

Electronic Supplementary Information

to

Magnifying the ESIPT process in tris(salicylideneanilines) by steric effect - a pathway to the molecules with the panchromatic fluorescence

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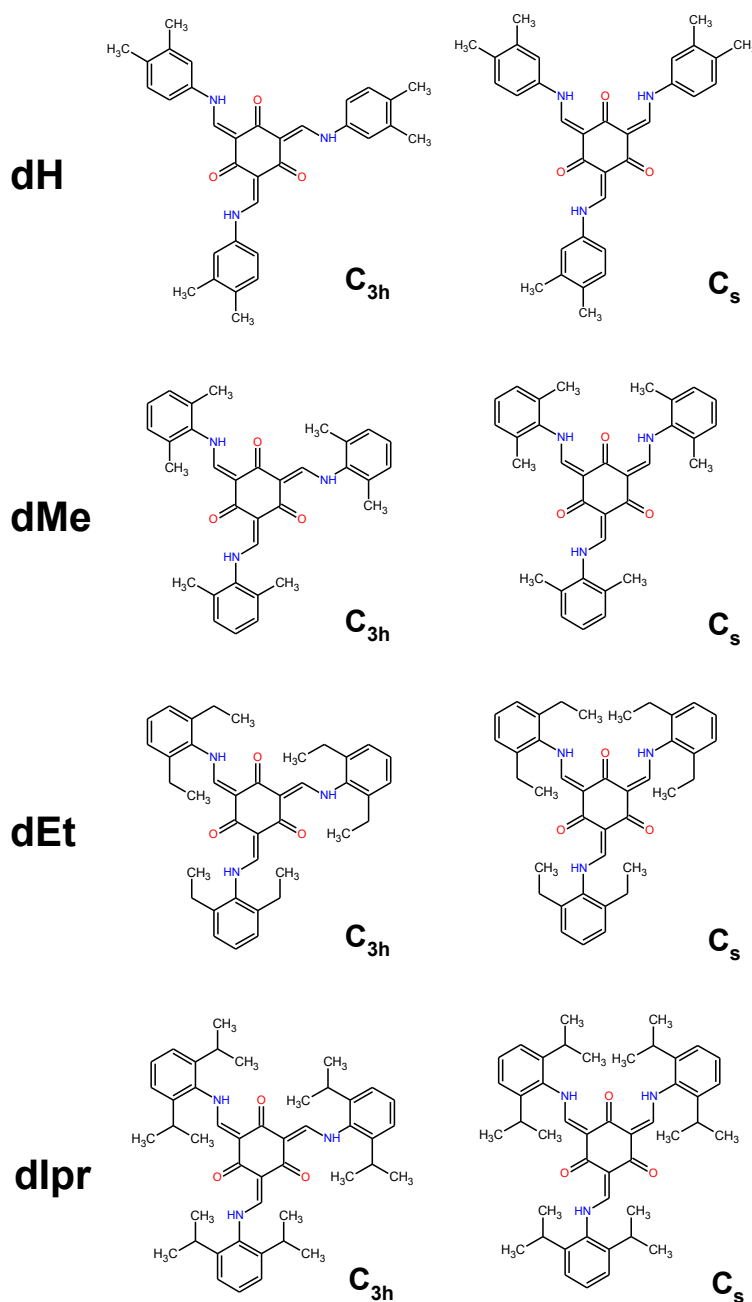


Figure S1. Full structures of the studied TSANs (two diastereoisomers)

Theoretical results

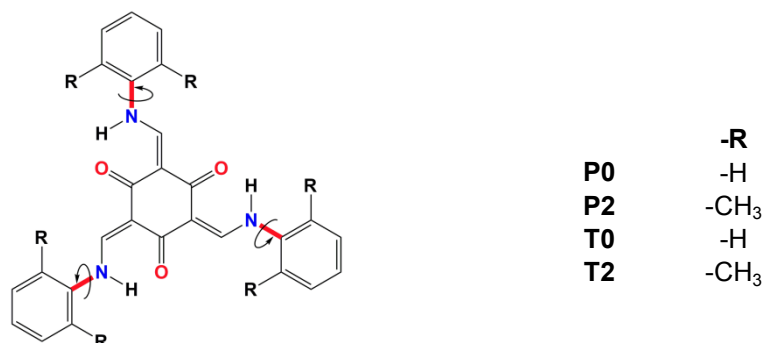


Figure S2. Planar molecular structures for prototype molecules with C_{3h} symmetry used for theoretical exploration. Twisted molecules have the aniline ring perpendicular to the salicylidene core through the rotation along bonds marked in red by 90 degrees.

Table S1. Vertical transition energy (ΔE), oscillator strength (f), dipole moment (μ), and leading electronic configurations of planar and perpendicular *tris*(*N*-salicylideneanilines) computed with ADC(2)/cc-pVDZ method at the MP2/cc-pVDZ equilibrium geometry of the ground state.

	State	$\Delta E/eV$	f	$\mu/Debye$	el. conf.
P0	S_0	0.00	-	0.00	$(33a'')^2$
	${}^1\pi\pi^*$	3.33	0.98	1.76	0.82(17a''-19a'')
	${}^1\pi\pi^*$	3.33	0.98	1.77	0.82(18a''-19a'')
	${}^1n\pi^*$	3.90	0.00	0.00	0.61(16a''-19a'')
P2	S_0	0.01	-		$(24a'')^2$
	${}^1\pi\pi^*$	3.26	0.96	1.85	0.81(23a''-25a'')
	${}^1\pi\pi^*$	3.26	0.96	1.85	0.86(23a''-25a'')
	${}^1n\pi^*$	3.57	0.00	0.00	0.86(114a'-25a'')
T0	S_0	0.52	-	0.00	$(33a'')^2$
	${}^1\pi\pi^*$	3.94	0.70	1.00	0.90(33a''-34a'')
	${}^1\pi\pi^*$	3.94	0.70	1.00	0.90(32a''-34a'')
	${}^1n\pi^*$	4.36	0.00	0.00	0.65(28a'-34a'')
T2	S_0	0.00	-	0.00	$(45a'')^2$
	${}^1n\pi^*$	3.67	0.00	0.00	0.92(44a''-46a'')
	${}^1\pi\pi^*$	3.88	0.68	1.15	0.92(45a''-46a'')
	${}^1n\pi^*$	3.88	0.68	1.15	0.83(90a'-46a'')

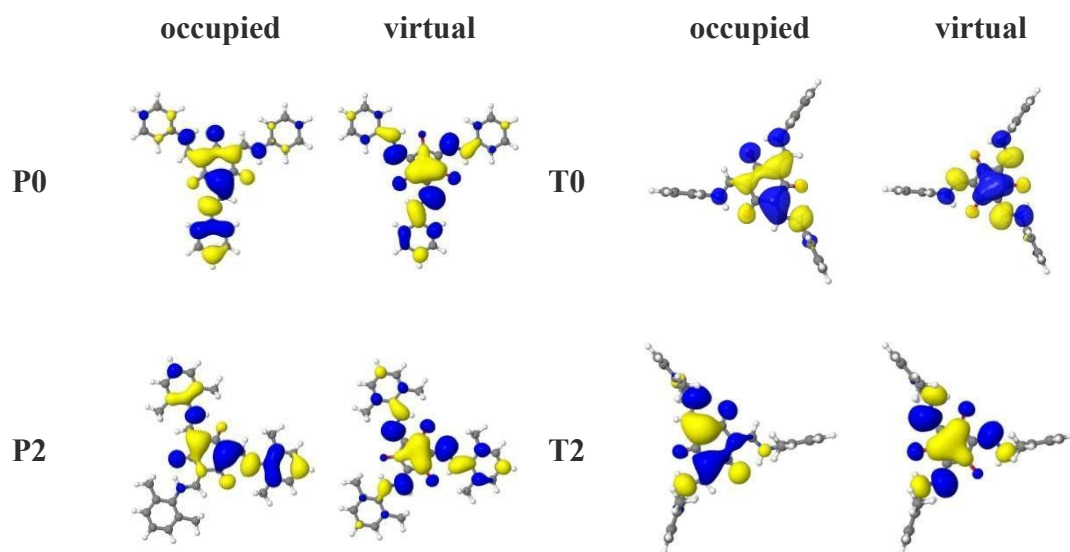


Figure S3. Natural transition orbitals computed for the first vertical electronic transition at MP2/ADC(2)/cc-pVDZ level of theory.

Table S2. Vertical transition energy (ΔE), oscillator strength (f) and dipole moments ($\mu(S_I)$ and $\mu(S_0)$), computed with ADC(2)/cc-pVDZ method at the equilibrium geometry of the S_I state of TSANs.

		$\Delta E/\text{eV}$	f	$\mu(S_I)/\text{Debye}$	$\mu(S_0)/\text{Debye}$
P0	<i>kkk</i>	3.12	1.15	1.44	0.00
	<i>kke</i>	2.25	0.53	6.57	6.41
P2	<i>kkk</i>	2.89	0.89	1.95	0.89
	<i>kke</i>	2.25	0.53	6.57	6.48
T0	<i>kkk</i>	3.38	0.52	1.30	0.31
	<i>kke</i>	2.23	0.52	6.97	6.12
T2	<i>kkk</i>	3.38	0.54	1.14	0.17
	<i>kke</i>	2.62	0.30	4.97	6.56

Experimental results

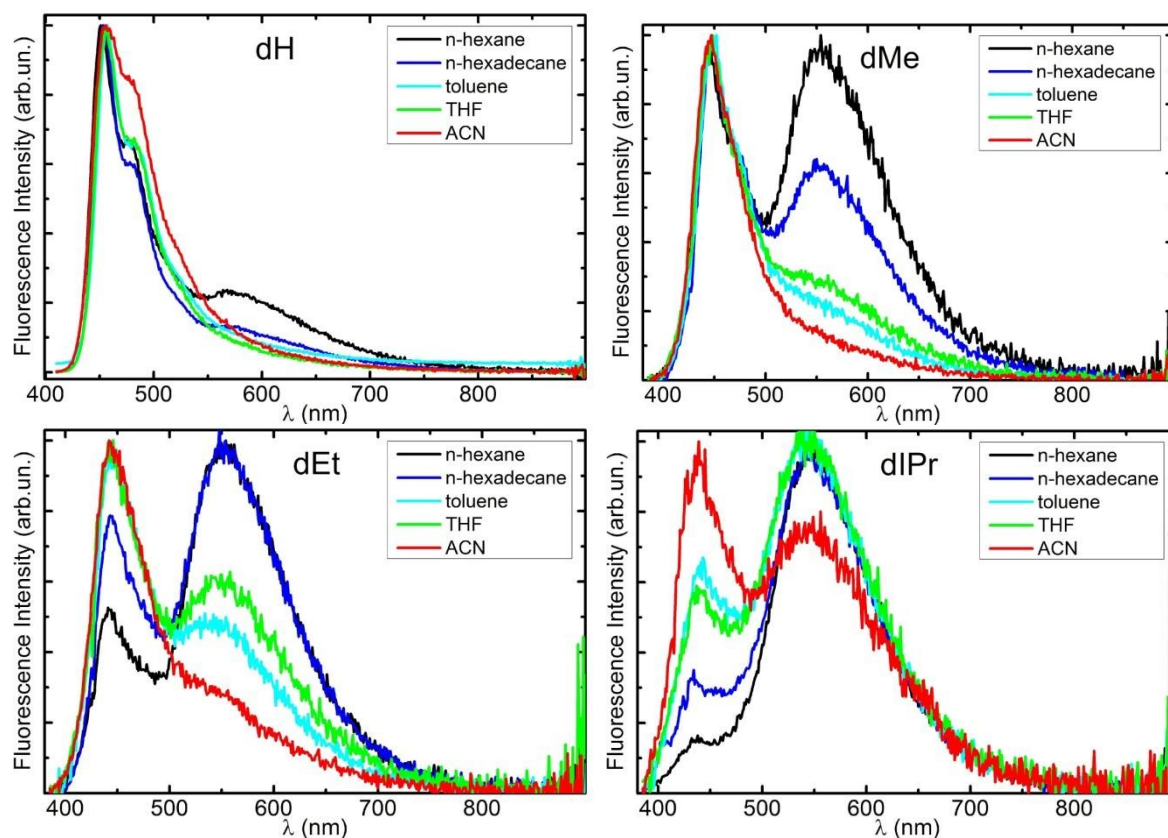


Figure S4. Fluorescence spectra of **dH**, **dMe**, **dEt** and **dIPr** measured in *n*-hexane, *n*-hexadecane, toluene, THF and ACN solutions.

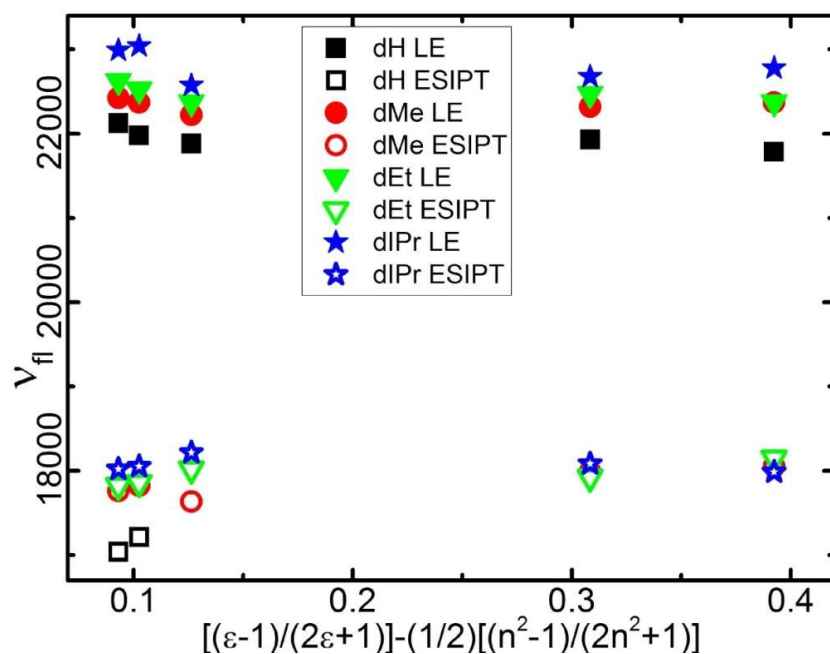


Figure S5. Solvatochromism of the LE and ESIPT fluorescence bands for **dH**, **dMe**, **dEt** and **dIPr** compounds expressed as wavenumber of the maximum of emission band, ν_{fl} , versus modified Lippert-Mataga polarity parameter $f(\epsilon, n) = [(\epsilon - 1)/(2\epsilon + 1)] - \frac{1}{2}[(n^2 - 1)/(2n^2 + 1)]$.

Table S3. Parameters of two exponential decays obtained from deconvolution of fluorescence decays for **dH**, **dMe**, **dEt** and **dIPr** in five solvents. Wavelength of decay observation, τ_{obs} , is expressed in nanometers and decay times, τ_1 and τ_2 , in picoseconds. Excitation at 390 nm.

Molecule	Solvent	Flu. band	$\lambda_{\text{obs}}/\text{nm}$	τ_1/ps	τ_2/ps	A_1	A_2
dH	<i>n</i> -hexane	LE	452	25	263	4.6	17.7
		ESIPT	600	31	251	-21	20.73
	<i>n</i> -hexadecane	LE	454	292	523	12.3	2.64
		ESIPT	600	312	614	-16	15.56
	Toluene	LE	457	288			
	THF	LE	456	198			
ACN	LE	456	164				
dMe	<i>n</i> -hexane	LE	444	28	163	16	19.3
		ESIPT	550	29	160	-38	37.8
	<i>n</i> -hexadecane	LE	448	23	170	10.4	20
		ESIPT	555	20	165	-31	31.36
	Toluene	LE	450	42	82	5.2	11.9
		ESIPT	600	37	73	-39	39.4
THF	LE	450	73				
ACN	LE	450	46				
dEt	<i>n</i> -hexane	LE	430	14	226	40.3	10.92
		ESIPT	600	31	231	-25	26.8
	<i>n</i> -hexadecane	LE	481	36	233	16.7	14.51
		ESIPT	555	25	236	-42	42.19
	Toluene	LE	450	16	98	33.6	31.6
		ESIPT	600	20.5	101	-28	28.6
	THF	LE	450	21	113	9.9	7.13
		ESIPT	582	27	99	-20	23.9
ACN	LE	450	32	63	14.9	22.2	
	ESIPT	582	31	62	-95	94.9	
dIPr	<i>n</i> -hexane	LE	430	0.53	353	997	5
		ESIPT	550	28	354	-16	19.5
	<i>n</i> -hexadecane	LE	430	13.5	280	28.7	3.3
		ESIPT	550	27	127	-9.9	9.74
	Toluene	LE	430	1.5	169	314	7.27
		ESIPT	600	31	166	-28	28.2
	THF	LE	430	2.5	164	247	7.8
		ESIPT	600	30	160	-28	28.05
ACN	LE	420	3.1	84	633	30.9	
	ESIPT	600	28	84	-41	41.54	

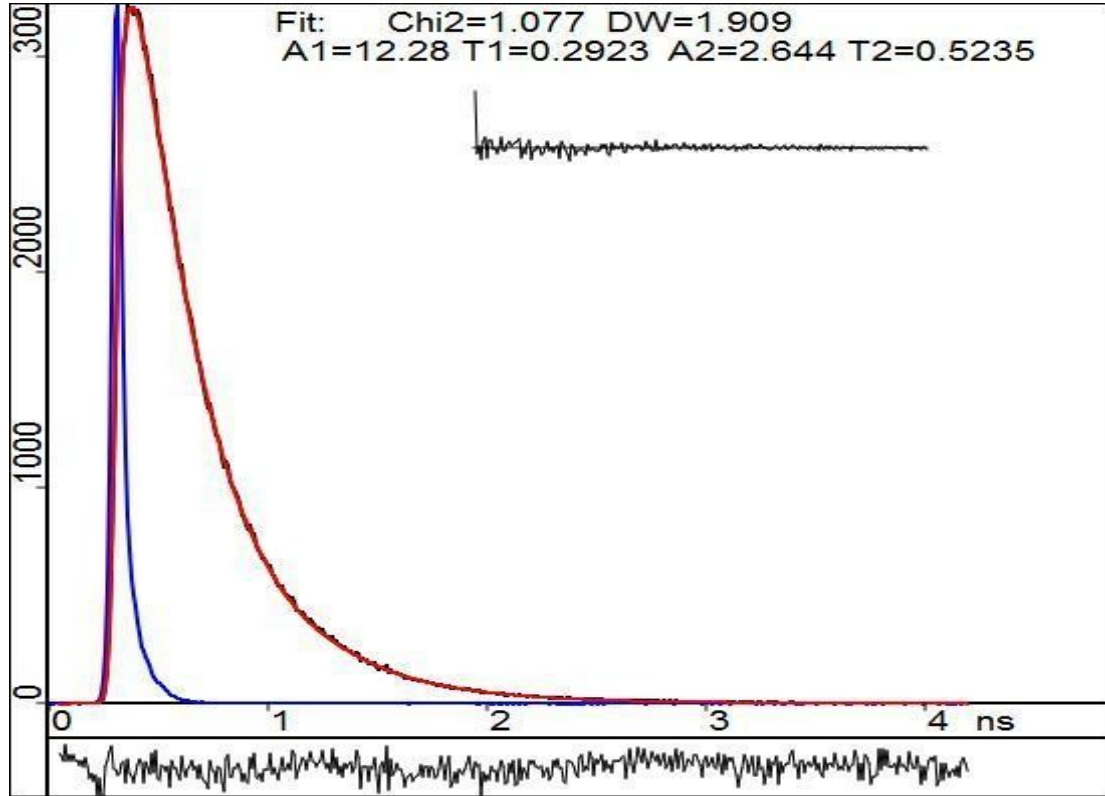


Figure S6. Two exponential decay fit (red line) to fluorescence profile (black) of **dH** in *n*-hexadecane. Fluorescence recorded at 454 nm with temporal resolution 1.53 ps per channel. Excitation pulse (IRF) is plotted in blue, residuals and the autocorrelation function in black.

