Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Heterocyclic bismuth(III) compounds with transannular N→Bi interactions as catalysts for the oxidation of thiophenol to diphenyldisulfide

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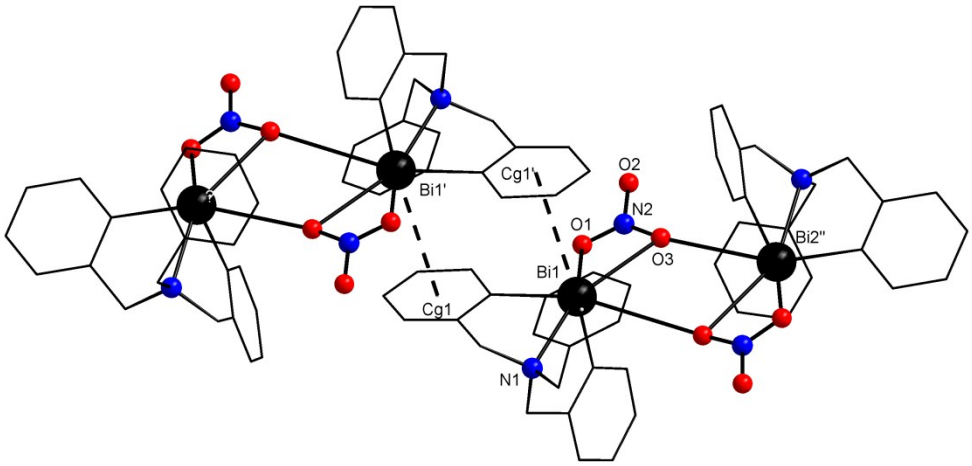


Figure S1. Intermolecular Bi···π arene interactions in **3**

Bi1···Cg1'(C1'-C6') 3.586 Å Symmetry equivalent positions *1-x*, *2-y*, *1-z* are given by "prime".

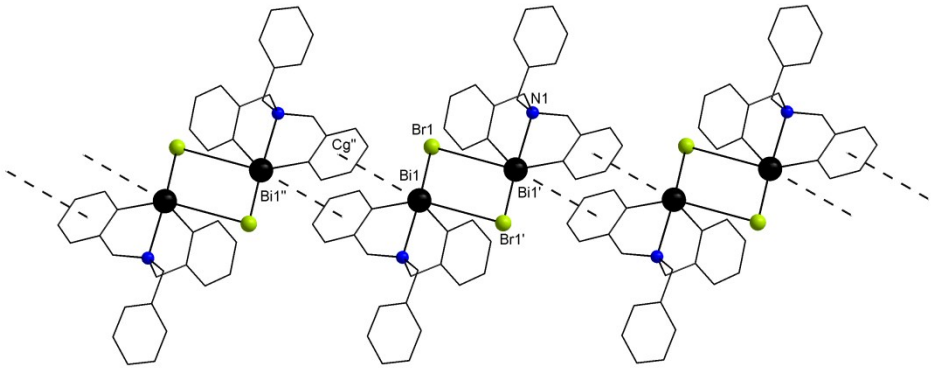


Figure S2. Intermolecular Bi···Br and Bi···π arene interactions in **1**[1]

Bi1···Cg"(C1"-C6") 4.097 Å (1-x, 2-y, 2-z)

Bi1···Br1' 2.7653(7) Å (1-x, 2-y, 2-z)

Symmetry equivalent positions *1-x*, *1-y*, *2-z* and *1-x*, *2-y*, *2-z* are given by "prime" and "second", respectively.

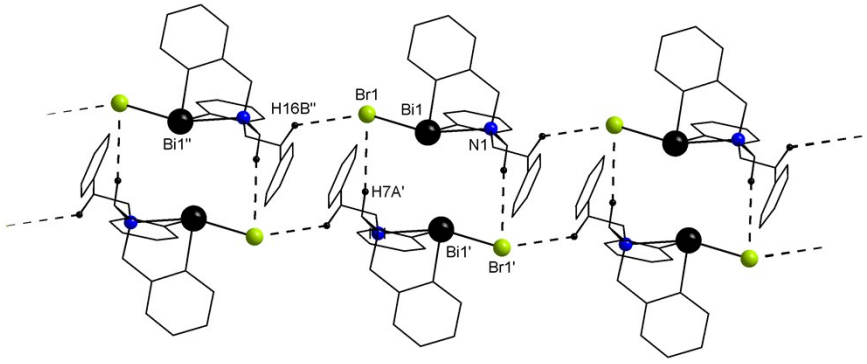


Figure S3. View of a polymeric chain in **2** [1]

Intra-dimers interactions	Br1···H7A'	3.037 Å (-x, 1-y, -z), Σr_{vdW}(H,Br) 3.15 Å[2]
Inter-dimers interactions	Br1···H16B"	2.889 Å (x, 1+y, z)

1. A. M. Toma, A. Pop, A. Silvestru, T. Rüffer, H. Lang, M. Mehring, *Dalton Trans*., *in press*, DOI: 10.1039/c7dt00188f.
2. J. Emsley, *Die Elemente*, **1993**, Walter de Gruyter, Oldenburg.

