Electronic Supplementary Material (ESI) for Dalton Transactions

ELECTRONIC SUPPORTING INFORMATION

Table S1. Crystal Data.

	trans-$[PtCl_2(EtCN)_2]$	*trans*-**1**	*trans*-**2**	**4**	**5**
empirical formula	$C_6H_{10}Cl_4N_2Pt$	$C_{12}H_{12}Cl_4N_4O_4Pt$	$C_{12}H_{16}Cl_4N_4O_6Pt$	$C_{12}H_{15}C_{l4}N_4O_2Pt$	$C_{18}H_{22}Cl_4N_6O_4Pt$
fw	447.05	613.15	649.17	584.17	723.31
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)
λ(Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	5.9682(2)	9.6189(2) Å	5.8898(2)	15.0633(8)	6.59770(10)
b (Å)	8.8714(5)	8.7091(2) Å	18.3306(7)	8.5041(4)	7.9991(2)
c (Å)	11.9058(6)	11.1019(3)	8.9748(3)	14.8670(5)	11.9255(2)
α (deg)	90	90	90	90	73.9520(10)
β (deg)	103.931(3)	114.029(2)	98.3540(10)	104.787(3)	82.1570(10)
γ (deg)	90	90	90	90	75.8260(10)
V ($Å^3$)	611.83(5)	849.43(4)	958.67(6)	1841.39(14)	584.84(2)
Z	2	2	2	4	1
ρ_{calc} (Mg/m^3)	2.427	2.397	2.235	2.107	2.054
μ(Mo Kα) (mm^{-1})	12.300	8.916	7.913	8.212	6.494
No. reflns.	11915	27697	21370	31328	15751
Unique reflns.	1570	2477	3256	3235	4457
GOOF (F^2)	1.097	1.038	1.293	1.134	1.034
R_{int}	0.0347	0.0351	0.0373	0.0608	0.0342
R1[a] ($I \geq 2\sigma$)	0.0221	0.0162	0.0273	0.0445	0.0206
wR2[b] ($I \geq 2\sigma$)	0.0521	0.0345	0.0556	0.1015	0.0408

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Table S2. Crystal Data.

	6	**8**	**10**	**11**
empirical formula	$C_{12}H_{16}Cl_4N_4O_2Pt$	$C_{18}H_{22}Cl_3N_6O_5Pt$	$C_9H_{17}Cl_4N_3O_5Pt$	$C_{13}H_{20}Cl_4N_4O_3Pt$
fw	585.18	703.86	584.15	617.22
temp (K)	100(2)	100(2)	100(2)	100(2)
λ(Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	Trigonal	Monoclinic	Triclinic	triclinic
space group	$P3_2$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.8439(3)	15.9646(7)	6.7248(7)	6.59850(10)
b (Å)	7.8439(3)	11.9025(5)	8.0570(5)	7.95740(10)
c (Å)	25.4480(7)	13.2546(6)	16.8733(13)	19.0913(4)
α (deg)	90	90	79.899(6)	87.0580(10)
β (deg)	90	93.4980(10)	81.282(7)	86.2180(10)
γ (deg)	120	90	72.243(6)	74.5110(10)
V (Å^3)	1355.96(8)	2513.93(19)	852.47(12)	963.32(3)
Z	3	4	2	2
ρ_{calc} (Mg/m^3)	2.150	1.860	2.276	2.128
μ(Mo Kα) (mm^{-1})	8.364	5.940	8.879	7.858
No. reflns.	8574	19613	16984	18919
Unique reflns.	2958	5771	5811	5860
GOOF (F^2)	1.050	1.067	1.051	1.081
R_{int}	0.0442	0.0355	0.0309	0.0436
R1[a] ($I \geq 2\sigma$)	0.0230	0.0319	0.0274	0.0349
wR2[b] ($I \geq 2\sigma$)	0.0506	0.0730	0.0475	0.0603

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

The structure of *trans*-[$PtCl_4(EtCN)_2$]

