

Supporting Information

Halogen Bonding Helicates Encompassing Iodonium Cations

*Alan Vanderkooy, Arvind Kumar Gupta, Tamás Földes, Sofia Lindblad, Andreas Orthaber, Imre Pápai, and Máté Erdélyi**

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Author Contributions

A.V. Data curation: Lead; Funding acquisition: Equal; Investigation: Lead; Writing—Original Draft: Lead; Writing—Review & Editing: Equal

A.G. Data curation: Supporting; Visualization: Supporting; Writing—Original Draft: Supporting

T.F. Data curation: Supporting; Formal analysis: Supporting

S.L. Data curation: Supporting; Formal analysis: Supporting

A.O. Formal analysis: Supporting; Visualization: Supporting; Writing—Original Draft: Supporting

I.P. Formal analysis: Supporting; Software: Supporting; Supervision: Supporting; Visualization: Supporting; Writing—Original Draft: Supporting

M.E. Formal analysis: Supporting; Funding acquisition: Lead; Investigation: Supporting; Methodology: Supporting; Project administration: Lead; Resources: Lead; Supervision: Lead; Writing—Original Draft: Supporting; Writing—Review & Editing: Supporting.

Supporting Information

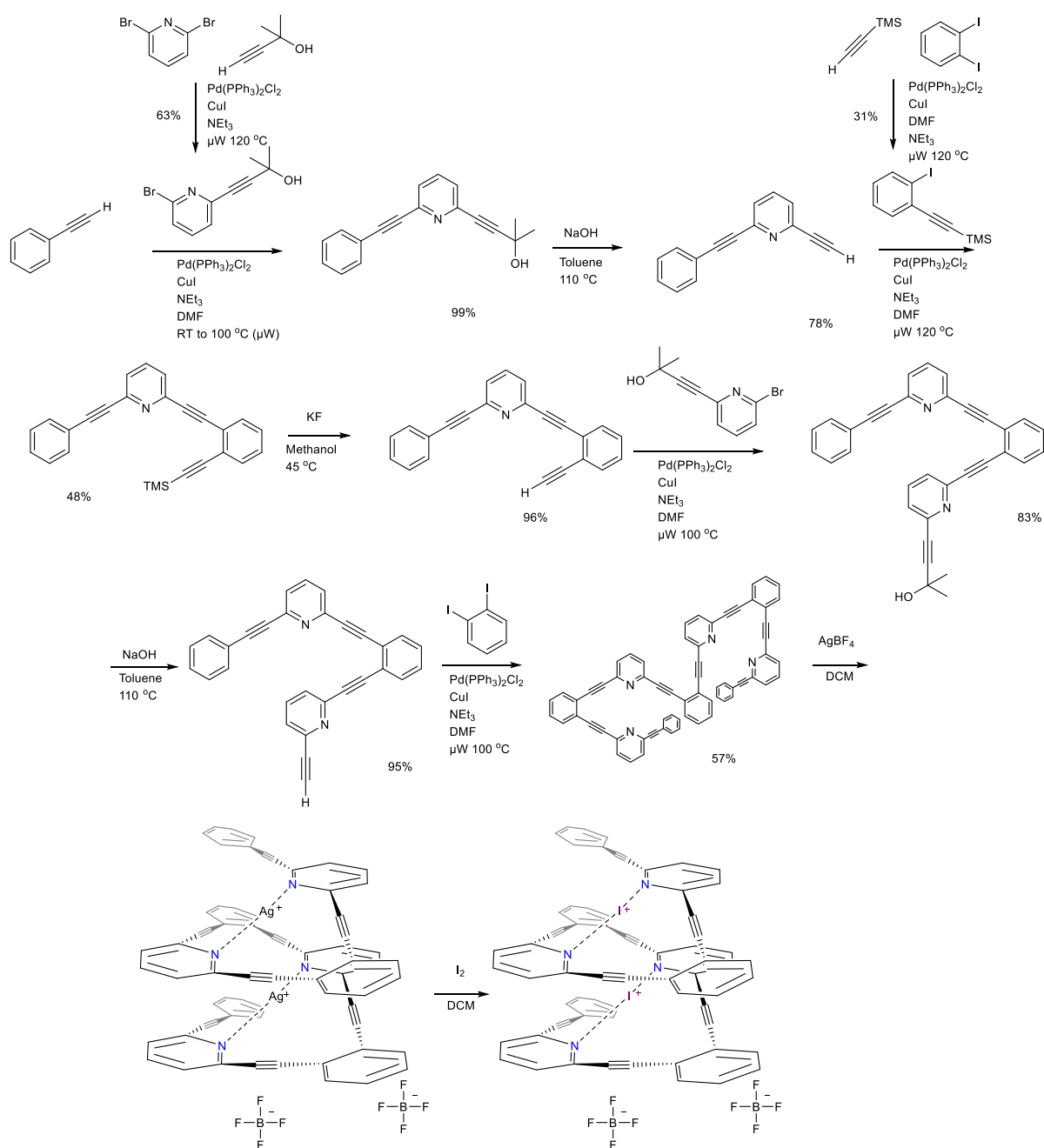
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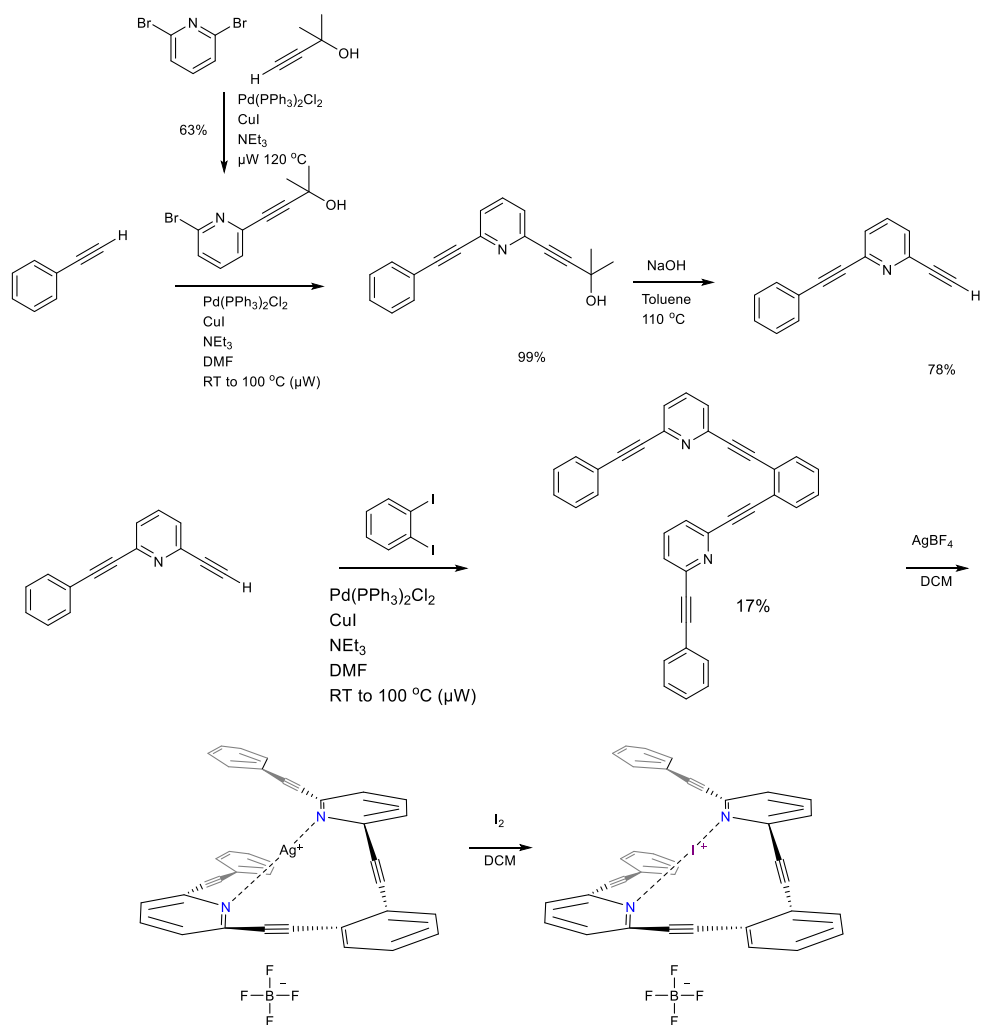
General Information

Unless otherwise indicated, reactions were carried out without effort to exclude air or water. Chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. Pyridine was distilled prior to use. Anhydrous DCM was obtained by distillation over CaH_2 and subsequently stored over 3Å molecular sieves. Anhydrous deuterated DCM (CD_2Cl_2) was obtained by adding 3Å molecular sieves to a bottle of CD_2Cl_2 and storing the bottle in a glove box. Anhydrous hexane was obtained by distillation over sodium metal/benzophenone in the presence of tetraglyme and stored over 3Å molecular sieves. Glassware for the synthesis of N-I-N complexes was dried in an oven prior to use. Microwave heating was performed with a Biotage Initiator+ using fixed hold times. Reactions were monitored by thin layer chromatography, LCMS, GCMS, and/or NMR. Silica gel (40 – 63 μm) was used for column chromatography. Flash chromatography was run on a Biotage IsoleraOne apparatus. IsoElute C18(EC) cartridges were used for reverse-phase filtration. LCMS analysis was performed using a Waters micromass ZQ spectrometer connected to an Agilent 1100 series LC system with a Waters 2700 Sample Manager autosampler equipped with either a InertSustain C18 or a Grace C8 column. A mobile phase gradient of water and acetonitrile with 0.1% formic acid was used (gradient 5% MeCN \rightarrow 95%). GCMS analysis was performed with a Varian Saturn 2200 spectrometer connected to a Varian CP-3800 gas chromatograph with helium as the mobile phase. HRMS data was obtained by Stenhagen Analyslab AB, Gothenburg, Sweden. HRMS samples were eluted through analytical columns (either SunShell C18 or Halo RP Amide C18) before being analysed on a Sciex QStar XL, TOF. UV-vis data were collected using a Cary 100 Bio UV-visible spectrophotometer with a cuvette of 2 mm thickness. FTIR spectra were recorded with a PerkinElmer Spectrum 100 FT-IR Spectrometer equipped with a Universal ATR Sampling Accessory. FTIR spectral features given as follows: wavenumber (cm^{-1}); intensity (s-strong, m-medium, w-weak, br-broad). NMR spectra were recorded on the following spectrometers: 400 MHz Agilent MR400-DD2 with a OneNMR probe, 500 MHz Bruker Avance Neo with a TXO cryogenic probe, and a 600 MHz Bruker Avance Neo with a TCI cryogenic probe. The spectra were processed using MestReNova. Chemical shifts are reported on the δ scale (ppm). ^1H and ^{13}C chemical shifts are referenced to the solvent peaks (CD_2Cl_2 : 5.32 and 53.84) (CDCl_3 7.26 and 77.16). ^{15}N NMR chemical shifts in ^1H - ^{15}N HMBC NMR spectra were referenced relative to the ^1H chemical shift using the Absolute Reference function in MestReNova (MeNO_2 reference scale). NMR spectral features are given in the following order: chemical shift (ppm), multiplicity, number of hydrogens, and coupling constant (J Hz). Multiplicities are denoted as follows; s-singlet, d-doublet, t-triplet, q-quartet, quin-quintet, m-complex multiplet, app - apparent, br- broad.

Synthesis

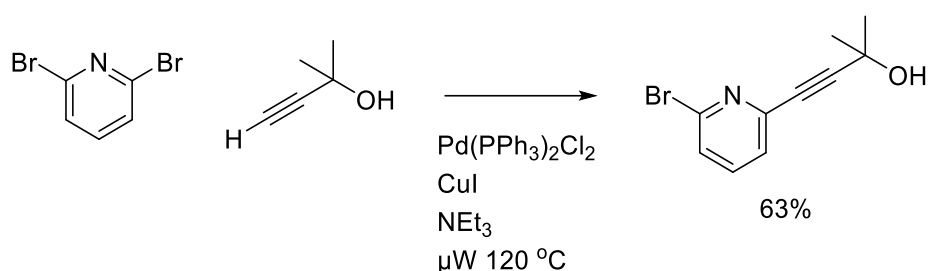


Scheme S1: Synthetic strategy for producing ligand **6**, silver complex **8**, and iodonium complex **4**.



Scheme S2: Synthetic strategy for producing ligand **5**, silver complex **7**, and iodonium complex **3**.

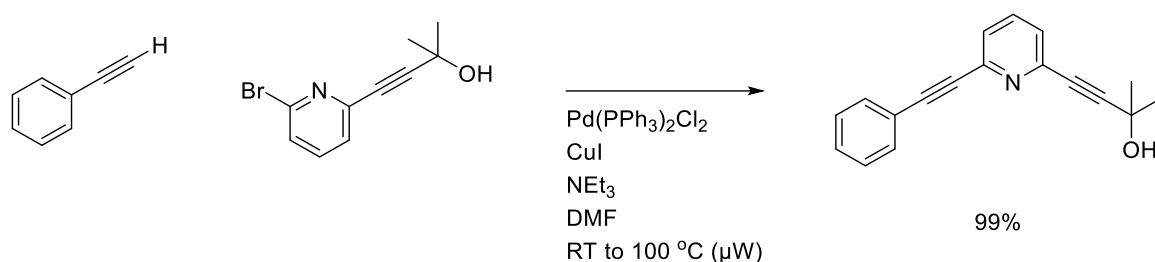
4-(6-bromopyridin-2-yl)-2-methylbut-3-yn-2-ol



The synthesis of 4-(6-bromopyridin-2-yl)-2-methylbut-3-yn-2-ol was achieved through a Sonogashira coupling procedure. 2,6-Dibromopyridine (2.088 g, 8.81 mmol) was dissolved in DMF (2 mL) and triethylamine (9 mL). The solution was degassed with a stream of argon for several minutes. Subsequently, bis(triphenylphosphine) palladium(II) chloride (102 mg, 0.15 mmol, 0.02 equiv), copper(I) iodide (17 mg, 0.09 mmol, 0.01 equiv), and 2-methylbut-3-yn-2-ol (0.85 mL, 8.77 mmol, 1 equiv) were added. The solution was stirred and degassing with a stream of argon was continued for a few minutes. The reaction vial was then sealed and heated under microwave irradiation for 10 minutes at 100 °C. The reaction mixture was diluted with 50 mL of DCM and washed with 50 mL of water. The aqueous phase was extracted 4 times with 10 mL portions of DCM. The combined DCM portions were dried with sodium sulfate, filtered, and evaporated. Thin layer chromatography on silica gel with hexane/ethyl acetate (2:1) gave a retention factor (*R_f*) of 0.21 for the product. The product was isolated by gradient elution in flash chromatography (hexane/EtAc; 5% EtAc → 50% EtAc). 4-(6-Bromopyridin-2-yl)-2-methylbut-3-yn-2-ol was collected as a white solid (1.333 g, 5.55 mmol, 63% yield). Characterization data were consistent with previously reported syntheses.^[1]

¹H NMR (400 MHz, CD₂Cl₂) δ 7.52 (dd, *J* = 7.5, 8.0 Hz, 1H), 7.43 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.37 (dd, *J* = 7.5, 1.0 Hz, 1H), 2.26 (s, 1H), 1.60 (s, 6H). ¹³C NMR (100 MHz, CD₂Cl₂) 143.7, 141.9, 138.9, 128.0, 126.4, 95.6, 80.5, 65.7, 31.3.

2-methyl-4-(6-(phenylethynyl)pyridin-2-yl)but-3-yn-2-ol

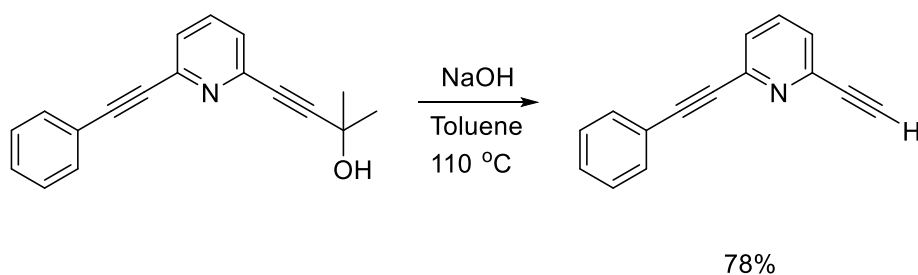


2-Methyl-4-(6-(phenylethynyl)pyridin-2-yl)but-3-yn-2-ol was synthesized via a Sonogashira coupling. 4-(6-bromopyridin-2-yl)-2-methylbut-3-yn-2-ol (1.514 g, 6.31 mmol) was dissolved in anhydrous DMF (2 mL) and triethylamine (8 mL). The solution was degassed with a stream of argon for several minutes. Subsequently, bis(triphenylphosphine) palladium(II) chloride (84 mg, 0.12 mmol, 0.02 equiv), copper(I) iodide (11 mg, 0.06 mmol, 0.01 equiv), and phenylacetylene (0.80 mL, 7.3 mmol, 1.2 equiv) were added. The solution was stirred and degassing with a stream of argon was continued for a few minutes. The reaction vial was seal and allowed to react at room temperature for half an hour before

heating under microwave irradiation for 5 minutes at 100 °C. The reaction was diluted with 75 mL of DCM and washed with 75 mL of water. The aqueous phase was extracted 3 times with 10 mL portions of DCM. The combined DCM portions were dried with sodium sulfate, filtered, and evaporated. Thin layer chromatography on silica gel with hexane/ethyl acetate (2:1) gave a retention factor (R_f) of 0.2 for the product. The product was isolated by gradient elution in flash chromatography on silica stationary phase (hexane/EtAc; 8% EtAc → 66% EtAc). 2-Methyl-4-(6-(phenylethynyl)pyridin-2-yl)but-3-yn-2-ol was collected as a brown oil/resin (1.630 g, 6.24 mmol, 99% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 7.8, 7.8$ Hz, 1H), 7.60 – 7.57 (m, 2H), 7.46 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.38 – 7.35 (m, 4H), 2.10 (s, 1H), 1.64 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 143.5, 136.6, 132.3, 129.3, 128.5, 126.6, 126.3, 122.2, 94.2, 89.9, 88.3, 81.4, 65.7, 31.3. FTIR (cm^{-1}): 3330 (br w), 3059 (w), 2980 (w), 2930 (w), 2220 (w), 1598 (w), 1577 (m), 1557 (s), 1491 (m), 1441 (s), 1374 (m), 1361 (m), 1323 (w), 1267 (m), 1197 (w), 1165 (s), 1084 (w), 1070 (w), 1026 (w), 981 (w), 947 (m), 912 (w), 878 (w), 842 (w), 806 (s), 755 (s), 731 (s), 689 (s), 663 (w). HRMS calculated m/z for $(\text{C}_{19}\text{H}_{15}\text{NO})^+$ $[\text{M}+\text{H}]$ 262.1226; found 262.1233.

2-Ethynyl-6-(phenylethynyl)pyridine

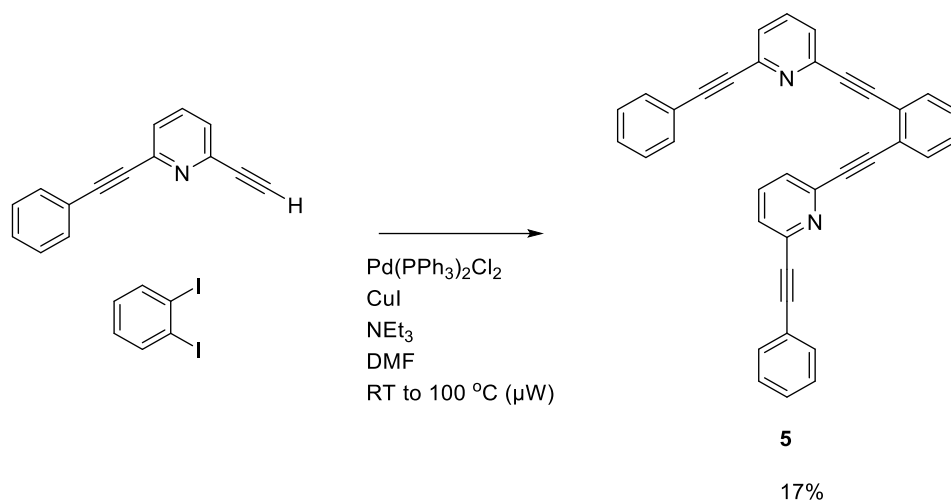


The deprotection of the alkyne to form 2-ethynyl-6-(phenylethynyl)pyridine was guided by a previously reported procedure.^[2] The 2-methyl-4-(6-(phenylethynyl)pyridin-2-yl)but-3-yn-2-ol (1.63 g, 6.24 mmol) starting material was dissolved in toluene (30 mL). Sodium hydroxide (3.1 g, 78 mmol, 12.5 equiv) was ground to a powder with a mortar and pestle and subsequently added to the solution. The reaction was then stirred in a 110 °C oil bath for 40 minutes. The crude reaction mixture was diluted with 75 mL of toluene and washed with 60 mL of water. The aqueous phase was extracted 3 times with 25 mL portions of toluene. The combined organic phases were dried with sodium sulfate, filtered, and evaporated. The product 2-ethynyl-6-(phenylethynyl)pyridine was collected as a brown solid (0.989 g, 4.87 mmol, 78%). Further purification was not necessary for the continuation of the synthetic route, however, the product could be recrystallized from hot hexane to obtain a yellow solid (MP 82 – 84 °C).

^1H NMR (500 MHz, CDCl_3) δ 7.66 (dd, $J = 7.8, 7.8$ Hz, 1H), 7.60 – 7.58 (m, 2H), 7.50 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.43 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.39 – 7.35 (m, 3H), 3.17 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.1, 142.8, 136.6, 132.3, 129.3, 128.6, 127.0, 126.5, 122.2, 89.9, 88.2, 82.4, 77.8. FTIR (solid, cm^{-1}): 3297 (w), 3285 (m), 3058 (w), 2581 (w), 2210 (w), 2110 (w), 1974 (w), 1598 (w), 1574 (m), 1554 (m), 1489 (m), 1440 (s), 1384 (w), 1311 (w), 1274 (w), 1241 (m), 1214 (w), 1167 (m), 1070 (m), 1025 (m), 1000 (w), 986 (m), 925 (m), 908 (w), 819 (m), 808 (s), 758 (s), 733 (m), 691 (s), 668 (m), 652 (s). HRMS calculated m/z for $(\text{C}_{15}\text{H}_{10}\text{N})^+$ $[\text{M}+\text{H}]$ 204.0808; found 204.0815.

Compound 5

1,2-Bis((6-(phenylethynyl)pyridin-2-yl)ethynyl)benzene

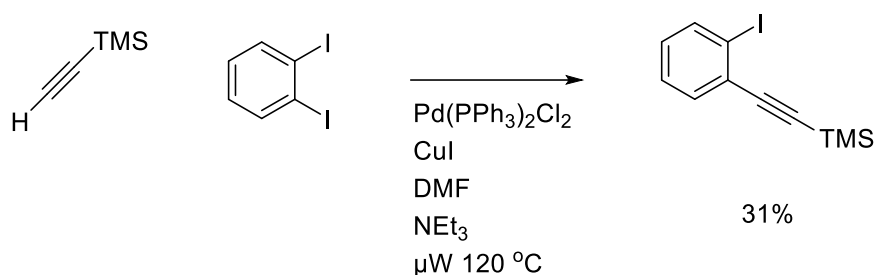


2-Ethynyl-6-(phenylethynyl)pyridine (888 mg, 4.37 mmol) was dissolved in DMF (1.75 mL) and triethylamine (4.5 mL) in a microwave vial. A solution of 1,2-diodobenzene (723 mg, 2.19 mmol, 0.5 equiv) in triethylamine (4 mL) was added. The solution was degassed with a stream of argon for several minutes. Subsequently, bis(triphenylphosphine) palladium(II) chloride (79 mg, 0.11 mmol, 0.03 equiv) and copper(I) iodide (11 mg, 0.06 mmol, 0.01 equiv) were added. The solution was stirred and degassing with a stream of argon was continued for five minutes. The reaction vial was seal and allowed to react at room temperature for twenty minutes before heating under microwave irradiation for 10 minutes at 120 °C. The reaction was diluted with DCM (50 mL) and washed with 50 mL of water. The aqueous phase was extracted 3 times with 15 mL portions of DCM. The combined DCM portions were dried with sodium sulfate, filtered, and evaporated. Thin layer chromatography on silica gel with hexane/ethyl acetate (2:1) gave a retention factor (R_f) of 0.38 for the product. Adding 1% triethylamine to this mobile phase resulted in a retention factor (R_f) of 0.27. The product was isolated by running it through two columns in gradient elution in flash chromatography on silica stationary phase (1st column: hexane/EtAc, 8% EtAc → 55% EtAc; second column hexane/EtAc/1% NEt₃, 8% EtAc → 50% EtAc). After evaporating the product containing fractions, **5** was obtained as a reddish brown solid (179 mg, 0.37 mmol, 17%).*

¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, J = 7.8, 1.1 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.61 – 7.59 (m, 2H), 7.45 (dd, J = 7.8, 1.0 Hz, 1H), 7.40 – 7.37 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 143.9, 143.8, 136.8, 132.2, 132.2, 129.3, 129.1, 128.6, 127.3, 126.6, 125.7, 122.3, 93.0, 89.6, 88.6, 88.3. ¹H- ¹⁵N HMBC NMR (51 MHz, CDCl₃) δ -65.2 FTIR (solid, cm⁻¹): 3054 (w), 2923 (w), 2214 (w), 1598 (w), 1575 (m), 1555 (s), 1490 (m), 1482 (m), 1451 (m), 1439 (s), 1330 (w), 1294 (w), 1278 (w), 1239 (w), 1167(m), 1096 (w), 1084 (w), 1070 (w), 1026 (w), 984 (w), 916 (w), 804 (s), 753 (s), 731 (m), 688 (s). HRMS calculated m/z for (C₃₆H₂₁N₂)⁺ [M+H] 481.1699; found 481.1705.

* Our study was focused on the structure of the helices. The synthesis of **5** has not been optimized. We expect that greater yields are possible.

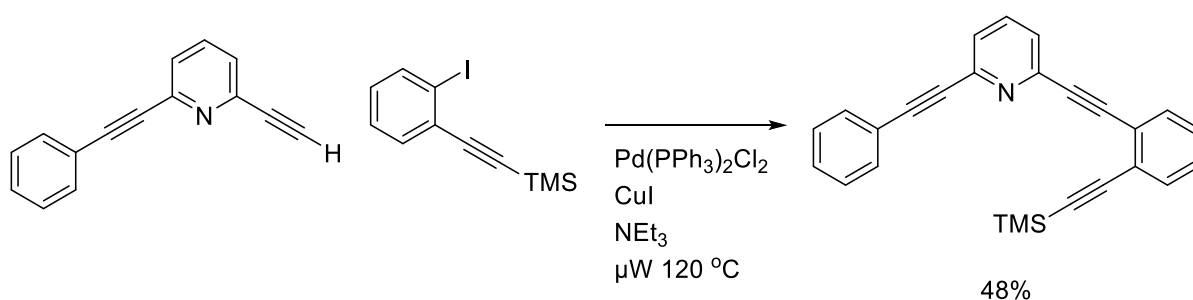
((2-Iodophenyl)ethynyl)trimethylsilane



The synthesis of ((2-iodophenyl)ethynyl)trimethylsilane was guided by previously reported procedures.^[3] 1,2-Diiodobenzene (0.853 g, 2.59 mmol), triethylamine (5 mL), bis(triphenylphosphine) palladium(II) chloride (35 mg, 0.05 mmol, 0.02 equiv), and copper iodide (6 mg, 0.03 mmol, 0.01 equiv) were combined in a vial. The solution was stirred and degassed with a stream of argon for several minutes. Subsequently, (trimethylsilyl)acetylene (0.35 mL, 2.52 mmol, 1 equiv) was added slowly. The reaction vial was sealed and stirred at room temperature for 5 minutes before heating under microwave irradiation for 10 minutes at 120 °C. The crude reaction mixture was diluted with 5 mL of DCM followed by 100 mL of diethyl ether. The solution was washed with 100 mL of water. The aqueous phase was extracted 3 times with 50 mL of diethyl ether. The organic phases were combined, dried with sodium sulfate, filtered, and evaporated. The product was isolated by column chromatography on silica using petroleum spirit (BP 40-60 °C) as eluent ($R_f \sim 0.2$). After evaporation, ((2-iodophenyl)ethynyl)trimethylsilane was collected as a yellow oil (234 mg, 0.78 mmol, 31%). Characterization data were consistent with a previously reported synthesis.^[3b]

$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 7.86 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.47 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.33 – 7.29 (m, 1H), 7.04 – 7.00 (m, 1H), 0.28 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CD_2Cl_2) δ 139.2, 133.1, 130.1, 130.0, 128.3, 106.8, 101.3, 99.2, -0.2.

2-(Phenylethynyl)-6-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine

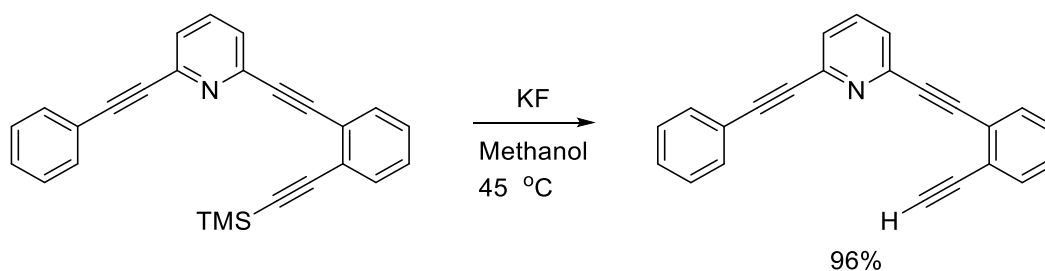


2-(Phenylethynyl)-6-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine was synthesized via a Sonogashira coupling. A 40 °C water bath was used to dissolve 2-ethynyl-6-(phenylethynyl)pyridine (34 mg, 0.17 mmol) and ((2-iodophenyl)ethynyl)trimethylsilane (57 mg, 0.19 mmol, 1.13 equiv) in triethylamine (0.4 mL) which had previously been dried over 3Å molecular sieves. The solution was stirred and degassed with a stream of argon. Bis(triphenylphosphine) palladium(II) chloride (3 mg, 0.004₃ mmol, 0.03 equiv), and copper iodide (0.7 mg, 0.003₇ mmol, 0.02 equiv) were added to the reaction vial. The reaction vial was sealed and heated under microwave irradiation for 10 minutes at 120 °C. The crude reaction mixture was diluted with DCM (40 mL) and washed with water (50 mL). The

aqueous phase was extracted 3 times with 20 mL of DCM. The combined DCM phases were dried using sodium sulfate, filtered, and evaporated. Thin layer chromatography on silica gel with hexane/ethyl acetate (10:1) gave a retention factor (R_f) of 0.3 for the product. The product was isolated by gradient elution in flash chromatography on a silica stationary phase (hexane/EtAc; 0% EtAc \rightarrow 18% EtAc). 2-(Phenylethynyl)-6-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine was isolated as a brown oil/resin (30 mg, 0.08 mmol, 48%).

^1H NMR (500 MHz, CDCl_3) δ 7.68 (dd, $J = 8, 8$ Hz, 1H), 7.62 – 7.59 (m, 3H), 7.52 – 7.47 (m, 3H), 7.39 – 7.36 (m, 3H), 7.32 – 7.30 (m, 2H), 0.28 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.0₄, 144.0₃, 136.4, 132.4, 132.3, 129.2, 128.8, 128.6, 128.4, 126.5, 126.4, 126.4, 125.1, 122.3, 103.3, 99.2, 92.2, 89.7, 88.5, 88.5, 0.2. FTIR (cm^{-1}): 3059 (w), 2957 (w), 2925 (w), 2898 (w), 2853 (w), 2215 (w), 2156 (w), 1598 (w), 1575 (m), 1555 (s), 1491 (m), 1477 (m), 1445 (s), 1437 (s), 1330 (w), 1295 (w), 1248 (m), 1213 (w), 1166 (m), 1097 (w), 1081 (w), 1070 (w), 1037 (w), 1026 (w), 999 (w), 983 (w), 946 (w), 862 (s), 837 (s), 805 (s), 753 (s), 730 (m), 688 (s). HRMS calculated m/z for $(\text{C}_{26}\text{H}_{22}\text{NSi})^+$ $[\text{M}+\text{H}]$ 376.1516; found 376.1525.

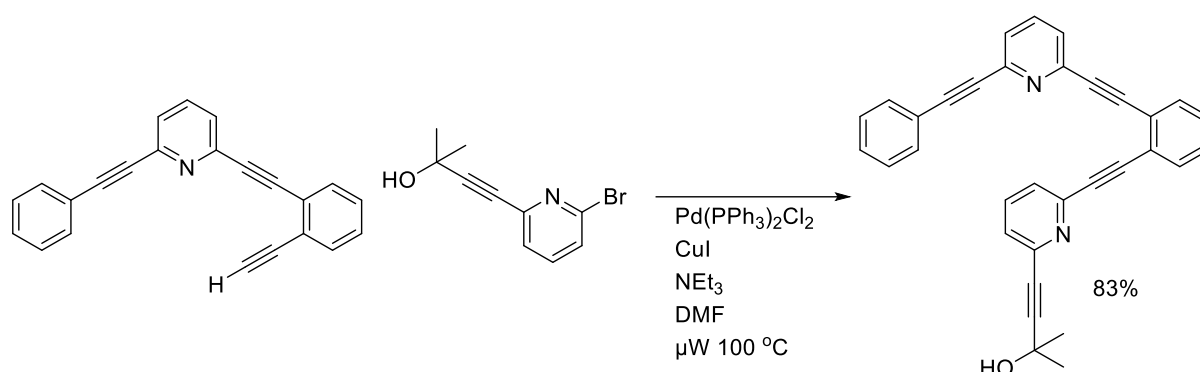
2-((2-Ethynylphenyl)ethynyl)-6-(phenylethynyl)pyridine



2-(Phenylethynyl)-6-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine (0.765 g, 2.04 mmol), potassium fluoride (1.095 g, 18.8 mmol, 9 equiv) and Methanol (60 mL) were combined in a round bottom flask and stirred while heating to 45 °C in water bath for 3 hours. The crude reaction mixture was evaporated to 5 mL, diluted with 80 mL of DCM, and washed with 100 mL of water. The aqueous phase was extracted 3 times with 10 mL of DCM. The combined DCM phases were dried with sodium sulfate, filtered, and evaporated. 2-((2-Ethynylphenyl)ethynyl)-6-(phenylethynyl)pyridine was collected as a brown solid (0.594 g, 96%).

