Supporting Information

Attractive Halogen•••Halogen Interactions in Crystal Structure of Trans-Dibromogold(III) Complex

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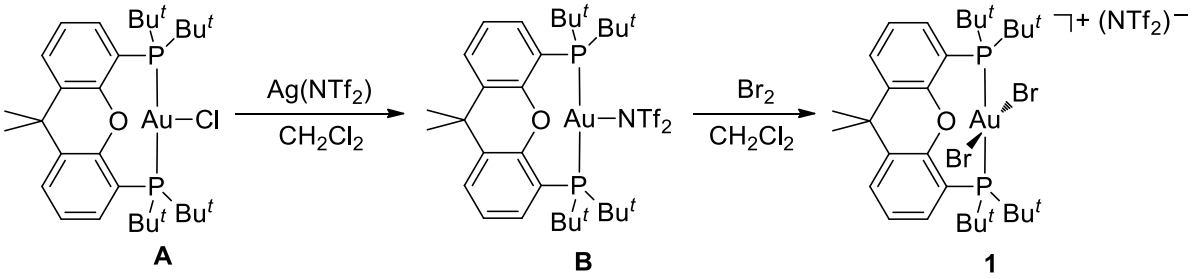
Synthetic part.

All the reagents used in this study were obtained from the commercial sources (Aldrich, TCI-Europe, Strem, ABCR). Complexes **A**, **B** and **1** were prepared similar to analogues complexes which were reported earlier.[1,2] C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNS/O analyzer. Mass-spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source; MeOH, CH_2Cl_2 or MeOH/CH_2Cl_2 mixture was used as a solvent.



Scheme S1. Synthesis of complex **1**.

1. Bromine (194 μmol, 10 μL) was added to the solution of complex **B** (67 μmol, 50 mg) in CH_2Cl_2 (2mL) and the resulting mixture evaporated to dryness. The formed precipitate was washed with Et_2O (3×2 mL) and dried under vacuum. Yield: 53 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52 (t, J = 8.9 Hz, 36H), 1.64 (s, 6 H), 7.44 (t, J = 7.8 Hz, 2H), 7.64–7.67 (m, 2H), 7.76 (d, J = 7.7 Hz, 2H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$): δ 28.53 (s), 31.04 (t, J = 4.0 Hz), 36.52 (s), 38.31 (t, J = 10.7 Hz), 116.97 (t, J = 18.9 Hz), 125.13 (s), 129.34 (s), 133.22 (s), 135.78 (s), 154.91 (s), signal from NTf_2 was not observed. Elem. anal. calcd for $C_{31}H_{44}AuBr_2F_6NO_5P_2S_2$: C 33.62; H 4.00; N 1.26. Found: C 34.06; H 4.42; N 0.94. MS (ESI$^+$), found: 827.3854 $[M - NTf_2]^+$; calcd for $C_{29}H_{44}AuBr_2OP_2$: 827.3814. Crystals, suitable for X-ray analysis, were obtained by layering CH_2Cl_2 solution of **1** with hexane.

Single crystal structure analysis of 1.

Identification code	**1**
Empirical formula	C33H48AuBr2F6NO5P2S2
Formula weight	1135.57
Temperature	120(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.2051(2) Å b = 15.0710(4) Å c = 17.6847(4) Å
Volume	2007.78(9) $Å^3$
Z	2
Density (calculated)	1.878 Mg/m^3
Absorption coefficient	11.543 mm^{-1}
F(000)	1116
Crystal size	0.161 x 0.080 x 0.033 mm^3
Theta range for data collection	2.721 to 77.168°.
Index ranges	-9<=h<=10, -19<=k<=19, -22<=l<=22
Reflections collected	57831
Independent reflections	8460 [R(int) = 0.0484]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.30988
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8460 / 0 / 483
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0246, wR2 = 0.0614
R indices (all data)	R1 = 0.0276, wR2 = 0.0632
Extinction coefficient	n/a
Largest diff. peak and hole	1.169 and -1.384 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	7139(1)	4233(1)	8186(1)	16(1)
Br(1)	10106(1)	4518(1)	8721(1)	24(1)
Br(2)	4168(1)	3990(1)	8175(1)	21(1)
P(1)	7196(1)	2552(1)	7444(1)	17(1)
P(2)	6633(1)	5829(1)	8257(1)	15(1)
O(1)	5650(3)	3984(1)	6665(1)	16(1)
C(1)	6987(4)	1784(2)	8075(2)	23(1)
C(2)	7371(5)	740(2)	7677(2)	29(1)
C(3)	8252(5)	2247(2)	8887(2)	26(1)
C(4)	5244(5)	1806(2)	8271(2)	28(1)
C(5)	8963(4)	2226(2)	6856(2)	22(1)
C(6)	8448(4)	1295(2)	6109(2)	26(1)
C(7)	10577(4)	2111(2)	7394(2)	26(1)
C(8)	9272(4)	3021(2)	6530(2)	25(1)
C(9)	5391(4)	2363(2)	6610(2)	19(1)
C(10)	4556(4)	1457(2)	6227(2)	23(1)
C(11)	3244(4)	1265(2)	5567(2)	25(1)
C(12)	2765(4)	1975(2)	5254(2)	22(1)
C(13)	3581(4)	2879(2)	5611(2)	19(1)
C(14)	3211(4)	3669(2)	5271(2)	19(1)
C(15)	4537(4)	3705(2)	4760(2)	25(1)
C(16)	1493(4)	3499(2)	4711(2)	24(1)
C(17)	3373(4)	4606(2)	6002(2)	15(1)
C(18)	2378(4)	5355(2)	6016(2)	20(1)
C(19)	2647(4)	6209(2)	6681(2)	19(1)
C(20)	3907(4)	6321(2)	7352(2)	19(1)
C(21)	4937(4)	5586(2)	7371(2)	15(1)
C(22)	4631(4)	4731(2)	6683(2)	16(1)
C(23)	4853(4)	3067(2)	6295(2)	17(1)
C(24)	8300(4)	6435(2)	7948(2)	21(1)
C(25)	8868(4)	5673(2)	7225(2)	25(1)
C(26)	7589(4)	7218(2)	7643(2)	25(1)
C(27)	9817(4)	6869(2)	8653(2)	26(1)
C(28)	6055(4)	6619(2)	9256(2)	21(1)
C(29)	7295(5)	6416(3)	9931(2)	28(1)
C(30)	6210(5)	7688(2)	9406(2)	28(1)
C(31)	4282(4)	6351(3)	9313(2)	29(1)
S(1)	1359(1)	-943(1)	6848(1)	29(1)
S(2)	2940(1)	-539(1)	8472(1)	26(1)
F(1)	3786(4)	-704(2)	6121(2)	50(1)
F(2)	2466(3)	-2088(2)	5584(1)	39(1)