Despite the fact that the starting *trans*-[$PtCl_4(EtCN)_2$] complex is widely used in metal-mediated syntheses, its X-ray structure is yet unknown. We succeeded in obtaining crystals of this compound, which were characterized by X-ray diffraction (**Figure S1**), indicating that the Pt–N≡C group is linear, and the Pt(1)–N(1) bond lengths [1.966(3) Å] correspond to that of *cis*- and *trans*-[$PtCl_2(EtCN)_2$] [1.94(2) Å and 1.96(2) Å, respectively]; Pt–Cl distances [2.3172(9) Å, 2.3221(9) Å] are slightly longer that of *cis*- and *trans*-[$PtCl_2(EtCN)_2$] (2.263(5) Å and 2.285(5) Å, correspondingly).[S1]

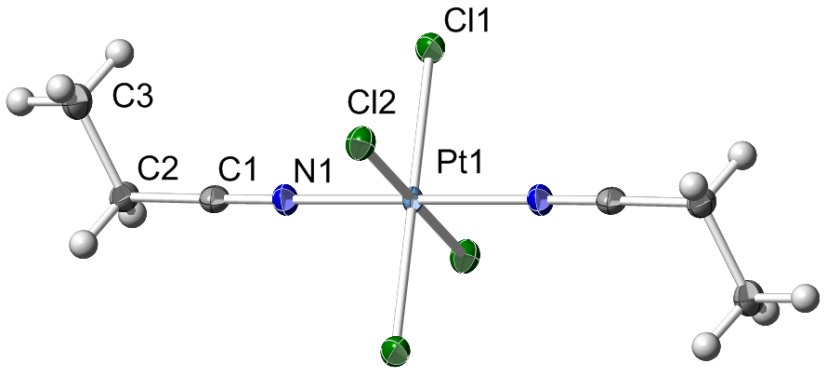

Figure S1. Molecular structure of *trans*-[$PtCl_4(EtCN)_2$] with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 1.966(3), Pt(1)–Cl(1) 2.3221(9), Pt(1)–Cl(2) 2.3172(9), N(1)–C(1) 1.127(5), N(1)–Pt(1)–Cl(2) 89.21(10), Cl(2)–Pt(1)–Cl(1) 89.77(3), C(1)–N(1)–Pt(1) 176.0(3).

The structures of *trans*-1, *trans*-2, 6, 10, and 11

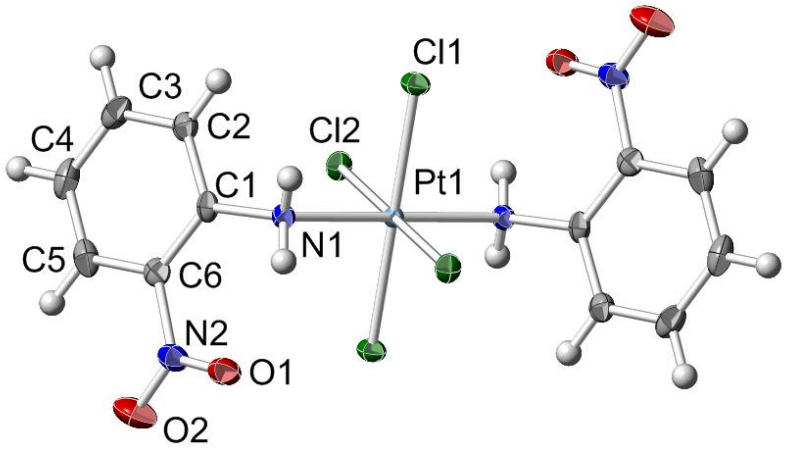

Figure S2. Molecular structure of *trans*-**1** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 2.0856(19), Pt(1)–Cl(1) 2.3112(5), Pt(1)–Cl(2) 2.3153(6), N(1)–C(1) 1.433(3), N(2)–C(6) 1.462(3), N(1)–Pt(1)–Cl(1) 92.55(6), N(1)–Pt(1)–Cl(2) 83.11(6), Cl(1)–Pt(1)–Cl(2) 90.41(2).

