# **Electronic Supplementary Information**

# Modulating Photoswitch Performance with Halogen, Coordinative and Hydrogen Bonding: A Comparison of Relative Bond Strengths

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## Overview



**Figure S1.** Overview of the photoirradiations performed in this work. No isomerization was observed upon irradiation of **1-Ag**. However, *t*-**1** was converted to **1-Ag** in the presence of AgBF<sub>4</sub>. Upon irradiation of **1-I**, decomposition into **1-H** was observed, a compound which was sequentially partially converted into *t*-**1-H** upon continuous irradiation. The non-photoswitchable control compound **2-I** is insensitive to irradiation.

### **1. SYNTHESIS**

#### **1.1. General information**

All chemicals were purchased from commercial suppliers and, unless stated otherwise, used without further purification. CD<sub>2</sub>Cl<sub>2</sub> was dried over molecular sieves (3 Å) and stored in a glovebox. All equipment to be used in a glovebox was dried overnight, *in vacuo* or in an oven (150 °C). LCMS analysis was done on an Agilent 1100 Series HPLC system (C8 column from GRACE Genesis Light) with a Waters MicroMass ZQ mass spectrometer. Acetonitrile with 1% formic acid in MQ-water was used as mobile phase, eluting over 10 min with a gradient of 5-95% acetonitrile. Photoirradiation was performed using an Oriel 1000W Xe ARC light source. NMR spectra were recorded on an Agilent MR-400 with an OneNMR probe, or a Bruker Avance Neo 500 with a TXO cryogenic probe. Chemical shifts are reported on the  $\delta$  scale (ppm), where the residual solvent signal has been used as an internal reference; CDCl<sub>3</sub> ( $\delta^{H}$  7.26,  $\delta^{C}$  77.16), CD<sub>2</sub>Cl<sub>2</sub> ( $\delta^{H}$  5.32,  $\delta^{C}$  53.84) and CD<sub>3</sub>CN ( $\delta^{H}$  1.94,  $\delta^{C}$  118.26, 1.32). The <sup>15</sup>N chemical shifts are referenced to nitromethane ( $\delta^{N}$  0.0 ppm) using the absolute reference function in MestreNova 11.0. Chemical shift ( $\delta$ ), splitting patterns, coupling constants (*J* Hz) and integrals (number of hydrogens) were used to assign the <sup>1</sup>H NMR signals, when necessary supported by 2D NMR data. Resonance multiplicity is denoted as s (singlet), d (doublet), and m (multiplet). The NMR spectra were processed using the software MestreNova 11.0.

#### 1.2. Synthesis



#### (Z)-1,6-Bis(pyridin-2-yl)hexa-3-en-1,5-diyne (1)

Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.610 g, 0.87 mmol) and CuI (0.223 g, 1.17 mmol) was weighed up in a 50 mL round bottom flask with a stir bar. The flask was flushed with Ar (g), sealed with a septum, fitted with an Ar (g) balloon, and continuously flushed for 15 min. It was then placed in an ice bath, and a degassed solution of THF (~20 mL) and *n*-BuNH<sub>2</sub> (1.5 mL, 15.18 mmol) was added. By syringe, *cis*-1,2-dichloroethene (0.39 mL, 5.17 mmol) followed by 2-ethynylpyridine (1.15 mL, 11.39 mmol) was added. The mixture was then left stirring, allowing the ice bath to melt and reach room temperature. After 1 day, more 2-ethynylpyridine (0.50 mL, 4.95 mmol) was added. After an additional 3 days, the solution was concentrated by blowing with air, and purified on a silica column using air pressure, eluting with CH<sub>3</sub>CN. Further purification by prepTLC (EtOAc, 2 mm silica layer) yielded **1** (70.8 mg, 0.31 mmol, 6%).<sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>)  $\delta$  8.62 (m, 2H, H2/2'), 7.66 (ddd, *J* = 7.7, 7.6 and 1.8 Hz, 2H, H4/4'), 7.58 (m, 2H, 5/5'), 7.24 (ddd, *J* = 7.6, 4.9, and 1.2 Hz) 2H, H3/3'), 6.20 (s, 2H, H9/9'); <sup>13</sup>C NMR (101 MHz, 25 °C, CDCl<sub>3</sub>)  $\delta$  150.3 (C2/2'), 143.3 (C6/6'), 136.2 (C4/4'), 127.8 (C5/5'), 123.2 (C3/3'), 120.7 (C9/9'), 97.0 (C7/7'), 86.6 (C8/8'); <sup>15</sup>N NMR (51 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -62.0 (N1/1'); MS (ESI) *m/z* 231.2 [M+H]<sup>+</sup>.



#### [(Z)-1,6-Bis(pyridin-2-yl)hexa-3-en-1,5-diyne silver(I)]<sup>+</sup> tetrafluoroborate (1-Ag) in CD<sub>2</sub>Cl<sub>2</sub>

**1** (6.0 mg, 0.026 mmol) was dried *in vacuo* in an NMR tube overnight. In a glovebox, it was dissolved in dry CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL). The solution was transferred to a 4 mL glass vial with AgBF<sub>4</sub> (5.4 mg, 0.028 mmol). The vial was shaken to allow AgBF<sub>4</sub> to dissolve. The solution, containing **1-Ag**, was transferred back to the NMR tube, which was sealed with a septum and parafilm. <sup>1</sup>H NMR (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.98 (m, 2H, H2/2'), 7.97 (m, 2H, H4/4'), 7.74 (m, 2H, H5/5'), 7.62 (m, 2H, H3/3'), 6.42 (s, 2H, H9/9'); <sup>13</sup>C NMR (126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  153.8 (C2/2'), 143.1 (C6/6'), 139.9 (C4/4'), 128.9 (C5/5'), 126.0 (C3/3'), 121.9 (C9/9'), 97.2 (C7/7' or C8/8'), 89.9 (C8/8' or C7/7'); <sup>15</sup>N NMR (51 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -115.1 (N1/1').



