

Electronic supplementary information for:

**Redox-driven ligand ejection in nickel(II)-
diiminosemiquinonate radical complexes**

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General

Materials and methods: All operations were performed under anaerobic conditions under a pure argon atmosphere using standard Schlenk techniques. Anhydrous toluene and triethylamine were distilled over CaH_2 under an argon atmosphere prior to use. Anhydrous dichloromethane, acetonitrile, methanol were purchased from Acros. High-pressure reactions were carried out using a 0.6 L Parr Instrument stainless steel vessel. 3,5-Di-*tert*-butyl-2-nitrobromobenzene **3** was prepared according to a reported procedure.¹ All other chemicals were purchased from Acros, Alfa-Aesar, Sigma-Aldrich or TCI and were used as received. NMR spectra were recorded on a Bruker Avance 400 (^1H at 400 MHz, ^{13}C at 100 MHz). Chemical shifts are given relative to solvent residual peaks. Mass spectra were recorded on a Bruker Esquire 3000 (ESI/Ion Trap) equipment. Melting points were measured with a Büchi B-545 apparatus and weren't corrected. Microanalyses were performed by the Service Central d'Analyse du CNRS (Lyon, France). Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer equipped with an ATR sampling accessory. UV/Vis visible spectra at 298K were recorded on a Varian Cary 50 spectrometer. X-band EPR spectra were recorded on an EMX plus spectrometer equipped with an Oxford Helium cryostat. Spectra were treated using the Bruker SIMFONIA software. Cyclic voltammetry curves were recorded on a CH Instruments 620 potentiostat in a standard three-electrode cell under argon atmosphere in CH_2Cl_2 solutions containing 0.1M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. An Ag/AgNO_3 (0.01 M) reference electrode was used. All the potentials given in the text are referred to the regular Fc^+/Fc redox couple used as an internal reference. A glassy carbon disc electrode (5 mm diameter), polished with 1 μm diamond paste, was used as the working electrode. Electrochemical oxidations were performed on an EG&G PAR 273A potentiostat, under an argon atmosphere at 298 K, using a carbon felt working electrode.

Crystal structure analysis: Crystals were mounted on a Kappa CCD Nonius diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a cryostream cooler. The collected reflections were corrected for absorption (SADABS). Crystal structural solution (direct method) and refinement (by full-matrix least squares on F) was performed using the OLEX 2 analysis package. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms, with isotropic thermal parameters.

Crystallographic data and structure refinement for complexes **1** & **2**

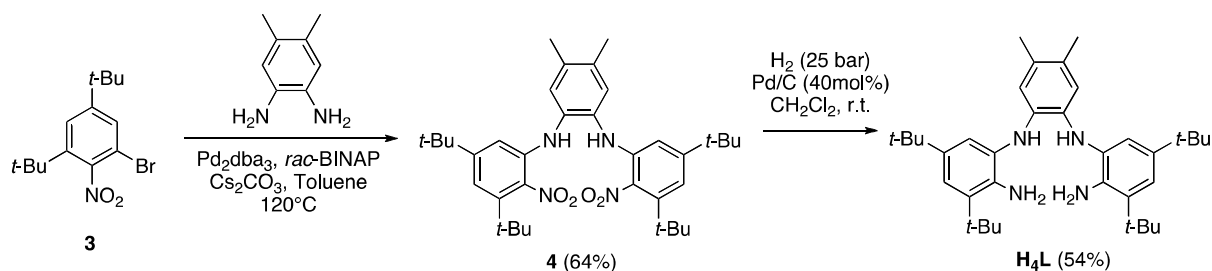
	2 [1], 3 CH₃OH	[2], C₆H₆
Empirical formula	C ₇₅ H ₁₁₂ N ₈ Ni ₂ O ₃	C ₇₈ H ₁₁₀ N ₈ Ni
Fw	1291.15	1218.45
Temperature/K	200	200
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /n
a/Å	32.632(7)	13.686(3)
b/Å	8.9933(18)	23.219(5)
c/Å	24.821(5)	23.157(5)
α /°	90.00	90.00
β /°	94.39(3)	96.26(3)
γ /°	90.00	90.00
Volume/Å ³	7263(3)	7315(3)
Z	4	4
ρ_{calc} /mg/mm ³	1.181	1.106
m /mm ⁻¹	0.569	0.311
F(000)	2792.0	2648.0
Crystal size/mm ³	0.55 × 0.46 × 0.16	0.55 × 0.46 × 0.16
2 θ range for data collection	4.7 to 52°	2.5 to 52°
Index ranges	-40 ≤ h ≤ 36, -11 ≤ k ≤ 9, -30 ≤ l ≤ 27	-16 ≤ h ≤ 14, -28 ≤ k ≤ 28, -28 ≤ l ≤ 28
Reflections collected	32177	63601
Independent reflections	7082[R(int) = 0.0671]	14101[R(int) = 0.0684]
Data/restraints/parameters	7082/9/453	14101/281/962
Goodness-of-fit on F ²	1.100	1.025
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0572, wR ₂ = 0.1228	R ₁ = 0.0551, wR ₂ = 0.1194
Final R indexes [all data]	R ₁ = 0.0889, wR ₂ = 0.1346	R ₁ = 0.1415, wR ₂ = 0.1466
Largest diff. peak/hole / e Å ⁻³	0.48/-0.54	0.41/-0.28

