

# Azoimidazole functionalized Ni-porphyrins for molecular spin switching and light responsive MRI contrast agents.

---

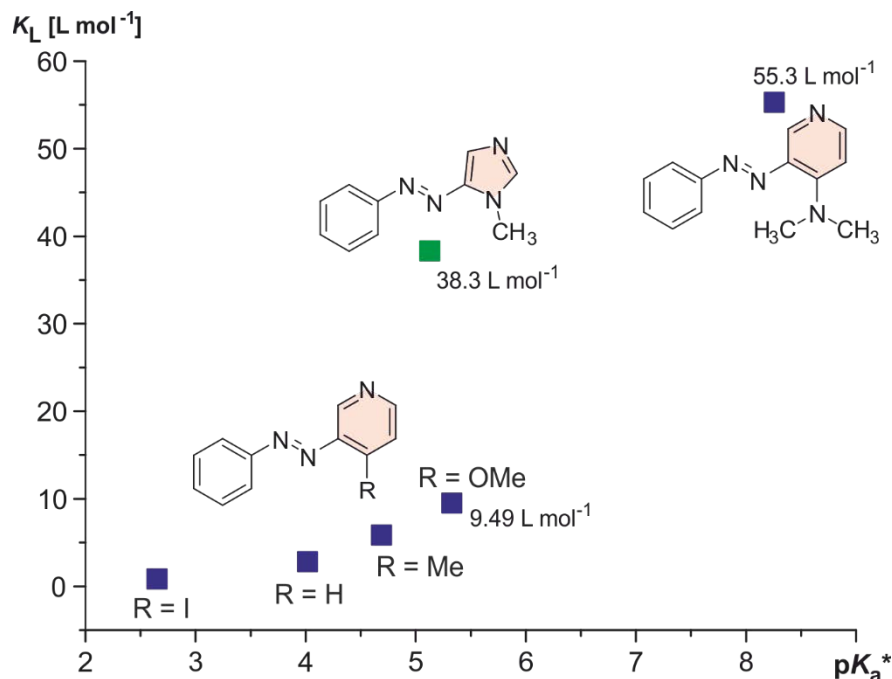
Gernot Heitmann, Christian Schütt, Jens Gröbner, Lukas Huber and Rainer Herges

## Table of Contents

<b>I.</b>	<b>Coordination strength and basicity of pyridine- and imidazole-based PDLs.....</b>	<b>S1</b>
<b>II.</b>	<b>Computational Details</b>	
	II.1 Complex Formation Energy of the Reference System.....	S2
	II.2 Energy Difference of the Magnetic Conformers in <i>cis</i> Configuration.....	S2
	II.3 XYZ Coordinates of TPSSh/SVP optimized Reference System .....	S3
	II.4 XYZ Coordinates of TPSSh/SVP optimized Record Player Type Molecules	
	II.4.1 Magnetic Conformers of Biphenyl RP <b>4</b> .....	S5
	II.4.2 Magnetic Conformers of Biphenyl Thioether RP <b>5</b> .....	S7
<b>III.</b>	<b>Experimental Section</b>	
	III.1 General Information.....	S9
	III.2 Synthetic Procedures .....	S10
	III.3 NMR Spectra.....	S21
	III.4 UV-vis spectra and UV-vis switching experiments.....	S34
	III.5 NMR switching experiments.....	S36
	III.6 Thermal half-lives of <i>cis</i> - <b>4</b> and <i>cis</i> - <b>5</b> and of tonearms <i>cis</i> - <b>13</b> and <i>cis</i> - <b>16</b> .....	S38
	III.7 Intramolecular coordination in <i>cis</i> record players <b>4</b> and <b>5</b> .....	S39
	III.8. MRI measurements with record players <b>4</b> and <b>5</b> . .....	S42
<b>IV.</b>	<b>Literature.....</b>	<b>S43</b>

## I. Coordination Strength and Basicity of Pyridine- and Imidazole-based PDLs

Light-driven coordination-induced spin state switching (LD-CISS) in water requires a photoswitchable ligand with a high binding affinity ( $K_L$ ) to the metal center while exhibiting a low basicity (corresponding to the  $pK_a$ ). Figure S1 shows the association constants ( $K_L$ ) of several 3-(phenylazo)-pyridine ligands<sup>1</sup> and the parent phenylazoimidazole ligand<sup>2</sup> to NiTPPF<sub>20</sub> in toluene-d<sub>8</sub> in correlation to their predicted<sup>3</sup> basicity ( $pK_a^*$ ). The azoimidazole ligand provides the most favourable  $K_L/pK_a$  ratio and will most likely not be protonated in water ( $pK_a^* = 5.13$ ). The dimethylamino-substituted azopyridine ligand binds stronger to the nickel in toluene; however, its predicted basicity ( $pK_a^* = 8.26$ ) suggests that it will be completely protonated in aqueous media and therefore will not bind.



**Figure S1:** Association constants ( $K_L$ ) of 3-(phenylazo)pyridines<sup>1</sup> and 5-(phenylazo)-1-methylimidazole<sup>2</sup> to Ni(II)TPPF<sub>20</sub> in toluene in correlation to their calculated<sup>3</sup>  $pK_a$  values. The imidazole derivative provides the most favourable  $K_L/pK_a$  ratio.

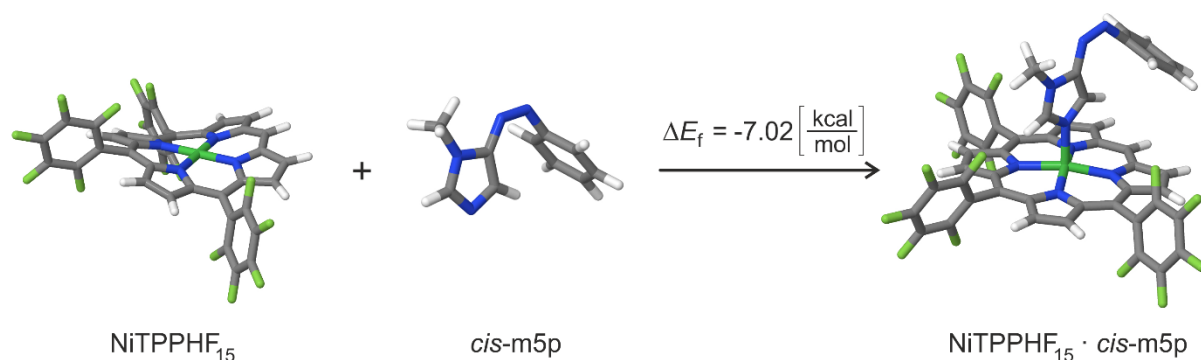
## II. Computational Details

### II.1 Complex Formation Energy of the Reference System

All calculations have been conducted using Turbomole 6.6.<sup>4</sup> The geometry optimizations were performed at the TPSSh/SVP level of theory. Single point energies using a larger basis set (TPSSh/def2TZVP) were calculated at the optimized geometries. The calculated complex formation energy ( $\Delta E_f$ ) for the formation of the five coordinate complex of tris-pentafluorophenyl-porphyrin (NiTPPHF<sub>15</sub>) with the most stable conformation of *cis*-1-methyl-5-phenylazoimidazole (*cis*-m5p)<sup>2</sup> is given in Figure S2 and Table S1.

**Table S1.** Complex formation energy ( $\Delta E_f$ ) of the reference system calculated at the TPSSh/def2TZVP//TPSSh/SVP level of theory.  $\Delta E_f$  is defined according to the following equation: NiTPPHF<sub>15</sub> (singlet) + *cis*-m5p (singlet)  $\rightarrow$  NiTPPHF<sub>15</sub> · *cis*-m5p (triplet).

$E_{\text{abs}}$ m5p singlet [a.u.]	$E_{\text{abs}}$ NiTPPHF <sub>15</sub> singlet [a.u.]	$E_{\text{abs}}$ NiTPPHF <sub>15</sub> singlet [a.u.]	$\Delta E_f$ [kcal/mol]
-606.28355311	-5286.05067482	-4679.75594046	-7.02



**Figure S2:** Calculated (TPSSh/def2TZVP//TPSSh/SVP) complex formation energy of the five coordinate complex of *cis*-m5p with NiTPPHF<sub>15</sub> in kcal/mol.

### II.2 Energy Difference of the Magnetic Conformers in *cis* Configuration

The energy difference ( $\Delta\Delta E_f$ ) of the uncoordinated diamagnetic (*cis*-s-u) and the coordinated paramagnetic *cis* isomer (*cis*-t-k) is indicative of the amount of paramagnetic *cis* species. A higher difference in energy of the magnetic conformers gives rise to a stabilization upon coordination and thus a stronger coordination of the tone arm.

**Table S2.** Calculated (TPSSh/def2TZVP//TPSSh/SVP) energy difference of the uncoordinated *cis* (singlet) and coordinated *cis* (triplet) species for 1a-c. ( $\Delta\Delta E_{f,\text{calc}} = \Delta E_{f,\text{calc-}cis\text{-s-u}} - \Delta E_{f,\text{calc-}cis\text{-t-k}}$ ).

	$E_{\text{abs},cis\text{-s-u}}$ [Hartree]	$E_{\text{abs},cis\text{-t-k}}$ [Hartree]	$\Delta\Delta E_f$ [kcal/mol]
Biphenyl <b>4</b>	-5515.98617580	-5515.98958307	2.14
Biarylthioether <b>5</b>	-5914.20203374	-5914.20847273	4.04

### II.3 XYZ Coordinates of TPSSh/SVP Optimized Reference System.

#### NiTPPHF<sub>15</sub> · 1 cis-m5p

E<sub>TPSSh/SVP</sub> = -5281.59352739 Hartree

NImag = 0

C	0.266560	-3.468100	4.108400
C	-1.033430	-3.799430	3.687930
C	-1.235560	-4.930670	2.893870
C	-0.151520	-5.730600	2.510350
C	1.139590	-5.402250	2.940570
C	1.351960	-4.283980	3.752260
N	0.478370	-2.385780	5.012410
N	0.390980	-1.186690	4.653060
C	0.192970	-0.754850	3.347150
C	0.184630	-1.260280	2.043190
N	0.057630	0.629080	3.199960
N	0.048050	-0.232430	1.164390
C	-0.032760	0.886720	1.885560
H	-1.876780	-3.173230	3.991600
H	-2.249170	-5.186540	2.570760
H	-0.314900	-6.614460	1.886810
H	1.990320	-6.026860	2.651550
H	2.352960	-4.029760	4.110330
H	0.277500	-2.287570	1.703360
H	-0.160100	1.888560	1.476580
C	1.217600	2.516540	-1.136420
N	1.408950	1.161040	-1.173020
C	2.491890	3.205340	-1.186160
C	3.452510	2.240790	-1.266240
C	2.763530	0.966090	-1.249540
C	-0.032650	3.160200	-1.059390
C	-1.282940	2.513540	-1.050510
C	-2.557690	3.201460	-1.031920
C	-3.520820	2.235690	-1.034130
C	-2.832140	0.960640	-1.054780
N	-1.475320	1.157180	-1.065860
Ni	-0.021980	-0.287040	-0.895610
N	1.420570	-1.721340	-1.184440
C	1.220520	-3.076040	-1.229530
C	2.485320	-3.769380	-1.347760
C	3.453980	-2.807770	-1.381550
C	2.772100	-1.531730	-1.279890
C	-3.478910	-0.288930	-1.059980
C	-2.830950	-1.539160	-1.083680
C	-3.512320	-2.818660	-1.149460
C	-2.539940	-3.776030	-1.184230
C	-1.273110	-3.078020	-1.146060
N	-1.475820	-1.724280	-1.082590
C	-0.026110	-3.706580	-1.196280
C	3.412420	-0.279930	-1.303170
H	-4.600830	2.374830	-1.025090
H	-2.696870	4.281800	-1.034080
H	-4.591780	-2.960520	-1.182500
H	-2.659030	-4.858010	-1.247650
H	4.530820	-2.942380	-1.477270
H	2.604560	-4.851400	-1.409480

#### cis-m5p

E<sub>TPSSh/SVP</sub> = -605.618593002 Hartree

Nimag = 0

C	1.537060	0.035830	0.606520
C	2.073990	-1.140650	0.058860
C	2.984140	-1.060000	-0.999180
C	3.372690	0.185210	-1.507880
C	2.850830	1.355900	-0.944250
C	1.939170	1.287940	0.113220
N	0.680020	-0.038310	1.744680
N	-0.570700	-0.081390	1.628610
C	-1.265670	-0.070460	0.431930
C	-1.026140	-0.030040	-0.952930
N	-2.661640	-0.119390	0.543340
N	-2.193300	-0.051820	-1.639540
C	-3.147540	-0.104580	-0.717030
H	1.772610	-2.108920	0.467600
H	3.395640	-1.979730	-1.426770
H	4.086900	0.243490	-2.334420
H	3.157440	2.333710	-1.328830
H	1.533550	2.197940	0.563780
H	-4.218570	-0.133770	-0.925460
C	-3.422460	-0.173220	1.785870
H	-4.039260	-1.086400	1.812770
H	-2.698900	-0.187000	2.612850
H	-4.071830	0.713440	1.872470
H	-0.068020	0.012210	-1.466200

#### NiTPPHF<sub>15</sub>

E<sub>TPSSh/SVP</sub> = -4675.95096384 Hartree

NImag = 0

C	-0.352450	-0.078880	3.463820
N	0.686240	0.257860	2.626100
C	0.062380	-0.010250	4.844310
C	1.351160	0.434500	4.841470
C	1.739540	0.558660	3.460080
C	-1.661250	-0.328840	3.043230
C	-2.066710	-0.080570	1.729870
C	-3.447090	0.019360	1.325690
C	-3.445320	0.480280	0.043150
C	-2.063450	0.589170	-0.353110
N	-1.229840	0.256860	0.689930
Ni	0.698330	0.256320	0.690200
N	2.631190	0.248150	0.686840
C	3.468830	-0.078650	-0.352830
C	4.850290	0.012970	0.054990
C	4.846050	0.452000	1.346130
C	3.464400	0.558330	1.738660
C	-1.651310	0.837040	-1.664760
C	-0.340610	0.591120	-2.079470
C	0.062680	0.494490	-3.460360
C	1.342300	0.028590	-3.460720
C	1.746970	-0.068460	-2.080040
N	0.703070	0.261430	-1.243390

H	2.634060	4.284840	-1.170140	C	3.057000	-0.319410	-1.666490
H	4.531060	2.378760	-1.328920	C	3.044010	0.783200	3.042000
C	-0.026380	4.649340	-0.957330	H	-4.298790	0.693660	-0.598280
C	4.901940	-0.259750	-1.418940	H	-4.302670	-0.199590	1.962390
C	-4.971590	-0.288720	-1.054990	H	-0.570110	0.718970	-4.316850
C	-5.697080	-0.645190	0.089190	H	1.973820	-0.196570	-4.317900
C	-7.093460	-0.645720	0.108760	H	5.694410	0.658280	1.998490
C	-7.796970	-0.284550	-1.042310	H	5.705130	-0.197040	-0.585950
C	-7.102790	0.074140	-2.199800	H	-0.567890	-0.245130	5.700080
C	-5.706010	0.068470	-2.193830	H	2.006850	0.626860	5.690490
F	-5.051310	-0.991620	1.204020	C	-2.681960	-0.776730	4.031740
F	-7.757840	-0.982020	1.212570	C	-2.671610	1.265930	-2.663270
F	-9.125630	-0.281700	-1.035960	C	4.071290	-0.760740	-2.664820
F	-7.776200	0.413400	-3.296410	C	4.513320	-2.090740	-2.679430
F	-5.070260	0.415080	-3.312320	C	5.458520	-2.543440	-3.601470
C	5.726030	-0.319070	-0.289080	C	5.986450	-1.652110	-4.537920
C	7.117400	-0.249450	-0.387980	C	5.570570	-0.318550	-4.543820
C	7.711980	-0.129710	-1.645980	C	4.624310	0.111250	-3.611020
C	6.915620	-0.075390	-2.792090	F	4.023850	-2.962570	-1.799980
C	5.526380	-0.144460	-2.666910	F	5.854280	-3.813260	-3.597470
F	5.185520	-0.430790	0.924670	F	6.883330	-2.074210	-5.421400
F	7.877910	-0.293040	0.703750	F	6.077670	0.532170	-5.432260
F	9.034850	-0.063430	-1.751690	F	4.248740	1.389760	-3.638720
F	7.483160	0.042790	-3.990040	C	-3.222700	0.383080	-3.600800
F	4.789860	-0.087560	-3.774890	C	-4.180110	0.798050	-4.529020
C	0.270280	5.466110	-2.056040	C	-4.609280	2.127420	-4.527880
C	0.312750	6.858500	-1.950390	C	-4.083070	3.029390	-3.600670
C	0.046670	7.465180	-0.720800	C	-3.126520	2.591420	-2.682970
C	-0.257190	6.678490	0.392910	F	-2.835940	-0.892090	-3.623140
C	-0.291640	5.289950	0.259330	F	-4.685470	-0.062610	-5.408760
F	0.529620	4.917400	-3.241160	F	-5.517310	2.534970	-5.406800
F	0.604460	7.607990	-3.009570	F	-4.491270	4.295300	-3.601080
F	0.085350	8.788100	-0.608800	F	-2.640600	3.472630	-1.810930
F	-0.501620	7.254870	1.567950	C	-3.237560	0.089760	4.981470
F	-0.578130	4.562650	1.348210	C	-4.196360	-0.342250	5.900290
C	0.018240	1.604050	4.285490	C	-4.620510	-1.673050	5.878090
H	-0.883430	1.452110	4.898000	C	-4.089210	-2.559170	4.938570
H	0.905670	1.480700	4.922510	C	-3.132170	-2.104170	4.029930
H	0.002820	2.609230	3.839320	F	-2.855330	1.365830	5.023150
H	-0.026990	-4.798800	-1.242210	F	-4.707500	0.503820	6.790830
				F	-5.528830	-2.097350	6.748750
				F	-4.492910	-3.826370	4.919180
				F	-2.641010	-2.970850	3.146350
				H	3.797780	1.014840	3.797490

## II.4 XYZ Coordinates of TPSSh/SVP Optimized Record Player Type Molecules.

### II.4.1 Magnetic Conformers of Biphenyl RP 4

*cis*<sub>dia</sub>

E<sub>TPSSh/SVP</sub> = -5511.28035583 Hartree

NImag = 0

C	-0.772220	-2.996780	2.692220
N	-1.509020	-2.058540	2.004550
C	-1.503850	-4.232880	2.816510
C	-2.680320	-4.056940	2.152290
C	-2.688730	-2.692840	1.685730
C	0.549540	-2.832030	3.103780
C	1.318520	-1.738870	2.698810
C	2.752120	-1.683080	2.829600
C	3.165460	-0.593240	2.122490
C	1.975640	0.051820	1.624870
N	0.850500	-0.662150	1.979610
Ni	-0.991060	-0.247450	1.560250
N	-2.838290	0.186880	1.195400
C	-3.393550	1.442390	1.096800
C	-4.813270	1.356860	0.858230
C	-5.109770	0.031990	0.747740
C	-3.883490	-0.685460	0.992930
C	1.979060	1.273930	0.945490
C	0.796970	1.994440	0.757400
C	0.770620	3.392720	0.405210
C	-0.514580	3.812590	0.570810
C	-1.282070	2.651650	0.945620
N	-0.470650	1.546330	1.064930
C	-2.674720	2.637450	1.052940
C	-3.810290	-2.071280	1.135730
H	4.180720	-0.234570	1.963850
H	3.360330	-2.411720	3.363120
H	1.642540	3.975560	0.114460
H	-0.920950	4.811940	0.426350
H	-6.075290	-0.428860	0.546160
H	-5.481800	2.209020	0.747660
H	-1.142690	-5.125180	3.325240
H	-3.492680	-4.768920	2.015620
C	1.202930	-3.925190	3.880200
C	-5.015390	-2.891410	0.822430
C	3.284000	1.901190	0.559850
C	-3.436500	3.917820	1.002430
C	-3.981320	4.464940	2.171630
C	-4.731610	5.642270	2.153620
C	-4.950420	6.299320	0.940890
C	-4.418680	5.778720	-0.241280
C	-3.670280	4.600350	-0.198180
F	-3.793310	3.856570	3.341420
F	-5.235560	6.140520	3.279350
F	-5.666790	7.417070	0.912360
F	-4.631690	6.402810	-1.397010
F	-3.182700	4.121480	-1.341340
C	-6.024160	-3.102920	1.770460
C	-7.162980	-3.855960	1.477530

*cis*<sub>para</sub>

E<sub>TPSSh/SVP</sub> = -5511.29817707 Hartree

NImag = 0

C	3.350850	0.546430	3.653890
C	3.856360	0.086790	2.423440
C	4.641320	0.930260	1.618740
C	4.903240	2.240820	2.063180
C	4.396250	2.697180	3.283190
C	3.638990	1.849610	4.092450
N	2.703830	-0.320620	4.583580
N	1.601340	-0.881000	4.372330
C	0.793590	-0.697020	3.261380
C	0.743850	0.083830	2.105770
N	-0.372640	-1.473770	3.223120
N	-0.373320	-0.224570	1.396900
C	-1.024000	-1.159120	2.091970
H	3.662120	-0.942130	2.108410
H	5.510340	2.905200	1.441540
H	4.606060	3.718990	3.612900
H	3.267050	2.176740	5.066650
H	1.450130	0.825820	1.747670
H	-1.956370	-1.628130	1.782410
C	-0.762190	-2.490440	4.198060
C	0.782560	2.796850	-0.932280
N	0.976550	1.443410	-0.847930
C	2.055680	3.482200	-1.010010
C	3.020820	2.519420	-0.971110
C	2.336940	1.247820	-0.857930
C	-0.467550	3.445450	-0.937320
C	-1.717840	2.803480	-0.918570
C	-2.990430	3.496890	-0.957450
C	-3.957490	2.536910	-0.956820
C	-3.272400	1.260010	-0.932850
N	-1.916510	1.448600	-0.901340
Ni	-0.479580	0.010370	-0.661850
N	0.978390	-1.434630	-0.869330
C	0.778090	-2.788290	-0.855890
C	2.046280	-3.483750	-0.781550
C	3.014930	-2.524000	-0.733050
C	2.335160	-1.244610	-0.793480
C	-3.921660	0.013050	-0.964750
C	-3.274070	-1.235640	-0.989720
C	-3.959890	-2.508540	-1.067750
C	-2.995640	-3.473690	-1.049570
C	-1.722420	-2.786970	-0.972970
N	-1.918330	-1.429580	-0.942410
C	-0.474130	-3.431320	-0.907710
C	2.992470	0.002560	-0.780090
H	-5.036760	2.679430	-0.981530
H	-3.125780	4.576770	-0.991930
H	-5.037960	-2.646190	-1.137960
H	-3.136370	-4.552510	-1.094270

