From Antiaromatic Norcorrolatonickel(II) to Aromatic and Non-aromatic Zwitterions: Innocent Ligands with Unbalanced Charge of the Core

Supporting Information

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Figure S90. Thermal ellipsoid plots of the crystal structure of 5

Table S3. Electrochemical potentials for 3-R, 4-R, and 5

Table S4. Computational details for structures discussed in the paper

References
General methods and instrumentation

Commercial reagents were used without further purification. Solvents were freshly distilled from the appropriate drying agents or purified under nitrogen with the mBraun MBSPS-800 before use. The analytical TLCs were performed with silica gel 60 F254 plates. Column chromatography was performed by using silica gel 60 (200-300 mesh ASTM). The NMR spectra were recorded on a Bruker Avance II spectrometer, operating at 500 MHz for $^1$H and 125 MHz for $^{13}$C or a Bruker Avance II spectrometer operating at 600 MHz for $^1$H and 150 MHz for $^{13}$C. TMS was used as an internal reference for $^1$H and $^{13}$C chemical shifts and CDCl$_3$ was used as solvent. For $^{31}$P NMR the 85% H$_3$PO$_4$ solution in water was used as external standard. Standard pulse programs from the Bruker library were used for 2D experiments. Mass spectrometry measurements were conducted by using the electrospray ionization technique on a Bruker apex ultra FT or Finnigan LCQ Advantage MAX mass spectrometer. Absorption UV/Vis/NIR spectra were recorded by using a Varian Cary 50 Bio and Jasco V-770 spectrophotometers. EPR spectra (X-band) were recorded on a Bruker ELEXSYS E500 spectrometer and were simulated using WinEPR Simfonia v.1.25 (shareware version) by Bruker. The applied dichloromethane was freshly distilled over calcium hydride. HPLC separations were carried out by means of Chirex 3010 analytical column (25 cm length, 4.6 mm i.d.) packed with 5 mm silica gel coated with covalently bound (S)-valine and dinitroaniline using Shimadzu chromatographic system or Merck-Hitachi LaChrom series connected to a flow-cell mounted on Jasco J-1500 spectropolarimeter. HPLC-grade hexane was used. Circular dichroism spectra were obtained directly in the flow cell by means of pseudo stopped-flow technique using a Jasco J-1500 spectropolarimeter. Electrochemical measurements were performed by means of Autolab (Metrohm) potentiosstat/galvanostat system for dichloromethane solutions with a glassy carbon, a platinum wire, and Ag/AgCl as the working, auxiliary, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. The potentials were referenced with the ferrocene/ferrocenium couple used as internal standard.

Crystals of 3-Et were obtained by slow diffusion of the dichloromethane solution into hexane while crystal of 5 were obtained by slow evaporation of the dichloroethane/hexane solution. Data collection of 3-Et was performed at the Bruker APEX-II CCD diffractometer at room temperature with synchrotron radiation (monochromatic wavelength of 0.6525 Å). Crystal data for 5 was collected at low temperature using XtaLAB Synergy R, HyPix diffractometer with Cu Kα radiation ($\lambda = 1.54184$ Å). Data reduction and analysis were carried out with the SAINIT$^{[1]}$ and CrysAlisPRO programs$^{[2]}$. The structure was solved by using the SHELXT$^{[3]}$ and refined by the full-matrix least-squares method on all F$^2$ data using the SHELXL$^{[4]}$. All hydrogen atoms, including those located in the difference density map, were placed in calculated positions and refined as the riding model. See Table S1 for detailed data. The full structure and diffraction data are available in Cambridge Crystallographic Data Center under the CCDC numbers 2040257 (3-Et) and 2040258 (5).

Computational methods

Density functional theory (DFT) calculations were performed by using the Gaussian 09.E01 program$^{[5]}$. DFT geometry optimizations were carried out in the unconstrained C$_1$ symmetry by using the X-ray structure, molecular mechanics, or semiempirical models as starting geometries. DFT geometries were refined with the polarizable continuum model of solvation (PCM, standard dichloromethane
parametrization) to meet standard convergence criteria, and the existence of a local minimum was verified by a normal mode frequency calculation. DFT calculations were performed by using the hybrid B3LYP functional\cite{6-8} functional combined with the 6-31G(d,p) basis set for organic part of analyzed molecules and LANL2DZ pseudopotential for nickel(II) center. The structure optimization results are collected in the Table S3. The electronic spectra were simulated by means of time-dependent density functional theory (TD-DFT) using the Tamm-Dancoff approximation for 50 states. The electronic transitions and UV/Vis/NIR as well as CD spectra were analyzed by means of the GaussSum program.\cite{9} The transitions were convoluted by Gaussian curves with 2000 cm$^{-1}$ half line width. The population analysis was performed with NBO5.0 package implemented in Gaussian. The charge distribution was analyzed with Multiwfn 3.7. The graphic representation was obtained with an application of Multiwfn package and GaussView5.0 with using a formatted check point files.
From antiaromatic norcorrolatonickel(II) to aromatic and non-aromatic diamagnetic zwitterions: innocent ligands with unbalanced charge of the core

