SUPPORTING INFORMATION

Twisted Acceptors in the Design of Deep-Blue TADF Emitters: Crucial Role of the Excited-State Relaxation on the Photophysics of Methyl Substituted *s*-Triphenyltriazine Derivatives

Illia E. Serdiuk[1,2],* Chi Hyun Ryoo,[2] Karol Kozakiewicz,[3] Michał Mońka,[1] Beata Liberek,[3]

Soo Young Park[2]

[1] Faculty of Mathematics, Physics and Informatics, University of Gdańsk, Wita Stwosza 57, 80-308 Gdańsk, Poland

[2] Center for Supramolecular Optoelectronic Materials, Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Republic of Korea

[3] Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland

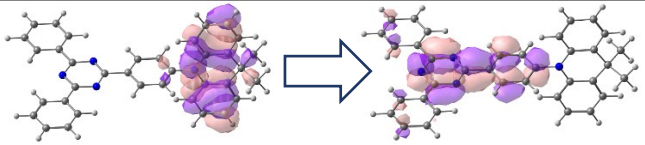
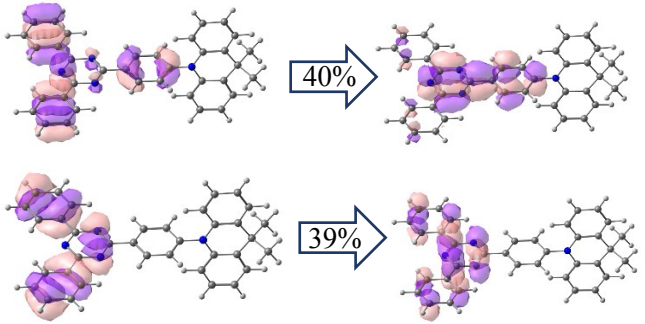
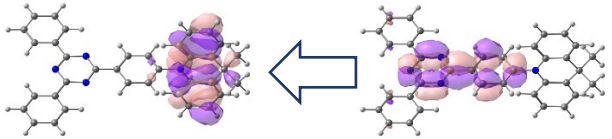
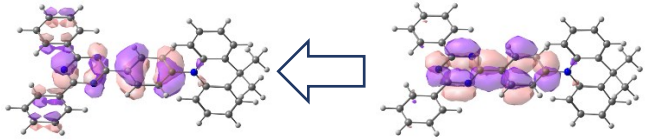
*Correspondence e-mail: illia.serdiuk@gmail.com

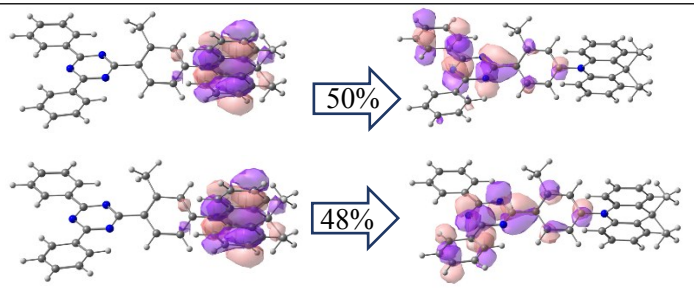
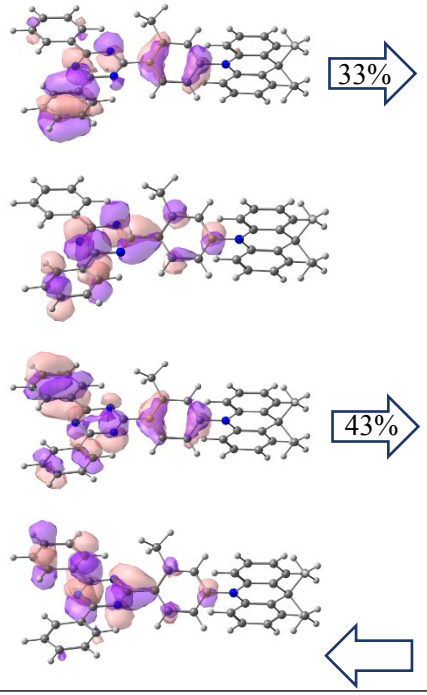
Contents

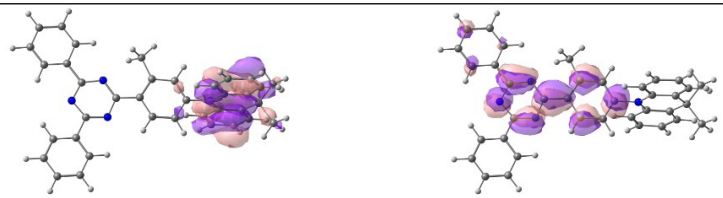
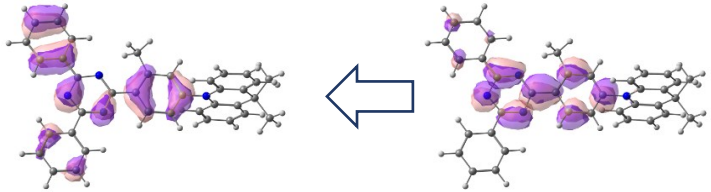
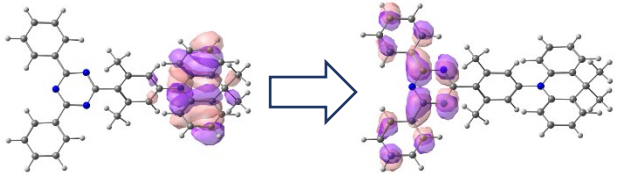
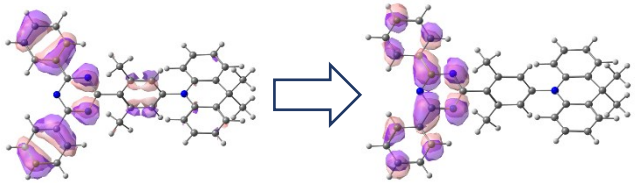
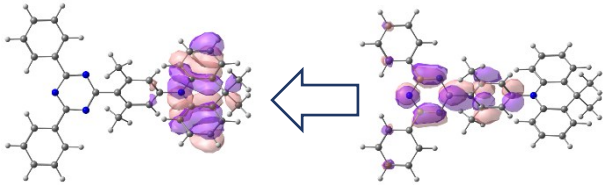
DFT/TDDFT calculations

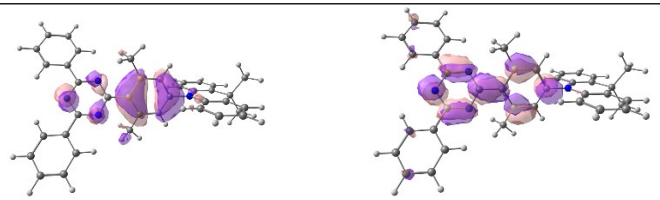
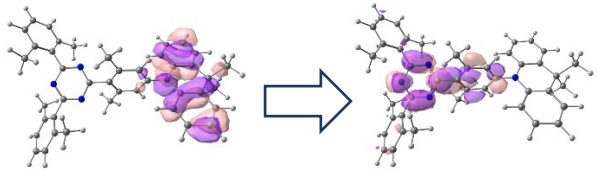
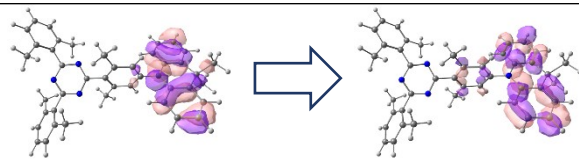
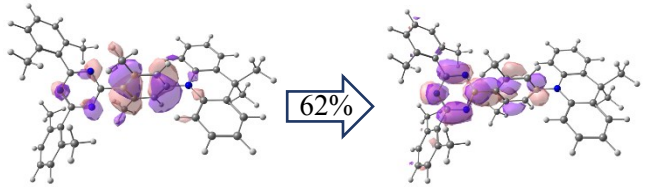
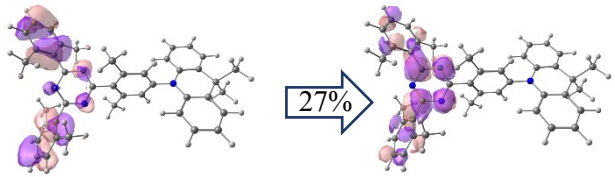
Table S1. Orbitals involved in the electronic transitions

*geometries of the ^{1}CT and ^{3}CT states are very similar so only the ^{1}CT one is shown

Cmpd	Opt. geometry*	State	Orbitals involved
DMAC-TRZ	**S_0**	**CT**	
		^{3}LE	
	S_1 and T_1 (CT)	**CT**	
	T_2 (^{3}LE)	**^{3}LE**	

2	**S_0**	**CT**	
		^{3}LE	

	S_1 and T_1 (CT)	CT	
	T_2 (^{3}LE)	^{3}LE	
4	S_0	CT	
		^{3}LE	
	S_1 and T_1 (CT)	CT	

	T_2 (^{3}LE)	**^{3}LE**	
6	**S_0**	**CT**	
		T_2 (^{3}LE donor)	
		T_3 (^{3}LE acceptor)	 

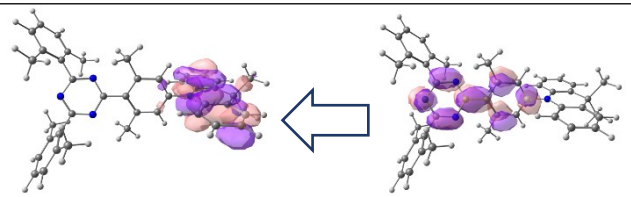
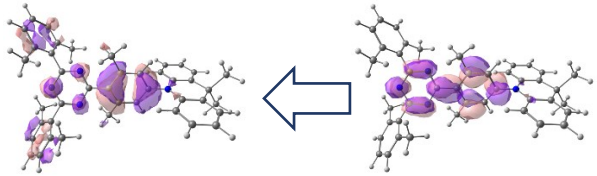
	S_1 and T_1 (CT)	**CT**	
	T_2 (^{3}LE)	**LE**	