F(3)	4224(3)	-1713(2)	6728(1)	36(1)
F(4)	-140(3)	-715(2)	8647(2)	47(1)
F(5)	1006(3)	702(2)	9248(2)	49(1)
F(6)	1687(4)	-374(2)	9762(2)	57(1)
O(2)	472(4)	-421(2)	6393(2)	50(1)
O(3)	547(3)	-1787(2)	6845(2)	37(1)
O(4)	2997(4)	-1538(2)	8293(2)	34(1)
O(5)	4335(4)	85(2)	8981(2)	38(1)
N(1)	2295(4)	-230(2)	7708(2)	30(1)
C(32)	3053(5)	-1383(2)	6293(2)	29(1)
C(33)	1272(5)	-210(3)	9065(2)	34(1)

Table 4. Bond lengths [Å] and angles [°] for **1**.

Au(1)-P(2)	2.4067(7)
Au(1)-P(1)	2.4126(7)
Au(1)-Br(1)	2.4252(3)
Au(1)-Br(2)	2.4585(3)
P(1)-C(9)	1.835(3)
P(1)-C(1)	1.894(3)
P(1)-C(5)	1.901(3)
P(2)-C(21)	1.826(3)
P(2)-C(28)	1.895(3)
P(2)-C(24)	1.899(3)
O(1)-C(22)	1.402(3)
O(1)-C(23)	1.402(3)
C(1)-C(4)	1.528(5)
C(1)-C(2)	1.542(5)
C(1)-C(3)	1.542(4)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-C(7)	1.536(5)
C(5)-C(8)	1.538(4)
C(5)-C(6)	1.542(4)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.402(4)
C(9)-C(23)	1.402(4)
C(10)-C(11)	1.384(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.395(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.391(4)
C(12)-H(12)	0.9500
C(13)-C(23)	1.392(4)
C(13)-C(14)	1.522(4)

C(14)-C(17)	1.528(4)
C(14)-C(16)	1.533(4)
C(14)-C(15)	1.546(4)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(22)	1.394(4)
C(17)-C(18)	1.394(4)
C(18)-C(19)	1.387(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.387(4)
C(19)-H(19)	0.9500
C(20)-C(21)	1.404(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.408(4)
C(24)-C(25)	1.535(5)
C(24)-C(26)	1.539(4)
C(24)-C(27)	1.546(4)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(31)	1.537(5)
C(28)-C(30)	1.538(4)
C(28)-C(29)	1.542(4)
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
S(1)-O(2)	1.428(3)
S(1)-O(3)	1.431(3)
S(1)-N(1)	1.574(3)
S(1)-C(32)	1.836(4)
S(2)-O(5)	1.423(3)
S(2)-O(4)	1.428(3)
S(2)-N(1)	1.586(3)
S(2)-C(33)	1.837(4)

F(1)-C(32)	1.334(4)
F(2)-C(32)	1.331(4)
F(3)-C(32)	1.333(4)
F(4)-C(33)	1.325(5)
F(5)-C(33)	1.325(4)
F(6)-C(33)	1.328(5)

