

Supporting Information

Mechanistic Insight into Catalyst-Transfer Polymerization of unusual Anion-Radical Naphthalene Diimide Monomers: an Observation of Ni(0) Intermediates

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Instrumentation.

^1H (500.13 MHz), ^{13}C (125.77 MHz) and ^{31}P (202.46 MHz) NMR spectra were recorded on a Bruker Avance III spectrometer using a 5 mm $^1\text{H}/^{13}\text{C}/^{19}\text{F}/^{31}\text{P}$ gradient probe at 303 K (unless otherwise noted). The NMR spectra were recorded from THF- d_8 solutions and referenced to the solvent peak ($\delta(^1\text{H}) = 1.72$ ppm, $\delta(^{13}\text{C}) = 25.2$ ppm). The ^{31}P NMR spectra were referenced to external H_3PO_4 ($\delta = 0$ ppm). The samples for in-situ experiments were prepared in a glovebox under argon atmosphere.

GPC measurements were carried out on an Agilent 1100 Series (Agilent, USA) normal-temperature size exclusion chromatograph, equipped with refractive index detector and one column PL Gel MIXED-B (Polymer Laboratories, UK). Chloroform was used as eluent and the flow rate was 1 mL/min. Number average molecular weights (M_n) and polydispersity indexes (PDI) of obtained polymers were determined based on calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

Materials.

2,6-bis(2-thienyl)naphthalene-1,4,5,8-tetracarboxylic-*N,N'*-bis(2-octyldodecyl) diimide (Ar_1), 2-(2-bromothien-5-yl)naphthalene-1,4,5,8-tetracarboxylic-*N,N'*-bis(2-octyldodecyl) diimide ($\text{Ar}_1\text{-Br}$) and 2,6-bis(2-bromothien-5-yl)naphthalene-1,4,5,8-tetracarboxylic-*N,N'*-bis(2-octyldodecyl) diimide ($\text{Br-Ar}_1\text{-Br}$) were synthesized as described elsewhere.¹ Rieke zinc was prepared by the reduction of ZnCl_2 with sodium naphthalenide.² Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. All other chemicals were purchased from Aldrich and used as received.

General procedure for polymerization of $\text{Br-Ar}_1\text{-Br/Zn}$. All operations were done under an inert gas atmosphere. The charge-transfer monomer was prepared as follows: $\text{Br-Ar}_1\text{-Br}$ (0.1 mmol) was placed in a round-bottomed flask equipped with a magnetic stirrer and a septum, and the atmosphere was replaced with argon. Dry THF (20 mL) and active Zn (1.05 mmol) were added via a syringe and the mixture was stirred at room temperature for 1 h. Afterwards, a catalytic amount of Ni(dppe)Br_2 (0.001-0.01 mmol) was added. In general, polymerization times ranged between 1 to 24 hours at temperatures from 0°C to 50°C.

For particular kinetic experiment documented in the Table S1, 0.04 mol % of Ni(dppe)Br_2 was taken and the polymerization was conducted at room temperature (about 23°C). 8 samples were withdrawn after 1,2,3,4,5,6,9,72 hours of the polymerization. The reaction mixtures were quenched with 5 M HCl and extracted with CHCl_3 . The organic layers were washed with water, dried over anhydrous MgSO_4 and concentrated under reduced pressure to give the crude polymers containing also some unreacted monomers and oligomers (if any). For preparation of pure polymer samples, acetone was added and the precipitates were washed with warm acetone, collected by filtration and dried in vacuo at 40 °C to give pure $(\text{Ar}_1)_n$ samples.

Table S1. Kinetic polymerization experiment; polymerization of $\text{Br-Ar}_1\text{-Br/Zn}$ was conducted in the presence of 0.04 mol % of Ni(dppe)Br_2 .

Sample	Time, [h]	Monomer conversion, [%]	M_n (PS standard)	M_n (oligo-(TNDIT) standard)	M_w (PS standard) [g/mol]	M_w (oligo-(TNDIT) standard)	PDI (oligo-(TNDIT) standard)
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¹ Senkovskyy, V.; Tkachov, R.; Komber, H.; Sommer, M.; Heuken, M.; Voit, B.; Huck, W. T. S.; Kataev, V.; Petr, A.; Kiriy, A. *J. Am. Chem. Soc.* **2011**, *131*, 19966-19970.

² Sodium naphthalenide was prepared according to the protocol published in the work of Rieke with the only difference that sodium was used instead of lithium: Chen, T.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233-244.

			[g/mol]	[g/mol]		[g/mol]	
1	1	10	4500	2750	5570	3070	1.1
2	2	15	4531	2790	5600	3150	1.15
3	3	23	6800	3690	13170	5250	1.4
4	4	31	10400	5150	22750	7600	1.5
5	5	50	19200	7650	40800	10700	1.4
6	6	55	38200	11800	56100	14400	1.2
7	9	79	44150	13350	83100	18250	1.4
8	72	100	94690	23050	221800	36450	1.6

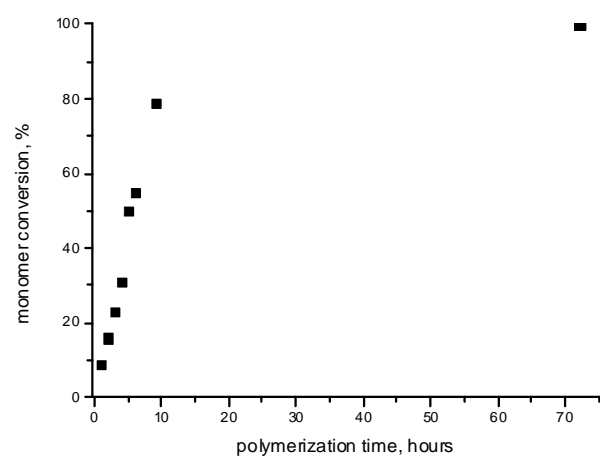


Figure S1a. Monomer conversion versus polymer time plot for polymerization of Br-Ar₁-Br/Zn conducted in the presence of 0.04 mol % of Ni(dppe)Br₂.

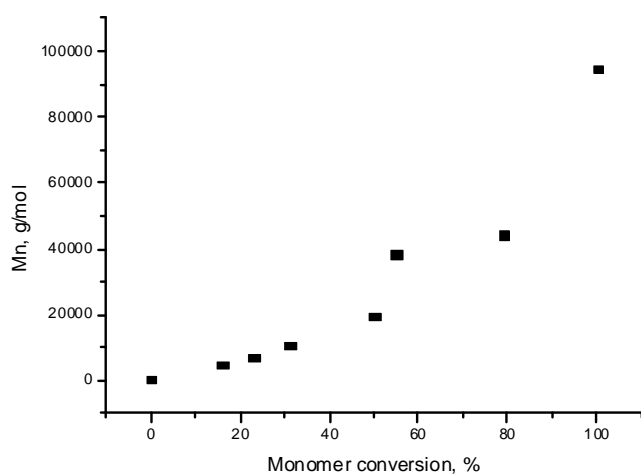


Figure S1b. Number-average molecular weight (determined against PS standards) versus monomer conversion plot for the same polymerization as in Figure S1a.

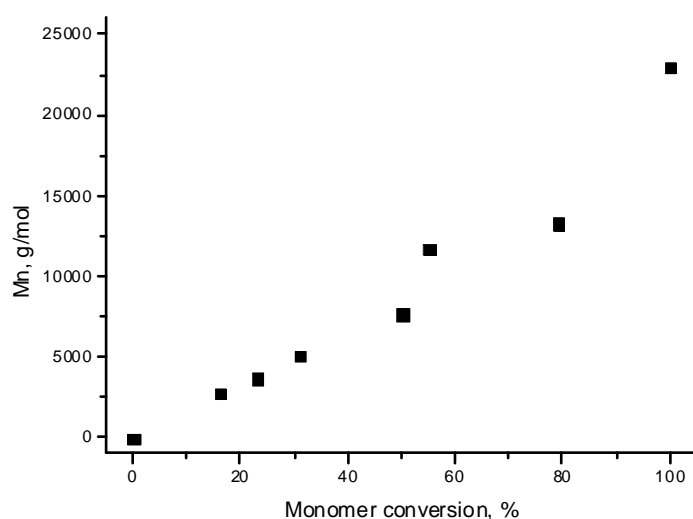


Figure S1c. Number-average molecular weight (determined against oligo-(TNDIT) standards) versus monomer conversion plot for the same polymerization as in Figures S1a,b.

Chain-extension experiment was conducted similarly to the kinetic polymerization experiment described above with the only difference that the monomer was added in two portions. To this end, the first portion of Br-Ar₁-Br/Zn was polymerized in the presence of 0.06 mol % Ni(dppe)Br₂. The monomer conversion of about 80% was reached in 4 hours of the polymerization (GPC data, Figure S2). Afterwards, the second portion of the monomer equal to the first one was added. Several samples were withdrawn from the polymerization mixture at different polymerization times, treated as described above and investigated by GPC.