#### [(Z)-1,6-Bis(pyridin-2-yl)hexa-3-en-1,5-diyne silver(I)]<sup>+</sup> tetrafluoroborate (1-Ag) in CD<sub>3</sub>CN

**1** (1.9 mg, 0.008 mmol) was dissolved in CD<sub>3</sub>CN (0.5 mL). The solution was transferred to a 4 mL glass vial with AgBF<sub>4</sub> (1.6 mg, 0.008 mmol). The vial was shaken to allow AgBF<sub>4</sub> to dissolve. The solution, containing **1-Ag**, was transferred to an NMR tube. <sup>1</sup>H NMR (400 MHz, 25 °C, CD<sub>3</sub>CN)  $\delta$  8.67 (m, 2H, H2/2'), 7.96 (ddd, *J* = 7.8, 7.7 and 1.7 Hz, 2H, H4/4'), 7.73 (m, 2H, H5/5'), 7.56 (m, 2H, H3/3'), 6.44 (s, 2H, H9/9'); <sup>13</sup>C NMR (101 MHz, 25 °C, CD<sub>3</sub>CN)  $\delta$  152.5 (C2/2'), 143.5 (C6/6'), 139.7 (C4/4'), 129.3 (C5/5'), 125.9 (C3/3'), 122.4 (C9/9'), 94.6 (C7/7' or C8/8'), 89.0 (C8/8' or C7/7').



#### [(Z)-1,6-Bis(pyridin-2-yl)hexa-3-en-1,5-diyne iodine(I)]<sup>+</sup> tetrafluoroborate (1-I)

**1** (4.5 mg, 0.020 mmol) was dried *in vacuo* in an NMR tube overnight. In a glovebox, it was dissolved in dry CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL). The solution was transferred to a 4 mL glass vial with AgBF<sub>4</sub> (6.3 mg, 0.032 mmol), washing the tube with CD<sub>2</sub>Cl<sub>2</sub> (0.1 mL). I<sub>2</sub> (6.8 mg, 0.027 mmol) was added, and the vial was shaken to allow AgI to precipitate. The slightly pink supernatant, containing **1-I**, was transferred back to the NMR tube, which was sealed with a septum and parafilm. <sup>1</sup>H NMR (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.88 (ddd, *J* = 5.6, 1.4, 0.6 Hz, 2H, H2/2'), 8.16 (ddd, *J* = 7.9, 7.8, 1.4 Hz, 2H, H4/4'), 7.80 (ddd, *J* = 7.9, 1.3, 0.6 Hz, 2H, H5/5'), 7.51 (ddd, *J* = 7.8, 5.6, 1.3 Hz, 2H, H3/3'), 6.47 (s, 2H, H9/9'); <sup>13</sup>C NMR (126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  151.6 (C2/2'), 142.7 (C4/4'), 142.5 (C6/6'), 130.9 (C5/5'), 127.4 (C3/3'), 123.7 (C9/9'), 97.6 (C8/8'), 95.4 (C7/7'); <sup>15</sup>N NMR (51 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -161.0 (N1/1').



#### (Z)-2-(6-(Pyridin-2-yl)hexa-3-en-1,5-diyn-1-yl)pyridin-1-ium tetrafluoroborate (1-H)

**1** (3.0 mg, 0.013 mmol) was dissolved in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL). The solution was transferred to a 4 mL glass vial with I<sub>2</sub> (3.2 mg, 0.013 mmol) and H<sub>2</sub>O (1 drop) was added. The resulting solution was transferred to another vial with AgBF<sub>4</sub> (2.5 mg, 0.013 mmol). After shaking the vial, the solution was filtered by syringe filter into an NMR tube. The tube was then allowed to stand for 4 days. <sup>1</sup>H NMR (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.78 (m, 2H, H2/2'), 8.00 (ddd, *J* = 7.8, 7.7 and 1.6 Hz, 2H, H4/4'), 7.73 (m, 2H, H5/5'), 7.58 (ddd, *J* = 7.7, 5.2 and 1.2 Hz, 2H, H3/3'), 6.37 (s, 2H, H9/9').



### 1,2-Bis(pyridin-2-ylethynyl)benzene (2)

Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.542 g, 0.77 mmol) and CuI (0.161 g, 0.85 mmol) was added to a microwave vial and kept under Ar (g). Et<sub>3</sub>N (12 mL, 86.10 mmol), 1,2-diiodobenzene (1 mL, 7.65 mmol) and DMF (4 mL) was added by syringe, and the mixture was shortly stirred. 2-ethynylpyridine (1.8 mL, 17.82 mmol) was then added, followed by immediate irradiation by microwave for 9 min at 120 °C. The black reaction mixture was filtered through celite, washing with CH<sub>2</sub>Cl<sub>2</sub> (~120 mL). EDTA (0.560 g, 1.92 mmol) was added, and the solution stirred for 55 min before it was filtered through celite again, washing with more CH<sub>2</sub>Cl<sub>2</sub> (~50 mL). The solution was then washed with H<sub>2</sub>O (115 mL), and the resulting aqueous phase was extracted 3 times with CH<sub>2</sub>Cl<sub>2</sub> (tot. ~100 mL). The combined organic phases were concentrated *in vacuo* to give a black liquid crude, which was purified two sequential times on silica using column chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>:EtOAc 95:5→80:20 and EtOAc:hexanes 2:3→7:3, respectively. This generated **2** as an orange solid (1.366 g, 4.87 mmol, 64 %). <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>)  $\delta$  8.64 (m, H2/2'), 7.63-7.72 (m, H5/5', H4/4', and H10/10'), 7.37 (BB' part of AA'BB', H11/11'), 7.27 (m, H3/3').



