Supporting Information

Unusual C-N Coupling Reactivity of Thiopyridazines – Efficient Synthesis of Iron Diorganotrisulfide Complexes

Michael Tüchler,[a] Stefan Holler,[a] Jörg A. Schachner,[a] Ferdinand Belaj,[a] and Nadia C. Mösch-Zanetti*[a]

[a] Institute of Chemistry, University of Graz. Schubertstrasse 1, 8010 Graz/Austria

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UV-Vis Spectroscopy

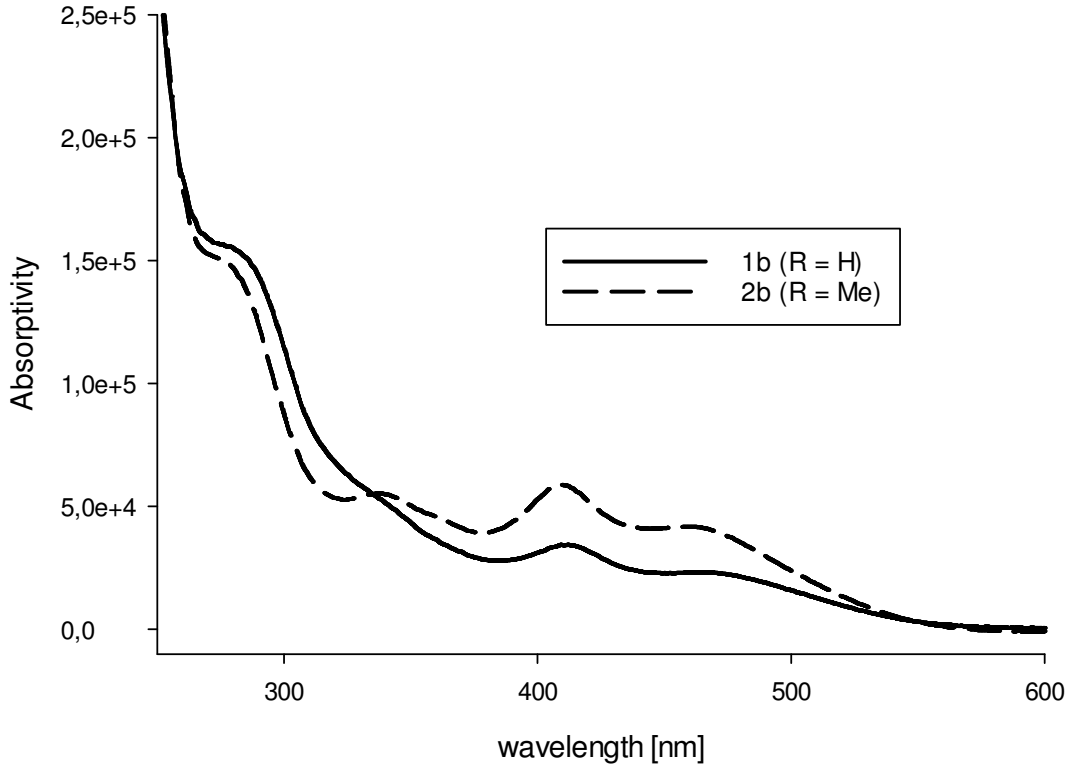

Figure S1. UV-Vis spectra of complexes **1b** and **2b**, measured as 0.346 µM (**1b**) and 0.374 µM (**2b**) solutions in acetonitrile

Table S1. Absorption maxima and absorptivities of complexes **1b** and **2b**, measured as 0.346 µM (**1b**) and 0.374 µM (**2b**) solutions in acetonitrile

1b		**2b**	
λ [nm]	**ε** [$Lmol^{-1}cm^{-1}$]	**λ** [nm]	**ε** [$Lmol^{-1}cm^{-1}$]
223	45780	207	65800
280	15500	278	13400
345	5700	340	5000
412	3500	409	5500
472	2300	465	3900

