Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI)

Synthesis and Coordination Behaviour of 1*H*-1,2,3-Triazole-4,5-Dithiolates

David Schallenberg,[a] Nils Pardemann,[a] Alexander Villinger[a] and Wolfram W. Seidel*[a,b]

[a]Institut für Chemie, Universität Rostock, Albert-Einstein-Straße 3a, 18059 Rostock, Germany.
Email: wolfram.seidel@uni-rostock.de
[b]Leibniz Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany

1. Crystallographic details

Single crystals suitable for X-ray diffraction analysis were selected in Fomblin YR-1800 perfluoropolyether oil (Alfa Aesar) at ambient temperature and mounted on a glass fiber. During the measurement, the samples were cooled to 123(2) K. Diffraction data were collected on a Bruker D8 QUEST diffractometer and a Bruker Kappa Apex II diffractometer using graphite monochromated Mo-K_α radiation. Structure solutions were found by direct methods (SHELXS-97 or SHELXS-2013)[S1] and were refined by full-matrix least-squares procedures on F^2 (SHELXL-2013).[S2] All non-hydrogen atoms were anisotropically refined unless stated otherwise. Hydrogen atoms were included at calculated positions with fixed thermal parameters unless stated otherwise. The unit cell of complex **12** contains four disordered dichloromethane molecules, which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

1.1 Overview

Table S1. Crystallographic details for **2**, **3** and **5**.

	2	**3**	**5**
empirical formula	$C_{24}H_{23}N_3S_2$	$C_{23}H_{21}N_3S_2$	$C_{30}H_{44}N_6S_4Si_2$
M_W / g·mol^{-1}	417.57	403.55	673.13
colour, habit	colourless, block	colourless, block	yellow, stick
crystal system	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	$P2_1/c$
a / Å	7.7879(4)	8.5292(5)	13.5190(4)
b / Å	8.0677(4)	8.8087(6)	16.6351(5)
c / Å	17.5632(8)	15.2170(10)	16.6347(5)
α / °	82.267(2)	82.215(2)	90
β / °	84.301(2)	75.818(2)	92.0320(10)
γ / °	80.255(2)	67.935(2)	90
V / Å^3	1074.38(9)	1026.04(12)	3738.62(19)
Z	2	2	4
$\rho_{\text{calcd.}}$ / g·cm^{-1}	1.291	1.306	1.196
μ / mm^{-1}	0.263	0.273	0.346
$\lambda_{\text{MoK}\alpha}$ / Å	0.71073	0.71073	0.71073
T / K	173(2)	173(2)	153(2)
collected refl.	26470	25599	40882
unique refl.	7407	6539	9958
refl. $I > 2\sigma(I)$	5812	5073	7562
R_{int}	0.0290	0.0388	0.0359
parameters/restraints	264/0	253/0	389/0
R_1 [$I > 2\sigma$(I)]	0.0389	0.0385	0.0383
wR_2 (all data)	0.1058	0.1026	0.0989

GooF	1.021	1.030	1.017
resid. density [eÅ^{-3}]	0.374/-0.226	0.293/-0.346	0.341/-0.309
CCDC	2145136	2145137	2145135

Table S2. Crystallographic details for **10, 11** and **12**.

	10	**11**	**12**
empirical formula	$C_{20}H_{19}N_3S_2Ti$	$C_{36}H_{33}N_3NiP_2S_2$	$C_{35}H_{31}N_3NiP_2S_2 \cdot CH_2Cl_2$
M_W / g·mol^{-1}	413.40	692.42	763.32
colour, habit	black, block	brown, block	yellow, plate
crystal system	Triclinic	Triclinic	Monoclinic
space group	*P -1*	*P -1*	$P2_1/c$
a / Å	7.7274(5)	9.3214(7)	9.9178(4)
b / Å	8.8234(5)	11.2004(9)	16.9500(7)
c / Å	14.3988(8)	17.4208(15)	20.6572(9)
α / °	99.292(3)	73.090(4)	90
β / °	102.649(3)	85.479(4)	96.336(2)
γ / °	93.060(3)	67.171(4)	90
V / Å^3	941.32(10)	1602.6(2)	3451.4(2)
Z	2	2	4
$\rho_{calcd.}$ / g·cm^{-1}	1.459	1.435	1.469
μ / mm^{-1}	0.685	0.867	0.962
$\lambda_{MoK\alpha}$ / Å	0.71073	0.71073	0.71073
T / K	173(2)	173(2)	173(2)
collected refl.	26305	52898	42838
unique refl.	5722	11572	9095
refl. $I > 2\sigma(I)$	3910	8994	5555
R_{int}	0.0457	0.0376	0.0658
parameters/restraints	283/278	399/0	419/325
R_1 [$I > 2\sigma$(I)]	0.0371	0.0366	0.0558
wR_2 (all data)	0.0858	0.1007	0.1334
GooF	1.014	1.039	1.007
resid. density [eÅ^{-3}]	0.356/-0.328	0.683/-0.317	0.609/-0.466
CCDC	2145138	2145139	2145142

Table S3. Crystallographic details for **13**, [**14**]$^{2-}$, [**14**]$^{-}$.

	13	[(NEt$_4$)$_2$**14**]	[(NEt$_4$)**14**]
empirical formula	$C_{35}H_{31}N_3P_2PdS_2{\cdot}CHCl_3$	$[C_8H_{20}N]_2$ $[C_{20}H_{18}N_6NiS_4]$	$[C_8H_{20}N]$ $[C_{20}H_{18}N_6NiS_4]$
M_W / g·mol^{-1}	845.45	789.85	659.60
colour, habit	red, block	brown, block	green, plate
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$
a / Å	11.3911(4)	12.1647(13)	26.082(2)
b / Å	28.1153(10)	9.8068(12)	7.5934(6)
c / Å	11.9438(3)	17.4762(18)	15.7003(17)
α / °	90	90	90
β / °	110.1700(10)	103.615(4)	98.061(4)
γ / °	90	90	90
V / Å^3	3590.6(2)	2026.3(4)	3078.7(5)
Z	4	2	4
$\rho_{\text{calcd.}}$ / g·cm^{-1}	1.564	1.295	1.423
μ / mm^{-1}	0.977	0.721	0.933
$\lambda_{\text{MoK}\alpha}$ / Å	0.71073	0.71073	0.71073
T / K	173(2)	173(2)	123(2)
collected refl.	63084	19908	5946
unique refl.	12438	5118	5946
refl. $I > 2\sigma(I)$	11144	3268	4268
R_{int}	0.0248	0.0519	0.1206
parameters/restraints	461/6	311/402	188/0
R_1 [$I > 2\sigma(I)$]	0.0316	0.0441	0.0529
wR_2 (all data)	0.0684	0.1096	0.1146
GooF	1.173	1.009	1.030
resid. density [eÅ^{-3}]	0.672/-0.953	0.634/-0.507	0.634/-0.488
CCDC	2145141	2145140	2184381

1.2 Molecular structures of 2, 3, 5, 12 and $[14]^{2-}$

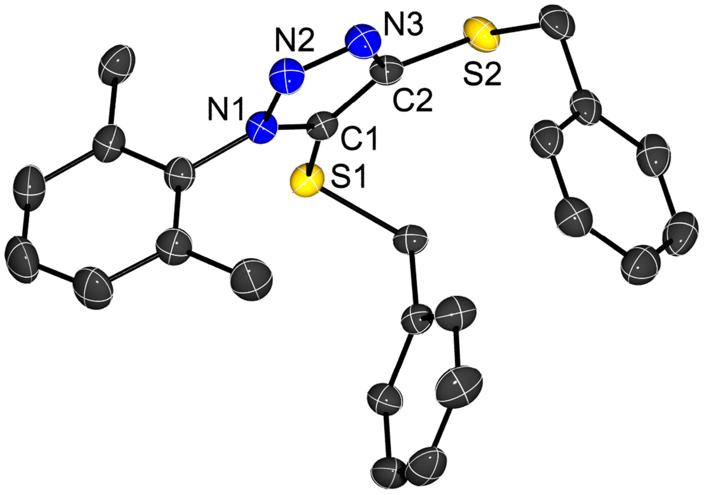


Figure S1. Molecular structure of **2** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms were omitted of clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: C1-S1 1.741(1), C2-S2 1.746(1), C1-C2 1.383(2), C1-N1 1.363(1), C2-N3 1.360(2), N1-N2 1.349(1), N3-N2 1.314(1), S1-S2 3.6601(5), S2-C2-C1 128.23(9), S1-C1-C2 133.34(9), S2-C2-N3-N2 176.92(9), S1-C1-N1-N2 -175.99(8), S1-C1-C2-S2 -1.5(2).

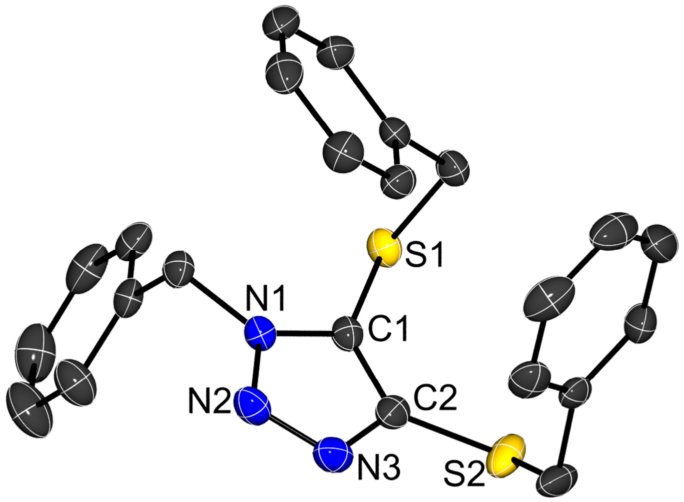


Figure S2. Molecular structure of **3** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms were omitted of clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: C1-S1 1.735(1), C2-S2 1.734(1), C1-C2 1.378(2), C1-N1 1.357(2), C2-N3 1.356(2), N1-N2 1.339(2), N3-N2 1.317(2), S1-S2 3.5884(5), S2-C2-C1 126.7(1), S1-C1-C2 132.2(1), S2-C2-N3-N2 -176.9(1), S1-C1-N1-N2 -177.90(9), S1-C1-C2-S2 -5.5(2).

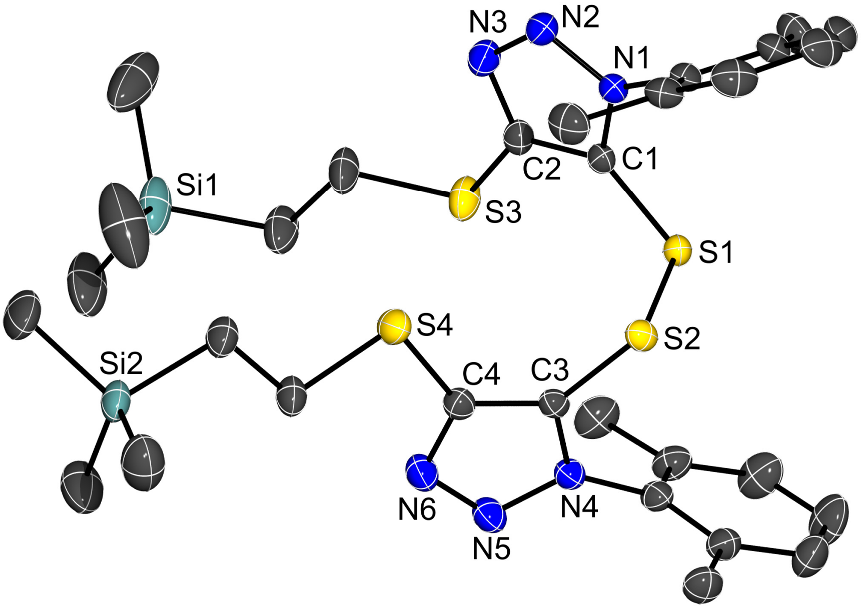


Figure S3. Molecular structure of **5** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms were omitted of clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: C1-S1 1.7384(15), C2-S3 1.7471(16), C3-S2 1.7378(15), C4-S4 1.7448(16), C1-C2 1.378(2), C3-C4 1.377(2), S1-S2 2.0794(5), S3-S1 3.5957(6), S4-S2 3.5732(5), S3-C2-C1 127.14(12), S1-C1-C2 131.87(12), S2-C3-C4 131.12(12), S4-C4-C3 127.06(12), S1-S2-C3 101.25(5), S2-S1-C1 102.15(5), S3-C2-C1-S1 4.1(2), S4-C4-C3-S2 -1.8(2), C1-S1-S2-C3 89.16(7).

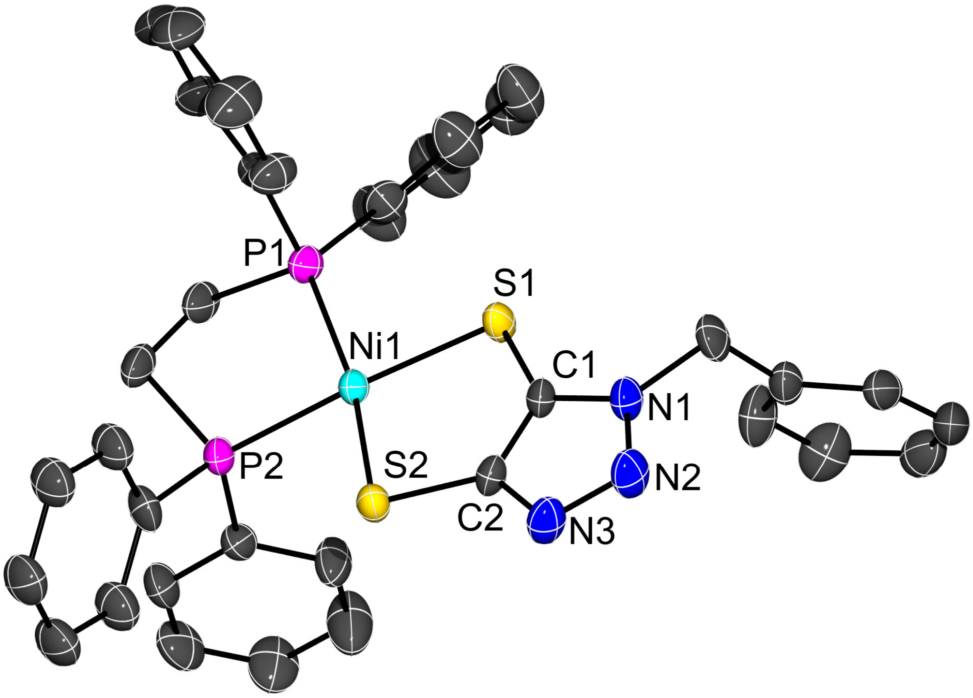


Figure S4. Molecular structure of **12** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms were omitted of clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: C2-S2 1.719(3), C1-S1 1.750(3), S2-Ni1 2.1982(8), S1-Ni1 2.1925(9), Ni1-P1 2.1577(8), Ni1-P2 2.1697(9), C2-C1 1.370(4), S1-S2 3.265(1), P2-Ni1-S2 170.50(3), P1-Ni1-S1 167.15(3), P1-Ni1-P2 86.10(3), P1-Ni1-S2 91.57(3), P2-Ni1-S1 87.94(3), S2-C2-C1 125.2(2), S1-C1-C2 121.0(2), S2-C2-C1-S1 -2.7(4), S1-C1-N1-N2 -178.9(2), S2-C2-N3-N2 -178.1(2), P2-Ni1-S2-C2 167.5(1), P1-Ni1-S1-C1 172.6(1).

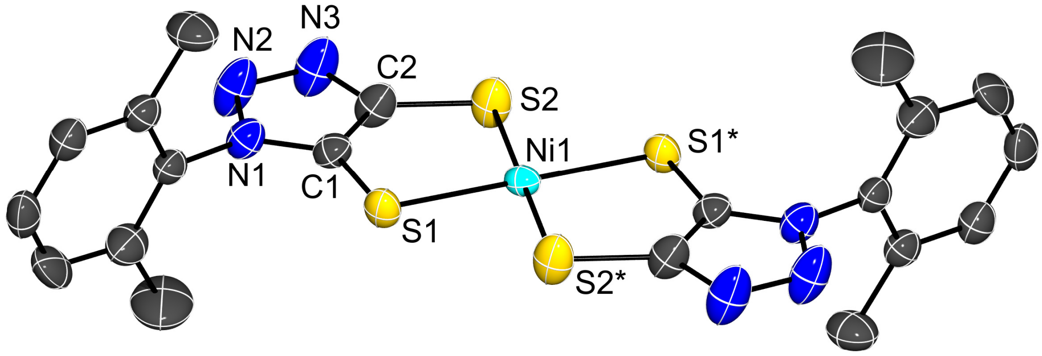


Figure S5. Molecular structure of $(NEt_4)_2$**14** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms and tetra-ethylammonium were omitted of clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: C1-C2 1.370(4), C2-S2 1.751(2), C1-S1 1.715(3), S2-Ni1 2.2139(7), S1-Ni1 2.2132(6), S1-S2 3.259(1), S2-C2-C1 120.8(2), S1-C1-C2 125.3(2), S2-Ni1-S1 94.81(2), C2-S2-Ni1 99.96(9), C1-S1-Ni1 99.13(8), S2-C2-C1-S1 -0.4(3).

2. Experimental section

Materials

All operations were carried out in an atmosphere of dry argon using Schlenk and glove box techniques. Solvents were dried and saturated with argon by standard methods and freshly distilled prior to use. Bis(benzylthio)acetylene, bis(trimethylsilylethylthio)acetylene, 2,6-dimethylphenylazide, benzylazide, [Cp*Ru(COD)Cl], 1-benzyl-3-*n*-butyl-1*H*-benzo[*d*]imidazoliumiodide, [(dppe)NiCl$_2$] and [(dppe)PdCl$_2$] were prepared according to literature methods.[S3-S9] All other chemicals (at least of reaction grade quality) were obtained from commercial sources and used as received. Analytical thin layer chromatography was performed on silica gel (Silica 60 F254) coated aluminium plates. Column chromatography was performed using silica gel 60 (pore size 0.063–0.2 mm) purchased from Merck as the column stationary phase.

