

Supplementary Material

Pseudo-five-component synthesis of indolone-3-aminopropenylidene merocyanine dimers and their attenuated aggregation-induced emission

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1. General Considerations

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere. By using MBraun system MB-SPS-800 dry acetonitrile was obtained. Triethylamine was suspended with sodium sulfate, filtrated and refluxed under argon atmosphere over sodium. Afterwards it was distilled and stored in a Schlenk flask with potassium hydroxide pallets under argon atmosphere.

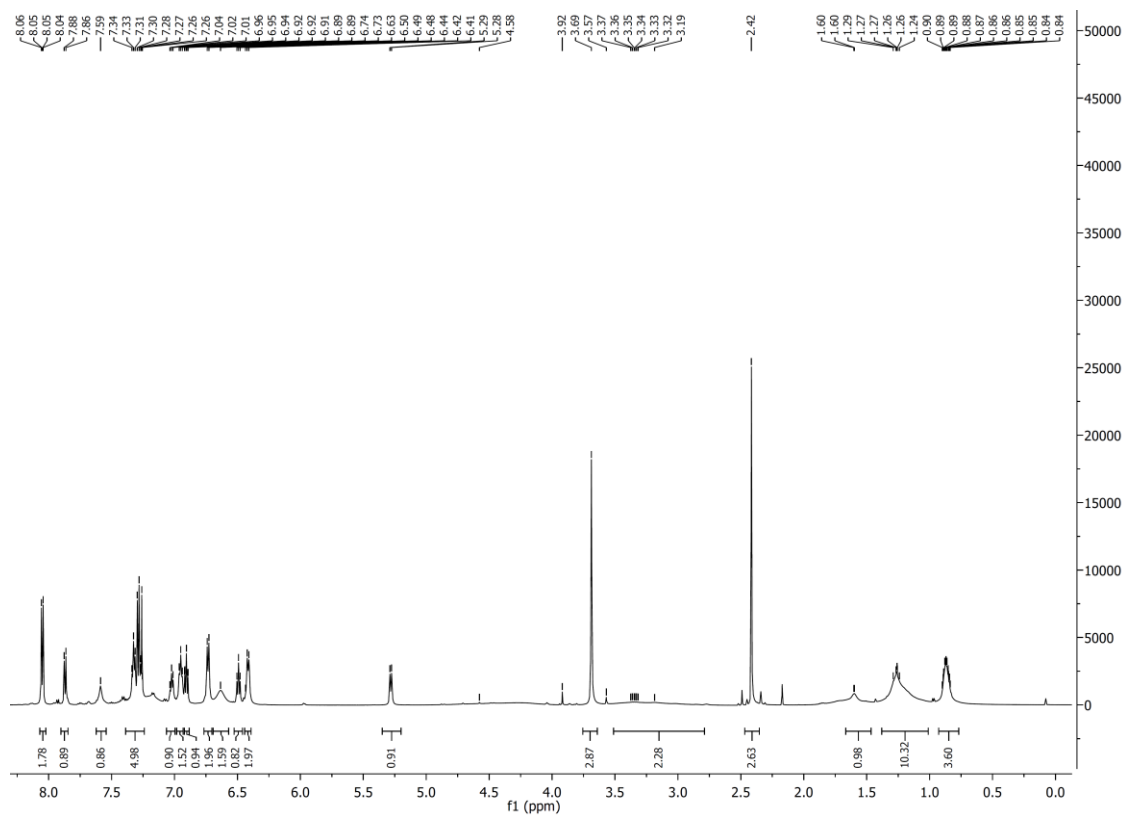
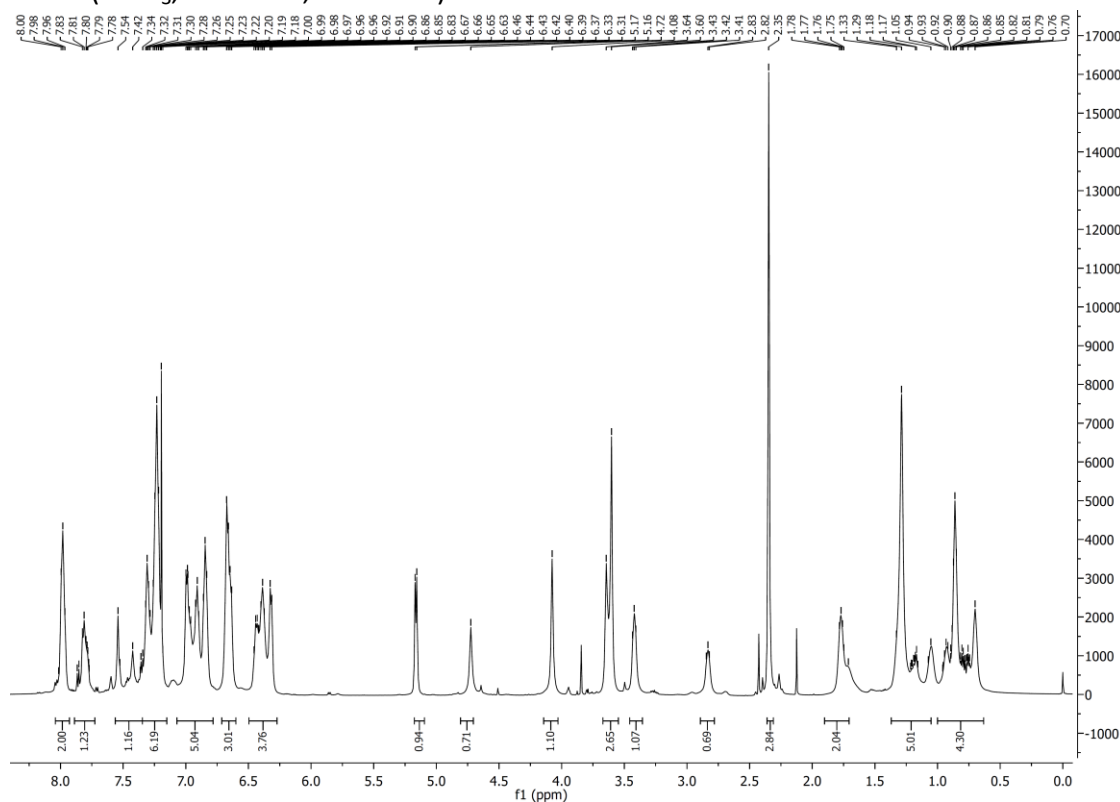
Bis(triphenylphosphane)palladium(0)dichloride, copper iodide, and all precursors were commercially available and were purchased from *Acros Organics*, *ABCR GmbH & Co. KG*, *Alfa Aesar GmbH*, *Sigma-Aldrich Chemie GmbH* and *Merck Serono KGaA*. *N*-(2-Bromophenyl)-3-phenyl-*N*-tosylpropiolamide (**4**),¹ 1-ethynyl-4-methoxybenzene (**5a**),^{2,3} 1-ethynyl-4-methylbenzene (**5c**),⁴ *N*-benzyl hexan-1-amine (**6**),⁵ *N,N'*-(1,4-phenylenebis(methylene))bis(hexan-1-amine) (**7a**),⁶ and *N,N'*-(1,4-phenylenebis(methylene))bis(propan-2-amine) (**7b**)⁶ were synthesized according to literature procedures.

