Synthesis and crystal structures of *D*-annulated pentacyclic steroids: looking within and beyond AR signalling in prostate cancer.

Svetlana K. Vorontsova,[†] Igor V. Zavarzin,[†] Valerii Z. Shirinian,[†] Eugene I. Bozhenko,[†] Alexander M. Scherbakov,[‡] Olga E. Andreeva,[‡] Danila V. Sorokin[‡] and Mikhail E. Minyaev[,†]*

[†] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., Moscow, 119991, Russian Federation.

[‡] Department of Experimental Tumor Biology, Blokhin N.N. National Medical Research Center of Oncology, 24 Kashirskoye sh., Moscow 115522, Russian Federation.

CrystEngComm

Electronic Supplementary Information

2022

Table of contents

S1. X-ray studies

S1.1. X-ray structure determination

X-ray diffraction data for all studied compounds were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector, using shutterless φ- and ω-scan technique and graphite-monochromatized Mo K_α-radiation (0.71073Å). The intensity data of collected reflections were integrated by the *SAINT* program[1] and semi-empirically corrected for absorption and decay by multi-scan methods, using *SADABS*.[2] The structure was solved by direct methods using *SHELXT*[3] and was refined by the full-matrix least-squares method on F^2 using *SHELXL-2018*.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. Positions of all hydrogen atoms (except those in a disordered phenyl group in **1g**) were found from the electron density-difference map. However all these atoms, except H-atoms of a water molecule in **1g**, were placed in geometrically ideal calculated positions (initial C-H distances: 0.950 Å for aromatic, 0.980 Å for methyl, 0.990 Å for methylene and 1.000 Å for tertiary hydrogen atoms) and refined as riding atoms (the C-H distances were also refined with the exception of the disordered fragment in **1g**) with relative isotropic displacement parameters (U_{iso}(H)=1.5 U_{eq}(C) for methyl hydrogen atoms, 1.2 U_{eq}(C) otherwise). A rotating group model was applied for methyl groups. The initial positions for H3A and H3B in **1g** were found the electron density-difference map, then their positions were restrained at the distance of 0.85(2)Å from atom O3. These atoms were refined with relative isotropic displacement parameters (U_{iso}(H)=1.5 U_{eq}(O)). The SHELXTL program suite[1] was used for molecular graphics. Intensities of reflections (0 5 11) in **1b**, (0 0 2) in **2a** and **2b**, (1 2 0, 1 0 7) in **3e**, (0 5 6) in **3f**, and (1 0 1) in **3g** were affected by the beam-stop, therefore these reflections were omitted from the final steps of the refinement. The absolute structure parameter was determined by quotients [(I+)-(I-)]/[(I+)+(I-)].[5]

The 4-Br-phenyl fragment in **1g** exhibited a disorder over three positions with a disorder ratio of 0.4651(24):0.3061(18):0.2286(25). A close inspection of final data allows us to suppose that the entire molecule is slightly disordered, which was reflected in elongated thermal ellipsoids for some atoms. The modeling of the remaining disorder was found to be unreasonable.

The *SHELXTL* program suite[1] was used for molecular graphics for SI. Crystal data, data collection and structure refinement details are summarized in Table S1.

Table S1. Crystal data, data collection and structure refinement details.

Compound	**1b**	**1c**	**1g**•½H_2O	**2a**	**2b**	**2c**
Empirical formula	$C_{28}H_{31}FO_2$	$C_{28}H_{31}FO_2$	$C_{28}H_{31}BrO_2$•0.5(H_2O)	$C_{28}H_{33}ClO_2$	$C_{28}H_{32}ClFO_2$	$C_{28}H_{32}ClFO_2$
M_r	418.53	418.53	488.44	436.99	454.98	454.98
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.1444(1)	8.2415(3)	16.9823(3)	7.3570(1)	7.3425(4)	8.1994(2)
b (Å)	14.7371(2)	14.6409(6)	19.7469(4)	15.9989(3)	19.7162(12)	9.5995(2)
c (Å)	18.1313(3)	17.9646(8)	7.0709(1)	19.5774(4)	31.4052(19)	29.1554(7)
V (Å^3)	2176.21(5)	2167.66(15)	2371.21(7)	2304.34(7)	4546.4(5)	2294.83(9)
Z	4	4	4	4	8	4
Density(calc) (g•cm^{-3})	1.277	1.282	1.368	1.260	1.329	1.317
μ (mm^{-1})	0.084	0.084	1.758	0.188	0.200	0.198
Crystal size (mm)	0.54×0.35×0.28	0.25×0.13×0.09	0.58×0.23×0.17	0.47×0.14×0.11	0.51×0.25×0.05	0.35×0.20×0.17
T_{min}, T_{max}	0.718, 0.749	0.713, 0.863	0.350, 0.501	0.680, 0.747	0.610, 0.747	0.685, 0.747
F(000)	896	896	1020	936	1936	968
Θ range (°)	2.64 to 42.10	2.27 to 37.04	2.39 to 39.50	2.44 to 35.01	2.44 to 34.35	2.23 to 35.63
Completeness to Θ_{full}, Θ_{max}	0.996, 0.999	0.998, 0.999	0.998, 0.993	0.998, 0.999	0.998, 0.999	1.000 to 1.000
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.943	0.848	0.895	0.807	0.794	0.820

Table S1 (cont.). Crystal data, data collection and structure refinement details

Compound	**1b**	**1c**	**1g**•½H_2O	**2a**	**2b**	**2c**
Index ranges	-15 ≤ h ≤ 15 -27 ≤ k ≤ 27 -34 ≤ l ≤ 34	-13 ≤ h ≤ 13 -24 ≤ k ≤ 24 -30 ≤ l ≤ 30	-30 ≤ h ≤ 30 -35 ≤ k ≤ 35 -12 ≤ l ≤ 12	-11 ≤ h ≤ 11 -25 ≤ k ≤ 25 -31 ≤ l ≤ 31	-11 ≤ h ≤ 11 -31 ≤ k ≤ 31 -46 ≤ l ≤ 49	-13 ≤ h ≤ 13 -15 ≤ k ≤ 15 -47 ≤ l ≤ 47
Reflections						
measured	155860	81162	110634	110054	126091	81722
independent [R_{int}]	15305 [0.0305]	11059 [0.0873]	14229 [0.0378]	10116 [0.0544]	19060 [0.0840]	10589 [0.048]
observed [I > 2σ(I)]	14388	8787	10976	8919	14999	9139
Data, restraints, parameters	15305, 302, 0	11059, 302, 0	14229, 357, 27	10116, 303, 0	19060, 621, 0	10589, 311, 0
R indices [F^2>2σ(F^2)]	0.0329, 0.0883	0.0498, 0.1137	0.0437, 0.1099	0.0402, 0.0988	0.0637, 0.1540	0.0403, 0.0945
R indices [*all data*]	0.0366, 0.0919	0.0728, 0.1280	0.0631, 0.1210	0.0497, 0.1061	0.0867, 0.1694	0.0538, 0.1027
Goodness-of-fit on F^2	1.093	1.036	1.031	1.029	1.027	1.068
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e•Å^{-3})	0.463, -0.173	0.513, -0.247	0.775, -0.985	0.440, -0.272	1.402, -0.439	0.351, -0.214
Flack	0.13(7)	0.4(3)	-0.0058(16)	-0.022(13)	0.00(2)	-0.010(15)
Quotients	6230	3322	4108	3654	5401	3603
CCDC number	2060473	2060474	2060475	2060476	2060477	2060478

Table S1 (cont.). Crystal data, data collection and structure refinement details

Compound	**2g**	**2h**	**3d**	**3e**	**3f**	**3g**
Empirical formula	$C_{28}H_{32}BrClO_2$	$C_{28}H_{32}BrClO_2$	$C_{28}H_{33}ClO_2$	$C_{28}H_{32}ClFO_2$	$C_{28}H_{32}Cl_2O_2$	$C_{28}H_{32}Cl_2O_2$
M_r	515.89	515.89	436.99	454.98	471.43	481.45
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell						
a (Å)	7.4163(2)	7.5079(2)	9.5984(2)	9.6037(2)	7.5823(2)	9.6737(2)
b (Å)	24.3559(6)	10.4189(3)	13.7895(4)	14.6224(4)	12.3043(4)	13.7426(3)
c (Å)	26.0244(6)	30.1049(9)	17.3969(4)	16.3071(4)	24.7321(8)	17.4902(4)
V (Å^3)	4700.8(2)	2354.93(12)	2302.60 (10)	2289.99 (10)	2307.38 (12)	2325.18 (9)
Z	8	4	4	4	4	4
Density(calc) (g•cm^{-3})	1.458	1.455	1.261	1.320	1.357	1.375
μ (mm^{-1})	1.886	1.883	0.189	0.199	0.306	1.790
Crystal size (mm)	0.33×0.20×0.18	0.28×0.13×0.01	0.40×0.11×0.08	0.55×0.38×0.34	0.57×0.09×0.07	0.41×0.36×0.31
T_{min}, T_{max}	0.070, 0.109	0.075, 0.112	0.712, 0.757	0.714, 0.747	0.612, 0.639	0.491, 0.598
F(000)	2144	1072	936	968	1000	1008
Θ range (°)	2.49 to 29.00	2.07 to 30.50	2.34 to 32.05	2.46 to 36.36	2.34 to 31.52	2.58 to 33.75
Completeness to Θ_{full}, Θ_{max}	0.999, 0.999	1.000, 1.000	0.999, 1.000	0.997, 0.998	0.999, 0.999	0.998, 0.999
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.682	0.714	0.747	0.834	0.736	0.782

Table S1 (cont.). Crystal data, data collection and structure refinement details

Compound	**2g**	**2h**	**3d**	**3e**	**3f**	**3g**
	$-10 \le h \le 10$	$-10 \le h \le 10$	$-14 \le h \le 14$	$-15 \le h \le 15$	$-11 \le h \le 11$	$-15 \le h \le 15$
Index ranges	$-33 \le k \le 33$	$-14 \le k \le 14$	$-20 \le k \le 20$	$-24 \le k \le 24$	$-18 \le k \le 18$	$-21 \le k \le 21$
	$-35 \le l \le 35$	$-42 \le l \le 42$	$-25 \le l \le 25$	$-27 \le l \le 27$	$-36 \le l \le 36$	$-27 \le l \le 27$
Reflections						
measured	95224	65027	97543	103490	77290	76577
independent [R_{int}]	12469 [0.0852]	7197 [0.0819]	8024 [0.0460]	11117 [0.0479]	7682 [0.0501]	9291 [0.0418]
observed [$I > 2\sigma(I)$]	10288	5948	7458	10073	6919	8270
Data, restraints, parameters	12469, 621, 0	7197, 311, 0	8024, 303, 0	11117, 318, 2	7682, 311, 0	9291, 302, 0
R indices [$F^2>2\sigma(F^2)$]	0.0387, 0.0670	0.0386, 0.0788	0.0352, 0.0836	0.0386, 0.1030	0.0387, 0.0891	0.0311, 0.0753
R indices [*all data*]	0.0574, 0.0754	0.0553, 0.0873	0.0403, 0.0877	0.0453, 0.1085	0.0471, 0.0949	0.0383, 0.0781
Goodness-of-fit on F^2	1.056	1.018	1.054	1.065	1.043	1.054
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($e \bullet Å^{-3}$)	0.360, -0.395	0.534, -0.562	0.315, -0.178	0.323, -0.334	0.539, -0.456	0.671, -0.570
Flack	-0.013(3)	-0.009(4)	0.014(13)	-0.042(18)	0.001(16)	0.000(2)
Quotients	3865	2192	3112	4150	2766	3333
CCDC number	2060479	2060480	2060481	2060482	2060483	2060484

Radiation type: Mo Kα (λ= 0.71073Å), Θ_{full} = 25.24°, collection temperature = 100K.

S1.2. The structures of chalcones.

S1.2.1. The structure of 1b.

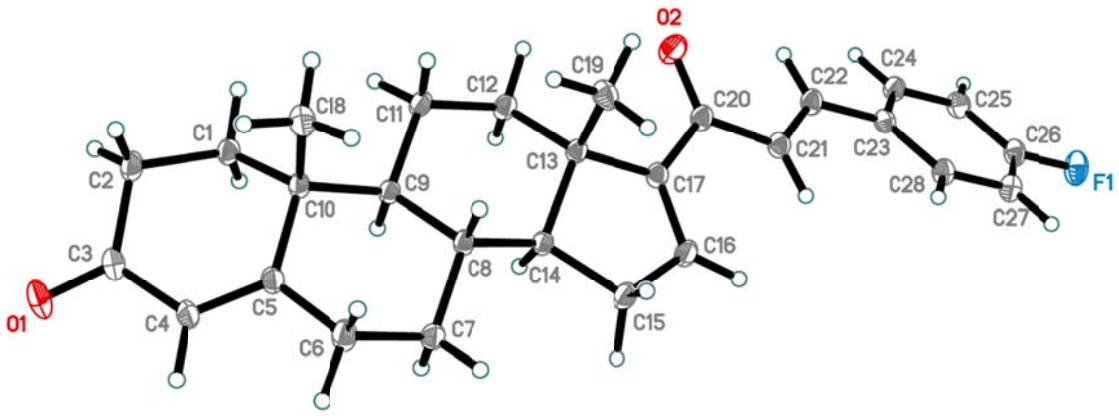


Fig. S1. The structure of **1b** (p=50%).

Table S2. Bond lengths [Å] for **1b**.

Bond	Length	Bond	Length	Bond	Length
C(1)-C(2)	1.5295(9)	C(9)-C(11)	1.5408(9)	C(18)-H(18B)	0.946(9)
C(1)-C(10)	1.5431(9)	C(9)-C(10)	1.5661(8)	C(18)-H(18C)	0.946(9)
C(1)-H(1A)	0.980(10)	C(9)-H(9)	0.997(13)	C(19)-H(19A)	0.965(10)
C(1)-H(1B)	0.980(10)	C(10)-C(18)	1.5470(10)	C(19)-H(19B)	0.965(10)
C(2)-C(3)	1.5068(11)	C(11)-C(12)	1.5425(9)	C(19)-H(19C)	0.965(10)
C(2)-H(2A)	0.953(10)	C(11)-H(11A)	1.002(10)	C(20)-O(2)	1.2296(9)
C(2)-H(2B)	0.953(11)	C(11)-H(11B)	1.002(10)	C(20)-C(21)	1.4891(9)
C(3)-O(1)	1.2285(9)	C(12)-C(13)	1.5294(9)	C(21)-C(22)	1.3420(10)
C(3)-C(4)	1.4604(10)	C(12)-H(12B)	0.993(10)	C(21)-H(21)	0.971(15)
C(4)-C(5)	1.3489(9)	C(12)-H(12A)	0.993(10)	C(22)-C(23)	1.4646(9)
C(4)-H(4)	0.997(15)	C(13)-C(17)	1.5282(8)	C(22)-H(22)	0.954(15)
C(5)-C(6)	1.5016(9)	C(13)-C(19)	1.5429(10)	C(23)-C(24)	1.4044(9)
C(5)-C(10)	1.5213(9)	C(13)-C(14)	1.5457(9)	C(23)-C(28)	1.4017(10)
C(6)-C(7)	1.5313(10)	C(14)-C(15)	1.5367(9)	C(24)-C(25)	1.3938(10)
C(6)-H(6B)	1.000(11)	C(14)-H(14)	1.008(14)	C(24)-H(24)	0.975(15)
C(6)-H(6A)	1.000(11)	C(15)-C(16)	1.5116(10)	C(25)-C(26)	1.3828(11)
C(7)-C(8)	1.5265(9)	C(15)-H(15A)	0.995(11)	C(25)-H(25)	0.966(16)
C(7)-H(7A)	0.974(11)	C(15)-H(15B)	0.995(11)	C(26)-F(1)	1.3544(8)
C(7)-H(7B)	0.974(11)	C(16)-C(17)	1.3501(9)	C(26)-C(27)	1.3853(11)

C(8)-C(14)	1.5242(9)	C(16)-H(16)	0.976(15)	C(27)-C(28)	1.3894(10)
C(8)-C(9)	1.5494(8)	C(17)-C(20)	1.4787(9)	C(27)-H(27)	0.971(16)
C(8)-H(8)	0.977(14)	C(18)-H(18A)	0.946(10)	C(28)-H(28)	0.942(16)

Table S3. Bond angles [°] for **1b**.

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	114.01(5)	C(5)-C(10)-C(18)	107.51(5)	C(16)-C(17)-C(20)	126.31(6)
C(3)-C(2)-C(1)	111.26(6)	C(1)-C(10)-C(18)	109.32(5)	C(16)-C(17)-C(13)	109.69(5)
O(1)-C(3)-C(4)	121.12(7)	C(5)-C(10)-C(9)	108.64(5)	C(20)-C(17)-C(13)	123.38(6)
O(1)-C(3)-C(2)	122.43(7)	C(1)-C(10)-C(9)	108.70(5)	O(2)-C(20)-C(17)	120.51(6)
C(4)-C(3)-C(2)	116.41(6)	C(18)-C(10)-C(9)	112.58(5)	O(2)-C(20)-C(21)	120.88(6)
C(5)-C(4)-C(3)	123.88(6)	C(9)-C(11)-C(12)	114.86(5)	C(17)-C(20)-C(21)	118.61(6)
C(4)-C(5)-C(6)	119.70(6)	C(13)-C(12)-C(11)	110.32(5)	C(22)-C(21)-C(20)	120.36(6)
C(4)-C(5)-C(10)	122.91(6)	C(17)-C(13)-C(12)	119.52(5)	C(21)-C(22)-C(23)	125.90(6)
C(6)-C(5)-C(10)	117.35(5)	C(17)-C(13)-C(19)	105.89(5)	C(28)-C(23)-C(24)	118.51(6)
C(5)-C(6)-C(7)	112.14(6)	C(12)-C(13)-C(19)	110.45(6)	C(28)-C(23)-C(22)	122.16(6)
C(8)-C(7)-C(6)	110.45(6)	C(17)-C(13)-C(14)	100.16(5)	C(24)-C(23)-C(22)	119.33(6)
C(14)-C(8)-C(7)	111.88(5)	C(12)-C(13)-C(14)	107.06(5)	C(25)-C(24)-C(23)	121.47(6)
C(14)-C(8)-C(9)	107.07(5)	C(19)-C(13)-C(14)	113.59(5)	C(26)-C(25)-C(24)	117.71(6)
C(7)-C(8)-C(9)	109.82(5)	C(8)-C(14)-C(15)	121.67(5)	F(1)-C(26)-C(25)	119.25(7)
C(11)-C(9)-C(8)	111.94(5)	C(8)-C(14)-C(13)	113.11(5)	F(1)-C(26)-C(27)	117.83(7)
C(11)-C(9)-C(10)	112.43(5)	C(15)-C(14)-C(13)	104.24(5)	C(25)-C(26)-C(27)	122.92(6)
C(8)-C(9)-C(10)	113.56(5)	C(16)-C(15)-C(14)	100.68(5)	C(26)-C(27)-C(28)	118.54(7)
C(5)-C(10)-C(1)	110.09(5)	C(17)-C(16)-C(15)	111.97(6)	C(27)-C(28)-C(23)	120.85(6)

Table S4. Torsion angles [°] for **1b**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-54.10(8)	C(7)-C(8)-C(14)-C(13)	-177.30(5)
C(1)-C(2)-C(3)-O(1)	-149.04(7)	C(9)-C(8)-C(14)-C(13)	62.34(7)
C(1)-C(2)-C(3)-C(4)	33.46(9)	C(17)-C(13)-C(14)-C(8)	169.49(5)
O(1)-C(3)-C(4)-C(5)	176.91(8)	C(12)-C(13)-C(14)-C(8)	-65.15(7)
C(2)-C(3)-C(4)-C(5)	-5.56(11)	C(19)-C(13)-C(14)-C(8)	57.04(7)
C(3)-C(4)-C(5)-C(6)	174.17(7)	C(17)-C(13)-C(14)-C(15)	35.29(6)
C(3)-C(4)-C(5)-C(10)	-3.49(11)	C(12)-C(13)-C(14)-C(15)	160.65(6)
C(4)-C(5)-C(6)-C(7)	131.13(7)	C(19)-C(13)-C(14)-C(15)	-77.16(7)
C(10)-C(5)-C(6)-C(7)	-51.07(9)	C(8)-C(14)-C(15)-C(16)	-162.31(6)
C(5)-C(6)-C(7)-C(8)	54.57(9)	C(13)-C(14)-C(15)-C(16)	-33.09(7)

C(6)-C(7)-C(8)-C(14)	-176.57(6)	C(14)-C(15)-C(16)-C(17)	18.50(8)
C(6)-C(7)-C(8)-C(9)	-57.83(8)	C(15)-C(16)-C(17)-C(20)	175.34(7)
C(14)-C(8)-C(9)-C(11)	-52.44(7)	C(15)-C(16)-C(17)-C(13)	4.15(8)
C(7)-C(8)-C(9)-C(11)	-174.11(6)	C(12)-C(13)-C(17)-C(16)	-141.12(7)
C(14)-C(8)-C(9)-C(10)	178.92(5)	C(19)-C(13)-C(17)-C(16)	93.52(7)
C(7)-C(8)-C(9)-C(10)	57.26(7)	C(14)-C(13)-C(17)-C(16)	-24.76(7)
C(4)-C(5)-C(10)-C(1)	-16.10(9)	C(12)-C(13)-C(17)-C(20)	47.37(9)
C(6)-C(5)-C(10)-C(1)	166.18(6)	C(19)-C(13)-C(17)-C(20)	-77.98(8)
C(4)-C(5)-C(10)-C(18)	102.89(8)	C(14)-C(13)-C(17)-C(20)	163.74(6)
C(6)-C(5)-C(10)-C(18)	-74.83(7)	C(16)-C(17)-C(20)-O(2)	-174.76(8)
C(4)-C(5)-C(10)-C(9)	-135.02(7)	C(13)-C(17)-C(20)-O(2)	-4.70(11)
C(6)-C(5)-C(10)-C(9)	47.27(8)	C(16)-C(17)-C(20)-C(21)	4.83(11)
C(2)-C(1)-C(10)-C(5)	44.61(8)	C(13)-C(17)-C(20)-C(21)	174.88(6)
C(2)-C(1)-C(10)-C(18)	-73.28(7)	O(2)-C(20)-C(21)-C(22)	-9.20(11)
C(2)-C(1)-C(10)-C(9)	163.48(6)	C(17)-C(20)-C(21)-C(22)	171.22(7)
C(11)-C(9)-C(10)-C(5)	-178.27(5)	C(20)-C(21)-C(22)-C(23)	179.32(7)
C(8)-C(9)-C(10)-C(5)	-49.88(7)	C(21)-C(22)-C(23)-C(28)	-20.22(12)
C(11)-C(9)-C(10)-C(1)	61.94(7)	C(21)-C(22)-C(23)-C(24)	159.38(7)
C(8)-C(9)-C(10)-C(1)	-169.67(5)	C(28)-C(23)-C(24)-C(25)	-0.27(11)
C(11)-C(9)-C(10)-C(18)	-59.32(7)	C(22)-C(23)-C(24)-C(25)	-179.88(7)
C(8)-C(9)-C(10)-C(18)	69.07(7)	C(23)-C(24)-C(25)-C(26)	-0.44(11)
C(8)-C(9)-C(11)-C(12)	50.01(8)	C(24)-C(25)-C(26)-F(1)	-178.52(7)
C(10)-C(9)-C(11)-C(12)	179.24(6)	C(24)-C(25)-C(26)-C(27)	0.80(11)
C(9)-C(11)-C(12)-C(13)	-51.94(8)	F(1)-C(26)-C(27)-C(28)	178.90(7)
C(11)-C(12)-C(13)-C(17)	168.95(6)	C(25)-C(26)-C(27)-C(28)	-0.43(11)
C(11)-C(12)-C(13)-C(19)	-67.89(7)	C(26)-C(27)-C(28)-C(23)	-0.32(11)
C(11)-C(12)-C(13)-C(14)	56.25(7)	C(24)-C(23)-C(28)-C(27)	0.66(11)
C(7)-C(8)-C(14)-C(15)	-52.03(8)	C(22)-C(23)-C(28)-C(27)	-179.74(7)
C(9)-C(8)-C(14)-C(15)	-172.39(6)		

S1.2.2. The structure of 1c.

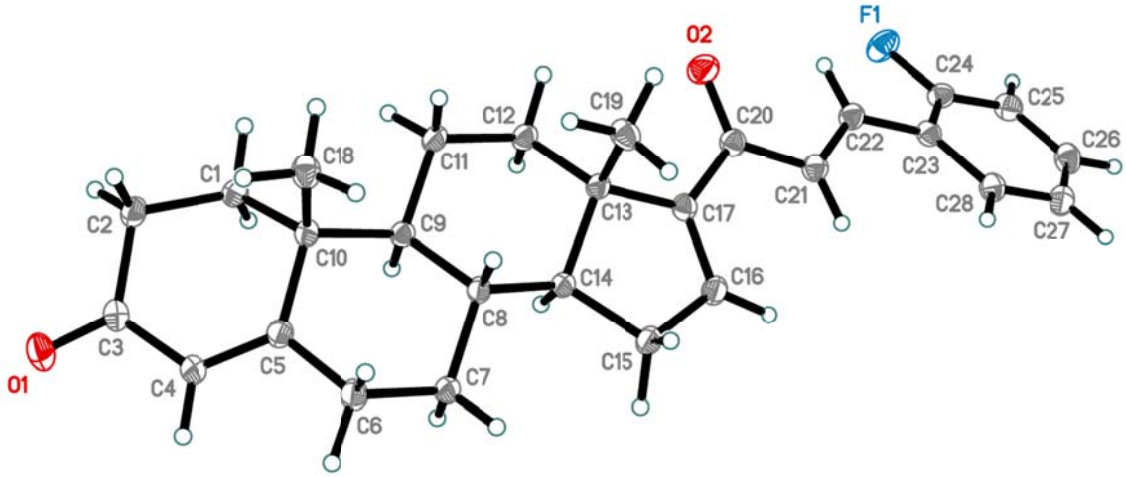


Fig. S2. The structure of **1c** (p=50%).

Table S5. Bond lengths [Å] for **1c**.

Bond	Length	Bond	Length	Bond	Length
C(1)-C(2)	1.527(2)	C(9)-C(11)	1.542(2)	C(18)-H(18B)	0.947(15)
C(1)-C(10)	1.540(2)	C(9)-C(10)	1.566(2)	C(18)-H(18C)	0.947(15)
C(1)-H(1A)	1.009(16)	C(9)-H(9)	1.03(2)	C(19)-H(19A)	0.966(15)
C(1)-H(1B)	1.009(16)	C(10)-C(18)	1.548(2)	C(19)-H(19B)	0.966(15)
C(2)-C(3)	1.505(2)	C(11)-C(12)	1.541(2)	C(19)-H(19C)	0.966(15)
C(2)-H(2A)	0.986(17)	C(11)-H(11A)	0.992(17)	C(20)-O(2)	1.226(2)
C(2)-H(2B)	0.986(17)	C(11)-H(11B)	0.992(17)	C(20)-C(21)	1.490(2)
C(3)-O(1)	1.227(2)	C(12)-C(13)	1.528(2)	C(21)-C(22)	1.342(2)
C(3)-C(4)	1.465(2)	C(12)-H(12B)	0.994(17)	C(21)-H(21)	0.97(2)
C(4)-C(5)	1.345(2)	C(12)-H(12A)	0.994(17)	C(22)-C(23)	1.465(2)
C(4)-H(4)	0.95(3)	C(13)-C(17)	1.528(2)	C(22)-H(22)	0.94(2)
C(5)-C(6)	1.501(2)	C(13)-C(19)	1.543(2)	C(23)-C(24)	1.393(2)
C(5)-C(10)	1.521(2)	C(13)-C(14)	1.547(2)	C(23)-C(28)	1.400(2)
C(6)-C(7)	1.532(2)	C(14)-C(15)	1.537(2)	C(24)-F(1)	1.3566(19)
C(6)-H(6B)	0.993(17)	C(14)-H(14)	1.00(2)	C(24)-C(25)	1.381(2)
C(6)-H(6A)	0.993(17)	C(15)-C(16)	1.508(2)	C(25)-C(26)	1.389(3)
C(7)-C(8)	1.525(2)	C(15)-H(15A)	1.035(17)	C(25)-H(25)	0.92(3)
C(7)-H(7A)	0.980(17)	C(15)-H(15B)	1.035(17)	C(26)-C(27)	1.391(3)
C(7)-H(7B)	0.980(17)	C(16)-C(17)	1.349(2)	C(26)-H(26)	0.94(3)
C(8)-C(14)	1.524(2)	C(16)-H(16)	0.97(2)	C(27)-C(28)	1.387(2)
C(8)-C(9)	1.545(2)	C(17)-C(20)	1.475(2)	C(27)-H(27)	0.94(3)
C(8)-H(8)	0.98(2)	C(18)-H(18A)	0.947(15)	C(28)-H(28)	0.99(2)

Table S6. Bond angles [°] for **1c**.

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	114.04(13)	C(5)-C(10)-C(18)	107.60(13)	C(16)-C(17)-C(20)	126.04(14)
C(3)-C(2)-C(1)	111.07(13)	C(1)-C(10)-C(18)	109.28(12)	C(16)-C(17)-C(13)	109.79(13)
O(1)-C(3)-C(4)	121.00(15)	C(5)-C(10)-C(9)	108.65(12)	C(20)-C(17)-C(13)	123.51(13)
O(1)-C(3)-C(2)	122.54(15)	C(1)-C(10)-C(9)	108.65(12)	O(2)-C(20)-C(17)	120.60(14)
C(4)-C(3)-C(2)	116.39(14)	C(18)-C(10)-C(9)	112.62(12)	O(2)-C(20)-C(21)	120.77(14)
C(5)-C(4)-C(3)	123.76(14)	C(12)-C(11)-C(9)	114.87(12)	C(17)-C(20)-C(21)	118.63(13)
C(4)-C(5)-C(6)	119.71(14)	C(13)-C(12)-C(11)	110.38(12)	C(22)-C(21)-C(20)	119.89(14)
C(4)-C(5)-C(10)	122.91(14)	C(17)-C(13)-C(12)	119.61(12)	C(21)-C(22)-C(23)	125.52(15)
C(6)-C(5)-C(10)	117.35(13)	C(17)-C(13)-C(19)	105.84(12)	C(24)-C(23)-C(28)	116.54(14)
C(5)-C(6)-C(7)	112.16(13)	C(12)-C(13)-C(19)	110.49(13)	C(24)-C(23)-C(22)	119.72(14)
C(8)-C(7)-C(6)	110.25(13)	C(17)-C(13)-C(14)	100.08(11)	C(28)-C(23)-C(22)	123.75(14)
C(14)-C(8)-C(7)	111.82(12)	C(12)-C(13)-C(14)	107.21(12)	F(1)-C(24)-C(25)	117.91(14)
C(14)-C(8)-C(9)	107.14(11)	C(19)-C(13)-C(14)	113.42(13)	F(1)-C(24)-C(23)	117.99(14)
C(7)-C(8)-C(9)	110.11(12)	C(8)-C(14)-C(15)	121.87(12)	C(25)-C(24)-C(23)	124.09(15)
C(11)-C(9)-C(8)	112.21(12)	C(8)-C(14)-C(13)	112.94(12)	C(24)-C(25)-C(26)	117.68(15)
C(11)-C(9)-C(10)	112.36(12)	C(15)-C(14)-C(13)	104.23(12)	C(25)-C(26)-C(27)	120.48(16)
C(8)-C(9)-C(10)	113.55(11)	C(16)-C(15)-C(14)	100.81(12)	C(28)-C(27)-C(26)	120.30(16)
C(5)-C(10)-C(1)	110.02(12)	C(17)-C(16)-C(15)	112.01(13)	C(27)-C(28)-C(23)	120.91(15)

Table S7. Torsion angles [°] for **1c**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-54.53(18)	C(7)-C(8)-C(14)-C(13)	-177.07(12)
C(1)-C(2)-C(3)-O(1)	-149.59(16)	C(9)-C(8)-C(14)-C(13)	62.19(15)
C(1)-C(2)-C(3)-C(4)	33.40(19)	C(17)-C(13)-C(14)-C(8)	169.37(12)
O(1)-C(3)-C(4)-C(5)	177.85(17)	C(12)-C(13)-C(14)-C(8)	-65.15(16)
C(2)-C(3)-C(4)-C(5)	-5.1(2)	C(19)-C(13)-C(14)-C(8)	57.09(16)
C(3)-C(4)-C(5)-C(6)	173.94(15)	C(17)-C(13)-C(14)-C(15)	35.04(14)
C(3)-C(4)-C(5)-C(10)	-4.0(3)	C(12)-C(13)-C(14)-C(15)	160.52(13)
C(4)-C(5)-C(6)-C(7)	130.76(17)	C(19)-C(13)-C(14)-C(15)	-77.24(15)
C(10)-C(5)-C(6)-C(7)	-51.2(2)	C(8)-C(14)-C(15)-C(16)	-161.98(14)
C(5)-C(6)-C(7)-C(8)	54.56(19)	C(13)-C(14)-C(15)-C(16)	-32.84(15)
C(6)-C(7)-C(8)-C(14)	-176.83(13)	C(14)-C(15)-C(16)-C(17)	18.28(18)
C(6)-C(7)-C(8)-C(9)	-57.83(17)	C(15)-C(16)-C(17)-C(20)	175.13(15)
C(14)-C(8)-C(9)-C(11)	-52.24(16)	C(15)-C(16)-C(17)-C(13)	4.28(19)

C(7)-C(8)-C(9)-C(11)	-174.05(13)	C(12)-C(13)-C(17)-C(16)	-141.23(15)
C(14)-C(8)-C(9)-C(10)	178.99(12)	C(19)-C(13)-C(17)-C(16)	93.34(16)
C(7)-C(8)-C(9)-C(10)	57.17(16)	C(14)-C(13)-C(17)-C(16)	-24.70(16)
C(4)-C(5)-C(10)-C(1)	-16.0(2)	C(12)-C(13)-C(17)-C(20)	47.6(2)
C(6)-C(5)-C(10)-C(1)	166.00(14)	C(19)-C(13)-C(17)-C(20)	-77.79(18)
C(4)-C(5)-C(10)-C(18)	102.97(17)	C(14)-C(13)-C(17)-C(20)	164.17(14)
C(6)-C(5)-C(10)-C(18)	-75.04(17)	C(16)-C(17)-C(20)-O(2)	-174.06(17)
C(4)-C(5)-C(10)-C(9)	-134.83(16)	C(13)-C(17)-C(20)-O(2)	-4.4(2)
C(6)-C(5)-C(10)-C(9)	47.16(17)	C(16)-C(17)-C(20)-C(21)	5.4(2)
C(2)-C(1)-C(10)-C(5)	45.04(17)	C(13)-C(17)-C(20)-C(21)	175.08(14)
C(2)-C(1)-C(10)-C(18)	-72.89(17)	O(2)-C(20)-C(21)-C(22)	-7.6(2)
C(2)-C(1)-C(10)-C(9)	163.87(13)	C(17)-C(20)-C(21)-C(22)	172.89(15)
C(11)-C(9)-C(10)-C(5)	-178.33(12)	C(20)-C(21)-C(22)-C(23)	179.60(15)
C(8)-C(9)-C(10)-C(5)	-49.63(16)	C(21)-C(22)-C(23)-C(24)	156.00(17)
C(11)-C(9)-C(10)-C(1)	61.98(16)	C(21)-C(22)-C(23)-C(28)	-23.6(3)
C(8)-C(9)-C(10)-C(1)	-169.32(12)	C(28)-C(23)-C(24)-F(1)	178.60(15)
C(11)-C(9)-C(10)-C(18)	-59.22(16)	C(22)-C(23)-C(24)-F(1)	-1.0(2)
C(8)-C(9)-C(10)-C(18)	69.48(16)	C(28)-C(23)-C(24)-C(25)	-0.8(2)
C(8)-C(9)-C(11)-C(12)	49.58(18)	C(22)-C(23)-C(24)-C(25)	179.56(16)
C(10)-C(9)-C(11)-C(12)	178.98(13)	F(1)-C(24)-C(25)-C(26)	-179.28(15)
C(9)-C(11)-C(12)-C(13)	-51.51(19)	C(23)-C(24)-C(25)-C(26)	0.2(3)
C(11)-C(12)-C(13)-C(17)	168.98(13)	C(24)-C(25)-C(26)-C(27)	0.5(3)
C(11)-C(12)-C(13)-C(19)	-67.83(17)	C(25)-C(26)-C(27)-C(28)	-0.5(3)
C(11)-C(12)-C(13)-C(14)	56.23(16)	C(26)-C(27)-C(28)-C(23)	-0.2(3)
C(7)-C(8)-C(14)-C(15)	-51.80(19)	C(24)-C(23)-C(28)-C(27)	0.8(2)
C(9)-C(8)-C(14)-C(15)	-172.53(13)	C(22)-C(23)-C(28)-C(27)	-179.57(16)

S1.2.3. The structure of 1g•½H_2O.

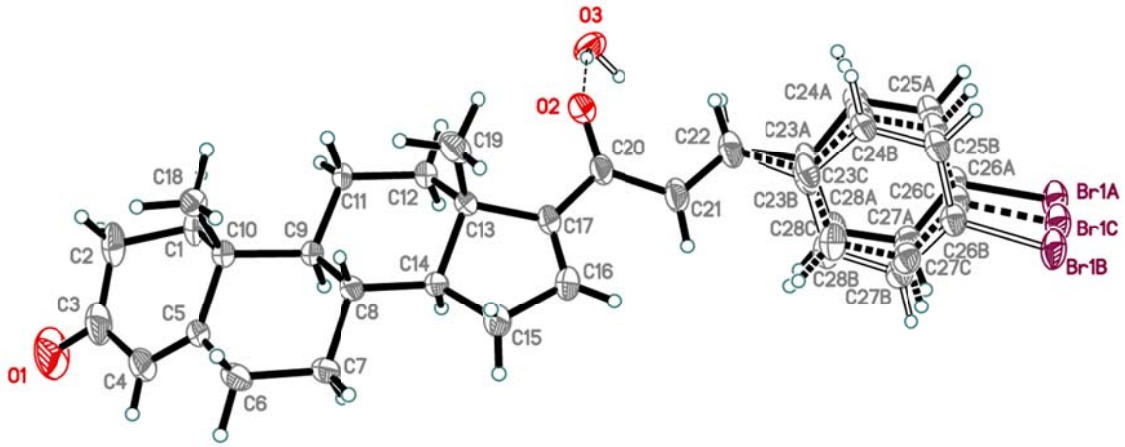


Fig. S3. The structure of **1g**•0.5H_2O (p=50%). The disorder ratio for the *p*-bromophenyl group (positions A/B/C) is 0.4651(24):0.3061(18):0.2286(25).

Table S8. Bond lengths [Å] for **1g**•0.5H_2O.

