Supporting information

Halogen Bond Asymmetry in Solution

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References
1. SYNTHESIS

1.1. General information

Reagents and solvents were obtained from commercial suppliers and, unless otherwise specified, used without further purification. Anhydrous DMF was provided by Sigma-Aldrich and redistilled. Et₂NH (99.5%) was purchased from Sigma-Aldrich or Acros Organics. Dry DCM was freshly distilled from CaH₂ in the presence of tetraethylene glycol dimethyl ether, dry n-hexane was freshly distilled from sodium metal/benzophenone; both were then stored over molecular sieves in a glove box. In the deuteration reaction and in the syntheses of the [N-I-N]⁺ complexes all used glassware were pre-dried overnight in an oven at 150 °C. Microwave-assisted reactions were performed on a Biotage Initiator instrument, using capped vials and fixed hold-time. Thin layer chromatography (TLC) and liquid chromatography-mass spectrometry (LC-MS) were used for monitoring the reactions. Merck neutral, silica gel-coated aluminum sheets, grade F254 were used for analytical TLC, and the spots were visualized by UV (254 nm). LC-MS analyses were done on an API SCIEX 150 EX Perkin Elmer ESI-MS (30 eV) attached to a Perkin Elmer gradient pump system and a C8 column (Gemini), using acetonitrile and 1% formic acid in MQ-water (gradient elution using 5- 95% acetonitrile over 4 min) as mobile phases. VWR Chemicals Silica gel (40-63 μm) or Davisil® Chromatographic Silica Media (LC60Å 40-63 micron) were used for column chromatography. A Heraeus Christ Labofuge A centrifuge was used for centrifugations. For structural NMR assignments, ¹H NMR and ¹³C NMR spectra were recorded on either a Varian (400MR or VNMRS 500) or a Bruker (Avance III HD 800 or 900) spectrometer at 25 °C in CD₃CN, CD₂Cl₂ (dried over molecular sieves (3 Å) and stored in a glove box), or CDCl₃, at 400, 500, 800, or 900 MHz for ¹H NMR, and 101, 126, 201, or 226 MHz for ¹³C NMR. Reported chemical shifts are on the δ scale (ppm), with the residual solvent signal as internal standard; CDCl₃ (δH 7.26, δC 77.16), CD₂Cl₂ (δH 5.32, δC 53.84), CD₃CN (δH 1.94, δC 118.26, 1.32). For assignment of the ¹H and ¹³C signals ¹H-¹H COSY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC NMR experiments were used. Each ¹H NMR resonance was assigned according to the conventions: chemical shift (δ) measured in ppm, observed multiplicity, observed coupling constant (J Hz), number of hydrogens, and assignment. Designation of multiplicities is: s (singlet), d (doublet), t (triplet), q (quartet), h (heptet), and m (multiplet). Structure numbering refers to numbers used in the NMR assignments. To obtain ¹⁵N NMR chemical shifts a Varian VNMRS 500 spectrometer, equipped with a ¹H-¹⁹F/¹⁵N-³¹P 5 mm PFG dual broadband probe, or a Bruker Avance III HD 900 spectrometer, equipped with a 5mm TCI cryogenic probe, were used to record ¹H-¹⁵NgHMBCAD NMR spectra at 25 °C. A sealed capillary with nitromethane (δN 0.0 ppm) was used as external chemical shift reference. High resolution mass spectrometry (HRMS) data were obtained by Stenhagen Analyslab AB, Gothenburg, Sweden, on a Q-TOF-MS, with detection in the positive ion mode at 50-1000 Da. Samples were dissolved in acetonitrile, and run on an analytical Halo RP-Amide column using 5-95% H₂O/mixACN/MeOH 1:1. For detection a QSTAR XL TOF detector, with external mass reference, was used.
1.2. The synthesis of [(4-methyl-2-((2-((4-(trifluoromethyl)pyridin-2-yl)ethynyl)phenyl)-ethynyl)pyridine)iodine]•tetrafluoroborate

2-Deutero-4-methyl-6-chloropyridine (3-d). To dry n-hexane (44 mL), kept under an argon atmosphere while being stirred and cooled (-78 °C), DMAE (8 mL, 79.52 mmol) was added by syringe. n-BuLi (2.5 M in hexanes, 63 mL, 157.50 mmol) was added dropwise by syringe over 45 min, after which the solution was stirred (100 min) during continuous cooling at -78 °C. A solution of 2-chloro-4-methylpyridine (2.63 mL, 23.54 mmol) in dry n-hexane (44 mL) was prepared and added dropwise by syringe, over 1 h, which made the colorless solution to orange yellow while losing its clearness. The cooled (-78 °C) solution was stirred (45 min), and then quenched with CH₃OD (17.5 mL, 430.48 mmol) added dropwise by syringe, over 15 min. The solution darkened and received a brown color. It was stirred (15 min) while cooling (-78 °C), and then further stirred (35 min) and allowed to reach room temperature, during which the color brightened to orange-yellow. The solution was washed with H₂O (150 mL). The aqueous phase was then extracted with Et₂O (3 x 50 mL), and the combined neon orange organic phases dried over Na₂SO₄, filtered, and concentrated in vacuo to give the crude product (3.074 g) as an orange liquid. The crude was purified by column chromatography (silica), eluting with Et₂O:hexane (2:3) providing 3-d (1.876 g, 62%, with ≥ 90% deuteration) as an orange oil, which solidified upon storage in the freezer (-20 °C). ¹H (400 MHz, CDCl₃) δ 7.15 (dq, J = 1.5, 0.7 Hz, 1H, H-5), 7.02 (dqt, J = 1.5, 0.7, 0.7 Hz, 1H, H-3), 2.34 (dd, J = 0.7, 0.7 Hz, 3H, H-12); ¹³C (126 MHz, CDCl₃) δ 151.7 (t, 2JCD = 2.0 Hz, C-6), 150.5 (t, 3JCD = 1.1 Hz, C-4), 149.1 (t, 4JCD = 27.6 Hz, C-2), 125.0 (C-5), 123.4 (t, 5JCD = 1.0 Hz, C-3), 20.9 (C-12); MS (ESI) m/z 129.1 [M+H]+, calcd 129.6 (C₆H₆DNCl)+.

4-Methyl-2-[2-(trimethylsilyl)-ethynyl]pyridine (4). Five separate microwave vials (20 mL), each equipped with a magnetic stir bar, containing PPh₃ (1: 0.414 g, 1.58 mmol; 2: 0.447 g, 1.70 mmol; 3: 0.414 g, 1.58 mmol; 4: 0.432 g, 1.65 mmol; 5: 0.497 g, 1.89 mmol), and Pd(Ph₃)₂Cl₂ (1: 0.452 g, 0.64 mmol; 2: 0.449 g, 0.64 mmol; 3: 0.443 g, 0.63 mmol; 4: 0.457 g, 0.65 mmol; 5: 0.477 g, 0.68 mmol) were prepared. The vials were capped with microwave vial cap with septum, and purged with Ar (g). The vials were uncapped in a glove box, and CuI (1: 0.193 g, 1.01 mmol; 2: 0.193 g, 1.01 mmol; 3: 0.196 g, 1.03 mmol; 4: 0.196 g, 1.03 mmol; 5: 0.21 g, 1.10 mmol) was added. After recapping with new microwave vial caps with septum and removing the vials from the glove box, the vials were kept under an Ar (g) atmosphere. Et₂NH (1-5: 10 mL, 96.72 mmol), DMF (1-5: 4 mL), 2-chloro-4-methylpyridine 3 (1-5: 0.88 mL, 7.88 mmol), and ethynyltrimethylsilane (1-5: 1.4 mL, 10.11 mmol) was added by syringe, while stirring the solution. The vials were irradiated by microwave for 27 min at 120 °C (60 s pre-stirring, fixed hold time). The reaction mixtures were filtered through Celite, being washed with DCM (~300 mL). The solution was then washed with H₂O (150 mL). The aqueous phase was extracted with DCM three times (tot. ~125 mL), after which the combined organic phases were washed with brine (120 mL), dried
over MgSO₄, filtered, and concentrated in vacuo to give the crude product as a brown-black liquid. The crude was purified by column chromatography (silica) twice, eluting with Et₂O:hexane (3:7). Compound 4 (5.595 g, 75%) was obtained as a dark brown liquid. 

1H (500 MHz, CDCl₃) δ 8.41 (dd, J = 5.1, 0.7 Hz, 1H, H-2), 7.29 (ddq, J = 1.7, 0.9, 0.7 Hz, 1H, H-5), 7.04 (ddq, J = 5.1, 1.7, 0.8 Hz, 1H, H-3), 2.32 (dd, J = 0.9, 0.8 Hz, 3H, H-12), 0.26 (s, 9H, H-14); 13C (126 MHz, CDCl₃) δ 149.8 (C-2), 147.4 (C-4), 143.0 (C-6), 128.3 (C-5), 124.2 (C-3), 104.0 (C-7), 94.4 (C-8), 20.9 (C-12), -0.1 (C-14); MS (ESI) m/z 189.8 [M+H]+, calcd 190.3 (C₁₁H₁₆NSi).
2-Ethynyl-4-methylpyridine (5). Compound 4 (5.602 g, 29.59 mmol), MeOH (140 mL), and KF (5.212 g, 89.71 mmol) were stirred at room temperature (2.5 h). The solution was concentrated *in vacuo* to give a black, wet-looking solid that was dissolved in DCM (200 mL). The solution was washed with H₂O (150 mL), the aqueous phase extracted with DCM three times (3 x 50 mL), and the combined organic phases washed with brine (100 mL) dried over Na₂SO₄, filtered, and concentrated *in vacuo*. Compound 5 (3.436 g, 99%) was obtained as a black-brown liquid. ¹H (500 MHz, CDCl₃) δ 8.43 (dd, J = 5.0, 0.5 Hz, 1H, H-2), 7.32 (dqd, J = 1.6, 0.8, 0.5 Hz, 1H, H-5), 7.08 (ddq, J = 5.0, 1.6, 0.6 Hz, 1H, H-3), 3.11 (s, 1H, H-8), 2.34 (dd, J = 0.8, 0.6 Hz, 1H, H-12); ¹³C (126 MHz, CDCl₃) δ 149.9 (C-2), 147.6 (C-4), 142.3 (C-6), 128.5 (C-5), 124.6 (C-3), 83.1 (C-7), 76.8 (C-8), 20.9 (C-12); MS (ESI) m/z 118.0 [M+H]+, calcd 118.2 (C₈H₈N)+.

2-Deutero-6-ethynyl-4-methylpyridine (5-d). Compound 4-d (5.819 g, 30.57 mmol), MeOH (150 mL), and KF (5.494 g, 94.56 mmol) were stirred at room temperature (13.5 h). The solution was concentrated *in vacuo* to give a black, wet-looking solid that was dissolved in DCM (150 mL). The solution was washed with H₂O (150 mL), the aqueous phase extracted with DCM three times (tot. 140 mL), and the combined yellow-black organic phases dried over Na₂SO₄, filtered, and concentrated *in vacuo*. Compound 5-d (2.866 g, 79%) was obtained as a thick, black oil. ¹H (500 MHz, CDCl₃) δ 7.32 (d, J = 1.5 Hz, 1H, H-5), 7.08 (d, J = 1.5 Hz, 1H, H-3), 3.11 (s, 1H, H-8), 2.34 (s, 1H, H-12); ¹³C (126 MHz, CDCl₃) δ 149.6 (t, J_CD = 26.7 Hz, C-2), 147.6 (C-4), 142.3 (t, J_CD = 1.9 Hz, C-6), 128.5 (C-5), 124.5 (t, J_CD = 1.0 Hz, C-3), 83.1 (C-7), 76.8 (C-8), 21.0 (C-12); MS (ESI) m/z 119.3 [M+H]+, calcd 119.2 (C₈H₇DN)+.

2-[2-(2-Iodophenyl)ethynyl]-4-methylpyridine (6). To two separate microwave vials (20 mL), each equipped with a magnetic stir bar, Pd(Ph₃)₂Cl₂ (1: 0.499 g, 0.71 mmol; 2: 0.450 g, 0.64 mmol) was added. The vials were capped with microwave vial caps with septum, and purged with Ar (g). In a glove box, the vials were uncapped and CuI (1: 0.46 g, 2.42 mmol; 2: 0.22 g, 1.16 mmol) was added. After recapping with a new microwave vial caps with septum and removing the vials from the glovebox, the vials were kept under an Ar (g) atmosphere. Et₂NH (1: 12 mL, 116.06 mmol; 2: 12 mL, 116.06 mmol) and 1,2-diiodobenzene (1: 1.4 mL, 10.71 mmol; 2: 1.4 mL, 10.71 mmol) were added by syringe under stirring. Compound 5 (2.062 g, 17.60 mmol) was dissolved in DMF (8 mL), and the solution was divided equally between the two vials, being added by syringe under
continuous stirring. The vials were irradiated by microwave for 5 min at 120 °C (60 s pre-stirring, fixed hold time) in succession. The brown-black reaction mixture was filtered through Celite, washed with DCM, and the solution was transferred to a separatory funnel, washing the round bottom flask with additional DCM (~300 mL in total). The solution was washed with H2O (150 mL), the aqueous phase was then extracted with DCM three times (3 x 50 mL), after which the combined organic phases were washed with brine (150 mL), dried over MgSO4, filtered, and concentrated in vacuo to give the crude product as a dark brown oil. The crude was purified by column chromatography (silica) two times, eluting with pentane:EtOAc (2:1) to provide 6 (1.953 g, 35%) as an orange solid. 

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\begin{align*}
\text{H} & \quad \delta \quad 8.49 \text{ (dd, } J = 5.1, 0.8 \text{ Hz, } 1\text{H, } H-2), \quad 7.88 \text{ (dd, } J = 8.0, 1.2 \text{ Hz, } 1\text{H, H-10}), \quad 7.61 \text{ (dd, } J = 7.7, 1.7 \text{ Hz, } 1\text{H, H-10}), \quad 7.46 \text{ (ddq, } J = 1.7, 0.8, 0.8 \text{ Hz, } 1\text{H, H-5}), \quad 7.34 \text{ (ddd, } J = 7.7, 7.5, 1.2 \text{ Hz, } 1\text{H, H-11}), \quad 7.09 \text{ (ddq, } J = 5.1, 1.7, 0.9 \text{ Hz, } 1\text{H, H-3}), \quad 7.05 \text{ (ddd, } J = 8.1, 7.5, 1.7 \text{ Hz, } 1\text{H, H-11'}), \\
\text{C} & \quad \delta \quad 150.0 \text{ (C-2), } 147.6 \text{ (C-4), } 143.1 \text{ (C-6), } 138.9 \text{ (C-10), } 133.3 \text{ (C-10), } 129.2 \text{ (C-9), } 128.5 \text{ (C-5), } 128.0 \text{ (C-11), } 124.3 \text{ (C-3), } 101.3 \text{ (C-9'), } 92.2 \text{ (C-7), } 90.9 \text{ (C-8), } 21.0 \text{ (C-12); MS (ESI) } m/z 319.9 \text{ [M+H]}. 
\end{align*}
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2-Deutero-6-[2-(2-iodophenyl)ethynyl]-4-methylpyridine (6-d). To a microwave vial (20 mL), equipped with a magnetic stir bar, Pd(Ph3)2Cl2 (0.407 g, 0.58 mmol) was added. The vial was capped with a microwave vial cap with septum, and purged with Ar (g). The vial was uncapped in a glove box, and CuI (0.188 g, 0.99 mmol) was added. After recapping with a new microwave vial cap with septum and removing the vial from the glovebox, the vial was kept under an Ar (g) atmosphere. Et2NH (11 mL, 106.39 mmol) was added (a few mL of it was added, then the solution was stirred quickly before adding the rest) by syringe, after which the solution was bubbled through with Ar (g) via a needle. 1,2-Diiodobenzene (1.43 mL, 10.94 mmol) was added via a syringe, and the solution was bubbled through with Ar (g). Compound 5-d (0.859 g, 7.27 mmol) was dissolved in DMF (3.75 mL), and transferred into the vial via a syringe. The solution was bubbled through with Ar (g) and was then irradiated by microwave for 5 min at 120 °C (30 s pre-stirring, fixed hold time). The brown-black reaction mixture was filtered through Celite, and washed with DCM, after which the solution was transferred to a separatory funnel, washing the round bottom flask with additional DCM (~100 mL in total). The solution was washed with H2O (70 mL). The aqueous phase was then extracted with DCM three times (tot. 100 mL), after which the combined organic phases were dried over Na2SO4, filtered, and concentrated in vacuo to give the crude product as a black, thick liquid. The crude was purified by column chromatography (silica) two times, the first time eluting with Et2O:hexane (1:2) and changing to Et2O:hexane (1:1) after first solvent refill, and the second time with Et2O:hexane (1:2) only. Compound 6-d (0.839 g, 36%) was obtained as pale brown crystals. 

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\begin{align*}
\text{H} & \quad \delta \quad 7.89 \text{ (dd, } J = 8.0, 1.2 \text{ Hz, } 1\text{H, H-10}), \quad 7.61 \text{ (dd, } J = 7.7, 1.7 \text{ Hz, } 1\text{H, H-10}), \quad 7.47 \text{ (dq, } J = 1.6, 0.7 \text{ Hz, } 1\text{H, H-5}), \quad 7.35 \text{ (ddd, } J = 7.7, 7.5, 1.2 \text{ Hz, } 1\text{H, H-11}), \quad 7.09 \text{ (dq, } J = 1.6, 0.6 \text{ Hz, } 1\text{H, H-3}), \quad 7.05 \text{ (ddd, } J = 8.0, 7.5, 1.7 \text{ Hz, } 1\text{H, H-11'}), \quad 2.38 \text{ (dd, } J = 0.7, 0.6 \text{ Hz, } 3\text{H, H-12}); \\
\text{C} & \quad \delta \quad 149.5 \text{ (t, } J_{CD} = 28.0 \text{ Hz, C-2), } 147.9 \text{ (t, } J_{CD} = 3.2 \text{ Hz, C-4), } 142.9 \text{ (t, } J_{CD} = 2.2 \text{ Hz, C-6), } 138.9 \text{ (C-10'), } 133.3 \text{ (C-10), } 130.2 \text{ (C-11').}
\end{align*}
\]
129.1 (C-9), 128.5 (C-5), 128.0 (C-11), 124.2 (C-3), 101.3 (C-9'), 92.0 (C-7), 91.1 (C-8), 21.1 (C-12); HRMS m/z 320.9999 [M+H]+, calcd 321.1596 (C_{14}H_{10}DNI)+.

