Supplementary Information

Click and shift: triazole effect on solvatochromic dyes

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1. General information

- **Synthesis, Purification, and Characterization**

Commercially available reagents and solvents were purchased and used as supplied. Reactions were monitored by analytical thin-layer chromatography (TLC) on a silica gel 60 F_{254}, Merck precoated silica gel plate, which were revealed by using a UV lamp. Flash-column chromatography was performed on Selekt flash chromatography systems (Biotage), using silica gel SNAP KP-Sil single-use column and solid deposition of the crude reaction.

NMR spectra were recorded at room temperature on a Bruker Avance NEO spectrometer, operating at 600 and 151 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts are reported as values (ppm) with reference to the peak of DMSO-d_6. Abbreviation for the ^{1}H NMR data are as follows: chemical shift δ, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants J.

High-resolution mass spectrometry measurements were performed with a Waters SYNAPT G2-Si mass spectrometer.

- **Optical spectroscopy**

Spectroscopic grade solvents were employed for all the photophysical studies. Methanol-d_4 (99 atom % D) was purchased at Sigma-Aldrich. Experiments were performed at room temperature with air-equilibrated optically diluted (absorption below 0.1, implying concentration equal to or below 10 µM) or 10 µM solutions using 1 cm pathlength quartz cuvettes.

Absorption spectra (UV–vis) were recorded with a Cary 50 UV-vis-NIR spectrophotometer.

Fluorescence spectra were performed on a Cary Eclipse fluorescence spectrophotometer. Fluorescence quantum yield in solution were referenced with **PRODAN** in 1,4-dioxane (φ_f = 0.75) for samples with 360 nm excitation, and in acetone (ϕ_f = 0.8) for samples with 380 nm excitation.[1] The quantum yield values were corrected for the refractive index of the solvent, according classical procedure.[2]

For the emission lifetime measurements, a pulsed laser diode having an excitation wavelength of 405 nm, connected to spectrofluorometer (FLS 1000, Edinburgh Instruments) was used. The instrument response function of these lifetime measurements had a FWHM of 130 ps.

Photostability measurements were made by recording fluorescence kinetics of sample in solution for 60 minutes, with a 365 nm LED as light source (P = 4.5 mW/cm^2).

- **Theoretical calculations**

Gaussian 16A03[3] was employed for calculations. The geometrical parameters for the ground (S_0) and the excited (S_1) states have been determined with the density functional level of theory (DFT), employing the mPW1PW91 functional[4] and the 6-31+G(d) basis set. DFT was performed both in vacuum and considering solvent effects by including the solvation model based on density (SMD). [5]The absolute nature of the energetic minima was established by the absence of a negative frequency in the vibrational analysis. Energy parameters were calculated only in vacuum as vertical electronic excitations from the S_0 minima structure using the linear response (LR) approach and the time-dependent density functional response theory (TD-DFT).[6] These calculations were carried out for the fifteen first excited states at the mPW1PW91/6-311+G(2d,p) level. The EDD representations have been done with Multiwfn 3.8dev.[7] Calculations were performed both in vacuum and considering solvent

effects (toluene, dichloromethane and acetonitrile) by means of the solvation model based on density (SMD). [5]

- **Two-photon absorption measurements**

Experiments were carried out on a Zeiss LSM 710 epi-fluorescence microscope equipped with an InSight DeepSee (Spectra-Physics) tunable wavelength laser system, delivering 100-ps pulses at 80 MHz. Excitation and emission light were transmitted through a Plan-Apochromat 10x/0.45, ∞/0.17 objective with a working distance of 2.0 mm and focused at the air/liquid boundary, allowing the simultaneous detection of sample and background fluorescence. Emission spectra were measured in a laser power regime where the fluorescence was proportional to the square of the laser excitation power and using a dynamic wide emission detection window between 420-670 nm in intervals of 10 nm or 3 nm. Emission spectral data for compound and background regions of interest (ROIs) were registered using ImageJ software[8,9].

To determine the multiplicity of the multiphoton absorption process, emission was recorded as detailed above at different excitation intensities, and the integrated emission in the emission wavelength range were plotted as a function of relative excitation power.

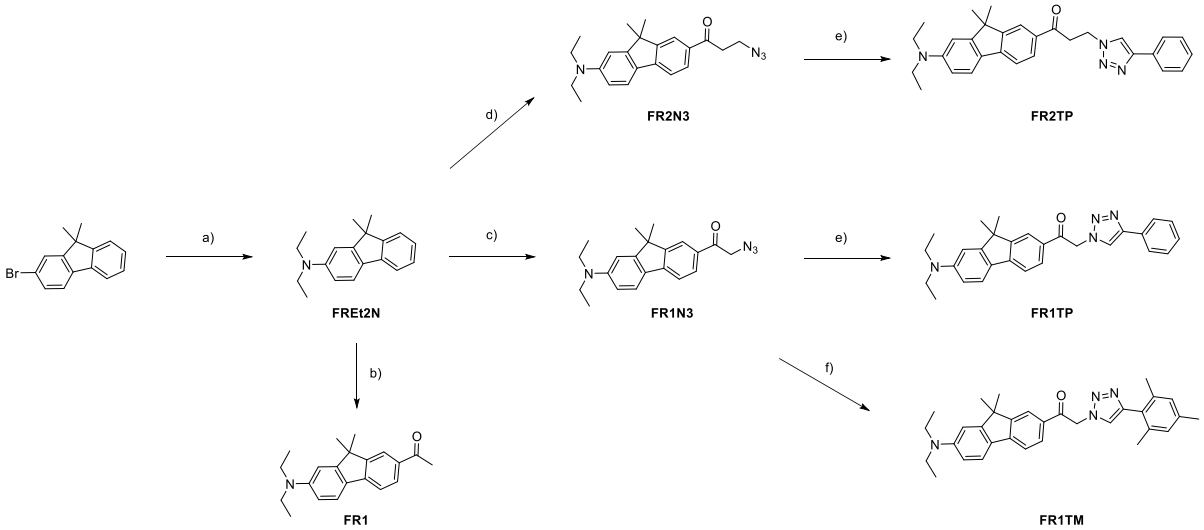
The two-photon absorption cross sections were determined by two-photon induced fluorescence method[10,11] and according to the following equation:

$$\sigma_{2PA,s} = \sigma_{2PA,r} \frac{C_r \eta_r \phi_{f,r} F_s}{C_s \eta_s \phi_{f,s} F_r}$$

where σ_{2PA} is the two-photon absorption cross-section, C is the concentration of the species, ϕ_f is the fluorescence quantum yield, η is the refractive index of the used solvent, and F is the integrated emission spectrum recorded at each wavelength. The letters *s* and *r* are used to denote sample and reference, respectively.

As reference, rhodamine 6G in methanol (ϕ_f = 70%[2])two-photon cross section data was taken from reference[12] was used assuming that fluorescence quantum yields remain the same regardless of the excitation mechanism.

2. Synthesis



Scheme S1. Synthesis of fluorophores. Reagents and conditions: a) Et_2NH, BINAP, $Pd(OAc)_2$, NaO^tBu, toluene, 110°C, overnight, 76%; b) Acetyl chloride, $AlCl_3$, DCM, 0°C to rt, overnight, 59%; c) 1. Bromoacetyl bromide, TfOH, 0°C, 1h; 2. NaN_3, DMSO, rt, 10 min., 66%; d) 1. 3-Chloropropionyl chloride, TfOH, 0°C, 1h; 2. NaN_3, DMSO, rt, 10 min., 51%; e) Phenyl acetylene, $[Cu(CH_3CN)_4]PF_6$, TBTA, $CHCl_3$, rt, overnight, 86% for **FR1TP** and 84% for **FR2TP**; f) 2-Ethynyl-1,3,5-trimethylbenzene, $[Cu(CH_3CN)_4]PF_6$, TBTA, $CHCl_3$, rt, overnight, 83%.

FREt2N

BINAP (470 mg, 0.75 mmol), palladium(II) acetate (36.7 mg, 0.16 mmol), sodium tert-butoxide (781.3 mg, 8.13 mmol) and 2-bromo-9,9-dimethylfluorene (2.019 g, 7.79 mmol) were added in a round bottom flask and placed under nitrogen. Toluene (15 mL) and diethylamine (1 mL, 9.65 mmol) were added and nitrogen was bubbled in the solution for 5 minutes. The mixture was heated at 110°C overnight. Then, the reaction was cooled to room temperature. The reaction mixture was diluted with DCM, filtered through a plug of celite, and rinsed three times with DCM. Solvents were removed under vacuum. Crude product was purified by flash column chromatography (pentane to pentane/EtOAc, 9:1 (v/v))* to give compound **FREt2N** (1.49 g, 76%) as an off-white powder. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 7.61 – 7.49 (m, 2H), 7.41 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.22 (td, *J* = 7.4, 1.1 Hz, 1H), 7.12 (td, *J* = 7.4, 1.1 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.39 (q, *J* = 7.0 Hz, 4H), 1.39 (s, 6H), 1.12 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 155.0, 152.1, 147.6, 139.5, 126.7, 126.0, 124.8, 122.3, 120.9, 118.1, 110.4, 105.6, 46.2, 43.9, 27.3, 12.5. **HRMS (ESI)**, calculated mass for $[M+H]^+$:266.1909 found 266.1913 (Δ = 1.50 ppm)

**Alternatively, this product can be obtained with satisfactory purity by trituration with methanol.*

FR1

Aluminum trichloride (1.9 g, 14.2 mmol) was placed in a round bottom flask under nitrogen atmosphere and suspended in 30 mL of dry DCM. The suspension was cooled down to 0°C, andacetyl chloride (1 mL, 14 mmol) was added. To this mixture, a solution of **FREt2N** (1.49 g, 5.61 mmol) in DCM (10 mL) was dropwise added. The reaction mixture was allowed to warm slowly to room temperature while stirring overnight. Then, the reaction mass was cooled at 0°C and quenched with a saturated solution of Na_2CO_3 (50 mL). DCM (50 mL) was added, and the organic layer was washed with brine and water, dried over $MgSO_4$, filtered, and solvents were removed under vacuum. Crude product was purified by

flash column chromatography (pentane to pentane/EtOAc, 4:1 (v/v)) to give compound **FR1** (1.024 g, 59%) as yellow powder. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 7.98 (d, *J* = 1.6 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.66 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.42 (q, *J* = 7.0 Hz, 4H), 2.58 (s, 3H), 1.43 (s, 6H), 1.13 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 197.2, 156.8, 152.4, 148.5, 144.7, 133.5, 128.3, 124.5, 122.3, 121.9, 117.8, 110.6, 105.2, 46.3, 44.0, 27.0, 26.7, 12.5. **HRMS (ESI)** calculated mass for $[M+H]^+$: 308.2014, found 308.2013 (Δ = -0.32 ppm)

FR1N3

Triflic acid (15 mL) was added to **FREt2** (485 mg, 1.82 mmol) under nitrogen atmosphere, and the resulting solution was cooled to 0°C. Bromoacetyl bromide (0.4 mL, 2.19 mmol) was added dropwise, and the solution was allowed to warm to room temperature while stirring for 1 hour. Then, ice-cold water (100 mL) and 100 mL of EtOAc were added. The biphasic mixture was strongly stirred, and a saturated solution of sodium bicarbonate was added until reaching a pH between 5 and 7. The phases were separated, and the aqueous layer was extracted EtOAc (2 x 75mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and solvents were removed under vacuum. Then, the resultant crude was dissolved in DMSO (5 mL). Sodium azide (227 mg, 3.49 mmol) was added, and the solution was stirred 10 minutes at room temperature. The reaction mixture was poured in water (100 mL) and extracted with EtOAc (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered, and solvents were removed under vacuum. Crude product was purified by flash column chromatography (pentane to pentane/EtOAc, 4:1 (v/v)) to give compound **FR1N3** (417 mg, 66%) as yellow powder.**^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 7.99 (d, *J* = 1.6 Hz, 1H), 7.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.88 (s, 2H), 3.43 (q, *J* = 7.0 Hz, 4H), 1.43 (s, 6H), 1.14 (t, *J* = 7.0 Hz, 6H).**^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 193.5, 156.9, 152.5, 148.7, 145.5, 130.7, 128.0, 124.3, 122.5, 121.8, 117.9, 110.7, 105.1, 54.6, 46.3, 44.0, 27.0, 12.5.**HRMS (ESI**) calculated for $[M+H]^+$ at 349.2029, found 349.2035 (Δ = 1.72 ppm)

FR2N3

Triflic acid (1 mL) was added to **FREt2** (78.5 mg, 0.30 mmol) under nitrogen atmosphere, and the resulting solution was cooled to 0°C. 3-Chloropropionyl chloride (0.43 mL, 0.44 mmol) was added dropwise, and the solution was allowed to warm to room temperature while stirring for 1 hour. Then, ice-cold water (50 mL) and 50 mL of EtOAc were added. The biphasic mixture was strongly stirred, and a saturated solution of sodium bicarbonate was added until reaching a pH between 5 and 7. The phases were separated, and the aqueous layer was extracted with EtOAc (2 x 30mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and solvents were removed under vacuum. Then, the resultant crude was dissolved in DMSO (1 mL). Sodium azide (43.2 mg, 0.67 mmol) was added, and the solution was stirred 10 minutes at room temperature. The reaction mixture was poured in water (50 mL) and extracted with EtOAc (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered and solvents were removed under vacuum. Crude product was purified by flash column chromatography (pentane to pentane/EtOAc, 4:1 (v/v)) to give compound **FR2N3** (55 mg, 51%) as yellow powder. **^{1}H NMR (600 MHz, DMSO)** δ 8.03 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.67 (t, *J* = 6.2 Hz, 2H), 3.43 (q, *J* = 7.0 Hz, 4H), 3.37 (t, *J* = 6.2 Hz, 2H), 1.44 (s, 6H), 1.14 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (151 MHz, DMSO)** δ 196.9, 156.8, 152.5, 148.6, 145.0, 132.8, 128.1, 124.4, 122.4, 121.8, 117.8, 110.7, 105.2, 46.3, 46.1, 44.0, 37.1, 26.9, 12.5. **HRMS (ESI)** calculated mass for $[M+H]^+$:363.2185, found 363.2194 (Δ = 2.48 ppm)

General protocol for copper-catalyzed azide–alkyne cycloaddition

Corresponding azide (1 eq.), tris[(1-benzyl-*1H*-1,2,3- triazol-4-yl)methyl]amine (TBTA) (0.5 eq.) and $[Cu(CH_3CN)_4]PF_6$ (0.5 eq.) were added and placed under nitrogen atmosphere. Then, 5 mL of $CHCl_3$ and corresponding alkyne (2 eq) were added. The solution was stirred overnight at room temperature. Then, solvents were removed under vacuum. Crude product was purified by flash column chromatography (pentane/EtOAc, 4:1 to 7:3 (v/v)) to give the corresponding triazole derivative.

FR1TP was synthetized according the general protocol with **FR1N3** (37 mg, 0.11 mmol), $[Cu(CH_3CN)_4]PF_6$ (22 mg, 0.06 mmol), TBTA (37 mg, 0.06 mmol) and phenyl acetylene (24 µL, 0.21 mmol), to give the compound (41 mg, 86%) as yellow powder. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 8.53 (s, 1H), 8.14 (d, *J* = 1.7 Hz, 1H), 8.03 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.24 (s, 2H), 3.44 (q, *J* = 7.0 Hz, 4H), 1.47 (s, 6H), 1.15 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 191.1, 157.0, 152.6, 148.8, 146.2, 145.8, 130.8, 130.4, 129.0, 128.3, 127.8, 125.1, 124.2, 123.1, 122.7, 122.1, 118.1, 110.7, 105.1, 55.9, 46.4, 44.0, 26.9, 12.5. **HRMS (ESI)** calculated for $[M+H]^+$: 451.2498, found 451.2492 (Δ = -1.32 ppm)

FR1TM was synthetized according the general protocol with **FR1N3** (11.8 mg, 0.034 mmol), $[Cu(CH_3CN)_4]PF_6$ (9.3 mg, 0.024 mmol), TBTA (12 mg, 0.023 mmol) and 2-ethynyl-1,3,5-trimethylbenzene (6 µL, 0.040 mmol), to give the compound (14 mg, 83%) as yellow powder. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 8.13 (d, *J* = 1.6 Hz, 1H), 8.07 (s, 1H), 8.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 1.1 Hz, 2H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.22 (s, 2H), 3.44 (q, *J* = 7.0 Hz, 4H), 2.28 (s, 3H), 2.09 (s, 6H), 1.46 (s, 6H), 1.15 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 191.2, 157.0, 152.6, 148.8, 145.7, 143.9, 137.1, 137.0, 130.5, 128.3, 128.1, 127.7, 125.7, 124.3, 122.7, 122.11 118.0, 110.7, 105.2, 55.7, 46.4, 44.0, 26.9, 20.7, 20.4, 12.5. **HRMS (ESI)** calculated for $[M+H]^+$:493.2967, found 493.2974 (Δ = 1.42 ppm)

FR2TP was synthetized according the general protocol with **FR2N3** (61 mg, 0.17 mmol), $[Cu(CH_3CN)_4]PF_6$ (35 mg, 0.09 mmol), TBTA (37 mg, 0.07 mmol) and phenyl acetylene (37 µL, 0.34 mmol), to give the compound (66 mg, 84%) as yellow powder. **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 8.63 (s, 1H), 8.03 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 8.3, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.28 (m, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.66 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.77 (t, *J* = 6.7 Hz, 2H), 3.80 (t, *J* = 6.8 Hz, 2H), 3.42 (q, *J* = 7.0 Hz, 4H), 1.42 (s, 6H), 1.13 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 196.2, 156.9, 152.5, 148.6, 146.2, 145.1, 132.6, 130.8, 128.9, 128.1, 127.8, 125.1, 124.4, 122.4, 121.9, 121.8, 117.9, 110.7, 105.2, 46.3, 45.1, 44.0, 40.0, 37.8, 26.9, 12.5. **HRMS (ESI)** calculated for $[M+H]^+$:465.2654, found 465.2654 (Δ = -0.43 ppm).

3. NMR and HRMS spectra

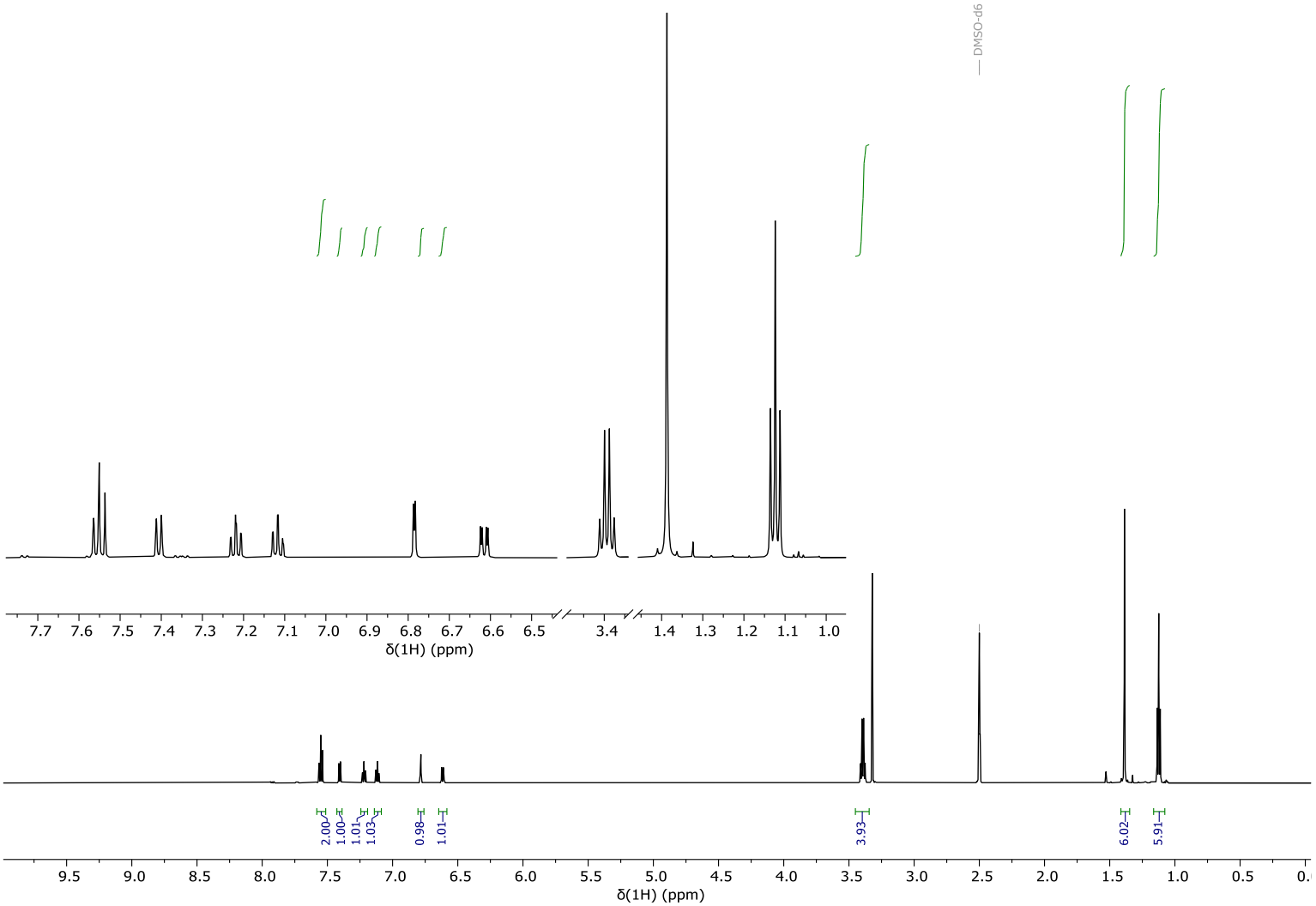


Fig. S1. ^{1}H NMR spectrum of **FREt2N** (DMSO-d_6, 600 MHz).