Bond	Length	Bond	Length	Bond	Length
C(1)-C(2)	1.527(2)	C(13)-C(17)	1.527(2)	C(25A)-H(25A)	0.9500
C(1)-C(10)	1.538(2)	C(13)-C(19)	1.541(3)	C(26A)-C(27A)	1.382(5)
C(1)-H(1A)	0.98(2)	C(13)-C(14)	1.542(2)	C(26A)-Br(1A)	1.895(2)
C(1)-H(1B)	0.98(2)	C(14)-C(15)	1.537(3)	C(27A)-C(28A)	1.394(3)
C(2)-C(3)	1.494(4)	C(14)-H(14)	0.98(3)	C(27A)-H(27A)	0.9500
C(2)-H(2A)	0.99(2)	C(15)-C(16)	1.505(3)	C(28A)-H(28A)	0.9500
C(2)-H(2B)	0.99(2)	C(15)-H(15A)	0.92(3)	C(23B)-C(28B)	1.392(5)
C(3)-O(1)	1.229(2)	C(15)-H(15B)	0.92(3)	C(23B)-C(24B)	1.401(4)
C(3)-C(4)	1.470(3)	C(16)-C(17)	1.344(3)	C(24B)-C(25B)	1.396(4)
C(4)-C(5)	1.346(2)	C(16)-H(16)	0.87(4)	C(24B)-H(24B)	0.9500
C(4)-H(4)	0.90(3)	C(17)-C(20)	1.465(3)	C(25B)-C(26B)	1.388(6)
C(5)-C(6)	1.498(3)	C(18)-H(18A)	0.978(17)	C(25B)-H(25B)	0.9500
C(5)-C(10)	1.518(2)	C(18)-H(18B)	0.978(17)	C(26B)-C(27B)	1.382(5)
C(6)-C(7)	1.526(3)	C(18)-H(18C)	0.978(17)	C(26B)-Br(1B)	1.896(3)
C(6)-H(6A)	1.04(2)	C(19)-H(19A)	0.97(2)	C(27B)-C(28B)	1.395(4)
C(6)-H(6B)	1.04(2)	C(19)-H(19B)	0.97(2)	C(27B)-H(27B)	0.9500
C(7)-C(8)	1.527(2)	C(19)-H(19C)	0.97(2)	C(28B)-H(28B)	0.9500
C(7)-H(7A)	0.97(2)	C(20)-O(2)	1.231(2)	C(23C)-C(28C)	1.391(5)
C(7)-H(7B)	0.97(2)	C(20)-C(21)	1.485(2)	C(23C)-C(24C)	1.400(4)
C(8)-C(14)	1.520(2)	C(21)-C(22)	1.331(3)	C(24C)-C(25C)	1.394(4)
C(8)-C(9)	1.543(2)	C(21)-H(21)	0.94(3)	C(24C)-H(24C)	0.9500
C(8)-H(8)	1.02(3)	C(22)-C(23A)	1.477(3)	C(25C)-C(26C)	1.389(6)

C(9)-C(11)	1.544(2)	C(22)-C(23C)	1.480(4)	C(25C)-H(25C)	0.9500
C(9)-C(10)	1.5603(19)	C(22)-C(23B)	1.483(3)	C(26C)-C(27C)	1.383(5)
C(9)-H(9)	1.00(3)	C(22)-H(22A)	0.9500	C(26C)-Br(1C)	1.896(3)
C(10)-C(18)	1.538(2)	C(22)-H(22B)	0.9500	C(27C)-C(28C)	1.395(4)
C(11)-C(12)	1.535(2)	C(22)-H(22C)	0.9500	C(27C)-H(27C)	0.9500
C(11)-H(11A)	1.019(19)	C(23A)-C(28A)	1.388(4)	C(28C)-H(28C)	0.9500
C(11)-H(11B)	1.019(19)	C(23A)-C(24A)	1.398(3)	O(3)-H(3A)	0.87(3)
C(12)-C(13)	1.527(2)	C(24A)-C(25A)	1.393(4)	O(3)-H(3B)	0.86(3)
C(12)-H(12A)	0.962(19)	C(24A)-H(24A)	0.9500		
C(12)-H(12B)	0.962(19)	C(25A)-C(26A)	1.390(5)		

Table S9. Bond angles [°] for **1g**•0.5H_2O.

Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	113.04(15)	C(20)-C(17)-C(13)	123.89(15)
C(3)-C(2)-C(1)	111.09(17)	O(2)-C(20)-C(17)	120.46(16)
O(1)-C(3)-C(4)	121.8(3)	O(2)-C(20)-C(21)	121.53(18)
O(1)-C(3)-C(2)	121.6(2)	C(17)-C(20)-C(21)	117.99(16)
C(4)-C(3)-C(2)	116.53(15)	C(22)-C(21)-C(20)	121.54(19)
C(5)-C(4)-C(3)	123.11(18)	C(21)-C(22)-C(23A)	132.5(3)
C(4)-C(5)-C(6)	120.70(16)	C(21)-C(22)-C(23C)	122.7(4)
C(4)-C(5)-C(10)	122.82(16)	C(21)-C(22)-C(23B)	117.5(3)
C(6)-C(5)-C(10)	116.41(13)	C(28A)-C(23A)-C(24A)	122.3(4)
C(5)-C(6)-C(7)	113.26(18)	C(28A)-C(23A)-C(22)	116.7(3)
C(6)-C(7)-C(8)	112.03(14)	C(24A)-C(23A)-C(22)	120.6(4)
C(14)-C(8)-C(7)	111.30(14)	C(25A)-C(24A)-C(23A)	119.6(4)
C(14)-C(8)-C(9)	107.38(15)	C(26A)-C(25A)-C(24A)	117.9(3)
C(7)-C(8)-C(9)	108.91(13)	C(27A)-C(26A)-C(25A)	122.3(3)
C(8)-C(9)-C(11)	112.62(12)	C(27A)-C(26A)-Br(1A)	118.9(3)
C(8)-C(9)-C(10)	113.01(13)	C(25A)-C(26A)-Br(1A)	118.8(3)
C(11)-C(9)-C(10)	112.84(11)	C(26A)-C(27A)-C(28A)	120.3(5)
C(5)-C(10)-C(1)	110.35(13)	C(23A)-C(28A)-C(27A)	117.6(5)
C(5)-C(10)-C(18)	107.92(13)	C(28B)-C(23B)-C(24B)	115.2(5)
C(1)-C(10)-C(18)	109.70(13)	C(28B)-C(23B)-C(22)	127.9(5)
C(5)-C(10)-C(9)	108.43(11)	C(24B)-C(23B)-C(22)	116.9(5)
C(1)-C(10)-C(9)	108.41(12)	C(25B)-C(24B)-C(23B)	122.9(5)
C(18)-C(10)-C(9)	112.02(12)	C(26B)-C(25B)-C(24B)	118.1(5)
C(12)-C(11)-C(9)	114.03(12)	C(27B)-C(26B)-C(25B)	122.3(4)
C(13)-C(12)-C(11)	110.33(15)	C(27B)-C(26B)-Br(1B)	118.3(4)
C(17)-C(13)-C(12)	118.58(16)	C(25B)-C(26B)-Br(1B)	119.4(4)

C(17)-C(13)-C(19)	107.27(13)	C(26B)-C(27B)-C(28B)	116.8(7)
C(12)-C(13)-C(19)	110.30(14)	C(23B)-C(28B)-C(27B)	124.7(7)
C(17)-C(13)-C(14)	99.47(12)	C(28C)-C(23C)-C(24C)	116.8(6)
C(12)-C(13)-C(14)	106.96(13)	C(28C)-C(23C)-C(22)	125.0(7)
C(19)-C(13)-C(14)	114.09(17)	C(24C)-C(23C)-C(22)	118.0(6)
C(8)-C(14)-C(15)	121.6(2)	C(25C)-C(24C)-C(23C)	122.9(7)
C(8)-C(14)-C(13)	113.79(12)	C(26C)-C(25C)-C(24C)	117.6(7)
C(15)-C(14)-C(13)	103.50(13)	C(27C)-C(26C)-C(25C)	121.8(6)
C(16)-C(15)-C(14)	100.27(19)	C(27C)-C(26C)-Br(1C)	118.9(6)
C(17)-C(16)-C(15)	111.75(16)	C(25C)-C(26C)-Br(1C)	119.3(5)
C(16)-C(17)-C(20)	125.87(16)	C(26C)-C(27C)-C(28C)	118.6(9)
C(16)-C(17)-C(13)	109.66(17)	C(23C)-C(28C)-C(27C)	122.2(9)

Table S10. Torsion angles [°] for **1g**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-55.9(2)	C(12)-C(13)-C(17)-C(16)	-141.65(19)
C(1)-C(2)-C(3)-O(1)	-148.2(2)	C(19)-C(13)-C(17)-C(16)	92.7(2)
C(1)-C(2)-C(3)-C(4)	34.4(3)	C(14)-C(13)-C(17)-C(16)	-26.3(2)
O(1)-C(3)-C(4)-C(5)	178.2(2)	C(12)-C(13)-C(17)-C(20)	46.6(2)
C(2)-C(3)-C(4)-C(5)	-4.5(3)	C(19)-C(13)-C(17)-C(20)	-79.0(2)
C(3)-C(4)-C(5)-C(6)	171.4(2)	C(14)-C(13)-C(17)-C(20)	161.95(18)
C(3)-C(4)-C(5)-C(10)	-5.5(3)	C(16)-C(17)-C(20)-O(2)	-163.5(2)
C(4)-C(5)-C(6)-C(7)	134.16(19)	C(13)-C(17)-C(20)-O(2)	6.9(3)
C(10)-C(5)-C(6)-C(7)	-48.8(2)	C(16)-C(17)-C(20)-C(21)	14.9(3)
C(5)-C(6)-C(7)-C(8)	51.0(3)	C(13)-C(17)-C(20)-C(21)	-174.71(16)
C(6)-C(7)-C(8)-C(14)	-173.8(2)	O(2)-C(20)-C(21)-C(22)	15.8(3)
C(6)-C(7)-C(8)-C(9)	-55.6(3)	C(17)-C(20)-C(21)-C(22)	-162.60(18)
C(14)-C(8)-C(9)-C(11)	-51.20(18)	C(20)-C(21)-C(22)-C(23A)	176.3(4)
C(7)-C(8)-C(9)-C(11)	-171.83(16)	C(20)-C(21)-C(22)-C(23C)	168.4(10)
C(14)-C(8)-C(9)-C(10)	179.47(13)	C(20)-C(21)-C(22)-C(23B)	170.2(7)
C(7)-C(8)-C(9)-C(10)	58.83(19)	C(21)-C(22)-C(23A)-C(28A)	9.2(8)
C(4)-C(5)-C(10)-C(1)	-15.4(2)	C(21)-C(22)-C(23A)-C(24A)	-163.5(4)
C(6)-C(5)-C(10)-C(1)	167.58(16)	C(28A)-C(23A)-C(24A)-C(25A)	1.0(9)
C(4)-C(5)-C(10)-C(18)	104.42(19)	C(22)-C(23A)-C(24A)-C(25A)	173.3(5)
C(6)-C(5)-C(10)-C(18)	-72.56(18)	C(23A)-C(24A)-C(25A)-C(26A)	-2.3(7)
C(4)-C(5)-C(10)-C(9)	-134.03(17)	C(24A)-C(25A)-C(26A)-C(27A)	1.3(7)
C(6)-C(5)-C(10)-C(9)	49.0(2)	C(24A)-C(25A)-C(26A)-Br(1A)	179.1(4)
C(2)-C(1)-C(10)-C(5)	45.7(2)	C(25A)-C(26A)-C(27A)-C(28A)	1.0(9)
C(2)-C(1)-C(10)-C(18)	-73.1(2)	Br(1A)-C(26A)-C(27A)-C(28A)	-176.8(6)

C(2)-C(1)-C(10)-C(9)	164.28(16)	C(24A)-C(23A)-C(28A)-C(27A)	1.3(11)
C(8)-C(9)-C(10)-C(5)	-54.26(16)	C(22)-C(23A)-C(28A)-C(27A)	-171.3(6)
C(11)-C(9)-C(10)-C(5)	176.52(14)	C(26A)-C(27A)-C(28A)-C(23A)	-2.3(11)
C(8)-C(9)-C(10)-C(1)	-174.08(13)	C(21)-C(22)-C(23B)-C(28B)	21.8(19)
C(11)-C(9)-C(10)-C(1)	56.70(18)	C(21)-C(22)-C(23B)-C(24B)	-160.2(8)
C(8)-C(9)-C(10)-C(18)	64.73(16)	C(28B)-C(23B)-C(24B)-C(25B)	-1.3(18)
C(11)-C(9)-C(10)-C(18)	-64.49(18)	C(22)-C(23B)-C(24B)-C(25B)	-179.5(9)
C(8)-C(9)-C(11)-C(12)	50.2(2)	C(23B)-C(24B)-C(25B)-C(26B)	0.3(13)
C(10)-C(9)-C(11)-C(12)	179.67(15)	C(24B)-C(25B)-C(26B)-C(27B)	1.7(10)
C(9)-C(11)-C(12)-C(13)	-53.19(19)	C(24B)-C(25B)-C(26B)-Br(1B)	-176.9(5)
C(11)-C(12)-C(13)-C(17)	168.49(13)	C(25B)-C(26B)-C(27B)-C(28B)	-2.5(14)
C(11)-C(12)-C(13)-C(19)	-67.33(16)	Br(1B)-C(26B)-C(27B)-C(28B)	176.1(9)
C(11)-C(12)-C(13)-C(14)	57.26(18)	C(24B)-C(23B)-C(28B)-C(27B)	0(2)
C(7)-C(8)-C(14)-C(15)	-55.6(3)	C(22)-C(23B)-C(28B)-C(27B)	178.3(13)
C(9)-C(8)-C(14)-C(15)	-174.72(18)	C(26B)-C(27B)-C(28B)-C(23B)	2(2)
C(7)-C(8)-C(14)-C(13)	179.55(18)	C(21)-C(22)-C(23C)-C(28C)	19(2)
C(9)-C(8)-C(14)-C(13)	60.4(2)	C(21)-C(22)-C(23C)-C(24C)	-165.8(10)
C(17)-C(13)-C(14)-C(8)	171.74(18)	C(28C)-C(23C)-C(24C)-C(25C)	-3(2)
C(12)-C(13)-C(14)-C(8)	-64.4(2)	C(22)-C(23C)-C(24C)-C(25C)	-178.8(12)
C(19)-C(13)-C(14)-C(8)	57.9(2)	C(23C)-C(24C)-C(25C)-C(26C)	2.9(18)
C(17)-C(13)-C(14)-C(15)	37.7(2)	C(24C)-C(25C)-C(26C)-C(27C)	0.4(15)
C(12)-C(13)-C(14)-C(15)	161.58(19)	C(24C)-C(25C)-C(26C)-Br(1C)	-179.2(8)
C(19)-C(13)-C(14)-C(15)	-76.2(2)	C(25C)-C(26C)-C(27C)-C(28C)	-3(2)
C(8)-C(14)-C(15)-C(16)	-165.08(19)	Br(1C)-C(26C)-C(27C)-C(28C)	176.3(14)
C(13)-C(14)-C(15)-C(16)	-35.6(3)	C(24C)-C(23C)-C(28C)-C(27C)	0(3)
C(14)-C(15)-C(16)-C(17)	20.1(3)	C(22)-C(23C)-C(28C)-C(27C)	175.4(18)
C(15)-C(16)-C(17)-C(20)	175.6(2)	C(26C)-C(27C)-C(28C)-C(23C)	3(3)
C(15)-C(16)-C(17)-C(13)	4.1(3)		

Table S11. Hydrogen bonds for **1g** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3A)...O(2)	0.87(3)	2.13(3)	2.983(5)	167(11)
O(3)-H(3B)...O(2)#1	0.86(3)	1.85(3)	2.698(5)	171(10)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, z

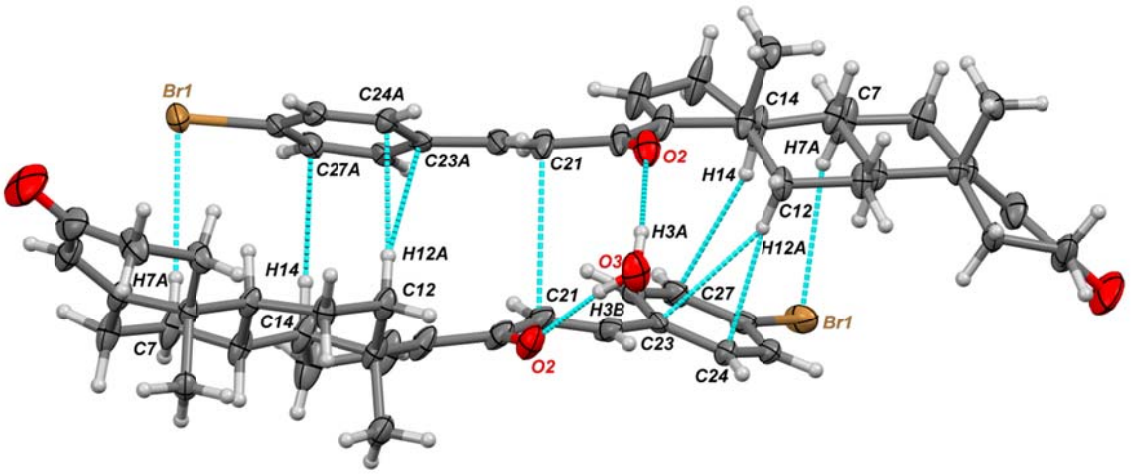


Fig. S4. The hydrogen bonds and non-covalent interactions within the associate $(\mathbf{1g})_2 \cdot H_2O$. Only interacting atoms are labeled. The disorders of the 4-bromophenyl group and of the water molecule are omitted for clarity.

Table S12. Some short-range interactions within the $(\mathbf{1g})_2 \cdot H_2O$ associate [Å].

Interaction	Length
Br(1A)..H(7A)#1	3.048
C(27A)..H(14)#1	2.871
C(24A)..H(12A)#1	2.627
C(23A)..H(12A)#1	2.840
C(21)..C(21)#1	3.363(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, z

Table S13. Selected torsion angles [°] within the -CH=C-CO-CH=CH-C_6H_4Hal fragment for **1b**, **1c** and **1g**.

	C16-C17-C20-O2	O2-C20-C21-C22	C21-C22-C23-C24	C21-C22-C23-C28
1b	-174.76(8)	-9.20(11)	159.38(7)	-20.22(12)
1c	-174.06(17)	-7.6(2)	156.00(17)	-23.6(3)
1g	-163.5(2)	15.8(3)	-160.2(8)..-165.8(10)*	9.2(8)..21.8(19)*

* The listed range for **1g** is due to disorder the -C_6H_4H-Br fragment (see Fig. S3).

S1.3. The structures of chlorine-containing D-annulated pentacyclic steroids.

S1.3.1. The structure of 2a.

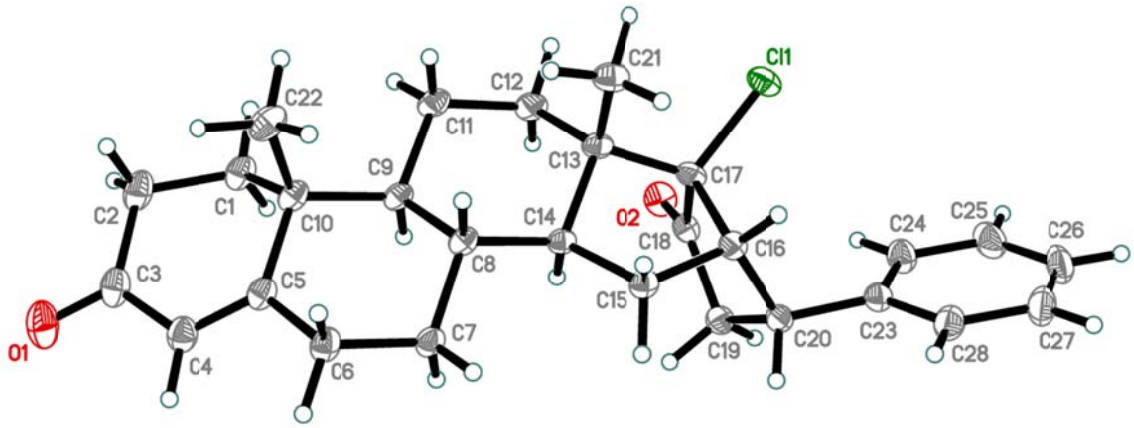


Fig. S5. The structure of **2a** (p=50%).

Table S14. Bond lengths [Å] for **2a**.

Bond	Length	Bond	Length	Bond	Length
Cl(1)-C(17)	1.8015(14)	C(8)-H(8)	1.03(2)	C(18)-C(19)	1.511(2)
O(1)-C(3)	1.225(2)	C(9)-C(11)	1.542(2)	C(19)-C(20)	1.529(2)
O(2)-C(18)	1.2100(19)	C(9)-C(10)	1.560(2)	C(19)-H(19A)	0.971(16)
C(1)-C(2)	1.521(2)	C(9)-H(9)	1.01(2)	C(19)-H(19B)	0.971(16)
C(1)-C(10)	1.543(2)	C(10)-C(21)	1.542(2)	C(20)-C(23)	1.518(2)
C(1)-H(1A)	0.986(17)	C(11)-C(12)	1.538(2)	C(20)-H(20)	1.01(2)
C(1)-H(1B)	0.986(17)	C(11)-H(11B)	0.984(18)	C(21)-H(21A)	1.004(15)
C(2)-C(3)	1.504(3)	C(11)-H(11A)	0.984(17)	C(21)-H(21B)	1.004(15)
C(2)-H(2A)	1.012(19)	C(12)-C(13)	1.530(2)	C(21)-H(21C)	1.004(15)
C(2)-H(2B)	1.012(19)	C(12)-H(12B)	0.995(17)	C(22)-H(22A)	0.983(15)
C(3)-C(4)	1.464(2)	C(12)-H(12A)	0.995(17)	C(22)-H(22B)	0.983(15)
C(4)-C(5)	1.342(2)	C(13)-C(14)	1.5402(19)	C(22)-H(22C)	0.983(16)
C(4)-H(4)	0.97(3)	C(13)-C(22)	1.541(2)	C(23)-C(24)	1.394(2)
C(5)-C(6)	1.504(2)	C(13)-C(17)	1.549(2)	C(23)-C(28)	1.398(2)
C(5)-C(10)	1.531(2)	C(14)-C(15)	1.5340(19)	C(24)-C(25)	1.394(2)
C(6)-C(7)	1.528(2)	C(14)-H(14)	1.00(2)	C(24)-H(24)	1.01(3)
C(6)-H(6B)	0.988(17)	C(15)-C(16)	1.559(2)	C(25)-C(26)	1.390(3)
C(6)-H(6A)	0.988(17)	C(15)-H(15B)	0.971(16)	C(25)-H(25)	0.97(3)

C(7)-C(8)	1.527(2)	C(15)-H(15A)	0.971(16)	C(26)-C(27)	1.384(3)
C(7)-H(7A)	0.985(17)	C(16)-C(20)	1.553(2)	C(26)-H(26)	1.03(3)
C(7)-H(7B)	0.985(17)	C(16)-C(17)	1.555(2)	C(27)-C(28)	1.391(2)
C(8)-C(14)	1.524(2)	C(16)-H(16)	1.00(2)	C(27)-H(27)	0.99(3)
C(8)-C(9)	1.5455(18)	C(17)-C(18)	1.554(2)	C(28)-H(28)	0.96(3)

Table S15. Bond angles [°] for **2a**.

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	113.55(13)	C(5)-C(10)-C(9)	109.78(11)	C(18)-C(17)-C(16)	103.61(11)
C(3)-C(2)-C(1)	112.51(14)	C(21)-C(10)-C(9)	111.64(13)	C(13)-C(17)-Cl(1)	113.11(10)
O(1)-C(3)-C(4)	121.59(17)	C(1)-C(10)-C(9)	108.51(11)	C(18)-C(17)-Cl(1)	105.51(9)
O(1)-C(3)-C(2)	121.74(16)	C(12)-C(11)-C(9)	112.76(12)	C(16)-C(17)-Cl(1)	113.98(10)
C(4)-C(3)-C(2)	116.58(14)	C(13)-C(12)-C(11)	110.54(12)	O(2)-C(18)-C(19)	126.12(14)
C(5)-C(4)-C(3)	123.44(16)	C(12)-C(13)-C(14)	109.10(12)	O(2)-C(18)-C(17)	124.91(14)
C(4)-C(5)-C(6)	119.60(14)	C(12)-C(13)-C(22)	110.33(12)	C(19)-C(18)-C(17)	108.97(12)
C(4)-C(5)-C(10)	123.25(13)	C(14)-C(13)-C(22)	111.95(12)	C(18)-C(19)-C(20)	105.76(12)
C(6)-C(5)-C(10)	117.06(13)	C(12)-C(13)-C(17)	117.47(12)	C(23)-C(20)-C(19)	113.85(12)
C(5)-C(6)-C(7)	112.34(12)	C(14)-C(13)-C(17)	98.70(11)	C(23)-C(20)-C(16)	113.47(12)
C(8)-C(7)-C(6)	111.27(12)	C(22)-C(13)-C(17)	108.84(12)	C(19)-C(20)-C(16)	103.05(11)
C(14)-C(8)-C(7)	110.79(11)	C(8)-C(14)-C(15)	119.18(11)	C(24)-C(23)-C(28)	118.40(14)
C(14)-C(8)-C(9)	108.23(11)	C(8)-C(14)-C(13)	114.19(12)	C(24)-C(23)-C(20)	123.22(14)
C(7)-C(8)-C(9)	110.38(11)	C(15)-C(14)-C(13)	103.55(11)	C(28)-C(23)-C(20)	118.38(14)
C(11)-C(9)-C(8)	111.22(12)	C(14)-C(15)-C(16)	105.25(11)	C(23)-C(24)-C(25)	120.96(17)
C(11)-C(9)-C(10)	112.90(11)	C(20)-C(16)-C(17)	106.62(11)	C(26)-C(25)-C(24)	119.71(18)
C(8)-C(9)-C(10)	113.82(11)	C(20)-C(16)-C(15)	112.88(12)	C(27)-C(26)-C(25)	120.03(16)
C(5)-C(10)-C(21)	107.85(12)	C(17)-C(16)-C(15)	103.89(11)	C(26)-C(27)-C(28)	120.07(17)
C(5)-C(10)-C(1)	109.09(13)	C(13)-C(17)-C(18)	114.91(11)	C(27)-C(28)-C(23)	120.82(17)
C(21)-C(10)-C(1)	109.94(13)	C(13)-C(17)-C(16)	105.55(11)		

Table S16. Torsion angles [°] for **2a**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-53.2(2)	C(17)-C(13)-C(14)-C(15)	47.06(13)
C(1)-C(2)-C(3)-O(1)	-154.95(17)	C(8)-C(14)-C(15)-C(16)	-162.69(12)
C(1)-C(2)-C(3)-C(4)	28.4(2)	C(13)-C(14)-C(15)-C(16)	-34.56(14)
O(1)-C(3)-C(4)-C(5)	-176.37(17)	C(14)-C(15)-C(16)-C(20)	-107.70(13)

C(2)-C(3)-C(4)-C(5)	0.3(2)	C(14)-C(15)-C(16)-C(17)	7.40(14)
C(3)-C(4)-C(5)-C(6)	171.55(15)	C(12)-C(13)-C(17)-C(18)	-46.08(17)
C(3)-C(4)-C(5)-C(10)	-4.9(2)	C(14)-C(13)-C(17)-C(18)	70.84(13)
C(4)-C(5)-C(6)-C(7)	133.70(16)	C(22)-C(13)-C(17)-C(18)	-172.30(12)
C(10)-C(5)-C(6)-C(7)	-49.62(19)	C(12)-C(13)-C(17)-C(16)	-159.56(12)
C(5)-C(6)-C(7)-C(8)	53.79(17)	C(14)-C(13)-C(17)-C(16)	-42.65(13)
C(6)-C(7)-C(8)-C(14)	-176.64(12)	C(22)-C(13)-C(17)-C(16)	74.21(14)
C(6)-C(7)-C(8)-C(9)	-56.78(16)	C(12)-C(13)-C(17)-Cl(1)	75.17(14)
C(14)-C(8)-C(9)-C(11)	-54.37(14)	C(14)-C(13)-C(17)-Cl(1)	-167.91(9)
C(7)-C(8)-C(9)-C(11)	-175.77(12)	C(22)-C(13)-C(17)-Cl(1)	-51.05(13)
C(14)-C(8)-C(9)-C(10)	176.75(12)	C(20)-C(16)-C(17)-C(13)	141.72(11)
C(7)-C(8)-C(9)-C(10)	55.35(15)	C(15)-C(16)-C(17)-C(13)	22.26(14)
C(4)-C(5)-C(10)-C(21)	100.52(17)	C(20)-C(16)-C(17)-C(18)	20.57(14)
C(6)-C(5)-C(10)-C(21)	-76.04(16)	C(15)-C(16)-C(17)-C(18)	-98.89(12)
C(4)-C(5)-C(10)-C(1)	-18.9(2)	C(20)-C(16)-C(17)-Cl(1)	-93.56(12)
C(6)-C(5)-C(10)-C(1)	164.58(13)	C(15)-C(16)-C(17)-Cl(1)	146.98(10)
C(4)-C(5)-C(10)-C(9)	-137.65(15)	C(13)-C(17)-C(18)-O(2)	66.09(18)
C(6)-C(5)-C(10)-C(9)	45.80(17)	C(16)-C(17)-C(18)-O(2)	-179.30(13)
C(2)-C(1)-C(10)-C(5)	47.13(18)	Cl(1)-C(17)-C(18)-O(2)	-59.23(16)
C(2)-C(1)-C(10)-C(21)	-70.94(18)	C(13)-C(17)-C(18)-C(19)	-114.33(13)
C(2)-C(1)-C(10)-C(9)	166.70(14)	C(16)-C(17)-C(18)-C(19)	0.28(14)
C(11)-C(9)-C(10)-C(5)	-176.28(12)	Cl(1)-C(17)-C(18)-C(19)	120.35(10)
C(8)-C(9)-C(10)-C(5)	-48.25(15)	O(2)-C(18)-C(19)-C(20)	158.30(14)
C(11)-C(9)-C(10)-C(21)	-56.73(15)	C(17)-C(18)-C(19)-C(20)	-21.28(15)
C(8)-C(9)-C(10)-C(21)	71.29(15)	C(18)-C(19)-C(20)-C(23)	-90.05(15)
C(11)-C(9)-C(10)-C(1)	64.58(16)	C(18)-C(19)-C(20)-C(16)	33.29(14)
C(8)-C(9)-C(10)-C(1)	-167.39(12)	C(17)-C(16)-C(20)-C(23)	90.04(14)
C(8)-C(9)-C(11)-C(12)	55.31(16)	C(15)-C(16)-C(20)-C(23)	-156.52(12)
C(10)-C(9)-C(11)-C(12)	-175.32(12)	C(17)-C(16)-C(20)-C(19)	-33.55(14)
C(9)-C(11)-C(12)-C(13)	-55.33(17)	C(15)-C(16)-C(20)-C(19)	79.89(13)
C(11)-C(12)-C(13)-C(14)	54.80(16)	C(19)-C(20)-C(23)-C(24)	20.7(2)
C(11)-C(12)-C(13)-C(22)	-68.57(16)	C(16)-C(20)-C(23)-C(24)	-96.75(17)
C(11)-C(12)-C(13)-C(17)	165.93(12)	C(19)-C(20)-C(23)-C(28)	-158.99(14)
C(7)-C(8)-C(14)-C(15)	-58.05(16)	C(16)-C(20)-C(23)-C(28)	83.55(17)
C(9)-C(8)-C(14)-C(15)	-179.19(12)	C(28)-C(23)-C(24)-C(25)	0.5(3)
C(7)-C(8)-C(14)-C(13)	178.93(11)	C(20)-C(23)-C(24)-C(25)	-179.19(16)

C(9)-C(8)-C(14)-C(13)	57.78(15)	C(23)-C(24)-C(25)-C(26)	0.0(3)
C(12)-C(13)-C(14)-C(8)	-58.64(15)	C(24)-C(25)-C(26)-C(27)	-0.5(3)
C(22)-C(13)-C(14)-C(8)	63.76(16)	C(25)-C(26)-C(27)-C(28)	0.4(3)
C(17)-C(13)-C(14)-C(8)	178.21(11)	C(26)-C(27)-C(28)-C(23)	0.2(3)
C(12)-C(13)-C(14)-C(15)	170.21(12)	C(24)-C(23)-C(28)-C(27)	-0.6(2)
C(22)-C(13)-C(14)-C(15)	-67.39(15)	C(20)-C(23)-C(28)-C(27)	179.08(15)

S1.3.2. The structure of 2b.

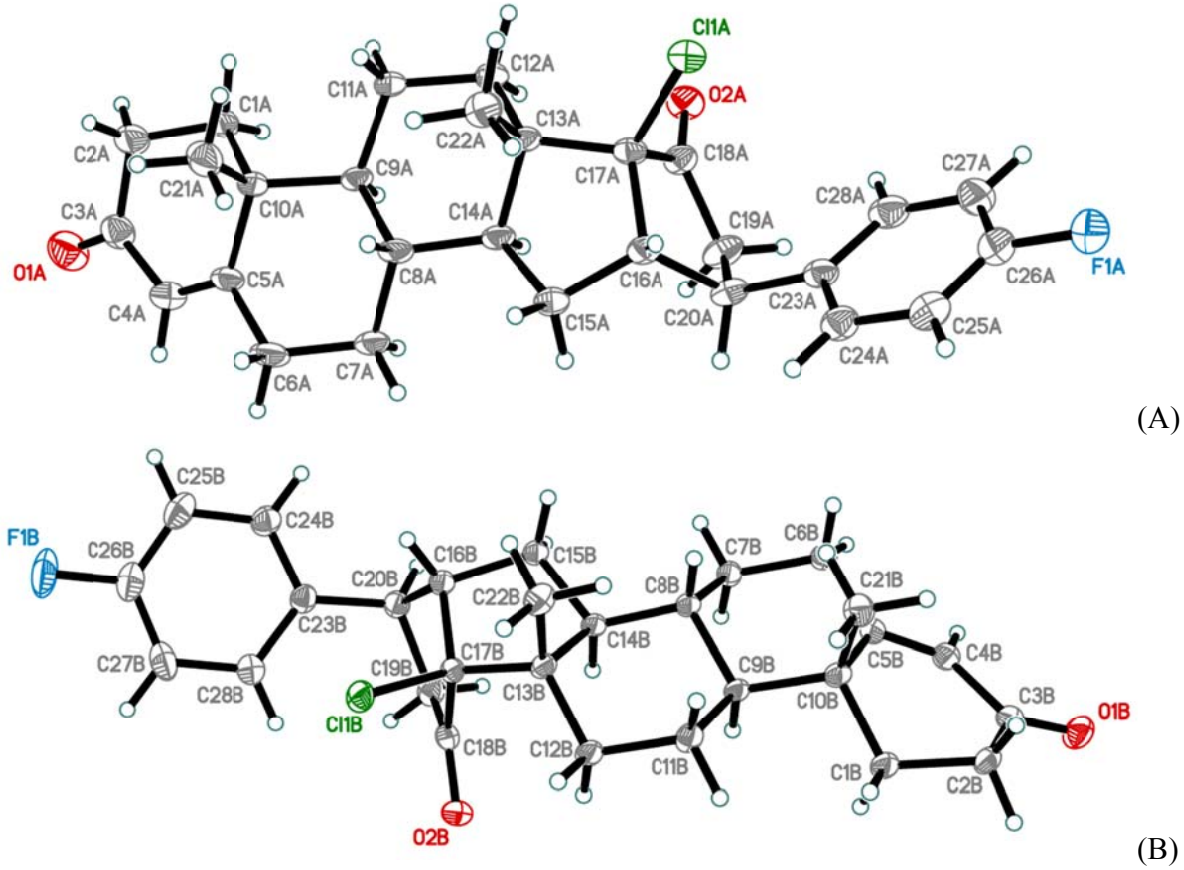


Fig. S6. The structures of two crystallographically unique molecules (***A*** and ***B***) of **2b** (p=50%).

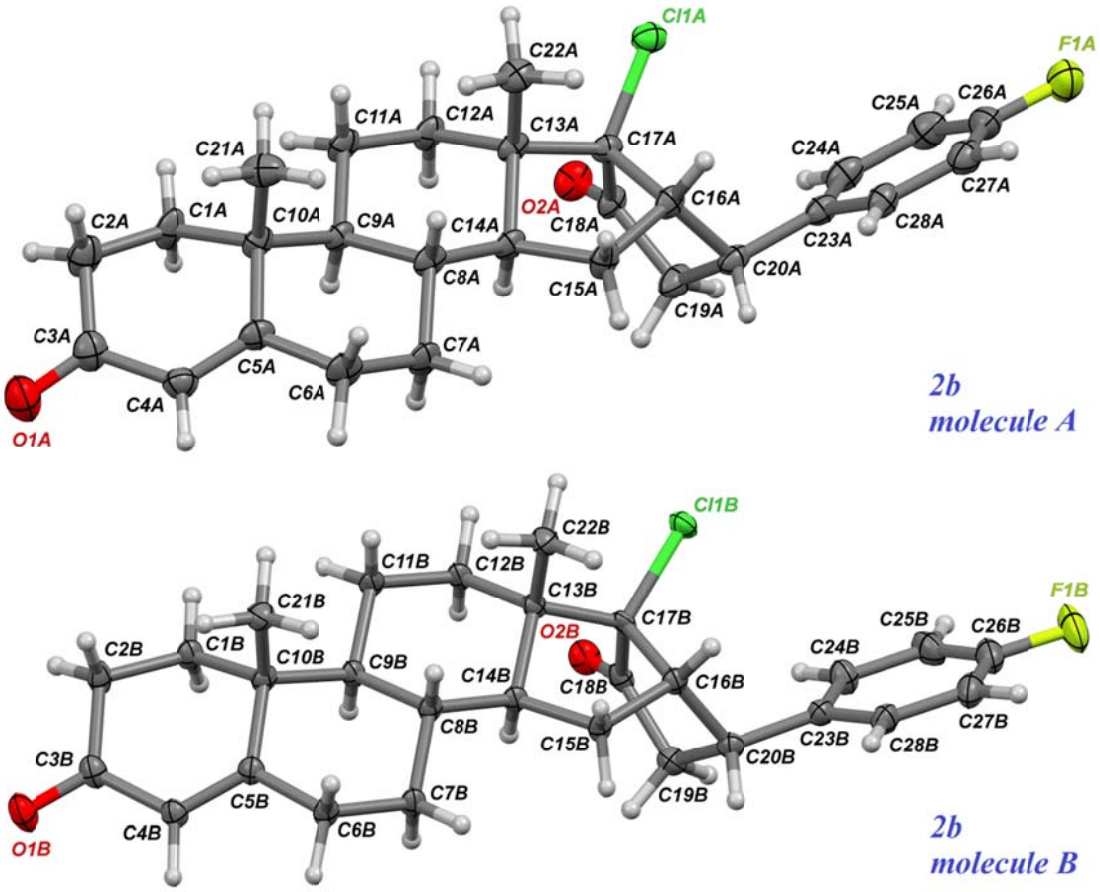


Fig. S7. The structures of two crystallographically unique molecules (***A*** and ***B***) of **2b**, similarly oriented in space (p=50%).

Table S17. Bond lengths [Å] for **2b**.