4-methyl-2-(2-(2-(trimethylsilyl)ethynyl)phenyl)-ethynyl)pyridine (7). To a microwave vial (20 mL), equipped with a magnetic stir bar, Pd(Ph3)2Cl2 (0.199 g, 0.28 mmol) and 6 (1.118 g, 3.50 mmol) were added. The vial was capped with a microwave vial cap with septum, and purged with Ar (g). In a glove box, the vial was uncapped and CuI (0.088 g, 0.46 mmol) was added. After recapping with a new microwave vial cap with septum and removing the vial from the glovebox, the vial was kept under an Ar (g) atmosphere. Et2NH (5.4 mL, 52.23 mmol) was added by syringe, after which the solution was stirred. DMF (1.8 mL) and ethynyltrimethylsilane (0.59 mL, 4.26 mmol) was added, also by syringe. The dark, red-brown solution was given a gentle stir, and was then irradiated by microwave for 36 min at 120 °C (60 s pre-stirring, fixed hold time). The brown-black reaction mixture was transferred to a separatory funnel, washing the vial with DCM (140 mL). The solution was washed with H2O (70 mL). The aqueous phase was then extracted with DCM two times (tot. 65 mL), after which the combined organic phases were dried over Na2SO4, filtered, and concentrated in vacuo to give the crude product as a brown-black liquid (2.847 g). The crude was purified by column chromatography (silica), eluting with DCM. The residue was dissolved in DCM (10 mL), EDTA (0.275 g, 0.94 mmol) was added, and the resulting solution was stirred in room temperature (25 min). (This step is necessary to avoid Glaser coupling, catalyzed by residual Cu(I) upon deprotection of the TMS). The solution was subsequently concentrated in vacuo, and again purified by column chromatography (silica), eluting with DCM. Compound 7 (0.653 g, 65%) was obtained as a dark, red-black liquid. 1H (500 MHz, CDCl3) δ 8.49 (d, J = 4.0 Hz, 1H, H-2), 7.58-7.60 (m, 1H, H-10), 7.50-7.52 (m, 1H, H-10'), 7.42 (s, 1H, H-5), 7.28-7.31 (m, 2H, H-11 and H-11'), 7.08 (d, J = 4.0 Hz, 1H, H-3), 2.35 (s, 3H, H-12), 0.28 (s, 9H, H-14); 13C (126 MHz, CDCl3) δ 149.9 (C-2), 147.3 (C-4), 143.4 (C-6), 132.4 (C-10), 132.3 (C-10), 128.6 (C-11' and C-5), 128.4 (C-11), 126.2 (C-9), 125.3 (C-9'), 124.2 (C-3), 103.5 (C-8'), 99.0 (C-7'), 87.8 (C-8), 92.7 (C-7), 20.9 (C-12), 0.2 (C-14); HRMS m/z 290.1365 [M+H]+, calcd 290.4610 (C_{19}H_{20}NSi)+.

2-Deutero-4-methyl-6-(2-(2-(trimethylsilyl)ethynyl)phenyl)-ethynyl)pyridine (7-d). To two separate microwave vials (20 mL), each equipped with a magnetic stir bar, Pd(Ph3)2Cl2 (1: 0.325 g, 0.46 mmol; 2: 0.323 g, 0.46 mmol) was added. The vials were capped with microwave vial caps with septum, and purged with Ar (g).
The vials were uncapped in a glove box and CuI (1: 0.153 g, 0.80 mmol; 2: 0.166 g, 0.87 mmol) was added. After recapping with new microwave vial caps with septum and removing the vials from the glove box, the vials were kept under an Ar (g) atmosphere. Et₂NH (1: 8.75 mL, 84.63 mmol; 2: 8.75 mL, 84.63 mmol) was added (first a few mL, then the solutions were stirred quickly before adding the rest) by syringe, after which the solutions were bubbled through with Ar (g) by needle. Compound 6-d (3.650 g, 11.40 mmol) was dissolved in DMF (5.75 mL), and the resulting solution was divided equally between the two vials, adding it by syringe. Next, the solutions were bubbled through with Ar (g) and ethynyltrimethylsilane (0.95 mL, 6.86 mmol) was added to one of the vials, after which the resulting dark red solution was immediately irradiated by microwave for 30 min at 120 °C (30 s pre-stirring, fixed hold time). Ethynyltrimethylsilane (0.95 mL, 6.86 mmol) was then added to the second vial, repeating the same procedure as above. The brown-black reaction mixtures were filtered through Celite, washed with DCM (85 mL). EDTA (1.038 g, 3.55 mmol) was added along with a magnetic stir bar, and the resulting brown-black solution was stirred at room temperature for 15 min. The solution was filtered through Celite, washed with DCM (80 mL) and transferred to a separatory funnel. The round bottom flask was washed with additional DCM (50 mL), and the combined DCM solution was washed with H₂O (150 mL). The aqueous phase was extracted with DCM (3 x 30 mL), after which the combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuo to give the crude product (6.287 g) as a black liquid. The crude was purified by column chromatography (silica) three times, the first and second columns being eluted with DCM, and the third with Et₂O:hexane (1:2). Compound 7-d (2.103 g, 64%) was obtained as a red, thick oil, which solidified upon storage in the freezer. ¹H (400 MHz, CDCl₃) δ 7.58-7.60 (m, 1H, H-10), 7.49-7.52 (m, 1H, H-10'), 7.41 (dq, J = 1.4, 0.7 Hz, 1H, H-5), 7.27-7.32 (m, 2H, H-11 and H-11'), 7.07 (dq, J = 1.4, 0.6 Hz, 1H, H-3), 2.36 (dd, J = 0.7, 0.6 Hz, 3H, H-12), 0.28 (s, 9H, H-14); ¹³C (126 MHz, CDCl₃) δ 149.6 (t, ¹JCD = 27.4 Hz, C-2), 147.4 (t, ¹JCD = 1.2 Hz, C-4), 143.4 (t, ¹JCD = C-6), 132.4 (C-10'), 132.3 (C-10), 128.6 (C-5), 128.5 (C-11'), 128.4 (C-11), 126.2 (C-9), 125.4 (C-9'), 123.9 (C-3), 103.5 (C-8'), 99.0 (C-7'), 92.7 (C-7), 87.7 (C-8), 20.9 (C-12), 0.2 (C-14); HRMS m/z 291.1428 [M+H]+, calcld 291.4671 (C₁₉H₁₉DNSi)+.

2-[2-(2-Ethynylphenyl)ethynyl]-4-methylpyridine (8). Compound 7 (0.650 g, 2.25 mmol), MeOH (13 mL), and KF (0.405 g, 6.97 mmol) were stirred at room temperature (2.5 h). The solution was concentrated in vacuo to give a black, wet-looking solid that was dissolved in DCM (50 mL). The solution was washed with H₂O (50 mL), the aqueous phase extracted with DCM two times (tot. 40 mL), and the combined yellow-brown-black organic phases dried over Na₂SO₄, filtered, and concentrated in vacuo. Compound 8 (0.468 g, 96%) was obtained as a black-brown thick oil with some black crystals. ¹H (400 MHz, CDCl₃) δ 8.48 (d, J = 5.1 Hz, 1H, H-2), 7.60-7.63 (m, 1H, H-10), 7.53-7.56 (m, 1H, H-10'), 7.41 (dq, J = 1.8, 0.7 Hz, 1H, H-5), 7.30-7.37 (m, 2H, H-11 and H-11'), 7.08 (ddq, J = 5.1, 1.8, 0.80, Hz, 1H, H-3), 3.40 (s, 1H, H-7'), 2.37 (dd, J = 0.8, 0.7 Hz, 3H, H-12); ¹³C (201 MHz, CDCl₃) δ 150.0 (C-2), 147.5 (C-4), 143.3 (C-6), 132.8 (C-10'), 132.5 (C-10), 128.7 (C-11),
128.7 (C11'), 128.6 (C-5), 125.6 (C-9), 125.1 (C-9'), 124.2 (C-3), 92.8 (C-7), 87.2 (C-8), 82.1 (C-8'), 81.6 (C-7), 21.0 (C-12); HRMS m/z 218.0969 [M+H]⁺, calcd 218.2790 (C16H12N)+.

2-Deutero-6-[2-(2-ethynylphenyl)ethynyl]-4-methylpyridine (8-d). Compound 7-d (2.103 g, 7.24 mmol), MeOH (40 mL), and KF (1.293 g, 22.25 mmol) were stirred at room temperature (16.5 h). The solution was concentrated in vacuo to give a black, wet-looking solid that was dissolved in DCM (~150 mL). The solution was washed with H₂O (150 mL), the aqueous phase extracted with DCM three times (tot. 90 mL), and the combined yellow-brown-black organic phases dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was obtained as a black thick liquid, which was purified by column chromatography (silica), eluting with Et₂O, to give 8-d (1.058 g, 67%) as pale orange crystals. ¹H (400 MHz, CDCl₃) δ 7.60-7.62 (m, 1H, H-10), 7.53- 7.55 (m, 1H, H-10'), 7.40 (d, J = 1.5, 0.7 Hz, 1H, H-5), 7.31-7.35 (m, 2H, H-11 and H-11'), 7.07 (dq, J = 1.5, 0.8 Hz, 1H, H-3), 3.39 (s, 1H, H-7'), 2.37 (dd, J = 0.8, 0.7 Hz, 3H, H-12); ¹³C (126 MHz, CDCl₃) δ 149.6 (t, ¹JCD = 26.9 Hz, C-2), 147.5 (C-4), 143.2 (t, ¹JCD = 1.5 Hz, C-6), 132.8 (C-10'), 132.6 (C-10), 128.7 (C-11), 128.7 (C11'), 128.6 (C-5), 125.6 (C-9), 125.1 (C-9'), 124.0 (C-3), 92.7 (C-7), 87.3 (C-8), 82.1 (C-8'), 81.6 (C-7), 21.0 (C-12); HRMS m/z 219.1032 [M+H]⁺, calcd 219.2851 (C16H11DN)+.

4-Methyl-2-[2-[2-(2-[4-(trifluoromethyl)pyridin-2-yl]-ethynyl}phenyl]ethynyl]pyridine (9). To a microwave vial (5-8 mL), equipped with a magnetic stir bar, Pd(Ph₃)₂Cl₂ (0.231g, 0.33 mmol) was added. The vial was capped with a microwave vial cap with septum, and purged with Ar (g). The vial was uncapped in a glovebox and CuI (0.095g, 0.50 mmol) was added. After recapping with a new microwave vial cap with septum and removing the vial from the glovebox, the vial was kept under an Ar (g) atmosphere. Et₂NH (3.3 mL, 31.92 mmol) was added (first a few mL, then the solution was stirred quickly before adding the rest) via a syringe, after which the solution was bubbled through with Ar (g) via a needle. 2-Chloro-4-(trifluoromethyl)pyridine (0.34 mL, 2.64 mmol) was added via a syringe, and the solution was bubbled through with Ar (g). Compound 8 (0.468 g, 2.15 mmol) was dissolved in DMF (1.1 mL), and transferred to the vial by syringe, washing the round
bottom flask with Et$_2$NH (2 mL). The dark solution was stirred quickly, and then irradiated by microwave for 20 min at 120 °C (30s pre-stirring, fixed hold time). The brown-black reaction mixture was filtered through Celite, being washed with DCM, after which the solution was transferred to a separatory funnel, washing the round bottom flask with more DCM (~200 mL in total). The solution was washed with H$_2$O (120 mL). The aqueous phase was then extracted with DCM three times (tot. 50 mL), after which the combined organic phases were dried over Na$_2$SO$_4$, filtered, and concentrated 	extit{in vacuo} to give the crude product as a brown-black oil. The crude was purified by column chromatography (silica) three times, the first and second column being eluted with DCM and changing to DCM:MeOH (100:1) towards the end, and the third with EtOAc:hexane (1:6). Compound 9 (0.053 g, 7%) was obtained as a thick brown-red oil, which solidified upon storage in the freezer. $^1$H (500 MHz, CDCl$_3$) $\delta$ 8.81 (d, $J = 5.1$ Hz, 1H, H-2'), 8.51 (d, $J = 5.0$ Hz, 1H, H-5'), 7.65-7.68 (m, 2H, H-10 and H-10'), 7.52 (dq, $J = 2.0$, 0.7 Hz, 1H, H-5), 7.47 (dd, $J = 5.1$, 1.9 Hz, 1H, H-3'), 7.37-7.41 (m, 2H, H-11 and H-11'), 7.10 (ddq, $J = 5.0$, 2.0, 0.8 Hz, 1H, H-3), 2.36 (dd, $J = 0.8$, 0.7 Hz, 3H, H-12); $^{13}$C (126 MHz, CDCl$_3$) $\delta$ 151.0 (C-2'), 150.1 (C-2), 147.6 (C-4), 145.0 (C-6'), 143.1 (C-6), 138.7 (C-4'), 132.4 (C10 or C10'), 132.3 (C10 or C10'), 129.4 (C11 or C11'), 128.9 (C11 or C11'), 128.4 (C-5), 126.1 (C9 or 9'), 125.0 (C9 or 9'), 124.3 (C-3), 123.7 (q, $^{3}J_{CF} = 3.6$ Hz, C-5'), 121.6 (C-12'), 118.3 (q, $^{3}J_{CF} = 3.5$ Hz, C-3'), 93.6 (C-7), 92.1(C-7'), 89.9 (C-8 or C-8'), 87.2 (C-8 or C-8), 20.9 (C-12); $^{15}$N (51 MHz, CDCl$_3$) $\delta$ -55.5 (N-1'), -73.4 (N-1); HRMS m/z 363.1109 [M+H$^+$], calcd 363.3632 (C$_{22}$H$_{14}$N$_{2}$F$_{3}$)+.

2-Deutero-4-methyl-6-[2-[2-[4-(trifluoromethyl)pyridin-2-yl]-ethynyl]phenyl]ethynyl|pyridine (9-d). To two separate microwave vials (20 mL), each equipped with a magnetic stir bar, Pd(Ph$_3$)$_2$Cl$_2$ (I: 0.187 g, 0.27 mmol; 2: 0.186 g, 0.26 mmol) was added. The vials were capped and purged with Ar (g). The vials were uncapped in a glove box and CuI (I: 0.088 g, 0.46 mmol; 2: 0.092 g, 0.48 mmol) was added. After recapping with new microwave vial caps with septum, and removing the vials from the glovebox, the vials were kept under an Ar (g) atmosphere. Et$_2$NH (I: 3.5 mL, 33.85 mmol; 2: 3.5 mL, 33.85 mmol) was added (a few mL of it was added, then the solutions were stirred quickly before adding the rest) by syringe, after which the solutions were bubbled through with Ar (g) by needle. 2-Chloro-4-(trifluoromethyl)pyridine (I: 0.45 mL, 3.50 mmol; 2: 0.45 mL, 3.50 mmol) was added via a syringe, and the solutions were bubbled through with Ar (g). The vials were then allowed to stand at room temperature (~1 hr). Compound 8-d (0.752 g, 3.45 mmol) was dissolved in DMF (1.8 mL); half of the resulting solution was added to one of the vials, after which the vial was immediately irradiated by microwaves at 100 °C, for 12 min (5s pre-stirring with fixed hold time). The remaining 8-d solution was added to the second vial, after which the same procedure as above was repeated. The brown-black reaction mixtures were filtered through Celite, and washed with DCM (~160 mL). The solution was transferred to a
separatory funnel, the round bottom flask washed with additional DCM (~50 mL), and the combined solution was washed with H2O (120 mL). The aqueous phase was then extracted with DCM (3 x 30 mL), after which the combined organic phases were dried over Na2SO4, filtered, and concentrated in vacuo to give the crude product (1.791 g) as a black, thick oil. The crude was purified by column chromatography (silica) three times, the first column being eluted with DCM, and the second and third with EtOAc:hexane (1:6). Compound 9-d (0.240 g, 19%) was obtained as a beige solid. 1H (400 MHz, CDCl3) δ 8.81 (dq, J = 5.1, 0.7 Hz, 1H, H-2'), 8.07 (dq, J = 1.7, 0.8, 0.7 Hz, 1H, H-5'), 7.65-7.68 (m, 2H, H-10 and H-10'), 7.52 (dd, J = 1.7 and 0.8 Hz, 1H, H-5), 7.46 (ddq, J = 5.1, 1.7, 0.7 Hz, 1H, H-3'), 7.37-7.43 (m, 2H, H-11 and H-11'), 7.10 (dq, J = 1.7, 0.8 Hz, 1H, H-3), 2.36 (dd, J = 0.8, 0.8 Hz, 3H, H-12); 13C (201 MHz, CD2Cl2) δ 151.4 (C-2'), 150.0 (t, 1JCD = 27.1 Hz, C-2), 148.0 (C-4), 145.0 (C-6'), 143.2 (C-6), 138.8 (q, 3JC = 34.3 Hz, C-4'), 132.6 (C10 or C10'), 132.4 (C10 or C10'), 129.8 (C11 or C11'), 129.2 (C11 or 11' ), 128.8 (C-5), 126.2 (C9 or 9'), 125.1 (C9 or 9'), 124.5 (C-3), 124.0 (q, 3JC = 3.8 Hz, C-5'), 123.1 (q, 1JC = 272.5 Hz, C-12'), 118.7 (q, 3JC = 4.0 Hz, C-3'), 94.1 (C-7), 92.4 (C-7), 89.5 (C-8 or C-8'), 86.8 (C-8 or C-8), 20.9 (C-12); 15N (81 MHz, CD2Cl2) δ -53.7 (N-1'), -71.8 (N-1); HRMS m/z 364.1172 [M+H]+, calcd 364.3693 (C22H13DN2F3)+.

(4-Methyl-2-[2-(2-{2-[4-(trifluoromethyl)pyridin-2-yl]ethynyl}phenyl)ethynyl]pyridine)-iodonium tetrafluoroborate (1a). In a glovebox 9 (0.093 g, 0.26 mmol) dissolved in dry DCM (10 mL) was added by syringe to AgBF4 (0.052 g, 0.27 mmol) in a centrifuge vial (40 mL). The resulting yellow solution was stirred until the AgBF4 had dissolved, and the clear solution turned slightly cloudy. Dry n-hexane (20 mL) was added by syringe to generate precipitation. The vial was then centrifuged for 10 min at 2000 rpm. The supernatant was removed, and the pellet was washed with dry n-hexane (2 mL) and dried in vacuo over night. The slightly yellow solid (0.118 g) was dissolved in dry DCM (13 mL), and I2 (0.059 g, 0.23 mmol) was added. After being stirred (30 min) to allow AgI to precipitate, the vial was again centrifuged for 10 min at 2000 rpm. The supernatant was transferred to another centrifuge vial (40 mL), and dry n-hexane (26 mL) was added via a syringe to generate precipitation of 1a. The purple-pink solution with white, flakey solid was centrifuged for 10 min at 2500 rpm, the supernatant was removed, and the remaining pellet was washed with dry n-hexane (3 mL) and dried in vacuo for 35 min to generate 1a (0.073 g, 55%) as a slightly yellow powder. 1H (900 MHz, CD2Cl2) δ 9.09 (d, J = 5.7 Hz, 1H, H-2, 5.7 Hz, 1H, H-2'), 8.77 (d, J = 5.9 Hz, 1H, H-2) 8.07 (d, J = 1.9 Hz, 1H, H-5'), 7.80-7.83 (m, 2H, H-10 and H-10'), 7.75 (dq, J = 2.0, 0.8 Hz, 1H, H-5), 7.71 (dd, J = 5.7, 1.9 Hz, 1H, H-3'), 7.61-7.65 (m, 2H, H-11 and H-11'), 7.33 (ddq, J = 5.9, 2.0, 0.7 Hz, 1H, H-3), 2.55 (dd, J = 0.8, 0.7 Hz, 3H, H-12); 13C (226 MHz, CD2Cl2) δ 156.5 (C-4), 152.6 (C-2'), 151.0 (C-2), 144.4 (C-6), 143.3 (q, 3JC = 37.7 Hz, C-4'), 142.7 (C-6), 135.0 (C-10 or C-10'), 134.8...
(C-10 or C-10'), 131.8 (C-11 or C-11'), 131.5 (C-11 or C-11'), 131.4 (C-5), 128.2 (C-3), 126.3 (q, $^3J_{CF} = 3.6$ Hz, C-5'), 124.7 (C-9 or C-9'), 124.1 (C-9 or C-9'), 122.4 (q, $^3J_{CF} = 2.8$ Hz, C-3'), 121.9 (q, $^3J_{CF} = 272.4$ Hz, C-12'), 100.5 (C-8 or C-8'), 98.6 (C-8 or C-8'), 90.9 (C-7), 90.4 (C-7'), 21.9 (C-12); $^{15}\text{N}$ (91 MHz, CD$_2$Cl$_2$) $\delta$ -145.1(N-1'), -182.9 (N-1); HRMS m/z 489.0076 [M-BF$_4^-$]+, calcd 489.2591 (C$_{22}$H$_{13}$N$_2$F$_3$I$^+$).