Relations of the observed fluorescence decay times (τ_1, τ_2) and amplitudes (A, B, C) to rate constants k_1, k_{12}, k_2, k_{21} and initial population $[S1]_0$:

$$\lambda_{1,2} = \frac{1}{2}(k_1 + k_{12} + k_2 + k_{21} \mp \sqrt{[(k_2 + k_{21} - k_1 - k_{12})^2 + 4k_{12}k_{21}]}) \quad (S1)$$

$$A = [S1]_0 \frac{\lambda_2 - k_1 - k_{12}}{\lambda_2 - \lambda_1} \quad (S2)$$

$$B = [S1]_0 \frac{k_2 + k_{21} - \lambda_1}{\lambda_2 - \lambda_1} \quad (S3)$$

$$C = [S1]_0 \frac{k_{12}}{\lambda_2 - \lambda_1} \quad (S4)$$

can be used to determine the sums of rate constants:

$$k_1 + k_{12} = \frac{A\lambda_1 + B\lambda_2}{A+B} \quad (S5)$$

$$k_2 + k_{21} = \lambda_1 + \lambda_2 - k_1 - k_{12} \quad (S6)$$

$$k_{21} = \frac{(\lambda_1 - \lambda_2)^2 - (k_1 + k_{12} - k_2 - k_{21})^2}{4k_{12}} \quad (S7)$$

Knowing k_1 for a molecule/solvent where ESIPT does not occur one may calculate with (S5) k_{12} and then with (S6) and (S7) – the rest of rate constants for this molecule in other solvents.

Table S4. Rate constants of the forward and backward ESIPT, k_{12} and k_{21} for **dH**, **dMe**, **dEt** and **dIPr** and their deuterated counterparts in *n*-hexane at temperature 21°C. Kinetic isotope effect (KIE) is calculated for both rates: $\text{KIE}(k_{12}) = k_{12}(\text{H})/k_{12}(\text{D})$ and $\text{KIE}(k_{21}) = k_{21}(\text{H})/k_{21}(\text{D})$.

Compound	$k_{12}(\text{H})$	$k_{21}(\text{H})$	$k_{12}(\text{D})$	$k_{21}(\text{D})$	KIE(k_{12})	KIE(k_{21})
	10^9s^{-1}	10^9s^{-1}	10^9s^{-1}	10^9s^{-1}		
dH	7.8	27.5	1.2	4.4	6.4	6.2
dMe	53.4	25.2	10.7	11.0	5.0	2.3
dEt	253.7	14.0	55.5	7.5	4.6	1.8
dIPr	1874.0	9.4	281.4	6.0	6.6	1.5

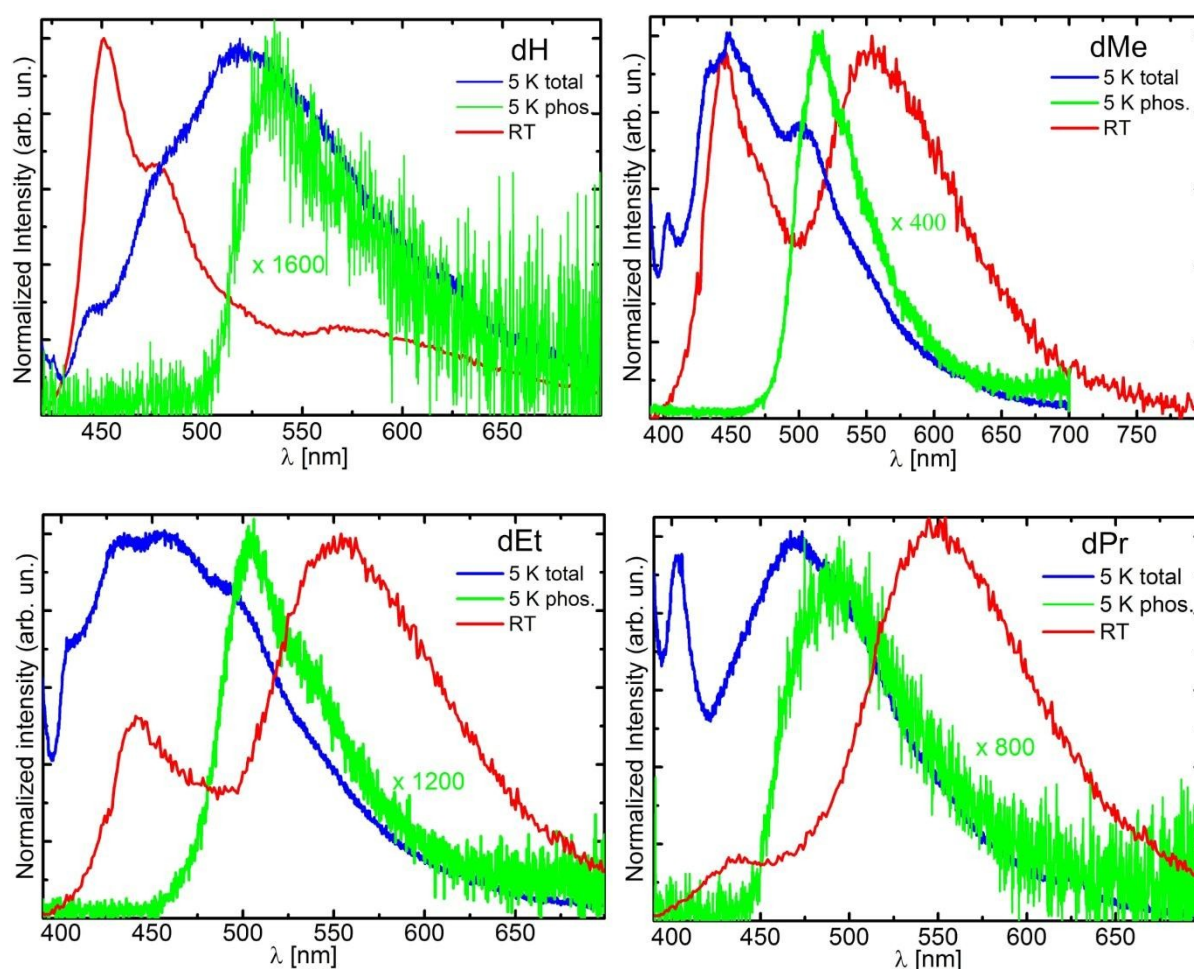


Figure S7. The spectra of **dH**, **dMe**, **dEt** and **dIPr** in *n*-hexane. Total (“in phase”) emission (blue line), long-living (“out of phase”) emission (red line) at **5 K** and fluorescence spectrum at room temperature (red line). 5 K spectra taken with excitation at 405 nm, for the RT spectrum excitation was at 380 nm.

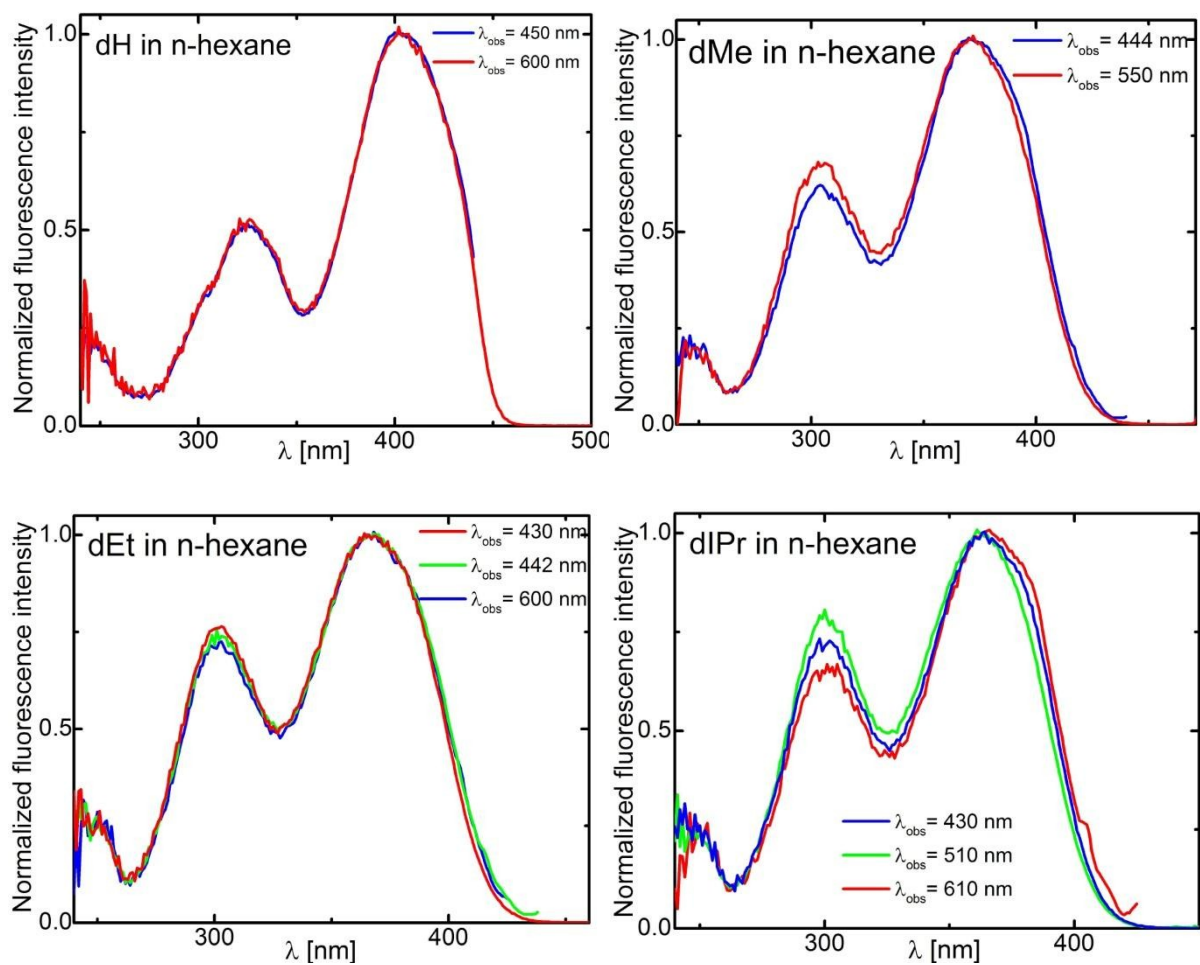


Figure S8. The normalised fluorescence excitation spectra of **dH**, **dMe**, **dEt** and **dIPr** in *n*-hexane at room temperature using indicated excitation wavelengths.

Instruments and methods

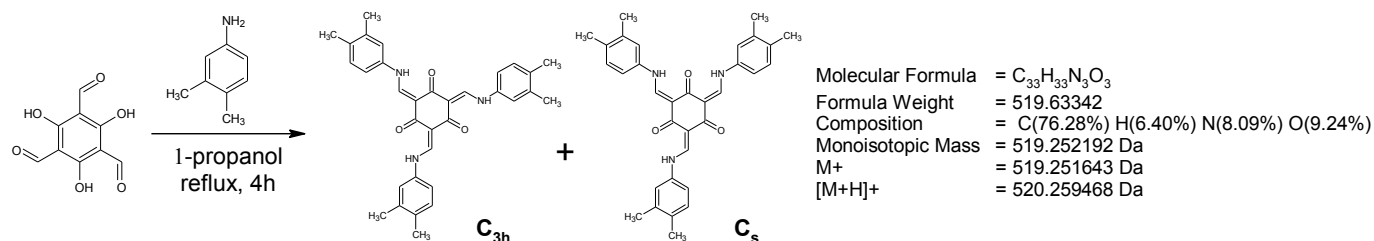
¹H FT-NMR spectra were recorded using Bruker AVANCE 500 MHz spectrometer. The chemical shifts are given vs. TMS as an internal standard. The coupling constants were calculated by using chemical shifts reported in Hz unit (ChemSketch 12.0). FT infrared spectra were recorded using Thermo-Nicolet Nexus 670 FTIR spectrometer. Low and high resolution mass spectra ((LRMS and HRMS (EI⁺)) were obtained with a Waters AutoSpec Premier mass spectrometer. Melting points were obtained with an A. KRÜSS Optronic KSP1N melting point meter. Elemental analysis was conducted with an Elementar Vario EL III analyzer. Thin layer chromatography (TLC) analysis was carried out using Merck Silica gel 60 F 254 TLC plates and spots were visualised under UV light (365 or 254 nm). Silica gel column chromatography (CC) was performed with short 1 inch diameter columns packed with Silica gel 60 (Merck) suspended in hexane.

Synthesis and purification of compounds

All chemicals and solvents were purchased from Aldrich or Fluorochem with the exception of the 1,3,5-triformylphloroglucinol which was purchased from Carbosynth. All reactants were used as received. None of the reactions and purifications required oxygen, water and ambient light exclusion.

Synthesis of **dH**

(2E,4E,6E)-2,4,6-tris{[(3,4-dimethylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (C_{3h} diastereoisomer) and (2Z)-2,4,6-tris{[(3,4-dimethylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (C_s diastereoisomer)



In a one necked round bottoms flask (100 ml) was put magnetic stir bar (ellipsoidal, 10 x 20 mm), 1,3,5-triformylphloroglucinol (0.42 g; 2 mmol) and 3,4-dimethylaniline (0.97 g; 8 mmol; 4 eq.) and 1-propanol (40 ml). The mixture while stirred was heated to reflux. After 30 minutes the product dominated in the reaction mixture (a few drops of the reaction mixture were diluted in acetone, TLC - DCM) and it was manifested by the appearance of the precipitate. Dioxane (10 ml) was added and the reaction was conducted for 4 hours in total. After that, the suspension was cooled below 50 °C and diluted with methanol (~60 ml). The precipitate was filtered off after 15 minutes of stirring on a sinter funnel (G4, 1 inch wide), washed with methanol (ambient temperature, 4 x 30 ml) and dried in air for 16 h (preferably overnight). The yellow powder (0.92 g) was then suspended in methanol (75 ml) in a round bottom flask (100 ml) and stirred with reflux for 2 hours and filtered off again after cooling below 50 °C on a sinter funnel (G4, 1 inch wide), washed with methanol (ambient temperature, 4 x 30 ml) and dried in air for 16 h (preferably overnight). Finally the product was dried in vacuum desiccator for at least 8 hours (75 °C, 2 mbar). Pale yellow

amorphous solid (858 mg, 82%). The product has very high affinity to the polar and protic solvents. ^1H NMR analysis indicates that the compound exists in the form of two isomers. The product stains TLC plates with intensive yellow colour (two spots).

HRMS (EI⁺): calculated (M⁺): 519.2516, found: 519.2504, error: -2.31 ppm.

^1H NMR (CDCl₃ + TMS, 298 K, 500 Mhz): 13.34 (doublet, J = 13.1 Hz, N-H proton of C_{3h} diastereoisomer), 13.30 (doublet, J = 13.4 Hz, N-H proton of C_s diastereoisomer, partially overlaps with signal at 13.34 ppm), 12.92 (doublet, J = 13.0 Hz, N-H proton of C_s diastereoisomer), 12.91 (doublet, J = 13.1 Hz, N-H proton of C_s diastereoisomer, partially overlaps with signal at 12.92 ppm), 8.78 (doublet, J = 13.4 Hz, =C-H proton of C_s diastereoisomer), 8.77 (doublet, J = 13.3 Hz, =C-H proton of C_s diastereoisomer, partially overlaps with signal at 8.78 ppm): 8.72 (doublet, J = 13.2 Hz, =C-H proton of C_{3h} diastereoisomer), 8.69 (doublet, J = 12.6 Hz, =C-H proton of C_s diastereoisomer, partially overlaps with signal at 8.72 ppm), 6.98-7.15 (multiplet, 9H, J_{ortho} = 8.1 Hz, J_{meta} = 2.3 Hz, phenyl substituent), 2.22-2.29 (multiplet resulting from the overlap of several singlets at 2.23 ppm, 2.24 ppm, 2.27 ppm and 2.28 ppm, 18H, CH₃ groups).