^1H NMR (500 MHz, CDCl_3) δ 7.68 (dd, $J = 7.8, 7.8$ Hz, 1H), 7.63 – 7.60 (m, 3H), 7.56 – 7.54 (m, 1H), 7.52 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.48 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.38 – 7.33 (m, 5H), 3.39 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.0, 143.9, 136.5, 132.8, 132.6, 132.3, 129.2, 128.9, 128.8, 128.5, 126.8, 126.6, 125.2₉, 125.2₅, 122.3, 92.1, 89.8, 88.4, 88.1, 82.1, 81.7. FTIR (solid, cm^{-1}): 3287 (w), 3058 (w), 2923 (w), 2215 (w), 1598 (w), 1575 (m), 1556 (s), 1490 (m), 1478 (m), 1445 (s), 1436 (s), 1329 (w), 1293 (w), 1262 (w), 1235 (w), 1166 (m), 1094 (s), 1094 (s), 1082 (s), 1070 (s), 983 (m), 951 (m), 916 (m), 805 (s), 730 (m), 689 (s). HRMS calculated m/z for $(\text{C}_{23}\text{H}_{13}\text{N})^+$ $[\text{M}+\text{H}]$ 304.1121; found 304.1118.

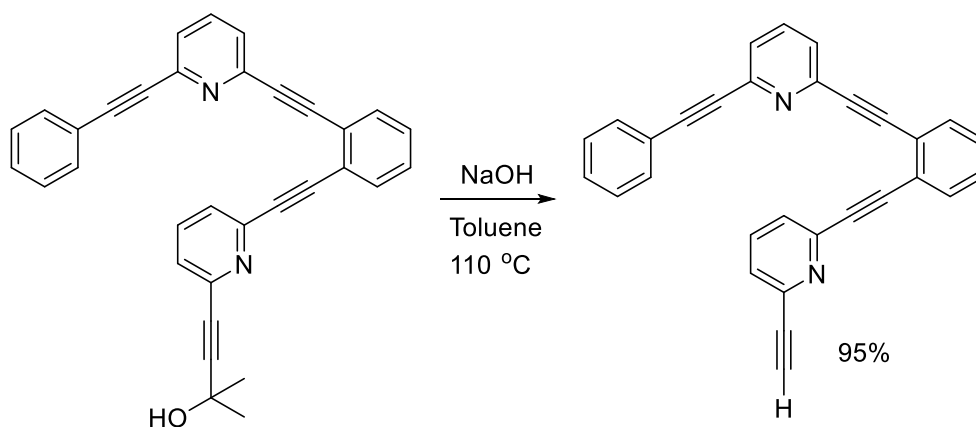
2-Methyl-4-(6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)but-3-yn-2-ol



4-(6-Bromopyridin-2-yl)-2-methylbut-3-yn-2-ol (1.33 g, 5.54 mmol, 2.8 equiv) was dissolved in DMF (2 mL) and combined with 2-((2-ethynylphenyl)ethynyl)-6-(phenylethynyl)pyridine (0.594 g, 1.96 mmol) and triethylamine (4.5 mL). The solution was stirred and degassed with a stream of argon. Bis(triphenylphosphine) palladium(II) chloride (15 mg, 0.02 mmol, 0.01 equiv), and copper iodide (2 mg, 0.01 mmol, 0.005 equiv) were added to the reaction vial. After stirring for another 2 minutes with a degassing stream of argon, the reaction vial was sealed and stirred without heating for 30 minutes. Subsequently, the reaction was heated under microwave irradiation for 10 minutes at 100 °C. The crude reaction mixture was diluted with DCM (70 mL) and washed with water (100 mL). The aqueous phase was extracted 3 times with 10 mL of DCM. The combined DCM phases were dried with sodium sulfate, filtered, and evaporated. 2-Methyl-4-(6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)but-3-yn-2-ol was isolated by reverse phase chromatography on C18-coated silica gel using a water/acetonitrile mobile phase (gradient elution: 33% MeCN → 77% MeCN). The product containing fractions were evaporated to yield 2-methyl-4-(6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)but-3-yn-2-ol as a yellow solid (0.749 g, 1.62 mmol, 83%).

¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.66 – 7.62 (m, 3H), 7.60 – 7.58 (m, 2H), 7.49 (d, *J* = 7.5, 1H), 7.40 – 7.36 (m, 5H), 7.31 (d, *J* = 7.8 Hz, 1H), 2.16 (s, 1H), 1.64 (s, 6H).
¹³C NMR (126 MHz, CDCl₃) δ 143.9, 143.9, 143.8, 143.3, 136.7₃, 136.7₁, 132.3, 132.2₃, 132.2₁, 129.3, 129.0₄, 129.0₂, 128.6, 127.6, 127.0, 126.6, 126.5, 125.7, 125.6, 122.3, 94.0, 92.9, 89.5, 88.7, 88.3, 88.2, 81.6, 65.6, 31.4. FTIR (solid, cm⁻¹): 3313 (w br), 3056 (w), 2979 (w), 2929 (w), 2854 (w), 2215 (w), 1575 (m), 1556 (s), 1490 (m), 1481 (m), 1451 (m), 1440 (s), 1374 (w), 1361 (w), 1327 (w), 1271 (m), 1252 (w), 1237 (w), 1197 (w), 1167 (s), 1084 (w), 1070 (w), 1026 (w), 983 (m), 948 (m), 909 (m), 880 (w), 805 (s), 754 (s), 728 (s), 689 (s). HRMS calculated *m/z* for (C₃₃H₂₃N₂O)⁺ [M+H] 463.1805; found 463.1808.

2-Ethynyl-6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridine

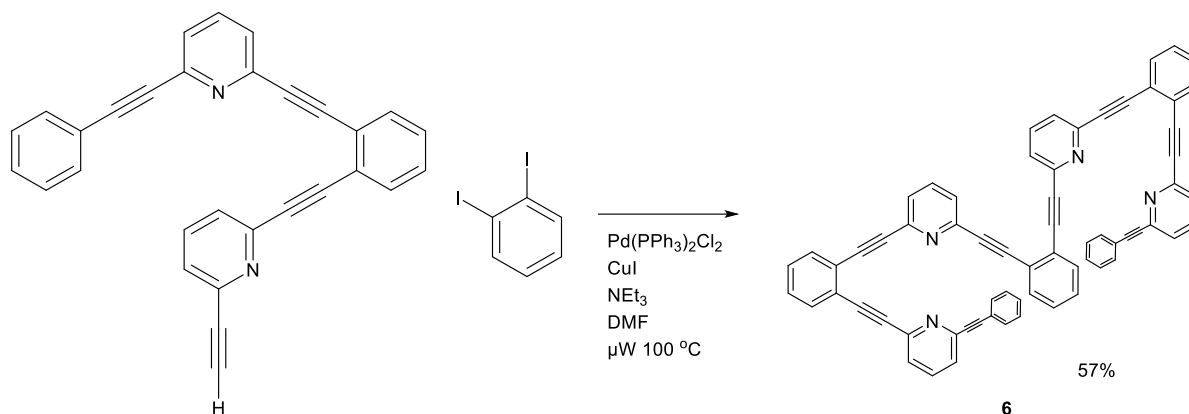


The deprotection of the alkyne was guided by a previously reported procedure.^[2] 2-Methyl-4-(6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)but-3-yn-2-ol (0.749 g, 1.62 mmol) was dissolved in toluene (50 mL). Sodium hydroxide (5.5 g, 137 mmol, 85 equiv) was ground with a mortar and pestle and added to the solution. The reaction was stirred in a 110 °C oil bath for 1 hour and subsequently allowed to cool slowly while continuing to stir. The crude mixture was diluted with toluene (50 mL) and washed with water (50 mL). The aqueous phase was extracted 3 times with 30 mL portions of toluene. The combined organic phases were dried with sodium sulfate, filtered, and evaporated. 2-Ethynyl-6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridine was collected as a lightly yellow solid (623 mg, 95%).

¹H NMR (500 MHz, CD₂Cl₂) δ 7.87 (m, 2H), 7.77 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.72 – 7.66 (m, 3H), 7.63 – 7.60 (m, 2H), 7.52 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.45 – 7.39 (m, 6H), 3.24 (s, 1H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 144.0, 144.0, 143.9, 142.9, 137.2, 132.5, 132.4, 129.6, 129.5₃, 129.4₇, 129.0, 128.2, 127.5, 127.2, 126.9, 125.9, 125.7, 122.5, 93.3, 93.0, 89.3, 88.8, 88.1, 87.9, 82.9, 77.3. FTIR (solid, cm⁻¹): 3285 (w), 3053 (w), 2213 (w), 2107 (w), 1574 (m), 1555 (s), 1490 (m), 1481 (m), 1451 (m), 1439 (s), 1330 (w), 1321 (w), 1294 (w), 1278 (w), 1256 (w), 1238 (w), 1218 (w), 1168 (m), 1082 (w), 1070 (w), 1026 (w), 983 (m), 946 (w), 929 (w), 916 (w), 805 (s), 754 (s), 730 (m), 689 (s), 656 (m). HRMS calculated *m/z* for (C₃₀H₁₇N₂)⁺ [M+H] 405.1386; found 405.1397.

Compound 6

1,2-Bis((6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)ethynyl)benzene

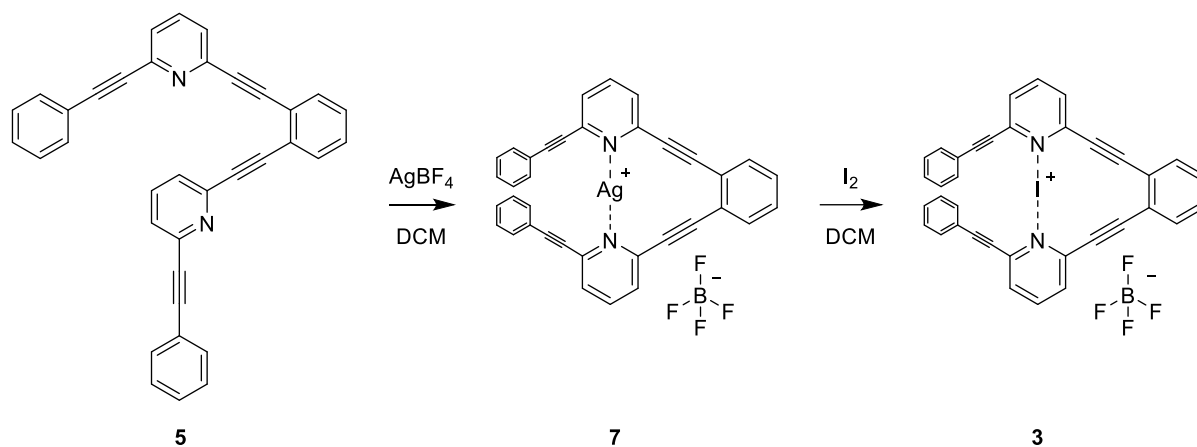


2-Ethynyl-6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridine (0.342 g, 0.846 mmol, 2.2 equiv) was dissolved in DMF (2 mL) and triethylamine (6 mL). 1,2-Diodobenzene (126 mg, 0.382 mmol, 1 equiv) was added as a solution in triethylamine (0.5 mL). The solution was stirred and degassed with a stream of argon for 18 minutes. Bis(triphenylphosphine) palladium(II) chloride (24 mg, 0.03 mmol, 0.08 equiv), and copper iodide (3 mg, 0.02 mmol, 0.05 equiv) were added to the reaction vial. After stirring for another 3 minutes with a degassing stream of argon, the reaction vial was sealed and heated under microwave irradiation for 20 minutes at 100 °C. The reaction mixture was diluted with DCM (50 mL) and washed with water (80 mL). The aqueous phase was extracted three times with 25 mL of DCM. The combined DCM phases were dried with sodium sulfate, filtered, and evaporated. The product was re-dissolved in DCM (20 mL) and precipitated in methanol (500 mL) at room temperature. The precipitate was stored at -20 °C overnight before being separated from the supernatant by filtration. The product (**6**) was re-dissolved in DCM and evaporated to obtain a black solid (192 mg, 0.217 mmol, 57%).

¹H NMR (500 MHz, CDCl₃) δ 7.84 (dd, *J* = 7.8, 1.0 Hz, 2H), 7.76 (dd, *J* = 7.0, 1.9 Hz, 2H), 7.72 – 7.64 (m, 10H), 7.62 – 7.60 (m, 2H), 7.57 – 7.55 (m, 4H), 7.42 – 7.31 (m, 14H). ¹³C NMR (126 MHz, CDCl₃) δ 143.8₀, 143.7₈, 143.7₇, 143.6₉, 136.9, 136.8, 132.3, 132.2, 132.2, 129.2, 129.1, 129.0, 129.0, 128.6, 127.4₀, 127.3₇, 127.2₅, 126.6, 125.8, 125.7₃, 125.7₀, 122.3, 93.4, 93.2, 93.1, 89.5, 88.6, 88.2, 88.0, 87.9. ¹H-¹⁵N HMBC NMR (51 MHz, CDCl₃) δ -64.1, -65.3. FTIR (solid, cm⁻¹): 3055 (w), 2213 (w), 1597 (w), 1574 (m), 1555 (s), 1481 (m), 1450 (m), 1438 (s), 1330 (w), 1295 (w), 1237 (w), 1168 (m), 983 (w), 911 (w), 874 (w), 805 (s), 754 (s), 728 (m), 689 (m). HRMS calculated *m/z* for (C₆₆H₃₅N₄)⁺ [M+H] 883.2856; found 883.2833.

Complex 3

1,2-Bis((6-(phenylethynyl)pyridin-2-yl)ethynyl)benzene iodonium tetrafluoroborate



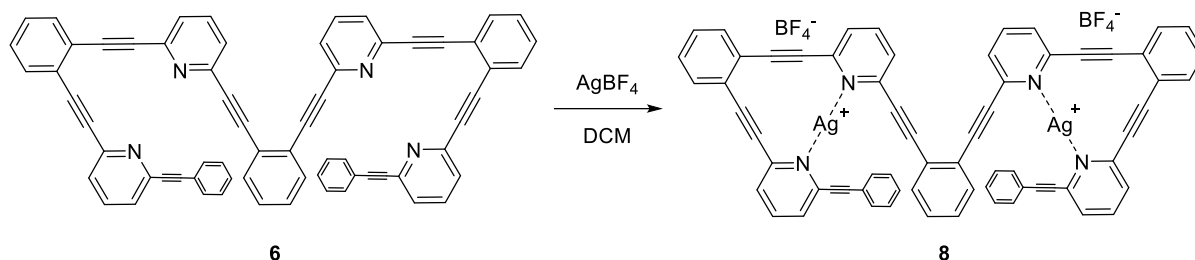
The silver complex **7** was formed by dissolving **5** (9.4 mg, 0.20 mmol, 1.2 equiv) in DCM (3.0 mL) and adding this solution to silver tetrafluoroborate (3.3 mg, 0.17 mmol, 1 equiv). The solution was stirred for 40 minutes at room temperature before filtering through a 0.45 micron PTFE syringe filter. The silver complex **7** was subsequently precipitated by adding hexane (6 mL) while stirring vigorously. The precipitate was centrifuged at 1000 rcf for 10 minutes, and the supernatant was removed. The silver complex **7** dried under high vacuum overnight before being transferred into a glovebox. A solution of iodine (5.2 mg, 0.21 mmol, 1.2 equiv) in deuterated DCM (1 mL, dried over 3Å molecular sieves) was added to the solid silver complex.[†] The solution was stirred for 15 minutes. The precipitated silver iodide was removed by filtration through a syringe filter (0.45 micron, PTFE) to obtain a dark coloured solution containing complex **3**. Crystals for X-ray diffraction were grown by preparing the iodonium complex in anhydrous 1,2-dichloroethane followed by vapour diffusion against dry hexane at -35 °C.

^1H NMR (600 MHz, CD_2Cl_2) δ 8.05 (dd, $J = 7.8, 7.9$ Hz, 2H), 7.80 – 7.79 (m, 2H), 7.77 (d, $J = 7.9$ Hz, 2H), 7.66 (d, $J = 7.8$ Hz, 2H), 7.62 – 7.61 (m, 2H), 7.40 (d, $J = 7.4$ Hz, 4H), 7.24 (t, $J = 7.5$ Hz, 2H), 7.12 (dd, $J = 7.4, 7.5$ Hz, 4H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.8, 143.9, 141.9, 134.6, 132.7, 131.5, 131.0, 129.7, 129.3, 128.8, 124.7, 120.0, 101.3, 98.8, 91.9, 87.7. ^1H - ^{15}N HMBC NMR (61 MHz, CDCl_3) δ - 158.8.

[†] Samples of the helical iodonium complexes for NMR spectroscopy were prepared directly in deuterated DCM by the addition of iodine. We found that the typical hexane precipitation for isolating N-X-N complexes led to less pure samples, presumably due to product decomposition.

Complex **8**

1,2-Bis((6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)ethynyl)benzene bis(silver tetrafluoroborate)[‡]



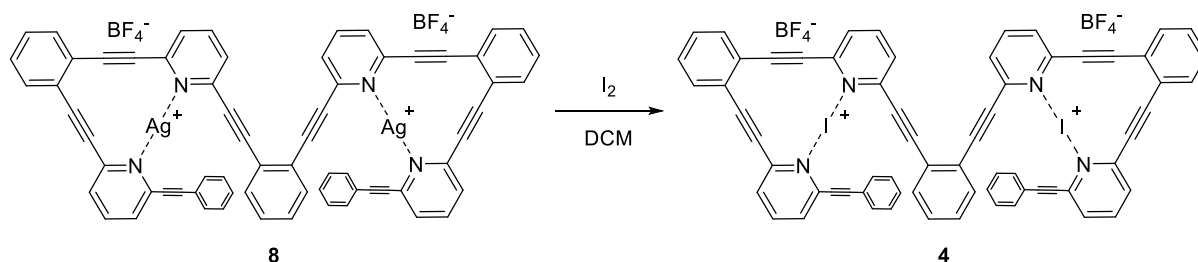
Compound **6** (10.1 mg, 11 μmol) was dissolved in DCM (4.0 mL) and added to silver tetrafluoroborate (4.2 mg, 22 μmol , 2 equiv). The solution was stirred for 30 minutes before being filter through a syringe filter (0.45 microns, PTFE). Hexane (8 mL) was subsequently added to the solution to precipitate the product while stirring vigorously. The solution was centrifuged at 1000 rcf for 12 minutes and the supernatant was removed. The pellet was evaporated under high vacuum overnight to yield complex **8** as a brown solid (13.5 mg, 10.6 μmol 96%). Crystals for X-ray diffraction were grown by vapour diffusion of a CD_2Cl_2 solution of the silver complex against hexane at 4 °C.

^1H NMR (500 MHz, CD_2Cl_2) δ 8.12 – 8.07 (m, 4H), 7.96 (d, J = 7.7 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 7.5 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.35 (d, J = 7.3 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.20 – 7.17 (m, 2H), 7.12 (dd, J = 7.4, 8 Hz, 4H), 7.05 – 7.02 (m, 6H), 6.85 – 6.79 (m, 4H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 144.9, 144.8, 144.1, 143.7, 142.8, 141.7, 133.6, 133.3, 133.1, 132.3, 131.0, 130.9, 130.6, 130.3, 129.4, 129.1, 128.7, 128.3, 128.2, 123.3₃, 123.2₈, 123.0, 119.9, 96.6, 95.1, 93.4, 93.0, 91.7, 91.4, 87.3. ^1H - ^{15}N HMBC NMR (51 MHz, CD_2Cl_2) δ – 122.3, – 122.2. FTIR (solid, cm^{-1}): 3074 (w), 2209 (m), 1581 (m), 1557 (s), 1491 (m), 1449 (m), 1397 (w), 1281 (w), 1243 (m), 1184 (m), 1048 (s), 947 (w), 848 (w), 805 (s), 754 (s), 732 (m), 689 (s).

[‡] We suspected that the multivalent silver **8** would require slow formation in order to properly fold into a helix, however, both slow and fast introduction of silver tetrafluoroborate led to helical X-ray crystal structures and the same NMR spectra (Slow addition of silver salt was performed by adding 2.2 equivalents of silver tetrafluoroborate dissolved in acetonitrile by syringe pump over 16 hours to a DCM solution of the ligand while stirring. Fast introduction of silver was achieved by adding a DCM solution of ligand to solid silver tetrafluoroborate powder and stirring for half an hour.)

Complex 4

1,2-Bis((6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)ethynyl)benzene bis(iodonium tetrafluoroborate)



Complex **8** (8.5 mg, 6.7 μmol) was evaporated under high vacuum and transferred into a glove box. The silver complex was dissolved in CD_2Cl_2 (0.85 mL), which had been dried previously over 3Å molecular sieves. The solution was filtered through a 0.45 μm syringe filter (PTFE). A solution of iodine in CD_2Cl_2 was added (0.25 mL, 8.4 mg/mL, 2.1 mg, 8.3 μmol , 1.2 equiv) under stirring.⁵ The stirring was continued for 15 minutes before the solution was filtered through a 0.45 μm syringe filter (PTFE) to remove the silver iodide precipitate. After one day, a second addition of iodine solution in CD_2Cl_2 was added (0.15 mL, 15 mg/mL, 2.3 mg, 9.1 μmol , 1.4 equiv).^{**} The solution was again stirred for 15 minutes before filtration to remove the yellow precipitate. A brown solution containing complex **4** was obtained and characterized by NMR spectroscopy. Single crystals for X-ray diffraction analysis were grown from a 1,2-dichloroethane solution via vapour diffusion against hexane at -35°C .

¹H NMR (500 MHz, CD_2Cl_2) δ 8.15 (dd, $J = 7.8, 7.8$ Hz, 2H), 7.87 (dd, $J = 7.8, 7.8$ Hz, 2H), 7.73 – 7.71 (m, 4H), 7.66 (d, $J = 7.8$ Hz, 2H), 7.61 (d, $J = 7.8$ Hz, 2H), 7.38 – 7.35 (m, 4H), 7.28 – 7.25 (m, 6H), 7.21 – 7.18 (m, 4H), 7.06 (m, 4H), 6.98 – 6.94 (m, 2H), 6.91 – 6.88 (m, 2H). ¹³C NMR (126 MHz, CD_2Cl_2) δ 144.0₂, 143.9₈, 143.9₆, 143.4, 142.9, 142.3, 134.4, 134.3, 133.3, 132.4, 131.2, 131.0, 130.9, 130.5, 130.0, 129.9, 129.2, 128.9, 128.8, 124.3, 124.2, 123.3, 119.8, 100.8, 99.5, 99.3, 99.2, 92.0, 91.3, 90.6, 87.3. ¹H- ¹⁵N HMBC NMR (51 MHz, CD_2Cl_2) δ – 153.9, – 159.7.

⁵ Samples of the helical iodonium complexes for NMR spectroscopy were prepared directly in deuterated DCM by the addition of iodine. We found that the typical hexane precipitation for isolating N-X-N complexes led to less pure samples, presumably due to product decomposition.

^{**} The addition of iodine could be performed via multiple methods to obtain the iodonium product, however, the two separate additions of iodine produced the best NMR spectra. Other successful methods include a single, quick addition of an iodine solution to either a solution of the silver complex or to an undissolved, solid sample of the silver complex, as well as slow addition of an iodine solution by syringe pump over two hours to a solution of the silver complex.

1-Dimensional NOESY NMR

One-dimensional NOESY NMR data indicate proximity of distinct pyridyl groups in ligand **6** and in complexes **4** and **8**. The ^1H , ^{13}C , and ^{15}N NMR for these complexes indicate symmetry across the central aryl groups. Therefore, these complexes must contain two instances of pyridyl groups which are close to each other in space. This is only possible to achieve in the helical conformations.

Two-dimensional NOESY NMR spectroscopy was also performed on complexes **4** and **8**, however, the crosspeaks associated with protons on overlying aryl groups were too weak to rely on. Therefore, the more sensitive one-dimensional NOE experiments were conducted in order to analyze the complexes.

The ^1H NMR spectrum of ligand **6** in CD_2Cl_2 contained too much spectral overlap to be applicable for NOESY analysis. Therefore CDCl_3 was used as solvent for NOESY analysis of ligand **6**.

Silver complex **8**: ^1H 1D-NOESY NMR (500 MHz, CD_2Cl_2)

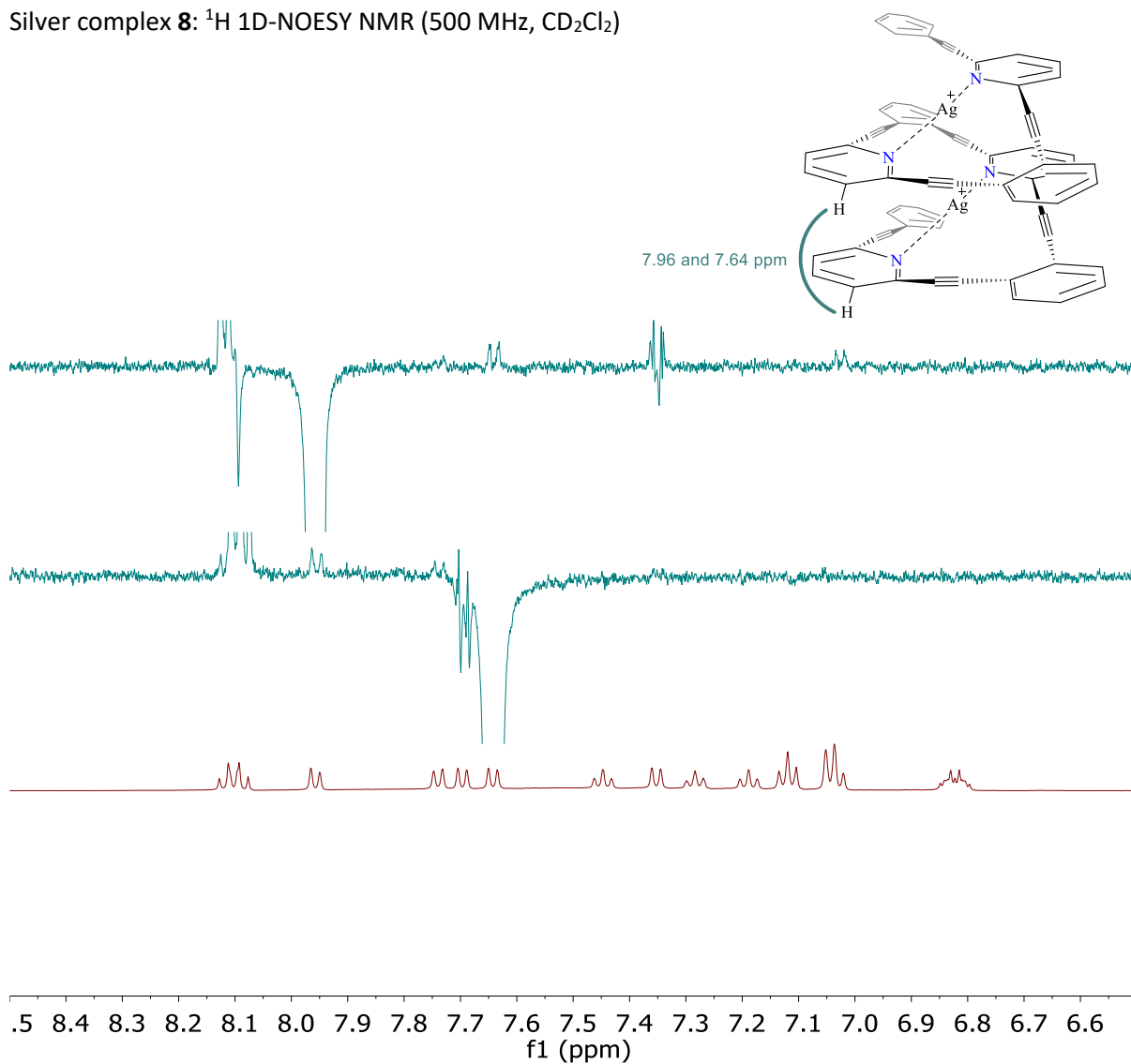


Figure S1: *Top and middle:* one-dimensional selective gradient NOESY ^1H NMR spectrum (pulse sequence selnogpzs.2) of complex **8** collected with a mixing time of 1.2 seconds and selective excitation at 7.96 (top) and 7.64 ppm (middle). *Bottom:* ^1H NMR spectrum of the same complex for comparison.

Iodonium complex **4**: ^1H 1D-NOESY NMR (600 MHz, CD_2Cl_2)

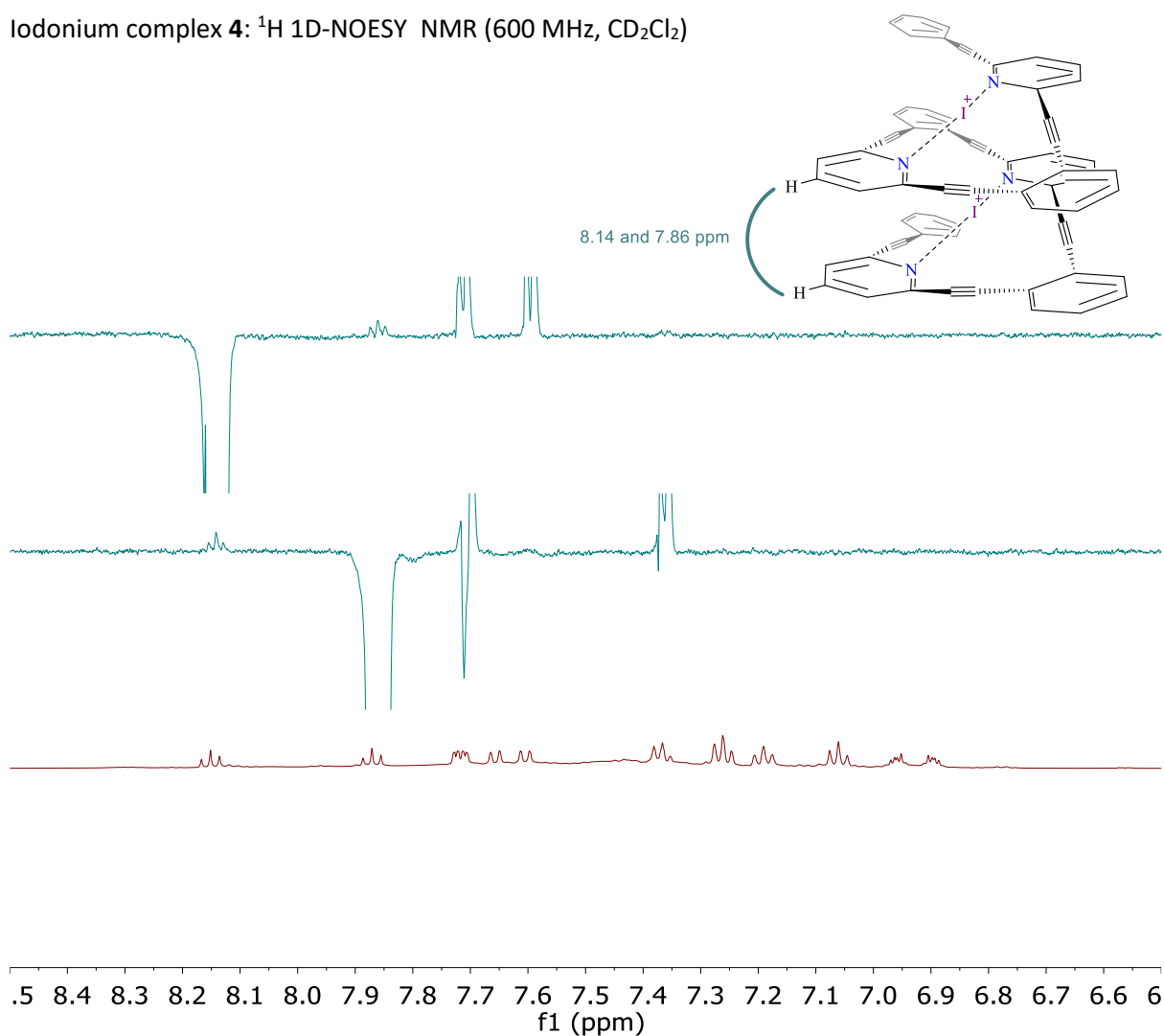


Figure S2: *Top and Middle:* One-dimensional selective gradient NOESY ^1H NMR spectra (pulse sequence selnogpzs.2) of complex **4** collected with a mixing time of 1.2 seconds. Selective excitations were at 8.14 (top) and 7.86 ppm (middle). *Bottom:* ^1H NMR spectrum of the same complex for comparison.