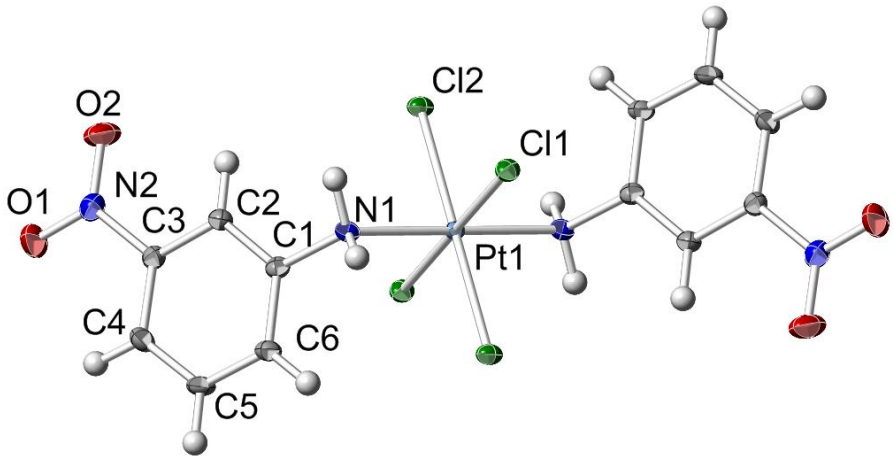

Figure S3. Molecular structure of *trans*-**2** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 2.082(3), Pt(1)–Cl(1) 2.3087(7), Pt(1)–Cl(2) 2.3085(7), N(1)–C(1) 1.436(4), N(2)–C(3) 1.469(4), N(1)–Pt(1)–Cl(1) 95.09(8), N(1)–Pt(1)–Cl(2) 89.29(8), Cl(1)–Pt(1)–Cl(2) 89.15(3)

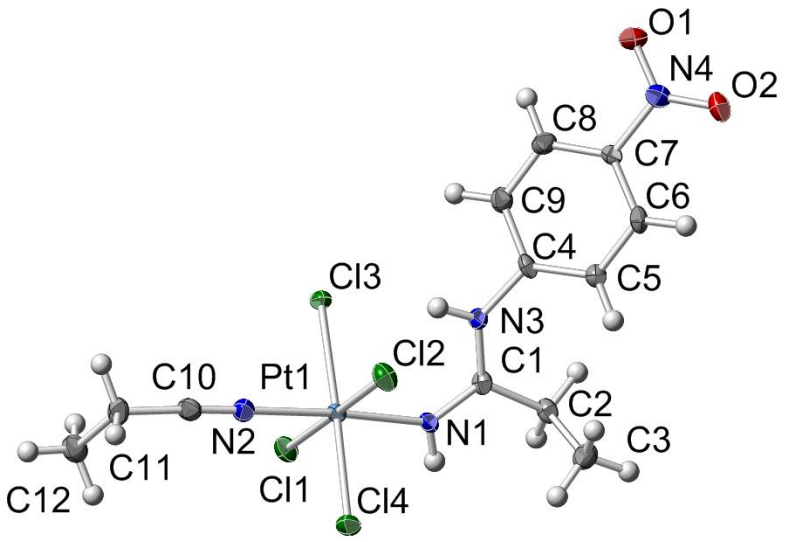

Figure S4. Molecular structure of **6** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 2.009(5), Pt(1)–N(2) 2.005(5), Pt(1)–Cl(1) 2.3202(15), Pt(1)–Cl(2) 2.3205(15), Pt(1)–Cl(3) 2.3297(14), Pt(1)–Cl(4) 2.3064(15), N(1)–C(1) 1.303(7), N(2)–C(10) 1.128(8), N(3)–C(1) 1.340(8), N(2)–Pt(1)–N(1) 176.2(2), Cl(1)–Pt(1)–Cl(2) 178.93(6), Cl(4)–Pt(1)–Cl(3) 178.28(6).

