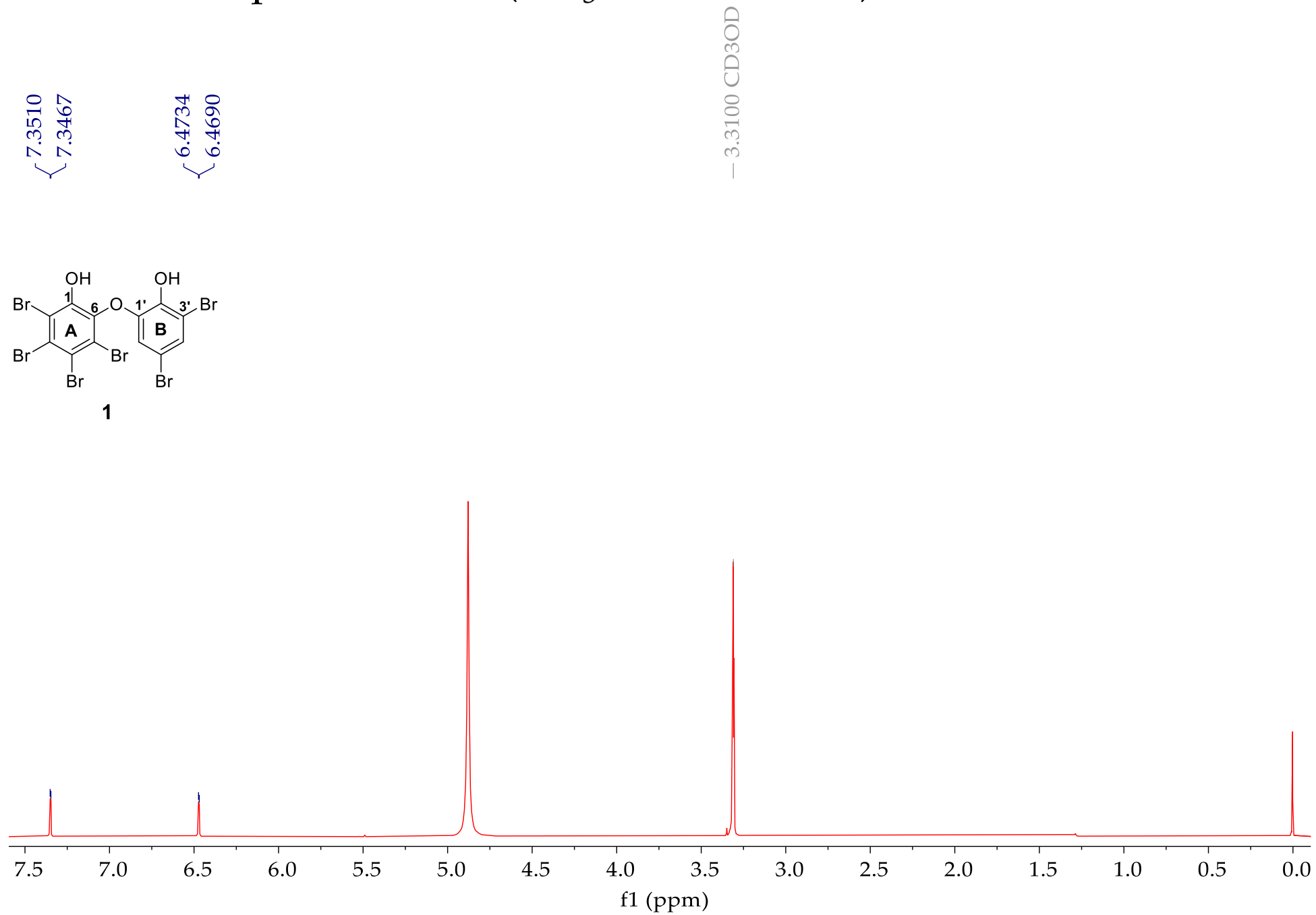
Figure S3. Crystal Structure of **1**
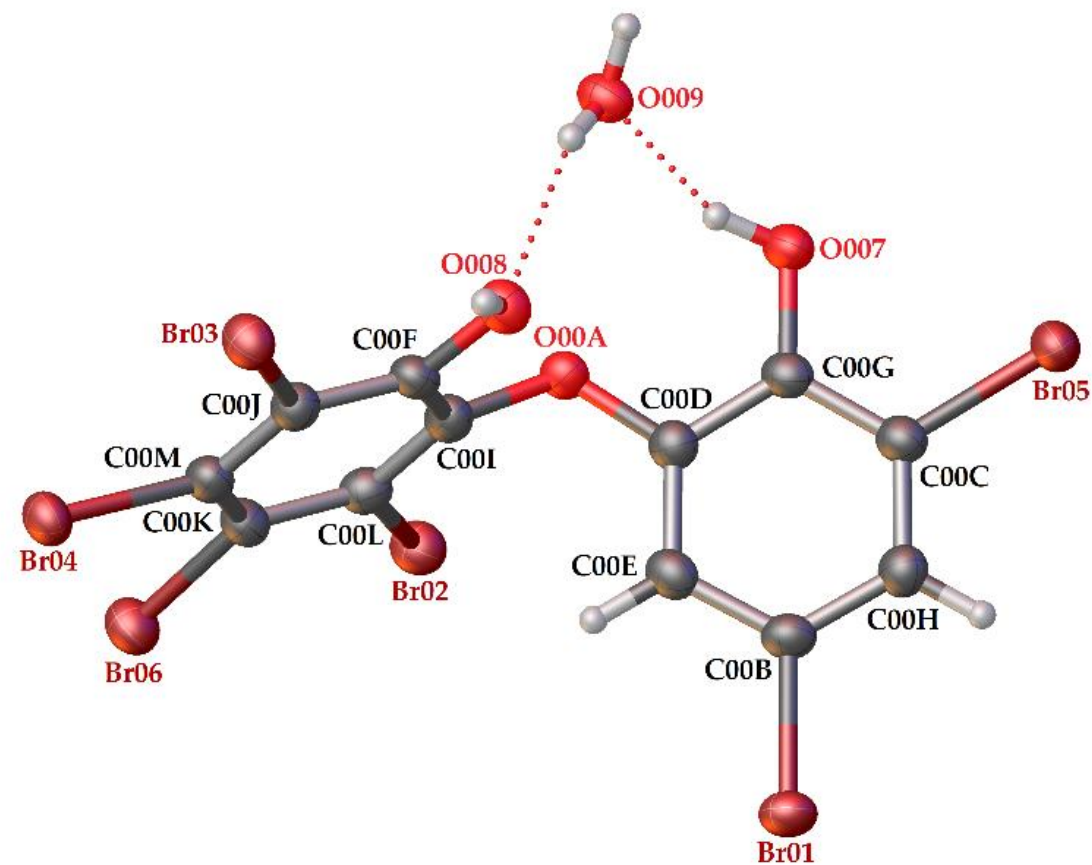
2, 3, 4, 5-tetrabromo-6-(3', 5'-dibromo-2'-hydroxyphenoxy) phenol

Table S1. Crystal Data & Structure Refinement for **1**

Identification code	180726irai
Empirical formula	$C_{12}H_6Br_6O_4$
Formula weight	693.63
Temperature/K	123.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	4.74979(10)
b/Å	18.7360(3)
c/Å	18.3463(4)
$\alpha/°$	90
$\beta/°$	91.6135(19)
$\gamma/°$	90
Volume/Å^3	1632.02(6)
Z	4
ϱ_{calc}g/cm^3	2.823
μ/mm^{-1}	14.772
F(000)	1280.0
Crystal size/mm^3	0.281 × 0.279 × 0.221
Radiation	$MoK\alpha$ ($\lambda = 0.71073$)
2Θ range for data collection/°	3.108 to 62.354
Index ranges	$-6 \le h \le 6$, $-25 \le k \le 25$, $-26 \le l \le 25$
Reflections collected	20780
Independent reflections	4898 [$R_{int} = 0.0374$, $R_{sigma} = 0.0252$]
Data/restraints/parameters	4898/0/208
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	$R_1 = 0.0435$, $wR_2 = 0.1179$
Final R indexes [all data]	$R_1 = 0.0526$, $wR_2 = 0.1269$
Largest diff. peak/hole / e Å^{-3}	1.42/-0.77

Table S2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	x	y	z	U(eq)
Br01	-227.5(9)	8111.4(2)	6204.8(3)	34.75(12)
Br02	7616.6(9)	6700.4(2)	8071.2(3)	34.93(12)
Br03	-790.8(10)	3995.6(3)	7420.9(3)	34.86(12)
Br04	-89.4(10)	4628.6(2)	9099.8(2)	34.71(12)
Br05	6901.4(10)	6977.5(3)	4062.1(3)	36.74(13)
Br06	4059.1(11)	5999.0(3)	9432.1(3)	37.98(13)
O00A	6453(6)	5900.9(16)	6644.2(17)	29.8(6)
O007	8319(7)	5945.1(17)	5269.5(19)	34.9(7)
O008	2752(7)	4874.0(18)	6353.4(17)	33.3(6)
C00B	2409(9)	7428(2)	5905(2)	30.4(8)
C00C	5445(9)	6955(2)	5004(3)	31.1(8)
C00D	5283(9)	6417(2)	6184(2)	29.1(8)
C00E	3283(9)	6900(2)	6398(3)	31.4(8)
C00F	2945(9)	5093(2)	7060(2)	28.8(8)
C00G	6383(9)	6428(2)	5484(2)	29.7(8)
C00H	3461(9)	7463(2)	5213(3)	32.7(9)
C00I	4826(9)	5659(2)	7212(2)	29.7(8)
C00J	1528(9)	4788(2)	7626(2)	29.3(8)
C00K	3673(9)	5619(2)	8478(2)	30.9(8)
C00L	5196(9)	5926(2)	7910(2)	29.6(8)
C00M	1877(9)	5049(2)	8338(2)	31.0(8)
O009	7827(7)	4570.4(18)	5686.3(19)	33.8(7)

Table S3. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **1**.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br01	31.5(2)	30.9(2)	42.1(3)	-1.96(17)	6.89(17)	4.77(16)
Br02	33.7(2)	33.4(2)	37.9(2)	-2.53(17)	4.49(17)	-4.54(17)
Br03	36.4(2)	34.0(2)	34.4(2)	-0.82(16)	6.55(17)	-7.00(17)
Br04	38.1(2)	35.6(2)	30.9(2)	1.45(16)	9.31(17)	-2.63(17)
Br05	44.1(3)	34.4(2)	32.3(2)	2.96(16)	10.48(18)	4.25(18)
Br06	43.6(3)	38.1(3)	32.4(2)	-3.13(17)	5.03(18)	-4.09(19)
O00A	26.9(14)	30.5(14)	32.2(15)	2.5(12)	6.2(11)	1.3(11)
O007	39.7(17)	29.3(15)	36.2(17)	1.9(12)	12.3(13)	4.3(13)
O008	30.4(15)	36.2(16)	33.5(16)	-1.4(13)	3.7(12)	-4.4(13)
C00B	25.9(18)	29(2)	37(2)	-2.7(16)	4.4(15)	1.9(15)
C00C	32(2)	29(2)	33(2)	-1.1(16)	6.9(16)	-0.1(16)
C00D	26.7(18)	28.7(19)	32(2)	1.2(15)	4.0(15)	-2.0(15)
C00E	29.5(19)	32(2)	33(2)	-2.3(16)	7.3(16)	-3.5(16)
C00F	28.2(18)	29.7(19)	28.6(19)	-2.4(15)	5.7(15)	2.8(15)
C00G	30.0(19)	26.3(18)	33(2)	-2.4(15)	5.7(15)	-1.0(15)
C00H	32(2)	32(2)	34(2)	3.7(17)	4.3(16)	-0.1(17)
C00I	26.7(18)	29.4(19)	33(2)	3.7(16)	6.2(15)	1.4(15)
C00J	28.6(18)	27.6(19)	32(2)	1.2(15)	2.8(15)	-0.5(15)
C00K	33(2)	32(2)	27.5(19)	-1.5(16)	4.4(15)	1.6(17)
C00L	26.0(18)	26.6(19)	36(2)	-1.1(16)	2.6(15)	-0.4(15)
C00M	31(2)	31(2)	32(2)	2.2(16)	7.2(16)	3.7(16)
O009	32.8(16)	33.0(16)	36.0(17)	-4.2(13)	9.6(13)	-1.7(13)

Table S4. Bond Lengths for **1**

Atom	Atom	Length/Å
Br01	C00B	1.884(4)
Br02	C00L	1.869(4)
Br03	C00J	1.881(4)
Br04	C00M	1.876(4)
Br05	C00C	1.880(5)
Br06	C00K	1.893(4)
O00A	C00D	1.389(5)
O00A	C00I	1.390(5)
O007	C00G	1.357(5)
O008	C00F	1.361(5)
C00B	C00E	1.396(6)
C00B	C00H	1.380(6)
C00C	C00G	1.387(6)
C00C	C00H	1.400(6)
C00D	C00E	1.378(6)
C00D	C00G	1.400(6)
C00F	C00I	1.410(6)
C00F	C00J	1.377(6)
C00I	C00L	1.382(6)
C00J	C00M	1.400(6)
C00K	C00L	1.408(6)
C00K	C00M	1.386(6)

Table S5. Bond Angles for 1

Atom	Atom	Atom	Angle/°
C00D	O00A	C00I	117.5(3)
C00E	C00B	Br01	118.7(3)
C00H	C00B	Br01	119.8(3)
C00H	C00B	C00E	121.5(4)
C00G	C00C	Br05	118.6(3)
C00G	C00C	C00H	121.1(4)
C00H	C00C	Br05	120.3(3)
O00A	C00D	C00G	114.6(4)
C00E	C00D	O00A	123.4(4)
C00E	C00D	C00G	122.0(4)
C00D	C00E	C00B	118.4(4)
O008	C00F	C00I	116.1(4)
O008	C00F	C00J	124.9(4)
C00J	C00F	C00I	118.9(4)
O007	C00G	C00C	120.0(4)
O007	C00G	C00D	121.9(4)
C00C	C00G	C00D	118.1(4)

Atom	Atom	Atom	Angle/°
C00B	C00H	C00C	118.9(4)
O00A	C00I	C00F	117.4(4)
C00L	C00I	O00A	121.2(4)
C00L	C00I	C00F	121.2(4)
C00F	C00J	Br03	118.2(3)
C00F	C00J	C00M	120.8(4)
C00M	C00J	Br03	121.1(3)
C00L	C00K	Br06	119.5(3)
C00M	C00K	Br06	120.3(3)
C00M	C00K	C00L	120.3(4)
C00I	C00L	Br02	119.2(3)
C00I	C00L	C00K	118.9(4)
C00K	C00L	Br02	121.8(3)
C00J	C00M	Br04	120.0(3)
C00K	C00M	Br04	120.2(3)
C00K	C00M	C00J	119.9(4)

Table S6. Torsion Angles for 1

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br01	C00B	C00E	C00D	-177.8(3)	C00E	C00B	C00H	C00C	0.1(7)
Br01	C00B	C00H	C00C	179.2(3)	C00E	C00D	C00G	O007	-178.9(4)
Br03	C00J	C00M	Br04	-2.3(5)	C00E	C00D	C00G	C00C	1.3(7)
Br03	C00J	C00M	C00K	177.8(3)	C00F	C00I	C00L	Br02	-177.7(3)
Br05	C00C	C00G	O007	0.2(6)	C00F	C00I	C00L	C00K	0.5(7)
Br05	C00C	C00G	C00D	-179.9(3)	C00F	C00J	C00M	Br04	179.7(3)
Br05	C00C	C00H	C00B	179.3(3)	C00F	C00J	C00M	C00K	-0.2(7)
Br06	C00K	C00L	Br02	0.3(5)	C00G	C00C	C00H	C00B	-0.8(7)
Br06	C00K	C00L	C00I	-177.9(3)	C00G	C00D	C00E	C00B	-2.0(7)
Br06	C00K	C00M	Br04	-2.2(5)	C00H	C00B	C00E	C00D	1.3(7)
Br06	C00K	C00M	C00J	177.7(3)	C00H	C00C	C00G	O007	-179.6(4)
O00A	C00D	C00E	C00B	175.4(4)	C00H	C00C	C00G	C00D	0.2(7)
O00A	C00D	C00G	O007	3.5(6)	C00I	O00A	C00D	C00E	27.7(6)
O00A	C00D	C00G	C00C	-176.3(4)	C00I	O00A	C00D	C00G	-154.8(4)
O00A	C00I	C00L	Br02	7.4(6)	C00I	C00F	C00J	Br03	-176.1(3)
O00A	C00I	C00L	C00K	-174.4(4)	C00I	C00F	C00J	C00M	1.9(6)
O008	C00F	C00I	O00A	-4.9(6)	C00J	C00F	C00I	O00A	173.0(4)
O008	C00F	C00I	C00L	-180.0(4)	C00J	C00F	C00I	C00L	-2.1(6)
O008	C00F	C00J	Br03	1.6(6)	C00L	C00K	C00M	Br04	178.7(3)
O008	C00F	C00J	C00M	179.6(4)	C00L	C00K	C00M	C00J	-1.5(7)
C00D	O00A	C00I	C00F	86.5(5)	C00M	C00K	C00L	Br02	179.4(3)
C00D	O00A	C00I	C00L	-98.5(5)	C00M	C00K	C00L	C00I	1.3(7)

Table S7. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for **1**

Atom	x	y	z	U(eq)
H007	8230	5579	5532	52
H008	1318	4616	6292	50
H00E	2518	6874	6871	38
H00H	2849	7826	4883	39
H00A	6146	4500	5816	51
H00B	8140(110)	4250(30)	5380(30)	31(13)

Table S8. Refinement Model Description of **1**

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

   At 1.2 times of: All C(H) groups

   At 1.5 times of: All O(H) groups

2a. Free rotating group: O009(H00A)

2b. Aromatic/amide H refined with riding coordinates: C00E(H00E), C00H(H00H)

2c. Idealized tetrahedral OH refined as rotating group: O007(H007), O008(H008)

Table S9. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 1

```
SPARTAN'20 Quantum Mechanics Driver:   (Win/64b)              Release  1.0.0

Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 717
Number of electrons: 310
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step        Energy         Max Grad.       Max Dist.
           1     -16130.324682      0.029469        0.075204
           2     -16130.331007      0.007593        0.063575
           3     -16130.331542      0.001578        0.004060
           4     -16130.331567      0.000786        0.008361
           5     -16130.331582      0.000337        0.001851


  Reason for exit: Successful completion
  Quantum Calculation CPU Time :   5:01:41.34
  Quantum Calculation Wall Time:     20:20.21
```

Figure S4. HOMO-LUMO of **1**
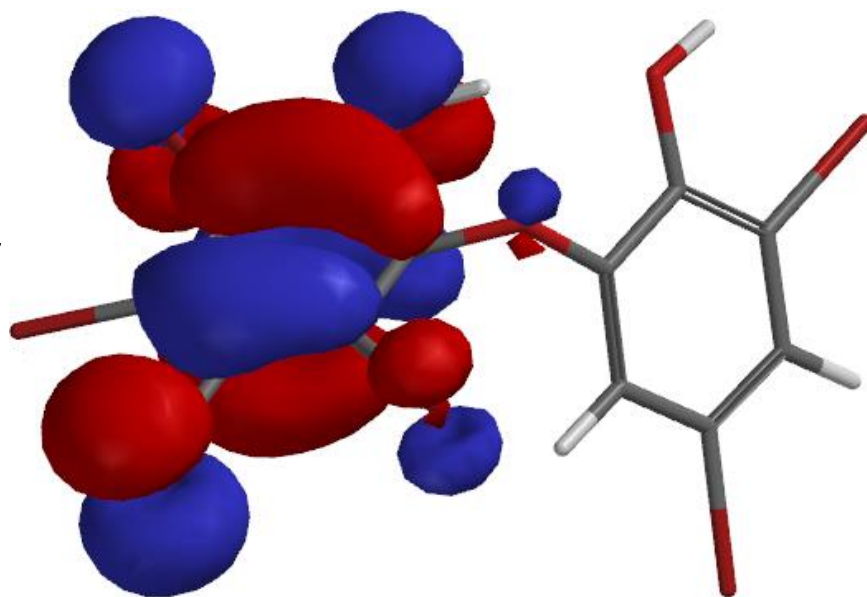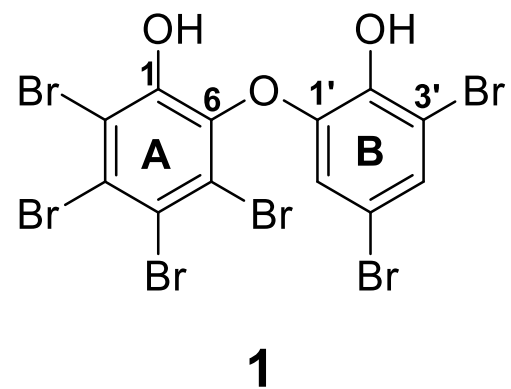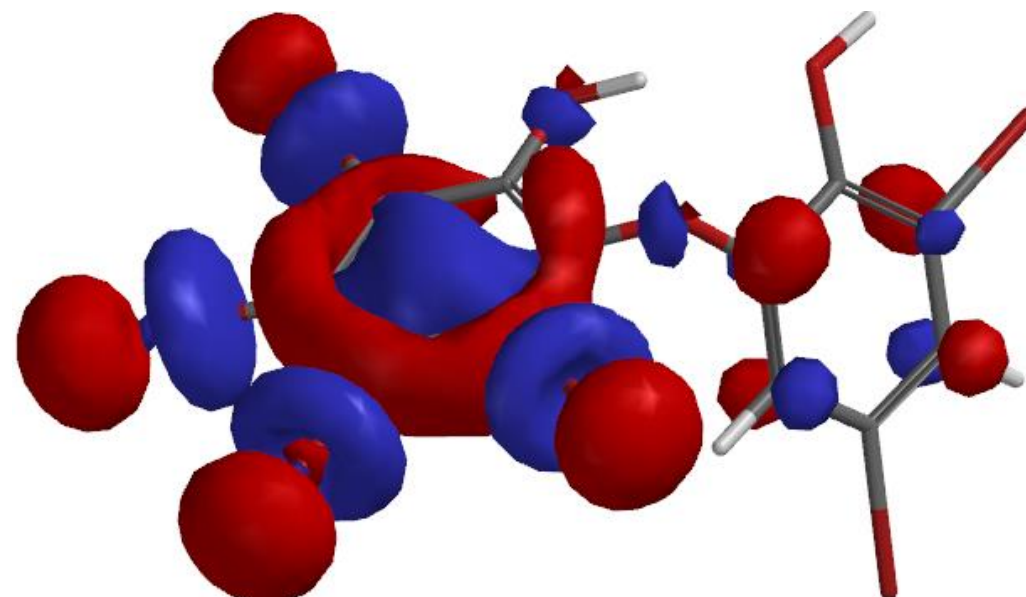
HOMO 1 **LUMO 1**

Figure S5. Calculated ^{13}C NMR Chemical Shift of **1**
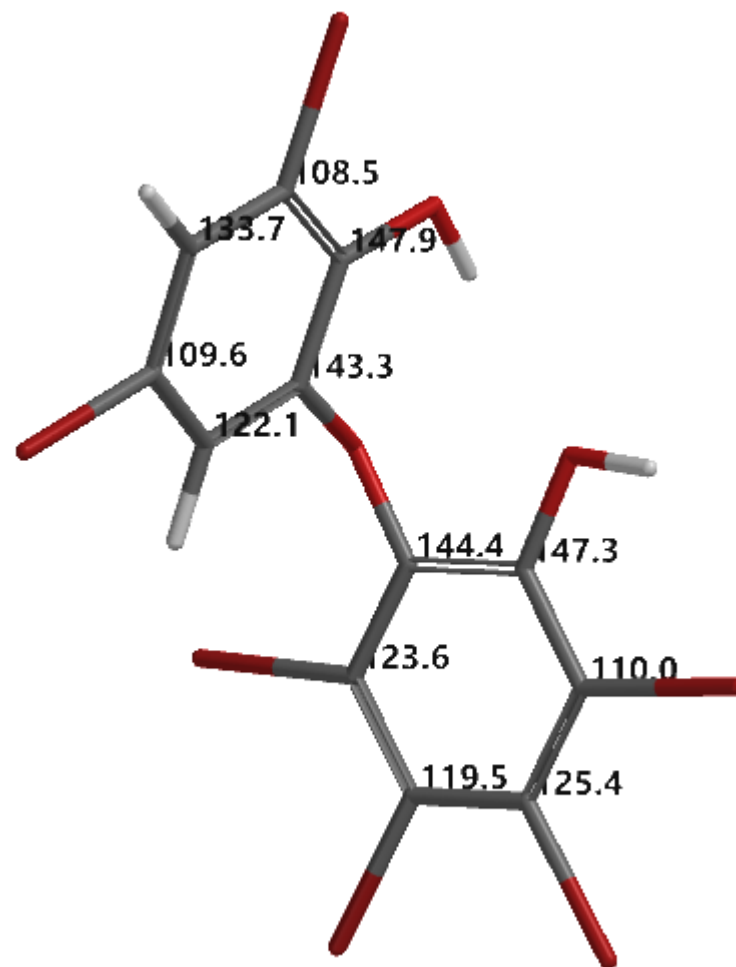
Figure S6. ^{1}H NMR spectrum of **2** (Me$_2$CO-d_6, 500 MHz)
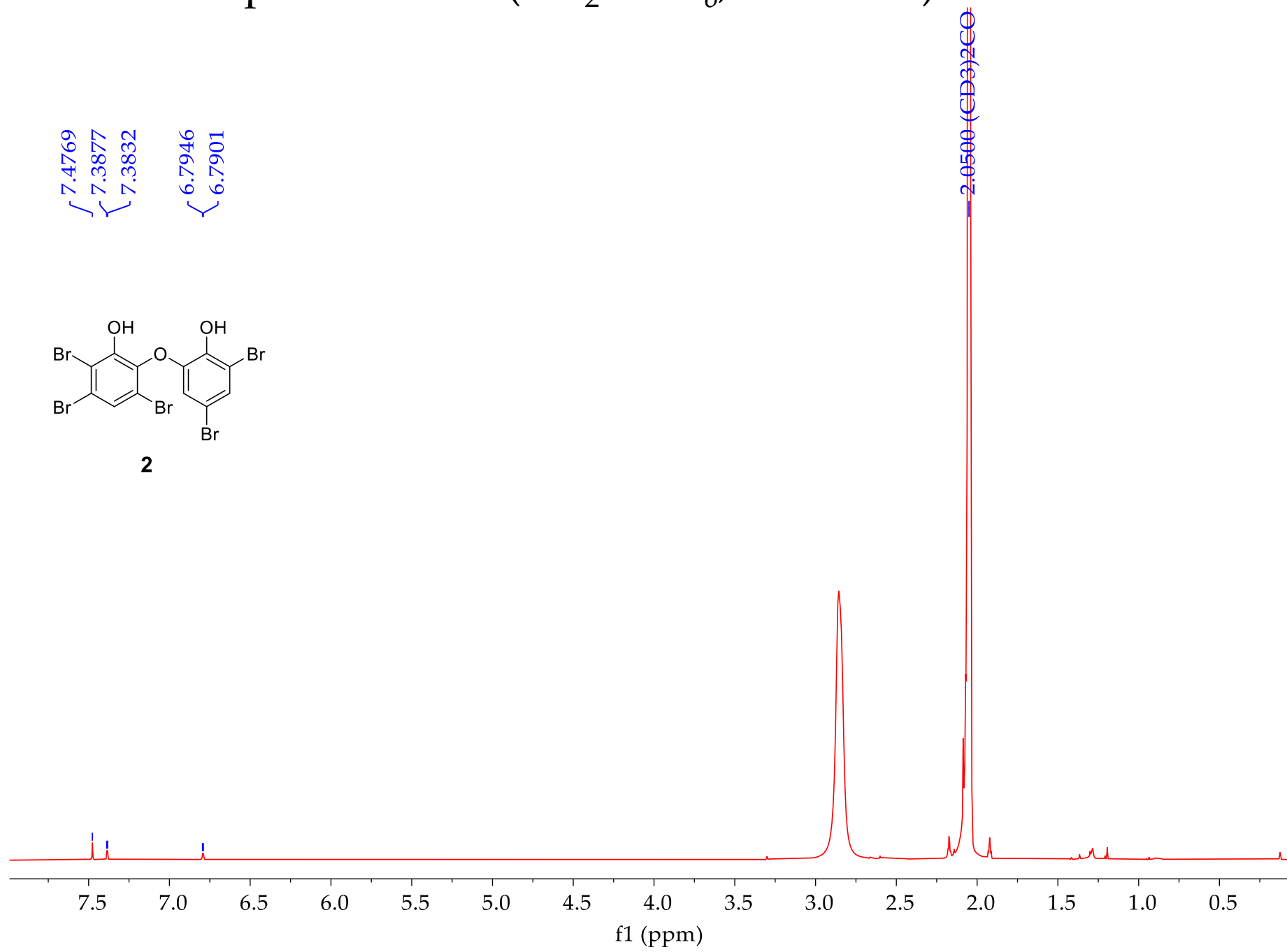
Table S10. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 2

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 675
Number of electrons: 276
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step       Energy         Max Grad.      Max Dist.
            1    -13556.767302      0.022717       0.081068
            2    -13556.772247      0.007810       0.053125
            3    -13556.772709      0.001135       0.001814
            4    -13556.772720      0.000908       0.013479
            5    -13556.772746      0.000390       0.002851
            6    -13556.772747      0.000208       0.001519
```

Figure S7. HOMO-LUMO of **2**

2
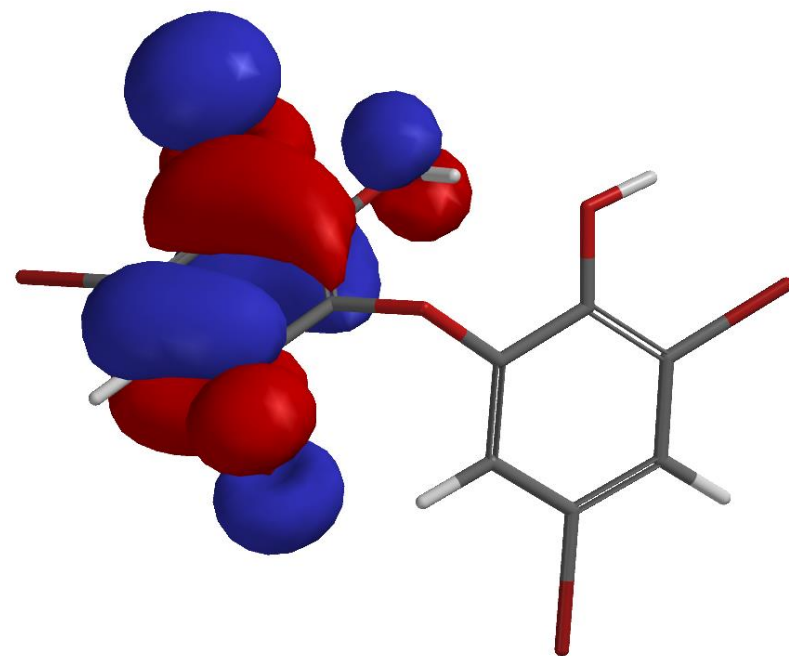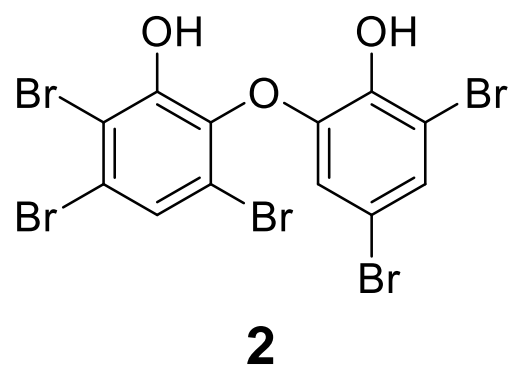
HOMO 2
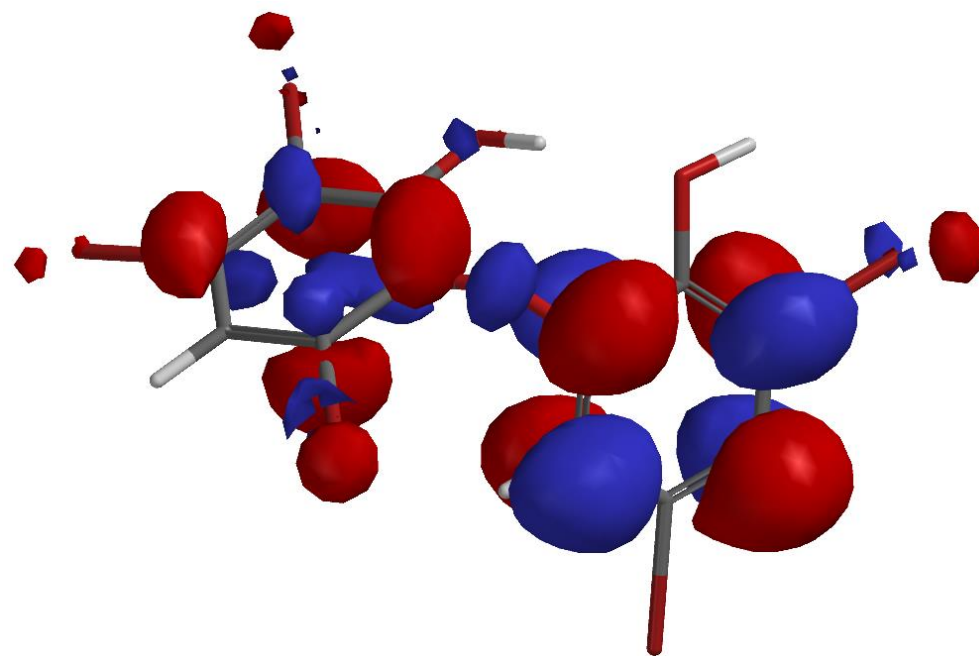
LUMO 2

Figure S8. Calculated ^{13}C NMR Chemical Shift of **2**
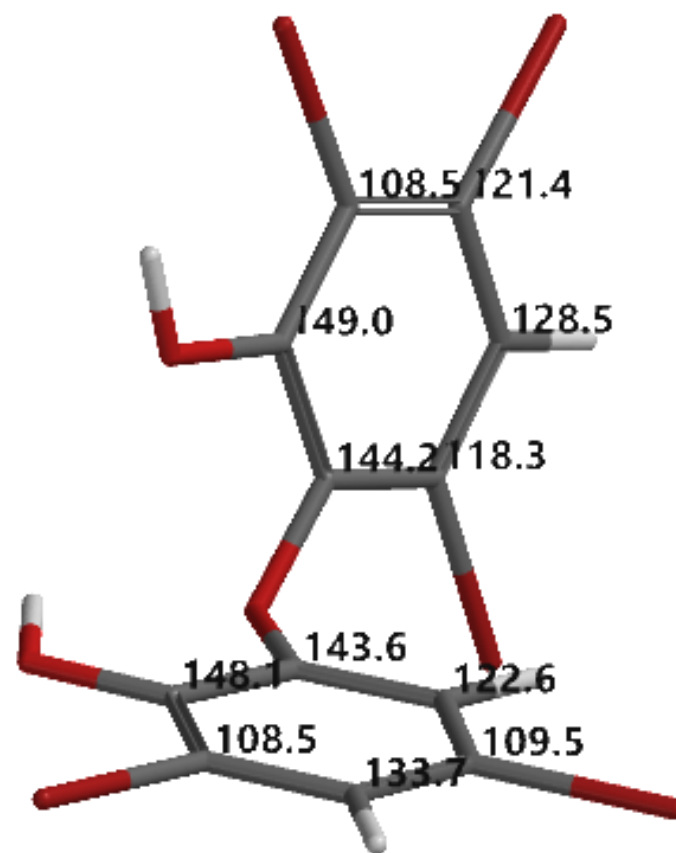
Figure S9. ^{1}H NMR spectrum of **3** (CDCl$_3$, 500 MHz)
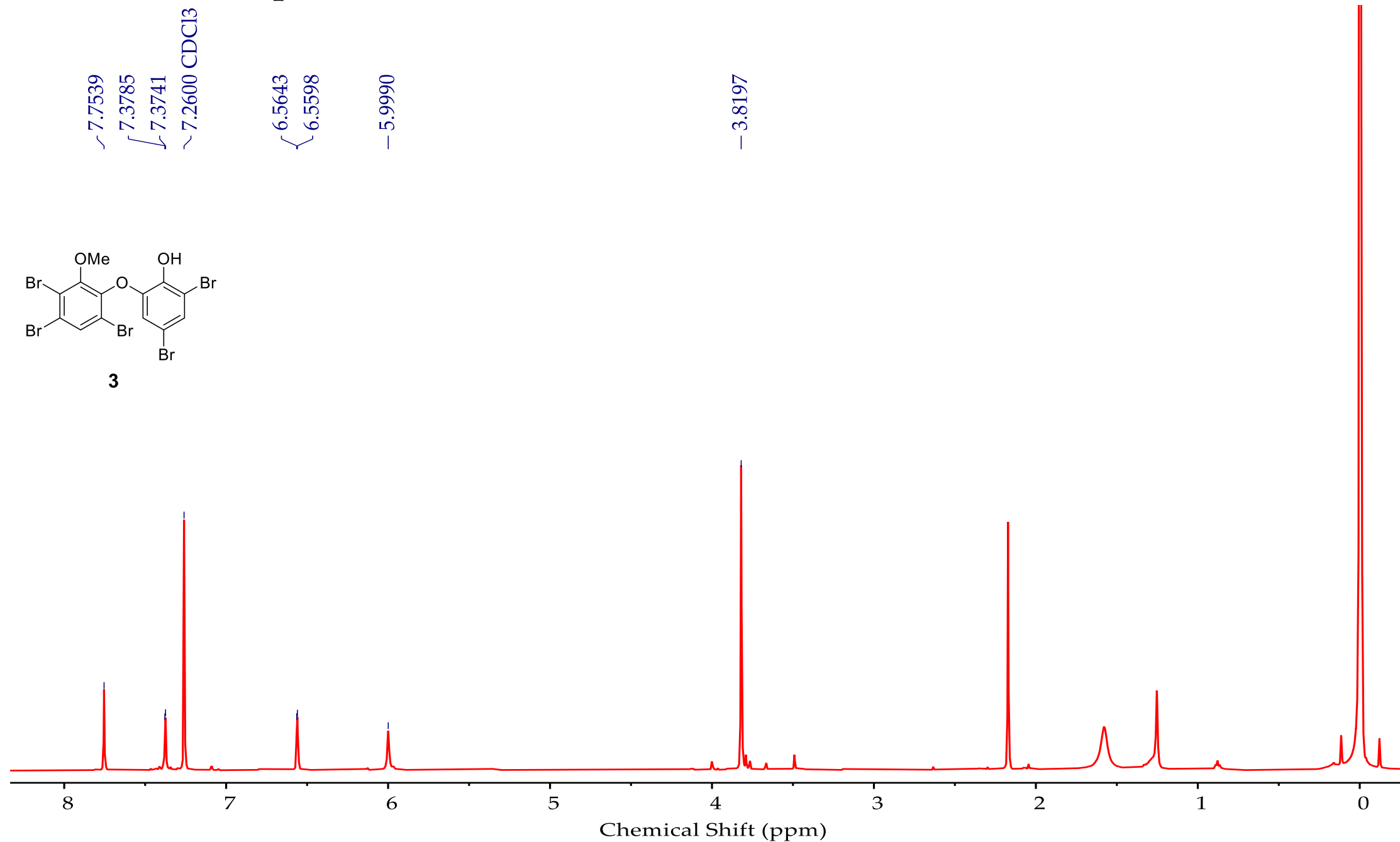
Table S11. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 3

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 714
Number of electrons: 284
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step      Energy          Max Grad.        Max Dist.
          1    -13596.053627      0.022713         0.083976
          2    -13596.059595      0.007325         0.138126
          3    -13596.060478      0.001646         0.025831
          4    -13596.060560      0.001320         0.153568
          5    -13596.060814      0.001554         0.062408
          6    -13596.060876      0.001640         0.049467
          7    -13596.060903      0.001004         0.038755
          8    -13596.060924      0.000578         0.008867
          9    -13596.060929      0.000183         0.003442
```

Figure S10. HOMO-LUMO of **3**
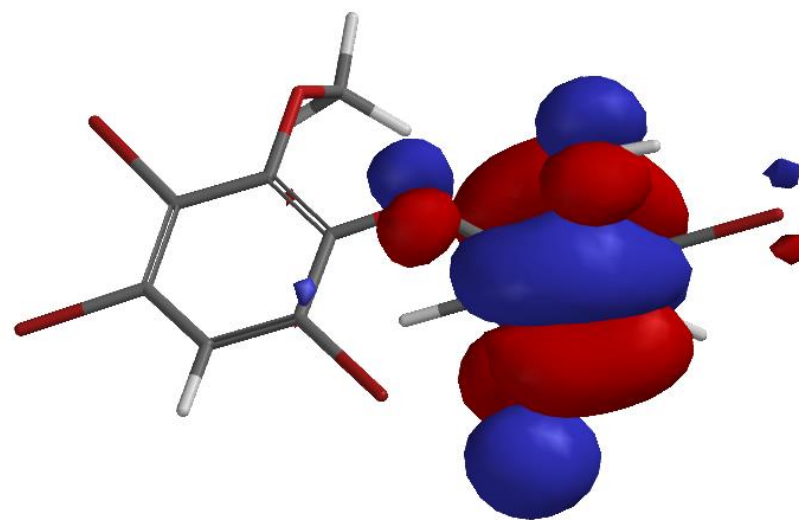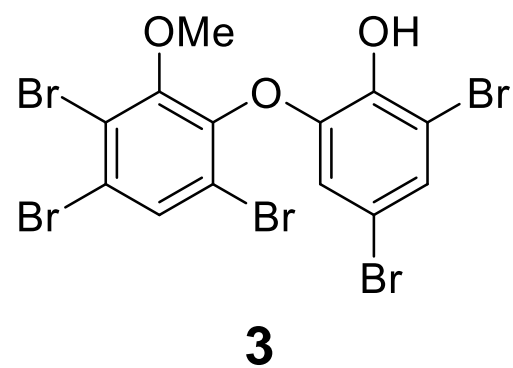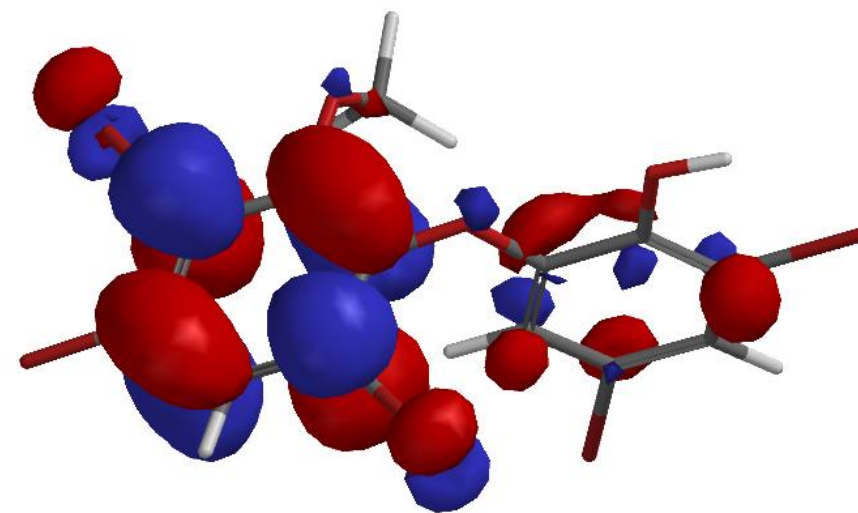
HOMO 3　　　　**LUMO 3**

Figure S11. Calculated ^{13}C NMR Chemical Shift of **3**
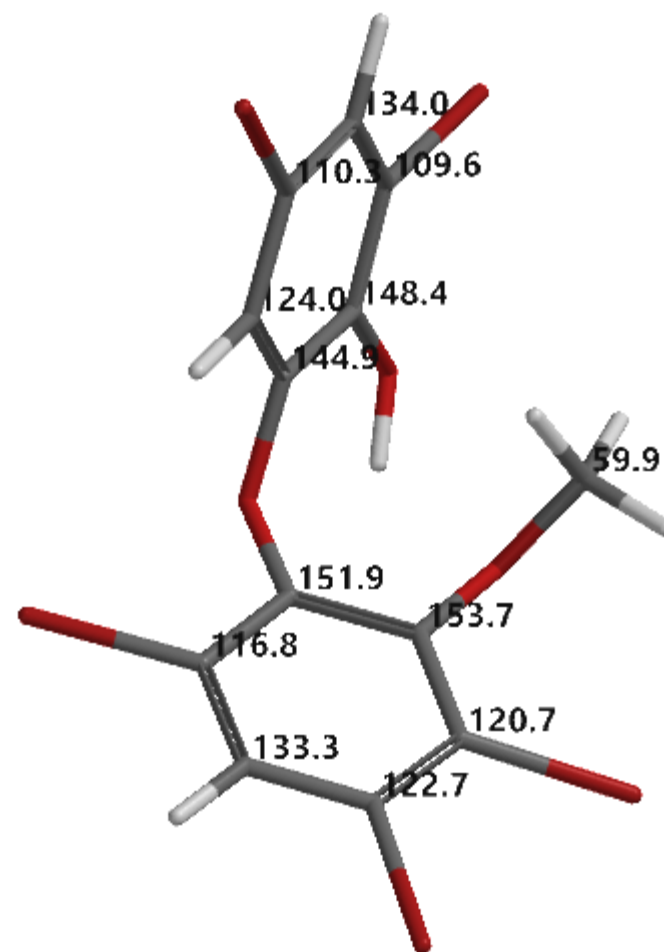
Figure S12. ¹H NMR spectrum of **4** (Me$_2$CO-d_6, 500 MHz)

Table S12. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 4

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 714
Number of electrons: 284
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step       Energy          Max Grad.        Max Dist.
           1    -13596.056101        0.022110         0.075185
           2    -13596.061698        0.008615         0.116440
           3    -13596.062567        0.003925         0.073192
           4    -13596.062888        0.004495         0.088281
           5    -13596.063157        0.003611         0.080883
           6    -13596.063326        0.001687         0.060938
           7    -13596.063428        0.001079         0.119373
           8    -13596.063575        0.003974         0.042723
           9    -13596.063618        0.003396         0.071338
          10    -13596.063520        0.005150         0.048847
          11    -13596.063706        0.000446         0.010202
          12    -13596.063710        0.000324         0.001582
```

Figure S13. HOMO-LUMO of **4**
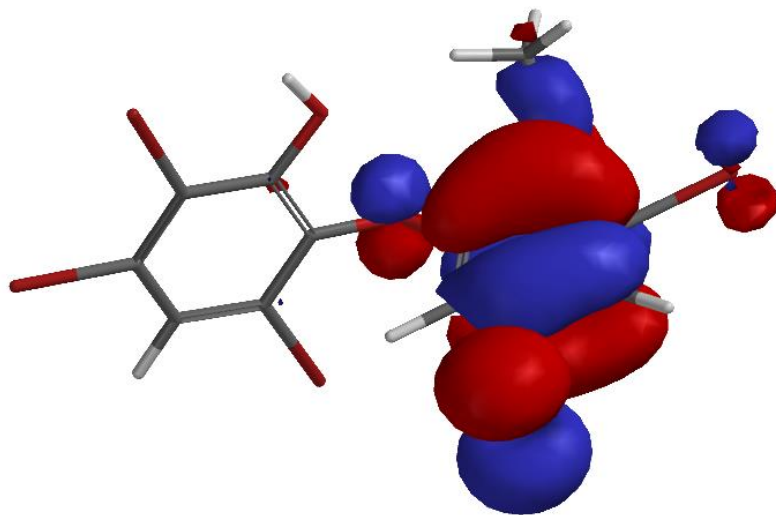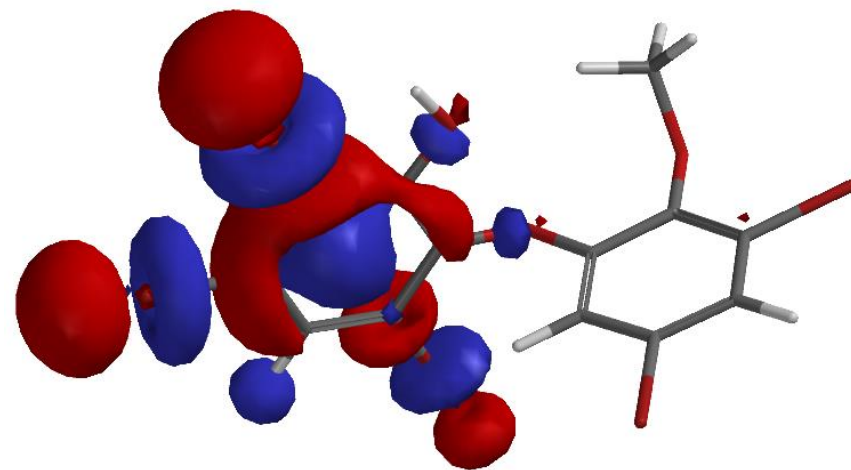
HOMO 4   **LUMO 4**

Figure S14. Calculated ^{13}C NMR Chemical Shift of **4**
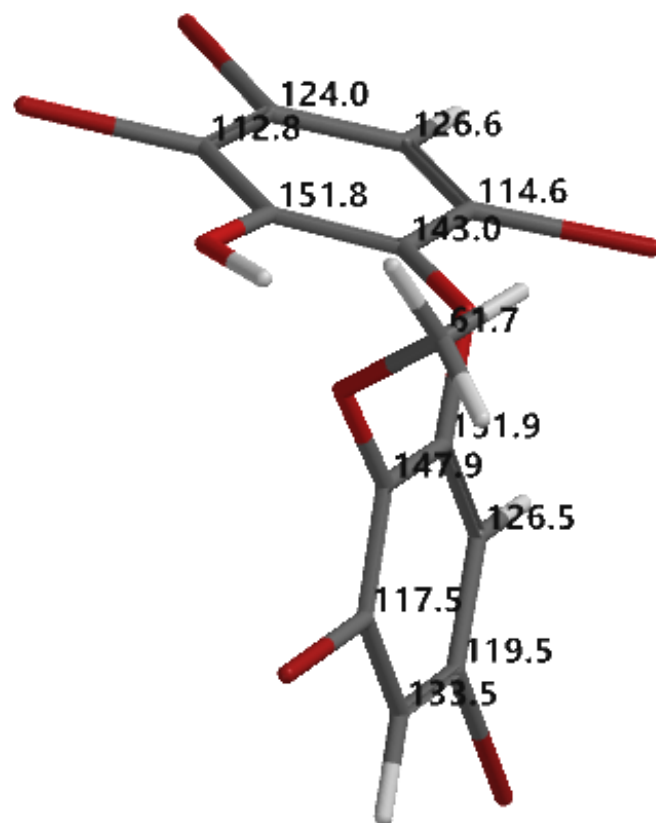
Figure S15. ^{1}H NMR spectrum of **5** (CDCl$_3$, 500 MHz)
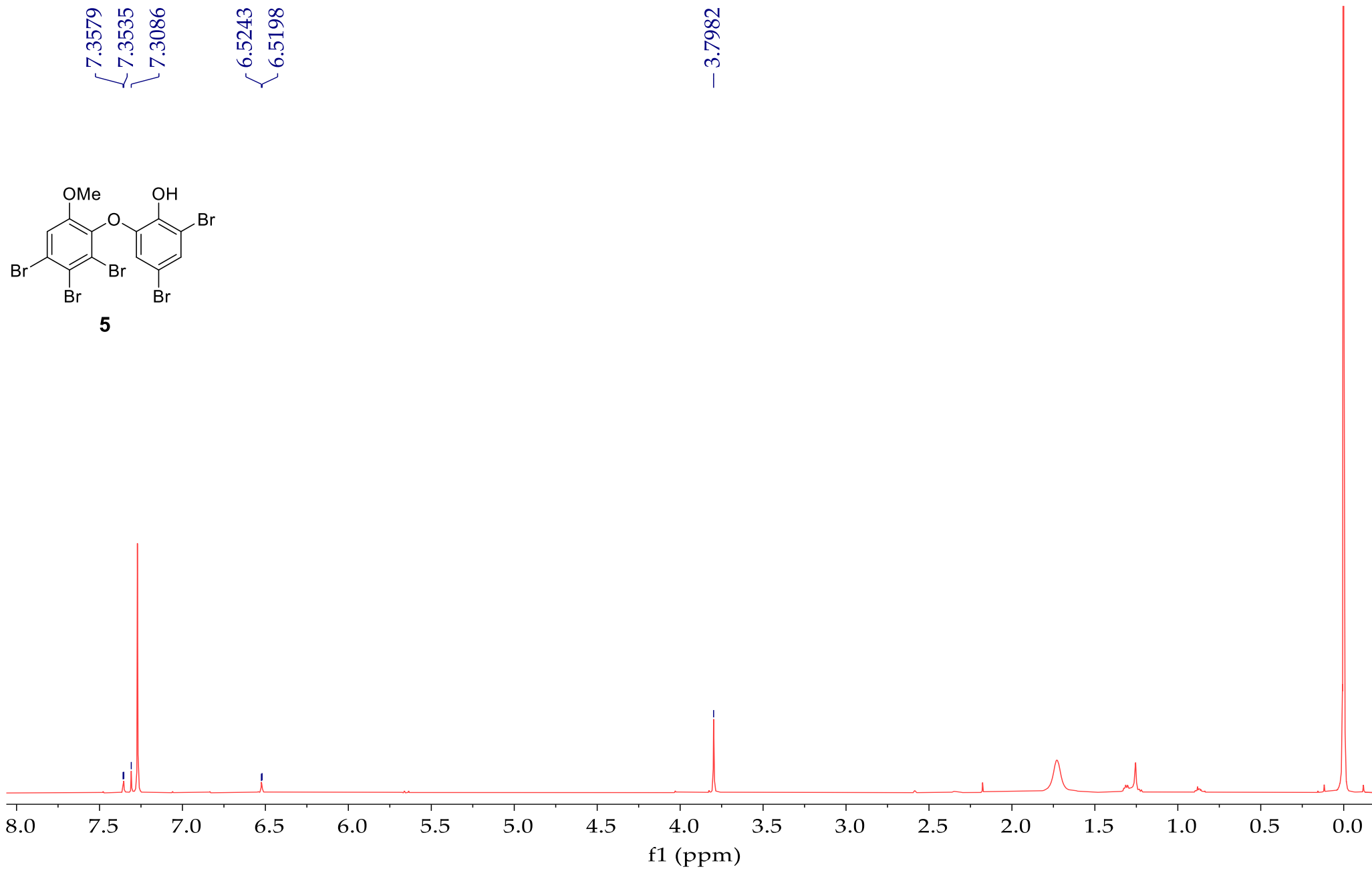
Table S13. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **5**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 714
Number of electrons: 284
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step      Energy           Max Grad.       Max Dist.
          1     -13596.053210       0.024364        0.077730
          2     -13596.058728       0.007035        0.047576
          3     -13596.059286       0.002251        0.011393
          4     -13596.059338       0.002116        0.055522
          5     -13596.059466       0.000895        0.037523
          6     -13596.059496       0.001018        0.008389
          7     -13596.059503       0.000458        0.008994
```

