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DESIGNED SYNTHESIS OF "L" SHAPED 17-HALO-ARYL-ETHYNYL STEROIDS.

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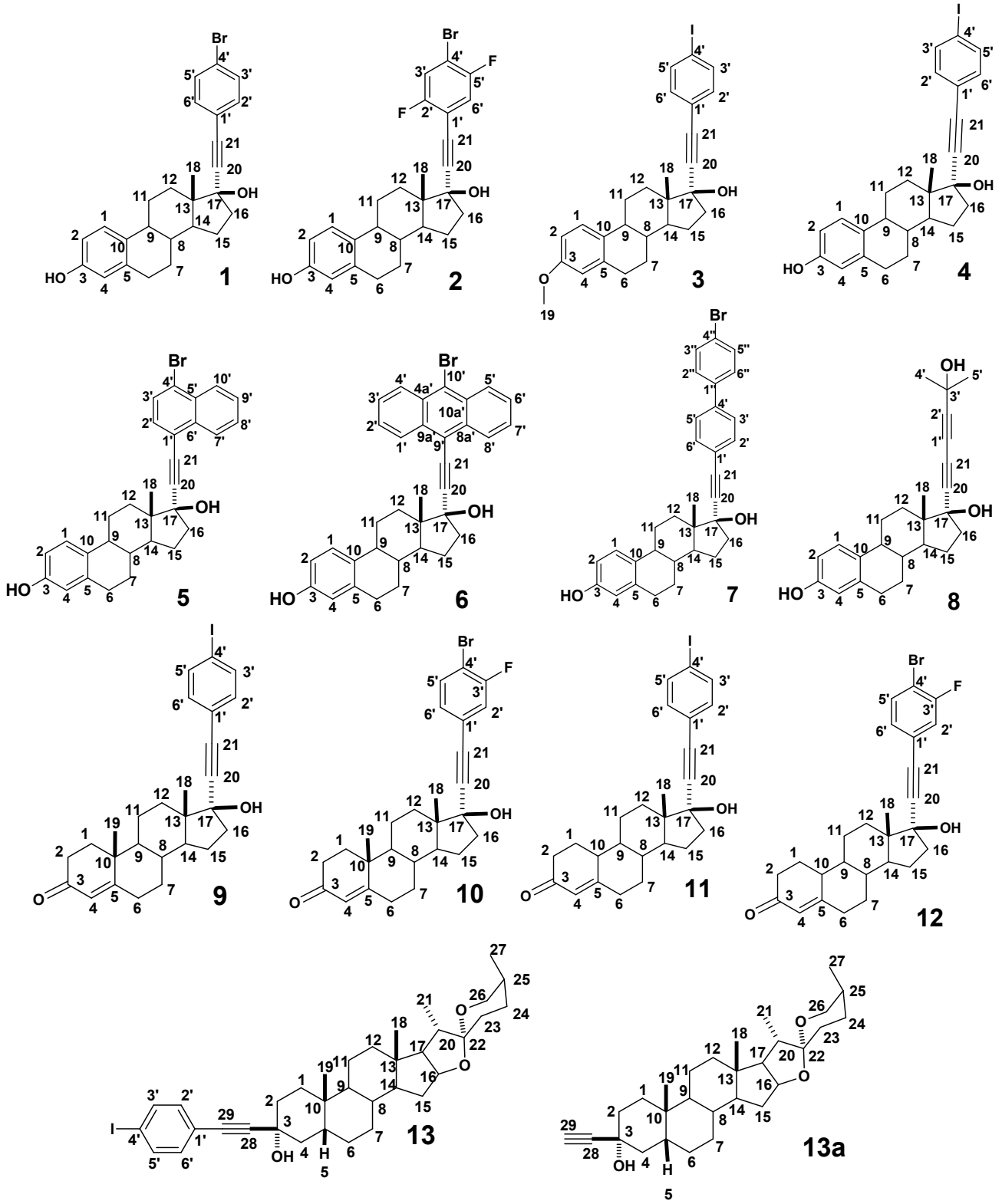


Scheme S1. Schematic numbering for all 13 derivatives used for ^{1}H and ^{13}C NMR spectra.

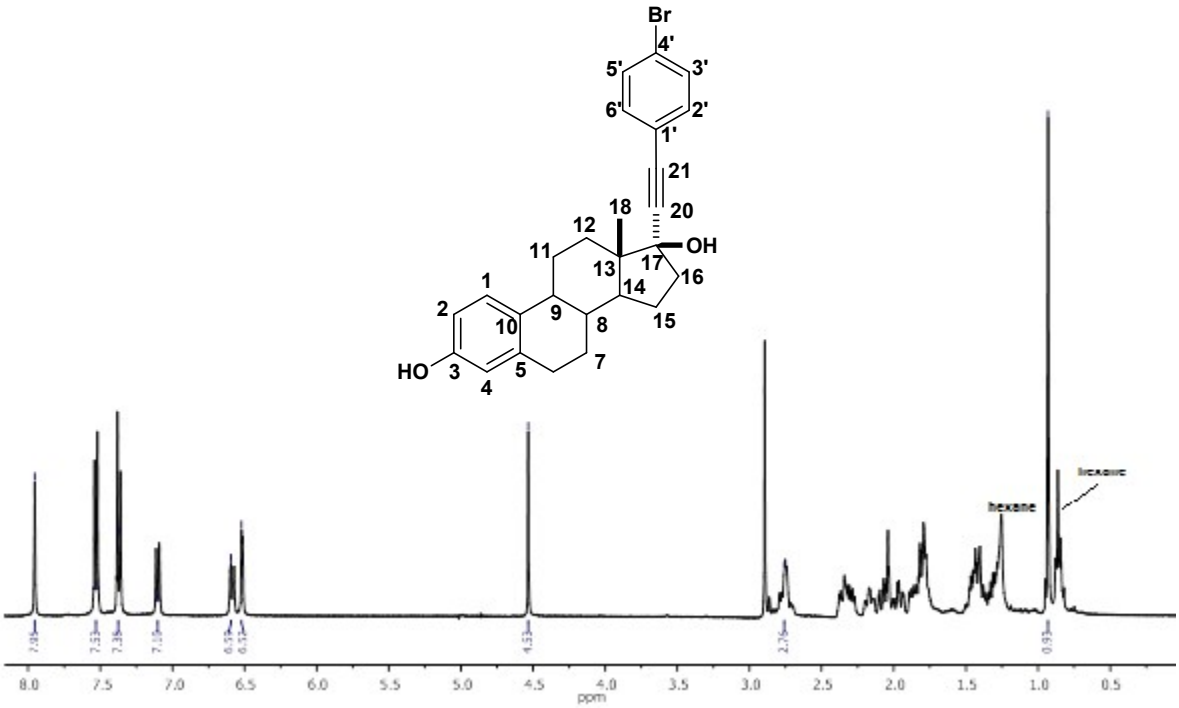


Figure S1. ^{1}H NMR spectrum for compound **1** (400 MHz, acetone-d_6).

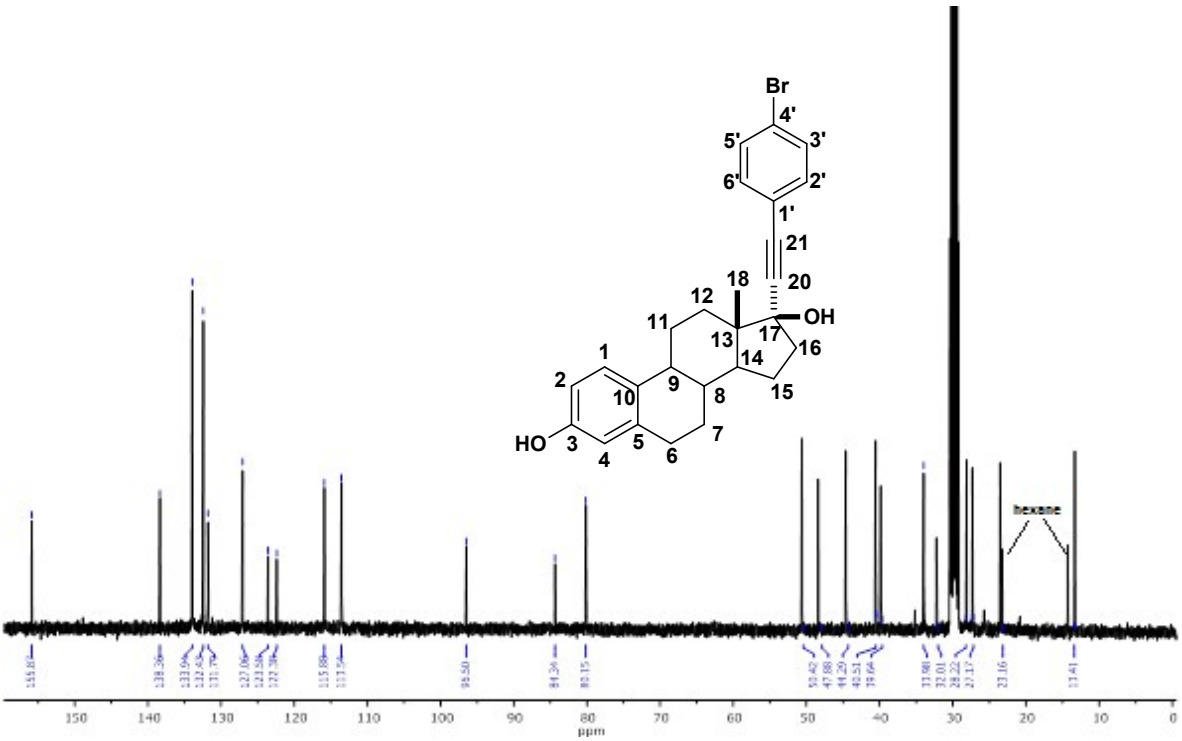


Figure S2. ^{13}C NMR spectrum for compound **1** (100 MHz, acetone-d_6).

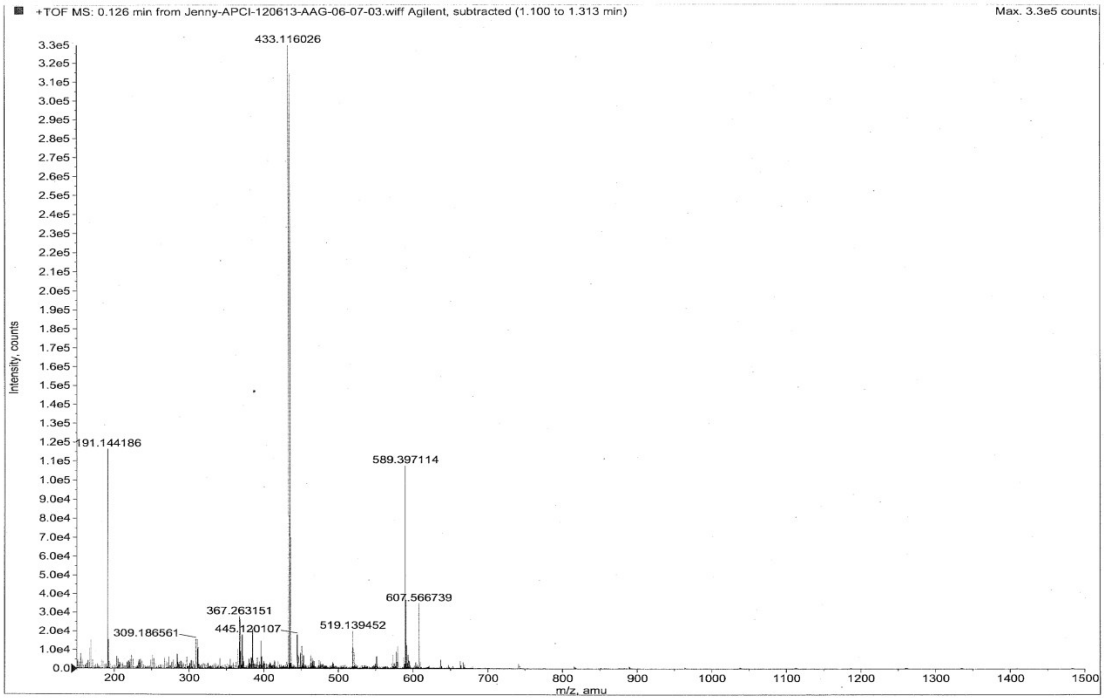


Figure S3. High resolution mass spectrum for compound **1** $[(C_{26}H_{27}O_2Br\text{-}H_2O)+H]^+$.

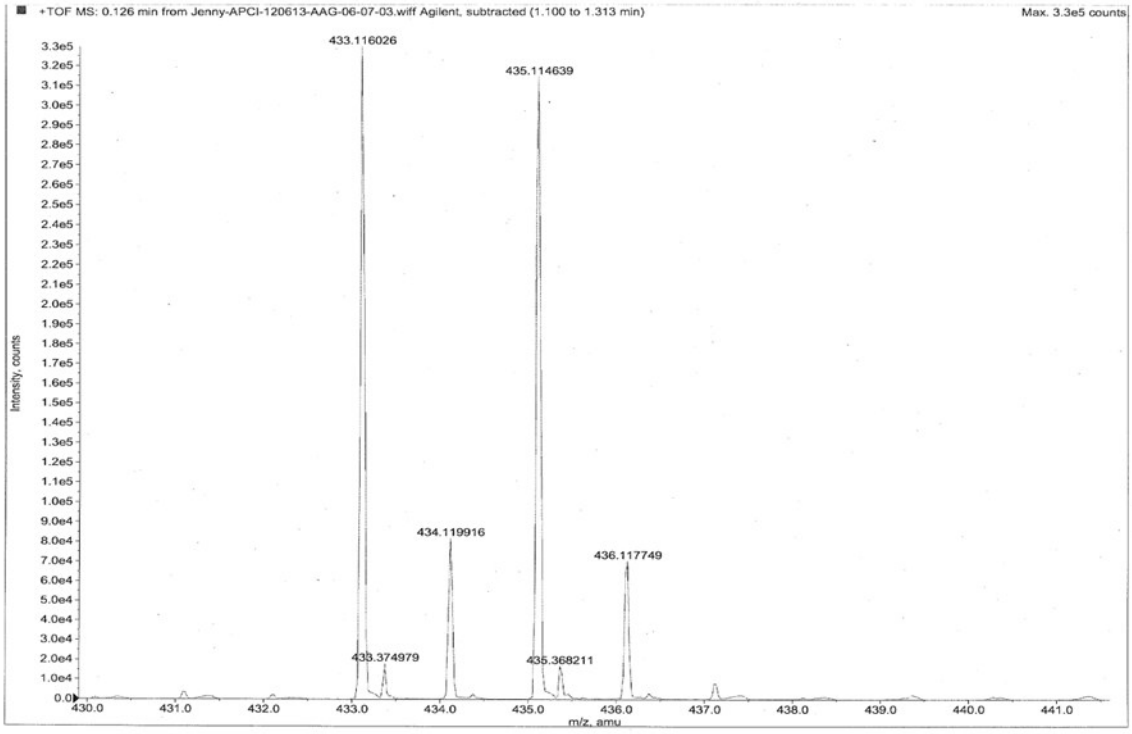


Figure S3a. High resolution mass spectrum for compound **1**

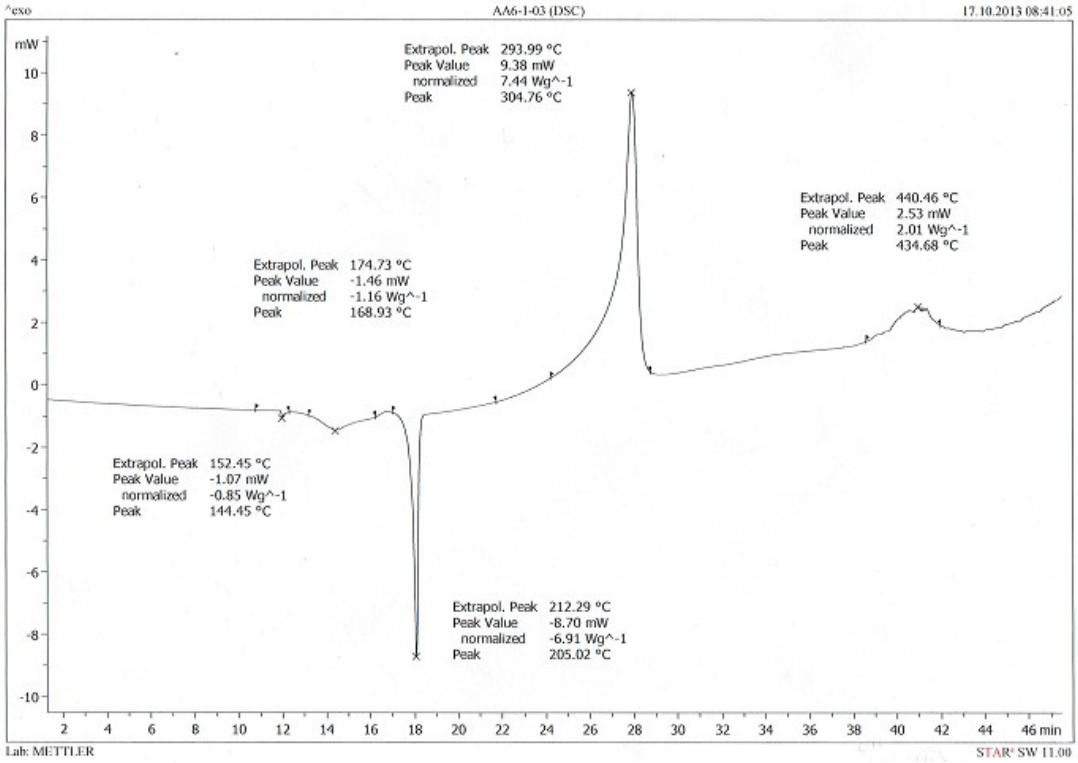


Figure S4. DSC for compound **1**.

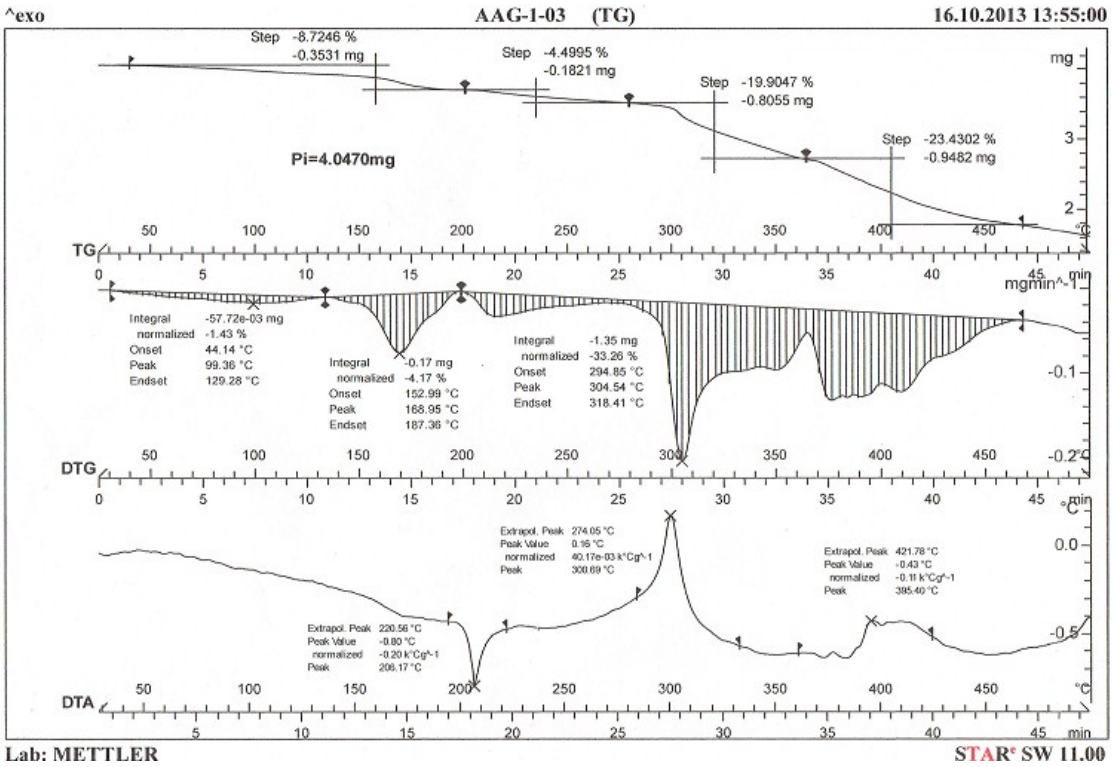


Figure S5. TGA for compound **1**.

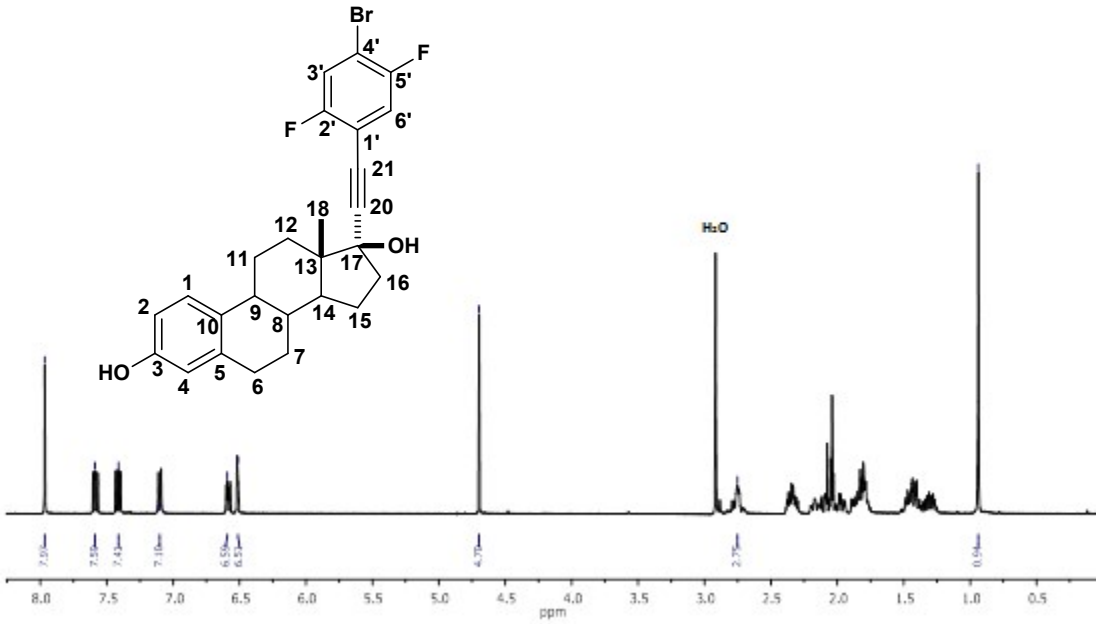


Figure S6. ^{1}H NMR spectrum for compound **2** (400 MHz, acetone-d_6).