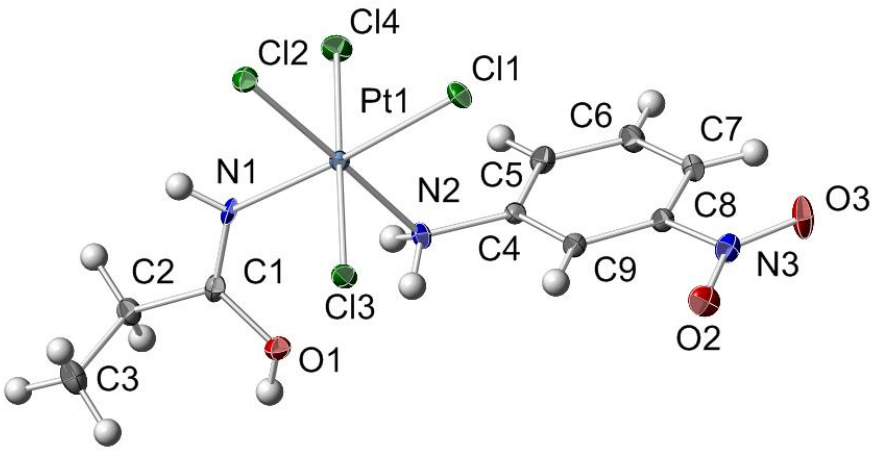

Figure S5. Molecular structure of **10** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 2.031(2), Pt(1)–N(2) 2.114(2), Pt(1)–Cl(1) 2.3227(7), Pt(1)–Cl(2) 2.3200(8), Pt(1)–Cl(3) 2.3276(7), Pt(1)–Cl(4) 2.3095(8), O(1)–C(1) 1.311(4), N(1)–Pt(1)–N(2) 90.28(9), Cl(2)–Pt(1)–Cl(1) 88.69(3), Cl(4)–Pt(1)–Cl(3) 178.53(3), C(1)–N(1)–Pt(1) 130.7(2), C(4)–N(2)–Pt(1) 119.80(18), N(1)–C(1)–O(1)118.4(3), N(1)–C(1)–C(2) 122.4(3).

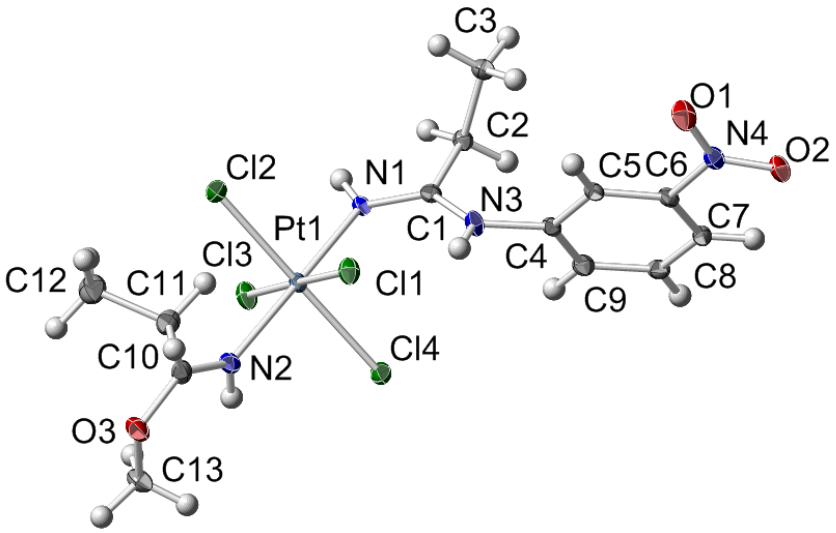

Figure S6. Molecular structure of **11** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 2.017(3), Pt(1)–N(2) 2.034(3), Pt(1)–Cl(1) 2.3249(10), Pt(1)–Cl(2) 2.3089(11), Pt(1)–Cl(3) 2.3118(10), Pt(1)–Cl(4) 2.3217(11), N(1)–C(1) 1.299(5), N(2)–C(10) 1.291(5), N(3)–C(1) 1.343(5), O(3)–C(10) 1.334(5), N(1)–Pt(1)–N(2) 172.49(14), N(1)–Pt(1)–Cl(2) 87.01(10), N(2)–Pt(1)–Cl(2) 94.25(10).

