Tuning the emission of carbazole-triazine based emitters through aryl substituents: towards efficient TADF emitters

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Contents

1. Materials and equipment

All reagents were purchased from Sigma-Aldrich or Oakwood Chemical and used without purification. 2,4,6-trichloro-1,3,5-triazine, 9*H*-carbazole, sodium hydride 60% w/w, (2,6-dimethylphenyl)boronic acid, (4-methoxyphenyl)boronic acid, (4-fluorophenyl)boronic acid, (4-(trifluoromethyl)phenyl)boronic acid, tetrakis(triphenylphosphine)palladium, sodium carbonate, and anhydrous sodium sulphate were used as received. Hexane, dichloromethane (DCM), cyclohexane, and methanol solvents were analytical grade and distilled before use and toluene and tetrahydrofuran (THF) were distilled and dried under molecular sieves (3 Å). Anhydrous and freeze−pump−thawed toluene for photophysical characterization was obtained from an Innovative Technology SPS-400-4 solvent purification system. Milli-Q-Millipore water was employed in all the experiments. Silica gel (0.063–0.200 mm) was used in column chromatography.

The ^{1}H and $^{13}C\{^{1}H\}$ nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV III HD 400 MHz spectrometer with chloroform-*d* ($CDCl_3$) as solvent with TMS as internal standard. Coupling constants are given in Hz and chemical shifts are reported in δ values in ppm. Gas chromatography-mass spectroscopy (GC – MS) analysis were performed employing an electronic impact (EI) ionization method and a 25mx0.2mmx0.33μm column with a 5% phenylpolysiloxane phase. All unknown products were further characterized by high-resolution mass spectrometry (HRMS) using Agilent1200 HPLC system (Agilent Technologies, Wilmington, USA) coupled with a high-resolution mass spectrometer Bruker micrOTOF-QII (Bruker Daltonics, Billerica, MA, USA) with an electrospray ionization source (ESI) available in UMYMFOR, UBA, Argentina. Thermogravimetric analyses (TGA) were performed in TA Instruments-Discovery TGA 55 (UNITEFA-CONICET-UNC).

Photophysical characterization: Absorbance measurements were obtained using a Cary 60 spectrometer available at University of British Columbia (UBC), Canada and in a Shimadzu UV-2101 PC available at National University of Córdoba (UNC), Argentina. Fluorescence measurements and lifetimes were obtained from Edinburgh Instruments FS5 and FLS1000 spectrofluorometer (UBC, Canada) and in Horiba Nanolog (UNC, Argentina). Lifetime (τ_p, τ_d) decays were obtained using an EPLED (λ_{ex} = 313 nm) coupled with a time-correlated single photon counting (TCSPC) detector, or a pulsed Xe microsecond flash lamp (Xe μF) coupled with a multichannel scaling (MCS) detector. Absolute photoluminescence quantum yields were determined using Edinburgh Instruments FS5 spectrofluorometer with the SC-30 Integrating Sphere Module.

Anhydrous and oxygen-free toluene for inert measurements in solution was obtained from an Innovative Technology SPS-400-4 solvent purification system.

2. Photophysical characterization

All measurements were conducted under air atmosphere, in quartz cuvettes, at room temperature. Solutions in toluene were prepared at time of use. UV-vis spectra were recorded (Figures S1-4). Absorption and emission spectra of in different solvents **DCzTRZAr-DiMe**, **DCzTRZAr-OMe**, **DCzTRZAr-F** and **DCzTRZAr-CF$_3$**.

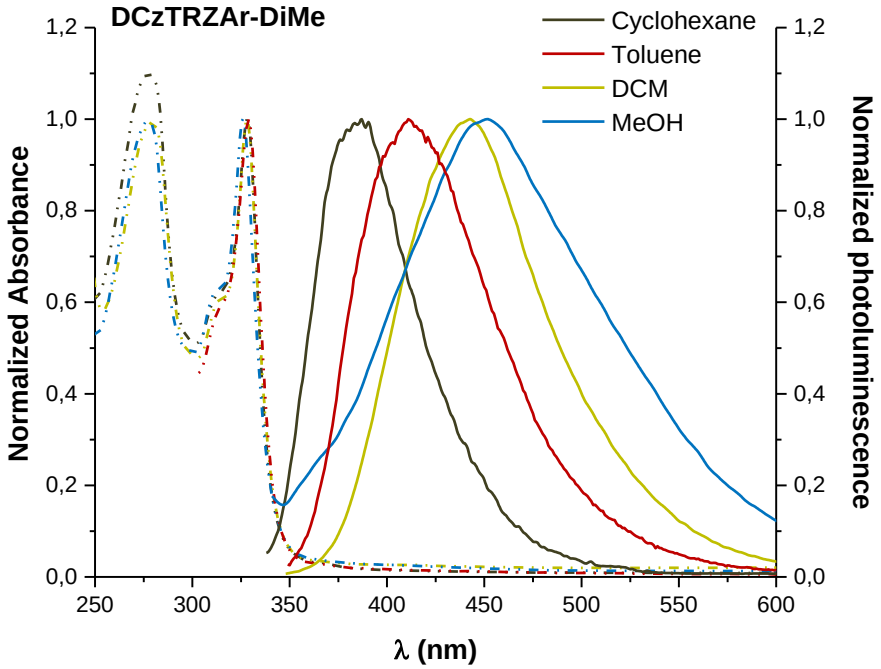


Figure S1: UV-visible (dashed) and photoluminescence spectra (solid) of **DCzTRZAr-DiMe** in different solvents, measured in 10^{-5} M solutions for UV and 10^{-6} M solutions for photoluminescence. Excitation wavelengths: λ_{exc} (cyclohexane)=328 nm, λ_{exc} (toluene) = 329 nm, λ_{exc} (DCM) = 328 nm and λ_{exc} (MeOH) = 326 nm

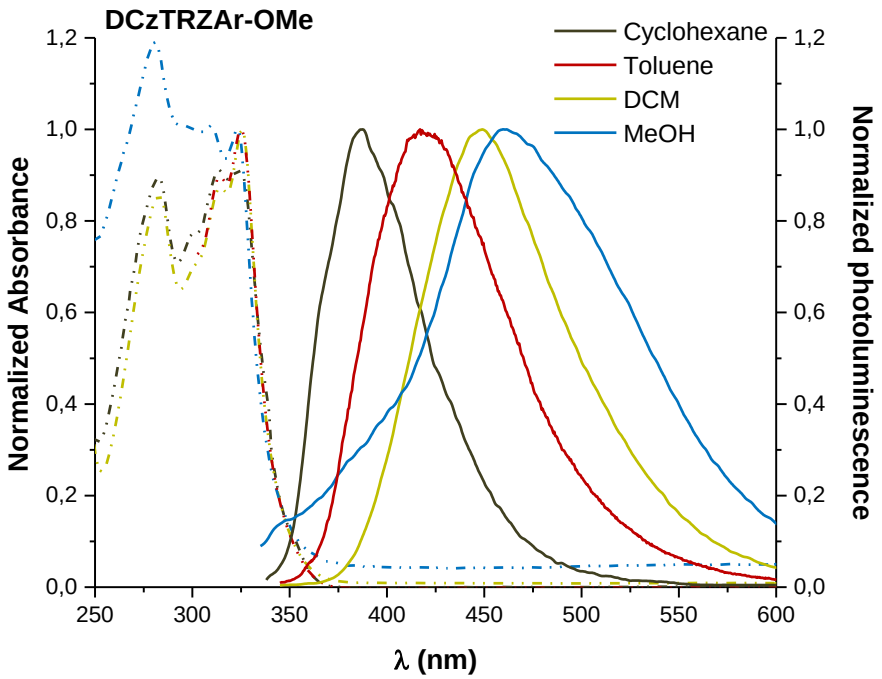


Figure S2: UV-visible (dashed) and photoluminescence spectra (solid) of **DCzTRZAr-OMe** in different solvents, measured in 10^{-5} M solutions for UV and 10^{-6} M solutions for photoluminescence. Excitation wavelengths: λ_{exc} (cyclohexane)=324 nm, λ_{exc} (toluene) = 325 nm, λ_{exc} (DCM) = 326 nm and λ_{exc} (MeOH) = 323 nm

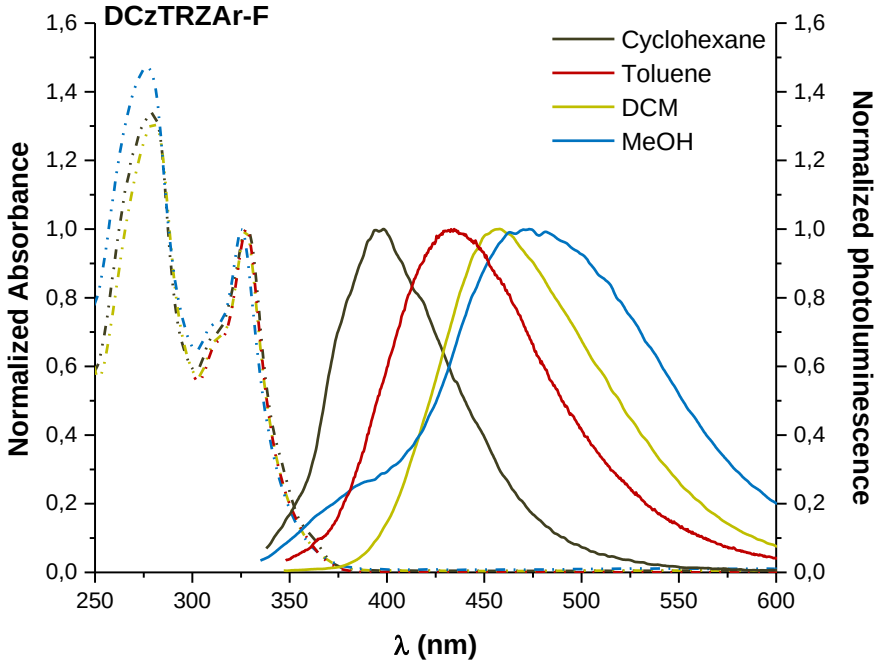


Figure S3: UV-visible (dashed) and photoluminescence spectra (solid) of **DCzTRZAr-F** in different solvents, measured in 10^{-5} M solutions for UV and 10^{-6} M solutions for photoluminescence. Excitation wavelengths: λ_{exc} (cyclohexane)=326 nm, λ_{exc} (toluene) = 326 nm, λ_{exc} (DCM) = 326 nm and λ_{exc} (MeOH) = 325 nm

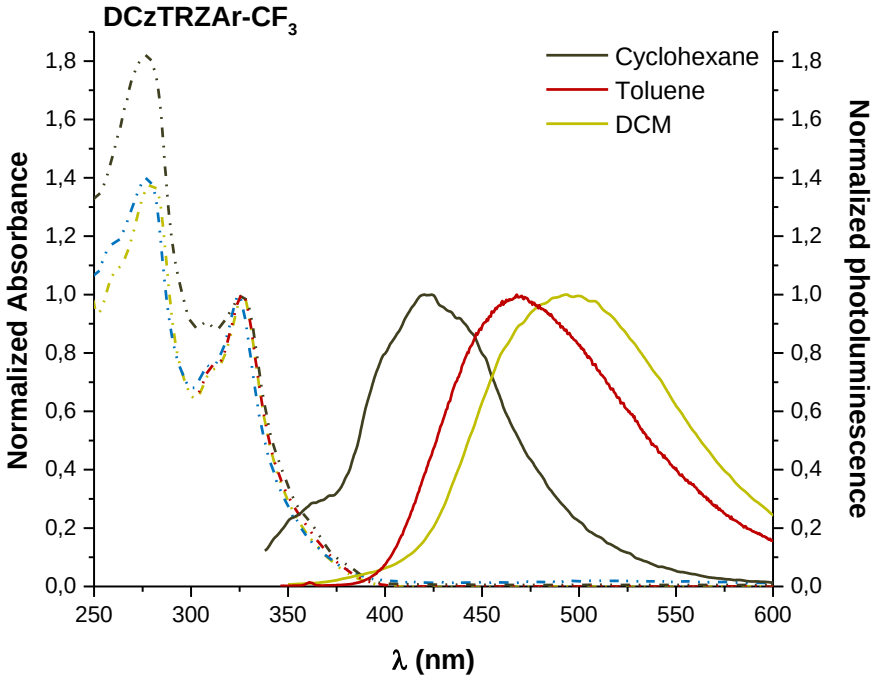


Figure S4: UV-visible (dashed) and photoluminescence spectra (solid) of **DCzTRZAr-CF$_3$** in different solvents, measured in 10^{-5} M solutions for UV and 10^{-6} M solutions for photoluminescence. Excitation wavelengths: λ_{exc} (cyclohexane)=327 nm, λ_{exc} (toluene) = 326 nm, λ_{exc} (DCM) = 326 nm

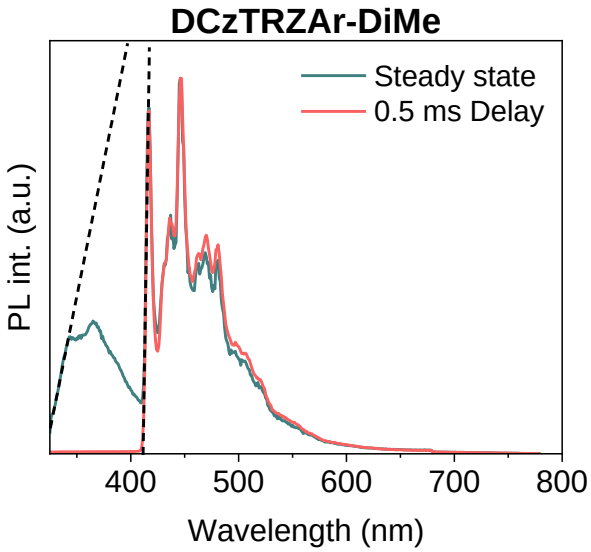


Figure S5: Time-resolved (0.5 ms delay, red trace) and steady-state emission (no delay, green trace) spectra measured in 2-methyltetrahydrofuran at 77 K for **DCzTRZAr-DiMe**

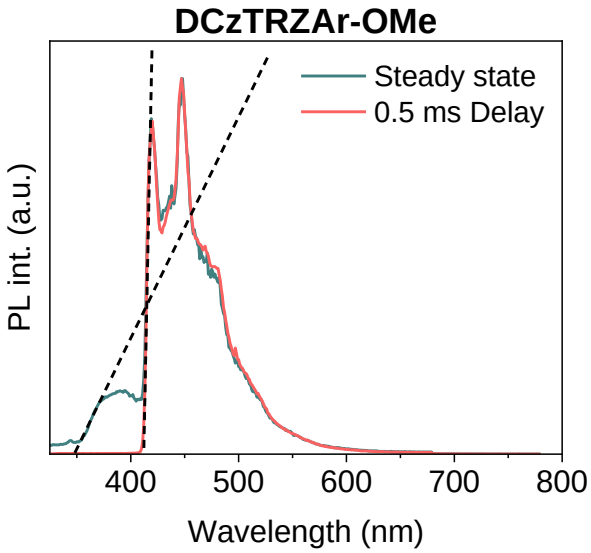


Figure S6: Time-resolved (0.5 ms delay, red trace) and steady-state emission (no delay, green trace) spectra measured in 2-methyltetrahydrofuran at 77 K for **DCzTRZAr-OMe**

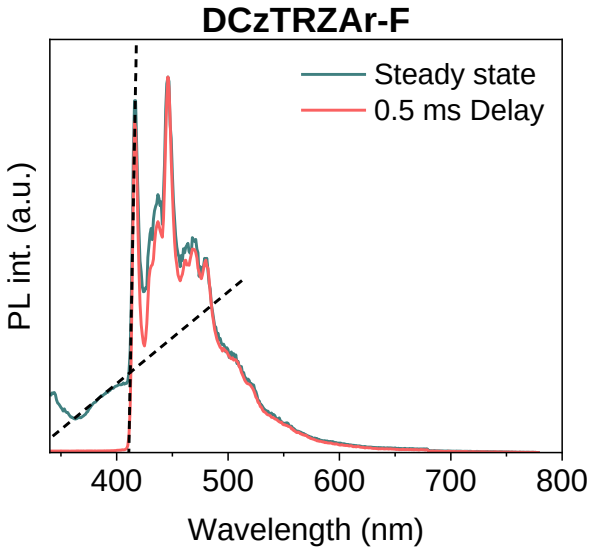


Figure S7: Time-resolved (0.5 ms delay, red trace) and steady-state emission (no delay, green trace) spectra measured in 2-methyltetrahydrofuran at 77 K for **DCzTRZAr-F**