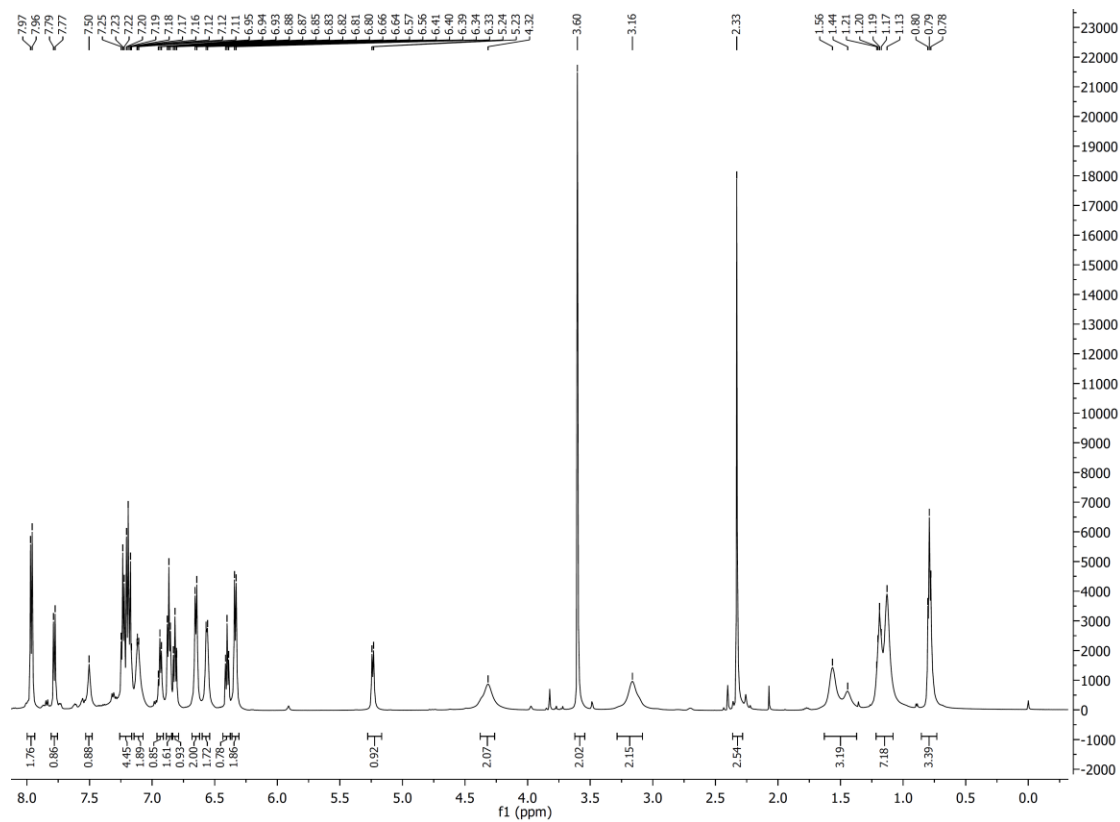
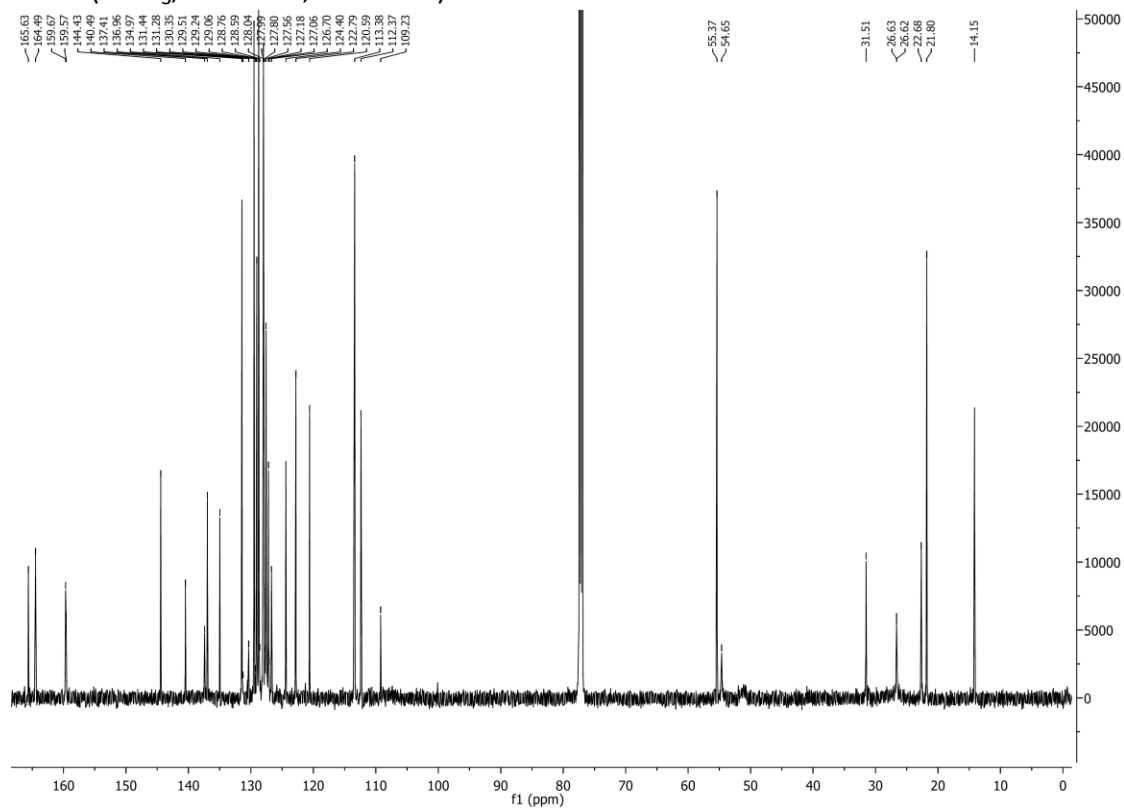
For purification of the reaction mixtures, a flash chromatography was performed on silica gel 60 (0.015-0.040 mm) from *Macherey-Nagel GmbH & Co. KG* under a pressure of 2 bar. Therefore, the crude reaction mixtures were absorbed on Celite® 545 (0.02-0.10 mm) from *Macherey-Nagel GmbH & Co. KG*. For TLC Silica gel 60 F₂₅₄ 6 x 6 cm aluminum sheets by *Macherey-Nagel GmbH & Co. KG* were used. The spots were detected with UV light at 254 and 365 nm.

¹H, ¹³C and 135-DEPT NMR spectra were recorded on Bruker Avance III 600 spectrometer. CDCl₃ was used as a deuterated solvent. For ¹H spectra the residual proton signal of the deuterated solvent was locked as internal standard (CDCl₃, δ_H 7.26, δ_C 77.16). The multiplicities of signals were abbreviated as follows: s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublet of doublets of doublets, dt doublet of triplets, td: triplet of doublets, tt: triplet of triplets, q: quartet, and quint: quintet. The types of carbon atoms were abbreviated as follows: CH₃: primary carbon atom, CH₂: secondary carbon atom, CH: tertiary carbon atom and C_{quat}: quaternary carbon atom. For determination 135-DEPT NMR spectra was used. For structure elucidation in some cases ROESY NMR spectra were used.

