**Supporting Information**

for

**Ferrocenophanes with two nitrogen atoms in bridging positions *via* olefin metathesis: synthesis, structure, and solution dynamics**

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**Experimental details, characterization of amino dienes 1, amino aldehydes S, additional X-ray data, VT 1H NMR spectra, 2D NMR spectra, and details of theoretical calculations**

**General remarks**. *N*-allyl-4-methoxyaniline [[[1]](#endnote-1)] and *N*-allyl-2-ethoxyaniline [[[2]](#endnote-2)] were synthesized according to published procedures. Compounds **1a**, **1e**, **1f**, and **S1** were described previously [[[3]](#endnote-3)]. Reductive amination reactions were carried out using Schlenk tube techniques under an argon atmosphere according to the general conditions described by Abdel-Magid *et al*. [[[4]](#endnote-4)]. The resulting products were isolated without exclusion of air. The progress of the reactions was monitored using TLC (hexanes:ethyl acetate, 4:1, v/v). 1,2-Dichloroetane (DCE) and dichloromethane were distilled from CaH2. All other reagents and solvents were commercial and were used as received. Column chromatography was performed on silica gel 60 (230–400 mesh). The NMR spectra were recorded on a Varian V NMRS 500 MHz spectrometer at ambient temperature unless otherwise noted. The VT NMR spectra were measured on an Avance III 600 MHz Bruker Spectrometer.

**Synthesis of diamine****1b**



*N*-allyl-4-methoxyaniline (0.850 g, 5.21 mmol), 1,2-dichloroetane (20 mL), 1,1′-ferrocene-dicarboxaldehyde (0.360 g, 1.50 mmol) and NaBH(OAc)3 (0.850 g, 4.01 mmol) were placed in a dry Schlenk tube equipped with a stirring bar. The resulting mixture was stirred at room temperature for 24 h. An aqueous solution of NaOH (100 mL, 1M) was added. The organic phase was separated. The aqueous phase was extracted with CH2Cl2 (3 × 20 mL). The combined organic solutions were dried over MgSO4. The volatiles were removed on a rotary evaporator to obtain a brown-red oil. This residue was subjected to column chromatography (SiO2, hexanes:ethyl acetate, 4:1, v/v). Three coloured fractions were collected which were further purified by crystallization from *n*-hexane at −70°C.

**Diamine 1b**: yellow crystals, 0.430 g (0.80 mmol, 53%). mp: 68-71 °C (from *n*-hexane). 1H NMR (500 MHz, CDCl3) *δ* (ppm): 6.80 (dt, *J* = 9.0, 2.5 Hz, 4H, C6H4), 6.74 (dt, *J* = 9.0, 2.5 Hz, 4H, C6H4), 5.80 (ddt, *J* = 16.0, 11.5, 5.5 Hz, 2H, -CH=), 5.16 (dd, *J* = 11.5, 1.5 Hz, 2H, =CH2), 5.14-5.12 (m, 2H, =CH2), 4.17 (s, 4H, -CH2-N), 4.06 (app. t, *J* = 1.5 Hz, 4H, C5H4), 4.03 (app. t, *J* = 2.0 Hz, 4H, C5H4), 3.76 (d, *J* = 5.5 Hz, 4H, -C*H*2-CH=), 3.75 (s, 6H, OCH3). 13C{1H} NMR (126 MHz, CDCl3) *δ* (ppm): 152.04 (*p*-C6H4), 143.53 (*ipso*-C6H4), 134.86 (-CH=), 116.41 (=CH2), 116.18 (C6H4), 114.46 (C6H4), 84.49 (C5H4), 69.80 (C5H4), 68.44 (C5H4), 55.67 (OCH3), 52.88 (-*C*H2-N), 50.97 (-*C*H2-CH=). HR MS (ESI) *m/z* found for C32H3656FeN2O2Na [M+Na]+ 559.2028 (Calc. 559.2024). Anal. Calc. for C32H36FeN2O2: C 71.64, H 6.76, N 5.22; Found: C 71.12, H 6.48, N 5.18.

**Amino aldehyde S2**: red crystals, 0.200 g (0.51 mmol, 34%). mp: 41-43 °C (from ethyl acetate/*n*-hexane). 1H NMR (500 MHz, CDCl3) *δ* (ppm): 9.95 (s, 1H, CHO), 6.79 (dt, *J* = 9.5, 2.5 Hz, 2H, C6H4), 6.71 (dt, *J* = 9.0, 2.0 Hz, 2H, C6H4), 5.79 (ddt, *J* = 17.0, 10.5, 5.5 Hz, 1H, -CH=), 5.17 (dq, *J* = 7.7, 1.6 Hz, 1H, =CH2), 5.14 (app. t, *J* = 1.6 Hz, 1H, =CH2), 4.75 (app. t, *J* = 2.0 Hz, 2H, C5H4), 4.57 (app. t, *J* = 2.0 Hz, 2H, C5H4), 4.21 (app. t, *J* = 2,0 Hz, 2H, C5H4), 4.18 (app. t, *J* = 2.0 Hz, 2H, C5H4), 4.10 (s, 2H, -CH2-N), 3.75 (s, OCH3) overlapping with 3.74 (dt, -C*H*2-CH=), 5H. 13C{1H} NMR (126 MHz, CDCl3) *δ* (ppm): 193.42 (-CHO=), 152.49 (*p*-C6H4), 143.38 (*ipso*-C6H4), 134.89 (-CH=), 116.82 (=CH2), 116.68 (C6H4), 114.66 (C6H4), 86.58 (C5H4), 79.85 (C5H4), 73.94 (C5H4), 70.84 (C5H4), 70.30 (C5H4), 69.53 (C5H4), 55.82 (OCH3), 53.43 (-*C*H2-CH=), 50.62 (-CH2-N). MS (EI) *m/z* (%), 56Fe: 389 (47, M+), 348 (22), 254 (12), 227 (100), 199 (71), 121 (43). HR MS (EI) *m/z* found for C22H2356FeNO2 [M]+ 389.1085 (Calc. 389.1078). Anal. Calc. for C22H23FeNO2: C 67.88, H 5.96, N 3.60; Found: C 68.19, H 5.91, N 3.64.