Ligand **6**: ^1H 1D-NOESY NMR (500 MHz, CD_3Cl)

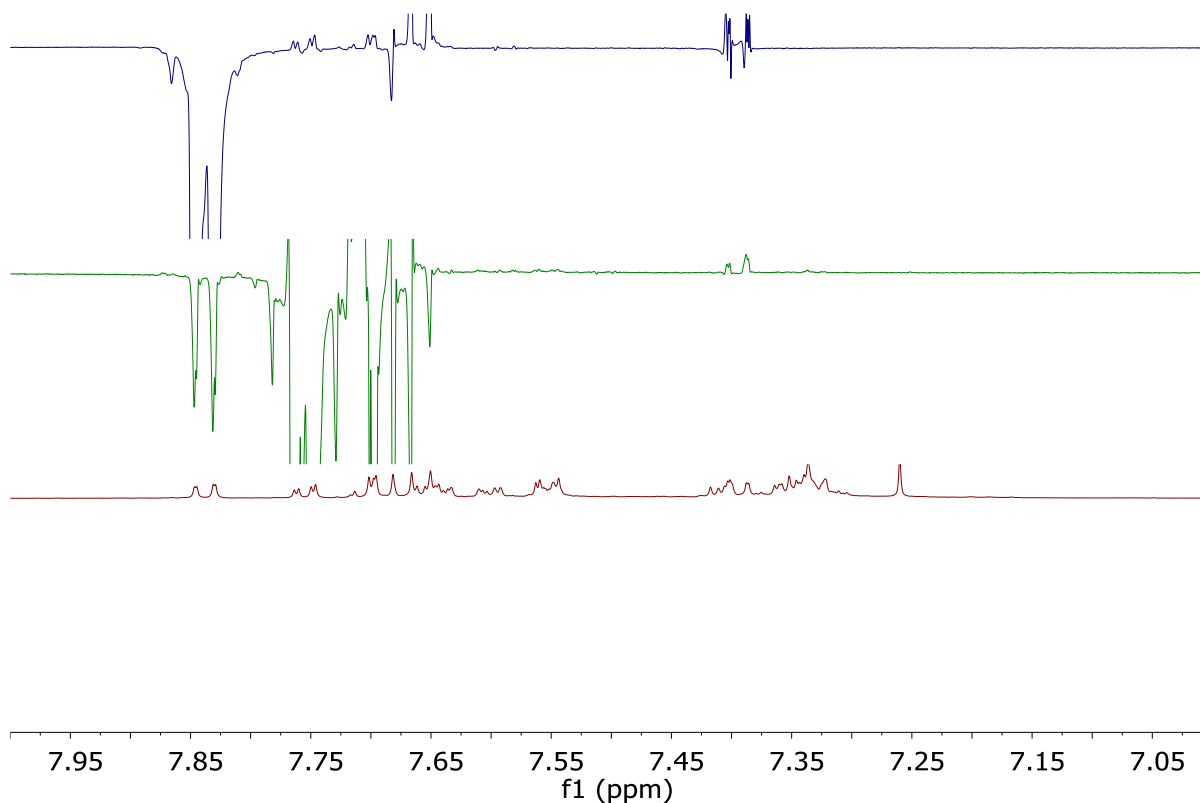
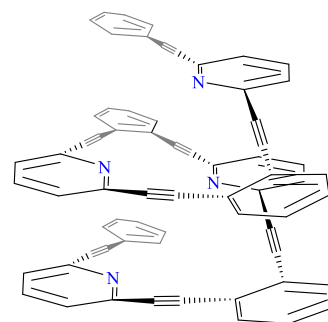
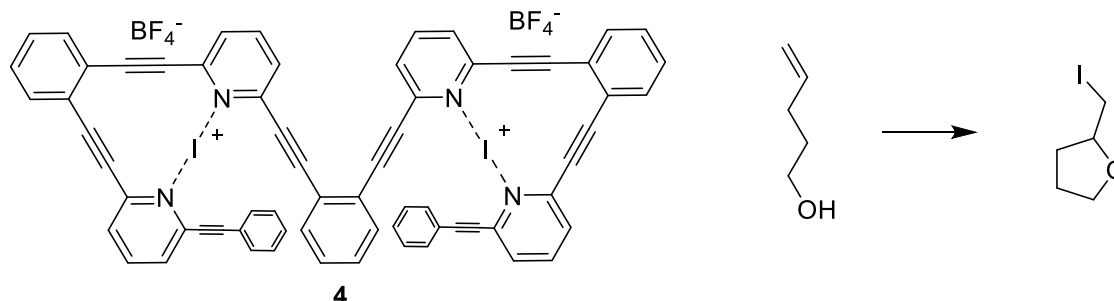


Figure S3: *Top and Middle:* One-dimensional selective gradient NOESY ^1H NMR spectra (pulse sequence selnoggps.2) of ligand **6** collected with a mixing time of 1.2 seconds. Selective excitations were at 7.84 (top) and 7.76 ppm (middle). *Bottom:* ^1H NMR spectrum of the ligand **6** for comparison.

^1H - ^{15}N HMBC NMR shows that the two distinct pyridines in **6** have resonances at 7.40, 7.67, 7.84 and 7.68, 7.71, 7.76 ppm respectively (see the NMR appendix). The correlations between 7.84 and 7.76 ppm and between 7.76 and 7.40 ppm are evidence for a helix conformation.

Halocyclization Reactions

Reaction of Complex **4** with 4-penten-1-ol



The halocyclization of 4-penten-1-ol to form the 2-(iodomethyl)tetrahydrofuran was performed by adding a solution of 4-penten-1-ol in CDCl_3 (0.1 mL, 14 mg/mL, 16 μmol), to an NMR sample of complex **4** in CD_2Cl_2 which had been derived by starting from 8 mg of the silver complex **8** (6 μmol).

^1H NMR (400 MHz, CD_2Cl_2)

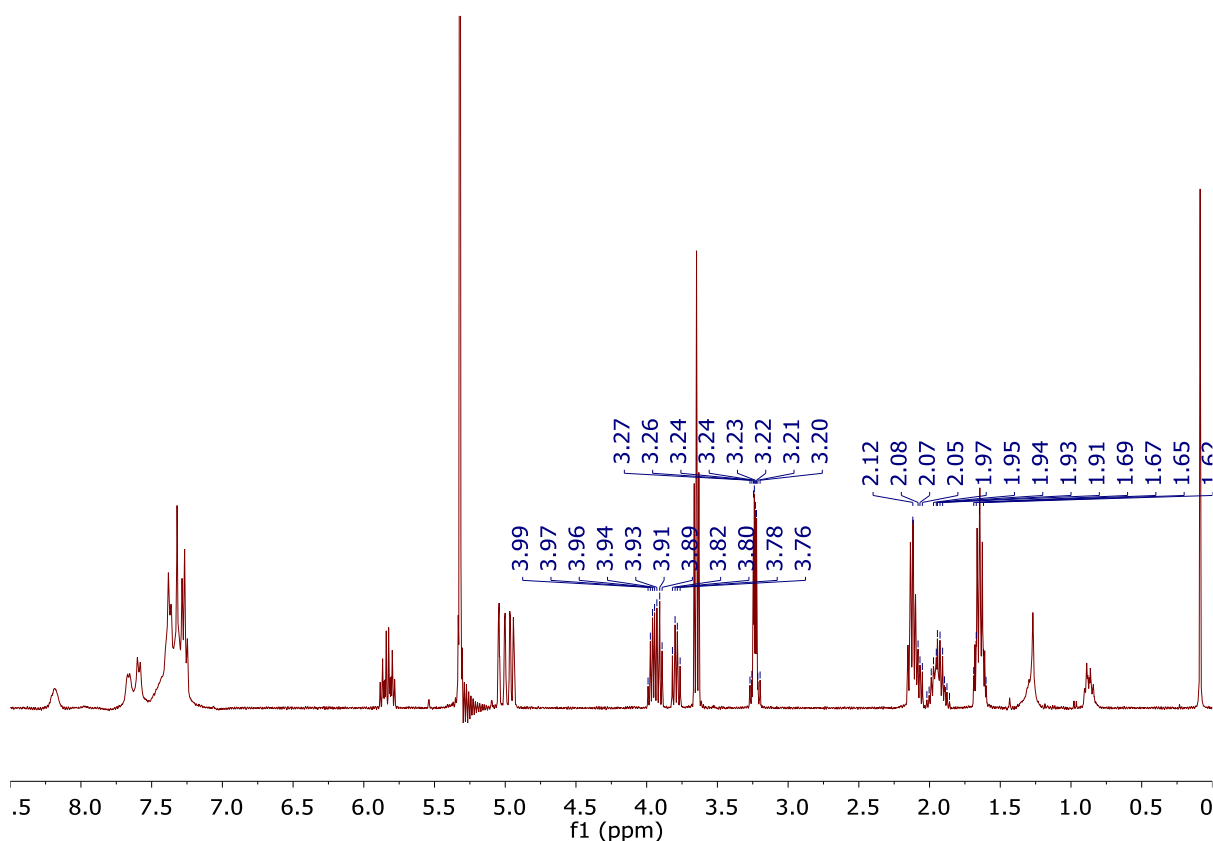


Figure S4: ^1H NMR spectrum of crude reaction mixture of 4-penten-1-ol mixed with complex **4**. The peaks corresponding to the product 2-(iodomethyl)tetrahydrofuran have been labelled and are consistent with those previously reported in the literature.^[4] It should be noted that some peaks are not visible due to overlap of the multiplets with the spectrum of the unreacted 4-penten-1-ol starting material (shown below).

4-penten-1-ol ^1H NMR (400 MHz CDCl_3)

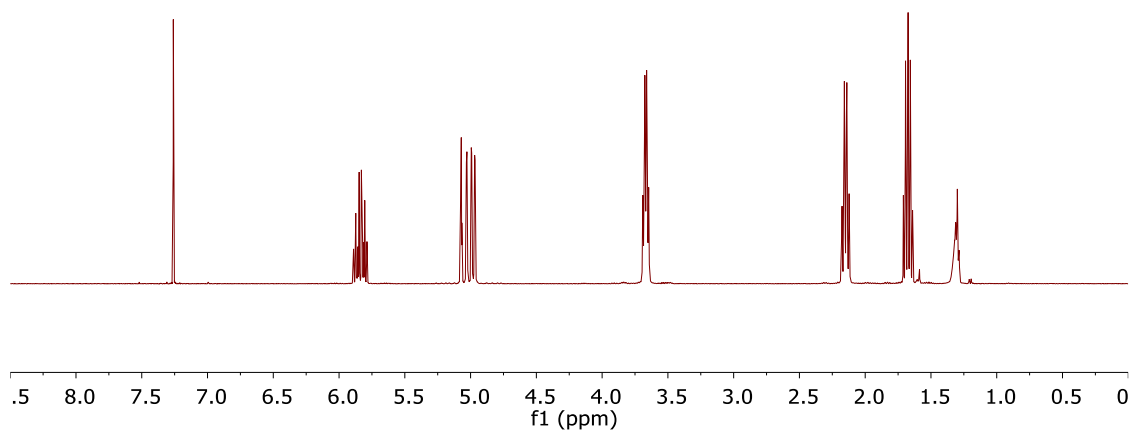
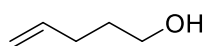


Figure S5: ^1H NMR spectrum of 4-penten-1-ol in CDCl_3

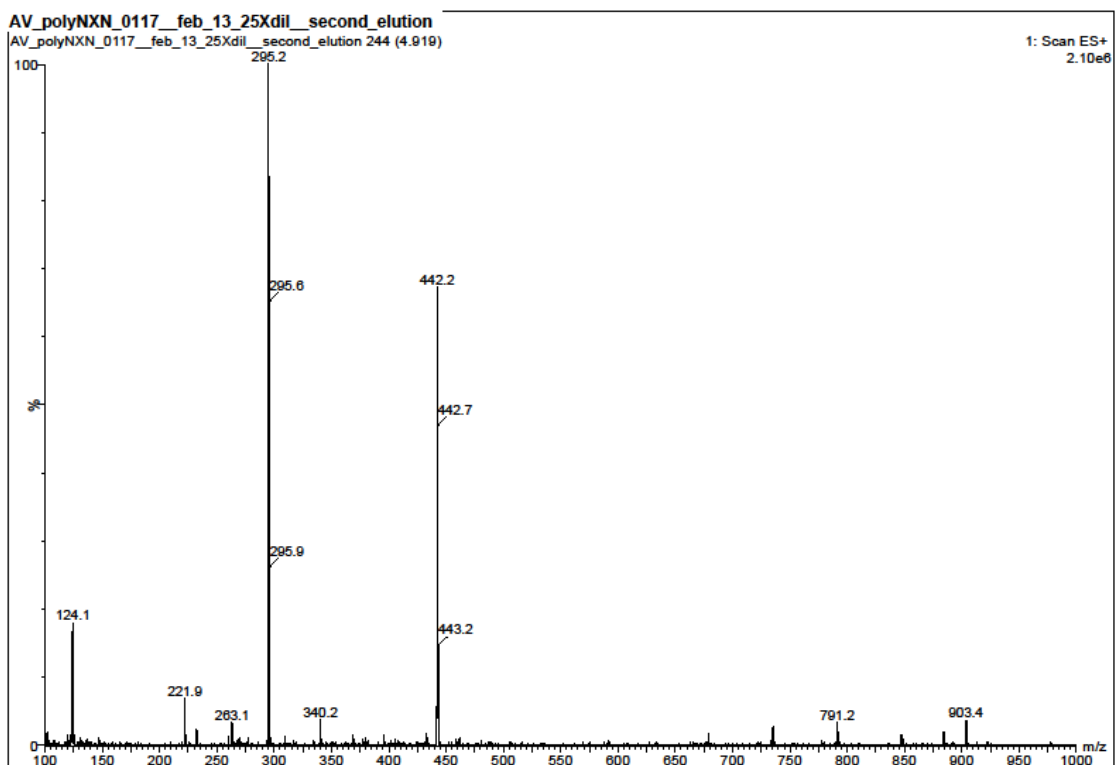
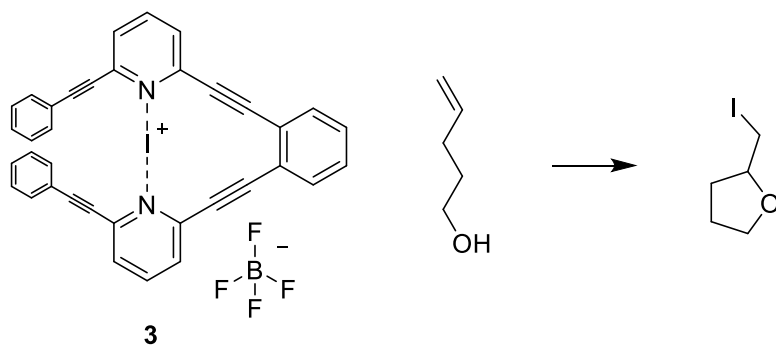


Figure S6: Positive ionization mode electrospray mass spectrum obtained from LCMS of the crude reaction mixture of complex **4** with 4-penten-1-ol. The peaks corresponding to the protonated ligand **6** $[\text{M}+3\text{H}]^{3+}$ and $[\text{M}+2\text{H}]^{2+}$ can be seen at 295 and 442 m/z , which indicates survival of the ligand through the reaction.

Reaction of Complex **3** with 4-penten-1-ol



The halocyclization of 4-penten-1-ol to form the 2-(iodomethyl)tetrahydrofuran was performed by adding of a solution of 4-penten-1-ol in CD_2Cl_2 (0.2 mL, 7.8 mg/mL, 19 μmol), to an NMR sample of complex **3** in CD_2Cl_2 which had been derived by starting from 3 mg of silver tetrafluoroborate (15 μmol).

^1H NMR (400 MHz, CD_2Cl_2)

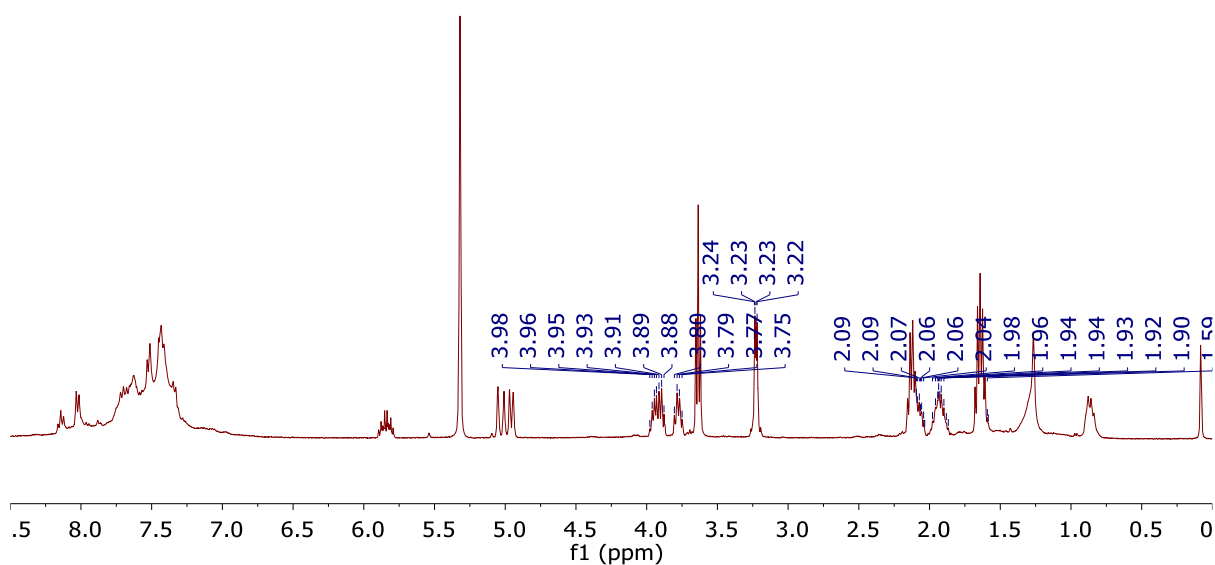


Figure S7: ^1H NMR spectrum of crude reaction mixture from mixing 4-penten-1-ol with complex **3**. The peaks corresponding to the product 2-(iodomethyl)tetrahydrofuran have been labelled and are consistent with those previously reported in the literature.^[4] It should be noted that some peaks are not visible due to overlap of the multiplets with the spectrum of the unreacted 4-penten-1-ol starting material (Figure S5).

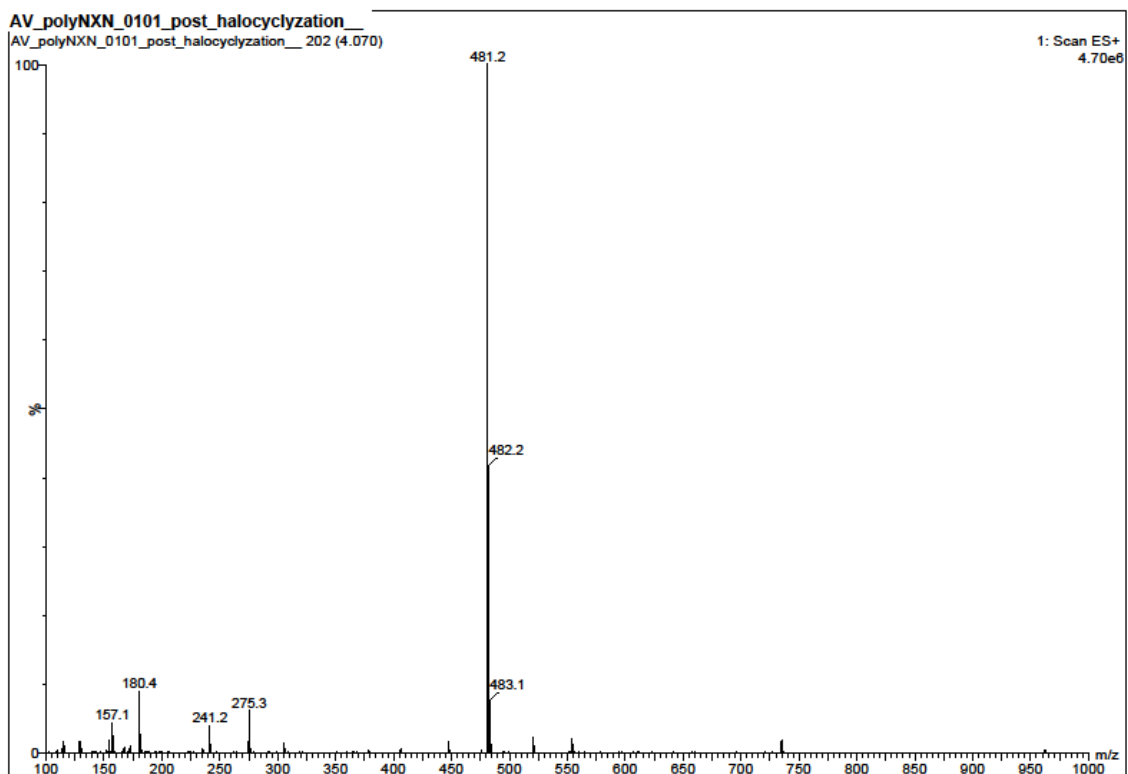


Figure S8: Positive ionization mode electrospray mass spectrum obtained from LCMS of the crude reaction mixture of complex **3** with 4-penten-1-ol. The peak corresponding to the protonated ligand **5** $[M+H]^+$ can be seen at 481 m/z, which indicates survival of the ligand through the reaction.

X-ray Crystallography

Single crystals of **3**, **4**, and **8** have been collected on a Bruker D8 APEX-II equipped with a CCD camera using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystals were mounted on a fibre loop and fixated using Fomblin oil. Data reduction was performed with SAINT,^[5] Absorption corrections for the area detector were performed using SADABS.^[6] Structures were solved by direct methods and refined by least squares methods on F2 using the SHELX and the OLEX2 suit of programs.^[7] The data collections for **3**, **8** and **4** (M-enantiomer, CCDC = 1905846) were collected at 150(2) K, while **4** (P-enantiomer, CCDC = 1905848) was collected at 100(2) K. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained in geometrical positions to their parent atoms. Some of the solvent molecules in **3** (DCE) and **8** (DCM) showed diffuse scattering and could not be modelled satisfactorily. Their impact were treated as diffuse contribution to the overall scattering without specific atom positions and masked by the Olex2 program similar to the SQUEEZE/PLATON.^[8]

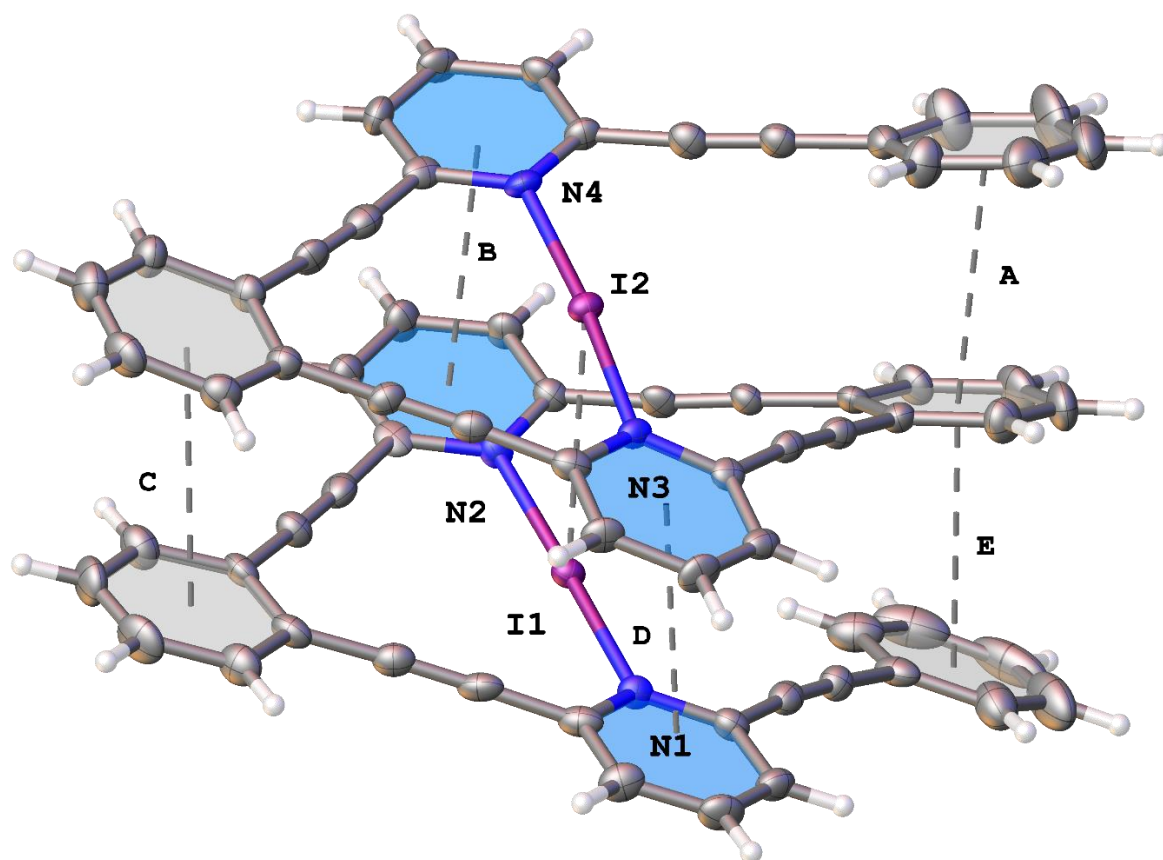
Compound **4** crystallized by self-sorting in the enantiomeric pair of space groups P6(1) and P6(5) as the P- and M-enantiomer, respectively. The absolute structures were determined from anomalous scattering using the Flack parameter. The M-enantiomer was measured at 150 K and gave a Flack value of 0.006(3) based on 6599 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$, while the P-enantiomer (measured at 100 K) computed a Flack value of 0.003(6) from 6074 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$.^[9]

Compound	3 6(C ₂ H ₄ Cl ₂) (racemic)	4 4(C ₂ H ₄ Cl ₂) (M-enantiomer)	4 4(C ₂ H ₄ Cl ₂) (P-enantiomer)	8 2.5(CH ₂ Cl ₂) (racemic)
CCDC	1905847	1905846	1905848	1905845
Chemical formula	C ₁₉₂ H ₁₂₄ B ₅ Cl ₁₂ F ₂₀ I ₅ N ₁₀	C ₇₄ H ₅₀ B ₂ Cl ₈ F ₈ I ₂ N ₄	C ₇₄ H ₅₀ B ₂ Cl ₈ F ₈ I ₂ N ₄	C _{68.5} H ₃₉ Ag ₂ B ₂ Cl ₅ F ₈ N ₄
Formula weight	4064.95	1706.20	1706.20	1484.64
Temperature (K)	150(2)	150(2)	100(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Hexagonal	Hexagonal	Monoclinic
Space group	P-1	P6(5)	P6(1)	P2(1)/c
a (Å); α (°)	18.86(15); 95.53(3)	16.3587(10); 90	16.3052(8); 90	33.79(3); 90
b (Å); β (°)	20.208(17); 92.748(3)	16.3587(10); 90	16.3052(8); 90	13.088(12); 98.34(2)
c (Å); γ (°)	29.203(2); 115.796(3)	45.847(3); 120	45.535(12); 120	30.496(3); 90
V (Å ³); Z	9923.9(14); 2	10625.3(15); 6	13550.3(5); 6	13345(2); 8
ρ (calc.) mg m ⁻³	1.360	1.600	1.621	1.478
μ (Mo K α) mm ⁻¹	1.014	1.258	1.275	1.605
2 θ _{max} (°)	50	50	50	50
R(int)	0.1176	0.0489	0.0835	0.0815
Completeness to θ	100%	100%	100%	99.9%
Data / param.	35925 / 2197	14303 / 883	14101 / 883	26918 / 1612
GOF	1.013	1.185	1.074	1.076
R1 [F > 4 σ (F)]	0.0601	0.0325	0.0338	0.0804
wR2 (all data)	0.1501	0.0710	0.0678	0.1878
Max. peak/hole (e.Å ⁻³)	1.445 / -1.384	0.802 / -0.732	0.716 / -0.658	1.554 / -1.126
Flack Parameter		0.006(3)	0.003(6)	

Table S1. Crystallographic data for **3**, **4**, and **8**

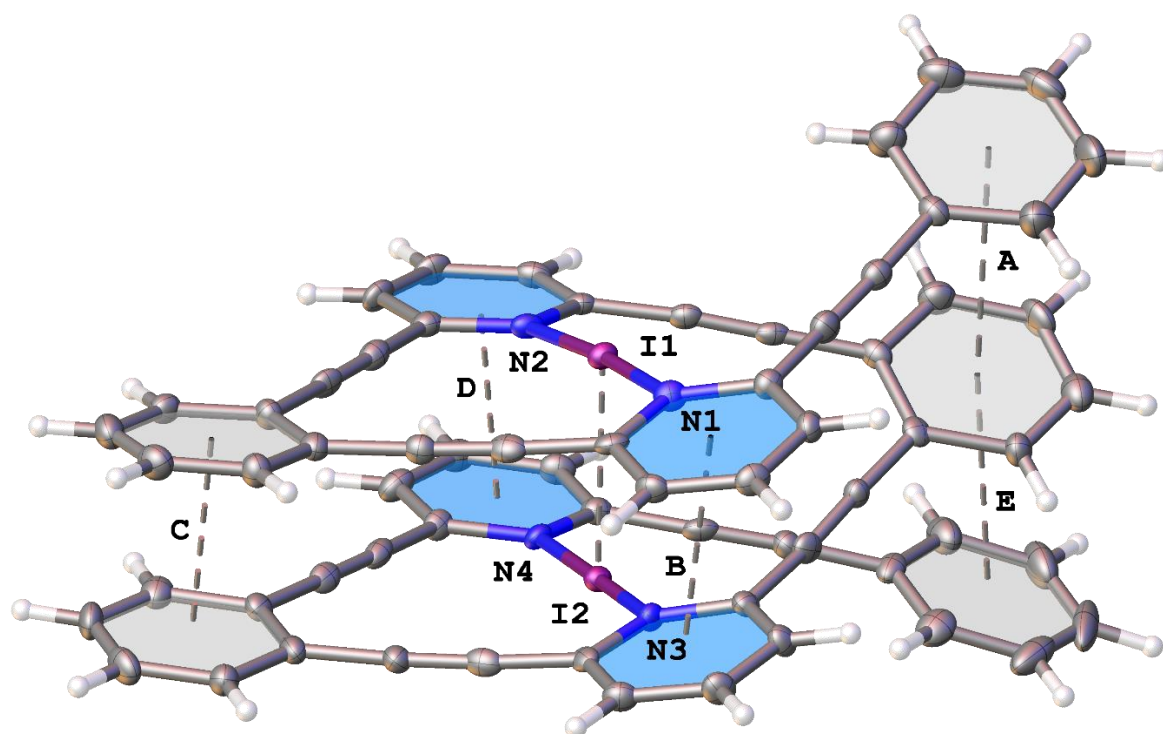
Measured Angles and Distances in the Crystal Structures

Complex 4: (M-helix, measured at 150K)



	Centroid to centroid distance	Angle between ring planes
A:	3.840(4) Å	4.2(3)
B:	3.740(3) Å	5.26(19)
C:	3.913(4) Å	6.8(2)
D:	3.665(3) Å	7.05(19)
E:	3.914(4) Å	18.7(2)
N3-I2-N4: 2.253(5) Å, 2.302(5) Å, 175.37(18)		
N1-I1-N2: 2.260(5) Å, 2.255(5) Å, 176.77(17)		
I1-I2: 3.887(1) Å		

Complex 4: (P-helix, measured at 100K)



	Centroid to centroid distance	Angle between ring planes
A:	3.809(4) Å	4.5(2)
B:	3.720(3) Å	5.40(18)
C:	3.905(3) Å	7.18(19)
D:	3.641(3) Å	6.97(18)
E:	3.911(4) Å	19.2(2)

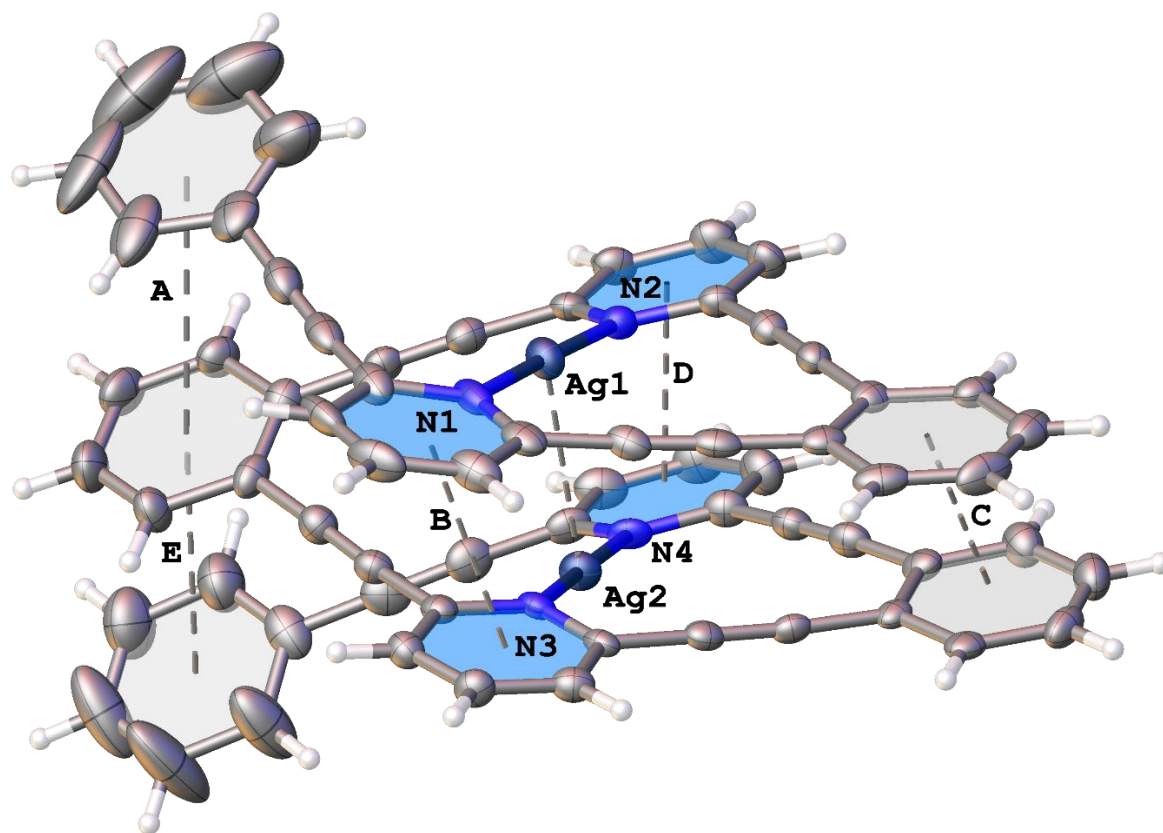
N1-I1-N2: 2.302(5) Å, 2.248(5) Å, 175.26(18)