Bond	Length	Bond	Length	Bond	Length
Cl(1A)-C(17A)	1.803(3)	C(8A)-C(9A)	1.549(4)	C(17A)-C(18A)	1.555(4)
F(1A)-C(26A)	1.360(5)	C(8A)-H(8A)	0.98(5)	C(18A)-C(19A)	1.514(5)
O(1A)-C(3A)	1.223(5)	C(9A)-C(11A)	1.542(4)	C(19A)-C(20A)	1.535(5)
O(2A)-C(18A)	1.204(4)	C(9A)-C(10A)	1.555(4)	C(19A)-H(19A)	0.99(3)
C(1A)-C(2A)	1.526(5)	C(9A)-H(9A)	0.99(4)	C(19A)-H(19B)	0.99(3)
C(1A)-C(10A)	1.540(5)	C(10A)-C(21A)	1.550(5)	C(20A)-C(23A)	1.514(5)
C(1A)-H(1A)	0.92(3)	C(11A)-C(12A)	1.537(5)	C(20A)-H(20A)	0.94(5)
C(1A)-H(1B)	0.92(3)	C(11A)-H(11B)	1.01(3)	C(21A)-H(21A)	0.94(3)
C(2A)-C(3A)	1.504(5)	C(11A)-H(11A)	1.01(3)	C(21A)-H(21B)	0.94(3)
C(2A)-H(2A)	0.98(4)	C(12A)-C(13A)	1.533(4)	C(21A)-H(21C)	0.94(3)
C(2A)-H(2B)	0.98(4)	C(12A)-H(12B)	1.01(3)	C(22A)-H(22A)	0.97(3)

C(3A)-C(4A)	1.457(5)	C(12A)-H(12A)	1.01(3)	C(22A)-H(22B)	0.97(3)
C(4A)-C(5A)	1.338(5)	C(13A)-C(22A)	1.538(4)	C(22A)-H(22C)	0.97(3)
C(4A)-H(4A)	0.94(5)	C(13A)-C(14A)	1.541(4)	C(23A)-C(24A)	1.392(5)
C(5A)-C(6A)	1.506(5)	C(13A)-C(17A)	1.544(5)	C(23A)-C(28A)	1.404(4)
C(5A)-C(10A)	1.522(4)	C(14A)-C(15A)	1.537(4)	C(24A)-C(25A)	1.393(6)
C(6A)-C(7A)	1.532(5)	C(14A)-H(14A)	1.00(4)	C(24A)-H(24A)	0.89(5)
C(6A)-H(6B)	1.00(3)	C(15A)-C(16A)	1.554(5)	C(25A)-C(26A)	1.374(6)
C(6A)-H(6A)	1.00(3)	C(15A)-H(15B)	0.93(3)	C(25A)-H(25A)	1.06(5)
C(7A)-C(8A)	1.533(5)	C(15A)-H(15A)	0.93(3)	C(26A)-C(27A)	1.374(6)
C(7A)-H(7A)	1.01(3)	C(16A)-C(20A)	1.552(5)	C(27A)-C(28A)	1.384(5)
C(7A)-H(7B)	1.01(3)	C(16A)-C(17A)	1.557(4)	C(27A)-H(27A)	0.99(5)
C(8A)-C(14A)	1.520(5)	C(16A)-H(16A)	0.96(4)	C(28A)-H(28A)	0.98(5)
Cl(1B)-C(17B)	1.800(3)	C(8B)-C(9B)	1.548(4)	C(17B)-C(18B)	1.555(4)
F(1B)-C(26B)	1.365(4)	C(8B)-H(8B)	0.96(4)	C(18B)-C(19B)	1.512(5)
O(1B)-C(3B)	1.224(4)	C(9B)-C(11B)	1.539(4)	C(19B)-C(20B)	1.532(5)
O(2B)-C(18B)	1.205(4)	C(9B)-C(10B)	1.562(4)	C(19B)-H(19C)	0.98(3)
C(1B)-C(2B)	1.529(4)	C(9B)-H(9B)	0.93(4)	C(19B)-H(19D)	0.98(3)
C(1B)-C(10B)	1.541(4)	C(10B)-C(21B)	1.545(4)	C(20B)-C(23B)	1.512(4)
C(1B)-H(1C)	0.91(3)	C(11B)-C(12B)	1.536(4)	C(20B)-H(20B)	0.97(5)
C(1B)-H(1D)	0.91(3)	C(11B)-H(11D)	1.00(3)	C(21B)-H(21D)	0.98(3)
C(2B)-C(3B)	1.505(5)	C(11B)-H(11C)	1.00(3)	C(21B)-H(21E)	0.98(3)
C(2B)-H(2C)	0.97(3)	C(12B)-C(13B)	1.526(4)	C(21B)-H(21F)	0.98(3)
C(2B)-H(2D)	0.97(3)	C(12B)-H(12D)	0.98(3)	C(22B)-H(22D)	0.97(3)
C(3B)-C(4B)	1.466(4)	C(12B)-H(12C)	0.98(3)	C(22B)-H(22E)	0.97(3)
C(4B)-C(5B)	1.347(4)	C(13B)-C(14B)	1.539(4)	C(22B)-H(22F)	0.97(3)
C(4B)-H(4B)	0.98(5)	C(13B)-C(22B)	1.544(4)	C(23B)-C(24B)	1.390(5)
C(5B)-C(6B)	1.501(4)	C(13B)-C(17B)	1.546(4)	C(23B)-C(28B)	1.396(4)
C(5B)-C(10B)	1.519(4)	C(14B)-C(15B)	1.536(4)	C(24B)-C(25B)	1.405(5)
C(6B)-C(7B)	1.531(4)	C(14B)-H(14B)	0.95(4)	C(24B)-H(24B)	0.94(5)
C(6B)-H(6D)	0.97(3)	C(15B)-C(16B)	1.563(4)	C(25B)-C(26B)	1.367(6)
C(6B)-H(6C)	0.97(3)	C(15B)-H(15D)	0.94(3)	C(25B)-H(25B)	0.95(5)
C(7B)-C(8B)	1.523(4)	C(15B)-H(15C)	0.94(3)	C(26B)-C(27B)	1.381(6)
C(7B)-H(7C)	0.99(3)	C(16B)-C(17B)	1.549(4)	C(27B)-C(28B)	1.396(5)
C(7B)-H(7D)	0.99(3)	C(16B)-C(20B)	1.561(4)	C(27B)-H(27B)	1.04(5)
C(8B)-C(14B)	1.524(4)	C(16B)-H(16B)	0.94(4)	C(28B)-H(28B)	0.93(5)

Table S18. Bond angles [°] for **2b**.

Atoms	Angle	Atoms	Angle
C(2A)-C(1A)-C(10A)	113.6(3)	C(8A)-C(14A)-C(15A)	116.8(3)
C(3A)-C(2A)-C(1A)	112.2(3)	C(8A)-C(14A)-C(13A)	112.9(3)
O(1A)-C(3A)-C(4A)	121.7(4)	C(15A)-C(14A)-C(13A)	104.0(3)
O(1A)-C(3A)-C(2A)	122.4(4)	C(14A)-C(15A)-C(16A)	105.7(2)
C(4A)-C(3A)-C(2A)	115.9(3)	C(20A)-C(16A)-C(15A)	114.2(3)
C(5A)-C(4A)-C(3A)	124.6(3)	C(20A)-C(16A)-C(17A)	106.6(2)
C(4A)-C(5A)-C(6A)	119.9(3)	C(15A)-C(16A)-C(17A)	104.6(3)
C(4A)-C(5A)-C(10A)	122.7(3)	C(13A)-C(17A)-C(18A)	115.8(3)
C(6A)-C(5A)-C(10A)	117.3(3)	C(13A)-C(17A)-C(16A)	105.6(2)
C(5A)-C(6A)-C(7A)	113.3(3)	C(18A)-C(17A)-C(16A)	104.2(2)
C(6A)-C(7A)-C(8A)	110.3(3)	C(13A)-C(17A)-Cl(1A)	113.4(2)
C(14A)-C(8A)-C(7A)	112.6(3)	C(18A)-C(17A)-Cl(1A)	104.8(2)
C(14A)-C(8A)-C(9A)	110.6(2)	C(16A)-C(17A)-Cl(1A)	112.9(2)
C(7A)-C(8A)-C(9A)	108.6(3)	O(2A)-C(18A)-C(19A)	126.5(3)
C(11A)-C(9A)-C(8A)	113.2(3)	O(2A)-C(18A)-C(17A)	124.7(3)
C(11A)-C(9A)-C(10A)	112.7(2)	C(19A)-C(18A)-C(17A)	108.8(3)
C(8A)-C(9A)-C(10A)	111.9(2)	C(18A)-C(19A)-C(20A)	106.3(3)
C(5A)-C(10A)-C(1A)	109.5(3)	C(23A)-C(20A)-C(19A)	115.2(3)
C(5A)-C(10A)-C(21A)	107.2(3)	C(23A)-C(20A)-C(16A)	111.6(3)
C(1A)-C(10A)-C(21A)	110.0(3)	C(19A)-C(20A)-C(16A)	103.6(3)
C(5A)-C(10A)-C(9A)	109.1(3)	C(24A)-C(23A)-C(28A)	118.4(3)
C(1A)-C(10A)-C(9A)	109.0(2)	C(24A)-C(23A)-C(20A)	124.4(3)
C(21A)-C(10A)-C(9A)	112.1(3)	C(28A)-C(23A)-C(20A)	117.2(3)
C(12A)-C(11A)-C(9A)	114.6(3)	C(23A)-C(24A)-C(25A)	120.8(3)
C(13A)-C(12A)-C(11A)	109.3(3)	C(26A)-C(25A)-C(24A)	118.3(4)
C(12A)-C(13A)-C(22A)	109.7(3)	F(1A)-C(26A)-C(25A)	118.0(4)
C(12A)-C(13A)-C(14A)	107.5(3)	F(1A)-C(26A)-C(27A)	118.9(4)
C(22A)-C(13A)-C(14A)	112.7(3)	C(25A)-C(26A)-C(27A)	123.1(4)
C(12A)-C(13A)-C(17A)	118.6(2)	C(26A)-C(27A)-C(28A)	117.9(4)
C(22A)-C(13A)-C(17A)	107.9(3)	C(27A)-C(28A)-C(23A)	121.3(3)
C(14A)-C(13A)-C(17A)	100.2(2)		
C(2B)-C(1B)-C(10B)	112.7(2)	C(8B)-C(14B)-C(15B)	117.8(2)

C(3B)-C(2B)-C(1B)	112.1(3)	C(8B)-C(14B)-C(13B)	114.1(2)
O(1B)-C(3B)-C(4B)	121.5(3)	C(15B)-C(14B)-C(13B)	103.8(2)
O(1B)-C(3B)-C(2B)	122.1(3)	C(14B)-C(15B)-C(16B)	105.2(2)
C(4B)-C(3B)-C(2B)	116.3(3)	C(17B)-C(16B)-C(20B)	106.5(2)
C(5B)-C(4B)-C(3B)	123.6(3)	C(17B)-C(16B)-C(15B)	103.6(2)
C(4B)-C(5B)-C(6B)	120.2(3)	C(20B)-C(16B)-C(15B)	112.9(2)
C(4B)-C(5B)-C(10B)	122.6(3)	C(13B)-C(17B)-C(16B)	105.8(2)
C(6B)-C(5B)-C(10B)	117.1(3)	C(13B)-C(17B)-C(18B)	114.3(2)
C(5B)-C(6B)-C(7B)	112.5(2)	C(16B)-C(17B)-C(18B)	103.9(2)
C(8B)-C(7B)-C(6B)	111.1(2)	C(13B)-C(17B)-Cl(1B)	113.9(2)
C(7B)-C(8B)-C(14B)	111.0(2)	C(16B)-C(17B)-Cl(1B)	113.3(2)
C(7B)-C(8B)-C(9B)	109.3(2)	C(18B)-C(17B)-Cl(1B)	105.40(19)
C(14B)-C(8B)-C(9B)	109.0(2)	O(2B)-C(18B)-C(19B)	126.3(3)
C(11B)-C(9B)-C(8B)	112.3(2)	O(2B)-C(18B)-C(17B)	125.0(3)
C(11B)-C(9B)-C(10B)	112.4(2)	C(19B)-C(18B)-C(17B)	108.7(3)
C(8B)-C(9B)-C(10B)	112.3(2)	C(18B)-C(19B)-C(20B)	106.6(3)
C(5B)-C(10B)-C(1B)	109.8(2)	C(23B)-C(20B)-C(19B)	114.8(3)
C(5B)-C(10B)-C(21B)	108.2(2)	C(23B)-C(20B)-C(16B)	113.2(2)
C(1B)-C(10B)-C(21B)	109.6(2)	C(19B)-C(20B)-C(16B)	102.7(2)
C(5B)-C(10B)-C(9B)	108.4(2)	C(24B)-C(23B)-C(28B)	118.4(3)
C(1B)-C(10B)-C(9B)	108.6(2)	C(24B)-C(23B)-C(20B)	123.2(3)
C(21B)-C(10B)-C(9B)	112.2(2)	C(28B)-C(23B)-C(20B)	118.4(3)
C(12B)-C(11B)-C(9B)	113.5(2)	C(23B)-C(24B)-C(25B)	121.2(3)
C(13B)-C(12B)-C(11B)	110.4(2)	C(26B)-C(25B)-C(24B)	117.9(3)
C(12B)-C(13B)-C(14B)	108.9(2)	F(1B)-C(26B)-C(25B)	118.5(4)
C(12B)-C(13B)-C(22B)	109.4(2)	F(1B)-C(26B)-C(27B)	118.0(4)
C(14B)-C(13B)-C(22B)	112.3(2)	C(25B)-C(26B)-C(27B)	123.5(3)
C(12B)-C(13B)-C(17B)	118.3(2)	C(26B)-C(27B)-C(28B)	117.5(3)
C(14B)-C(13B)-C(17B)	98.3(2)	C(27B)-C(28B)-C(23B)	121.6(3)
C(22B)-C(13B)-C(17B)	109.2(2)		

Table S19. Torsion angles [°] for **2b**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10A)-C(1A)-C(2A)-C(3A)	-53.6(5)	C(8A)-C(14A)-C(15A)-C(16A)	-156.8(3)
C(1A)-C(2A)-C(3A)-O(1A)	-152.3(4)	C(13A)-C(14A)-C(15A)-C(16A)	-31.7(3)

C(1A)-C(2A)-C(3A)-C(4A)	30.1(5)
O(1A)-C(3A)-C(4A)-C(5A)	-179.3(4)
C(2A)-C(3A)-C(4A)-C(5A)	-1.7(6)
C(3A)-C(4A)-C(5A)-C(6A)	172.1(4)
C(3A)-C(4A)-C(5A)-C(10A)	-4.3(6)
C(4A)-C(5A)-C(6A)-C(7A)	136.8(4)
C(10A)-C(5A)-C(6A)-C(7A)	-46.5(4)
C(5A)-C(6A)-C(7A)-C(8A)	52.0(4)
C(6A)-C(7A)-C(8A)-C(14A)	177.7(3)
C(6A)-C(7A)-C(8A)-C(9A)	-59.5(4)
C(14A)-C(8A)-C(9A)-C(11A)	-45.3(4)
C(7A)-C(8A)-C(9A)-C(11A)	-169.2(3)
C(14A)-C(8A)-C(9A)-C(10A)	-173.9(3)
C(7A)-C(8A)-C(9A)-C(10A)	62.1(3)
C(4A)-C(5A)-C(10A)-C(1A)	-18.2(5)
C(6A)-C(5A)-C(10A)-C(1A)	165.3(3)
C(4A)-C(5A)-C(10A)-C(21A)	101.1(4)
C(6A)-C(5A)-C(10A)-C(21A)	-75.5(4)
C(4A)-C(5A)-C(10A)-C(9A)	-137.4(3)
C(6A)-C(5A)-C(10A)-C(9A)	46.1(4)
C(2A)-C(1A)-C(10A)-C(5A)	46.4(4)
C(2A)-C(1A)-C(10A)-C(21A)	-71.1(4)
C(2A)-C(1A)-C(10A)-C(9A)	165.6(3)
C(11A)-C(9A)-C(10A)-C(5A)	177.5(3)
C(8A)-C(9A)-C(10A)-C(5A)	-53.6(3)
C(11A)-C(9A)-C(10A)-C(1A)	58.0(4)
C(8A)-C(9A)-C(10A)-C(1A)	-173.1(3)
C(11A)-C(9A)-C(10A)-C(21A)	-64.0(3)
C(8A)-C(9A)-C(10A)-C(21A)	65.0(3)
C(8A)-C(9A)-C(11A)-C(12A)	46.3(4)
C(10A)-C(9A)-C(11A)-C(12A)	174.6(3)
C(9A)-C(11A)-C(12A)-C(13A)	-54.2(4)
C(11A)-C(12A)-C(13A)-C(22A)	-62.3(3)
C(11A)-C(12A)-C(13A)-C(14A)	60.6(3)
C(11A)-C(12A)-C(13A)-C(17A)	173.1(3)
C(7A)-C(8A)-C(14A)-C(15A)	-62.3(4)
C(14A)-C(15A)-C(16A)-C(20A)	-109.9(3)
C(14A)-C(15A)-C(16A)-C(17A)	6.2(3)
C(12A)-C(13A)-C(17A)-C(18A)	-42.0(4)
C(22A)-C(13A)-C(17A)-C(18A)	-167.5(3)
C(14A)-C(13A)-C(17A)-C(18A)	74.4(3)
C(12A)-C(13A)-C(17A)-C(16A)	-156.7(3)
C(22A)-C(13A)-C(17A)-C(16A)	77.8(3)
C(14A)-C(13A)-C(17A)-C(16A)	-40.3(3)
C(12A)-C(13A)-C(17A)-Cl(1A)	79.2(3)
C(22A)-C(13A)-C(17A)-Cl(1A)	-46.3(3)
C(14A)-C(13A)-C(17A)-Cl(1A)	-164.3(2)
C(20A)-C(16A)-C(17A)-C(13A)	142.7(3)
C(15A)-C(16A)-C(17A)-C(13A)	21.4(3)
C(20A)-C(16A)-C(17A)-C(18A)	20.2(3)
C(15A)-C(16A)-C(17A)-C(18A)	-101.1(3)
C(20A)-C(16A)-C(17A)-Cl(1A)	-92.9(3)
C(15A)-C(16A)-C(17A)-Cl(1A)	145.8(2)
C(13A)-C(17A)-C(18A)-O(2A)	65.3(4)
C(16A)-C(17A)-C(18A)-O(2A)	-179.2(3)
Cl(1A)-C(17A)-C(18A)-O(2A)	-60.5(4)
C(13A)-C(17A)-C(18A)-C(19A)	-116.4(3)
C(16A)-C(17A)-C(18A)-C(19A)	-0.9(4)
Cl(1A)-C(17A)-C(18A)-C(19A)	117.8(3)
O(2A)-C(18A)-C(19A)-C(20A)	159.4(4)
C(17A)-C(18A)-C(19A)-C(20A)	-18.8(4)
C(18A)-C(19A)-C(20A)-C(23A)	-91.4(3)
C(18A)-C(19A)-C(20A)-C(16A)	30.8(4)
C(15A)-C(16A)-C(20A)-C(23A)	-152.2(3)
C(17A)-C(16A)-C(20A)-C(23A)	92.9(3)
C(15A)-C(16A)-C(20A)-C(19A)	83.3(3)
C(17A)-C(16A)-C(20A)-C(19A)	-31.7(3)
C(19A)-C(20A)-C(23A)-C(24A)	8.5(5)
C(16A)-C(20A)-C(23A)-C(24A)	-109.3(4)
C(19A)-C(20A)-C(23A)-C(28A)	-170.8(3)
C(16A)-C(20A)-C(23A)-C(28A)	71.5(4)
C(28A)-C(23A)-C(24A)-C(25A)	-0.2(5)

C(9A)-C(8A)-C(14A)-C(15A)	176.0(3)	C(20A)-C(23A)-C(24A)-C(25A)	-179.5(3)
C(7A)-C(8A)-C(14A)-C(13A)	177.2(3)	C(23A)-C(24A)-C(25A)-C(26A)	-0.1(6)
C(9A)-C(8A)-C(14A)-C(13A)	55.5(3)	C(24A)-C(25A)-C(26A)-F(1A)	179.6(3)
C(12A)-C(13A)-C(14A)-C(8A)	-63.9(3)	C(24A)-C(25A)-C(26A)-C(27A)	0.4(6)
C(22A)-C(13A)-C(14A)-C(8A)	57.2(4)	F(1A)-C(26A)-C(27A)-C(28A)	-179.6(3)
C(17A)-C(13A)-C(14A)-C(8A)	171.6(3)	C(25A)-C(26A)-C(27A)-C(28A)	-0.4(6)
C(12A)-C(13A)-C(14A)-C(15A)	168.6(3)	C(26A)-C(27A)-C(28A)-C(23A)	0.0(5)
C(22A)-C(13A)-C(14A)-C(15A)	-70.4(3)	C(24A)-C(23A)-C(28A)-C(27A)	0.3(5)
C(17A)-C(13A)-C(14A)-C(15A)	44.0(3)	C(20A)-C(23A)-C(28A)-C(27A)	179.6(3)
C(10B)-C(1B)-C(2B)-C(3B)	-54.4(4)	C(8B)-C(14B)-C(15B)-C(16B)	-160.7(3)
C(1B)-C(2B)-C(3B)-O(1B)	-155.2(3)	C(13B)-C(14B)-C(15B)-C(16B)	-33.4(3)
C(1B)-C(2B)-C(3B)-C(4B)	28.1(4)	C(14B)-C(15B)-C(16B)-C(17B)	5.6(3)
O(1B)-C(3B)-C(4B)-C(5B)	-173.5(3)	C(14B)-C(15B)-C(16B)-C(20B)	-109.2(3)
C(2B)-C(3B)-C(4B)-C(5B)	3.2(5)	C(12B)-C(13B)-C(17B)-C(16B)	-160.6(2)
C(3B)-C(4B)-C(5B)-C(6B)	166.7(3)	C(14B)-C(13B)-C(17B)-C(16B)	-43.8(3)
C(3B)-C(4B)-C(5B)-C(10B)	-8.8(5)	C(22B)-C(13B)-C(17B)-C(16B)	73.4(3)
C(4B)-C(5B)-C(6B)-C(7B)	135.0(3)	C(12B)-C(13B)-C(17B)-C(18B)	-46.9(3)
C(10B)-C(5B)-C(6B)-C(7B)	-49.3(4)	C(14B)-C(13B)-C(17B)-C(18B)	69.9(3)
C(5B)-C(6B)-C(7B)-C(8B)	52.3(4)	C(22B)-C(13B)-C(17B)-C(18B)	-172.9(2)
C(6B)-C(7B)-C(8B)-C(14B)	-178.0(2)	C(12B)-C(13B)-C(17B)-Cl(1B)	74.3(3)
C(6B)-C(7B)-C(8B)-C(9B)	-57.7(3)	C(14B)-C(13B)-C(17B)-Cl(1B)	-168.89(19)
C(7B)-C(8B)-C(9B)-C(11B)	-172.3(3)	C(22B)-C(13B)-C(17B)-Cl(1B)	-51.7(3)
C(14B)-C(8B)-C(9B)-C(11B)	-50.8(3)	C(20B)-C(16B)-C(17B)-C(13B)	143.4(2)
C(7B)-C(8B)-C(9B)-C(10B)	59.8(3)	C(15B)-C(16B)-C(17B)-C(13B)	24.1(3)
C(14B)-C(8B)-C(9B)-C(10B)	-178.6(2)	C(20B)-C(16B)-C(17B)-C(18B)	22.7(3)
C(4B)-C(5B)-C(10B)-C(1B)	-17.3(4)	C(15B)-C(16B)-C(17B)-C(18B)	-96.6(3)
C(6B)-C(5B)-C(10B)-C(1B)	167.1(3)	C(20B)-C(16B)-C(17B)-Cl(1B)	-91.2(3)
C(4B)-C(5B)-C(10B)-C(21B)	102.3(3)	C(15B)-C(16B)-C(17B)-Cl(1B)	149.5(2)
C(6B)-C(5B)-C(10B)-C(21B)	-73.3(3)	C(13B)-C(17B)-C(18B)-O(2B)	61.1(4)
C(4B)-C(5B)-C(10B)-C(9B)	-135.8(3)	C(16B)-C(17B)-C(18B)-O(2B)	175.9(3)
C(6B)-C(5B)-C(10B)-C(9B)	48.6(3)	Cl(1B)-C(17B)-C(18B)-O(2B)	-64.7(3)
C(2B)-C(1B)-C(10B)-C(5B)	48.0(4)	C(13B)-C(17B)-C(18B)-C(19B)	-117.7(3)
C(2B)-C(1B)-C(10B)-C(21B)	-70.7(3)	C(16B)-C(17B)-C(18B)-C(19B)	-2.9(3)
C(2B)-C(1B)-C(10B)-C(9B)	166.4(3)	Cl(1B)-C(17B)-C(18B)-C(19B)	116.5(2)
C(11B)-C(9B)-C(10B)-C(5B)	178.9(2)	O(2B)-C(18B)-C(19B)-C(20B)	162.9(3)

C(8B)-C(9B)-C(10B)-C(5B)	-53.4(3)	C(17B)-C(18B)-C(19B)-C(20B)	-18.3(3)
C(11B)-C(9B)-C(10B)-C(1B)	59.7(3)	C(18B)-C(19B)-C(20B)-C(23B)	-91.7(3)
C(8B)-C(9B)-C(10B)-C(1B)	-172.6(2)	C(18B)-C(19B)-C(20B)-C(16B)	31.6(3)
C(11B)-C(9B)-C(10B)-C(21B)	-61.7(3)	C(17B)-C(16B)-C(20B)-C(23B)	90.6(3)
C(8B)-C(9B)-C(10B)-C(21B)	66.1(3)	C(15B)-C(16B)-C(20B)-C(23B)	-156.3(2)
C(8B)-C(9B)-C(11B)-C(12B)	52.1(3)	C(17B)-C(16B)-C(20B)-C(19B)	-33.8(3)
C(10B)-C(9B)-C(11B)-C(12B)	179.8(2)	C(15B)-C(16B)-C(20B)-C(19B)	79.3(3)
C(9B)-C(11B)-C(12B)-C(13B)	-54.7(3)	C(19B)-C(20B)-C(23B)-C(24B)	15.9(4)
C(11B)-C(12B)-C(13B)-C(14B)	56.3(3)	C(16B)-C(20B)-C(23B)-C(24B)	-101.5(4)
C(11B)-C(12B)-C(13B)-C(22B)	-66.8(3)	C(19B)-C(20B)-C(23B)-C(28B)	-162.7(3)
C(11B)-C(12B)-C(13B)-C(17B)	167.3(2)	C(16B)-C(20B)-C(23B)-C(28B)	79.8(3)
C(7B)-C(8B)-C(14B)-C(15B)	-61.2(3)	C(28B)-C(23B)-C(24B)-C(25B)	-0.1(5)
C(9B)-C(8B)-C(14B)-C(15B)	178.3(3)	C(20B)-C(23B)-C(24B)-C(25B)	-178.8(3)
C(7B)-C(8B)-C(14B)-C(13B)	176.7(2)	C(23B)-C(24B)-C(25B)-C(26B)	-0.3(6)
C(9B)-C(8B)-C(14B)-C(13B)	56.2(3)	C(24B)-C(25B)-C(26B)-F(1B)	179.4(3)
C(12B)-C(13B)-C(14B)-C(8B)	-59.7(3)	C(24B)-C(25B)-C(26B)-C(27B)	0.0(6)
C(22B)-C(13B)-C(14B)-C(8B)	61.6(3)	F(1B)-C(26B)-C(27B)-C(28B)	-178.6(3)
C(17B)-C(13B)-C(14B)-C(8B)	176.4(2)	C(25B)-C(26B)-C(27B)-C(28B)	0.8(6)
C(12B)-C(13B)-C(14B)-C(15B)	170.8(2)	C(26B)-C(27B)-C(28B)-C(23B)	-1.3(5)
C(22B)-C(13B)-C(14B)-C(15B)	-67.9(3)	C(24B)-C(23B)-C(28B)-C(27B)	1.0(5)
C(17B)-C(13B)-C(14B)-C(15B)	46.9(3)	C(20B)-C(23B)-C(28B)-C(27B)	179.7(3)

S1.3.3. The structure of 2c.

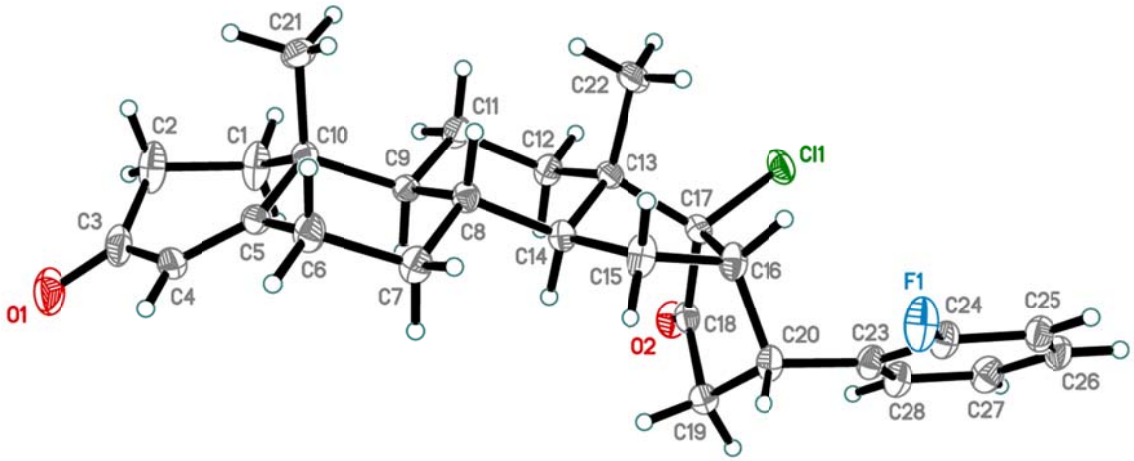


Fig. S8. The structure of **2c** (p=50%).

Table S20. Bond lengths [Å] for **2c**.

Bond	Length	Bond	Length	Bond	Length
Cl(1)-C(17)	1.7976(14)	C(9)-C(11)	1.542(2)	C(18)-C(19)	1.517(2)
C(1)-C(2)	1.533(2)	C(9)-C(10)	1.558(2)	C(19)-C(20)	1.530(2)
C(1)-C(10)	1.537(2)	C(9)-H(9)	1.00(2)	C(19)-H(19A)	0.981(16)
C(1)-H(1A)	0.949(18)	C(10)-C(21)	1.541(2)	C(19)-H(19B)	0.981(16)
C(1)-H(1B)	0.949(18)	C(11)-C(12)	1.537(2)	C(20)-C(23)	1.516(2)
C(2)-C(3)	1.499(3)	C(11)-H(11B)	0.958(16)	C(20)-H(20)	0.98(2)
C(2)-H(2A)	1.01(2)	C(11)-H(11A)	0.958(16)	C(21)-H(21A)	0.966(15)
C(2)-H(2B)	1.01(2)	C(12)-C(13)	1.526(2)	C(21)-H(21B)	0.966(15)
C(3)-O(1)	1.228(2)	C(12)-H(12B)	0.981(16)	C(21)-H(21C)	0.966(15)
C(3)-C(4)	1.462(3)	C(12)-H(12A)	0.981(16)	C(22)-H(22A)	0.980(15)
C(4)-C(5)	1.344(2)	C(13)-C(22)	1.536(2)	C(22)-H(22B)	0.980(15)
C(4)-H(4)	0.97(2)	C(13)-C(14)	1.542(2)	C(22)-H(22C)	0.980(15)
C(5)-C(6)	1.507(2)	C(13)-C(17)	1.550(2)	C(23)-C(24)	1.391(2)
C(5)-C(10)	1.519(2)	C(14)-C(15)	1.535(2)	C(23)-C(28)	1.396(2)
C(6)-C(7)	1.534(2)	C(14)-H(14)	0.97(2)	C(24)-F(1)	1.3597(19)
C(6)-H(6B)	0.965(17)	C(15)-C(16)	1.555(2)	C(24)-C(25)	1.379(2)
C(6)-H(6A)	0.965(17)	C(15)-H(15B)	0.973(16)	C(25)-C(26)	1.388(2)
C(7)-C(8)	1.528(2)	C(15)-H(15A)	0.973(17)	C(25)-H(25)	0.98(2)
C(7)-H(7A)	0.986(16)	C(16)-C(17)	1.553(2)	C(26)-C(27)	1.390(3)
C(7)-H(7B)	0.986(16)	C(16)-C(20)	1.559(2)	C(26)-H(26)	0.94(2)
C(8)-C(14)	1.528(2)	C(16)-H(16)	1.01(2)	C(27)-C(28)	1.391(2)
C(8)-C(9)	1.5483(19)	C(17)-C(18)	1.552(2)	C(27)-H(27)	0.93(2)
C(8)-H(8)	0.98(2)	C(18)-O(2)	1.2038(18)	C(28)-H(28)	0.99(2)

Table S21. Bond angles [°] for **2c**.

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	112.94(14)	C(1)-C(10)-C(9)	108.43(12)	C(13)-C(17)-Cl(1)	112.95(10)
C(3)-C(2)-C(1)	110.16(16)	C(21)-C(10)-C(9)	111.48(12)	C(18)-C(17)-Cl(1)	105.46(9)
O(1)-C(3)-C(4)	121.69(19)	C(12)-C(11)-C(9)	111.62(12)	C(16)-C(17)-Cl(1)	113.20(10)
O(1)-C(3)-C(2)	122.68(19)	C(13)-C(12)-C(11)	109.90(13)	O(2)-C(18)-C(19)	126.21(15)
C(4)-C(3)-C(2)	115.56(14)	C(12)-C(13)-C(22)	110.46(14)	O(2)-C(18)-C(17)	125.19(14)
C(5)-C(4)-C(3)	122.89(15)	C(12)-C(13)-C(14)	108.55(11)	C(19)-C(18)-C(17)	108.53(12)

C(4)-C(5)-C(6)	120.47(14)	C(22)-C(13)-C(14)	112.65(13)	C(18)-C(19)-C(20)	103.99(12)
C(4)-C(5)-C(10)	123.57(15)	C(12)-C(13)-C(17)	116.63(12)	C(23)-C(20)-C(19)	113.73(13)
C(6)-C(5)-C(10)	115.95(12)	C(22)-C(13)-C(17)	108.85(12)	C(23)-C(20)-C(16)	111.12(13)
C(5)-C(6)-C(7)	111.97(13)	C(14)-C(13)-C(17)	99.34(11)	C(19)-C(20)-C(16)	103.27(12)
C(8)-C(7)-C(6)	111.52(13)	C(8)-C(14)-C(15)	119.72(12)	C(24)-C(23)-C(28)	115.98(14)
C(14)-C(8)-C(7)	110.76(12)	C(8)-C(14)-C(13)	113.45(12)	C(24)-C(23)-C(20)	118.91(14)
C(14)-C(8)-C(9)	107.81(11)	C(15)-C(14)-C(13)	103.65(12)	C(28)-C(23)-C(20)	125.09(14)
C(7)-C(8)-C(9)	110.61(12)	C(14)-C(15)-C(16)	105.01(12)	F(1)-C(24)-C(25)	118.42(14)
C(11)-C(9)-C(8)	111.17(12)	C(17)-C(16)-C(15)	104.62(11)	F(1)-C(24)-C(23)	117.16(13)
C(11)-C(9)-C(10)	112.84(11)	C(17)-C(16)-C(20)	105.50(12)	C(25)-C(24)-C(23)	124.40(15)
C(8)-C(9)-C(10)	113.80(12)	C(15)-C(16)-C(20)	113.77(14)	C(24)-C(25)-C(26)	117.98(15)
C(5)-C(10)-C(1)	110.55(13)	C(13)-C(17)-C(18)	115.14(11)	C(25)-C(26)-C(27)	120.07(15)
C(5)-C(10)-C(21)	108.00(13)	C(13)-C(17)-C(16)	105.65(11)	C(26)-C(27)-C(28)	120.15(16)
C(1)-C(10)-C(21)	109.89(15)	C(18)-C(17)-C(16)	104.31(12)	C(27)-C(28)-C(23)	121.42(15)
C(5)-C(10)-C(9)	108.48(12)				

Table S22. Torsion angles [°] for **2c**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-57.9(2)	C(13)-C(14)-C(15)-C(16)	-34.96(16)
C(1)-C(2)-C(3)-O(1)	-141.92(19)	C(14)-C(15)-C(16)-C(17)	9.14(17)
C(1)-C(2)-C(3)-C(4)	41.1(2)	C(14)-C(15)-C(16)-C(20)	-105.49(15)
O(1)-C(3)-C(4)-C(5)	172.25(16)	C(12)-C(13)-C(17)-C(18)	-42.25(18)
C(2)-C(3)-C(4)-C(5)	-10.7(2)	C(22)-C(13)-C(17)-C(18)	-168.00(13)
C(3)-C(4)-C(5)-C(6)	173.62(15)	C(14)-C(13)-C(17)-C(18)	74.06(14)
C(3)-C(4)-C(5)-C(10)	-5.2(2)	C(12)-C(13)-C(17)-C(16)	-156.76(13)
C(4)-C(5)-C(6)-C(7)	127.75(15)	C(22)-C(13)-C(17)-C(16)	77.48(15)
C(10)-C(5)-C(6)-C(7)	-53.31(19)	C(14)-C(13)-C(17)-C(16)	-40.46(13)
C(5)-C(6)-C(7)-C(8)	53.05(19)	C(12)-C(13)-C(17)-Cl(1)	78.98(14)
C(6)-C(7)-C(8)-C(14)	-173.44(13)	C(22)-C(13)-C(17)-Cl(1)	-46.77(15)
C(6)-C(7)-C(8)-C(9)	-53.97(17)	C(14)-C(13)-C(17)-Cl(1)	-164.71(9)
C(14)-C(8)-C(9)-C(11)	-55.12(15)	C(15)-C(16)-C(17)-C(13)	19.81(16)
C(7)-C(8)-C(9)-C(11)	-176.35(13)	C(20)-C(16)-C(17)-C(13)	140.12(12)
C(14)-C(8)-C(9)-C(10)	176.14(12)	C(15)-C(16)-C(17)-C(18)	-101.97(13)
C(7)-C(8)-C(9)-C(10)	54.91(16)	C(20)-C(16)-C(17)-C(18)	18.33(14)
C(4)-C(5)-C(10)-C(1)	-11.1(2)	C(15)-C(16)-C(17)-Cl(1)	143.91(11)

C(6)-C(5)-C(10)-C(1)	170.05(14)	C(20)-C(16)-C(17)-Cl(1)	-95.78(12)
C(4)-C(5)-C(10)-C(21)	109.21(17)	C(13)-C(17)-C(18)-O(2)	72.43(19)
C(6)-C(5)-C(10)-C(21)	-69.69(17)	C(16)-C(17)-C(18)-O(2)	-172.28(14)
C(4)-C(5)-C(10)-C(9)	-129.83(15)	Cl(1)-C(17)-C(18)-O(2)	-52.78(17)
C(6)-C(5)-C(10)-C(9)	51.27(17)	C(13)-C(17)-C(18)-C(19)	-110.23(14)
C(2)-C(1)-C(10)-C(5)	42.2(2)	C(16)-C(17)-C(18)-C(19)	5.06(14)
C(2)-C(1)-C(10)-C(21)	-76.9(2)	Cl(1)-C(17)-C(18)-C(19)	124.55(11)
C(2)-C(1)-C(10)-C(9)	161.02(16)	O(2)-C(18)-C(19)-C(20)	150.49(15)
C(11)-C(9)-C(10)-C(5)	-179.66(12)	C(17)-C(18)-C(19)-C(20)	-26.81(15)
C(8)-C(9)-C(10)-C(5)	-51.78(16)	C(18)-C(19)-C(20)-C(23)	-83.00(15)
C(11)-C(9)-C(10)-C(1)	60.24(17)	C(18)-C(19)-C(20)-C(16)	37.54(14)
C(8)-C(9)-C(10)-C(1)	-171.88(14)	C(17)-C(16)-C(20)-C(23)	87.43(14)
C(11)-C(9)-C(10)-C(21)	-60.86(18)	C(15)-C(16)-C(20)-C(23)	-158.47(12)
C(8)-C(9)-C(10)-C(21)	67.02(16)	C(17)-C(16)-C(20)-C(19)	-34.87(14)
C(8)-C(9)-C(11)-C(12)	56.88(17)	C(15)-C(16)-C(20)-C(19)	79.23(14)
C(10)-C(9)-C(11)-C(12)	-173.87(13)	C(19)-C(20)-C(23)-C(24)	-173.14(14)
C(9)-C(11)-C(12)-C(13)	-57.82(17)	C(16)-C(20)-C(23)-C(24)	70.85(18)
C(11)-C(12)-C(13)-C(22)	-66.40(16)	C(19)-C(20)-C(23)-C(28)	8.2(2)
C(11)-C(12)-C(13)-C(14)	57.57(16)	C(16)-C(20)-C(23)-C(28)	-107.78(18)
C(11)-C(12)-C(13)-C(17)	168.66(12)	C(28)-C(23)-C(24)-F(1)	-177.74(14)
C(7)-C(8)-C(14)-C(15)	-57.79(18)	C(20)-C(23)-C(24)-F(1)	3.5(2)
C(9)-C(8)-C(14)-C(15)	-178.93(13)	C(28)-C(23)-C(24)-C(25)	0.7(2)
C(7)-C(8)-C(14)-C(13)	179.27(12)	C(20)-C(23)-C(24)-C(25)	-178.08(16)
C(9)-C(8)-C(14)-C(13)	58.13(15)	F(1)-C(24)-C(25)-C(26)	177.84(15)
C(12)-C(13)-C(14)-C(8)	-60.17(15)	C(23)-C(24)-C(25)-C(26)	-0.6(3)
C(22)-C(13)-C(14)-C(8)	62.48(16)	C(24)-C(25)-C(26)-C(27)	0.1(2)
C(17)-C(13)-C(14)-C(8)	177.53(11)	C(25)-C(26)-C(27)-C(28)	0.1(3)
C(12)-C(13)-C(14)-C(15)	168.42(13)	C(26)-C(27)-C(28)-C(23)	0.0(3)
C(22)-C(13)-C(14)-C(15)	-68.93(16)	C(24)-C(23)-C(28)-C(27)	-0.4(2)
C(17)-C(13)-C(14)-C(15)	46.12(13)	C(20)-C(23)-C(28)-C(27)	178.29(16)
C(8)-C(14)-C(15)-C(16)	-162.56(13)		

S1.3.4. The structure of 2g.