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-927235 and 927236 (for **1** and **2**, respectively). Copies of the data can be obtained

free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033) or via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

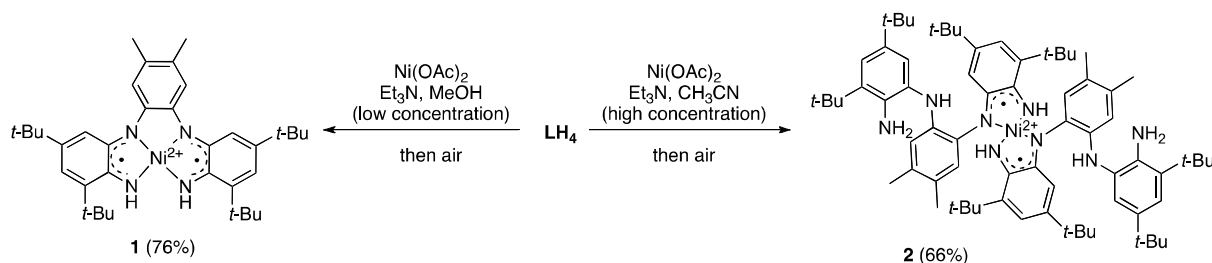
Synthesis of the ligand H₄L and complexes 1 & 2

General comment: The ligand H₄L was prepared in two steps starting from 3,5-di-*tert*-butyl-2-nitrobromobenzene **3** (Scheme 1). A reliable procedure recently reported by the Beifuss' group² allowed the Pd-catalyzed *N*-arylation of **3** with 4,5-dimethyl-*o*-phenylenediamine. The adjusted conditions led to the isolation of the *N,N'*-bis(3,5-di-*tert*-butyl-2-nitrophenyl)-4,5-dimethyl-*o*-phenylenediamine **4** in a convenient yield. Subsequent reduction of **4** by catalytic hydrogenation and recrystallization from methanol cleanly led to the targeted ligand H₄L in a moderate yield.



Scheme 1

The reaction between H₄L and Ni(OAc)₂ in the presence of an excess of Et₃N was performed in either anhydrous MeOH or anhydrous CH₃CN (Scheme 2). While the nature of the solvents has no influence on the outcome of the reaction, the concentration revealed to be a decisive parameter. Indeed, at low concentration, only complex [NiL]⁰ **1** was isolated whereas [NiH₂L₂]⁰ **2** preferentially formed at high concentration.



Scheme 2

Synthetic procedures:

***N,N'*-bis(3,5-di-*tert*-butyl-2-nitrophenyl)-4,5-dimethyl-*o*-phenylenediamine (4).** In a flame-dried resealable tube under argon atmosphere were added compound **3** (2.77g, 8.82 mmol, 2.4 equiv.), 4,5-dimethyl-*o*-phenylenediamine (500 mg, 3.68 mmol, 1.0 equiv.), Cs₂CO₃ (4.78 g, 14.67 mmol, 4.0 equiv.) and freshly distilled toluene (31 mL). After degassing the solution, Pd₂dba₃ (336 mg, 0.37 mmol, 10 mol%) and *rac*-Binap (343 mg, 0.55 mmol, 15 mol%) were added. The tube was immediately sealed and heated to 120°C during 24 hours. After cooling to r.t. the mixture was filtrated through a pad of Celite and abundantly washed with CH₂Cl₂ until getting a colorless filtrate. The organic phase was concentrated under reduced pressure and the remaining crude product was purified by column chromatography on silica gel (CH₂Cl₂/Pentane; 3:1 to 1:1, v:v) to give an orange solid (1.41 g, 64% yield). Pure analytical sample was obtained by crystallization from methanol; m.p. 200-203°C (Decomp., MeOH); ¹H NMR (400MHz, CDCl₃) : δ (ppm)= 7.05 (d, *J*= 1.8Hz, 2H), 6.93 (s, 2H), 6.86 (d, *J*= 1.8Hz, 2H), 5.80 (sl, 2H), 2.18 (s, 6H), 1.39 (s, 18H), 1.21 (s, 18H). ¹³C NMR (100MHz, CDCl₃): δ (ppm)= 153.2, 142.1, 140.3, 136.3, 132.5, 131.5, 123.4, 117.4, 113.3, 36.2, 35.1, 31.1, 31.0, 19.3. MS (ESI): *m/z*= 601 [M-H]⁻. IR: ν (cm⁻¹) 3390, 2962, 2870, 1580, 1530. Anal. Calcd for C₃₆H₅₀N₄O₄: C, 71.73; H, 8.36; N, 9.29. Found: C, 71.60; H, 8.36; N, 9.17.

