Electronic Supplementary Material (ESI) for Dalton Transactions.

Chirality at metal and helical ligand folding in optical isomers of chiral *bis*(napthaldiminato)nickel(II) complexes

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Table S1. ESI (+)-MS (*m*/*z* (%)) spectral data of the compounds [a].

Compounds	**1*R***	**1*S***	**2*R***	**2*S***		**3*S*** [b]
$[M+H]^+$	607 (30)	607 (20)	667 (15)	667 (5)	$[M]^+$	764 (10)
$[M\text{-HL}]^+$	331 (58)	331 (45)			$[M\text{-HL}]^+$	411 (100)
$[HL+H]^+$			306 (10)	306 (10)	$[HL]^+$	353 (30)
$[C_{10}H_6(CHNH)(O)Ni]$	228 (100)	228 (100)			$[C_{10}H_6(CHNH)(O)Ni+H]$	229 (22)
$[CH(CH_3)(C_6H_4OCH_3)]^+$			135 (100)	135 (100)	$[C_6H_4(Br)(CHCH_3)]^+$	183 (30)
$[C_6H_4(Br)(CHCH_3)]^+$					$[C_{10}H_6(O)(CHNH)]^+$	170 (60)
$[CH(C_6H_5)(CH_3)]^+$	105 (33)	105 (25)	105 (15)	105 (20)	$[CH(C_6H_5)(CH_3)\text{-}H]^+$	104 (60)

[a] Isotopic distribution patterns for $^{58/60}$Ni (in **1*R***/**1*S*** and **2*R***/**2*S***) and combined $^{58/60}$Ni + $^{79/81}$Br (**3*R***/**3*S***) containing ions are clearly visible in the mass spectra; [b] EI-MS spectra.

Table S2. ^{1}H NMR (400 MHz) spectral data of the compounds in $CDCl_3$ at 20 ^{o}C.

Entity	C*H*$_3$	OC*H*$_3$	Ar-*H*	C*H*N
1*R*	1.97 (d, *J* = 6.5Hz, 6H)	-	6.64 (d, *J* = 9.2Hz, 2H), 6.78 (t, *J* = 7.4Hz, 2H), 7.05 (d, *J* = 8.4Hz, 2H), 7.34 (d, *J* = 8.4Hz, 4H), 7.42 (t, *J* = 7.4Hz, 4H), 7.60 (m, 6H), 7.74 (d, *J* = 8.8Hz, 2H)	11.05 (br, 2H)
1*S*	1.97 (d, *J* = 6.5Hz, 6H)	-	6.62 (d, *J* = 9.2Hz, 2H), 6.76 (t, *J* = 7.4Hz, 2H), 7.05 (d, *J* = 8.4Hz, 2H), 7.32 (d, *J* = 8.4Hz, 4H), 7.41 (t, *J* = 7.4Hz, 4H), 7.59 (m, 6H), 7.72 (d, *J* = 8.8Hz, 2H)	11.02 (br, 2H)
2*R*	2.01 (d, *J* = 6.5Hz, 6H)	3.83 (s, 6H)	6.56 (d, *J* = 7.2Hz, 2H), 6.96 (m, 6H), 7.09 (d, *J* = 8.4Hz, 2H), 7.36 (d, *J* = 8.4Hz, 2H), 7.56 (d, *J* = 7.4Hz, 4H), 7.61 (d, *J* = 8.4Hz, 2H), 7.88 (d, *J* = 8.8Hz, 2H)	12.81 (br, 2H)
3*R*	1.94 (d, *J* = 6.0Hz, 6H)	-	6.63 (d, *J* = 8.8Hz, 2H), 6.88 (d, *J* = 7.2Hz, 2H), 7.12 (t, *J* = 6.8Hz, 2H), 7.37 (d, *J* = 7.4Hz, 4H), 7.55 (d, *J* = 8.4Hz, 6H), 7.67 (d, *J* = 7.0Hz, 2H), 7.82 (d, *J* = 8.4Hz, 2H)	11.27 (br, 2H)