N3-I2-N4:: 2.249(5) Å, 2.258(5) Å, 177.03(17)

I1-I2: 3.8621(7) Å

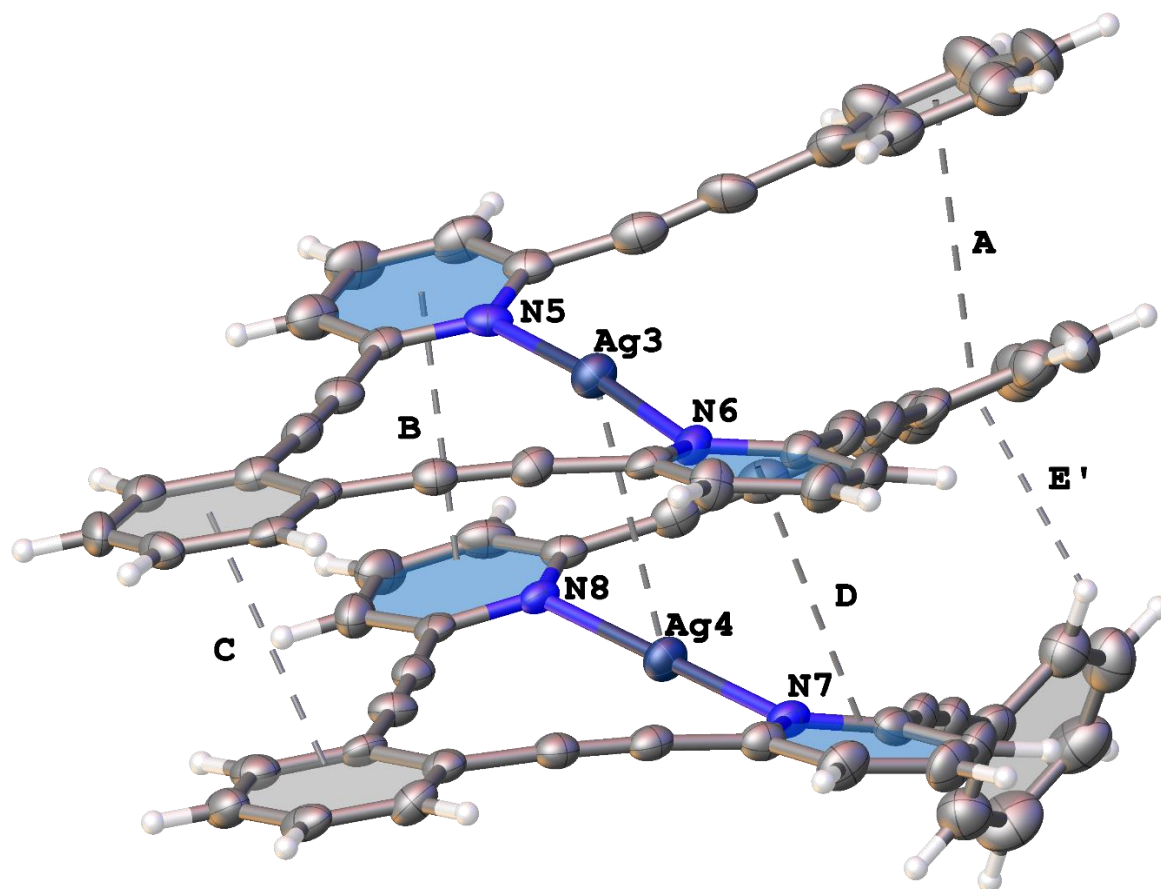
Silver Complex 8:

Helix A

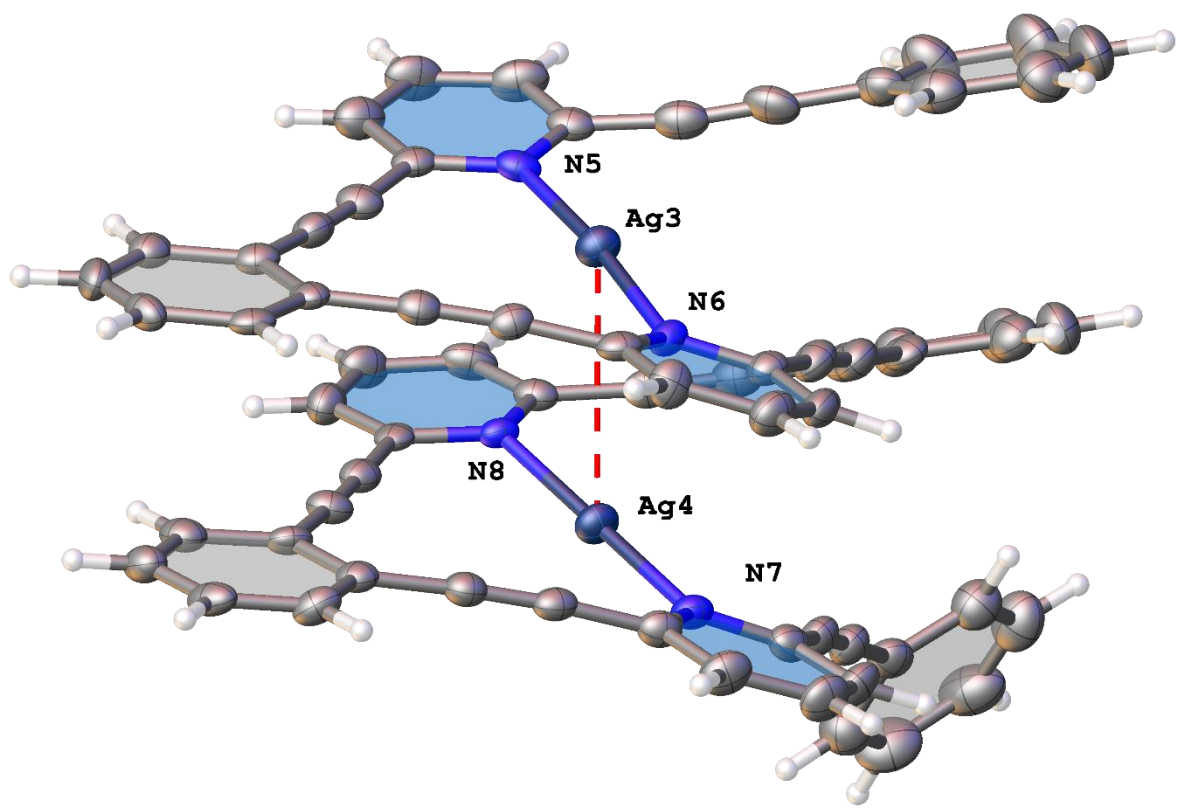


	Centroid to centroid distance	Angle between ring planes
A:	4.067(7) A	5.9(4)
B:	3.636(4) A	4.0(2)
C:	3.628(4) A	3.7(2)
D:	3.719(4) A	1.9(2)
E:	3.962(6) A	15.2(4)
N1-Ag1-N2: 2.151(5) A, 2.146(5) A, 178.7(2)		
N3-Ag2-N4: 2.146(5) A, 2.159(5) A, 177.6(2)		
Ag1-Ag2	3.5541(8) A	

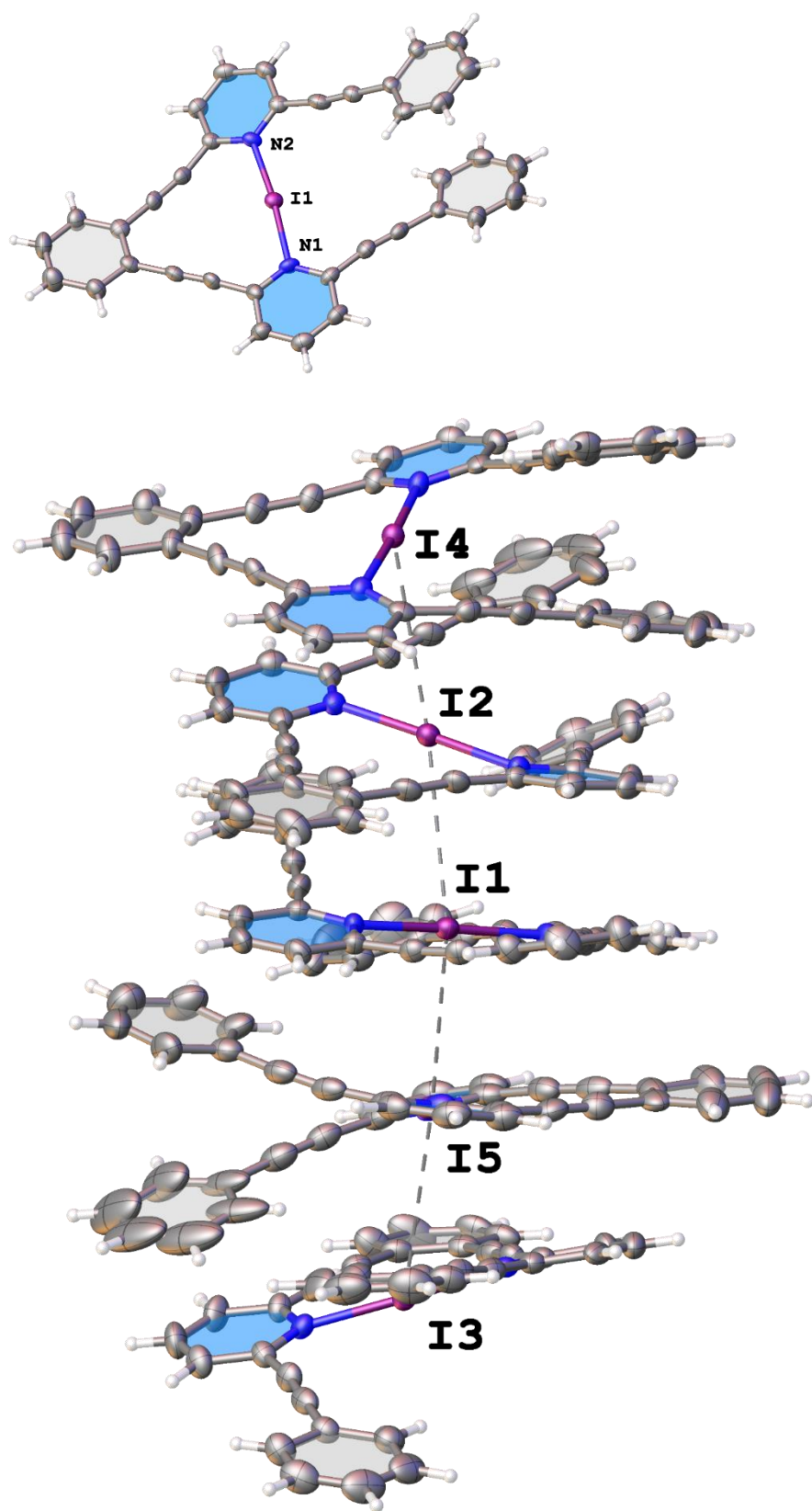
Helix B



	Centroid to centroid distance	Angle between ring planes
A:	3.710(5) A	8.7(3)
B:	3.628(4) A	4.4(2)
C:	3.731(4) A	2.0(2)
D:	3.793(4) A	1.8(2)
E':	2.827(3) A (CH- π interaction)	37.2(3)
N5-Ag3-N6: 2.154(5) A, 2.165(5) A, 174.9(2)		
N7-Ag4-N8: 2.156(5) A, 2.164(5) A, 178.3(2)		
Ag3-Ag4: 3.6351(8) A		



Complex 3:



3:

	Centroid to centroid distance	Angle between ring planes
Terminal phenyls (intramolecular):	3.933(4)	21.7(3)
Pyr -> Terminal phenyl (inter)	3.541(5) A	2.9(3)
Terminal Ph -> pyr (inter)	3.978(4)	8.5(2)
N5-I3-N6: 2.276(5) A , 2.290(5) A, 174.75(19)		

5:

	Centroid to centroid distance	Angle between ring planes
Terminal phenyls (intramolecular):	3.972(5)	20.5(3)
Pyr -> Terminal phenyl (inter)	3.664(4)A	6.6(3)
Ph -> Pyr (inter)	4.049(4)	8.3(2)
N9-I5-N10: 2.289(6)A, 2.278(6) A, 175.8(2)		

1:

	Centroid to centroid distance	Angle between ring planes
Terminal phenyls (intramolecular):	3.877(4)	17.3(3)
Pyr -> phenyl (inter)	3.991(4)	0.9(2)
Terminal Ph -> pyr (inter)	3.679(4)	3.8(2)
N1-I1-N2: 2.316(5)A, 2.256(5)A, 174.1(2)		

2:

	Centroid to centroid distance	Angle between ring planes
Terminal phenyls (intramolecular):	3.678(4)	12.9(3)
Pyr -> Terminal phenyl (inter)	3.663(4)	2.5(2)
Terminal Ph -> pyr (inter)	3.688(4)	5.7(2)
N3-I2-N4: 2.271(5) A, 2.302(5) A 174.8(2)		

4:

	Centroid to centroid distance	Angle between ring planes
Terminal phenyls (intramolecular):	3.919(4)	14.7(2)
N7-I4-N8: 2.275(5) Å, 2.277(5) Å, 176.17(18)		

Intermolecular distance I - I distances:

I3-I5:	4.3464(6)
I5-I1:	4.3099(7)
I1-I2:	4.1149(6)
I2-I4:	4.2947(6)

Computational Details

Density functional theory (DFT) calculations were carried out to identify the most stable forms of compound **4**. The weakly coordinating BF_4^- counterions were not included in the molecular models, as previous studies on analogous systems indicated that the presence of the counterion does not influence the structure of the $[\text{N-I-N}]^+$ halogen bonded complexes.^[10] We thus assume that the relative stabilities of various conformers of the "bare" halogen bonded cation (denoted as $\mathbf{4}^{2+}$) would not change in the presence of the BF_4^- counterions.

The geometry optimizations were performed by using the dispersion-corrected, range-separated hybrid ωB97XD exchange-correlation functional^[11] along with the Def2SVP basis set.^[12] For each optimized structure, an additional single-point energy calculation was performed at the $\omega\text{B97XD}/\text{Def2TZVPP}$ level to increase the accuracy of the electronic structure calculations.

The relative stabilities reported in the manuscript refer to solution-phase Gibbs free energies as obtained from

$$G = E_0' + (G_0 - E_0) + (G_{\text{sol}} - E_0)$$

where E_0 and E_0' refer to electronic energies computed at $\omega\text{B97XD}/\text{Def2SVP}$ and $\omega\text{B97XD}/\text{Def2TZVPP}$ levels of DFT; G_0 denotes gas-phase Gibbs free energy; G_{sol} is the energy in solution-phase (both computed at $\omega\text{B97XD}/\text{Def2SVP}$ level). The thermal and entropic contributions in G_0 were estimated within the ideal gas - rigid rotor - harmonic oscillator approximation for $T = 298.15$ K. The solvent effects were taken into account by computing the solvation free energies via the SMD solvation model^[13] using dichloromethane as a solvent. All DFT calculations were carried out with the *Gaussian16* software package.^[14]

The charge distribution in the most stable form of $\mathbf{4}^{2+}$ was analyzed via NPA (natural population analysis)^[15] with the *NBO 3.1* program as included in *Gaussian16*. The topology of the electron density was characterized via AIM (atoms in molecules) analysis^[16] as implemented in *Multiwfn* software.^[17] The same software was used to compute the Mayer bond orders^[18] as well.

Computational results

Conformations of cation $\mathbf{4}^{2+}$

The most stable form of cation $\mathbf{4}^{2+}$ corresponds to a folded regular helix structure with aligned N-I-N units and multiple π -stacking interactions between the aromatic rings (see $\mathbf{4a}^{2+}$ in Figure S9). Another folded structure ($\mathbf{4b}^{2+}$), wherein the helicity is switched at the central ortho-phenylene group could also be identified computationally, however, this conformer involves a notably distorted acetylenic unit (highlighted by an arrow in Figure S9) and it is predicted to be 6.0 kcal/mol less stable than $\mathbf{4a}^{2+}$. The unfolded structure with reduced van der Waals contacts ($\mathbf{4c}^{2+}$) is found to be 7.0 kcal/mol less stable than $\mathbf{4a}^{2+}$ pointing to the importance of stabilizing noncovalent interactions in the helix structure. The two strong three-center four-electron $[\text{N-I-N}]^+$ halogen bonds represent significant stabilizing effect for the formation of the helical structure, which is clearly demonstrated by the highly destabilized structure of $\mathbf{4d}^{2+}$, in which one of the $[\text{N-I-N}]^+$ bonds is broken.

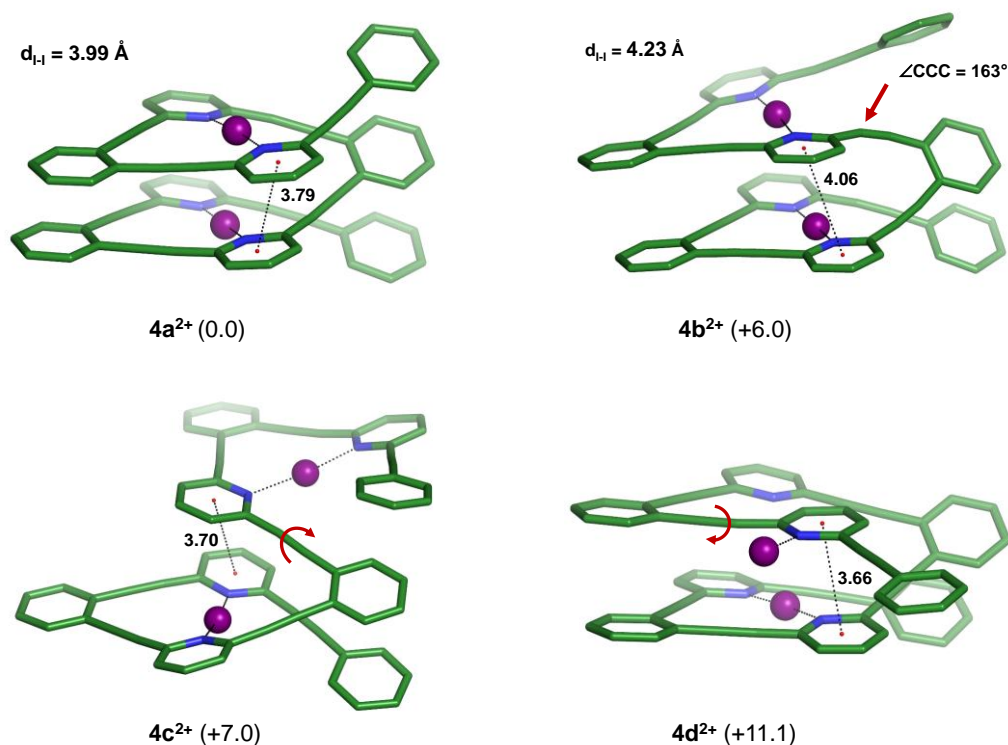


Figure S9. Structural isomers identified computationally for the cationic component of compound **4**. Relative stabilities are shown in parenthesis (in kcal/mol; with respect to the most stable form). Distances measured between the centers of the interacting aromatic rings are given in Å; d_{I-I} denotes distance between the I atoms. The red arrows are meant to highlight the structural changes with respect to structure **4a²⁺**. All H atoms are omitted for clarity.

On the enhanced stability of the helical conformer

Given the cationic nature of iodine involved in the $[N-I-N]^+$ halogen bond, the distance measured between the iodonium centers of the helical conformer **4a²⁺** is surprisingly short ($d_{I-I} = 3.99$ Å), and it is actually comparable to the sum of van der Waals radii.^{††[19]} The computed equilibrium structure of **4a²⁺** matches well with the crystallographic structure (see comparison in Figure S10), but the iodonium ions are found to be slightly closer in the measured X-ray structure. Namely, $d_{I-I} = 3.86$ – 3.89 Å, which is clearly shorter than the sum of van der Waals radii.^{††} We note, however, that the positive charge of iodonium is significantly reduced via the interaction with the N atoms of the pyridylene units. The net atomic charges obtained from NPA population analysis for the centers involved in the symmetric N-I-N unit are $Q_I = +0.45$ and $Q_N = -0.51$.

^{††} The van der Waals radius of I ranges between 1.98 and 2.15 Å depending on the definition; see: S. S. Batsanov, *Inorg. Mat.*, 2001, **37**, 871.

^{††} The small deviation between the computed and measured I-I distances is likely due to crystal packing forces. Test calculations carried out for a model that includes the BF_4^- counterions as well indicates that the presence of the counterions may slightly influence the optimized structure of **4a²⁺**, but the computed I-I distance is still longer than that in the crystallographic structure.

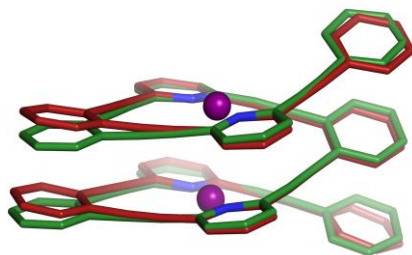


Figure S10. Superimposition of computed (green) and crystallographic (red) structures of $4a^{2+}$. The overlay was obtained by root mean square fitting of the positions of the N and I atoms.

To provide insight into the nature of interactions in $4a^{2+}$, we performed AIM topology analysis and computed the Mayer bond orders (see Figure S11). Although the AIM analysis reveals a bond critical point (bcp) between the two iodonium ions (bcp **6** in Figure S11b), the low electron density ($\rho = 0.007$) and the small value of the bond order (BO = 0.009) suggest very weak orbital overlaps between the iodonium centers. For the same reasons, the direct orbital interactions between the I and N centers in bcp's **5** and **7** are expected to be very weak as well. The electrostatic interaction between the two N-I-N units can be estimated as the sum of Coulombic interactions between the point charges centered on the atoms (using the atomic charges $Q_I = +0.45$ and $Q_N = -0.51$ data), and the overall interaction is found to be repulsive ($\Delta E_{\text{elstat}} = +21.9$ kcal/mol).

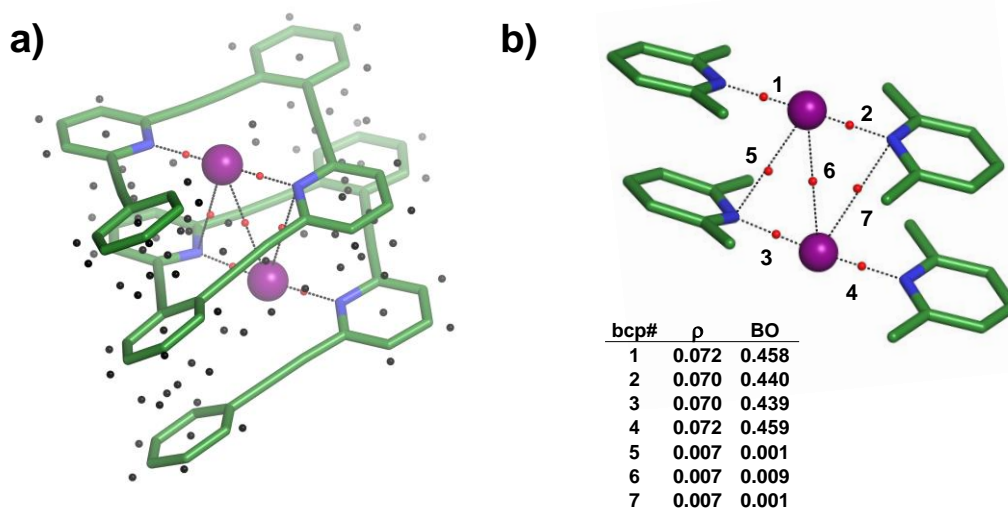


Figure S11. Results of AIM topology analysis carried out for $4a^{2+}$: a) The entire set of critical points identified via the AIM analysis; b) Bond critical points (bcp's) associated with the aligned the N-I-N units. The values of the electron density at the bcp points along with the related bond orders (BO) are listed in a table.

It thus appears that the enhanced stability of the helical conformer of the 4^{2+} cation arises from attractive van der Waals forces, which is clearly manifested in the stacking arrangement of adjacent aromatic rings. Calculations carried out for the molecule that does not involve the I^+ ions support this view, as the helical structure is preserved upon the geometry optimization, and the aryl-aryl contacts are further adjusted to maximize the stabilizing noncovalent interactions (see Figure

S12). For instance, the distance between the centers of the interacting pyridylene rings become slightly shortened in the neutral helix.

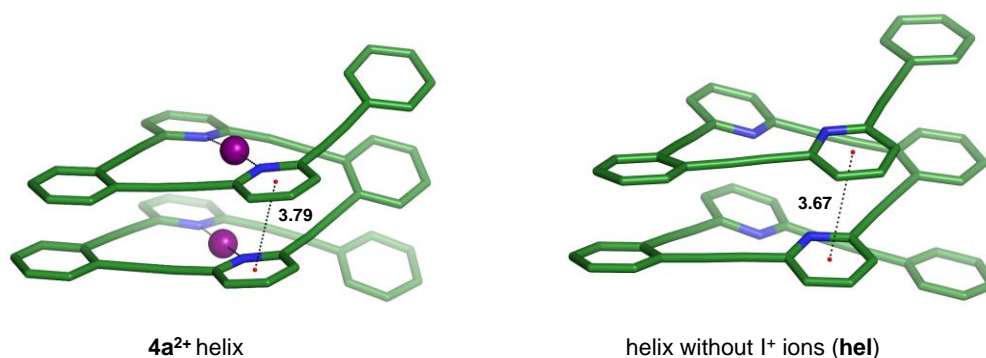


Figure S12. Helical structures of $4a^{2+}$ and the analogous neutral molecule (**hel**) derived by omitting the iodonium ions from $4a^{2+}$.

Due to the extended intramolecular van der Waals contacts in $4a^{2+}$, dispersion forces are expected to play an important role in the stabilization of the helical structure.^[20] To assess the effect of dispersion interactions, we carried out DFT calculations using the B3LYP functional,^[21] which is known to underestimate dispersion effects.^[22] The geometry optimization carried out at the B3LYP/Def2SVP level for the neutral helix **hel** resulted in a spontaneous unfolding of the helical structure (see Figure S13a). Similarly, B3LYP/Def2SVP calculations performed for the $4a^{2+}$ cation gave an unfolded structure with the N-I-N units displaced apart (Figure S13b).

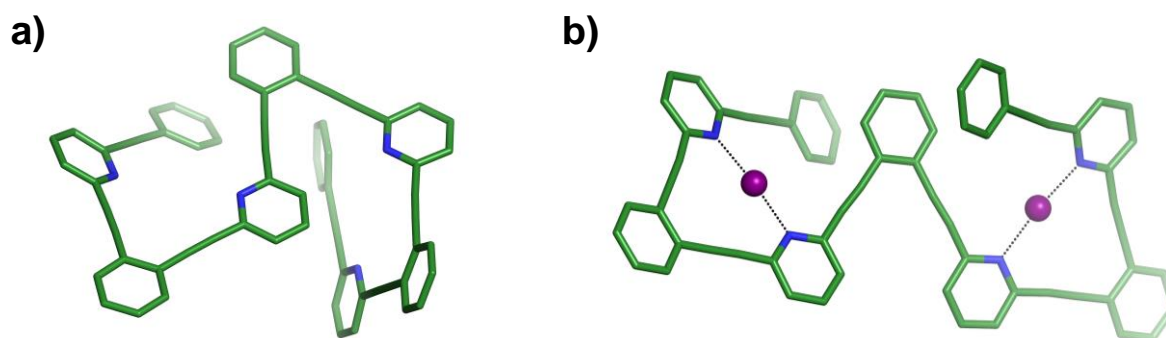


Figure S13. Unfolded structures obtained via B3LYP/Def2SVP geometry optimizations from initial helix structures (**hel** and $4a^{2+}$ respectively).

The presented results indicate that the formation of the stable helix structure of 4^{2+} cation is driven by two types of stabilizing interactions. The strong [N-I-N]⁺ halogen bonds generate relatively rigid triangular units involving three aromatic rings, which are then organized into a compact helical structure via dispersion interactions.

Energy data

Table S2. Various energy contributions computed for the optimized structures of conformers of **4²⁺** and the molecule obtained by omitting the iodonium ions from **4a²⁺** (all energy data are in hartree).

	E_0	G_0	G_{sol}	E_0'	G
4a	-3346.2599	-3345.5585	-3346.4718	-3349.1691	-3348.6796
4b	-3346.2470	-3345.5465	-3346.4591	-3349.1586	-3348.6701
4c	-3346.2423	-3345.5459	-3346.4513	-3349.1558	-3348.6684
4d	-3346.2283	-3345.5317	-3346.4435	-3349.1433	-3348.6619
hel	-2751.1488	-2750.4524	-2751.2333	-2754.0512	-2753.4393

Cartesian coordinates

Cartesian coordinates of the optimized geometries are given below in standard XYZ format (units are in Å). The first two lines indicates the total number of atoms and labelling.