Measurements

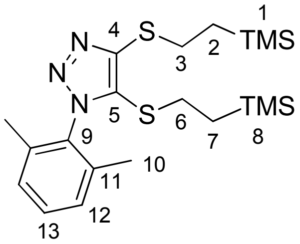
One- and two-dimensional NMR spectra were recorded at 300 K with a BrukerAvance 250, 300, 400 or 500 MHz spectrometer, respectively. In ^1H and $^{13}C\{^1H\}$ NMR the chemical shifts (δ in ppm) were internally referenced to the solvent residual peak (^1H NMR: 7.26 ppm in $CDCl_3$, 7.15 ppm in C_6D_6, 5.32 ppm in CD_2Cl_2 and 2.74 ppm in d^7-DMF; ^{13}C NMR: 77.0 ppm in $CDCl_3$, 128.0 ppm in C_6D_6, 53.8 ppm in CD_2Cl_2 and 30.1 ppm in d^7-DMF). For the $^{31}P\{^1H\}$ NMR and ^{29}Si NMR respectively were used H_3PO_4 (85 %) and $Si(CH_3)_4$ as external standard (0 ppm). The EPR spectrum was recorded on a Bruker ElexSys E 500 CW spectrometer and a Bruker Magnettech ESR 5000. The simulation of the spectrum was performed using the freeware EPR simulation program EasySpin.[S10] IR spectroscopy was conducted on a Nicolet 380 FT-IR with a Smart Orbit ATR module. UV/vis-spectroscopy was carried out with a Perkin Elmer Lambda 19 spectrometer. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 Series, determination of sulphur being excluded for compounds with fluorine content. DSC-TGA measurements were conducted on a Setaram Instruments LABSYS D/LABTG-1A under an atmosphere of argon with a heat flow of 10 K/min. Mass spectrometry by Electrospray Ionization (HRMS-ESI) was obtained with an Agilent 6210 Time-of-Flight LC/MS or with a Thermo Electron Finnigan MAT 95-XP spectrometer. MALDI mass spectra were obtained with a Bruker Reflex IV spectrometer using 2,5-dihydroxybenzoic acid as matrix. Cyclic voltammetry was performed using a Princeton Applied Research VersaSTAT 3. A three electrode arrangement with a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl in CH_3CN reference electrode and 0.15 M n-Bu_4NPF_6 as supporting electrolyte was employed. The Fc/Fc^+ redox couple was used as internal standard.

<u>Standard operation procedure for the synthesis of 1*H*-1,2,3-triazole-4,5-dithiolenes **1**, **2** and **3**:</u>

<u>With Ru-catalysis:</u> A solution containing the alkyne (1.6 mmol) and the azide (1.6 mmol) in toluene (14 mL) was added to a solution of [Cp*(cod)RuCl] (30 mg, 0.08 mmol) in toluene (1 mL) and the reaction mixture was stirred at ambient temperature overnight. The solvent was removed in vacuo and the residue was purified by column chromatography on silica applying the adapted eluent ratio of *n*-hexane/EtOAc to afford the pure triazole.

<u>With Cu-catalysis:</u> A mixture containing the alkyne and the azide as well as CuI (3 %), KO*t*-Bu (3 %) and 1-benzyl-3-*n*-butyl-1*H*-benzo[*d*]imidazoliumiodide (3 %) was stirred neat at 90 °C for 3 d followed by the addition of CH_2Cl_2 (10 mL). The solvent was removed in vacuo and the residue was purified by column chromatography on silica applying the adapted eluent of *n*-hexane/EtOAc to afford the pure triazole. Non reacted alkyne can be regained in the first fraction.

1-(2,6-Dimethylphenyl)-4,5-bis(2-(trimethylsilyl)ethylsulfanyl)-1*H*-1,2,3-triazole (**1**)



Reactants for Ru-catalysis: bis(trimethylsilylethylthio)acetylene (444 mg, 1.53 mmol), 2,6-dimethylphenylazide (226 mg, 1.54 mmol), [Cp*(cod)RuCl] (28 mg, 0.07 mmol); 8:1 *n*-hexane/EtOAc, $R_f = 0.68$. Yield: 484 mg (72 %).

Anal. Calc. for $C_{20}H_{35}N_3S_2Si_2$: C, 54.87; H, 8.06; N, 9.60; S, 14.65. Found: C, 54.44; H, 7.71; N, 9.50; S, 14.12.

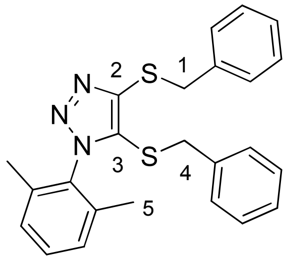
^1H NMR ($CDCl_3$, 300 MHz): δ 7.33 (m, 1 H, *H*-13), 7.18 (d, $^3J_{HH} = 7.6$ Hz, 2 H, *H*-12), 3.18 (m, 2 H, *H*-3), 2.75 (m, 2 H, *H*-6), 1.98 (s, 6 H, *H*-10), 0.99 (m, 2 H, *H*-2), 0.74 (m, 2 H, *H*-7), 0.04 (s, 9 H, *H*-1), 0.05 (s, 9 H, *H*-8) ppm.

^{13}C NMR (C_6D_6, 100 MHz): δ 146.0 (*C*-4), 136.3 (*C*-11), 135.8 (*C*-9), 132.7 (*C*-12), 131.4 (*C*-11, *C*-13), 128.6 (*C*-5), 30.9 (*C*-6), 29.9 (*C*-3), 18.1 (*C*-2), 17.9 (*C*-7), 17.4 (*C*-10), −1.8 (*C*-8), −2.0 (*C*-1) ppm.

^{29}Si NMR (C_6D_6, 80 MHz) δ 1.1 (*Si*-8), 1.0 (*Si*-1) ppm.

MS (MALDI) *m/z*: 437 ([M]).

1-(2,6-Dimethylphenyl)-4,5-bis(benzylsulfanyl)-1*H*-1,2,3-triazole (**2**)



Reactants for Ru-catalysis: bis(benzylthio)acetylene (434 mg, 1.60 mmol), 2,6-dimethylphenylazide (236 mg, 1.60 mmol), [Cp*(cod)RuCl] (30 mg, 0.08 mmol); 4:1 *n*-hexane/EtOAc, R_f = 0.51. Yielded **2** (457 mg 68 %).

Reactants for Cu-catalysis: bis(benzylthio)acetylene (7.54 g, 27.90 mmol), 2,6-dimethylphenylazide (4.11 g, 27.90 mmol), CuI (160 mg, 0.84 mmol), KO*t*-Bu (95 mg, 0.84 mmol), 1-benzyl-3-*n*-butyl-1*H*-benzo[*d*]imidazolium-iodide (331 mg, 0.84 mmol); 4:1 *n*-hexane/EtOAc, R_f = 0.51. Yield: 4.6 g (40 %). Single crystals of **2** suitable for XRD analysis were obtained by slow evaporation of a solution of **5** in CH_2Cl_2/*n*-hexane.

Conversion of **1** into **2**: A yellow MeOH solution (10 ml) of **1** (111 mg, 0.25 mmol) and TBAF · H_2O (151 mg, 0.54 mmol) was stirred overnight. The volatile components were removed in vacuo and the oily brown residue was dissolved in thf (10 mL). Benzyl bromide (87 mg, 61 μL, 0.51 mmol) was added at −78 °C and the reaction mixture was stirred at ambient temperature overnight followed by the removal of the volatile components in vacuo. The residue was dissolved in toluene (5 mL), washed with H_2O (3 x 5 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuo to afford the converted air stable triazole derivate. Yield: 92 mg (88 %).

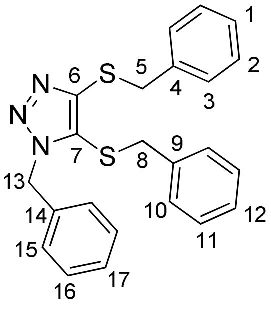
Anal. Calc. for $C_{24}H_{23}N_3S_2$: C, 69.03; H, 5.55; N, 10.06.; S, 15.36. Found: C, 69.01; H, 5.50; N, 9.73; S, 15.49.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.21 - 6.77 (m, 13 H, C_6H_5, C_6H_3), 4.26 (s, 2 H, *H*-1), 3.53 (s, 2 H, *H*-4), 1.60 (s, 6 H, *H*-5) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ 144.0 (*C*-2), 138.5 (C_6H_5), 136.6 (C_6H_5), 136.4 (C_6H_3), 135.5 (C_6H_3), 131.7 (*C*-3), 130.1 (C_6H_3), 129.5 (C_6H_5), 129.2 (C_6H_5), 128.8 (C_6H_5), 128.6 (C_6H_5), 128.4 (C_6H_3), 127.7 (C_6H_5), 127.3 (C_6H_5), 38.5 (*C*-1), 38.3 (*C*-4), 17.3 (*C*-5) ppm.

MS (EI+) *m*/*z*: 417 ([M]$^+$).

1-Benzyl-4,5-bis(benzylsulfanyl)-1*H*-1,2,3-triazole (**3**)



Reactants for Cu-catalysis: bis(benzylthio)acetylene (10.4 g, 38.50 mmol), benzylazide (5.1 g, 38.40 mmol), CuI (200 mg, 1.05 mmol), KO*t*-Bu (118 mg, 1.04 mmol), 1-benzyl-3-*n*-butyl-1*H*-benzo[*d*]imidazoliumiodide (420 mg, 1.06 mmol); 5:1 *n*-hexane/EtOAc, R_f = 0.44. Yield: 6.0 g (39 %). Single crystals of **3** suitable for XRD analysis were obtained from a saturated solution of **3** in Et_2O upon cooling to −26 °C.

Anal. Calc. for $C_{23}H_{21}N_3S_2$: C, 68.45; H, 5.24; N, 10.41, S, 15.89. Found: C, 69.04; H, 5.27; N, 10.43; S, 15.75.

^{1}H NMR (C_6D_6, 300 MHz): δ 7.23 - 7.19 (m, 15 H, C_6H_5), 4.81 (s, 2 H, *H*-13), 4.23 (s, 2 H, *H*-5), 3.25 (s, 2 H, *H*-8) ppm.

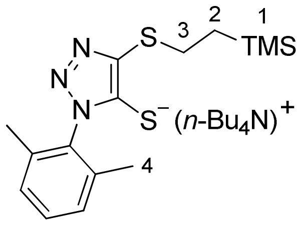
^{13}C NMR (C_6D_6, 62.9 MHz): δ 146.5 (*C*-6), 138.5 (*C*-4), 136.9 (*C*-9), 135.7 (*C*-14), 129.4 (*C*-3), 129.1 (*C*-10), 128.9 (*C*-15), 128.8 (*C*-2), 128.5 (*C*-11), 128.4 (*C*-7), 128.2 (*C*-1), 127.8 (*C*-16), 127.7 (*C*-12), 127.3 (*C*-17), 51.9 (*C*-13), 39.6 (*C*-8), 37.8 (*C*-5) ppm.

MS (MALDI) *m/z*: 404 ($[M+H]^+$).

UV/vis (MeCN) λ (ε/dm^3·mol^{-1}·cm^{-1}): 210 (26300), 262 (5300) nm.

Melting point (DSC): 67 °C.

Tetra-*n*-butylammonium-1-(2,6-dimethylphenyl)-4-(2-(trimethylsilyl)ethylsulfanyl)-1*H*-1,2,3-triazole-5-thiolate (*n*-Bu$_4$N-**4**)



A yellow solution of **1** (233 mg, 0.53 mmol) and TBAF · H_2O (315 mg, 1.13 mmol) in THF (10 mL) was stirred at ambient temperature overnight. Solid exchanger resin DOWEX® 50WX8-200 (705 mg), $CaCO_3$ (239 mg) and MeOH (2 mL) were added. The suspension was stirred overnight, filtered over celite, washed with THF and the solvents were removed in vacuo. The oily residue was washed with degassed H_2O (2 x 5 mL) and dried in vacuo to afford *n*-Bu$_4$N-**4** as air sensitive green-brown solid (308 mg, 98 %).

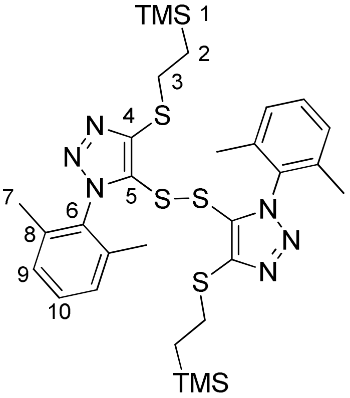
^{1}H NMR (C_6D_6, 400 MHz): δ 7.01 (m, 3 H, C_6H_3), 3.32 (m, 2 H, *H*-3), 3.10 (m, 8 H, *n*-Bu$_4$N$^+$-CH_2), 2.20 (s, 6 H, *H*-4), 1.37 (m, 8 H, *n*-Bu$_4$N$^+$-CH_2), 1.20 (m, 8 H, *n*-Bu$_4$N$^+$-CH_2), 1.06 (m, 2 H, *H*-2), 0.84 (t, $^3J_{HH}$ = 7.30 Hz, 12 H, *n*-Bu$_4$N$^+$-CH_3), 0.01 (s, 9 H, *H*-1) ppm.

^{13}C NMR (C_6D_6, 100 MHz): δ 139.6 (C_6H_3), 137.4 (C_6H_3), 128.4 (C_6H_3), 127.9 (C_6H_3), 59.2 (*n*-Bu$_4$N$^+$-CH_2), 28.5 (*C*-3), 24.7 (*n*-Bu$_4$N$^+$-CH_2), 20.4 (*n*-Bu$_4$N$^+$-CH_2), 18.5 (*C*-4), 18.3 (*C*-2), 14.0 (*n*-Bu$_4$N$^+$-CH_3), −1.5 (*C*-1) ppm.

^{29}Si NMR (C_6D_6, 80 MHz): δ 0.8 (*Si*-1) ppm.

MS (MALDI) *m/z*: 337 ($[M+H]^+$), 242 ([*n*-Bu$_4$N$^+$]).

4-(2-(Trimethylsilyl)ethylsulfanyl)-5-(2-(5-(2-trimethylsilyl)ethylsulfanyl)-1-(2,6-dimethylphenyl)-3*H*-1,2,3-triazole-4-yl)disulfanyl)-1-(2,6-dimethylphenyl)-1*H*-1,2,3-triazole) (**5**)



A hydrogen peroxide solution in degassed H_2O (612 μL, 3-%) was added to a solution of *n*-Bu_4N-**4** (730 mg, 1.23 mmol) in degassed glacial acetic acid (30 mL) and after 5 min a colour change to bright yellow occurred. The reaction mixture was stirred overnight and the solvents were removed in vacuo. The residue was purified by column chromatography on silica (4:1 *n*-hexane/EtOAc, $R_f = 0.65$) to afford **5** as air stabile yellow solid (284 mg, 69 %). Single crystals of **5** suitable for XRD analysis were obtained by slow evaporation of a solution of **5** in *n*-hexane/EtOAc (4:1).

Anal. Calc. for $C_{30}H_{44}N_6S_4Si_2$: C, 53.53; H, 6.59; N, 12.48. Found: C, 53.81; H, 6.63; N, 12.48.

^{1}H NMR (C_6D_6, 300 MHz): δ 6.95 (t, $^3J_{HH}$ = 7.55 Hz, 2 H, *H*-10), 6.79 (d, $^3J_{HH}$ = 7.55 Hz, 4 H, *H*-9), 3.38 (m, 4 H, *H*-3), 1.93 (s, 12 H, *H*-7), 1.08 (m, 4 H, *H*-2), −0.05 (s, 18 H, *H*-1) ppm.

^{13}C NMR (C_6D_6, 75.5 MHz): δ 149.9 (*C*-4), 136.5 (*C*-6), 135.0 (*C*-8), 130.4 (*C*-10), 128.7 (*C*-9), 128.3 (*C*-5), 29.7 (*C*-3), 18.1 (*C*-2), 17.9 (*C*-7), −1.8 (*C*-1) ppm.

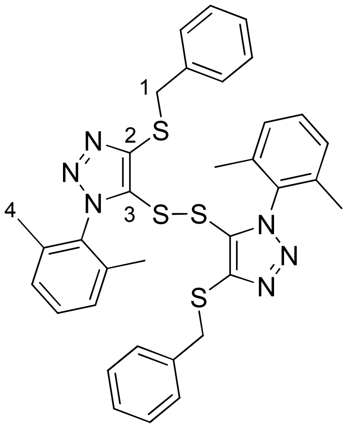
^{29}Si NMR (C_6D_6, 59.6 MHz): δ 1.0 (*Si-1*) ppm.

MS (ESI+) *m/z*: 695 ([M+Na]$^+$), 673 ([M+H]$^+$).

General procedure for the conversion of **1** into **2** and into **7** and of **5** into **6**:

A yellow solution of **1** (or **5**) and TBAF · H_2O in MeOH (10 mL) was stirred at ambient temperature overnight. The volatile components were removed in vacuo and the oily brown residue was dissolved in THF (10 mL). The respective alkylating agent was added at −78 °C and the reaction mixture was stirred at ambient temperature overnight followed by the removal of the volatile components in vacuo. The residue was dissolved in toluene (5 mL), washed with H_2O (3 x 5 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuo to afford the converted air stable triazole derivate.