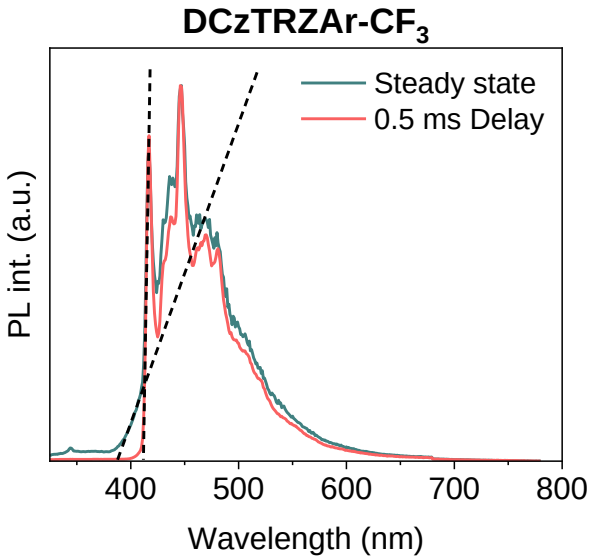


Figure S8: Time-resolved (0.5 ms delay, red trace) and steady-state emission (no delay, green trace) spectra measured in 2-methyltetrahydrofuran at 77 K for **DCzTRZAr-CF$_3$**

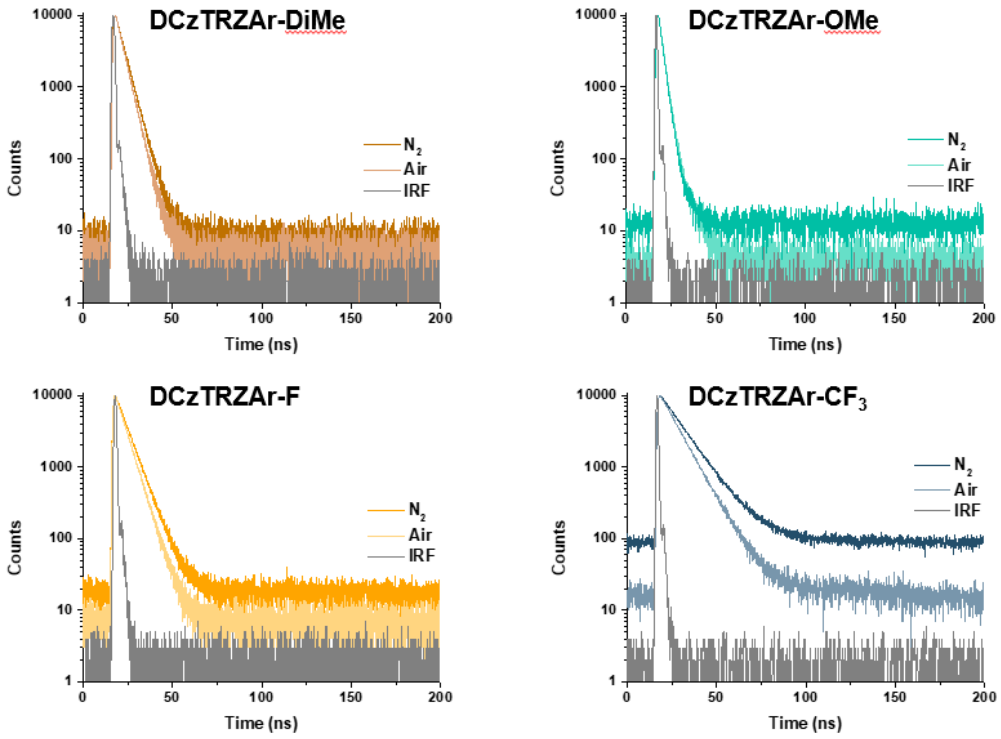


Figure S9*:* Prompt PL decays for **DCzTRZAr** compounds in toluene solutions (optical densities of 0.12 at the excitation wavelength) under N_2 (darker coloured trace) and air (lighter coloured trace). All measurements were performed using TCSPC with a 313 nm EPLED source

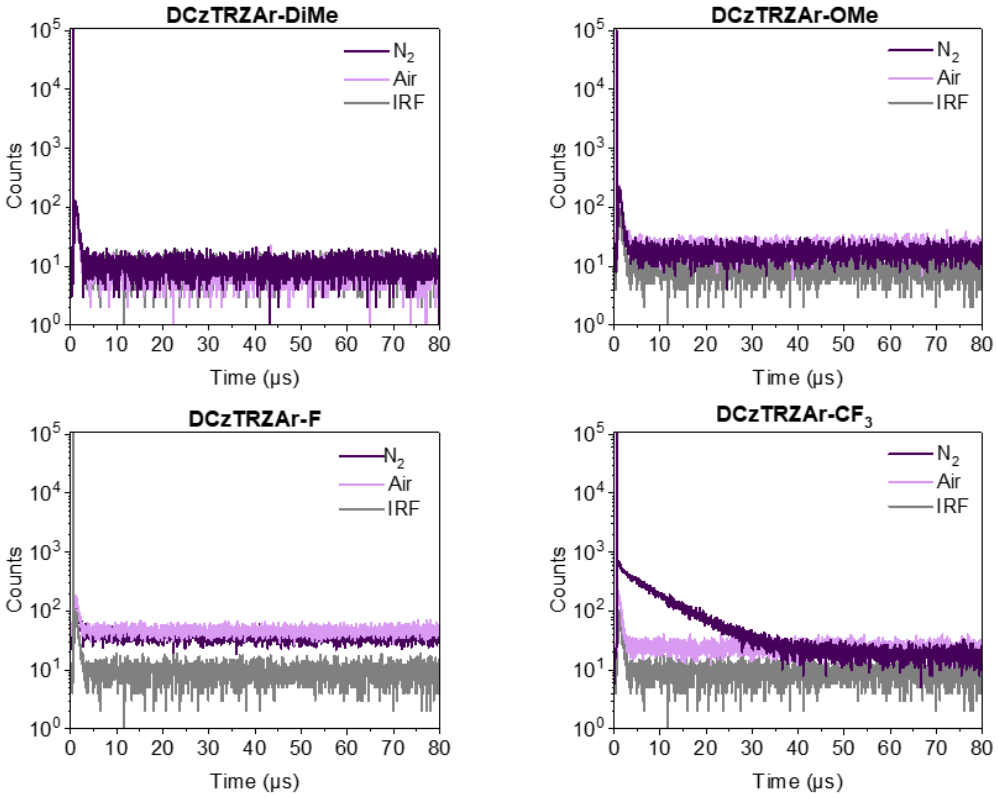


Figure S10: PL decays for **DCzTRZAr** compounds in toluene solutions (optical densities of 0.12 at the excitation wavelength) under N_2 (darker coloured trace) and air (lighter coloured trace). All measurements were performed using a 313 nm EPLED source coupled with multichannel scaling (MCS) detector.

The PL decay data for **DCzTRZAr-CF$_3$** were fitted by a bi-exponential function (equation 1) using data shown in Figure S10 under nitrogen. B_1 and B_2 are the pre-exponential for lifetimes τ_1 and τ_2, respectively. R_p and R_d are individual component ratio for prompt and delayed fluorescence and are calculated as $R_p = \tau_1B_1/(\tau_1B_1 + \tau_2B_2)$ and $R_d=1 - R_p$.

$$R(t) = B_1 e^{\frac{-t}{\tau_1}} + B_2 e^{\frac{-t}{\tau_2}} \qquad \text{equation (1)}$$

The values obtained for B_1, B_2, τ_1, τ_2, R_p and R_d are:

B_1= 2791071.25 B_2= 542.34

τ_1=12 ns τ_2=8.29 μs

Rp= 0.88 R_d= 0.12

The rate constants and quantum efficiencies were determined using the following equations according to Adachi's method.[37-43]

$\Phi_p = \Phi_{PL}R_p$ equation (2)

$\Phi_d = \Phi_{PL}R_d$ equation (3)

$k_p = 1/\tau_p$ equation (4)

$k_d = 1/\tau_d$ equation (5)

$$k_F = \Phi_p/\tau_p \qquad \text{equation (6)}$$

$$k_{\mathrm{RISC}} = \frac{k_p+k_d}{2} - \sqrt{\left(\frac{k_p+k_d}{2}\right)^2 - k_p k_d\left(1+\frac{\Phi_d}{\Phi_p}\right)} \qquad \text{equation (7)}$$

$$k_{ISC} = (k_p k_d \Phi_d)/(k_{RISC}\Phi_p) \qquad \text{equation (8)}$$

3. Theoretical calculations

Figure S11 shows HOMO and LUMO distributions in gas phase.

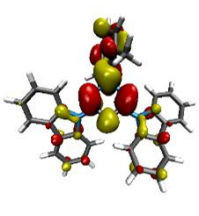
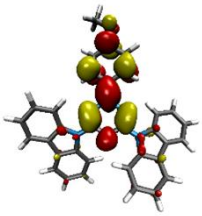
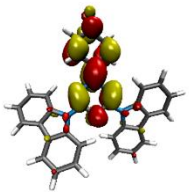
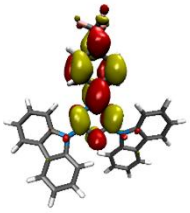
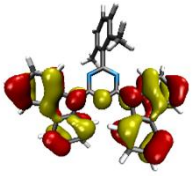
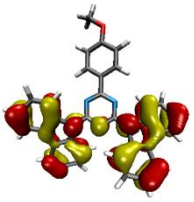
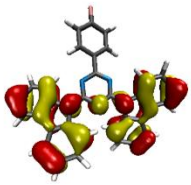
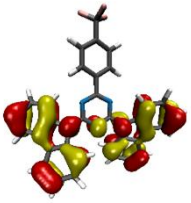
	DCzTRZAr-DiMe	**DCzTRZAr-OMe**	**DCzTRZAr-F**	**DCzTRZAr-CF_3**
	-0.52 eV	-0.76 eV	-0.98 eV	-1.31 eV
LUMO				
HOMO				
	-7.40 eV	-7.33 eV	-7.45 eV	-7.53 eV

***Figure S11**:* HOMO – LUMO distributions of **DCzTRZAr-DiMe**, **DCzTRZAr-OMe**, **DCzTRZAr-F** and **DCzTRZAr-CF_3** in gas phase

Tables S1 – S12 show cartesian coordinates of ground state, singlet excited state and triplet state of **DCzTRZAr** compounds, calculated at the CAM-B3LYP/6-31+G(d) level in toluene, using PCM.

Table S1. Cartesian coordinates [Å] of the optimized structure of ground state for **DCzTRZAr-DiMe**

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.0005	1.9214	-0.0006	**C**	3.3993	-4.6089	1.1501	**H**	1.3457	-5.0047	1.6620
N	1.1798	1.3045	0.0266	**C**	2.0494	-4.2684	1.2854	**H**	0.5312	-2.7603	1.0575
C	1.1242	-0.0304	0.0346	**C**	1.5769	-3.0040	0.9485	**H**	-0.5328	-2.7582	-1.0610
N	-0.0003	-0.7440	-0.0002	**C**	-1.5784	-3.0020	-0.9512	**H**	-1.3480	-5.0020	-1.6670
C	-1.1244	-0.0296	-0.0353	**C**	-2.0513	-4.2661	-1.2889	**H**	-3.7367	-5.6034	-1.4214
N	-1.1792	1.3051	-0.0277	**C**	-3.4011	-4.6066	-1.1526	**H**	-5.3647	-3.9193	-0.5900
C	0.0008	3.4131	-0.0009	**C**	-4.3119	-3.6698	-0.6843	**H**	-3.2460	1.8720	0.8041
N	-2.3229	-0.7147	-0.0868	**C**	-3.9698	1.0774	0.7066	**H**	-5.6169	2.2725	1.3573
N	2.3224	-0.7158	0.0869	**C**	-5.3109	1.2904	1.0093	**H**	-7.3062	0.4807	1.1124
C	-2.4953	-2.0711	-0.4648	**C**	-6.2672	0.2791	0.8708	**H**	-6.6228	-1.7736	0.3186
C	-3.8569	-2.3972	-0.3459	**C**	-5.8892	-0.9799	0.4258	**H**	0.8644	6.0398	1.9607
C	-4.5499	-1.2135	0.1213	**C**	0.5038	4.1013	1.1156	**H**	-0.8631	6.0392	-1.9632
C	-3.5969	-0.1896	0.2577	**C**	0.4883	5.4961	1.0984	**H**	0.0004	7.2775	-0.0013
C	2.4943	-2.0726	0.4640	**C**	0.0005	6.1913	-0.0012	**C**	1.0373	3.3746	2.3260
C	3.8560	-2.3987	0.3462	**C**	-0.4871	5.4958	-1.1007	**H**	0.3331	2.6184	2.6893
C	4.5496	-1.2146	-0.1192	**C**	-0.5023	4.1009	-1.1176	**H**	1.9750	2.8586	2.1002
C	3.5970	-0.1905	-0.2558	**H**	6.6227	-1.7749	-0.3149	**H**	1.2219	4.0774	3.1426
C	5.8893	-0.9811	-0.4221	**H**	7.3072	0.4799	-1.1061	**C**	-1.0358	3.3740	-2.3279
C	6.2679	0.2783	-0.8657	**H**	5.6185	2.2722	-1.3513	**H**	-0.3333	2.6155	-2.6892
C	5.3120	1.2899	-1.0044	**H**	3.2469	1.8716	-0.8010	**H**	-1.9753	2.8608	-2.1027
C	3.9705	1.0768	-0.7033	**H**	5.3635	-3.9210	0.5904	**H**	-1.2175	4.0763	-3.1456
C	4.3106	-3.6716	0.6838	**H**	3.7346	-5.6060	1.4183				

Table S2. Cartesian coordinates [Å] of the optimized structure of ground state for **DCzTRZAr-OMe**

	X	Y	Z		X	Y	Z		X	Y	Z
C	1.4771	-0.7229	0.0234	**C**	1.2986	5.8515	0.3276	**H**	-2.5295	1.6922	-1.1286
N	1.4056	0.6098	-0.0376	**C**	2.5731	5.6765	0.8478	**H**	0.9000	6.8481	0.1614
C	0.1743	1.1160	-0.0434	**C**	3.0697	4.3875	1.0709	**H**	3.1853	6.5403	1.0877
N	-0.9480	0.3993	0.0071	**C**	2.3210	3.2537	0.7730	**H**	4.0654	4.2621	1.4857
C	-0.7688	-0.9199	0.0657	**C**	-3.6341	-0.0759	1.0382	**H**	2.7189	2.2647	0.9435
N	0.4146	-1.5307	0.0763	**C**	-4.9661	0.0239	1.4263	**H**	-2.9734	0.7749	1.1088
C	2.8150	-1.3425	0.0307	**C**	-5.8422	-1.0631	1.3354	**H**	-5.3286	0.9741	1.8070
N	-1.8997	-1.7149	0.1250	**C**	-5.3889	-2.2854	0.8594	**H**	-6.8771	-0.9501	1.6434
N	0.0489	2.4927	-0.1137	**C**	-0.9966	-3.9451	-0.7349	**H**	-6.0582	-3.1384	0.7970
C	-3.1882	-1.3032	0.5488	**C**	-1.3725	-5.2508	-1.0324	**H**	0.0179	-3.6105	-0.8902
C	-4.0564	-2.4057	0.4699	**C**	-2.6803	-5.7043	-0.8286	**H**	-0.6261	-5.9315	-1.4310
C	-3.2894	-3.5294	-0.0289	**C**	-3.6463	-4.8428	-0.3280	**H**	-2.9394	-6.7311	-1.0675
C	-1.9694	-3.0874	-0.2223	**C**	2.9693	-2.7112	0.2967	**H**	-4.6667	-5.1827	-0.1768
C	1.0452	3.4363	0.2402	**C**	4.2221	-3.2924	0.3045	**H**	2.0919	-3.3116	0.5084
C	0.5317	4.7272	0.0280	**C**	5.3578	-2.5172	0.0379	**H**	4.3507	-4.3486	0.5167
C	-0.8141	4.5810	-0.4890	**C**	5.2204	-1.1537	-0.2319	**H**	6.0833	-0.5352	-0.4456
C	-1.0921	3.2051	-0.5600	**C**	3.9539	-0.5800	-0.2296	**H**	3.8449	0.4769	-0.4449
C	-1.7619	5.5160	-0.9005	**O**	6.5418	-3.1742	0.0635	**C**	7.7321	-2.4456	-0.1957
C	-2.9799	5.0669	-1.3910	**H**	-1.5451	6.5787	-0.8438	**H**	8.5444	-3.1681	-0.1231
C	-3.2408	3.6948	-1.4740	**H**	-3.7309	5.7802	-1.7163	**H**	7.7172	-2.0117	-1.2015
C	-2.3091	2.7470	-1.0638	**H**	-4.1942	3.3533	-1.8661	**H**	7.8792	-1.6540	0.5471