Table S2. Chain-extension experiment; the first portion of Br-Ar₁-Br/Zn was polymerized in the presence of 0.06 mol % of Ni(dppe)Br₂ and afterwards the second monomer portion was added.

Sample	Time [h]	Monomer conversion, [%]	M _n (oligo- (NDIT ₂) standard) [g/mol]	M _w (oligo- (NDIT ₂) standard) [g/mol]	PDI (oligo- (NDIT ₂) standard)
Polymerization of the first portion					
1	4	80	19400	29100	1.5
Polymerization of the second portion					

2	0	43	20150	34250	1.7
3	0.25	44	21200	36040	1.7
4	0.75	49	21800	40300	1.85
5	1.25	52	22700	38100	1.68
6	2	55	22900	51067	2.23
7	3	65	23100	50300	2.18
8	6	90	24300	53200	2.19
9	12	100	29100	67500	2.32

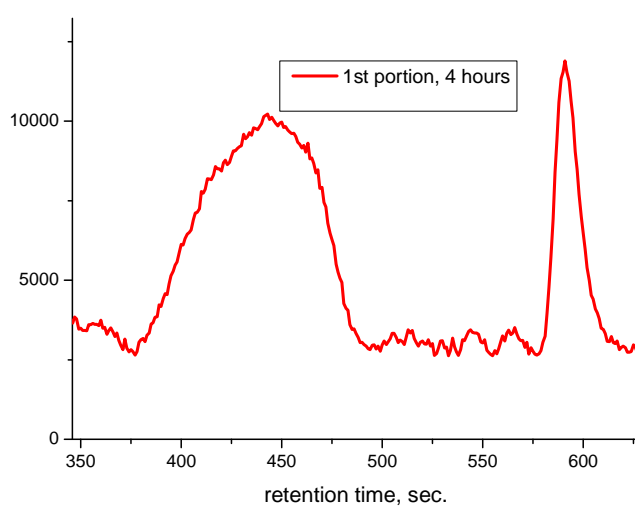


Figure S2a. The first portion of the monomer was significantly consumed after 5 hours of the polymerization.

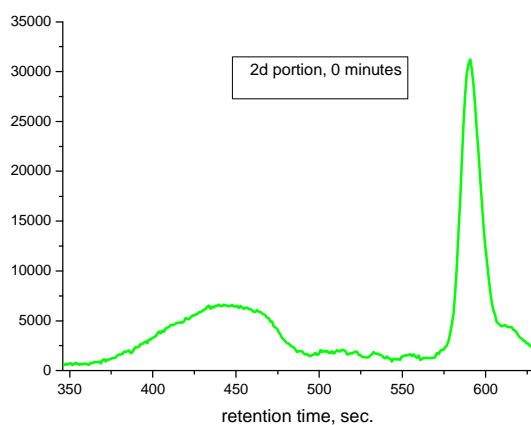


Figure S2b. GPC trace of the polymerization mixture right after addition of the second monomer portion: intensity of the monomer peak was significantly increased.

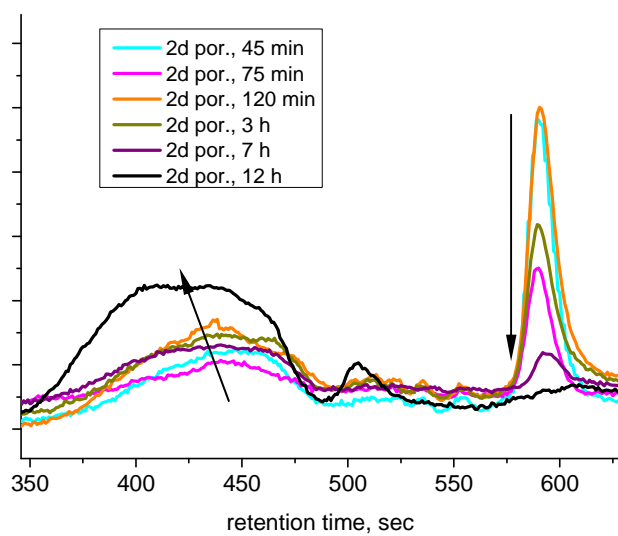


Figure S2c. Polymerization of the second monomer portion: monomer consumption leads to growth of the polymer peak and a slight shift toward higher molecular weights.

Yamamoto polymerization of Br-Ar₁-Br. All operations were done under an inert gas atmosphere. Br-Ar₁-Br (150 mg, 0.1 mmol) was placed in a round-bottomed flask equipped with a magnetic stirrer and a septum, and the atmosphere was replaced with argon. Dry THF (20 mL), Ni(COD)₂ (27.5 mg, 0.1 mmol) and bipy (15.6 mg, 0.1 mmol) were added via a syringe and the mixture was stirred at room temperature for 12 hours. Three samples were withdrawn in 10 minutes, 1 hour and 12 hours after the polymerization start. The mixtures were quenched with 5 M HCl and extracted with CHCl₃. The organic layers were washed with water, dried over anhydrous MgSO₄ and concentrated under reduced pressure to give polymerization products. The resulting samples were analyzed by GPC.

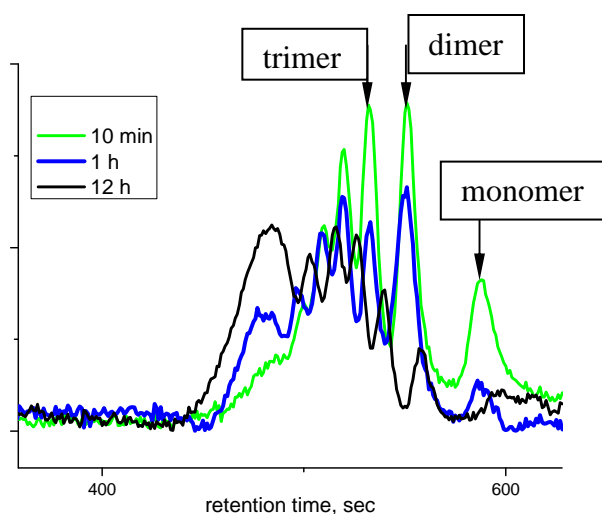


Figure S3. GPC data for the Yamamoto polymerization of Br-Ar₁-Br with equimolar amounts of Ni(COD)₂/bipy. Three samples were analyzed at different reaction time: 10 minutes (green), 1 hour (blue) and 10 hours (black). The monomer is almost fully consumed early in the reaction, when no polymer was formed which is typical for step-growth polymerizations.

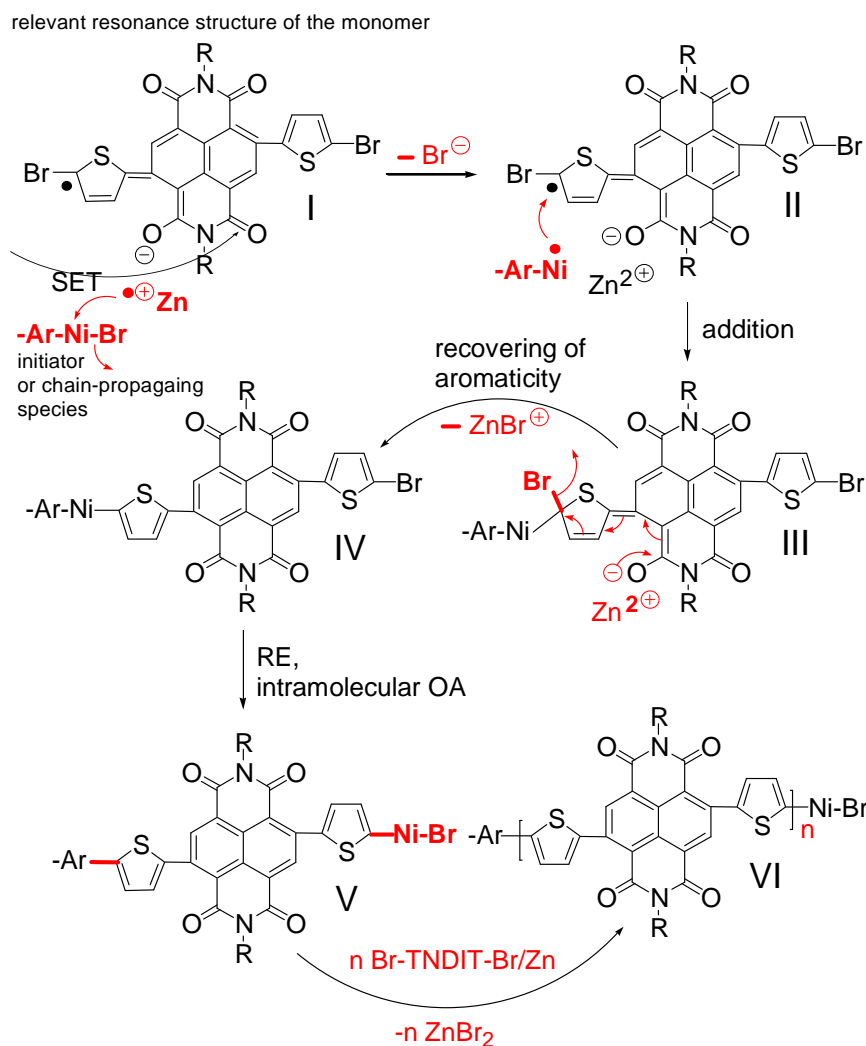
Density functional Theory calculations.

