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Heteroternary Cucurbit[8]uril Complexes as Supramolecular Scaffolds for Self-assembled Bifunctional Photoredoxcatalysts

Fabian Lutz,[a] Nerea Lorenzo-Parodi,[b] Torsten C. Schmidt,[b] Jochen Niemeyer*[a]

[a] Faculty of Chemistry, Organic Chemistry and Center for Nanointegration Duisburg- Essen (CENIDE), University of Duisburg-Essen, Universitätsstrasse. 7, 45141 Essen, Germany. jochen.niemeyer@uni-due.de

[b] Instrumental Analytical Chemistry and Centre for Water and Environmental Research (ZWU), Universitätsstrasse 5, 45141 Essen, Germany

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1. General informations

1.1 Materials and Methods

For all described experiments, thin-layer chromatography (TLC) was performed using Polygram® SIL G/UV254 TLC plates (silica gel 0.2 mm, 40 × 80 mm). The spots were visualized by placing them in a dark box under a 254 nm UV light source. Flash column chromatography was carried out using silica gel 60M (40 – 63 µm), purchased from MACHEREY-NAGEL GmbH & Co. KG under an argon pressure of 0.5 bar.

Reactions under inert conditions were conducted by heating the flask for at least 10 minutes over hot air (> 200 °C) under vacuum and flushing it with argon three times before use.

4,4'-Dimethyl-2,2'-bipyridine (sold as 2,2'-Bi-4-picoline) and 1,3-dibromopropane were purchased from Fluorochem Ltd and used without further purification.

Selenium dioxide, Eosin Y and potassium tetrachloroplatinate(II) were purchased from Alfa Aesar and used without further purification.

Iodomethane, trimethylamine, triethanolamine and cucurbit[8]uril hydrate were purchased from Sigma Aldrich and used without further purification. CB8 was titrated against cobaltocene before use to determine its purity, following literature procedure.[1]

n-Butyllithium (2.7 M in toluene) was purchased from ACROS Organics and used without further purification.

Bis(acetonitrile)dichloropalladium(II), bis(bipyridinium)ruthenium(II) chloride and dichlorotetrakis(2-(2-pyridinyl)phenyl)diiridium(III) were purchased from ABCR GmbH and used without further purification.

Sodium tris(acetoxy)borohydride was purchased from Carbolution Chemicals GmbH and used without further purification.

Ethyl acetate was purchased in technical grade and distilled before use. All other solvents were purchased as p.a. grade. Dry THF was stirred over sodium and distilled before use. Deuterated solvents for NMR were purchased from Deutero GmbH. [D_6]-dimethyl sulfoxide was stored over 3 Å molecular sieve.

1.2 Analytical methods

NMR spectroscopy was conducted with a Bruker DMX 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75.5 MHz), Bruker DMX 600 spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz) or Bruker Avance Neo 400 (^{1}H: 400 MHz, ^{13}C: 100.7 MHz). All measurements were performed at room temperature unless noted otherwise in deuterated solvents. The chemical shifts are referenced relative to the solvent´s residual proton signals (for ^{1}H NMR) or to the solvent signal (for ^{13}C) as follows:

Solvent	^{1}H-NMR	^{13}C-NMR
[D_1]-Chloroform	7.26	77.16
[D_6]-Dimethyl sulfoxide	2.50	39.52

Fine structure of the spectra is described as follows: s = singlet, br s = broad singlet, d = doublet, t = triplet, m = multiplet. Coupling constants, where applicable, are given in Hertz.

Mass spectrometry was conducted on a Bruker Amazon SL spectrometer (ESI low-resolution) or Bruker Maxis 4G spectrometer with HPLC (ESI high-resolution). High-resolution spectra were recorded with an internal standard for calibration.

UV-Vis absorption spectroscopy was conducted on a JASCO V-660 spectrophotometer. The cuvettes were purchased from Hellma Analytics, type 100-QS (10 mm light path). The used solvents were Millipore water and triethanolamine in analytical grade. Spectra were recorded five times and the results averaged for a higher signal to noise ratio.

Fluorescence spectroscopy was conducted on a Varian Cary Eclipse Fluorescence Spectrophotometer. The cuvettes were purchased from Hellma Analytics, type 115F-QS SD (10x2 mm). The used solvents were Millipore water and triethanolamine in analytical grade.

MPLC purification was performed on a Gilson PLC 2050 with an auto sampler on reused C18 reverse-phase silica gel type (YMC*Gel ODS-AQ-HG, 15 µm particle size, 12 nm pore size).
Gas chromatography was conducted on a Shimadzu GC-2014 with TCD. The column used was an Agilent J&W GC CP-Molsieve 5A with a length of 50 m, inner diameter of 0.32 mm and a film thickness of 30 µm (CP7540). Argon was used as carrier gas. The obtained data was analysed with OriginPro 2019b. For the quantitative runs, the injector was heated to a temperature of 250 °C, the TCD was fixed at 100 °C with a sampling rate of 200 ms. The column was preheated to 40 °C, then increased by 10 °C per minute for five minutes and kept at 90 °C for two minutes. The flow parameters were as follows: 210 kPa pressure, 16.1 mL / min total flow with 2.0 mL / min purge flow and a split ratio of 5, leading to a column flow of 2.35 mL / min and a linear velocity of 35 cm / sec. The hydrogen signal was detected at 3.5 minutes.

1.3 Irradiation experiments

For irradiation experiments, a self-built setup, adapted from *König* and coworkers, was used. The samples were irradiated in 20 mm crimp top vials (38.5 mm · 22 mm) with 20 mm crimp caps with a silicone/PTFE septum of 3.0 mm thickness. These vials were placed in an aluminium heating block that was connected to a thermostat and irradiated by either an OSRAM Oslon SSL 80 blue on star (for photosensitizer **2**, λ_{max} = 470 nm, 1120 mW), OSRAM Oslon SSL 80 green on star (for photosensitizer **1**, λ_{max} = 528 nm, 1120 mW) or SSC VIOSYS UV 365nm CUN66A1B on star LED (for photosensitizer **3**, λ_{max} = 365 nm, 1260 mW).

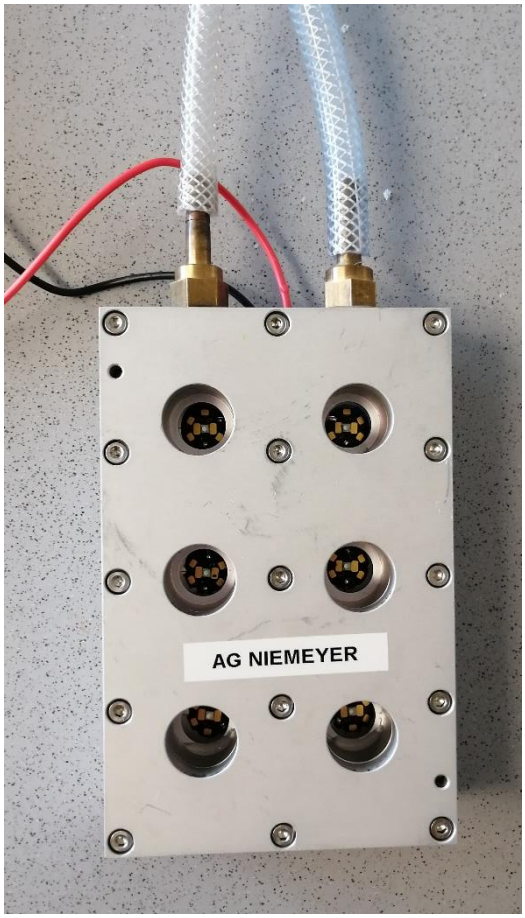


Figure S1: *Irradiation setup with LED lights and aluminium heating block.*

2. Synthetic procedures

2.1 Overview

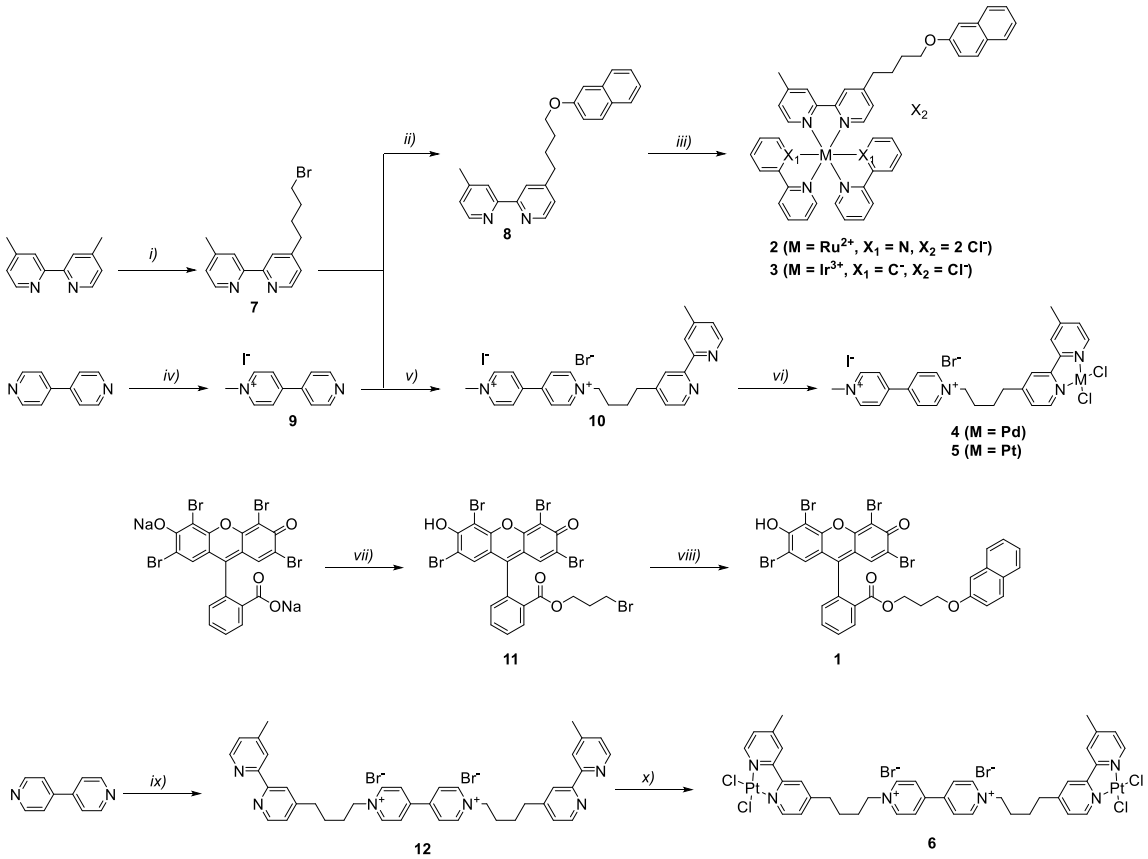
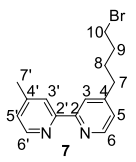


Figure S2: *Synthesis of the photosensitizers **1**, **2** and **3** and the water reducing catalysts **4**, **5** and **6**. i) 4,4'-Dimethyl-2,2'-bipyridine, DIPA, THF, then n-BuLi, then 4,4'-dimethyl-2,2'-bipyridine, THF, then 1,3-dibromopropane, 54%. ii) **7**, 2-Naphthol, Cs_2CO_3, acetonitrile, 53%. iii) $[Ru(bipy)_2Cl_2]$, $AgNO_3$, methanol, then **8**, NH_4PF_6, ion exchange chromatography, 85% for **2**; $[Ir_2(ppy)_4Cl_2]$, **8**, chloroform, methanol, NH_4PF_6, ion exchange chromatography, 95% for **3**. iv) 4,4'-bipyridine, iodomethane, acetone, 78%. v) **7**, **9**, acetonitrile, 44%. vi) **10**, $[Pd(CH_3CN)_2Cl_2]$, acetonitrile, 93% for **4**; **10**, $[Pt(DMSO)_2Cl_2]$, methanol, 79% for **5**. vii) Eosin Y, 1,3-dibromopropane, dimethylformamide, 51%. viii) **11**, 2-naphthol, $CaCO_3$, acetonitrile, 31%. ix) 4,4'-bipyridine, **7**, acetonitrile, 48%. x) **12**, $[Pt(DMSO)_2Cl_2]$, methanol, 81%.*

7[2], **9**[3], **10**[4] and **12**[5] were synthesized according to literature procedures and are only listed for the sake of completeness.

2.2 Synthesis of 4-(4-bromobutyl)-4'-methyl-2,2'-bipyridine (7)[2]

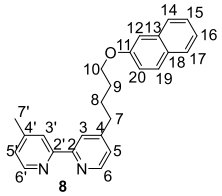


In a flame-dried flask filled with argon at -78 °C, freshly distilled dry diisopropylamine (2.30 mL, 16.0 mmol, 1.25 eq.) was dissolved in dry tetrahydrofurane (28.0 mL) before the slow addition of *n*-butyllithium (2.7 M in toluene, 6.10 mL, 16.0 mmol, 1.25 eq.). This mixture was stirred for about 15 minutes, until a slightly yellow colour occurred. 4,4'-dimethyl-2,2'-bipyridine (2.50 g, 13.6 mmol, 1 eq.), dissolved in dry tetrahydrofurane (60 mL) was then added dropwise over 10 minutes. This was stirred for one hour at -78 °C before the rapid addition of 1,3-dibromopropane (5.51 mL, 54.3 mmol, 4 eq.). After one more hour, the cooling bath was removed and the mixture was stirred at room temperature, changing its colour from blue to green to yellow. After 3 hours, phosphate buffer (50 mM mM, pH = 7.00, 100 mL) was added and the aqueous phase was extracted with diethyl ether (2 x 150 mL). The organic phase was dried over magnesium sulfate before the removal of the solvent under reduced pressure. The resulting orange oil was further purified via reverse-phase MPLC (120 g, 25 mL/min, 30 – 60% methanol in water with 0.05% trifluoroacetic acid, 120 minutes). After removal of the solvent under reduced pressure, the product was received as an off-white solid (2.23 g, 7.31 mmol, 53.8% yield).

$C_{15}H_{17}BrN_2$: 305.22 g/mol

^{1}H-NMR (400 MHz, [D_1]-chloroform, 300 K): δ = 8.57 (d, *J* = 5.1 Hz, 1H, H-6), 8.54 (d, *J* = 5.0 Hz, 1H, H-6'), 8.24 (s, 2H, H-3 + H-3'), 7.17 – 7.12 (m, 2H, H-5,H-5'), 3.42 (t, *J* = 6.4 Hz, 2H, H-10), 2.73 (t, *J* = 7.4 Hz, 2H, H-7), 2.44 (s, 3H, H-7'), 1.97 – 1.81 (m, 4H, H-8 + H-9).

2.3 Synthesis of 4-methyl-4'-(4-(naphthalen-2-yloxy)butyl)-2,2'-bipyridine (8)



Bromobutyl bipyridine **7** (300 mg, 0.983 mmol, 1 eq.), 2-naphthol (283 mg, 1.97 mmol, 2 eq.) and caesium carbonate (1.28 g, 3.93 mmol, 4 eq.) were dissolved in acetonitrile (8.0 mL) and the mixture was heated to reflux. After 16 hours, the precipitate was removed by filtration and ethyl acetate (20 mL) was added. This led to formation of further precipitate, which was again removed by filtration. The organic filtrate was washed with water (15 mL), dried over sodium sulphate and the solvent was removed under reduced pressure. The product was further purified by column chromatography (1.5 x 25 cm, SiO_2, 3:1 cyclohexane : ethyl acetate) to give the product as an off-white solid (190 mg, 0.516 mmol, 52.9% yield).

$C_{25}H_{24}N_2O$: 368.48 g/mol

^{1}H-NMR (600 MHz, [D_1]-chloroform, 300 K): δ = 8.58 (d, ^3J = 5.0 Hz, 1H, H-6), 8.55 (d, ^3J = 5.0 Hz, 1H, H-6'), 8.31 (s, 1H, H-3), 8.26 (s, 1H, H-3'), 7.75 (d, ^3J = 8.2 Hz, 1H, H-17), 7.73 (d, ^3J = 9.2 Hz, 1H, H-19), 7.71 (d, ^3J = 7.8 Hz, 1H, H-14), 7.42 (ddd, ^3J = 8.2, 6.7 Hz, ^5J = 1.3 Hz, 1H, H-15), 7.32 (ddd, ^3J = 8.0, 6.8 Hz, ^5J = 1.1 Hz, 1H, H-16), 7.19 (dd, ^3J = 5.0 Hz, ^5J = 1.7 Hz, 1H, H-5), 7.16 (d, ^3J = 4.8 Hz, H-5'), 7.14 (dd, ^3J = 8.9 Hz, ^5J = 2.8 Hz, 1H, H-20), 7.11 (d, ^5J = 2.5 Hz, 1H, H-12), 4.11 (t, ^3J = 5.9 Hz, 2H, H-10), 2.82 (t, ^3J = 7.3 Hz, 2H, H-7), 2.45 (s, 3H, H-7'), 2.01 – 1.88 (m, 4H, H-8 + H-9).

^{13}C NMR (151 MHz, [D_1]-chloroform, 300 K): δ = 157.1 (C-11), 152.7 (C-4, from HMBC), 149.1 (C-6), 148.9 (C-6'), 148.6 (C-4'), 134.7 (C-13), 129.5 (C-19), 129.1 (C-18), 127.8 (C-17), 126.9 (C-14), 126.5 (C-15), 124.9 (C-5'), 124.2 (C-5), 123.7 (C-16), 122.4 (C-3'), 121.6 (C-3), 119.1 (C-20), 106.7 (C-12), 67.7 (C-10), 35.3 (C-7), 29.0 (C-8 / 9), 27.1 (C-8 / 9), 21.4 (C-7'). Signals for C-2, C-2' and C-4 could not be detected.

COSY (600 MHz/600 MHz, [D_1]-chloroform, 300 K): δ = 8.58 / 7.19 (H-6 / H-5), 8.55 / 7.16 (H-6' / H-5'), 7.75 / 7.32 (H-17 / H-16), 7.73 / 7.14 (H-19 / H-20), 7.71 / 7.42 (H-14 / H-15), 7.42 / 7.71, 7.32 (H-15 / H-14, H-16), 7.32 / 7.75, 7.42 (H-16 / H-17, H-15), 7.19 / 8.58 (H-5 / H-6), 7.16 / 8.55 (H-5' / H-6'), 7.14 / 7.73 (H-20 / H-19), 4.11 / 2.01 – 1.88 (H-10 / H-8 + H-9), 2.82 / 2.01 – 1.88 (H-7 / H-8 + H-9), 2.01 – 1.88 / 4.11, 2.82 (H-8 + H-9 / H-10, H-7).

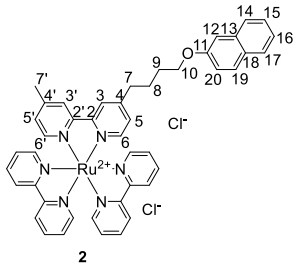
HSQC (600 MHz/151 MHz, [D_1]-chloroform, 300 K): δ = 8.58 / 149.1 (H-6 / C-6), 8.55 / 148.9 (H-6' / C-6'), 8.31 / 121.6 (H-3 / C-3), 8.26 / 122.4 (H-3' / C-3'), 7.75 / 127.8 (H-17 / C-17), 7.73 / 129.5 (H-19 / C-19), 7.71 / 126.9 (H-14 / C-14), 7.42 / 126.5 (H-15 / C-15), 7.32 / 123.7 (H-16 / C-16), 7.19 / 124.2 (H-5 / C-5), 7.16 / 124.9 (H-5' / C-5'), 7.14 / 119.1 (H-20 / C-20), 7.11 / 106.7 (H-12 / C-12), 4.11 / 67.7 (H-10 / C-10), 2.82 / 35.3 (H-7 / C-7), 2.45 / 21.4 (H-7' / C-7'), 1.94 / 29.0, 27.1 (H-8 + H-9 / C-8 + C-9).

HMBC (600 MHz/151 MHz, [D_1]-chloroform, 300 K): δ = 8.58 / 124.2 (H-6 / C-5), 8.55 / 124.9 (H-6' / C-5'), 8.26 / 21.4 (H-3' / C-7'), 7.75 / 134.7, 129.5, 126.5 (H-17 / C-13, C-19, C-15), 7.73 / 157.1, 134.7, 127.8 (H-19 / C-11, C-13, C-17), 7.71 / 129.1, 123.7, 106.7 (H-14 / C-18, C-16, C-12), 7.42 / 134.7, 127.8 (H-15 / C-13, C-17), 7.32 / 129.1, 126.9 (H-16 / C-18, C-14), 7.14 / 129.1, 106.7 (H-20 / C-18, C-12), 7.11 / 157.1, 129.1, 126.9, 119.1 (H-12 / C-11, C-18, C-14, C-20), 4.11 / 157.1, 29.0, 27.1 (H-10 / C-11, C-8, C-9), 2.82 / 152.7, 124.2, 121.6, 29.0, 27.1 (H 7 / C-4, C-5, C-3, C-8, C-9), 2.45 / 148.9, 124.9, 122.4 (H-7' / C-6', C-5', C-3'), 2.01 – 1.88 / 29.0, 27.1 (H 8 + H-9 / C-8, C-9).

HR-MS [ESI-pos, chloroform/methanol]: m/z = 369.1979 $[M+H]^+$, calculated 369.1961 for $[C_{25}H_{25}N_2O]^+$.

IR (ATR) ῡ 3055, 2941, 2864, 1628, 1599, 1554, 1510 ,1461, 1390, 1259, 1217, 1179, 1120, 813 cm^{-1}.

2.4 Synthesis of Bis(2,2'bipyridine)(4-methyl-4'-(4-(naphthalen-2-yloxy)butyl)-2,2'-bipyridine) ruthenium(II) chloride (2)



2

Bis(bipyridinium)ruthenium(II) chloride (80.0 mg, 0.165 mmol, 1 eq.) and silver nitrate (60.0 mg, 0.353 mmol, 2.1 eq.) were dissolved in methanol (10.0 mL). After stirring at room temperature for one hour, the resulting precipitate was removed by filtration and washed with 5 mL of methanol. The solution was added to the functionalized bipyridine **8** (70.0 mg, 0.190 mmol, 1.15 eq.) and the mixture was heated to reflux for 16 hours. The reaction mixture was allowed to cool to room temperature and the hexafluorophosphate-salt of the product was precipitated by the addition of a saturated aqueous solution of ammonium hexafluorophosphate (5.0 mL). The precipitate was isolated by filtration and washed with water (2 x 5.0 mL). The resulting dark red solid was dissolved in a mixture of methanol and ethanol (1:1, 5.0 mL) and further purified via ion-exchange chromatography (Amberlite IRA-400 chloride form, 3 x 10 cm, methanol : ethanol, 1 : 1). The dark-red coloured fractions were combined and after removal of the solvent under reduced pressure, the product was obtained as a dark red solid (120 mg, 0.141 mmol, 85.5% yield).

$C_{45}H_{40}Cl_2N_6ORu$: 852.83 g/mol

^{1}H-NMR (600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.93 – 8.79 (m, 4H, $H_{arom.}$), 8.20 – 8.10 (m, 4H, $H_{arom.}$), 7.84 – 7.69 (m, 8H, $H_{arom.}$), 7.57 (d, *J* = 5.8 Hz, 1H, $H_{arom.}$), 7.55 – 7.49 (m, 4H, $H_{arom.}$), 7.47 – 7.40 (m, 2H, $H_{arom.}$), 7.37 (d, *J* = 5.7 Hz, 1H, $H_{arom.}$), 7.35 – 7.28 (m, 3H, $H_{arom.}$), 7.13 (dd, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H, $H_{arom.}$), 4.14 (t, *J* = 6.2 Hz, 2H, H-10), 2.89 (t, *J* = 7.5 Hz, 2H, H-7), 2.52 (s, 3H, H-7'), 1.94 – 1.78 (m, 4H, H-8 + H-9).

^{13}C NMR (151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 156.63, 156.57, 156.5, 156.4, 156.2, 156.1, 153.7, 151.2, 151.13, 151.07, 151.0, 150.5, 150.2, 149.7, 137.7, 134.3, 129.3, 128.6, 128.4, 127.8, 127.5, 126.6, 126.4, 125.3, 124.5, 123.5, 118.7, 106.7 (all $C_{arom.}$), 67.2 (C-10), 34.1 (C-7), 28.3, 26.1 (C-8 + C-9), 20.7 (C-7').

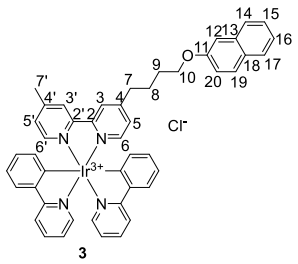
Comment: Due to the strong overlap of signals in the ^{1}H and ^{13}C NMR spectra, a full analysis of the 2D-NMR data was not possible.

HR-MS [ESI-pos, methanol]: m/z = 391.1164 $[M\text{-}2Cl^-]^{2+}$, calculated 391.1148 for $[C_{45}H_{40}N_6ORu]^{2+}$.

IR (ATR) ῡ 3640, 3062, 2931, 2861, 1974, 1612, 1550, 1504, 1457, 1427, 1388, 1349, 1311, 1257, 1218, 1172, 1118, 1025 ,956, 825, 755.

UV-Vis (85% water, 15% $N(EtOH)_3$): λ_{max}(***ε***) = 461 nm (10429 M^{-1} cm^{-1}), 426 nm (8806 M^{-1} cm^{-1}), 329 nm (sh, 9626 M^{-1} cm^{-1}), 288 nm (61353 M^{-1} cm^{-1}).

