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Supporting Information

Artificial Supramolecular Pumps Powered by Light

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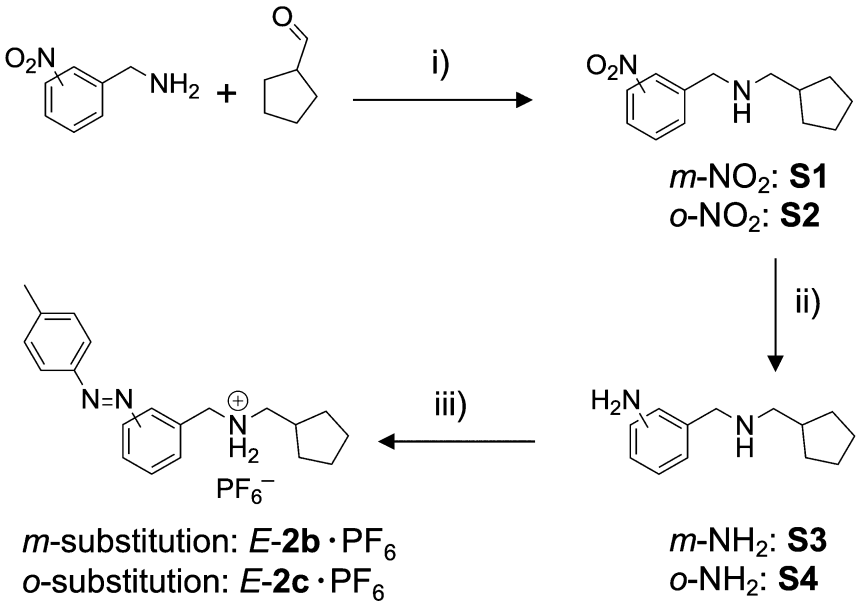
SUPPORTING INFORMATION

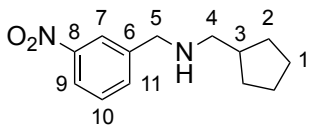
1. Synthetic procedures and analytical data



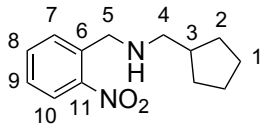
Scheme S1. Synthetic route towards compounds *E*-**2b**·PF_6 and *E*-**2c**·PF_6. i) 1) molecular sieves 3 Å, EtOH. 2) $NaCNBH_3$, r.t. ii) H_2 (10 bar), 10% Pd/C, MeOH, r.t. iii) 1) 4-nitrosotoluene, AcOH, r.t. 2) NH_4PF_6, H_2O.

General procedure for reductive amination

Nitrobenzylamine hydrochloride (0.51 g, 2.70 mmol) and NaOH (0.11 g, 2.75 mmol) were suspended in absolute EtOH (20 mL), under a nitrogen atmosphere and the mixture stirred for 30 min. Cyclopentancarbaldehyde (0.22 g, 2.24 mmol) was added along with 3 Å molecular sieves and the resulting mixture was stirred for 2 hours. $NaCNBH_3$ (0.10 g, 2.64 mmol) was added portionwise and the resulting mixture stirred overnight. The mixture was filtered and the filtrate concentrated under reduced pressure. The residue was suspended in EtOAc (25 mL) and washed with water (3 x 20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (Cyclohexane:EtOAc; 1:1) to yield the titled compound as a yellow oil.



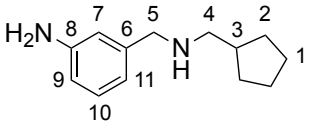
1-cyclopentyl-N-(3-nitrobenzyl)methanamine **S1**: 0.30 g, 57%, **^{1}H NMR (500 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 8.21 (s, 1H, H_7), 8.10 (d, *J* = 8.1 Hz, 1H, H_9), 7.68 (d, *J* = 7.5 Hz, 1H, H_{11}), 7.49 (t, *J* = 7.9 Hz, 1H, H_{10}), 3.90 (s, 2H, H_5), 2.55 (d, *J* = 7.1 Hz, 2H, H_4), 2.04 (p, *J* = 7.7 Hz, 1H, H_3), 1.85 – 1.71 (m, 2H), 1.65 – 1.49 (m, 3H), 1.24 – 1.10 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 148.2, 142.1, 134.1, 129.1, 122.8, 121.9, 54.7, 52.8, 39.6, 30.7, 25.1.



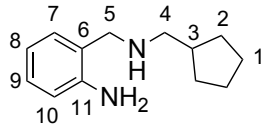
1-cyclopentyl-N-(2-nitrobenzyl)methanamine **S2**: 0.41 g, 63%, **^{1}H NMR (500 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 7.94 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 4.03 (s, 2H, H_5), 2.55 (d, *J* = 7.2 Hz, 2H, H_4), 2.06-1.98 (m, 1H), 1.80-1.74 (m, 2H), 1.60-1.51 (m, 4H), 1.18-1.14 (m, 2H). **^{13}C NMR (125 MHz, 298 K, $CDCl_3$):** *δ (ppm)* 149.2, 136.0, 133.1, 131.3, 127.9, 124.7, 55.5, 51.1, 40.1, 30.9, 25.4.

General procedure for flow hydrogenation

Compound **S1** or **S2** was dissolved in MeOH (~10 mg mL^{-1}) and hydrogenation was carried out at 25 °C on a Thales NANO flow hydrogenator using 10% Pd/C as catalyst with 10 bar of hydrogen, at a flow rate of 1 mL min^{-1}. The solvent was removed under reduced pressure and the corresponding aniline was used without further purification.



1-cyclopentyl-N-(3-aminobenzyl)methanamine **S3:** 0.18 g, 70%. **^{1}H NMR (500 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 7.10 (t, *J* = 7.7 Hz, 1H, H_{10}), 6.70 (d, *J* = 7.7 Hz, 1H, H_9), 6.69 (t, *J* = 2.1 Hz, 1H, H_7), 6.58 (dd, *J* = 7.9, 2.1 Hz, 1H, H_{11}), 3.72 (s, 2H, H_5), 2.55 (d, *J* = 7.2 Hz, 2H, H_4), 2.06 – 2.02 (m, 1H, H_3), 1.79 – 1.75 (m, 2H), 1.59-1.53 (m, 4H), 1.17-1.13 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 146.9, 137.5, 129.5, 118.9, 115.4, 114.6, 52.8, 50.5, 38.7, 30.9, 25.2.

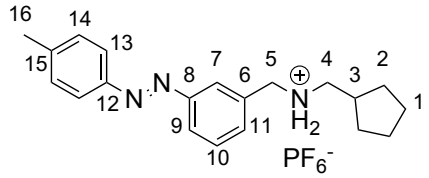


1-cyclopentyl-N-(2-aminobenzyl)methanamine **S4:** 0.30 g, 86%. **^{1}H NMR (500 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 7.08 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.69-6.65 (m, 2H), 3.80 (s, 2H), 2.55 (d, *J* = 7.2 Hz, 2H), 2.04-1.98 (m, 1H), 1.78-1.72 (m, 2H), 1.61-1.51 (m, 4H), 1.20-1.13 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 147.2, 129.8, 128.3, 124.6, 117.7, 115.8, 55.3, 53.6, 40.2, 31.0, 25.5.

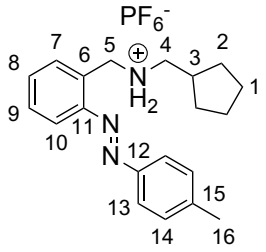
General procedure for Mill's coupling

4-nitrosotoluene (1.5 equivalents) and the desired aniline (1 equivalent) were dissolved in acetic acid (10 mL). The resulting mixture was stirred in the dark for 48 hours. Volatiles were removed under vacuum and the residue neutralized with aqueous $NaHCO_3$ (sat. solution). The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic layers were washed with

$NaHCO_3$ (sat. 2 x 100 mL) and water (2 x 100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. Purification by flash chromatography (Cyclohexane/EtOAc, 7:3) afforded the free amine as an orange oil. The oil was suspended in acetone and protonated adding some drops of concentrated hydrochloric acid (37%). An orange solid precipitates, the supernatant was decanted and the residue was triturated with acetone (3x). The hydrochloride salt was then dissolved in hot water and a saturated solution of NH_4PF_6 was added. The precipitate was recovered, washed with water and dried under vacuum to afford the product as an orange solid.



E-**2b**·PF_6: (0.53 g, 29%). **^{1}H NMR (500 MHz, CD_3CN, 298 K):** *δ (ppm)* 8.01 (t, J = 1.9 Hz, 1H, H_7), 7.97 (dt, *J* = 7.9, 1.7 Hz, 1H, H_9), 7.84 (d, J = 8.3 Hz, 2H, H_{13}), 7.66 (t, J = 7.7 Hz, 1H, H_{10}), 7.62 (dt, J = 7.8, 1.5 Hz, 1H, H_{11}), 7.41 (d, J = 8.0 Hz, 1H, H_{14}), 4.28 (s, 2H, H_5), 3.05 (d, J = 7.5 Hz, 2H, H_4), 2.45 (s, 3H, H_{16}), 2.18 (dt, *J* = 15.5, 7.7 Hz, 1H, H_3), 1.90 – 1.80 (m, 2H), 1.72 – 1.52 (m, 4H), 1.32 – 1.16 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 153.8, 151.5, 143.8, 133.5, 132.8, 131.1, 131.0, 125.0, 124.8, 123.8, 118.3, 54.0, 52.6, 37.8, 31.1, 25.7, 21.5. **HRMS (ESI+)** *m/z* calculated for $C_{20}H_{26}N_3^+$ $[M]^+$ 309.2205; found: 309.2205.