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4a²⁺

```
C 3.772188 1.263117 -2.288560
C 2.648656 0.543109 -1.867509
N 2.752579 -0.764671 -1.538338
C 3.919358 -1.427315 -1.702155
C 5.071905 -0.748961 -2.116312
C 4.995072 0.611116 -2.390779
C 1.363096 1.163740 -1.825023
C 0.272179 1.694713 -1.861963
C -1.003240 2.336007 -1.928084
C -2.198535 1.638342 -1.617972
C -3.427622 2.305635 -1.722144
C -3.477854 3.640846 -2.109266
C -2.300532 4.329610 -2.399699
C -1.073275 3.681434 -2.314482
C -2.173802 0.284356 -1.157713
C -2.167472 -0.848115 -0.718918
C -2.194003 -2.157042 -0.144931
C -3.411077 -2.757832 0.191196
C -3.407691 -4.028453 0.757098
C -2.199956 -4.672665 0.987415
C -1.002562 -4.027831 0.647761
N -1.022579 -2.799154 0.078887
I 0.910807 -1.817222 -0.649967
H -4.348178 -4.509842 1.031892
H 5.885577 1.159684 -2.702621
C 3.936330 -2.843114 -1.516238
H -2.155288 -5.658712 1.449223
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H -4.338176 -2.213713 0.012537
H -0.150647 4.214975 -2.546961
H -2.338337 5.379787 -2.694185
```

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H	3.662861	2.319312	-2.532404
C	1.325348	-5.104753	1.258662
C	2.602648	-5.592930	1.675061
C	3.635776	-4.676000	1.937147
C	4.869188	-5.133527	2.386085
C	5.082855	-6.500037	2.574029
C	4.063126	-7.413677	2.305874
C	2.824423	-6.967284	1.858032
H	3.454849	-3.608916	1.796795
H	5.666002	-4.420045	2.604584
H	6.048641	-6.854841	2.939688
H	4.231396	-8.481455	2.457403
H	2.019914	-7.676700	1.656952
C	3.951478	-4.056810	-1.499390
C	3.973679	-5.485581	-1.477364
C	2.853308	-6.243386	-1.901450
C	2.912807	-7.641823	-1.854491
C	4.059613	-8.284254	-1.401710
C	5.161691	-7.539271	-0.986253
C	5.120357	-6.150153	-1.024703
C	1.667739	-5.605187	-2.380419
H	2.052154	-8.221291	-2.190623
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C	-2.939694	-4.153418	-2.966661
C	-1.791093	-4.899536	-2.731871
C	-1.415220	-1.088716	-4.415706
H	-3.704624	-2.258536	-3.699470
H	-3.918129	-4.549246	-2.688897
H	-1.829958	-5.877402	-2.252659
C	-1.303029	0.061831	-4.785947
C	-1.193276	1.423655	-5.205232
C	0.066386	2.011016	-5.488003
C	0.122831	3.358565	-5.872344
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C	-2.280555	3.527328	-5.727247
C	-2.355850	2.196138	-5.332580
C	1.274465	1.247269	-5.433987
H	1.092150	3.807138	-6.095297
H	-0.981832	5.154223	-6.304287
H	-3.195245	4.113726	-5.829706
H	-3.322567	1.738369	-5.118317

C	2.303143	0.601576	-5.440766
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C	4.537073	-3.619201	-5.148698
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H	6.830755	0.234133	-6.210903
H	4.706487	1.568217	-6.073191
C	4.451051	-4.828544	-5.071625
C	4.285809	-6.247685	-5.027424
C	3.043385	-6.805289	-5.377023
C	2.881445	-8.185840	-5.381251
C	3.948787	-9.016922	-5.037098
C	5.180526	-8.467003	-4.680919
C	5.354681	-7.087175	-4.674885
H	2.218558	-6.146829	-5.654807
H	1.921231	-8.618834	-5.667980
H	3.821953	-10.101343	-5.054425
H	6.014866	-9.119121	-4.416237
H	6.319006	-6.652043	-4.407167

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4b²⁺

C	-7.079616	-0.390128	2.102444
C	-6.252929	0.658792	1.680539
N	-4.923353	0.634826	1.928027
C	-4.379289	-0.377205	2.642894
C	-5.160623	-1.456112	3.071085
C	-6.520859	-1.463007	2.785659
C	-6.819864	1.780512	0.997815
C	-7.360899	2.707553	0.429382
C	-8.005245	3.769608	-0.279917
C	-7.259064	4.847026	-0.819182
C	-7.917428	5.840047	-1.557265
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C	-10.030371	4.725093	-1.212109
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C	-5.845954	4.930779	-0.629180
C	-4.644080	5.004640	-0.479703
C	-3.229338	5.144119	-0.355502
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C	-1.232830	6.463581	-0.595686
C	-0.498926	5.404629	-0.083409
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I	-3.612476	2.323137	0.996669
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H	-7.146840	-2.297588	3.106857
C	-3.004234	-0.279154	3.023655
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C	2.707725	-1.344862	1.122927
C	3.249630	-0.096547	1.431023
C	2.457010	1.044432	1.365544
H	-0.483703	-0.399008	0.390726
H	0.947425	-2.433578	0.503598
H	3.337271	-2.236153	1.162770
H	4.300450	-0.011642	1.714075
H	2.877178	2.024762	1.596312
C	-1.887454	-0.117585	3.472025
C	-0.609976	0.246711	4.004469
C	-0.447630	1.557283	4.531634
C	0.809794	1.966438	4.983185
C	1.882122	1.079534	4.955405
C	1.712167	-0.221232	4.482666
C	0.473970	-0.636583	4.002479
H	0.935846	2.973168	5.376978
H	2.857208	1.406280	5.321062
H	2.552551	-0.916841	4.477325
H	0.343355	-1.645325	3.610032
C	-2.371255	9.562686	1.064450
C	-3.024823	8.493136	1.685434
N	-2.351648	7.654314	2.508152
C	-1.038507	7.851528	2.767576
C	-0.338169	8.899276	2.154035
C	-1.014115	9.757481	1.297533
C	-4.420737	8.282666	1.460780
C	-5.615365	8.177878	1.269597
C	-7.030478	8.096040	1.080249
C	-7.794290	7.077347	1.703896
C	-9.185812	7.062213	1.541459
C	-9.816111	8.032967	0.770333
C	-9.064775	9.027150	0.143941
C	-7.682171	9.059394	0.297291
C	-7.165259	6.062169	2.486826
C	-6.635333	5.187819	3.140450
C	-6.071827	4.101511	3.874068

C	-6.900362	3.078272	4.348350
C	-6.334107	2.003788	5.021768
C	-4.955331	1.949348	5.177059
C	-4.164860	2.989593	4.669239
N	-4.733185	4.056659	4.070076
I	-3.470227	5.830641	3.356853
H	-6.964852	1.203317	5.412779
H	-0.488542	10.588628	0.823498
C	-0.395000	7.000526	3.711182
H	-4.464738	1.111032	5.670849
C	-2.744095	2.834219	4.696494
H	-7.974007	3.148053	4.177486
H	-7.094106	9.845971	-0.178089
H	-9.559696	9.790483	-0.459056
H	-10.901496	8.014190	0.657702
H	-9.768765	6.278372	2.026979
H	0.718689	9.033511	2.383315
H	-2.941097	10.228264	0.416488
C	-1.625630	2.363168	4.639049
C	0.136988	6.359425	4.594856
C	0.702036	5.614422	5.676144
C	-0.147848	5.074567	6.658307
C	0.391290	4.368390	7.728255
C	1.772733	4.192240	7.826238
C	2.619982	4.724272	6.852311
C	2.092112	5.436403	5.779520
H	-0.268151	3.955605	8.493634
H	2.192532	3.642025	8.670594
H	3.700392	4.593264	6.936564
H	2.750510	5.863281	5.021052
H	-1.226111	5.218939	6.573890

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4c²⁺

C	4.174602	-6.327130	-4.398686
C	2.905752	-6.768007	-4.814390
C	2.646351	-8.129049	-4.922004
C	3.643930	-9.057878	-4.619981
C	4.904264	-8.625090	-4.207477
C	5.173848	-7.265218	-4.094876
C	4.433441	-4.924384	-4.310629
C	4.597822	-3.721669	-4.263848
C	4.793383	-2.312641	-4.323057
C	6.079266	-1.758318	-4.255215
C	6.235924	-0.386507	-4.389027
C	5.119229	0.413383	-4.609152
C	3.854320	-0.178935	-4.655764
N	3.711624	-1.516045	-4.485890
C	2.688989	0.609585	-4.911701
C	1.718346	1.276546	-5.209832
C	0.594252	2.070461	-5.601416

C	0.804736	3.392591	-6.019825
C	-0.261777	4.182823	-6.435505
C	-1.556496	3.664423	-6.439924
C	-1.786243	2.356762	-6.025050
C	-0.724215	1.544924	-5.601038
C	-0.999015	0.211760	-5.161162
C	-1.256648	-0.908703	-4.769807
C	-1.579161	-2.183901	-4.209669
N	-0.571067	-2.962682	-3.752874
C	-0.830435	-4.110721	-3.084339
C	-3.186821	-3.806572	-3.454185
C	-2.910210	-2.598596	-4.082875
C	0.272724	-4.814852	-2.508339
C	1.223805	-5.359124	-1.986060
C	2.381871	-6.008886	-1.456710
C	2.422966	-7.408820	-1.404040
C	3.571644	-8.065581	-0.978634
C	4.704021	-7.334509	-0.621237
C	4.679901	-5.946406	-0.664746
C	3.518247	-5.265585	-1.052528
C	3.512614	-3.837583	-1.013975
C	3.564001	-2.625999	-0.943230
C	3.550797	-1.201210	-1.027164
N	4.726573	-0.535224	-1.058862
C	4.749006	0.796095	-1.299645
C	3.561204	1.520184	-1.452634
C	2.345345	0.856444	-1.351618
C	2.334700	-0.516421	-1.144810
C	6.009106	1.454378	-1.448949
C	7.050148	2.042611	-1.661637
C	8.273211	2.727148	-1.944656
C	8.236547	4.025746	-2.472651
C	9.416076	4.698554	-2.774403
C	10.649007	4.084550	-2.553129
C	10.705275	2.799264	-2.023756
C	9.527082	2.106482	-1.711431
C	9.604531	0.800864	-1.133811
C	9.674237	-0.293934	-0.613474
C	9.832669	-1.527185	0.090764
C	11.109982	-1.958026	0.461321
C	11.246353	-3.127221	1.200917
C	10.111859	-3.834718	1.572694
C	8.850700	-3.369868	1.177845
N	8.734213	-2.248652	0.426588
C	7.671748	-4.058508	1.583887
C	6.696421	-4.647542	2.005575
C	5.510163	-5.329075	2.418121
C	4.273699	-4.664526	2.360939
C	3.105094	-5.351282	2.667983
C	3.159870	-6.696063	3.037136
C	4.387903	-7.354753	3.113131

C	5.563244	-6.677358	2.807581
I	6.714949	-1.521681	-0.325919
I	1.588060	-2.333581	-4.200678
H	6.159201	-6.920052	-3.777263
H	5.684755	-9.353462	-3.979769
H	3.440006	-10.126274	-4.716040
H	1.663941	-8.470210	-5.253795
H	2.134918	-6.033258	-5.053830
H	3.588568	-9.156045	-0.944792
H	1.547459	-7.977936	-1.718773
H	5.612627	-7.849728	-0.305524
H	5.562107	-5.368268	-0.389200
H	-2.326452	-5.496311	-2.397088
H	-4.218479	-4.147644	-3.351338
H	-3.704283	-1.961457	-4.471414
H	-2.798075	1.948846	-6.026514
H	-2.393463	4.282321	-6.769413
H	-0.081013	5.208125	-6.762613
H	1.819872	3.792405	-6.024541
H	1.404533	-1.079158	-1.085737
H	1.407862	1.405680	-1.451884
H	3.614120	2.591571	-1.643397
H	7.270863	4.504754	-2.641462
H	9.373646	5.709654	-3.182792
H	11.574106	4.613048	-2.789318
H	11.668391	2.320498	-1.841048
H	11.973758	-1.360275	0.172028
H	12.236068	-3.476316	1.500501
H	10.173574	-4.740206	2.175587
H	6.526460	-7.188151	2.859992
H	4.428783	-8.402654	3.415711
H	2.240076	-7.232747	3.277796
H	2.144243	-4.835602	2.620273
H	4.239733	-3.616406	2.058206
H	5.207134	1.490829	-4.744176
H	7.229140	0.062192	-4.332626
H	6.931612	-2.421051	-4.110974
C	-2.144190	-4.564252	-2.931402

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4d²⁺

C	-6.961766	-5.837693	-1.493401
C	-5.733323	-6.339948	-1.025571
C	-5.636667	-7.678329	-0.602845
C	-6.757549	-8.498453	-0.650281
C	-7.973507	-7.995673	-1.116525
C	-8.074785	-6.668124	-1.537159
C	-4.589371	-5.491499	-0.980634
C	-3.625195	-4.748720	-0.960487
C	-2.440530	-3.978219	-0.942120
N	-2.478827	-2.639283	-1.238660

C	-1.341325	-1.875795	-1.286550
C	-0.103412	-2.466770	-1.020706
C	-0.046099	-3.810835	-0.677472
C	-1.210406	-4.566569	-0.640220
C	-1.416256	-0.497422	-1.589812
C	-1.331479	0.696724	-1.795133
C	-1.176430	2.091538	-2.027828
C	0.134218	2.629582	-2.107512
C	0.289009	4.001569	-2.340927
C	-0.827057	4.822566	-2.479667
C	-2.114370	4.290095	-2.390241
C	-2.290556	2.929578	-2.168489
C	1.262139	1.767712	-1.939468
C	2.175806	0.985534	-1.781407
C	3.268055	0.066560	-1.613090
N	2.965978	-1.237717	-1.554706
C	3.963756	-2.117451	-1.423804
C	5.310381	-1.727381	-1.332765
C	5.615712	-0.373331	-1.379516
C	4.583037	0.546103	-1.527125
C	3.645049	-3.520530	-1.389627
C	3.503515	-4.726013	-1.383367
C	3.423361	-6.154922	-1.351395
C	2.434034	-6.863793	-2.074049
C	2.418720	-8.266997	-2.031117
C	3.359105	-8.961983	-1.281276
C	4.327951	-8.263827	-0.559739
C	4.360952	-6.874548	-0.596092
C	1.415479	-6.184756	-2.810861
C	0.489114	-5.655029	-3.392549
C	-0.748801	-5.147189	-3.893083
N	-0.853285	-3.844561	-4.232009
C	-2.057081	-3.326521	-4.569958
C	-3.200615	-4.131821	-4.627749
C	-3.092865	-5.484697	-4.329167
C	-1.861172	-5.999101	-3.949534
C	-2.163431	-1.925588	-4.833298
C	-2.326919	-0.736416	-5.016333
C	-2.529926	0.661620	-5.233850
C	-1.431141	1.548209	-5.358954
C	-1.667825	2.907954	-5.598534
C	-2.968229	3.389641	-5.704811
C	-4.051227	2.520901	-5.570120
C	-3.834041	1.166261	-5.338475
C	-0.088680	1.075443	-5.241404
C	1.053647	0.682130	-5.133837
C	2.423451	0.289717	-5.051656
N	2.731918	-1.017121	-4.873942
C	4.024217	-1.425159	-4.846237
C	5.064297	-0.494737	-4.955331
C	4.761669	0.850775	-5.111265

C	3.432104	1.250187	-5.168375
C	4.294113	-2.816349	-4.732092
C	4.502494	-4.010860	-4.676680
C	4.671415	-5.428030	-4.622022
C	5.722267	-5.998825	-3.887294
C	5.854661	-7.381835	-3.830230
C	4.952345	-8.200224	-4.510270
C	3.911453	-7.636631	-5.249416
C	3.763723	-6.255801	-5.304753
I	1.044413	-2.475990	-4.525410
H	6.650866	-0.036180	-1.299665
H	1.293804	4.422642	-2.397905
H	-0.690643	5.892157	-2.649887
H	-2.984291	4.940841	-2.492601
H	-3.292632	2.503057	-2.104227
H	6.088271	-2.483201	-1.222952
H	4.774950	1.618696	-1.567255
H	1.658025	-8.806515	-2.597466
H	3.335377	-10.052724	-1.256376
H	5.064554	-8.806560	0.035398
H	5.120401	-6.326937	-0.036158
H	-4.151615	-3.682938	-4.912824
H	-3.970321	-6.132075	-4.376421
H	-1.738981	-7.047741	-3.680182
H	-0.818306	3.585244	-5.696285
H	-3.138166	4.450501	-5.896714
H	-5.071189	2.898955	-5.659222
H	-4.677914	0.479942	-5.251569
H	6.092841	-0.853013	-4.930868
H	5.561580	1.587561	-5.203754
H	3.151937	2.293555	-5.307529
H	2.952326	-5.804964	-5.878472
H	3.213291	-8.279033	-5.789344
H	5.066608	-9.285297	-4.470012
H	6.671341	-7.825584	-3.258126
H	6.426867	-5.352475	-3.361110
H	-1.196362	-5.627734	-0.395096
H	0.919961	-4.268721	-0.458575
H	0.806443	-1.862100	-1.103510
H	-4.684738	-8.062949	-0.232570
H	-6.686027	-9.535493	-0.318145
H	-8.851632	-8.643521	-1.149338
H	-9.029326	-6.280072	-1.896624
H	-7.034418	-4.796965	-1.814453
I	-4.326829	-1.724565	-1.568586

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model without I⁺

C	3.768658	1.446609	-1.547207
C	2.621434	0.655519	-1.729945
N	2.660767	-0.677233	-1.772520

C	3.838668	-1.284051	-1.618255
C	5.036781	-0.579267	-1.409033
C	4.991653	0.808788	-1.379088
C	1.332203	1.282066	-1.849726
C	0.250783	1.825748	-1.909111
C	-1.049138	2.413878	-1.979166
C	-2.196443	1.636228	-1.680936
C	-3.465461	2.224219	-1.783787
C	-3.603569	3.557090	-2.155664
C	-2.472418	4.325145	-2.433211
C	-1.207071	3.756717	-2.348712
C	-2.053281	0.276913	-1.262683
C	-1.884936	-0.863345	-0.887111
C	-1.711314	-2.229347	-0.470315
C	-2.782912	-3.129265	-0.581963
C	-2.583271	-4.446846	-0.187417
C	-1.337831	-4.823494	0.296258
C	-0.327997	-3.848615	0.376208
N	-0.515233	-2.580518	0.008872
H	-3.391959	-5.176519	-0.265412
H	5.903062	1.390129	-1.224049
C	3.856860	-2.721105	-1.656513
H	-1.128018	-5.847831	0.605560
C	0.974571	-4.221440	0.859635
H	-3.739003	-2.789443	-0.981011
H	-0.318980	4.345188	-2.583932
H	-2.577448	5.371119	-2.727979
H	-4.599109	4.000223	-2.225969
H	-4.344722	1.619048	-1.556405
H	5.972347	-1.125174	-1.281773
H	3.681677	2.533493	-1.525416
C	2.062744	-4.590778	1.246134
C	3.365490	-5.018799	1.658134
C	4.426135	-4.099691	1.720589
C	5.699001	-4.526541	2.084051
C	5.930622	-5.868069	2.392263
C	4.880968	-6.784322	2.336308
C	3.605450	-6.365871	1.970877
H	4.238305	-3.055415	1.465961
H	6.518692	-3.805946	2.127708
H	6.931681	-6.199019	2.677830
H	5.058330	-7.835714	2.572521
H	2.783843	-7.081574	1.910161
C	3.902976	-3.932446	-1.661029
C	3.921182	-5.359020	-1.598092
C	2.744332	-6.105409	-1.848631
C	2.774251	-7.499463	-1.705154
C	3.946227	-8.150798	-1.340418
C	5.111642	-7.417561	-1.116899
C	5.097221	-6.033787	-1.242544
C	1.551231	-5.453892	-2.286211

H	1.866111	-8.068389	-1.909547
H	3.953217	-9.238187	-1.243283
H	6.034478	-7.925275	-0.829692
H	5.997136	-5.450884	-1.041188
C	0.565199	-4.894487	-2.715597
C	-0.616391	-4.271444	-3.247322
N	-0.543302	-2.976989	-3.561322
C	-1.625912	-2.382574	-4.065396
C	-2.843142	-3.056766	-4.263436
C	-2.911022	-4.406899	-3.942166
C	-1.782868	-5.034440	-3.429104
C	-1.505727	-0.999047	-4.440182
H	-3.700164	-2.521898	-4.674278
H	-3.836892	-4.966268	-4.092245
H	-1.786781	-6.091846	-3.161972
C	-1.413482	0.154859	-4.798822
C	-1.250263	1.513510	-5.208807
C	0.047568	2.032341	-5.446405
C	0.187628	3.376634	-5.820437
C	-0.928512	4.191631	-5.975457
C	-2.205813	3.674946	-5.756584
C	-2.363985	2.348506	-5.373228
C	1.192726	1.185832	-5.323226
H	1.189694	3.770716	-5.998153
H	-0.801405	5.234800	-6.272175
H	-3.084029	4.312738	-5.874826
H	-3.358223	1.942877	-5.180146
C	2.133912	0.427342	-5.231333
C	3.268261	-0.447108	-5.095811
N	3.045937	-1.761483	-5.174752
C	4.081028	-2.588713	-5.025520
C	5.394046	-2.136477	-4.806510
C	5.619674	-0.768268	-4.742138
C	4.543975	0.099929	-4.886163
C	3.821607	-4.002612	-5.079273
H	6.202720	-2.857896	-4.685874
H	6.625768	-0.379333	-4.571959
H	4.669293	1.181564	-4.829735
C	3.646927	-5.202333	-5.088202
C	3.415861	-6.615027	-5.057892
C	2.116485	-7.123666	-5.221006
C	1.889922	-8.494247	-5.152856
C	2.950519	-9.372891	-4.926053
C	4.243154	-8.874390	-4.767707
C	4.477653	-7.504542	-4.831426
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H	0.876247	-8.881321	-5.278093
H	2.768364	-10.448669	-4.873937
H	5.075401	-9.557755	-4.585893
H	5.484760	-7.107845	-4.692440

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hel optimized at B3LYP/Def2SVP level

C	-0.349244	0.494139	-3.094317
C	-0.499450	-0.022490	-1.787940
N	-0.375507	-1.328808	-1.510522
C	-0.108121	-2.172017	-2.519946
C	0.043919	-1.749647	-3.859582
C	-0.074543	-0.389088	-4.136099
C	-0.805398	0.871044	-0.705709
C	-1.079783	1.671309	0.171940
C	-1.428731	2.647703	1.149782
C	-1.478147	2.339180	2.542662
C	-1.854850	3.349679	3.452471
C	-2.168060	4.634375	3.016280
C	-2.113253	4.939643	1.650698
C	-1.749264	3.957643	0.733264
C	-1.151686	1.042499	3.038241
C	-0.868241	-0.043759	3.512476
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H	-1.317192	-3.198502	6.857784
H	0.052679	-0.025537	-5.157704
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C	0.488128	-7.016281	-2.996160

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C	0.470617	-8.119429	-0.405104
C	0.316847	-6.744724	-0.572223
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H	0.196163	-6.091661	0.293998
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C	0.493486	-5.397524	-6.738825
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C	0.250965	-3.530942	-8.078904
C	0.429870	-4.293138	-9.253262
C	0.652245	-5.662910	-9.131317
C	0.684383	-6.232581	-7.861532
C	0.008584	-2.117653	-8.190808
H	0.394382	-3.804815	-10.228115
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C	6.048153	-7.672778	-3.424238
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C	7.005918	-5.478962	-3.798991
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H	3.915581	-7.842650	-3.760978
H	6.168577	-8.721170	-3.139526
H	8.143519	-7.195561	-3.160661
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4a²⁺ optimized at B3LYP/Def2SVP level

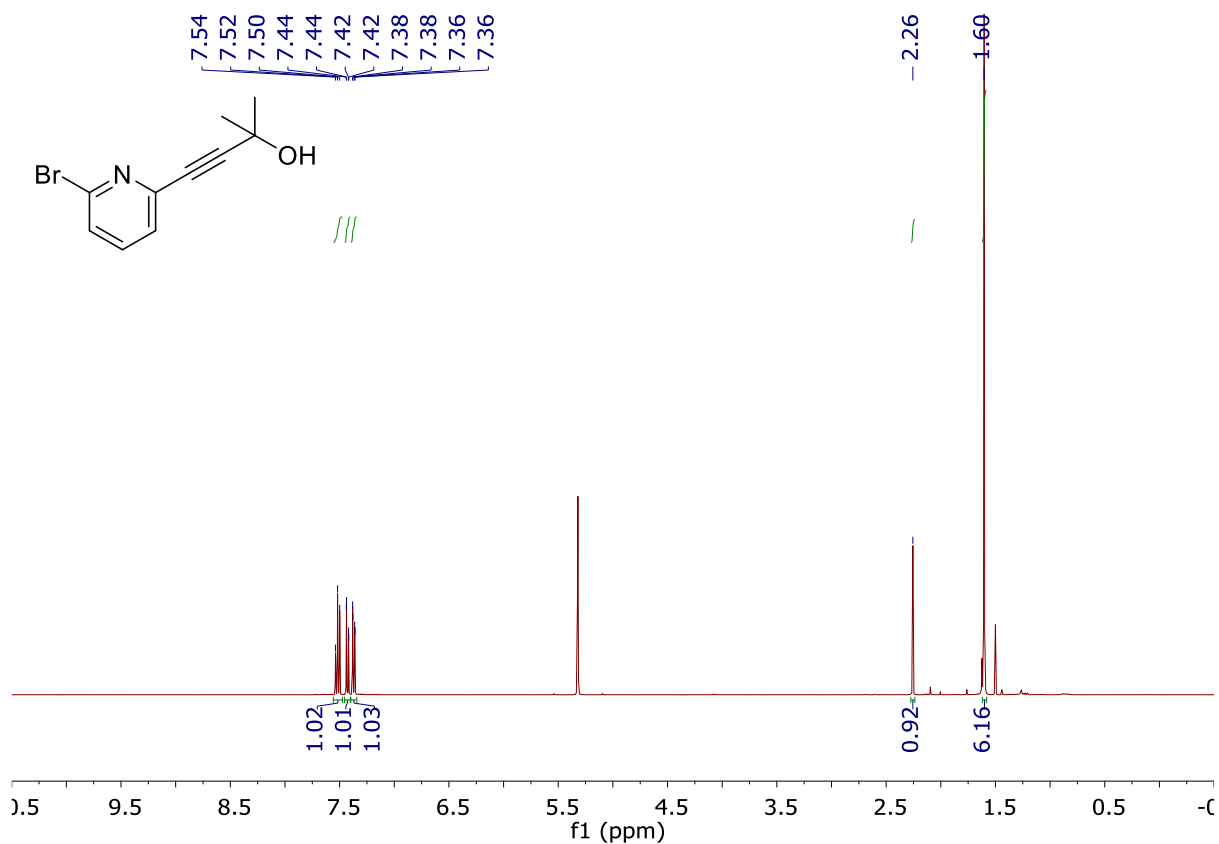
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C	-2.748249	0.846824	-0.944171
C	-3.271757	-0.303444	2.549328
C	-3.888490	-0.429837	3.595810
C	-4.613406	-0.613926	4.806445
C	-4.124162	-1.483139	5.831880
C	-4.889005	-1.662695	7.001082
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C	-6.578456	-0.140317	6.166427
C	-5.841232	0.050233	4.998662
C	-2.871410	-2.143302	5.693164
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C	-0.506432	-3.309662	5.577661
C	-0.103218	-4.092216	6.674851
C	1.176273	-4.642563	6.693343
C	2.045193	-4.387316	5.637225
C	1.612421	-3.598528	4.551906
N	0.341774	-3.109440	4.526228
I	-0.507884	-2.046235	2.667982
H	1.500339	-5.253644	7.538770
H	-3.195583	1.531441	-1.668340
C	-0.029679	-1.683325	-0.729284
H	3.064894	-4.772256	5.629947
C	2.519292	-3.278550	3.506645
H	-0.802625	-4.243017	7.497112
H	-6.211654	0.715588	4.216731
H	-7.528825	0.381470	6.298309
H	-6.683569	-1.149265	8.079128
H	-4.514717	-2.327502	7.781532
H	-1.232684	0.084930	-2.300861
H	-4.150181	1.318567	0.643591
C	3.418424	-3.010330	2.724583
C	4.480294	-2.676281	1.835746
C	4.327853	-1.634218	0.893492
C	5.378388	-1.307401	0.037928
C	6.588453	-2.008085	0.107715
C	6.748826	-3.042159	1.037896
C	5.705871	-3.377833	1.898901
H	3.383543	-1.088371	0.848049
H	5.258161	-0.496573	-0.684302

H	7.411508	-1.743371	-0.560427
H	7.695384	-3.584567	1.095471
H	5.829054	-4.179379	2.629897
C	0.810199	-2.450199	-1.173737
C	1.775865	-3.408857	-1.595814
C	2.341429	-3.398358	-2.907344
C	3.257099	-4.408564	-3.265645
C	3.612329	-5.407682	-2.360868
C	3.058769	-5.418137	-1.075633
C	2.151946	-4.429313	-0.698238
C	2.026212	-2.394765	-3.866661
H	3.687793	-4.392838	-4.268154
H	4.324168	-6.180631	-2.657422
H	3.332969	-6.202092	-0.366184
H	1.718216	-4.433978	0.303079
C	1.842676	-1.568758	-4.747402
C	1.672025	-0.492302	-5.665085
N	2.245745	-0.564346	-6.894017
C	2.208541	0.503671	-7.738800
C	1.508081	1.673949	-7.380415
C	0.871138	1.739889	-6.145336
C	0.962378	0.658757	-5.272449
C	2.912916	0.458062	-8.972965
H	1.483507	2.508437	-8.081295
H	0.321340	2.639222	-5.858706
H	0.506468	0.680705	-4.282912
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C	5.751307	0.872406	-13.618627
C	5.009927	1.962027	-13.144749
C	4.273130	1.848802	-11.966666
C	5.007068	-1.713164	-11.031077
H	6.328202	-1.183697	-13.286656
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H	5.008152	2.904781	-13.696170
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C	4.973295	-2.787004	-10.451054
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N	4.145909	-4.362999	-8.820577
C	4.011668	-5.634603	-8.351609
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C	5.587668	-6.425680	-10.013601
C	5.673910	-5.128817	-10.513395
I	3.190031	-2.558213	-7.754250
C	3.098952	-5.926259	-7.301368
H	4.623956	-7.692862	-8.536916
H	6.159590	-7.233808	-10.475056
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C	2.297937	-6.349709	-6.480684

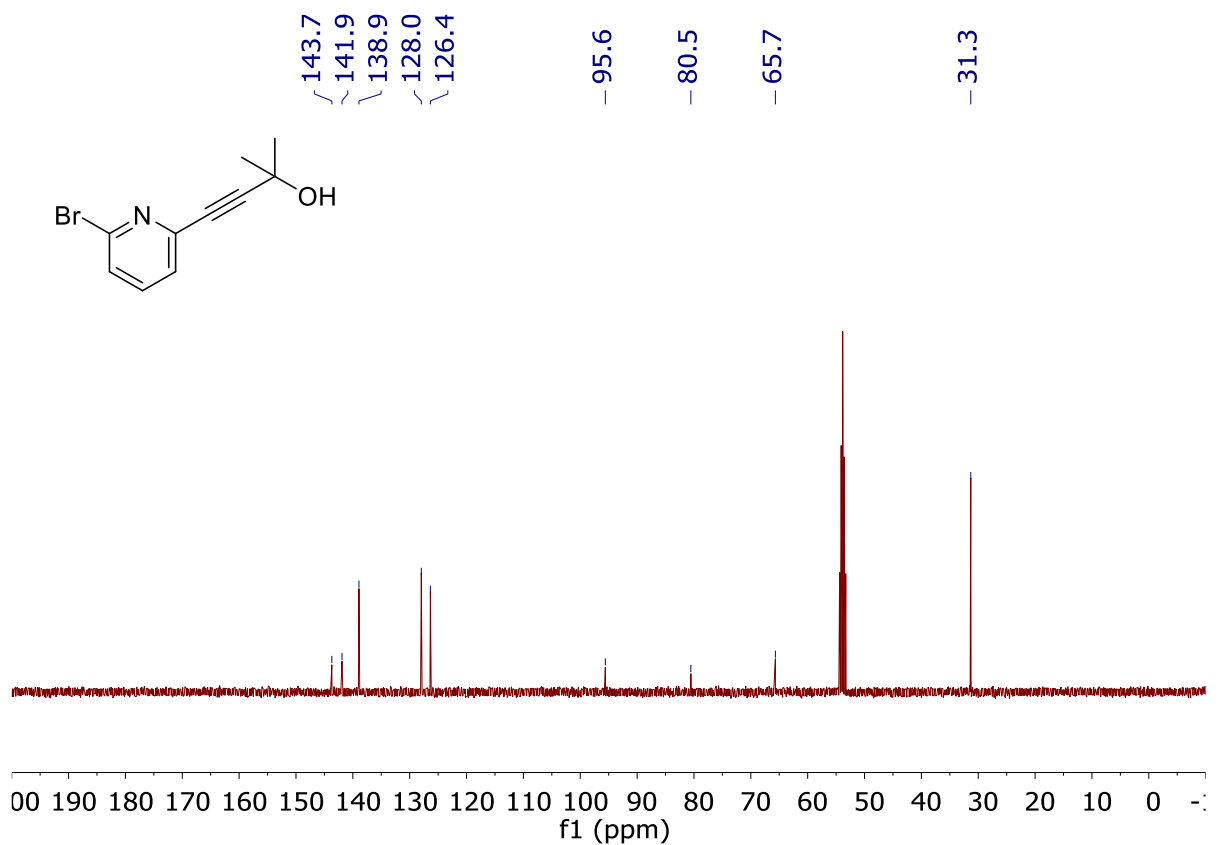
C	1.332931	-6.847329	-5.558425
C	0.254432	-6.035110	-5.139981
C	-0.691946	-6.536501	-4.248056
C	-0.578169	-7.844984	-3.762556
C	0.486071	-8.657174	-4.172636
C	1.437756	-8.167649	-5.065301
H	0.172941	-5.017098	-5.525786
H	-1.528729	-5.908514	-3.933575
H	-1.326598	-8.236087	-3.069093
H	0.569529	-9.679963	-3.797871
H	2.264103	-8.801061	-5.394349

NMR Spectra

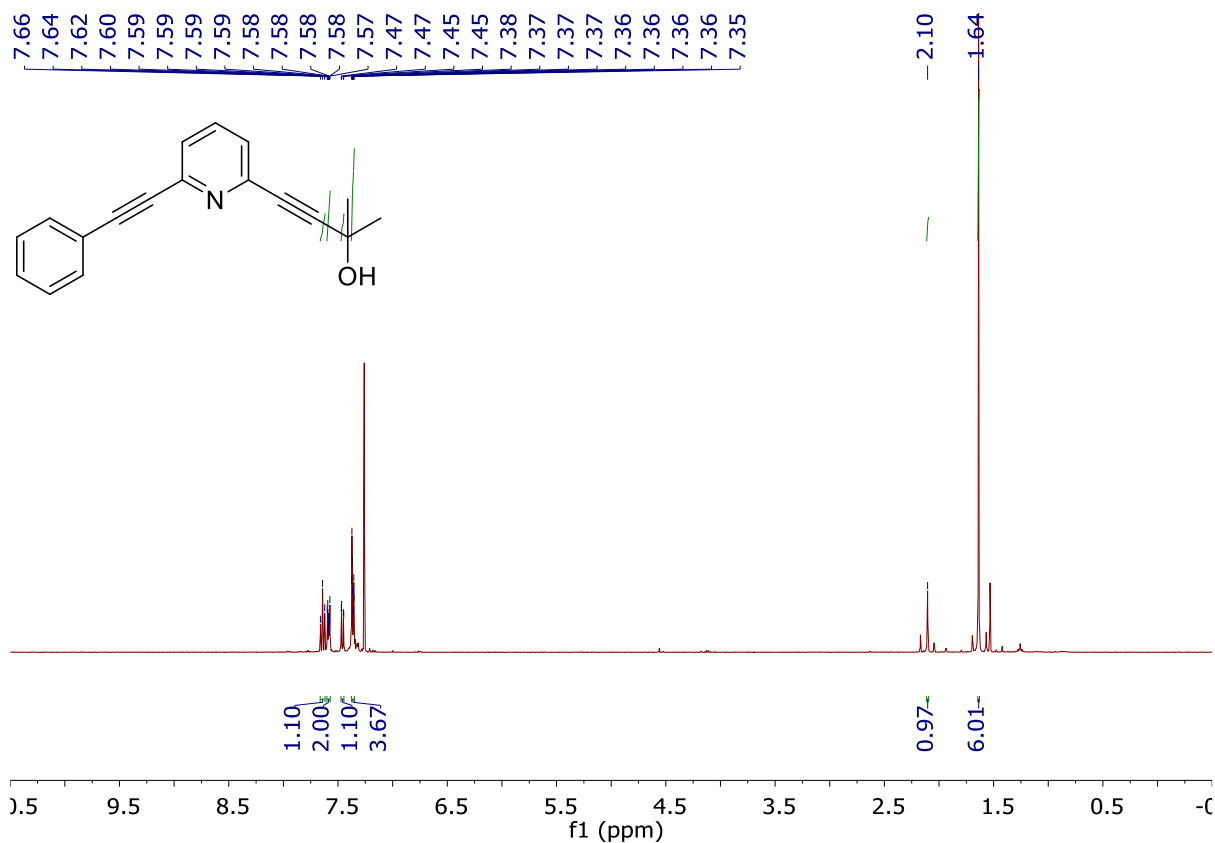
4-(6-bromopyridin-2-yl)-2-methylbut-3-yn-2-ol: ^1H NMR (400 MHz, CD_2Cl_2)