***N,N'*-bis(3,5-di-*tert*-butyl-2-aminophenyl)-4,5-dimethyl-*o*-phenylenediamine (H₄L).** In a Paar pressure vessel, Pd/C (40 mol%) was added to a solution of the dinitro compound (0.03 M) in a CH₂Cl₂/MeOH mixture (1:1, v:v). The resulting suspension was stirred at r.t. under H₂ (25 bars) during 24 hours. After complete consumption of the material (TLC monitoring) the mixture was filtrated through celite and abundantly washed with CH₂Cl₂. The combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The remaining residue was recrystallized from MeOH to afford white crystals. Yield: 54%; m.p. 211-213°C (MeOH); ¹H NMR (400 MHz, CD₃OD): δ (ppm)= 7.02 (d, *J*= 2.3 Hz, 2H), 6.81 (d, *J*= 2.3 Hz, 2H), 6.52 (s, 2H), 2.12 (s, 6H), 1.43 (s, 18H), 1.21 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm)= 141.1, 135.5, 134.3, 132.8, 131.3, 129.6, 119.8, 118.5, 116.9, 34.9, 34.5, 31.8, 30.2, 19.3. MS (ESI): *m/z*= 543 [M+H]⁺. IR: ν (cm⁻¹) 3481, 3348, 2950, 2867, 1580, 1514. Anal. Calcd for C₃₆H₅₄N₄, 0.5 MeOH: C, 78.44; H, 10.10; N, 10.03. Found: C, 78.15; H, 10.07; N, 9.92.

[NiL]⁰ (1). Under argon, the ligand H₄L (50mg, 0.09 mmol, 1.0 equiv.) and Et₃N (103 μL, 0.74 mmol, 8.0 eq) were added to a degassed solution of Ni(OAc)₂·4H₂O (23 mg, 0.09 mmol, 1.0 equiv.) in dry MeOH (30 mL). The mixture was refluxed during 1 hour under argon, then exposed to air upon cooling to r.t. and stirred 2 hours. The black precipitate that formed was

filtrated, washed with MeOH and dried under vacuum; yield: 76%. Suitable crystals for X-ray analysis were obtained by slow evaporation at r.t. of an Et₂O/MeOH solution; m.p. >250°C; MS (ESI): m/z= 597 [M+H]⁺. IR: ν (cm⁻¹) 3414, 2949, 2905, 2870, 1477, 1356, 1106. Anal. Calcd for C₃₆H₅₀N₄Ni, 0.5MeOH, 0.5CH₂Cl₂: C, 67.74; H, 8.14; N, 8.54. Found: C, 68.04; H, 8.00; N, 8.61.

[NiH₂L₂]⁰ (2). Under argon, Ni(OAc)₂·4H₂O (32 mg, 0.13 mmol, 1.0 equiv.) and Et₃N (72 μ L, 0.52 mmol, 4.0 eq) were added to a degassed solution of ligand **3** (70mg, 0.13 mmol, 1.0 equiv.) in dry CH₃CN (5 mL). The mixture was refluxed during 1 hour under argon, then exposed to air upon cooling to r.t. and stirred 2 hours. The blue green precipitate that formed was filtrated, washed with CH₃CN and dried under vacuum; yield: 66%. Suitable crystals for X-ray analysis were obtained by vapor diffusion of CH₃CN in a benzene solution at r.t.; m.p. >250°C; MS (ESI): m/z= 1140 [M+H]⁺. IR: ν (cm⁻¹) 3481, 3383, 3348, 2952, 2908, 2870, 1584, 1309, 1236, 1163, 1106. Anal. Calcd for C₇₂H₁₀₄N₈Ni, C₆H₆: C, 76.89; H, 9.10; N, 9.20. Found: C, 76.56; H, 9.14; N, 9.19.