2.5 Synthesis of Bis(2-phenylpyridine)(4-methyl-4'-(4-(naphthalen-2-yloxy)butyl)-2,2'-bipyridine) iridium(III) chloride (3)



3

Tetrakis(2-(2-pyridinyl)phenyl)diiridium(III)dichloride (66.0 mg, 61.6 µmol, 1 eq.) and the functionalized bipyridine **8** (50.0 mg, 136 µmol, 2.2 eq.) were dissolved in a mixture of chloroform and methanol (1 : 1, 10.0 mL) and stirred at 65 °C. After 16 hours, the solvents were removed under reduced pressure and the resulting solid was dissolved in water (3.0 mL). The hexafluorophosphate-salt of the product was precipitated by the addition of a saturated aqueous solution of ammonium hexafluorophosphate (5.0 mL). The precipitate was isolated by filtration and washed with water (2 x 5.0 mL). The resulting solid was dissolved in a mixture of methanol and ethanol (1:1, 5.0 mL) and further purified via ion-exchange chromatography (Amberlite IRA-400, 3 x 10 cm, methanol : ethanol, 1 : 1). The brightly-yellow coloured fractions were combined and after removal of the solvent under reduced pressure, the product was obtained as a bright yellow solid (100 mg, 110 µmol, 89.3% yield).

$C_{47}H_{40}ClIrN_4O$: 904.53 g/mol

^{1}H-NMR (600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.80 (s, 1H, H-3'), 8.78 (s, 1H, H-3), 8.25 (d, *J* = 8.2 Hz, 2H, H-ppy), 7.95 – 7.88 (m, 4H, H-ppy), 7.82, 7.80 (each d, each ^3J = 7.0 Hz, 2H, H-17 + H-19), 7.77 (d, ^3J = 8.2 Hz, 1H, H-14), 7.72 (d, ^3J = 5.6 Hz, 1H, H-6), 7.68 (d, ^3J = 5.6 Hz, 1H, H-6'), 7.62 (d, *J* = 5.6 Hz, 1H, H-ppy), 7.60 (d, *J* = 5.7 Hz, 1H, H-ppy), 7.59 (d, ^3J = 5.0 Hz, 1H, H-5), 7.51 (d, ^3J = 5.3 Hz, 1H, H-5'), 7.44 (t, ^3J = 7.2 Hz, 1H, H-15), 7.33 (t, ^3J = 7.2 Hz, 1H, H-16), 7.29 (d, ^4J = 2.1 Hz, 1H, H-12), 7.19 – 7.11 (m, 3H, H-20, H-ppy), 7.01 (t, *J* = 7.3 Hz, 2H, H-ppy), 6.89 (t, *J* = 7.2 Hz, 2H, H-ppy), 6.19 (t, *J* = 8.4 Hz, 2H, H-ppy), 4.13 (t, ^3J = 5.9 Hz, 2H, H-10), 2.89 (t, ^3J = 7.5 Hz, 2H, H-7), 2.52 (s, 3H, H-7'), 1.94 – 1.83 (m, 4H, H-8 + H-9).

^{13}C NMR (151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 166.9 (C-ppy), 156.5 (C-11), 155.4 (C-2), 155.2 (C-4), 155.1 (C-4'), 151.5 (C-2'), 150.8 (C-ppy), 149.1 (b, C-6), 149.0 (b, C-6'), 148.9 (b, C-ppy), 148.7 (b, C-ppy), 143.8 (C-ppy), 138.7 (C-ppy), 134.3 (C-13), 131.1 (C-ppy), 130.2 (C-ppy), 129.3 (C-19), 129.2 (C-5'), 128.4 (C-5 (b) + C-18), 127.5 (C-17), 126.6 (C-14), 126.4 (C-15), 125.6 (C-3'), 125.1 (C-ppy), 124.8 (C-3), 123.9 (C-ppy), 123.5 (C-16), 122.2 (C-ppy), 120.0 (C-ppy), 118.7 (C-20), 106.6 (C-12), 67.2 (C-10), 34.3 (C-7), 28.3 (C-8 / 9), 26.1 (C-8 / 9), 20.9 (C-7').

Due to strong signals overlaps, not all ^{13}C signals for the ppy-units could be detected individually.

COSY (600 MHz/600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.25 / 7.95-7.88 (H-ppy / H-ppy), 7.95-7.88/ 8.25, , 7.19-7.11, 7.01 (H-ppy / H-ppy, H-ppy, H-ppy), 7.82, 7.80 / 7.44, 7.33, 7.19-7.11 (H-17 + H-19 / H-15, H-16, H-20), 7.77 / 7.44 (H-14 / H-15), 7.72 / 7.59 (H-6, H-5), 7.68 / 7.51 (H-´6' / H-5'), 7.62 / 7.19-7.11 (H-ppy / H-ppy), 7.59 / 7.72 (H-5 / H-6), 7.51 / 7.68 (H-5' / H-6'), 7.44 / 7.77, 7.33 (H-15 / H-14, H-16), 7.33 / 7.82, 7.80 , 7.44 (H-16 / H-17, H-15), 7.19-7.11/ 7.95-7.88, 7.82, 7.80 , 7.62 (H-20 + H-ppy / H-19, H-ppy, H-ppy), 7.01 / 7.95-7.88, 6.89 (H-ppy / H-ppy, H-ppy), 6.89 / 7.01 (H-ppy / H-ppy), 4.13 / 1.94-1.83 (H-10 / H-9), 2.89 / 1.94-1.83 (H-7 / H-8), 1.94-1.83/ 4.13, 2.89 (H-8 + H-9 / H-10, H-7).

HSQC (600 MHz/151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.80 / 125.6 (H-3' / C-3'), 8.78 / 124.8 (H-3 / C-3), 8.25 / 120.0 (H-ppy / C-ppy), 7.95-7.88/ 138.7, 125.1 (H-ppy / C-ppy, C-ppy), 7.82, 7.80 / 129.3, 127.5 (H-17 + H-19 / C-19 + C-17), 7.77 / 126.6 (H-14 / C-14), 7.72 / 149.1 (H-6 / C-6), 7.68 / 149.0 (H-6' / C-6'), 7.62, 7.60 / 148.9, 148.7 (H-ppy, H-ppy / C-ppy, C-ppy), 7.59 / 128.4 (H-5 / C-5), 7.51 / 129.2 (H-5' / C-5'), 7.44 / 126.4 (H-15 / C-15), 7.33 / 123.5 (H-16 / C-16), 7.29 / 106.6 (H-12 / C-12), 7.19-7.11/ 123.9, 118.7 (H-20 + H-ppy / C-ppy, C-20), 7.01 / 122.2 (H-ppy / C-ppy), 6.89 / 130.2 (H-ppy / C-ppy), 6.19 / 131.1 (H-ppy / C-ppy), 4.13 / 67.2 (H-10 / C-10), 2.89 / 34.3 (H-7 / C-7), 2.52 / 20.9 (H-7' / C-7'),1.94-1.83/ 28.3, 26.1 (H-8 + H-9 / C-8 + C-9).

HMBC (600 MHz/151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.80 / 129.2, 20.9 (H-3' / C-5', C-7'), 8.78 / 155.2, 34.3 (H-3 / C-4, C-7), 8.25 / 166.9, 123.9 (H-ppy /C-ppy, C-ppy), 7.95-7.88/ 166.9, 150.8, 148.7, 130.2 (H-ppy / C-ppy, C-ppy, C-ppy, C-ppy), 7.82, 7.80 / 156.5, 134.3, 129.3, 127.5, 126.4 (H-17 + H-19 / C-11, C-13, C-19, C-17, C-15), 7.77 / 128.4, 123.5, 106.6 (H-14 / C-18, C-16, C-12), 7.72 /

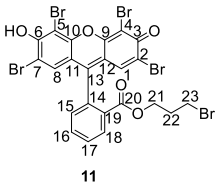
155.4, 155.2, 128.4 (H-6 / C-2, C-4, C-5), 7.68 / 155.1, 151.5, 129.2 (H-6‘ / C-4‘, C-2‘, C-5‘), 7.62 / 166.9, 138.7, 123.9 (H-ppy / C-ppy, C-ppy, C-ppy), 7.60 / 166.9, 138.7 (H-ppy / C-ppy, C-ppy), 7.59 / 124.8 (H-5 / C-3), 7.51 / 149.0, 125.6 (H-5‘ / C-6‘, C-3‘), 7.44 / 134.3, 128.4, 127.5 (H-15 / C-13, C-18, C-17), 7.33 / 128.4, 126.6 (H-16 / C-18, C-14), 7.29 / 128.4, 126.6, 118.7 (H-12 / C-18, C-14, C-20), 7.19-7.11/ 156.5, 128.4, 122.2, 120.0, 106.6 (H-20, H-ppy, H-ppy, H-ppy / C-11, C-18, C-ppy, C-ppy, C-12), 7.01 / 143.8, 131.1, 130.2 (H-ppy / C-ppy, C-ppy, C-ppy), 6.89 / 150.8, 125.1 (H-ppy / C-ppy, C-ppy), 6.19 / 150.8, 143.8, 122.2 (H-ppy / C-ppy, C-ppy, C-ppy), 4.13 / 26.1 (H-10 / C-8 or C-9), 2.89 / 155.4, 128.4, 124.8, 28.3, 26.1 (H-7 /C-2, C-5, C-3, C-8, C-9), 2.52 / 151.5, 129.2, 125.6 (H-7‘ / C-2‘, C-5‘, C-3‘), 1.94-1.83/ 28.3, 26.1 (H-8 + H-9 / C-8, C-9).

HR-MS [ESI-pos, methanol]: m/z = 869.2842 $[M\text{-}Cl^-]^+$, calculated 869.2826 for $[C_{47}H_{40}IrN_4O]^+$.

IR (ATR) ῡ 3046, 2931, 2861, 2113, 2067, 1604, 1550, 1511, 1473, 1419, 1357, 1311, 1265, 1218, 1172, 1118, 1049, 1025, 971, 833, 748, 617.

UV-Vis (85% water, 15% $N(EtOH)_3$): $\lambda_{max}(\varepsilon)$ = 311 nm (br, 28624 M^{-1} cm^{-1}).

2.6 Synthesis of 4-bromobutyl 2-(2,4,5,7-tetrabromo-6-hydroxy-3-oxo-3H-xanthen-9-yl)benzoate (11)



11

Eosin Y (1.00 g, 1.45 mmol, 1 eq.) and 1,3-dibromopropane (2.92 g, 1474 µL, 14.5 mmol, 10 eq.) were dissolved in dimethylformamide (40 mL) and stirred at 80 °C. After 18 hours, the solvent was removed under reduced pressure and the resulting slurry dissolved in diethyl ether (60 mL) and stirred at room temperature. After 48 hours, the precipitate was removed by filtration and the filtrate collected. After removal of the solvent under reduced pressure, the dark residue was further purified via column-chromatography (SiO_2, 3 x 25 cm, dichloromethane : methanol 1 : 1). After removal of the solvent under reduced pressure, the product was obtained as a dark red film (580 mg, 733 µmol, ~51% yield).

Comment: The product was obtained in ca. 90% purity due to difficult purification on SiO_2 (smearing behaviour). This contamination was accepted as the next step proved to be undisturbed by this and product **12** was easier to purify.

$C_{23}H_{13}Br_5O_5$: 768.89 g/mol

^{1}H-NMR (600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.21 (dd, ^3J = 7.9 Hz, ^4J = 1.0 Hz, 1H, H-18), 7.87 (td, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, H-16), 7.79 (td, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, H-17), 7.50 (dd, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 1H, H-15), 6.97 (s, 2H, H-1 + H-8), 4.08 (t, ^3J = 6.0 Hz, 2H, H-21), 3.28 (t, ^3J = 6.6 Hz, 2H, H-23), 1.89 (p, ^3J = 6.4 Hz, 2H, H-22).

^{13}C NMR (151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 167.7 (C-3 + C-6), 165.0 (C-20), 152.8 (C-9 + C-10), 150.6 (C-13), 133.10 (C-14 + C-16), 130.8 (C-18), 130.7 (C-15), 130.2 (C-17), 129.9 (C-19), 129.2 (C-1 + C-8), 118.3 (C-2 + C-7), 110.2 (C-11 + C-12), 99.7 (C-4 + C-5), 63.2 (C-21), 31.0 (C-22), 30.3 (C-23).

COSY (600 MHz/600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.21 / 7.79 (H-18 / H-17), 7.87 / 7.79, 7.50 (H-16 / H-17, H-15), 7.79 / 8.21, 7.87, 7.50 (H-17 / H-18, H-16, H-15), 7.50 / 7.87, 7.79 (H-15 / H 16, H-17), 4.08 / 1.89 (H-21 / H-22), 3.28 / 1.89 (H-23 /H-22), 1.89 / 4.08, 3.28 (H-22 / H-21, H-23).

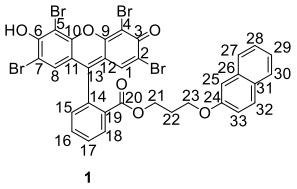
HSQC (600 MHz/151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.21 / 130.8 (H-18 / C-18), 7.87 / 133.06 (H-16 / C-16), 7.79 / 130.2 (H-17 / C-17), 7.50 / 130.7 (H-15 / C-15), 6.97 / 129.2 (H-1 + H-8 / C-1 + C 8), 4.08 / 63.2 (H-21 / C-21), 3.28 / 30.3 (H-23 / C-23), 1.89 / 31.0 (H-22 / C-22).

HMBC (600 MHz/151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.21 / 165.0, 133.1 (H-18 / C-20, C-16, C-14), 7.87 / 133.10, 130.8 (H-16 / C-14, C-18), 7.79 / 130.7, 129.9 (H-17 / C-15, C-19), 7.50 / 150.6, 130.2, 129.9 (H-15 / C-13, C-17, C-19), 6.97 / 167.7, 152.8, 150.6, 118.3, 99.7 (H-1, H-8 / C-3 + C-6, C-9 + C-10, C-13, C-2 + C-7, C-4 + C-5), 4.08 / 165.0, 31.0, 30.3 (H-21 / C-20, C-22, C-23), 3.28 / 63.2, 31.0 (H-23 / C-21, C-22), 1.89 / 63.2, 30.3 (H-22 / C-21, C-23).

HR-MS [ESI-pos, methanol/water]: m/z = 764.6727 $[M+H]^+$, calculated 764.6753 for $[C_{23}H_{14}Br_5O_5]^+$.

IR (ATR) ῡ 3371 (br), 3157 (sh, br), 3057, 2956, 2762, 2441, 1716, 1616, 1547, 1502, 1439, 1340, 1267, 1228, 1169, 1132, 1079, 1057, 1022, 972, 881 cm^{-1}.

2.7 Synthesis of 3-(naphthalen-2-yloxy)propyl 2-(2,4,5,7-tetrabromo-6-hydroxy-3-oxo-3H-xanthen-9-yl)benzoate (1)



1

Functionalized eosin **11** (150 mg, 195 µmol, 1 eq.), 2-naphthol (140 mg, 975 µmol, 5 eq.) and calcium carbonate (309 mg, 950 µmol, 4.9 eq.) were suspended in acetonitrile (10.0 mL) and the mixture was heated to reflux. After 20 hours, the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was further purified by column chromatography (SiO_2, 3 x 30 cm, chloroform : acetonitrile 2 : 1). After removal of the solvent under reduced pressure, the product was obtained as a dark red film (50.0 mg, 60.1 µmol, 30.8% yield).

$C_{33}H_{20}Br_4O_6$: 832.13 g/mol

^{1}H-NMR (400 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.18 (d, ^3J = 7.9 Hz, 1H, H-18), 7.90 – 7.83 (m, 2H, H-16 + H-27), 7.83 – 7.74 (m, 3H, H-17 + H-30 + H-32), 7.52 (d, ^3J = 7.5 Hz, 1H, H-15), 7.44 (t, ^3J = 7.8 Hz, 1H, H-28), 7.32 (t, ^3J = 7.5 Hz, 1H, H-29), 7.10 (d, ^4J = 2.5 Hz, 1H, H-25), 7.05 (dd, ^3J = 8.9 Hz, J = 2.5 Hz, 1H, H-33), 6.96 (s, 2H, H-1 + H-8), 4.18 (t, ^3J = 5.9 Hz, 2H, H-21), 3.81 (t, ^3J = 5.8 Hz, 2H, H-23), 1.80 (p, ^3J = 5.9 Hz, 2H, H-22).

^{13}C NMR (101 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 168.4 (C-3 + C-6), 165.1 (C-20), 156.1 (C-24), 152.9 (C-9 + C-10), 150.7 (C-13), 134.2 (C-26), 133.2 (C-14), 133.0 (C-16), 130.8 (C-18), 130.6 (C-15), 130.1 (C-17), 130.0 (C-19), 129.2 (C-32), 129.1 (C-1 + C-8), 128.5 (C-31), 127.4 (C-30), 127.0 (C-27), 126.3 (C-28), 123.5 (C-29), 118.63 (C-2 + C-7), 118.55 (C-33), 109.3 (C-11 + C-12), 106.4 (C-25), 99.6 (C-4 + C-5), 63.6 (C-23), 62.1 (C-21), 27.9 (C-22).

COSY (400 MHz/400 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.18 / 7.83-7.74 (H-19 / H-17), 7.90-7.83 / 7.83-7.74, 7.52, 7.44 (H-16 + H-27 / H-17 + H-15 + H-28), 7.83-7.74 / 8.18, 7.90-7.83, 7.32, 7.05 (H-17 + H-30 + H-32 / H-18, H-16, H-29, H-33), 7.52 / 7.90-7.83 (H-15 / H-16), 7.44 / 7.90-7.83, 7.32 (H-28 / H-27, H-29), 7.32 / 7.83-7.74, 7.44 (H-29 / H-30, H-28), 7.05 / 7.83-7.74 (H-33 / H-32), 4.18 / 1.80 (H-21 / H-22), 3.81 / 1.80 (H-23 / H-22), 1.80 / 4.18, 3.81 (H-22 / H-21, H-23).

HSQC (400 MHz/101 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.18 / 130.8 (H-18 / C-18), 7.90-7.83 / 133.0, 127.0 (H-16 + H-27 / C-16, C-27), 7.83-7.74 / 130.1, 129.2, 127.4 (H-17 + H-30 + H-32 / C-17, C-32, C-30), 7.52 / 130.6 (H-15 / C-15), 7.44 / 126.3 (H-28 / C-28), 7.32 / 123.5 (H-29 / C-29), 7.10 / 106.4 (H-25 / C-25), 7.05 / 118.55 (H-33 / C-33), 6.96 / 129.1 (H-1 + H-8 / C-1 + C-8), 4.18 / 62.1 (H-21 / C-21), 3.81 / 63.6 (H-23 / C-23), 1.80 / 27.9 (H-22 / C-22).

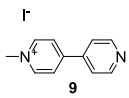
HMBC (400 MHz/101 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 8.18 / 133.2, 133.0 (H-18 / C-14, C-16), 7.90-7.83 / 133.2, 130.8, 128.5, 123.5, 106.4 (H-16 + H-27 / C-14, C-18, C-31, C-29, C-25), 7.83-7.74 / 156.1, 134.2, 130.6, 130.0, 129.2, 127.4, 126.3 (H-17 + H-30 + H-32 / C-24, C-26, C-15, C-19, C-32, C-30, C-28), 7.52 / 150.7, 130.1, 130.0 (H-15 / C-13, C-17, C-19), 7.44 / 134.2, 127.4 (H-28 / C-26, C-30), 7.32 / 128.5, 127.0 (H-29 / C-31, C-27), 7.10 / 128.5, 118.55 (H-25 / C-31, C-33), 7.05 / 128.5 (H-33 / C-31), 6.96 / 168.4, 152.9, 150.7, 118.63 (H-1 + H-8 / C-3 + C-6, C-9 + C-10, C-13, C-2 + C-7), 4.18 / 63.6 (H-21 / C-23), 3.81 / 62.1 (H-23 / C-21).

HR-MS [ESI-pos, methanol]: m/z = 828.8044 $[M+H]^+$, calculated 828.8066 for $[C_{33}H_{21}Br_4O_6]^+$.

IR (ATR) ῡ 3610, 3370, 3054, 2954, 2923, 2607, 2522, 2437, 1712, 1619, 1550, 1450, 1342, 1226, 1172, 1126, 1072, 1049, 971, 879, 833, 809, 755, 709, 640.

UV-Vis (85% water, 15% $N(EtOH)_3$): $\lambda_{max}(\varepsilon)$ = 532 nm (5834 M^{-1} cm^{-1}), 498 nm (sh, 1877 M^{-1} cm^{-1}), 308 nm (1082 M^{-1} cm^{-1}).

2.8 Synthesis of *N*-methyl-4,4'-bipyridinium iodide (9)[3]



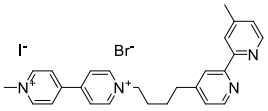
9

4,4'-bipyridine (2.50 g, 16.0 mmol, 1 eq.) and iodomethane (2.60 g, 1.14 mL, 18.3 mmol, 1.15 eq.) were dissolved in acetone (40 mL) and stirred at room temperature. After 24 hours, the resulting yellow precipitate was isolated by filtration, washed with acetone (4 x 20 mL) and resuspended in methanol (20 mL). After careful removal of the solvent under reduced pressure, the product was obtained as a yellow solid (3.70 g, 12.4 mmol, 77.5% yield).

$C_{11}H_{11}IN_2$: 298.13 g/mol

^{1}H-NMR (300 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.13 (d, *J* = 6.8 Hz, 2H), 8.87 (d, *J* = 6.3 Hz, 2H), 8.61 (d, *J* = 6.9 Hz, 2H), 8.03 (d, *J* = 6.3 Hz, 2H), 4.38 (s, 3H).

2.9 Synthesis of *N*-methyl-*N*-(hex-5-ynyl)-4,4'-bipyridinium bromide iodide (10)[4]



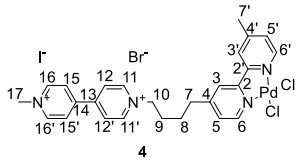
10

Bromobutyl bipyridine **7** (300 mg, 983 µmol, 1.1 eq.) and *N*-methyl-4,4'-bipyridinium iodide (**9**) (270 mg, 906 µmol, 1.0 eq.) were dissolved in acetonitrile (20 mL) and the mixture was heated to reflux. After 20 hours, the mixture was cooled to room temperature and filtrated. The precipitate was isolated by filtration, washed with water (2 x 5.0 mL) and dried under reduced pressure to give the product as an orange solid (240 mg, 400 µmol, 44.2% yield).

$C_{26}H_{28}BrIN_4$: 603.35 g/mol

^{1}H-NMR (300 MHz, [D_1]-chloroform, 300 K): δ = 9.36 (d, *J* = 6.4 Hz, 2H), 9.26 (d, *J* = 6.3 Hz, 2H), 8.74 (d, *J* = 6.5 Hz, 2H), 8.71 (d, *J* = 6.5 Hz, 2H), 8.56 (d, *J* = 5.0 Hz, 1H), 8.51 (d, *J* = 4.9 Hz, 1H), 8.25 (s, 1H), 8.22 (s, 1H), 7.29 (t, *J* = 5.3 Hz, 1H), 7.28 (t, *J* = 5.3 Hz, 1H), 4.73 (t, *J* = 7.2 Hz, 2H), 4.43 (s, 3H), 2.77 (t, *J* = 7.9 Hz, 2H), 2.41 (s, 3H), 2.04 (q, *J* = 7.8 Hz, 2H), 1.73 (q, *J* = 7.9 Hz, 2H).

2.10 Synthesis of (*N*-methyl-*N*-(4-(4'-methyl-[2,2'-bipyridine]-4-yl)butyl)-4,4'-bipyridinium) palladium(II) dichloride bromide iodide (4)



Viologen-bipyridine **10** (60.0 mg, 99.4 µmol, 1 eq.) and bis(acetonitrile)palladium(II) chloride (23 mg, 88.7 µmol, 0.9 eq.) were dissolved in acetonitrile (5.0 mL) and the mixture was heated to reflux. After 18 hours, the mixture was cooled to room temperature and centrifuged for 5 minutes (6153 x g). After removal of the supernatant, the precipitate was suspended and centrifuged again for 5 minutes each (6153 x g) using acetonitrile (5.0 mL) and diethyl ether (5.0 mL). After removal of solvent residues under reduced pressure, the product was obtained as a crème-coloured solid (64.0 mg, 82.0 µmol, 92.4% yield).

$C_{26}H_{28}BrCl_2IN_4Pd$: 780.67 g/mol

^{1}H-NMR (600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.35 (d, ^3J = 6.3 Hz, 2H, H-11 + H-11'), 9.27 (d, ^3J = 6.4 Hz, 2H, H-16 + H-16'), 8.94 (d, ^3J = 5.9 Hz, 1H, H-6), 8.89 (d, ^3J = 5.9 Hz, 1H, H-6'), 8.76 (d, ^3J = 6.2 Hz, 2H, H-12 + H-12'), 8.73 (d, ^3J = 6.5 Hz, 2H, H-15 + H-15'), 8.45 (s, 1H, H-3), 8.44 (s, 1H, H-3'), 7.64 (d, ^3J = 5.9 Hz, 1H, H-5), 7.63 (d, ^3J = 5.9 Hz, 1H, H-5'), 4. 71 (t, ^3J = 7.2 Hz, 2H, H-10), 4.43 (s, 3H, H-17), 2.88 (t, ^3J = 7.2 Hz, 2H, H-7), 2.52 (s, 3H, H-7'), 2.02 (p, ^3J = 7.4 Hz, 2H, H-9), 1.78 (p, ^3J = 7.5 Hz, 2H, H-8).