Figure S16. HOMO-LUMO of 5
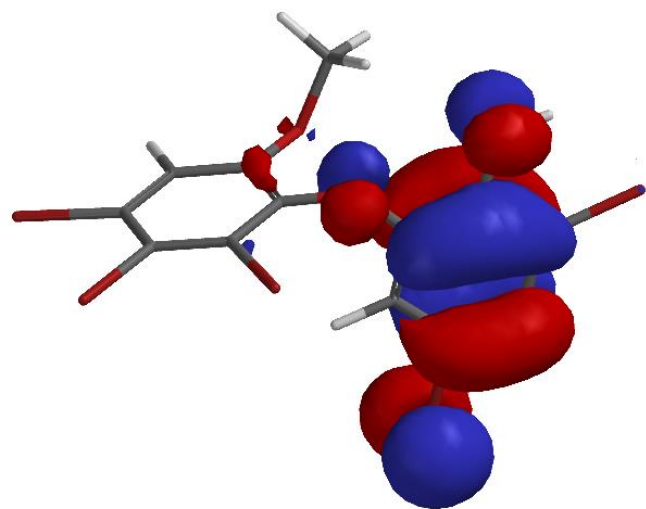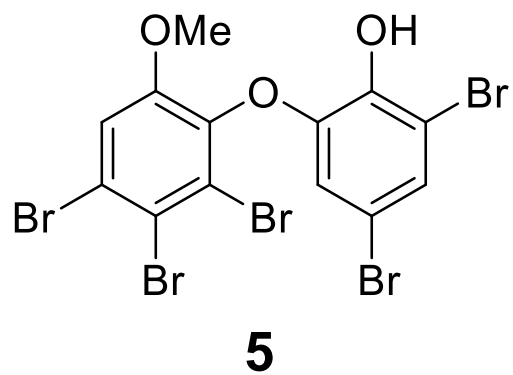
HOMO 5
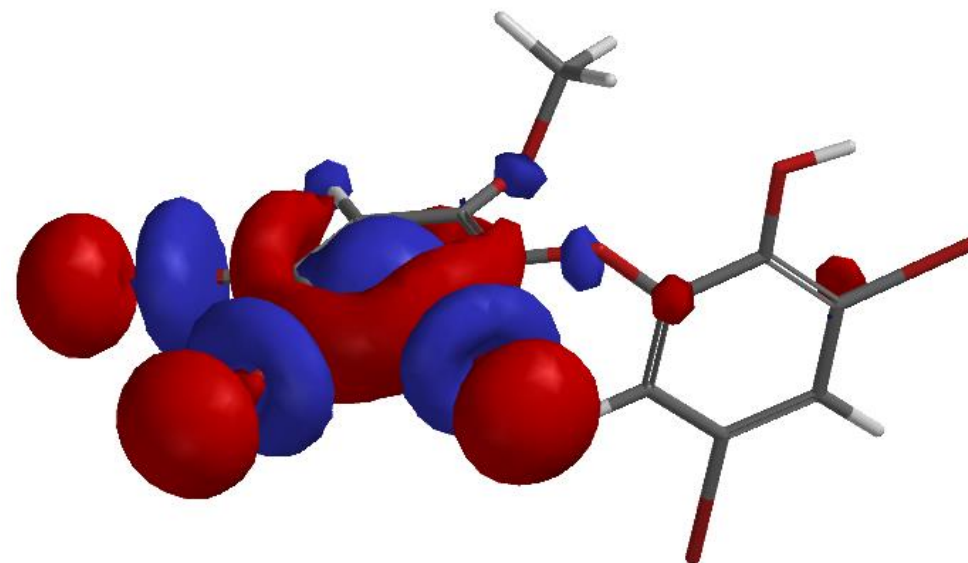
LUMO 5

Figure S17. Calculated ¹³C NMR Chemical Shift of **5**
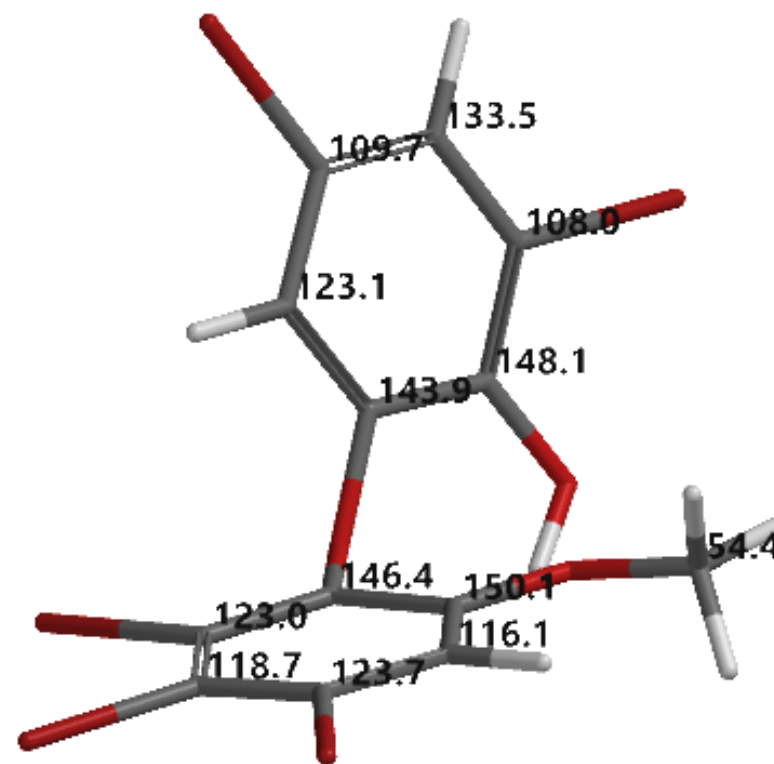
Figure S19. ^{13}C NMR spectrum of **6** (Me$_2$CO-d_6, 500 MHz)
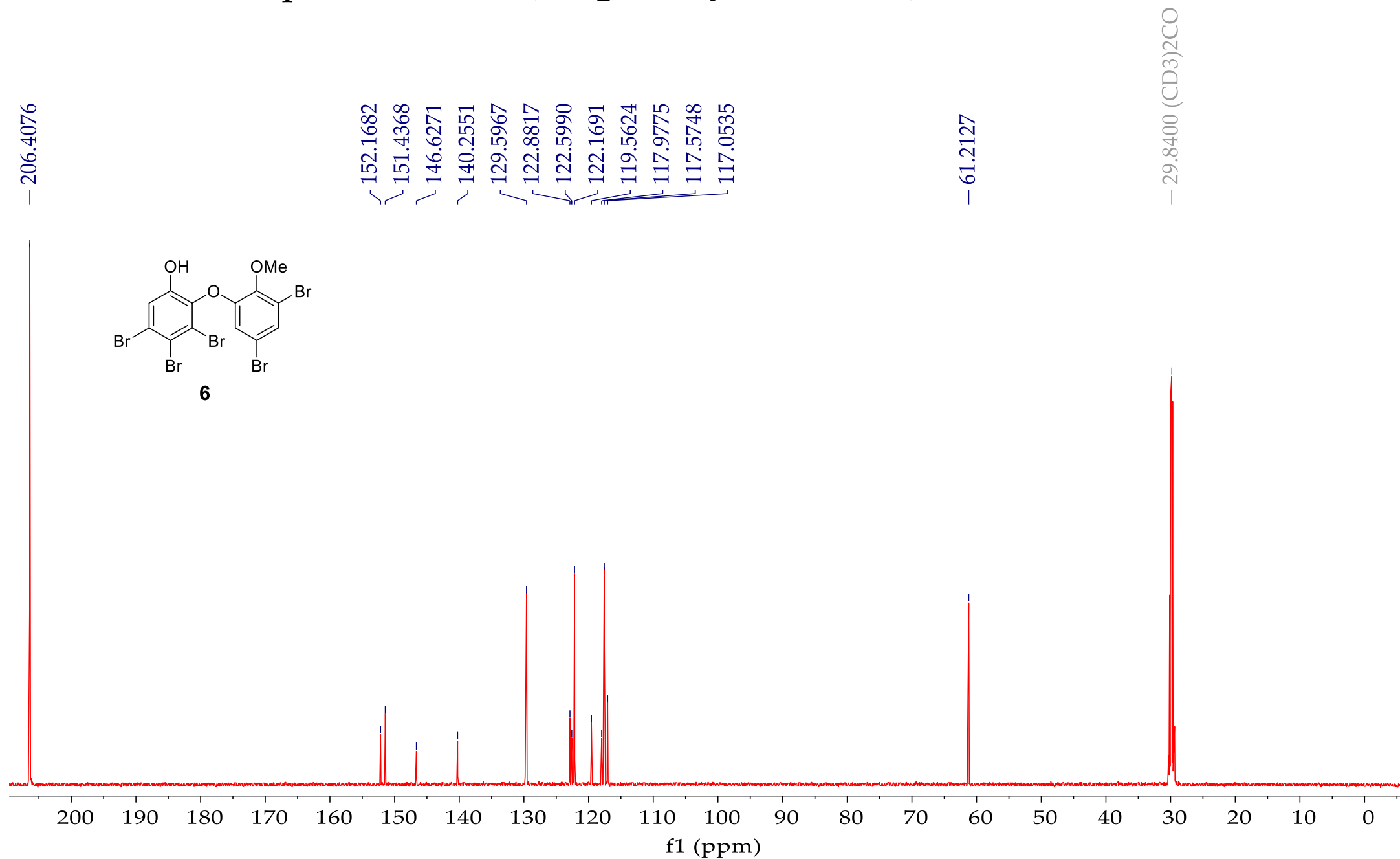
Figure S20. ^{1}H-^{13}C HSQC spectrum of **6** (Me$_2$CO-*d$_6$*, 500 MHz)

{2.05,29.84}(CD3)2CO
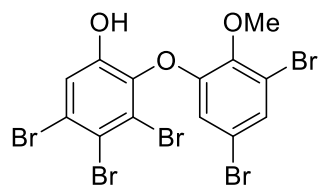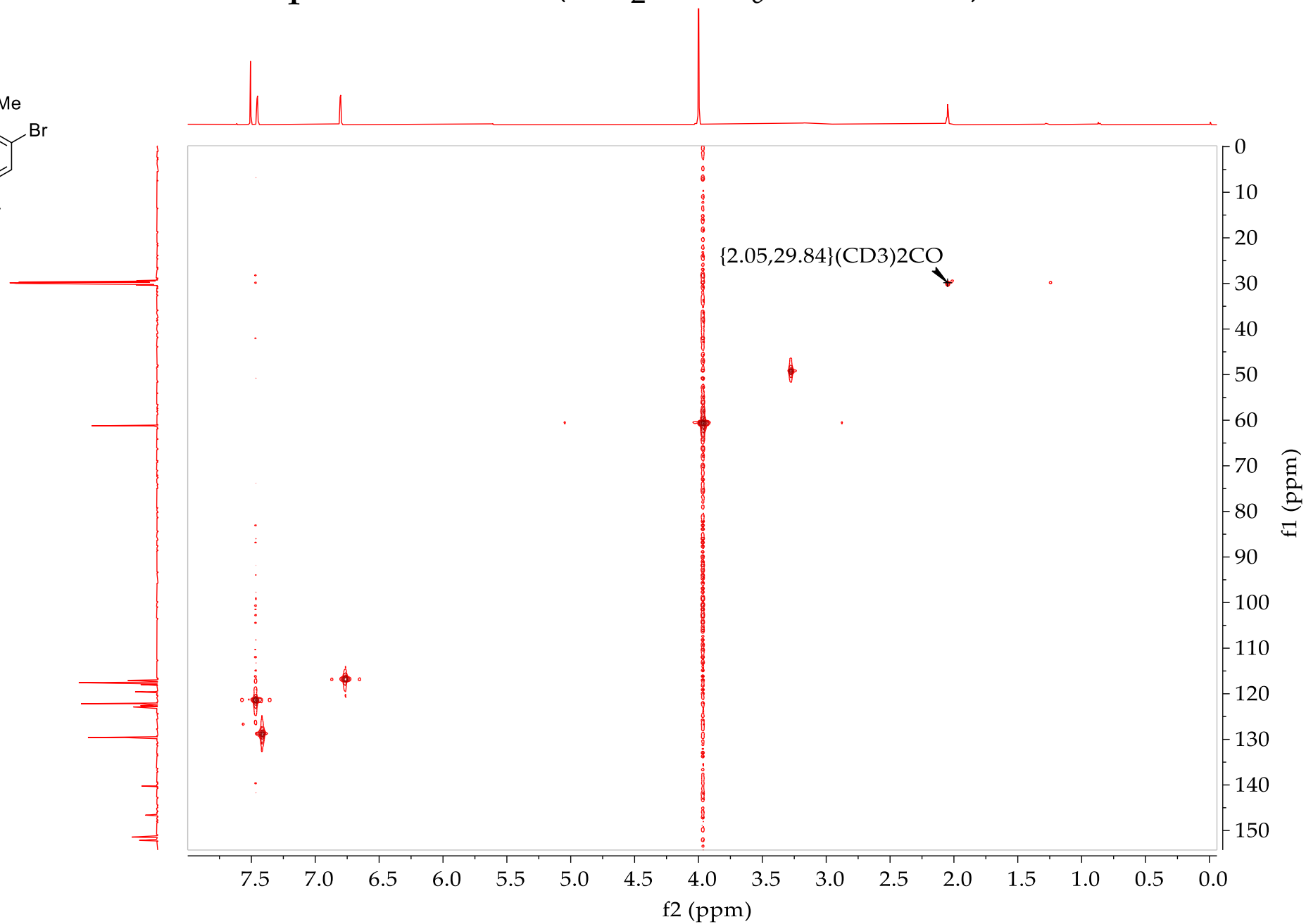
Figure S21. ^{1}H-^{13}C HMBC spectrum of **6** (Me$_2$CO-d_6, 500 MHz)

Figure S22. HREIMS of **6**

ターミナル1

SAMPLE : NH-C35-1356
SAMPLE NO.: 770   SCAN NO.: 27

                                                    PAGE   1

NO. PKNO.   P.C. M/Z(OBS.) ER(MU)   US ELEMENTS

  1   234   10.1   603.0111
  2   235   79.8   604.9632
  3   236   8.2   605.6311 - 0.0   8.0   C13 H7 Br5 O3
  4   237   31.3   605.9715
  5   238   5.2   606.6461   7.1   7.5   C13 H8 Br5 O3
  6   239   54.1   607.6294   0.2   8.0   C13 H7 Br4 Br*1 O3
  7   240   16.8   608.6710
  8   241   79.7   609.6229 - 4.1   8.0   C13 H7 Br3 Br*2 O3
  9   242   9.2   609.9897
 10   243   14.3   610.6332
 11   244   6.8   611.0001
 12   245   100.0   611.6311
 13   246   7.9   611.8050
 14   247   8.3   612.0046
 15   248   15.6   612.6488
 16   249   51.1   613.6411
 17   250   10.4   613.9119
 18   251   14.2   614.6598
 19   252   10.1   614.9887

+60

+18.1

6

Table S14. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 6

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 714
Number of electrons: 284
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step       Energy         Max Grad.        Max Dist.
           1    -13596.053628       0.025644         0.082958
           2    -13596.058798       0.006105         0.058462
           3    -13596.059382       0.001715         0.006906
           4    -13596.059418       0.001786         0.042893
           5    -13596.059498       0.001193         0.010775
           6    -13596.059513       0.000694         0.015156


 Reason for exit: Successful completion
 Quantum Calculation CPU Time :    6:33:10.28
 Quantum Calculation Wall Time:      26:25.66
```

Figure S23. HOMO-LUMO of 6
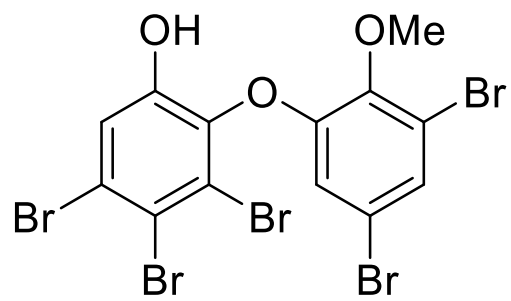
6
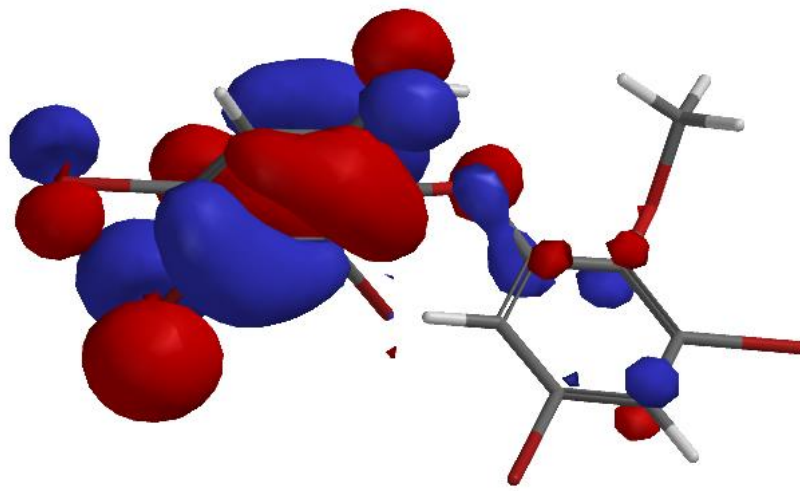
HOMO 6
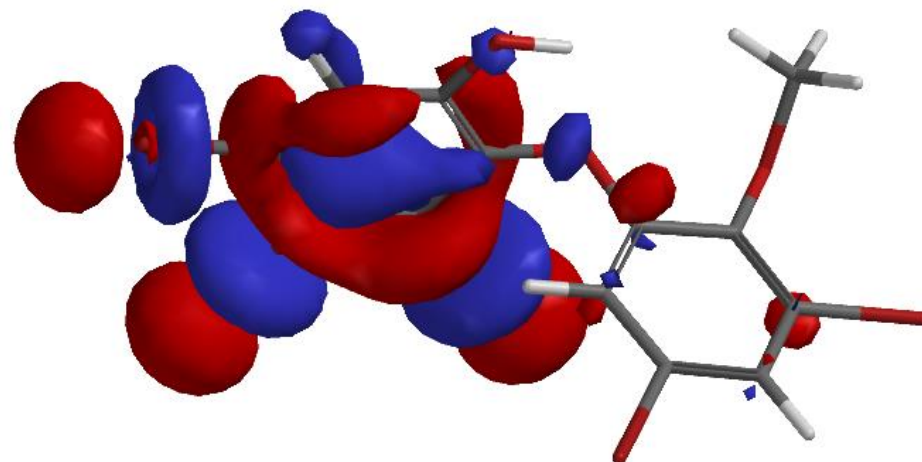
LUMO 6

Figure S24. Calculated ^{13}C NMR Chemical Shift of **6**
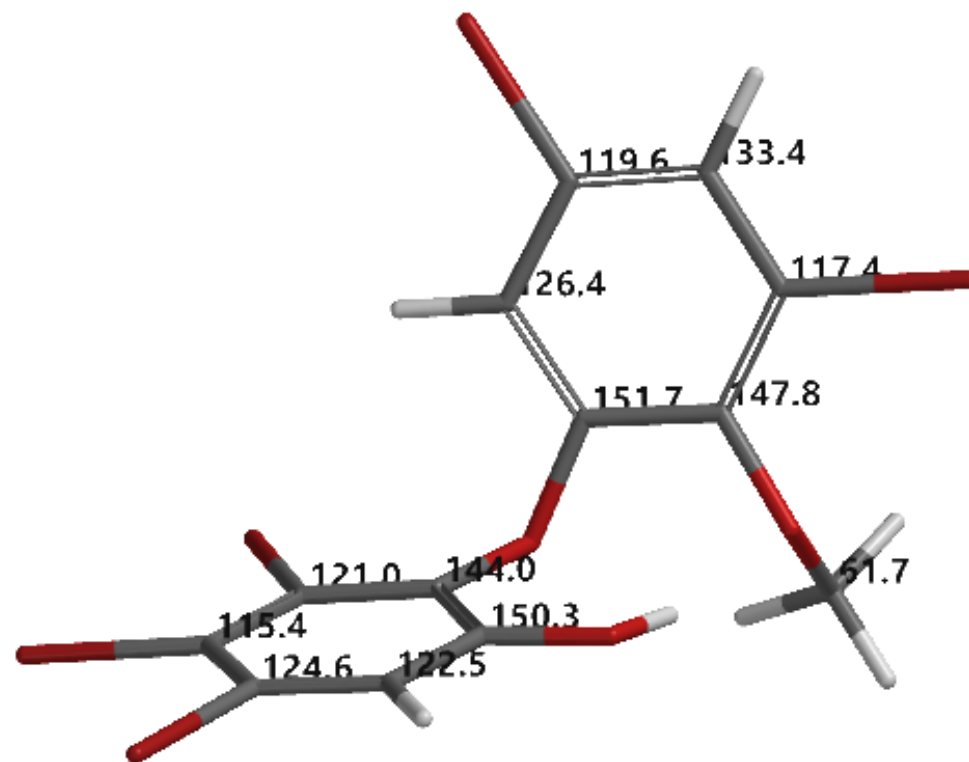
Figure S25. ^{1}H NMR spectrum of **7** (Me$_2$CO-d_6, 500 MHz)
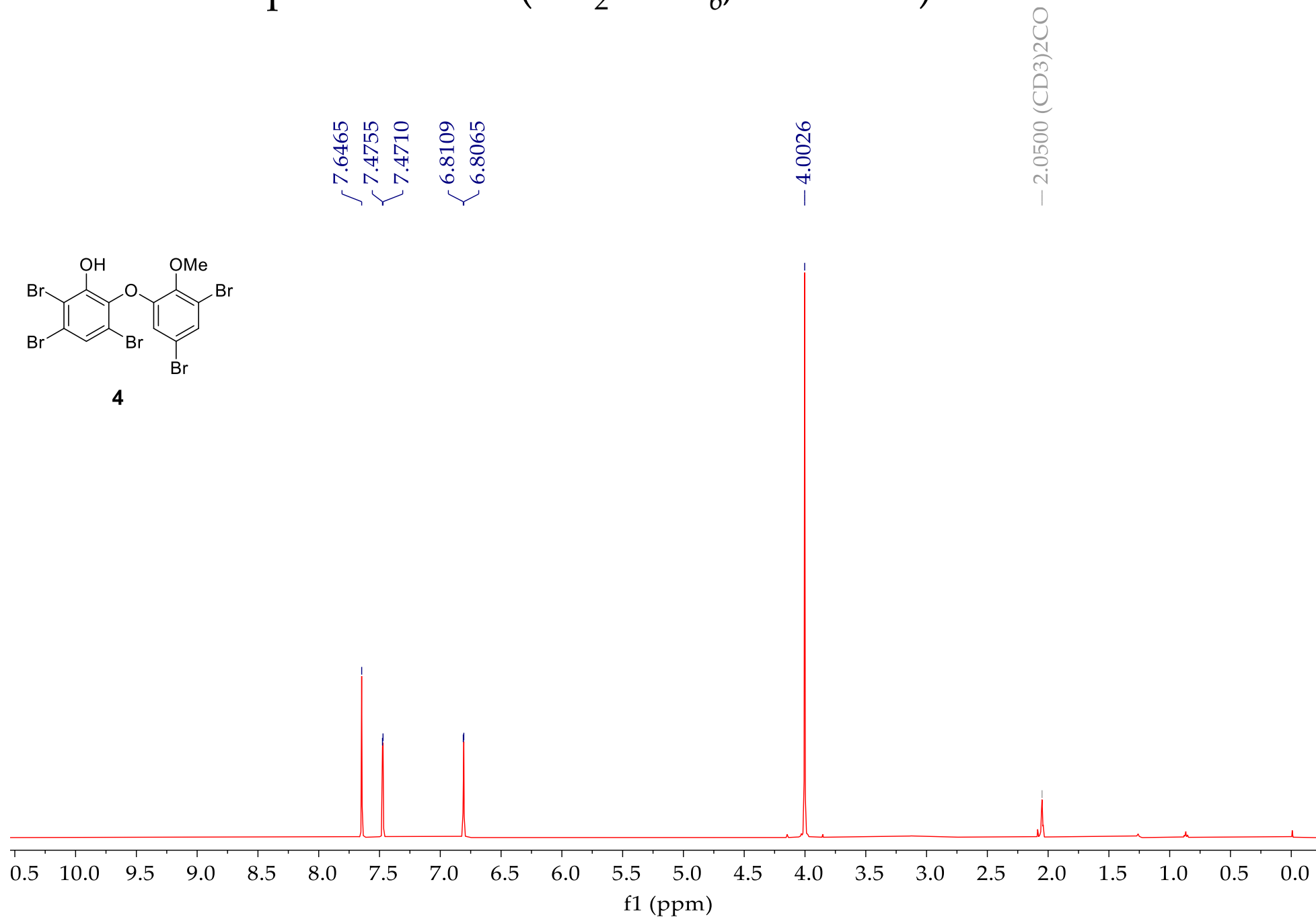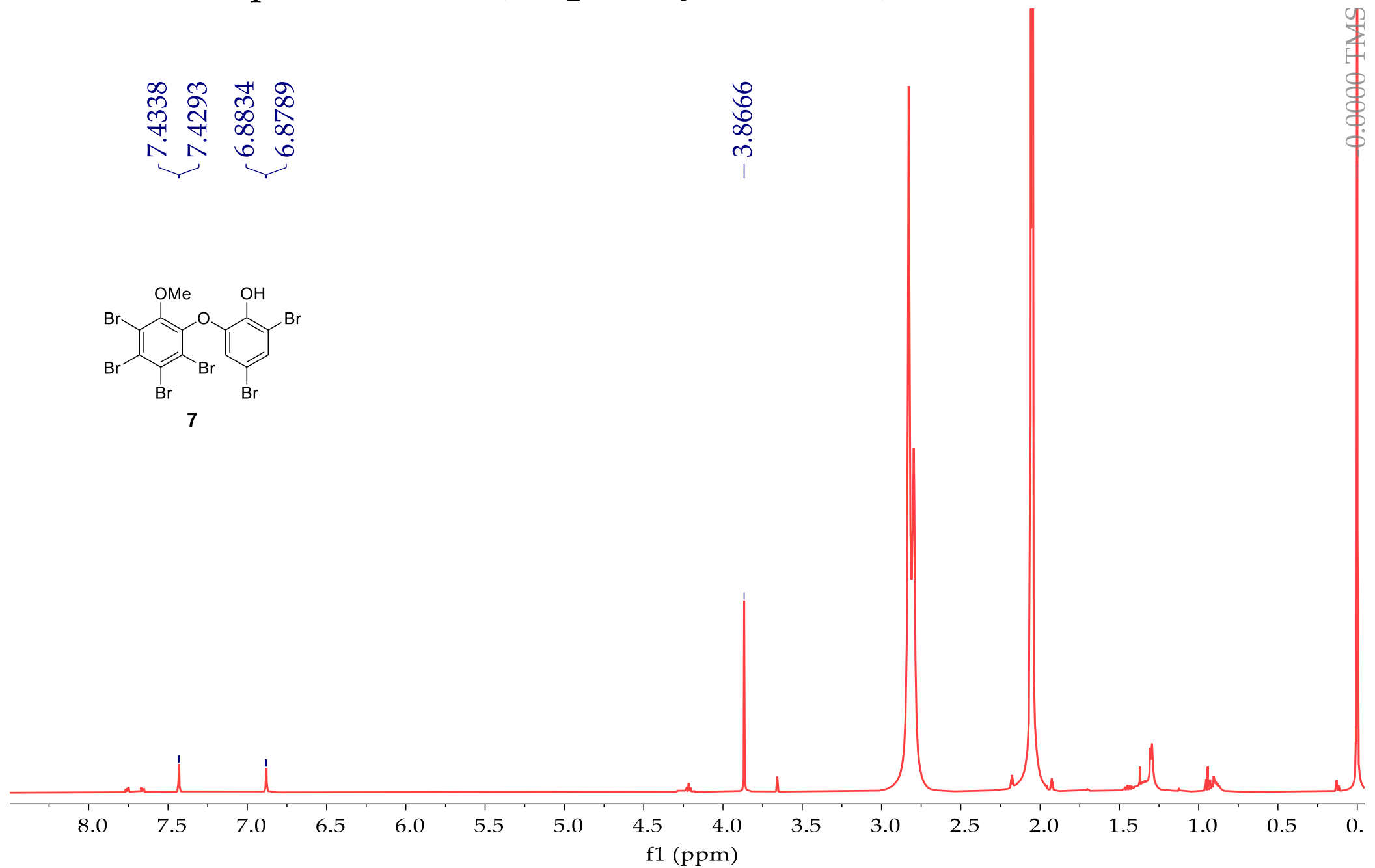
Figure S26. HRESIMS of 7
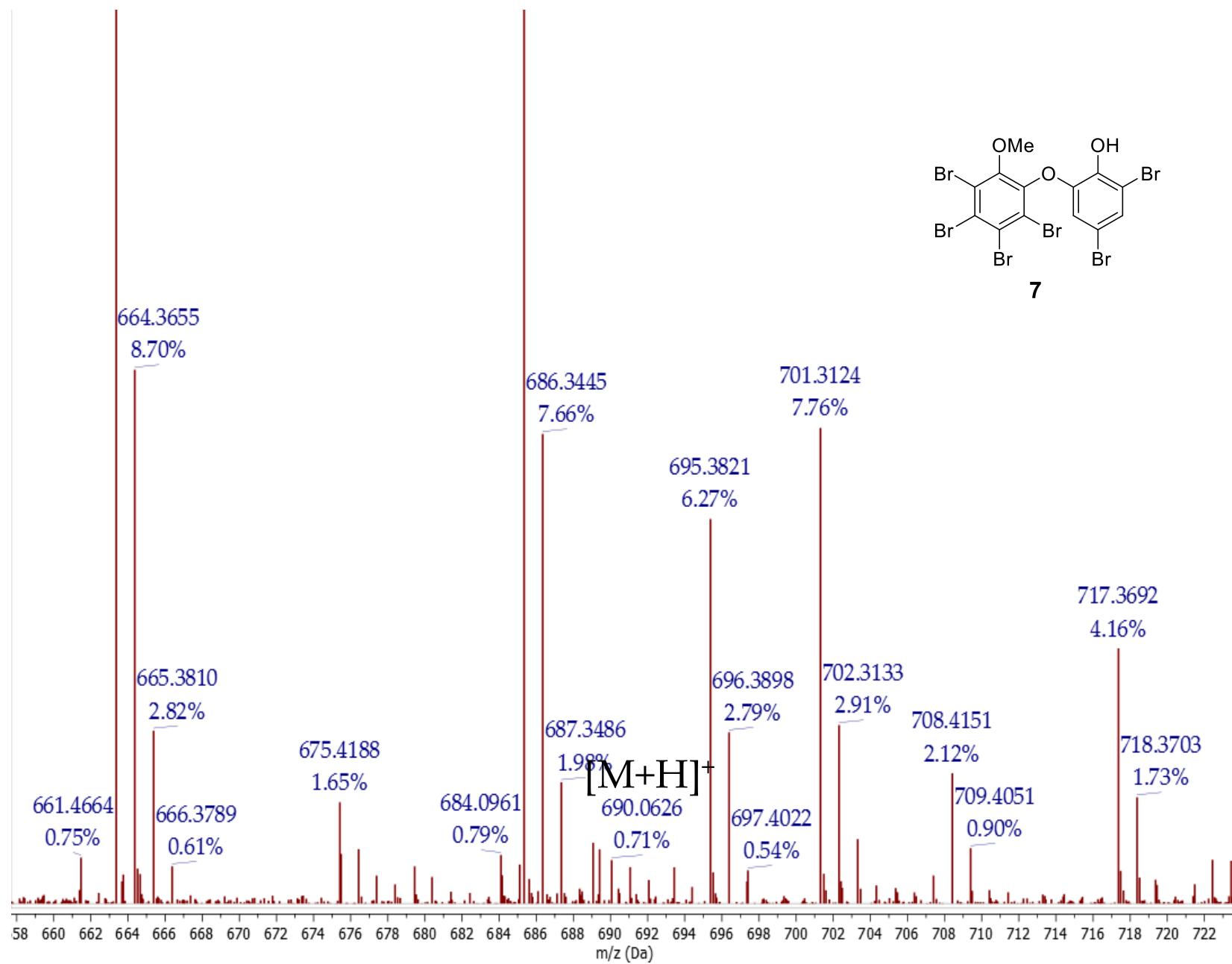
Table S15. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 7

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 756
Number of electrons: 318
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step        Energy          Max Grad.        Max Dist.
          1      -16169.610850       0.028599         0.093509
          2      -16169.618486       0.008688         0.139524
          3      -16169.619389       0.001766         0.099035
          4      -16169.619639       0.001159         0.150255
          5      -16169.619796       0.001193         0.060879
          6      -16169.619824       0.001191         0.020720
          7      -16169.619839       0.000708         0.006034
          8      -16169.619843       0.000359         0.007205
```
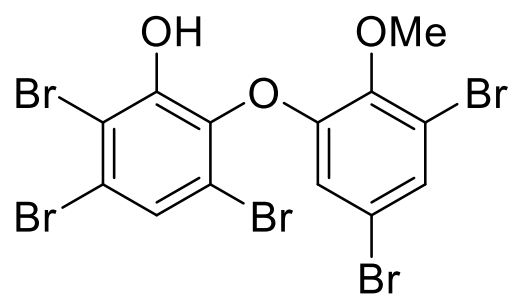
Figure S27. HOMO-LUMO of **7**
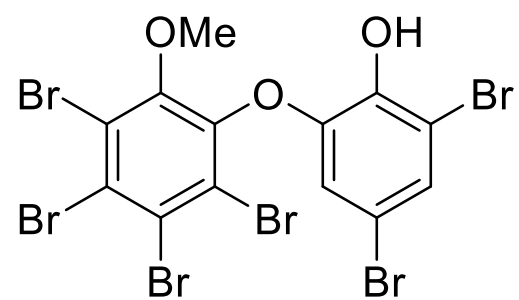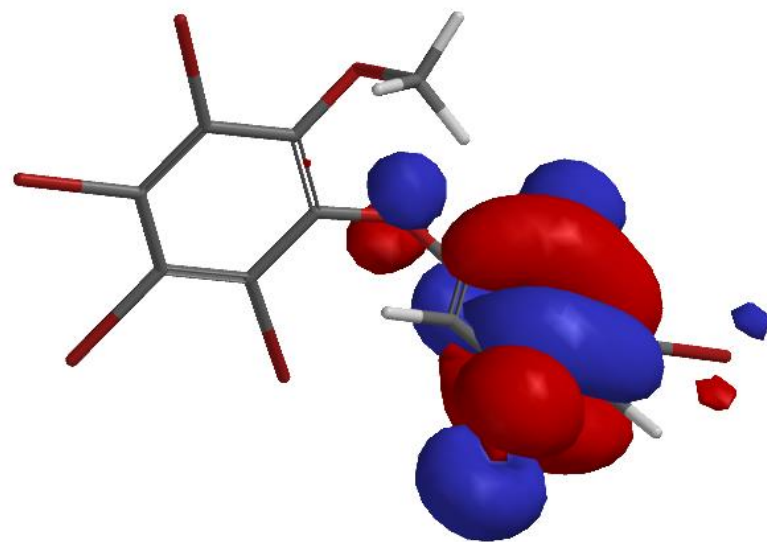
HOMO 7
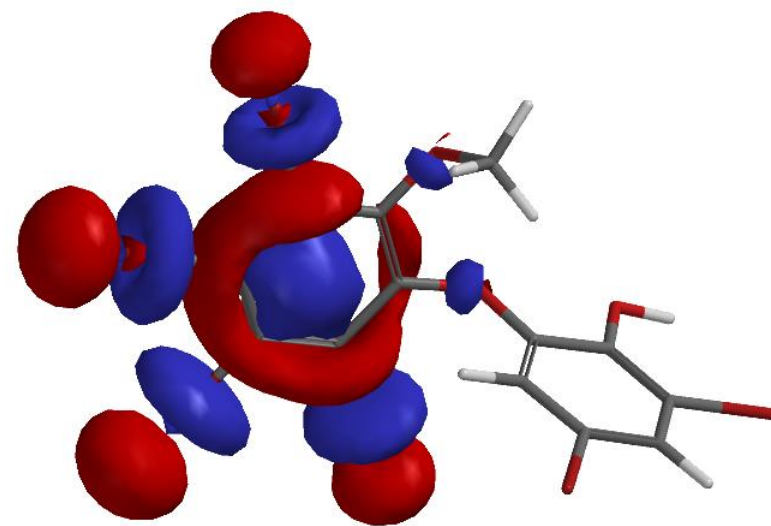
LUMO 7

Figure S28. Calculated ^{13}C NMR Chemical Shift of **7**
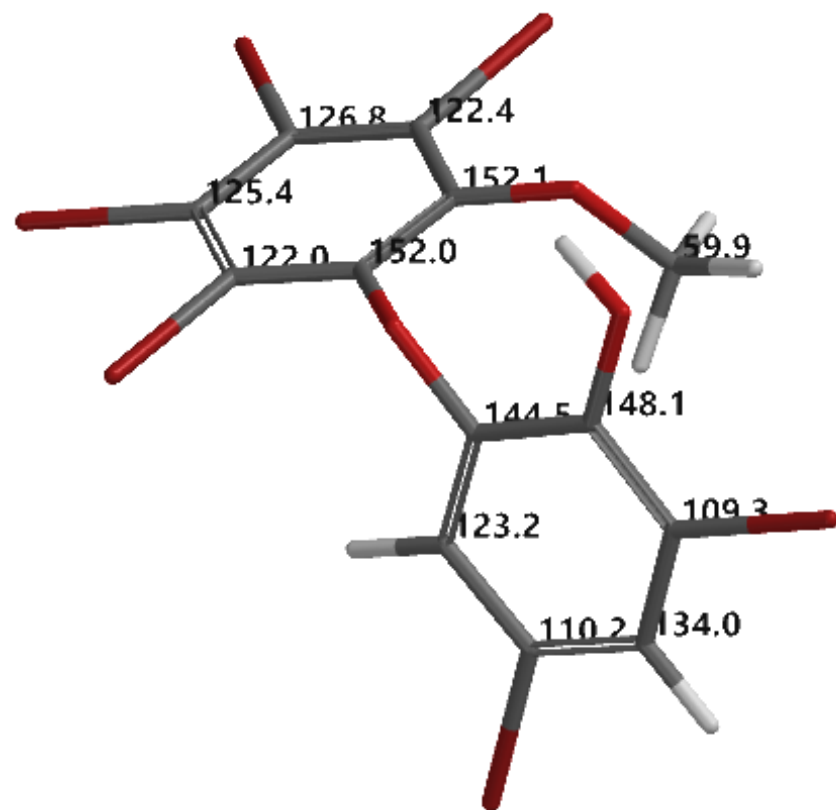
Figure S29. ¹H NMR spectrum of **8** (CDCl₃, 500 MHz)
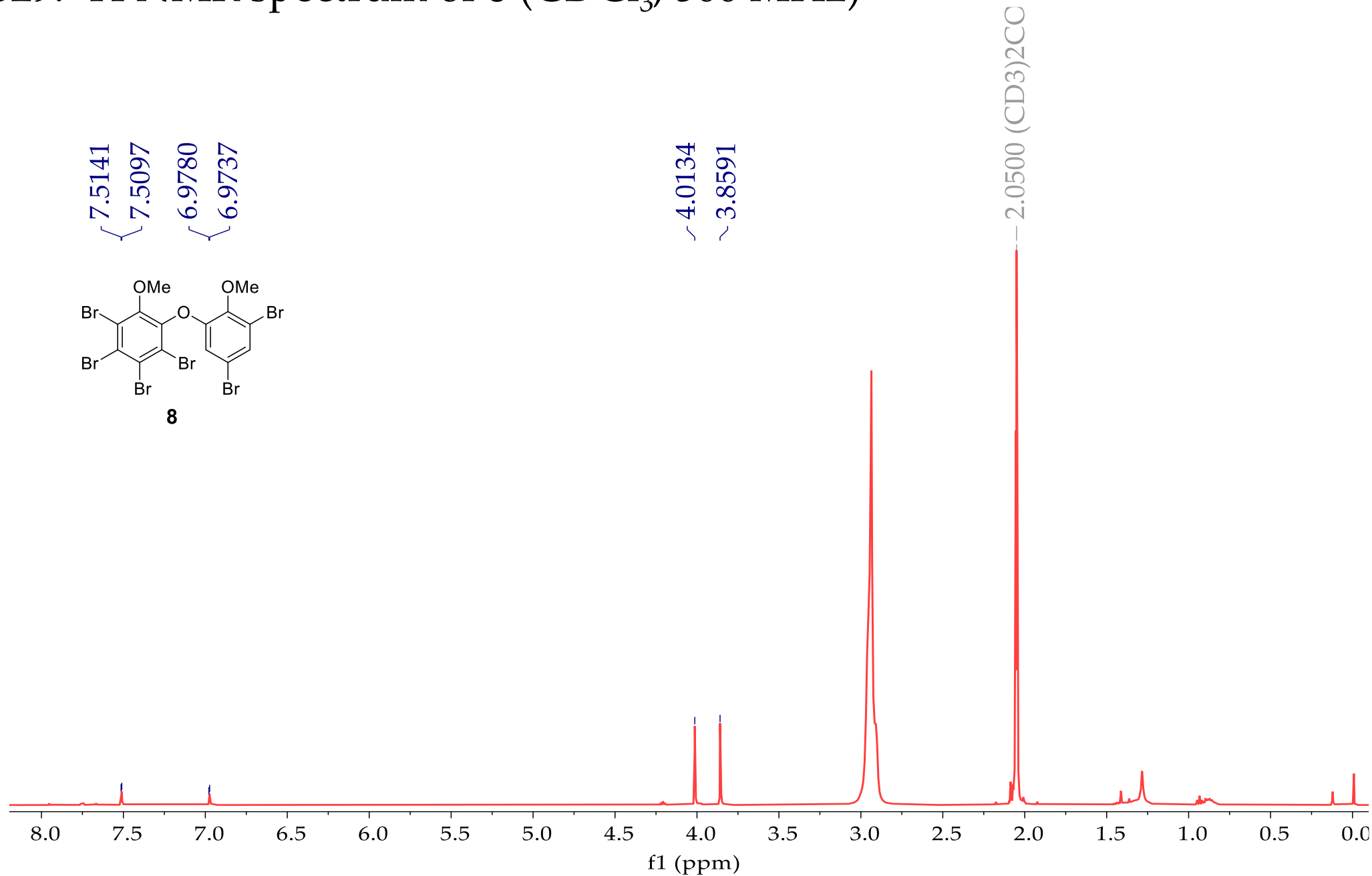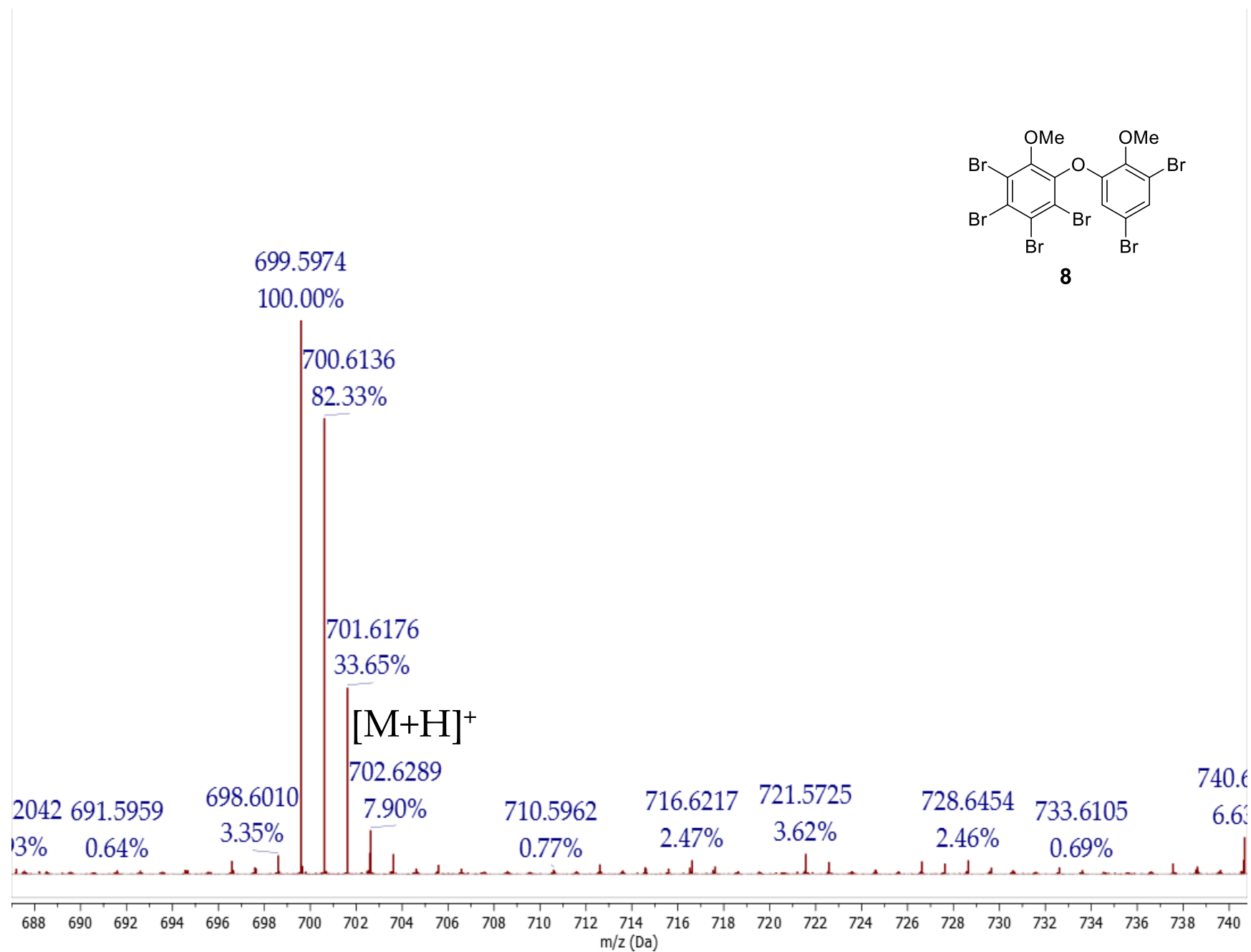
Figure S31. Crystal Structure of **8**
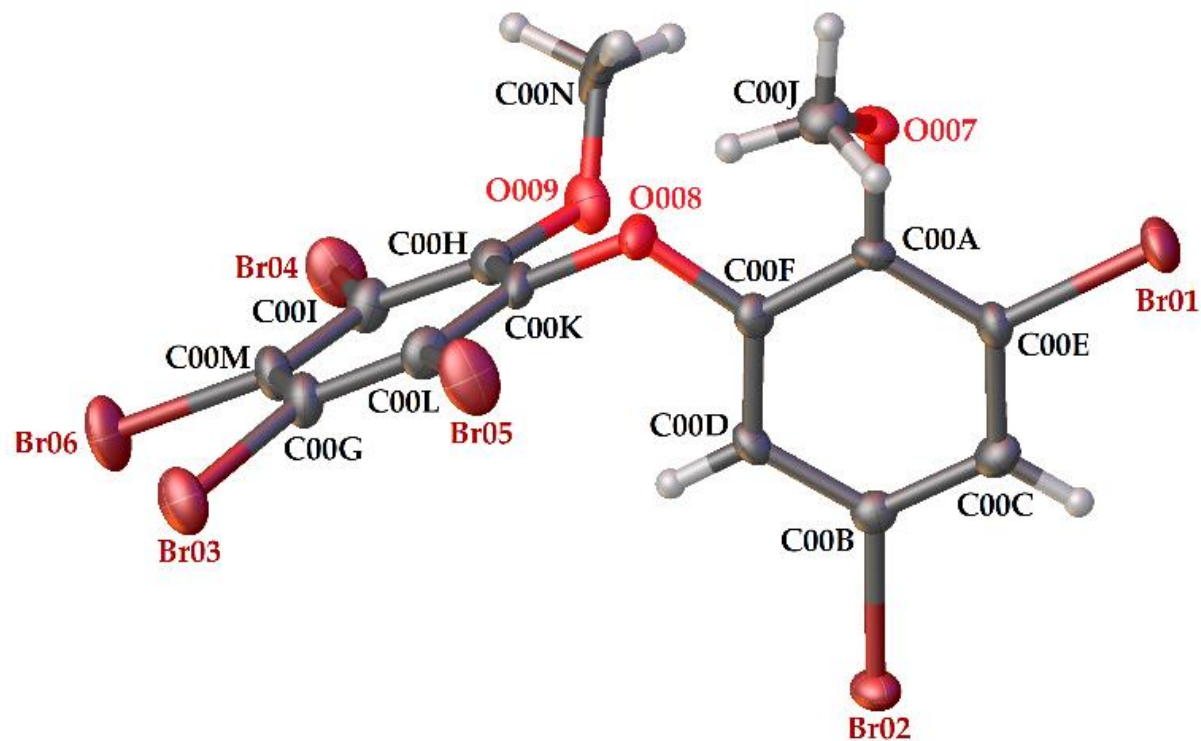
2,3,4,5-tetrabromo-6-(3',5'-dibromo-2'-methoxyphenoxy) anisole

Table S16. Crystal Data & Structure Refinement for 8

Identification code	190412irai-TN-2-1
Empirical formula	$C_{14}H_8Br_6O_3$
Formula weight	703.66
Temperature/K	113
Crystal system	triclinic
Space group	P-1
a/Å	8.733(3)
b/Å	8.911(3)
c/Å	12.769(4)
$\alpha/°$	104.185(4)
$\beta/°$	100.011(3)
$\gamma/°$	101.892(3)
Volume/Å^3	916.0(5)
Z	2
ϱ_{calc}g/cm^3	2.551
μ/mm^{-1}	13.158
F(000)	652.0
Crystal size/mm^3	0.317 × 0.229 × 0.21
Radiation	MoKα (λ = 0.71075)
2Θ range for data collection/°	6.588 to 54.968
Index ranges	-10 ≤ h ≤ 11, -11 ≤ k ≤ 11, -15 ≤ l ≤ 16
Reflections collected	7554
Independent reflections	4046 [R_{int} = 0.0369, R_{sigma} = 0.0427]
Data/restraints/parameters	4046/3/210
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.0964
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.0997
Largest diff. peak/hole / e Å^{-3}	1.42/-1.20

Table S17. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 8. Ueq is defined as 1/3 of the trace of the orthogonalized UIJ tensor.