Table S2. Vertical transition energies grouped by the nature of transition. Calculated for the optimized geometries of respective electronic states*

Cmpd	State	Vertical transition energy (nm)			
		^{3}CT	^{1}CT	^{3}LE (A)	^{3}LE (D)
DMAC-TRZ	S_0	517.1	515.7	413.0	390.0
	S_1 (^{1}CT)	613.6	611.6	448.3	405.5
	T_1 (^{3}CT)	613.5	611.5	448.5	405.4
1	S_0	508.7	507.3	404.5	390.0
	S_1 (^{1}CT)	611.0	609.0	447.9	405.4
	T_1 (^{3}CT)	610.9	608.9	448.1	405.3
2	S_0	501.6	500.4	408.2	390.4
	S_1 (^{1}CT)	609.0	607.1	448.5	405.9
	T_1 (^{3}CT)	608.9	607.0	448.8	405.7
3	S_0	490.3	489.0	397.8	390.4
	S_1 (^{1}CT)	605.1	603.1	446.9	405.6
	T_1 (^{3}CT)	605.0	603.0	447.2	405.5
4	S_0	492.3	492.2	403.2	390.9
	S_1 (^{1}CT)	572.9	571.6	425.9	406.6
	T_1 (^{3}CT)	573.2	571.7	426.4	406.5
5	S_0	468.4	468.3	394.7	390.9
	S_1 (^{1}CT)	572.1	570.7	425.1	406.5
	T_1 (^{3}CT)	572.4	570.8	425.6	406.3
6	S_0	501.6	500.4	408.2	390.4
	S_1 (^{1}CT)	592.4	590.6	430.6	406.3
	T_1 (^{3}CT)	592.5	590.6	431.0	406.1

***^{3}LE (A)** – transition localized on the acceptor fragment; **^{3}LE (D)** – transition localized on the donor (DMAC) fragment.

Photoluminescence spectra and decays

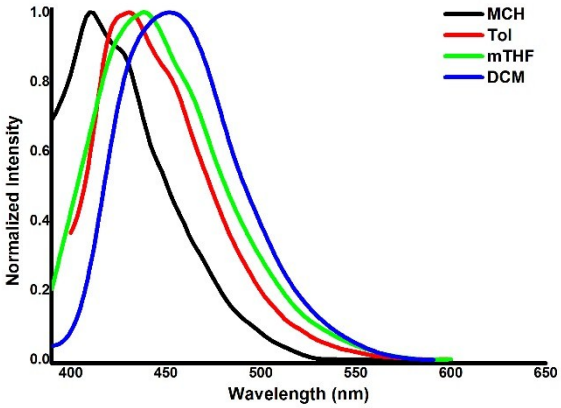


Figure S1. Fluorescence spectra of **5** in various solvents at 78 K.

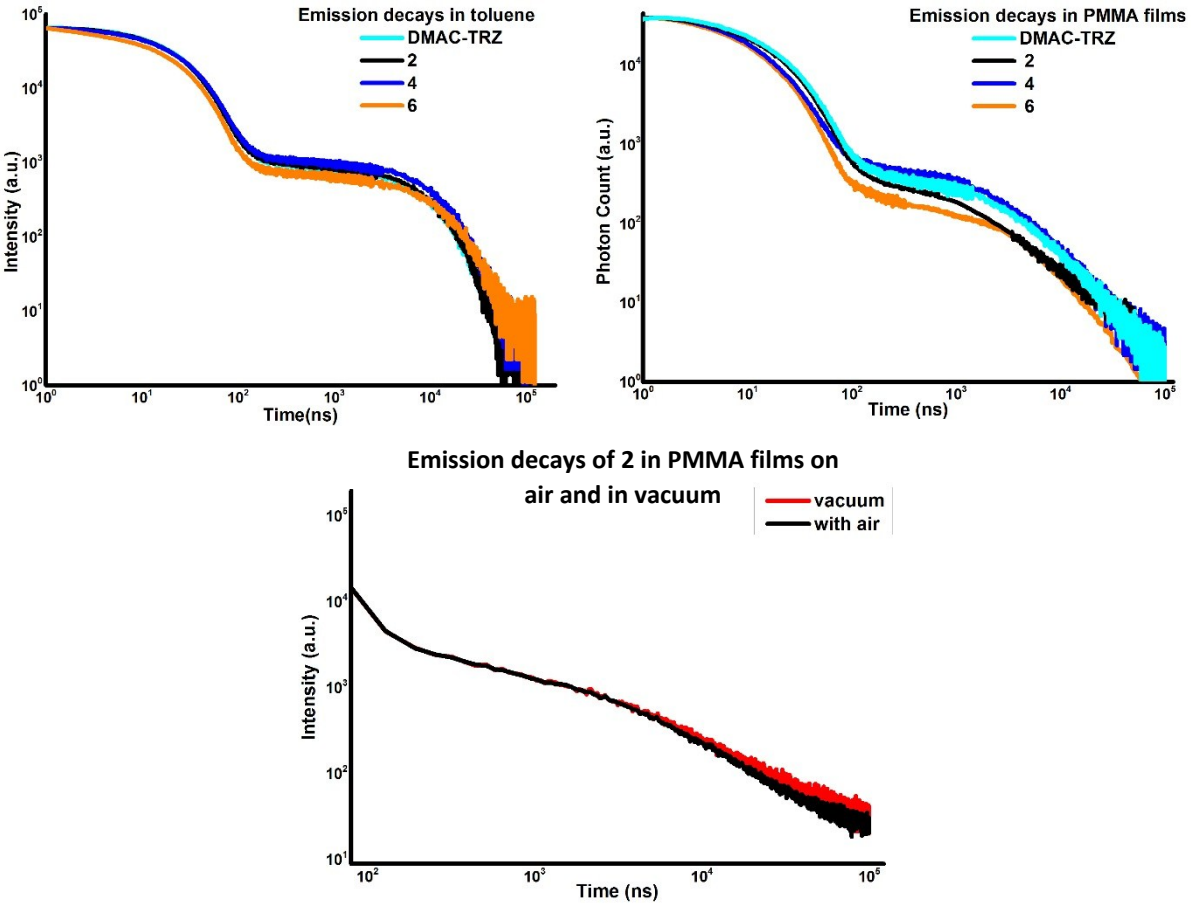


Figure S2. Emission decays at RT

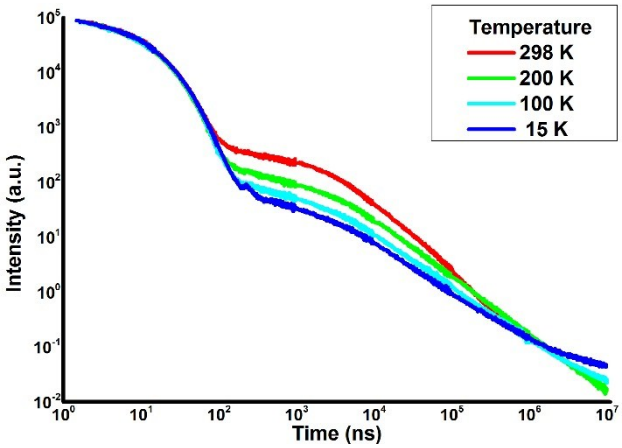


Figure S3. Emission decays of **6** in PMMA film at various temperatures.

Table S3. Oscillator strengths calculated from the experimental absorption and emission bands corresponding to the S_1–S_0 transitions

Cmpd	f_{abs}	f_{em}
DMAC-TRZ	0.035	0.026
1	0.040	0.033
2	0.025	0.023
3	0.031	0.021
4	0.010	0.018
5	0.009	0.022
6	0.007	0.020