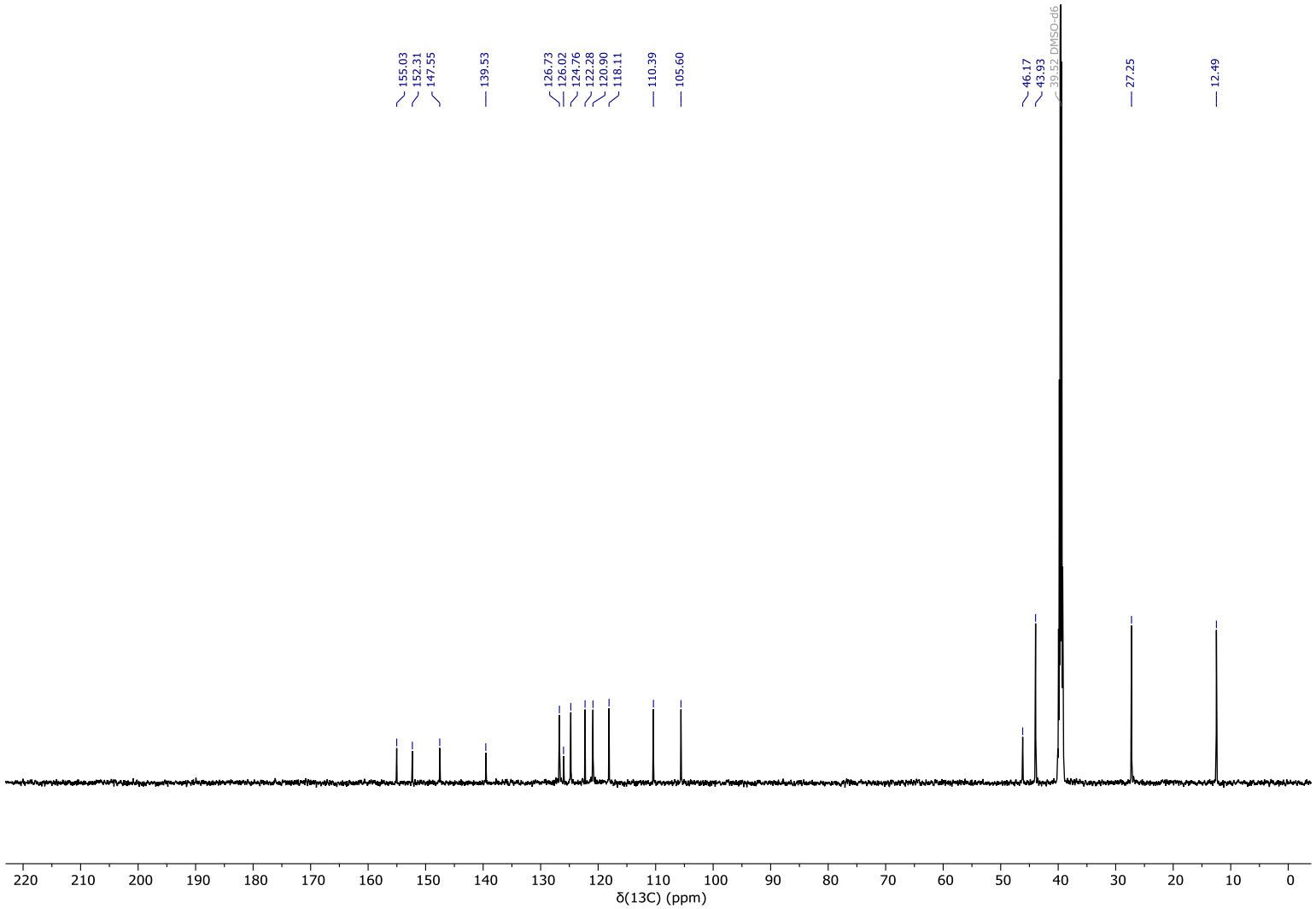


Fig. S2. ^{13}C NMR spectrum of **FREt2N** (DMSO-d_6, 151 MHz).

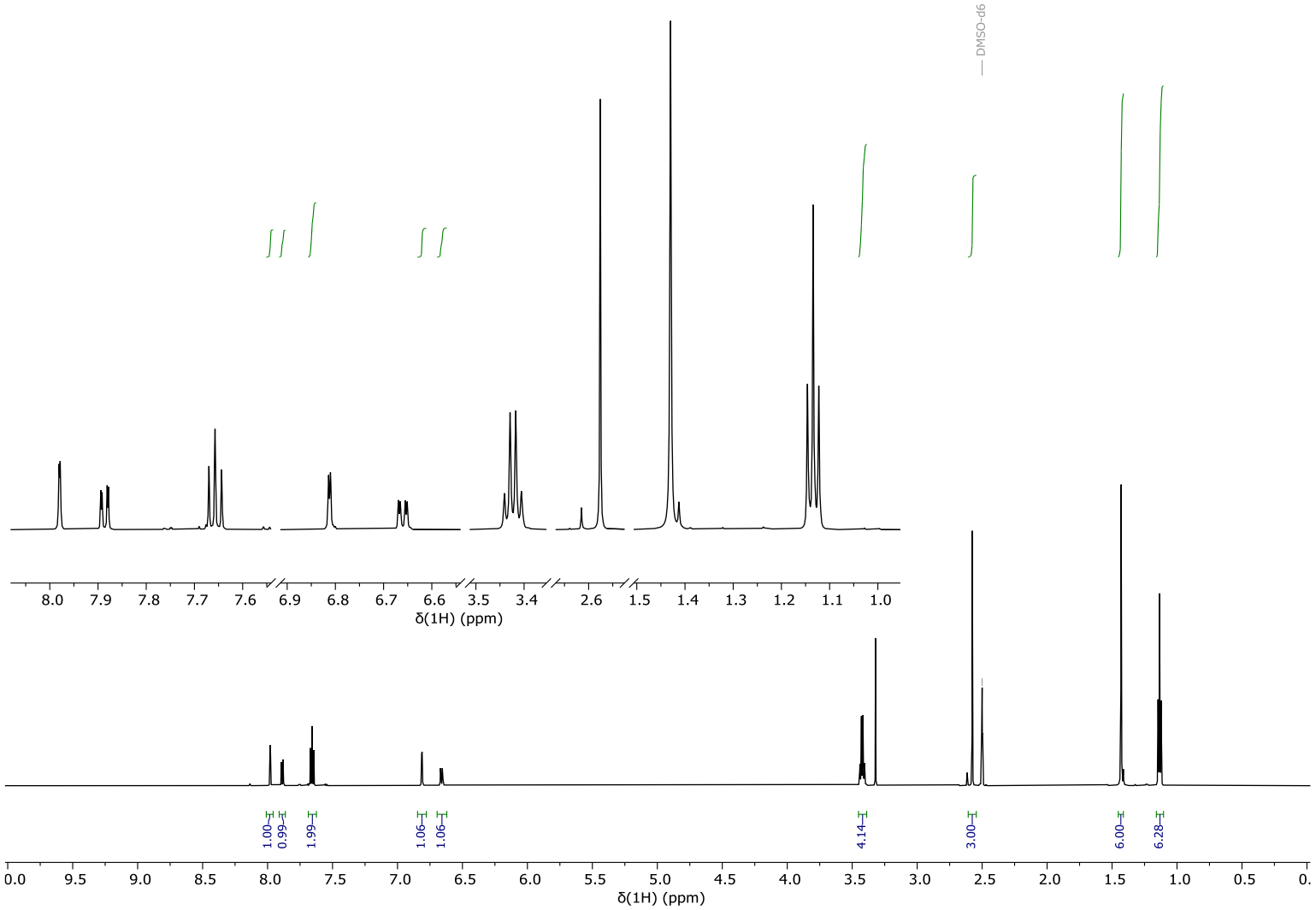


Fig. S3. ^{1}H NMR spectrum of **FR1** (DMSO-d_6, 600 MHz).

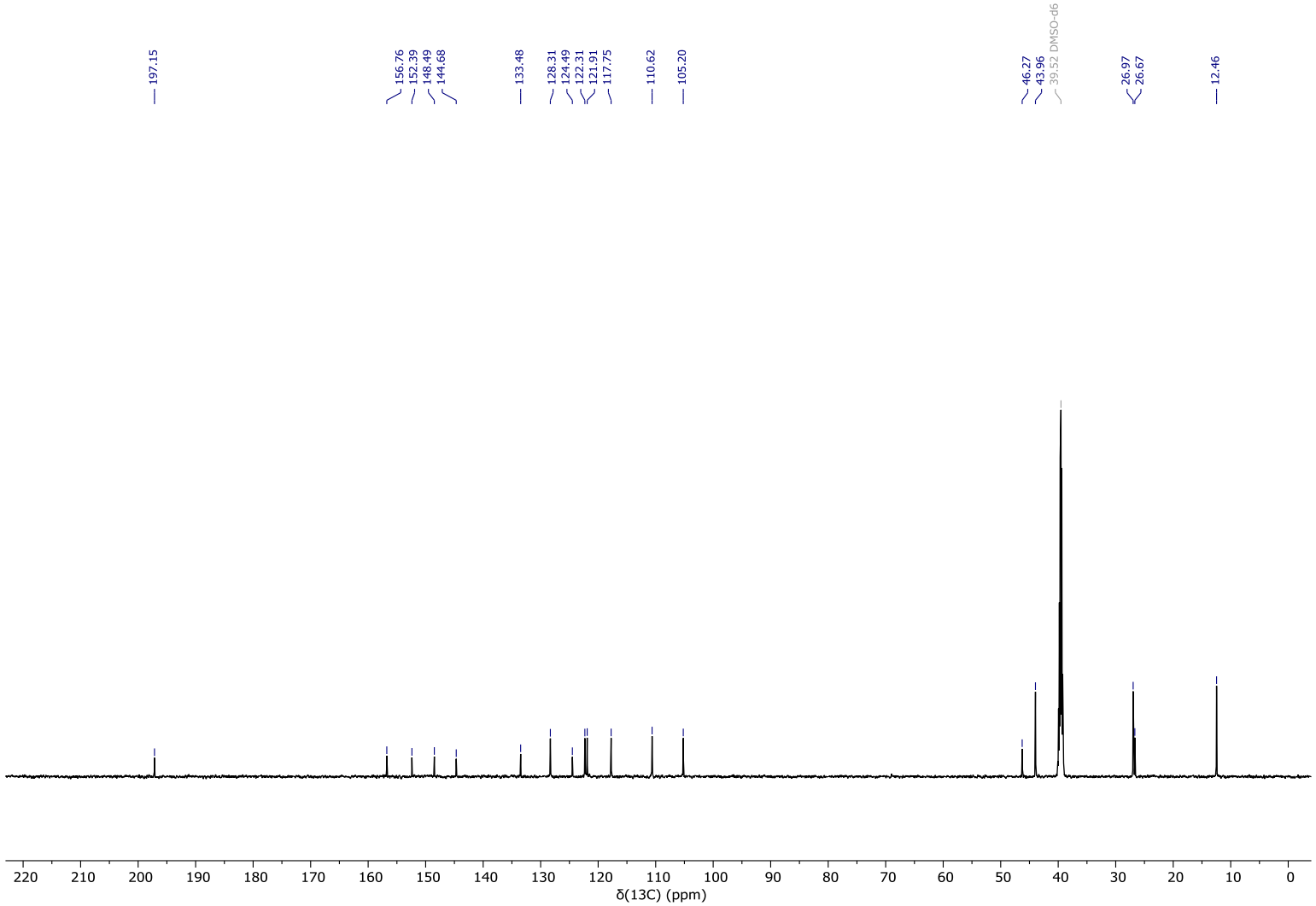


Fig. S4. ^{13}C NMR spectrum of **FR1** (DMSO-d6, 151 MHz).

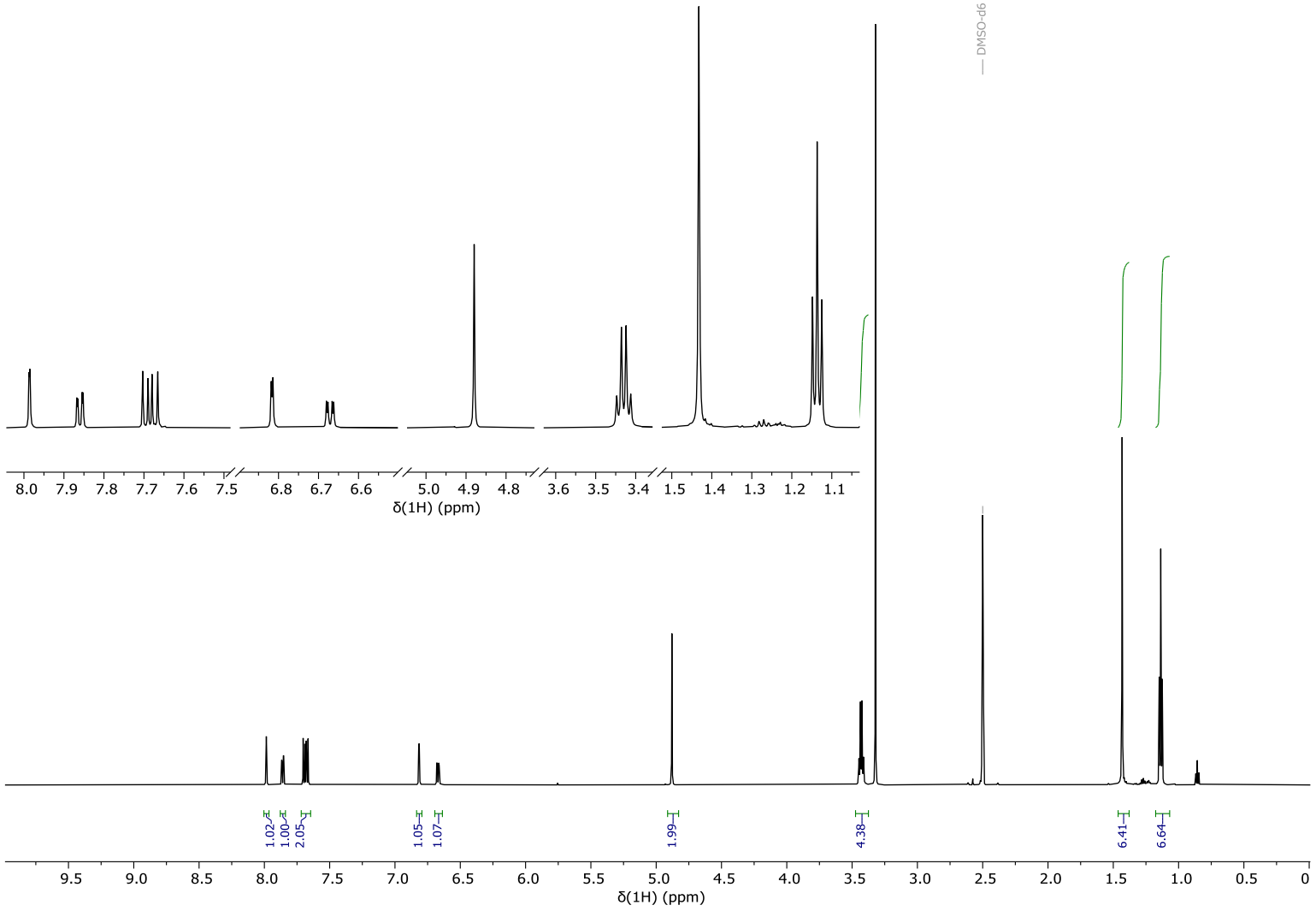


Fig. S5. ^{1}H NMR spectrum of **FR1N3** (DMSO-d_6, 600 MHz).

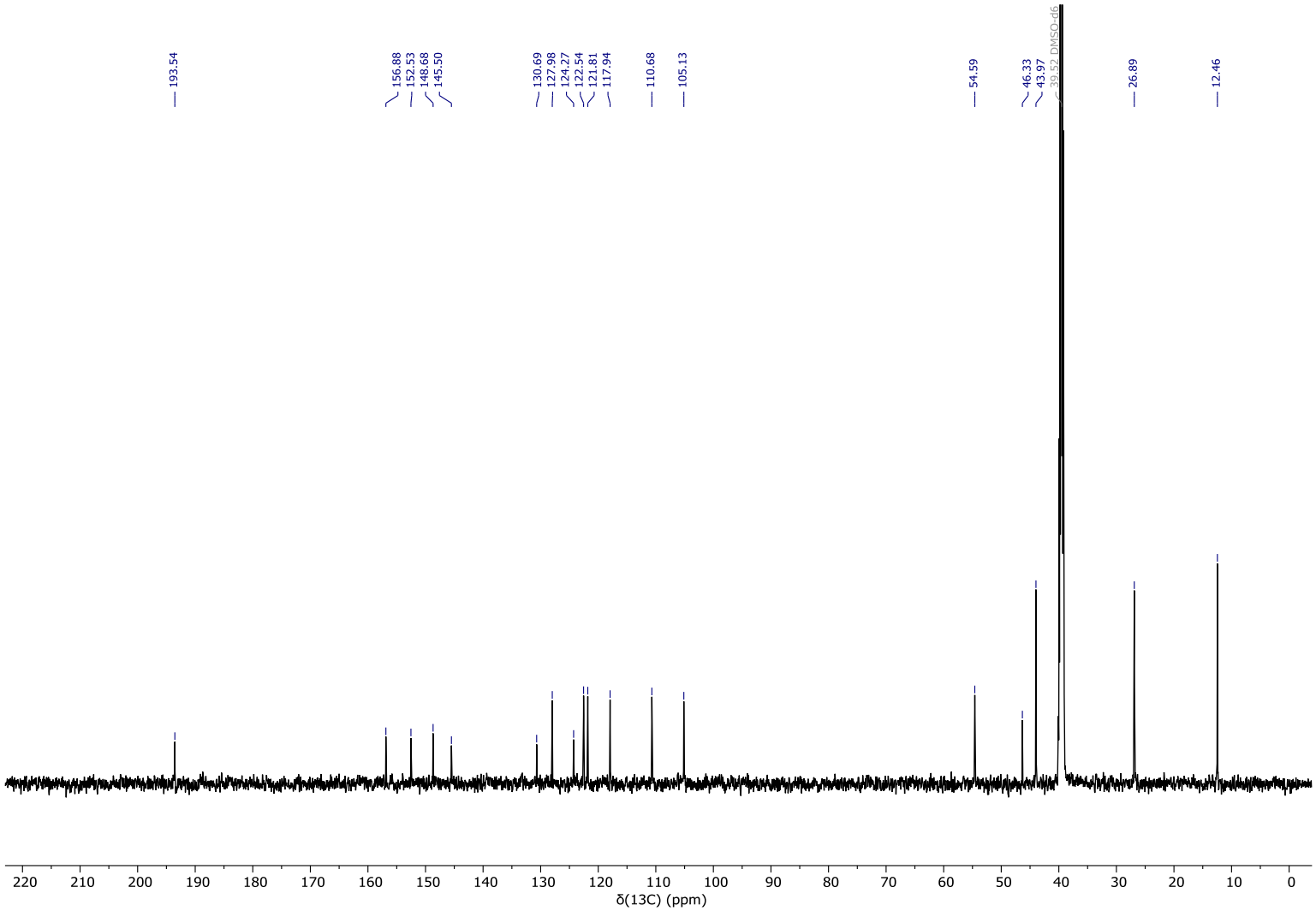


Fig. S6. ^{13}C NMR spectrum of **FR1N3** (DMSO-d_6, 151 MHz).

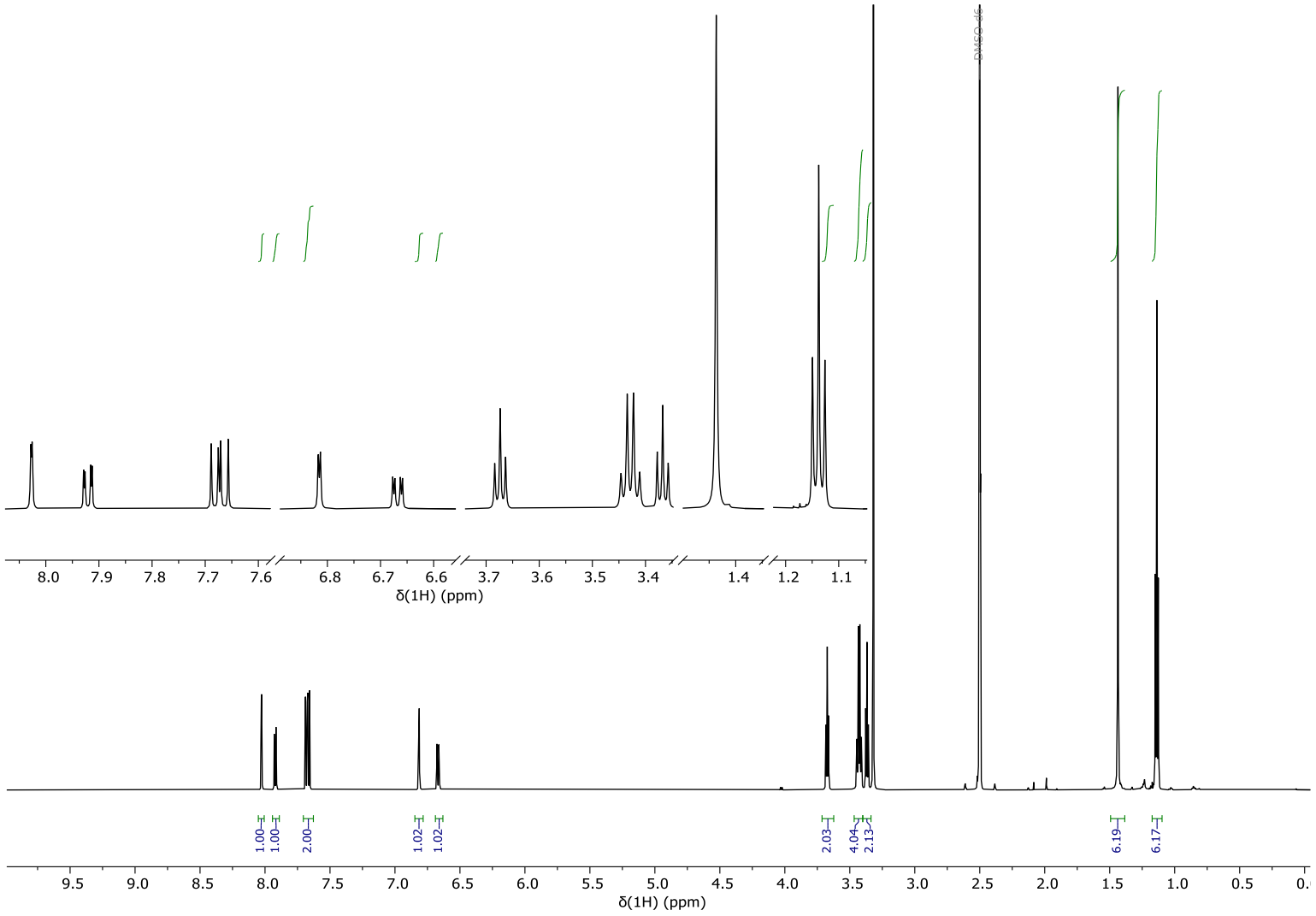


Fig. S7. ^{1}H NMR spectrum of **FR2N3** (DMSO-d_6, 600 MHz).