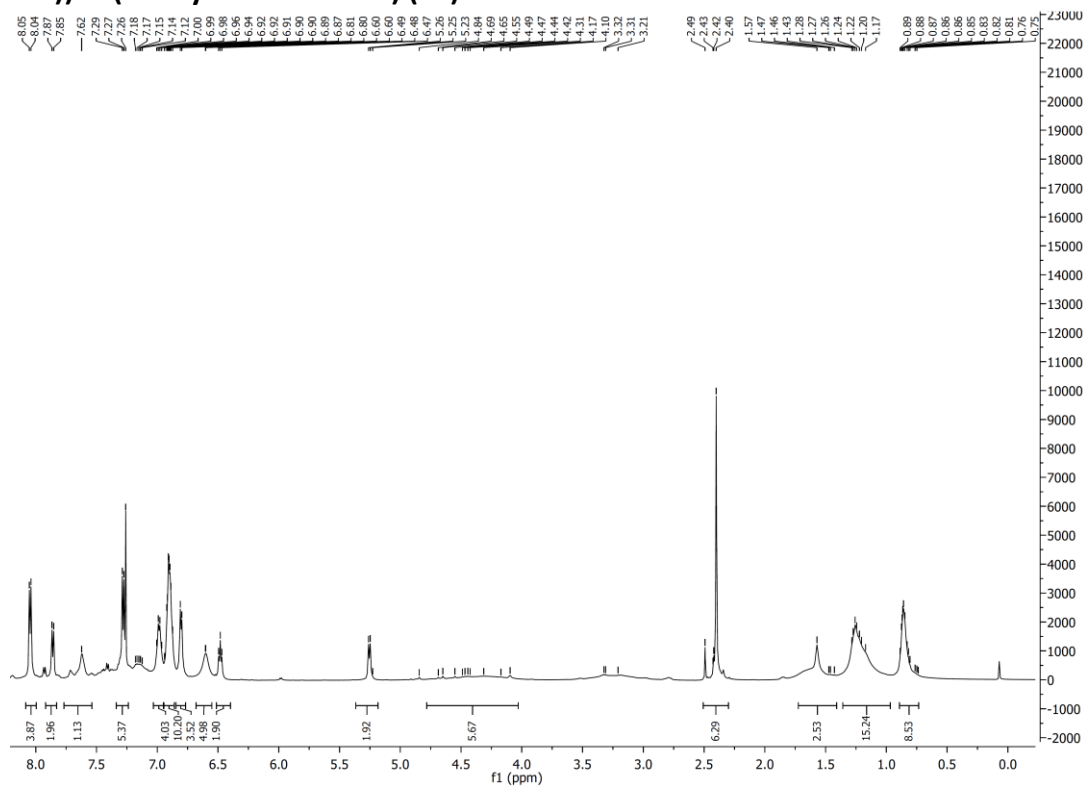
Mass spectra were measured on Finnigan MAT 8200 (EI), Finnigan LCQ Deca (Thermo Quest) (ESI) or Bruker-Ultraflex I (MALDI-TOF). High resolution mass spectra were recorded on UHR-QTOF maXis 4G Bruker Daltronics. All Peaks with an intensity of >10% corresponding to the base peak were stated. IR spectra were measured on IRAffinity-1 by *Shimadzu*. The intensity of signals is abbreviated as follows: vs: very strong, s: strong, m: medium and w: weak. The melting points (uncorrected) were measured on Rechart-Jung Thermovar. Elementary analysis was carried out in the micro analytical laboratory of Institut für Pharmazeutische und Medizinische Chemie der Heinrich-Heine-Universität, Düsseldorf.

Absorption spectra were recorded with a UV/Vis/NIR spectrometer Lambda 19 from Perkin Elmer and emission spectra with an F-7000 fluorescence spectrophotometer from Hitachi at the Institut für Organische Chemie und Makromolekulare Chemie der Heinrich-Heine-Universität Düsseldorf using the emission correction curve provided by the instrument manufacturer. The dichloromethane solvent used corresponded to the HPLC purity. All solution spectra were recorded with dyes dissolved in spectroscopic grade solvents at 298 K using 1 cm-quartz cuvettes from Hellma GmbH. The molar extinction coefficients of dye solutions of known dye concentration were determined by five point regression line.

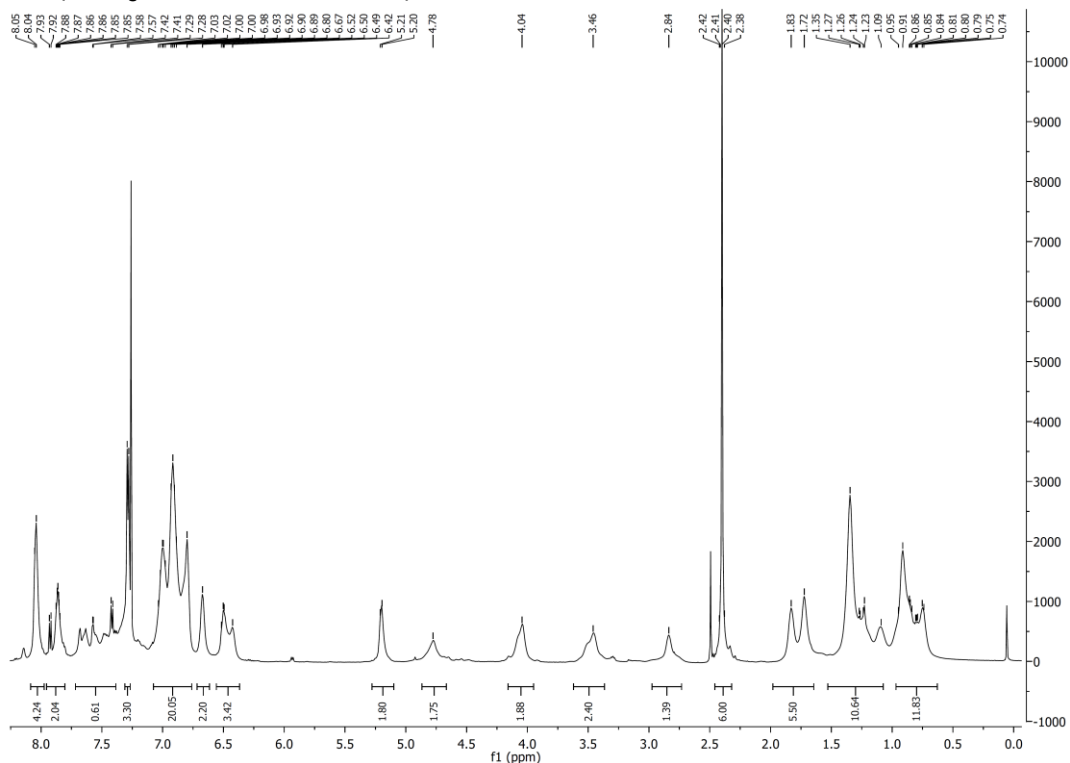
2. ^1H and ^{13}C NMR Spectra of Compounds 1a and 82.1 (*E*)-3-((*E*)-3-(Benzyl(hexyl)amino)-3-(4-methoxyphenyl)-1-phenylallylidene)-1-tosylindolin-2-one (1a) ^1H NMR spectrum (CDCl₃, 600 MHz, *T* = 263 K) ^1H NMR spectrum (CDCl₃, 600 MHz, *T* = 263 K)