#### [(1,2-Bis(pyridin-2-ylethynyl)benzene)iodine(I)]<sup>+</sup> tetrafluoroborate (2-I)

1,2-Bis(pyridin-2-ylethynyl)benzene (5.1 mg, 0.018 mmol) was dried *in vacuo* overnight. In a glovebox, it was dissolved in dry CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL). The solution was transferred to a 4 mL glass vial with AgBF<sub>4</sub> (4.0 mg, 0.021 mmol). I<sub>2</sub> (5.4 mg, 0.021 mmol) was added, and the vial was shaken to allow AgI to precipitate. The slightly pink supernatant, containing **2-I**, was filtered by syringe to an NMR tube, which was sealed with a septum and parafilm. <sup>1</sup>H NMR (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.82 (ddd, *J* = 5.6, 1.5 and 0.8 Hz, 2H, H2/2'), 8.16 (ddd, *J* = 7.9, 7.7 and 1.5 Hz) 2H, H4/4'), 7.88 (ddd, *J* = 7.9, 1.4 and 0.8 Hz, 2H, H5/5'), 7.75 (AA' part of AA'BB', 2H, H10/10'), 7.56 (BB' part of AA'BB', 2H, H11/11'), 7.47 (ddd, *J* = 7.7, 5.6 and 1.4 Hz, 2H, H3/3'); <sup>15</sup>N NMR (51 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  –164.7 (N1/1').

## **1.3.** Photoirradiation

For the photoirradiation, an Oriel 1000 W Xe ARC light source was used. The sample was placed into an NMR tube, which was clamped over a crystallization dish with dry ice for cooling (Fig. S2).



**Figure S2.** Illustration of the set up used for photoirradiation. A Xe ARC 1000 W lamp equipped with water-cooling, and a lens to focus the irradiation on to the sample was used to irradiate a sample in an NMR tube that is held over a crystallization dish filled with dry ice for cooling.

## 2. NMR SPECTRA

# 2.1. Synthesized compounds



Figure S3. The <sup>1</sup>H NMR spectrum of 1 (400 MHz, 25 °C, CDCl<sub>3</sub>).



Figure S4. The <sup>13</sup>C NMR spectrum of 1 (101 MHz, 25 °C, CDCl<sub>3</sub>).



Figure S5. The TOCSY spectrum of 1 (400 MHz, 25 °C, CDCl<sub>3</sub>).



Figure S6. The <sup>1</sup>H,<sup>13</sup>C HSQC spectrum of **1** (400 and 101 MHz, 25 °C, CDCl<sub>3</sub>).



Figure S7. The  ${}^{1}$ H, ${}^{13}$ C HMBC spectrum of 1 (400 and 101 MHz, 25 °C, CDCl<sub>3</sub>).



Figure S8. The <sup>1</sup>H NMR spectrum of 1 (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S9. The <sup>13</sup>C NMR spectrum of 1 (126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S10. The  ${}^{1}$ H, ${}^{13}$ C HSQC spectrum of 1 (500 and 126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



**Figure S11.** The <sup>1</sup>H,<sup>13</sup>C HMBC spectrum of **1** (500 and 126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S12. The  ${}^{1}$ H, ${}^{15}$ N HMBC spectrum of 1 (500 and 51 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S13. The <sup>1</sup>H NMR spectrum of 1 (400 MHz, 25 °C, CD<sub>3</sub>CN).



Figure S14. The  ${}^{13}$ C NMR spectrum of 1 (101 MHz, 25 °C, CD<sub>3</sub>CN).



Figure S15. The <sup>1</sup>H NMR spectrum of 1-I (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S16. The  ${}^{13}$ C NMR spectrum of 1-I (126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S17. The <sup>1</sup>H,<sup>13</sup>C HSQC spectrum of 1-I (500 and 126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



**Figure S18.** The <sup>1</sup>H,<sup>13</sup>C HMBC spectrum of **1-I** (500 and 126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



**Figure S19.** The <sup>1</sup>H,<sup>15</sup>N HMBC spectrum of **1-I** (500 and 51 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S20. The <sup>1</sup>H NMR spectrum of 1-Ag (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S21. The  ${}^{13}$ C NMR spectrum of 1-Ag (126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S22. The  ${}^{1}$ H, ${}^{13}$ C HSQC spectrum of 1-Ag (500 and 126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S23. The <sup>1</sup>H,<sup>15</sup>N HMBC spectrum of 1-Ag (500 and 51 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S24. The <sup>1</sup>H NMR spectrum of 1-Ag (400 MHz, 25 °C, CD<sub>3</sub>CN).



Figure S25. The  ${}^{13}$ C NMR spectrum of 1-Ag (101 MHz, 25 °C, CD<sub>3</sub>CN).



Figure S26. The <sup>1</sup>H NMR spectrum of 1-H (400 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S27. The <sup>1</sup>H NMR spectrum of 2-I (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



**Figure S28.** The <sup>1</sup>H,<sup>15</sup>N HMBC spectrum of **2-I** (500 and 51 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>).



Figure S29. The <sup>1</sup>H NMR spectrum of 2 (400 MHz, 25 °C, CDCl<sub>3</sub>).



.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 f1 (ppm)

**Figure S30.** Breaking the iodine(I) complex **1-I** (19.5  $\mu$ mol, lowest spectrum) by sequential addition of H<sub>2</sub>O (~20  $\mu$ L, second lowest spectrum) and TFA (~2  $\mu$ L, second top spectrum) gave only a small amount of protonated complex as observed by <sup>1</sup>H NMR (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>). Conversion to the protonated form was observed directly upon addition of TFA. The day after (top spectrum) the **1-H** complex had formed almost completely, while trace amounts of iodine(I) complex **1-I** could still be detected. The **1-H** complex is marked by the blue lines, and **1-I** of the two spectra on top is marked by pink.