C	-7.305390	-4.418180	0.206630	H	4.092550	-2.664600	-0.670080
C	-6.314030	-4.226750	-0.758010	H	2.179260	-4.564780	-0.773840
C	-5.184120	-3.469140	-0.441800	H	2.193300	4.559180	-1.092020
F	-5.910310	-2.574030	2.987730	H	4.099750	2.650700	-1.030420
F	-8.108350	-4.039740	2.395250	C	-0.470970	4.938280	-0.975070
F	-8.384270	-5.134760	-0.086440	C	4.492330	0.002990	-0.768050
F	-6.454150	-4.763960	-1.966940	C	-5.414360	0.008570	-0.973190
F	-4.255120	-3.298880	-1.380260	C	-0.484760	-4.923340	-0.856730
C	4.039860	2.544630	1.556090	C	-0.232180	-5.607150	0.339190
C	5.242570	3.188500	1.255880	C	-0.265890	-7.000070	0.420230
C	5.705880	3.197180	-0.063280	C	-0.561080	-7.745760	-0.723540
C	4.964430	2.563310	-1.061620	C	-0.818050	-7.094630	-1.932060
C	3.750070	1.905320	-0.779340	C	-0.773040	-5.699450	-1.986680
C	1.873330	-4.975840	3.241490	C	-6.141700	-0.356460	0.167200
C	2.489190	-6.000790	3.962110	C	-7.537790	-0.367470	0.182750
C	2.440910	-5.983810	5.358140	C	-8.239550	-0.008450	-0.970250
C	1.777640	-4.949810	6.022660	C	-7.543800	0.357800	-2.124440
C	1.167540	-3.935970	5.279880	C	-6.146780	0.362630	-2.113880
F	1.934780	-5.012220	1.910940	C	5.253000	0.456420	0.338950
F	3.119790	-6.988780	3.332630	C	6.657180	0.481740	0.230770
F	3.027250	-6.952450	6.052090	C	7.310210	0.059280	-0.928910
F	1.732560	-4.936710	7.352340	C	6.559500	-0.397260	-2.016370
F	0.541820	-2.960810	5.935900	C	5.165820	-0.419880	-1.929620
H	3.660680	2.546660	2.582440	C	-0.152590	5.644250	-2.142540
H	5.811180	3.683280	2.048820	C	-0.165080	7.040300	-2.187980
H	6.648840	3.691090	-0.316130	C	-0.505070	7.762530	-1.042060
H	5.341340	2.551280	-2.088580	C	-0.828660	7.087410	0.136790
C	3.016230	1.247580	-1.898990	C	-0.806880	5.691270	0.157700
C	2.849770	1.935210	-3.115090	H	-1.821930	-2.355340	4.463680
C	2.522860	-0.067780	-1.798420	H	-0.125330	-2.360310	5.083170
C	1.864860	-0.663440	-2.878930	H	-0.606740	-3.494240	3.770950
C	1.704030	0.022130	-4.085040	F	-8.215910	0.694060	-3.222550
C	2.221520	1.320970	-4.207140	F	-9.568060	-0.015680	-0.968790
H	3.203950	2.964420	-3.219490	F	-8.203620	-0.712490	1.282820
H	2.667110	-0.635870	-0.877520	F	-5.495850	-0.705540	1.282780
H	1.480190	-1.683130	-2.780980	F	-5.509430	0.715250	-3.229370
H	1.189520	-0.438200	-4.932470	F	-1.103080	-7.805590	-3.019720
N	2.019030	2.061520	-5.410060	F	-1.023530	-5.107710	-3.153580
N	2.825090	1.970660	-6.371000	F	-0.599780	-9.072070	-0.661220
C	3.976990	1.198810	-6.374670	F	-0.027750	-7.618880	1.574900
N	4.708680	1.245290	-7.564020	F	0.044990	-4.919670	1.453490
C	4.727150	0.355630	-5.534550	F	-1.120770	5.073800	1.297080
N	5.840800	-0.081260	-6.170220	F	-1.150900	7.777900	1.228380
C	5.797060	0.466370	-7.379170	F	0.172840	4.980980	-3.251680
C	4.342860	1.992890	-8.758900	F	0.139380	7.686210	-3.311390
H	4.505450	0.055130	-4.512630	F	-0.520830	9.090860	-1.073010
H	6.544700	0.320820	-8.161270	H	4.571830	-0.754980	-2.785000
H	4.229470	3.060130	-8.516620	H	7.054700	-0.727560	-2.934410
H	3.389070	1.621400	-9.163880	H	8.402810	0.083950	-0.979940
H	5.141430	1.859770	-9.504300	H	7.242440	0.824630	1.089420

## II.4.2 Magnetic Conformers of Biphenyl Thioether RP 5

*cis*<sub>dia</sub>

E<sub>TPSSH/SVP</sub> = -5909.35804047 Hartree

NImag = 0

C	-0.679150	-3.306580	2.911930
N	-1.487480	-2.363040	2.322040
C	-1.416030	-4.519950	3.166710
C	-2.668710	-4.328100	2.663530
C	-2.712520	-2.971870	2.176950
C	0.702100	-3.184090	3.081460
C	1.422090	-2.146250	2.484380
C	2.854480	-2.145060	2.317240
C	3.150150	-1.099860	1.494170
C	1.906830	-0.416070	1.233450
N	0.857420	-1.070730	1.836610
Ni	-1.002650	-0.576630	1.788140
N	-2.865790	-0.088260	1.745030
C	-3.396160	1.180530	1.751890
C	-4.837030	1.129220	1.704850
C	-5.177520	-0.186260	1.600270
C	-3.947920	-0.935490	1.664730
C	1.827330	0.825330	0.592850
C	0.680640	1.619130	0.702030
C	0.643210	3.028260	0.397200
C	-0.564550	3.489430	0.829310
C	-1.297010	2.343780	1.308210
N	-0.517060	1.210720	1.247410
C	-2.657250	2.360650	1.630940
C	-3.882670	-2.325920	1.773240
H	4.122600	-0.782880	1.121590
H	3.536500	-2.876350	2.747720
H	1.458770	3.588850	-0.055520
H	-0.946580	4.507990	0.792690
H	-6.172900	-0.619610	1.518720
H	-5.495680	1.996050	1.705960
H	-1.007290	-5.414110	3.634830
H	-3.506900	-5.023160	2.654160
C	1.427200	-4.268070	3.802650
C	-5.112220	-3.135300	1.539880
C	3.027400	1.340560	-0.136000
C	-3.391520	3.655340	1.706390
C	-3.843160	4.146000	2.939350
C	-4.578520	5.329190	3.038240
C	-4.875020	6.052650	1.881070
C	-4.438210	5.589610	0.638060
C	-3.706750	4.402530	0.563500
F	-3.577880	3.474010	4.058300
F	-4.996070	5.770670	4.221570
F	-5.574660	7.178770	1.960290
F	-4.729520	6.276750	-0.463740
F	-3.318450	3.978830	-0.638860
C	-6.099100	-3.310830	2.517250
C	-7.248290	-4.066800	2.273160
C	-7.425890	-4.664840	1.023240
C	-6.456500	-4.509770	0.030220

*cis*<sub>para</sub>

E<sub>TPSSH/SVP</sub> = -5909.37624370 Hartree

NImag = 0

H	-2.351860	-4.763160	-0.708790
H	-4.273350	-2.866890	-0.722840
C	-4.675250	-0.196540	-0.787290
C	-3.175620	-0.198440	-0.756440
C	-0.954900	-2.983160	-0.736400
H	4.849830	2.462620	-1.358820
H	2.932020	4.352550	-1.415800
C	0.289080	4.710870	-1.317820
H	-4.279260	2.468890	-0.916190
H	-2.366470	4.353890	-1.179320
C	-3.201300	2.324000	-0.951260
C	-2.521080	1.045740	-0.872040
C	-2.234170	3.277210	-1.080800
C	-0.964590	2.582530	-1.073530
N	-1.161700	1.232880	-0.941600
C	0.282110	3.221250	-1.204440
C	1.532540	2.579900	-1.240090
C	2.801190	3.273960	-1.340960
C	3.771710	2.317050	-1.312190
C	3.091760	1.041280	-1.207450
N	1.735640	1.228500	-1.167330
C	3.741970	-0.205210	-1.147850
C	5.233540	-0.211050	-1.147660
C	3.094460	-1.452540	-1.060880
N	1.741270	-1.637080	-0.951520
C	1.542010	-2.991020	-0.888610
C	2.808350	-3.688410	-0.970520
C	3.774800	-2.730780	-1.078380
H	4.848970	-2.877820	-1.182470
H	2.939950	-4.769560	-0.961180
C	0.293570	-3.627330	-0.774290
C	-2.224240	-3.681440	-0.711390
C	-3.194160	-2.724360	-0.716250
C	-2.515020	-1.443160	-0.729270
N	-1.155790	-1.628010	-0.749890
Ni	0.310250	-0.183440	-0.726690
N	0.531930	-0.024180	1.314840
C	-0.403230	0.452860	2.174630
C	1.558990	-0.447620	2.053630
N	1.326790	-0.259870	3.363710
C	0.055530	0.310790	3.487480
C	2.217380	-0.605160	4.467470
H	-1.336890	0.866760	1.808490
H	2.475710	-0.884960	1.659900
N	-0.331180	0.613880	4.788240
H	3.208510	-0.834580	4.049610
H	1.828180	-1.480770	5.010540
H	2.281610	0.244350	5.161790
N	-1.448290	1.081820	5.122750
C	-2.496550	1.267360	4.173950
C	-2.955920	2.568790	3.920180



C	-5.315470	-3.751510	0.298160	C	-3.105050	0.165460	3.554680
F	-5.954910	-2.747430	3.716030	C	-4.138860	0.367960	2.630110
F	-8.171890	-4.220640	3.218510	C	-4.586890	1.670330	2.352520
F	-8.517110	-5.380760	0.777360	C	-3.990830	2.757200	2.999230
F	-6.628060	-5.079250	-1.159530	H	-2.485660	3.414020	4.428090
F	-4.407730	-3.614060	-0.665910	H	-2.740110	-0.844940	3.758790
C	3.877490	2.303530	0.431900	S	-4.835070	-1.096320	1.887680
C	4.991190	2.785380	-0.263050	H	-5.399680	1.828720	1.639560
C	5.273890	2.291280	-1.541730	H	-4.343460	3.770330	2.783980
C	4.453790	1.316830	-2.114830	C	-5.494360	-0.529850	0.320810
C	3.325420	0.843680	-1.427240	C	-5.313550	0.144640	-1.994800
C	2.117620	-5.281980	3.126050	C	-6.706010	0.143590	-2.118410
C	2.774090	-6.307170	3.810240	C	-7.502420	-0.196080	-1.021330
C	2.747590	-6.329510	5.206570	C	-6.893820	-0.526940	0.192300
C	2.066260	-5.333010	5.908850	H	-4.691690	0.398520	-2.858050
C	1.415460	-4.318910	5.202890	H	-7.165470	0.402510	-3.076980
F	2.153790	-5.288440	1.794000	H	-8.593130	-0.201880	-1.105330
F	3.418590	-7.262660	3.145280	H	-7.499400	-0.787750	1.064440
F	3.370050	-7.300280	5.865050	C	0.309710	-5.118840	-0.679760
F	2.043890	-5.355150	7.239020	C	0.416510	-5.754400	0.562830
F	0.770920	-3.381260	5.895000	C	0.484050	-7.144090	0.678010
H	3.650840	2.676640	1.435290	C	0.436470	-7.930760	-0.475080
H	6.139150	2.653990	-2.104650	C	0.325610	-7.325430	-1.728760
H	4.690240	0.923370	-3.105590	C	0.259270	-5.932800	-1.817470
S	2.252310	-0.430270	-2.075650	F	0.469610	-5.025860	1.678800
C	2.457650	-0.316560	-3.846950	F	0.596570	-7.720940	1.872670
C	2.184680	0.870610	-4.541390	F	0.500660	-9.254510	-0.379990
C	2.783900	-1.487260	-4.551360	F	0.287290	-8.077290	-2.826070
C	2.810070	-1.468790	-5.950970	F	0.155330	-5.382480	-3.026060
C	2.533180	-0.293190	-6.652490	C	0.194590	5.529730	-0.185960
C	2.250150	0.887060	-5.943920	C	0.251220	6.922120	-0.276350
H	1.907290	1.777590	-3.998270	C	0.390970	7.524240	-1.528710
H	3.001890	-2.405840	-4.000500	C	0.479330	6.733820	-2.676830
H	3.048460	-2.384620	-6.500150	C	0.425970	5.343130	-2.559740
H	2.536990	-0.272310	-7.745140	F	0.613720	7.308510	-3.869740
N	1.868940	2.056730	-6.664140	F	0.516610	4.613520	-3.670490
N	2.569580	3.100060	-6.657670	F	0.060340	4.982320	1.022480
C	3.830900	3.203850	-6.093280	F	0.177660	7.676650	0.818170
N	4.360520	4.493440	-6.015550	F	0.443220	8.848380	-1.626890
C	4.879040	2.366360	-5.680680	C	5.949820	-0.538960	0.011330
N	5.973820	3.096940	-5.356840	C	7.344920	-0.550250	0.045510
C	5.625540	4.363280	-5.555010	C	8.060520	-0.221640	-1.108250
C	3.645840	5.724410	-6.324990	C	7.377770	0.110840	-2.280290
H	4.887020	1.278760	-5.640410	C	5.980640	0.111090	-2.288550
H	6.267070	5.226870	-5.371930	F	8.062040	0.420550	-3.378210
H	3.037640	6.047990	-5.463560	F	5.358680	0.427950	-3.422980
H	2.979800	5.537550	-7.179120	F	5.292650	-0.849380	1.136240
H	4.379440	6.505970	-6.572580	F	7.996190	-0.862320	1.164050
H	5.637050	3.539740	0.195570	F	9.388690	-0.225620	-1.090130

### III. Experimental Section

#### III.1 General Information

Commercially available solvents and starting materials were used as received. THF was distilled from benzophenone-Na. Dichloromethane was distilled from CaH<sub>2</sub>. Column chromatography was carried out using 0.04 – 0.063 mm mesh silica gel (Merck). *R<sub>f</sub>* values were determined by thin layer chromatography on Polygram® Sil G/UV<sub>254</sub> (Macherey-Nagel, 0.2 mm particle size).

NMR spectra were measured in Schott Economic NMR tubes using deuterated solvents (Deutero). The degree of deuteration is given in parentheses. Chemical shifts are calibrated to residual protonated solvent signals (<sup>1</sup>H: δ (CHCl<sub>3</sub>) = 7.26 ppm, δ (CD<sub>2</sub>Cl<sub>2</sub>) = 5.32 ppm, δ (CD<sub>3</sub>CN) = 1.94 ppm, δ (acetone-d<sub>6</sub>) = 2.05 ppm, δ (DMSO-d<sub>6</sub>) = 2.50 ppm; <sup>13</sup>C: δ (CHCl<sub>3</sub>) = 77.16 ppm, δ (CD<sub>2</sub>Cl<sub>2</sub>) = 53.84 ppm, δ (CD<sub>3</sub>CN) = 1.32 ppm, δ (acetone-d<sub>6</sub>) = 29.84 ppm, δ (DMSO-d<sub>6</sub>) = 39.52 ppm; deuteration grade 99.8 %). Reference for <sup>19</sup>F NMR spectra is CCl<sub>3</sub>F to which the spectrometer frequency is calibrated. The signal multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet) and br (broad signal). Measurements were performed with a Bruker DRX 500 (<sup>1</sup>H NMR: 500 MHz, <sup>13</sup>C NMR: 125 MHz, <sup>19</sup>F NMR: 470 MHz) and a Bruker AV 600 (<sup>1</sup>H NMR: 600 MHz, <sup>13</sup>C NMR: 150 MHz).

The high resolution (HR) mass spectra were measured with an APEX 3 FT-ICR with a 7.05 T magnet by co. Bruker Daltonics (ESI) or with an AccuTOF by co. Jeol (EI). Low resolution mass spectra were measured with a MAT 8230 by co. Finnigan (EI/CI), an AccuTOF by co. Jeol (EI), an LCQ Classic by co. Thermo Finnigan (ESI) or an AutoflexSpeed by co. Bruker (MALDI-TOF).

Infrared spectra were recorded on a Perkin-Elmer ATR spectrometer with a Golden-Gate-Diamond-ATR A531-G for neat samples. Signal intensities were abbreviated with w (weak), m (medium), s (strong) and vs (very strong). Broad signals are additionally labeled with br.

UV-visible absorption spectra were recorded on a Perkin-Elmer Lambda-14 spectrophotometer with a Büchi thermostat using quartz cells of 1 cm path length.

The amount of carbon, hydrogen, sulfur and nitrogen in a compound was determined with a CHNS-Elementaranalysator Euro EA 3000 Series by co. Euro Vector.

Irradiation experiments were performed with LED light sources.

Melting points were measured with a Melting Point B-540 by co. Büchi.

### III.2 Synthetic procedures

**3-Bromobenzenediazonium tetrafluoroborate (8).**<sup>5</sup> A suspension of 3-bromoaniline (**6**) (8.25 g, 48.0 mmol) in tetrafluoroboric acid (50 wt-%, 30 mL) was diluted with water until a clear solution was obtained. The solution was cooled to 0 °C and a solution of sodium nitrite (3.71 g, 53.8 mmol) in water (7.5 mL) was added dropwise under vigorous stirring. The precipitate was filtered off and was consecutively washed with water (50 mL), ethanol (50 mL) and diethyl ether (150 mL) before being dried in vacuo. The desired product (11.9 g, 43.8 mmol, 91 %) was obtained as a white solid.

**Mp:** 139 °C (decomp.).

**IR (ATR):**  $\nu$  = 3098 (m), 2304 (m), 1575 (w), 1562 (w), 1463 (m), 1422 (w), 1281 (w), 1173 (w), 1024 (ss, br), 887 (m), 788 (s), 664 (m), 651 (s), 556 (m), 521 (s), 504 (w)  $\text{cm}^{-1}$ .

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 300 K):**  $\delta$  = 8.63 (t, <sup>4</sup>*J* = 2.00 Hz, 1H, 2-H), 8.49 (ddd, <sup>3</sup>*J* = 8.38 Hz, <sup>4</sup>*J* = 2.05 Hz, <sup>4</sup>*J* = 0.93 Hz, 1H, 4-H), 8.40 (ddd, <sup>3</sup>*J* = 8.29 Hz, <sup>4</sup>*J* = 1.91 Hz, <sup>4</sup>*J* = 0.94 Hz, 1H, 6-H), 7.84 (t, <sup>3</sup>*J* = 8.35, 1H, 5-H) ppm.

**<sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 300 K):**  $\delta$  = 146.3 (C-6), 134.9 (C-2), 134.1 (C-5), 132.6 (C-4), 124.5 (C-3), 117.1 (C-1) ppm.

**MS (EI, 70 eV):** *m/z* (%) = 175.9/173.9 (99/100) [C<sub>6</sub>H<sub>4</sub>BrF]<sup>+</sup>.

**HR-MS (EI):** *m/z* [M]<sup>+</sup> calcd for C<sub>6</sub>H<sub>4</sub><sup>79</sup>BrF, 173.9480; found 173.9481; calcd for C<sub>6</sub>H<sub>4</sub><sup>81</sup>BrF, 175.9460; found 175.9460.

Diazonium tetrafluoroborates undergo a BALTZ SCHIEMANN reaction during the vaporization process in EI-MS. Therefore, only the fluorinated derivative is found.

**5-(3'-Bromophenylazo)-1-(*N,N*-dimethylsulfamoyl)imidazole (9).** 1-(*N,N*-Dimethylsulfamoyl)imidazole<sup>6</sup> (**7**) (1.50 g, 8.57 mmol) was dissolved in dry THF (45 mL) and cooled to -78 °C. *n*-Butyllithium (3.45 mL, 8.63 mmol) in *n*-hexane was added dropwise over a period of 15 minutes. After 30 minutes of stirring at -78 °C, dimethylhexylchlorosilane (1.86 mL, 12.5 mmol) was added. The reaction mixture was stirred at -78 °C for 60 minutes and at room temperature for 16 hours. It was again cooled to -78 °C and *n*-butyllithium (3.75 mL, 9.38 mmol) in *n*-hexane was added dropwise over a period of 10 minutes. After 30 minutes of stirring at -78 °C, 3-bromobenzenediazonium tetrafluoroborate (**8**) (2.31 g, 8.52 mmol) was added as a solid in one portion, and the reaction mixture immediately turned from light yellow to deep red. It was stirred at -78 °C for 60 minutes and at room temperature for 7 hours. Then, half saturated aqueous sodium bicarbonate solution (60 mL) was added, layers were separated and the aqueous layer was extracted once with THF (40 mL). The combined organic layers were treated with tetra-*n*-butylammoniumfluoride trihydrate (2.93 g, 9.27 mmol) and the mixture was stirred at room temperature for 16 hours. Then, half saturated aqueous sodium bicarbonate solution (60 mL) was added,

layers were separated and the aqueous layer was extracted three times with chloroform (each 40 mL). The combined organic layers were dried over magnesium sulfate and evaporated. The resulting crude product was purified via column chromatography on silica gel (methylene chloride, 10 vol-% ethyl acetate,  $R_f = 0.58$ ). The desired product was obtained as orange solid (1.83 g, 5.11 mmol, 60 %).

**Mp:** 105 – 106 °C.

**IR (ATR):**  $\nu = 3130$  (w), 1470 (m), 1450 (m), 1383 (s), 1342 (m), 1274 (m), 1252 (m), 1171 (s), 1117 (m), 1089 (s), 1055 (m), 976 (s), 896 (m), 870 (m), 844 (m), 813 (m), 796 (s), 726 (s), 679 (m), 664 (m), 637 (m), 593 (s), 564 (s), 546 (s), 505 (s)  $\text{cm}^{-1}$ .

**$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta = 8.15$  (d,  $^4J = 0.60$  Hz, 1H, 2-*H*), 7.96 (t,  $^4J = 1.85$  Hz, 1H, 2'-*H*), 7.78 (ddd,  $^3J = 8.00$  Hz,  $^4J = 1.70$  Hz,  $^4J = 1.00$  Hz, 1H, 6'-*H*), 7.60 (ddd,  $^3J = 7.94$  Hz,  $^4J = 1.86$  Hz,  $^4J = 0.96$  Hz, 1H, 4'-*H*), 7.53 (d,  $^4J = 0.65$  Hz, 1H, 4-*H*), 7.34 (t,  $^3J = 7.95$  Hz, 1H, 5'-*H*), 2.99 (s, 6H, - $\text{N}(\text{CH}_3)_2$ ) ppm.

**$^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ , 300 K):**  $\delta = 153.9$  (C-3'), 145.0 (C-5), 141.6 (C-2), 134.4 (C-4'), 130.8 (C-5'), 125.5 (C-2'), 123.4 (C-1'), 122.4 (C-6'), 119.7 (C-4), 38.5 (- $\text{N}(\text{CH}_3)_2$ ) ppm.

**MS (EI, 70 eV):**  $m/z$  (%) = 359.0/357.0 (12/12)  $[\text{M}]^{+}$ , 252.0/250.0 (31/34)  $[\text{M-SO}_2\text{N}(\text{CH}_3)_2+\text{H}]^{+}$ , 157.0/155.0 (58/61)  $[\text{PhBr}]^{+}$ , 108.0 (100)  $[\text{SO}_2\text{N}(\text{CH}_3)_2]^{+}$ .

**HR-MS (EI):**  $m/z$   $[\text{M}]^{+}$  calcd for  $\text{C}_{11}\text{H}_{12}\text{N}_5\text{O}_2\text{S}^{79}\text{Br}$ , 356.9895; found 356.9887; calcd for  $\text{C}_6\text{H}_4^{81}\text{BrF}$ , 358.9875; found 358.9867.