Table S3. Cartesian coordinates [Å] of the optimized structure of ground state for **DCzTRZAr-F**

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.0039	1.8924	0.0001	**C**	-3.9634	1.0129	-0.7458	**H**	-7.3108	0.4288	-1.0622
N	-1.1770	1.2757	0.0519	**C**	-4.3127	-3.6605	0.8728	**H**	-5.6092	2.1845	-1.4430
C	-1.1236	-0.0569	0.0538	**C**	-3.3962	-4.5866	1.3510	**H**	-3.2322	1.7899	-0.9091
N	-0.0024	-0.7747	0.0031	**C**	-2.0405	-4.2527	1.4374	**H**	-5.3691	-3.9057	0.8140
C	1.1222	-0.0623	-0.0500	**C**	-1.5676	-3.0056	1.0421	**H**	-3.7312	-5.5705	1.6643
N	1.1819	1.2697	-0.0509	**C**	3.9656	0.9931	0.7534	**H**	-1.3323	-4.9814	1.8202
C	0.0085	3.3729	-0.0008	**C**	5.3099	1.1970	1.0472	**H**	-0.5170	-2.7674	1.1099
N	2.3160	-0.7553	-0.1150	**C**	6.2689	0.2016	0.8315	**H**	3.2374	1.7725	0.9191
N	-2.3206	-0.7442	0.1192	**C**	5.8898	-1.0327	0.3228	**H**	5.6164	2.1565	1.4529
C	3.5931	-0.2454	0.2321	**C**	1.5529	-3.0103	-1.0440	**H**	7.3107	0.3949	1.0677
C	4.5467	-1.2570	0.0274	**C**	2.0200	-4.2581	-1.4439	**H**	6.6253	-1.8154	0.1625
C	3.8465	-2.4209	-0.4778	**C**	3.3744	-4.5979	-1.3597	**H**	0.5031	-2.7674	-1.1100
C	2.4814	-2.0952	-0.5496	**C**	4.2952	-3.6776	-0.8788	**H**	1.3085	-4.9826	-1.8286
C	-2.4917	-2.0846	0.5500	**C**	1.1829	4.0745	-0.2912	**H**	3.7051	-5.5821	-1.6768
C	-3.8582	-2.4044	0.4768	**C**	1.1947	5.4630	-0.2977	**H**	5.3505	-3.9278	-0.8216
C	-4.5533	-1.2363	-0.0256	**C**	0.0176	6.1299	-0.0029	**H**	2.0868	3.5231	-0.5222
C	-3.5957	-0.2281	-0.2275	**C**	-1.1640	5.4712	0.2927	**H**	2.0931	6.0250	-0.5277
C	-5.8955	-1.0062	-0.3205	**C**	-1.1613	4.0827	0.2884	**H**	-2.0586	6.0396	0.5217
C	-6.2698	0.2308	-0.8263	**F**	0.0219	7.4825	-0.0040	**H**	-2.0688	3.5378	0.5202
C	-5.3068	1.2228	-1.0396	**H**	-6.6340	-1.7865	-0.1616				

Table S4. Cartesian coordinates [Å] of the optimized structure of ground state for **DCzTRZAr-CF$_3$**

	X	Y	Z		X	Y	Z		X	Y	Z
C	1.1919	-0.0109	0.0090	**C**	-4.3424	4.3297	0.8569	**H**	-4.5821	5.3874	0.7987
N	0.5836	1.1723	0.0588	**C**	-5.2758	3.4170	1.3283	**H**	-6.2596	3.7567	1.6367
C	-0.7507	1.1254	0.0542	**C**	-4.9495	2.0595	1.4143	**H**	-5.6839	1.3545	1.7921
N	-1.4711	0.0060	0.0008	**C**	-3.7024	1.5812	1.0252	**H**	-3.4699	0.5293	1.0934
C	-0.7645	-1.1223	-0.0483	**C**	0.2822	-3.9702	0.7527	**H**	1.0658	-3.2460	0.9165
N	0.5690	-1.1863	-0.0445	**C**	0.4801	-5.3151	1.0477	**H**	1.4388	-5.6259	1.4520
C	2.6773	-0.0198	0.0134	**C**	-0.5203	-6.2694	0.8347	**H**	-0.3317	-7.3119	1.0719
N	-1.4604	-2.3126	-0.1146	**C**	-1.7535	-5.8849	0.3274	**H**	-2.5401	-6.6167	0.1690
N	-1.4316	2.3243	0.1168	**C**	-3.7129	-1.5413	-1.0442	**H**	-3.4654	-0.4929	-1.1134
C	-0.9553	-3.5923	0.2331	**C**	-4.9629	-2.0038	-1.4427	**H**	-5.6843	-1.2899	-1.8289
C	-1.9716	-4.5411	0.0308	**C**	-5.3085	-3.3564	-1.3556	**H**	-6.2942	-3.6835	-1.6717
C	-3.1332	-3.8363	-0.4740	**C**	-4.3918	-4.2804	-0.8736	**H**	-4.6464	-5.3346	-0.8147
C	-2.8019	-2.4728	-0.5482	**C**	3.3744	-1.1901	-0.2940	**H**	2.8218	-2.0889	-0.5409
C	-2.7746	2.5015	0.5399	**C**	4.7627	-1.1999	-0.2925	**H**	5.2997	-2.1103	-0.5349
C	-3.0866	3.8696	0.4669	**C**	5.4598	-0.0376	0.0269	**H**	5.3205	2.0357	0.5934
C	-1.9115	4.5600	-0.0263	**C**	4.7739	1.1344	0.3378	**H**	2.8426	2.0466	0.5738
C	-0.9065	3.5981	-0.2233	**C**	3.3863	1.1422	0.3273	**C**	6.9603	-0.0296	-0.0111
C	-1.6729	5.9016	-0.3167	**H**	-2.4508	6.6436	-0.1622	**F**	7.4875	-1.2476	0.2246
C	-0.4306	6.2711	-0.8129	**H**	-0.2261	7.3116	-1.0451	**F**	7.4306	0.3654	-1.2182
C	0.5584	5.3040	-1.0211	**H**	1.5244	5.6029	-1.4169	**F**	7.4902	0.8143	0.8980
C	0.3400	3.9609	-0.7318	**H**	1.1150	3.2267	-0.8918				

Table S5. Cartesian coordinates [Å] of the optimized structure of singlet excited state for **DCzTRZAr-DiMe**

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.3107	1.8654	-0.3294	**C**	2.3547	-5.3661	-0.5256	**H**	0.2378	-5.4399	-0.9109
N	1.3572	0.9983	-0.4091	**C**	1.0866	-4.7972	-0.6946	**H**	-0.1068	-3.0000	-0.7042
C	1.0177	-0.2966	-0.2699	**C**	0.8770	-3.4268	-0.5877	**H**	-2.4974	-0.3258	-2.8293
N	-0.2023	-0.7777	-0.1991	**C**	-3.4115	-0.6041	-2.3194	**H**	-4.5523	-1.0276	-4.0896
C	-1.1718	0.1826	-0.4134	**C**	-4.5612	-0.9961	-3.0058	**H**	-6.5998	-1.6467	-2.8709
N	-0.9554	1.5364	-0.2933	**C**	-5.7182	-1.3458	-2.3147	**H**	-6.6913	-1.5979	-0.3944
C	0.6650	3.3194	-0.2908	**C**	-5.7761	-1.3197	-0.9067	**H**	-1.2648	0.2206	2.4386
N	-2.4864	-0.2357	-0.0427	**C**	-2.2971	-0.1048	2.4400	**H**	-2.5216	-0.1169	4.5765
N	2.0807	-1.2113	-0.1773	**C**	-3.0097	-0.2981	3.6253	**H**	-4.8668	-0.8635	4.5349
C	-3.4829	-0.5832	-0.9285	**C**	-4.3354	-0.7210	3.5998	**H**	-6.0408	-1.3009	2.3946
C	-4.6528	-0.9363	-0.2121	**C**	-5.0069	-0.9709	2.3874	**H**	1.6441	5.7351	1.8819
C	-4.3193	-0.7858	1.2092	**C**	1.0259	3.9135	0.9269	**H**	0.9856	5.9985	-2.3480
C	-2.9746	-0.3535	1.2519	**C**	1.3649	5.2671	0.9414	**H**	1.6190	7.0689	-0.2057
C	1.9782	-2.6118	-0.3111	**C**	1.3502	6.0165	-0.2294	**C**	1.0369	3.1133	2.2052
C	3.2568	-3.1778	-0.1455	**C**	0.9933	5.4153	-1.4306	**H**	0.0339	2.7440	2.4471
C	4.1771	-2.0921	0.1093	**C**	0.6469	4.0641	-1.4784	**H**	1.6925	2.2405	2.1235
C	3.4347	-0.8962	0.0759	**H**	6.1132	-3.0032	0.3834	**H**	1.3829	3.7228	3.0446
C	5.5490	-2.0750	0.3604	**H**	7.2447	-0.8242	0.7781	**C**	0.2648	3.4216	-2.7886
C	6.1773	-0.8587	0.5813	**H**	5.9341	1.2768	0.7174	**H**	0.8786	2.5377	-2.9909
C	5.4336	0.3276	0.5480	**H**	3.5054	1.2518	0.2514	**H**	-0.7799	3.0938	-2.7793
C	4.0668	0.3314	0.2954	**H**	4.4360	-4.9836	-0.1205	**H**	0.3949	4.1223	-3.6181
C	3.4459	-4.5553	-0.2498	**H**	2.4824	-6.4410	-0.6115				

Table S6. Cartesian coordinates [Å] of the optimized structure of singlet excited state for **DCzTRZAr-OMe**

	X	Y	Z		X	Y	Z		X	Y	Z
C	1.0426	-1.2306	-0.3403	**C**	3.2517	4.8963	0.7144	**H**	-1.7598	2.6227	-1.2136
N	1.4542	0.0724	-0.4003	**C**	4.3367	4.2004	1.2265	**H**	3.2645	5.9815	0.6625
C	0.4737	0.9724	-0.2423	**C**	4.3029	2.8009	1.2988	**H**	5.2126	4.7387	1.5757
N	-0.8163	0.7329	-0.1661	**C**	3.2054	2.0721	0.8578	**H**	5.1566	2.2669	1.7066
C	-1.1150	-0.5988	-0.3765	**C**	-2.2205	-0.9289	2.4739	**H**	3.1908	0.9929	0.9028
N	-0.2099	-1.6190	-0.2903	**C**	-2.9292	-1.1237	3.6613	**H**	-1.1730	-0.6560	2.4696
C	2.1031	-2.2664	-0.3480	**C**	-4.2768	-1.4706	3.6391	**H**	-2.4211	-1.0009	4.6113
N	-2.4476	-0.9572	-0.0082	**C**	-4.9760	-1.6387	2.4280	**H**	-4.8048	-1.6148	4.5759
N	0.8775	2.3178	-0.1420	**C**	-3.4213	-1.1804	-2.2841	**H**	-6.0274	-1.9075	2.4381
C	-2.9249	-1.0997	1.2874	**C**	-4.6002	-1.4789	-2.9678	**H**	-2.4989	-0.9366	-2.7967
C	-4.2926	-1.4525	1.2478	**C**	-5.7657	-1.7932	-2.2737	**H**	-4.6069	-1.4674	-4.0521
C	-4.6519	-1.5281	-0.1732	**C**	-5.8038	-1.8217	-0.8652	**H**	-6.6694	-2.0233	-2.8283
C	-3.4740	-1.2111	-0.8927	**C**	1.7864	-3.6264	-0.2167	**H**	-6.7260	-2.0710	-0.3506
C	2.1182	2.7760	0.3347	**C**	2.7754	-4.5920	-0.2222	**H**	0.7464	-3.9135	-0.1094
C	2.1370	4.1830	0.2722	**C**	4.1182	-4.2227	-0.3659	**H**	2.5333	-5.6451	-0.1182
C	0.8644	4.6023	-0.2736	**C**	4.4518	-2.8774	-0.5040	**H**	5.4820	-2.5637	-0.6225
C	0.1085	3.4365	-0.5050	**C**	3.4431	-1.9138	-0.4927	**H**	3.6990	-0.8669	-0.6076
C	0.3397	5.8580	-0.5805	**O**	5.0202	-5.2440	-0.3607	**C**	6.3932	-4.9293	-0.5083
C	-0.9343	5.9413	-1.1229	**H**	0.9245	6.7558	-0.4006	**H**	6.9239	-5.8809	-0.4781
C	-1.6763	4.7755	-1.3561	**H**	-1.3588	6.9102	-1.3681	**H**	6.5860	-4.4347	-1.4672
C	-1.1747	3.5161	-1.0509	**H**	-2.6731	4.8539	-1.7811	**H**	6.7439	-4.2903	0.3103

Table S7. Cartesian coordinates [Å] of the optimized structure of singlet excited state for **DCzTRZAr-F**

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.3020	1.9060	-0.0826	C	-4.0854	0.2479	-0.6428	H	-7.2834	-0.9330	-0.8271
N	-1.3635	1.0219	0.0616	C	-3.5216	-4.3859	1.0269	H	-5.9388	1.0947	-1.2851
C	-1.0695	-0.2514	0.0644	C	-2.4343	-5.1242	1.4701	H	-3.5075	1.1395	-0.8330
N	0.1671	-0.7989	-0.0356	C	-1.1583	-4.5472	1.4915	H	-4.5173	-4.8202	1.0124
C	1.1104	0.1714	-0.1201	C	-0.9377	-3.2410	1.0703	H	-2.5710	-6.1485	1.8036
N	0.9701	1.4645	-0.1653	C	3.4055	0.8688	1.8113	H	-0.3135	-5.1325	1.8435
C	-0.5666	3.3277	-0.1050	C	4.5730	1.0244	2.5571	H	0.0515	-2.8089	1.0784
N	2.4597	-0.3209	-0.1703	C	5.7412	0.3496	2.2091	H	2.4940	1.3981	2.0567
N	-2.1262	-1.1668	0.1715	C	5.7883	-0.5159	1.0987	H	4.5701	1.6845	3.4173
C	3.4658	0.0069	0.7152	C	2.2509	-1.7874	-2.1759	H	6.6368	0.4925	2.8042
C	4.6457	-0.6875	0.3503	C	2.9705	-2.6641	-2.9858	H	6.7098	-1.0320	0.8494
C	4.3021	-1.4827	-0.8300	C	4.3112	-2.9415	-2.7274	H	1.2057	-1.5683	-2.3501
C	2.9379	-1.2120	-1.1037	C	4.9924	-2.3509	-1.6442	H	2.4771	-3.1370	-3.8276
C	-2.0340	-2.5014	0.6201	C	0.4708	4.2640	-0.3023	H	4.8471	-3.6279	-3.3743
C	-3.3214	-3.0716	0.6054	C	0.2151	5.6264	-0.3278	H	6.0377	-2.5817	-1.4674
C	-4.2344	-2.0602	0.1187	C	-1.0887	6.0640	-0.1529	H	1.4839	3.9044	-0.4403
C	-3.4777	-0.9002	-0.1306	C	-2.1392	5.1852	0.0466	H	1.0105	6.3481	-0.4828
C	-5.6070	-2.0788	-0.1272	C	-1.8756	3.8221	0.0700	H	-3.1453	5.5678	0.1840
C	-6.2156	-0.9381	-0.6299	F	-1.3424	7.4039	-0.1776	H	-2.6832	3.1194	0.2355
C	-5.4532	0.2082	-0.8873	H	-6.1875	-2.9760	0.0683				

Table S8. Cartesian coordinates [Å] of the optimized structure of singlet excited state for **DCzTRZAr-CF$_3$**

