# Electronic Supplementary Information

for

# "Super stable" Blatter radicals through ArLi addition: Surprising chemistry of 7-(trifluoromethyl)benzo[*e*][1,2,4]triazine

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## 1. Computational details

Quantum-mechanical calculations were carried out using Gaussian 09 suite of programs.[1] Geometry optimizations were undertaken at the B3LYP/6-31G(2d,p) level of theory using tight convergence limits and no symmetry constraints. Natural charges were obtained from population analysis performed with the NBO method at the B3LYP/6-31+G(2d,p) // B3LYP/6-31G(2d,p) level of theory. Solvent effects were implemented with the PCM model[2] using the SCRF(solvent=THF) keyword. Isotropic Fermi contact coupling constants for radicals **1** were calculated using the UCAM-B3LYP/EPR-III // UB3LYP/6-31G(2d,p) method in benzene dielectric medium requested with the SCRF(Solvent=Benzene) keyword (PCM model).[2]

## 2. Experimental details

**General**. Commercially available solvents and reagents were used as received. NMR spectra were recorded on a Bruker AVIII: $^1$H NMR (600 MHz); $^{13}$C NMR (151 MHz); $^{19}$F NMR (565 MHz), unless specified otherwise. Chemical shifts are given relative to residual not deuterated solvent peaks (for $CDCl_3$: $^1$H NMR $\delta = 7.26$ ppm, $^{13}$C NMR $\delta = 77.16$ ppm; for DMSO-$d_6$: $^1$H NMR $\delta = 2.50$ ppm, $^{13}$C NMR $\delta = 39.52$ ppm)[3] or to $CFCl_3$ ($^{19}$F NMR $\delta = 0.00$ ppm) used as the external standard. The IR spectra were measured for neat compounds with an NEXUS FT-IR in KBr or Agilent Cary 630 FTIR spectrometers. Mass spectra were measured with a Varian 500-MS LC Ion Trap. High-resolution MS spectra were registered on Waters SYNAPT HDMS (ES+) or Waters SYNAPT G2-Si (AP+) mass spectrometers. Elemental analyses were obtained with a Vario EL III (Elementar Analysensysteme GmbH) instrument. Melting points were determined in capillaries with a Melt-Temp II apparatus and are uncorrected. Acquisition and full details of simulation of EPR spectra are described in the ESI.

**Addition of ArLi to 3-phenyl-7-(trifluoromethyl)benzo[*e*][1,2,4]triazine (2). General procedure for preparation of radicals 1. Method A**. Bromoarene (0.70 mmol) was dissolved in anh. THF (1.0 mL) and a 1.9 M solution of *t*-BuLi in pentane (0.70 mL, 1.40 mmol) was added dropwise at –78 °C. After 15 min. the generated aryllithium solution was added dropwise at –78 °C to the solution of 3-phenyl-7-(trifluoromethyl)benzo[*e*][1,2,4]triazine (**2**, 138 mg, 0.50 mmol) dissolved in anh. THF (2 mL). The reaction mixture was warmed to ambient temperature, and the stirring was continued overnight. The pink and green byproducts started to appear after 30 min. The reaction mixture was quenched with water (5 mL), opened to air and left stirring for 1 hr. Reaction products were extracted with $CH_2Cl_2$ (4×) and the combined extracts were dried ($Na_2SO_4$). Solvents were removed and the resulting mixture of products was separated using preparative layer chromatography plates (PLC) coated with $SiO_2$ and pet. ether/$CH_2Cl_2$ (1:4) as the eluent. The least polar green fraction comprised of compound **3**, the middle brown fraction contained radical **1**, and the last pink fraction consisted of radical **4**.

**Method B**. The reaction was carried out as described in Method A, except for the temperature of quenching with water: addition of ArLi, stirring (1 hr), and quenching with $H_2O$ before areal oxidation all were conducted at –78°C. Also the reaction time after ArLi addition was extended to 1 hr. The obtained crude radical **1** was purified by filtration trough a $SiO_2$ pad using pet. ether with increased amounts of $CH_2Cl_2$ (0–70%) as the eluent.

**1,3-Diphenyl-7-trifluoromethyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (1a).** Yield: 65 mg (range 33–37%) with Method A and 158 mg (range 84–94%) with Method B; dark brown crystals. Mp 148–151°C (pet. ether/$Et_2O$), $R_f$ = 0.70 ($SiO_2$, $CH_2Cl_2$/pet. ether 3:7). EPR (benzene) $a_N$ = 7.58, 4.87 and 4.77, $a_F$ = 3.49 G, $g$ = 2.0034. IR (KBr) $\nu$ 3063w, 3053w, 1594m, 1492m, 1420m, 1394s, 1353s, 1315s, 1258s, 1157m, 1150m, 1119s, 1062m, 900m, 688s $cm^{-1}$. UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (*log* ε) 274.5 (4.53), 323 (3.79), 373 (3.67), 431 (3.45), 495 (3.10) nm. HRMS (TOF ES+) *m/z* $[M]^+$ calcd. for $C_{20}H_{13}F_3N_3$: 352.1062, found 352.1061. Anal. Calcd. for $C_{20}H_{13}F_3N_3$ (352.34): C, 68.18; H, 3.72; N, 11.93. Found: C, 68.31; H, 3.58; N, 11.98.

**1-(Biphenyl-4-yl)-3-phenyl-7-trifluoromethyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (1b)**. Yield: 71 mg (range 29–33%) with Method A and 199 mg (range 90–93%) with Method B; dark brown crystals. Mp 193–195°C (pet. ether/$Et_2O$), $R_f$ = 0.79 ($SiO_2$, $CH_2Cl_2$/pet. ether 3:7). EPR (benzene) $a_N$ = 7.56, 4.93 and 4.84, $a_F$ = 3.21 G, $g$ = 2.0023. IR (KBr) $\nu$ 3072w, 3053w, 3034w, 1489m, 1394s, 1353m, 1315s, 1258m, 1169m, 1116s, 1065m, 767m, 691m $cm^{-1}$. HRMS (TOF ES+) *m/z* $[M]^+$ calcd. for $C_{26}H_{17}F_3N_3$: 428.1375, found 428.1375. Anal. Calcd. for $C_{26}H_{17}F_3N_3$ (428.44): C, 72.89; H, 4.00; N, 9.81. Found: C, 72.79; H, 4.18; N, 9.91.

**3-Phenyl-7-(trifluoromethyl)benzo[1,2,4]triazine (2)**. *N*'-(2-Nitro-5-trifluoromethylphenyl)benzhydrazide (**6**, 3.23 g, 10.0 mmol) was dissolved in glacial AcOH (100 mL), Sn powder (4.76 g, 40.0 mmol) was added, and the solution was left stirring vigorously at rt for 2 hr. The reaction mixture was then heated at 115–125°C for 30 min and cooled. AcOEt (100 mL) and $H_2O$ (200 mL) were added, and the resulting biphasic mixture was passed through a layer of Cellite. The organic layer was separated, and the aqueous layer was extracted with AcOEt (2×50 mL). The combined organic extracts were washed with sat. $NaHCO_3$ and dried ($Na_2SO_4$). The solvent was removed, the solid residue was dissolved in a MeOH/$CH_2Cl_2$ mixture (1:1, 40 mL), and solid $NaIO_4$ (3.2 g, 15 mmol) was added. The mixture was stirred until the initial dihydro derivative was no longer observed by TLC (about 30 min). Inorganic salts were filtered, solvents were evaporated, and the resulting yellow solid residue was passed through a short $SiO_2$ column ($CH_2Cl_2$/hexane, 1:1, $R_f = 0.82$ in $CH_2Cl_2$). The obtained product was recrystallized from a $CH_2Cl_2$/cyclohexane mixture. Yield: 2.38 g (85%) after chromatography and 2.00 g (73%) after crystallization; orange crystals. Mp. 160–162°C. $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.26 (s, 1H), 8.76–8.71 (m, 2H), 8.19 (d, $J$ = 8.9 Hz, 1H), 8.09 (dd, $J_1$ = 8.9 Hz, $J_2$ = 2.0, Hz 1H), 7.61–7.55 (m 3H) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 160.9, 145.3, 142.1, 134.9, 132.3, 131.8 (q, $J_{CF}$ = 34.0 Hz), 130.97, 130.94, 129.22, 129.20, 127.9 (q, $J_{CF}$ = 27.9 Hz), 123.2 (q, $J_{CF}$ = 271.0 Hz) ppm. $^{19}$F NMR ($CDCl_3$, 375 MHz) δ –62.48 (s) ppm. IR (neat) $v$ 3079w, 1633m, 1506m, 1428m, 1320s, 1234m, 1170m, 1118s, 1055m, 1010m, 894s, 849s, 768m cm$^{-1}$. HRMS (TOF AP+) $m/z$ $[M+1]^+$ calcd. for $C_{14}H_9F_3N_3$: 276.0749, found 276.0750. Anal. Calcd. for $C_{14}H_8F_3N_3$ (275.23): C, 61.09; H, 2.93; N, 15.27. Found: C, 61.22; H, 2.81; N, 15.19.

**"Trimer" 3a**. Yield: 65 mg (range 25–32%, Method A); dark green crystals. Mp 136–139°C (cyclohexane/$Et_2O$). $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.12–8.10 (m, 2H), 7.56 (d, $J$ = 8.0 Hz, 2H), 7.50–7.30 (m, 19H), 7.24–7.19 (m, 2H), 7.10–6.97 (m, 7H), 6.42 (d, $J$ = 8.0 Hz, 1H), 6.37 (d, $J$ = 8.0 Hz, 1H), 6.32–6.31 (m, 2H), 5.88 (t, $J$ = 8.0 Hz, 2H), 5.62 (d, $J$ = 2.0 Hz, 1H) ppm. $^{13}$C{$^1$H,$^{19}$F} NMR ($CDCl_3$, 125 MHz) δ 160.53, 150.86, 145.93, 145.77, 142.93, 142.82, 141.69, 138.60, 138.53, 138.25, 135.35, 135.28, 134.73, 133.25, 133.21, 133.04, 131.68, 130.05, 129.73, 129.65, 129.61, 129.55, 128.67, 128.51, 128.17, 127.81, 127.50, 127.43, 126.39 ($^2J_{CF}$ = 33 Hz), 126.17 (q, $^2J_{CF}$ = 32 Hz), 126.13, 125.94, 126.69, 124.40, 124.10, 123.83 ($^1J_{CF}$ = 270 Hz), 123.75 ($^1J_{CF}$ = 270 Hz), 118.76 ($^3J_{CF}$ ≈ 3 Hz), 118.56 ($^3J_{CF}$ ≈ 3 Hz), 115.65, 115.35, 107.84, 107.59, 94.00 ppm. $^{19}$F NMR ($CDCl_3$, 470 MHz) δ –62.95 (s, 3F), –63.04 (s, 3F) ppm. IR (KBr) $v$ 1591m, 1543m, 1492s, 1426m, 1315s, 1245m, 1169m, 1116s, 691s cm$^{-1}$. UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (*log* ε) 246 (4.69), 320 (4.60), 444 (3.89), 678.5 (3.99), 745 sh (3.86) nm. HRMS (TOF AP+) $m/z$ $[M+1]^+$ calcd $C_{60}H_{40}F_6N_9$: 1000.3311, found: 1000.3317. Anal. Calcd. for $C_{60}H_{39}F_6N_9$ (1000.0): C, 72.06; H, 3.93; N, 12.61. Found: 72.06; H, 3.33; N, 12.70.

**"Trimer" 3b**. Yield: 90 mg (range 36–44%, Method A); dark green crystals. Mp. 285–287°C (cyclohexane/$Et_2O$). $^1$H NMR ($CDCl_3$, 600 MHz) δ 8.13–8.15 (m, 2H), 7.67 (d, $J$ = 9.0 Hz, 2H), 7.63 (d, $J$ = 9.0 Hz, 2H), 7.52–7.58 (m, 10H), 7.38–7.49 (m, 18H), 7.31–7.35 (m, 3H), 7.05–7.15 (m, 6H), 7.02 (d, $J$ = 4.8 Hz, 1H), 6.46–6.49 (m, 3H), 6.41(dd, $J_1$ = 8.5 Hz, $J_2$ = 2.0 Hz, 1H), 5.95 (d, $J$ = 7.8 Hz, 1H), 5.93 (d, $J$ = 8.4 Hz, 1H), 5.82 (d, $J$ = 1.8 Hz, 1H) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$, 150 MHz) major signals δ 129.1, 128.93, 128.92, 128.2, 127.2, 127.12, 127.09, 124.3, 124.1, 94.2, ppm. $^{19}$F NMR ($CDCl_3$, 565 MHz) δ –62.91 (s, 3F), –63.02 (s, 3F) ppm. IR (neat) ν 3060w, 3028w, 1600w, 1537m, 1515m, 1489s, 1426m, 1315s, 1245m, 1169m, 1119m, 694m cm$^{-1}$. HRMS (TOF

AP+) *m/z* $[M+1]^+$ calcd. for $C_{78}H_{52}F_6N_9$: 1228.4250, found 1228.4260. Anal. Calcd. for $C_{78}H_{51}F_6N_9$ (1228.3): C, 76.27; H, 4.19; N, 10.26. Found: 76.39; H, 4.13; N, 8.76.

**Radical 4a**. Yield: 41 mg (range 18–25%, Method A), dark pink powder. Mp. 164–165°C (pet. ether). IR (KBr) ν 1594s, 1530s, 1499s, 1401m, 1340s, 1315s, 1166m, 1122s, 694m $cm^{-1}$. UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (*log* ε) 304 (4.63), 522 (3.80), 775 (3.04) nm. HRMS (TOF AP+) *m/z* $[M+1]^+$ calcd for $C_{40}H_{27}F_3N_6$: 648.2249, found 648.2250. Anal. Calcd. for $C_{40}H_{26}F_3N_6$ (647.67): C, 74.18; H, 4.05; N, 12.98. Calcd. for $C_{40}H_{26}F_3N_6 \cdot 0.5H_2O$: C, 73.16; H, 4.14; N, 12.80. Found: C, 73.64; H, 4.11; N, 11.17.

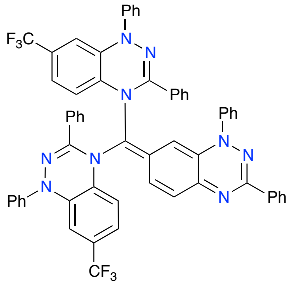
**Radical 4b**. Yield: 36 mg (range 22–23%, Method A); dark pink microcrystals. Mp 179–180 °C (pet. ether/$Et_2O$). IR (KBr) *ν* 1594s, 1518s, 1486s, 1394m, 1334s, 1315s, 1245m, 1220m, 1169m, 1128s, 761m, 688m $cm^{-1}$. HRMS (TOF AP+) *m/z* $[M+1]^+$ calcd $C_{52}H_{35}F_3N_6$: 800.2875, found: 800.2863. Anal. Calcd. for $C_{52}H_{34}F_3N_6$ (799.86): C, 78.08; H, 4.28; N, 10.51; Calcd. for $C_{52}H_{34}F_3N_6 \cdot H_2O$ (817.88): C, 76.36; H, 4.44; N, 10.28. Found: C, 76.43; H, 4.15; N, 8.74.

***N*'-2-(2-Nitro-5-trifluoromethylphenyl)benzhydrazide (6)**. The mixture of benzhydrazide (4.22 g, 31.0 mmol) and 2-fluoro-1-nitro-4-(trifluoromethyl)benzene (**5**, 6.27 g, 30.0 mmol) was heated in DMSO (12 mL) at 70°C over 36 hr. The reaction mixture was cooled, diluted with AcOEt (100 mL) and then water was added. The organic layer was separated and the aqueous was washed with AcOEt (2×50 mL). The combined organic layers were dried ($Na_2SO_4$) and solvents were evaporated under reduced pressure. The residue was crystallized from a mixture EtOH/$H_2O$. Yield: 7.62 g (78%); orange crystals. Mp. 176–178°C (EtOH/$H_2O$). $^1H$ NMR (DMSO-$d_6$, 600 MHz) δ 10.86 (s, 1H), 9.68 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.38 (s, 1H), 7.18 (d, *J* = 9.0 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, 150 MHz) δ 166.2, 145.1, 135.2 (q, $J_{CF}$ = 31.5 Hz), 133.7, 132.2, 132.0 128.6, 127.8, 127.5, 123.0 (q, $J_{CF}$ = 273.0 Hz), 113.5 (q, $J_{CF}$ = 3 Hz), 111.8 (q, $J_{CF}$ = 4.5 Hz). $^{19}F$ NMR (DMSO-$d_6$, 565 MHz) δ –62.65 (s) ppm. IR (neat) *ν* 3377m, 3295m, 1647s, 1613s, 1573s, 1528s, 1683s, 1413m, 1342s, 1275vs, 1234vs, 1162w, 1039w $cm^{-1}$. HRMS (TOF AP+) *m/z* $[M+1]^+$ calcd. for $C_{14}H_{11}F_3N_3O_3$: 326.0753, found 326.0754. Anal. Calcd. for $C_{14}H_{10}F_3N_3O_3$: C, 51.70; H, 3.10; N, 12.92. Found: C, 51.70; H, 2.91; N, 12.61.