**UV/Vis (toluene):**  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ) = 360 (4.177) nm.

**Anal. Calcd.** For  $\text{C}_{11}\text{H}_{12}\text{N}_5\text{O}_2\text{SBr}$  (356.99): cal. C 36.88, H 3.38, N 19.55, S 8.95, found C 37.15, H 3.34, N 19.43, S 8.91 %.

**4(5)-(3'-Bromophenylazo)imidazole (10).** The sulfamoyl-protected azoimidazole **9** (697 mg, 1.95 mmol) was dissolved in ethanol (30 mL) and ethanolic hydrochloric acid (4 M, 30 mL) was added. The reaction mixture was stirred at 55 °C for 1 hour. It was then cooled to 0 °C and potassium hydroxide solution (40 %, 10 mL) was added dropwise. The solution was treated with saturated aqueous sodium bicarbonate solution (80 mL) and stirring at 0 °C was continued for 15 minutes. Chloroform (100 mL) was added and the layers were separated. The aqueous layer was extracted twice with chloroform (50 mL) and the combined organic layers were dried over magnesium sulfate before being evaporated to dryness. The obtained crude product may be purified via column chromatography on silica gel (ethyl acetate,  $R_f = 0.20$ ) to give the desired deprotected azoimidazole **10** (390 mg, 1.55 mmol, 80 %) as yellow powder. However, using the crude product in the following step has found to give comparable yields so that purification on this stage is not essential.

**Mp:** 135 – 140 °C (decomp.).

**IR (ATR):**  $\nu$  (cm<sup>-1</sup>) = 1568 (w), 1514 (m), 1450 (w), 1427 (s), 1322 (w), 1308 (w), 1296 (w), 1234 (m), 1151 (m), 1094 (m), 1059 (w), 1003 (m), 913 (m), 838 (s), 801 (s), 772 (s), 700 (m), 671 (s), 624 (s), 588 (m), 565 (m), 534 (m), 517 (w) cm<sup>-1</sup>.

**<sup>1</sup>H-NMR (600 MHz, DMSO-d<sub>6</sub>, 298 K):**  $\delta$  = 12.66 (s, br, 1H, NH), 7.98 (s, 1H, 4-H), 7.88 (s, 1H, 2-H), 7.87-7.85 (m, 1H, 2'-H), 7.82-7.77 (m, 1H, 6'-H), 7.67-7.63 (m, 1H, 4'-H), 7.51 (t, <sup>3</sup>J = 7.92 Hz, 1H, 5'-H) ppm.

**<sup>13</sup>C-NMR (150 MHz, DMSO-d<sub>6</sub>, 298 K):**  $\delta$  = 153.8 (C-1', C-4(5)), 137.3 (C-2), 132.5 (C-4'), 131.5 (C-5'), 122.9 (C-2'), 122.5 (C-6', C-3'), 118.9 (C-5(4)) ppm.

**MS (EI, 70 eV):** m/z (%) = 252.0/250.0 (46/46) [M]<sup>+</sup>, 171.1 (18) [M-Br]<sup>+</sup>, 157.0/155.0 (39/40) [PhBr]<sup>+</sup>, 95.0 (100) [C<sub>3</sub>H<sub>3</sub>N<sub>4</sub>]<sup>+</sup>.

**HR-MS (EI):** m/z [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>7</sub>N<sub>4</sub><sup>79</sup>Br, 249.9854; found 249.9846; calcd for C<sub>9</sub>H<sub>7</sub>N<sub>4</sub><sup>81</sup>Br, 251.9834; found 251.9834.

**UV/Vis (toluene):**  $\lambda_{\max}$  (lg  $\epsilon$ ) = 351 (4.337) nm.

**4-(3'-Bromophenylazo)-1-(triphenylmethyl)imidazole (11).** A suspension of 4(5)-(3'-bromophenylazo)imidazole (**10**) (346 mg, 1.38 mmol) and triphenylchloromethane (404 mg, 1.45 mmol) in methylene chloride (15 mL) was treated with 12rimethylamine (248  $\mu$ L, 1.79 mmol). Stirring at room temperature for 16 hours gave a deep red solution which was diluted with ethyl acetate (50 mL) and washed three times with half saturated sodium bicarbonate solution (each 30 mL). The organic layer was dried over magnesium sulfate and evaporated to dryness. Purification of the crude product via column chromatography on silica gel (cyclohexane/ethyl acetate, 3:1,  $R_f$  = 0.17) gave an orange solid (666 mg, 1.35 mmol, 98 %).

**Mp:** 68 – 70 °C.

**IR (ATR):**  $\nu$  (cm<sup>-1</sup>) = 1568 (w), 1489 (m), 1444 (m), 1287 (m), 1118 (m), 1087 (m), 991 (m), 904 (m), 865 (m), 745 (s), 698 (s), 676 (s), 658 (s), 638 (m), 616 (m), 560 (m), 506 (m) cm<sup>-1</sup>.

**<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, 298 K):**  $\delta$  = 8.00 (t, <sup>4</sup>J = 1.83 Hz, 1H, 2'-H), 7.87 (ddd, <sup>3</sup>J = 7.95 Hz, <sup>4</sup>J = 1.56 Hz, <sup>4</sup>J = 0.95 Hz, 1H, 6'-H), 7.62 (d, <sup>4</sup>J = 1.33 Hz, 1H, 5-H), 7.54 (d, <sup>4</sup>J = 1.35 Hz, 1H, 2-H), 7.52 (ddd, <sup>3</sup>J = 7.92 Hz, <sup>4</sup>J = 1.71 Hz, <sup>4</sup>J = 0.84 Hz, 1H, 4'-H), 7.40-7.36 (m, 9H, Tr-*m*-H, Tr-*p*-H), 7.34 (t, <sup>3</sup>J = 7.98 Hz, 1H, 5'-H), 7.22-7.18 (m, 6H, Tr-*o*-H) ppm.

**<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, 298 K):**  $\delta$  = 154.1 (C-1'), 152.9 (C-4), 141.7 (C-*i*-Tr), 139.6 (C-2), 132.9 (C-4'), 130.3 (C-5'), 129.8 (C-*o*-Tr), 128.5 (C-*p*-Tr), 128.4 (C-*m*-Tr), 123.8 (C-2'), 123.5 (C-5), 123.4 (C-6'), 123.0 (C-3'), 76.4 (-CPh<sub>3</sub>) ppm.

**MS (EI, 70 eV):**  $m/z$  (%) = 250.0 (1)  $[M - C(Ph)_3 + H]^+$ , 243.1 (100)  $[C(Ph)_3]^+$ .

**MS (CI, isobutane):**  $m/z$  (%) = 495.0/493.0 (7/6)  $[M + H]^+$ , 243.1 (100)  $[C(Ph)_3]^+$ , 167.1 (34)  $[C(Ph)_2 + H]^+$ .

**4-(3'-(2''-Formylphenyl)phenylazo)-1-(triphenylmethyl)imidazole (12).** 4-(3'-Bromophenylazo)-1-(triphenylmethyl)imidazole (**11**) (230 mg, 466  $\mu$ mol) was dissolved in toluene (15 mL) and purged with nitrogen for 20 min. 2-Formylphenylboronic acid (77.0 mg, 514  $\mu$ mol) and [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (17.0 mg, 23.3  $\mu$ mol) were added and purging with nitrogen was continued for another 15 min. Potassium carbonate (212 mg, 1.54 mmol, in 4 mL H<sub>2</sub>O) was added and the reaction mixture was stirred at 95 °C overnight under an atmosphere of nitrogen. After cooling down to room temperature ethyl acetate (50 mL) was added, followed by filtration over celite. The organic layer was washed three times with water (each 50 mL), dried over magnesium sulfate and evaporated to dryness. Purification via column chromatography on silica gel (chloroform,  $R_f$  = 0.36) gave a yellow solid (236 mg, 455  $\mu$ mol, 98 %).

**Mp:** 86 – 88 °C.

**IR (ATR):**  $\nu$  (cm<sup>-1</sup>) = 3080 (w), 2843 (w), 1695 (m), 1595 (m), 1490 (m), 1441 (m), 1389 (w), 1297 (m), 1197 (m), 1121 (m), 1036 (w), 1001 (w), 911 (w), 805 (w), 762 (s), 749 (s), 699 (s), 661 (s), 640 (m), 617 (m), 562 (w), 519 (w), 510 (m) cm<sup>-1</sup>.

**<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  = 10.02 (d, <sup>4</sup> $J$  = 0.75 Hz, 1H, -CHO), 8.03 (dd, <sup>3</sup> $J$  = 7.78 Hz, <sup>4</sup> $J$  = 1.03 Hz, 1H, 3''-H), 8.00 (ddd, <sup>3</sup> $J$  = 8.00 Hz, <sup>4</sup> $J$  = 1.90 Hz, <sup>4</sup> $J$  = 1.10 Hz, 1H, 6'-H), 7.92 (t, <sup>4</sup> $J$  = 1.75 Hz, 1H, 2'-H), 7.63 (td, <sup>3</sup> $J$  = 7.53 Hz, <sup>4</sup> $J$  = 1.45 Hz, 1H, 5''-H), 7.61 (d, <sup>4</sup> $J$  = 1.45 Hz, 1H, 5-H), 7.57 (t, <sup>3</sup> $J$  = 7.78 Hz, 1H, 5'-H), 7.54 (d, <sup>4</sup> $J$  = 1.45 Hz, 1H, 2-H), 7.52-7.46 (m, 2H, 4''-H, 6''-H), 7.41 (ddd, <sup>3</sup> $J$  = 7.53 Hz, <sup>4</sup> $J$  = 1.73 Hz, <sup>4</sup> $J$  = 1.13 Hz, 1H, 4'-H), 7.40-7.35 (m, 9H, Tr-*m*-H, Tr-*p*-H), 7.23-7.17 (m, 6H, Tr-*o*-H) ppm.

**<sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  = 192.2 (-CHO), 153.1 (C-1'), 153.0 (C-4), 145.3 (C-1''), 141.7 (C-*i*-Tr), 139.5 (C-2), 138.6 (C-3'), 133.7 (C-2''), 133.6 (C-5''), 131.8 (C-4'), 130.8 (C-6''), 129.8 (C-*o*-Tr), 129.1 (C-5'), 128.4 (C-*p*-Tr), 128.3 (C-*m*-Tr), 128.0 (C-4''), 127.6 (C-3''), 123.2 (C-6', C-5, C-2'), 76.3 (-CPh<sub>3</sub>) ppm.

**MS (EI, 70 eV):**  $m/z$  (%) = 518.1 (<1)  $[M + H]^+$ , 276.1 (4)  $[M - C(Ph)_3 + H]^+$ , 243.1 (100)  $[C(Ph)_3]^+$ .

**MS (CI, isobutane):**  $m/z$  (%) = 519.1 (2)  $[M + H]^+$ , 243.1 (100)  $[C(Ph)_3]^+$ .

**Anal. Calcd.** For [C<sub>35</sub>H<sub>26</sub>N<sub>4</sub>O + 0.45 CHCl<sub>3</sub>] (572.32): cal. C 74.39, H 4.66, N 9.79, found C 74.34, H 4.41, N 9.86 %.

**5-(3'-(2''-Formylphenyl)phenylazo)-1-methylimidazole (13).** The tritylated biphenylazoimidazole **12** (530 mg, 1.02 mmol) was dissolved in dry methylene chloride (12 mL) and methyl trifluoromethanesulfonate (170  $\mu$ L, 1.50 mmol) was added under an atmosphere of nitrogen. It was stirred at room temperature overnight, followed by the addition of acetone/H<sub>2</sub>O (2:1, 36 mL) and further stirring for 4 h at 40 °C. Saturated sodium bicarbonate solution (5 mL) was added, layers were separated and the aqueous layer was extracted twice with dichloromethane (each 20 mL). The combined organic layers were dried over magnesium sulfate and were evaporated to dryness. Purification via column chromatography on silica gel (ethyl acetate,  $R_f$  = 0.27) gave an orange solid (271 mg, 933  $\mu$ mol, 91 %).

**Mp:** 119 °C.

**IR (ATR):**  $\nu$  (cm<sup>-1</sup>) = 3113 (w), 3062 (w), 2924 (m), 2852 (m), 2751 (w), 16889 (vs), 1596 (m), 1518 (m), 1505 (m), 1467 (m), 1402 (m), 1340 (s), 1282 (m), 1223 (s), 1196 (m), 1115 (vs), 907 (m), 820 (m), 764 (s), 728 (s), 699 (s), 648 (s), 518 (m) cm<sup>-1</sup>.

**<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, 298 K):**  $\delta$  = 10.03 (s, 1H, -CHO), 8.05 (dd, <sup>3</sup> $J$  = 7.83 Hz, <sup>4</sup> $J$  = 1.05 Hz 1H, 3''-H), 7.90 (ddd, <sup>3</sup> $J$  = 7.98 Hz, <sup>4</sup> $J$  = 1.65 Hz, <sup>4</sup> $J$  = 1.08 Hz 1H, 6'-H), 7.83 (t, <sup>4</sup> $J$  = 1.71 Hz, 1H, 2'-H), 7.67 (dt, <sup>3</sup> $J$  = 7.50 Hz, <sup>4</sup> $J$  = 1.38 Hz, 1H, 5''-H), 7.62 (s, 2H, 2-H, 4-H), 7.59 (t, <sup>3</sup> $J$  = 7.77 Hz, 1H, 5'-H), 7.54 (t, <sup>3</sup> $J$  = 7.59 Hz, 1H, 4''-H), 7.50 (d, <sup>3</sup> $J$  = 7.62 Hz, 1H, 6''-H), 7.44 (td, <sup>3</sup> $J$  = 7.50 Hz, <sup>4</sup> $J$  = 1.26 Hz, 1H, 4'-H), 3.96 (s, 3H, -CH<sub>3</sub>) ppm.

**<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, 300 K):**  $\delta$  = 192.1 (-CHO), 152.9 (C-1'), 145.2 (C-5), 145.0 (C-1''), 140.9 (C-2), 138.8 (C-3'), 133.8-133.6 (C-5'', C-2''), 131.9 (C-4'), 130.7 (C-6''), 129.2 (C-5'), 128.2 (C-4''), 127.8 (C-3''), 124.2 (C-4), 123.4 (C-2'), 122.4 (C-6'), 32.6 (-CH<sub>3</sub>) ppm.

**MS (EI, 70 eV):**  $m/z$  (%) = 290.1 (100) [M]<sup>+</sup>, 195.1 (40) [C<sub>13</sub>H<sub>9</sub>ON]<sup>+</sup>, 152 (70) [C<sub>12</sub>H<sub>8</sub>]<sup>+</sup>, 109 (73) [C<sub>4</sub>H<sub>5</sub>N<sub>4</sub>]<sup>+</sup>.

**HR-MS (EI):**  $m/z$  [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>N<sub>4</sub>O, 290.1168; found 290.1167.

**UV/Vis (acetonitrile):**  $\lambda_{\max}$  (lg  $\epsilon$ ) = 210 (4.431), 228 (4.396), 362 (4.373) nm.

**5-(Biphenylazo-*N*-methylimidazole)-10,15,20-tris(pentafluorophenyl)porphyrin (mf-4).** To a solution of biphenyl tonearm **13** (453 mg, 1.56 mmol) and pentafluorobenzaldehyde (306 mg, 1.56 mmol) in chloroform (200 mL) was added borontrifluoride diethyletherate (406  $\mu$ L, 3.20 mmol) under an atmosphere of nitrogen. Pentafluorophenyl dipyrromethane (974 mg, 3.12 mmol) in chloroform (20 mL) was added to the stirred solution over 1 h at room temperature. Stirring under nitrogen at room temperature was continued for additional 6 h and the solution turned from dark red to black. Afterwards, chloranil (808 mg, 3.28 mmol) was added and the solution was stirred at reflux for 16 h. After cooling down to room temperature 14rimethylamine (880  $\mu$ L) was added and stirring was continued for 30 min. The solution was filtrated over celite and evaporated to dryness. Filtration of the

crude product over silica gel (chloroform) and subsequent column chromatography on silica gel (cyclohexane/ethyl acetate, 6:4,  $R_f = 0.19$ ) gave a purple solid (77.0 mg, 72.0  $\mu\text{mol}$ , 5 %).

**Mp:** 251 °C.

**IR (ATR):**  $\nu$  ( $\text{cm}^{-1}$ ) = 2922 (w), 1725 (w), 1650 (w), 1515 (s), 1494 (vs), 1438 (m), 1342 (m), 1224 (m), 1112 (m), 1077 (m), 1044 (m), 987 (vs), 973 (s), 917 (vs), 903 (m), 804 (s), 765 (s), 750 (s), 724 (s), 699 (m), 650(m), 549 (m)  $\text{cm}^{-1}$ .

**$^1\text{H-NMR}$  (500 MHz, acetone- $d_6$ , 300 K):**  $\delta$  = 9.25 (s, br, 4H, 12-*H*, 13-*H*, 17-*H*, 18-*H*), 9.16 (s, br, 2H, 3-*H*, 7-*H*), 9.08 (d,  $^3J = 4.30$  Hz, 2H, 2-*H*, 8-*H*), 8.31 (dd,  $^3J = 7.53$  Hz,  $^4J = 0.98$  Hz, 1H, 6'-*H*), 8.04 (td,  $^3J = 7.70$  Hz,  $^4J = 1.32$  Hz, 1H, 4'-*H*), 7.99 (dd,  $^3J = 7.93$  Hz,  $^4J = 1.13$  Hz, 1H, 3'-*H*), 7.88 (td,  $^3J = 7.51$  Hz,  $^4J = 1.45$  Hz, 1H, 5'-*H*), 7.54 (t,  $^4J = 1.73$  Hz, 1H, 2''-*H*), 7.50 (s, 1H, 2'''-*H*), 7.22 (ddd,  $^3J = 7.81$  Hz,  $^4J = 1.66$  Hz,  $^4J = 1.14$  Hz, 1H, 6''-*H*), 6.93 (ddd,  $^3J = 7.93$  Hz,  $^4J = 1.93$  Hz,  $^4J = 1.10$  Hz, 1H, 4''-*H*), 6.89 (d,  $^4J = 0.75$  Hz, 1H, 4'''-*H*), 6.67 (t,  $^3J = 7.88$  Hz, 1H, 5''-*H*), 3.30 (s, 3H,  $-\text{CH}_3$ ), -2.91 (s, 2H, pyrrole-NH) ppm.

**$^{19}\text{F-NMR}$  (470 MHz, acetone- $d_6$ , 300 K)**  $\delta$  = -139.74 (dd,  $^3J = 23.6$  Hz,  $^4J = 6.52$  Hz, 2F, A-*o*-F), -139.84 (dd,  $^3J = 23.9$  Hz,  $^4J = 7.72$  Hz, 1F, B-*o*-F), -140.01 (dd,  $^3J = 24.4$  Hz,  $^4J = 7.69$  Hz, 1F, B-*o'*-F), -140.12 (dd,  $^3J = 23.4$  Hz,  $^4J = 7.29$  Hz, 2F, A-*o'*-F), -155.69 (t,  $^3J = 20.2$  Hz, 2F, A-*p*-F), -155.76 (t,  $^3J = 20.0$  Hz, 1F, B-*p*-F), -164.53 (td,  $^3J = 22.1$  Hz,  $^4J = 7.72$  Hz, 2F, B-*m*-F, B-*m'*-F), -164.60 to -164.85 (m, 4F, A-*m*-F, A-*m'*-F) ppm.

**MS (EI, 70 eV):**  $m/z$  (%) = 1068.1 (100)  $[\text{M}]^{+}$ , 958.6 (4)  $[\text{M-C}_4\text{H}_5\text{N}_4]^{+}$ , 534.0 (15)  $[\text{M}]^{2+}$ .

**MS (CI, isobutane):**  $m/z$  (%) = 1069.4 (72)  $[\text{M+H}]^{+}$ .

**5-(Biphenylazo-*N*-methylimidazole)-10,15,20-tris(pentafluorophenyl)nickel(II)porphyrin (4).** The metal free biphenyl record player (77.0 mg, 72.0  $\mu\text{mol}$ ) was dissolved in toluene (80 mL) and nickel(II)acetylacetonate (185 mg, 720  $\mu\text{mol}$ ) was added. The resulting mixture was stirred at reflux for 3 d after which time no starting material was detectable via MALDI-TOF-MS. The reaction mixture was evaporated to dryness and the crude product was purified via column chromatography on silica gel (chloroform,  $R_f = 0.76$  (*cis*), 0.22 (*trans*)). The product was obtained as purple solid (56.0 mg, 49.8  $\mu\text{mol}$ , 69 %) which is deep red in solution.

**Mp:** 255 °C.

**IR (ATR):**  $\nu$  ( $\text{cm}^{-1}$ ) = 2951 (m), 2923 (m), 2853 (m), 1650 (w), 1518 (s), 1489 (s), 1342 (m), 1261 (m), 1226 (w), 1163 (w), 1071 (m), 1053 (m), 986 (vs), 956 (m), 938 (s), 799 (m), 762 (s), 743 (m), 705 (m)  $\text{cm}^{-1}$ .

**$^1\text{H-NMR}$  (600 MHz, acetone- $d_6$ , 300 K):**  $\delta$  = 10.57-8.52 (s, br, 8H, pyrrole-*H*), 8.27 (d,  $^3J = 7.32$ , 1H, 6'-*H*), 7.99 (t,  $^3J = 7.71$  Hz, 1H, 4'-*H*), 7.91 (d,  $^3J = 7.50$  Hz, 1H, 3'-*H*), 7.87 (t,  $^3J = 7.26$  Hz, 1H, 5'-*H*),



7.34 (s, br, 1H, 2''-H), 7.07 (d,  $^3J = 7.50$  Hz, 1H, 6''-H), 6.96 (d,  $^3J = 7.68$  Hz, 1H, 4''-H), 6.71 (t,  $^3J = 7.71$  Hz, 1H, 5''-H), 3.08 (s, br, 3H, -CH<sub>3</sub>) ppm.

The <sup>1</sup>H NMR signals experience strong line broadening which is due to intermolecular coordination. The imidazole protons (2'''-H, 4'''-H) are too broad and cannot be assigned. Trifluoroacetic acid (TFA, 10 μL) was added to protonate the imidazole and consequently inhibit intermolecular coordination.

**<sup>1</sup>H-NMR (500 MHz, acetone-d<sub>6</sub>, TFA, 300 K):** δ = 9.17-9.13 (m, 4H, pyrrole-H), 9.09 (s, br, 1H, 2'''-H), 9.06 (d,  $^3J = 4.95$  Hz, 2H, pyrrole-H), 8.99 (d,  $^3J = 5.00$  Hz, 2H, pyrrole-H), 8.35 (m, 1H, 6'-H), 8.01 (m, 1H, 4'-H), 7.93-7.88 (m, 2H, 3'-H, 5'-H), 7.50 (d, 4J = 1.35 Hz, 1H, 4'''-H), 7.36 (t,  $^4J = 1.75$  Hz, 1H, 2''-H), 7.34 (m, 1H, 6''-H), 7.14 (ddd,  $^3J = 7.94$  Hz,  $^4J = 1.91$  Hz,  $^4J = 1.09$  Hz, 1H, 4''-H), 6.90 (t,  $^3J = 7.90$  Hz, 1H, 5''-H), 3.54 (s, 3H, -CH<sub>3</sub>) ppm.