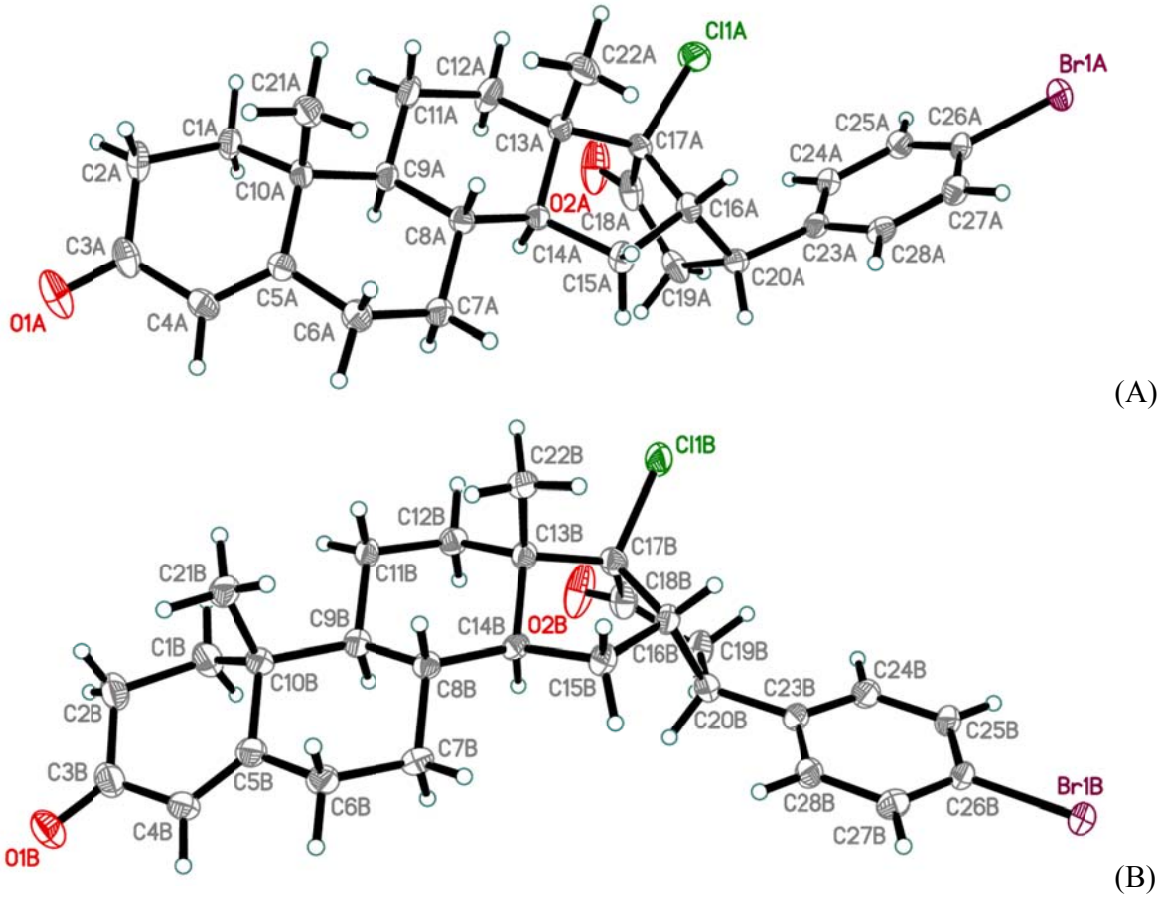


Fig. S9. The structures of two crystallographically unique molecules (***A*** and ***B***) of **2g** (p=50%).

Table S23. Bond lengths [Å] for **2g**.

Bond	Length	Bond	Length	Bond	Length
Br(1A)-C(26A)	1.897(3)	C(8A)-C(9A)	1.540(5)	C(17A)-C(18A)	1.539(6)
Cl(1A)-C(17A)	1.812(4)	C(8A)-H(8A)	0.94(4)	C(18A)-C(19A)	1.514(6)
O(1A)-C(3A)	1.228(4)	C(9A)-C(11A)	1.537(5)	C(19A)-C(20A)	1.523(5)
O(2A)-C(18A)	1.196(5)	C(9A)-C(10A)	1.569(5)	C(19A)-H(19A)	0.93(3)
C(1A)-C(2A)	1.526(5)	C(9A)-H(9A)	0.98(4)	C(19A)-H(19B)	0.93(3)
C(1A)-C(10A)	1.533(5)	C(10A)-C(21A)	1.547(5)	C(20A)-C(23A)	1.514(4)
C(1A)-H(1A)	1.00(3)	C(11A)-C(12A)	1.542(5)	C(20A)-H(20A)	0.91(4)
C(1A)-H(1B)	1.00(3)	C(11A)-H(11A)	0.95(3)	C(21A)-H(21A)	0.94(2)
C(2A)-C(3A)	1.497(6)	C(11A)-H(11B)	0.95(3)	C(21A)-H(21B)	0.94(2)
C(2A)-H(2A)	0.94(3)	C(12A)-C(13A)	1.524(5)	C(21A)-H(21C)	0.94(2)
C(2A)-H(2B)	0.94(3)	C(12A)-H(12B)	0.91(3)	C(22A)-H(22A)	0.97(2)

C(3A)-C(4A)	1.456(6)	C(12A)-H(12A)	0.91(3)	C(22A)-H(22B)	0.97(2)
C(4A)-C(5A)	1.341(5)	C(13A)-C(14A)	1.531(5)	C(22A)-H(22C)	0.97(2)
C(4A)-H(4A)	0.93(4)	C(13A)-C(22A)	1.534(6)	C(23A)-C(24A)	1.391(5)
C(5A)-C(6A)	1.499(5)	C(13A)-C(17A)	1.544(5)	C(23A)-C(28A)	1.393(5)
C(5A)-C(10A)	1.518(5)	C(14A)-C(15A)	1.539(5)	C(24A)-C(25A)	1.392(5)
C(6A)-C(7A)	1.524(5)	C(14A)-H(14A)	0.94(4)	C(24A)-H(24A)	0.89(4)
C(6A)-H(6B)	0.99(3)	C(15A)-C(16A)	1.559(5)	C(25A)-C(26A)	1.376(5)
C(6A)-H(6A)	0.99(3)	C(15A)-H(15B)	0.97(3)	C(25A)-H(25A)	0.98(4)
C(7A)-C(8A)	1.522(5)	C(15A)-H(15A)	0.97(3)	C(26A)-C(27A)	1.387(5)
C(7A)-H(7A)	0.94(3)	C(16A)-C(17A)	1.539(5)	C(27A)-C(28A)	1.382(5)
C(7A)-H(7B)	0.94(3)	C(16A)-C(20A)	1.550(5)	C(27A)-H(27A)	0.92(4)
C(8A)-C(14A)	1.520(5)	C(16A)-H(16A)	0.96(4)	C(28A)-H(28A)	0.92(4)
Br(1B)-C(26B)	1.905(3)	C(8B)-C(9B)	1.538(5)	C(17B)-C(18B)	1.554(6)
Cl(1B)-C(17B)	1.819(4)	C(8B)-H(8B)	1.00(4)	C(18B)-C(19B)	1.502(5)
O(1B)-C(3B)	1.221(5)	C(9B)-C(11B)	1.537(5)	C(19B)-C(20B)	1.534(5)
O(2B)-C(18B)	1.202(5)	C(9B)-C(10B)	1.560(5)	C(19B)-H(19C)	0.97(3)
C(1B)-C(2B)	1.526(5)	C(9B)-H(9B)	1.02(4)	C(19B)-H(19D)	0.97(3)
C(1B)-C(10B)	1.539(6)	C(10B)-C(21B)	1.538(5)	C(20B)-C(23B)	1.514(5)
C(1B)-H(1C)	1.00(3)	C(11B)-C(12B)	1.527(5)	C(20B)-H(20B)	1.00(4)
C(1B)-H(1D)	1.00(3)	C(11B)-H(11D)	0.95(3)	C(21B)-H(21D)	0.98(2)
C(2B)-C(3B)	1.497(6)	C(11B)-H(11C)	0.95(3)	C(21B)-H(21E)	0.98(2)
C(2B)-H(2C)	0.95(3)	C(12B)-C(13B)	1.523(5)	C(21B)-H(21F)	0.98(2)
C(2B)-H(2D)	0.95(3)	C(12B)-H(12D)	0.95(3)	C(22B)-H(22D)	0.94(2)
C(3B)-C(4B)	1.466(5)	C(12B)-H(12C)	0.95(3)	C(22B)-H(22E)	0.94(2)
C(4B)-C(5B)	1.341(5)	C(13B)-C(22B)	1.533(5)	C(22B)-H(22F)	0.94(2)
C(4B)-H(4B)	0.95(4)	C(13B)-C(17B)	1.538(5)	C(23B)-C(24B)	1.390(5)
C(5B)-C(6B)	1.496(6)	C(13B)-C(14B)	1.544(5)	C(23B)-C(28B)	1.394(5)
C(5B)-C(10B)	1.518(5)	C(14B)-C(15B)	1.537(5)	C(24B)-C(25B)	1.386(5)
C(6B)-C(7B)	1.527(5)	C(14B)-H(14B)	1.04(4)	C(24B)-H(24B)	0.97(4)
C(6B)-H(6D)	0.96(3)	C(15B)-C(16B)	1.547(5)	C(25B)-C(26B)	1.369(5)
C(6B)-H(6C)	0.96(3)	C(15B)-H(15D)	0.91(3)	C(25B)-H(25B)	0.90(4)
C(7B)-C(8B)	1.523(5)	C(15B)-H(15C)	0.91(3)	C(26B)-C(27B)	1.387(5)
C(7B)-H(7C)	0.96(3)	C(16B)-C(17B)	1.560(5)	C(27B)-C(28B)	1.386(5)
C(7B)-H(7D)	0.96(3)	C(16B)-C(20B)	1.564(5)	C(27B)-H(27B)	0.98(4)
C(8B)-C(14B)	1.534(5)	C(16B)-H(16B)	0.97(4)	C(28B)-H(28B)	0.93(4)

Table S24. Bond angles [°] for **2g**.

Atoms	Angle	Atoms	Angle
C(2A)-C(1A)-C(10A)	112.7(3)	C(8A)-C(14A)-C(13A)	112.4(3)
C(3A)-C(2A)-C(1A)	110.2(3)	C(8A)-C(14A)-C(15A)	118.0(3)
O(1A)-C(3A)-C(4A)	121.8(4)	C(13A)-C(14A)-C(15A)	105.0(3)
O(1A)-C(3A)-C(2A)	122.0(4)	C(14A)-C(15A)-C(16A)	105.8(3)
C(4A)-C(3A)-C(2A)	116.1(3)	C(17A)-C(16A)-C(20A)	106.3(3)
C(5A)-C(4A)-C(3A)	123.4(4)	C(17A)-C(16A)-C(15A)	103.8(3)
C(4A)-C(5A)-C(6A)	120.6(4)	C(20A)-C(16A)-C(15A)	113.5(3)
C(4A)-C(5A)-C(10A)	122.7(3)	C(16A)-C(17A)-C(18A)	103.8(3)
C(6A)-C(5A)-C(10A)	116.7(3)	C(16A)-C(17A)-C(13A)	105.2(3)
C(5A)-C(6A)-C(7A)	112.6(3)	C(18A)-C(17A)-C(13A)	118.2(3)
C(8A)-C(7A)-C(6A)	110.4(3)	C(16A)-C(17A)-Cl(1A)	113.3(3)
C(14A)-C(8A)-C(7A)	111.7(3)	C(18A)-C(17A)-Cl(1A)	103.7(3)
C(14A)-C(8A)-C(9A)	109.2(3)	C(13A)-C(17A)-Cl(1A)	112.6(3)
C(7A)-C(8A)-C(9A)	110.2(3)	O(2A)-C(18A)-C(19A)	125.6(4)
C(11A)-C(9A)-C(8A)	113.4(3)	O(2A)-C(18A)-C(17A)	125.5(4)
C(11A)-C(9A)-C(10A)	112.9(3)	C(19A)-C(18A)-C(17A)	108.8(3)
C(8A)-C(9A)-C(10A)	112.8(3)	C(18A)-C(19A)-C(20A)	106.1(3)
C(5A)-C(10A)-C(1A)	110.1(3)	C(23A)-C(20A)-C(19A)	116.7(3)
C(5A)-C(10A)-C(21A)	108.7(3)	C(23A)-C(20A)-C(16A)	111.0(3)
C(1A)-C(10A)-C(21A)	109.6(3)	C(19A)-C(20A)-C(16A)	102.6(3)
C(5A)-C(10A)-C(9A)	107.9(3)	C(24A)-C(23A)-C(28A)	118.0(3)
C(1A)-C(10A)-C(9A)	108.7(3)	C(24A)-C(23A)-C(20A)	124.0(3)
C(21A)-C(10A)-C(9A)	111.8(3)	C(28A)-C(23A)-C(20A)	117.8(3)
C(9A)-C(11A)-C(12A)	113.8(3)	C(23A)-C(24A)-C(25A)	121.2(4)
C(13A)-C(12A)-C(11A)	110.2(4)	C(26A)-C(25A)-C(24A)	118.9(4)
C(12A)-C(13A)-C(14A)	107.6(3)	C(25A)-C(26A)-C(27A)	121.5(3)
C(12A)-C(13A)-C(22A)	110.9(4)	C(25A)-C(26A)-Br(1A)	119.6(3)
C(14A)-C(13A)-C(22A)	112.3(3)	C(27A)-C(26A)-Br(1A)	118.9(3)
C(12A)-C(13A)-C(17A)	118.0(3)	C(28A)-C(27A)-C(26A)	118.6(4)
C(14A)-C(13A)-C(17A)	99.4(3)	C(27A)-C(28A)-C(23A)	121.8(4)
C(22A)-C(13A)-C(17A)	108.2(3)		
C(2B)-C(1B)-C(10B)	112.7(3)	C(8B)-C(14B)-C(15B)	120.0(3)
C(3B)-C(2B)-C(1B)	112.2(4)	C(8B)-C(14B)-C(13B)	113.8(3)

O(1B)-C(3B)-C(4B)	122.1(4)	C(15B)-C(14B)-C(13B)	102.6(3)
O(1B)-C(3B)-C(2B)	122.0(4)	C(14B)-C(15B)-C(16B)	103.1(3)
C(4B)-C(3B)-C(2B)	115.9(3)	C(15B)-C(16B)-C(17B)	104.8(3)
C(5B)-C(4B)-C(3B)	124.5(4)	C(15B)-C(16B)-C(20B)	112.9(3)
C(4B)-C(5B)-C(6B)	120.9(4)	C(17B)-C(16B)-C(20B)	106.6(3)
C(4B)-C(5B)-C(10B)	122.0(4)	C(13B)-C(17B)-C(18B)	119.6(3)
C(6B)-C(5B)-C(10B)	116.9(3)	C(13B)-C(17B)-C(16B)	106.4(3)
C(5B)-C(6B)-C(7B)	113.2(3)	C(18B)-C(17B)-C(16B)	104.5(3)
C(8B)-C(7B)-C(6B)	110.7(3)	C(13B)-C(17B)-Cl(1B)	111.7(3)
C(7B)-C(8B)-C(14B)	112.4(3)	C(18B)-C(17B)-Cl(1B)	100.9(3)
C(7B)-C(8B)-C(9B)	110.0(3)	C(16B)-C(17B)-Cl(1B)	113.7(3)
C(14B)-C(8B)-C(9B)	108.5(3)	O(2B)-C(18B)-C(19B)	126.4(4)
C(11B)-C(9B)-C(8B)	111.6(3)	O(2B)-C(18B)-C(17B)	126.3(4)
C(11B)-C(9B)-C(10B)	111.5(3)	C(19B)-C(18B)-C(17B)	107.2(3)
C(8B)-C(9B)-C(10B)	115.2(3)	C(18B)-C(19B)-C(20B)	104.3(3)
C(5B)-C(10B)-C(21B)	108.4(3)	C(23B)-C(20B)-C(19B)	116.1(3)
C(5B)-C(10B)-C(1B)	109.0(3)	C(23B)-C(20B)-C(16B)	113.7(3)
C(21B)-C(10B)-C(1B)	110.2(3)	C(19B)-C(20B)-C(16B)	105.1(3)
C(5B)-C(10B)-C(9B)	110.2(3)	C(24B)-C(23B)-C(28B)	117.5(3)
C(21B)-C(10B)-C(9B)	110.9(3)	C(24B)-C(23B)-C(20B)	122.8(3)
C(1B)-C(10B)-C(9B)	108.2(3)	C(28B)-C(23B)-C(20B)	119.7(3)
C(12B)-C(11B)-C(9B)	111.3(3)	C(25B)-C(24B)-C(23B)	121.6(4)
C(13B)-C(12B)-C(11B)	110.2(3)	C(26B)-C(25B)-C(24B)	119.2(4)
C(12B)-C(13B)-C(22B)	109.9(3)	C(25B)-C(26B)-C(27B)	121.3(3)
C(12B)-C(13B)-C(17B)	117.2(3)	C(25B)-C(26B)-Br(1B)	118.6(3)
C(22B)-C(13B)-C(17B)	109.3(3)	C(27B)-C(26B)-Br(1B)	120.0(3)
C(12B)-C(13B)-C(14B)	109.0(3)	C(28B)-C(27B)-C(26B)	118.5(4)
C(22B)-C(13B)-C(14B)	111.4(3)	C(27B)-C(28B)-C(23B)	121.8(3)
C(17B)-C(13B)-C(14B)	99.7(3)		

Table S25. Torsion angles [°] for **2g**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10A)-C(1A)-C(2A)-C(3A)	-58.0(5)	C(8A)-C(14A)-C(15A)-C(16A)	-151.4(3)
C(1A)-C(2A)-C(3A)-O(1A)	-147.6(4)	C(13A)-C(14A)-C(15A)-C(16A)	-25.3(4)
C(1A)-C(2A)-C(3A)-C(4A)	36.4(4)	C(14A)-C(15A)-C(16A)-C(17A)	-2.5(4)

O(1A)-C(3A)-C(4A)-C(5A)	179.8(4)	C(14A)-C(15A)-C(16A)-C(20A)	-117.5(3)
C(2A)-C(3A)-C(4A)-C(5A)	-4.2(5)	C(20A)-C(16A)-C(17A)-C(18A)	24.4(4)
C(3A)-C(4A)-C(5A)-C(6A)	170.7(4)	C(15A)-C(16A)-C(17A)-C(18A)	-95.6(3)
C(3A)-C(4A)-C(5A)-C(10A)	-8.4(6)	C(20A)-C(16A)-C(17A)-C(13A)	149.2(3)
C(4A)-C(5A)-C(6A)-C(7A)	129.0(4)	C(15A)-C(16A)-C(17A)-C(13A)	29.3(4)
C(10A)-C(5A)-C(6A)-C(7A)	-51.8(5)	C(20A)-C(16A)-C(17A)-Cl(1A)	-87.4(3)
C(5A)-C(6A)-C(7A)-C(8A)	53.4(5)	C(15A)-C(16A)-C(17A)-Cl(1A)	152.6(3)
C(6A)-C(7A)-C(8A)-C(14A)	-178.6(3)	C(12A)-C(13A)-C(17A)-C(16A)	-160.1(3)
C(6A)-C(7A)-C(8A)-C(9A)	-57.0(4)	C(14A)-C(13A)-C(17A)-C(16A)	-44.3(4)
C(14A)-C(8A)-C(9A)-C(11A)	-48.7(4)	C(22A)-C(13A)-C(17A)-C(16A)	73.1(4)
C(7A)-C(8A)-C(9A)-C(11A)	-171.7(3)	C(12A)-C(13A)-C(17A)-C(18A)	-44.8(5)
C(14A)-C(8A)-C(9A)-C(10A)	-178.6(3)	C(14A)-C(13A)-C(17A)-C(18A)	71.0(4)
C(7A)-C(8A)-C(9A)-C(10A)	58.3(4)	C(22A)-C(13A)-C(17A)-C(18A)	-171.7(4)
C(4A)-C(5A)-C(10A)-C(1A)	-12.8(5)	C(12A)-C(13A)-C(17A)-Cl(1A)	76.1(4)
C(6A)-C(5A)-C(10A)-C(1A)	168.0(3)	C(14A)-C(13A)-C(17A)-Cl(1A)	-168.1(3)
C(4A)-C(5A)-C(10A)-C(21A)	107.2(4)	C(22A)-C(13A)-C(17A)-Cl(1A)	-50.8(4)
C(6A)-C(5A)-C(10A)-C(21A)	-71.9(4)	C(16A)-C(17A)-C(18A)-O(2A)	176.5(4)
C(4A)-C(5A)-C(10A)-C(9A)	-131.3(4)	C(13A)-C(17A)-C(18A)-O(2A)	60.5(6)
C(6A)-C(5A)-C(10A)-C(9A)	49.5(4)	Cl(1A)-C(17A)-C(18A)-O(2A)	-64.8(5)
C(2A)-C(1A)-C(10A)-C(5A)	45.6(5)	C(16A)-C(17A)-C(18A)-C(19A)	-4.4(4)
C(2A)-C(1A)-C(10A)-C(21A)	-74.0(4)	C(13A)-C(17A)-C(18A)-C(19A)	-120.4(4)
C(2A)-C(1A)-C(10A)-C(9A)	163.6(3)	Cl(1A)-C(17A)-C(18A)-C(19A)	114.2(3)
C(11A)-C(9A)-C(10A)-C(5A)	177.4(3)	O(2A)-C(18A)-C(19A)-C(20A)	161.5(4)
C(8A)-C(9A)-C(10A)-C(5A)	-52.4(4)	C(17A)-C(18A)-C(19A)-C(20A)	-17.6(4)
C(11A)-C(9A)-C(10A)-C(1A)	58.0(4)	C(18A)-C(19A)-C(20A)-C(23A)	-89.6(4)
C(8A)-C(9A)-C(10A)-C(1A)	-171.7(3)	C(18A)-C(19A)-C(20A)-C(16A)	31.9(4)
C(11A)-C(9A)-C(10A)-C(21A)	-63.1(4)	C(17A)-C(16A)-C(20A)-C(23A)	90.2(4)
C(8A)-C(9A)-C(10A)-C(21A)	67.1(4)	C(15A)-C(16A)-C(20A)-C(23A)	-156.4(3)
C(8A)-C(9A)-C(11A)-C(12A)	47.2(5)	C(17A)-C(16A)-C(20A)-C(19A)	-35.1(4)
C(10A)-C(9A)-C(11A)-C(12A)	177.1(4)	C(15A)-C(16A)-C(20A)-C(19A)	78.3(4)
C(9A)-C(11A)-C(12A)-C(13A)	-52.4(5)	C(19A)-C(20A)-C(23A)-C(24A)	15.7(6)
C(11A)-C(12A)-C(13A)-C(14A)	59.2(5)	C(16A)-C(20A)-C(23A)-C(24A)	-101.3(4)
C(11A)-C(12A)-C(13A)-C(22A)	-64.0(4)	C(19A)-C(20A)-C(23A)-C(28A)	-169.7(3)
C(11A)-C(12A)-C(13A)-C(17A)	170.5(4)	C(16A)-C(20A)-C(23A)-C(28A)	73.3(4)
C(7A)-C(8A)-C(14A)-C(13A)	-179.2(3)	C(28A)-C(23A)-C(24A)-C(25A)	-1.4(6)
C(9A)-C(8A)-C(14A)-C(13A)	58.6(4)	C(20A)-C(23A)-C(24A)-C(25A)	173.2(4)

C(7A)-C(8A)-C(14A)-C(15A)	-56.7(5)	C(23A)-C(24A)-C(25A)-C(26A)	-0.8(6)
C(9A)-C(8A)-C(14A)-C(15A)	-178.9(3)	C(24A)-C(25A)-C(26A)-C(27A)	2.1(6)
C(12A)-C(13A)-C(14A)-C(8A)	-64.8(4)	C(24A)-C(25A)-C(26A)-Br(1A)	-179.4(3)
C(22A)-C(13A)-C(14A)-C(8A)	57.6(4)	C(25A)-C(26A)-C(27A)-C(28A)	-1.1(6)
C(17A)-C(13A)-C(14A)-C(8A)	171.8(3)	Br(1A)-C(26A)-C(27A)-C(28A)	-179.6(3)
C(12A)-C(13A)-C(14A)-C(15A)	165.7(3)	C(26A)-C(27A)-C(28A)-C(23A)	-1.2(6)
C(22A)-C(13A)-C(14A)-C(15A)	-72.0(4)	C(24A)-C(23A)-C(28A)-C(27A)	2.5(6)
C(17A)-C(13A)-C(14A)-C(15A)	42.2(4)	C(20A)-C(23A)-C(28A)-C(27A)	-172.5(3)
C(10B)-C(1B)-C(2B)-C(3B)	-54.5(5)	C(8B)-C(14B)-C(15B)-C(16B)	-170.3(3)
C(1B)-C(2B)-C(3B)-O(1B)	-154.9(4)	C(13B)-C(14B)-C(15B)-C(16B)	-42.9(3)
C(1B)-C(2B)-C(3B)-C(4B)	27.4(5)	C(14B)-C(15B)-C(16B)-C(17B)	20.4(4)
O(1B)-C(3B)-C(4B)-C(5B)	-176.1(4)	C(14B)-C(15B)-C(16B)-C(20B)	-95.3(3)
C(2B)-C(3B)-C(4B)-C(5B)	1.5(6)	C(12B)-C(13B)-C(17B)-C(18B)	-34.3(5)
C(3B)-C(4B)-C(5B)-C(6B)	171.8(4)	C(22B)-C(13B)-C(17B)-C(18B)	-160.2(3)
C(3B)-C(4B)-C(5B)-C(10B)	-4.0(6)	C(14B)-C(13B)-C(17B)-C(18B)	83.0(4)
C(4B)-C(5B)-C(6B)-C(7B)	134.7(4)	C(12B)-C(13B)-C(17B)-C(16B)	-152.2(3)
C(10B)-C(5B)-C(6B)-C(7B)	-49.3(5)	C(22B)-C(13B)-C(17B)-C(16B)	81.9(4)
C(5B)-C(6B)-C(7B)-C(8B)	54.8(4)	C(14B)-C(13B)-C(17B)-C(16B)	-34.9(4)
C(6B)-C(7B)-C(8B)-C(14B)	-177.5(3)	C(12B)-C(13B)-C(17B)-Cl(1B)	83.2(4)
C(6B)-C(7B)-C(8B)-C(9B)	-56.5(4)	C(22B)-C(13B)-C(17B)-Cl(1B)	-42.7(4)
C(7B)-C(8B)-C(9B)-C(11B)	-177.6(3)	C(14B)-C(13B)-C(17B)-Cl(1B)	-159.5(2)
C(14B)-C(8B)-C(9B)-C(11B)	-54.2(4)	C(15B)-C(16B)-C(17B)-C(13B)	9.4(4)
C(7B)-C(8B)-C(9B)-C(10B)	54.0(4)	C(20B)-C(16B)-C(17B)-C(13B)	129.3(3)
C(14B)-C(8B)-C(9B)-C(10B)	177.3(3)	C(15B)-C(16B)-C(17B)-C(18B)	-118.1(3)
C(4B)-C(5B)-C(10B)-C(21B)	97.9(4)	C(20B)-C(16B)-C(17B)-C(18B)	1.8(4)
C(6B)-C(5B)-C(10B)-C(21B)	-78.1(4)	C(15B)-C(16B)-C(17B)-Cl(1B)	132.8(3)
C(4B)-C(5B)-C(10B)-C(1B)	-22.1(5)	C(20B)-C(16B)-C(17B)-Cl(1B)	-107.3(3)
C(6B)-C(5B)-C(10B)-C(1B)	161.9(3)	C(13B)-C(17B)-C(18B)-O(2B)	40.5(6)
C(4B)-C(5B)-C(10B)-C(9B)	-140.7(4)	C(16B)-C(17B)-C(18B)-O(2B)	159.4(4)
C(6B)-C(5B)-C(10B)-C(9B)	43.4(4)	Cl(1B)-C(17B)-C(18B)-O(2B)	-82.4(5)
C(2B)-C(1B)-C(10B)-C(5B)	50.5(5)	C(13B)-C(17B)-C(18B)-C(19B)	-141.6(4)
C(2B)-C(1B)-C(10B)-C(21B)	-68.3(4)	C(16B)-C(17B)-C(18B)-C(19B)	-22.7(4)
C(2B)-C(1B)-C(10B)-C(9B)	170.3(3)	Cl(1B)-C(17B)-C(18B)-C(19B)	95.4(3)
C(11B)-C(9B)-C(10B)-C(5B)	-174.5(3)	O(2B)-C(18B)-C(19B)-C(20B)	-147.2(5)
C(8B)-C(9B)-C(10B)-C(5B)	-46.0(4)	C(17B)-C(18B)-C(19B)-C(20B)	35.0(4)

C(11B)-C(9B)-C(10B)-C(21B)	-54.5(4)	C(18B)-C(19B)-C(20B)-C(23B)	-159.7(3)
C(8B)-C(9B)-C(10B)-C(21B)	74.0(4)	C(18B)-C(19B)-C(20B)-C(16B)	-33.0(4)
C(11B)-C(9B)-C(10B)-C(1B)	66.5(4)	C(15B)-C(16B)-C(20B)-C(23B)	-98.4(4)
C(8B)-C(9B)-C(10B)-C(1B)	-165.1(3)	C(17B)-C(16B)-C(20B)-C(23B)	147.0(3)
C(8B)-C(9B)-C(11B)-C(12B)	57.5(4)	C(15B)-C(16B)-C(20B)-C(19B)	133.6(3)
C(10B)-C(9B)-C(11B)-C(12B)	-172.1(3)	C(17B)-C(16B)-C(20B)-C(19B)	19.0(4)
C(9B)-C(11B)-C(12B)-C(13B)	-58.7(4)	C(19B)-C(20B)-C(23B)-C(24B)	14.0(6)
C(11B)-C(12B)-C(13B)-C(22B)	-65.0(4)	C(16B)-C(20B)-C(23B)-C(24B)	-108.2(4)
C(11B)-C(12B)-C(13B)-C(17B)	169.3(3)	C(19B)-C(20B)-C(23B)-C(28B)	-165.5(4)
C(11B)-C(12B)-C(13B)-C(14B)	57.2(4)	C(16B)-C(20B)-C(23B)-C(28B)	72.3(5)
C(7B)-C(8B)-C(14B)-C(15B)	-60.7(4)	C(28B)-C(23B)-C(24B)-C(25B)	-1.0(6)
C(9B)-C(8B)-C(14B)-C(15B)	177.5(3)	C(20B)-C(23B)-C(24B)-C(25B)	179.5(4)
C(7B)-C(8B)-C(14B)-C(13B)	177.3(3)	C(23B)-C(24B)-C(25B)-C(26B)	1.2(6)
C(9B)-C(8B)-C(14B)-C(13B)	55.5(4)	C(24B)-C(25B)-C(26B)-C(27B)	-0.8(6)
C(12B)-C(13B)-C(14B)-C(8B)	-57.6(4)	C(24B)-C(25B)-C(26B)-Br(1B)	178.3(3)
C(22B)-C(13B)-C(14B)-C(8B)	63.8(4)	C(25B)-C(26B)-C(27B)-C(28B)	0.3(6)
C(17B)-C(13B)-C(14B)-C(8B)	179.1(3)	Br(1B)-C(26B)-C(27B)-C(28B)	-178.8(3)
C(12B)-C(13B)-C(14B)-C(15B)	171.2(3)	C(26B)-C(27B)-C(28B)-C(23B)	0.0(6)
C(22B)-C(13B)-C(14B)-C(15B)	-67.4(4)	C(24B)-C(23B)-C(28B)-C(27B)	0.4(6)
C(17B)-C(13B)-C(14B)-C(15B)	47.9(3)	C(20B)-C(23B)-C(28B)-C(27B)	179.9(4)

S1.3.5. The structure of 2h.

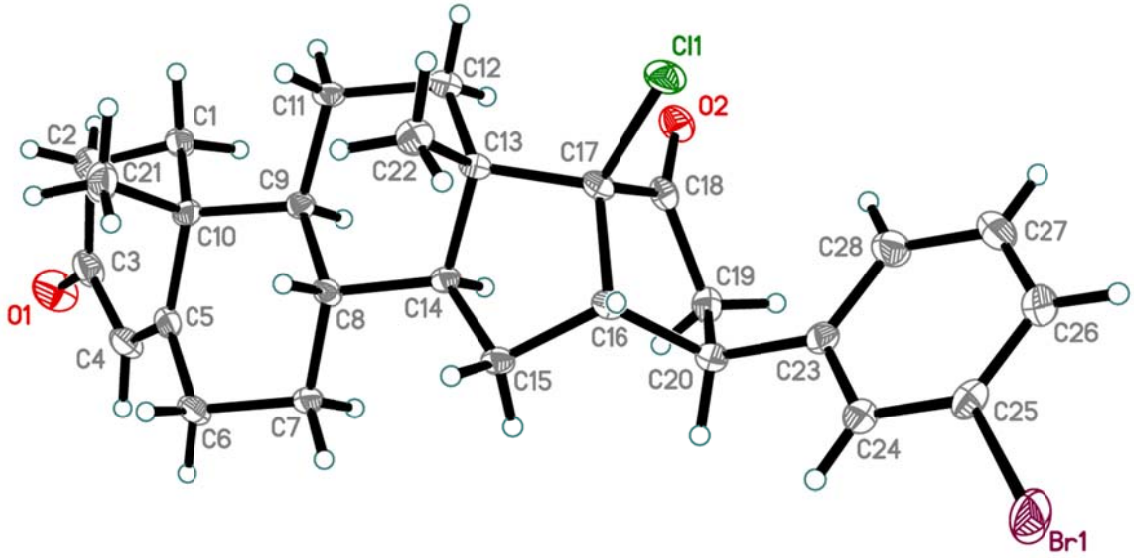


Fig. S10. The structure of **2h** (p=50%).

Table S26. Bond lengths [Å] for **2h**.

Bond	Length	Bond	Length	Bond	Length
Br(1)-C(25)	1.903(3)	C(8)-C(9)	1.549(4)	C(17)-C(18)	1.553(4)
Cl(1)-C(17)	1.798(3)	C(8)-H(8)	0.95(4)	C(18)-C(19)	1.510(4)
O(1)-C(3)	1.223(4)	C(9)-C(11)	1.538(4)	C(19)-C(20)	1.535(4)
O(2)-C(18)	1.204(4)	C(9)-C(10)	1.566(4)	C(19)-H(19A)	0.97(3)
C(1)-C(2)	1.530(5)	C(9)-H(9)	0.96(4)	C(19)-H(19B)	0.97(3)
C(1)-C(10)	1.538(4)	C(10)-C(21)	1.550(5)	C(20)-C(23)	1.518(4)
C(1)-H(1A)	0.98(3)	C(11)-C(12)	1.536(4)	C(20)-H(20)	0.97(4)
C(1)-H(1B)	0.98(3)	C(11)-H(11B)	0.94(3)	C(21)-H(21A)	0.95(2)
C(2)-C(3)	1.501(5)	C(11)-H(11A)	0.94(3)	C(21)-H(21B)	0.95(2)
C(2)-H(2A)	0.95(3)	C(12)-C(13)	1.529(4)	C(21)-H(21C)	0.95(2)
C(2)-H(2B)	0.95(3)	C(12)-H(12B)	0.93(3)	C(22)-H(22A)	0.91(2)
C(3)-C(4)	1.462(5)	C(12)-H(12A)	0.93(3)	C(22)-H(22B)	0.91(2)
C(4)-C(5)	1.338(5)	C(13)-C(22)	1.537(4)	C(22)-H(22C)	0.91(2)
C(4)-H(4)	0.93(4)	C(13)-C(17)	1.539(4)	C(23)-C(28)	1.388(5)
C(5)-C(6)	1.504(4)	C(13)-C(14)	1.544(4)	C(23)-C(24)	1.399(5)
C(5)-C(10)	1.528(4)	C(14)-C(15)	1.532(4)	C(24)-C(25)	1.386(4)
C(6)-C(7)	1.528(4)	C(14)-H(14)	1.00(4)	C(24)-H(24)	0.91(4)
C(6)-H(6B)	0.96(3)	C(15)-C(16)	1.556(4)	C(25)-C(26)	1.372(5)

C(6)-H(6A)	0.96(3)	C(15)-H(15B)	0.94(3)	C(26)-C(27)	1.387(5)
C(7)-C(8)	1.526(4)	C(15)-H(15A)	0.94(3)	C(26)-H(26)	0.94(4)
C(7)-H(7A)	1.01(3)	C(16)-C(20)	1.556(4)	C(27)-C(28)	1.379(5)
C(7)-H(7B)	1.01(3)	C(16)-C(17)	1.559(4)	C(27)-H(27)	0.86(4)
C(8)-C(14)	1.526(4)	C(16)-H(16)	0.88(4)	C(28)-H(28)	0.91(4)

Table S27. Bond angles [°] for **2h**.