NMR Spectroscopy

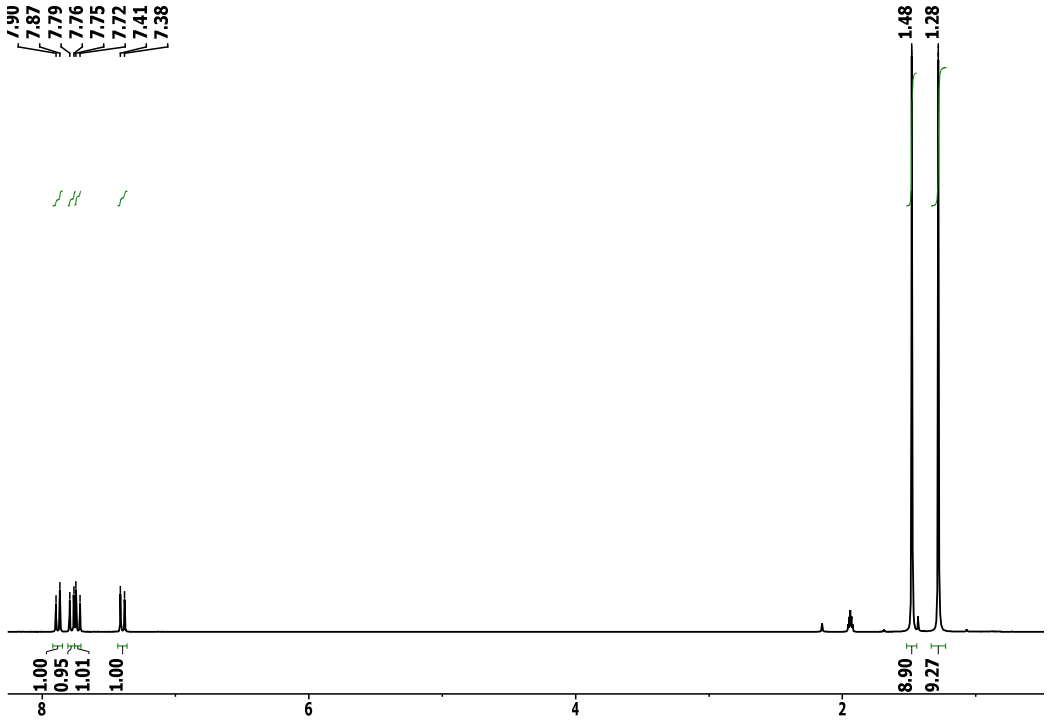

Figure S2. ^{1}H NMR spectrum of **3** in acetonitrile-d3.