**<sup>19</sup>F-NMR (470 MHz, acetone-d<sub>6</sub>, 300 K)** δ = -139.10 to -139.70 (m, 3F, A-*o*-F, B-*o*-F), -139.80 to -140.25 (m, 3F, B-*o'*-F, A-*o'*-F), -155.60 to -155.85 (m, 3F, A-*p*-F, B-*p*-F), -164.10 to -164.80 (m, 6F, B-*m*-F, B-*m'*-F, A-*m*-F, A-*m'*-F) ppm.

**MS (EI, 70 eV):** m/z (%) = 1124.0 (100) [M]<sup>+</sup>, 1015.3 (20) [M-C<sub>4</sub>H<sub>5</sub>N<sub>4</sub>]<sup>+</sup>, 562.0 (7) [M]<sup>2+</sup>.

**MS (CI, isobutane):** m/z (%) = 1125.1 (51) [M+H]<sup>+</sup>.

**HR-MS (ESI, EtOH, 0.1 % HCOOH):** m/z [M+H]<sup>+</sup> calcd for [C<sub>54</sub>H<sub>21</sub>F<sub>15</sub>N<sub>8</sub>Ni+H]<sup>+</sup>, 1125.108; found 1125.107.

**UV/Vis (acetonitrile):** λ<sub>max</sub> (lg ε) = 406 (5.264), 524 (4.156), 557 (3.966) nm.

**4-(3'-(Triisopropylsilylthio)phenylazo)-1-(triphenylmethyl)imidazole (14).** Under an atmosphere of nitrogen the tritylated azoimidazole **11** (200 mg, 0.405 mmol) was dissolved in dry toluene (11 mL) and Cesium carbonate (172 mg, 0.527 mmol), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (15.0 mg, 20.3 μmol) and triisopropylsilylthiole (113 μL, 0.537 mmol) were then added subsequently. The resulting mixture was stirred at 100 °C for 4 h, [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (15.0 mg, 20.3 μmol) was added again and stirring at 100 °C was continued for another 5 h. After cooling down to room temperature and further stirring at room temperature overnight ethyl acetate (40 mL) was added. The reaction mixture was filtrated over celite and evaporated to dryness. Purification of the crude product via column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1, R<sub>f</sub> = 0.25) gave a yellow solid (224 mg, 0.373 mmol, 92 %).

**Mp:** 253 °C.

**IR (ATR):** ν (cm<sup>-1</sup>) = 2943 (m), 2865 (m), 1738 (w), 1582 (w), 1522 (m), 1493 (m), 1438 (s), 1349 (m), 1280 (m), 1227 (m), 1186 (m), 1152 (m), 1117 (m), 1086 (m), 991 (m), 881 (m), 856 (m), 792 (s), 748 (s), 699 (s), 683 (s), 657 (s), 639 (s), 577 (m), 547 (m), 512 (s), 490 (m), 456 (m) cm<sup>-1</sup>.

**<sup>1</sup>H-NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):** δ = 7.95 (t, <sup>4</sup>J = 1.74 Hz, 1H, 2'-H), 7.65 (ddd, <sup>3</sup>J = 7.98 Hz, <sup>4</sup>J = 1.77 Hz, <sup>4</sup>J = 0.99 Hz, 1H, 6'-H), 7.55 (d, <sup>4</sup>J = 1.38 Hz, 1H, 5-H), 7.55-7.52 (m, 2H, 4'-H, 2-H), 7.42-7.38 (m, 9H, *m*-Tr-H, *p*-Tr-H), 7.32 (t, <sup>3</sup>J = 7.80 Hz, 1H, 5'-H), 7.25-7.21 (m, 6H, *o*-Tr-H), 1.28 (sept., <sup>3</sup>J = 7.45 Hz, 3H, 3x -CH(CH<sub>3</sub>)<sub>2</sub>), 1.08 (d, <sup>3</sup>J = 7.50 Hz, 18H, 3x -CH(CH<sub>3</sub>)<sub>2</sub>) ppm.

**<sup>13</sup>C-NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):** δ = 153.9 (C-4), 153.6 (C-1'), 142.3 (C-*i*-Tr), 139.6 (C-2), 137.4 (C-4'), 133.3 (C-3'), 130.2 (C-*o*-Tr), 130.1 (C-2'), 129.4 (C-5'), 128.7 (C-*p*-Tr, C-*m*-Tr), 121.9 (C-5), 120.7 (C-6'), 76.6 (-CPh<sub>3</sub>), 18.6 (-CH(CH<sub>3</sub>)<sub>2</sub>), 13.5 (-CH(CH<sub>3</sub>)<sub>2</sub>) ppm.

**MS (ESI, methanol):** m/z (%) = 642.0 (4) [M+K]<sup>+</sup>, 625.0 (31) [M+Na]<sup>+</sup>, 602.7 (12) [M+H]<sup>+</sup>, 243.1 (100) [CPh<sub>3</sub>]<sup>+</sup>.

**Anal. Calcd.** For [C<sub>37</sub>H<sub>42</sub>N<sub>4</sub>Ssi + 0.25 EtOAc] (624.93): cal. C 73.03, H 7.10, N 8.97, S 5.13, found C 72.99, H 7.14, N 9.19, S 4.92 %.

**4-(3'-(2''-Formylthiophenyl)phenylazo)-1-(triphenylmethyl)imidazole (15).** Under an atmosphere of nitrogen the thiol-functionalized azoimidazole **14** (576 mg, 955 μmol) was dissolved in DMF (25 mL). Potassium carbonate (145 mg, 1.05 mmol) and cesium fluoride (160 mg, 1.05 mmol) were added and the resulting mixture was stirred for 10 min at room temperature. 2-Fluorobenzaldehyde (111 μL, 1.05 mmol) was added and the mixture was heated to 100 °C for 5 h. After cooling down to room temperature half saturated ammonium chloride solution (aq., 40 mL) and diethyl ether (40 mL) were added and layers were separated. The aqueous layer was extracted once with diethylether (30 mL) and the combined organic layers were washed two times with water (each 50 mL), dried over magnesium sulfate and evaporated to dryness. Purification of the crude product via column chromatography on silica gel (cyclohexane/ethyl acetate, 7:3, R<sub>f</sub> = 0.32) gave a yellow solid (457 mg, 0.830 mmol, 87 %).

**Mp:** 216 °C.

**IR (ATR):** ν (cm<sup>-1</sup>) = 3122 (w), 3058 (w), 2864 (w), 2161 (w), 1736 (w), 1695 (s), 1588 (m), 1561 (w), 1524 (w), 1489 (m), 1464 (w), 1437 (s), 1410 (w), 1391 (w), 1327 (w), 1275 (s), 1241 (w), 1200 (m), 1188 (m), 1155 (m), 1128 (s), 1087 (w), 1056 (m), 1034 (m), 1001 (m), 988 (m), 921 (m), 904 (w), 889 (w), 863 (m), 849 (w), 826 (m), 785 (m), 760 (vs), 751 (vs), 701 (vs), 687 (s), 677 (s), 657 (s), 640 (s), 556 (m), 509 (m), 432 (m), 409 (m) cm<sup>-1</sup>.

**<sup>1</sup>H-NMR (600 MHz, DMSO-d<sub>6</sub>, 298 K):** δ = 10.26 (s, 1H, -CHO), 7.97 (dd, <sup>3</sup>J = 7.62 Hz, <sup>4</sup>J = 1.44 Hz, 1H, 3''-H), 7.82 (d, <sup>3</sup>J = 7.92 Hz, 1H, 6'-H), 7.76 (t, <sup>4</sup>J = 1.71 Hz, 1H, 2'-H), 7.65-7.61 (m, 3H, 2-H, 5-H, 5'-H), 7.58-7.54 (m, 2H, 4'-H, 5''-H), 7.49-7.37 (m, 10H, 4''-H, *m*-Tr-H, *p*-Tr-H), 7.20-7.15 (m, 6H, *o*-Tr-H), 7.07 (d, <sup>3</sup>J = 7.92 Hz, 1H, 6''-H) ppm.

**<sup>13</sup>C-NMR (150 MHz, DMSO-d<sub>6</sub>, 298 K):** δ = 192.1 (-CHO), 153.4 (C-1'), 152.9 (C-4), 141.6 (C-*i*-Tr), 139.7 (C-1''), 139.4 (C-2), 134.9 (C-4'), 134.6 (C-5''), 133.9 (C-3'), 133.3 (C-3''), 133.2 (C-2''), 131.1 (C-5'), 129.4 (C-6''), 129.2 (C-*o*-Tr), 128.5 (C-*m*-Tr), 128.3 (C-*p*-Tr), 126.7 (C-4''), 125.7 (C-2'), 123.1

(C-6'), 120.8 (C-5), 75.7 (-CPh<sub>3</sub>) ppm.

**MS (ESI, methanol):** m/z (%) = 588.9 (8) [M+K]<sup>+</sup>, 573.0 (82) [M+Na]<sup>+</sup>, 550.7 (9) [M+H]<sup>+</sup>, 243.1 (100) [CPh<sub>3</sub>].

**Anal. Calcd.** For [C<sub>35</sub>H<sub>26</sub>N<sub>4</sub>OS + 0.25 EtOAc] (572.70): cal. C 75.50, H 4.93, N 9.78, S 5.47, found C 75.38, H 4.89, N 10.02, S 5.47 %.

**5-(3'-(2''-Formylthiophenyl)phenylazo)-1-methylimidazole (16).** Under an atmosphere of nitrogen the biphenylthioether azoimidazole **15** (347 mg, 630 μmol) was dissolved in dry methylene chloride (12 mL). Methyl trifluoromethanesulfonate (71.0 μL, 630 μmol) was added dropwise and it was stirred at room temperature for 90 min. Acetone/H<sub>2</sub>O (2:1, 36 mL) was added and stirring was continued for 16 h. Saturated Sodium bicarbonate solution (aq., 5 mL) was added, layers were separated and the aqueous layer was extracted two times with methylene chloride (each 20 mL). The combined organic layers were dried over magnesium sulfate and evaporated to dryness. Purification via column chromatography on silica gel (ethyl acetate, R<sub>f</sub> = 0.15) gave an orange solid (176 mg, 546 μmol, 87 %).

**Mp:** 135 °C.

**IR (ATR):** ν (cm<sup>-1</sup>) = 3112 (w), 2848 (w), 2747 (m), 1698 (m), 1678 (vs), 1588 (m), 1557 (m), 1504 (m), 1458 (m), 1410 (m), 1395 (m), 1339 (s), 1293 (s), 1225 (s), 1198 (vs), 1125 (vs), 1043 (s), 996 (m), 971 (m), 909 (s), 846 (s), 827 (s), 772 (vs), 687 (s), 677 (s), 658 (vs), 639 (vs), 597 (m), 531 (vs), 468 (m) cm<sup>-1</sup>.

**<sup>1</sup>H-NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):** δ = 10.39 (s, 1H, -CHO), 7.91 (dd, <sup>3</sup>J = 7.65 Hz, <sup>4</sup>J = 1.60 Hz, 1H, 3''-H), 7.87 (t, <sup>4</sup>J = 1.83 Hz, 1H, 2'-H), 7.82 (ddd, <sup>3</sup>J = 7.82 Hz, <sup>4</sup>J = 1.95 Hz, <sup>4</sup>J = 1.19 Hz, 1H, 6'-H), 7.61 (s, 1H, 2-H), 7.55-7.50 (m, 2H, 4-H, 5'-H), 7.49-7.45 (m, 2H, 4'-H, 5''-H), 7.39 (dt, <sup>3</sup>J = 7.49 Hz, <sup>4</sup>J = 1.11 Hz, 1H, 4''-H), 7.23 (dd, <sup>3</sup>J = 7.93 Hz, <sup>4</sup>J = 1.13 Hz, 1H, 6''-H), 3.91 (s, 3H, -CH<sub>3</sub>) ppm.

**<sup>13</sup>C-NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):** δ = 191.8 (-CHO), 154.4 (C-1'), 145.8 (C-5), 141.6 (C-2), 140.7 (C-1''), 135.6 (C-3'), 134.7-134.5 (C-4', C-2'', C-5''), 132.3 (C-3''), 131.4 (C-6''), 130.7 (C-5'), 127.3 (C-4''), 126.0 (C-2'), 124.0 (C-4), 123.1 (C-6'), 32.8 (-CH<sub>3</sub>) ppm.

**MS (EI):** m/z (%) = 322.1 (100) [M]<sup>+</sup>, 293.1 (20) [M-CHO]<sup>+</sup>, 227.0 (24) [M-C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>]<sup>+</sup>, 184.0 (51) [C<sub>12</sub>H<sub>8</sub>S]<sup>+</sup>, 109.1 (76) [C<sub>4</sub>H<sub>5</sub>N<sub>4</sub>]<sup>+</sup>.

**HR-MS (EI):** m/z [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>N<sub>4</sub>OS, 322.0888; found 322.0881.

**UV/Vis (acetonitrile):** λ<sub>max</sub> (lg ε) = 210 (4.460), 236 (4.380), 362 (4.365) nm.

**Anal. Calcd.** For [C<sub>17</sub>H<sub>14</sub>N<sub>4</sub>OS + 0.2 EtOAc] (340.01): cal. C 62.88, H 4.62, N 16.48, S 9.43, found C 63.08, H 4.34, N 16.32, S 9.63 %.

**5-(Phenyl-2'-(thiophenyl-3''-(azo-*N*-methylimidazole)))-10,15,20-tris(pentafluorophenyl)-porphyrin (mf-5).** To a solution of biphenylthioether tonearm **16** (484 mg, 1.52 mmol) and pentafluorobenzaldehyde (271 mg, 1.38 mmol) in methylene chloride (200 mL) was added borontrifluoride diethyletherate (257  $\mu$ L, 2.03 mmol) under an atmosphere of nitrogen. Pentafluorophenyl dipyrromethane (862 mg, 2.76 mmol) in methylene chloride (40 mL) was added to the stirred solution over 1 h at room temperature. Stirring under nitrogen at room temperature was continued for additional 6 h and the solution turned from dark red to black. Afterwards, chloranil (713 mg, 2.90 mmol) was added and the solution was stirred at reflux for 2 h and at room temperature for 16 h. Triethylamine (1 mL) was added and stirring was continued for 30 min. The reaction mixture was evaporated to dryness and the crude product was filtrated over silica gel (methylene chloride). Subsequent column chromatography on silica gel (cyclohexane/ethyl acetate, 6:4  $\rightarrow$  1:1,  $R_f$  = 0.22  $\rightarrow$  0:1) gave a purple solid (44.0 mg, 40.0  $\mu$ mol, 3 %).

**Mp:** 154 °C.

**IR (ATR):**  $\nu$  (cm<sup>-1</sup>) = 3316 (w), 2963 (w), 2926 (w), 2855 (w), 1981 (w), 1728 (w), 1704 (w), 1652 (w), 1679 (w), 1517 (s), 1495 (s), 1435 (m), 1403 (m), 1341 (m), 1259 (s), 1226 (m), 1192 (w), 1143 (m), 1113 (m), 1079 (s), 1063 (s), 1043 (s), 1033 (s), 1026 (s), 985 (vs), 936 (m), 917 (s), 801 (s), 756 (vs), 740 (s), 687 (s), 644 (m), 531 (m), 497 (m), 432 (m), 423 (m) cm<sup>-1</sup>.

**<sup>1</sup>H-NMR (600 MHz, acetone-d<sub>6</sub>, 300 K):**  $\delta$  = 9.28 (s, br, 4H, pyrrole-*H*), 9.15 (s, br, 2H, pyrrole-*H*), 8.90 (s, br, 2H, pyrrole-*H*), 8.31 (dd, <sup>3</sup>*J* = 7.41 Hz, <sup>4</sup>*J* = 1.23 Hz, 1H, 6'-*H*), 7.93 (td, <sup>3</sup>*J* = 7.46 Hz, <sup>4</sup>*J* = 1.35 Hz, 1H, 4'-*H*), 7.88 (dd, <sup>3</sup>*J* = 8.16 Hz, <sup>4</sup>*J* = 1.14 Hz, 1H, 3'-*H*), 7.84 (td, <sup>3</sup>*J* = 7.85 Hz, <sup>4</sup>*J* = 1.49 Hz, 1H, 5'-*H*), 7.68 (s, 1H, 2-*H*), 7.38 (ddd, <sup>3</sup>*J* = 7.83 Hz, <sup>4</sup>*J* = 1.62 Hz, <sup>4</sup>*J* = 1.00 Hz, 1H, 4''-*H*), 7.21 (s, 1H, 4-*H*), 7.14 (t, <sup>4</sup>*J* = 1.68 Hz, 1H, 2''-*H*), 7.03 (t, <sup>3</sup>*J* = 7.83 Hz, 1H, 5''-*H*), 6.90 (ddd, <sup>3</sup>*J* = 7.72 Hz, <sup>4</sup>*J* = 1.66 Hz, <sup>4</sup>*J* = 1.04 Hz, 1H, 6''-*H*), 3.55 (s, 3H, -CH<sub>3</sub>), -2.83 (s, 2H, pyrrole-NH) ppm.

**<sup>19</sup>F-NMR (470 MHz, acetone-d<sub>6</sub>, 300 K)**  $\delta$  = -139.57 (dd, <sup>3</sup>*J* = 24.2 Hz, <sup>4</sup>*J* = 7.65 Hz, 2F, A-*o*-F), -139.69 (dd, <sup>3</sup>*J* = 23.8 Hz, <sup>4</sup>*J* = 7.63 Hz, 1F, B-*o*-F), -139.98 (dd, <sup>3</sup>*J* = 23.7 Hz, <sup>4</sup>*J* = 7.53 Hz, 1F, B-*o'*-F), -140.09 (dd, <sup>3</sup>*J* = 23.8 Hz, <sup>4</sup>*J* = 7.51 Hz, 2F, A-*o'*-F), -155.66 (t, <sup>3</sup>*J* = 20.3 Hz, 2F, A-*p*-F), -155.69 (t, <sup>3</sup>*J* = 20.2 Hz, 1F, B-*p*-F), -164.51 to -164.80 (m, 6F, B-*m*-F, B-*m'*-F, A-*m*-F, A-*m'*-F) ppm.

**MS (MALDI-TOF):**  $m/z$  (%) = 1123.7 (12) [M + Na]<sup>+</sup>, 1101.7 (100) [M + H]<sup>+</sup>.

**5-(Phenyl-2'-(thiophenyl-3''-(azo-*N*-methylimidazole)))-10,15,20-tris(pentafluorophenyl)-nickel(II)porphyrin (5).** The metal free biphenylthioether record player (39.0 mg, 35.4  $\mu$ mol) was dissolved in toluene (40 mL) and nickel(II)acetylacetonate (91.0 mg, 354  $\mu$ mol) was added. The resulting mixture was stirred at reflux for 2.5 d after which time no starting material was detectable via MALDI-TOF-MS. The reaction mixture was evaporated to dryness and the crude product was purified

via column chromatography on silica gel (chloroform → chloroform, 5 % methanol,  $R_f = 0.50$  (*cis*), 0.25 (*trans*)). The product was obtained as purple solid (10.0 mg, 8.64  $\mu\text{mol}$ , 24 %) which is deep red in solution.

**Mp:** 253 °C.

**IR (ATR):**  $\nu$  ( $\text{cm}^{-1}$ ) = 1652 (w), 1583 (w), 1518 (s), 1486 (s), 1429 (m), 1342 (m), 1317 (w), 1278 (w), 1262 (w), 1225 (m), 1164 (w), 1142 (w), 1114 (m), 1074 (m), 1060 (m), 1005 (m), 984 (vs), 958 (s), 938 (s), 925 (s), 854 (m), 839 (m), 799 (m), 762 (vs), 745 (s), 703 (s), 686 (m), 641 (m), 585 (w), 503 (w)  $\text{cm}^{-1}$ .

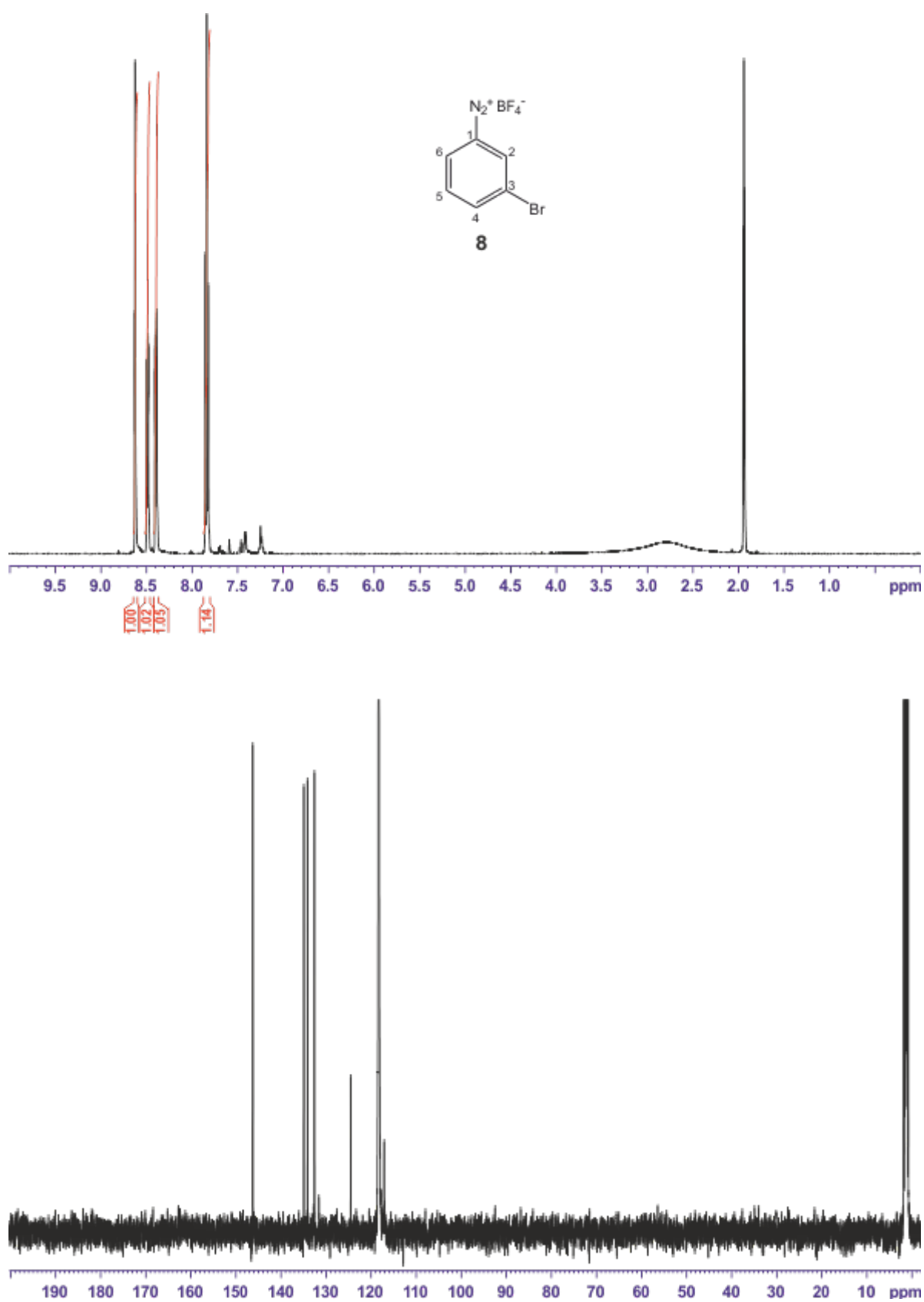
**$^1\text{H-NMR}$  (600 MHz, acetone- $d_6$ , 300 K):**  $\delta$  = 9.44 (s, br, 4H, pyrrole-*H*), 9.32 (s, br, 2H, pyrrole-*H*), 9.09 (s, br, 2H, pyrrole-*H*), 8.24 (dd,  $^3J = 7.35$  Hz,  $^4J = 1.23$  Hz, 1H, 6'-*H*), 7.96 (s, br, 1H, 2-*H*), 7.86 (td,  $^3J = 7.84$  Hz,  $^4J = 1.32$  Hz, 1H, 4'-*H*), 7.81 (td,  $^3J = 7.53$  Hz,  $^4J = 1.39$  Hz, 1H, 5'-*H*), 7.79 (dd,  $^3J = 7.83$  Hz,  $^4J = 1.25$  Hz, 1H, 3'-*H*), 7.62 (s, br, 1H, 4-*H*), 7.31 (d,  $^3J = 8.22$  Hz, 1H, 4''-*H*), 7.08-7.06 (m, 1H, 2''-*H*), 6.99 (t,  $^3J = 7.77$  Hz, 1H, 5''-*H*), 6.90 (d,  $^3J = 7.86$  Hz, 6''-*H*), 3.60 (s, 3H, - $\text{CH}_3$ ) ppm.