(2-deutero-4-methyl-6-[2-(2-[4-(trifluoromethyl)pyridin-2-yl]-ethynyl)phenyl]ethynyl]pyridine)-iodonium tetrafluoroborate (1a-d). Compound 9-d (0.105 g, 0.29 mmol) dissolved in dry DCM (10 mL) was added by syringe to AgBF$_4$ (0.057 g, 0.29 mmol) in a centrifuge vial (40 mL) in a glovebox. The resulting yellow solution was stirred until the AgBF$_4$ had dissolved, and the clear solution turned slightly cloudy. Dry n-hexane (20 mL) was added by syringe to generate precipitation. The vial was then centrifuged for 10 min at 2000 rpm. The supernatant was removed, and the pellet was washed with dry n-hexane (2 mL) and dried in vacuo overnight. The white solid (0.151 g) was dissolved in dry DCM (13 mL), and I$_2$ (0.069 g, 0.27 mmol) was added. After being stirred (30 min) to allow AgI to precipitate, the vial was again centrifuged for 10 min at 2000 rpm. The supernatant was transferred into another centrifuge vial (40 mL), and dry n-hexane (26 mL) was added by syringe to generate precipitation of 1a-d. The purple-pink solution with white, flakey solid was centrifuged for 10 min at 2500 rpm. The supernatant was removed, and the remaining pellet was washed with dry n-hexane (3 mL) and dried in vacuo (35 min) to generate 1a-d (0.139 g, 89%, ≥95% deuteration) as a white powder. $^1\text{H}$ (900 MHz, CD$_2$Cl$_2$) $\delta$ 9.09 (d, $J = 5.8$ Hz, 1H, H-2'), 8.06 (d, $J = 1.9$ Hz, 1H, H-5'), 7.79-7.82 (m, 2H, H-10 and H-10'), 7.75 (dq, $J = 2.0$, 0.9 Hz, 1H, H-5) 7.70 (dd, $J = 5.8$, and 1.9 Hz, 1H, H-3'), 7.60-7.63 (m, 2H, H-11 and H-11'), 7.32 (dq, $J = 2.0$, 0.8 Hz, 1H, H-3), 2.54 (dd, $J = 0.9$, 0.8 Hz, 3H, H-12); $^{13}\text{C}$ (226 MHz, CD$_2$Cl$_2$) $\delta$ 156.5 (C-4), 152.7 (C-2'), 150.7 (t, $^1J_{CD}$ = 28.7 Hz, C-2), 144.4 (C-6'), 143.2 (q, $^3J_{CF} = 35.84$, 35.80, and 35.80 Hz, C-4'), 142.7 (C-6), 135.0 (C-10 or C-10'), 134.8 (C-10 or C-10'), 131.8 (C-11 or C-11'), 131.4 (C-5, and C-11 or C-11'), 128.1 (C-3), 126.3 (q, $^3J_{CF} = 3.8$ Hz, C-5'), 124.7 (C-9 or C-9'), 124.1 (C-9 or C-9'), 122.4 (q, $^3J_{CF} = 3.8$ Hz, C-3'), 121.9 (q, $^3J_{CF} = 272.6$ Hz, C-12'), 100.5 (C-8 or C-8'), 98.6 (C-8 or C-8'), 91.0 (C-7), 90.4 (C-7'), 21.9 (C-12); $^{15}\text{N}$ (91 MHz, CD$_2$Cl$_2$) $\delta$ -145.1 (N-1'), -183.1 (N-1); HRMS m/z 490.0138 [M-BF$_4^-$]+, calcd 490.2652 (C$_{22}$H$_{12}$DN$_2$F$_3$I$^+$).
1.3. The synthesis of \([2,2'-(9,10-dimethoxyphenanthrene-3,6-diyl)dipyridine iodine (I)]\) tetrafluoroborate (2a)

3,6-Dibromo-9,10-dimethoxyphenanthrene (11). 3,6-dibromo-phenanthrenequinone (0.850 g, 2.32 mmol), tetrabutylammonium bromide (0.300 g, 0.92 mmol), sodium dithionite (0.640 g, 9.40 mmol), THF (20 mL), and water (20 mL) was added into a round bottom flask (100 mL). The mixture was stirred for 5 min, after which dimethyl sulfate (1.5 mL, 15.90 mmol), followed by an aqueous solution of NaCl (14 M, 4 mL, 56.00 mmol) were added. The reaction mixture was stirred for 15 min and EtOAc (30 mL) was added. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with H₂O (30 mL), NH₃ (aq. 15 % w/v, 2 x 15 mL), and brine (30 mL) sequentially, dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (silica), eluting with DCM:hexane (1:1), to give 11 as a colorless solid (0.770 g, 84%). ¹H NMR (500 MHz, CDCl₃) δ 8.61 (d, \(J = 1.9\) Hz, 2H, H₁₂), 8.07 (d, \(J = 8.8\) Hz, 2H, H-9), 7.70 (dd, \(J = 8.8, 1.9\) Hz, 2H, H-8), 4.06 (s, 6H, H-14); ¹³C NMR (126 MHz, CDCl₃) δ 143.9 (C-13 and C-13'), 130.7 (C-8), 129.0 (C-10 and C-10'), 128.3 (C-11), 125.5 (C-12), 124.1 (C-9), 120.6 (C-7), 61.1 (C-14); MS (ESI) m/z 397.3 [M+H]+, calcd 397.1 (C₂₆H₂₁N₂O₂)+.

2,2'-(9,10-Dimethoxyphenanthrene-3,6-diyl)dipyridine (12). THF (15 mL) was added to a mixture of Pd(PPh₃)₄ (0.204 g, 0.18 mmol), and compound 11 (0.350 g, 0.88 mmol) into a round bottom flask (50 mL). 2-Pyridylzinc bromide (0.5 M in THF, 1.3 mL, 2.65 mmol) was added via a syringe, and the reaction mixture was stirred overnight at 50 °C. DCM (30 mL) and NH₃ (aq. 28 % w/v, 30 mL) was added, after which the aqueous phase was separated and extracted three times with DCM (3 x 30 mL). The combined organic phases were washed with H₂O (30 mL) and brine (30 mL) sequentially, dried over MgSO₄, filtered, and concentrated in vacuo. The crude was purified by flash chromatography (silica), eluting with DCM:MeOH (30:1) to give 12 as a white solid (0.230 g, 67%). ¹H NMR (400 MHz, CDCl₃) δ 9.43 (dd, \(J = 1.6, 0.5\) Hz, 2H, H-12), 8.79 (dd, \(J = 4.8, 1.8, 0.9\) Hz, 2H, H-2), 8.35 (dd, \(J = 8.5, 0.5\) Hz, 2H, H-9), 8.27 (dd, \(J = 8.5, 1.6\) Hz, 2H, H-8), 7.98 (dd, \(J = 8.0, 1.1, 0.9\) Hz, 2H, H-5), 7.83 (dd, \(J = 8.0, 7.5, 1.8\) Hz, 2H, H-4), 7.29 (dd, \(J = 7.5, 4.8, 1.1\) Hz, 2H, H-3), 4.14 (s, 6H, H-14); ¹³C NMR (101 MHz, CDCl₃) δ 157.6 (C-6), 149.9 (C-2), 144.5 (C-13), 137.0 (C-7), 136.9 (C-4), 129.8 (C-10), 129.3 (C-11), 125.7 (C-9), 122.9 (C-8), 122.3 (C-3), 121.7 (C-12), 121.1 (C-5), 61.2 (C-14); MS (ESI) m/z 393.5 [M+H]+, calcd 393.5 (C₂₆H₂₁N₂O₂)+.
[2,2'-9,10-Dimethoxyphenanthrene-3,6-diyl]dipyridine silver (I) tetrafluoroborate (13). To a microwave vial (5 mL), AgBF₄ (9.9 mg, 0.51 mmol), and 12 (18.1 mg, 0.05 mmol) were added. The vial was evacuated and filled with Ar (g). Dry DCM (6 mL) was added, and the reaction mixture was stirred (10 min). Dry n-hexane (12 mL) was added to cause precipitation. The vial was centrifuged (5 min, 2500 rpm), the supernatant removed by syringe and the solid dried under vacuum (2 h), to afford 13 as a white precipitate. ¹H NMR (400 MHz, CD₃CN) δ 9.28 (d, J = 1.7 Hz, 2H, H-12), 8.21-8.23 (m, 4H, H-2, H-2', H-9), 7.98 (dd, J = 8.5, 1.7 Hz, 2H, H-8), 7.78-7.79 (m, 2H, H-4), 7.77-7.77 (m, 2H, H-5), 7.14-7.20 (m, 2H, H-3), 4.11 (s, 6H, H-14); ¹³C NMR (101 MHz, CD₃CN) δ 158.2 (C-6), 151.1 (C-2), 145.3 (C-13), 138.9 (C-4), 138.5 (C-11), 130.6 (C-10), 129.2 (C-7), 126.8 (C-8), 123.8 (C-9), 123.7 (C-3), 123.3 (C-5), 122.1 (C-12), 61.7 (C-14).

[2,2'-9,10-Dimethoxyphenanthrene-3,6-diyl]dipyridine iodine (I) tetrafluoroborate (2). Complex 11 (~0.05 mmol) was transferred to a dry NMR tube (5 mm) fitted with a rubber septum, and dissolved in CD₃CN (10 mL). The tube was cooled to -78 °C, and a cold (-35 °C) solution of I₂ (15 mg, 0.06 mmol) in CD₃CN was added by syringe, and the solution was allowed to warm to -40 °C and form AgI precipitate, leaving 10 in solution. The tube was centrifuged at -40 °C, and inserted into the pre-cooled (-40 °C) NMR probe. ¹H NMR (500 MHz, CD₃CN, -40°C) δ 9.09 (br s, 2H, H-12), 8.12 (br s, 2H, H-2), 7.69 (br s, 4H; H-4 and H-8), 7.50 (br s, 4H, H-9 and H-5), 7.02 (br s, 2H, H-3), 4.07 (br s, 6H, OCH₃).
2. NMR SPECTRA

2.1. Synthesis of compound 1a and 1a-d.

Figure S1. The $^1$H NMR spectra of 3-d acquired at 25 °C in CDCl$_3$ at 400 MHz.

Figure S2. The $^{13}$C NMR spectra of 3-d acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S3. The $^1$H NMR spectra of 4 acquired at 25 °C in CDCl$_3$ at 500 MHz.

Figure S4. The $^{13}$C NMR spectra of 4 acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S5. The $^1$H NMR spectra of 4-d acquired at 25 °C in CDCl$_3$ at 400 MHz.

Figure S6. The $^{13}$C NMR spectra of 4-d acquired at 25 °C in CDCl$_3$ at 126 MHz.
**Figure S7.** The $^1$H NMR spectra of 5 acquired at 25 °C in CDCl$_3$ at 500 MHz.

**Figure S8.** The $^{13}$C NMR spectra of 5 acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S9. The $^1$H NMR spectra of 5-d acquired at 25 °C in CDCl$_3$ at 500 MHz.

Figure S10. The $^{13}$C NMR spectra of 5-d acquired at 25 °C in CDCl$_3$ at 126 MHz.
**Figure S11.** The $^1$H NMR spectra of 6 acquired at 25 °C in CDCl$_3$ at 500 MHz.

**Figure S12.** The $^{13}$C NMR spectra of 6 acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S13. The $^1$H NMR spectra of 6-$d$ acquired at 25 °C in CDCl$_3$ at 400 MHz.

Figure S14. The $^{13}$C NMR spectra of 6-$d$ acquired at 25 °C in CDCl$_3$ at 201 MHz.
**Figure S15.** The $^1$H NMR spectra of 7 acquired at 25 °C in CDCl$_3$ at 500 MHz.

**Figure S16.** The $^{13}$C NMR spectra of 7 acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S17. The $^1$H NMR spectra of 7-d acquired at 25 °C in CDCl$_3$ at 400 MHz.

Figure S18. The $^{13}$C NMR spectra of 7-d acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S19. The $^1$H NMR spectra of 8 acquired at 25 °C in CDCl$_3$ at 400 MHz.

Figure S20. The $^{13}$C NMR spectra of 8 acquired at 25 °C in CDCl$_3$ at 201 MHz.
Figure S21. The $^1$H NMR spectra of $8\text{-}d$ acquired at 25 °C in CDCl$_3$ at 400 MHz.

Figure S22. The $^{13}$C NMR spectra of $8\text{-}d$ acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S23. The $^1$H NMR spectra of 9 acquired at 25 °C in CDCl$_3$ at 500 MHz.

Figure S24. The $^{13}$C NMR spectra of 9 acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S25. The $^1$H-$^{15}$N HMBC NMR spectrum of 9 acquired at 25 °C in CDCl$_3$ at 51 MHz.

Figure S26. The $^1$H NMR spectra of 9-d acquired at 25 °C in CDCl$_3$ at 400 MHz.
Figure S27. The $^{13}$C NMR spectra of 9-d acquired at 25 °C in CD$_2$Cl$_2$ at 201 MHz.

Figure S28. The $^1$H-$^{15}$N HMBC NMR spectra of 9-d acquired at 25 °C in CD$_2$Cl$_2$ at 81 MHz.
Figure S29. The $^1$H NMR spectra of 1a acquired at 25 °C in CD$_2$Cl$_2$ at 900 MHz.

Figure S30. The $^{13}$C NMR spectra of 1a acquired at 25 °C in CD$_2$Cl$_2$ at 226 MHz.
Figure S31. The $^1$H-$^{15}$N NMR spectra of 1a acquired at 25 °C in CD$_2$Cl$_2$ at 91 MHz.

Figure S32. The $^1$H NMR spectra of 1a-d acquired at 25 °C in CD$_2$Cl$_2$ at 900 MHz.
Figure S33. The $^{13}$C NMR spectra of 1a-d acquired at 25 °C in CD$_2$Cl$_2$ at 226 MHz.

Figure S34. The $^1$H-$^{15}$N HMBC NMR spectra of 1a-d acquired at 25 °C in CD$_2$Cl$_2$ at 91 MHz.
2.2. [2,2’-(9,10-dimethoxyphenanthrene-3,6-diyl)dipyridine iodine (I)] tetrafluoroborate and intermediates

Figure S35. The $^1$H NMR spectra of 11 acquired at 25 °C in CDCl$_3$ at 500 MHz.

Figure S36. The $^{13}$C NMR spectra of 11 acquired at 25 °C in CDCl$_3$ at 126 MHz.
Figure S37. The $^1$H NMR spectra of 12 acquired at 25 °C in CDCl$_3$ at 400 MHz.

Figure S38. The $^{13}$C NMR spectra of 12 acquired at 25 °C in CDCl$_3$ at 101 MHz.
**Figure S39.** The $^1$H NMR spectra of 13 acquired at 25 °C in CD$_3$CN at 400 MHz.

**Figure S40.** The $^{13}$C NMR spectra of 13 acquired at 25 °C in CD$_3$CN at 101 MHz.
Figure S41. The $^1$H NMR spectra of 2a acquired at -40 °C in CD$_3$CN at 500 MHz.
3. IPE NMR

3.1 General information

The samples for the IPE NMR experiments were prepared in a glove box, with a 2:1 ratio of the deuterated and corresponding non-deuterated compounds, using CD$_2$Cl$_2$ (dried over molecular sieves (3 Å) and stored in a glove box) as solvent. The NMR tubes and septas had been dried under vacuum overnight, and were subsequently stored in a glove box prior to use. All other glass ware had been pre-dried overnight in the oven at 150 °C. $^1$H and $^{13}$C spectra were recorded on a Bruker Avance III HD 800 MHz spectrometer, with a $^{13}$C/$^{15}$N-$^1$H/$^2$H 5 mm CPTXO dual broadband cryogenic probe, in the temperature interval -32 °C to 40 °C. A 10 min wait at each new temperature was allowed to ensure the sample obtained the desired temperature. The $^{13}$C NMR spectra were obtained at 201 MHz, with broadband $^1$H and inverse-gated $^2$H decoupling.
3.2. $^{13}$C NMR chemical shifts and their temperature dependence

Table S1. The $^{13}$C NMR chemical shifts of 1a / 1a-d at various temperatures.

| Temp. (K) | $\frac{1}{T}$ (K$^{-1}$) | $\delta$ (ppm) | $\delta$ (ppm) | $\delta$ (ppm) | $\delta$ (ppm) | $\delta$ (ppm) | $\delta$ (ppm) | $\delta$ (ppm) | $\delta$ (ppm) |
|-----------|-------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 241       | 0.004149378             | -0.3347        | -0.1511        | 0.0239         | 0              | -0.0317        |
| 253       | 0.003952569             | -0.3343        | -0.1472        | 0.0234         | 0              | -0.0312        |
| 263       | 0.003802281             | -0.3320        | -0.1461        | 0.0236         | 0              | -0.0303        |
| 273       | 0.003663004             | -0.3312        | -0.1452        | 0.0230         | 0              | -0.0300        |
| 283       | 0.003533569             | -0.3312        | -0.1445        | 0.0225         | 0              | -0.0302        |
| 293       | 0.003412969             | -0.3293        | -0.1425        | 0.0226         | 0              | -0.0292        |
| 303       | 0.003300330             | -0.3286        | -0.1423        | 0.0223         | 0              | -0.0280        |
| 313       | 0.003194888             | -0.3281        | -0.1405        | 0.0224         | 0              | -0.0290        |

Table S2. The $^2$H-isotope effects on $^{13}$C NMR chemical shifts of 1a / 1a-d at various temperatures.

| Temp. (K) | $1/T$ (K$^{-1}$) | $\Delta$obs (ppm) | $\Delta$obs (ppm) | $\Delta$obs (ppm) | $\Delta$obs (ppm) |
|-----------|-----------------|--------------------|--------------------|--------------------|--------------------|
| 241       | 0.004149378     | -0.3347            | -0.1511            | 0.0239             | 0                  |
| 253       | 0.003952569     | -0.3343            | -0.1472            | 0.0234             | 0                  |
| 263       | 0.003802281     | -0.3320            | -0.1461            | 0.0236             | 0                  |
| 273       | 0.003663004     | -0.3312            | -0.1452            | 0.0230             | 0                  |
| 283       | 0.003533569     | -0.3312            | -0.1445            | 0.0225             | 0                  |
| 293       | 0.003412969     | -0.3293            | -0.1425            | 0.0226             | 0                  |
| 303       | 0.003300330     | -0.3286            | -0.1423            | 0.0223             | 0                  |
| 313       | 0.003194888     | -0.3281            | -0.1405            | 0.0224             | 0                  |
Figure S42. The C-2 $^{13}$C NMR isotope shift of 1a / 1a-d at various temperatures.

Figure S43. The C-3 $^{13}$C NMR isotope shift of 1a / 1a-d at various temperatures.
Figure S44. The C-4 $^{13}$C NMR isotope shift of 1a / 1a-$d$ at various temperatures.