4-(Benzylsulfanyl)-5-(2-(5-benzylsulfanyl)-3-(2,6-dimethylphenyl)-3*H*-1,2,3-triazole-4-yl)-di-sulfanyl)-1-(2,6-dimethylphenyl)-1*H*-1,2,3-triazole (**6**)



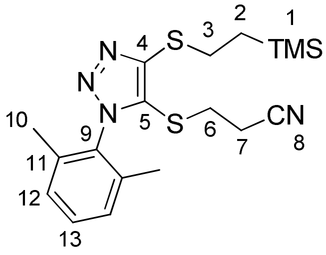
Reactants: **5** (135 mg, 0.20 mmol), TBAF $\cdot$ H_2O (248 mg, 0.89 mmol), benzyl bromide (72 mg, 51 μL, 0.42 mmol). The crude product was purified by column chromatography on silica (*n*-hexane/EtOAc, 2:1, R_f = 0.53) to afford **6** as orange oil (96 mg, 75 %).

^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.35 - 7.08 (m, 16 H, C_6H_3, C_6H_5), 4.01 (s, 4 H, *H*-1), 1.86 (s, 12 H, *H*-4) ppm.

^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 144.1 (*C*-2), 136.1 (C_6H_3), 136.0 (C_6H_5), 135.5 (C_6H_3), 134.5 (*C*-3), 130.4 (C_6H_5), 130.2 (C_6H_3), 127.9 (C_6H_3), 127.7 (C_6H_5), 127.2 (C_6H_5), 38.9 (*C*-1), 17.5 (*C*-4) ppm.

MS (ESI+) *m*/*z*: 675 ([M+Na]$^+$), 653 ([M+H]$^+$).

1-(2,6-Dimethylphenyl)-4-(2-(trimethylsilyl)ethylsulfanyl)-5-(2-(cyano)ethylsulfanyl)-1*H*-1,2,3-triazole (**7**)



Reactants: **1** (225 mg, 0.52 mmol), TBAF $\cdot$ H_2O (318 mg, 1.14 mmol), 2-bromopropanenitrile (138 mg, 85 μL, 1.03 mmol). Yield: 172 mg air stable brown oil (78 %).

Anal. Calc. for $C_{18}H_{26}N_4S_2Si$: C, 55.34; H, 6.71; N, 14.34; S, 16.42. Found: C, 55.39; H, 6.48; N, 14.30; S, 17.65.

^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.36 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, *H*-13), 7.21 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, *H*-12), 3.23 (m, 2 H, *H*-3), 2.93 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *H*-6), 2.54 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *H*-7), 1.97 (s, 6 H, *H*-10), 0.99 (m, 2 H, *H*-2), 0.05 (s, 9 H, *H*-1) ppm.

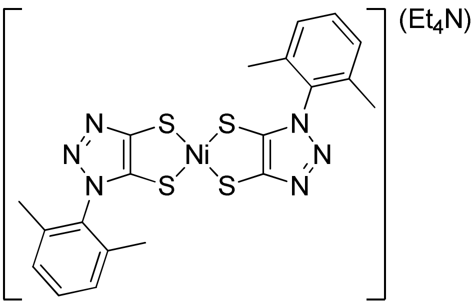
^{13}C NMR (CDCl$_3$, 75 MHz): δ 146.2 (*C*-4), 135.7 (*C*-9), 134.2 (*C*-5), 130.5 (*C*-11), 128.6 (*C*-13), 127.6 (*C*-12), 117.0 (*C*-8), 29.9 (*C*-3), 29.6 (*C*-6), 18.6 (*C*-7), 17.6 (*C*-2), 17.5 (*C*-10), -1.8 (*C*-1) ppm.

^{29}Si NMR (C_6D_6, 80 MHz): δ 1.6 (*Si*-1) ppm.

IR (CH_2Cl_2): $\tilde{\nu}$ 2256 (C≡N) cm^{-1}.

MS (MALDI) *m*/*z*: 391 ([M+H]$^+$).

Tetraethylammonium[bis(1-(2,6-dimethylphenyl)-1*H*-1,2,3-triazole-4,5-dithiolato)nickelate(II)]
(Et_4N**14**)



Ligand H_2-**8** (154 mg, 0.65 mmol) and KOH (110 mg, 1.96 mmol) were dissolved in MeOH (20 mL). After addition of $NiCl_2$ (45 mg, 0.35 mmol) the reaction mixture was stirred at ambient temperature for 2 h. A solution of $(Et_4N)Br$ (216 mg, 1.03 mmol) in degassed H_2O (15 mL) was added dropwise. The red solution was concentrated to the half of volume. The resulted brown precipitate was filtered, washed subsequently with degassed H_2O (6 x 3 mL) and dried in vacuo overnight. At air 20 mg of [$(Et_4N)_2$**14**] were solved in 15 ml MeOH. Through slowly evaporate of MeOH small green crystals were collected. This single crystals of [**14**]$^-$ are suitable for XRD analysis.

UV/vis (MeOH) λ (ε/dm^3·mol^{-1}·cm^{-1}): 518 (109), 645 (105), 988 (330) nm.

2.1 NMR spectroscopy and cyclic voltammetry

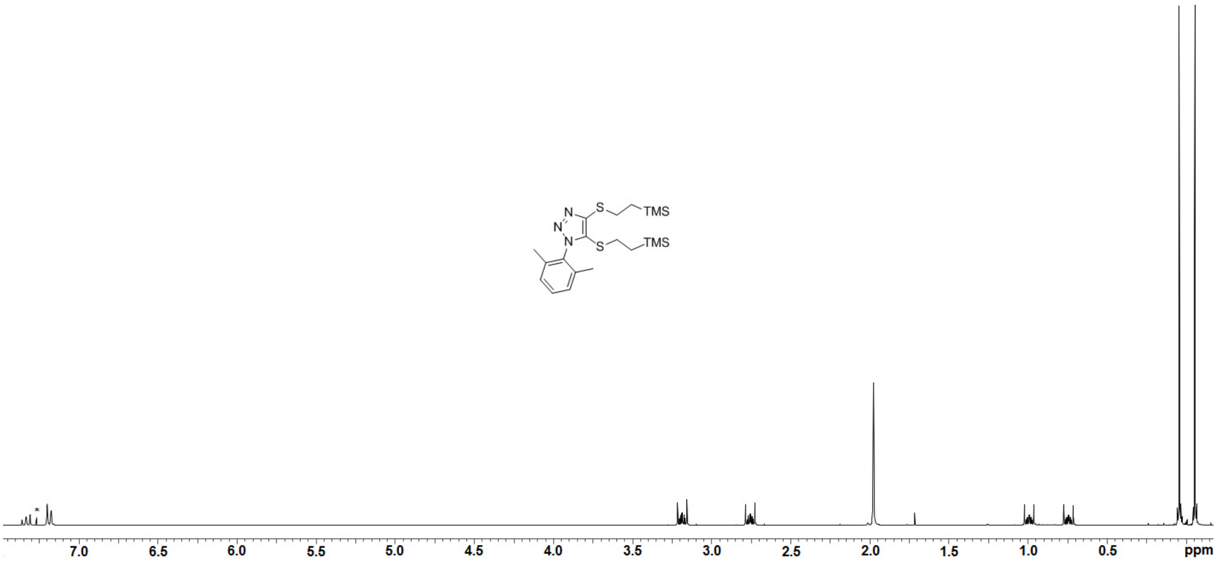


Figure S6. ^{1}H NMR spectrum (300 MHz) of **1** in C_6D_6 (*) at 300 K.

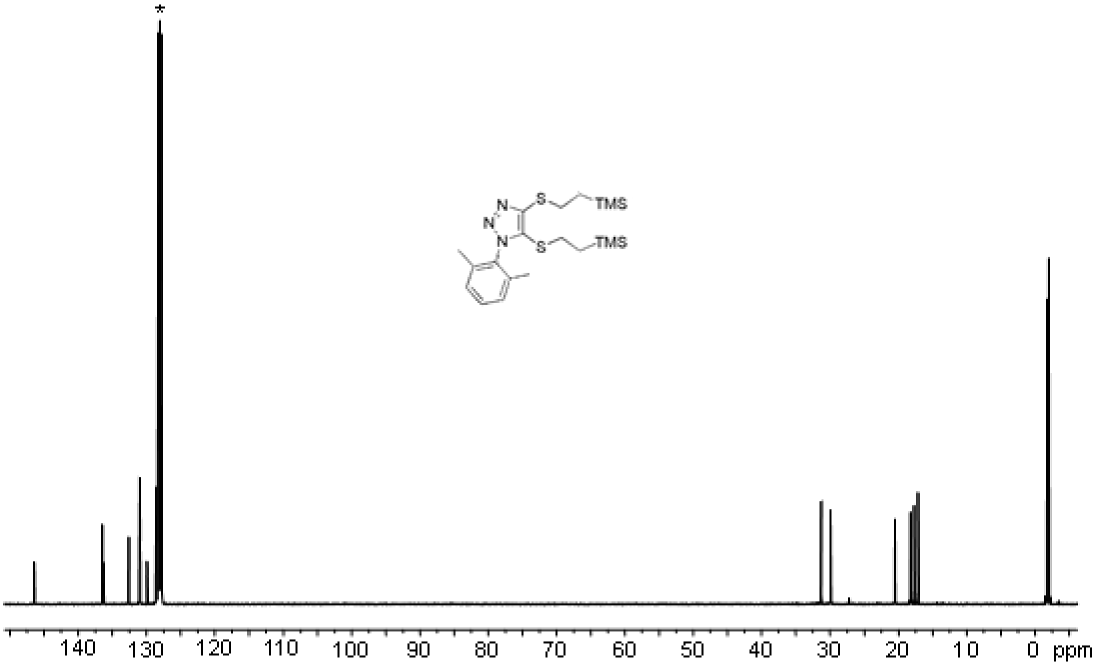


Figure S7. ^{13}C NMR spectrum (100 MHz) of **1** in C_6D_6 (*) at 300 K.

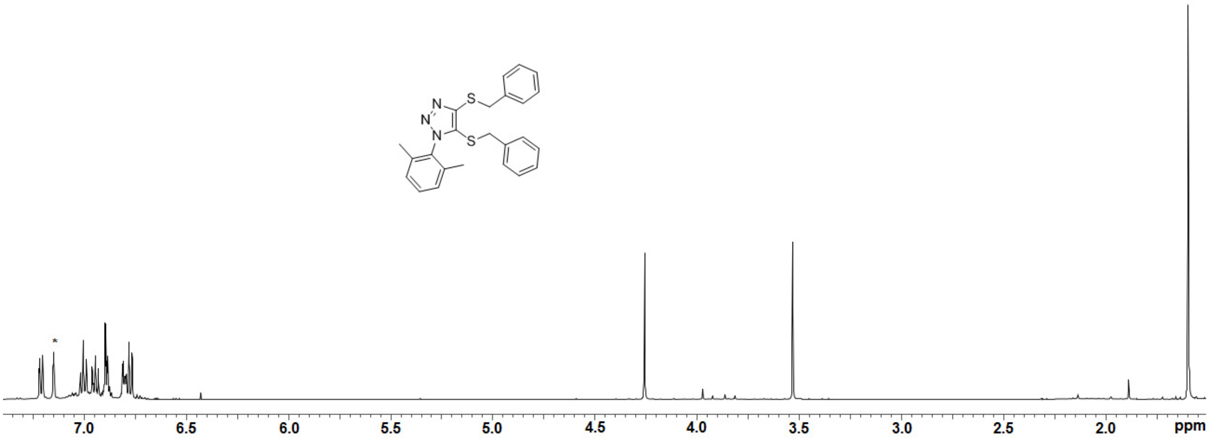


Figure S8. ^{1}H NMR spectrum (500 MHz) of **2** in C_6D_6 (*) at 300 K.

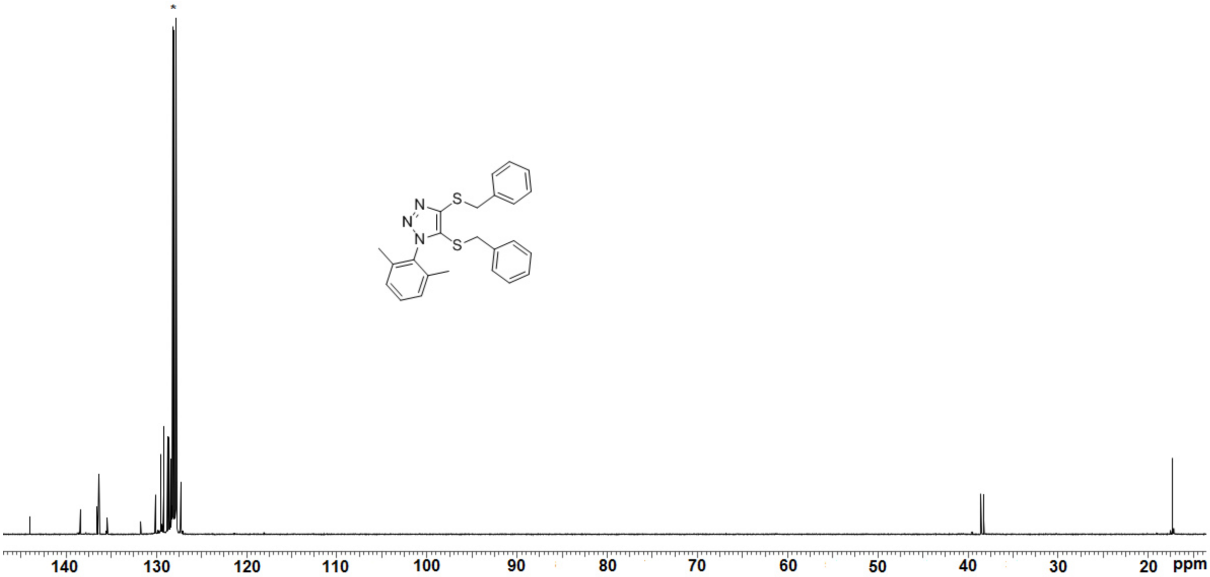


Figure S9. ^{13}C NMR spectrum (100 MHz) of **2** in C_6D_6 (*) at 300 K.

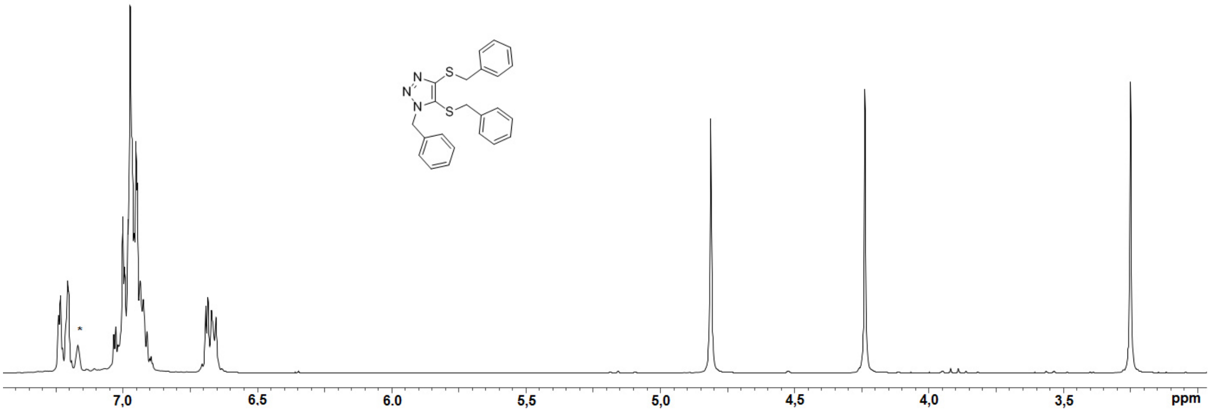


Figure S10. ^{1}H NMR spectrum (200 MHz) of **3** in C_6D_6 (*) at 300 K.

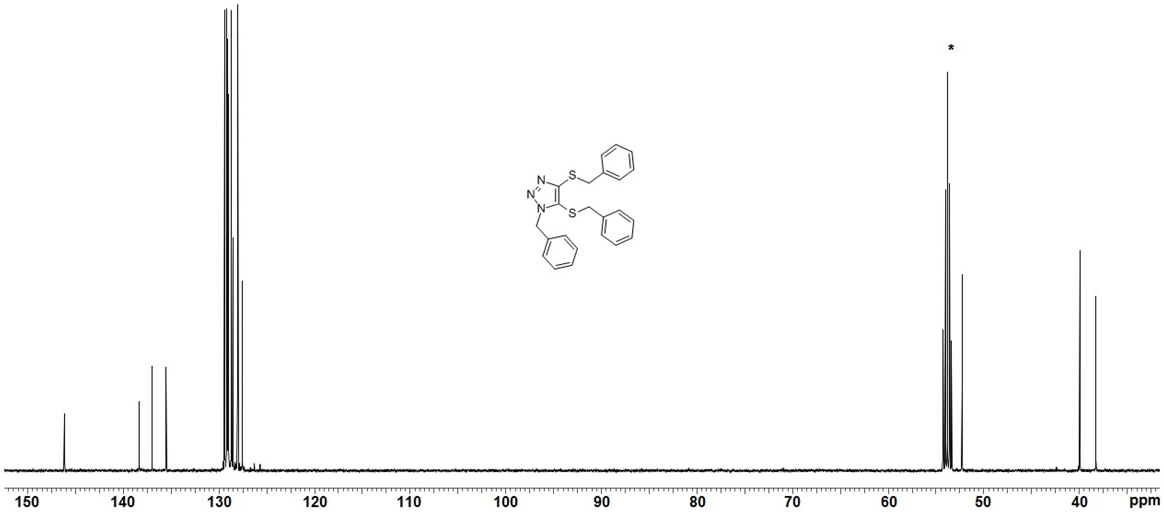


Figure S11. ^{13}C NMR spectrum (125 MHz) of **3** in CD_2Cl_2 (*) at 300 K.