**$^{19}\text{F-NMR}$  (470 MHz, acetone- $d_6$ , 300 K)**  $\delta$  = -139.44 (dd,  $^3J = 23.4$  Hz,  $^4J = 7.01$  Hz, 2F, A-*o*-F), -139.74 (dd,  $^3J = 23.6$  Hz,  $^4J = 7.20$  Hz, 1F, B-*o*-F), -139.87 (dd,  $^3J = 23.7$  Hz,  $^4J = 7.10$  Hz, 1F, B-*o'*-F), -140.22 (dd,  $^3J = 23.1$  Hz,  $^4J = 6.82$  Hz, 2F, A-*o'*-F), -155.74 (t,  $^3J = 20.4$  Hz, 2F, A-*p*-F), -155.76 (t,  $^3J = 20.2$  Hz, 1F, B-*p*-F), -164.35 to -164.72 (m, 6F, B-*m*-F, B-*m'*-F, A-*m*-F, A-*m'*-F) ppm.

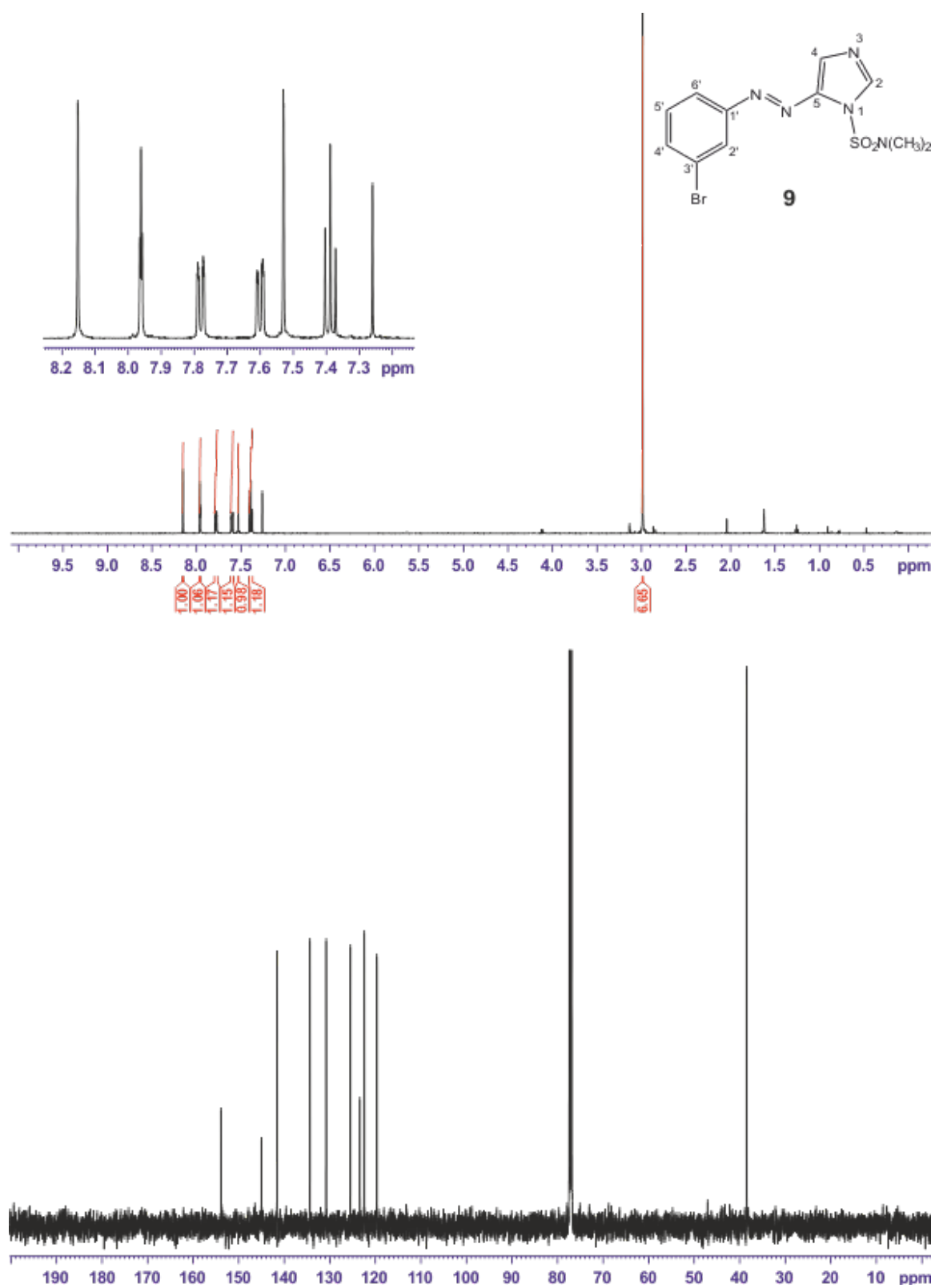
**HR-MS** (ESI, EtOH, 0.1 % HCOOH):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{54}\text{H}_{21}\text{F}_{15}\text{N}_8\text{S}\text{Ni}+\text{H}]$ , 1157.079; found 1157.078.

**UV/Vis (acetonitrile):**  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ) = 406 (5.184), 524 (4.085), 558 (3.951) nm.

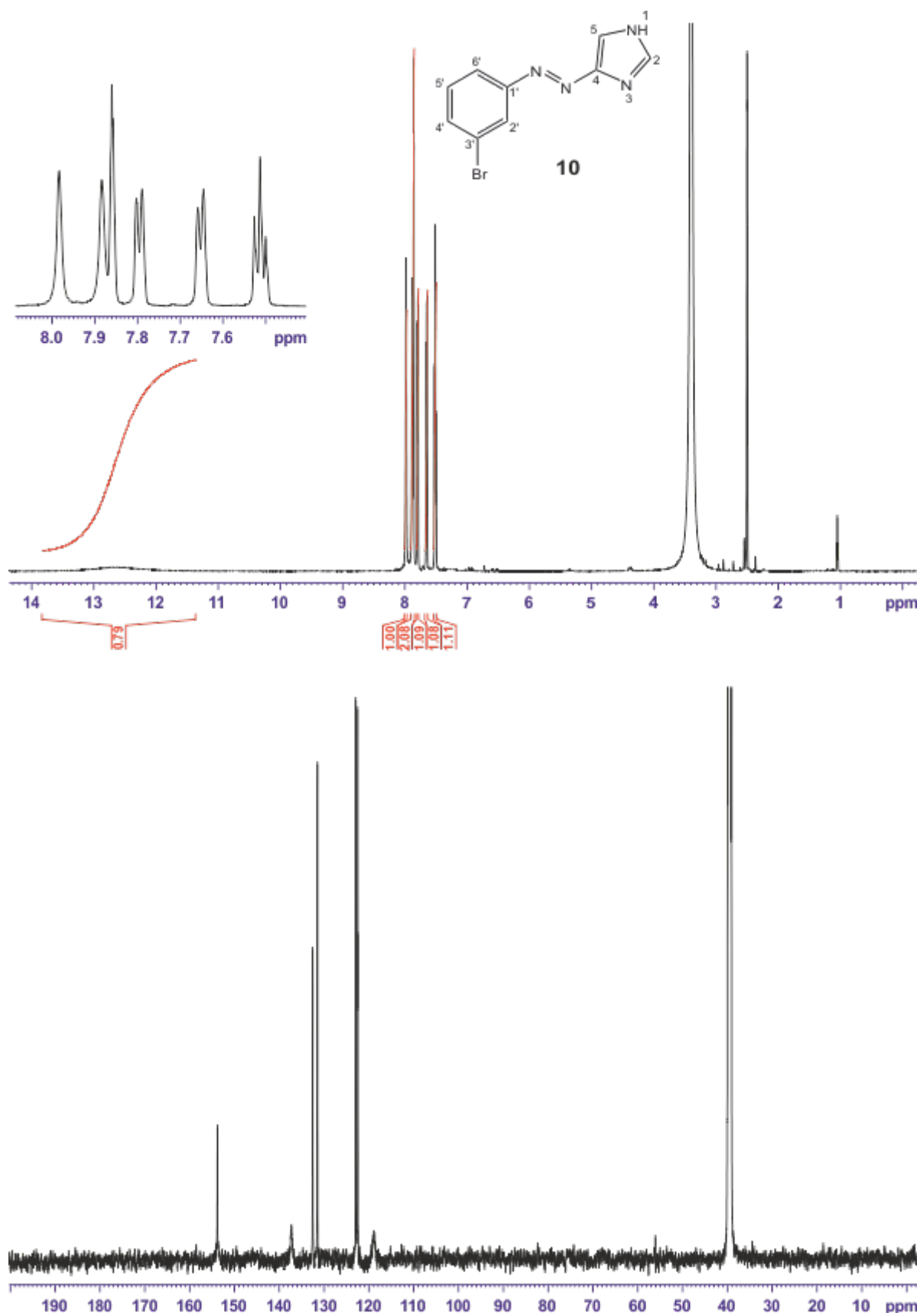
### III.3 NMR spectra



**Figure S3:**  $^1H$  NMR (top) and  $^{13}C$  NMR (bottom) spectra of 3-bromobenzenediazonium tetrafluoroborate **8**. Spectra were measured in acetonitrile- $d_3$  at 300 K.

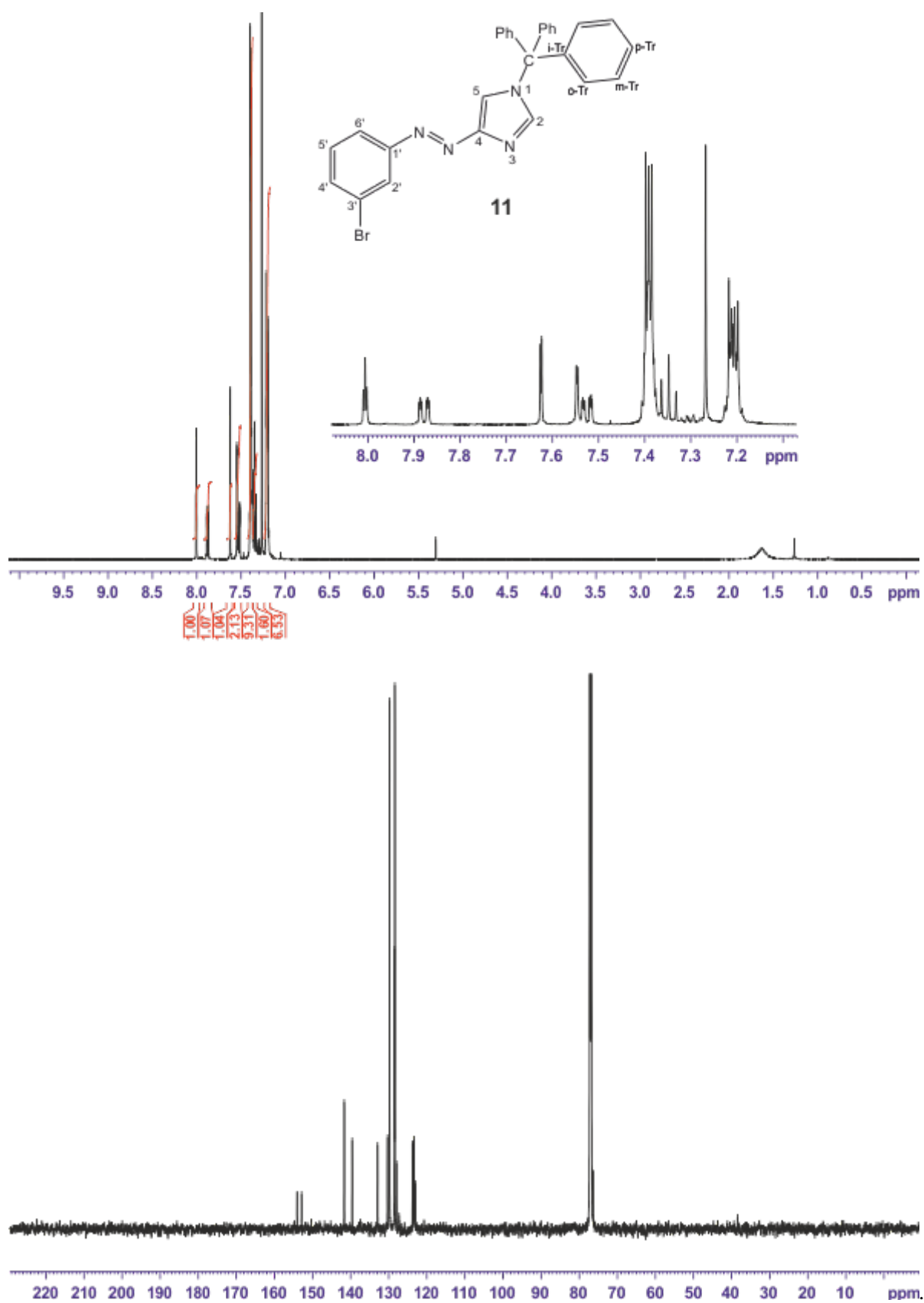


**Figure S4:** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of 5-(3'-Bromophenylazo)-1-(*N,N*-dimethylsulfamoyl)imidazole (**9**). Spectra were measured in CDCl<sub>3</sub> at 300 K.

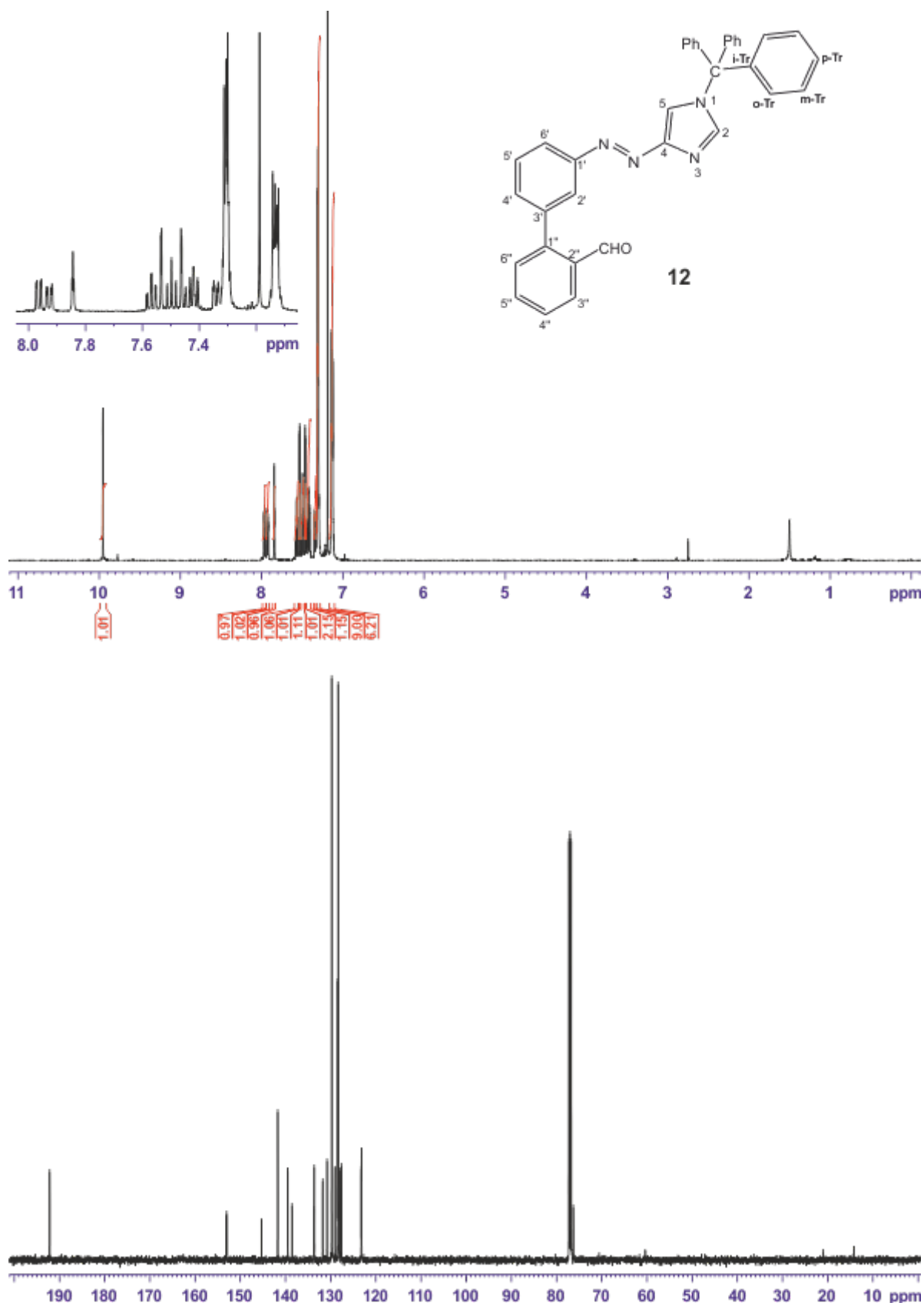


**Figure S5:** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of 4(5)-(3'-Bromophenylazo)imidazole (**10**). Spectra were measured in DMSO-d<sub>6</sub> at 298 K.

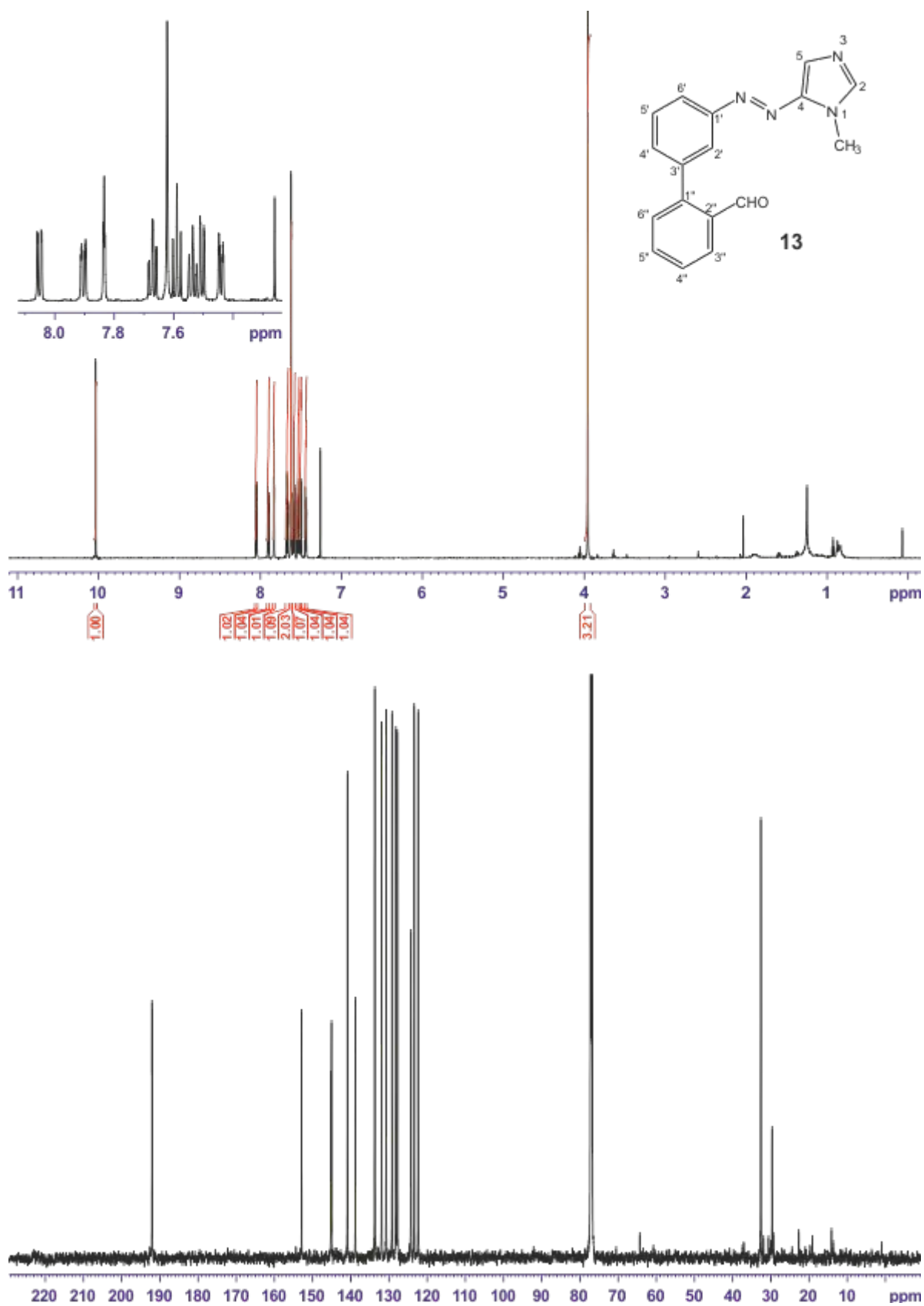




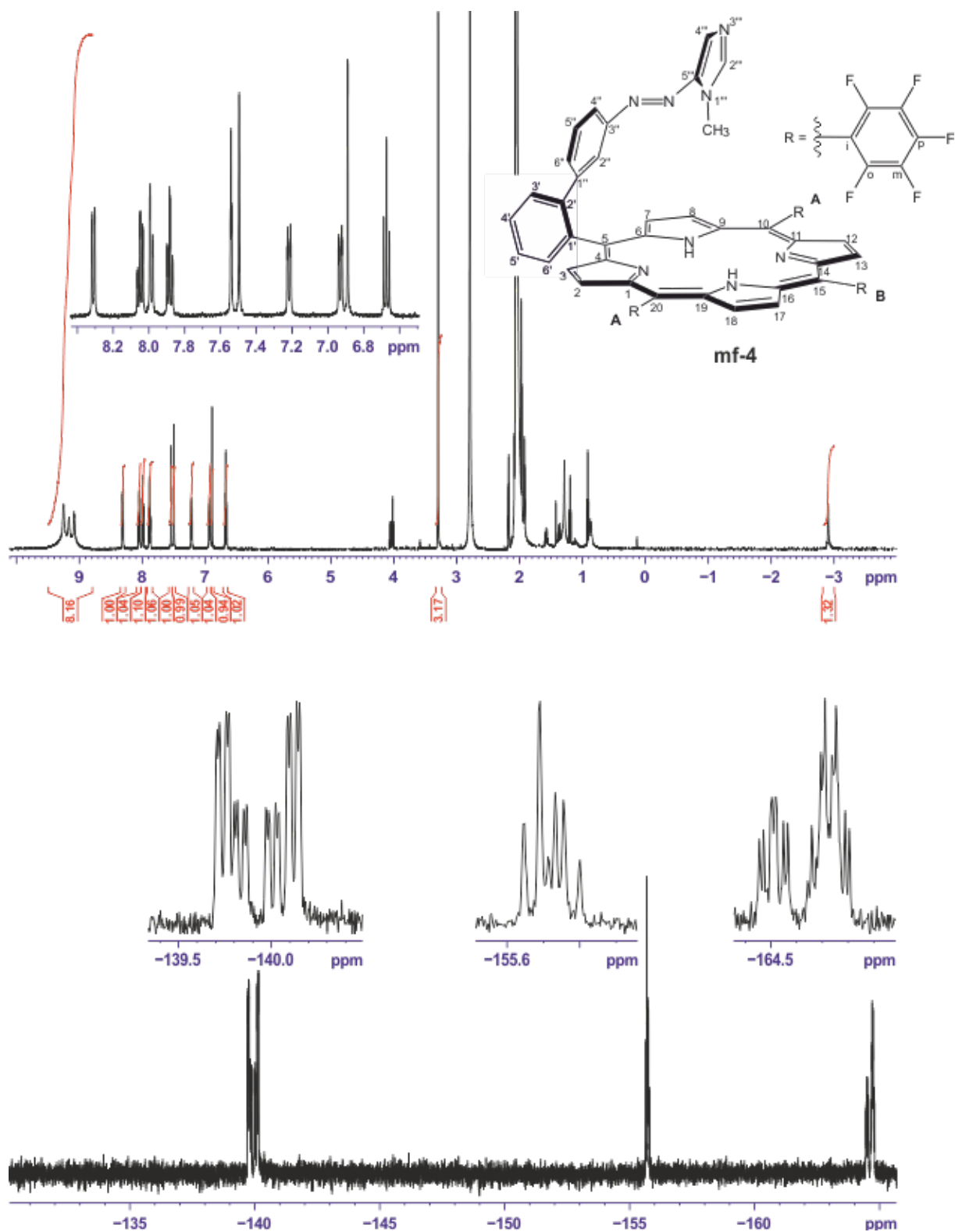
**Figure S6:** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of 4-(3'-Bromophenylazo)-1-(triphenylmethyl)imidazole (**11**). Spectra were measured in CDCl<sub>3</sub> at 298 K.