Figure S45. The C-4 $^{13}$C NMR isotope shift of 1a / 1a-$d$ at various temperatures.
Table S3. The $^{13}$C NMR chemical shifts of $9 / 9$-$d$ at various temperatures.

| Temp. (K) | $1/T$ (K$^{-1}$) | $^{1}$Δ$_{obs}$ (ppm) δ(C2-D-C2-H) | $^{2}$Δ$_{obs}$ (ppm) δ(C3-D-C3-H) | $^{3}$Δ$_{obs}$ (ppm) δ(C4-D-C4-H) | $^{4}$Δ$_{obs}$ (ppm) δ(C5-D-C5-H) | $^{5}$Δ$_{obs}$ (ppm) δ(C6-D-C6-H) |
|-----------|-----------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| 241       | 0.004149378     | -0.3337                            | -0.1374                            | 0.0138                             | 0                                  | -0.0171                            |
| 253       | 0.003952569     | -0.3338                            | -0.1366                            | 0.0133                             | 0                                  | -0.0149                            |
| 263       | 0.003802281     | -0.3336                            | -0.1365                            | 0.0122                             | 0                                  | -0.0140                            |
| 273       | 0.003663004     | -0.3323                            | -0.1357                            | 0.0116                             | 0                                  | -0.0137                            |
| 283       | 0.003533569     | -0.3314                            | -0.1344                            | 0.0107                             | 0                                  | -0.0127                            |
| 293       | 0.003412969     | -0.3294                            | -0.1333                            | 0.0100                             | 0                                  | -0.0128                            |
| 303       | 0.003300330     | -0.3300                            | -0.1329                            | 0.0093                             | 0                                  | -0.0107                            |
| 313       | 0.003194888     | -0.3276                            | -0.1310                            | 0.0083                             | 0                                  | -0.0114                            |

Table S4. The $^{2}$H-isotope effects on $^{13}$C NMR chemical shifts of $9 / 9$-$d$ at various temperatures.
Figure S46. The C-2 $^{13}$C NMR isotope shift of 9 / 9-$d$ at various temperatures.

\[
y = -6.495x - 0.3079 \\
R^2 = 0.8639
\]

Figure S47. The C-3 $^{13}$C NMR isotope shift of 9 / 9-$d$ at various temperatures.

\[
y = -6.4507x - 0.1113 \\
R^2 = 0.9256
\]
Figure S48. The C-4 $^{13}$C NMR isotope shift of 9 / 9-d at various temperatures.

Figure S49. The C-6 $^{13}$C NMR isotope shift of 9 / 9-d at various temperatures.
Table S5. The $^{13}$C NMR chemical shifts of 1b / 1b-$d$ at various temperatures

| Temp. (K) | $\Delta$ (ppm) C2 (H) | $\Delta$ (ppm) C2 (D) | $\Delta$ (ppm) C3 (H) | $\Delta$ (ppm) C3 (D) | $\Delta$ (ppm) C4 (H) | $\Delta$ (ppm) C4 (D) | $\Delta$ (ppm) C5 (H) | $\Delta$ (ppm) C5 (D) | $\Delta$ (ppm) C6 (H) | $\Delta$ (ppm) C6 (D) |
|-----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| 241       | 143.2491               | 142.9535               | 126.1410               | 126.0025               | 156.6484               | 156.6570               | 130.6435               | 130.6435               | 135.9769               | 135.9334               |
| 253       | 143.5624               | 143.2671               | 126.1408               | 126.0024               | 156.4180               | 156.4348               | 130.6587               | 130.6587               | 136.3806               | 136.3400               |
| 263       | 143.8470               | 143.5507               | 126.1340               | 125.9993               | 156.2012               | 156.2253               | 130.6670               | 130.6670               | 136.7489               | 136.7058               |
| 273       | 144.1296               | 143.8320               | 126.1229               | 125.9884               | 155.9831               | 155.9931               | 130.6728               | 130.6728               | 137.1000               | 137.0640               |
| 283       | 144.4177               | 144.1207               | 126.1141               | 125.9796               | 155.7621               | 155.7909               | 130.6707               | 130.6707               | 137.4563               | 137.4227               |
| 293       | 144.7021               | 144.4019               | 126.0992               | 125.9680               | 155.5408               | 155.5717               | 130.6654               | 130.6654               | 137.8093               | 137.7741               |
| 303       | 144.9841               | 144.6837               | 126.0883               | 125.9569               | 155.3226               | 155.3520               | 130.6284               | 130.6284               | 138.1571               | 138.1235               |
| 313       | 145.2613               | 144.9612               | 126.0729               | 125.9445               | 155.1022               | 155.1332               | 130.5997               | 130.5997               | 138.5027               | 138.4667               |

Table S6. The $^2$H-isotope effects on $^{13}$C NMR chemical shifts of 1b / 1b-$d$ at various temperatures.

| Temp. (K) | $1/T (K^{-1})$ | $^1$A_{obs} (ppm) $\delta$(C2$_{D}$-C2$_{H}$) | $^2$A_{obs} (ppm) $\delta$(C3$_{D}$-C3$_{H}$) | $^3$A_{obs} (ppm) $\delta$(C4$_{D}$-C4$_{H}$) | $^4$A_{obs} (ppm) $\delta$(C5$_{D}$-C5$_{H}$) | $^5$A_{obs} (ppm) $\delta$(C6$_{D}$-C6$_{H}$) |
|-----------|----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 241       | 0.004149378   | -0.2956                         | -0.1385                         | 0.0086                          | 0                               | -0.0435                        |
| 253       | 0.003952569   | -0.2953                         | -0.1384                         | 0.0168                          | 0                               | -0.0406                        |
| 263       | 0.003802281   | -0.2963                         | -0.1347                         | 0.0241                          | 0                               | -0.0431                        |
| 273       | 0.003663004   | -0.2976                         | -0.1345                         | 0.0192                          | 0                               | -0.0360                        |
| 283       | 0.0035353569  | -0.2970                         | -0.1345                         | 0.0288                          | 0                               | -0.0336                        |
| 293       | 0.003412969   | -0.3002                         | -0.1312                         | 0.0309                          | 0                               | -0.0352                        |
| 303       | 0.003300330   | -0.3004                         | -0.1314                         | 0.0294                          | 0                               | -0.0336                        |
| 313       | 0.003194888   | -0.3001                         | -0.1284                         | 0.0310                          | 0                               | -0.0360                        |
Figure S50. The C-2 $^{13}$C NMR isotope shift of 1b / 1b-$d$ at various temperatures.

Figure S51. The C-3 $^{13}$C NMR isotope shift of 1b / 1b-$d$ at various temperatures
Figure S52. The C-4 $^{13}$C NMR isotope shift of $\text{1b} / \text{1b-d}$ at various temperatures.

Figure S53. The C-6 $^{13}$C NMR isotope shift of $\text{1b} / \text{1b-d}$ at various temperatures.
3.3. IPE NMR spectra

![Figure S54. Part of the $^2$H coupled $^{13}$C NMR spectra of 1a /1a-d acquired at 241 K in CD$_2$Cl$_2$ at 201 MHz.](image)

![Figure S55. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1a / 1a-d acquired at 241 K in CD$_2$Cl$_2$ at 201 MHz.](image)
**Figure S56.** Part of the $^2$H decoupled $^{13}$C NMR spectra of 1a/1a-d acquired at 253 K in CD$_2$Cl$_2$ at 201 MHz.

**Figure S57.** Part of the $^2$H decoupled $^{13}$C NMR spectra of 1a/1a-d acquired at 263 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S58. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1a /1a-d acquired at 273 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S59. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1a /1a-d acquired at 283 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S60. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1a /1a-$d$ acquired at 293 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S61. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1a /1a-$d$ acquired at 303 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S62. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1a / 1a-d acquired at 313 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S63. Part of the $^2$H decoupled $^{13}$C NMR spectra of 9 / 9-d acquired at 241 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S64. Part of the $^2$H decoupled $^{13}$C NMR spectra of 9 / 9-$d$ acquired at 253 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S65. Part of the $^2$H decoupled $^{13}$C NMR spectra of 9 / 9-$d$ acquired at 263 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S66. Part of the $^2$H decoupled $^{13}$C NMR spectra of 9 / 9-d acquired at 273 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S67. Part of the $^2$H decoupled $^{13}$C NMR spectra of 9 / 9-d acquired at 283 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S68. Part of the $^2$H decoupled $^{13}$C NMR spectra of 9 / 9-d acquired at 293 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S69. Part of the $^2$H decoupled $^{13}$C NMR spectra of 9 / 9-d acquired at 303 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S70. Part of the $^2$H decoupled $^{13}$C NMR spectra of 9 / 9-$d$ acquired at 313 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S71. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1b / 1b-$d$ acquired at 241 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S72. Part of the $^2\text{H}$ decoupled $^{13}\text{C}$ NMR spectra of 1b / 1b-d acquired at 253 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S73. Part of the $^2\text{H}$ decoupled $^{13}\text{C}$ NMR spectra of 1b / 1b-d acquired at 263 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S74. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1b / 1b-d acquired at 273 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S75. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1b / 1b-d acquired at 283 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S76. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1b / 1b-d acquired at 293 K in CD$_2$Cl$_2$ at 201 MHz.

Figure S77. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1b / 1b-d acquired at 303 K in CD$_2$Cl$_2$ at 201 MHz.
Figure S78. Part of the $^2$H decoupled $^{13}$C NMR spectra of 1b / 1b-d acquired at 313 K in CD$_2$Cl$_2$ at 201 MHz.
4. COMPUTATION

4.1 General

**Computational model.** All quantum-chemical calculations were performed with Density Functional Theory (DFT). For geometry optimizations and thermochemical calculations we used the M06 exchange and correlation (XC) functional and a mixed-level basis set constructed in the following way: The atoms involved in the [N–X–N]⁺ bond were described with valence triple-zeta basis sets and diffuse functions, specifically, the 6-311+G(d,p) basis set for I and Jensen’s aug-pc-2 basis set for H and N. The C atoms that are nearest neighbors to the N atoms were described with the pc-2 basis set, all other atoms, with the pc-1 basis set. This basis set provides an accurate description of the [N–X–N]⁺ at a reasonable computational cost. Solvent effects were covered with the Polarizable Continuum Model (PCM). For all geometries, vibrational frequencies were calculated to characterize the structures and to determine thermochemical corrections. The latter were calculated for 233 K, corresponding to the experimental conditions. The basis-set interaction error (BSSE) for the dimer structures was corrected by the counterpoise (CP) method.

¹⁵N NMR chemical shieldings were calculated at the optimized geometries obtained as above, using the gauge-independent atomic orbitals (GIAO) method. For the NMR calculations, the modification by Wilson et al. of the Becke 97 XC functional was employed. The basis set was constructed analogously as above except that Jensen’s pcS basis sets were used. For the computation of chemical shifts, pyridine was used as a secondary reference with an experimental shift of δ_{exp}(N) = -67.0.

All calculations were performed with the Gaussian09 programming package.

**Energy surfaces and potential curves for bis(pyridine) model systems.** The energy surfaces shown in Figure 3 and used for the construction of Figures 4a,b were obtained by rigid potential scans. We started by optimizing the respective I⁺ complex with a planar conformation of the two pyridine rings enforced. Then, the rigid scans were performed in the way that the two N–X distances were varied from 0.6 Å to 3.0 Å (H⁺ complexes) or 1.6 Å to 4.0 Å (I⁺ complexes) in steps of 0.1 Å while the two pyridines (or pyridine derivatives) were kept at the geometry found in the optimization of the respective I⁺ complex. In some cases, refined plots (step width 0.05 Å) were performed in the region close to the stationary geometries. For the generation of Figure 3, an additional scan was performed where r_{NN} was varied from 3.2 Å to 7.0 Å and Δr from -r_{NN} + 1.6 Å to r_{NN} – 1.6 Å.

All complexes were optimized with the two pyridine rings coplanar to model the situations in real complexes. However, the ground state for bis(pyridine) complexes is often twisted. Therefore, many of the structures show several imaginary frequencies that refer to the twisting of the pyridine rings or, in consequence, the rotation of CH₃ or CF₃ groups.

The potential curves in Figure 4a for the model systems (i.e. with variable r_{NN}) were constructed according to

\[ E_{\text{var}}(\Delta r) = \min_{r_{NN}} E(r_{NN}, \Delta r), \quad (S5) \]

the dissociation curve shown in Figure 3 (right border plane) according to

\[ E_{\text{bond}}(r_{NN}) = \min_{\Delta r} E(r_{NN}, \Delta r). \quad (S6) \]
The values for $E_{\text{var}}$ and $E_{\text{bond}}$, respectively, were found by five-point polynomial interpolations using the $E$ values from the scan. The obtained $E_{\text{var}}$ values were in addition smoothed by a five-point Savitzky-Golay filter prior to plotting.

**Energies of the bis(pyridinylethynyl)benzene systems.** The full optimization of the complexes for the bis(pyridinylethynyl)benzene derivatives with was not possible due to problems of the optimization algorithm in Gaussian 09 for nearly (but not fully) planar geometries. We therefore performed the optimizations in the way that we enforced $C_2$ or $C_s$ symmetry, respectively, for the geometry, resulting in a strictly planar backbone. As a consequence, some of the geometries show one or more additional imaginary frequencies in the range $i10\ \text{cm}^{-1} \ldots i100\ \text{cm}^{-1}$, which belong to rotations of the CH$_3$ and CF$_3$ groups. We expect this constraint to have only negligible impact on the calculated energy balances.

**4.2 Definition of relative energies and its components**

The relative energies for the conformers of 2a and 2b were calculated as stabilization energies relative to the [N−X−N]$^+$ bonds in 14a,b. That is, they are given as reaction energies for the formal reaction shown in Figure S79 for the example of 2a-sym-1. (For the formation of a dimer, one would have two molecules each of 12 and 14a on the left hand side and four pyridines on the right hand side). Note that the sign of the energies follows the usual conventions, i.e., a conformer is less stable the more positive its stabilization energy is.

![Figure S79. Formal reaction for the definition of stabilization energies with conformer 2a-sym-1 as example.](image)

For a more detailed discussion of the halogen bonds in different conformers, the obtained stabilization energies were decomposed into the intrinsic energy of the halonium bond $\Delta E_{\text{bond}}$, the strain energy of the backbone $\Delta E_{\text{strain}}$, and (for dimers) the van der Waals energy $\Delta E_{\text{vdW}}$. To determine these energy contributions we consider the formal reaction of the fictitious species shown in Figure S80, where the X$^+$ has been removed but all ligands are kept in the geometry they had in the reaction in Figure S79.

![Figure S80. Formal reaction for the determination of $\Delta E_{\text{strain}}$ with conformer 2a-sym-1 as example.](image)

To get the correct $\Delta E_{\text{strain}}$ from the energy balance of this reaction, three energy contributions need to be eliminated: (i) the strain energies of the pyridine rings (we are interested in the straining of the backbone only), (ii) the energy of the Coulomb repulsion between the partial charges of the N atoms, which is screened and thus
vanishes in the complexes (see Ref. 25 in the main text) and (iii) for dimers, the van der Waals interaction $E_{vdW}$ between the two ligands, which will be specified separately. To handle (i) och (ii), for each ligand $\text{lig}$ we construct a system $\text{lig:Pyr}_2$ where the two pyridines are in the same geometry and mutual position as in $\text{lig}$ and the backbone is omitted (see Figure S81). The unsaturated bonds in the pyridines are saturated with a H atom each, the position of which is optimized (shown in bold).

![Figure S81](image-url)

**Figure S81.** Structures used for the “purification” of $\Delta E_{strain}$ with conformers $2a$-sym-$1$ and $(2a)_2$-par as examples. The shaded parts of the molecules are omitted, the position of the bold-faced H atoms is reoptimized.

Then, the “purified” energy

$$E_{pur}(\text{lig}) = E(\text{lig}) - \left[ E(\text{lig:Pyr}_2) - 2E(\text{Pyr}) \right]$$  (S1)

where $\text{Pyr}$ is a pyridine in its equilibrium geometry is the energy of $\text{lig}$ corrected according to (i) and (ii).

For a dimer containing two ligands $\text{lig}_1$, $\text{lig}_2$, $E_{pur}$ is simply

$$E_{pur}(\text{lig}_1+\text{lig}_2) = E_{pur}(\text{lig}_1) + E_{pur}(\text{lig}_2).$$  (S2)

To determine the van der Waals energy for a dimer, we additionally calculated the energy of the dimer $\text{lig}_1+\text{lig}_2$ and that of the pyridine tetramer $\text{lig}_1+\text{lig}_2: \text{Pyr}_4$, which is constructed in analogy to $\text{lig:Pyr}_2$ (see Figure S81). $E_{vdW}$ can then be determined as follows:

$$E_{vdW}(\text{lig}_1+\text{lig}_2) = E(\text{lig}_1+\text{lig}_2) - E_{pur}(\text{lig}_1+\text{lig}_2),$$  (S3a)

$$E(\text{lig}_1+\text{lig}_2) = E(\text{lig}_1+\text{lig}_2) - [E(\text{lig}_1+\text{lig}_2: \text{Pyr}_4) - 4E(\text{Pyr})] + \text{BSSE}(\text{lig}_1, \text{lig}_2).$$  (S3b)

Here, $\text{BSSE}(\text{lig}_1, \text{lig}_2)$ is the BSSE between $\text{lig}_1$ and $\text{lig}_2$, which is calculated with the CP method. The BSSE values calculated for the ligand pair were also used to correct the $E$ and $G^{233}$ values of the corresponding complexes. The BSSE for the pyridine oligomers was neglected.

Finally, $E_{bond}$ is calculated as

$$E_{bond} = E - E_{strain} - E_{vdW}.$$  (S4)
4.3 Supplementary results

In this section, some results are presented in greater detail and/or extent than in the main part of the paper.

4.3.1 Potential curves for the bis(pyridine) complexes and their derivatives

Figure S82. Potential curves for bis(pyridine)iodinium (a) and bis(pyridine)proton (b) complexes and their derivatives.

Figure S82 is an extension of Figure 4a to all derivatives of the bis(pyridine) complexes under investigation. It demonstrates the fact discussed in the main text that symmetric substitution has only minor effects on the potential curves whereas asymmetric substitution results in asymmetric single or double potential wells.

4.3.2 Geometries and stabilities of the bis(pyridine) (Pyr2) and 1,2-bis(pyridine-2-ylethynyl)benzene (Pyr2EB) complexes and their derivatives

Table S7. The auxiliary energies used for the decomposition of relative bond energies. See Sec. 4.1 for definitions. $^{a}$GM = global minimum, LM = local minimum, d = degenerate, TS = transition state. $^{b}$Stabilization energy relative to the corresponding state (values in square brackets: to the ground state) of the corresponding compound with $R = R' = H$. $^{c}$For compounds with more than one equilibrium structure, the energy of the present structure relative to the ground-state energy. $^{d}$Stabilization energy of the Pyr2EB complex relative to the corresponding state of the corresponding Pyr2 complex.

Table S7 is an extension of Table 3 in the main text. It presents in addition to Table 3 the N–X bond distances for the Pyr2 complexes and the stabilization energies of the Pyr2EB complexes relative to their Pyr2 counterparts.
The results show that the bond distances in corresponding Pyr2 and PyrEB complexes generally differ by 0.03 Å or less, except for the case X = H, R = CH3, R’= CF3. Also, the stabilization energies for the ground-state geometries are similar in most cases. These findings confirm the conclusion drawn in Ref. 25 (main text) that the backbone in the Pyr2EB complexes is flexible and shows no considerable strain energy. In contrast, the energy barriers for the TS are considerably higher in the Pyr2EB than the Pyr2 complexes. This can be explained by the geometrical constraints the backbone imposes on the two pyridine rings, which result in an unfavorable geometry for the [N–X–N]+ moiety and a weaker bond. Finally, one sees that the backbone in the Pyr2BE complex destabilizes the [N–X–N]+ bonds by 12 to 17 kJ mol⁻¹, which again can be traced back to the constraints the backbone imposes on the geometry of the bispyridine moiety. (We have shown earlier²⁵ that the strain energy of the backbone is just a few kJ mol⁻¹.)