Molecular structure and unit cells in crystal phase

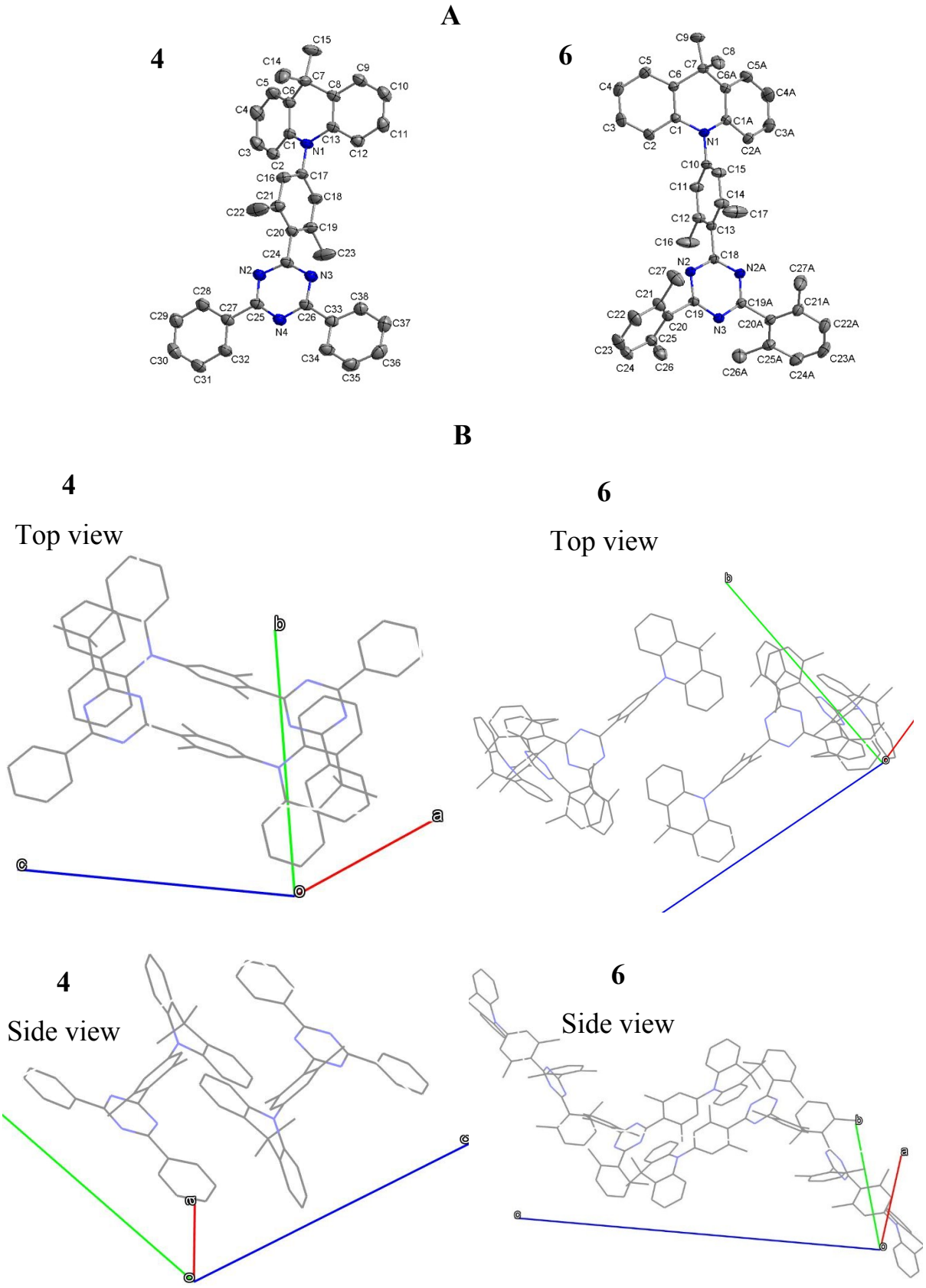


Figure S4. Crystal molecular structures (A) and unit cells (B) of **4** and **6**

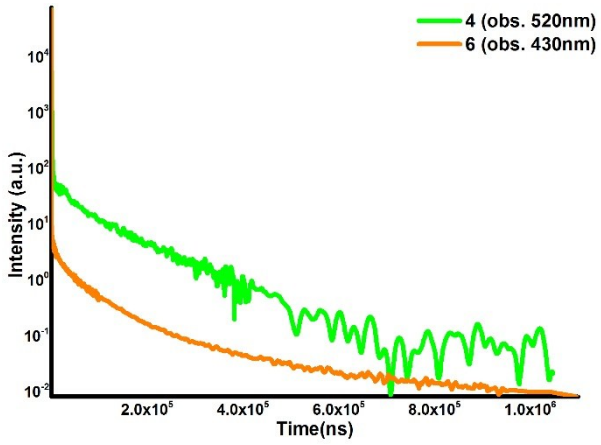


Figure S5. Emission decays of **4** and **6** in crystal phase.

HOMO LUMO

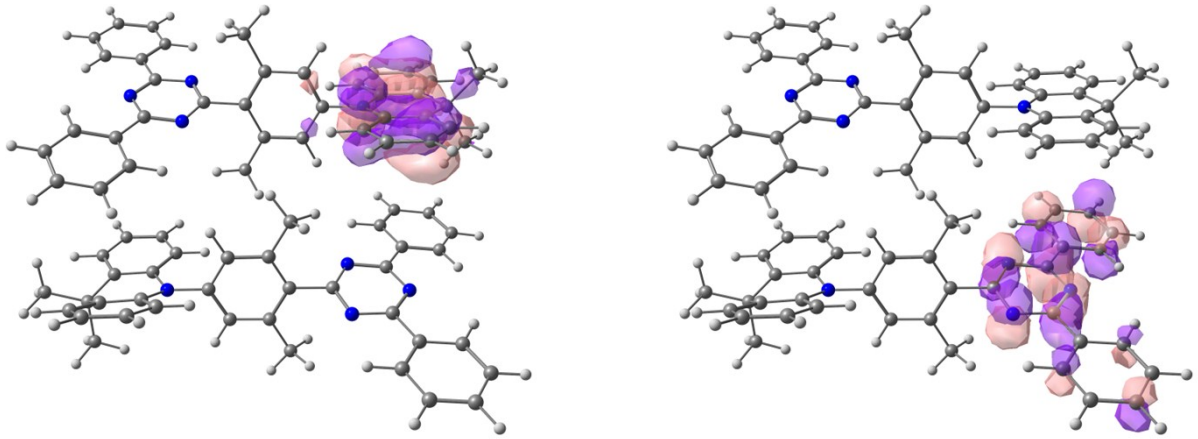


Figure S6. Frontier orbitals of the crystal dimer of **4**.

Parameters of OLED devices

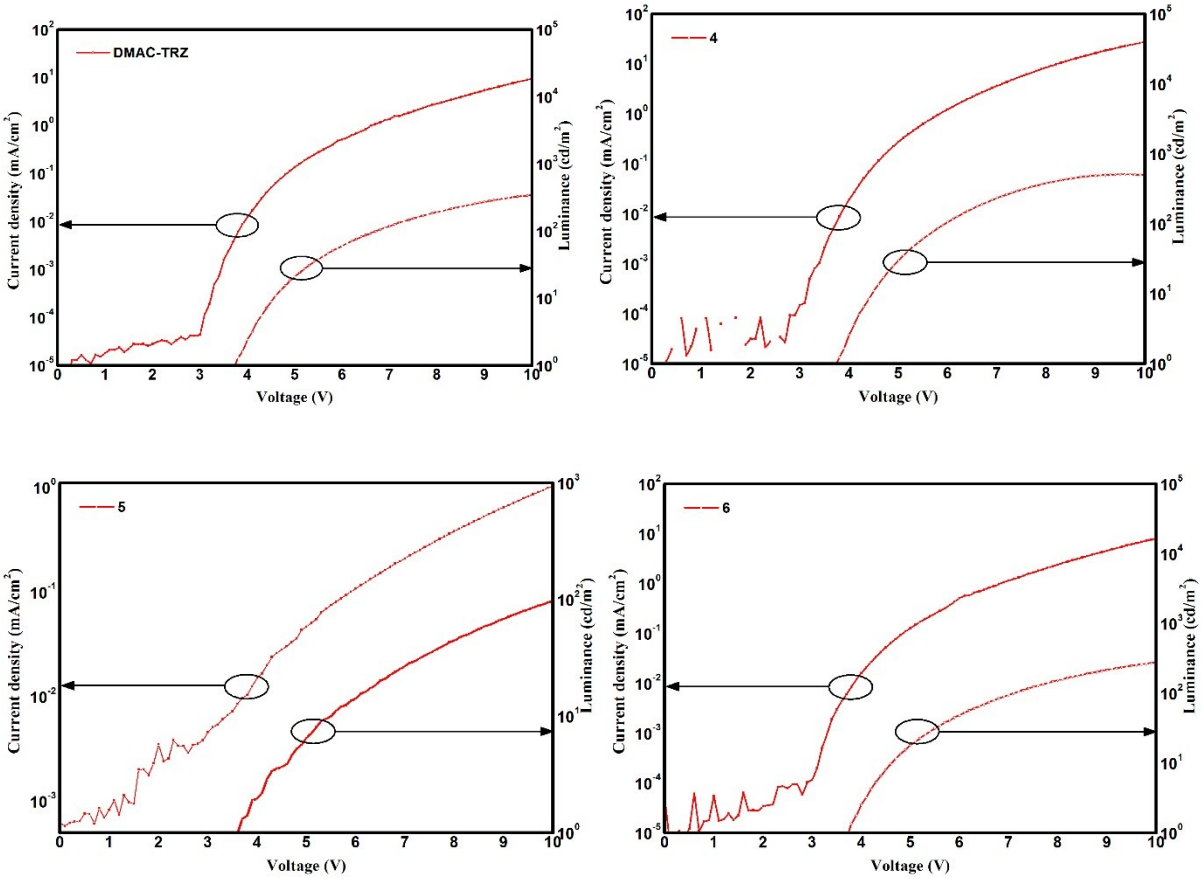


Figure S6. Current density-voltage-luminance diagram of the investigated OLEDs

Synthetic procedures and results of analyses

2,6-Dimethylbenzamidine. A suspension of ammonium chloride (6.7 g, 0.127 mol) in dry toluene (135 ml) was purged with Ar and cooled down to –15°C. 2M solution of trimethylaluminum in toluene (63.4 ml, 0.127 mol) was added dropwise maintaining the mixture temperature below –10°C. Mixture was stirred for 30 min at –10°C, let to heat up to RT and stirred until gas evolution finished. 2,6-Dimethylbenzonitrile (5 g, 0.038 mol) was added and the mixture was refluxed under Ar for 3 days. The mixture was cooled to 0°C, methanol (50 ml) was added dropwise and stirring continued for 30 min. Solvents were evaporated under reduced pressure. The precipitate was washed thoroughly with toluene and then separately with hot isopropanol. Alcohol fractions were combined and evaporated to afford title compound as a free base after recrystallization from isopropanol/toluene mixture. Toluene fractions containing unreacted 2,6-dimethylbenzonitrile can be used in repeated synthesis. White powder, yield 41% (2.3 g). ^{1}H-NMR (300 MHz, DMSO-d6, δ): 2.82 (s, 6H), 6.11 (broad s, 2H), 7.00 (d, 2H, J = 7.6 Hz), 7.10 (dd, 1H, J = 8.5 Hz, J = 8.5 Hz), 8.32 (s, 1H).

General procedure for 2-(4-bromoaryl)-4,6-diaryl-1,3,5-triazines. Benzamidine hydrochloride (11 mmol) and potassium tert-butoxide (10.8 mmol) were mixed in DMSO and stirred at RT for 30 min. 4-Bromobenzaldehyde (5 mmol) was added and the mixture was stirred at 70–100°C for 15–40h. After cooling to RT, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (5 mmol) was added and mixture was stirred at 50°C for another hour. 50% aqueous methanol was added and the precipitate was collected by filtration. Column chromatography using 30–50% $CHCl_3$ in hexane afforded pure title compounds.