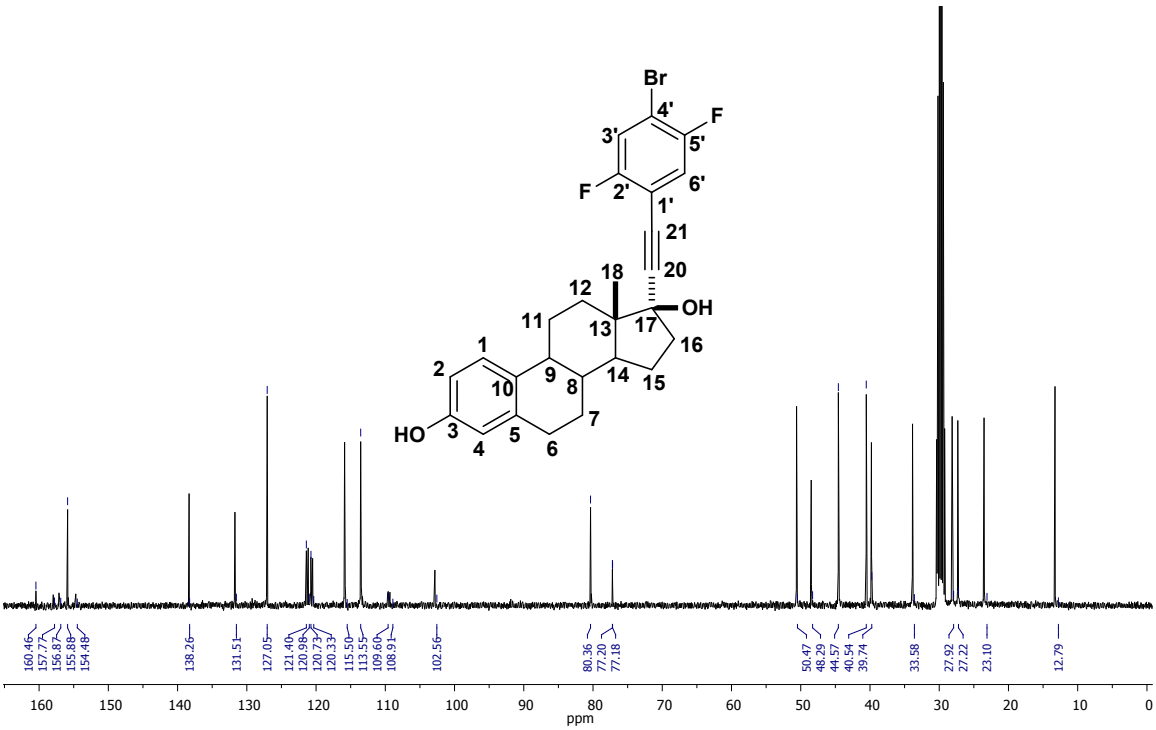


Figure S7. ^{13}C NMR spectrum for compound **2** (100 MHz, acetone-d_6).

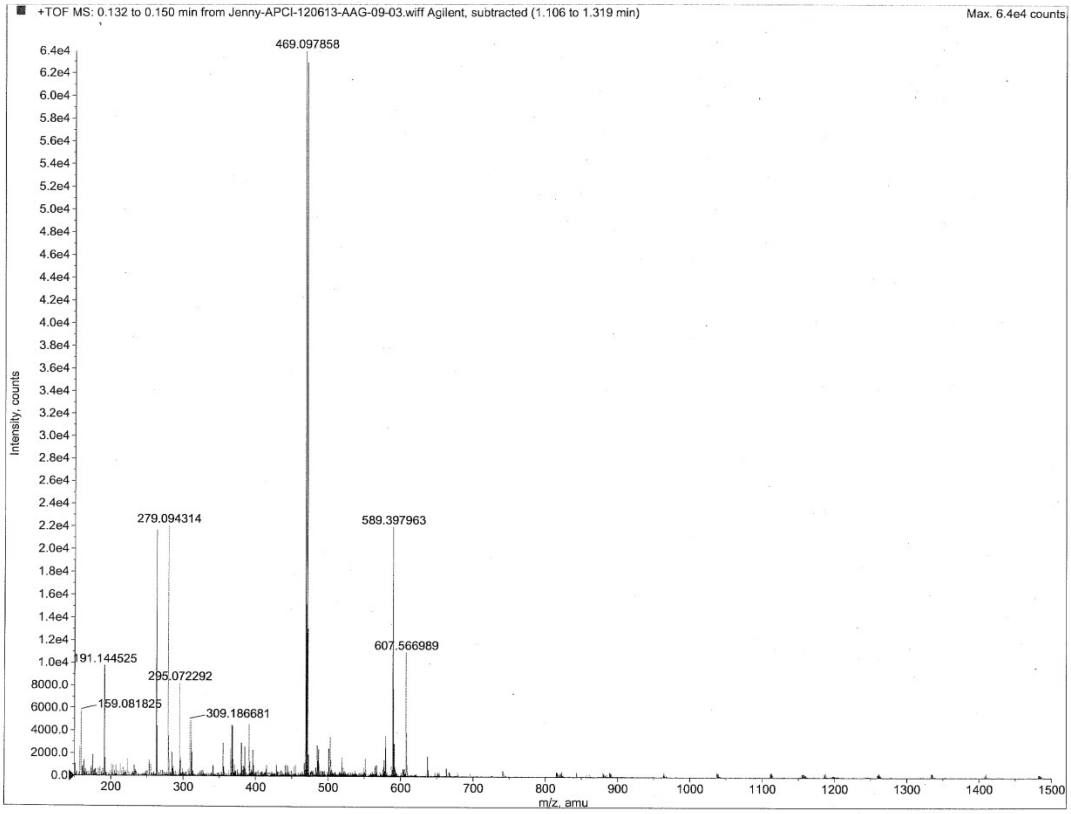


Figure S8. High resolution mass spectrum for compound **2** $[(C_{26}H_{25}O_2F_2Br–H_2O)+H]^+$**.**

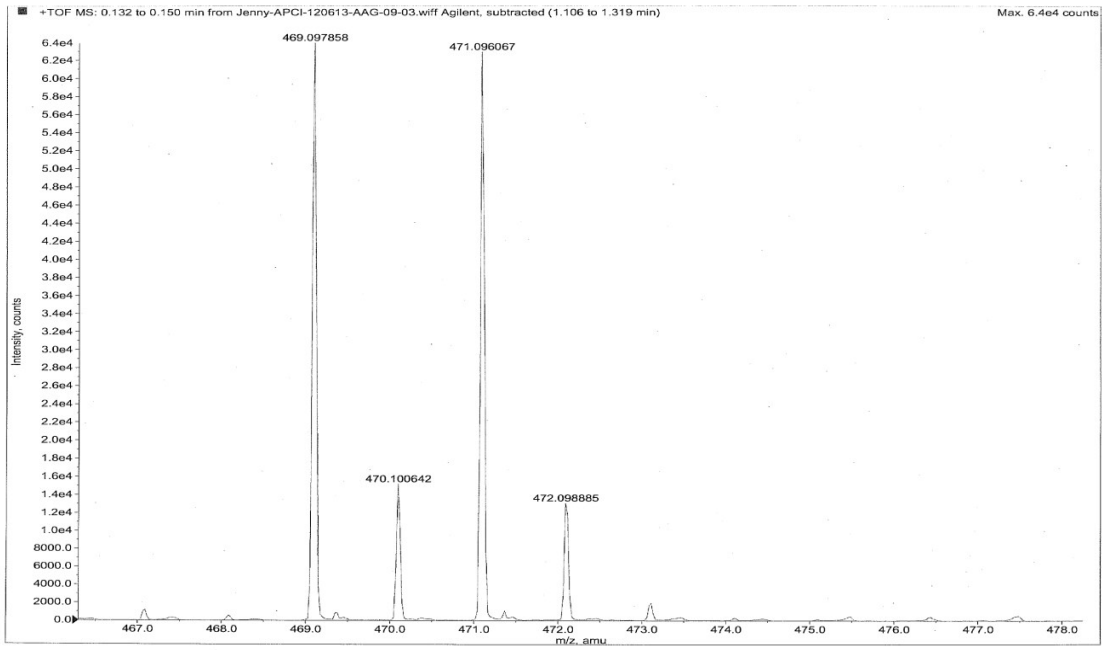


Figure S8a. High resolution mass spectrum for compound **2**

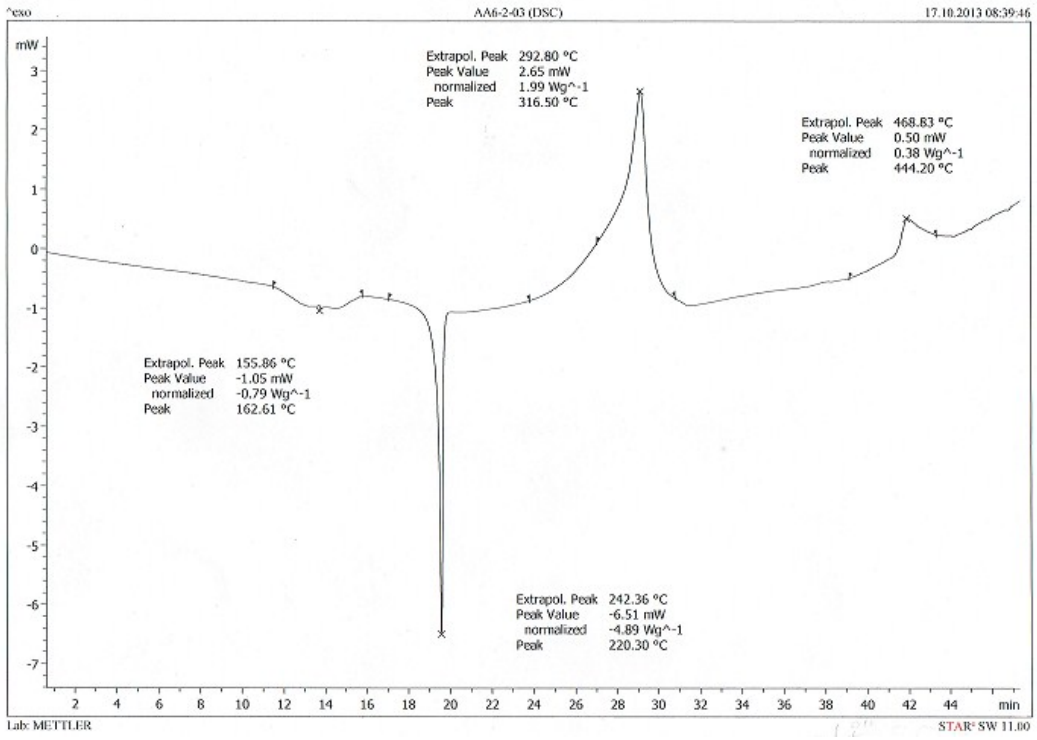


Figure S9. DSC for Compound **2**.

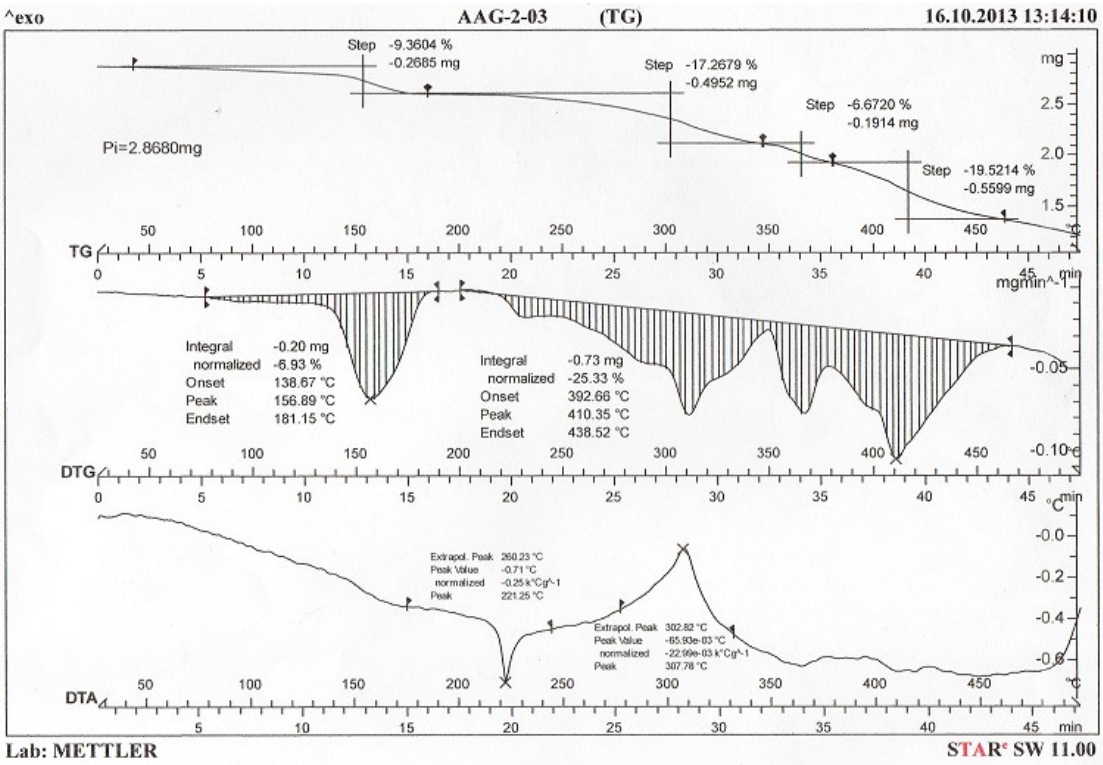


Figure S10. TGA for Compound **2**.

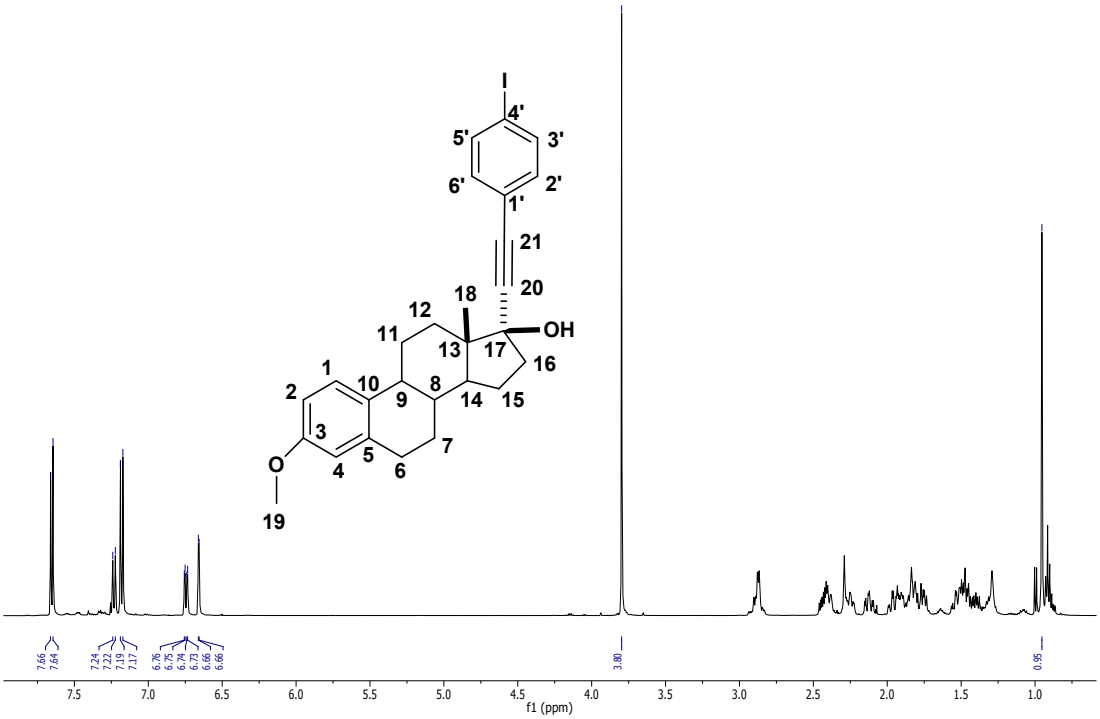


Figure S11. ^{1}H NMR spectrum for compound **3** (500 MHz, $CDCl_3$).

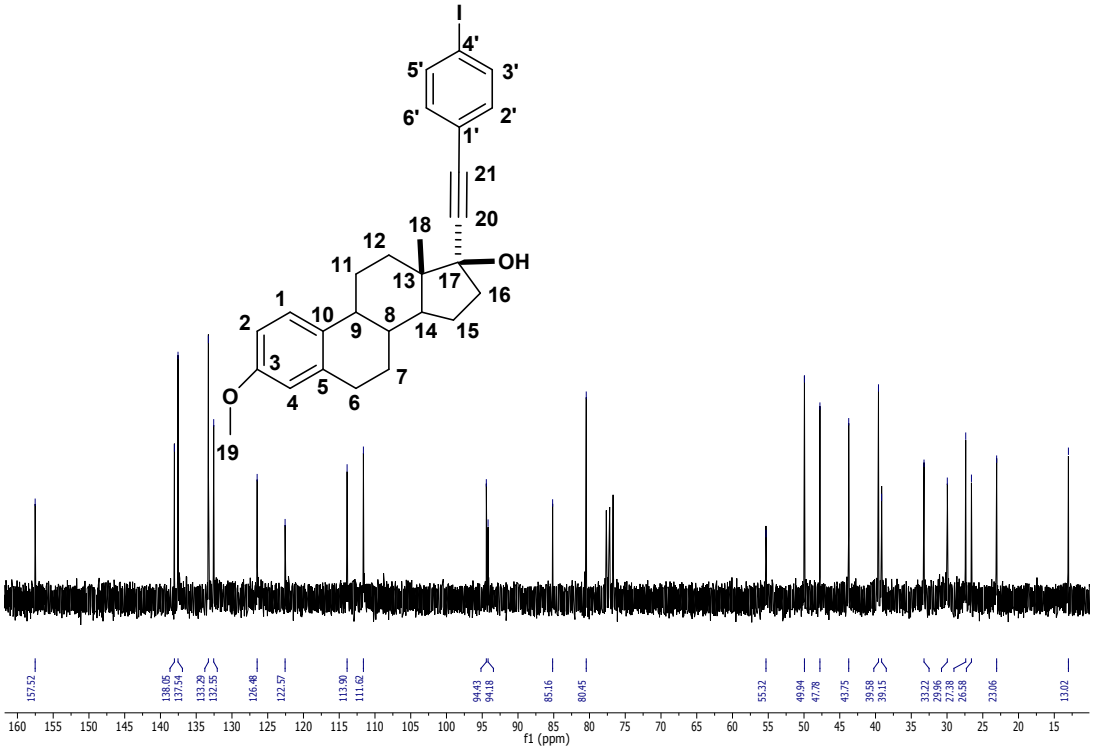


Figure S12. ^{13}C NMR spectrum for compound **3** (125.76 MHz, $CDCl_3$).

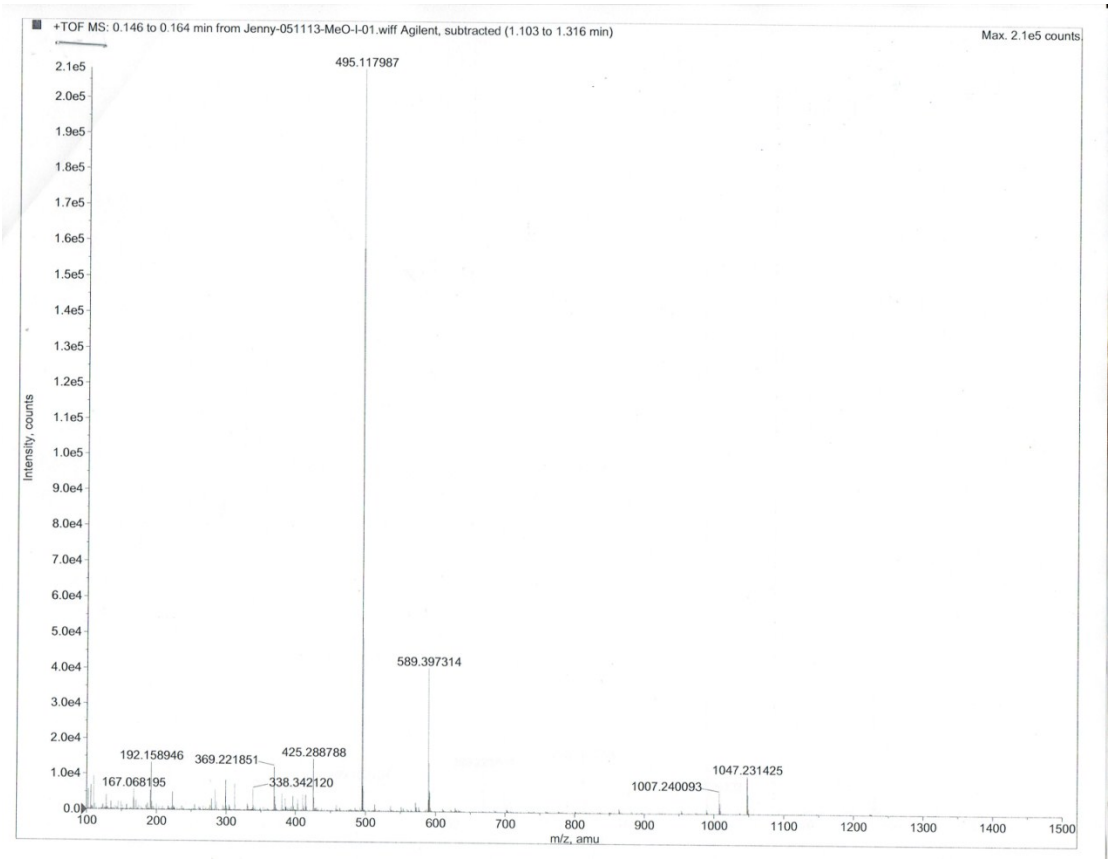


Figure S13. High resolution mass spectrum for compound **3** $[(C_{27}H_{29}IO_2 - H_2O)+H]^+$**.**

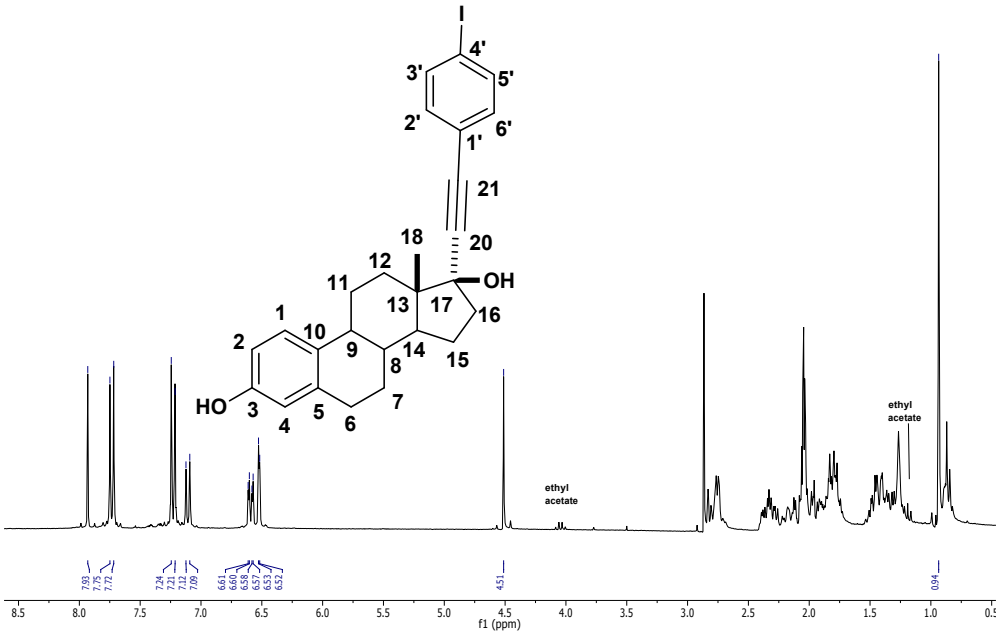


Figure S14. ^{1}H NMR spectrum for compound **4** (270 MHz, $CDCl_3$) .