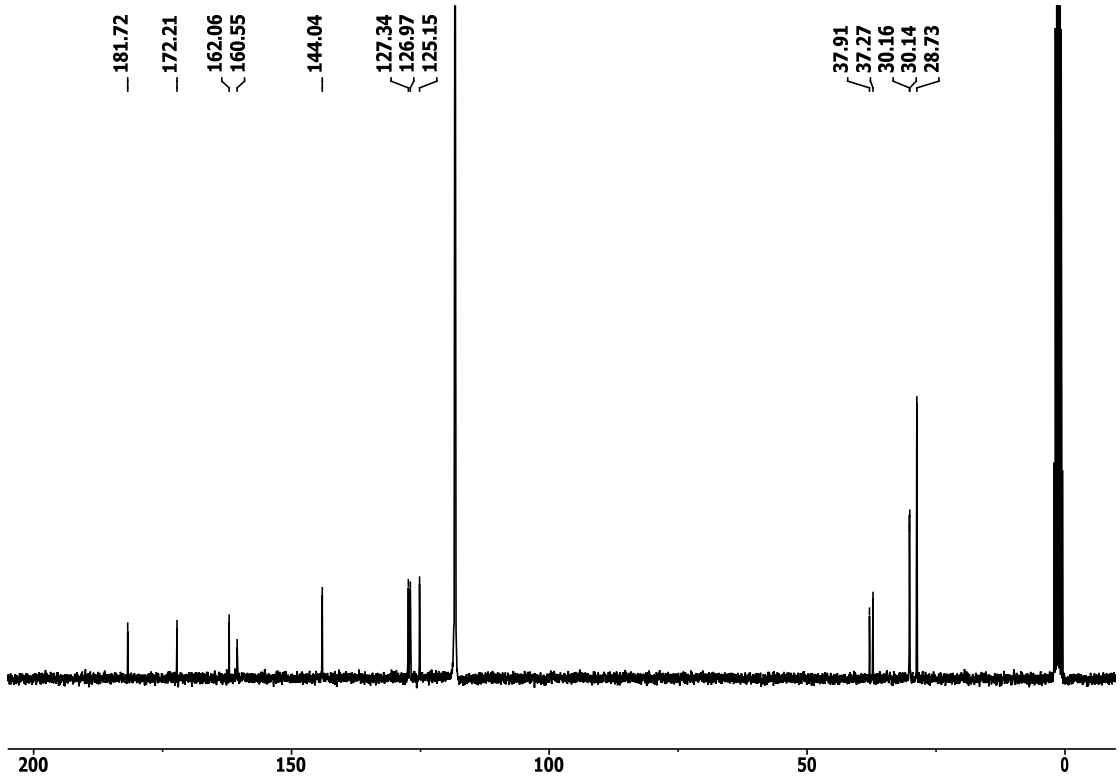

Figure S3. ^{13}C NMR spectrum of **3** in acetonitrile-d3.

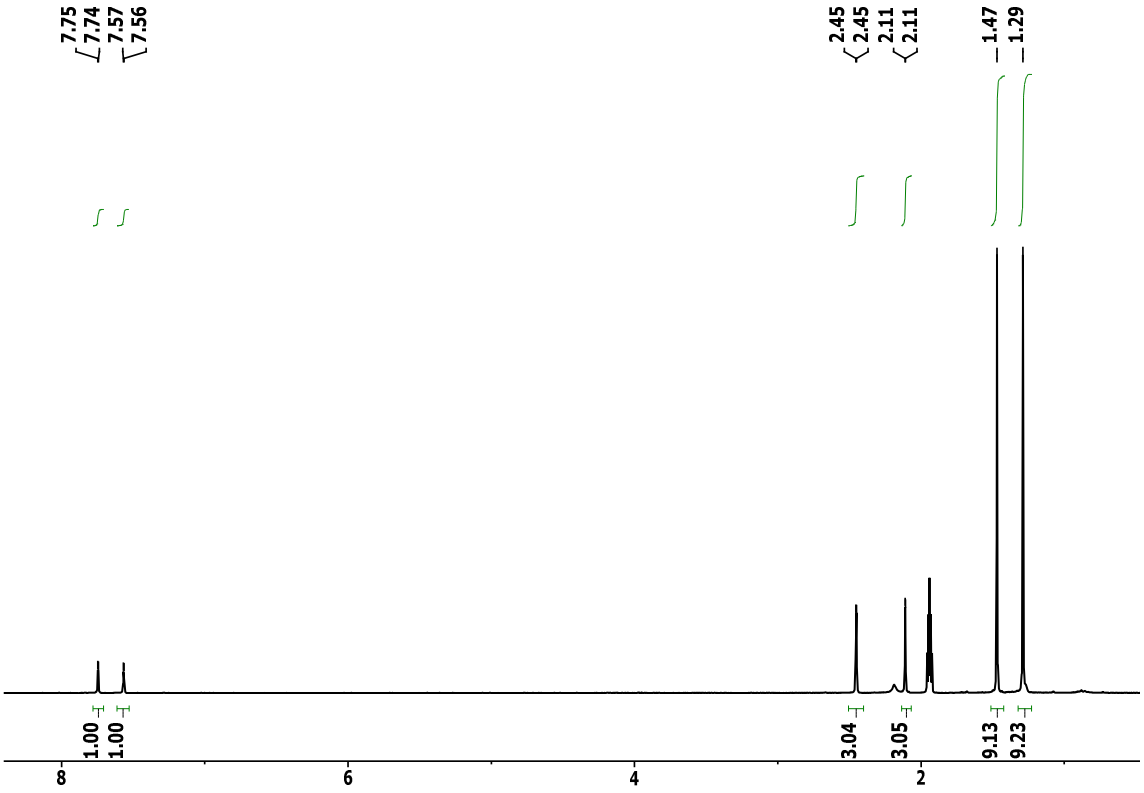

Figure S4. ^{1}H NMR spectrum of **4** in acetonitrile-d3.