Atom	x	y	z	U(eq)
Br01	2276.2(7)	1367.2(7)	10563.0(4)	28.28(14)
Br02	7526.5(6)	3871.0(7)	8927.1(4)	25.11(13)
Br03	2872.1(8)	3874.3(7)	3447.4(4)	33.07(15)
Br04	3773.5(8)	9527.4(6)	7030.9(5)	36.51(16)
Br05	1413.9(9)	1719.4(7)	5016.7(5)	39.38(17)
Br06	3877.1(9)	7832.3(7)	4419.8(5)	36.83(16)
O007	394(4)	2350(4)	8712(3)	20.7(7)
O008	1522(4)	3791(4)	7275(3)	21.4(7)
O009	2645(5)	7055(5)	8153(3)	28.2(8)
C00A	2004(6)	2697(6)	8750(4)	16.8(9)
C00B	5293(6)	3424(5)	8861(4)	18.2(9)
C00C	4734(6)	2704(6)	9618(4)	20.8(10)
C00D	4274(6)	3806(6)	8068(4)	17.8(9)
C00E	3078(6)	2350(6)	9543(4)	18.4(9)
C00F	2663(6)	3457(6)	8034(4)	18.3(9)
C00G	2705(6)	4899(6)	4885(4)	24.4(11)
C00H	2594(6)	6365(6)	7068(4)	20.4(10)
C00I	3110(6)	7292(6)	6400(4)	23.2(10)
C00J	-555(6)	1008(6)	7776(4)	26.0(11)
C00K	2103(6)	4710(6)	6627(4)	19.8(10)
C00L	2141(6)	3969(6)	5543(4)	23.2(10)
C00M	3146(6)	6553(6)	5305(4)	22.9(10)
C00N	1244(9)	7187(8)	8383(4)	40.6(16)

Table S18. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br01	29.0(3)	35.4(3)	23.5(3)	16.9(2)	9.2(2)	2.7(2)
Br02	15.9(2)	32.0(3)	26.8(3)	8.9(2)	5.92(19)	3.8(2)
Br03	42.7(3)	28.1(3)	21.7(3)	4.5(2)	6.5(2)	-1.0(2)
Br04	52.9(4)	15.5(3)	37.7(3)	4.4(2)	15.4(3)	1.6(2)
Br05	56.5(4)	17.4(3)	36.1(3)	4.3(2)	12.5(3)	-5.0(3)
Br06	57.8(4)	23.9(3)	30.2(3)	15.1(2)	14.4(3)	1.7(3)
O007	14.4(16)	24.4(18)	22.8(18)	6.5(14)	6.6(13)	2.1(14)
O008	18.0(16)	24.4(18)	24.9(18)	15.2(15)	4.4(14)	3.2(14)
O009	33(2)	27(2)	17.9(17)	4.4(15)	2.2(15)	0.4(16)
C00A	14(2)	17(2)	19(2)	3.8(18)	6.5(17)	3.1(17)
C00B	18(2)	14(2)	21(2)	2.8(18)	3.1(18)	1.8(18)
C00C	18(2)	21(2)	20(2)	3.2(19)	0.0(19)	4.0(19)
C00D	19(2)	16(2)	17(2)	5.3(18)	7.3(18)	0.4(18)
C00E	22(2)	19(2)	14(2)	5.4(18)	4.6(18)	3.3(19)
C00F	21(2)	14(2)	20(2)	6.7(18)	5.2(19)	2.9(18)
C00G	29(3)	23(3)	19(2)	8(2)	3(2)	3(2)
C00H	18(2)	21(2)	19(2)	5.2(19)	1.1(18)	2.0(19)
C00I	27(3)	16(2)	22(2)	5.8(19)	0(2)	2(2)
C00J	20(2)	24(3)	29(3)	6(2)	2(2)	1(2)
C00K	17(2)	23(2)	20(2)	13(2)	1.5(18)	2.0(19)
C00L	26(3)	13(2)	27(3)	5.8(19)	3(2)	1.6(19)
C00M	27(3)	22(2)	18(2)	9(2)	5(2)	0(2)
C00N	76(4)	42(3)	13(2)	6(2)	2(3)	44(3)

Table S19. Bond Lengths for 8

Atom	Atom	Length/Å
Br01	C00E	1.891(5)
Br02	C00B	1.891(5)
Br03	C00G	1.885(5)
Br04	C00I	1.878(5)
Br05	C00L	1.882(5)
Br06	C00M	1.889(5)
O007	C00A	1.366(6)
O007	C00J	1.447(6)
O008	C00F	1.396(6)
O008	C00K	1.385(6)
O009	C00H	1.359(6)
O009	C00N	1.329(8)
C00A	C00E	1.394(7)
C00A	C00F	1.397(7)
C00B	C00C	1.387(7)
C00B	C00D	1.384(7)
C00C	C00E	1.396(7)
C00D	C00F	1.368(7)
C00G	C00L	1.397(7)
C00G	C00M	1.383(7)
C00H	C00I	1.392(7)
C00H	C00K	1.387(7)
C00I	C00M	1.401(7)
C00K	C00L	1.390(7)

Table S20. Bond Angles for 8

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00A	O007	C00J	113.6(4)	C00M	C00G	Br03	121.3(4)
C00K	O008	C00F	116.9(4)	C00M	C00G	C00L	119.4(5)
C00N	O009	C00H	115.8(4)	O009	C00H	C00I	120.9(5)
O007	C00A	C00E	120.7(4)	O009	C00H	C00K	120.1(5)
O007	C00A	C00F	122.4(4)	C00K	C00H	C00I	118.9(5)
C00E	C00A	C00F	116.9(4)	C00H	C00I	Br04	117.6(4)
C00C	C00B	Br02	118.0(4)	C00H	C00I	C00M	120.1(5)
C00D	C00B	Br02	119.8(4)	C00M	C00I	Br04	122.2(4)
C00D	C00B	C00C	122.2(5)	O008	C00K	C00H	119.0(4)
C00B	C00C	C00E	117.3(4)	O008	C00K	C00L	119.8(5)
C00F	C00D	C00B	118.5(5)	C00H	C00K	C00L	121.2(5)
C00A	C00E	Br01	119.2(4)	C00G	C00L	Br05	122.4(4)
C00A	C00E	C00C	122.5(5)	C00K	C00L	Br05	117.8(4)
C00C	C00E	Br01	118.3(4)	C00K	C00L	C00G	119.7(5)
O008	C00F	C00A	113.7(4)	C00G	C00M	Br06	120.1(4)
C00D	C00F	O008	123.7(4)	C00G	C00M	C00I	120.5(5)
C00D	C00F	C00A	122.6(4)	C00I	C00M	Br06	119.4(4)
C00L	C00G	Br03	119.3(4)				

Table S21. Torsion Angles for 8

A	B	C	D	Angle/°
Br02	C00B	C00C	C00E	-178.6(3)
Br02	C00B	C00D	C00F	179.5(3)
Br03	C00G	C00L	Br05	-3.9(6)
Br03	C00G	C00L	C00K	176.2(4)
Br03	C00G	C00M	Br06	1.8(6)
Br03	C00G	C00M	C00I	-176.0(4)
Br04	C00I	C00M	Br06	-0.3(6)
Br04	C00I	C00M	C00G	177.5(4)
O007	C00A	C00E	Br01	0.7(6)
O007	C00A	C00E	C00C	-179.2(4)
O007	C00A	C00F	O008	-1.2(6)
O007	C00A	C00F	C00D	-180.0(4)
O008	C00K	C00L	Br05	-0.8(6)
O008	C00K	C00L	C00G	179.1(4)
O009	C00H	C00I	Br04	-3.1(7)
O009	C00H	C00I	C00M	175.9(5)
O009	C00H	C00K	O008	6.2(7)
O009	C00H	C00K	C00L	-175.7(5)
C00B	C00C	C00E	Br01	-180.0(3)
C00B	C00C	C00E	C00A	-0.1(7)
C00B	C00D	C00F	O008	179.8(4)
C00B	C00D	C00F	C00A	-1.6(7)
C00C	C00B	C00D	C00F	0.0(7)
C00D	C00B	C00C	C00E	0.9(7)

A	B	C	D	Angle/°
C00E	C00A	C00F	O008	-179.0(4)
C00E	C00A	C00F	C00D	2.2(7)
C00F	O008	C00K	C00H	-82.3(6)
C00F	O008	C00K	C00L	99.6(5)
C00F	C00A	C00E	Br01	178.5(3)
C00F	C00A	C00E	C00C	-1.3(7)
C00H	C00I	C00M	Br06	-179.2(4)
C00H	C00I	C00M	C00G	-1.4(8)
C00H	C00K	C00L	Br05	-179.0(4)
C00H	C00K	C00L	C00G	1.0(8)
C00I	C00H	C00K	O008	-177.1(4)
C00I	C00H	C00K	C00L	1.0(7)
C00J	O007	C00A	C00E	-107.6(5)
C00J	O007	C00A	C00F	74.6(6)
C00K	O008	C00F	C00A	172.6(4)
C00K	O008	C00F	C00D	-8.6(7)
C00K	C00H	C00I	Br04	-179.7(4)
C00K	C00H	C00I	C00M	-0.8(8)
C00L	C00G	C00M	Br06	-178.9(4)
C00L	C00G	C00M	C00I	3.3(8)
C00M	C00G	C00L	Br05	176.8(4)
C00M	C00G	C00L	C00K	-3.1(8)
C00N	O009	C00H	C00I	103.5(6)
C00N	O009	C00H	C00K	-79.9(6)

Table S22. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **8**

Atom	x	y	z	U(eq)
H00C	5433.13	2465.87	10153.75	25
H00D	4675.83	4290.02	7569.01	21
H00A	-447.93	1253.01	7096.84	39
H00B	-1665.7	805.46	7809.42	39
H00E	-180.51	73.77	7800.72	39
H00F	812.91	7854.42	7989.34	61
H00G	1400.96	7657.17	9167.9	61
H00H	504.42	6142.63	8158.12	61

Table S23. Refinement Model Description of **8**

Number of restraints - 3, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of: All C(H) groups

At 1.5 times of: All C(H,H,H) groups

2. Rigid body (RIGU) restrains O009, C00N with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

3.a Aromatic/amide H refined with riding coordinates: C00C(H00C), C00D(H00D)

3.b Idealized Me refined as rotating group: C00J(H00A,H00B,H00E), C00N(H00F,H00G,H00H)

Table S24. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 8

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 795
Number of electrons: 326
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step      Energy         Max Grad.      Max Dist.
           1    -16208.904060     0.031123       0.116981
           2    -16208.911301     0.008252       0.121129
           3    -16208.912230     0.003044       0.006869
           4    -16208.912278     0.003037       0.093174
           5    -16208.912575     0.002268       0.020735
           6    -16208.912629     0.001779       0.016953
           7    -16208.912658     0.001025       0.017400
           8    -16208.912668     0.000458       0.007091
```

Figure S32. HOMO-LUMO of **8**
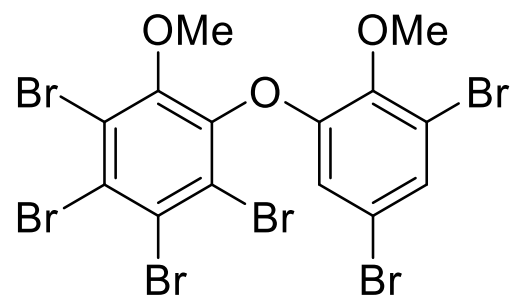
8
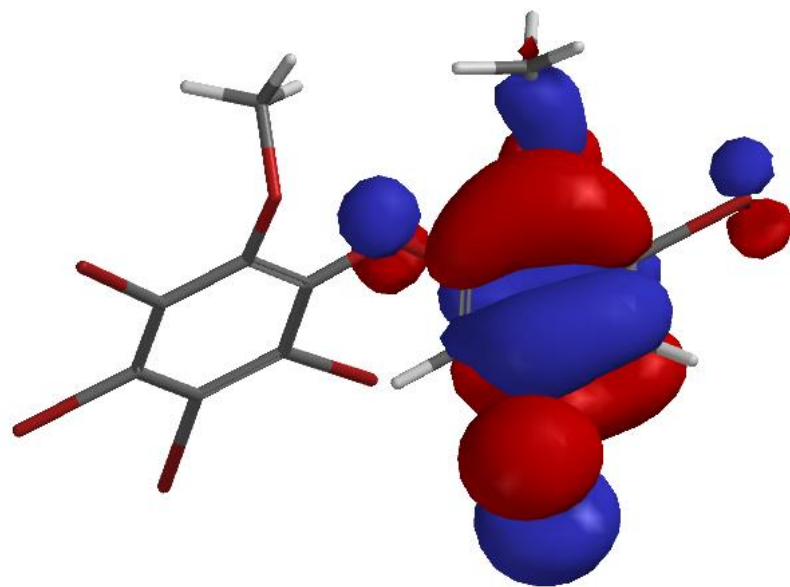
HOMO 8

LUMO 8

Figure S33. Calculated ^{13}C NMR Chemical Shift of **8**

Figure S34. ^{1}H NMR spectrum of 9 (CDCl$_3$, 500 MHz)

Figure S35. HRESIMS of 9

Figure S36. Crystal Structure of **9**

2,3,4,5-tetrabromo-6-(3',5'-dibromo-2'-methoxyphenoxy) anisole

Table S25. Crystal Data and Structure Refinement for 9

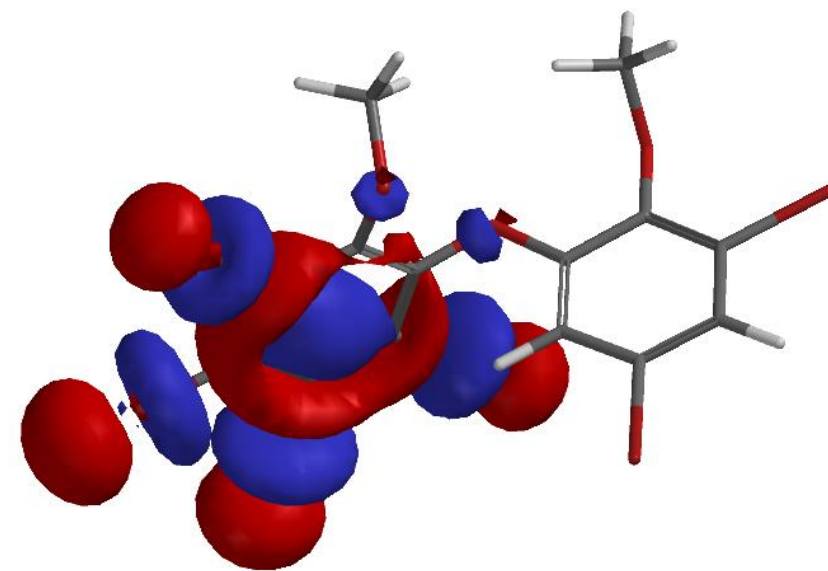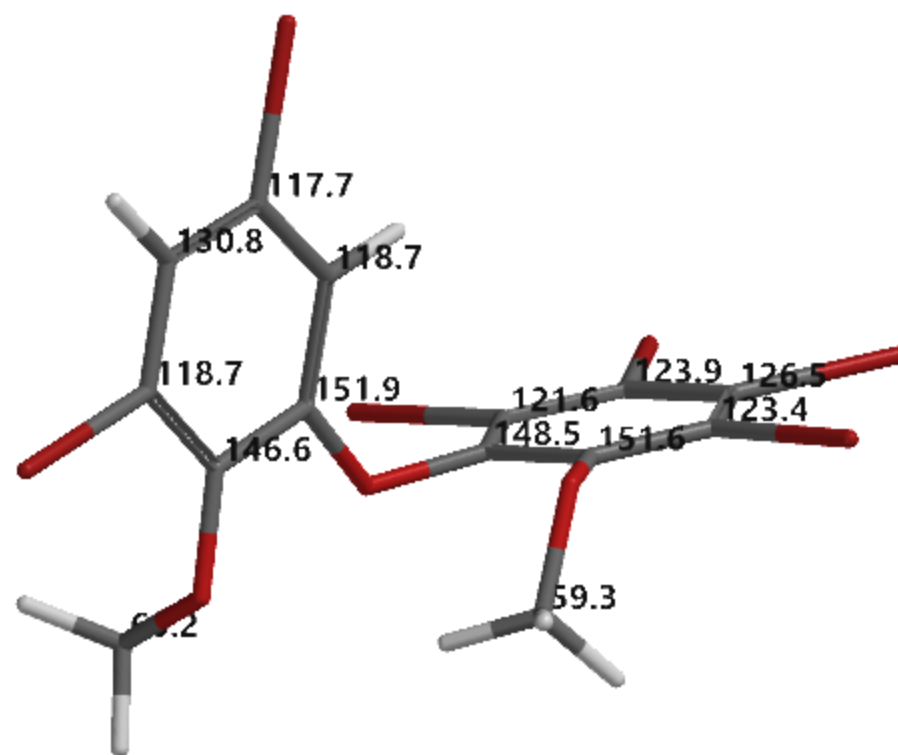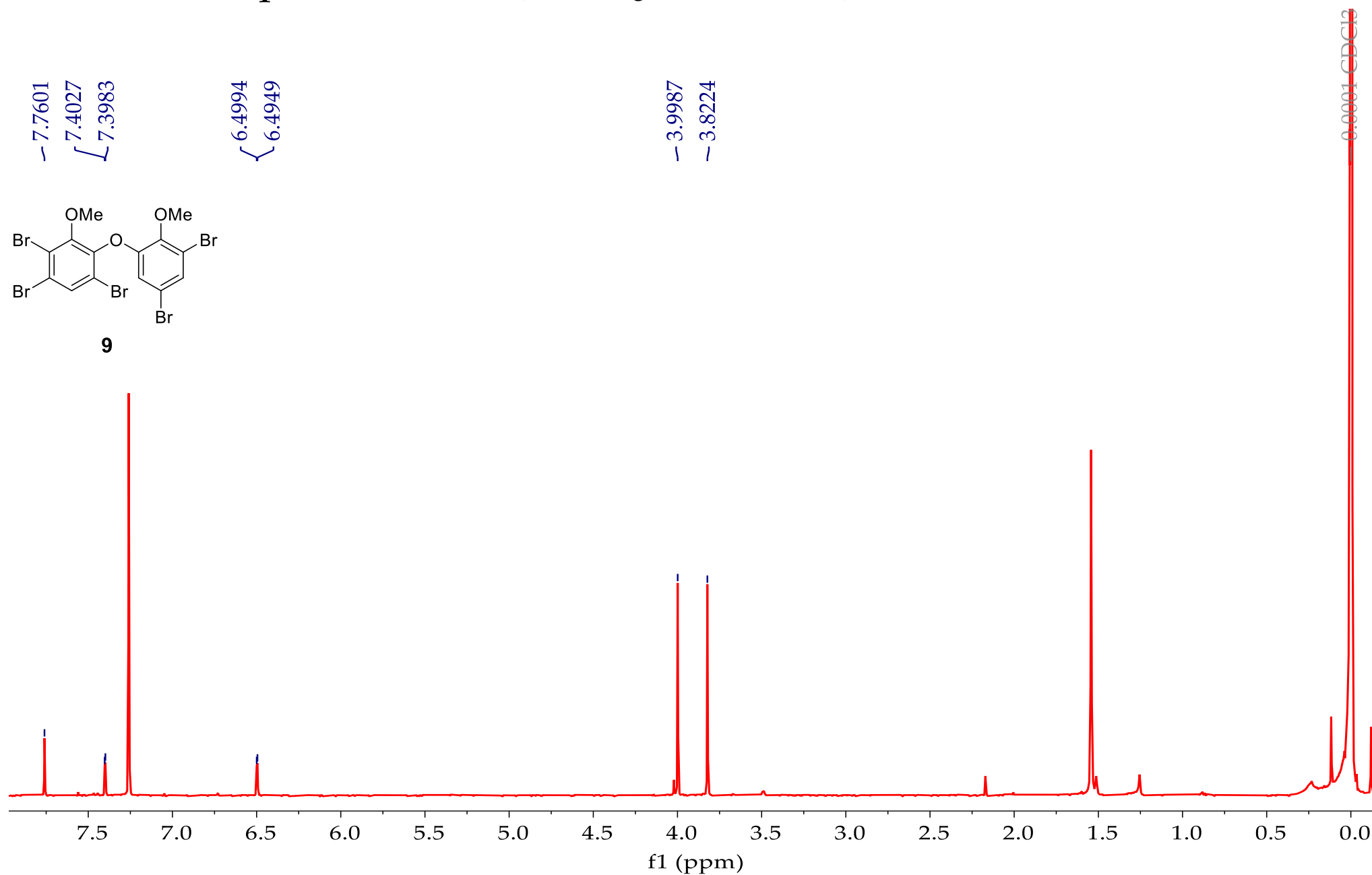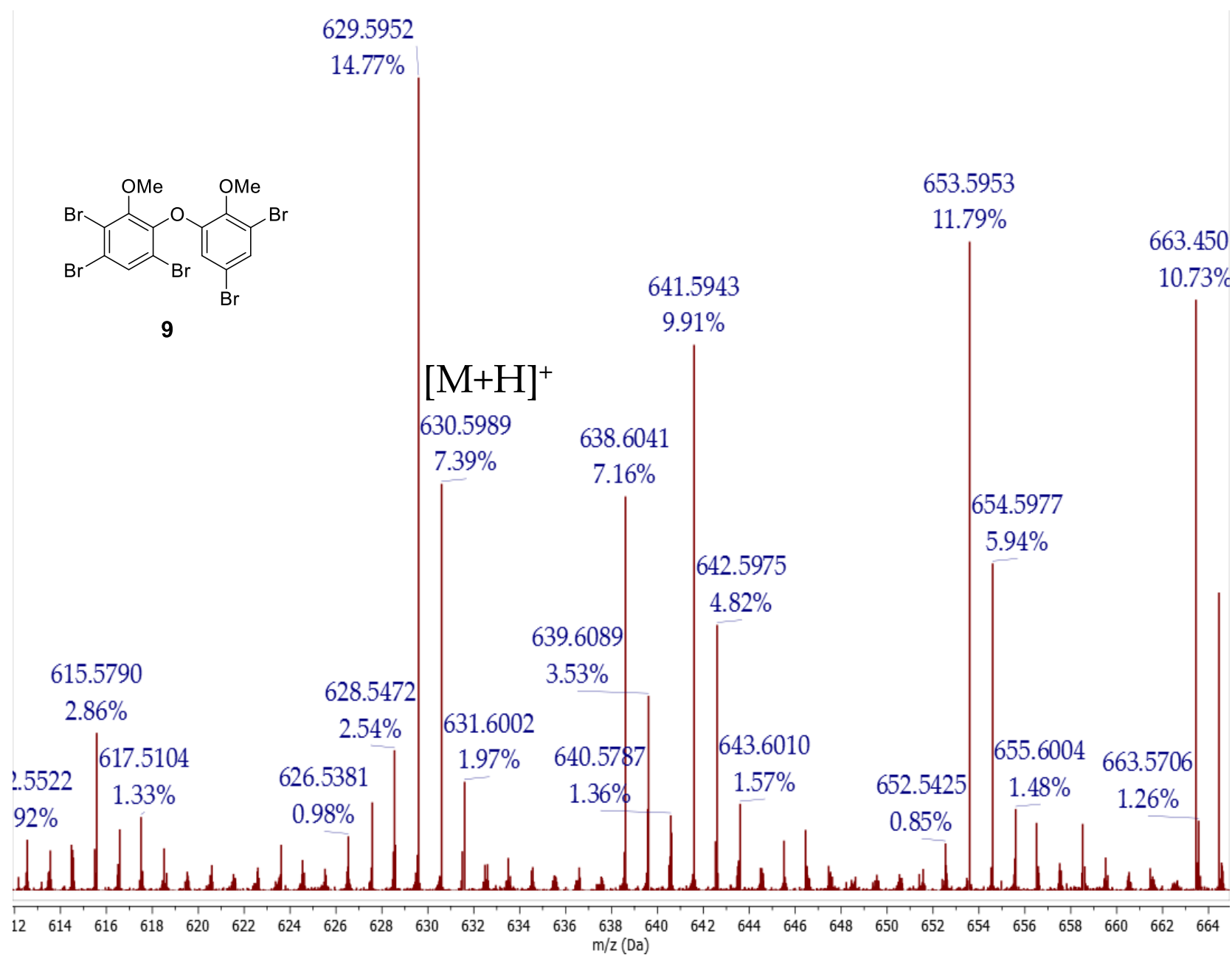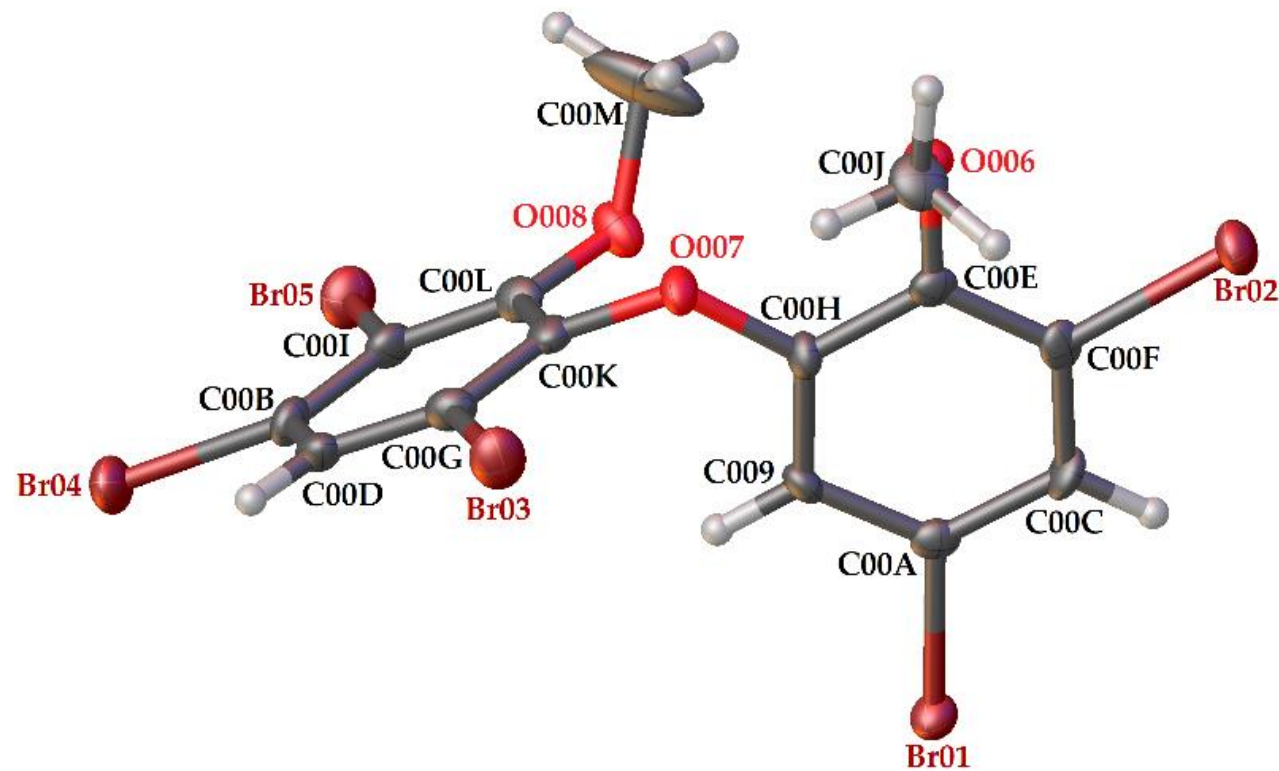|	
Identification code	190412irai-TN-7
Empirical formula	$C_{14}H_9Br_5O_3$
Formula weight	624.76
Temperature/K	113.15
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	6.9014(15)
b/Å	11.940(3)
c/Å	21.090(5)
$\alpha/°$	90
$\beta/°$	90
$\gamma/°$	90
Volume/Å^3	1737.9(7)
Z	4
ϱ_{calc}g/cm^3	2.388
μ/mm^{-1}	11.569
F(000)	1168.0
Crystal size/mm^3	0.26 × 0.11 × 0.06
Radiation	MoKα (λ = 0.71075)
2Θ range for data collection/°	6.82 to 54.952
Index ranges	-8 ≤ h ≤ 8, -15 ≤ k ≤ 15, -27 ≤ l ≤ 22
Reflections collected	17770
Independent reflections	3584 [R_{int} = 0.0623, R_{sigma} = 0.0509]
Data/restraints/parameters	3584/1/201
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0648
Final R indexes [all data]	R_1 = 0.0480, wR_2 = 0.0681
Largest diff. peak/hole / e Å^{-3}	0.61/-0.60
Flack parameter	0.087(12)

Table S26. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **9**. Ueq is defined as 1/3 of the trace of the orthogonalized UIJ tensor.

Atom	x	y	z	U(eq)
Br01	7455.4(13)	530.8(7)	6203.2(4)	22.52(18)
Br02	3198.4(13)	3974.1(8)	7432.3(4)	25.8(2)
Br03	-533.9(14)	1031.0(8)	4576.7(4)	31.2(2)
Br04	4843.4(15)	1132.5(8)	2567.4(4)	31.9(2)
Br05	7279.5(13)	3188.6(9)	3310.0(5)	31.0(2)
O006	1251(8)	4088(4)	6129(3)	21.0(13)
O007	2018(8)	2887(5)	5088(3)	21.0(14)
O008	5380(8)	3753(5)	4563(3)	25.0(14)
C009	4541(12)	1838(7)	5627(4)	17.4(18)
C00A	5516(11)	1669(6)	6191(4)	18.3(17)
C00B	4003(12)	1709(7)	3355(4)	20.5(18)
C00C	5164(12)	2280(8)	6735(4)	20.8(19)
C00D	2306(14)	1270(7)	3609(4)	24(2)
C00E	2669(12)	3275(6)	6161(4)	18.6(17)
C00F	3731(12)	3093(7)	6702(4)	19.7(19)
C00G	1700(13)	1665(7)	4195(4)	21.8(19)
C00H	3120(12)	2656(7)	5621(4)	16.9(17)
C00I	5014(12)	2548(8)	3671(4)	23.8(19)
C00J	-666(11)	3639(8)	6221(5)	28(2)
C00K	2702(13)	2498(7)	4511(4)	21.1(18)
C00L	4356(12)	2961(7)	4245(4)	20.0(19)
C00M	4487(17)	4814(10)	4615(8)	74(5)

Table S27. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **9**. The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br01	22.8(4)	24.8(4)	19.9(4)	0.8(4)	-0.4(4)	6.5(4)
Br02	31.2(5)	28.5(5)	17.6(4)	-5.9(4)	1.9(4)	2.8(4)
Br03	34.9(5)	30.9(6)	27.7(5)	1.3(5)	4.9(4)	-9.7(4)
Br04	48.0(6)	31.8(5)	15.9(4)	-1.9(4)	4.2(4)	3.6(4)
Br05	30.7(5)	36.2(6)	26.0(5)	2.7(4)	5.5(4)	-3.4(4)
O006	23(3)	17(3)	23(3)	0(3)	1(3)	3(2)
O007	23(3)	26(3)	14(3)	-4(3)	0(2)	7(2)
O008	21(3)	27(4)	28(3)	-10(3)	-2(3)	0(3)
C009	22(4)	13(4)	17(4)	-5(3)	2(3)	0(4)
C00A	18(4)	15(4)	22(5)	5(4)	4(4)	-2(3)
C00B	25(4)	25(5)	12(4)	4(4)	2(4)	1(4)
C00C	18(4)	29(5)	15(4)	3(4)	-7(4)	1(4)
C00D	39(5)	14(4)	20(5)	2(4)	-5(4)	0(4)
C00E	22(4)	15(4)	19(4)	5(4)	4(4)	-1(4)
C00F	24(4)	21(5)	14(4)	3(3)	6(4)	-6(4)
C00G	24(5)	17(4)	25(5)	3(4)	-1(4)	-2(4)
C00H	17(4)	21(5)	13(4)	-3(3)	-2(3)	-1(4)
C00I	32(5)	20(5)	19(4)	6(4)	4(4)	1(4)
C00J	18(4)	34(5)	31(5)	-2(4)	7(4)	4(4)
C00K	27(5)	18(4)	19(4)	1(4)	-3(4)	8(4)
C00L	15(4)	21(5)	23(5)	0(4)	-5(3)	0(4)
C00M	37(6)	28(6)	156(14)	-39(8)	-13(8)	-3(5)

Table S28. Bond Lengths for 9

Atom	Atom	Length/Å
Br01	C00A	1.907(8)
Br02	C00F	1.901(8)
Br03	C00G	1.898(9)
Br04	C00B	1.890(9)
Br05	C00I	1.899(9)
O006	C00E	1.380(9)
O006	C00J	1.441(10)
O007	C00H	1.386(10)
O007	C00K	1.385(10)
O008	C00L	1.358(10)
O008	C00M	1.413(12)
C009	C00A	1.381(12)
C009	C00H	1.385(11)
C00A	C00C	1.381(12)
C00B	C00D	1.390(12)
C00B	C00I	1.391(13)
C00C	C00F	1.388(12)
C00D	C00G	1.387(12)
C00E	C00F	1.373(12)
C00E	C00H	1.394(11)
C00G	C00K	1.383(12)
C00I	C00L	1.384(12)
C00K	C00L	1.386(12)

Table S29. Bond Angles for **9**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00E	O006	C00J	112.5(6)	C00E	C00F	C00C	122.2(8)
C00K	O007	C00H	117.3(6)	C00D	C00G	Br03	119.2(7)
C00L	O008	C00M	115.8(7)	C00K	C00G	Br03	119.2(7)
C00A	C009	C00H	117.1(8)	C00K	C00G	C00D	121.6(8)
C009	C00A	Br01	117.2(6)	O007	C00H	C00E	115.8(7)
C00C	C00A	Br01	119.2(6)	C009	C00H	O007	122.5(7)
C00C	C00A	C009	123.6(7)	C009	C00H	C00E	121.6(8)
C00D	C00B	Br04	117.3(7)	C00B	C00I	Br05	120.8(7)
C00D	C00B	C00I	120.7(8)	C00L	C00I	Br05	118.5(7)
C00I	C00B	Br04	121.9(6)	C00L	C00I	C00B	120.7(8)
C00A	C00C	C00F	117.0(7)	O007	C00K	C00L	120.2(8)
C00G	C00D	C00B	117.9(8)	C00G	C00K	O007	119.6(8)
O006	C00E	C00H	119.4(8)	C00G	C00K	C00L	120.2(8)
C00F	C00E	O006	122.1(8)	O008	C00L	C00I	120.6(8)
C00F	C00E	C00H	118.5(8)	O008	C00L	C00K	120.4(8)
C00C	C00F	Br02	119.0(6)	C00I	C00L	C00K	118.8(8)
C00E	C00F	Br02	118.8(7)				

Table S30. Torsion Angles for 9

A	B	C	D	Angle/°
Br01	C00A	C00C	C00F	-179.6(6)
Br03	C00G	C00K	O007	-2.6(11)
Br03	C00G	C00K	C00L	179.0(6)
Br04	C00B	C00D	C00G	178.4(7)
Br04	C00B	C00I	Br05	1.6(11)
Br04	C00B	C00I	C00L	179.5(7)
Br05	C00I	C00L	O008	-4.4(11)
Br05	C00I	C00L	C00K	179.9(6)
O006	C00E	C00F	Br02	1.1(11)
O006	C00E	C00F	C00C	-179.6(8)
O006	C00E	C00H	O007	-2.5(11)
O006	C00E	C00H	C009	179.4(7)
O007	C00K	C00L	O008	3.8(12)
O007	C00K	C00L	C00I	179.5(8)
C009	C00A	C00C	C00F	0.8(13)
C00A	C009	C00H	O007	-178.7(7)
C00A	C009	C00H	C00E	-0.8(12)
C00A	C00C	C00F	Br02	-179.3(6)
C00A	C00C	C00F	C00E	1.4(13)
C00B	C00D	C00G	Br03	-176.7(6)
C00B	C00D	C00G	C00K	2.3(13)
C00B	C00I	C00L	O008	177.7(8)

A	B	C	D	Angle/°
C00B	C00I	C00L	C00K	2.0(13)
C00D	C00B	C00I	Br05	-177.6(6)
C00D	C00B	C00I	C00L	0.3(13)
C00D	C00G	C00K	O007	178.4(8)
C00D	C00G	C00K	C00L	0.0(13)
C00F	C00E	C00H	O007	-179.1(7)
C00F	C00E	C00H	C009	2.9(12)
C00G	C00K	C00L	O008	-177.8(8)
C00G	C00K	C00L	C00I	-2.1(13)
C00H	O007	C00K	C00G	112.5(9)
C00H	O007	C00K	C00L	-69.1(10)
C00H	C009	C00A	Br01	179.3(6)
C00H	C009	C00A	C00C	-1.1(13)
C00H	C00E	C00F	Br02	177.5(6)
C00H	C00E	C00F	C00C	-3.2(13)
C00I	C00B	C00D	C00G	-2.4(12)
C00J	O006	C00E	C00F	-98.5(9)
C00J	O006	C00E	C00H	85.1(9)
C00K	O007	C00H	C009	-17.0(11)
C00K	O007	C00H	C00E	164.9(7)
C00M	O008	C00L	C00I	113.5(11)
C00M	O008	C00L	C00K	-70.9(12)

Table S31. Hydrogen Atom Coordinates ($\text{Å}\times10^4$) and Isotropic Displacement Parameters ($\text{Å}^2\times10^3$) for **9**

Atom	x	y	z	U(eq)
H009	4827.61	1419.61	5266.82	21
H00C	5856.47	2151.82	7106.42	25
H00D	1599.05	728.47	3392.07	29
H00A	-993.9	3162.57	5870.23	42
H00B	-1581.68	4242.78	6246.43	42
H00E	-699.22	3213.84	6606.7	42
H00F	4394.88	5149.86	4203.06	111
H00G	5246.52	5284.57	4887.94	111
H00H	3211.6	4726.98	4790.67	111

Table S32. Refinement model description for **9**

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of: All C(H) groups

At 1.5 times of: All C(H,H,H) groups

2.a Aromatic/amide H refined with riding coordinates: C009(H009), C00C(H00C), C00D(H00D)

2.b Idealized Me refined as rotating group: C00J(H00A,H00B,H00E), C00M(H00F,H00G,H00H)

Table S33. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 9

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 753
Number of electrons: 292
Parallel Job: 16 threads


SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
         Step      Energy         Max Grad.      Max Dist.
           1   -13635.346267      0.025715       0.101967
           2   -13635.352033      0.007462       0.126962
           3   -13635.352956      0.002650       0.005913
           4   -13635.352998      0.002584       0.083121
           5   -13635.353359      0.003436       0.044216
           6   -13635.353470      0.002677       0.038853
           7   -13635.353545      0.001050       0.030200
           8   -13635.353572      0.000731       0.011531
           9   -13635.353579      0.000452       0.007713
```

Figure S37. HOMO-LUMO of **9**
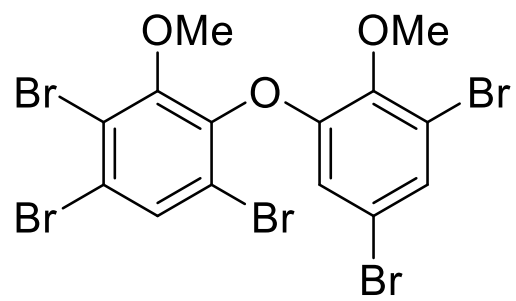
9
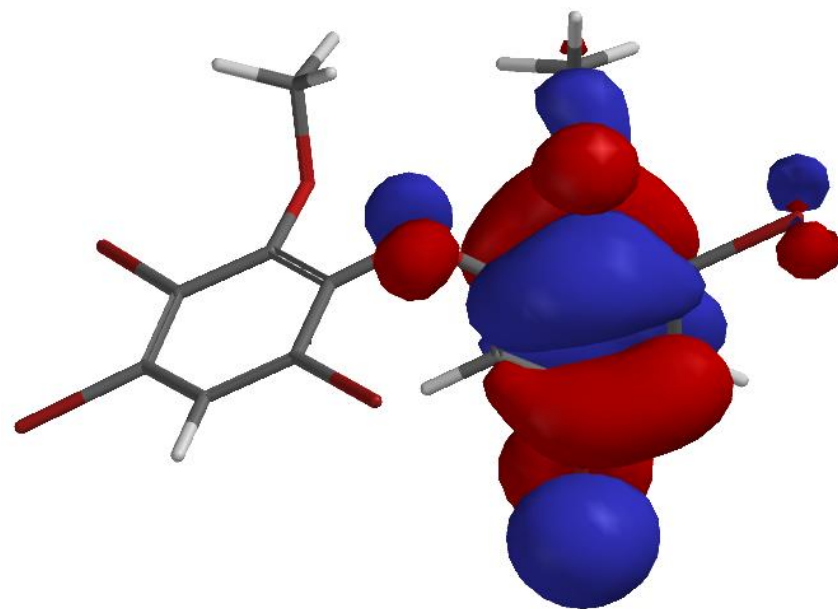
HOMO 9
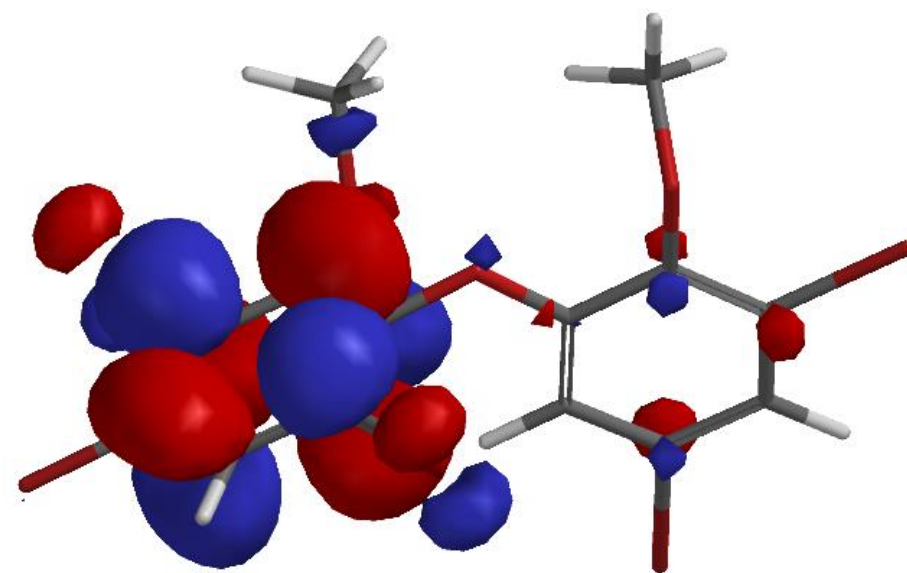
LUMO 9