	X	Y	Z		X	Y	Z		X	Y	Z
C	1,2335	-0,0707	-0,0322	**C**	-4,2276	4,4258	1,0091	**H**	-4,4408	5,4906	0,9775
N	0,5959	1,1437	0,0998	**C**	-5,1814	3,5268	1,4633	**H**	-6,1544	3,8829	1,7877
C	-0,7068	1,1419	0,1008	**C**	-4,8879	2,1582	1,5096	**H**	-5,6396	1,4630	1,8724
N	-1,5076	0,0388	0,0084	**C**	-3,6564	1,6591	1,1016	**H**	-3,4447	0,6009	1,1325
C	-0,7721	-1,0743	-0,0895	**C**	-0,3273	-3,6474	1,5541	**H**	0,4084	-2,8898	1,7862
N	0,5109	-1,2337	-0,1317	**C**	-0,3263	-4,8907	2,1820	**H**	0,4243	-5,1037	2,9349
C	2,6622	-0,1321	-0,0432	**C**	-1,2686	-5,8625	1,8523	**H**	-1,2419	-6,8241	2,3534
N	-1,5497	-2,2878	-0,1569	**C**	-2,2600	-5,6245	0,8801	**H**	-2,9859	-6,3953	0,6428
N	-1,3750	2,3666	0,1963	**C**	-3,2020	-1,6109	-1,9133	**H**	-2,8042	-0,6148	-2,0512
C	-1,3147	-3,4226	0,5889	**C**	-4,3019	-2,0735	-2,6331	**H**	-4,7693	-1,4222	-3,3631
C	-2,2832	-4,4015	0,2496	**C**	-4,8077	-3,3553	-2,4279	**H**	-5,6649	-3,6895	-3,0025
C	-3,1399	-3,7956	-0,7684	**C**	-4,2274	-4,2320	-1,4915	**H**	-4,6341	-5,2283	-1,3526
C	-2,6410	-2,4870	-0,9803	**C**	3,3461	-1,3616	-0,2162	**H**	2,7693	-2,2696	-0,3450
C	-2,7009	2,5665	0,6375	**C**	4,7258	-1,4148	-0,2284	**H**	5,2249	-2,3690	-0,3644
C	-2,9843	3,9452	0,5999	**C**	5,4843	-0,2498	-0,0608	**H**	5,4045	1,8839	0,2463
C	-1,7992	4,6156	0,1099	**C**	4,8267	0,9752	0,1110	**H**	2,9489	1,9860	0,2701
C	-0,8250	3,6269	-0,1201	**C**	3,4477	1,0360	0,1213	**C**	6,9675	-0,3047	-0,1292
C	-1,5234	5,9568	-0,1532	**H**	-2,2772	6,7179	0,0273	**F**	7,4702	-1,4824	0,3141
C	-0,2758	6,3010	-0,6530	**H**	-0,0419	7,3403	-0,8631	**F**	7,4507	-0,1604	-1,3972
C	0,6836	5,3090	-0,8906	**H**	1,6557	5,5894	-1,2857	**F**	7,5640	0,6704	0,5963
C	0,4296	3,9676	-0,6286	**H**	1,1804	3,2119	-0,8033				

Table S9. Cartesian coordinates [Å] of the optimized structure of triplet state for **DCzTRZAr-DiMe**

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.0000	2.0179	0.0000	**C**	3.2532	-4.5727	1.3986	**H**	1.2334	-4.8163	2.0977
N	1.1863	1.3317	0.1706	**C**	1.9418	-4.1459	1.6212	**H**	0.5064	-2.5418	1.4377
C	1.1261	0.0440	0.1443	**C**	1.5193	-2.8709	1.2550	**H**	-0.5062	-2.5418	-1.4374
N	0.0000	-0.7438	0.0001	**C**	-1.5192	-2.8710	-1.2548	**H**	-1.2332	-4.8163	-2.0975
C	-1.1261	0.0440	-0.1442	**C**	-1.9417	-4.1460	-1.6211	**H**	-3.5534	-5.5710	-1.7009
N	-1.1863	1.3317	-0.1705	**C**	-3.2531	-4.5727	-1.3986	**H**	-5.2081	-4.0442	-0.6503
C	0.0000	3.4792	0.0000	**C**	-4.1837	-3.7196	-0.8061	**H**	-3.2172	1.7772	0.8806
N	-2.3147	-0.7082	-0.1846	**C**	-3.9299	0.9674	0.8183	**H**	-5.5570	2.0649	1.6685
N	2.3146	-0.7082	0.1846	**C**	-5.2456	1.1147	1.2461	**H**	-7.1934	0.2245	1.4687
C	-2.4487	-2.0324	-0.6366	**C**	-6.1724	0.0741	1.1322	**H**	-6.5192	-1.9614	0.5015
C	-3.7804	-2.4466	-0.4297	**C**	-5.7986	-1.1536	0.5871	**H**	1.3653	6.1357	1.6493
C	-4.4893	-1.3235	0.1608	**C**	0.7857	4.2010	0.9390	**H**	-1.3653	6.1357	-1.6492
C	-3.5627	-0.2671	0.2787	**C**	0.7719	5.5943	0.9164	**H**	0.0000	7.3856	0.0001
C	2.4487	-2.0324	0.6367	**C**	0.0000	6.2992	0.0001	**C**	1.5925	3.5166	2.0161
C	3.7804	-2.4465	0.4297	**C**	-0.7718	5.5943	-0.9163	**H**	1.0169	2.7244	2.5054
C	4.4893	-1.3235	-0.1610	**C**	-0.7857	4.2010	-0.9389	**H**	2.4941	3.0425	1.6192
C	3.5626	-0.2671	-0.2787	**H**	6.5191	-1.9613	-0.5018	**H**	1.8918	4.2420	2.7788
C	5.7986	-1.1535	-0.5873	**H**	7.1932	0.2245	-1.4690	**C**	-1.5924	3.5166	-2.0160
C	6.1722	0.0742	-1.1325	**H**	5.5568	2.0649	-1.6687	**H**	-1.0168	2.7244	-2.5053
C	5.2454	1.1147	-1.2463	**H**	3.2170	1.7772	-0.8807	**H**	-2.4941	3.0426	-1.6193
C	3.9298	0.9674	-0.8184	**H**	5.2082	-4.0442	0.6501	**H**	-1.8916	4.2420	-2.7788
C	4.1838	-3.7196	0.8061	**H**	3.5536	-5.5710	1.7010				

Table S10. Cartesian coordinates [Å] of the optimized structure of triplet state for **DCzTRZAr-OMe**

	X	Y	Z		X	Y	Z		X	Y	Z
C	1.4869	-0.8465	0.0640	**C**	1.4950	5.8006	0.1628	**H**	-2.4540	1.7154	-1.1578
N	1.4189	0.5357	-0.1037	**C**	2.7682	5.5947	0.6741	**H**	1.1286	6.8065	-0.0224
C	0.2404	1.0780	-0.0799	**C**	3.2265	4.2931	0.9162	**H**	3.4115	6.4427	0.8887
N	-0.9528	0.4260	0.0627	**C**	2.4404	3.1788	0.6480	**H**	4.2244	4.1447	1.3189
C	-0.7598	-0.9098	0.1519	**C**	-3.3439	-0.1589	1.6953	**H**	2.8063	2.1777	0.8218
N	0.3370	-1.5910	0.1734	**C**	-4.6022	-0.0234	2.2757	**H**	-2.5573	0.5671	1.8502
C	2.7659	-1.4945	0.0931	**C**	-5.6025	-0.9708	2.0580	**H**	-4.8025	0.8328	2.9107
N	-1.9894	-1.6582	0.2000	**C**	-5.3765	-2.0994	1.2495	**H**	-6.5724	-0.8416	2.5273
N	0.1430	2.4736	-0.1921	**C**	-1.3481	-3.6084	-1.2521	**H**	-6.1624	-2.8333	1.1030
C	-3.1358	-1.2740	0.8765	**C**	-1.8498	-4.7805	-1.8121	**H**	-0.3293	-3.2838	-1.4146
C	-4.1408	-2.2487	0.6614	**C**	-3.1602	-5.1927	-1.5695	**H**	-1.2057	-5.3831	-2.4433
C	-3.5473	-3.2738	-0.1964	**C**	-4.0243	-4.4376	-0.7579	**H**	-3.5224	-6.1129	-2.0165
C	-2.2143	-2.8674	-0.4438	**C**	2.8846	-2.8914	0.3027	**H**	-5.0435	-4.7688	-0.5868
C	1.1611	3.3911	0.1303	**C**	4.1167	-3.5126	0.3324	**H**	1.9842	-3.4778	0.4512
C	0.6879	4.6956	-0.1062	**C**	5.2936	-2.7732	0.1532	**H**	4.1964	-4.5832	0.4980
C	-0.6633	4.5753	-0.6097	**C**	5.2074	-1.3973	-0.0562	**H**	6.0986	-0.7975	-0.2018
C	-0.9740	3.2018	-0.6474	**C**	3.9636	-0.7722	-0.0847	**H**	3.9100	0.2964	-0.2588
C	-1.5938	5.5244	-1.0323	**O**	6.4641	-3.4839	0.2007	**C**	7.6768	-2.7783	0.0305
C	-2.8282	5.0972	-1.4993	**H**	-1.3498	6.5826	-1.0011	**H**	8.4720	-3.5207	0.1052
C	-3.1245	3.7288	-1.5464	**H**	-3.5640	5.8219	-1.8342	**H**	7.7227	-2.2947	-0.9529
C	-2.2128	2.7677	-1.1259	**H**	-4.0913	3.4045	-1.9209	**H**	7.8115	-2.0219	0.8132

Table S11. Cartesian coordinates [Å] of the optimized structure of triplet state for **DCzTRZAr-F**

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.0002	2.0048	0.0000	**C**	-3.9493	0.9176	-0.7655	**H**	-7.2226	0.1440	-1.3211
N	-1.1874	1.3227	0.1964	**C**	-4.1415	-3.7274	0.9831	**H**	-5.5992	1.9837	-1.6118
C	-1.1226	0.0346	0.1684	**C**	-3.1918	-4.5625	1.5709	**H**	-3.2421	1.7276	-0.8706
N	-0.0001	-0.7434	0.0002	**C**	-1.8772	-4.1256	1.7495	**H**	-5.1679	-4.0599	0.8608
C	1.1226	0.0343	-0.1684	**C**	-1.4703	-2.8574	1.3434	**H**	-3.4794	-5.5547	1.9039
N	1.1876	1.3224	-0.1965	**C**	3.9494	0.9168	0.7653	**H**	-1.1534	-4.7818	2.2226
C	0.0004	3.4356	0.0000	**C**	5.2746	1.0469	1.1681	**H**	-0.4543	-2.5210	1.4930
N	2.3039	-0.7237	-0.2456	**C**	6.1936	0.0061	1.0036	**H**	3.2424	1.7269	0.8704
N	-2.3041	-0.7232	0.2456	**C**	5.8015	-1.2045	0.4340	**H**	5.5996	1.9827	1.6115
C	3.5645	-0.2995	0.1985	**C**	1.4697	-2.8578	-1.3434	**H**	7.2226	0.1427	1.3209
C	4.4821	-1.3571	0.0329	**C**	1.8763	-4.1260	-1.7494	**H**	6.5156	-2.0130	0.3108
C	3.7534	-2.4624	-0.5674	**C**	3.1908	-4.5632	-1.5707	**H**	0.4538	-2.5212	-1.4930
C	2.4193	-2.0383	-0.7312	**C**	4.1407	-3.7282	-0.9830	**H**	1.1524	-4.7821	-2.2224
C	-2.4197	-2.0378	0.7312	**C**	1.1853	4.1695	-0.2550	**H**	3.4783	-5.5555	-1.9037
C	-3.7539	-2.4616	0.5674	**C**	1.1871	5.5554	-0.2565	**H**	5.1671	-4.0609	-0.8607
C	-4.4824	-1.3562	-0.0329	**C**	0.0007	6.2267	0.0000	**H**	2.1015	3.6297	-0.4639
C	-3.5646	-0.2988	-0.1986	**C**	-1.1858	5.5557	0.2566	**H**	2.0929	6.1187	-0.4564
C	-5.8017	-1.2034	-0.4340	**C**	-1.1844	4.1698	0.2550	**H**	-2.0915	6.1192	0.4565
C	-6.1936	0.0073	-1.0037	**F**	0.0009	7.5896	0.0001	**H**	-2.1007	3.6303	0.4639
C	-5.2744	1.0478	-1.1683	**H**	-6.5160	-2.0118	-0.3109				

Table S12. Cartesian coordinates [Å] of the optimized structure of triplet state for **DCzTRZAr-CF$_3$**

	X	Y	Z		X	Y	Z		X	Y	Z
C	1.2993	-0.0093	0.0133	**C**	-4.4134	4.1569	0.9770	**H**	-4.7413	5.1849	0.8565
N	0.6224	1.1811	0.2013	**C**	-5.2556	3.2087	1.5604	**H**	-6.2472	3.5010	1.8909
C	-0.6682	1.1164	0.1666	**C**	-4.8268	1.8918	1.7369	**H**	-5.4884	1.1705	2.2060
N	-1.4435	0.0039	0.0026	**C**	-3.5596	1.4792	1.3330	**H**	-3.2280	0.4615	1.4803
C	-0.6776	-1.1159	-0.1555	**C**	0.1910	-3.9501	0.7762	**H**	1.0025	-3.2457	0.8876
N	0.6124	-1.1931	-0.1800	**C**	0.3144	-5.2766	1.1763	**H**	1.2467	-5.6058	1.6241
C	2.7251	-0.0161	0.0189	**C**	-0.7284	-6.1913	1.0038	**H**	-0.5972	-7.2214	1.3195
N	-1.4389	-2.2988	-0.2419	**C**	-1.9357	-5.7941	0.4284	**H**	-2.7455	-6.5058	0.2998
N	-1.4186	2.3066	0.2463	**C**	-3.5635	-1.4499	-1.3442	**H**	-3.2210	-0.4352	-1.4882
C	-1.0214	-3.5603	0.2030	**C**	-4.8316	-1.8498	-1.7580	**H**	-5.4826	-1.1218	-2.2315
C	-2.0816	-4.4743	0.0298	**C**	-5.2745	-3.1626	-1.5859	**H**	-6.2664	-3.4451	-1.9240
C	-3.1813	-3.7396	-0.5745	**C**	-4.4459	-4.1194	-0.9969	**H**	-4.7846	-5.1443	-0.8797
C	-2.7504	-2.4061	-0.7322	**C**	3.4574	-1.2056	-0.2285	**H**	2.9158	-2.1213	-0.4347
C	-2.7326	2.4271	0.7265	**C**	4.8384	-1.2084	-0.2229	**H**	5.3746	-2.1318	-0.4177
C	-3.1494	3.7645	0.5644	**C**	5.5499	-0.0305	0.0361	**H**	5.3900	2.0733	0.4874
C	-2.0381	4.4879	-0.0322	**C**	4.8466	1.1563	0.2814	**H**	2.9313	2.0864	0.4801
C	-0.9855	3.5636	-0.1966	**C**	3.4664	1.1669	0.2739	**C**	7.0368	-0.0197	-0.0109
C	-1.8764	5.8060	-0.4311	**H**	-2.6802	6.5256	-0.3092	**F**	7.5799	-1.2269	0.2691
C	-0.6611	6.1908	-0.9979	**H**	-0.5176	7.2192	-1.3137	**F**	7.5270	0.3280	-1.2346
C	0.3740	5.2658	-1.1618	**H**	1.3127	5.5854	-1.6031	**F**	7.5816	0.8639	0.8593
C	0.2348	3.9410	-0.7612	**H**	1.0402	3.2287	-0.8660				

Table S13 shows the difference of energy between HOMO and LUMO and excitation properties in gas phase.

Table S13. Difference of energy between HOMO and LUMO, excitation wavelengths and oscillator strengths (f) in gas phase at the CAM-B3LYP/6-31G+(d) level

Compound	$\Delta E_{HOMO-LUMO}$ (eV)	λ_{abs} (nm)	f
DCzTRZAr-DiMe	6.88	283	0.6480
DCzTRZAr-OMe	6.58	279	0.5757
DCzTRZAr-F	6.47	290	0.4911
DCzTRZAr-CF_3	6.22	298	0.3429

Table S14 and Table S15 show the excitation wavelengths and the corresponding oscillator strength (f) with the associated electronic transitions for each one of them in toluene and gas phase, respectively.

