

## Electronic Supporting Information

### Substituent effects on the photophysical properties of tris(salicylideneanilines)

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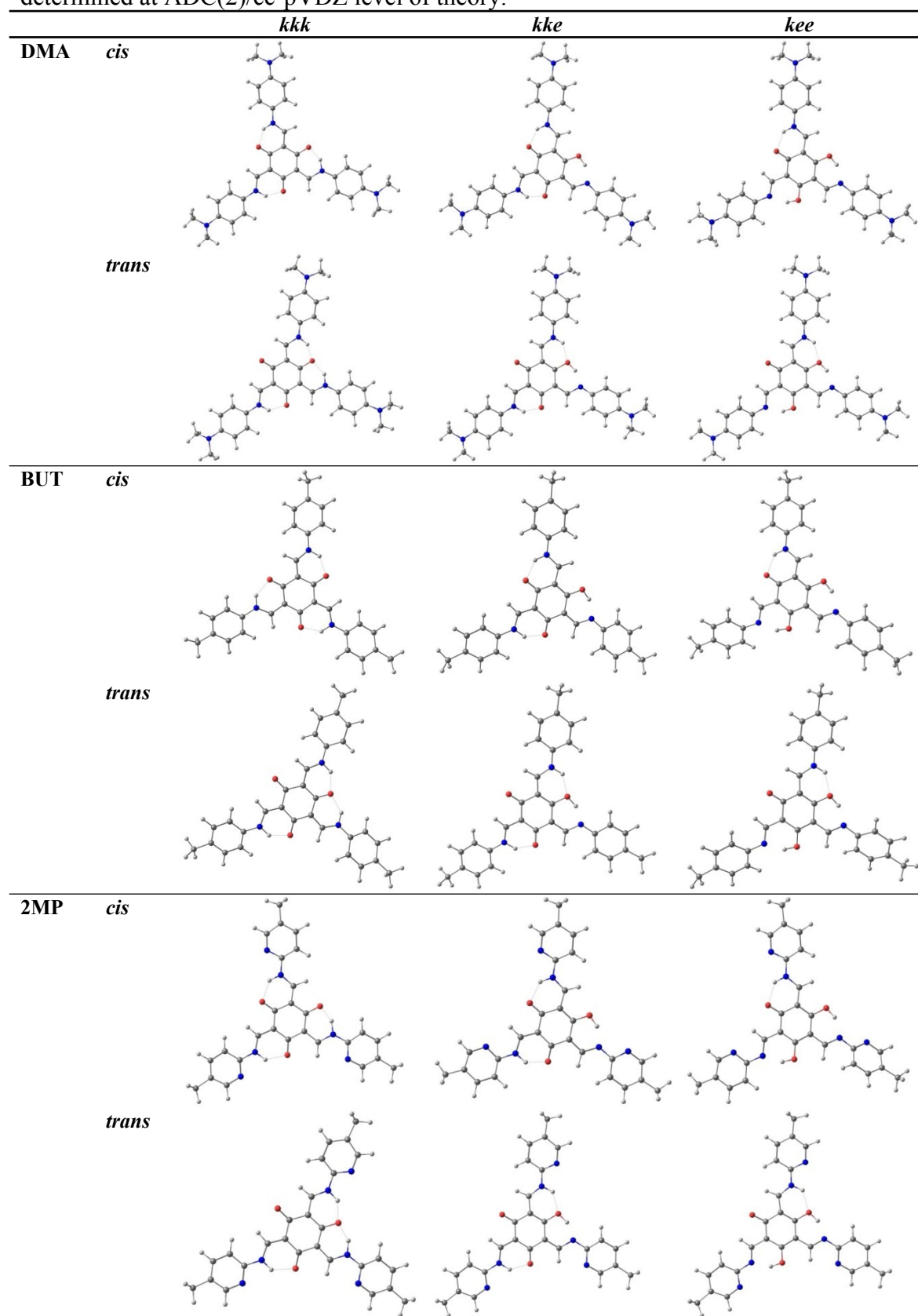
and **2MP** computed at MP2/ADC(2)/cc-pVDZ level of theory. Solid levels denote the adiabatic (optimised) energy of a given state and dashed levels denote the vertical energy of the absorbing/fluorescing state computed at the optimised geometry of the respective states. Barriers are shown in red. Energy (in eV) is given with respect to the ground-state equilibrium of the respective *trans-**kkk*** isomers.

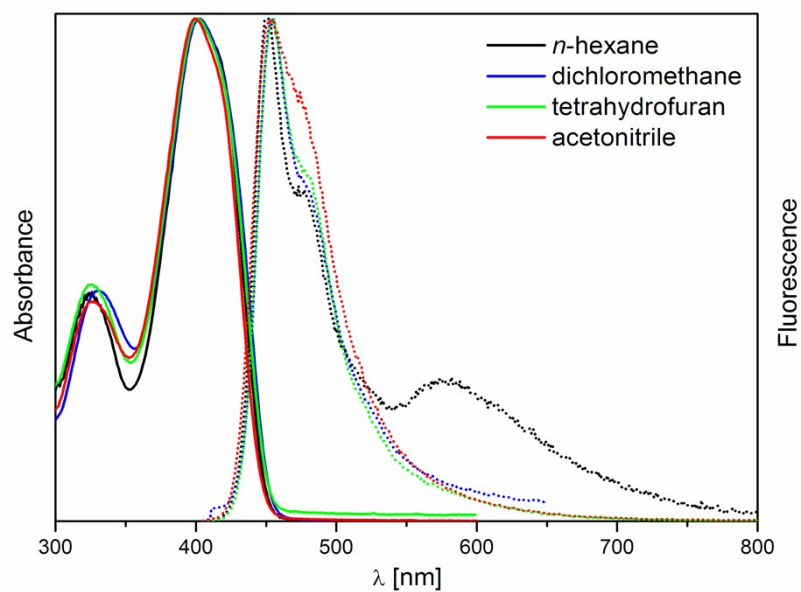
**Figure S9a.**  $S_1$ - $S_0$  electron density difference computed at ADC(2)/cc-pVDZ level of theory. Red (blue) indicates electron acceptor (donor) regions. **b.** Minimum energy profiles for hydrogen transfer in the  $S_1$  state of **DMA**, computed at ADC(2)/cc-pVDZ level of theory. Vertical profiles of the ground state computed at the relevant excited-state geometries are denoted by open symbols connected by dashed line.

**Figure S10.** Minimum energy profiles for *cis-**kkk***  $\rightarrow$  *trans-**kkk*** reaction of **DMA** and **2MP** computed at MP2/ADC(2)/cc-pVDZ level of theory, respectively. Symbols connected by solid line denote energy profile optimised in the  $S_1$  state, while dashed lines denotes vertical energy of the  $S_0$ .

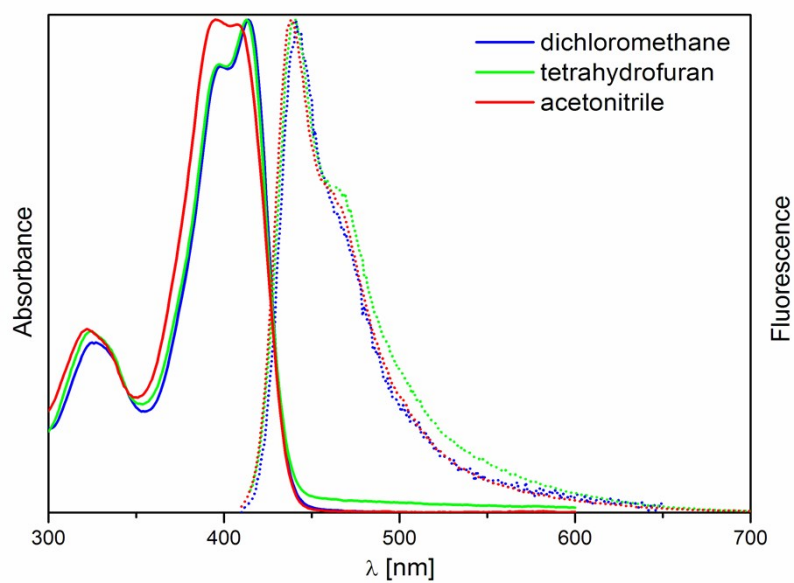
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**Table S1.** Photophysically relevant conformers of tris(salicylideneaniline) derivatives, determined at ADC(2)/cc-pVDZ level of theory.



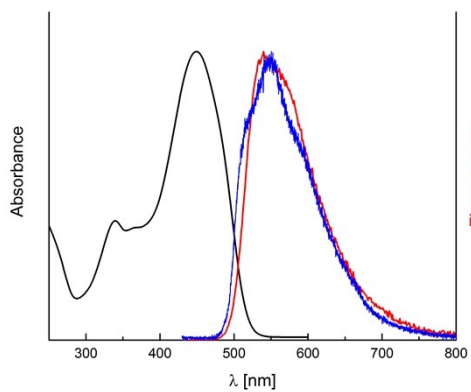


### TBU

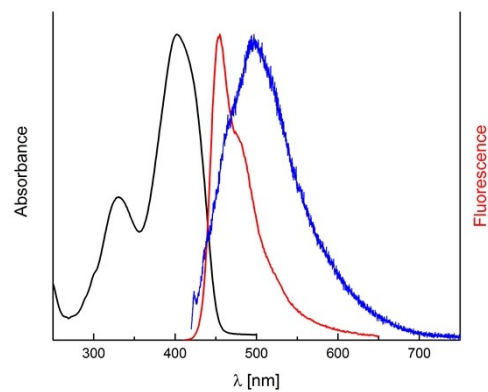


### 2MP

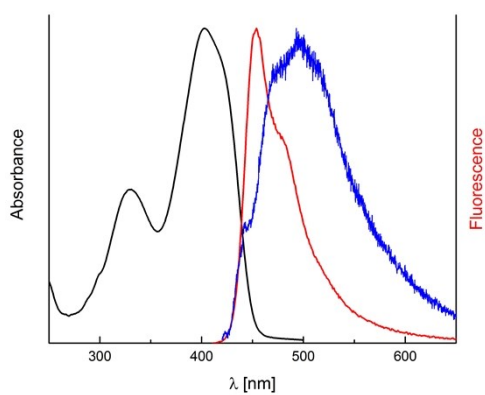
**Figure S1.** Steady-state absorption and emission spectra of **TBU** and **2MP** measured in *n*-hexane, dichloromethane, tetrahydrofuran and acetonitrile solution.



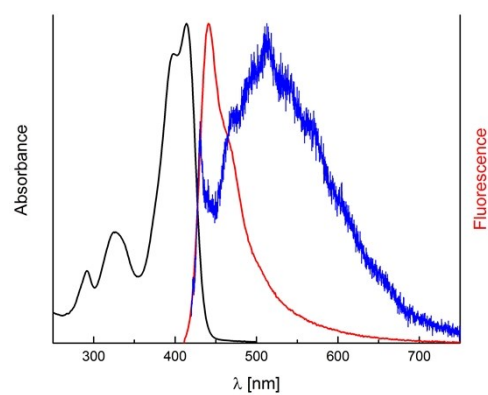
**DMA**



**BUT**

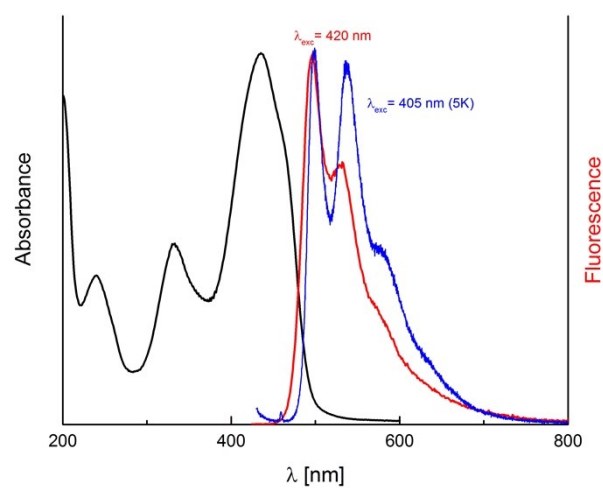


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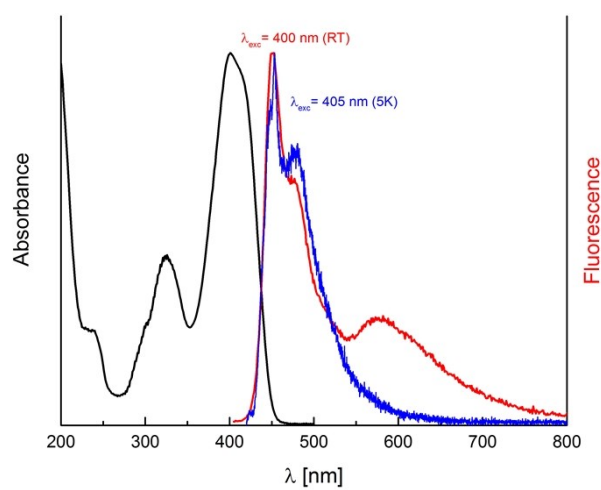


**2MP**

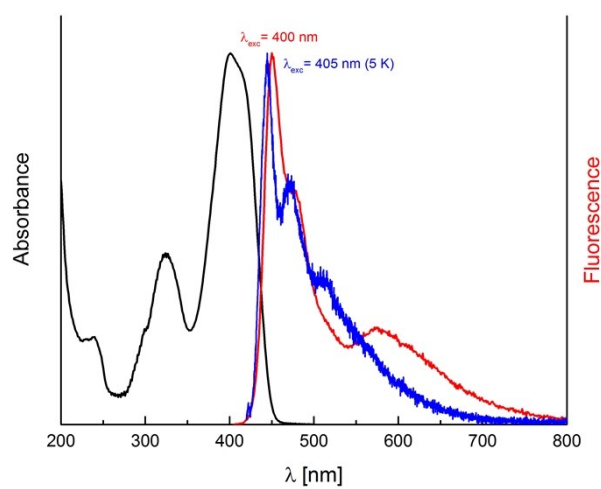
**Figure S2.** Absorption (black) and emission spectra of **DMA**, **BUT**, **TBU** and **2MP** measured in dichloromethane solution at room (blue) and 5 Kelvin (green) temperature.



**DMA**

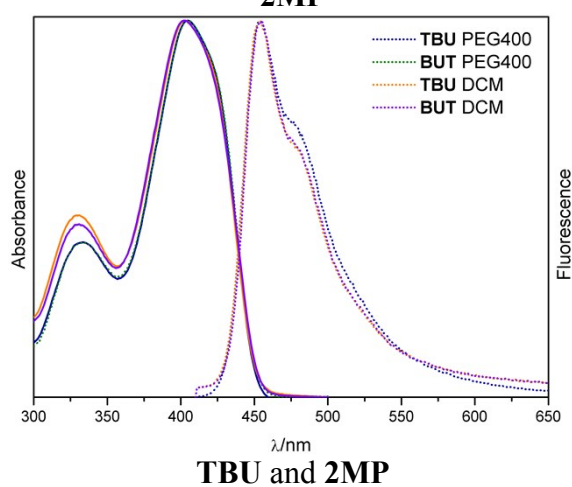
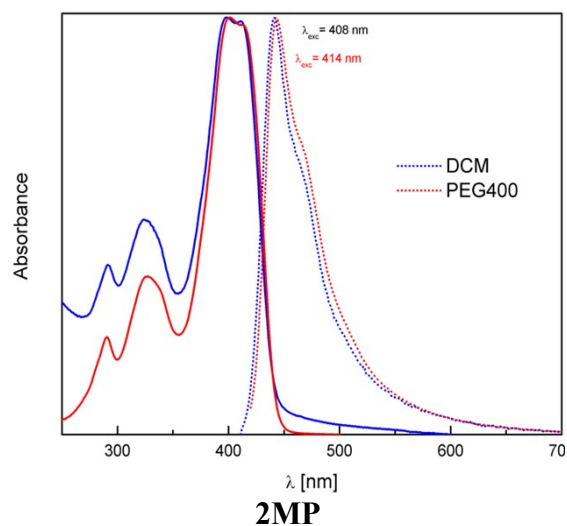


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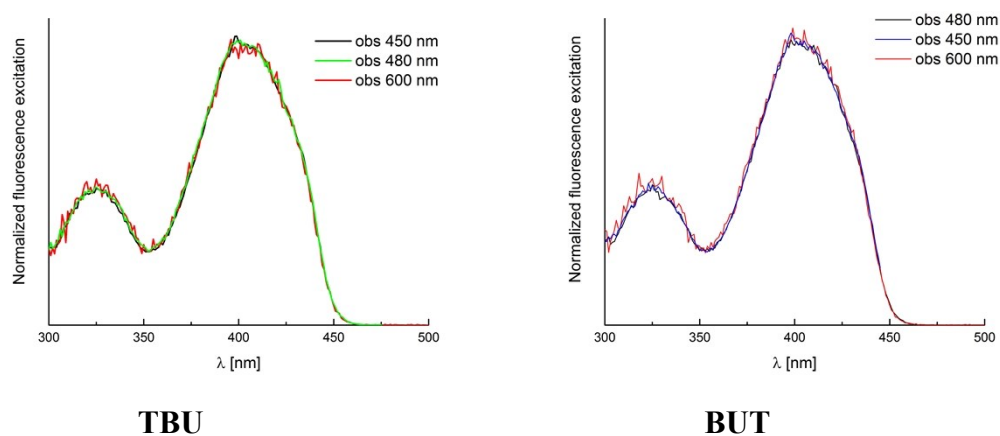


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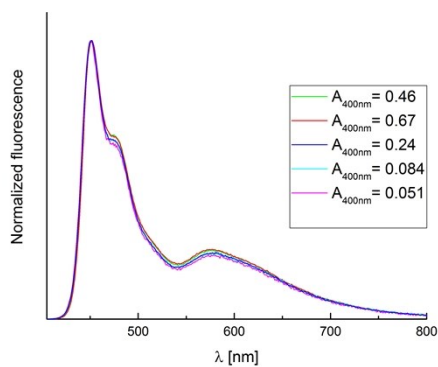
**Figure S3.** Absorption (black) and emission spectra of **DMA**, **BUT** and **TBU** measured in *n*-hexane at room (red) and 5 K (blue) temperature.