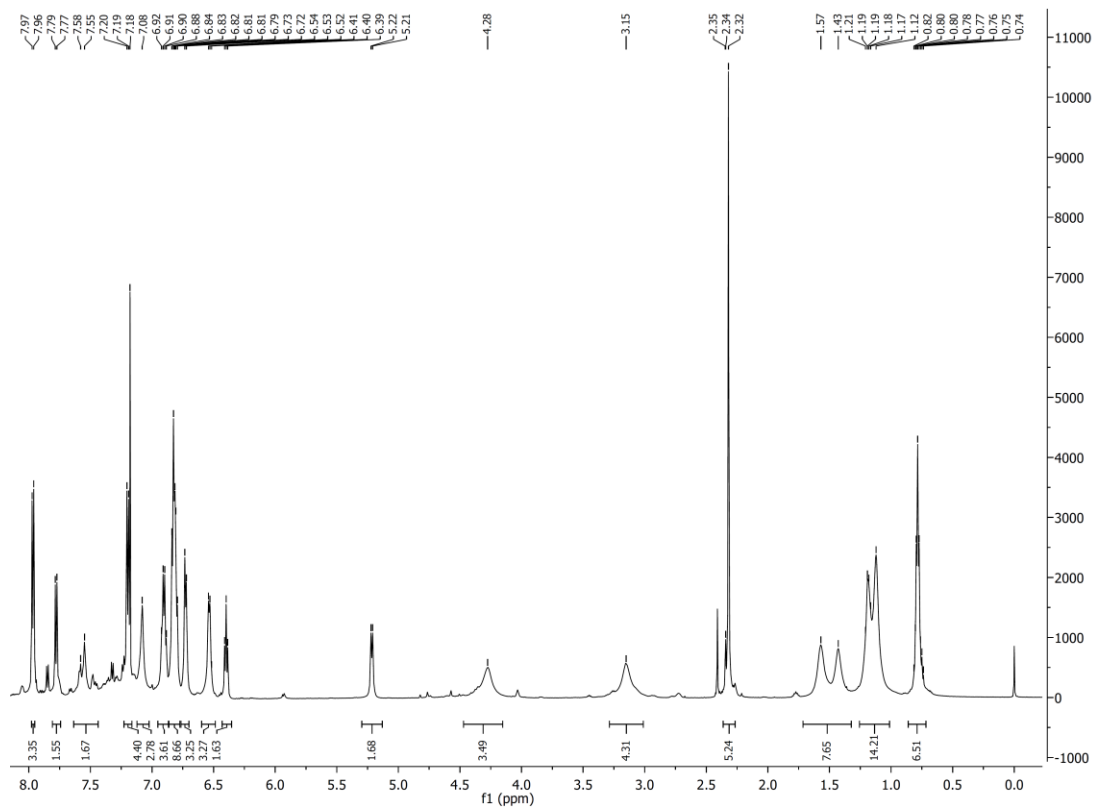
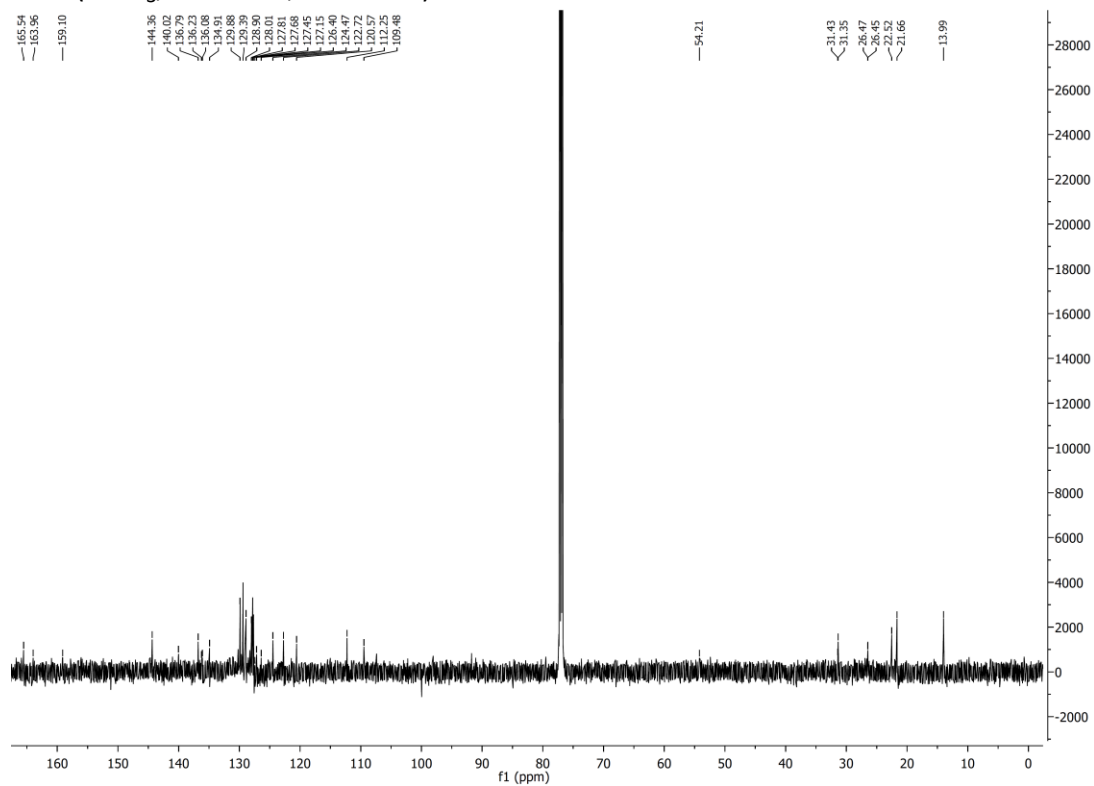
¹H NMR spectrum (CDCl₃, 600 MHz, T = 323 K)¹³C NMR spectrum (CDCl₃, 150 MHz, T = 293 K)