2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine. White powder, yield 87%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.58 (t, 2H, J = 7.3 Hz), 7.62 (t, 2H, J = 7.3 Hz), 7.70 (d, 2H, J = 8.6 Hz), 8,64 (d, 2H, J = 8.2Hz), 8.75 (d, 2H, J = 7.8 Hz).

2-(4-Bromophenyl)-4,6-bis(2-methylphenyl)-1,3,5-triazine. White powder, yield 65%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.82 (s, 6H), 7.35–7.40 (m, 4H), 7.45 (t, 2H, J = 7.7 Hz), 7.68 (d, 2H, J = 8.7 Hz), 8.27 (d, 2H, J = 7.7 Hz), 8.55 (d, 2H, J = 7.6 Hz).

2-(4-Bromo-2-methylphenyl)-4,6-diphenyl-1,3,5-triazine. White powder, yield 54%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.84 (s, 3H), 7.50–7.64 (m, 8H), 7.24 (d, 1H, J = 8.5 Hz), 8.72 (d, 4H, J = 7.6 Hz).

2-(4-Bromo-2-methylphenyl)-4,6-bis(2-methylphenyl)-1,3,5-triazine. White powder, yield 57%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.77 (s, 9H), 7.33–7.39 (m, 4H), 7.44 (t, 2H, J = 7.4 Hz), 7.49–7.52 (m, 2H), 8.14 (d, 1H, J = 8.2 Hz), 8.22 (d, 2H, J = 7.7 Hz).

2-(4-Bromo-2,6-dimethylphenyl)-4,6-diphenyl-1,3,5-triazine. White powder, yield 63%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.28 (s, 6H), 7.35 (s, 2H), 7.35 (t, 4H, J = 7.5 Hz), 7.61 (t, 2H, J = 7.2 Hz), 8.69 (d, 4H, J = 8.2 Hz).

2-(4-Bromo-2,6-dimethylphenyl)-4,6-bis(2-methylphenyl)-1,3,5-triazine. White powder, yield 43%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.34 (s, 6H), 2.74 (s, 6H), 7.31–7.37 (m, 6H), 7.43 (t, 2H, J = 7.5 Hz), 8.21 (d, 2H, J = 7.8 Hz).

2-(4-Bromo-2,6-dimethylphenyl)-4,6-bis(2,6-dimethylphenyl)-1,3,5-triazine. White powder, yield 27%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.2 (s broad, 18H), 7.12 (d, 4H, J = 7.6 Hz), 7.21–7.27 (m, 2H), 7.30 (s, 2H).

General procedure for 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (DMAC-TRZ) and its derivatives (1-6). Mixture of 9,9-dimethyl-9,10-dihydroacridine (1 mmol, 209 mg) 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (1.03 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.05 mmol, 46mg) and tri-tert-butylphosphonium tetrafluoroborate (0.1 mmol, 29 mg) were dissolved in dry toluene under Ar atmosphere. Potassium tert-butoxide (1.5 mmol) was added and the mixture was stirred at 90°C for 10–20h. Solvent was removed by evaporation, the residue was

washed by water and purified by column chromatography with 30–50% $CHCl_3$ in hexane as eluent.

10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydro-acridine (DMAC-TRZ). Yellow powder, yield 91%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.72 (s, 6H), 6.38 (dd, 2H, J = 7.9 Hz; J = 1.5 Hz), 6.96–6.99 (m, 4H), 7,49 (dd, 2H, J = 7.9 Hz; J = 1.5 Hz), 7.55–7.59 (m, 8H), 8.81–8.84 (m, 4H), 9.03 (d, 2H, J = 8.6 Hz),. ^{13}C NMR (250 MHz, $CDCl_3$, δ): 172.0, 171.3, 145.6, 140.8, 136.4, 132.9, 131.8, 131.7, 130.5, 129.2, 128.9, 126.7, 125.6, 121.1, 114.4, 36.3, 31.5 HRMS *m/z*: calcd for $C_{36}H_{28}N_4$, 517.2387 $[M+H]^+$; found, 517.2394. Elem. Anal. Calcd for $C_{36}H_{28}N_4$, %: C 83.69; H 5.46; N 10.84. Found, %: C 80.17; H 6.19; N 10.90.

10-(4-(4,6-bis(2-methylphenyl)-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (1). Yellow powder, yield 91%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.71 (s, 6H), 2.87 (s, 6H), 6.37 (d, 2H, J = 8.0 Hz), 6.93–7.01 (m, 4H), 7.37–7.42 (m, 4H), 7.44–7.49 (m, 4H), 7.54 (d, 2H, J = 8.5 Hz), 8.32 (d, 2H, J = 7.7 Hz), 8.93 (d, 2H, J = 8.5 Hz). ^{13}C NMR (250 MHz, $CDCl_3$, δ): 174.6, 170.4, 145.6, 140.8, 139.3, 136.3, 136.2, 132.1, 131.8, 131.7, 131.5, 131.3, 130.5, 126.6, 126.4, 125.5, 121.1, 114.4, 36.3, 31.4, 22.7. HRMS *m/z*: calcd for $C_{38}H_{32}N_4$, 545.2700 $[M+H]^+$; found, 545.2703. Elem. Anal. Calcd for $C_{38}H_{32}N_4$, %: C 83.79; H 5.92; N 10.29. Found, %: C 83.17; H 5.88; N 9.88.

10-(3-methyl-4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (2). Pale yellow powder, yield 88%. ^{1}H NMR ($CDCl_3$, δ): 1.72 (s, 6H), 2.92 (s, 3H), 6.43 (d, 2H, J = 8.0 Hz), 6.95 (t, 2H, J = 7.4 Hz), 7.01 (t, 2H, J = 7.4 Hz), 7.36–7.42 (m, 2H), 7.48 (d, 2H, J = 7.6 Hz), 7.56–7.66 (m, 6H), 8.59 (d, 1H, J = 8.0 Hz), 8.78 (d, 4H, J = 8.0 Hz). ^{13}C NMR (250 MHz, $CDCl_3$, δ): 174.2, 171.7, 143.9, 142.5, 140.8, 136.3, 134.5, 134.1, 132.9, 130.3, 129.3, 129.1, 129.0, 126.6, 125.5, 120.9, 114.5, 36.2, 31.6, 22.7. HRMS *m/z*: calcd for

$C_{37}H_{30}N_4$, 531.2543 [*M*+H]$^+$; found, 531.2547. Elem. Anal. Calcd for $C_{37}H_{30}N_4$, %: C 83.74; H 5.70; N 9.88. Found, %: C 83.22; H 5.62; N 9.52.

10-(3-methyl-4-(4,6-bis(2-methylphenyl)-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (3). Pale yellow powder, yield 85%. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.71 (s, 6H), 2.83 (s, 6H), 2.86 (s, 3H), 6.40 (d, 2H, J = 8.1 Hz), 6.94 (t, 2H, J = 7.5 Hz), 7.00 (t, 2H, J = 7.8 Hz), 7.33–7.41 (m, 6H), 7.44–7.48 (m, 4H), 8.26 (d, 2H, J = 7.6 Hz), 8.48 (d, 1H, J = 7.9 Hz). ^{13}C NMR (250 MHz, $CDCl_3$, δ):174.3, 173.5, 143.7, 142.3, 140.8, 139.1, 136.3, 136.2, 134.4, 134.1, 132.1, 131.5, 131.2, 130.3, 129.0, 126.6, 126.4, 125.5, 120.9, 114.4, 36.2, 31.5, 22.6, 22.5. HRMS *m/z*: calcd for $C_{39}H_{34}N_4$, 559.2856 [*M*+H]$^+$; found, 559.2849. Elem. Anal. Calcd for $C_{39}H_{34}N_4$, %: C 83.84; H 6.13; N 10.03. Found, %: C 83.51; H 5.99; N 9.83.

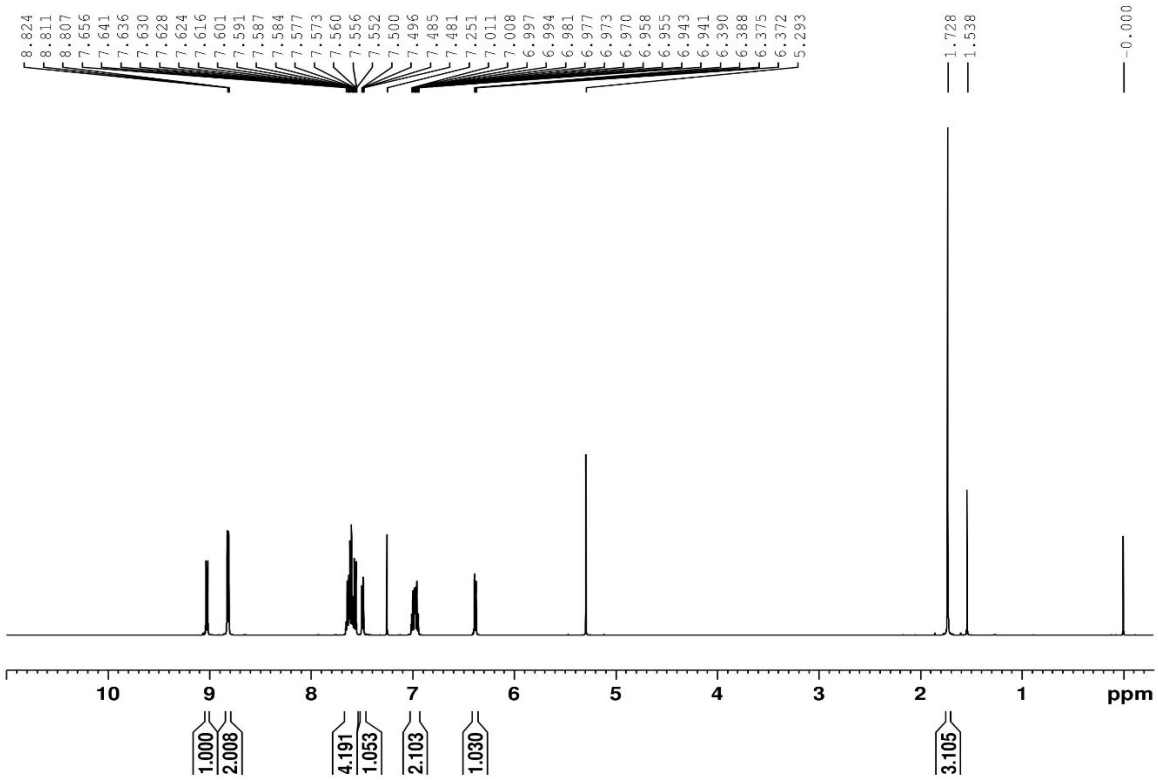
10-(3,5-dimethyl-4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (4). White powder, yield 85%. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.72 (s, 6H), 2.40 (s, 6H), 6.50 (d, 2H, J = 8.2 Hz), 6.95 (t, 2H, J = 7.5 Hz), 7.05 (t, 2H, J = 7.6 Hz), 7.17 (s, 2H), 7.47 (d, 2H, J = 7.6 Hz), 7.57–7.61 (m, 4H), 7.62–7.66 (m, 2H), 8.74–8.76 (m, 4H). ^{13}C NMR (250 MHz, $CDCl_3$, δ): 176.1, 172.0, 141.8, 140.9, 139.6, 137.6, 136.1, 133.1, 130.8, 130.1, 129.3, 129.0, 126.6, 125.5, 120.7, 114.6, 36.2, 31.7, 20.8. HRMS *m/z*: calcd for $C_{38}H_{32}N_4$, 545.2700 [*M*+H]$^+$; found, 545.2709. Elem. Anal. Calcd for $C_{38}H_{32}N_4$, %: C 83.79; H 5.92; N 10.29. Found, %: C 83.69; H 5.91; N 10.11.