Figure S38. Calculated ^{13}C NMR Chemical Shift of **9**
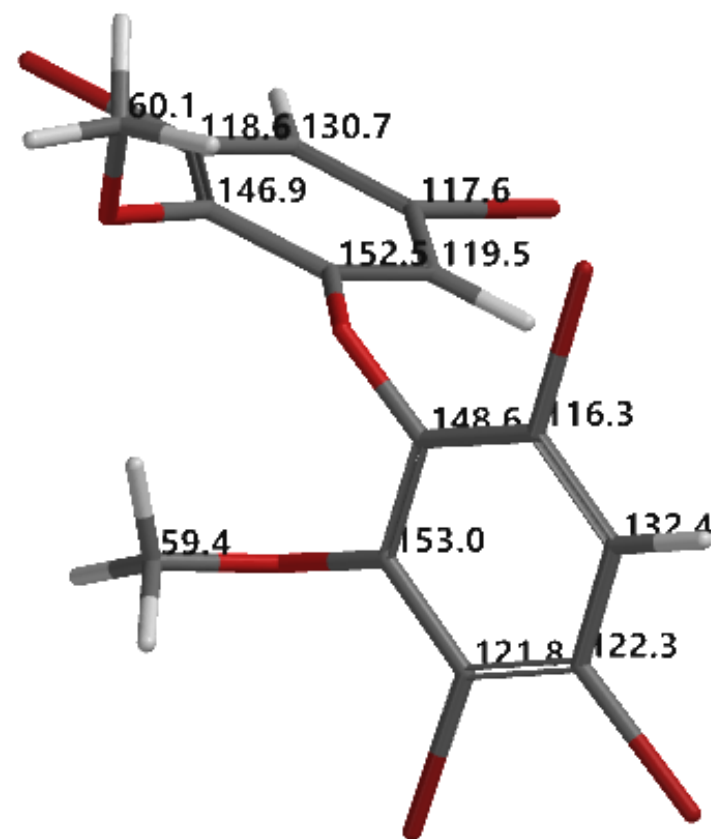
Figure S39. ^{1}H NMR spectrum of **10** (Me$_2$CO-d_6, 500 MHz)
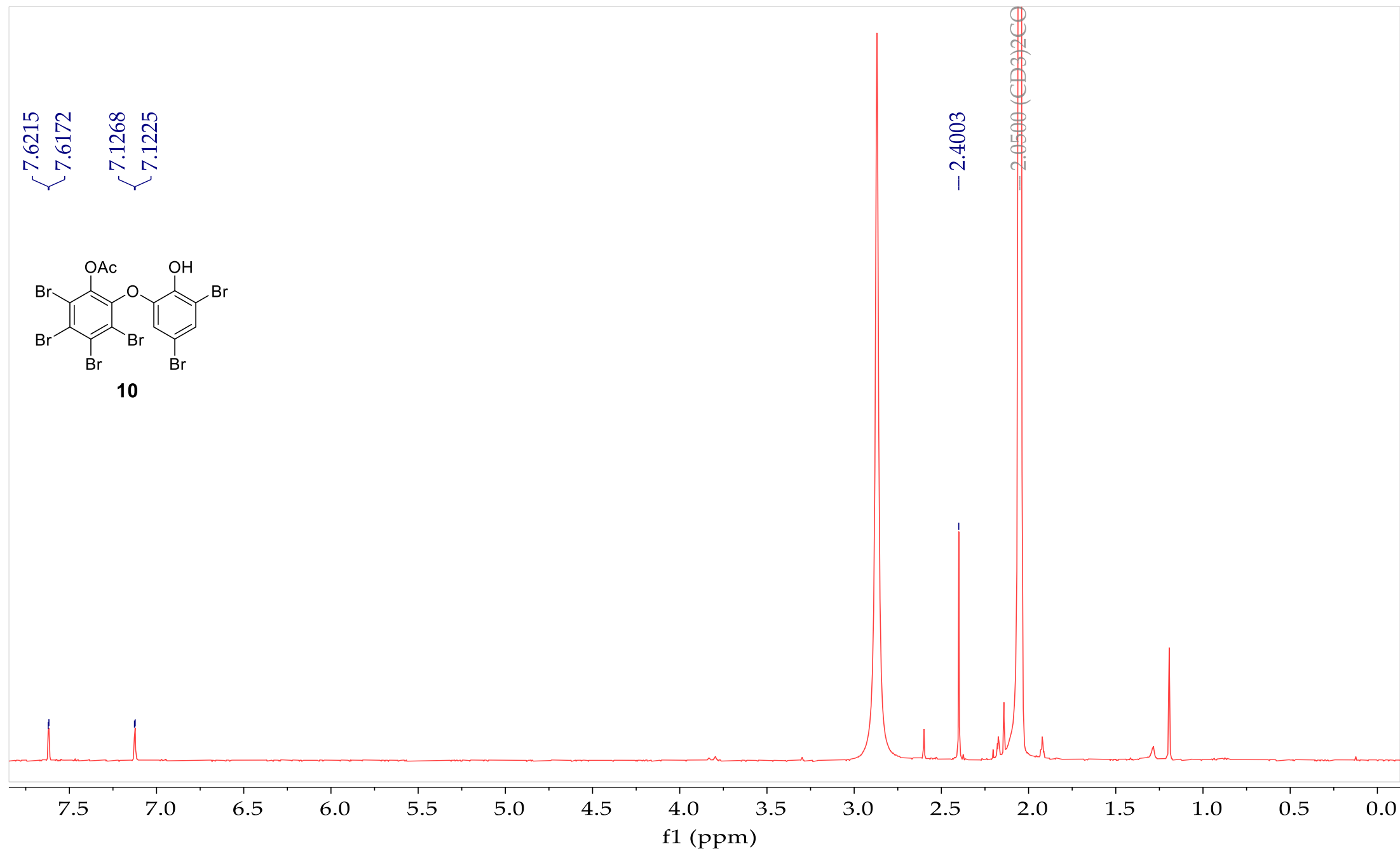
Figure S40. ^{1}H NMR spectrum of **10** (CDCl$_3$, 500 MHz)
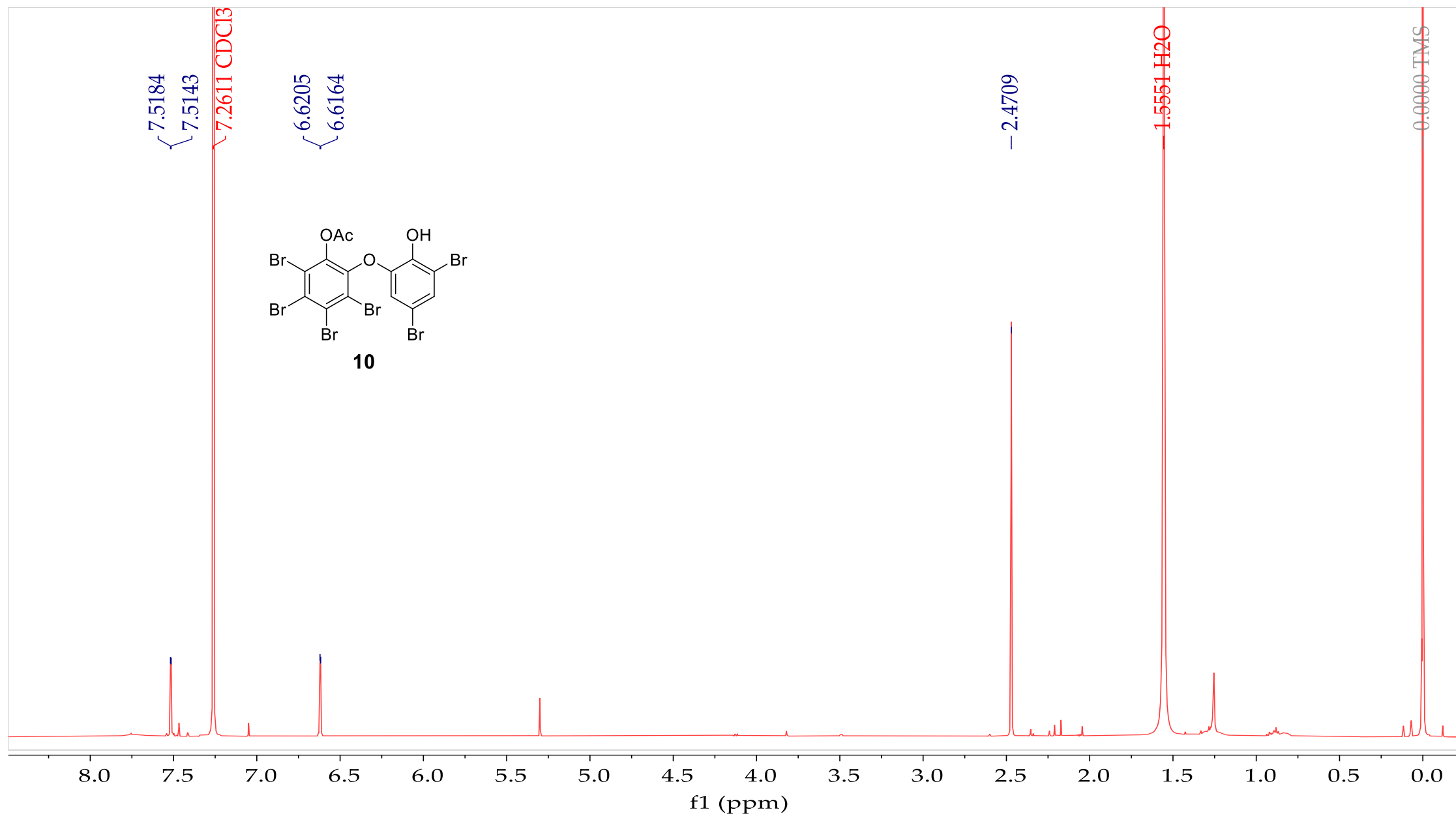
Figure S41. ^{1}H-^{1}H COSY spectrum of **10** (CDCl$_3$, 500 MHz)
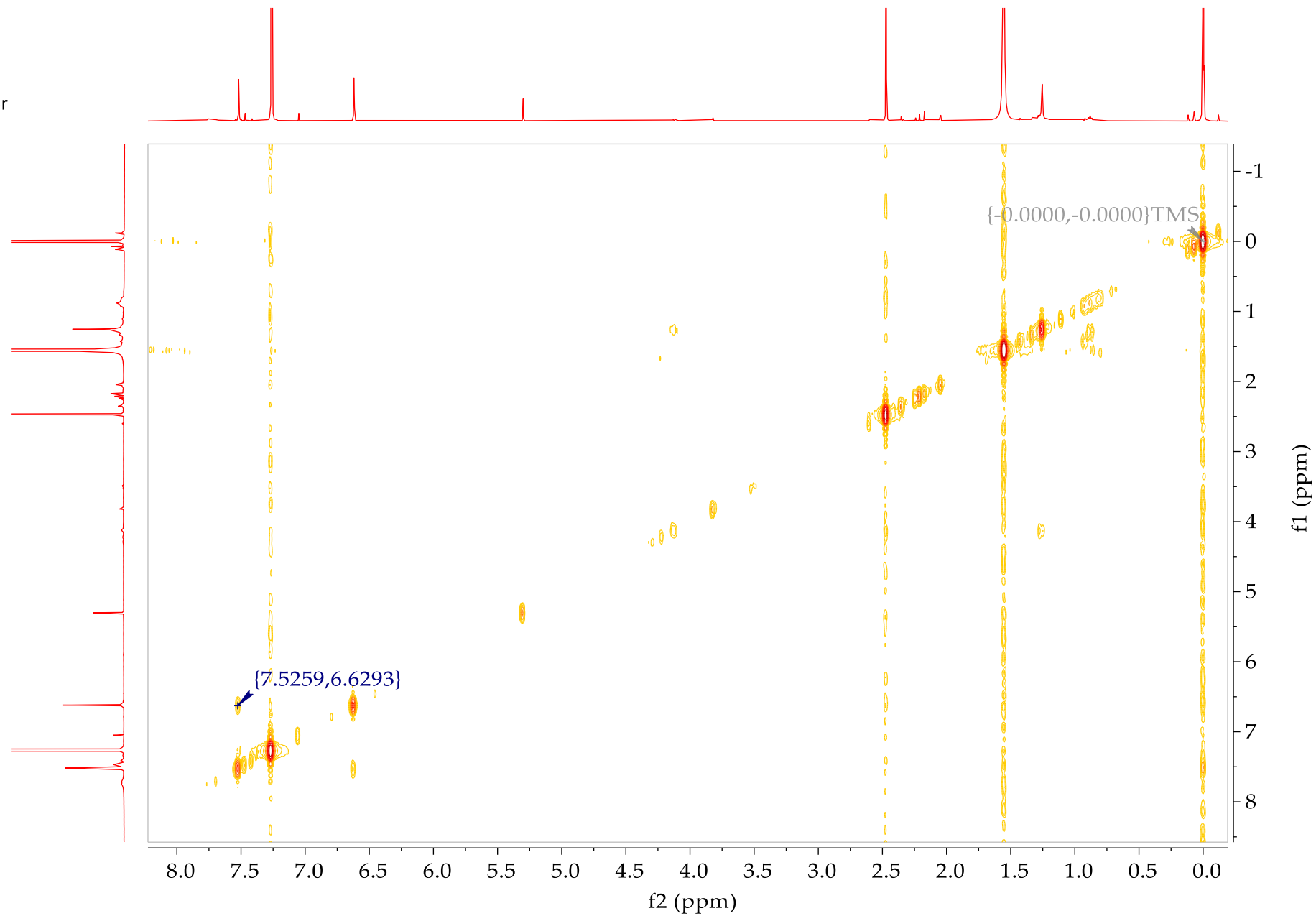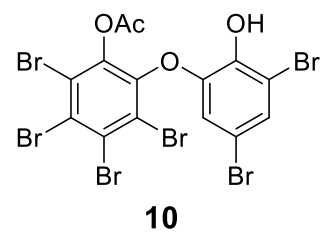
Figure S42. ^1H-^{13}C HSQC spectrum of **10** (CDCl$_3$, 500 MHz)
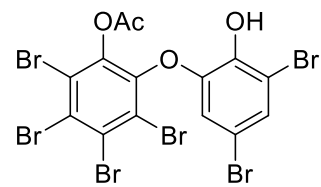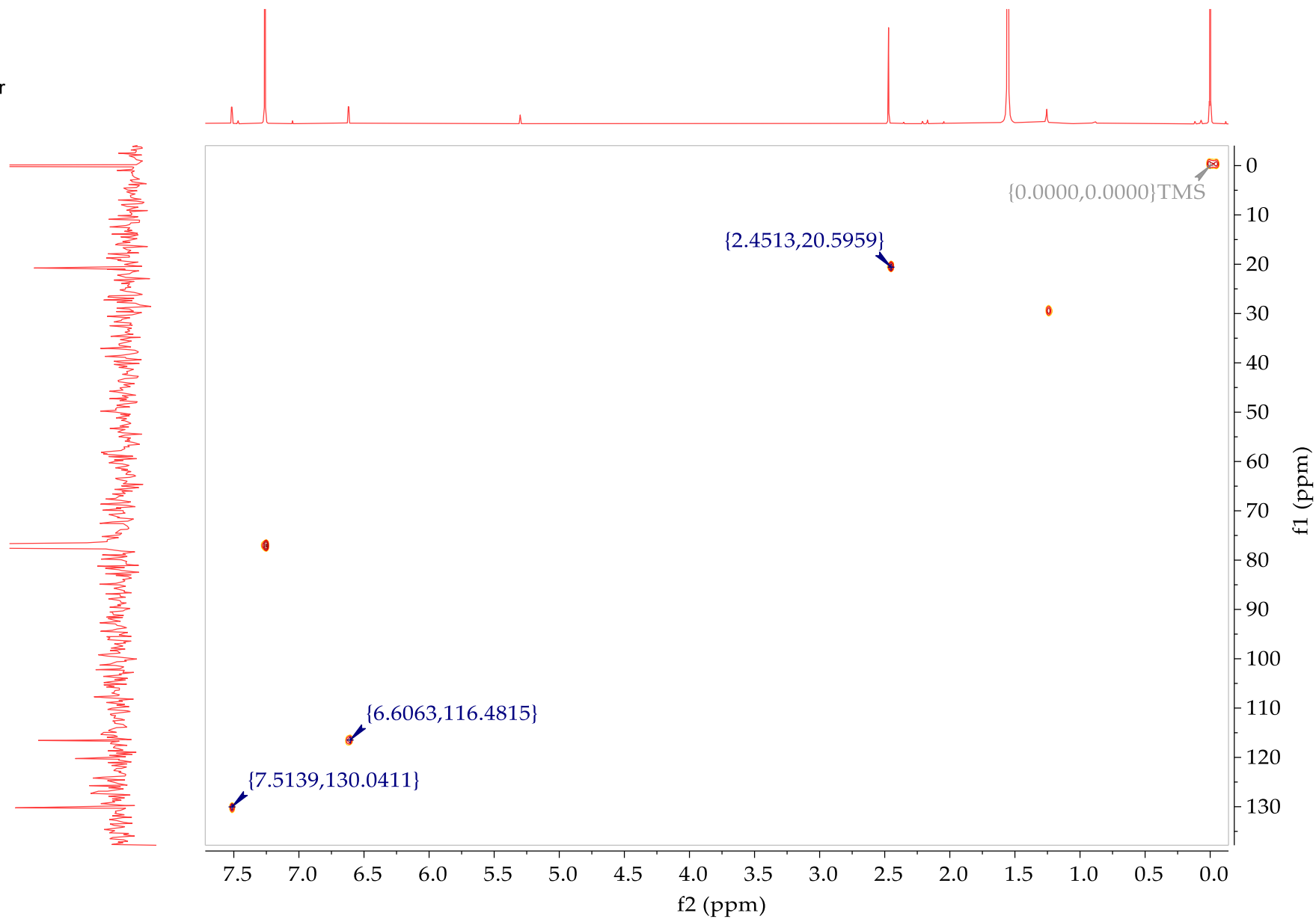
Figure S43. ^1H-^{13}C HMBC spectrum of **10** (CDCl$_3$, 500 MHz)
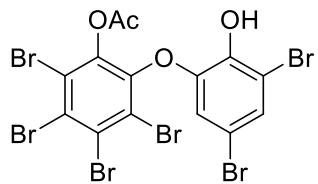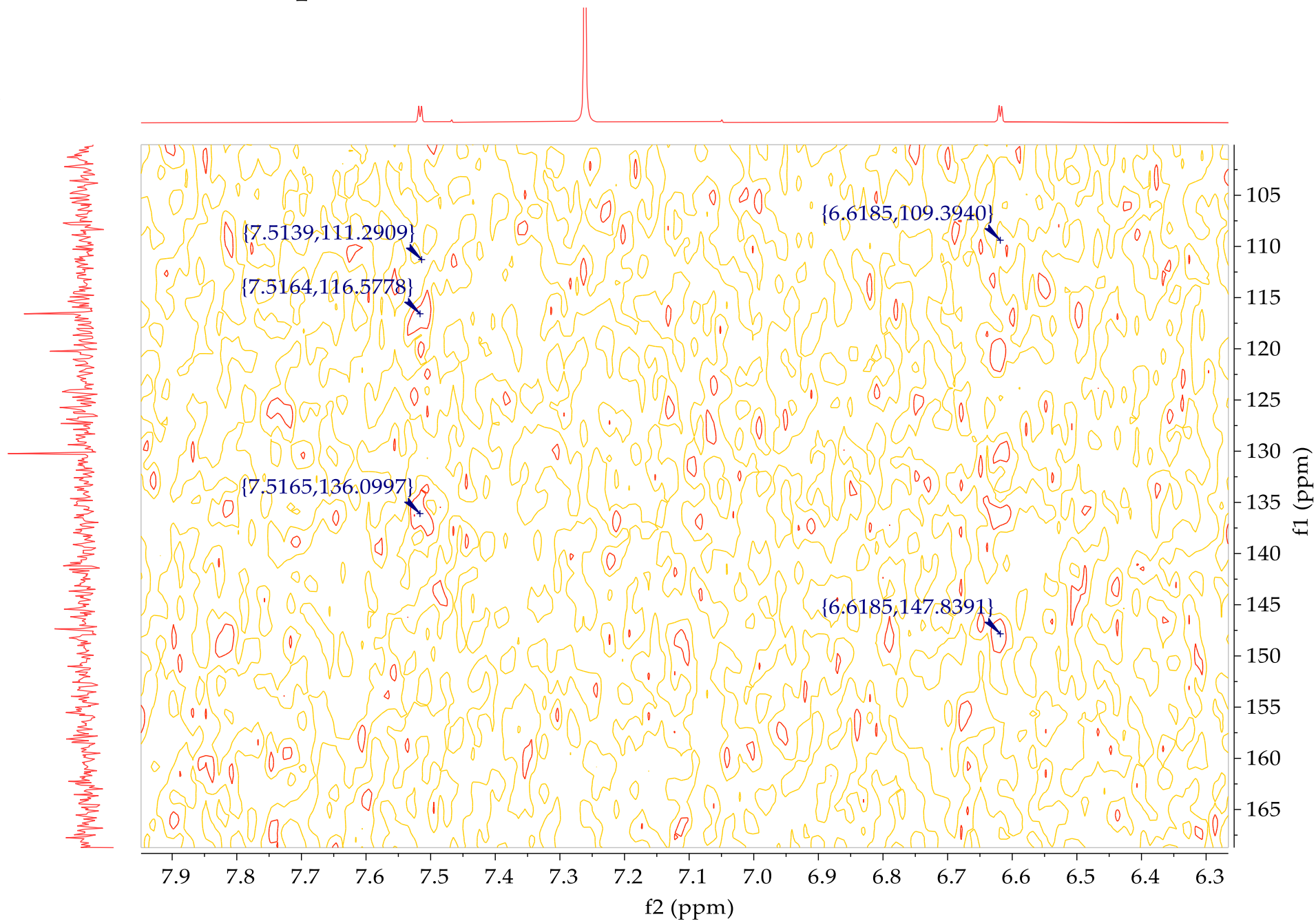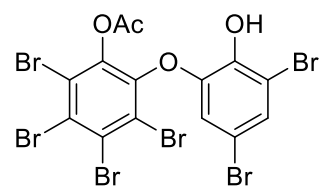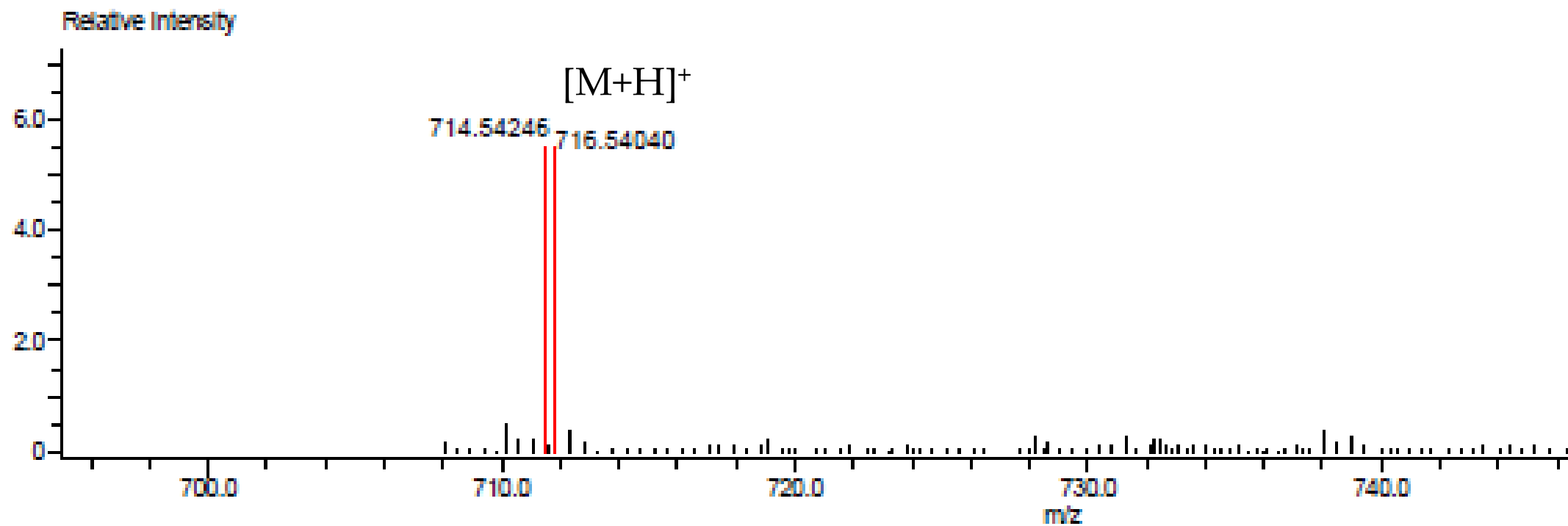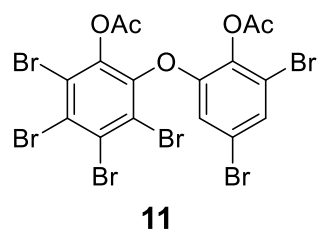
Table S34. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **10**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 810
Number of electrons: 332
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step        Energy         Max Grad.        Max Dist.
          1    -16282.961523       0.039596         0.099841
          2    -16282.973455       0.009160         0.056260
          3    -16282.974471       0.004227         0.035504
          4    -16282.974697       0.001591         0.011823
          5    -16282.974728       0.000611         0.013237
          6    -16282.974736       0.000430         0.011420
```
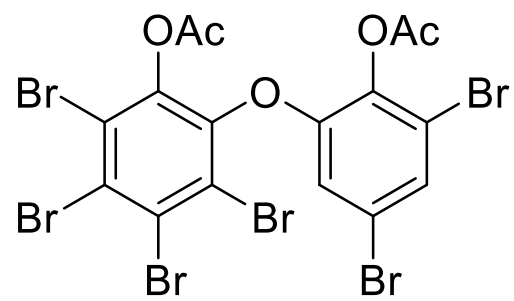
Figure 45. HOMO-LUMO of 10

HOMO 10

LUMO 10
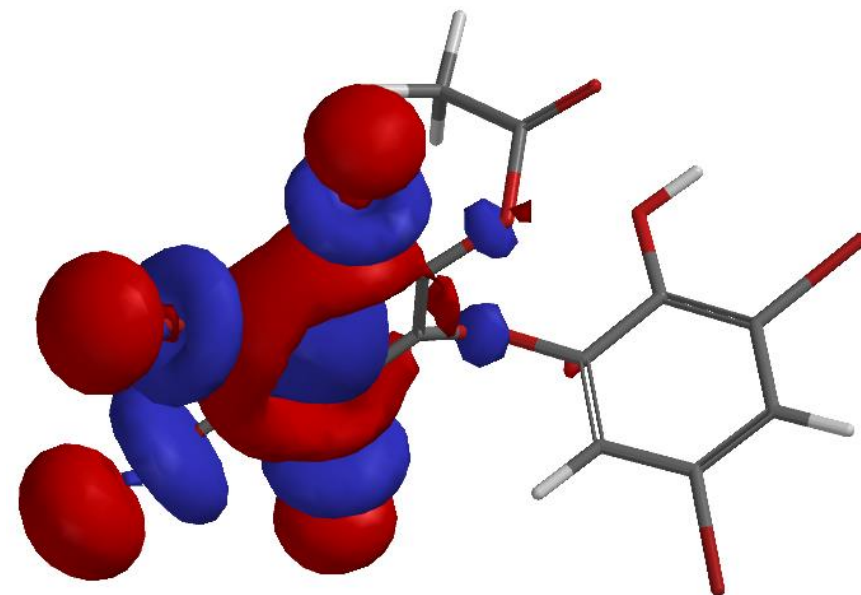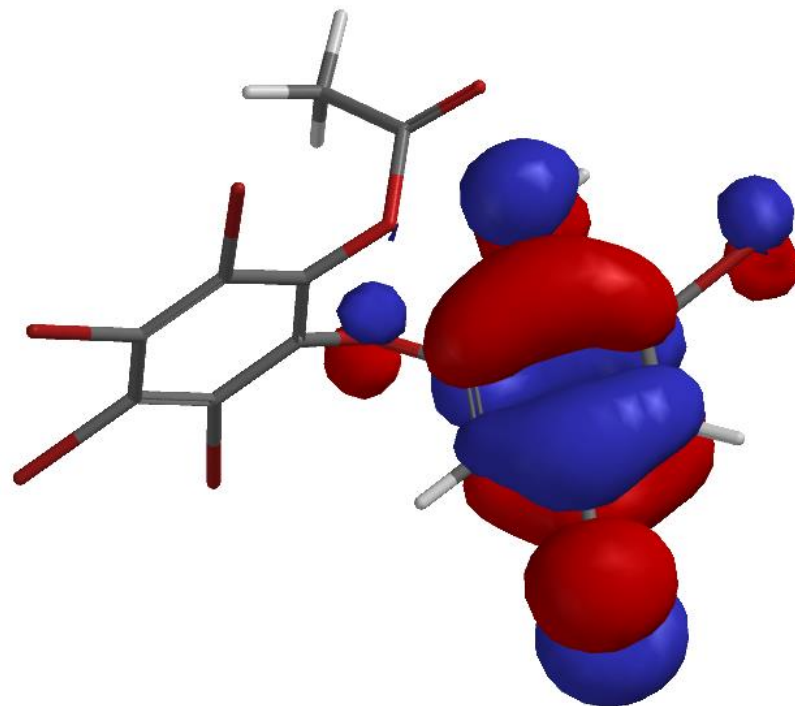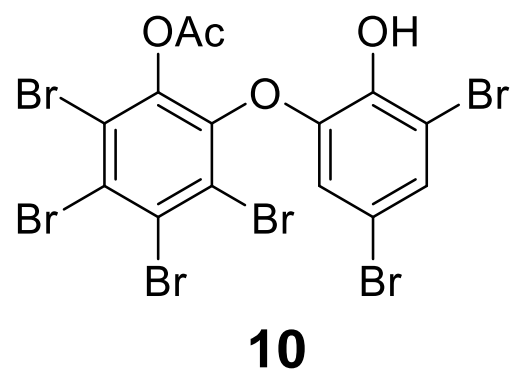
Figure S46. Calculated ^{13}C NMR Chemical Shift of **10**
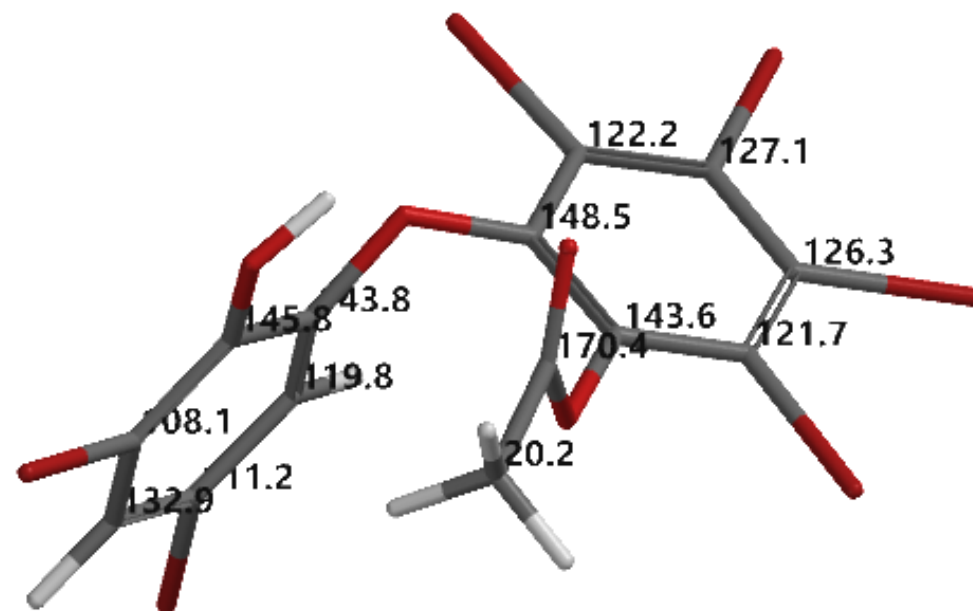
Figure S47. ^{1}H NMR spectrum of **11** (Me$_2$CO-d_6, 500 MHz)

7.6443
7.6401
7.1422
7.1409

2.3639
2.2403
2.0500 (CD3)2CO

f1 (ppm)
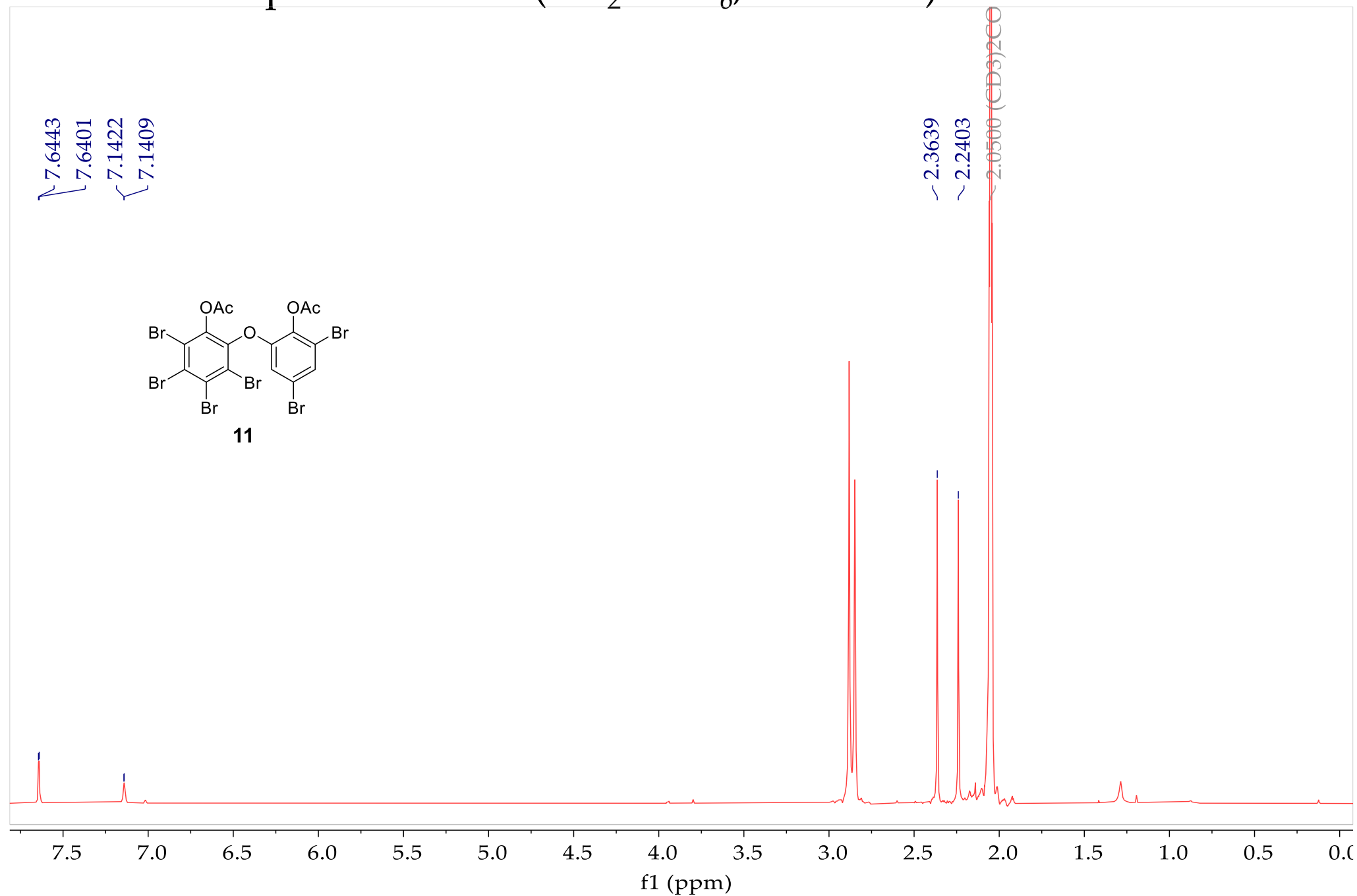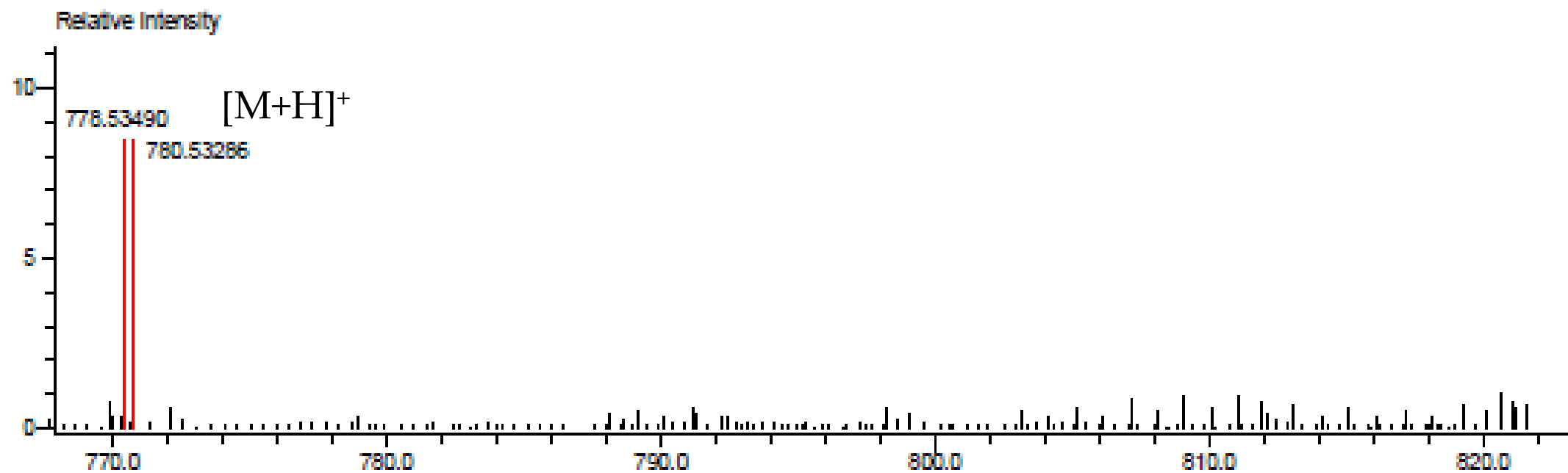
Table S35. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **11**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 903
Number of electrons: 354
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step      Energy         Max Grad.      Max Dist.
           1    -16435.596645    0.053312       0.109488
           2    -16435.613906    0.009515       0.084379
           3    -16435.615225    0.005318       0.043742
           4    -16435.615707    0.005185       0.060976
           5    -16435.615985    0.005939       0.074446
           6    -16435.616297    0.004642       0.075823
           7    -16435.616595    0.003118       0.101938
           8    -16435.616834    0.003743       0.090140
           9    -16435.617030    0.004368       0.036928
          10    -16435.617070    0.002291       0.040489
          11    -16435.617133    0.000930       0.015841
          12    -16435.617140    0.000620       0.014268
```

Figure S49. HOMO-LUMO of **11**
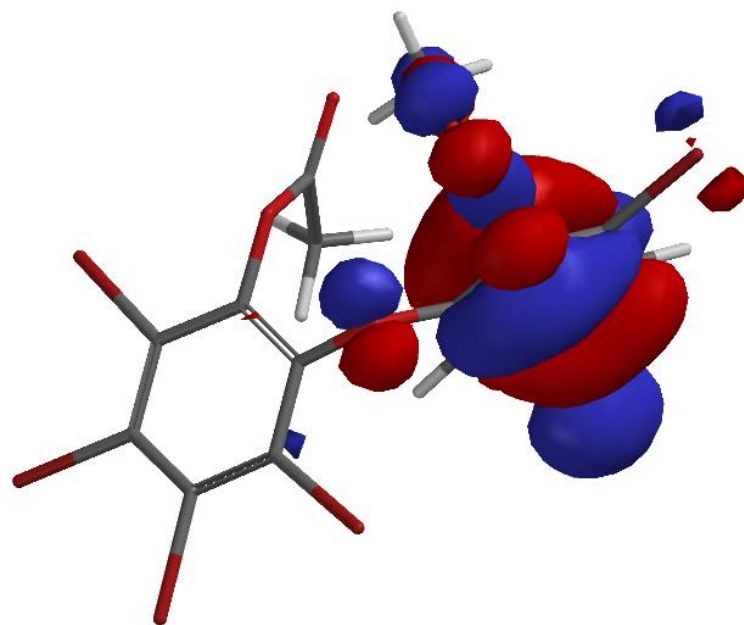
HOMO 11
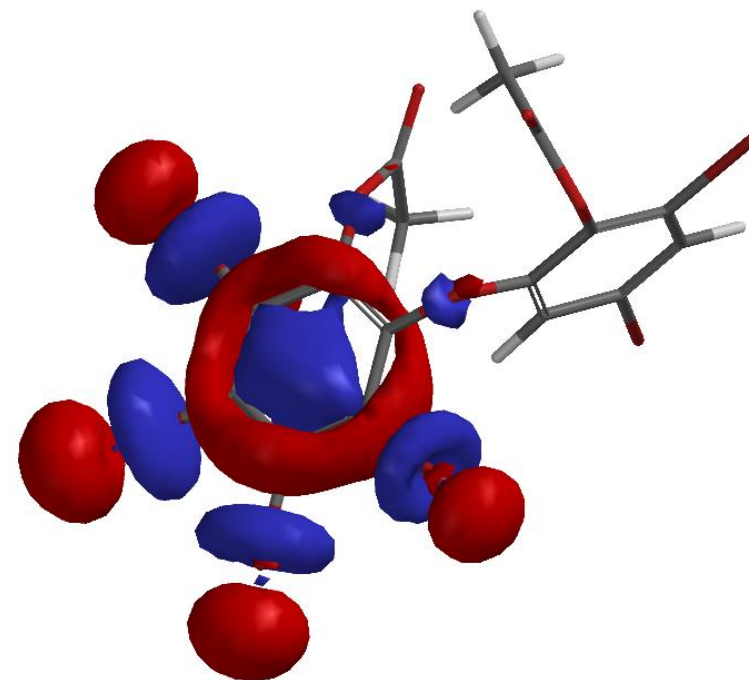
LUMO 11

Figure S50. Calculated ^{13}C NMR Chemical Shift of **11**
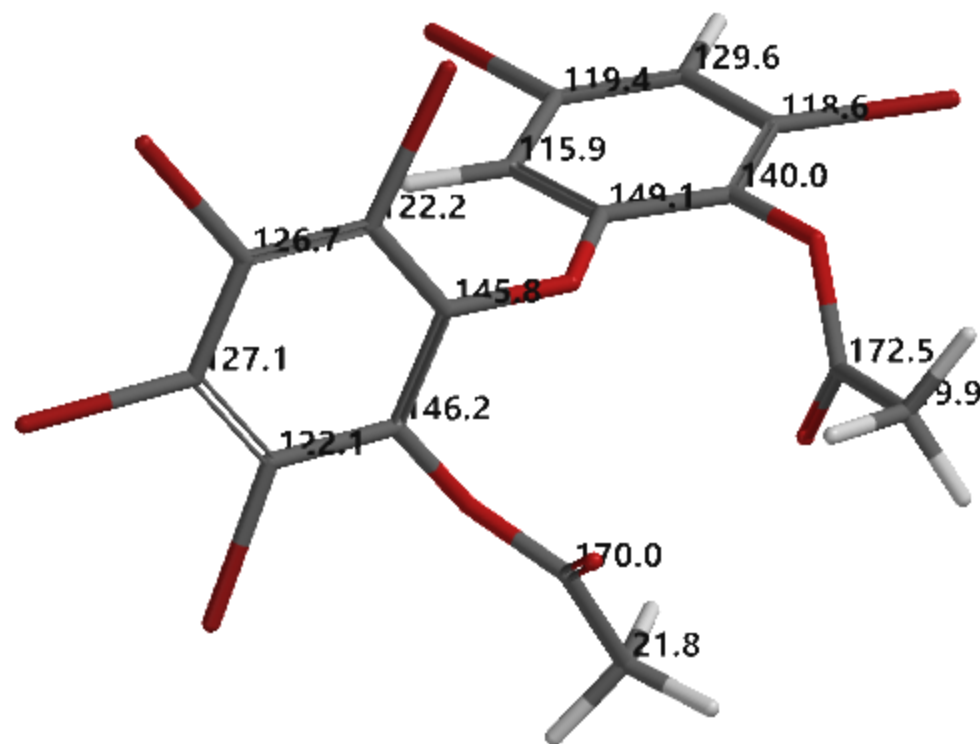
Figure S51. ^{1}H NMR spectrum of **12** (Me$_2$CO-d_6, 500 MHz)
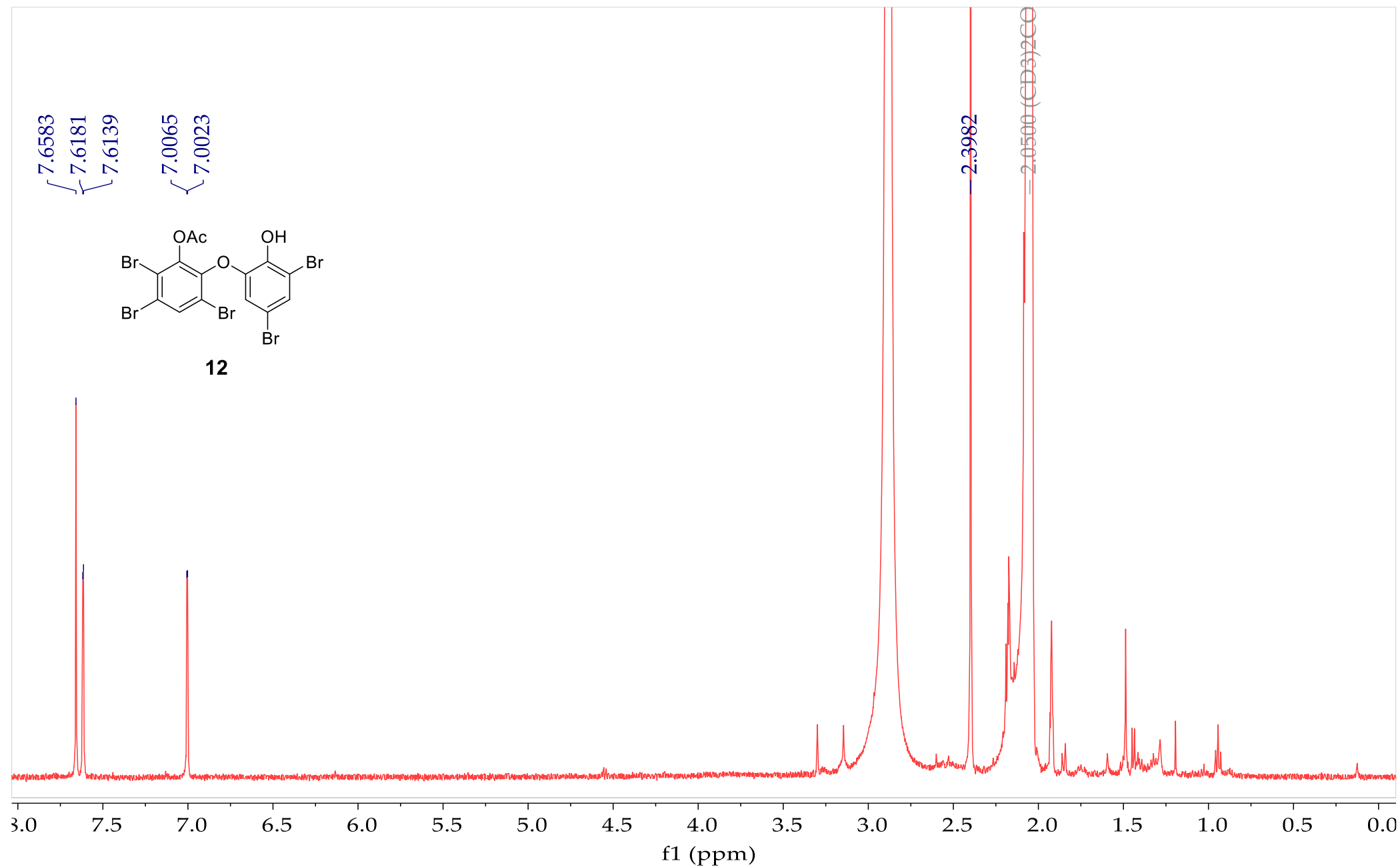
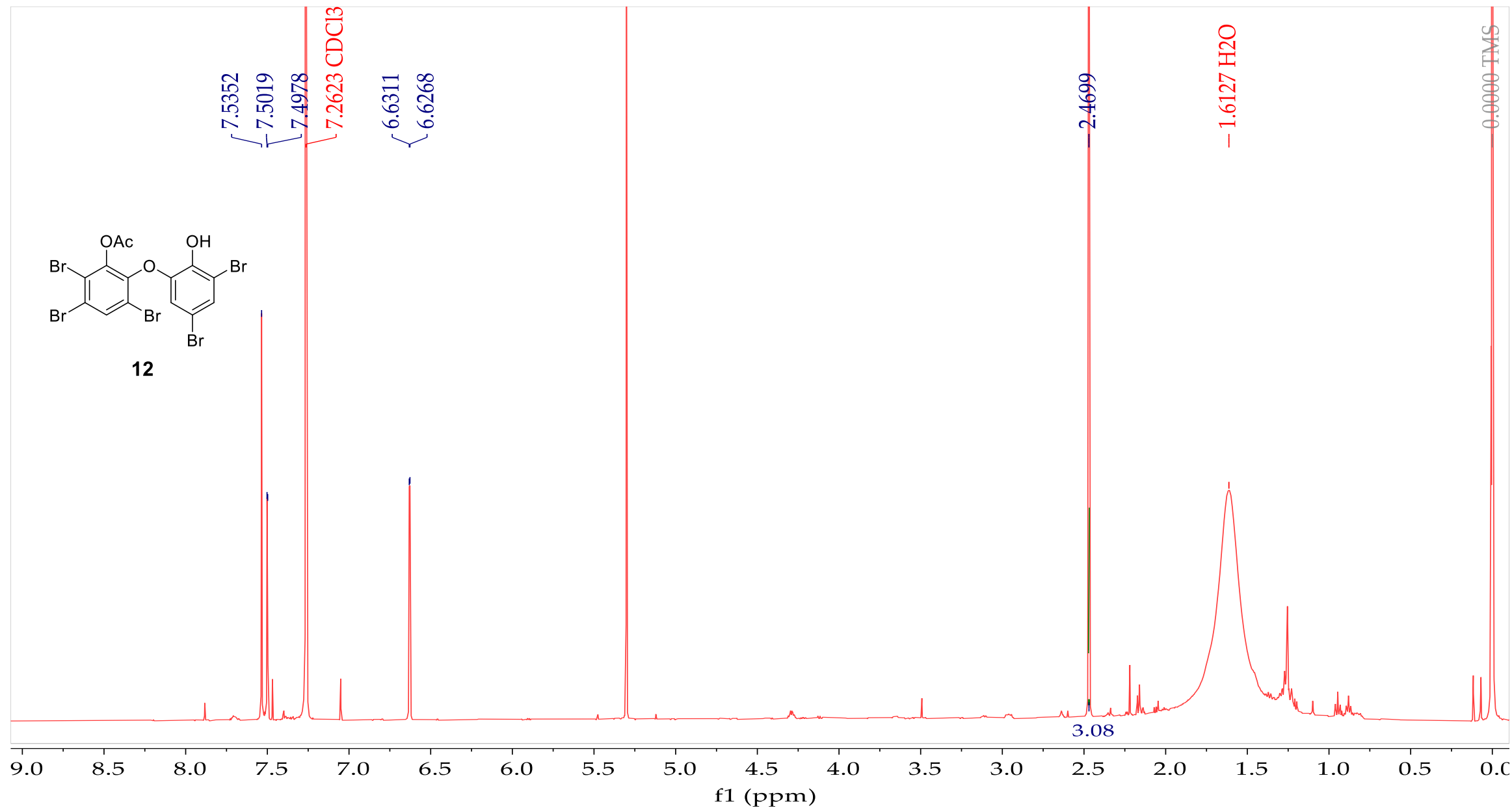Figure S52. ^{1}H NMR spectrum of **12** (CDCl$_3$, 500 MHz)

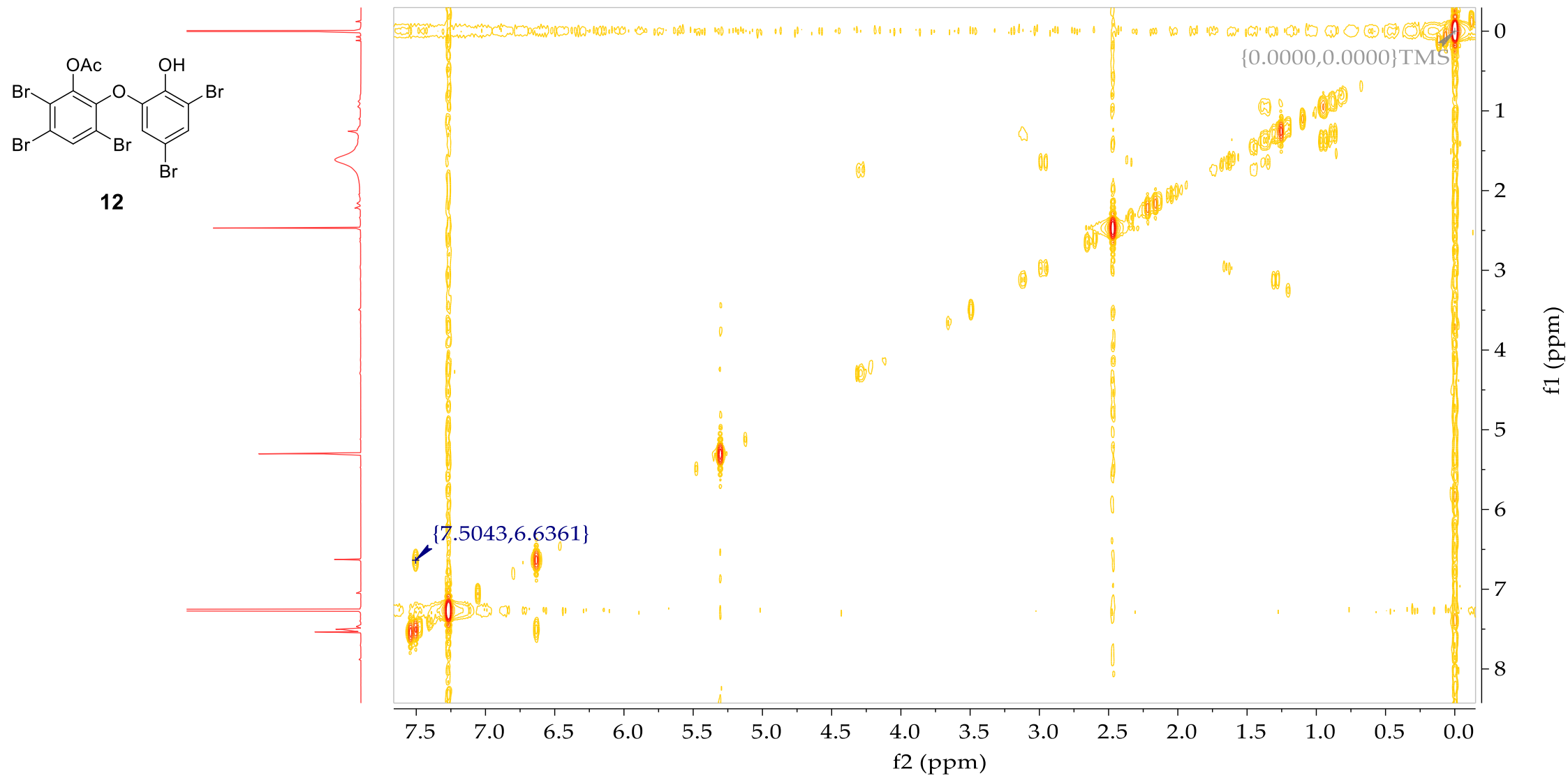Figure S53. ¹H-¹H COSY spectrum of **12** (CDCl$_3$, 500 MHz)

{7.5043,6.6361}

{0.0000,0.0000}TMS

f1 (ppm)

f2 (ppm)

Figure S54. ^{1}H-^{13}C HSQC spectrum of **12** (CDCl$_3$, 500 MHz)
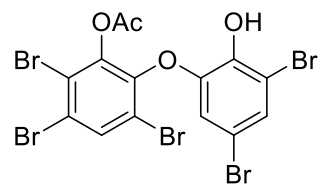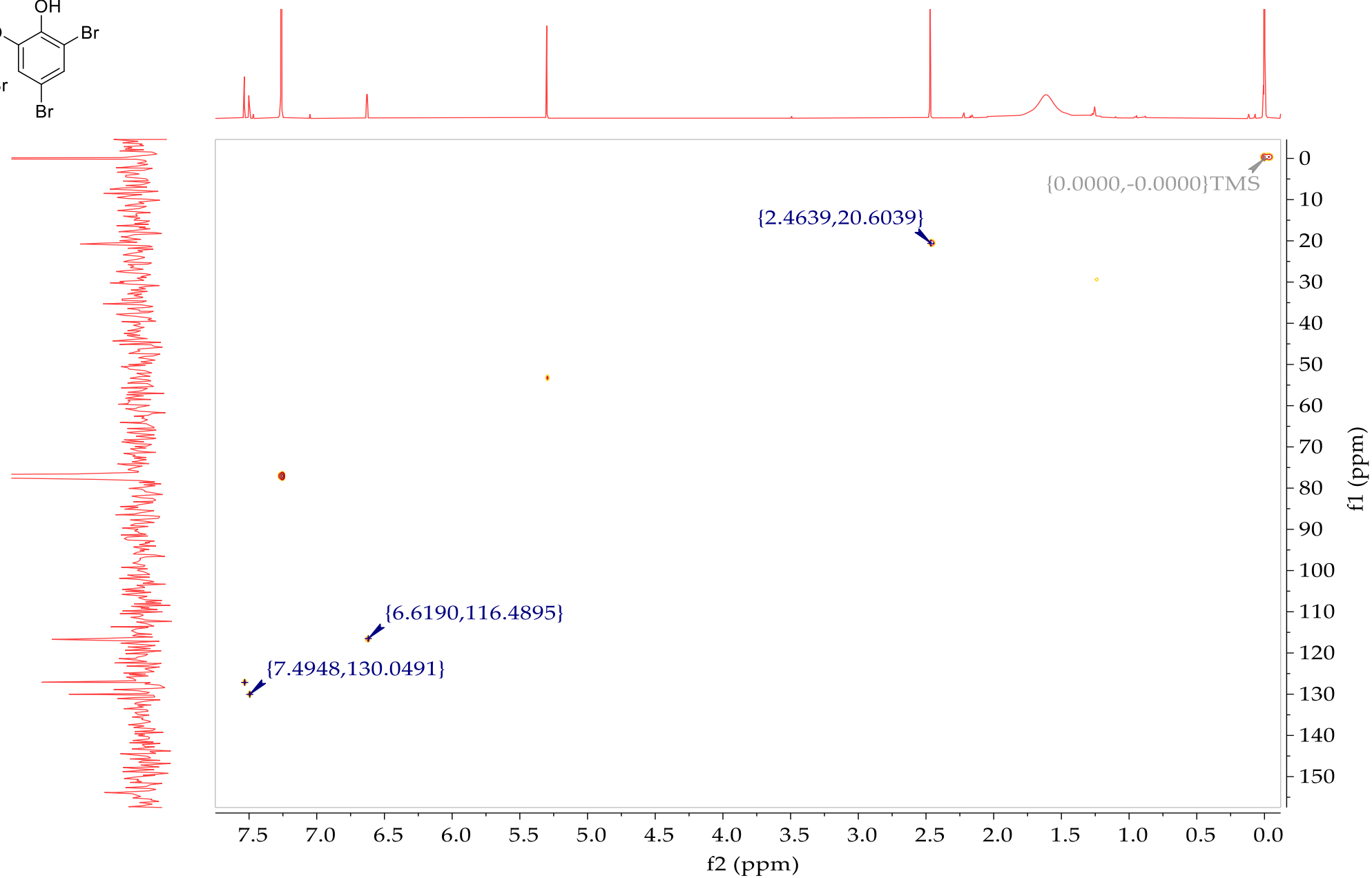
Figure S55. ^{1}H-^{13}C HMBC spectrum of **12** (CDCl$_3$, 500 MHz)

{0.0000,-0.0000}TMS

{6.6301,111.2302}

{6.6290,119.8976}

{6.6286,136.4091}

{6.6286,148.6755}

{2.4697,169.8201}
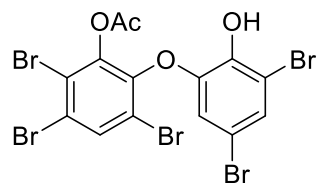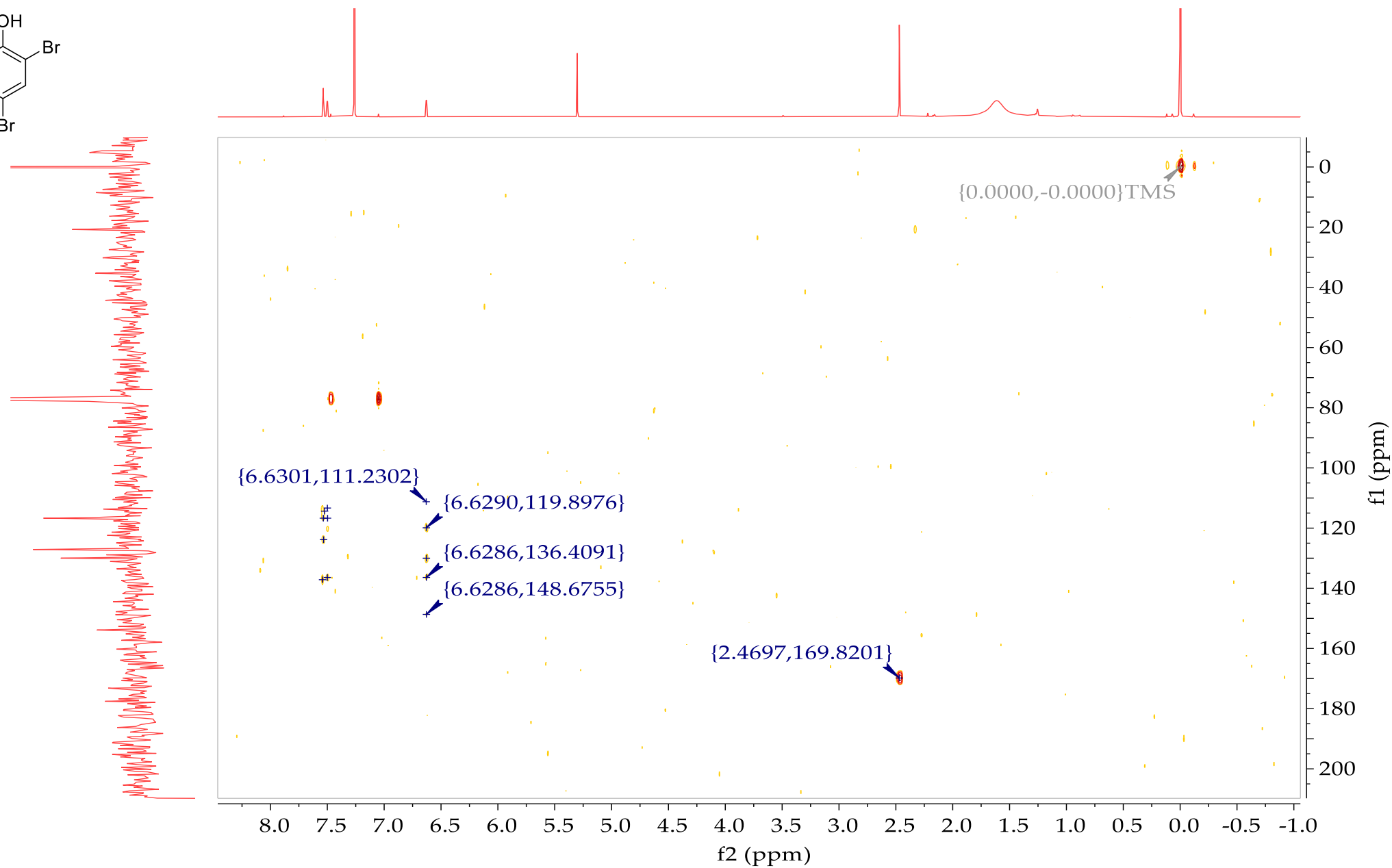
Figure S56. HRESIMS of **12**

12

Relative Intensity

[M+H]⁺

638.62989

640.62785

m/z
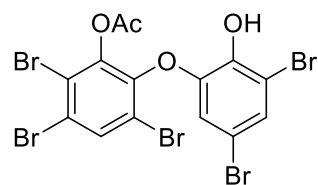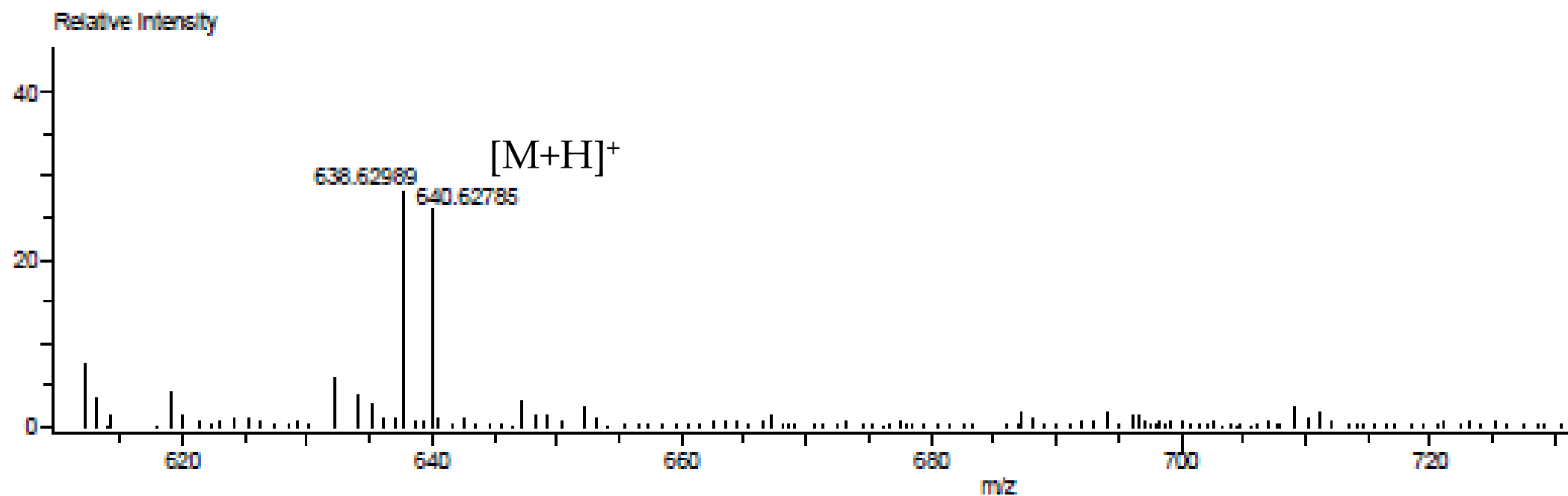
Table S36. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **12**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 768
Number of electrons: 298
Parallel Job: 16 threads


SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
        Step       Energy        Max Grad.      Max Dist.
          1    -13709.404352     0.038647       0.111242
          2    -13709.414372     0.014645       0.050709
          3    -13709.415618     0.004164       0.040775
          4    -13709.415825     0.001370       0.009811
          5    -13709.415855     0.000568       0.007578
          6    -13709.415859     0.000290       0.008302
```
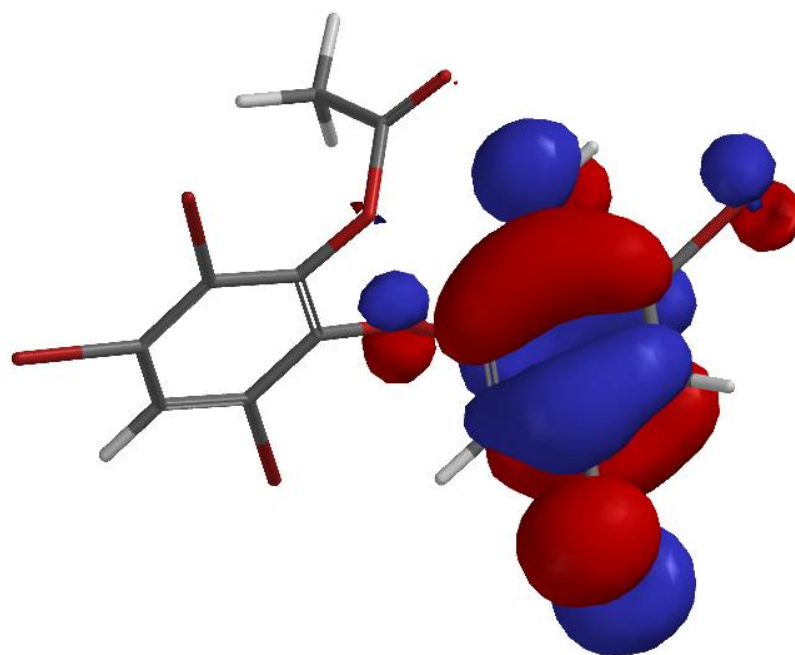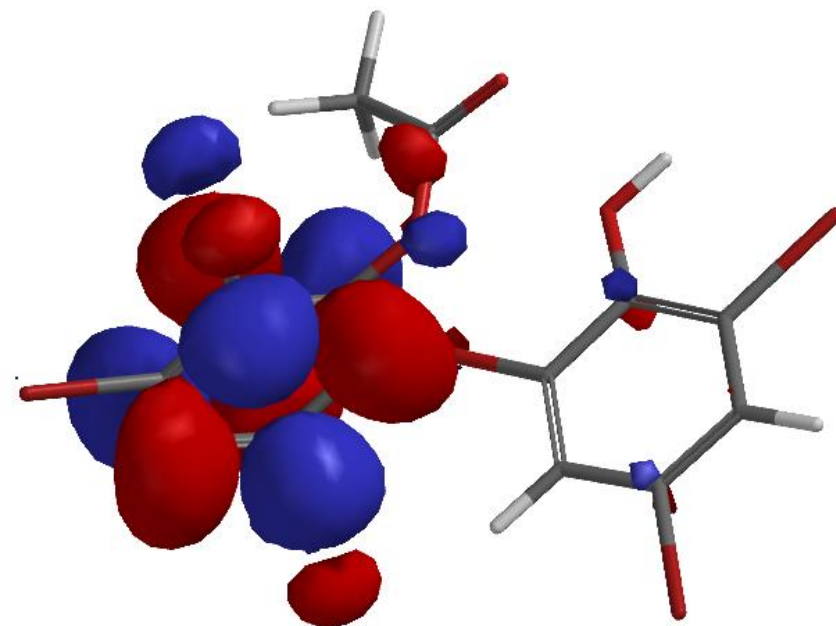
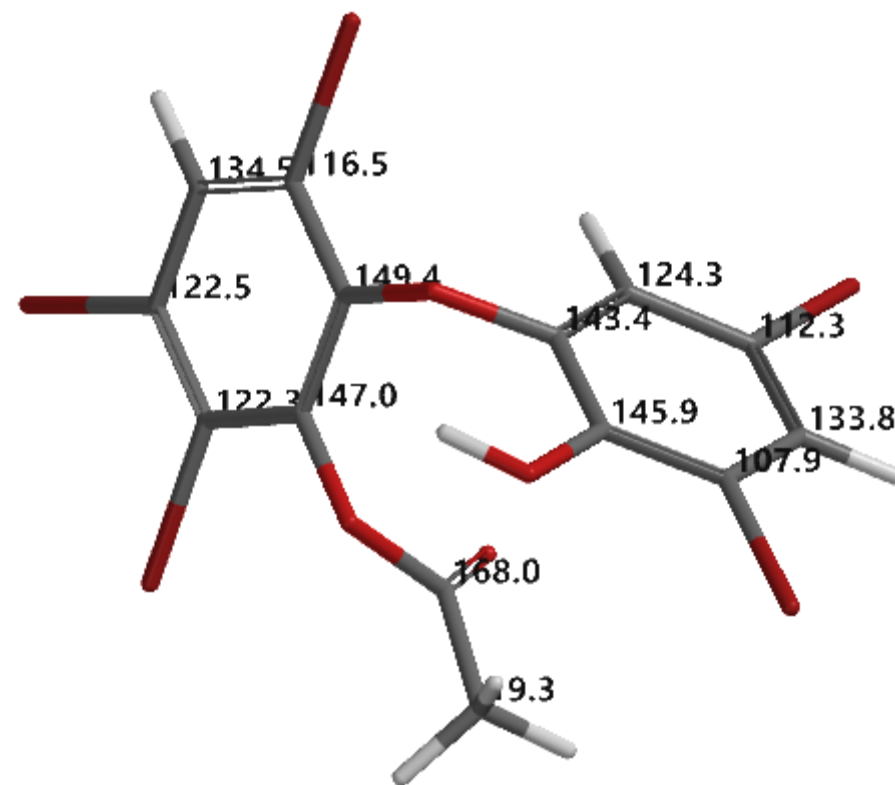Figure S57. HOMO-LUMO of **12**
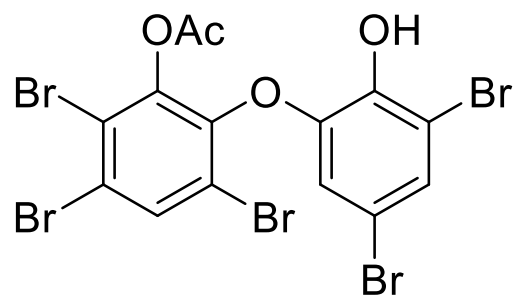
12

HOMO 12

LUMO 12

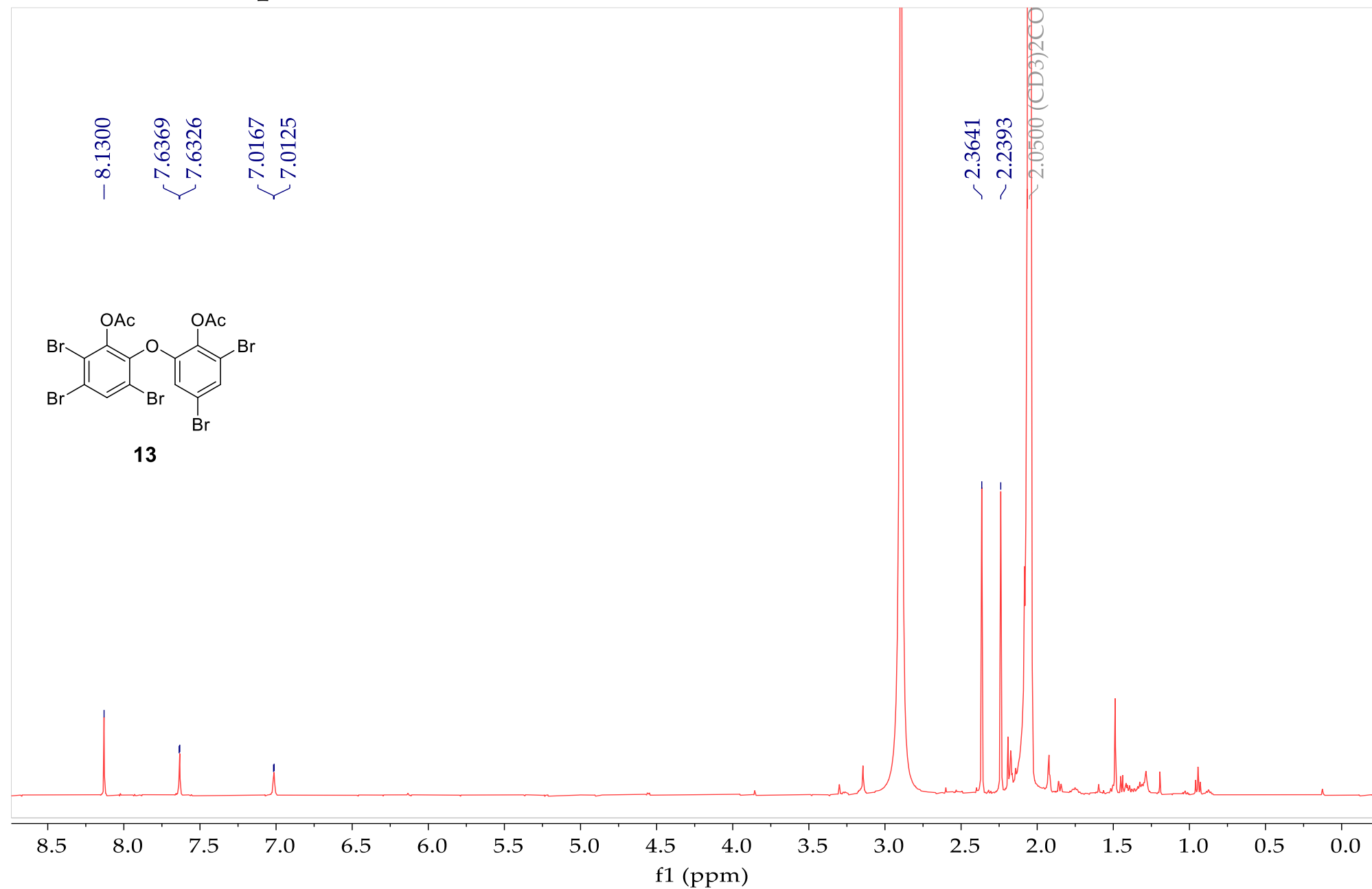# Figure S59. ^{1}H NMR spectrum of **13** (Me$_2$CO-d_6, 500 MHz)

Figure S60. ^{1}H NMR spectrum of **13** (CDCl$_3$, 500 MHz)
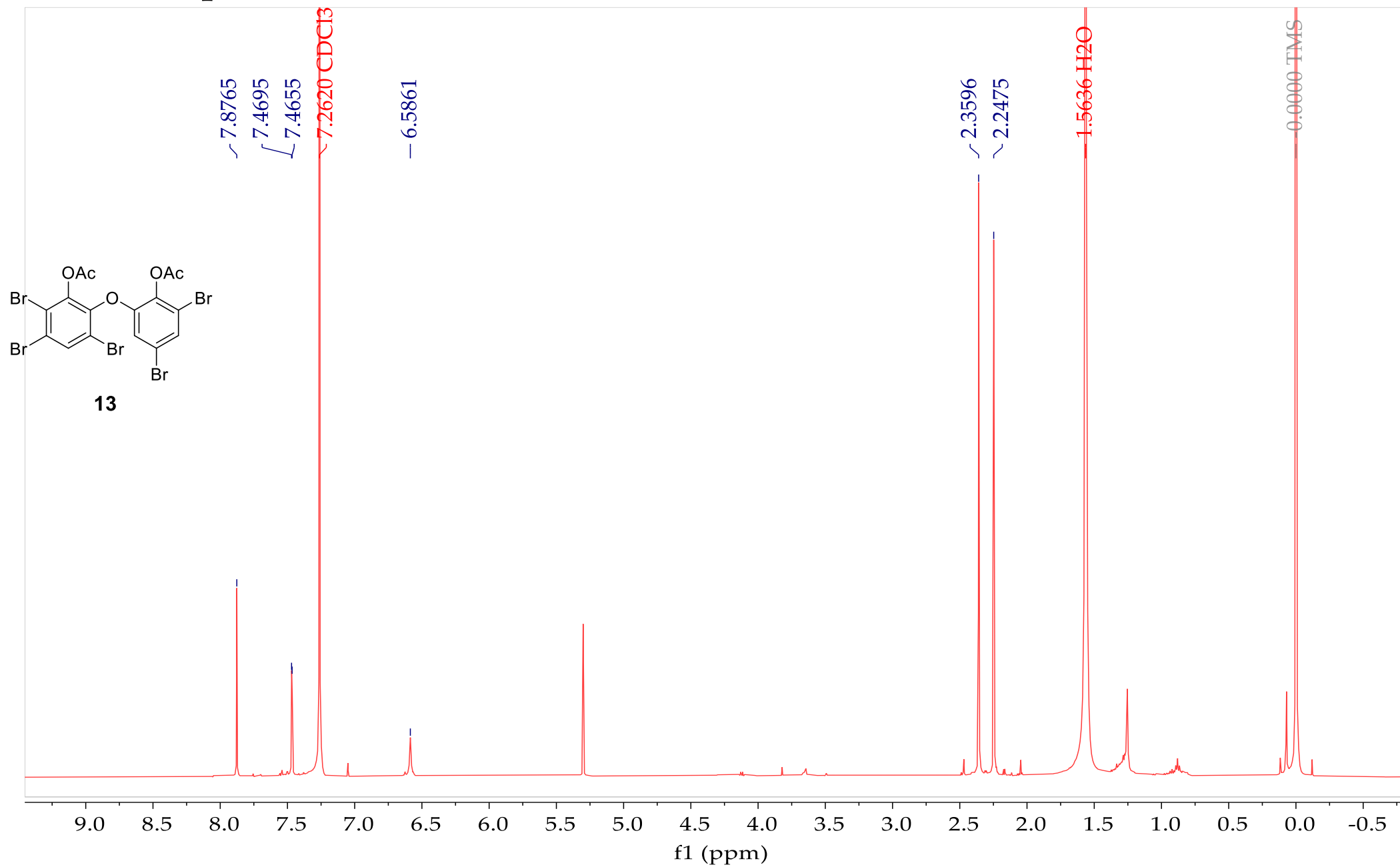
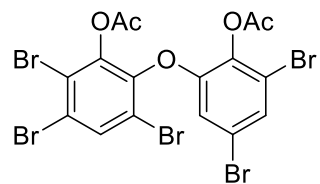Figure S61. ^{1}H-^{1}H COSY spectrum of **13** (CDCl$_3$, 500 MHz)

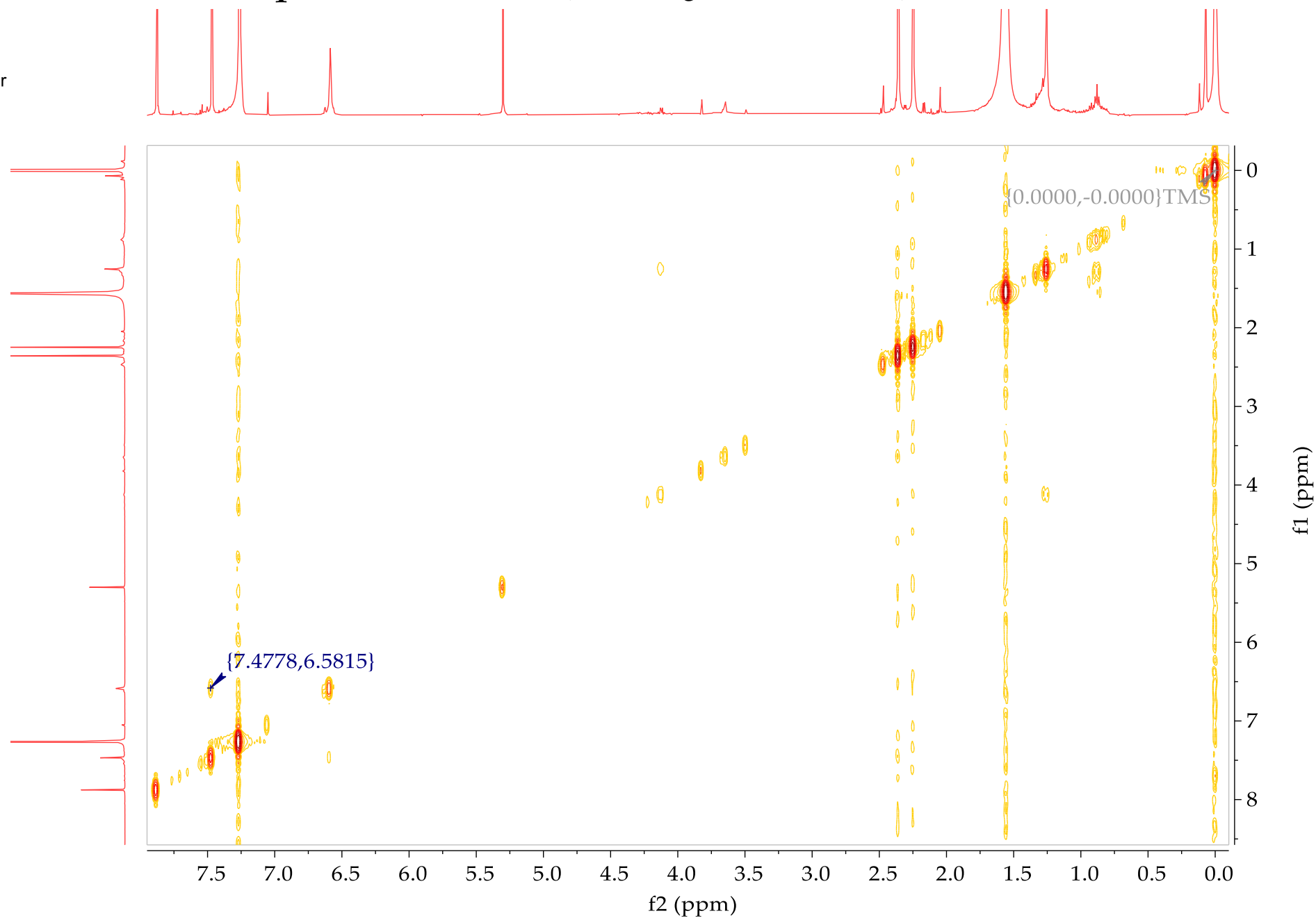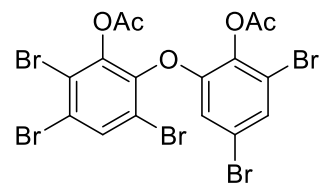# Figure S62. ¹H-¹³C HSQC spectrum of **13** (CDCl₃, 500 MHz)

{0.0000,0.0000}TMS

{2.3593,20.2644}   {2.2474,20.2644}
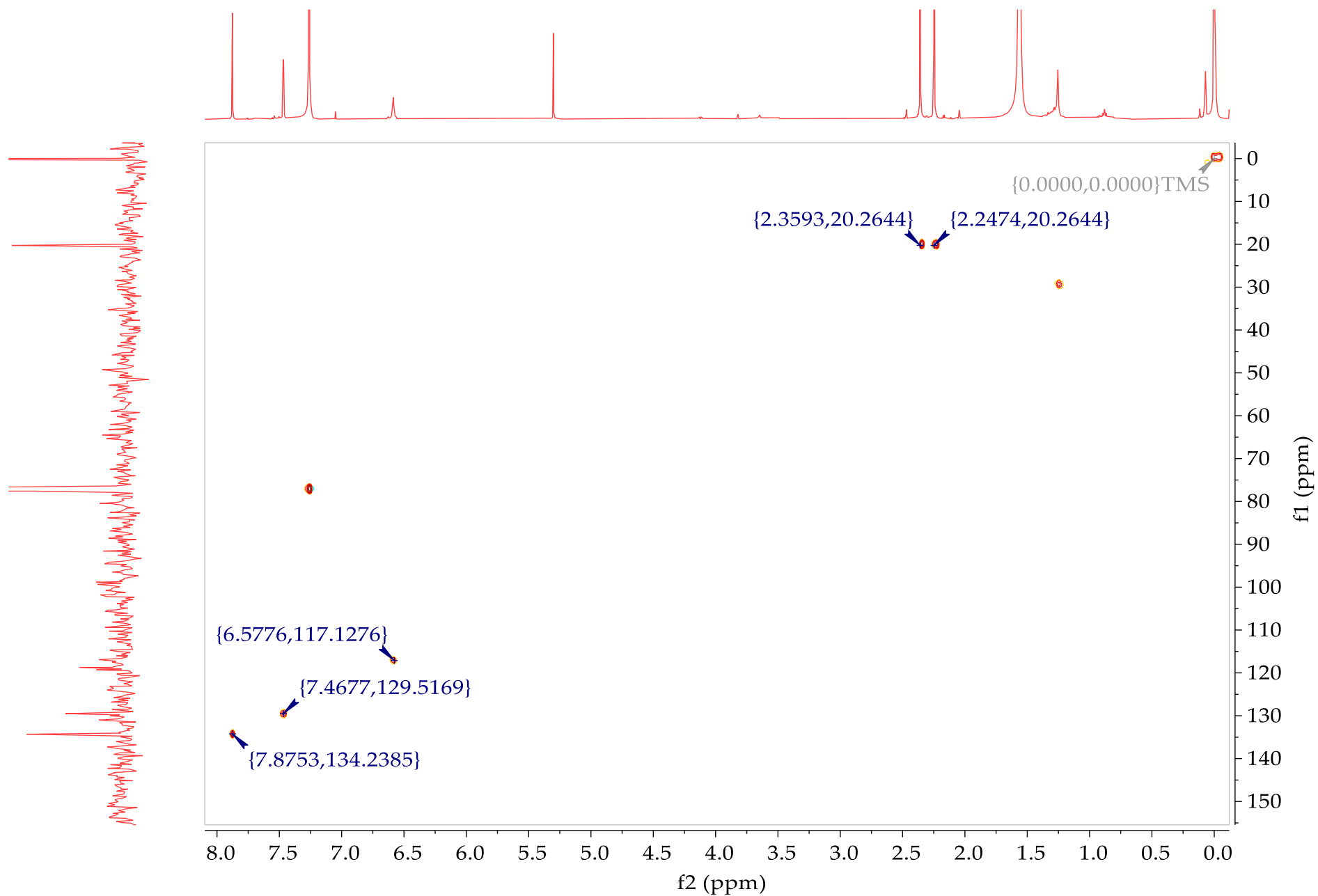
{6.5776,117.1276}

{7.4677,129.5169}

{7.8753,134.2385}
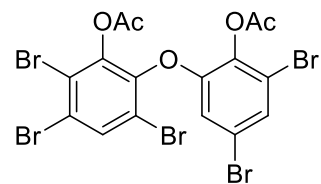
Figure S63. ^{1}H-^{13}C HMBC spectrum of **13** (CDCl$_3$, 500 MHz)
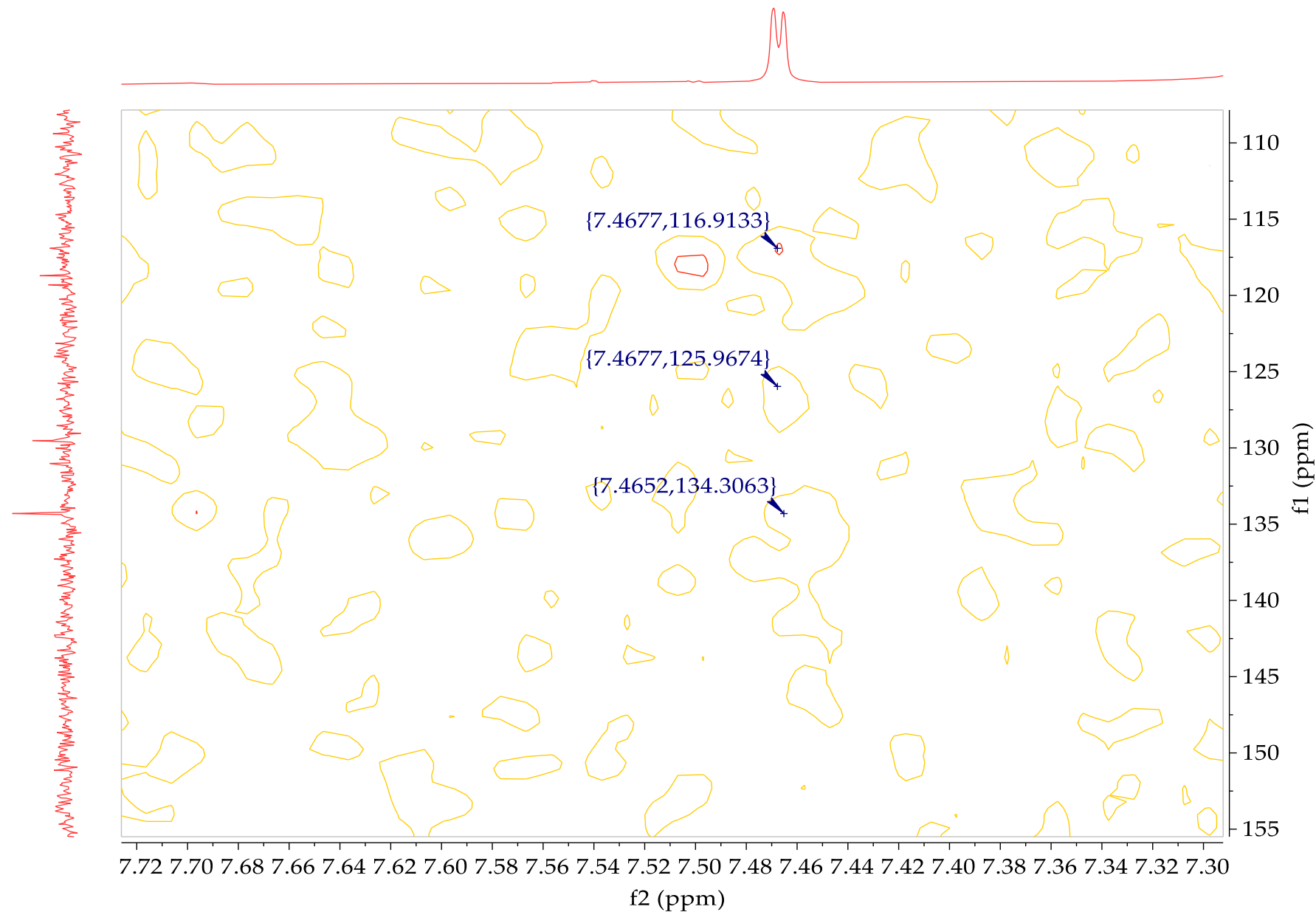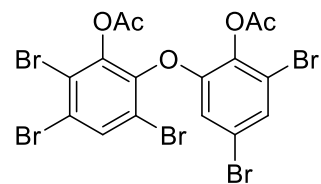
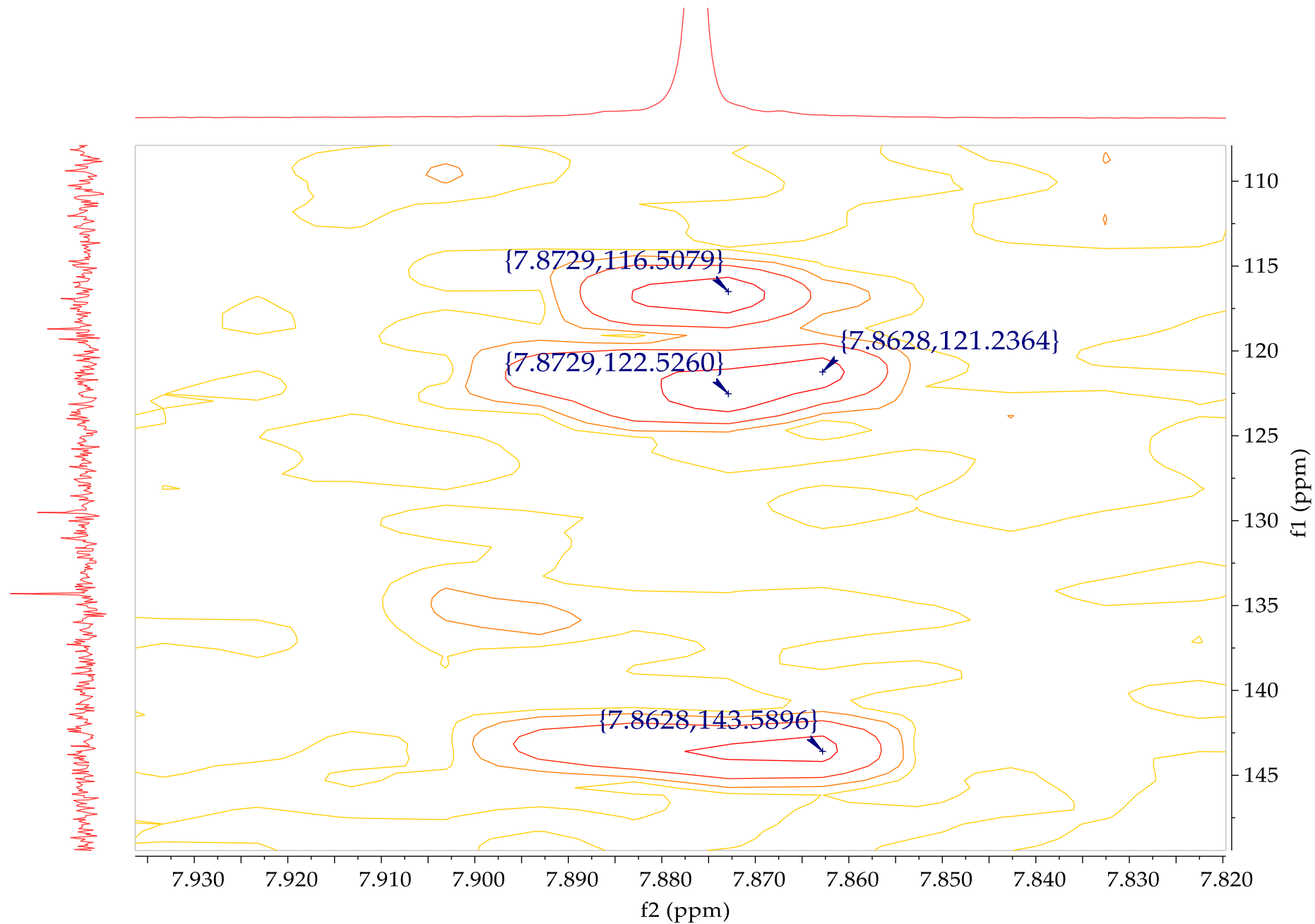Figure S64. ¹H-¹³C HMBC spectrum of **13** (CDCl₃, 500 MHz)

Figure S65. HRESIMS of **13**

Table S37. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **13**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 861
Number of electrons: 320
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step       Energy          Max Grad.        Max Dist.
          1    -13862.043081        0.045313         0.117283
          2    -13862.058089        0.010116         0.074929
          3    -13862.059689        0.005803         0.033053
          4    -13862.059993        0.001959         0.034129
          5    -13862.060035        0.001562         0.008661
          6    -13862.060046        0.000761         0.014733
          7    -13862.060050        0.000256         0.008008
```

Figure S66. HOMO-LUMO of **13**

13

HOMO 13
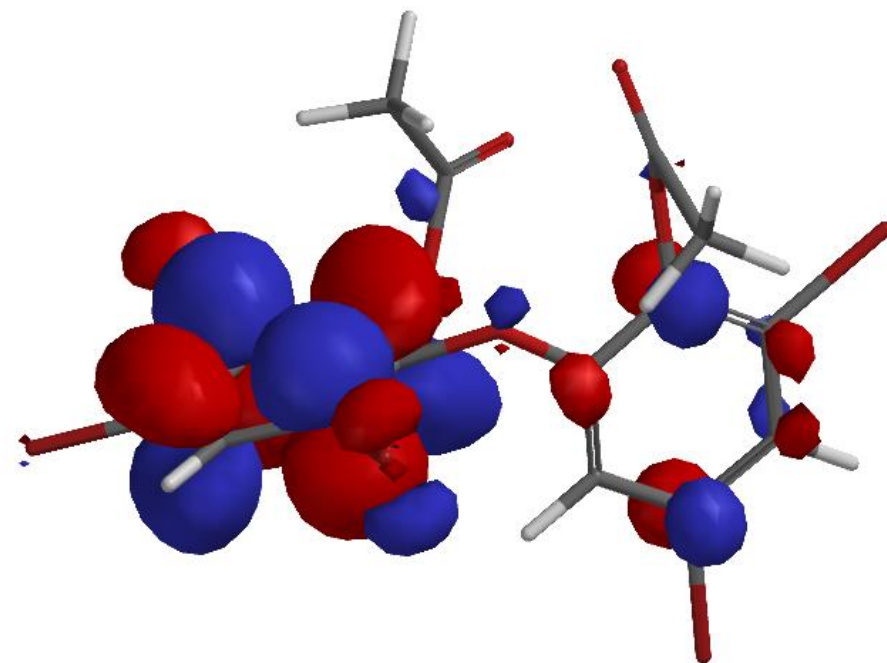
LUMO 13

Figure S67. Calculated ¹³C NMR Chemical Shift of **13**

Figure S68. ^{1}H NMR spectrum of **14** (as a mixture with compound 2) (CD$_3$OD, 500 MHz)
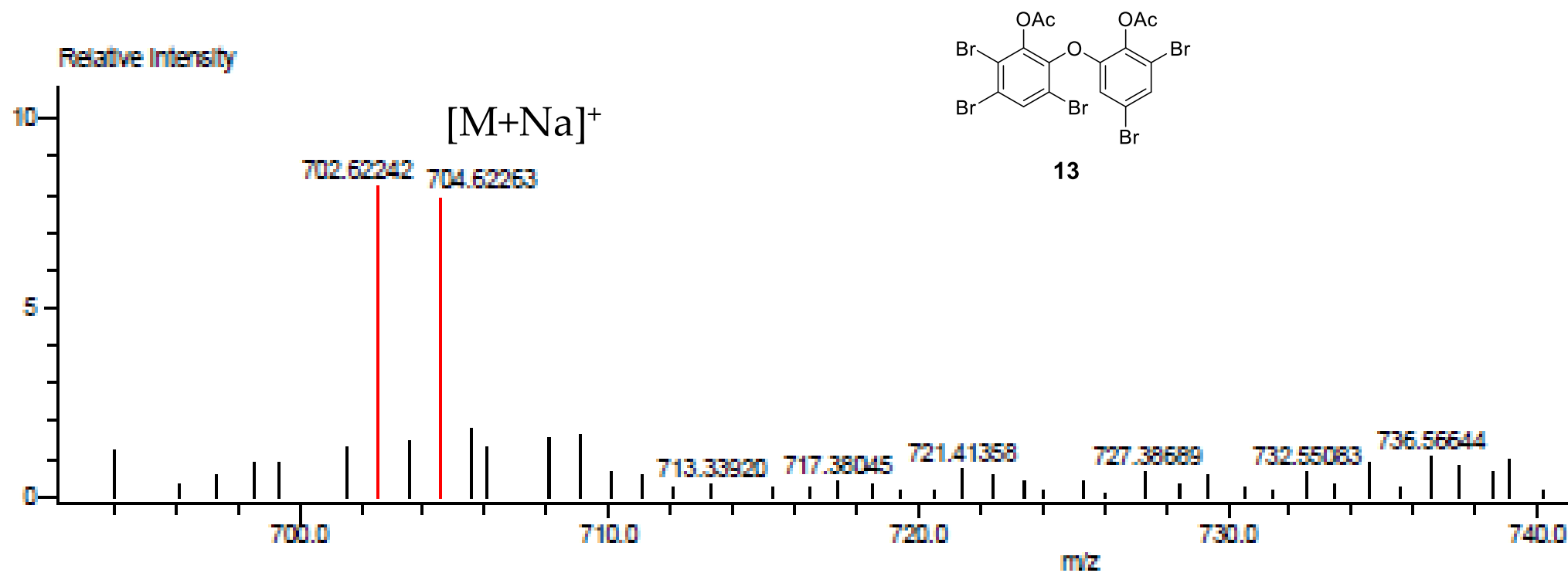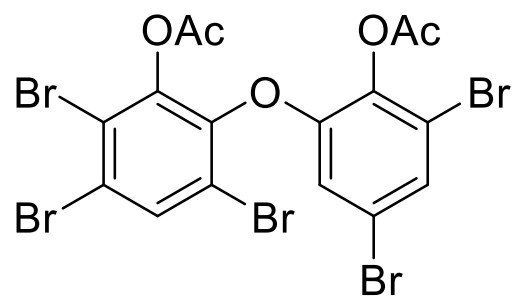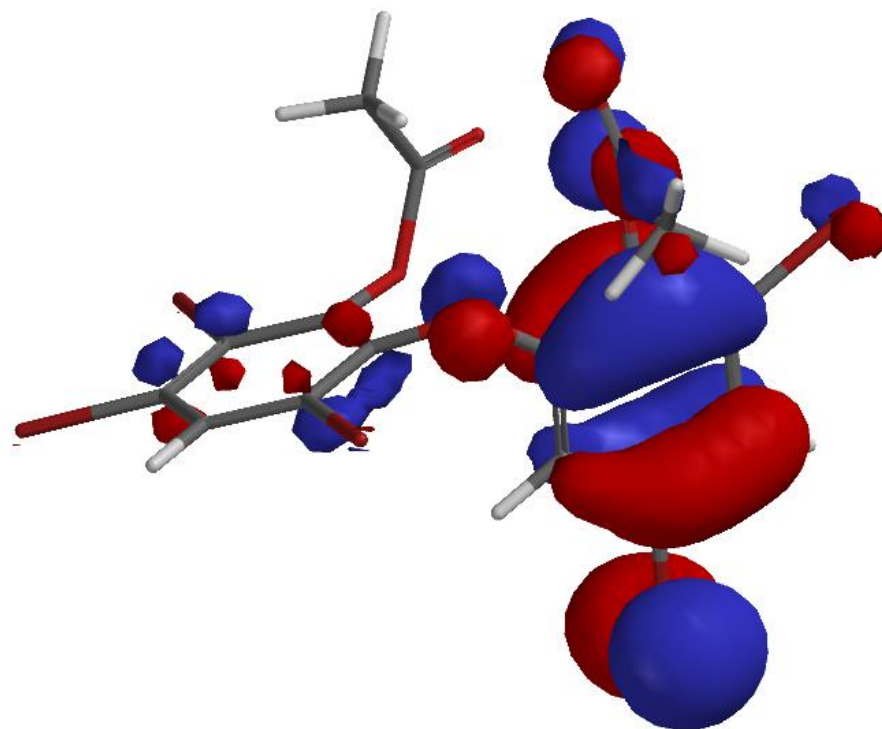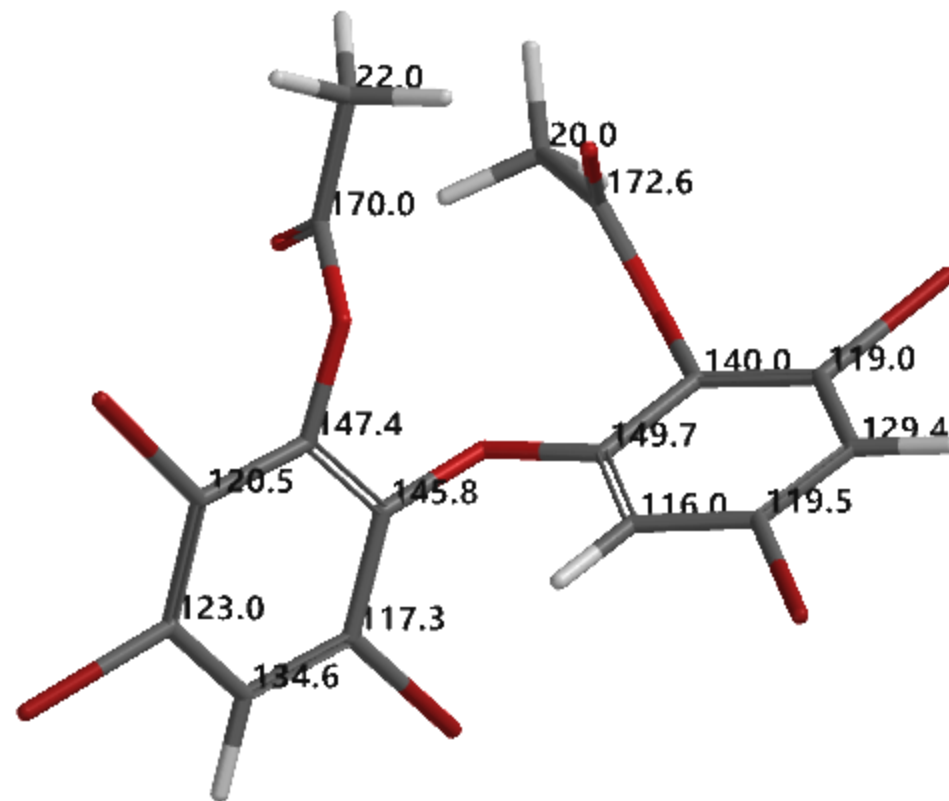
Table S38. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **14**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 675
Number of electrons: 276
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step        Energy          Max Grad.       Max Dist.
         1      -13556.764367       0.026802        0.092144
         2      -13556.769213       0.008273        0.054314
         3      -13556.769651       0.001336        0.001260
         4      -13556.769660       0.001153        0.010465
         5      -13556.769685       0.000329        0.002076
         6      -13556.769686       0.000126        0.000620
```

Figure S69. HOMO-LUMO of **14**

14

HOMO 14

LUMO 14

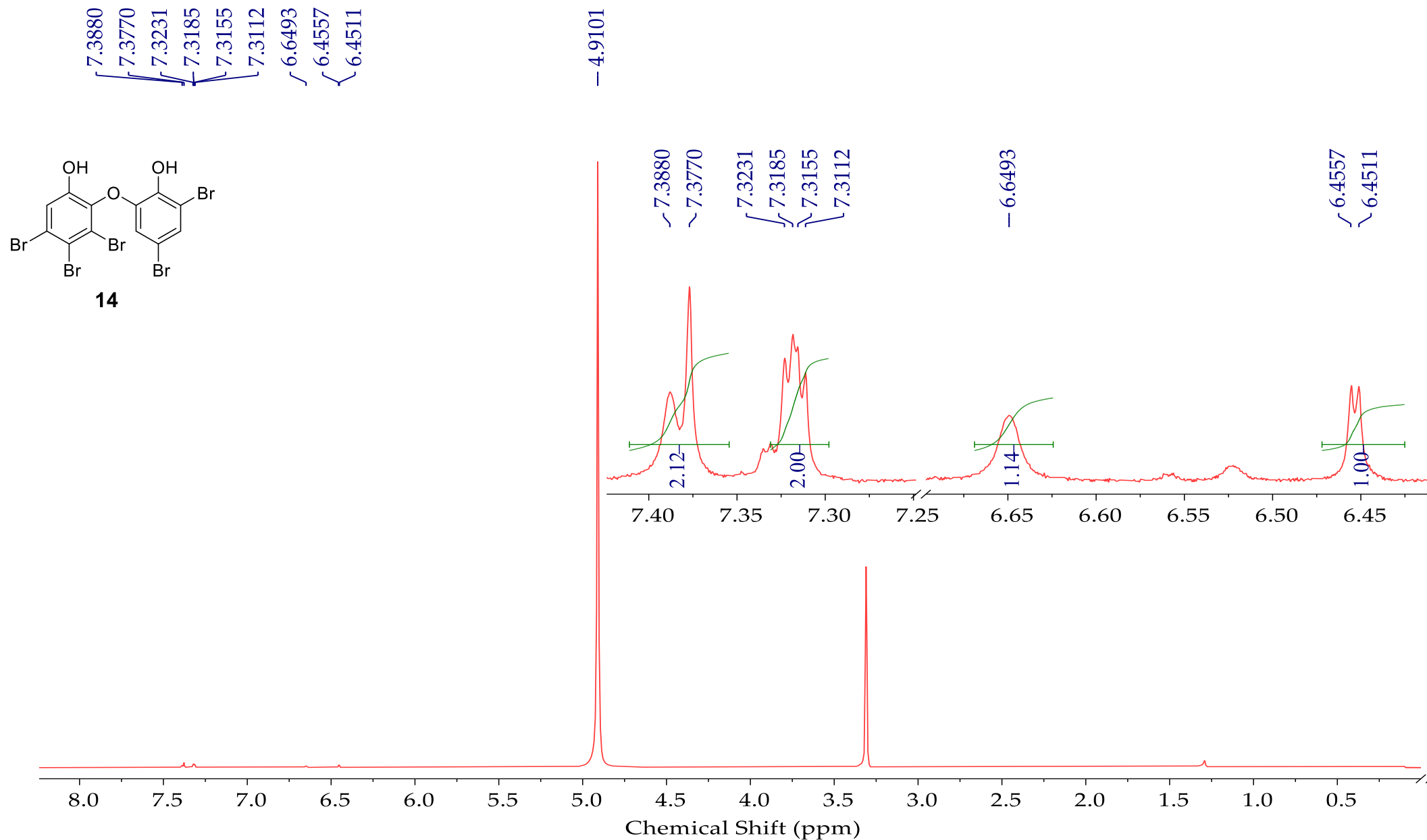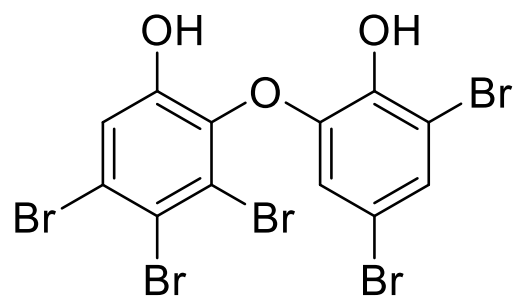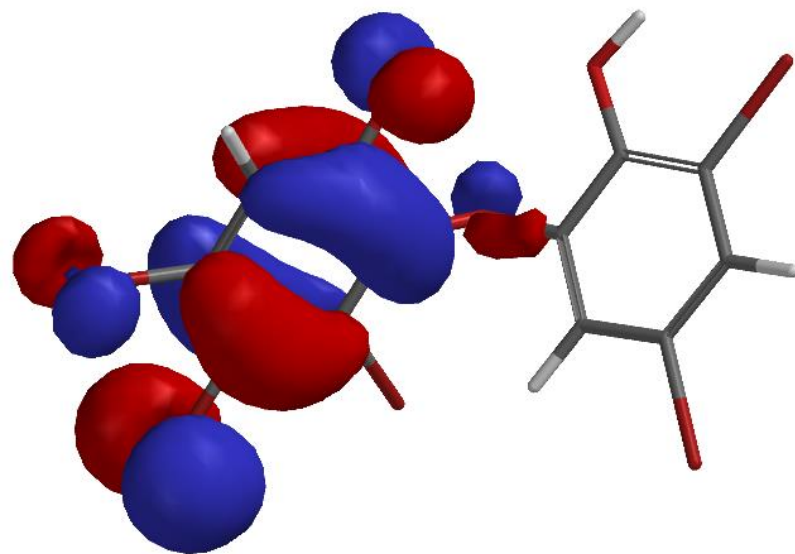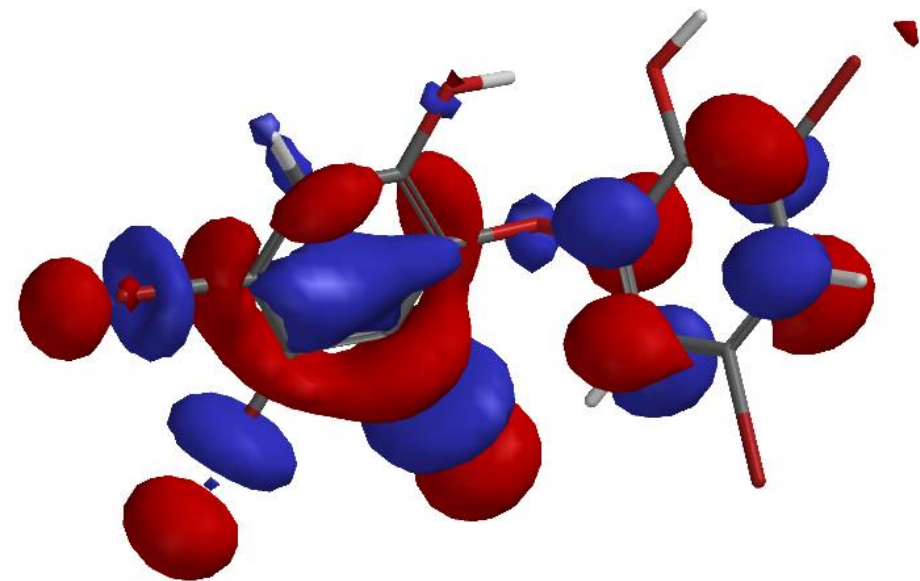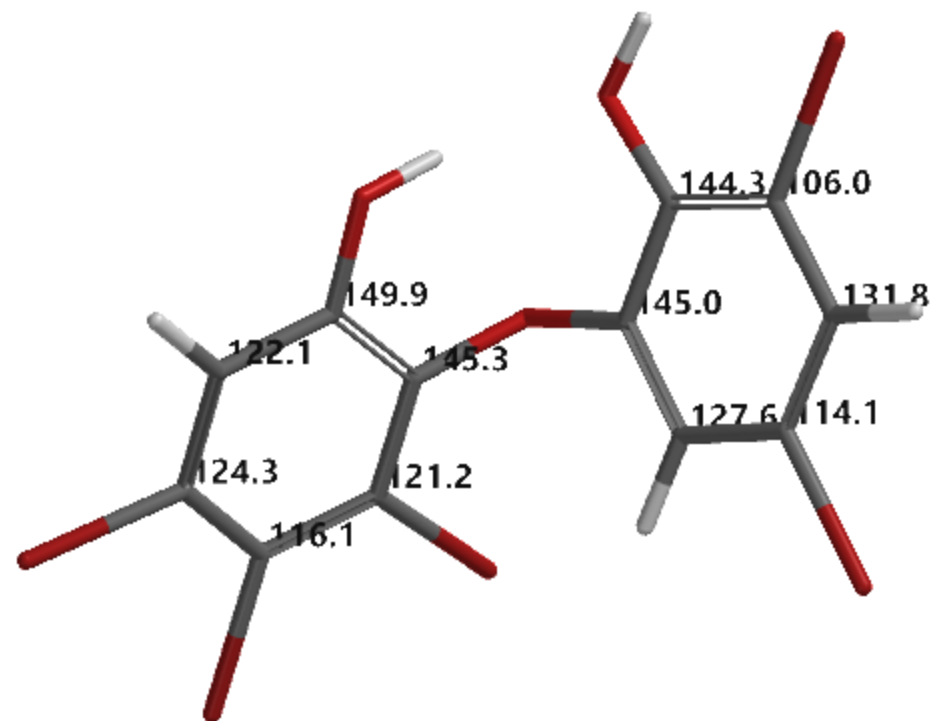# Figure S70. Calculated ^{13}C NMR Chemical Shift of **14**

Table S39. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **15**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 675
Number of electrons: 276
Parallel Job: 16 threads


SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
        Step      Energy           Max Grad.        Max Dist.
          1    -13556.762016       0.021476         0.076590
          2    -13556.766688       0.007328         0.035406
          3    -13556.767190       0.001804         0.014344
          4    -13556.767172       0.001841         0.123542
          5    -13556.767366       0.001495         0.052741
          6    -13556.767419       0.001206         0.007993
          7    -13556.767443       0.000188         0.002668
          8    -13556.767443       0.000053         0.001092
```

Figure S71. HOMO-LUMO of **15**
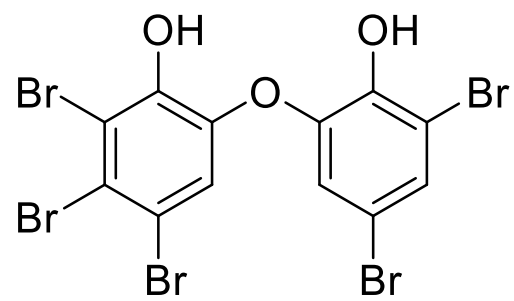
15
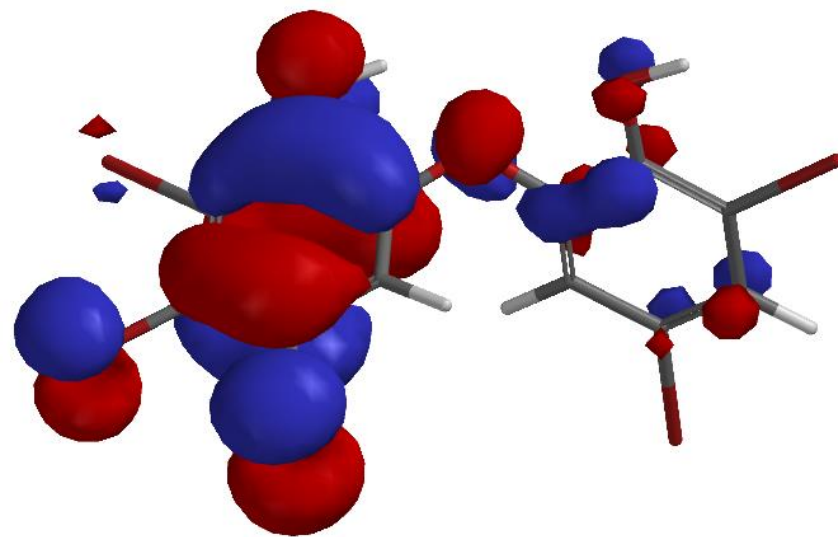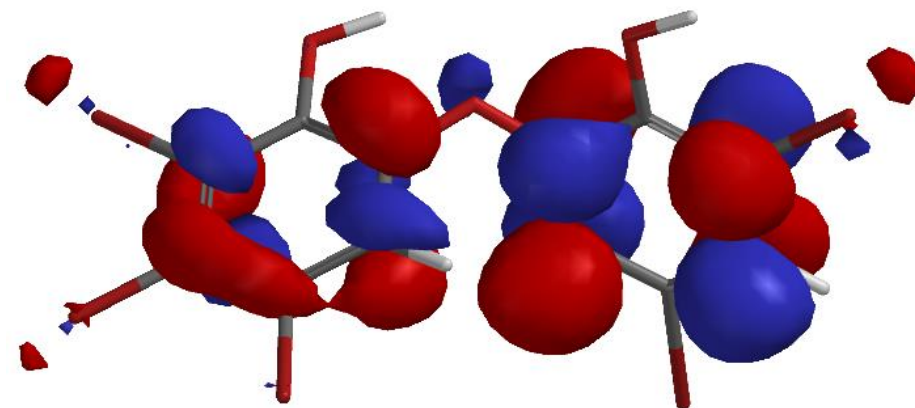
HOMO 15   **LUMO 15**
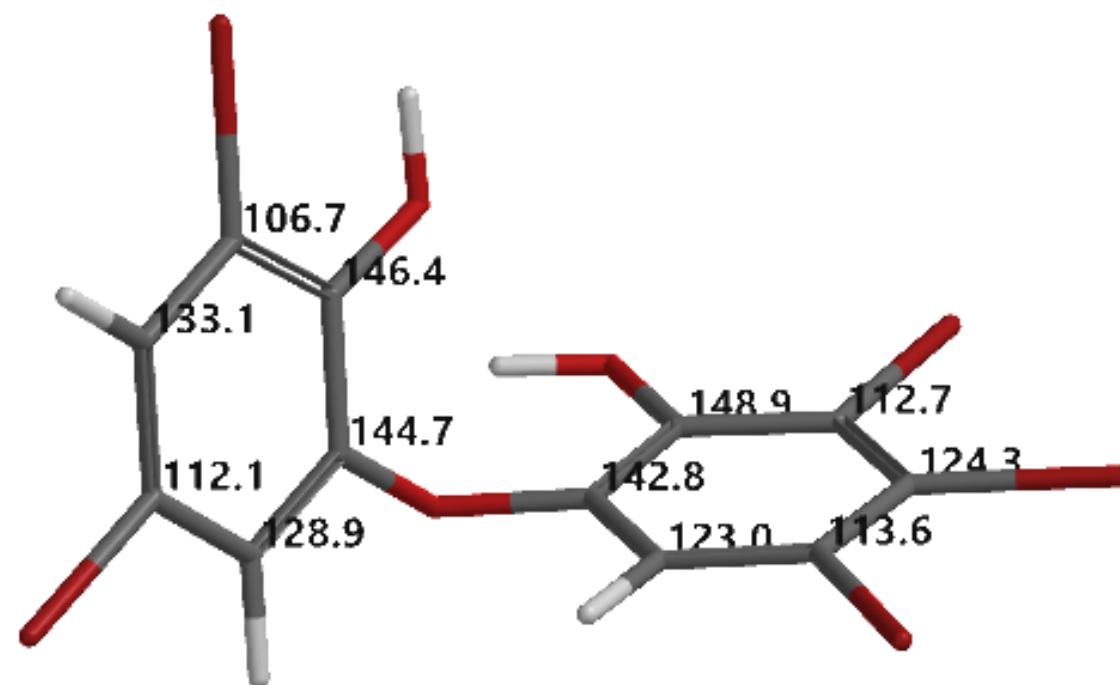
Figure S73. ^{1}H NMR spectrum of **16** (Me$_2$CO-d_6, 500 MHz)