**Generation of the anion $1a^-$. Investigation of the anion stability**. Radical **1a** (13.0 mg, 0.037 mmol) was dissolved in anhydrous THF (2 mL). Pd(10%)/C (4 mg) and NaH (60% in mineral oil, 5.0 mg, 0.13 mmol) were added under $H_2$ atmosphere. The reaction mixture was stirred for 3 hr at room temperature. The solution was decanted and left stirring overnight opened to air. TLC test showed two major spots, brown and pink. Separation of the mixture on a TLC plate using $CH_2Cl_2$/pet. ether (4:1) mixture gave radical **1a** (5.0 mg, 38%) and "pink" **4a** (2.5 mg, 21%). MS analysis confirmed the identity of the isolated products by direct comparison with the authentic samples. Both samples of **4a** run one after another gave identical MS spectra: HRMS (TOF ESI+) *m/z* $[M+1]^+$ calcd for $C_{40}H_{27}F_3N_6$: 648.2249, found 648.2238.

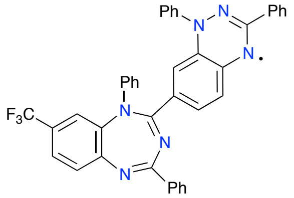
**Generation of 4a-*leuco*.** Ascorbic acid (1.8 mg, 0.0102 mmol) was added at room temperature to the solution of "pink" radical (**4a**, 4.4 mg, 0.0068 mmol) dissolved in a mixture of DMSO-$d_6$, $CDCl_3$ and $D_2O$ (1.0 mL, 2:1:2), and the mixture was shaken for 10 min. The organic layer was withdrawn with a pipette, dried ($Na_2SO_4$), and transferred to NMR tube. $^1$H and $^{19}$F NMR spectra were recorded immediately. $^1$H NMR (DMSO-$d_6$/$CDCl_3$, 600 MHz) δ 8.51 (s, 1H), 7.95–7.93 (m, 2H), 7.75–7.73 (m, 2H), 7.60 (d, $J$ = 8.4 Hz, 1H), 7.55–7.52 (m, 2H), 7.37–7.28 (m, 9H), 7.26–7.23 (m, 3H), 7.07–7.04 (m, 2H), 6.72–6.67 (m, 2H), 6.50 (d, $J$ = 9.6 Hz, 2H) ppm. $^{19}$F NMR (DMSO-$d_6$/$CDCl_3$, 565 MHz): δ –61.77 ppm.

### 3. Systematic naming of compounds 3a and 4a



**3a**

4,4'-[(1,3-Diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-ylidene)methylene]-bis[1,3-diphenyl-7-(trifluoromethyl)-1,4-dihydrobenzo[*e*][1,2,4]triazine]



**4a**

1,3-Diphenyl-7-[1,4-diphenyl-8-(trifluoromethyl)-1*H*-benzo[*f*][1,3,5]triazepin-2-yl]-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl

## 4. NMR Spectra

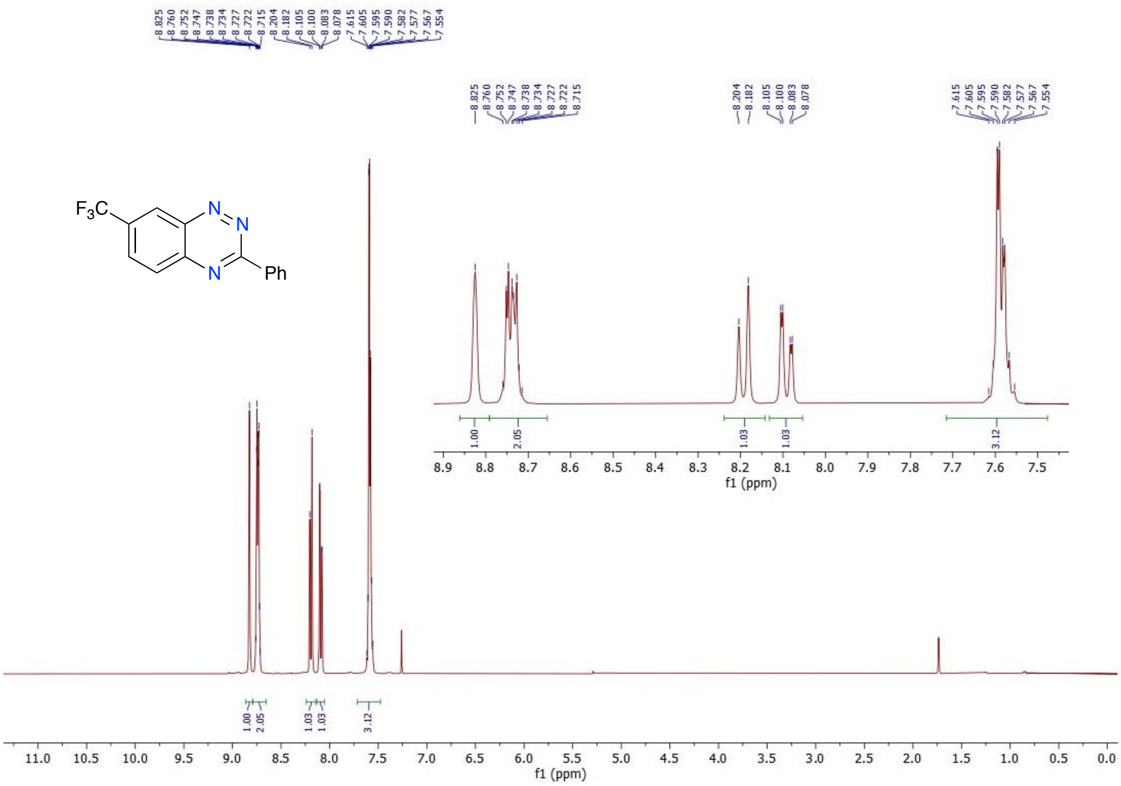


**Figure S1.** $^{1}$H NMR (400 MHz, CDCl$_3$) spectrum of *3-phenyl-7-(trifluoromethyl)benzo[e][1,2,4]triazine (***2***)*.

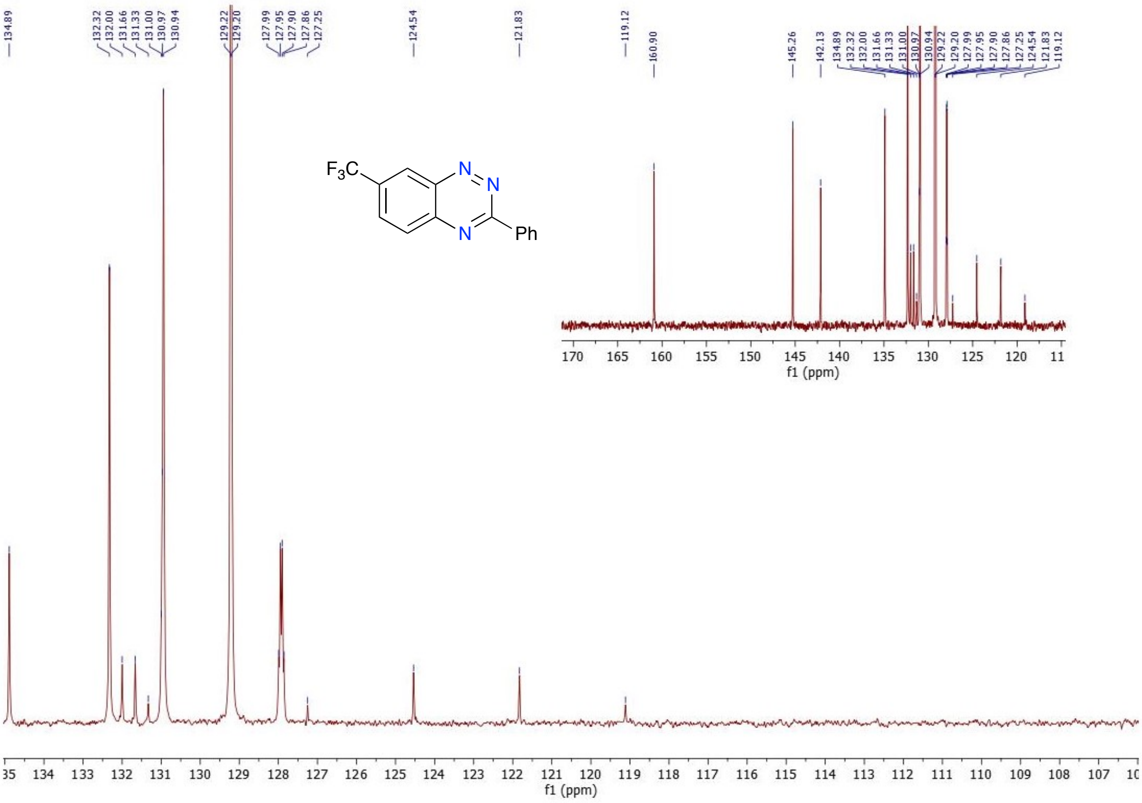


**Figure S2.** $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) spectrum of *3-phenyl-7-(trifluoromethyl)benzo[e][1,2,4]triazine* (**2**)

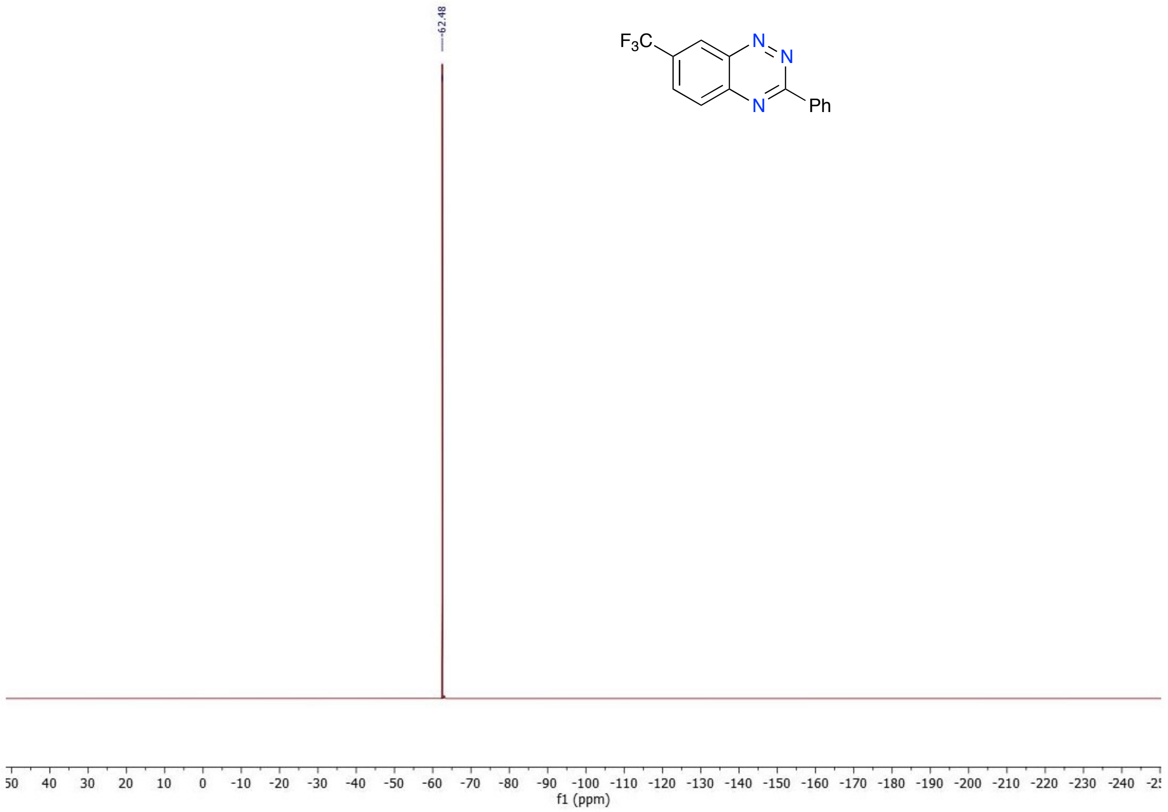


**Figure S3.** $^{19}$F NMR (375 MHz, $CDCl_3$) spectrum of
*3-phenyl-7-(trifluoromethyl)benzo[e][1,2,4]triazine* (**2**).

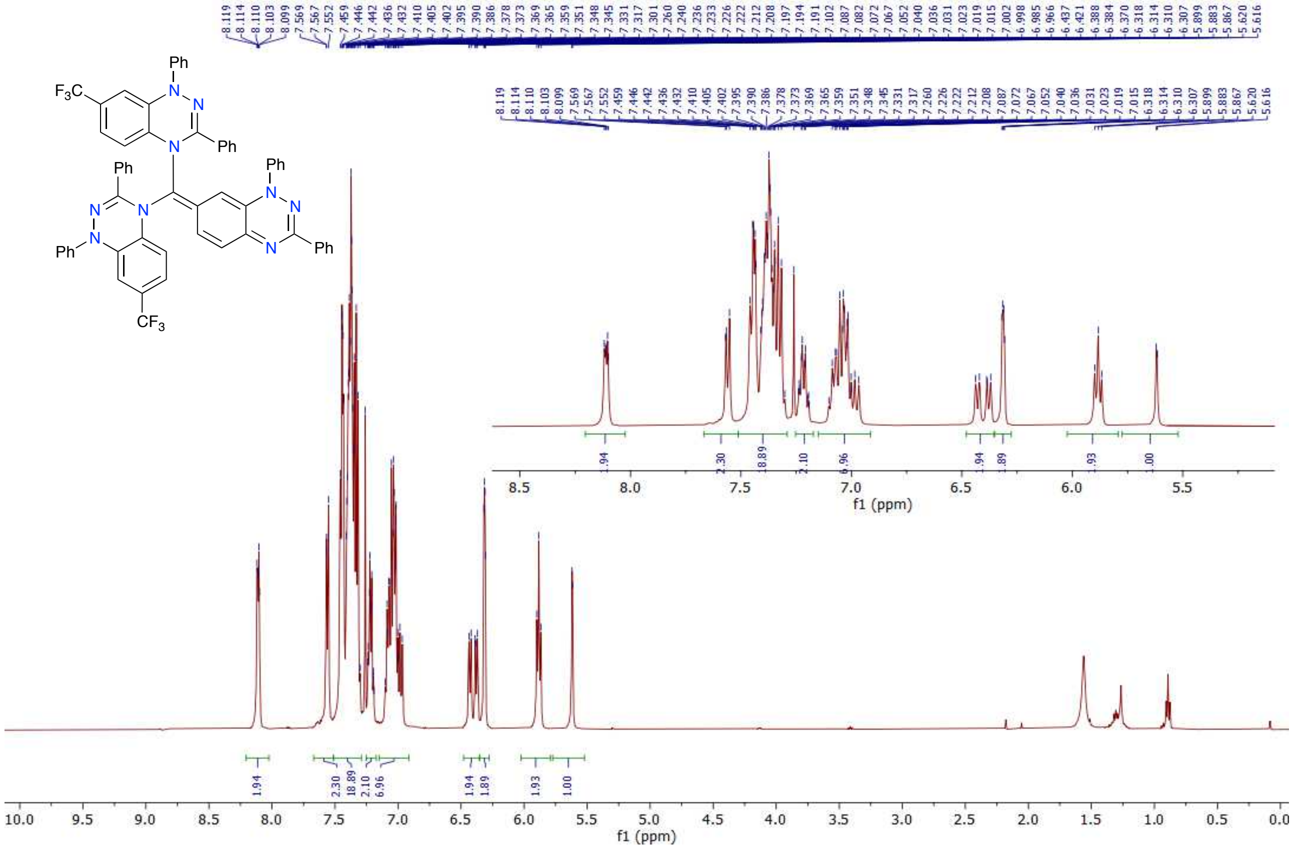


**Figure S4.** $^1$H NMR (500 MHz, $CDCl_3$) spectrum of ‘trimer’ **3a**. Residual pentane solvent visible in the low field region of the spectrum.