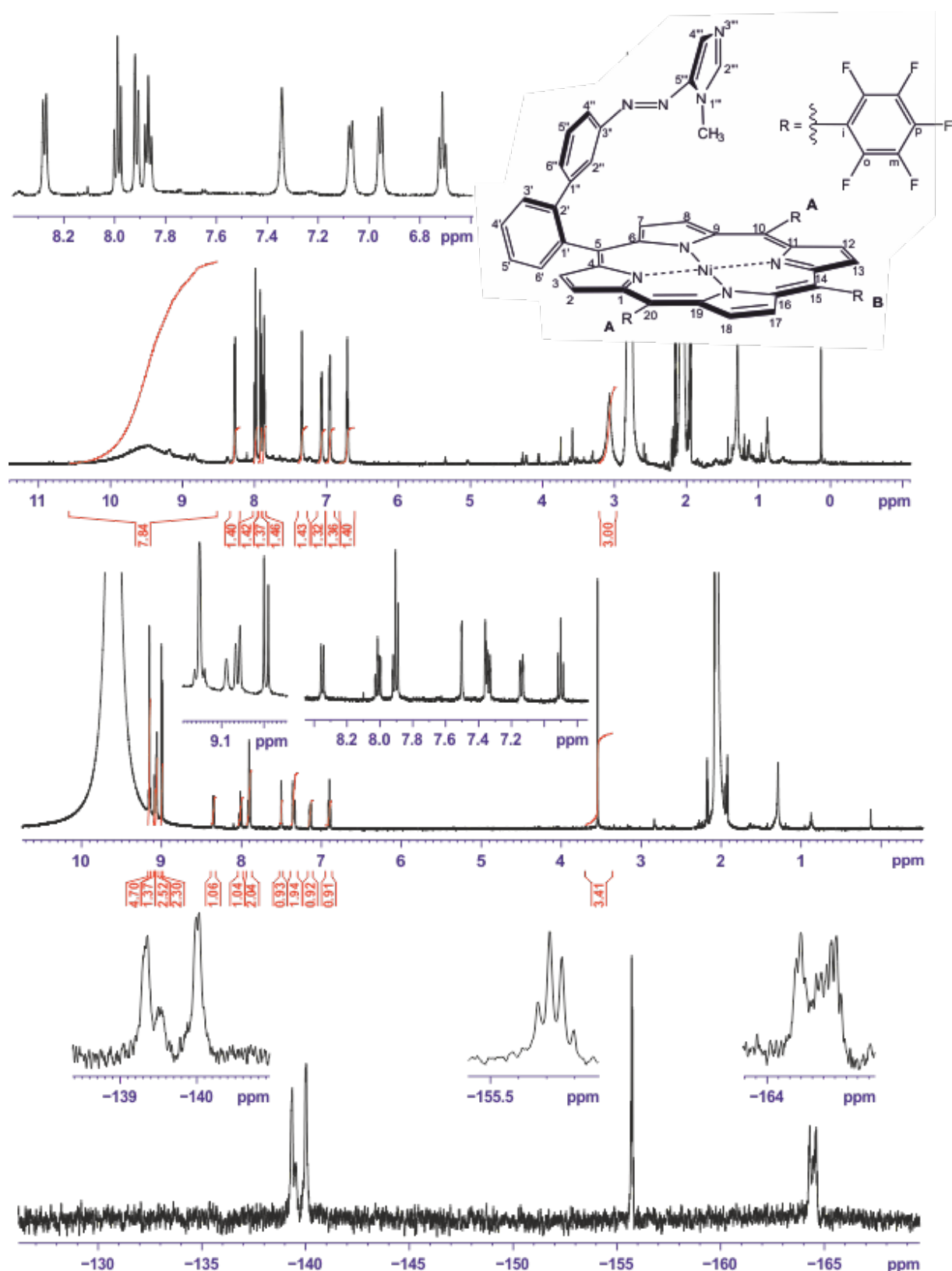
**Figure S7:**  $^1\text{H}$  NMR (top) and  $^{13}\text{C}$  NMR (bottom) spectra of 4-(3'-(2''-formylphenyl)phenylazo)-1-(triphenylmethyl)imidazole (**12**). Spectra were measured in  $\text{CDCl}_3$  at 300 K.



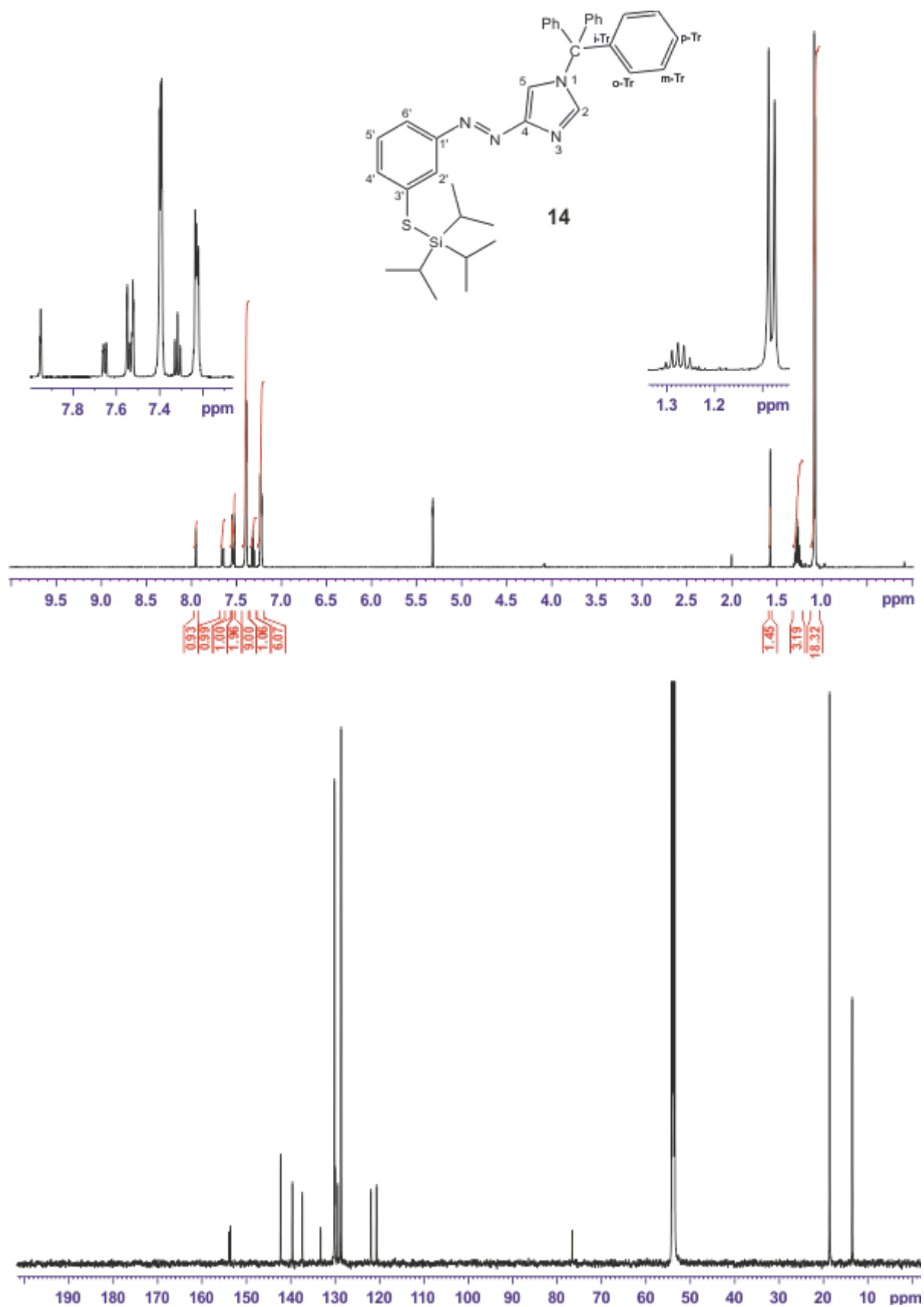
**Figure S8:** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of 5-(3'-(2''-formylphenyl)phenylazo)-1-methylimidazole (**13**). Spectra were measured in CDCl<sub>3</sub> at 298 K.



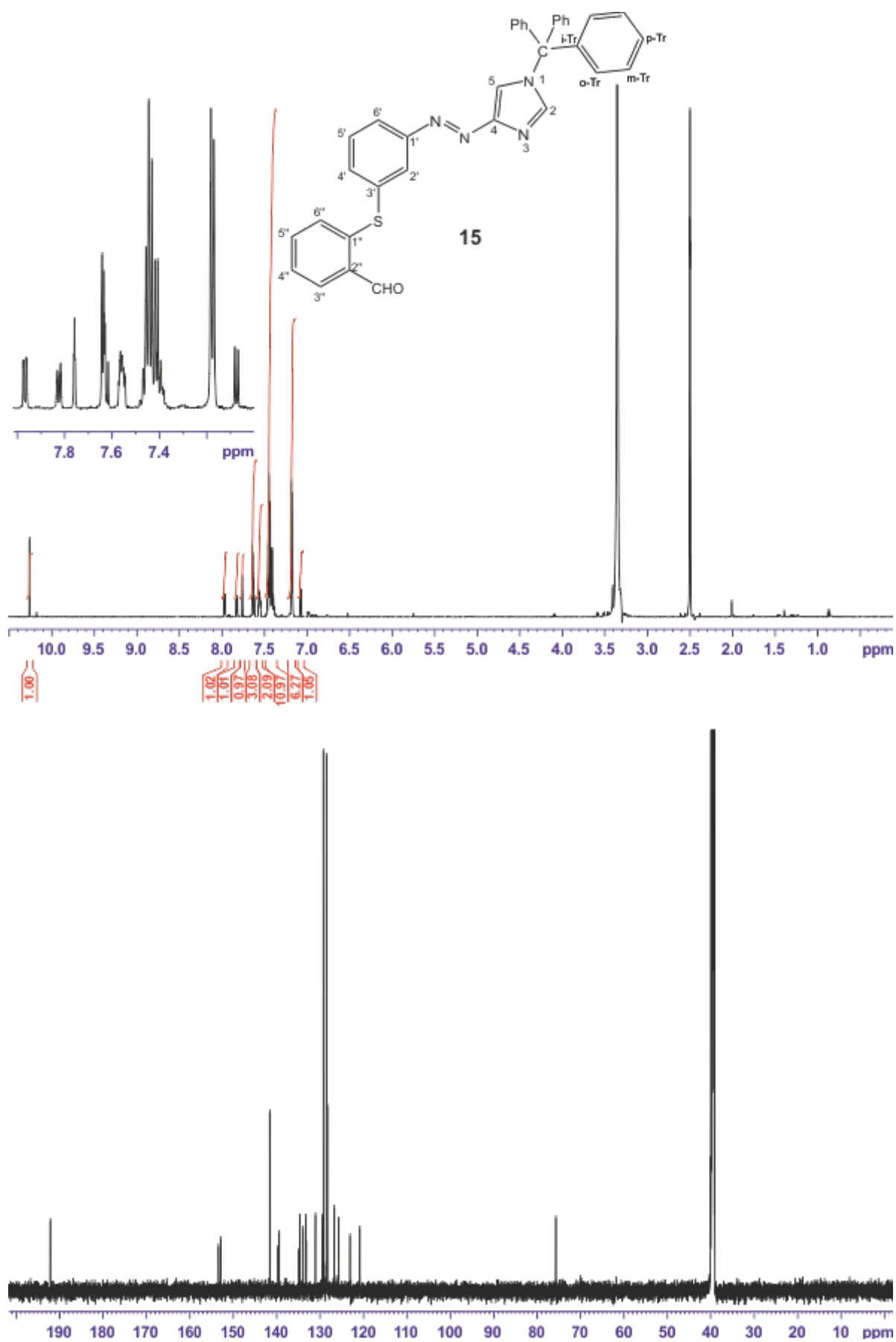
**Figure S9:** <sup>1</sup>H NMR (top) and <sup>19</sup>F NMR (bottom) spectra of metal-free biphenyl record player (mf-4). Spectra were measured in acetone-d<sub>6</sub> at 300 K.



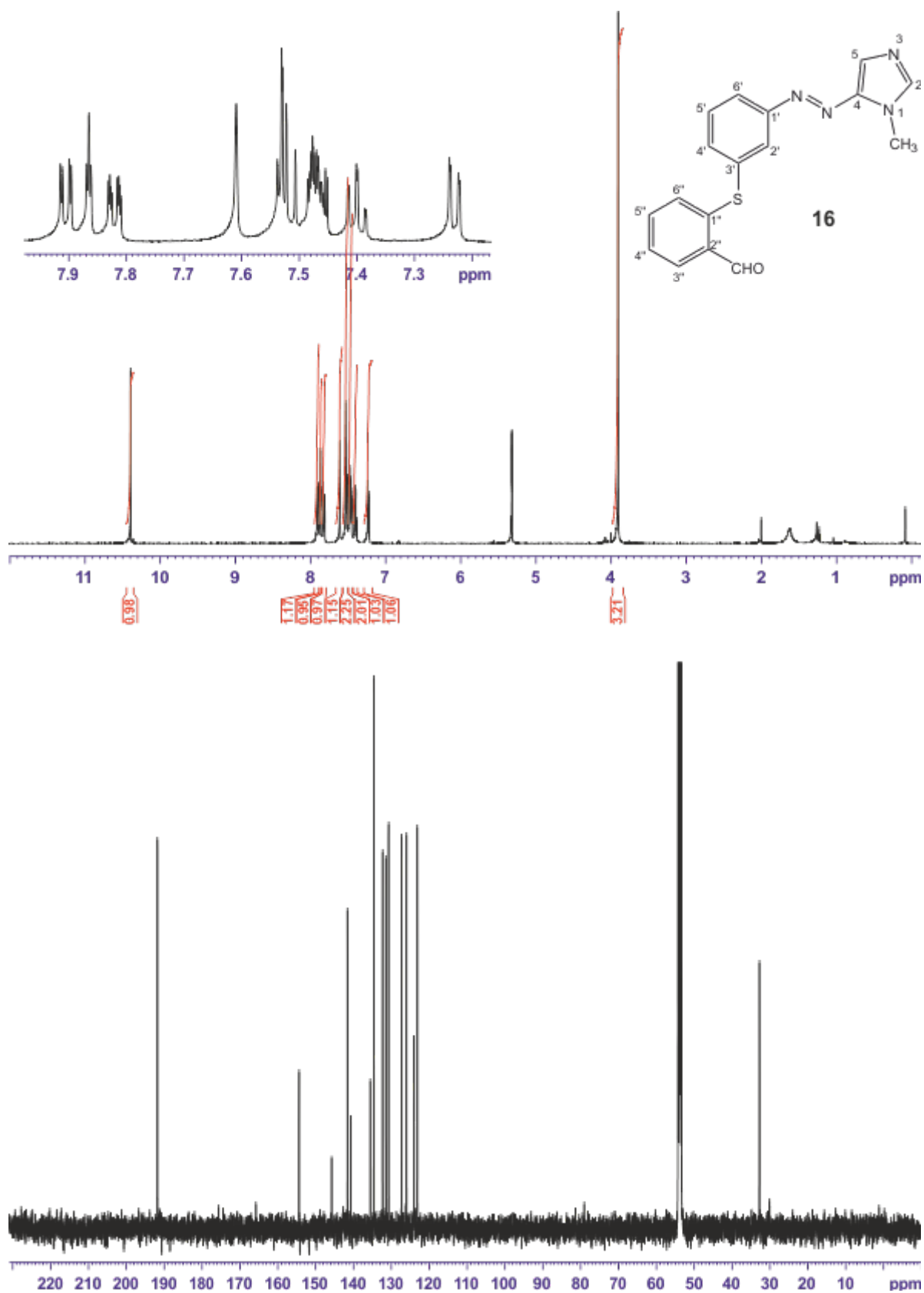
**Figure S10:** <sup>1</sup>H NMR (top), <sup>1</sup>H NMR with 10 μL trifluoroacetic acid (middle) and <sup>19</sup>F NMR (bottom) spectra of *trans* biphenyl record player (4). Spectra were measured in acetone-*d*<sub>6</sub> at 300 K.



**Figure S11:**  $^1\text{H}$  NMR (top) and  $^{13}\text{C}$  NMR (bottom) spectra of 4-(3'-(triisopropylsilylthio)phenylazo)-1-(triphenylmethyl)imidazole (**14**). Spectra were measured in  $\text{CD}_2\text{Cl}_2$  at 298 K.

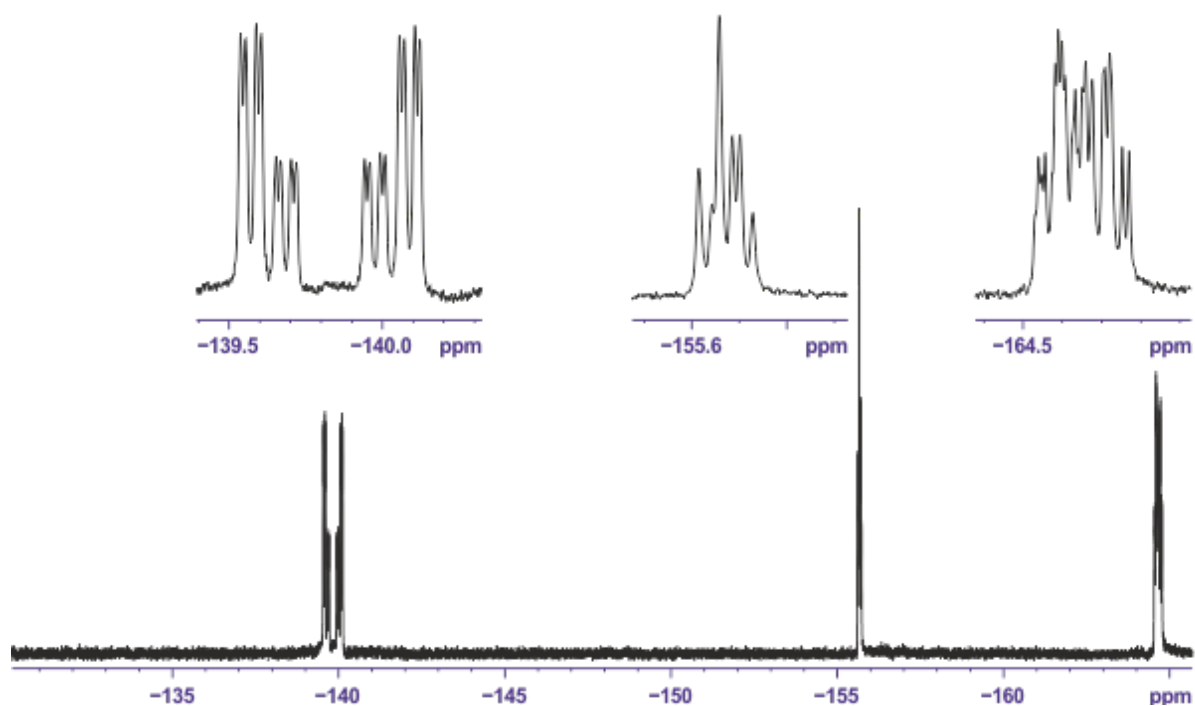
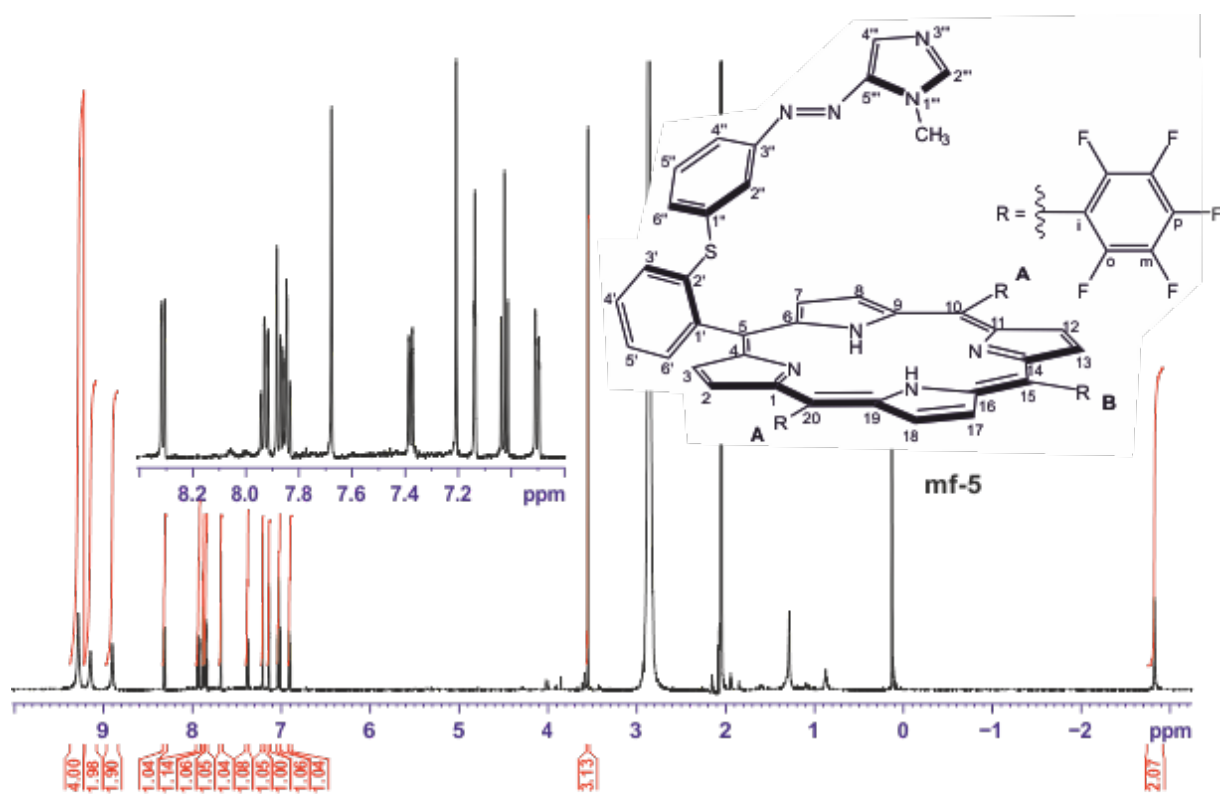


**Figure S12:** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of 4-(3'-(2''-formylthiophenyl)phenylazo)-1-(triphenylmethyl)imidazole (**15**). Spectra were measured in DMSO-d<sub>6</sub> at 298 K.