7.3950
7.3904
7.3839
7.3795
7.2575
7.2529
6.6556
6.6513

2.8445
2.0590
2.0547
2.0500
2.0500 (CD3)2CO
2.0455
2.0412
1.3428

16

8.0   7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   0.5   0.0
f1 (ppm)
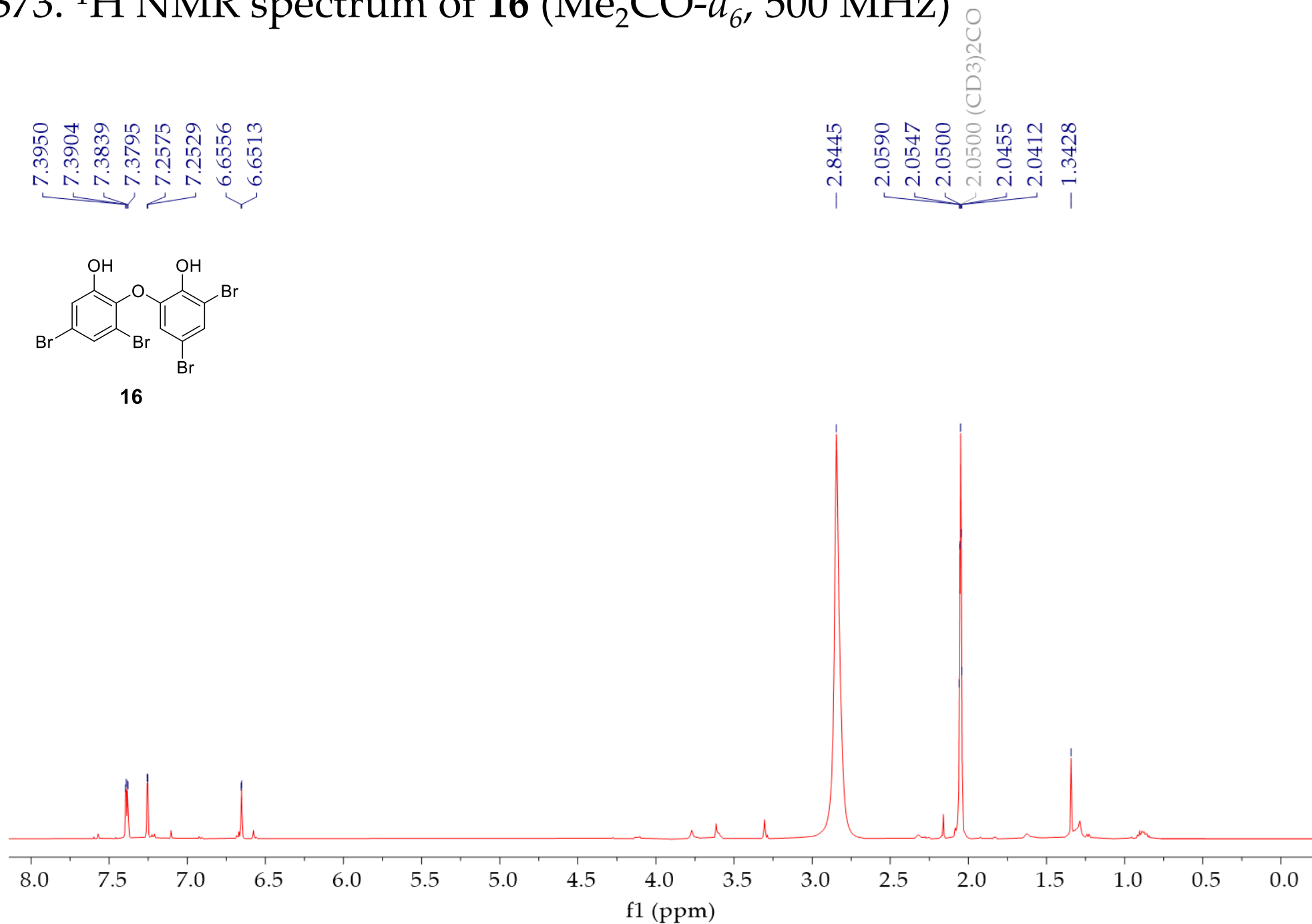
Figure S74. ^{1}H NMR spectrum of **16** (Me$_2$CO-d_6, 500 MHz)
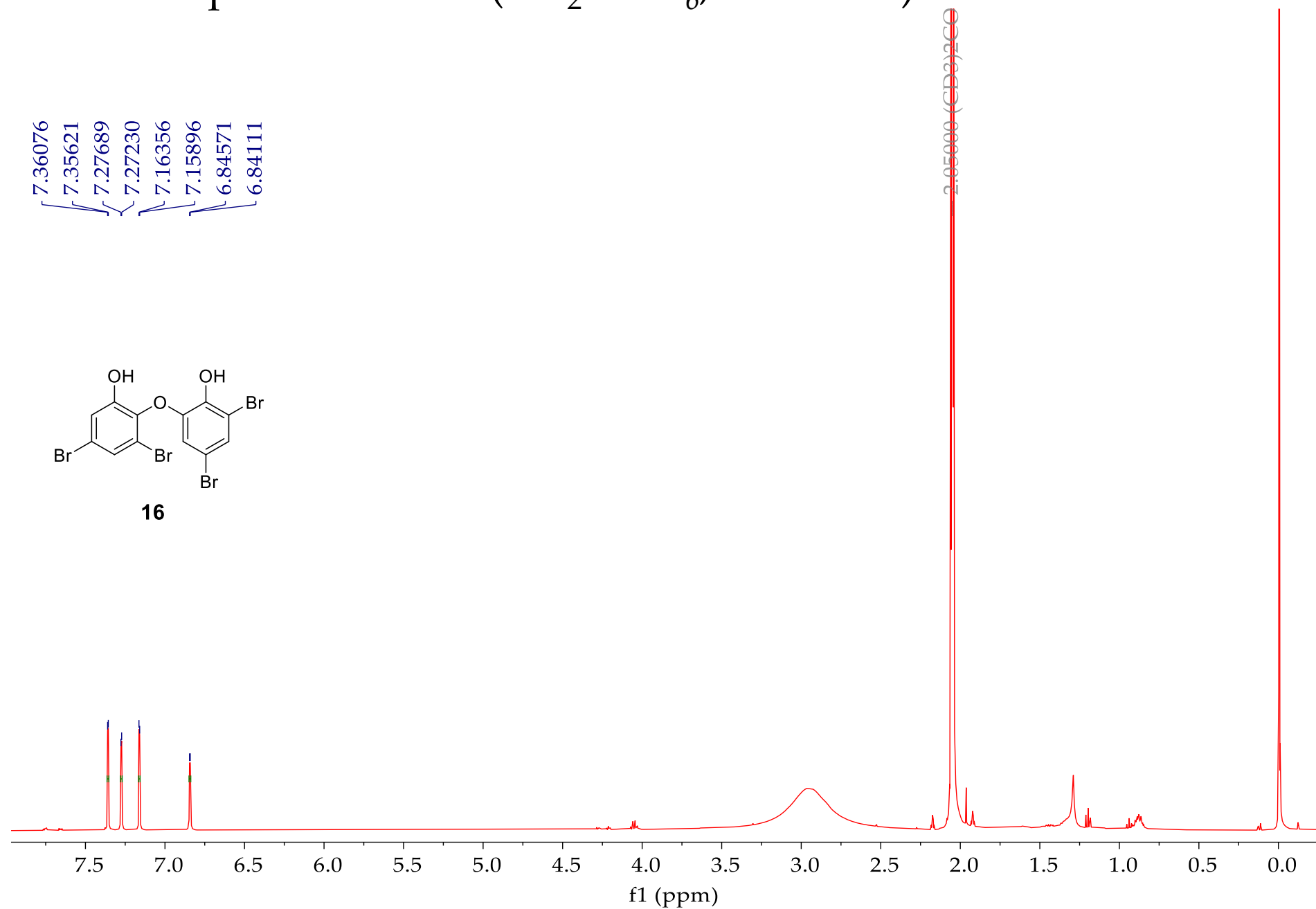
Figure S75. ^{1}H-^{1}H COSY spectrum of **16** (Me$_2$CO-d_6, 500 MHz)

{0.00000,0.00000}TMS

{6.84715,7.36240}

{7.16540,7.27946}

16
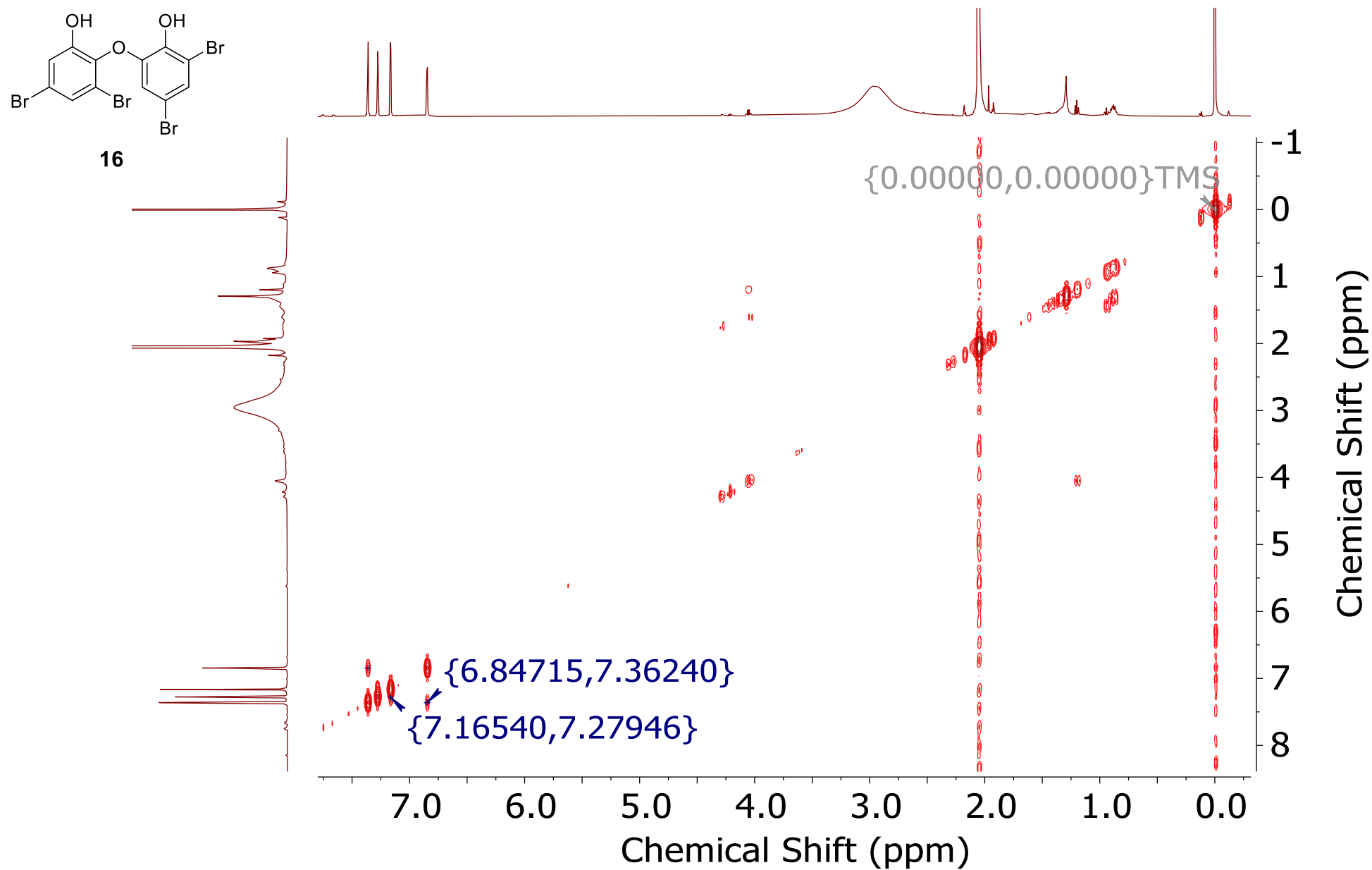
Figure S76. ^1H-^{13}C HSQC spectrum of **16** (Me$_2$CO-d_6, 500 MHz)
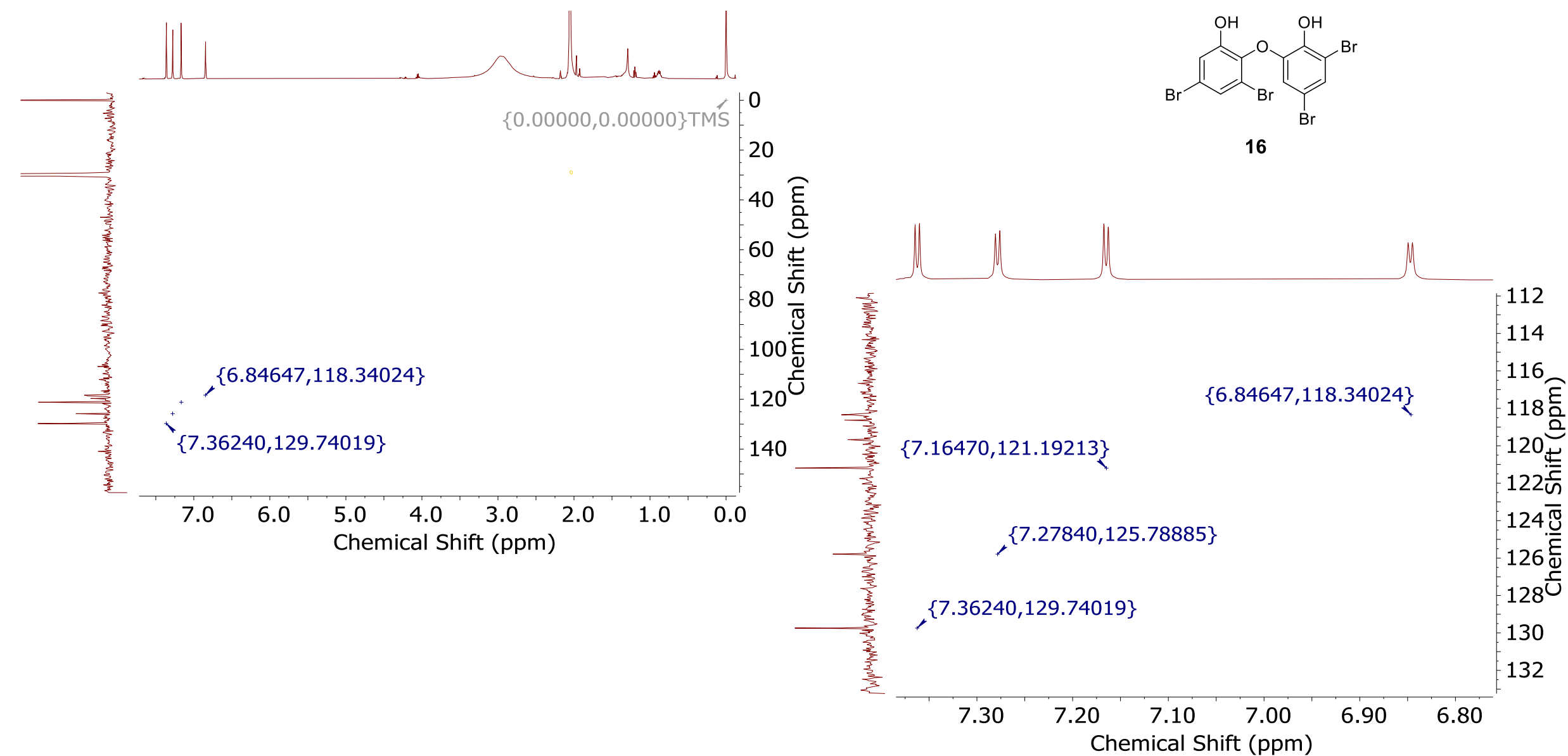
Figure S77. ^{1}H-^{13}C HMBC spectrum of **16** (Me$_2$CO-d_6, 500 MHz)

{0.0000,-0.0000}TMS

{7.3618,111.3426}
{6.8476,129.7404}
{6.8455,145.6917}
{7.1644,153.2181}

16

{7.3541,108.0675}
{6.8455,108.0675}
{7.3618,111.3426}
{7.3557,117.3811}
{7.1640,118.2408}
{7.1641,125.7890}
{6.8476,129.7404}
{7.2759,139.7343}
{7.1640,139.7343}
{6.8455,145.6917}
{7.3618,145.3928}
{7.1644,153.2181}

Figure S78. HREIMS of 16


```
ターミナル1

SAMPLE : PBDE-192C-3
SAMPLE NO.: 772     SCAN NO.: 15
                                                        PAGE   1
NO. PKNO.     P.C. M/Z(OBS.) ER(MU)   US ELEMENTS

  1   205     8.0  504.9696
  2   206    17.6  513.6962 - 8.7    8.0  C12 H6 Br4 O3
  3   207     2.8  514.7133
  4   208    69.4  515.7007 - 2.2    8.0  C12 H6 Br3 Br*1 O3
  5   209    10.5  516.7071   0.8    8.0  C11 C*1 H6 Br3 Br*1 O3
  6   210     4.9  516.9696
  7   211   100.0  517.6907 -10.1    8.0  C12 H6 Br2 Br*2 O3
  8   212     1.1  517.9964
  9   213    14.4  518.6998 - 4.4    8.0  C11 C*1 H6 Br2 Br*2 O3
 10   214    59.7  519.6914 - 7.4    8.0  C12 H6 Br1 Br*3 O3
 11   215     8.2  520.7143
 12   216    22.9  521.6952 - 1.6    8.0  C12 H6 Br*4 O3
 13   217     1.8  522.7074
 14   218     2.2  523.9968
 15   219     1.8  528.9992
 16   220     7.5  530.9664
 17   221     1.3  537.0021
 18   222     1.8  541.0110
 19   223     1.0  542.6993
```
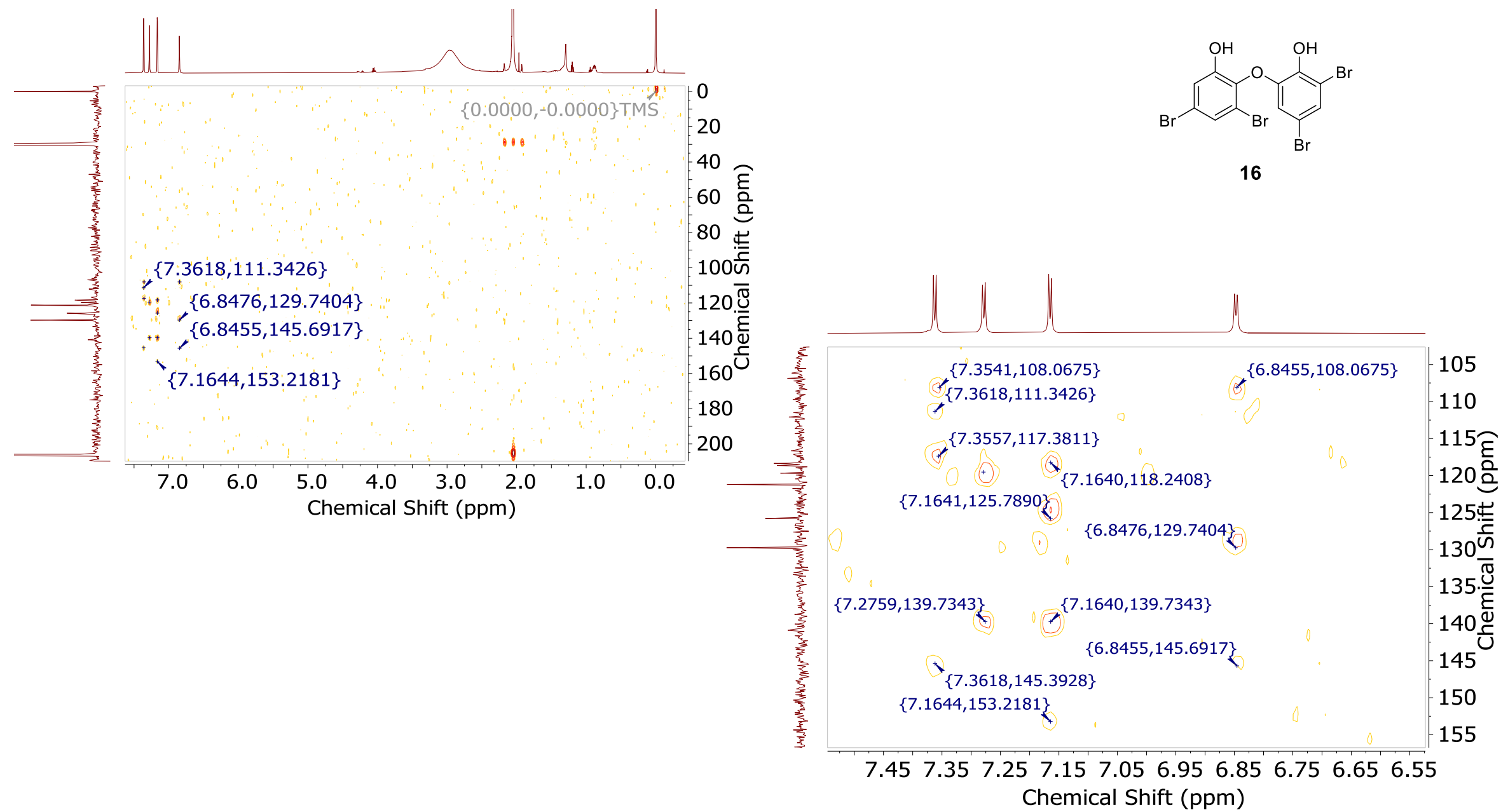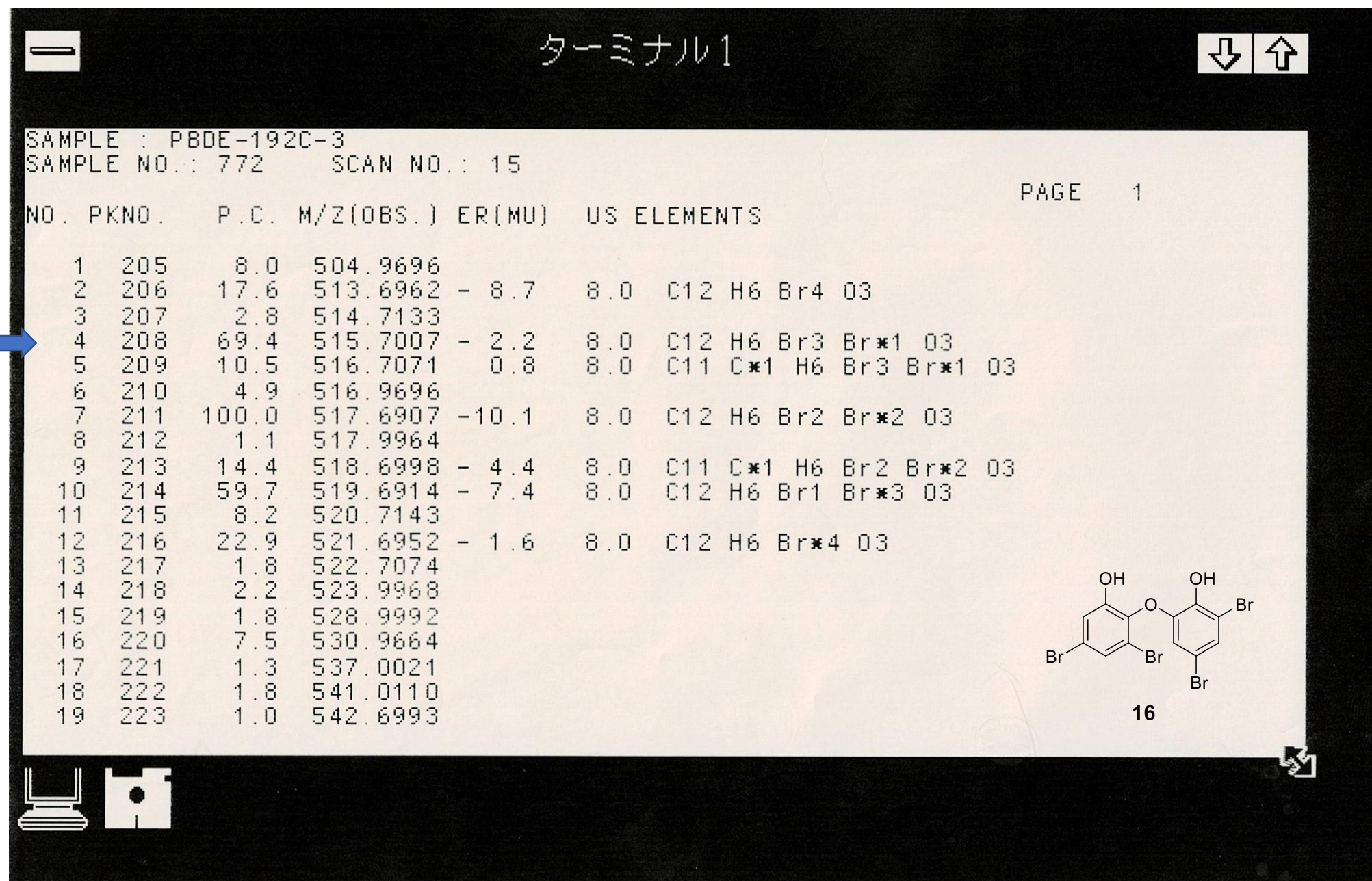
Table S40. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **16**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 633
Number of electrons: 242
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step       Energy          Max Grad.       Max Dist.
           1    -10983.204306       0.019514        0.105574
           2    -10983.208599       0.006637        0.048535
           3    -10983.208980       0.001289        0.001567
           4    -10983.208992       0.001103        0.009585
           5    -10983.209019       0.000365        0.001983
           6    -10983.209019       0.000137        0.000376
```
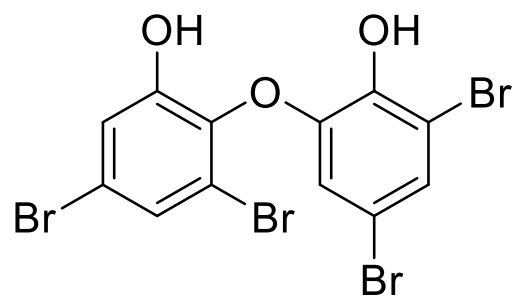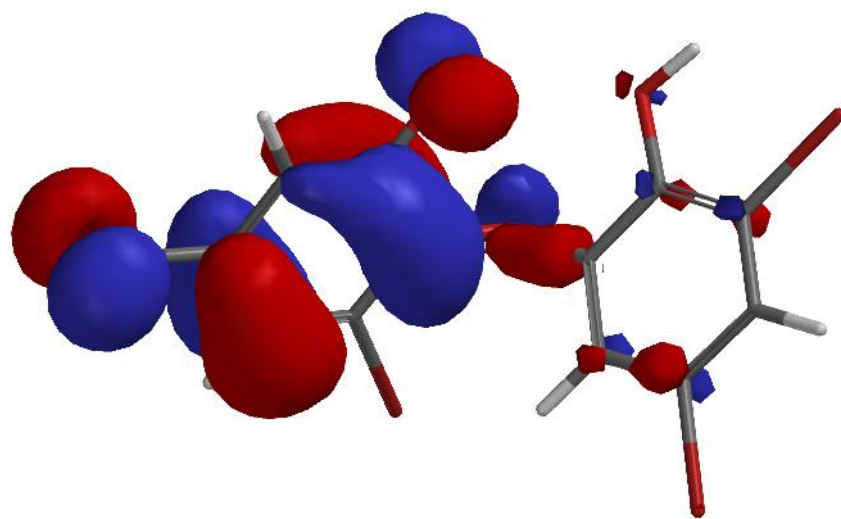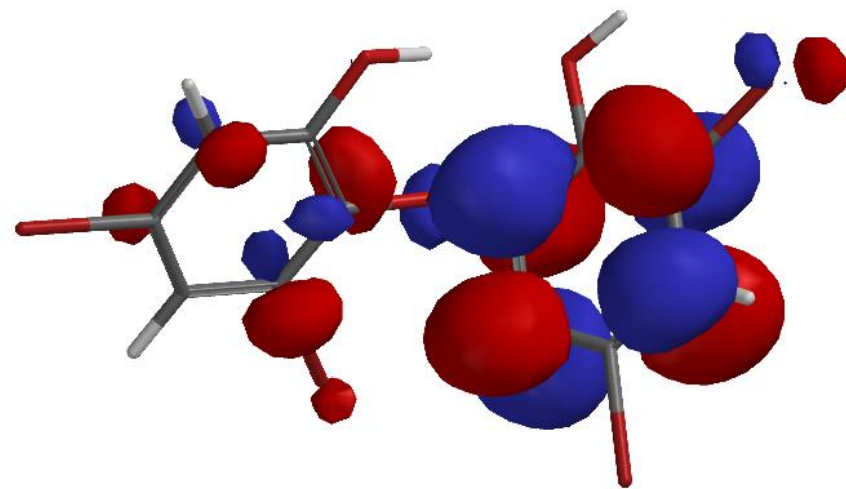
Figure S79. HOMO-LUMO of 16

16

HOMO 16

LUMO 16
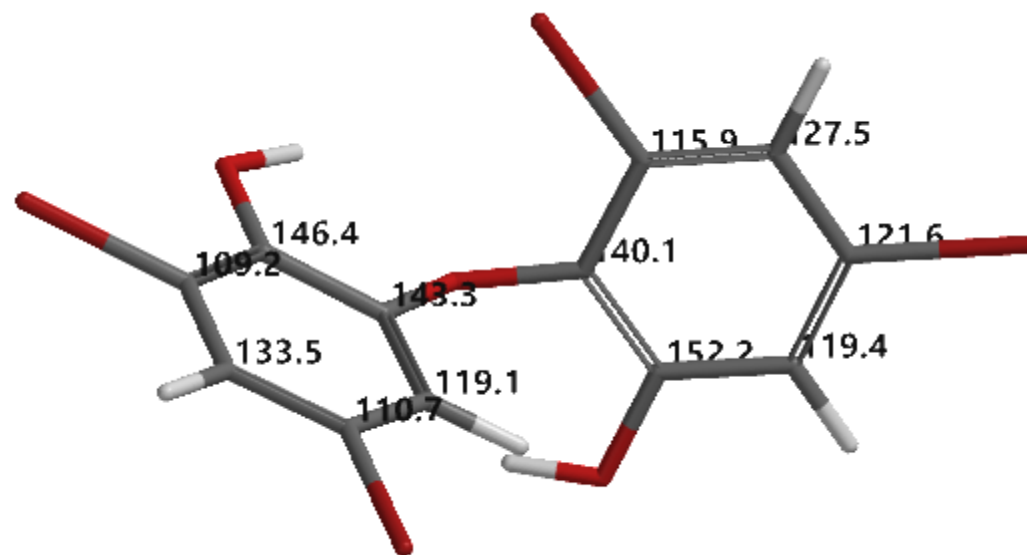
Figure S80. Calculated ¹³C NMR Chemical Shift of 16

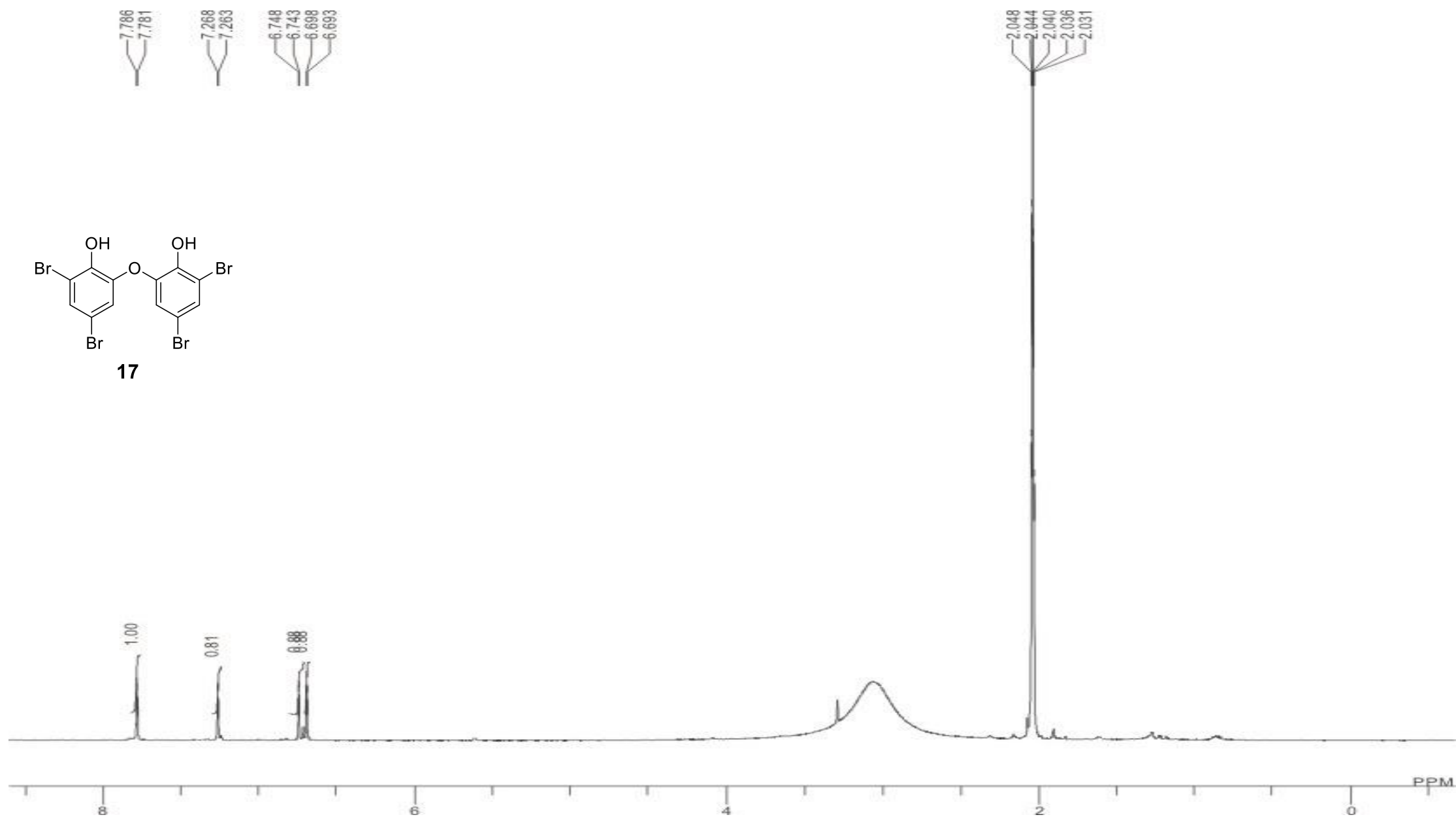# Figure S81. ^{1}H NMR spectrum of **17** (Me$_2$CO-d_6, 500 MHz)
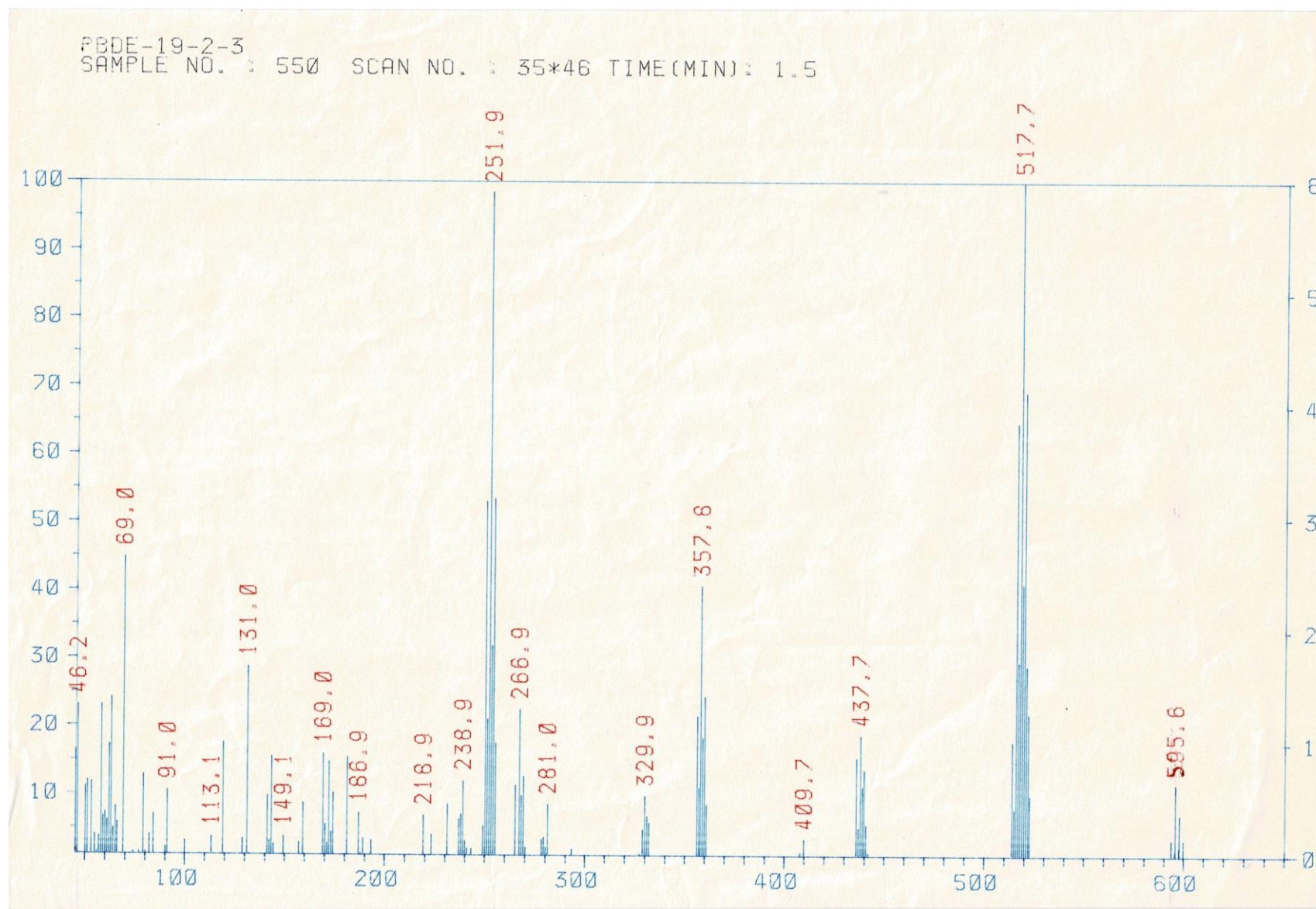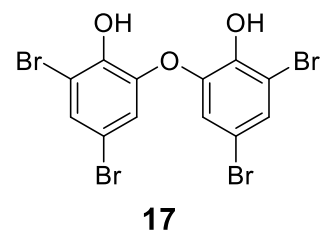
Figure S82. LREIMS of 17

Table S41. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **17**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 633
Number of electrons: 242
Parallel Job: 16 threads


SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
         Step       Energy          Max Grad.        Max Dist.
           1    -10983.201771       0.019121         0.075432
           2    -10983.205709       0.007524         0.038952
           3    -10983.206070       0.001657         0.012114
           4    -10983.206114       0.001665         0.159896
           5    -10983.206307       0.002395         0.019355
           6    -10983.206382       0.001516         0.019983
           7    -10983.206418       0.000385         0.010043
           8    -10983.206423       0.000390         0.030467
```
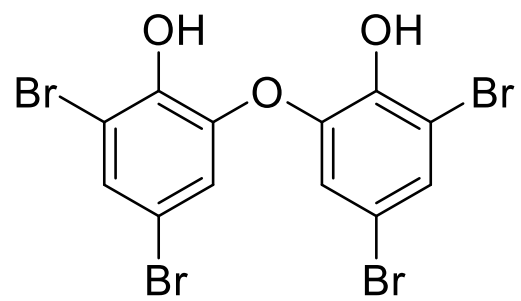
Figure S83. HOMO-LUMO of **17**

17
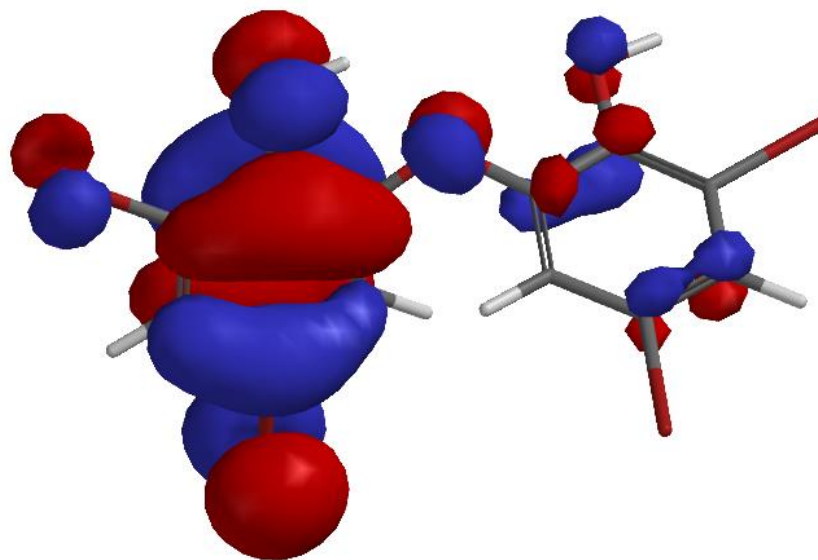
HOMO 17
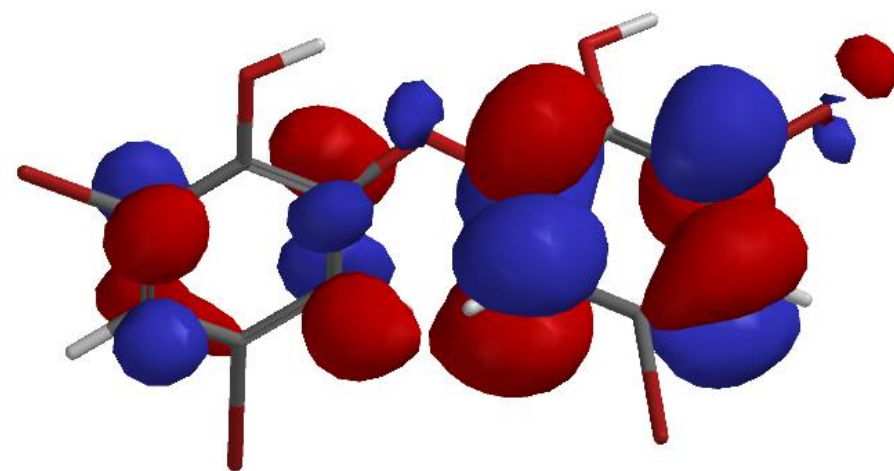
LUMO 17

Figure S84. Calculated ^{13}C NMR Chemical Shift of **17**
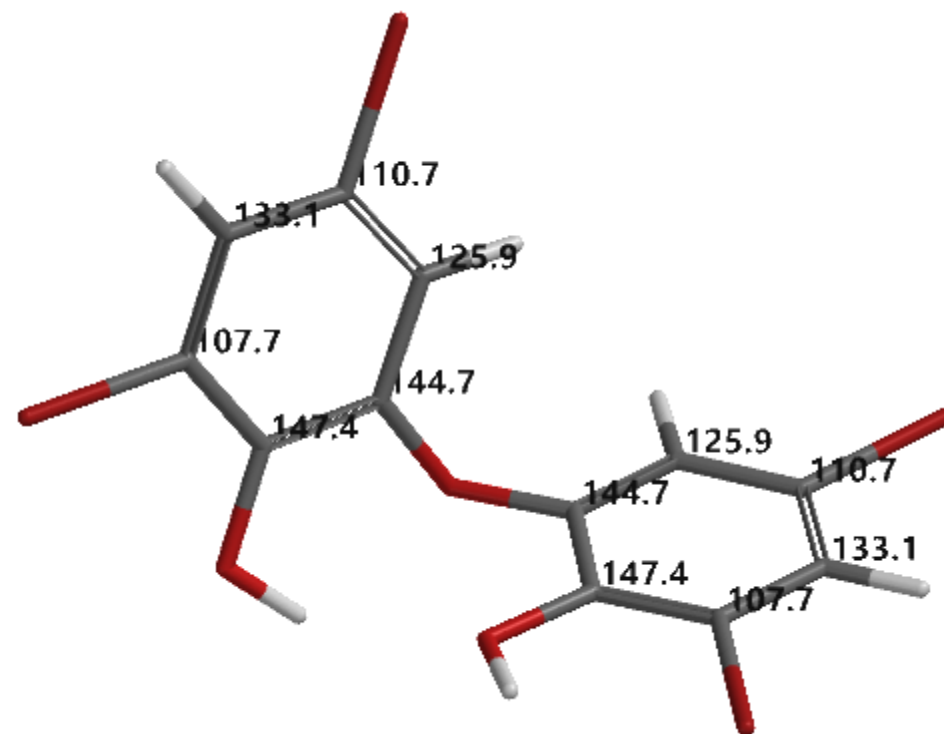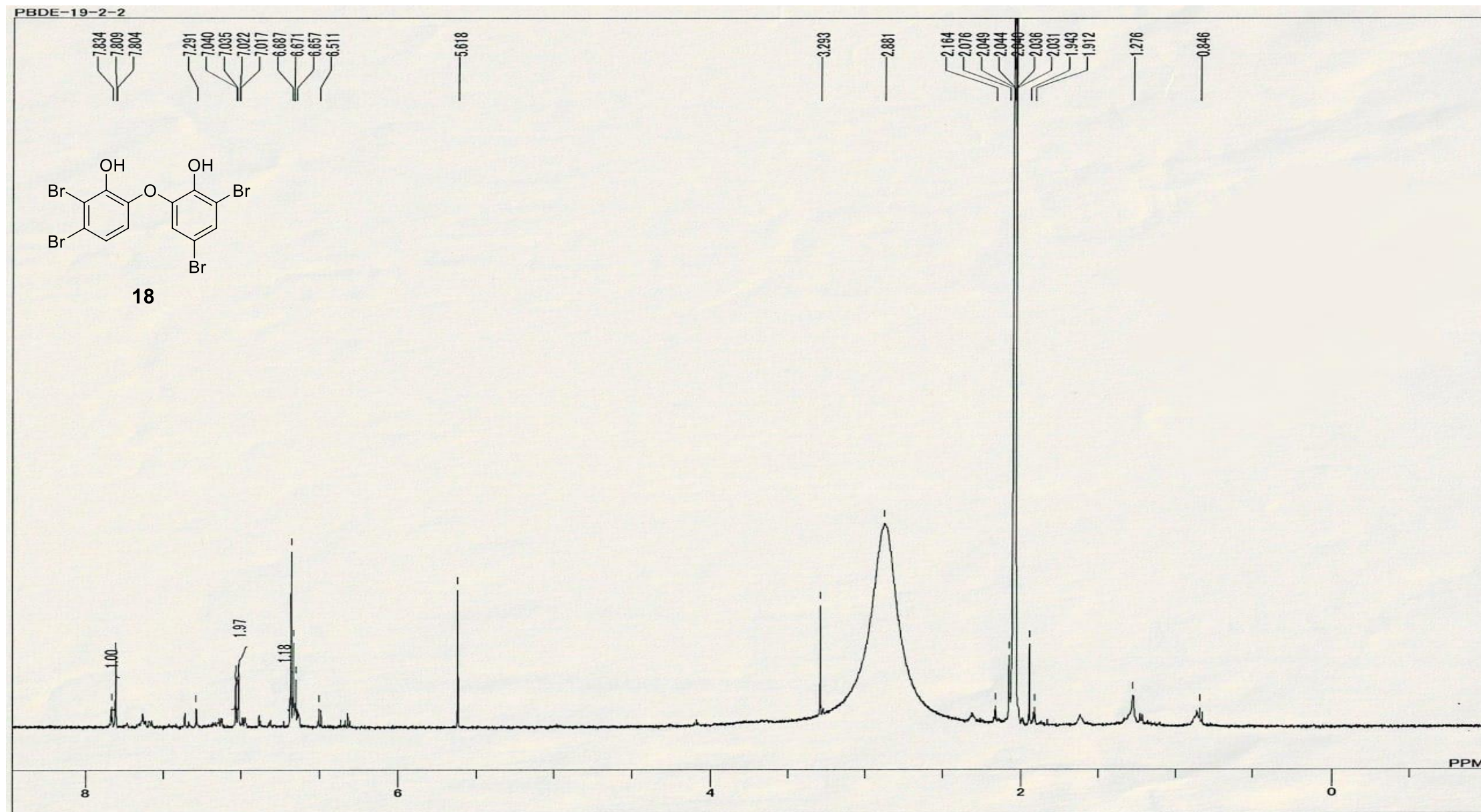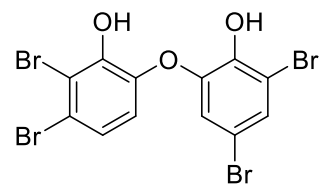
Figure S86. LREIMS of **18**

Table S42. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 18

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 633
Number of electrons: 242
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step      Energy         Max Grad.      Max Dist.
          1    -10983.197652      0.019940       0.073170
          2    -10983.202008      0.007085       0.029451
          3    -10983.202442      0.001721       0.012466
          4    -10983.202490      0.001711       0.135443
          5    -10983.202707      0.001536       0.016656
          6    -10983.202752      0.000794       0.024183
          7    -10983.202769      0.000340       0.018511
```

Figure S87. HOMO-LUMO of **18**
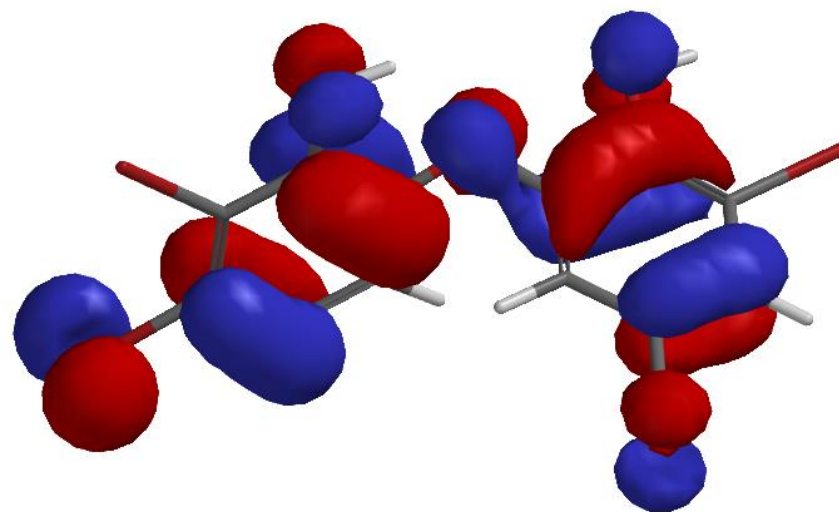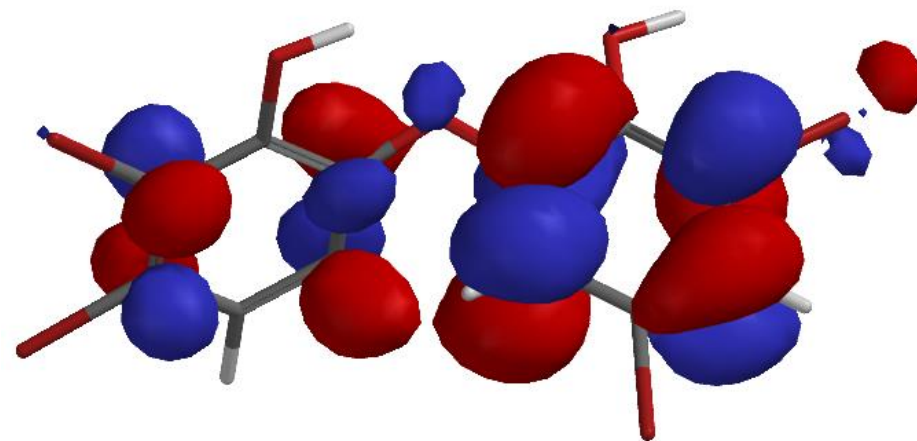
HOMO 18   **LUMO 18**

Figure S88. Calculated ^{13}C NMR Chemical Shift of **18**
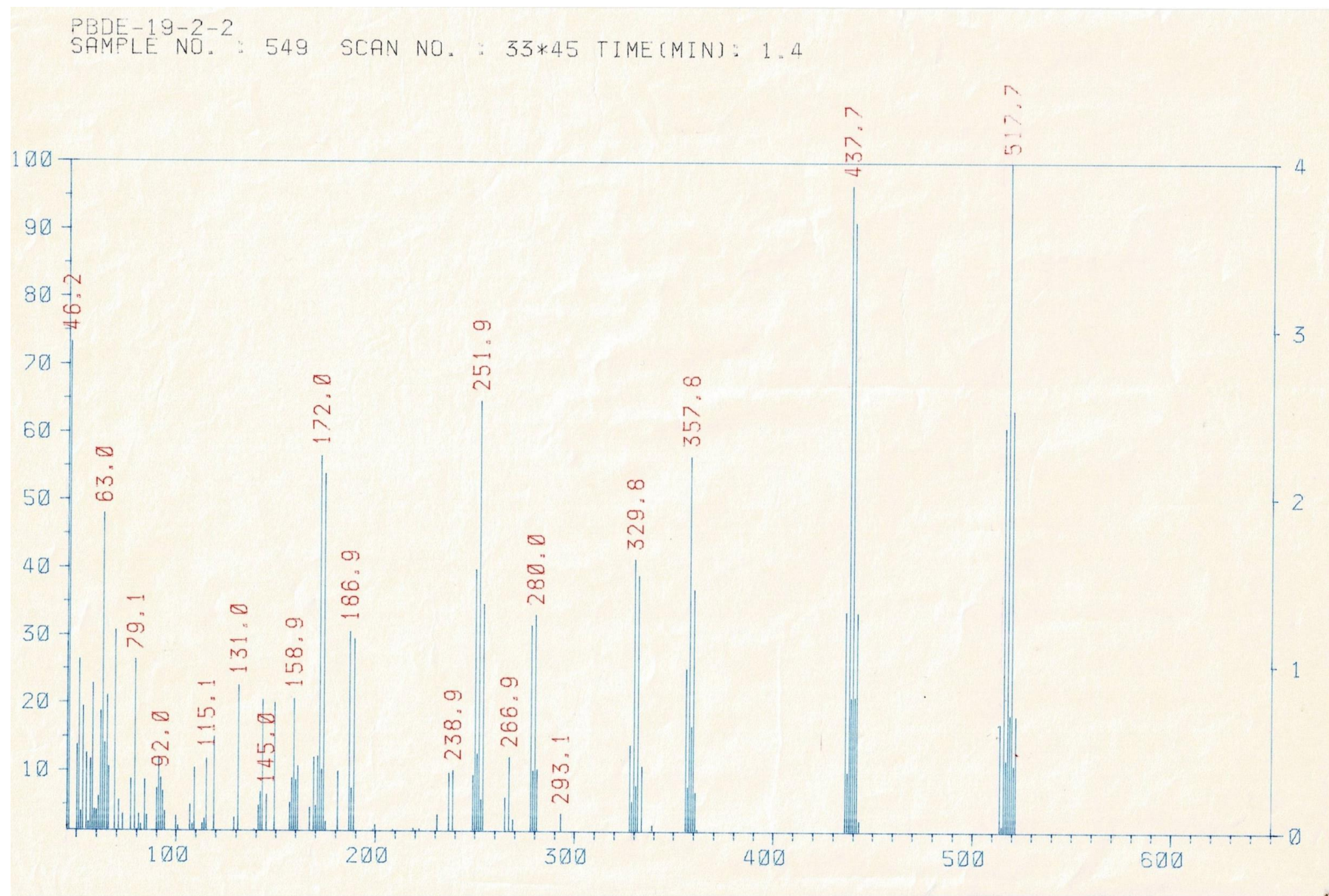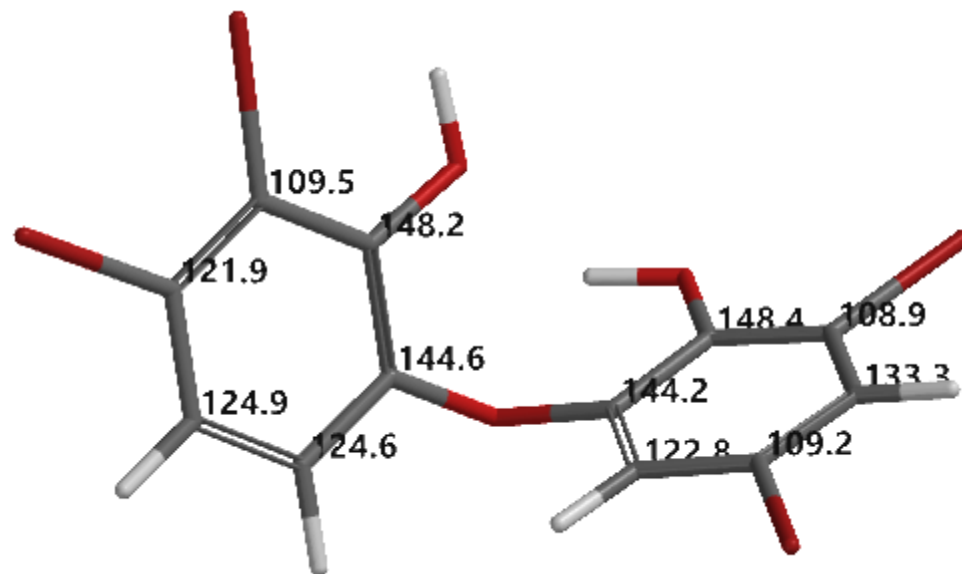
Table S43. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **19**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 633
Number of electrons: 242
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step        Energy          Max Grad.       Max Dist.
          1     -10983.200602       0.016693        0.073750
          2     -10983.204147       0.006753        0.031396
          3     -10983.204508       0.001359        0.003948
          4     -10983.204523       0.001317        0.090499
          5     -10983.204695       0.001149        0.027379
          6     -10983.204725       0.000761        0.027626
          7     -10983.204743       0.000361        0.013578
```
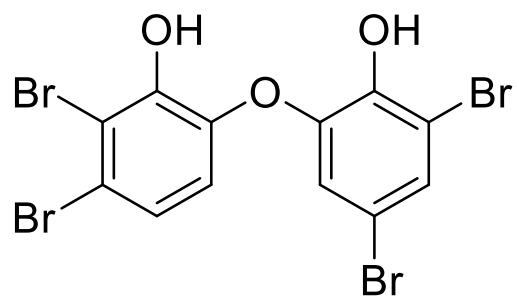
Figure S89. HOMO-LUMO of **19**
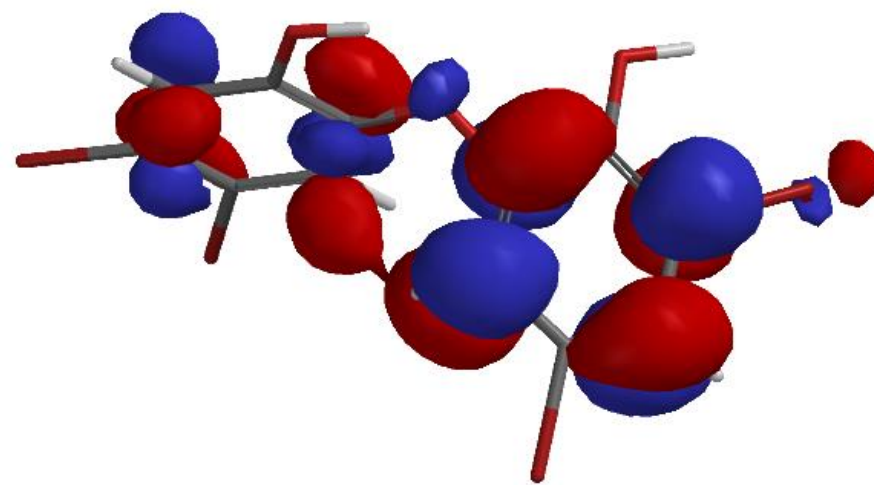
HOMO 19   **LUMO 19**