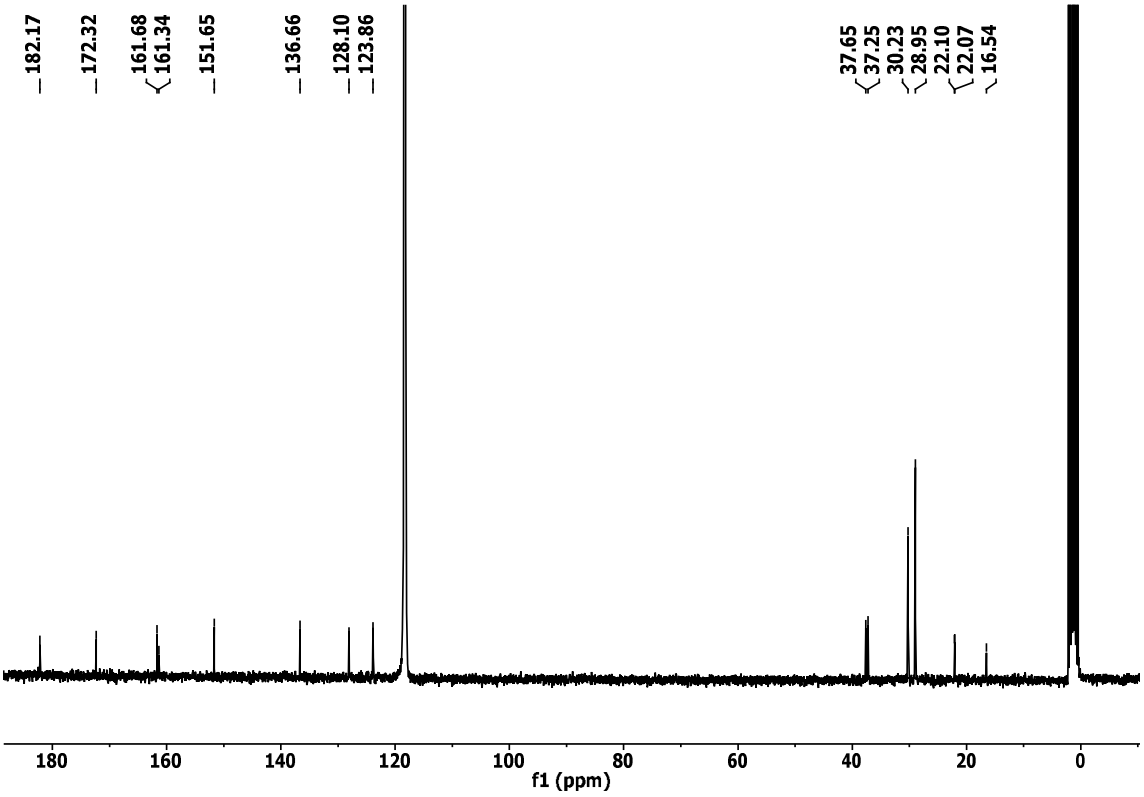

Figure S5. ^{13}C NMR spectrum of **4** in acetonitrile-d3.

Molecular Structures

The pyridazine disulfide was crystallized by slow evaporation of a dichloromethane solution.

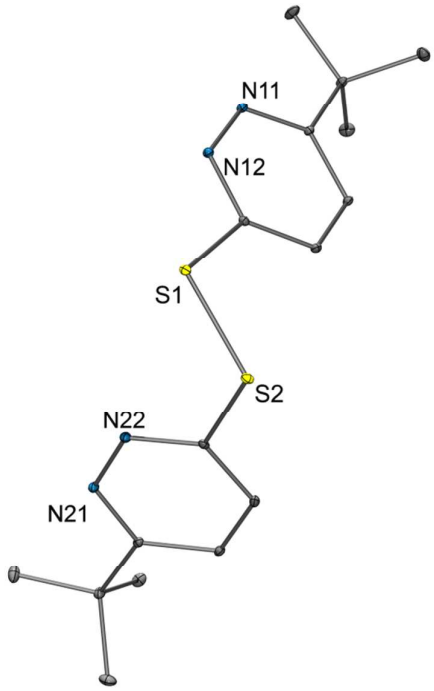

Figure S6. Molecular structure and atom numbering scheme of the pyridazine-disulfide (PnS_2Pn). Hydrogen atoms have been omitted for clarity.