**Figure S31.** The <sup>13</sup>C spectrum (126 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>) of **1-I** (19.5 µmol, lowest) did not change directly after addition of H<sub>2</sub>O (~20 µL) and TFA (~2 µL, second lowest spectrum). However, after standing for 4 days (middle spectrum), conversion to **1-H** was observed. The chemical shifts are readily influenced by addition of aqueous NaOH (top and second top spectra), indicating that the **1-H** complex was formed upon standing for 4 days.

**Table S1.** The <sup>15</sup>N chemical shift (51 MHz, 25 °C,  $CD_2Cl_2$ ) of **1-I** was not influenced by the addition of H<sub>2</sub>O or TFA until the sample had been standing for 4 days; giving the **1-H** complex enough time to form. Addition of aqueous solution of NaOH affected the chemical shift in agreement with changing the degree of protonation.

Addition	<sup>15</sup> Ν δ
c-1-I	-161.0
$+ H_2O (20 \ \mu L)$	-161.4
+ H <sub>2</sub> O (20 µL) + TFA (2 µL)	-161.7
+ H <sub>2</sub> O (20 µL) + TFA (2 µL) + 4 days	-155.9
+ H <sub>2</sub> O (20 µL) + TFA (2 µL) + 4 days + NaOH (6 M aq. 2 µL)	-149.9
+ H <sub>2</sub> O (20 $\mu$ L) + TFA (2 $\mu$ L) + 4 days + NaOH (6 M aq. 6 $\mu$ L)	-131.3

### 2.2. Photoirradiation



**Figure S32 (see Figure 2 in manuscript).** The stacked <sup>1</sup>H NMR spectra (400 MHz, 25 °C,  $CD_2Cl_2$ ) of **1** before (bottom), after 15 min (second lowest), 25 min (second top), and 40 min (top) non-selective irradiation, with indicated *trans:cis* ratios.



**Figure S33.** Stacked <sup>1</sup>H NMR spectra (500 MHz, 25 °C,  $CD_2Cl_2$ ) of **1-I** (~8.7 µmol, bottom) being exposed to non-selective irradiation for four times. The total irradiation time when the spectrum was recorded is indicated in their left corners. This caused the iodine(I) complex **1-I** (marked with pink lines) to decompose into protonated ligand (marked with blue lines). Indicated by the blue arrow is what could be the appearing signal of the extra proton on the pyridyl nitrogen of the protonated ligand.



).6 9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6. f1 (ppm)

**Figure S34.** When applying non-selective irradiation to **2-I**, no change was observed in the resulting <sup>1</sup>H NMR spectra (500 MHz, 25 °C,  $CD_2Cl_2$ ). After 7 min and 22 min irradiation time (the two spectra on top), sign of pyridine protonation appears, which could indicate minor decomposition, yielding a protonated complex. However, the majority remains halogen bonded. Indicated by the blue arrow is what could be the signal of the extra proton on the pyridyl nitrogen of the protonated ligand.



**Figure S35.** The stacked <sup>1</sup>H NMR spectra (500 MHz, 25 °C,  $CD_2Cl_2$ ) of **1-Ag** after applying nonselective irradiation for different times (bottom to top: 0 min, 2 min, 4.5 min, and 16.5 min). The only difference between the spectra is their ratio of **1-Ag**-signals to the solvent residue peak (integral normalized to 1 in the picture), due to precipitation.



Figure S36. The <sup>1</sup>H NMR spectrum (500 MHz, 25 °C) of 1-Ag in CD<sub>2</sub>Cl<sub>2</sub> after 16.5 min non-selective irradiation (bottom), and after further concentration and re-dissolving in CD<sub>3</sub>CN (middle). As a reference, **1-Ag** formed from the *cis*-ligand **1** directly in  $CD_3CN$  is included as well (top). Dissolving the precipitate formed during irradiation did not generate two major species, which indicates that the trans-isomer did not form, further supported by the similarity of the observed shifts (middle) to the reference 1-Ag in CD<sub>3</sub>CN.



Figure S37 (Figure 3 in manuscript). Stacked <sup>1</sup>H NMR spectra (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>) of the ligand 1 after irradiation to reach its photostationary state (bottom), then after addition of  $AgBF_4$  to that same sample (second bottom), and after sequential irradiation for 10 min (second top). Also shown is a reference spectrum of **1-Ag** (top). *t*-**1** is marked by brown lines, showing that the *trans*-isomer does not seem to interact with the silver(I) of AgBF<sub>4</sub>. The *cis*-isomer, however, is forming **1-Ag** (marked by grey lines). Upon irradiation, the *t*-1 signals disappear, leaving behind only those of 1-Ag.



.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 f1 (ppm)

**Figure S38.** The stacked <sup>1</sup>H NMR spectra (400 MHz, 25 °C,  $CD_2Cl_2$ ) recorded upon irradiation of the proton complex **1-H** (total irradiation time indicated in left corners). The appearance of the *trans*-isomer is indicated by relative integrals of the isomers alkene protons.



**Figure S39.** The <sup>1</sup>H NMR spectrum (25 °C,  $CD_2Cl_2$ ) recorded after irradiation of **1-H** and neutralization with NaOH (aq.) (bottom, 400 MHz) compared with the spectrum (25 °C,  $CD_2Cl_2$ ) of **1** after irradiation to reach the photostationary state (top, 500 MHz). Both the signals for **1** and *t*-**1** (the latter indicated by green lines) match.

## **3. UV SPECTRA**



Figure S40. The UV spectrum (UV absorbance against wavelength (nm)) recorded for 1 in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S41. The UV spectrum (UV absorbance against wavelength (nm)) recorded for 1-Ag in  $CD_2Cl_2$ .