^{13}C NMR (151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 156.5 (C-4), 156.0 (C-2), 155.7 (C-2'), 153.3 (C-4'), 149.1 (C-6), 148.9 (C-6'), 148.6 (C-13), 148.1 (C-14), 146.7 (C-16 + C-16'), 145.8 (C-11 + C-11'), 127.7 (C-5'), 127.0 (C-5), 126.5 (C-12 + C-12'), 126.0 (C-15 + C-15'), 124.4 (C-3'), 123.8 (C-3), 60.6 (C-10), 48.1 (C-17), 33.7 (C-7), 29.9 (C-9), 25.6 (C-8), 21.0 (C-7').

COSY (600 MHz/600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.35 / 8.76 (H-11 + H-11' / H-12 + H-12'), 9.27 / 8.73 (H-16 + H-16' / H-15 + H-15'), 8.94 / 7.64 (H-6 / H-5), 8.89 / 7.63 (H-6' / H-5'), 8.76 / 9.35 (H-12 + H-12' / H-11 + H-11'), 8.73 / 9.27 (H-15 + H-15' / H-16 + H-16'), 8.45 / 7.64 (H-3 / H-5), 8.44 / 7.63 (H-3' / H-5'), 7.64, 7.63 / 8.94, 8.89, 8.45, 8.44 (H-5 + H-5' / H-6, H-6', H-3, H-3'), 4.71 / 2.02 (H-10 / H-9), 2.88 / 1.78 (H-7 / H-8), 2.02 / 4.71, 1.78 (H-9 / H-10, H-8), 1.78 / 2.88, 2.02 (H-8 / H-7, H-9).

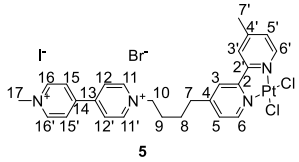
HSQC (600 MHz/151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.35 / 145.8 (H-11 + H-11' / C-11 + C-11'), 9.27 / 146.7 (H-16 + H-16' / C-16 + C-16'), 8.94 / 149.1 (H-6 / C-6), 8.89 / 148.9 (H-6' / C-6'), 8.76 / 126.5 (H-12 + H-12' / C-12 + C-12'), 8.73 / 126.0 (H-15 + H-15' / C-15 + C-15'), 8.45 / 123.8 (H-3 / C-3), 8.44 / 124.4 (H-3' / C-3'), 7.64 / 127.0 (H-5 / C-5), 7.63 / 127.5 (H-5' / C-5'), 4.71 / 60.6 (H-10 / C-10), 4.43 / 48.1 (H-17 / C-17), 2.88 / 33.7 (H-7 / C-7), 2.52 / 21.0 (H-7' / C-7'), 2.02 / 29.9 (H-9 / C-9), 1.78 / 25.6 (H-8 / C-8).

HMBC (600 MHz/151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.35 / 148.6, 145.8, 126.5, 60.6 (H-11 + H-11' / C-13, C-11 + C-11', C-12 + C-12', C-10), 9.27 / 148.1, 146.7, 126.0, 48.1 (H-16 + H-16' / C-14, C-16 + C-16', C-15 + C-15', C-17), 8.94 / 156.5, 156.0, 127.0 (H-6 / C-4, C-2, C-5), 8.89 / 155.7, 153.3, 127.7 (H-6' / C-2', C-4', C-5'), 8.76 / 148.1, 145.8, 126.5 (H-12 + C-12' / C-14, C-11 + C-11', C-12 + C-12'), 8.73 / 148.6, 146.7, 126.0 (H-15 + H-15' / C-13, C-16 + C-16', C-15 + C-15'), 8.45 / 156.0, 127.0, 33.7 (H-3 / C-2, C-5, C-7), 8.44 / 155.7, 127.7, 21.0 (H-3' / C-2', C-5', C-7'), 7.64, 7.63 / 149.1, 148.9, 124.4, 123.8, 33.7, 21.0 (H-5 + H-5' / C-6, C-6', C-3', C-3, C-7, C-7'), 4.71 / 145.8, 29.9, 25.6 (H-10 / C-11 + C-11', C-9, C-8), 4.43 / 146.7 (H-17 / C-16 + C-16'), 2.88 / 156.5, 127.0, 123.8, 29.9, 25.6 (H-7 / C-4, C-5, C-3, C-9, C-8), 2.52 /153.3, 127.7, 124.4 (H-7' / C-4', C-5', C-3'), 1.78 / 156.5, 60.6, 33.7, 29.9 (H-8 / C-4, C-10, C-7, C-9).

HR-MS [ESI-pos, acetonitrile/water]: m/z = 286.03557 $[M\text{-}Br\text{-}I]^{2+}$, calculated 286.03575 for $[C_{26}H_{28}Cl_2N_4Pd]^{2+}$.

IR (ATR) ῡ 3134, 3064, 2945, 2252, 1641, 1614, 1566, 1450, 1277, 1223, 1188, 1109, 1041, 1026, 1009, 820 cm^{-1}.

2.11 Synthesis of (*N*-methyl-*N*-(4-(4'-methyl-[2,2'-bipyridine]-4-yl)butyl)-4,4'-bipyridinium) platinum(II) dichloride bromide iodide (5)



5

Viologen-bipyridine **10** (60.0 mg, 99.4 µmol, 1.1 eq.) and bis(dimethylsulfoxido)platinum(II) chloride (37.0 mg, 87.6 µmol, 1 eq.) were dissolved in methanol (5 mL) and the mixture was heated to reflux. After 18 hours, the mixture was cooled to room temperature and centrifuged for 5 minutes (6153 x g). After removal of the supernatant, the precipitate was washed and centrifuged again with acetonitrile (5 mL) and diethyl ether (5 mL) for 5 minutes each (6153 x g). After removal of solvent residues under reduced pressure, the product was obtained as a yellow solid (60.0 mg, 69.0 µmol, 78.8% yield).

$C_{26}H_{28}BrCl_2IN_4Pt$: 869.33 g/mol

^{1}H-NMR (600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.35 (d, ^3J = 6.4 Hz, 2H, H-11 + H-11'), 9.29-9.25 (m, 3H, H-6 + H-16 + H-16'), 9.23 (d, ^3J = 6.0 Hz, 1H, H-6'), 8.76 (d, ^3J = 6.8 Hz, H-12 + H-12'), 8.73 (d, ^3J = 6.8 Hz, 2H, H-15 + H-15'), 8.44 (d, ^4J = 1.9 Hz, 1H, H-3), 8.43 (d, ^4J = 1.9 Hz, 1H, H-3'), 7.67 (t, ^3J = 6.3 Hz, 1H, H-5), 7.66 (t, ^3J = 6.3 Hz, 1H, H-5'), 4.71 (t, ^3J = 7.4 Hz, 2H, H-10), 4.43 (s, 3H, H-17), 2.85 (t, ^3J = 7.4 Hz, 2H, H-7), 2.48 (s, 3H, H-7'), 2.02 (p, ^3J = 7.6 Hz, 2H, H-9), 1.80 (p, ^3J = 7.6 Hz, 2H, H-8).

^{13}C NMR (151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 156.4 (C-2), 156.1 (C-4'), 155.7 (C-4), 152.5 (C-2'), 148.6 (C-13), 148.1 (C-14), 147.7 (C-6), 147.5 (C-6'), 146.7 (C-16 + C-16'), 145.8 (C-11 + C-11'), 128.1 (C-5'), 127.4 (C-5), 126.5 (C-12 + C-12'), 126.0 (C-15 + C-15'), 124.7 (C-3'), 124.1 (C-3), 60.6 (C-10), 48.1 (C-17), 33.8 (C-7), 29.9 (C-9), 25.4 (C-8), 21.1 (C-7').

COSY (600 MHz/600 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.35 / 8.76 (H-11 + H-11' / H-12 + H-12'), 9.29-9.25 / 8.73, 7.67, 4.43 (H-6, H-16 + H-16' / H-15 + H-15', H-5, H-17), 9.23 / 7.66, 2.48 (H-6' / H-5', H-7'), 8.76 / 9.35 (H-12 + H-12' / H-11 + H-11'), 8.73 / 9.29-9.25 (H-15+ H-15' / H-16 + H-16'), 8.44 / 7.67, 2.85 (H-3 / H-5, H-7), 8.43 / 7.66, 2.48 (H-3' / H-5', H-7'), 7.67, 7.66 / 9.29-9.25, 9.23, 8.44, 8.43, 2.48 (H-5 + H-5' / H-6, H-6', H-3, H-3', H-7'), 4.71 / 2.02 (H-10 / H-9), 2.85 / 8.44, 1.80 (H-7 / H-3, H-8), 2.48 / 8.43, 7.66 (H-7' / H-3', H-5'), 2.02 / 4.71, 1.80 (H-9 / H-10, H-8), 1.80 / 2.85, 2.02 (H-8 / H-7, H-9).

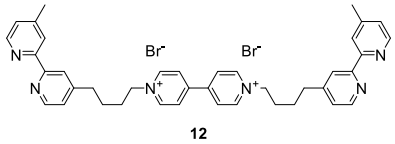
HSQC (600 MHz/151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.35 / 145.8 (H-11 + H-11' / C-11 + C-11'), 9.29-9.25 / 147.7, 146.7 (H-6 + H-16 + H-16' / C-6, C-16 + C-16'), 9.23 / 147.5 (H-6' / C-6'),8.76 / 126.5 (H-12 + H-12' / C-12 + C-12'), 8.73 / 126.0 (H-15 + H-15' / C-15 + C-15'), 8.44 / 124.1 (H-3 / C-3), 8.43 / 124.7 (H-3' / C-3'), 7.67 / 127.4 (H-5 / C-5), 7.66 / 128.1 (H-5' / C-5'), 4.71 / 60.6 (H-10 / C-10), 4.43 / 48.1 (H-17 / C-17), 2.85 / 33.8 (H-7 / C-7), 2.48 / 21.1 (H-7' / C-7'), 2.02 / 29.9 (H-9 / C-9), 1.80 / 25.4 (H-8 / C-8).

HMBC (600 MHz/151 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.35 / 148.6, 145.8, 60.6 (H-11 + C-11' / C-13, C-11 + C-11', C-10), 9.29-9.25 / 148.1, 146.7, 127.4, 126.0, 48.1 (H-6 + H-16 + H-16' / C-14, C-16 + C-16', C-5, C-15 + C-15', C-17), 9.23 / 156.1, 152.5 (H-6' / C-4', C-2'), 8.76 / 148.1, 145.8, 126.5 (H-12 + H-12' / C-14, C-11 + C-11', C-12 + C-12'), 8.73 / 148.6, 146.7, 126.0 (H-15 + H-15' / C-13, C-16 + C-16', C-15 + C-15'), 8.44 / 156.4, 127.4 (H-3 / C-2, C-5), 8.43 / 156.1, 128.1, 21.1 (H-3' / C-4', C-5', C-7'), 7.67, 7.66 / 147.7, 147.5, 124.7, 124.1 (H-5 + H-5' / C-6, C-6', C-3', C-3), 4.71 / 29.9, 25.4 (H-10 / C-9, C-8), 2.85 / 155.7, 127.4, 124.1, 29.9, 25.4 (H-7 / C-4, C-5, C-3, C-9, C-8), 2.48 / 152.5, 128.1, 124.7 (H-7' / C-2', C-5', C-3'), 2.02 / 60.6, 33.8, 25.4 (H-9 / C-10, C-7, C-8), 1.80 / 155.7, 60.6, 33.8, 29.9 (H-8 / C-4, C-10, C-7, C-9).

HR-MS [ESI-pos, acetonitrile/water]: m/z = 330.56658 $[M\text{-}Br\text{-}I]^{2+}$, calculated 330.56640 for $[C_{26}H_{28}N_4Cl_2Pt]^{2+}$.

IR (ATR) ῡ 3110, 3030 (br), 2985, 2922, 2854, 1637, 1618, 1560, 1543, 1509, 1483, 1450, 1435, 1361, 1302, 1282, 1273, 1248, 1225, 1182, 1178, 1122, 1076, 1036, 918, 895, 835, 823 cm^{-1}.

2.12 Synthesis of *N,N*-bis(4-(4'-methyl-[2,2'-bipyridine]-4-yl)butyl)-4,4'-bipyridinium bromide (12)[5]



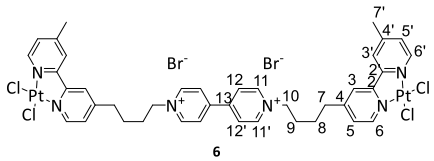
12

Bromobutyl bipyridine **7** (400 mg, 1.31 mmol, 3 eq.) and 4,4'-bipyridin (68.0 mg, 0.435 mmol, 1 eq.) were dissolved in acetonitrile (10.0 mL) and the mixture was heated to reflux. After 80 hours, the yellow precipitate was isolated by filtration and resuspended in acetonitrile (5 mL). The solid was isolated by centrifugation (2 x 5 minutes, 6153 x g). After drying of the damp solid under vacuum, the product was obtained as a yellow solid (160 mg, 208 µmol, 47.8% yield).

$C_{40}H_{42}Br_2N_6$: 766.63 g/mol

^{1}H-NMR (300 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.37 (d, ^3J = 6.9 Hz, 4H), 8.74 (d, ^3J = 6.9 Hz, 4H), 8.55 (d, ^3J = 5.0 Hz, 2H), 8.49 (d, ^3J = 4.9 Hz, 2H), 8.22 (d, ^3J = 7.1 Hz, 4H), 7.31 – 7.24 (m, 4H), 4.73 (t, ^3J = 7.1 Hz, 4H), 2.76 (t, ^3J = 7.5 Hz, 4H), 2.40 (s, 6H), 2.04 (p, ^3J = 7.6 Hz, 4H), 1.69 (p, J = 7.3 Hz, 4H).

2.13 Synthesis of (*N,N*-bis(4-(4'-methyl-[2,2'-bipyridine]-4-yl)butyl)-4,4'-bipyridinium)diplatinum(II) tetra-chloride dibromide (6)



6

Bis bipyridin functionalised viologen **12** (36.0 mg, 47.0 µmol, 1 eq.) and bis(dimethylsulfoxido) platinum(II) chloride (40.0 mg, 94.7 µmol, 2 eq.) were dissolved in methanol (5.0 mL) and the mixture was heated to reflux. After 18 hours, the solvent was removed under reduced pressure and the yellow solid was suspended in acetonitrile (10.0 mL) and isolated by centrifugation (5 minutes, 6153 x g). The resulting crude product was suspended and centrifuged again using acetonitrile (10.0 mL) and diethylether (10.0 mL) for 5 minute each (6153 x g). After drying of the damp solid under reduced pressure, the product was obtained as a yellow solid (49.0 mg, 37.8 µmol, 80.4% yield).

The product contains ca. 5% of an impurity that could not be removed (most likely the mono-Pt complex).

Comment 2: As the product was insoluble in solvents suitable for mass spectrometry, an aliquot of the product was dissolved in a minute amount of water, precipitated by addition of an excess of potassium hexafluorophosphate and washed thoroughly with water. The hexafluorophosphate-salt was then analyzed by ESI-MS.

$C_{40}H_{42}Br_2Cl_4N_6Pt_2$: 1298.59 g/mol

^{1}H-NMR (400 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.38 (d, ^3J = 6.9 Hz, 4H, H-11 + H-11'), 9.28 (d, ^3J = 6.1 Hz, 2H, H-6), 9.24 (d, ^3J = 6.1 Hz, 2H, H-6'), 8.76 (d, ^3J = 6.9 Hz, 4H, H-12 + H-12'), 8.49 (s, 4H, H-3 + H-3'), 7.73 – 7.60 (m, 4H, H-5 + H-5'), 4.73 (t, ^3J = 7.4 Hz, 4H, H-10), 2.85 (t, ^3J = 7.3 Hz, 4H, H-7), 2.48 (s, 6H, H-7'), 2.02 (p, ^3J = 7.7 Hz, 4H, H-9), 1.80 (p, ^3J = 7.3 Hz, 4H, H-8).

^{13}C NMR (101 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 156.5 (C-2), 156.2 (C-2'), 155.7 (C-4), 152.6 (C-4'), 148.5 (C-13), 147.8 (C-6), 147.6 (C-6'), 145.9 (C-11 + C-11'), 128.1 (C-5'), 127.4 (C-5), 126.6 (C-12 + C-12'), 124.7 (C-3'), 124.1 (C-3), 60.6 (C-10), 33.8 (C-7), 29.9 (C-9), 25.4 (C-8), 21.1 (C-7').

COSY (400 MHz/400 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.38 / 8.76 (H-11 + H-11'/ H-12 + H-12'), 9.28 / 7.66 (H-6 / H-5), 8.76 / 9.38 (H-12 + H-12' / H-11 + H-11'), 8.49 / 7.73 – 7.60, 2.48 (H-3 + H-3' / H-5 + H-5', H-7'), 7.73 – 7.60 / 9.28, 9.24, 8.49 (H-5 + H-5' / H-6, H-6', H-3 + H-3'), 4.73 / 2.02 (H-10 / H-9), 2.85 / 1.80 (H-7 / H-8), 2.48 / 8.49 (H-7' / H-3'), 2.02 / 4.73, 1.80 (H-9 / H-10, H-8), 1.80 / 2.85, 2.02 (H-8 / H-7, H-9).

HSQC (400 MHz/101 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.38 / 145.9 (H-11 + H-11‘ / C-11 + C-11‘), 9.28 / 147.8 (H-6 / C-6), 9.24 / 147.6 (H-6‘ / C-6‘), 8.76 / 126.6 (H-12 + H-12‘/ C-12 + C-12‘), 8.49 / 124.7, 124.1 (H-3 + H-3‘ / C-3‘, C-3), 7.73 – 7.60 / 128.1, 127.4 (H-5 + H-5‘ / H-5‘, H-5), 4.73 / 60.6 (H-10 / C-10), 2.85 / 33.8 (H-7 / C-7), 2.48 / 21.1 (H-7‘ / C-7‘), 2.02 / 29.9 (H-9 / C-9), 1.80 / 25.4 (H-8 / C-8).
HMBC (400 MHz/101 MHz, [D_6]-dimethyl sulfoxide, 300 K): δ = 9.38 / 148.5, 145.9, 126.6, 60.6 (H-11 + H-11‘ / C-13, C-11 + C-11‘, C-12 + C-12‘, C-10), 9.28 / 156.5, 155.7, 127.4 (H-6 / C-2, C-4, C-5), 9.24 / 156.2, 152.6, 127.4 (H-6‘ / C-2‘, C-4‘, C-5‘), 8.76 / 148.5, 145.9, 126.6 (H-12 + H-12‘ / C-13, C-11 + C-11‘, C-12 + C-12‘), 8.49 / 156.5, 156.2, 128.1, 127.4, 33.8, 21.1 (H-3 + H-3‘ / C-2, C-2‘, C-5‘, C-5, C-7, C-7‘), 7.73 – 7.60 / 147.8, 147.6, 124.7, 124.1, 33.8, 21.1 (H-5 + H-5‘ / C-6, C-6‘, C-3‘, C-3, C-7, C-7‘), 4.73 / 145.9, 29.9, 25.4 (H-10 / C-11 + C-11‘, C-9, C-8), 2.85 / 155.7, 127.4, 124.1, 29.9, 25.4 (H-7 / C-4, C-5, C-3, C-9, C-8), 2.48 / 152.6, 128.1, 124.7 (H-7‘ / C-4‘, C-5‘, C-3‘), 1.80 / 60.6 (H-8 / C-10).
HR-MS [ESI-pos, acetonitrile/water]: m/z = 568.0723 $[M\text{-}2\ PF_6]^{2+}$, calculated 568.0755 for $[C_{40}H_{42}Cl_4N_6Pt_2]^{2+}$; 1135.1392 $[M\text{-}2\ PF_6\text{-}H]^{+}$, calculated 1135.1443 for $[C_{40}H_{41}Cl_4N_6Pt_2]^{+}$.
IR (ATR) ῡ 3552 (br), 3114, 3037, 3010, 2991, 2916, 2858, 2252, 2121, 1633, 1620, 1554, 1502, 1483, 1433, 1377, 1344, 1308, 1300, 1277, 1244, 1217, 1169, 1153, 1126, 1016, 982, 924, 920, 825 cm^{-1}.