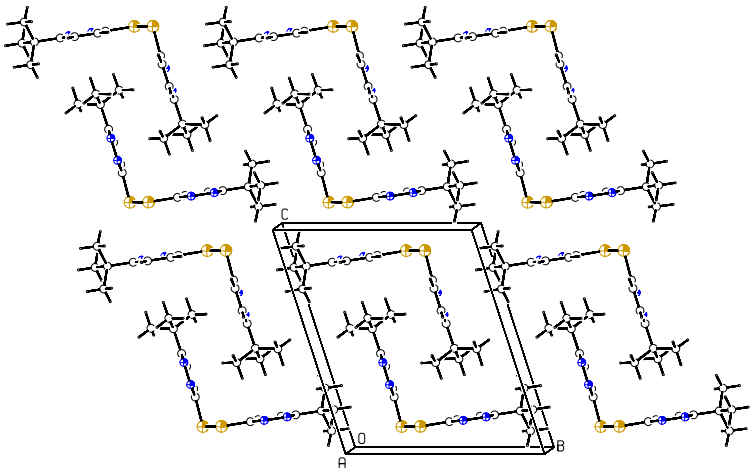

Figure S7. ORTEP plot of the packing of PnS_2Pn. The atoms are drawn with arbitrary radii.

Table S2. Crystal data, data collection and refinement for PnS_2Pn

Crystal data	**PnS_2Pn**
Empirical formula	$C_{16}H_{22}N_4S_2$
Formula weight	334.49
Crystal description	needle, colourless
Crystal size	0.33 x 0.17 x 0.05mm
Crystal system, space group	triclinic, P -1
Unit cell dimensions:	
a	5.82840(10)Å
b	11.5363(3)Å
c	13.7476(3)Å
α	107.9297(10)°
β	95.8257(9)°
γ	95.3949(9)°
Volume	867.23(3)Å^3
Z	2
Calculated density	1.281Mg/m^3
F(000)	356
Linear absorption coefficient μ	0.309mm^{-1}
Max. and min. transmission	1.000 and 0.837
Unit cell determination	2.80° < θ < 30.60°
	4764 reflections used at 100K
Data collection	
Temperature	100 K
Diffractometer	Bruker APEX-II CCD
Radiation source	fine-focus sealed tube
Radiation and wavelength	MoK_α, 0.71073Å
Monochromator	graphite
Scan type	φ and ω scans
θ range for data collection	2.80 to 30.00°
Reflections collected / unique	9787 / 5038
Significant unique reflections	4216 with I > 2σ(I)
R(int), R(sigma)	0.0214, 0.0323
Completeness (θ)	99.6% (30.0°)
Refinement	
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restraints	5038 / 213 / 0
Goodness-of-fit on F^2	1.038
Final R indices [I > 2σ(I)]	R1 = 0.0345, wR2 = 0.0859
R indices (all data)	R1 = 0.0448, wR2 = 0.0908
Extinction expression	none
Largest Δ/ σ in last cycle	0.001
Largest difference peak and hole	0.545 and -0.281e/Å^3
Structure Solution Program	SHELXS-97[1]
Structure Refinement Program	SHELXL-2014/6[1]
CCDC number	1532936

Complex **1a** was crystallized from slow evaporation of a dichloromethane solution. The structure could not be solved by direct methods, but by interpretation of the patterson map and subsequent structure expansion (SHELXS-97).[1] Several attempts with different superposition vectors had to be made to overcome the pseudo-symmetry problem and to get a correct solution. Full-matrix least-squares refinements of F^2 values against all reflections were performed by direct methods (SHELXL-97).[1]

The asymmetric unit consists of one cationic complex (**A**) lying on a general position, two cationic complexes (**B**, **C**) lying with their Fe centres on inversion centres (Figure S8), 4 triflate anions, and 6 dichloromethane solvent molecules. The structure is composed of layers normal to the long c-axis, where layers consisting of complexes **A** alternate with layers consisting of **B** and **C** (Figure S9). This results in pseudo-symmetry, but no disorder was detected. The differences between **A**, **B** and **C** are mainly the orientations of the *tert*-butyl groups.