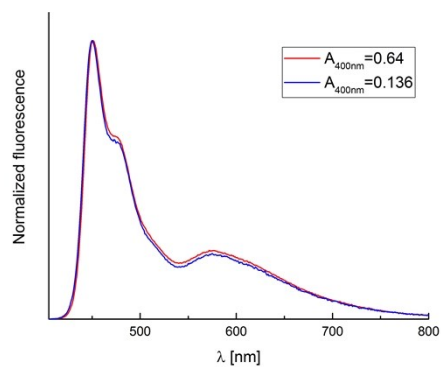
**Figure S4.** Absorption and emission spectra of **2MP**, **TBU** and **BUT** measured in dichloromethane solution and poly(ethylene glycol) 400.



**Figure S5.** Normalised fluorescence excitation spectra of **TBU** and **BUT** measured in *n*-hexane at room temperature.

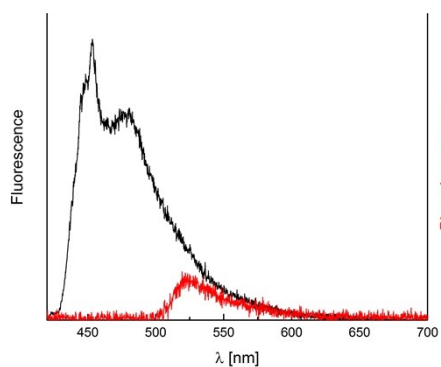


**BUT**

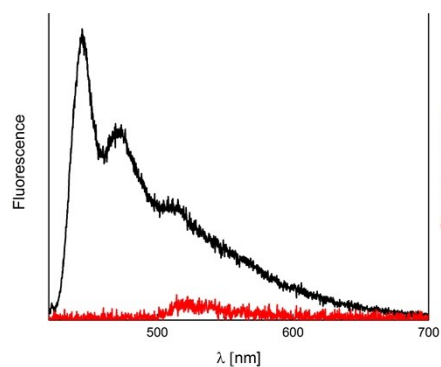


**TBU**

**Figure S6.** Normalised fluorescence spectra of **BUT** and **TBU** measured in *n*-hexane for different concentrations at room temperature.



**BUT**



**TBU**

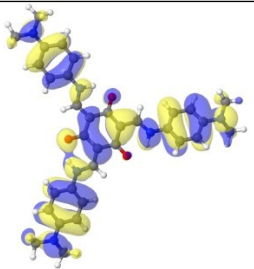
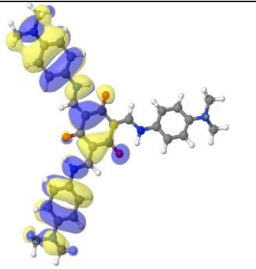
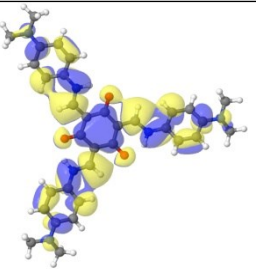
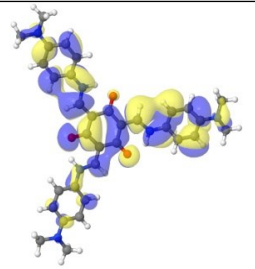
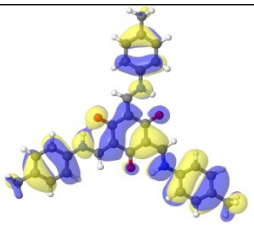
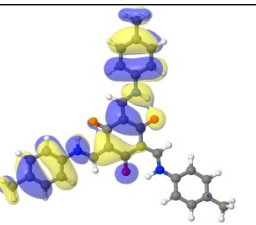
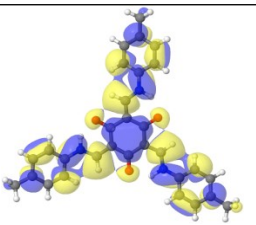
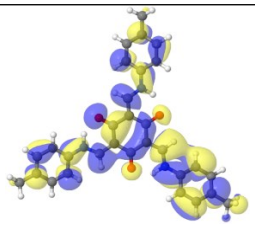
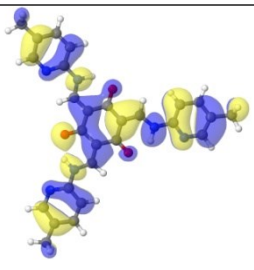
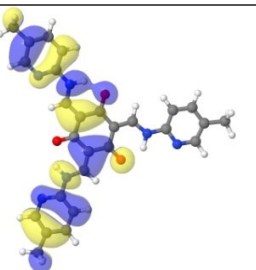
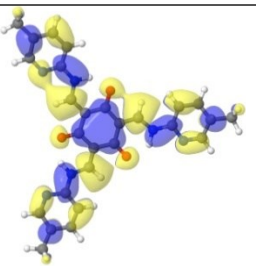
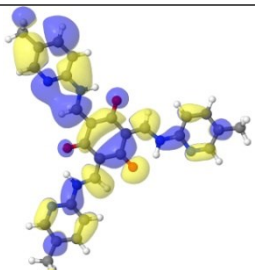
**Figure S7.** Emission spectra (phosphorescence – red; fluorescence – black) of **BUT** and **TBU** in *n*-hexane at 5K obtained with  $\lambda_{\text{exc}} = 405$  nm. Measured phosphorescence lifetimes for **BUT** in *n*-hexane and dichloromethane ( $\lambda_{\text{obs}} = 523$  nm) were 140 ms and 115 ms, respectively.



**Table S2a.** Vertical transition energy ( $\Delta E$ ), oscillator strength ( $f$ ), dipole moment ( $\mu$ ), and leading electronic configurations of *cis-**kkk*** isomers of **DMA**, **BUT** and **2MP** computed with ADC(2)/cc-pVDZ method at the MP2/cc-pVDZ equilibrium geometry of the ground state.

State	$\Delta E/eV$	$f$	$\mu/\text{Debye}$	el. conf.
<b>DMA</b>				
$S_0$	0.00	-	1.22	(150a) <sup>2</sup>
$^1\pi\pi^*$	3.13	1.12	4.98	0.84(150a-151a)
$^1\pi\pi^*$	3.19	1.13	2.14	0.83(149a-151a)
$^1n\pi^*$	3.56	0.00	1.27	0.85(141a-151a)
<b>BUT</b>				
$S_0$	0.00	-	0.05	(126a) <sup>2</sup>
$^1\pi\pi^*$	3.33	1.04	1.88	0.85 (126a-127a)
$^1\pi\pi^*$	3.33	1.04	1.85	0.85 (125a-127a)
$^1n\pi^*$	3.52	0.00	0.02	0.87 (117a-127a)
<b>2MP</b>				
$S_0$	0.00	-	2.98	(126a) <sup>2</sup>
$^1\pi\pi^*$	3.36	1.05	3.98	0.65 (125a-127a)
$^1\pi\pi^*$	3.40	1.06	1.45	0.63 (126a-127a)
$^1n\pi^*$	3.93	0.00	3.10	0.64 (124a-127a)

**Table S2b.** Relevant molecular  $\pi$  orbitals involved into the lowest electronic excitations.

HOMO		LUMO	
<b>DMA</b>			
<i>149a</i>	<i>150a</i>	<i>151a</i>	<i>152a</i>
			
<b>BUT</b>			
<i>125a</i>	<i>126a</i>	<i>127a</i>	<i>128a</i>
			
<b>2MP</b>			
<i>125a</i>	<i>126a</i>	<i>127a</i>	<i>128a</i>
			

**Table S3.** Vertical transition energy ( $\Delta E$ ), oscillator strength ( $f$ ), dipole moment ( $\mu$ ), and leading electronic configurations of *trans-kkk* isomers of **DMA**, **BUT** and **2MP** computed with ADC(2)/cc-pVDZ method at the MP2/cc-pVDZ equilibrium geometry of the ground state.

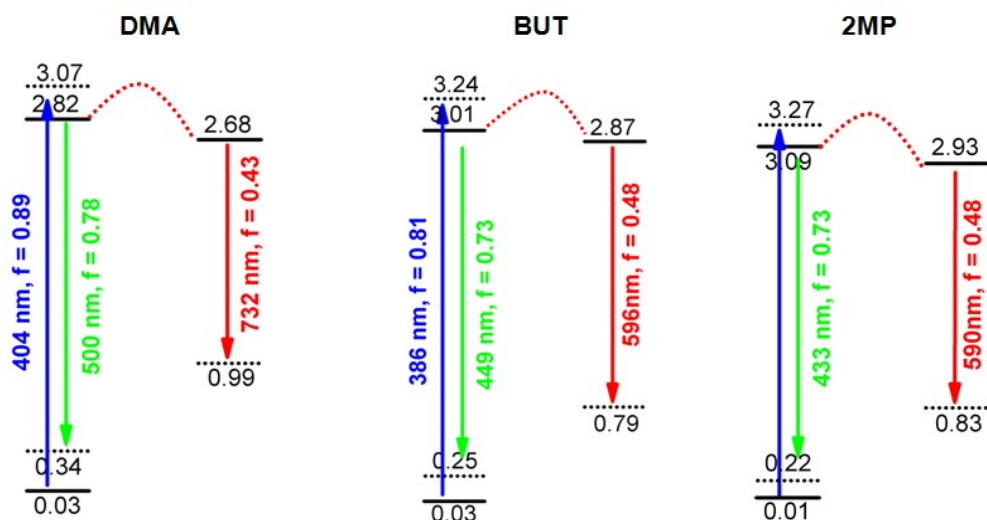
State	$\Delta E/eV$	$f$	$\mu/\text{Debye}$	el. conf.
<b>DMA</b>				
$S_0$	0.03	-	2.18	(150a) <sup>2</sup>
$^1\pi\pi^*$	3.07	0.89	4.34	0.82(149a-151a)
$^1\pi\pi^*$	3.22	1.21	3.46	0.74(150a-151a)
$^1n\pi^*$	3.53	0.00	0.50	0.85(141a-151a)
<b>BUT</b>				
$S_0$	0.03	-	2.32	(126a) <sup>2</sup>
$^1\pi\pi^*$	3.21	0.81	2.72	0.85(126a-127a)
$^1\pi\pi^*$	3.40	1.15	1.24	0.76(125a-127a)
$^1n\pi^*$	3.48	0.00	0.36	0.86(117a-127a)
<b>2MP</b>				
$S_0$	0.01	-	2.68	(126a) <sup>2</sup>
$^1\pi\pi^*$	3.26	0.83	2.69	0.86(126a-127a)
$^1n\pi^*$	3.35	0.00	2.18	0.87(117a-127a)
$^1\pi\pi^*$	3.47	1.23	2.59	0.78(125a-127a)

**Table S4.** Adiabatic energy of the fluorescing state ( $E(S_1)$ ), vertical transition energy ( $\Delta E$ ), oscillator strength ( $f$ ) and dipole moments ( $\mu(S_1)$  and  $\mu(S_0)$ ), computed with ADC(2)/cc-pVDZ method at the equilibrium geometry of the  $S_1$  state of **DMA** and **2MP**.

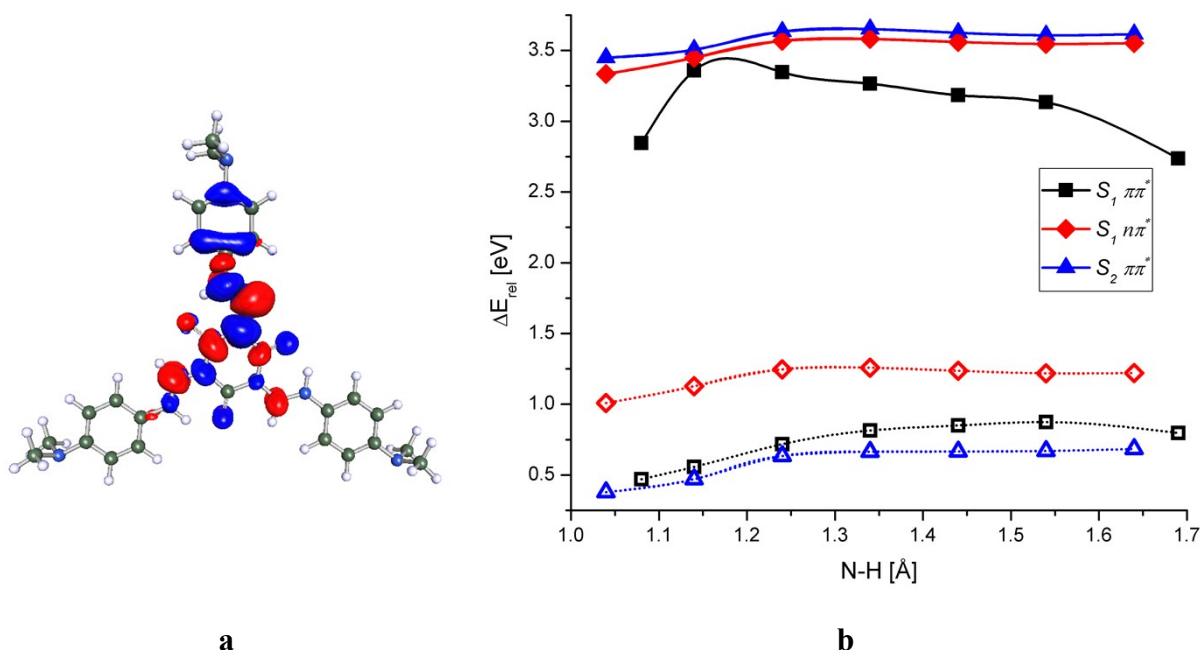
Isomer	$E(S_1)/eV$	$\Delta E/eV$	$f$	$\mu(S_1)/D$	$\mu(S_0)/D$
<b>DMA</b>					
<i>cis-kkk</i>	2.85	2.44	0.86	10.97	1.09
<i>trans-kkk</i>	2.82	2.48	0.78	7.61	1.95
<i>cis-kke</i>	2.67	1.86	0.54	12.42	6.40
<i>trans-kke</i>	2.68	1.69	0.43	13.16	5.40
<b>BUT</b>					
<i>cis-kkk</i>	3.11	2.88	0.95	1.80	1.24
<i>trans-kkk</i>	2.98	2.76	0.73	1.86	1.66
<i>cis-kke</i>	2.88	2.21	0.57	4.10	6.64
<i>trans-kke</i>	2.87	2.08	0.48	5.87	4.97
<b>2MP</b>					
<i>cis-kkk</i>	3.19	2.97	0.91	2.86	3.55
<i>trans-kkk</i>	3.09	2.86	0.73	1.65	3.14
<i>cis-kke</i>	3.05	2.33	0.61	8.45	3.75
<i>trans-kke</i>	2.93	2.10	0.48	2.77	8.32

**Table S5.** Selected molecular structural parameters of optimised  $^1\pi\pi^*$ ,  $^1n\pi^*$ ,  $^3\pi\pi^*$ ,  $^3n\pi^*$  excited states of **BUT** and **DMA** obtained at ADC(2)/cc-pVDZ level of theory. Labels are shown in the Scheme 1.