**Amino alcohol S2-2H**: brown oil, 0.060 g (0.15 mmol, 10%). 1H NMR (500 MHz, CDCl3) *δ* (ppm): 6.80 (dt, *J* = 9.0, 3.0 Hz, 2H, C6H4), 6.76 (dt, *J* = 9.5, 3.0 Hz, 2H, C6H4), 5.81 (ddt, *J* = 17.1, 10.7, 5.5 Hz, 1H, CH=), 5.17 (dq, *J* = 9.5, 1.5 Hz, 1H, =CH2), 5.14 (app. sextet, *J* = 1.5 Hz, 1H, =CH2), 4.34 (d, *J* = 4.5 Hz, 2H, C*H*2-OH), 4.18 (app. t, *J* = 2.0 Hz, 2H, C5H4), 4.16 (s, 2H, ‑CH2-N), 4.14 (app. t, *J* = 1.5 Hz, 2H, C5H4), 4.10 (app. t, *J* = 1.5 Hz, 2H, C5H4), 4.08 (t, *J* = 2.0 Hz, 2H, C5H4), 3.77 (dt, *J* = 5.0 Hz, 1.7 Hz, 2H, -C*H*2-CH=), 3.75 (s, 3H, OCH3), 1.82 (bs, 1H, OH). 13C{1H} NMR (126 MHz, CDCl3) *δ* (ppm): 151.56 (*p*-C6H4), 142.59 (*ipso*-C6H4), 133.84 (‑CH=), 115.93 (C6H4 or =CH2), 115.88 (C6H4 or =CH2), 113.63 (C6H4), 87.84 (C5H4), 84.20 (C5H4), 68.58 (C5H4), 68.08 (C5H4), 67.47 (C5H4), 67.11 (C5H4), 59.84 (CH2OH), 54.82 (OCH3), 53.00 (CH2N), 50.03 (CH2-CH=). HR MS (ESI) *m/z* found for C22H2556FeNO2Na [M+Na]+ 414.1125 (Calc. 414.1132). Anal. Calc. for C22H23FeNO2 × 0.5 H2O: C 66.03, H 6.00, N 3.50; Found: C 66.66, H 6.10, N 3.90.

**Synthesis of diamine 1d**



Similarly as described above, *N*-allyl-2-ethoxyaniline (1.14 g, 7.09 mmol), 1,2-dichloroetane (30 mL), 1,1′-ferrocenedicarboxaldehyde (0.400 g, 1.65 mmol) and NaBH(OAc)3 (0.800 g, 3.37 mmol) were stirred at room temperature for 1 week. The usual work-up and column chromatography (SiO2, hexanes:ethyl acetate, 4:1, v/v) provided two compounds.

**Diamine 1d**: yellow crystals from *n*-hexane at −70 °C; 204 mg (0.361 mmol, 22%). mp: 58-61 °C (from *n*-hexane). 1H NMR (500 MHz, CDCl3) *δ* (ppm): 6.92 (m, 2H, C6H4), 6.85 (dd, *J* = 8.1, 1.5 Hz, 2H, C6H4), 6.79 (m, 2H, C6H4), 6.71 (dd, *J* = 7.9, 1.6 Hz, 2H, C6H4), 5.83 (ddt, *J* = 16.3, 10.2, 6.1 Hz, 2H, -CH=), 5.17 (dq, *J* = 17.2, 1.8 Hz, 2H, =CH2), 5.11 (dq, *J* = 10, 2 Hz, 2H, =CH2), 4.12 (q, *J* = 6.7 Hz, 4H, O-CH2-) overlapping with: 4.10 (s, 4H, -CH2-N), 3.92 (app. t, *J* = 1.8 Hz, 4H, C5H4), 3.84 (app t, *J* = 1.8 Hz, 4H, C5H4), 3.60 (dt, *J* = 6.1, 1.3 Hz, 4H, -C*H2*-CH=), 1.48 (t, *J* = 7.0 Hz, 6H, -CH3). 13C{1H} NMR (126 MHz, CDCl3) *δ* (ppm): 151.99 (C6H4), 139.94 (C6H4), 136.22 (CH=), 122.34 (C6H4), 121.84 (C6H4), 120.52 (C6H4), 116.83 (=CH2), 113.01 (C6H4), 83.26 (C5H4), 70.27 (C5H4), 68.06 (C5H4), 63.80 (O-CH2-), 53.34 (-CH2-N), 50.64 (-*C*H2-CH=), 15.15 (-CH2-*C*H3). HR MS (ESI) *m/z* found for C34H4056FeN2O2 [M]+ 564.2435 (Calc. 564.2439). Anal. Calc. for C34H40FeN2O2 × 0.5 H2O: C 71.20, H 7.15, N 4.88; Found: C 71.21, H 6.58, N 5.10.

**Amino aldehyde S3**: red micro-crystalline solid, 170 mg (0.422 mmol, 25%). mp: 44-45 °C (from ethyl acetate/*n*-hexane). 1H NMR (500 MHz, CDCl3) *δ* (ppm): 9.89 (s, 1H, CHO), 6.94 (m, 1H, C6H4), 6.87 (dd, *J* = 8.1, 1.5 Hz, 1H, C6H4), 6.79 (td, *J* = 7.5, 1.3 Hz, 1H, C6H4), 6.70 (dd, *J* = 7.9, 1.6 Hz, 1H, C6H4), 5.84 (ddt, *J* = 16.3, 10.2, 6.1 Hz, 1H, -CH=), 5.18 (dq, *J* = 17.3, 1.6 Hz, 1H, =CH2), 5.14 (dq, *J* = 10.3, 1.5 Hz, 1H, =CH2), 4.68 (app. t, *J* = 2.0 Hz, 2H, C5H4), 4.50 (app. t, *J* = 2.0 Hz, 2H, C5H4), 4.14 (q, *J* = 7.0 Hz, 2H, O-CH2-) overlapping with 4.13 (app. t, *J* = 1.7 Hz, 2H, C5H4), 4.08 (s, 2H, -CH2-N), 4.03 (app. t, *J* = 1.8 Hz, 2H, C5H4), 3.60 (dt, *J* = 6.1, 1.4 Hz, 2H, -C*H2*-CH=), 1.52 (t, *J* = 7.0 Hz, 3H, -CH3). 13C{1H} NMR (126 MHz, CDCl3) *δ* (ppm): 193.20 (CHO), 152.12 (C6H4), 139.48 (C6H4), 136.01 (CH=), 122.76 (C6H4), 122.00 (C6H4), 120.54 (C6H4), 117.10 (=CH2), 113.02 (C6H4), 85.56 (C5H4), 79.60 (C5H4), 73.63 (C5H4), 71.21 (C5H4), 69.93 (C5H4), 69.25 (C5H4), 63.85 (O-CH2-), 53.85 (-*C*H2-CH=), 49.92 (-CH2-N), 15.14 (-CH2-*C*H3). HR MS (ESI) *m/z* found for C23H2456FeNO2Na [M+Na]+ 426.1133 (Calc. 426.1132). Anal. Calc. for C23H25FeNO2: C 68.50, H 6.25, N 3.47; Found: C 68.12, H 5.85, N 3.61.