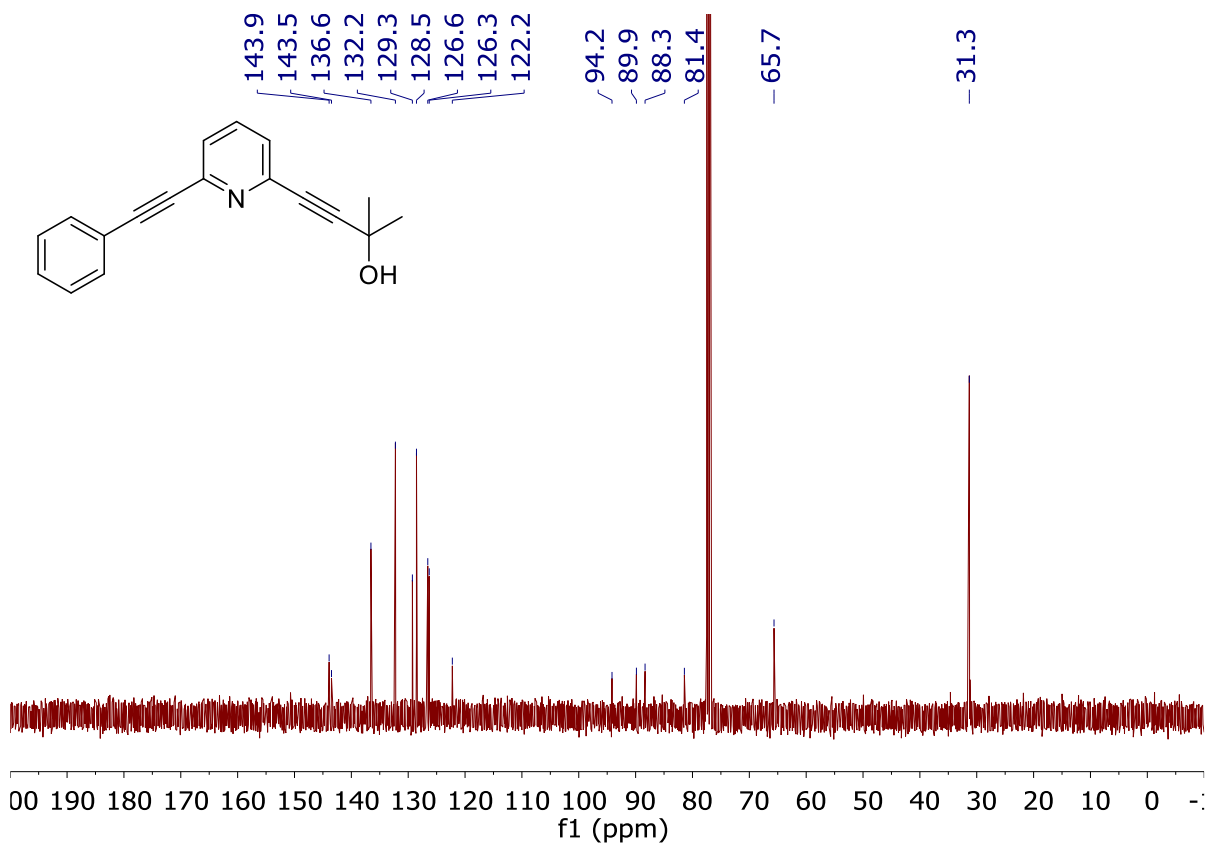
4-(6-bromopyridin-2-yl)-2-methylbut-3-yn-2-ol: ^{13}C NMR (100 MHz, CD_2Cl_2)



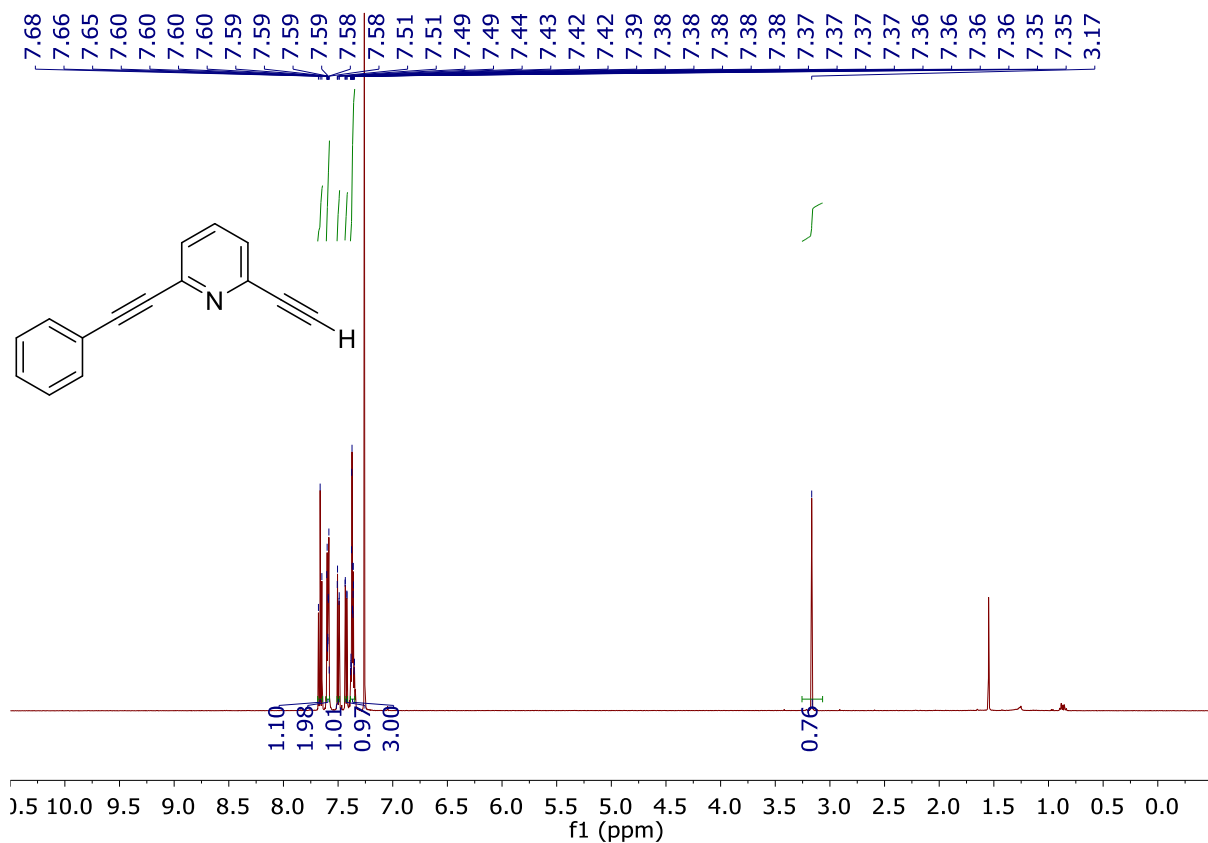
2-methyl-4-(6-(phenylethynyl)pyridin-2-yl)but-3-yn-2-ol: ^1H NMR (400 MHz, CDCl_3)



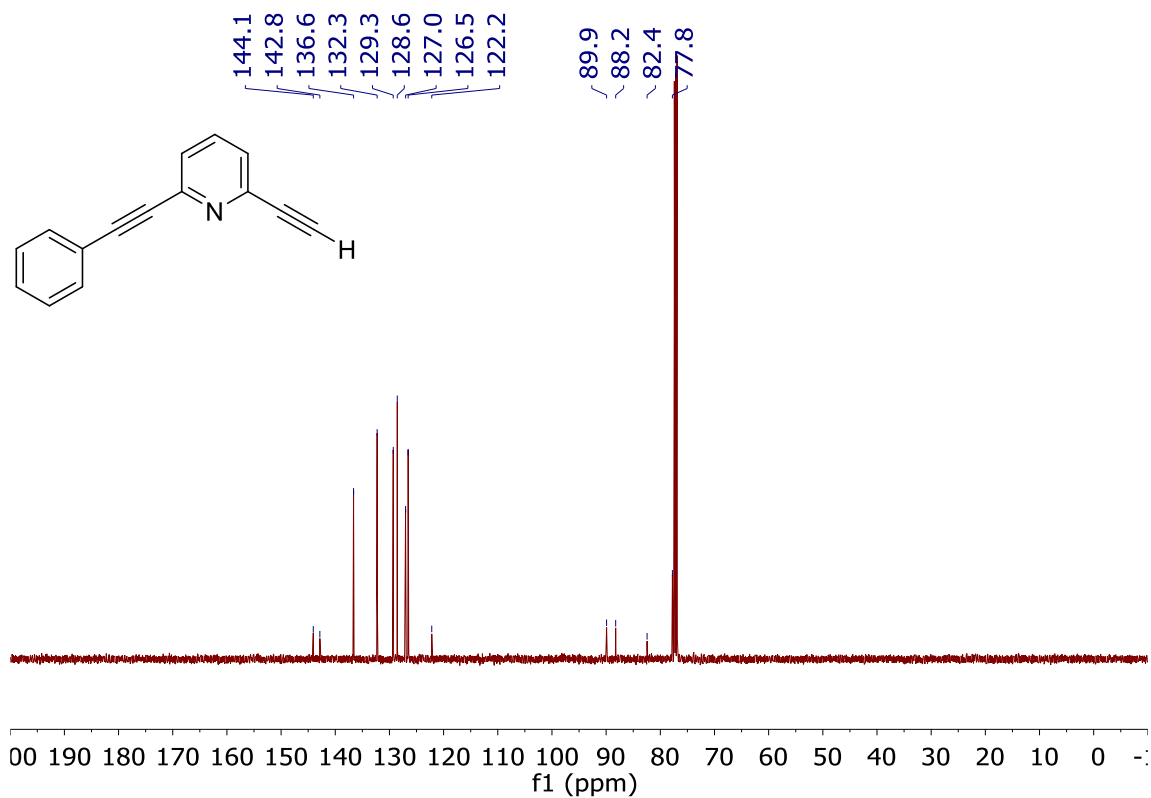
2-methyl-4-(6-(phenylethynyl)pyridin-2-yl)but-3-yn-2-ol: ^{13}C NMR (100 MHz, CDCl_3)



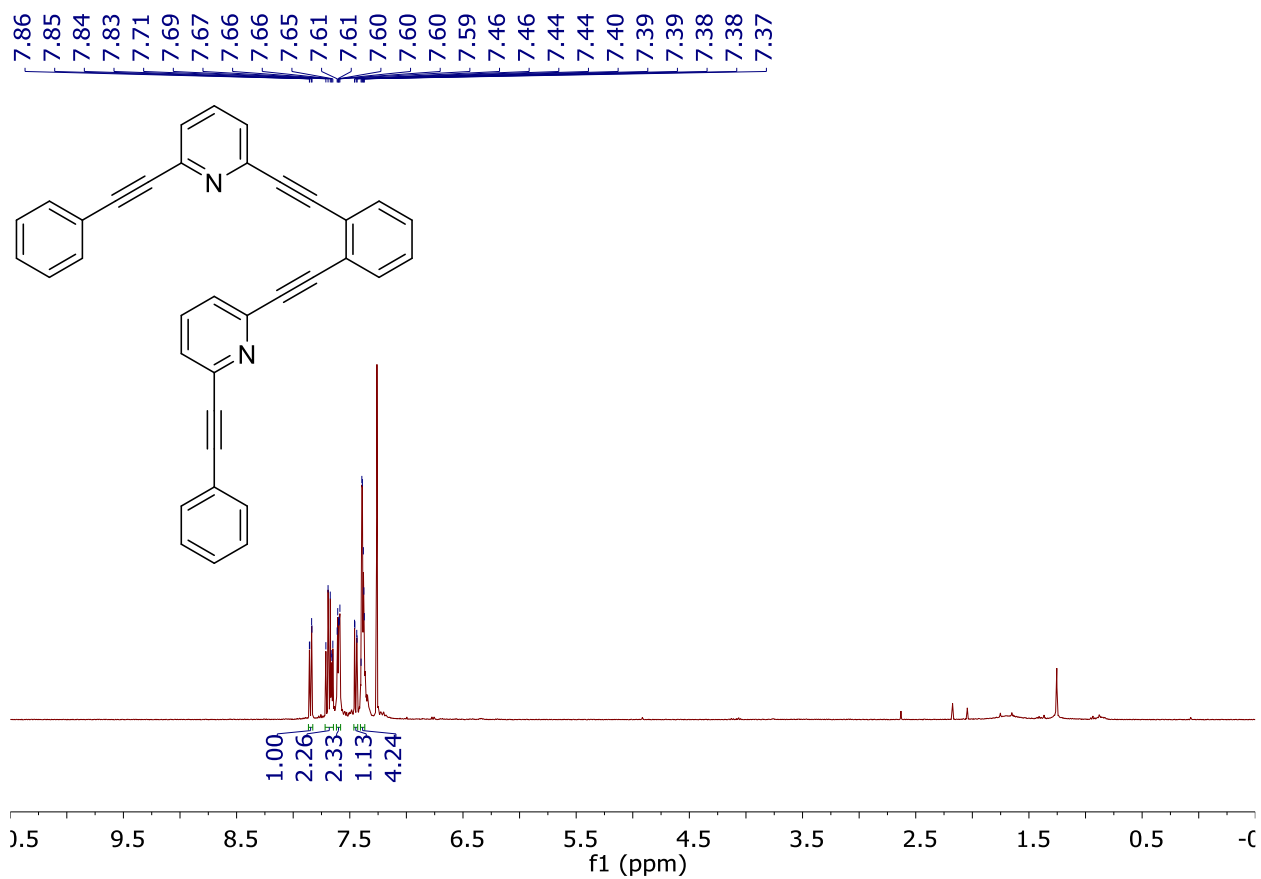
2-Ethynyl-6-(phenylethynyl)pyridine: ¹H NMR (500 MHz, CDCl₃)



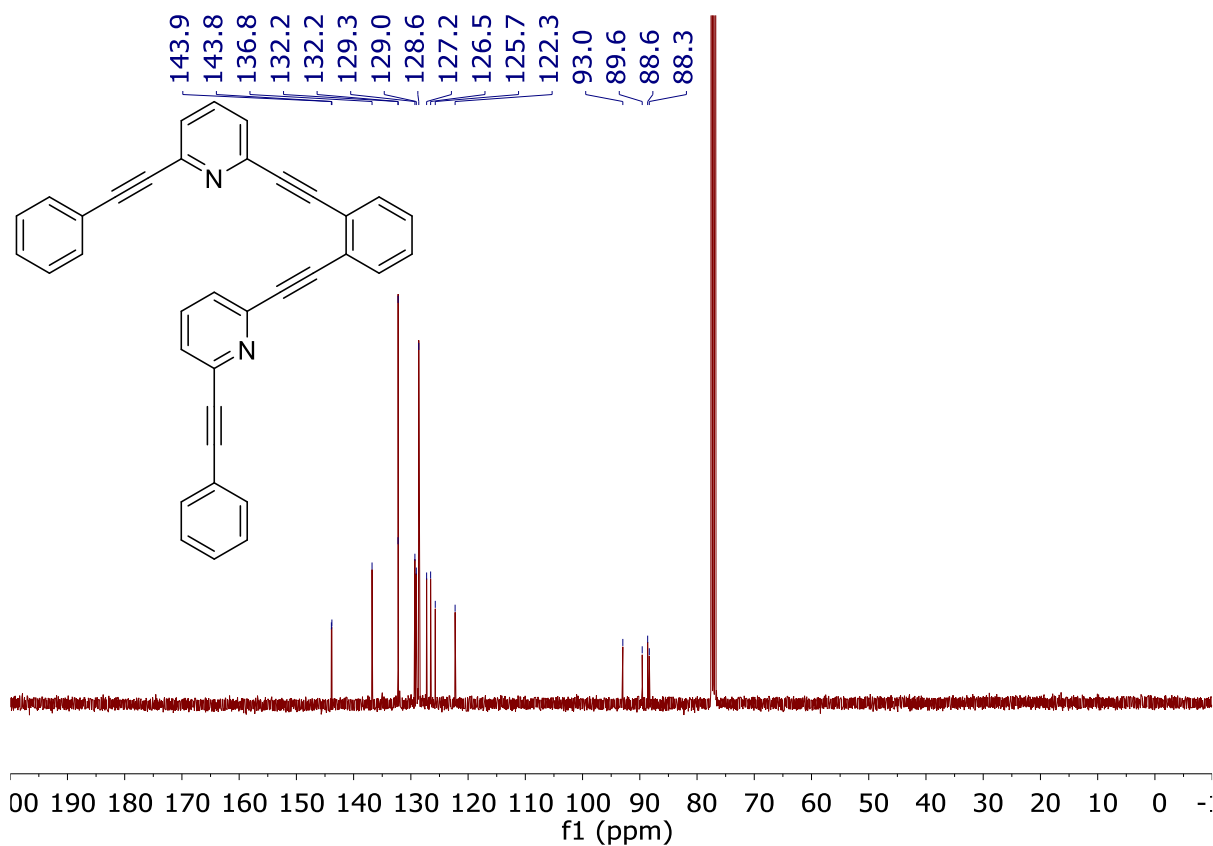
2-Ethynyl-6-(phenylethynyl)pyridine: ¹³C NMR (126 MHz, CDCl₃)



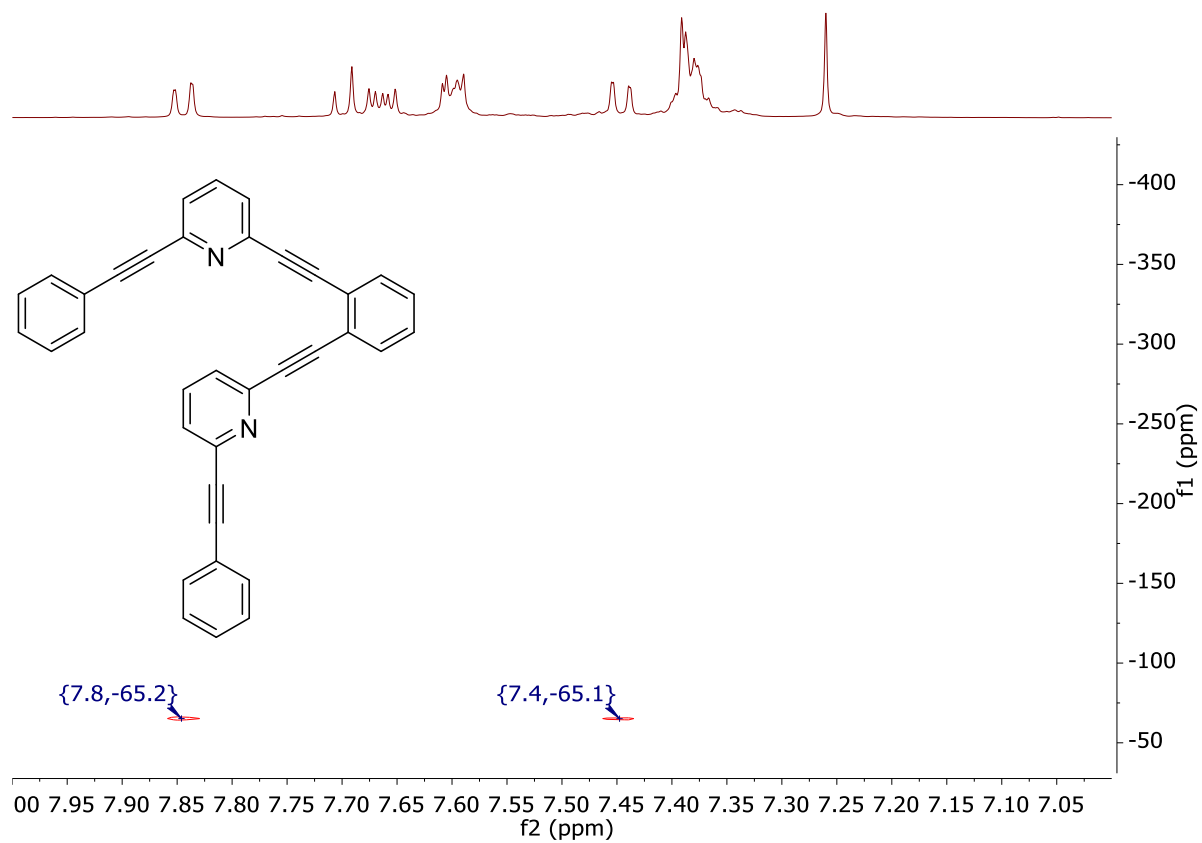
Compound 5: ^1H NMR (400 MHz, CDCl_3)



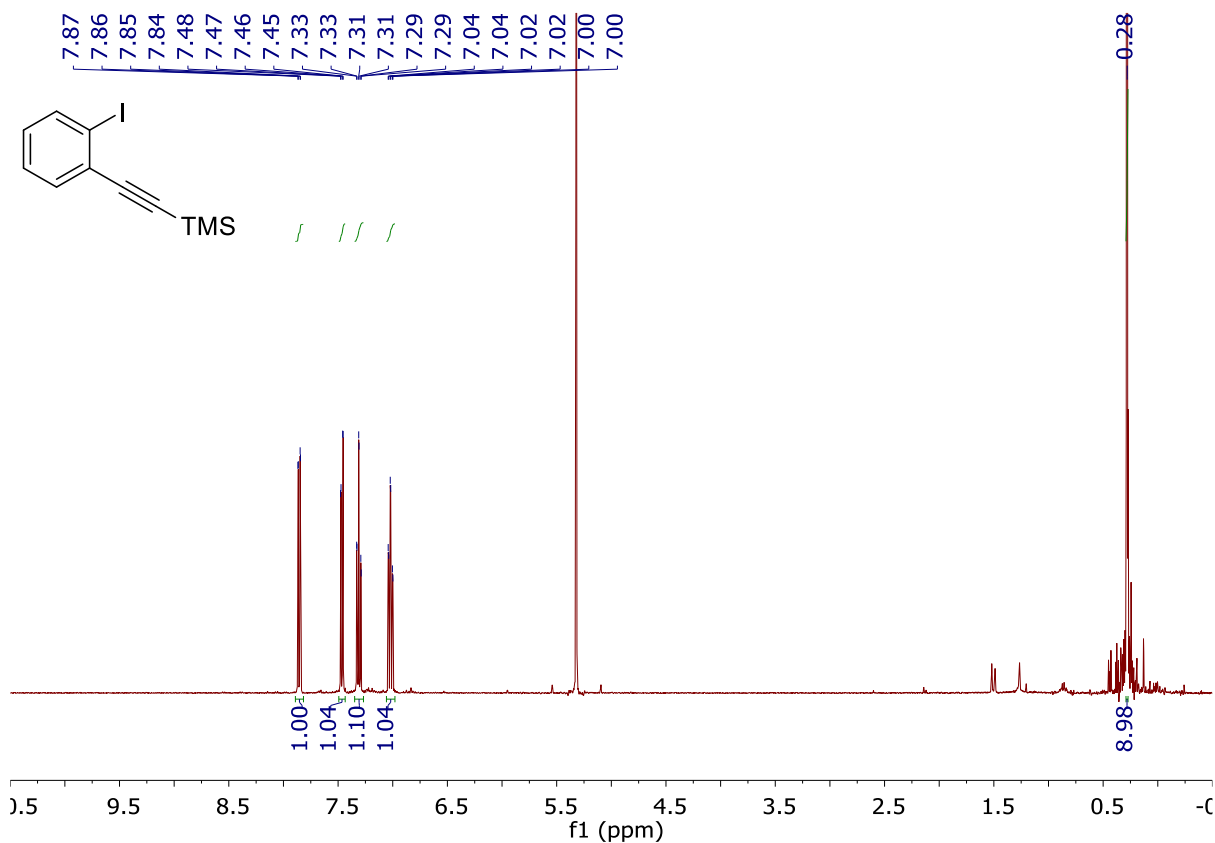
Compound 5: ^{13}C NMR (101 MHz, CDCl_3)



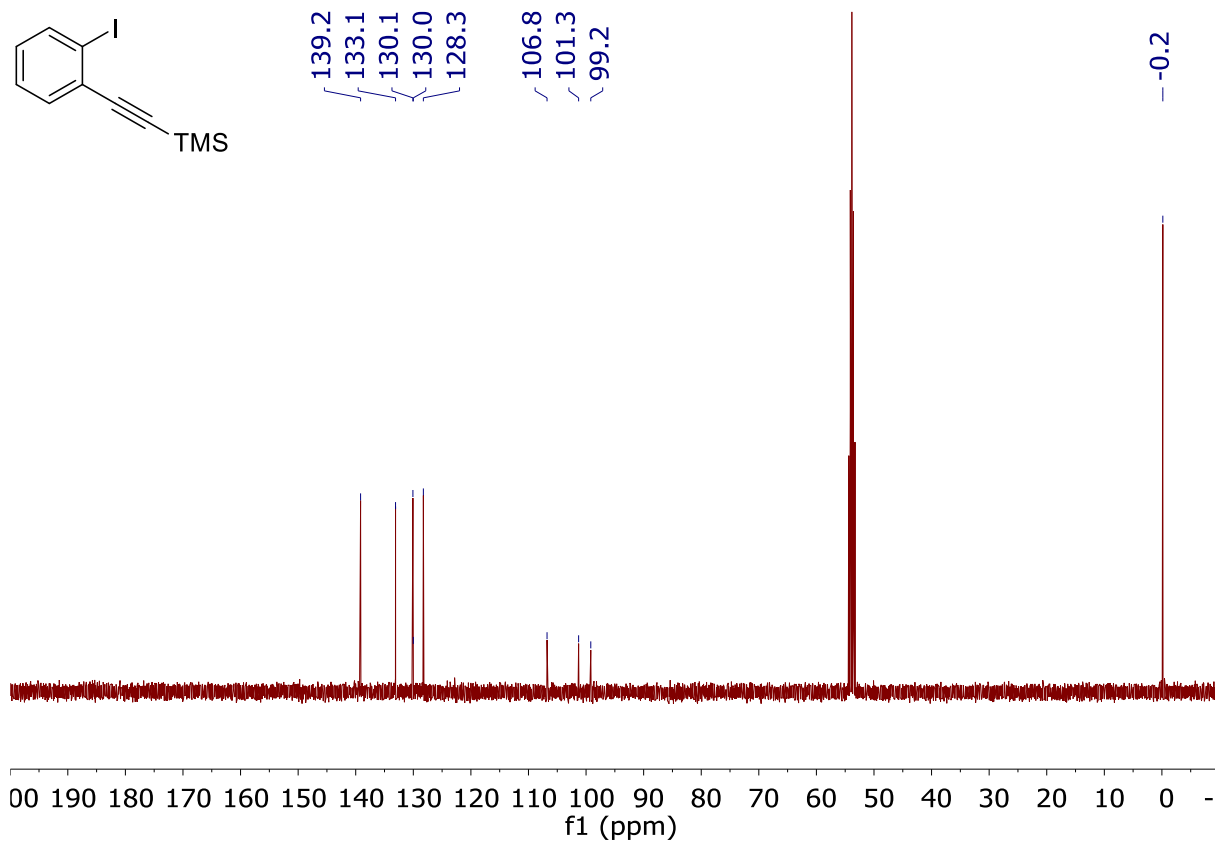
Compound 5: ^1H - ^{15}N HMBC NMR



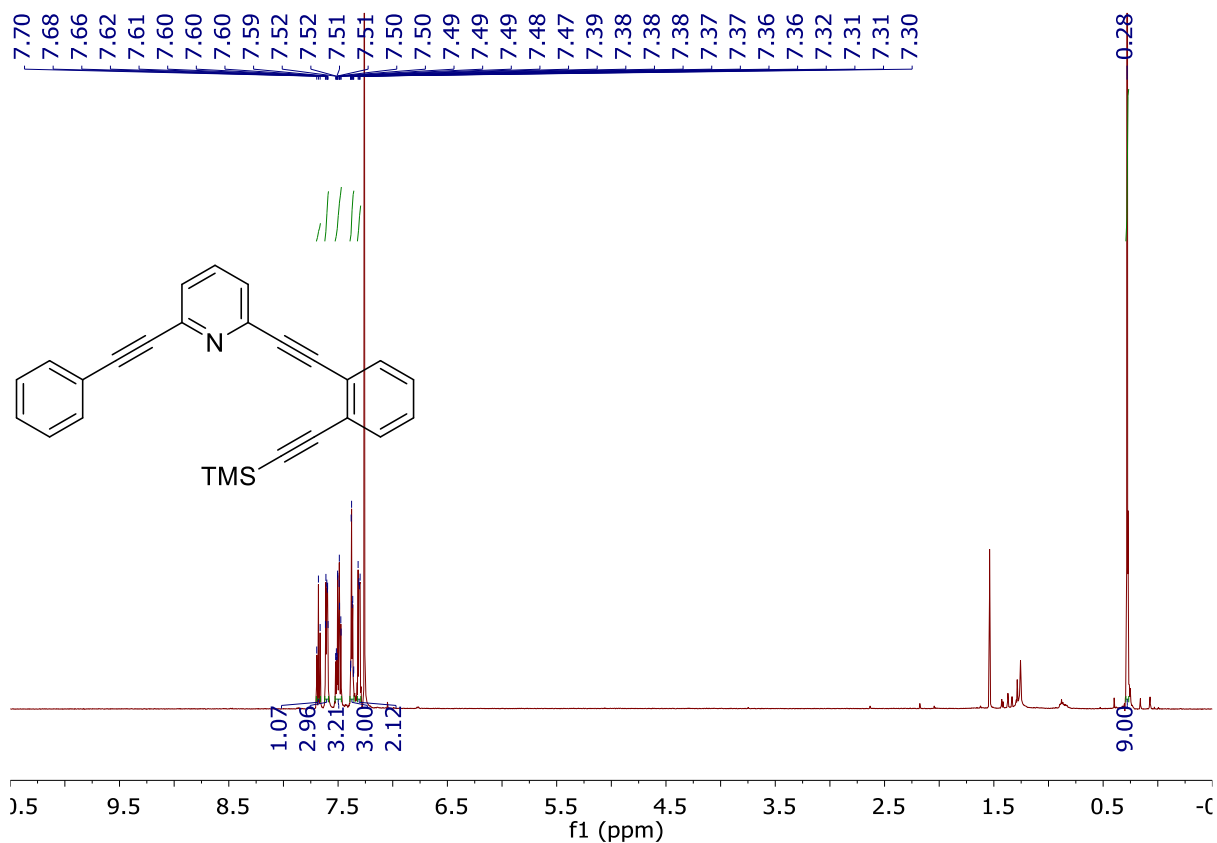
((2-Iodophenyl)ethynyl)trimethylsilane: ^1H NMR (400 MHz, CD_2Cl_2)



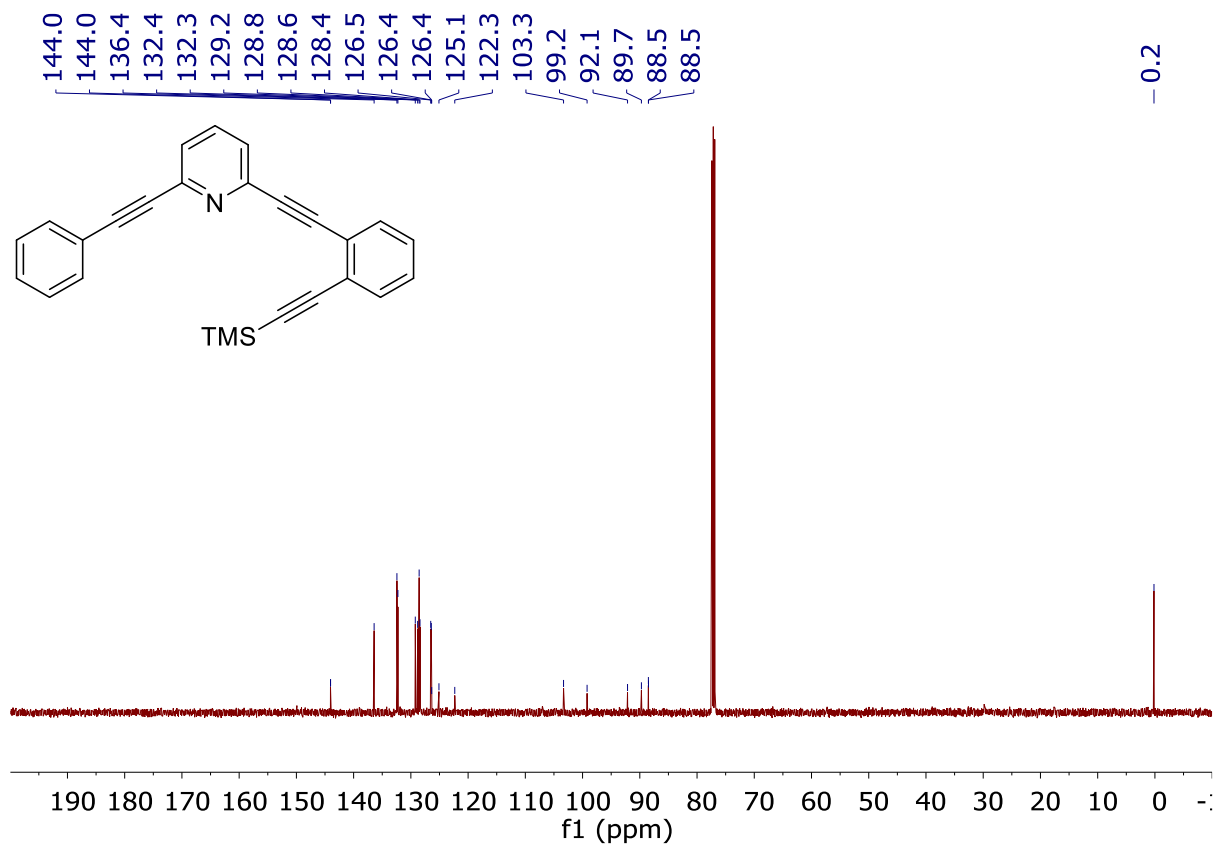
((2-Iodophenyl)ethynyl)trimethylsilane: ^{13}C NMR (100 MHz, CD_2Cl_2)