Figure S42. The UV spectrum (UV absorbance against wavelength (nm)) recorded for 1-H in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S43. The UV spectrum (UV absorbance against wavelength (nm)) recorded for 1-I in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S44. The UV spectrum (UV absorbance against wavelength (nm)) recorded for 2-I in  $CD_2Cl_2$ .

### **4. COMPUTATIONS**

A dual-level strategy was employed to obtain accurate rotational barriers of complex A-C; 1, 1-X (Figure S45). Minimum and transition state geometries were optimized at the lower computational method, while the energetics (Table S1) were calculated at the coupled cluster level. This strategy was chosen as the best compromise in describing the mechanism of large systems while at the same time providing reliable energetics.<sup>1-3</sup> For complex A-C, the multiconfigurational complete active space selfconsistent field (CASSCF) method<sup>4</sup> in combination with the 6-31G\* basis set<sup>5,6</sup> was used to obtain minimum and transition state geometries. All available  $\pi$  and  $\pi^*$  molecular orbitals were included in the active space. The multiconfigurational method was used as it is known to account for the nondynamical electron correlations in transition states of cis to trans rotation.<sup>7</sup> Due to the size of the systems of interest, for complexes 1 and 1-X, minimum geometries (Figure S45) were optimized using the  $\omega$ B97X-D density functional<sup>8</sup> in combination with the aug-cc-pVDZ basis set.<sup>9,10</sup> The aug-cc-pVDZ basis set was chosen as it is known to provide a good balance between accuracy and computational cost in predicting geometries of complexes.<sup>11-13</sup> For heavy atoms (e.g., Ag and I), scalar relativistic effects were taken into account using the Stuggard-Dresden effective core potential.<sup>9</sup> Dichloromethane solvent effects were taken into account using the polarizable continuum model (PCM) of Tomasi and co-workers.<sup>14</sup> Transition state geometries of complex 1 and 1-X were optimized with fixed dihedral angles, where the dihedral value was taken from the transition state geometry of complex C obtained at the CASSCF level. Vibrational analysis was performed on each transition state geometry, and showed that each correspond to a maximum structure on the potential energy surface with only one imaginary frequency. The intrinsic reaction coordinate (IRC) calculations were performed to ensure the corresponding transition state geometries linking cis to trans rotation. However, due to the size of interest, the IRC calculations were done for complexes A and B (Fig. S45) only. The corresponding energetics, shown in Table S1, were calculated at the DLPNO-CCSD(T) level<sup>15,16</sup> in combination with the Def2-TZVP basis set.<sup>17</sup> The potential energy profiles for the *cis* to *trans* isomerization of complexes A and B are shown in Figures S46 and S47, respectively.

DFT calculations were performed using the Gaussian Rev C.01 package.<sup>18</sup> The geometry optimization calculations were performed using ultrafine grid integration and tight convergence criteria for the forces and displacement.<sup>19</sup> For the coupled cluster calculations, the ORCA 4.2.1 package<sup>15</sup> was used, whereas for multiconfigurational calculations, the CASSCF calculations were carried out using the OpenMolcas 19.11 package.<sup>20</sup>



Figure S45. Structures used to determine rotational barriers.

Table S1.	Energetics	(kcal/mol)	for the rota	tional barrier	s of compl	lexes A-C,	<b>1</b> and <b>1-X</b>	calculated at
the DLPN	O-CCSD(T	)/def2-TZV	/P//ω-B97X	L-D//aug-cc-	VDZ leve	el of theory		

Complex	Ebarrier
Α	79.46
В	81.85
С	68.80
1	64.38
1-Ag	126.61
1-I	100.78
1-H	82.96

We used the simplified model systems A-C and 1 to investigate the evolution of the potential energy surface of *cis-trans* isomerization of enedyenes. The *cis* to *trans* isomerization energies, shown in Table S1, indicate that an extended conjugation eases the photoisomerization ( $E_{barrier}$ : B > C > 1), and thus  $\pi$ -conjugation stabilizes the transition state. A multiconfigurational analysis revealed that the in-plane  $\pi$ -orbitals of the alkyne fragment are less involved in the photoisomerization process. The three-center, four-electron halogen bond (1-I), the coordinative bond (1-Ag) and the hydrogen bond (1-H) all increase the rotational barrier as compared to 1.

Figure S46 and S47 show the simplified ground state ( $S_0$ ) and first excited ( $S_1$ ) potential energy surfaces of a one-dimensional torsional *cis-trans* isomerization for ethylene (A) and 2-butene (B). A planar geometry is preferred in the ground electronic state, whereas the first excited state favours a twisted geometry. The energy gaps between ground ( $S_0$ ) and first excited ( $S_1$ ) state for complexes A and B at the purely twisted geometry are larger than 1 eV. It is generally accepted that the *cis-trans* isomerization occurs close to the twisting angle (ca. 90° torsional angle) with the help of pyramidalization. A proper description of photochemical *cis-trans* isomerization requires at least two coordinates and three electronic states.<sup>21</sup>



**Figure S46**. Potential energy profile from *cis* to *trans* isomerization of complex **A** calculated at the CASSCF/6-31G\* level of theory.



**Figure S47**. Potential energy profile from *cis* to *trans* isomerization of complex **B** calculated at the CASSCF/6-31G\* level of theory.

The topological analysis of electron density ( $\rho_{(r)}$ ) and energy density ( $H_{(r)}$ ) at the [N-I-N]<sup>+</sup> bond critical points (Table S2) were carried out using the AIMALL version 19.10.12 program.<sup>22</sup> Here, we used the Cremer-Kraka criteria that are based on the total electron energy density at the [N-X-N]<sup>+</sup> bond critical point to identify the covalent character of a bond, where a negative value of the energy density indicates a covalent bond and a positive value of the energy density denotes an electrostatic interaction.<sup>23,24</sup> The outcome of this analysis is in agreement with previous literature analyses of analogous systems.<sup>25-27</sup>

Complex	R (Å)	$\rho_{(\mathbf{r})}$	$H_{(\mathbf{r})}$
1-Ag	2.144	0.599	-0.176
1-I	2.300	0.524	-0.177
<b>1-H</b>	1.050	2.108	-3.450
	1.856	0.273	-0.051

**Table S2**. N-X bond distances (R) in Å (X= Ag, I or H), topological analysis of electron density ( $\rho_{(r)}$ ) in e/Å<sup>3</sup> and energy density ( $H_{(r)}$ ) in h/Å<sup>3</sup> at the [N-X-N]<sup>+</sup> bond critical points.