**Synthesis of diamine 1c**

*Method A*



*N*-allylaniline (0.060 g, 0.510 mmol), 1,2-dichloroetane (20 mL), amino aldehyde **S2** (0.200 g, 0.510 mmol) and NaBH(OAc)3 (0.100 g, 0.500 mmol) were placed in a dry Schlenk tube equipped with a stirring bar. The resulting mixture was stirred at room temperature for 24 h. An aqueous solution of NaOH (100 mL, 1M) was added. The phases were separated, the aqueous phase was extracted with CH2Cl2 (3 × 20 mL). The combined organic solutions were dried over MgSO4. The volatiles were removed on a rotary evaporator. The product was isolated by column chromatography (SiO2 (hexanes:ethyl acetate, 4:1, v/v). A yellow fraction was collected which was further purified by crystallization from *n*-hexane at −70 °C. The product **1c** was obtained as yellow-orange oil at room temperature that solidified upon standing at 4 °C. Yield: 0.160 g (0.316 mmol, 62%).

*Method B*



Compound **1c** was also similarly obtained from amino aldehyde **S1** [3] and *N*-allyl-4-methoxyaniline [1].

**Diamine 1c**: 1H NMR (500 MHz, CDCl3) *δ* (ppm): 7.21 (d, *J* = 7.5 Hz, 1H, C6H5), 7.19 (d, *J* = 7.5 Hz, 1H, C6H5), 6.80 (d, *J* = 9.5 Hz, 2H, C6H4), 6.78–6.76 (m, 2H, C6H5), 6.74 (d, *J* = 9.0 Hz, 2H, C6H4), 6.69 (dt, *J* = 7.2, 1.0 Hz, 1H, C6H5), 5.85–5.75 (m, 2H, -CH=), 5.19-5.12 (m, 4H, -CH2=), 4.26 (s, 2H, -CH2-N), 4.19 (s, 2H, -CH2-N), 4.14 (app. t, *J* = 2.0 Hz, 2H, C5H4), 4.09 (t, *J* = 2.0 Hz, 2H, C5H4), 4.07-4.04 (two overlapping triplets, 4H, C5H4), 3.89 (dt, *J* = 5.0, 2.0 Hz, 2H, -C*H*2-CH=), 3.77 (dt, *J* = 5.0, 1.5 Hz, 2H, -C*H*2-CH=), 3.75 (s, 3H, OCH3). 13C{1H} NMR (126 MHz, CDCl3) *δ* (ppm): 151.26, 147.81, 142.70, 134.04, 133.31, 128.19, 115.74, 115.62, 115.40, 115.34, 113.65, 112.15 (12 signals, C6H5, C6H4, or CH=CH), 84.11 (C5H4), 83.75 (C5H4), 69.02 (C5H4), 68.79 (C5H4), 67.68 (two overlapping signals, C5H4), 54.84 (OCH3), 52.09 (‑CH2-N), 51.18 (‑CH2-N), 50.18 (-*C*H2-CH=), 48.65 (-*C*H2-CH=). HR MS (ESI) *m/z* found for C31H3456FeN2ONa [M+Na]+ 529.1920 (Calc. 529.1918). Anal. Calc. for C31H34FeN2O × 0.5 H2O: C 72.23, H 6.79, N 5.43; Found: C 71.78, H 6.49, N 5.39.

**Synthesis of diamine 1g**



Obtained from amino aldehyde **S1** (139 mg, 0.386 mmol) and *N*-allylmethylamine (90 μL, 66.7 mg, 0.94 mmol). Eluted with hexanes:ethyl acetate 50:50 containing 1% Et3N. Yield: 144 mg, (0.347 mmol, 90%), yellow oil. 1H NMR (500 MHz, CDCl3) *δ* (ppm): 7.22 – 7.18 (m, 2H, C6H5), 6.76 (d, *J* = 7.9 Hz, 2H, C6H5), 6.68 (t, *J* = 7.2 Hz, 1H, C6H5), 5.91 – 5.75 (m, 2H, =CH2), 5.22 – 5.11 (m, 4H, -CH=), 4.25 (s, 2H, C5H4-C*H*2-N), 4.14 (app. t, *J* = 1.7 Hz, 2H, C5H4), 4.13 (app. t, *J* = 1.8 Hz, 2H, C5H4), 4.11 (app. t, *J* = 1.8 Hz, 2H, C5H4), 4.04 (app. t, *J* = 1.8 Hz, 2H, C5H4), 3.89 (m, 2H, -C*H2*-CH=), 3.40 (s, 2H, C5H4-C*H*2-N), 2.97 (d, *J* = 6.4 Hz, 2H, -C*H2*-CH=), 2.15 (s, 3H, N-CH3). 13C{1H} NMR (126 MHz, CDCl3) *δ* (ppm): 148.82 (C6H5), 136.17 (=CH2), 134.34 (=CH2), 129.19 (C6H5), 117.67 (-CH=), 116.70 (-CH=), 116.32 (C6H5), 113.13 (C6H5), 85.04 (C5H4), 83.35 (C5H4), 70.98 (C5H4), 69.78 (C5H4), 68.93 (C5H4), 68.62 (C5H4), 59.99 (-C*H2*-CH=), 56.58 (C5H4-C*H*2-N), 52.15 (-C*H2*-CH=), 49.60 (C5H4-C*H*2-N), 41.73 (N-CH3). HR MS (ESI) *m/z* found for C25H3056FeN2Na [M+Na]+ 437.1652 (Calc. 437.1656). Anal. Calc. for C25H30FeN2 × 0.25 H2O: C 71.69, H 7.28, N 6.68; Found: C 71.73, H 7.05, N 6.54.