From our chemical intuition we have chosen selected conformations of the complexes and reference molecules and have expressed the geometry of the molecules by means of standard values for bond lengths and bond angles. Our atomistic electronic structure calculations are based on the self consistent Kohn-Sham Density Functional Theory using the PBE³ functional. This functional was created by Adamo as a 25 % exchange and 75 % correlation weighting functional following the originally pure 1996 functional of Perdew, Burke and

³ Adamo C.; Barone, V. *J. Chem. Phys.* **1999**, 110, 6158-69.

Ernzerhof⁴, which is implemented in GAUSSIAN under the keyword PBE1PBE. We use this functional in conjunction with Dunning's⁵ correlation consistent basis set cc-pVDZ, which includes polarization functions by definition. The starting geometries were optimized searching for a potential energy minimum until the GAUSSIAN standard conditions for convergence were satisfied. For the stationary points calculations of the vibration frequencies were performed to ensure the location of a local minimum (no imaginary frequency) and to calculate the thermochemical correction to the zero temperature electronic energy. The stabilization energies were calculated as the differences of the Gibbs free energy at 298 K between complexes and the composing molecules.

Scheme S1. A plausible mechanism of Ni-initiated catalyst-transfer polymerization of Br-TNDIT-Br/Zn (dppe ligand is omitted).



⁴ Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865-68. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **1997**, 78, 1396.

⁵ Dunning, T. H. *J. Chem. Phys.* **1989**, 90, 1007-23.

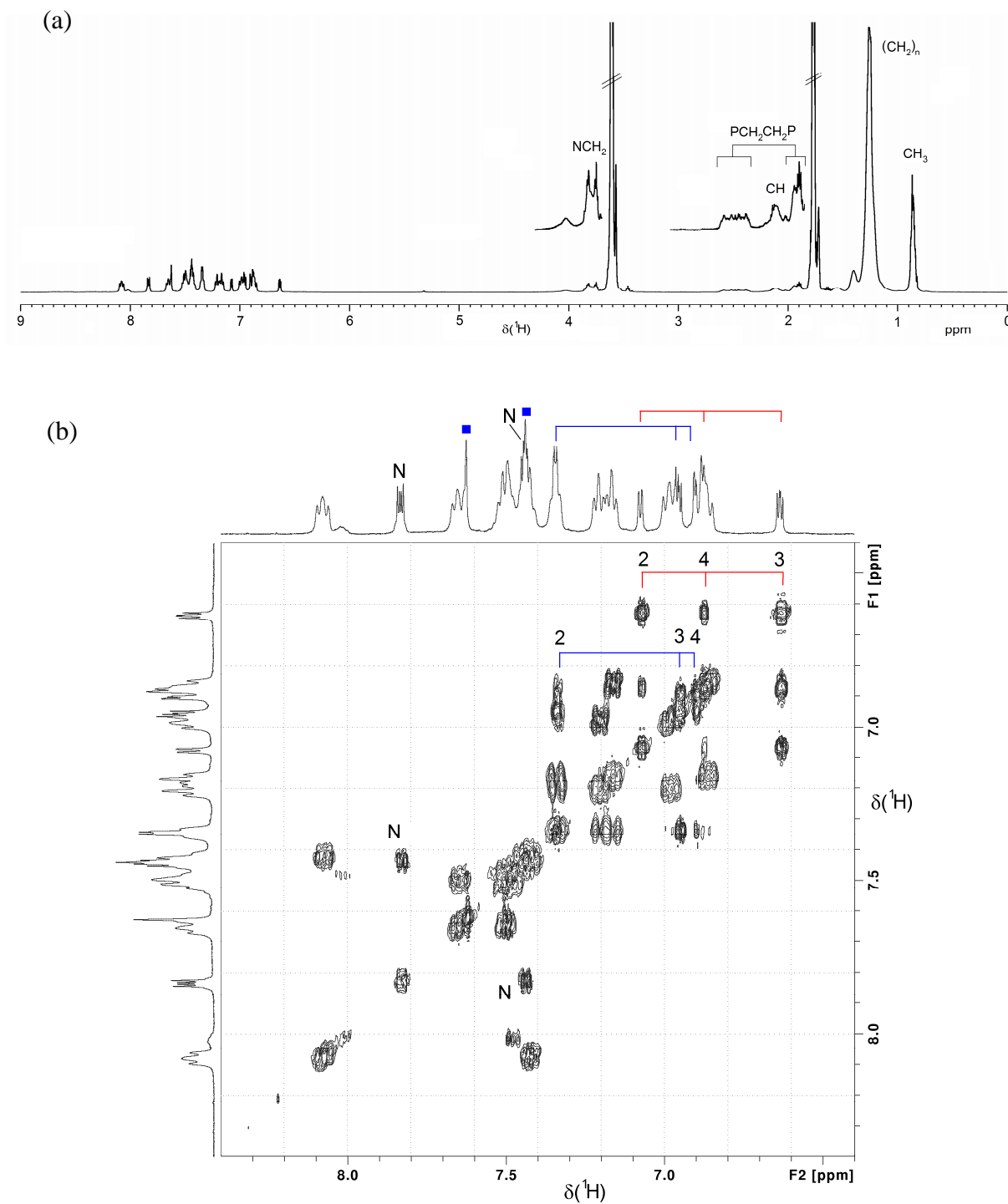


Figure S4. ^1H NMR spectrum (a) and COSY spectrum (b, aromatic protons) of $(\eta^2\text{-Ar}_1)(\text{dppe})\text{Ni}^0$ synthesized from $\text{Ni}(\text{dppe})\text{Br}_2$ and Ar_1/Zn (solvent THF-d_8 , 273 K). The enlarged aromatic protons region is depicted as top spectrum in the COSY plot. The two different thiophene moieties with protons H_2 , H_3 and H_4 are indicated by blue and red lines. Two singlets due to the aromatic NDI core protons are marked by colored squares. Naphthalene signals from Ar_1/Zn synthesis are marked by N. All other signals are due to the four non-equivalent phenyl rings of $\text{Ni}^0(\text{dppe})$.