P(2)-Au(1)-P(1)	152.65(2)
P(2)-Au(1)-Br(1)	96.88(2)
P(1)-Au(1)-Br(1)	95.61(2)
P(2)-Au(1)-Br(2)	87.57(2)
P(1)-Au(1)-Br(2)	89.59(2)
Br(1)-Au(1)-Br(2)	158.635(12)
C(9)-P(1)-C(1)	112.21(14)
C(9)-P(1)-C(5)	102.05(14)
C(1)-P(1)-C(5)	112.58(14)
C(9)-P(1)-Au(1)	100.12(10)
C(1)-P(1)-Au(1)	114.15(10)
C(5)-P(1)-Au(1)	114.35(10)
C(21)-P(2)-C(28)	112.82(14)
C(21)-P(2)-C(24)	101.51(13)
C(28)-P(2)-C(24)	112.05(14)
C(21)-P(2)-Au(1)	100.25(9)
C(28)-P(2)-Au(1)	114.37(10)
C(24)-P(2)-Au(1)	114.50(10)
C(22)-O(1)-C(23)	115.7(2)
C(4)-C(1)-C(2)	108.8(3)
C(4)-C(1)-C(3)	108.7(3)
C(2)-C(1)-C(3)	108.5(3)
C(4)-C(1)-P(1)	110.3(2)
C(2)-C(1)-P(1)	114.9(2)
C(3)-C(1)-P(1)	105.4(2)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(1)-C(4)-H(4A)	109.5
C(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5

C(7)-C(5)-C(8)	109.2(3)
C(7)-C(5)-C(6)	109.4(3)
C(8)-C(5)-C(6)	108.0(3)
C(7)-C(5)-P(1)	112.6(2)
C(8)-C(5)-P(1)	108.0(2)
C(6)-C(5)-P(1)	109.6(2)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(5)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(23)	117.4(3)
C(10)-C(9)-P(1)	119.1(2)
C(23)-C(9)-P(1)	123.4(2)
C(11)-C(10)-C(9)	121.3(3)
C(11)-C(10)-H(10)	119.3
C(9)-C(10)-H(10)	119.3
C(10)-C(11)-C(12)	119.9(3)
C(10)-C(11)-H(11)	120.1
C(12)-C(11)-H(11)	120.1
C(13)-C(12)-C(11)	120.4(3)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(12)-C(13)-C(23)	118.7(3)
C(12)-C(13)-C(14)	123.5(3)
C(23)-C(13)-C(14)	117.7(3)
C(13)-C(14)-C(17)	107.7(2)
C(13)-C(14)-C(16)	112.3(3)
C(17)-C(14)-C(16)	111.5(3)
C(13)-C(14)-C(15)	108.0(3)
C(17)-C(14)-C(15)	108.8(2)
C(16)-C(14)-C(15)	108.4(3)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(22)-C(17)-C(18)	118.2(3)
C(22)-C(17)-C(14)	118.0(3)
C(18)-C(17)-C(14)	123.8(3)
C(19)-C(18)-C(17)	121.0(3)
C(19)-C(18)-H(18)	119.5
C(17)-C(18)-H(18)	119.5
C(20)-C(19)-C(18)	120.0(3)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	121.2(3)
C(19)-C(20)-H(20)	119.4
C(21)-C(20)-H(20)	119.4
C(20)-C(21)-C(22)	117.2(3)
C(20)-C(21)-P(2)	117.8(2)
C(22)-C(21)-P(2)	125.0(2)
C(17)-C(22)-O(1)	118.2(3)
C(17)-C(22)-C(21)	122.4(3)
O(1)-C(22)-C(21)	119.3(3)
C(13)-C(23)-O(1)	118.7(3)
C(13)-C(23)-C(9)	122.2(3)
O(1)-C(23)-C(9)	119.1(3)
C(25)-C(24)-C(26)	107.8(3)
C(25)-C(24)-C(27)	109.2(3)
C(26)-C(24)-C(27)	109.1(3)
C(25)-C(24)-P(2)	106.8(2)
C(26)-C(24)-P(2)	110.9(2)
C(27)-C(24)-P(2)	113.0(2)
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(24)-C(27)-H(27A)	109.5
C(24)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(24)-C(27)-H(27C)	109.5

H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(31)-C(28)-C(30)	108.4(3)
C(31)-C(28)-C(29)	108.9(3)
C(30)-C(28)-C(29)	109.2(3)
C(31)-C(28)-P(2)	111.6(2)
C(30)-C(28)-P(2)	114.3(2)
C(29)-C(28)-P(2)	104.3(2)
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(28)-C(30)-H(30A)	109.5
C(28)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(28)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(28)-C(31)-H(31A)	109.5
C(28)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(28)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
O(2)-S(1)-O(3)	118.3(2)
O(2)-S(1)-N(1)	109.40(17)
O(3)-S(1)-N(1)	116.60(17)
O(2)-S(1)-C(32)	103.2(2)
O(3)-S(1)-C(32)	103.77(16)
N(1)-S(1)-C(32)	103.20(18)
O(5)-S(2)-O(4)	119.38(18)
O(5)-S(2)-N(1)	108.63(17)
O(4)-S(2)-N(1)	115.84(16)
O(5)-S(2)-C(33)	104.46(18)
O(4)-S(2)-C(33)	103.94(17)
N(1)-S(2)-C(33)	102.33(19)
S(1)-N(1)-S(2)	123.29(18)
F(2)-C(32)-F(3)	107.8(3)
F(2)-C(32)-F(1)	107.7(3)
F(3)-C(32)-F(1)	107.4(3)
F(2)-C(32)-S(1)	110.1(3)
F(3)-C(32)-S(1)	111.7(2)
F(1)-C(32)-S(1)	111.9(3)
F(5)-C(33)-F(4)	108.0(3)
F(5)-C(33)-F(6)	108.5(3)
F(4)-C(33)-F(6)	108.2(4)
F(5)-C(33)-S(2)	111.4(3)
F(4)-C(33)-S(2)	111.1(3)