**Attempted metathesis of 1g**

Diamine **1g** (40.2 mg, 0.097 mmol) and CH2Cl2 (10 mL) were placed in a Schlenk tube equipped with a stirring bar. Then, the second-generation Grubbs catalyst **GII** (4.0 mg, 5% mol) was added. The mixture was stirred at 50 °C and at room temperature for 48 h under an argon atmosphere. Then, a small amount of ethyl-vinyl ether was added to deactivate the catalyst. A black-green solid was obtained after removal of the solvent on a rotary evaporator. This solid was dissolved in toluene and filtered through a Celite® pad and washed with additional portions of toluene. A dark green filtrate was obtained which was reduced in volume. This solution was subjected to column chromatography (Al2O3, toluene:ethyl acetate, 19:1, v/v). Two yellow fractions were collected. The amino aldehyde **S4** was the main component of the first fraction according to 1H NMR, the second one was identified as **1g** (20.0 mg, 50% recovered yield).



**Figure S1**: The olefinic range of the 1H NMR (500 MHz, CDCl3) spectrum of the crude reaction mixture of amino diene **1a** with catalyst **GII** showing that only one isomer of the newly formed C=C bond is present. Residual CH2Cl2 marked with an asterisk (\*).

Obraz zawierający tekst, niebo, dzień

Opis wygenerowany automatycznie

**Figure S2**: The selected range of 1H NMR (500 MHz, CDCl3) spectra of **1g** (lower trace) and **1g** with 10 mol% of catalyst **GII** (upper trace). Signals assigned to the aliphatic part of the molecule are marked.

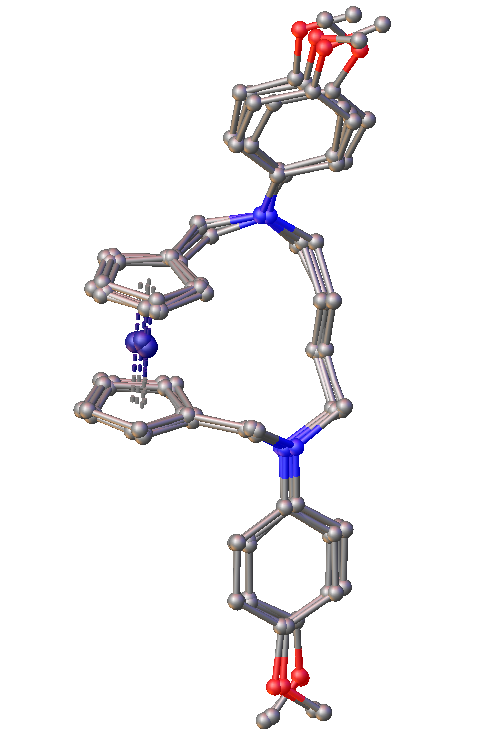
**Table S1**. Reactions of compound **1f** with ruthenium alkylidenes. Metathesis products were not detected under all studied conditions.

|  |  |  |  |
| --- | --- | --- | --- |
| Catalyst | Solvent | Temperature [°C­] | Additive |
| GI | C6H6 | 20 | - |
| GII | CH2Cl2 | 20 | - |
| GII | CH2Cl2 | 40 | - |
| GII | C7H8 | 80 | - |
| GII | CH2Cl2 | 40 | Ti(O-*i*Pr)4 [[[5]](#endnote-5)] |
| GII | CH2Cl2 | 40 | NaCl [[[6]](#endnote-6)] |
| Grubbs-Hoveyda II | CH2Cl2 | 20 | - |
| Grubbs-Hoveyda II | CH2Cl2 | 40 | HCl/Et2O [[[7]](#endnote-7)] |
| Grubbs-Hoveyda II | CH2Cl2 | 40 | Ti(O-*i*Pr)4 [5] |
| Grubbs-Hoveyda II | C7H8 | 80 | - |

**X-ray crystal structure determination**

Single crystals suitable for X-ray diffraction measurements were grown from *n*-hexane (**1a**, **1b**) at −70 °C or dichloromethane/*n*-hexane (**2a**, **2b**, **3b**) at 4 °C. Crystals suitable for diffraction experiments were selected under a polarizing microscope and glued with a two-component epoxy resin to cactus needles (**1a, 1b** and **2a**) or mounted on a MiTeGen MicroLoopsTM using a perfluorinated oil (**2b** and **3b**). Diffraction data were collected at room temperature using a Rigaku Oxford Diffraction Gemini A Ultra diffractometer with Mo Kα radiation. CrysAlisPRO software suite was used for controlling diffractometer as well as data collection and reduction. Crystal structures were solved using ShelxT and independent atom model refinements were carried out with ShelxL invoked from Olex2 program [[[8]](#endnote-8),[[9]](#endnote-9),[[10]](#endnote-10)]. Crystal structure of compound **2b** contained heavily disordered solvent molecules which were impossible to model. Therefore, SQUEEZE procedure implemented in PLATON has been applied [[[11]](#endnote-11)]. It revealed two solvent accessible voids with volumes of 435 and 149 Å3 and electron counts of 129 and 55, respectively. The larger void forms channels and might contain three molecules of dichloromethane per asymmetric unit, whereas the smaller one is discreet and may contain a molecule of hexane. Note that this is only tentative proposal of void contents. Single crystals of **2b** diffracted X-rays weakly, and the obtained diffraction data are only significantly different from zero to ~1 Å which makes the derivation of any geometrical parameters of the structure impossible. Crystal structure and refinement details are given in Table S4.

CCDC 2222236-2222238 and 2242035-2242036 contain the supplementary crystallographic data for this paper. All the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>. Raw diffraction data are available at <https://doi.org/10.5281/zenodo.7330815>.



**Figure S3**: The overlay of four molecules, depicted in a ball-and-stick model, present in the asymmetric unitof compound **2b**. Hydrogen atoms are omitted for clarity.