10-(3,5-dimethyl-4-(4,6-bis(2-methylphenyl)-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (5). White powder, yield 98%. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.70 (s, 6H), 2.35 (s, 6H), 2.78 (s, 6H), 6.45 (d, 2H, J = 8.1 Hz), 6.93 (t, 2H, J = 7.5 Hz), 7.01 (t, 2H, J = 7.6 Hz), 7.14 (s, 2H), 7.35–7.40 (m, 4H), 7.45 (t, 4H, J = 6.1 Hz), 8.19 (d, 2H, J = 7.8 Hz). ^{13}C NMR (250 MHz, $CDCl_3$, δ): 175.5, 174.8, 141.7, 140.9, 139.0, 138.9, 137.8, 136.0, 132.1, 131.5, 131.4, 130.6, 130.1, 126.6, 126.4, 125.5, 120.7, 114.6, 36.2, 31.7, 22.3, 20.5. HRMS *m/z*:

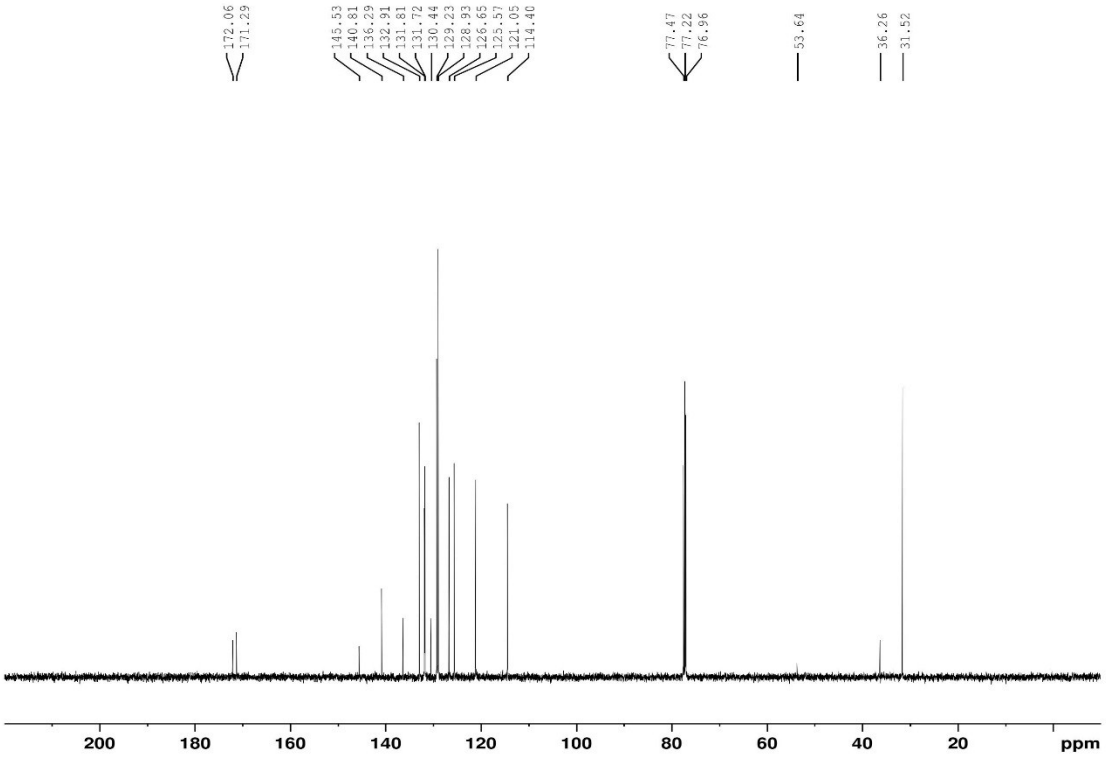
calcd for $C_{40}H_{36}N_4$, 573.3013 [M+H]$^+$; found, 573.3018. Elem. Anal. Calcd for $C_{40}H_{36}N_4$, %: C 83.88; H 6.34; N 9.78. Found, %: C 83.71; H 6.35; N 9.48.

10-(3,5-dimethyl-4-(4,6-bis(2,6-dimethylphenyl)-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (6). White powder, yield 90%. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 1.69 (s, 6H), 2.26 (s, 12H), 2.30 (s, 6H), 6.36 (d, 4H, J = 7.7 Hz), 6.87–7.00 (m, 4H), 7.11–7.18 (m, 6H), 7.23–7.29 (m, 2H), 7.44 (d, 2H, J = 7.6 Hz). ^{13}C NMR (250 MHz, $CDCl_3$, δ): 177.8, 177.0, 142.1, 140.8, 138.3, 137.2, 137.1, 134.9, 130.6, 130.0, 129.5, 128.1, 126.6, 125.5, 120.7, 114.5, 36.1, 31.8, 20.2, 20.1. HRMS *m/z*: calcd for $C_{42}H_{40}N_4$, 601.3326 [M+H]$^+$; found, 601.3330. Elem. Anal. Calcd for $C_{42}H_{40}N_4$, %: C 83.96; H 6.71; N 9.33. Found, %: C 83.90; H 6.79; N 9.43.

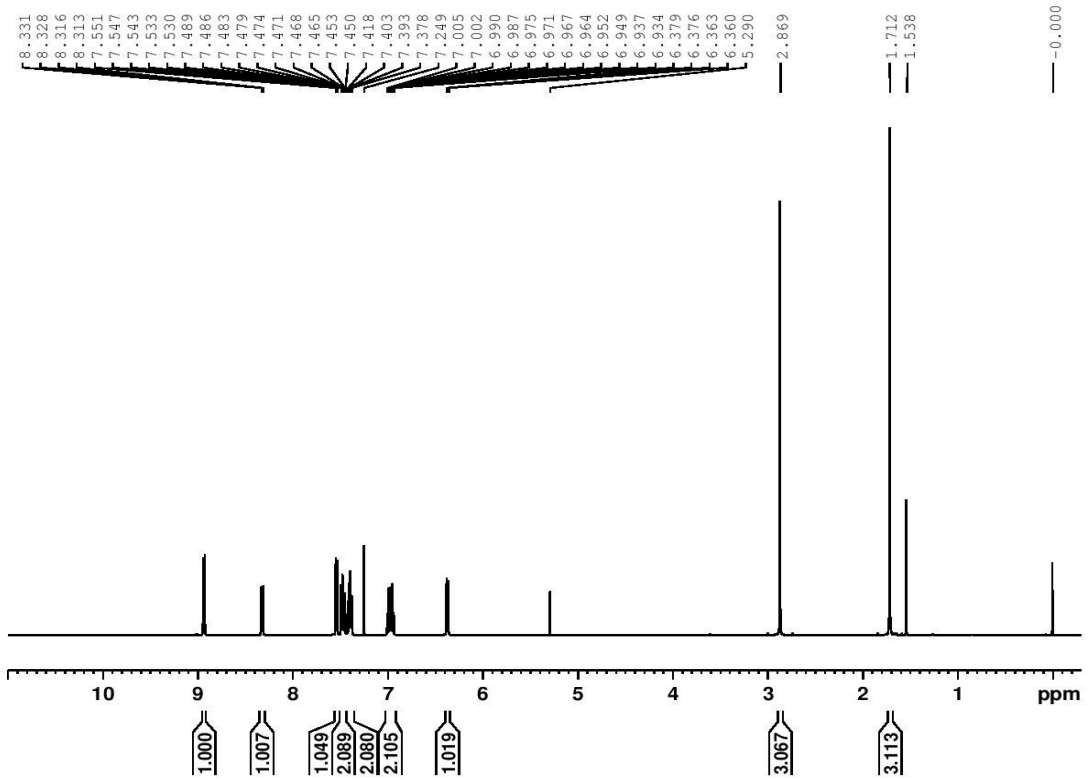
^{1}H NMR spectra of **DMAC-TRZ** in $CDCl_3$