3. NMR-Spectra

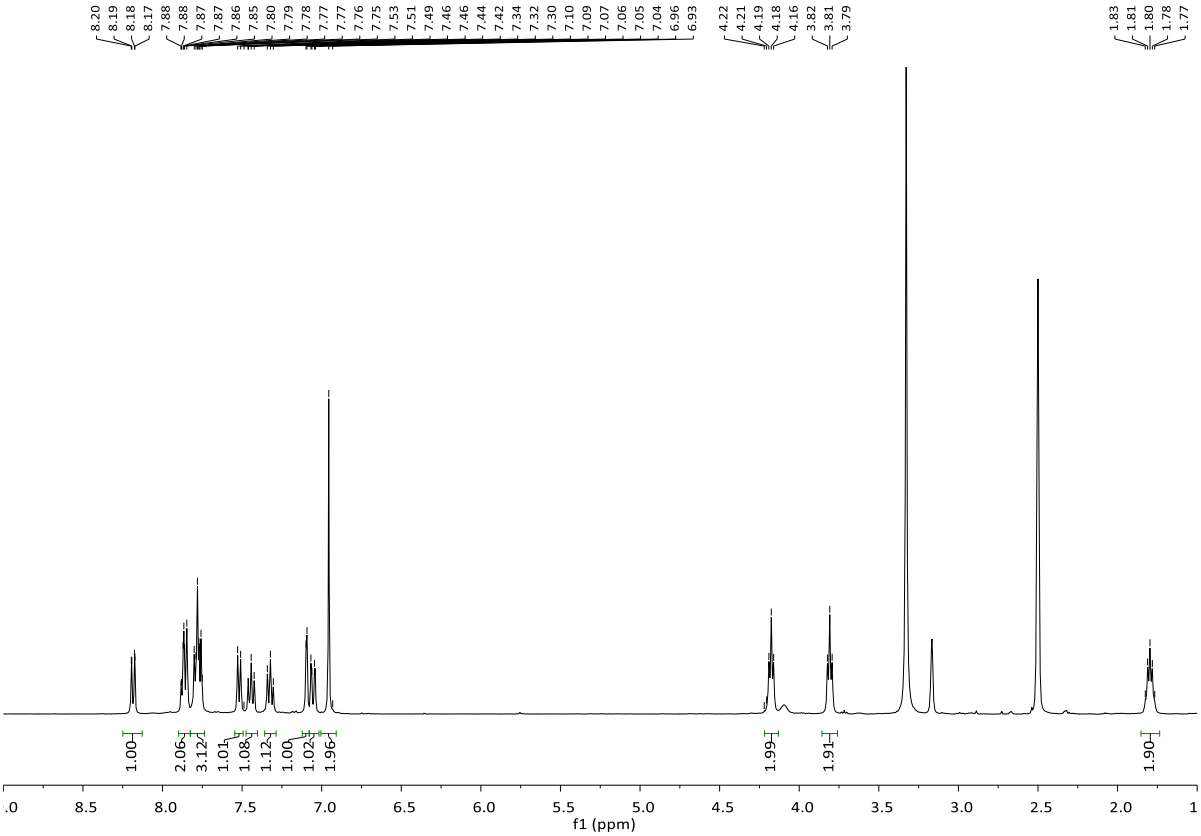


Figure S3: *^{1}H-NMR spectrum of **1** ([D$_6$]-DMSO, 400 MHz, 300 K).*

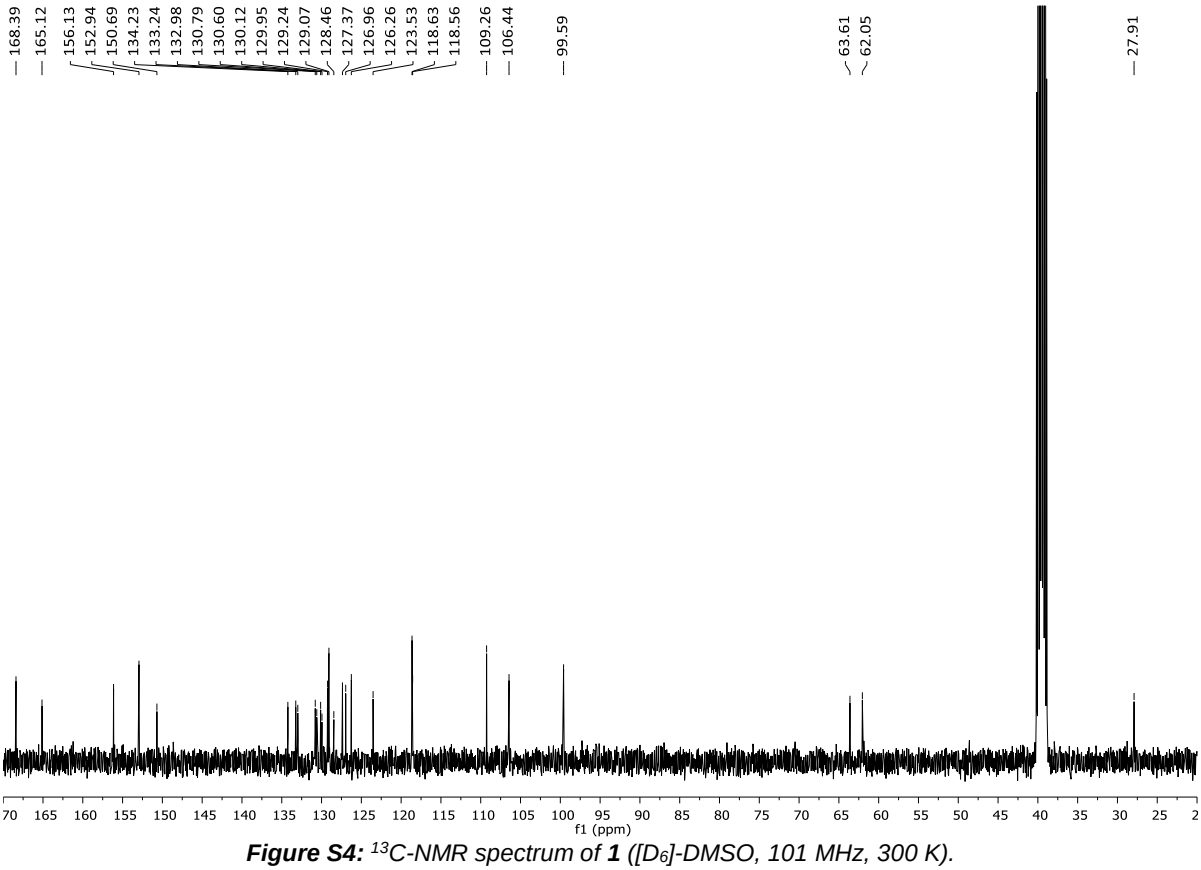


Figure S4: *^{13}C-NMR spectrum of **1** ([D$_6$]-DMSO, 101 MHz, 300 K).*

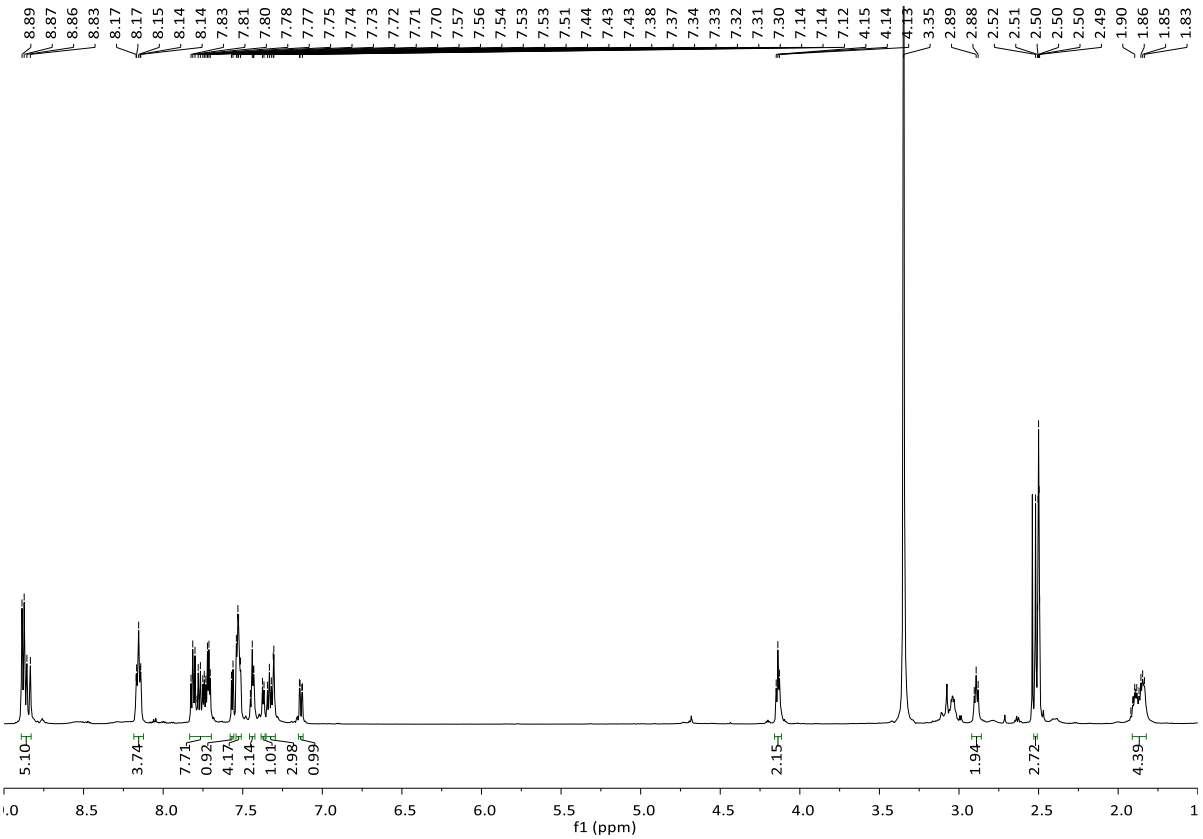


Figure S5: *^{1}H-NMR spectrum of-* ***2*** *([D$_6$]-DMSO, 600 MHz, 300 K).*

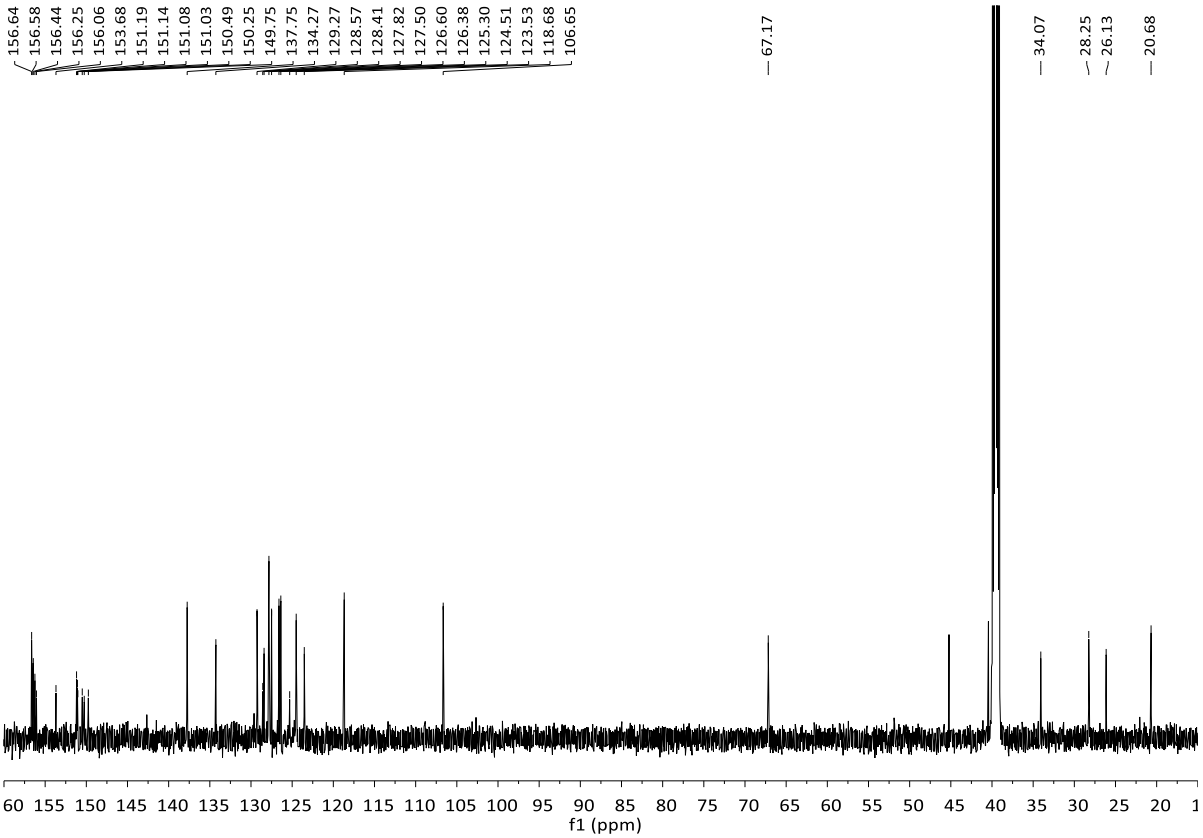


Figure S6: *^{13}C-NMR spectrum of* ***2*** *([D$_6$]-DMSO, 151 MHz, 300 K).*

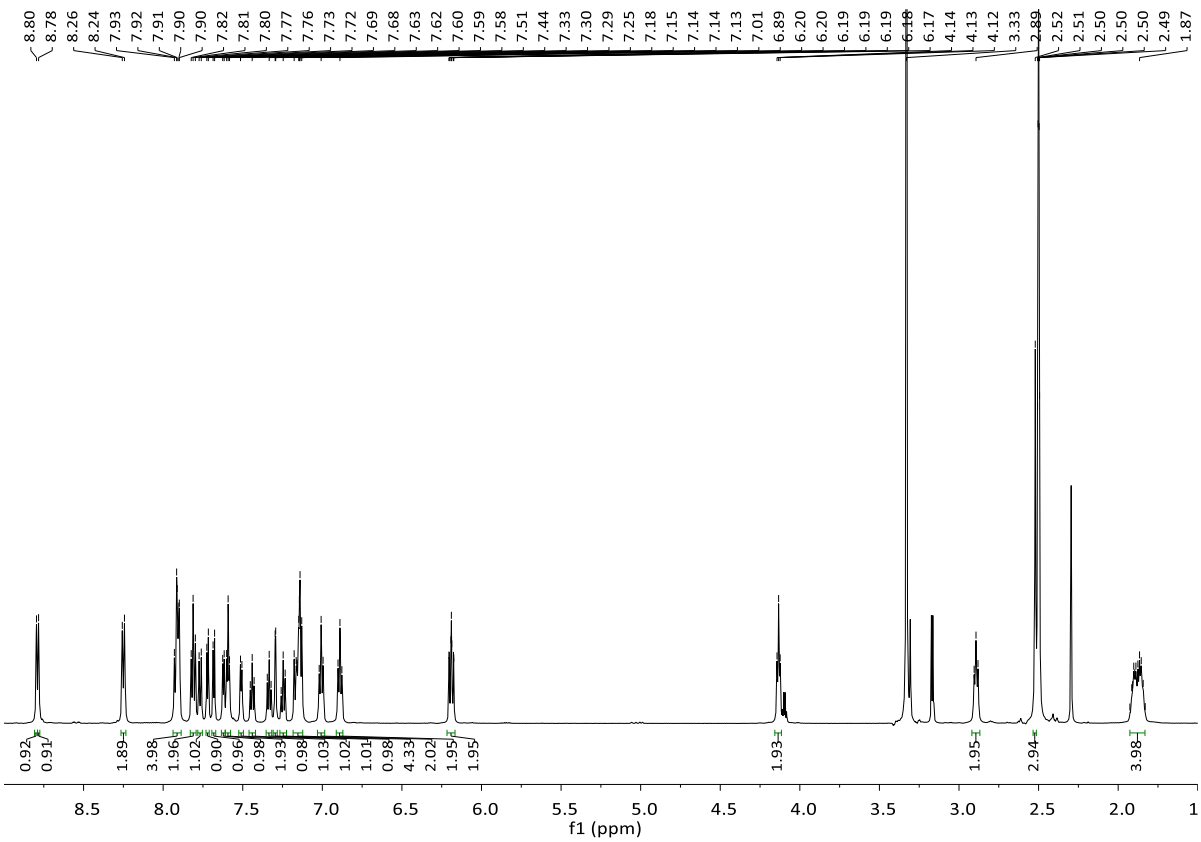


Figure S7: *^{1}H-NMR spectrum of **3** ([D$_6$]-DMSO, 600 MHz, 300 K).*

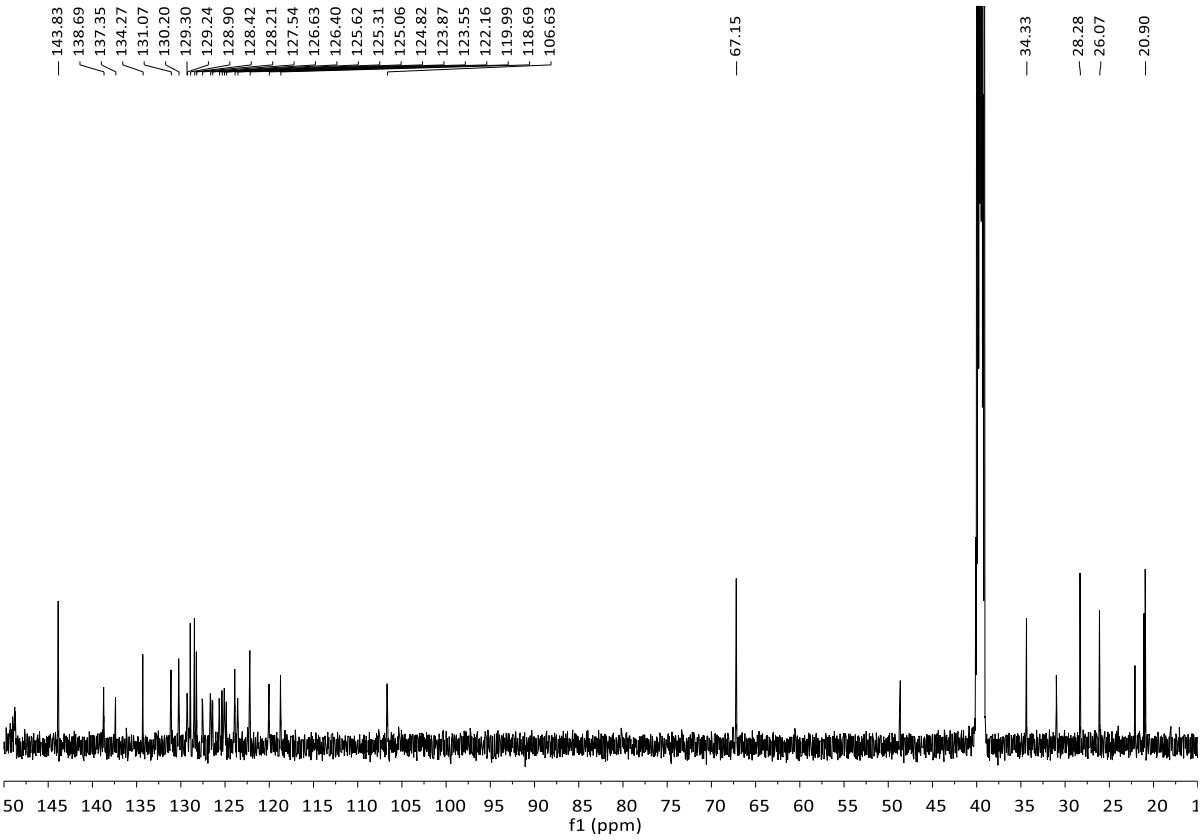


Figure S8: *^{13}C-NMR spectrum of **3** ([D$_6$]-DMSO, 151 MHz, 300 K).*

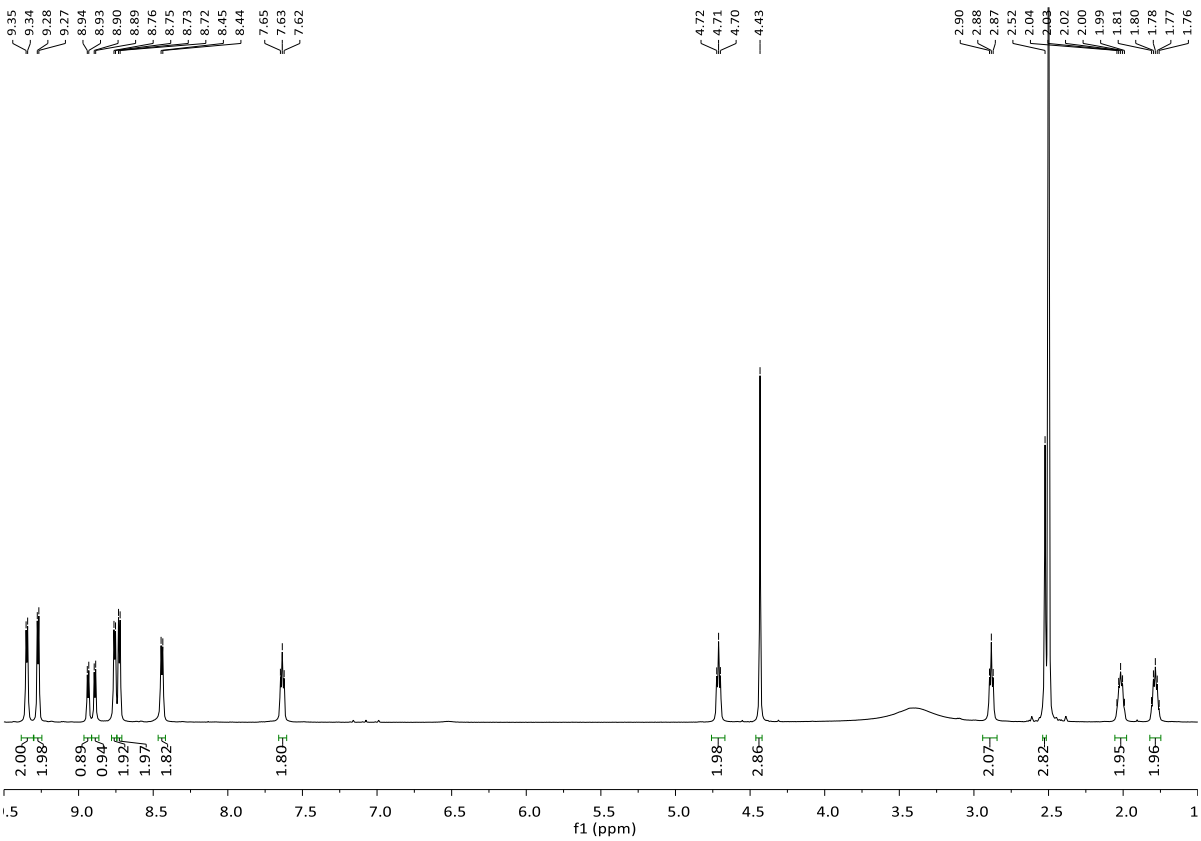


Figure S9: *^{1}H-NMR spectrum of **4** ([D$_6$]-DMSO, 600 MHz, 300 K).*

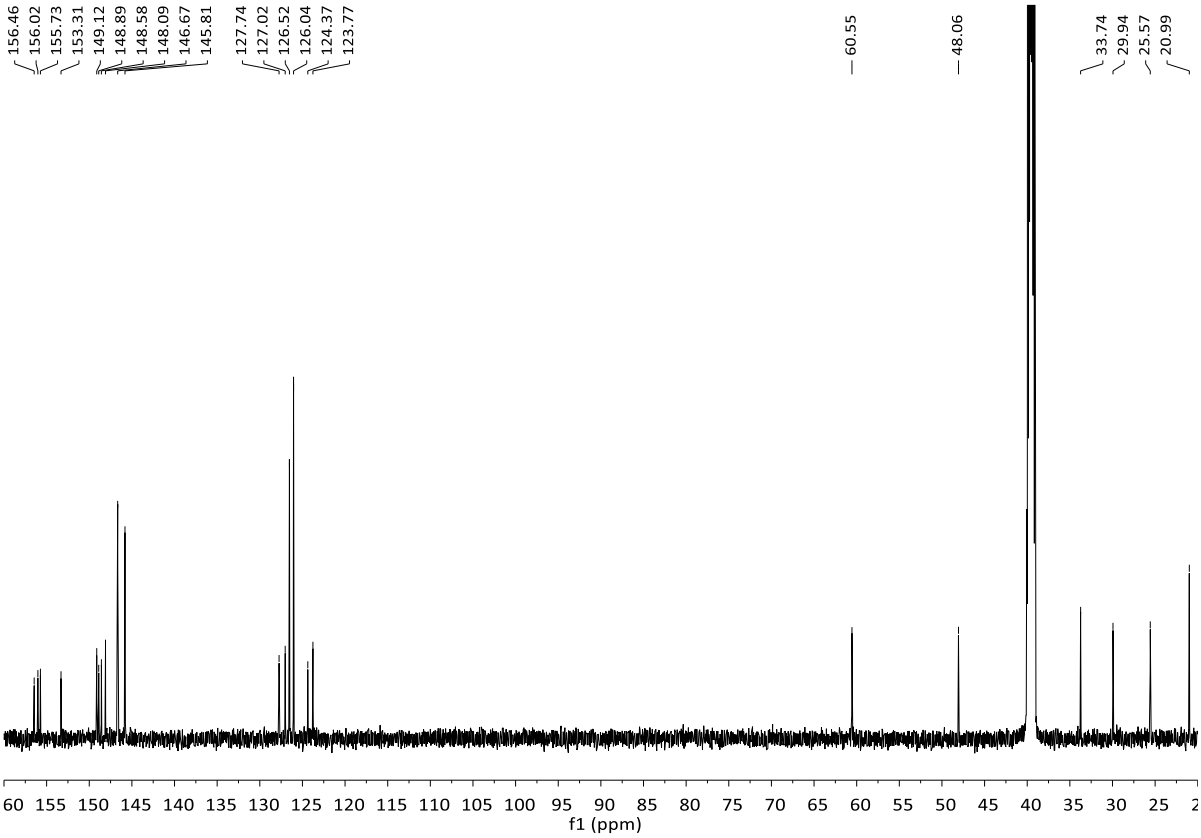


Figure S10: *^{13}C-NMR spectrum of **4** ([D$_6$]-DMSO, 151 MHz, 300 K).*

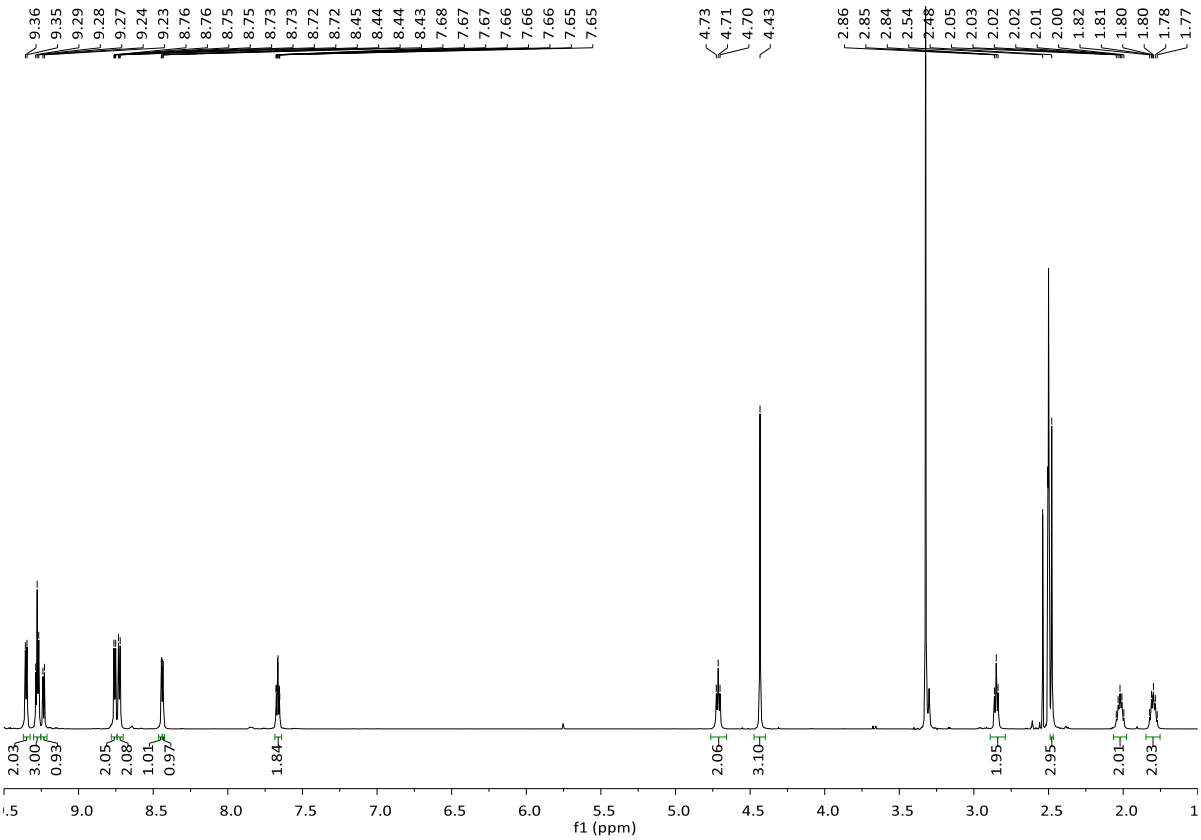


Figure S11: *^{1}H-NMR spectrum of **5** ([D$_6$]-DMSO, 600 MHz, 300 K).*

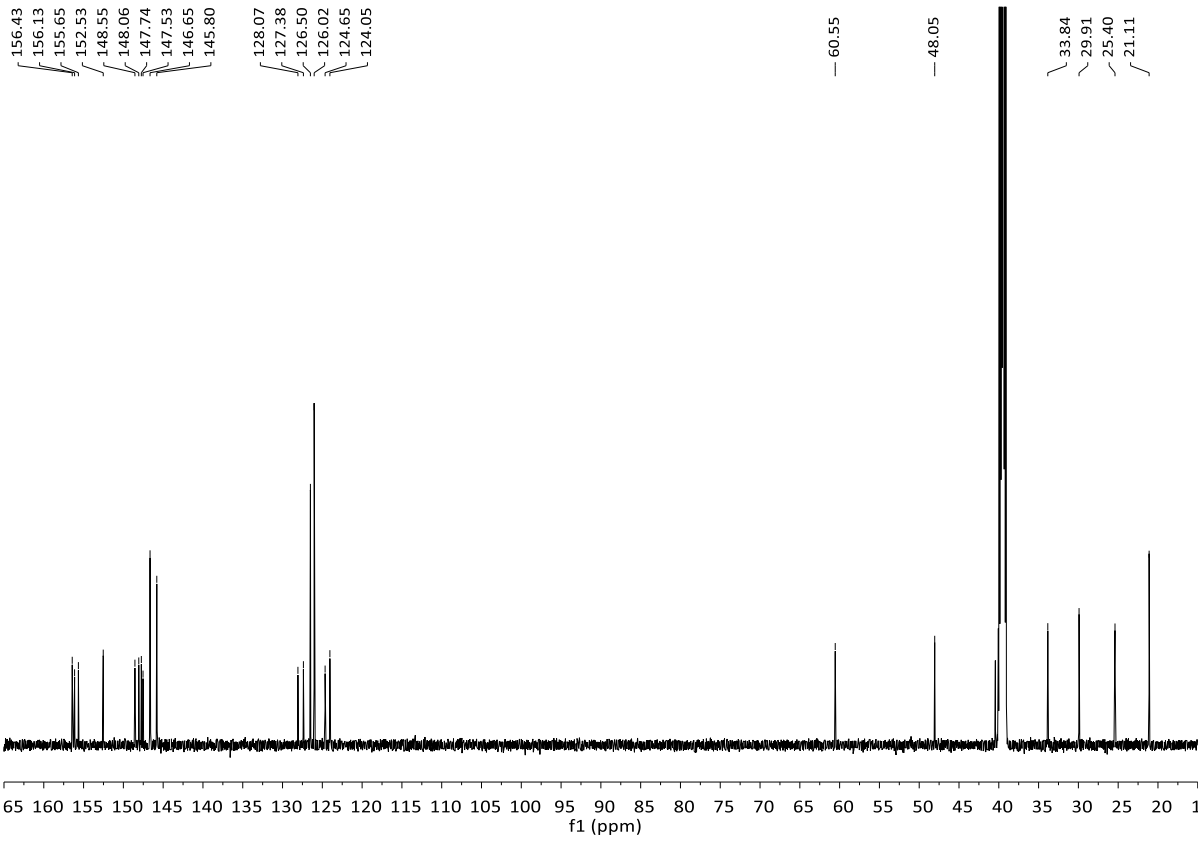


Figure S12: *^{13}C-NMR spectrum of **5** ([D$_6$]-DMSO, 151 MHz, 300 K).*

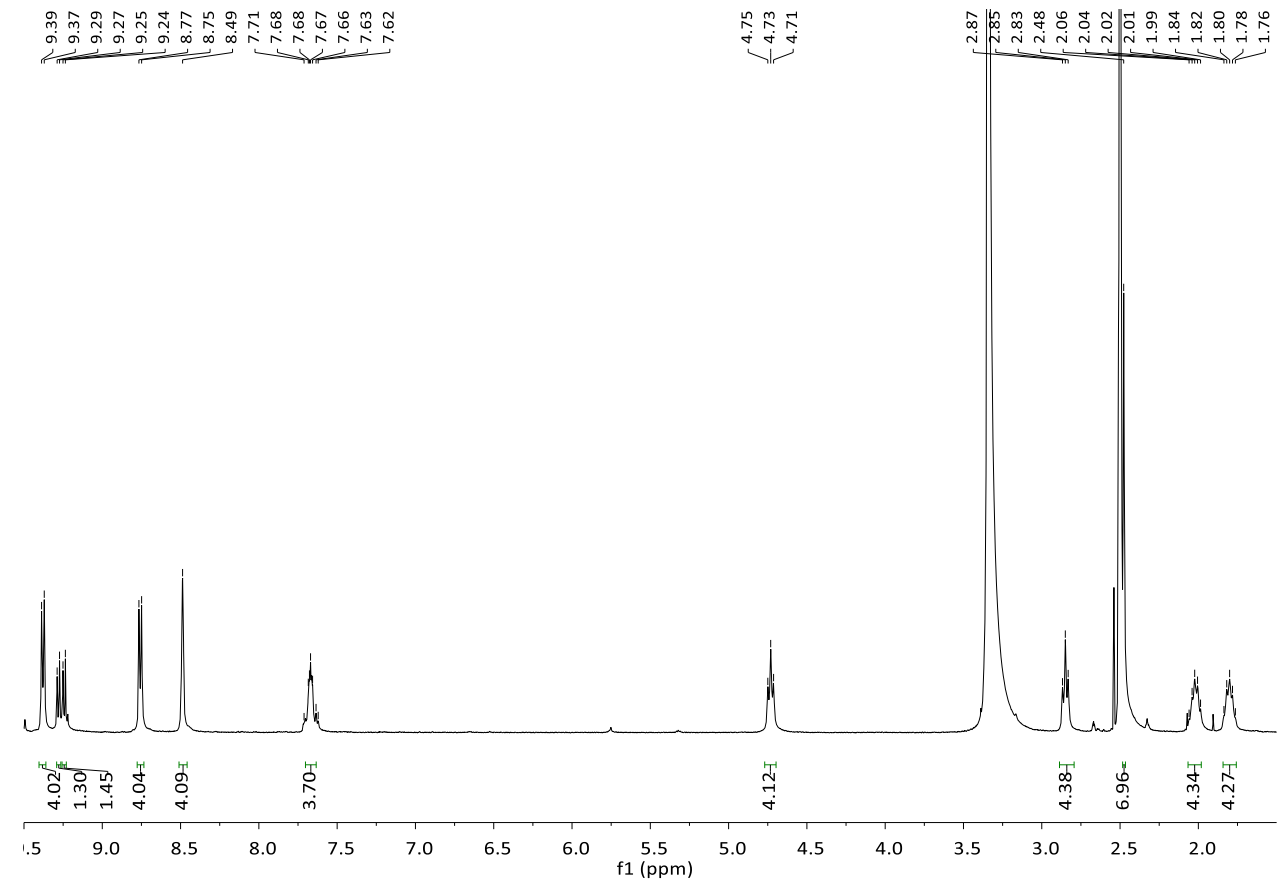


Figure S13: *^{1}H-NMR spectrum of **6** ([D$_6$]-DMSO, 400 MHz, 300 K).*

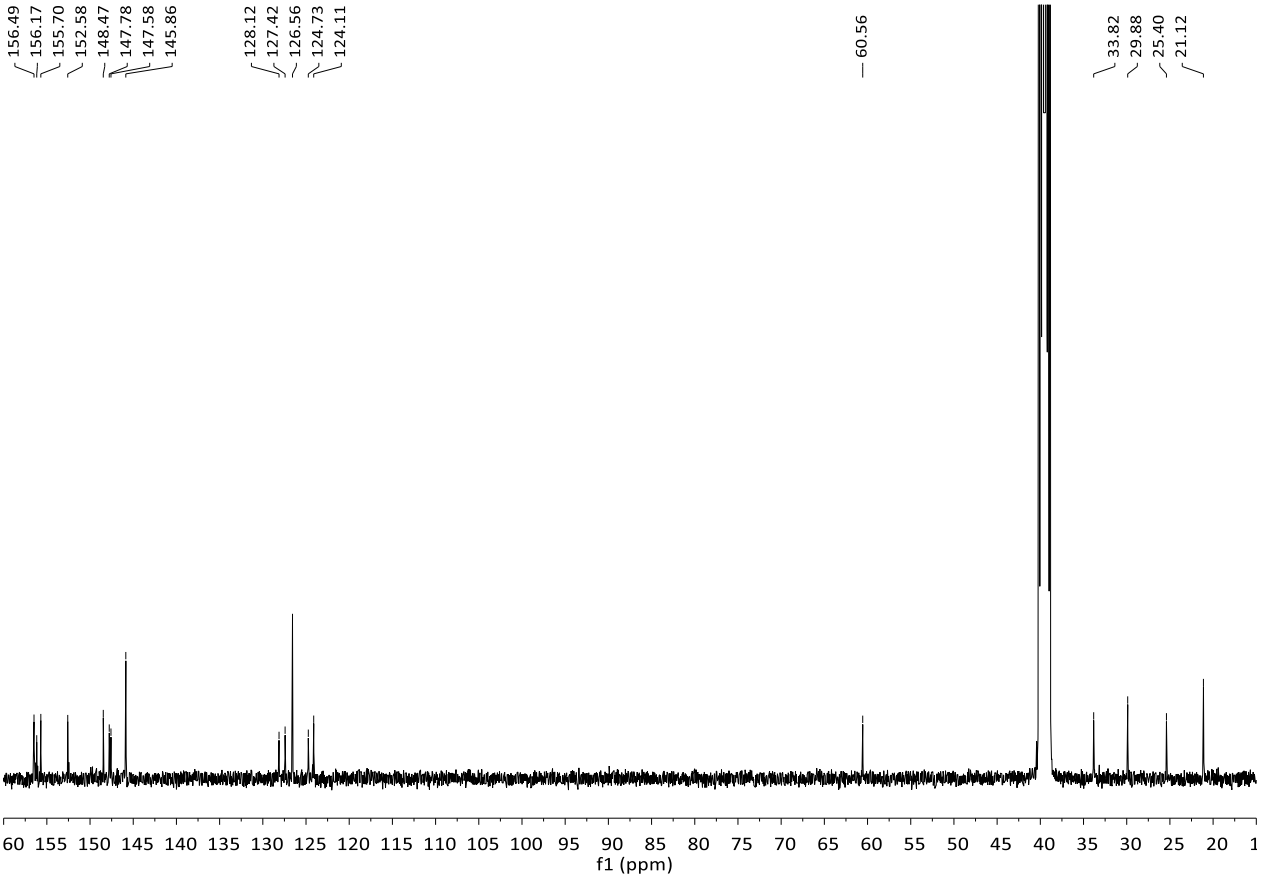


Figure S14: *^{13}C-NMR spectrum of **6** ([D$_6$]-DMSO, 101 MHz, 300 K).*

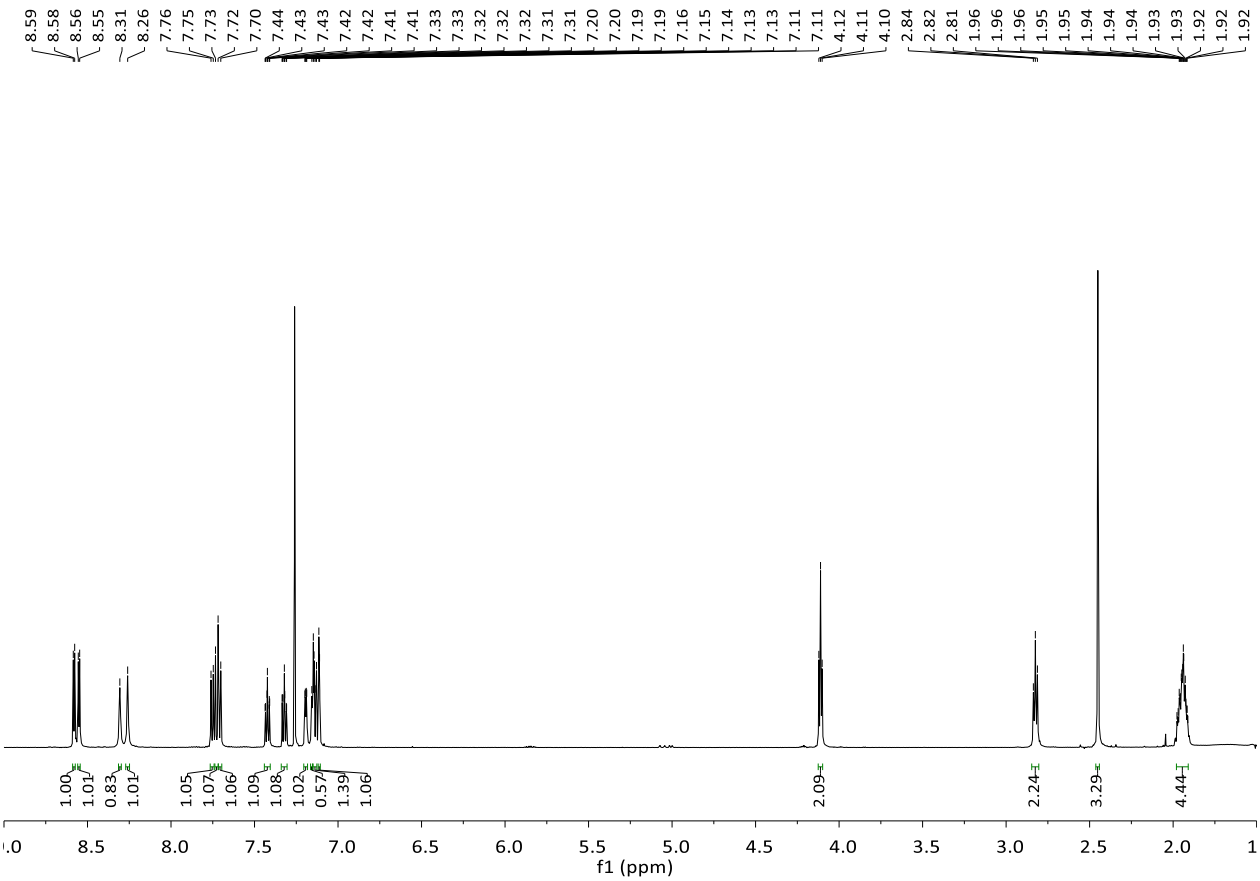