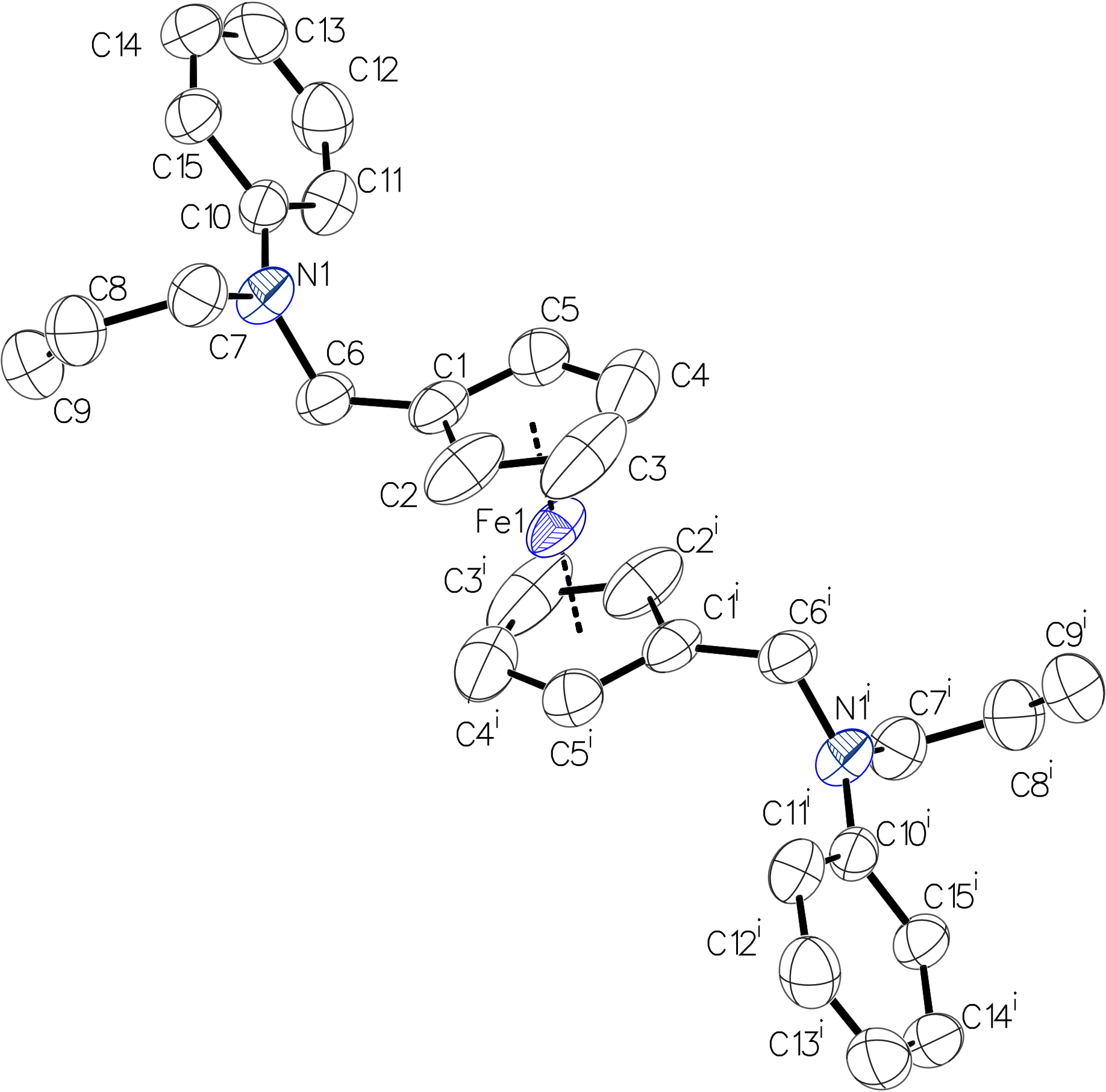
Obraz zawierający origami, sztuka, design

Opis wygenerowany automatycznie przy średnim poziomie pewności

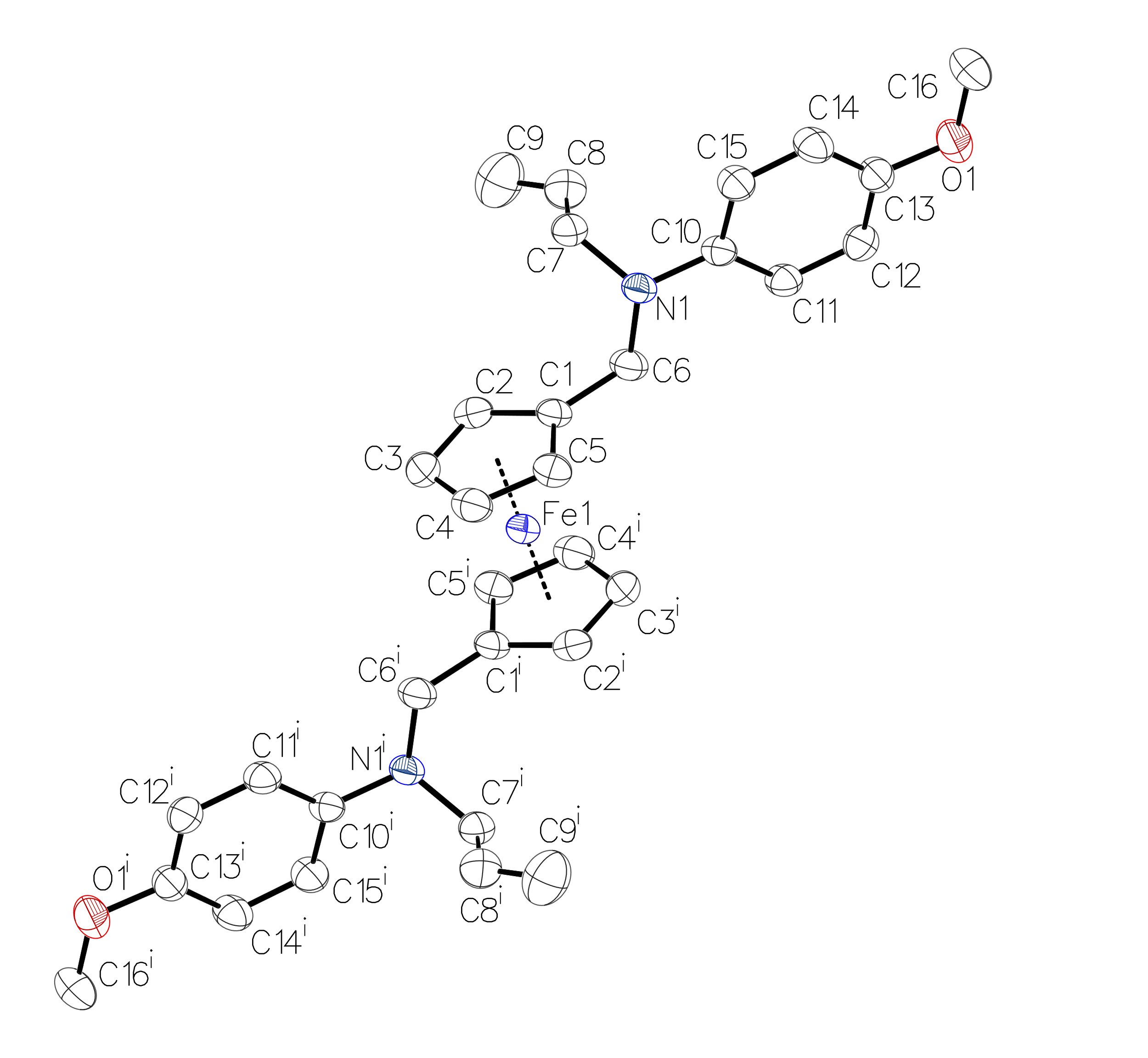
**Figure S4**: The calculated size of the cavity (defined as the distance between the two nitrogen atoms) in compound **2b** for two conformers with different orientations of the aromatic substituents. See below for details of theoretical calculations.