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Table S1 Crystal data for 3-Et

| Crystal data                      |                  |
|----------------------------------|------------------|
| Chemical formula                 | C_{56}H_{66}N_{5}NiO_{6}P |
| $M_r$                            | 994.81           |
| Crystal system, space group      | Monoclinic, P2_1/c |
| Temperature (K)                  | 273              |
| $a$, $b$, $c$ (Å)                | 13.739 (1), 14.663(1), 25.820(2) |
| $β$ (°)                          | 103.17 (4)       |
| $V$ (Å³)                         | 5064.8 (8)       |
| $Z$                              | 4                |
| Radiation type                   | $λ = 0.6525$ Å   |
| $μ$ (mm⁻¹)                       | 0.38             |
| Crystal size (mm)                | 0.24 × 0.2 × 0.16 |

| Data collection                  |                  |
|----------------------------------|------------------|
| Diffractometer                   | Bruker APEX-II CCD |
| No. of measured, independent and |                  |
| observed [$I > 2σ(I)$] reflections| 56988, 8729, 7406 |
| $R_{int}$                        | 0.070            |
| $(\sin θ/λ)_{\text{max}}$ (Å⁻¹) | 0.603            |

| Refinement                      |                  |
|----------------------------------|------------------|
| $R(F^2 > 2σ(F^2))$, $wR(F^2)$, $S$| 0.139, 0.308, 1.14 |
| No. of reflections               | 8729             |
| No. of parameters                | 634              |
| No. of restraints                | 411              |
| H-atom treatment                 | H-atom parameters constrained |
| $w = 1/[σ^2(F_o^2) + (0.0282P)^2 + 56.3031P]$ | |
| $Δρ_{\text{max}}$, $Δρ_{\text{min}}$ (e Å⁻³) | 1.43, −0.99 |
Table S2 Crystal data for 5

| Crystal data                                      |                                         |
|--------------------------------------------------|-----------------------------------------|
| Chemical formula                                 | $2\text{C}_{48}\text{H}_{56}\text{N}_{5}\text{NiO}_{2}\text{P} \cdot \text{C}_{2}\text{H}_{4}\text{Cl}_{2}$ |
| $M_r$                                            | 1748.26                                  |
| Crystal system, space group                      | Triclinic, $P\bar{1}$                   |
| Temperature (K)                                  | 170                                      |
| $a$, $b$, $c$ (Å)                                | 11.437(1), 14.614 (1), 27.058(2)         |
| $\alpha$, $\beta$, $\gamma$ (°)                 | 96.28 (1), 96.34 (1), 101.03 (1)         |
| $V$ (Å$^3$)                                      | 4372.34 (6)                              |
| $Z$                                              | 2                                        |
| Radiation type                                   | Cu Kα                                    |
| $\mu$ (mm$^{-1}$)                                | 1.90                                     |
| Crystal size (mm)                                | $0.37 \times 0.18 \times 0.03$           |

Data collection

| Diffractometer                                   | XtaLAB Synergy R, HyPix                  |
| No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections | 63192, 17396, 16667                      |
| $R_{int}$                                        | 0.026                                    |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å$^{-1}$) | 0.628                                    |

Refinement

| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$           | 0.046, 0.128, 1.03                        |
| No. of reflections                                | 17396                                    |
| No. of parameters                                 | 1080                                     |
| H-atom treatment                                  | H-atom parameters constrained            |
| $\Delta_{\text{pmax}}$, $\Delta_{\text{pmin}}$ (e Å$^{-3}$) | 1.01, −0.99                              |
Synthesis and characterization

Synthesis of the precursor. Starting norcorrolatonickel(II) complex 1 and its 3-nitro-derivative were obtained as described previously.\textsuperscript{[10,11]}

Scheme S1. Addition of dialkylacetylenedicarboxylate and tributylphosphine to 3-nitro-5,14-dimezytyl-norcorrolatonickel(II)

General procedure for addition of dialkyl acetylenedicarboxylate and tributyl phosphine to 3-nitrocorrolatonickel(II) 1-NO$_2$

A solution of NO$_2$-norcorrole nickel complex 1-NO$_2$ (31 mg, 0.05 mmol), Bu$_3$P (62 mg, 0.25 mmol) and dimethyl acetylenedicarboxylate (62 mg, 0.5 mmol) or diethyl acetylenedicarboxylate (80 mg, 0.5 mmol) in 4 mL of dichloromethane was stirred at room temperature for 2 h. The solvent was then evaporated under vacuum. The residue was chromatographed on a silica gel column with dichloromethane as eluent. Green product fraction was collected. After solvent removal, the solid was washed with hexane to afford the desired product as a brown powder for 3-Me in 52% yield (24 mg) and 3-Et in 51% yield (25 mg).

Selected data for 3-Me and 3-Et:
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21.1, 20.9, 20.6, 13.0. "31P NMR (202 MHz, CDCl3, 298 K) δP = 28.3. UV-vis (CH2Cl2) λmax/nm (ε/1000): 250 (sh), 313 (sh), 336 (42.9), 451 (37.8), 472 (sh), 573 (sh), 615 (25.1), 663 (sh). ESI-HRMS calc. for [C54H62N5NiO6P]+ (M+H)+: 966.3864, Found 966.3851.