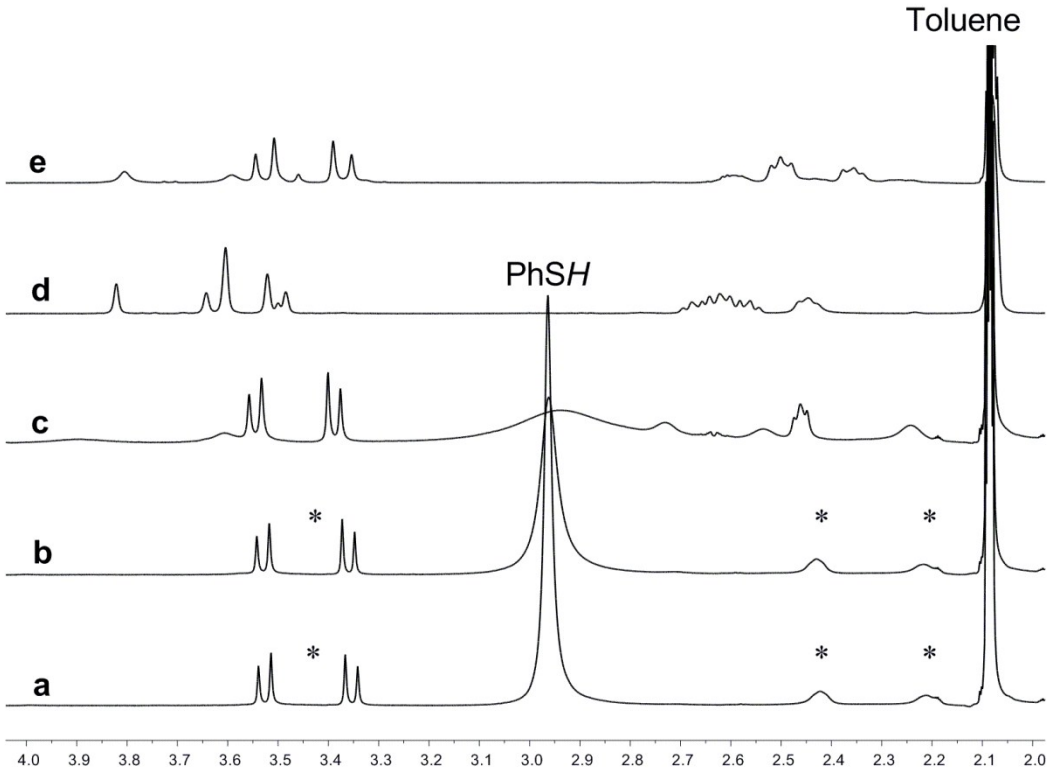


Figure S4. Detail of the aliphatic region in the ^{1}H NMR spectra of a mixture of PhSH and compound **6** (*) showing the disappearance of the S*H* resonance from PhSH due to the formation of Ph_2S_2, as well as the dynamic behaviour of the Bi(III) complex **6**: (a) immediately after adding the solvent, at 20 °C, (b) after 2 hours at 20 °C, (c) after 24 hours at 20 °C, (d) at 80 °C, (e) again at 20 °C. The resonances corresponding to **6** are denoted with an asterisk in spectra **a** and **b**. In spectra **c** – **e** the resonances corresponding to the Bi(III) intermediates formed in solution could not be unambiguously assigned. Spectra **a** - **c** are recorded on a 600 MHz NMR spectrometer, while spectra **d** and **e** on a 400 MHz NMR spectrometer.

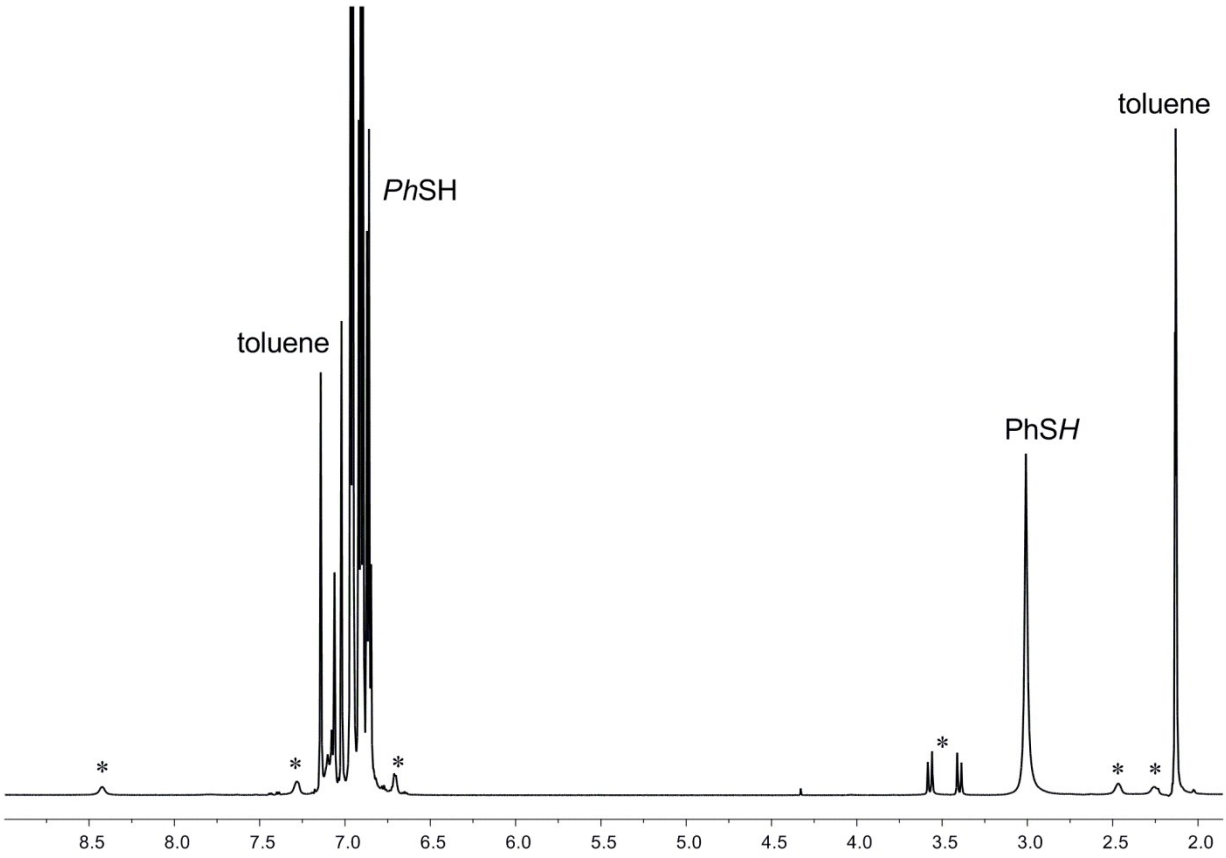


Figure S5. ^{1}H NMR spectrum of a mixture of PhSH and compound **6**. immediately after adding the solvent (20°C, toluene-d_8, 600 MHz). The resonances noted with an asterisk correspond to compound **6**.