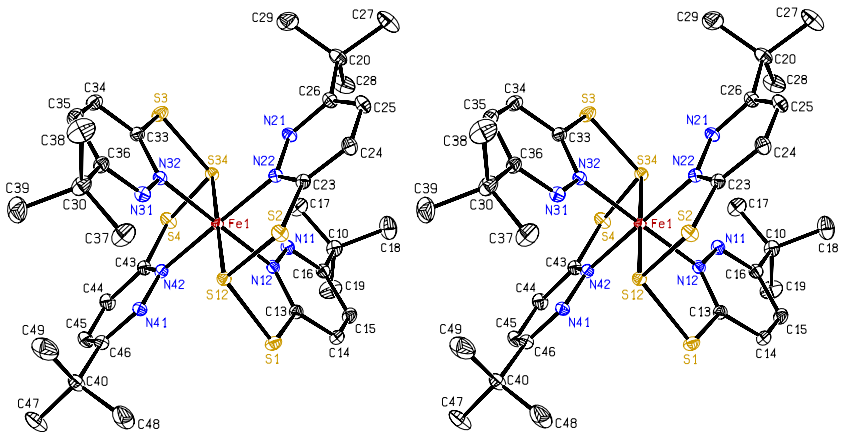

Figure S8. Stereoscopic ORTEP plot of one of the three cationic complexes of the asymmetric unit of **1a,** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms, solvent molecules and triflate anions were omitted for clarity reasons.

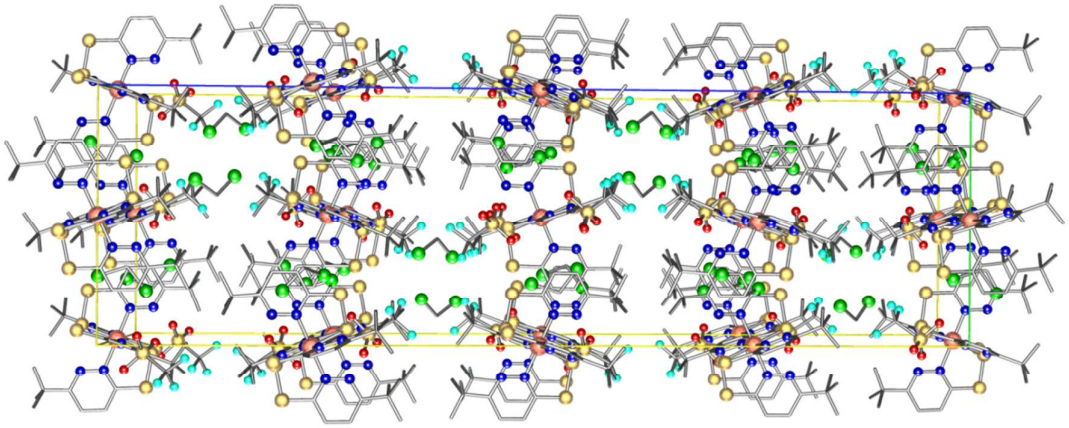

Figure S9. Plot of the packing of **1a**. The H atoms were omitted for clarity reasons. The other atoms are drawn with arbitrary radii.

Complex **2a** was crystallized from slow evaporation of a dichloromethane solution.

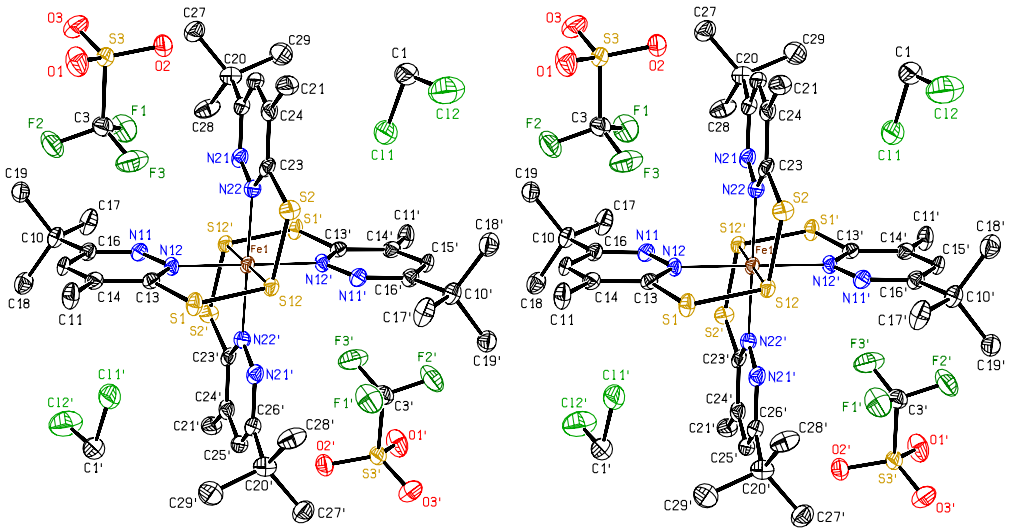

Figure S10. Stereoscopic ORTEP plot of **2a**, showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons.