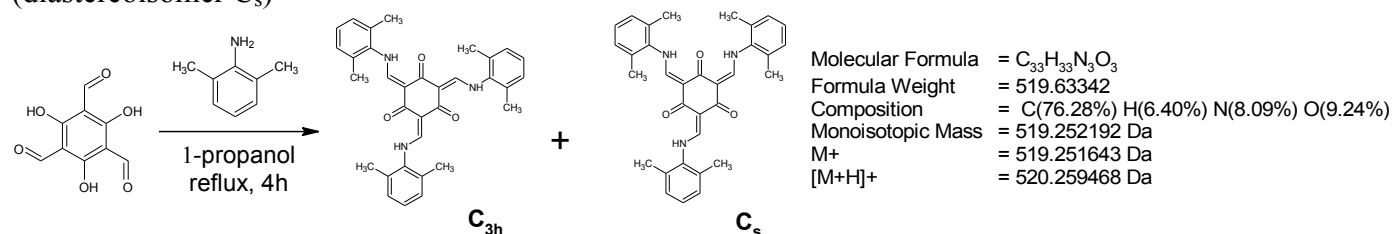
IR (KBr, cm⁻¹): 3013, 2964, 2921, 2855, 1621 (CO), 1601, 1579, 1554, 1512, 1448, 1409, 1339, 1288, 1279, 1249, 1219, 1189, 1168, 1119, 1096, 1039, 1021, 988, 861, 847, 801.

Elemental analysis: (C₃₃H₃₃N₃O₃), calculated: C(76.28%), H(6.40%), N(8.09%), O(9.24%), found: C(76.20%), H(6.27%), N(8.06%).

Melting point: (dioxane:methanol precipitate): 316-317 °C.

Synthesis of dMe

(2E,4E,6E)-2,4,6-tris{[(2,6-dimethylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (diastereoisomer C_{3h}) and
(2Z)-2,4,6-tris{[(2,6-dimethylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (diastereoisomer C_s)



In a one necked round bottoms flask (100 ml) was put magnetic stir bar (ellipsoidal, 10 x 20 mm), 1,3,5-triformylphloroglucinol (0.42 g; 2 mmol) and 2,6-dimethylaniline (0.97 g; 8 mmol; 4 eq.) and 1-propanol (40 ml). The mixture while stirred was heated to reflux. After 30 minutes the product dominated in the reaction mixture reaction mixture (a few drops of the reaction mixture were diluted in acetone, TLC - DCM) and the reaction was conducted for 4 hours in total. After that, the orange-brown solution was cooled below 50 °C and diluted with methanol (~60 ml) and further cooled to the ambient temperature to obtain a precipitate. The precipitate was filtered off after 15 minutes of stirring on a on a sinter funnel (G4, 1 inch wide), washed with methanol (ambient temperature, 4 x 30 ml) and dried in air for 16 h (preferably overnight). The beige powder (0.95 g) was easily dissolved in chloroform (15 ml) (the solubility in dichloromethane is too low for CC) and put onto chromatography column [10 cm high, 50 ml SiO₂ suspended in hexanes, 1 inch wide column]. The product was eluted with chloroform + 4% of ethyl acetate (Chloroform alone is not polar enough to elute the product in a narrow fraction). The bright yellow colour fraction was collected (*ca.* 120 ml) directly into the receiving flask (100 ml) and evaporated to dryness to yield a bright yellow

solid. In the same flask, the product was crystallised by dissolving it in hot tetrahydrofuran (20 ml, Uvasol) and rapid consecutive addition of 1-propanol (20 ml, ACS reagent grade) and methanol (2 x 30 ml, Uvasol). The crystallisation began promptly and the flask was put into the freezer for 24 hours (-25 °C). The next day the crystals were filtered off on a sinter funnel (G4, 1 inch wide), washed with methanol (ambient temperature, 4 x 30 ml) and dried in air for 16 h (preferably overnight). Finally the product was dried in vacuum desiccator for at least 8 hours (75 °C, 2 mbar). Pale yellow crystalline solid (837 mg, 80%). The product has very high affinity to the polar and protic solvents. ¹H NMR analysis indicates that the compound exists in the form of two isomers. The product stains TLC plates with poorly visible pale yellow colour (two spots).

HRMS (EI⁺): calculated (M⁺): 519.2516, found: 519.2512, error: -0.77 ppm.

¹H NMR (CDCl₃ + TMS, 298 K, 500 Mhz): 12.88 (doublet, J = 13.3 Hz, N-H proton of C_{3h} diastereoisomer), 12.83 (doublet, J = 13.4 Hz, N-H proton of C_s diastereoisomer partially overlaps with signal at 12.88 ppm), 12.52 (doublet, J = 13.4 Hz, two perfectly overlapping doublets of N-H protons of C_s diastereoisomer), 8.42 (doublet, J = 13.4 Hz, =C-H proton of C_s diastereoisomer), 8.40 (doublet, J = 13.4 Hz, =C-H proton of C_s diastereoisomer, partially overlaps with signal at 8.42 ppm), 8.35 (doublet, J = 13.3 Hz, =C-H proton of C_{3h} diastereoisomer), 8.34 (doublet, J = 13.4 Hz, =C-H proton of C_s diastereoisomer, partially overlaps with signal at 8.35 ppm), 7.07-7.15 (multiplet, 9H, phenyl substituent), 2.35-2.42 (multiplet resulting from the overlap of four singlets at 2.36 ppm, 2.38 ppm, 2.39 ppm and 2.41 ppm, 18H, CH₃ groups).

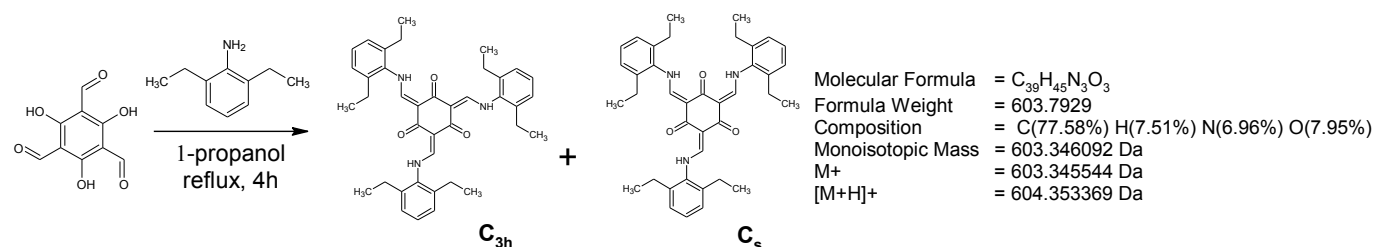
IR (KBr, cm⁻¹): 3029, 2965, 2922, 2851, 1607 (CO), 1581, 1554, 1473, 1450, 1426, 1380, 1298, 1256, 1244, 1221, 1191, 1165, 1093, 1030, 1007, 991, 922, 835, 772, 738.

Elemental analysis: (C₃₃H₃₃N₃O₃), calculated: C(76.28%), H(6.40%), N(8.09%), O(9.24%), found: C(75.07%), H(6.35%), N(7.75%).

Melting point: (THF:1-PrOH:MeOH 1:1:3): 242-244 °C.

Synthesis of dEt

(2E,4E,6E)-2,4,6-tris{[(2,6-diethylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (diastereoisomer C_{3h}) and
(2Z)-2,4,6-tris{[(2,6-diethylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (diastereoisomer C_s)



In a one necked round bottoms flask (100 ml) was put magnetic stir bar (ellipsoidal, 10 x 20 mm), 1,3,5-triformylphloroglucinol (0.42 g; 2 mmol) and 2,6-diethylaniline (1.19 g; 8 mmol; 4 eq.) and 1-propanol (40 ml). The mixture while stirred was heated to reflux. After 30 minutes the product dominated in the reaction mixture reaction mixture (a few drops of the reaction mixture were diluted in acetone, TLC - DCM) and the reaction was conducted for 4 hours in total. After that, the orange-brown solution was cooled below 50 °C and diluted with

methanol (~60 ml) and further cooled in the freezer (-25 °C) to obtain a precipitate. The precipitate was filtered off the next day on a sinter funnel (G4, 1 inch wide), washed with methanol (ambient temperature, 4 x 30 ml) and dried in air for 16 h (preferably overnight). The beige powder (0.93 g) was easily dissolved in dichloromethane (15 ml) and put onto chromatography column [10 cm high, 50 ml SiO₂ suspended in hexanes, 1 inch wide column]. The product was eluted with dichloromethane + 2% of ethyl acetate (DCM alone is not polar enough to elute the product in a narrow fraction). The bright yellow colour fraction was collected (*ca.* 120 ml) directly into the receiving flask (100 ml) and evaporated to dryness to yield a yellow resin. In the same flask, the product was crystallised by dissolving it in boiling 1-propanol (30 ml, ACS reagent grade) and rapid consecutive addition of methanol (2 x 30 ml, Uvasol). The flask was put into the freezer for 48 hours (-25 °C). After two days the crystals were filtered off on a sinter funnel (G4, 1 inch wide), washed with methanol (ambient temperature, 4 x 30 ml) and dried in air for 16 h (preferably overnight). Finally the product was dried in vacuum desiccator for 8 hours (75 °C, 2 mbar). Pale yellow solid (843 mg, 70%). The product has high affinity to the polar and protic solvents. ¹H NMR analysis indicates that the compound exists in the form of two isomers. The product stains TLC plates with barely visible pale yellow colour (two spots).

HRMS (EI⁺): calculated (M⁺): 603.3455, found: 603.3487, error: 5.30 ppm.

¹H NMR (CDCl₃ + TMS, 298 K, 500 Mhz): 12.86 (doublet, J = 13.3 Hz, N-H proton of C_{3h} diastereoisomer), 12.82 (doublet, J = 13.2 Hz, N-H proton of C_s diastereoisomer, partially overlaps with signal at 12.86 ppm), 12.58 (doublet, J = 13.4 Hz, N-H proton of C_s diastereoisomer), 12.57 (doublet, J = 13.3 Hz, N-H proton of C_s diastereoisomer, partially overlaps with signal at 12.58 ppm), 8.37 (doublet, J = 13.1 Hz, =C-H proton of C_s diastereoisomer), 8.34 (doublet, J = 13.3 Hz, =C-H proton of C_s diastereoisomer, partially overlaps with signal at 8.37 ppm forming apparent triplet), 8.30 (doublet, J = 13.5 Hz, =C-H proton of C_s diastereoisomer), 8.29 (doublet, J = 13.3 Hz, =C-H proton of C_{3h} diastereoisomer, partially overlaps with signal at 8.30 ppm), 7.12-7.25 (multiplet, 9H, phenyl substituent), 2.65-2.78 (multiplet resulting from the overlap of four quartets, J = 7.5 Hz, 12H, CH₂ groups), 1.20-1.30 (multiplet resulting from the overlap of four triplets, J = 7.5 Hz, 18H, CH₃ groups).

IR (KBr, cm⁻¹): 3026, 2966, 2932, 2873, 1602 (CO), 1579, 1550, 1470, 1437, 1378, 1294, 1256, 1215, 1183, 1168, 1105, 1099, 1079, 1059, 1014, 907, 851, 836, 829, 801, 764, 738.

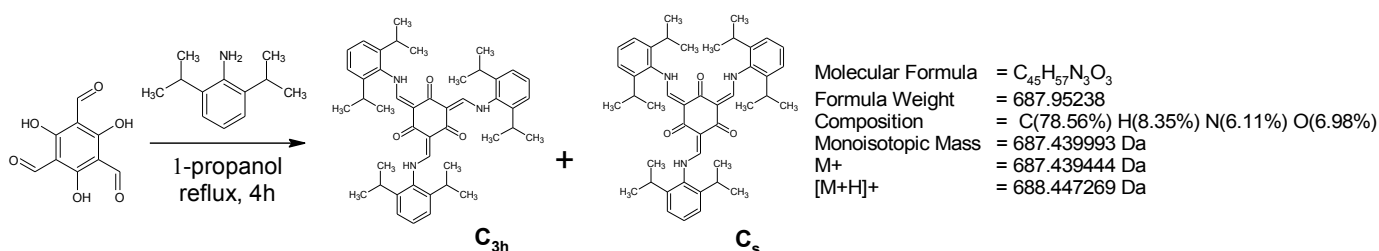
Elemental analysis: (C₃₉H₄₅N₃O₃), calculated: C(77.58%), H(7.51%), N(6.96%), O(7.95%), found: C(77.25%), H(7.01%), N(7.08%).

Melting point: (1-PrOH:MeOH 1:2): 215-216 °C.

Synthesis of **dIpr**

(2E,4E,6E)-2,4,6-tris{[(2,6-diisopropylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (diastereoisomer C_{3h}) and

(2Z)-2,4,6-tris{[(2,6-diisopropylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (diastereoisomer C_s)



In a one necked round bottoms flask (100 ml) was put magnetic stir bar (ellipsoidal, 10 x 20 mm), 1,3,5-triformylphloroglucinol (0.42 g; 2 mmol) and 2,6-diethylaniline (1.42 g; 8 mmol; 4 eq.) and 1-propanol (40 ml). The mixture while stirred was heated to reflux. After 30 minutes the product dominated in the reaction mixture reaction mixture (a few drops of the reaction mixture were diluted in acetone, TLC - DCM) and the reaction was conducted for 4 hours in total. After that, the orange solution was cooled below 50 °C and diluted with methanol (~60 ml) and further cooled in the freezer (-25 °C) to obtain a precipitate. The precipitate was filtered off the next day on a sinter funnel (G4, 1 inch wide), washed with methanol (ambient temperature, 4 x 30 ml) and dried in air for 16 h (preferably overnight). The beige powder (1.1 g) was easily dissolved in dichloromethane (15 ml) and put onto chromatography column [10 cm high, 50 ml SiO₂ suspended in hexanes, 1 inch wide column]. The product was eluted with dichloromethane + 1% of ethyl acetate (DCM alone is not polar enough to elute the product in a narrow fraction). The bright yellow colour fraction was collected (*ca.* 120 ml) directly into the receiving flask (100 ml) and evaporated to dryness to yield a yellow resin. In the same flask, the product was crystallised by dissolving it in boiling 1-propanol (30 ml, ACS reagent grade) and rapid consecutive addition of methanol (2 x 30 ml, Uvasol). The flask was put into the freezer for 48 hours (-25 °C). After two days the crystals were filtered off a on a sinter funnel (G4, 1 inch wide), washed with methanol (ambient temperature, 4 x 30 ml) and dried in air for 16 h (preferably overnight). Finally the product was dried in vacuum desiccator for 8 hours (75 °C, 2 mbar). Pale yellow microcrystalline solid (841 mg, 61%). The product has high affinity to the polar and protic solvents. ¹H NMR analysis indicates that the compound exists in the form of two isomers. The product stains TLC plates with almost not visible pale yellow colour (two spots).