4.3.3 Calculated ¹⁵N chemical shieldings

| Pyridine:  | σ(N) = -79.0857 | δexp(N) = -67.0 |
|-----------|-----------------|-----------------|
| CH3       | -7.4424         | -75.6917        |
| CF3       | -22.6142        | -95.4694        |
| CF3       | 1.3627          | -95.4597        |

Table S8. Computed ¹⁵N NMR shieldings for the studied [N-I-N]+ complexes and ligands.
4.3.4 Ligand energies etc. used for the decomposition of the bonding energies

|                  | $E$             | $G^{233}$ | $E$(lig) | BSSE     | $E$(lig:Pyr2) | [E(lig:Pyr3)] |
|------------------|-----------------|-----------|----------|-----------|---------------|---------------|
| Pyr 12           | -248.13185009   | -248.063579 | -248.13185009 | -496.26261967 |               |               |
| 14a              | -1261.81581559  | -1261.460234 | -1261.81581559 | -496.26083135 |               |               |
| 2a-sym-1         | -7415.37982146  | -7415.227785 | -496.26108590 | 0.00025455   | -496.25857391 |               |
| 2a-sym-2 (TS)    | -8180.88070942  | -8180.521084 | -1261.78256656 | -496.25834904 |               |               |
| 2a-1             | -8180.88708577  | -8180.531471 | -1261.80785091 | -496.25625258 |               |               |
| 2a-asy (TS)      | -8180.88699433  | -8180.531067 | -1261.80783702 | -496.25836092 |               |               |
| (2a)$_2$-par     | -8180.87734608  | -8180.517454 | -1261.79489551 | -496.25783690 |               |               |
| lig1             | -1261.80603022  | -1261.80602676 | -496.25998047 |               |               |
| lig2             | -1261.80602676  | -496.25978902 |               |               |               |
| (2a)$_2$-tw      | -16361.83791980 | -16361.103283 | -2523.61157692 | 0.00130416   | -992.51949182 |               |
| lig1             | -1261.80676266  | -496.25916876 |               |               |               |
| lig2             | -1261.80676251  | -496.25916140 |               |               |               |
| 14b              | -496.72018194   | -496.556704 | -496.24565502 | 0.00097998   | -496.24467504 |               |
| 2b               | -1262.25494565  | -1261.81015106 | -496.25692989 |               |               |
| (2b)$_2$-par     | -1261.8054603   | -1261.80954603 | -496.25836424 |               |               |
| lig1             | -1261.80954603  | -496.25833553 |               |               |               |
| lig2             | -1261.80958219  |               |               |               |               |
| (2b)$_2$-tw      | -2524.55855180  | -2523.787407 | -2523.63088583 | 0.01147743   | -992.49743291 |               |
| lig1             | -1261.81006888  | -496.2584433 |               |               |               |
| lig2             | -1261.81007428  | -496.25845031 |               |               |               |
| lig1+lig2        | -2524.55083299  | -2523.787515 | -2523.61809991 | 0.00852754   | -992.49392305 |               |
| (2a) lig1+lig2   | -1261.81015106  | -2523.61809991 | 0.00852754 |               |               |
| (2b) lig1+lig2   | -1261.80954603  | -496.25836424 |               |               |               |
| Table S9. The auxiliary energies used for the decomposition of relative bond energies. See Sec. 4.2 for definitions.

4.4 Geometries and thermochemical data for individual compounds

In this section, the geometries, energies and if applicable thermochemical data and lowest frequencies (up to and including the first real frequency) are given. All geometry parameters are given in Ångström and degrees, energies in Hartree units, vibrational frequencies in cm$^{-1}$, and NMR shieldings in ppm.

4.4.1 Bis(pyridine) complexes and their derivatives

We provide the Z-matrixes obtained by geometry optimization for the ground states of the bis(pyridine) complexes and used as a starting point for both the potential scans and the calculation. For the scans, the values for R11 and R12 were changed stepwise as described in Section 4.1. The geometries and energies of the local minima and TS were determined by a constrained optimization where only the N–X distances were allowed to vary. Thus, for the non-ground-state geometries, only the values for R1 and R2 are given below, along with the energies and vibration frequencies.

The data for pyridine and its derivatives, which are required for the calculation of stabilization energies etc., are given in Section 4.4.3.
X = I, R = H, R' = H

Number of atoms: 23
Point group: D2H

I
N  1  R11
C  2  R2  1  A1
N  1  R12  2  A180  3  D0  0
C  4  R2  2  A1  3  D0  0
C  4  R2  2  A1  3  D180  0
C  2  R2  4  A1  5  D180  0
C  3  R3  2  A2  1  D180  0
C  7  R3  2  A2  1  D180  0
C  5  R3  4  A2  1  D180  0
C  6  R3  4  A2  1  D180  0
C  2  R4  1  A180  5  D0  0
C  4  R4  1  A180  3  D0  0
H  3  R5  2  A3  1  D0  0
H  7  R5  2  A3  1  D0  0
H  5  R5  4  A3  1  D0  0
H  6  R5  4  A3  1  D0  0
H  8  R6  3  A4  2  D180  0
H  9  R6  7  A4  2  D180  0
H  10  R6  5  A4  4  D180  0
H  11  R6  6  A4  4  D180  0
H  12  R7  2  A180  3  D0  0
H  13  R7  4  A180  5  D0  0

R11  2.275372
R12  2.275372
R2  1.334550
R3  1.377805
R4  2.740128
R5  1.084102
R6  1.087428
R7  1.088702
A180  180.000000
A1  119.674824
A2  121.263285
A3  116.680733
A4  119.773551
D0  0.000000
D180  180.000000

Electronic energy: -7415.37985512

Lowest frequency:
B3U  38.0229

X = H, R = H, R' = H

Number of atoms: 23
Point group: C2V

R11  1.061125
R12 1.741370

Electronic energy: -496.71817222

Lowest frequencies:
A" -144.4116
A" -49.1543
A'  58.1387

-----------------------------------------------------------------

Point group: C2V

R11 1.287162
R12 1.287162

Electronic energy: -496.71554916

Lowest frequencies:
A' -570.6132
A" -126.7329
A"  36.2004

=================================================================

X = I, R = CH₃, R' = CH₃

-----------------------------------------------------------------

Number of atoms: 29
Point group: C2H

| I | N   | 1   | R11          |
|---|-----|-----|--------------|
|  | C   | 2   | R21          |
|  | N   | 1   | R12          |
|  | C   | 4   | R22          |
|  | C   | 3   | R31          |
|  | C   | 7   | R32          |
|  | C   | 6   | R31          |
|  | C   | 2   | R4           |
|  | C   | 4   | R4           |
|  | H   | 3   | R51          |
|  | H   | 7   | R52          |
|  | H   | 5   | R52          |
|  | H   | 6   | R51          |
|  | H   | 8   | R61          |
|  | H   | 9   | R62          |
|  | H   | 10  | R62          |
|  | H   | 11  | R61          |
|  | H   | 12  | R7           |
|  | H   | 13  | R7           |
|  | H   | 22  | R8           |
|  | H   | 22  | R9           |
|  | H   | 22  | R9           |
|  | H   | 23  | R8           |
|  | H   | 23  | R9           |
|  | H   | 23  | R9           |

R11 2.272677
R12  2.272677
R21  1.333751
R22  1.336643
R31  1.376182
R32  1.373462
R4   2.769133
R51  1.084255
R52  1.084164
R61  1.088897
R62  1.089433
R7   1.487943
R8   1.094772
R9   1.097873
A180 180.000000
A11  119.961149
A12  120.064609
A21  121.501614
A22  121.473902
A31  116.688019
A32  116.627455
A41  119.501015
A42  119.534551
A5   121.869568
A6   111.812892
A7   110.512733
A101 59.999661
D0   0.000000
D180 180.000000
D1   120.958970

Electronic energy:  
-7493.94484558

Lowest frequencies:
AU   -76.1638
BG   -75.3282
AU   23.0196

-----------------------------------------------------------------
X = H, R = CH3, R' = CH3
-----------------------------------------------------------------

Number of atoms: 29
Point group: CS

R11  1.060052
R12  1.739492

Electronic energy:  
-575.28293045

Lowest frequencies:
A"   -128.9053
A"   -41.6426
A"   20.1928

-----------------------------------------------------------------
Point group: CS

R11  1.287869
R12  1.287869
Electronic energy: -575.28018746

Lowest frequencies:
A' -723.9467
A" -72.9785
A" -71.1804
A" -39.4838
A' -31.1852
A" 19.4154

=================================================================
X = I, R = CF3, R' = CF3
=================================================================

Number of atoms: 29
Point group: C2h

I
N  1  R11
C  2  R21  1  A11
N  1  R12  2  A180  3  D0  0
C  4  R22  2  A12  3  D0  0
C  4  R21  2  A11  3  D180  0
C  2  R22  4  A12  5  D180  0
C  3  R31  2  A21  1  D180  0
C  7  R32  2  A22  1  D180  0
C  5  R32  4  A22  1  D180  0
C  6  R31  4  A21  1  D180  0
C  2  R4  7  A101  9  D0  0
C  4  R4  5  A101  10  D0  0
H  3  R51  2  A31  1  D0  0
H  7  R52  2  A32  1  D0  0
H  5  R52  4  A32  1  D0  0
H  6  R51  4  A31  1  D0  0
H  8  R61  3  A41  2  D180  0
H  9  R62  7  A42  2  D180  0
H 10  R62  5  A42  4  D180  0
H 11  R61  6  A41  4  D180  0
C 12  R7  8  A5  3  D180  0
C 13  R7  11  A5  6  D180  0
F  22  R8  12  A6  8  D0  0
F  22  R9  12  A7  8  D1  0
F  22  R9  12  A7  8  -D1  0
F  23  R8  13  A6  11  D0  0
F  23  R9  13  A7  11  D1  0
F  23  R9  13  A7  11  -D1  0
R11 2.280013
R12 2.280013
R21 1.331335
R22 1.334306
R31 1.379484
R32 1.375591
R4 2.727869
R51 1.083732
R52 1.083691
R61 1.087414
R62 1.088561
R7 1.504431
R8 1.330502
| X = H, R = CF₃, R' = CF₃ |
|--------------------------|
| **Electronic energy:**   | -8089.10873435 |
| **Lowest frequencies:**  |
| A\u2032 | -35.0605 |
| A\u2032 | -12.045  |
| B\u2032 |  2.6267  |
|--------------------------|
| X = I, R = CH₃, R' = CF₃ |
|--------------------------|
| **Electronic energy:**   | -1170.44885059 |
| **Lowest frequencies:**  |
| A\u2032 | -96.8337 |
| A\u2032 | -18.2973 |
| A\u2032 |  15.0897 |
|--------------------------|
| X = I, R = CH₃, R' = CF₃ |
|--------------------------|
| **Electronic energy:**   | -1170.44612238 |
| **Lowest frequencies:**  |
| A\u2032 | -458.6589 |
| A\u2032 | -52.4768 |
| A"  |  5.9812  |
Number of atoms: 29
Point group: CS

| I | N  | R11  | 1  | A11  |
|---|-----|------|----|------|
|   | C  | R21  | 2  | A101 | D0  | 0  |
|   | N  | R12  | 2  | A101 | 3   | 0  |
|   | C  | R22  | 2  | A12  | 3   | 0  |
|   | C  | R23  | 2  | A13  | 3   | 180 0 |
|   | C  | R24  | 4  | A14  | 5   | 180 0 |
|   | C  | R31  | 2  | A21  | 1   | 180 0 |
|   | C  | R32  | 2  | A22  | 1   | 180 0 |
|   | C  | R33  | 4  | A23  | 1   | 180 0 |
|   | C  | R34  | 4  | A24  | 1   | 180 0 |
|   | C  | R41  | 7  | A102 | 9   | 0  |
|   | C  | R42  | 5  | A103 | 10  | 0  |
|   | H  | R51  | 2  | A31  | 1   | 0  |
|   | H  | R52  | 2  | A32  | 1   | 0  |
|   | H  | R53  | 4  | A33  | 1   | 0  |
|   | H  | R54  | 4  | A34  | 1   | 0  |
|   | H  | R61  | 3  | A41  | 2   | 180 0 |
|   | H  | R62  | 7  | A42  | 2   | 180 0 |
|   | H  | R63  | 5  | A43  | 4   | 180 0 |
|   | H  | R64  | 6  | A44  | 4   | 180 0 |
|   | C  | R71  | 8  | A51  | 3   | 180 0 |
|   | C  | R72  | 11 | A52  | 6   | 180 0 |
|   | H  | R81  | 12 | A61  | 8   | 0  |
|   | H  | R91  | 12 | A71  | 8   | 11 0 |
|   | H  | R91  | 12 | A71  | 8   | -11 0 |
|   | F  | R82  | 13 | A62  | 11  | 0  |
|   | F  | R92  | 13 | A72  | 11  | 12 0 |
|   | F  | R92  | 13 | A72  | 11  | -12 0 |

R11  2.233868
R12  2.323375
R21  1.334924
R22  1.333327
R23  1.329804
R24  1.337821
R31  1.375538
R32  1.372312
R33  1.375824
R34  1.380724
R41  2.766633
R42  2.730283
R51  1.083862
R52  1.083862
R53  1.083914
R54  1.084093
R61  1.088799
R62  1.089238
R63  1.088646
R64  1.087168
R71  1.487180
R72  1.503656
R81  1.094720
R82  1.330669
R91  1.097766
R92  1.336387
A101 179.973588
A11  120.105158
A12  119.317439
A13  119.955153
A14  119.724501
A21  121.289033
A22  121.332194
A23  121.391961
A24  121.501090
A31  116.736443
A32  116.683057
A33  116.926413
A34  116.893786
A41  119.367889
A42  119.520876
A43  120.258474
A44  120.280521
A51  121.837770
A52  121.582177
A61  111.795051
A62  112.379910
A71  110.480740
A72  110.650704
A102 60.086892
A103 60.397763
D0  0.000000
D180 180.000000
D11  121.000141
D12  120.633775

Electronic energy:  -7791.52733551
Lowest frequencies:
A"   -37.1722
A"   16.3103

-----------------------------------------------------------------
X = H, R = CH3, R' = CF3
-----------------------------------------------------------------
Number of atoms:  29
Point group: CS
R11  1.048336
R12  1.809170
Electronic energy:  -872.87007142
Lowest frequencies:
A"   -59.5555
A"   -13.6334
A"    23.4082

-----------------------------------------------------------------
Point group: CS
R11  1.599225
R12  1.095662
Electronic energy:  -872.86206314
Lowest frequencies:
A"       -69.4863
A"       -23.1956
A"        13.6596

-----------------------------------------------

Point group: CS

R11   1.450571
R12   1.164725

Electronic energy:                          -872.86178472

Lowest frequencies:
A'       -724.2087
A'        -45.0994
A"       -24.5476
A"        18.8520
4.4.2 1,2-bis(pyridine-2-ylethynyl)benzene ligands and complexes and their derivatives

For complexes where NMR properties were calculated we specify in addition the energy of the NMR calculation as well as the $^{15}$N chemical shieldings. (A summary of the NMR shieldings is given in Section 4.3.3). The NMR data for pyridine are given in Section 4.4.3.

X = I, R = H, R' = H

Number of atoms: 23
Point group: D2H

I
N 1 R11
C 2 R2 1 A1
N 1 R12 2 A180 3 D0 0
C 4 R2 2 A1 3 D0 0
C 4 R2 2 A1 3 D180 0
C 2 R2 4 A1 5 D180 0
C 3 R3 2 A2 1 D180 0
C 7 R3 2 A2 1 D180 0
C 5 R3 4 A2 1 D180 0
C 6 R3 4 A2 1 D180 0
C 2 R4 1 A180 5 D0 0
C 4 R4 1 A180 3 D0 0
H 3 R5 2 A3 1 D0 0
H 7 R5 2 A3 1 D0 0
H 5 R5 4 A3 1 D0 0
H 6 R5 4 A3 1 D0 0
H 8 R6 3 A4 2 D180 0
H 9 R6 7 A4 2 D180 0
H 10 R6 5 A4 4 D180 0
H 11 R6 6 A4 4 D180 0
H 12 R7 2 A180 3 D0 0
H 13 R7 4 A180 5 D0 0

R11 2.275372
R12 2.275372
R2 1.334550
R3 1.377805
R4 2.740128
R5 1.084102
R6 1.087428
R7 1.088702
A180 180.00000
A1 119.674824
A2 121.263285
A3 116.680733
A4 119.773551
D0 0.000000
D180 180.00000

Electronic energy: -7415.37985512

Lowest frequency:
B3U 38.0229
X = H, R = H, R' = H

Number of atoms: 23
Point group: C2V

R11        1.061125
R12        1.741370

Electronic energy: -496.71817222

Lowest frequencies:
A"        -144.4116
A"         -49.1543
A'          58.1387

Point group: C2V

R11        1.287162
R12        1.287162

Electronic energy: -496.71554916

Lowest frequencies:
A'        -570.6132
A"        -126.7329
A"          36.2004

X = I, R = CH3, R' = CH3

Number of atoms: 29
Point group: C2H

I
N 1    R11
C 2    R21
C 4    R22
C 2    R21
C 4    R22
C 2    R22
C 3    R31
C 7    R32
C 5    R32
C 6    R31
C 2    R4
C 4    R4
H 3    R51
H 7    R52
H 5    R52
H 6    R51
H 8    R61
H 9    R62
H 10   R62
H 11   R61
C 12   R7
C 13   R7
H 22   R8

| X | H | R | 22 | R9 | 12 | A7 | 8 | D1 | 0 |
|---|---|---|----|----|----|----|---|----|---|
| H | 22 | R9 | 12  | A7 | 8  | -D1| 0 |
| H | 23 | R8 | 13  | A6 | 11 | D0 | 0 |
| H | 23 | R9 | 13  | A7 | 11 | D1 | 0 |
| H | 23 | R9 | 13  | A7 | 11 | -D1| 0 |

| R11 | 2.272677 |
| R12 | 2.272677 |
| R21 | 1.333751 |
| R22 | 1.336643 |
| R31 | 1.376182 |
| R32 | 1.373462 |
| R4  | 2.769133 |
| R51 | 1.084255 |
| R52 | 1.084164 |
| R61 | 1.088897 |
| R62 | 1.089433 |
| R7  | 1.487943 |
| R8  | 1.094772 |
| R9  | 1.097873 |
| A110 | 180.000000 |
| A12  | 119.961149 |
| A21  | 121.501614 |
| A22  | 121.473902 |
| A31  | 116.688019 |
| A32  | 116.627455 |
| A41  | 119.501015 |
| A42  | 119.534551 |
| A5   | 121.869568 |
| A6   | 111.812892 |
| A7   | 110.512733 |
| A101 | 59.999661 |
| D0   | 0.000000 |
| D180 | 180.000000 |
| D1   | 120.958970 |

Electronic energy: \(-7493.94484558\)

Lowest frequencies:

| AU  | -76.1638 |
| BG  | -75.3282 |
| AU  | 23.0196  |

---

X = H, R = CH3, R' = CH3

---

Number of atoms: 29
Point group: CS

| R11 | 1.060052 |
| R12 | 1.739492 |

Electronic energy: \(-575.28293045\)

Lowest frequencies:

| A"   | -128.9053 |
| A"   | -41.6426  |
| A"   | 20.1928   |
Point group: CS

R11 1.287869
R12 1.287869

Electronic energy: -575.28018746

Lowest frequencies:
A' -723.9467
A" -72.9785
A" -71.1804
A' -39.4838
A" -31.1852
A" 19.4154