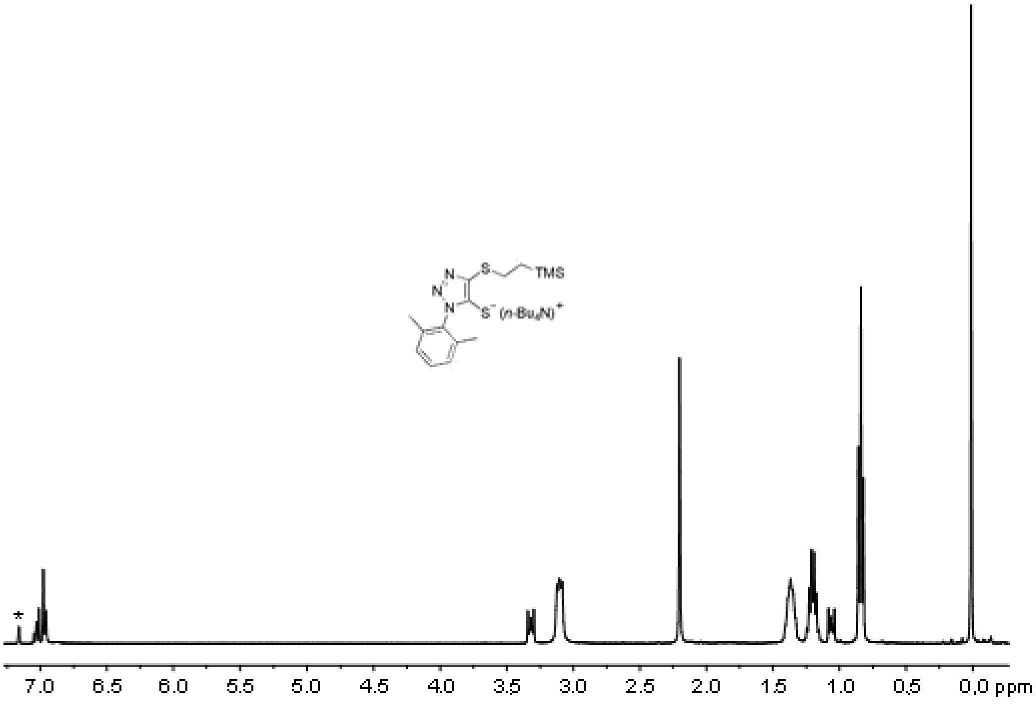


Figure S12. ^{1}H NMR spectrum (400 MHz) of *n*-Bu$_4$N-**4** in C_6D_6 (*) at 300 K.

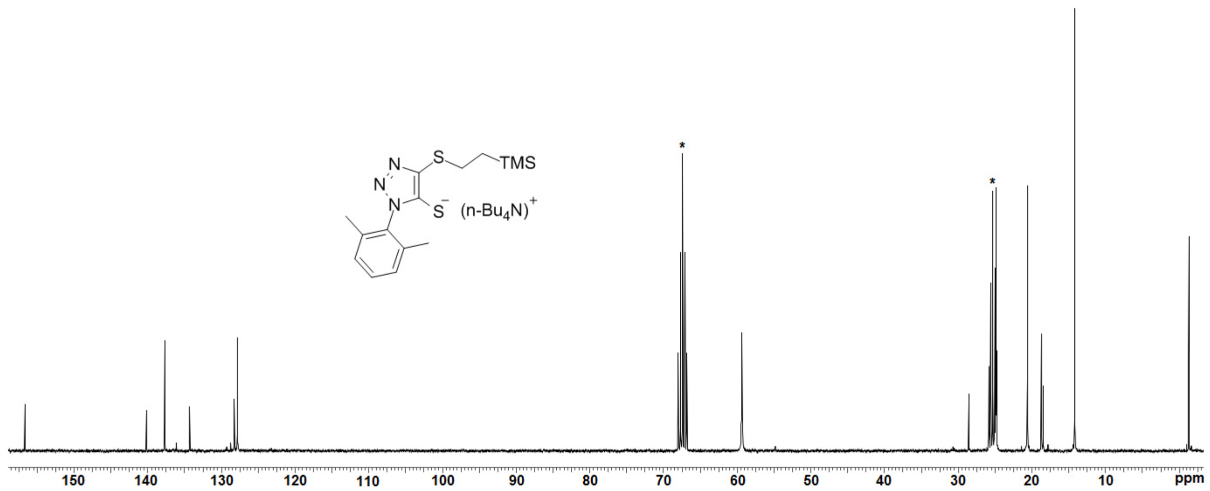


Figure S13. ^{13}C NMR spectrum (75 MHz) of *n*-Bu$_4$N-**4** in THF-D$_8$ (*) at 300 K.

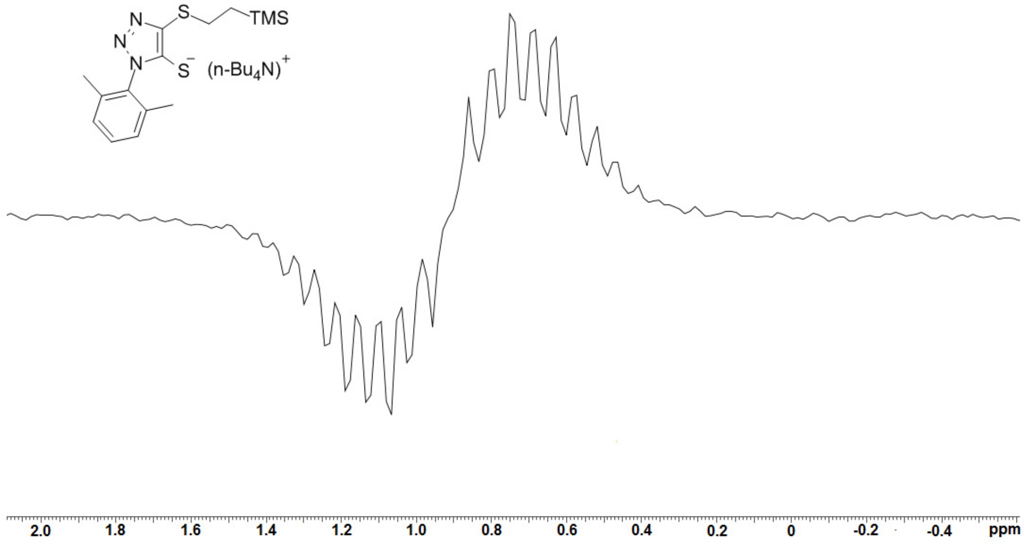


Figure S14. ^{29}Si NMR spectrum (60 MHz) of *n*-Bu$_4$N-**4** in THF-D$_8$ at 300 K.

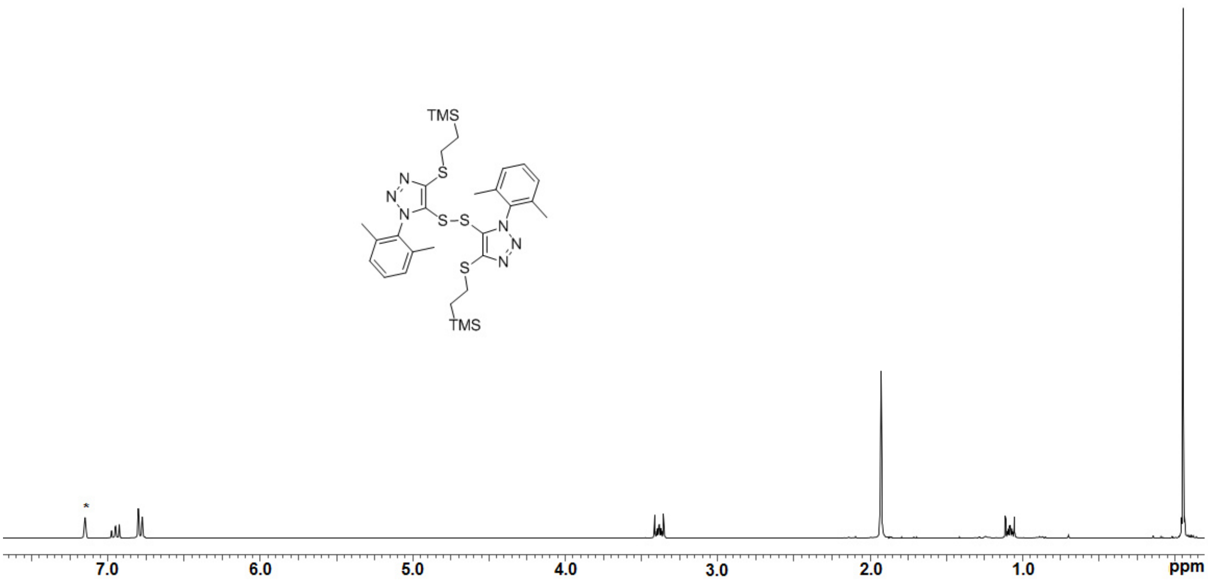


Figure S15. ^{1}H NMR spectrum (300 MHz) of **5** in CDCl$_3$ (*) at 300 K.

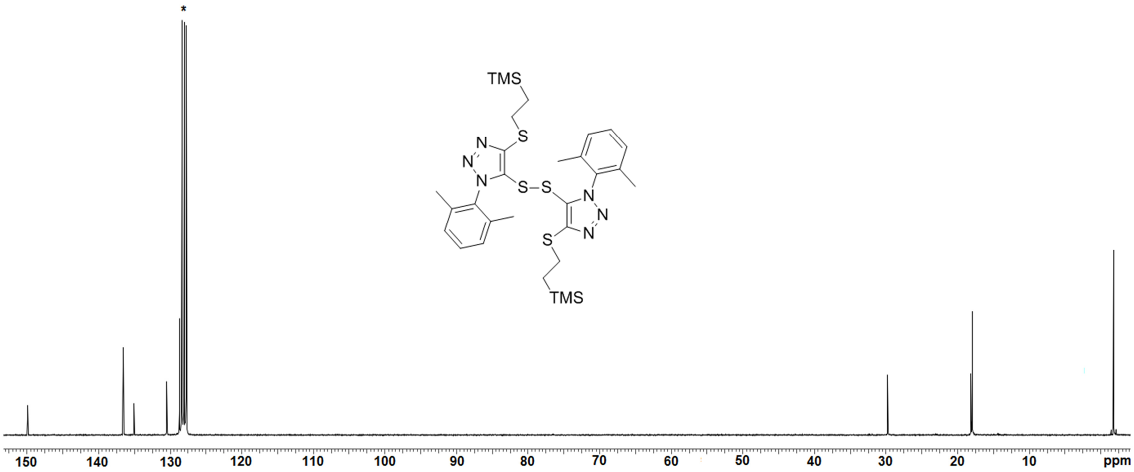


Figure S16. ^{13}C NMR spectrum (75 MHz) of **5** in C_6D_6 (*) at 300 K.

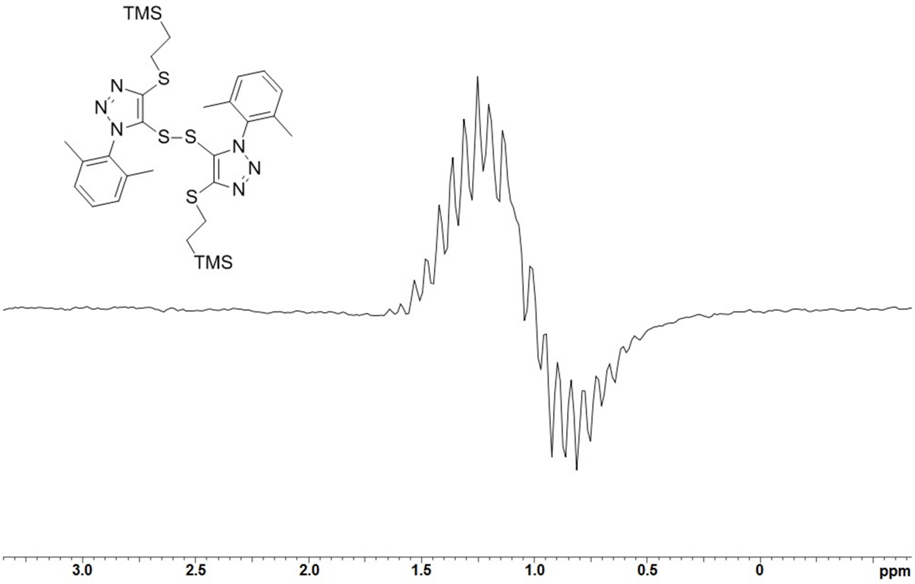


Figure S17. ^{29}Si NMR spectrum (60 MHz) of **5** in C_6D_6 at 300 K.

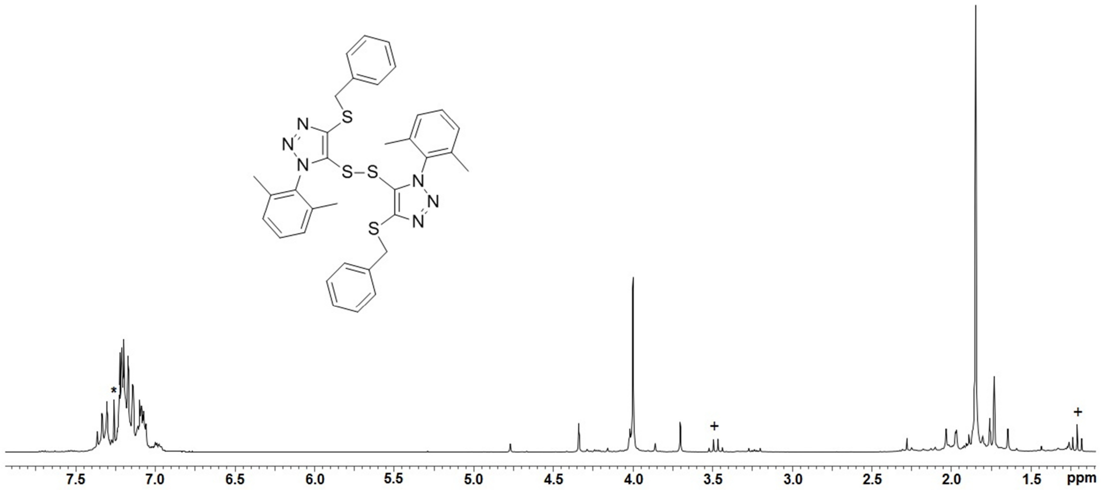


Figure S18. ^{1}H NMR spectrum (250 MHz) of **6** in $CDCl_3$ (*) with traces of Et_2O (+) at 300 K.

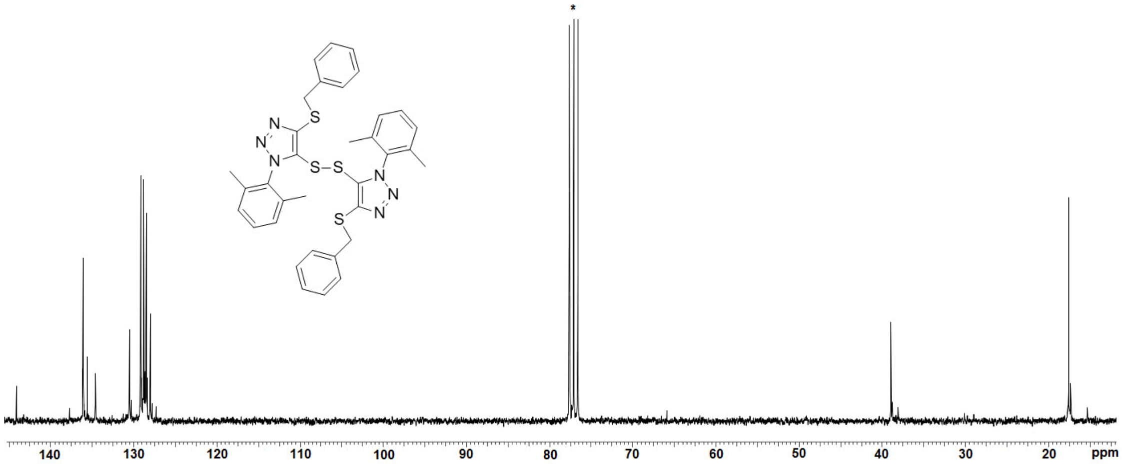


Figure S19. ^{13}C NMR spectrum (64 MHz) of **6** in $CDCl_3$ (*) at 300 K.

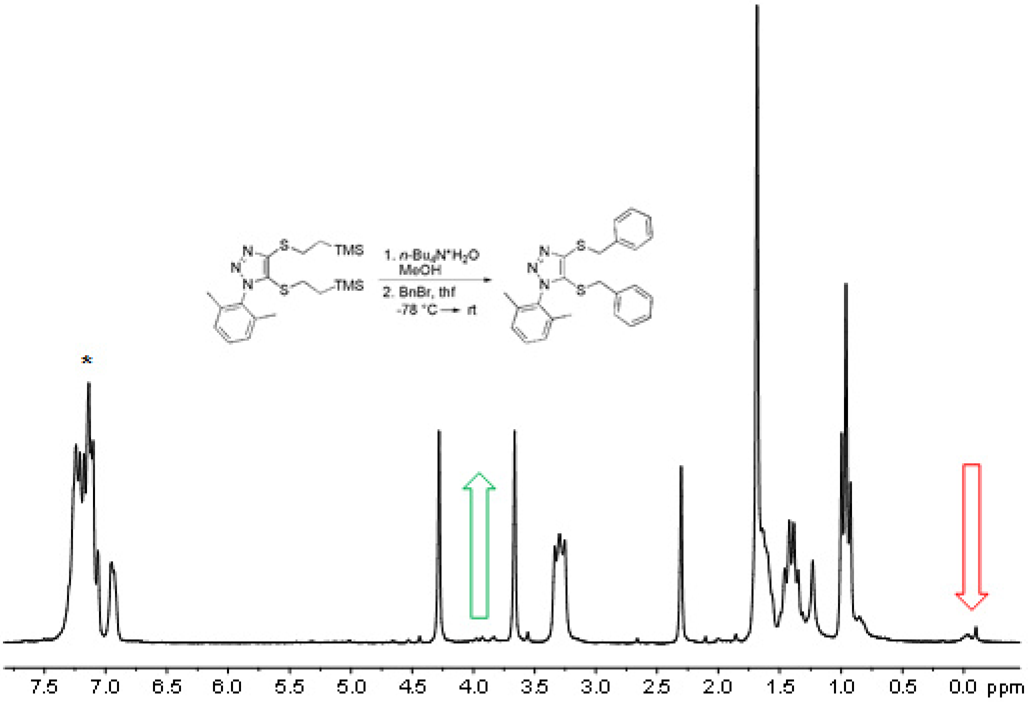


Figure S20. ^{1}H NMR spectrum (300 MHz) after the conversion of **1** into **2** in C_6D_6(*) at 300 K.