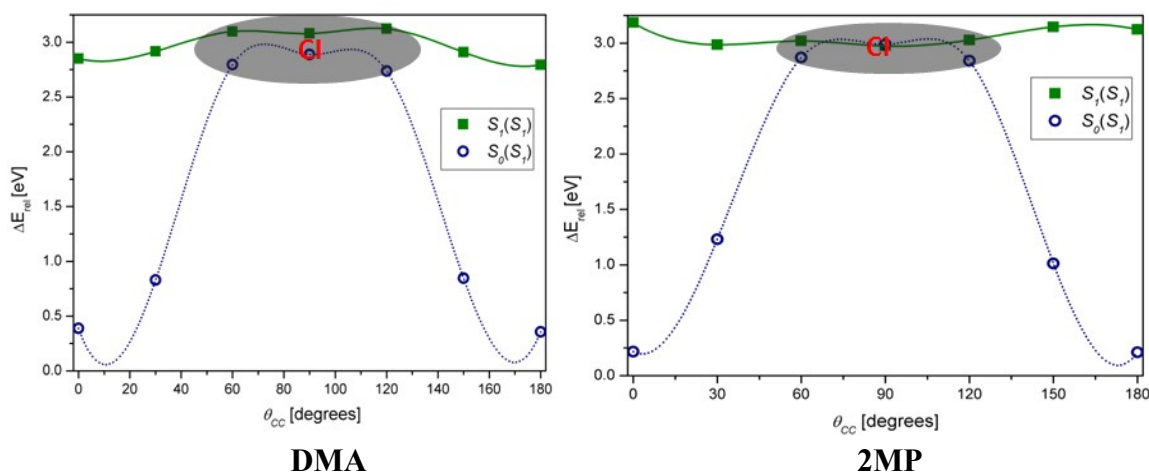
Bond length [Å]	$^1\pi\pi^*$	$^1n\pi^*$	$^3\pi\pi^*$	$^3n\pi^*$
<b>BUT</b>				
<b>N<sub>10</sub>-H<sub>11</sub></b>	1.07	1.03	1.05	1.03
<b>O<sub>12</sub>-H<sub>11</sub></b>	1.56	1.82	1.68	1.82
<b>N<sub>4</sub>-H<sub>5</sub></b>	1.04	1.03	1.04	1.04
<b>O<sub>6</sub>-H<sub>5</sub></b>	1.77	1.77	1.77	1.77
<b>N<sub>7</sub>-H<sub>8</sub></b>	1.04	1.02	1.04	1.02
<b>O<sub>9</sub>-H<sub>8</sub></b>	1.75	1.99	1.75	1.99
<b>DMA</b>				
<b>N<sub>10</sub>-H<sub>11</sub></b>	1.07	1.03	1.07	1.03
<b>O<sub>12</sub>-H<sub>11</sub></b>	1.59	1.86	1.58	1.81
<b>N<sub>4</sub>-H<sub>5</sub></b>	1.04	1.03	1.04	1.04
<b>O<sub>6</sub>-H<sub>5</sub></b>	1.76	1.80	1.75	1.76
<b>N<sub>7</sub>-H<sub>8</sub></b>	1.04	1.02	1.04	1.02
<b>O<sub>9</sub>-H<sub>8</sub></b>	1.72	1.99	1.73	1.99



**Figure S8.** General photophysical scheme for *trans* isomers of **DMA**, **BUT** and **2MP** computed at MP2/ADC(2)/cc-pVDZ level of theory. Solid levels denote the adiabatic (optimised) energy of a given state and dashed levels denote the vertical energy of the absorbing/fluorescing state computed at the optimised geometry of the respective states. Barriers are shown in red. Energy (in eV) is given with respect to the ground-state equilibrium of the respective *trans*-*kkk* isomers.



**Figure S9a.**  $S_1$ - $S_0$  electron density difference computed at ADC(2)/cc-pVDZ level of theory. Red (blue) indicates electron acceptor (donor) regions. **b.** Minimum energy profiles for hydrogen transfer in the  $S_1$  state of **DMA**, computed at ADC(2)/cc-pVDZ level of theory. Vertical profiles of the ground state computed at the relevant excited-state geometries are denoted by open symbols connected by dashed line.



**Figure S10.** Minimum energy profiles for *cis- $kkk$*   $\rightarrow$  *trans- $kkk$*  reaction of **DMA** and **2MP** computed at MP2/ADC(2)/cc-pVDZ level of theory, respectively. Symbols connected by solid line denote energy profile optimised in the  $S_1$  state, while dashed lines denotes vertical energy of the  $S_0$ .

## Instruments and methods

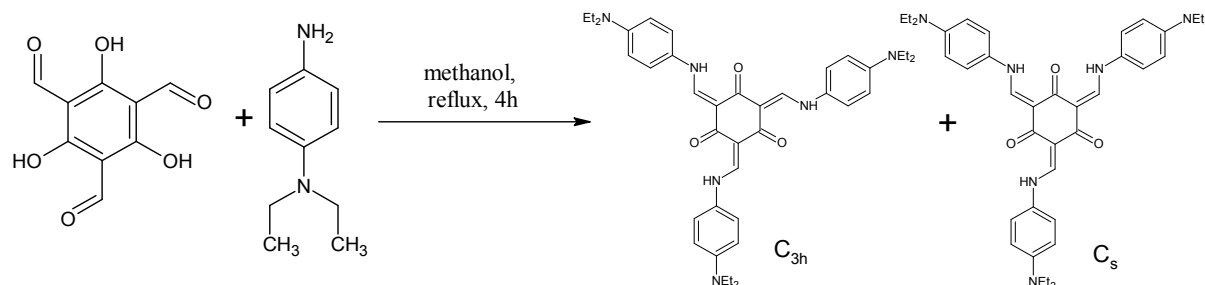
<sup>1</sup>H FT-NMR spectra were recorded using Bruker AVANCE 500 MHz spectrometer. The chemical shifts are given vs. TMS as an internal standard. The coupling constants were calculated by using chemical shifts reported in Hz unit. FT infrared spectra were recorded using Thermo-Nicolet Nexus 670 FTIR 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. 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 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 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 and water exclusion.

### 1. DMA

(2E,4E,6E)-2,4,6-tris {[4-(diethylamino)phenylamino]methylidene} cyclohexane-1,3,5-trione (**C<sub>3h</sub>** isomer) and (2Z)-2,4,6-tris {[4-(diethylamino)phenylamino]methylidene} cyclohexane-1,3,5-trione (**C<sub>s</sub>** isomer)



**Scheme S1.** Synthesis of **DMA**.

In a one necked round bottoms flask (250 ml) was put 1,3,5-triformylphloroglucinol (0.21 g, 1 mmol) and *N,N*-diethyl-4-aminoaniline (*N,N*-diethyl-*p*-phenylenediamine) (0.99 g, 6 mmol, 6 eq. assuming 100% purity of the amine) and methanol (60 ml). The mixture while stirring was heated to reflux. After 15 minutes the product is already present in the reaction mixture (TLC - DCM or DCM+5% ethyl acetate). After 4 hours the very dark black solution was cooled slightly and methanol was gradually added (4 x 30 ml). Next, the black solution was mandatorily put in the freezer for minimum 16 hours (-25°C, preferably overnight). The next day the black supernatant liquid was decanted as well as possible. (This is the only convenient method to get rid of the excess of the amine and black dyes resulting from oxidation of commercial *N,N*-diethyl-4-aminoaniline.) The residue (black tar) was dried at 50°C on the rotary evaporator and dissolved in dichloromethane (10 ml) and put onto column chromatography [50 ml SiO<sub>2</sub> suspended in hexanes, 1 inch wide column]. First eluent used

was dichloromethane (25 ml) followed by dichloromethane + 5% ethyl acetate (100 ml) to elute the dark brown impurities. Then the product was eluted with dichloromethane + 10-15% ethyl acetate (the product has a very strong affinity to silica gel). The dark brown coloured fraction (F1) was collected (125 ml) and evaporated to give red-brown foil (0.56 g, 82%). Additional fraction (F2) was collected (25 ml) which contained impure product and the column was finally eluted with neat ethyl acetate (or acetone) to recover anything adsorbed on the silica gel (50 ml) (F3). These two last fractions (F2, F3) were discarded after determining of the final yield since the attempt to repeat the column required too polar eluent to give satisfactory separation. The obtained product (0.56 g, 82%) from the evaporation (F1) was dissolved in boiling methanol (80 ml) in the round bottom flask (100 ml) and left in the freezer (-25°C) for at least 16 hours (preferably overnight). The next day the product appeared as a red-orange solid adsorbed on the surface of the flask. The supernatant liquid was quickly decanted while still cold. The residue was evaporated to dryness at 50°C on the rotary evaporator to accelerate removal of remaining methanol. The mother liquor was kept and evaporated to dryness. Finally, the product was removed from the flask with the aid of metal spatula and dried in the vacuum desiccator for 24 hours at ambient temperature followed by drying in the vacuum oven at 40°C for 6 hours. Red-orange solid (crushed thin film) (0.47 g; 72%). The product stains TLC plates with orange colour. TLC and <sup>1</sup>H NMR analysis indicates that the compound exists in the form of two isomers.

HRMS (EI): calculated [M]<sup>+</sup>: 648.3782, found: 648.3785, error: 0.46 ppm.

<sup>1</sup>H FT-NMR (CDCl<sub>3</sub>+TMS, 298 K, 500 Mhz): 13.51 (doublet, J = 13.3 Hz, N-H proton of C<sub>3h</sub> diastereoisomer), 13.44 (doublet, J = 13.4 Hz, N-H proton of C<sub>s</sub> diastereoisomer), 13.02 (doublet, J = 13.5 Hz, two ideally overlapping N-H protons of C<sub>s</sub> diastereoisomer), 8.75 (doublet, J = 13.2 Hz, =C-H proton of C<sub>s</sub> diastereoisomer), 8.73 (doublet, J = 13.5 Hz, =C-H proton of C<sub>s</sub> diastereoisomer, partially overlaps with peak at 8.75 ppm), 8.67 (doublet, J = 13.2 Hz, =C-H proton of C<sub>3h</sub> diastereoisomer), 8.63 (doublet, J = 13.3 Hz, =C-H proton of C<sub>s</sub> diastereoisomer), 7.16-7.20 (aromatic, complicated multiplet, 6H), 6.66-6.70 (aromatic, complicated multiplet, 6H), 3.34-3.39 (-CH<sub>2</sub>-, multiplet resulting from overlapping quartets, J = 7.1 Hz, 12H), 1.15-1.20 (-CH<sub>3</sub>, multiplet resulting from overlapping triplets, J = 7.2 Hz, 18H).

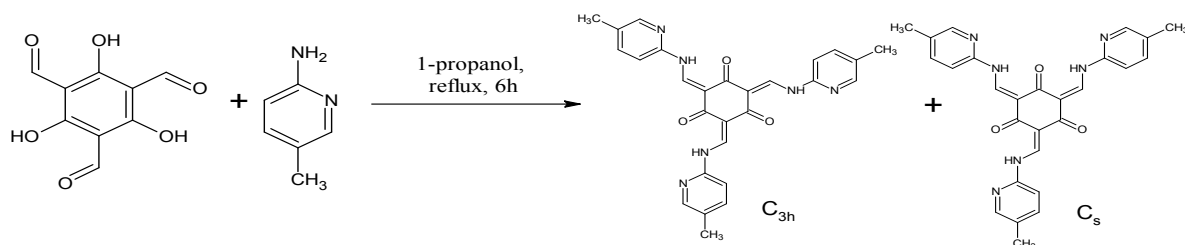
IR (KBr, cm<sup>-1</sup>): 3077, 3048, 2970, 2929, 2890, 2869, 1604, 1573, 1548, 1521, 1452, 1428, 1400, 1374, 1357, 1299, 1263, 1239, 1197, 1155, 1093, 1078, 1035, 1014, 1001, 811, 786.

Elemental analysis: calculated: (C<sub>39</sub>H<sub>48</sub>N<sub>6</sub>O<sub>3</sub>) C(72.19%) H(7.46%) N(12.95%) O(7.40%), found: C(71.45%) H(7.55%) N(12.78%).

Melting point (MeOH): turns into resin in the 128-140°C range, turns dark and becomes much less viscous at 194-196 °C.

## 2. 2MP

(2E,4E,6E)-2,4,6-tris[(5-methyl-2-pyridyl)amino]methylidene)cyclohexane-1,3,5-trione (**C<sub>3h</sub>** isomer) and (2Z)-2,4,6-tris((5-methyl-2-pyridylamino)methylidene)cyclohexane -1,3,5-trione (**C<sub>s</sub>** isomer)



**Scheme S2.** Synthesis of **2MP**.

In a one necked round bottoms flask (not smaller than 250 ml) equipped with large magnetic stir bar (preferably egg-shaped of size not smaller than 3/2 inch  $\times$  1/2 inch) was put 1,3,5-triformylphloroglucinol (0.22 g; 1.05 mmol) and 5-methyl-2-aminopyridine (0.65 g, 6 mmol, 6 equivalents) and 1-propanol (not less than 100 ml). The mixture was heated to reflux and after 15 minutes a very heavy pale yellow precipitate appeared. (The precipitation slows the stirring bar thus more solvent may be added or better dioxane (40 ml)). and the suspension was gently refluxed for 6 hours. Overheating may result in strong bumping. The flask was cooled to 50°C and diluted with methanol to the full volume. After 15 minutes of stirring the mixture was filtered warm on a sinter funnel (G4, 1 inch wide, tedious) and washed with warm methanol (3 x 30 ml). The resulting yellow solid (0.39 g; 77%) was dried overnight in air. Next the powder was transferred to the round bottom flask (100 ml) and stirred with acetone (80 ml) for 16 hours (preferably overnight) at ambient temperature. The suspension was filtered off on a sinter funnel (G4, 1 inch wide) and washed with acetone (3 x 30 ml). (Like in previous filtration, the product darkened somewhat and was difficult to quantitatively remove from the funnel which resulted in some losses. Filtering on narrower funnel would be too tedious as the pores of the sinter funnel get clogged easily.) Mother liquor was evaporated to dryness and kept. Finally, the product was dried in the vacuum desiccator for 24 hours at ambient temperature followed by drying in the vacuum oven at 60°C for 6 hours. Pale yellow amorphous powder (324 mg; 65%). The product stains TLC plates with pale yellow colour. TLC and  $^1\text{H}$  NMR analysis indicates that the compound exists in the form of two isomers.

**HRMS (EI):** calculated  $[\text{M}]^+$ : 480.1904 Da, found: 480.1919, error: 3.12 ppm.

**$^1\text{H}$  NMR (CDCl<sub>3</sub> + TMS, 298 K, 500 Mhz):** 13.40 (doublet,  $J = 13.4$  Hz, N-H proton of **C<sub>3h</sub>** diastereoisomer, almost perfectly overlaps with peak from N-H proton of **C<sub>s</sub>** diastereoisomer), 13.04 (triplet resulting from an overlap from two doublets from two N-H protons of **C<sub>s</sub>** diastereoisomer,  $J_1 = 13.5$  Hz,  $J_2 = 13.5$  Hz), 9.40 (doublet,  $J = 13.4$  Hz, =C-H proton of **C<sub>s</sub>** diastereoisomer), 9.38 (doublet,  $J = 12.6$  Hz, =C-H proton of **C<sub>s</sub>** diastereoisomer, partially overlaps with peak at 9.40 ppm), 9.30 (doublet,  $J = 12.8$  Hz, =C-H proton of **C<sub>3h</sub>** diastereoisomer), 9.28 (doublet,  $J = 12.9$  Hz, =C-H proton of **C<sub>s</sub>** diastereoisomer which partially overlaps with peak at 9.30 ppm), 8.23-8.25 (pyridine ring, multiplet, 3H), 7.54



(pyridine ring, doublet of triplet of doublets,  $J_{ortho} = 8.1$  Hz,  $J_{meta} = 2.3$  Hz,  $J_{benzylic} = 0.6$  Hz,  $C_s$  diastereoisomer), 7.50 (pyridine ring, doublet of doublets of doublets,  $J_{ortho} = 8.0$  Hz,  $J_{meta} = 2.2$  Hz,  $J_{benzylic} = 0.6$  Hz,  $C_{3h}$  diastereoisomer), 7.05 (pyridine ring, doublet,  $J_{ortho} = 8.1$  Hz,  $C_s$  diastereoisomer), 7.00 (pyridine ring, doublet,  $J_{ortho} = 8.3$  Hz,  $C_s$  diastereoisomer), 6.94 (pyridine ring, doublet,  $J_{ortho} = 8.2$  Hz,  $C_s$  diastereoisomer), 6.92 (pyridine ring, doublet,  $J_{ortho} = 8.2$  Hz,  $C_{3h}$  diastereoisomer, partially overlaps with peak at 6.94 ppm), 2.32-2.34 (-CH<sub>3</sub>, multiplet resulting from two singlets at 2.33 and 2.34 ppm, 9H).