E-**2c**·PF_6: (0.42 g, 21%). **^{1}H NMR (500 MHz, CD_3CN, 298 K):** *δ (ppm)* 7.87 (dd, J = 8.3, 2.3 Hz, 3H), 7.69 – 7.58 (m, 3H), 7.44 (dt, J = 8.1, 0.8 Hz, 2H), 4.65 (s, 2H), 3.10 (d, J = 7.5 Hz, 2H), 2.46 (s, 3H), 2.21 (dq, J = 16.0, 8.0 Hz, 1H), 1.87 – 1.76 (m, 2H), 1.68 – 1.50 (m, 2H), 1.20 (dq, J = 12.1, 7.6 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$, 298 K):** *δ (ppm)* 151.5, 151.3, 144.6, 133.3, 132.7, 132.1, 131.1, 129.9, 124.3, 53.8, 49.8, 37.5, 31.1, 25.7, 21.6. **HRMS (ESI+)** *m/z* calculated for $C_{20}H_{26}N_3^+$ $[M]^+$ 309.2205; found: 309.2205.

2. ^{1}H NMR Characterization

2.1. ^{1}H NMR Characterization of *Z*-configured axles

^{1}H NMR spectra of axles were recorded after exhaustive irradiation at 365 nm. The data for *E*-**2a** and *Z*-**2a** were previously reported.[1]

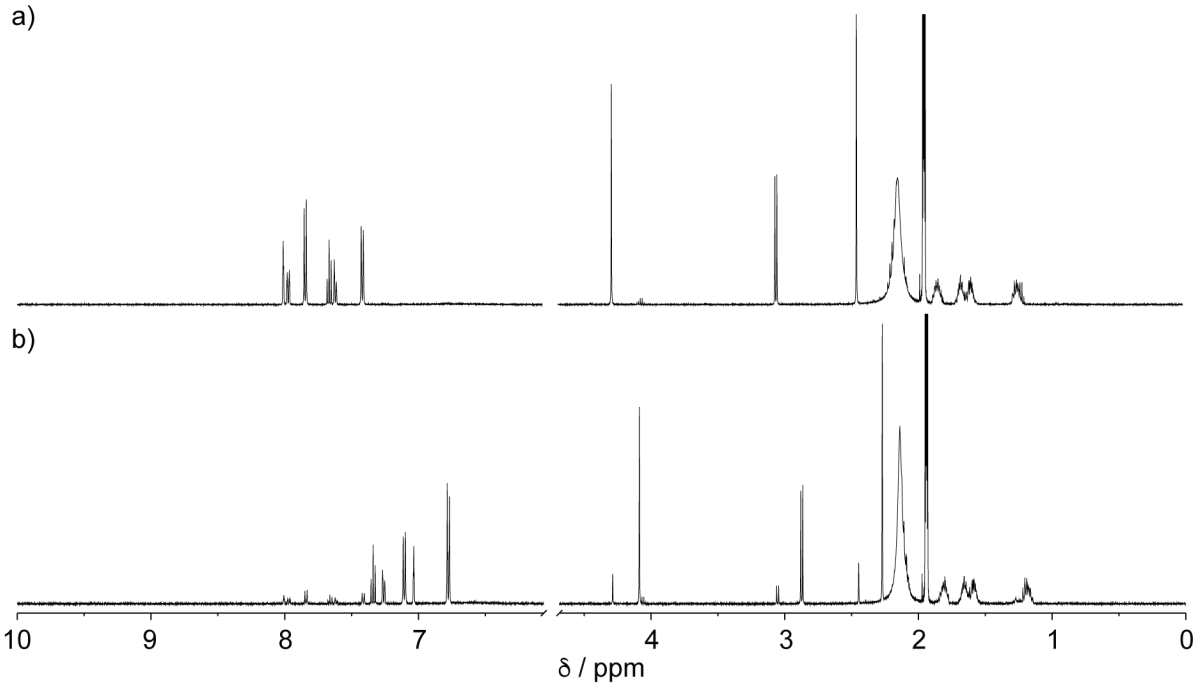


Figure S1. Partial ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of a) *E*-**2b** and b) the same sample after irradiation (30 min, λ_{irr} = 365 nm).

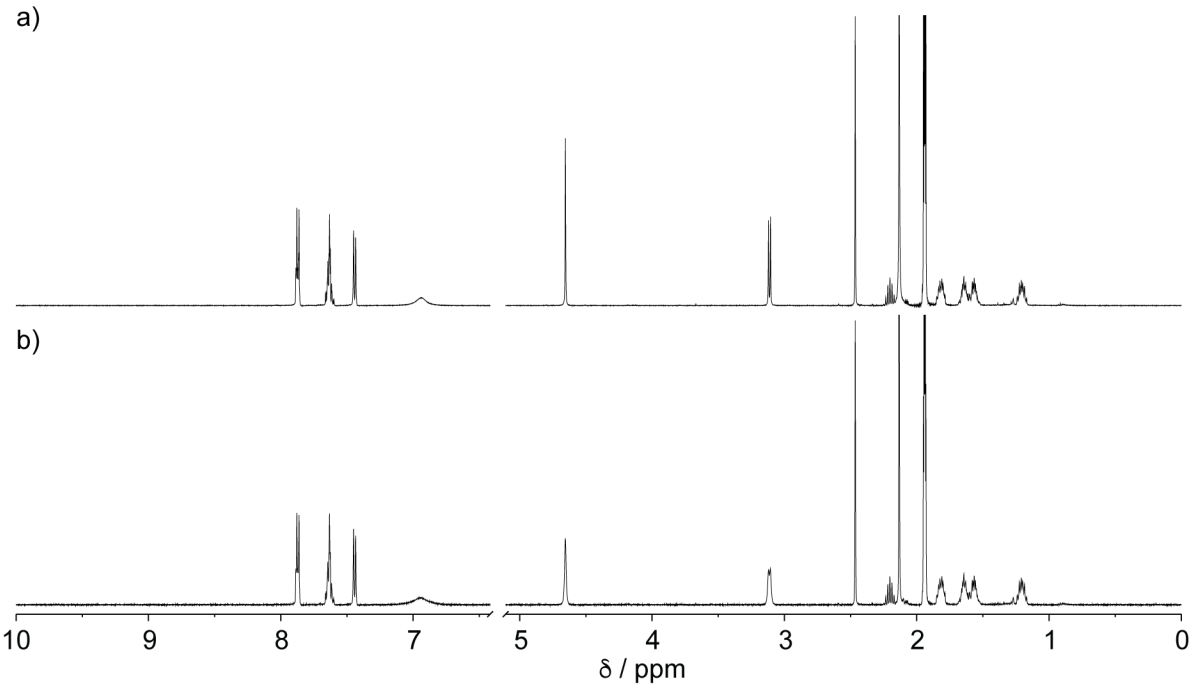


Figure S2. Partial ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of a) *E*-**2c** and b) the same sample after irradiation (30 min, λ_{irr} = 365 nm).

2.2. ^{1}H NMR Characterization of the supramolecular complexes

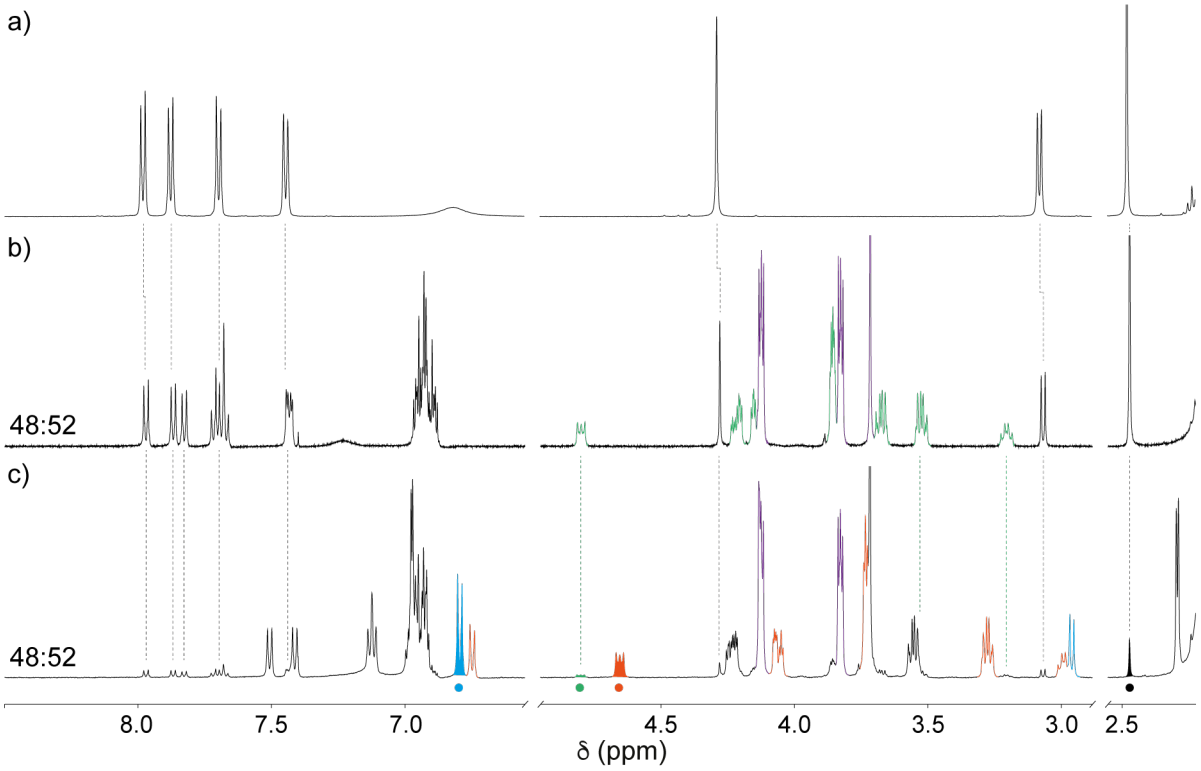


Figure S3. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of a) *E*-**2a**. b) A 1:1 mixture of *E*-**2a** and **1** (10 mM); the signals univocally associated with the complex are highlighted in green, the signals of free **1** are highlighted in purple. c) The same sample after exhaustive irradiation (λ_{irr} = 369 nm, 30 min) and equilibration for 3 hours in the dark. The signals of free *Z*-**2a** are highlighted in cyan, those univocally attributed to the *Z*-complex are highlighted in orange. The dots underneath the filled signals in (c) mark the signals univocally assigned to a species that were followed for the kinetic measurements: green, [**1**⊃*E*-**2a**]; orange, [**1**⊃*Z*-**2a**]; cyan, *Z*-**2a**; black, *E*-**2a**. The ratios in (b) and (c) indicate respectively the associated fraction of the *E*- and *Z*-complex (complex:axle), obtained by integration of univocally identified, non-overlapping, signals for complex and free axle.

