#### **Supporting Information**

## for

# Chirality transfer based on reversible C-C bond formation/breaking in nickel complexes

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# **Synthetic procedures**

**General procedures.** All of the synthetic reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere. The reagents were commercial samples and were not purified further.

NMR spectra were recorded with a ECP-300 spectrometer using tetramethylsilane as internal standard ( $\delta$  0). UV/vis/NIR spectra were measured on a JASCO V 570 spectrophotometer. CD spectra were measured on a JASCO J-725 spectrometer. The X-ray crystal diffraction measurements of the single crystals were made on a Rigaku RAXIS RAPID. Elemental analyses were performed on Perkin Elmer 2400 CHN analyzer.

Synthesis of 1. A sample of (1R)-(-)-myrtenal (0.57 g, 3.6 mmol) was added to a solution of 2-aminobenzenethiol (0.49 g, 3.9 mmol) in 20 cm<sup>3</sup> of ethanol. The mixture was heated under reflux for 3 h and cooled to room temperature. A sample of Ni(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O (0.46 g, 1.9 mmol) was then added to this reaction solution that

was confirmed to contain (1*R*)-(–)-myrtenal-derived benzothiazoline by <sup>1</sup>H NMR spectroscopy. The mixture was stirred at room temperature overnight and the resulting brown powder (1) was collected by filtration and then washed with methanol and *N*,*N*-dimethylformamide. Yield: 0.31 g, 29%. Anal. Found for 1: C, 66.98; H, 6.30; N, 4.93%. Calcd for C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>NiS<sub>2</sub>: C, 67.26; H, 6.35; N, 4.90%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.06 (1H, s), 7.47 (1H, s, azomethine-H), 7.41 (1H, d, *J* = 8.1, benzene), 7.02 (1H, t, *J* = 7.4, benzene), 6.96 (1H, d, *J* = 7.3, benzene), 6.81 (1H, t, *J* = 7.0, benzene), 2.55 – 2.47 (2H, m), 2.36 (1H, br), 2.29 (1H, br), 2.07 (1H, br), 1.32 (3H, s, CH<sub>3</sub>), 1.03 (1H, d, *J* = 8.4), 0.81 (3H, s, CH<sub>3</sub>). UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}/nm$  ( $\Delta\epsilon/M^{-1}$  cm<sup>-1</sup>); 637 (–2.75), 521 (+7.31), 369 (–13.7), 319 (–28.4).

Synthesis of 2. A suspension of 1 (0.50 g, 8.8 mmol) in 30 cm<sup>3</sup> of THF was stirred at 30~40 °C for 4 h. After filtration, the dark brown filtrate was evaporated to dryness. The resulting dark brown powder was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) and then poured onto a silica gel column. The elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) gave mainly three bands (dark violet, yellow and dark brown bands). The first violet band was collected and evaporated to dryness to give a violet powder (2). Single-crystals of 2 suitable for X-ray analysis were grown by slow evaporation of a pentane solution of a violet powder. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.68 (1H, d, *J* = 8.0, benzene), 7.47 (1H, d, *J* = 8.6, benzene), 7.20 (1H, t, *J* = 7.1, benzene), 7.13 (1H, t, *J* = 7.6, benzene), 5.52 (1H, s), 5.13 (1H, s), 2.30 – 2.22 (2H, m), 2.17 – 2.14 (2H, m), 2.02 (2H, br), 1.19 (3H, s, CH<sub>3</sub>), 0.94 (3H, s, CH<sub>3</sub>).

Synthesis of 3. A suspension of 1 (0.63 g, 1.1 mmol) in 30 cm<sup>3</sup> of toluene was heated under reflux for 45 min. After filtration, the dark brown filtrate was evaporated to dryness. The resulting dark brown powder was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) and then poured onto a silica gel column. The elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) gave mainly three bands (dark violet, brown and dark brown bands). The first violet band was collected and evaporated to dryness to give a dark violet powder (A), which was found to be a 1:1 mixture of 2 and 3 by NMR spectral measurement. When a pentane solution of this powder was allowed to stand at room temperature in a vessel, dark violet crystals of **3** appeared at the side of the vessel with the concomitant appearance of brown crystals of 1 at the bottom of the vessel. One of the crystals of 3 thus obtained was used for X-ray analysis. Single-crystals of 1 suitable for X-ray analysis were obtained by the slow diffusion of pentane into a CH<sub>3</sub>CN solution of a dark violet powder (A). Anal. Found for 3: C, 67.48; H, 6.70; N, 4.86%. Calcd for  $C_{32}H_{36}N_2NiS_2$ : C, 67.26; H, 6.35; N, 4.90%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.68 (1H, d, J = 8.2, benzene), 7.42 (1H, d, J = 8.6, benzene), 7.19 (1H, t, J = 7.4, benzene), 7.13 (1H, t, J = 7.7, benzene), 5.54 (1H, s), 5.01 (1H, s), 2.45 - 2.36 (2H, m), 2.19 -2.14 (2H, m), 2.05 - 2.00 (2H, m), 1.16 (3H, s, CH<sub>3</sub>), 0.37 (3H, s, CH<sub>3</sub>). UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}/nm$  ( $\epsilon/M^{-1}$  cm<sup>-1</sup>); 836 (3.4 × 10<sup>4</sup>), 359<sup>sh</sup> (4.7 × 10<sup>3</sup>). CD (CHCl<sub>3</sub>):  $\lambda_{max}/nm$  ( $\Delta\epsilon/M^{-1}$  cm<sup>-1</sup>); 738 (-4.46), 615 (-0.221), 578 (-1.70), 512 (+1.42), 454<sup>sh</sup> (+1.04), 369 (-4.14), 337 (+2.64), 312 (-4.40).