X = I, R = CF3, R' = CF3

Number of atoms: 29
Point group: C2H

I
N 1 R11
C 2 R21 1 A11
N 1 R12 2 A180 3 D0 0
C 4 R22 2 A12 3 D0 0
C 4 R21 2 A11 3 D180 0
C 2 R22 4 A12 5 D180 0
C 3 R31 2 A21 1 D180 0
C 7 R32 2 A22 1 D180 0
C 5 R32 4 A22 1 D180 0
C 6 R31 4 A21 1 D180 0
C 2 R4 7 A101 9 D0 0
C 4 R4 5 A101 10 D0 0
H 3 R51 2 A31 1 D0 0
H 7 R52 2 A32 1 D0 0
H 5 R52 4 A32 1 D0 0
H 6 R51 4 A31 1 D0 0
H 8 R61 3 A41 2 D180 0
H 9 R62 7 A42 2 D180 0
H 10 R62 5 A42 4 D180 0
H 11 R61 6 A41 4 D180 0
C 12 R7 8 A5 3 D180 0
C 13 R7 11 A5 6 D180 0
F 22 R8 12 A6 8 D0 0
F 22 R9 12 A7 8 D1 0
F 22 R9 12 A7 8 -D1 0
F 23 R8 13 A6 11 D0 0
F 23 R9 13 A7 11 D1 0
F 23 R9 13 A7 11 -D1 0

R11 2.280013
R12 2.280013
R21 1.331335
R22 1.334306
R31 1.379484
R32 1.375591
|       | Value      |
|-------|-----------|
| R4    | 2.727869  |
| R51   | 1.083732  |
| R52   | 1.083691  |
| R61   | 1.087414  |
| R62   | 1.088561  |
| R7    | 1.504431  |
| R8    | 1.330502  |
| R9    | 1.335528  |
| A180  | 180.000000|
| A11   | 119.569556|
| A12   | 119.497472|
| A21   | 121.351844|
| A22   | 121.176819|
| A31   | 116.951921|
| A32   | 117.045801|
| A41   | 120.292342|
| A42   | 120.113758|
| A5    | 121.501214|
| A6    | 112.203044|
| A7    | 110.627570|
| A101  | 60.516561 |
| D0    | 0.000000  |
| D180  | 180.000000|
| D1    | 120.589819|

Electronic energy: \(-8089.10873435\)

Lowest frequencies:
- AU: -35.0605
- AU: -12.2045
- BU: 2.6267

X = H, R = CF3, R’ = CF3

Number of atoms: 29
Point group: CS

|       | Value      |
|-------|-----------|
| R11   | 1.063646  |
| R12   | 1.737498  |

Electronic energy: \(-1170.44885059\)

Lowest frequencies:
- A": -96.8337
- A": -18.2973
- A": 15.0897

Point group: CS

|       | Value      |
|-------|-----------|
| R11   | 1.291045  |
| R12   | 1.291045  |

Electronic energy: \(-1170.44612238\)

Lowest frequencies:
- A': -458.6589
\[ A^" = -52.4768 \]
\[ A^" = 5.9812 \]

=================================================================
Number of atoms: 29
Point group: CS

I
N 1  R11
C 2  R21  1  A11
N 1  R12  2  A101  3  D0  0
C 4  R22  2  A12  3  D0  0
C 4  R23  2  A13  3  D180  0
C 2  R24  4  A14  5  D180  0
C 3  R31  2  A21  1  D180  0
C 7  R32  2  A22  1  D180  0
C 5  R33  4  A23  1  D180  0
C 6  R34  4  A24  1  D180  0
C 2  R41  7  A102  9  D0  0
C 4  R42  5  A103  10  D0  0
H 3  R51  2  A31  1  D0  0
H 7  R52  2  A32  1  D0  0
H 5  R53  4  A33  1  D0  0
H 6  R54  4  A34  1  D0  0
H 8  R61  3  A41  2  D180  0
H 9  R62  7  A42  2  D180  0
H 10 R63  5  A43  4  D180  0
H 11 R64  6  A44  4  D180  0
C 12 R71  8  A51  3  D180  0
C 13 R72  11  A52  6  D180  0
H 22 R81  12  A61  8  D0  0
H 22 R91  12  A71  8  D11  0
H 22 R91  12  A71  8  -D11  0
F 23 R82  13  A62  11  D0  0
F 23 R92  13  A72  11  D12  0
F 23 R92  13  A72  11  -D12  0

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| R11   | 2.233868 |
| R12   | 2.323375 |
| R21   | 1.334924 |
| R22   | 1.333327 |
| R23   | 1.329804 |
| R24   | 1.337821 |
| R31   | 1.375538 |
| R32   | 1.372312 |
| R33   | 1.375824 |
| R34   | 1.380724 |
| R41   | 2.766633 |
| R42   | 2.730283 |
| R51   | 1.083862 |
| R52   | 1.083862 |
| R53   | 1.083914 |
| R54   | 1.084093 |
| R61   | 1.088799 |
| R62   | 1.089238 |
| R63   | 1.088646 |
| R64   | 1.087168 |
| R71   | 1.487180 |
Electronic energy:  \(-7791.5273351\)

Lowest frequencies:
\(A''\)  \(-37.1722\)
\(A''\)  \(16.3103\)

-----------------------------------------------
\(X = H, R = CH_3, R' = CF_3\)
-----------------------------------------------

Number of atoms:  29
Point group:  CS

R11  1.048336
R12  1.809170

Electronic energy:  \(-872.87007142\)

Lowest frequencies:
\(A''\)  \(-59.5555\)
\(A''\)  \(-13.6334\)
\(A''\)  \(23.4082\)

-----------------------------------------------
Point group: CS

R11  1.599225  
R12  1.095662  

Electronic energy:  -872.86206314  

Lowest frequencies:  
A"      -69.4863  
A"      -23.1956  
A"      13.6596  

-----------------------------------------------------------------

Point group: CS

R11  1.450571  
R12  1.164725  

Electronic energy:  -872.86178472  

Lowest frequencies:  
A'      -724.2087  
A'      -45.0994  
A"      -24.5476  
A"      18.8520
4.4.3 Conformers of 2a and 2b

In addition to the geometries and thermochemical data the data for the energy decomposition according to Sec. 4.4.3 are given. For the ligands, only the energies are given, the geometries can be derived from those of the complexes by omitting the I⁺ or H⁺ ions. For the pyridine oligomers, besides the energies, the position of the saturating H atom is given in Z-matrix coordinates where the anchoring atoms for the Z matrix are chosen as shown in Figure S83. The pyridine moieties are numbered in the order in which their N atoms occur in the geometry. Regarding notation, note that Pyr2 denotes pyridine moiety number 2 whereas Pyr_2 denotes a pyridine dimer.

A summary of the energy components is given in Section 4.3.4.

Figure S83. Definition of the Z-matrix coordinates for the saturating H atoms in the pyridine oligomers.

=================================================================
Pyridine
=================================================================

Number of atoms:  11
Point group: C2V

0 1
N  0.00000000  0.00000000  1.40676553
C  0.00000000  1.13720389  0.71815804
C  0.00000000  1.19292979 -0.66595287
C  0.00000000  0.00000000 -1.37483295
C  0.00000000 -1.19292979 -0.66595287
C  0.00000000 -1.13720389  0.71815804
H  0.00000000  2.05582629  1.29980274
H  0.00000000  2.15439161 -1.17813799
H  0.00000000  0.00000000 -2.46504241
H  0.00000000 -2.15439161 -1.17813799
H  0.00000000 -2.05582629  1.29980274

Electronic energy: -248.13185009
Zero-point correction= 0.088231
Sum of electronic and zero-point Energies= -248.043619
Sum of electronic and thermal Energies= -248.039320
Sum of electronic and thermal Enthalpies= -248.038376
Sum of electronic and thermal Free Energies= -248.070364

Lowest frequency:
A2  380.6281

Electronic energy (NMR): -248.21443757

15N shieldings:
N  1  -79.0857

=================================================================
Number of atoms:  51  
Point group: C1  

|   |   |   |   |   |
|---|---|---|---|---|
| 1 | C | 2.94759388 | -0.96437032 | -0.01359440 |
| 1 | C | 1.72238495 | -0.31678087 | 0.28207720 |
| 1 | C | 0.51536866 | -1.11255256 | 0.40313588 |
| 1 | C | 0.59581002 | -2.52244579 | 0.26196490 |
| 1 | C | 1.85824779 | -3.14475350 | -0.00288195 |
| 1 | C | 2.99242008 | -2.39511388 | -0.16421077 |
| 1 | C | -0.74056773 | -0.54497086 | 0.65309627 |
| 1 | C | -1.88054725 | -1.32513626 | 0.74381799 |
| 1 | C | -1.78938770 | -2.72365051 | 0.63271732 |
| 1 | C | -0.56972905 | -3.30610432 | 0.38877890 |
| 1 | C | 4.11717979 | -0.19443445 | -0.15578488 |
| 1 | C | 4.08198168 | 1.17179458 | -0.01661427 |
| 1 | C | 2.87375486 | 1.83454399 | 0.27425024 |
| 1 | C | 1.72242768 | 1.07963290 | 0.42239567 |
| 1 | C | -3.17803582 | -0.69557922 | 1.00398332 |
| 1 | C | 2.81588042 | 3.03064888 | 0.42013198 |
| 1 | O | 1.89605230 | -4.50710867 | -0.08560519 |
| 1 | C | 4.20835394 | -2.91713276 | -0.42753948 |
| 1 | O | 3.2931297 | -3.94924137 | -1.40552353 |
| 1 | N | -3.69938660 | 0.20828012 | 0.13601626 |
| 1 | C | -4.86136074 | 0.84986589 | 0.38450473 |
| 1 | C | -5.57838736 | 0.59146752 | 1.52118659 |
| 1 | C | -5.09803042 | -0.35665132 | 2.41660079 |
| 1 | C | -3.89835317 | -0.99062100 | 2.15085184 |
| 1 | C | 3.77237951 | 4.13128184 | -0.16593534 |
| 1 | C | 3.67129111 | 5.50281417 | 0.00345633 |
| 1 | C | 2.61821948 | 6.01257107 | 0.74845893 |
| 1 | C | 1.70892283 | 5.11328939 | 1.28210941 |
| 1 | N | 1.79776988 | 3.80112625 | 1.12670722 |
| 1 | H | -0.83180760 | 0.53174946 | 0.78908754 |
| 1 | H | -2.68750112 | -3.33621542 | 0.71538155 |
| 1 | H | -0.48908237 | -4.38593950 | 0.27628753 |
| 1 | C | 5.05467275 | -0.70328497 | -0.37102818 |
| 1 | H | 5.00801231 | 1.73000353 | -0.1139168 |
| 1 | C | 0.80218417 | 1.61331810 | 0.65185940 |
| 1 | H | 2.30616745 | -6.21224541 | 0.94182227 |
| 1 | C | 3.31908590 | -4.81135219 | 1.41253178 |
| 1 | H | 1.60577321 | -4.90121524 | 1.94152561 |
| 1 | C | 5.34752451 | -3.87248546 | -1.79917109 |
| 1 | H | 4.17808556 | -4.94294259 | -0.96825482 |
| 1 | H | 3.60777039 | -3.79684306 | -2.21818707 |
| 1 | H | -5.19325667 | 1.55914950 | -0.36122589 |
| 1 | H | -6.51004577 | 1.12371925 | 1.69335905 |
| 1 | H | -5.65033255 | -0.59079722 | 3.32491018 |
| 1 | H | -3.47458476 | -1.7178308 | 2.84717648 |
| 1 | H | 4.57982981 | 3.71410778 | -0.76554056 |
| 1 | H | 4.40694119 | 6.16740208 | -0.44948058 |
| 1 | H | 2.50078587 | 7.08281158 | 0.90879873 |
| 1 | H | 0.86746429 | 5.47506539 | 1.86811274 |
| 1 | I | -2.83252729 | 0.57145127 | -1.73123853 |

Electronic energy:  -8180.88699433  
Zero-point correction=  0.397554  
Sum of electronic and zero-point Energies=  -8180.489440
Sum of electronic and thermal Energies = -8180.463337
Sum of electronic and thermal Enthalpies = -8180.462393
Sum of electronic and thermal Free Energies = -8180.548763

Lowest frequency:
A 13.1483

Ligand energies:
E(lig) = -1261.80783702
E(lig:Pyr_2) = -496.25836092

Geometry parameters for saturating H atoms at pyridines:

| Lig | Pyr1 | r   | phi  | tau  |
|-----|------|-----|------|------|
|     |      | 1.0836 | 118.12 | -178.65 |
|     |      | 1.0860 | 117.24 | 179.93  |

Number of atoms: 51
Point group: C1

S83
H     1.62219742  -4.88287313  1.96199857
H     5.34119822  -3.88048989  -1.80270127
H     4.17303608  -4.94579652  -0.96320570
H     3.60083244  -3.80669280  -2.21887538
H     -5.19600243   1.55253390  -0.36654810
H     -6.52245794  1.10989765   1.67978718
H     -5.66431433  -0.60050587   3.31605785
H     -3.48174612  -1.71274975   2.85004761
H     -4.90801366   3.55710420   0.88938629
H     -4.71550473   6.01909085  1.11725076
H     -2.46973135   7.09494273   0.77667761
H     -0.53856132   5.62969113   0.23141345
I     -2.82203678  0.57770607  -1.72363255

Electronic energy:                                -8180.88708577
Zero-point correction=                                0.397393
Sum of electronic and zero-point Energies=        -8180.489693
Sum of electronic and thermal Energies=           -8180.463579
Sum of electronic and thermal Enthalpies=         -8180.462635
Sum of electronic and thermal Free Energies=      -8180.549211

Lowest frequency:
A           10.9151

Ligand energies:
E(lig)                 -1261.80785091
E(lig:Pyr_2)            -496.25834904

Geometry parameters for saturating H atoms at pyridines:

| Lig | Pyr1     | r   | phi  | tau  |
|-----|----------|-----|------|------|
| Lig |         | 1.0836| 118.11| -178.67 |
| Pyr2|         | 1.0860| 117.23| 179.93  |

=================================================================
2a-sym-1
=================================================================

Number of atoms:  51
Point group: C1

S84
C  -5.19620620  -5.37856485  -0.68854468
C  -4.82013020  -6.69752282  -0.58470467
C  -3.53876698  -6.98161084  -0.13517377
C  -2.69437495  -5.93400582   0.18174271
C  -7.11127525   2.01556745   0.21315404
C  -8.84927236   1.85472492  -0.09742586
C  -8.44227275  -0.62521352  -0.56915939
C  -7.96279195  -0.38800932  -0.69543707
N  -6.66797743   0.23271250  -0.39644810
H  -3.61239634  -2.33322646   1.36466283
H   0.45714297  -4.47247912  -0.57485498
H   0.97148720  -2.46944589  -0.44505684
H  -2.3559570   3.29258995  -0.47513066
H  -4.68823195  3.13386261  -0.60507095
H  -4.53451284  -0.65130527  1.38396931
H   3.30319394  -0.03741714   0.61474885
H   2.15012059   1.09172657  1.39349294
H   2.01943090  -0.67527472  1.68905919
H   0.97398857   3.57334500  -1.60609609
H   2.00411394   2.28326146  -0.91540572
H   0.73399236   1.87094526  -2.10708999
H  -6.18943819  -5.11158657  -1.03002396
H  -5.52382321  -7.48334371  -0.84806455
H  -3.20137492  -8.01119122  -0.02627149
H  -1.68877885  -6.12429093   0.55287894
H  -6.74092877   2.96351493   0.59939142
H  -9.14594694   2.68164796   0.03171501
H  -9.92443659   0.44563673  -0.83171218
H  -3.26101476  -1.36647793  -1.05357300
H  -5.47382371  -2.27537549  -0.58103314

Electronic energy:                              -8180.88070942
Zero-point correction=                           0.398164
Sum of electronic and zero-point Energies=        -8180.482545
Sum of electronic and thermal Energies=           -8180.457019
Sum of electronic and thermal Enthalpies=         -8180.456075
Sum of electronic and thermal Free Energies=      -8180.537759

Lowest frequency:
  A           39.8403

Ligand energies:
E(lig)                 -1261.78256656
E(lig:Pyr_2)            -496.25857391

Geometry parameters for saturating H atoms at pyridines:

| Lig | Pyr1 | r     | phi   | tau  |
|-----|------|-------|-------|------|
|     |      | 1.0840| 117.76| -179.84|
| Pyr2|      | 1.0841| 117.71| -179.99|

=================================================================
2a-sym-2 (TS)
=================================================================
Number of atoms:  51
Point group: C2

| 1 1 |
|-----|
| C  -0.13326308  0.67923569  -3.94353824 |
| C  0.13326308  -0.67923569  -3.94353824 |
| O  -0.30554201  1.34922961  -5.11475422 |
| O  0.30554201  -1.34922961  -5.11475422 |
C   -0.20922624  1.43399630  -2.71765147
C   -0.01608558  0.71198867  -1.53686986
C    0.20760568  1.37481448  -0.33763106
C   -0.04838688  2.70650754  -0.15137194
C   -0.40173575  3.43475532  -1.32227401
C   -0.41957051  2.82851266  -2.56950544
H    0.65912458  0.80619849   0.45411753
H   -0.64114757  4.49676529  -1.26856374
H   -0.62610388  3.43213416  -3.45315322
C   -0.01608558  0.71198867  -1.53686986
C   -0.20922624  1.43399630  -2.71765147
C    0.20760568  1.37481448  -0.33763106
C   -0.04838688  2.70650754  -0.15137194
C   -0.40173575  3.43475532  -1.32227401
C   -0.41957051  2.82851266  -2.56950544
H    0.65912458  0.80619849   0.45411753
H   -0.64114757  4.49676529  -1.26856374
H   -0.62610388  3.43213416  -3.45315322
C    0.33116127  4.36269133   3.74907866
C    0.28364889  5.19699831   2.64450168
C    0.16123708  4.63266990   1.38909053
C    0.07827928  3.25334795   1.21642400
N    0.12353070  2.45057589   2.32588183
C    0.25241710   3.00540418   3.53704572
H    0.42907764  4.74741853   4.76111611
H    0.34919717  6.27826818   2.75457922
H    0.14822725  5.27135654   0.50872987
H    0.28991706  2.32559473   4.37969929
C   -0.33116127  4.36269133   3.74907866
C   -0.25241710  5.19699831   2.64450168
N   -0.12353070  2.45057589   2.32588183
C   -0.07827928  3.25334795   1.21642400
C   -0.16123708  4.63266990   1.38909053
C   -0.28364889  5.19699831   2.64450168
H   -0.42907764  4.74741853   4.76111611
H   -0.28991706  2.32559473   4.37969929
H   -0.14822725  5.27135654   0.50872987
H   -0.34919717  6.27826818   2.75457922
I     0.00000000  0.00000000   0.00000000
C    0.90347491  1.63167799  -5.81697900
C   -0.90347491  1.63167799  -5.81697900
H    0.62318271  2.19964909  -6.70868141
H   1.57483109  2.24128799  -5.19358754
H   1.41008621  0.70349982  -6.11374231
H   -0.62318271  2.19964909  -6.70868141
H  -1.57483109  2.24128799  -5.19358754
H  -1.41008621  0.70349982  -6.11374231

Electronic energy: -8180.85376157
Zero-point correction= 0.397794
Sum of electronic and zero-point Energies= -8180.455968
Sum of electronic and thermal Energies= -8180.430635
Sum of electronic and thermal Enthalpies= -8180.429690
Sum of electronic and thermal Free Energies= -8180.512345