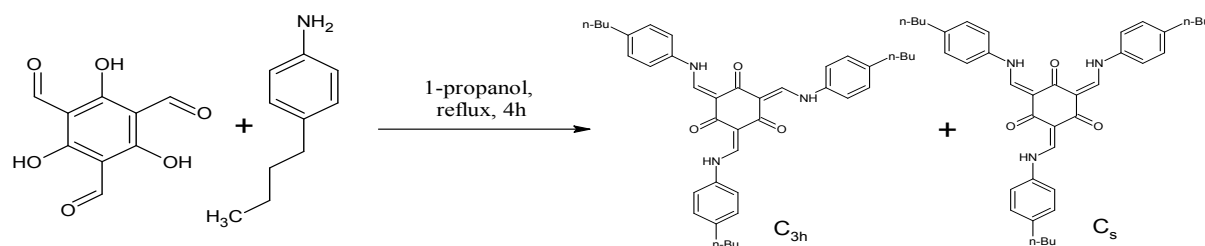
IR (KBr, cm<sup>-1</sup>): 3077, 3006, 2923, 2865, 1615, 1598, 1574, 1488, 1449, 1380, 1337, 1312, 1279, 1253, 1235, 1134, 1092, 1031, 1005, 870, 821, 742.

Elemental analysis: calculated: (C<sub>27</sub>H<sub>24</sub>N<sub>6</sub>O<sub>3</sub>) C(67.49%) H(5.03%) N(17.49%) O(9.99%), found: C(67.02%) H(5.11%) N(17.17%).

Melting point (precipitated from 1-PrOH): 331-332 °C, gradually darkens to black 250-330 °C.

### 3. BUT

(2E,4E,6E)-2,4,6-tris{[(4-*n*-butylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (**C<sub>3h</sub>** isomer) and (2Z)-2,4,6-tris{[(4-*n*-butylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (**C<sub>s</sub>** isomer)



**Scheme S3.** Synthesis of **BUT**.

In a one necked round bottoms flask (250 ml) was put 1,3,5-triformylphloroglucinol (0.42 g; 2 mmol) and 4-*n*-butylaniline (1.20 g; 8 mmol; 4 eq.) and 1-propanol (40 ml). The mixture while stirring was heated to reflux. After 15 minutes the product is already present in the reaction mixture (TLC - DCM) and the reaction was conducted for 4 hours. After that, the dark brown solution was cooled and evaporated to dryness. The residue was dissolved in dichloromethane (10 ml) and put onto column chromatography [50 ml SiO<sub>2</sub> suspended in hexanes, 1 inch wide column]. Dichloromethane (20 ml) was used to elute the excess of the amine. Next, the product was eluted with dichloromethane + 5% of ethyl acetate. The orange coloured fraction was collected (*ca.* 100 ml) and evaporated to dryness to yield bright orange resin. The crystallisation of the product due to its high solubility is slightly difficult and requires some patience. The product was dissolved in hot 2-propanol (40 ml) and after gradual cooling in the fridge and then freezer (-25°C) heavy precipitate appeared. Methanol (60 ml) was gradually added with swirling and cautious crushing of some agglomerated lumps and after 48 hours in the freezer the precipitate was immediately collected on a sinter

funnel (G4, 1 inch wide) and rapidly washed with mandatorily chilled methanol (-25°C, 2 x 30 ml). The product darkened somewhat shortly after filtration. The mother liquor was kept and evaporated to dryness. Finally, the product was dried in the vacuum desiccator for 24 hours at ambient temperature followed by drying in the vacuum oven at 40°C for 6 hours. Yellow micro needles, fibres and turnings (1.097 g; 91 %). The product stains TLC plates with intensive yellow colour. TLC and <sup>1</sup>H NMR analysis indicates that the compound exists in the form of two isomers.

HRMS (EI): calculated [M]<sup>+</sup>: 603.3455 Da, found: 603.3445, error: -1.66 ppm.

<sup>1</sup>H FT-NMR (CDCl<sub>3</sub>+TMS, 298 K, 500 Mhz): 13.38 (doublet, J = 13.4 Hz, N-H proton of diastereoisomer C<sub>3h</sub>), 13.33 (doublet, J = 13.1 Hz, N-H proton of C<sub>s</sub> diastereoisomer), 12.97 (doublet, J = 13.3 Hz, peak from two perfectly overlapping N-H protons of C<sub>s</sub> diastereoisomer), 8.81 (doublet, J = 13.2 Hz, =C-H proton of C<sub>s</sub> diastereoisomer), 8.79 (doublet, J = 13.4 Hz, =C-H proton of C<sub>s</sub> diastereoisomer, partially overlapping with peak at 8.81 ppm), 8.74 (doublet, J = 12.9 Hz, =C-H proton of C<sub>3h</sub> diastereoisomer), 8.71 (doublet, J = 13.2 Hz, =C-H proton of C<sub>s</sub> diastereoisomer, partially overlapping with peak at 8.74 ppm), 7.19-7.24 (multiplet, 12 H), 2.61 (deformed triplet, J = 7.5 Hz, 6H), 1.56-1.64 (complicated multiplet, 6H), 1.41-1.33 (complicated multiplet, J = 7.5 Hz, 6H), 0.92-0.96 (complicated multiplet, J = 7.3 Hz, 9H).

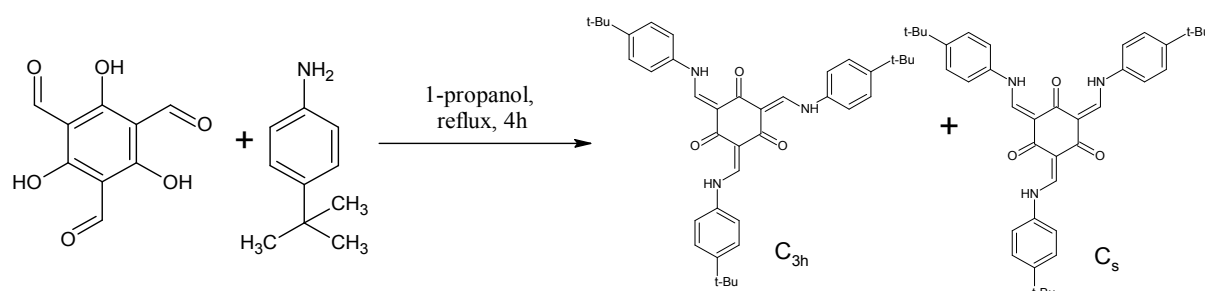
IR (KBr, cm<sup>-1</sup>): 3032, 2956, 2928, 2857, 1621, 1603, 1581, 1551, 1518, 1456, 1422, 1293, 1260, 1234, 1124, 1096, 1019, 993, 830.

Elemental analysis: calculated: (C<sub>39</sub>H<sub>45</sub>N<sub>3</sub>O<sub>3</sub>) C(77.58%), H(7.51%), N(6.96%), O(7.95%), found: C(76.10%), H(7.69%), N(6.91%).

Melting point (2-propanol): 80-81°C.

#### 4. TBU

(2E,4E,6E)-2,4,6-tris{[(4-*t*-butylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (**C<sub>3h</sub>** isomer) and (2Z)-2,4,6-tris{[(4-*t*-butylphenyl)amino]methylidene}cyclohexane-1,3,5-trione (**C<sub>s</sub>** isomer)



**Scheme S4.** Synthesis of TBU.

In a one necked round bottoms flask (250 ml) was put 1,3,5-triformylphloroglucinol (0.42 g; 2 mmol) and 4-*t*-butylaniline (1.20 g; 8 mmol; 4 eq.) and 1-propanol (40 ml). The mixture while stirring was heated to reflux. After 15 minutes the product is already present in the reaction mixture (TLC - DCM) and the reaction was conducted for 4 hours. After that, the dark brown solution was cooled and evaporated to dryness. The residue was dissolved in dichloromethane (10 ml) and put onto column chromatography [50 ml SiO<sub>2</sub> suspended in hexanes, 1 inch wide column]. Dichloromethane (20 ml) was used to elute the excess of the amine. Next, the product was eluted with dichloromethane + 5% of ethyl acetate. The orange coloured fraction was collected (*ca.* 100 ml) and evaporated to dryness to yield bright orange resin. The crystallisation of the product due to its high solubility is slightly difficult and requires some patience. The product was dissolved in hot 2-propanol (40 ml) and after gradual cooling in the fridge and then freezer (-25°C) heavy precipitate appeared. Methanol (60 ml) was gradually added with swirling and cautious crushing of some agglomerated lumps and after 48 hours in the freezer the precipitate was immediately collected on a sinter funnel (G4, 1 inch wide) and rapidly washed with mandatorily chilled methanol (-25°C, 2 x 30 ml). The product darkened somewhat shortly after filtration. The mother liquor was kept and evaporated to dryness. Finally, the product was dried in the vacuum desiccator for 24 hours at ambient temperature followed by drying in the vacuum oven at 60°C for 6 hours. Yellow amorphous solid (1.03 g; 85 %). The product stains TLC plates with intensive yellow colour. TLC and <sup>1</sup>H NMR analysis indicates that the compound exists in the form of two isomers.

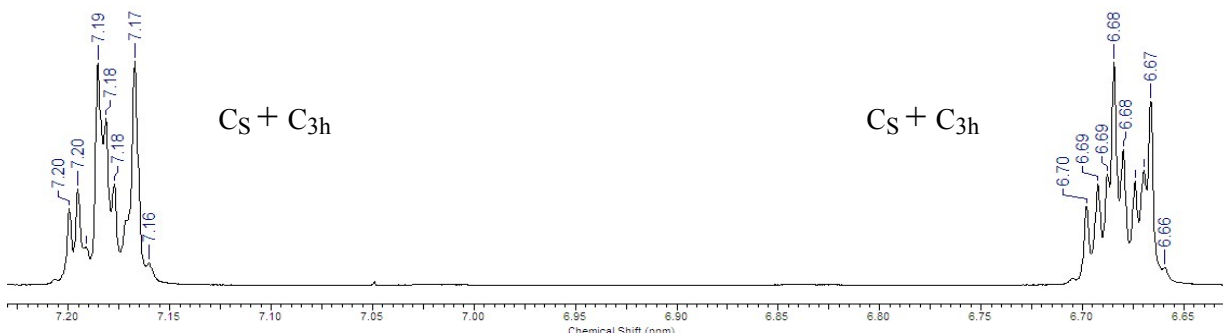
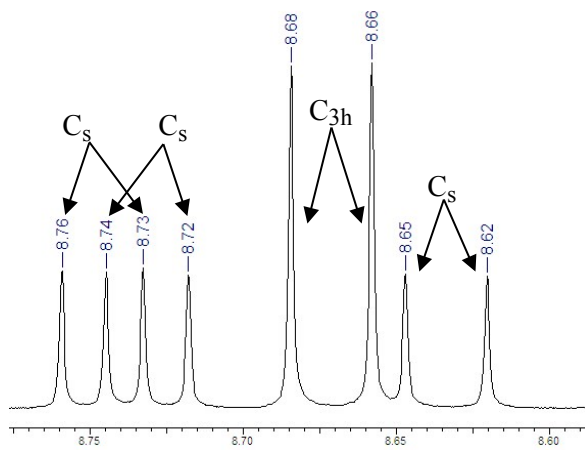
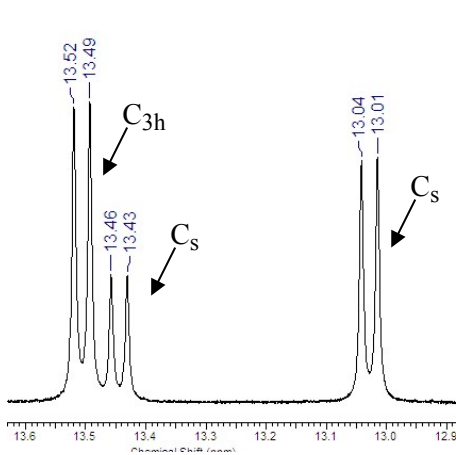
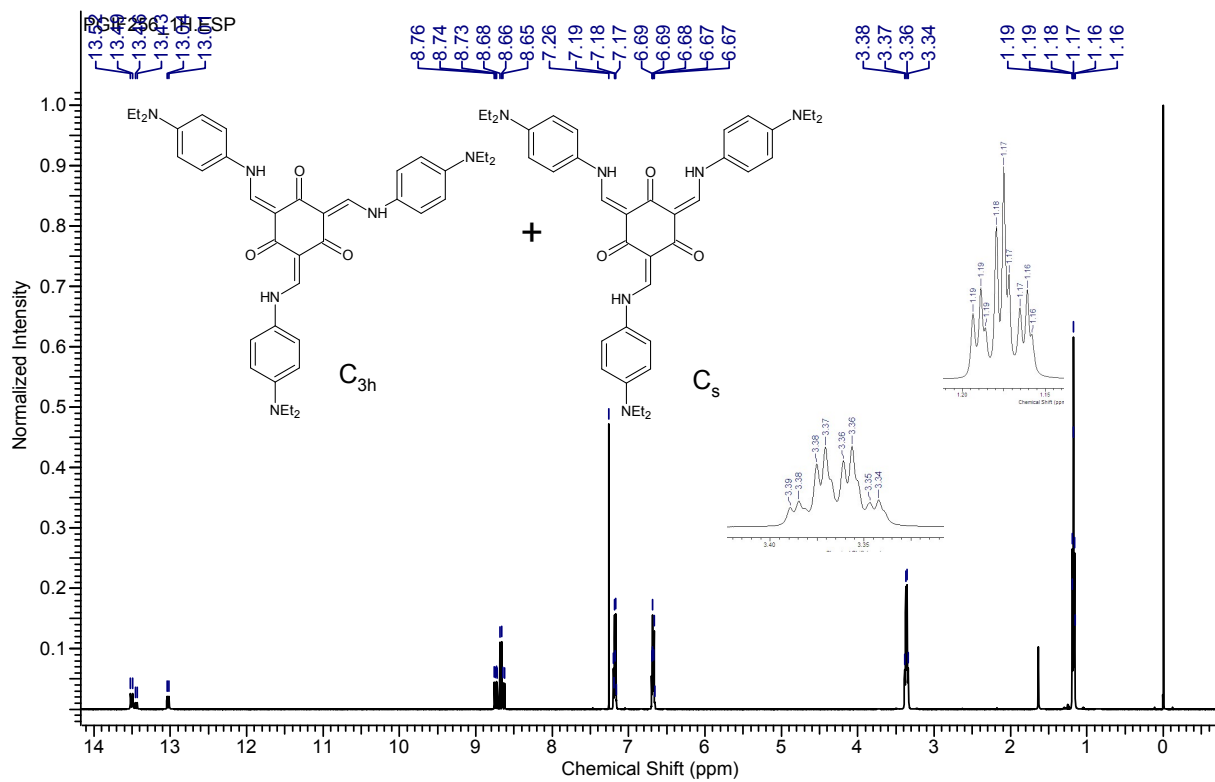
HRMS (EI): calculated [M]<sup>+</sup>: 603.3455 Da, found: 603.3466, error: 1.82 ppm.

<sup>1</sup>H FT-NMR (CDCl<sub>3</sub>+TMS, 298 K, 500 Mhz): 13.41 (doublet, J = 13.1 Hz, N-H proton of C<sub>3h</sub> diastereoisomer), 13.35 (doublet, J = 13.2 Hz, N-H proton of C<sub>s</sub> diastereoisomer), 12.98 (doublet, J = 13.3 Hz, N-H proton of C<sub>s</sub> diastereoisomer), 12.96 (doublet, J = 13.4 Hz, N-H proton of C<sub>s</sub> diastereoisomer, partially overlapping with peak at 12.98 ppm), 8.84 (doublet, J = 13.2 Hz, =C-H proton of C<sub>s</sub> diastereoisomer), 8.82 (doublet, J = 13.3 Hz, =C-H proton of C<sub>s</sub> diastereoisomer, partially overlapping with peak at 8.84 ppm), 8.76 ppm (doublet, J = 13.1 Hz, =C-H proton of C<sub>3h</sub> diastereoisomer), 8.73 (doublet, J = 13.5 Hz, =C-H proton of C<sub>s</sub> diastereoisomer, partially overlapping with peak at 8.76 ppm), 7.39-7.44 (complicated multiplet, 6H), 7.21-7.26 (complicated multiplet, partially overlapping with solvent peak, 6H), 1.32-1.34 (multiplet consisting of three overlapping singlets at 1.34, 1.33 and 1.33 ppm, 27H).