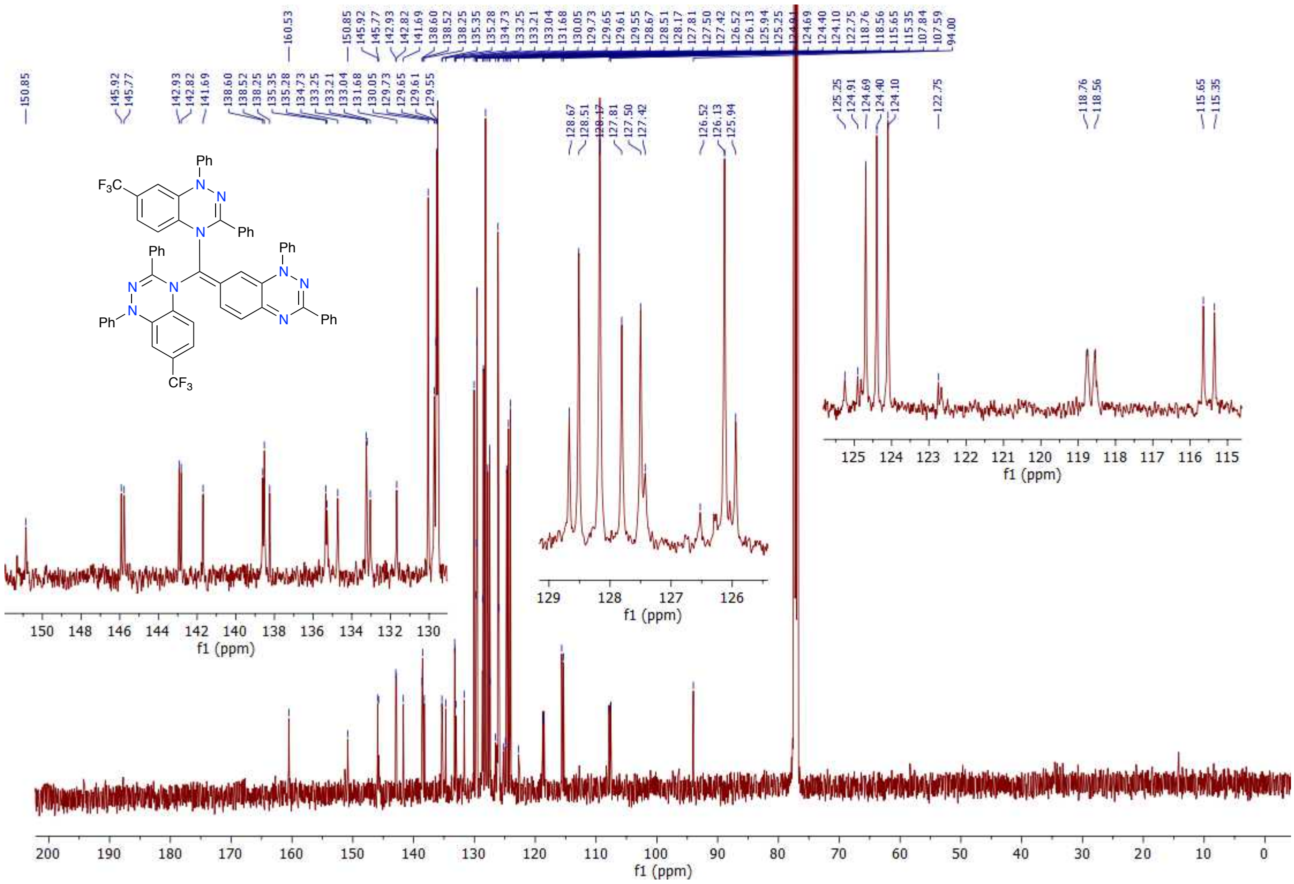


**Figure S5.** $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl$_3$) spectrum of 'trimer' **3a**.

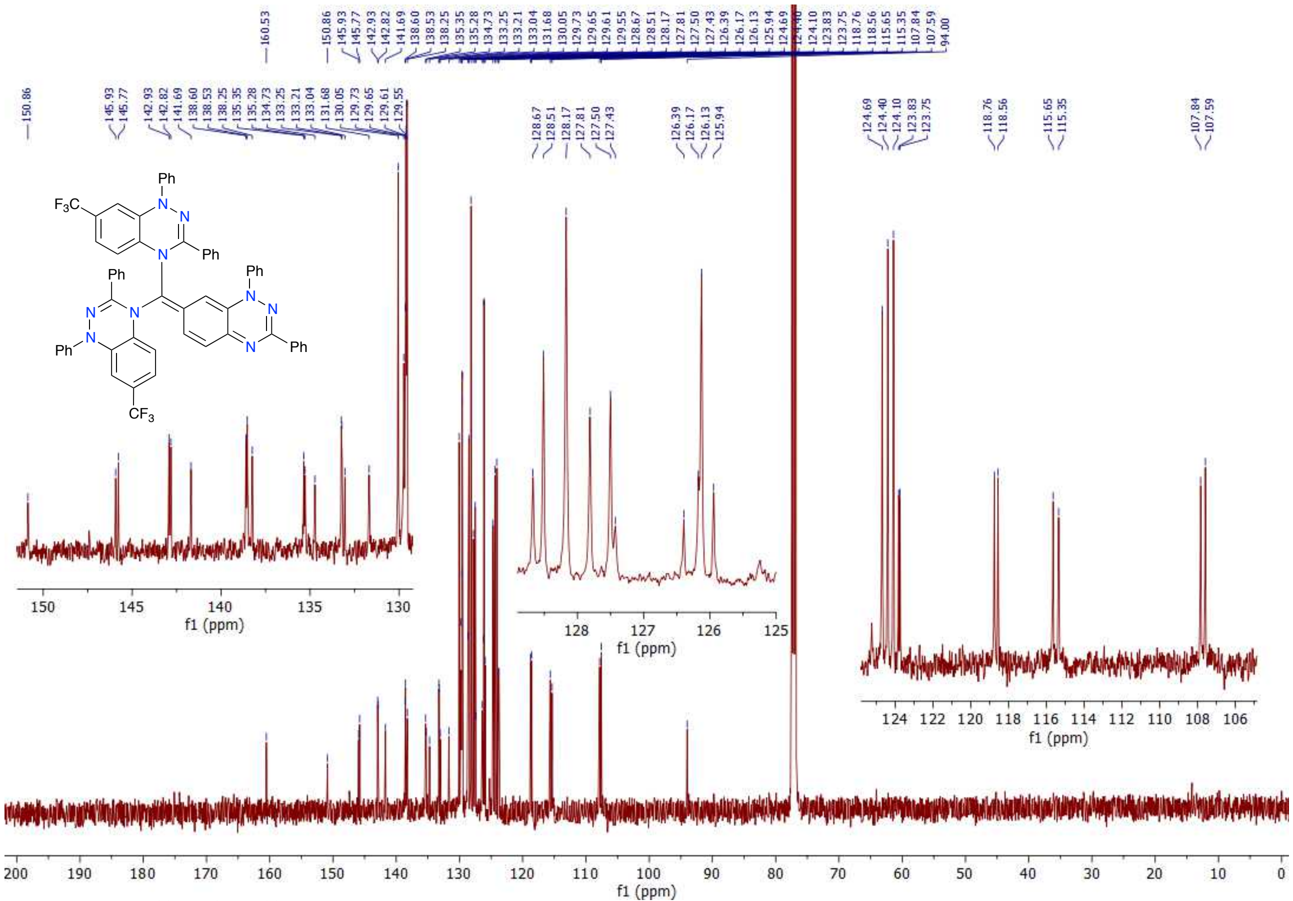


**Figure S6.** $^{13}C\{^{1}H, ^{19}F\}$ NMR (125 MHz, CDCl$_3$) spectrum of 'trimer' **3a**.

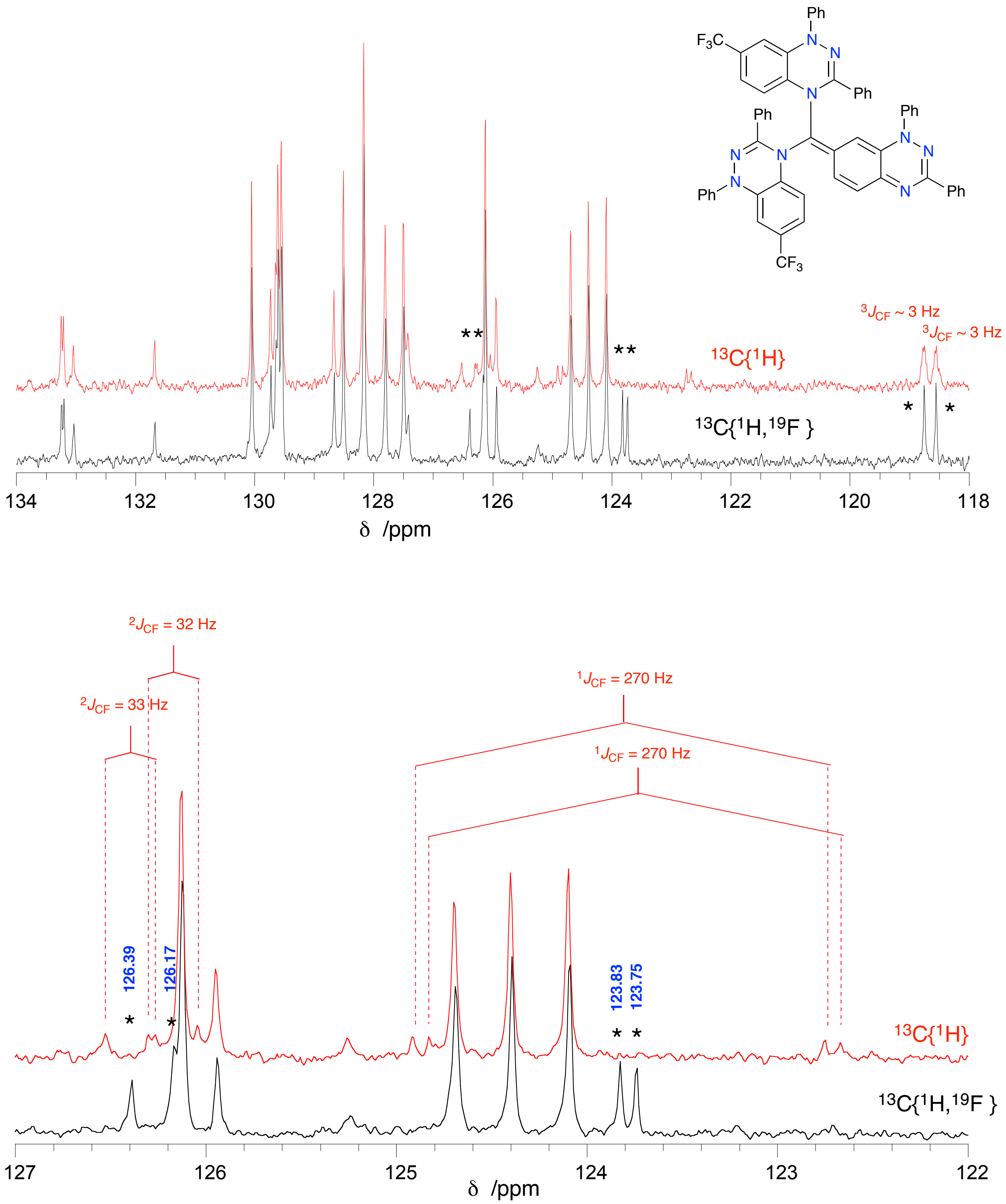


**Figure S7.** Two expansions of overlaid $^{13}$C{$^1$H, $^{19}$F} (black) and $^{13}$C{$^1$H} NMR (red; 125 MHz, CDCl$_3$) spectra of ‘trimer’ **3a** showing two main components of quartets resulting form $^1J_{CF}$ and $^2J_{CF}$ coupling of two nonequivalent CF$_3$ groups. The top graph also shows two poorly resolved quartets at 118.76 and 118.56 ppm resulting from $^3J_{CF}$. The asterisks indicate signals of F-decoupled C atoms with given chemical shifts (blue).