The C-N coupled thiopyridazine **3** was crystallized by slow evaporation of an acetonitrile solution.

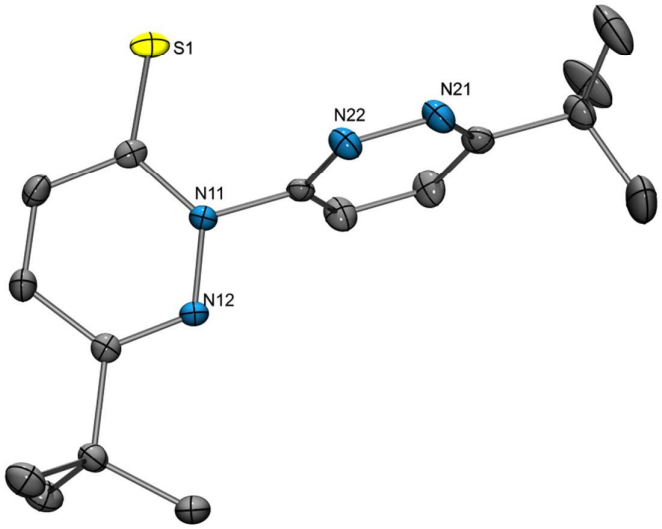

Figure S11. Molecular structure of **3**, showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The orientation, having the smaller site occupation factor of 0.265(3) of the disordered *tert*-butyl group and hydrogen atoms are omitted for clarity.

The C-N coupled, substituted thiopyridazine **4** was crystallized by slow evaporation of an acetonitrile solution.

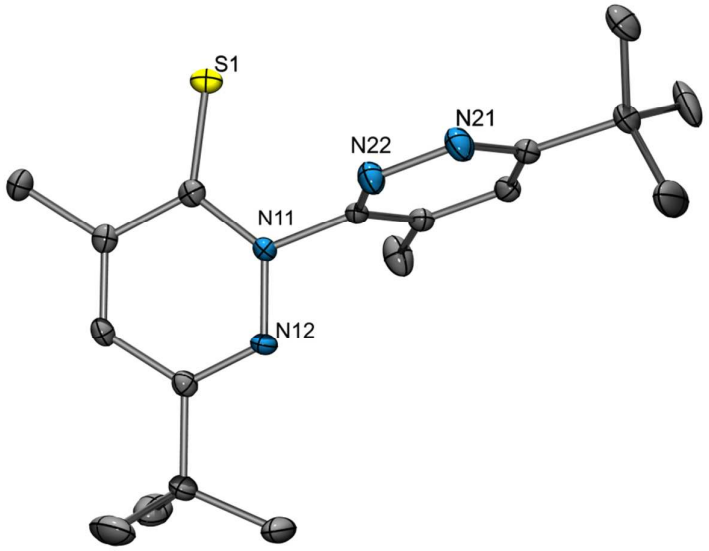

Figure S12. Molecular structure of **4**, showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S3. Crystal data, data collection and refinement for complexes **1a** and **2a**