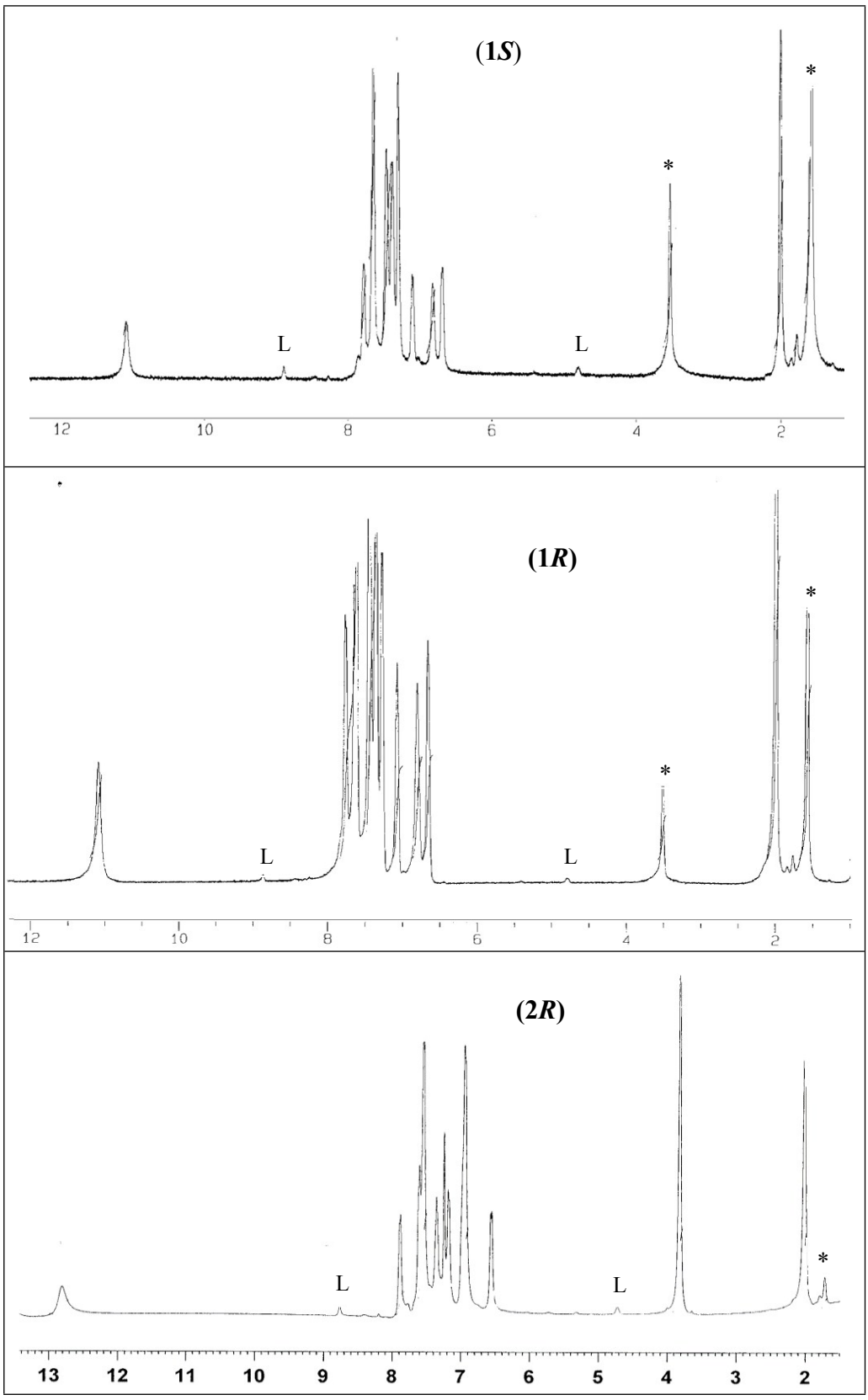


Figure S1. ^{1}H NMR (400 MHz) spectra of **1*S*** (top), **1*R*** (middle) and **2*R*** (bottom) in $CDCl_3$ at 20 ^{o}C. Peaks marked as "L" are due to free ligands, while asterisked peaks to methanol or water.