# **Optimized geometries**

Optimized geometries were obtained at the CASSCF/6-31G\* level of theory for complex A-C and obtained at the  $\omega$ B97X-D/aug-cc-pVDZ level of theory for complex 1 and 1-X.

# A (cis)

С	0.00000000	-0.67262219	0.00000000
Η	0.91344348	-1.23788653	0.00000000
Η	-0.91344348	-1.23788653	0.00000000
С	-0.00000000	0.67262219	0.00000000
Η	-0.91344348	1.23788653	0.00000000
Η	0.91344348	1.23788653	0.00000000

# A (Transition State)

С	0.00719763	-0.72362356	-0.02254106
Η	0.71620675	-1.29837123	0.54630470
Η	-0.69309134	-1.27550711	-0.62390356
С	-0.00628931	0.72457478	0.02209031
Η	-0.59776267	1.25925296	0.74404854
Н	0.57373894	1.31367416	-0.66599893

# **B** (cis)

С	-0.67163000	0.66723400	-0.00000800
Н	-1.17572500	1.63437100	-0.00000500
С	0.67163800	0.66722200	0.00000000
Н	1.17576100	1.63434600	0.00002500
С	-1.59337200	-0.52337500	0.00000200
Н	-1.05642800	-1.47612300	-0.00007000
Н	-2.25014400	-0.51070200	0.88100800
Н	-2.25027700	-0.51062700	-0.88090300
С	1.59336100	-0.52338400	-0.00000300
Н	2.25072200	-0.51024200	-0.88056400
Н	2.24969400	-0.51107900	0.88134100
Н	1.05641700	-1.47612600	-0.00077600

# **B** (transition state)

С	-0.72606973	0.66084919	-0.04749073
Η	-1.22162509	0.65319059	-1.00589922
С	0.72440896	0.71223340	0.00557722
Η	1.21840365	1.67080749	0.01573083
С	-1.60580212	0.64432455	1.17250858
Η	-1.02011249	0.64253197	2.08514176
Η	-2.26274313	1.51271692	1.20249520
Η	-2.25029360	-0.23329551	1.18894252
С	1.60707257	-0.50643008	0.02346004
Η	2.26540317	-0.53244472	-0.84353959
Η	2.24833530	-0.52085583	0.90295149
Η	1.02305358	-1.41941913	0.02273767

# C (cis)

С	2.25397800	-0.36056900	0.00005300
С	1.51018900	0.60510400	-0.00002800
С	0.68006900	1.75453300	-0.00003500
С	-2.25400000	-0.36056200	0.00006300
С	-1.51019600	0.60509900	0.00005500
С	-0.68007900	1.75452900	-0.00000400
Н	1.18331100	2.71969700	-0.00006800
Н	-1.18332600	2.71969200	-0.00000400
С	3.13003400	-1.52754700	-0.00000300
Н	4.18784400	-1.23738100	0.00171400
Н	2.95884200	-2.15661900	0.88285600
Н	2.96121100	-2.15472400	-0.88465300
С	-3.13001100	-1.52756600	-0.00004600
Н	-2.96287000	-2.15359600	0.88574700
Н	-4.18782100	-1.23743300	-0.00416600
Н	-2.95709100	-2.15775800	-0.88175600

# **C** (transition state)

С	-0.73566753	0.58273247	-0.05608603
Η	-1.16785383	0.55292990	-1.04017995
С	0.73215460	0.71864980	0.07951534
Η	1.16178571	1.70383662	0.11308400
С	1.58786678	-0.38567636	0.14469275
С	-1.58795378	0.52144686	1.05055302
С	-2.33835460	0.47172562	2.01904890
С	2.34212067	-1.34912809	0.19903809
С	3.24170123	-2.51134795	0.27921121
Η	4.17431344	-2.31282011	-0.23653511
Η	3.47244527	-2.74970771	1.31172807
Η	2.78330583	-3.38307160	-0.17321078
С	-3.23289893	0.39278524	3.18575076
Η	-4.12413487	0.98938053	3.02855050
Η	-3.54117436	-0.63106101	3.36658511
Н	-2.73348801	0.75682575	4.07575210

# **1** (cis)

Ν	0.00000000	2.38609300	-1.15724400
С	0.00000000	2.99808400	0.04061300
С	0.00000000	4.39192600	0.18707400
С	0.00000000	5.18098900	-0.95802600
С	0.00000000	4.55558800	-2.20166100
С	0.00000000	3.16077700	-2.24289600
Н	0.00000000	4.83476100	1.18105600
Н	0.00000000	5.13076200	-3.12597800
Н	0.00000000	2.64059700	-3.20219200
Ν	0.00000000	-2.38609300	-1.15724400
С	0.00000000	-2.99808400	0.04061300
С	0.00000000	-4.39192600	0.18707400
С	0.00000000	-5.18098900	-0.95802600

С	0.00000000	-4.55558800	-2.20166100
С	0.00000000	-3.16077700	-2.24289600
Н	0.00000000	-4.83476100	1.18105600
Н	0.00000000	-5.13076200	-3.12597800
Н	0.00000000	-2.64059700	-3.20219200
С	0.00000000	2.15677400	1.20595100
С	0.00000000	1.47533100	2.21243000
С	0.00000000	0.67593500	3.38698500
С	0.00000000	-2.15677400	1.20595100
С	0.00000000	-1.47533100	2.21243000
С	0.00000000	-0.67593500	3.38698500
Н	0.00000000	6.26765200	-0.87875400
Н	0.00000000	-6.26765200	-0.87875400
Н	0.00000000	1.19901600	4.34375500
Н	0.00000000	-1.19901600	4.34375500