Figure S90. Calculated ^{13}C NMR Chemical Shift of **19**
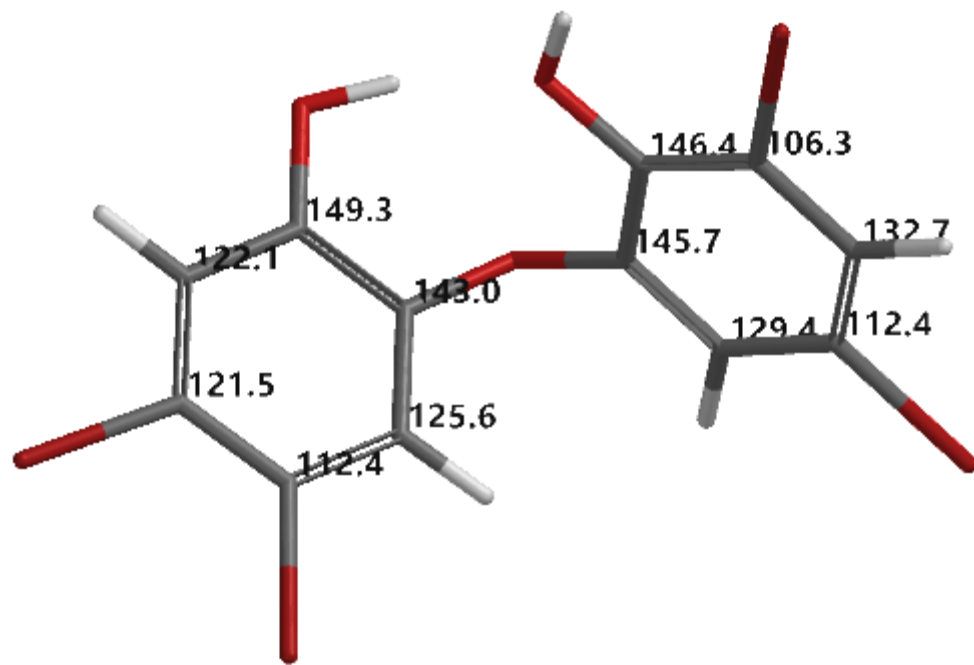
Figure S91. ^{1}H NMR spectrum of **20** (Me$_2$CO-d_6, 500 MHz)

7.3720
7.3675
7.2743
7.2698
7.0724
7.0679
7.0553
7.0505
6.9187
6.9016
6.6027
6.5980

2.0500 (CD3)2CO

f1 (ppm)
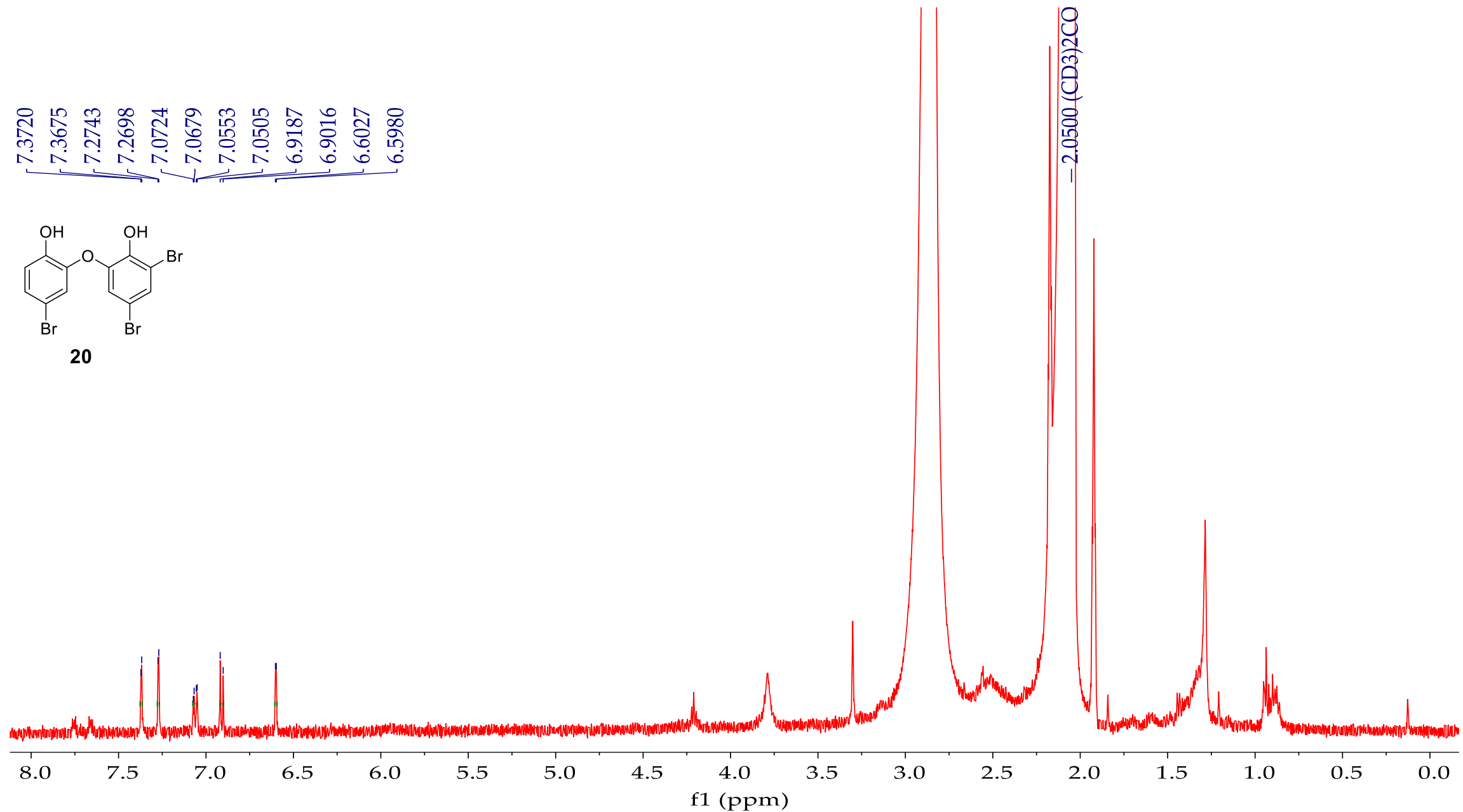
Figure S92. ¹H NMR spectrum of 20 (CD₃OD, 500 MHz)

Figure S93. HRESIMS of **20**

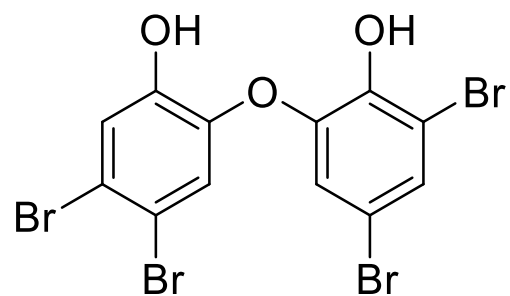C:\Users\HP\Do....3-ESI-pos.7rw\ Injection 1 TOF   50.00-15...terval; CURRENT MS + spectrum 0.73

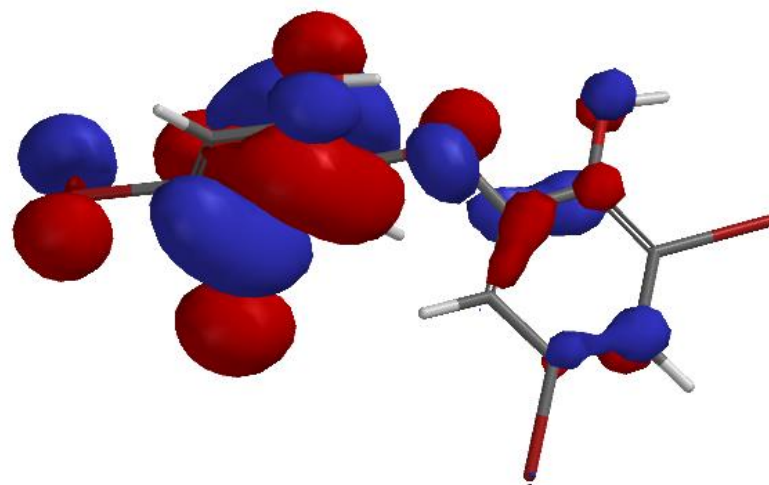# Table S44. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **20**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 591
Number of electrons: 208
Parallel Job: 16 threads


SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
        Step        Energy         Max Grad.        Max Dist.
         1      -8409.634220       0.017535         0.085287
         2      -8409.637712       0.006305         0.030190
         3      -8409.638038       0.001863         0.014808
         4      -8409.638082       0.001851         0.137845
         5      -8409.638268       0.001677         0.035937
         6      -8409.638312       0.001098         0.028919
         7      -8409.638336       0.000524         0.018643
         8      -8409.638346       0.000611         0.120349
```

Figure S94. HOMO-LUMO of **20**

20
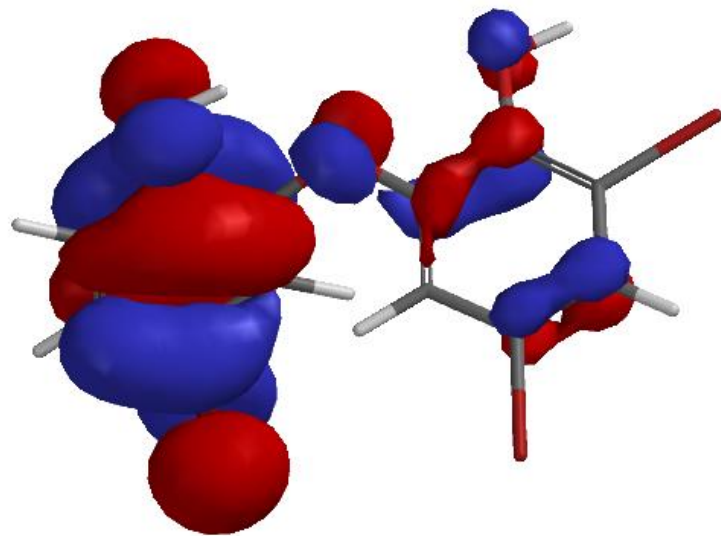
HOMO 20
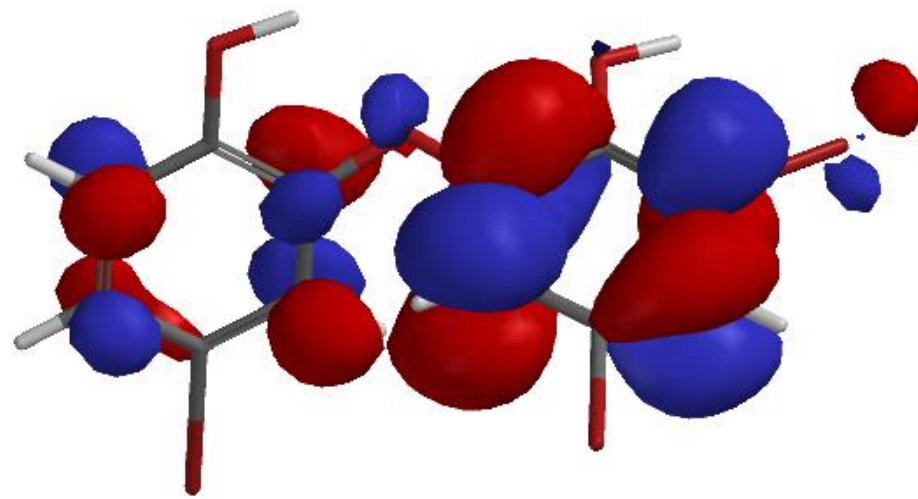
LUMO 20

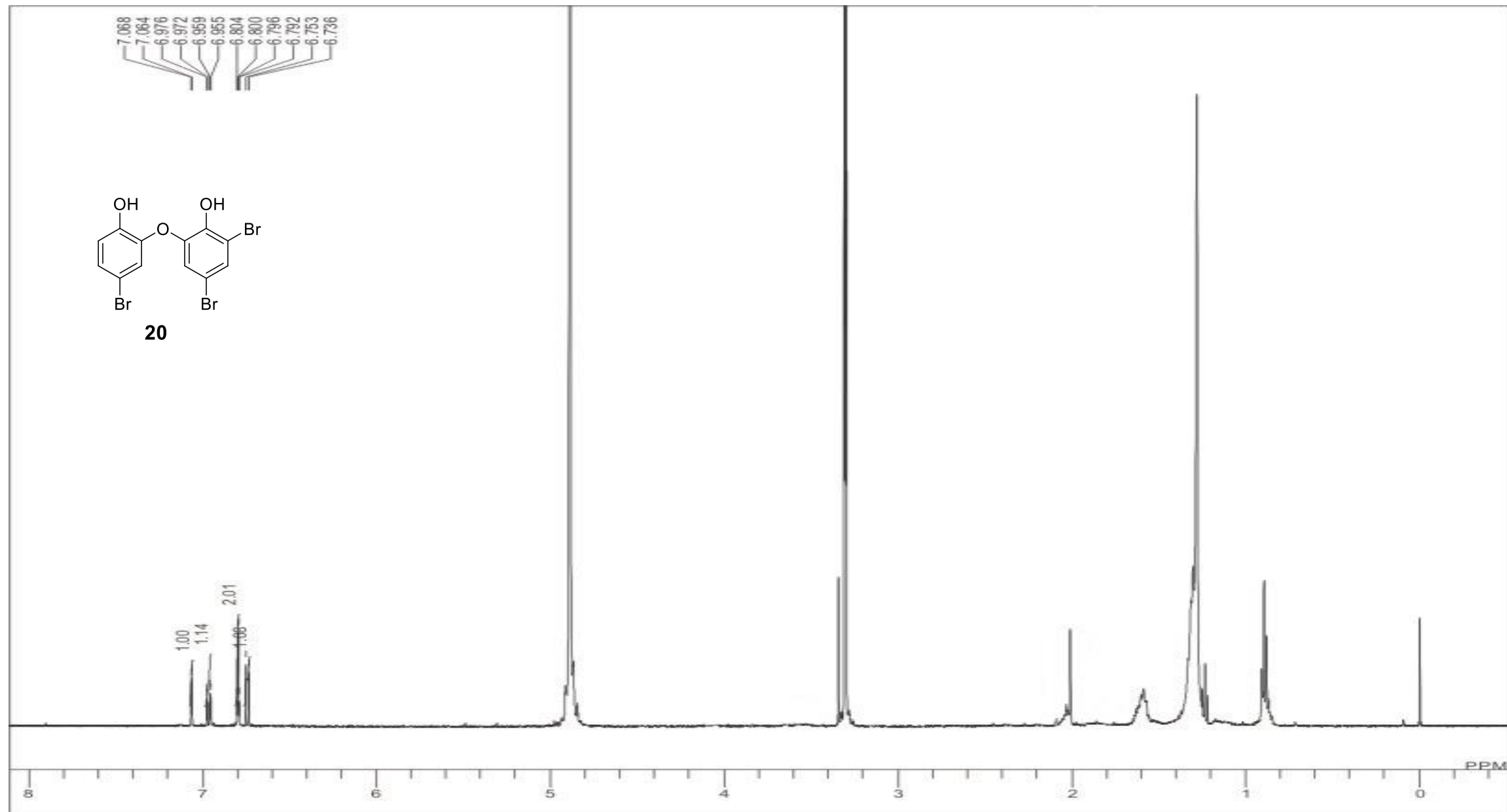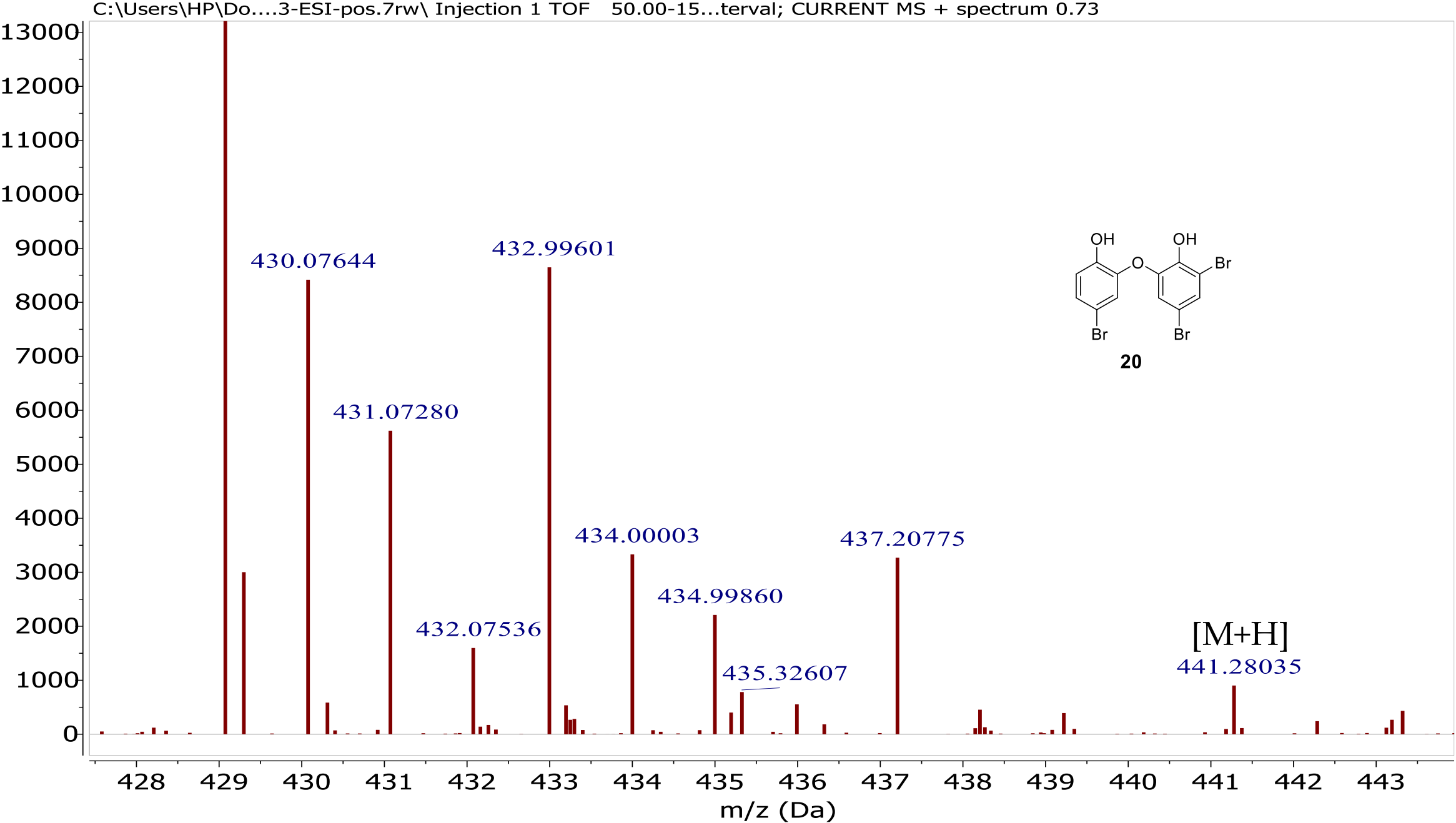# Figure S95. Calculated ^{13}C NMR Chemical Shift of **20**
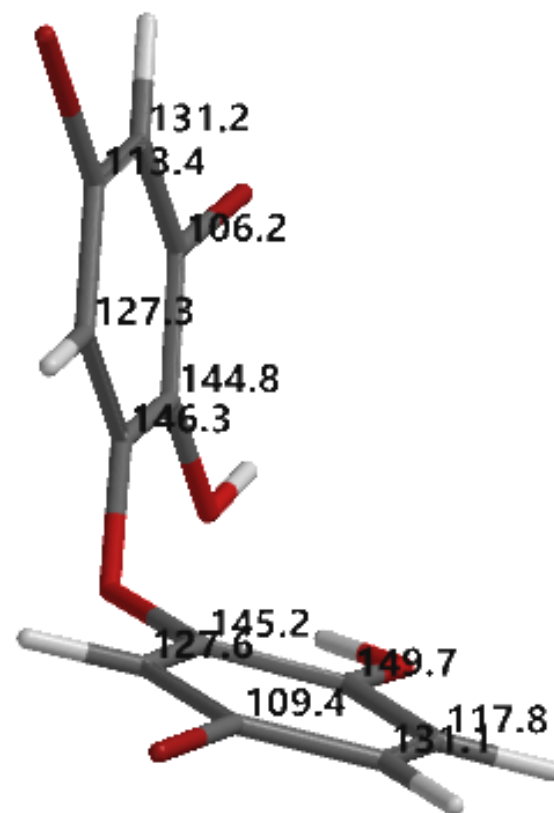
Table S45. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 21

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 591
Number of electrons: 208
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step        Energy          Max Grad.       Max Dist.
          1      -8409.632240       0.017496        0.095000
          2      -8409.636292       0.005800        0.091007
          3      -8409.636732       0.001794        0.005237
          4      -8409.636767       0.000924        0.007042
          5      -8409.636781       0.000384        0.003723
```
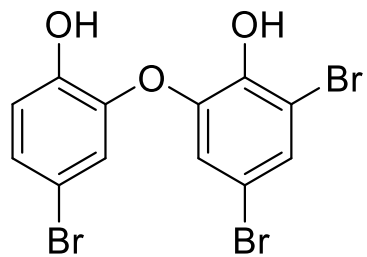
Figure S96. HOMO-LUMO of 21
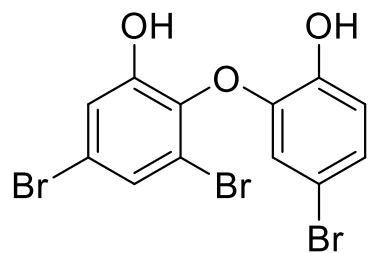
HOMO 21
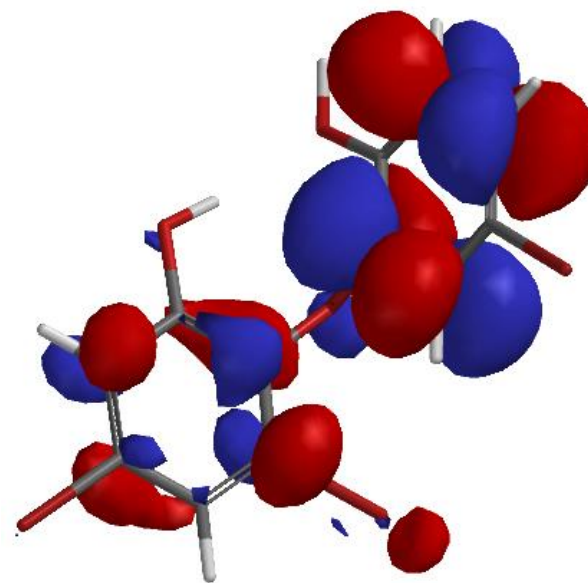
LUMO 21
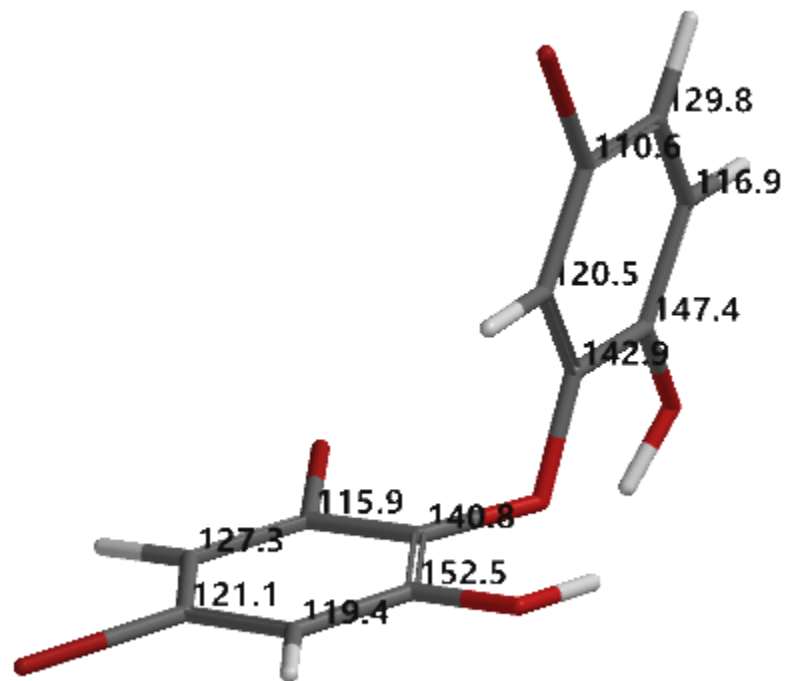
Table S46. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **22**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 591
Number of electrons: 208
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step       Energy          Max Grad.        Max Dist.
          1     -8409.634727       0.015772         0.105842
          2     -8409.639110       0.006119         0.052560
          3     -8409.639489       0.001724         0.004920
          4     -8409.639516       0.000940         0.005607
          5     -8409.639524       0.000223         0.002318
```

Figure S98. HOMO-LUMO of **22**

HOMO 22   **LUMO 22**

Figure S99. Calculated ¹³C NMR Chemical Shift of **22**
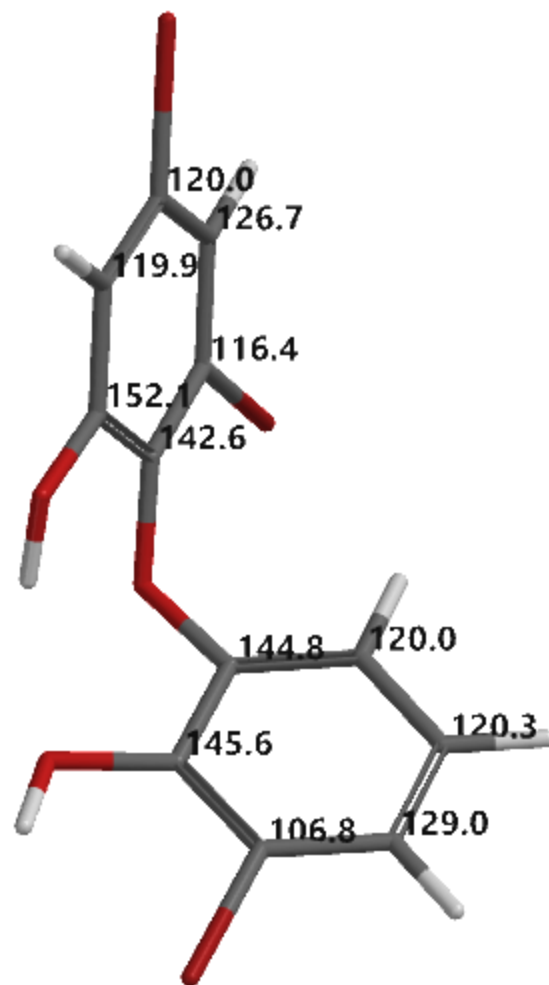
Figure S100. ^{1}H NMR spectrum of **23** (Me$_2$CO-d_6, 500 MHz)

Figure S101. HREIMS of **23**

Table S47. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **23**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 591
Number of electrons: 208
Parallel Job: 16 threads


SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
        Step      Energy         Max Grad.      Max Dist.
          1     -8409.634389     0.016739       0.065263
          2     -8409.637882     0.006159       0.034225
          3     -8409.638259     0.002213       0.011345
          4     -8409.638300     0.002233       0.185322
          5     -8409.638611     0.001981       0.018988
          6     -8409.638682     0.001090       0.087197
          7     -8409.638765     0.001048       0.030177
          8     -8409.638795     0.000857       0.119546
          9     -8409.638899     0.001216       0.127146
         10     -8409.638961     0.002789       0.048644
         11     -8409.639026     0.001687       0.083467
         12     -8409.639074     0.001206       0.052942
         13     -8409.639073     0.001148       0.034654
         14     -8409.639087     0.000590       0.012529
```
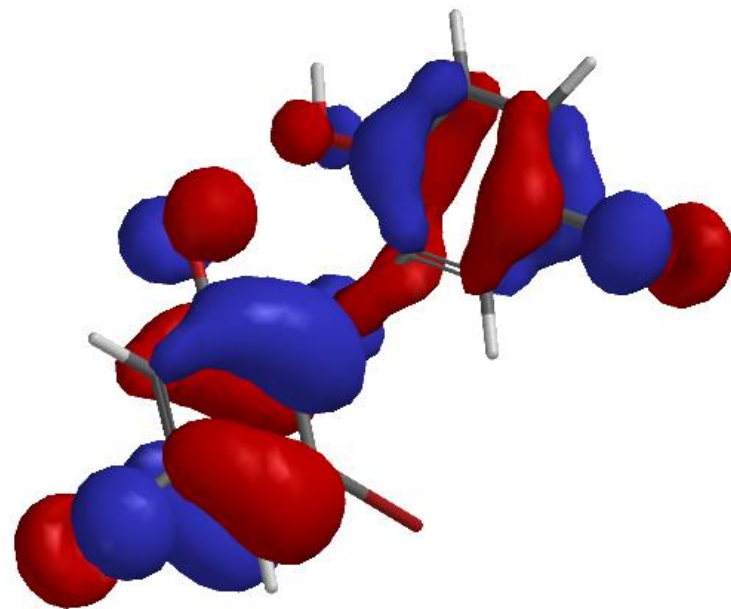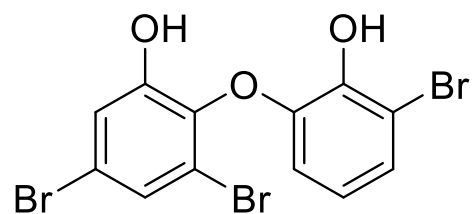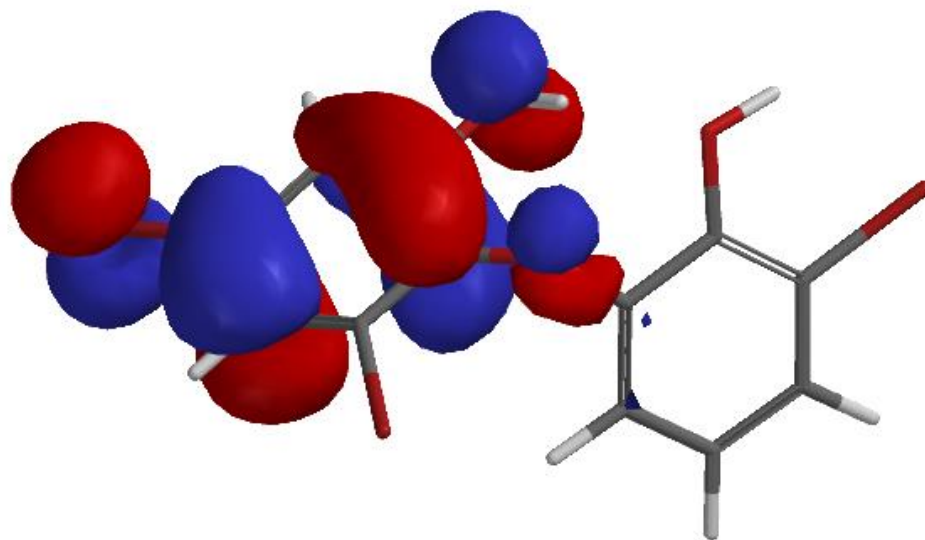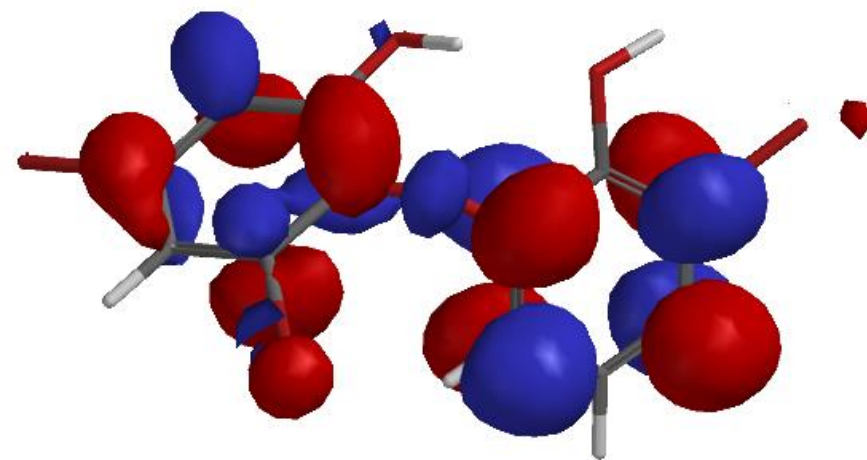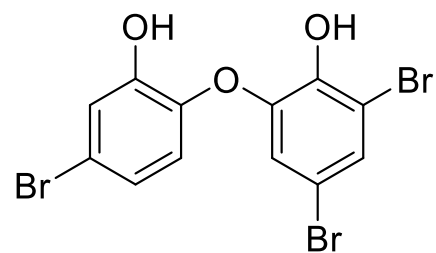
23
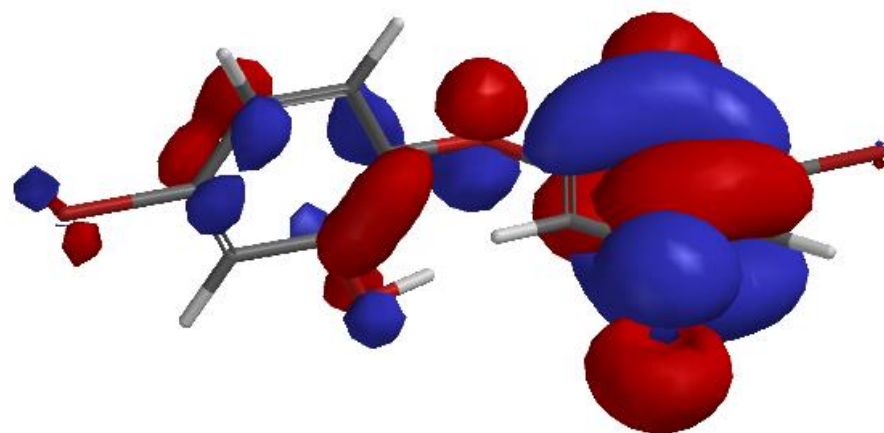
HOMO 23
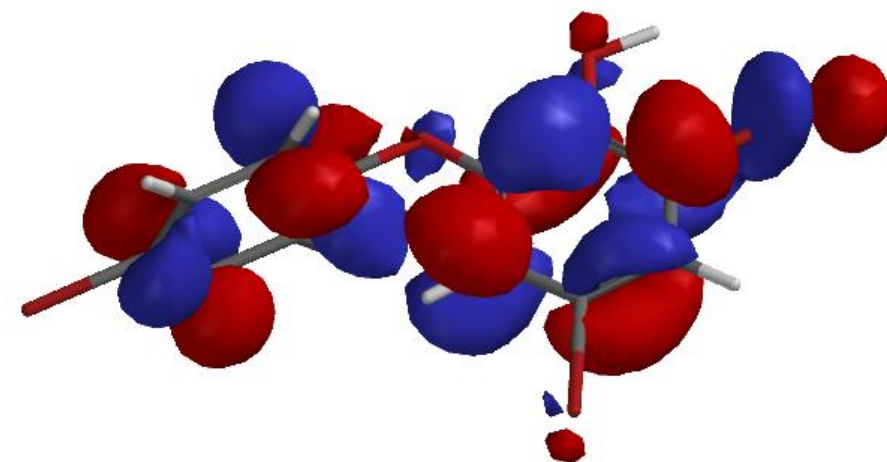
LUMO 23

Figure S103. Calculated ^{13}C NMR Chemical Shift of **23**
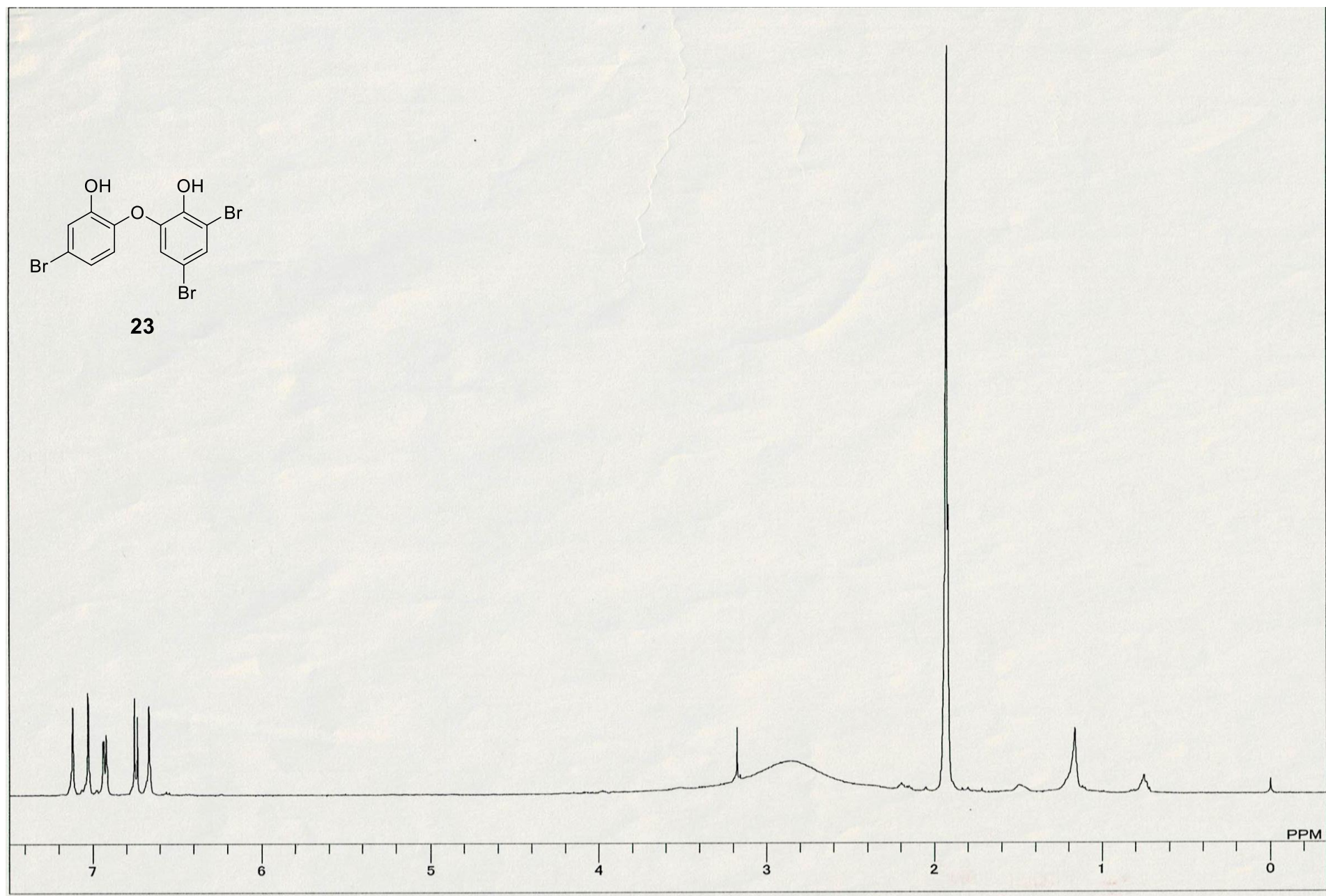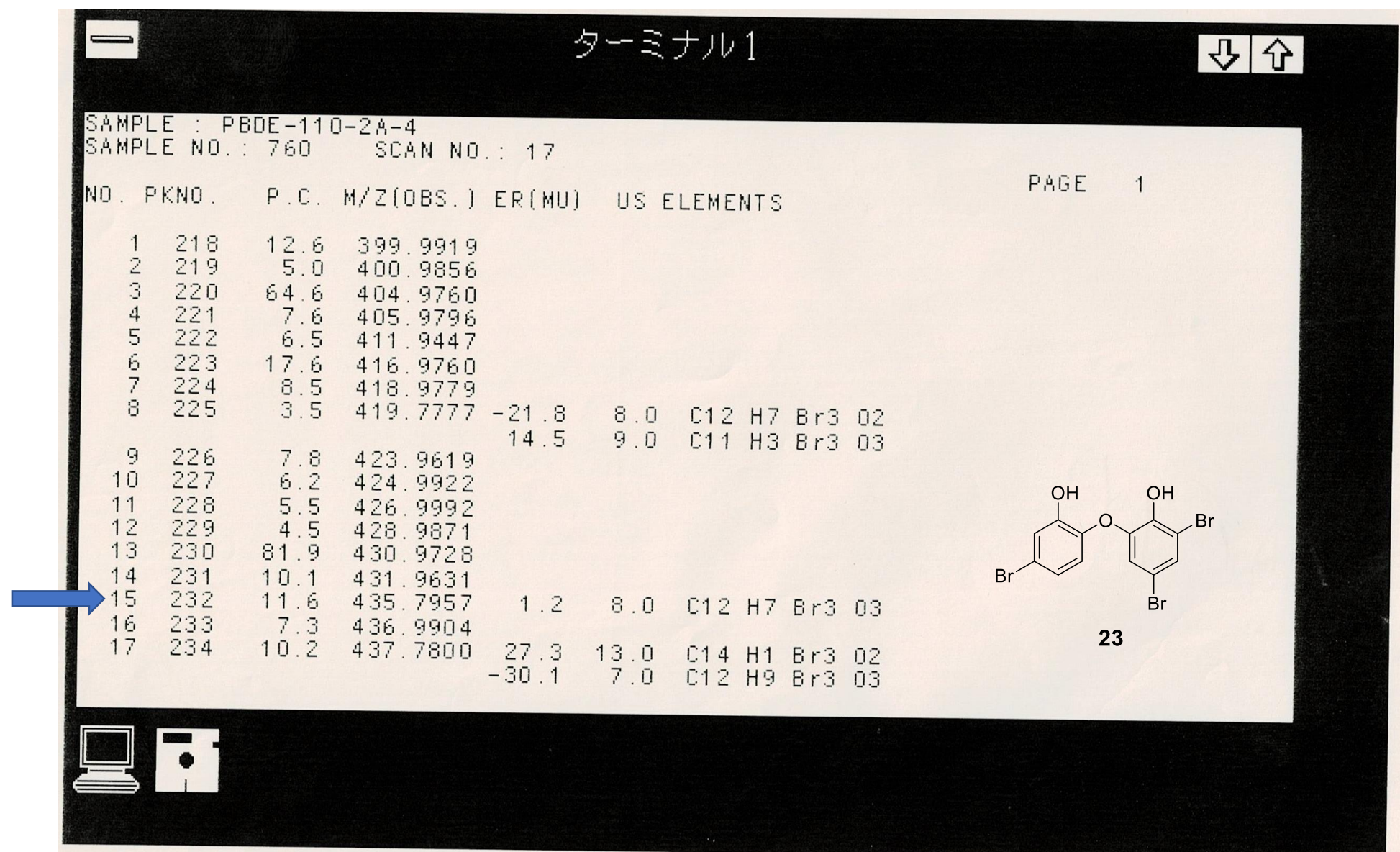
Table S48. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **24**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 591
Number of electrons: 208
Parallel Job: 16 threads


SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
         Step       Energy        Max Grad.      Max Dist.
          1      -8409.632444     0.016787       0.082560
          2      -8409.636402     0.007465       0.031322
          3      -8409.636768     0.001545       0.010429
          4      -8409.636797     0.001521       0.126229
          5      -8409.636910     0.001247       0.049118
          6      -8409.636960     0.000858       0.059241
          7      -8409.636992     0.000807       0.028110
          8      -8409.637008     0.000818       0.125739
          9      -8409.637075     0.001628       0.045330
         10      -8409.637126     0.002153       0.154828
         11      -8409.637395     0.003611       0.155314
         12      -8409.637600     0.005031       0.224109
         13      -8409.637523     0.010662       0.147016
         14      -8409.638102     0.003629       0.018859
         15      -8409.638261     0.002728       0.132207
         16      -8409.638372     0.003278       0.032379
         17      -8409.638441     0.002243       0.133479
         18      -8409.638608     0.001795       0.136145
         19      -8409.638762     0.001576       0.099217
         20      -8409.638863     0.001767       0.036126
         21      -8409.638910     0.001083       0.044834
         22      -8409.638912     0.000696       0.023248
```

Figure S104. HOMO-LUMO of 24
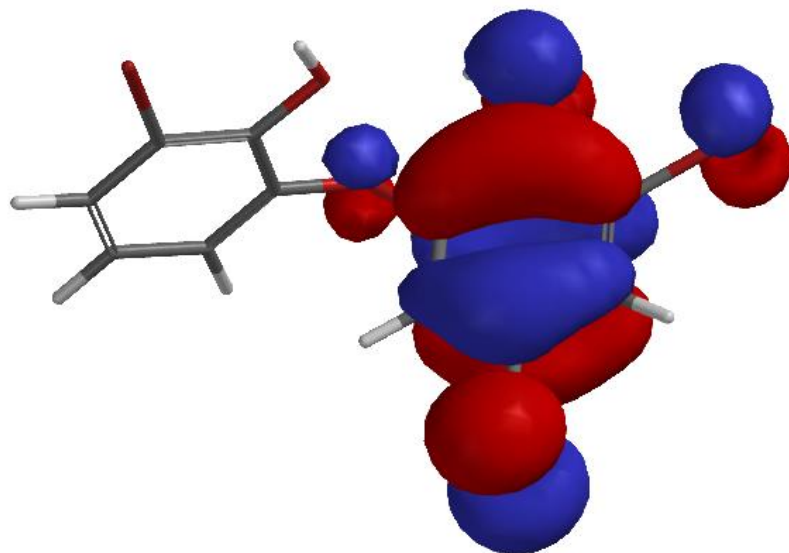
HOMO 24
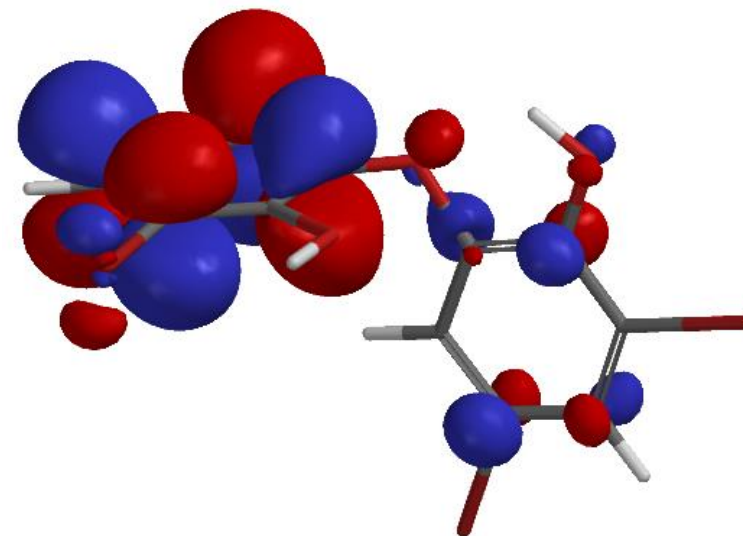
LUMO 24

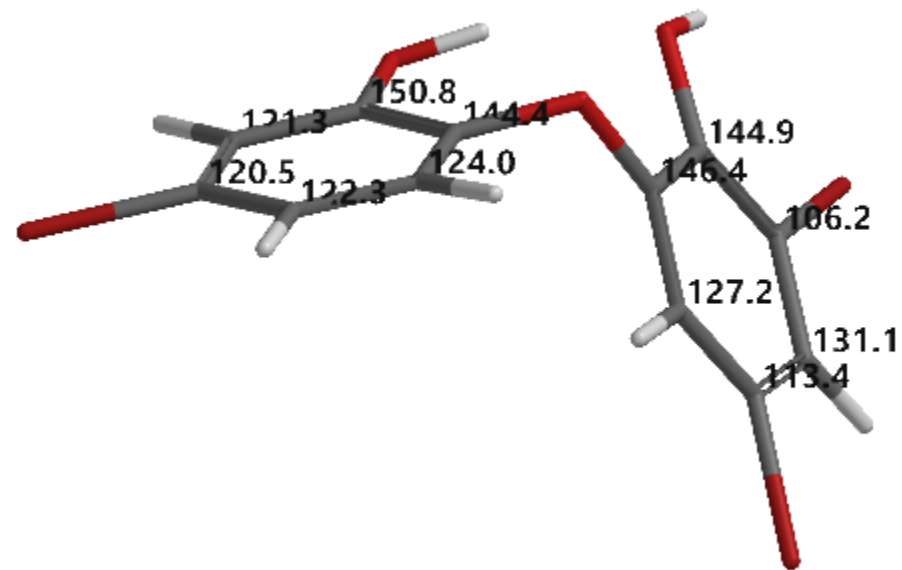# Figure S105. Calculated ^{13}C NMR Chemical Shift of **24**
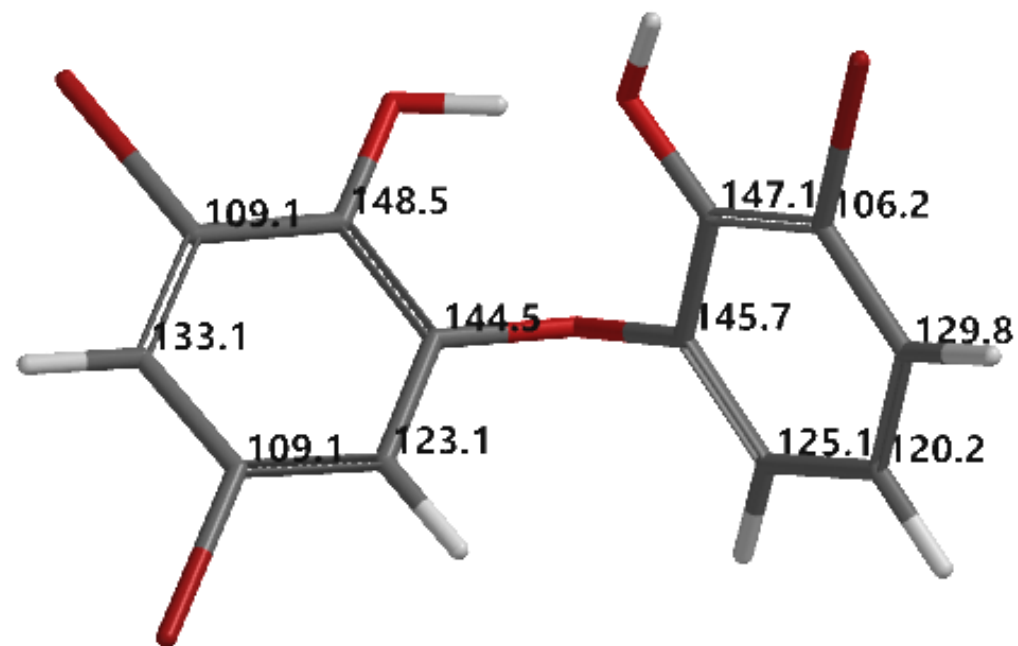
Table S49. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 25

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 549
Number of electrons: 174
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
        Step       Energy        Max Grad.      Max Dist.
          1     -5836.062719      0.016246       0.054932
          2     -5836.065642      0.006155       0.026482
          3     -5836.065966      0.001450       0.017384
          4     -5836.066013      0.001454       0.087323
          5     -5836.066128      0.001001       0.061258
          6     -5836.066146      0.000780       0.087930
          7     -5836.066193      0.000980       0.038614
          8     -5836.066212      0.000899       0.081279
          9     -5836.066254      0.000949       0.190805
         10     -5836.063372      0.027098       0.122667
         11     -5836.066322      0.001013       0.113282
         12     -5836.066419      0.003404       0.047946
         13     -5836.066492      0.002043       0.036870
         14     -5836.066518      0.000259       0.014888
         15     -5836.066519      0.000223       0.008911
```
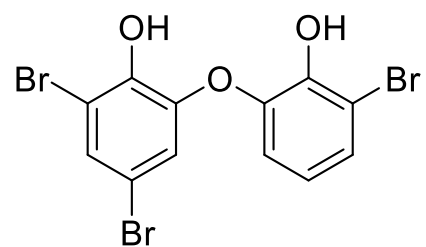
Figure S106. HOMO-LUMO of 25
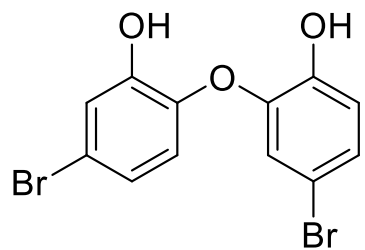
25
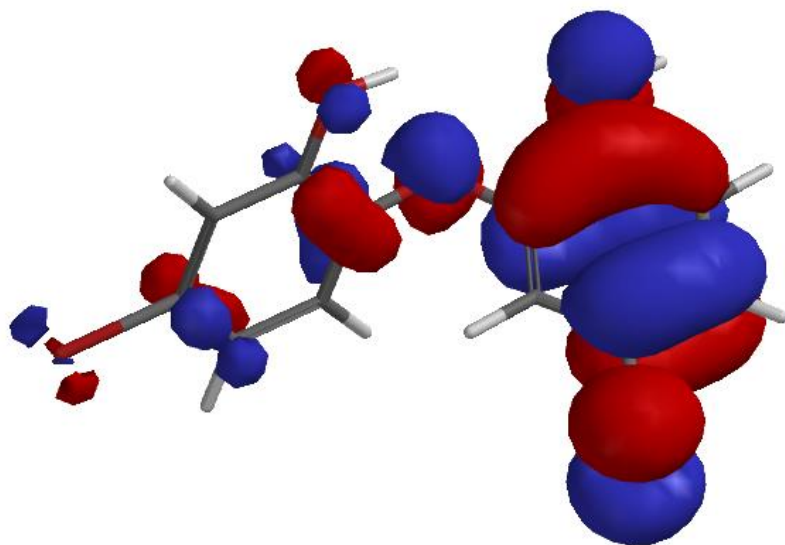
HOMO 25
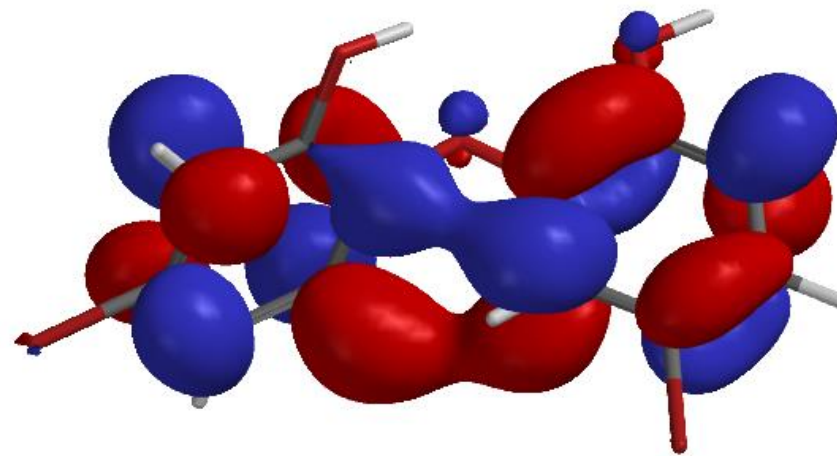
LUMO 25