Lowest frequencies:
B   -95.4225
B    7.9379

Ligand energies:
E(lig)                 -1261.78353216
E(lig:Pyr_2)            -496.25625258

Geometry parameters for saturating H atoms at pyridines:

| Lig | Pyr1 | r     | phi   | tau  |
|-----|------|-------|-------|------|
|     |      | 1.0831| 117.90| 179.67|
| Pyr2|      | 1.0831| 117.90| 179.67|

2a-asym (TS)

Number of atoms: 51
Point group: C1

1  1  
C  -2.00837047  1.30402028  0.22220871 0.22220871
C  -2.72086197  0.11586978  0.49908708 0.49908708
C  -2.03017276 -1.15181571  0.46810212 0.46810212
C  -0.67519739 -1.19389905  0.07411158 0.07411158
C   0.05853687  0.03361740 -0.04362215 -0.04362215
C  -0.57831648  1.24661266  0.03811591 0.03811591
C  -2.72407273 -2.35733155  0.61613728 0.61613728
C  -2.21323462 -3.54968624  0.14334360 0.14334360
C   -0.86427491 -3.58547610 -0.27570971 -0.27570971
C  -0.09977509 -2.44184473 -0.25074063 -0.25074063
C  -2.72978753  2.49945339  0.02932199 0.02932199
C  -4.10753778  2.49529589 -0.00959249 -0.00959249
C  -4.82463811  1.30205327  0.20459728 0.20459728
C  -4.1196172  0.16496072  0.53540889 0.53540889
C  -3.06759931 -4.73043224  0.00173867 0.00173867
C  -6.27842939  1.18271504 -0.01819594 -0.01819594
O   1.40302694 -0.04679721 -0.27060926 -0.27060926
C   2.17585097 -0.03295524  0.92454589 0.92454589
O   0.03213366  2.44253632 -0.08057391 -0.08057391
C   1.05068727  2.63211817 -1.06098710 -1.06098710
N   -4.34033904  4.65351099 -0.48802887 0.48802887
C  -5.09292008 -5.76244683  0.65409524 0.65409524
C  -4.61956159 -7.01112182 -0.35579015 -0.35579015
C  -3.33025237  7.12980623  0.14727268 0.14727268
C  -2.57204310 -5.98984585  0.32114811 0.32114811
C   -7.14311251  2.24011512  0.24540833 0.24540833
C   -8.49908504  2.08439931  0.00748842 0.00748842
C   -8.95715399  0.87242802 -0.48712462 -0.48712462
C  -8.02973048 -1.12811333  0.71955465 0.71955465
N  -6.72732250  0.01116705 -0.50056416 0.50056416
H   -3.70130185 -2.36415909  1.08642687 -1.08642687
H  -0.43218848 -4.51426210  0.64883960 0.64883960
H   0.94229783  2.47379302  0.56595455 0.56595455
H  -2.17921942  3.41699439 -0.16943873 -0.16943873
H   -4.63626822  3.41557549 -0.26292782 -0.26292782
H   -4.69319389  0.73087198  0.74438712 0.74438712
H   3.22400249 -0.13391748  0.62678735 0.62678735
H   2.03976568  0.91345867  1.46995551 1.46995551
H   1.89963775 -0.87259363  1.58053011 1.58053011
H   1.07614209  3.70801707 -1.25882050 -1.25882050
H   2.03156212  2.30198942 -0.70062354 -0.70062354
H   0.80181107  2.09462390 -1.58499112 -1.58499112
H  -6.09049574 -5.61257512 -1.04356017 -1.04356017
H  -5.26042542  7.87437299 -0.51370639 -0.51370639
H  -2.92192155 -8.10401612  0.41049095 0.41049095
H  -1.56949380 -6.04951949  0.73952303 0.73952303
H  -6.75551513  3.17213635  0.65541711 0.65541711
H  -9.19148975   2.90003646   0.21389053
H  -10.01290131   0.70238744  -0.68932134
H  -8.35541189  -1.08985614  -1.10722817
I  -5.35929622  -2.84789738  -1.02459781

Electronic energy:                                -8180.87734608
Zero-point correction=                                0.398092
Sum of electronic and zero-point Energies=        -8180.479254
Sum of electronic and thermal Energies=           -8180.454383
Sum of electronic and thermal Enthalpies=         -8180.453439
Sum of electronic and thermal Free Energies=      -8180.533881

Lowest frequencies:
A             -36.9795
A             37.6951

Ligand energies:
E(lig)                 -1261.79489551
E(lig:Pyr_2)            -496.25783690

Geometry parameters for saturating H atoms at pyridines:

| Lig | Pyr1  | 1.0830 | 118.24 | -179.71 |
|-----|-------|--------|--------|---------|
|     | Pyr2  | 1.0857 | 117.08 | 179.68  |

Number of atoms: 102
Point group: C1
N 4.49689013 0.75730785 -2.17379063
H -0.97101238 1.80115948 -2.50929965
H -4.64281137 3.0786068 -0.89856131
H -3.38446685 4.75168003 0.80384421
H 4.61865050 3.34660528 -0.74151478
H 1.01515829 1.87237737 -2.52508262
H -2.14382940 7.63164485 2.00651389
H -0.56534565 7.54280475 3.72837888
H -2.07520387 1.1698874 0.29221482
H 1.90699907 5.95868330 3.72837888
H 0.24187226 6.50488399 3.68357010
H 0.59886258 4.76575182 3.50048514
H -5.81744527 -0.83521020 -2.56254349
H -5.73838235 -0.60484730 -5.03593115
H -4.16879154 1.09708408 -6.02249941
H -2.82163357 2.51971280 -4.47617606
H 2.89517469 2.66730557 4.39756211
H 4.30389443 1.32343088 -5.96232662
H 5.88790995 -0.37544936 5.00946486
H 5.91660831 -0.69297313 2.53664299
I 4.42809319 -0.00240893 -0.01514649
I 4.46542725 0.00958090 0.00509283
C 1.3981670 -4.08526275 -0.04458648
C 0.71883590 -3.27575869 0.89798715
C -0.73077622 -3.26266162 0.91180457
C -1.43391317 -4.09403930 0.00340050
C -0.71374804 -4.92801803 -0.91388470
C 0.65231264 -4.91268742 -0.95755221
C -1.48057251 -2.45804751 1.78885609
C -2.86151889 -2.45679627 1.7641208
C -3.54754375 -3.29651015 0.86824118
C -2.84366095 -4.1016064 0.00865376
C 2.80719407 -4.09264370 -0.07912192
C 3.53459495 -3.30871938 0.78071462
C 2.87267902 -2.49678423 1.71893769
C 1.49325196 -2.49756010 1.77811041
C -3.61884622 -1.59723310 2.69103510
C 3.65408448 -1.67669697 2.66198644
O -1.43233281 -5.73650651 -1.74499304
C -1.53429045 -7.0929649 -1.27988620
C 1.38585503 -5.67158252 -1.80236115
C 1.02108643 -5.7188716 -3.18039180
O -4.44718890 -0.66461480 2.19091147
C -5.19081133 0.09371226 3.00298876
C -5.13865556 -0.03477806 4.37159145
C -4.26895102 -0.97112945 4.91397324
C -3.50756241 -1.75695153 4.06477033
C 3.55968546 -1.88485263 4.03051057
C 4.34391747 -1.14157742 4.89696922
C 5.22122205 -0.19998810 4.37656370
C 5.25649683 -0.02292471 3.01287812
N 4.48903809 -0.73837248 2.18414435
H -0.97750423 -1.79648511 2.49426788
H -4.63781335 -3.31325623 0.86697999
H -3.36845189 -4.75368853 -0.68685865
H 3.30986140 -4.73463034 -0.79899430
H 4.62433845 -3.32738828 0.75257917
H 1.00875758 -1.86277760 2.51953607
H -2.11399008 -7.63025882 -2.02652109
H -0.53955885 -7.53718915 -1.17595364
H  -2.05674701  -7.11534198  -0.31197353
H   1.93988887  -5.94595161  -3.73017846
H   0.27481051  -6.49703889  -3.37758978
H   0.62722726  -4.74787324  -3.50813242
H  -5.83150036   0.82648914   2.52580823
H  -5.76305857   0.59597115   4.99951064
H  -4.19319728  -1.09668305   5.99297718
H  -2.83505687  -2.52032750   4.45258627
H   2.88247092  -2.65271269   4.40068012
H   4.28047610  -1.30505259   5.97168590
H   5.86419838   0.39813073   5.01755557
H   5.90314206   0.71577178   2.55341059

Electronic energy:                               -16361.83791980
Zero-point correction=                                0.797323
Sum of electronic and zero-point Energies=       -16361.040597
Sum of electronic and thermal Energies=          -16360.986805
Sum of electronic and thermal Enthalpies=        -16360.985861
Sum of electronic and thermal Free Energies=     -16361.133052

Lowest frequency:
A            7.3729

Ligand energies:
E(lig1+lig2)           -2523.61157692
E(lig1+lig2:Pyr_4)      -992.51949182
E(lig1)                -1261.80602676
E(lig1:Pyr_2)           -496.25987902
BSSE                       0.00130416

Geometry parameters for saturating H atoms at pyridines:

| Lig1+Lig2 | Pyr1 | r    | phi  | tau  |
|-----------|------|------|------|------|
|           |      | 1.0848 | 117.67 | 179.11 |
| Pyr2      |      | 1.0848 | 117.67 | -179.07 |
| Pyr3      |      | 1.0848 | 117.67 | 179.11 |
| Pyr4      |      | 1.0848 | 117.67 | -179.07 |
| Lig1      | Pyr1 | 1.0849 | 117.71 | 179.16 |
|           | Pyr2 | 1.0849 | 117.72 | -179.06 |
| Lig2      | Pyr3 | 1.0849 | 117.71 | 179.16 |
|           | Pyr4 | 1.0849 | 117.72 | -179.06 |

(2a)2-tw

Number of atoms: 102
Point group: C1
|   |          |          |          |
|---|----------|----------|----------|
| C | -3.07012998 | -4.43825425 | 0.96221013 |
| C | -2.80095432 | -3.07891993 | 0.67537609 |
| C | -1.47029357 | -2.68410035 | 0.27391290 |
| C | -0.51310327 | -3.68451729 | -0.01831487 |
| C | -0.83118158 | -5.06162659 | 0.22509388 |
| C | -2.04129941 | -5.42531515 | 0.75732009 |
| C | -1.09646163 | -1.33975851 | 0.14894034 |
| C | 0.11977286 | -0.96908791 | -0.39574756 |
| C | 1.04084234 | -1.97675194 | -0.74676170 |
| C | 0.74115200 | -3.30194763 | -0.53405099 |
| C | -4.35863625 | -4.80736226 | 1.39446248 |
| C | -5.36575736 | -3.87527400 | 1.48841055 |
| C | -5.12682069 | -2.53169307 | 1.14034471 |
| C | -3.86001757 | -2.16071023 | 0.73069763 |
| O | 0.11538252 | -5.99612959 | -0.07295923 |
| C | -0.09387166 | -6.63788225 | -1.32775225 |
| O | -2.38964871 | -6.69718138 | 1.04387317 |
| C | -1.45045749 | -7.54373731 | 1.70654739 |
| H | -1.77106599 | -0.56969430 | 0.51563377 |
| H | 2.00001066 | -1.70535076 | -1.18822839 |
| H | 1.46983029 | -4.07537079 | -0.77262103 |
| H | -4.55038807 | -5.84990359 | 1.64034182 |
| H | -6.35476072 | -4.18115269 | 1.83044088 |
| H | -3.69419012 | -1.13963617 | 0.39202757 |
| H | 0.70575916 | -7.37569561 | -1.44272243 |
| H | -1.06942488 | -7.14561256 | -1.35394672 |
| H | -0.03951556 | -5.90867207 | -2.15047598 |
| H | -2.04437481 | -8.29213045 | 2.23985340 |
| H | -0.78196393 | -8.04326884 | 0.99614485 |
| H | -0.85332648 | -6.96741938 | 2.42480502 |

Electronic energy: -16361.83795890
Zero-point correction: 0.800549
Sum of electronic and zero-point Energies: -16361.037410
Sum of electronic and thermal Energies: -16360.985120
Sum of electronic and thermal Enthalpies: -16360.984176
Sum of electronic and thermal Free Energies: -16361.122520

Lowest frequency:
A  21.0667

Ligand energies:
E(lig1+lig2) -2523.62427019
E(lig1+lig2:Pyr_4) -992.52154410
E(lig1) -1261.80676266
E(lig1:Pyr_2) -496.25916876
E(lig2) -1261.80676521
E(lig2:Pyr_2) -496.25916140
BSSE  0.00406434

Geometry parameters for saturating H atoms at pyridines:

| r   | phi  | tau  |
|-----|------|------|
| Lig1+Lig2 Pyr1 | 1.0843 | 117.84 | 179.30 |
| Pyr2 | 1.0845 | 117.83 | 179.26 |
| Pyr3 | 1.0845 | 117.83 | 179.19 |
| Pyr4 | 1.0843 | 117.83 | 179.33 |
| Lig1 Pyr1 | 1.0843 | 117.88 | 179.22 |
| Pyr2 | 1.0844 | 117.86 | 179.46 |
| Lig2 Pyr3 | 1.0844 | 117.86 | 179.38 |
| Pyr4 | 1.0843 | 117.89 | 179.35 |

=================================================================
Number of atoms: 51
Point group: C1

C  2.94653844 -0.96025602 -0.06538408
C  1.72187328 -0.31417045  0.23659785
C  0.52083151 -1.11450281  0.38540261
C  0.61290025 -2.52687445  0.28059431
C  1.87450666 -3.14775388  0.01569670
C  3.00114191 -2.39408248 -0.18033500
C -0.73706612 -0.55086113  0.63434619
C -1.87207812 -1.33445195  0.78588349
C -1.76298482 -2.73739140  0.69726593
C -0.54591666 -3.31434176  0.44165411
C  4.10570533 -0.18525498 -0.25251949
C  4.06725694  1.18230232 -0.12860238
C  2.8645893  1.84207781  0.19183001
C  1.71848024  1.08343989  0.36042371
C -3.16944494 -0.72306271  1.04206531
C  2.80560940  3.1109485  0.34072568
O  1.92160247 -4.51166514 -0.02753058
C  2.32562002 -5.10061163  1.20451525
O  4.21863977 -2.91114776 -0.43977958
C  4.3468655  -3.97646368 -1.38097938
N -3.44297869  0.47290156  0.47943939
C -4.58573953  1.15295481  0.66257238
C -5.56878058  0.62659768  1.45322760
C -5.34782754 -0.61785305  2.04285810
C -4.15500602 -1.28732102  1.83957821
C  3.94562728  4.06153583  0.62408177
C  3.83393608  5.43705085  0.74837192
C  2.58849458  6.02707912  0.59276821
C  1.50964290  5.19934853  0.32648441
N  1.60744517  3.88453401  0.20245457
H -0.81277710  0.52964131  0.75295718
H -2.64957936 -3.36349235  0.79078631
H -0.46022560 -4.39496842  0.34152680
H  5.03558273 -0.68984846 -0.50684128
H  4.97868752  1.75336787 -0.30191381
H  0.80148643  1.61621476  0.60543852
H  2.34116718 -6.18373607  1.04973640
H  3.32964928 -4.75731250  1.49550105
H  1.61168666 -4.85655364  2.00607545
H  5.36285615 -3.90833881 -1.77631362
H  4.19854533 -4.95503882 -0.91047542
H  3.62409713 -3.85436468 -2.19965286
H -4.66789861  2.10085444  0.14935327
H -6.49503166  1.17319776  1.60399086
H -6.11248408 -1.06154181  2.67843404
H -3.96438900 -2.24144281  2.32483273
H  4.91173018  3.58002560  0.76695940
H  4.71349342  6.04083703  0.97139239
H  2.45441282  7.10381867  0.68036866
H  0.51581157  5.62380371  0.20532168
H -2.75266666  0.86603827 -0.14795320

Electronic energy: -1262.25494565
Zero-point correction= 0.410123
Sum of electronic and zero-point Energies= -1261.844823
Sum of electronic and thermal Energies= -1261.820589
Sum of electronic and thermal Enthalpies= -1261.819645
Sum of electronic and thermal Free Energies= -1261.899402

Lowest frequency:
A  29.9441

Ligand energies:
E(lig)                 -1261.81015106
E(lig:Pyr_2)            -496.25692989

Geometry parameters for saturating H atoms at pyridines:

| Lig | Pyr1 | r    | phi  | tau    |
|-----|------|------|------|--------|
|     |      | 1.0838 | 118.49 | -179.19 |
| Pyr2| 1.0860 | 117.24 | -179.95 |