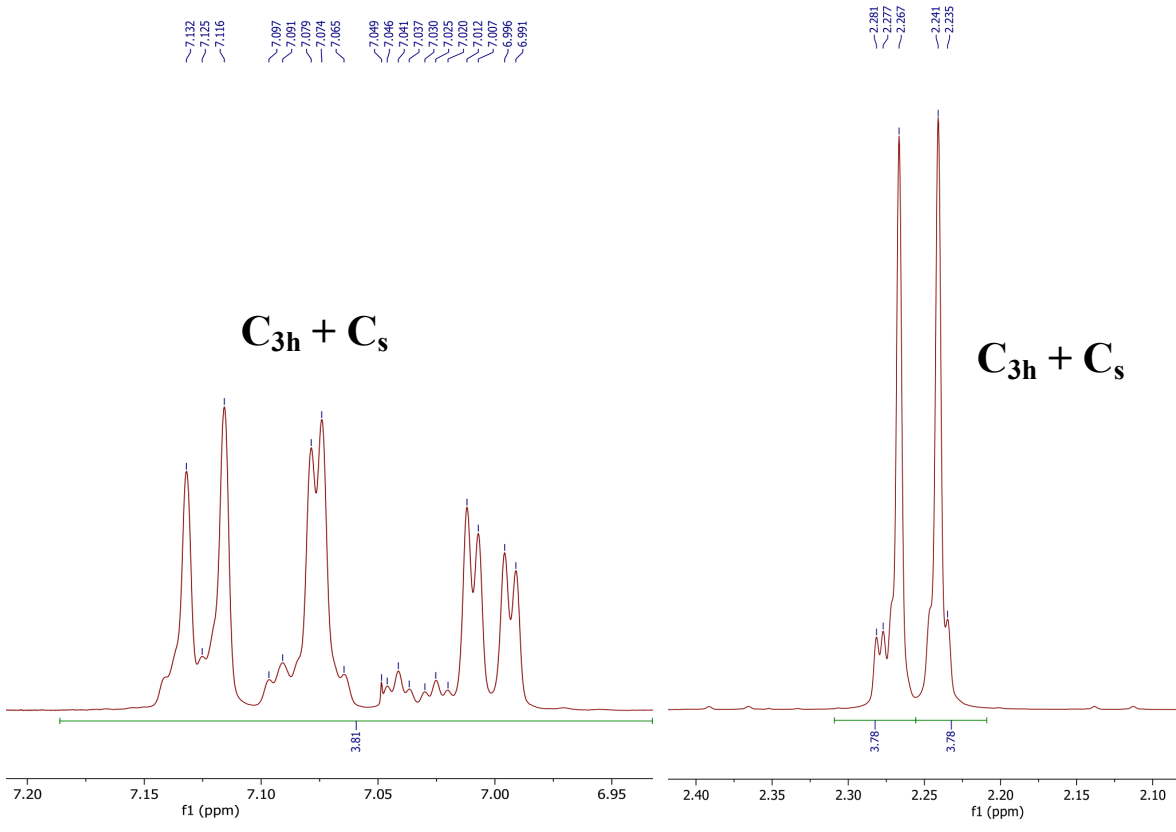
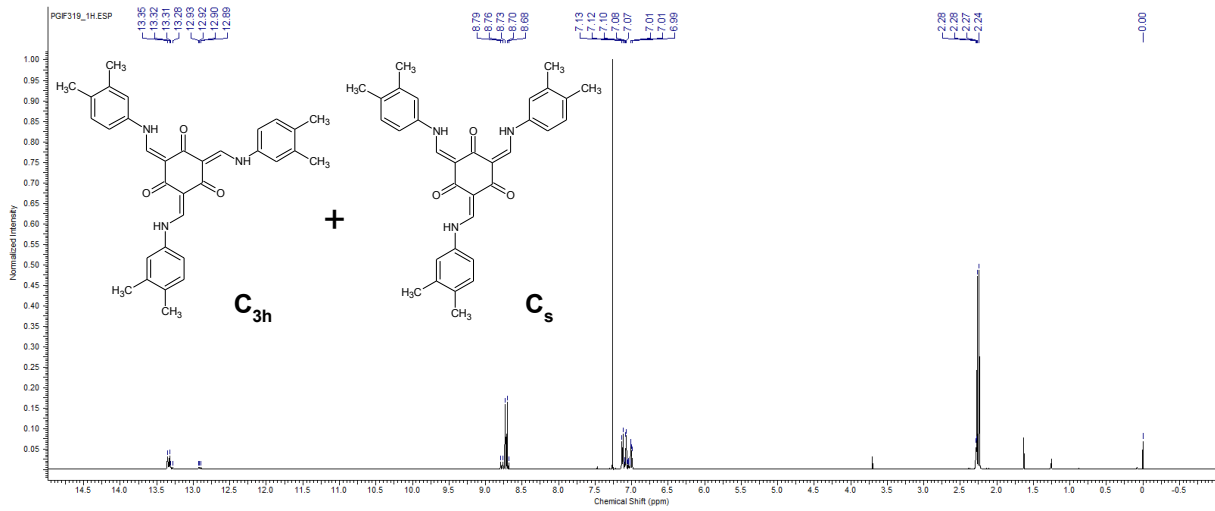
HRMS (EI⁺): calculated (M⁺): 687.4394, found: 687.4406, error: 1.75 ppm.

¹H NMR (CDCl₃ + TMS, 298 K, 500 Mhz): 12.86 (doublet, J = 13.3 Hz, N-H proton of C_{3h} diastereoisomer), 12.80 (doublet, J = 13.6 Hz, N-H proton of C_s diastereoisomer, partially overlaps with signal at 12.86 ppm), 12.58 (doublet, J = 13.3 Hz, N-H proton of C_s diastereoisomer), 12.57 (doublet, J = 13.4 Hz, N-H proton of C_s diastereoisomer, partially overlaps with signal at 12.58 ppm), 8.32 (doublet, J = 13.4 Hz, =C-H proton of C_s diastereoisomer), 8.29 (doublet, J = 13.4 Hz, =C-H proton of C_s diastereoisomer, partially overlaps with signal at 8.32 ppm), 8.26 (doublet, J = 13.3 Hz, =C-H proton of C_{3h} diastereoisomer, partially overlaps with signal at 8.29 ppm), 8.25 (doublet, J = 13.2 Hz, =C-H proton of C_{3h} diastereoisomer, partially overlaps with signal at 8.26 ppm), 7.27-7.34 (multiplet, 6H, phenyl substituent), 7.17-7.25 (multiplet, 3H, phenyl substituent), 3.13-3.28 (multiplet resulting from the overlap of four septets, J = 6.8 Hz, 6H, CH groups), 1.19-1.30 (multiplet resulting from the overlap of four doublets, J = 6.9 Hz, 36H, CH₃ groups).

IR (KBr, cm⁻¹): 3072, 2964, 2928, 2872, 1601 (CO), 1580, 1554, 1475, 1461, 1437, 1387, 1365, 1336, 1291, 1260, 1249, 1218, 1182, 1147, 1100, 1058, 1034, 1015, 935, 836, 801, 758.

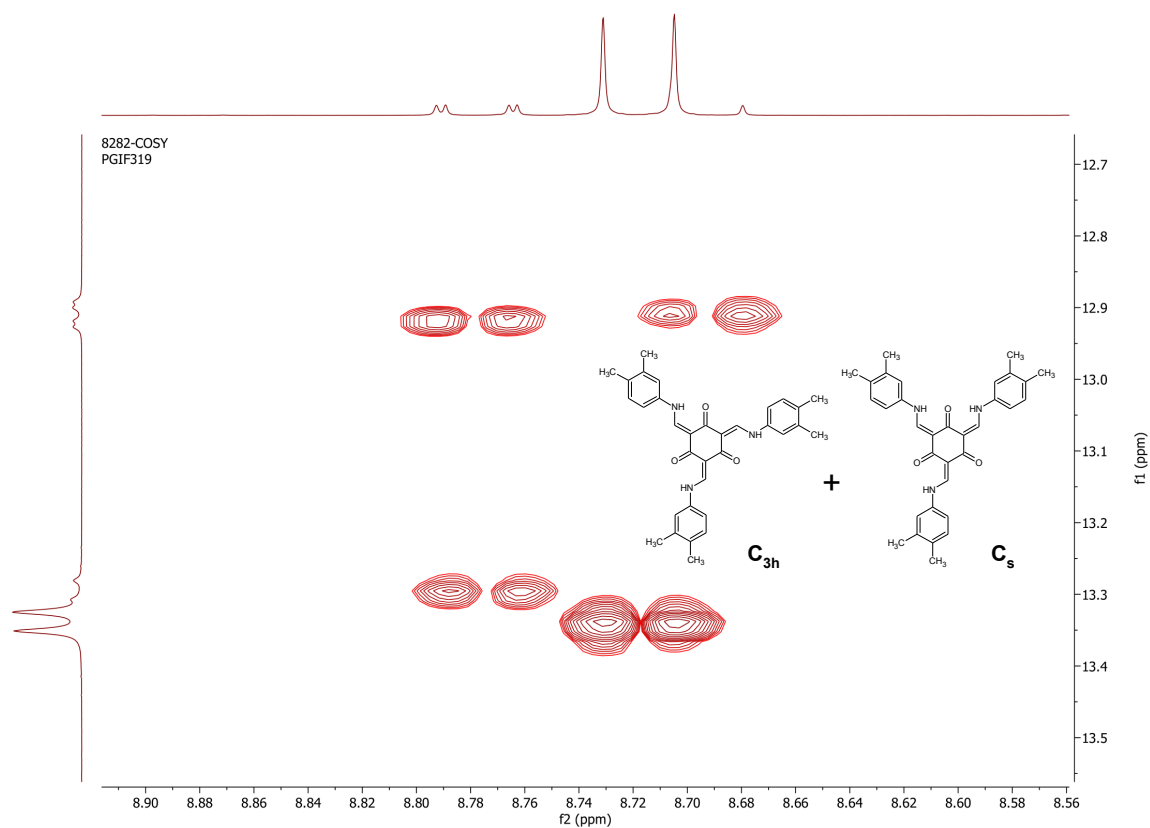
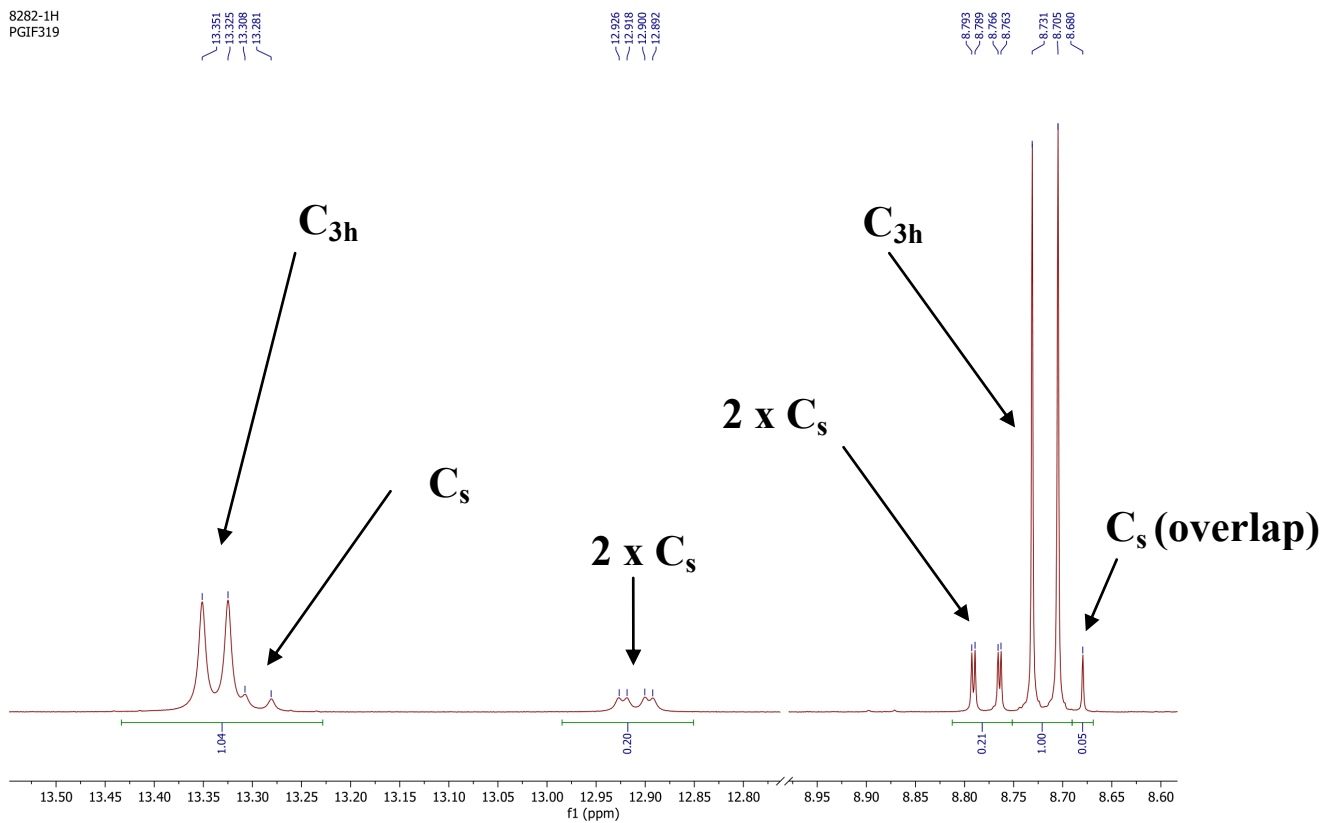
Elemental analysis: (C₄₅H₅₇N₃O₃), calculated: C(78.56%), H(8.35%), N(6.11%), O(6.98%), found: C(78.58%), H(8.05%), N(6.20%).

Melting point: (1-PrOH:MeOH 1:2): 288-289 °C.

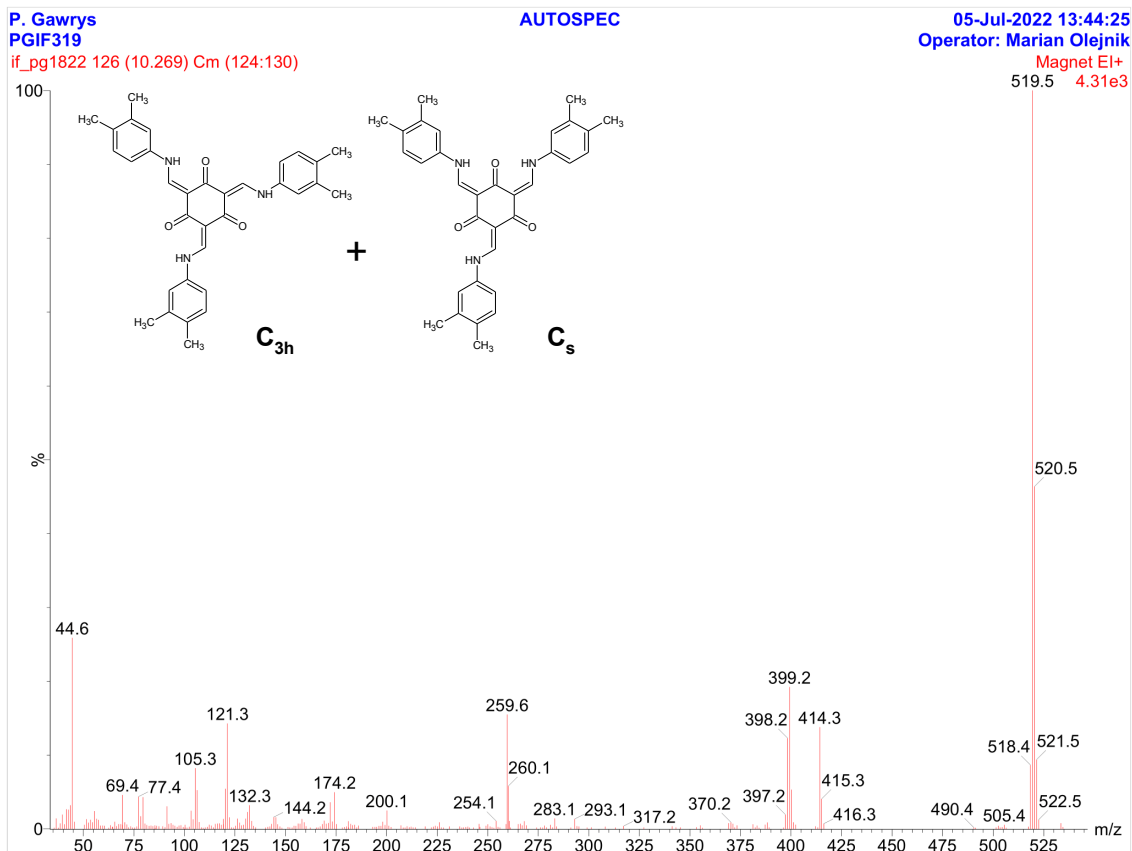


Spectrum S1. ¹H FT-NMR spectrum of **dH** (CDCl₃) (with extended diagnostic region)

8282-1H
PGIF319



Spectrum S2. ¹H-¹H COSY FT-NMR spectrum of **dH** (CDCl₃) (diagnostic region)



Spectrum S3. LR-MS spectrum of **dH** (EI^+)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 40.0 PPM / DBE: min = -1.5, max = 80.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