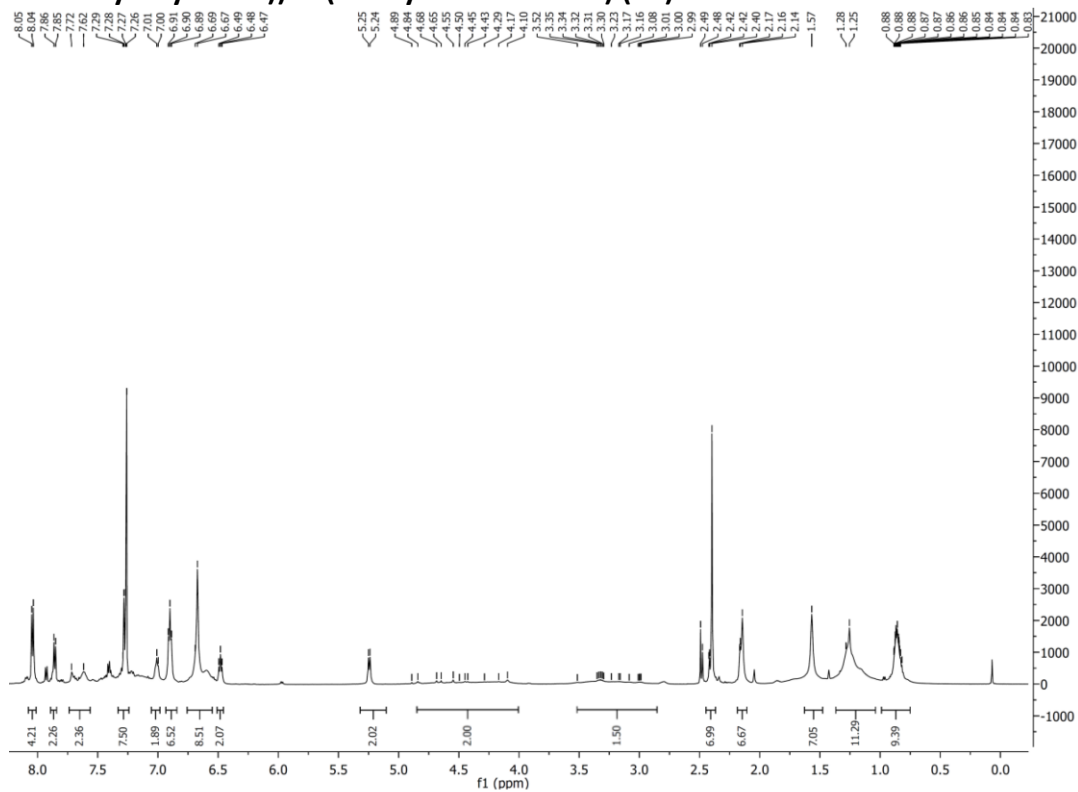
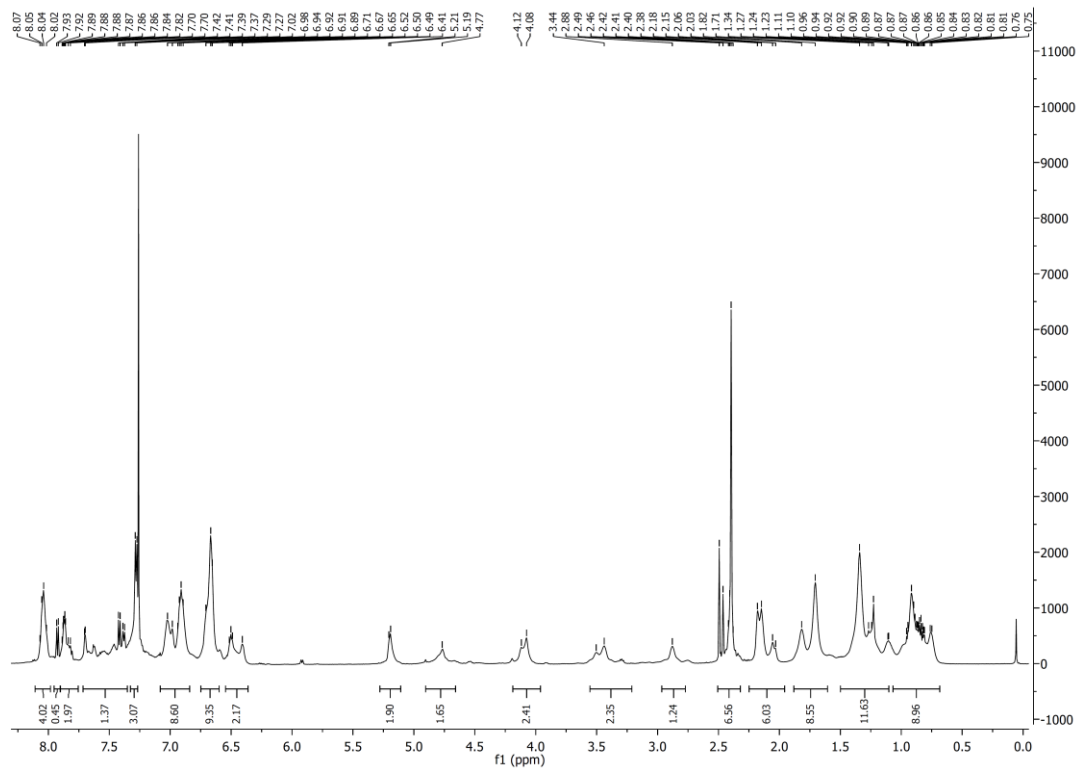
2.2. ((3*E*,3'*E*)-3,3'-((2*E*,2'*E*)-((1,4-Phenylenebis(methylene))bis(hexylazanediy))bis(1,3-diphenylprop-2-en-3-yl-1-ylidene))bis(1-tosylindolin-2-one) (8a)