# 1 (transition state)

С	0.55623000	2.44928000	0.48801800
Н	0.50998000	3.12905900	1.34275700
С	-0.55621100	2.44929300	-0.48814200
Н	-0.50990200	3.12898600	-1.34294600
С	-1.64471800	1.63571000	-0.34099200
С	1.64467800	1.63560800	0.34092700
С	2.61070400	0.88378800	0.16911900
С	-2.61073500	0.88388600	-0.16915900
С	-3.74590200	0.03813700	-0.02810200
С	-4.76933500	0.06842200	-0.99270200
Ν	-3.78339800	-0.77176200	1.05314400
С	-5.86489500	-0.76985600	-0.82856800
Н	-4.69060600	0.73945000	-1.84574900
С	-4.84401700	-1.56584600	1.18818300
С	-5.90818800	-1.60710400	0.28385000

Н	-6.67322300	-0.76947500	-1.55921700
Н	-4.85055300	-2.21026000	2.06913600
Н	-6.74557900	-2.28134800	0.45486100
С	3.74593600	0.03815500	0.02805100
С	4.76946600	0.06864000	0.99256400
Ν	3.78327300	-0.77201100	-1.05298500
С	5.86501800	-0.76964500	0.82848900
Н	4.69082000	0.73984100	1.84548400
С	4.84388700	-1.56611300	-1.18794900
С	5.90818600	-1.60713300	-0.28375300
Н	6.67343400	-0.76908900	1.55903800
Н	4.85030800	-2.21070400	-2.06876900
Н	6.74557500	-2.28139500	-0.45471900

# 1-Ag (cis)

Ν	2.14781700	0.79475100	0.02352700
С	2.84997900	-0.36312200	-0.00632700
С	4.24618800	-0.37935900	-0.02604900
С	4.93406100	0.82856600	-0.01346200
С	4.21046500	2.01677100	0.02143000
С	2.82234500	1.95291200	0.03898600
Н	4.77042500	-1.33138900	-0.05114500
Н	4.70571400	2.98491700	0.03425500
Н	2.22282200	2.86016900	0.06739900
Ag	0.00000000	0.74073900	0.00002600
Ν	-2.14781700	0.79475100	-0.02352400
С	-2.84997900	-0.36312100	0.00631000
С	-4.24618900	-0.37935900	0.02600200
С	-4.93406100	0.82856600	0.01340700
С	-4.21046500	2.01677200	-0.02146300
С	-2.82234500	1.95291200	-0.03899000
Н	-4.77042600	-1.33138900	0.05108100

Н	-4.70571400	2.98491800	-0.03429100
Н	-2.22282100	2.86017000	-0.06738400
С	2.09854500	-1.57898300	-0.01382000
С	1.45571400	-2.60996100	-0.01165000
С	0.67591900	-3.79635900	-0.00644300
С	-2.09854500	-1.57898300	0.01381500
С	-1.45571400	-2.60996100	0.01165600
С	-0.67591900	-3.79635900	0.00642600
Н	6.02272000	0.84023500	-0.02976600
Н	-6.02272100	0.84023500	0.02968800
Н	1.20821100	-4.74735300	-0.01184500
Н	-1.20821100	-4.74735300	0.01181200

**1-Ag** (transition state)

С	0.04560000	3.04288300	-0.17886700
Н	-0.07780900	4.03432300	0.26274500
С	-0.97603700	2.52499000	-1.11646300
Н	-0.90140700	2.79420900	-2.17289600
С	-2.03316400	1.77484900	-0.68368100
С	1.16655300	2.31265800	0.09196900
С	2.14462800	1.58636900	0.30318300
С	-2.95663400	1.07594500	-0.25159200
С	-4.04924900	0.28254600	0.19744900
С	-5.05548300	-0.10433200	-0.70496400
Ν	-4.06028000	-0.06624700	1.50303000
С	-6.11011400	-0.87710000	-0.23407000
Н	-4.99970200	0.20537000	-1.74661900
С	-5.08105200	-0.80705700	1.93002900
С	-6.12787800	-1.23852500	1.11061100
Н	-6.90697100	-1.19086700	-0.90750500
Н	-5.06927000	-1.07519200	2.98786600
Н	-6.93338800	-1.84182600	1.52536600

С	3.20302900	0.67898900	0.54675500
С	4.35070300	1.05368400	1.25875200
Ν	3.04637400	-0.57974500	0.05447000
С	5.35333500	0.11386800	1.46085200
Н	4.43763100	2.06873700	1.63871500
С	4.02063200	-1.47191000	0.25692600
С	5.18978800	-1.17183100	0.95066400
Н	6.25366300	0.38302100	2.01105500
Н	3.85615500	-2.46660400	-0.15280900
Н	5.94958300	-1.93842500	1.08452600
Ag	1.12725400	-1.04482900	-0.95868600

**1-I** (cis)

Ν	0.00000000	2.28490900	0.76358300
С	0.00000000	2.91588400	-0.43556500
С	0.00000000	4.31093400	-0.50247400
С	0.00000000	5.04937500	0.67515900
С	0.00000000	4.38222600	1.89732700
С	0.00000000	2.99487300	1.89828500
Н	0.00000000	4.79382300	-1.47632400
Н	0.00000000	4.92009900	2.84219200
Н	0.00000000	2.42580300	2.82586700
Ι	0.00000000	0.00000000	0.83042800
Ν	0.00000000	-2.28490900	0.76358300
С	0.00000000	-2.91588400	-0.43556500
С	0.00000000	-4.31093400	-0.50247400
С	0.00000000	-5.04937500	0.67515900
С	0.00000000	-4.38222600	1.89732700
С	0.00000000	-2.99487300	1.89828500
Н	0.00000000	-4.79382300	-1.47632400
Н	0.00000000	-4.92009900	2.84219200
Н	0.00000000	-2.42580300	2.82586700