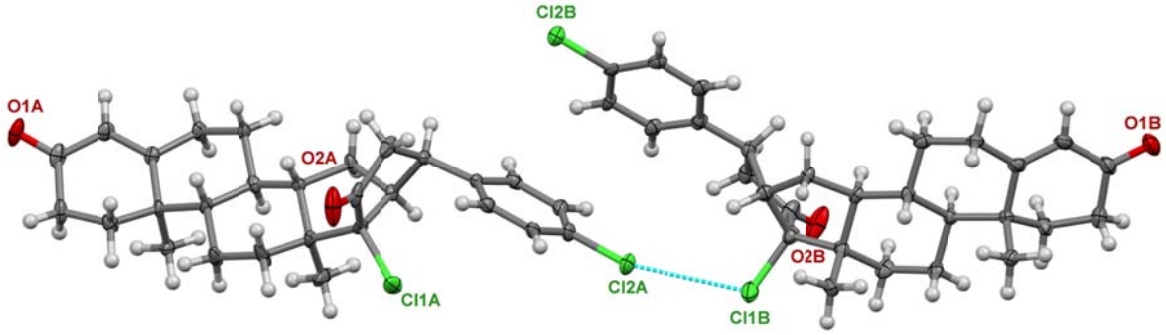
Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	113.2(3)	C(1)-C(10)-C(9)	108.6(2)	C(13)-C(17)-Cl(1)	113.8(2)
C(3)-C(2)-C(1)	112.1(3)	C(21)-C(10)-C(9)	111.3(3)	C(18)-C(17)-Cl(1)	105.49(19)
O(1)-C(3)-C(4)	122.0(3)	C(12)-C(11)-C(9)	112.8(2)	C(16)-C(17)-Cl(1)	112.8(2)
O(1)-C(3)-C(2)	122.2(3)	C(13)-C(12)-C(11)	110.6(2)	O(2)-C(18)-C(19)	125.9(3)
C(4)-C(3)-C(2)	115.8(3)	C(12)-C(13)-C(22)	109.4(3)	O(2)-C(18)-C(17)	125.3(3)
C(5)-C(4)-C(3)	124.2(3)	C(12)-C(13)-C(17)	118.0(2)	C(19)-C(18)-C(17)	108.8(3)
C(4)-C(5)-C(6)	120.2(3)	C(22)-C(13)-C(17)	108.9(2)	C(18)-C(19)-C(20)	105.9(3)
C(4)-C(5)-C(10)	122.8(3)	C(12)-C(13)-C(14)	108.9(2)	C(23)-C(20)-C(19)	113.1(3)
C(6)-C(5)-C(10)	117.0(3)	C(22)-C(13)-C(14)	112.3(2)	C(23)-C(20)-C(16)	113.8(2)
C(5)-C(6)-C(7)	111.9(3)	C(17)-C(13)-C(14)	99.0(2)	C(19)-C(20)-C(16)	102.8(2)
C(8)-C(7)-C(6)	111.0(3)	C(8)-C(14)-C(15)	118.8(2)	C(28)-C(23)-C(24)	118.3(3)
C(7)-C(8)-C(14)	110.7(3)	C(8)-C(14)-C(13)	113.7(2)	C(28)-C(23)-C(20)	123.0(3)
C(7)-C(8)-C(9)	110.1(2)	C(15)-C(14)-C(13)	103.7(2)	C(24)-C(23)-C(20)	118.7(3)
C(14)-C(8)-C(9)	108.4(2)	C(14)-C(15)-C(16)	105.4(2)	C(25)-C(24)-C(23)	119.2(3)
C(11)-C(9)-C(8)	112.0(2)	C(20)-C(16)-C(15)	113.3(2)	C(26)-C(25)-C(24)	122.6(3)
C(11)-C(9)-C(10)	112.8(3)	C(20)-C(16)-C(17)	106.6(2)	C(26)-C(25)-Br(1)	118.3(3)
C(8)-C(9)-C(10)	113.3(2)	C(15)-C(16)-C(17)	103.8(2)	C(24)-C(25)-Br(1)	119.0(3)
C(5)-C(10)-C(1)	110.1(3)	C(13)-C(17)-C(18)	114.5(2)	C(25)-C(26)-C(27)	117.7(3)
C(5)-C(10)-C(21)	108.3(3)	C(13)-C(17)-C(16)	106.2(2)	C(28)-C(27)-C(26)	120.9(3)
C(1)-C(10)-C(21)	109.6(3)	C(18)-C(17)-C(16)	103.9(2)	C(27)-C(28)-C(23)	121.2(3)
C(5)-C(10)-C(9)	108.9(2)				

Table S28. Torsion angles [°] for **2h**.

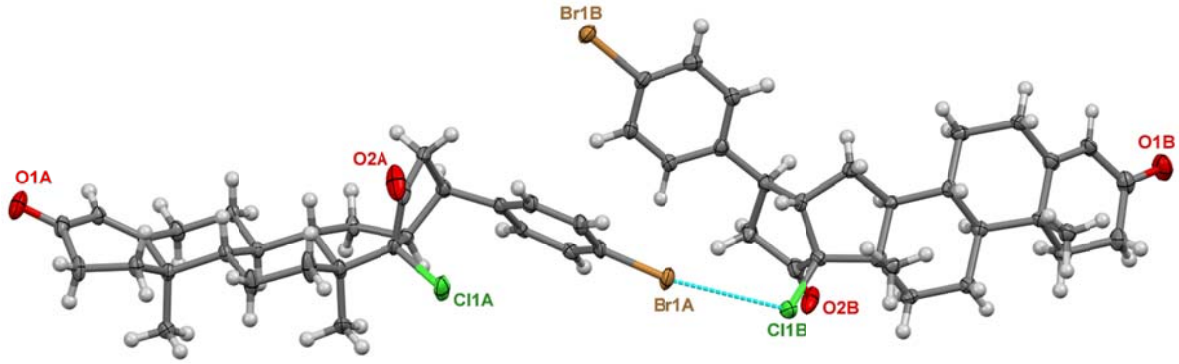
Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-54.6(4)	C(8)-C(14)-C(15)-C(16)	-161.8(3)
C(1)-C(2)-C(3)-O(1)	-150.1(3)	C(13)-C(14)-C(15)-C(16)	-34.5(3)
C(1)-C(2)-C(3)-C(4)	32.7(4)	C(14)-C(15)-C(16)-C(20)	-106.8(3)
O(1)-C(3)-C(4)-C(5)	179.6(3)	C(14)-C(15)-C(16)-C(17)	8.4(3)
C(2)-C(3)-C(4)-C(5)	-3.2(5)	C(12)-C(13)-C(17)-C(18)	-44.3(4)
C(3)-C(4)-C(5)-C(6)	171.8(3)	C(22)-C(13)-C(17)-C(18)	-169.8(2)
C(3)-C(4)-C(5)-C(10)	-5.7(5)	C(14)-C(13)-C(17)-C(18)	72.8(3)
C(4)-C(5)-C(6)-C(7)	131.1(3)	C(12)-C(13)-C(17)-C(16)	-158.2(3)
C(10)-C(5)-C(6)-C(7)	-51.3(4)	C(22)-C(13)-C(17)-C(16)	76.2(3)
C(5)-C(6)-C(7)-C(8)	54.5(4)	C(14)-C(13)-C(17)-C(16)	-41.1(3)
C(6)-C(7)-C(8)-C(14)	-177.3(3)	C(12)-C(13)-C(17)-Cl(1)	77.1(3)
C(6)-C(7)-C(8)-C(9)	-57.5(3)	C(22)-C(13)-C(17)-Cl(1)	-48.4(3)
C(7)-C(8)-C(9)-C(11)	-174.4(3)	C(14)-C(13)-C(17)-Cl(1)	-165.8(2)
C(14)-C(8)-C(9)-C(11)	-53.2(3)	C(20)-C(16)-C(17)-C(13)	140.7(2)
C(7)-C(8)-C(9)-C(10)	56.7(3)	C(15)-C(16)-C(17)-C(13)	20.8(3)
C(14)-C(8)-C(9)-C(10)	177.9(3)	C(20)-C(16)-C(17)-C(18)	19.7(3)
C(4)-C(5)-C(10)-C(1)	-15.7(4)	C(15)-C(16)-C(17)-C(18)	-100.2(3)
C(6)-C(5)-C(10)-C(1)	166.8(3)	C(20)-C(16)-C(17)-Cl(1)	-94.0(2)
C(4)-C(5)-C(10)-C(21)	104.2(4)	C(15)-C(16)-C(17)-Cl(1)	146.1(2)
C(6)-C(5)-C(10)-C(21)	-73.3(3)	C(13)-C(17)-C(18)-O(2)	66.0(4)
C(4)-C(5)-C(10)-C(9)	-134.6(3)	C(16)-C(17)-C(18)-O(2)	-178.7(3)
C(6)-C(5)-C(10)-C(9)	47.9(4)	Cl(1)-C(17)-C(18)-O(2)	-59.9(3)
C(2)-C(1)-C(10)-C(5)	44.9(4)	C(13)-C(17)-C(18)-C(19)	-113.8(3)
C(2)-C(1)-C(10)-C(21)	-74.1(4)	C(16)-C(17)-C(18)-C(19)	1.5(3)
C(2)-C(1)-C(10)-C(9)	164.0(3)	Cl(1)-C(17)-C(18)-C(19)	120.4(2)
C(11)-C(9)-C(10)-C(5)	-178.5(2)	O(2)-C(18)-C(19)-C(20)	157.9(3)
C(8)-C(9)-C(10)-C(5)	-50.0(3)	C(17)-C(18)-C(19)-C(20)	-22.4(3)
C(11)-C(9)-C(10)-C(1)	61.6(3)	C(18)-C(19)-C(20)-C(23)	-89.4(3)
C(8)-C(9)-C(10)-C(1)	-169.9(3)	C(18)-C(19)-C(20)-C(16)	33.8(3)
C(11)-C(9)-C(10)-C(21)	-59.2(3)	C(15)-C(16)-C(20)-C(23)	-157.0(3)
C(8)-C(9)-C(10)-C(21)	69.4(3)	C(17)-C(16)-C(20)-C(23)	89.6(3)
C(8)-C(9)-C(11)-C(12)	53.9(3)	C(15)-C(16)-C(20)-C(19)	80.4(3)
C(10)-C(9)-C(11)-C(12)	-176.9(3)	C(17)-C(16)-C(20)-C(19)	-33.1(3)

C(9)-C(11)-C(12)-C(13)	-55.1(3)	C(19)-C(20)-C(23)-C(28)	24.1(4)
C(11)-C(12)-C(13)-C(22)	-67.1(3)	C(16)-C(20)-C(23)-C(28)	-92.8(4)
C(11)-C(12)-C(13)-C(17)	167.7(3)	C(19)-C(20)-C(23)-C(24)	-155.9(3)
C(11)-C(12)-C(13)-C(14)	56.0(3)	C(16)-C(20)-C(23)-C(24)	87.3(3)
C(7)-C(8)-C(14)-C(15)	-59.4(4)	C(28)-C(23)-C(24)-C(25)	0.8(5)
C(9)-C(8)-C(14)-C(15)	179.9(3)	C(20)-C(23)-C(24)-C(25)	-179.2(3)
C(7)-C(8)-C(14)-C(13)	178.2(2)	C(23)-C(24)-C(25)-C(26)	-0.5(5)
C(9)-C(8)-C(14)-C(13)	57.4(3)	C(23)-C(24)-C(25)-Br(1)	-179.9(2)
C(12)-C(13)-C(14)-C(8)	-59.6(3)	C(24)-C(25)-C(26)-C(27)	-0.1(6)
C(22)-C(13)-C(14)-C(8)	61.7(3)	Br(1)-C(25)-C(26)-C(27)	179.3(3)
C(17)-C(13)-C(14)-C(8)	176.6(2)	C(25)-C(26)-C(27)-C(28)	0.4(6)
C(12)-C(13)-C(14)-C(15)	170.0(2)	C(26)-C(27)-C(28)-C(23)	0.0(6)
C(22)-C(13)-C(14)-C(15)	-68.7(3)	C(24)-C(23)-C(28)-C(27)	-0.6(5)
C(17)-C(13)-C(14)-C(15)	46.1(3)	C(20)-C(23)-C(28)-C(27)	179.5(3)

S1.3.5. Non-covalent interactions in 2d and 2g.



2d



2g

Fig. S11. The C17B-Cl1B···Hal-C26A interaction in isostructural crystals of previously published **2d** (CSD refcode MUXRAB; CCDC deposition number 1990621) and **2g** (p=50%). The Cl1B···Br1A distance is 3.288(1)Å in **2g**, and the Cl1B···Cl2A distance is 3.264(6)Å in **2g**.

S1.4. The structures of reduced *D*-annulated pentacyclic steroids.

S1.4.1. The structure of 3d.

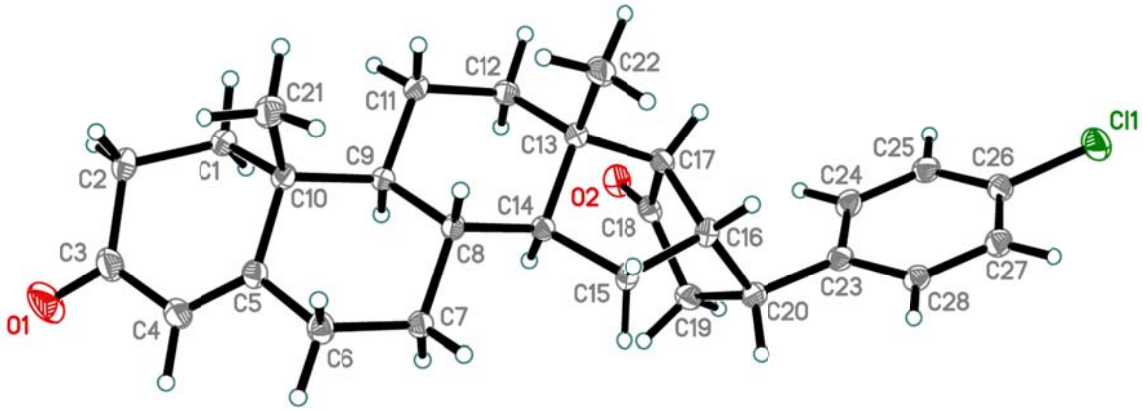


Fig. S12. The structure of **3d** (p=50%).

Table S29. Bond lengths [Å] for **3d**.

Bond	Length	Bond	Length	Bond	Length
Cl(1)-C(26)	1.7386(16)	C(8)-H(8)	0.98(2)	C(17)-H(17)	0.96(2)
O(1)-C(3)	1.223(2)	C(9)-C(11)	1.537(2)	C(18)-C(19)	1.516(2)
O(2)-C(18)	1.2122(19)	C(9)-C(10)	1.559(2)	C(19)-C(20)	1.531(2)
C(1)-C(2)	1.525(2)	C(9)-H(9)	0.94(2)	C(19)-H(19A)	0.998(15)
C(1)-C(10)	1.546(2)	C(10)-C(21)	1.548(2)	C(19)-H(19B)	0.998(15)
C(1)-H(1A)	0.962(15)	C(11)-C(12)	1.535(2)	C(20)-C(23)	1.518(2)
C(1)-H(1B)	0.962(15)	C(11)-H(11B)	0.972(16)	C(20)-H(20)	0.97(2)
C(2)-C(3)	1.504(2)	C(11)-H(11A)	0.972(16)	C(21)-H(21A)	0.970(14)
C(2)-H(2A)	0.982(16)	C(12)-C(13)	1.529(2)	C(21)-H(21B)	0.970(14)
C(2)-H(2B)	0.982(16)	C(12)-H(12B)	0.985(15)	C(21)-H(21C)	0.970(14)
C(3)-C(4)	1.466(2)	C(12)-H(12A)	0.985(15)	C(22)-H(22A)	0.993(13)
C(4)-C(5)	1.343(2)	C(13)-C(14)	1.540(2)	C(22)-H(22B)	0.993(13)
C(4)-H(4)	1.02(2)	C(13)-C(22)	1.543(2)	C(22)-H(22C)	0.993(13)
C(5)-C(6)	1.505(2)	C(13)-C(17)	1.544(2)	C(23)-C(24)	1.395(2)
C(5)-C(10)	1.519(2)	C(14)-C(15)	1.541(2)	C(23)-C(28)	1.401(2)
C(6)-C(7)	1.530(2)	C(14)-H(14)	1.02(2)	C(24)-C(25)	1.395(2)
C(6)-H(6B)	1.023(15)	C(15)-C(16)	1.563(2)	C(24)-H(24)	0.96(2)

C(6)-H(6A)	1.023(15)	C(15)-H(15B)	0.963(14)	C(25)-C(26)	1.385(2)
C(7)-C(8)	1.527(2)	C(15)-H(15A)	0.963(14)	C(25)-H(25)	0.98(2)
C(7)-H(7A)	0.974(14)	C(16)-C(17)	1.552(2)	C(26)-C(27)	1.387(2)
C(7)-H(7B)	0.974(14)	C(16)-C(20)	1.560(2)	C(27)-C(28)	1.395(2)
C(8)-C(14)	1.528(2)	C(16)-H(16)	0.97(2)	C(27)-H(27)	0.98(2)
C(8)-C(9)	1.548(2)	C(17)-C(18)	1.536(2)	C(28)-H(28)	0.93(2)

Table S30. Bond angles [°] for **3d**.

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	113.37(13)	C(5)-C(10)-C(9)	108.33(11)	C(18)-C(17)-C(16)	103.65(11)
C(3)-C(2)-C(1)	111.13(13)	C(1)-C(10)-C(9)	108.60(12)	C(13)-C(17)-C(16)	104.83(11)
O(1)-C(3)-C(4)	121.77(17)	C(21)-C(10)-C(9)	112.26(12)	O(2)-C(18)-C(19)	124.82(14)
O(1)-C(3)-C(2)	122.29(16)	C(12)-C(11)-C(9)	112.73(12)	O(2)-C(18)-C(17)	125.69(14)
C(4)-C(3)-C(2)	115.92(14)	C(13)-C(12)-C(11)	110.88(13)	C(19)-C(18)-C(17)	109.49(12)
C(5)-C(4)-C(3)	122.92(15)	C(12)-C(13)-C(14)	109.04(12)	C(18)-C(19)-C(20)	104.86(12)
C(4)-C(5)-C(6)	119.74(14)	C(12)-C(13)-C(22)	109.99(12)	C(23)-C(20)-C(19)	113.44(13)
C(4)-C(5)-C(10)	123.83(14)	C(14)-C(13)-C(22)	112.63(13)	C(23)-C(20)-C(16)	110.12(12)
C(6)-C(5)-C(10)	116.43(13)	C(12)-C(13)-C(17)	117.63(13)	C(19)-C(20)-C(16)	102.56(12)
C(5)-C(6)-C(7)	112.51(13)	C(14)-C(13)-C(17)	99.96(11)	C(24)-C(23)-C(28)	117.75(14)
C(8)-C(7)-C(6)	112.31(12)	C(22)-C(13)-C(17)	107.34(12)	C(24)-C(23)-C(20)	123.53(13)
C(7)-C(8)-C(14)	111.11(11)	C(8)-C(14)-C(13)	113.58(11)	C(28)-C(23)-C(20)	118.67(14)
C(7)-C(8)-C(9)	110.24(11)	C(8)-C(14)-C(15)	119.83(12)	C(23)-C(24)-C(25)	121.60(15)
C(14)-C(8)-C(9)	107.97(11)	C(13)-C(14)-C(15)	104.47(12)	C(26)-C(25)-C(24)	118.94(15)
C(11)-C(9)-C(8)	111.81(12)	C(14)-C(15)-C(16)	105.06(12)	C(25)-C(26)-C(27)	121.31(15)
C(11)-C(9)-C(10)	112.53(12)	C(17)-C(16)-C(20)	105.11(12)	C(25)-C(26)-Cl(1)	118.94(13)
C(8)-C(9)-C(10)	114.27(12)	C(17)-C(16)-C(15)	104.81(11)	C(27)-C(26)-Cl(1)	119.75(12)
C(5)-C(10)-C(1)	110.34(12)	C(20)-C(16)-C(15)	115.13(12)	C(26)-C(27)-C(28)	118.81(14)
C(5)-C(10)-C(21)	108.20(13)	C(18)-C(17)-C(13)	115.19(12)	C(27)-C(28)-C(23)	121.59(15)
C(1)-C(10)-C(21)	109.12(12)				

Table S31. Torsion angles [°] for **3d**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-55.84(18)	C(12)-C(13)-C(14)-C(15)	168.22(12)
C(1)-C(2)-C(3)-O(1)	-144.50(19)	C(22)-C(13)-C(14)-C(15)	-69.39(14)
C(1)-C(2)-C(3)-C(4)	37.5(2)	C(17)-C(13)-C(14)-C(15)	44.25(13)
O(1)-C(3)-C(4)-C(5)	174.30(18)	C(8)-C(14)-C(15)-C(16)	-158.01(12)
C(2)-C(3)-C(4)-C(5)	-7.7(2)	C(13)-C(14)-C(15)-C(16)	-29.38(15)
C(3)-C(4)-C(5)-C(6)	173.33(15)	C(14)-C(15)-C(16)-C(17)	2.56(15)
C(3)-C(4)-C(5)-C(10)	-5.5(3)	C(14)-C(15)-C(16)-C(20)	-112.39(13)
C(4)-C(5)-C(6)-C(7)	129.58(16)	C(12)-C(13)-C(17)-C(18)	-47.10(18)
C(10)-C(5)-C(6)-C(7)	-51.49(17)	C(14)-C(13)-C(17)-C(18)	70.66(15)
C(5)-C(6)-C(7)-C(8)	51.53(17)	C(22)-C(13)-C(17)-C(18)	-171.69(12)
C(6)-C(7)-C(8)-C(14)	-172.73(11)	C(12)-C(13)-C(17)-C(16)	-160.33(12)
C(6)-C(7)-C(8)-C(9)	-53.08(15)	C(14)-C(13)-C(17)-C(16)	-42.57(13)
C(7)-C(8)-C(9)-C(11)	-175.84(12)	C(22)-C(13)-C(17)-C(16)	75.08(14)
C(14)-C(8)-C(9)-C(11)	-54.30(15)	C(20)-C(16)-C(17)-C(18)	25.67(14)
C(7)-C(8)-C(9)-C(10)	54.87(15)	C(15)-C(16)-C(17)-C(18)	-96.09(13)
C(14)-C(8)-C(9)-C(10)	176.41(11)	C(20)-C(16)-C(17)-C(13)	146.83(11)
C(4)-C(5)-C(10)-C(1)	-12.2(2)	C(15)-C(16)-C(17)-C(13)	25.07(14)
C(6)-C(5)-C(10)-C(1)	168.89(12)	C(13)-C(17)-C(18)-O(2)	62.8(2)
C(4)-C(5)-C(10)-C(21)	107.08(17)	C(16)-C(17)-C(18)-O(2)	176.70(15)
C(6)-C(5)-C(10)-C(21)	-71.80(16)	C(13)-C(17)-C(18)-C(19)	-118.04(13)
C(4)-C(5)-C(10)-C(9)	-130.98(15)	C(16)-C(17)-C(18)-C(19)	-4.12(15)
C(6)-C(5)-C(10)-C(9)	50.14(16)	O(2)-C(18)-C(19)-C(20)	159.81(15)
C(2)-C(1)-C(10)-C(5)	42.49(17)	C(17)-C(18)-C(19)-C(20)	-19.38(16)
C(2)-C(1)-C(10)-C(21)	-76.26(16)	C(18)-C(19)-C(20)-C(23)	-84.17(15)
C(2)-C(1)-C(10)-C(9)	161.08(12)	C(18)-C(19)-C(20)-C(16)	34.56(15)
C(11)-C(9)-C(10)-C(5)	179.26(12)	C(17)-C(16)-C(20)-C(23)	83.39(14)
C(8)-C(9)-C(10)-C(5)	-51.81(15)	C(15)-C(16)-C(20)-C(23)	-161.84(12)
C(11)-C(9)-C(10)-C(1)	59.41(15)	C(17)-C(16)-C(20)-C(19)	-37.65(14)
C(8)-C(9)-C(10)-C(1)	-171.66(11)	C(15)-C(16)-C(20)-C(19)	77.13(15)
C(11)-C(9)-C(10)-C(21)	-61.33(17)	C(19)-C(20)-C(23)-C(24)	24.3(2)
C(8)-C(9)-C(10)-C(21)	67.60(16)	C(16)-C(20)-C(23)-C(24)	-89.99(17)
C(8)-C(9)-C(11)-C(12)	54.38(17)	C(19)-C(20)-C(23)-C(28)	-158.49(13)
C(10)-C(9)-C(11)-C(12)	-175.43(12)	C(16)-C(20)-C(23)-C(28)	87.23(15)

C(9)-C(11)-C(12)-C(13)	-54.50(17)	C(28)-C(23)-C(24)-C(25)	-0.3(2)
C(11)-C(12)-C(13)-C(14)	55.17(16)	C(20)-C(23)-C(24)-C(25)	176.98(14)
C(11)-C(12)-C(13)-C(22)	-68.79(16)	C(23)-C(24)-C(25)-C(26)	-0.7(2)
C(11)-C(12)-C(13)-C(17)	167.95(13)	C(24)-C(25)-C(26)-C(27)	1.1(2)
C(7)-C(8)-C(14)-C(13)	179.24(12)	C(24)-C(25)-C(26)-Cl(1)	-179.12(12)
C(9)-C(8)-C(14)-C(13)	58.24(15)	C(25)-C(26)-C(27)-C(28)	-0.4(2)
C(7)-C(8)-C(14)-C(15)	-56.38(17)	Cl(1)-C(26)-C(27)-C(28)	179.75(11)
C(9)-C(8)-C(14)-C(15)	-177.38(12)	C(26)-C(27)-C(28)-C(23)	-0.6(2)
C(12)-C(13)-C(14)-C(8)	-59.46(16)	C(24)-C(23)-C(28)-C(27)	0.9(2)
C(22)-C(13)-C(14)-C(8)	62.93(16)	C(20)-C(23)-C(28)-C(27)	-176.46(13)
C(17)-C(13)-C(14)-C(8)	176.57(11)		

S1.4.2. The structure of 3e.

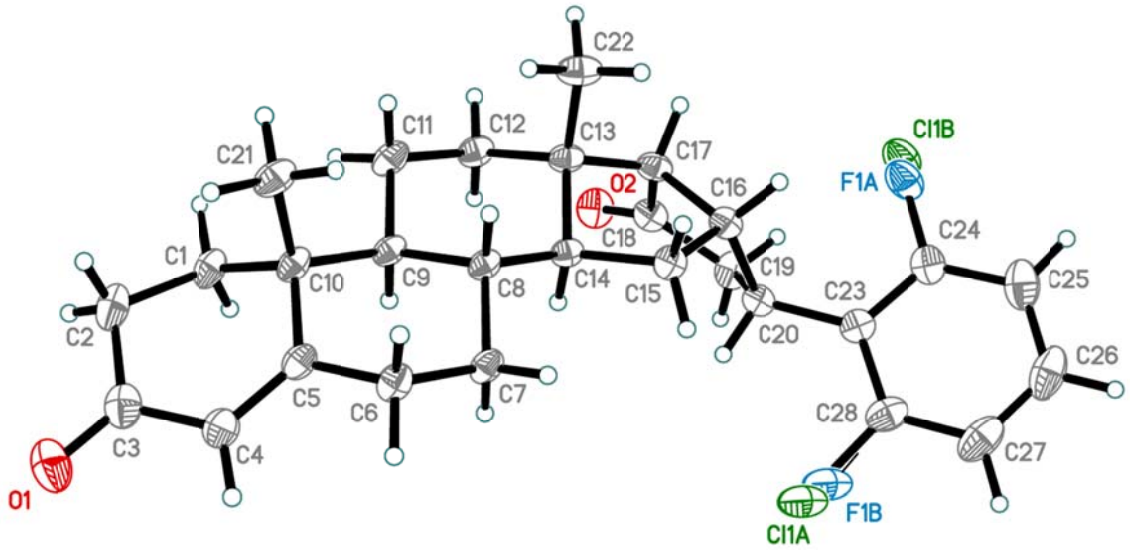


Fig. S13. The structure of **3e** (p=50%). The Cl/F disorder ratio (positions A/B) is 0.7248(19):0.2752(19).

Table S32. Bond lengths [Å] for **3e**.

Bond	Length	Bond	Length	Bond	Length
Cl(1A)-C(28)	1.7607(14)	C(8)-C(14)	1.5244(15)	C(17)-C(18)	1.5236(17)
F(1A)-C(24)	1.347(2)	C(8)-C(9)	1.5459(15)	C(17)-H(17)	1.00(2)
Cl(1B)-C(24)	1.753(2)	C(8)-H(8)	0.96(2)	C(18)-C(19)	1.511(2)
F(1B)-C(28)	1.342(3)	C(9)-C(11)	1.5398(17)	C(19)-C(20)	1.5375(18)
O(1)-C(3)	1.2213(19)	C(9)-C(10)	1.5644(16)	C(19)-H(19A)	0.960(16)
O(2)-C(18)	1.2120(15)	C(9)-H(9)	0.97(2)	C(19)-H(19B)	0.960(16)
C(1)-C(2)	1.524(2)	C(10)-C(21)	1.5456(17)	C(20)-C(23)	1.5057(18)
C(1)-C(10)	1.5406(16)	C(11)-C(12)	1.5364(19)	C(20)-H(20)	0.97(2)
C(1)-H(1A)	0.983(15)	C(11)-H(11B)	0.982(15)	C(21)-H(21A)	0.991(14)
C(1)-H(1B)	0.983(15)	C(11)-H(11A)	0.982(15)	C(21)-H(21B)	0.991(14)
C(2)-C(3)	1.501(2)	C(12)-C(13)	1.5297(17)	C(21)-H(21C)	0.991(14)
C(2)-H(2A)	0.944(16)	C(12)-H(12B)	0.942(15)	C(22)-H(22A)	0.968(14)
C(2)-H(2B)	0.944(16)	C(12)-H(12A)	0.942(14)	C(22)-H(22B)	0.968(14)
C(3)-C(4)	1.4651(19)	C(13)-C(14)	1.5428(15)	C(22)-H(22C)	0.968(14)
C(4)-C(5)	1.3504(17)	C(13)-C(22)	1.5436(17)	C(23)-C(24)	1.3935(18)
C(4)-H(4)	0.98(2)	C(13)-C(17)	1.5487(18)	C(23)-C(28)	1.4010(18)
C(5)-C(6)	1.5040(16)	C(14)-C(15)	1.5306(15)	C(24)-C(25)	1.386(2)
C(5)-C(10)	1.5213(17)	C(14)-H(14)	1.010(19)	C(25)-C(26)	1.392(3)
C(6)-C(7)	1.5285(16)	C(15)-C(16)	1.5477(16)	C(25)-H(25)	0.97(3)
C(6)-H(6B)	1.011(15)	C(15)-H(15B)	0.968(14)	C(26)-C(27)	1.381(3)
C(6)-H(6A)	1.011(15)	C(15)-H(15A)	0.968(14)	C(26)-H(26)	0.97(3)
C(7)-C(8)	1.5255(16)	C(16)-C(17)	1.5614(16)	C(27)-C(28)	1.390(2)
C(7)-H(7A)	0.953(14)	C(16)-C(20)	1.5618(17)	C(27)-H(27)	0.97(3)
C(7)-H(7B)	0.953(14)	C(16)-H(16)	1.02(2)		

Table S33. Bond angles [°] for **3e**.

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	113.38(11)	C(21)-C(10)-C(9)	111.98(10)	C(19)-C(18)-C(17)	108.80(10)
C(3)-C(2)-C(1)	112.32(11)	C(12)-C(11)-C(9)	112.65(10)	C(18)-C(19)-C(20)	103.54(10)
O(1)-C(3)-C(4)	121.13(15)	C(13)-C(12)-C(11)	110.44(10)	C(23)-C(20)-C(19)	115.58(10)
O(1)-C(3)-C(2)	121.94(14)	C(12)-C(13)-C(14)	108.32(9)	C(23)-C(20)-C(16)	113.58(10)
C(4)-C(3)-C(2)	116.80(12)	C(12)-C(13)-C(22)	110.14(10)	C(19)-C(20)-C(16)	106.57(10)
C(5)-C(4)-C(3)	123.26(13)	C(14)-C(13)-C(22)	112.76(10)	C(24)-C(23)-C(28)	114.65(12)

C(4)-C(5)-C(6)	120.20(11)	C(12)-C(13)-C(17)	118.44(10)	C(24)-C(23)-C(20)	122.74(11)
C(4)-C(5)-C(10)	122.71(11)	C(14)-C(13)-C(17)	100.94(9)	C(28)-C(23)-C(20)	122.58(12)
C(6)-C(5)-C(10)	117.03(10)	C(22)-C(13)-C(17)	106.06(10)	F(1A)-C(24)-C(25)	118.04(16)
C(5)-C(6)-C(7)	111.90(9)	C(8)-C(14)-C(15)	118.15(9)	F(1A)-C(24)-C(23)	117.44(15)
C(8)-C(7)-C(6)	110.69(9)	C(8)-C(14)-C(13)	113.68(9)	C(25)-C(24)-C(23)	124.49(14)
C(14)-C(8)-C(7)	111.12(9)	C(15)-C(14)-C(13)	103.96(9)	C(25)-C(24)-Cl(1B)	115.85(14)
C(14)-C(8)-C(9)	108.88(8)	C(14)-C(15)-C(16)	103.28(9)	C(23)-C(24)-Cl(1B)	119.50(13)
C(7)-C(8)-C(9)	110.03(9)	C(15)-C(16)-C(17)	106.32(9)	C(24)-C(25)-C(26)	118.16(15)
C(11)-C(9)-C(8)	111.97(10)	C(15)-C(16)-C(20)	112.26(9)	C(27)-C(26)-C(25)	120.21(14)
C(11)-C(9)-C(10)	112.92(9)	C(17)-C(16)-C(20)	105.84(9)	C(26)-C(27)-C(28)	119.52(15)
C(8)-C(9)-C(10)	113.92(9)	C(18)-C(17)-C(13)	119.51(10)	F(1B)-C(28)-C(27)	113.9(3)
C(5)-C(10)-C(1)	109.97(10)	C(18)-C(17)-C(16)	105.46(10)	F(1B)-C(28)-C(23)	123.1(3)
C(5)-C(10)-C(21)	107.68(9)	C(13)-C(17)-C(16)	105.45(9)	C(27)-C(28)-C(23)	122.98(14)
C(1)-C(10)-C(21)	109.85(10)	O(2)-C(18)-C(19)	124.87(12)	C(27)-C(28)-Cl(1A)	117.64(12)
C(5)-C(10)-C(9)	108.88(9)	O(2)-C(18)-C(17)	126.31(12)	C(23)-C(28)-Cl(1A)	119.38(11)
C(1)-C(10)-C(9)	108.47(9)				

Table S34. Torsion angles [°] for **3e**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-53.12(16)	C(14)-C(15)-C(16)-C(17)	18.06(12)
C(1)-C(2)-C(3)-O(1)	-156.19(14)	C(14)-C(15)-C(16)-C(20)	-97.23(11)
C(1)-C(2)-C(3)-C(4)	27.96(17)	C(12)-C(13)-C(17)-C(18)	-32.52(15)
O(1)-C(3)-C(4)-C(5)	-173.62(13)	C(14)-C(13)-C(17)-C(18)	85.43(12)
C(2)-C(3)-C(4)-C(5)	2.26(19)	C(22)-C(13)-C(17)-C(18)	-156.82(11)
C(3)-C(4)-C(5)-C(6)	169.14(11)	C(12)-C(13)-C(17)-C(16)	-150.83(10)
C(3)-C(4)-C(5)-C(10)	-7.97(18)	C(14)-C(13)-C(17)-C(16)	-32.88(11)
C(4)-C(5)-C(6)-C(7)	131.03(12)	C(22)-C(13)-C(17)-C(16)	84.87(11)
C(10)-C(5)-C(6)-C(7)	-51.70(14)	C(15)-C(16)-C(17)-C(18)	-117.84(10)
C(5)-C(6)-C(7)-C(8)	55.02(13)	C(20)-C(16)-C(17)-C(18)	1.72(12)
C(6)-C(7)-C(8)-C(14)	-178.03(9)	C(15)-C(16)-C(17)-C(13)	9.51(11)
C(6)-C(7)-C(8)-C(9)	-57.36(12)	C(20)-C(16)-C(17)-C(13)	129.07(9)
C(14)-C(8)-C(9)-C(11)	-52.29(12)	C(13)-C(17)-C(18)-O(2)	42.75(17)
C(7)-C(8)-C(9)-C(11)	-174.30(9)	C(16)-C(17)-C(18)-O(2)	161.05(12)
C(14)-C(8)-C(9)-C(10)	178.04(9)	C(13)-C(17)-C(18)-C(19)	-139.01(11)
C(7)-C(8)-C(9)-C(10)	56.03(12)	C(16)-C(17)-C(18)-C(19)	-20.71(13)

C(4)-C(5)-C(10)-C(1)	-16.74(15)	O(2)-C(18)-C(19)-C(20)	-150.42(13)
C(6)-C(5)-C(10)-C(1)	166.06(10)	C(17)-C(18)-C(19)-C(20)	31.31(13)
C(4)-C(5)-C(10)-C(21)	102.92(13)	C(18)-C(19)-C(20)-C(23)	-156.66(11)
C(6)-C(5)-C(10)-C(21)	-74.27(12)	C(18)-C(19)-C(20)-C(16)	-29.43(13)
C(4)-C(5)-C(10)-C(9)	-135.47(11)	C(15)-C(16)-C(20)-C(23)	-98.78(11)
C(6)-C(5)-C(10)-C(9)	47.34(13)	C(17)-C(16)-C(20)-C(23)	145.64(10)
C(2)-C(1)-C(10)-C(5)	46.60(14)	C(15)-C(16)-C(20)-C(19)	132.81(10)
C(2)-C(1)-C(10)-C(21)	-71.74(14)	C(17)-C(16)-C(20)-C(19)	17.23(12)
C(2)-C(1)-C(10)-C(9)	165.58(11)	C(19)-C(20)-C(23)-C(24)	61.61(16)
C(11)-C(9)-C(10)-C(5)	-178.34(10)	C(16)-C(20)-C(23)-C(24)	-62.03(15)
C(8)-C(9)-C(10)-C(5)	-49.15(12)	C(19)-C(20)-C(23)-C(28)	-120.26(13)
C(11)-C(9)-C(10)-C(1)	62.00(13)	C(16)-C(20)-C(23)-C(28)	116.10(13)
C(8)-C(9)-C(10)-C(1)	-168.80(10)	C(28)-C(23)-C(24)-F(1A)	-177.87(15)
C(11)-C(9)-C(10)-C(21)	-59.38(13)	C(20)-C(23)-C(24)-F(1A)	0.4(2)
C(8)-C(9)-C(10)-C(21)	69.81(12)	C(28)-C(23)-C(24)-C(25)	-0.2(2)
C(8)-C(9)-C(11)-C(12)	53.41(13)	C(20)-C(23)-C(24)-C(25)	178.08(13)
C(10)-C(9)-C(11)-C(12)	-176.40(10)	C(28)-C(23)-C(24)-Cl(1B)	175.03(13)
C(9)-C(11)-C(12)-C(13)	-55.91(14)	C(20)-C(23)-C(24)-Cl(1B)	-6.7(2)
C(11)-C(12)-C(13)-C(14)	57.17(13)	F(1A)-C(24)-C(25)-C(26)	177.71(16)
C(11)-C(12)-C(13)-C(22)	-66.58(13)	C(23)-C(24)-C(25)-C(26)	0.0(2)
C(11)-C(12)-C(13)-C(17)	171.16(10)	Cl(1B)-C(24)-C(25)-C(26)	-175.34(14)
C(7)-C(8)-C(14)-C(15)	-59.28(13)	C(24)-C(25)-C(26)-C(27)	0.0(2)
C(9)-C(8)-C(14)-C(15)	179.38(10)	C(25)-C(26)-C(27)-C(28)	0.1(2)
C(7)-C(8)-C(14)-C(13)	178.48(9)	C(26)-C(27)-C(28)-F(1B)	179.9(3)
C(9)-C(8)-C(14)-C(13)	57.14(12)	C(26)-C(27)-C(28)-C(23)	-0.3(2)
C(12)-C(13)-C(14)-C(8)	-60.12(12)	C(26)-C(27)-C(28)-Cl(1A)	179.41(12)
C(22)-C(13)-C(14)-C(8)	62.04(13)	C(24)-C(23)-C(28)-F(1B)	-179.9(3)
C(17)-C(13)-C(14)-C(8)	174.79(9)	C(20)-C(23)-C(28)-F(1B)	1.8(4)
C(12)-C(13)-C(14)-C(15)	170.09(9)	C(24)-C(23)-C(28)-C(27)	0.32(19)
C(22)-C(13)-C(14)-C(15)	-67.75(13)	C(20)-C(23)-C(28)-C(27)	-177.95(13)
C(17)-C(13)-C(14)-C(15)	45.00(10)	C(24)-C(23)-C(28)-Cl(1A)	-179.40(10)
C(8)-C(14)-C(15)-C(16)	-166.43(9)	C(20)-C(23)-C(28)-Cl(1A)	2.33(17)
C(13)-C(14)-C(15)-C(16)	-39.39(11)		

S1.4.3. The structure of 3f.