F(6)-C(33)-S(2)	109.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	14(1)	17(1)	17(1)	6(1)	0(1)	2(1)
Br(1)	15(1)	25(1)	27(1)	9(1)	-3(1)	2(1)
Br(2)	16(1)	23(1)	25(1)	10(1)	5(1)	1(1)
P(1)	15(1)	16(1)	18(1)	6(1)	0(1)	3(1)
P(2)	13(1)	16(1)	15(1)	5(1)	1(1)	1(1)
O(1)	14(1)	13(1)	19(1)	5(1)	0(1)	2(1)
C(1)	25(2)	22(2)	23(2)	11(1)	2(1)	3(1)
C(2)	34(2)	23(2)	32(2)	15(1)	1(1)	4(1)
C(3)	30(2)	27(2)	24(2)	13(1)	1(1)	4(1)
C(4)	28(2)	28(2)	33(2)	17(1)	7(1)	1(1)
C(5)	19(2)	22(1)	23(2)	7(1)	5(1)	6(1)
C(6)	26(2)	24(2)	24(2)	5(1)	3(1)	7(1)
C(7)	20(2)	28(2)	31(2)	10(1)	4(1)	9(1)
C(8)	26(2)	26(2)	27(2)	11(1)	10(1)	6(1)
C(9)	19(2)	17(1)	20(1)	6(1)	2(1)	2(1)
C(10)	25(2)	16(1)	28(2)	8(1)	1(1)	1(1)
C(11)	24(2)	17(1)	30(2)	5(1)	-1(1)	-3(1)
C(12)	20(2)	21(2)	21(1)	5(1)	-2(1)	-1(1)
C(13)	17(2)	19(1)	19(1)	5(1)	1(1)	2(1)
C(14)	17(2)	18(1)	18(1)	5(1)	-3(1)	0(1)
C(15)	30(2)	27(2)	19(1)	9(1)	7(1)	5(1)
C(16)	22(2)	23(2)	22(2)	6(1)	-6(1)	0(1)
C(17)	12(1)	16(1)	18(1)	5(1)	4(1)	2(1)
C(18)	14(1)	24(2)	21(1)	11(1)	0(1)	1(1)
C(19)	15(2)	19(1)	27(2)	10(1)	4(1)	5(1)
C(20)	16(2)	18(1)	22(1)	7(1)	4(1)	1(1)
C(21)	14(1)	17(1)	16(1)	7(1)	1(1)	0(1)
C(22)	12(1)	17(1)	21(1)	9(1)	4(1)	2(1)
C(23)	16(1)	16(1)	19(1)	5(1)	4(1)	2(1)
C(24)	18(2)	22(1)	23(1)	10(1)	3(1)	-2(1)
C(25)	20(2)	30(2)	26(2)	9(1)	6(1)	-1(1)
C(26)	22(2)	26(2)	28(2)	12(1)	-1(1)	-4(1)
C(27)	16(2)	28(2)	33(2)	12(1)	-2(1)	-5(1)
C(28)	18(2)	24(2)	18(1)	5(1)	1(1)	2(1)
C(29)	26(2)	36(2)	18(1)	8(1)	1(1)	5(1)
C(30)	31(2)	22(2)	23(2)	1(1)	0(1)	5(1)
C(31)	22(2)	33(2)	25(2)	3(1)	7(1)	4(1)
S(1)	29(1)	20(1)	29(1)	2(1)	-6(1)	6(1)
S(2)	26(1)	22(1)	28(1)	9(1)	0(1)	2(1)
F(1)	62(2)	41(1)	51(2)	24(1)	7(1)	-12(1)
F(2)	48(1)	32(1)	27(1)	3(1)	4(1)	-2(1)
F(3)	31(1)	44(1)	35(1)	16(1)	7(1)	12(1)

F(4)	32(1)	41(1)	56(2)	1(1)	11(1)	-4(1)
F(5)	48(2)	28(1)	54(2)	-3(1)	6(1)	10(1)
F(6)	60(2)	76(2)	43(1)	26(1)	20(1)	20(2)
O(2)	59(2)	37(2)	37(2)	6(1)	-15(1)	22(1)
O(3)	28(1)	29(1)	43(2)	-2(1)	4(1)	-6(1)
O(4)	40(2)	27(1)	38(1)	15(1)	9(1)	10(1)
O(5)	32(2)	46(2)	33(1)	16(1)	-6(1)	-10(1)
N(1)	40(2)	17(1)	26(1)	5(1)	-5(1)	2(1)
C(32)	33(2)	24(2)	28(2)	9(1)	1(1)	-3(1)
C(33)	36(2)	24(2)	35(2)	2(1)	4(2)	2(2)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1**.