Figure S15: *^{1}H-NMR spectrum of **8** ([D$_6$]-DMSO, 600 MHz, 300 K).*

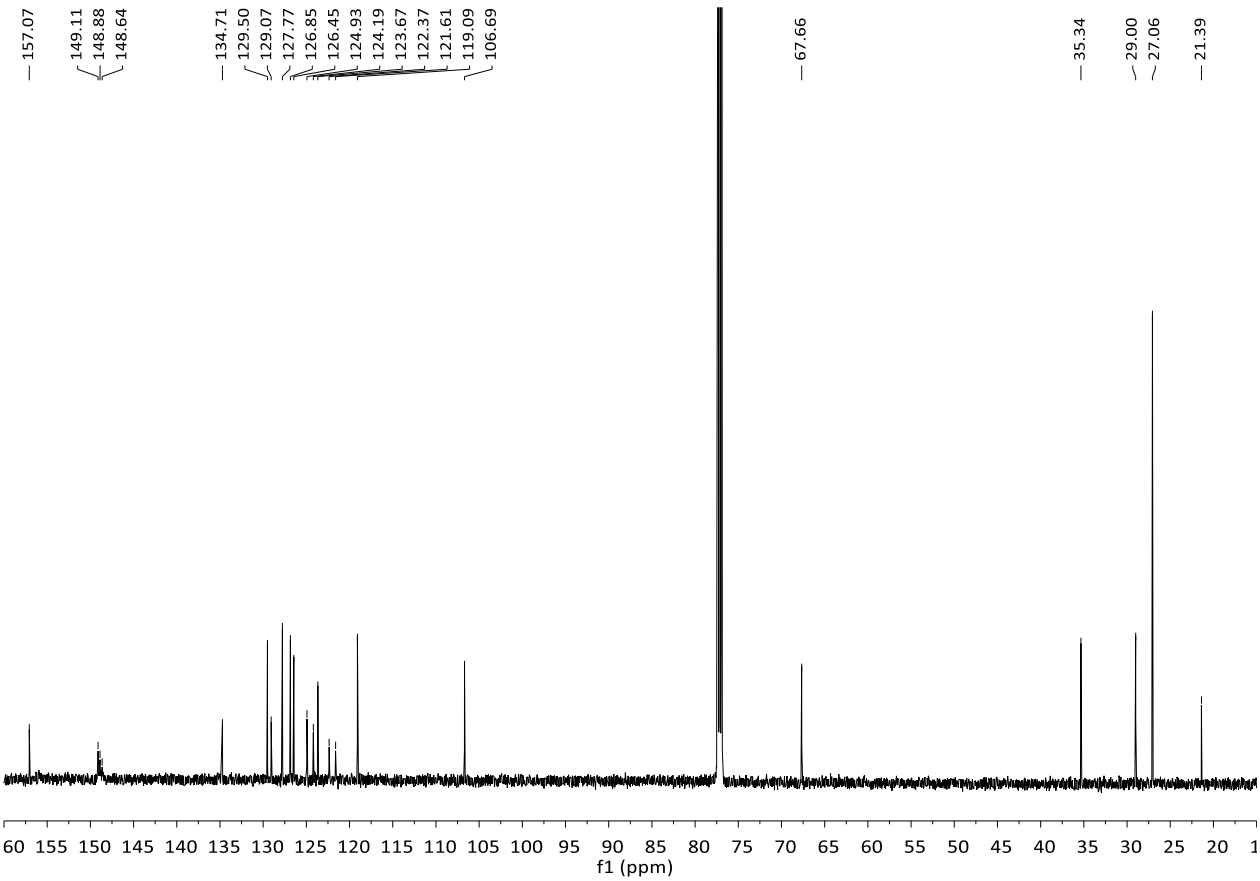


Figure S16: *^{13}C-NMR spectrum of **8** ([D$_6$]-DMSO, 151 MHz, 300 K).*

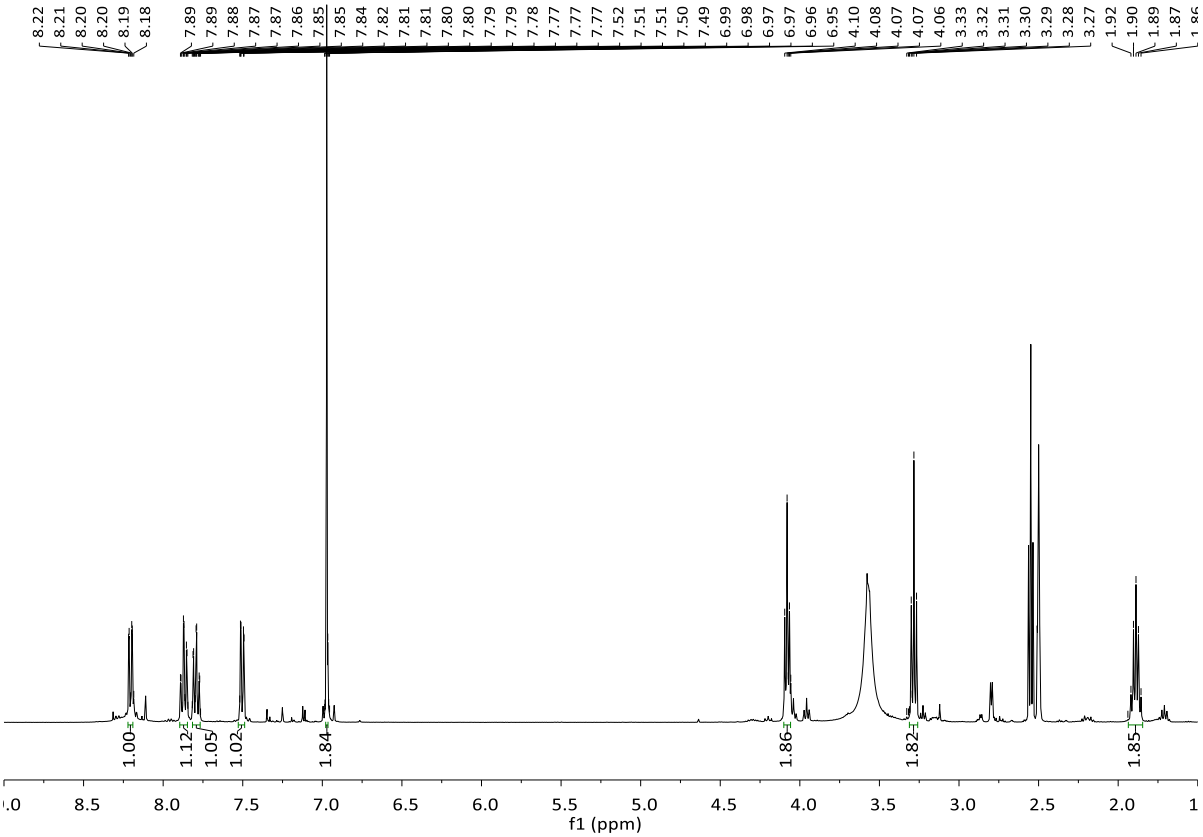


Figure S17: *^{1}H-NMR spectrum of **11** ([D$_6$]-DMSO, 400 MHz, 300 K).*

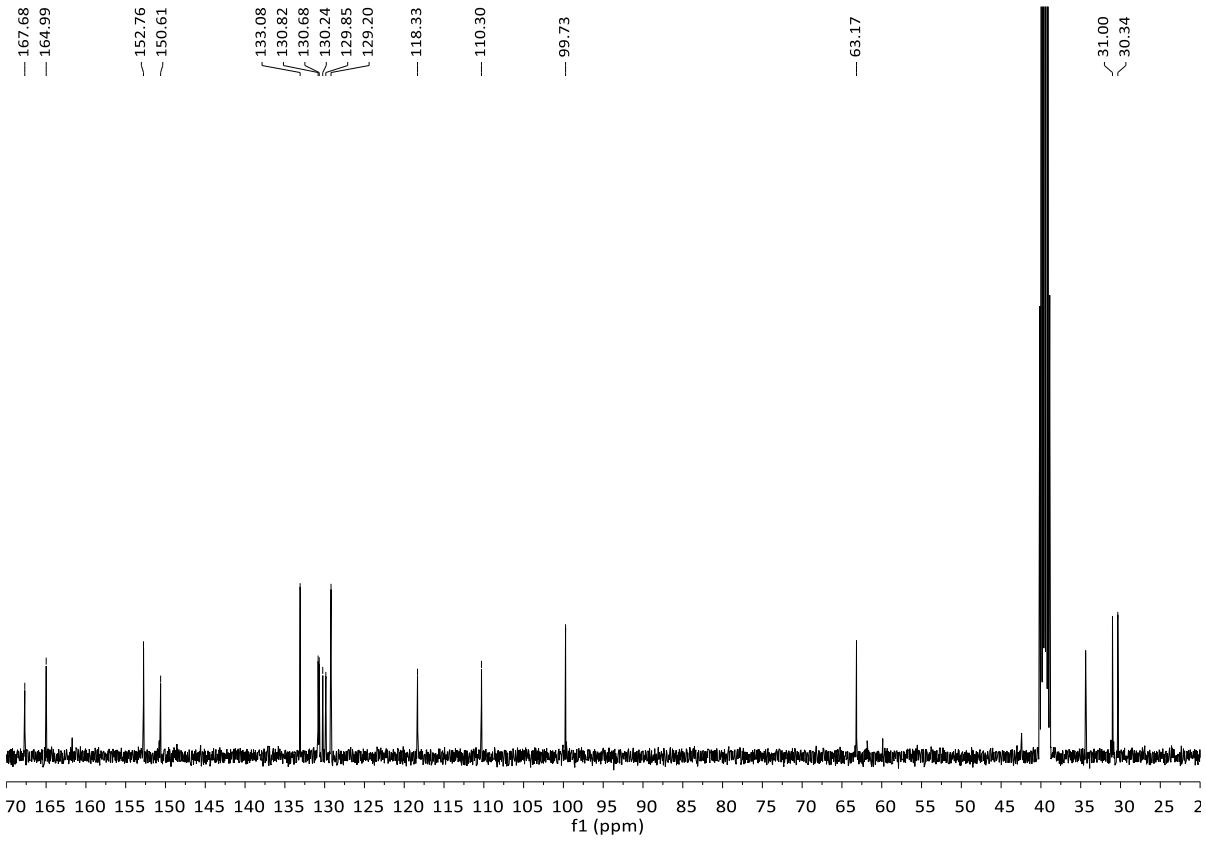


Figure S18: *^{13}C-NMR spectrum of **11** ([D$_6$]-DMSO, 101 MHz, 300 K).*

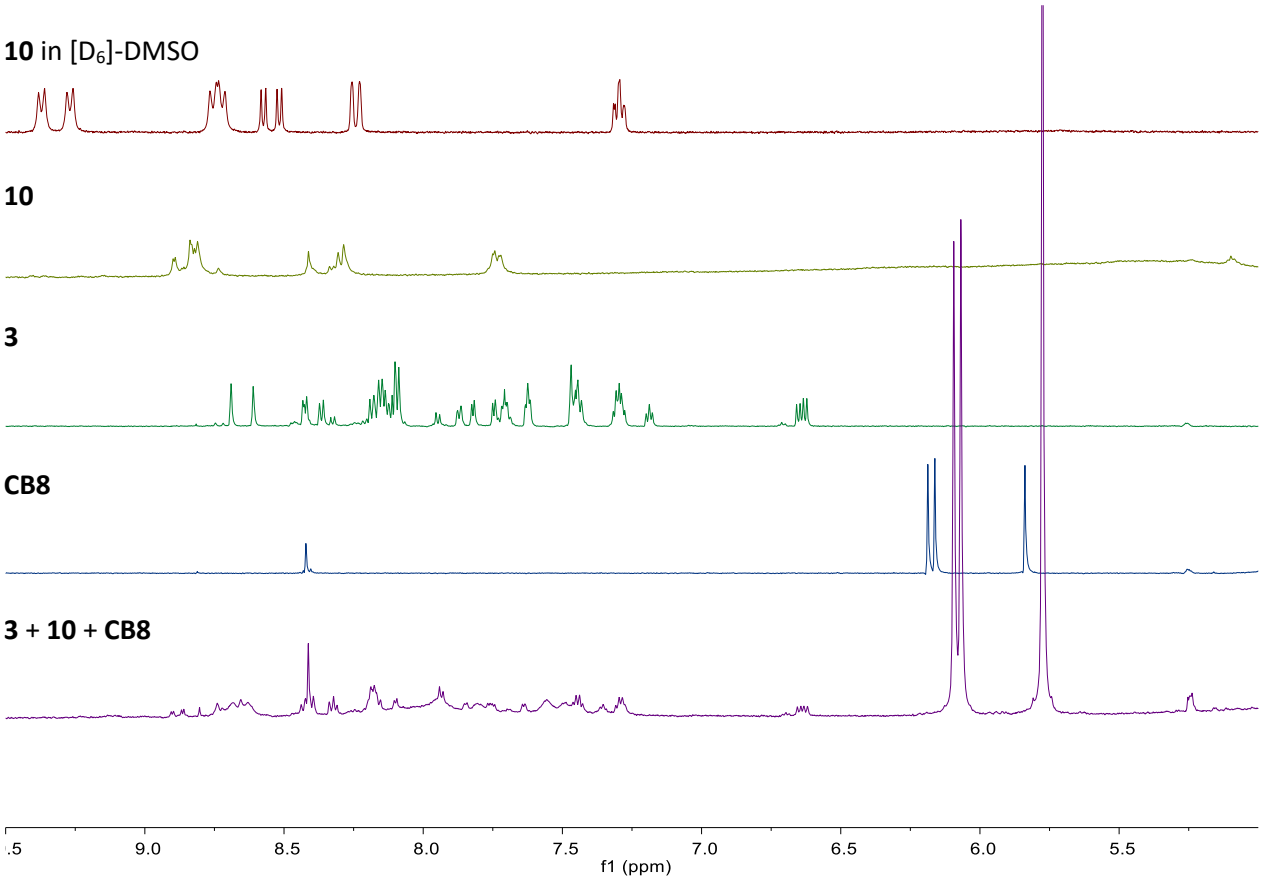


Figure S19: *^{1}H-NMR spectra of **10** ([D$_6$]-DMSO, 300 MHz, 300 K), furthermore **10, 3**, **CB8,** and their equimolar mixture (0.25 mM, 85% D$_2$O, 15% N(EtOH)$_3$, 600 MHz, 300 K). The spectra are cut off below 5 ppm due to the overbearing signals of N(EtOH)$_3$. The spectrum of 10 is additionally shown in [D$_6$]-DMSO to prove its purity because the spectrum in 85% D$_2$O, 15% N(EtOH)$_3$ shows broadening, most probably due to reduction of the viologen-unit.*

4. Catalytic application

4.1 H_2-Calibration curve

To quantify the amount of H_2 detected by headspace gas chromatography, a calibration curve was generated by dissolving different amounts of sodium tris(acetoxy)borohydride in 2 N hydrochloric acid under an argon atmosphere. The vials had a total inner volume of 9.6 mL and a headspace volume of 8.6 mL after addition of 1 mL of solution. The same vials were also used for the irradiation experiments. From this, a small sample of 200 µL of gas was transferred by a gas-tight 1 mL Hamilton syringe from the vial into the gas chromatograph by hand.