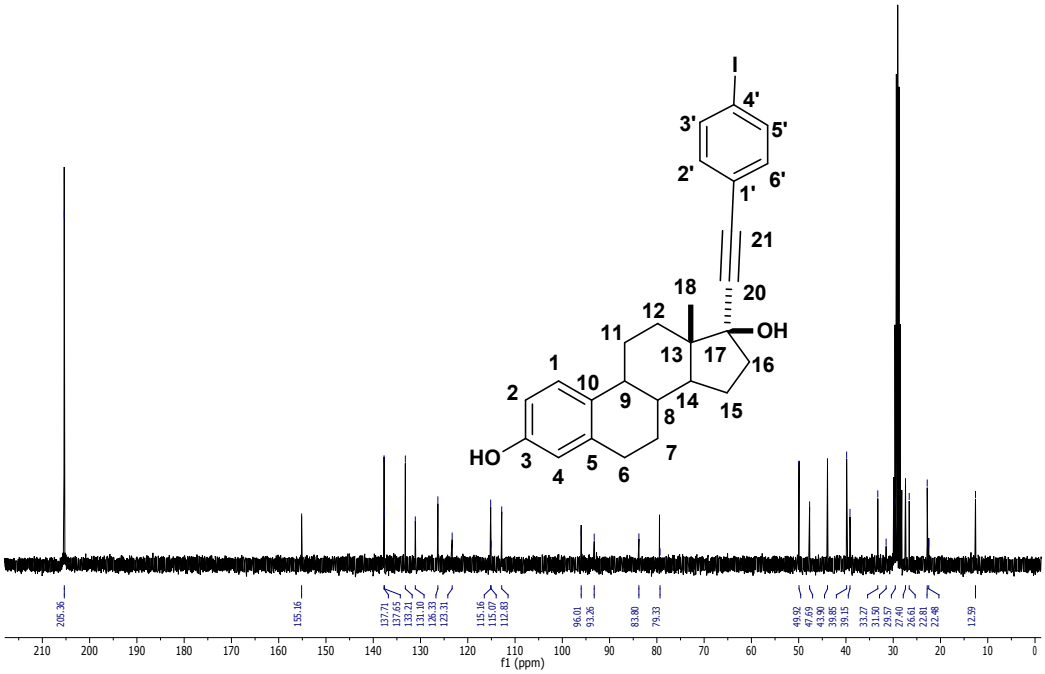


Figure S15. ^{13}C NMR spectrum for compound **4** (67.93 MHz, $CDCl_3$).

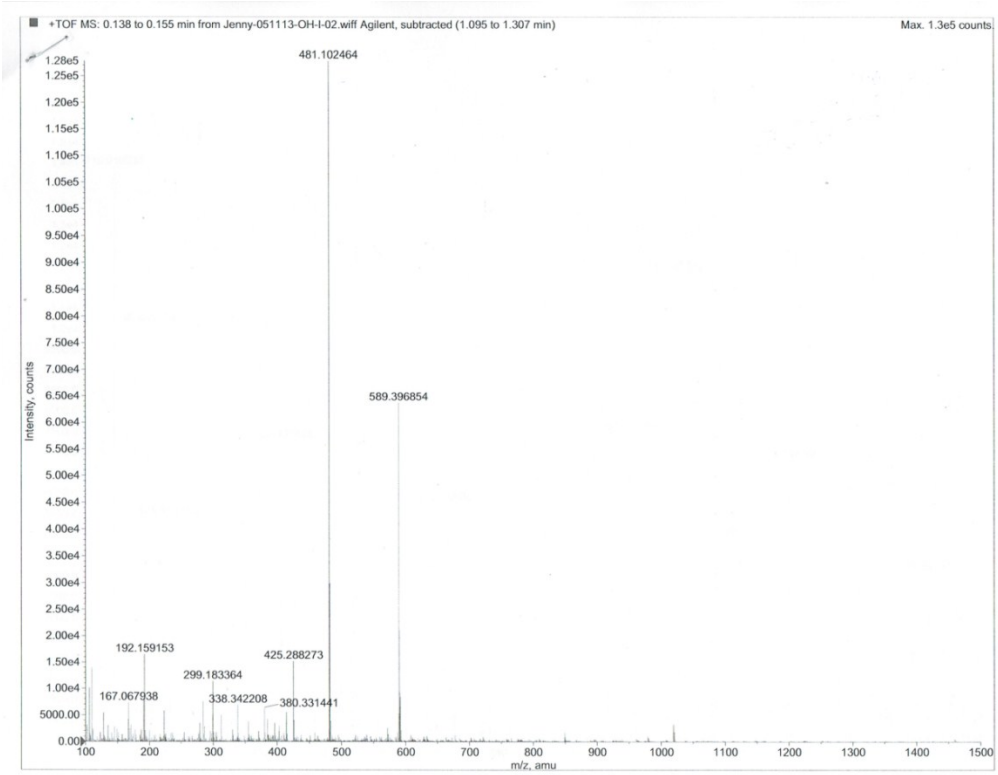


Figure S16. High resolution mass spectrum for compound **4** $[(C_{26}H_{27}IO_2–H_2O)+H]^+$**.**

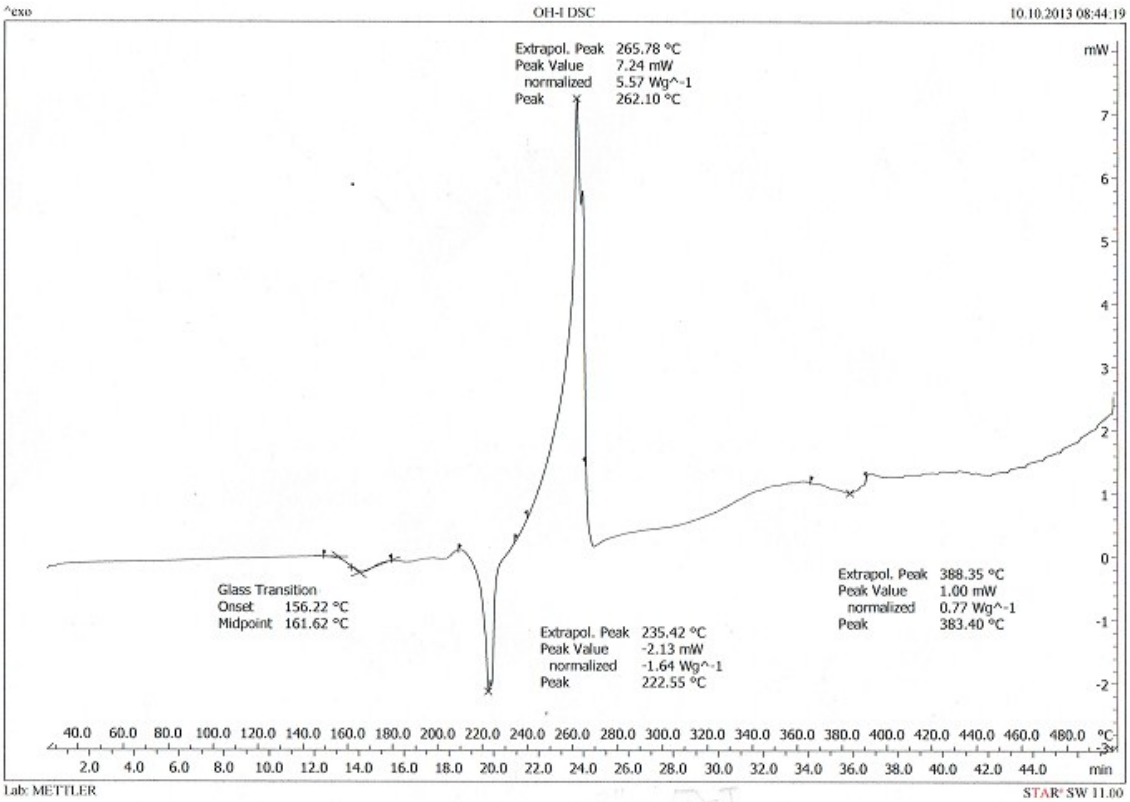


Figure S17. DSC for Compound **4**.

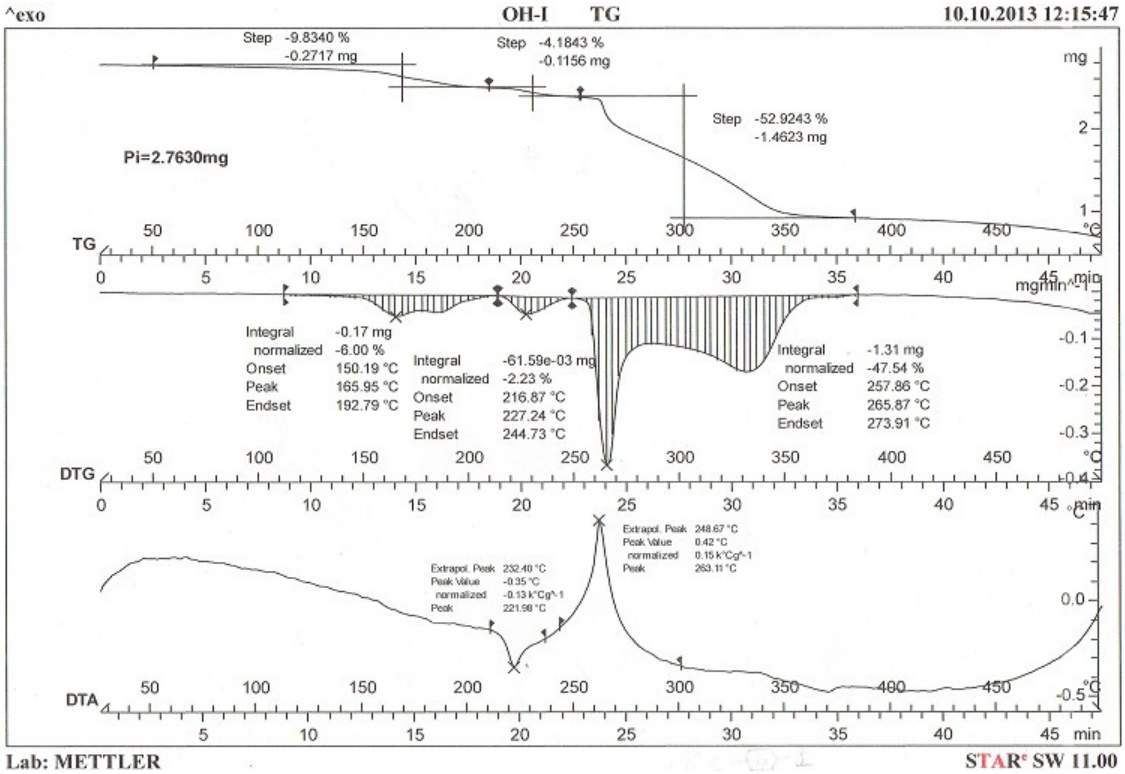


Figure S18. TGA for Compound **4**.

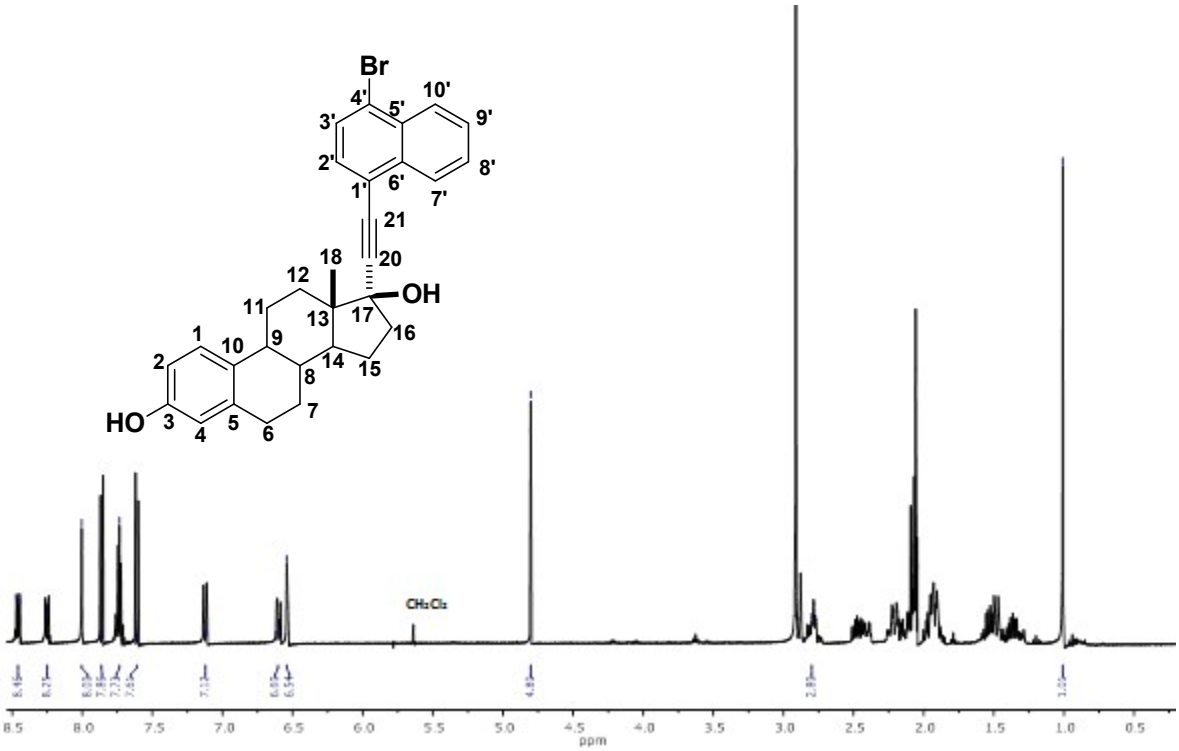


Figure S19. ^{1}H NMR spectrum for compound **5** (400 MHz, acetone-d_6).

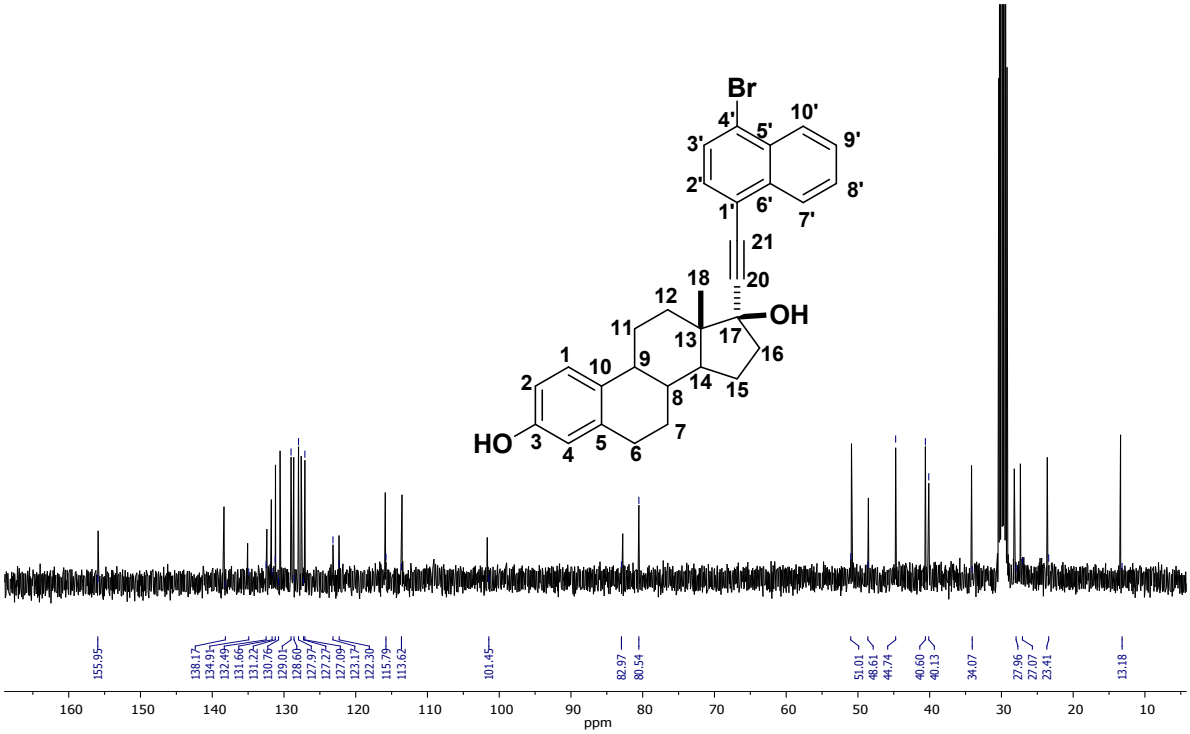


Figure S20. ^{13}C NMR spectrum for compound **5** (100 MHz, acetone-d_6).

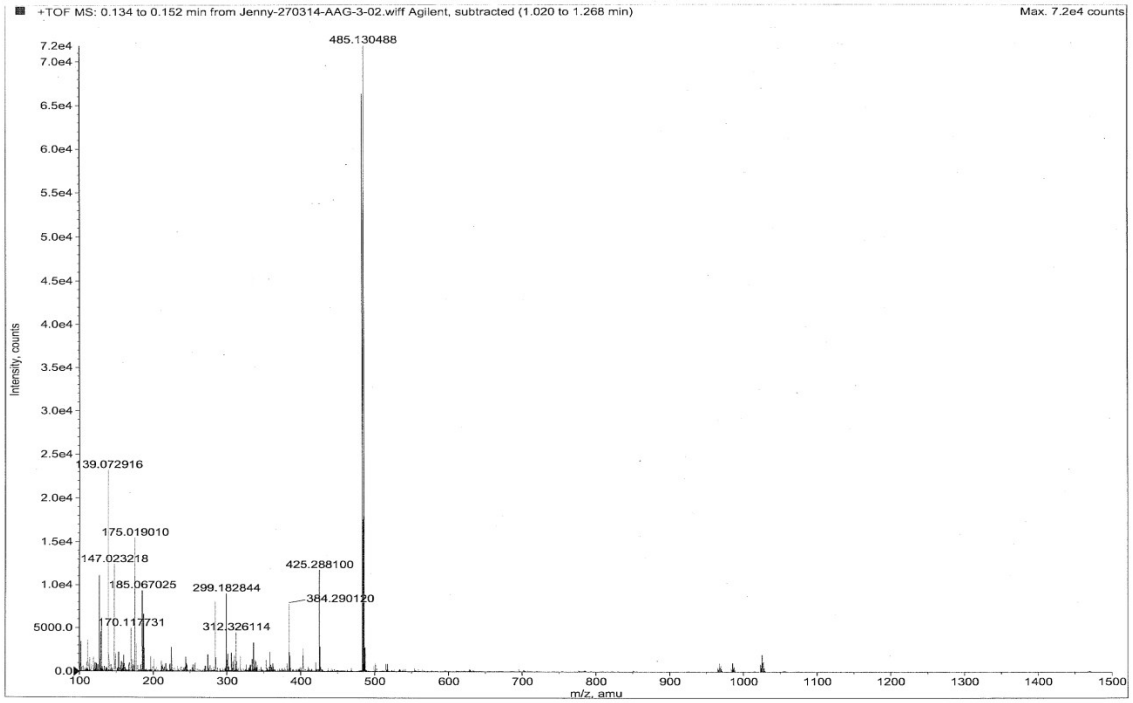


Figure S21. High resolution mass spectrum for compound **5** for $[C_{30}H_{29}O_2Br\text{-}H_2O)+H]^+$.