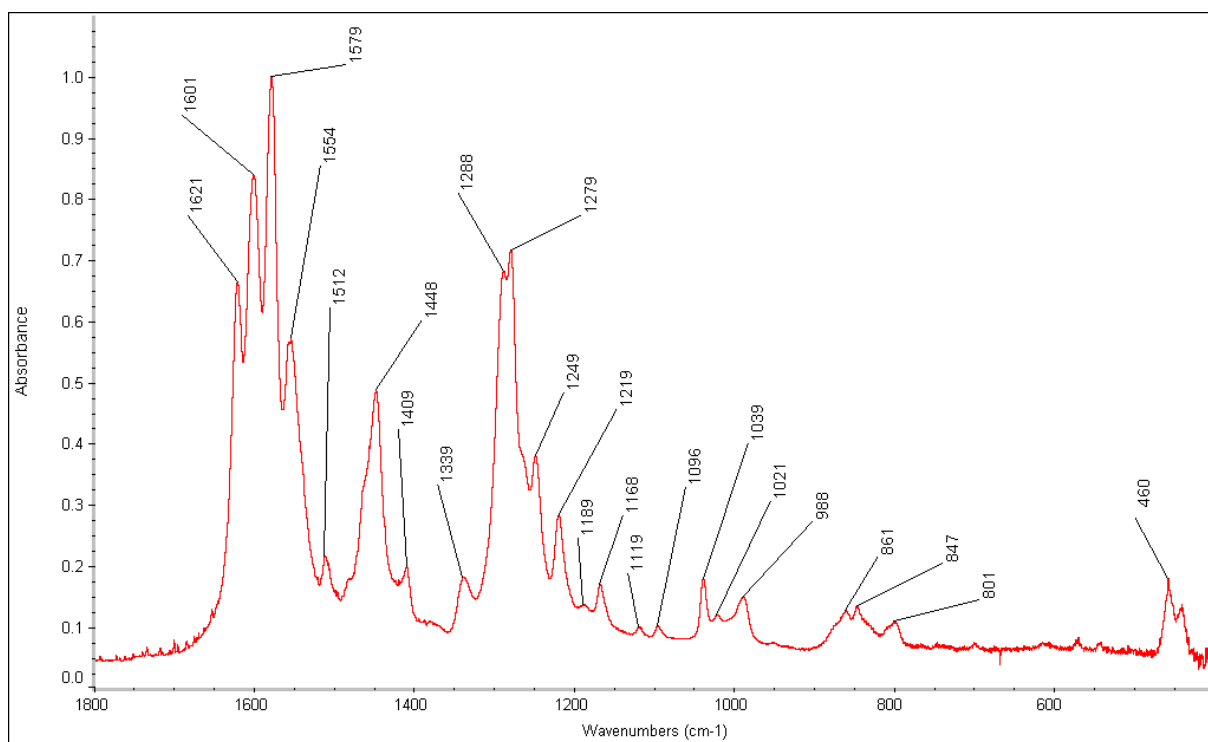
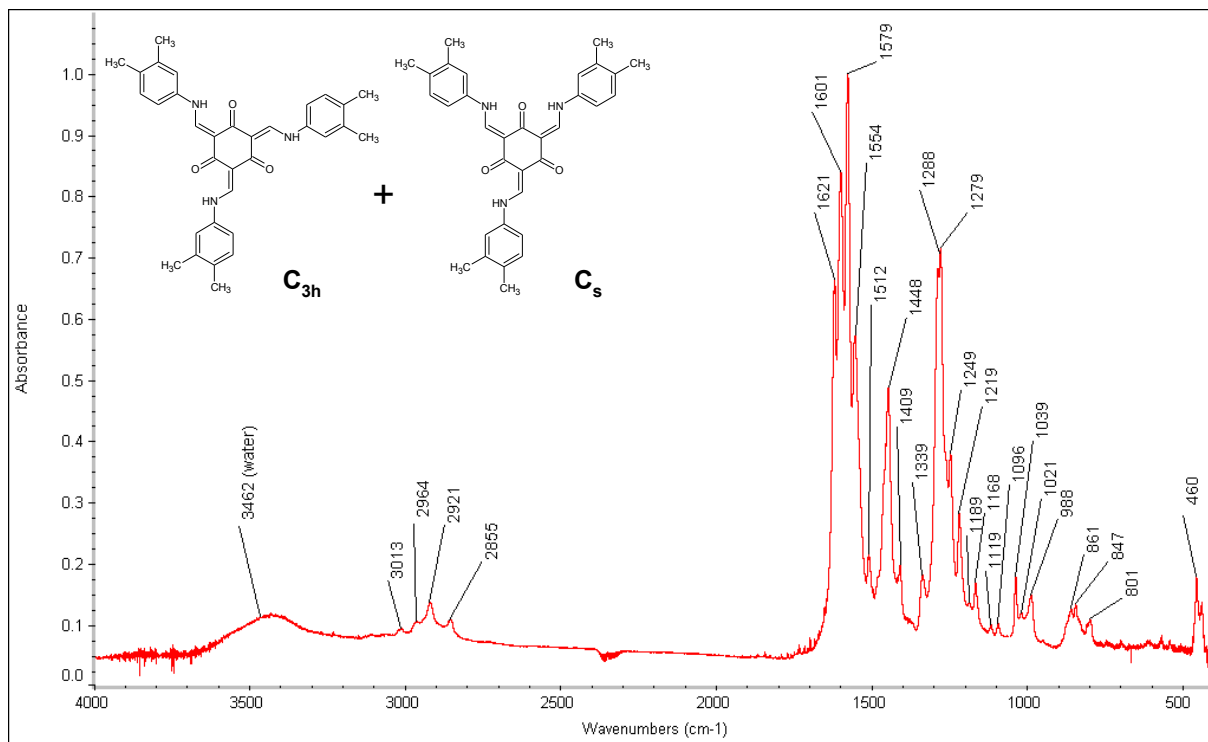
C: 0-100 H: 0-200 N: 3-3 O: 3-3

P. Gawrys
PGIF319
if_pg1822h 239 (9.115) Cm (226:242)

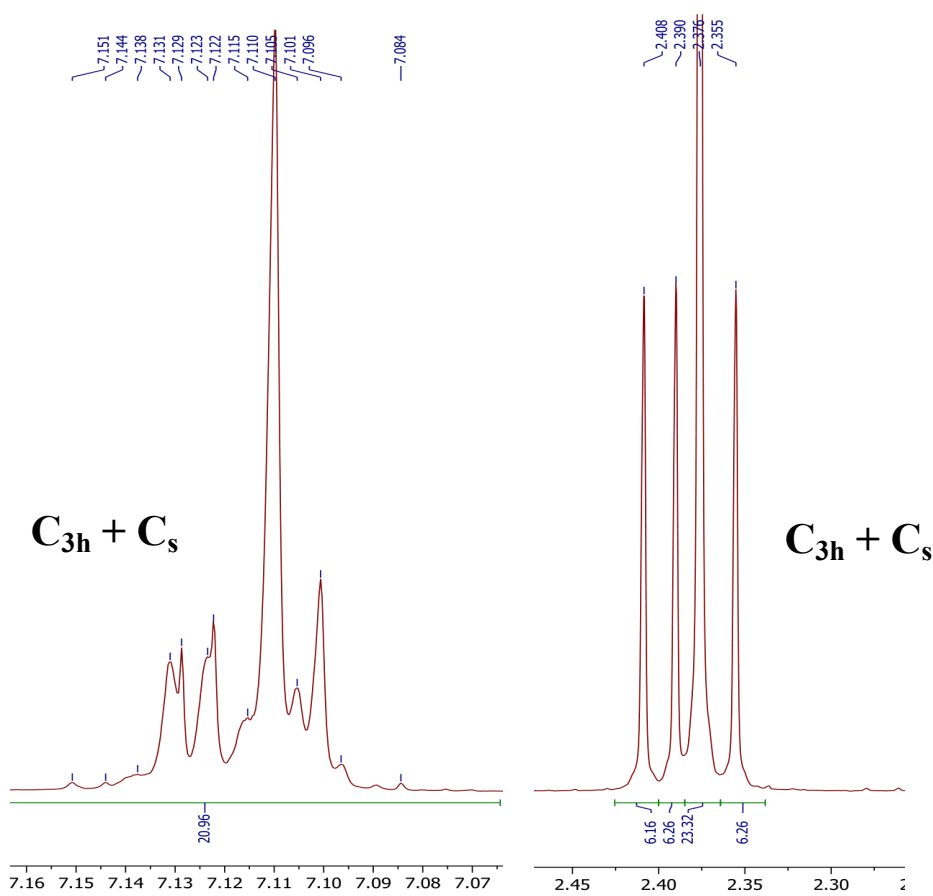
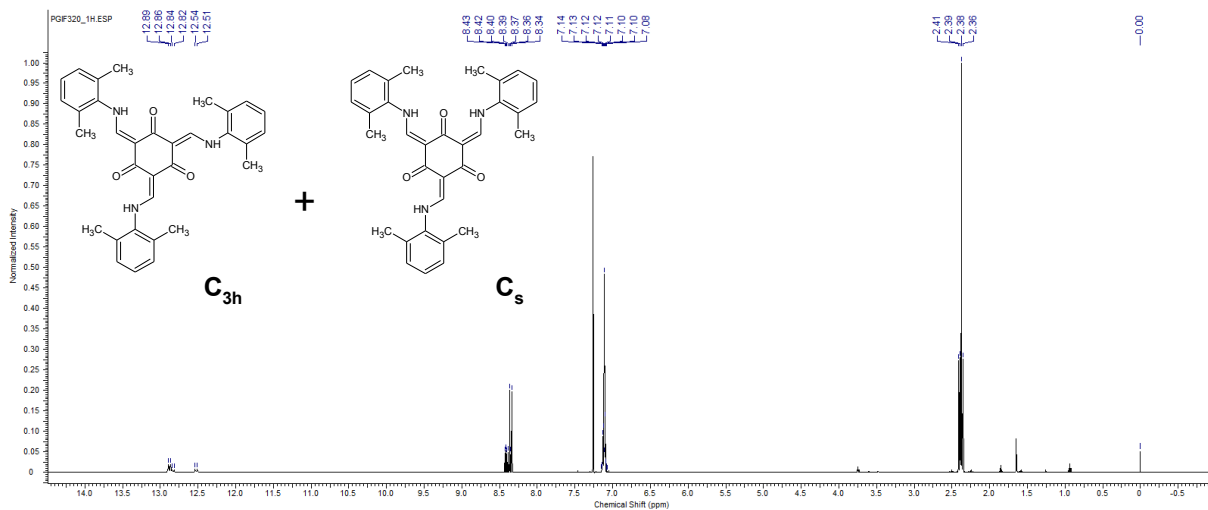
AUTOSPEC

06-Jul-2022 17:00:13
Operator: Marian Olejnik
Voltage EI+
151

Spectrum S4. HR-MS spectrum of **dH** (EI^+)

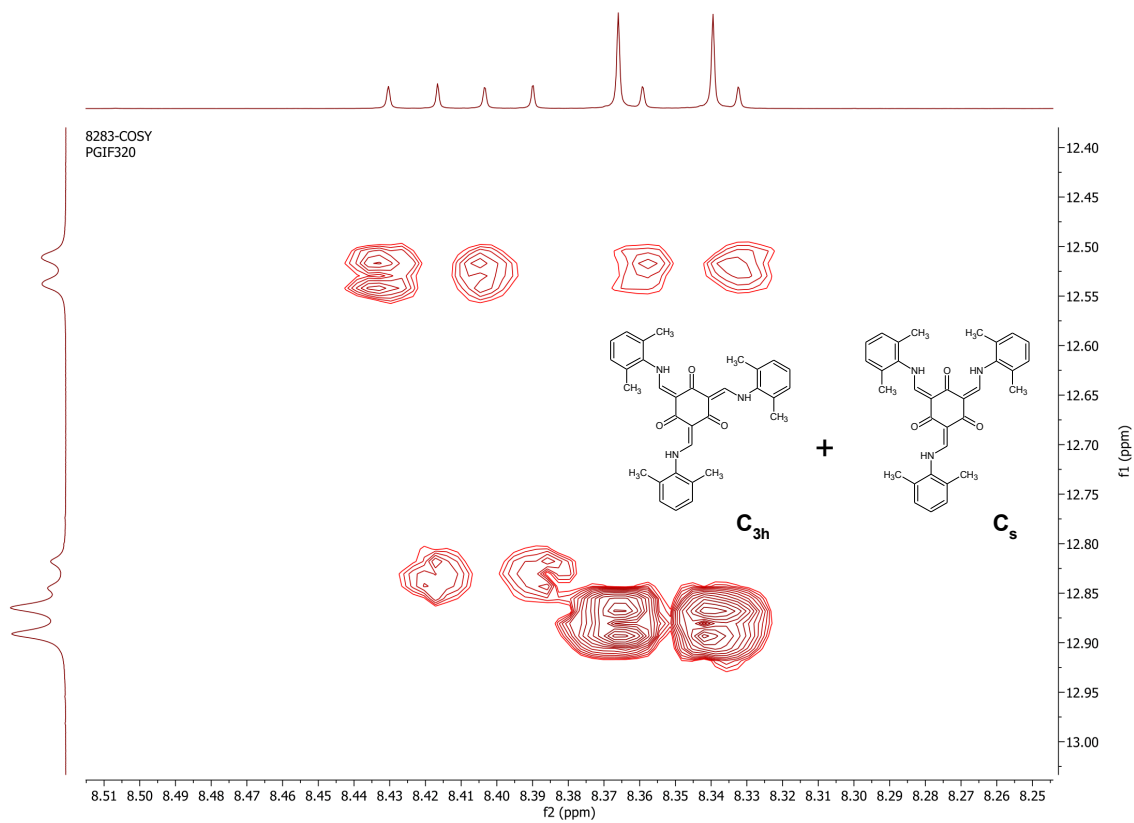
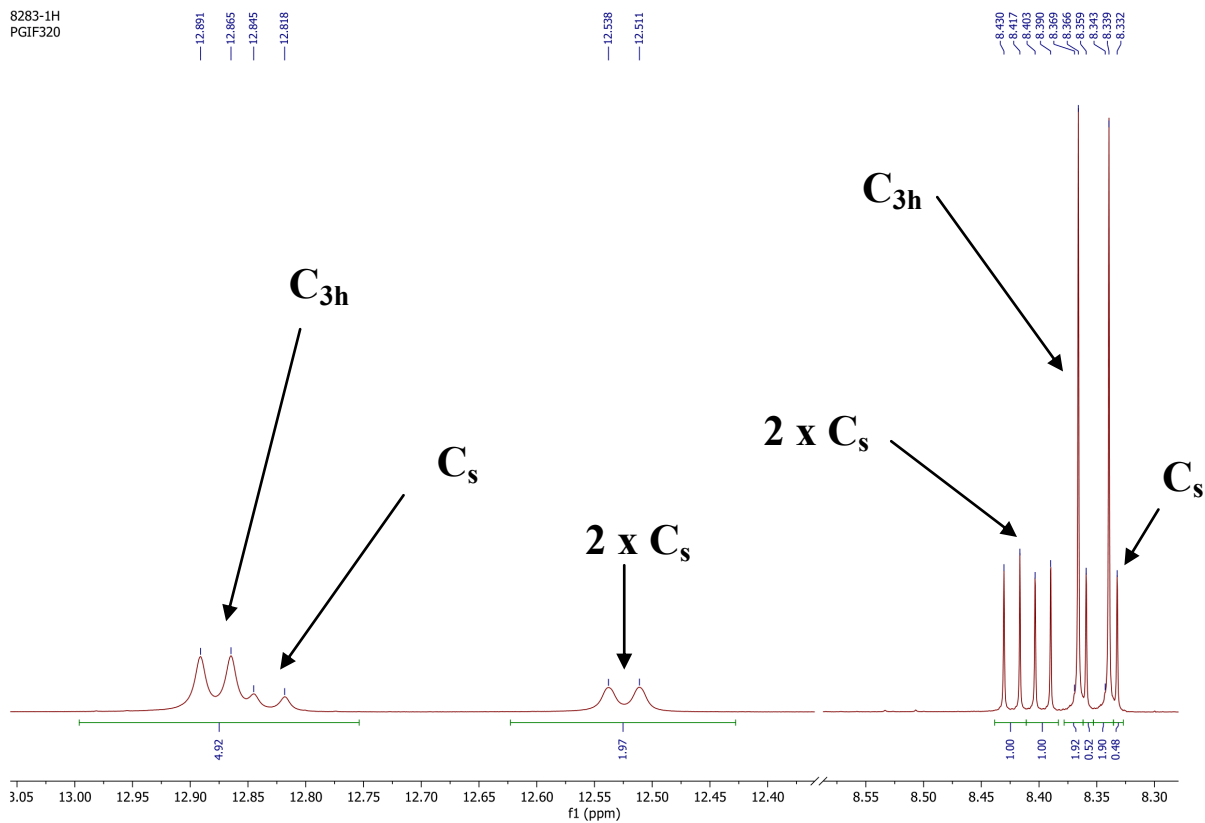


Spectrum S5. IR spectrum of **dH** (KBr)

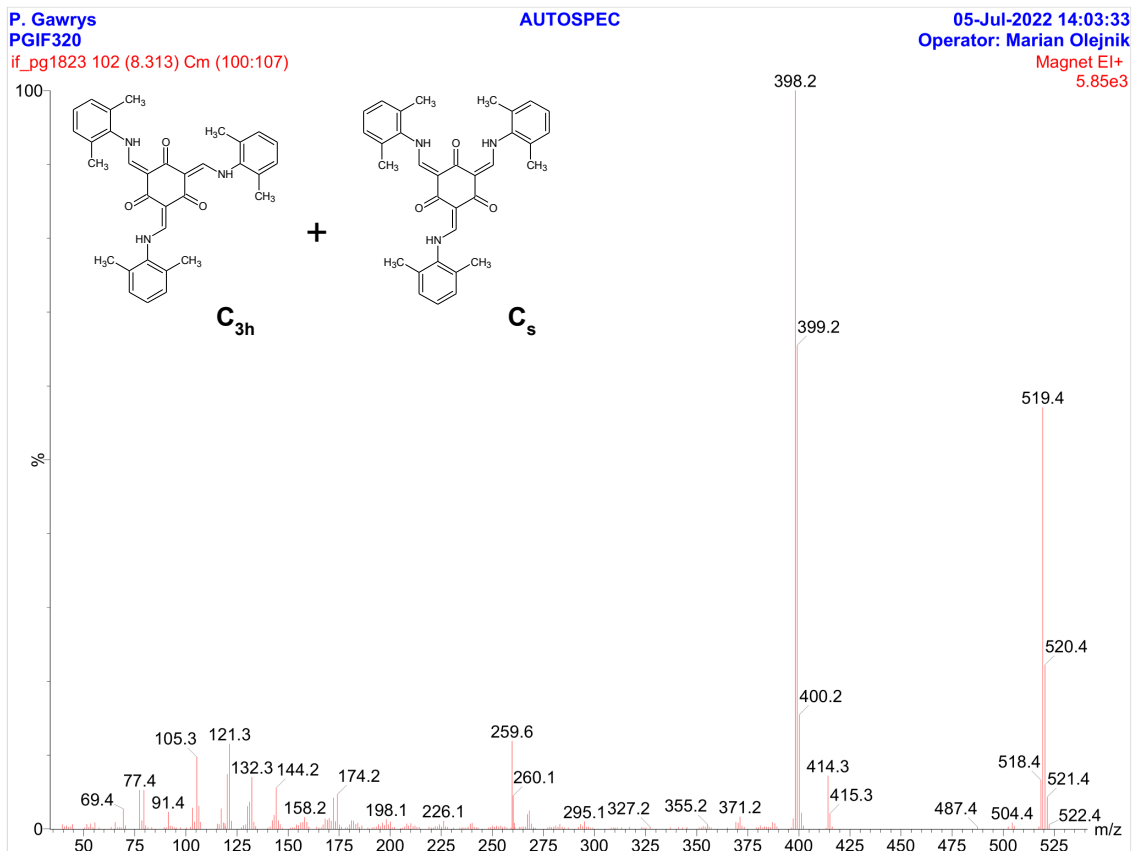


Spectrum S6. ^1H FT-NMR spectrum of **dMe** (CDCl_3) (with extended diagnostic region)