(2b)2-tw

Number of atoms: 102
Point group: C1

2  1
C  4.28037164 -0.71168065  1.35710501
C  3.07829214 -0.41099916  0.67125063
C  3.10635457  0.51210027 -0.44521462
C  4.34662549  1.06324802 -0.85466063
C  5.54879075  0.71967837 -0.15537293
C  5.51919280 -0.11256334  0.93233994
C  1.95305694  0.88059145 -1.14906808
C  2.00047199  1.74568531 -2.23006440
C  3.23814357  2.28906831 -2.62612737
C  4.38364541  1.95095851 -1.95035034
C  4.25081079 -1.60175344  2.44860191
C  3.07317583 -2.18383666  2.85701814
C  1.86940072 -1.88538409  2.19268599
C  1.89488170 -1.01749754  1.11635511
C  0.77502922  2.08306284 -2.94932905
C  0.57726948 -2.44680218  2.62782365
O  6.72285844  1.24629076 -0.60539597
C  7.46589091  0.35193989 -1.9309257
C  6.60995993 -0.46231243  1.64332080
C  7.56370134  0.53940736  1.99898632
N -0.15817994  1.12236802 -3.08897961
C -1.33370543  1.31567680 -3.70102500
C -1.64168465  2.53984113 -4.23238066
C -0.69819166  3.56017167 -4.12850578
C  0.50772994  3.33241420 -3.48800894
C  0.43568395  3.77765690  3.00005143
C -0.81922146  4.23923864  3.36798200
C -1.89454449  3.36096122  3.35345601
C -1.66128339  2.05053855  2.98170559
N -0.46091251  1.60211962  2.62970568
H  0.98755033  0.49094887 -0.8375935
H  3.29143198  2.95831568 -3.48457927
H  5.34294541  2.36548701 -2.25560353
H  5.18075860 -1.81559512  2.97135881
H  3.06865314 -2.85620669  3.71557755
H  0.95655499 -0.82607610  0.60038230
H  8.38979238  0.86924002 -1.70531623
| H | 7.70958057 | -0.57389201 | -0.88795716 |
| H | 6.90030458 | 0.10314560  | 2.91079463 |
| H | 8.05007940 | 0.68328131  | 1.21437779 |
| H | 7.06100928 | 1.49379267  | 2.20110951 |
| H | -1.99000840| 0.45517158  | -3.75307282|
| H | -2.59642204| 2.69401654  | -4.72682313|
| H | -0.91169935| 4.54422627  | -4.54290237|
| H | 1.24081110 | 4.12826142  | -3.76863320|
| H | -2.89458593 | -3.68552534 | 3.63320021 |
| H | -2.46909825 | -1.32181741 | 2.97428709 |
| H | 0.07403317 | 0.14853195  | -2.78244945|
| H | -0.07442791 | 0.17019219  | 2.77850719 |
| C | -0.57347672 | -2.46860770 | -2.61128481|
| C | -0.77903601 | 2.10477307  | 2.93002562 |
| N | 0.46351878 | -1.62249387 | -2.61870876|
| C | 1.66465719 | -2.07169778 | -2.96704610|
| C | 1.89990666 | -3.38436330 | -3.32953666|
| C | 0.82581796 | -4.26421474 | -3.33713218|
| C | -0.42987341 | -3.80184621 | -2.97407599|
| C | -0.51405183 | 3.35884408  | 3.45882397 |
| C | 0.69148328  | 3.59392089  | 4.09738798 |
| C | 1.63692290 | 2.57623474  | 4.20903292 |
| C | 1.33120860 | 1.34735637  | 3.68746583 |
| N | 0.15599060 | 1.14697650  | 3.07710678 |
| H | 2.47148154 | -1.34184095 | -2.96428983|
| H | 2.90050491 | -3.70948927 | -3.60662861|
| H | 0.96590868 | -5.30787174 | -3.61644661|
| H | -1.28572494| -4.47490979 | -2.94772864|
| H | -1.24863918 | 4.15240948 | 3.34147901 |
| H | 0.90314244  | 4.58160834  | 4.50401843 |
| H | 2.59141574  | 2.73610436  | 4.70281264 |
| H | 1.98915206 | 0.48853106  | 3.74619780 |
| C | -4.27948220 | -0.72952140 | -1.35449419|
| C | -3.07798563 | -0.42175112 | -0.67075127|
| C | -3.10765972 | 0.50998857  | 0.43847081 |
| C | -4.34886737 | 1.06229275  | 0.84349704 |
| C | -5.55040673 | 0.71136221  | 0.14679260 |
| C | -5.51933117 | -0.12914441 | -0.9349682 |
| C | -1.95500705 | 0.88597119  | 1.13941646 |
| C | -2.00390650 | 1.75949224  | 2.21354348 |
| C | -3.24252993 | 2.30380240  | 2.60534600 |
| C | -4.38743478 | 1.95846372  | 1.93222206 |
| C | -4.24834824 | -1.62783725 | -2.43916313|
| C | -3.06973022 | -2.21122100 | -2.84294338|
| C | -1.86559594 | -1.90588707 | -2.18064337|
| C | -1.89357397 | -1.02990350 | -1.11090923|
| C | -6.72537199 | 1.23945657  | 0.59272360 |
| C | -7.46694808 | 0.35020290  | 1.42420861 |
| C | -6.60939223 | -0.48610238 | -1.64297659|
| C | -7.56490727 | 0.51119994  | -2.00620913|
| O | -0.98837037 | 0.49555574  | 0.83075145 |
| O | -3.29693549 | 2.97963677  | 3.45854693 |
| O | -5.34744107 | 2.37374105  | 2.23421606 |
| O | -5.17787099 | -1.84709647 | -2.96042996|
| O | -3.06399442 | -2.89001116 | -3.69639251|
| O | -0.95565688 | -0.83332158 | -0.59612282|
| O | -8.39173478 | 0.86804105  | 1.69542196 |
| O | -7.70905646 | -0.58016545 | 0.88917341 |
H     -6.90100327   0.10933259   2.33704361
H     -8.05072946   0.14389845  -2.91517948
H     -8.31612197   0.65981119  -1.22267456
H     -7.06388301   1.46487155  -2.21571043

Electronic energy:                                -2524.55083299
Zero-point correction=                                0.820742
Sum of electronic and zero-point Energies=        -2523.730091
Sum of electronic and thermal Energies=           -2523.680244
Sum of electronic and thermal Enthalpies=         -2523.679300
Sum of electronic and thermal Free Energies=      -2523.814869

Lowest frequency:
A           14.0586

Ligand energies:
E(lig1+lig2)           -2523.61809991
E(lig1+lig2:Pyr_4)      -992.49392305
E(lig1)                -1261.81006888
E(lig2)                -1261.81007428
E(lig2:Pyr_2)           -496.25845031
BSSE                       0.00852754

Geometry parameters for saturating H atoms at pyridines:

|   | r    | phi  | tau  |
|---|------|------|------|
| Lig1+Lig2| Pyr1 | 1.0854 | 118.16 | 178.87 |
|     | Pyr2 | 1.0869 | 117.03 | 178.53 |
|     | Pyr3 | 1.0869 | 117.03 | 178.53 |
|     | Pyr4 | 1.0854 | 118.16 | 178.87 |
| Lig1 | Pyr1 | 1.0842 | 118.23 | 179.32 |
|     | Pyr2 | 1.0859 | 117.05 | 179.46 |
| Lig2 | Pyr3 | 1.0859 | 117.05 | 179.46 |
|     | Pyr4 | 1.0842 | 118.23 | 179.32 |

=================================================================
(2b)2-par

Number of atoms: 102
Point group: C1
| Element | X-coordinates | Y-coordinates | Z-coordinates |
|---------|---------------|---------------|---------------|
| C       | 0.96038919    | 4.40838152    | 3.89232925    |
| N       | -4.89567567   | 0.0255862     | -1.47510935   |
| C       | -5.65786655   | -0.80941319   | -2.17396934   |
| C       | -5.32171166   | -1.26658006   | -3.4339777    |
| C       | -4.12812171   | -0.82688117   | -3.99150511   |
| C       | -3.33274697   | 0.05224906    | -3.2743755    |
| C       | 3.20936942    | 0.06169577    | -3.2188738    |
| C       | 4.01794552    | -0.78792915   | -3.95351579   |
| H       | -1.07356438   | 0.56668116    | -1.78343507   |
| H       | -4.68729835   | 2.40646795    | -0.41862536   |
| C       | -3.41905903   | 0.59713980    | -1.78888323   |
| H       | -2.09656575   | 6.46994958    | 2.73370159    |
| H       | -0.49474748   | 6.34367422    | 1.94066199    |
| C       | -1.99143590   | 6.01446408    | 1.00425156    |
| H       | 1.87499118    | 4.61402624    | 4.45721623    |
| H       | 0.21233245    | 5.17879689    | 4.11256975    |
| H       | 0.56289776    | 3.42574611    | 4.18012867    |
| H       | -6.5758508    | -1.13893179   | -1.69498384   |
| H       | -5.9760469    | -1.95191828   | -3.96562245   |
| H       | -3.82511035   | -1.15731889   | -4.98454315   |
| H       | -2.40631103   | 0.43763950    | -3.69709756   |
| H       | 2.30278564    | 0.47951623    | -3.65042194   |
| H       | 3.73257892    | -1.06282315   | -4.96777715   |
| H       | 5.86052294    | -1.93500296   | -3.96550042   |
| H       | 6.40769384    | -1.26186271   | -1.60849287   |
| H       | -4.92639254   | -0.02882863   | 0.41064345    |
| H       | 4.92008997    | 0.03501900    | -0.42159557   |
| C       | 1.48575806    | -2.94590606   | -0.64788190   |
| C       | 0.79636238    | -2.09317216   | 0.2596242     |
| C       | -0.65475736   | -2.06194976   | 0.22015892    |
| C       | -1.33950604   | -2.89453790   | -0.70453202   |
| C       | -0.60814049   | -3.71367675   | -1.62243931   |
| C       | 0.75951961    | -3.72271230   | -1.61581036   |
| C       | -1.42218560   | -1.26271487   | 1.08068695    |
| C       | -2.80781222   | -1.29444738   | 1.05969399    |
| C       | -3.47001390   | -2.16751698   | 0.17408717    |
| C       | -2.74812094   | -2.93945334   | -0.69730943   |
| C       | 2.88997155    | -3.04401406   | -0.58088148   |
| C       | 3.59901450    | -2.29027741   | 0.31748210    |
| C       | 2.94138404    | -1.37634177   | 1.16275759    |
| C       | 1.55985452    | -1.30551836   | 1.13292229    |
| C       | -3.57737801   | -0.39948884   | 1.91776101    |
| C       | 3.74031465    | -0.46770915   | 2.00388842    |
| C       | -1.31416242   | -4.49989285   | -2.48476968   |
| C       | -1.42504721   | -5.85365449   | -2.05068841   |
| O       | 1.50977085    | -4.46810694   | -2.45512940   |
| C       | 1.18628843    | -4.47567418   | -3.84441606   |
| N       | -4.72339097   | 0.10813694    | 1.42284570    |
| C       | -5.52394149   | 0.93449082    | 2.10809850    |
| C       | -5.19487610   | 1.31593117    | 3.38098312    |
| O       | -4.00802598   | 0.83236504    | 3.92910020    |
| C       | -3.20545223   | -0.02853912   | 3.20174970    |
| C       | 3.32211577    | -0.06344969   | 3.26722977    |
| C       | 4.11390948    | 0.81652885    | 3.98703661    |
| C       | 5.30709543    | 1.26020529    | 3.43185748    |
C      5.64616658   0.80620998   2.17137128
N      4.88614253  -0.02801034   1.46933303
H     -0.92865653  -0.57413787   1.76550768
H     -4.55513958  -2.25474702   0.19910033
H     -3.25600596  -3.60800924  -1.39058139
H      3.39891739  -3.73284610  -1.25201930
H      4.68148297  -2.39141208   0.38467270
H      1.06407448  -0.58857269   1.78845448
H     -2.01124064  -6.38246097  -2.80808163
H     -0.43413240  -6.32207348  -1.95853838
H     -1.94488687  -5.90760744  -1.08207062
H      2.12272408  -4.68090449  -4.37274453
H      0.45120618   -5.25111468  -4.08757990
H      0.79601905   -3.49676389  -4.15231862
H     -6.40721316   1.28284828  1.58898149
H     -5.84755005   1.98446116   3.93507275
H     -3.71742873   1.11950030   4.93843131
H     -2.29794228  -0.44337110   3.63425708
H      2.39674771  -0.45356754   3.68916637
H      3.80873540   1.14429206   4.98044732
H      5.96190335   1.94579183   3.96574622
H     -6.56409595   1.13856014   1.69448982

Electronic energy:                                -2524.55855180
Zero-point correction=                                0.824066
Sum of electronic and zero-point Energies=        -2523.734486
Sum of electronic and thermal Energies=           -2523.686091
Sum of electronic and thermal Enthalpies=         -2523.685147
Sum of electronic and thermal Free Energies=      -2523.813121

Lowest frequency:
A           19.1942

Ligand energies:
E(lig1+lig2)           -2523.63088583
E(lig1+lig2:Pyr_4)      -992.49743291
E(lig1)                -1261.80954603
E(lig1:Pyr_2)           -496.25836424
E(lig2)                -1261.80958219
E(lig2:Pyr_2)           -496.25833553
BSSE                       0.01147743

Geometry parameters for saturating H atoms at pyridines:

|          | r   |  phi |  tau |
|----------|-----|------|------|
| Lig1+Lig2 Pyr1 | 1.0872 | 116.93 | 179.34 |
| Pyr2   | 1.0853 | 118.10 | -179.18 |
| Pyr3   | 1.0853 | 118.12 | 179.19 |
| Pyr4   | 1.0872 | 116.92 | -179.32 |
| Lig1   Pyr1 | 1.0856 | 117.13 | 179.58 |
| Pyr2   | 1.0840 | 118.28 | -179.38 |
| Lig2   Pyr3 | 1.0840 | 118.30 | 179.39 |
| Pyr4   | 1.0856 | 117.12 | -179.56 |

=================================================================
12
-----------------------------------------------------------------
Number of atoms:  50
Point group: C2
0   1
C     -4.54944306  -0.68157358  -0.02422179

S98
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -4.5494306| 0.68157358| 0.02422179|
| O    | -5.72436348| -1.37251808| -0.07875838|
| C    | -5.72436348| 1.37251808| 0.07875838|
| C    | -3.31941064| -1.41837885| -0.04346854|
| C    | -2.08109221| -0.72547716| -0.02617642|
| C    | -0.89791293| -1.48040661| -0.05824809|
| C    | -0.90781872| 0.72547716| 0.02617642|
| C    | -3.32456110| 2.82531286| 0.09255927|
| H    | 0.07079315| -0.98382176| -0.05415953|
| C    | -2.18240907| 4.62211088| 0.16504474|
| C    | -3.34237529| -0.13246288|
| C    | -3.1941064| 1.41837885| 0.04346854|
| C    | -3.2456110| 2.82531286| 0.09255927|
| C    | -2.14783875| 3.53423168| 0.10754974|
| C    | -0.90781872| 2.86466816| 0.09016284|
| C    | -0.89791293| 1.48040661| 0.05824809|
| C    | -2.08109221| 0.72547716| 0.02617642|
| C    | -3.31941064| -1.41837885| -0.04346854|
| C    | -2.08109221| -0.72547716| -0.02617642|
| C    | -0.89791293| -1.48040661| -0.05824809|
| C    | -0.90781872| 0.72547716| 0.02617642|
| C    | -3.32456110| 2.82531286| 0.09255927|
| H    | 3.75056205| 5.38471101| -0.26613976|
| H    | 1.77944008| -6.56942911| 0.74920452|
| C    | 3.41947058| -3.07181406| -1.1148198|
| C    | 2.77405510| 4.90722916| 0.20415673|
| C    | 2.58648572| 3.61771283| 0.6745131|
| C    | 1.68208537| -5.55946933| 0.35031853|
| C    | 0.46242647| -4.90375438| 0.39917843|
| C    | 0.36667255| -3.61006254| -0.11289769|
| N    | 1.42451509| -2.98362479| -0.63380922|
| C    | 2.58648572| -3.61771283| -0.6745131|
| C    | 3.75056205| -5.38471101| -0.26613976|
| H    | 1.77944008| -6.56942911| 0.74920452|
| C    | 3.41947058| -3.07181406| -1.1148198|
| C    | 2.77405510| 4.90722916| 0.20415673|
| C    | 2.58648572| 3.61771283| 0.6745131|
| C    | 1.68208537| -5.55946933| 0.35031853|
| C    | 0.36667255| -3.61006254| -0.11289769|
| N    | 1.42451509| -2.98362479| -0.63380922|
| C    | 3.41947058| -3.07181406| -1.1148198|
| C    | 1.77944008| -5.69429111| -0.74920452|
| C    | -6.33551303| -1.56951307| 1.19094690|
| C    | -6.33551303| 1.56951307| -1.19094690|
| H    | -7.26175720| -2.12473254| 1.01476975|
| H    | -5.67877420| -2.15771842| 1.85019658|
| H    | -6.57137458| -0.60780213| 1.66736493|
| H    | -7.26175720| 2.12473254| -1.01476975|
| H    | -5.67877420| 2.15771842| -1.85019658|
| H    | -6.57137458| 0.60780213| -1.66736493|

Electronic energy: \(-1261.81581559\)
Zero-point correction= \(0.394665\)
Sum of electronic and zero-point Energies= \(-1261.421151\)
Sum of electronic and thermal Energies= \(-1261.396496\)
Sum of electronic and thermal Enthalpies= \(-1261.395552\)
Sum of electronic and thermal Free Energies= \(-1261.476889\)

Lowest frequency:
A \(25.1238\)

Ligand energies:

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Electronic energy: \(-1261.81581559\)
Zero-point correction= \(0.394665\)
Sum of electronic and zero-point Energies= \(-1261.421151\)
Sum of electronic and thermal Energies= \(-1261.396496\)
Sum of electronic and thermal Enthalpies= \(-1261.395552\)
Sum of electronic and thermal Free Energies= \(-1261.476889\)

Lowest frequency:
A \(25.1238\)

Ligand energies:
**Geometry parameters for saturating H atoms at pyridines:**

| Lig | Pyr1 | r       | phi     | tau     |
|-----|------|---------|---------|---------|
| Lig | Pyr1 | 1.0860  | 117.29  | -179.95 |
| Pyr2|      | 1.0860  | 117.29  | -179.95 |

Number of atoms: 23
Point group: D2D

Electronic energy: -7415.37982146
Zero-point correction= 0.180585
Sum of electronic and zero-point Energies= -7415.199236
Sum of electronic and thermal Energies= -7415.187446
Sum of electronic and thermal Enthalpies= -7415.186502
Sum of electronic and thermal Free Energies= -7415.238667

Lowest frequency:
E  44.0193

Ligand energies:
E(lig)                  -496.26108590
E(lig:Pyr_2)            -248.13067359
BSSE                       0.00025455

Number of atoms: 23
Point group: C2V
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | 0.00000000 | 0.00000000 | 0.33094818 |
| N    | 0.00000000 | 0.00000000 | 1.39374256 |
| C    | 0.00000000 | 1.17066964 | 2.03593123 |
| C    | 0.00000000 | 1.20306866 | 3.40931231 |
| C    | 0.00000000 | -1.20306866| 3.40931231 |
| C    | 0.00000000 | -1.17066964| 2.03593123 |
| N    | 0.00000000 | 0.00000000 | -1.36958088|
| C    | 1.14487034 | 0.00000000 | -2.04875828|
| C    | 1.19526408 | 0.00000000 | -3.42982316|
| C    | 0.00000000 | 0.00000000 | -4.13541744|
| C    | -1.19526408| 0.00000000 | -3.42982316|
| C    | -1.14487034| 0.00000000 | -2.04875828|
| H    | 0.00000000 | 2.05807087 | 1.41648774 |
| H    | 0.00000000 | 2.15741118 | 3.92890170 |
| H    | 0.00000000 | 0.00000000 | 5.19381392 |
| H    | 0.00000000 | -2.15741118| 3.92890170 |
| H    | 0.00000000 | -2.05807087| 1.41648774 |
| H    | 2.05751580 | 0.00000000 | -1.46067655|
| H    | 2.15449892 | 0.00000000 | -3.94378021|
| H    | 0.00000000 | 0.00000000 | -5.22486811|
| H    | -2.15449892| 0.00000000 | -3.94378021|
| H    | -2.05751580| 0.00000000 | -1.46067655|

Electronic energy: -496.72018194
Zero-point correction= 0.191201
Sum of electronic and zero-point Energies= -496.528980
Sum of electronic and thermal Energies= -496.518573
Sum of electronic and thermal Enthalpies= -496.517629
Sum of electronic and thermal Free Energies= -496.567044

Lowest frequency:
A2  37.0262

Ligand energies:
E(lig)                   -496.24565502
E(lig:Pyr_2)             -248.13170572
BSSE                      0.00097998

Number of atoms: 12
Point group: C2V
Sum of electronic and zero-point Energies=  -7167.116213
Sum of electronic and thermal Energies=  -7167.110334
Sum of electronic and thermal Enthalpies=  -7167.109390
Sum of electronic and thermal Free Energies=  -7167.147306

Lowest frequency:
B1         134.1904

Ligand energies:
E(lig)                  -248.12444332

Number of atoms:  12
Point group: C2V

1   1
H  0.00000000  0.00000000  0.50420527
N  0.00000000  0.00000000 -0.50700120
C  0.00000000  1.17847125 -1.14325757
C  0.00000000  1.20426083 -2.51493567
C  0.00000000  0.00000000 -3.20933531
C  0.00000000 -1.20426083 -2.51493567
C  0.00000000 -1.17847125 -1.14325757
H  0.00000000  2.06468928 -0.52438525
H  0.00000000  2.15839807 -3.03429178
H  0.00000000  0.00000000 -4.29775222
H  0.00000000 -2.15839807 -3.03429178
H  0.00000000 -2.06468928 -0.52438525

Electronic energy:                                 -248.57035438
Zero-point correction=                                0.102738
Sum of electronic and zero-point Energies=         -248.467616
Sum of electronic and thermal Energies=            -248.463247
Sum of electronic and thermal Enthalpies=          -248.462303
Sum of electronic and thermal Free Energies=       -248.494441

Lowest frequency:
B1         392.3641

Ligand energies:
E(lig)                  -248.12372926
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