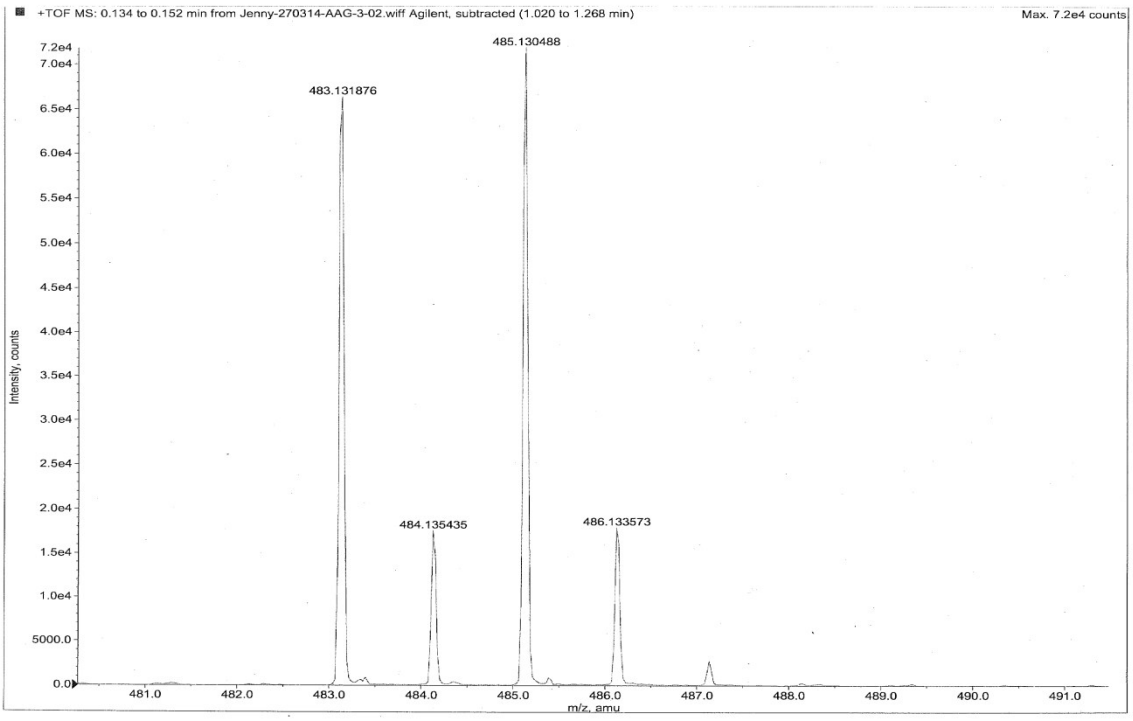


Figure S21a. High resolution mass spectrum for compound **5**

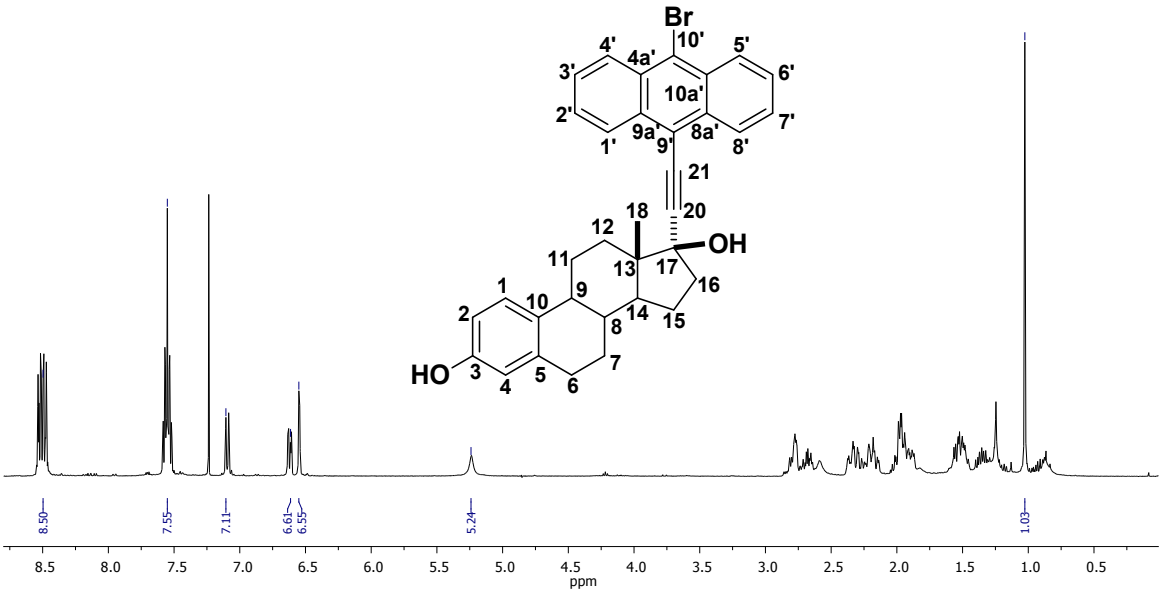


Figure S22. ^{1}H NMR spectrum for compound **6** (400 MHz, $CDCl_3$).

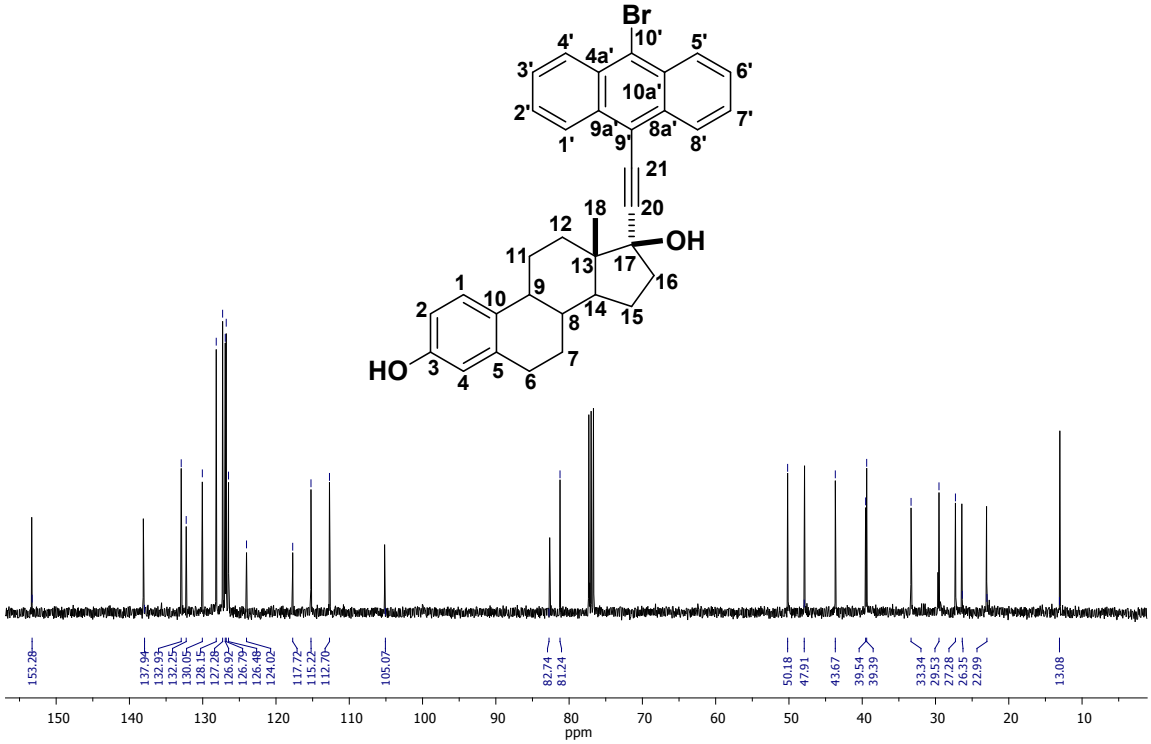


Figure S23. ^{13}C NMR spectrum for compound **6** (100 MHz, $CDCl_3$).

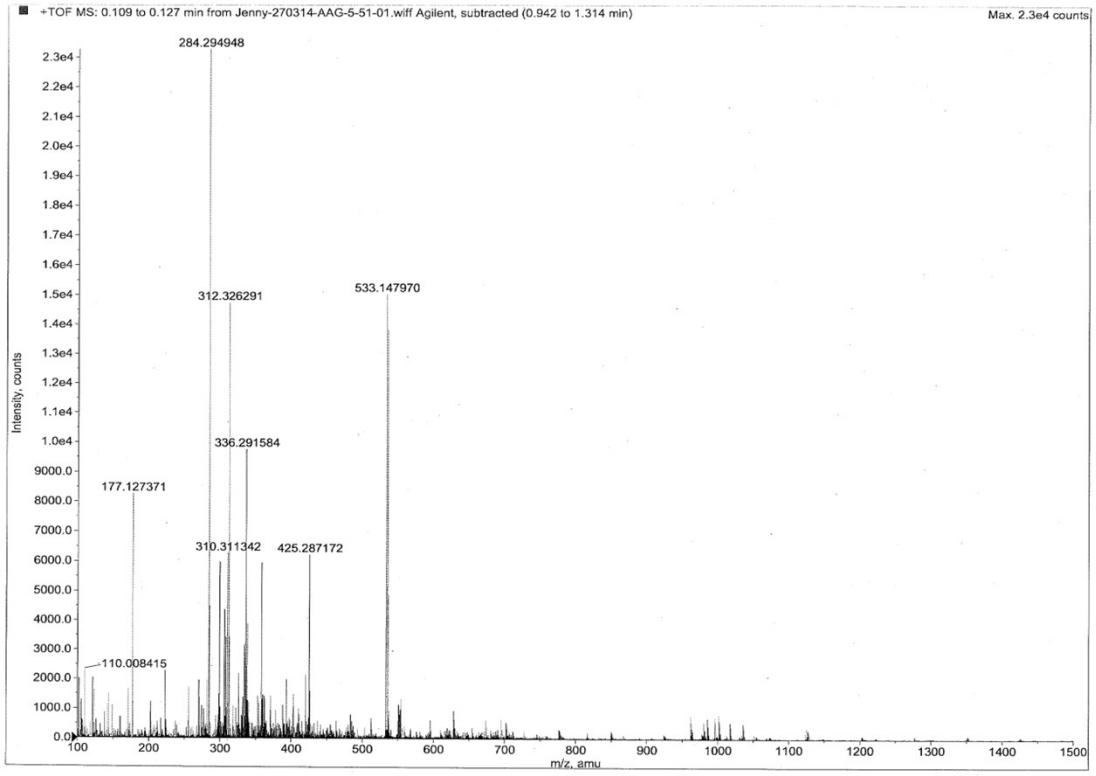


Figure S24. High resolution mass spectrum for compound **6** $[(C_{34}H_{31}O_2Br–H_2O)+H]^+$

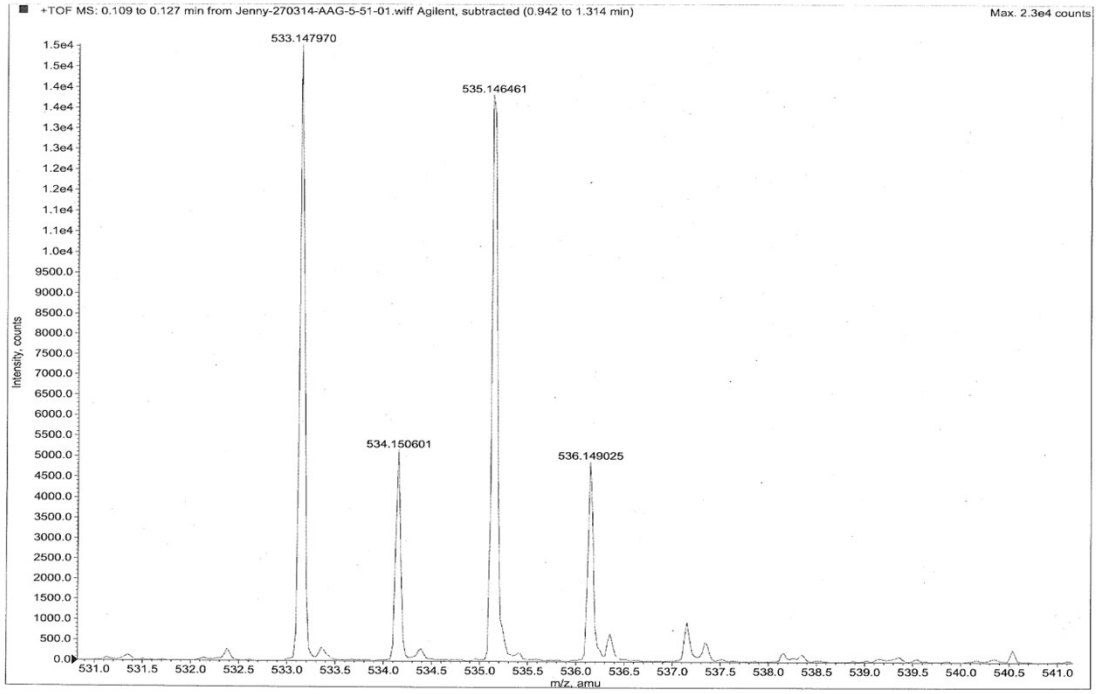


Figure S24a. High resolution mass spectrum for compound **6**

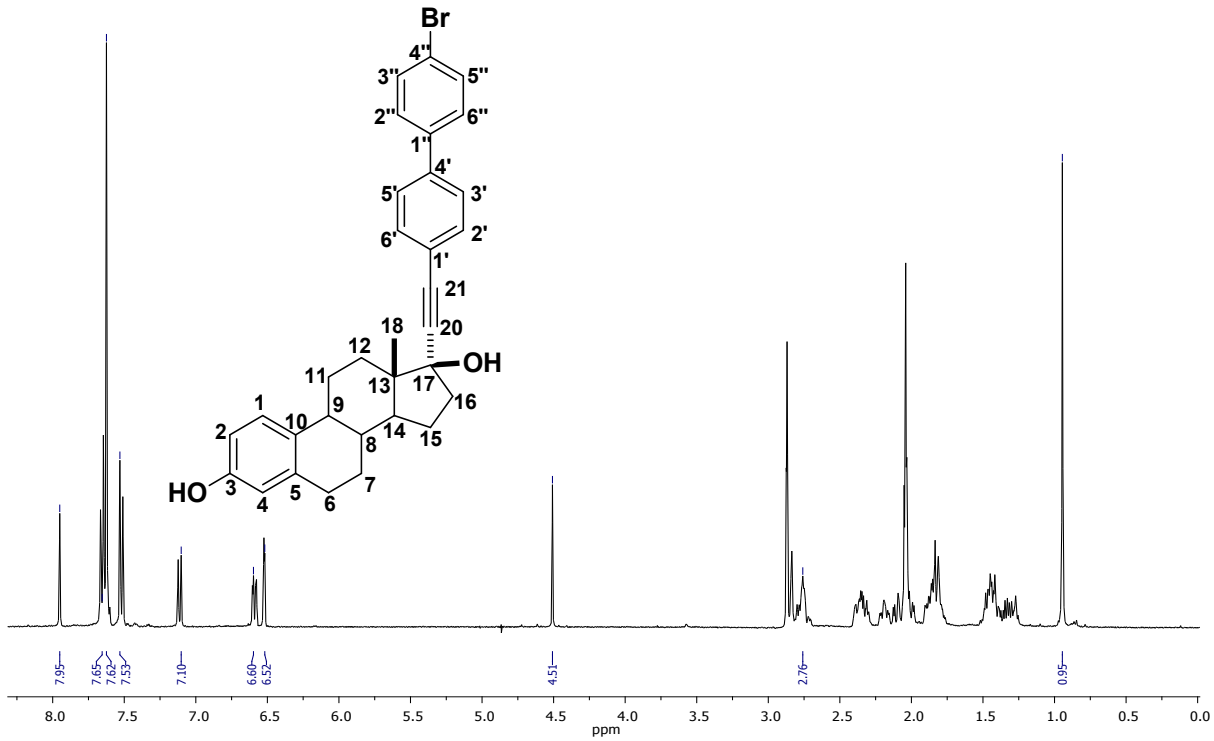


Figure S25. ^{1}H NMR spectrum for compound **7** (400 MHz, acetone-d_6).

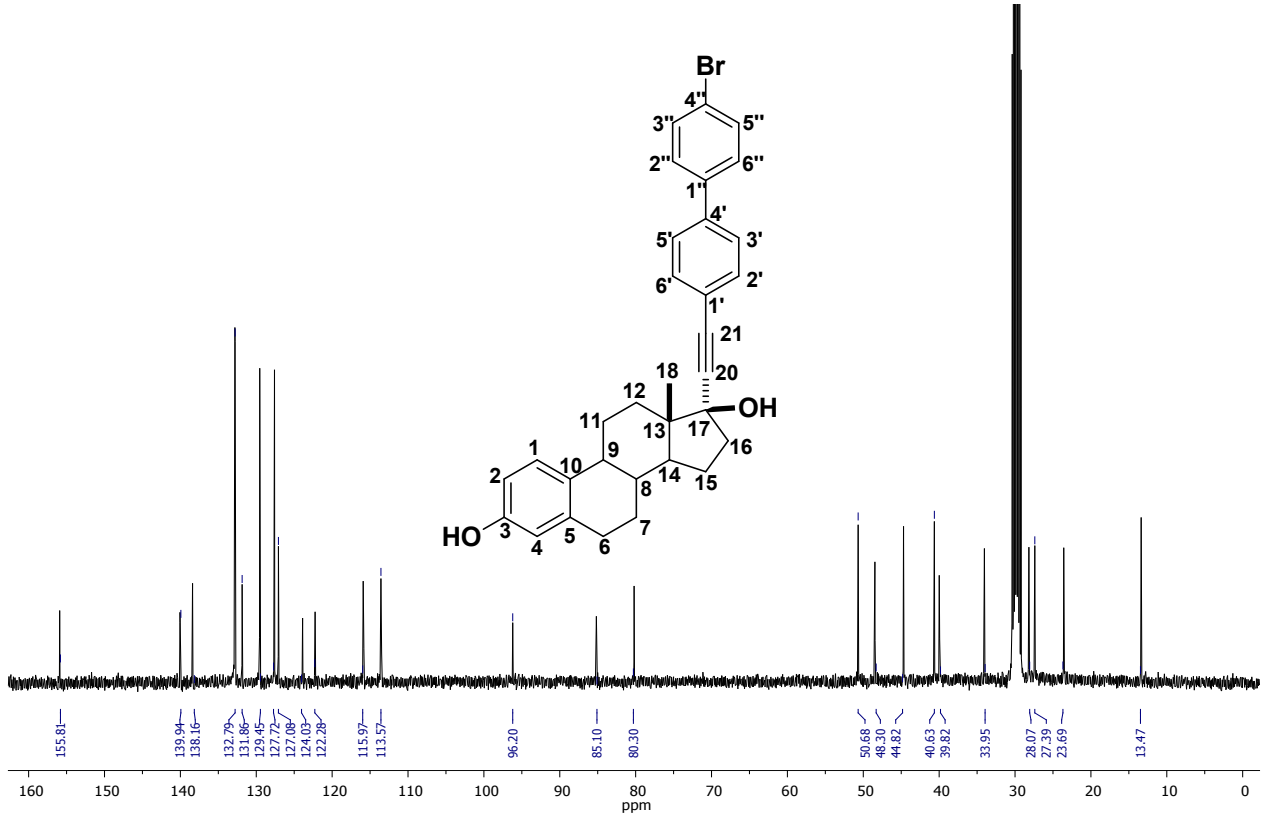


Figure S26. ^{13}C NMR spectrum for compound **7** (100 MHz, acetone-d_6).

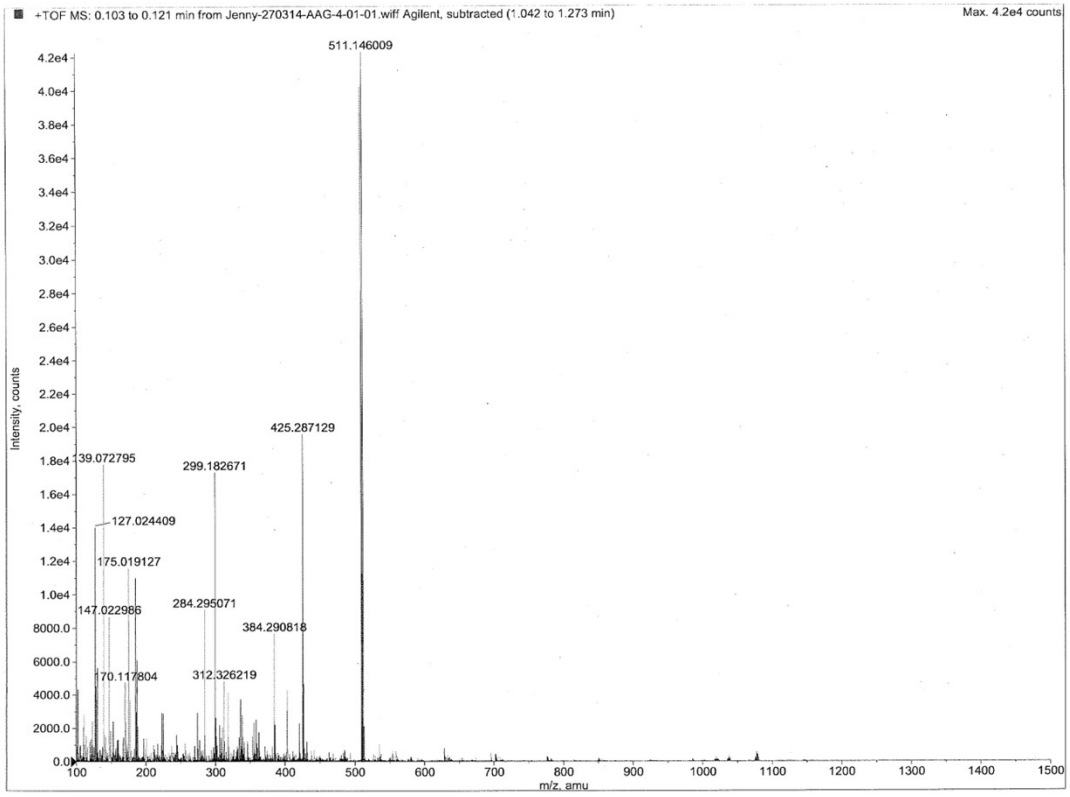


Figure S27. High resolution mass spectrum for compound **7** $[(C_{32}H_{31}O_2Br\text{-}H_2O)+H]^+$.