Scheme S2. Hydrolysis of 3-R.

Hydrolysis of 3-R

A sample of 20 mg of 3-Me or 3-Et was dissolved in 2 mL of chloroform/ethanol mixture (80/20 v/v) and 50 mg of basic alumina (Brockman 3°) was added. The slurry was sonicated in ultrasonic bath for 1-3 h. The solid was then separated from the solution by filtration and washed with 2 portion of 5 mL of chloroform. The filtrate was then evaporated to dryness, dissolved in dichloromethane and passed a short silica-gel column. The red eluate was collected and evaporated to 10% of its original volume. The product 4 was precipitated by addition of hexane.
and collected by filtration. Yields: 17 mg (90%) for 4-Me and 17.2 mg (93%) for 4-Et.

Selected data for 4-Me and 4-Et:

4-Me: \( ^1H \) NMR (600MHz, CDCl\(_3\), 298K): \( \delta_H = 9.084 (s, 1H, \beta-2/2a), 9.079 (s, 1H, \beta-2/2a), 8.41 (d, \( \begin{array}{l} J = 4.3 \text{ Hz, 1H, } \beta-18/18a \end{array} \)), 8.40 (d, \( \begin{array}{l} J = 4.3 \text{ Hz, 1H, } \beta-18/18a \end{array} \)), 8.29 (d, \( \begin{array}{l} J = 5.1 \text{ Hz, 1H, } \beta-8/12 \end{array} \)), 8.25 (d, \( \begin{array}{l} J = 5.0 \text{ Hz, 1H, } \beta-7/13 \end{array} \)), 8.24 (d, \( \begin{array}{l} J = 5.2 \text{ Hz, 1H, } \beta-8/12 \end{array} \)), 8.19 (d, \( \begin{array}{l} J = 5.0 \text{ Hz, 1H, } \beta-7/13 \end{array} \)), 8.14 (d, \( \begin{array}{l} J = 5.1 \text{ Hz, 1H, } \beta-7/13 \end{array} \)), 8.12 (d, \( \begin{array}{l} J = 4.7 \text{ Hz, 1H, } \beta-7/13 \end{array} \)), 7.99 (d, \( \begin{array}{l} J = 4.2 \text{ Hz, 2H, } \beta-8/12 \end{array} \)), 7.934 (d, \( \begin{array}{l} J = 4.3 \text{ Hz, 1H, } \beta-17/17a \end{array} \)), 7.15 (s, 1H, \( m_\text{-Mes} \)), 7.14 (s, 2H, \( m_\text{-Mes} \)), 7.12 (s, 1H, \( m_\text{-Mes} \)), 7.10 (s, 1H, \( m_\text{-Mes} \)), 7.08 (s, 1H, \( m_\text{-Mes} \)), 7.06 (s, 1H, \( m_\text{-Mes} \)), 7.04 (s, 1H, \( m_\text{-Mes} \)), 6.68 (d, \( \begin{array}{l} J_{HP} = 16.5 \text{ Hz, 1H, } 1^\prime/1^\prime a \end{array} \)), 6.64 (d, \( \begin{array}{l} J_{HP} = 16.5 \text{ Hz, 1H, } 1^\prime/1^\prime a \end{array} \)), 3.82 (s, 3H, \( 2^-/2^-2a \)), 2.53 (s, 6H, \( p_\text{-Me} \)), 2.48 (s, 3H, \( p_\text{-Me} \)), 2.22 (m, 6H, \( 1^\prime/1^\prime a \)), 1.97 (s, 3H, \( o_\text{-Me} \)), 1.96 (m, 6H, \( 1^\prime/1^\prime a \)), 1.95 (s, 3H, \( o_\text{-Me} \)), 1.91 (s, 3H, \( o_\text{-Me} \)), 1.85 (s, 3H, \( o_\text{-Me} \)), 1.84 (s, 3H, \( o_\text{-Me} \)), 1.81 (s, 3H, \( o_\text{-Me} \)), 1.75 (s, 3H, \( o_\text{-Me} \)), 1.69 (s, 3H, \( o_\text{-Me} \)), 1.12 (m, 6H, \( 2^-/2^-2a \)), 1.06 (m, 18H, \( 3^\prime/3^-3a \)), 0.96 (m, 6H, \( 2^-/2^-2a \)), 0.557 (t, \( \begin{array}{l} J = 7.2 \text{ Hz, 9H, } 4^-/4^\prime a \end{array} \)), 0.554 (t, \( \begin{array}{l} J = 7.2 \text{ Hz, 9H, } 4^-/4^\prime a \end{array} \)). \( ^{13}C(\text{H}) \) NMR (125MHz, CDCl\(_3\), 298 K) \( \delta_C = 171.7, 142.64, 142.56, 142.4, 141.4, 141.1, 139.4, 139.3, 139.0, 138.9, 138.6, 138.5, 138.4, 138.4, 138.3, 137.9, 136.8, 136.8, 136.0, \), 135.5, 133.49, 132.35, 132.30, 132.2, 129.33, 129.27, 127.6, 127.4, 127.3, 127.1, 126.8, 126.7, 126.4, 126.2, 121.8, 121.7, 121.2, 120.6, 117.8, 117.0, 115.0, 112.9, 89.0, 54.1, 47.2 (d, \( \begin{array}{l} J_{HP} = 44.8 \text{ Hz} \end{array} \)), 46.9 (d, \( \begin{array}{l} J_{HP} = 44.8 \text{ Hz} \end{array} \)), 29.7, 23.7, 23.6, 21.6, 21.4, 21.3, 21.2, 21.0, 20.94, 20.87, 20.7, 19.93, 19.8, 19.6, 19.5, 12.8. \( ^{31}P(\text{H}) \) NMR (202 MHz, CDCl\(_3\), 298 K) \( \delta_P = 35.8, 35.5 \). UV-vis (CHCl\(_3\)) \( \lambda_{\text{max}} \text{/nm (} \epsilon/1000 \text{): 315 (15.3), 333 (14.7), 386 (41.1), 450 (34.8), 617 (21.9). ESI-HRMS calc. for [\text{C}_{25}H_{60}N_5NiO_4P]^+ (M)^+: 907.3731, Found 907.3631. \)
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Scheme S3. Addition of tributylphosphine to 3-nitro-5,14-dimezytl-norcorrolatonickel(II)