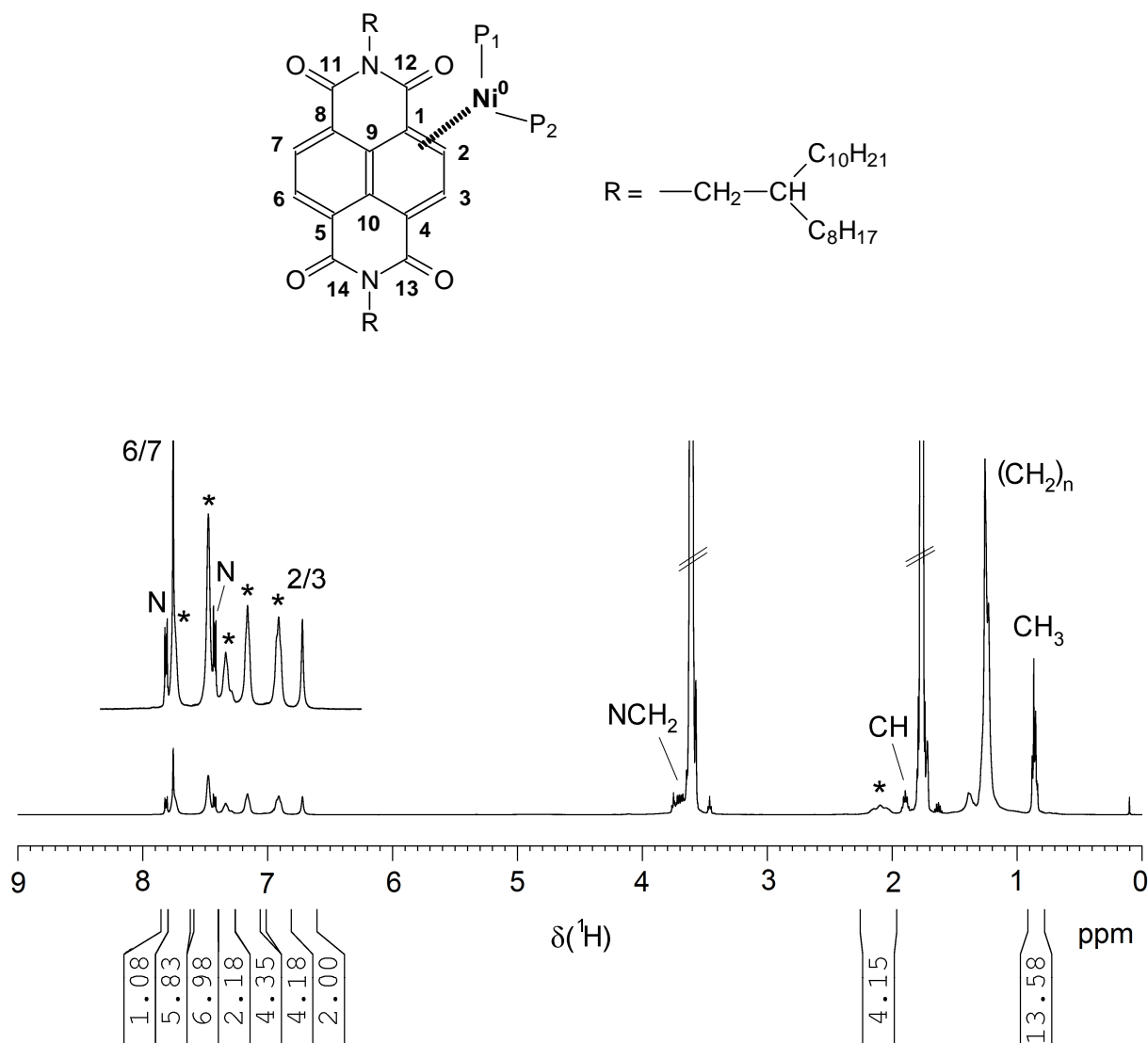


Figure S5. ^1H NMR spectrum of $(\eta^2\text{-NDI})(\text{dppe})\text{Ni}^0$ (R = OD) measured in THF-d_8 at 303 K. The signals 2/3 and 6/7 are from the aromatic core of NDI. Signals marked with * are due to signals of $\text{Ni}^0(\text{dppe})$. At this temperature a pairwise fast exchange takes place (see also Figure S6a). Thus, two of the four phenyl rings are equivalent and only two different phenyl rings can be observed. Naphtalene signals from NDI/Zn synthesis are marked by N.

The signal integration proves the 1:1 stoichiometry of $\eta^2\text{-NDI}:\text{dppe}$. The intensity of one $\eta^2\text{-NDI}$ is 1 as deduced from the signal of 2/3 at 6.7 ppm. The intensity of all phenyl proton signals of dppe (6.8 – 7.8 ppm; corrected by the intensity of N (1.08) and 6/7 (2.00)) is 20.44 in good agreement with the theoretical value of 20 for 1:1 stoichiometry of $\eta^2\text{-NDI}:\text{dppe}$. Moreover, this stoichiometry also follows from the integral of the four protons of the aliphatic bridge in dppe (~2.1 ppm; I = 4.15; 1 H = 1.04) and the methyl group signal (0.85 ppm; 12 protons; I = 13.58; 1 H = 1.13) of the octadecyl moiety.

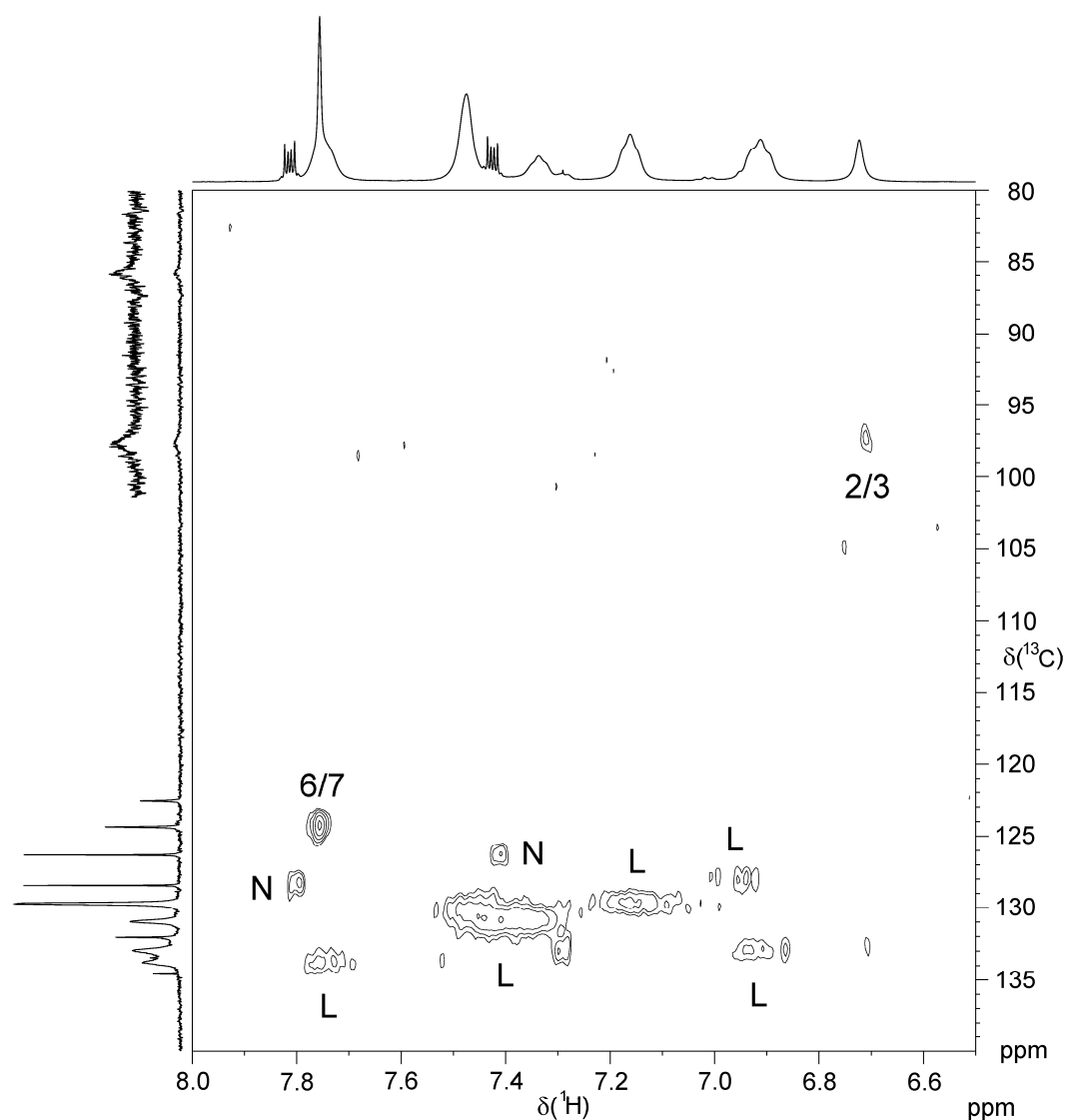


Figure S6. HSQC spectrum of (η^2 -NDI)(dppe)Ni⁰ (R = OD) measured in THF-d₈ at 323 K. L – signals of the dppe ligand, N – signals of naphthalene from the synthesis of Rieke zinc used in NDI (R = OD)/Zn monomer synthesis. The spectrum shows the ¹H-¹³C correlations for the CH groups 2/3 and 6/7. The ¹H and ¹³C spectrum are from 1D NMR measurements showing also non-protonated carbons in the ¹³C trace.