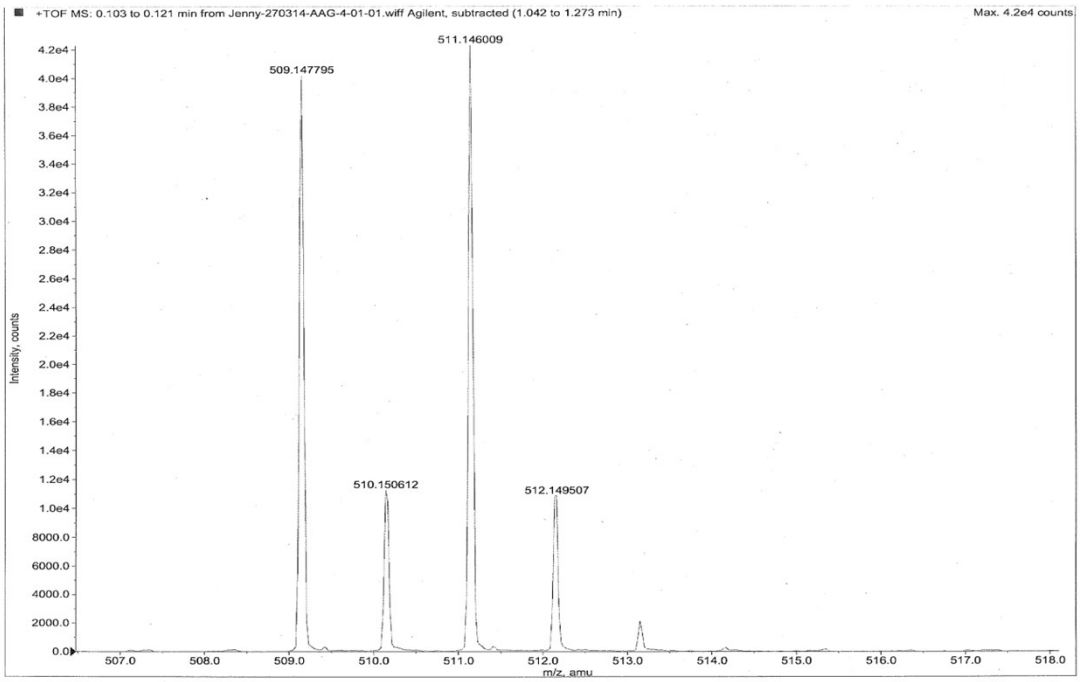


Figure S27a. High resolution mass spectrum for compound **7**

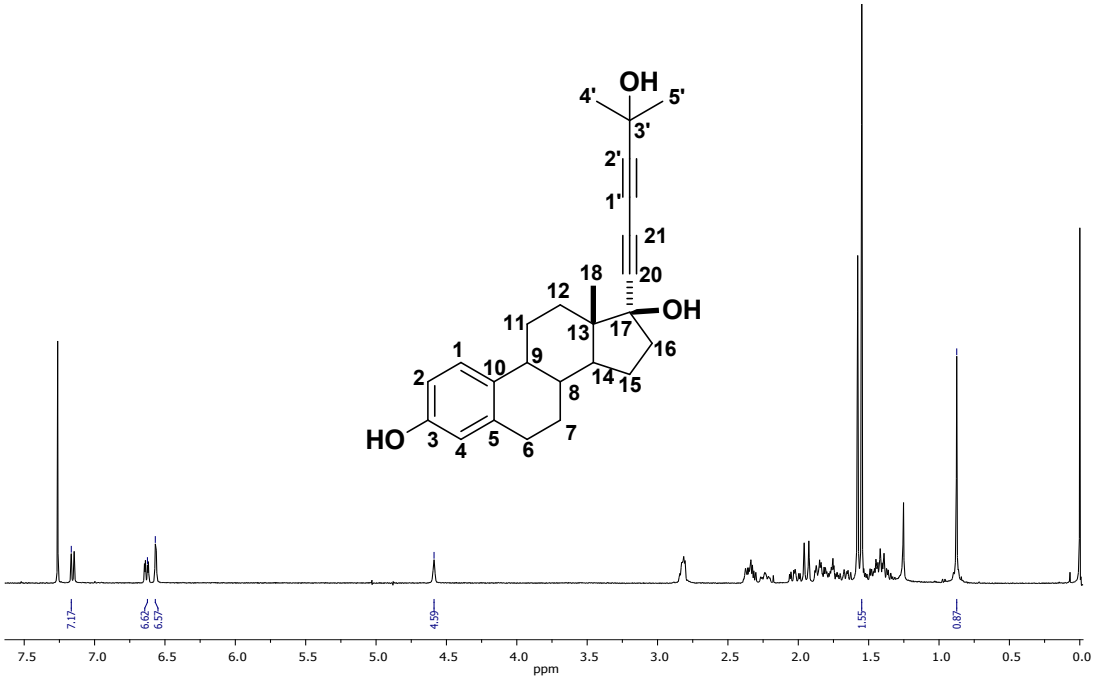


Figure S28. ^{1}H NMR spectrum for compound **8** (400 MHz, $CDCl_3$).

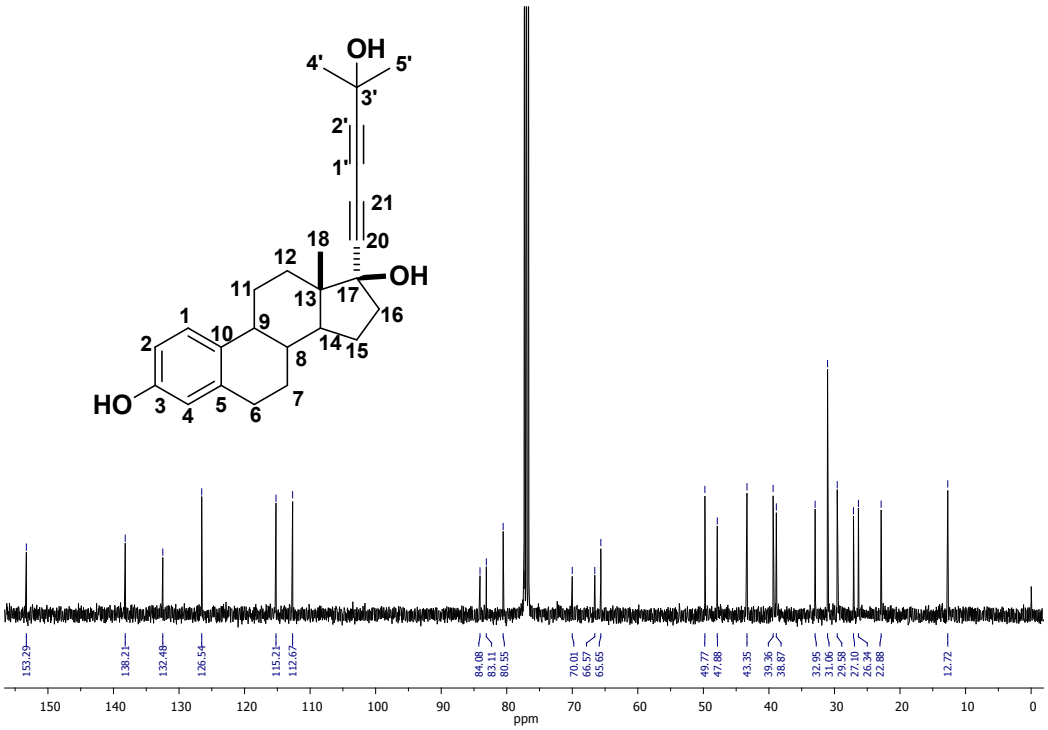


Figure S29. ^{13}C NMR spectrum for compound **8** (100 MHz, $CDCl_3$).

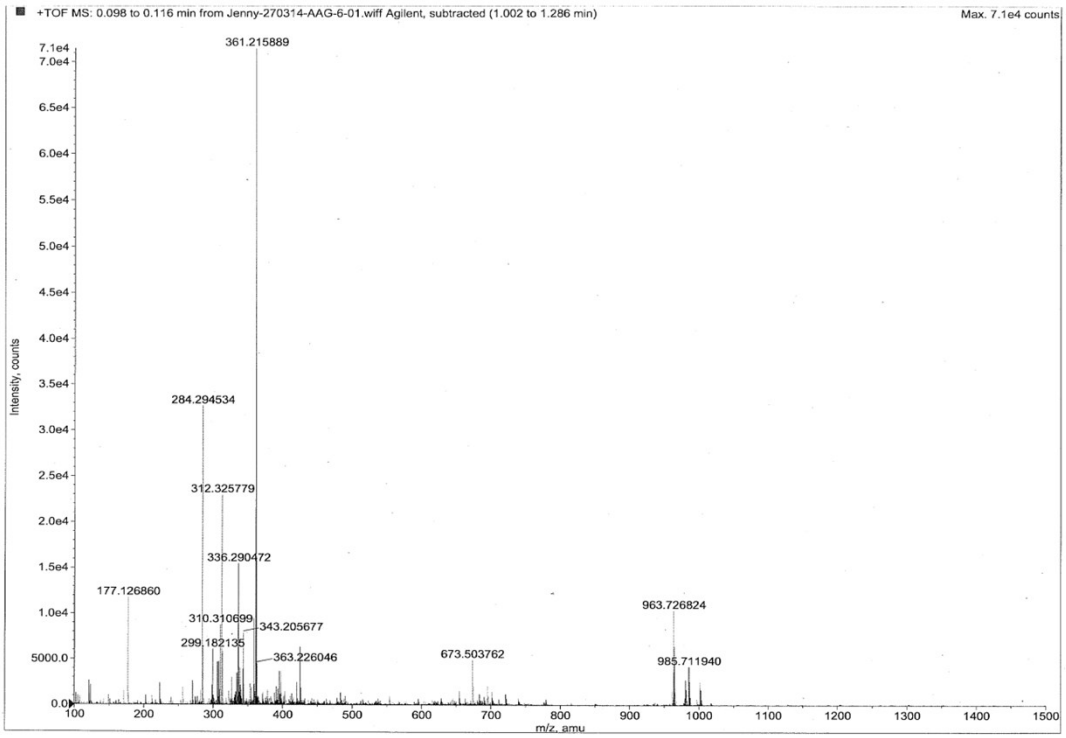


Figure S30. High resolution mass spectrum for compound **8** $[C_{25}H_{30}O_3\text{-}H_2O)+H]^+$.

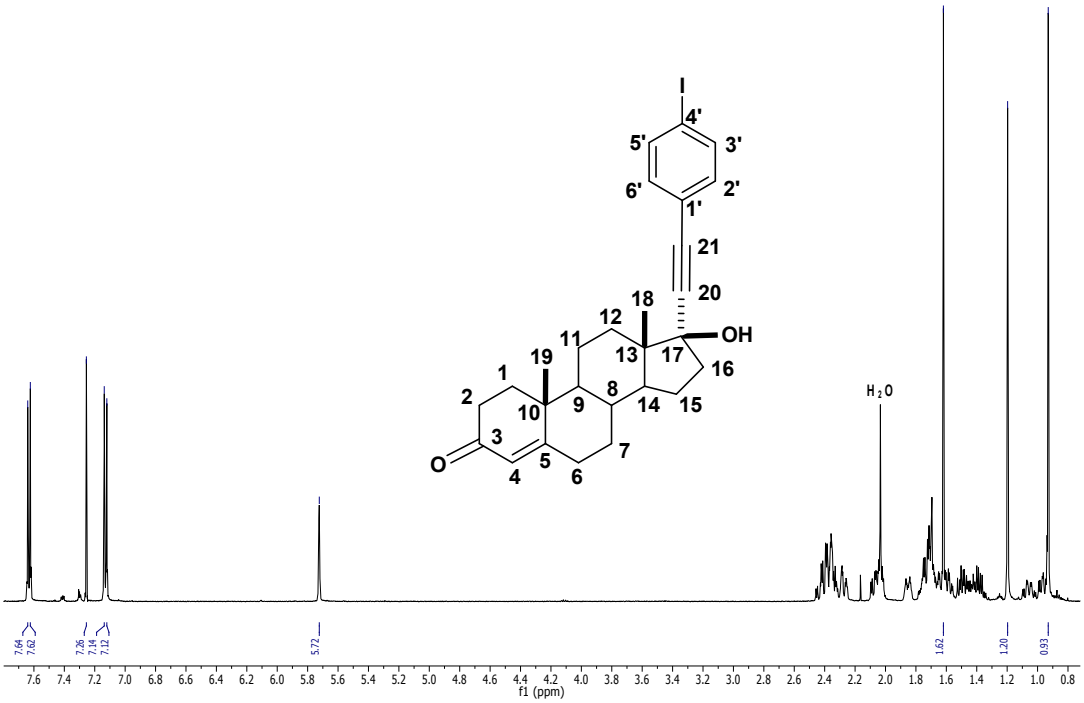


Figure S31. ^{1}H NMR spectrum for compound **9** (500 MHz, $CDCl_3$).

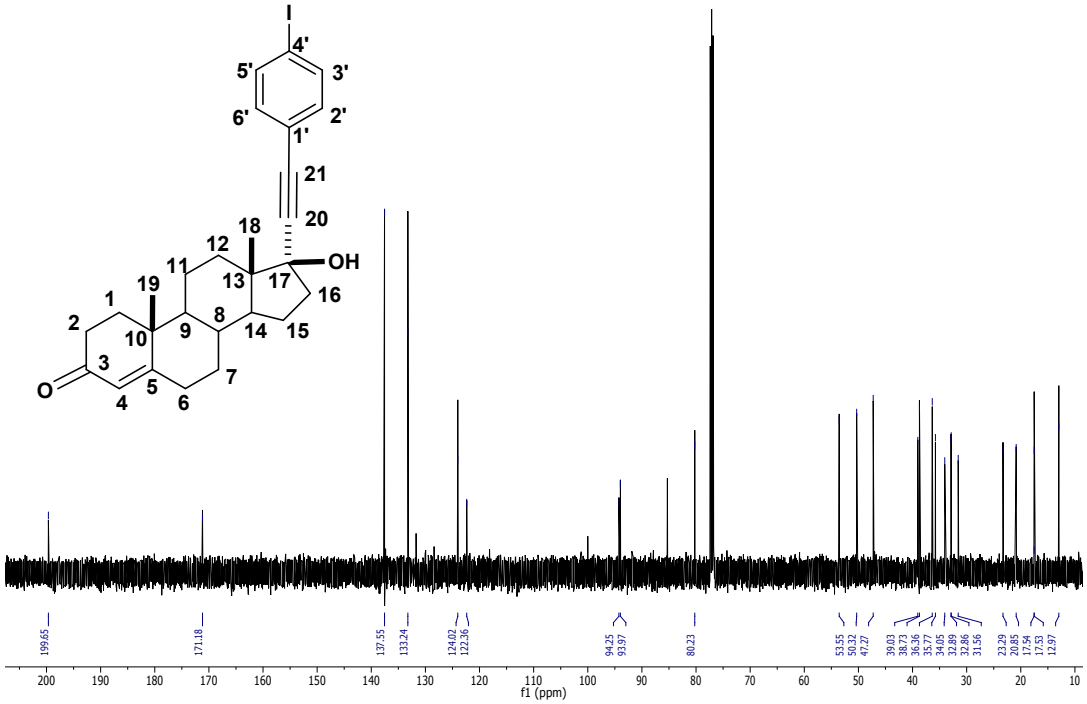


Figure S32. ^{13}C NMR spectrum for compound **9** (125.76 MHz, $CDCl_3$).

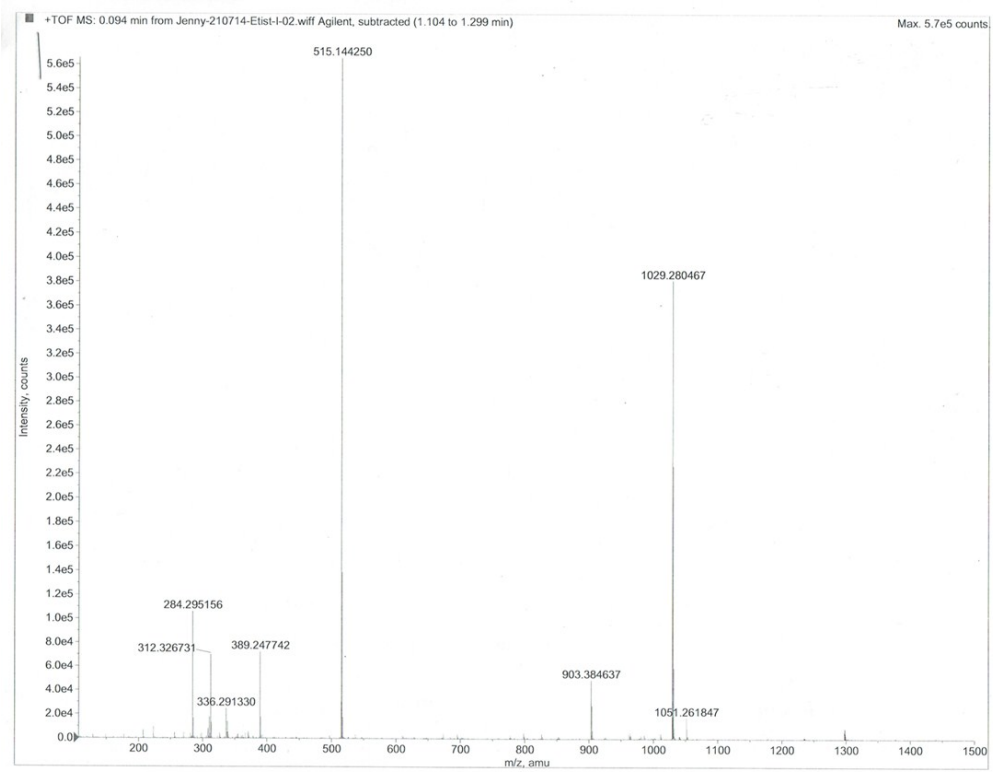


Figure S33. High resolution mass spectrum for compound **9** $[C_{27}H_{31}IO_2+H]^+$

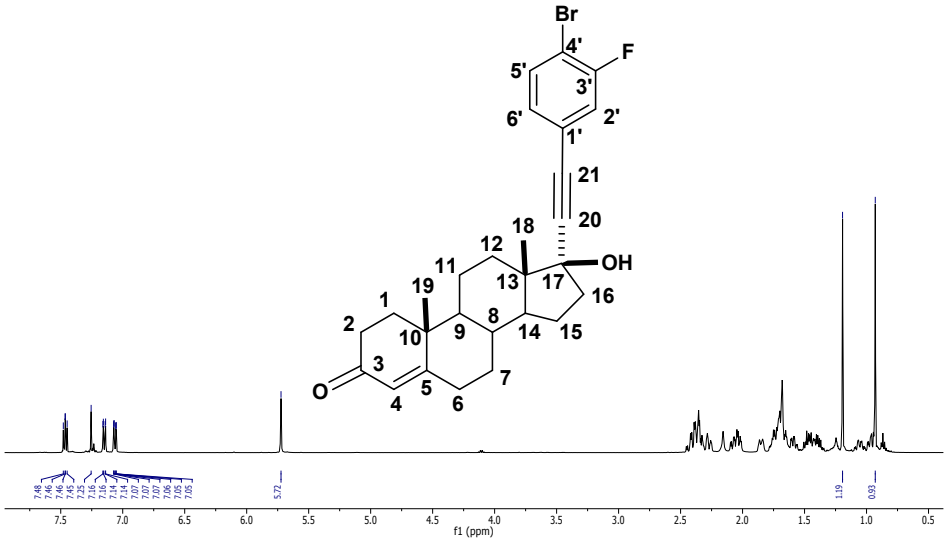


Figure S34. ^{1}H NMR spectrum for compound **10** (500 MHz, $CDCl_3$)

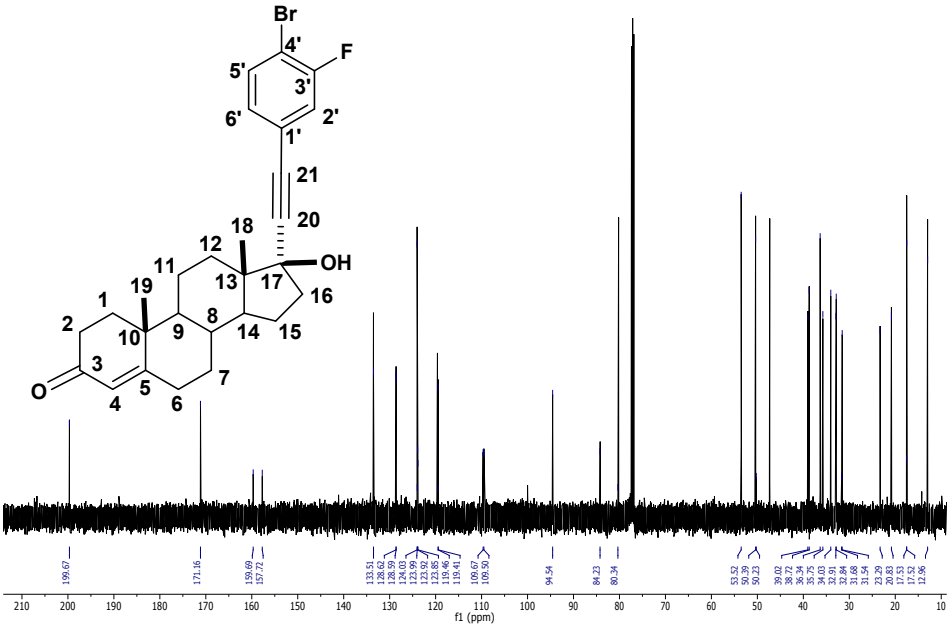


Figure S35. ^{13}C NMR spectrum for compound **10** (125.76 MHz, $CDCl_3$).