Addition of tributyl phosphine to 3-nitrocorrolatonickel(II) 1-NO$_2$

A sample of 12 mg (0.02 mmol) of 1-NO$_2$ was dissolved in 1 mL of chloroform and 10 µL of tributylphosphine (8 mg, 0.04 mmol) was added. The sample turned blue after 5 minutes. The reaction mixture was allowed to react for 2 h at room temperature until TLC analysis indicated disappearance of the starting material. The sample was then passed down a short silica column with dichloromethane as eluent and the purple fraction was collected. The product was precipitated by addition of hexane and collected by filtration. Yield: 7.5 mg (47%). The crystals suitable for X-ray diffraction analysis were obtained by a slow diffusion od hexane into dichloroethane solution of 5.

Selected properties of 5:

$^1$H NMR (500MHz, CDCl$_3$, 298K): $\delta$ = 7.05 (s, 1H, $\beta$-2), 6.92 (s, 3H, m-Mes), 6.56 (s, 1H, m-Mes), 6.50 (d, $^3$$J_{H,P}$=3.8 Hz, 1H, $\beta$-8), 6.45 (d, $^3$$J_{H,H}$=4.2 Hz, 1H, $\beta$-11/17), 6.43 (d, $^3$$J_{H,H}$=4.1 Hz, 1H, $\beta$-12/16), 6.42 (d, $^3$$J_{H,H}$=4.1 Hz, 1H, $\beta$-12/16), 6.38 (d, $^3$$J_{H,H}$=4.1 Hz, 1H, $\beta$-11/17), 5.69 (s, 1H, meso-5), 2.89 (s, 3H, o-Me), 2.35 (s, 3H, o-Me), 2.23 (s, 3H, o-Me), 2.18 (s, 6H, p-Me), 1.88 (s, 3H, 1”), 1.70 (s, 3H, o-Me), 1.50 (m, 3H, 1”), 1.35 (m, $^3$$J_{H,H}$=7.4 Hz, 6H, 3”), 1.23 (m, 3H, 2”), 1.20 (m, 3H, 2”), 0.90 (t, $^3$$J_{H,H}$=7.4 Hz, 9H, 4”). $^{13}$C NMR (125MHz, CDCl$_3$, 298 K) $\delta$C = 154.6, 153.9, 153.3, 146.3, 146.2, 140.5, 140.1, 139.2, 138.9, 137.7, 137.6, 137.1, 137.02, 136.9, 134.9, 134.5, 134.1, 132.6, 131.4, 131.0, 129.5, 129.4, 128.7, 127.7, 127.1, 114.2, 114.1, 113.8, 112.4, 108.3, 85.5, 84.8, 45.1, 29.7, 23.91, 23.89, 23.7, 23.6, 23.4, 21.1, 20.9, 20.7, 20.4, 20.3, 13.6. $^{31}$PNMR (202 MHz, CDCl$_3$, 298 K) $\delta_P$ = 16.9. UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$/nm (ε/1000): 273 (66.0), 343 (sh), 406 (sh), 425 (62.6), 516 (sh), 552 (16.5), 649 (22.1), 705 (69.4). ESI-HRMS calc. for [C$_{48}$H$_{53}$N$_5$O$_2$P]$^+$ (M–H)$^+$: 822.3441, Found 822.3418.
Scheme S4. A plausible mechanism of addition of dialkylacetylenedicarboxylate and tributylphosphine to 3-nitro-5,14-mesityl-norcorrolatonickel(II).
Figure S1. ¹H NMR spectrum (500 MHz, CDCl₃, 298 K) of 3-Me; s, residual CHCl₃ signal; w, dissolved water signal.