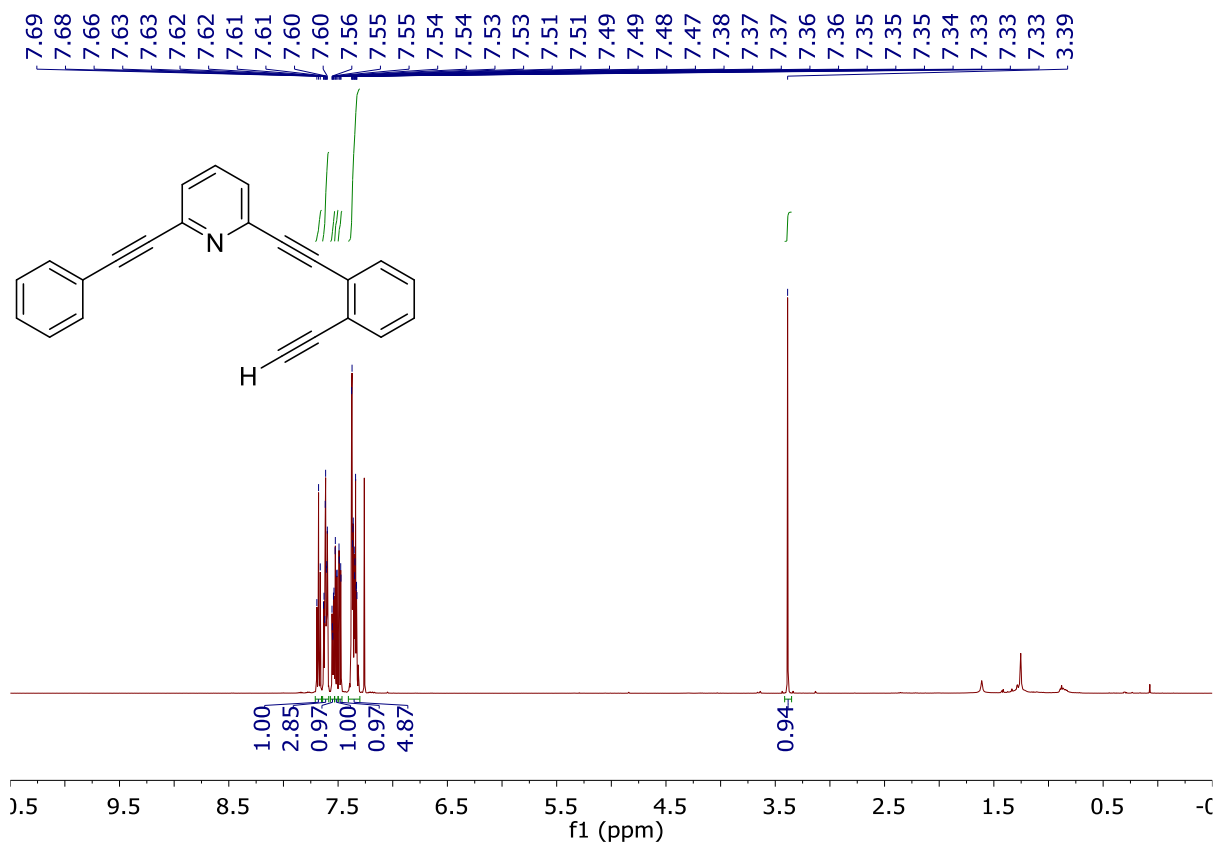
2-(Phenylethynyl)-6-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine: ^1H NMR (500 MHz, CDCl_3)



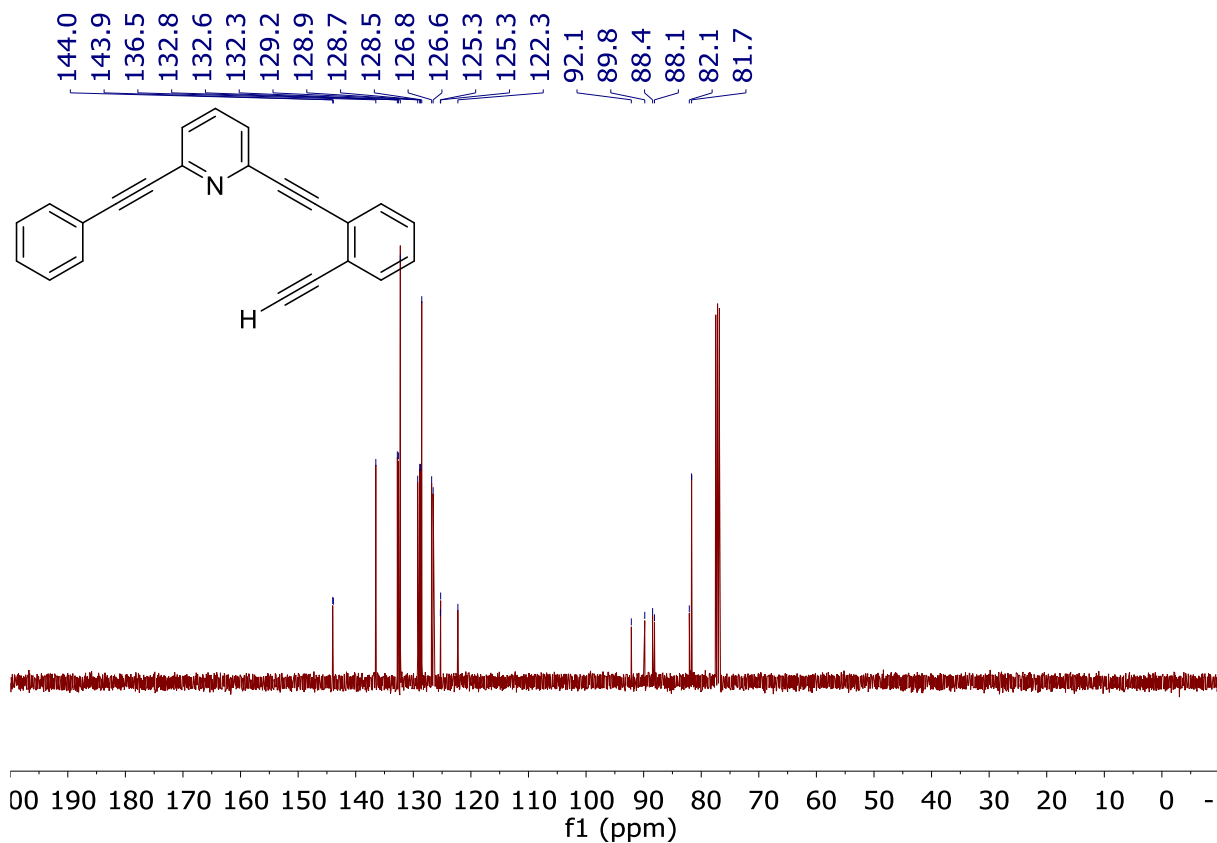
2-(Phenylethynyl)-6-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine: ^{13}C NMR (126 MHz, CDCl_3)



2-((2-Ethynylphenyl)ethynyl)-6-(phenylethynyl)pyridine: ^1H NMR (500 MHz, CDCl_3)

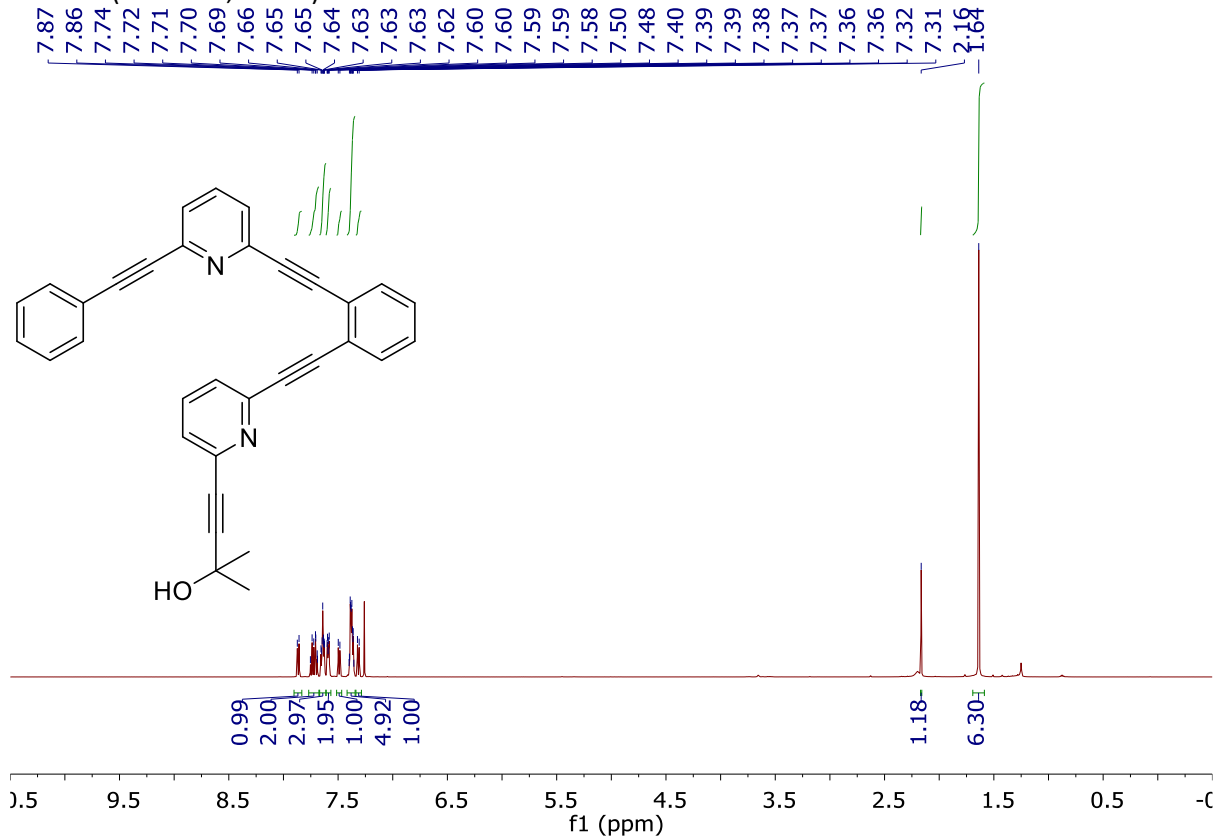


2-((2-Ethynylphenyl)ethynyl)-6-(phenylethynyl)pyridine: ^{13}C NMR (101 MHz, CDCl_3)



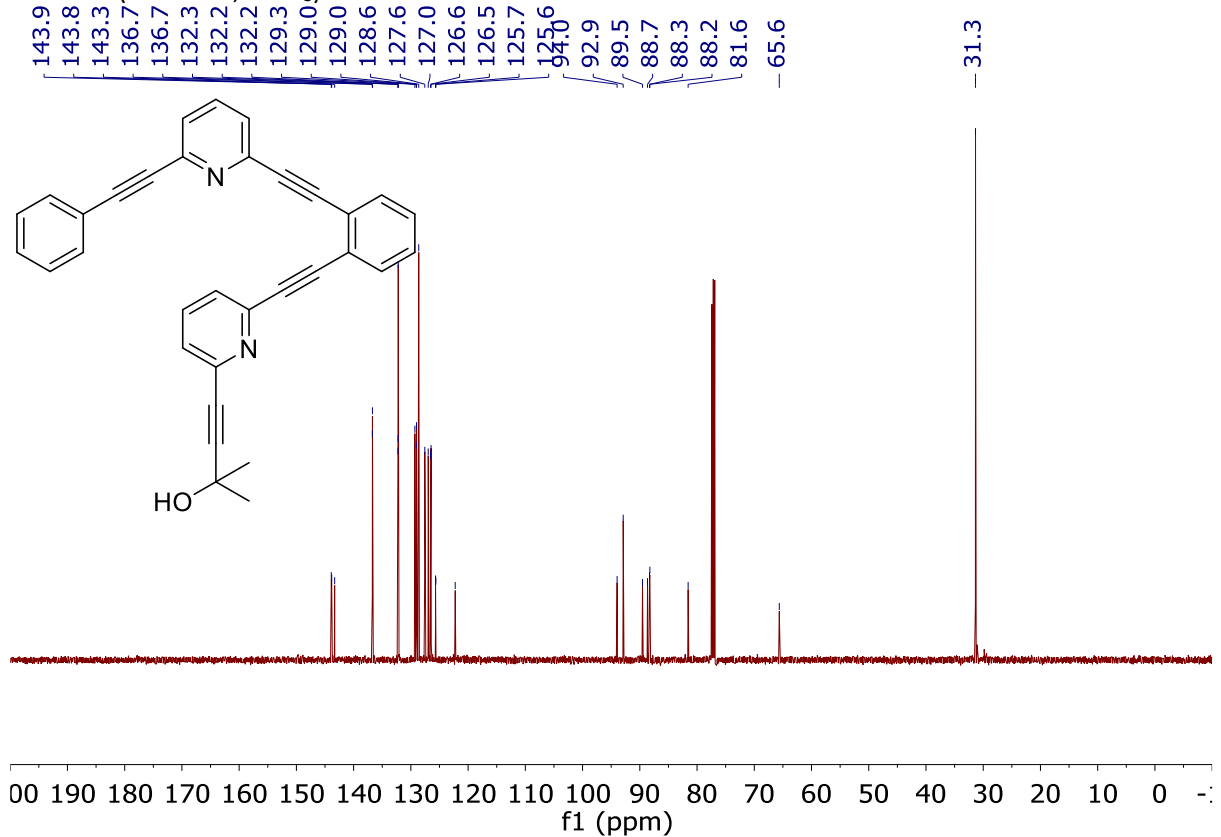
2-Methyl-4-(6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)but-3-yn-2-ol:

¹H NMR (500 MHz, CDCl₃)

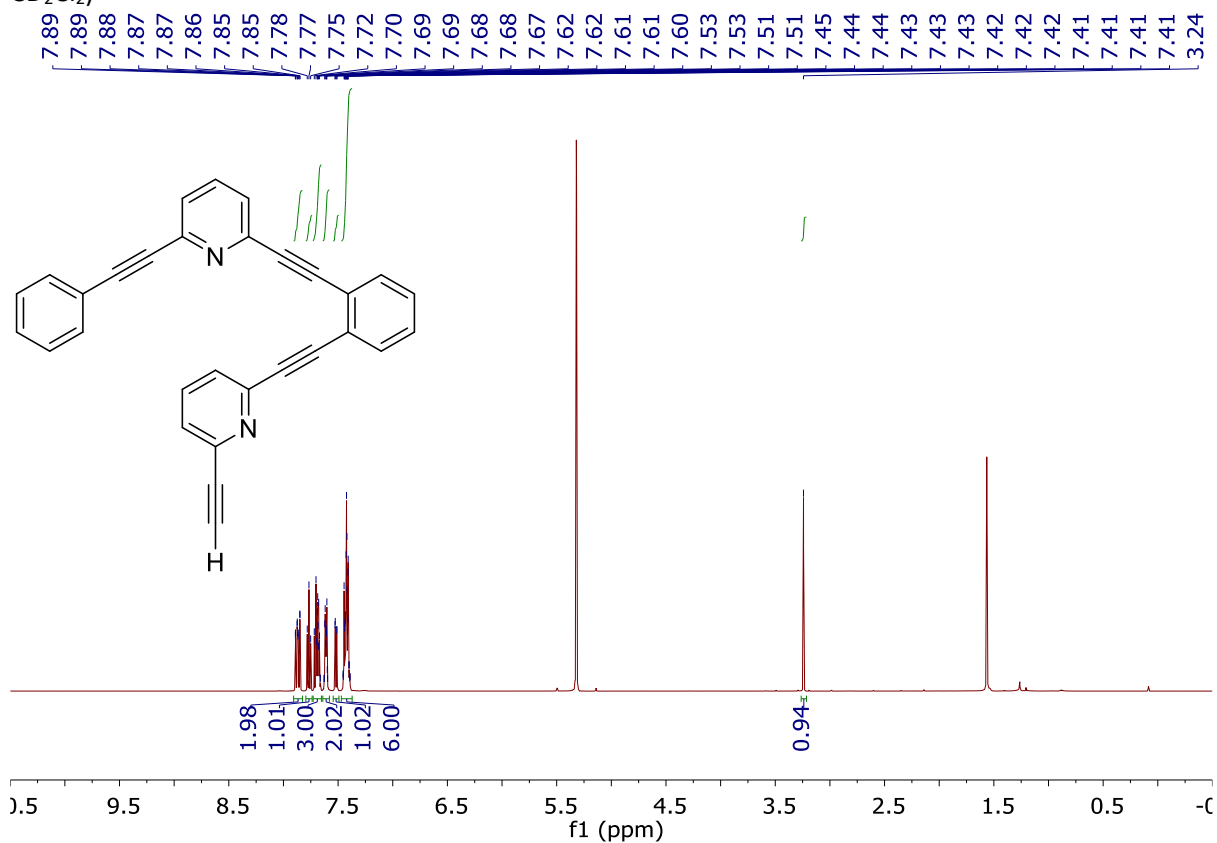


2-Methyl-4-(6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridin-2-yl)but-3-yn-2-ol:

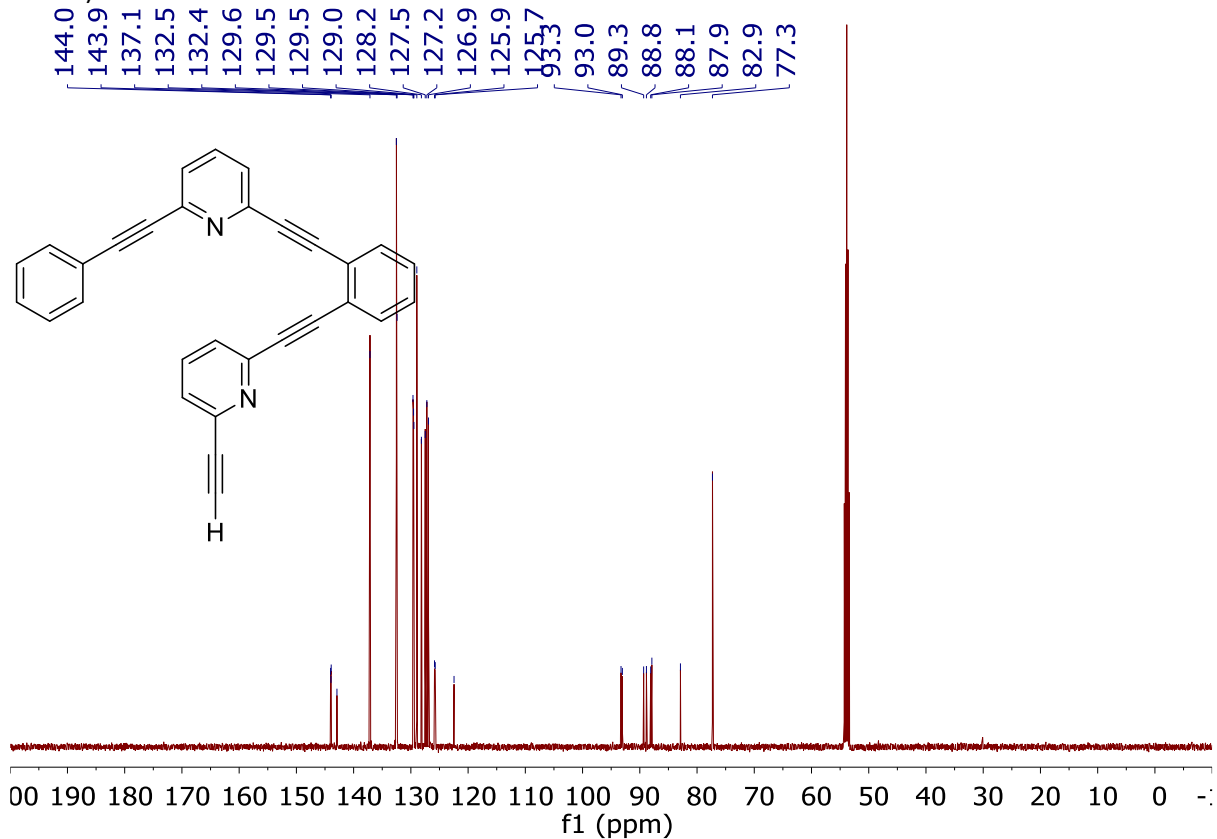
¹³C NMR (126 MHz, CDCl₃)



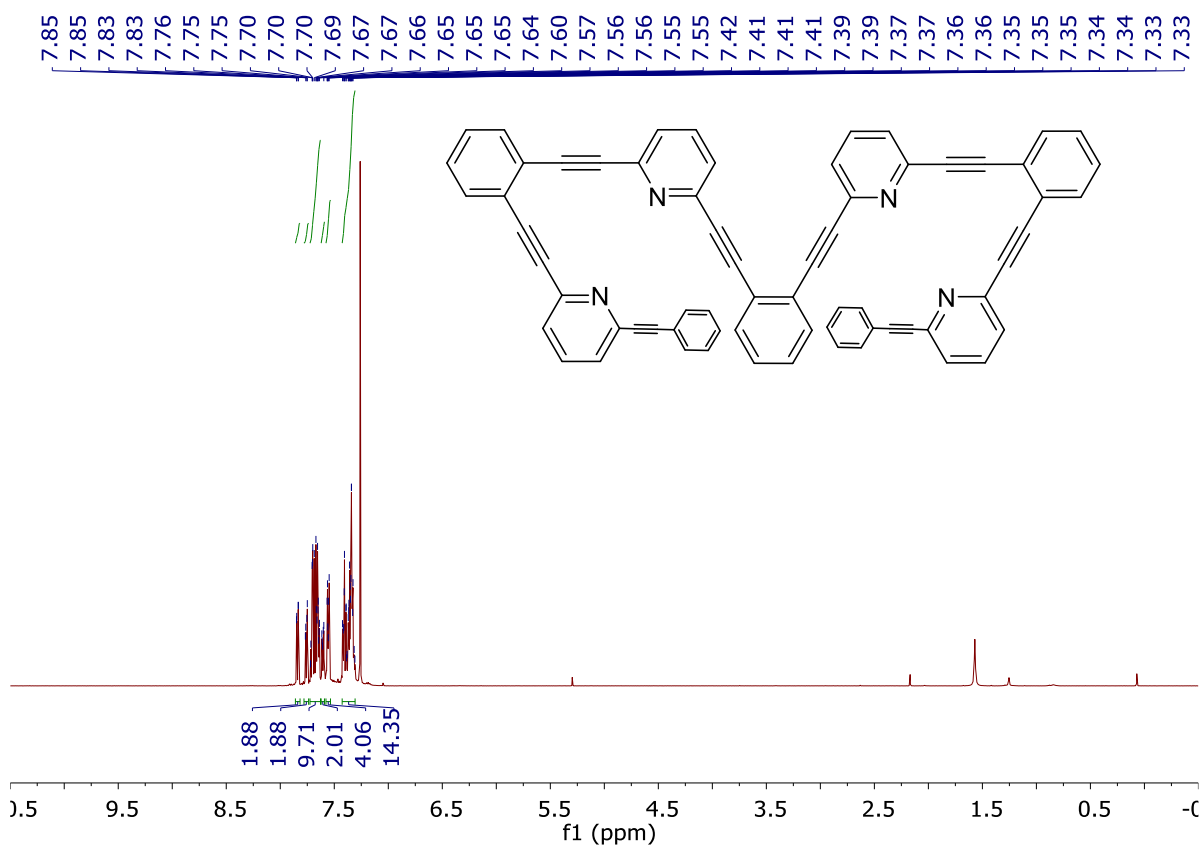
2-Ethynyl-6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridine: ^1H NMR (500 MHz, CD_2Cl_2)



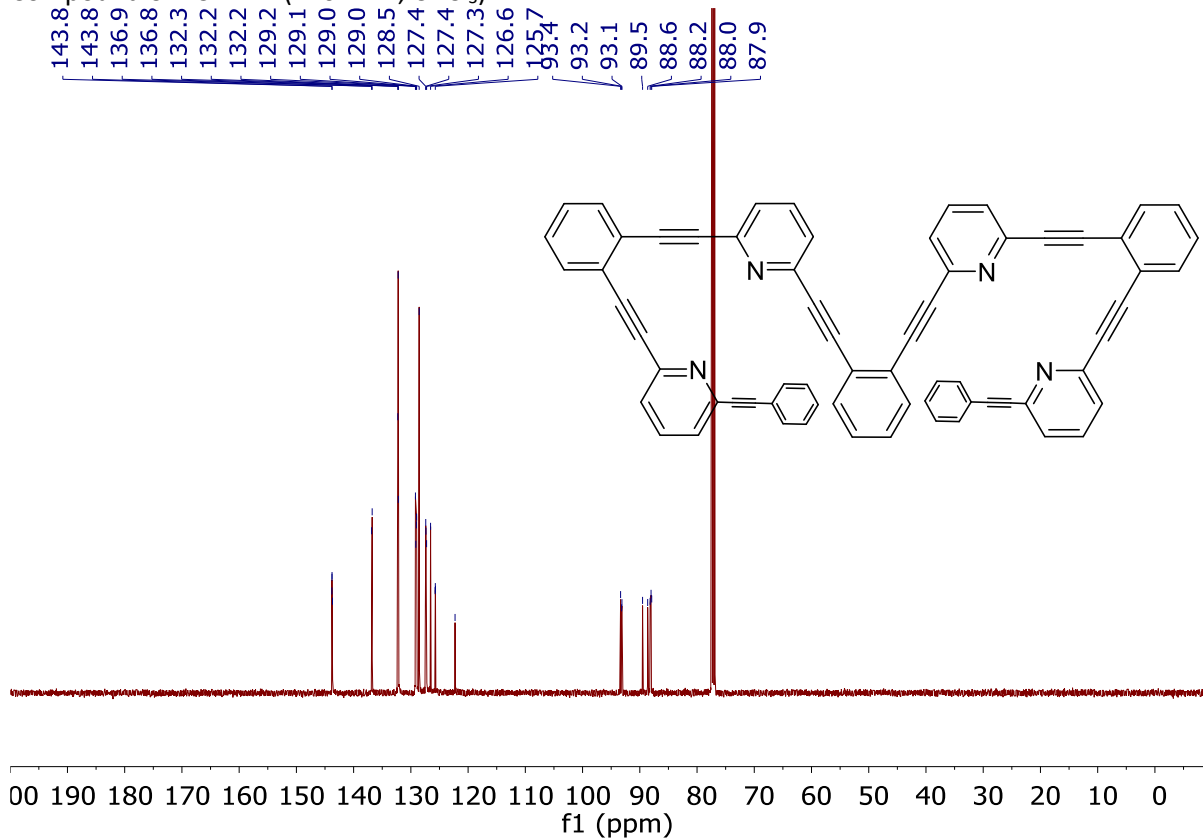
2-Ethynyl-6-((2-((6-(phenylethynyl)pyridin-2-yl)ethynyl)phenyl)ethynyl)pyridine: ^{13}C NMR (126 MHz, CD_2Cl_2)



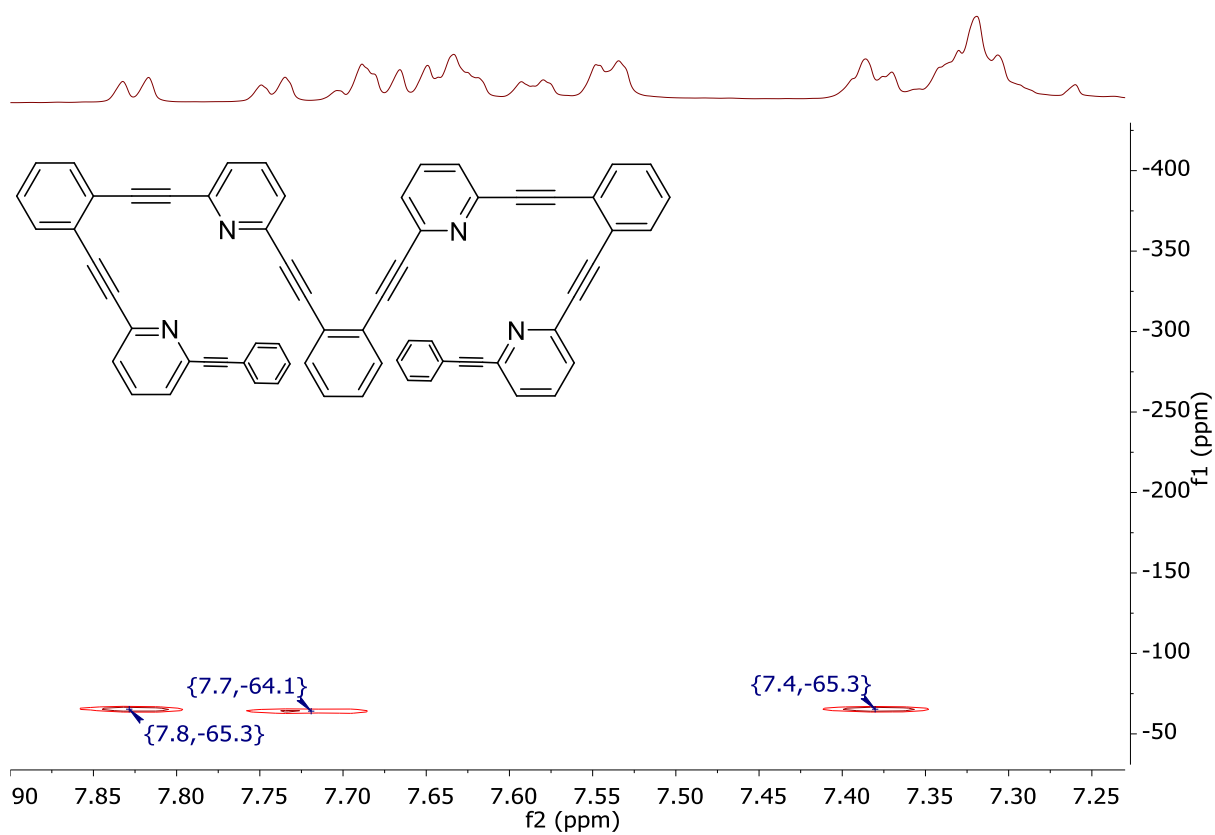
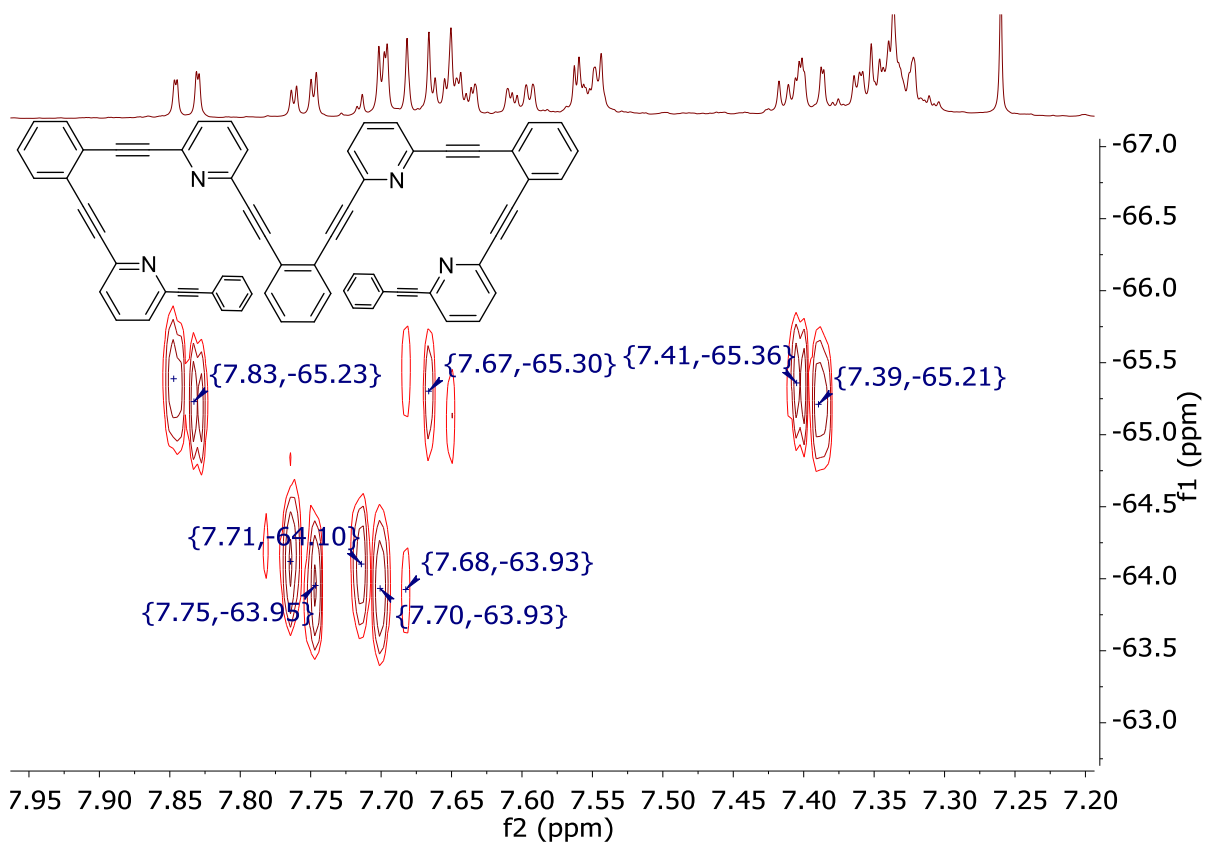
Compound 6: ^1H NMR (500 MHz, CDCl_3)