Table S14. Vertical transitions of compounds in toluene

Compound	λ_{abs} (nm)	f	Assignments
DCzTRZAr-DiMe	337	0.0941	HOMO - 12 → LUMO (2.00%) HOMO - 3 → LUMO (30.81%) HOMO - 2 → LUMO (5.42%) HOMO - 1 → LUMO (55.43%)
	284	0.1397	HOMO → LUMO + 3 (83.72%)
	280	0.4398	HOMO - 11 → LUMO (4.39%) HOMO - 10 → LUMO (3.03%) HOMO - 5 → LUMO (12.51%) HOMO - 3 → LUMO + 1 (23.30%) HOMO - 3 → LUMO + 2 (2.23%) HOMO - 2 → LUMO + 1 (4.40%) HOMO - 1 → LUMO + 1 (27.61%) HOMO - 1 → LUMO + 2 (2.79%) HOMO → LUMO + 1 (4.88%)
DCzTRZAr-OMe	289	0.7520	HOMO - 1 → LUMO (49.43%)

	284	0.9111	HOMO - 1 → LUMO + 2 (4.00%) HOMO - 1 → LUMO + 10 (2.04%) HOMO → LUMO + 1 (33.12%) HOMO - 4 → LUMO (44.69%) HOMO - 1 → LUMO + 1 (20.18%) HOMO → LUMO (21.31%) HOMO → LUMO + 2 (3.24%)
	260	0.3840	HOMO - 3 → LUMO + 1 (25.35%) HOMO - 3 → LUMO + 3 (8.19%) HOMO - 2 → LUMO (19.94%) HOMO - 2 → LUMO + 1 (3.07%) HOMO - 2 → LUMO + 2 (18.76%) HOMO - 1 → LUMO + 1 (2.39%) HOMO → LUMO + 3 (4.03%)
DCzTRZAr-F	293	0.7133	HOMO - 12 → LUMO (2.36%) HOMO - 3 → LUMO (3.64%) HOMO - 1 → LUMO (55.70%) HOMO - 1 → LUMO + 2 (2.91%) HOMO - 1 → LUMO + 7 (2.35%) HOMO → LUMO + 1 (26.10%)
	280	0.3106	HOMO - 4 → LUMO (4.40%) HOMO - 1 → LUMO + 1 (21.81%) HOMO → LUMO (52.96%) HOMO → LUMO + 2 (6.52%)
	258	0.5136	HOMO - 12 → LUMO (2.14%) HOMO - 1 → LUMO (29.06%) HOMO - 1 → LUMO + 2 (5.68%) HOMO → LUMO + 1 (49.63%)
DCzTRZAr-CF_3	300	0.5290	HOMO - 12 → LUMO (1.48%) HOMO - 3 → LUMO (3.32%) HOMO - 1 → LUMO (67.75%) HOMO - 1 → LUMO + 5 (2.06%) HOMO → LUMO + 1 (5.92%)
	279	0.2834	HOMO - 1 → LUMO (7.27%) HOMO - 1 → LUMO + 2 (2.71%) HOMO → LUMO + 1 (63.76%)
	256	0.2667	HOMO - 3 → LUMO (4.29%) HOMO - 3 → LUMO + 2 (16.60%) HOMO - 3 → LUMO + 5 (1.03%) HOMO - 2 → LUMO + 1 (1.64%)

			HOMO - 2 → LUMO + 3 (15.21%) HOMO → LUMO + 3 (3.15%)

Table S15: Vertical transitions of compounds in gas phase

Compound	λ_{abs} (nm)	f	Assignments
DCzTRZAr-DiMe	283	0.6480	HOMO - 3 → LUMO (4.65%) HOMO - 1 → LUMO (31.19%) HOMO - 1 → LUMO + 2 (3.86%) HOMO → LUMO + 1 (48.37%)
	272	0.1550	HOMO - 5 → LUMO (2.11%) HOMO - 3 → LUMO + 1 (2.81%) HOMO - 3 → LUMO + 8 (2.12%) HOMO - 2 → LUMO + 10 (4.37%) HOMO - 1 → LUMO + 1 (32.84%) HOMO - 1 → LUMO + 3 (5.49%) HOMO → LUMO (4.37%) HOMO → LUMO + 2 (14.58%)
	252	0.2764	HOMO - 7 → LUMO + 1 (2.92%) HOMO - 6 → LUMO + 2 (2.47%) HOMO - 5 → LUMO (2.54%) HOMO - 3 → LUMO + 3 (22.90%) HOMO - 2 → LUMO (2.72%) HOMO - 2 → LUMO + 2 (26.51%) HOMO - 1 → LUMO + 1 (5.53%) HOMO - 1 → LUMO + 3 (14.05%)
DCzTRZAr-OMe	286	0.5355	HOMO - 12 → LUMO (2.17%) HOMO - 3 → LUMO (2.39%) HOMO - 1 → LUMO (54.77%) HOMO - 1 → LUMO + 2 (3.24%) HOMO → LUMO + 1 (25.96%)
	279	0.5757	HOMO - 4 → LUMO (29.64%) HOMO - 1 → LUMO + 1 (20.88%) HOMO → LUMO (31.79%) HOMO → LUMO + 2 (4.43%)
	258	0.1788	HOMO - 3 → LUMO (20.73%) HOMO - 3 → LUMO + 1 (18.85%) HOMO - 3 → LUMO + 2 (8.78%) HOMO - 2 → LUMO (2.94%) HOMO - 2 → LUMO + 1 (10.82%)

			HOMO - 1 → LUMO + 2 (3.24%) HOMO → LUMO + 1 (3.04%) HOMO → LUMO + 3 (11.76%)
DCzTRZAr-F	290	0.4911	HOMO - 12 → LUMO (2.62%) HOMO - 3 → LUMO (5.73%) HOMO - 1 → LUMO (61.98%) HOMO - 1 → LUMO + 2 (2.17%) HOMO → LUMO + 1 (9.18%)
	278	0.1712	HOMO - 4 → LUMO (2.38%) HOMO - 1 → LUMO + 1 (16.71%) HOMO → LUMO (65.55%) HOMO → LUMO + 2 (5.81%)
	256	0.1799	HOMO - 10 → LUMO (7.72%) HOMO - 9 → LUMO (2.61%) HOMO - 5 → LUMO (3.26%) HOMO - 4 → LUMO (7.98%) HOMO - 3 → LUMO + 1 (1.07%) HOMO - 3 → LUMO + 3 (1.28%) HOMO - 2 → LUMO (1.39%) HOMO - 1 → LUMO + 1 (7.77%) HOMO - 1 → LUMO + 3 (5.84%) HOMO → LUMO (1.23%) HOMO → LUMO + 2 (4.39%)
DCzTRZAr-CF_3	298	0.3429	HOMO - 12 → LUMO (1.55%) HOMO - 3 → LUMO (5.79%) HOMO - 1 → LUMO (69.05%) HOMO - 1 → LUMO + 5 (1.70%) HOMO → LUMO + 1 (3.28%)
	278	0.2679	HOMO - 3 → LUMO + 2 (1.34%) HOMO - 1 → LUMO (4.66%) HOMO - 1 → LUMO + 2 (2.38%) HOMO → LUMO + 1 (70.19%)
	254	0.1913	HOMO - 2 → LUMO + 1 (2.56%) HOMO - 3 → LUMO (2.38%) HOMO - 3 → LUMO + 2 (15.71%) HOMO - 2 → LUMO + 1 (5.60%) HOMO - 2 → LUMO + 3 (14.12%) HOMO - 1 → LUMO + 2 (1.58%) HOMO → LUMO + 3 (3.14%)

Figures S12-23 show the distribution of orbitals that contribute the most to each vertical transition of the four compounds. These transitions were calculated in toluene and are the ones marked with grey in Table S14.

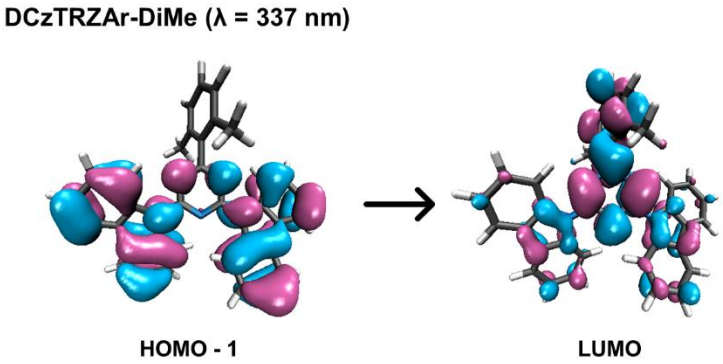


Figure S12: Molecular orbitals involved in transition with λ_{exc} = 337 nm for compound **DCzTRZAr-DiMe**

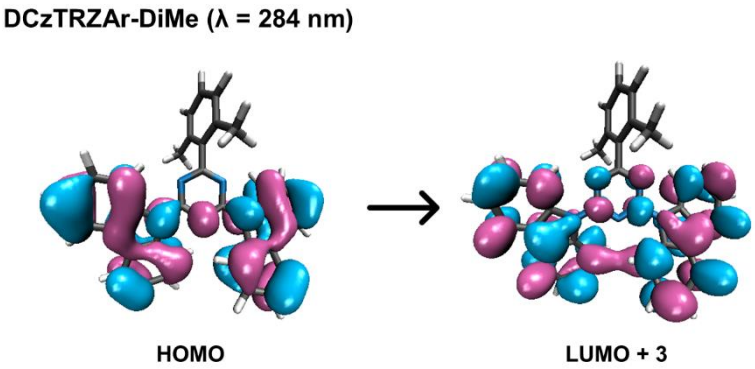


Figure S13: Molecular orbitals involved in transition with λ_{exc} = 284 nm for compound **DCzTRZAr-DiMe**

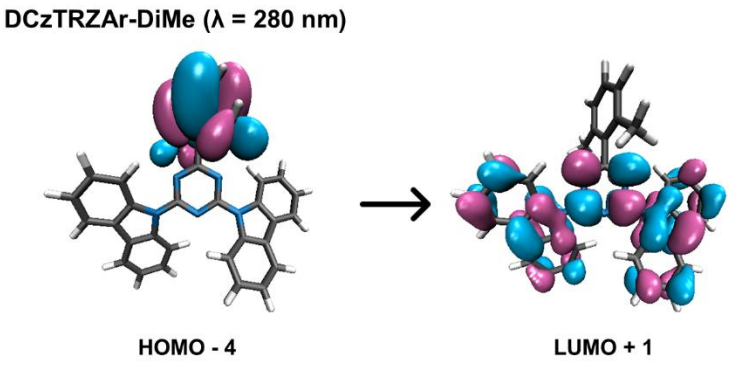


Figure S14: Molecular orbitals involved in transition with λ_{exc} = 280 nm for compound **DCzTRZAr-DiMe**

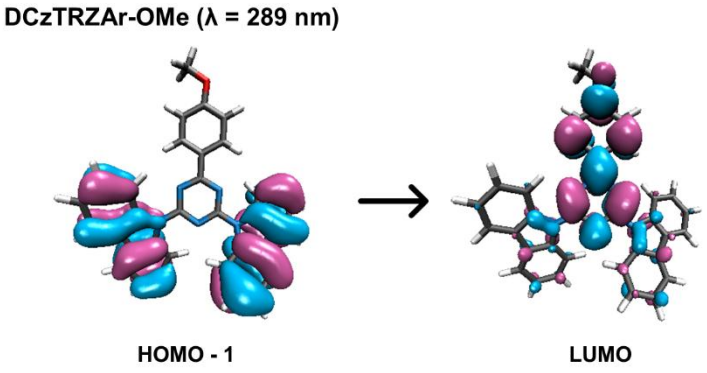


Figure S15: Molecular orbitals involved in transition with λ_{exc} = 289 nm for compound **DCzTRZAr-OMe**

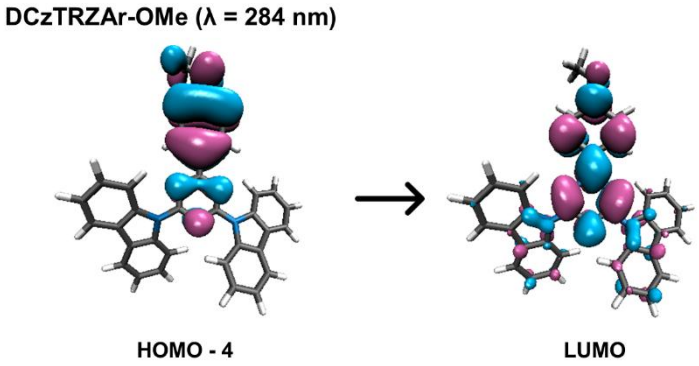


Figure S16: Molecular orbitals involved in transition with λ_{exc} = 284 nm for compound **DCzTRZAr-OMe**

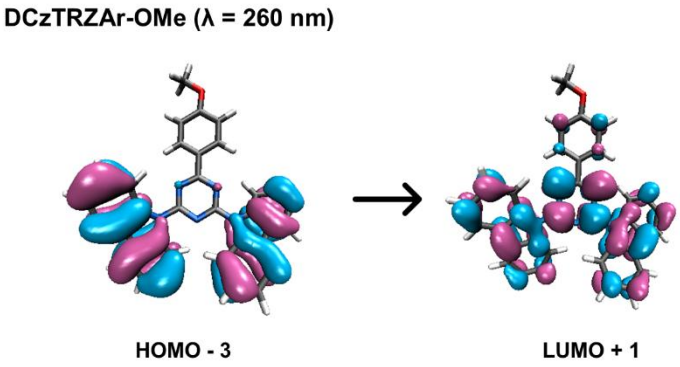


Figure S17: Molecular orbitals involved in transition with λ_{exc} = 260 nm for compound **DCzTRZAr-OMe**

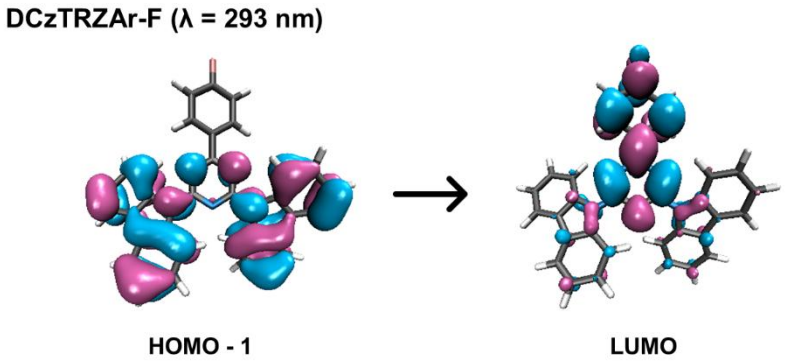


Figure S18: Molecular orbitals involved in transition with λ_{exc} = 293 nm for compound **DCzTRZAr-F**

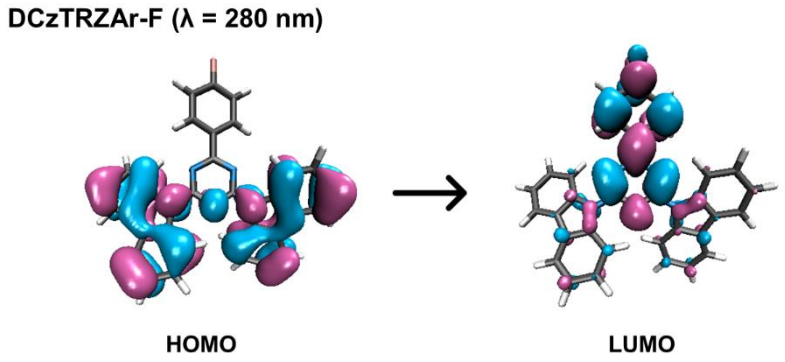


Figure S19: Molecular orbitals involved in transition with λ_{exc} = 280 nm for compound **DCzTRZAr-F**

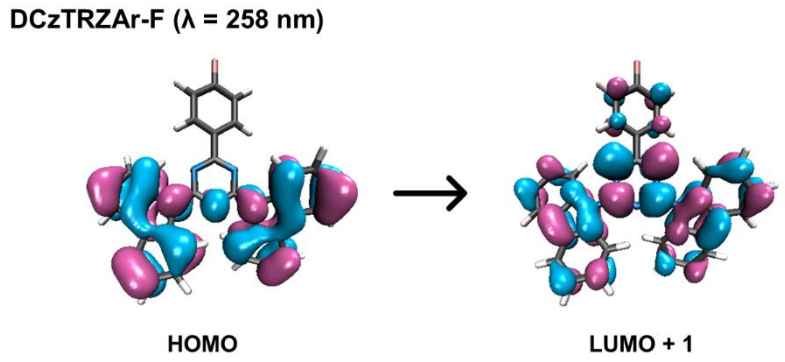


Figure S20: Molecular orbitals involved in transition with λ_{exc} = 258 nm for compound **DCzTRZAr-F**