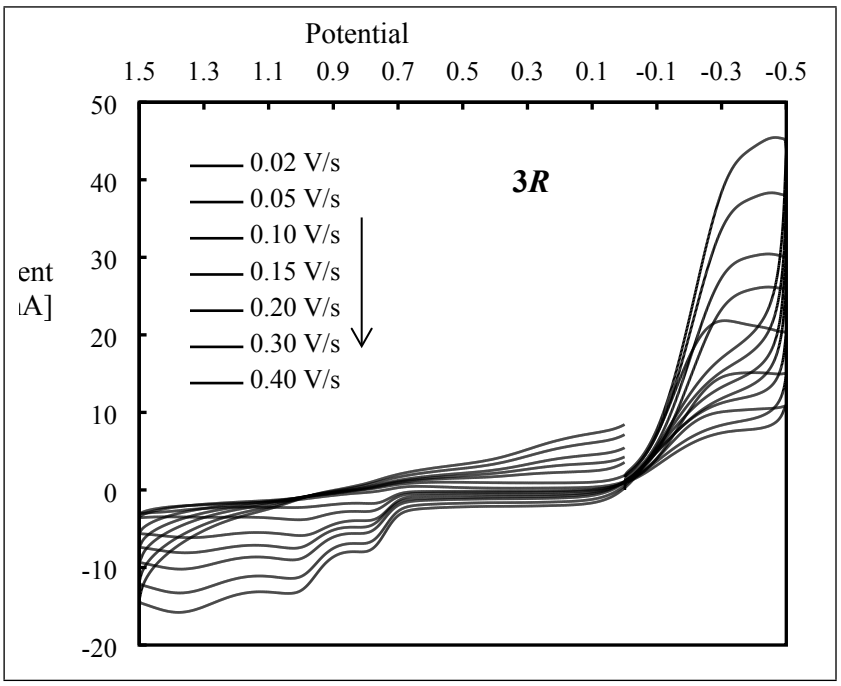


Figure S2. Cyclic voltammograms of ***3R*** (1.0 mmol/L); TBAP (0.1 mol/L) at varying scan rates in acetonitrile at 25 °C.