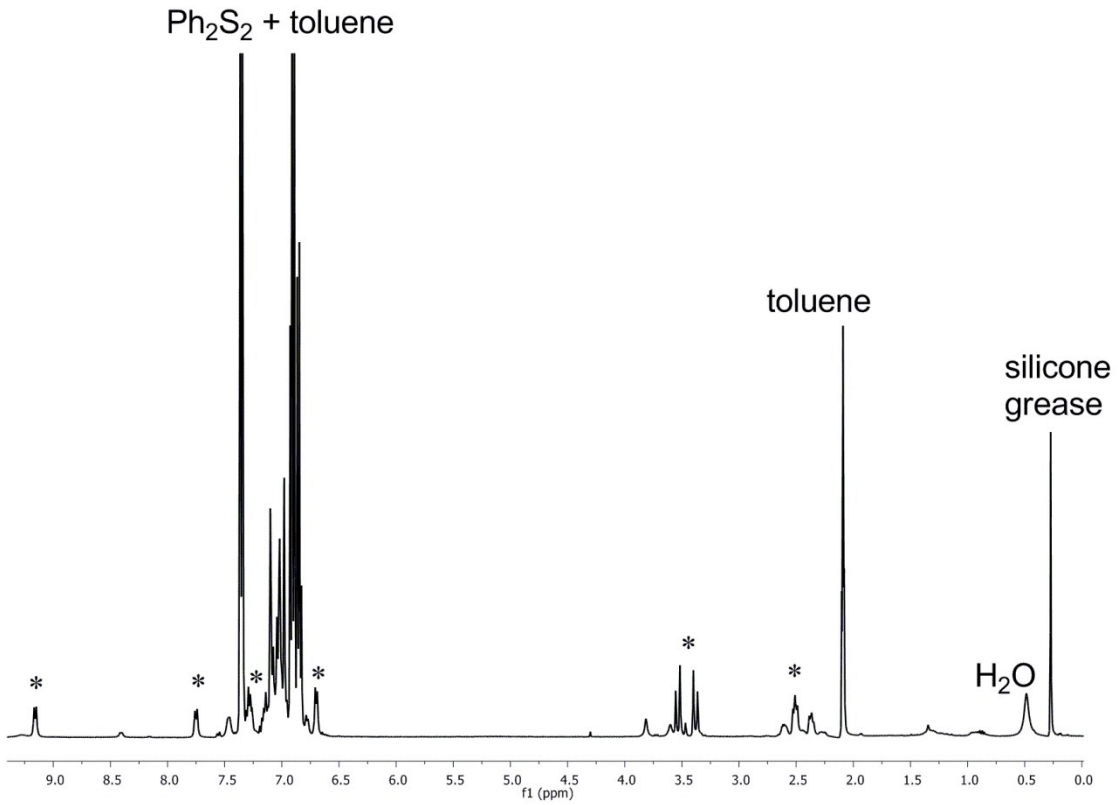
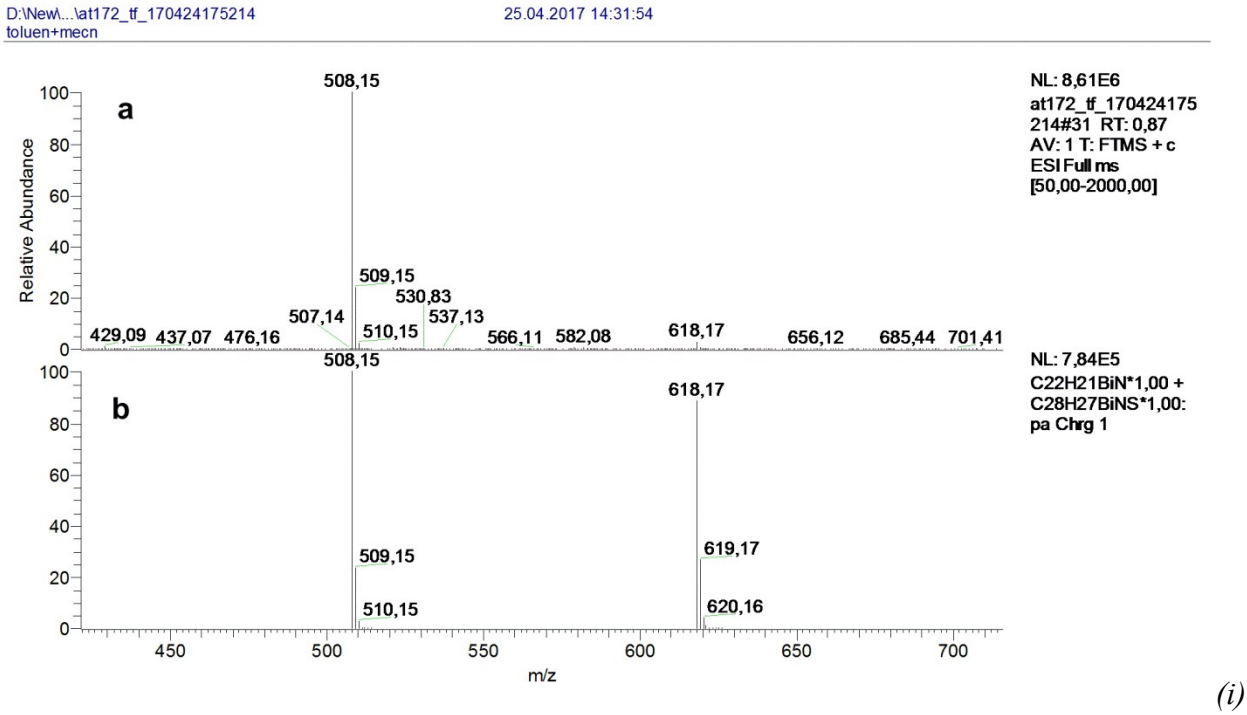
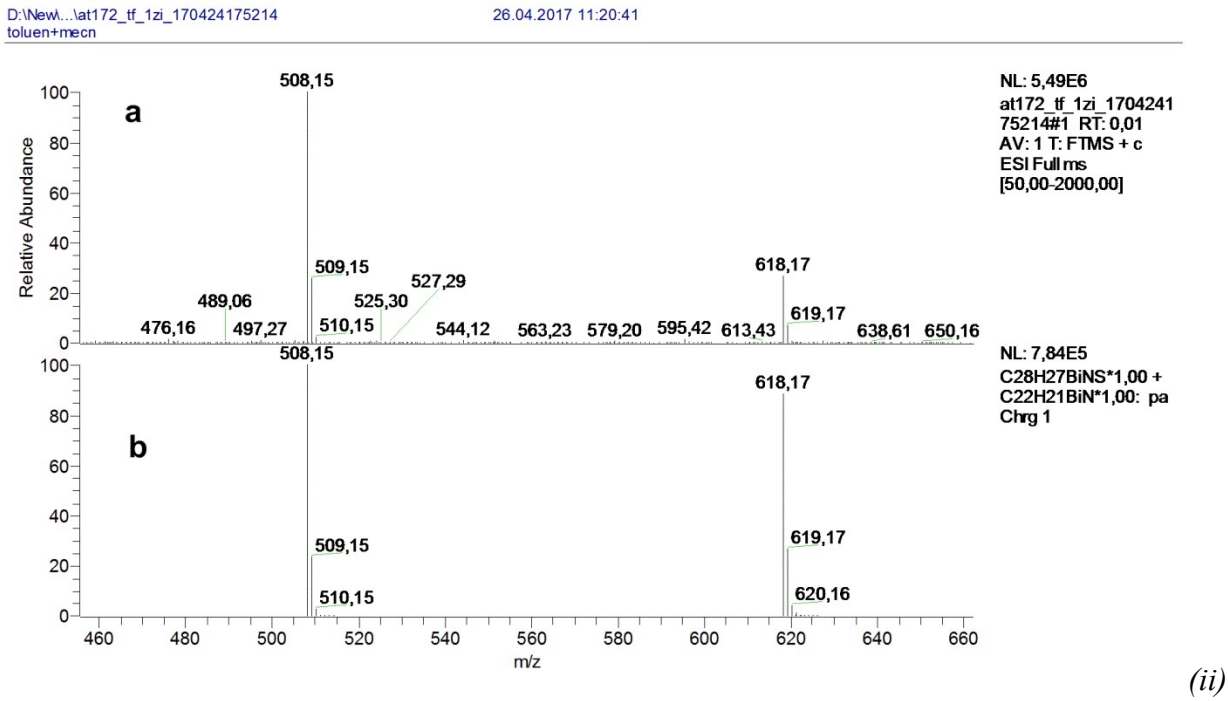