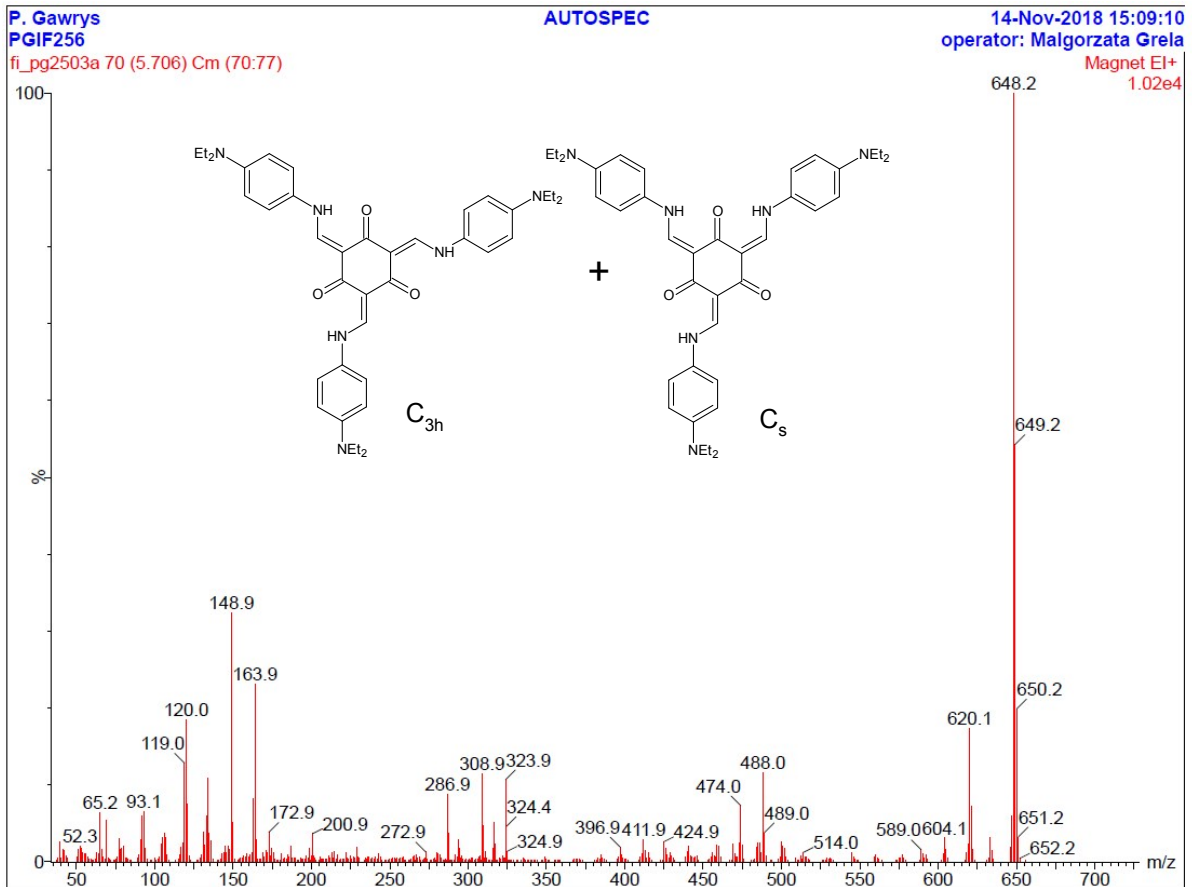
IR (KBr, cm<sup>-1</sup>): 3069, 3036, 2962, 2904, 2870, 1617, 1602, 1579, 1553, 1519, 1454, 1417, 1393, 1365, 1294, 1259, 1238, 1186, 1112, 1094, 1035, 1014, 994, 826.

Elemental analysis: calculated: (C<sub>39</sub>H<sub>45</sub>N<sub>3</sub>O<sub>3</sub>) C(77.58%), H(7.51%), N(6.96%), O(7.95%); found: C(76.94%), H(7.51%), N(6.94%).

Melting point (2-propanol): 192-193°C.



Spectrum S1.  $^1\text{H}$  FT-NMR spectrum of **DMA** (extended diagnostic and aromatic region).



Spectrum S2. LR-MS spectrum of **DMA**.

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

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

Elements Used:

C: 0-70 H: 0-100 N: 6-6 O: 0-4

P. Gawrys

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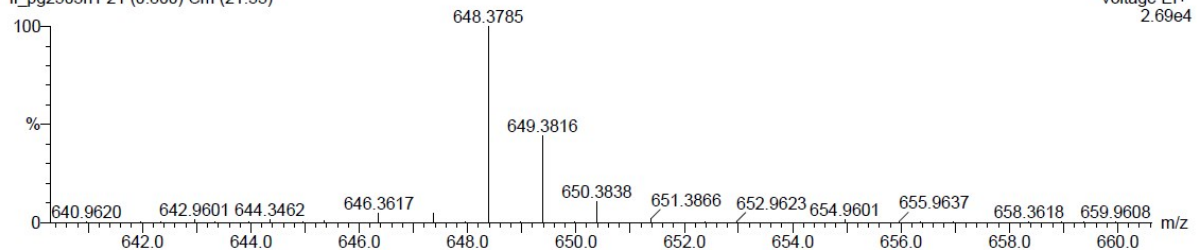
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operator: Malgorzata Grela

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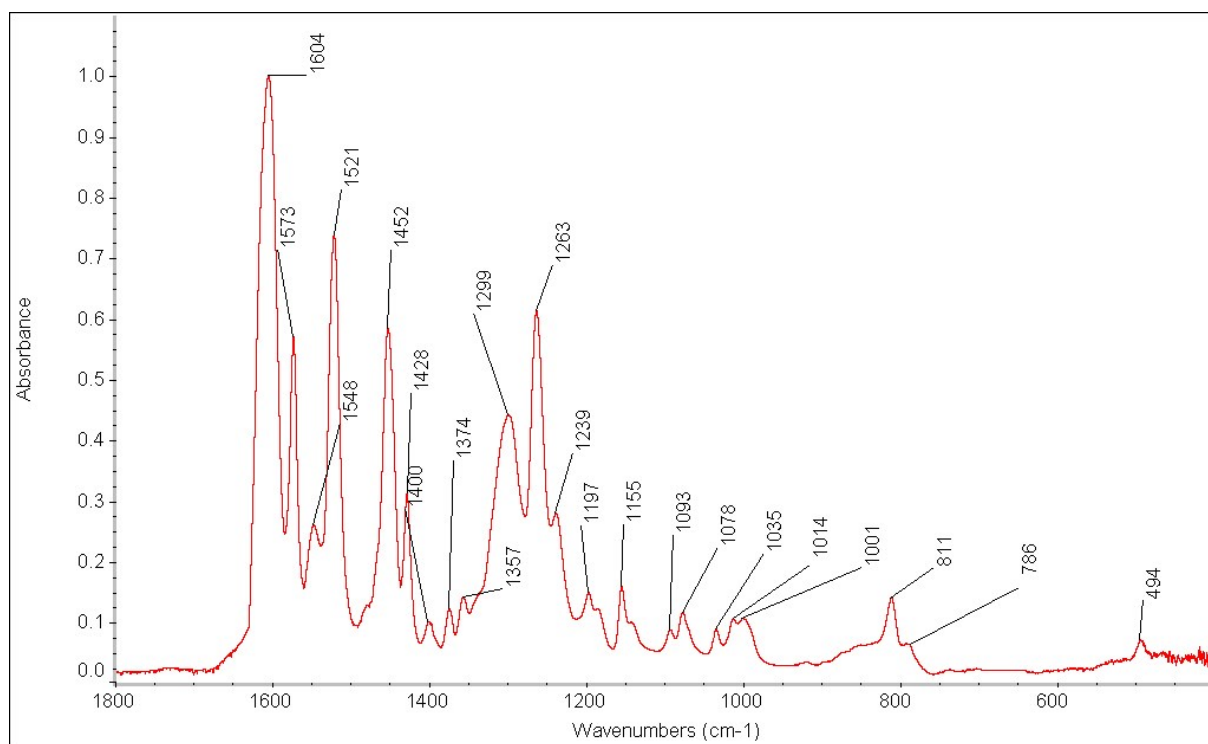
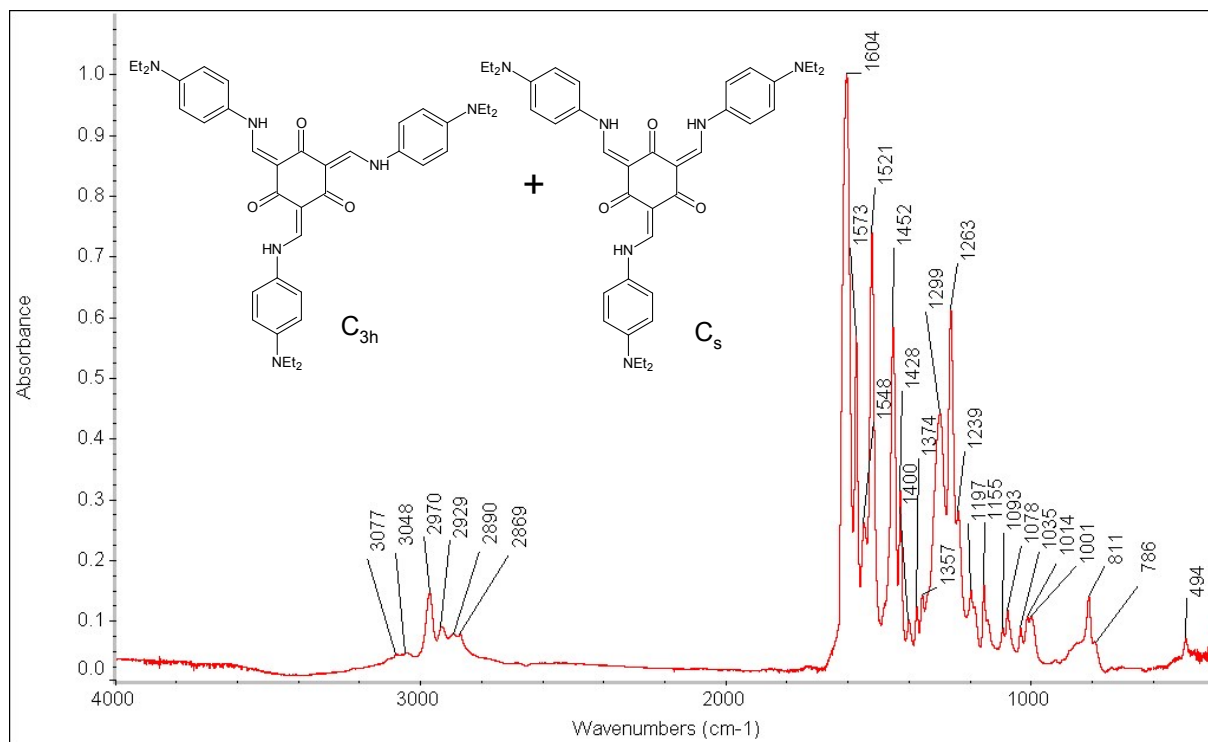
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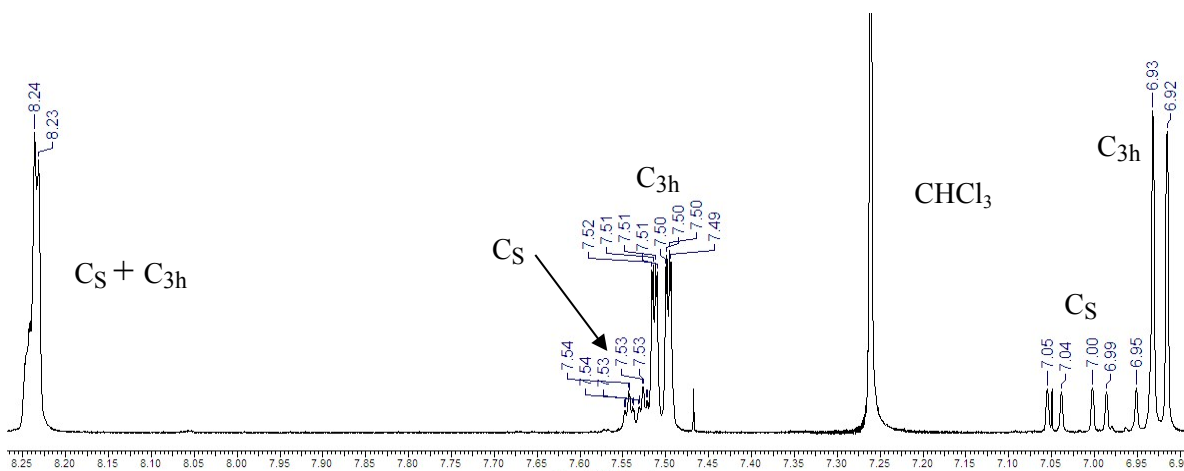
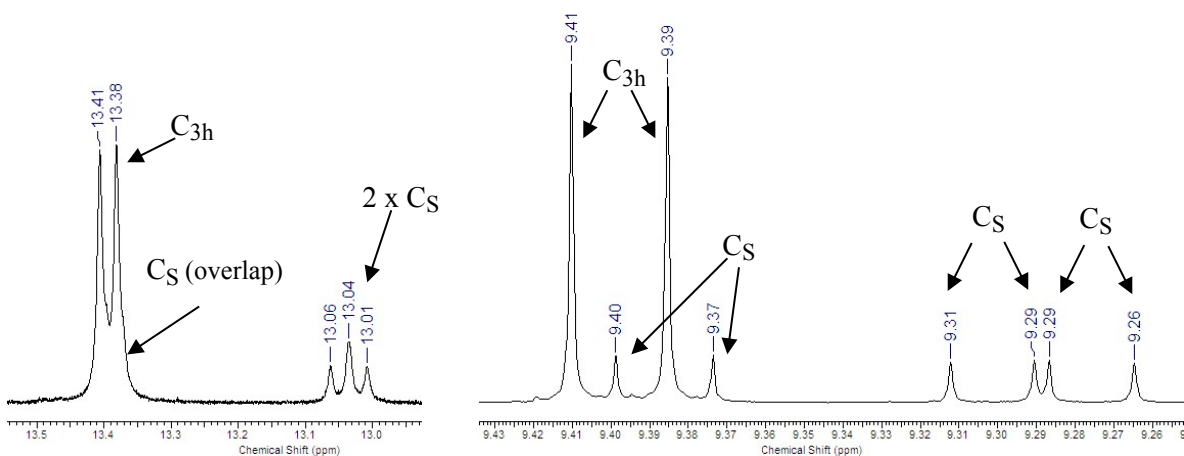
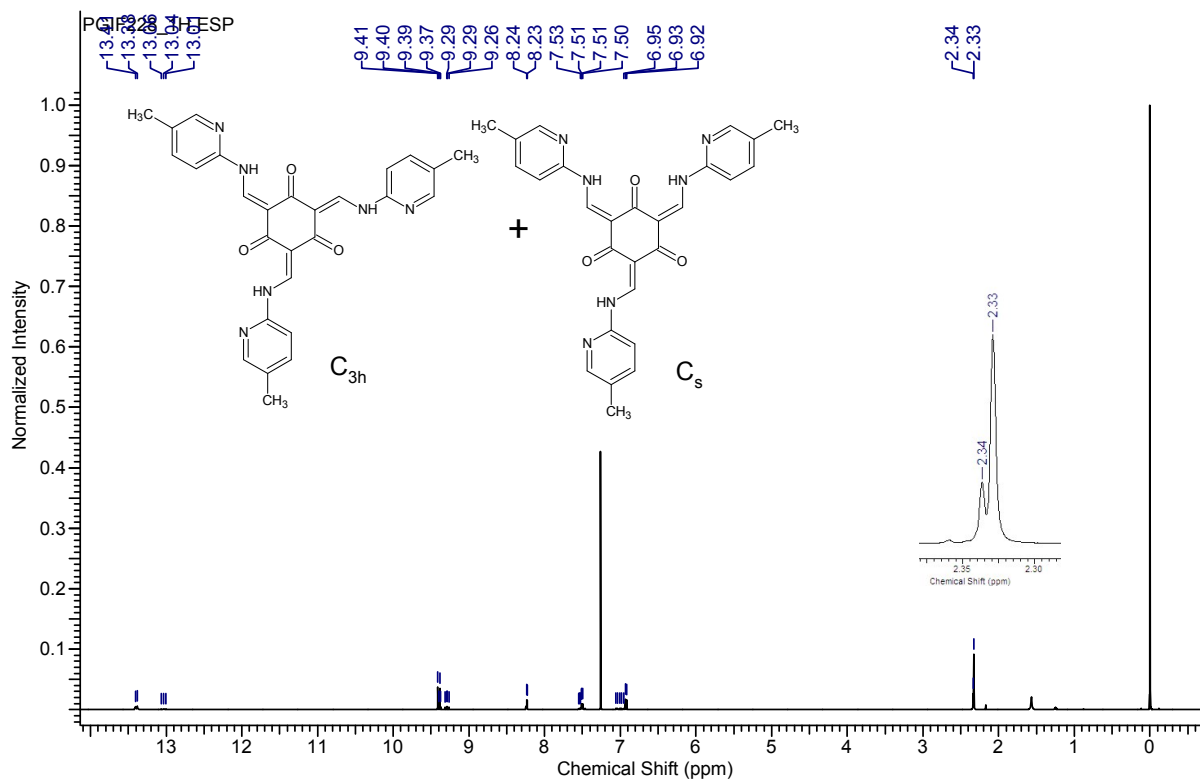
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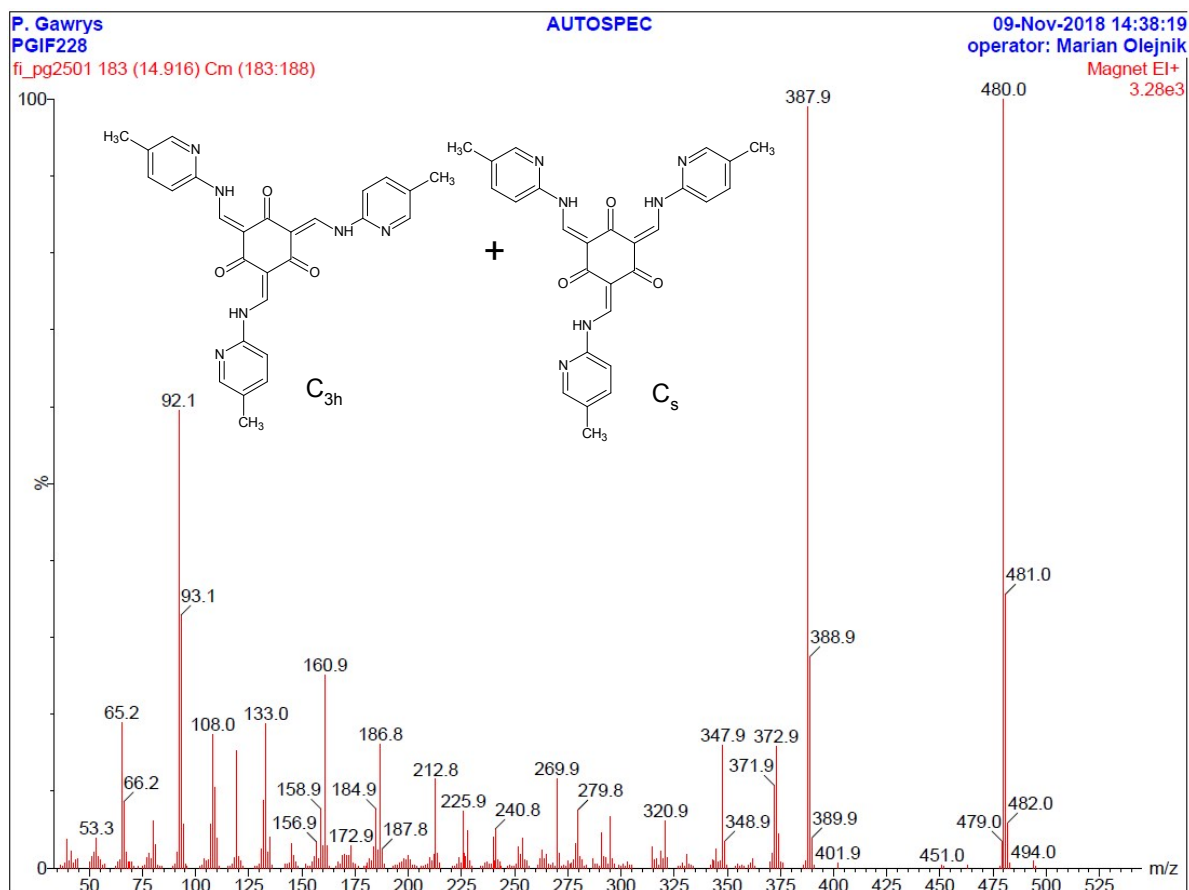
Spectrum S3. HR-MS spectrum of **DMA**.