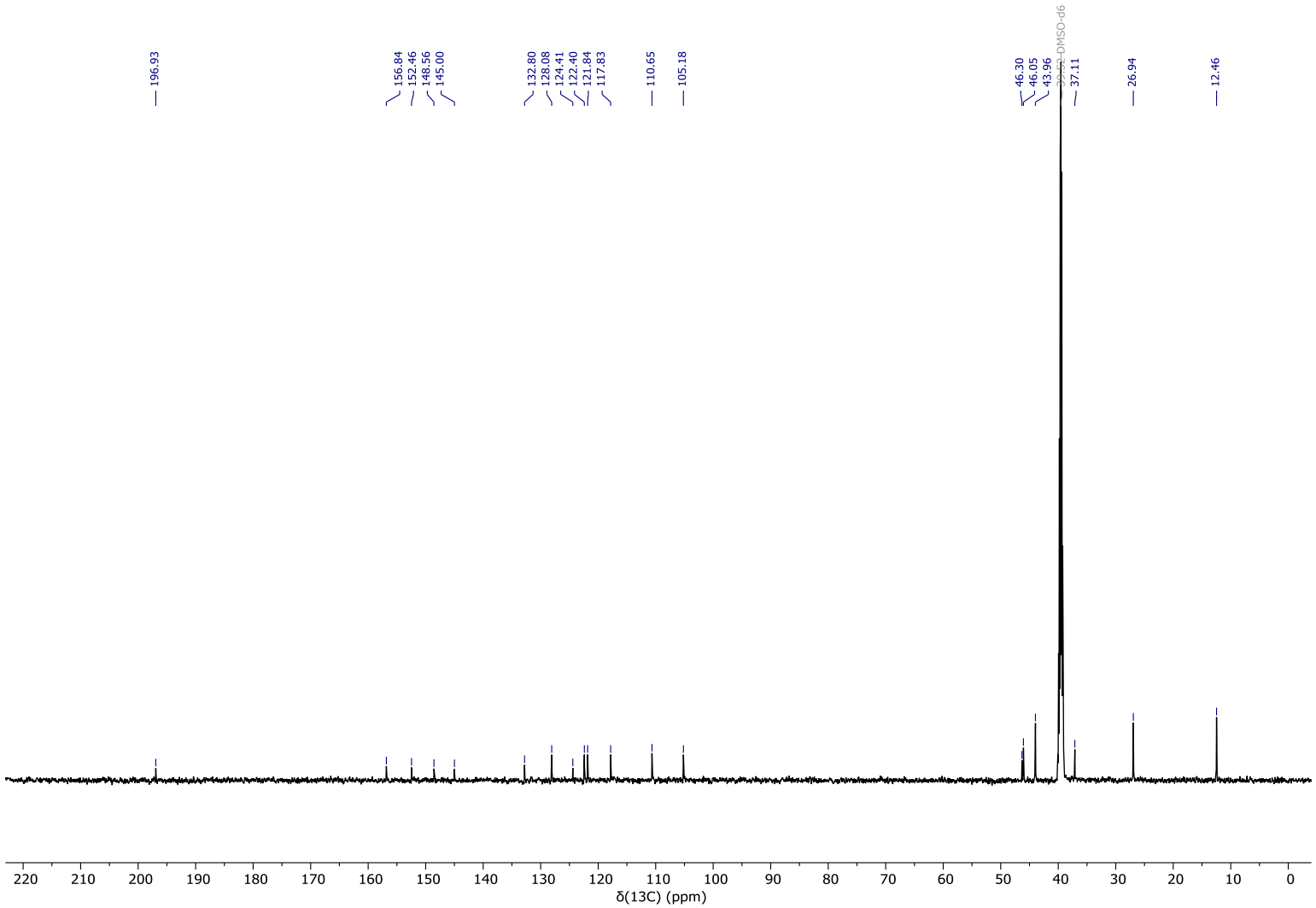


Fig. S8. ^{13}C NMR spectrum of **FR2N3** (DMSO-d_6, 151 MHz).

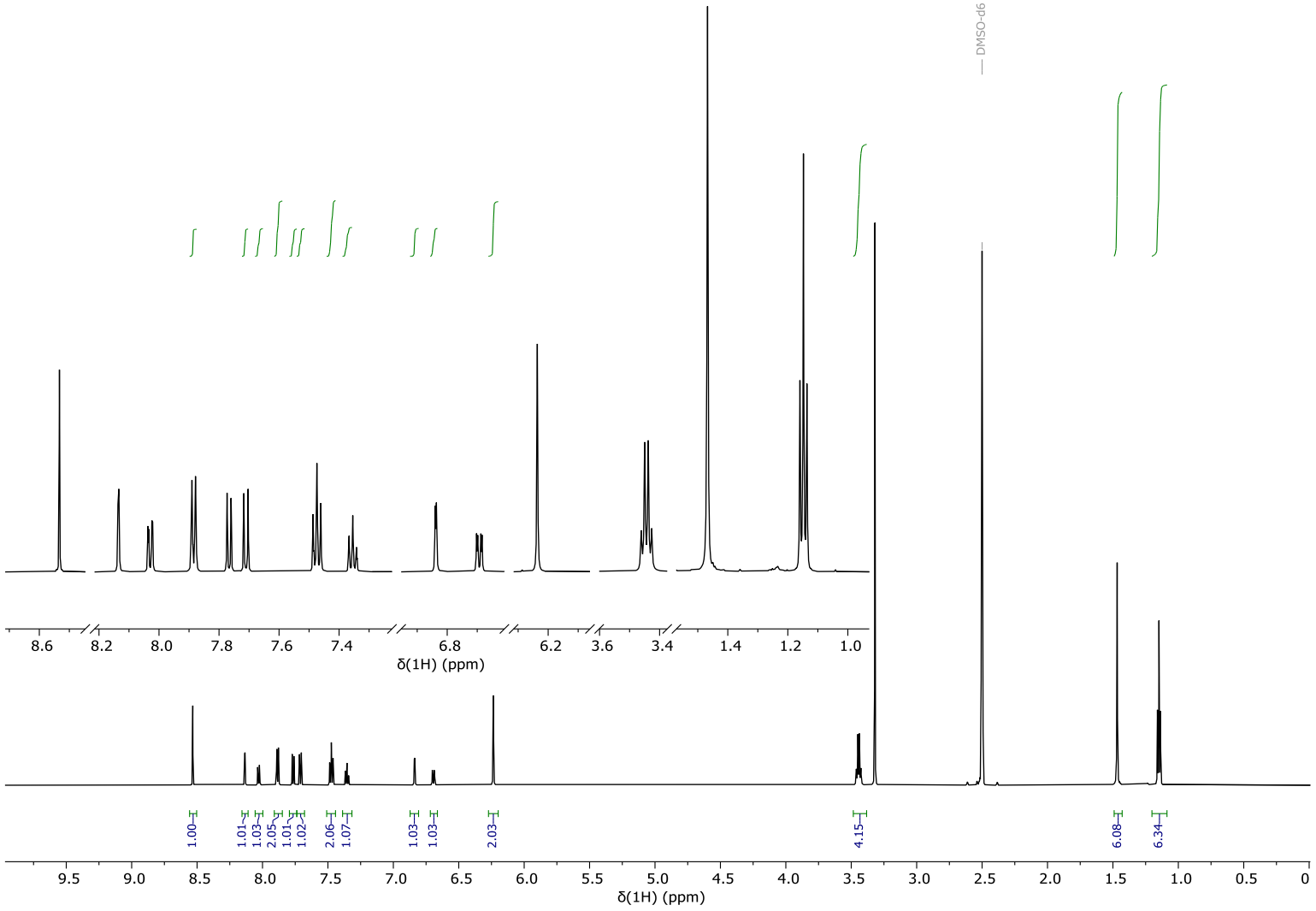


Fig. S9. ^{1}H NMR spectrum of **FR1TP** (DMSO-d_6, 600 MHz).

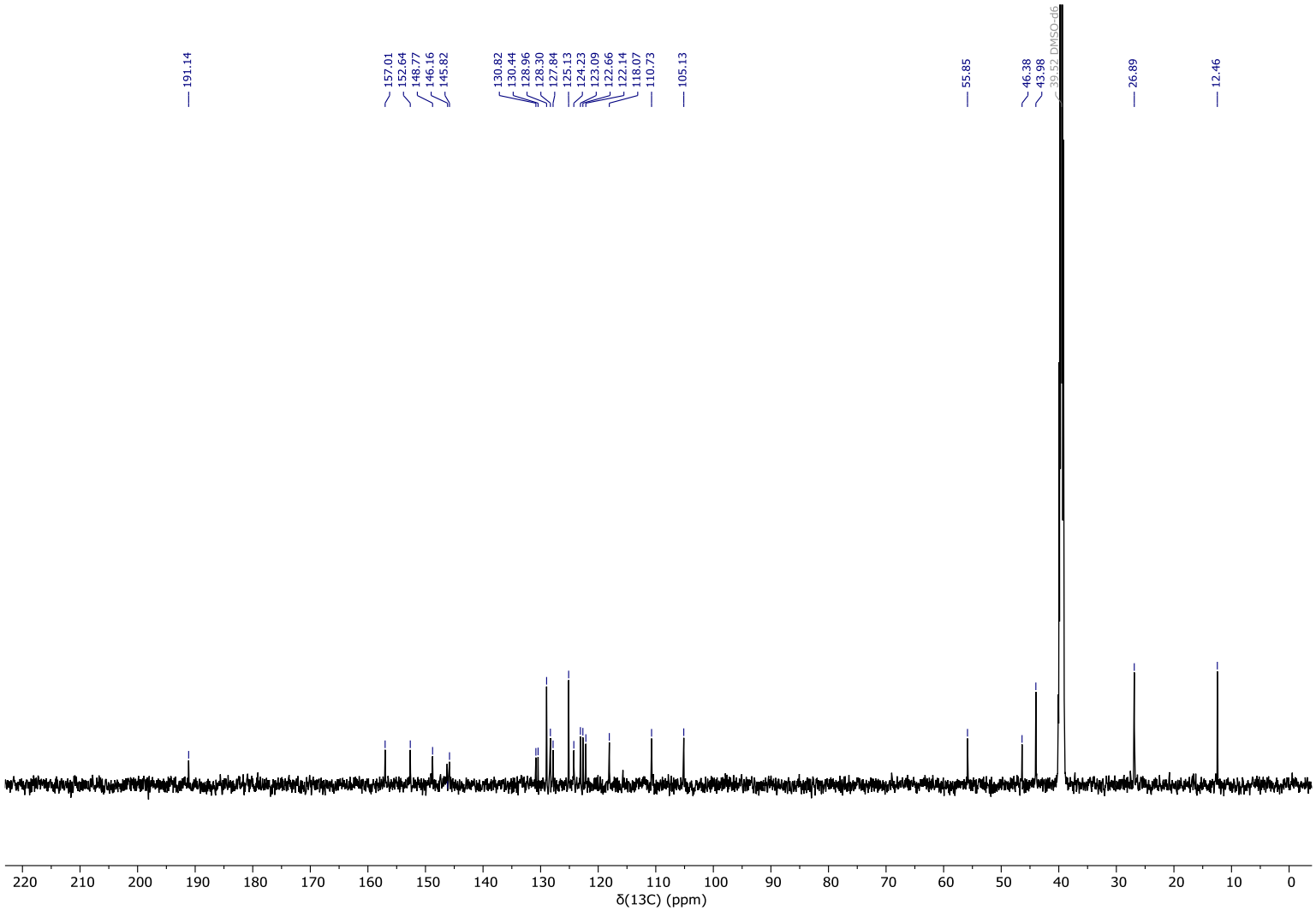


Fig. S10. ^{13}C NMR spectrum of **FR1TP** (DMSO-d_6, 151 MHz).

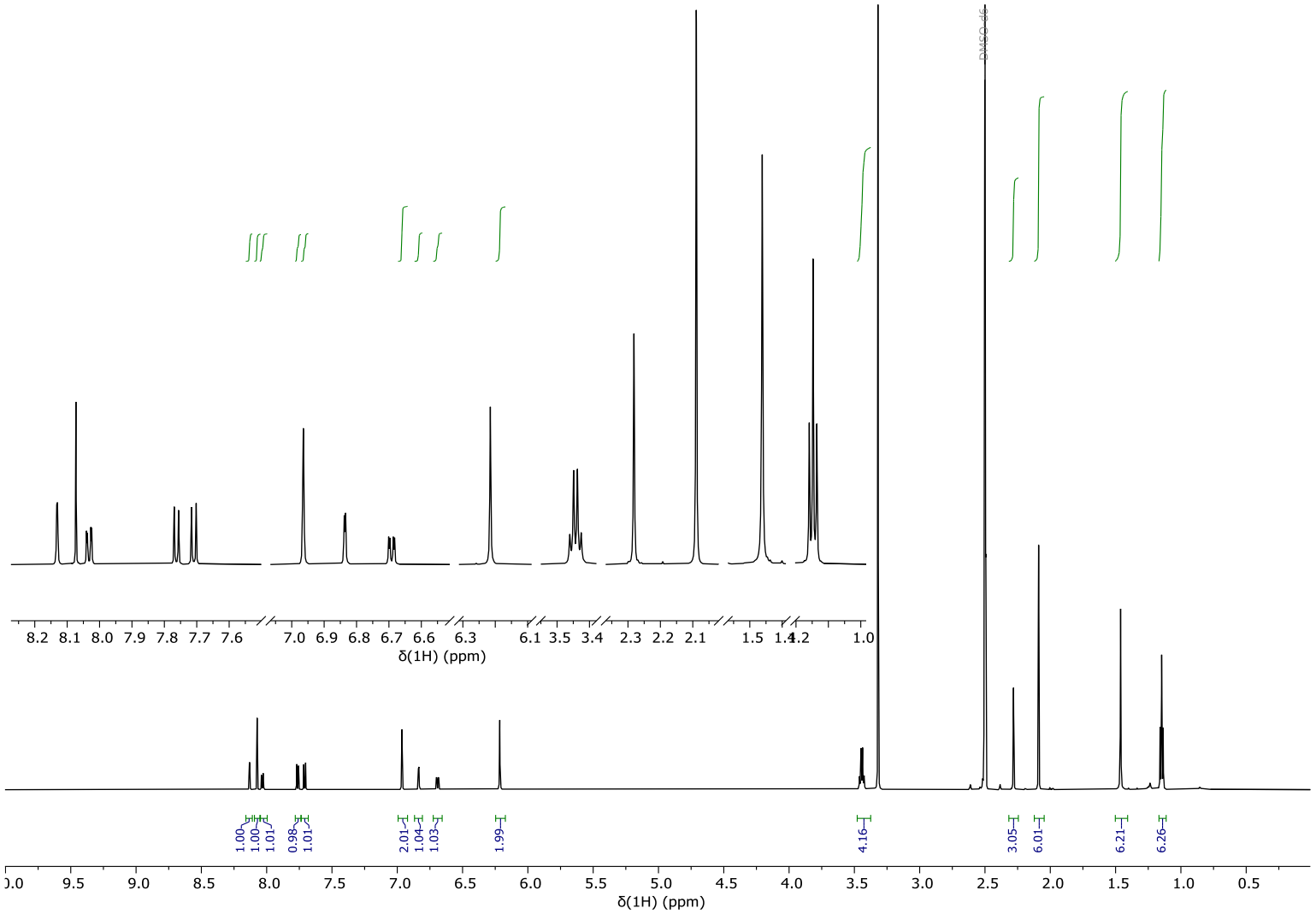


Fig. S11. ^{1}H NMR spectrum of **FR1TM** (DMSO-d_6, 600 MHz).

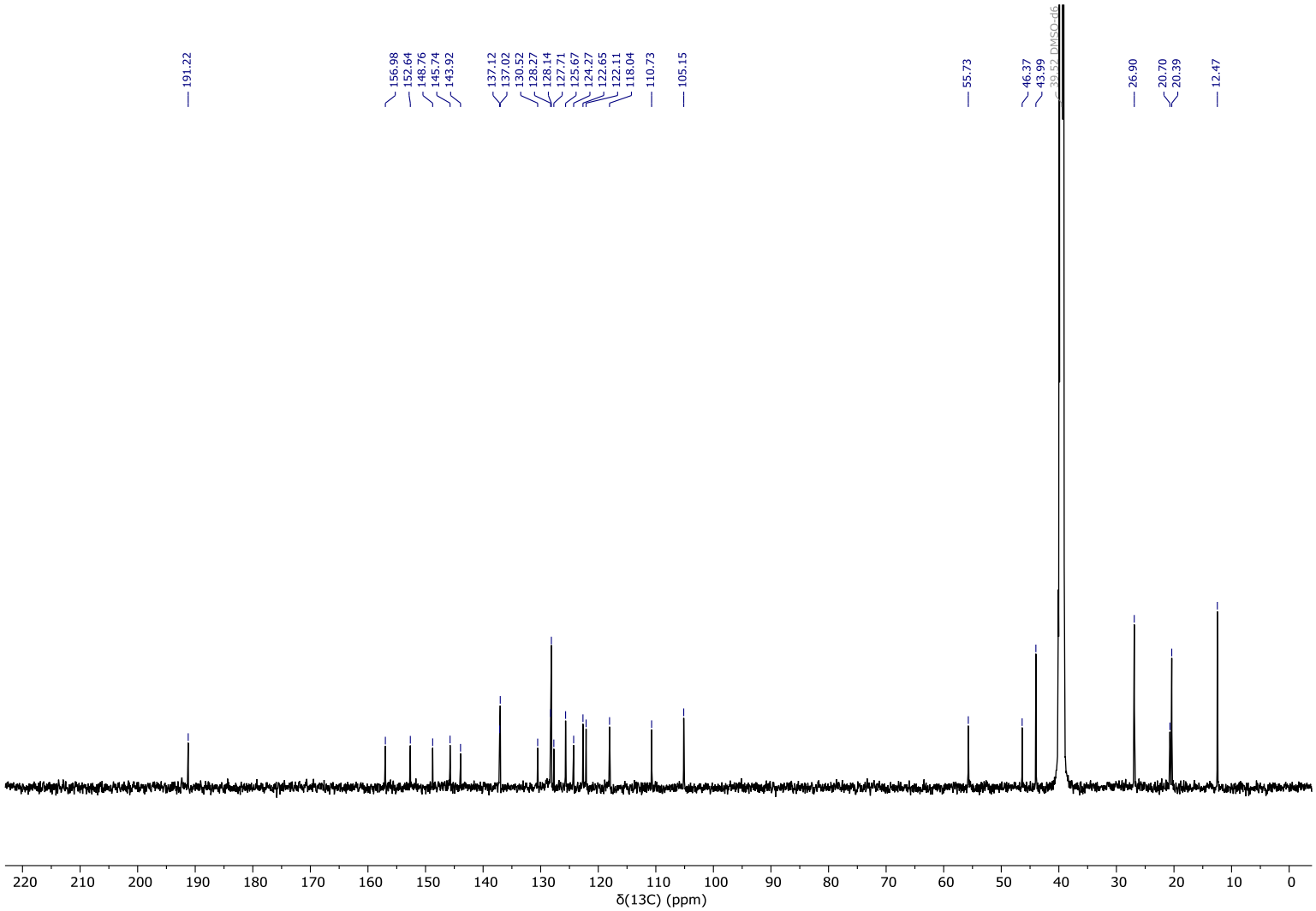


Fig. S12. ^{13}C NMR spectrum of **FR1TM** (DMSO-d_6, 151 MHz).