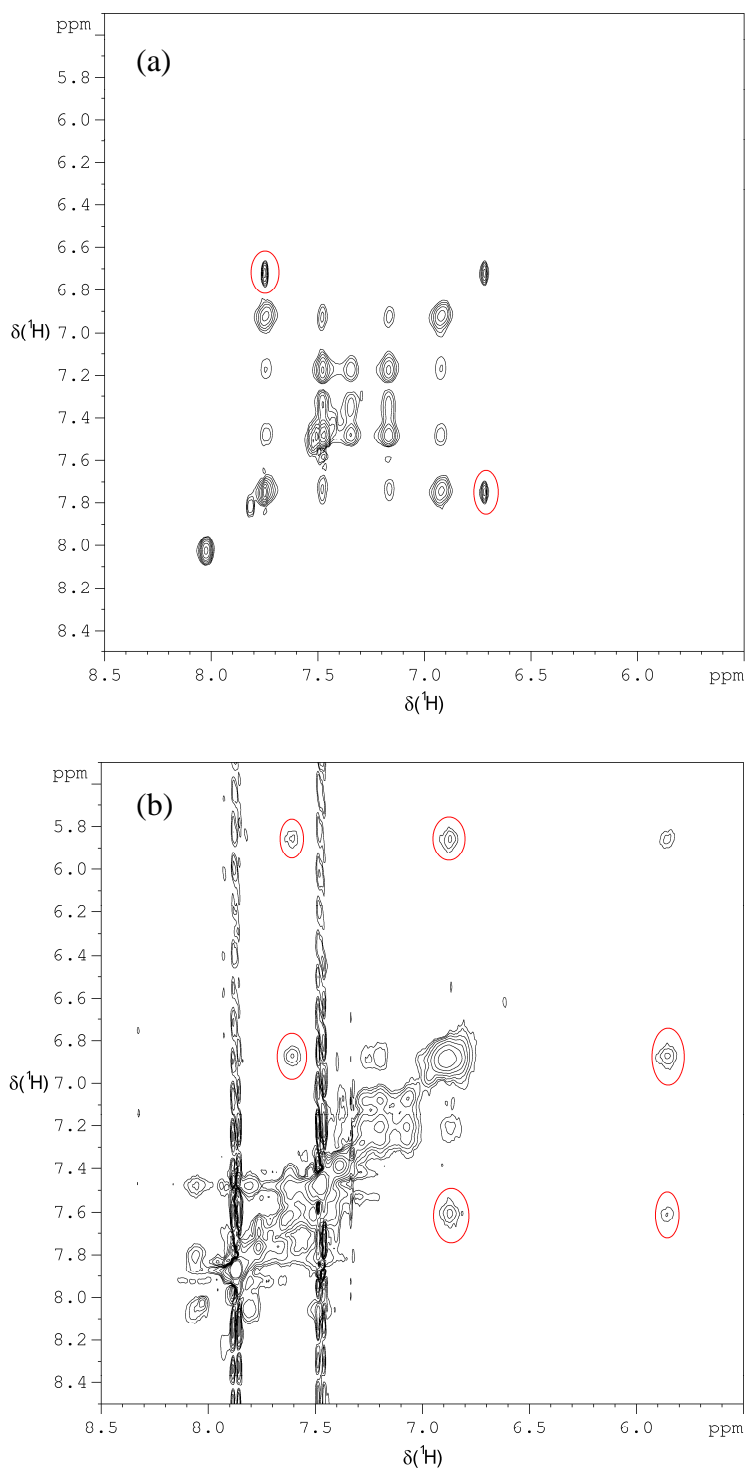


Figure S7. tr-ROESY spectra of $(\eta^2\text{-NDI})(\text{dppe})\text{Ni}^0$ (R = OD) measured in THF- d_8 at 303 K (a) and 213 K (b). The circled peaks indicate in (a) slow exchange processes between protons 2/3 and 6/7 at 303 K and in (b) between 2, 3, 6 and 7 at 213 K. Whereas signal broadening and splitting in the 1D spectrum clearly indicates that exchange processes were frozen with decreasing temperature the assignment of the new signals remains still open because of intense signal overlap of broadened signals in the 6.7 – 8.2 ppm region (see Figure 2b). Non-assigned exchange peaks are due to slow exchange of the phenyl protons of the dppe ligand.

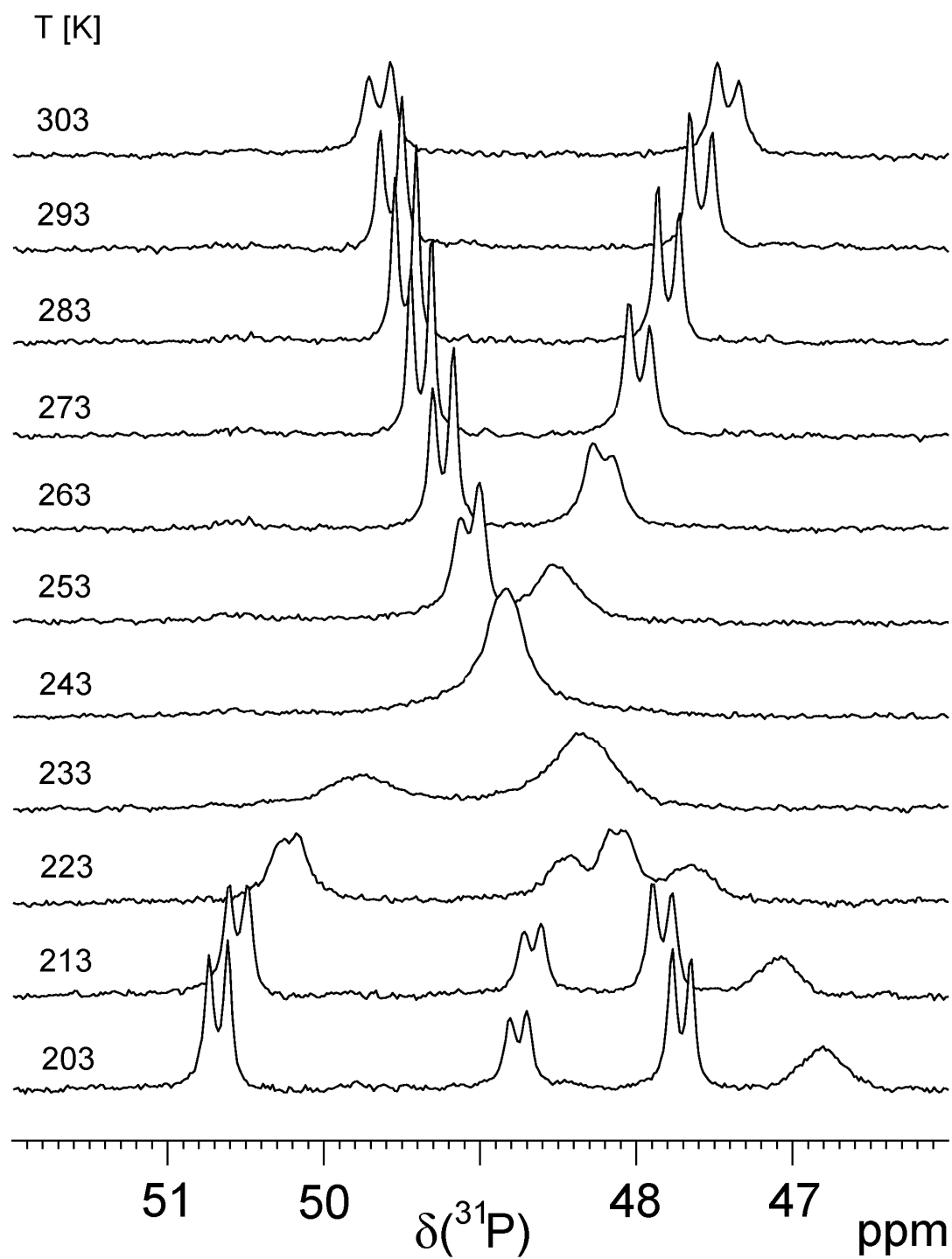


Figure S8. Temperature-dependent ^{31}P NMR measurements on $(\eta^2\text{-NDI})(\text{dppe})\text{Ni}^0$ ($\text{R} = \text{OD}$) in THF-d_8 showing fluxional behaviour of this compound.