Figure S6. ^{1}H NMR spectrum of a mixture of Ph_2S_2 and diorganobismuth(III) intermediates formed in the NMR tube, at 80°C. The resonances noted with an asterisk correspond to diorganobismuth(III) intermediates.



(i)



(ii)

Figure S7. (a) Experimentaly determined and (b) simulated ESI+ MS spectra of a mixture of **6** and PhSH: *(i)* after 2 hours and *(ii)* after 24 hours, at room temperature.

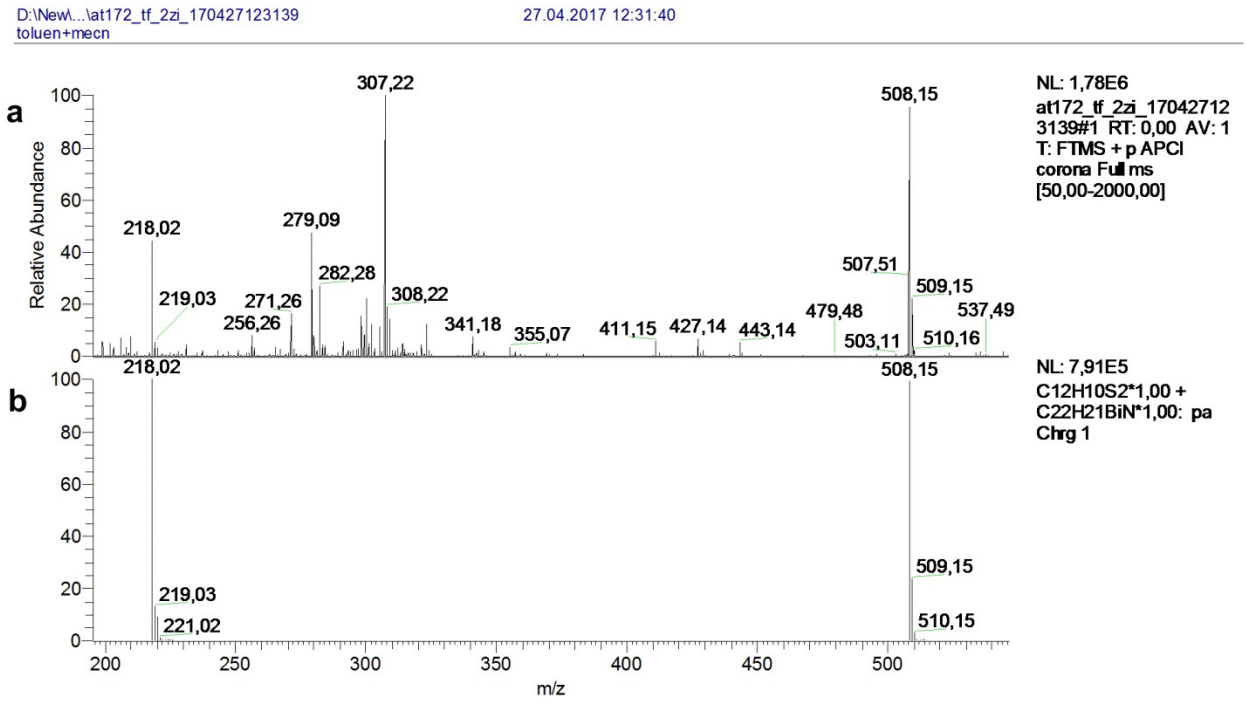