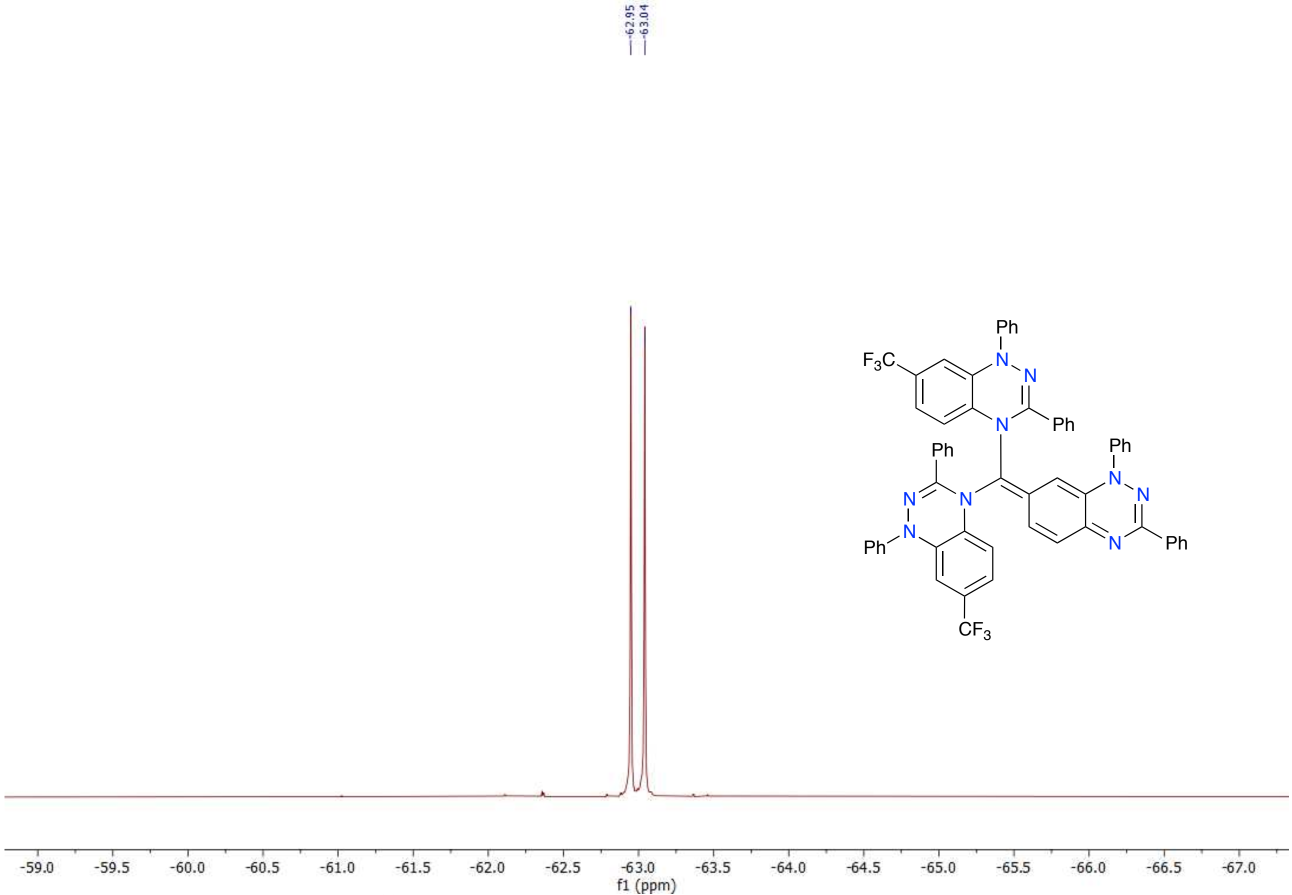


**Figure S8.** $^{19}$F NMR (470 MHz, CDCl$_3$) spectrum of 'trimer' **3a**.

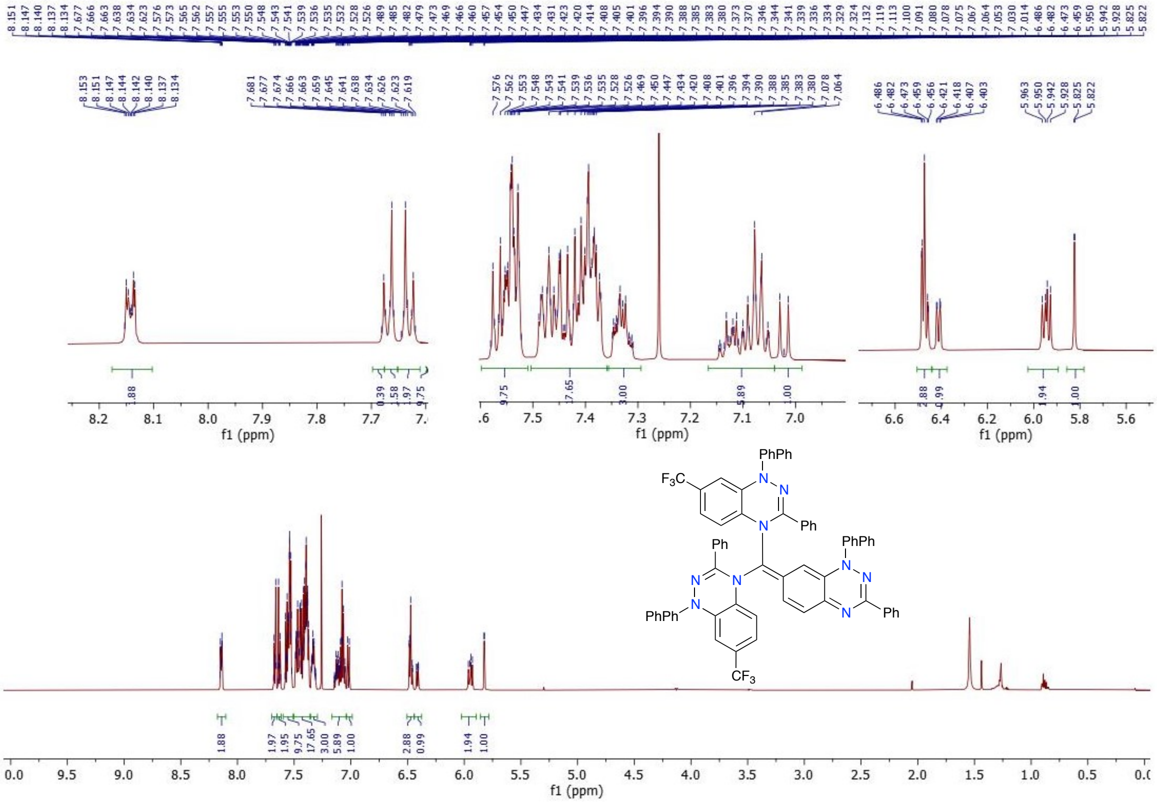


**Figure S9.** $^{1}$H NMR (600 MHz, CDCl$_3$) spectrum of 'trimer' **3b**.

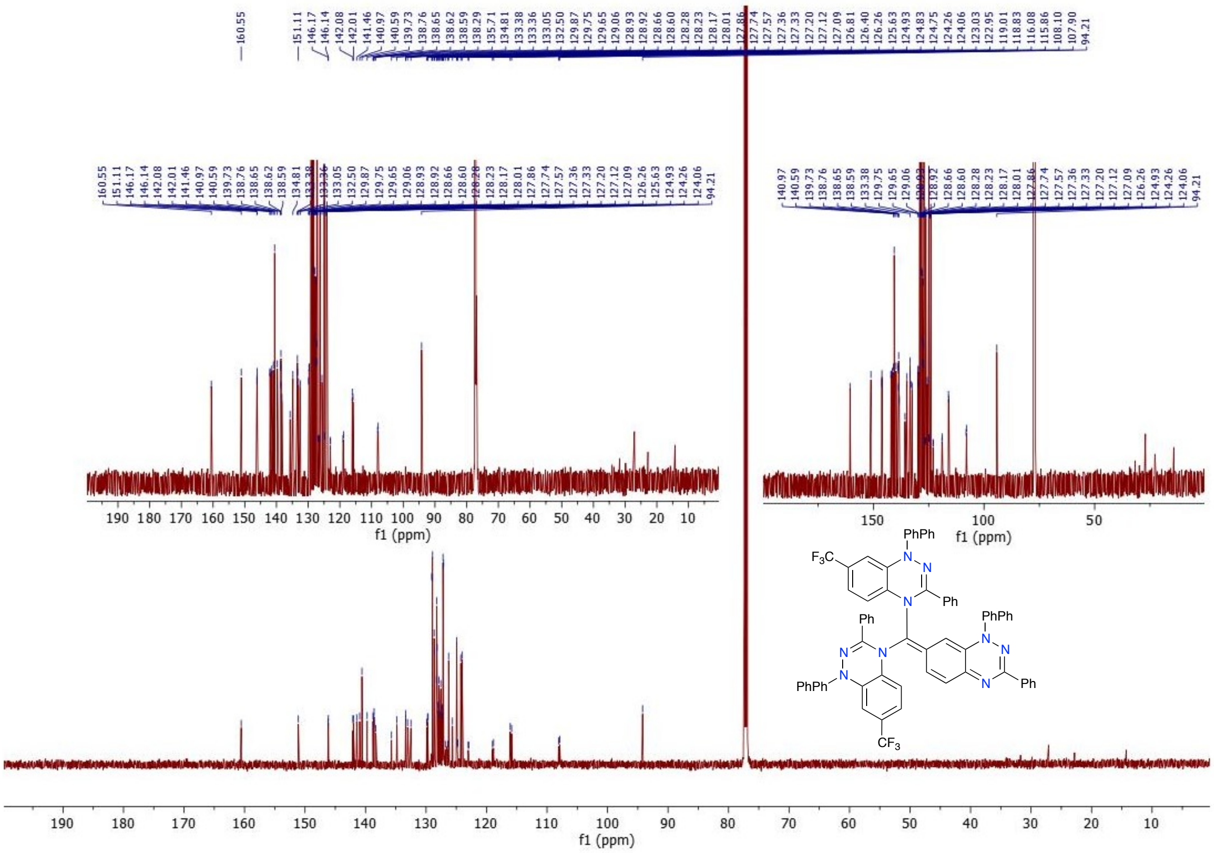


**Figure S10.** $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) spectrum of ‘trimer’ **3b**.

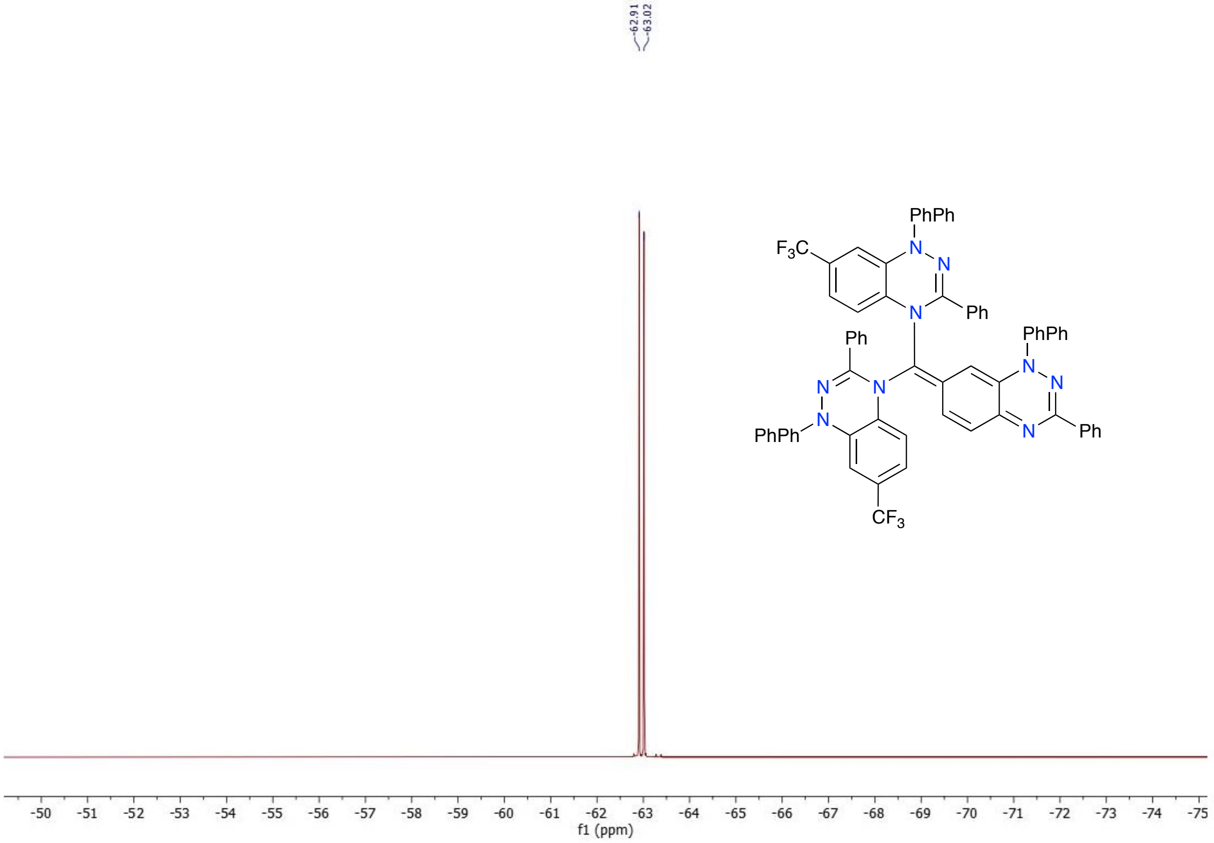


**Figure S11.** $^{19}F$ NMR (565 MHz, DMSO-$d_6$) spectrum of ‘trimer’ **3b**.

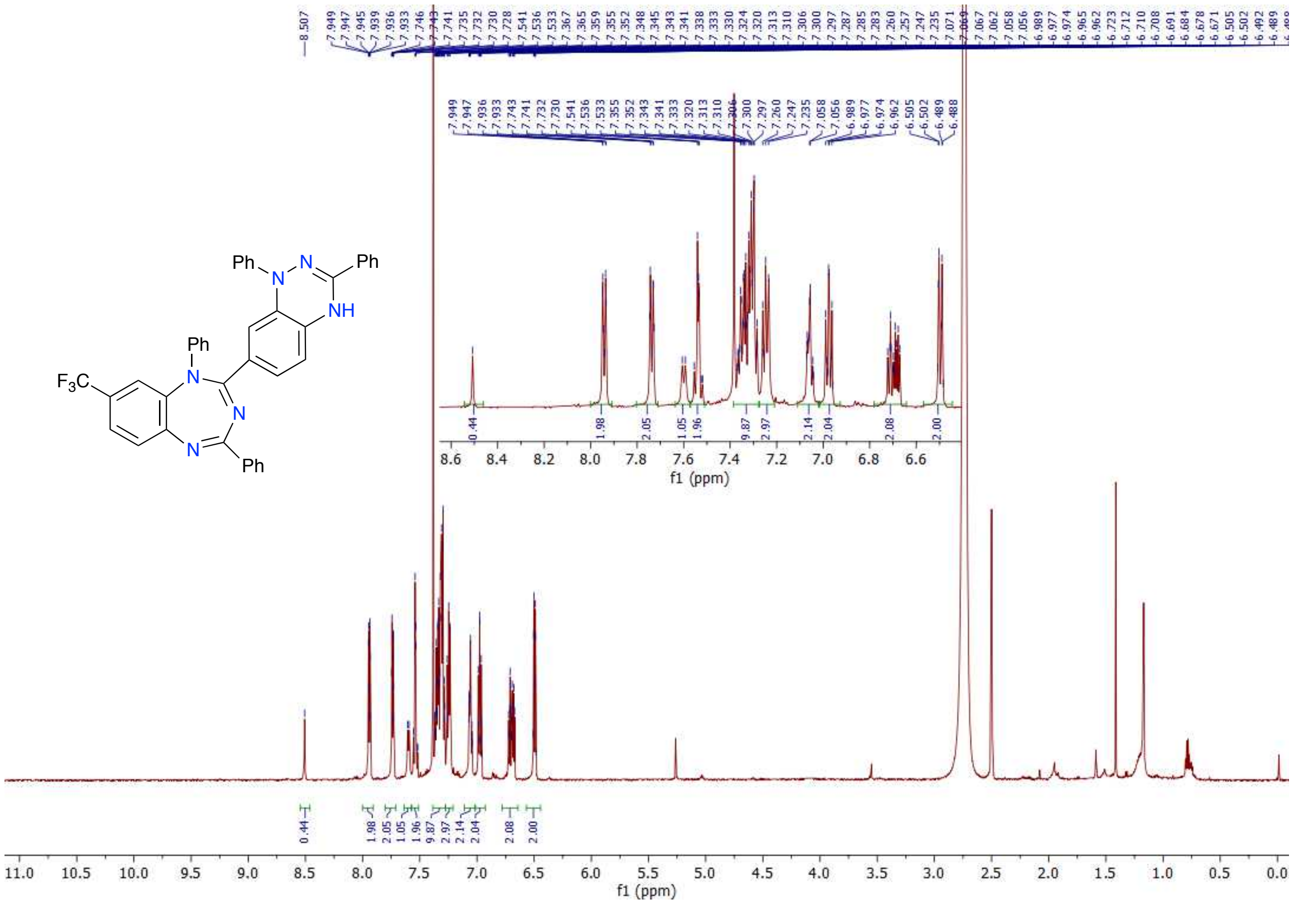


**Figure S12.** $^{1}$H NMR (600 MHz, DMSO-$d_6$/CDCl$_3$) spectrum of **4a-*leuco***.

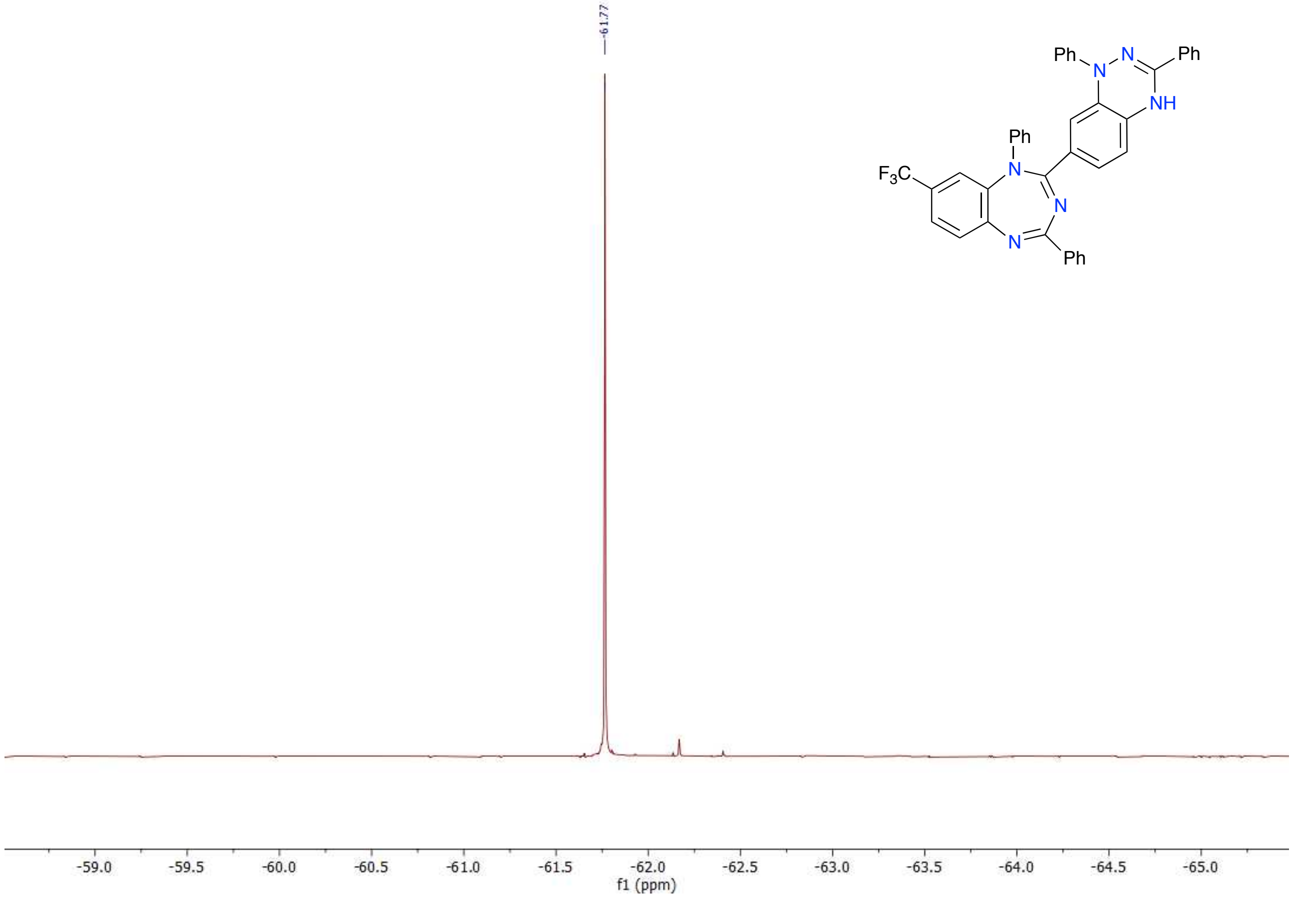


**Figure S13.** $^{19}$F NMR (565 MHz, DMSO-$d_6$/CDCl$_3$) spectrum of **4a-*leuco***.

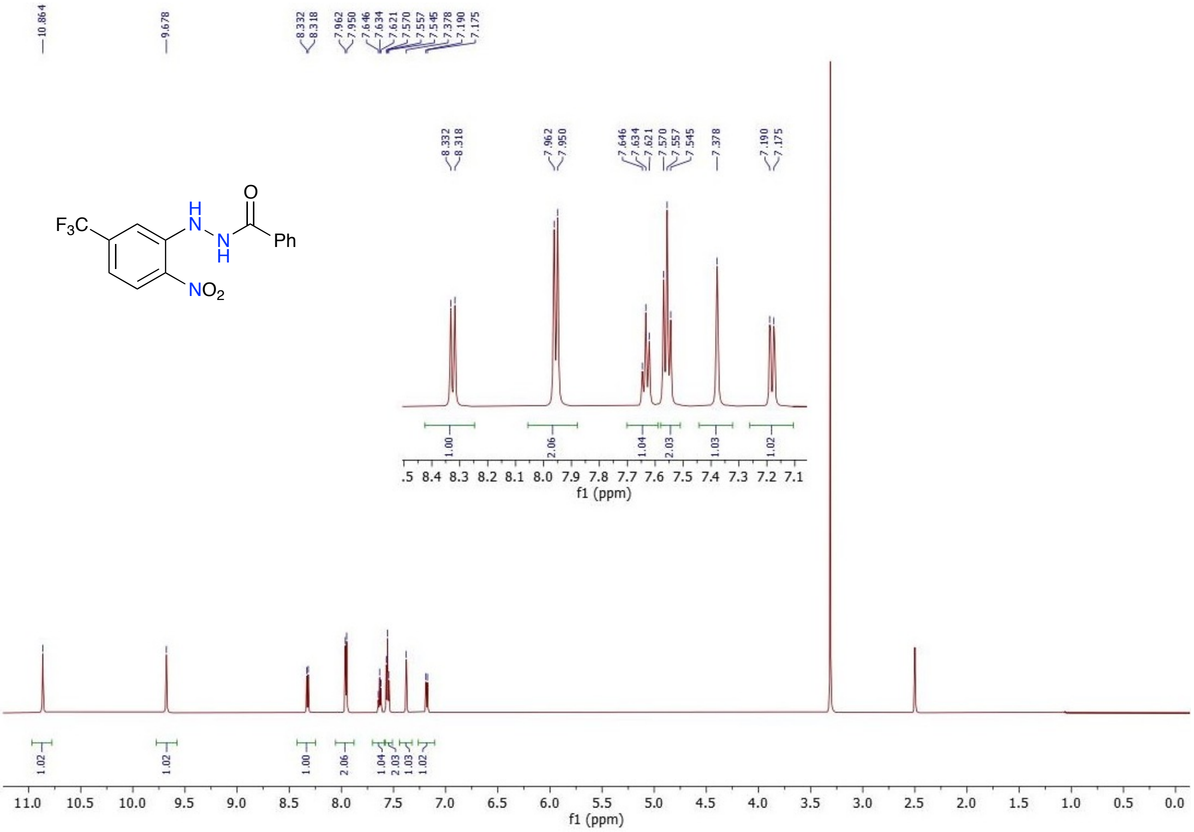


**Figure S14.** $^{1}$H NMR (600 MHz, DMSO-$d_6$) spectrum of *N'-2-[2-nitro-5-(trifluoromethyl)phenyl]benzhydrazide* (**6**).

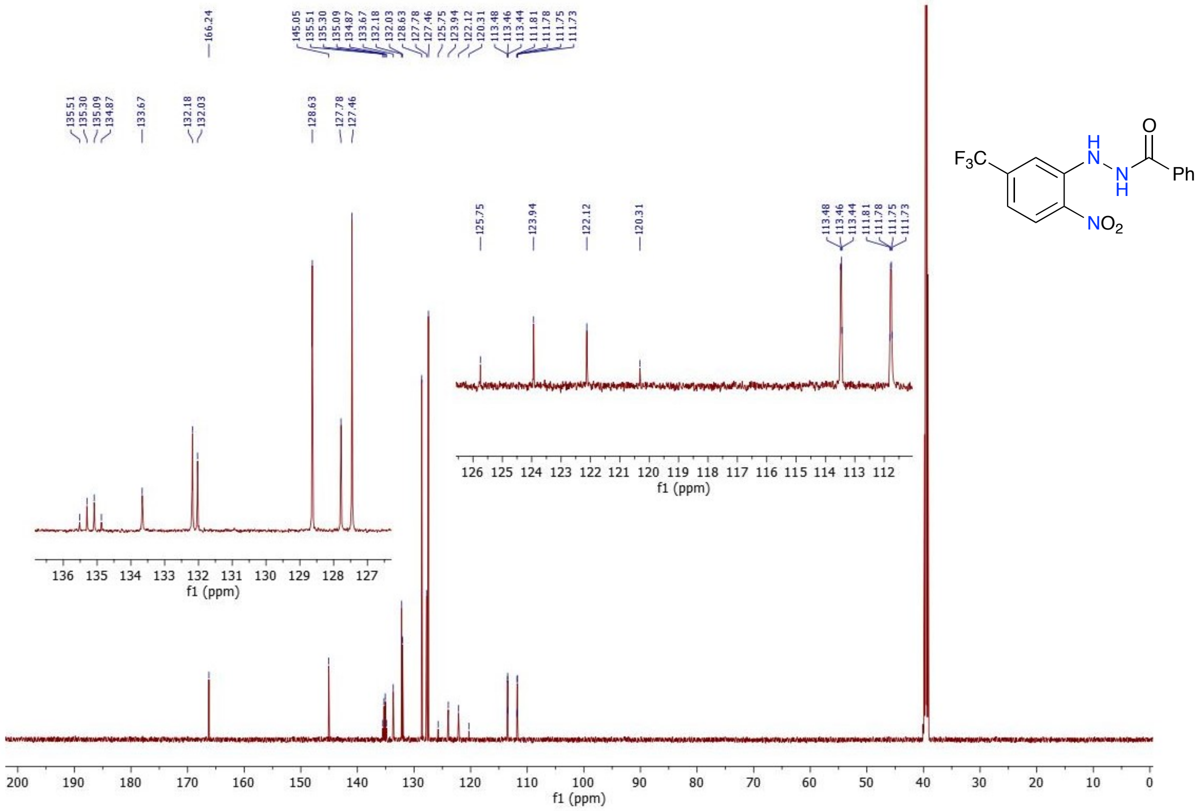


**Figure S15.** $^{13}$C NMR (600 MHz, DMSO-$d_6$) spectrum of *N'-2-[2-nitro-5-(trifluoromethyl)phenyl]benzhydrazide* (**6**).

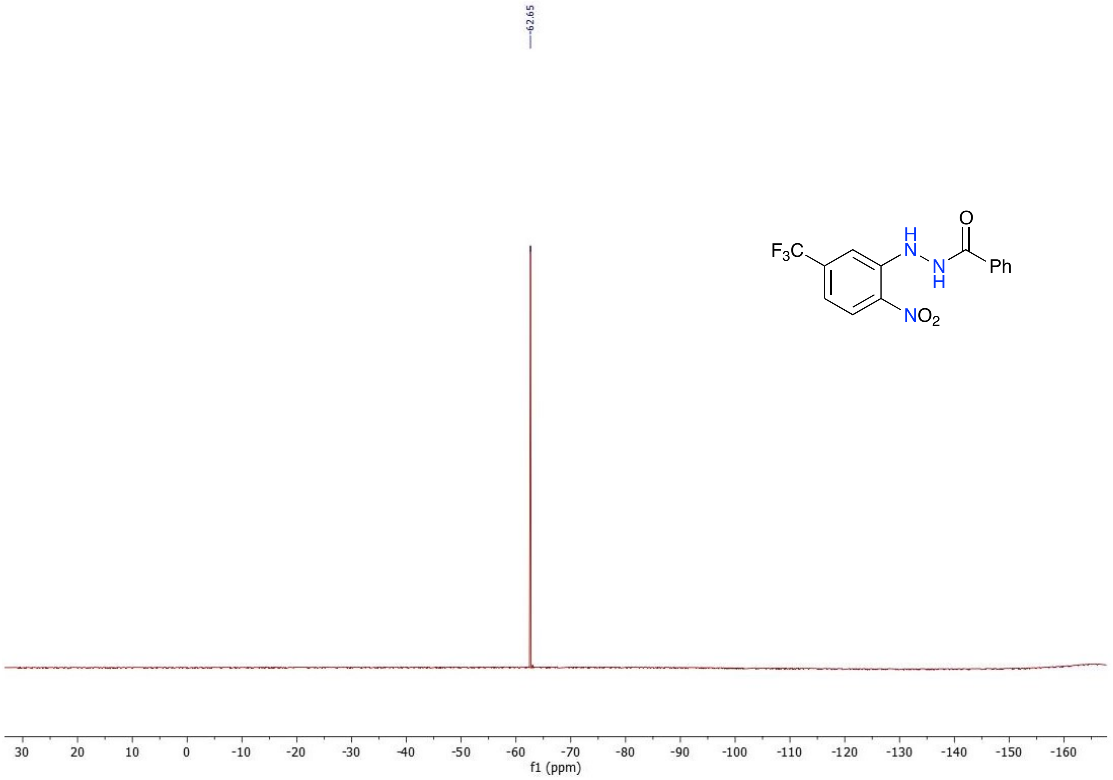


**Figure S16.** $^{19}$F NMR (600 MHz, DMSO-$d_6$) spectrum of *N'-2-[2-nitro-5-(trifluoromethyl)phenyl]benzhydrazide* (**6**).

## 5. Single crystal XRD data collection, refinement and results

### *Collection*

Single-crystal XRD measurements for **4a** were performed with a Rigaku XtalAB Synergy, Pilatus 300K diffractometer at 104(2) K using the Cu$K_\alpha$ radiation ($\lambda$ = 1.54184 Å). The data was integrated using CrysAlisPro program,[4] and intensities for absorption were corrected using multi-scan method as in SCALE3 ABSPACK scaling algorithm implemented in CrysAlisPro program.[4] The single crystal of **3a** was measured using Bruker-Nonius X8 Kappa APEX II diffractometer at 100.0(1) K using the Mo$K_\alpha$ radiation ($\lambda$ = 0.71073Å). The data were integrated using SAINT program,[5] while intensities for absorption were corrected using multi-scan method as in SADABS scaling algorithm.[6]

**Table S1. Selected structural data for 3a and 4a.**

| | **3a**<br>CCDC:<br>2169664 | **4a**<br>CCDC:<br>2238097 |
|---|---|---|
| Formula | $C_{60.5}H_{40}ClF_6N_9$ | $C_{40}H_{26}F_3N_6$ |
| Formula Weight | 1042.46 | 647.67 |
| Crystal System | monoclinic | triclinic |
| Space Group | *C*2/c | $P\bar{1}$ |
| *a* /Å | 14.4385(6) | 9.2476(6) |
| *b* /Å | 28.091(1) | 10.8175(8) |
| *c* /Å | 28.302(1) | 18.2214(10) |
| *α* /° | 90 | 101.258(5) |
| *β* /° | 104.453(2) | 93.429(5) |
| *γ* /° | 90 | 112.966(7) |
| Volume /Å$^3$ | 11115.6(8) | 1627.2(2) |
| Z | 8 | 2 |
| 2θ range for data coll. /° | 2.9 to 47.064 | 9.142 to 148.886 |
| Index ranges | $-16 \le h \le 16$,<br>$-29 \le k \le 31$,<br>$-31 \le l \le 31$ | $-11 \le h \le 11$,<br>$-13 \le k \le 12$,<br>$-22 \le l \le 22$ |
| No. of measured, independent, and obs. [$I>2\sigma(I)$] reflections | 123103, 8259, 6860 | 32475, 6446, 3928 |
| *R*int | 0.0440 | 0.1220 |
| Goodness-of-fit on $F^2$ | 1.068 | 1.093 |