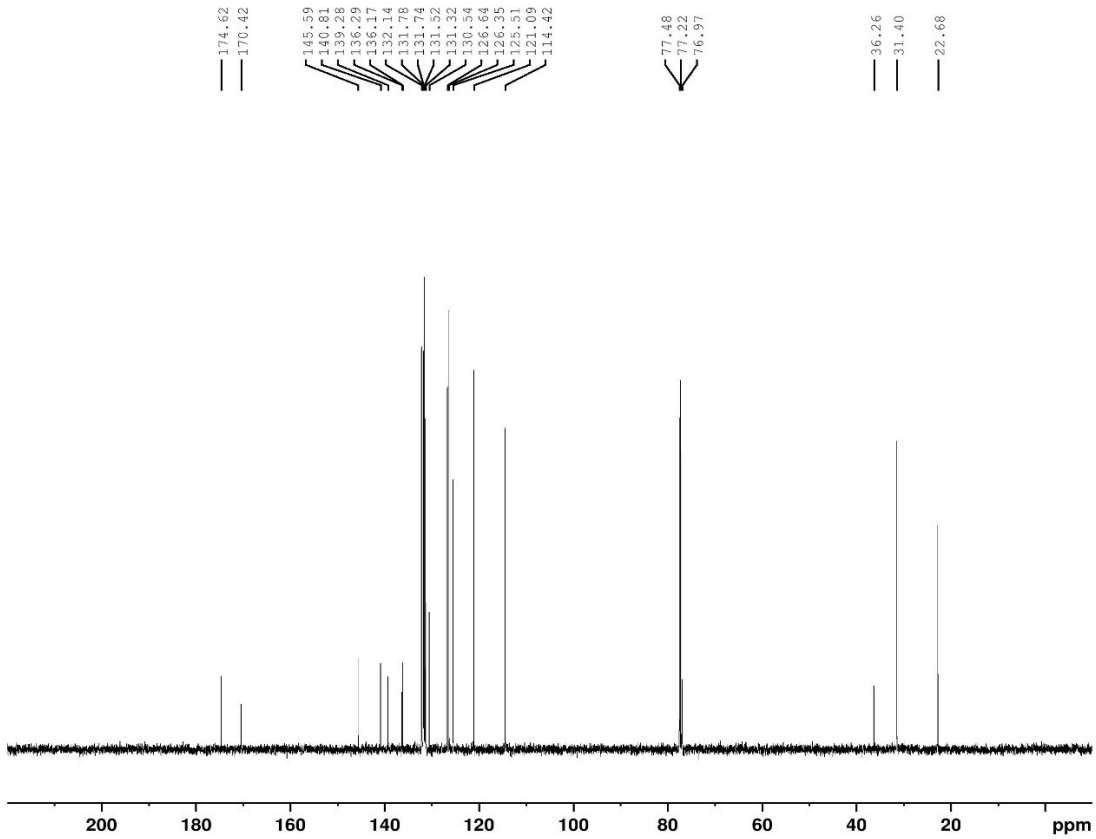
^{13}C NMR spectra of **DMAC-TRZ** in $CDCl_3$