Figure S8. Experimentaly determined (a) and simulated (b) APCI+ MS spectra of a mixture of **6** and PhSH after 24 hours at room temperature and warming at 80°C.

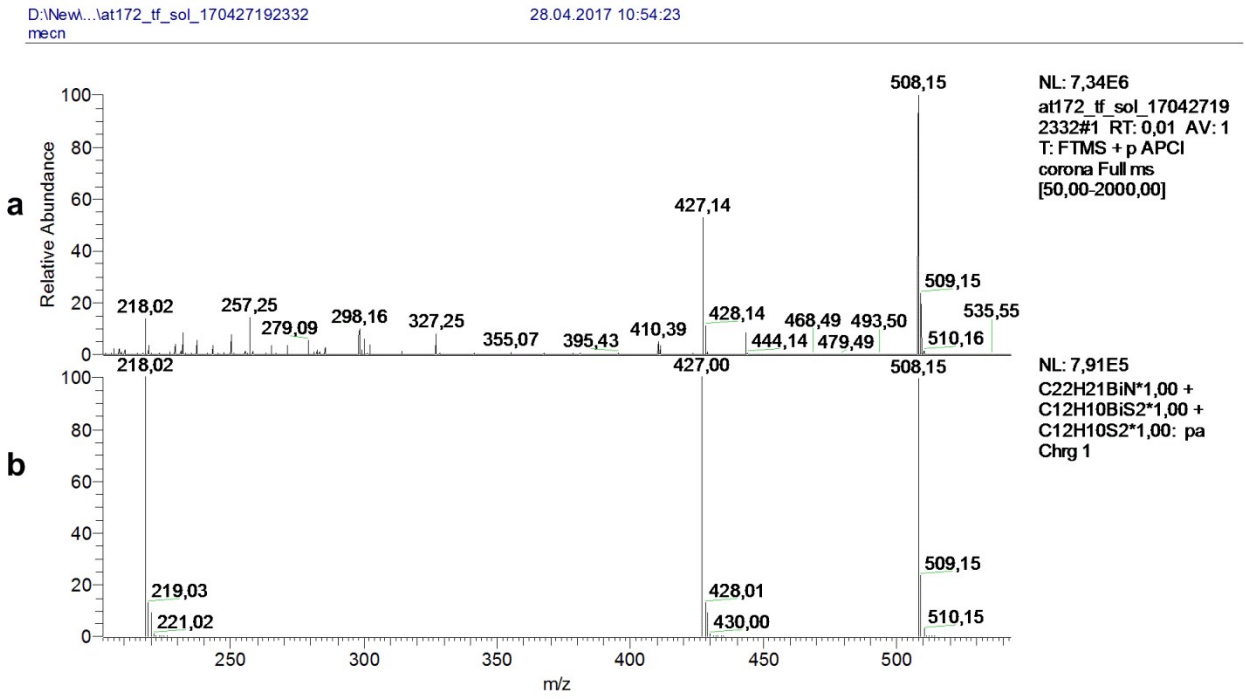


Figure S9. Experimentaly determined (a) and simulated (b) APCI+ MS spectra of the solution remained after 15 min. reflux in toluene.

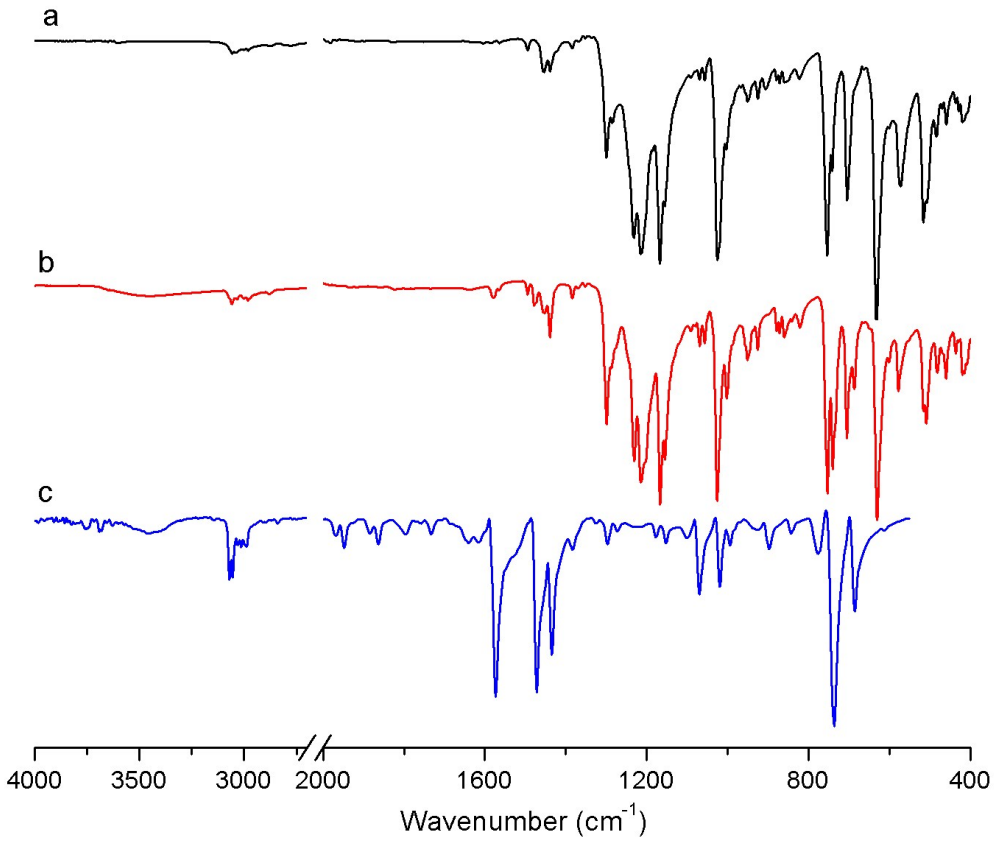


Figure S10. IR spectra of compound **4** (a), compound **4** + PhSH (b) and Ph_2S_2 (commercial product) (c).