| Final *R* indexes [$F^2 > 2\sigma(F^2)$] | $R_1$ =0.0887,<br>w$R_2$ = 0.2252 | *R1* =0.1384<br>*wR2* = 0.3917 |
| Final *R* indexes [all data] | $R_1$ =0.1046,<br>w$R_2$ = 0.2388 | $R_1$ =0.1842,<br>$wR_2$ = 0.4354 |
| Data/restraints/ parameters | 8259/867/870 | 6446/12/470 |
| Largest diff. peak/hole /Å$^{-3}$ | 0.39/-1.65 | 0.75/-0.56 |

### *Structure solution and refinement*

The structures were solved with the ShelXT[7] structure solution program using Intrinsic Phasing and refined in the ShelXle[8] by the full-matrix least-squares minimization on $F^2$ with the ShelXL[9] refinement package. All non-hydrogen atoms were refined anisotropically and C–H hydrogens were generated geometrically using the HFIX command as in ShelXL. Hydrogen atoms were refined isotropically and constrained to ride on their parent atoms. In **3a** and **4a** disordered $CF_3$ groups were identified. Sums of occupancies of relevant sites were set equal to 1 and refined using free variables. PART instruction was applied to exclude bonding between equivalent disordered atoms. Constraints and restraints such as EADP, SADI, DFIX, DANG, RIGU, and SIMU were used to aid disorders modeling. The $CF_3$ group in **3a** and **4a** was refined over two sites with occupancy ratio 0.58(2):0.42(2) and 0.51(1):0.49(1). Additionally, three phenyl groups in **3a** are identified as disordered over two sides each. Relevant occupancy ratios for the disordered phenyl rings are 0.61(3):0.39(3), 0.55(2):0.45(2) and 0.82(2):0.18(2).

Psuedomerohedral twinning in **3a** was detected using TWINROTMAT in PLATON.[10] Twin Law: -1 0 0 0 -1 0 1 0 1 resulted in a very low BASF value, *ca*. 1%. Visual observations suggested desolvation of the sample, which are corroborated by large voids in structure that carry random, diffuse electron density. One $CH_2Cl_2$ molecule can be located in the difference map, but refined poorly. SQUEEZE was used to calculate the remaining solvent accessible voids in the structure and to estimate the electron count in that space. A void volume of 1519 $Å^3$ and electron count of 389 is consistent with approximately 8 $CH_2Cl_2$ molecules in the void of the unit cell. The reported formula is an appropriate conclusion based on the analysis with SQUEEZE tool.[11] Similarly, a strongly disordered solvent molecule in **4a** was removed from the model using SQUEEZE procedure causing a discrepancy between the reported and the checkcif formula. In this structure, a void volume of 99 $Å^3$ and electron count of 23 is consistent with approximately one ethanol molecule per unit cell. Single-crystal XRD measurement for **4a** resulted in very weak intensities of recorded reflections. Therefore, the resolution of the measurement is low (*i.e.* > 0.9 Å). However, data is of sufficient quality for the structure confirmation and crystal packing discussion. The crystal data and structure refinement descriptors are presented in Table S1. Partial packing diagrams for **3a** and **4a** are shown in Figures S17–S19.