	x	y	z	U(eq)
H(2A)	6584	437	7156	43
H(2B)	7267	401	8050	43
H(2C)	8505	717	7571	43
H(3A)	9378	2224	8771	40
H(3B)	8165	1900	9256	40
H(3C)	8017	2910	9151	40
H(4A)	5019	2466	8560	42
H(4B)	5170	1433	8620	42
H(4C)	4425	1535	7757	42
H(6A)	8124	793	6298	39
H(6B)	9386	1105	5828	39
H(6C)	7508	1394	5728	39
H(7A)	10844	2677	7897	39
H(7B)	11484	2034	7088	39
H(7C)	10433	1549	7539	39
H(8A)	8226	3130	6220	38
H(8B)	10084	2833	6169	38
H(8C)	9702	3608	6995	38
H(10)	4897	964	6424	28
H(11)	2670	652	5326	30
H(12)	1876	1839	4795	27
H(15A)	5640	3844	5116	37
H(15B)	4314	4204	4528	37
H(15C)	4498	3090	4312	37
H(16A)	1426	2891	4252	37
H(16B)	1320	4015	4495	37
H(16C)	635	3482	5028	37
H(18)	1502	5280	5562	24
H(19)	1969	6716	6677	23
H(20)	4078	6907	7806	23
H(25A)	9453	5205	7419	38
H(25B)	9617	5973	6996	38
H(25C)	7898	5353	6798	38
H(26A)	6689	6937	7165	38
H(26B)	8468	7519	7486	38
H(26C)	7157	7697	8084	38
H(27A)	9481	7396	9096	40
H(27B)	10688	7105	8443	40
H(27C)	10243	6381	8868	40
H(29A)	7135	5746	9866	41
H(29B)	7106	6820	10474	41

H(29C)	8433	6553	9882	41
H(30A)	7335	7871	9372	42
H(30B)	5993	8051	9954	42
H(30C)	5402	7822	8988	42
H(31A)	3503	6363	8827	43
H(31B)	3988	6808	9811	43
H(31C)	4225	5711	9335	43

Table 7. Torsion angles [°] for **1**.

C(9)-P(1)-C(1)-C(4)	-44.7(3)
C(5)-P(1)-C(1)-C(4)	-159.2(2)
Au(1)-P(1)-C(1)-C(4)	68.3(2)
C(9)-P(1)-C(1)-C(2)	78.8(3)
C(5)-P(1)-C(1)-C(2)	-35.7(3)
Au(1)-P(1)-C(1)-C(2)	-168.2(2)
C(9)-P(1)-C(1)-C(3)	-161.9(2)
C(5)-P(1)-C(1)-C(3)	83.6(2)
Au(1)-P(1)-C(1)-C(3)	-48.9(2)
C(1)-P(1)-C(9)-C(10)	-33.1(3)
C(5)-P(1)-C(9)-C(10)	87.7(3)
Au(1)-P(1)-C(9)-C(10)	-154.5(2)
C(1)-P(1)-C(9)-C(23)	151.1(3)
C(5)-P(1)-C(9)-C(23)	-88.2(3)
Au(1)-P(1)-C(9)-C(23)	29.6(3)
C(23)-C(9)-C(10)-C(11)	-0.4(5)
P(1)-C(9)-C(10)-C(11)	-176.5(3)
C(9)-C(10)-C(11)-C(12)	2.0(5)
C(10)-C(11)-C(12)-C(13)	-1.0(5)
C(11)-C(12)-C(13)-C(23)	-1.6(5)
C(11)-C(12)-C(13)-C(14)	175.7(3)
C(12)-C(13)-C(14)-C(17)	143.7(3)
C(23)-C(13)-C(14)-C(17)	-39.0(4)
C(12)-C(13)-C(14)-C(16)	20.6(4)
C(23)-C(13)-C(14)-C(16)	-162.1(3)
C(12)-C(13)-C(14)-C(15)	-98.9(4)
C(23)-C(13)-C(14)-C(15)	78.4(3)
C(13)-C(14)-C(17)-C(22)	37.7(4)
C(16)-C(14)-C(17)-C(22)	161.4(3)
C(15)-C(14)-C(17)-C(22)	-79.1(3)
C(13)-C(14)-C(17)-C(18)	-144.8(3)
C(16)-C(14)-C(17)-C(18)	-21.2(4)
C(15)-C(14)-C(17)-C(18)	98.3(3)
C(22)-C(17)-C(18)-C(19)	1.1(4)
C(14)-C(17)-C(18)-C(19)	-176.4(3)
C(17)-C(18)-C(19)-C(20)	-0.9(5)
C(18)-C(19)-C(20)-C(21)	0.5(5)
C(19)-C(20)-C(21)-C(22)	-0.2(4)
C(19)-C(20)-C(21)-P(2)	176.6(2)
C(28)-P(2)-C(21)-C(20)	36.8(3)
C(24)-P(2)-C(21)-C(20)	-83.3(3)
Au(1)-P(2)-C(21)-C(20)	158.9(2)
C(28)-P(2)-C(21)-C(22)	-146.7(2)
C(24)-P(2)-C(21)-C(22)	93.2(3)
Au(1)-P(2)-C(21)-C(22)	-24.6(3)
C(18)-C(17)-C(22)-O(1)	-179.0(3)
C(14)-C(17)-C(22)-O(1)	-1.4(4)
C(18)-C(17)-C(22)-C(21)	-0.8(4)