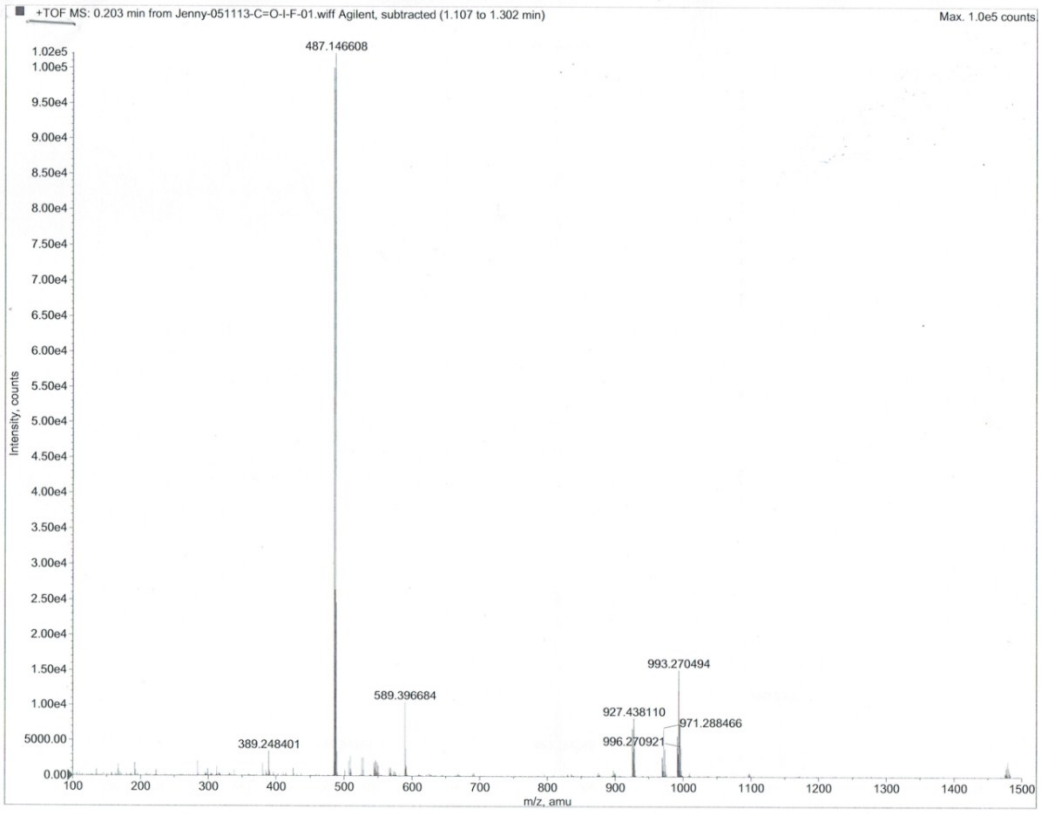


Figure S36. High resolution mass spectrum for compound **10** $[C_{27}H_{30}BrFO_2+H]^+$

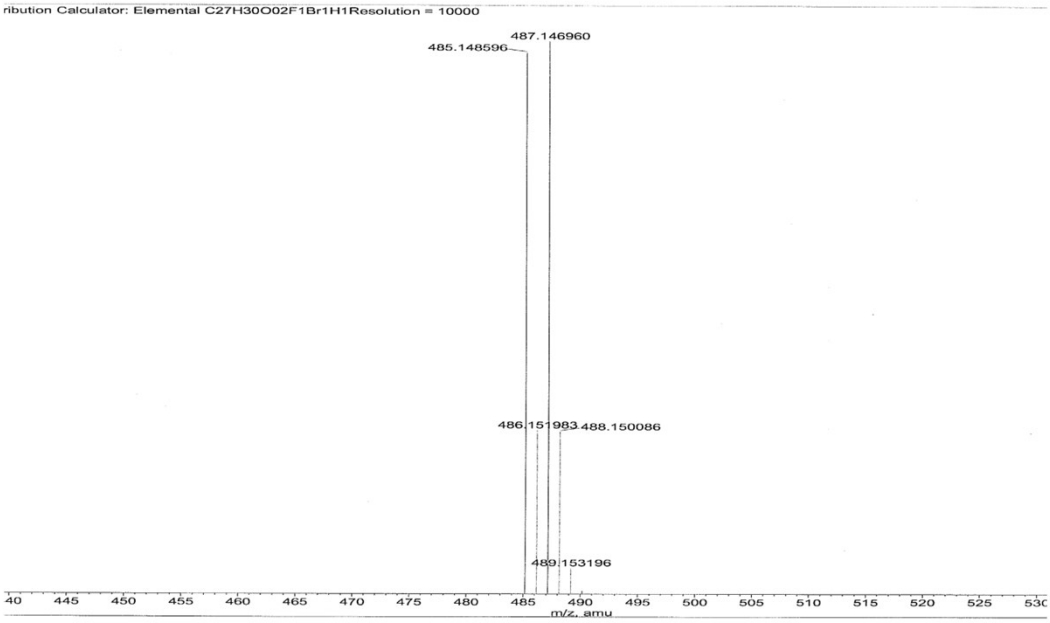


Figure S36a. High resolution mass spectrum for compound **10.**

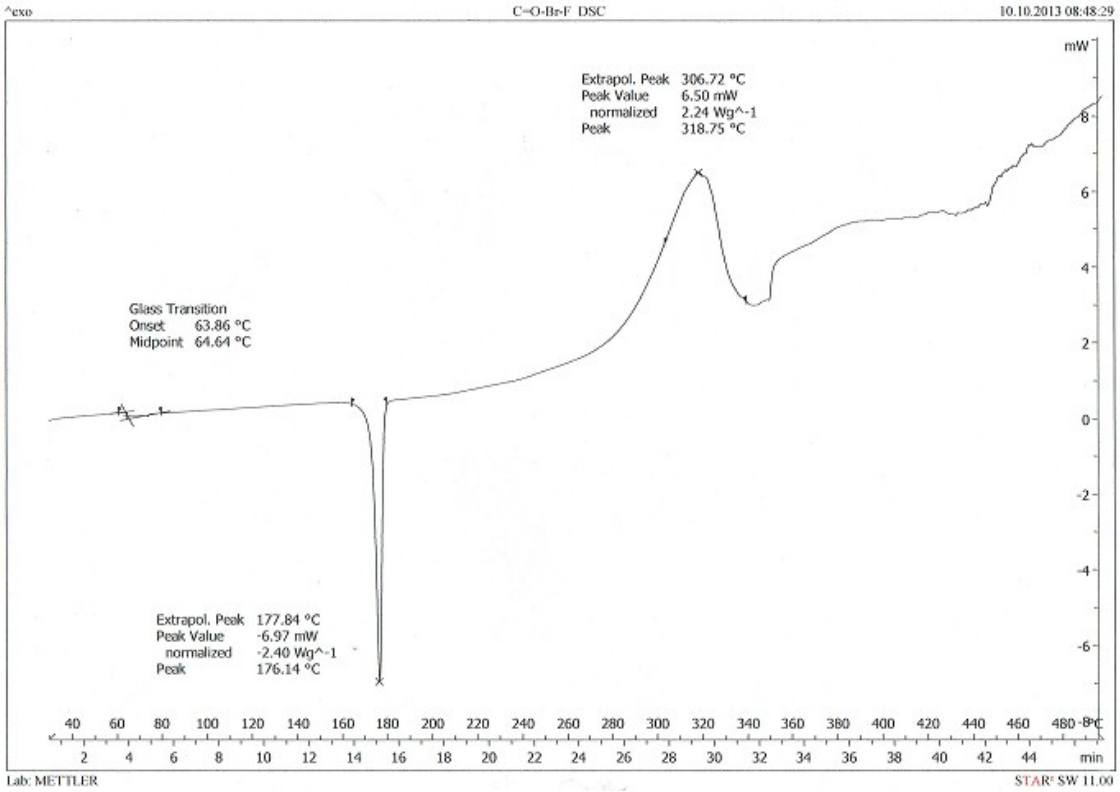


Figure S37. DSC for Compound **10.**

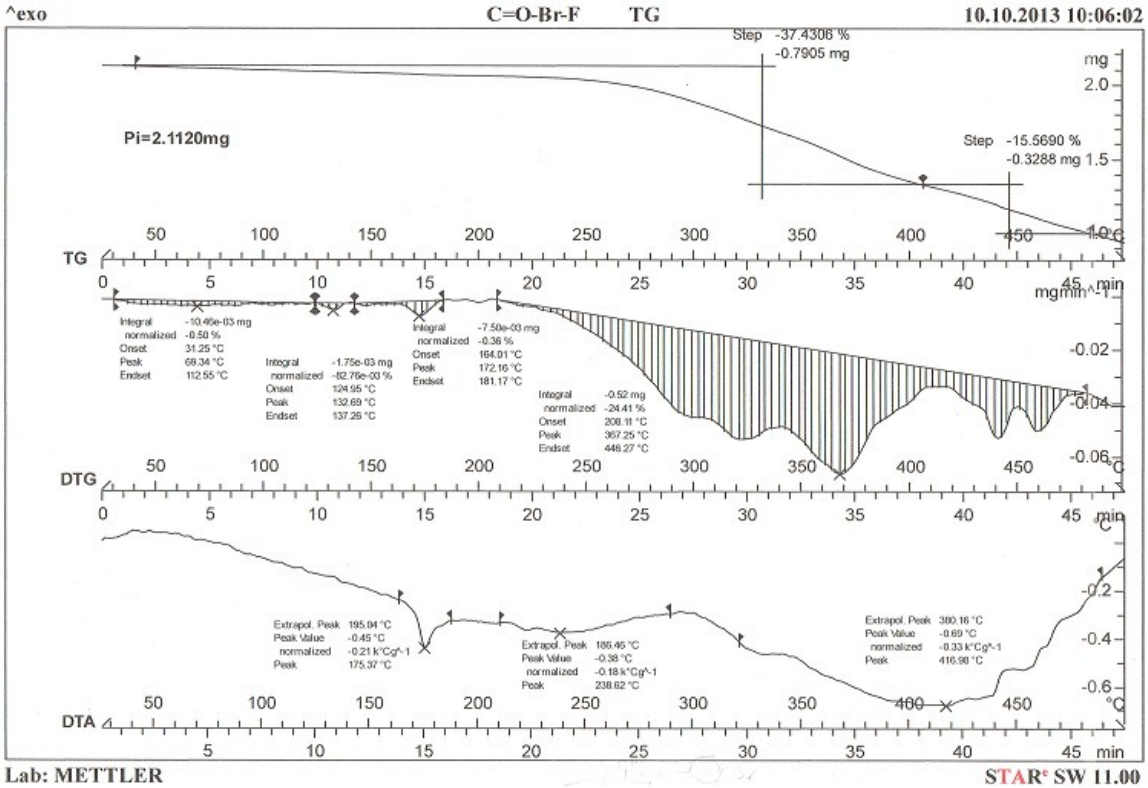


Figure S38. TGA for Compound **10.**

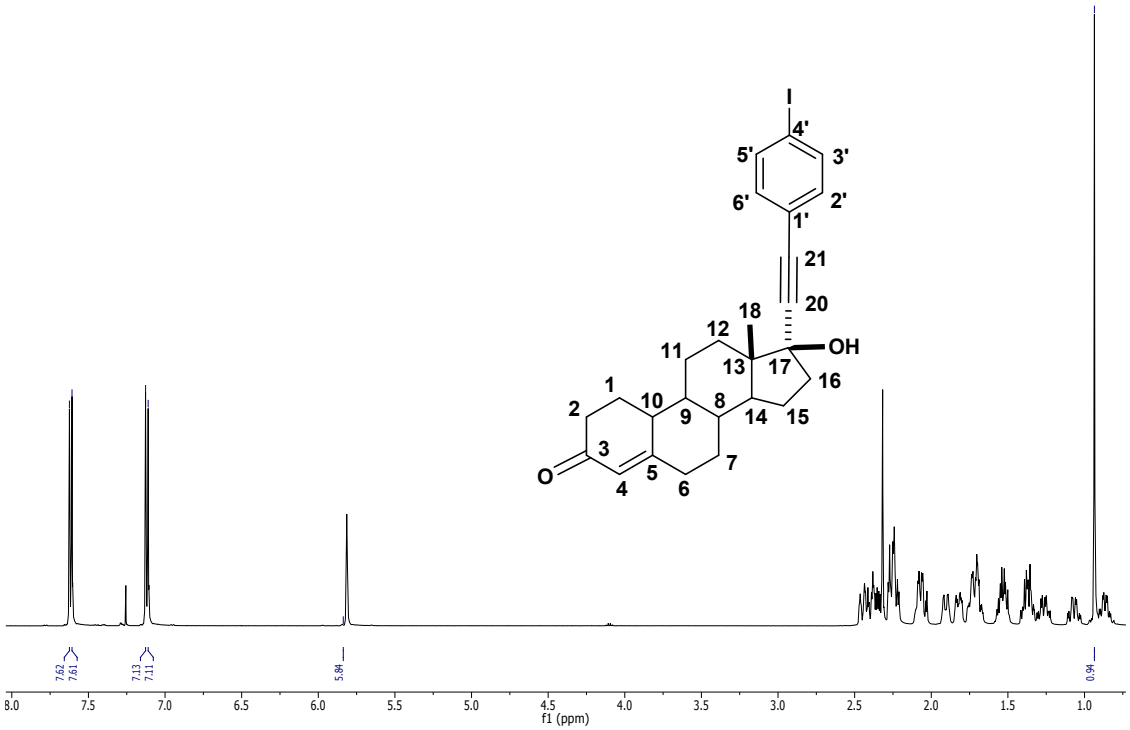


Figure S39. ^{1}H NMR spectrum for compound **11** (500 MHz, $CDCl_3$).

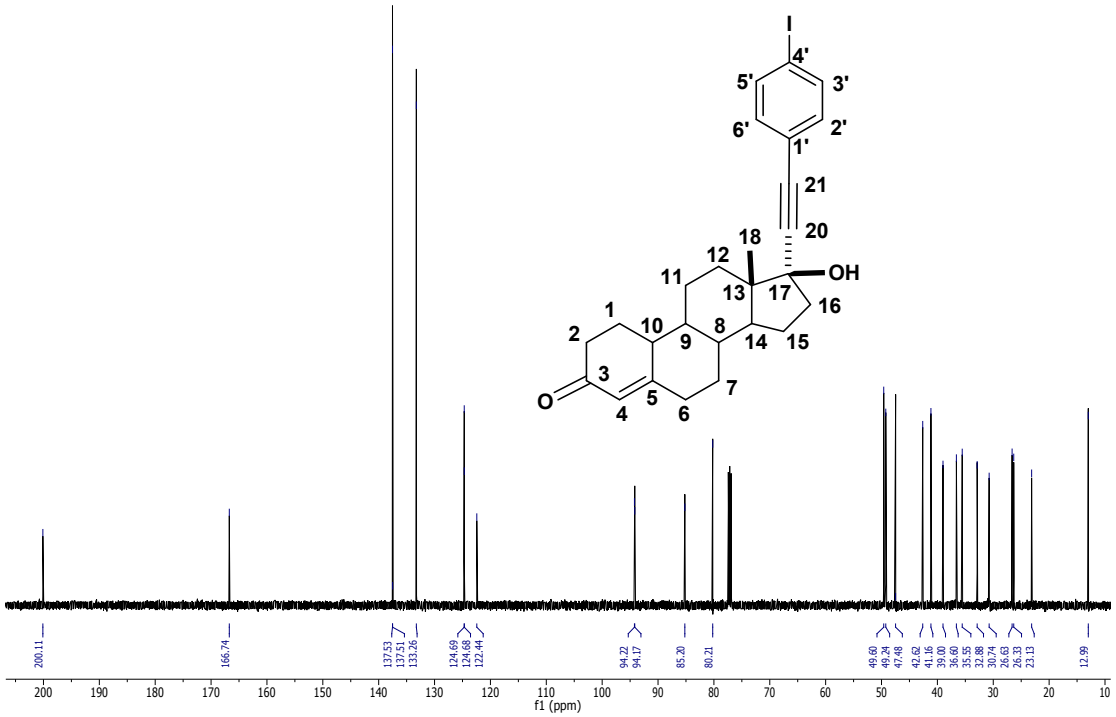


Figure S40. ^{13}C NMR spectrum for compound **11** (125.76 MHz, $CDCl_3$).

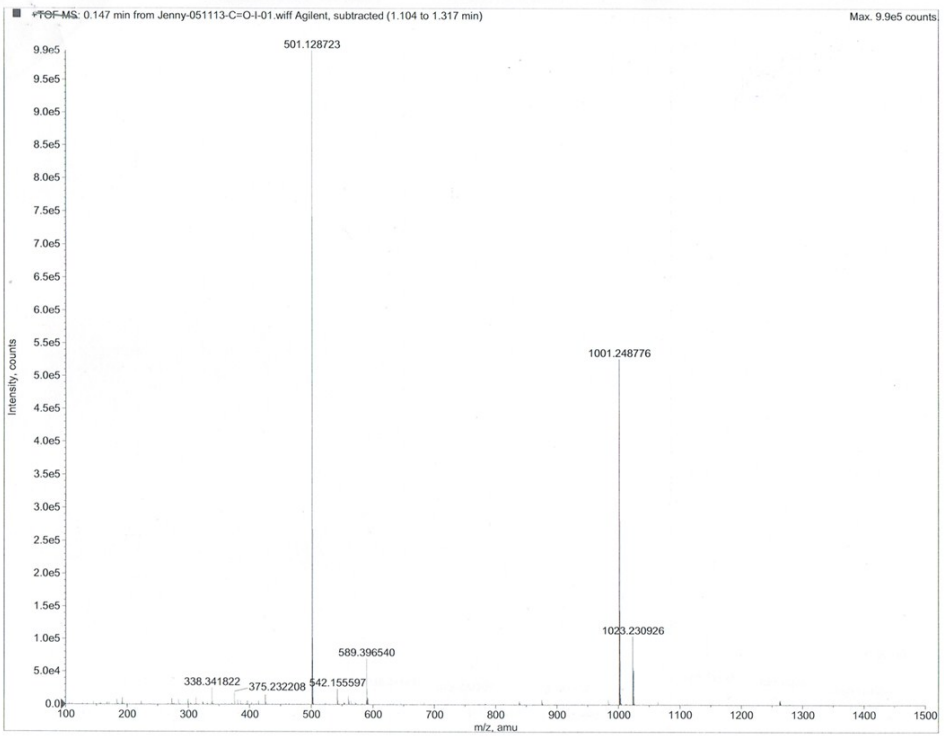


Figure S41. High resolution mass spectrum for compound **11** $[C_{26}H_{29}IO_2+H]^+$**.**

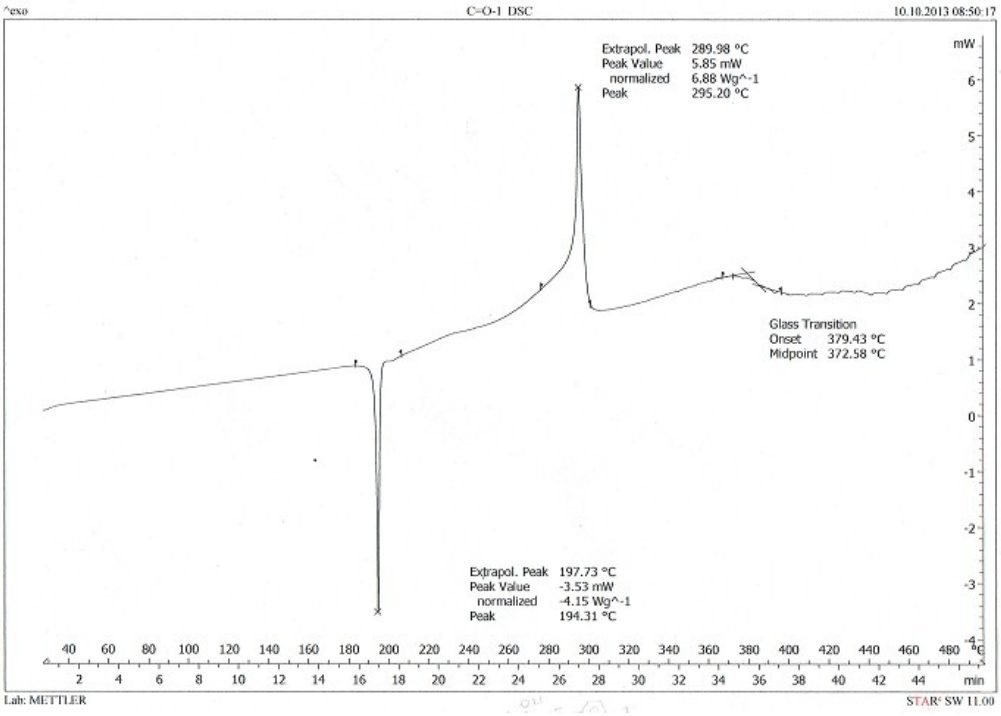


Figure S42. DSC for Compound **11.**

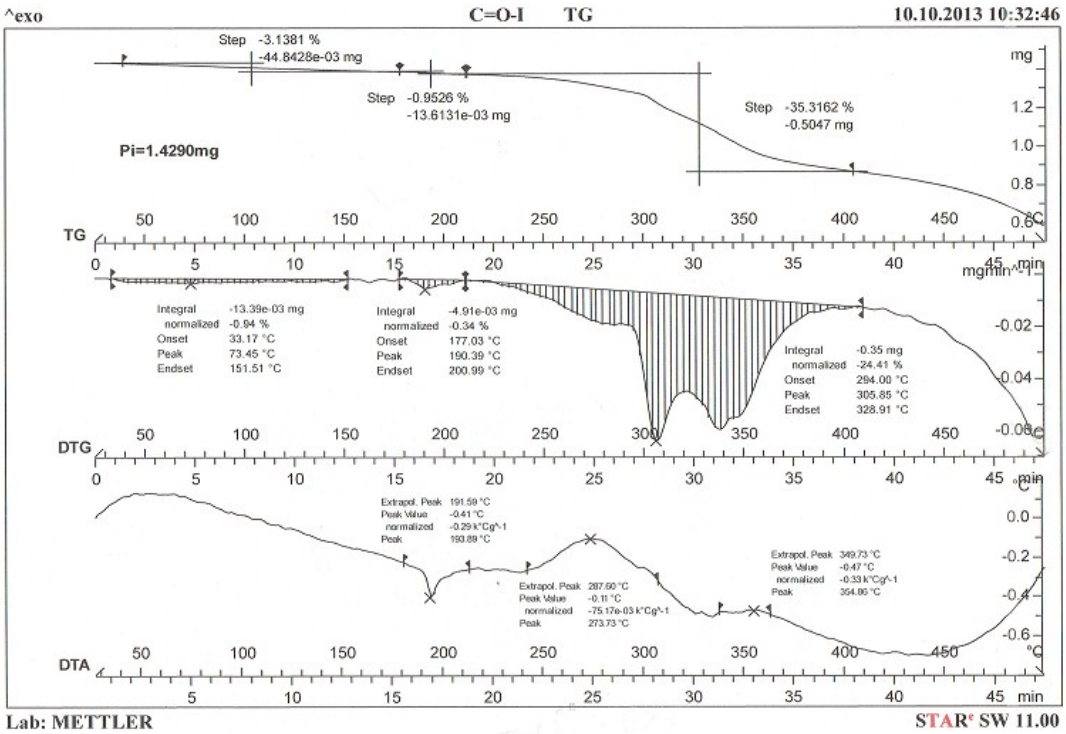


Figure S43.TGA for Compound **11.**

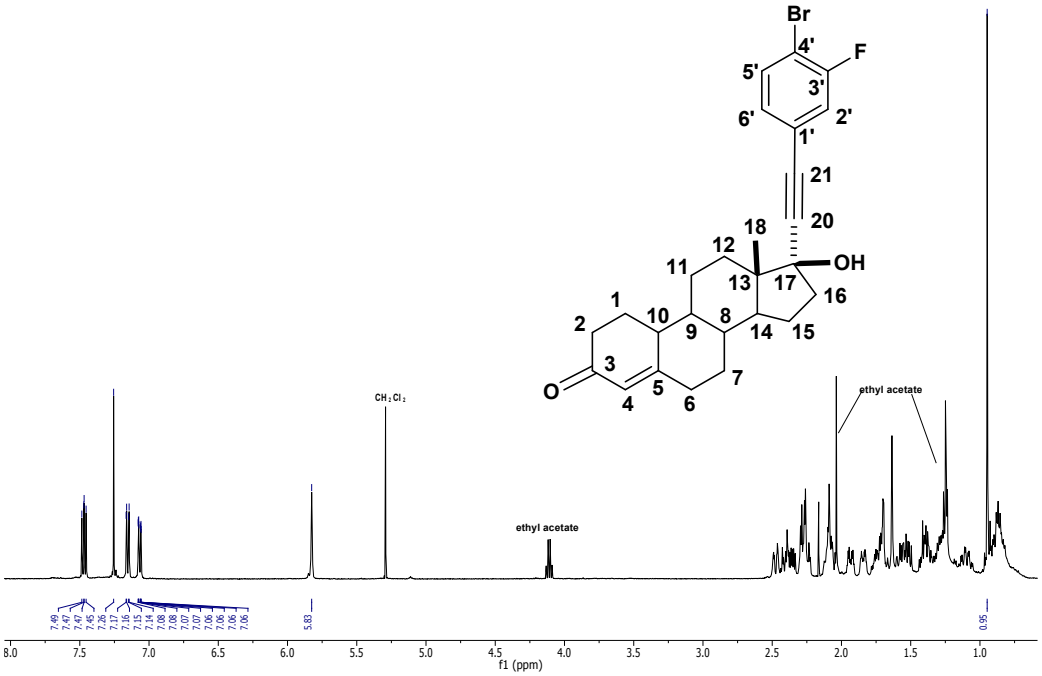


Figure S44. ^{1}H NMR spectrum for compound **12** (500 MHz, $CDCl_3$)