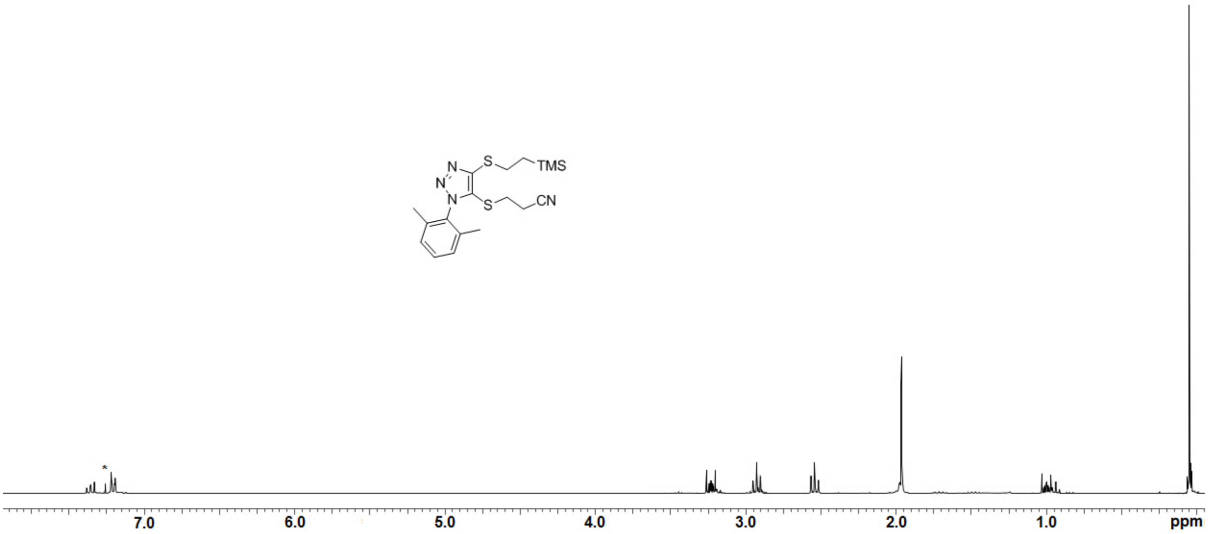


Figure S21. ^{1}H NMR spectrum (300 MHz) after the conversion of **1** into **7** in $CDCl_3$ (*) at 300 K.

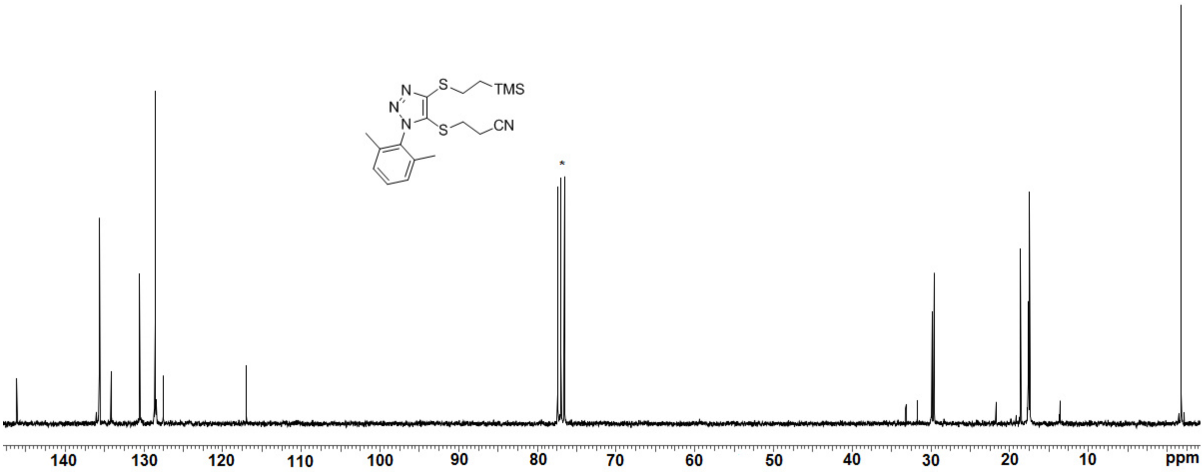


Figure S22. ^{13}C NMR spectrum (75 MHz) after the conversion of **1** into **7** in C_6D_6(*) at 300 K.

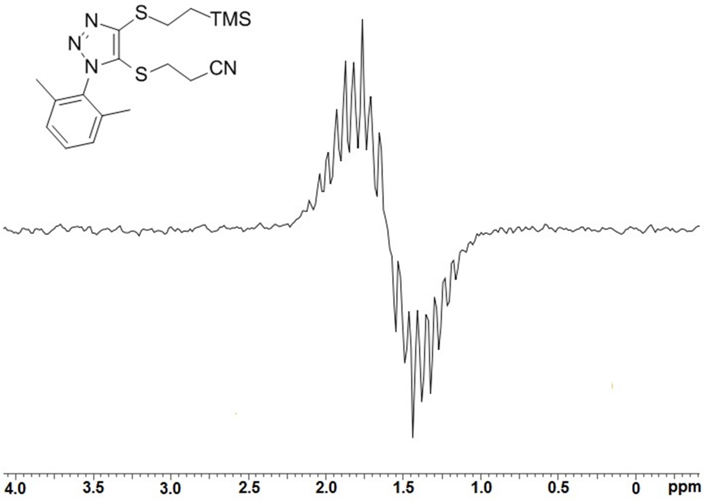


Figure S23. ^{29}Si NMR spectrum (60 MHz) of **7** in $CDCl_3$ at 300 K.

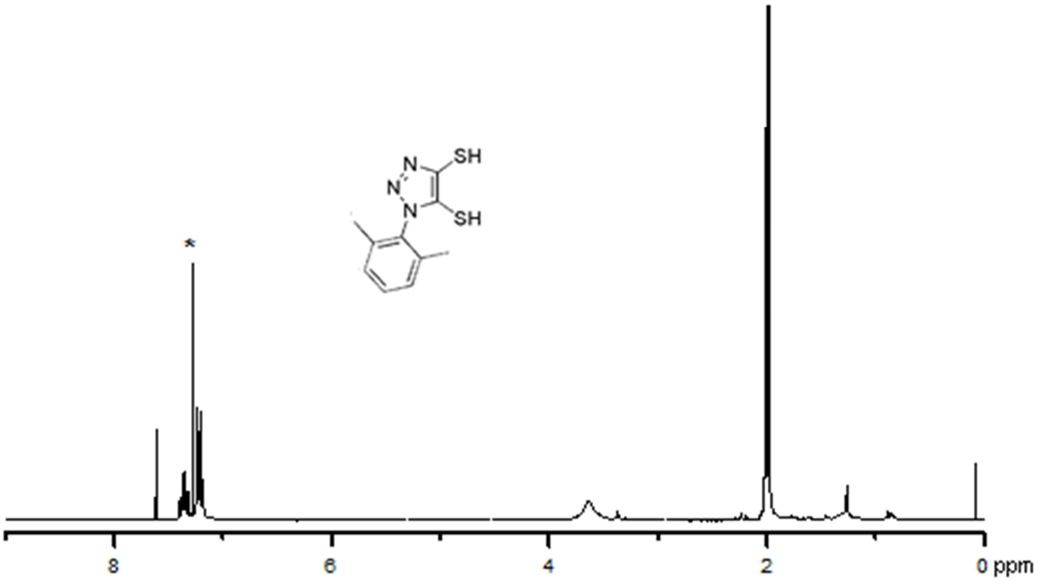


Figure S24. ^{1}H NMR spectrum (300 MHz) of H$_2$-**8** in CDCl$_3$(*) at 300 K.

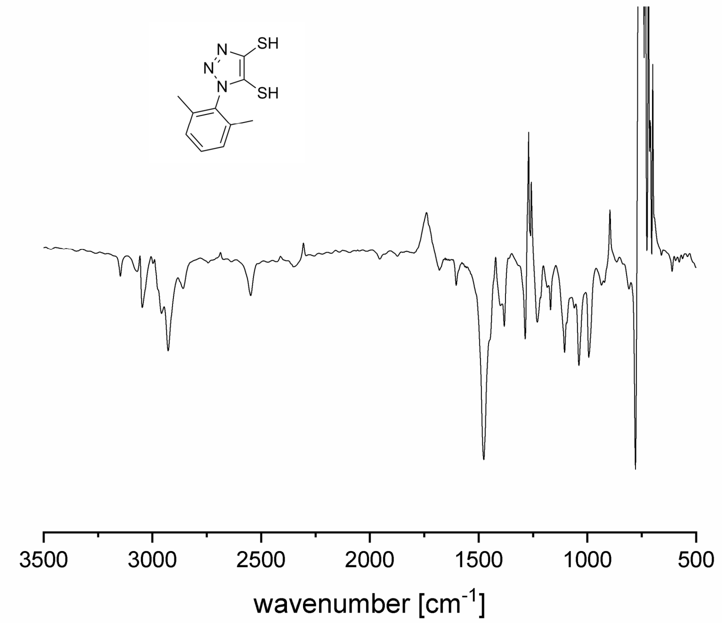


Figure S25. IR spectrum of H$_2$-**8** in CH$_2$Cl$_2$.

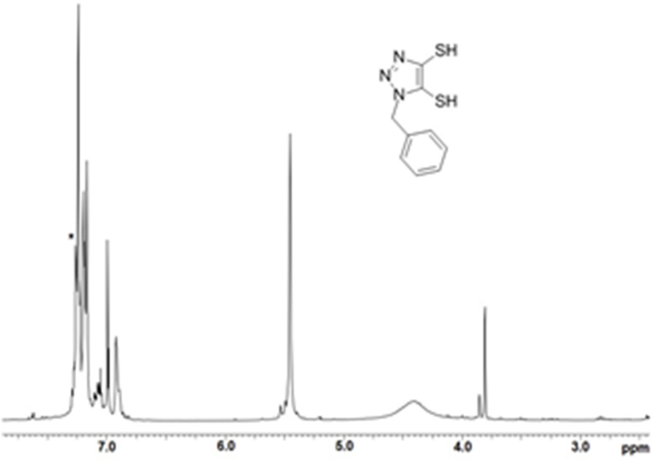


Figure S26. ^{1}H NMR spectrum (300 MHz) of H_2-**9** in $CDCl_3$ (*) at 300 K.

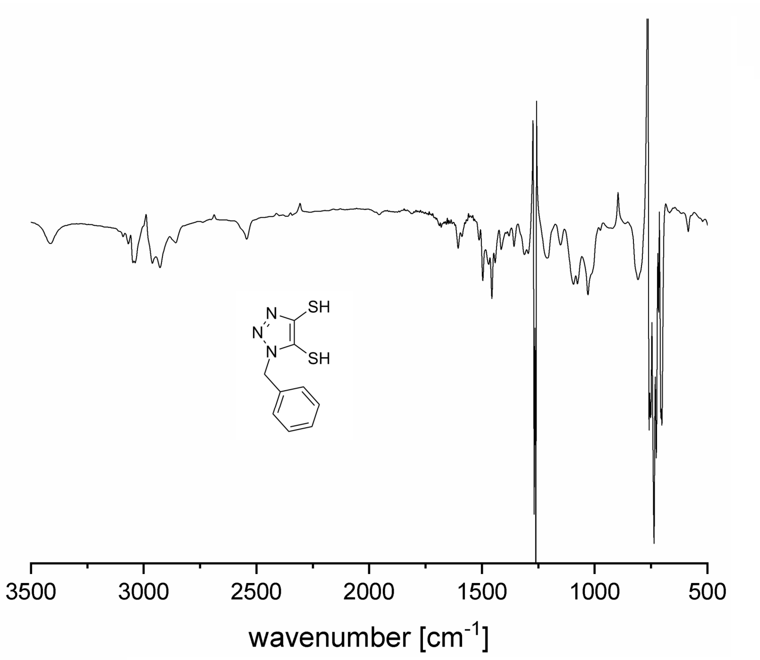


Figure S27. IR spectrum of H_2-**9** in CH_2Cl_2.

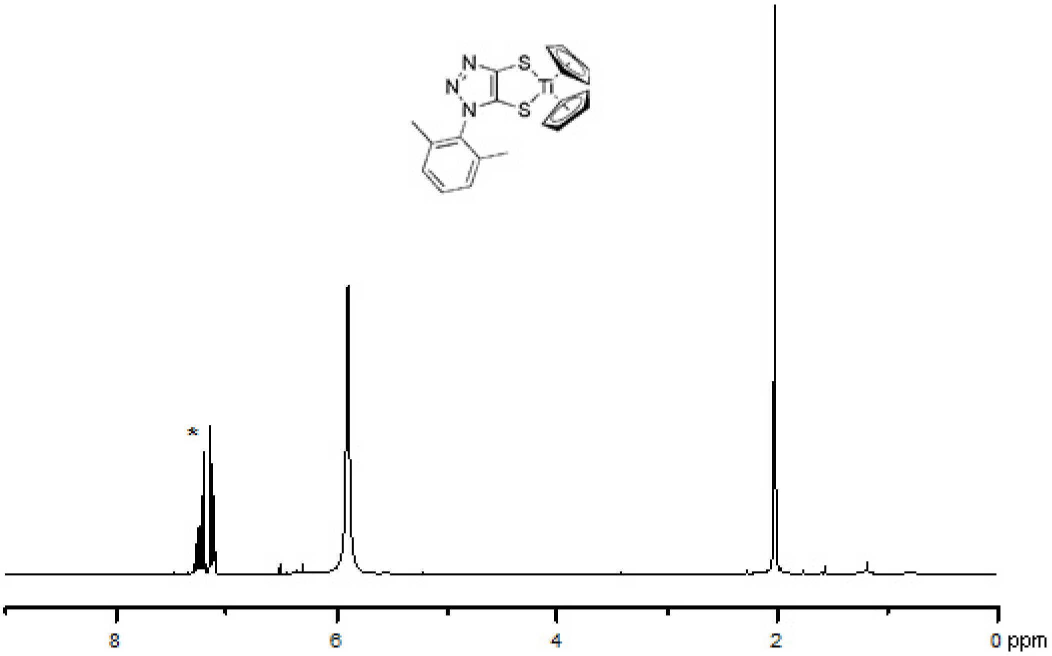


Figure S28. ^{1}H NMR spectrum (250 MHz) of **10** in CDCl$_3$(*) at 300 K.

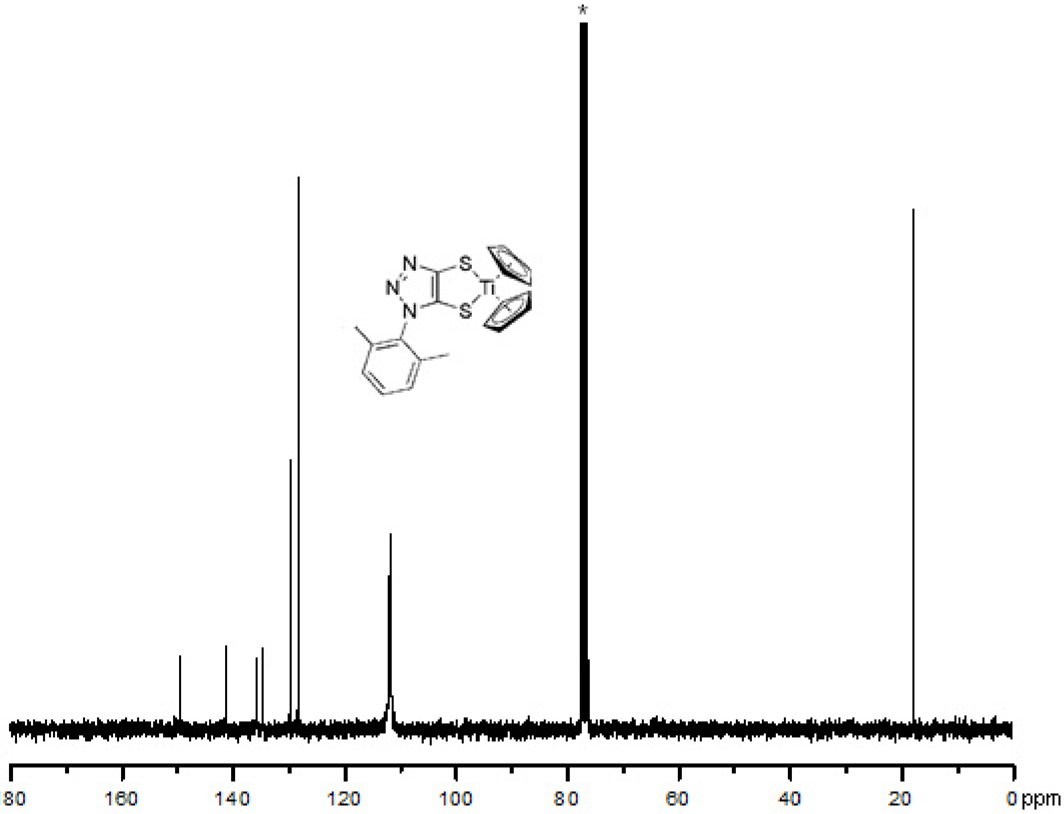


Figure S29. ^{13}C NMR spectrum (63 MHz) of **10** in CDCl$_3$(*) at 300 K.