Figure S107. Calculated ¹³C NMR Chemical Shift of 25

Figure S108. ^{1}H NMR spectrum of **26** (CD$_3$OD, 500 MHz)

Figure S109. HREIMS of 26

SAMPLE : PBDE-110-31
SAMPLE NO.: 759   SCAN NO.: 10

PAGE   3

NO. PKNO.   P.C. M/Z(OBS.) ER(MU)   US ELEMENTS

36	254	0.6	338.0081			
37	255	0.5	339.0316			
38	256	0.6	339.8710	-38.7	8.0	C13 H10 Br2 O1
				- 2.3	9.0	C12 H6 Br2 O2
				34.0	10.0	C11 H2 Br2 O3
39	257	0.4	341.0106			
40	258	0.4	341.8780	-11.0	8.0	C12 H8 Br2 O2
				25.3	9.0	C11 H4 Br2 O3
41	259	43.1	342.9792			
42	260	5.2	343.9887			
43	261	1.0	344.9995			
44	262	2.2	346.9730			
45	263	0.4	347.9721			
46	264	0.7	348.9776			
47	265	0.6	349.9687			
48	266	1.1	351.0080			
49	267	11.1	354.9792			
50	268	2.0	355.9720			
51	269	0.7	356.9661			
52	270	1.8	357.8824	- 1.5	8.0	C12 H8 Br2 O3

26

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 549
Number of electrons: 174
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
         Step       Energy        Max Grad.      Max Dist.
          1      -5836.061537      0.017002       0.108180
          2      -5836.065659      0.005031       0.109740
          3      -5836.066063      0.002040       0.007664
          4      -5836.066100      0.000938       0.005806
          5      -5836.066109      0.000241       0.003234
```
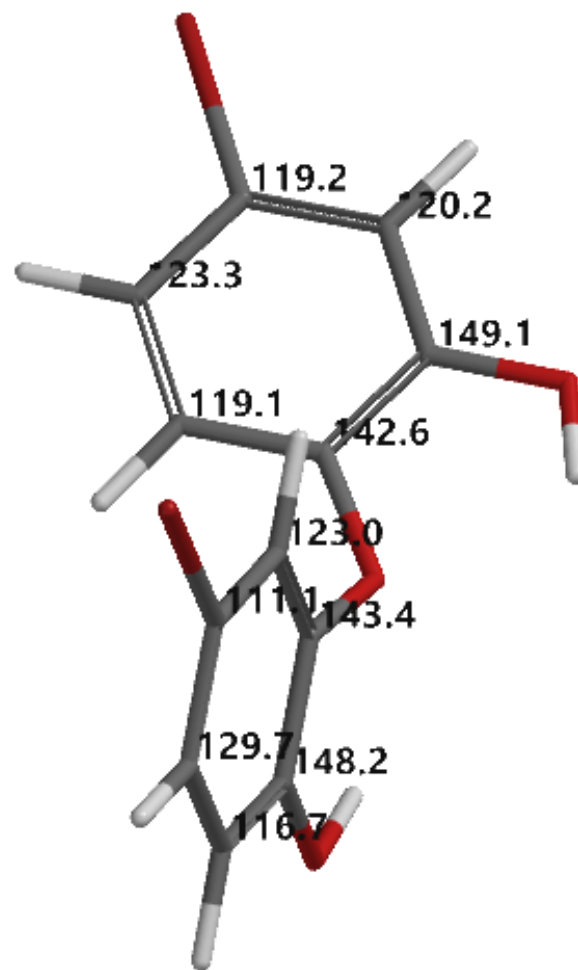
Figure S110. HOMO-LUMO of **26**

26

HOMO 26
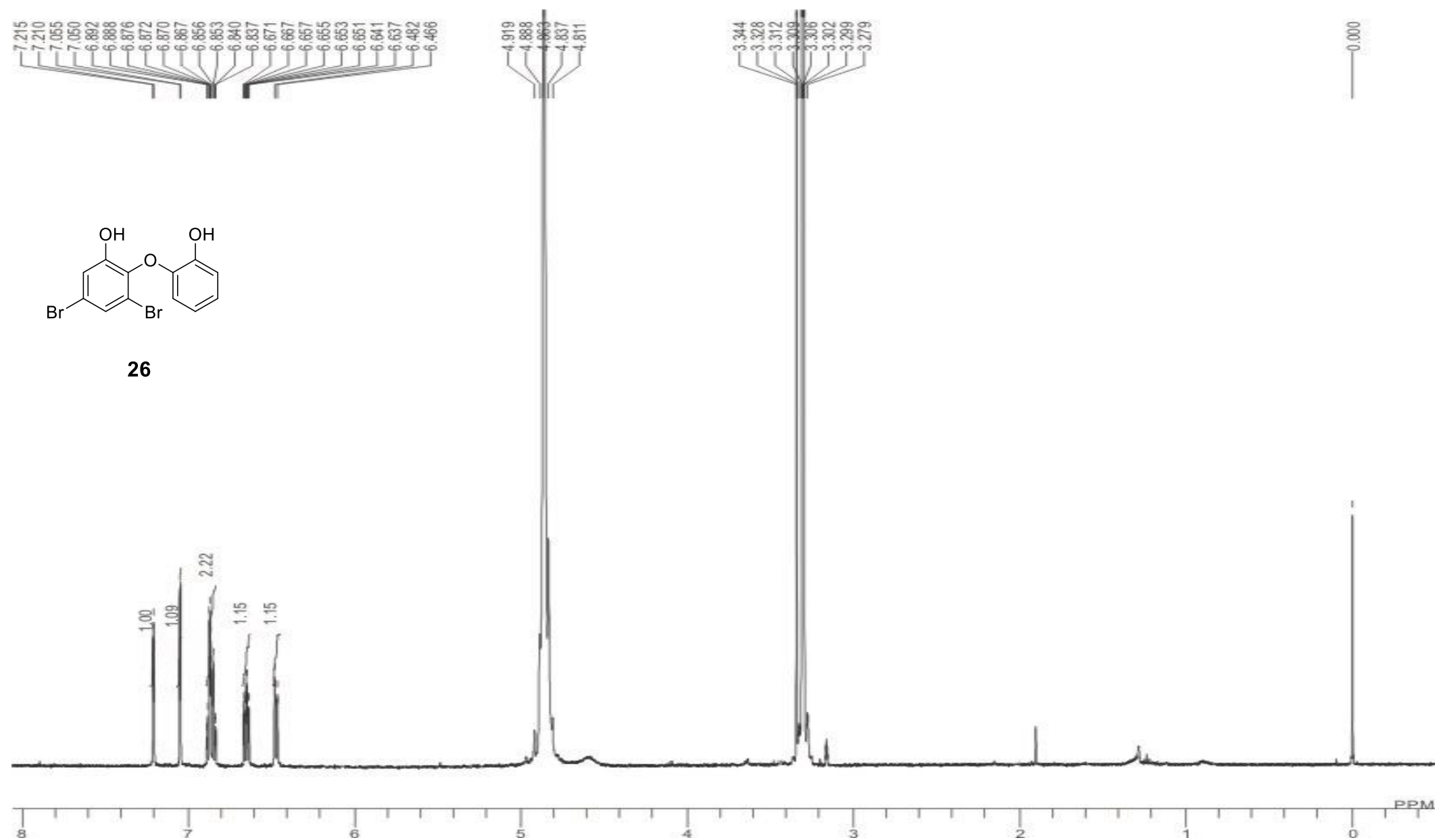
LUMO 26

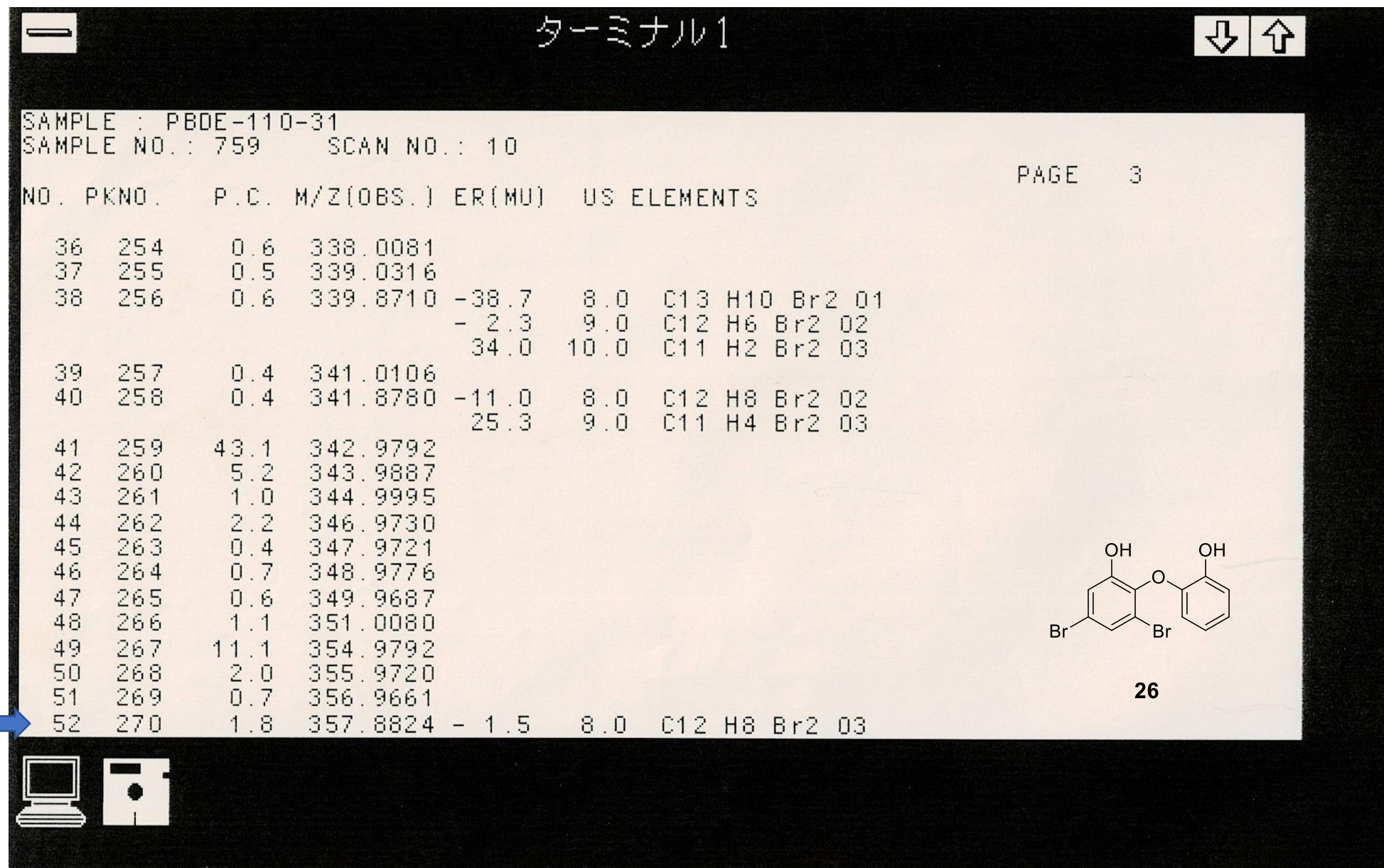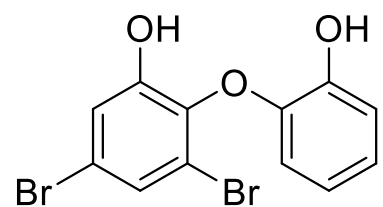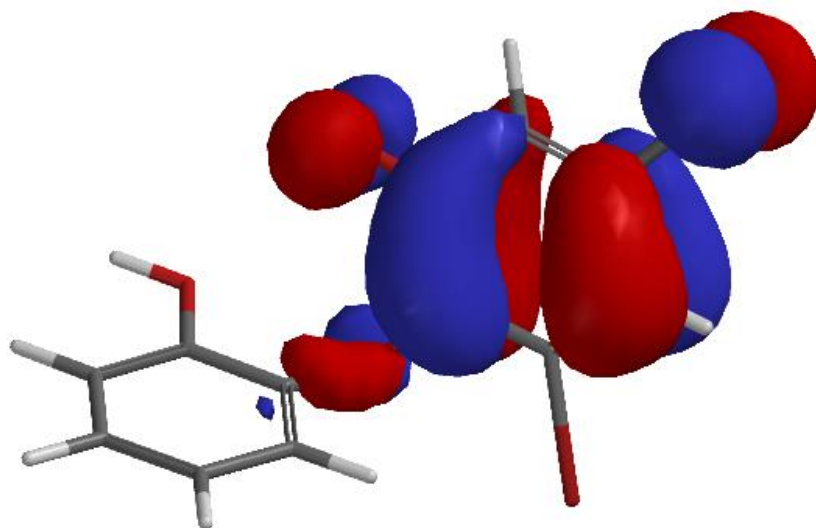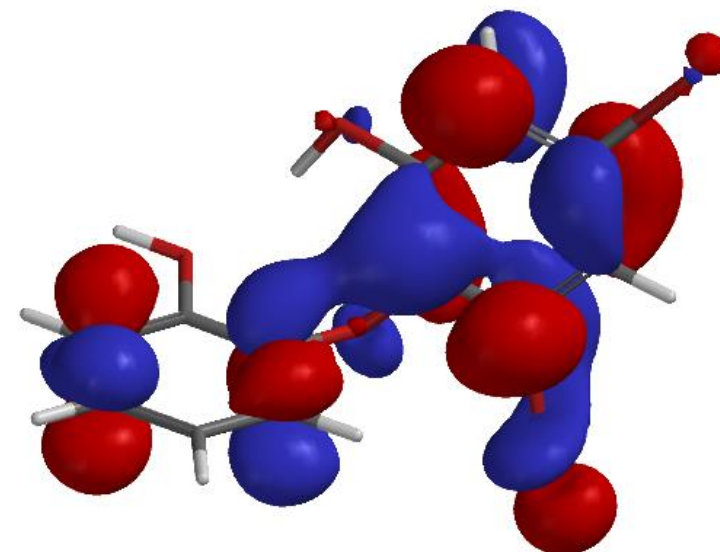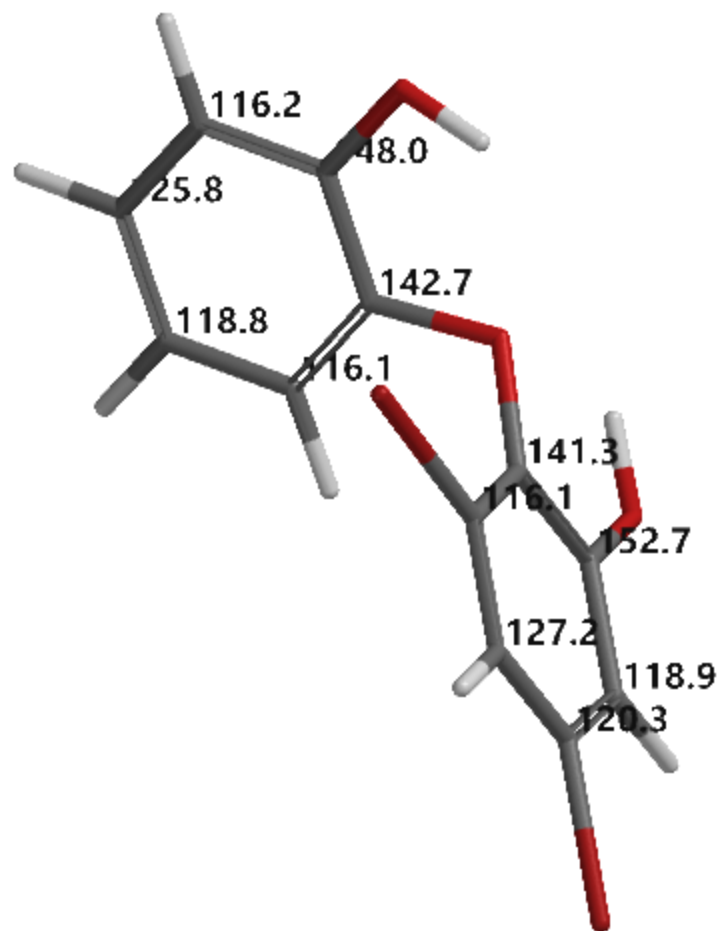# Figure S111. Calculated ^{13}C NMR Chemical Shift of **26**

Table S51. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of 27

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 549
Number of electrons: 174
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization


Optimization:
       Step        Energy         Max Grad.      Max Dist.
         1      -5836.063149      0.017000       0.060994
         2      -5836.066525      0.006244       0.029606
         3      -5836.066856      0.001845       0.014476
         4      -5836.066899      0.001919       0.167341
         5      -5836.067112      0.001970       0.050329
         6      -5836.067205      0.001829       0.157225
         7      -5836.067413      0.002573       0.085936
         8      -5836.067511      0.004582       0.057463
         9      -5836.067630      0.002905       0.075926
        10      -5836.067774      0.001150       0.044421
        11      -5836.067822      0.000970       0.021432
        12      -5836.067830      0.000263       0.012001
```
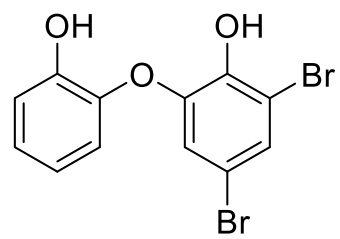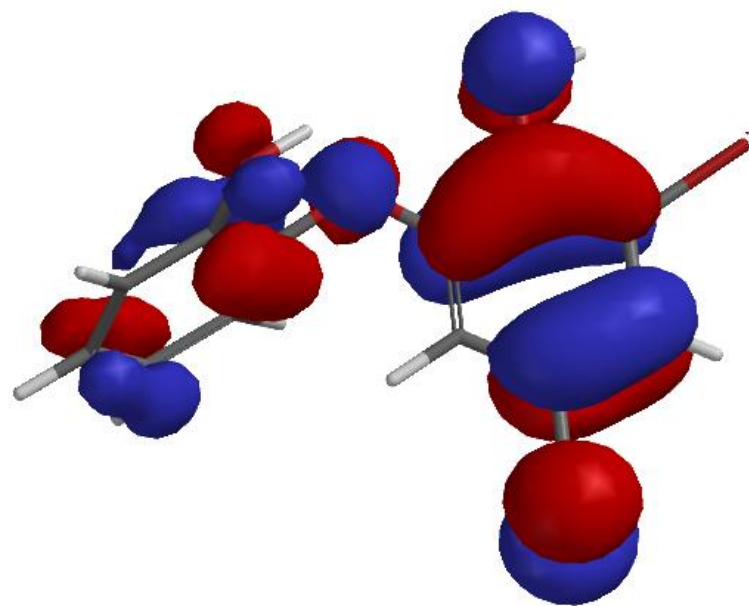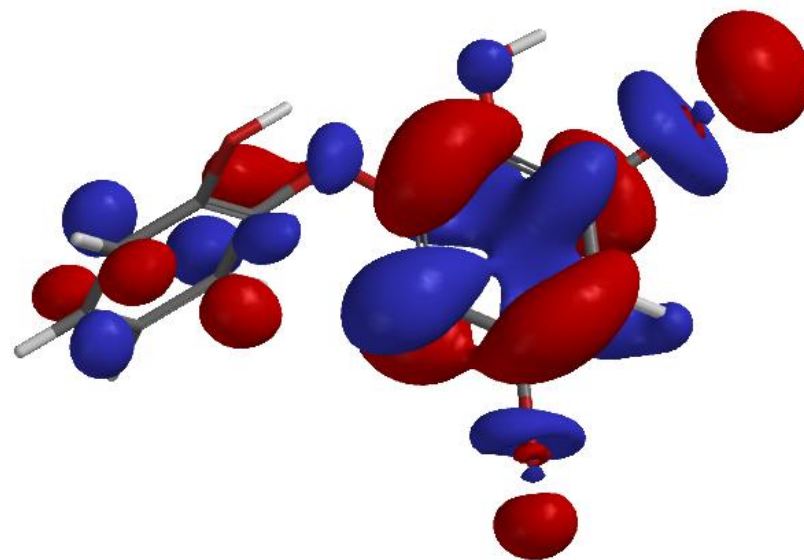
Figure S112. HOMO-LUMO of 27

27

HOMO 27

LUMO 27

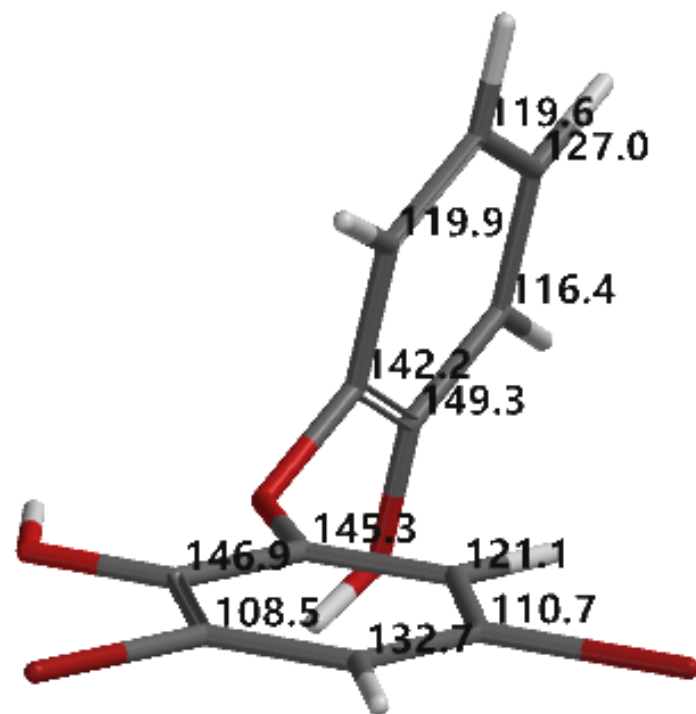# Figure S113. Calculated ^{13}C NMR Chemical Shift of **27**

Table S52. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **28**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 507
Number of electrons: 140
Parallel Job: 16 threads


SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
        Step       Energy        Max Grad.        Max Dist.
          1     -3262.491099      0.016820         0.061238
          2     -3262.493993      0.006810         0.029800
          3     -3262.494318      0.001731         0.018173
          4     -3262.494368      0.001732         0.125139
          5     -3262.494530      0.001178         0.068377
          6     -3262.494592      0.000941         0.091630
          7     -3262.494643      0.001489         0.152496
          8     -3262.494801      0.002630         0.146192
          9     -3262.494680      0.005622         0.109539
         10     -3262.494877      0.001934         0.013981
         11     -3262.494916      0.001601         0.055904
         12     -3262.494984      0.000956         0.048517
         13     -3262.495022      0.000974         0.043055
         14     -3262.495030      0.000291         0.015718
```
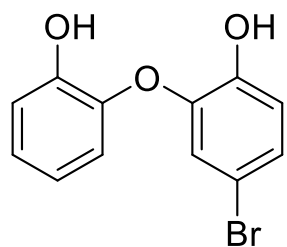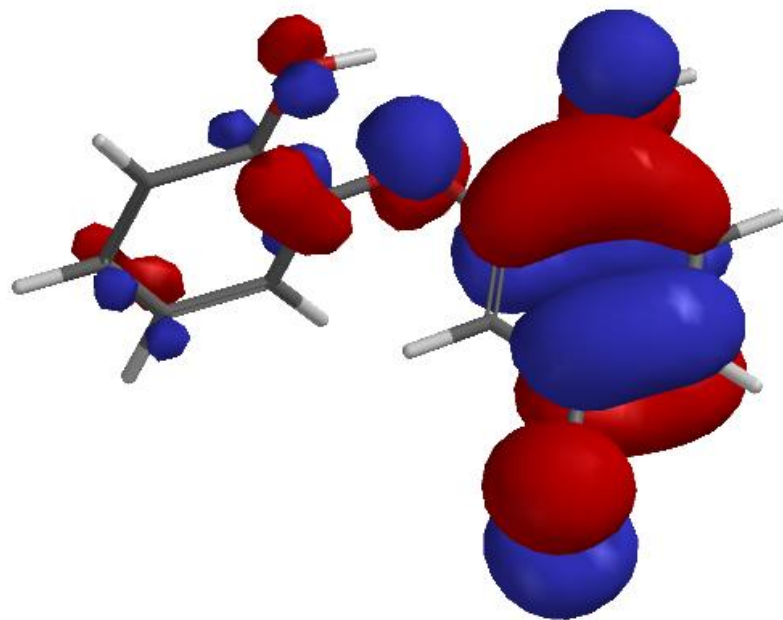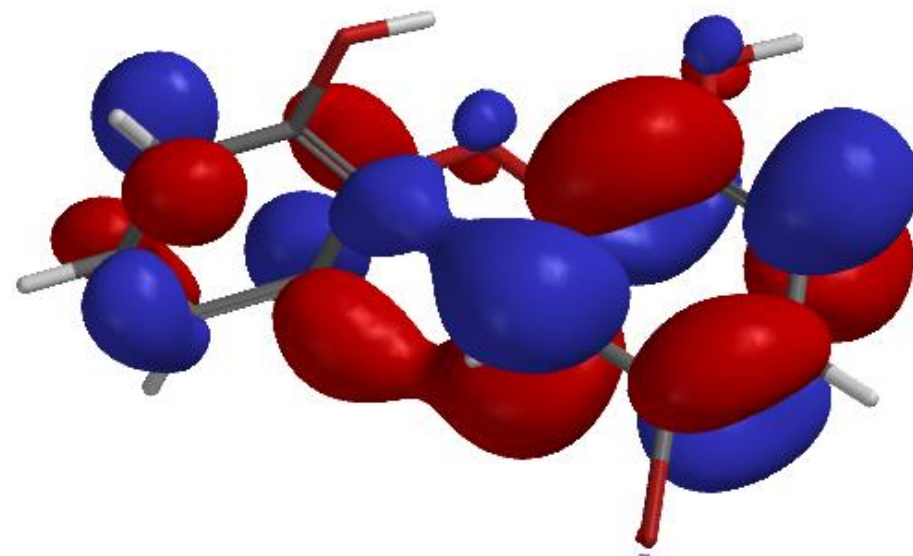
Figure S114. HOMO-LUMO of **28**

28

HOMO 28

LUMO 28

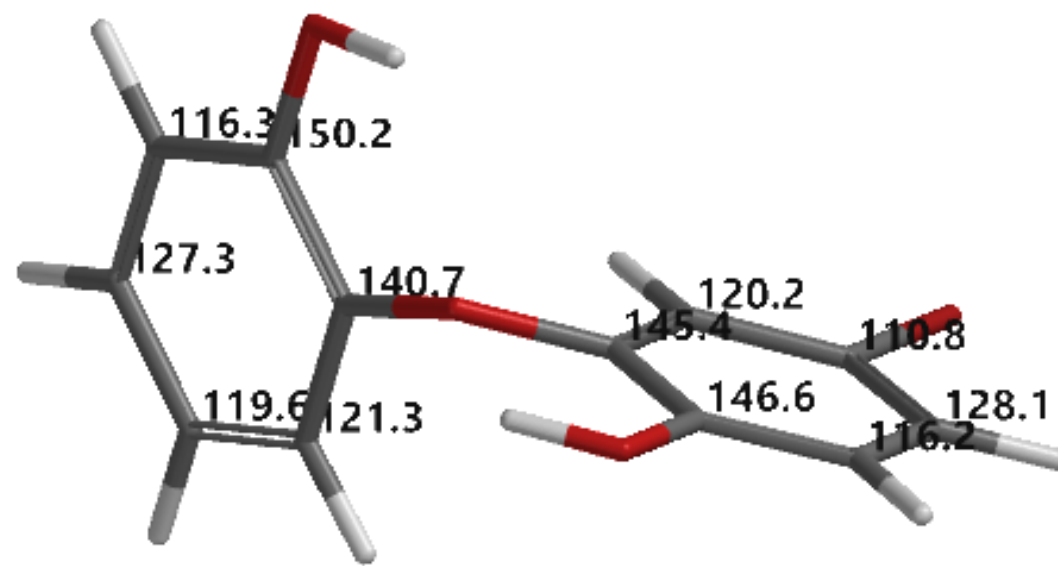Figure S115. Calculated ¹³C NMR Chemical Shift of **28**

Table S53. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **29**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 507
Number of electrons: 140
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
          Step      Energy        Max Grad.      Max Dist.
           1     -3262.493067     0.016774       0.060603
           2     -3262.496457     0.006546       0.032003
           3     -3262.496841     0.001784       0.011009
           4     -3262.496872     0.001785       0.135742
           5     -3262.497002     0.001114       0.021546
           6     -3262.497030     0.000804       0.051283
           7     -3262.497098     0.000724       0.103100
           8     -3262.497164     0.001238       0.161182
           9     -3262.497355     0.001839       0.149424
          10     -3262.497318     0.004700       0.087265
          11     -3262.497447     0.001239       0.032768
          12     -3262.497478     0.000822       0.052254
          13     -3262.497503     0.000267       0.019419
          14     -3262.497505     0.000102       0.002946
```
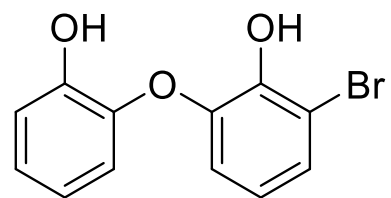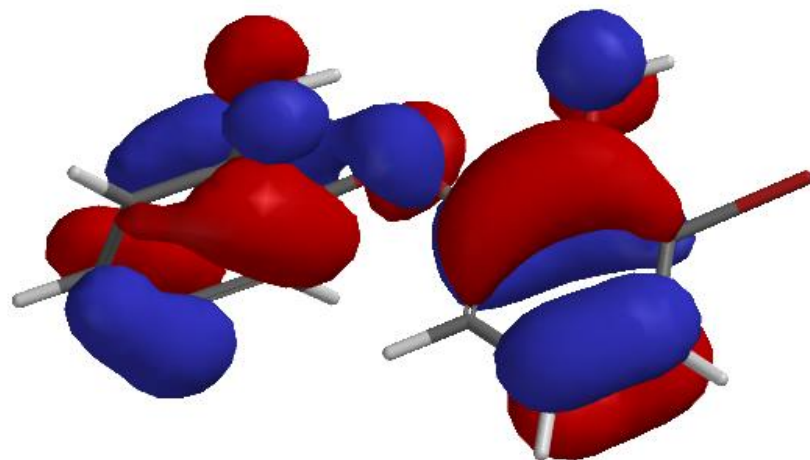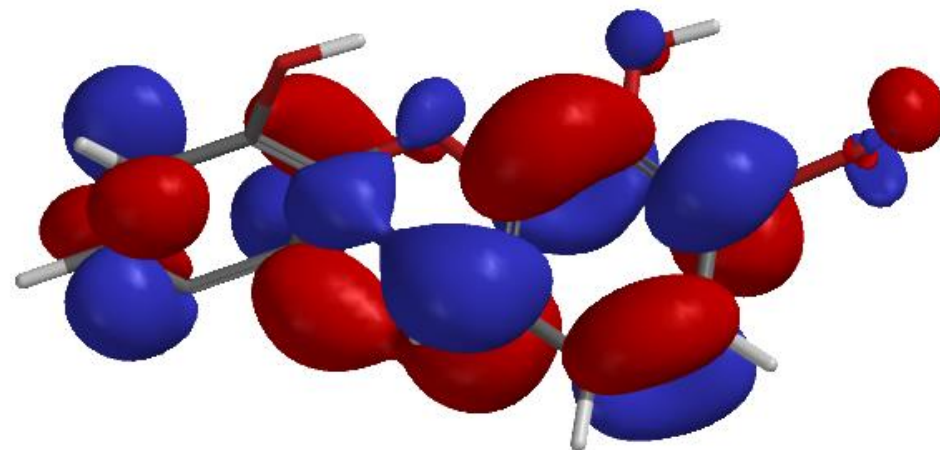
Figure S116. HOMO-LUMO of **29**

29

HOMO 29

LUMO 29

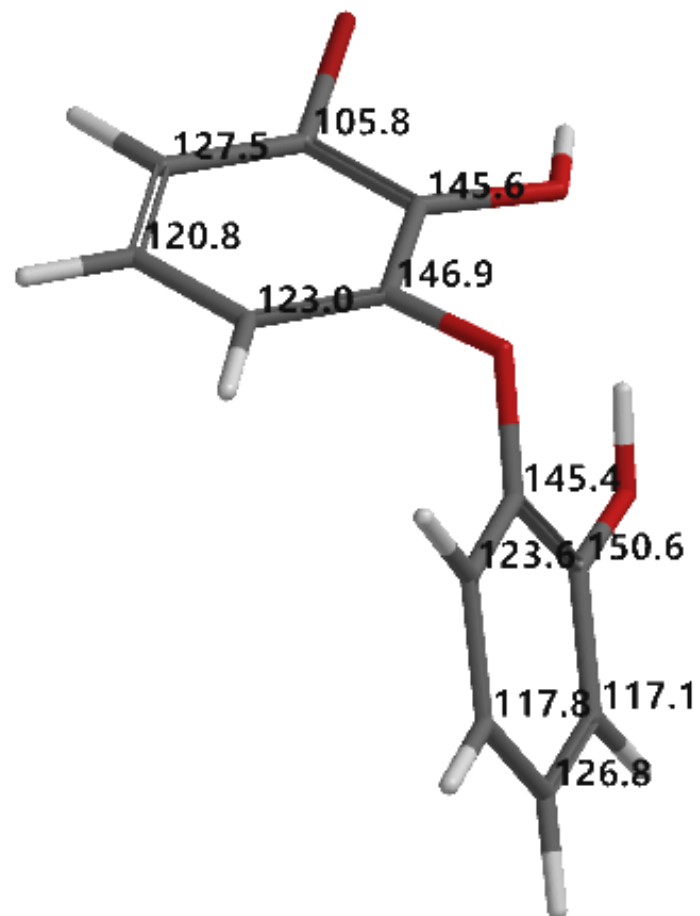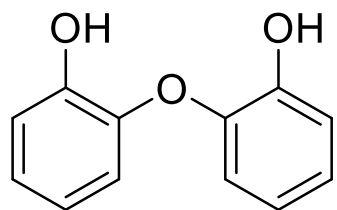Figure S117. Calculated ¹³C NMR Chemical Shift of **29**

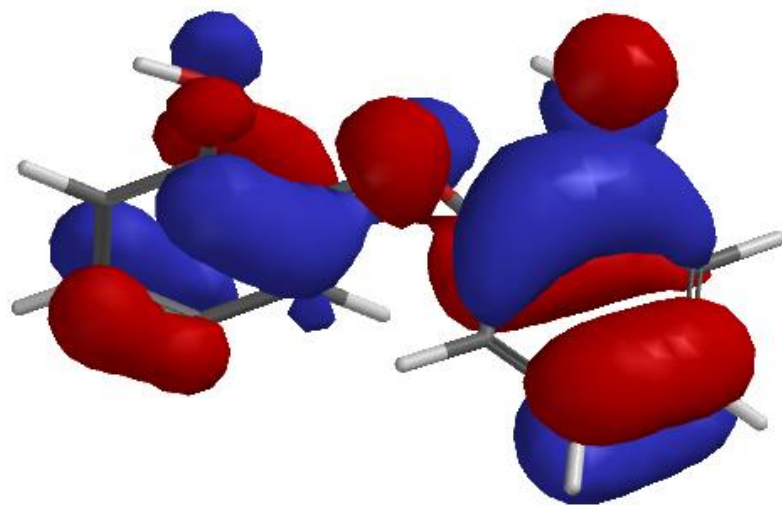# Table S54. Equilibrium Geometry DFT ωB97X-D/6-311+G(2d,p) of **30**

```
Job type: Geometry optimization.
Method: RWB97X-D
Basis set: 6-311+G(2D,P)
Number of basis functions: 465
Number of electrons: 106
Parallel Job: 16 threads

SCF model:
 A restricted hybrid HF-DFT SCF calculation will be
 performed using Pulay DIIS + Geometric Direct Minimization



Optimization:
          Step        Energy           Max Grad.        Max Dist.
           1       -688.920186         0.016180         0.049697
           2       -688.922801         0.007123         0.022371
           3       -688.923050         0.001042         0.004455
           4       -688.923061         0.000928         0.051355
           5       -688.923115         0.000467         0.029738
           6       -688.923131         0.000541         0.039364
```
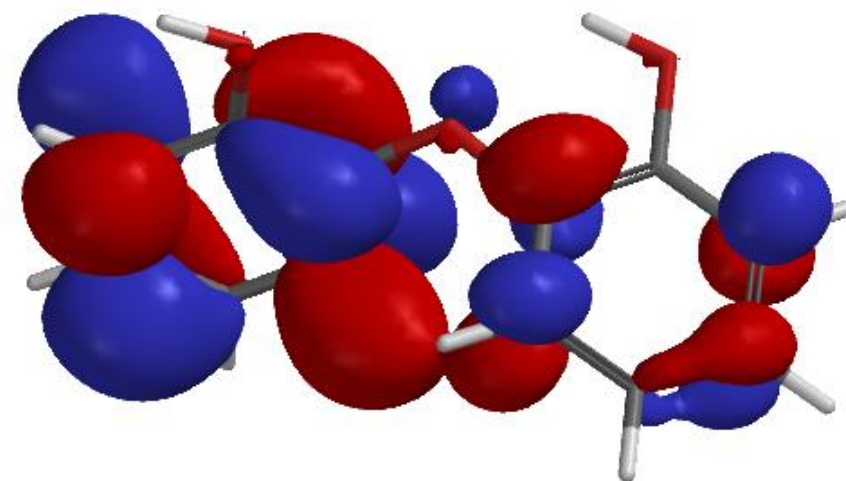
Figure S118. HOMO-LUMO of **30**

30

HOMO 30

LUMO 30
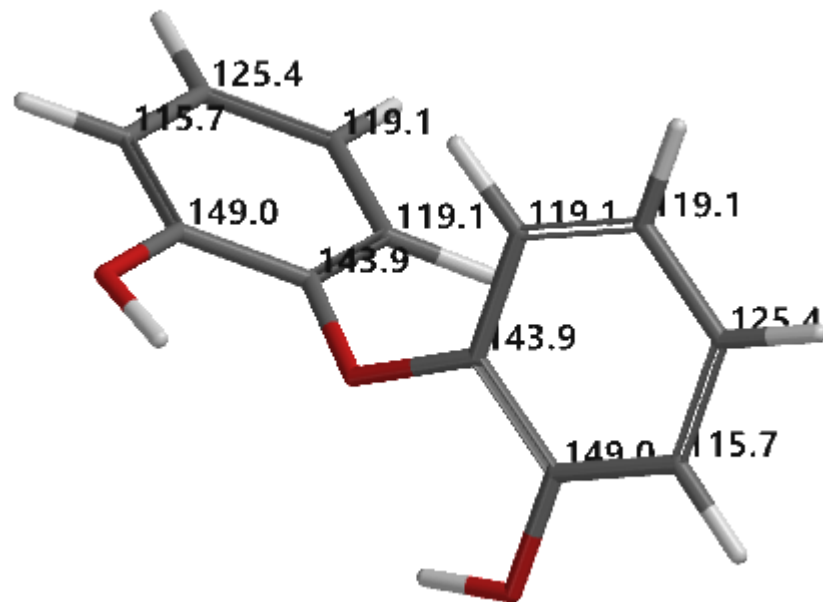
Table S55. ^{1}H NMR Data of **1–5**

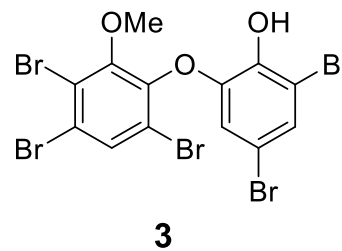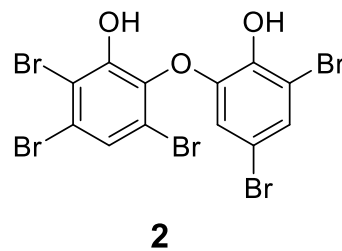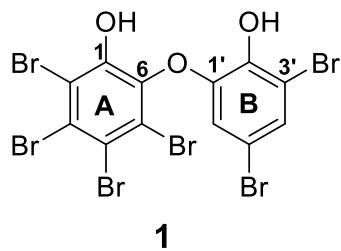| Pos	1 (Me$_2$CO-d_6)	1 (CD$_3$OD)	2 (Me$_2$CO-d_6)	3 (CDCl$_3$)	4 (Me$_2$CO-d_6)	5 (CDCl$_3$)
			Compound			
H4′	7.40 (1H, d, J = 2.2 Hz)	7.35 (1H, d, J = 2.2 Hz)	7.38 (1H, d, J = 2.3 Hz)	7.38 (1H, d, J = 2.3 Hz)	7.47 (1H, d, J = 2.3 Hz)	7.47 (1H, d, J = 2.3 Hz)
H6′	6.83 (1H, d, J = 2.2 Hz)	6.47 (1H, d, J = 2.2 Hz)	6.79 (1H, d, J = 2.3 Hz)	6.56 (1H, d, J = 2.3 Hz)	6.81 (1H, d, J = 2.3 Hz)	6.52 (1H, d, J = 2.3 Hz)
H2	-	-	-	-	-	7.31 (1H, s)
H4	-	-	7.47 (1H, s)	7.75 (1H, s)	7.64 (1H, s)	-
OMe′ (Ring B)	-	-	-	-	4.00 (3H, s)	-
OMe (Ring A)	-	-	-	3.81 (3H, s)	-	3.79 (3H, s)

Table S56. NMR Data of **6** in Me$_2$CO-d_6

6
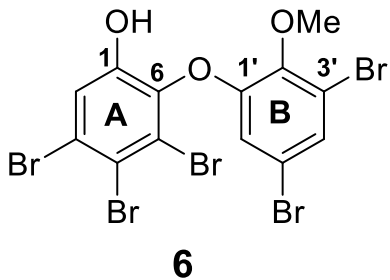
Pos	δ_C (mult.)	δ_H (J in Hz)	HMBC
1	151.3 C		
2	122.0 CH	7.50 (1H, s)	1, 3, 4, 6
3	122.5 C		
4	116.9 C		
5	122.7 C		
6	140.1 C		
2'-OMe (Ring B)	61.1 CH$_3$	3.99 (3H, s)	2'
1'	152.0 C		
2'	146.5 C		
3'	119.4 C		
4'	129.4 CH	7.40 (1H, d, J = 2.5)	2', 3', 5', 6'
5'	117.8 C		
6'	117.4 CH	6.78 (1H, d, J = 2.5)	1', 2', 3', 5'

Table S57. ¹H NMR Data of **7–9**

	7	**8**	**9**
		Compound	
Pos	**7**	**8**	**9**
	(Me$_2$CO-d_6)	(CDCl$_3$)	(CDCl$_3$)
H4'	7.43	7.50	7.40
	(1H, d, J = 2.2 Hz)	(1H, d, J = 2.2 Hz)	(1H, d, J = 2.2 Hz)
H6'	6.88	6.97	6.50
	(1H, d, J = 2.2 Hz)	(1H, d, J = 2.2 Hz)	(1H, d, J = 2.2 Hz)
H2	-	-	-
H4	-	-	7.76
			(1H, s)
OMe' (Ring B)	-	4.00 (3H, s)	4.00 (3H, s)
OMe (Ring A)	3.87 (3H, s)	3.85 (3H, s)	3.82 (3H, s)

Table S58. ¹H NMR Data of 10–13

Pos	10 (CDCl₃)	10 (Me₂CO-d_6)	11 (Me₂CO-d_6)	12 (CDCl₃)	12 (Me₂CO-d_6)	13 (CDCl₃)	13 (Me₂CO-d_6)
			Compound				
H4′	7.51 (1H, d, J = 2.1 Hz)	7.62 (1H, d, J = 2.2 Hz)	7.64 (1H, d, J = 2.1 Hz)	7.50 (1H, d, J = 2.1 Hz)	7.62 (1H, d, J = 2,1 Hz)	7.47 (1H, d, J = 2.0 Hz)	7.63 (1H, d, J = 2.1 Hz)
H6′	6.62 (1H, d, J = 2.1 Hz)	7.12 (1H, d, J = 2.2 Hz)	7.14 (1H, d, J = 2.1 Hz)	6.63 (1H, d, J = 2.1 Hz)	7.00 (1H, d, J = 2,1 Hz)	6.58 (1H, d, J = 2.0 Hz)	7.01 (1H, d, J = 2.1 Hz)
H2	-	-	-	-	-	-	-
H4	-	-	-	7.54 (1H, s)	7.66 (1H, s)	7.87 (s, 1H)	8.13 (s, 1H)
OAc′ (Ring B)	-	-	2.36 (3H, s)	-	-	2.36 (s, 3H)	2.36 (s, 3H)
OAc (Ring A)	2.47 (3H, s)	2.40 (3H, s)	2.24 (3H, s)	2.47 (3H, s)	2.40 (3H, s)	2.25 (s, 3H)	2.24 (s, 3H)

Table S59. ¹H NMR Data of **2, 14, 16–18**

Pos	Compound					
	2 (CD$_3$OD)	**14** (CD$_3$OD)	**16** (Me$_2$CO-d_6)	**16** (Me$_2$CO-d_6)	**17** (Me$_2$CO-d_6)	**18** (Me$_2$CO-d_6)
H4′	7.32 (1H, d, J = 2.3 Hz)	7.31 (1H, d, J = 2.3 Hz)	7.38 (1H, d, J = 2.5 Hz)	7.36 (1H, d, J = 2.3 Hz)	7.27 (1H, d, J = 2.5 Hz)	7.81 (1H, d, J = 2.5 Hz)
H6′	6.65 (1H, bs)	6.45 (1H, d, J = 2.3 Hz)	6.64 (1H, d, J = 2.5 Hz)	6.84 (1H, d, J = 2.3 Hz)	6.69 (1H, d, J = 2.5 Hz)	6.67 (d, overlapped)
H2	-	7.38 (1H, s)	7.24 (1H, d, J = 2.5 Hz)	7.16 (1H, d, J = 2.3 Hz)		-
H3	-	-	-	-	7.78 (1H, d, J = 2.5 Hz)	-
H4	7.39 (1H, bs)	-	7.37 (1H, d, J = 2.5 Hz)	7.27 (1H, d, J = 2.3 Hz)	-	7.03 (1H, dd, J = 8.5 Hz)
H5	-	-	-	-	6.74 (1H, d, J = 2.5 Hz)	7.03 (1H, dd, J = 8.5 Hz)

Table S60. ^{1}H NMR Data of **20, 24, 26**

20 **23** **26**
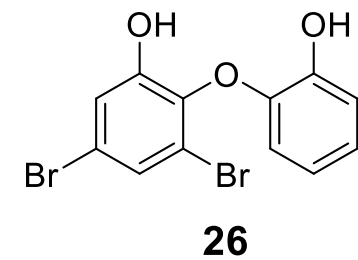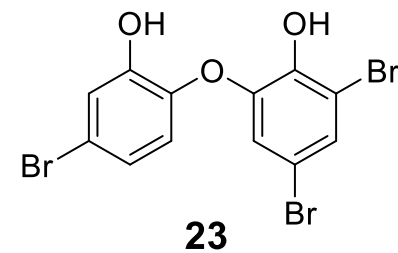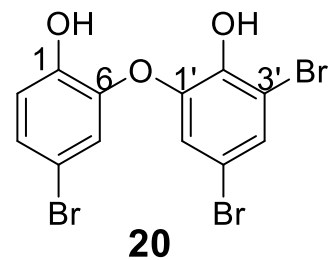
Pos	20 (Me$_2$CO-d$_6$)	20 (CD$_3$OD)	23 (Me$_2$CO-d$_6$)	26 (CD$_3$OD)
H3′	-	-		6.87 (1H, d, J = 2.0 Hz)
H4′	7.37 (1H, d, J = 2.3 Hz)	7.07 (1H, d, J = 2.0 Hz)	7.03 (1H, d, J = 2.0 Hz)	6.87 (1H, dq, J = 8.0, 2.0 Hz)
H5′	-	-		6.62 (1H, td, J = 8.0, 2.0 Hz)
H6′	6.60 (1H, d, J = 2.3 Hz)	6.79 (1H, q, J = 2.0 Hz)	6.67 (1H, d, J = 2.0 Hz)	6.48 (1H, d, J = 8.0 Hz)
H2	6.91 (1H, d, J = 8.5 Hz)	6.74 (1H, d, J = 8.5 Hz)	7.12 (1H, d, J = 2.0 Hz)	7.05 (1H, d, J = 2.5 Hz)
H3	7.06 (1H, dd, J = 8.5, 2.3 Hz)	6.97 (1H, dd, J = 8.5, 2.0 Hz)		-
H4	-	-	6.93 (1H, dd, J = 8.5, 2.0 Hz)	7.22 (1H, d, J = 2.5 Hz)
H5	7.27 (1H, d, J = 2.3 Hz)	6.79 (1H, q, J = 2.0 Hz)	6.75 (1H, d, J = 8.5 Hz)	-

Table S61. E_{HOMO}, E_{LUMO}, and ΔE for **1–30**

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (E_{LUMO}-E_{HOMO}) (eV)
1	-8.67	-0.05	8.62
2	-8.75	0.27	9.02
3	-8.48	0.33	8.81
4	-8.65	0.21	8.86
5	-8.48	0.28	8.76
6	-8.79	0.22	9.01
7	-8.52	-0.08	8.44
8	-8.74	-0.12	8.62
9	-8.71	0.29	9.00
10	-8.60	-0.26	8.34
11	-9.12	-0.47	8.65
12	-8.56	0.14	8.70
13	-9.10	-0.02	9.08
14	-8.62	0.20	8.82
15	-8.48	0.18	8.66
16	-8.76	0.38	9.14
17	-8.44	0.27	8.71
18	-8.51	0.35	8.86
19	-8.37	0.29	8.66
20	-8.30	0.43	8.73
21	-8.67	0.60	9.27
22	-8.66	0.63	9.29
23	-8.52	0.56	9.08
24	-8.27	0.59	8.86
25	-8.31	0.72	9.03
26	-8.56	0.82	9.38
27	-8.39	0.71	9.10
28	-8.19	0.94	9.13
29	-8.34	0.99	9.33
30	-7.99	1.13	9.12