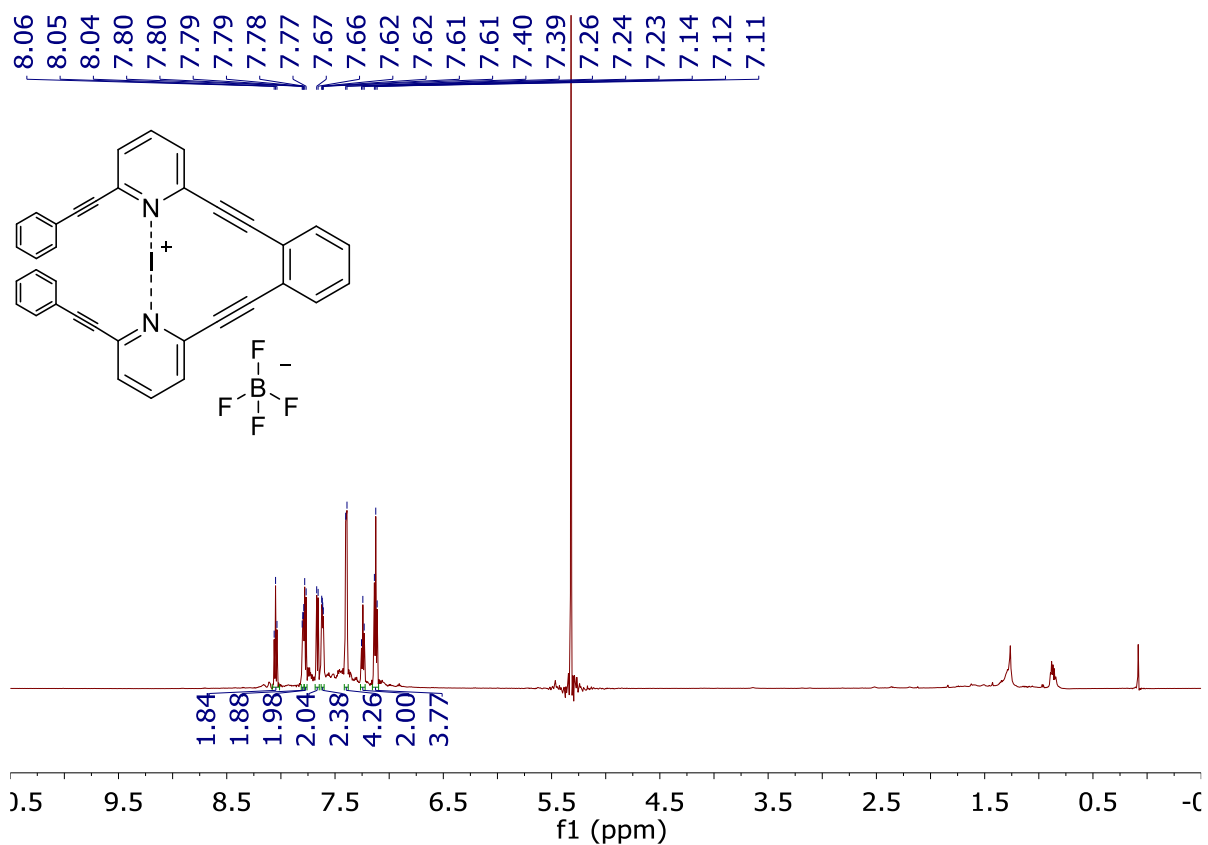
Compound 6: ^{13}C NMR (126 MHz, CDCl_3)



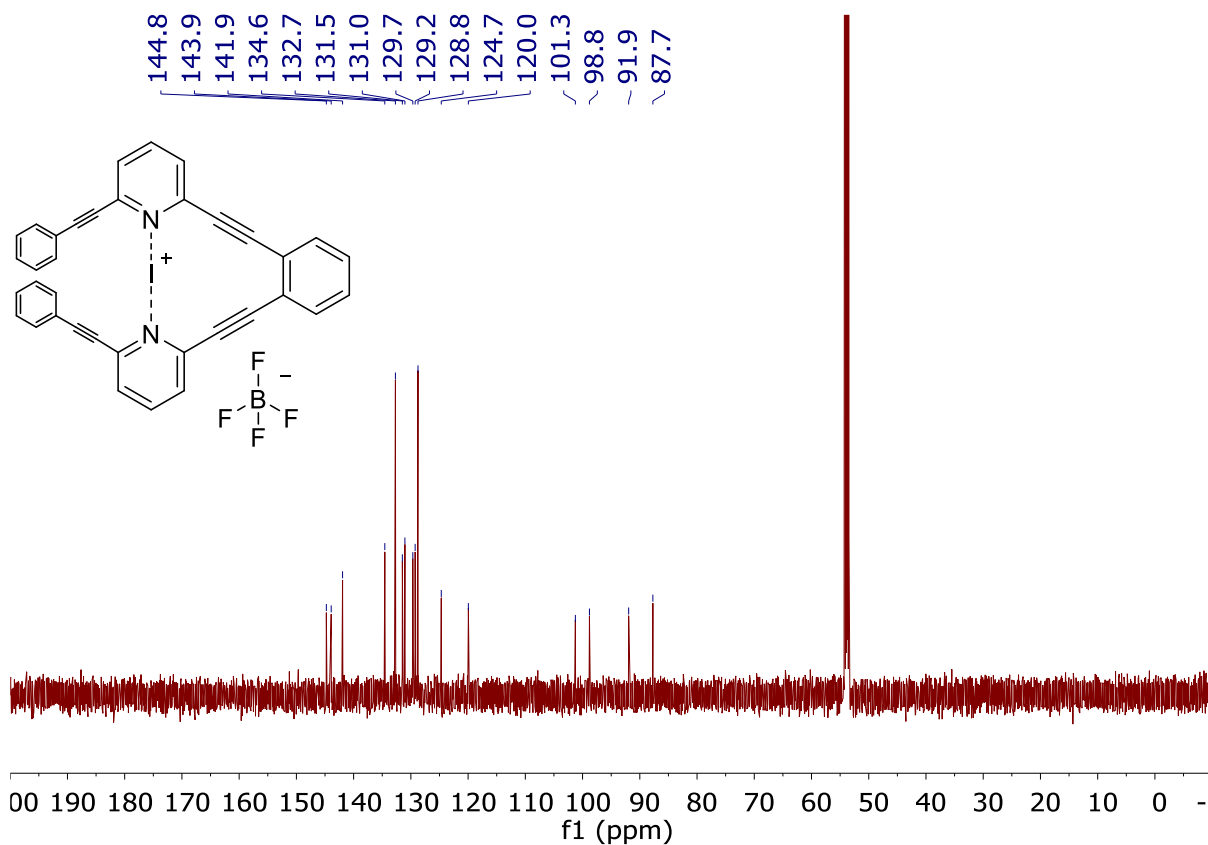
Compound 6: ^1H - ^{15}N HMBC NMR (51 MHz, CDCl_3)



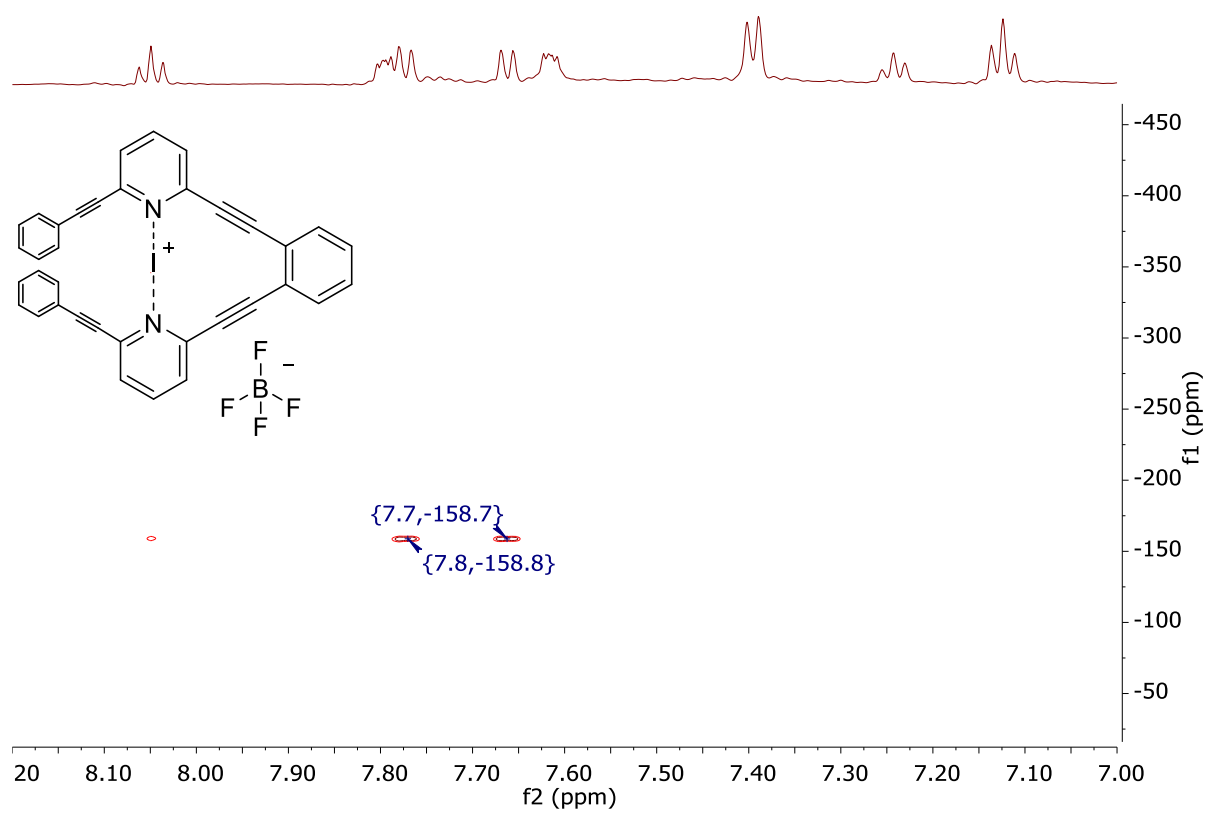
Complex 3: ^1H NMR (600 MHz, CD_2Cl_2)



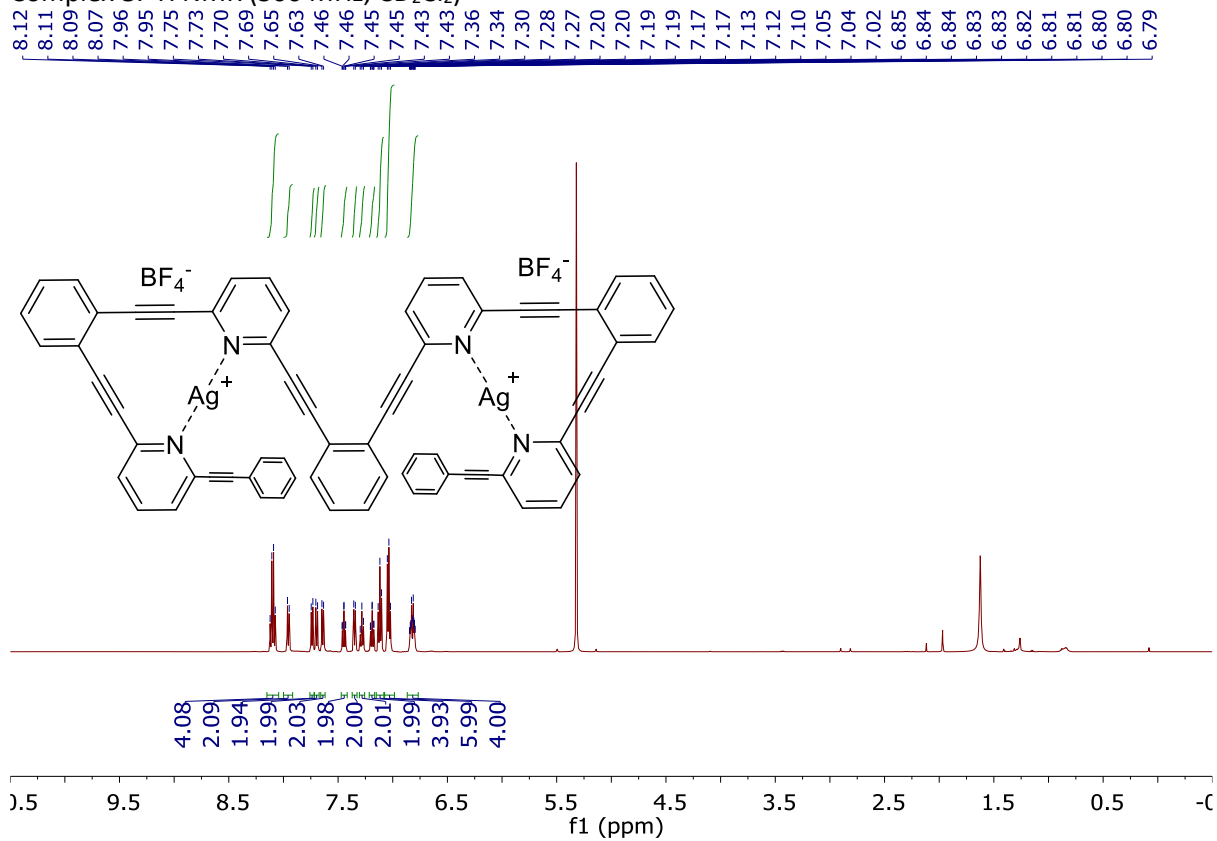
Complex 3: ^{13}C NMR (151 MHz, CD_2Cl_2)



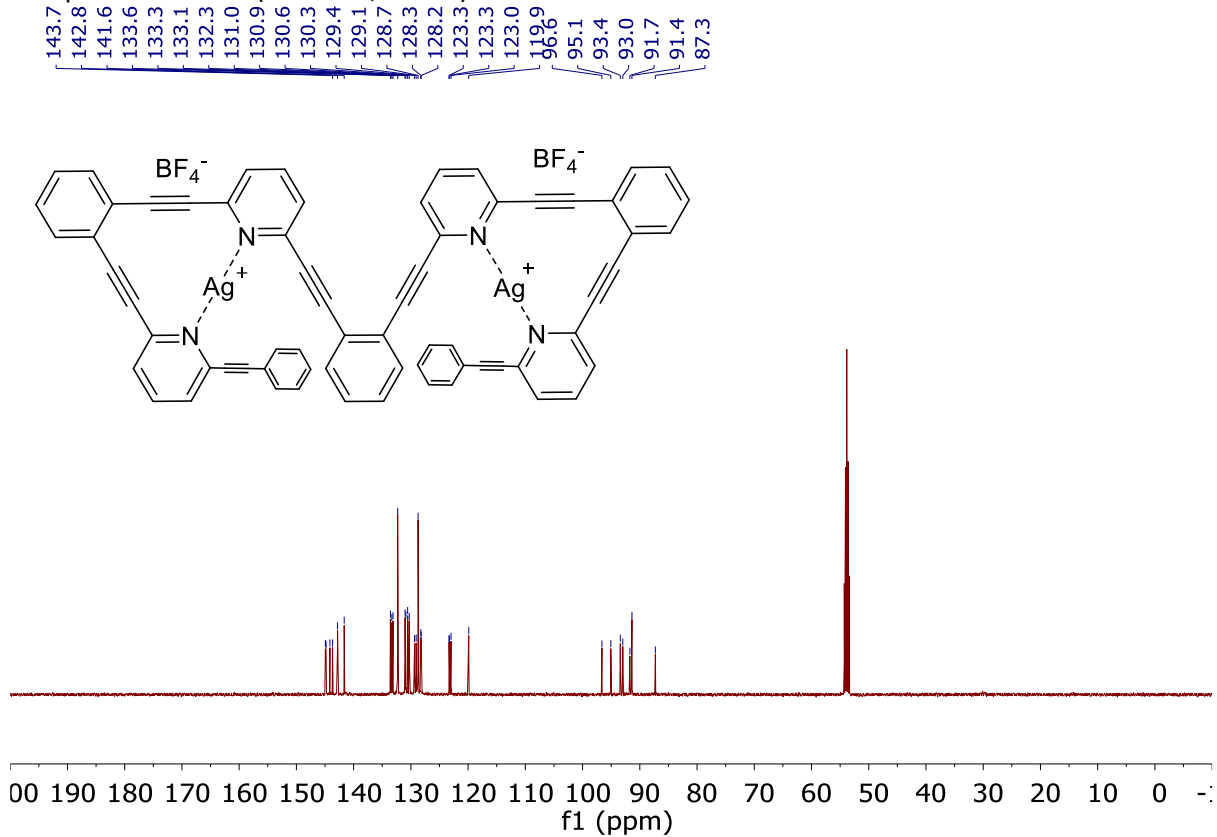
Complex 3: ^1H - ^{15}N HMBC NMR (61 MHz, CD_2Cl_2)



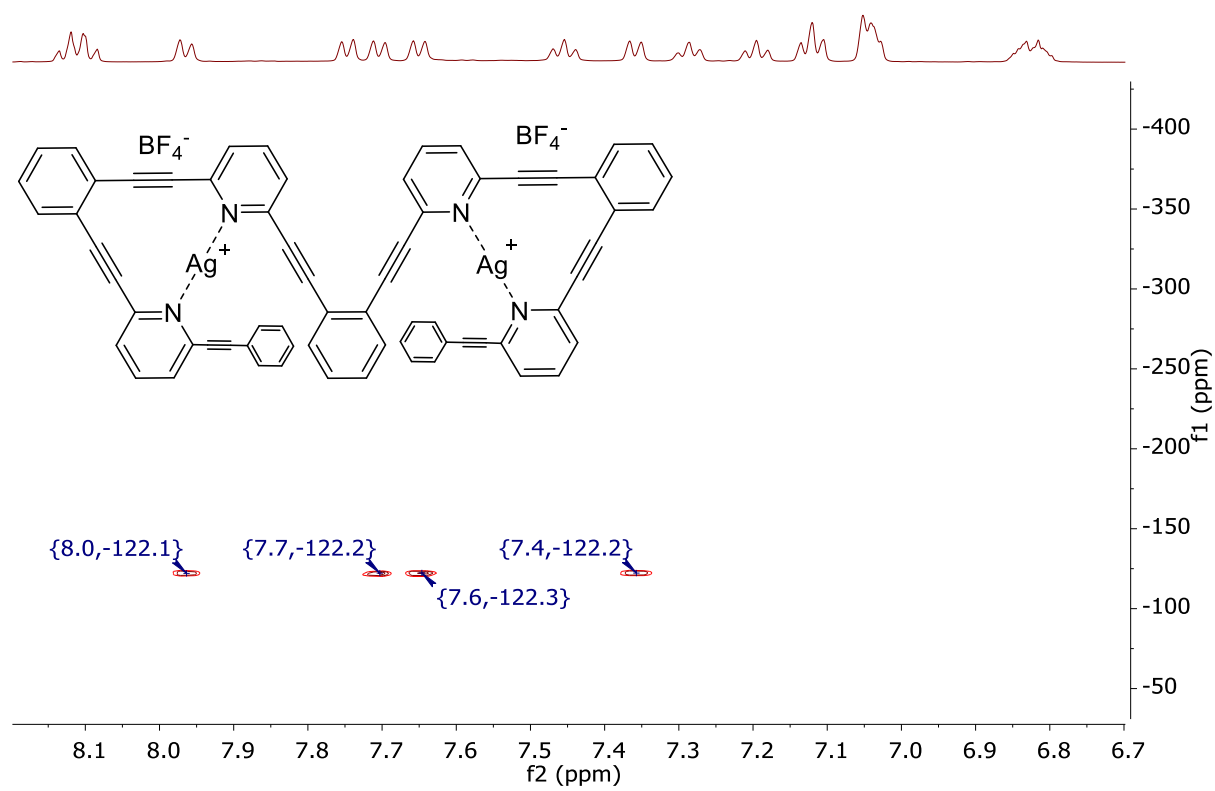
Complex 8: ^1H NMR (500 MHz, CD_2Cl_2)



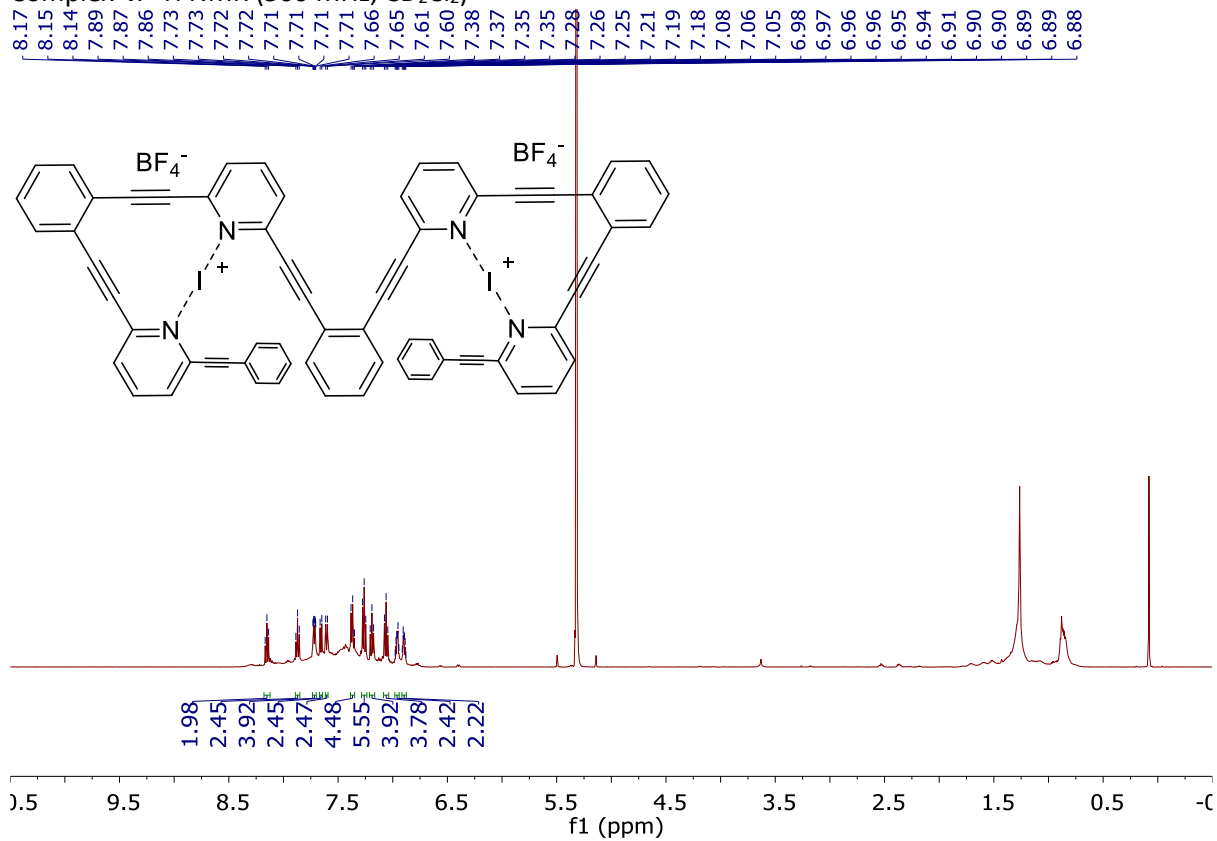
Complex 8: ^{13}C NMR (126 MHz, CD_2Cl_2)



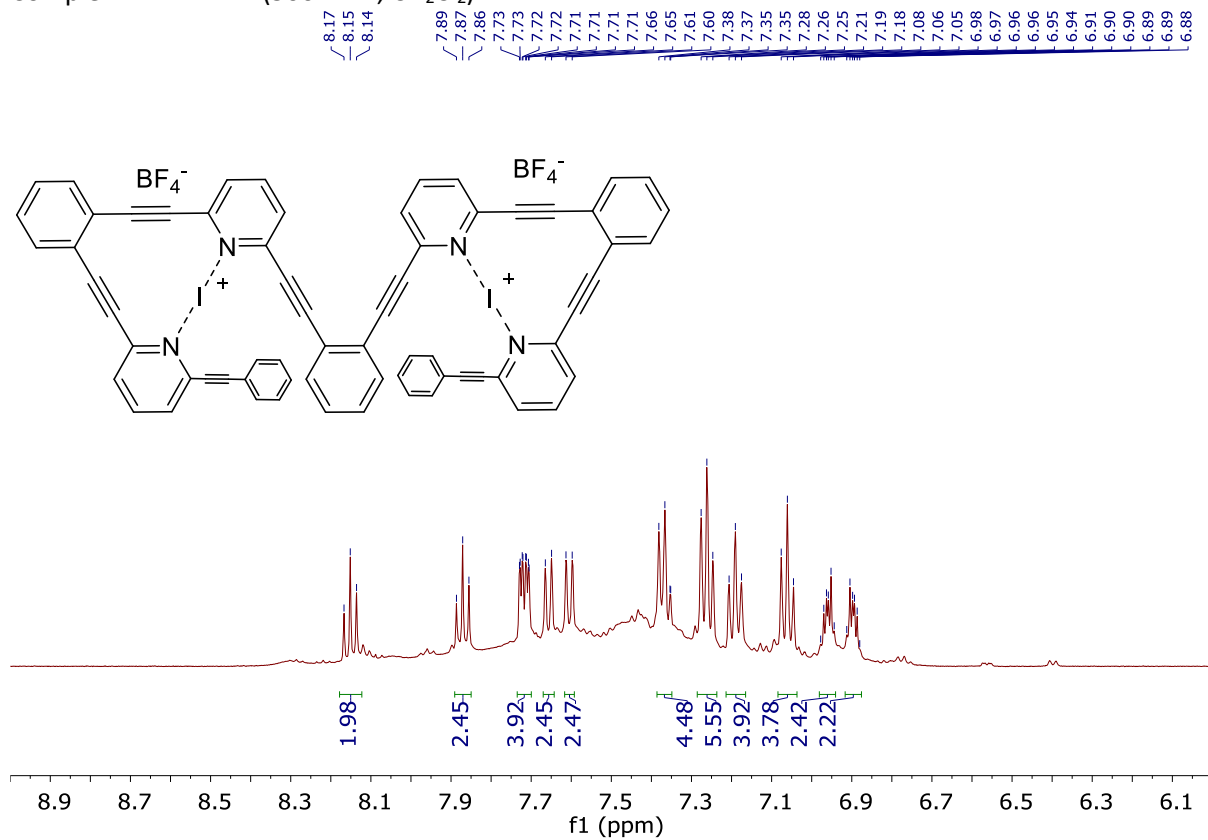
Complex **8**: ^1H - ^{15}N HMBC NMR (51 MHz, CD_2Cl_2)



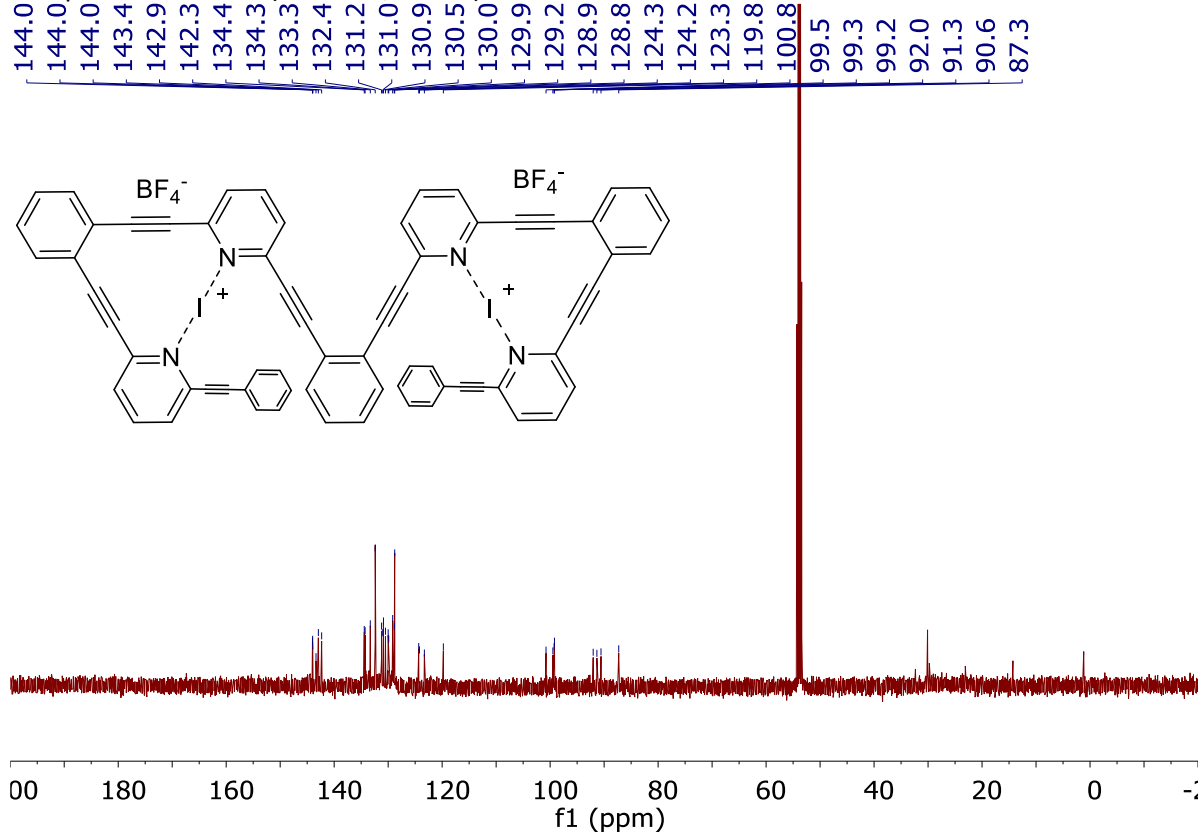
Complex 4: ^1H NMR (500 MHz, CD_2Cl_2)



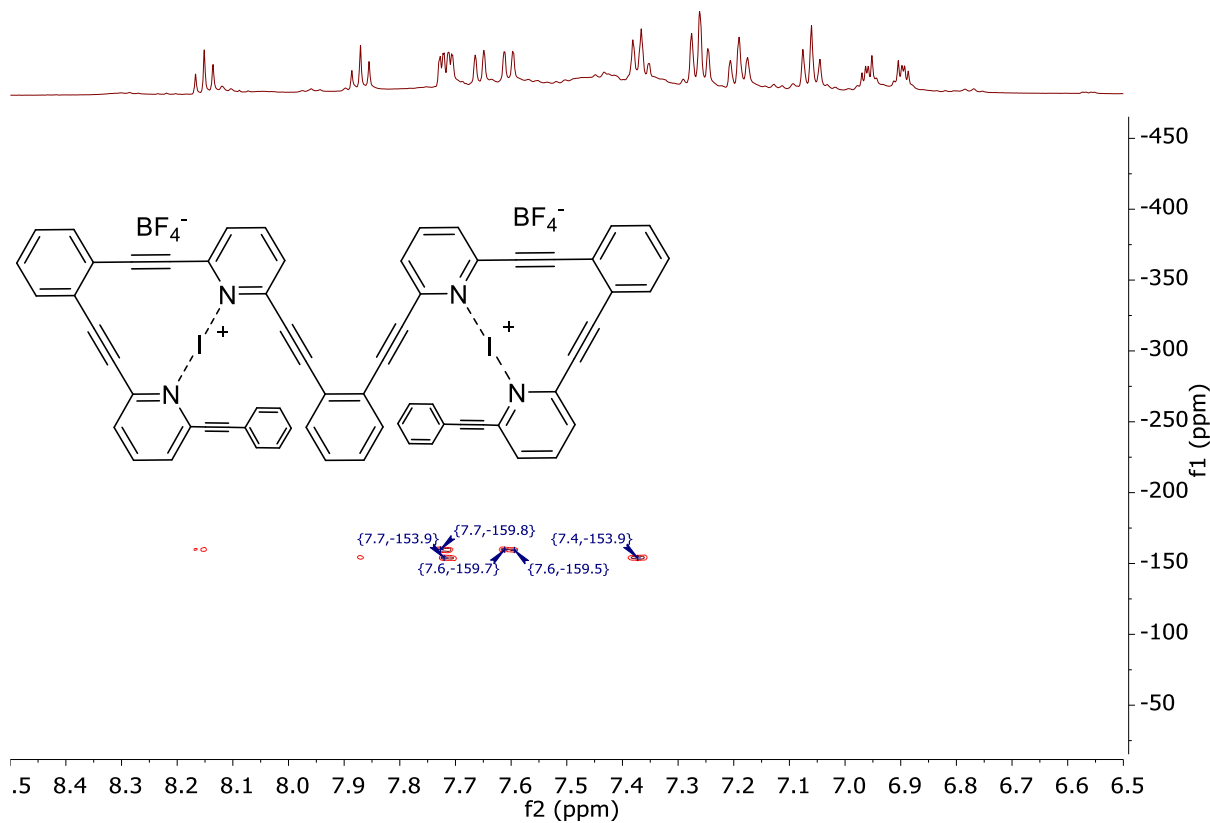
Complex 4: ^1H NMR (500 MHz, CD_2Cl_2)



Complex 4: ^{13}C NMR (126 MHz, CD_2Cl_2)



Complex 4: ^1H - ^{15}N HMBC NMR (51 MHz, CD_2Cl_2)



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