Electrochemical experiments

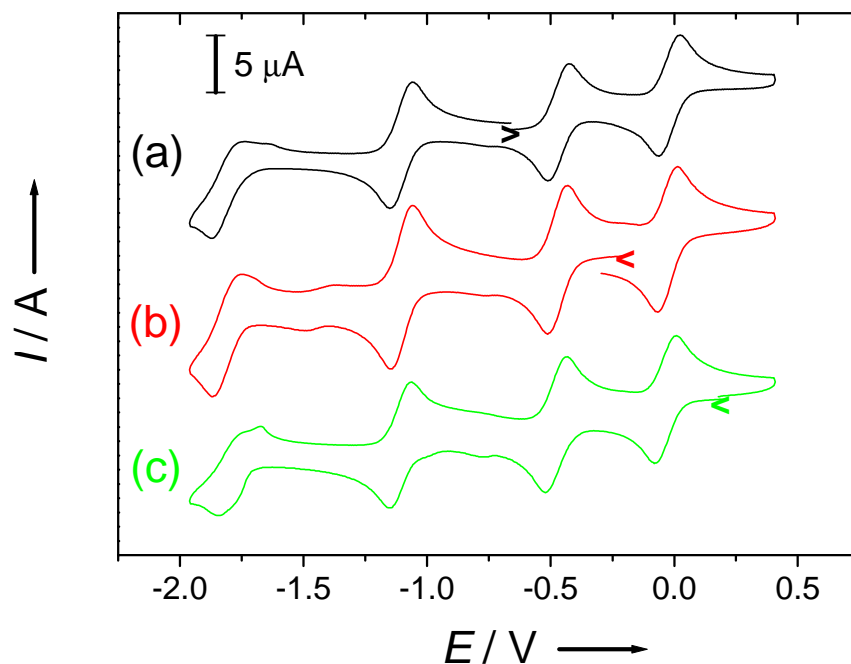


Figure S1 Cyclic voltammograms of 0.5 mM CH_2Cl_2 (+0.1 M TBAP) solutions of (a) **1**; (b) electrochemically generated 1^+ ; (c) electrochemically generated 1^{2+} . Scan rate = 0.1 V / s. $T = 298$ K. The potentials are referenced vs. Fc/Fc^+ .

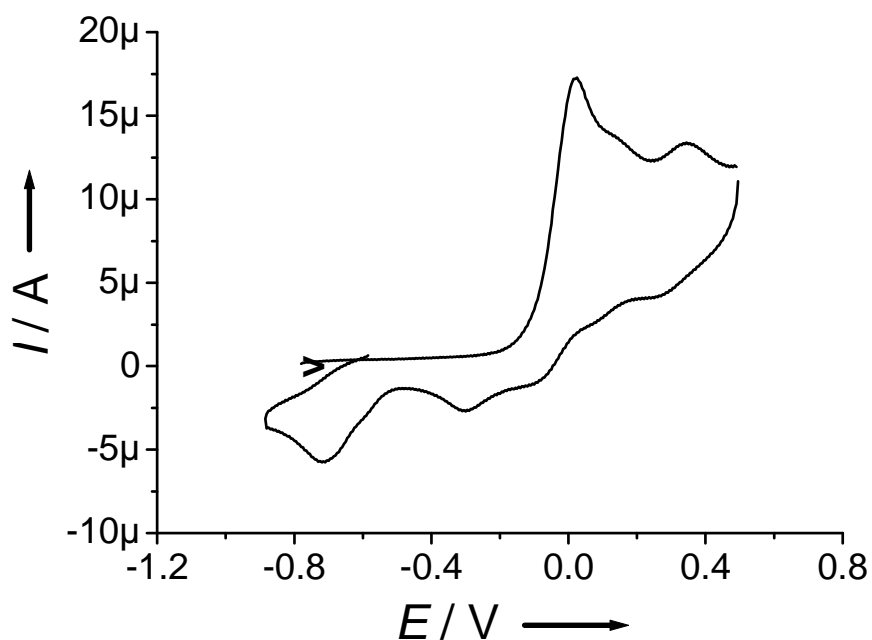


Figure S2 Cyclic voltammogram of a 0.5 mM CH_2Cl_2 (+0.1 M TBAP) solution of H_4L . Scan rate = 0.1 V / s. $T = 298$ K. The potentials are referenced vs. Fc/Fc^+ .