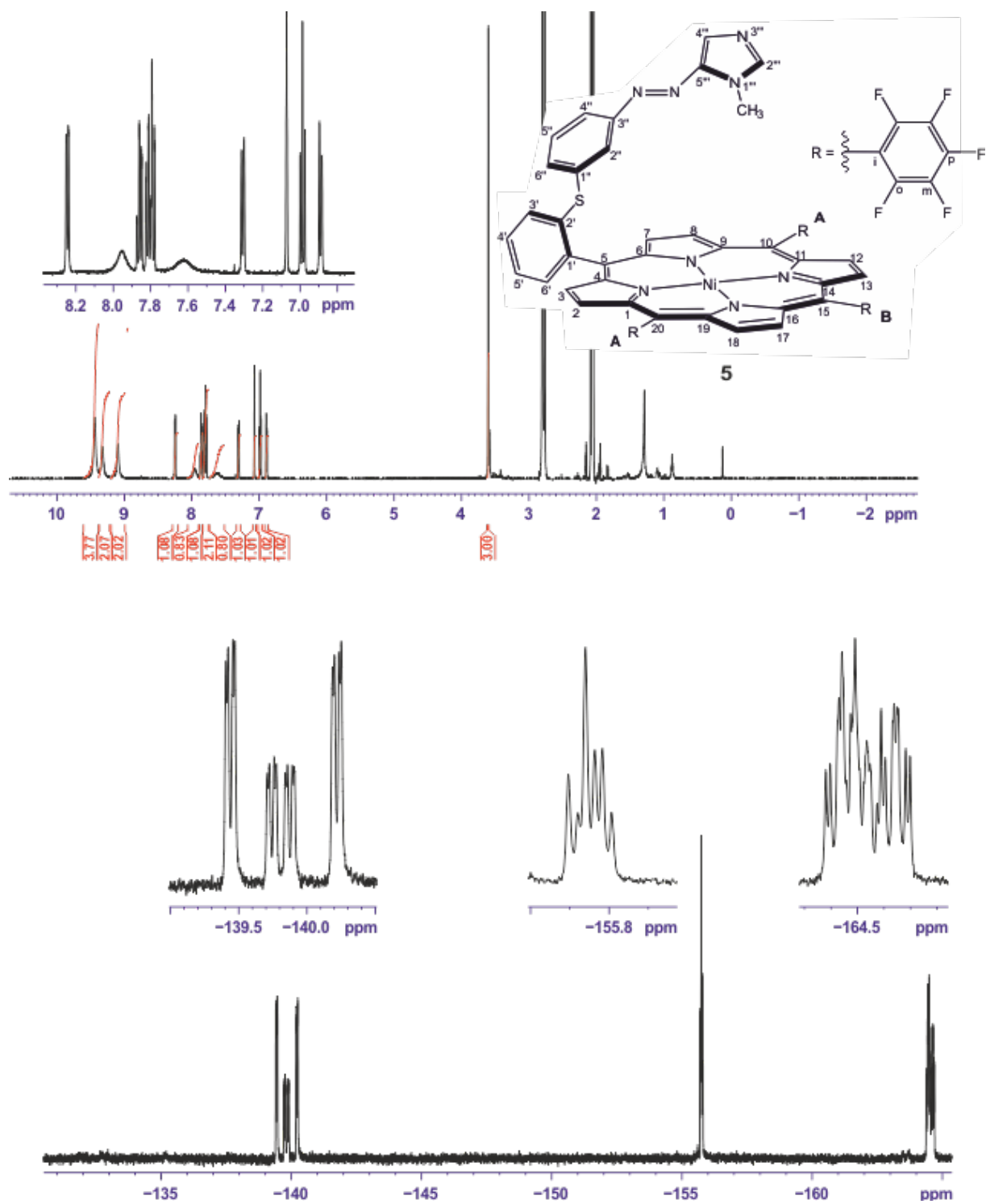


**Figure S13:**  $^1\text{H}$  NMR (top) and  $^{13}\text{C}$  NMR (bottom) spectra of 5-(3'-(2''-formylthiophenyl)phenylazo)-1-methylimidazole (**16**). Spectra were measured in dichloromethane- $\text{d}_2$  at 300 K.





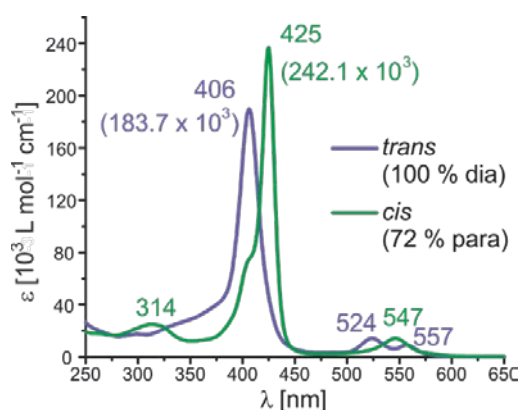
**Figure S14:**  $^1\text{H}$  NMR (top) and  $^{19}\text{F}$  NMR (bottom) spectra of metal-free biphenyl thioether record player (mf-5). Spectra were measured in acetone- $d_6$  at 300 K.



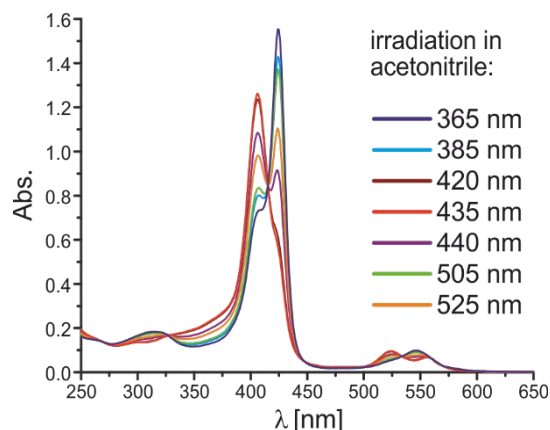
**Figure S15:**  $^1\text{H}$  NMR (top) and  $^{19}\text{F}$  NMR (bottom) spectra of biphenyl thioether record player (**5**). Spectra were measured in acetone- $\text{d}_6$  at 300 K.

### III.4 UV-vis spectra and UV-vis switching experiments.

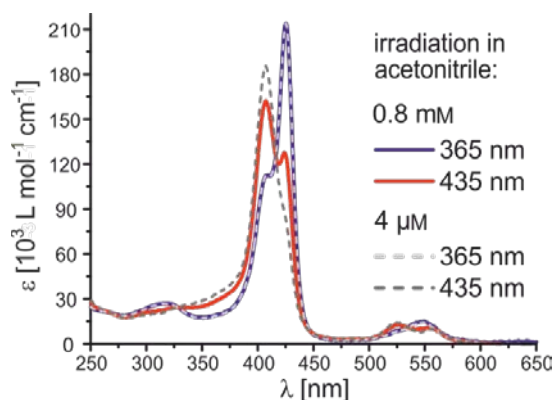
#### III.4.1 UV-vis spectra and switching experiments of biphenyl record player (**4**).



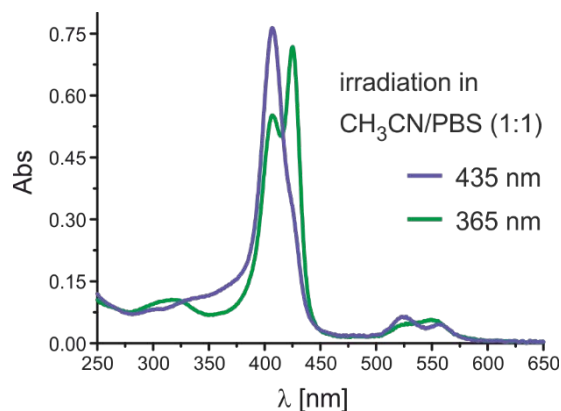
**Figure S16:** Extinction coefficients of *trans*-**4** (red) and *cis*-**4** (blue) in acetonitrile. The extinction coefficients of pure *trans*-**4** were measured after storage in the dark at 40 °C for 2 weeks. The extinction coefficients of *cis*-**4** were determined by subtracting the absorption of residual *trans*-**4** (15%) from the PSS-365 solutions.



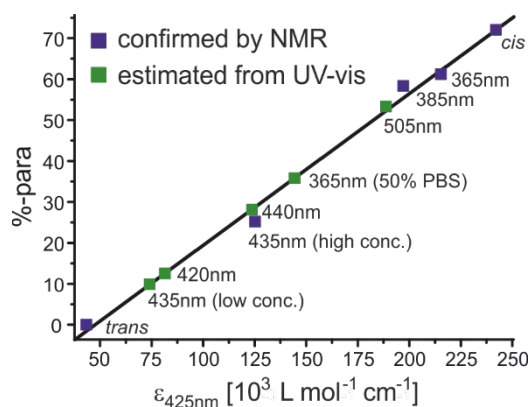
**Figure S17:** Switching experiments of a 7  $\mu\text{M}$  solution of **4** in acetonitrile (irradiation time: > 1 min). *Trans*→*cis* isomerization is most effective with 365 nm, followed by 385 nm and 505 nm. Back isomerization (*cis*→*trans*) is achieved by irradiation with 435 nm or 420 nm.



**Figure S18:** Concentration dependency of photostationary states (365 nm and 435 nm) of **4**. *Cis*→*trans* isomerization with 435 nm is reduced at higher concentrations whereas *trans*→*cis* isomerization with 365 nm remains unaffected (irradiation times: > 30 min).

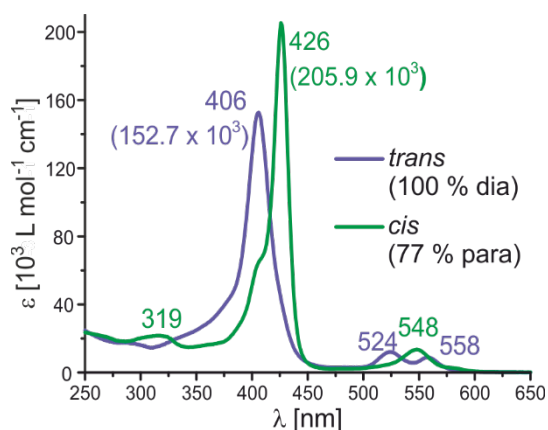


**Figure S19:** Switching experiments of a 4  $\mu\text{M}$  solution of **4** in acetonitrile/PBS (pH 7.4) (1:1). Intramolecular coordination of *cis*-**4** is reduced in comparison to the measurements in pure acetonitrile (irradiation time: > 1 min).

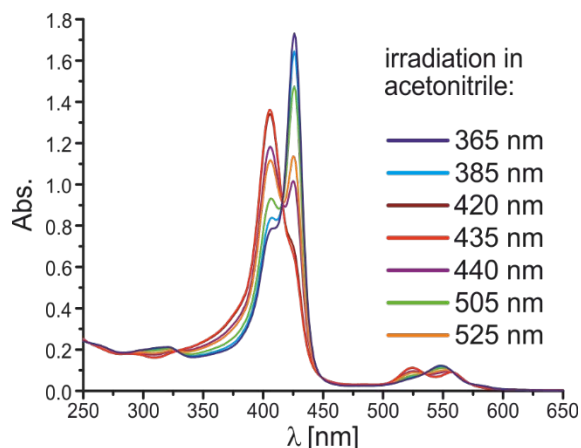


**Figure S20:** Amount of paramagnetic species (%-para) of **4** in correlation to the UV-vis extinction ( $\epsilon_{425\text{nm}}$ ) at 426 nm (Soret band of the paramagnetic species). A linear relationship between %-para and  $\epsilon_{426\text{nm}}$  allows the estimation of %-para for samples which are not measurable with NMR.

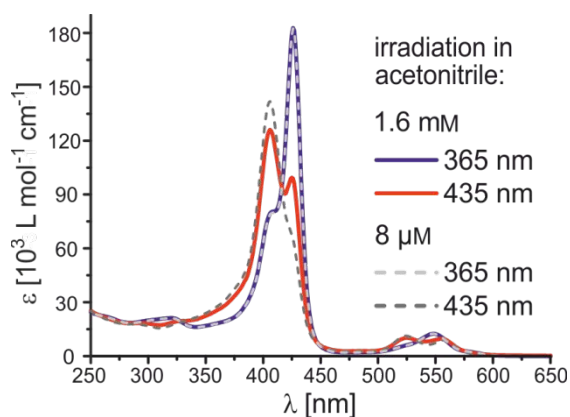
### III.4.2 UV-vis spectra and switching experiments of biphenyl thioether record player (**5**).



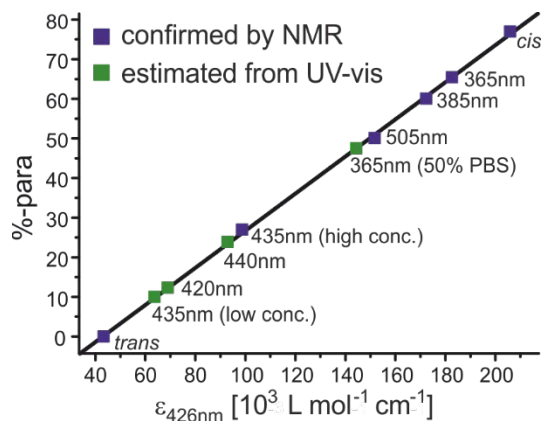
**Figure S21:** Extinction coefficients of *trans*-**5** (red) and *cis*-**5** (blue) in acetonitrile. The extinction coefficients of pure *trans*-**5** were measured after storage in the dark at 40 °C for 2 weeks. The extinction coefficients of *cis*-**5** were determined by subtracting the absorption of residual *trans*-**5** (15%) from the PSS-365 solutions.



**Figure S22:** Switching experiments of a 10  $\mu\text{M}$  solution of **5** in acetonitrile (irradiation time: > 1 min). *Trans*→*cis* isomerization is most effective with 365 nm, followed by 385 nm and 505 nm. Back isomerization (*cis*→*trans*) is achieved by irradiation with 435 nm or 420 nm.

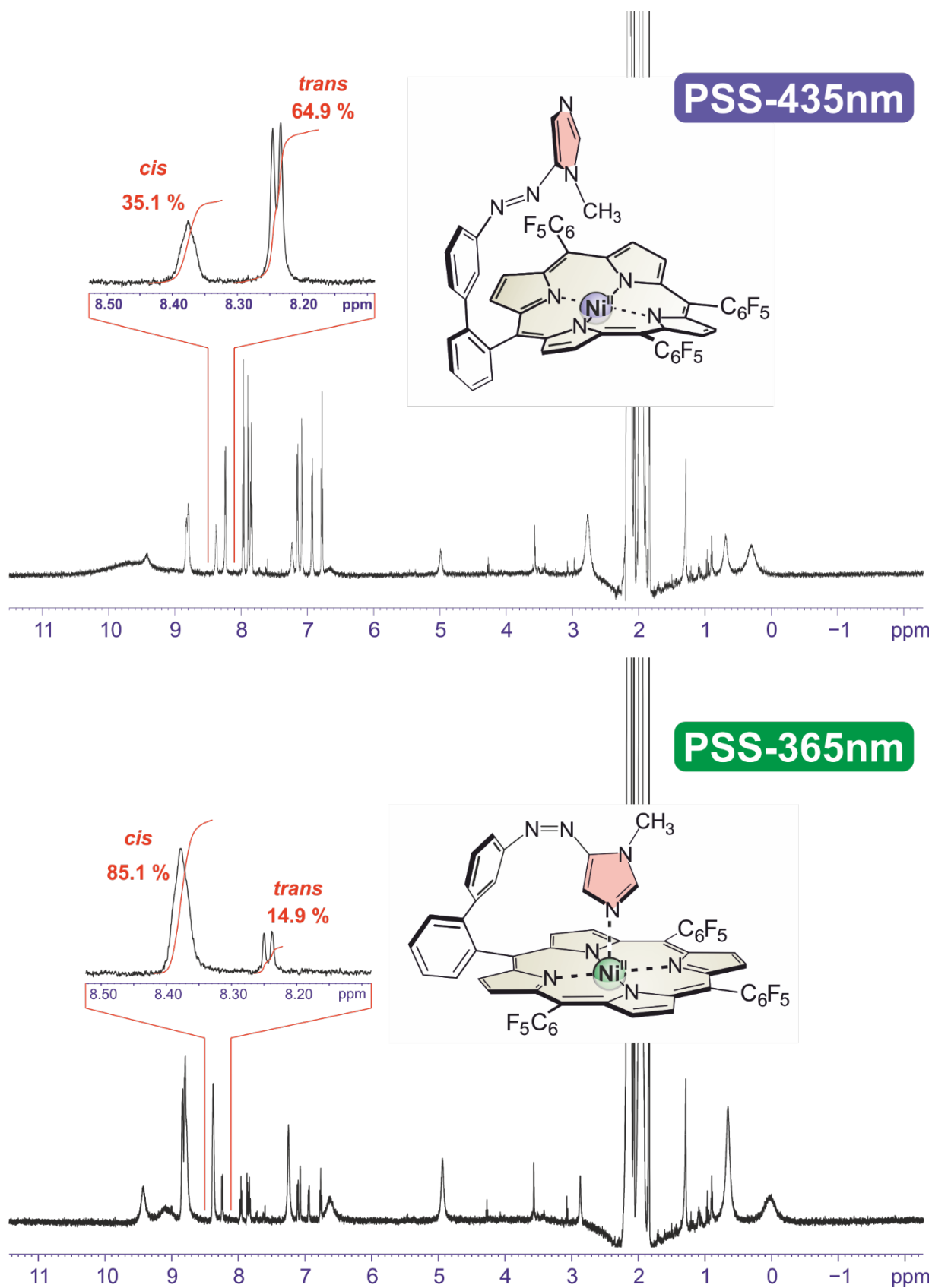


**Figure S23:** Concentration dependency of photostationary states (365 nm and 435 nm) of **5**. *Cis*→*trans* isomerization with 435 nm is reduced at higher concentrations whereas *trans*→*cis* isomerization with 365 nm remains unaffected (irradiation time: > 30 min).