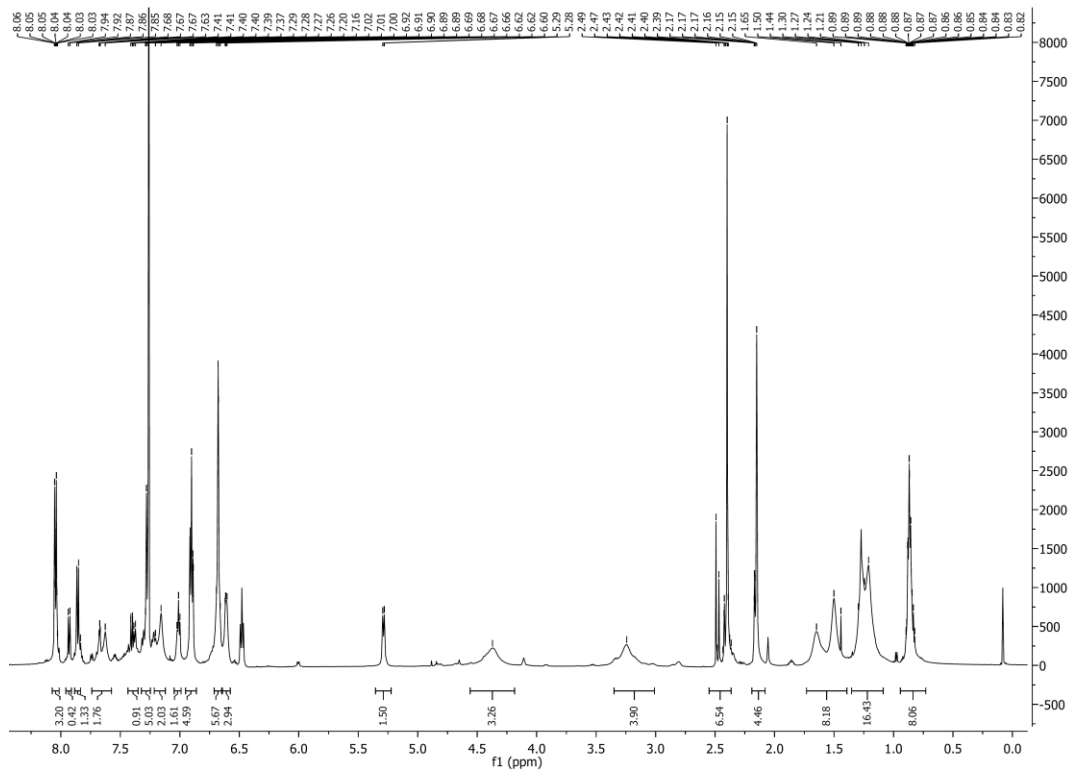
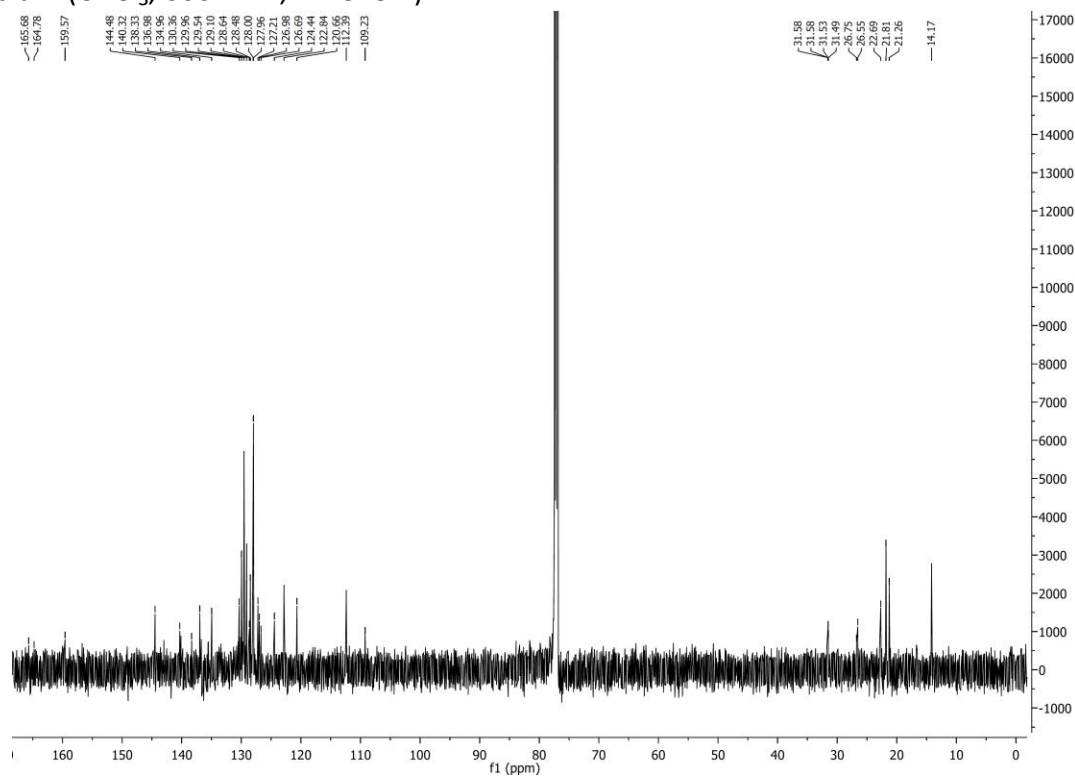


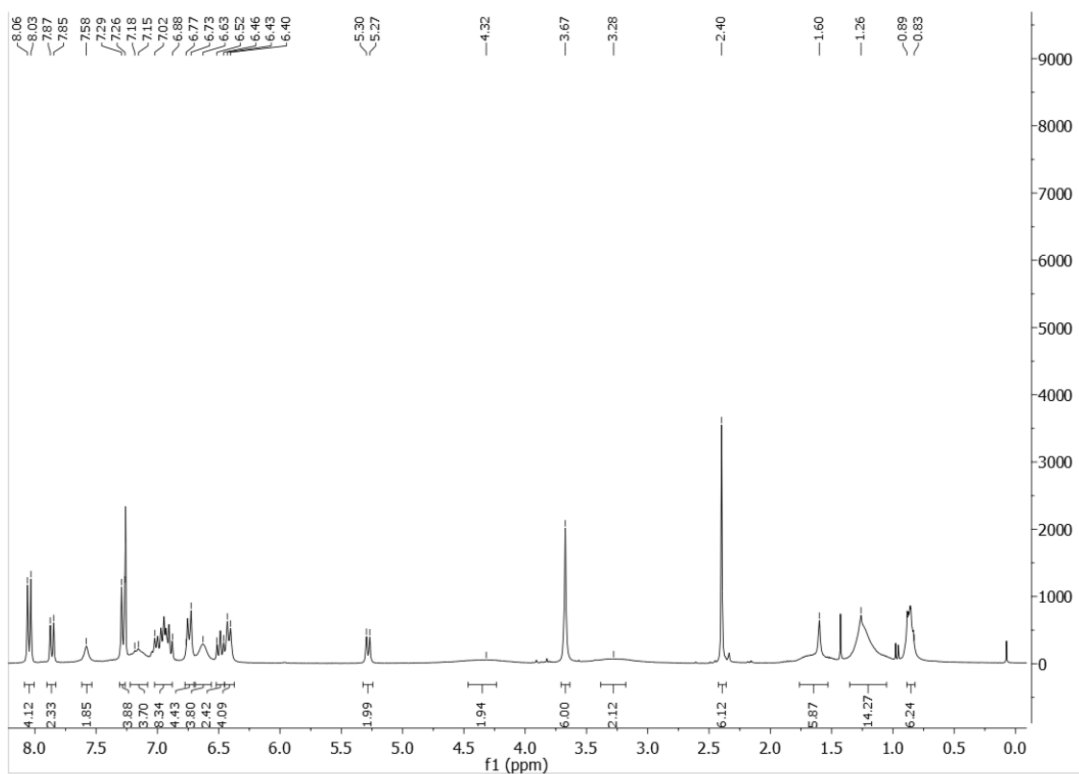
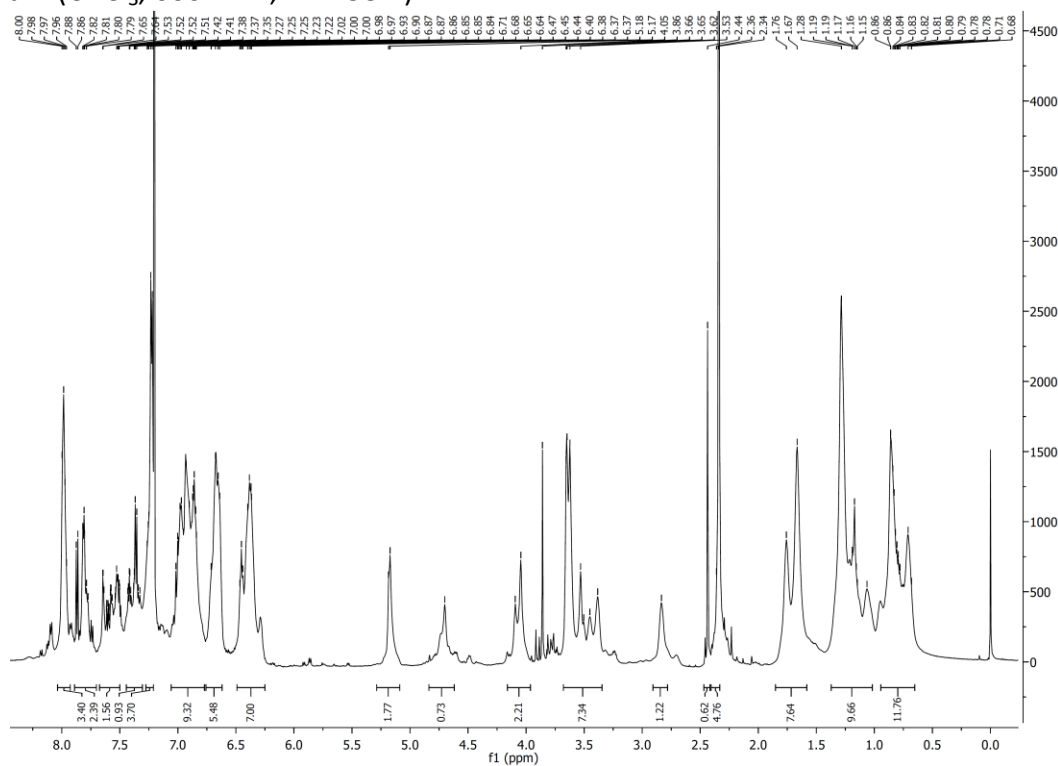
¹H NMR spectrum (CDCl₃, 600 MHz, *T* = 263 K)