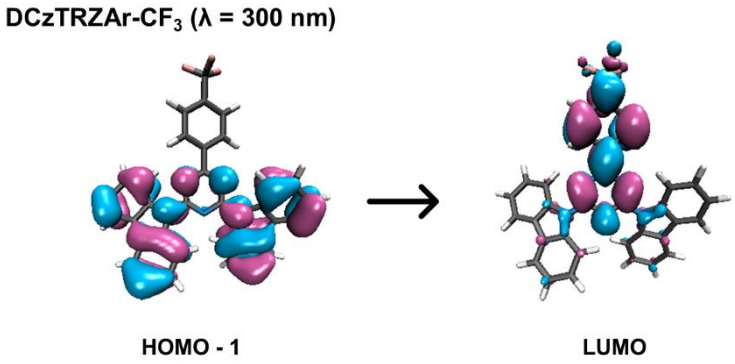


Figure S21: Molecular orbitals involved in transition with λ_{exc} = 300 nm for compound **DCzTRZAr-CF$_3$**

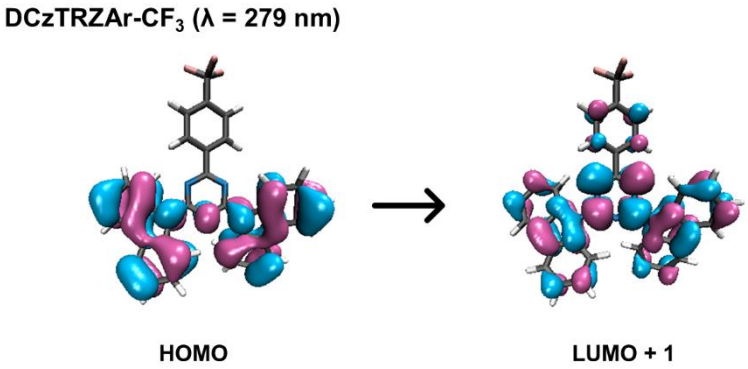


Figure S22: Molecular orbitals involved in transition with λ_{exc} = 279 nm for compound **DCzTRZAr-CF$_3$**

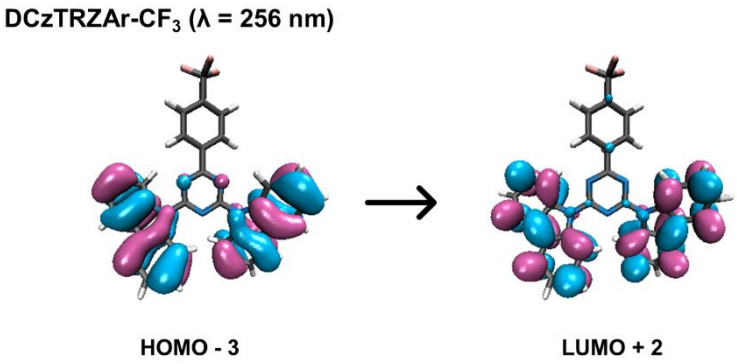


Figure S23: Molecular orbitals involved in transition with λ_{exc} = 256 nm for compound **DCzTRZAr-CF$_3$**

Table S16 shows the difference of energy between triplet state and excited singlet state for the four compounds, in toluene.

Table S16: Difference of energy between triplet state and excited singlet state (ΔE_{ST} (eV)) in toluene at CAM-B3LYP/6-31+G(d), M062X/6-31+G(d), M062X/def2tzvp, ωB97xd/6-31+G(d) levels

Compound	CAM-B3LYP/ 6-31+G(d)	M062X/ 6-31+G(d)	M062X/ Def2TZVP	ωB97xd/ 6-31+G(d)
DCzTRZAr-DiMe	0.330	0.311	0.323	0.319
DCzTRZAr-OMe	0.539	0.797	0.840	1.014
DCzTRZAr-F	0.510	0.325	0.337	0.500
DCzTRZAr-CF_3	0.491	0.315	0.326	0.593

Figures S24-27 show the optimized geometries in the ground state (S_0) and excited singlet state (S_1) in toluene of the four compounds with the numbers corresponding to the atoms forming the analyzed dihedral angles. These values are in Table 4 in the manuscript.

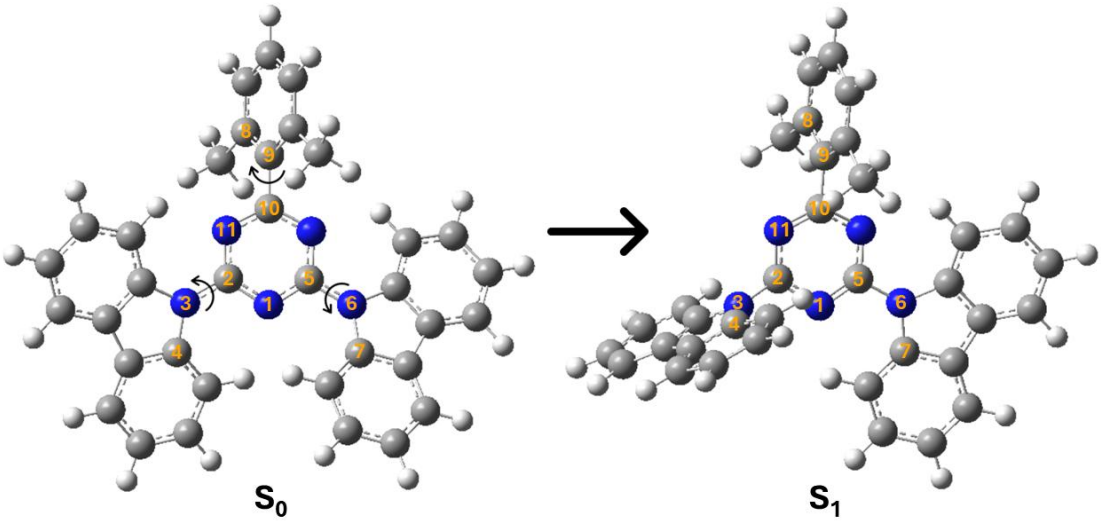


Figure S24: Optimized geometries of ground state (S_0) and excited singlet state (S_1) of **DiCzTRZ-DiMe** in toluene

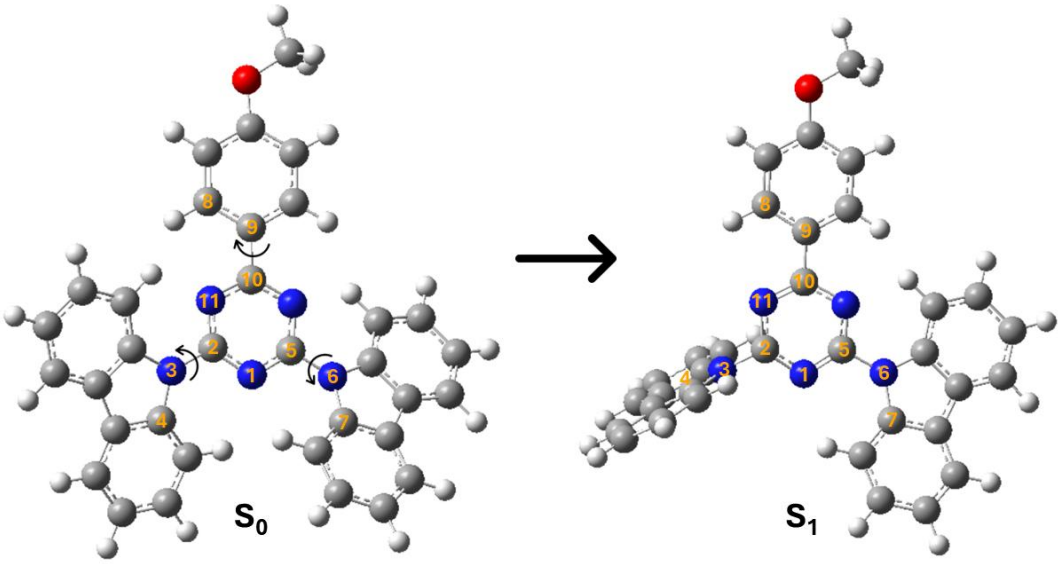


Figure S25: Optimized geometries of ground state (S_0) and excited singlet state (S_1) of **DiCzTRZ-OMe** in toluene

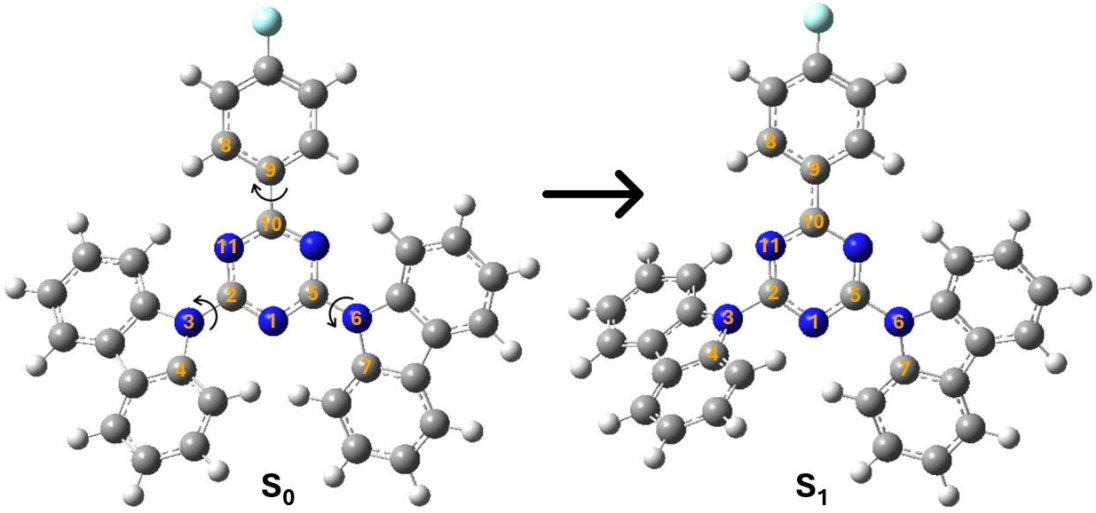


Figure S26: Optimized geometries of ground state (S_0) and excited singlet state (S_1) of **DiCzTRZ-F** in toluene

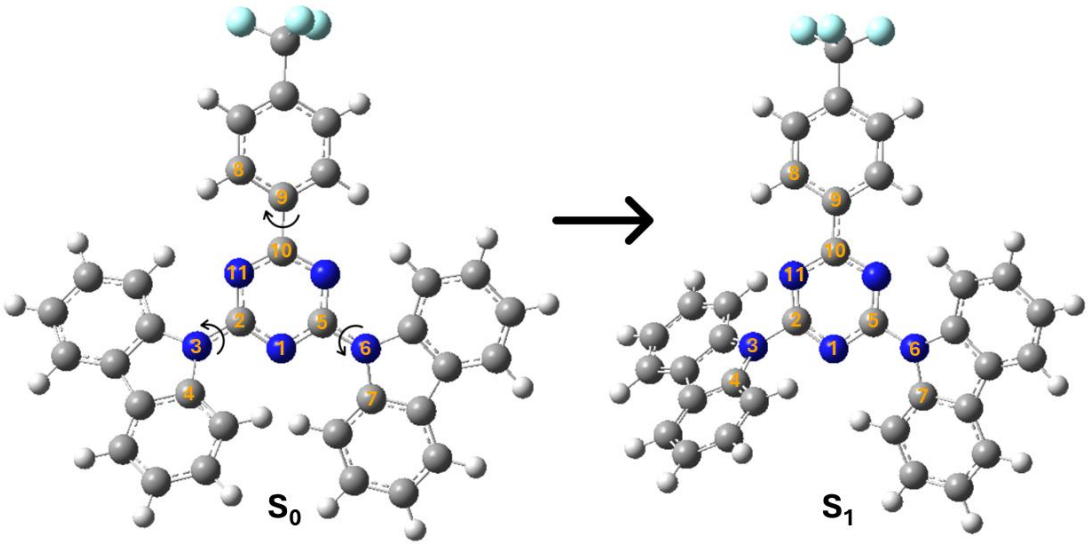


Figure S27: Optimized geometries of ground state (S_0) and excited singlet state (S_1) of **DiCzTRZ-CF_3** in toluene

Table S17 shows dihedral angles calculated in gas phase for the four compounds.

Table S17. angles in ground state and excited singlet state in gas phase

Compound	Atoms	Angle (S_0)	Angle (S_1)
DCzTRZAr-DiMe	N1-C2-N3-C4	17.7°	75.6°
	N1-C5-N6-C7	17.5°	0.4°
	C8-C9-C10-N11	62.6°	68.2°
DCzTRZAr-OMe	N1-C2-N3-C4	20.8°	53.9
	N1-C5-N6-C7	21.2°	22.1°
	C8-C9-C10-N11	11.1°	4.9°
DCzTRZAr-F	N1-C2-N3-C4	21.1°	52.3°
	N1-C5-N6-C7	20.7°	22.7°
	C8-C9-C10-N11	12.4°	4.4°
DCzTRZAr-CF_3	N1-C2-N3-C4	20.8°	49.3°
	N1-C5-N6-C7	20.2°	22.0°
	C8-C9-C10-N11	13.6°	3.9°

Figures S28-31 show the optimized geometries in the ground state (S_0) and excited singlet state (S_1) in gas phase of the four compounds with the numbers corresponding to the atoms forming the analyzed dihedral angles. These values are in Table S4.

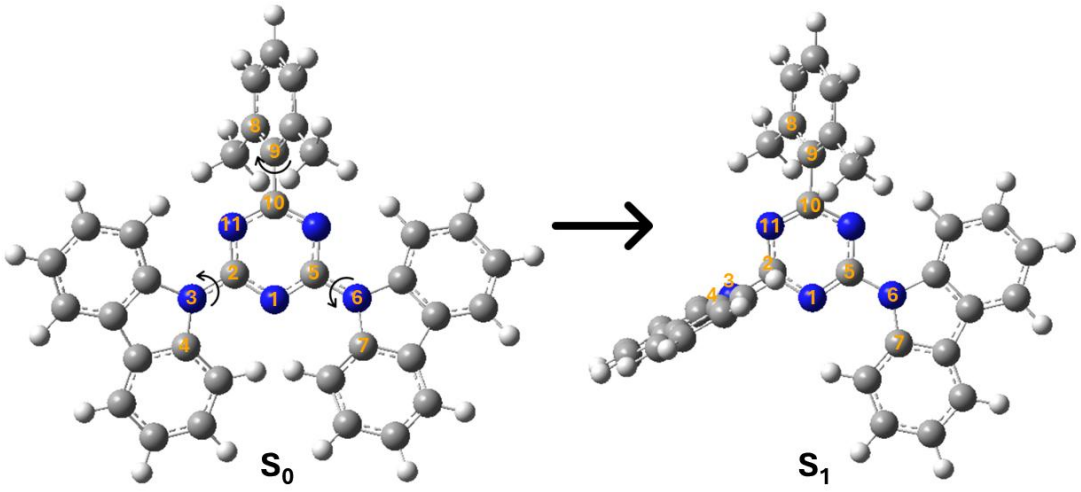


Figure S28: Optimized geometries of ground state (S_0) and excited singlet state (S_1) of **DiCzTRZ-DiMe** in gas phase