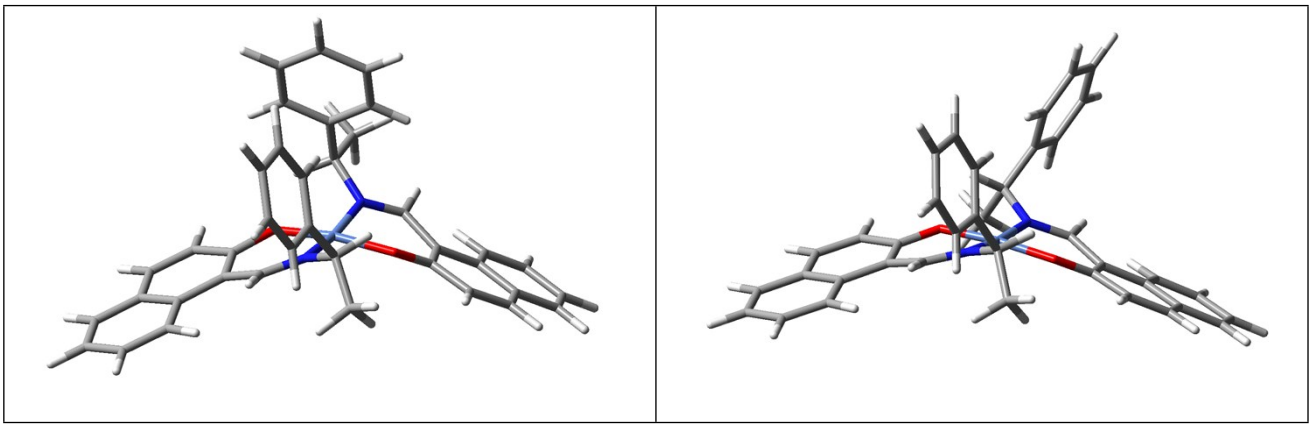


Figure S3. Lowest-energy DFT conformations calculated at B3LYP/6-31G(d) level for compound **Δ-Ni-1*R***. Left: absolute minimum; right, second minimum, +0.16 kcal/mol.

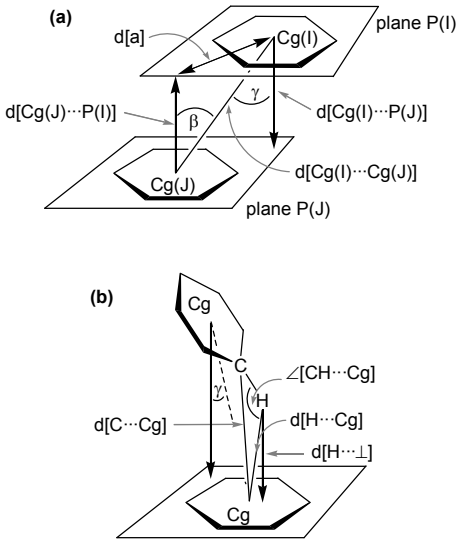
Analysis of supramolecular interactions in the crystals:

The supramolecular packing analyses are tabulated below.

The listed "Analysis of Short Ring-Interactions" in the PLATON geometry calculation for possible π-stacking interactions yielded rather rather long centroid-centroid distances (>4.0 Å) together with non-parallel ring planes (alpha >> 0°) and large slip angles (β, γ > 30°).

In comparison, significant π-stackings show rather short centroid-centroid contacts (<3.8 Å), near parallel ring planes (alpha < 10° to ~0° or even exactly 0° by symmetry), small slip angles (β, γ < 25°) and vertical displacements (slippage < 1.5 Å) which translate into a sizable overlap of the aryl-plane areas.[1]

Significant intermolecular C-H···π contacts start below 2.7 Å for the (C-)H···ring centroid distances with H-perp also below 2.6-2.7 Å and C-H··Cg > 145°.[1,2,3]



Scheme S1 Graphical presentation of the parameters used for the description of (a) π- π stacking and (b) CH-π interactions.

Packing Analysis for **Ni-*R*-L1 (1*R*)** for possible **CH-π interactions:**

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==========================================================================================
Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma <  30.0 Deg)
==========================================================================================
- Cg(J)   = Center of gravity of ring J (Plane number above)
- H-Perp  = Perpendicular distance of H to ring plane J
- Gamma   = Angle between Cg-H vector and ring J normal
- X-H..Cg = X-H-Cg angle (degrees)
- X..Cg   = Distance of X to Cg (Angstrom)
- X-H, Pi = Angle of the X-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees)
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X--H(I)	Res(I)	Cg(J) [ARU(J)]	H..Cg	H-Perp	Gamma	X-H..Cg	X..Cg	X-H,Pi
C(15) -H(15)	[1] ->	Cg(6) [2545.01]	2.83	-2.81	7.35	136	3.581(4)	41
C(18) -H(18)	[1] ->	Cg(6) [2645.01]	2.93	2.92	4.48	128	3.593(4)	40