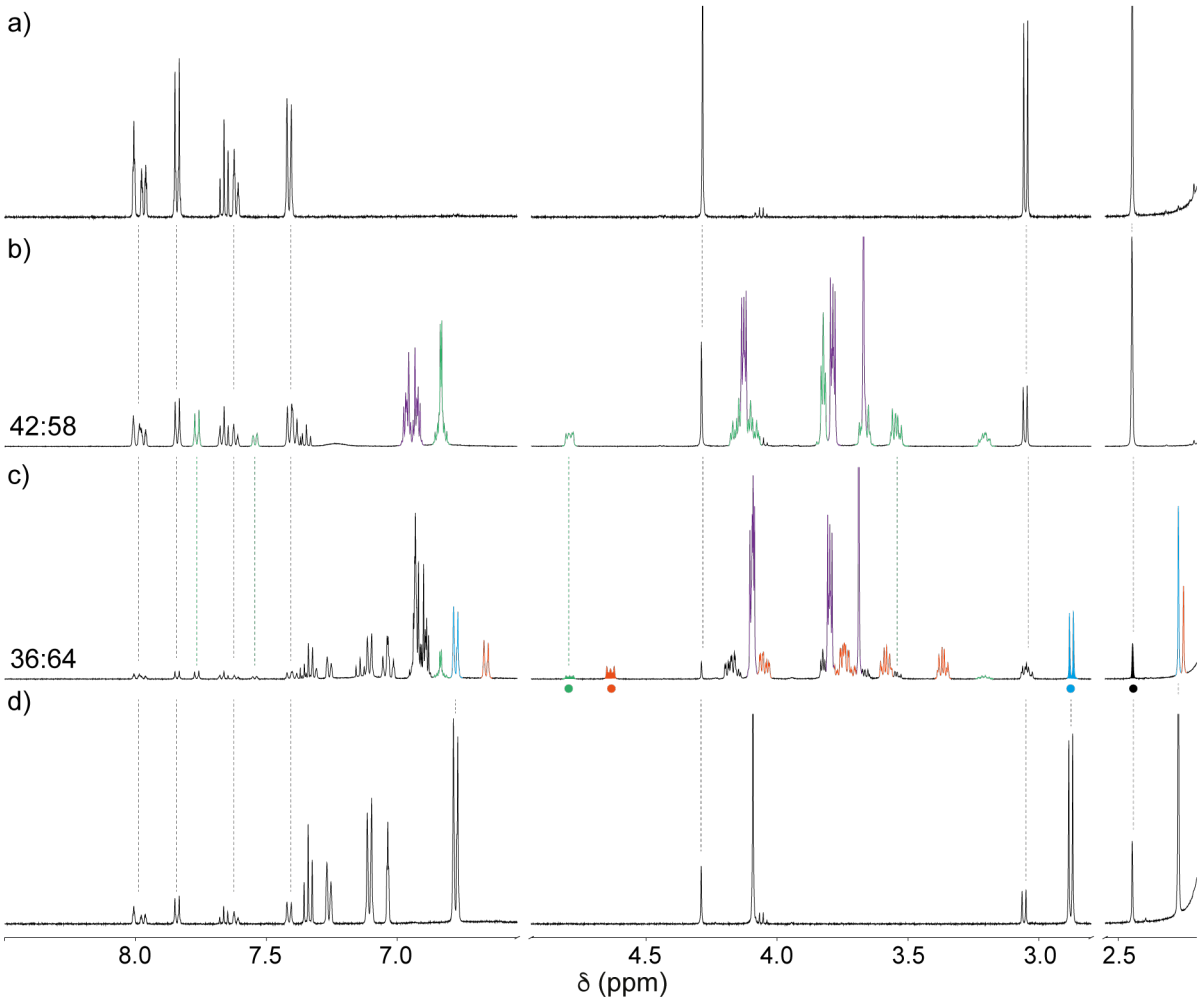


Figure S4. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of a) *E*-**2b**. b) A 1:1 mixture of *E*-**2b** and **1** (5 mM); the signals univocally associated with the complex are highlighted in green, the signals of free **1** are highlighted in purple. c) The same sample after exhaustive irradiation (λ_{irr} = 365 nm, 30 min) and equilibration for 3 hours in the dark. The signals of free *Z*-**2b** are highlighted in cyan, those univocally attributed to the *Z*-complex are highlighted in orange. d) Same sample as (a) after exhaustive irradiation (λ_{irr} = 365 nm, 30 min). The dots underneath the filled signals in (c) mark the signals univocally assigned to a species that were followed for the kinetic measurements: green, [**1**⊃*E*-**2b**]; orange, [**1**⊃*Z*-**2b**]; cyan, *Z*-**2b**; black, *E*-**2b**. The ratios in (b) and (c) indicate respectively the associated fraction of the *E*- and *Z*-complex (complex:axle), obtained by integration of univocally identified, non-overlapping, signals for complex and free axle.

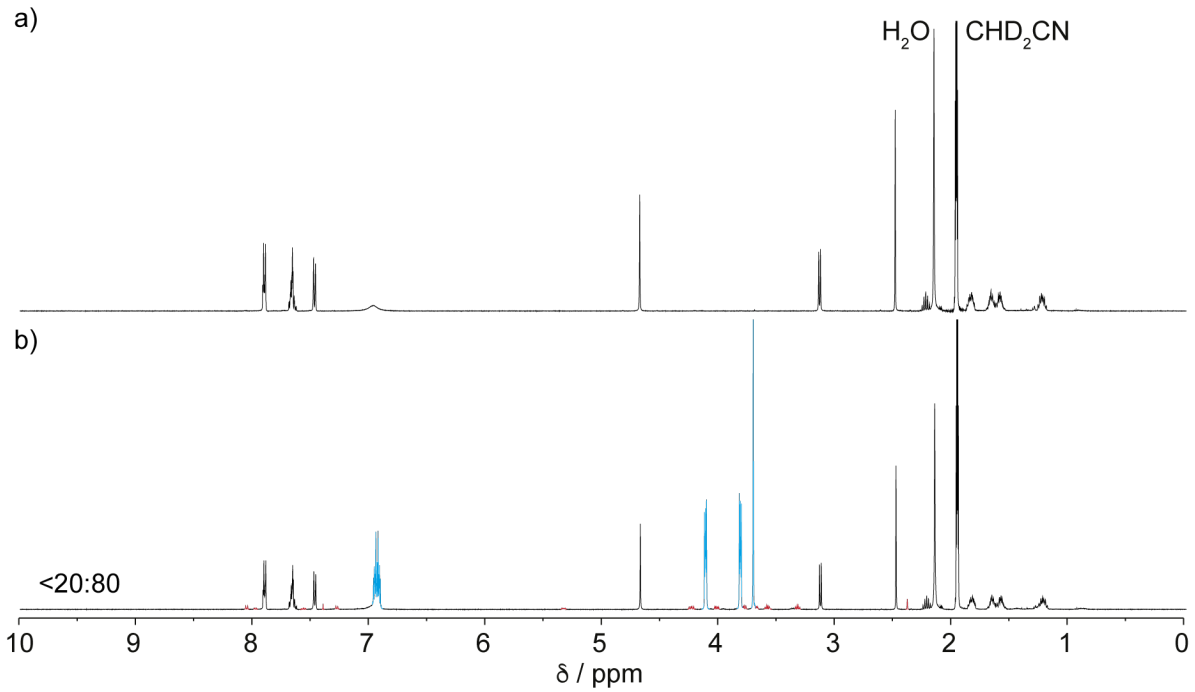


Figure S5. ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of a) *E*-**2c**. b) A 1:1 mixture of *E*-**2c** and **1** (5 mM); the signals associated with the complex are highlighted in red, the signals of free **1** are highlighted in cyan. The ratio in (b) indicates the associated fraction of complex obtained by integration of univocally identified, non-overlapping signals for the complex and the free axle.