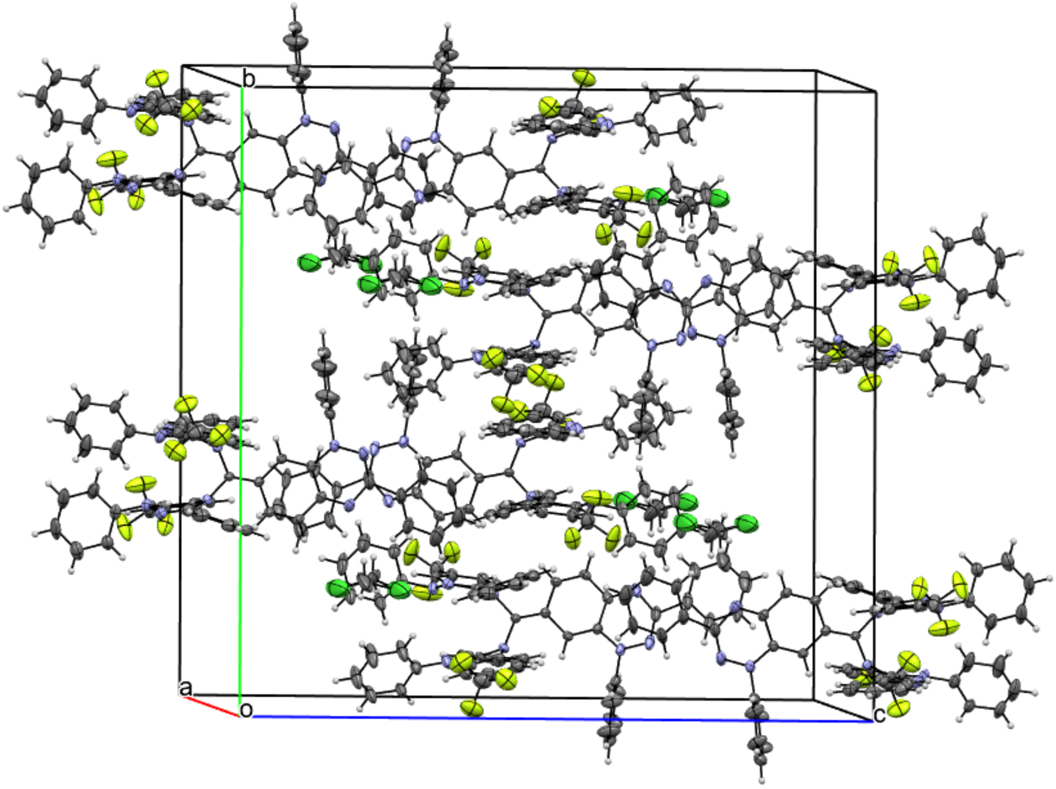


**Figure S17**. Unit cell packing diagram for **3a**. Color code: F-light green, N-blue, Cl-green.

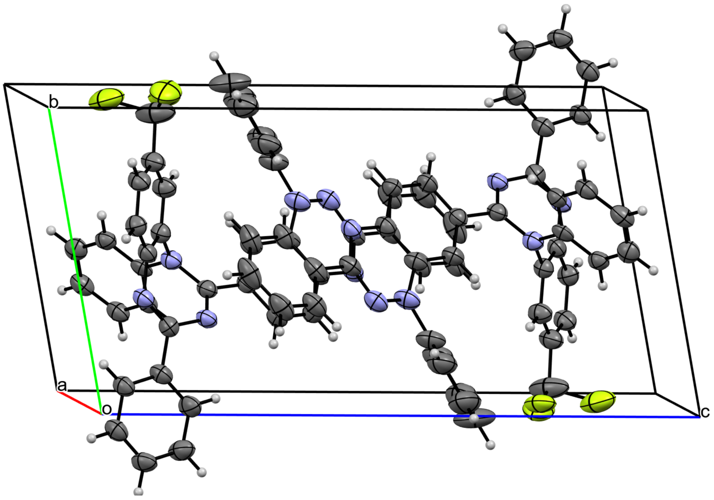


**Figure S18**. Unit cell packing diagram for **4a**. Color code: F-light green, N-blue.

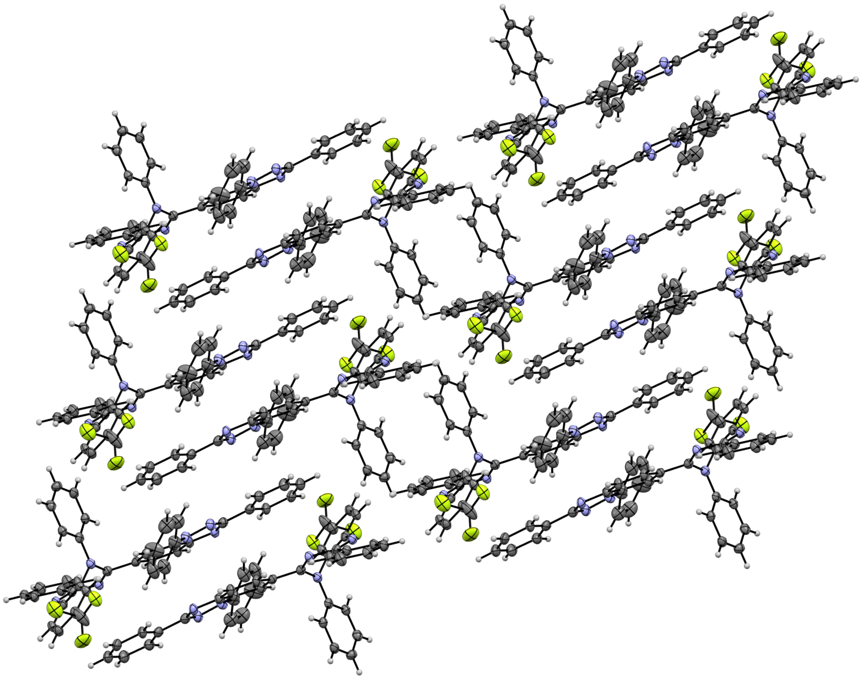


**Figure S19**. Slipped stacks of **4a**. Adjacent stacks are assembled parallel to each other. Color code: F-light green, N-blue.

Slippage angle - of 33.8° was calculated as an angle defined by C(3)$^{\cdots}$C(3)$^{\cdots}$C(8a) minus 90°. The two carbon atoms C(3) used for the measurements were for two molecules in the stack with same orientation.

***Results***

The structure of **3a** and **4a** was confirmed with low temperature single-crystal X–ray diffraction methods. Dark-green crystals of **3a** were grown from hexane/$CH_2Cl_2$ at 0 $^{o}$C, and **4a** was crystalized from a mixture of MeOH/EtOH at ambient temperature. "Trimer" **3a** crystallized in a monoclinic, C2/c space group, while derivative **4a** forms triclinic crystals with the *P*-1 space group. Results are shown in the main text Fig. 2 and also in Table S1.

Crystal structures of both compounds contain one molecule in the asymmetric unit, while the unit cell contains either 8 (**3a**) or 2 (**4a**) molecules. Both derivative exhibit rotational disorder of the $CF_3$ groups, which is refined over two sites with almost equal occupancy in the ratio 0.58(2):0.42(2) for **3a** and 0.51(2):0.49(2) for **4a**. In addition, "trimer" **3a** exhibits rotational disorder of three Ph groups. Each molecule of **3a** is associated with 0.5 molecule of $CH_2Cl_2$ disordered over two sites about the 2-fold axis. Moreover, the crystal structure of **3a** contains solvent accessible voids with the volume of 1519 Å$^3$ and electron count of 389, as determined by the SQUEEZE procedure. These parameters are consistent with approximately 8 molecules of $CH_2Cl_2$ in the void of the unit cell. In the structure of **4a**, the void and electron count are smaller, 99 Å$^3$ and 23 e$^-$, respectively, and are consistent with one molecule of EtOH per unit cell.

Compounds **3a** and **4a** represent unique structures. The quinoid form of the benzo[*e*][1,2,4]triazine ring in the former is approximately planar with a small bend/warp ring system up to about 10° and resembles that of the C(7)–dicyanomethyle derivative[12] with similar molecular dimensions. The methylene group is bonded to the C(7) position of the benzo[*e*][1,2,4]triazine (BT) with a distance of 1.359(6) Å, which is well reproduced by DFT calculations (1.385 Å). The two BT units are bonded to the C(7)–methylene carbon atom with their N(4) nitrogen atoms and distances of 1.437(6) and 1.442(5) Å (DFT: 1.418 and 1.419 Å). Both BT substituents are approximately parallel to each other with relative *anti* orientation, and both are orthogonal to the quinoid system. This tight molecular arrangement is helped with the puckered geometry of the 8-π electron [1,2,4]triazinyl system of the BT substituents. The experimental puckering angle, defined by an interplanar angle between the N(1)–N(2)–C(3)–N(4) and N(4)–C(4a)–C(8a)–N(1) planes is 23°, while the DFT calculated angle is 27.5°.

**Table S1**: Selected interatomic distances (Å) and angles (°) for investigated derivatives.[a]

| | **3a** [b] | | **4a** [c] |
|---|---|---|---|
| | quinoind [d] | BT [e] | |
| N(1)–N(2) | 1.357(5) | 1.374(6), 1.406(6) | 1.355(8) |
| N(2)–C(3) | 1.294(6) | 1.288(5), 1.285(6) | 1.336(9) |
| C(3)–N(4) | 1.385(6) | 1.434(6), 1.408(5) | 1.323(6) |
| N(4)–C(4a) | 1.316(6) | 1.426(6), 1.432(6) | 1.372(8) |
| C(4a)–C(8a) | 1.450(6) | 1.403(6), 1.397(6) | 1.412(9) |
| C(8a)–N(1) | 1.386(5) | 1.412(7), 1.395(5) | 1.385(6) |
| N(1)–$C_{Ar}$ | 1.442(5) | 1.429(7), 1.42(1) | 1.43(1) |
| C(3)–$C_{Ph}$ | 1.50(3) | 1.467(6), 1.489(7) | 1.494(9) |
| C(7)–X | – | 1.483(8), 1.489(8) | 1.487(8) |
| N(1)–N(2)–C(3) | 117.0(4) | 118.7(4), 116.7(4) | 115.3(6) |
| N(1)Ar···BT [f] | 89.42 | 55.95, 83.65 | 47 |
| C(3)Ph···BT [g] | 14.72 | 19.19, 25.11 | 9.3 |

[a] Numbering according to chemical structures. [b] Distances for main disorder components. [c] Parameters for the benzo[*e*][1,2,4]triazinyl fragment. Benzo[*f*][1,3,5]triazepine ring is described in Fig. 5. [d] Dimenstion of the quinoid benzo[*e*][1,2,4]triazine fragment. [e] Dimenstion of the benzo[*e*][1,2,4]triazin-4-yl (BT) fragment. [f] Angle between planes of the N(1) aryl ring (Ar) and the benzo[*e*][1,2,4]triazine (BT) defined by all non-hydrogen atoms. [g] Angle between planes of the C(3) phenyl ring (Ph) and the benzo[*e*][1,2,4]triazine (BT) defined by all non-hydrogen atoms.

The structure of the "pink" radical **4a** consists of two fragments: a benzo[*e*][1,2,4]triazinyl radical and the connected at the C(7) position benzo[*f*][1,3,5]triazepin-2-yl system. While the geometry of Blatter radical fragment is typical,[13] the latter has only one experimentally known close analogue.[14] Analysis of the [1,3,5]triazepine ring geometry indicates that the double bonds are localized, the ring is puckered by 61° along the N(1)···N(5) line to avoid conjugation of 8 p electrons, and the N(2)–Ph group is in the axial position, while the NC(4)–Ph group is nearly coplanar to the N(3)–C(4)–N(5) fragment (9.3°, Fig. 5). Similar features and interatomic distances are found in the previously reported close analogue in which the puckering angle is 48° and the interplanar angle between NC(4)–Ph and N(3)–C(4)–N(5) is 13.7°.[14]

## 6. Electronic absorption spectroscopy

Electronic absorption spectra for radicals **1a**, green "trimer" **3a** and "pink" radical **4a** were recorded in spectroscopic grade $CH_2Cl_2$ at concentrations in a range 1.5–10× $10^{-5}$ M and fitted to the Beer–Lambert law. Results are shown in Figures S20–S22.

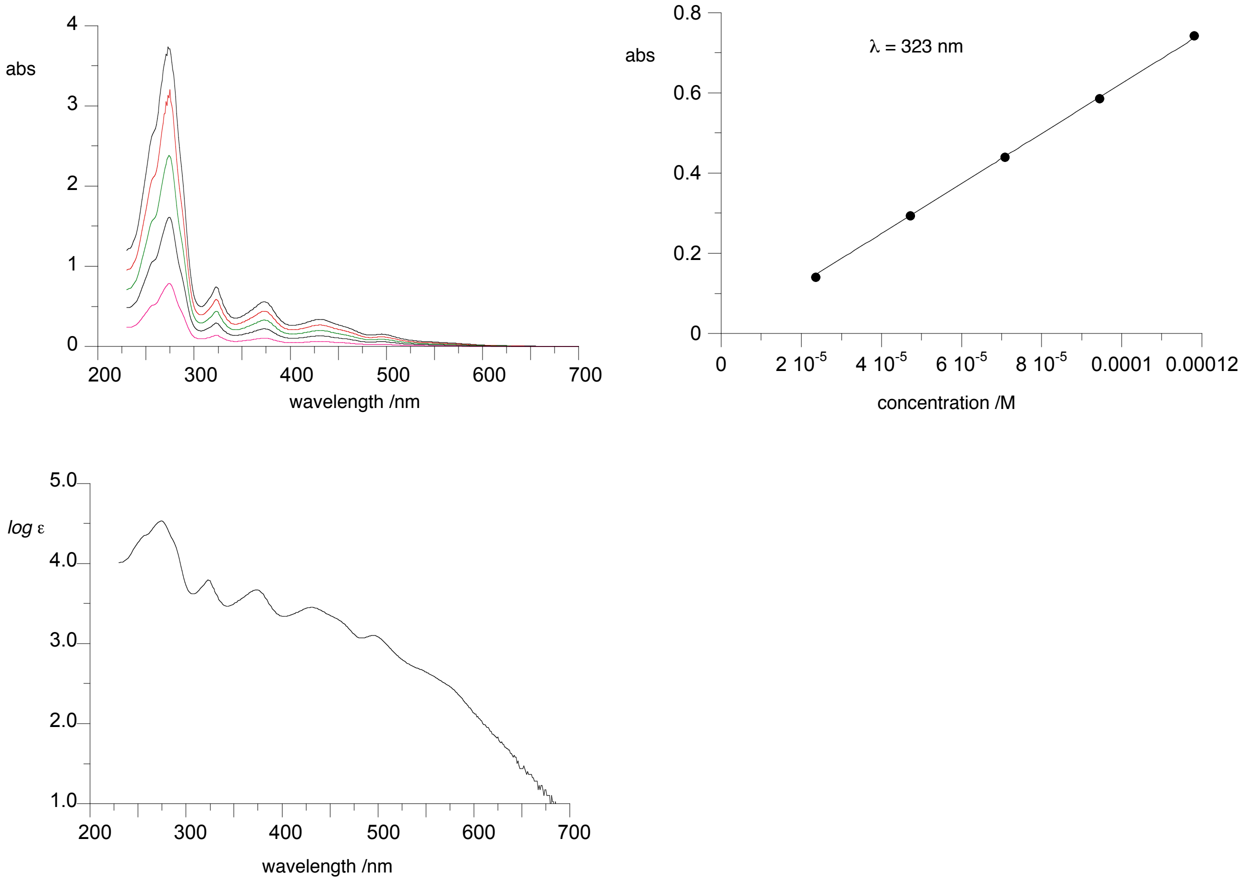


**Figure S20**. Clockwise: electronic absorption spectra for **1a** in $CH_2Cl_2$ for four concentrations, determination of molar extinction coefficient ε at λ = 323 nm (best fit function: ε = 6238(28)×conc, $r^2$ = 0.9996), and molar extinction *log* (ε) plot.