Substitution of the nitrile in *trans*-[$PtCl_4(EtCN)_2$] with *o*-, *m*-, and *p*-NAs

1:1 ratio. A ratio between *cis*- and *trans*-isomers (2:3, 1:3, and 1:2 for **1**, **2**, and **3**, correspondingly) was determined by ^{1}H NMR integration. All *cis*-[$PtCl_4(NA)_2$] (*cis*-**1**–**3**) in the mixtures of isomers were completely isomerized to the corresponding *trans*-isomers (*trans*-**1**–**3**) in the solid state (1d, 50 °C) or in solution (1d, acetone, 40 °C); the isomerization was monitored by TLC, ^{1}H and ^{13}C{^{1}H} NMR.

1:2 ratio. A ratio between *cis*- and *trans*-isomers (3:5, 1:3, and 2:3 for **1**, **2**, and **3**, correspondingly) was determined by ^{1}H NMR integration. All *cis*-[$PtCl_4(NA)_2$] (*cis*-**1**–**3**) were completely isomerized to the corresponding *trans*-isomers (*trans*-**1**–**3**) in the solid state (1d, 50 °C) or in solution (1d, acetone, 40 °C); the isomerization was monitored by TLC, ^{1}H and ^{13}C{^{1}H} NMR.

All obtained compounds were characterized by ESI-MS, IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopic techniques and also by C, H, and N elemental analyses. The substitution products *cis*- and *trans*-**1**–**3** have different R_f for the corresponding *cis*- and *trans*-isomer in the each pair,

which allows the distinguishing these species. *Cis/trans*-**1**–**3** exhibit satisfactory elemental analyses; in the ESI⁻-MS the typical ions are $[M - H]^-$. The IR spectra display a medium intensity bands at 3212–3168 cm^{-1}, which can be attributed to the N−H stretching vibrations. In the ^1H NMR spectra NH resonances appears as a broad singlet at 8.73–8.79 for *cis*- and *trans*-**2**,**3** and at 8.99 and 9.23 ppm for *cis*- and *trans*-**1**, such low-field signal position for the latter can be explained by formation of intramolecular hydrogen bonding with *o*-NO_2 group.

Complexes *trans*-**1** and *trans*-**2** were also characterized by X-ray diffraction (**Figures S2**–**S3**); both complexes exhibit a slightly distorted octahedral geometry with the two *trans*-*N*-donor ligands.

***cis/trans*-[$PtCl_4$($NH_2C_6H_4NO_2$-*o*)$_2$]** (*cis/trans*-**1**). Found: C, 23.39; H, 1.86; N, 9.03 (Calcd. for $C_{12}H_{12}N_4Cl_4O_4Pt$: C, 23.51; H, 1.97; N, 9.14). ESI⁻-MS, *m/z*: 610.9212; calcd for $[M - H]^-$ 610.9134. IR spectrum in KBr (selected bands, cm^{-1}): 3390 m and 3181 m ν(N−H), 3083 w ν(C−H), 1617 s and 1487 s ν(C=C_{Ar}), 1526 s ν_{asymm}(N=O), 1345 s ν_{symm}(N=O), 752 w δ(C–H_{Ar}). TLC: R_f = 0.43 (*cis*-**1**) and 0.60 (*trans*-**1**) (Me_2CO:$CHCl_3$ = 1:20, v/v). ^1H NMR spectrum in $(CD_3)_2CO$, δ: (*cis*-**1**): 8.99 (s, br, 4H, NH_2), 8.26 (d, 8.2 Hz, 2H), 7.97 (d, 8.1 Hz, 2H) (*o*- and *m*-H from Ar), 7.83 (t, 8.1 Hz, 2H), 7.67 (t, 8.1 Hz, 2H) (*m*- and *p*-H from Ar); (*trans*-**1**): 9.23 (s, br, 4H, NH_2), 8.49 (d, 4.0 Hz, 2H), 8.20 (d, 4.0 Hz, 2H) (*o*- and *m*-H from Ar), 8.05 (t, 4.0 Hz, 2H), 7.90 (t, 4.0 Hz, 2H) (*m*- and *p*-H from Ar). $^{13}C\{^1H\}$ NMR spectrum in $(CD_3)_2CO$, δ: (*cis*-**1**): 142.9, 134.1 (C_{ipso}); 132.9, 129.0, 128.8, 125.3 (C_{Ar}); (*trans*-**1**): 142.6, 134.5 (C_{ipso}); 133.5, 128.9, 128.8, 125.2 (C_{Ar}).