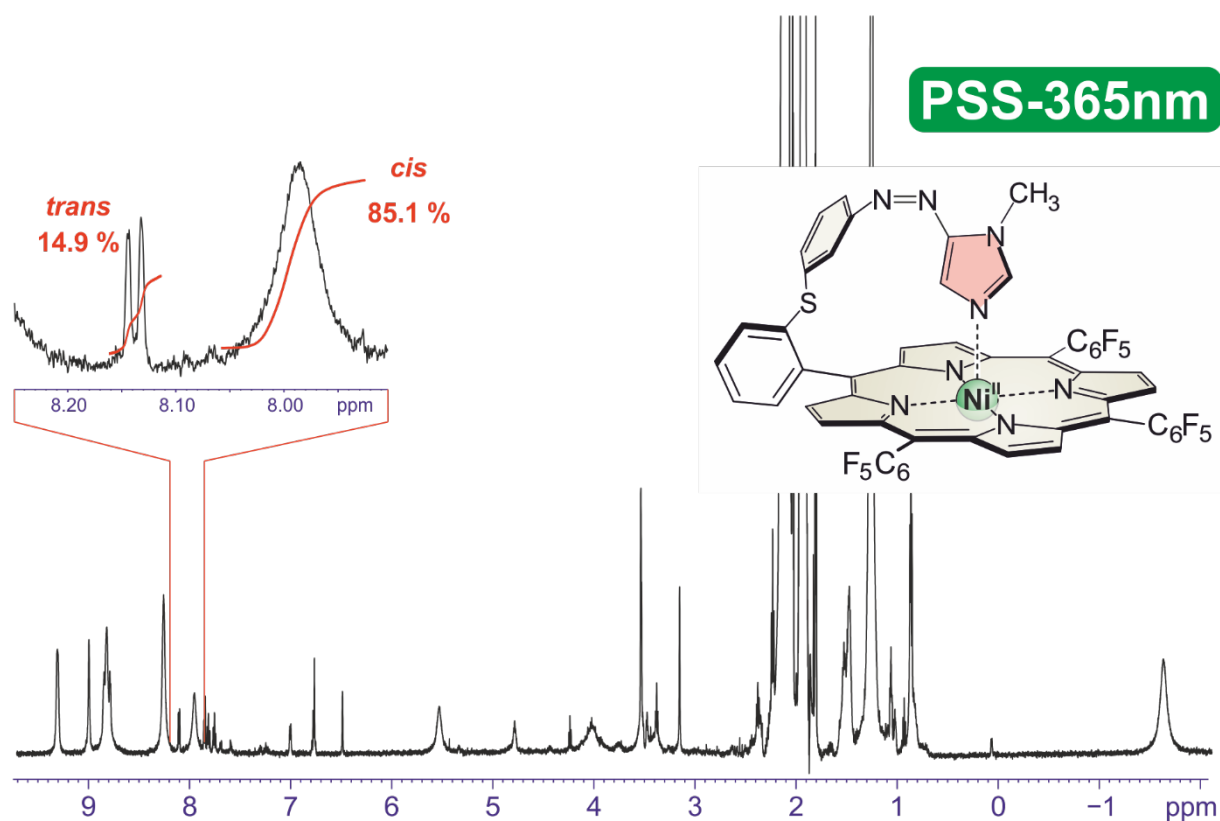
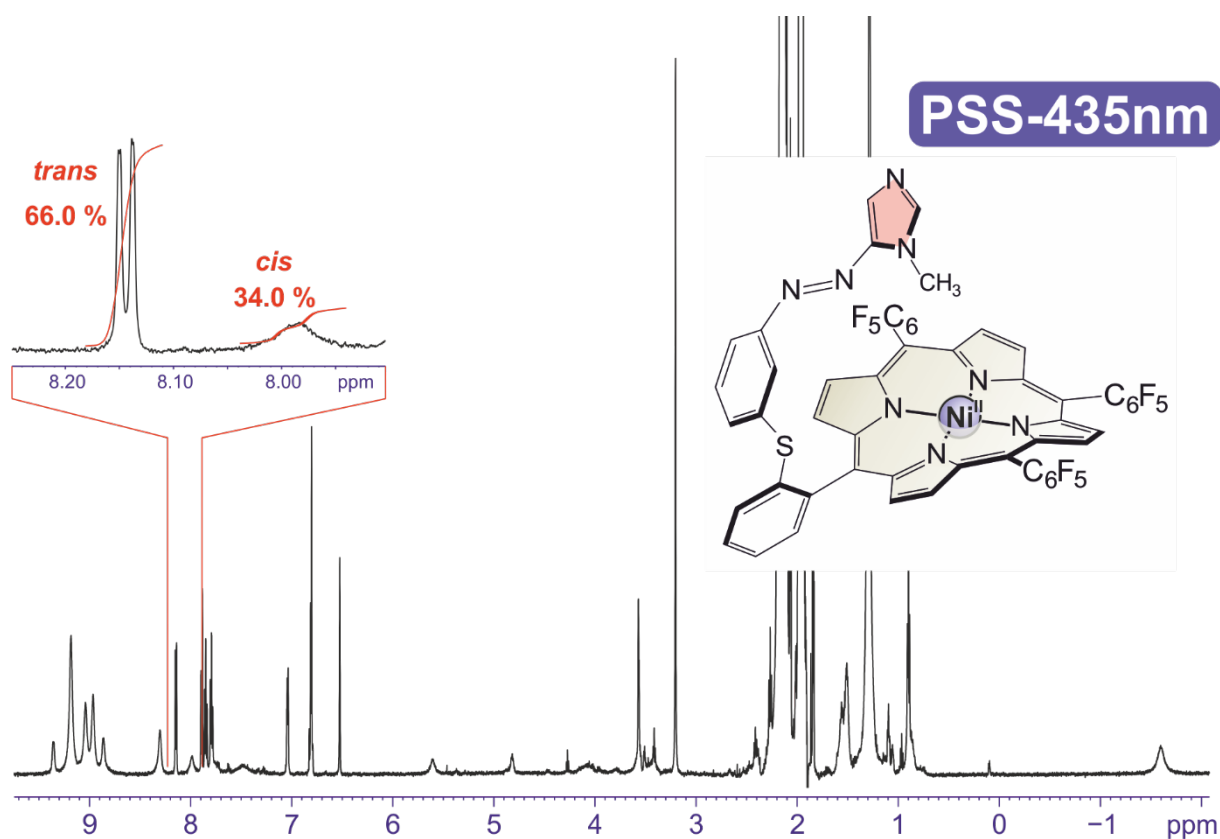


**Figure S24:** Amount of paramagnetic species (%-para) of **5** in correlation to the UV-vis extinction ( $\epsilon_{426\text{nm}}$ ) at 426 nm (Soret band of the paramagnetic species). A linear relationship between %-para and  $\epsilon_{426\text{nm}}$  allows the estimation of %-para for samples which are not measurable with NMR.

### III.5 NMR switching experiments.

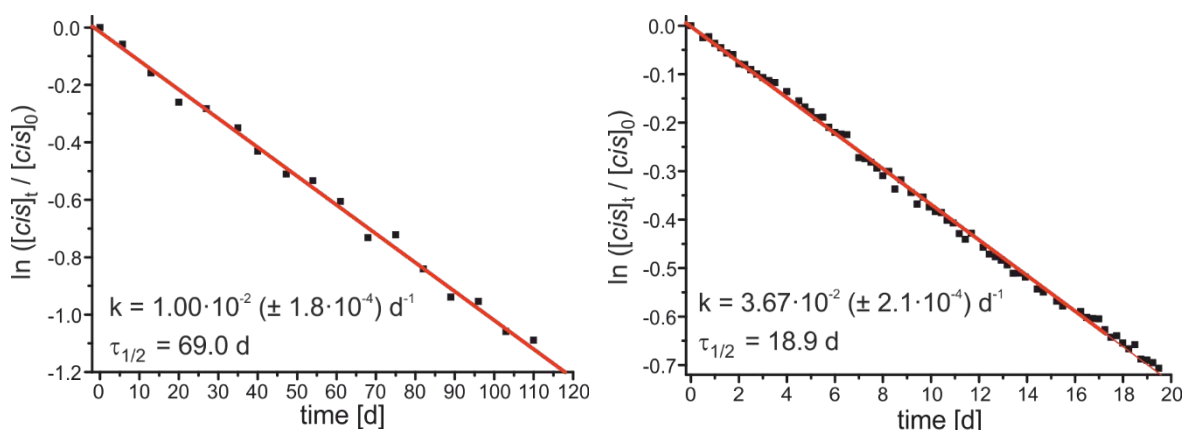


**Figure S25:**  $^1\text{H}$  NMR spectra of biphenyl record player (**4**) upon irradiation with 435 nm (top) and 365 nm (bottom). The predominant species of each PSS is shown as molecular structure. Spectra were measured in acetonitrile- $d_3$  at 300 K.

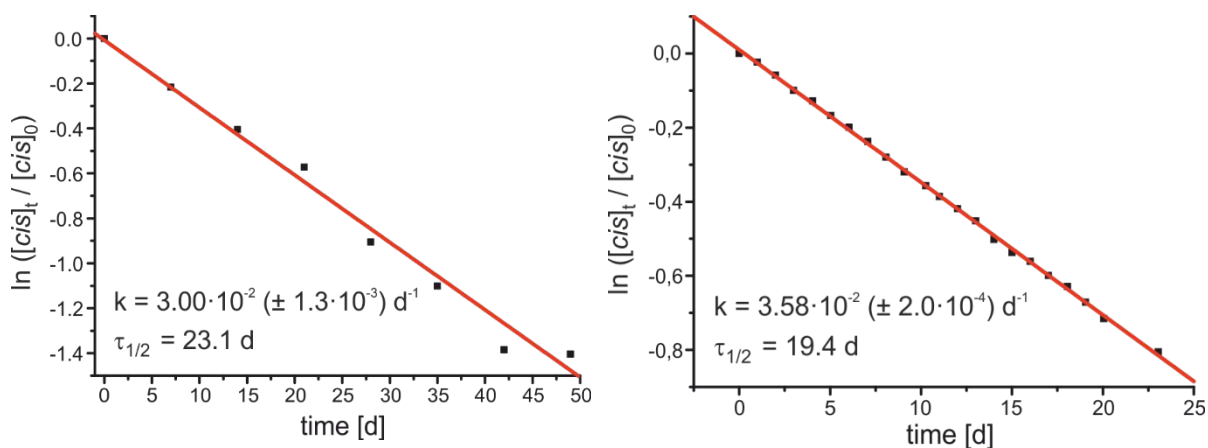


**Figure S26:**  $^1\text{H}$  NMR spectra of biphenyl record player (**5**) upon irradiation with 435 nm (top) and 365 nm (bottom). The predominant species of each PSS is shown as molecular structure. Spectra were measured in acetonitrile- $d_3$  at 300 K.

### III.6 Thermal half-lives of *cis*-4 and *cis*-5 and of tonearms *cis*-13 and *cis*-16.



**Figure S27:** First order kinetics plot for the thermal reversion of *cis*-biphenyl **4** (left) and of the respective *cis*-biphenyl tonearm **13** (right) in DMSO- $d_6$  at 25 °C.

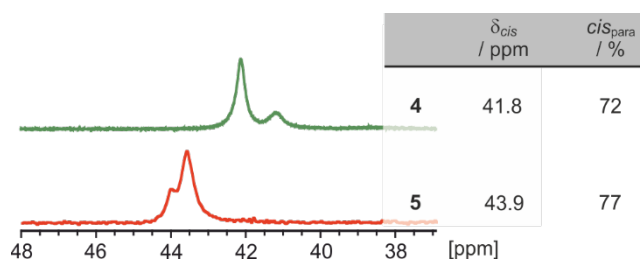


**Figure S28:** First order kinetics plot for the thermal reversion of *cis*-biphenyl thioether **5** (left) and of the respective *cis*-biphenyl thioether tonearm **16** (right) in DMSO- $d_6$  at 25 °C.

### III.7 Intramolecular coordination in *cis* record players 4 and 5.

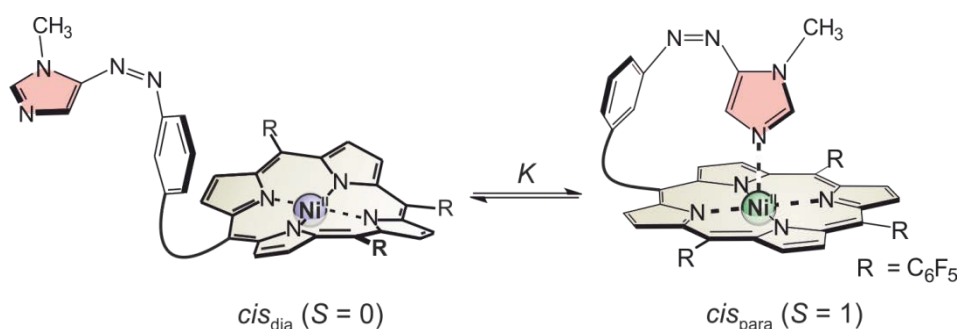
As we described earlier the ratio of the paramagnetic *cis*-species can easily be derived from the NMR shift ( $\delta$ ) of the pyrrole protons of the porphyrin system.<sup>7,8</sup> In a diamagnetic, square planar coordination sphere the pyrrole protons signals appear at 9 ppm ( $\delta_{\text{dia}}$ ) and are shifted to ca. 54.5 ppm ( $\delta_{\text{para}}$ ) in the paramagnetic, octahedral complex with two additional axial ligands (at 300 K). Since the coordination/de-coordination of axial ligands is fast on nmr time scale only the time-averaged pyrrole shift is observed which represents the respective equilibrium between both magnetic species (see figure S29). The ratio of paramagnetic *cis* species ( $cis_{\text{para}}$ ) correlates linearly with the time-averaged *cis* pyrrole shift ( $\delta_{\text{cis}}$ ) following equation S1.

$$cis_{\text{para}} = \frac{\delta_{\text{cis}} - \delta_{\text{dia}}}{\delta_{\text{para}} - \delta_{\text{dia}}} \quad (\text{S1})$$



**Figure S29:** Averaged pyrrole protons shifts ( $\delta_{\text{cis}}$ ) of *cis*-4 and *cis*-5 in acetonitrile- $d_3$  at 300 K. The ratios ( $cis_{\text{para}}$ ) of paramagnetic *cis* species correlate linearly with  $\delta_{\text{cis}}$  following equation S1.

To determine the thermodynamic parameters  $\Delta H$  and  $\Delta S$  of the coordination event in *cis* record players 4 and 5 (see figure S30) the respective association constant ( $K$ ) was measured as a function of temperature in acetonitrile- $d_3$  (see tables S3 and S4).  $K$  can be calculated from the pyrrole protons NMR shifts of the *cis* isomer ( $\delta_{\text{cis}}$ ) of the record player molecule (see equation S2).<sup>8</sup> The maximum pyrrole protons shifts ( $\delta_{\text{para}}$ ) were measured by an analogous experiment in pure pyridine- $d_5$  for each temperature. The thermodynamic parameters  $\Delta H$  and  $\Delta S$  were then obtained by Gibbs free enthalpy plots (see equation S3, figures S31 and S32).



**Figure S30:** Equilibrium between the magnetic conformers  $cis_{\text{dia}}$  and  $cis_{\text{para}}$  of imidazole “record player” molecules.

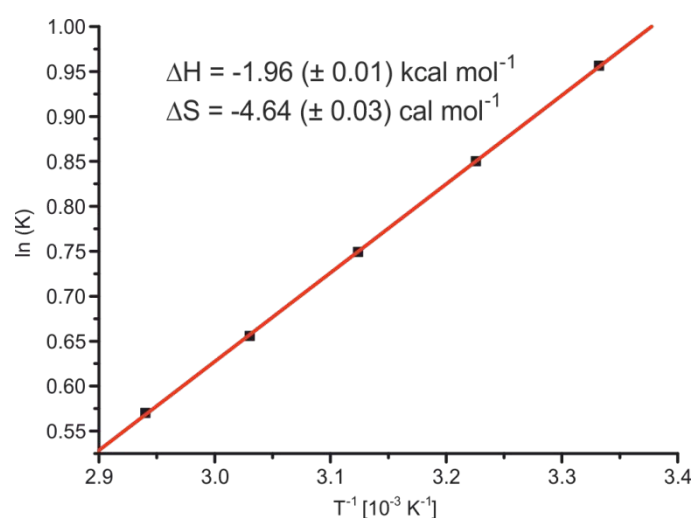
$$K = \frac{cis_{\text{para}}}{cis_{\text{dia}}} = \frac{\delta_{\text{cis}} - \delta_{\text{dia}}}{\delta_{\text{para}} - \delta_{\text{cis}}} \quad (\text{S2})$$

$$\Delta G = \Delta H - T\Delta S = -RT \ln(K) \quad (\text{S3})$$



**Table S3.** Determination of intramolecular association constants of biphenyl record player (**4**) in acetonitrile-d<sub>3</sub> from *cis*-pyrrole proton shifts ( $\delta_{cis}$ ). The respective maximum shift ( $\delta_{max}$ ) was found by measurement in pure pyridine-d<sub>5</sub>.

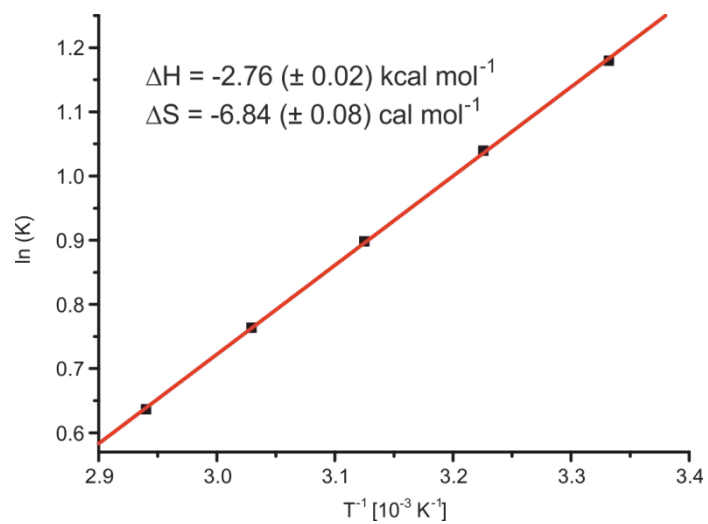
T / K	T <sup>-1</sup> / K <sup>-1</sup>	$\delta_{cis}$ / ppm	$\delta_{max}$ / ppm	<i>cis</i> -4 <sub>para</sub> / %	<i>cis</i> -4 <sub>dia</sub> / %	K	ln(K)
300.1	0.00333	41.81	54.42	72.2	27.8	2.6019	0.9562
310.0	0.00323	39.65	52.75	70.1	29.9	2.3397	0.8500
320.1	0.00312	37.70	51.27	67.9	32.1	2.1150	0.7490
330.0	0.00303	36.07	50.12	65.8	34.2	1.9267	0.6558
340.1	0.00294	34.48	48.89	63.9	36.1	1.7682	0.5700



**Figure S31:** Gibbs free enthalpy plot for the determination of thermodynamic parameters  $\Delta H$  and  $\Delta S$  for the coordination event in *cis*-biphenyl rp (**4**).

**Table S4.** Determination of intramolecular association constants of biphenyl thioether record player (**5**) in acetonitrile-d<sub>3</sub> from *cis*-pyrrole proton shifts ( $\delta_{cis}$ ). The respective maximum shift ( $\delta_{max}$ ) was found by measurement in pure pyridine-d<sub>5</sub>.

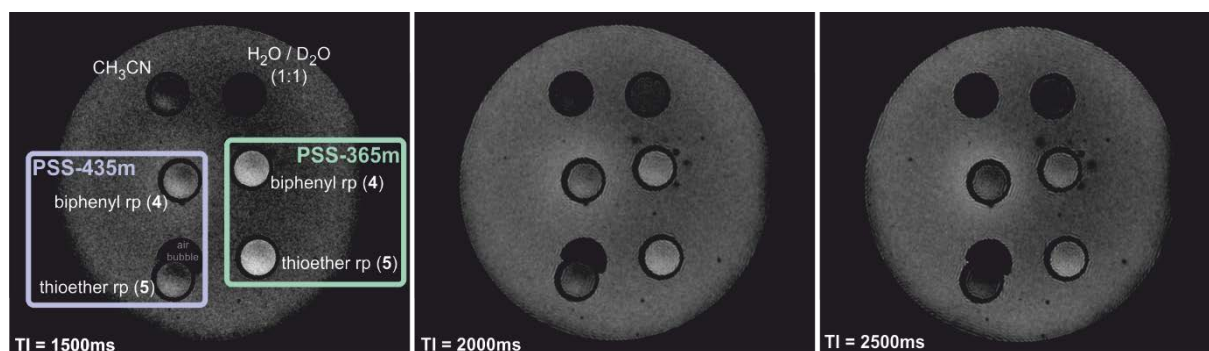
T / K	T <sup>-1</sup> / K <sup>-1</sup>	$\delta_{cis}$ / ppm	$\delta_{max}$ / ppm	<i>cis</i> -5 <sub>para</sub> / %	<i>cis</i> -5 <sub>dia</sub> / %	K	ln(K)
300.1	0.00333	43.87	54.59	76.5	23.5	3.2528	1.1795
310.0	0.00323	41.46	52.94	73.9	26.1	2.8275	1.0394
320.0	0.00313	39.17	51.46	71.1	28.9	2.4548	0.8981
330.1	0.00303	36.96	49.99	68.2	31.8	2.1458	0.7635
340.1	0.00294	35.06	48.85	65.4	34.6	1.8898	0.6365



**Figure S32:** Gibbs free enthalpy plot for the determination of thermodynamic parameters  $\Delta H$  and  $\Delta S$  for the coordination event in *cis*-biphenyl thioether rp (**5**).

### III.8 MRI measurements with record players 4 and 5.

MRI experiments were performed on a 7T small animal MRI system (ClinScan 70/30 USR by co. Bruker Biospin, Ettlingen, Germany). Samples of record players **4** and **5** were irradiated with the respective wavelengths (435nm or 365nm, irradiation time > 2h) and transferred into NMR tubes which were immobilized in an agarose gel phantom (1 wt.-% agarose in H<sub>2</sub>O/D<sub>2</sub>O, 1:1). Acetonitrile and H<sub>2</sub>O/D<sub>2</sub>O (1:1) in NMR tubes were placed into the phantom as well for reference measurements. We used H<sub>2</sub>O/D<sub>2</sub>O (1:1) instead of pure H<sub>2</sub>O to adjust the proton density and therefore the signal strength of the phantom and reference to that of acetonitrile. Measurements were performed with an inversion recovery gradient echo sequence (scan parameters: acquisition type = 2D, TE = 6.3 ms, TR = 3000 ms, flip angle = 90°, FoV = 39 mm<sup>2</sup>, matrix = 208×208 px, slice thickness = 2 mm, BW = 775 Hz/px, averages = 5) with varying inversion times (TI = 1500 ms, 2000 ms, 2500 ms). The obtained MR images are shown in figure S33. The signal intensities of all samples were quantified within a 0.1cm<sup>2</sup> area in the centre of the respective sample spot and were referenced to acetonitrile (signal intensity of acetonitrile = 100 % for every TI, see table S5). The thioether record player (**5**) allows switching of the signal intensity from 115 % (PSS-435nm) to 139-133 % (PSS-365nm) with respect to pure acetonitrile and therefore provides an MRI contrast switching efficiency of 24-18 % depending on the inversion time (TI). The biphenyl record player (**4**) switches the signal intensity from 122-123 % (PSS-435nm) to 133-128 % (PSS-365nm) and therefore provides an MRI contrast switching efficiency of 11-5 %. The highest contrast switching efficiencies (24 % for **5**, 11 % for **4**) were obtained for TI = 1500 ms.



**Figure S33:** Magnetic resonance images (gradient echo sequence) of record players **4** (location within phantom: middle) and **5** (bottom) in both switching states, plus acetonitrile (top left) and H<sub>2</sub>O/D<sub>2</sub>O (1:1) (top right) as references with three different inversion times (left image: 1500 ms, middle: 2000 ms, right: 2500 ms). The samples were placed in an agarose gel phantom (1 wt.-% in H<sub>2</sub>O/D<sub>2</sub>O, 1:1).

**Table S5:** Inversion time (TI) dependent signal intensities (arbitrary units) within a 0.1cm<sup>2</sup> area in the center of the respective sample spot. For a better comparability the signal intensities were referenced to 100 % signal intensity of the acetonitrile reference.

TI / ms	Signal intensity / a.u.			signal intensity / %		
	1500	2000	2500	1500	2000	2500
acetonitrile	52.21	92.18	128.86	100	100	100
H <sub>2</sub> O / D <sub>2</sub> O (1:1)	47.77	98.94	145.40	91	107	113
<b>4</b> (PSS-435nm)	63.51	113.34	158.51	122	123	123
<b>4</b> (PSS-365nm)	69.69	119.92	164.34	133	130	128
<b>5</b> (PSS-435nm)	59.90	105.96	148.67	115	115	115
<b>5</b> (PSS-365nm)	72.34	124.38	170.99	139	135	133
noise	2.42	2.62	2.66	4.6	2.8	2.1

#### IV. Literature

- 1 S. Thies, H. Sell, C. Bornholdt, C. Schütt, F. Köhler, F. Tuczek and R. Herges, *Chem. Eur. J.*, 2012, **18**, 16358–16368.
- 2 C. Schütt, G. Heitmann, T. Wendler, B. Krahwinkel and R. Herges, *J. Org. Chem.*, 2016, **81**, 1206–1215.
- 3 *Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs).*
- 4 *TURBOMOLE V6.6 2014, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.*
- 5 M. F. W. Dunker, E. B. Starkey and G. L. Jenkins, *Journal of the American Chemical Society*, 1936, **58**, 2308–2309.
- 6 D. J. Chadwick and R. I. Ngochindo, *J. Chem. Soc. Perkin Trans. 1*, 1984, 481–486.
- 7 S. Thies, H. Sell, C. Schütt, C. Bornholdt, C. Näther, F. Tuczek and R. Herges, *J. Am. Chem. Soc.*, 2011, **133**, 16243–16250.
- 8 M. Dommaschk, C. Schütt, S. Venkataramani, U. Jana, C. Näther, F. D. Sönnichsen and R. Herges, *Dalton Trans.*, 2014, **43**, 17395–17405.