EPR and UV-Vis spectra

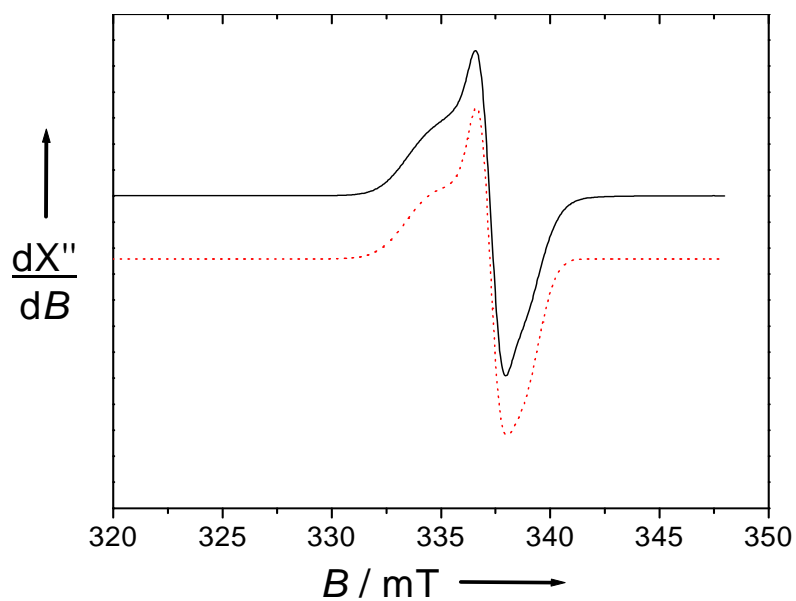


Figure S3 X-Band EPR spectrum of a 0.5 mM CH_2Cl_2 (+ 0.1 M TBAP) of the electrochemically generated 1^+ . Black: Experimental spectrum; Red: Simulation using the parameters $g_1 = 1.994$, $g_2 = 2.004$, $g_3 = 2.021$. Microwave Freq: 9.42 GHz, power: 5 mW, Mod. Freq: 100 KHz, Amp. 0.1 mT, $T = 10$ K.

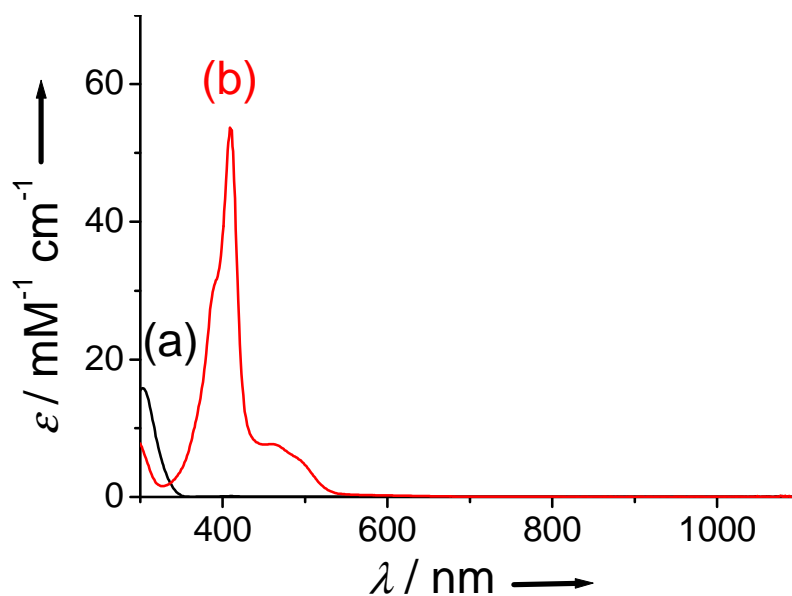


Figure S4 UV-Vis spectra of H_4L in CH_2Cl_2 solution (+ 0.1 M TBAP). Black (a): H_4L before electrolysis, Red (b): After electrochemical oxidation at 0.21 V. $T = 298$ K.