***cis/trans*-[$PtCl_4$($NH_2C_6H_4NO_2$-*m*)$_2$]** (*cis/trans*-**2**). Found: C, 23.47; H, 1.89; N, 9.10 (Calcd. for $C_{12}H_{12}N_4Cl_4O_4Pt$: C, 23.51; H, 1.97; N, 9.14). ESI⁻-MS, *m/z*: 610.9197; calcd for $[M - H]^-$ 610.9134. IR spectrum in KBr (selected bands, cm^{-1}): 3194 m and 3168 m ν(N−H), 3091 w ν(C−H), 1630 s ν(C=C_{Ar}), 1534 s ν_{asymm}(N=O), 1356 s ν_{symm}(N=O), 749 w δ(C–H_{Ar}). TLC: R_f= 0.40 (*cis*-**2**) and 0.61 (*trans*-**2**) (Me_2CO:$CHCl_3$ = 1:20, v/v). ^1H NMR spectrum in $(CD_3)_2CO$, δ: (*cis*-**2**): 8.75 (s, br, 4H, NH_2), 8.54 (s, 2H, *o*-H from Ar), 8.23 (d, 8.0 Hz, 2H), 7.88 (d, 8.0 Hz, 2H) (*o*- and *p*-H from Ar), 7.70 (t, 2H, 8.0 Hz, *m*-H from Ar); (*trans*-**2**): 8.76 (s, br, 4H, NH_2), 8.49 (s, 2H, *o*-H from Ar), 8.25 (d, 4.0 Hz, 2H), 7.99 (d, 4.0 Hz, 2H) (*o*- and *p*-H from Ar), 7.68 (t, 4.0 Hz, 2H, *m*-H from Ar). $^{13}C\{^1H\}$ spectrum in $(CD_3)_2CO$, δ: (*cis*-**2**): 148.8, 142.0

(C_{ipso}); 131.8, 123.5, 123.3, 120.4 (C_{Ar}); (*trans*-**2**): 144.3, 141.9 (C_{ipso}); 134.1, 129.7, 124.8, 122.4 (C_{Ar}).

***cis/trans*-[$PtCl_4$(*N*$NH_2C_6H_4NO_2$-*p*)$_2$]** (*cis/trans*-**3**). Found: C, 23.43; H, 1.92; N, 9.08 (Calcd. for $C_{12}H_{12}N_4Cl_4O_4Pt$: C, 23.51; H, 1.97; N, 9.14). ESI$^-$-MS, *m/z*: 610.9236; calcd for $[M - H]^-$ 610.9134. IR spectrum in KBr (selected bands, cm^{-1}): 3212 m and 3181 m and 3112 w ν(N−H), 3028 w ν(C−H), 1621 s ν(C=C_{Ar}), 1528 s ν_{asymm}(N=O), 1352 s ν_{symm}(N=O), 753 w δ(C–H_{Ar}). TLC: R_f = 0.41 (*cis*-**3**) and 0.60 (*trans*-**3**) (Me_2CO:$CHCl_3$ = 1:20, v/v). ^{1}H NMR spectrum ($(CD_3)_2CO$, δ): (*cis*-**3**): 8.85 (s, 4H, NH_2), 8.40 (d, 8.5 Hz, 4H), 7.94 (d, 8.5 Hz, 4H) (H from Ar); (*trans*-**3**): 8.79 (s, br, 4H, NH_2), 8.27 (d, 4.4 Hz, 4H), 7.82 (d, 4.4 Hz, 4H) (H from Ar). $^{13}C\{^1H\}$ spectrum ($(CD_3)_2CO$, δ): (*cis*-**3**): 146.8, 146.6 (C_{ipso}); 126.6, 125.3 (C_{Ar}); (*trans*-**3**): 147.2, 146.2 (C_{ipso}), 126.5, 124.2 (C_{Ar}).

S1 P. Svensson, K. Lövqvist, V.Yu. Kukushkin, Å. Oskarsson, *Acta Chem. Scand.*, 1995, 49, 72–75.