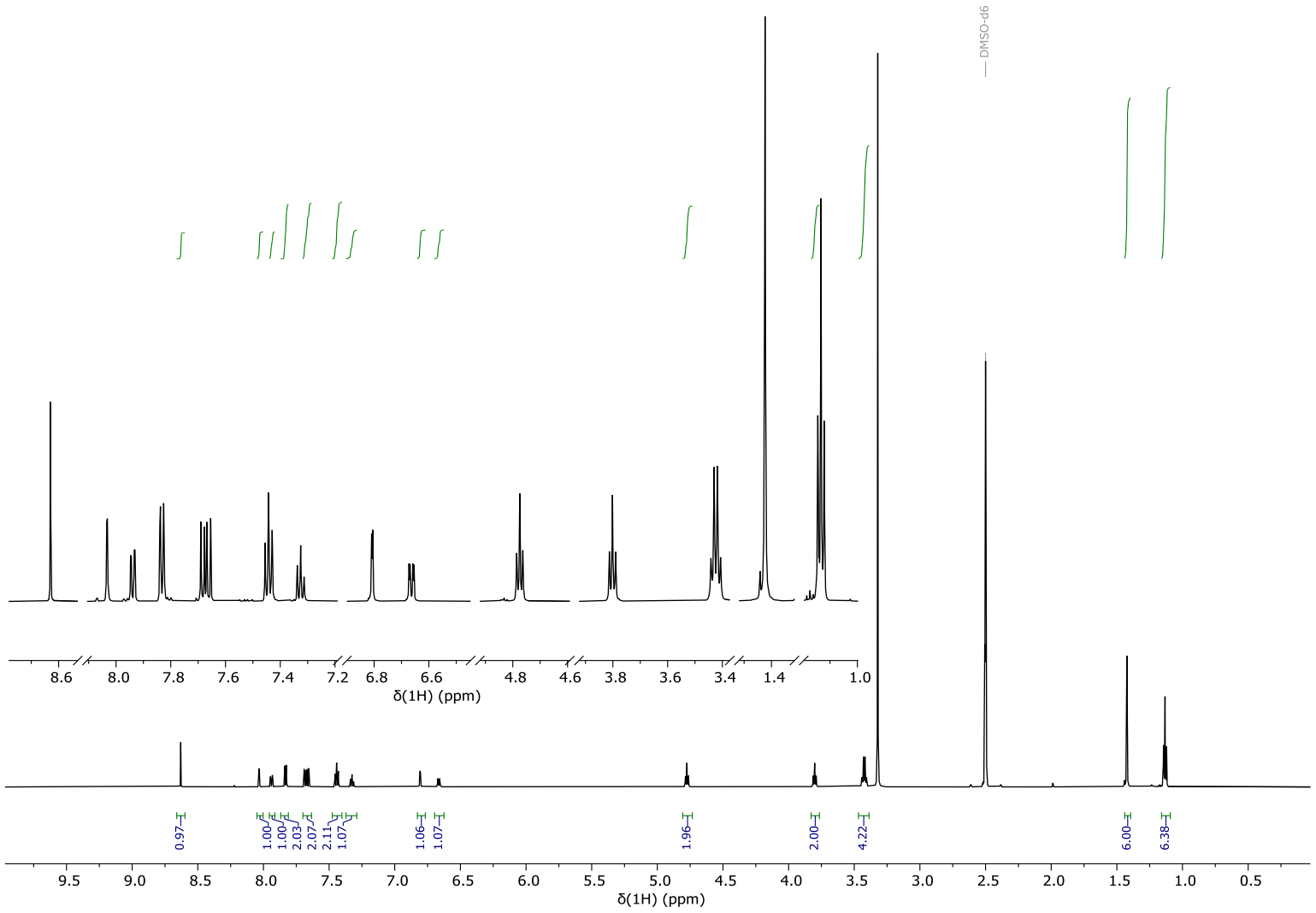


Fig. S13. ^{1}H NMR spectrum of **FR2TP** (DMSO-d_6, 600 MHz).

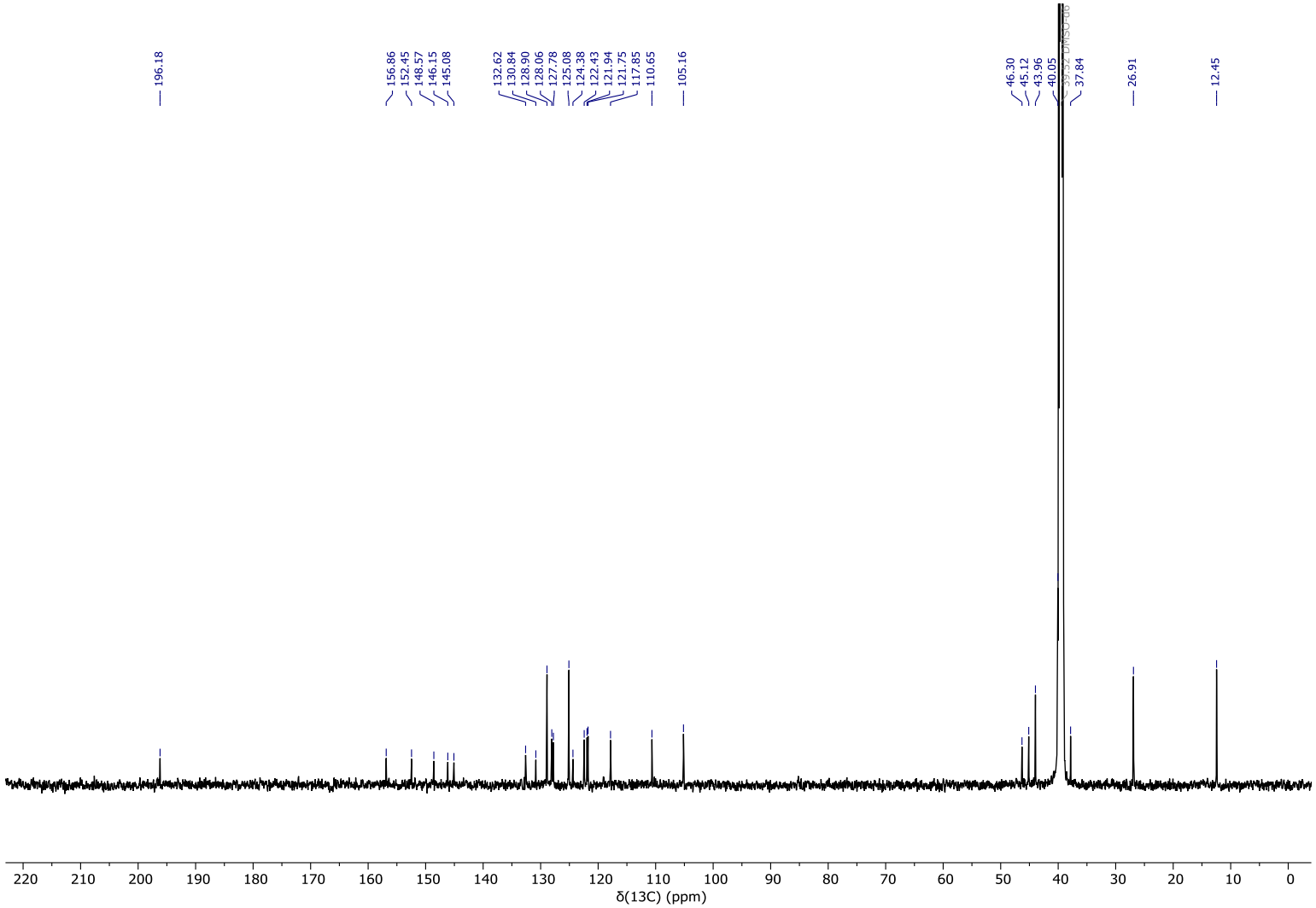


Fig. S14. ^{13}C NMR spectrum of **FR2TP** (DMSO-d_6, 151 MHz).

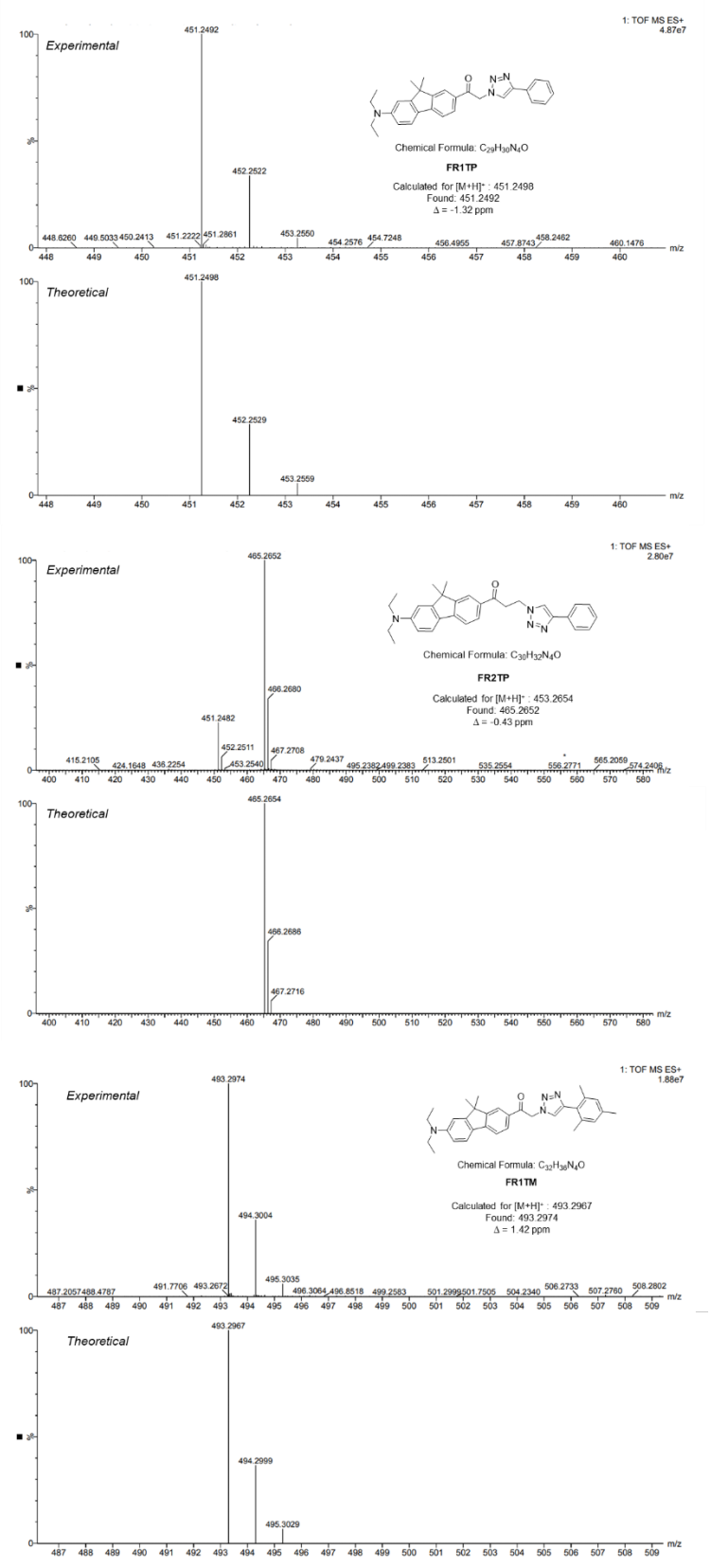


Fig. S15. HRMS of **FR1TP**, **FR2TP** and **FR1TM**.

4. Spectroscopic study details

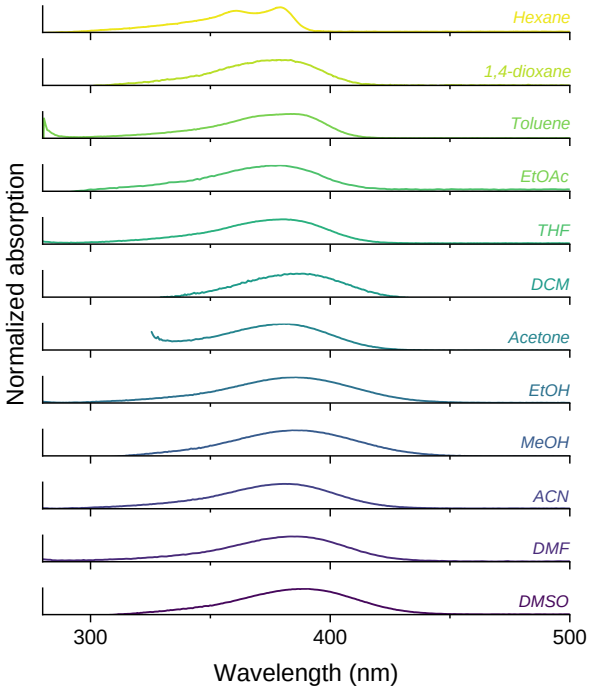


Fig. S16. Normalized absorption spectra of **FR1** in a series of organic solvents.

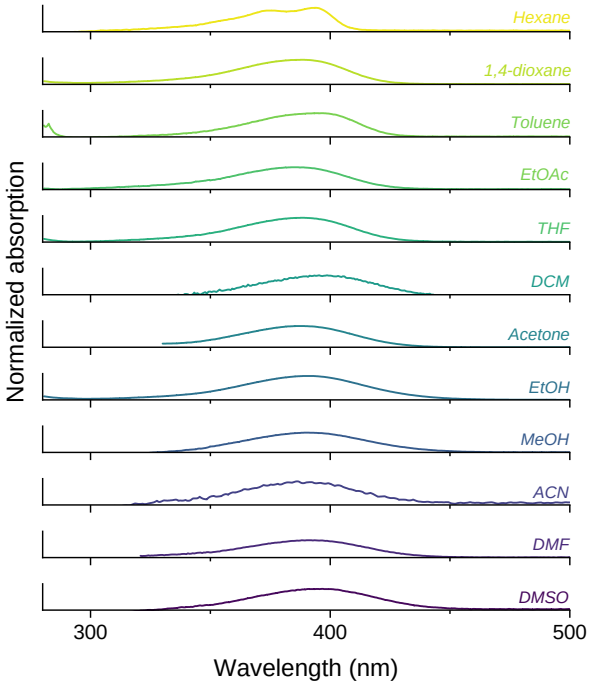


Fig. S17. Normalized absorption spectra of **FR2TP** in a series of organic solvents.

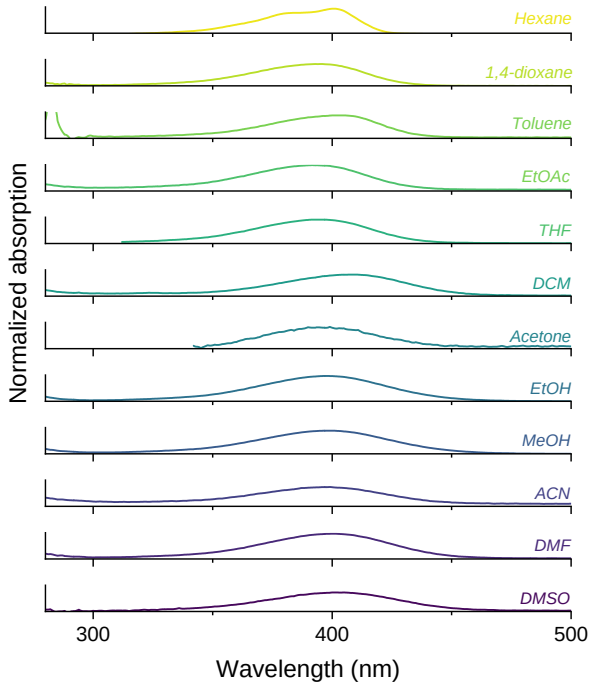


Fig. S18. Normalized absorption spectra of **FR1TP** in a series of organic solvents.

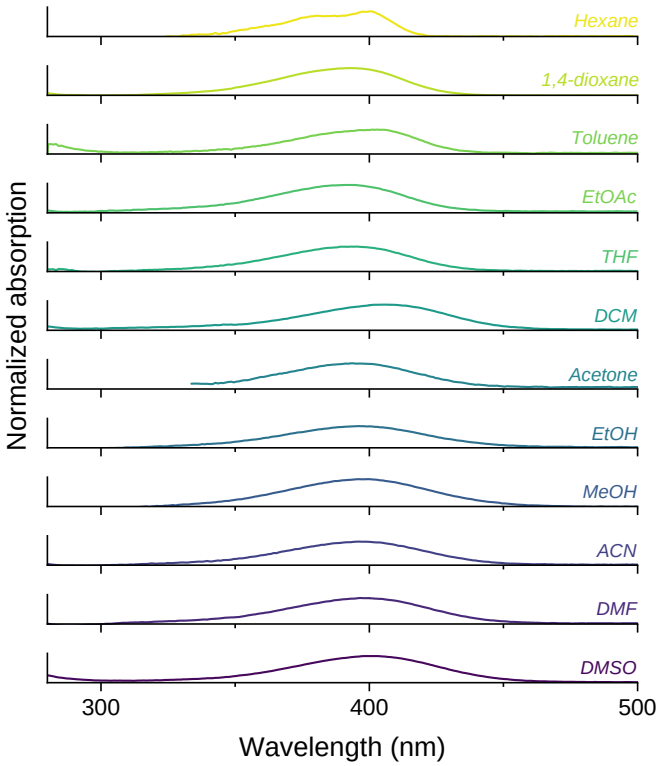


Fig. S19. Normalized absorption spectra of **FR1TM** in a series of organic solvents.

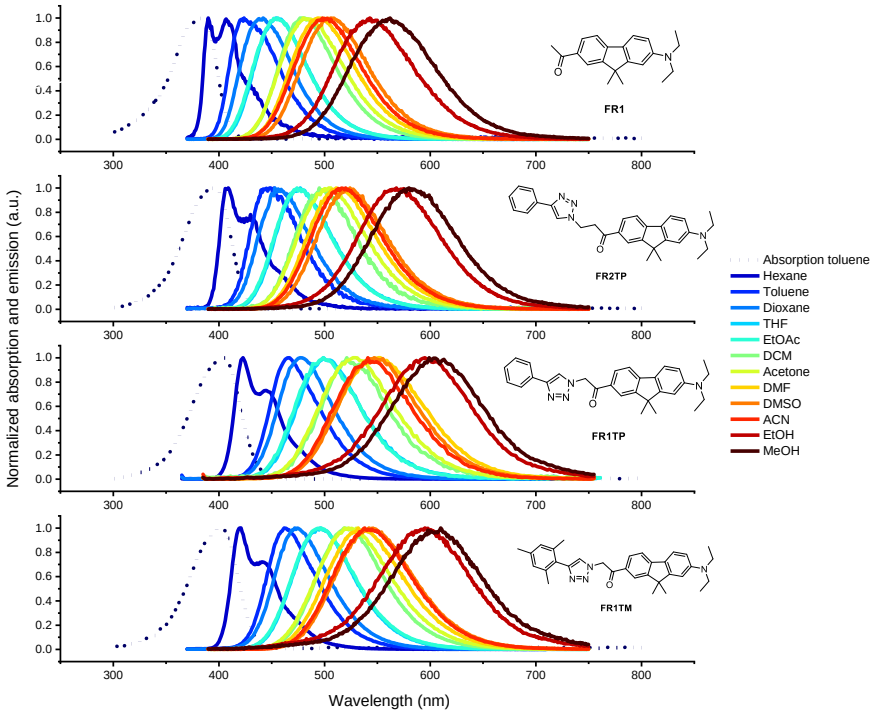


Fig. S20. Absorption (dotted line) spectra in toluene and normalized fluorescence (solid) spectra of a) **FR1**, b) **FR2TP**, c) **FR1TP** and d) **FR1TM** in a series of organic solvents. Concentration around 10^{-5} M. Excitation for emission readout at 360 nm in n-Hexane, Toluene, and Dioxane, and at 380 nm for all other solvents.

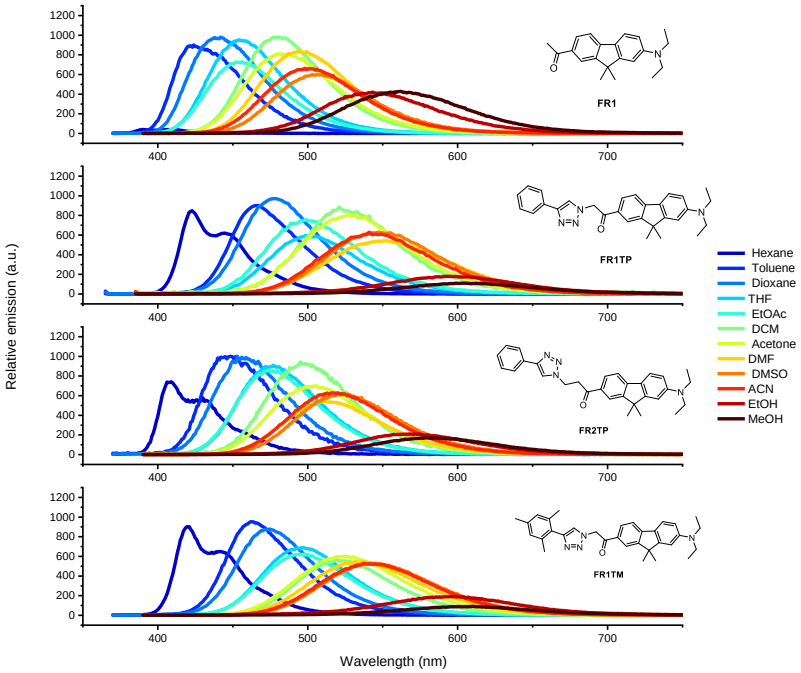


Fig. S21. Relative fluorescence spectra of a) **FR1**, b) **FR1TP**, c) **FR2TP** and d) **FR1TM** in a series of organic solvents.