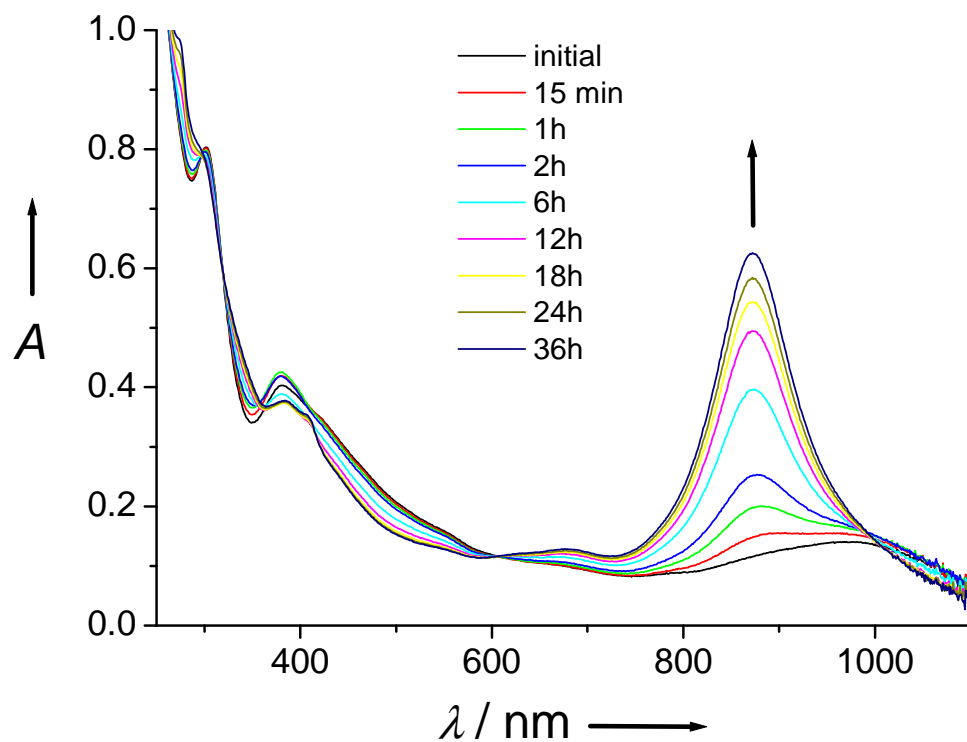
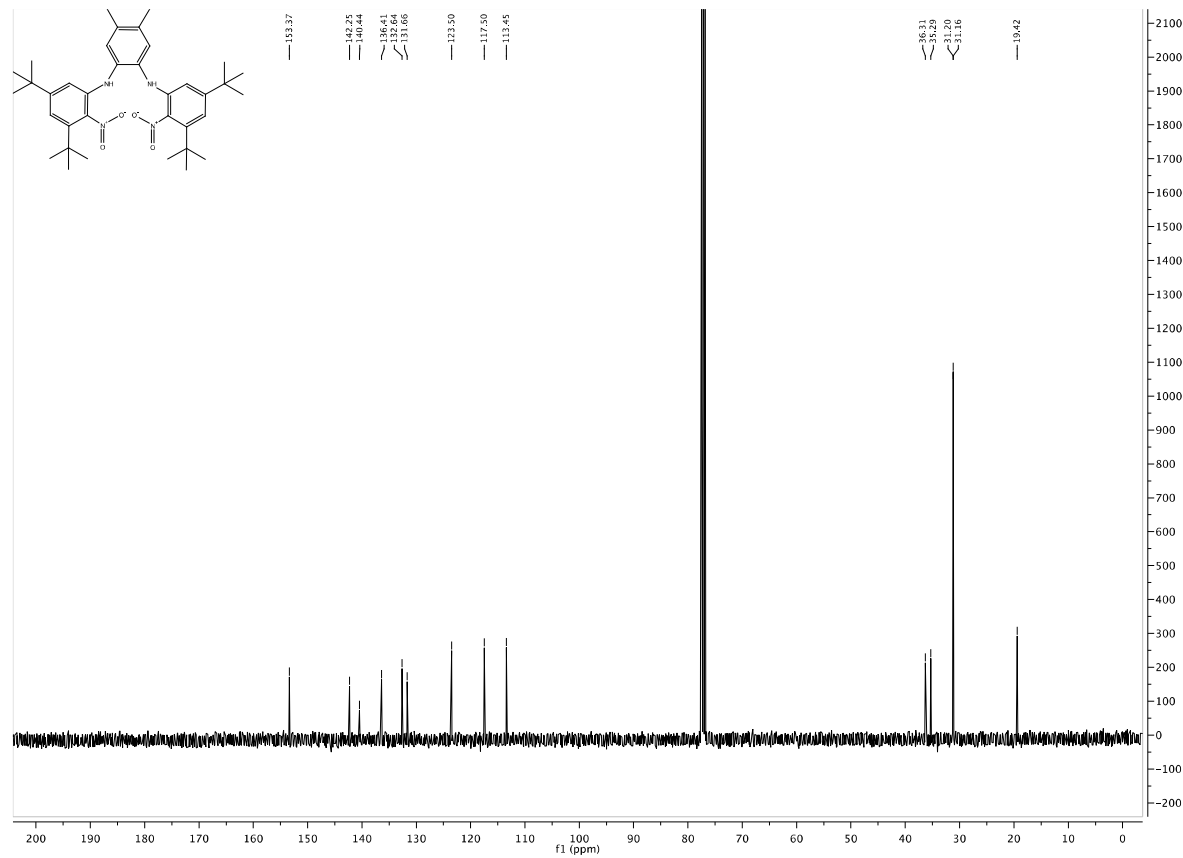
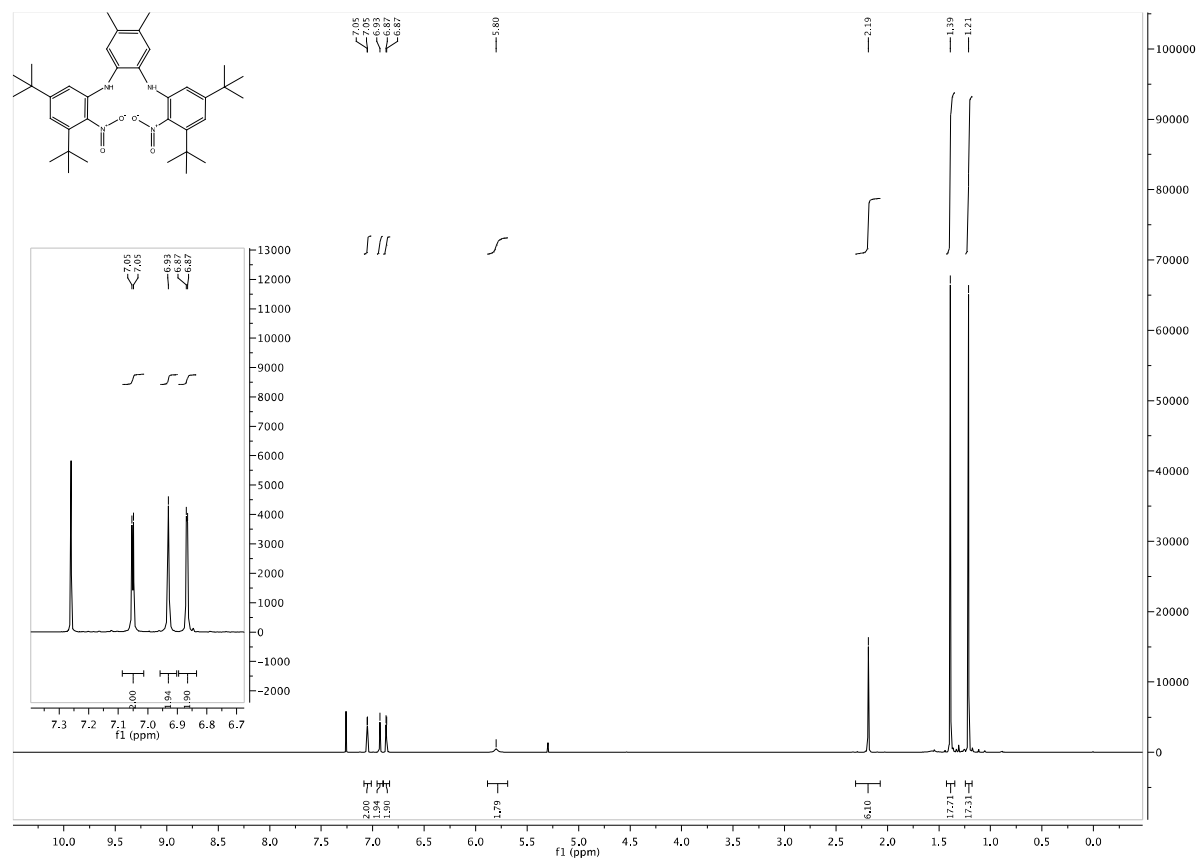
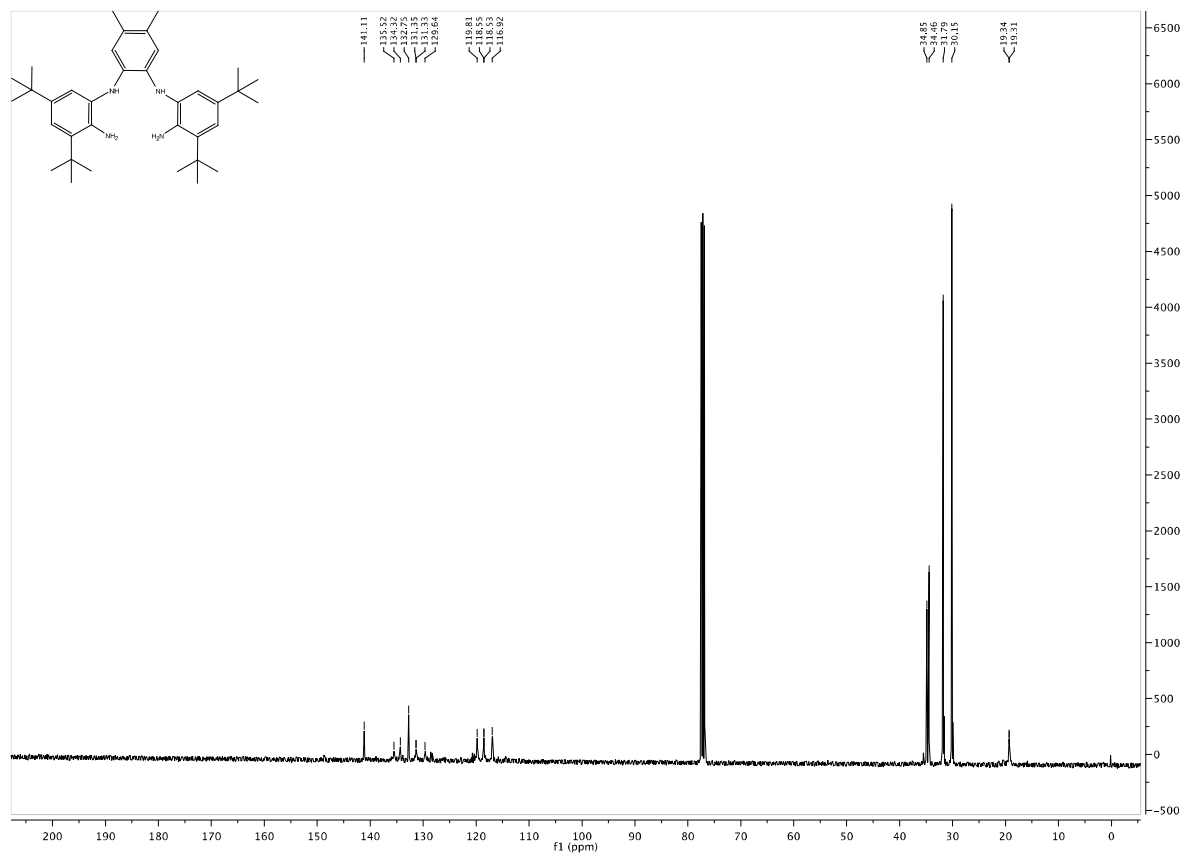