Crystal data	**1a**	**2a**
Empirical formula	$C_{32}H_{44}FeN_8S_6^{+2}$ $(CF_3SO_3S^-)_2$ · $3CH_2Cl_2$	$C_{36}H_{52}FeN_8S_6^{+2}(CF_3O_3S^-)_2$ · $2CH_2Cl_2$
Formula weight	1341.88	1313.05
Crystal description	block, orange	block, red
Crystal size	0.32 x 0.25 x 0.21mm	0.21 x 0.16 x 0.09mm
Crystal system, space group	monoclinic, P 2_1/c	triclinic, P -1
Unit cell dimensions:		
a	15.2993(4)Å	9.392(4)Å
b	14.6458(4)Å	13.237(5)Å
c	50.0036(13)Å	13.440(5)Å
α		105.154(9)°
β	96.2896(9)°	110.447(9)°
γ		105.533(10)°
Volume	11136.9(5)$Å^3$	1386.9(10)$Å^3$
Z	8	1
Calculated density	1.601Mg/m^3	1.572Mg/m^3
F(000)	5488	676
Linear absorption coefficient μ	0.929mm^{-1}	0.837mm^{-1}
Max. and min. transmission	1.0000 and 0.8626	1.000 and 0.531
Unit cell determination	2.48° < θ < 30.75°	2.34° < θ < 26.92°
	9748 reflections used at 100K	9771 reflections used at 100K
Data collection		
Temperature	100K	
Diffractometer	Bruker APEX-II CCD	
Radiation source	fine-focus sealed tube	Incoatec microfocus sealed tube
Radiation and wavelength	MoKα, 0.71073Å	
Monochromator	graphite	multilayer monochromator
Scan type	φ and ω scans	
θ range for data collection	2.15 to 30.00°	2.43 to 25.00°
Reflections collected / unique	96005 / 32325	20837 / 4871
Significant unique reflections	23702 with I > 2σ(I)	3805 with I > 2σ(I)
R(int), R(sigma)	0.0260, 0.0361	0.0686, 0.0664
Completeness (θ)	99.4% (30°)	99.8% (25°)
Refinement		
Refinement method	Full-matrix least-squares on F^2	
Data / parameters / restraints	32325 / 1362 / 0	4871 / 345 / 0
Goodness-of-fit on F^2	1.030	1.106
Final R indices [I > 2σ(I)]	R1 = 0.0372, wR2 = 0.0865	R1 = 0.0641, wR2 = 0.1683
R indices (all data)	R1 = 0.0580, wR2 = 0.0931	R1 = 0.0824, wR2 = 0.1829
Extinction expression	none	none
Largest Δ/ σ in last cycle	0.003	0.000
Largest difference peak and hole	0.903 and -0.715e/$Å^3$	1.197 and -0.652e/$Å^3$
Structure Solution Program	SHELXS-97[1]	
Structure Refinement Program	SHELXL-2014/6[1]	
CCDC number	1532932	1532933

Table S4. Crystal data, data collection and refinement for the C-N coupled thiopyridazines **3** and **4**

Crystal data	**3**	**4**
Empirical formula	$C_{16}H_{22}N_4S$	$C_{18}H_{26}N_4S$
Formula weight	302.43	330.49
Crystal description	board, yellow	needle, orange
Crystal size	0.36 x 0.25 x 0.06mm	0.28 x 0.11 x 0.09mm
Crystal system, space group	monoclinic, P 2_1/c	monoclinic, C 2/c
Unit cell dimensions:		
a	10.8122(6)Å	24.385(18)Å
b	6.0819(3)Å	13.956(5)Å
c	25.7395(14)Å	11.314(4)Å
β	98.431(3)°	95.677(12)°
Volume	1674.31(15)Å^3	3831(3)Å^3
Z	4	8
Calculated density	1.200Mg/m^3	1.146Mg/m^3
F(000)	648	1424
Linear absorption coefficient μ	0.193mm^{-1}	0.174mm^{-1}
Max. and min. transmission	1.000 and 0.880	1.000 and 0.773
Unit cell determination	2.66° < θ < 30.65°	2.53° < θ < 27.78°
	5086 reflections used at 100K	6131 reflections used at 100K
Data collection		
Temperature	100K	
Diffractometer	Bruker APEX-II CCD	
Radiation source	Incoatec microfocus sealed tube	
Radiation and wavelength	MoKα, 0.71073Å	
Monochromator	multilayer monochromator	
Scan type	φ and ω scans	
θ range for data collection	3.20 to 26.00°	2.91 to 26.00°
Reflections collected / unique	13272 / 3285	23702 / 3752
Significant unique reflections	2771 with I > 2σ(I)	2932 with I > 2σ(I)
R(int), R(sigma)	0.0357, 0.0343	0.0671, 0.0460
Completeness (θ)	99.8% (26.0°)	99.8% (26.0°)
Refinement		
Refinement method	Full-matrix least-squares on F^2	
Data / parameters / restraints	3285 / 218 / 4	3752 / 226 / 0
Goodness-of-fit on F^2	1.065	1.047
Final R indices [I > 2σ(I)]	R1 = 0.0360, wR2 = 0.0826	R1 = 0.0389, wR2 = 0.0933
R indices (all data)	R1 = 0.0447, wR2 = 0.0868	R1 = 0.0552, wR2 = 0.1010
Extinction expression	none	
Largest Δ/ σ in last cycle	0.001	0.001
Largest difference peak and hole	0.337 and -0.230e/Å^3	0.247 and -0.259e/Å^3
Structure Solution Program	SHELXS-97[1]	
Structure Refinement Program	SHELXL-2014/6[1]	
CCDC number	1532934	1532935

References

(1) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.