С	0.00000000	2.12440100	-1.62519400
С	0.00000000	1.46812400	-2.64735700
С	0.00000000	0.67584100	-3.82692500
С	0.00000000	-2.12440100	-1.62519400
С	0.00000000	-1.46812400	-2.64735700
С	0.00000000	-0.67584100	-3.82692500
Н	0.00000000	6.13735200	0.63778500
Н	0.00000000	-6.13735200	0.63778500
Н	0.00000000	1.20385100	-4.78047700
Н	0.00000000	-1.20385100	-4.78047700

# 1-I (transition state)

С	-0.33568500	2.86608400	-1.03044500
Н	-0.49204700	3.93828800	-0.88707700
С	-1.32667200	2.07182500	-1.78944100
Н	-1.22125500	2.00717100	-2.87456100
С	-2.37795400	1.46656800	-1.16343900
С	0.78826000	2.28610200	-0.53170900
С	1.77181700	1.67241000	-0.10023100
С	-3.30508000	0.92749100	-0.54923400
С	-4.39723300	0.29225400	0.10497700
С	-5.36051800	-0.40110200	-0.64827000
Ν	-4.45008000	0.39366600	1.45140300
С	-6.41584800	-1.00916000	0.02095500
Н	-5.27054000	-0.45107800	-1.73154900
С	-5.47032200	-0.19766200	2.06949000
С	-6.47627800	-0.90822700	1.40841400
Н	-7.17989700	-1.55285800	-0.53354600
Н	-5.49278400	-0.10249500	3.15642200
Н	-7.28384900	-1.36740600	1.97579700
С	2.90763200	1.05962200	0.43453600
С	3.89218300	1.79323100	1.11769700

Ν	3.08112100	-0.29605400	0.30055600
С	5.00433400	1.15500100	1.63777700
Н	3.74979800	2.86564500	1.22066000
С	4.16236300	-0.92653400	0.80455500
С	5.14209200	-0.22645100	1.47877600
Н	5.76413900	1.72797000	2.16565700
Н	4.21882900	-2.00056500	0.65367200
Н	5.99886000	-0.76772400	1.87109900
Ι	1.65231900	-1.44356500	-0.69559900

# 1-H (cis)

Ν	1.45832500	-0.90416700	0.00998000
С	2.35254500	0.11532200	-0.01444700
С	3.71521200	-0.18216500	-0.02144000
С	4.12629400	-1.50930600	0.00022900
С	3.17757000	-2.53255400	0.03037600
С	1.83991000	-2.19101000	0.03337200
Н	4.43142100	0.63420500	-0.04255200
Η	3.46627100	-3.57946900	0.04959500
Н	1.04404800	-2.92825700	0.05479900
Η	0.42385600	-0.71527900	0.00762300
Ν	-1.42934500	-0.91428100	-0.00858100
С	-2.32976400	0.09157400	0.01055400
С	-3.71092200	-0.12789100	0.01482600
С	-4.18217300	-1.43568200	-0.00390900
С	-3.26048700	-2.47731000	-0.02736600
С	-1.90394900	-2.16322000	-0.02802700
Н	-4.39102800	0.72063400	0.03163600
Н	-3.57771300	-3.51758700	-0.04415700
Н	-1.16707800	-2.96538500	-0.04616900
С	1.85250700	1.44135600	-0.02652100
С	1.40300600	2.56920900	-0.02098300

С	0.69519600	3.79765500	-0.00867000
С	-1.81251900	1.42713900	0.02164400
С	-1.36938400	2.55777300	0.02208300
С	-0.65990100	3.78641200	0.01428900
Н	5.18872000	-1.74640400	-0.00494500
Н	-5.25246400	-1.63621100	-0.00121600
Н	1.24720100	4.73556400	-0.01624000
Н	-1.21493800	4.72351200	0.02576900

# **1-H** (transition state)

С	-0.51033500	2.49101600	-0.48385700
Н	-0.46122000	3.17407700	-1.33620000
С	0.58968200	2.47832300	0.50464700
Н	0.54239300	3.17344500	1.34590800
С	1.66842800	1.65486900	0.35583800
С	-1.60100500	1.68703400	-0.35399500
С	-2.57231000	0.93661500	-0.20626300
С	2.62209100	0.88795000	0.18316200
С	3.74835300	0.03185400	0.03151900
С	4.80303500	0.08779600	0.95924000
Ν	3.74243600	-0.81048100	-1.02504400
С	5.88946300	-0.76048600	0.78206200
Н	4.75717800	0.78604300	1.79259900
С	4.79441200	-1.61311500	-1.17307500
С	5.88977400	-1.63060100	-0.30501100
Н	6.72360700	-0.74132700	1.48258200
Н	4.76821500	-2.28424500	-2.03325100
Н	6.71864900	-2.31285600	-0.48515600
С	-3.68929500	0.09980600	-0.09517000
С	-4.75378000	0.09806300	-1.00647300
Ν	-3.75123400	-0.76537800	0.95786200
С	-5.81923800	-0.76949700	-0.81352500

Н	-4.72004600	0.78016100	-1.85133500
С	-4.77194500	-1.61347300	1.16413100
С	-5.83446100	-1.63796400	0.28364600
Н	-6.64669800	-0.77225200	-1.52098600
Н	-4.70030300	-2.25158100	2.04000500
Н	-6.65736400	-2.32589600	0.45559900
Н	-2.98003100	-0.76370000	1.61924500

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