3. UV-Vis Spectroscopic characterization

The photophysical and photochemical data for compounds *E*-**2a** and *Z*-**2a** in CH_3CN were reported previously.[1]

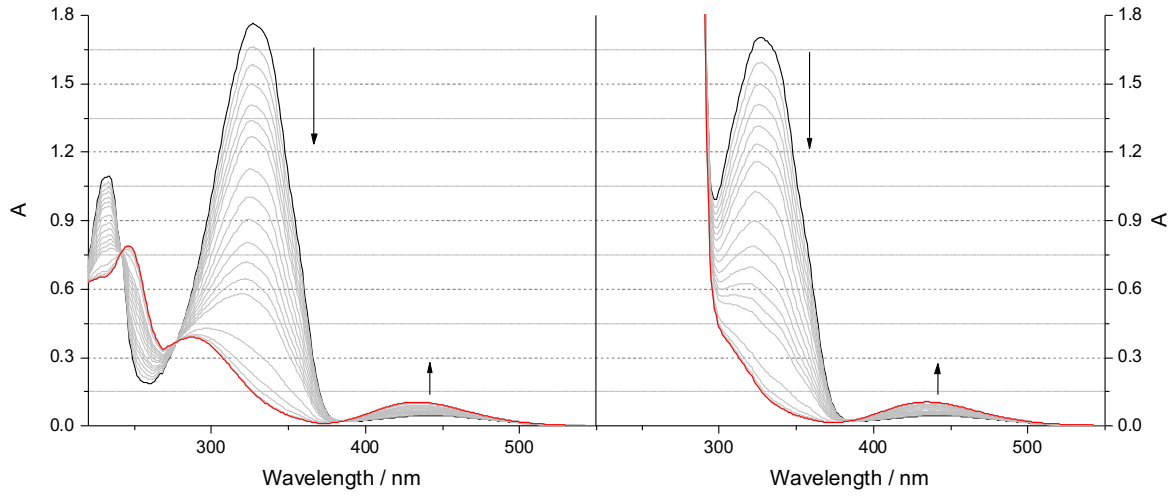


Figure S6. Absorption spectral changes of a solution of *E*-**2b** (left panel; 7.7×10^{-5} M) and [**1**⊃*E*-**2b**] (right panel; 7.7×10^{-5} M axle + 100 equiv. **1**) upon irradiation at 365 nm (air equilibrated CH_3CN, 298 K). Black and red spectra represent respectively the starting (*E*-configured compound) and final (PSS >95% *Z*-configured compound) states.

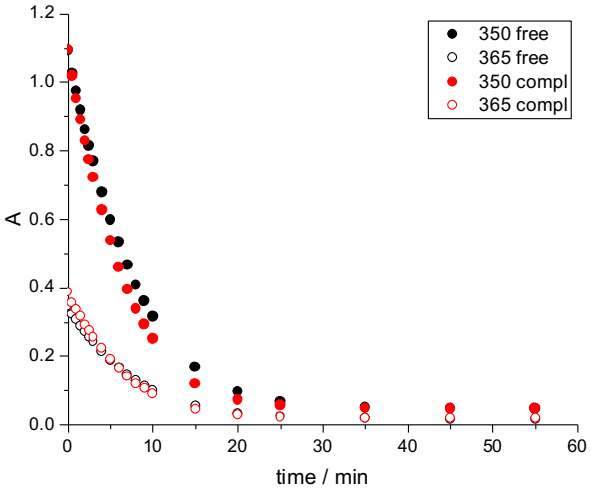


Figure S7. Time-dependent absorption spectral changes at 350 nm (full circles) and at 365 nm (empty circles) of a solution of *E*-**2b** (7.7×10^{-5} M, black) or [**1**⊃*E*-**2b**] (7.7×10^{-5} M axle + 100 equiv. **1**, red) upon irradiation at 365 nm (air equilibrated CH_3CN, 298 K).

4. Determination of the threading and dethreading rate constants

The threading and dethreading rate constants for compounds *E*-**2a** and *Z*-**2a** in CH_3CN were reported previously.[1]

4.1 Threading kinetics of *E*-2b

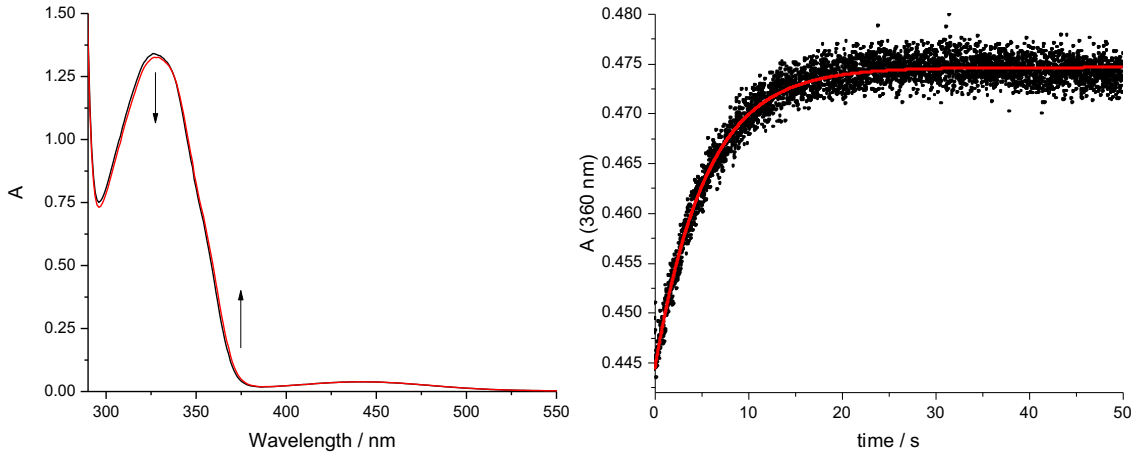


Figure S8. Left panel: absorption spectra of a solution of *E*-**2b** (6.6×10^{-5} M) before (black line) and after (red line) mixing with **1** (3.4×10^{-3} M) in CH_3CN at 298 K. Right panel: absorption spectral changes monitored at 360 nm in the stopped flow experiment. The red line is the least-squares fitting curve according to a mixed order kinetic model, providing a second-order threading rate constant of 16 M^{-1} s^{-1}.

4.2 Threading kinetics of *Z*-2b

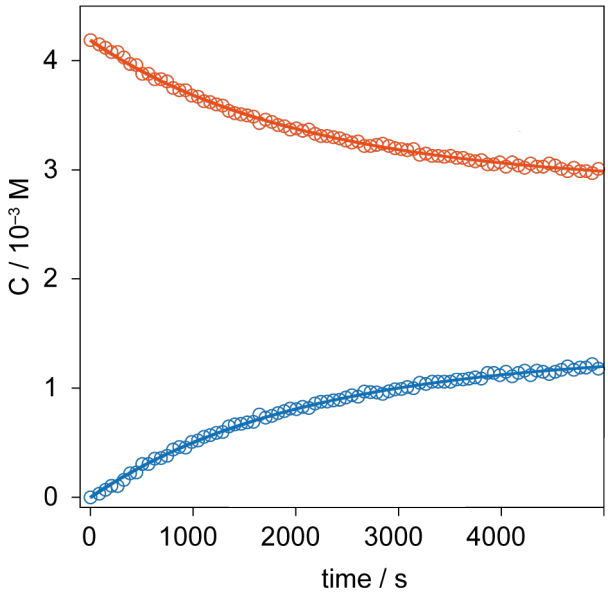


Figure S9. Time-dependent concentration profiles obtained from ^{1}H NMR data (500 MHz, CD_3CN, 298 K) on a solution of *Z*-**2b** (4.2 mM) upon the addition of **1** (5.0 mM), highlighting the slow threading of the ring over the cyclopentyl pseudo-stopper. Blue and orange circles represent the concentration of *Z*-**2b** and [**1**⊃*Z*-**2b**] respectively. Solid lines are the least-squares fitting curve according to a mixed order kinetic model.

Table S1. Thermodynamic, kinetic, spectroscopic and photochemical parameters for *E* and *Z* axles **2a-c** and for the corresponding [2]pseudorotaxanes in air equilibrated acetonitrile at 298 K.[‡]

	2a·PF_6 [a]		**2b**·PF_6		**2c**·PF_6	
	E	*Z*	*E*	*Z*	*E*	*Z*
K (M^{-1})[b]	225	230 196[c]	230	170 115[c]	<50	<10
k_{in} (M^{-1} s^{-1})	22[d]	5.1×10^{-2} [e]	16[d]	3.1×10^{-2} [e]	[f]	[f]
k_{out} (s^{-1})	0.1[d]	2.6×10^{-4} [e]	0.07[d]	2.7×10^{-4} [e]	[f]	[f]
$k_{\Delta,u}$ (s^{-1})[g]	[h]	1.9×10^{-6}	[h]	1.9×10^{-6}	[h]	8.3×10^{-3}
$k_{\Delta,c}$ (s^{-1})[g]	[h]	1.8×10^{-6}	[h]	4.8×10^{-6}	[h]	[f]
Φ_u[i]	0.17	[f]	0.23	0.58	[f]	[f]
Φ_c[i]	[f]	[f]	0.22	0.59	[f]	[f]
ε_u (M^{-1} cm^{-1})[j]	6800	<100[l]	3900	<100[k]	10100	[f]
ε_c (M^{-1} cm^{-1})[j]	[f]	[f]	4800	<100[k]	[f]	[f]

[‡]The indexes "u" and "c" denote that the corresponding quantity refers to the uncomplexed or complexed axle respectively. [a]Data from ref. [1]. [b]Determined by single point measurement of an equilibrated equimolar solution of the axle and **1**, unless noted otherwise. [c]Calculated as k_{in}/k_{out}. [d]Determined from stopped-flow UV-vis absorption experiments. [e]Determined from time-dependent ^{1}H NMR concentration profiles. [f]Not determined. [g]Rate constant of thermal $Z\rightarrow E$ isomerization. [h]The compound does not exhibit the corresponding process. [i]Quantum yield of the photochemical isomerization upon irradiation at 365 nm. [j]Molar absorption coefficient at 365 nm. [k]Upper limit estimated from the [*Z*]:[*E*] ratio at PSS.