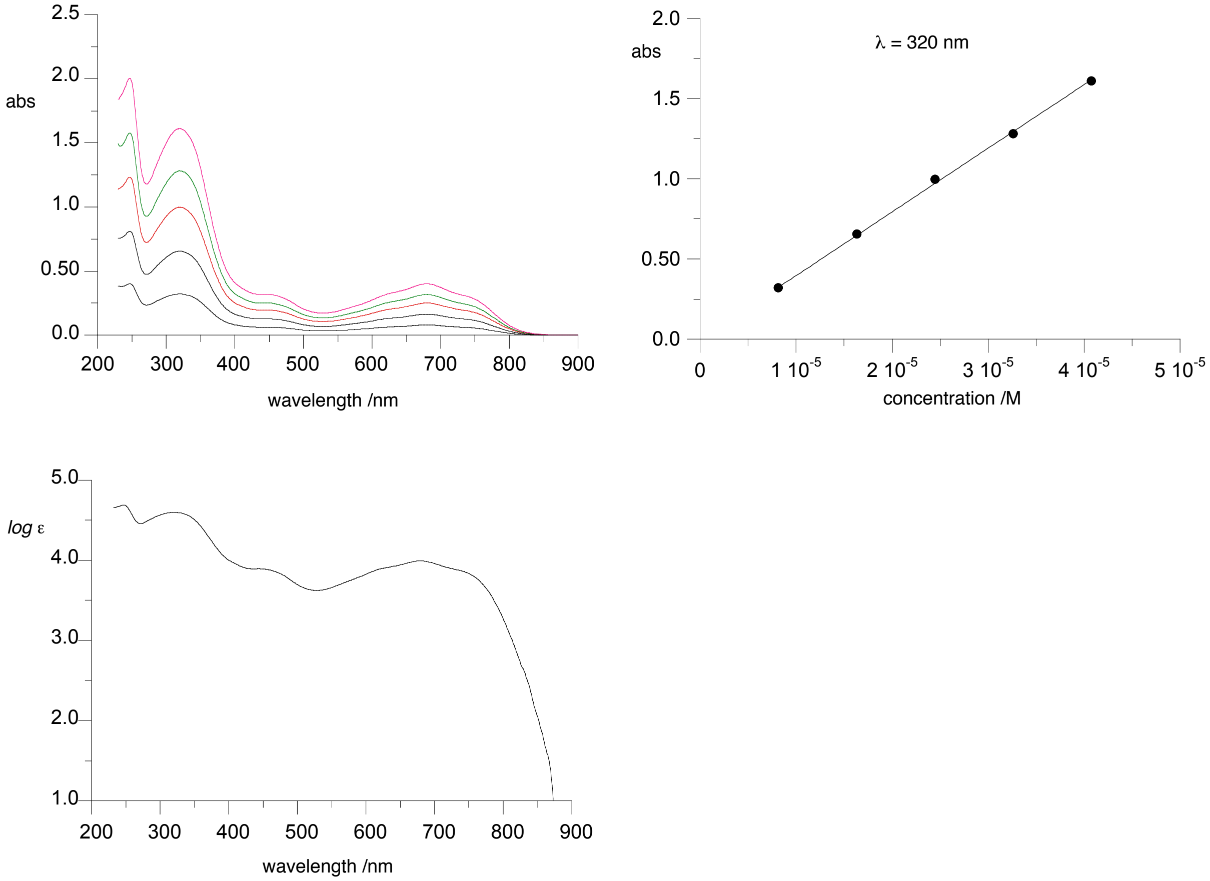
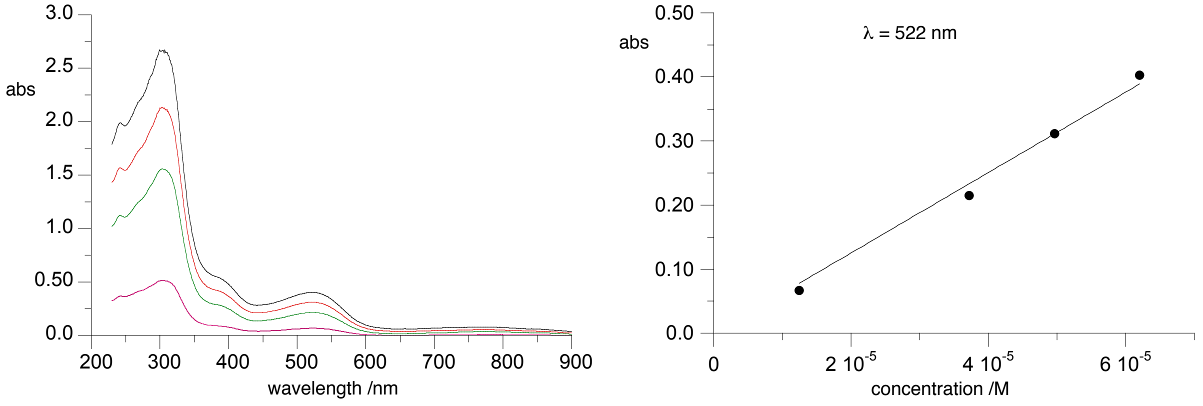


**Figure S21**. Clockwise: electronic absorption spectra for **3a** in $CH_2Cl_2$ for four concentrations, determination of molar extinction coefficient ε at λ = 323 nm (best fit function: $\varepsilon = 39688(263)\times\text{conc}$, $r^2 = 0.9990$), and molar extinction *log* (ε) plot.



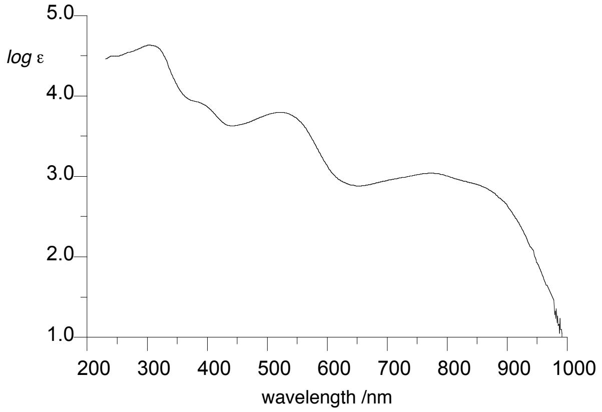


**Figure S22**. Clockwise: electronic absorption spectra for **4a** in $CH_2Cl_2$ for four concentrations, determination of molar extinction coefficient ε at λ = 522 nm (best fit function: ε = 6270(168)×conc, $r^2$ = 0.989), and molar extinction *log* (ε) plot.

## 7. EPR spectroscopy

EPR spectra for radicals **1** were recorded on an X-band EMX-Nano EPR spectrometer at *ca*. 20 °C using dilute and degassed solutions in distilled benzene in a concentration range of 2–5×$10^{-4}$ M. The microwave power was set with the Power Sweep program below the saturation of the signal, modulation frequency of 100 kHz, modulation amplitude of 0.5 $G_{pp}$ and spectral width of 100 G. Accurate g-values were obtained using TEMPO as EMX-Nano internal standard. Simulations of the spectra were performed with *Easy Spin* (Matlab) using DFT results (*vide infra*) as the starting point including all nitrogen atoms and up to 10 different hydrogen atoms. The resulting *hfcc* values were perturbed several times until a global minimum for the fit was achieved. Experimental and simulated spectra are shown in Figures S23 and S24 and resulting *hfcc* are listed in Table S2.

EPR spectrum of the "pink" radical **4a** is shown in Figure S25.

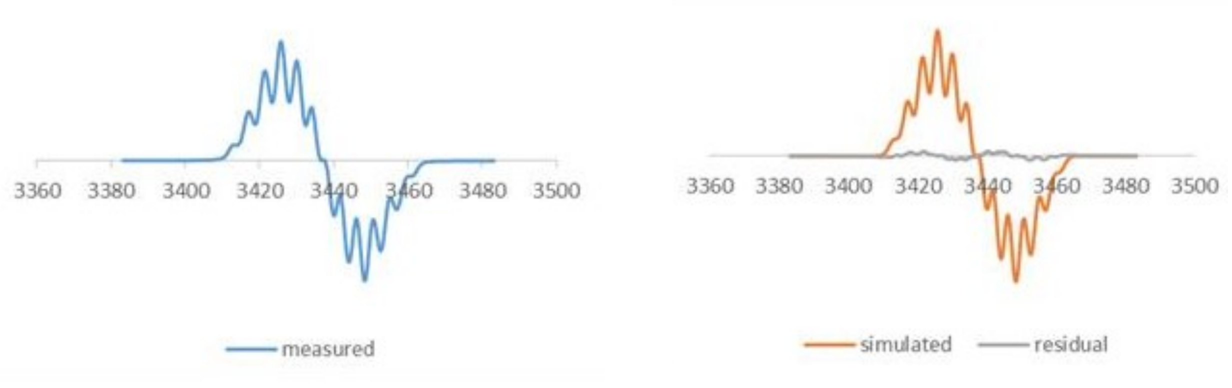


**Figure S23**. Experimental (blue, left), simulated (orange, right) and difference (grey, right) spectra for **1a** recorded in benzene at *ca* 20 °C.

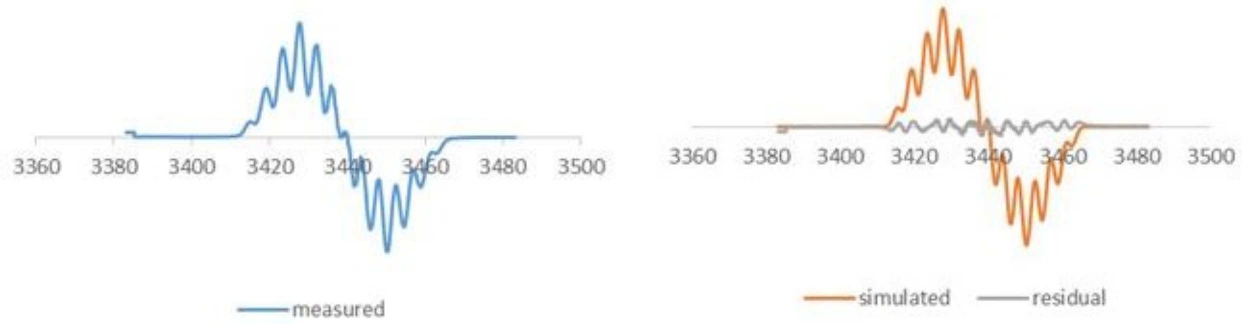


**Figure S24**. Experimental (blue, left), simulated (orange, right) and difference (grey, right) spectra for **1b** recorded in benzene at *ca* 20 °C.

**Table S2**. Experimental hyperfine coupling constants (G) and *g* values for radicals in series **1** recorded in benzene at 22 °C.[a]

| *hfcc* /G | **1a** | **1b** |
|---|---|---|
| $a_{N(1)}$ | 7.58 | 7.56 |
| $a_{N(2)}$ | 4.77 | 4.84 |
| $a_{N(4)}$ | 4.87 | 4.93 |
| 3×$a_F$ | 3.49 | 3.21 |
| $a_H$ | 1.01 | 1.10 |
| $a_H$ | 1.01 | 1.02 |
| $a_H$ | 0.96 | 1.02 |
| $a_H$ | 0.90 | 0.60 |
| $a_H$ | 0.06 | – |
| $a_H$ | – | – |
| $a_H$ | 0.43(×2) | 0.84(×2) |
| $a_H$ | 0.32(×2) | 0.61(×2) |
| 2×$a_H$ | 0.18 | 0.53 |
| 2×$a_H$ | 0.11 | 0.29 |
| 3×$a_F$ | – | – |
| *g* | 2.0034 | 2.0023 |

[a] Assignment of *hfcc* to N and F atoms is based on DFT results (*vide infra*)

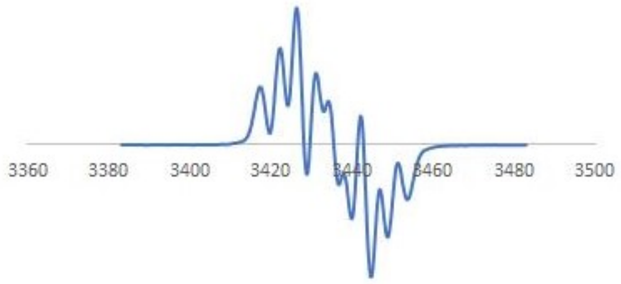


**Figure S25**. Experimental spectrum for **4a** recorded in benzene at *ca* 20 °C.

## 8. DFT-optimized molecular geometries.

Quantum-mechanical calculations were carried out using Gaussian 09 suite of programs.[1] Geometry optimizations were undertaken at the (U)B3LYP/6-31G(2d,p) level of theory using tight convergence limits and no symmetry constraints. The resulting equilibrium geometries for selected compounds are shown in Figures S26–S28.

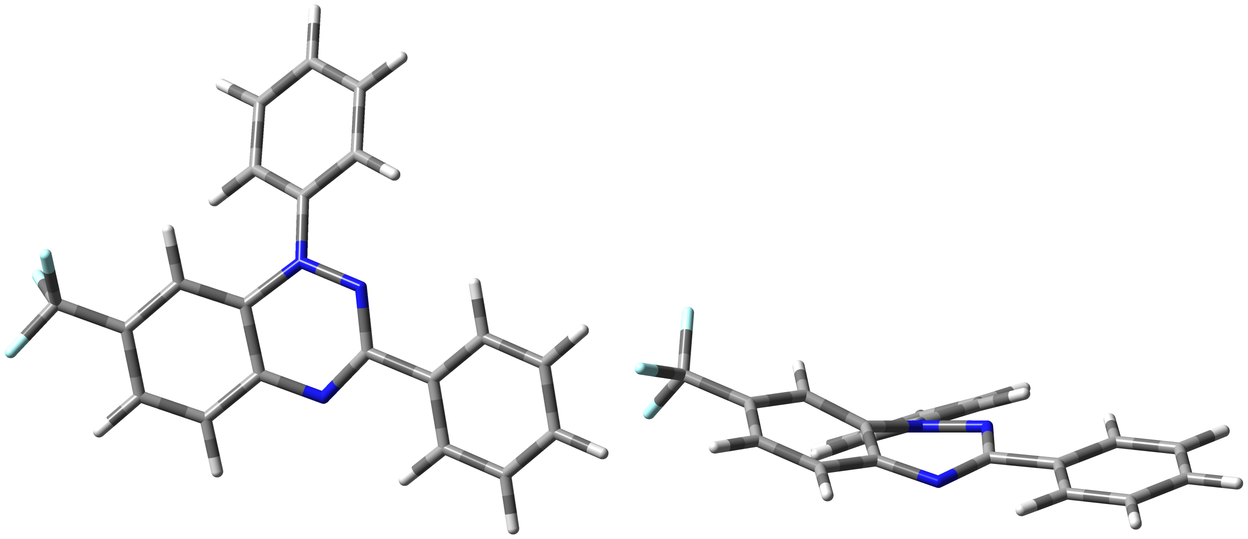


**Figure S26**. Two views of equilibrium geometry of anion $\mathbf{1a}^{-}$ at the B3LYP/6-31G(2d,p) level of theory.

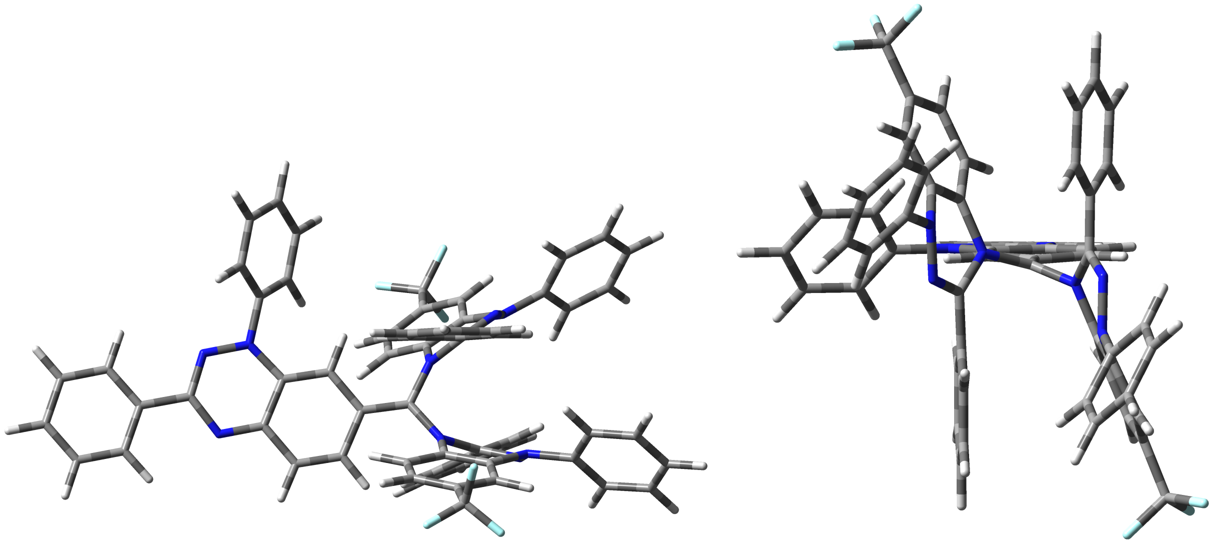


**Figure S27**. Two views of equilibrium geometry of “trimer” **3a** at the B3LYP/6-31G(2d,p) level of theory.

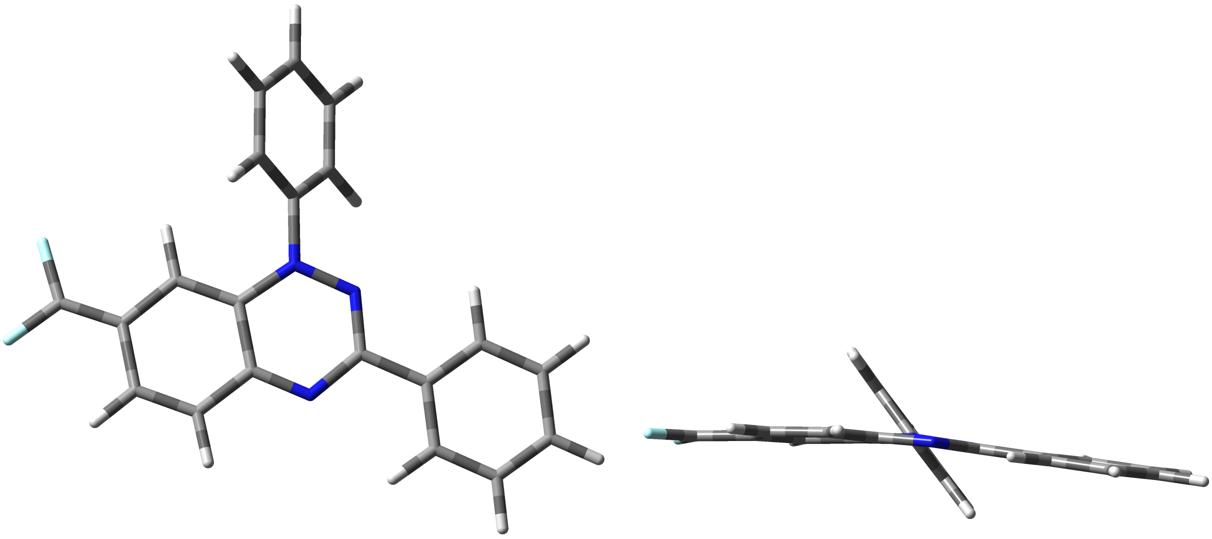


**Figure S28**. Two views of equilibrium geometry of Michael acceptor **7a** at the B3LYP/6-31G(2d,p) level of theory.

## 9. Archive for DFT calculations

**1a**

```
1\1\GINC-LOCALHOST\SP\UCAM-B3LYP\EPR-III\C20H13F3N3(2)\PIOTR\22-Sep-20
 22\0\\#P UCAM-B3LYP/EPR-III SCF=tight Geom(check, NoAngle, noDistance)
  #P SCRF(Solvent=Benzene) guess=check\\3-Ph-7-CF3-Benzotriazine C1\\0,
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 9211096494,-5.5742130032,0.240144177\H,0,-1.1061333184,-4.0211642539,0
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 9631\H,0,2.3592872943,-6.5632666043,0.3192649199\\Version=ES64L-G09Rev
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 .206e-09\Dipole=-0.030244,-0.8736846,0.6561394\Quadrupole=0.0101384,10
 .4050557,-10.415194,-3.9071117,1.685037,-3.0017171\PG=C01 [X(C20H13F3N
 3)]\\
```