	Absorption maximum (nm)					Emission maximum (nm)					ϕ_f (%)				
	FR8[a]	FR1	FR2TP	FR1TP	FR1TM	FR8[a]	FR1	FR2TP	FR1TP	FR1TM	FR8[a]	FR1	FR2TP	FR1TP	FR1TM
n-Hexane[b]	378	379	394	401	399	387	390	409	423	421	4	1	74	85	90
1.4-Dioxane[b]	378	379	394	394	393	435	438	453	478	472	98	<100	<100	<100	88
Toluene[b]	383	384	395	403	401	425	424	448	466	462	83	90	<100	93	<100
EtOAc	377	378	387	392	391	460	456	474	499	497	82	73	86	76	62
THF	378	380	389	395	393	449	454	477	501	496	90	96	91	77	69
DCM	384	386	395	407	405	479	479	495	525	519	85	99	94	88	56
Acetone	379	380	388	396	394	478	480	504	528	523	77	81	70	80	60
EtOH	383	386	389	399	396	536	542	568	595	595	47	42	21	18	19
MeOH	384	384	389	399	396	555	562	580	605	605	35	43	17	11	9
ACN	380	383	391	398	395	498	498	520	541	538	66	66	63	63	53
DMF	385	384	392	400	397	490	494	511	553	532	75	83	55	54	55
DMSO	387	388	397	400	400	503	505	524	548	542	70	62	62	63	53

a. Data taken from ref.[1] ; b. Excitation at 360 nm.

Table S1. Summary of spectroscopic properties of new triazoles based dyes (**FR1TP**, **FR1TM**, **FR2TP**) and **FR1** compared to former **FR8** (please note that (i) optically diluted solutions were used and the excitation wavelength was 380 nm unless otherwise stated, and (ii) fluorescence quantum yields with a value "< 100" are yields close to 100%, rounded up to the nearest unit).

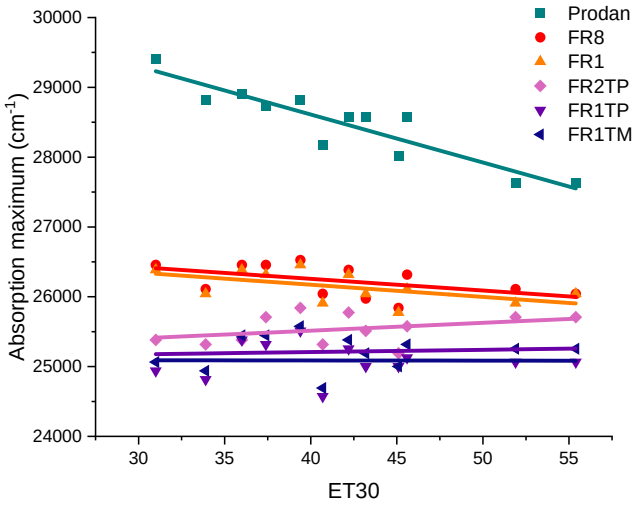


Fig. S22. Absorption maxima (dots) of **Prodan**, **FR8**, **FR1**, **FR2TP**, **FR1TP** and **FR1TM** *vs.* ET30 of the corresponding solvent and their linear fits (solid lines). Data of **Prodan** and **FR8** was taken from reference [1].

	Slope (cm^{-1})	χ^2
Prodan[a]	69	0.83
FR8[a]	17	0.27
FR1	17	0.30
FR2TP	11	0.37
FR1TP	0.29	0
FR1TM	3	0

a. Data taken from ref.[1]

Table S2. Slope of the linear fit of absorption maxima of **Prodan**, **FR8**, **FR1**, **FR2TP**, **FR1TP** and **FR1TM** *vs.* ET30 and the associated correlation coefficient χ^2.

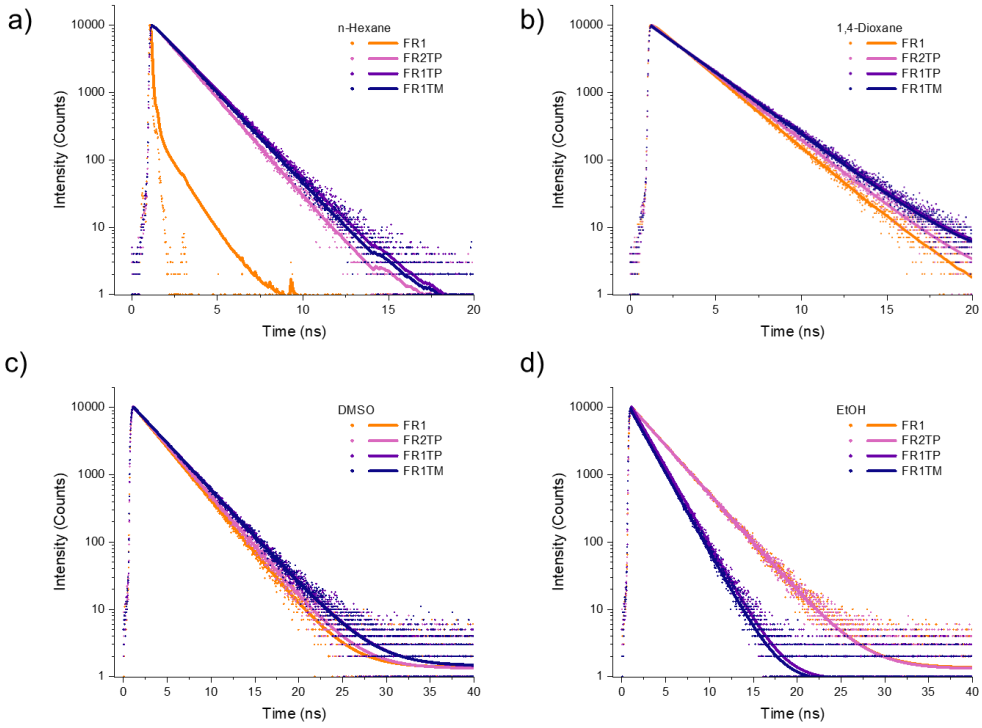


Fig. S23. Fluorescence decay traces (dotted lines) and fitted monoexponential decay traces of **FR1**, **FR2TP**, **FR1TP** and **FR1TM** in a) n-hexane, b) 1,4-dioxane, c) DMSO and d) ethanol.

	FR1		**FR2TP**		**FR1TP**		**FR1TM**	
	τ (ns)	χ^2	τ (ns)	χ^2	τ (ns)	χ^2	τ (ns)	χ^2
n-Hexane	0.21[a]	1.00	1.48	1.00	1.67	1.04	1.61	1.00
1,4-Dioxane	2.05	1.15	2.22	1.06	2.40	1.34	2.36	1.30
EtOH	2.99	1.07	2.99	1.06	1.89	0.95	1.85	0.98
DMSO	2.76	1.16	2.89	1.11	3.13	1.05	3.11	1.15

a. Average of biexponential fitting: 0.05 (84%) and 1.05 (16%).

Table S3. Fluorescence lifetimes obtained by monoexponential fitting of the fluorophores and their correlation coefficient χ^2.

	k_r (ns^{-1})				k_{nr} (ns^{-1})			
	FR1	**FR2TP**	**FR1TP**	**FR1TM**	**FR1**	**FR2TP**	**FR1TP**	**FR1TM**
n-Hexane	0.05	0.50	0.51	0.56	6.16	1.02	0.86	0.95
1,4-Dioxane	0.49	0.45	0.42	0.37	0.64	0.57	0.50	0.50
EtOH	0.14	0.07	0.10	0.10	0.35	0.34	0.56	0.57
DMSO	0.23	0.22	0.20	0.17	0.39	0.37	0.34	0.34

Table S4. Calculated radiative (k_r) and non-radiatives (k_{nr}) constants and of the fluorophores under study.

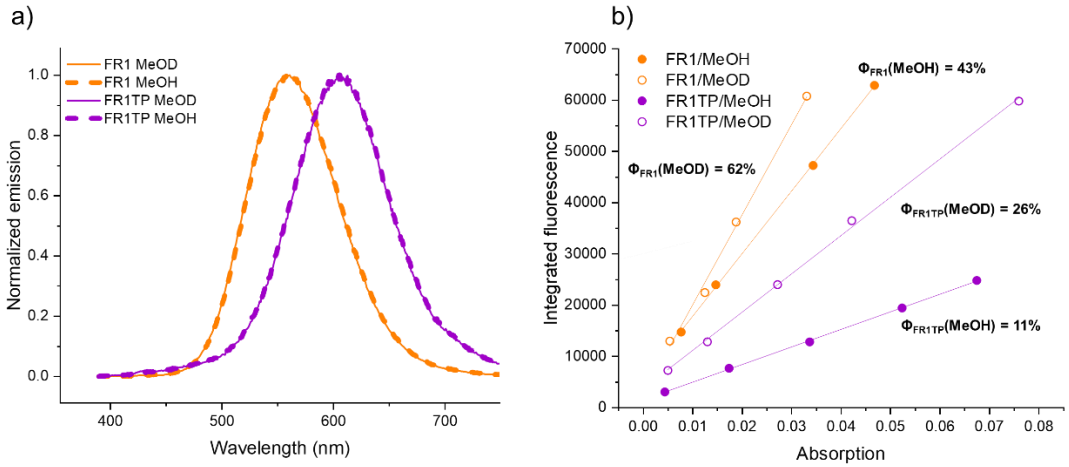


Fig. S24. a) Normalized fluorescence spectra of **FR1** (orange) and **FR1TP** (purple) in methanol (dotted line) and methanol-d_4 (solid line). b) Integrated fluorescence vs. absorption of **FR1** (orange) and **FR1TP** (purple) in methanol (full circle) and methanol-d_4 (white filled circle) and their linear fits. Associated calculated fluorescence quantum yield are displayed for both compound in methanol and methanol-d_4.

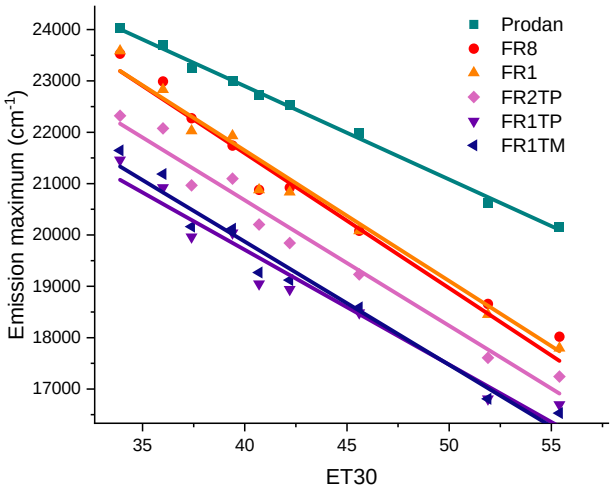


Fig. S25. Emission maxima (dots) of **Prodan**, **FR8**, **FR1**, **FR2TP**, **FR1TP** and **FR1TM** *vs.* ET30 of the corresponding solvent and their linear fits (solid lines). Data of **Prodan** and **FR8** was taken from reference [1].

	Slope (cm^{-1})	χ^2
Prodan[a]	180	1
FR8[a]	250	0.98
FR1	260	0.98
FR2TP	220	0.96
FR1TP	240	0.97
FR1TM	240	0.97

a. Data taken from ref.[1]

Table S5. Slope of the linear fit of emission maxima of **Prodan**, **FR8**, **FR1**, **FR1TP**, **FR2TP** and **FR1TM** vs. ET30 and the associated correlation coefficient χ^2. Data of **Prodan** and **FR8** was taken from reference [1].

	Stokes shift (cm^{-1})				
	FR8[a]	**FR1**	**FR2TP**	**FR1TP**	**FR1TM**
n-Hexane	620	740	930	1300	1310
1.4-Dioxane	3470	3550	3310	4460	4260
Toluene	2580	2460	3000	3350	3290
EtOAc	4790	4530	4740	5470	5450
THF	4180	4290	4740	5360	5280
DCM	5160	5030	5110	5520	5420
Acetone	5460	5480	5930	6310	6260
EtOH	7450	7460	8100	8260	8450
MeOH	8020	8250	8470	8530	8720
ACN	6240	6030	6340	6640	6730
DMF	5570	5800	5940	6920	6390
DMSO	5960	5970	6100	6750	6550

a. Data taken from ref.[1]

Table S6. Stokes shift values of **FR8**, **FR1**, **FR1TP**, **FR2TP** and **FR1TM**.

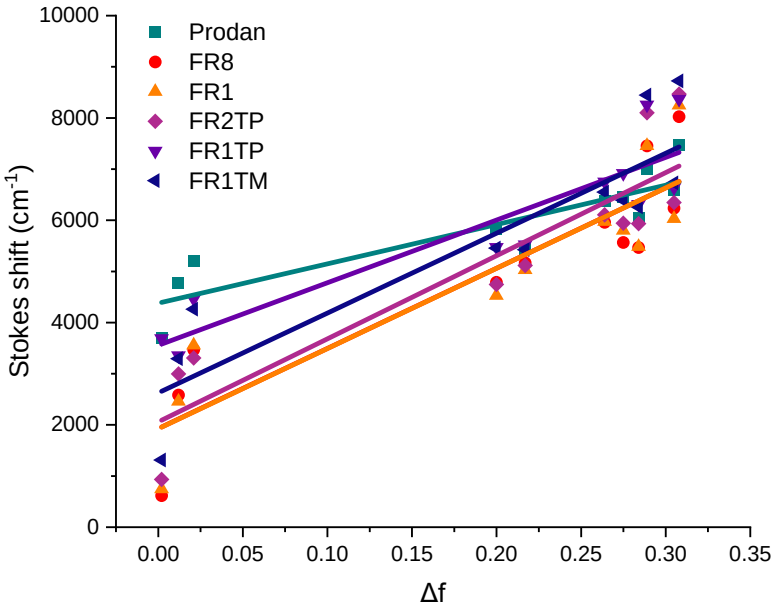


Fig. S26. Lippert-Mataga plots (*i.e.*, Stokes shift *vs.* orientation polarizability function of solvent) and the linear fits for **Prodan**, **FR8**, **FR1**, **FR2TP**, **FR1TP** and **FR1TM**. Data of **Prodan** and **FR8** was taken from reference [1].

	Slope	Intersection	χ^2	Onsager radius (Å)	Δμ (D)
Prodan[a]	7685	4377	0.80	-	7
FR8[a]	15682	1924	0.83	-	14
FR1	15697	1920	0.82	5.59	16
FR2TP	16244	2056	0.83	6.25	20
FR1TP	12249	3552	0.83	6.14	17
FR1TM	15613	2623	0.81	6.28	20

a. Data taken from ref.[1]; b. Calculated by DFT at the mPW1PW91/6-31+G(d) level or theory.

Table S7. Parameters of the linear fitting of Lippert-Mataga plots and calculated transition dipole moments for **Prodan**, **FR8**, **FR1**, **FR2TP**, **FR1TP** and **FR1TM**.

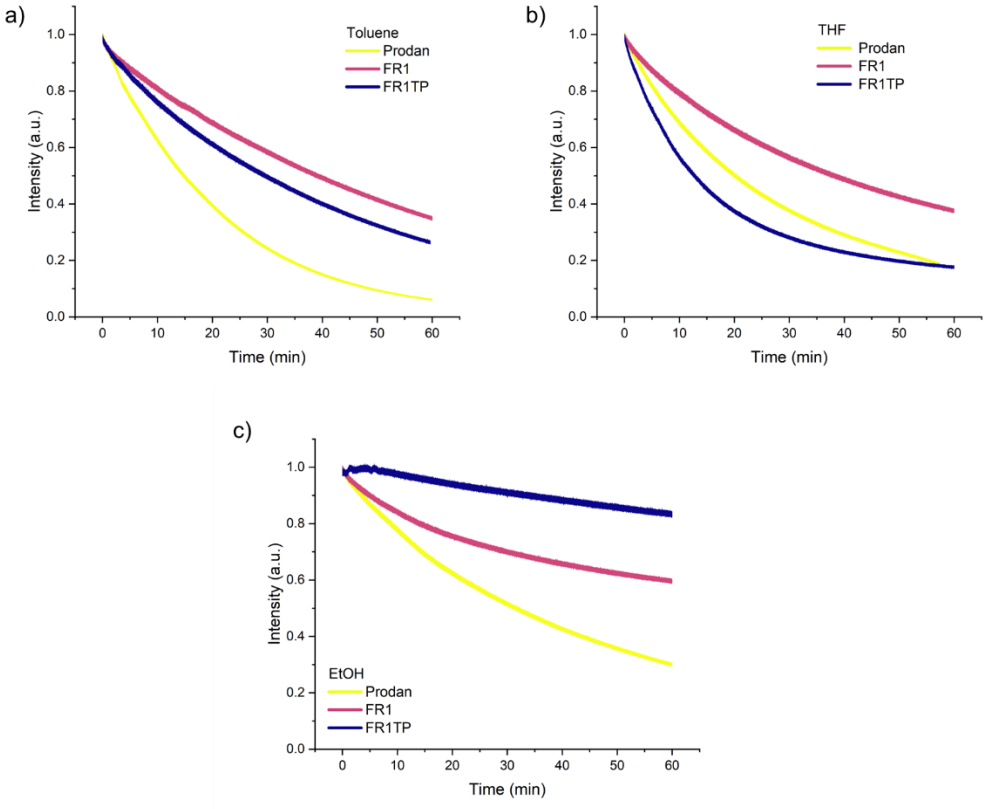


Fig. S27. Photodegradation decay curves *vs.* time of **Prodan**, **FR1** and **FR1TP** in a) toluene, b) THF and c) EtOH. (Irradiation with 365 nm LED as light source).

	Prodan		FR1		FR1TP	
	k (min)	*R* (%)	*k* (min)	*R* (%)	*k* (min)	*R* (%)
Toluene	22	6	62	35	45	27
THF	26	18	37	38	14	18
EtOH	35	30	28	60	-	84

Table S8. Photodegradation constant (*k*) and remaining fluorescence intensity (*R*) after 1 hour irradiation for **Prodan**, **FR1** and **FR1TP**.

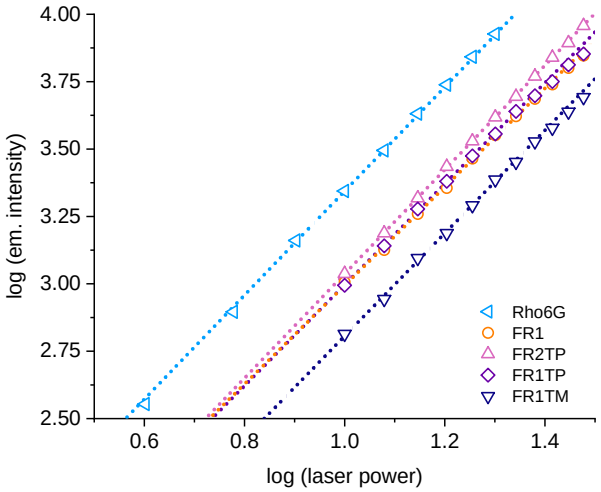


Fig. S28. Double logarithmic plot of the two-photon excited fluorescence *vs.* laser power of **FR1**, **FR2TP**, **FR1TP**, **FR1TM** and **Rho6G** (included as standard).

	Slope	χ^2
Rho6G	1.93±0.01	1.00
FR1	1.83±0.05	1.00
FR2TP	1.93±0.01	1.00
FR1TP	1.87±0.02	1.00
FR1TM	1.91±0.04	1.00

Table S9. Slope of the double logarithmic plot of the two-photon excited fluorescence vs. laser power of **FR1**, **FR2TP**, **FR1TP**, **FR1TM** and **Rho6G** (included as standard) and their associated correlation coefficient χ^2.

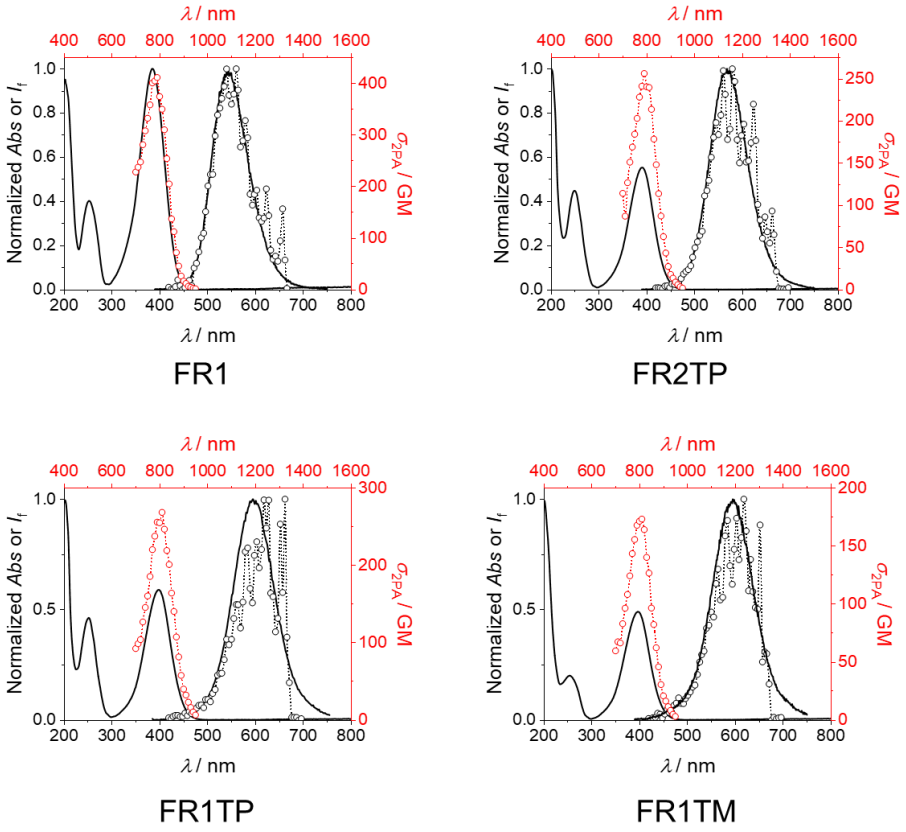


Fig. S29. Comparison between absorption and emission spectra of **FR1**, **FR2TP**, **FR1TP** and **FR1TM** obtained under different excitation conditions. Black solid lines represent one-photon absorption (left) and fluorescence (right) spectra of the compounds. Dotted lines relate to the two-photon absorption (red) and the two-photon induced emission (black) spectra. Fluorescence was recorded either upon one-photon excitation at 380 nm or two-photon excitation at 800 nm.