**Crystal structures of compound 1a** and**1b**

Compounds **1a** and **1b** (see Figure S4 and Figure S5 for molecular structures, respectively) crystallize in centrosymmetric space groups *P*21/*c* and , respectively. Both molecules lie in special positions, and they exhibit the exact symmetry of the point group . Consequently, ferrocene moiety adopts staggered conformation with parallel Cp rings. The nitrogen atom in molecule **1a** departs by only 0.0362(15) Å from the plane formed by the three adjacent carbon atoms. Analogous distance in compound **1b** of 0.3299(18) Å is significantly larger which points to lower conjugation of the nitrogen lone electron pair with the π electrons of the phenyl ring. This is the result of electron-donating properties of the methoxy group in *para* position with respect to the nitrogen atom.



**Figure S5**: Molecular structure of compound **1a**. One molecule from the asymmetric unit shown. Hydrogen atoms omitted for clarity. ADPs shown at the 50% probability level. Symmetry codes i = 1 − x, −y, 1 – z.



**Figure S6**: Molecular structure of compound **1b**. One molecule from the asymmetric unit shown. Hydrogen atoms omitted for clarity. ADPs shown at the 50% probability level. Symmetry codes i = 1 − x, −y, – z.

**Table S2.** The departure of nitrogen atoms from the plane of adjacent carbon atoms in Ångstroms.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **1a** | **1b** | **2a** |
| N1 | 0.0364(16) | 0.330(2) | 0.027(3) |
| N2 |  |  | 0.057(3) |

**Table S3.** Dihedral angle between planes of cyclopentadienyl rings in degrees.

|  |  |  |  |
| --- | --- | --- | --- |
| **1a** | **1b** | **2a** | **3b** |
| 0 | 0 | 0.99(13) | 9.61(12) |

**Table S4.** Crystal structure and refinement details for compound **1a**, **1b**, **2a**, **2b** and **3b**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **1a** | **1b** | **2a** | **2b** | **3b** |
| CCDC number | 2222237 | 2222238 | 2222236 | 2242035 | 2242036 |
| Molecular formula | C30H32FeN2 | C32H36FeN2O2 | C28H28FeN2 | C30H32FeN2O2 | C19H19FeNO |
| Formula weight | 476.42 | 536.48 | 448.37 | 508.42 | 333.20 |
| *T* /K | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) |
| Crystal system | monoclinic | triclinic | monoclinic | triclinic | orthorhombic |
| Space group | *P*21/*c* |  | *P*21/*c* |  | *Pbca* |
| *a* /Å | 10.2946(2) | 8.1888(2) | 13.5944(8) | 9.0866(2) | 19.3669(2) |
| *b* /Å | 10.13360(10) | 9.2298(4) | 9.3269(5) | 16.2580(3) | 7.51090(10) |
| *c* /Å | 12.3564(3) | 9.9792(5) | 18.0996(10) | 36.9507(9) | 20.7273(3) |
| *α* /° | 90 | 74.069(4) | 90 | 88.673(2) | 90 |
| *β* /° | 104.866(2) | 84.518(3) | 107.951(7) | 87.895(2) | 90 |
| *γ* /° | 90 | 67.755(4) | 90 | 81.185(2) | 90 |
| *V* /Å3 | 1245.89(4) | 671.26(5) | 2183.2(2) | 5389.8(2) | 3015.05(7) |
| *Z* | 2 | 1 | 4 | 8 | 8 |
| *ρ*calc /g/cm3 | 1.27 | 1.33 | 1.36 | 1.25 | 1.47 |
| μ/mm−1 | 0.625 | 0.594 | 0.709 | 0.588 | 1.00 |
| *F*(000) | 504 | 284 | 944 | 2144 | 1392 |
| Crystal size/mm3 | 0.51 × 0.38 × 0.26 | 0.42 × 0.20 × 0.05 | 0.59 × 0.20 × 0.03 | 0.35 × 0.15 × 0.024 | 0.48 × 0.38 × 0.12 |
| Radiation | Mo Kα (*λ* = 0.71073 Å) | | | | |  |
| 2Θ range for data collection/° | 6.8 to 65.7 | 6.4 to 66.0 | 6.4 to 57.2 | 4.9 to 55.0 | 6.9 to 65.7 |
| Index ranges | −15 ≤ *h* ≤ 15, −15 ≤ *k* ≤ 15, −18 ≤ *l* ≤ 18 | −12 ≤ *h* ≤ 12, −13 ≤ *k* ≤ 14, −14 ≤ *l* ≤ 15 | −17 ≤ *h* ≤ 18, −12 ≤ *k* ≤ 10, −23 ≤ *l* ≤ 19 | −11 ≤ *h* ≤ 11, −21 ≤ *k* ≤ 21, −47 ≤ *l* ≤ 47 | −28 ≤ *h* ≤ 29, −11 ≤ *k* ≤ 11, −31 ≤ *l* ≤ 29 |
| Reflections collected | 74020 | 30443 | 21873 | 137542 | 85694 |
| Independent reflections | 4514 [*R*int = 0.0359, *R*sigma = 0.0149] | 4756 [*R*int = 0.0540, *R*sigma = 0.0428] | 5006 [*R*int = 0.0418, *R*sigma = 0.0390] | 24739 [*R*int = 0.1072, *R*sigma = 0.0921] | 5438 [*R*int = 0.0372, *R*sigma = 0.0156] |
| Data/restraints/parameters | 4514/8/161 | 4756/0/170 | 5006/28/299 | 24739/0/1269 | 5438/0/200 |
| Goodness−of−fit on *F*2 | 1.010 | 1.034 | 1.068 | 0.979 | 1.031 |
| Final *R* indexes [*I≥*2*σ* (*I*)] | *R*1 = 0.0402, *wR*2 = 0.0929 | *R*1 = 0.0471, *wR*2 = 0.1077 | *R*1 = 0.0488, *wR*2 = 0.1115 | *R*1 = 0.0624, *wR*2 = 0.1454 | *R*1 = 0.0341, *wR*2 = 0.0818 |
| Final *R* indexes [all data] | *R*1 = 0.0663, *wR*2 = 0.1084 | *R*1 = 0.0768, *wR*2 = 0.1226 | *R*1 = 0.0859, *wR*2 = 0.1323 | *R*1 = 0.1400, *wR*2 = 0.1846 | *R*1 = 0.0481, *wR*2 = 0.0897 |
| Largest diff. peak/hole /eÅ−3 | +0.29/−0.21 | +0.38/−0.25 | +0.77/−0.46 | +0.41/−0.28 | +0.33/−0.27 |

**Obraz zawierający tekst, diagram, linia, Wykres

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**Figure S7**: VT 1H NMR (600 MHz, CD2Cl2) spectra of **2b** (R = 4-MeO-C6H4).