C(14)-C(17)-C(22)-C(21)	176.8(3)
C(23)-O(1)-C(22)-C(17)	-37.9(4)
C(23)-O(1)-C(22)-C(21)	143.9(3)
C(20)-C(21)-C(22)-C(17)	0.3(4)
P(2)-C(21)-C(22)-C(17)	-176.2(2)
C(20)-C(21)-C(22)-O(1)	178.5(3)
P(2)-C(21)-C(22)-O(1)	2.0(4)
C(12)-C(13)-C(23)-O(1)	-178.6(3)
C(14)-C(13)-C(23)-O(1)	4.0(4)
C(12)-C(13)-C(23)-C(9)	3.3(5)
C(14)-C(13)-C(23)-C(9)	-174.2(3)
C(22)-O(1)-C(23)-C(13)	36.7(4)
C(22)-O(1)-C(23)-C(9)	-145.1(3)
C(10)-C(9)-C(23)-C(13)	-2.3(5)
P(1)-C(9)-C(23)-C(13)	173.7(2)
C(10)-C(9)-C(23)-O(1)	179.6(3)
P(1)-C(9)-C(23)-O(1)	-4.5(4)
C(21)-P(2)-C(24)-C(25)	-69.1(2)
C(28)-P(2)-C(24)-C(25)	170.3(2)
Au(1)-P(2)-C(24)-C(25)	37.9(2)
C(21)-P(2)-C(24)-C(26)	48.1(2)
C(28)-P(2)-C(24)-C(26)	-72.6(2)
Au(1)-P(2)-C(24)-C(26)	155.07(19)
C(21)-P(2)-C(24)-C(27)	170.9(2)
C(28)-P(2)-C(24)-C(27)	50.3(3)
Au(1)-P(2)-C(24)-C(27)	-82.1(2)
C(21)-P(2)-C(28)-C(31)	40.8(3)
C(24)-P(2)-C(28)-C(31)	154.7(2)
Au(1)-P(2)-C(28)-C(31)	-72.9(2)
C(21)-P(2)-C(28)-C(30)	-82.6(3)
C(24)-P(2)-C(28)-C(30)	31.3(3)
Au(1)-P(2)-C(28)-C(30)	163.7(2)
C(21)-P(2)-C(28)-C(29)	158.2(2)
C(24)-P(2)-C(28)-C(29)	-87.9(2)
Au(1)-P(2)-C(28)-C(29)	44.5(2)
O(2)-S(1)-N(1)-S(2)	160.7(3)
O(3)-S(1)-N(1)-S(2)	23.1(3)
C(32)-S(1)-N(1)-S(2)	-90.0(3)
O(5)-S(2)-N(1)-S(1)	152.3(2)
O(4)-S(2)-N(1)-S(1)	14.7(3)
C(33)-S(2)-N(1)-S(1)	-97.6(3)
O(2)-S(1)-C(32)-F(2)	-73.9(3)
O(3)-S(1)-C(32)-F(2)	50.1(3)
N(1)-S(1)-C(32)-F(2)	172.2(2)
O(2)-S(1)-C(32)-F(3)	166.4(3)
O(3)-S(1)-C(32)-F(3)	-69.6(3)
N(1)-S(1)-C(32)-F(3)	52.5(3)
O(2)-S(1)-C(32)-F(1)	45.9(3)
O(3)-S(1)-C(32)-F(1)	170.0(3)
N(1)-S(1)-C(32)-F(1)	-68.0(3)

O(5)-S(2)-C(33)-F(5)	57.1(3)
O(4)-S(2)-C(33)-F(5)	-177.0(3)
N(1)-S(2)-C(33)-F(5)	-56.1(3)
O(5)-S(2)-C(33)-F(4)	177.5(3)
O(4)-S(2)-C(33)-F(4)	-56.6(3)
N(1)-S(2)-C(33)-F(4)	64.3(3)
O(5)-S(2)-C(33)-F(6)	-63.0(3)
O(4)-S(2)-C(33)-F(6)	62.9(3)
N(1)-S(2)-C(33)-F(6)	-176.2(3)

Symmetry transformations used to generate equivalent atoms:

Computational details

The single point calculations based on the experimental X-ray geometry of **1** have been carried out at the DFT level of theory using the dispersion-corrected hybrid functional ωB97XD [J.-D. Chai, M. Head-Gordon, *Chem. Chem. Phys.*, 2008, **10**, 6615−6620.] with the help of Gaussian-09 [M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, M. J. A.;, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, C. J.;, D. J. Fox, *Gaussian 09, Revision C.01,* Gaussian, Inc., Wallingford, CT, 2010.] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets [C. L. Barros, P. J. P. de Oliveira, F. E. Jorge, A. C. Neto, M. Campos, *Mol. Phys.*, 2010, **108**, 1965–1972. || A. C. Neto, F. E. Jorge, *Chem. Phys. Lett.*, 2013, **582**, 158–162. || R. C. de Berredo, F. E. Jorge, *J. Mol. Struct. – Theochem*, 2010, **961**, 107–112. || F. E. Jorge, A. C. Neto, G. G. Camiletti, S. F. Machado, *J. Chem. Phys.*, 2009, **130**, 064108.] for all atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader [R.F.W. Bader, *Chem. Rev.*, 1991, **91**, 893–928.] has been performed by using the Multiwfn program (version 3.6) [T. Lu, F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.]. The Cartesian

atomic coordinates for model supramolecular associate are presented in **Table S1**, Supporting Information.