5. DFT calculations

	Absorption				Emission				$\Delta E_{HOMO-LUMO}$ (eV) [e]	$\Delta\mu$ (D) [f]
	f [a]	HOMO→LUMO contribution (%) [b]	E_{calc} (eV) [c]	E_{exp} (eV) [d]	f [a]	LUMO→HOMO contribution (%) [b]	E_{calc} (eV) [c]	E_{exp} (eV) [d]		
FR1	0.730	99	3.40	3.27	0.790	99	3.26	3.17	3.86	9.8
FR2TP	0.665	99	3.20	3.16	0.660	98	3.04	3.03	3.64	11.6
FR1TP	0.700	99	3.13	3.09	0.709	99	3.00	2.93	3.55	11.9
FR1TM	0.700	99	3.14	3.10	0.711	99	3.01	2.94	3.56	11.8

a. Oscillator strength; b. Percentage contribution approximated by $2c_i^2 \times 100\%$; c. Calculated energies in the vacuum; d. Experimental energies determined in hexane (measured in optically diluted air-equilibrated solution); e. HOMO-LUMO energy band gap; g. Dipole moment change between first excited state and ground state calculated at the mPW1PW91/6-311+G(2d,p) level of theory.

Table S10. Calculated electronic properties of **FR1**, **FR1TP**, **FR2TP** and **FR1TM** at the mPW1PW91/6-311+G(2d.p) level of theory corresponding to the $S_0 \rightarrow S_1$ (absorption) and $S_1 \rightarrow S_0$ (emission) transitions.

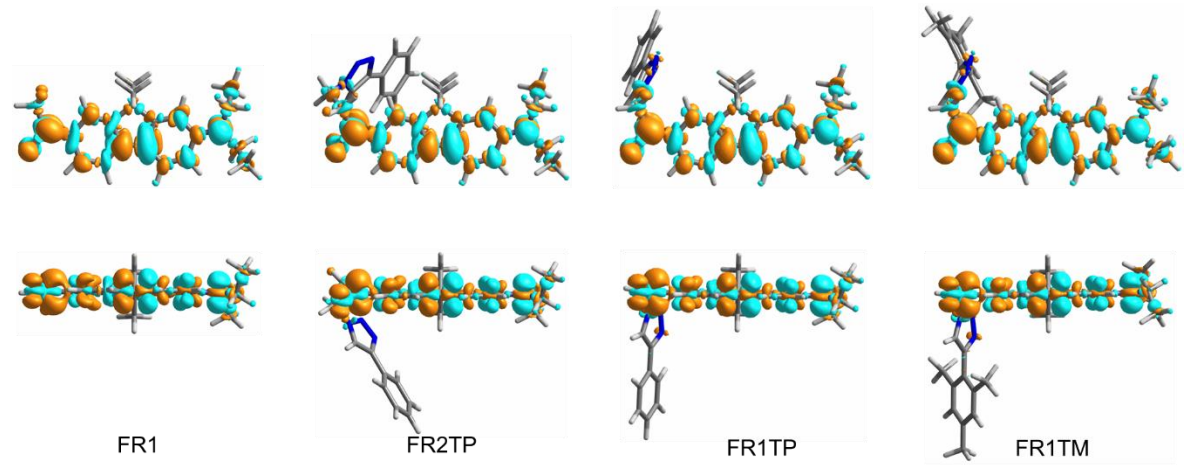


Fig. S30. Electronic Density Difference (EDD) plots at mPW1MP91/6-311+G(2d,p)//mPW1PW91/6-31+G(d) level between the first excited state (S_1) and the ground state (S_0) of **FR1**, **FR2TP**, **FR1TP** and **FR1TM**. The cyan and orange lobes represent region of decrease and increase of electronic density upon excitation. Contour threshold: 0.0015 au.

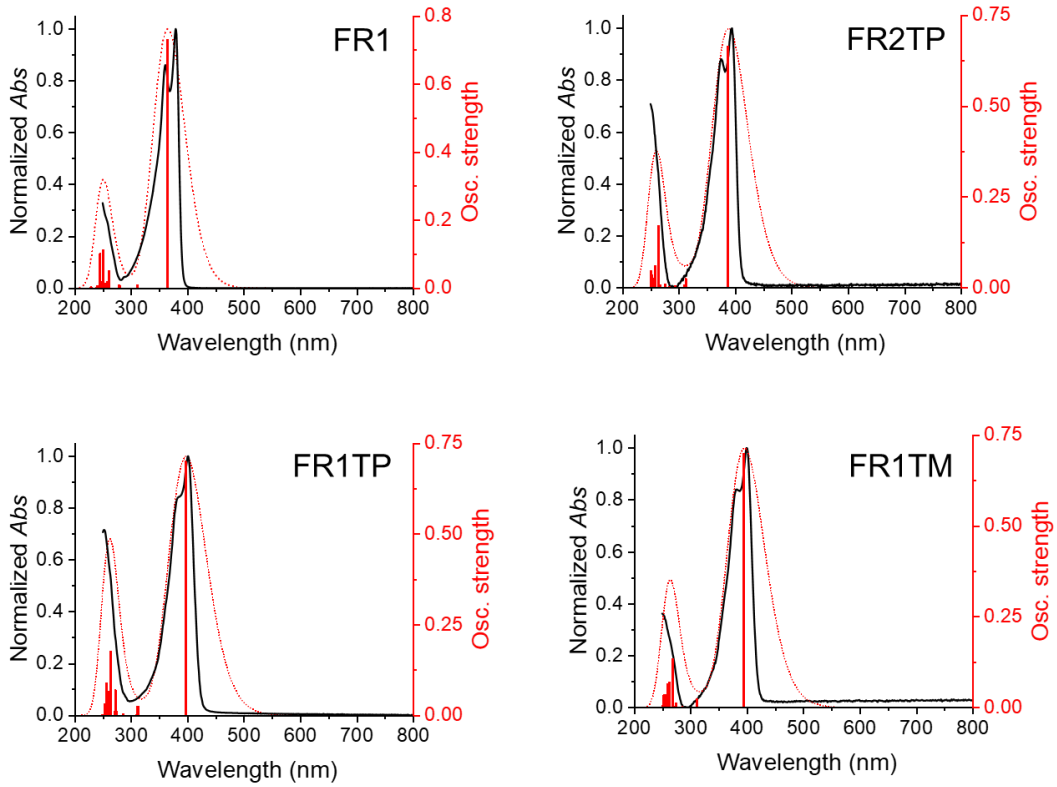


Fig. S31. Comparison between experimental absorption spectra of **FR1**, **FR1TP**, **FR2TP** and **FR1TM** in hexane (black solid lines) and simulated ones at the mPW1PW91/6-311+G(2d,p) level (red dotted lines). Oscillator strengths, calculated at the same theory level, are indicated as red bars for the first electronic transitions in each case.

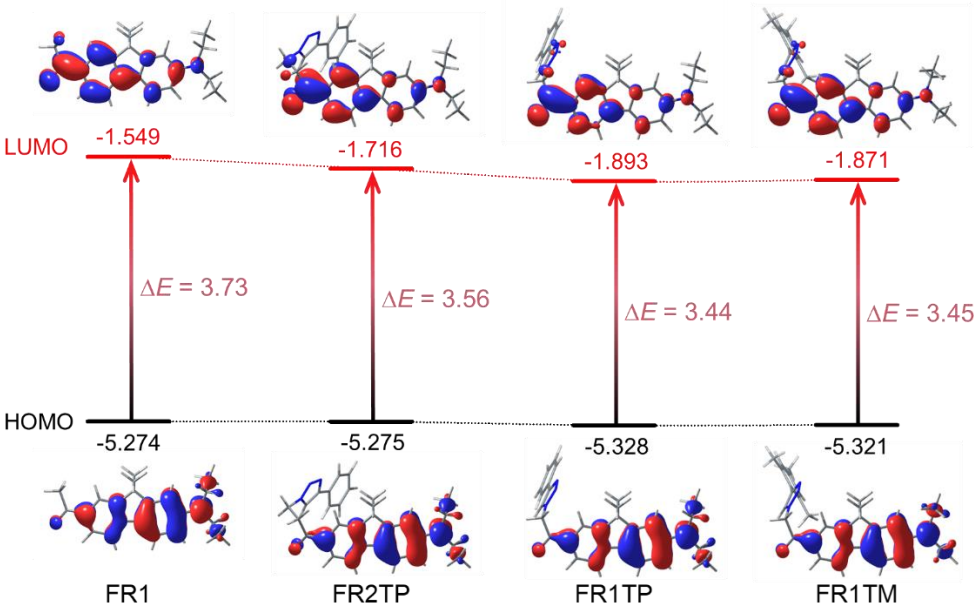


Fig. S32. Frontier molecular orbitals contour plots and energies for **FR1**, **FR2TP**, **FR1TP** and **FR1TM** at the SMD(toluene)/mPW1PW91/6-311+G(2d,p)//SMD(toluene)/mPW1PW91/6-31+G(d) level. Isosurface value: 0.03 a.u.

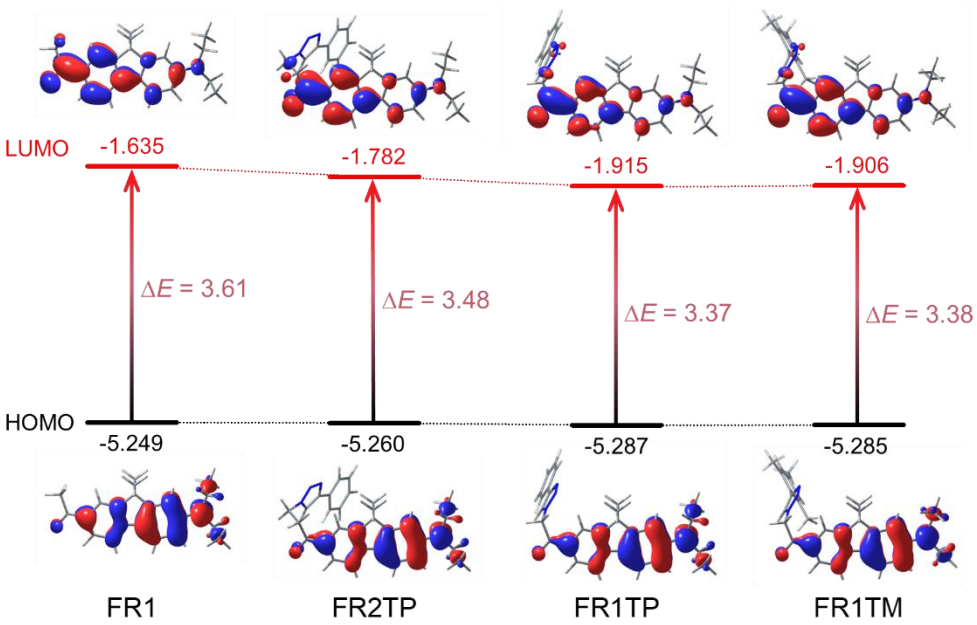


Fig. S33. Frontier molecular orbitals contour plots and energies for **FR1**, **FR2TP**, **FR1TP** and **FR1TM** at the SMD(dichloromethane)/mPW1PW91/6-311+G(2d,p)//SMD(dichloromethane)/mPW1PW91/6-31+G(d) level. Isosurface value: 0.03 a.u.

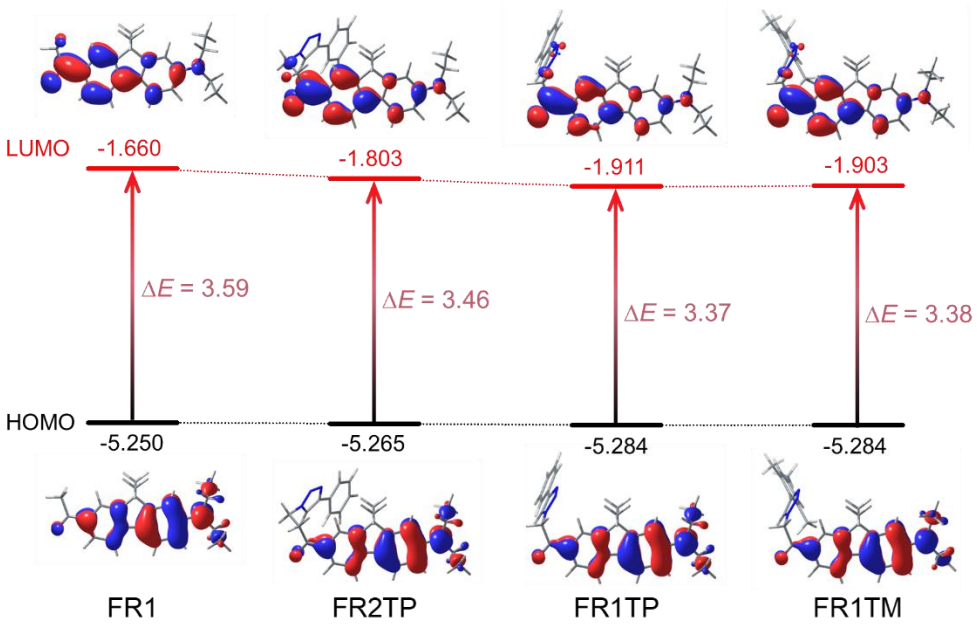


Fig. S34. Frontier molecular orbitals contour plots and energies for **FR1**, **FR2TP**, **FR1TP** and **FR1TM** at the SMD(acetonitrile)/mPW1PW91/6-311+G(2d,p)//SMD(acetonitrile)/mPW1PW91/6-31+G(d) level. Isosurface value: 0.03 a.u.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-4.09917	-0.41464	-0.03717
2	C	-3.63379	-1.72871	-0.20186
3	H	-4.37012	-2.51964	-0.29771
4	C	-2.27595	-2.01192	-0.24149
5	H	-1.9364	-3.03557	-0.36994
6	C	-1.36041	-0.96363	-0.11401
7	C	-1.81571	0.35819	0.05152
8	C	-3.17062	0.63357	0.08984
9	H	-3.5152	1.65578	0.21762
10	C	0.09519	-0.95138	-0.11744
11	C	0.53683	0.37087	0.04709
12	C	-0.64474	1.32344	0.16785
13	C	1.03853	-1.96863	-0.2498
14	H	0.73094	-3.00343	-0.37217
15	C	2.39212	-1.66743	-0.21447
16	H	3.09974	-2.48301	-0.29517
17	C	2.85487	-0.33745	-0.0535
18	C	1.88306	0.6843	0.07599
19	H	2.18621	1.71986	0.17916
20	C	-0.6533	2.3526	-0.97296
21	H	-0.65231	1.85769	-1.94811
22	H	0.22787	3.00049	-0.91591
23	H	-1.54202	2.98965	-0.91218
24	C	-0.64516	2.04145	1.5263
25	H	-1.53273	2.67479	1.62871
26	H	0.23765	2.6821	1.62475
27	H	-0.64005	1.32245	2.35023
28	N	4.20307	-0.05048	-0.0234
29	C	5.20867	-1.06141	-0.29356
30	H	4.84535	-1.73565	-1.07553
31	H	6.07783	-0.5525	-0.72505
32	C	5.64081	-1.85095	0.94052
33	H	4.79572	-2.37829	1.39138
34	H	6.06188	-1.1858	1.70113
35	H	6.40587	-2.58891	0.67639
36	C	4.69435	1.27951	0.28392
37	H	4.05155	1.73794	1.04229
38	H	5.67497	1.16621	0.75951
39	C	4.82174	2.19043	-0.93573
40	H	5.51418	1.76515	-1.66911
41	H	5.20278	3.17469	-0.64283
42	H	3.85705	2.32862	-1.43166
43	C	-5.56868	-0.18483	-0.00381
44	C	-6.08482	1.22721	0.1742
45	H	-7.17481	1.20255	0.17509
46	H	-5.74021	1.87898	-0.63569

47	H	-5.73375	1.66037	1.11685
48	O	-6.35455	-1.11311	-0.11711

Table S11. Atomic coordinates for the ground state (S_0) of compound **FR1** at the mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-4.10179	-0.41678	-0.03788
2	C	-3.63467	-1.73104	-0.20324
3	H	-4.3661	-2.5265	-0.30062
4	C	-2.27684	-2.01462	-0.24295
5	H	-1.93766	-3.03837	-0.37233
6	C	-1.36051	-0.96579	-0.11422
7	C	-1.81714	0.35683	0.05266
8	C	-3.17199	0.63208	0.09012
9	H	-3.51652	1.65407	0.21766
10	C	0.09428	-0.95318	-0.11797
11	C	0.53592	0.37028	0.04812
12	C	-0.64635	1.32273	0.17142
13	C	1.03906	-1.97071	-0.25219
14	H	0.732	-3.00582	-0.37526
15	C	2.39216	-1.66897	-0.21805
16	H	3.10052	-2.48379	-0.30029
17	C	2.85607	-0.33714	-0.05573
18	C	1.88199	0.68492	0.07652
19	H	2.1849	1.72034	0.1812
20	C	-0.65548	2.35674	-0.96422
21	H	-0.65446	1.86975	-1.94398
22	H	0.2256	3.00472	-0.90403
23	H	-1.5439	2.99431	-0.90022
24	C	-0.64753	2.0383	1.53083
25	H	-1.5349	2.67211	1.63416
26	H	0.23472	2.67977	1.63021
27	H	-0.64215	1.32073	2.35675
28	N	4.20077	-0.05114	-0.02744
29	C	5.20926	-1.06419	-0.29059
30	H	4.84829	-1.74551	-1.06703
31	H	6.07697	-0.55496	-0.72334
32	C	5.64059	-1.84168	0.9495
33	H	4.79883	-2.37373	1.40229
34	H	6.05772	-1.17004	1.70719
35	H	6.41075	-2.57684	0.6905
36	C	4.6957	1.28023	0.27819
37	H	4.05273	1.74358	1.03288
38	H	5.67483	1.1631	0.7546
39	C	4.82971	2.18505	-0.94328
40	H	5.52092	1.75467	-1.67541
41	H	5.21845	3.16677	-0.65013

42	H	3.8671	2.33363	-1.44133
43	C	-5.56892	-0.18125	-0.00422
44	C	-6.07845	1.23059	0.166
45	H	-7.16925	1.21588	0.16913
46	H	-5.73216	1.87597	-0.64853
47	H	-5.72432	1.66822	1.1056
48	O	-6.35984	-1.10982	-0.1126

Table S12. Atomic coordinates for the ground state (S_0) of compound **FR1** at the SMD(toluene)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-4.10328	-0.41773	-0.03752
2	C	-3.63558	-1.7332	-0.20205
3	H	-4.3636	-2.53211	-0.29966
4	C	-2.27744	-2.01786	-0.24133
5	H	-1.93733	-3.04148	-0.36999
6	C	-1.36102	-0.96757	-0.11274
7	C	-1.8183	0.35608	0.05395
8	C	-3.17301	0.63232	0.09101
9	H	-3.51615	1.65466	0.21784
10	C	0.09284	-0.95498	-0.11658
11	C	0.53441	0.36989	0.04968
12	C	-0.64795	1.32206	0.1725
13	C	1.03823	-1.97379	-0.25137
14	H	0.73028	-3.00883	-0.37439
15	C	2.39149	-1.67162	-0.21768
16	H	3.10063	-2.48583	-0.30097
17	C	2.85591	-0.33748	-0.05478
18	C	1.88028	0.68577	0.07852
19	H	2.18211	1.72139	0.18427
20	C	-0.65751	2.35651	-0.96296
21	H	-0.65616	1.87001	-1.94344
22	H	0.22424	3.00307	-0.8997
23	H	-1.54703	2.99207	-0.89617
24	C	-0.64989	2.03987	1.53087
25	H	-1.53809	2.67302	1.62966
26	H	0.23297	2.68089	1.62629
27	H	-0.64475	1.32388	2.35871
28	N	4.19754	-0.05189	-0.02691
29	C	5.20942	-1.06452	-0.28987
30	H	4.84652	-1.75299	-1.05857
31	H	6.07205	-0.55273	-0.72854
32	C	5.64932	-1.83097	0.95346
33	H	4.81358	-2.37179	1.40783
34	H	6.06124	-1.1502	1.706
35	H	6.42664	-2.55849	0.69431

36	C	4.69502	1.28184	0.27451
37	H	4.05108	1.75079	1.02434
38	H	5.67307	1.16174	0.75133
39	C	4.83335	2.17897	-0.95149
40	H	5.51961	1.73809	-1.68223
41	H	5.23218	3.15739	-0.66099
42	H	3.86957	2.33666	-1.44514
43	C	-5.56807	-0.17758	-0.00554
44	C	-6.07424	1.23212	0.16703
45	H	-7.16534	1.22316	0.17309
46	H	-5.72482	1.87576	-0.64748
47	H	-5.71294	1.66754	1.10481
48	O	-6.36203	-1.10765	-0.11857