By identifying and integrating the peak that corresponds to H_2, this resulted in a linear correlation between the measured integral and the amount of hydrogen in the sample. Apart from H_2, small amounts of two other trace gases were detected which probably correspond to O_2 and N_2 which were transferred into the gas chromatograph by the tip of the Hamilton syringe that was used to transfer the sample.

Further experiments with bigger amounts of gas showed a linear correlation between sample size and integral of the resulting peaks.

Comment: Due to a miscalculation, the total volume of the last two samples (99.37 µmol and 151.2 µmol) was slightly less than 1 mL. These divergences of 100 µL and 150 µL are small compared to the headspace volume of 8.6 mL.

Table S1: *Calibration data for the quantitative determination of H_2 in a gas-tight headspace vial by gas chromatography.*

$NaBH(OAc)_3$ [mg]	0.00	0.34	0.80	0.85	1.74	5.86	11.68	15.86	21.06	32.04
$NaBH(OAc)_3$ [µmol]	0.00	1.6	3.8	4.0	8.21	27.6	55.11	74.83	99.37	151.2
volume of 2 N HCl [mL]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.90	0.85
Integral	0	19.1	56.2	47.6	86.2	421	809	1300	1880	2630

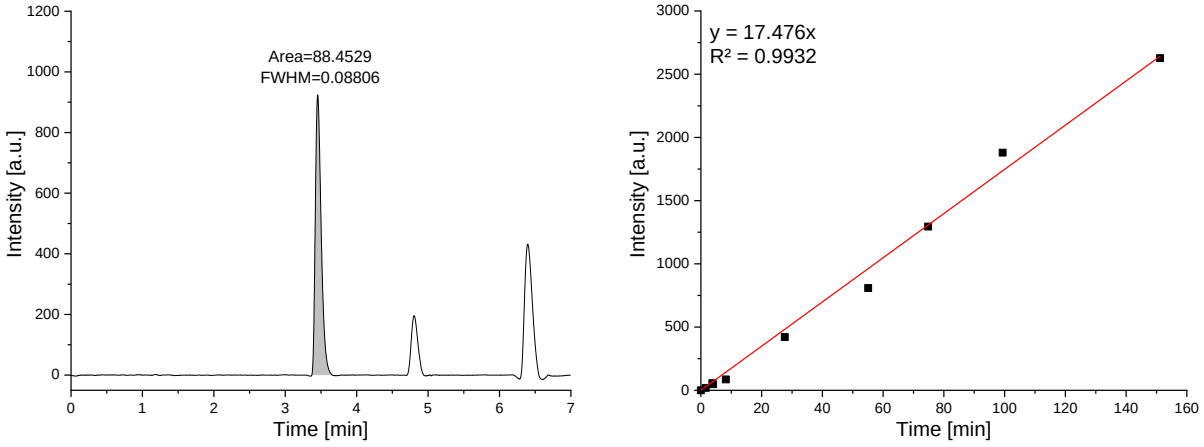


Figure S20: *Left: exemplary gas chromatogram of a sample containing ca. 10 µmol of molecular hydrogen in the vial. Right: Calibration curve for the quantitative determination of H_2 in a gas-tight headspace vial by gas chromatography.*

4.2 Irradiaton experiments

For the equimolar experiments, each single component had a concentration of 0.25 mM.
For the experiments with varying stoichiometries, one concentration was increased to 1 mM while the other concentrations were kept at 0.25 mM. The corresponding turnover number was calculated based on the concentration of the more diluted components at 0.25 mM. Due to the low amount of H_2 in most samples, 400 µL of headspace volume were taken from the vial, the corresponding TON was calculated respectively.

Eosin-based experiments

Table S2: *Turnover numbers of the equimolar photocatalytic reactions between **1** and **4**, and **1** and **5**, with and without **CB8**.*

number	equimolar	TON	average
	without CB8		
1	**1** + **4**	0.00	0.00
2	**1** + **5**	1.36	1.36
	with CB8		
3	**1** + **4** + **CB8**	0.00	0.00 ± 0.00
4	**1** + **4** + **CB8**	0.00	
5	**1** + **5** + **CB8**	1.33	1.315 ± 0.015
6	**1** + **5** + **CB8**	1.30	

Ruthenium-based experiments

Table S3: *Turnover numbers of the equimolar photocatalytic reactions between **2** and **4**, and **2** and **5**, with and without **CB8**.*

number	equimolar	TON	average
	without CB8		
7	**2** + **4**	0.00	0.00 ± 0.00
8	**2** + **4**	0.00	
9	**2** + **5**	0.48	0.50 ± 0.06
10	**2** + **5**	0.43	
11	**2** + **5**	0.58	
	with CB8		
12	**2** + **4** + **CB8**	0.00	0.00 ± 0.00
13	**2** + **4** + **CB8**	0.00	
14	**2** + **5** + **CB8**	2.38	1.19 ± 1.26
15	**2** + **5** + **CB8**	3.01	
16	**2** + **5** + **CB8**	0.12	
17	**2** + **5** + **CB8**	0.21	
18	**2** + **5** + **CB8**	0.12	

Table S4: *Turnover numbers of the investigations with varying stoichiometries of the photocatalytic reactions between **2** and **5**, with and without **CB8**.*

number	stoichiometrics	TON	average
	without CB8		
19	0.25 mM **2** + 1.0 mM **5**	10.12	9.38 ± 0.75
20	0.25 mM **2** + 1.0 mM **5**	8.63	
21	1.0 mM **2** + 0.25 mM **5**	0.32	0.29 ± 0.03
22	1.0 mM **2** + 0.25 mM **5**	0.26	
	with CB8		
23	0.25 mM **2** + 0.25 mM **5** + 1.0 mM **CB8**	0.32	
24	0.25 mM **2** + 0.25 mM **5** + 1.0 mM **CB8**	0.41	0.37 ± 0.05
25	0.25 mM **2** + 1.0 mM **5** + 0.25 mM **CB8**	11.39	11.8 ± 0.45
26	0.25 mM **2** + 1.0 mM **5** + 0.25 mM **CB8**	12.29	
27	1.0 mM **2** + 0.25 mM **5** + 0.25 mM **CB8**	0.20	0.27 ± 0.07
28	1.0 mM **2** + 0.25 mM **5** + 0.25 mM **CB8**	0.34	

Iridium-based experiments

Table S5: *Turnover numbers of the equimolar photocatalytic reactions between **3** and **4**, and **3** and **5**, with and without **CB8**.*

number	equimolar	TON	average
	without CB8		
29	**3** + **4**	0.00	0.00
30	**3** + **5**	1.98	1.26 ± 0.51
31	**3** + **5**	0.86	
32	**3** + **5**	0.93	
	with CB8		
33	**3** + **4** + **CB8**	0.21	0.11 ± 0.11
34	**3** + **4** + **CB8**	0.00	
35	**3** + **5** + **CB8**	3.10	3.11 ± 0.01
36	**3** + **5** + **CB8**	3.12	

Table S6: *Turnover numbers of the investigations with varying stoichiometries of the photocatalytic reactions between **3** and **5**, and **3** and **6**, with and without **CB8**.*

number	stoichiometrics	TON	average
	without CB8		
37	0.25 mM **3** + 1.0 mM **5**	1.72	1.66 ± 0.07
38	0.25 mM **3** + 1.0 mM **5**	1.59	
39	1.0 mM **3** + 0.25 mM **5**	7.59	6.43 ± 1.17
40	1.0 mM **3** + 0.25 mM **5**	5.26	
41	1.0 mM **3** + 0.25 mM **6**	6.31	4.23 ± 2.09
42	1.0 mM **3** + 0.25 mM **6**	2.14	
	with CB8		
43	0.25 mM **3** + 0.25 mM **5** + 1.0 mM **CB8**	6.00	3.34 ± 1.88
44	0.25 mM **3** + 0.25 mM **5** + 1.0 mM **CB8**	0.58	
45	0.25 mM **3** + 0.25 mM **5** + 1.0 mM **CB8**	4.89	
46	0.25 mM **3** + 0.25 mM **5** + 1.0 mM **CB8**	2.94	
47	0.25 mM **3** + 0.25 mM **5** + 1.0 mM **CB8**	0.95	
48	0.25 mM **3** + 0.25 mM **5** + 1.0 mM **CB8**	4.63	
49	0.25 mM **3** + 0.25 mM **5** + 1.0 mM **CB8**	3.36	
50	0.25 mM **3** + 1.0 mM **5** + 0.25 mM **CB8**	0.78	1.65 ± 0.87
51	0.25 mM **3** + 1.0 mM **5** + 0.25 mM **CB8**	2.52	
52	1.0 mM **3** + 0.25 mM **5** + 0.25 mM **CB8**	10.99	11.1 ± 0.11
53	1.0 mM **3** + 0.25 mM **5** + 0.25 mM **CB8**	12.21	
54	1.0 mM **3** + 0.25 mM **6** + 0.25 mM **CB8**	29.63	29.1 ± 0.53
55	1.0 mM **3** + 0.25 mM **6** + 0.25 mM **CB8**	28.57	

Table S7: *Turnover numbers of the mechanistic investigations of the photocatalytic reactions between **3** and **5**, **3** and ethylviologen, and **3** and ethylviologen and K_2PtCl_4, with and without **CB8**.*

number	control experiments	TON	average
56	**3** + **5** + **CB8,** dark	0.00	0.00
57	**3** + **5** + **CB8** + 100 µL Hg	4.21	3.72 ± 0.50
58	**3** + **5** + **CB8** + 100 µL Hg	3.22	
59	**3** + EV + **CB8**	0.77	0.72 ± 0.6
60	**3** + EV + **CB8**	0.66	
61	**3** + EV + **CB8** + [Pt(dmb)Cl_2]	3.83	3.77 ± 0.06
62	**3** + EV + **CB8** + [Pt(dmb)Cl_2]	3.71	
63	Naph + **5** + **CB8**	0.81	1.16 ± 0.34
64	Naph + **5** + **CB8**	1.50	
65	Naph + **5** + **CB8** + [Ir(ppy)2(dmb)Cl]	2.70	3.19 ± 0.49
66	Naph + **5** + **CB8** + [Ir(ppy)2(dmb)Cl]	3.67	
67	Naph + EV + CB8	0.00	0.07 ± 0.07
68	Naph + EV + CB8	0.15	

number	concentration of TEOA	TON	average
69	**3** + **5** + **CB8** + 0% **TEOA**	0.00	0.00
70	**3** + **5** + **CB8** + 0% **TEOA**	0.00	
71	**3** + **5** + **CB8** + 5% **TEOA**	0.99	1.17 ± 0.18
72	**3** + **5** + **CB8** + 5% **TEOA**	1.35	
73	**3** + **5** + **CB8** + 10% **TEOA**	3.87	3.93 ± 0.06
74	**3** + **5** + **CB8** + 10% **TEOA**	3.98	
35	**3** + **5** + **CB8** + 15% **TEOA**	3.11	3.11 ± 0.01
36	**3** + **5** + **CB8** + 15% **TEOA**	3.12	
75	**3** + **5** + **CB8** + 20% **TEOA**	5.96	4.86 ± 1.10
76	**3** + **5** + **CB8** + 20% **TEOA**	3.75	

Table S8: *Turnover numbers at different concentrations of triethanolamine for the system **3** + **5** + **CB8**.*

Comment for table S8: There is an almost linear increase of catalytic activity with increasing amounts of triethanolamine. Such behaviour is in line with the role of TEOA as the sacrificial electron-donor, which is needed to regenerate the reduced catalysts by intermolecular electron transfer.

4.2 GC-chromatograms

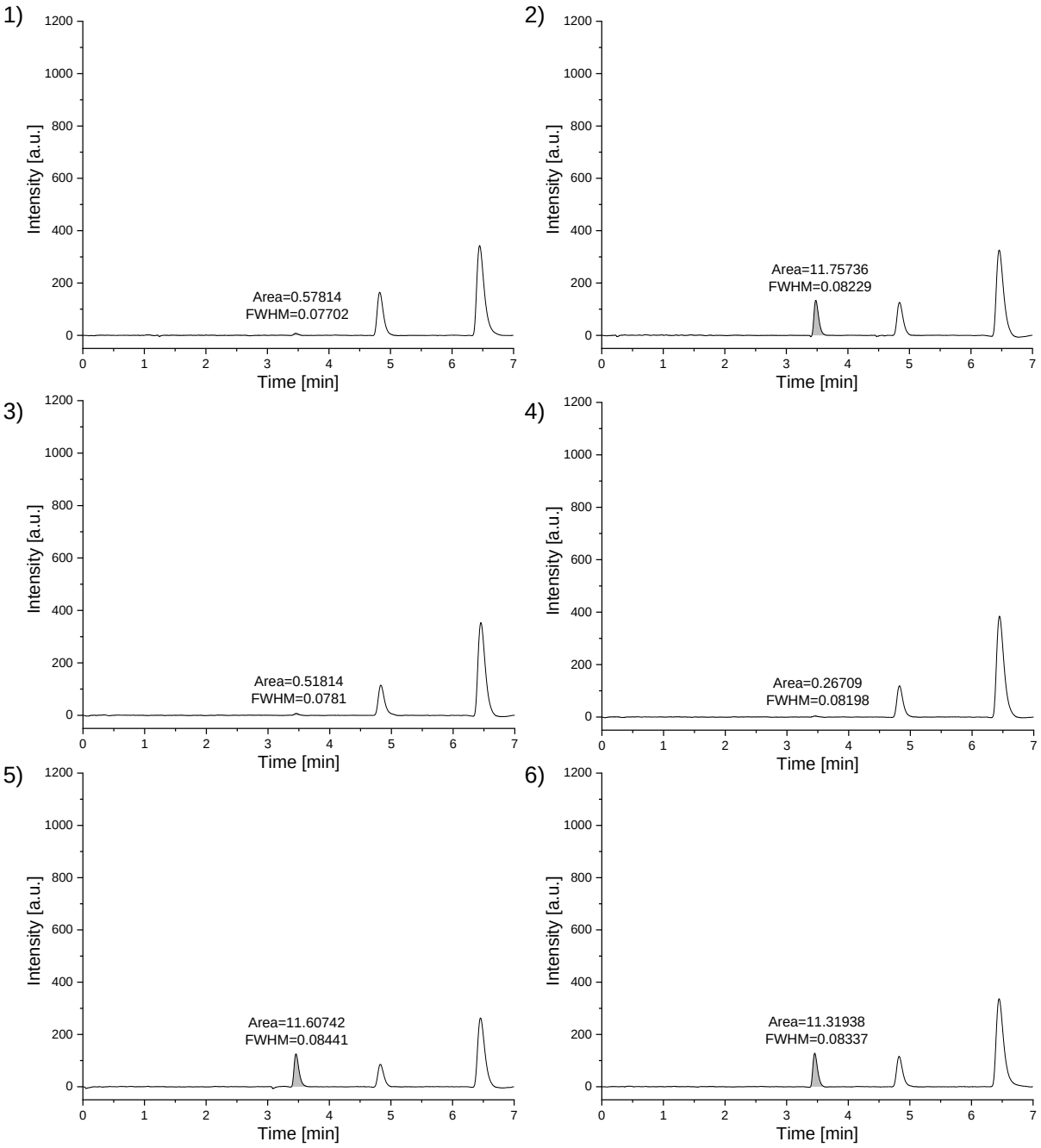


Figure S21: *Gas chromatograms of the equimolar photocatalytic reactions between **1** and **4**, and **1** and **5**, with and without **CB8** (see Table S2, entries 1-6).*

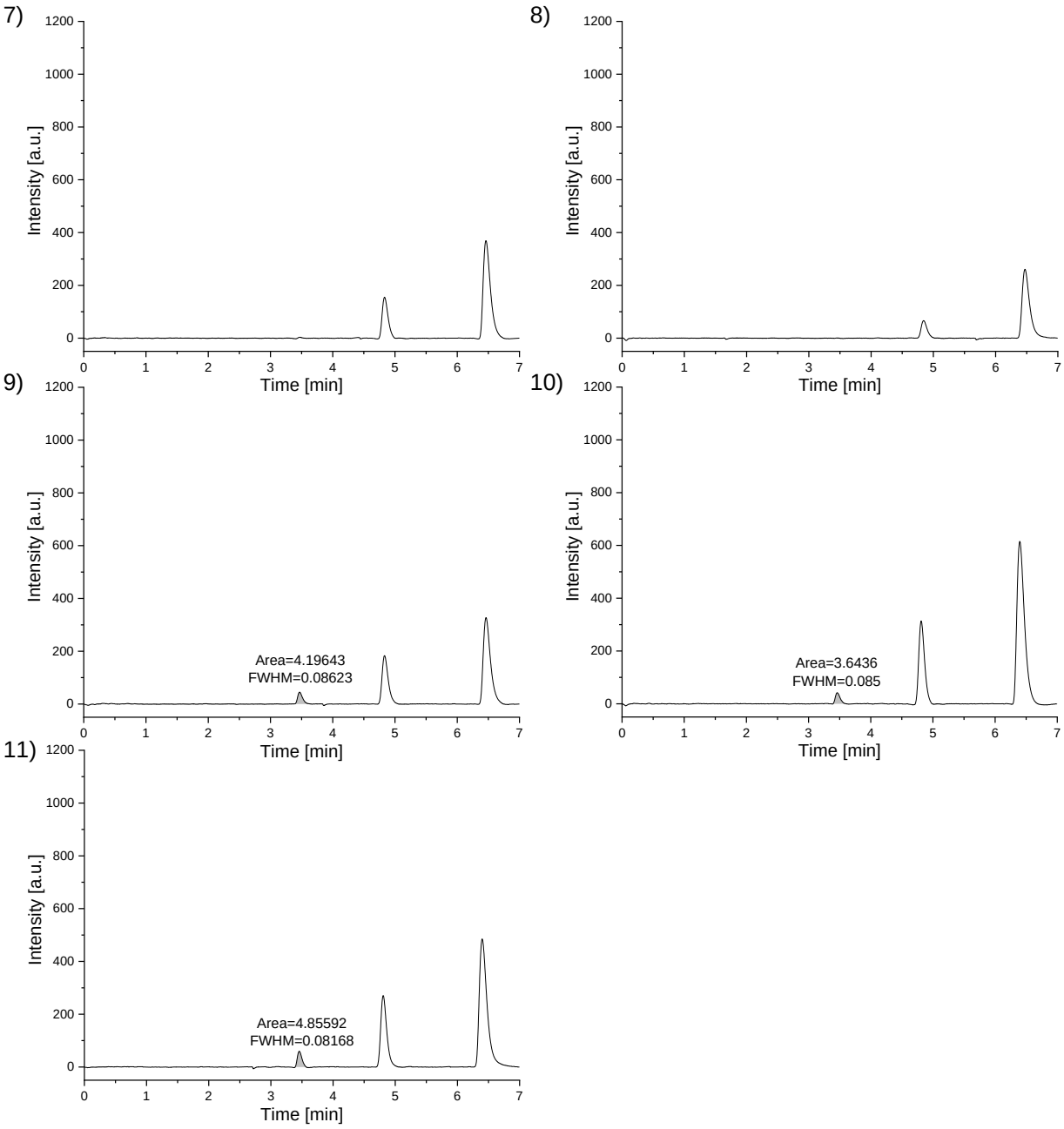


Figure S22: *Gas chromatograms of the equimolar photocatalytic reactions between* ***2*** *and* ***4****, and* ***2*** *and* ***5****, without* ***CB8*** *(see Table S3, entries 7-11).*

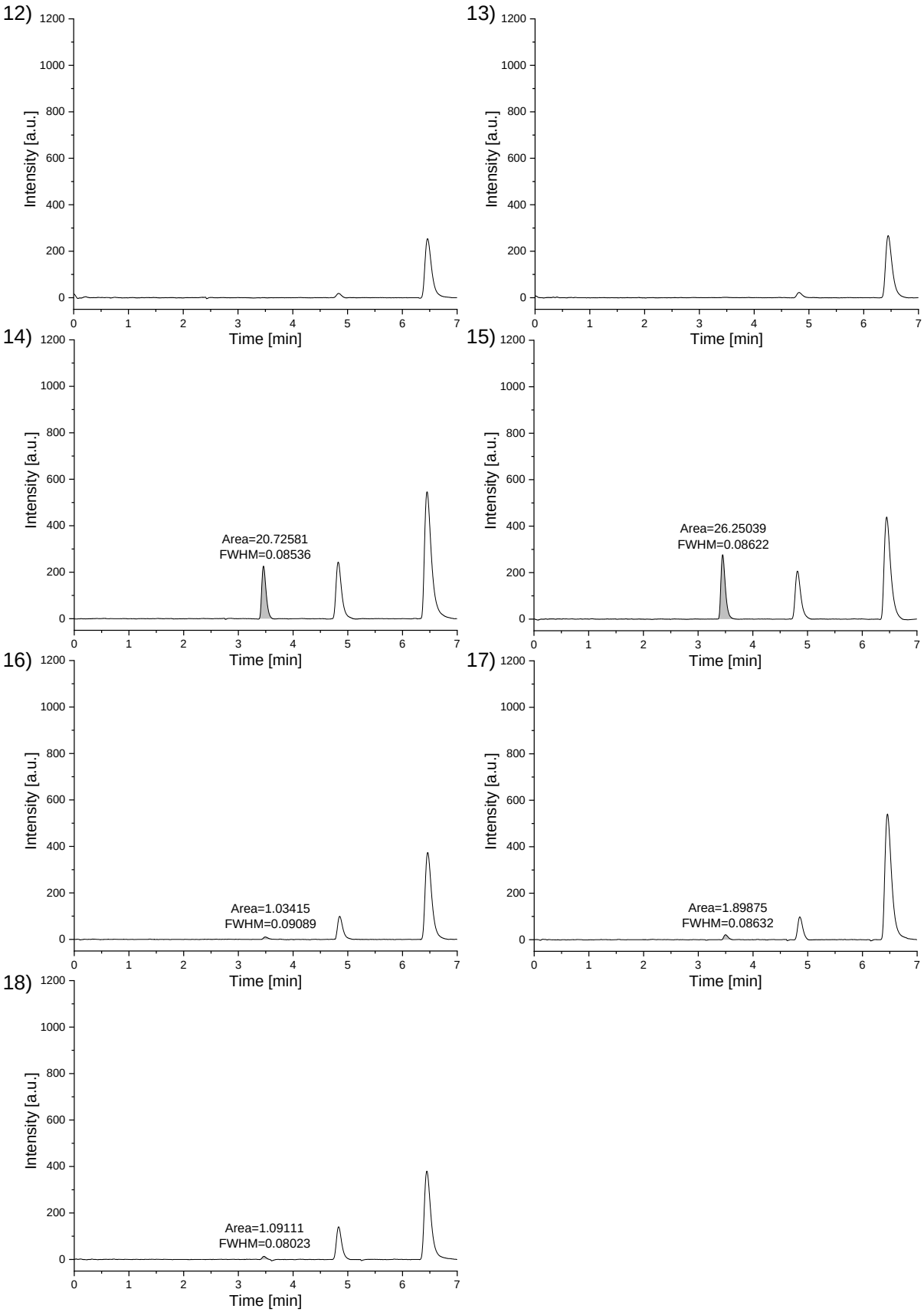


Figure S23: *Gas chromatograms of the equimolar photocatalytic reactions between **2** and **4**, and **2** and **5**, with **CB8** (see Table S3, entries 12-18).*