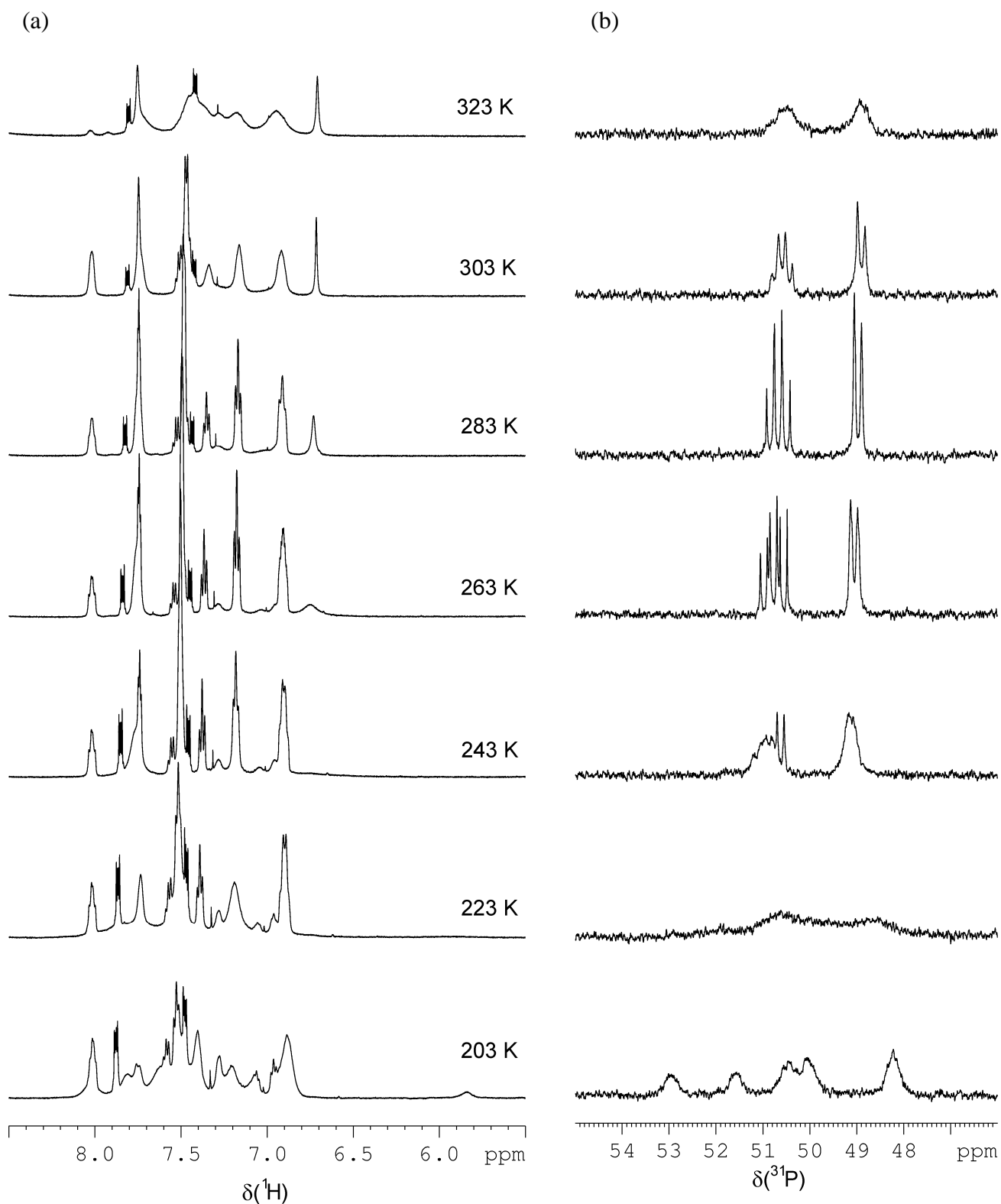


Figure S9. Temperature-dependent ^1H (a) and ^{31}P NMR (b) measurements on $(\eta^2\text{-NDI})\text{Ni}(\text{dppe})$ ($\text{R} = \text{EH}$) in THF-d_8 showing fluxional behaviour of this compound. Three pairs of doublets well observable at 263 K are attributed to location of Ni(0)dppe between ethyl/ethyl, ethyl/butyl and butyl/butyl residues of the two chiral 2-ethylhexyl substituents.

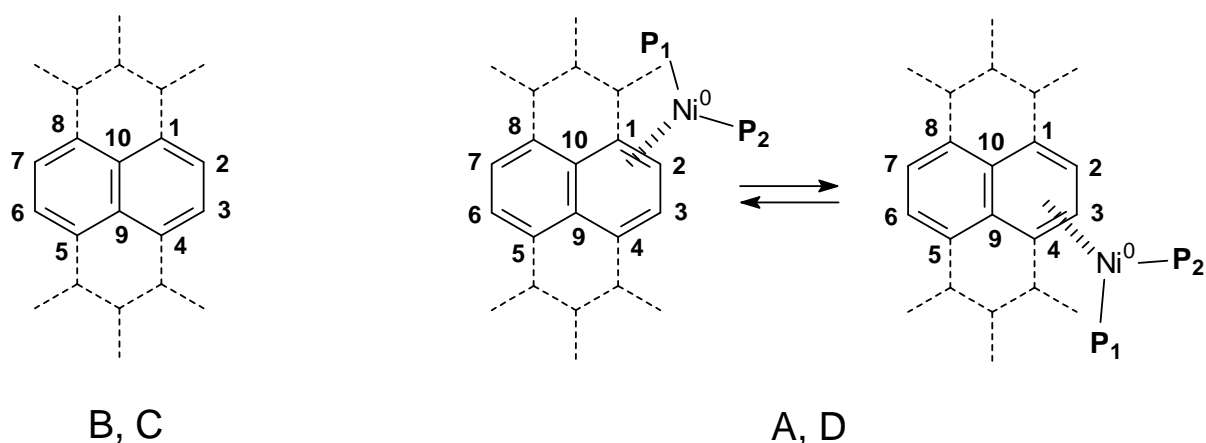
Estimation of ^{13}C chemical shifts of the naphthalene moiety in $(\eta^2\text{-NDI})(\text{dppe})\text{Ni}^0$ ($\text{R} = \text{OD}$) based on ^{13}C chemical shift increments

Procedure

a) based on the ^{13}C NMR data of the $(\eta^2\text{-naphthalene})(^i\text{Pr}_2\text{P}(\text{CH}_2)_2^i\text{Pr}_2\text{P})\text{Ni}^0$ complex (**A**) reported by Benn, R.; Mynott, R.; Topalovic, I.; Scott F. in *Organometallics* **1989**, 8, 2299-2305 (here: compound 2 in Table 1; conditions: solvent THF- d_8 , 183 K, 75.5 MHz) and the ^{13}C chemical shifts of naphthalene (**B**) in THF- d_8 (own measurement at 303 K, 125.3 MHz) the substituent chemical shifts (SCS) of $(^i\text{Pr}_2\text{P}(\text{CH}_2)_2^i\text{Pr}_2\text{P})\text{Ni}^0$ on the different atom positions of naphthalene were determined

b) based on these SCS values and the ^{13}C NMR data of the naphthalene moiety of NDI ($\text{R} = \text{OD}$) in THF- d_8 (**C**) (own measurement at 303 K, 125.3 MHz) the ^{13}C NMR data of the naphthalene moiety of $(\eta^2\text{-NDI})(\text{dppe})\text{Ni}^0$ complex (**D**) were estimated

c) the estimated ^{13}C NMR data of the naphthalene moiety of $(\eta^2\text{-NDI})(\text{dppe})\text{Ni}^0$ ($\text{R} = \text{OD}$) complex (**D**) were compared with the experimental data obtained at 323 K in THF- d_8 (Figure 3c).



Numbering of the atom positions for the naphthalene moiety. The dotted lines indicate the imide units present in **C** and **D**.

Table S3. Experimental and calculated ^{13}C chemical shifts of the naphthalene moiety of η^2 -naphthalene)($^i\text{Pr}_2\text{P}(\text{CH}_2)_2^i\text{Pr}_2\text{P}$) Ni^0 complex (**A**), naphthalene (**B**), NDI ($\text{R} = \text{OD}$) (**C**) and (η^2 -NDI)(dppe) Ni^0 ($\text{R} = \text{OD}$) (**D**) and substituent chemical shifts (SCS) For details see procedure part.

	$\delta(^{13}\text{C})_{\text{exp}}$	$\delta(^{13}\text{C})_{\text{exp}}$	SCS	$\delta(^{13}\text{C})_{\text{exp}}$	$\delta(^{13}\text{C})_{\text{calc}}$	$\delta(^{13}\text{C})_{\text{exp}}$	$\Delta\delta$
position	A	B		C	D	D	
1/4	84.9	128.5	-43.6	127.6	84.0	85.8	+1.8
2/3	91.3	126.4	-35.1	131.1	96.0	97.7	+1.8
5/8	125.9	128.5	-2.6	127.6	125.0	122.6	-2.4
6/7	123.4	126.4	-3.0	131.1	128.1	124.4	-3.7
9/10	137.5	134.5	+3.0	127.6	130.6	132.0	+1.4

Discussion

Keeping in mind the differences in bidentate ligand ($^i\text{Pr}_2\text{P}(\text{CH}_2)_2^i\text{Pr}_2\text{P}$ vs. dppe) and the additional imide substitution for the NDI compounds **C** and **D** there is a very good agreement between calculated and experimental ^{13}C chemical shift values for the naphthalene moiety of (η^2 -NDI)(dppe) Ni^0 ($\text{R} = \text{OD}$).

This confirms that the reported Ni complex is of comparable structure with the Ni^0 complexes reported by Benn et al. Moreover, the very slight deviations $\Delta\delta$ point to a very similar steric interaction between naphthalene ring and phosphorus ligand, i.e., the imide structures present in **D** are hardly involved in the NDI – ligand interaction. This is in agreement with the results of our DFT calculations of Ni(0) complexes.