Table S13. Atomic coordinates for the ground state (S_0) of compound **FR1** at the SMD(dichloromethane)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-4.10335	-0.41789	-0.03739
2	C	-3.63579	-1.73362	-0.2029
3	H	-4.36305	-2.53331	-0.30065
4	C	-2.27757	-2.01915	-0.24314
5	H	-1.93725	-3.04267	-0.37242
6	C	-1.36099	-0.96867	-0.11425
7	C	-1.81828	0.35518	0.05316
8	C	-3.17283	0.63233	0.0912
9	H	-3.51438	1.65498	0.21899
10	C	0.09266	-0.9561	-0.11791
11	C	0.53394	0.36927	0.04926
12	C	-0.64836	1.32109	0.17139
13	C	1.03846	-1.9751	-0.25284
14	H	0.7303	-3.01005	-0.37669
15	C	2.39182	-1.67258	-0.21808
16	H	3.1012	-2.48664	-0.30199
17	C	2.85593	-0.33754	-0.05385
18	C	1.87954	0.68598	0.07953
19	H	2.18029	1.72177	0.1866
20	C	-0.65815	2.35499	-0.96453
21	H	-0.65658	1.86808	-1.94504
22	H	0.22374	3.00113	-0.90027
23	H	-1.54836	2.98932	-0.89691
24	C	-0.65089	2.04071	1.52858
25	H	-1.54002	2.67283	1.62494
26	H	0.23201	2.68196	1.62176
27	H	-0.64546	1.32589	2.35772
28	N	4.19628	-0.0516	-0.02466
29	C	5.20969	-1.06346	-0.28769

30	H	4.84698	-1.75375	-1.05466
31	H	6.07114	-0.55026	-0.72653
32	C	5.6508	-1.82679	0.95677
33	H	4.81662	-2.37147	1.4098
34	H	6.05944	-1.14297	1.70837
35	H	6.43126	-2.55119	0.69848
36	C	4.6936	1.28345	0.27457
37	H	4.04817	1.75506	1.02121
38	H	5.67101	1.16346	0.75236
39	C	4.83329	2.17567	-0.95445
40	H	5.51861	1.73005	-1.68329
41	H	5.23452	3.1539	-0.66683
42	H	3.86897	2.33473	-1.44691
43	C	-5.56795	-0.17623	-0.004
44	C	-6.07107	1.23341	0.1698
45	H	-7.16225	1.22837	0.17548
46	H	-5.71794	1.87708	-0.64307
47	H	-5.70754	1.66657	1.10776
48	O	-6.36279	-1.10644	-0.11687

Table S14. Atomic coordinates for the ground state (S_0) of compound **FR1** at the SMD(acetonitrile)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-4.6231	0.0162	0.18035
2	C	-4.45397	-0.66654	1.41176
3	H	-5.27557	-0.73284	2.11386
4	C	-3.25714	-1.28274	1.74369
5	H	-3.1744	-1.79653	2.69745
6	C	-2.18551	-1.24711	0.8526
7	C	-2.33771	-0.57918	-0.37354
8	C	-3.52331	0.04554	-0.71132
9	H	-3.59485	0.57498	-1.65429
10	C	-0.83969	-1.79165	0.92408
11	C	-0.16327	-1.46427	-0.26704
12	C	-1.05477	-0.64671	-1.18955
13	C	-0.1894	-2.52039	1.92575
14	H	-0.70008	-2.77638	2.84942
15	C	1.12581	-2.91008	1.72707
16	H	1.66128	-3.46392	2.491
17	C	1.8036	-2.60696	0.53262
18	C	1.13986	-1.87665	-0.47159
19	H	1.65377	-1.60499	-1.38863
20	C	-1.27858	-1.3584	-2.53242
21	H	-1.97576	-0.79036	-3.15726
22	H	-1.69027	-2.3608	-2.38388
23	H	-0.33601	-1.44949	-3.082

24	C	-0.46914	0.75526	-1.42515
25	H	-1.14845	1.35536	-2.03993
26	H	0.49193	0.6949	-1.94493
27	H	-0.31123	1.27941	-0.4786
28	N	-5.81623	0.62825	-0.13604
29	C	-6.90362	0.73089	0.8198
30	H	-6.49342	0.89281	1.82156
31	H	-7.46476	1.6413	0.58155
32	C	-6.05259	1.21168	-1.44362
33	H	-5.57273	0.59347	-2.20896
34	H	-7.12786	1.14486	-1.64335
35	C	-5.60048	2.66571	-1.56402
36	H	-5.81099	3.05192	-2.56708
37	H	-4.52825	2.76623	-1.37501
38	H	-6.12599	3.29841	-0.8417
39	C	-7.84976	-0.4681	0.81196
40	H	-7.32084	-1.39378	1.05473
41	H	-8.30878	-0.59593	-0.17352
42	H	-8.65314	-0.32861	1.54324
43	C	3.21271	-3.03458	0.40831
44	O	3.86468	-3.38819	1.38352
45	C	3.90389	-3.04747	-0.95096
46	H	4.30931	-4.0571	-1.07848
47	H	3.22965	-2.85463	-1.78628
48	C	5.07664	-2.06813	-0.99241
49	H	5.6362	-2.1811	-1.92281
50	H	5.7481	-2.24903	-0.15111
51	N	4.63827	-0.6851	-0.92661
52	N	4.18936	-0.07369	-2.02967
53	N	3.80142	1.11655	-1.69045
54	C	3.98639	1.29286	-0.35116
55	C	4.52789	0.12325	0.14858
56	H	4.83781	-0.18909	1.13329
57	C	3.64418	2.54518	0.32676
58	C	3.3447	3.68874	-0.4246
59	H	3.36965	3.62614	-1.50712
60	C	3.02325	4.88427	0.20928
61	H	2.79527	5.76255	-0.3874
62	C	2.99733	4.96025	1.60103
63	H	2.74798	5.89491	2.09398
64	C	3.29206	3.8262	2.3557
65	H	3.26867	3.87167	3.44034
66	C	3.60978	2.62809	1.72431
67	H	3.82034	1.74835	2.32552

Table S15. Atomic coordinates for the ground state (S_0) of compound **FR2TP** at the mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-4.79823	0.23127	0.21653
2	C	-4.65756	-0.47683	1.4396
3	H	-5.48073	-0.51493	2.14217
4	C	-3.49011	-1.15201	1.76037
5	H	-3.43038	-1.68304	2.70655
6	C	-2.41767	-1.15251	0.86762
7	C	-2.5407	-0.45917	-0.349
8	C	-3.69687	0.22366	-0.67682
9	H	-3.74552	0.76954	-1.61176
10	C	-1.09882	-1.75953	0.9282
11	C	-0.40816	-1.4453	-0.25933
12	C	-1.26228	-0.57354	-1.1683
13	C	-0.48128	-2.53501	1.91657
14	H	-1.00197	-2.78344	2.8368
15	C	0.81404	-2.98221	1.70796
16	H	1.31815	-3.57563	2.46359
17	C	1.50639	-2.69102	0.51801
18	C	0.87475	-1.91342	-0.47256
19	H	1.39723	-1.65347	-1.38767
20	C	-1.51853	-1.25044	-2.52272
21	H	-2.18641	-0.63869	-3.13861
22	H	-1.97865	-2.23501	-2.39474
23	H	-0.58084	-1.37799	-3.07403
24	C	-0.61258	0.80228	-1.38498
25	H	-1.2637	1.44392	-1.98837
26	H	0.34209	0.70291	-1.91151
27	H	-0.42414	1.30664	-0.43259
28	N	-5.96077	0.8979	-0.08812
29	C	-7.04397	1.03515	0.87123
30	H	-6.62871	1.16423	1.87536
31	H	-7.56354	1.97178	0.64315
32	C	-6.1741	1.51663	-1.38561
33	H	-5.7204	0.89621	-2.16455
34	H	-7.25146	1.498	-1.58168
35	C	-5.66476	2.95214	-1.47549
36	H	-5.86325	3.36616	-2.47041
37	H	-4.58814	3.00891	-1.29046
38	H	-6.16348	3.59143	-0.73948
39	C	-8.041	-0.1194	0.84503
40	H	-7.55857	-1.07231	1.0815
41	H	-8.50304	-0.21549	-0.1431
42	H	-8.8401	0.04982	1.57546
43	C	2.892	-3.18759	0.38046
44	O	3.52178	-3.59933	1.34953
45	C	3.57358	-3.22352	-0.98148
46	H	3.84376	-4.27106	-1.15757

47	H	2.9253	-2.91579	-1.80222
48	C	4.86481	-2.40846	-1.00647
49	H	5.4126	-2.59723	-1.93157
50	H	5.50245	-2.67101	-0.1612
51	N	4.61391	-0.97687	-0.94183
52	N	4.18411	-0.32524	-2.02686
53	N	4.00536	0.91832	-1.6968
54	C	4.3159	1.08955	-0.38149
55	C	4.71101	-0.14156	0.11123
56	H	5.04304	-0.47823	1.08066
57	C	4.21917	2.39214	0.28359
58	C	3.90641	3.53875	-0.45873
59	H	3.7368	3.44691	-1.52624
60	C	3.81567	4.77986	0.16319
61	H	3.57249	5.65821	-0.42764
62	C	4.03647	4.89967	1.53462
63	H	3.9656	5.86918	2.01846
64	C	4.34774	3.76386	2.28063
65	H	4.51888	3.84371	3.35012
66	C	4.43693	2.52097	1.66172
67	H	4.67263	1.64517	2.25921

Table S16. Atomic coordinates for the ground state (S_0) of compound **FR2TP** at the SMD(toluene)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-4.81071	0.24121	0.20317
2	C	-4.67095	-0.46244	1.43159
3	H	-5.49402	-0.49411	2.13473
4	C	-3.50533	-1.14012	1.75491
5	H	-3.44553	-1.6673	2.70341
6	C	-2.43253	-1.14754	0.86051
7	C	-2.55457	-0.45983	-0.36066
8	C	-3.70843	0.22538	-0.69225
9	H	-3.75568	0.76557	-1.63054
10	C	-1.11583	-1.75732	0.92337
11	C	-0.42374	-1.45018	-0.26621
12	C	-1.27785	-0.58473	-1.18118
13	C	-0.50085	-2.53195	1.91526
14	H	-1.02368	-2.77654	2.83544
15	C	0.79359	-2.98353	1.70728
16	H	1.29128	-3.57915	2.46567
17	C	1.48981	-2.69595	0.51742
18	C	0.85922	-1.92028	-0.47672
19	H	1.37933	-1.66908	-1.39532
20	C	-1.53854	-1.27382	-2.52886
21	H	-2.2047	-0.66332	-3.14771

22	H	-2.00262	-2.2555	-2.39059
23	H	-0.60054	-1.41047	-3.07747
24	C	-0.62631	0.78721	-1.41498
25	H	-1.28079	1.4226	-2.02109
26	H	0.32397	0.6759	-1.94742
27	H	-0.43041	1.30069	-0.46847
28	N	-5.96868	0.90888	-0.1031
29	C	-7.05565	1.05143	0.85449
30	H	-6.64388	1.17567	1.86026
31	H	-7.56827	1.9904	0.62272
32	C	-6.18259	1.52527	-1.40406
33	H	-5.72807	0.90481	-2.182
34	H	-7.2601	1.5063	-1.5963
35	C	-5.67412	2.96051	-1.49509
36	H	-5.88149	3.37311	-2.48877
37	H	-4.59535	3.01656	-1.32082
38	H	-6.16958	3.59747	-0.75468
39	C	-8.05806	-0.09762	0.82154
40	H	-7.58324	-1.05204	1.06861
41	H	-8.51083	-0.19191	-0.17117
42	H	-8.86209	0.08079	1.5443
43	C	2.87387	-3.19826	0.38178
44	O	3.48558	-3.64092	1.35164
45	C	3.57252	-3.2072	-0.96946
46	H	3.83224	-4.25381	-1.16604
47	H	2.93687	-2.8754	-1.79048
48	C	4.87872	-2.41482	-0.96808
49	H	5.44054	-2.62008	-1.8805
50	H	5.49643	-2.68155	-0.10966
51	N	4.65923	-0.97574	-0.92015
52	N	4.34857	-0.3082	-2.03436
53	N	4.17158	0.94034	-1.71282
54	C	4.36302	1.09478	-0.3732
55	C	4.68099	-0.14948	0.143
56	H	4.92155	-0.4966	1.13578
57	C	4.23876	2.39281	0.29703
58	C	4.12751	3.5702	-0.45589
59	H	4.13541	3.51251	-1.53942
60	C	4.01201	4.80525	0.17596
61	H	3.92784	5.70745	-0.42301
62	C	4.00847	4.88732	1.56846
63	H	3.91932	5.85152	2.06005
64	C	4.11839	3.72048	2.32494
65	H	4.11199	3.77133	3.40985
66	C	4.22975	2.48348	1.69613
67	H	4.30107	1.58299	2.2992

Table S17. Atomic coordinates for the ground state (S_0) of compound **FR2TP** at the SMD(dichloromethane)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-4.7707	0.20599	0.21273
2	C	-4.60015	-0.42853	1.4758
3	H	-5.40754	-0.42449	2.19779
4	C	-3.42383	-1.08269	1.81005
5	H	-3.33892	-1.55519	2.7852
6	C	-2.37054	-1.13496	0.89301
7	C	-2.52443	-0.51831	-0.36291
8	C	-3.6893	0.14168	-0.70721
9	H	-3.76098	0.62584	-1.67421
10	C	-1.047	-1.72835	0.96186
11	C	-0.3819	-1.48117	-0.25739
12	C	-1.26631	-0.68336	-1.20403
13	C	-0.40378	-2.44118	1.98243
14	H	-0.90616	-2.64067	2.92471
15	C	0.89165	-2.89006	1.7724
16	H	1.40914	-3.43912	2.55245
17	C	1.56315	-2.65842	0.55563
18	C	0.90396	-1.94517	-0.46673
19	H	1.40201	-1.73907	-1.40852
20	C	-1.55132	-1.46028	-2.49765
21	H	-2.24007	-0.89743	-3.13648
22	H	-1.99989	-2.43614	-2.28502
23	H	-0.62471	-1.62221	-3.05856
24	C	-0.63676	0.67652	-1.5425
25	H	-1.31528	1.26493	-2.16906
26	H	0.29926	0.53769	-2.09345
27	H	-0.42037	1.251	-0.636
28	N	-5.93576	0.85343	-0.10285
29	C	-7.00076	1.04837	0.87103
30	H	-6.56657	1.22508	1.85935
31	H	-7.51834	1.97351	0.59956
32	C	-6.18113	1.3958	-1.43166
33	H	-5.74637	0.73184	-2.18459
34	H	-7.2629	1.36949	-1.59471
35	C	-5.6735	2.82183	-1.61589
36	H	-5.90957	3.17765	-2.62495
37	H	-4.58973	2.88426	-1.47769
38	H	-6.14798	3.49959	-0.89823
39	C	-8.00372	-0.09907	0.9213
40	H	-7.52413	-1.0393	1.21067
41	H	-8.47768	-0.24452	-0.05527
42	H	-8.79131	0.12052	1.65068
43	C	2.95133	-3.15265	0.42071
44	O	3.57307	-3.5639	1.39848

45	C	3.64035	-3.18803	-0.93424
46	H	3.93845	-4.23027	-1.0951
47	H	2.98811	-2.90936	-1.76204
48	C	4.91847	-2.35044	-0.97277
49	H	5.46386	-2.54839	-1.89653
50	H	5.56691	-2.58408	-0.12796
51	N	4.6522	-0.91863	-0.93506
52	N	4.30342	-0.26961	-2.04868
53	N	4.088	0.97464	-1.73206
54	C	4.29233	1.14447	-0.39618
55	C	4.66162	-0.08531	0.12223
56	H	4.92739	-0.41817	1.11351
57	C	4.1283	2.44074	0.26905
58	C	3.83782	3.59102	-0.47927
59	H	3.7373	3.51682	-1.55722
60	C	3.67908	4.82349	0.14913
61	H	3.45313	5.70326	-0.4466
62	C	3.80956	4.93059	1.5342
63	H	3.68605	5.89235	2.02321
64	C	4.10031	3.79145	2.28598
65	H	4.2032	3.86177	3.36494
66	C	4.25665	2.55693	1.66099
67	H	4.47725	1.67975	2.26223

Table S18. Atomic coordinates for the ground state (S_0) of compound **FR2TP** at the SMD(acetonitrile)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-1.24116	-2.72104	-0.17518
2	C	-0.51368	-3.1936	-1.2825
3	H	-0.97645	-3.94309	-1.91572
4	C	0.75904	-2.72071	-1.55886
5	H	1.30606	-3.09828	-2.41763
6	C	1.32077	-1.75329	-0.71802
7	C	0.59848	-1.27237	0.39198
8	C	-0.6682	-1.74892	0.66816
9	H	-1.21743	-1.3617	1.52087
10	C	2.60662	-1.07835	-0.75623
11	C	2.67934	-0.18284	0.32381
12	C	1.40027	-0.22369	1.14754
13	C	3.68787	-1.17603	-1.63141
14	H	3.66613	-1.86357	-2.47238
15	C	4.81572	-0.39674	-1.42704
16	H	5.64842	-0.51283	-2.10923
17	C	4.90383	0.51622	-0.34491
18	C	3.7955	0.60464	0.53259
19	H	3.80535	1.30354	1.3608

20	C	0.68236	1.13565	1.13861
21	H	0.48343	1.46775	0.11585
22	H	1.29558	1.89664	1.63281
23	H	-0.27226	1.07384	1.67017
24	C	1.67719	-0.66425	2.5933
25	H	0.74181	-0.74699	3.15609
26	H	2.3115	0.06815	3.10359
27	H	2.18362	-1.63332	2.6199
28	N	6.02868	1.28759	-0.15519
29	C	6.19143	2.12631	1.01824
30	H	5.7639	1.61917	1.88894
31	H	7.26553	2.20246	1.22039
32	C	5.60001	3.52619	0.86532
33	H	5.76007	4.11258	1.77637
34	H	4.52544	3.48508	0.66745
35	H	6.07093	4.05968	0.03361
36	C	7.11372	1.31385	-1.11931
37	H	6.70286	1.24678	-2.13153
38	H	7.58276	2.30205	-1.05761
39	C	8.16885	0.23316	-0.89268
40	H	8.6251	0.33521	0.09705
41	H	8.96475	0.31046	-1.64108
42	H	7.73333	-0.76776	-0.95623
43	C	-2.58544	-3.27884	0.05718
44	C	-3.43092	-2.76595	1.23385
45	H	-2.88639	-2.81398	2.17942
46	H	-4.31338	-3.40555	1.29751
47	O	-3.07163	-4.14962	-0.649
48	N	-3.83827	-1.38534	1.07195
49	N	-3.50504	-0.46655	1.98978
50	N	-3.98763	0.67002	1.60135
51	C	-4.64575	0.50853	0.41734
52	C	-4.55051	-0.82598	0.07079
53	H	-4.91625	-1.40494	-0.76251
54	C	-5.30212	1.62418	-0.26801
55	C	-5.36809	2.88057	0.34743
56	H	-4.92565	3.00721	1.32943
57	C	-5.99238	3.94637	-0.29172
58	H	-6.03592	4.91402	0.19915
59	C	-6.56179	3.77737	-1.55277
60	H	-7.04967	4.61032	-2.04959
61	C	-6.49939	2.53044	-2.17229
62	H	-6.93662	2.38762	-3.15585
63	C	-5.8735	1.46344	-1.53637
64	H	-5.82629	0.50041	-2.0364

Table S19. Atomic coordinates for the ground state (S_0) of compound **FR1TP** at the mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-1.27911	-2.75427	-0.20315
2	C	-0.54946	-3.20577	-1.31873
3	H	-1.00475	-3.94827	-1.96563
4	C	0.71985	-2.72186	-1.59159
5	H	1.26554	-3.08329	-2.45812
6	C	1.27968	-1.76496	-0.73606
7	C	0.55638	-1.30516	0.38384
8	C	-0.70798	-1.79126	0.65363
9	H	-1.25272	-1.427	1.51899
10	C	2.56247	-1.0857	-0.76511
11	C	2.63437	-0.20721	0.33045
12	C	1.35735	-0.26818	1.15738
13	C	3.64386	-1.16502	-1.64409
14	H	3.62405	-1.83893	-2.49628
15	C	4.76869	-0.38486	-1.42918
16	H	5.60073	-0.48601	-2.11465
17	C	4.85568	0.5136	-0.33207
18	C	3.74719	0.5821	0.55023
19	H	3.75593	1.26861	1.38862
20	C	0.63666	1.08876	1.17975
21	H	0.42683	1.44318	0.1661
22	H	1.25152	1.84187	1.68418
23	H	-0.31331	1.01484	1.71868
24	C	1.63899	-0.73464	2.59364
25	H	0.70516	-0.83177	3.15735
26	H	2.27092	-0.00913	3.11692
27	H	2.14978	-1.70232	2.60467
28	N	5.97398	1.28607	-0.1343
29	C	6.13469	2.1138	1.04987
30	H	5.71106	1.59642	1.91607
31	H	7.20867	2.19346	1.2482
32	C	5.53695	3.51077	0.91149
33	H	5.70042	4.08776	1.8285
34	H	4.46057	3.47051	0.72067
35	H	6.00259	4.05565	0.08361
36	C	7.06377	1.32565	-1.09584
37	H	6.65873	1.26643	-2.11057
38	H	7.52826	2.31434	-1.01989
39	C	8.12072	0.24799	-0.87368
40	H	8.5698	0.33945	0.12082
41	H	8.9221	0.34144	-1.6151
42	H	7.69449	-0.75609	-0.95652
43	C	-2.61672	-3.32686	0.02856
44	C	-3.48968	-2.79658	1.17535
45	H	-2.97715	-2.88752	2.13614
46	H	-4.39731	-3.40222	1.20141