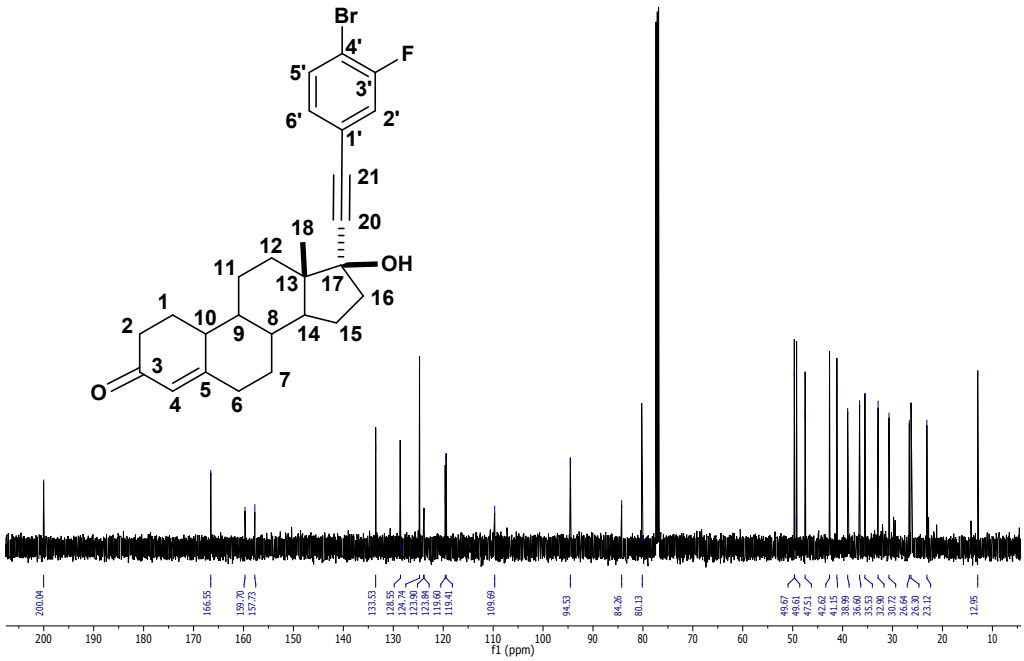


Figure S45. ^{13}C NMR spectrum for compound **12** (125.76 MHz, $CDCl_3$).

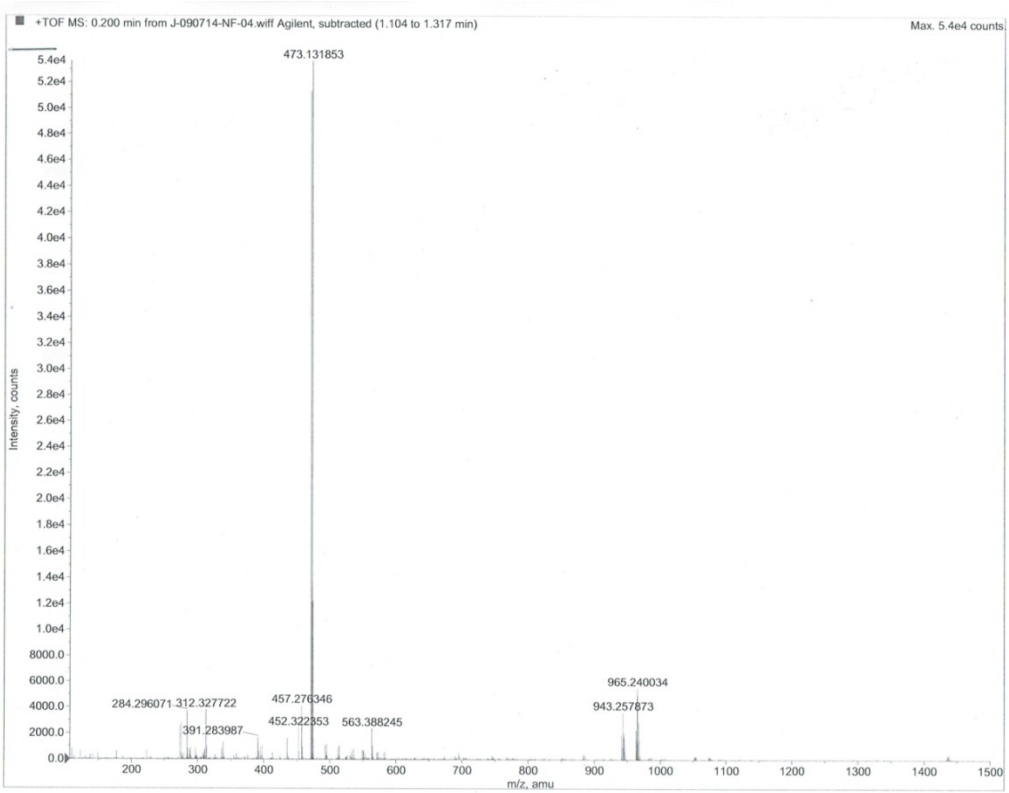


Figure S46. High resolution mass spectrum for compound **12** $[C_{26}H_{28}BrFO_2+H]^+$

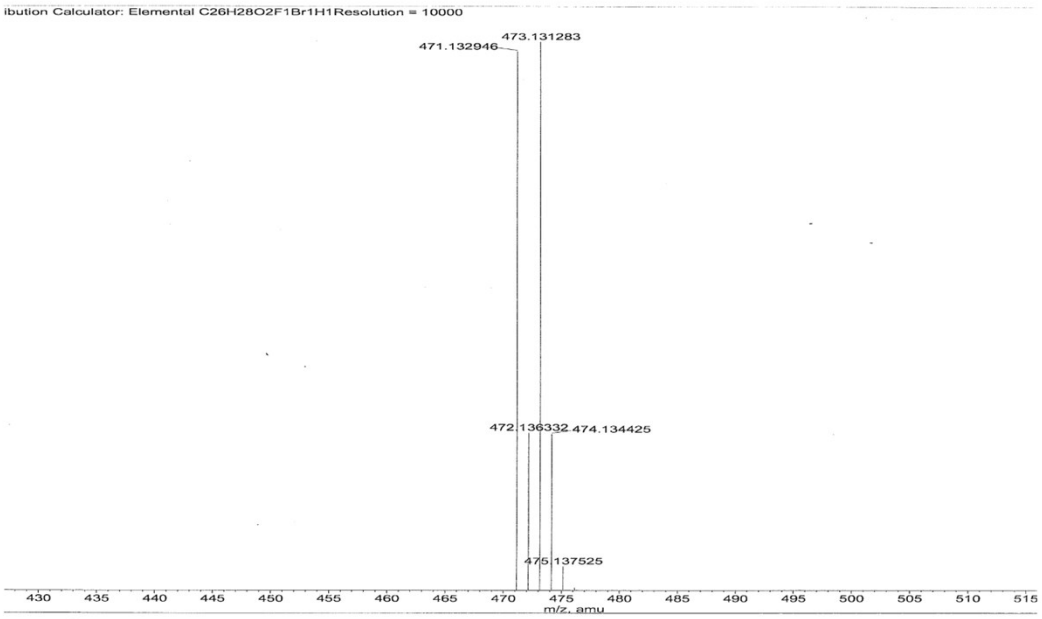


Figure S46a. High resolution mass spectrum for compound **12**

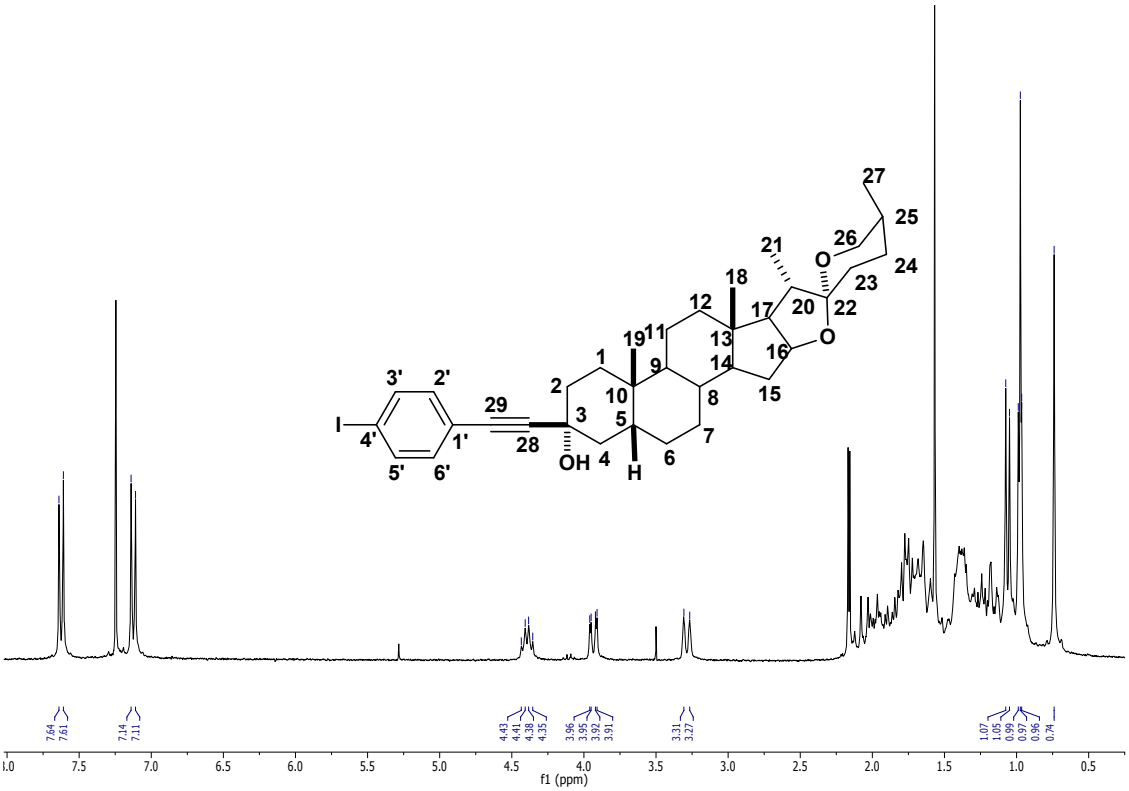


Figure S47.^{1}H NMR spectrum for compound **13** (270 MHz, $CDCl_3$).

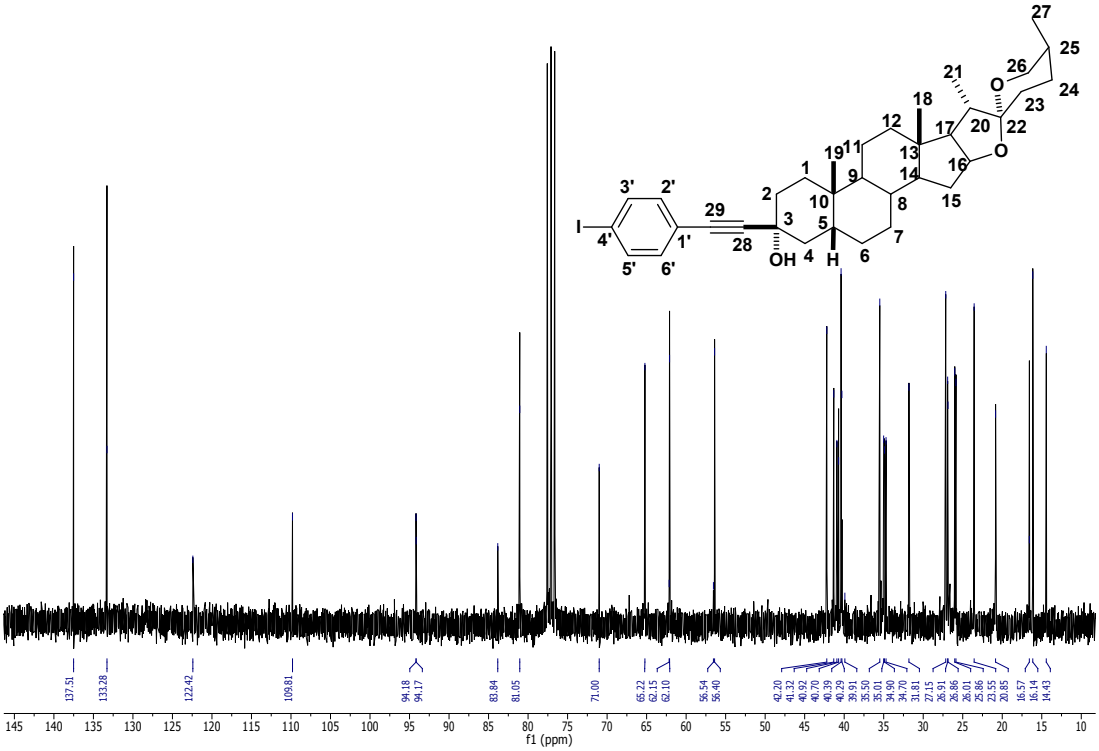


Figure S48. ^{13}C NMR spectrum for compound **13** (69.5 MHz, $CDCl_3$).

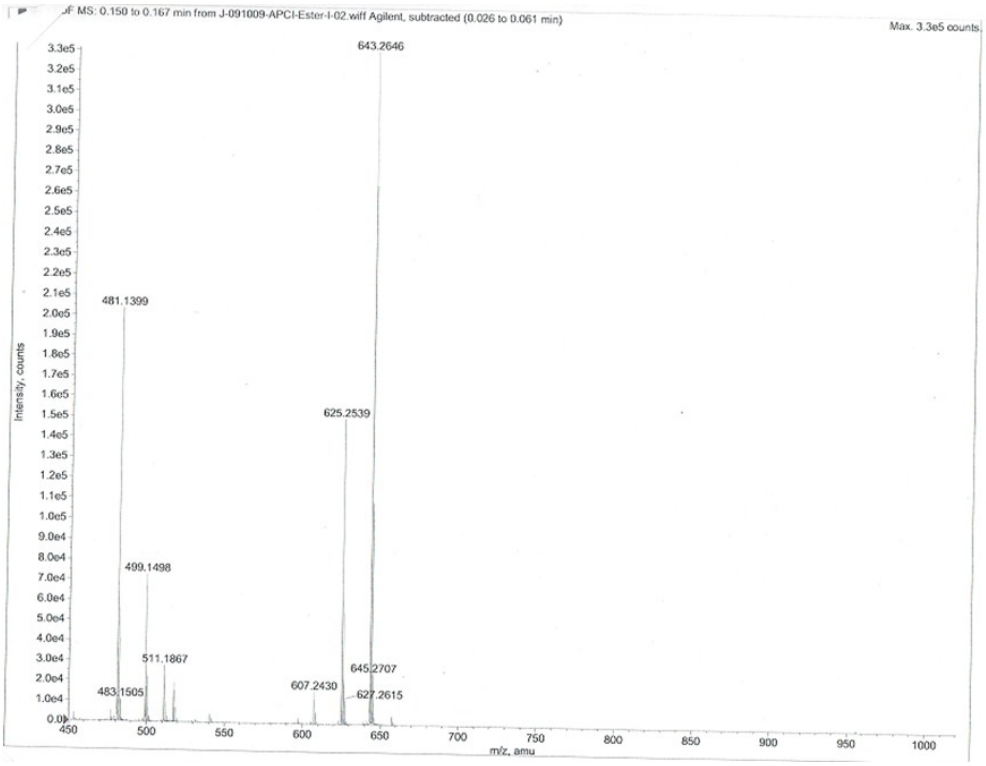


Figure S49. High resolution mass spectrum for compound **13** $[C_{35}H_{47}IO_3+H]^+$**.**

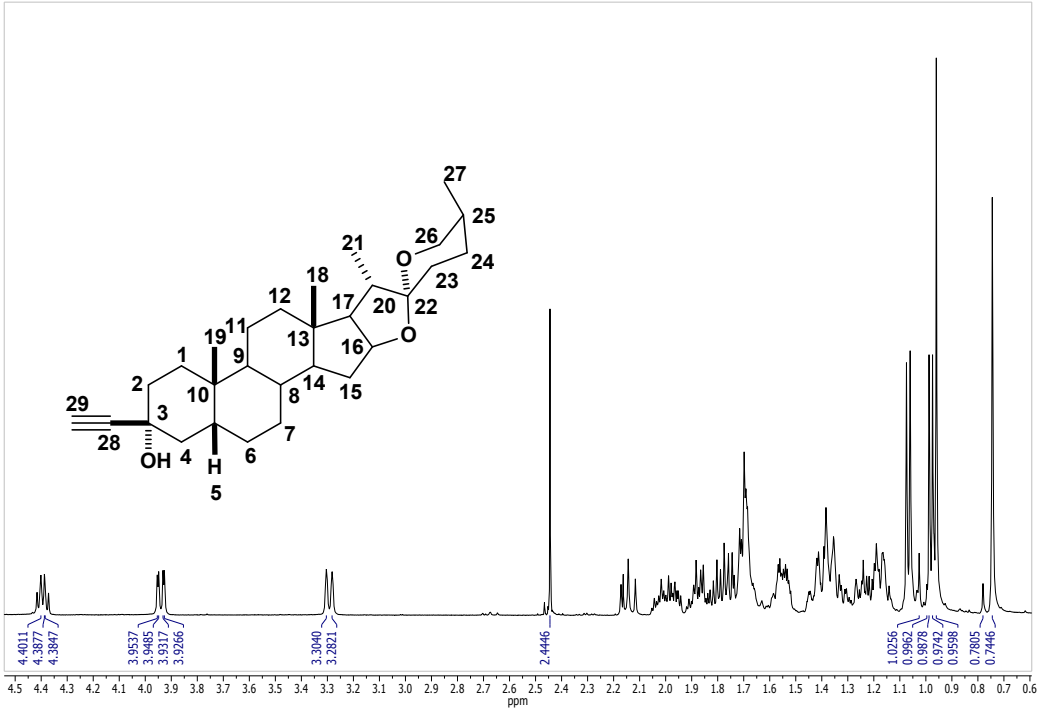


Figure S50. ^{1}H NMR spectrum for compound **(13a)** (500 MHz, $CDCl_3$).

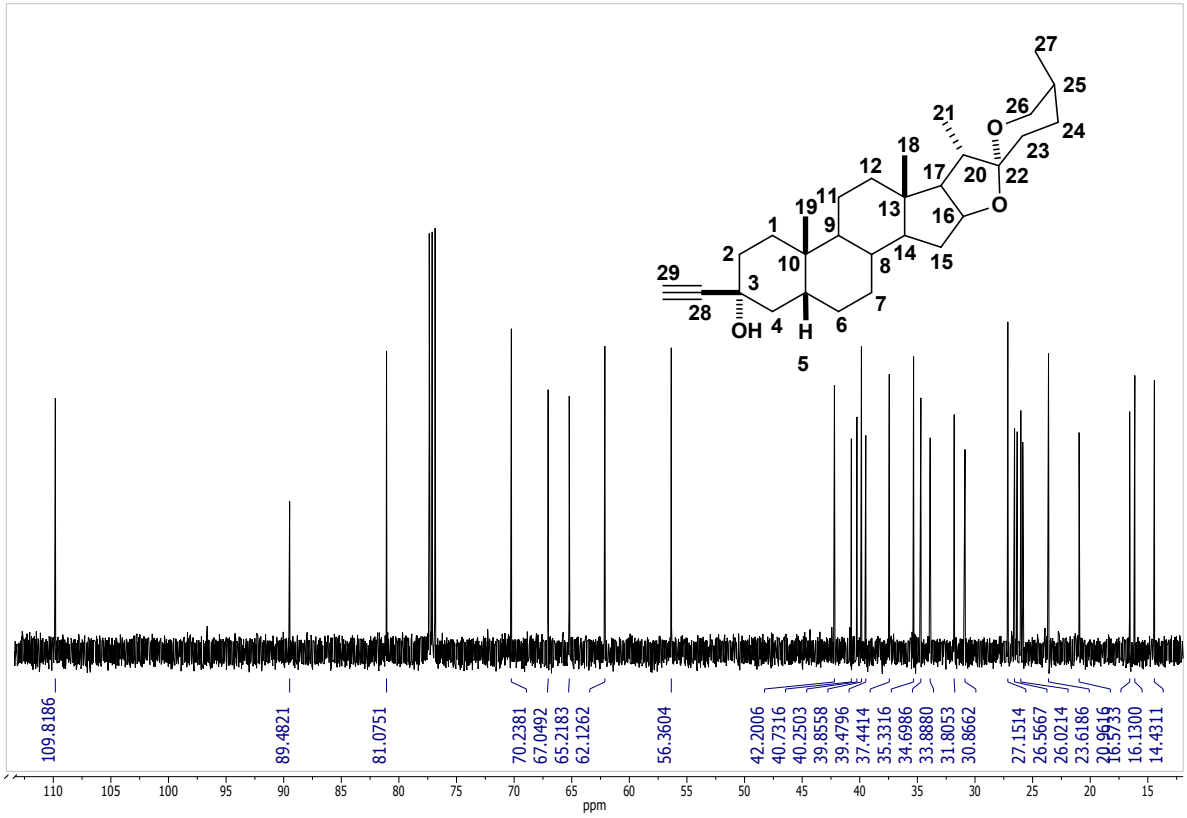


Figure S51. ^{13}C NMR spectrum for compound **(13a)** (125.76 MHz, $CDCl_3$).