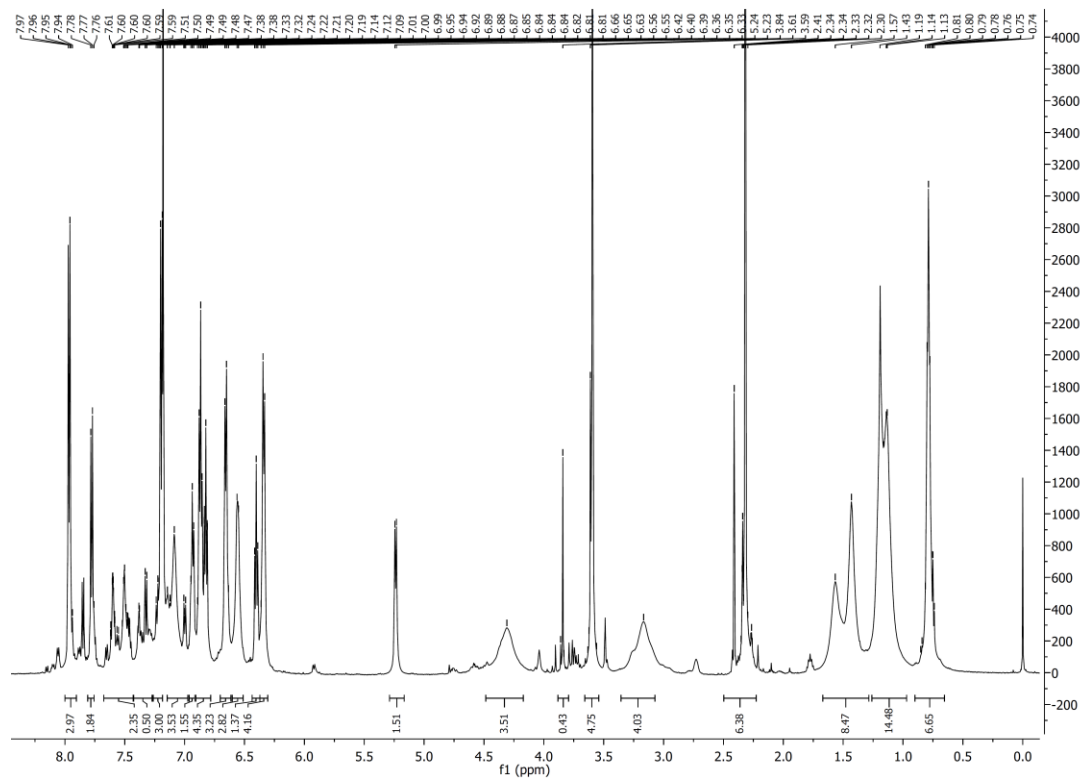
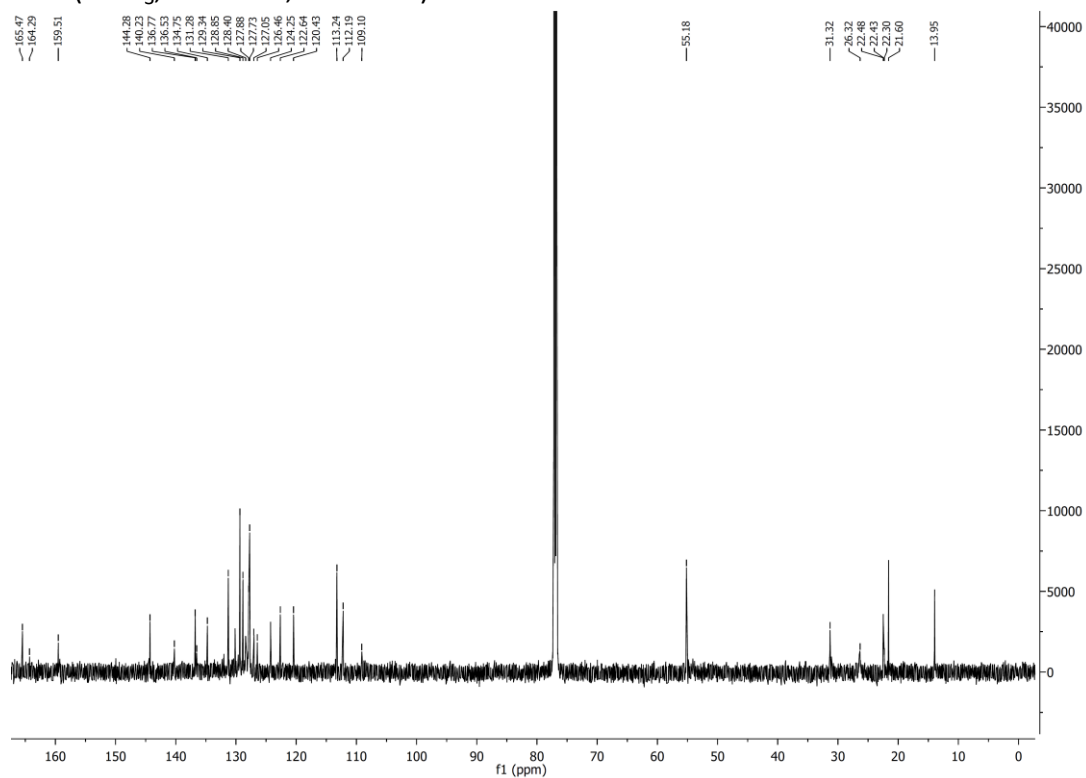