**Figure S8**: (a) 1H-13C HSQC NMR spectrum of **2b** (600 MHz, −93 °C, CD2Cl2); (b) 1H-13C HSQC NMR spectrum of **2b** (600 MHz, −80 °C, toluene-*d*8). Cross-peaks for CH2 are shown in blue; cross-peaks for CH and CH3 are shown in red.

**Theoretical calculations**

**Methods**

Theoretical calculations were performed using Orca 4.0 program [[[12]](#endnote-12)]. Molecules were optimized using BP86 method [[[13]](#endnote-13)] with def2-TZVPP basis set [[[14]](#endnote-14)] augmented with def2/J auxiliary basis set [[[15]](#endnote-15)]. Unless stated otherwise, the calculations were performed in the presence of the solvent field with the polarizable continuum model (PCM) using the CPCM polarizable conductor calculation model [[[16]](#endnote-16)]. The parameters of toluene were used. The starting geometries were adopted from the crystal structure or manually modified in the Avogadro program [[[17]](#endnote-17)], if crystal data was not available. Following geometry optimization, the vibrational frequencies were calculated, and the results showed that optimized structures are stable geometric structures (no imaginary frequencies). Gibbs free energies at 25 °C and –80 °C were obtained from the frequency calculations. NMR shieldings of 1H nuclei were calculated using default settings. In this method, the chemical shifts are calculated for rigid molecules in their lowest energy geometry. An optimized toluene molecule was used as a reference to calculate chemical shifts (shielding of the proton in *para* position was used as a reference).

**Geometry scan**: The scan was done using BP86 method [13] and def2-TZVP basis set [14], augmented with def2/J auxiliary basis set [15], with RI approximation [[[18]](#endnote-18)], without a solvation model. The atoms (1, 2, 3, 4) defining the dihedral angle subjected to the scan are shown in Figure S7. During the scan procedure, the molecule was optimized with the following dihedral angle values constrained: 0, –30, –60, –90, –110, –111, –112, –113, –114, –115, –120, –125, –130°. The bond length between atoms 2 and 3 (Figure S8) was computed for every scanned conformation. The conformation with the biggest bond length (conformation **D**, dihedral angle: –113°) was subjected to Gibbs free energy calculation and NMR shielding prediction.



**Figure** **S9**: Schematic representation of compound **2b** with the dihedral angle subjected to the scan shown in red. The dashed line represents the rest of the molecule.

**To get further insight into the dynamic processes that could account for the observed coalescence of signals on the VT NMR spectra, four possible conformations of compound 2b were considered (**Figure S10). **In conformation A, both phenyl rings were directed outside the cavity of the compound. This conformation was found in the crystal structure. In conformation B, one of the phenyl rings was directed towards the cavity. In conformation C, both rings were directed towards the cavity.** Conformation **D was derived from conformation A by rotating one of the phenyl rings, thus minimizing its** conjugation with the lone electron pair on the adjacent N atom. This conformation was unstable and it was generated via a geometry scan. It was meant to illustrate the ring rotation that takes place in a solution**.**

A picture containing scatter chart

Description automatically generated

**Figure S10**: The generated conformations of compound **2b**. Conformation **D** was derived from conformation **A** by rotating the aromatic ring shown in cyan.

In each conformation, the 11-membered ring of compound **2b** was in a conformation analogous to the chair conformation of cyclohexane. In conformation **A**, both aromatic rings were in pseudoequatorial positions. In conformation **B**, one of the aromatic rings was in pseudoaxial position, and the other was in pseudoequatorial position. In conformation **C**, both aromatic rings were in pseudoaxial positions.

**Relative energies of conformations A, B, C and D were calculated (Table S5).** The energy of the conformations increased in the order: E(**A**) < E(**B**) < E(**C**), that is the conformations with substituents in pseudoaxial positions had higher energies. Consequently, this behaviour was analogous to the behaviour of cyclohexane derivatives. **Conformation B had large entropy and its concentration significantly increased with the temperature. At** 25 °C, approximately 2% of compound **2b** could be present in this form.[[19]](#endnote-19) According to these calculations, conformations **C** and **D** are unlikely to be present in a solution in large amounts.

**Table S5**. Predicted relative free Gibbs energies of four conformations of compound **2b** at −80 °C and 25 °C.

|  |  |  |
| --- | --- | --- |
| **Conformation** | ***ΔG***0 [kJ/mol] | |
| −80 °C | 25 °C |
| **A** | **0** | **0** |
| **B** | **+13.1** | **+9.9** |
| **C** | **+28.4** | **+28.7** |
| **D** | **+16.3** | **+15.6** |

**The predicted NMR shifts of protons in each conformation were calculated. The protons that display considerable broadening or decoalescene at low temperature are** of particular interest. **The chemical shifts of these protons are shown on Figure S11.**

Obraz zawierający diagram

Opis wygenerowany automatycznie

**Figure S11**:The predicted chemical shifts (in ppm) for selected protons in **2b** (conformation **A**).

The predicted proton shifts in conformations **A**, **B** and **C** were generally similar. Therefore, it is unlikely that these conformations are the cause of shift changes observed at low temperatures. The complete list of calculated proton NMR chemical shifts for each conformation is shown on Figures S12-S15.