**1a**$^-$

```
1\1\GINC-LOCALHOST\SP\RB3LYP\6-31+G(2d,p)\C20H13F3N3(1-)\PIOTR\15-Apr-
 2022\0\\#P B3LYP/6-31+G(2d,p) SCF=tight SCRF(Solvent=THF) #P Geom=(NoD
 istance,NoAngle) Pop=NBO geom=check guess=check\\1,3-Diphenyl 7-CF3-Be
 nzotriazinyl anion in THF\\-1,1\N,0,0.9720578748,-0.1077079747,0.16348
 3975\N,0,-0.3558341187,-0.5765592218,0.3286024365\C,0,-1.266530351 3,0.
```

```
 2752226831,-0.0788778404\N,0,-1.117395086,1.5560789745,-0.4876214877\C
 ,0,0.0984468989,2.0946627193,-0.1966018461\C,0,1.1923155163,1.28602865
 84,0.2453148541\C,0,2.3442490379,1.8731772569,0.7420459705\C,0,2.51897
 20537,3.2717191415,0.6755440092\C,0,1.5042112153,4.0659336892,0.147999
 6945\C,0,0.3102270883,3.486372431,-0.2666091983\C,0,-2.67066225,-0.237
 6404255,-0.0404428793\C,0,-2.9650974712,-1.55417116,0.3402769941\C,0,-
 4.2795569618,-2.0093413653,0.3685071782\C,0,-5.3280985331,-1.160283404
 8,0.0098564083\C,0,-5.0445288934,0.1490200377,-0.3750897281\C,0,-3.728
 9955066,0.6072252781,-0.3969937566\C,0,1.9418702114,-1.0822163378,0.00
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 3.4281768198,0.11477572\C,0,3.873695728,-3.1350049393,-0.3626734608\C,
 0,4.1700831998,-1.8056206888,-0.6692989799\C,0,3.234821601,-0.79489525
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 3878901\H,0,-3.4823197467,1.6218534888,-0.6852269802\H,0,-5.8525119809
 ,0.8193328074,-0.6568691858\H,0,-6.3541794678,-1.5175171433,0.02983060
 42\H,0,-4.4879616834,-3.0327991915,0.6691893996\H,0,-2.1442153336,-2.2
 06494294,0.611872905\H,0,3.4922913789,0.219343223,-0.7650098445\H,0,5.
 1488350465,-1.5440852298,-1.0639372624\H,0,4.613821748,-3.9173211417,-
 0.497391254\H,0,2.3297969379,-4.4551300513,0.3551206142\H,0,0.65191007
 14,-2.6722134762,0.6542076418\C,0,3.8136179168,3.8633389649,1.09510336
 85\F,0,4.3158391909,3.2850537264,2.2156874427\F,0,4.8024973409,3.73429
 20946,0.1623528103\F,0,3.727092532,5.1910335139,1.347394131\\Version=E
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 96968,-0.5860748,0.0535588\Quadrupole=-5.9061561,-0.0296162,5.9357723,
 -7.0816952,-4.8510177,-4.6350171\PG=C01 [X(C20H13F3N3)]\\
```

**1c**

```
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 22\0\\#P UCAM-B3LYP/EPR-III SCF=tight Geom(check, NoAngle, noDistance)
  #P SCRF(Solvent=Benzene) guess=check\\3-Ph-7-CF3-1-(2CF3Ph)-Benzotria
 zinyl\\0,2\C,0,-2.075075267,-0.6172905124,-0.0441435731\C,0,-0.0097936
 503,-1.6250130229,-0.0303277338\C,0,0.6182397478,-0.350629387 7,-0.0628
 669232\C,0,0.8101321743,-2.7686276709,-0.0038828663\C,0,2.009357586,-0
 .2337408004,-0.0697040113\C,0,2.7862326699,-1.3868272608,-0.0350859362
 \C,0,2.1886878852,-2.654307718,-0.0054608445\C,0,-3.5557696387,-0.7228
 21845,-0.0325863069\C,0,-4.1615134615,-1.9831326841,0.0485610855\C,0,-
 4.3643617143,0.4200773336,-0.1028162862\C,0,-5.5477965996,-2.097108692
 ,0.0617402283\C,0,-5.7496651556,0.3014769503,-0.0897871576\C,0,-6.3463
 643187,-0.9564535701,-0.0067880977\N,0,-0.2358823115,0.742184885,-0.09
 0889153\N,0,-1.5888025491,0.6287831759,-0.0608845356\N,0,-1.3681932509
 ,-1.7524779918,-0.028574339\H,0,0.3212212964,-3.7355862072,0.014077443
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 741903,0.008572062\H,0,-3.5292774917,-2.8606308793,0.1000844011\H,0,-3
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 0.1254550778\H,0,-6.3656859597,1.1932357517,-0.1463468139\H,0,-7.42798
 38928,-1.0466446429,0.0029614791\C,0,4.2834682347,-1.2683960115,0.0229
 24502\F,0,4.7211623889,-0.1261664817,-0.5386875774\F,0,4.8903753604,-2
 .2912996076,-0.6056387221\F,0,4.7361252315,-1.273049243,1.295643856\C,
 0,0.2445744474,2.0947582849,-0.0546618182\C,0,0.4863086151,2.682222007
 4,1.182727138\C,0,0.4511286112,2.8222785379,-1.2342794559\C,0,0.935451
 7018,3.9989550744,1.2560106362\C,0,0.8988537284,4.1390685962,-1.151804
 0037\C,0,1.1412610305,4.7262459205,0.0879083244\H,0,0.3121747203,2.100
 9052118,2.0809463094\H,0,1.120514788,4.4515868542,2.2240332614\H,0,1.0
 567829307,4.699175572,-2.0643286075\H,0,1.4906468888,5.7516800315,0.13
 6627791\C,0,0.1936089068,2.2008915949,-2.5878490962\F,0,0.9358876877,1
 .0909445687,-2.7698681855\F,0,0.4984729941,3.0489938572,-3.584367583\F
 ,0,-1.0914222392,1.8477908168,-2.7417195443\\Version=ES64L-G09RevD.01\
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 e-09\Dipole=-0.2255751,1.4313684,0.9447215\Quadrupole=-8.9934092,15.31
 55851,-6.322176,6.2260898,-0.1725702,4.0323666\PG=C01 [X(C21H12F6N3)]\
```

**3a**

```
1\1\GINC-LOCALHOST\FOpt\RB3LYP\6-31G(2d,p)\C60H39F6N9\PIOTR\18-Apr-202
 2\0\\#P B3LYP/6-31G(2d,p) FOpt SCF=Direct Geom=(NoDistance,NoAngle) fc
```

```
heck\\3-Ph-7-CF3-Benzotriazine-trimer\\0,1\C,-6.4357435654,-0.70172333
42,-0.511941611\C,-4.2724071954,-0.8794986242,-1.2402388984\C,-3.80037
21794,-0.1231352155,-0.0882878664\C,-3.2778953823,-1.3577610264,-2.164
4657065\C,-2.4603937449,0.0648926457,0.1298900341\C,-1.4662315237,-0.4
582616921,-0.7767326215\C,-1.9560591246,-1.1677220329,-1.9382388354\C,
-7.8606206986,-1.0426507801,-0.7204382769\C,-8.2393833921,-1.819909887
7,-1.822664761\C,-8.8492537137,-0.5993303915,0.1710469171\C,-9.5769824
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962869\C,-10.5527167379,-1.7050535074,-1.1373200823\N,-4.8265921861,0.
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.5354941037,-1.1492009901,-1.4540762202\H,-3.6400613181,-1.8828466455,
-3.0406271633\H,-2.1267348328,0.6105754396,1.0001476241\H,-1.232908202
9,-1.5478518621,-2.6504011677\H,-7.4748027396,-2.1591138587,-2.5099278
496\H,-8.5581934973,0.0057882446,1.0210787365\H,-9.855939877,-2.750946
0051,-2.8851883808\H,-10.9372034919,-0.5783826136,0.659176557\H,-11.59
52082524,-1.9604575326,-1.2980248029\C,-4.5986254338,1.0996552708,1.92
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68651975\H,-3.4346780726,2.6264487171,0.9462965372\C,-4.2355366812,2.5
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66917\C,-0.1066060643,-0.2818692055,-0.5787094692\C,1.0424182137,-2.49
17275646,-0.9751243904\C,1.9720672291,-0.4544665552,-1.8588023509\C,-0
.010736819,-3.3856991289,-0.8179369992\C,2.3687011739,-2.9683580954,-0
.8995336432\C,0.2270831907,-4.7393492236,-0.5820431323\H,-1.0300301054
,-3.0340356584,-0.8517572792\C,2.6006150216,-4.3315980916,-0.723314374
6\C,1.5314847783,-5.2088959971,-0.5458350086\H,-0.603814802,-5.4187421
228,-0.441167091\H,3.6136734964,-4.7078834884,-0.7055452718\C,0.237171
5722,2.1197315978,0.05991716\C,1.301790932,0.3737642368,1.3367431965\C
,-0.8577219037,2.673054779,-0.5969213358\C,1.2657893271,2.9691309136,0
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180359141,0.2872274726\N,2.2298069934,1.1580094744,1.7481657868\N,2.39
87544391,2.3629720575,1.0921926556\N,0.8727798189,-1.0874878263,-1.213
0213648\N,3.1714667117,-0.9050181293,-1.8026384635\N,3.4057133017,-2.0
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748638433,1.7467702734,-2.7117906931\C,0.6025749927,0.9334239042,-3.45
8218894\C,2.5961281625,2.8760442202,-3.5073232279\H,3.637824204,1.6092
945708,-2.1083041867\C,0.454903856,2.0647849094,-4.2564964886\H,-0.168
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730217\H,3.3758263404,3.6308005215,-3.52359074\H,-0.4374913094,2.17847
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63946,-0.9166042939,2.0538180281\C,-0.0818225578,-1.5068425055,2.30675
31949\C,2.3189736128,-1.5355496599,2.5532339709\C,-0.1650390626,-2.690
4402637,3.0366986262\H,-0.9911228029,-1.0372703432,1.955543653\C,2.230
6197323,-2.7169227193,3.2792376231\H,3.2798734055,-1.0731459882,2.3630
02779\C,0.9873672785,-3.3030464006,3.5207408939\H,-1.1380200808,-3.130
562434,3.2292689897\H,3.1345480089,-3.1829058667,3.6585101838\H,0.9198
11454,-4.2289612224,4.0821184678\C,3.5470685865,3.0953540827,1.5009353
05\C,4.2069279069,3.9151188041,0.5774789551\C,4.0578765168,2.962453250
7,2.7954896076\C,5.3485613808,4.6137303597,0.9575078323\H,3.8285021931
,3.9917510599,-0.4354976678\C,5.2089830109,3.6550021297,3.1599279966\H
,3.5543513342,2.3088850648,3.4955784218\C,5.8566424499,4.4879650841,2.
2495625079\H,5.8503435691,5.2465865567,0.2326918577\H,5.5967588705,3.5
45334333,4.1677181011\H,6.7512358973,5.0277980562,2.5406941882\C,4.781
7345713,-2.3682242067,-0.9042252026\C,5.2343590029,-2.9670503291,0.276
8596619\C,5.6929956436,-2.0628043918,-1.9190544539\C,6.5821791584,-3.2
794952794,0.4263817786\H,4.5298844778,-3.1738691284,1.074309716\C,7.04
10828608,-2.3669052879,-1.7525451864\H,5.3367707776,-1.5797291804,-2.8
19481358\C,7.4927610649,-2.9811135712,-0.5858825685\H,6.9213935751,-3.
7444990406,1.3463501594\H,7.7409337935,-2.126482791,-2.546496834\H,8.5
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 288251\Quadrupole=13.836159,-26.7489211,12.9127621,8.0702388,-2.117311
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```

**7a**

```
1\1\GINC-LOCALHOST\SP\RB3LYP\6-31+G(2d,p)\C20H13F2N3\PIOTR\15-Apr-2022
 \0\\#P B3LYP/6-31+G(2d,p) SCF=tight Polar SCRF(Solvent=THF) #P Geom=(N
 oDistance,NoAngle) Pop=NBO geom=check guess=check\\3-Ph-7-CF2-Benzotri
 azine-chinoimine in THF\\0,1\C,0,1.8365907608,-0.5206995975,0.07828025
 74\C,0,-0.1467092133,-1.6662538495,0.1559469547\C,0,-0.8927167093,-0.4
 153561329,0.0467480782\C,0,-0.906182072,-2.8952046862,0.2106810525\C,0
 ,-2.2486344425,-0.4171531977,-0.0995385558\C,0,-2.9832431568,-1.664010
 0297,-0.0821937723\C,0,-2.2510134902,-2.8993468948,0.0934858314\C,0,3.
 3140526561,-0.5855197915,0.0281578695\C,0,3.9614705731,-1.82787392,0.0
 380874714\C,0,4.0889025488,0.5829679675,-0.0310917823\C,0,5.3512401326
 ,-1.8991150513,-0.0132248978\C,0,5.4747491974,0.506690727,-0.081009439
 8\C,0,6.1132192078,-0.7349909325,-0.0731290257\N,0,-0.0805014721,0.724
 2578672,0.0882393872\N,0,1.2784793052,0.6541075902,0.0320072307\N,0,1.
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 0.3264458069\H,0,-2.7982493727,0.5045864945,-0.2228221348\H,0,-2.80487
 58716,-3.8308803655,0.1222518402\H,0,3.3618718036,-2.7279527063,0.0867
 339024\H,0,3.5898926047,1.5444854023,-0.0338102062\H,0,5.8386723814,-2
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 01903\C,0,-2.0495255789,3.7576994814,0.9672699897\H,0,-1.9664617852,1.
 7340569233,1.6989876861\C,0,-1.5327928236,4.6833205816,0.0621502454\H,
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 092405\HyperPolar=3429.2028027,-2499.8429123,-283.2316985,387.5798199,
 88.1776643,-54.9543973,7.7411124,176.8770036,24.7049909,-19.9516845\Qu
 adrupole=-2.0370381,8.4153991,-6.3783611,-0.7350672,-4.0122003,-1.3477
 098\PG=C01 [X(C20H13F2N3)]\\
```

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