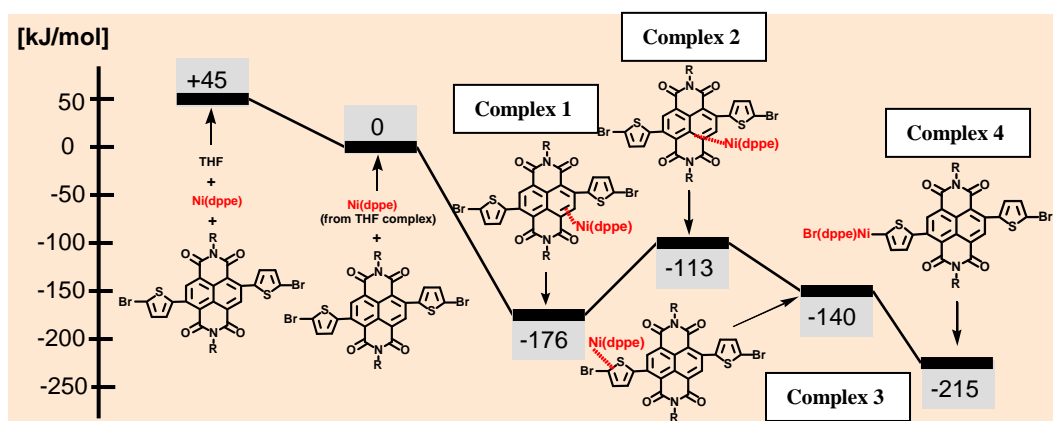
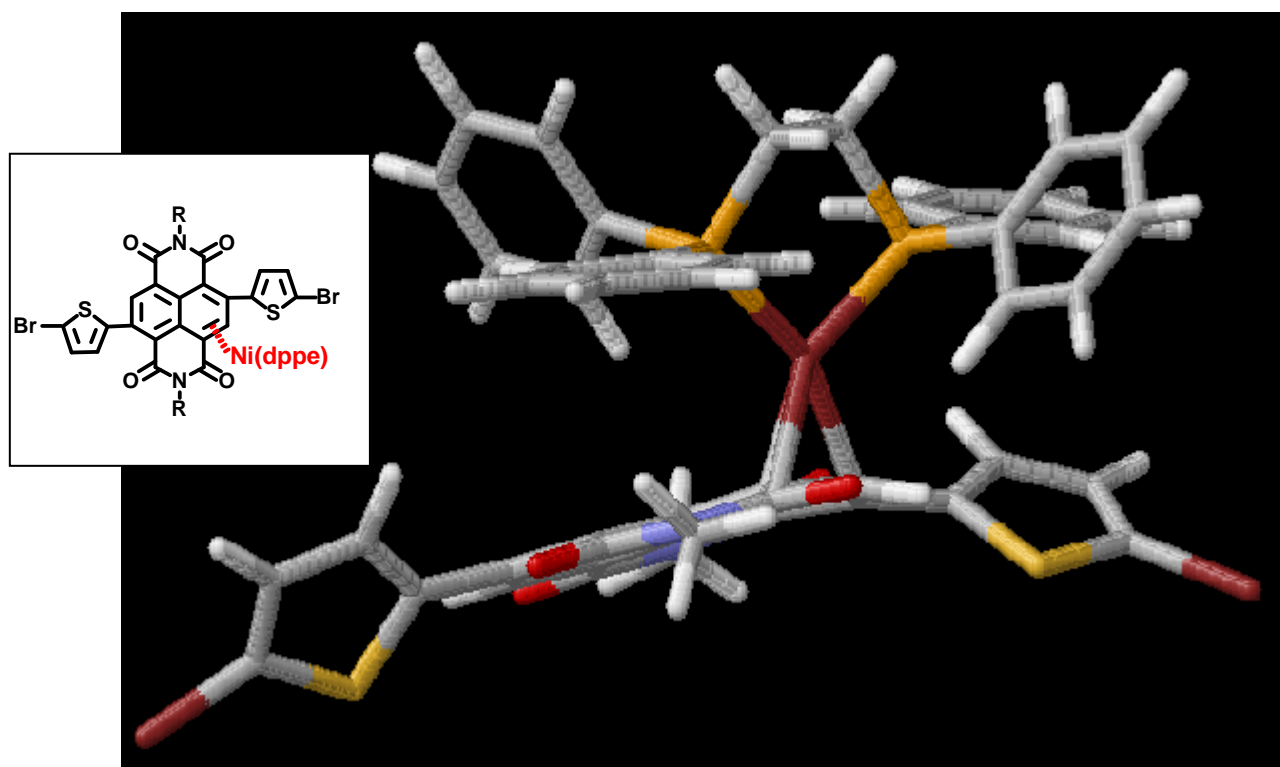


Figure S10. Relative energies for selected complexes between Ni(dppe) and 2,6-bis(2-bromothien-5-yl)naphthalene-1,4,5,8-tetracarboxylic-N,N'-bis(methyl) diimide for 0K temperatures (kJ/mol).

Complex 1, View 1:



Complex 1, View 2:

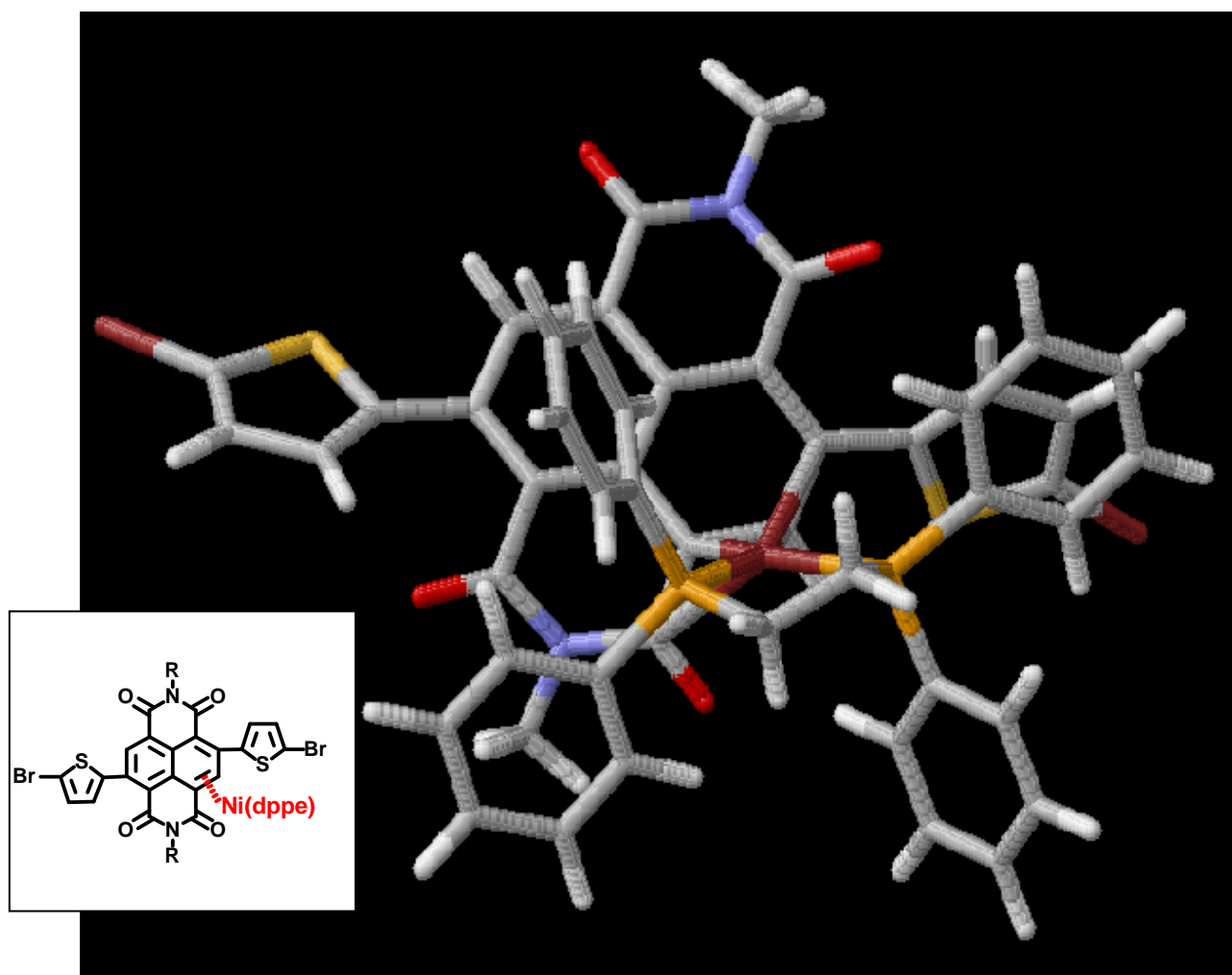
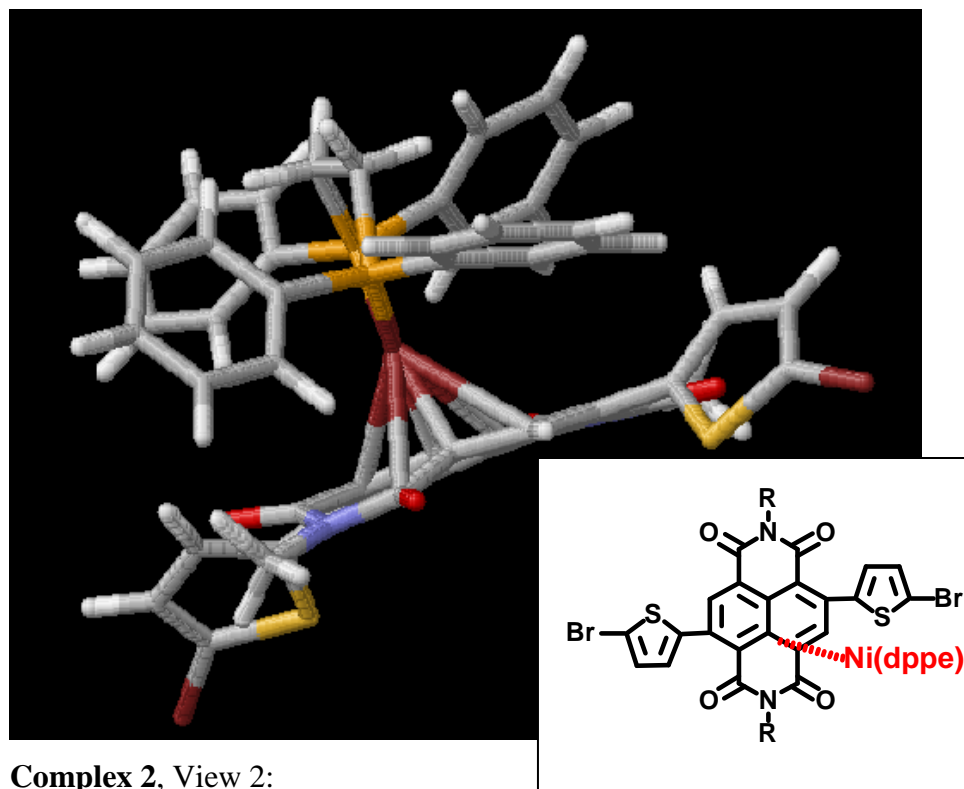