5. Observation of light-induced non-equilibrium states

The irradiation was performed in the NMR probe with a PMMA optical fiber (~5 m length) whose protective coating was removed for ca. 6 cm at the terminal end. The exposed PMMA core was sanded in order to diffuse light into solution. In a typical NMR experiment, the exposed core of the fiber was introduced into a tailor-made glass casing and immersed in 0.6 mL of an equimolar solution (8.9×10^{-3} M) of the axle and **1** inside an NMR tube. The other extremity of the fiber was connected to a LED source. The radiant power at the end of the optical fiber was 150 mW, corresponding to a photon flow higher than 10^{-7} Einstein s^{-1}.

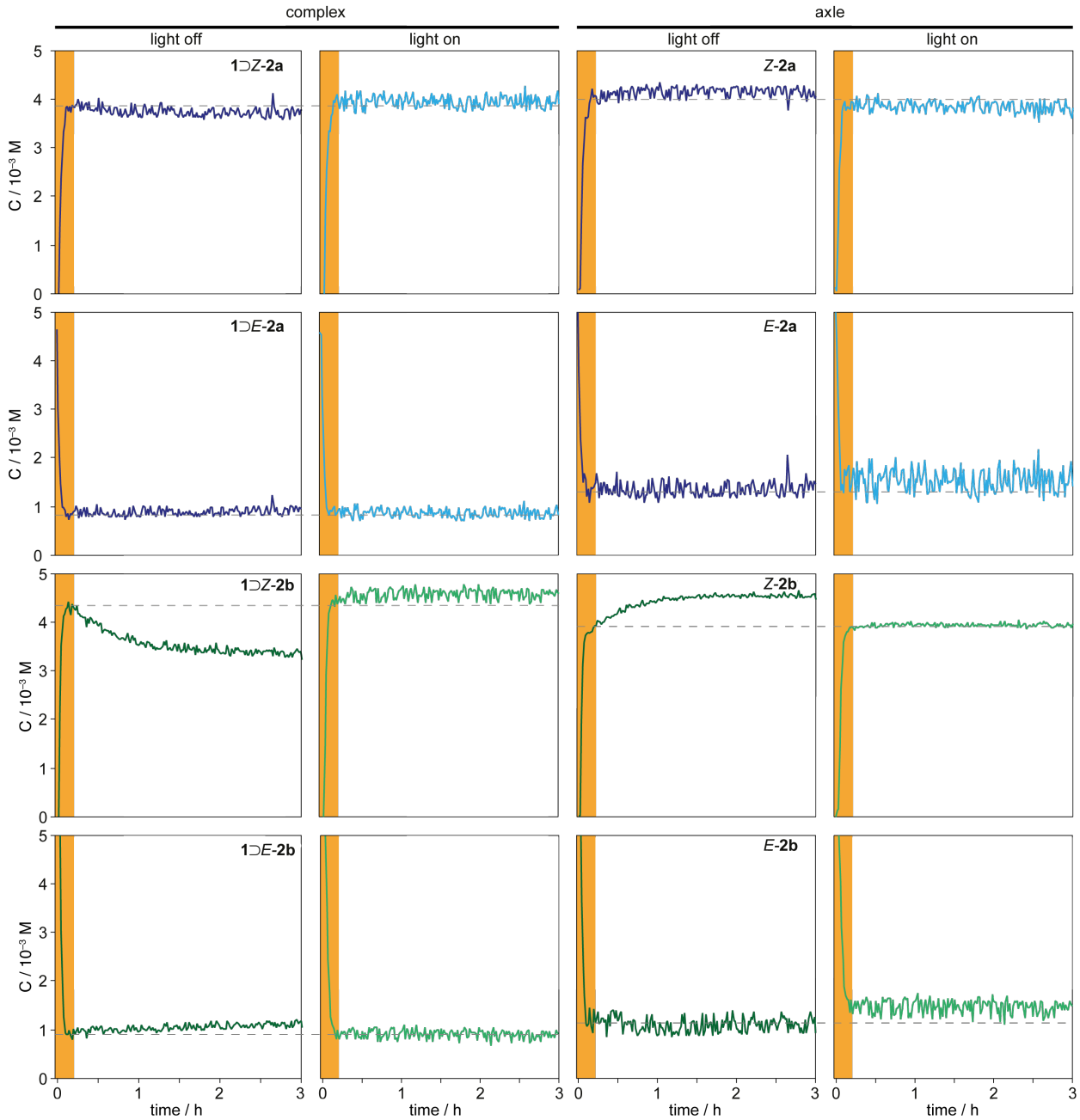


Figure S10. Experimental concentration profiles of all photoactive species (*Z* and *E* complexes, *Z* and *E* axles) after fast light-induced isomerization (orange band) of an equilibrated mixture of *E*-**2a** (blue traces) or *E*-**2b** (green traces) and **1**. Dark and light traces indicate system evolution in the dark or under constant illumination, respectively. Data obtained from ^{1}H NMR spectra (500 MHz, CD_3CN, *C* = 10 mM, 298 K).

6. NMR Spectra

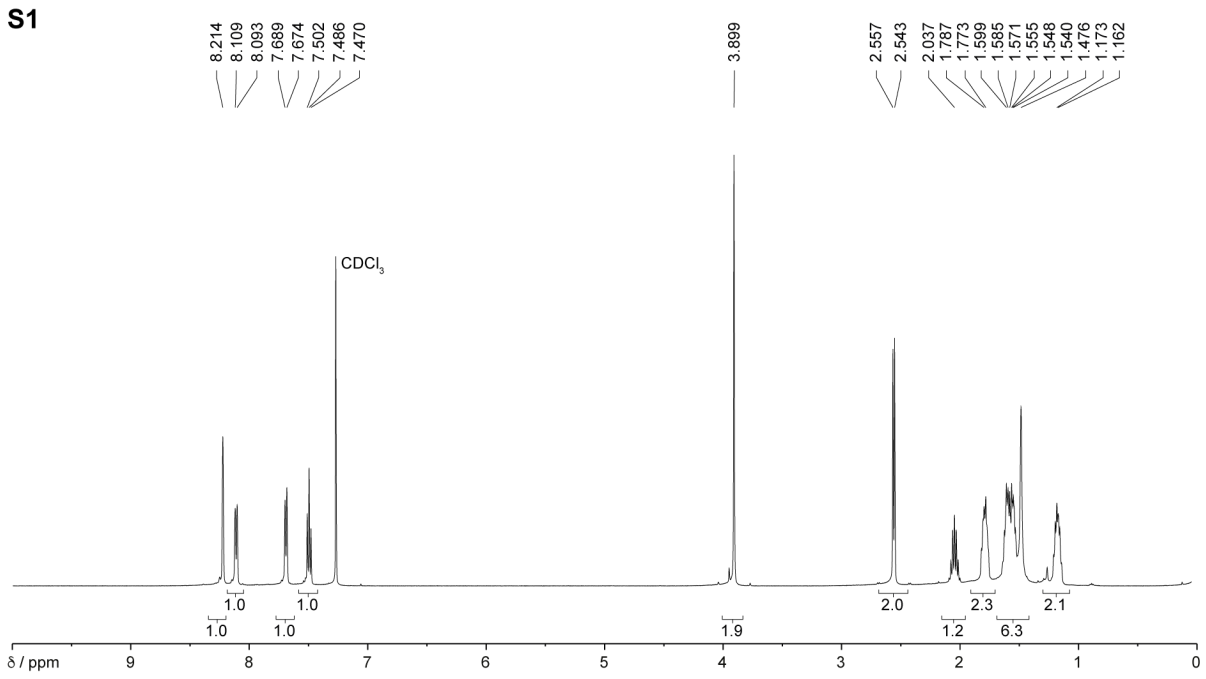


Figure S11. ^{1}H NMR spectrum of **S1** (500 MHz, $CDCl_3$, 298 K).

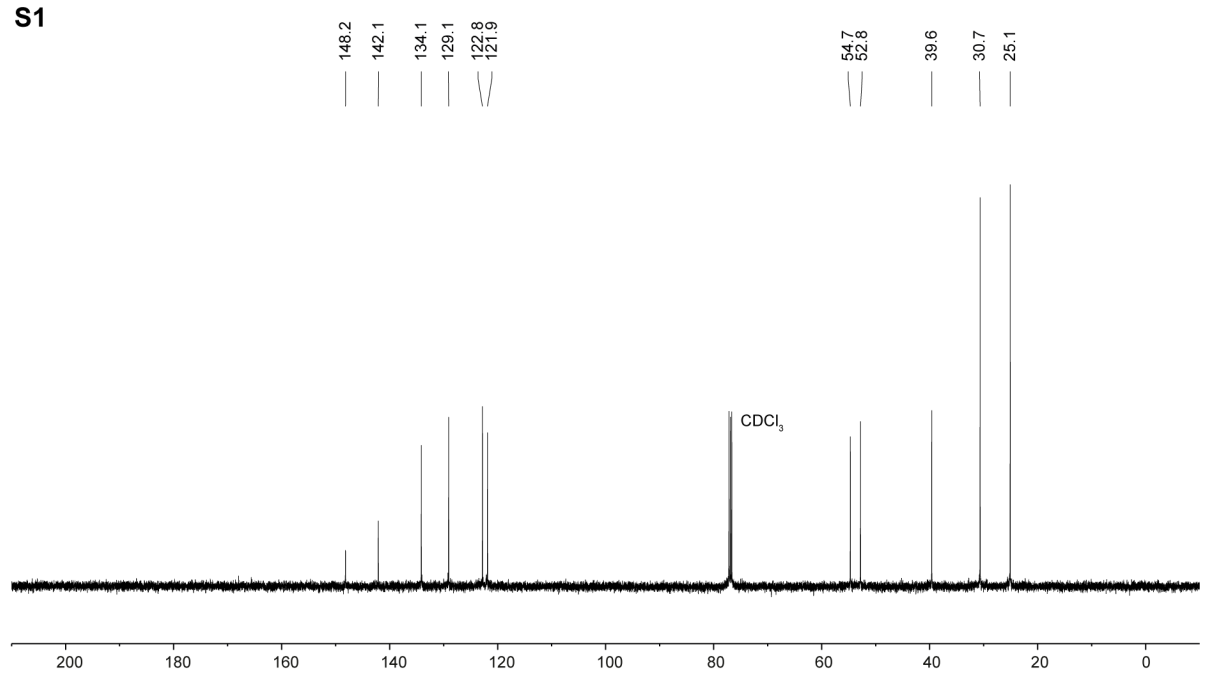


Figure S12. ^{13}C NMR spectrum of **S1** (125 MHz, $CDCl_3$, 298 K).