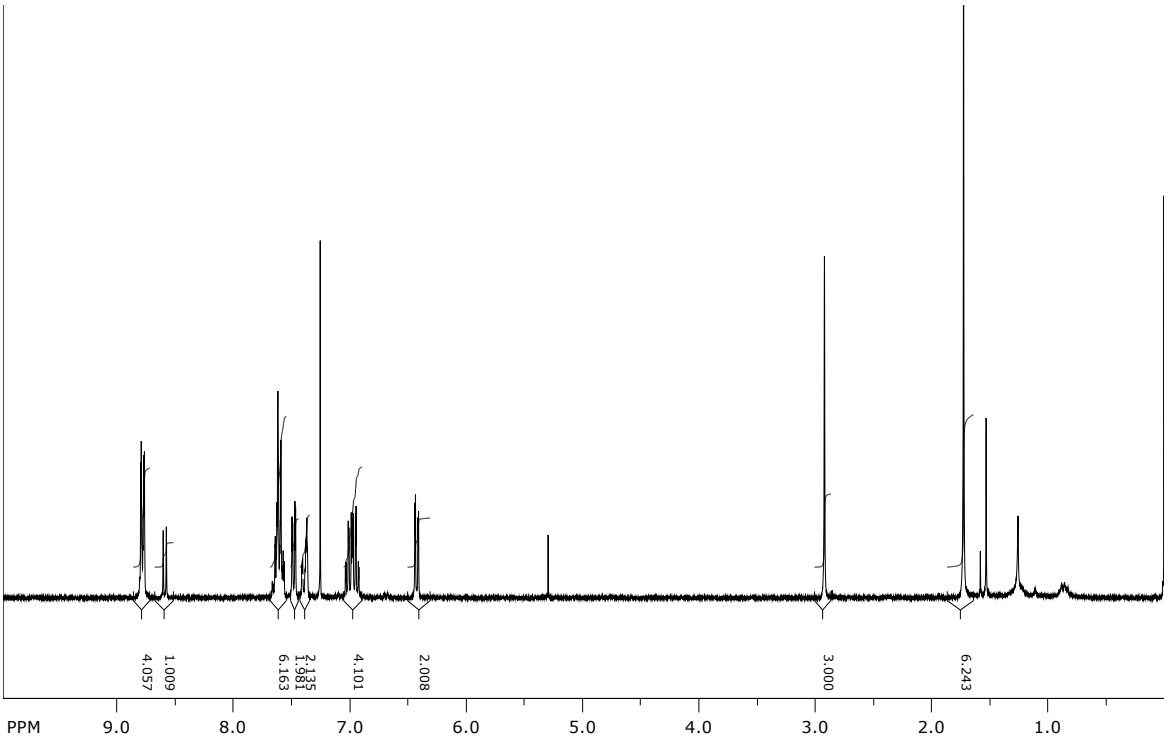
^{1}H NMR spectra of **1** in $CDCl_3$



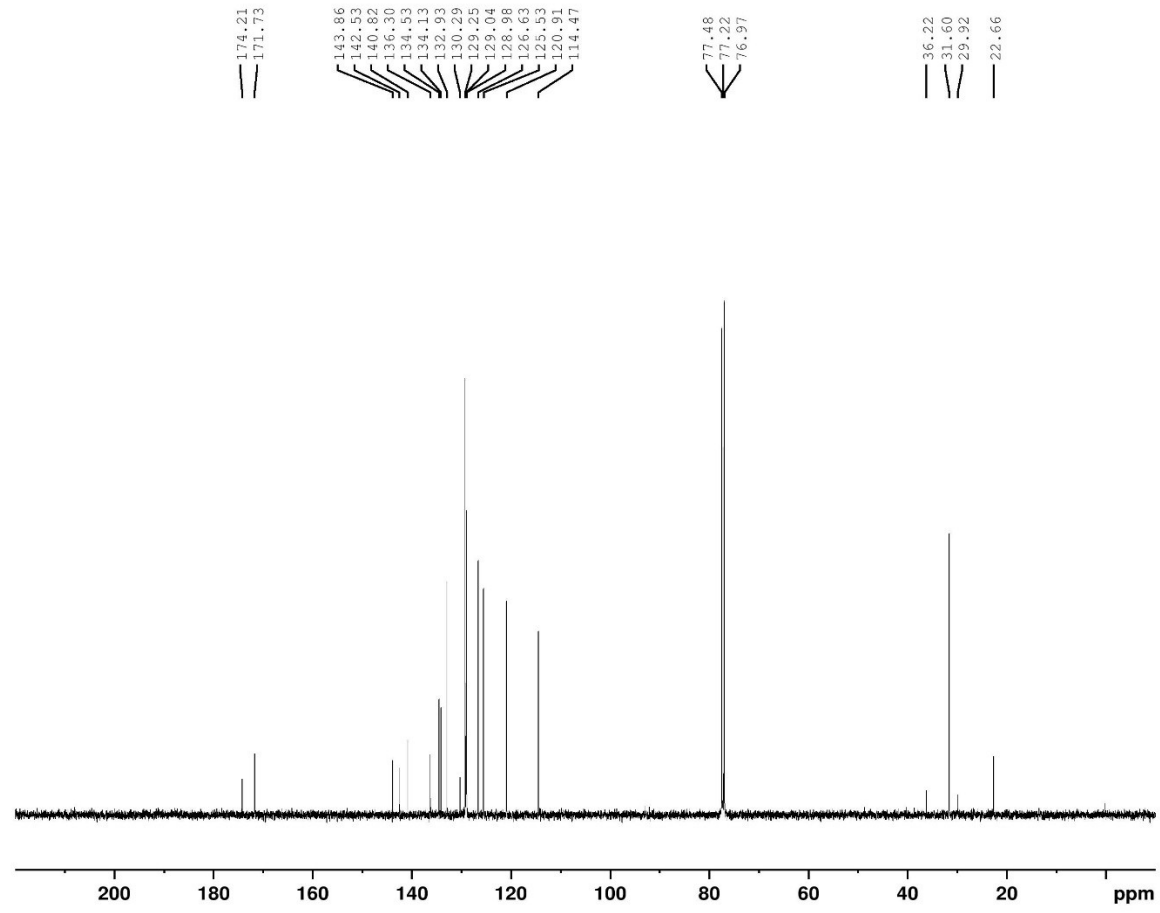
^{13}C NMR spectra of **1** in $CDCl_3$



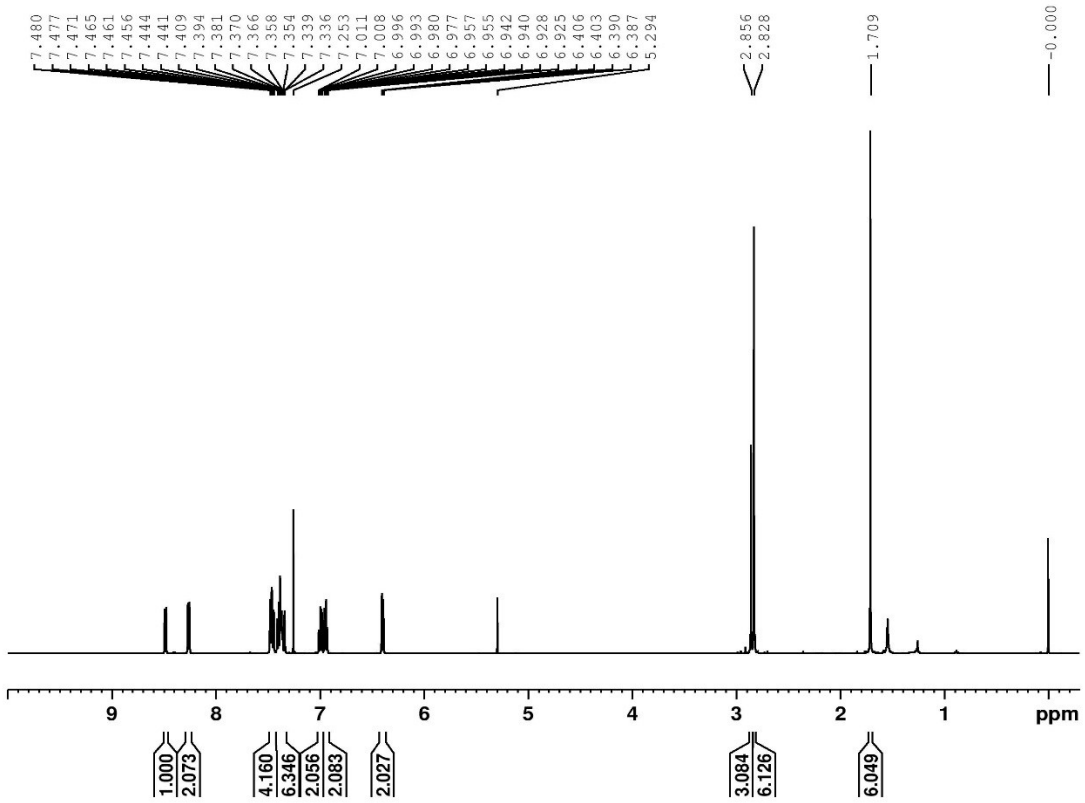
^{1}H NMR spectra of **2** in $CDCl_3$



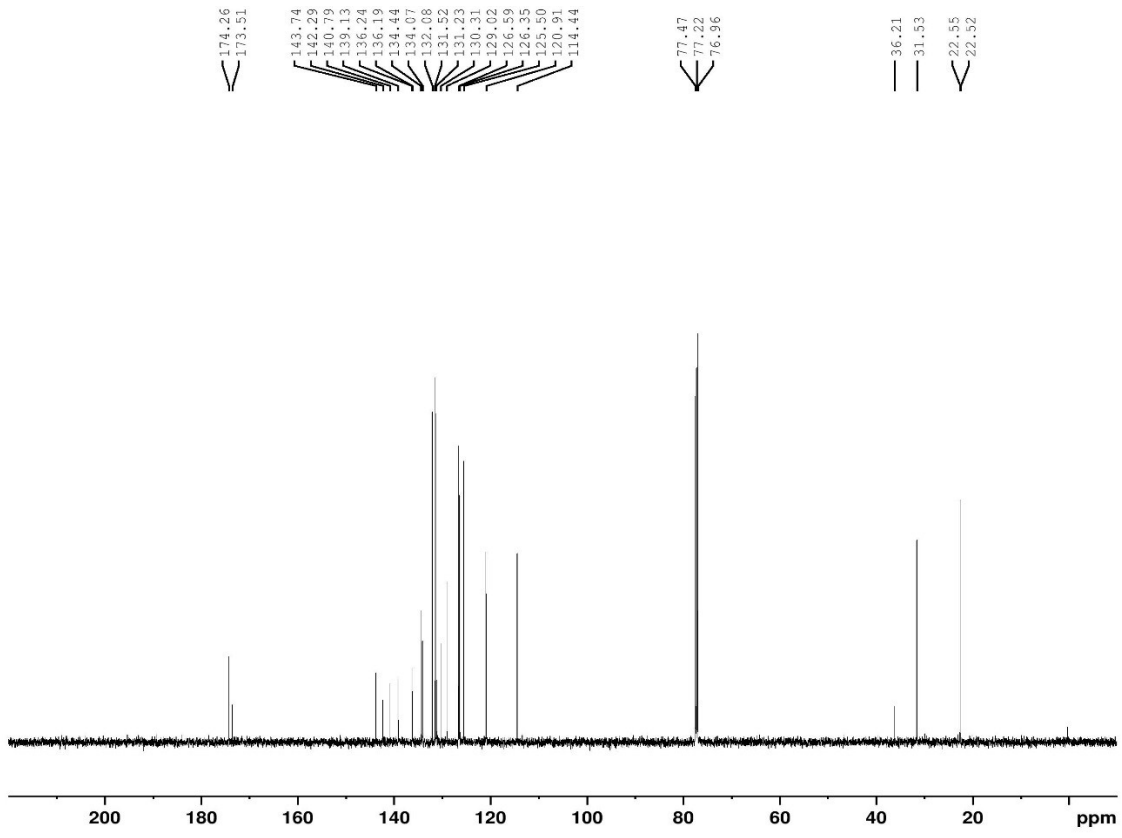
^{13}C NMR spectra of **2** in $CDCl_3$



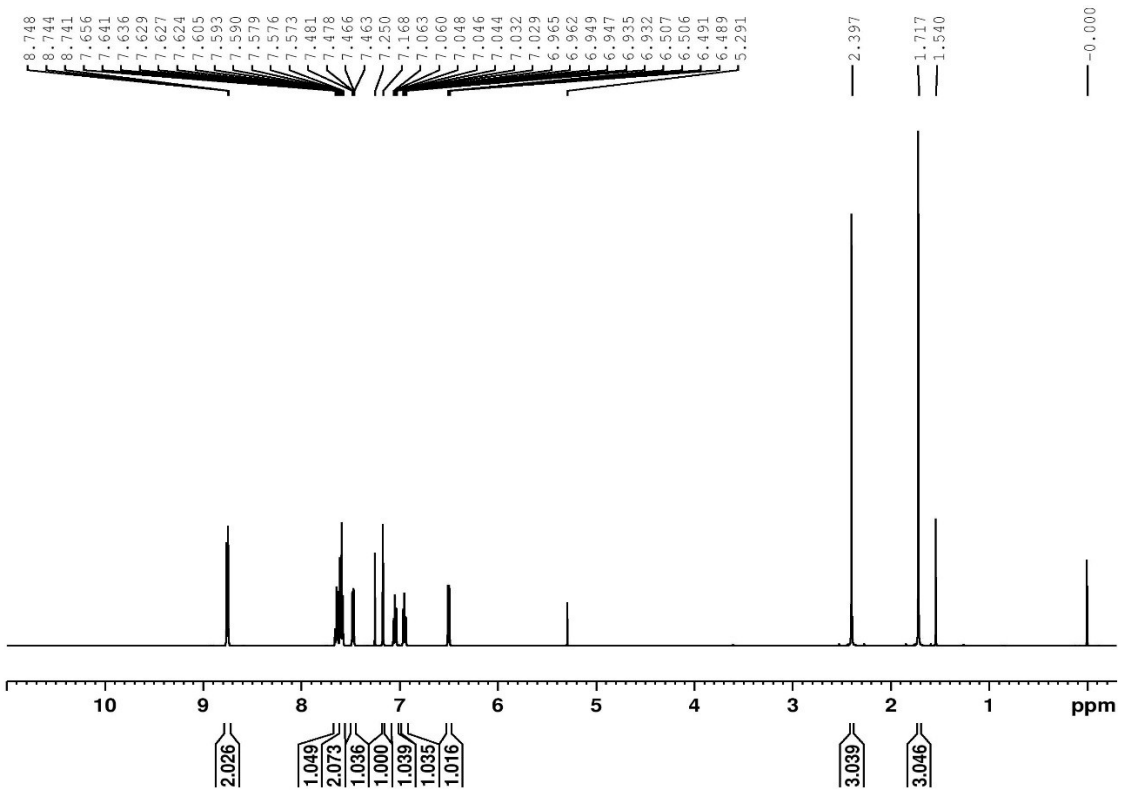
^{1}H NMR spectra of **3** in $CDCl_3$