Figure S11. Structure of one of the DFT-calculated Ni(0) complexes of Br-Ar₁-Br with Ni(dppe) located as shown in an inset.

Complex 2, View 1:



Complex 2, View 2:

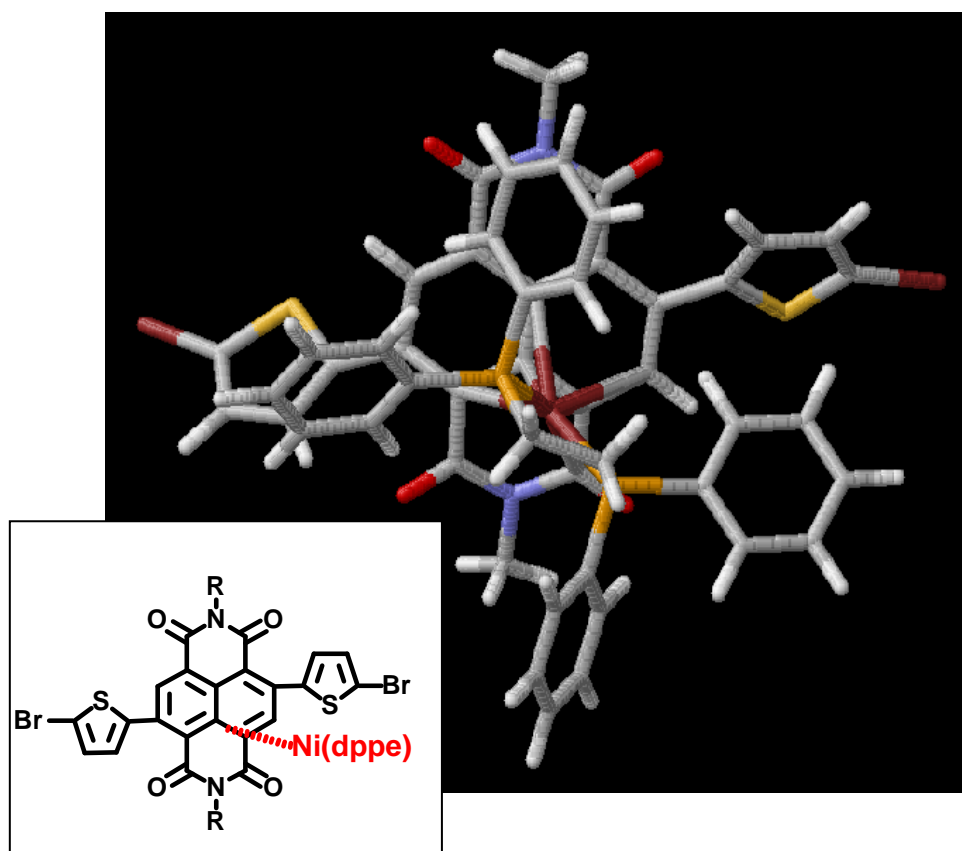


Figure S12. Structure of one of the DFT-calculated Ni(0) complexes of Br-Ar₁-Br with Ni(dppe) located as shown in an inset.

Complex 3, View 1:

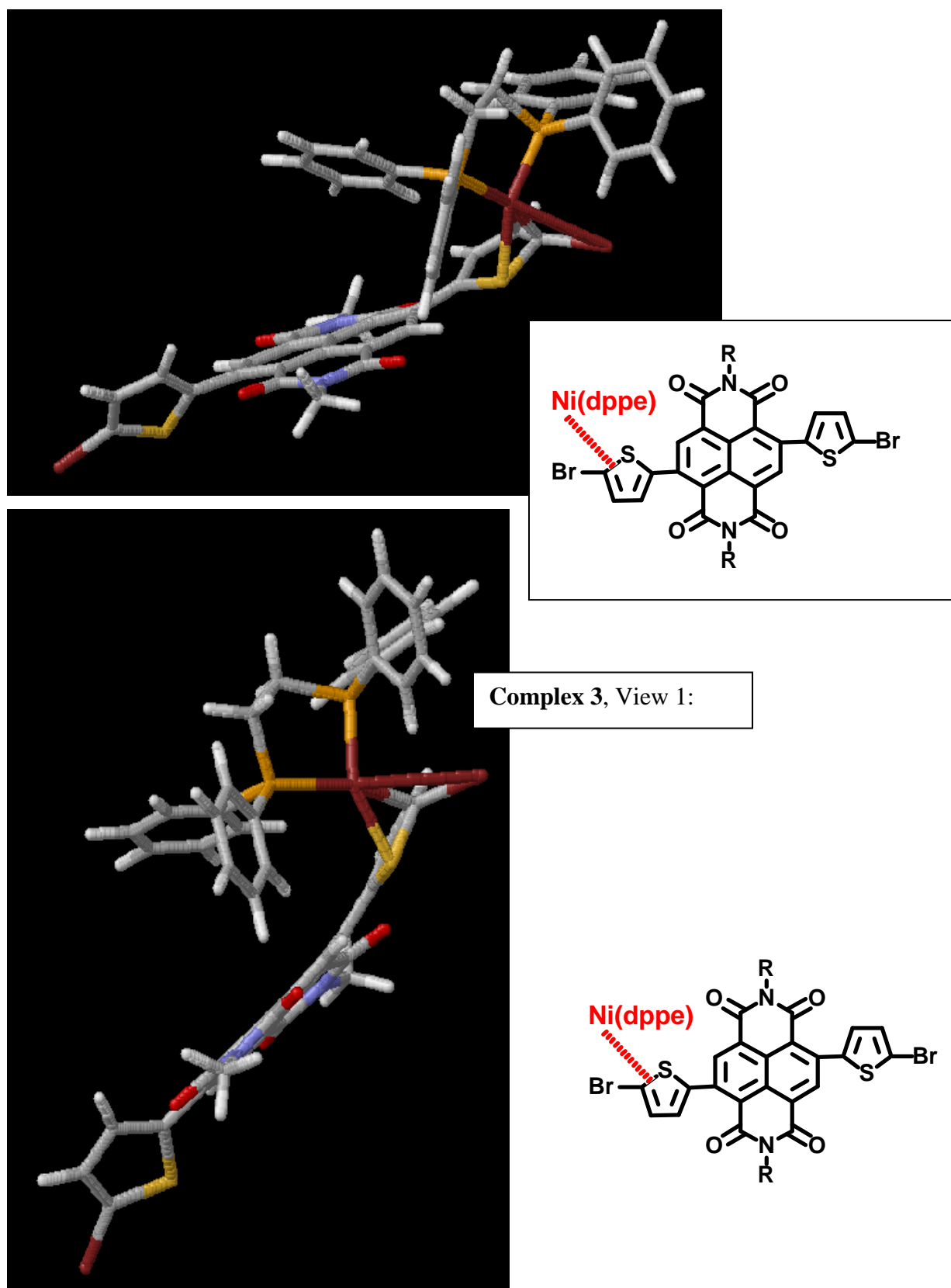


Figure S13. Structure of one of the DFT-calculated Ni(0) complexes of Br-Ar₁-Br with Ni(dppe) located as shown in an inset.