Table S1. Cartesian atomic coordinates for model supramolecular associate.

Atom	X	Y	Z
Au	1.711319	7.541720	2.931718
Br	4.141485	7.901685	2.951780
Br	-0.551428	7.443704	2.066117
P	1.411242	9.607132	4.136117
P	2.165849	5.182722	2.813770
O	2.454323	6.965903	5.401027
C	3.298334	5.846670	5.364947
C	3.278681	4.995234	4.248888
C	4.119560	3.876568	4.280114
H	4.124734	3.276213	3.543868
C	4.946681	3.628068	5.367374
H	5.513010	2.865081	5.370561
C	4.944366	4.492787	6.444602
H	5.517140	4.319275	7.182466
C	4.116943	5.616791	6.469842
C	4.014674	6.562064	7.656929
C	3.814383	7.970864	7.104724
C	4.355245	9.118891	7.681845
H	4.939515	9.041480	8.426974
C	4.047686	10.370949	7.177208
H	4.431556	11.146168	7.569366
C	3.183862	10.498320	6.106289
H	2.966614	11.365061	5.783849
C	2.624002	9.375731	5.487263
C	2.974456	8.114205	6.003226
C	2.765480	6.199082	8.490009
H	2.661018	6.844589	9.219897
H	2.872022	5.298946	8.862768
H	1.971861	6.223287	7.915994
C	5.238264	6.472292	8.562493
H	6.039851	6.713735	8.053245
H	5.328612	5.556500	8.899398
H	5.132151	7.088927	9.316715
C	1.762488	11.156045	3.118429

C	3.254329	11.247848	2.791442
H	3.765169	11.352452	3.621351
H	3.414676	12.020415	2.209936
H	3.539698	10.429747	2.333385
C	1.316076	12.480596	3.765769
H	0.355084	12.444699	3.953823
H	1.501610	13.222498	3.152843
H	1.807899	12.617346	4.602344
C	0.996837	10.961201	1.797214
H	1.291555	10.130578	1.368507
H	1.176918	11.717976	1.200920
H	0.035868	10.911223	1.980803
C	-0.222073	9.724453	5.093779
C	-0.045433	10.656291	6.308371
H	0.608555	10.267484	6.926119
H	-0.905206	10.761696	6.766816
H	0.272440	11.532130	6.004796
C	-1.383858	10.235965	4.220412
H	-1.231442	11.176891	3.992734
H	-2.225614	10.151494	4.714710
H	-1.432712	9.704726	3.398350
C	-0.569152	8.329649	5.621715
H	-0.783778	7.739613	4.869192
H	-1.342943	8.390192	6.220160
H	0.196576	7.966405	6.113603
C	2.963291	4.621498	1.198412
C	4.431434	5.060743	1.095997
H	4.478953	6.039434	1.076565
H	4.824333	4.698305	0.274582
H	4.927796	4.724926	1.871349
C	2.154318	5.346136	0.100798
H	1.208535	5.102135	0.177440
H	2.489971	5.080982	-0.780950
H	2.251822	6.315222	0.209508
C	2.903347	3.104799	0.956044
H	3.447139	2.644644	1.628835
H	3.249422	2.902842	0.061903
H	1.974047	2.800085	1.023108
C	0.711741	4.081494	3.306920
C	0.013663	4.772199	4.493036
H	0.681227	5.012287	5.169515
H	-0.644105	4.161383	4.885727

H	-0.438941	5.582464	4.178960
C	-0.305454	3.867147	2.179049
H	-0.583780	4.735874	1.820885
H	-1.087373	3.392534	2.530047
H	0.105918	3.336276	1.465179
C	1.205145	2.708683	3.808159
H	1.708898	2.262577	3.095697
H	0.435517	2.156433	4.059183
H	1.784871	2.834966	4.588236
Au	-6.478981	7.541720	2.931718
Br	-4.048815	7.901685	2.951780
Br	-8.741728	7.443704	2.066117
P	-6.779058	9.607132	4.136117
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C	-4.891966	5.846670	5.364947
C	-4.911619	4.995234	4.248888
C	-4.070740	3.876568	4.280114
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C	-4.073357	5.616791	6.469842
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C	-3.835055	9.118891	7.681845
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H	-3.758744	11.146168	7.569366
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H	-3.058149	7.088927	9.316715