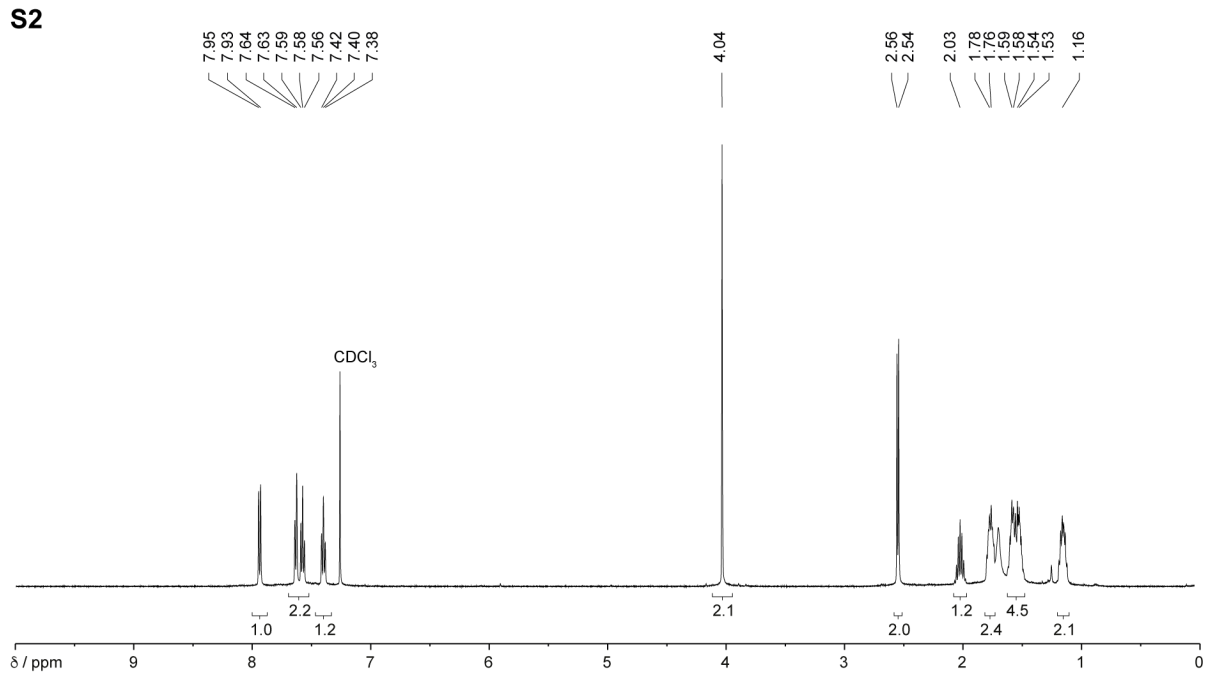


Figure S13. ^{1}H NMR spectrum of **S2** (500 MHz, $CDCl_3$, 298 K).

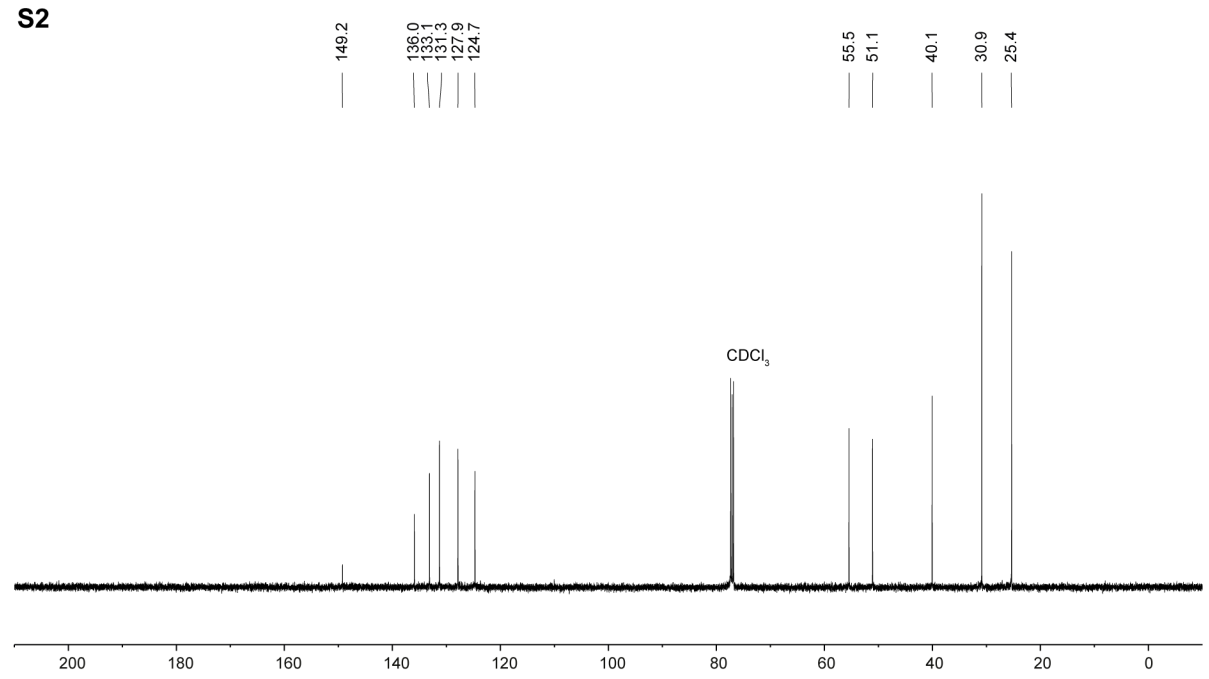


Figure S14. ^{13}C NMR spectrum of **S2** (125 MHz, $CDCl_3$, 298 K).

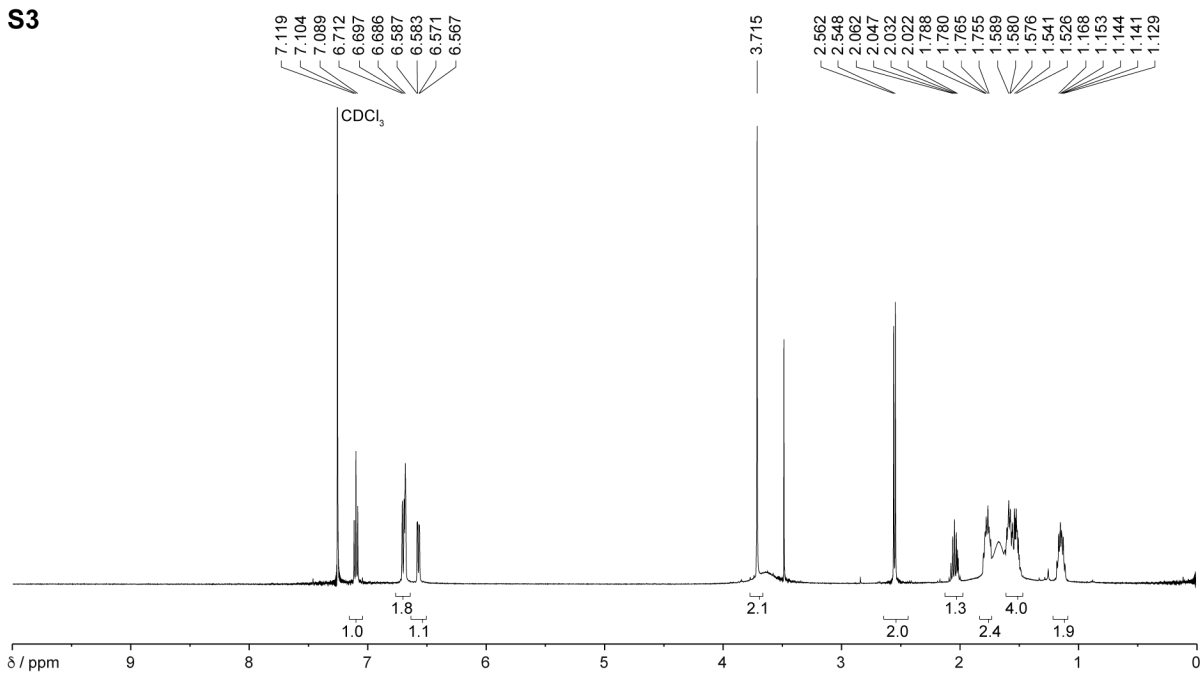


Figure S15. ^{1}H NMR spectrum of **S3** (500 MHz, $CDCl_3$, 298 K).