Figure S2. ¹³C NMR spectrum (125 MHz, CDCl₃, 298 K) of 3-Me.
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Figure S3. $^{31}$P NMR spectrum (202 MHz, CDCl$_3$, 298 K) of 3-Me.
Figure S4. $^1$H, $^1$H COSY spectrum (500 MHz, CDCl$_3$, 298 K) of 3-Me.
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Figure S5. $^1$H, $^1$H NOESY spectrum (500 MHz, CDCl$_3$, 298 K) of 3-Me.
Figure S6. $^1$H, $^{31}$P HMBC spectrum (500/202 MHz, CDCl$_3$, 298 K) of 3-Me. Correlation peak at about $\delta_H$ 6.6 ppm is due to the presence of small amount of hydrolysis product 4-Me formed during the data collection.
Figure S7. $^1$H, $^{13}$C HSQC spectrum (500/125 MHz, CDCl$_3$, 298 K) of 3-Me.
Figure S8. $^1$H, $^{13}$C HMBC spectrum (500/125 MHz, CDCl$_3$, 298 K) of 3-Me.
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**Figure S9.** $^1$H NMR spectrum (600 MHz, CDCl$_3$, 300 K) of 3-Et; s, residual CHCl$_3$ signal; w, dissolved water signal.

**Figure S10.** $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298 K) of 3-Et.
Figure S11. $^{31}$P NMR spectrum (202 MHz, CDCl$_3$, 298 K) of 3-Et.

Figure S12. $^{31}$P{$^{1}$H} NMR spectrum (202 MHz, CDCl$_3$, 298 K) of 3-Et. The weak signals near $\delta_p$ 35 are due to a small amount of hydrolysis products 4-Et that are formed during the data acquisition.
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Figure S13. $^1$H, $^1$H COSY spectrum (500 MHz, CDCl$_3$, 298 K) of 3-Et.
Figure S14. $^1$H, $^1$H NOESY spectrum (500 MHz, CDCl$_3$, 298 K) of 3-Et.
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Figure S15. $^1$H,$^{31}$P HMBC spectrum (500/202 MHz, CDCl$_3$, 298 K) of 3-Et. Correlation peaks at about $\delta_P$ 35 ppm is due to the presence of small amount of hydrolysis products 4-Et formed during the data acquisition.
Figure S16. $^1$H, $^{13}$C HSQC spectrum (600/150 MHz, CDCl$_3$, 298 K) of 3-Et.
Figure S17. $^1$H, $^{13}$C HMBC spectrum (600/150 MHz, CDCl$_3$, 298 K) of 3-Et.
Figure S18. ESI (+) HRMS spectrum 3-Me (experimental: red, upper trace; simulated: black, middle and bottom traces).
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Figure S19. ESI(+) HRMS spectrum 3-Et (experimental: magenta, upper trace; simulated: black, middle and bottom traces).
Figure S20. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 4-Me.

Figure S21. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 4-Me.
Figure S22. $^{13}$C NMR spectrum (150 MHz, CDCl$_3$, 298 K) of 4-Me.

Figure S23. $^{31}$P($^1$H) NMR spectrum (202 MHz, CDCl$_3$, 298 K) of 4-Me.
Figure S24. $^1$H, $^1$H COSY spectrum (500 MHz, CDCl$_3$, 298 K) of 4-Me.
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Figure S25. $^1$H, $^1$H NOESY spectrum (500 MHz, CDCl$_3$, 298 K) of 4-Me.
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Figure S26. $^1$H, $^{13}$C HSQC (red) and $^1$H, $^{13}$C HMBC (blue) spectra (500/125 MHz, CDCl$_3$, 298 K) of 4-Me.
Figure S27. $^1$H, $^{31}$P HMBC spectrum (500/202 MHz, CDCl$_3$, 298 K) of 4-Me.
**Figure S28.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 4-Et.

**Figure S29.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 4-Et.
Figure S30. $^{13}$C NMR spectrum (150 MHz, CDCl$_3$, 298 K) of 4-Et.

Figure S31. $^{31}$P($^1$H) NMR spectrum (202 MHz, CDCl$_3$, 298 K) of 4-Et.
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Figure S32. Selected region of the $^{31}$P{$^1$H} NMR spectrum (202 MHz, CDCl$_3$, 298 K) of 4-Et.
Figure S33. $^1$H, $^1$H COSY spectrum (500 MHz, CDCl$_3$, 298 K) of 4-Et.
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Figure S34. $^1$H, $^1$H NOESY spectrum (500 MHz, CDCl$_3$, 298 K) of 4-Et.
Figure S35. $^1$H, $^{13}$C HSQC (red) and $^1$H, $^{13}$C HMBC (blue) spectra (500/125 MHz, CDCl$_3$, 298 K) of 4-Et.
Figure S36. Selected region of $^1$H, $^{13}$C HSQC spectrum (500/125 MHz, CDCl$_3$, 298 K) of 4-Et.
Figure S37. $^1$H, $^{31}$P HMBC spectrum (500/202 MHz, CDCl$_3$, 298 K) of 4-Et.
Figure S38. Upper panel: ESI(+) HRMS spectrum of 4-Me (experimental: red, upper trace; simulated: black, middle and bottom traces). Lower panel: ESI(-) HRMS spectrum of 4-Me (experimental: green, upper trace; simulated: black, bottom trace).
Figure S39. ESI(+) HRMS spectrum of 4-Et (experimental: blue, upper trace; simulated: black, bottom trace).
Figure S40. ESI(-) HRMS spectrum 4-Et (experimental: upper trace; simulated: black, bottom trace).
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Figure S41. UV-vis spectrum of 3-Me in dichloromethane.