Spectrum S4. FT-IR spectrum of DMA.



Spectrum S5. <sup>1</sup>H FT-NMR spectrum of 2MP (extended diagnostic and aromatic region).



Spectrum S6. LR-MS spectrum of 2MP.

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

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

Elements Used:

C: 0-70 H: 0-100 N: 6-6 O: 0-4

P. Gawrys

PGIF228

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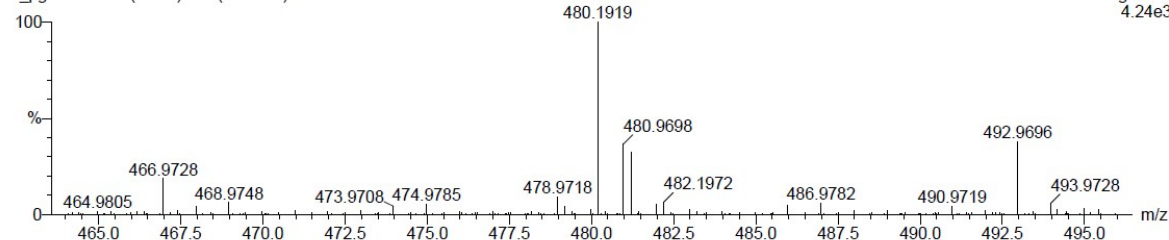
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operator: Malgorzata Grela

Voltage EI+

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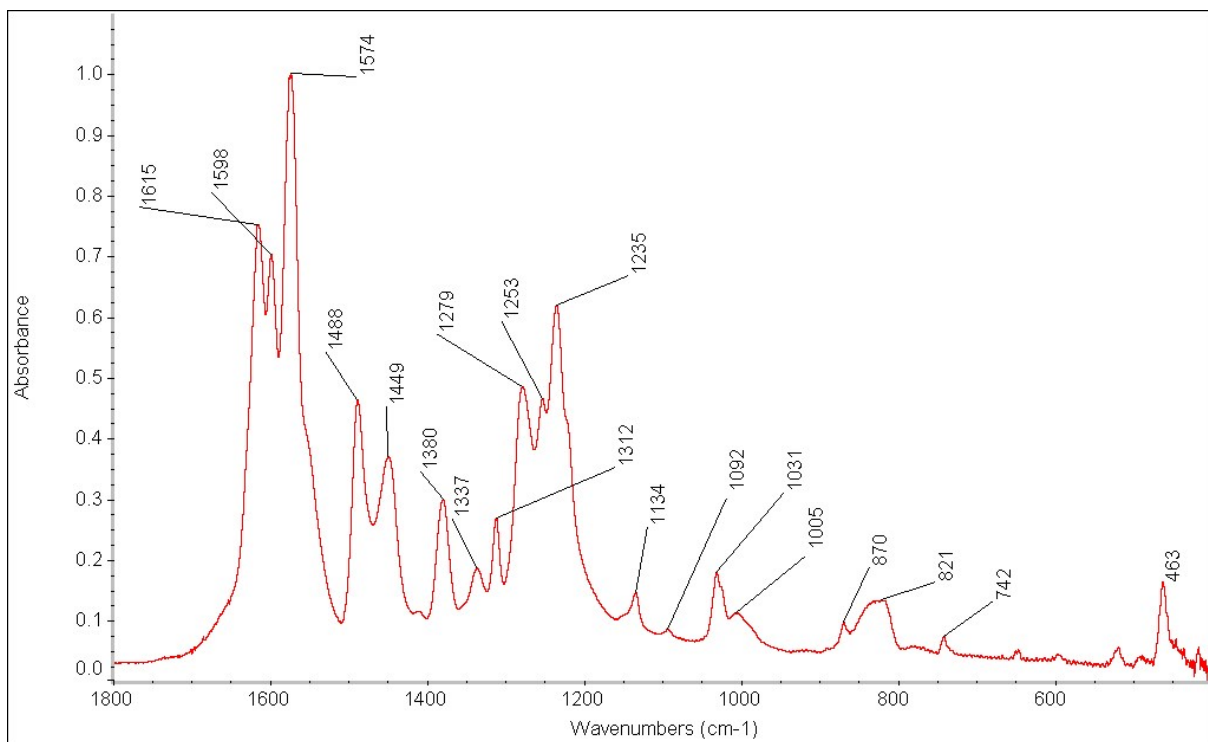
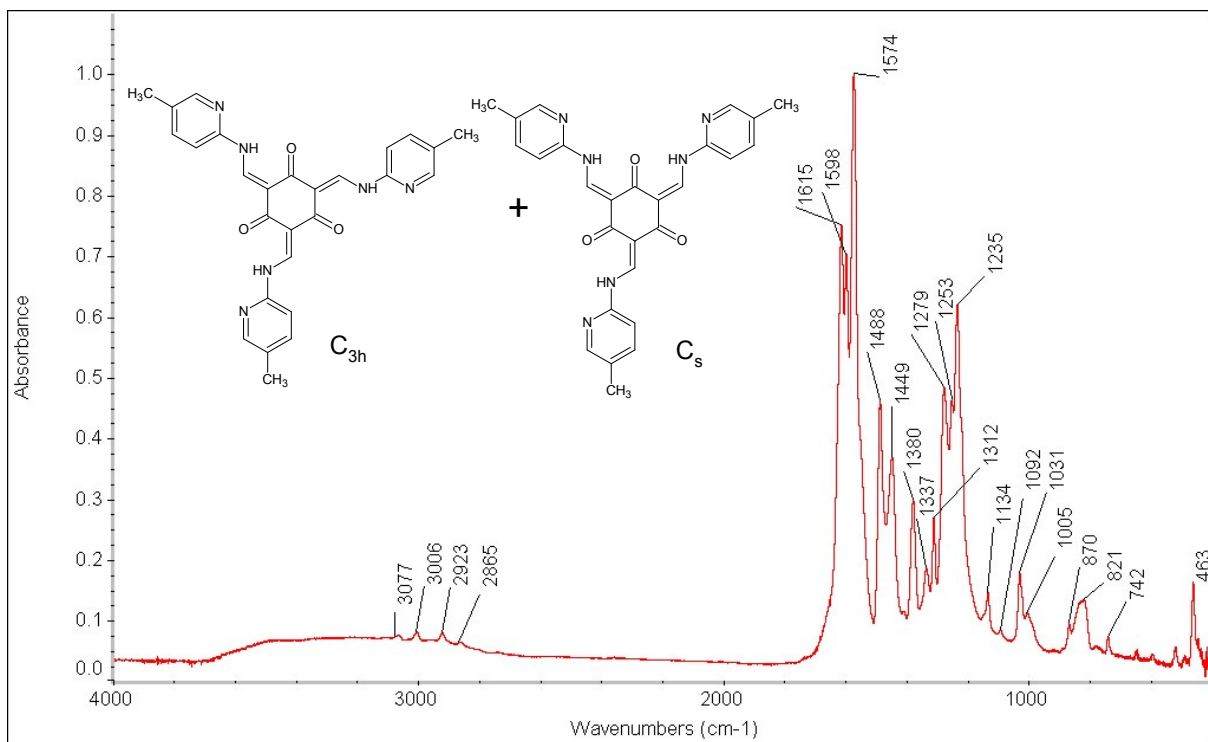
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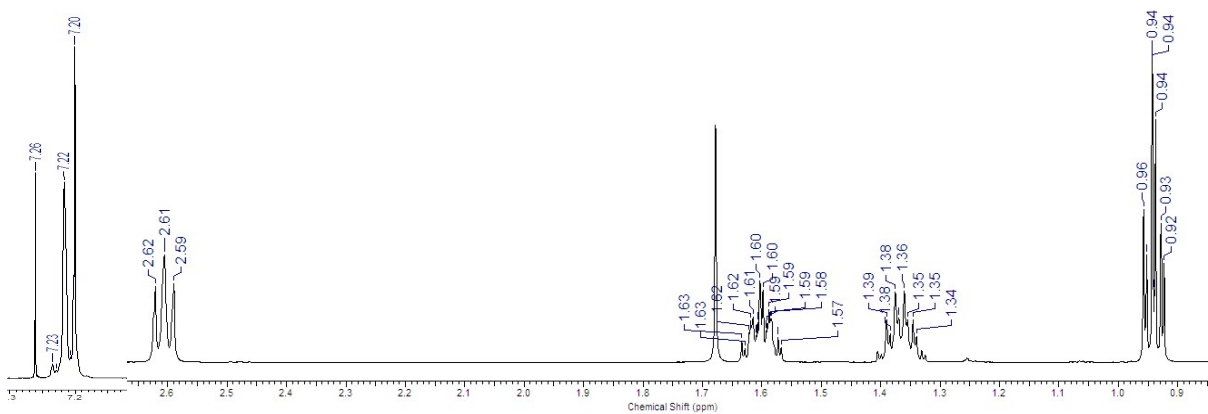
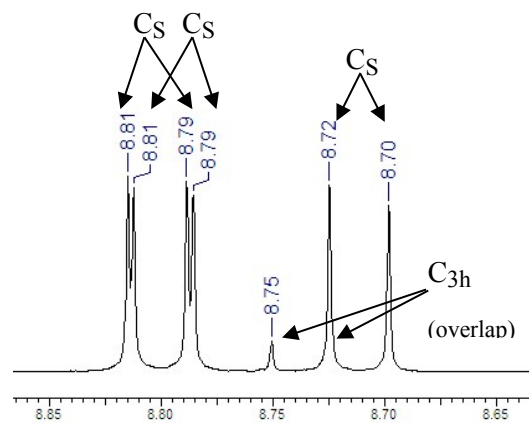
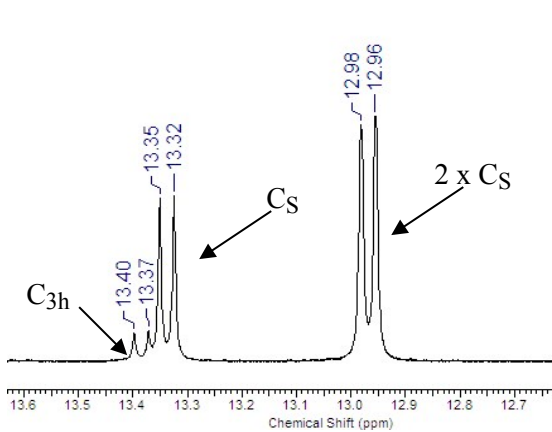
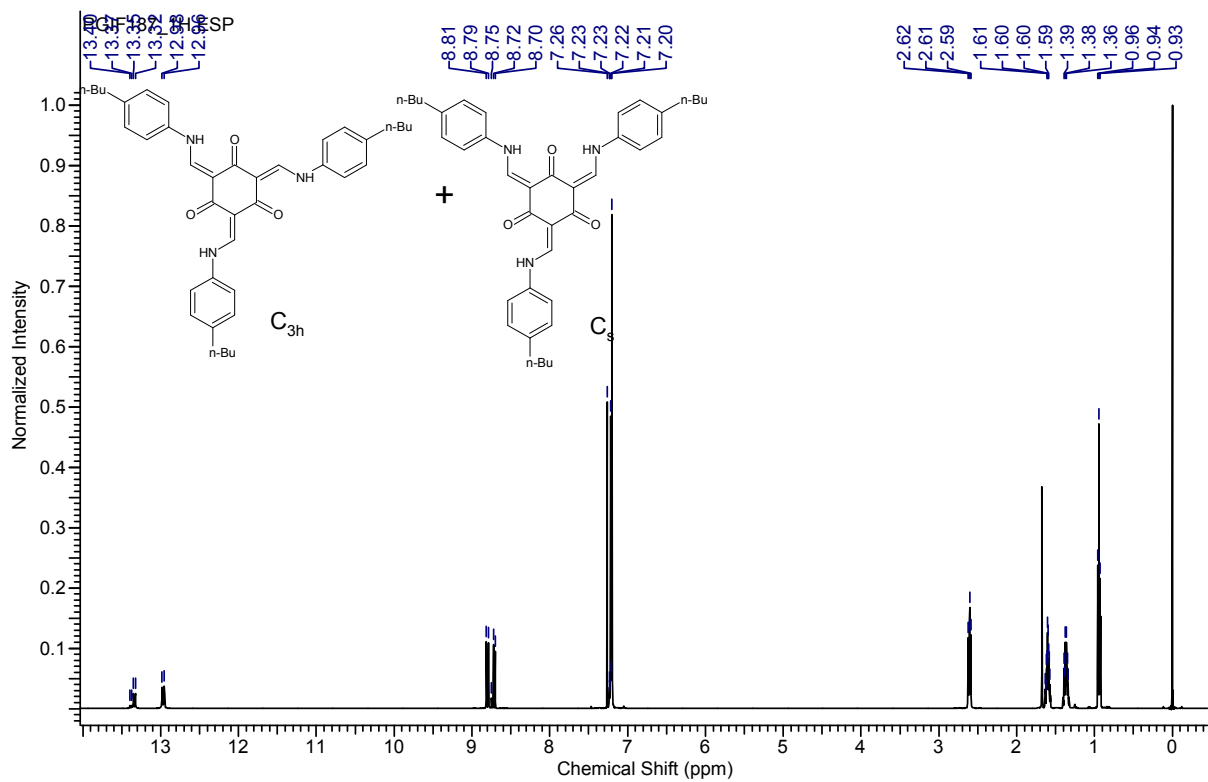
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
480.1919	480.1910	0.9	1.9	19.0	1.0	C <sub>27</sub> H <sub>24</sub> N <sub>6</sub> O <sub>3</sub>

Spectrum S7. HR-MS spectrum of 2MP.