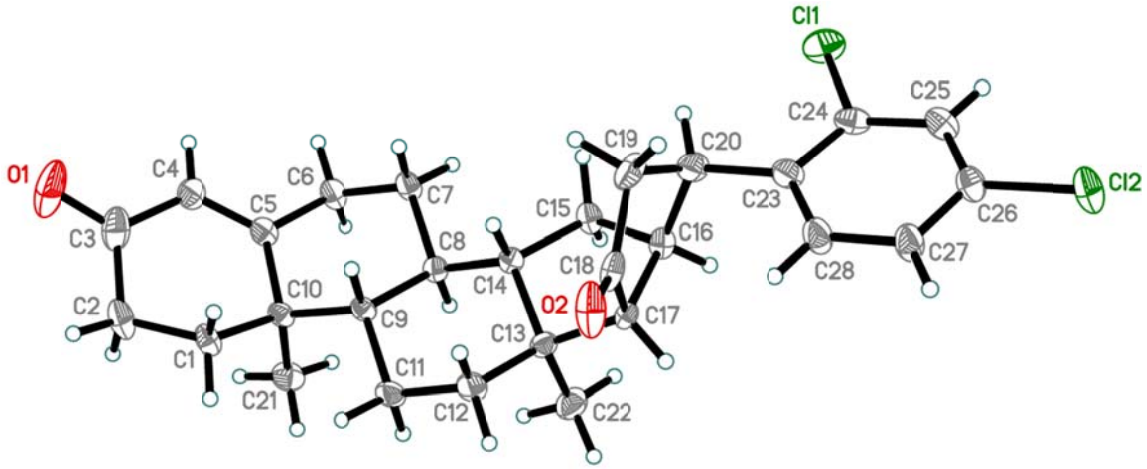


Fig. S14. The structure of **3f** (p=50%).

Table S35. Bond lengths [Å] for **3f**.

Bond	Length	Bond	Length	Bond	Length
Cl(1)-C(24)	1.740(2)	C(8)-C(9)	1.544(3)	C(17)-C(18)	1.525(3)
Cl(2)-C(26)	1.735(2)	C(8)-H(8)	1.00(3)	C(17)-H(17)	0.94(3)
O(1)-C(3)	1.221(3)	C(9)-C(11)	1.537(3)	C(18)-C(19)	1.504(3)
O(2)-C(18)	1.208(3)	C(9)-C(10)	1.562(3)	C(19)-C(20)	1.528(3)
C(1)-C(2)	1.527(3)	C(9)-H(9)	1.02(2)	C(19)-H(19A)	0.98(2)
C(1)-C(10)	1.541(3)	C(10)-C(21)	1.539(3)	C(19)-H(19B)	0.98(2)
C(1)-H(1A)	0.93(2)	C(11)-C(12)	1.540(3)	C(20)-C(23)	1.516(3)
C(1)-H(1B)	0.93(2)	C(11)-H(11A)	1.01(2)	C(20)-H(20)	0.98(3)
C(2)-C(3)	1.496(4)	C(11)-H(11B)	1.01(2)	C(21)-H(21A)	0.945(16)
C(2)-H(2A)	1.02(2)	C(12)-C(13)	1.527(3)	C(21)-H(21B)	0.945(16)
C(2)-H(2B)	1.02(2)	C(12)-H(12B)	0.94(2)	C(21)-H(21C)	0.945(16)
C(3)-C(4)	1.460(3)	C(12)-H(12A)	0.94(2)	C(22)-H(22A)	0.987(17)
C(4)-C(5)	1.342(3)	C(13)-C(22)	1.537(3)	C(22)-H(22B)	0.987(17)
C(4)-H(4)	0.94(3)	C(13)-C(14)	1.539(3)	C(22)-H(22C)	0.987(17)
C(5)-C(6)	1.504(3)	C(13)-C(17)	1.555(3)	C(23)-C(24)	1.394(3)
C(5)-C(10)	1.524(3)	C(14)-C(15)	1.535(3)	C(23)-C(28)	1.403(3)
C(6)-C(7)	1.531(3)	C(14)-H(14)	0.98(3)	C(24)-C(25)	1.389(3)
C(6)-H(6B)	0.98(2)	C(15)-C(16)	1.559(3)	C(25)-C(26)	1.384(3)

C(6)-H(6A)	0.98(2)	C(15)-H(15B)	1.001(19)	C(25)-H(25)	0.93(3)
C(7)-C(8)	1.527(3)	C(15)-H(15A)	1.001(19)	C(26)-C(27)	1.383(3)
C(7)-H(7A)	0.99(2)	C(16)-C(17)	1.560(3)	C(27)-C(28)	1.386(3)
C(7)-H(7B)	0.989(19)	C(16)-C(20)	1.565(3)	C(27)-H(27)	0.96(3)
C(8)-C(14)	1.529(3)	C(16)-H(16)	0.98(3)	C(28)-H(28)	0.94(3)

Table S36. Bond angles [°] for **3f**.

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	114.16(17)	C(5)-C(10)-C(9)	108.78(15)	C(13)-C(17)-C(16)	105.32(15)
C(3)-C(2)-C(1)	111.35(19)	C(21)-C(10)-C(9)	111.72(17)	O(2)-C(18)-C(19)	125.5(2)
O(1)-C(3)-C(4)	121.9(3)	C(1)-C(10)-C(9)	108.28(15)	O(2)-C(18)-C(17)	124.9(2)
O(1)-C(3)-C(2)	122.3(2)	C(9)-C(11)-C(12)	112.32(17)	C(19)-C(18)-C(17)	109.59(17)
C(4)-C(3)-C(2)	115.8(2)	C(13)-C(12)-C(11)	110.86(17)	C(18)-C(19)-C(20)	104.98(17)
C(5)-C(4)-C(3)	123.7(2)	C(12)-C(13)-C(22)	110.29(18)	C(23)-C(20)-C(19)	111.18(18)
C(4)-C(5)-C(6)	120.3(2)	C(12)-C(13)-C(14)	108.47(15)	C(23)-C(20)-C(16)	113.61(18)
C(4)-C(5)-C(10)	123.37(19)	C(22)-C(13)-C(14)	112.79(16)	C(19)-C(20)-C(16)	103.46(17)
C(6)-C(5)-C(10)	116.37(17)	C(12)-C(13)-C(17)	117.24(16)	C(24)-C(23)-C(28)	115.51(19)
C(5)-C(6)-C(7)	111.10(16)	C(22)-C(13)-C(17)	107.07(16)	C(24)-C(23)-C(20)	123.39(19)
C(8)-C(7)-C(6)	111.52(17)	C(14)-C(13)-C(17)	100.77(15)	C(28)-C(23)-C(20)	121.07(19)
C(7)-C(8)-C(14)	110.81(16)	C(8)-C(14)-C(15)	119.98(15)	C(25)-C(24)-C(23)	123.30(19)
C(7)-C(8)-C(9)	109.67(15)	C(8)-C(14)-C(13)	113.90(16)	C(25)-C(24)-Cl(1)	116.51(16)
C(14)-C(8)-C(9)	107.65(15)	C(15)-C(14)-C(13)	104.14(15)	C(23)-C(24)-Cl(1)	120.16(17)
C(11)-C(9)-C(8)	111.07(16)	C(14)-C(15)-C(16)	104.72(15)	C(26)-C(25)-C(24)	118.32(19)
C(11)-C(9)-C(10)	112.91(15)	C(15)-C(16)-C(17)	105.49(15)	C(27)-C(26)-C(25)	121.3(2)
C(8)-C(9)-C(10)	114.80(15)	C(15)-C(16)-C(20)	112.79(17)	C(27)-C(26)-Cl(2)	119.20(17)
C(5)-C(10)-C(21)	108.33(16)	C(17)-C(16)-C(20)	105.86(16)	C(25)-C(26)-Cl(2)	119.52(16)
C(5)-C(10)-C(1)	110.29(17)	C(18)-C(17)-C(13)	114.37(16)	C(26)-C(27)-C(28)	118.5(2)
C(21)-C(10)-C(1)	109.44(16)	C(18)-C(17)-C(16)	104.60(16)	C(27)-C(28)-C(23)	123.1(2)

Table S37. Torsion angles [°] for **3f**.

Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-54.6(3)	C(22)-C(13)-C(14)-C(15)	-69.4(2)
C(1)-C(2)-C(3)-O(1)	-144.4(3)	C(17)-C(13)-C(14)-C(15)	44.43(18)

C(1)-C(2)-C(3)-C(4)	37.3(3)	C(8)-C(14)-C(15)-C(16)	-163.68(17)
O(1)-C(3)-C(4)-C(5)	172.8(2)	C(13)-C(14)-C(15)-C(16)	-34.8(2)
C(2)-C(3)-C(4)-C(5)	-8.8(3)	C(14)-C(15)-C(16)-C(17)	11.0(2)
C(3)-C(4)-C(5)-C(6)	176.2(2)	C(14)-C(15)-C(16)-C(20)	-104.09(19)
C(3)-C(4)-C(5)-C(10)	-4.4(3)	C(12)-C(13)-C(17)-C(18)	-40.3(2)
C(4)-C(5)-C(6)-C(7)	125.8(2)	C(22)-C(13)-C(17)-C(18)	-164.78(17)
C(10)-C(5)-C(6)-C(7)	-53.6(2)	C(14)-C(13)-C(17)-C(18)	77.13(18)
C(5)-C(6)-C(7)-C(8)	56.0(2)	C(12)-C(13)-C(17)-C(16)	-154.57(17)
C(6)-C(7)-C(8)-C(14)	-174.94(17)	C(22)-C(13)-C(17)-C(16)	80.95(19)
C(6)-C(7)-C(8)-C(9)	-56.2(2)	C(14)-C(13)-C(17)-C(16)	-37.15(18)
C(7)-C(8)-C(9)-C(11)	-176.24(17)	C(15)-C(16)-C(17)-C(18)	-104.47(17)
C(14)-C(8)-C(9)-C(11)	-55.6(2)	C(20)-C(16)-C(17)-C(18)	15.3(2)
C(7)-C(8)-C(9)-C(10)	54.2(2)	C(15)-C(16)-C(17)-C(13)	16.4(2)
C(14)-C(8)-C(9)-C(10)	174.80(15)	C(20)-C(16)-C(17)-C(13)	136.20(16)
C(4)-C(5)-C(10)-C(21)	107.8(2)	C(13)-C(17)-C(18)-O(2)	73.5(3)
C(6)-C(5)-C(10)-C(21)	-72.8(2)	C(16)-C(17)-C(18)-O(2)	-171.8(2)
C(4)-C(5)-C(10)-C(1)	-11.9(3)	C(13)-C(17)-C(18)-C(19)	-108.78(18)
C(6)-C(5)-C(10)-C(1)	167.44(17)	C(16)-C(17)-C(18)-C(19)	5.9(2)
C(4)-C(5)-C(10)-C(9)	-130.6(2)	O(2)-C(18)-C(19)-C(20)	152.4(2)
C(6)-C(5)-C(10)-C(9)	48.8(2)	C(17)-C(18)-C(19)-C(20)	-25.3(2)
C(2)-C(1)-C(10)-C(5)	41.1(2)	C(18)-C(19)-C(20)-C(23)	-88.5(2)
C(2)-C(1)-C(10)-C(21)	-78.0(2)	C(18)-C(19)-C(20)-C(16)	33.8(2)
C(2)-C(1)-C(10)-C(9)	159.98(18)	C(15)-C(16)-C(20)-C(23)	-154.90(17)
C(11)-C(9)-C(10)-C(5)	-177.70(17)	C(17)-C(16)-C(20)-C(23)	90.2(2)
C(8)-C(9)-C(10)-C(5)	-49.0(2)	C(15)-C(16)-C(20)-C(19)	84.43(19)
C(11)-C(9)-C(10)-C(21)	-58.2(2)	C(17)-C(16)-C(20)-C(19)	-30.4(2)
C(8)-C(9)-C(10)-C(21)	70.5(2)	C(19)-C(20)-C(23)-C(24)	-135.7(2)
C(11)-C(9)-C(10)-C(1)	62.4(2)	C(16)-C(20)-C(23)-C(24)	108.1(2)
C(8)-C(9)-C(10)-C(1)	-168.89(16)	C(19)-C(20)-C(23)-C(28)	41.9(3)
C(8)-C(9)-C(11)-C(12)	56.0(2)	C(16)-C(20)-C(23)-C(28)	-74.3(3)
C(10)-C(9)-C(11)-C(12)	-173.42(17)	C(28)-C(23)-C(24)-C(25)	-0.2(3)
C(9)-C(11)-C(12)-C(13)	-55.7(2)	C(20)-C(23)-C(24)-C(25)	177.5(2)
C(11)-C(12)-C(13)-C(22)	-68.8(2)	C(28)-C(23)-C(24)-Cl(1)	-178.32(18)
C(11)-C(12)-C(13)-C(14)	55.2(2)	C(20)-C(23)-C(24)-Cl(1)	-0.6(3)
C(11)-C(12)-C(13)-C(17)	168.36(17)	C(23)-C(24)-C(25)-C(26)	-0.4(3)
C(7)-C(8)-C(14)-C(15)	-56.6(2)	Cl(1)-C(24)-C(25)-C(26)	177.81(17)

C(9)-C(8)-C(14)-C(15)	-176.57(17)	C(24)-C(25)-C(26)-C(27)	0.6(3)
C(7)-C(8)-C(14)-C(13)	179.02(16)	C(24)-C(25)-C(26)-Cl(2)	-178.98(16)
C(9)-C(8)-C(14)-C(13)	59.1(2)	C(25)-C(26)-C(27)-C(28)	-0.3(4)
C(12)-C(13)-C(14)-C(8)	-59.4(2)	Cl(2)-C(26)-C(27)-C(28)	179.34(19)
C(22)-C(13)-C(14)-C(8)	63.1(2)	C(26)-C(27)-C(28)-C(23)	-0.4(4)
C(17)-C(13)-C(14)-C(8)	176.90(15)	C(24)-C(23)-C(28)-C(27)	0.6(4)
C(12)-C(13)-C(14)-C(15)	168.12(16)	C(20)-C(23)-C(28)-C(27)	-177.2(2)

S1.4.4. The structure of 3g.

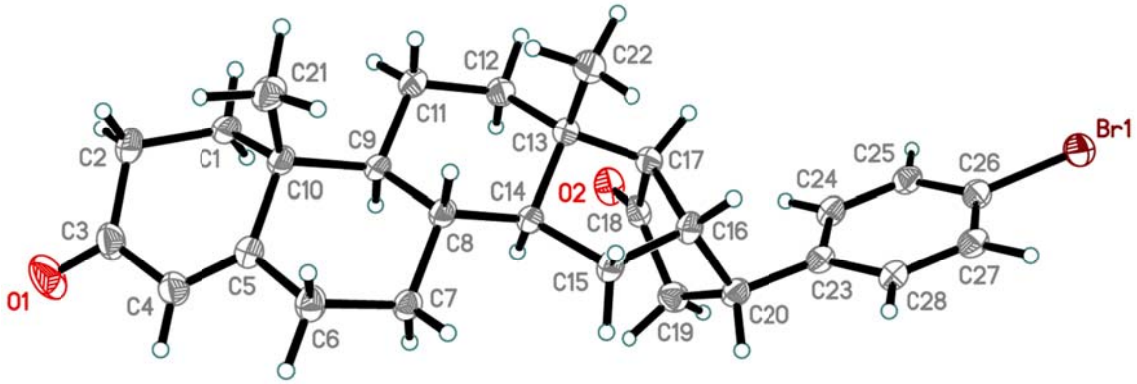


Fig. S15. The structure of **3g** (p=50%).

Table S38. Bond lengths [Å] for **3g**.

Bond	Length	Bond	Length	Bond	Length
Br(1)-C(26)	1.895(2)	C(8)-H(8)	1.04(3)	C(17)-H(17)	1.0000
O(1)-C(3)	1.223(3)	C(9)-C(11)	1.533(3)	C(18)-C(19)	1.514(3)
O(2)-C(18)	1.207(2)	C(9)-C(10)	1.559(3)	C(19)-C(20)	1.530(3)
C(1)-C(2)	1.527(3)	C(9)-H(9)	0.95(3)	C(19)-H(19A)	1.00(2)
C(1)-C(10)	1.542(3)	C(10)-C(21)	1.548(3)	C(19)-H(19B)	1.00(2)
C(1)-H(1A)	0.955(19)	C(11)-C(12)	1.537(3)	C(20)-C(23)	1.518(3)
C(1)-H(1B)	0.955(19)	C(11)-H(11A)	0.97(2)	C(20)-H(20)	1.00(3)
C(2)-C(3)	1.501(3)	C(11)-H(11B)	0.97(2)	C(21)-H(21A)	1.059(18)
C(2)-H(2A)	0.98(2)	C(12)-C(13)	1.530(3)	C(21)-H(21B)	1.059(19)
C(2)-H(2B)	0.98(2)	C(12)-H(12B)	0.99(2)	C(21)-H(21C)	1.059(18)
C(3)-C(4)	1.462(3)	C(12)-H(12A)	0.99(2)	C(22)-H(22A)	1.003(19)
C(4)-C(5)	1.340(3)	C(13)-C(17)	1.541(3)	C(22)-H(22B)	1.003(19)
C(4)-H(4)	0.95(3)	C(13)-C(14)	1.542(3)	C(22)-H(22C)	1.003(19)

C(5)-C(6)	1.509(3)	C(13)-C(22)	1.545(3)	C(23)-C(28)	1.397(3)
C(5)-C(10)	1.519(3)	C(14)-C(15)	1.544(3)	C(23)-C(24)	1.398(3)
C(6)-C(7)	1.526(3)	C(14)-H(14)	0.99(3)	C(24)-C(25)	1.393(3)
C(6)-H(6B)	1.04(2)	C(15)-C(16)	1.566(3)	C(24)-H(24)	0.95(3)
C(6)-H(6A)	1.04(2)	C(15)-H(15B)	1.013(19)	C(25)-C(26)	1.386(3)
C(7)-C(8)	1.521(3)	C(15)-H(15A)	1.013(19)	C(25)-H(25)	0.98(3)
C(7)-H(7A)	0.975(19)	C(16)-C(17)	1.547(3)	C(26)-C(27)	1.388(3)
C(7)-H(7B)	0.975(19)	C(16)-C(20)	1.561(3)	C(27)-C(28)	1.389(3)
C(8)-C(14)	1.524(3)	C(16)-H(16)	1.00(3)	C(27)-H(27)	1.05(3)
C(8)-C(9)	1.553(3)	C(17)-C(18)	1.541(3)	C(28)-H(28)	0.93(3)

Table S39. Bond angles [°] for **3g**.

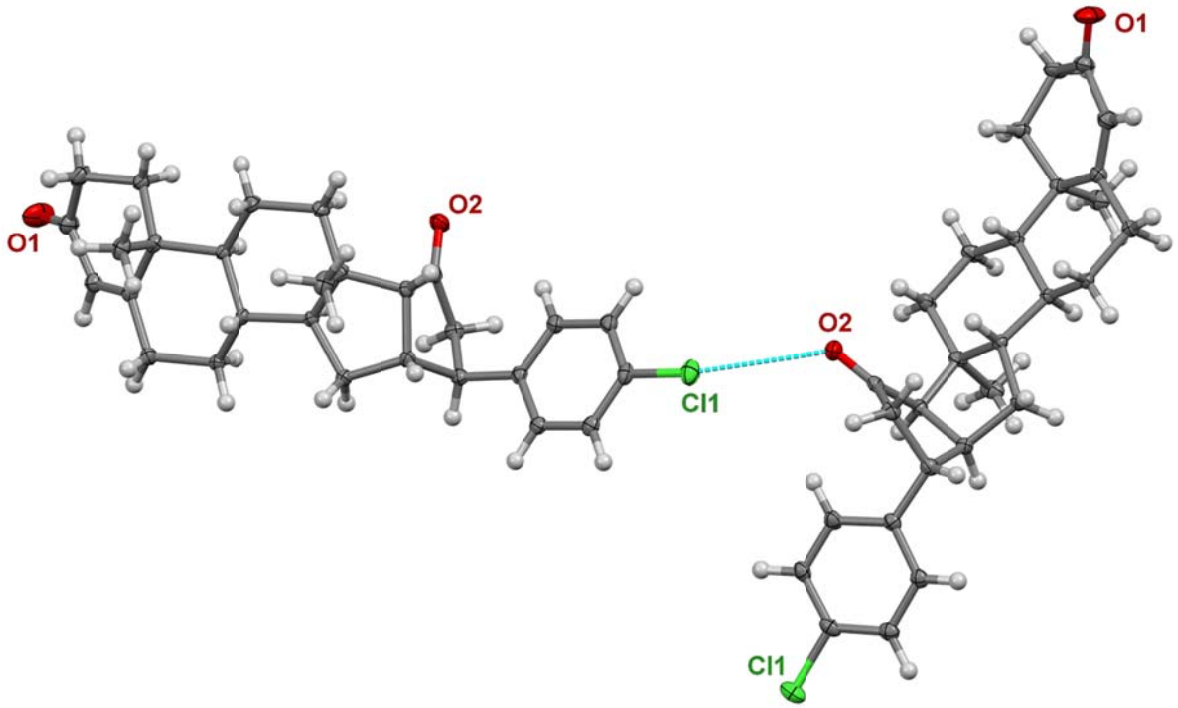
Atoms	Angle	Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(10)	113.27(18)	C(5)-C(10)-C(9)	108.72(15)	C(13)-C(17)-C(16)	104.89(16)
C(3)-C(2)-C(1)	111.05(17)	C(1)-C(10)-C(9)	108.51(17)	C(18)-C(17)-C(16)	103.52(15)
O(1)-C(3)-C(4)	121.9(2)	C(21)-C(10)-C(9)	112.02(16)	O(2)-C(18)-C(19)	125.04(19)
O(1)-C(3)-C(2)	122.1(2)	C(9)-C(11)-C(12)	113.06(16)	O(2)-C(18)-C(17)	125.66(19)
C(4)-C(3)-C(2)	116.04(18)	C(13)-C(12)-C(11)	110.83(18)	C(19)-C(18)-C(17)	109.30(15)
C(5)-C(4)-C(3)	123.0(2)	C(12)-C(13)-C(17)	117.71(18)	C(18)-C(19)-C(20)	104.91(16)
C(4)-C(5)-C(6)	120.18(19)	C(12)-C(13)-C(14)	108.94(16)	C(23)-C(20)-C(19)	113.57(17)
C(4)-C(5)-C(10)	123.71(18)	C(17)-C(13)-C(14)	100.22(15)	C(23)-C(20)-C(16)	110.07(16)
C(6)-C(5)-C(10)	116.10(17)	C(12)-C(13)-C(22)	109.88(17)	C(19)-C(20)-C(16)	102.25(15)
C(5)-C(6)-C(7)	112.85(17)	C(17)-C(13)-C(22)	107.28(16)	C(28)-C(23)-C(24)	117.65(18)
C(8)-C(7)-C(6)	112.51(16)	C(14)-C(13)-C(22)	112.58(18)	C(28)-C(23)-C(20)	118.74(17)
C(7)-C(8)-C(14)	111.23(15)	C(8)-C(14)-C(13)	113.81(15)	C(24)-C(23)-C(20)	123.55(17)
C(7)-C(8)-C(9)	110.19(15)	C(8)-C(14)-C(15)	119.86(16)	C(25)-C(24)-C(23)	121.57(18)
C(14)-C(8)-C(9)	107.90(15)	C(13)-C(14)-C(15)	104.32(15)	C(26)-C(25)-C(24)	118.92(19)
C(11)-C(9)-C(8)	111.73(16)	C(14)-C(15)-C(16)	105.01(16)	C(25)-C(26)-C(27)	121.20(19)
C(11)-C(9)-C(10)	112.76(15)	C(17)-C(16)-C(20)	105.25(16)	C(25)-C(26)-Br(1)	118.62(16)
C(8)-C(9)-C(10)	114.05(16)	C(17)-C(16)-C(15)	104.91(15)	C(27)-C(26)-Br(1)	120.18(15)
C(5)-C(10)-C(1)	110.30(16)	C(20)-C(16)-C(15)	114.93(17)	C(26)-C(27)-C(28)	118.82(18)
C(5)-C(10)-C(21)	108.13(17)	C(13)-C(17)-C(18)	115.13(16)	C(27)-C(28)-C(23)	121.82(18)
C(1)-C(10)-C(21)	109.17(15)				

Table S40. Torsion angles [°] for **3g**.

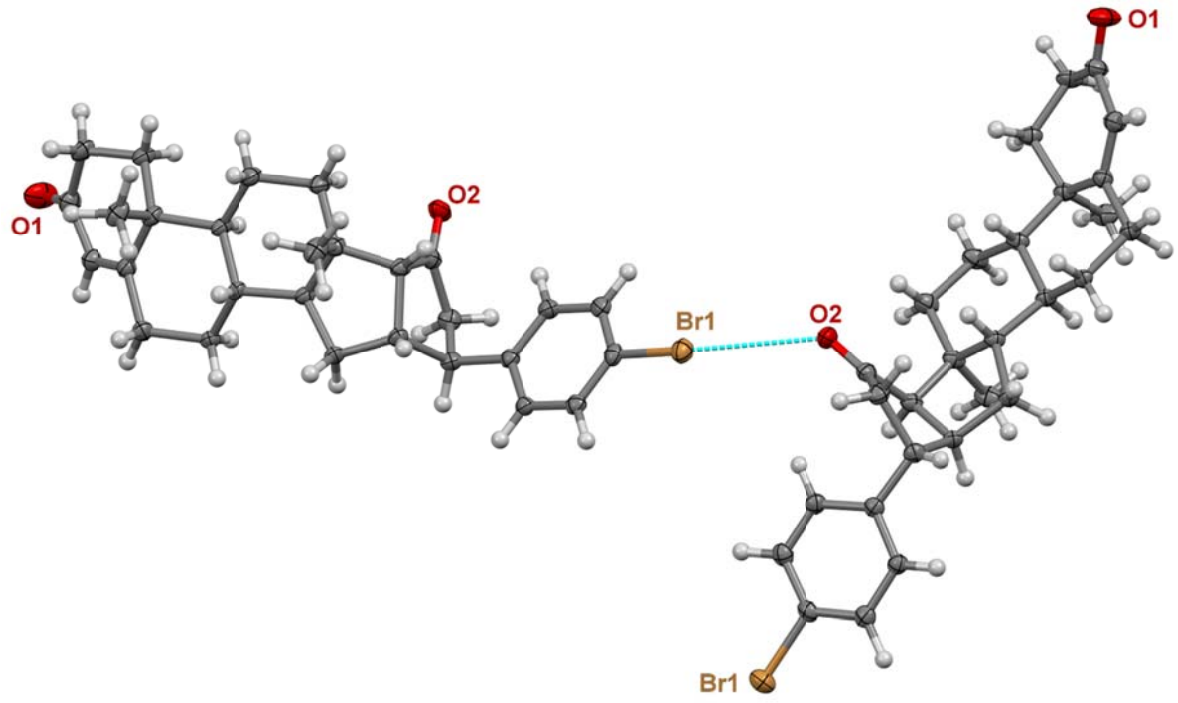
Atoms	Torsion Angle	Atoms	Torsion Angle
C(10)-C(1)-C(2)-C(3)	-55.9(2)	C(12)-C(13)-C(14)-C(15)	168.05(17)
C(1)-C(2)-C(3)-O(1)	-144.3(2)	C(17)-C(13)-C(14)-C(15)	43.89(19)
C(1)-C(2)-C(3)-C(4)	37.0(3)	C(22)-C(13)-C(14)-C(15)	-69.8(2)
O(1)-C(3)-C(4)-C(5)	174.4(2)	C(8)-C(14)-C(15)-C(16)	-157.61(17)
C(2)-C(3)-C(4)-C(5)	-7.0(3)	C(13)-C(14)-C(15)-C(16)	-28.8(2)
C(3)-C(4)-C(5)-C(6)	173.0(2)	C(14)-C(15)-C(16)-C(17)	2.1(2)
C(3)-C(4)-C(5)-C(10)	-5.9(3)	C(14)-C(15)-C(16)-C(20)	-112.97(17)
C(4)-C(5)-C(6)-C(7)	130.1(2)	C(12)-C(13)-C(17)-C(18)	-47.4(2)
C(10)-C(5)-C(6)-C(7)	-50.8(2)	C(14)-C(13)-C(17)-C(18)	70.45(19)
C(5)-C(6)-C(7)-C(8)	51.4(2)	C(22)-C(13)-C(17)-C(18)	-171.86(17)
C(6)-C(7)-C(8)-C(14)	-172.76(15)	C(12)-C(13)-C(17)-C(16)	-160.47(17)
C(6)-C(7)-C(8)-C(9)	-53.1(2)	C(14)-C(13)-C(17)-C(16)	-42.62(19)
C(7)-C(8)-C(9)-C(11)	-175.79(16)	C(22)-C(13)-C(17)-C(16)	75.07(19)
C(14)-C(8)-C(9)-C(11)	-54.2(2)	C(20)-C(16)-C(17)-C(13)	147.00(16)
C(7)-C(8)-C(9)-C(10)	54.9(2)	C(15)-C(16)-C(17)-C(13)	25.3(2)
C(14)-C(8)-C(9)-C(10)	176.49(15)	C(20)-C(16)-C(17)-C(18)	25.95(19)
C(4)-C(5)-C(10)-C(1)	-12.4(3)	C(15)-C(16)-C(17)-C(18)	-95.70(18)
C(6)-C(5)-C(10)-C(1)	168.55(17)	C(13)-C(17)-C(18)-O(2)	62.8(3)
C(4)-C(5)-C(10)-C(21)	106.9(2)	C(16)-C(17)-C(18)-O(2)	176.66(19)
C(6)-C(5)-C(10)-C(21)	-72.1(2)	C(13)-C(17)-C(18)-C(19)	-117.88(18)
C(4)-C(5)-C(10)-C(9)	-131.3(2)	C(16)-C(17)-C(18)-C(19)	-4.0(2)
C(6)-C(5)-C(10)-C(9)	49.7(2)	O(2)-C(18)-C(19)-C(20)	159.5(2)
C(2)-C(1)-C(10)-C(5)	42.9(2)	C(17)-C(18)-C(19)-C(20)	-19.8(2)
C(2)-C(1)-C(10)-C(21)	-75.8(2)	C(18)-C(19)-C(20)-C(23)	-83.45(19)
C(2)-C(1)-C(10)-C(9)	161.85(16)	C(18)-C(19)-C(20)-C(16)	35.1(2)
C(11)-C(9)-C(10)-C(5)	179.39(17)	C(17)-C(16)-C(20)-C(23)	82.81(18)
C(8)-C(9)-C(10)-C(5)	-51.8(2)	C(15)-C(16)-C(20)-C(23)	-162.30(16)
C(11)-C(9)-C(10)-C(1)	59.4(2)	C(17)-C(16)-C(20)-C(19)	-38.2(2)
C(8)-C(9)-C(10)-C(1)	-171.77(15)	C(15)-C(16)-C(20)-C(19)	76.7(2)
C(11)-C(9)-C(10)-C(21)	-61.2(2)	C(19)-C(20)-C(23)-C(28)	-160.11(18)
C(8)-C(9)-C(10)-C(21)	67.6(2)	C(16)-C(20)-C(23)-C(28)	85.9(2)
C(8)-C(9)-C(11)-C(12)	54.2(2)	C(19)-C(20)-C(23)-C(24)	22.7(3)
C(10)-C(9)-C(11)-C(12)	-175.82(17)	C(16)-C(20)-C(23)-C(24)	-91.3(2)

C(9)-C(11)-C(12)-C(13)	-54.3(2)	C(28)-C(23)-C(24)-C(25)	-0.5(3)
C(11)-C(12)-C(13)-C(17)	167.86(17)	C(20)-C(23)-C(24)-C(25)	176.71(18)
C(11)-C(12)-C(13)-C(14)	54.8(2)	C(23)-C(24)-C(25)-C(26)	-0.8(3)
C(11)-C(12)-C(13)-C(22)	-69.0(2)	C(24)-C(25)-C(26)-C(27)	1.5(3)
C(7)-C(8)-C(14)-C(13)	179.33(16)	C(24)-C(25)-C(26)-Br(1)	-178.98(15)
C(9)-C(8)-C(14)-C(13)	58.4(2)	C(25)-C(26)-C(27)-C(28)	-1.0(3)
C(7)-C(8)-C(14)-C(15)	-56.3(2)	Br(1)-C(26)-C(27)-C(28)	179.56(14)
C(9)-C(8)-C(14)-C(15)	-177.22(16)	C(26)-C(27)-C(28)-C(23)	-0.4(3)
C(12)-C(13)-C(14)-C(8)	-59.5(2)	C(24)-C(23)-C(28)-C(27)	1.1(3)
C(17)-C(13)-C(14)-C(8)	176.30(15)	C(20)-C(23)-C(28)-C(27)	-176.25(17)
C(22)-C(13)-C(14)-C(8)	62.6(2)		

S1.4.5. Non-covalent interactions in 3d and 3g.



3d



3g

Fig. S16. The intermolecular C17-Hal···O2=C20 interaction in isostructural crystals of **3d** and **3g** (p=50%). The Cl1···O2 distance is 3.249(2)Å in **3d**, and the Br1···O2 distance is 3.248(2)Å.

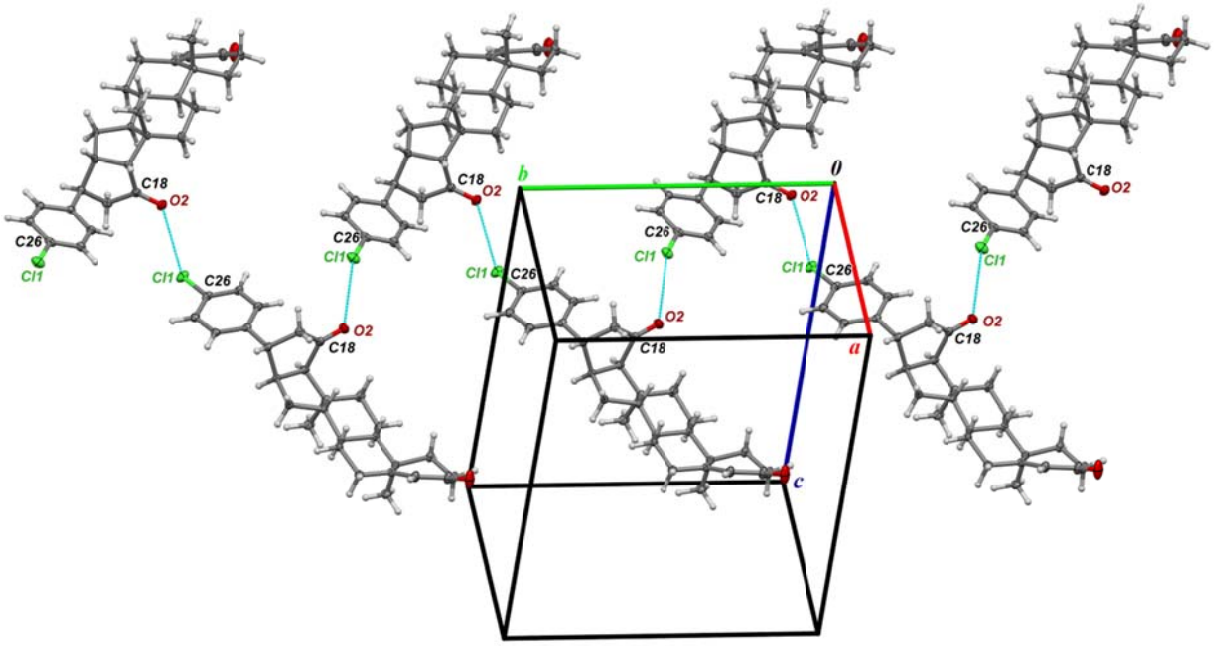


Fig. S17. The intermolecular C17-Hal···O2=C20 interaction in isostructural crystals of **3d** and **3g** (p=50%). The Cl1···O2 distance is 3.249(2)Å in **3d**, and the Br1···O2 distance is 3.248(2)Å.

S2. Geometry optimization and docking studies

The resulting geometries for quantum chemistry calculations and for docking studies are provided in a separate ZIP file for all compounds mentioned in Table 1 of the article. The contents of the ZIP file is following:

- The folder "Opt_XYZ\M16_Gas" contains resulting geometries in the XYZ format for the semi-empirical optimizations in the gas phase with MOPAC2016.
- The folder "Opt_XYZ\M16_Cryst" contains resulting geometries in the XYZ format for the semi-empirical optimizations in the crystalline state with MOPAC2016. The number of molecules in a unit cell (Z) is stated in each file title. The translation vectors are provided in separated XYZ files.
- The folder "Opt_XYZ\G09" contains resulting geometries in the XYZ format for the *ab initio* optimizations in the gas phase with GAUSSIAN09.
- The folder "Docking_pdb" contains resulting geometries in the PDB format for docking simulations for steroid binding against the human androgen receptor, performed with AutoDock Vina. Only geometries with the best ligand binding energies are provided for each ligand.

S2.1. Experimental details on quantum chemistry calculations

S2.1.1. Semi-empirical optimization for the gas phase.

The molecular geometries determined by the X-ray diffraction studies were optimized by semi-empirical quantum chemistry calculations with MOPAC2016[6] in the PM7[7] basis for the gas phase at 298K. For **1g** and **3e** having disordered fragments, atomic coordinates for the major parts of the disorders were only used. The resulting geometries were converted into the XYZ format.

S2.1.2. Semi-empirical optimization for the crystalline state.

The molecular geometries determined by the X-ray diffraction studies were optimized by semi-empirical quantum chemistry calculations with MOPAC2016[6] in the PM7[7] basis for crystals at 298K. The water molecule was removed from **1g**. For **1g** and **3e** having disordered

fragments, atomic coordinates for the major parts of the disorders were only used. The resulting geometries and corresponding translation vectors were converted into the XYZ format.

S2.1.3. *Ab initio* optimization for the gas phase.

The molecular geometries determined by the X-ray diffraction studies were optimized by *ab initio* calculations with GAUSSIAN09[8] using the ωB97XD functional[9] and the 6-31+G(d,p) basis set at the "FineGrid" integral precision level. For **1g** and **3e** having disordered fragments, atomic coordinates for the major parts of the disorders were only used. The resulting geometries were converted into the XYZ format.