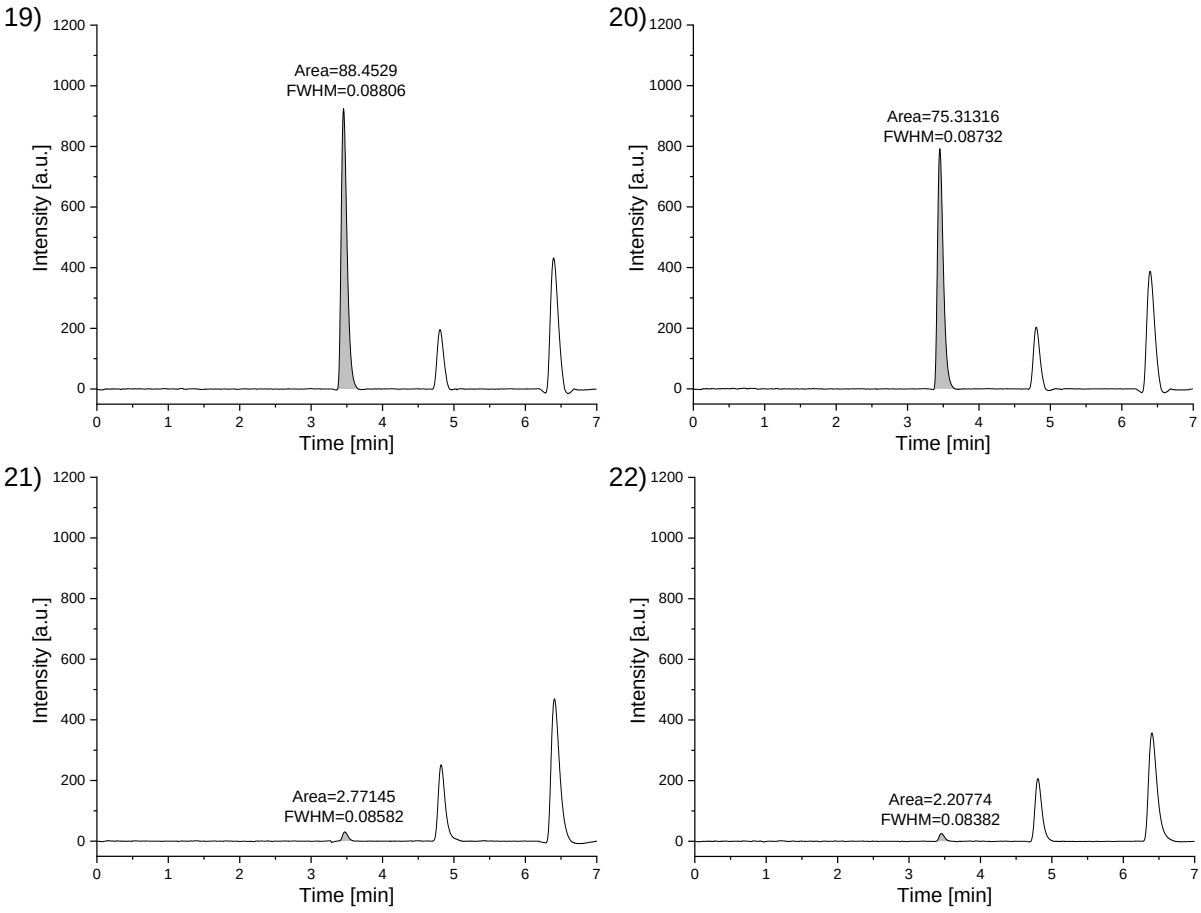


Figure S24: *Gas chromatograms of the stoichiometric investigation of the photocatalytic reactions between* ***2*** *and* ***5*** *without* ***CB8*** *(see Table S4, entries 19-22).*

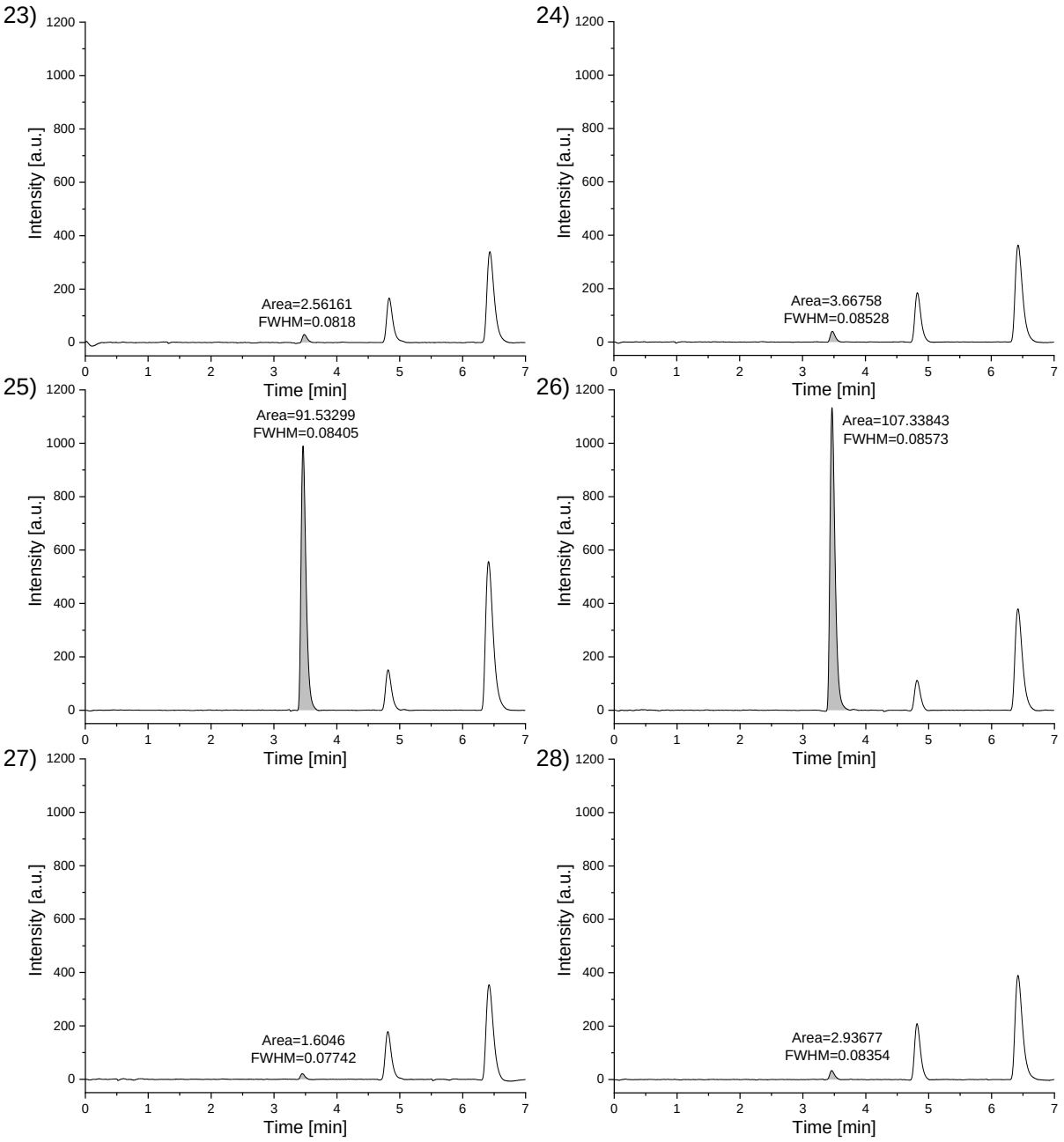


Figure 25: *Gas chromatograms of the stoichiometric investigation of the photocatalytic reactions between* ***2*** *and* ***5*** *with* ***CB8*** *(see Table S4, entries 23-28).*

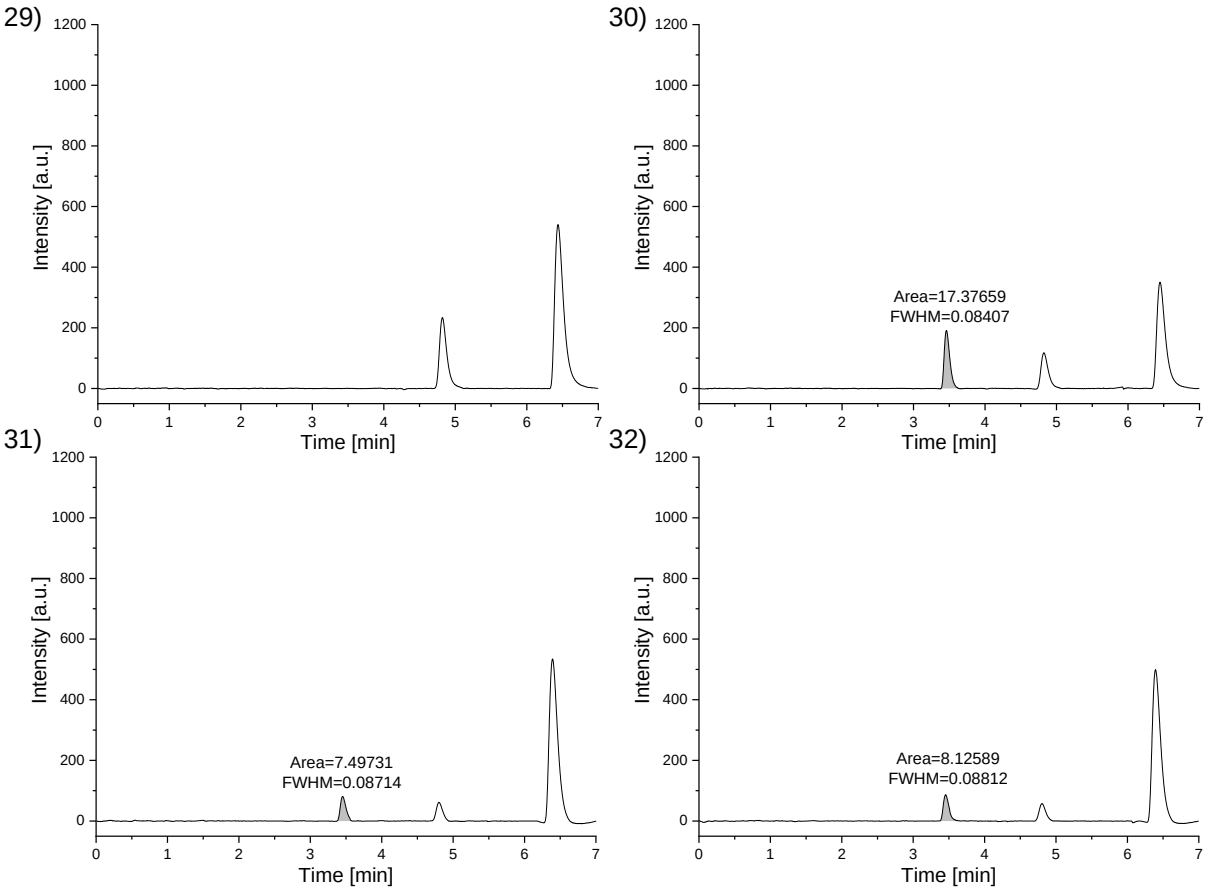


Figure S26: *Gas chromatograms of the equimolar photocatalytic reactions between **3** and **4**, and **3** and **5**, without **CB8** (see Table S5, entries 29-32).*

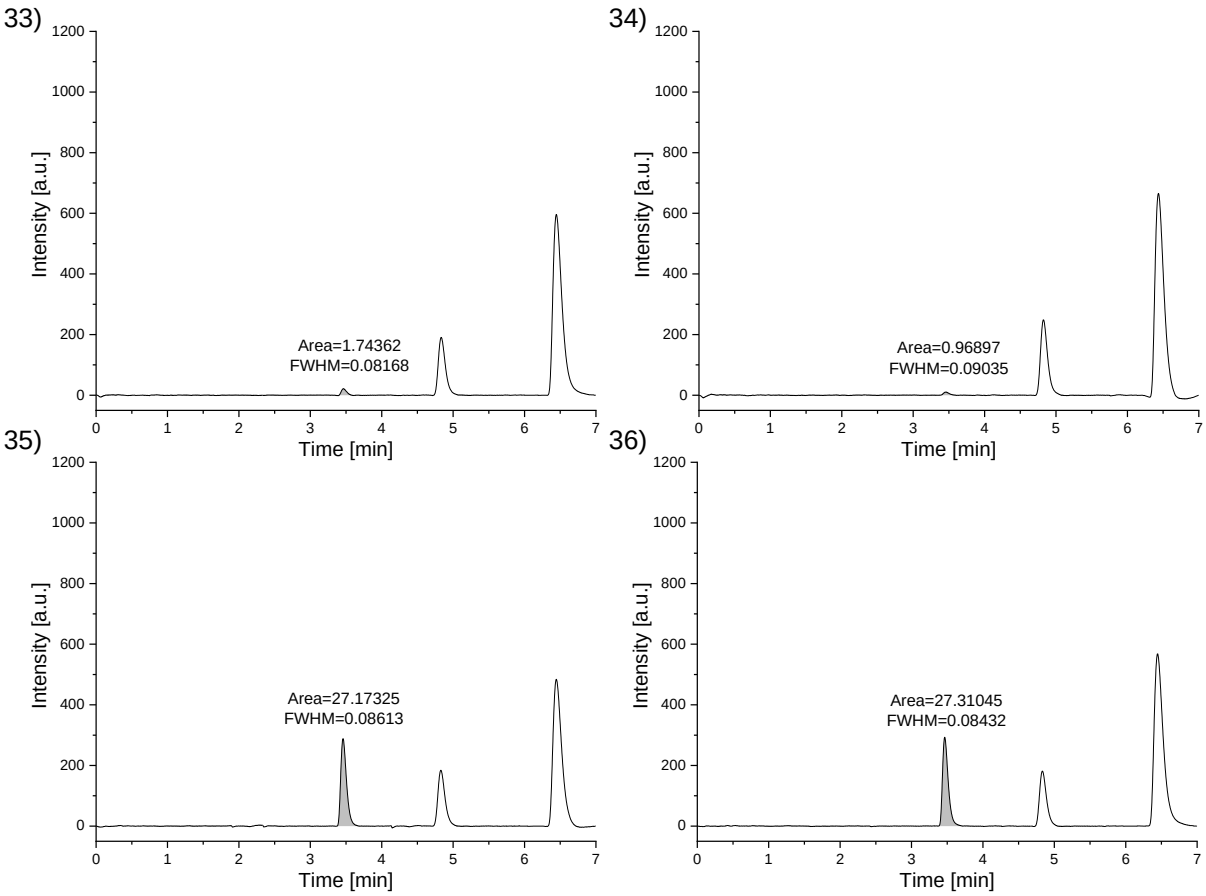


Figure S27: *Gas chromatograms of the equimolar photocatalytic reactions between **3** and **4**, and **3** and **5**, with **CB8** (see Table S5, entries 33-36).*

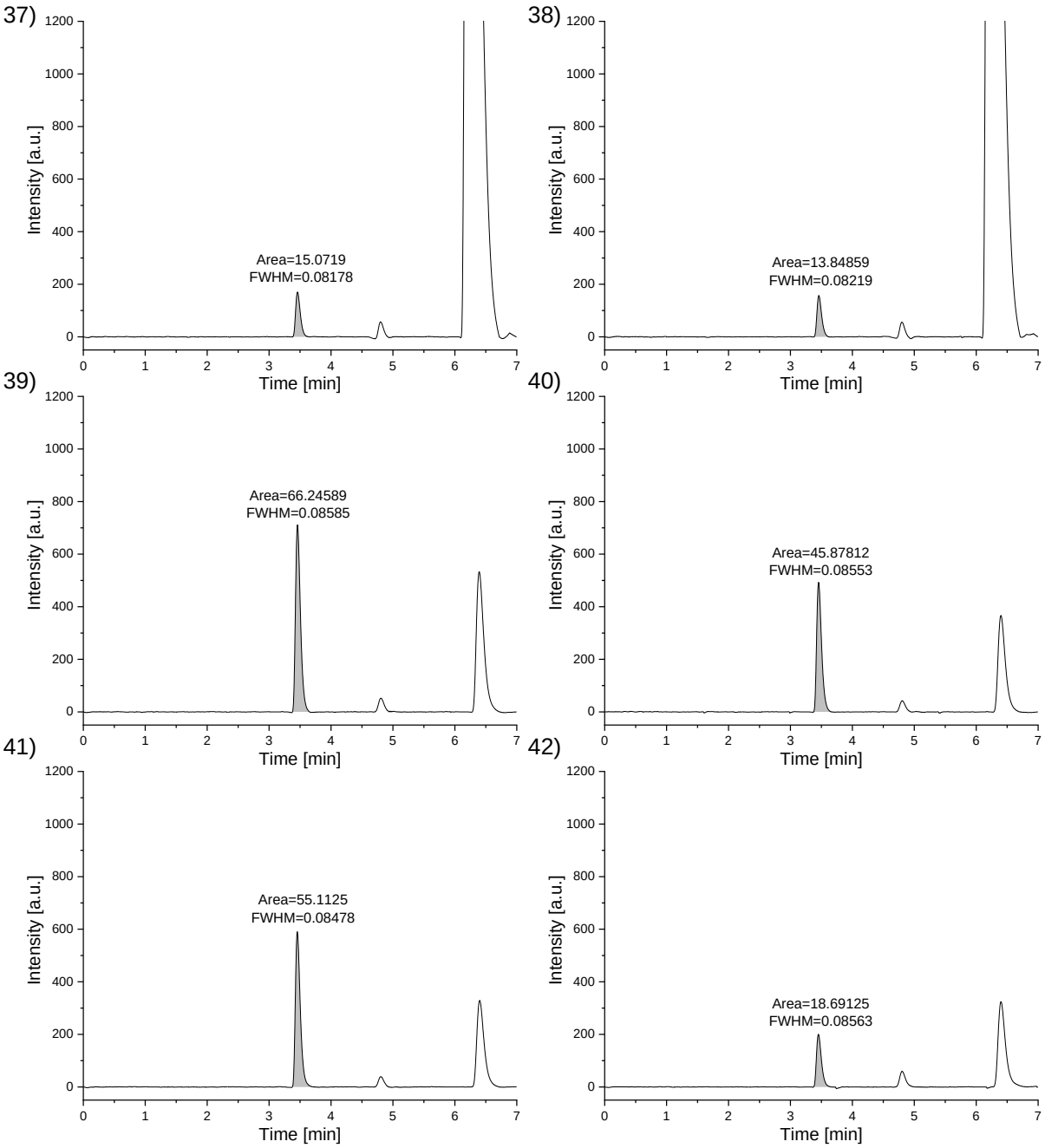


Figure S28: *Gas chromatograms of the stoichiometric investigation of the photocatalytic reactions between **3** and **5**, and **3** and **6**, without **CB8** (see Table S6, entries 37-42).*

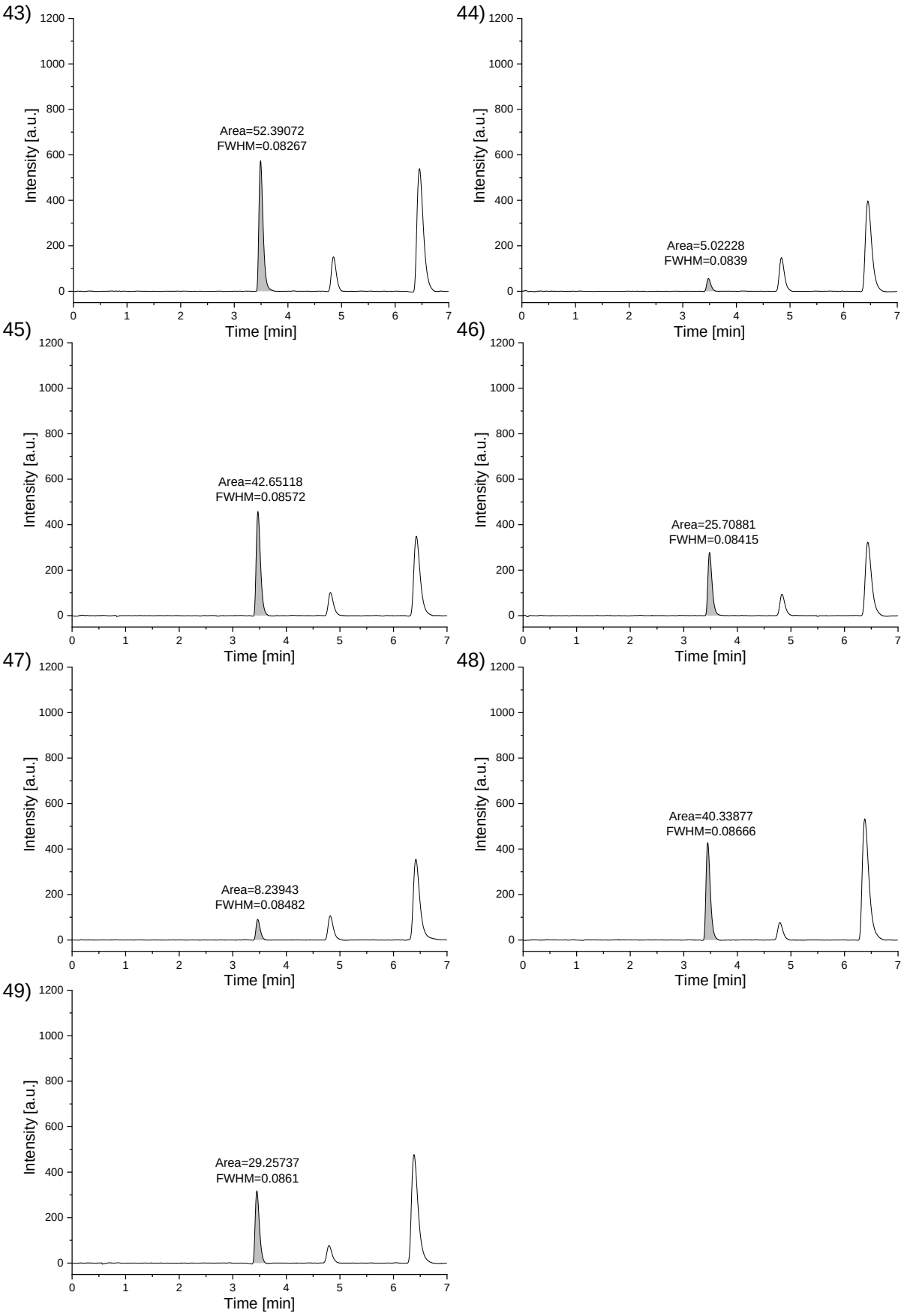


Figure S29: *Gas chromatograms of the stoichiometric investigation of the photocatalytic reactions between* ***3*** *and* ***5****, and* ***3*** *and* ***6****, with* ***CB8*** *(see Table S6, entries 43-49).*