Figure S42. UV-vis spectrum of 3-Et in dichloromethane.
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Figure S43. UV-vis spectrum of 4-Me in dichloromethane.

Figure S44. UV-vis spectrum of 4-Et in dichloromethane.
Figure S45. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 5; s, residual CHCl$_3$ signal; w, dissolved water signal; *, impurities.

Figure S46. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298 K) of 5.
Figure S47. $^{31}$P NMR spectrum (202 MHz, CDCl$_3$, 298 K) of S.
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Figure S48. $^1$H, $^1$H COSY spectrum (500 MHz, CDCl$_3$, 298 K) of 5.
Figure S49. $^1$H, $^1$H NOESY spectrum (500 MHz, CDCl$_3$, 298 K) of 5.
Figure S50. $^{1}H, ^{31}P$ HMBC spectrum (500/202 MHz, CDCl$_3$, 298 K) of 5.
**Figure S51.** $^1$H, $^{13}$C HSQC spectrum (500/125 MHz, CDCl$_3$, 298 K) of 5.
Figure S52. $^1$H, $^{13}$C HMBC spectrum (500/125 MHz, CDCl$_3$, 298 K) of 5.
Figure S53. ESI(+) HRMS spectrum 5 (experimental: red, upper trace; simulated: black, bottom trace).
Figure S54. UV-vis spectrum of 5 in dichloromethane.
Figure S55. Upper panel: A chiral stationary phase HPLC profile of 3-Et (mobile phase, 2% MeOH in DCM; flow 2 mL/min; detection wavelength 383 nm) with CD (top) and UV-vis absorption (bottom) detections. Lower panel: CD spectra of the enantiomers of 3-Et (black and red traces) and UV-vis spectrum of 3-Et in dichloromethane.
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Figure S56. Experimental (DCM, blue traces) and TD-DFT calculated (purple traces) UV-vis (top) and circular dichroism (bottom) spectra of P-3-Et. The green sticks represent a histogram of calculated optical active transitions.
Figure S57. Chiral stationary phase HPLC profiles of 4-Et with absorbance (bottom) and CD (top) detections at 383 nm and DCM/MeOH (98/2 v/v) as mobile phase. The upper panel presents an expansion of the peaks from the chiral stationary phase HPLC profile of 4-Et with ECD (bottom), absorbance (middle) detections, and 1st derivative of the absorbance (top), indicating the presence of four optically active stereoisomers (A); stereoisomers of 4- (C) DFT-optimized structures of R,S-4-Et with proton numbering and some interprotonic distances (top) and low field regions of the NOESY and COSY maps of 4-Et (600 MHz, CDCl₃, 300 K) with a partial signal assignments (C).
Figure S58. Top: A stopped-flow chiral stationary phase HPLC profile of 4-Et (DCM/MeOH 98/2, detection at 383 nm for both absorbance and CD channel) showing decay of the Cotton effect intensity (black trace) due to a racemization and stability of the absorbance over the racemization period (red trace). Bottom: A kinetic analysis of the racemization process of 4-Et. The red line were calculated as a best fit to the experimental data (black trace; blue trace shows deviation of the calculated curve from the experimental points) to the first-order kinetic equation with rate constant $k = 0.216 \text{ min}^{-1}$ (half-time 3.2 min).
Figure S59. Racemization of 4-Et may involve a tautomeric form 4'-Et with trigonal C1' (central structure) and calculated relative energy by 13.7 kcal/mol higher than that of 4-Et.

Figure S60. Correlations of the experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of 3-Et (left) and 4-Et (right).
Figure S61. Selected spectra (DCM, 298 K) taken upon spectrophotometric titration of 3-Et with trifloracetic acid (TFA). Black trace, 0 equiv; pink trace, 360 equiv of TFA.

Figure S62. Spectrophotometric titration (DCM, 246 K) of 3-Et with TFA, from 0 equiv (black trace) to 25 equiv (navy trace) of acid.
Figure S63. Selected regions of the $^1$H NMR spectra (CDCl$_3$, 223 K) taken upon titration of 3-Me with trifloracetic acid (TFA). A number of the acid equivalents added is given on the left margin of each spectrum.

Figure S64. COSY (left) and NOESY (right) spectra of [H-$^3$-Me]$^+$ (3-Me + 3.6 equiv TFA, CDCl$_3$, 223 K). The lower panel present expansions of a selected region of the respective maps with H-17–H-18 correlations.
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Figure S65. $^1$H, $^{13}$C HSQC (top) and $^1$H, $^{13}$C HMBC (bottom) spectra of [H-3-Me]$^+$ (3-Me + 3.6 equiv TFA, CDCl$_3$, 223 K).
**Figure S66.** ESI(+) mass spectrum of the sample obtained by addition of 4 equiv of TFA to the solution of 3-Me in DCM. The lower panel shows expansion of the spectrum in the region of the major peak (top) and simulation of the isotope pattern (bottom).
Figure S67. Selected $^1$H NMR spectra (CDCl$_3$, 223 K) taken upon titration of 3-Et with trifloracetic acid (TFA): blue, 0 equiv; red and black (red x 8), 1 equiv; green, 2 equiv; purple, 3.5 equiv of acid.