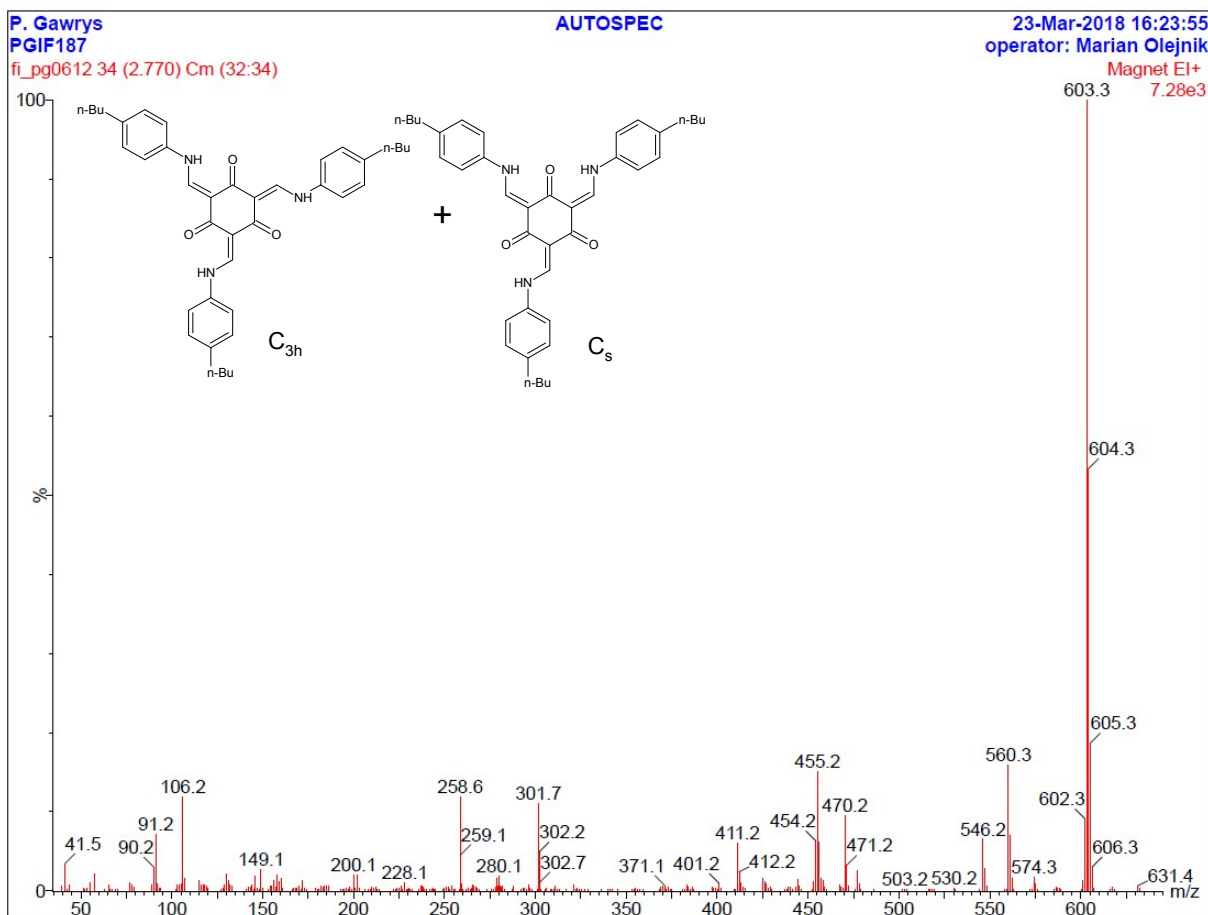




Spectrum S8. FT-IR spectrum of **2MP**.



Spectrum S9. <sup>1</sup>H FT-NMR spectrum of BUT (extended diagnostic and aromatic region).



Spectrum S10. LR-MS spectrum of BUT.

### Elemental Composition Report

Page 1

#### Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions  
109 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-80 H: 0-80 N: 0-3 O: 0-3

P. Gawrys

PGIF187

fi\_pg0612h 78 (2.975) Cm (78:103)

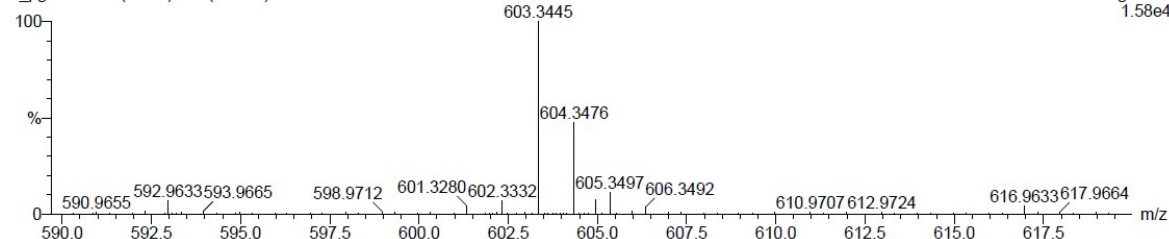
AUTOSPEC

29-Mar-2018 15:09:08

operator: Malgorzata Grela

Voltage EI+

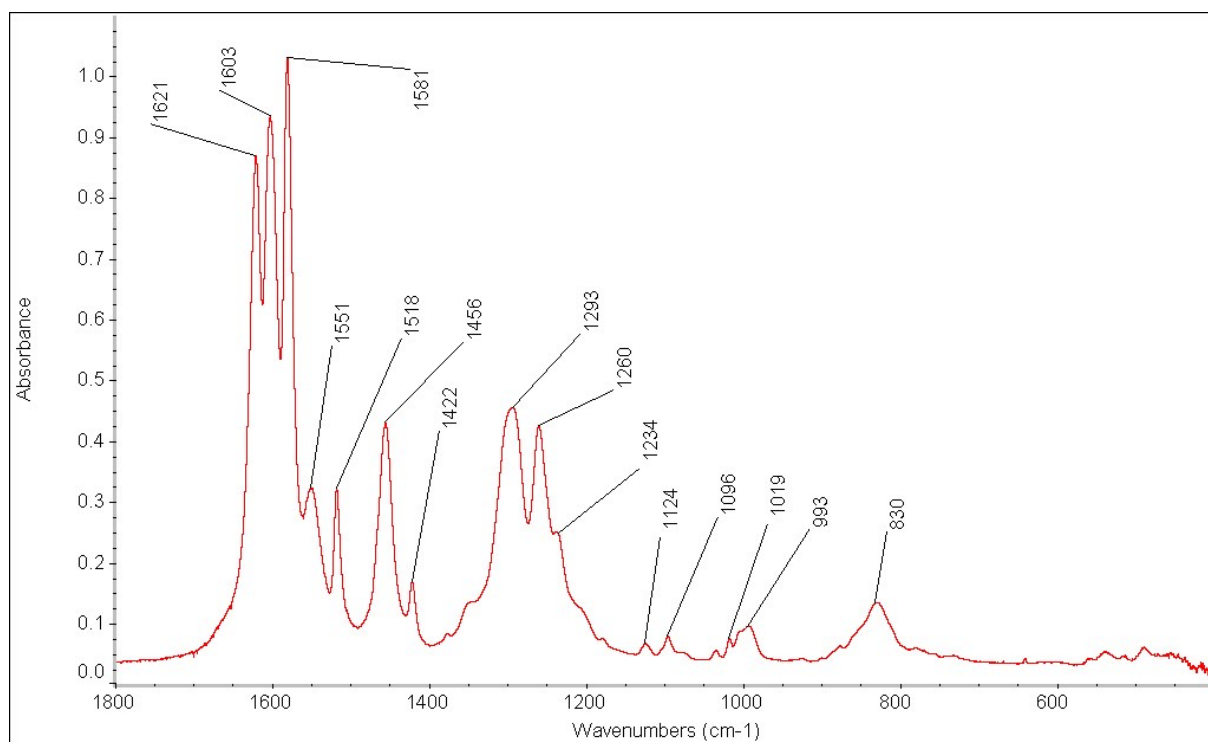
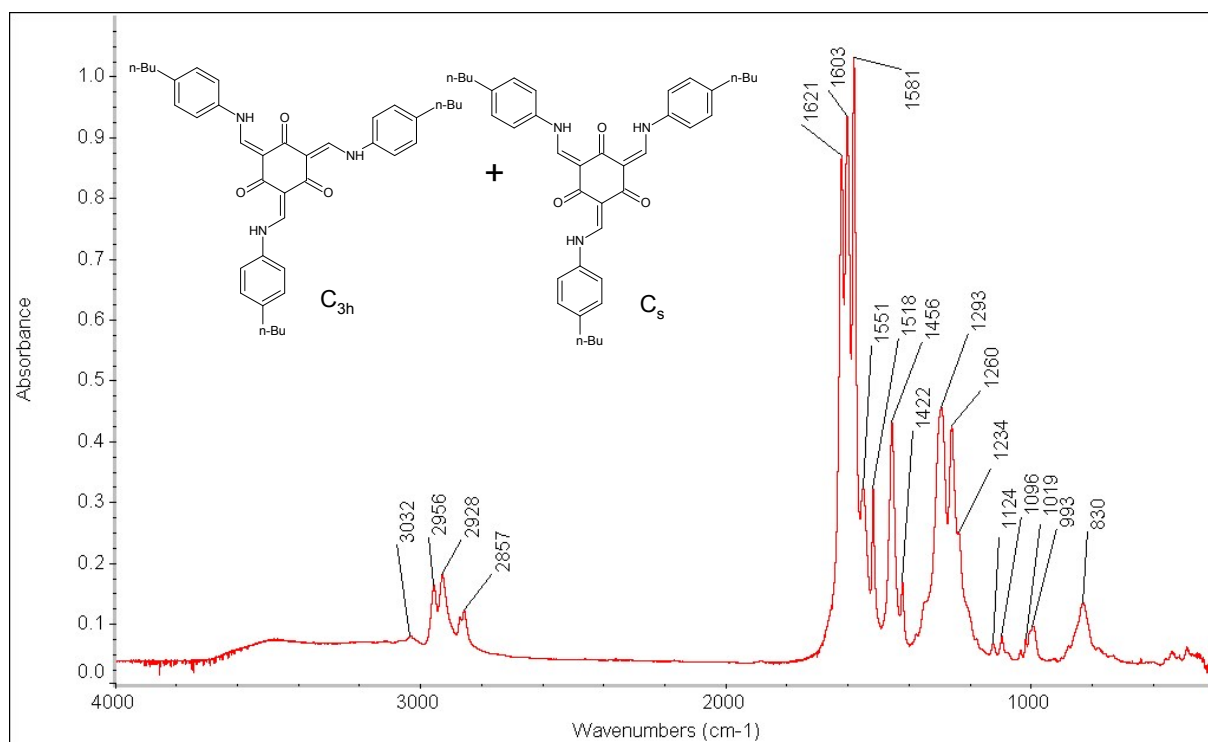
1.58e4



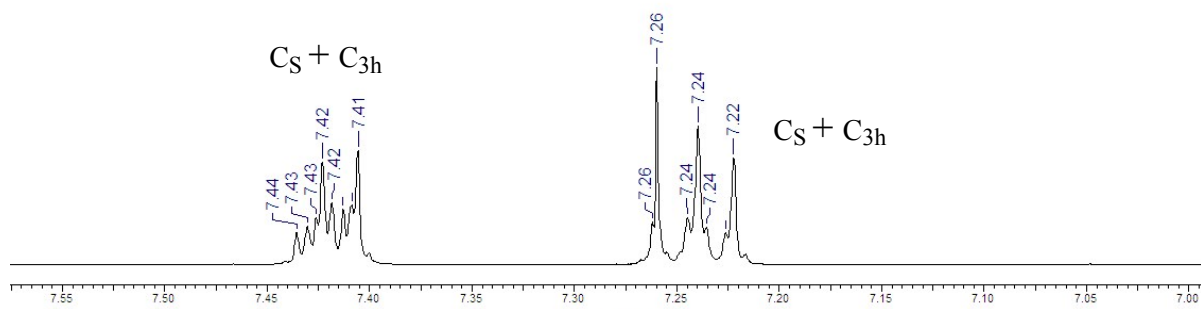
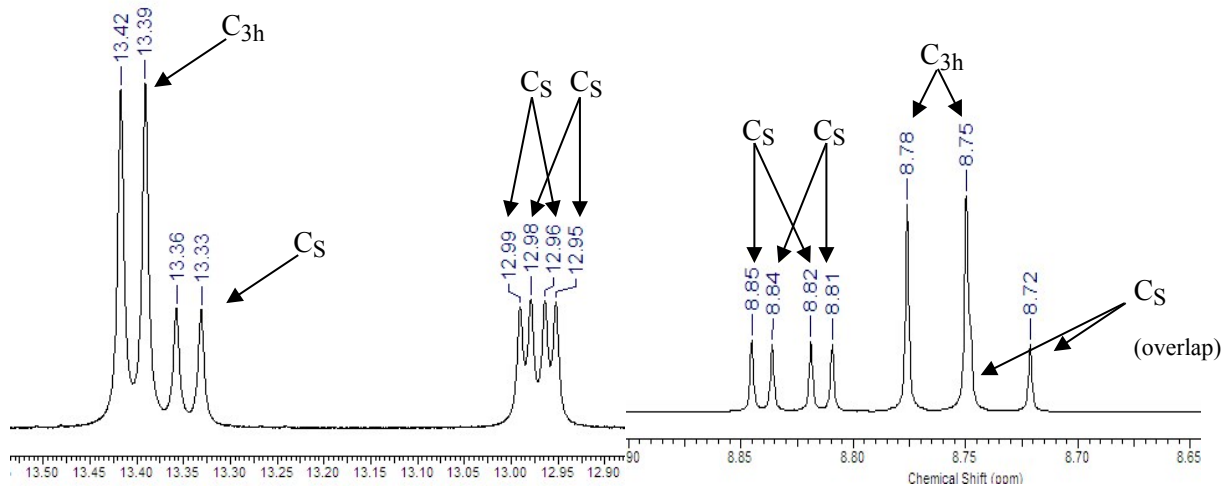
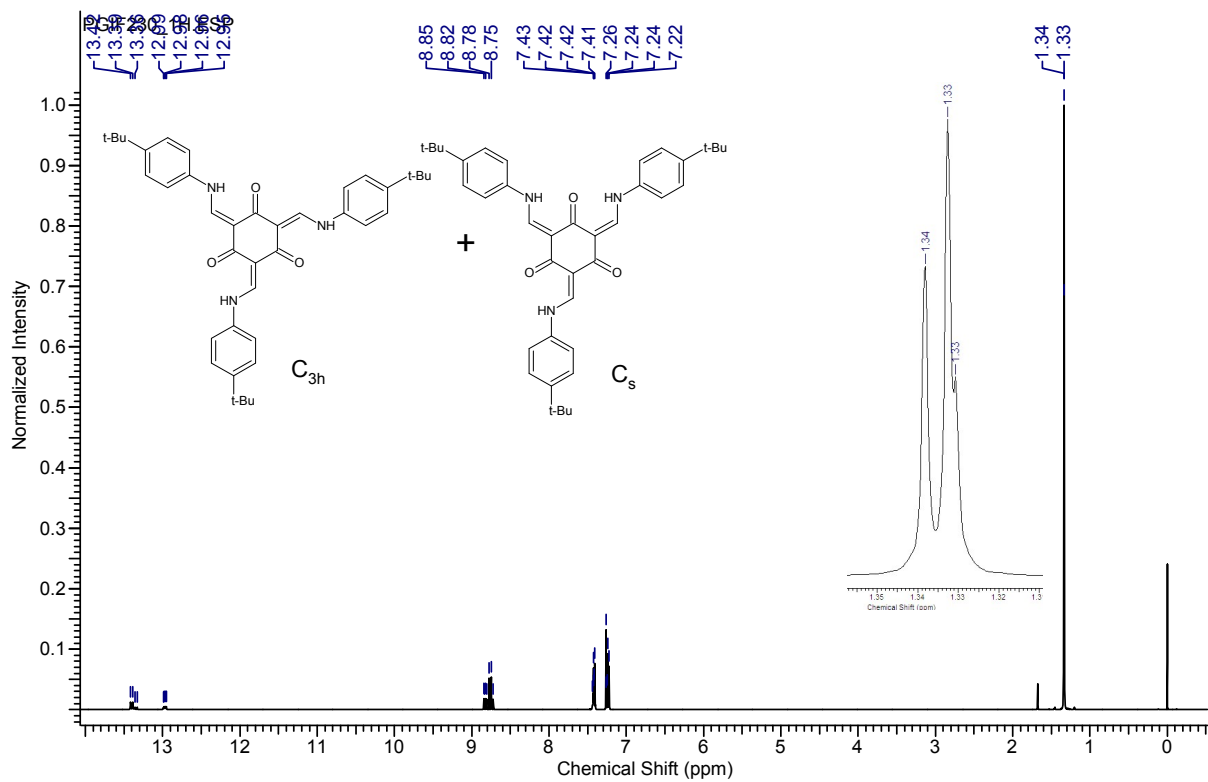
Minimum: -1.5  
Maximum: 10.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
603.3445	603.3461	-1.6	-2.7	19.0	5.2	C <sub>39</sub> H <sub>45</sub> N <sub>3</sub> O <sub>3</sub>
	603.3501	-5.6	-9.3	23.0	25.4	C <sub>44</sub> H <sub>45</sub> N O