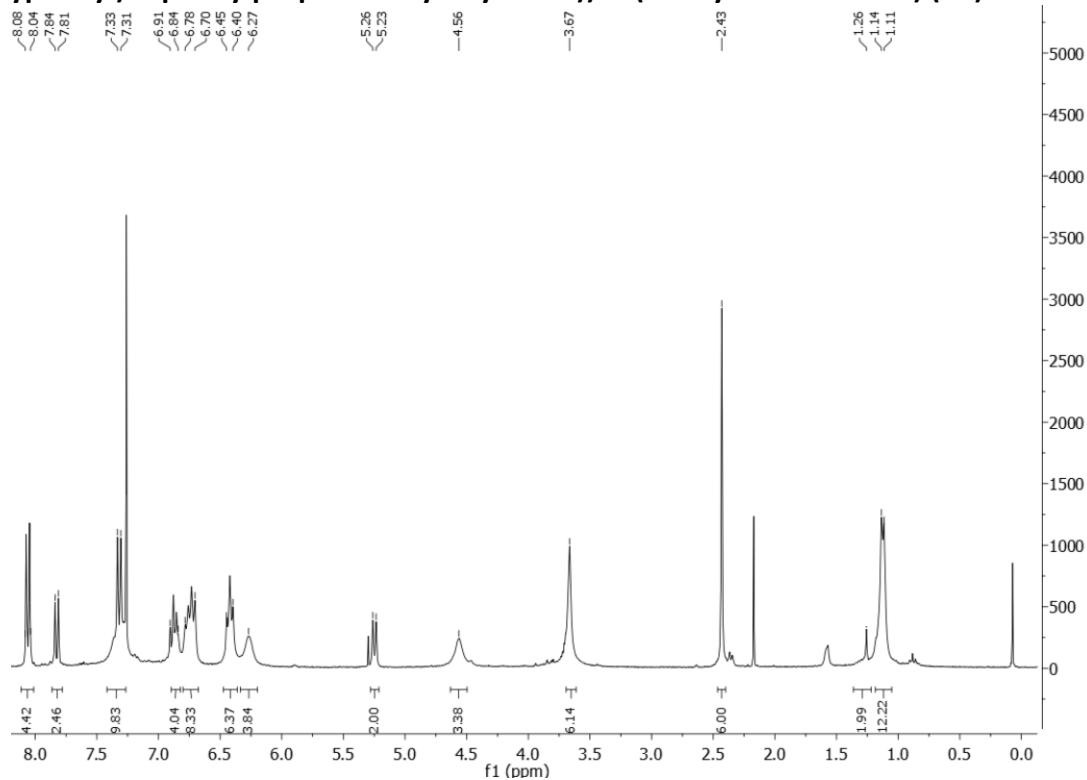
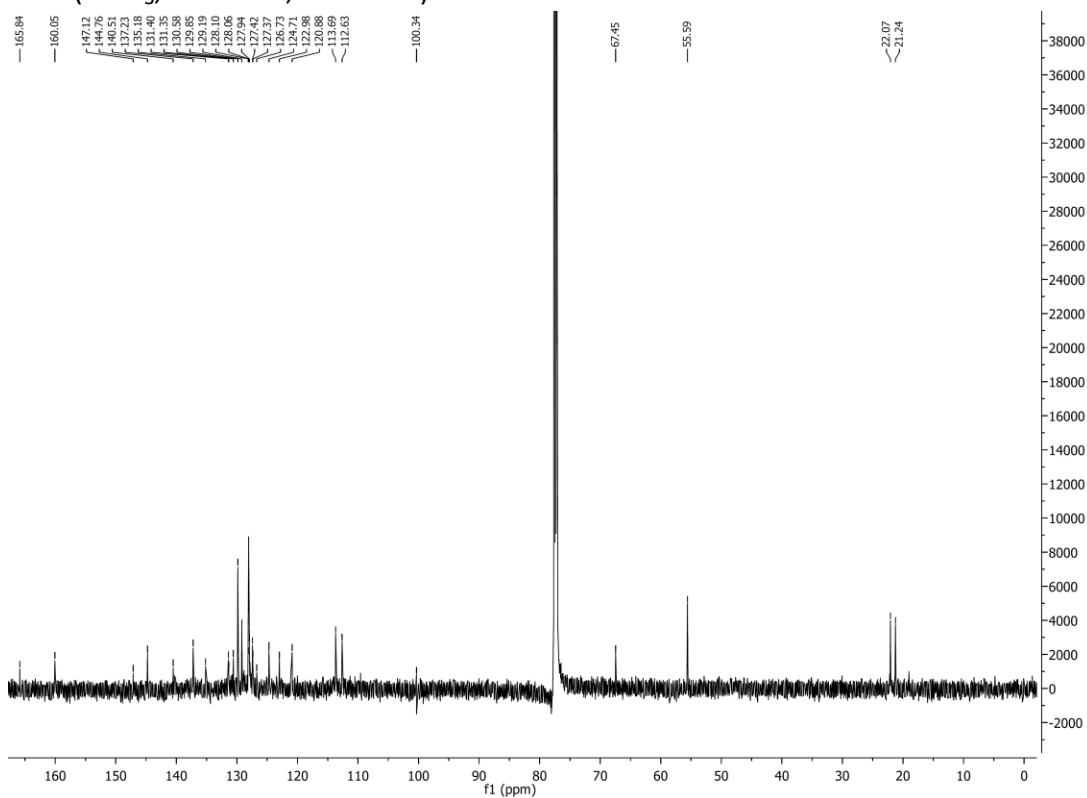
¹H NMR spectrum (CDCl₃, 600 MHz, T = 323 K)¹³C NMR spectrum (CDCl₃, 150 MHz, T = 293 K)

2.3. (3*E*,3'*E*)-3,3'-((2*E*,2'*E*)-((1,4-Phenylenebis(methylene))bis(hexylazanediyI))bis(1-phenyl-3-(p-tolyl)prop-2-en-3-yl-1-ylidene))bis(1-tosylindolin-2-one) (8b**)**¹H NMR spectrum (CDCl₃, 600 MHz, T = 293 K)¹H NMR spectrum (CDCl₃, 600 MHz, T = 263 K)

¹H NMR spectrum (CDCl₃, 600 MHz, T = 323 K)¹³C NMR spectrum (CDCl₃, 150 MHz, T = 293 K)

2.4. (3*E*,3'*E*)-3,3'-((2*E*,2'*E*)-((1,4-Phenylenebis(methylene))bis(hexylazanediy))bis(3-(4-methoxyphenyl)-1-phenylprop-2-en-3-yl-1-ylidene))bis(1-tosylindolin-2-one) (8c)¹H NMR spectrum (CDCl₃, 600 MHz, T = 293 K)¹H NMR spectrum (CDCl₃, 600 MHz, T = 263 K)

¹H NMR spectrum (CDCl₃, 600 MHz, T = 323 K)¹³C NMR spectrum (CDCl₃, 150 MHz, T = 293 K)

2.5. (3*E*,3'*E*)-3,3'-((2*E*,2'*E*)-((1,4-Phenylenebis(methylene))bis(isopropylazanediy))-bis(3-(4-methoxyphenyl)-1-phenylprop-2-en-3-yl-1-ylidene))bis(1-tosylindolin-2-one) (8d)¹H NMR spectrum (CDCl₃, 600 MHz, T = 293 K)¹³C NMR spectrum (CDCl₃, 150 MHz, T = 293 K)

3. References

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5. Stevens, J. R.; Plieger, P. G. *Dalton Trans.* **2011**, *40*, 12235–12241. DOI: 10.1039/c1dt10808e
6. Synthesized in analogy to ref 5.