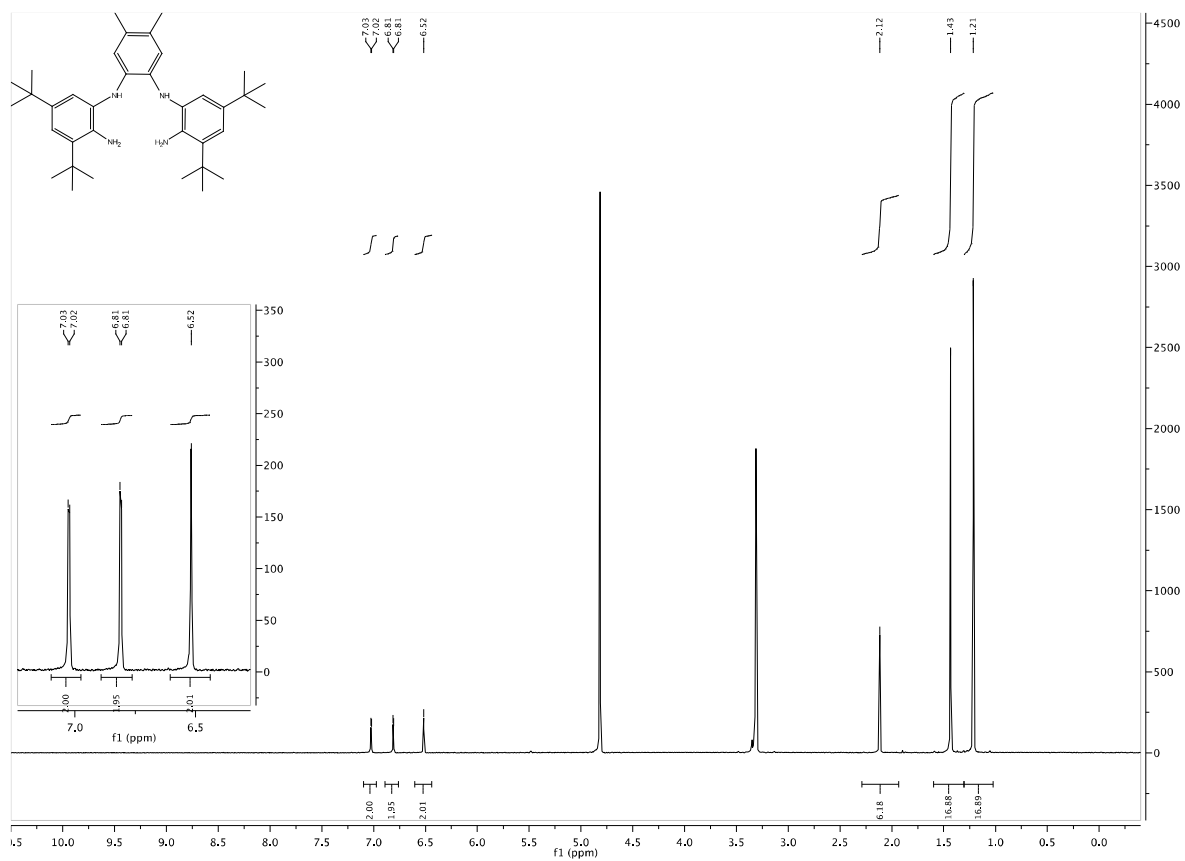


Figure S5 Evolution of the UV-Vis spectra of 1 after addition of one molar equivalent of H₄L in CH₂Cl₂ solution (+ 0.1 M TBAP). *T* = 298 K.

NMR Spectra





References

1 Rundel, W. *Chem. Ber.* **1963**, *96*, 636-637.

2 Tietze, M.; Iglesias, A.; Merisor, E.; Conrad, J.; Klaiber, I.; Beifuss, U. *Org. Lett.* **2005**, *7*, 1549-1552.