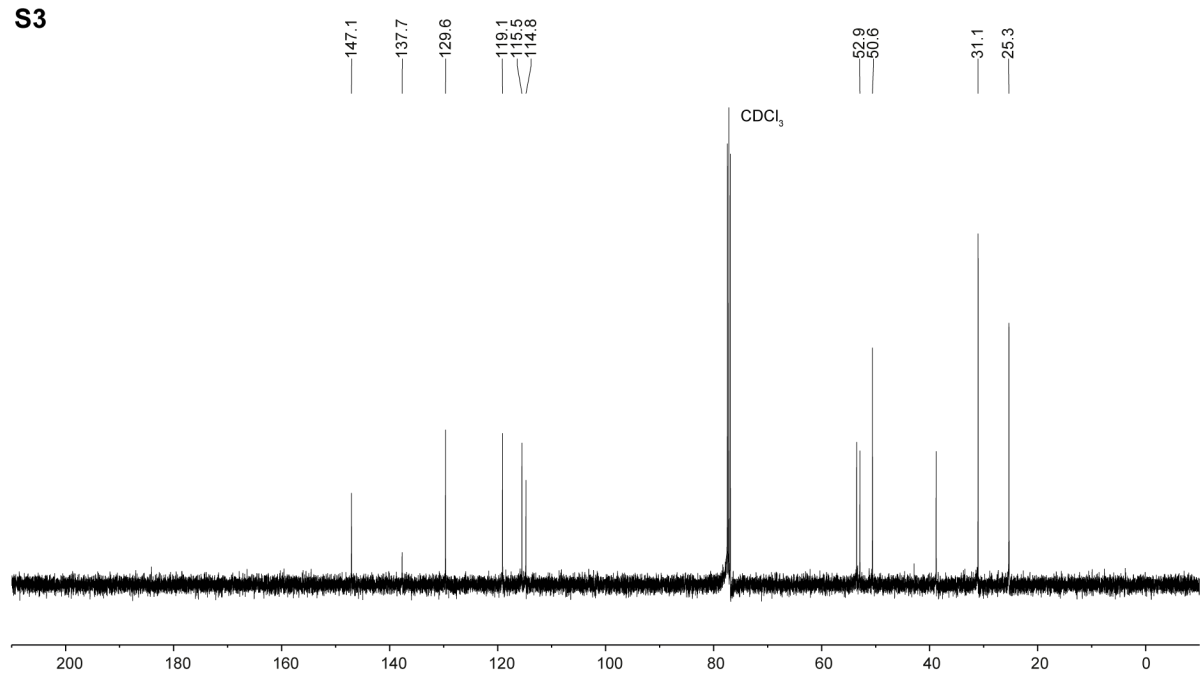


Figure S16. ^{13}C NMR spectrum of **S3** (125 MHz, $CDCl_3$, 298 K).

S4

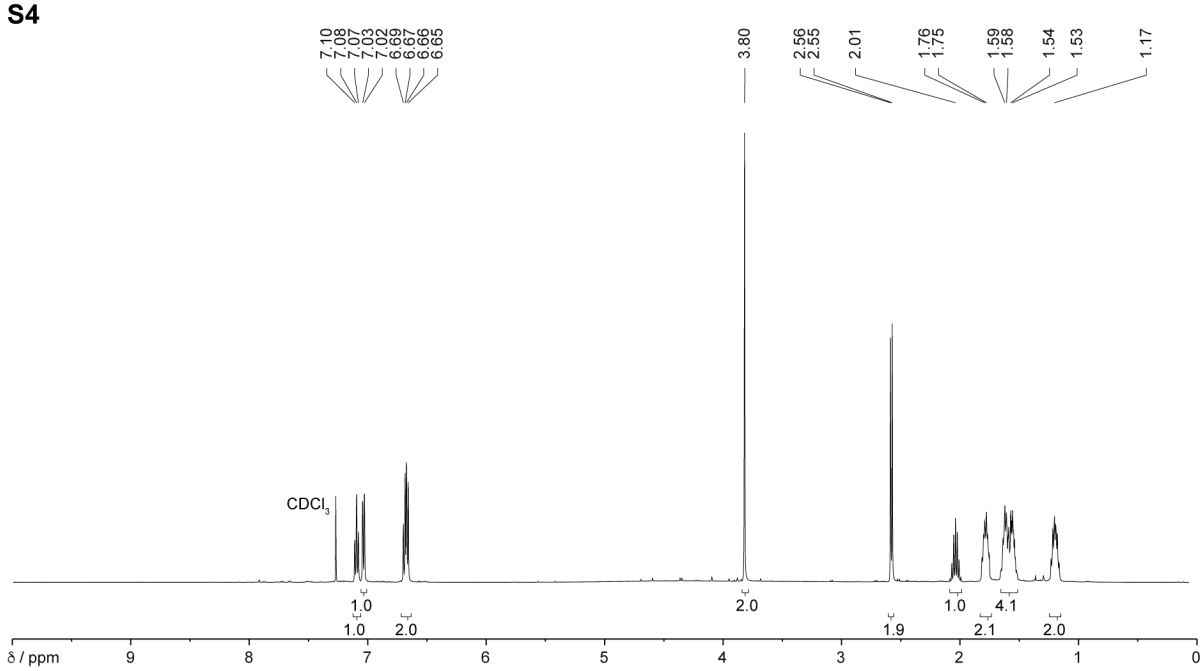


Figure S17. ^{1}H NMR spectrum of **S4** (500 MHz, $CDCl_3$, 298 K).

S4

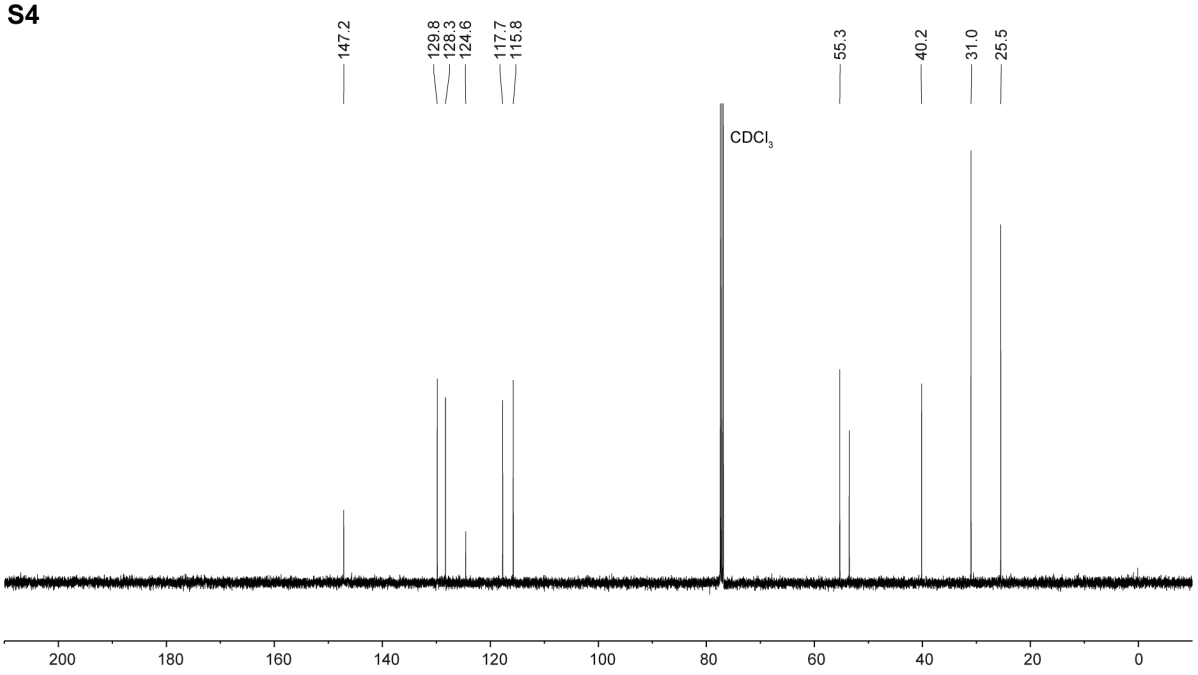


Figure S18. ^{13}C NMR spectrum of **S4** (125 MHz, $CDCl_3$, 298 K).

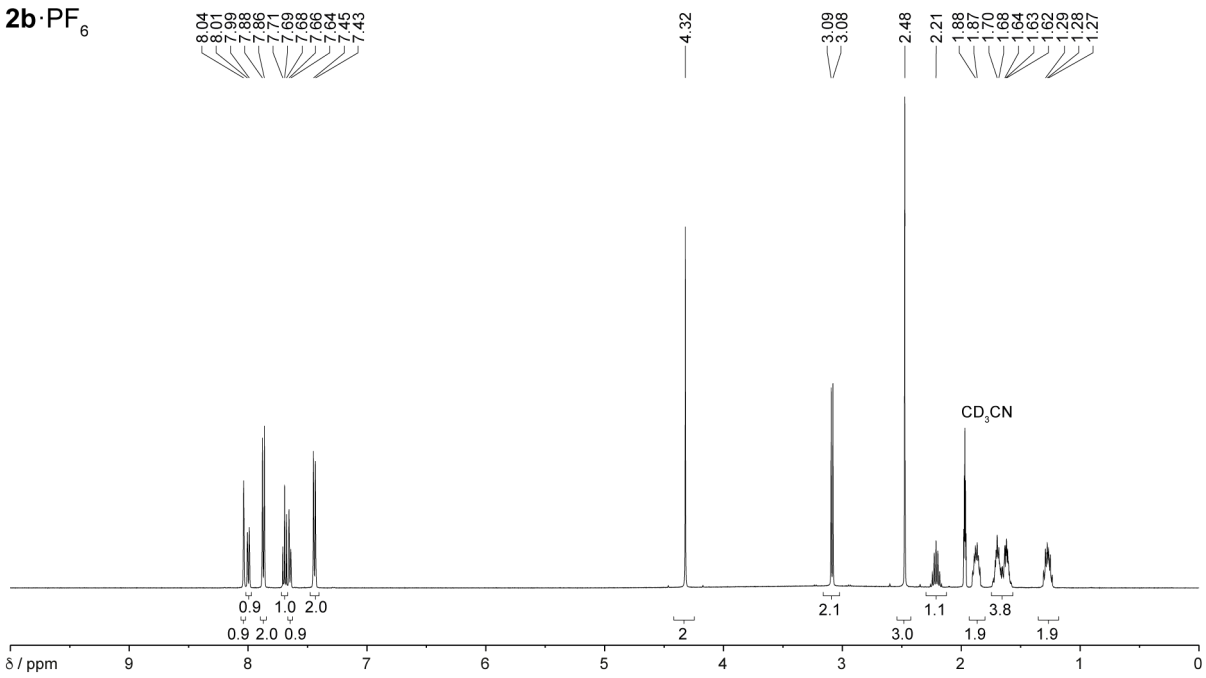


Figure S19. ^{1}H NMR spectrum of *E*-**2b**·PF_6 (500 MHz, CD_3CN, 298 K).