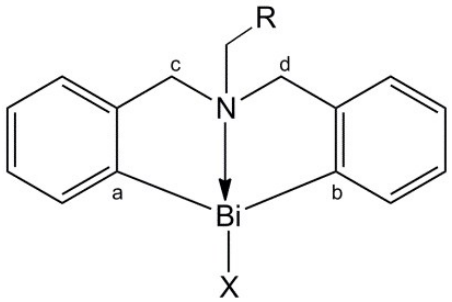
Table S1: Selected interatomic distances (Å)* and angles (°) in compounds **1** – **6**.

	1[1]	**3a**	**3b**	**4**	**5**	**2**[1]	**6**
Bi–C_a**	2.248(6)	2.275(9)	2.242(8)	2.217(4)	2.237(5)	2.247(14)	2.250(7)
Bi–C_b**	2.229(5)	2.230(9)	2.251(8)	2.256(5)	2.232(5)	2.225(13)	2.246(6)
N→Bi	2.531(4)	2.473(8)	2.453(7)	2.402(3)	2.454(4)	2.532(13)	2.479(5)
Bi−Br	2.7653(7)					2.729(2)	
Bi···Br (inter)	4.227						
Bi−O		2.377(8)	2.420(6)	2.474(3)	2.371(4)		2.424(5)
Bi···O (intra)		2.923	2.966				3.020(6)
Bi···O (inter)		3.537	3.212				3.341(7)
							3.408(7)
π Bi···Cg (intra)			3.895				
π Bi···Cg (inter)	4.097	3.586		3.535			
N−Bi−X***	157.64(10)	147.7(3)	147.9(2)	147.27(13)	144.79(14)	157.9(3)	149.20(17)
C_a−Bi−C_b	95.8(2)	93.4(3)	96.6(3)	96.44(16)	103.06(19)	97.3(5)	98.1(2)
C_c−N−C_d**	110.9(4)	109.6(8)	109.9(7)	110.4(4)	110.0(4)	111.4(11)	108.8(5)
C_a–Bi–O		80.3(4)	90.4(3)	84.18(14)	86.24(17)		86.4(2)
C_b–Bi–O		89.2(3)	81.7(3)	83.20(14)	82.89(18)		85.6(2)
C_a–Bi–N	72.28(17)	72.3(3)	72.5(3)	75.86(14)	73.13(17)	72.5(4)	74.9(2)
C_b–Bi–N	74.34(17)	75.9(3)	73.8(3)	73.74(15)	74.71(18)	73.4(4)	73.4(2)
C_6H_4/C_6H_4 dihedral angle	80.91	86.16	83.01	88.46	67.03	82.24	72.75

*Σr_{cov}(Bi,Br): 2.66 Å; Σr_{cov}(Bi,N): 1.92 Å; Σr_{cov}(Bi,O): 2.18 Å. Σr_{vdW}(Bi,Br): 4.35 Å; Σr_{vdW}(Bi,N): 3.94 Å; Σr_{vdW}(Bi,O): 3.80 Å.[50];

C_a, C_b, C_c, C_d correspond to the notation in Scheme S1. * X = Br for **1** and **2**, X = O for **3** – **6**.

1. A. M. Toma, A. Pop, A. Silvestru, T. Rüffer, H. Lang, M. Mehring, *Dalton Trans.,* 2017, **46**, 3953-3962.



Scheme S1.

Table S2. Crystal and structural refinement data for compounds **3- 6**

	3/ CCDC 1520802	**4**/ CCDC 1520801	**5**/ CCDC 1520800	**6**/ CCDC 1520799
Empirical formula	$C_{21}H_{19}BiN_2O_3$	$C_{22}H_{19}BiF_3NO_3S$	$C_{29}H_{26}BiNO_3S$	$C_{22}H_{21}BiN_2O_3$
Formula weight, g/mol	556.36	643.42	677.55	570.39
Temperature	110 K	110 K	294(2)K	297(2)K
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P 21/n	P 21/c
a [Å]	9.6340(4)	9.8797(6)	12.0680(11)	9.567(3)
b [Å]	10.1839(6)	10.1848(4)	14.0151(13)	18.155(5)
c [Å]	19.5747(10)	10.9733(5)	15.1158(14)	12.596(4)
α [°]	91.790(4)	78.190(4)	90	90
β [°]	104.227(4)	86.738(4)	91.579(2)	110.952(5)
γ [°]	93.993(4)	83.332(4)	90	90
Volume, $Å^3$	1854.76(17)	1072.86(9)	2555.6(4)	2043.1(10)
Z	4	2	4	4
Density (calculated), g/cm^3	1.992	1.992	1.761	1.854
Absorption coefficient, mm^{-1}	9.530	8.364	7.012	8.654
F(000)	1064	616	1320	1096
Crystal size, mm	0.36 x 0.34 x 0.28	0.36x0.22x0.10	0.58x 0.41x 0.37	0.34x0.29x0.24
Theta range for data collection	3.014 to 25.00°	3.063 to 24.999°	1.982 to 24.997 °	2.063 to 25.00°
Reflections collected/unique	13118 / 6521 [R(int) = 0.0293]	6582 / 3738 [R(int) = 0.0312]	23643 / 4497 [R(int) = 0.0714]	14421 / 3608 [R(int) = 0.0536]
Completeness to theta max.	99.8%	99.5%	99.8%	99.9%
Absorption correction	multi-scan			
Refinement method	Full-matrix least-squares on F^2			
Data / restrains / parameters	6521 / 0 / 475	3738 / 0 / 280	4497 / 0 / 316	3608 / 0 / 253
Goodness-of-fit on F^2 -S	1.075	1.037	0.973	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0459 wR2 = 0.0891	R1 = 0.0266 wR2 = 0.0503	R1 = 0.0330 wR2 = 0.0655	R1 = 0.0365 wR2 = 0.0726
R indices (all data)	R1 = 0.0560 wR2 = 0.0933	R1 = 0.0300 wR2 = 0.0516	R1 = 0.0466 wR2 = 0.0689	R1 = 0.0502 wR2 = 0.0782
Largest diff. peak and hole, $e/Å^3$	5.518 and -5.318	1.049 and -0.901	0.614 and -0.853	0.906 and -1.214