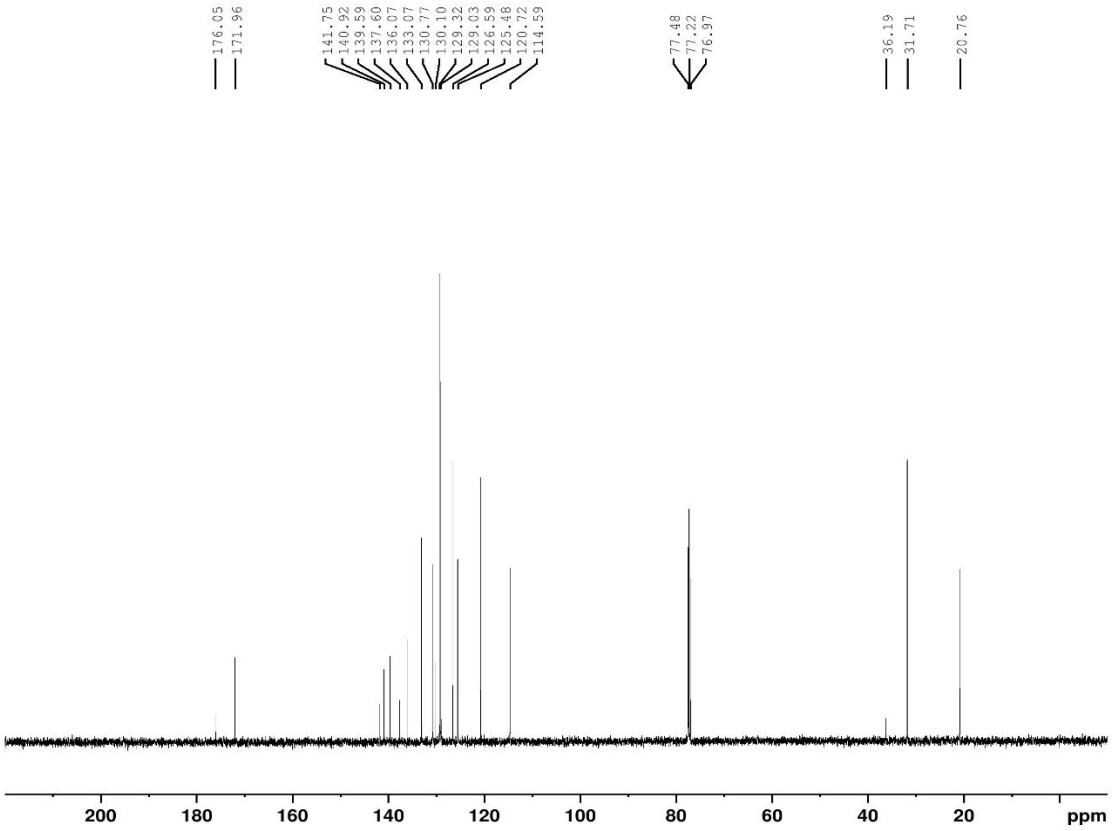
^{13}C NMR spectra of **3** in $CDCl_3$



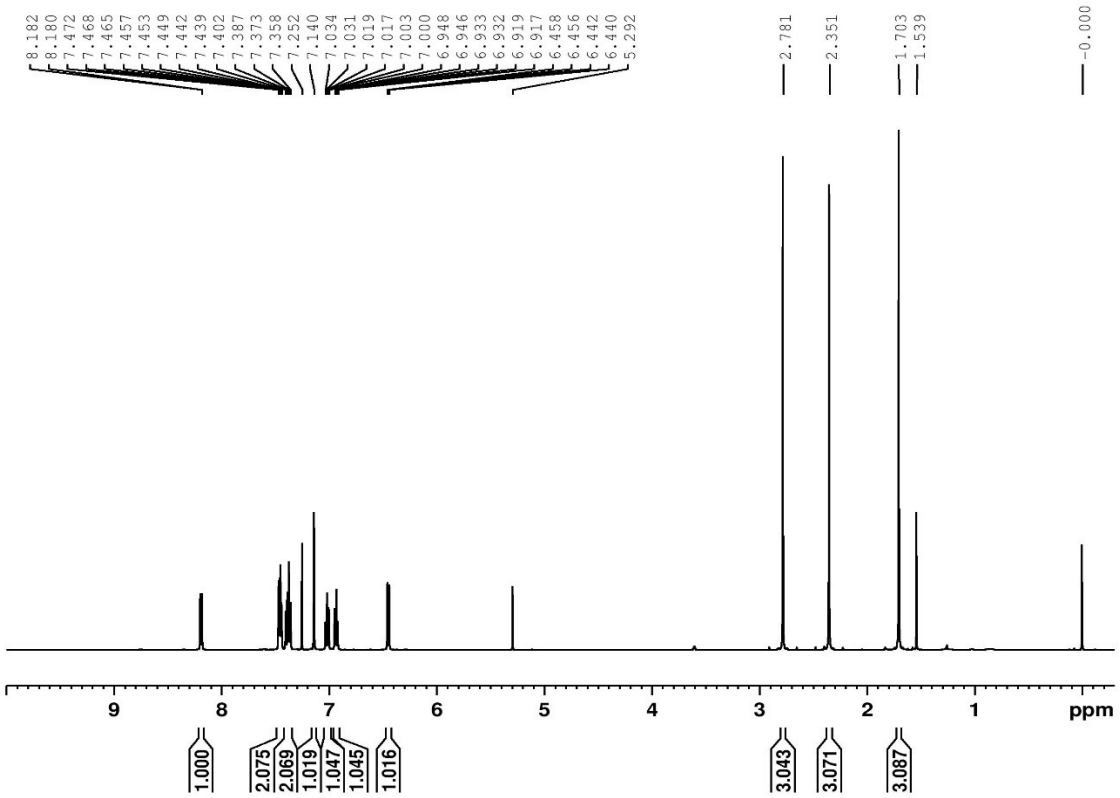
^{1}H NMR spectra of **4** in $CDCl_3$



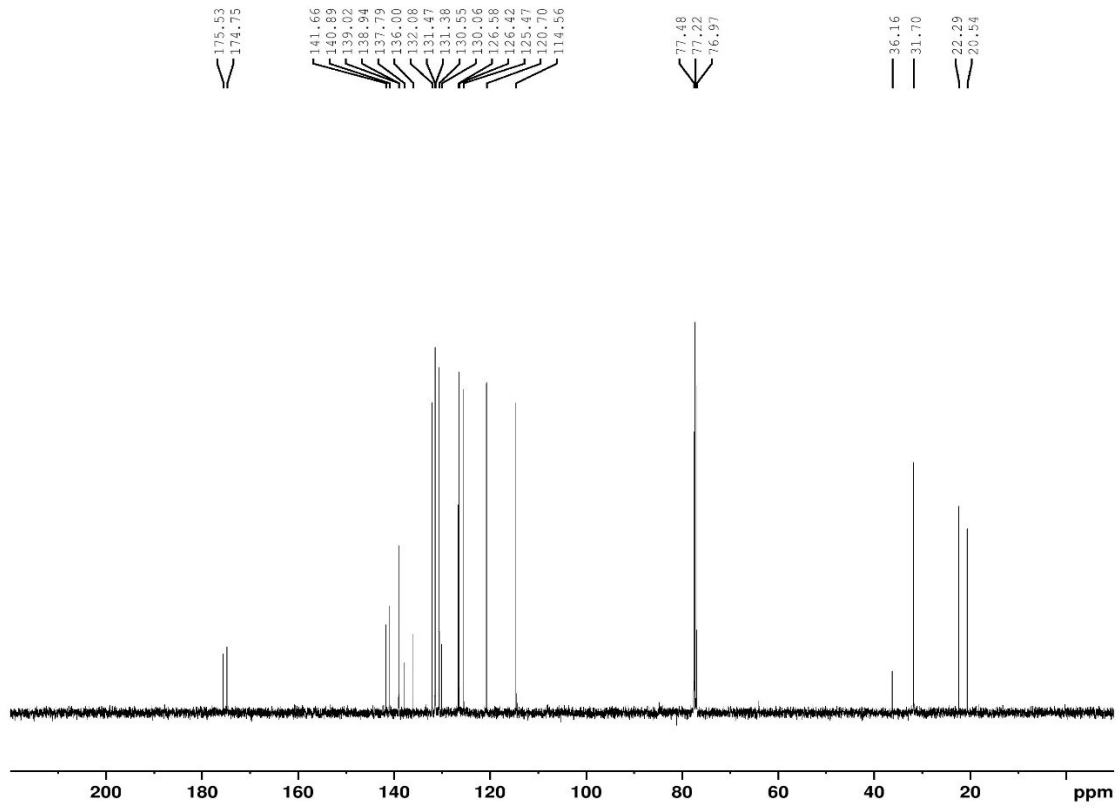
^{13}C NMR spectra of **4** in $CDCl_3$



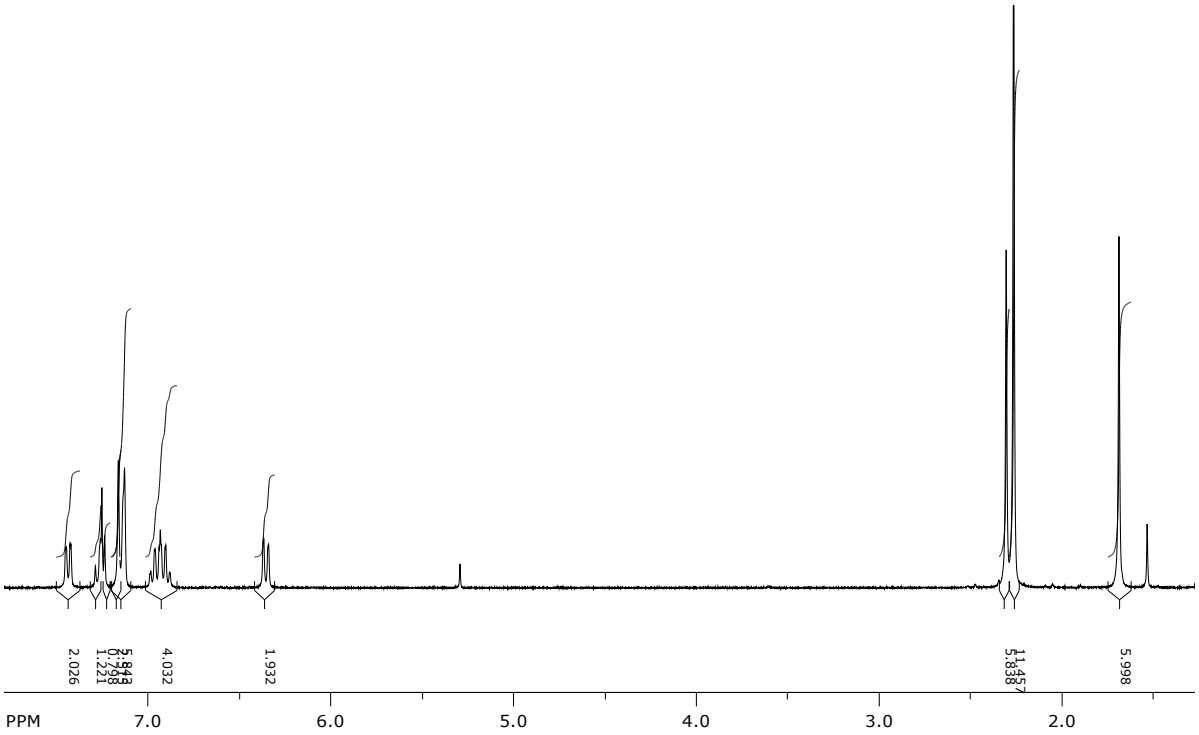
^{1}H NMR spectra of **5** in $CDCl_3$



^{13}C NMR spectra of **5** in $CDCl_3$



^{1}H NMR spectra of **6** in $CDCl_3$



^{13}C NMR spectra of **6** in $CDCl_3$