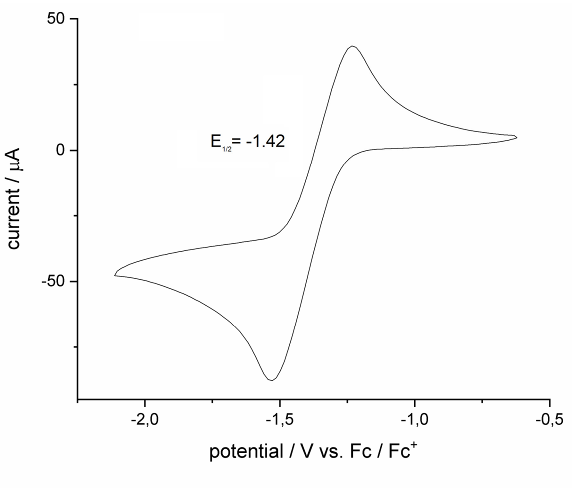


Figure S30. Cyclic voltammogram of **10** in CH_2Cl_2.

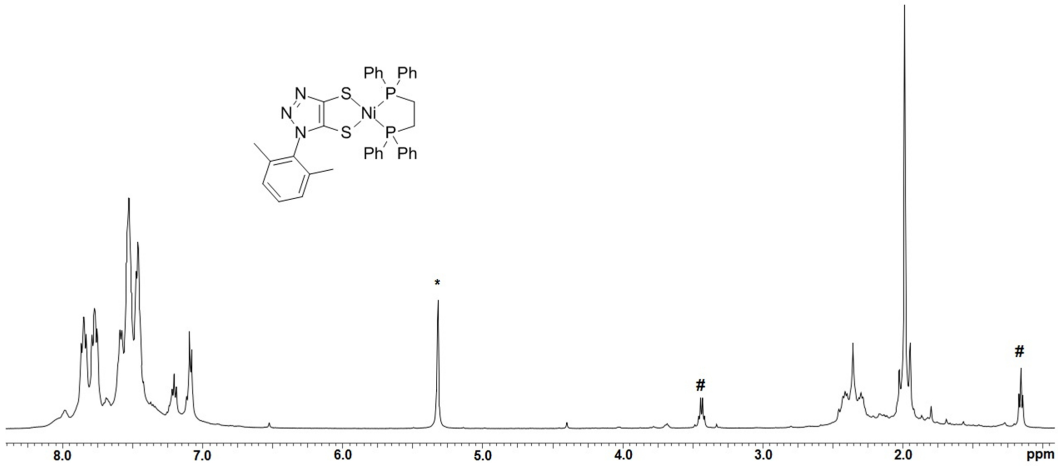


Figure S31. ^1H NMR spectrum (500 MHz) of **11** in CD_2Cl_2 (*) with traces of Et_2O (#) at 300 K.

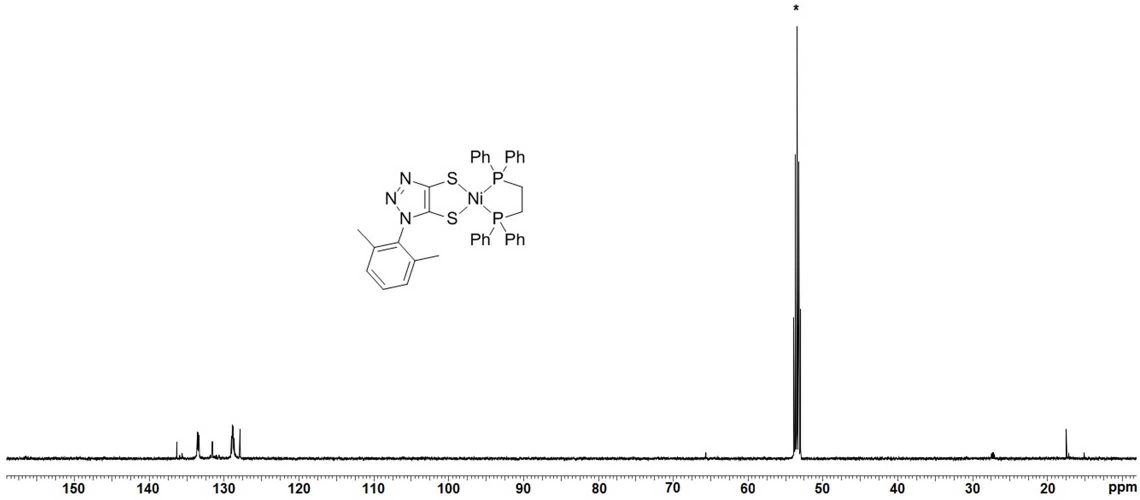


Figure S32. ^{13}C NMR spectrum (125 MHz) of **11** in CD_2Cl_2 (*) at 300 K.

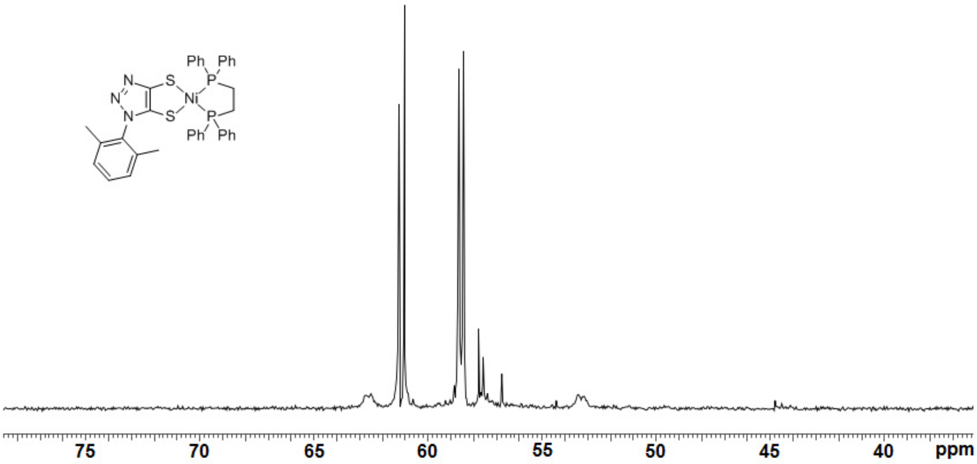


Figure S33. ^{31}P NMR spectrum (202 MHz) of **11** in CD_2Cl_2 at 300 K.

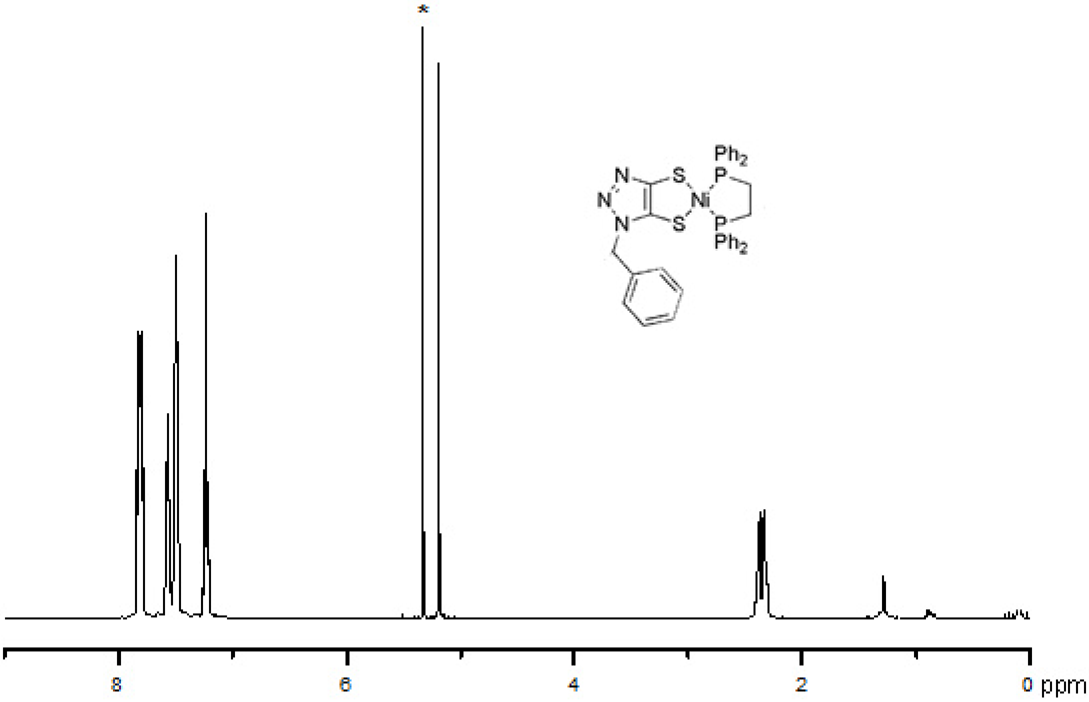


Figure S34. ^{1}H NMR spectrum (500 MHz) of **12** in CD_2Cl_2(*) at 300 K.

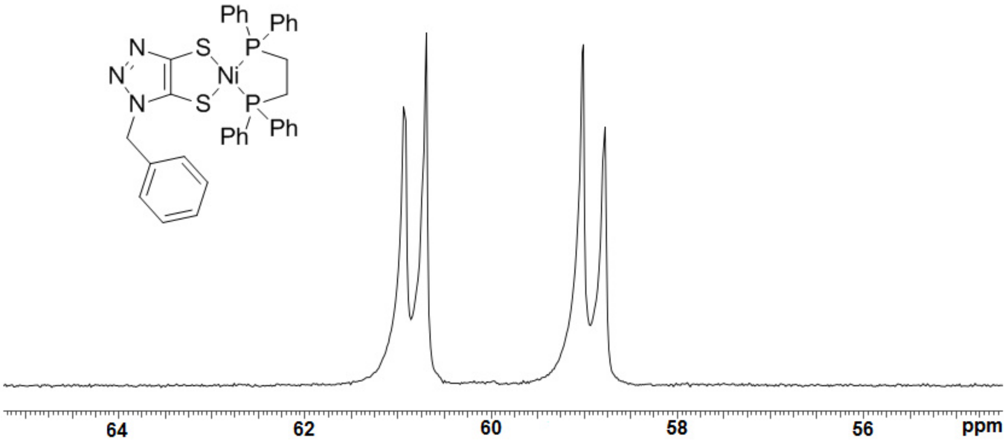


Figure S35. ^{31}P NMR spectrum (202 MHz) of **12** in CD_2Cl_2 at 300 K.

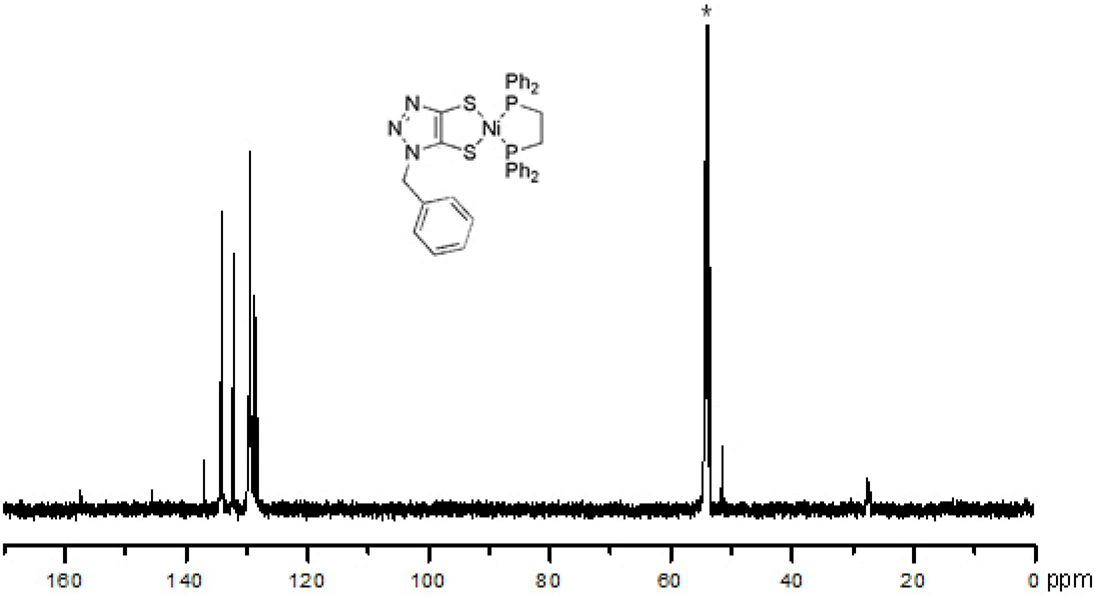


Figure S36. ^{13}C NMR spectrum (126 MHz) of **12** in CD_2Cl_2(*) at 300 K.

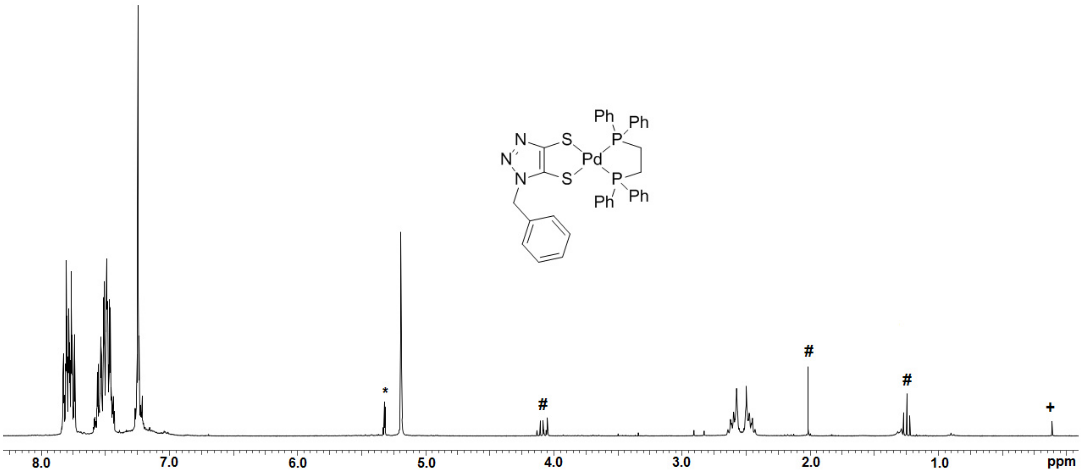


Figure S37. ^{1}H NMR spectrum (300 MHz) of **13** in CD_2Cl_2 (*) with traces of EtOAc (#) and Me_4Si (+) at 300 K.

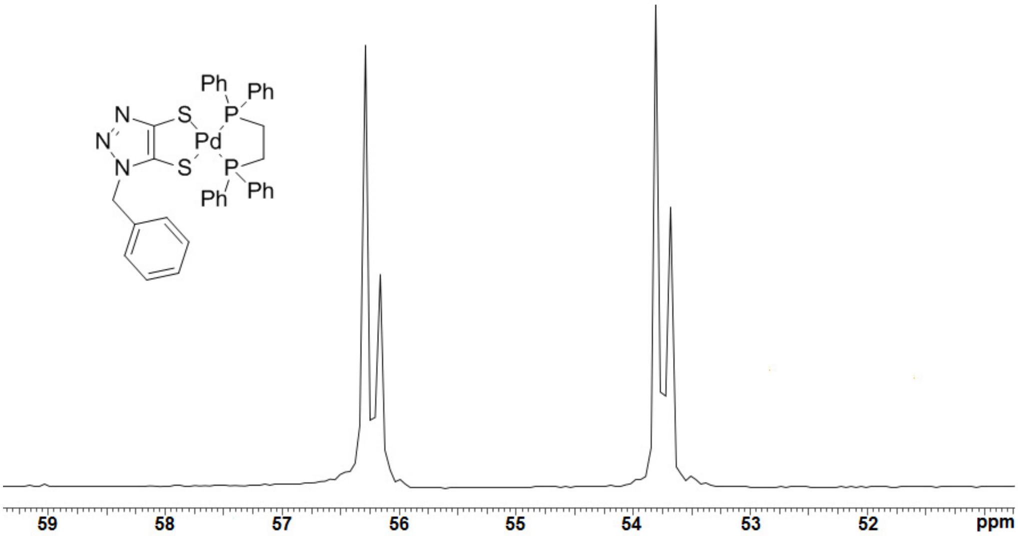


Figure S38. ^{31}P NMR spectrum (121 MHz) of **13** in $CDCl_3$ at 300 K.

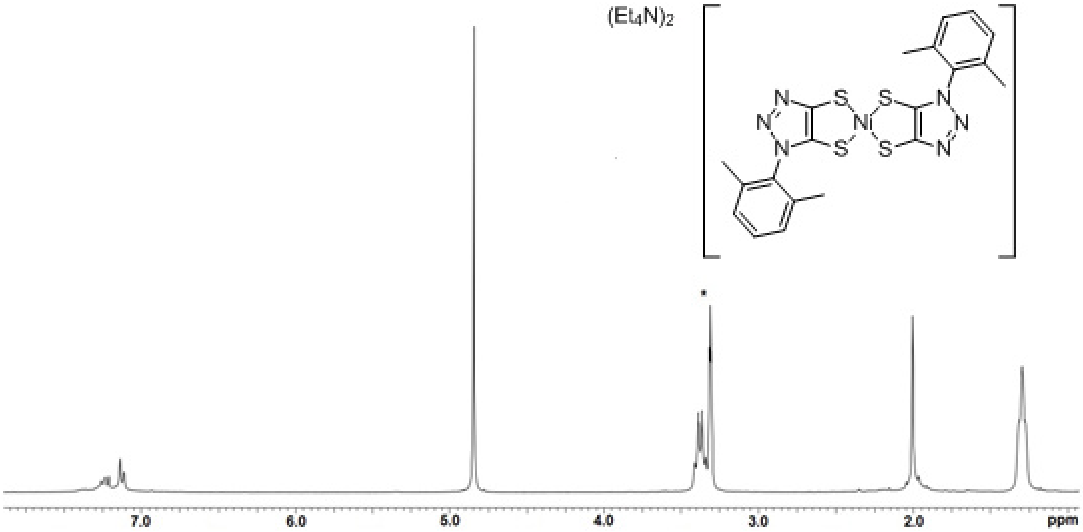


Figure S39. ^{1}H NMR spectrum (300 MHz) of $(Et_4N)_2$-**14** in MeOD (*) at 300 K.