Table S3. Cartesian coordinates (Å) of the calculated molecular structure of **1**.

Atom	x	y	z
Bi	0.237070000	-0.106958000	-0.695451000
N	-1.199688000	0.327648000	1.512973000
C	0.929742000	-1.536481000	0.927906000
C	1.699771000	-2.653239000	0.622238000
C	1.989231000	-3.599877000	1.600906000
C	1.502626000	-3.433959000	2.891277000
C	0.737433000	-2.316396000	3.202865000
C	0.451198000	-1.362151000	2.229560000
C	-0.290640000	-0.102555000	2.590548000
C	-1.354499000	1.786316000	1.471190000
C	-0.047389000	2.465477000	1.137389000
C	0.257702000	3.700881000	1.702872000
C	1.447626000	4.346311000	1.388535000
C	2.345852000	3.750270000	0.512765000
C	2.051299000	2.511051000	-0.048858000
C	0.860918000	1.863930000	0.259568000
C	-2.485797000	-0.393150000	1.614420000
H	2.094237000	-2.778806000	-0.378492000
H	2.591003000	-4.465323000	1.353384000
H	1.718225000	-4.170776000	3.654378000
H	0.365408000	-2.180072000	4.212208000
H	-0.841928000	-0.224416000	3.530950000
H	0.435578000	0.695459000	2.746872000
H	-2.096660000	2.015856000	0.704035000
H	-1.750764000	2.166292000	2.423417000
H	-0.436814000	4.157695000	2.399124000
H	1.674780000	5.306358000	1.833982000
H	3.278155000	4.244260000	0.269526000
H	2.754142000	2.044392000	-0.727544000
H	-2.243246000	-1.423506000	1.874056000
H	-3.072914000	0.025204000	2.443352000
C	-3.289008000	-0.380112000	0.343188000
C	-3.081617000	-1.369955000	-0.617855000
C	-4.233128000	0.612426000	0.088055000
C	-3.780224000	-1.353691000	-1.817314000
H	-2.369904000	-2.162705000	-0.419715000
C	-4.933091000	0.634830000	-1.112461000
H	-4.429212000	1.370015000	0.837194000
C	-4.703112000	-0.345203000	-2.070108000
H	-3.605420000	-2.127648000	-2.553098000
H	-5.660332000	1.414631000	-1.297613000
H	-5.247310000	-0.329230000	-3.005272000
Br	2.546131000	-0.398345000	-2.121980000

Table S4. Cartesian coordinates (Å) of the calculated molecular structure of **3**.

Atom	x	y	z
Bi	-0.239733000	-0.083243000	-0.661809000
N	1.124778000	0.278030000	1.544247000
C	-0.777206000	1.956925000	0.169022000
C	-1.432064000	2.913842000	-0.600649000
C	-1.613045000	4.205773000	-0.114890000
C	-1.128673000	4.548252000	1.141402000
C	-0.476178000	3.595959000	1.915457000
C	-0.303006000	2.298991000	1.438444000
C	0.304706000	1.235904000	2.315833000
C	1.089119000	-1.069288000	2.136016000
C	-0.302898000	-1.651238000	2.068672000
C	-0.774266000	-2.474018000	3.088209000
C	-2.051576000	-3.017155000	3.018027000
C	-2.869719000	-2.726718000	1.933276000
C	-2.406932000	-1.898059000	0.915652000
C	-1.127545000	-1.360035000	0.978888000
C	2.499126000	0.805584000	1.379862000
H	-1.820209000	2.650435000	-1.576534000
H	-2.127180000	4.942860000	-0.718729000
H	-1.258554000	5.554166000	1.519338000
H	-0.106146000	3.860757000	2.899654000
H	0.900508000	1.678926000	3.122102000
H	-0.501279000	0.671834000	2.785575000
H	1.781932000	-1.693950000	1.569188000
H	1.448545000	-1.048232000	3.173425000
H	-0.142975000	-2.684899000	3.944175000
H	-2.409882000	-3.656783000	3.814213000
H	-3.868654000	-3.140339000	1.879252000
H	-3.054621000	-1.665891000	0.080976000
H	2.397693000	1.872579000	1.182995000
H	3.042986000	0.694943000	2.326904000
C	3.261108000	0.165490000	0.252966000
C	3.170299000	0.699522000	-1.032873000
C	4.047091000	-0.967503000	0.454093000
C	3.823025000	0.097605000	-2.099892000
H	2.585995000	1.597672000	-1.195230000
C	4.701984000	-1.573876000	-0.611170000
H	4.154633000	-1.373933000	1.452342000
C	4.584826000	-1.046203000	-1.891289000
H	3.738547000	0.520979000	-3.092034000
H	5.305534000	-2.455798000	-0.440952000
H	5.092352000	-1.519040000	-2.721707000
O	-2.286705000	0.076806000	-1.701861000
N	-2.478733000	-0.946927000	-2.519626000
O	-1.632778000	-1.850315000	-2.501544000
O	-3.467108000	-0.933164000	-3.218781000

Table S5. Cartesian coordinates (Å) of the calculated molecular structure of **4**.