8283-1H
PGIF320



Spectrum S7. ^1H - ^1H COSY FT-NMR spectrum of dMe (CDCl_3) (diagnostic region)



Spectrum S8. LR-MS spectrum of **dMe** (EI⁺)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 40.0 PPM / DBE: min = -1.5, max = 80.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-100 H: 0-200 N: 3-3 O: 3-3

P. Gawrys

PGIF320

if_pg1823h 181 (6.903) Cm (181:200)

AUTOSPEC

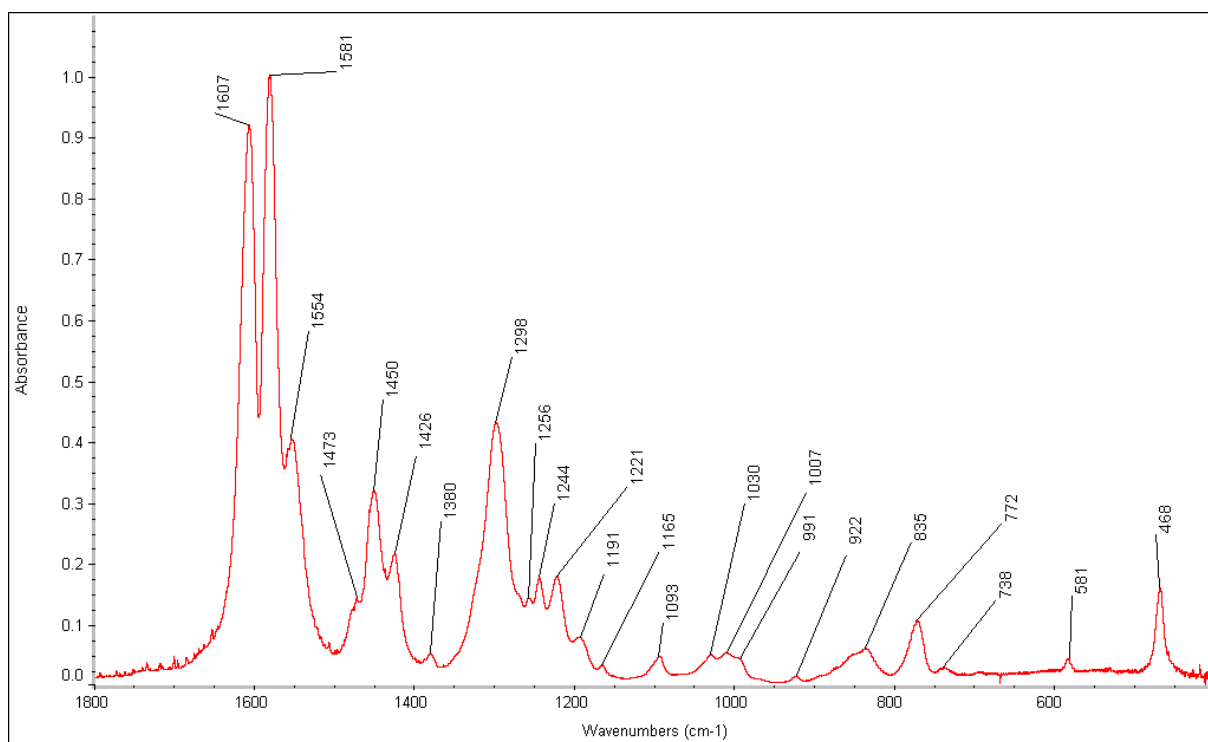
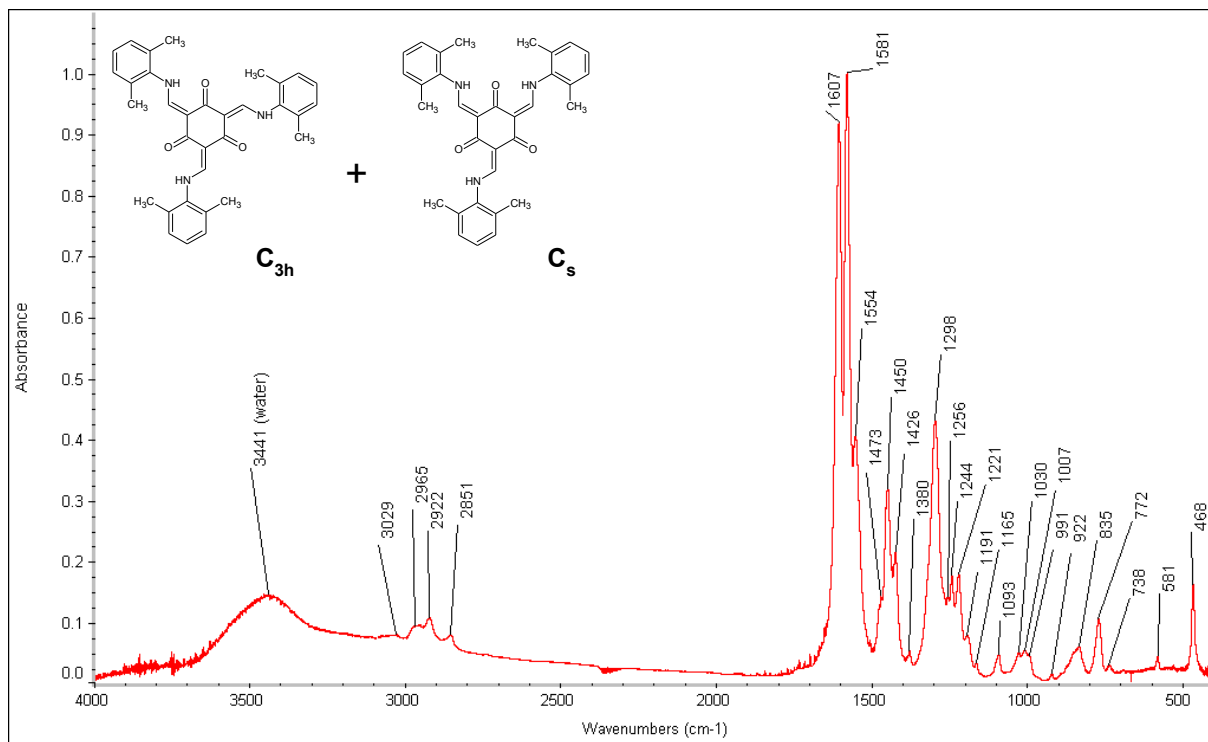
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Operator: Marian Olejnik

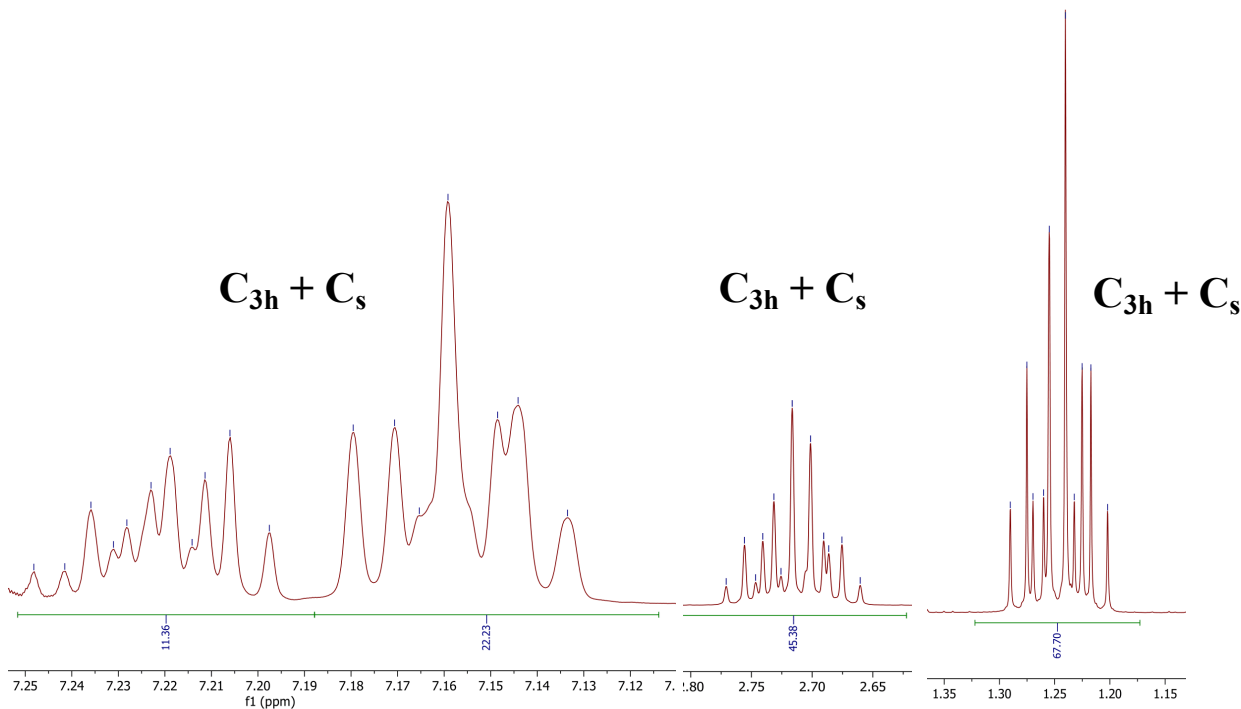
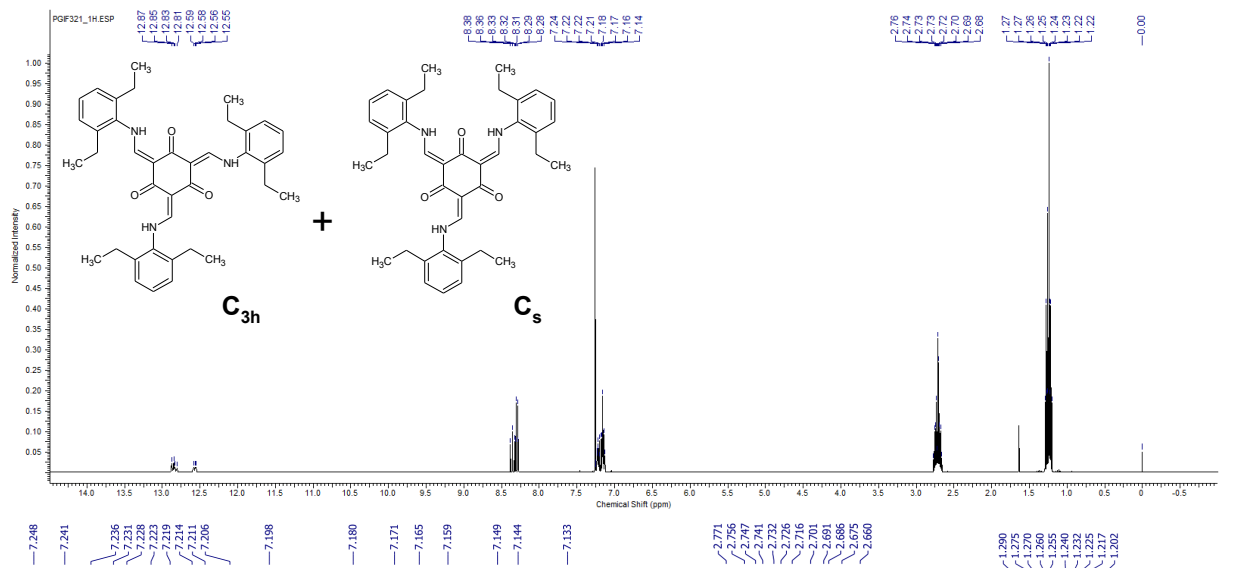
Voltage EI+

95

Spectrum S9. HR-MS spectrum of **dMe** (EI⁺)

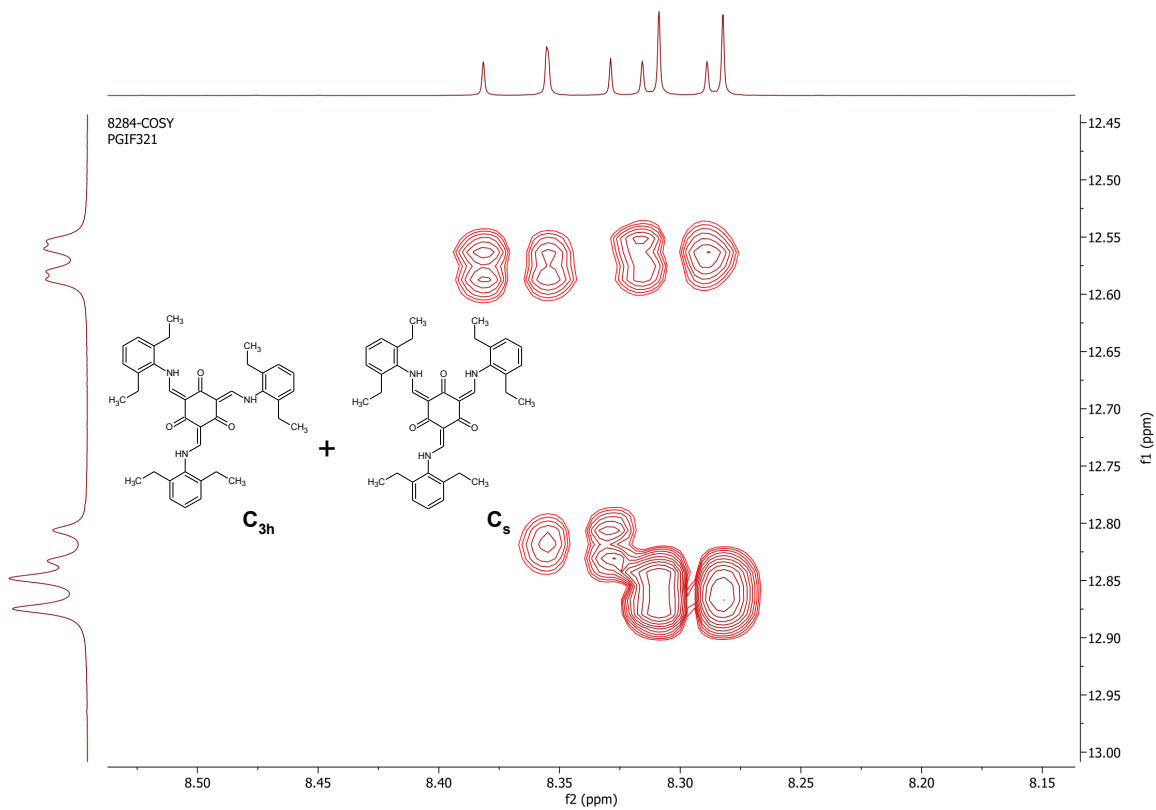
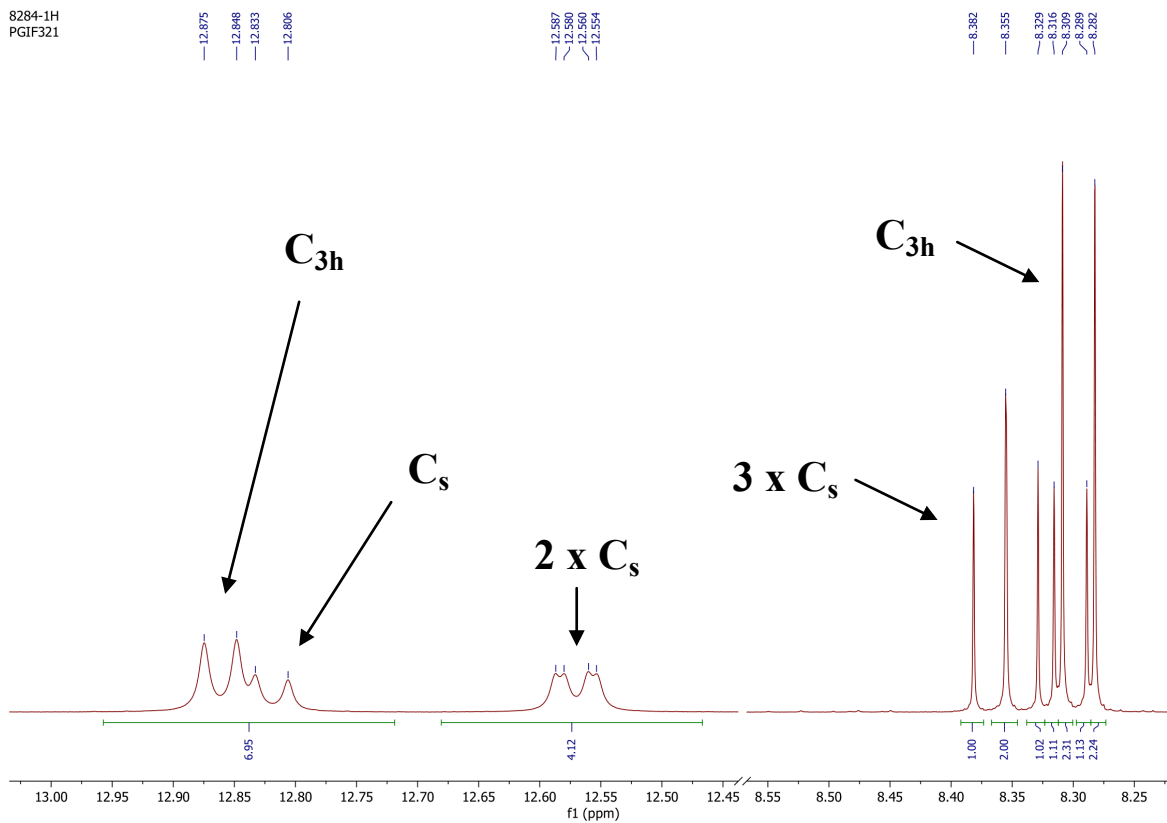