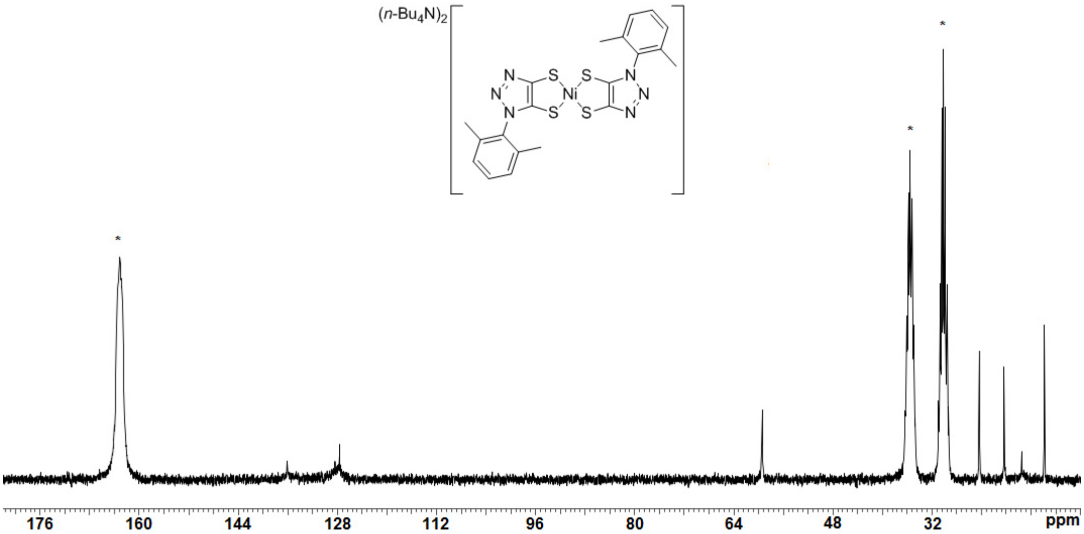


Figure S40. ^{13}C NMR spectrum (75.6 MHz) of [(*n*-$Bu_4N)_2$**14**] in DMF-D7 (*) at 300 K.

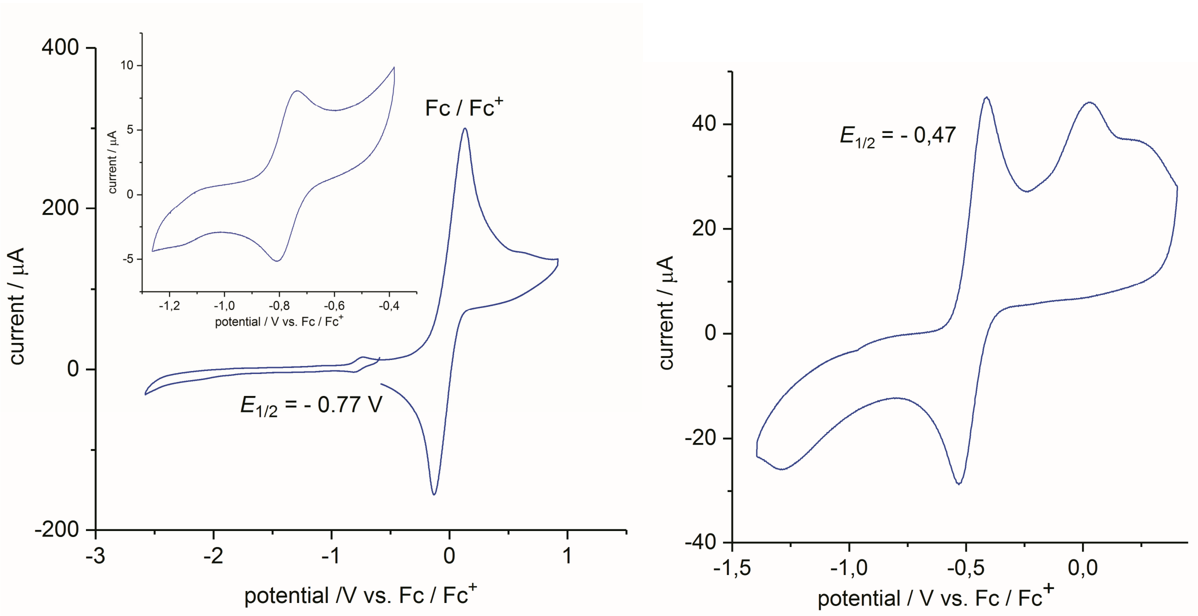


Figure S41: Cyclic voltammogram of $(NEt_4)_2$**14** in DMF (left) and in CH_3OH (right).

2.2 UV/vis absorption spectroscopy

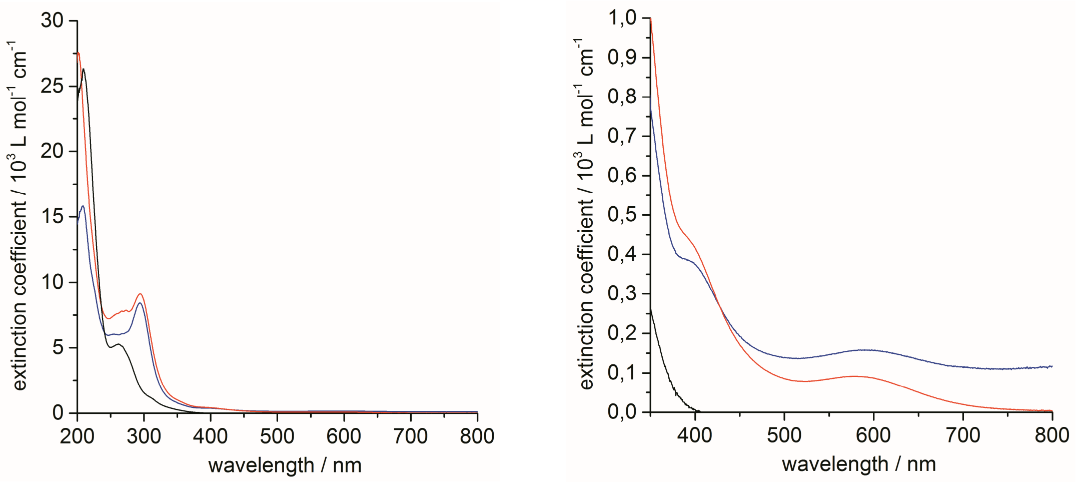


Figure S41. UV/vis spectra of **3** (black), **11** (red) and **12** (blue) at different concentrations.

UV-Vis spectra of $(NEt_4)_2$**14** and (NEt_4)**14** in Methanol are depicted in Figure S44 combined with the calculated spectra in the DFT part.

3. Computational details

DFT calculations with complex **11** (closed shell) and its anion **11**$^-$ (open shell, S = 1/2) were carried out using the G09RevE.01[S11] program package. Molecular geometries were optimized without truncation and symmetry constraints in the gas phase using either the PBE0 functional[S12] in combination with a split valence triple ζ-basis sets of the Ahlrich group (def2-TZVP)[S13] or the M06L functional[S14] in combination with related Pople basis sets 6-311+G(d,p).[S15] Dispersion was accounted for by the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).[S16] In doing so, an excellent match between the calculated and the experimentally determined structures for **11** was achieved with PBE0, while the results with M06L are reasonable et least (Table S4). In addition, essential bonding parameters of the anion **11**$^-$ are included in Table S4 for comparison. Frequency calculations were performed to identify all stationary points as minima. The molecular structures are depicted in Figure S43 and the Cartesian coordinates are given in Table S6. Accordingly, respective calculations with **12**, the Pd congeners **13** and **13**$^-$ (Fig. S44) as well as the homoleptic Ni complexes **14**$^{2-}$ and **14**$^-$ were performed using the PBE0/def2-TZVP combination. TD-DFT calculations were carried out for **12**, **13**, **14**$^{2-}$ and **14**$^-$ using the ORCA 4.2.1 program package.[S17] In all cases, ten transitions were accounted for, respectively (Table S5 and Fig. S45 and S46).

Table S4. Comparison of experimentally determined and calculated bond lengths and angles in **11** and [**11**]$^-$.

	11 (X-ray)	**11** (PBE0)	**11** (M06L)	[**11**]$^-$ (PBE0)	[**11**]$^-$ (M06L)
Ni–S1	2.2014(5)	2.1972	2.2314	2.3143	2.3493
Ni–S2	2.1845(4)	2.1863	2.2149	2.2711	2.2741
Ni–P1	2.1614(4)	2.1533	2.1701	2.2114	2.1880
Ni–P2	2.1560(4)	2.1493	2.1655	2.1815	2.1673
C1–S1	1.7221(15)	1.7188	1.7266	1.7162	1.7162
C2–S2	1.7351(15)	1.7375	1.7476	1.7405	1.7415

S1–Ni–S2	96.352(17)	96.409	96.100	97.045	95.842
P1–Ni–P2	87.371(17)	87.400	87.411	87.582	88.319
S1–S2–P2–P1	16.197(16)	18.061	19.720	71.648	72.460

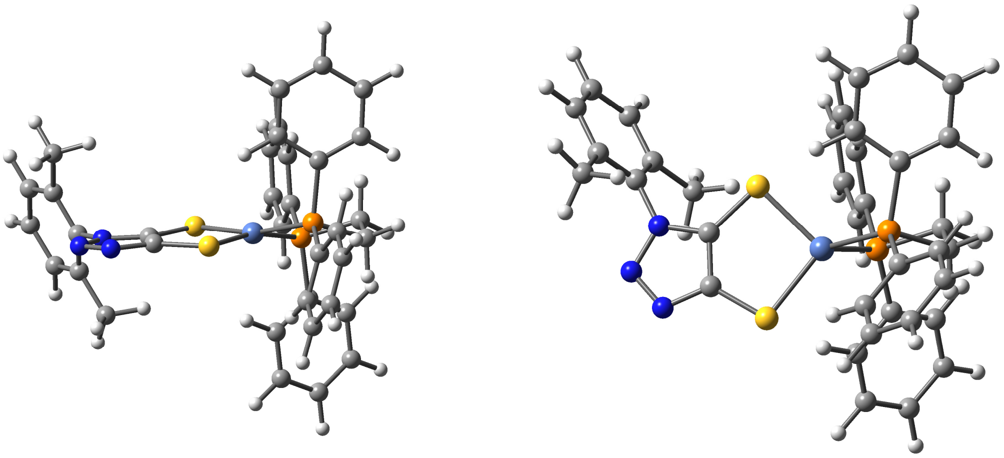


Figure S43. Calculated molecular structures of **11** (left) and **11**$^-$ (right); optimized at PBE0/def2-TZVP level.

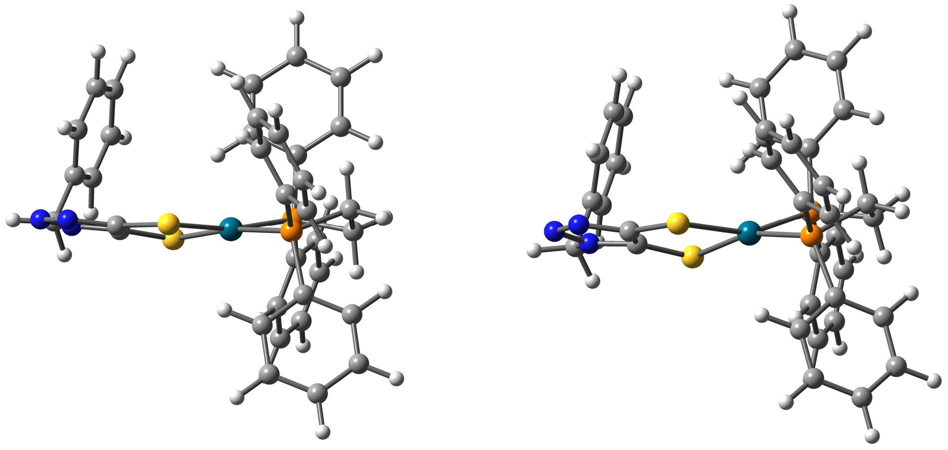


Figure S44. Calculated molecular structures of **13** (left) and **13**$^-$ (right); optimized at PBE0/def2-TZVP level.

Table S5. Calculated transitions with oscillator strength > 0.005 and respective essential assignments in **12** and **13**.

compound	state	wavelength	oscillator strength	assignment
12 (Ni)	1	623.4	0.0092	HOMO→LUMO: π(tazdt)→$\sigma^*(d_{X2\text{-}Y2})$
	4	443.2	0.0083	HOMO→π*(dppe-Ph)
	5	418.5	0.0057	HOMO→π*(dppe-Ph)
	6	406.2	0.0128	d→LUMO (d/d character)
	7	391.6	0.0106	HOMO→π*(dppe-Ph)
13 (Pd)	1	594.0	0.0097	HOMO→LUMO: π(tazdt)→$\sigma^*(d_{X2\text{-}Y2})$
	5	396.0	0.0098	HOMO→π*(dppe-Ph)
	6	384.2	0.0151	HOMO→π*(dppe-Ph)

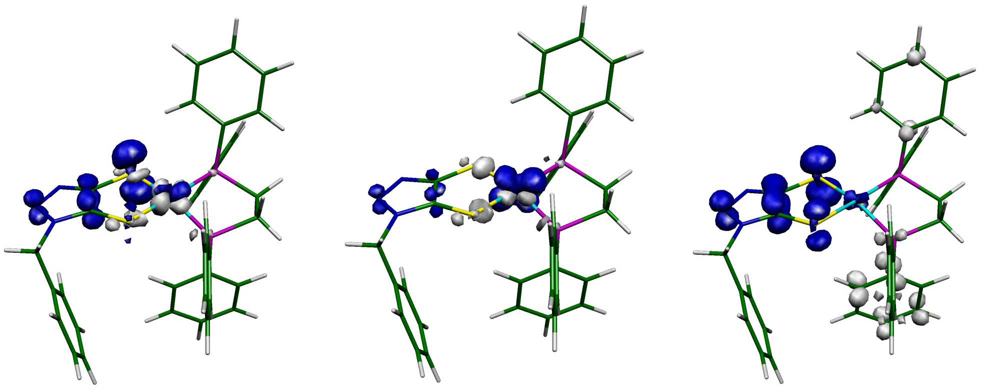


Figure S45. Difference electron densities of transitions in the Ni complex **12**: transitions 1 (left), 6 (middle) and 7 (right), calculated by TD-DFT (PBE0/def2-TZVP).

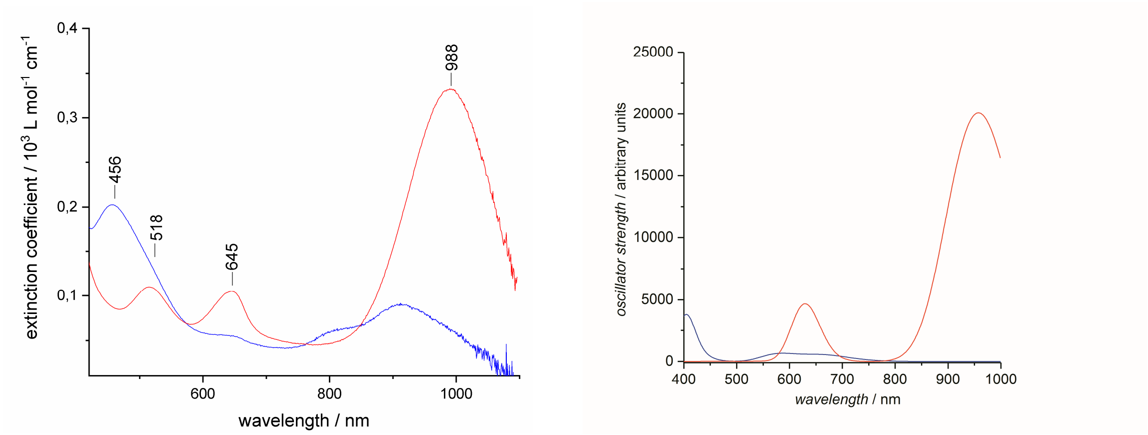


Figure S46. UV/vis spectra of $(NEt_4)_2$**14** (blue) and (NEt_4)**14** (red): experimental spectra in MeOH (left), calculated spectra by TD-DFT (right).

Table S6. Cartesian coordinates of the geometry optimized structures of **11** (left) and [**11**]$^-$ (right) in the gas phase; PBE0, def2-TZVP with empirical dispersion correction (GD3BJ).