Atom	x	y	z
Bi	0.028576000	0.103575000	-0.049743000
N	2.515724000	-0.428285000	0.276891000
C	0.231211000	-0.900578000	1.960841000
C	-0.784743000	-0.874421000	2.910508000
C	-0.560535000	-1.372839000	4.190498000
C	0.685732000	-1.887656000	4.526293000
C	1.702513000	-1.918334000	3.579130000
C	1.479320000	-1.432504000	2.293301000
C	2.533185000	-1.565589000	1.226236000
C	2.925696000	-0.852118000	-1.075134000
C	1.914312000	-1.802839000	-1.670713000
C	2.320007000	-2.824167000	-2.524917000
C	1.380640000	-3.678868000	-3.089839000
C	0.032479000	-3.523030000	-2.792269000
C	-0.378900000	-2.510080000	-1.930928000
C	0.557920000	-1.651494000	-1.369028000
C	3.335873000	0.687538000	0.812506000
H	-1.759424000	-0.480587000	2.652232000
H	-1.356119000	-1.353492000	4.924395000
H	0.867033000	-2.265920000	5.524008000
H	2.671398000	-2.329656000	3.839160000
H	3.532272000	-1.672041000	1.662516000
H	2.333838000	-2.470545000	0.651949000
H	3.000034000	0.045720000	-1.690692000
H	3.922563000	-1.310026000	-1.048585000
H	3.373210000	-2.955346000	-2.746399000
H	1.703097000	-4.469599000	-3.754759000
H	-0.701157000	-4.190173000	-3.226238000
H	-1.429481000	-2.401356000	-1.697407000
H	3.113517000	0.746595000	1.877614000
H	4.397074000	0.429653000	0.709980000
C	3.045227000	2.013466000	0.167494000
C	2.052395000	2.838801000	0.697101000
C	3.732012000	2.436166000	-0.969309000
C	1.728318000	4.042344000	0.085701000
H	1.533627000	2.537447000	1.599733000
C	3.410583000	3.639689000	-1.584777000
H	4.530142000	1.824457000	-1.371871000
C	2.402269000	4.440716000	-1.062606000
H	0.951298000	4.667539000	0.504950000
H	3.948764000	3.952788000	-2.469777000
H	2.148369000	5.376109000	-1.543365000
O	-2.184950000	-0.639178000	0.030806000
O	-2.465192000	0.783721000	-1.922873000
O	-4.160413000	-0.949374000	-1.376148000
S	-3.152871000	-0.027551000	-0.945913000
C	-4.020802000	1.191539000	0.156659000
F	-4.913386000	1.900279000	-0.534114000
F	-3.124994000	2.043312000	0.691385000
F	-4.648267000	0.570268000	1.159713000

Table S6. Cartesian coordinates (Å) of the calculated molecular structure of **5**.

Atom	x	y	z
Bi	0.184557000	-0.258601000	0.067533000
N	-2.132693000	0.910872000	-0.168120000
C	-0.134862000	1.033762000	1.898804000
C	0.642339000	0.888580000	3.043341000
C	0.330488000	1.595053000	4.201405000
C	-0.769191000	2.444274000	4.219923000
C	-1.546540000	2.596443000	3.077865000
C	-1.231655000	1.899232000	1.914034000
C	-2.001169000	2.140702000	0.641810000
C	-2.164948000	1.209802000	-1.609720000
C	-0.852698000	1.802373000	-2.067097000
C	-0.828262000	2.767632000	-3.069934000
C	0.381172000	3.298870000	-3.502085000
C	1.570436000	2.875346000	-2.922512000
C	1.553708000	1.918154000	-1.911846000
C	0.345602000	1.381603000	-1.482132000
C	-3.300671000	0.123527000	0.290598000
H	1.506302000	0.236270000	3.027580000
H	0.942212000	1.479234000	5.087295000
H	-1.021525000	2.988751000	5.120753000
H	-2.398126000	3.267532000	3.089827000
H	-2.990235000	2.564775000	0.849295000
H	-1.457966000	2.870365000	0.041033000
H	-2.353868000	0.271115000	-2.134079000
H	-2.997659000	1.884987000	-1.847112000
H	-1.758031000	3.109313000	-3.511016000
H	0.392287000	4.047151000	-4.284133000
H	2.514781000	3.289142000	-3.252333000
H	2.487861000	1.601497000	-1.467719000
H	-3.321082000	0.207451000	1.376812000
H	-4.219889000	0.584211000	-0.093159000
C	-3.234968000	-1.329650000	-0.088451000
C	-2.613737000	-2.237075000	0.770489000
C	-3.763833000	-1.798633000	-1.289334000
C	-2.497826000	-3.576690000	0.426168000
H	-2.221975000	-1.888041000	1.718635000
C	-3.647743000	-3.138646000	-1.639484000
H	-4.278565000	-1.114234000	-1.952496000
C	-3.008630000	-4.028597000	-0.784937000
H	-2.010428000	-4.266925000	1.102070000
H	-4.059208000	-3.487714000	-2.577485000
H	-2.916710000	-5.071653000	-1.057563000
O	2.409312000	-0.082521000	0.595012000
O	2.603051000	-1.619459000	-1.275031000
O	4.423326000	-0.008683000	-0.776562000
S	3.368023000	-0.864205000	-0.297286000
C	4.107370000	-2.005099000	0.831058000
C	3.975705000	-3.313671000	0.696175000
H	4.457063000	-3.997464000	1.383866000
H	3.390339000	-3.729166000	-0.113551000
H	4.690670000	-1.530006000	1.609458000