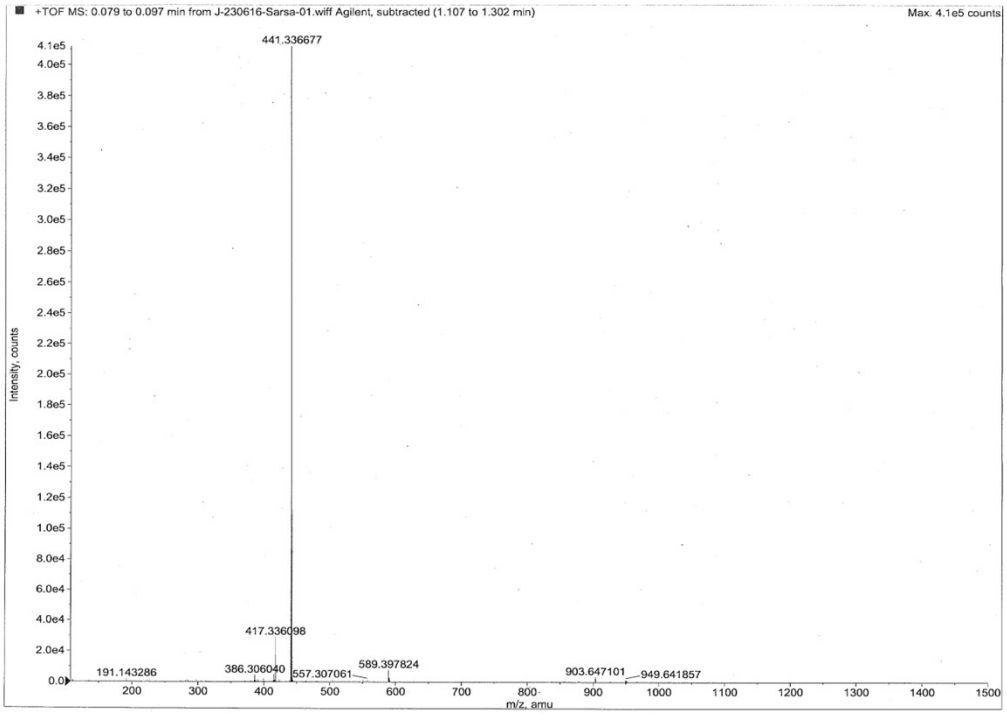


Figure S52. High resolution mass spectrum for compound **13a.**

Table S1. Crystallographic parameters for compounds **1-5, 7** and **9-13**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{26}H_{27}BrO_2$	$C_{26}H_{25}BrF_2O_2$	$C_{27}H_{29}IO_2$	$C_{26}H_{27}IO_2$
Formula weight	451.38	487.36	512.40	498.37
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
a (Å)	7.2984 (1)	7.3624 (1)	6.6335 (1)	7.3430 (2)
b (Å)	16.7188 (3)	16.7118 (3)	16.6143 (4)	17.0390 (4)
c (Å)	20.5514 (3)	20.7142 (4)	21.5766 (4)	20.654 (5)
α (º)	90.0	90.0	90.0	90.0
β (º)	90.0	90.0	90.0	90.0
γ (º)	90.0	90.0	90.0	90.0
Volume (Å)^3	2507.69 (7)	2548.65 (8)	2377.98 (8)	2584.2 (6)
Z	4	4	4	4
Crystal size (mm)	0.29×0.28×0.10	0.20x0.06x0.03	0.27x0.19x0.14	0.25x0.25x0.18
θ Range for data collection (º)	3.71 to 27.43	3.19 to 27.47	3.97 to 29.36	2.94 to 27.48
Index ranges	-9<=h<=9 -20<=k<=21 -22<=l<=26	-9<=h<=9 0<=k<=21 0<=l<=26	-7 ≤ h ≤ 9 -22 ≤ k ≤ 21 -29 ≤ l ≤ 29	-9<=h<=8 -22<=k<=21 -26<=l<=22
Reflections collected	28299	5796	30759	16039
Unique reflections (R_{int})	5694 (0.0992)	7596 (0.0000)	6212 (0.0068)	5819 (0.001)
D (mg/m^3)	1.196	1.270	1.431	1.255
Data/Restraints/ Parameters	5694/10/332	5796 / 312 / 299	6212/0/268	5816/2 / 265
Final *R* indices	R_1= *0.054* WR_2= *0.1318*	R_1= *0.0436* WR_2= *0.1112*	R_1= 0.049 WR_2= 0.0957	R_1= *0.0506* WR_2= *0.1275*
R indices (all data)	R_1= *0.0685* WR_2= *0.1422*	R_1= *0.0530* WR_2=*0.1162*	R_1= 0.0931 WR_2= 0.1105	R_1= *0.0676* WR_2=*0.1393*

Table S1. Continue

Compound	**5**	**7**	**9**	**10**
Empirical formula	$C_{30}H_{29}BrO_2$	$C_{32}H_{31}BrO_2$, C_2H_6O	$C_{27}H_{31}IO_2$	$C_{27}H_{30}BrFO_2$
Formula weight	501.43	573.54	514.42	485.42
Space Group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
a (Å)	7.7512 (16)	6.5925 (1)	6.4755 (2)	6.3958 (1)
b (Å)	14.839 (3)	22.2328 (6)	16.0635 (3)	16.2891 (3)
c (Å)	20.627 (4)	10.2751 (2)	22.8738 (3)	22.6776 (5)
α (º)	90	90	90.0	90.0
β (º)	90	100.232 (1)	90.0	90.0
γ (º)	90	90	90.0	90.0
Volume (Å)^3	2372.5 (8)	1482.07 (5)	2379.31 (9)	2362.59 (8)
Z	4	2	4	4
Crystal size (mm)	0.22x0.025x0.025	0.12x0.06x0.04	0.29×0.23×0.15	0.18×0.11×0.09
θ Range for data collection (º)	3.19 to 27.47	3.88 to 27.48	2.96 to 27.57	3.68 to 27.75
Index ranges	$-10 \le h \le 10$ $-19 \le k \le 17$ $-26 \le l \le 21$	$-8 \le h \le 7$ $-28 \le k \le 25$ $-13 \le l \le 13$	-8<=h<=8 -17<=k<=20 -29<=l<=23	0<=h<=8 0<=k<=21 0<=l<=28
Reflections collected	16939	15555	19231	20922
Unique reflections (R_{int})	5189 (0.1079)	5983 (0.0368)	5340 (0.0000)	5234 (0.0090)
D (mg/m^3)	1.404	1.244	1.436	1.365
Data/Restraints/Parameters	5189/212/404	5983/1/356	5340/0/274	5234/1/283
Final *R* indices	R_1= 0.1130 WR_2= 0.2821	R_1= 0.0406 WR_2= 0.0892	R_1= *0.042* WR_2= *0.1029*	R_1= *0.067* WR_2= *0.168*
R indices (all data)	R_1= 0.1985 WR_2= 0.3224	R_1= 0.0555 WR_2= 0.0975	R_1= *0.0503* WR_2= *0.1079*	R_1= *0.096* WR_2= *0.1897*

Table S1. Continue

Compound	**11**	**12**	**13**
Empirical formula	$C_{26}H_{29}IO_2$	$C_{26}H_{29}BrFO_2$	$C_{35}H_{47}IO_3$
Formula weight	500.39	472.39	642.62
Space Group	$P2_12_12_1$	$P2_12_12_1$	C2
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
a (Å)	6.3045 (1)	7.2612 (3)	20.9778 (4)
b (Å)	16.0693 (4)	15.8845 (6)	6.3136 (1)
c (Å)	22.1170 (6)	19.4007 (4)	23.9511 (5)
α (º)	90.0	90.0	90.0
β (º)	90.0	90.0	106.0550 (12)
γ (º)	90.0	90.0	90.0
Volume (Å)^3	2240.65 (9)	2237.69 (13)	3048.49 (10)
Z	4	4	4
Crystal size (mm)	0.12x0.08x0.04	0.24x0.15x0.10	0.07x0.04x0.02
θ Range for data collection (º)	3.11 to 27.55	3.95 to 27.49	3.03 to 27.49
Index ranges	$-8 \leq h \leq 6$ $-20 \leq k \leq 14$ $-28 \leq l \leq 21$	$-9 \leq h \leq 7$ $-18 \leq k \leq 20$ $-20 \leq l \leq 25$	-27<=h<=24 -8<=k<=8 -31<=l<=31
Reflections collected	16581	14795	20437
Unique reflections (R_{int})	5111 (0.0068)	4996 (0.0051)	6932 (0.0000)
D (mg/m^3)	1.244	1.402	1.400
Data/Restraints/Parameters	5111/1/267	4996/1/324	6932/2 / 361
Final *R* indices	R_1= 0.037 WR_2= 0.080	R_1= 0.053 WR_2= 0.1216	R_1= *0.044* WR_2= *0.075*
R indices (all data)	R_1= 0.048 WR_2= 0.085	R_1= 0.099 WR_2= 0.1422	R_1= *0.067* WR_2=*0.085*

Table S2. Selected bond distances (Å) for compounds **1-5**, **7** and **9-13**.

Bonds	Compound			
	1	**2**	**3**	**4**
C4A-Br1	1.883(5)	1.872(4)		
C17-O2	1.439(5)		1.432(7)	1.433(6)
C-17-C20	1.468 (6)	1.473(5)	1.470(8)	1.467(8)
C-20-C21	1.190(6)	1.185(5)	1.206(8)	1.192(8)
C-17-O17		1.438(4)		
F1-C3A		1.394(6)		
F2-C6A		1.298(6)		
C4A-I1			2.085(3)	2.079(6)

Bonds	Compound			
	5	**7**	**9**	**10**
C4A-Br1A	1.989(18)			1.891(6)
C4B-Br1B	1.859(12)			
C17-O2	1.448(14)			
C20A-C17	1.39(4)			
C20B-C17	1.60(4)			
C20A-C21A	1.18(2)			
C20B-C21B	1.18(2)			
C4AA-Br1		1.897(4)		
C17-O2		1.430(5)	1.433(4)	1.447(7)
C17-C20		1.474(5)	1.478(5)	1.466(8)
C20-C21		1.192(5)	1.196(5)	1.203(8)
C4A-I1			2.104(3)	
F1-C3A				1.296(9)

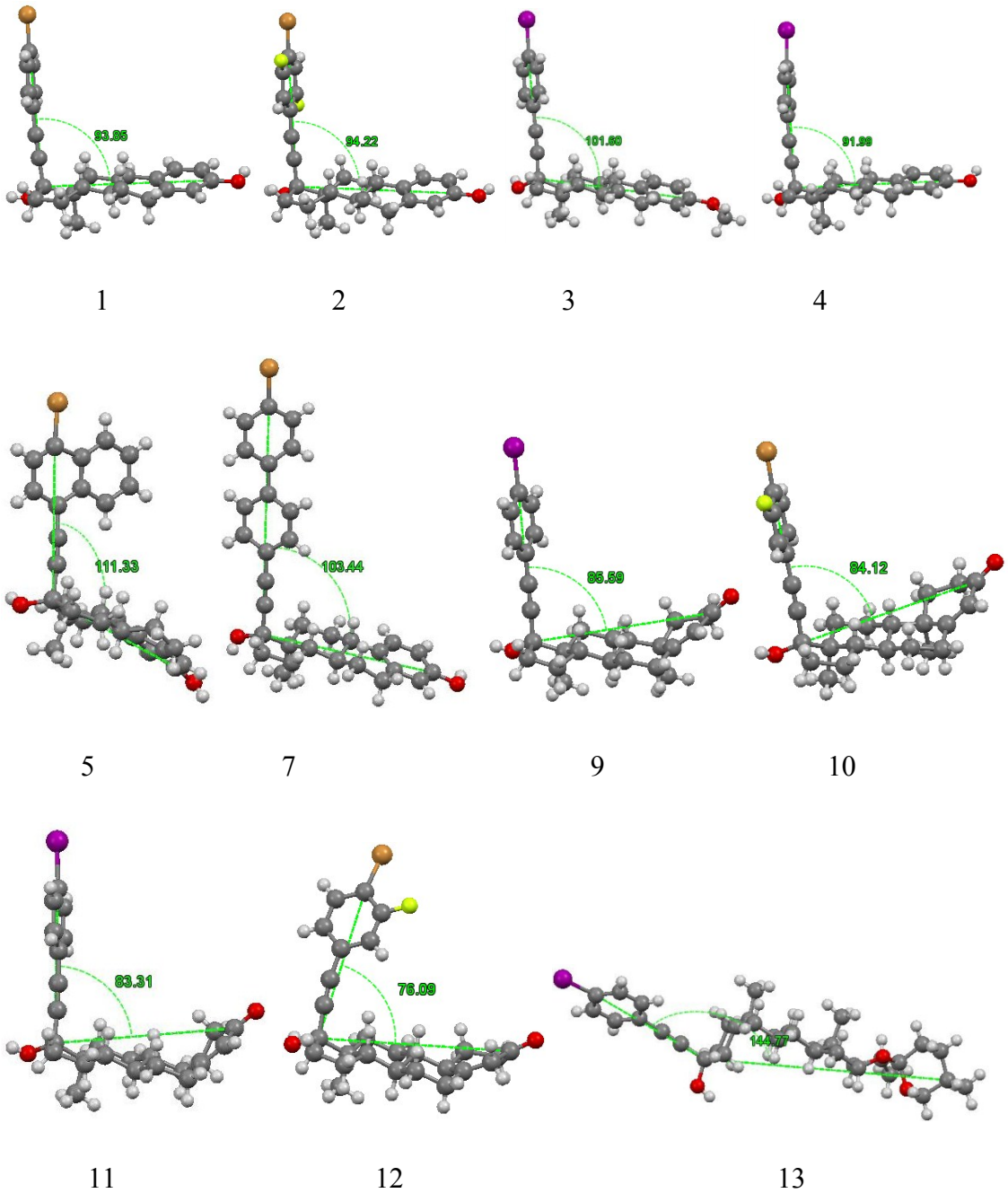
Bonds		Compound		
	11	**12**		**13**
C4A-Br1		1.888(5)	C4A-I1	2.102(5)
C4A-I1	2.102(5)		C3-C28	1.481(7)
C17-O2	1.433(5)	1.433(7)(O1)	C28-C29	1.194(7)
C-17-C20	1.472(6)	1.490(8)	C3-O1	1.439(7)
C-20-C21	1.193(7)	1.176(8)		
F1-C3A		1.339(7)		

Table S3. Selected bond angles (°) for compounds **1-5**, **7** and **9-13**.

Bond angles	Compound			
	1	**2**	**3**	**4**
C3A-C4A-Br1	120.7(4)	119.7(3)		
C5A-C4A-Br1	118.3(4)	121.2(3)		
C20-C17-C16	110.4(3)	110.0(3)	111.4(6)	110.9(5)
C20-C17-C13	111.2(3)	111.3(3)	112.0(4)	111.3(4)
C21 C20 C17	179.3(5)		177.2(6)	179.3(7)
O2-C17-C13	110.4(3)		113.7(5)	111.5(4)
O2-C17-C20	109.1(3)		108.9(5)	109.4(4)
O2-C17-C16	112.1(3)		107.7(5)	111.4(4)
O17-C17-C13		111.2(3)		
O17 C17 C16		112.0(3)		
O17-C17-C20		109.1(3)		
C4A C5A F1B		117.9(5)		
C6A C5A F1B		120.2(5)		
C2A C3A F1		120.8(5)		
C4A C3A F1		117.6(4)		
F2B C2A C3A		125.1(5)		
F2B C2A C1A		111.9(5)		
C3A-C4A-I1			120.0(2)	118.8(5)
C5A-C4A-I1			119.9(2)	121.9(6)

Bond angles	Compound			
	5	**7**	**9**	**10**
C5A C4A Br1A	102.6(13)			120.5(6)
C3A C4A Br1A	137.2(13)			120.4(6)
C20A C17 C16	106(2)			
C20A C17 C13	117.4(19)			
C21A C20A	174(4)			
C17	103(2)			
C20A C17 O2	112.9(10)			
O2 C17 C16				
C3AA C4AA		118.9(4)		
Br1		119.9(3)		
C5AA C4AA		105.8(3)	108.9(3)	108.3(4)
Br1		112.6(3)	112.1(2)	111.3(4)
O2 C17 C20		109.7(3)	110.4(3)	111.7(5)
O2 C17 C16		112.1(3)	111.6(2)	111.9(4)
C20 C17 C16		177.3(4)	178.2(2)	177.2(6)
C20 C17 C13	113.1(9)	114.0(3)	110.4(3)	110.4(5)
C21 C20 C17			119.5(3)	
O2 C17 C13			119.9(3)	
C3A C4A I1				119.5(7)
C5A C4A I1				118.1(7)
F1 C3A C2A				
F1 C3A C4A				

Bond angles	Compound			
	11	**12**		**13**
C5A C4A Br1		120.5(4)		
C3A C4A Br1		120.6(5)		
C5A C4A I1	119.2(3)			119.2(4)
C3A C4A I1	120.3(4)			119.9(4)
C20 C17 C16	111.3(4)	112.0(5)	C28 C3 C2	112.1(4)
C20 C17 C13	111.3(3)	109.1(4)	C28 C3 C4	109.3(4)
C21 C20 C17	177.8(5)	174.2(6)	C29 C28 C3	174.4(5)
C20 C17 O2	108.9(4)	109.9(5)(O1)	C28 C3 O1	107.3(4)
O2 C17 C16	111.6(3)	108.5(5)(O1)	O1 C3 C2	107.6(4)
O2 C17 C13	110.1(3)	114.6(4)(O1)	O1 C3 C4	110.6(4)
F1 C3A C2A		119.1(6)		
F1 C3A C4A		118.9(6)		



1 2 3 4

5 7 9 10

11 12 13

Figure S53. “L” Conformation observed all eleven steroidal structures analyzed by X-ray diffraction

TGA measurements and Porous comparison.

Table S4. TGA derived weight loss previous to decomposition for compounds **1**, **2** and **4**.

Compound	% of weight loss	Molecules of Water per unit cell	Temperature Range	Full Trace
1	4.17	4	135 to 187°C	Fig. S5
2	6.93	8	138 to 181 °C	Fig. S10
4	6.00	7	150 to 192 °C	Fig. S18

[a] The % is determined using the first derivative of TGA trace, please see full traces.

Table S5. Electron density and volumes derived from the mixed discrete atom and continuous solvent-area model refinement for compounds **1**, **2** and **4**.

Compound	Electron count in the Void region (# of e^-)[a]	Volume of void region (Å^3)[a]	Molecules of water[b]	Volume of guests (Å^3)	Remaining Volume (Å^3)
1	17 X 2	253 X 2	4	83 (160 [c])	423 (346 [c])
2	21 X 2	231 X 2	4	83 (160 [c])	379 (302 [c])
4	35 X 2	267 X 2	8	165 (320 [c])	369 (214 [c])

[a] These values are derived using PLATON SQUEEZE routine, the number of electron recovered by the BYPASS procedure depends on the quality of the data set especially for small angle (low order) reflections as these are more affected by disordered solvent, for compound **4** two MAIN cycles were applied. For a comparison between volumes calculate using these method those derived from procrystal electron density and experimental values see (Turner, M. J.; McKinnon, J. J.; Jayatilaka, D.; Spackman, M. A. Visualization and Characterization of Voids in Crystalline Materials. *CrystEngComm* **2011**, *13* (6), 1804–1813.).
[b] This value is calculated solely on recovered electron density, and round to consider complete water molecules, for TGA see table S2.
[c] These values consider the volume as 3 times the water molecule volume 20.63 Å^3 given in ref (Mitchell, A. S.; Spackman, M. A. Molecular Surfaces from the Promolecule: A Comparison with Hartree–Fock Ab Initio Electron Density Surfaces. *J. Comput. Chem.* **2000**, *21* (11), 933–942.).

Table S6. Benchmark values of surface areas for selected* classes of porous materials and calculated for compound **1**, **2**, **4**.

Type of Material	Sub- Classification	Surface Area (m^2 g^{-1}) BET	Calculated Surface Area (m^2 g^{-1})	Calculated Surface Area per Unit cell.[a] ($Å^2$)	Calculated Void Volume per Unit cell.[a] ($Å^3$)
Molecular Crystals	Intrinsically and Extrinsically Porous	3758([i])	3983.3	3508.8	11817.04
	Comp 1	---	1095.0	328.31	295.70
	Comp 2	---	979.2	316.99	287.94
	Comp 4	---	1038.4	343.75	307.48
Crystalline Solids	Covalent Frameworks	4210([ii])**	5053.4	4427.61	14697.50
	Coordination Polymers	7140 ([iii])	--	--	--
	PAFs	5600 ([iv])	--	--	--
	Bridged Polysilsesquioxanes	1880 ([v])	--	--	--
Amorphous	Porous graphitic carbon	4196 ([vi])	--	--	--
	Polymers of intrinsic porosity	1760 ([vii])	--	--	--

*This classification does not expect to be extensive and reader is referred to particular references and excellent review papers available on the subject (a) Holst, J. R.; Trewin, A.; Cooper, A. I. Porous Organic Molecules. *Nat Chem* **2010**, *2* (11), 915–920. b) Tian, J.; Thallapally, P. K.; McGrail, B. P. Porous Organic Molecular Materials. *CrystEngComm* **2012**, *14* (6), 1909–1919. c) McKeown, N. B. Nanoporous Molecular Crystals. *J. Mater. Chem.* **2010**, *20* (47), 10588–10597.). Characteristics as pores size distribution, chemical nature, and stability are not mentioned here but vary considerably between the different types of materials. The characterization methods also vary considerably. Either the number of publications and the variety of "acronyms" (MOF's,COF's, PAF's, ZIF's, PMC's, etc) given for types of materials that would lie in the same gross classification makes any broad classification a difficult task.

** Actually PAF 1 is the highest surface area of Covalent Frameworks reported see ref (II and IV)

[a]These values were calculated from Crystal Explorer using a 0.0003 au isosurface for the procrystal electron density. A clear comparison between these theoretically derived data and experimentally derive surface area and pore volumes is given in (Turner, M. J.; McKinnon, J. J.; Jayatilaka, D.; Spackman, M. A. Visualization and Characterization of Voids in Crystalline Materials. *CrystEngComm* **2011**, *13* (6), 1804–1813.).The calculation considers a completely evacuated perfect crystal lattice.

-- not experimentally determined, not calculated values.

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