Figure S68. COSY spectrum of [H-3-Et]$^+$ (3-Et + 3.5 equiv TFA, CDCl$_3$, 233 K). On the right, an expansion of a selected region of the COSY map with H-17–H-18 correlations is presented.
Figure S69. NOESY spectrum of [H-3-Et]+ (3-Et + 3.5 equiv TFA, CDCl₃, 233 K). On the bottom, expansions of the selected regions of the NOESY map with 2-H–18-H (left) and H-17–H-18 (right) correlations are presented.
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Figure S70. $^1$H,$^{13}$C HSQC spectrum of [H-3-Et]$^+$ (3-Me + 3.5 equiv TFA, CDCl$_3$, 233 K).
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Figure S71. $^1$H NMR spectra (600 MHz, CDCl$_3$, 213 K) of 4-Me (blue) and [H-4-Me]$^+$ (4-Me + 5 equiv TFA).

Figure S72. COSY (left) and NOESY (right) spectra of [H-4-Me]$^+$ (4-Me + 5 equiv TFA, CDCl$_3$, 213 K). The lower panel presents expansions of a selected region of the respective maps with H-17–H-18 correlations.
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**Figure S73.** Superimposed low-field regions of COSY (red) and NOESY (blue) spectra of $\text{[H-4-Me]}^+$ (4-Me + 5 equiv TFA, CDCl$_3$, 213 K).

**Figure S74.** $^1$H NMR spectra (600 MHz, CDCl$_3$, 233 K) of 4-Et (blue) and $\text{[H-4-Et]}^+$ (4-Me + 4 equiv TFA).
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Figure S75. Experimental (DCM, top) and TD-DFT calculated (bottom) spectra of 5.
Figure S76. DFT-calculated models of enantiomers of 5 and chiral stationary phase HPLC profiles of 5 with absorbance (bottom) and CD (top) detections at 291 nm and DCM mobile phase (2 mL/min).
Figure S77. Experimental spectra for the separated enantiomers of 5 (DCM, top) and TD-DFT calculated spectrum of S-5 (bottom).
Figure S78. Charge distribution (blue, negative charge; green, positive charge with isosurface value of 0.15) over the skeletons of S-5.
Figure S79. Cyclic (CV) and differential pulse (DP) voltammograms recorded for 3-Me in DCM with [Bu₄N]PF₆ as supporting electrolyte. The horizontal arrows indicate directions of the potential sweep, the green numbers are DP peak potentials in volts.

Figure S80. Cyclic (CV) and differential pulse (DP) voltammograms recorded for 3-Et in DCM with [Bu₄N]PF₆ as supporting electrolyte. The horizontal arrows indicate directions of the potential sweep, the green numbers are DP peak potentials in volts.
Figure S81. Cyclic (CV) and differential pulse (DP) voltammograms recorded for 4-Me in DCM with [Bu₄N]PF₆ as supporting electrolyte. The horizontal arrows indicate directions of the potential sweep, the green numbers are DP peak potentials in volts. The positions of the ferrocene/ferrocenium couple are marked with Fc symbol and oblique black arrows.
Figure S82. Cyclic (bottom) and differential pulse (top) voltammograms of 4-Et in DCM with [Bu₄N]PF₆ as supporting electrolyte. The horizontal arrows indicate directions of the potential sweep, the green numbers are DP peak potentials in volts. The blue line color in CV identifies the first scan, while the consecutive second scan is presented in pink.
Figure S83. Cyclic (bottom) and differential pulse (top) voltammograms of 5 in DCM with [Bu₄N]PF₆ as supporting electrolyte. The horizontal arrows indicate directions of the potential sweep, the green numbers are DP peak potentials in volts.
Figure 84. Charge distribution (blue, negative; green, positive charges; isosurface value, 0.15) over the skeletons of 3-Et (A), [H-3-Et]+ (B), [3*-Et]+(C), [3-Et-C]+ (D) and [3*-Et]− (E) calculated by Mulliken approach (Multiwfn package[49]) for the DFT-optimized structures.

Figure S85. Optical spectra (DCM, 298 K) recorded upon titration of 4-Et with iodine solution in DCM.
Figure S86. Experimental (top) and DFT calculated (bottom) electronic spectra of \([3^-\text{Et}]^+\). The experimental spectrum was generated by addition of \(I_2\) to a DCM solution of 3-Et at 298 K.
Figure S87. Fluid solution EPR spectrum of [3'-Et]^+ obtained by addition of I\(_2\) to a solution of 3-Et in dichloromethane at room temperature.