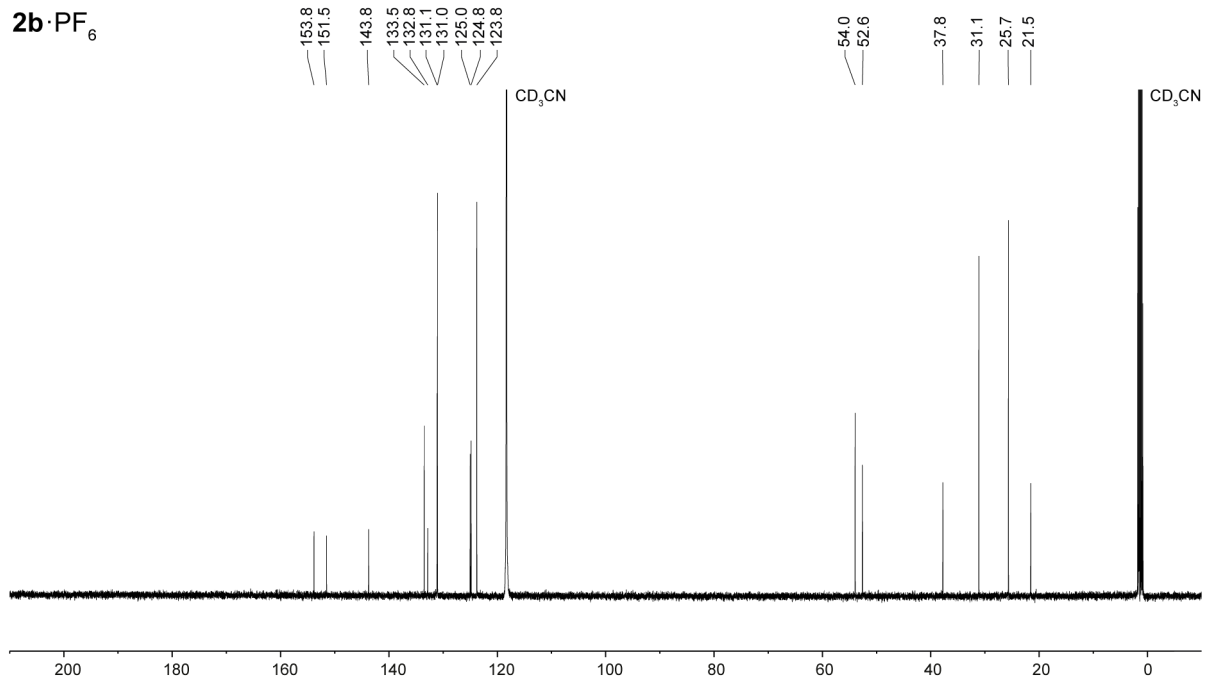


Figure S20. ^{13}C NMR spectrum of *E*-**2b**·PF_6 (125 MHz, CD_3CN, 298 K).

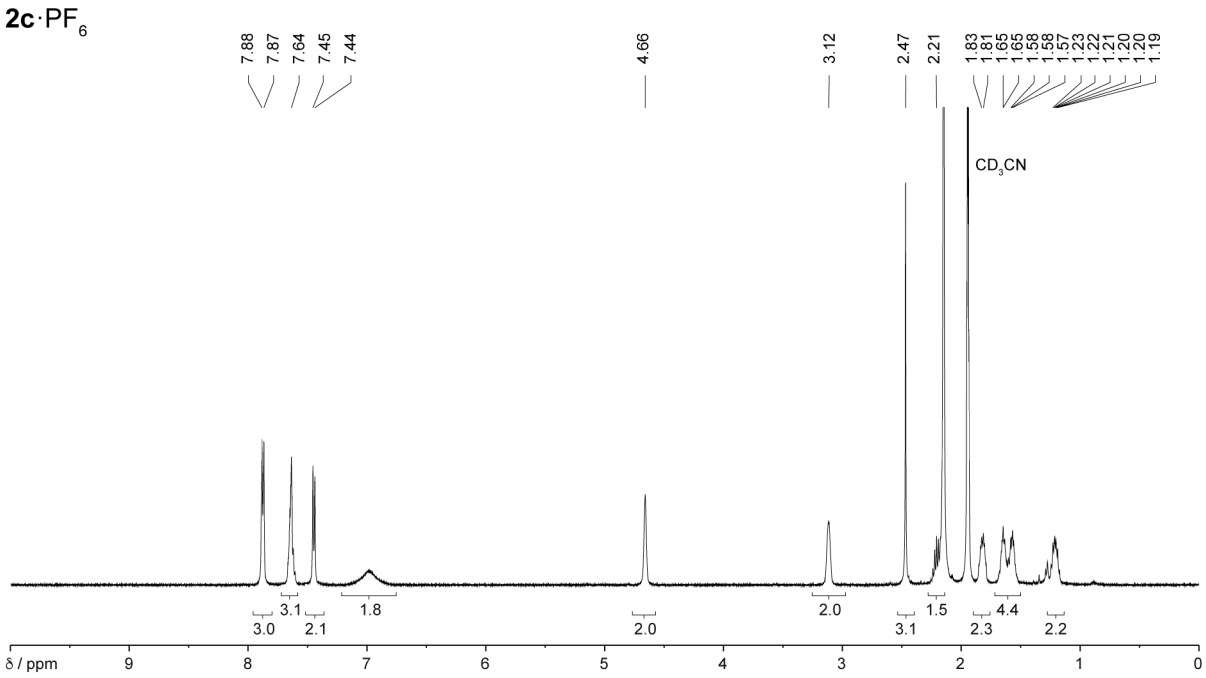


Figure S21. ^{1}H NMR spectrum of *E*-**2c**·PF_6 (500 MHz, CD_3CN, 298 K).

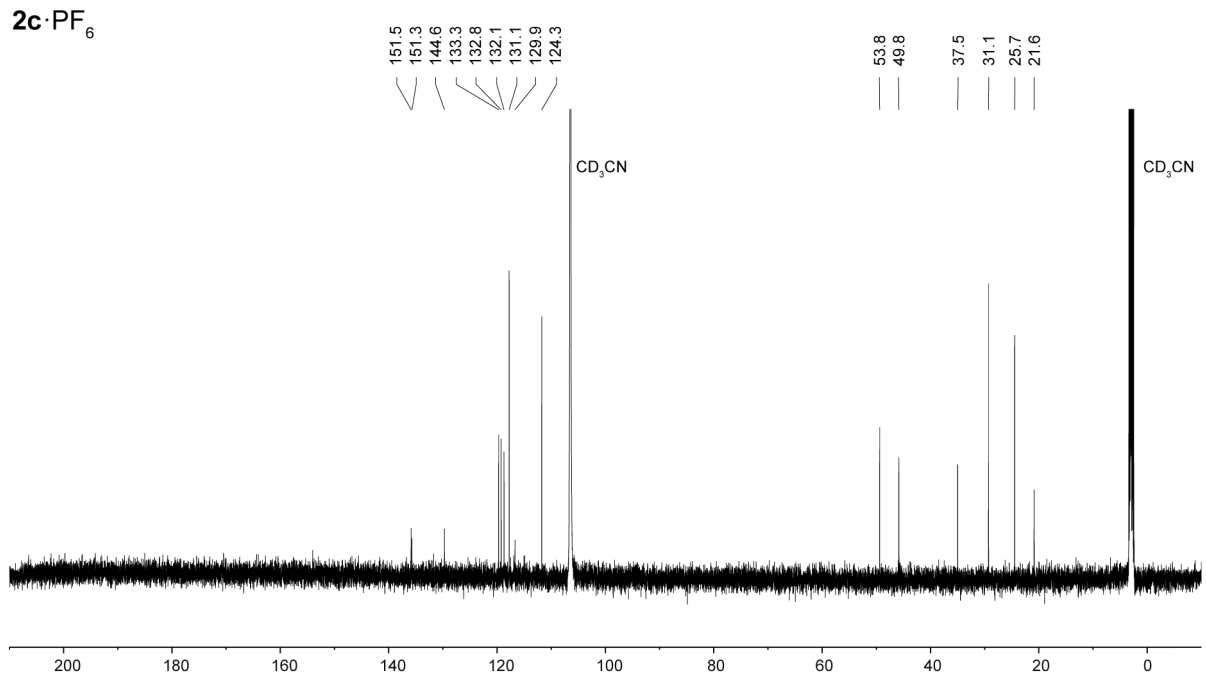


Figure S22. ^{13}C NMR spectrum of *E*-**2c**·PF_6 (125 MHz, CD_3CN, 298 K).

7. References

[1] M. Baroncini, S. Silvi, M. Venturi, A. Credi, *Angew. Chem. Int. Ed.* **2012**, *51*, 4223-4226; Angew. Chem. **2012**, *124*, 4299-4302