A picture containing chart

Description automatically generated

**proton** ***δ* [ppm]**

35 3.071

36 3.523

37 3.450

38 3.424

39 5.732

40 5.724

41 3.117

42 3.497

43 3.421

44 3.446

45 5.829

46 6.259

47 6.546

48 6.519

49 6.485

50 6.454

**proton** ***δ* [ppm]**

51 6.357

52 5.931

53 4.378

54 4.195

55 3.214

56 4.359

57 3.216

58 4.336

59 4.325

60 4.253

61 3.152

62 3.481

63 3.140

64 3.490

65 3.185

66 3.198

**Figure S12**:The predicted chemical shifts for all protons of in compound **2b** (conformation A).

Chart

Description automatically generated with medium confidence

**proton** ***δ* [ppm]**

35 2.828

36 3.746

37 3.458

38 3.505

39 5.698

40 5.818

41 3.818

42 3.623

43 3.495

44 3.594

45 6.236

46 6.456

47 6.637

48 6.718

49 6.259

50 6.308

**proton** ***δ* [ppm]**

51 6.337

52 6.216

53 4.098

54 3.944

55 3.625

56 4.239

57 3.009

58 3.976

59 3.258

60 4.434

61 3.253

62 3.535

63 3.236

64 3.496

65 3.175

66 3.171

**Figure S13**:The predicted chemical shifts for all protons of in compound **2b** (conformation B).

Chart

Description automatically generated

**proton** ***δ* [ppm]**

35 3.010

36 3.583

37 3.465

38 3.619

39 6.376

40 5.475

41 2.932

42 2.943

43 3.341

44 3.398

45 6.410

46 6.480

47 6.605

48 6.573

49 6.588

50 6.517

**proton** ***δ* [ppm]**

51 6.550

52 6.233

53 4.297

54 3.319

55 3.364

56 4.141

57 3.560

58 4.262

59 4.124

60 3.650

61 3.245

62 3.540

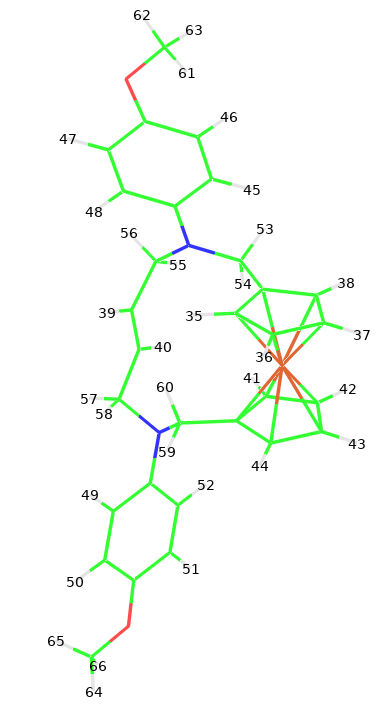
63 3.258

64 3.571

65 3.296

66 3.258

**Figure S14**:The predicted chemical shifts for all protons of in compound **2b** (conformation C).



**proton** ***δ* [ppm]**

35 2.958

36 3.432

37 3.373

38 3.462

39 5.758

40 5.777

41 3.680

42 3.703

43 3.214

44 3.154

45 5.844

46 6.227

47 6.549

48 6.530

49 7.148

50 6.621

**proton** ***δ* [ppm]**

51 6.474

52 6.672

53 4.419

54 4.366

55 3.281

56 4.226

57 3.300

58 2.965

59 3.193

60 4.505

61 3.184

62 3.487

63 3.137

64 3.596

65 3.292

66 3.249

**Figure S15**:The predicted chemical shifts for all protons of in compound **2b** (conformation D).

**References**

1. . Correa, A.; Tellitu, I.; Domínguez, E.; SanMartin, R. *J. Org. Chem*. **2006**, *71*, 8316–8319. [↑](#endnote-ref-1)
2. . Cadogan, J. I. G.; Hickson, C. L.; McNab, H. *J. Chem. Soc. Perkin Trans. I* **1985**, 1885–1889. [↑](#endnote-ref-2)
3. . Mazur, M.; Ziemkiewicz, K.; Rawiak, K.; Kisiel, K.; Wińska, P.; Deresz, K.; Jarzembska, K. N.; Buchowicz, W. *Eur. J. Inorg. Chem*. **2022**, e202101098. [↑](#endnote-ref-3)
4. . Abdel-Magid, A. F.; Carson, K. G.; Harris, B. D.; Maryanoff, C. A.; Shah, R. D. *J. Org. Chem.* **1996**, *61*, 3849–3862. [↑](#endnote-ref-4)
5. . For examples of Ti(O-*i*Pr)4 assisted ruthenium-catalyzed olefin metathesis, see: (a) Fürstner, A.; Langemann, K. *J. Am. Chem. Soc*. **1997**, *119*, 9130–9136. (b) Yang, Q.; Xiao, W.-J.; Yu, Z. *Org. Lett.,* **2005**, *7*, 871–874. (d) Au, C. W. G.; Pyne, S. J. *J. Org. Chem*. **2006**, *71*, 7097–7099. (d) Miller, B.; Mao, S.; Rosenker, K. M. G.; Pierce, J. G.; Wipf, P. *Beilstein J. Org.* *Chem.* **2012**, *8*, 1091–1097. [↑](#endnote-ref-5)
6. . For successful olefin metathesis in the presence of NaCl, see: Foster, J. C.; Grocott, M. C.; Arkinstall, L. A.; Varlas, S.; Redding, M. J.; Grayson, S. M.; O’Reilly, R. K. *J. Am. Chem. Soc*. **2020**, *142*, 13878−13885. [↑](#endnote-ref-6)
7. . For olefin metathesis of amine hydrochlorides, see (a) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857. (b) Hong, S. H.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 3508−3509. (c) Skowerski, K.; Szczepaniak, G.; Wierzbicka, C.; Gułajski, Ł.; Bieniek, M.; Grela, K. *Catal. Sci. Technol.* **2012**, *2*, 2424−2427. [↑](#endnote-ref-7)
8. . Sheldrick, G. *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8. [↑](#endnote-ref-8)
9. . Sheldrick, G. *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8. [↑](#endnote-ref-9)
10. . Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J. ; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. [↑](#endnote-ref-10)
11. . Spek, A. L. *Acta Crystallogr. Sect. C* **2015**, *71*, 9–18. [↑](#endnote-ref-11)
12. . Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. *J. Chem. Phys.* **2020**, *152*, 224108. [↑](#endnote-ref-12)
13. . Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. [↑](#endnote-ref-13)
14. . Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297. [↑](#endnote-ref-14)
15. . Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057. [↑](#endnote-ref-15)
16. . Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999–3094. [↑](#endnote-ref-16)
17. . Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. *J. Cheminformatics* **2012**, *4*, 17. [↑](#endnote-ref-17)
18. . Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 3396–3402. [↑](#endnote-ref-18)
19. . This was calculated using the Van ‘t Hoff equation. [↑](#endnote-ref-19)