Spectrum S10. IR spectrum of **dMe** (KBr)

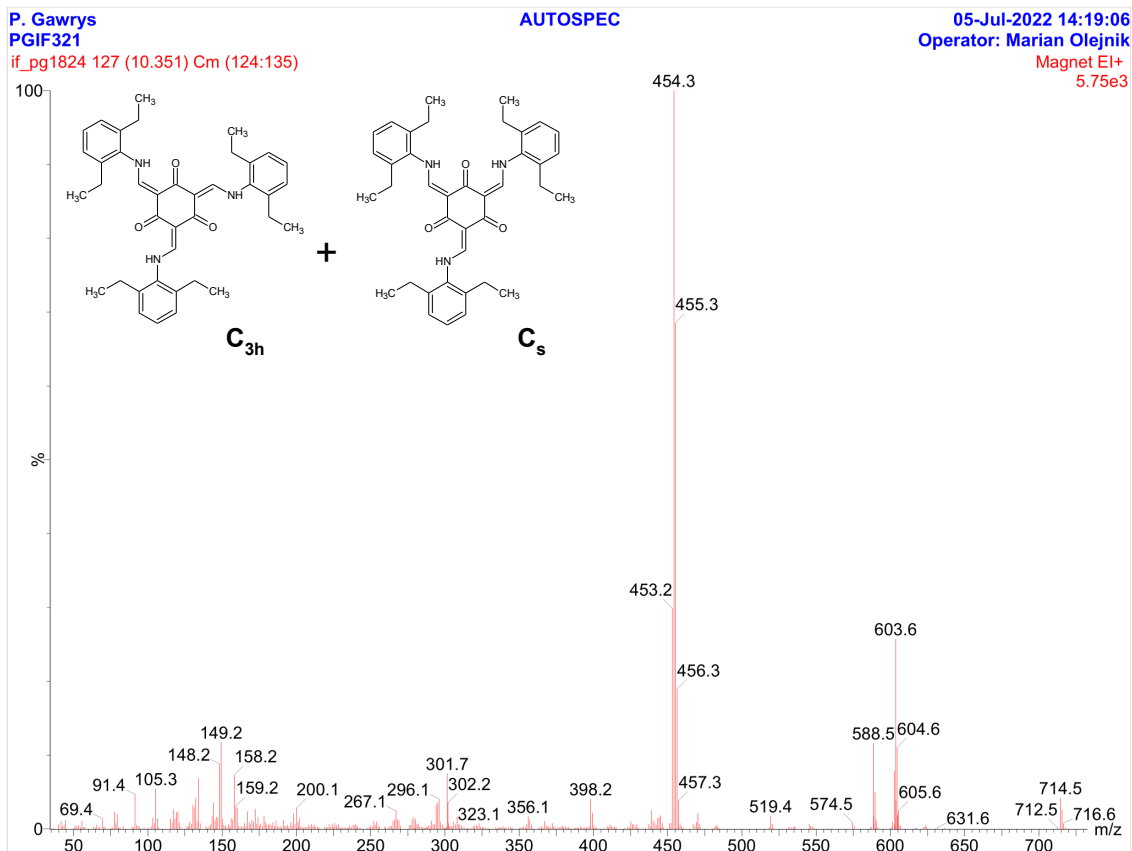


Spectrum S11. ^1H FT-NMR spectrum of **dEt** (CDCl_3) (with extended diagnostic region)

8284-1H
PGIF321



Spectrum S12. ^1H - ^1H COSY FT-NMR spectrum of **dEt** (CDCl_3) (diagnostic region)



Spectrum S13. LR-MS spectrum of **dEt** (EI⁺)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 40.0 PPM / DBE: min = -1.5, max = 80.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-100 H: 0-200 N: 3-3 O: 3-3

P. Gawrys

PGIF321

if_pg1824h 251 (9.573) Cm (233:251)

AUTOSPEC

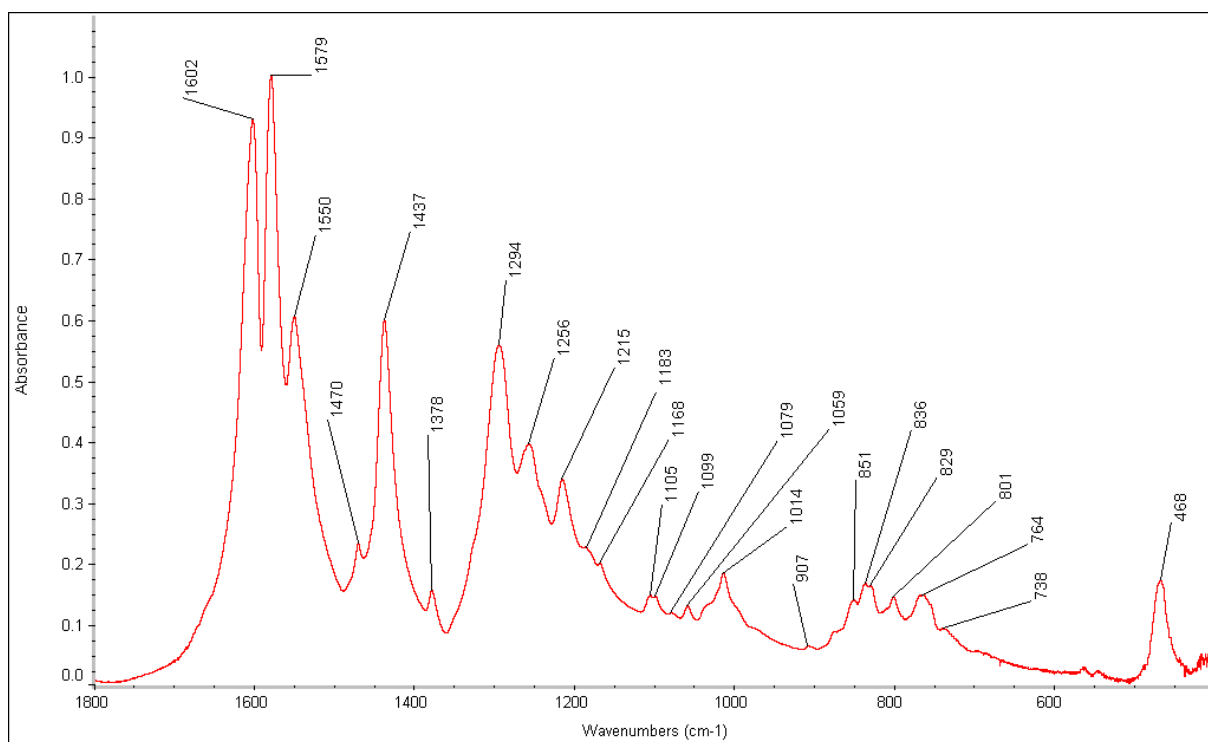
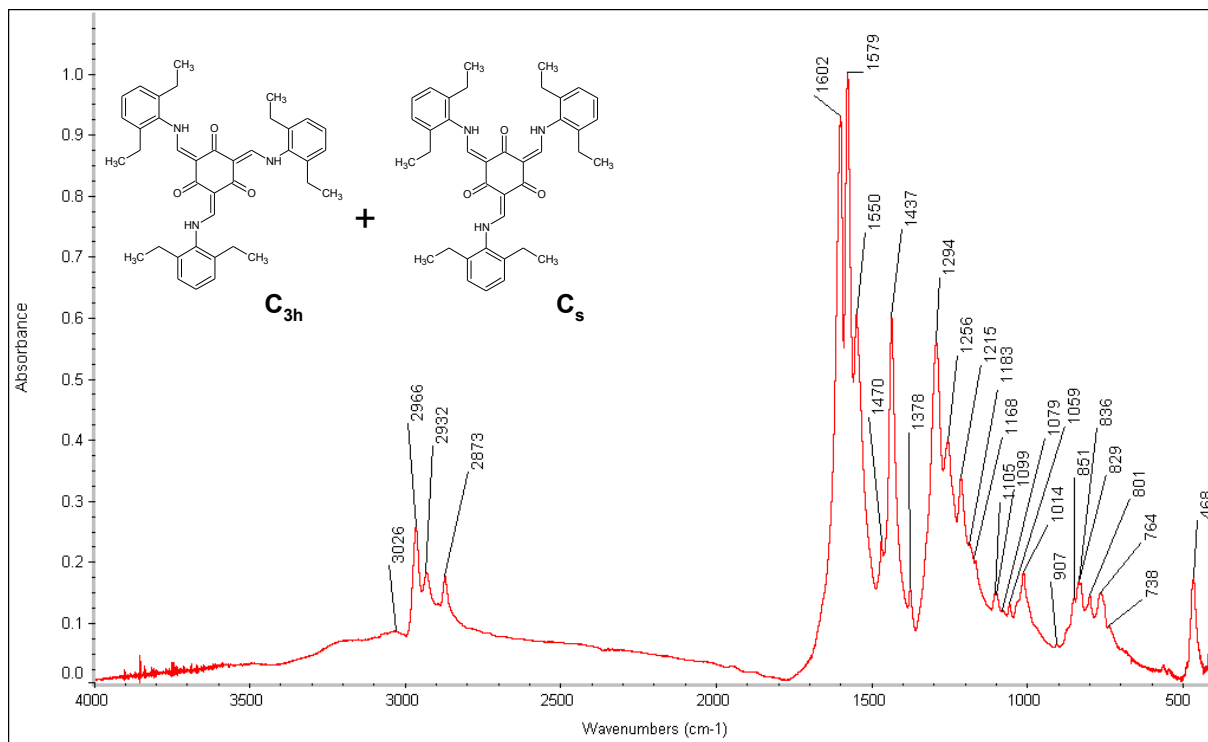
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Operator: Marian Olejnik

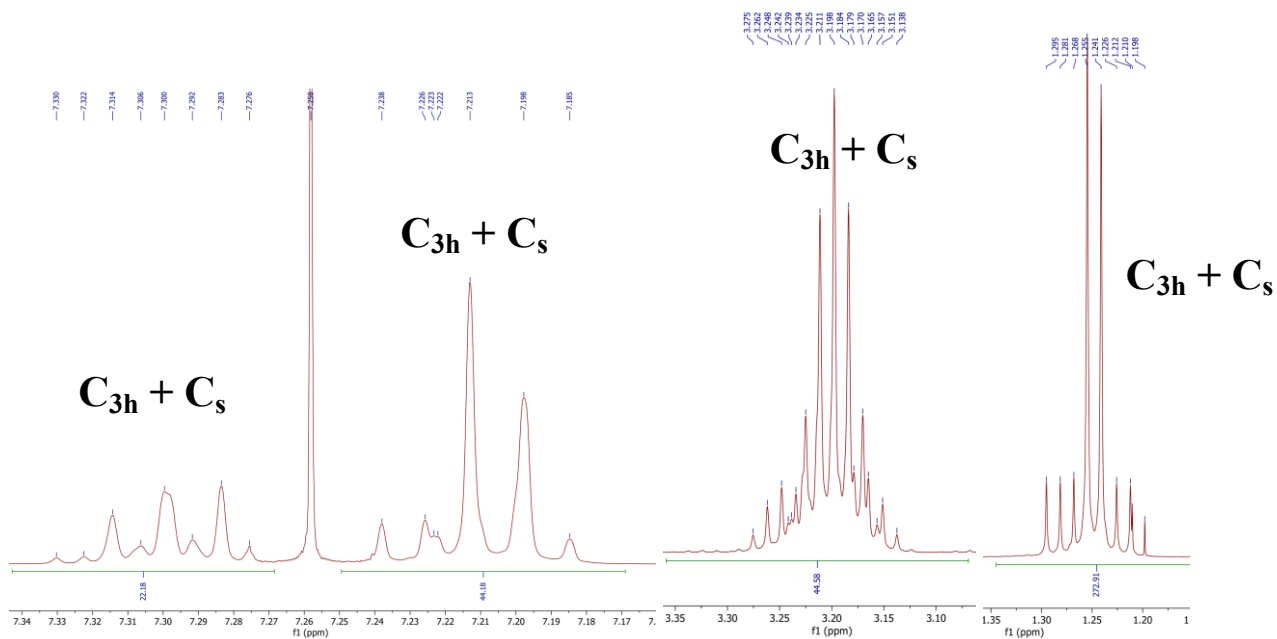
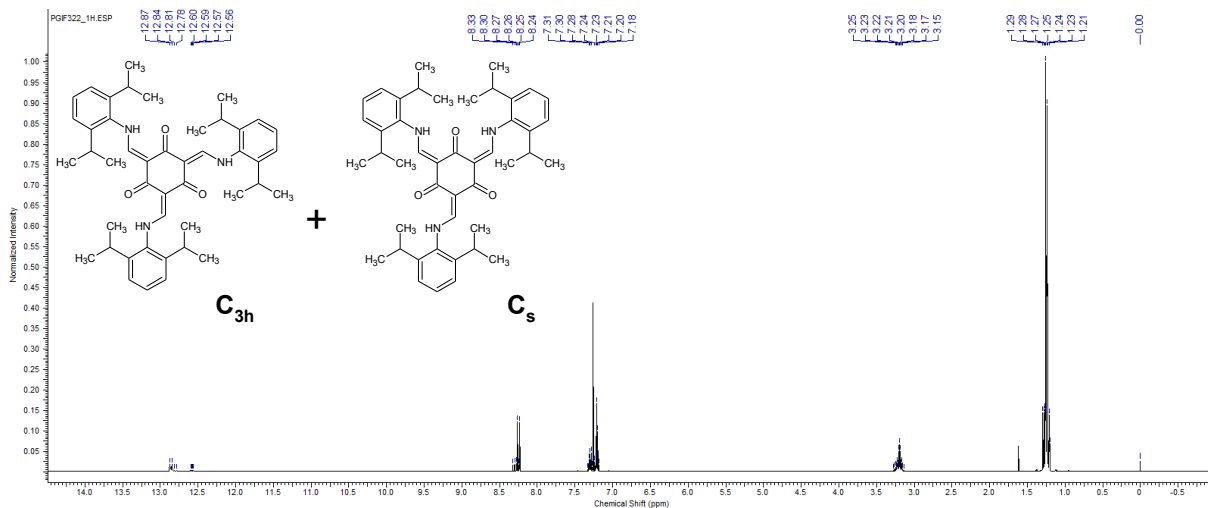
Voltage EI+

540

Spectrum S14. HR-MS spectrum of **dEt** (EI⁺)

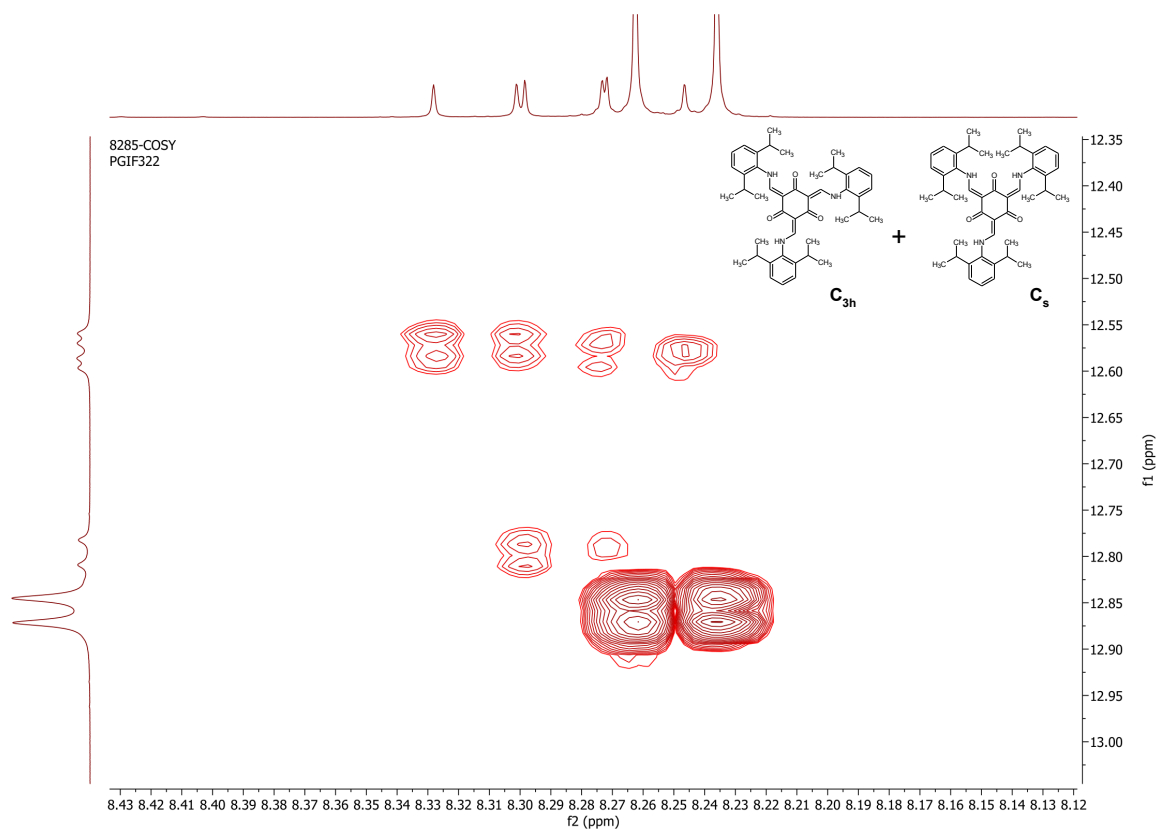
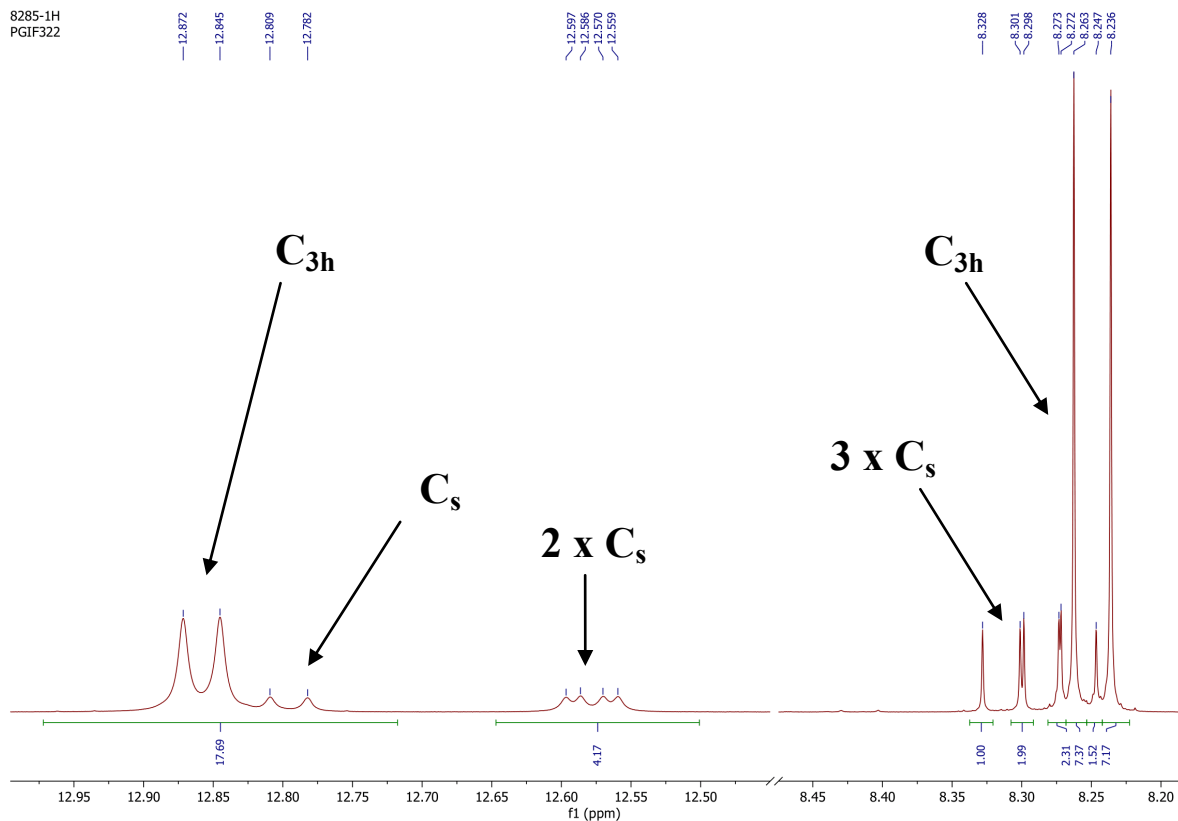