S2.2. Docking simulations

S2.2.1. Docking simulations for steroid binding against the human androgen receptor.

Molecular docking simulations were performed with the AutoDock Vina 1.1.2 software.[10] The human androgen receptor ligand-binding domain (hARLBD) was used as a target protein. The initial hARLBD structure was taken from the X-ray crystal structure of its complex with testosterone (TES-hARLBD)[11] (see also PDB code 2AM9; DOI: 10.2210/pdb2AM9/pdb; https://www.rcsb.org/structure/2am9). The so-called flexible docking was applied, in which not only a ligand molecule could change its pose within the ligand-binding pocket (LBP), but also some of the amino acid residues surrounding the LBP could change their conformations to minimize the energy of the complex formation. In the present study, side chains of the following 18 residues forming the LBP were assigned as "flexible" (or, more precisely, rotatable): Leu701, Leu704, Asn705, Leu707, Gln711, Trp741, Met742, Met745, Val746, Met749, Arg752, Phe764, Met780, Met787, Leu873, Phe876, Thr877, Met895. The rest of the residues and the backbone of the protein were considered to be rigid. The resulting geometries were converted into the PDB format.

An example of docking simulation is presented in Fig. S18, using **3d** as a ligand example.

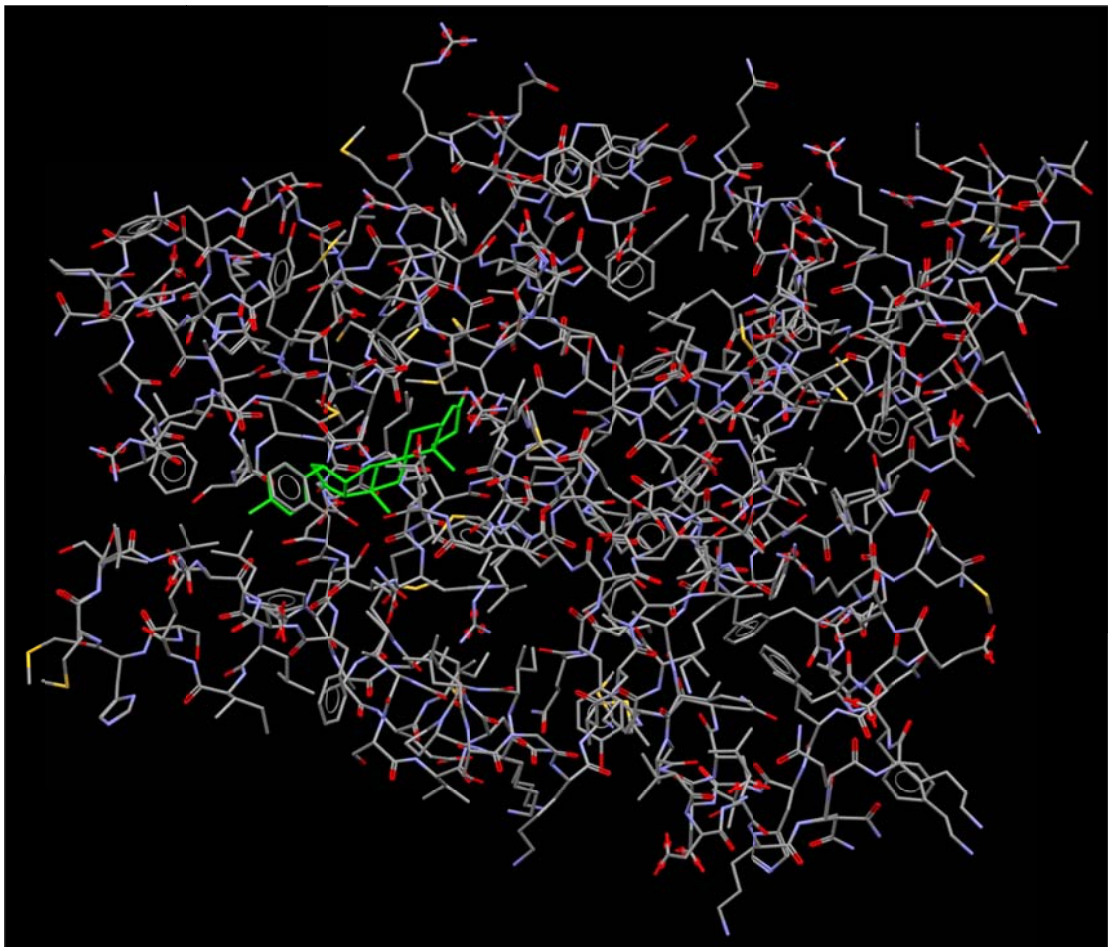


Fig. S18. The resulting geometry for docking **3d** (green) to hARLBD as a representative example.

S3. Experimental Section

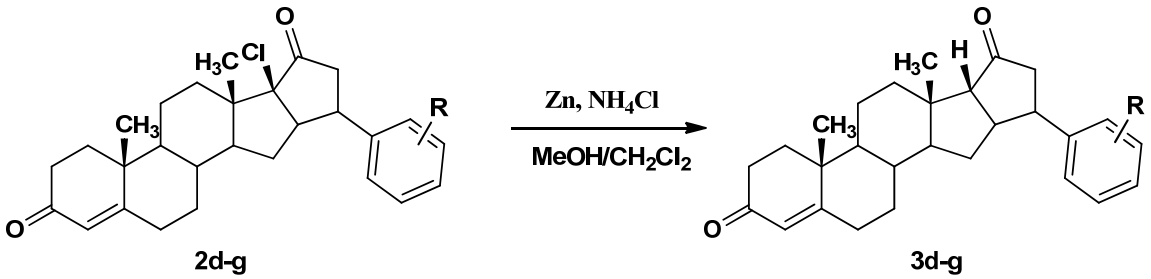
S3.1. Synthesis and crystallization of steroids

S3.1.1. General information.

The NMR spectra were recorded at 293 K in $CDCl_3$ on a Bruker AM-300 spectrometer operating at 300 MHz for ^1H, 75 MHz for ^{13}C. Mass spectra were obtained on a mass spectrometer (70 eV) with direct sample injection into the ion source. High resolution mass spectra were obtained on a Bruker MicroTOF II instrument in positive ion mode using electrospray ionisation (ESI). All chemicals and anhydrous solvents were purchased from commercial sources and used without further purification. Silica column chromatography was performed using silica gel 60 (70−230 mesh); TLC analysis was conducted on silica gel 60 F254 plates. Benzylidines **1a-h**[12] and pentacyclic steroids **2a-h**[13] were prepared according previously published methods. We report herein the synthesis of compounds **3**.

Crystals suitable for the X-ray diffraction method were obtained as follows. Crystals of benzylidines **1b**, **1c** and **1g** were grown from methanol. Crystals of **2** were obtained by slow solvent evaporation from the corresponding solutions in ethyl acetate (**2a**) or in acetonitrile (**2b**, **2c**). Crystals of **2g**, **2h**, **3d**, **3e**, **3f** and **3g** were obtained by a regular hot recrystallization from acetonitrile.

S3.1.2. Synthesis and characterization of pentacyclic steroids 3d-g



Scheme S1. Synthesis **3d-g** from **2d-g**.

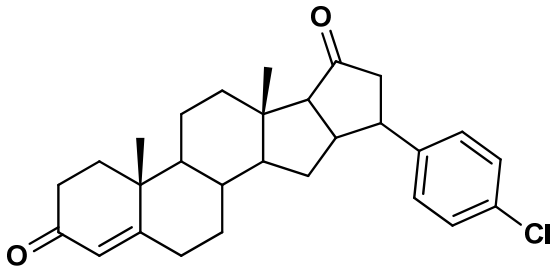
The configuration at atom C17 should retain upon reduction of **2** into **3** (Scheme S1) (see X-ray studies). However in case of formation of **3d** and **3g**, NMR studies points out to a presence of a small amount of the other isomer. A careful analysis of $^{13}C\{^1H\}$ NMR spectra of crude

products (before final recrystallization) suggests that this minor isomer is highly likely a diastereomer with the inverted configuration at C17. Therefore, we may suppose that the reduction proceeds stereoselectively but not stereospecifically. However, this minor isomer was neither detected by X-ray studies, nor isolated in its pure form. The spectral data below are presented for purified single diastereomers of **3d** and of **3g**, presented in the article.

The general method of synthesis.

A steroid **2** (1.0 mmol) was suspended in 20 mL of methanol and then CH_2Cl_2 (2-3 mL) was added dropwise until the substrate was completely dissolved. After obtaining a homogeneous solution, a pre-crushed mixture of zinc dust (4 mmol) and ammonium chloride (3.2 mmol) was added by portions. The reaction mixture was vigorously stirred at room temperature until the complete disappearance of the starting compound (monitored by TLC). After completion of the process, the reaction mixture was filtered and the precipitate was washed with methanol. The filtrate was evaporated; the residue was washed with water and dried. The product **3** was then recrystallized from CH_3CN.

(6aR,8aS)-11-(4-chlorophenyl)-6a,8a-dimethyl-1,2,5,6,6a,6b,7,8,8a,8b,10,11,11a,12,12a,12b-hexadecahydropentaleno[2,1-a]phenanthrene-4,9-dione (3d)

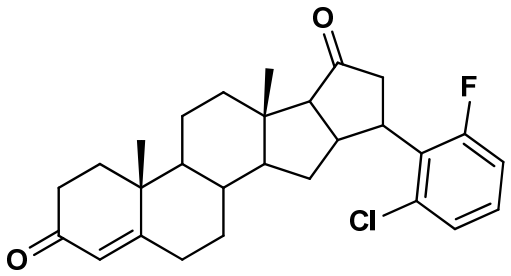


3d

3d was obtained as a light yellow powder; m.p. 175–177°C; Yield 80 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (s, 3H, *H22*), 0.86-0.95 (m, 1H), 0.98-1.16 (m, 2H), 1.13 (s, 3H, *H21*), 1.37-1.90 (m, 9H), 1.91-2.03 (m, 1H), 2.27-2.46 (m, 5H), 2.42 (d, 1H), 2.50-2.61 (m, 1H), 2.79-2.92 (m, 1H, *H16*), 3.03-3.14 (m, 1H, *H20*), 5.68 (s, 1H, *H4*), 7.04 (d, $^3J_{HH}$=8.2, 2H, *H24 and H28*), 7.21 (d, $^3J_{HH}$=8.2, 2H, *H25 and H27*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 17.5, 20.7, 20.8, 32.4, 32.8, 33.8, 34.0, 34.9, 35.8, 36.0, 38.7, 46.4, 47.1, 47.3, 47.5, 53.1, 53.6, 61.5, 124.1,

128.1, 129.0, 132.4, 144.1, 170.7, 199.5, 218.9. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{33}ClO_2$: 437.2248; Found: 437.2242. See Fig. S19, S24 and S25.

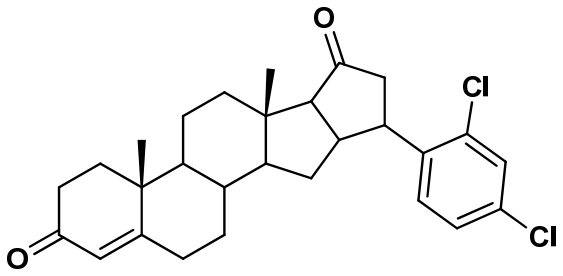
(6aR,8aS)-11-(2-chloro-6-fluorophenyl)-6a,8a-dimethyl-1,2,5,6,6a,6b,7,8,8a,8b,10,11,11a, 12,12a,12b-hexadecahydropentaleno[2,1-a]phenanthrene-4,9-dione (3e)



3e

3e was obtained as a light yellow powder; mp 165–167°C; Yield 74%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (s, 3H, *H22*), 0.90-1.02 (m, 1H), 1.07-1.22 (m, 2H), 1.18 (s, 3H, *H21*), 1.36-1.83 (m, 8H), 1.84-2.08 (m, 3H), 2.24-2.47 (m, 4H), 2.51-2.65 (m, 2H), 2.93-3.06 (m, 1H, *H20*), 3.62-3.76 (m, 1H, *H16*), 5.74 (s, 1H, *H4*), 6.91-7.05 (m, 1H, *H26*), 7.08-7.21 (m, 2H, *H25 and H27*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 17.5, 20.9, 21.3, 32.5, 32.9, 34.0, 34.4, 35.5, 35.8 (d, $^3J_{CF}$=3.9 Hz), 38.8, 41.5, 45.4 (d, $^4J_{CF}$=4.0 Hz), 45.7 (d, $^4J_{CF}$=1.3 Hz), 45.9, 52.9, 53.6, 62.9, 115.1 (d, $^2J_{CF}$=23.3 Hz), 124.1, 125.8 (d, $^4J_{CF}$=3.2 Hz), 128.3 (d, $^3J_{CF}$=10.1 Hz), 131.0 (d, $^2J_{CF}$=16.0 Hz), 134.5 (d, $^3J_{CF}$=7.5 Hz), 161.7 (d, $^1J_{CF}$=247.6 Hz), 171.1, 199.7, 218.9. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{32}ClFO_2$: 455.2139; Found: 455.2148. See Fig. S20, S26-S28.

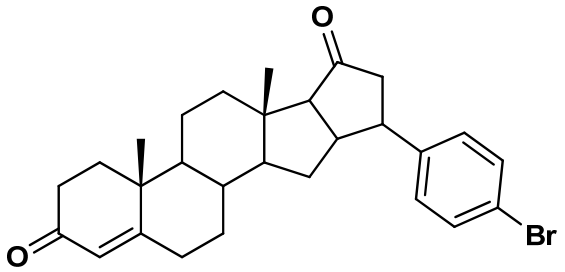
(6aR,8aS)-11-(2,4-dichlorophenyl)-6a,8a-dimethyl-1,2,5,6,6a,6b,7,8,8a,8b,10,11,11a, 12,12a,12b-hexadecahydropentaleno[2,1-a]phenanthrene-4,9-dione (3f)



3f

3f was obtained as a light yellow powder; mp 183–185°C; Yield 91 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 3H, *H22*), 0.83-0.99 (m, 1H), 1.06-1.26 (m,2H), 1.17 (s, 3H, *H21*), 1.40-1.75 (m, 6H), 1.82-1.93 (m, 3H), 1.97-2.06 (m, 1H), 2.23-2.52 (m, 6H), 2.59-2.72 (m, 1H), 2.84-2.97. (m, 1H, *H20*), 3.57-3.69 (m, 1H, *H16*), 5.73 (s, 1H, *H4*), 6.98 (d , $^{4}J_{HH}$ =8.4 Hz ,1H), 7.17 (dd, $^{3}J_{HH}$=8.4 Hz, $^{4}J_{HH}$=2.0 Hz, 1H), 7.40 (d, $^{3}J_{HH}$=2.0 Hz ,1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 17.5, 20.7, 32.4, 32.8, 33.7, 34.0, 35.2, 35.8, 36.2, 38.7, 43.4, 46.3, 46.7, 53.5, 53.6, 61.4, 124.1, 127.5, 129.8, 132.9, 134.5, 141.5, 170.7, 199.5, 219.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{32}Cl_2O_2$: 471.1857; Found: 471.1852. See Fig. S21, S22, S29 and S30.

(6aR,8aS)-11-(4-bromophenyl)-6a,8a-dimethyl-1,2,5,6,6a,6b,7,8,8a,8b,10,11,11a,12,12a,12b-hexadecahydropentaleno[2,1-a]phenanthrene-4,9-dione (3g)



3g

3g was obtained as a white powder; mp 215–217°C; Yield 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 3H, *H22*), 0.85-1.01 (m, 1H), 1.05-1.20 (m, 2H), 1.17 (s, 3H, *H21*), 1.35-1.95 (m, 9H), 1.95-2.08 (m, 1H), 2.23-2.53 (m, 6H), 2.55-2.69 (m, 1H), 2.82-2.94 (m, 1H, *H16*), 3.07-3.17 (m, 1H, *H20*), 5.76 (s, 1H, *H4*), 7.03 (d, $^{3}J_{HH}$=8.2, 2H, *H24 and H28*), 7.41 (d, $^{3}J_{HH}$=8.2, 2H, *H25 and H27*). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 17.5, 20.7, 20.8, 32.4, 32.9, 33.8, 34.0, 34.9, 35.7, 36.0, 38.8, 46.4, 47.1, 47.3, 47.4, 53.1, 53.6, 61.5, 120.4, 124.1, 128.5, 131.9, 144.6, 171.9, 200.4, 218.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{33}BrO_2$ 481.1719; Found: 481.1737. See Fig. S23, S31 and S32.

S3.1.3. HRMS spectra of 3d-g

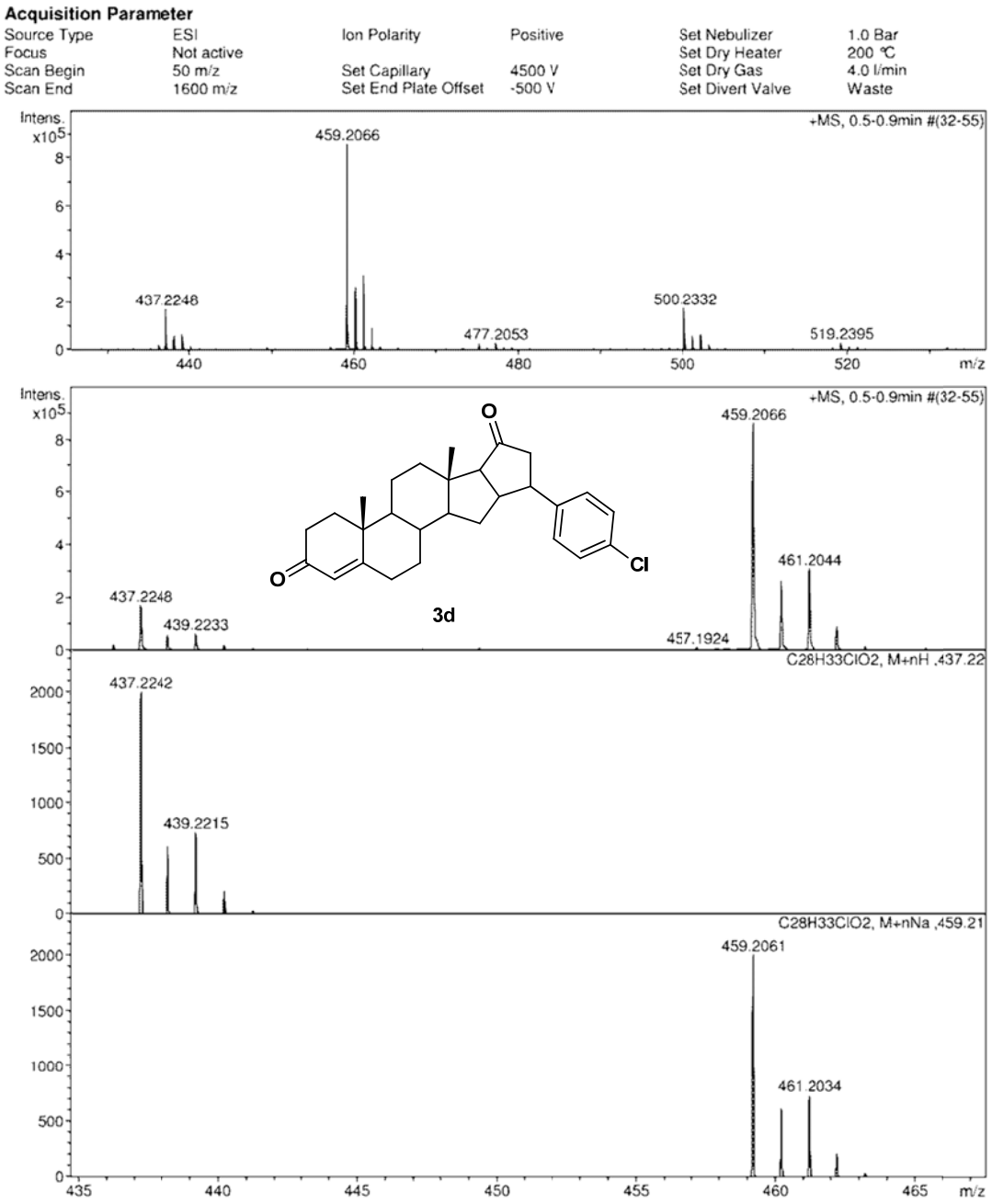


Fig. S19. The HRMS spectrum of **3d**.

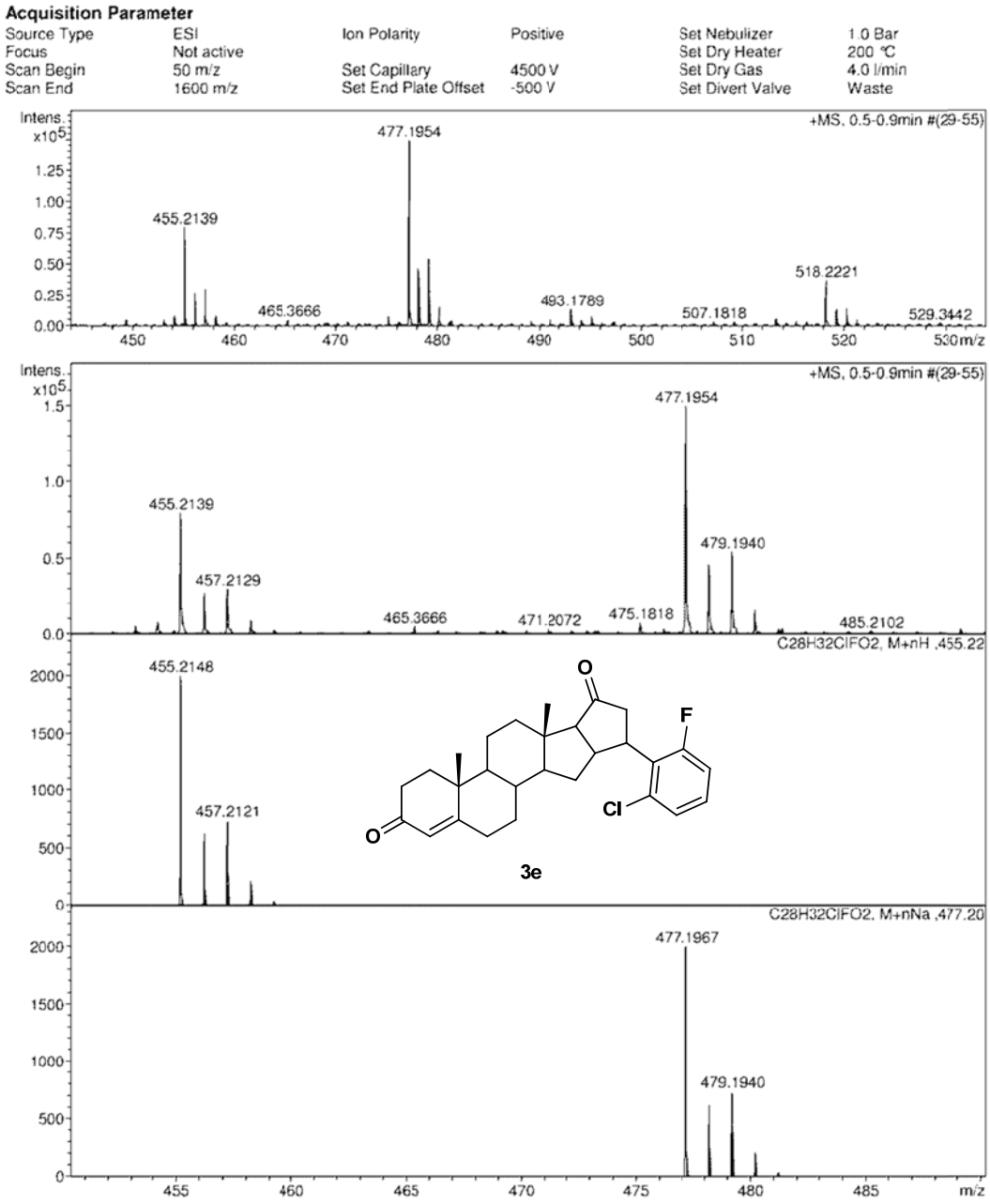


Fig. S20. The HRMS spectrum of **3e**.

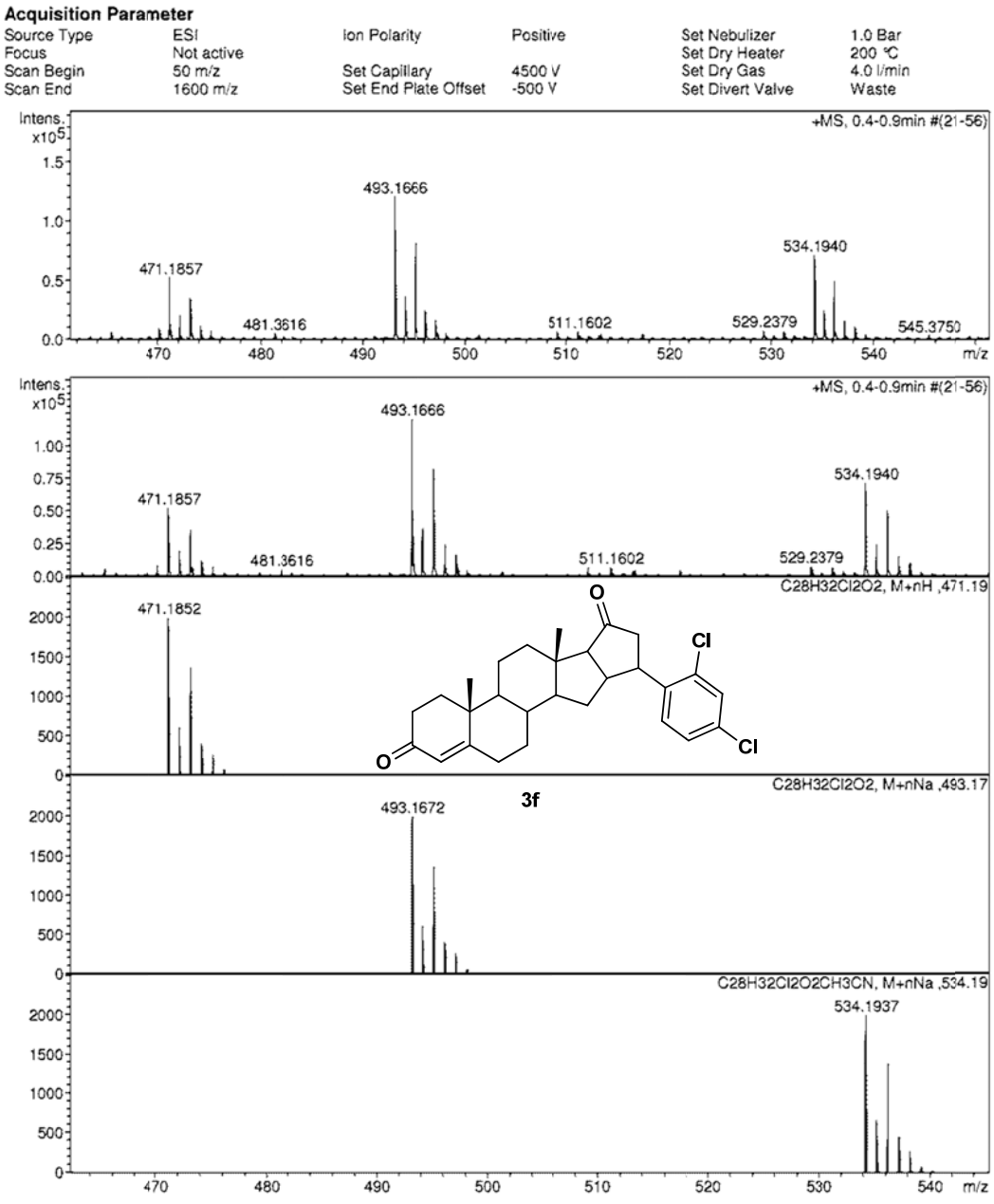


Fig. S21. The full HRMS spectrum of **3f**.

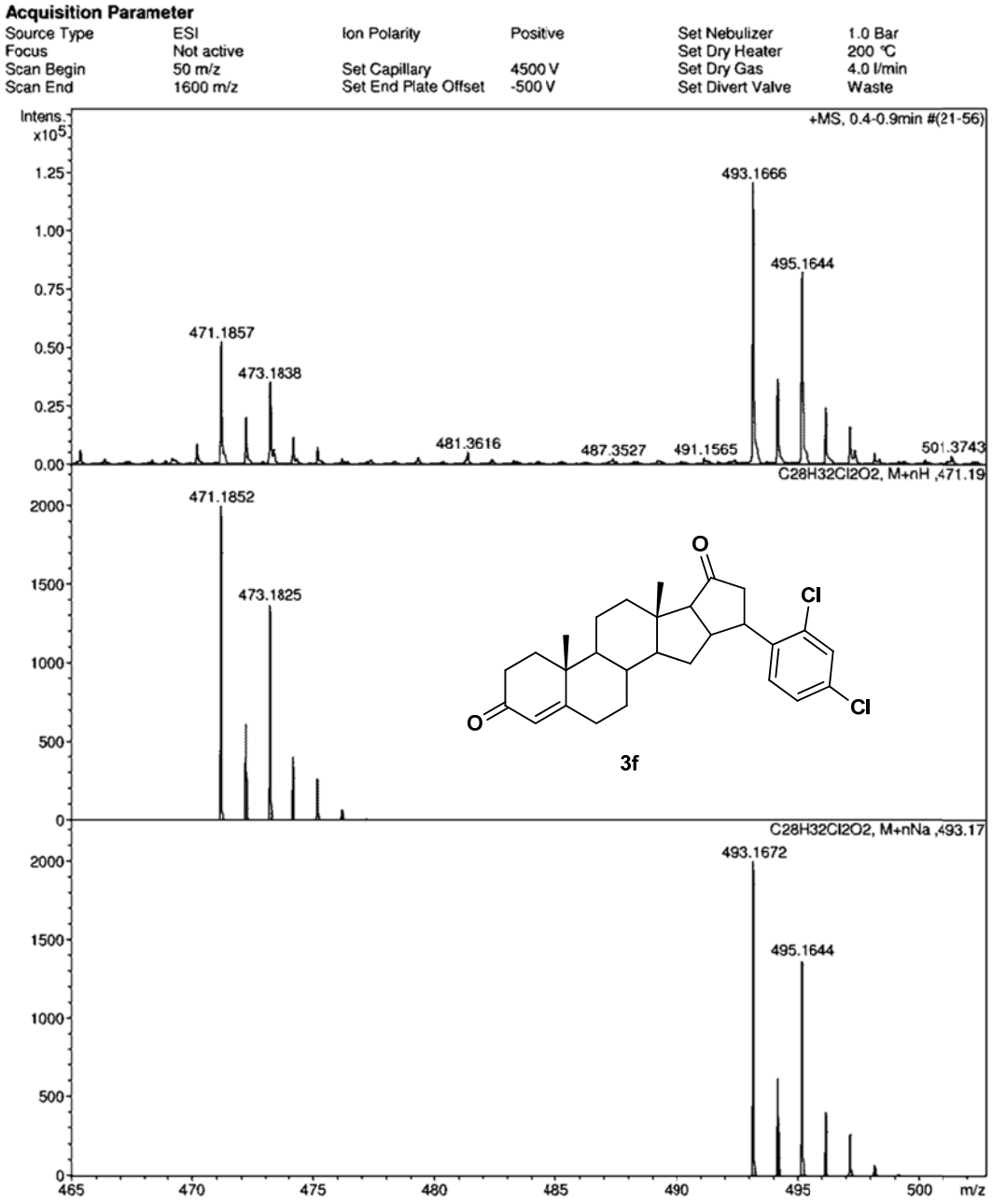


Fig. S22. The enlarged region (0-500 m/z) of HRMS spectrum of **3f**.

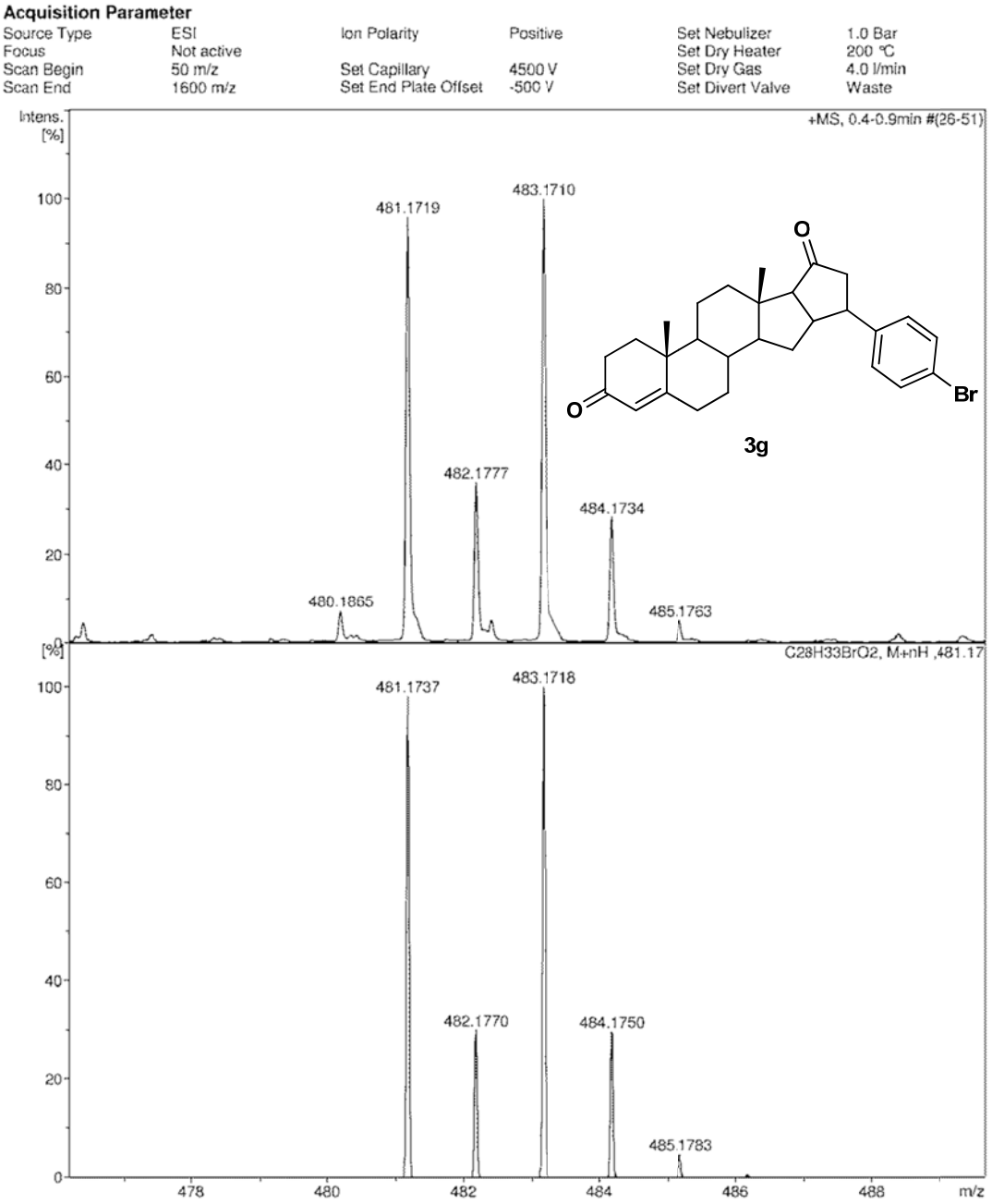


Fig. S23. The HRMS spectrum of **3g**.

S3.1.4. NMR spectra of 3d-g

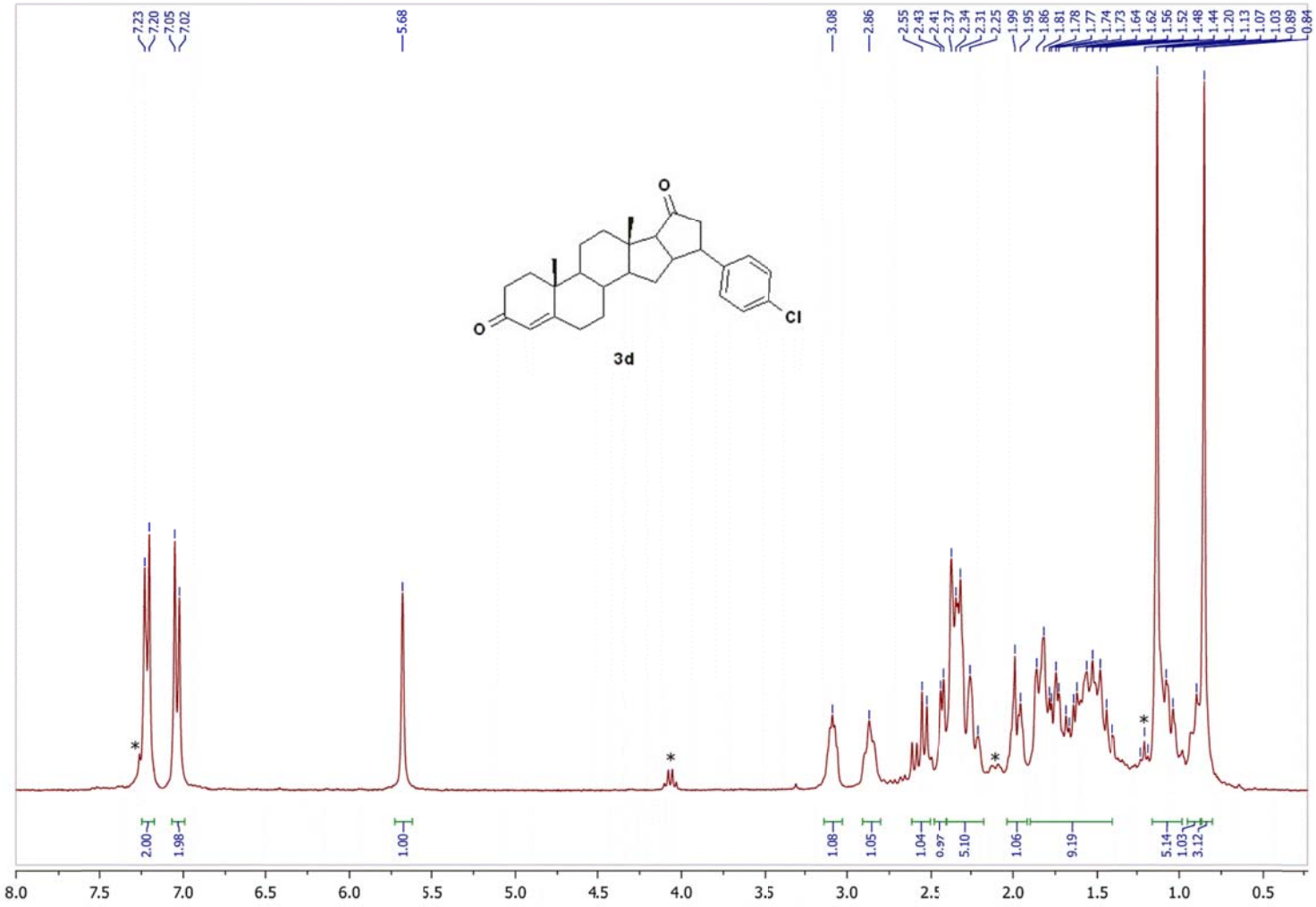


Fig. S24. The ^{1}H NMR spectrum of **3d**.