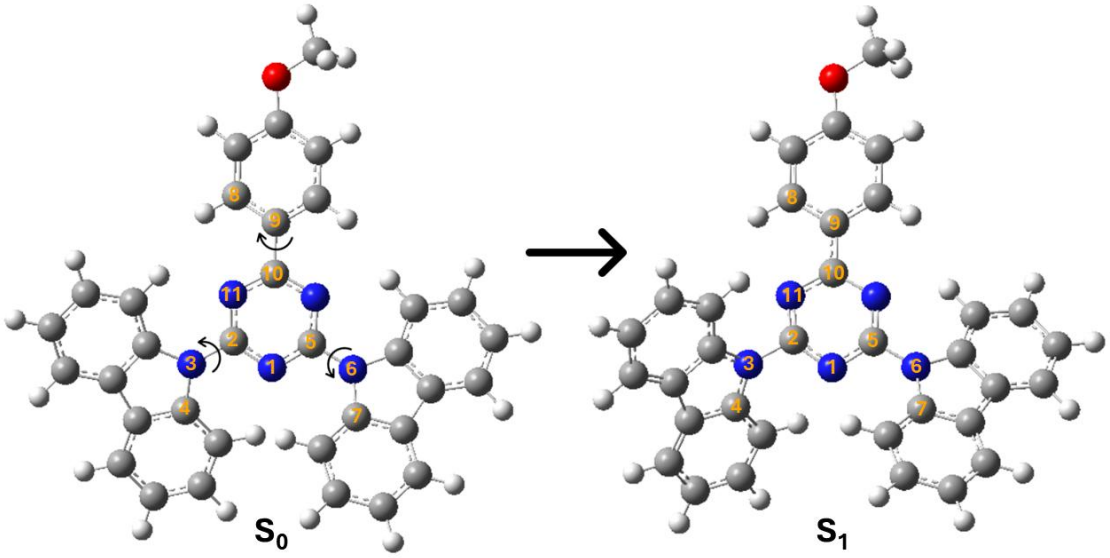


Figure S29: Optimized geometries of ground state (S_0) and excited singlet state (S_1) of **DiCzTRZ-OMe** in gas phase

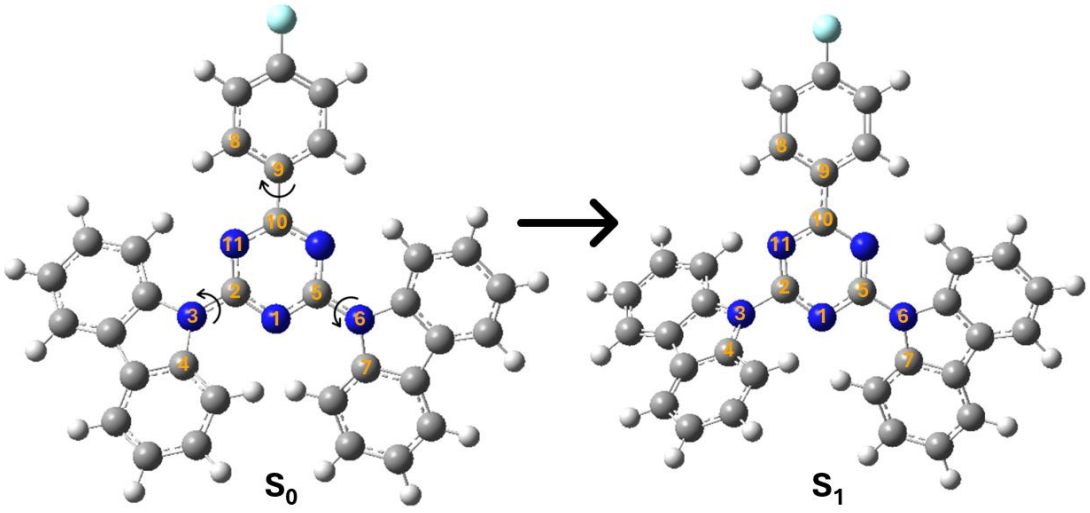


Figure S30: Optimized geometries of ground state (S_0) and excited singlet state (S_1) of **DiCzTRZ-F** in gas phase

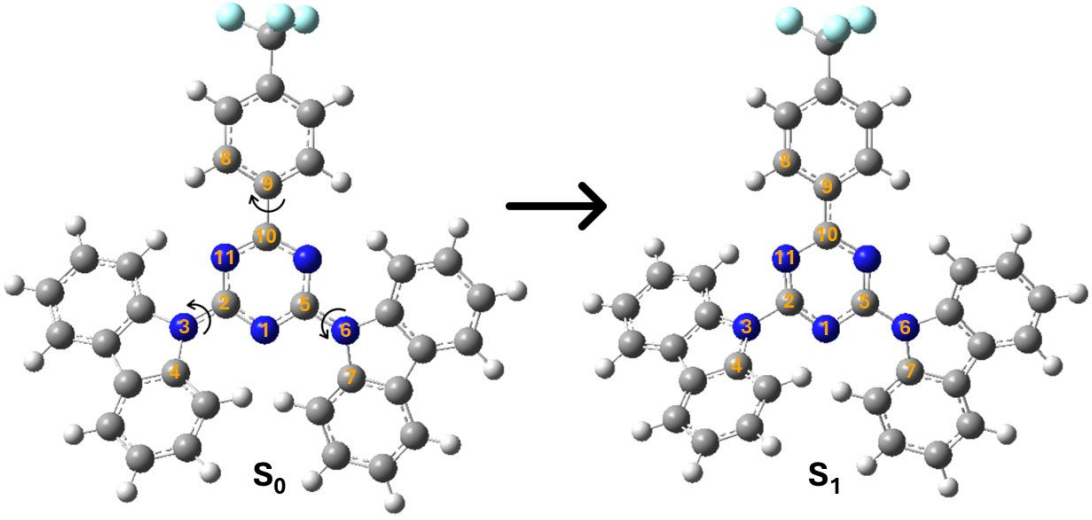


Figure S31: Optimized geometries of ground state (S_0) and excited singlet state (S_1) of **DiCzTRZ-CF_3** in gas phase

4. Electrochemical properties

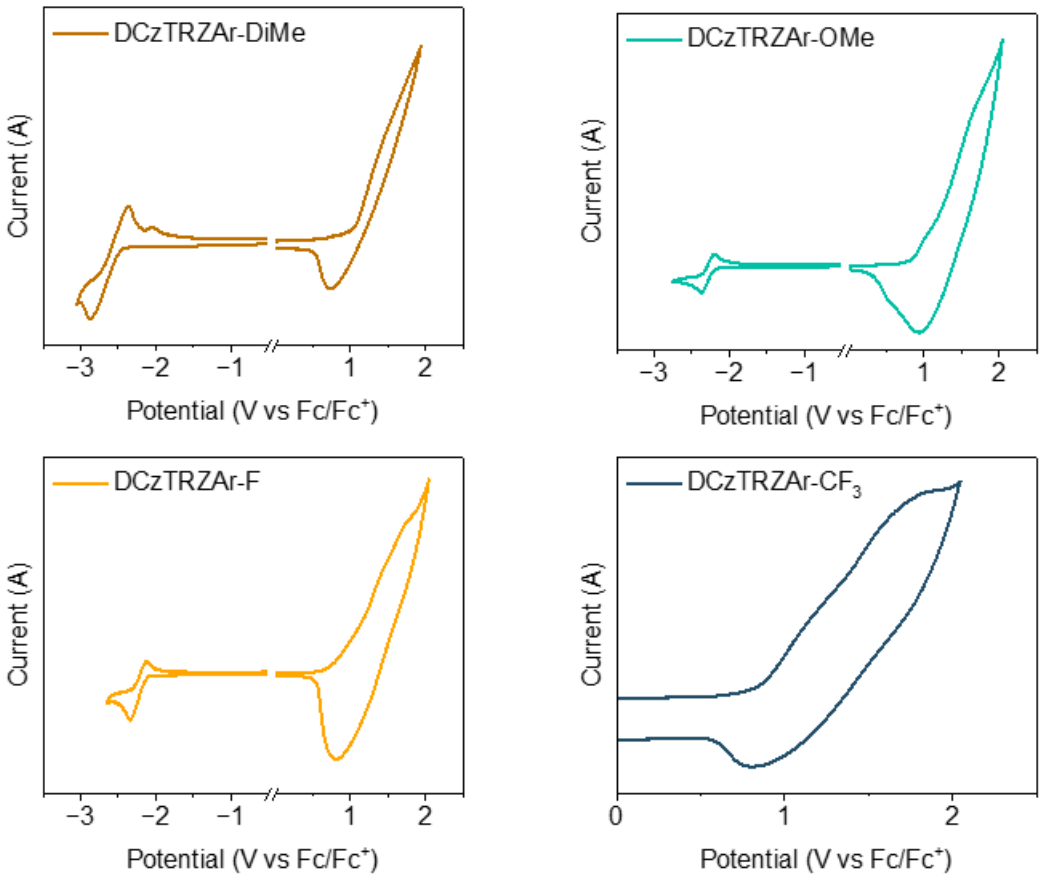


Figure S32: Cyclic voltammograms measured at 3 mM in degassed 1,2-difluorobenzene relative to Fc/Fc^+, with 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

5. Thermogravimetric analysis

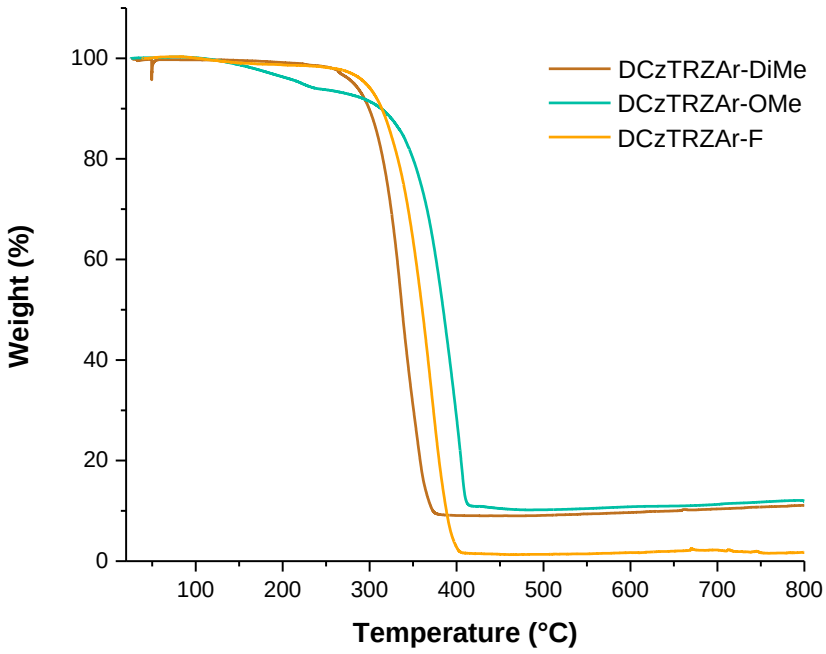


Figure S33: Thermogravimetric analysis of **DCzTRZAr**, obtained at 10°C /min under nitrogen at normal pressure

6. NMR spectra of DCzTRZAr compounds

DCzTRZAr-DiMe: 9,9'-(6-(2,6-dimethylphenyl)-1,3,5-triazine-2,4-diyl)bis(9*H*-carbazole)

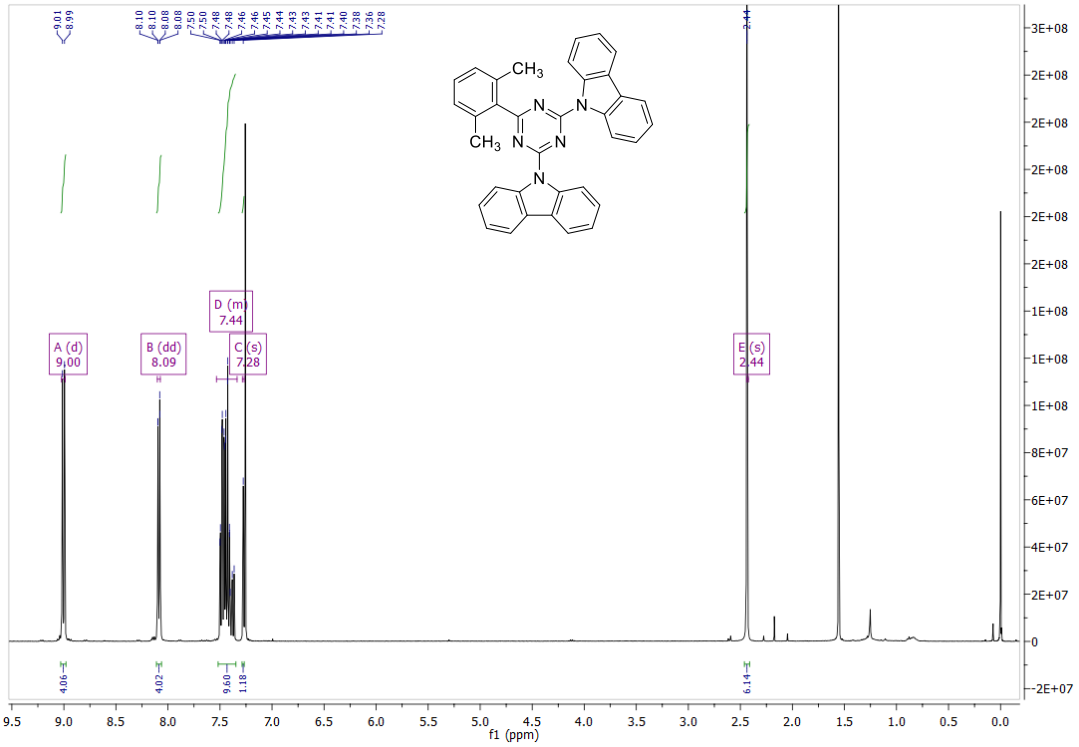


Figure S34. ^{1}H NMR (400 MHz) of **DCzTRZAr-DiMe** in $CDCl_3$

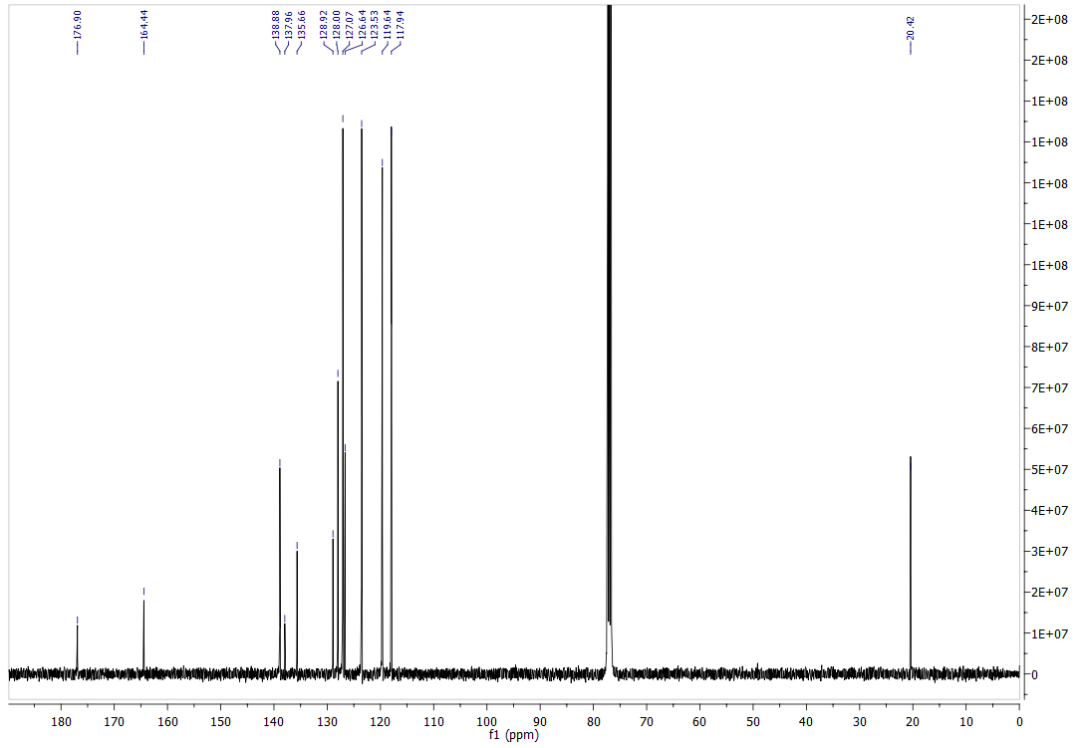


Figure S35. ^{13}C {^{1}H} NMR (101 MHz) of **DCzTRZAr-DiMe** in $CDCl_3$

DCzTRZAr-OMe: 9,9'-(6-(4-methoxyphenyl)-1,3,5-triazine-2,4-diyl)bis(9*H*-carbazole)