Figure S88. (A) Optical spectra (DCM, 298 K) recorded upon titration of 3-Et with iodine solution in DCM. (B) Frozen-solution EPR spectrum (DCM, 77 K) of [3'-Et]^+ (black trace) along with the spectrum simulated with indicated spin-hamiltonian parameters (red trace). (C) Spin density distribution calculated for [3'-Et]^+.
Figure S89. Thermal ellipsoid plots (at 50% probability level) of the crystal structure of 3-Et: top, aerial view; bottom, side view.
Figure S90. Thermal ellipsoid plots (at 50% probability level) of the crystal structure of 5: top, asymmetric part of the unit cell, bottom, side view of one of the molecules.
Table S3. Electrochemical potentials (in volts, referenced with ferrocene/ferrocenium couple) for 3-R, 4-R, and 5 in DCM.

| Compound | $E_{ox1}$ | $E_{ox2}$ | $E_{ox3}$ | $E_{red1}$ |
|----------|-----------|-----------|-----------|------------|
| 3-Me     | -0.13     | 0.59      | 1.25 $^a$ | -1.86 $^a$ |
| 3-Et     | -0.11     | 0.61      | 1.28 $^a$ | -1.82 $^a$ |
| 4-Me     | -0.07     | 0.62      | (1.05)$^c$ | -2.03 $^a$ |
| 4-Et     | -0.08     | 0.61      | (1.05)$^c$ | -2.04 $^a$ |
| 5        | 0.07      | 0.62      | -1.79     |            |
| 1$^b$    | 0.16      | 0.74      | -0.91     |            |
| 1-NO$_2$$^b$ | 0.47 | 0.87 | -0.69 |         |

[a] Irreversible couples. Potentials taken from differential pulse voltammetry. [b] Data from ref. 11 [c] Re-oxidation of the products of an irreversible reduction.

Table S3. Computational details for structures discussed in the paper. Optimizations were performed at the PCM(CH$_2$Cl)$_2$/B3LYP/6-31G(d,p) level of theory and LANL2DZ pseudopotential applied for nickel center.

| Structure | Code$^{[b]}$ | SCF $E^{[b]}$ | ZPV$^{[c]}$ | l. freq.$^{[d]}$ | G$^{[e]}$ | HOMO | LUMO | HLG $^{[f]}$ |
|-----------|--------------|---------------|------------|----------------|--------|------|------|---------|
| 3-Et      | PJC_2_001_n  | -3409.574404  | -3408.455183 | 10.74 | -3408.571999 | -4.46 | -2.09 | 2.37    |
| 3$^{**}$-Et | PJC_2_001_n_t | -3409.527222  | -3408.410798 | 15.07 | -3408.530000 | -5.85 | -3.59 | 2.14    |
| [3-Et]$^+$ | PJC_2_001_n_R | -3409.409023  | -3408.289775 | 13.78 | -3408.408825 | -5.73 | -3.59 | 2.14    |
| [H-3-Et]$^+$ | PJC_2_001_n_H | -3409.020994  | -3408.889677 | 8.17  | -3409.008065 | -5.73 | -3.59 | 2.14    |
| [3'-Et]$^+$ | PJC_2_001_n_m | -3409.650371  | -3408.534295 | 14.02 | -3408.652263 | -2.04$^f$ | -0.84 | 1.20    |
| [3-Et-C]$^+$ | PJC_2_001_n_C | -3106.436949  | -3105.312366 | 12.54 | -3105.425716 | -3.83 | -1.59 | 2.24    |
| 4-Et      | PJC_2_003    | -3142.401358  | -3141.352113 | 12.32 | -3141.459217 | -4.54 | -2.14 | 2.40    |
| [4'-Et]$^+$ | PJC_2_003_m  | -3142.479247  | -3141.433383 | 13.93 | -3141.541573 | -2.09$^f$ | -0.86 | 1.23    |
| 5         | PJC_2_001_phb | -2797.771115  | -2796.826438 | 11.03 | -2796.924090 | -4.41 | -2.06 | 2.35    |

[a] Optimized geometry available as <code>.pdb file. [b] Electronic energy. [c] Zero-point vibrational energy. [d] Lowest vibrational frequency. [e] Gibbs free energy. [f] SOMO
References

[1] G. M. Sheldrick, Acta Cryst. 2015, C71, 3-8.
[2] CrysAlis PRO 1.171.40.67a (Rigaku OD, 2019).
[3] G. M. Sheldrick, Acta Cryst. 2015, A71, 3.
[4] G. M. Sheldrick, Acta Cryst. 2015, C71, 3.
[5] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 Revision E.01.
[6] A. D. Becke, Phys.Rev.A, 1988, 38, 3098.
[7] A. D. Becke, J.Chem.Phys., 1993, 98, 5648.
[8] C. Lee, W. Yang, and R. G. Parr, Phys.Rev.B, 1988, 37, 785.
[9] N. M. O’Boyle, A. L. Tenderholt, and K. M. Langner, J.Comp.Chem., 2008, 29, 839.
[10] T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi, H. Shinokubo, Angew.Chem.Int.Ed. 2012, 51, 8542-8545.
[11] Z. Deng, X. Li, M. Stępień, P. J. Chmielewski, Chem.Eur.J. 2016, 22, 4231-4246.