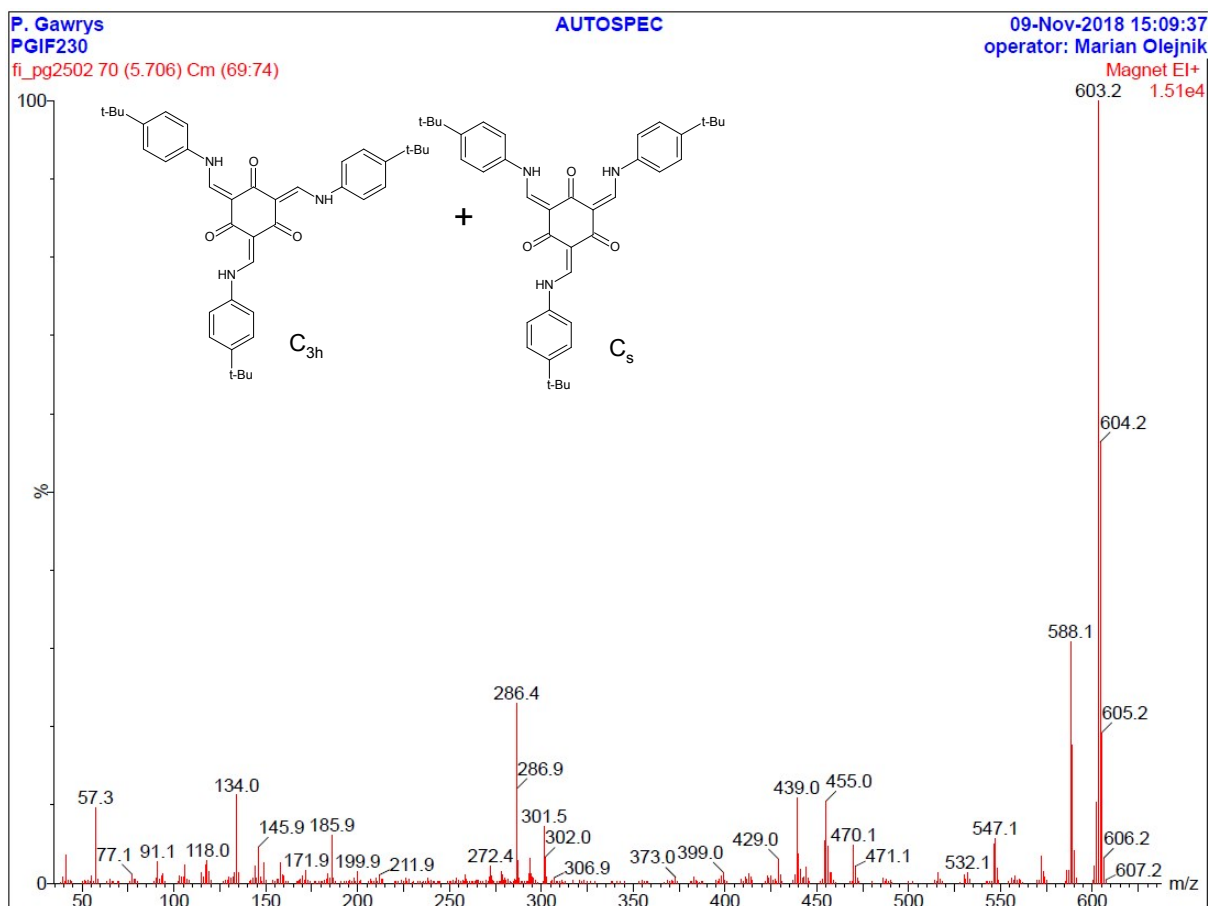
Spectrum S11. HR-MS spectrum of BUT.



Spectrum S12. FT-IR spectrum of **BUT**.



Spectrum S13.  $^1\text{H}$  FT-NMR spectrum of TBU (extended diagnostic and aromatic region).



Spectrum S14. LR-MS spectrum of TBU.

### Elemental Composition Report

Page 1

#### Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

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

Elements Used:

C: 0-70 H: 0-100 N: 3-3 O: 0-4

P. Gawrys

PGIF230

fi\_pg2502h 182 (6.942) Cm (182:210)

AUTOSPEC

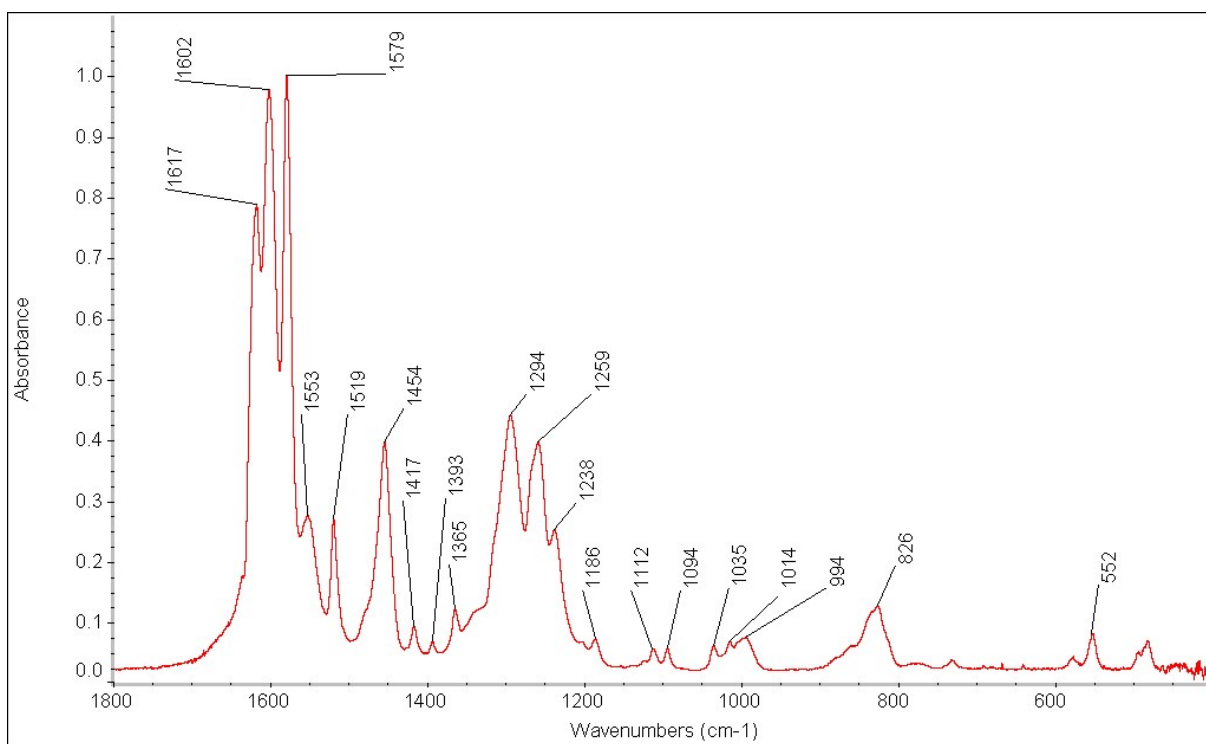
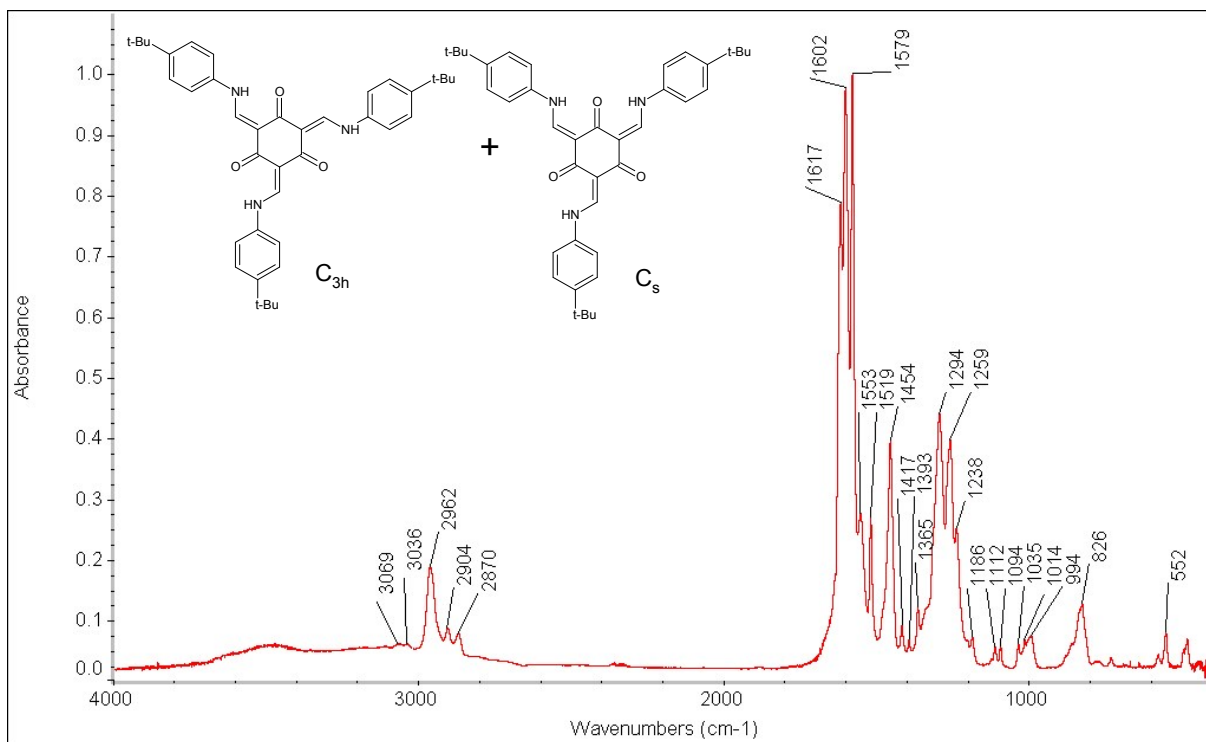
14-Nov-2018 14:35:22  
operator: Malgorzata Grela  
Voltage EI+  
4.72e3

Minimum:

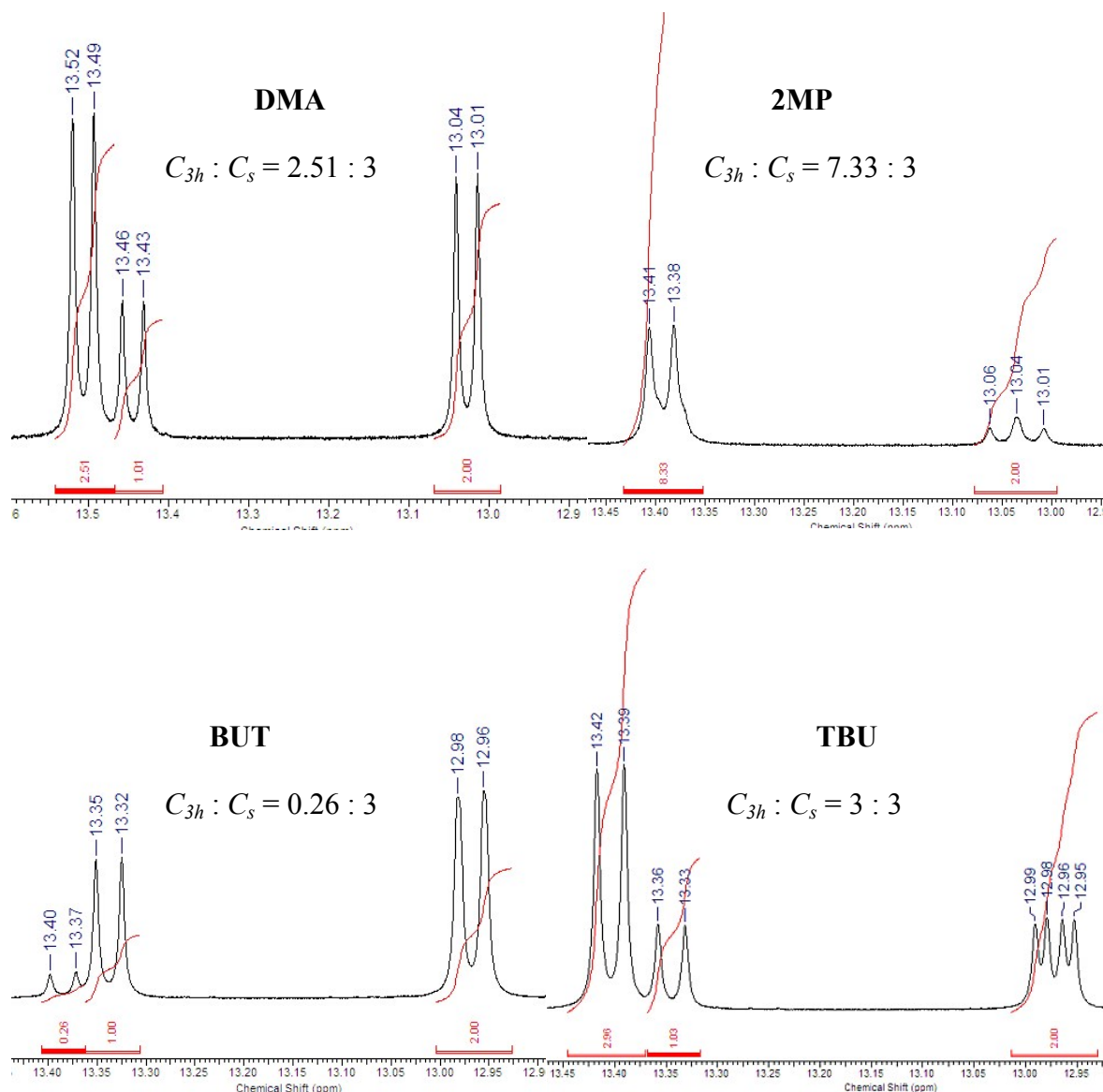
Maximum:

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
603.3466	603.3461	0.5	0.8	19.0	1.4	C39 H45 N3 O3

Spectrum S15. HR-MS spectrum of TBU.



Spectrum S16. FT-IR spectrum of **TBU**.



Spectrum S17. The integration values of NH protons of studied TSANs

Note: The ratio values were rounded to either first decimal place or to the value of 5 of the second decimal place. Percentage values were rounded to the nearest multiple of 5.

**DMA**  $C_{3h} : C_s = 2.51:3 \cong \underline{1:1.2} \cong C_{3h} (45\%) + C_s (55\%)$

**2MP**  $C_{3h} : C_s = (8.33-1) : 3 = 7.33 : 3 \cong 2.45:1 \cong \underline{1:0.4} \cong C_{3h} (70\%) + C_s (30\%)$

**BUT**  $C_{3h} : C_s = 0.26:3 \cong \underline{1:11.5} \cong C_{3h} (10\%) + C_s (90\%)$

**TBU**  $C_{3h} : C_s = 3:3 = \underline{1:1} \cong C_{3h} (50\%) + C_s (50\%)$