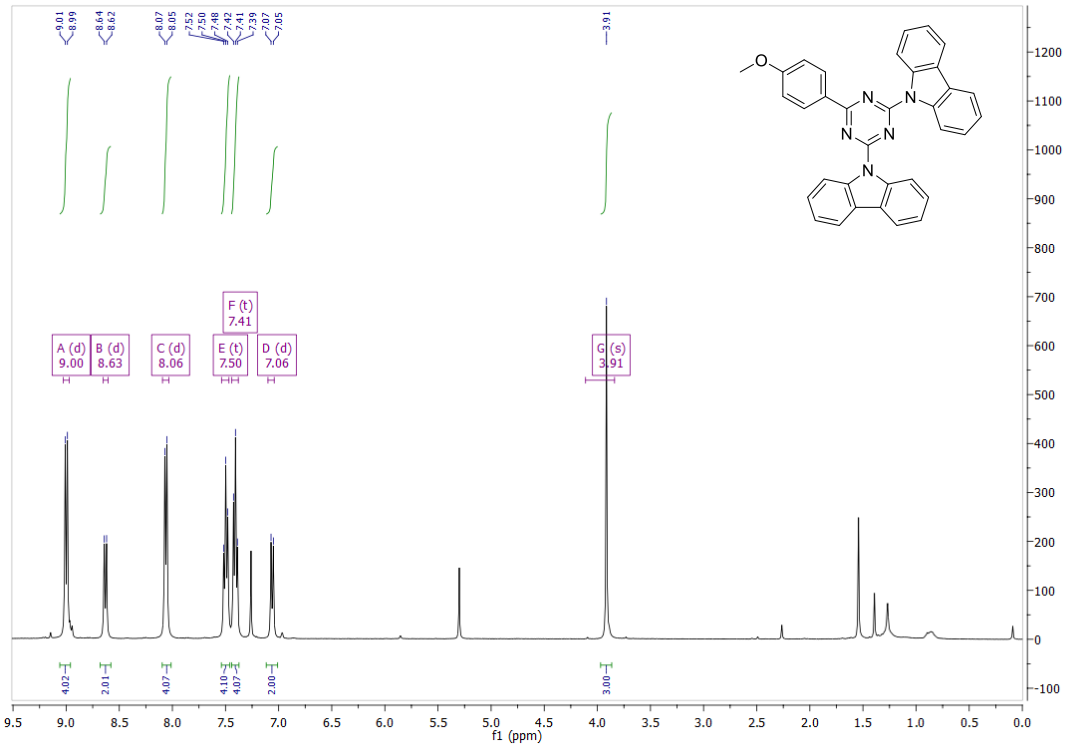


Figure S36. ^{1}H NMR (400 MHz) of **DCzTRZAr-OMe** in $CDCl_3$

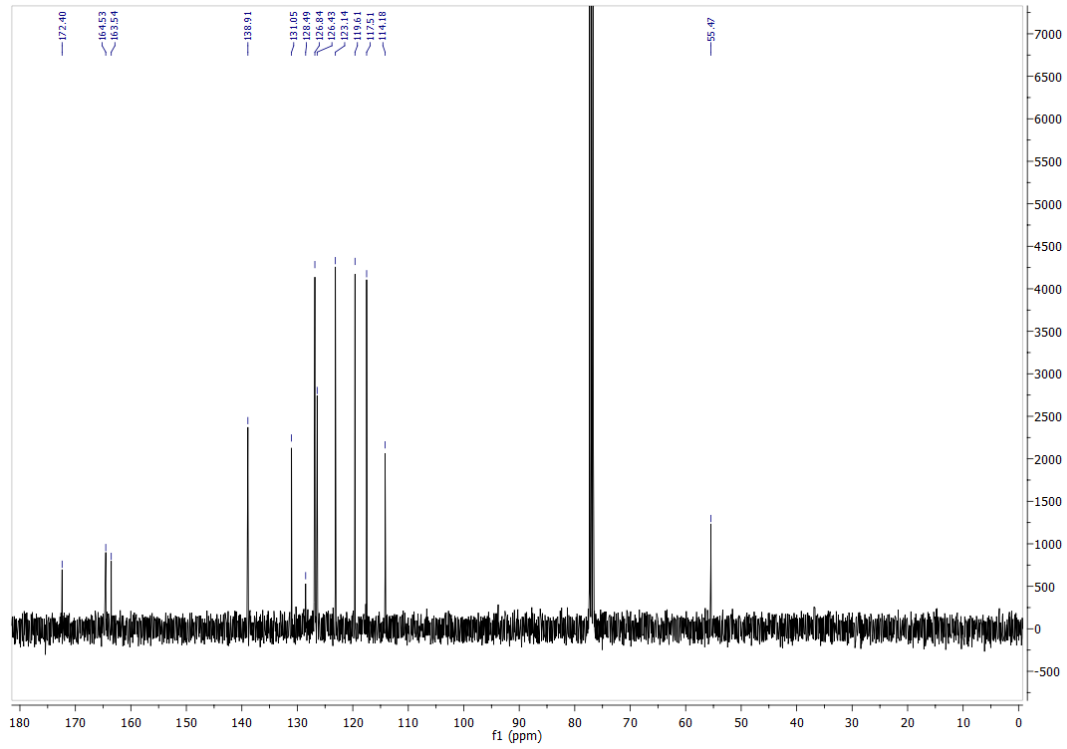


Figure S37. ^{13}C {^{1}H} NMR (101 MHz) of **DCzTRZAr-OMe** in $CDCl_3$

DCzTRZAr-F: 9,9'-(6-(4-fluorophenyl)-1,3,5-triazine-2,4-diyl)bis(9*H*-carbazole)

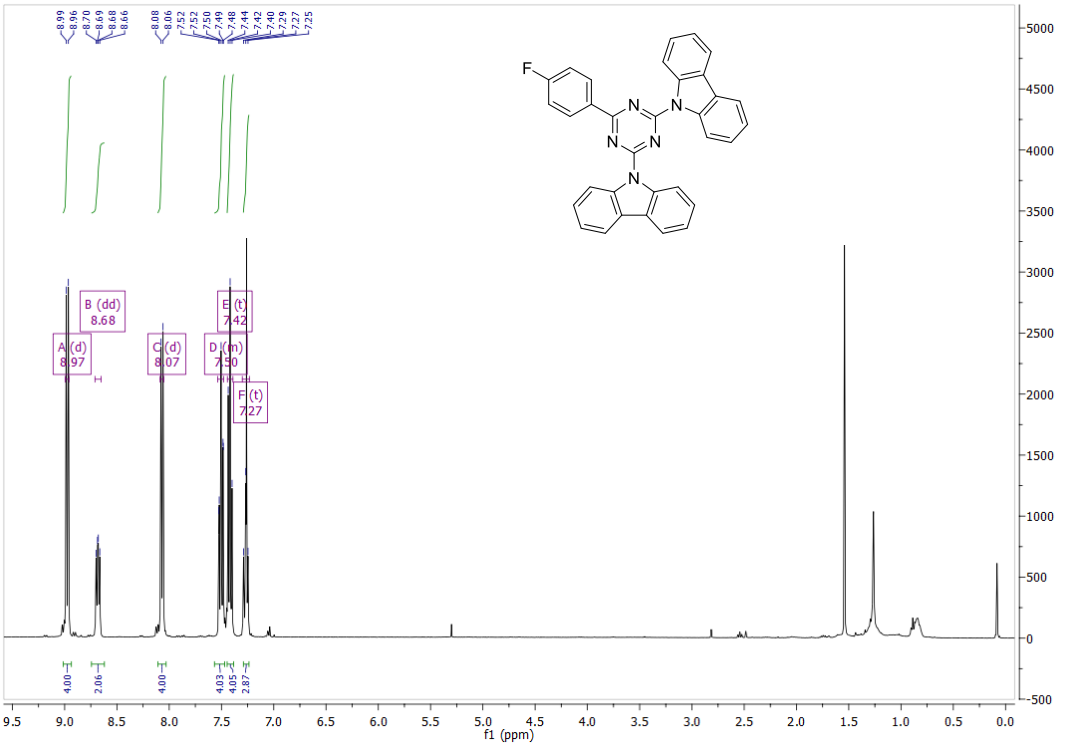


Figure S38. ^{1}H NMR (400 MHz) of **DCzTRZAr-F** in $CDCl_3$

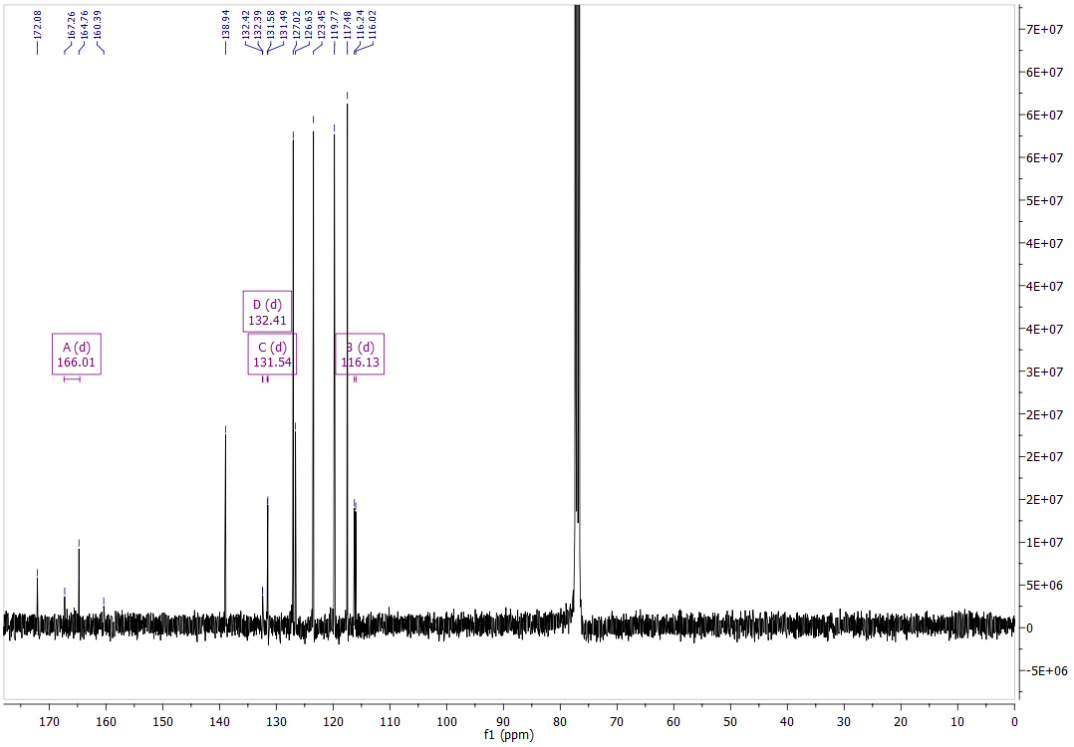


Figure S39 ^{13}C {^{1}H} NMR (101 MHz) of **DCzTRZAr-F** in $CDCl_3$

DCzTRZAr-CF$_3$: 9,9'-(6-(4-(trifluoromethyl)phenyl)-1,3,5-triazine-2,4-diyl)bis(9*H*-carbazole)

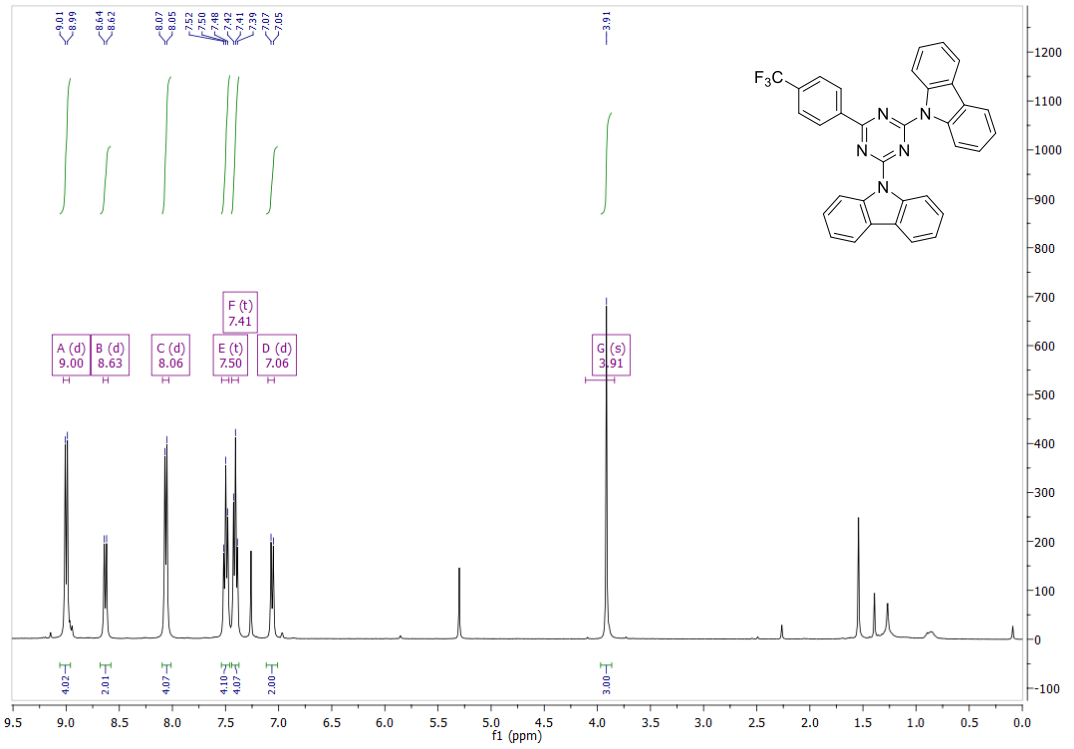


Figure S40. ^{1}H NMR (400 MHz) of **DCzTRZAr-CF$_3$** in $CDCl_3$

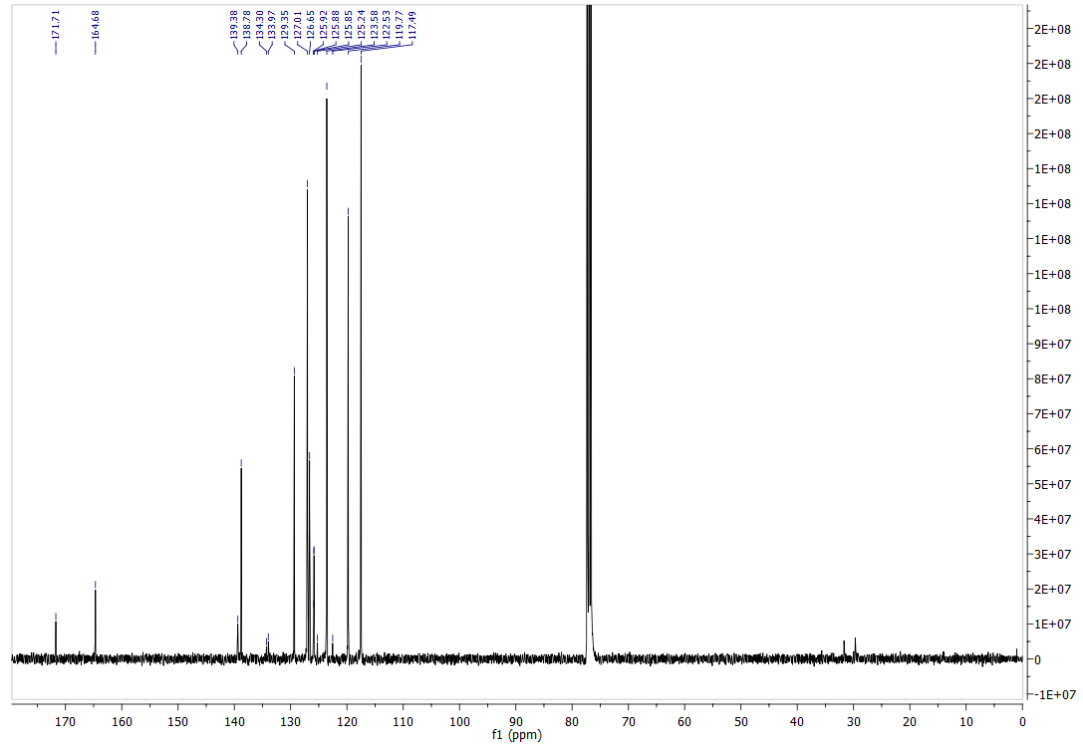


Figure S41. ^{13}C {^{1}H} NMR (101 MHz) of **DCzTRZAr-CF$_3$** in $CDCl_3$

7. References

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