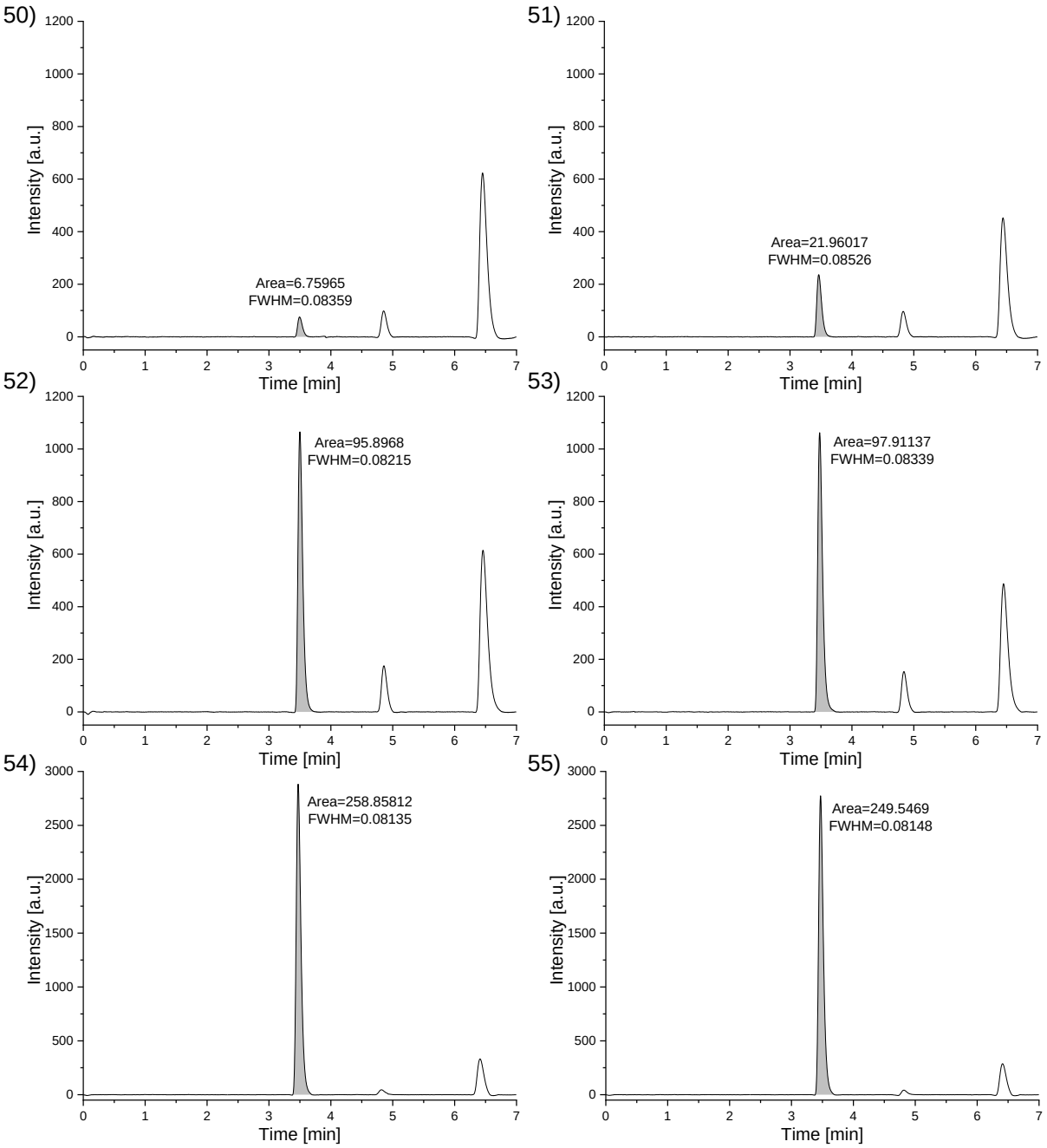


Figure S30: *Gas chromatograms of the stoichiometric investigation of the photocatalytic reactions between* ***3*** *and* ***5****, and* ***3*** *and* ***6****, with* ***CB8*** *(see Table S6, entries 50-55).*

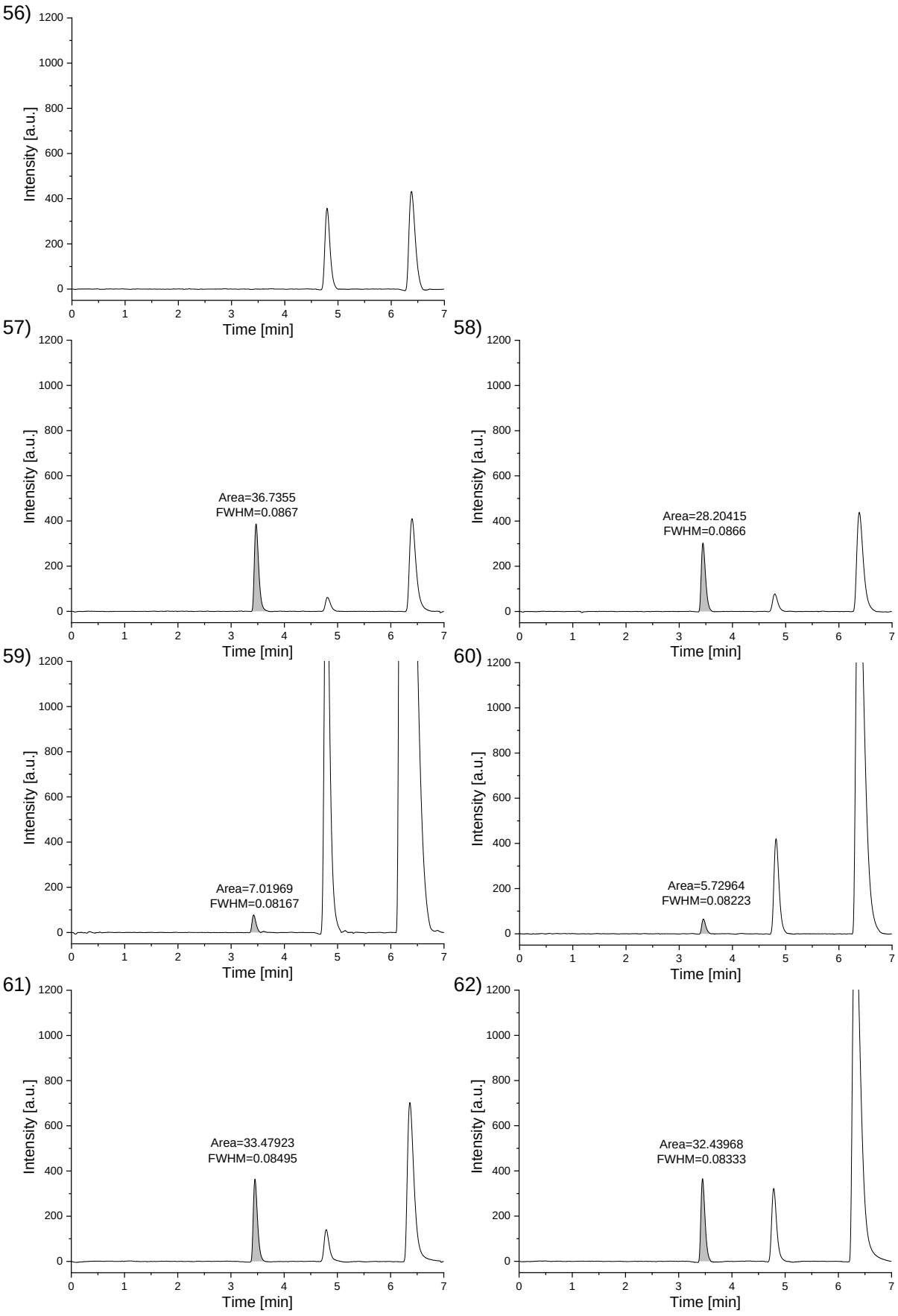


Figure S31: *Gas chromatograms of the mechanistic investigations of the photocatalytic reactions between* ***3*** *and* ***5*** *and the corresponding control reactions. (see Table S7, entries 56-62).*

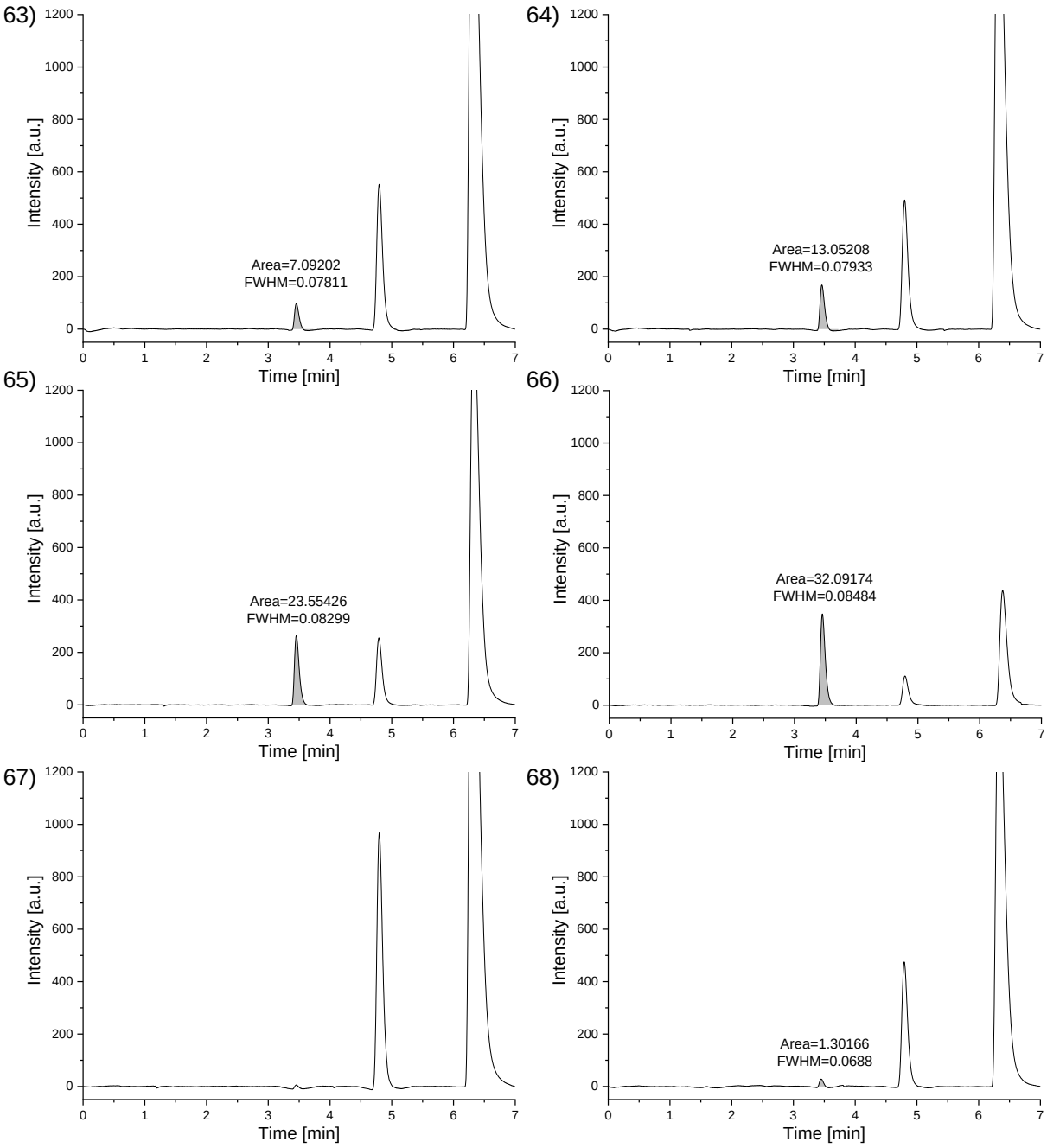


Figure S32: *Gas chromatograms of the mechanistic investigations of the photocatalytic reactions between **3** and **5** and the corresponding control reactions. (see Table S7, entries 63-68).*

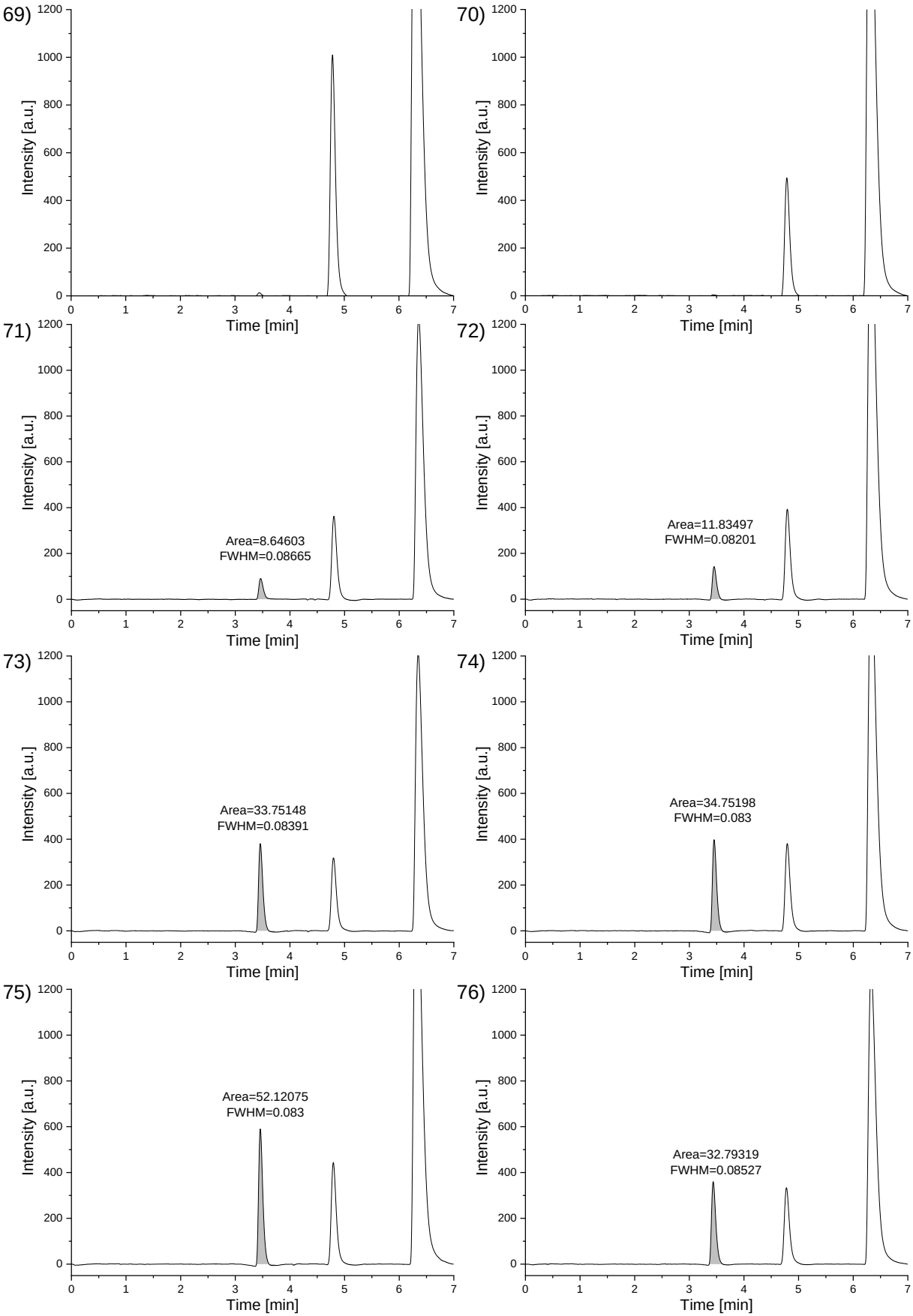


Figure S33: *Gas chromatograms of the studies at different concentrations of triethanolamine for the system* ***3*** + ***5*** + ***CB8*** *(see table S8, entries 69-76).*

5. Photophysical characterization

5.1 UV/Vis-spectra

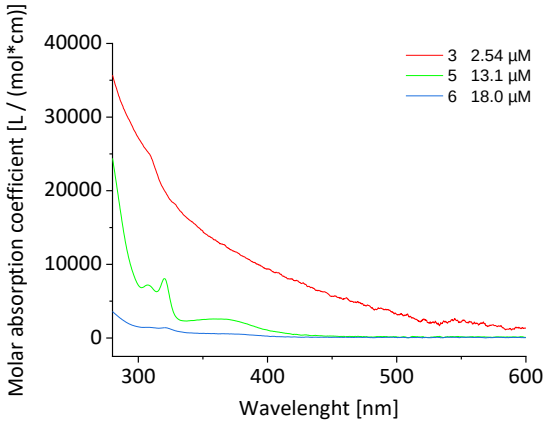


Figure S34: *UV/Vis absorption spectra coefficients of compounds **3**, **5**, and **6** in a mixture of 15:85 triethanolamine : water at room temperature. The different concentrations were chosen as the absorbance of the Pt-complexes **5** and **6** was very noisy at lower concentrations.*

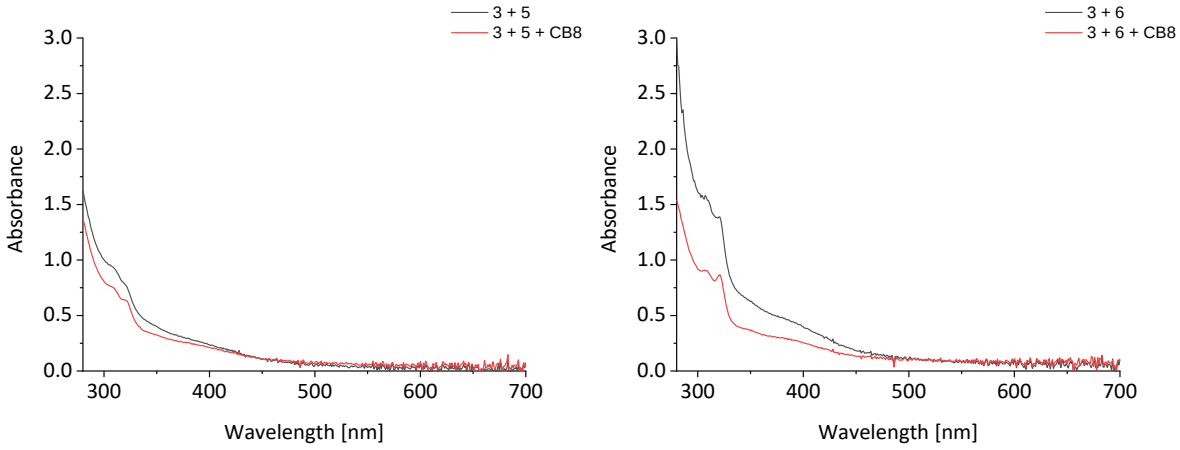


Figure S35: *Absorption spectra of the combinations of **3** + **5** and **3** + **6** in presence (red) and absence (black) of CB8 at concentrations of 0.25 mmol/l for each component in a mixture of 15:85 triethanolamine : water at 60 °C.*

5.2 Fluorescence spectra

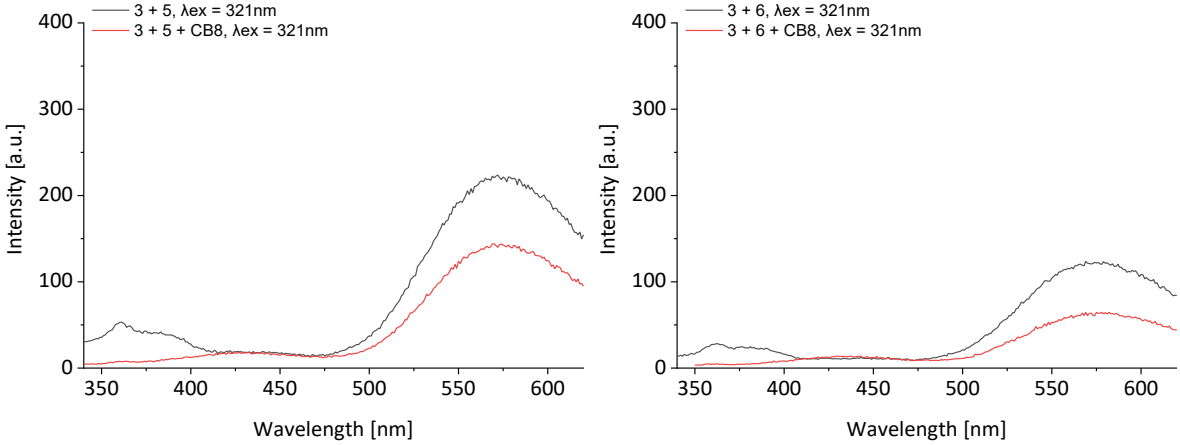


Figure S36: *Fluorescence spectra of the combinations of **3** + **5** and **3** + **6** in presence (red) and absence (black) of CB8 at concentrations of 0.25 mmol/l for each component in a mixture of 15:85 triethanolamine : water. The samples were irradiated at a wavelength of 321 nm at 60 °C.*

6. Calculations

Before employing the Bis-Pt complex **6**, we used available X-ray data to see if a threading into CB8 is possible (Schroedinger Suite, MacroModel 11.8, OPLS force field, solvent: water, the structures of CB8 and of the metal complexes were based on reported X-ray structures of related compounds from the literature[6-8]). The lateral size of the Me_2-bipy-$PtCl_2$ unit amounts to ca. 7 Å[6], while the opening of CB8 (portal diameter) also spans ca. 7 Å[7], so that threading (especially at 60 °C) should be possible. Furthermore, based on the X-ray data we have modelled the pseudorotaxane-structure of the complex of **6** with CB8 with different lateral positions of the CB8 macrocycle, showing that threading of **6** into CB8 should be possible as well as the formation of the heteroternary complex **3** + **6** + CB8.

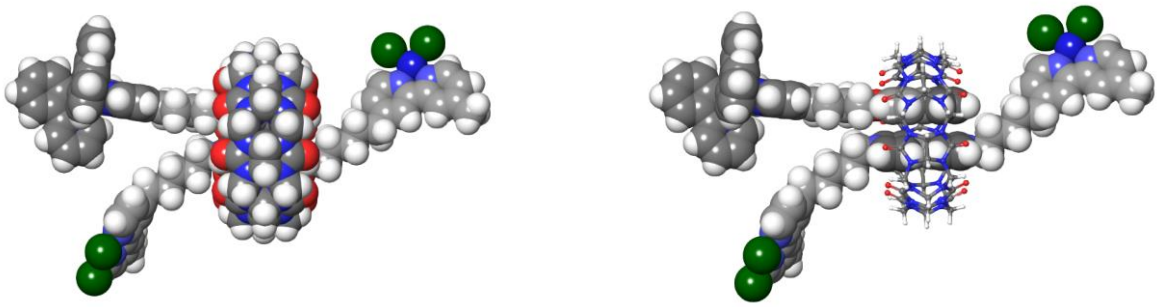


Figure S37: *Calculated structure of the heteroternary complex consisting of **3** + **5** + CB8.*

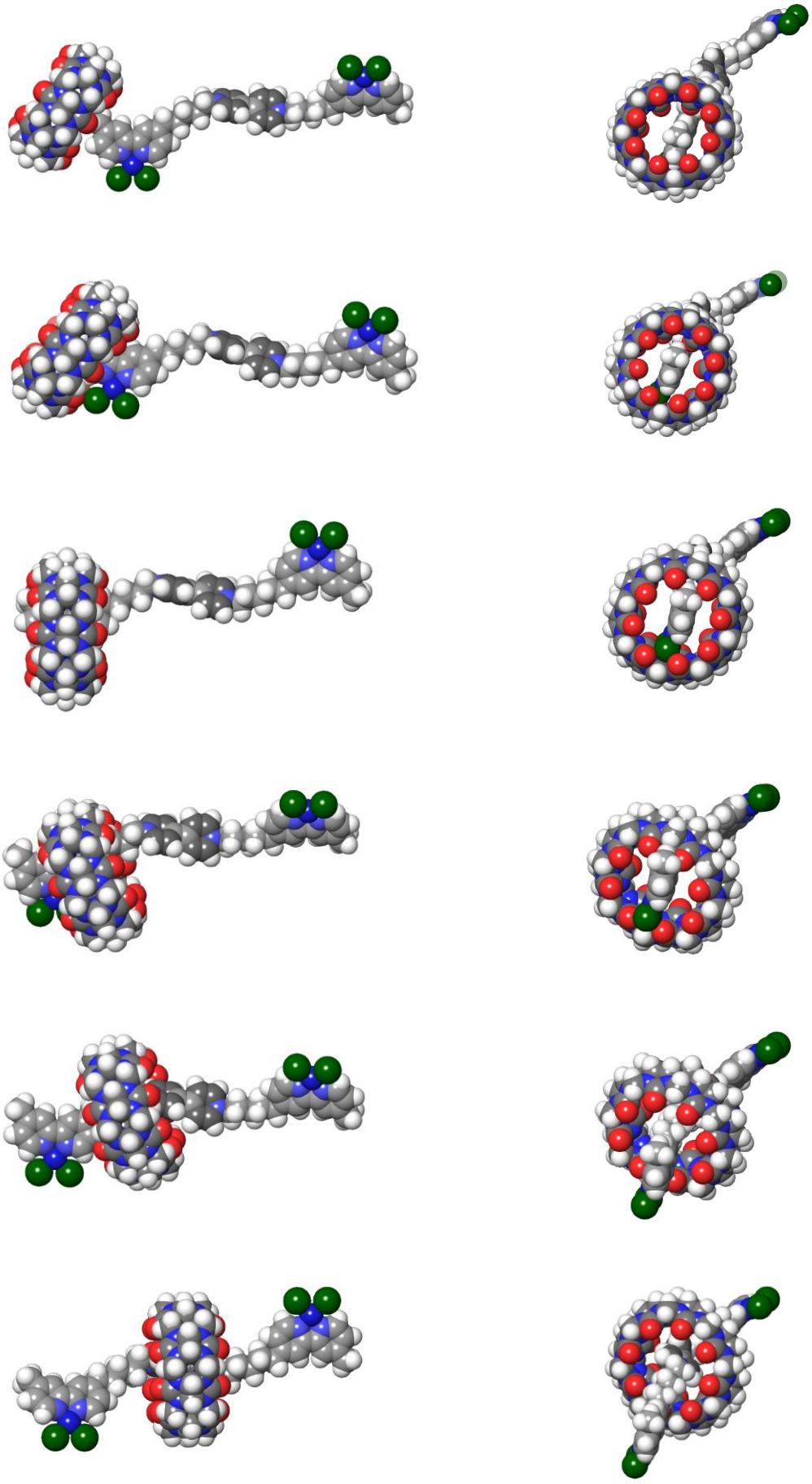


Figure S38: *Calculated structures for the threading of bisplatinated complex* ***6*** *into CB8.*

6. References

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