N	-3,22605	-2,18594	-0,6739	N	-3,4913	-0,93117	-1,57254
N	-3,05882	-3,41885	-1,21003	N	-3,7307	-0,73834	-2,89398
N	-1,78866	-3,60683	-1,38399	N	-2,58883	-0,47585	-3,45351
P	2,69517	-0,23161	0,10361	P	2,52698	-0,80553	0,25074
Ni	0,55805	-0,17035	-0,11622	Ni	0,61389	-0,12813	-0,54943
C	3,74875	-1,11843	-1,06583	C	3,74647	-1,71319	-0,76795
C	3,11346	-0,87563	1,74901	C	2,4703	-1,79528	1,79485
C	3,3369	1,49009	0,0729	C	3,46964	0,69675	0,76233
P	0,67558	1,94203	0,28475	P	0,97385	1,79822	0,47509
S	0,58194	-2,1625	-1,01664	S	0,0884	-0,16087	-2,7587
S	-1,61578	-0,06317	0,1845	S	-1,39565	-0,96828	0,23281
H	-0,33693	1,22222	-2,29768	H	0,53574	2,34382	-2,27675
C	4,84987	-1,86295	-0,65437	C	4,92615	-2,26235	-0,2696
C	3,44448	-1,02276	-2,42263	C	3,45862	-1,8337	-2,12539
C	4,0802	-0,29691	2,56833	C	3,39535	-1,71598	2,8343
C	2,4198	-1,99996	2,19758	C	1,37751	-2,65137	1,93595
H	4,36616	1,555	0,43075	H	4,35818	0,46948	1,35736
H	3,34584	1,77774	-0,98271	H	3,81119	1,15684	-0,1696

C	2,37285	2,36212	0,85937	C	2,50944	1,62332	1,49787
C	0,48233	2,89808	-1,24489	C	1,3039	3,2965	-0,51611
C	-0,42763	2,68631	1,50726	C	-0,26396	2,35222	1,69035
H	5,0762	-1,9588	0,40104	H	5,14642	-2,20096	0,7906
C	5,64814	-2,49465	-1,59508	C	5,81412	-2,90491	-1,11727
C	4,24895	-1,65075	-3,35825	C	4,34974	-2,47756	-2,97324
H	2,5584	-0,48311	-2,73765	H	2,51868	-1,43534	-2,50155
H	4,63385	0,57419	2,23924	H	4,243	-1,04358	2,76263
C	4,35039	-0,83369	3,81804	C	3,24203	-2,4824	3,98088
C	2,70232	-2,53997	3,44143	C	1,23143	-3,42751	3,0749
H	1,65989	-2,44152	1,55997	H	0,62083	-2,67074	1,1557
H	2,5818	3,42733	0,74612	H	2,96553	2,59001	1,72393
H	2,41292	2,1263	1,92612	H	2,20044	1,17295	2,44569
C	-0,04129	2,26372	-2,36854	C	0,964	3,25823	-1,86602
C	0,85386	4,24015	-1,32526	C	1,87121	4,45667	0,01139
C	-1,35939	3,66621	1,18417	C	-0,93746	3,5675	1,61331
C	-0,37555	2,18678	2,80856	C	-0,64839	1,43041	2,6666
H	6,50081	-3,07971	-1,27071	H	6,72966	-3,33041	-0,72001
C	5,35089	-2,38613	-2,94551	C	5,5281	-3,00983	-2,47281
H	4,00362	-1,5813	-4,41136	H	4,11296	-2,56882	-4,02749
H	5,10168	-0,37408	4,44981	H	3,96697	-2,40222	4,78408
C	3,66327	-1,95648	4,25492	C	2,1626	-3,34525	4,10099
H	2,16131	-3,41622	3,77879	H	0,37325	-4,08383	3,16701
C	0,7049	4,93508	-2,51358	C	2,09906	5,55884	-0,79648
H	1,24816	4,75232	-0,45446	H	2,12313	4,50706	1,06555
H	-1,42744	4,0363	0,16869	H	-0,67497	4,28094	0,84137
C	-2,21304	4,1595	2,15982	C	-1,95606	3,86629	2,508
C	-1,22275	2,6881	3,78036	C	-1,65403	1,73529	3,56651
H	0,31192	1,38371	3,05434	H	-0,17898	0,45268	2,69255
H	5,97262	-2,88708	-3,67853	H	6,22163	-3,51661	-3,13541
H	3,87541	-2,37511	5,23198	H	2,04058	-3,94204	4,9984
C	-2,14201	3,67726	3,45695	C	-2,31272	2,95566	3,49005
H	-1,17818	2,29419	4,78884	H	-1,94634	1,00322	4,31079
C	-1,12013	-2,50808	-0,96873	C	-1,60466	-0,48869	-2,52304
C	-2,02658	-1,58599	-0,49864	C	-2,17081	-0,79388	-1,28839
C	-4,513	-1,68247	-0,36145	C	-4,55054	-1,17501	-0,67218
C	-5,05812	-0,68934	-1,17396	C	-4,9316	-0,16637	0,21493
C	-6,31785	-0,20243	-0,84432	C	-5,97862	-0,43299	1,09105
H	-6,7642	0,56783	-1,46386	H	-6,28795	0,33877	1,78852
C	-7,00344	-0,69603	0,25276	C	-6,62516	-1,65773	1,07754
H	-7,9869	-0,3085	0,4941	H	-7,44157	-1,84717	1,76665
C	-6,43869	-1,68425	1,04243	C	-6,22956	-2,64218	0,18617
H	-6,97649	-2,06665	1,90314	H	-6,72956	-3,60548	0,17995
C	-5,1791	-2,19409	0,75145	C	-5,18198	-2,41839	-0,69951
C	-4,30743	-0,17034	-2,35885	C	-4,22885	1,15198	0,2211
H	-3,44591	0,42434	-2,03996	H	-3,21375	1,03694	0,61548
H	-4,95103	0,45675	-2,97668	H	-4,76583	1,87527	0,83693

H	-3,92426	-0,98999	-2,97068	H	-4,13189	1,54761	-0,79248
C	-4,54555	-3,24824	1,60245	C	-4,71564	-3,47939	-1,6451
H	-5,16147	-3,45815	2,47736	H	-5,25806	-4,41169	-1,47802
H	-3,55563	-2,93173	1,94132	H	-3,6464	-3,66486	-1,51334
H	-4,40473	-4,17296	1,0391	H	-4,85061	-3,16483	-2,68188
C	-0,18827	2,96264	-3,55766	C	1,1881	4,36633	-2,67253
H	-0,5969	2,46113	-4,42702	H	0,91821	4,32366	-3,72188
C	0,18508	4,29544	-3,63157	C	1,75654	5,51415	-2,14245
H	0,07056	4,8406	-4,56142	H	1,93464	6,37706	-2,77541
H	0,99335	5,97839	-2,56824	H	2,54131	6,45594	-0,37628
H	-2,94174	4,91857	1,90061	H	-2,47747	4,81414	2,42895
H	-2,81324	4,06171	4,21603	H	-3,11432	3,18631	4,18308

Table S7. Cartesian coordinates of the geometry optimized structures of **13** (left) and [**13**]⁻ (right) in the gas phase; PBE0, def2-TZVP with empirical dispersion correction (GD3BJ).

Pd	0.466705	-0.257737	-0.292363	Pd	0.523264	-0.344371	-0.258233
P	0.078349	1.856557	0.376154	P	0.059081	1.712439	0.581007
P	2.573157	0.065734	0.418395	P	2.680248	0.056287	0.307393
S	-1.631522	-0.349154	-1.288597	S	-1.590121	-0.363683	-1.467972
S	0.846112	-2.532565	-0.572780	S	0.664089	-2.748650	-0.375031
C	1.698176	2.635207	0.750782	C	1.653881	2.536715	1.001225
C	-0.748529	3.021615	-0.730769	C	-0.706240	2.916196	-0.546713
C	-0.873677	1.896822	1.920017	C	-0.966020	1.804561	2.064209
C	2.587860	1.603399	1.424125	C	2.672741	1.500586	1.456454
C	3.692805	0.373411	-0.974735	C	3.851190	0.498811	-0.997886
C	3.396172	-1.164967	1.451750	C	3.600662	-1.174145	1.282999
C	-1.709654	-2.058078	-1.466147	C	-1.787505	-2.066454	-1.462862
C	-0.705572	-2.968981	-1.228885	C	-0.901181	-3.055042	-1.058855
C	-1.544103	4.056456	-0.245890	C	-1.589280	3.908102	-0.126889
C	-0.553798	2.881242	-2.103050	C	-0.358288	2.842556	-1.895494
C	-2.055034	1.154910	1.968610	C	-2.278678	1.320701	1.957906
C	-0.479021	2.627149	3.038093	C	-0.496163	2.192410	3.321003
C	3.583168	-0.464753	-2.084590	C	4.096585	-0.472099	-1.979209
C	4.639926	1.394527	-0.978806	C	4.416016	1.766043	-1.160265
C	4.773167	-1.364543	1.398275	C	4.992220	-1.255865	1.272159
C	2.619879	-1.909775	2.337261	C	2.873924	-2.036761	2.102103
N	-2.749228	-2.817836	-1.872642	N	-2.879135	-2.761026	-1.861840
N	-1.169222	-4.208055	-1.509684	N	-1.495723	-4.260934	-1.244174
C	-2.125902	4.952642	-1.127919	C	-2.108654	4.814843	-1.037623
C	-1.134096	3.783176	-2.980095	C	-0.870832	3.756485	-2.801961
C	-2.831936	1.160294	3.114051	C	-3.099035	1.270597	3.068142
C	-1.254205	2.617720	4.188787	C	-1.319419	2.123131	4.434910
C	4.421236	-0.287731	-3.172711	C	4.906810	-0.190978	-3.061499
C	5.467496	1.576159	-2.076782	C	5.212794	2.050033	-2.259982
C	5.369926	-2.291412	2.237363	C	5.645982	-2.179509	2.072119
C	3.223386	-2.830830	3.177549	C	3.531722	-2.954862	2.905972
N	-2.407262	-4.120208	-1.887833	N	-2.694893	-4.088560	-1.715839
C	-4.107113	-2.401541	-2.089264	C	-4.163300	-2.228383	-2.192044

C	-1.918459	4.818776	-2.493548	C	-1.747473	4.744279	-2.376328
C	-2.432015	1.887473	4.226930	C	-2.625951	1.671102	4.314816
C	5.360828	0.733922	-3.173016	C	5.468985	1.074606	-3.212123
C	4.596585	-3.021489	3.128760	C	4.916916	-3.028509	2.894210
C	-4.733368	-1.845691	-0.835519	C	-4.870441	-1.619888	-1.005627
C	-4.524296	-2.471024	0.388865	C	-4.592088	-2.048485	0.286603
C	-5.514540	-0.699636	-0.885009	C	-5.816918	-0.620714	-1.194558
C	-5.095346	-1.959385	1.542477	C	-5.254183	-1.488971	1.368007
C	-6.090133	-0.186711	0.268193	C	-6.483748	-0.062276	-0.114922
C	-5.882698	-0.816832	1.485512	C	-6.203882	-0.496082	1.172684
H	2.108512	2.924695	-0.221093	H	1.976668	3.006817	0.068070
H	1.587087	3.549602	1.337424	H	1.514332	3.337565	1.732393
H	2.183981	1.312453	2.398236	H	2.386194	1.081240	2.425225
H	3.604114	1.965651	1.592915	H	3.676112	1.920861	1.571224
H	-1.719241	4.152220	0.819573	H	-1.877688	3.960991	0.916625
H	0.029626	2.047491	-2.477939	H	0.292806	2.040166	-2.227653
H	-2.357253	0.565944	1.107572	H	-2.636312	0.957425	0.998059
H	0.433928	3.210312	3.025034	H	0.519827	2.552083	3.438399
H	2.831822	-1.249401	-2.087664	H	3.622316	-1.445023	-1.888703
H	4.742896	2.057115	-0.127950	H	4.240773	2.541160	-0.423352
H	5.376003	-0.806656	0.691041	H	5.562799	-0.598384	0.625791
H	1.542638	-1.787956	2.337406	H	1.789449	-2.008306	2.068710
H	-2.748960	5.754055	-0.748177	H	-2.801448	5.578446	-0.700495
H	-0.986078	3.666121	-4.047120	H	-0.599459	3.682466	-3.849142
H	-3.748283	0.581969	3.132450	H	-4.110732	0.896193	2.958861
H	-0.935008	3.184270	5.055936	H	-0.936295	2.428527	5.403059
H	4.331416	-0.946376	-4.028542	H	5.088699	-0.958417	-3.805923
H	6.197643	2.377165	-2.073453	H	5.640522	3.041273	-2.368729
H	6.440832	-2.450641	2.188470	H	6.728993	-2.238863	2.051343
H	2.615417	-3.416098	3.857097	H	2.954381	-3.631025	3.526396
H	-4.638588	-3.290462	-2.436118	H	-4.744702	-3.061135	-2.597191
H	-4.138602	-1.652476	-2.884947	H	-4.050321	-1.471322	-2.973398
H	-2.380015	5.517702	-3.181626	H	-2.158132	5.451730	-3.088581
H	-3.036005	1.881122	5.127041	H	-3.267699	1.617390	5.187129
H	6.007930	0.876691	-4.030751	H	6.091665	1.298297	-4.070911
H	5.064803	-3.752543	3.777786	H	5.428917	-3.755404	3.515543
H	-3.897987	-3.355452	0.434697	H	-3.835647	-2.809016	0.441658
H	-5.659163	-0.192465	-1.833346	H	-6.016947	-0.259748	-2.198815
H	-4.924262	-2.455246	2.491403	H	-5.014429	-1.822984	2.371494
H	-6.693737	0.712264	0.215988	H	-7.211348	0.725419	-0.278188
H	-6.332621	-0.418473	2.388254	H	-6.715505	-0.053708	2.020767

Table S8. Cartesian coordinates of the geometry optimized structures of [**14**]$^{2-}$ (left) and [**14**]$^{-}$ (right) in the gas phase; PBE0, def2-TZVP with empirical dispersion correction (GD3BJ).

Ni	0.000000	0.000000	0.000000	Ni	0.000000	0.000000	0.000000
S	0.884921	0.218520	2.041448	S	0.839208	0.231896	2.025398
S	-0.884921	-0.218520	-2.041448	S	-0.839208	-0.231896	-2.025398
S	1.645434	1.149331	-1.003460	S	1.527512	1.217415	-0.975605

S	-1.645434	-1.149331	1.003460	S	-1.527512	-1.217415	0.975605
C	2.242901	1.185560	1.652137	C	2.163928	1.229761	1.651656
C	-2.242901	-1.185560	-1.652137	C	-2.163928	-1.229761	-1.651656
C	2.602895	1.586198	0.375728	C	2.488083	1.661015	0.373899
C	-2.602895	-1.586198	-0.375728	C	-2.488083	-1.661015	-0.373899
N	3.215059	1.711646	2.441571	N	3.128673	1.773247	2.430361
N	-3.215059	-1.711646	-2.441571	N	-3.128673	-1.773247	-2.430361
N	3.743559	2.307806	0.453874	N	3.608946	2.421742	0.441155
N	-3.743559	-2.307806	-0.453874	N	-3.608946	-2.421742	-0.441155
N	4.132369	2.394038	1.695149	N	3.999887	2.492520	1.670598
C	3.358254	1.624660	3.838142	C	3.303332	1.655450	3.829350
N	-4.132369	-2.394038	-1.695149	N	-3.999887	-2.492520	-1.670598
C	-3.358254	-1.624660	-3.838142	C	-3.303332	-1.655450	-3.829350
C	4.410356	0.870789	4.362892	C	4.319973	0.829218	4.307673
C	2.449770	2.294487	4.661344	C	2.449178	2.361182	4.675868
C	-4.410356	-0.870789	-4.362892	C	-4.319973	-0.829218	-4.307673
C	-2.449770	-2.294487	-4.661344	C	-2.449178	-2.361182	-4.675868
C	4.552796	0.808074	5.744203	C	4.480175	0.727052	5.684269
C	5.330075	0.127199	3.447353	C	5.188713	0.067844	3.357857
C	2.619082	2.197466	6.038907	C	2.638126	2.225315	6.046822
C	1.334675	3.087239	4.064145	C	1.367900	3.229661	4.118165
C	-4.552796	-0.808074	-5.744203	C	-4.480175	-0.727052	-5.684269
C	-5.330075	-0.127199	-3.447353	C	-5.188713	-0.067844	-3.357857
C	-2.619082	-2.197466	-6.038907	C	-2.638126	-2.225315	-6.046822
C	-1.334675	-3.087239	-4.064145	C	-1.367900	-3.229661	-4.118165
C	3.663040	1.465114	6.579671	C	3.645747	1.418313	6.547674
C	-3.663040	-1.465114	-6.579671	C	-3.645747	-1.418313	-6.547674
H	5.362545	0.218999	6.164270	H	5.262613	0.087278	6.078321
H	4.755306	-0.509727	2.769838	H	4.581206	-0.537201	2.679899
H	6.023023	-0.495608	4.017510	H	5.866810	-0.592500	3.899944
H	5.891928	0.817793	2.815595	H	5.775180	0.745727	2.734255
H	1.917725	2.709859	6.690228	H	1.984459	2.764701	6.723978
H	0.809231	3.657678	4.832836	H	0.903154	3.821205	4.907853
H	0.625838	2.421278	3.557409	H	0.594997	2.623765	3.635932
H	1.713006	3.773241	3.302262	H	1.762369	3.906518	3.356934
H	-5.362545	-0.218999	-6.164270	H	-5.262613	-0.087278	-6.078321
H	-4.755306	0.509727	-2.769838	H	-4.581206	0.537201	-2.679899
H	-6.023023	0.495608	-4.017510	H	-5.866810	0.592500	-3.899944
H	-5.891928	-0.817793	-2.815595	H	-5.775180	-0.745727	-2.734255
H	-1.917725	-2.709859	-6.690228	H	-1.984459	-2.764701	-6.723978
H	-0.809231	-3.657678	-4.832836	H	-0.903154	-3.821205	-4.907853
H	-0.625838	-2.421278	-3.557409	H	-0.594997	-2.623765	-3.635932
H	-1.713006	-3.773241	-3.302262	H	-1.762369	-3.906518	-3.356934
H	3.780207	1.400233	7.656889	H	3.779802	1.324121	7.619797
H	-3.780207	-1.400233	-7.656889	H	-3.779802	-1.324121	-7.619797

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