C(19) -H(19) [1] -> Cg(7) [2645.01]	2.71	2.66	11.22	130	3.397(4)	50
C(37) -H(37) [1] -> Cg(16) [2656.02]	2.83	2.80	8.04	133	3.543(4)	49
C(38) -H(38) [1] -> Cg(17) [2656.02]	2.60	2.59	5.30	148	3.443(4)	58
C(53) -H(53) [2] -> Cg(4) [2656.01]	2.63	2.60	8.18	140	3.413(4)	57
C(54) -H(54) [2] -> Cg(3) [2656.01]	2.97	2.95	6.11	133	3.683(4)	45
C(70) -H(70C) [2] -> Cg(13) [2646.02]	2.89	2.81	13.26	155	3.797(4)	57
C(74) -H(74) [2] -> Cg(13) [1655.02]	2.67	-2.60	12.79	163	3.587(5)	78
Min or Max	2.600	-2.809	4.48	163.00	3.397	78.00

[2545] = -X,-1/2+Y,-Z
[2645] = 1-X,-1/2+Y,-Z
[2656] = 1-X,1/2+Y,1-Z
[2656] = 1-X,1/2+Y,1-Z
[2646] = 1-X,-1/2+Y,1-Z
[1655] = 1+X,Y,Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in
Cg(3) = Ring C1-C2-C3-C4-C9-C10
Cg(4) = Ring C4-C5-C6-C7-C8-C9
Cg(6) = Ring C20-C21-C22-C23-C28-C29
Cg(7) = Ring C23-C24-C25-C26-C27-C28
Cg(13) = Ring C39-C40-C41-C42-C47-C48
Cg(16) = Ring C58-C59-C60-C61-C66-C67
Cg(17) = Ring C61-C62-C63-C64-C65-C66

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Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma < 30.0 Deg)

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- Cg(J) = Center of gravity of ring J (Plane number above)
- H-Perp = Perpendicular distance of H to ring plane J
- Gamma = Angle between Cg-H vector and ring J normal
- X-H..Cg = X-H-Cg angle (degrees)
- X..Cg = Distance of X to Cg (Angstrom)
- X-H, Pi = Angle of the X-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees)

X--H(I) Res(I) Cg(J) [ARU(J)]	H..Cg	H-Perp	Gamma	X-H..Cg	X..Cg	X-H,Pi
C(15) -H(15) [1] -> Cg(17) [1545.02]	2.60	-2.59	5.36	147	3.438(3)	58
C(16) -H(16) [1] -> Cg(16) [1545.02]	2.84	-2.81	8.39	133	3.551(4)	49
C(34) -H(34) [1] -> Cg(4) [2655.01]	2.70	2.65	10.86	130	3.394(3)	50
C(35) -H(35) [1] -> Cg(3) [2655.01]	2.93	2.92	4.36	128	3.587(3)	40
C(38) -H(38) [1] -> Cg(3) [2555.01]	2.84	-2.82	7.71	136	3.593(3)	41
C(56) -H(56) [2] -> Cg(6) [1555.01]	2.96	2.94	6.08	134	3.678(4)	45
C(57) -H(57) [2] -> Cg(7) [1555.01]	2.63	2.60	8.33	139	3.406(3)	57
C(70) -H(70C) [2] -> Cg(13) [2656.02]	2.89	-2.81	13.22	155	3.796(4)	57
C(74) -H(74) [2] -> Cg(13) [1455.02]	2.66	2.60	12.44	164	3.586(4)	78
Min or Max	2.600	-2.819	4.36	164.00	3.394	78.00

[1545] = X,-1+Y,Z
[2655] = 1-X,1/2+Y,-Z
[2555] = -X,1/2+Y,-Z
[1555] = X,Y,Z
[2656] = 1-X,1/2+Y,1-Z
[1455] = -1+X,Y,Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in
Cg(3) = Ring C1-C2-C3-C8-C9-C10
Cg(4) = Ring C3-C4-C5-C6-C7-C8
Cg(6) = Ring C20-C21-C22-C27-C28-C29
Cg(7) = Ring C22-C23-C24-C25-C26-C27
Cg(13) = Ring C39-C40-C41-C46-C47-C48
Cg(16) = Ring C58-C59-C60-C65-C66-C67

Cg(17) = Ring C60-C61-C62-C63-C64-C65

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