# X-ray crystallography

The crystallographic data and details of data collection for **1**, **2** and **3** are given in Table S1. X-ray crystallographic data for **1**, **2** and **3** were collected with the  $\omega$  scan technique on a Rigaku RAXIS-RAPID image plate diffractometer with graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71075$  Å) radiation at 200 K. Empirical absorption corrections were applied. The structures of **1** and **2** were solved by direct methods using SHELXS-97<sup>1</sup> and were refined with full-matrix least-squares on  $F^2$ . All calculations were performed using Yadokari-XG 2009 software package,<sup>2</sup> except the refinements that were performed using SHELXL-97.<sup>1</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms for **1** and **2** were included in calculated positions and refined using a riding model. The solution and refinement procedures for **3** were made with the CrystalStructure software package.<sup>3</sup> The structure of **3** was solved by direct methods using SIR 92<sup>4</sup> and refined anisotropically for all nonhydrogen atoms with full-matrix least-squares calculations on  $F^2$ . Hydrogen atoms for **3** were found by Fourier difference and then refined.

## **References:**

- 1 G. M. Sheldrick, Acta Cryst., 2008, A64, 112.
- 2 C. Kabuto, S. Akine, T. Nemoto and E. Kwon, J. Cryst. Soc. Jpn., 2009, 51, 218.
- 3 Rigaku/MSC, CrystalStructure. Version 3.6.0. Rigaku/MSC, The Woodlands, Texas, USA, 2004.
- 4 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.

	1	2	3
empirical formula	C <sub>32</sub> H <sub>36</sub> N <sub>2</sub> NiS <sub>2</sub>	C <sub>32</sub> H <sub>36</sub> N <sub>2</sub> NiS <sub>2</sub>	C <sub>32</sub> H <sub>36</sub> N <sub>2</sub> NiS <sub>2</sub>
formula weight	571.46	571.46	571.46
crystal system	monoclinic	orthorhombic	orthorhombic
space group	<i>C</i> 2	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
a, Å	19.657(13)	10.902(3)	11.963(3)
b, Å	6.820(4)	14.769(3)	12.171(4)
<i>c</i> , Å	11.259(7)	17.363(5)	19.720(6)
$\beta$ , deg.	115.435(11)		
$V, Å^3$	1363.2(14)	2795.6(12)	2871.4(15)
Ζ	2	4	4
<i>F</i> (000)	604	1208	1208
$D_{\rm calcd}$ , g cm <sup>-3</sup>	1.392	1.358	1.322
$\mu$ , mm <sup>-1</sup>	0.890	0.868	0.845
reflections collected	6694	26301	27958
indep. reflns ( $R_{int}$ )	2733 (0.0573)	6334 (0.3625)	6543 (0.0577)
$R1 (I > 2\sigma(I))$	0.0478	0.0772	0.0438
wR2 (all data)	0.1104	0.1119	0.0860
goodness-of-fit on $F^2$	1.061	0.919	1.046
Flack parameter	0.001(19)	0.03(3)	-0.021(12)

Table S1. Crystallographic data for 1, 2 and 3

Table S2. Selected bond distances  $(\text{\AA})$  of 1, 2 and 3

	1	2	3
Ni1-N1	1.904(3)	1.799(6)	1.813(2)
Ni1-N2		1.819(7)	1.807(2)
Ni1-S1	2.1748(13)	2.119(3)	2.1263(11)
Ni1-S2		2.118(2)	2.1328(11)
S1-C1	1.753(4)	1.720(8)	1.723(4)
S2-C17		1.715(10)	1.732(4)
N1-C6	1.438(4)	1.358(11)	1.357(4)
N1-C7	1.299(5)	1.472(10)	1.465(3)
N2-C22		1.354(10)	1.357(4)
N2-C23		1.465(8)	1.467(3)



Figure S1. Absorption (top) and CD (bottom) spectra of 1 and 3 in CHCl<sub>3</sub>.



**Figure S2.** <sup>1</sup>H NMR spectra of **2** in CDCl<sub>3</sub>; (a) just after the dissolution, (b) after 1 h, (c) after 4 h, (d) after 1 day.  $\times$  indicates CHCl<sub>3</sub> and impurity peaks.



**Figure S3.** <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>: a dark violet powder (**A**) obtained immediately after the elution (bottom) and a dark violet powder obtained after allowing the eluate to stand at room temperature overnight (top) in CDCl<sub>3</sub>.



Figure S4. CD spectra of 2 and 3 in CHCl<sub>3</sub>.