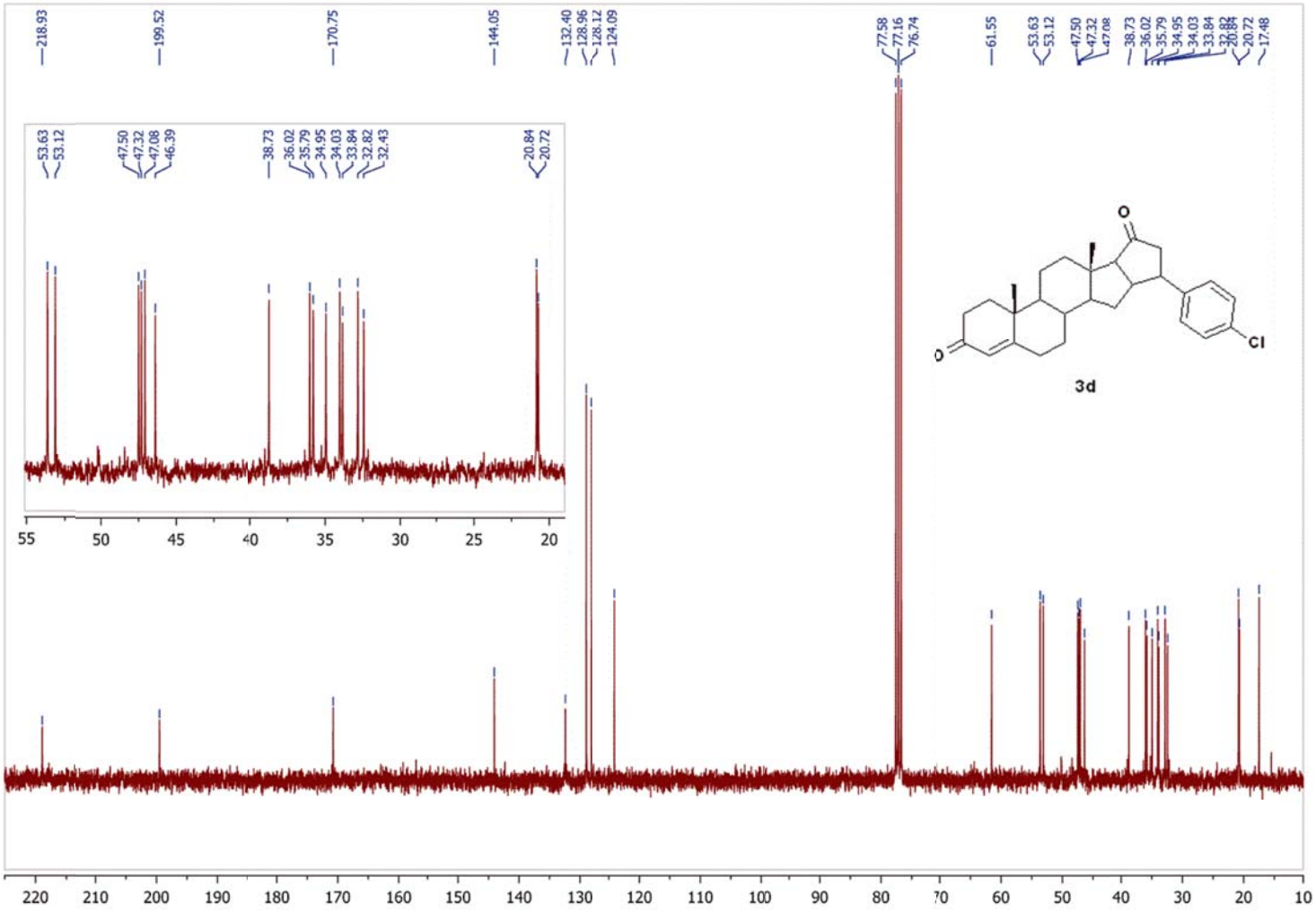


Fig. S25. The $^{13}C\{^{1}H\}$NMR spectrum of **3d**.

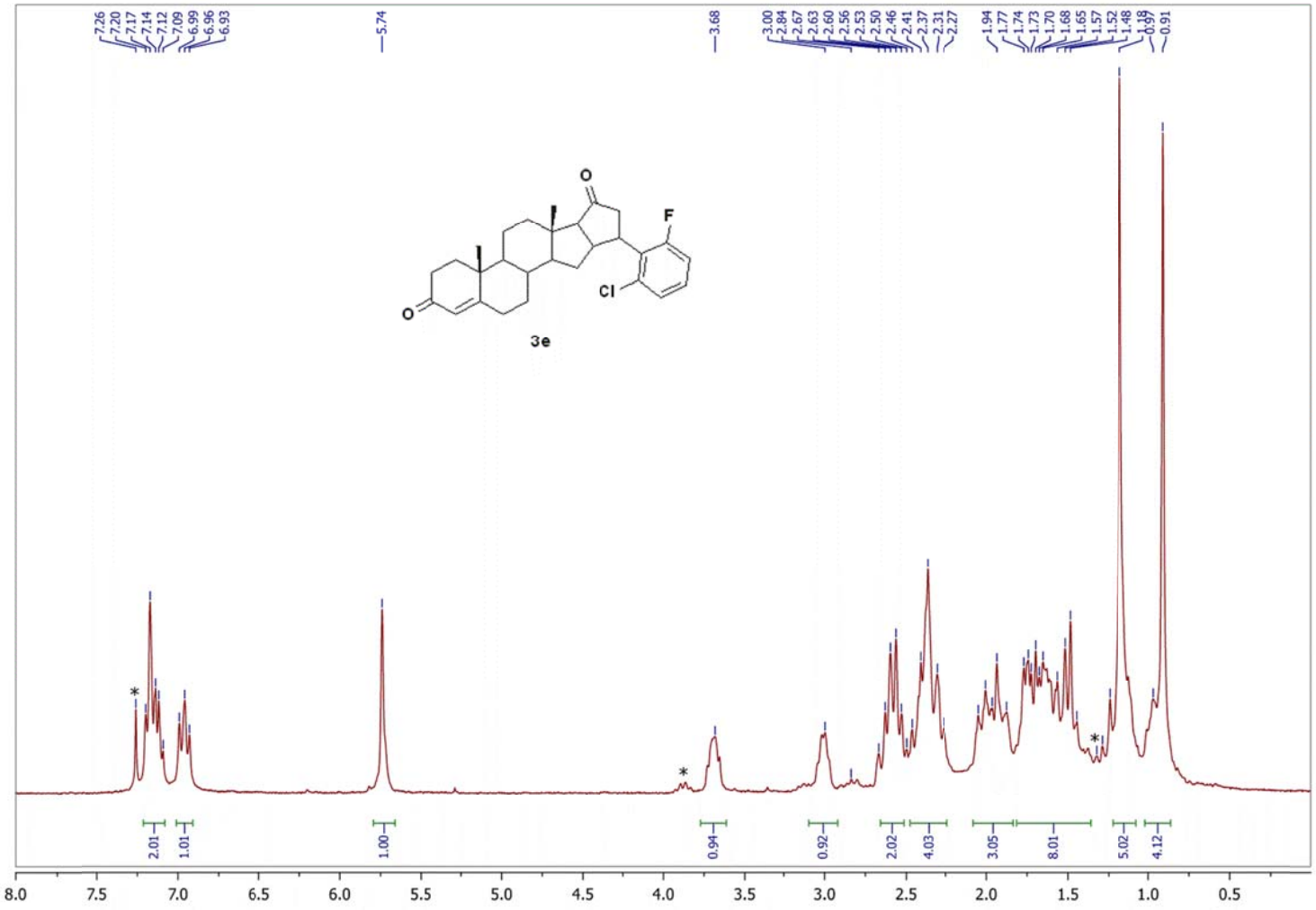


Fig. S26. The ^{1}H NMR spectrum of **3e**.

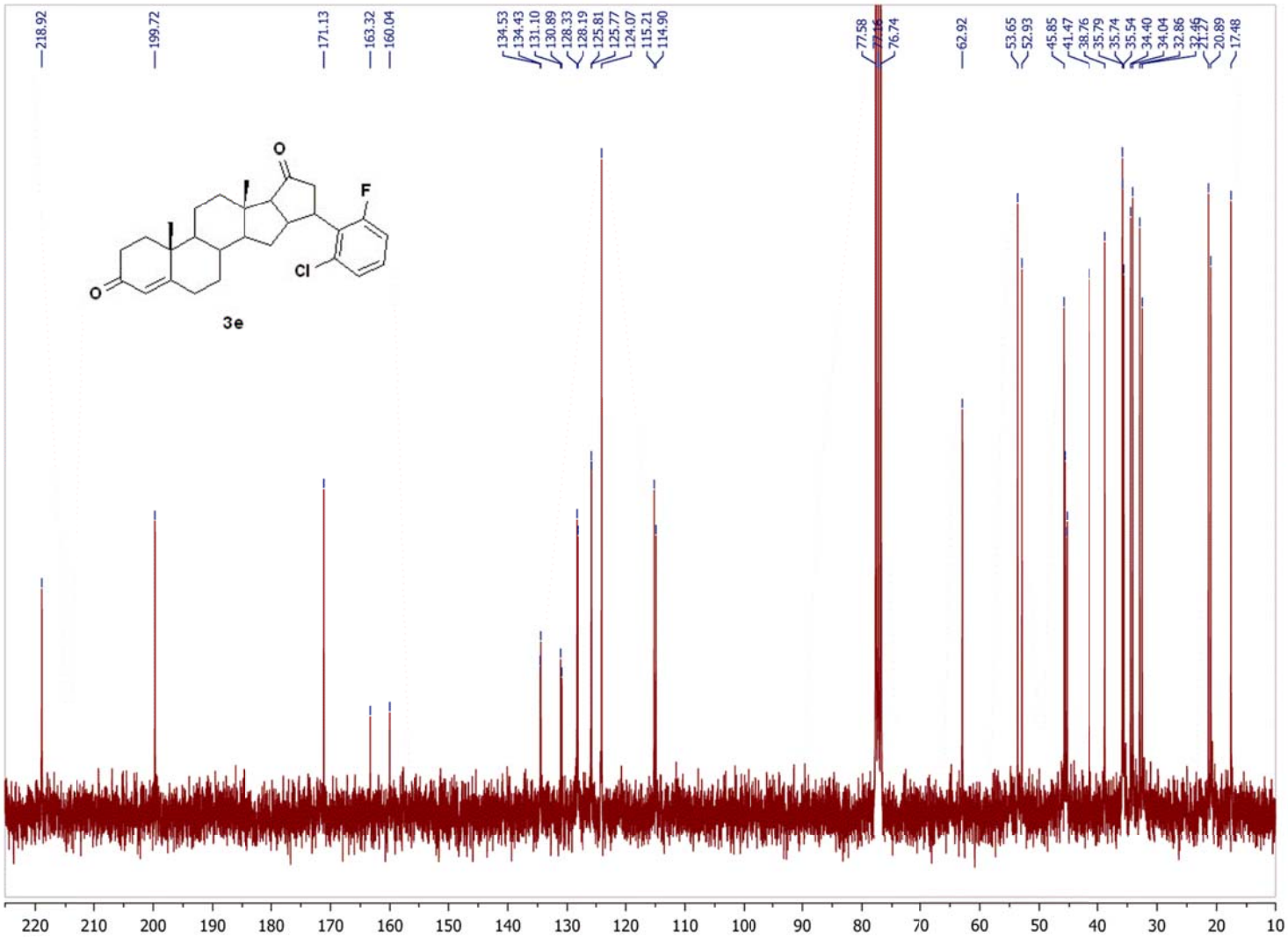


Fig. S27. The $^{13}C\{^{1}H\}$NMR spectrum of **3e**.

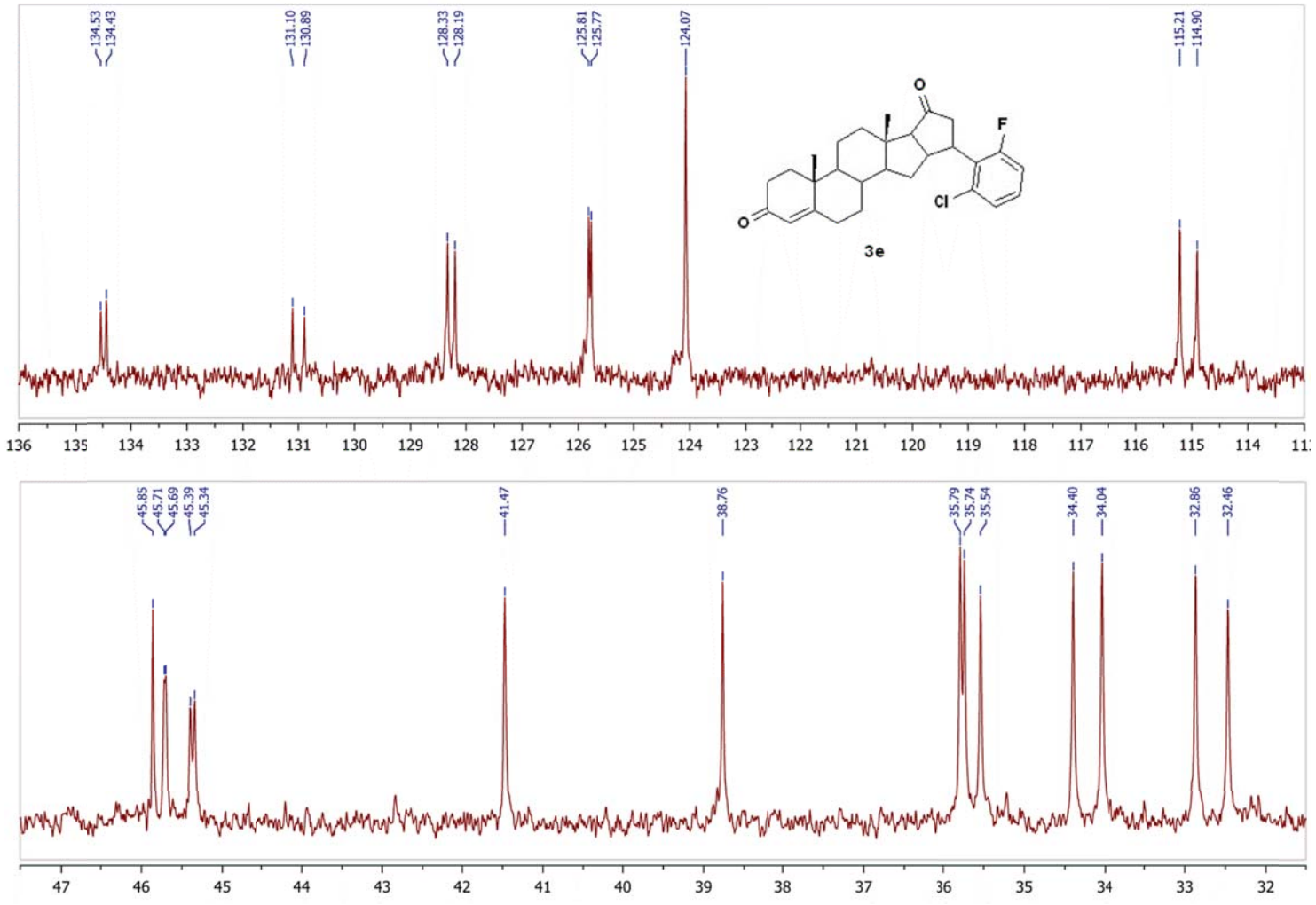


Fig. S28. The enlarged regions (23-47 and 114-135 ppm) for the $^{13}C\{^{1}H\}$NMR spectrum of **3e**.

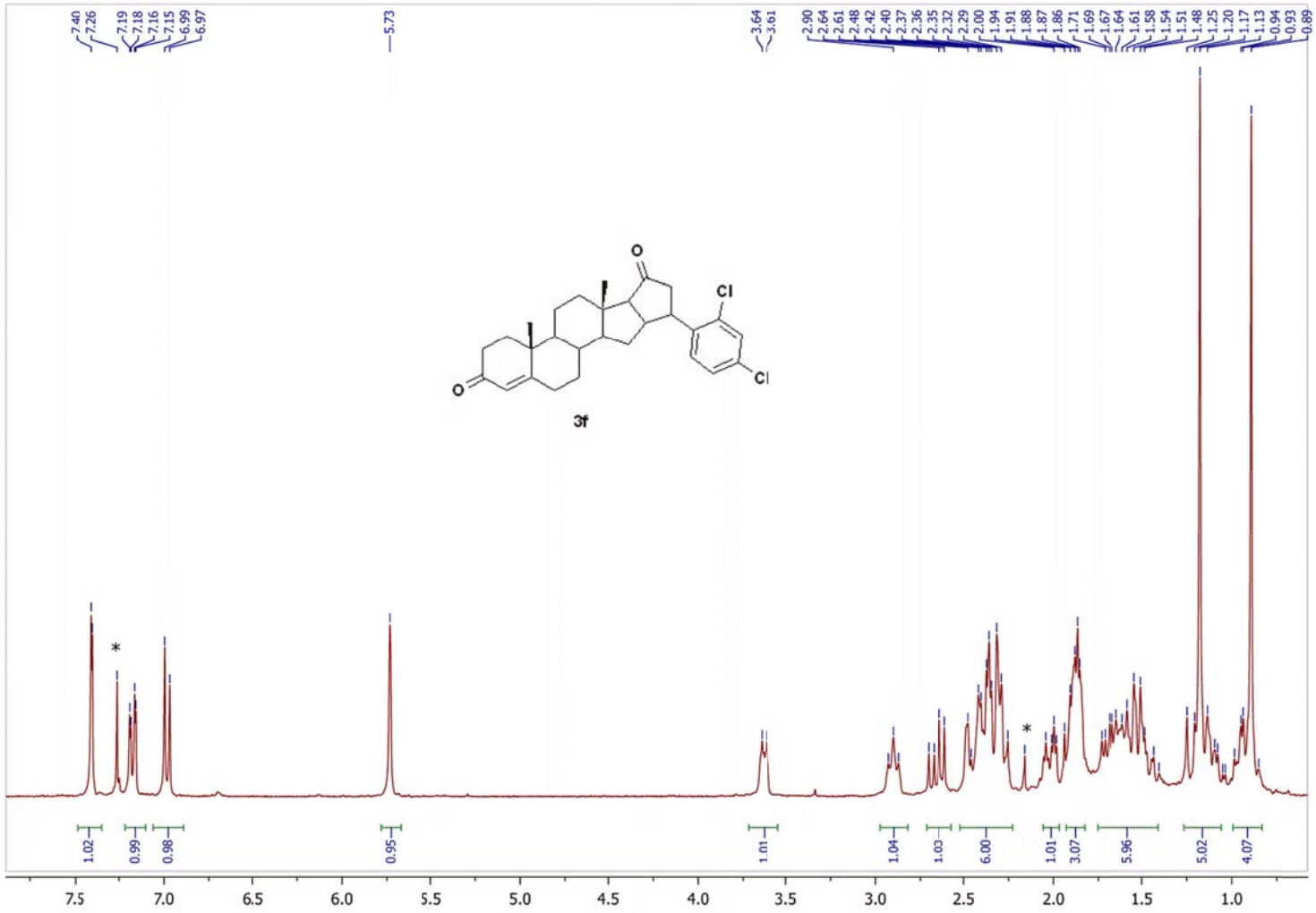


Fig. S29. The ^{1}H NMR spectrum of **3f**.

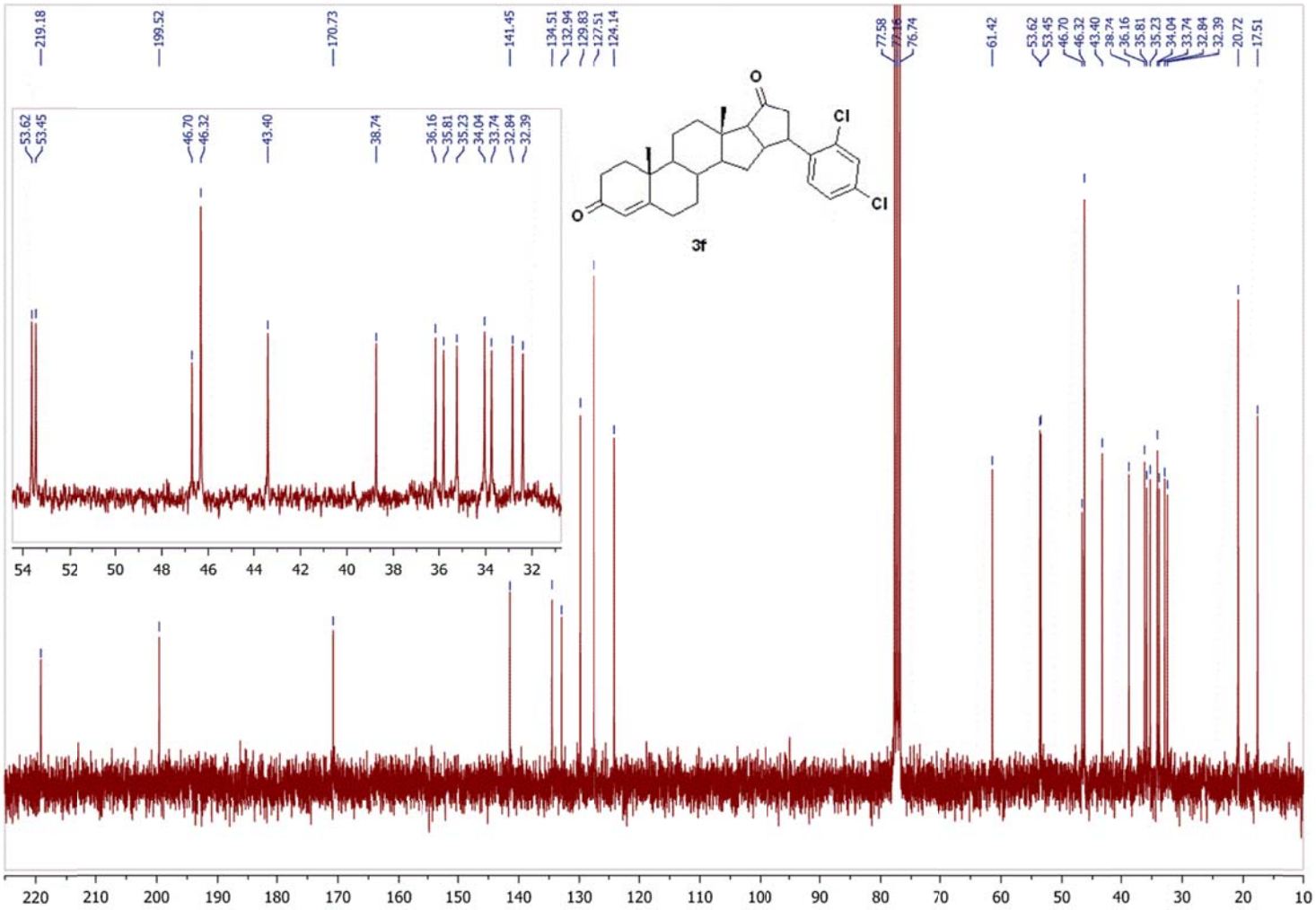


Fig. S30. The $^{13}C\{^{1}H\}$NMR spectrum of **3f**.

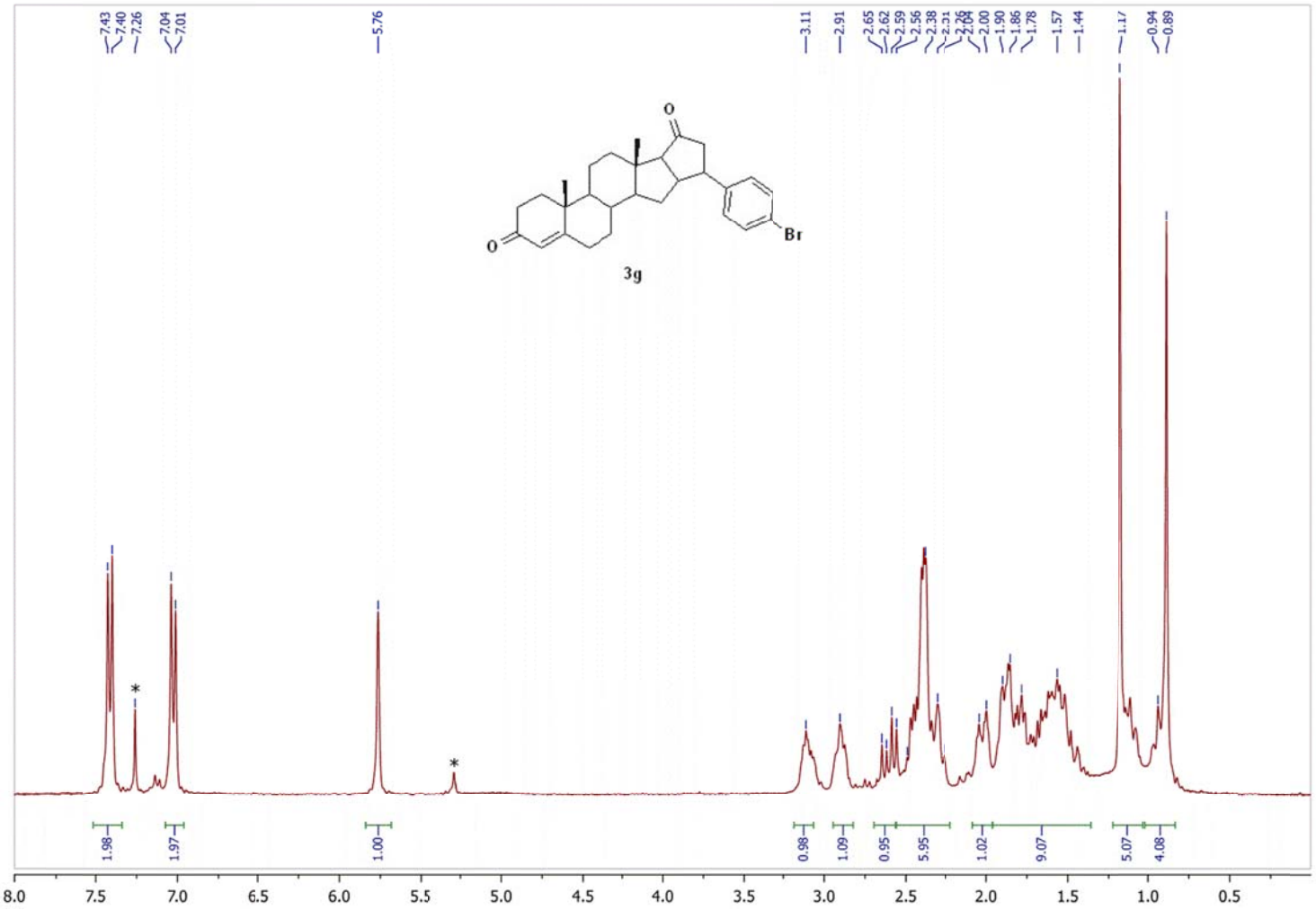


Fig. S31. The ^{1}H NMR spectrum of **3g**.

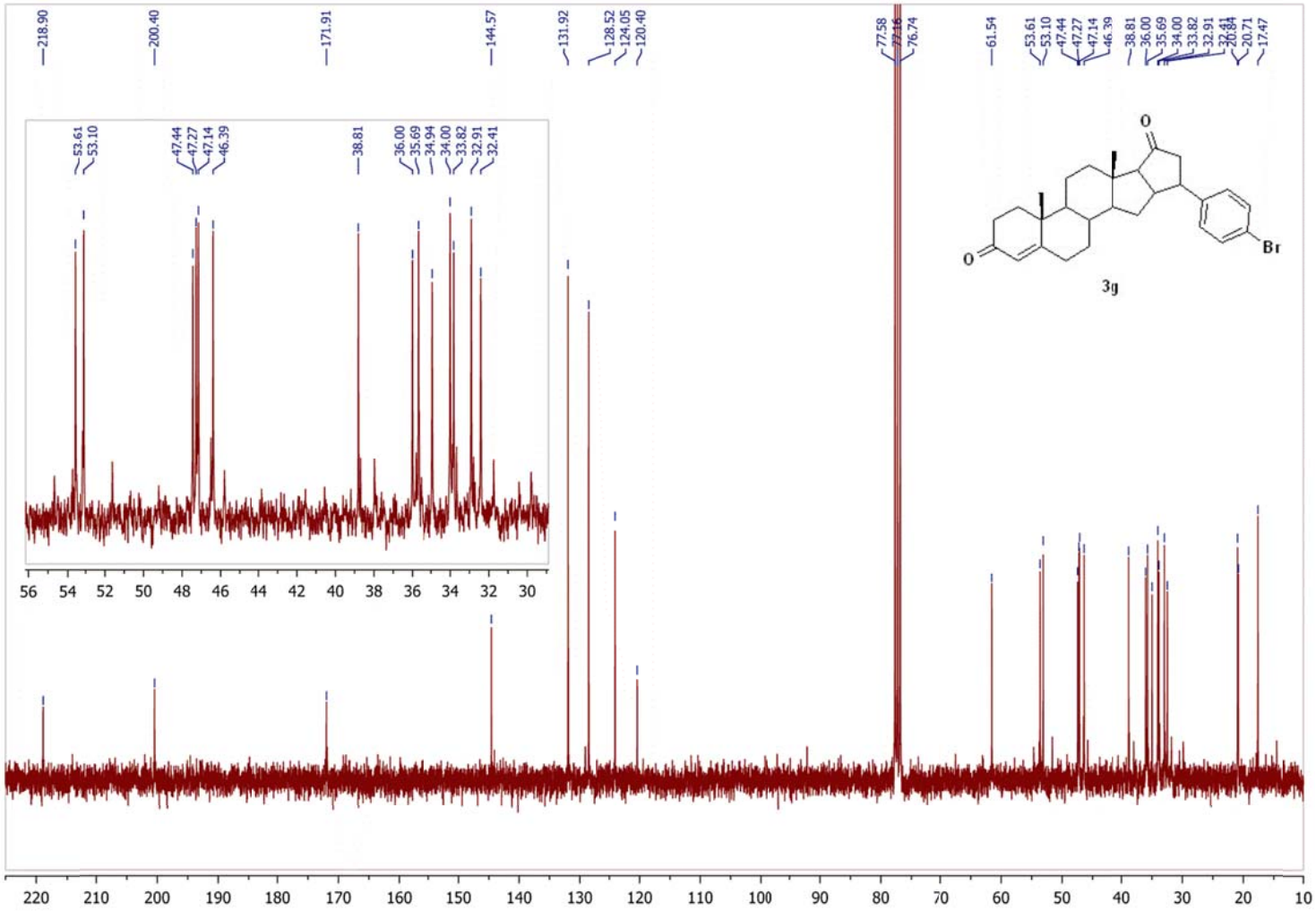


Fig. S32. The $^{13}C\{^{1}H\}$NMR spectrum of **3g**.

S3.2. Biological studies

S3.2.1. Cell line and evaluation of antiproliferative activity

The human prostate cancer cell line 22Rv1 (CRL-2505) was purchased from the ATCC collection. 22Rv1 cells bearing AR and ARV7 were cultured in standard RPMI-1640 medium (Gibco) supplemented with 10% fetal bovine serum (FBS, HyClone), RPMI-1640 Vitamins (PanEco) and 0.1 mg/mL sodium pyruvate (Santa Cruz) at 37 °C, 5% CO_2 and 80–85% humidity (NuAir CO_2 incubator). The cell growth was evaluated by the modified MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide) (Applichem) test[14] as described earlier.[15] 22Rv1 prostate cancer cells were seeded at a density of 10^5 cells per well in 24-well plates (TPP) in 900 μL of the medium. Antiandrogen bicalutamide (N-4-Cyano-3-(trifluoromethyl)phenyl-3-(4-fluorophenyl)sulfonyl-2-hydroxy-2-methylpropanamide) was used as a reference drug. The D-annulated carbocyclic steroids and bicalutamide were dissolved in DMSO (AppliChem) to 5 mM before experiments, and then the resulting solutions were diluted in the medium to the required concentrations. The solutions of the tested compounds and bicalutamide with different concentrations in 100 μL of the medium were added 24 h after the seeding, and the cells were grown for 72 h. After incubation with the compounds, the medium was removed, and the MTT reagent dissolved in the medium was added to the final concentration of 0.2 mg/mL to each well and incubated for 2 h. The cell supernatants were removed and the MTT formazan purple crystals were dissolved in DMSO (350 μL per well). Then the plates were gently shaken and the absorbance was measured at 571 nm with a MultiScan reader (ThermoFisher). The viability of the cells was assessed after subtraction of the blank value (the absorbance in the well w/o cells) from all wells. Dose-response curves were analyzed by regression analysis using sigmoidal curves (Log(concentration) *vs* normalized absorbance). The half-maximal inhibitory concentrations (IC_{50}) were determined with GraphPad Prism.

S3.2.2. AR activity

22Rv1 human prostate cancer cells were transfected with the ARE-LUC plasmid containing the luciferase reporter gene under the AR-dependent promoters, and co-transfected with β-galactosidase plasmid. Cell transfection for reporter gene products was carried out as

described earlier.[16] Briefly, 22Rv1 cells were plated (5.5×10^5 cells/well) onto a 24-well plate containing a standard cell culture medium. After 24-h incubation, cells were co-transfected with plasmids containing luciferase and β-galactosidase genes. Phenol-free RPMI-1640 medium supplemented with steroid-free serum (HyClone) was used for the ARE-LUC assay. The plasmids used in this work were kindly provided by Prof. P.Hartig.[17] The transfection was carried out for 6 h at 37°C using Lipofectamine 2000 in a medium supplemented with 2% steroid-free serum. Following transfection, a medium supplemented with 10 % steroid-free serum was added and cells were treated with synthesized compounds, bicalutamide or vehicle control. To induce AR transcriptional activity 22Rv1 cells were treated with 10 nM DHT.

The luciferase activity was measured according to a standard protocol (Promega) using a Tecan Infinite M200 Pro, β-galactosidase activity was analyzed by standard colourimetric assay using MultiScan FC as described in the reference.[18] The luciferase/β-galactosidase activities were normalized by the internal control values and represented as the mean ± SD for the three independent experiments. AR activity was calculated in arbitrary units as the ratio of luciferase/galactosidase activity.

S3.2.3. Immunoblotting

Immunoblotting with modifications was held as described earlier.[19] Expression levels of AR, ARV7, NKX3.1, PSA were determined using Cell Signalling Technology (CST) antibodies. Antibodies to α-tubulin (CST) were applied to normalize and to control the loading of samples into a gel. The detection was performed using secondary antibodies to rabbit Ig conjugated with horseradish peroxidase (Jackson ImmunoResearch) and ImageQuant LAS 4000 imager (GE Healthcare), as described in the Mruk's protocol.[20]

S4. References

1. *Bruker AXS Inc.*, Bruker.APEX-III, Madison, Wisconsin, USA, 2019.

2. L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D. Stalke, Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.* 2015, **48**, 3-10. http://dx.doi.org/10.1107/S1600576714022985

3. G.M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* 2015, **A71**, 3-8. http://dx.doi.org/10.1107/S2053273314026370

4. G.M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Cryst.* 2015, **C71**, 3-8. http://dx.doi.org/10.1107/S2053229614024218

5. S. Parsons, H.D. Flack, T. Wagner, Use of intensity quotients and differences in absolute structure refinement. *Acta Cryst.* 2013, **B69**, 249-259. http://dx.doi.org/10.1107/S2052519213010014

6. *MOPAC2016*, J.J.P. Stewart, , Stewart Computational Chemistry, Colorado Springs, CO, USA, 2016. http://OpenMOPAC.net

7. J.J.P. Stewart, Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters. *J. Mol. Model.* 2013, **19**, 1-32. http://dx.doi.org/10.1007/s00894-012-1667-x

8. *Gaussian 09, Revision D.01*, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

9. J.-D. Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* 2008, **10**, 6615-6620. http://dx.doi.org/10.1039/b810189b

10. O. Trott, A.J. Olson, AutoDock Vina: Improving the speed and accuracy of docking with a new scoring function, efficient optimization, and multithreading. *J. Comput. Chem.* 2010, **31**, 455-461. http://dx.doi.org/10.1002/jcc.21334

11. K.P. de Jésus-Tran, P.L. Côté, L. Cantin, J. Blanchet, F. Labrie, R. Breton, Comparison of crystal structures of human androgen receptor ligand-binding domain complexed with various agonists reveals molecular determinants responsible for binding affinity. *Protein Sci.* 2006, **15**, 987-999. http://dx.doi.org/10.1110/ps.051905906

12. A.M. Scherbakov, I.V. Zavarzin, S.K. Vorontsova, A. Hajra, O.E. Andreeva, A.V. Yadykov, I.S. Levina, Y.A. Volkova, V.Z. Shirinian, Synthesis and evaluation of the antiproliferative activity of benzylidenes of 16-dehydroprogesterone series. *Steroids* 2018, **138**, 91-101. http://dx.doi.org/10.1016/j.steroids.2018.06.013

13. S.K. Vorontsova, A.V. Yadykov, A.M. Scherbakov, M.E. Minyaev, I.V. Zavarzin, E.I. Mikhaevich, Y.A. Volkova, V.Z. Shirinian, Novel *D*-Annulated Pentacyclic Steroids: Regioselective Synthesis and Biological Evaluation in Breast Cancer Cells. *Molecules* 2020, **25**, Article No 3499. http://dx.doi.org/10.3390/molecules25153499

14. M. Iselt, W. Holtei, P. Hilgard, The tetrazolium dye assay for rapid *in vitro* assessment of cytotoxicity. *Arzneimittelforschung* 1989, **39**, 747-749.

15. Y.A. Volkova, Y.S. Antonov, A.V. Komkov, A.M. Scherbakov, A.S. Shashkov, L.G. Menchikov, E.I. Chernoburova, I.V. Zavarzin, Access to steroidal pyridazines *via* modified thiohydrazides. *RSC Advances* 2016, **6**, 42863-42868. http://dx.doi.org/10.1039/C6RA06881B

16. A.M. Scherbakov, L.B. Stefanova, D.V. Sorokin, S.E. Semina, L.M. Berstein, M.A. Krasil'nikov, Snail/beta-catenin signaling protects breast cancer cells from hypoxia attack. *Experim. Cell Res.* 2013, **319**, 3150-3159. http://dx.doi.org/10.1016/j.yexcr.2013.08.019

17. P.C. Hartig, K.L. Bobseine, B.H. Britt, M.C. Cardon, C.R. Lambright, V.S. Wilson, L.E. Gray, Jr., Development of two androgen receptor assays using adenoviral transduction of MMTV-luc reporter and/or hAR for endocrine screening. *Toxicol. Sci.: an Official Journal of the Society of Toxicology* 2002, **66**, 82-90.

18. A.M. Scherbakov, A.V. Komkov, A.S. Komendantova, M.A. Yastrebova, O.E. Andreeva, V.Z. Shirinian, A. Hajra, I.V. Zavarzin, Y.A. Volkova, Steroidal Pyrimidines and

Dihydrotriazines as Novel Classes of Anticancer Agents against Hormone-Dependent Breast Cancer Cells. *Front. Pharmacol.* 2017, **8**, Article No 979. http://dx.doi.org/10.3389/fphar.2017.00979

19. A.M. Scherbakov, V.N. Zhabinskii, V.A. Khripach, D.S. Shcherbinin, A.R. Mekhtiev, Y.Y. Shchegolev, A.P. Savochka, O.E. Andreeva, Biological Evaluation of a New Brassinosteroid: AntiproliferativeEffects and Targeting Estrogen Receptor α Pathways. *Chem. Biodiversity* 2019, **16**, Article No e1900332. http://dx.doi.org/10.1002/cbdv.201900332

20. D.D. Mruk, C.Y. Cheng, Enhanced chemiluminescence (ECL) for routine immunoblotting. An inexpensive alternative to commercially available kits. *Spermatogenesis* 2011, **1**, 121-122. http://dx.doi.org/10.4161/spmg.1.2.16606 PMCID: 3271654