C	-6.427812	11.156045	3.118429
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H	-4.425131	11.352452	3.621351
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H	-6.898745	10.130578	1.368507
H	-7.013382	11.717976	1.200920
H	-8.154432	10.911223	1.980803
C	-8.412373	9.724453	5.093779
C	-8.235733	10.656291	6.308371
H	-7.581745	10.267484	6.926119
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H	-7.917860	11.532130	6.004796
C	-9.574158	10.235965	4.220412
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H	-10.415914	10.151494	4.714710
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H	-7.993724	7.966405	6.113603
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C	-3.758866	5.060743	1.095997
H	-3.711347	6.039434	1.076565
H	-3.365967	4.698305	0.274582
H	-3.262504	4.724926	1.871349
C	-6.035982	5.346136	0.100798
H	-6.981765	5.102135	0.177440
H	-5.700329	5.080982	-0.780950
H	-5.938478	6.315222	0.209508
C	-5.286953	3.104799	0.956044
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H	-4.940878	2.902842	0.061903
H	-6.216253	2.800085	1.023108
C	-7.478559	4.081494	3.306920
C	-8.176637	4.772199	4.493036
H	-7.509073	5.012287	5.169515

H	-8.834405	4.161383	4.885727
H	-8.629241	5.582464	4.178960
C	-8.495754	3.867147	2.179049
H	-8.774080	4.735874	1.820885
H	-9.277673	3.392534	2.530047
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C	-6.985155	2.708683	3.808159
H	-6.481402	2.262577	3.095697
H	-7.754783	2.156433	4.059183
H	-6.405429	2.834966	4.588236

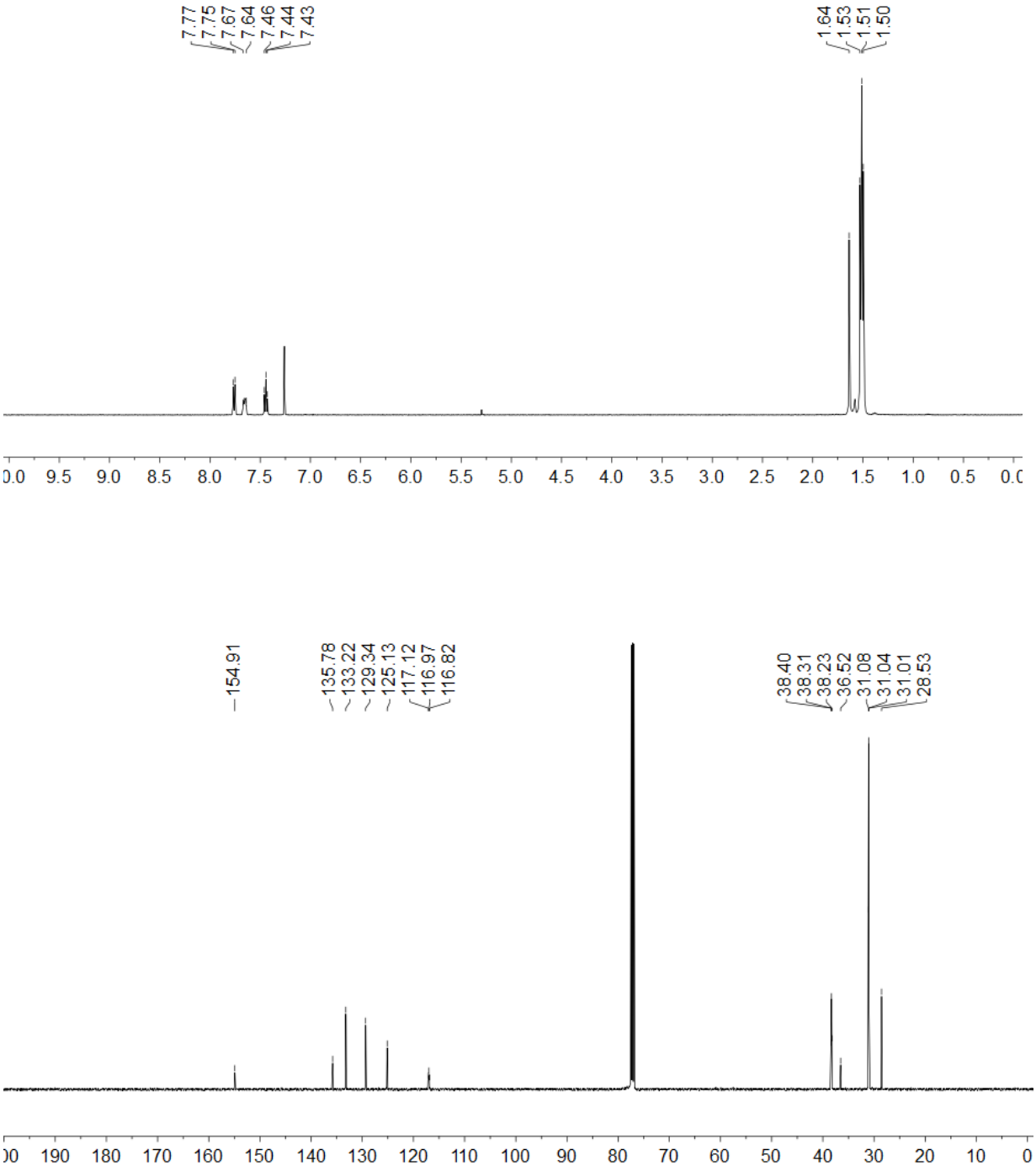

Figure S1. ^{1}H (top) and $^{13}C\{1H\}$ (bottom) NMR spectra of **1** ($CDCl_3$).