Spectrum S15. IR spectrum of **dEt** (KBr)

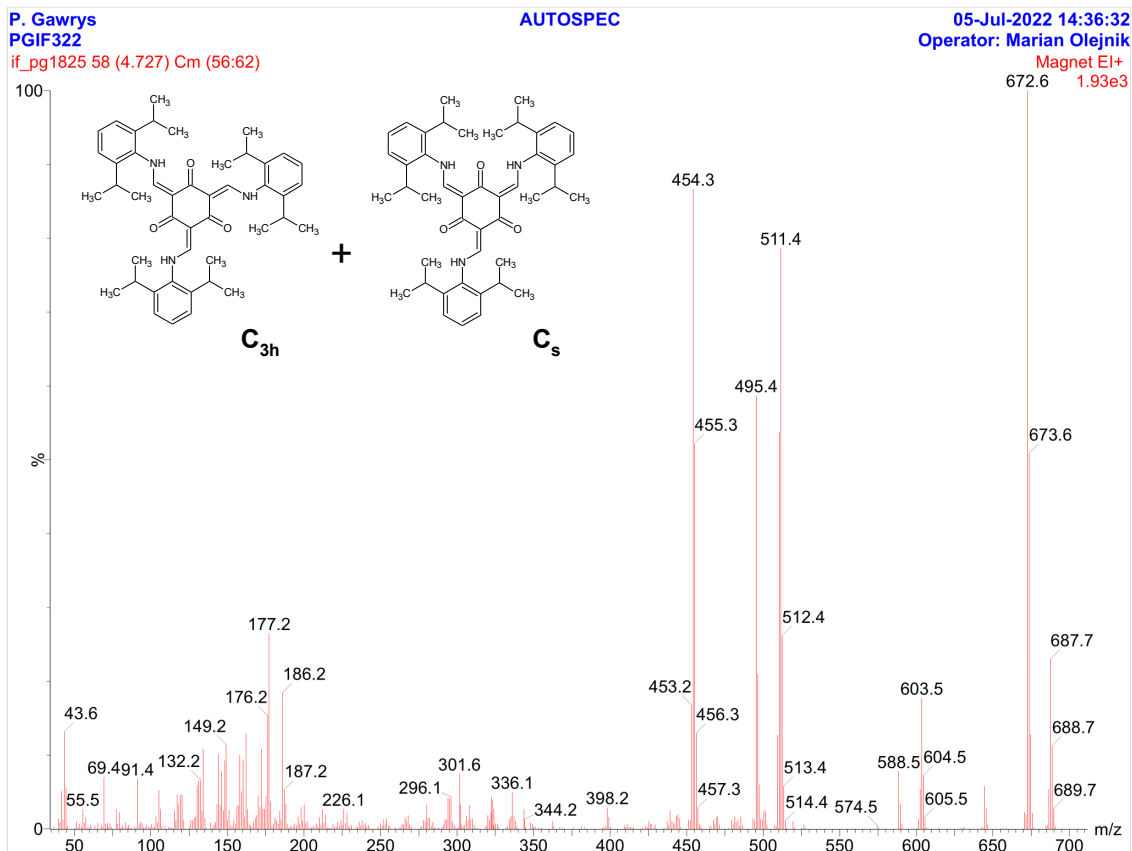


Spectrum S16. ^1H FT-NMR spectrum of **dIpr** (CDCl_3) (with extended diagnostic region)

8285-1H
PGIF322



Spectrum S17. ¹H-¹H COSY FT-NMR spectrum of **dIpr** (CDCl₃) (diagnostic region)



Spectrum S18. LR-MS spectrum of **dIpr** (EI^+)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 40.0 PPM / DBE: min = -1.5, max = 80.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

8 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-100 H: 0-200 N: 3-3 O: 3-3

P. Gawrys

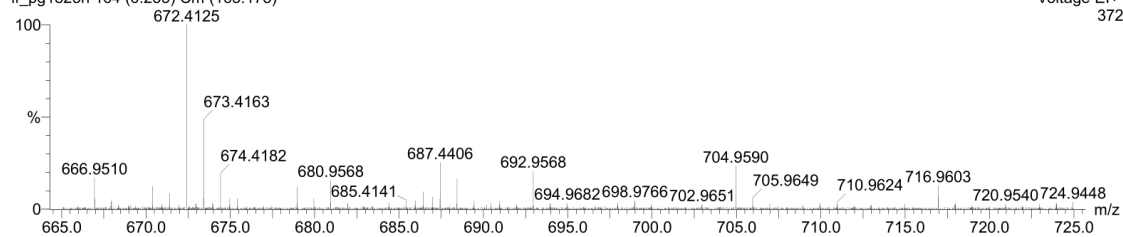
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06-Jul-2022 17:59:46

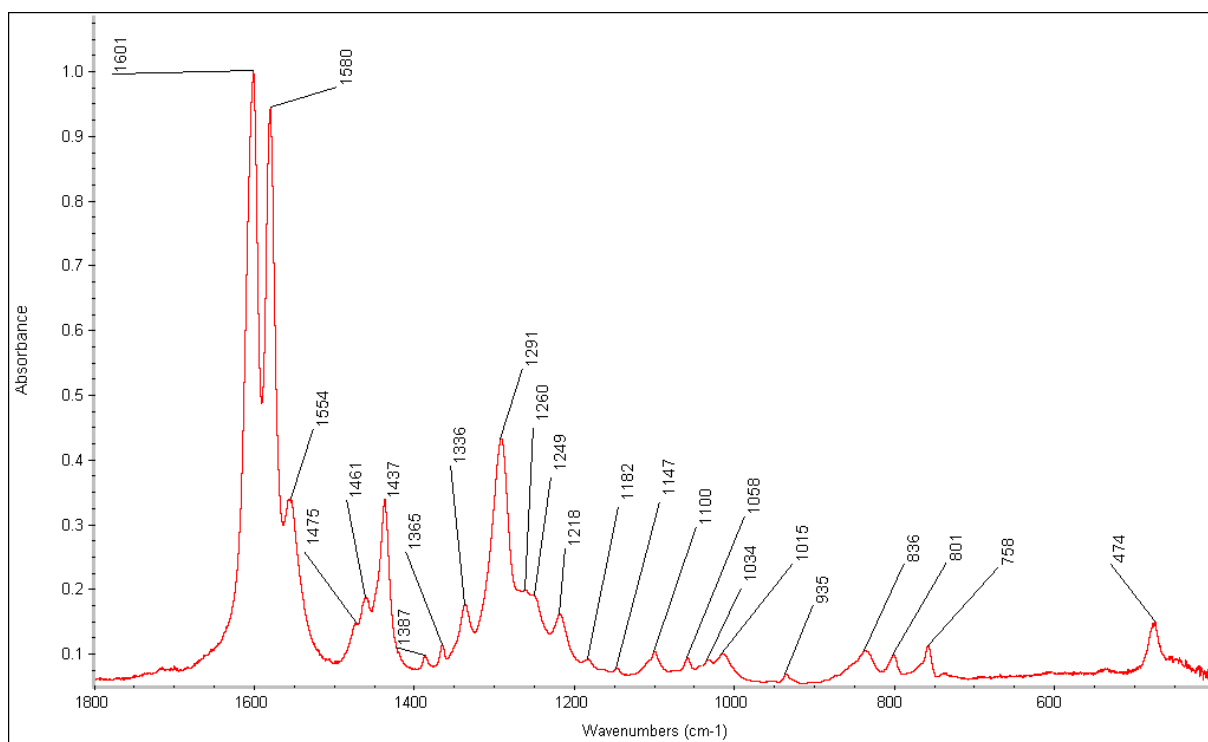
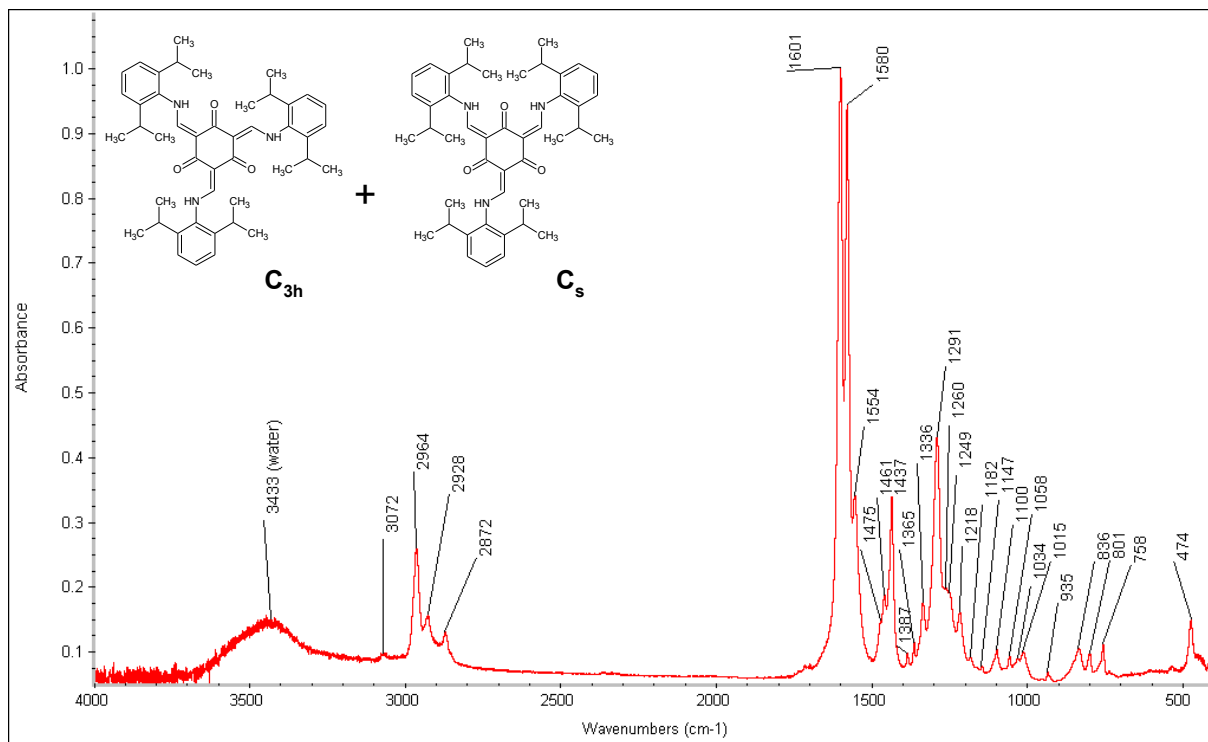
Operator: Marian Olejnik

Voltage EI+

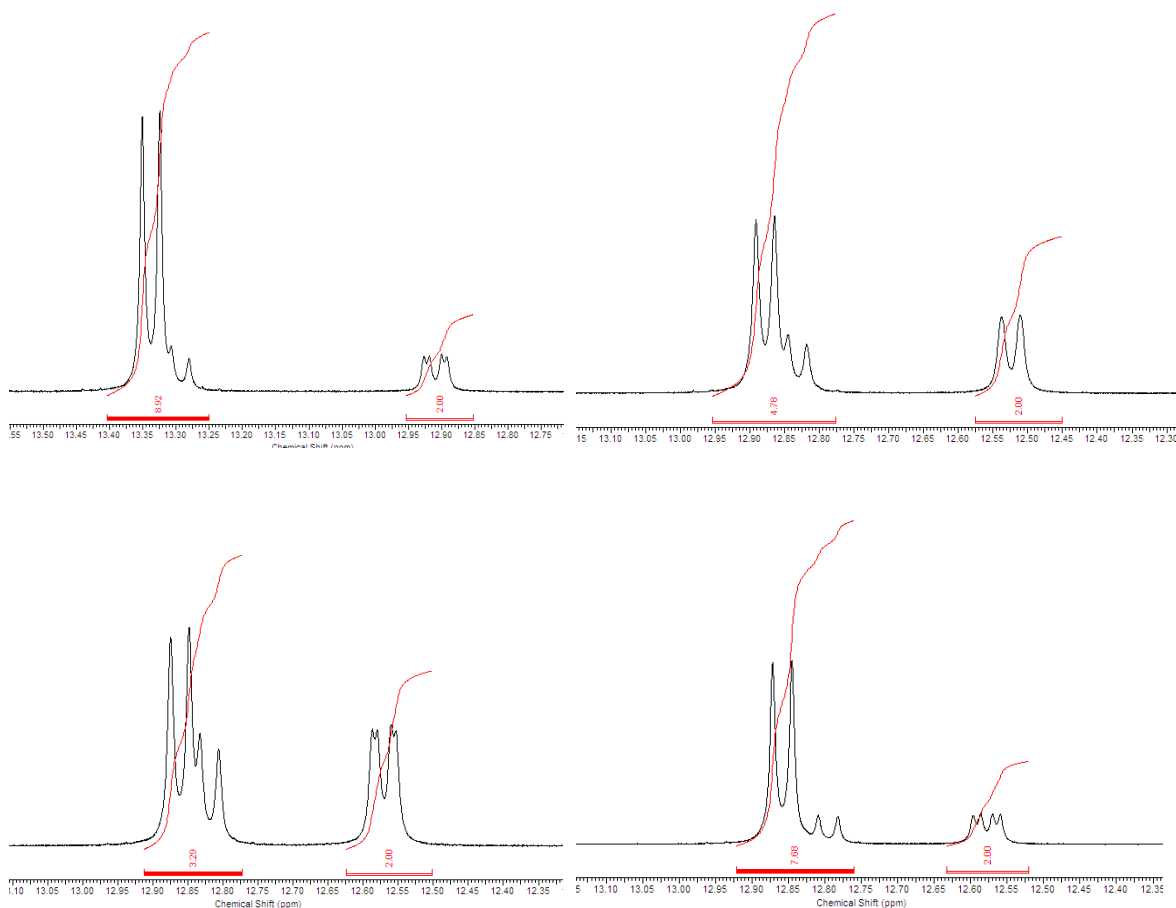
372



Spectrum S19. HR-MS spectrum of **dIpr** (EI^+)



Spectrum S20. IR spectrum of **dIpr** (KBr)



Spectrum S21. The integration values of NH protons of the studied TSANs used for the determination of the diastereoisomeric composition. It was arbitrarily established that the sum of the integration values of NH protons of the C_s diastereoisomer is equal to the value of 3.

Note: Percentage values were rounded to the nearest multiple of 5.

dH (up left) $C_{3h} : C_s = 8 : 3 \approx 70\% C_{3h}$ and $30\% C_s$

dMe (up right) $C_{3h} : C_s = (3.8) : 3 \approx 55\% C_{3h}$ and $45\% C_s$

dEt (down left) $C_{3h} : C_s = (2.3) : 3 \approx 45\% C_{3h}$ and $55\% C_s$

dIpr (down right) $C_{3h} : C_s = (6.7) : 3 \approx 70\% C_{3h}$ and $30\% C_s$