47	O	-3.07092	-4.23741	-0.65137
48	N	-3.84518	-1.39834	1.03296
49	N	-3.55702	-0.52496	2.00626
50	N	-4.00018	0.63616	1.63799
51	C	-4.58765	0.5339	0.41215
52	C	-4.48998	-0.78786	0.01797
53	H	-4.81776	-1.32371	-0.85914
54	C	-5.18753	1.68596	-0.26675
55	C	-5.29193	2.91569	0.3966
56	H	-4.92283	3.00131	1.41308
57	C	-5.86346	4.01354	-0.23864
58	H	-5.93728	4.95934	0.29003
59	C	-6.34146	3.90343	-1.54369
60	H	-6.78823	4.76108	-2.03755
61	C	-6.24079	2.68342	-2.2108
62	H	-6.60687	2.58652	-3.22863
63	C	-5.66732	1.58446	-1.57915
64	H	-5.58833	0.64349	-2.11566

Table S20. Atomic coordinates for the ground state (S_0) of compound **FR1TP** at the SMD(toluene)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-1.33065	-2.72664	-0.2478
2	C	-0.64916	-3.08398	-1.42693
3	H	-1.1305	-3.76975	-2.11663
4	C	0.60774	-2.57488	-1.71454
5	H	1.11496	-2.85787	-2.63224
6	C	1.20719	-1.6955	-0.80343
7	C	0.53441	-1.33386	0.38322
8	C	-0.72217	-1.8361	0.66119
9	H	-1.2258	-1.55226	1.57993
10	C	2.49238	-1.02188	-0.82701
11	C	2.62092	-0.2506	0.34277
12	C	1.37884	-0.37901	1.21419
13	C	3.53436	-1.02517	-1.75761
14	H	3.46891	-1.61508	-2.66799
15	C	4.67653	-0.27708	-1.51915
16	H	5.4774	-0.3182	-2.24693
17	C	4.82297	0.5102	-0.34303
18	C	3.75186	0.50447	0.58972
19	H	3.80429	1.10631	1.48945
20	C	0.67677	0.9758	1.39451
21	H	0.4268	1.42539	0.42842
22	H	1.32387	1.67124	1.93951
23	H	-0.24898	0.85593	1.96661
24	C	1.71468	-0.97848	2.58817

25	H	0.80254	-1.12058	3.17738
26	H	2.3758	-0.30735	3.14659
27	H	2.21452	-1.94714	2.48805
28	N	5.95825	1.24492	-0.11931
29	C	6.18766	1.9463	1.13519
30	H	5.78385	1.35564	1.96269
31	H	7.27057	1.98085	1.29144
32	C	5.62319	3.36309	1.15894
33	H	5.84722	3.8435	2.1179
34	H	4.53763	3.36556	1.0215
35	H	6.06605	3.9728	0.36428
36	C	7.00148	1.38564	-1.12505
37	H	6.54809	1.42745	-2.1196
38	H	7.47006	2.36247	-0.96818
39	C	8.06559	0.2948	-1.06361
40	H	8.55838	0.28479	-0.08569
41	H	8.83207	0.47091	-1.82657
42	H	7.63485	-0.69634	-1.23553
43	C	-2.65397	-3.32477	-0.00117
44	C	-3.53386	-2.80342	1.14045
45	H	-3.03607	-2.93384	2.10462
46	H	-4.45618	-3.38631	1.13875
47	O	-3.08882	-4.25405	-0.67097
48	N	-3.85613	-1.39407	1.02385
49	N	-3.58598	-0.54907	2.02496
50	N	-4.0042	0.62821	1.6708
51	C	-4.55644	0.56092	0.42638
52	C	-4.46265	-0.75323	0.00526
53	H	-4.76962	-1.26433	-0.8943
54	C	-5.12389	1.73282	-0.24758
55	C	-5.18929	2.96664	0.41468
56	H	-4.81524	3.04757	1.42993
57	C	-5.73061	4.08127	-0.21971
58	H	-5.77384	5.02935	0.30847
59	C	-6.21634	3.98392	-1.5236
60	H	-6.63914	4.85411	-2.01683
61	C	-6.15496	2.75958	-2.18942
62	H	-6.52861	2.67198	-3.20543
63	C	-5.61248	1.64362	-1.55863
64	H	-5.56762	0.69881	-2.09226

Table S21. Atomic coordinates for the ground state (S_0) of compound **FR1TP** at the SMD(dichloromethane)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-1.36642	-2.72801	-0.27393
2	C	-0.70034	-3.04794	-1.47231

3	H	-1.18996	-3.71106	-2.17826
4	C	0.55254	-2.52831	-1.76104
5	H	1.04773	-2.78041	-2.69427
6	C	1.16399	-1.67881	-0.82979
7	C	0.50689	-1.3557	0.37683
8	C	-0.74696	-1.86556	0.65459
9	H	-1.23638	-1.61468	1.59047
10	C	2.44972	-1.00589	-0.84775
11	C	2.59409	-0.27355	0.34531
12	C	1.3641	-0.4314	1.22872
13	C	3.4805	-0.98041	-1.79091
14	H	3.40188	-1.5404	-2.71905
15	C	4.62719	-0.24228	-1.54179
16	H	5.41879	-0.26032	-2.28064
17	C	4.78947	0.50627	-0.34172
18	C	3.72906	0.47171	0.60368
19	H	3.79373	1.04173	1.52312
20	C	0.66704	0.9163	1.46867
21	H	0.40278	1.40127	0.52347
22	H	1.32388	1.59	2.02898
23	H	-0.24962	0.77449	2.05046
24	C	1.71903	-1.07975	2.57536
25	H	0.8146	-1.24344	3.17078
26	H	2.38795	-0.42795	3.14718
27	H	2.21727	-2.04417	2.43345
28	N	5.92791	1.23088	-0.10744
29	C	6.16845	1.89911	1.16377
30	H	5.77207	1.28738	1.97934
31	H	7.2526	1.93127	1.30968
32	C	5.60283	3.31389	1.22813
33	H	5.83659	3.76999	2.19654
34	H	4.51561	3.31789	1.10325
35	H	6.03787	3.94286	0.44417
36	C	6.96688	1.39134	-1.11553
37	H	6.50904	1.46343	-2.10622
38	H	7.44425	2.35914	-0.93315
39	C	8.02159	0.29032	-1.08876
40	H	8.51705	0.24961	-0.11292
41	H	8.7867	0.48236	-1.84919
42	H	7.58186	-0.69174	-1.28859
43	C	-2.68459	-3.33884	-0.02573
44	C	-3.57452	-2.81479	1.10582
45	H	-3.09406	-2.97426	2.07468
46	H	-4.50957	-3.37619	1.08031
47	O	-3.10248	-4.28281	-0.68562
48	N	-3.8645	-1.39673	1.00878
49	N	-3.59833	-0.57453	2.02928
50	N	-3.98722	0.61727	1.68692

51	C	-4.51553	0.58102	0.43095
52	C	-4.43857	-0.72775	-0.00992
53	H	-4.73786	-1.21772	-0.92388
54	C	-5.04657	1.77331	-0.23686
55	C	-5.08813	3.00299	0.43542
56	H	-4.72312	3.06777	1.45522
57	C	-5.59537	4.13625	-0.1947
58	H	-5.62077	5.08062	0.34125
59	C	-6.06955	4.06179	-1.50456
60	H	-6.46572	4.94626	-1.99451
61	C	-6.03128	2.84169	-2.18036
62	H	-6.39658	2.77181	-3.20078
63	C	-5.52325	1.70692	-1.55394
64	H	-5.49773	0.76532	-2.09448

Table S22. Atomic coordinates for the ground state (S_0) of compound **FR1TP** at the SMD(acetonitrile)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-0.46021	-2.95925	-0.6217
2	C	0.2818	-3.1501	-1.80134
3	H	-0.12675	-3.80809	-2.561
4	C	1.5018	-2.52087	-1.99081
5	H	2.06127	-2.68172	-2.90758
6	C	1.99479	-1.68022	-0.9865
7	C	1.25746	-1.48159	0.19747
8	C	0.04348	-2.1134	0.38585
9	H	-0.51847	-1.94367	1.29912
10	C	3.21667	-0.89855	-0.90284
11	C	3.2327	-0.21501	0.32444
12	C	1.98116	-0.52519	1.13293
13	C	4.28672	-0.73957	-1.78273
14	H	4.30208	-1.24914	-2.74218
15	C	5.34554	0.08756	-1.44194
16	H	6.14996	0.20988	-2.15624
17	C	5.3795	0.78228	-0.20571
18	C	4.28615	0.60674	0.6774
19	H	4.27546	1.09946	1.64263
20	C	1.14848	0.74268	1.38333
21	H	1.70421	1.44881	2.00933
22	H	0.2134	0.49869	1.89687
23	H	0.90216	1.24223	0.44211
24	C	2.32572	-1.20165	2.46878
25	H	1.41305	-1.47194	3.00955
26	H	2.90339	-0.52368	3.10581
27	H	2.91542	-2.10913	2.31051
28	N	6.43853	1.59929	0.12215

29	C	6.42513	2.42666	1.31469
30	H	7.03667	3.31166	1.10681
31	H	5.41139	2.80316	1.48379
32	C	6.95397	1.72258	2.5627
33	H	6.36017	0.83601	2.80137
34	H	6.927	2.39732	3.42496
35	H	7.99003	1.39997	2.419
36	C	7.63013	1.68081	-0.70294
37	H	8.47073	1.91853	-0.04162
38	H	7.85338	0.69292	-1.11782
39	C	7.54373	2.72547	-1.81374
40	H	8.47317	2.74828	-2.39268
41	H	7.3808	3.72465	-1.39752
42	H	6.71788	2.51178	-2.49775
43	C	-1.74439	-3.67213	-0.49033
44	C	-2.61534	-3.45194	0.75636
45	H	-2.05783	-3.63213	1.67837
46	H	-3.44391	-4.16035	0.6972
47	O	-2.15747	-4.4495	-1.33775
48	N	-3.12989	-2.10153	0.85237
49	N	-2.85087	-1.34246	1.92179
50	N	-3.42114	-0.19153	1.74912
51	C	-4.0833	-0.18427	0.55438
52	C	-3.89666	-1.42134	-0.02729
53	H	-4.24051	-1.85618	-0.95276
54	C	-4.8403	0.98498	0.06565
55	C	-5.9237	1.47874	0.82107
56	C	-6.62964	2.58244	0.34683
57	H	-7.46877	2.95692	0.92943
58	C	-6.2939	3.21718	-0.85076
59	C	-5.21874	2.71345	-1.57836
60	H	-4.93547	3.19638	-2.51096
61	C	-4.4832	1.60772	-1.14327
62	C	-6.33592	0.83024	2.11539
63	H	-6.4924	-0.24664	1.99193
64	H	-7.26659	1.26747	2.48689
65	H	-5.56702	0.95017	2.88377
66	C	-3.32408	1.12498	-1.97636
67	H	-3.57601	0.22202	-2.54411
68	H	-2.4528	0.88408	-1.36089
69	H	-3.02782	1.88879	-2.70041
70	C	-7.06489	4.41873	-1.32583
71	H	-6.78015	4.69971	-2.34344
72	H	-6.88448	5.2851	-0.67917
73	H	-8.14337	4.22923	-1.31822

Table S23. Atomic coordinates for the ground state (S_0) of compound **FR1TM** at the mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-0.50341	-2.99183	-0.66685
2	C	0.22475	-3.13123	-1.86304
3	H	-0.18477	-3.76209	-2.64505
4	C	1.43576	-2.48349	-2.04718
5	H	1.98116	-2.60304	-2.97867
6	C	1.93838	-1.67844	-1.01765
7	C	1.21749	-1.53376	0.18569
8	C	0.00969	-2.17992	0.36513
9	H	-0.53479	-2.05717	1.29619
10	C	3.15482	-0.89144	-0.92245
11	C	3.18744	-0.25903	0.33295
12	C	1.95354	-0.61585	1.15069
13	C	4.20853	-0.68546	-1.81445
14	H	4.2114	-1.15498	-2.79443
15	C	5.26503	0.13772	-1.4588
16	H	6.05565	0.29722	-2.18132
17	C	5.31484	0.78431	-0.19472
18	C	4.23864	0.55892	0.70139
19	H	4.24131	1.01145	1.68609
20	C	1.12004	0.63203	1.48081
21	H	1.68618	1.31159	2.12683
22	H	0.19996	0.35699	2.00625
23	H	0.84454	1.17671	0.57271
24	C	2.32852	-1.35176	2.44602
25	H	1.42843	-1.6528	2.9923
26	H	2.91536	-0.70075	3.1028
27	H	2.9201	-2.2483	2.23697
28	N	6.36716	1.59897	0.14502
29	C	6.36928	2.37802	1.37218
30	H	6.96259	3.27917	1.18474
31	H	5.35456	2.72958	1.58203
32	C	6.94103	1.6325	2.57432
33	H	6.36562	0.72952	2.79834
34	H	6.92926	2.27461	3.46211
35	H	7.97757	1.33074	2.39098
36	C	7.53687	1.74365	-0.70592
37	H	8.38759	1.96704	-0.05357
38	H	7.76785	0.78277	-1.17538
39	C	7.40117	2.83926	-1.75923
40	H	8.31837	2.91128	-2.35435
41	H	7.22647	3.81346	-1.29078
42	H	6.56744	2.64138	-2.43929
43	C	-1.7771	-3.72277	-0.54102
44	C	-2.67396	-3.49566	0.68352
45	H	-2.14175	-3.7213	1.61091
46	H	-3.5259	-4.17189	0.59312

47	O	-2.15793	-4.53023	-1.37792
48	N	-3.14657	-2.13109	0.80444
49	N	-2.91489	-1.43011	1.92145
50	N	-3.45421	-0.25933	1.77266
51	C	-4.04745	-0.18205	0.54565
52	C	-3.8514	-1.39636	-0.08123
53	H	-4.1546	-1.78112	-1.04258
54	C	-4.75327	1.02607	0.0738
55	C	-5.84346	1.53183	0.81414
56	C	-6.49866	2.67417	0.35673
57	H	-7.3418	3.05784	0.92762
58	C	-6.10738	3.33618	-0.80967
59	C	-5.02756	2.82001	-1.5226
60	H	-4.70055	3.3234	-2.4297
61	C	-4.34108	1.67586	-1.10456
62	C	-6.31937	0.8615	2.07482
63	H	-6.46671	-0.21415	1.93117
64	H	-7.2697	1.2913	2.40376
65	H	-5.59563	0.97497	2.88763
66	C	-3.17712	1.1845	-1.92443
67	H	-3.44259	0.30984	-2.5294
68	H	-2.32648	0.8975	-1.29947
69	H	-2.84045	1.96267	-2.61512
70	C	-6.83093	4.57133	-1.27065
71	H	-6.43066	4.93878	-2.2198
72	H	-6.74363	5.37989	-0.53579
73	H	-7.90047	4.37787	-1.40999

Table S24. Atomic coordinates for the ground state (S_0) of compound **FR1TM** at the SMD(toluene)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-0.5112	-2.96	-0.72763
2	C	0.19284	-3.04011	-1.9443
3	H	-0.22779	-3.63489	-2.74862
4	C	1.39671	-2.37686	-2.12451
5	H	1.92311	-2.44814	-3.07182
6	C	1.9184	-1.62002	-1.06727
7	C	1.22162	-1.53448	0.15691
8	C	0.01876	-2.1919	0.32981
9	H	-0.50305	-2.12295	1.27899
10	C	3.13729	-0.83976	-0.95846
11	C	3.19763	-0.27139	0.32728
12	C	1.97909	-0.66617	1.15072
13	C	4.17482	-0.59281	-1.86103
14	H	4.15471	-1.01208	-2.8635
15	C	5.243	0.2062	-1.48451

16	H	6.02074	0.3989	-2.213
17	C	5.32154	0.78767	-0.18819
18	C	4.25952	0.52271	0.71719
19	H	4.28299	0.92356	1.72385
20	C	1.15671	0.56619	1.55802
21	H	1.74135	1.21174	2.22204
22	H	0.24942	0.26473	2.09147
23	H	0.86105	1.15319	0.68281
24	C	2.37697	-1.46372	2.40196
25	H	1.48521	-1.78998	2.94754
26	H	2.97632	-0.84305	3.07643
27	H	2.96343	-2.34978	2.1391
28	N	6.384	1.57545	0.17158
29	C	6.41627	2.2921	1.43805
30	H	7.01121	3.19757	1.28183
31	H	5.40813	2.6348	1.68847
32	C	7.01043	1.48336	2.58672
33	H	6.42965	0.57703	2.78294
34	H	7.02626	2.08375	3.50315
35	H	8.03939	1.18369	2.36132
36	C	7.54433	1.75221	-0.68984
37	H	8.40472	1.93442	-0.03806
38	H	7.75766	0.81561	-1.21314
39	C	7.40382	2.90272	-1.68131
40	H	8.31747	3.00063	-2.27819
41	H	7.23864	3.85061	-1.15832
42	H	6.56502	2.74318	-2.36567
43	C	-1.77103	-3.71338	-0.60238
44	C	-2.68176	-3.49734	0.61142
45	H	-2.15929	-3.75166	1.53718
46	H	-3.54125	-4.16026	0.49982
47	O	-2.12358	-4.54112	-1.43449
48	N	-3.14489	-2.13026	0.75753
49	N	-2.94728	-1.46568	1.90108
50	N	-3.49388	-0.29262	1.77626
51	C	-4.05765	-0.18242	0.53878
52	C	-3.83447	-1.37366	-0.12148
53	H	-4.10872	-1.72959	-1.10282
54	C	-4.76829	1.03383	0.09242
55	C	-5.95022	1.43261	0.7522
56	C	-6.6066	2.58706	0.32432
57	H	-7.52049	2.88865	0.83211
58	C	-6.12685	3.36064	-0.73659
59	C	-4.95831	2.94539	-1.37456
60	H	-4.56571	3.53401	-2.20067
61	C	-4.2676	1.79453	-0.98063
62	C	-6.52166	0.63486	1.89381
63	H	-6.60598	-0.42784	1.64237

64	H	-7.51777	1.0008	2.15759
65	H	-5.89172	0.70073	2.78684
66	C	-3.00788	1.40702	-1.70886
67	H	-3.16192	0.53106	-2.34901
68	H	-2.19677	1.16006	-1.01684
69	H	-2.66914	2.22548	-2.35008
70	C	-6.8492	4.60838	-1.16465
71	H	-6.40973	5.03252	-2.07183
72	H	-6.80825	5.37553	-0.38245
73	H	-7.90803	4.40784	-1.3616

Table S25. Atomic coordinates for the ground state (S_0) of compound **FR1TM** at the SMD(dichloromethane)/mPW1PW91/6-31+G(d) level of theory.

Tag	Symbol	Coordinates (Å)		
		X	Y	Z
1	C	-0.54219	-2.95352	-0.76614
2	C	0.13438	-2.97551	-2.0006
3	H	-0.30009	-3.5363	-2.82192
4	C	1.32896	-2.29426	-2.17954
5	H	1.83324	-2.31768	-3.14122
6	C	1.8705	-1.58234	-1.10125
7	C	1.20197	-1.55689	0.14144
8	C	0.0058	-2.2275	0.31159
9	H	-0.49244	-2.20727	1.27556
10	C	3.08806	-0.80097	-0.98456
11	C	3.17632	-0.29332	0.32506
12	C	1.98057	-0.73485	1.15773
13	C	4.10377	-0.50734	-1.89832
14	H	4.06132	-0.8794	-2.91864
15	C	5.17815	0.27752	-1.50892
16	H	5.93833	0.5071	-2.24528
17	C	5.28528	0.79718	-0.18778
18	C	4.24411	0.48622	0.72823
19	H	4.28845	0.83926	1.75198
20	C	1.16409	0.46967	1.64987
21	H	1.76443	1.08383	2.32938
22	H	0.27449	0.13356	2.19257
23	H	0.84024	1.09838	0.81426
24	C	2.41484	-1.59278	2.35583
25	H	1.5386	-1.95299	2.90513
26	H	3.02763	-1.00235	3.0451
27	H	2.99937	-2.46023	2.03287
28	N	6.35346	1.56936	0.1849
29	C	6.41535	2.22159	1.48532
30	H	7.00742	3.13353	1.36065
31	H	5.41346	2.5496	1.77688
32	C	7.03623	1.35593	2.57659

33	H	6.4573	0.44236	2.74326
34	H	7.07649	1.91095	3.52044
35	H	8.05852	1.06725	2.31009
36	C	7.49592	1.788	-0.69177
37	H	8.36894	1.94133	-0.04976
38	H	7.69861	0.87768	-1.26325
39	C	7.33333	2.98371	-1.62416
40	H	8.23538	3.11215	-2.23272
41	H	7.17688	3.90471	-1.0526
42	H	6.48244	2.85392	-2.29996
43	C	-1.79086	-3.72677	-0.64178
44	C	-2.70961	-3.51767	0.5662
45	H	-2.19669	-3.79808	1.49002
46	H	-3.57886	-4.16419	0.43709
47	O	-2.12423	-4.56543	-1.47068
48	N	-3.15305	-2.14619	0.73355
49	N	-2.95747	-1.50432	1.8897
50	N	-3.48819	-0.32152	1.77954
51	C	-4.03897	-0.18348	0.53917
52	C	-3.82443	-1.3664	-0.13874
53	H	-4.09273	-1.70253	-1.12875
54	C	-4.72891	1.04974	0.1077
55	C	-5.90441	1.45997	0.76919
56	C	-6.54003	2.63305	0.35469
57	H	-7.45174	2.94163	0.86187
58	C	-6.043	3.41254	-0.69222
59	C	-4.88137	2.98242	-1.33697
60	H	-4.47891	3.5728	-2.15728
61	C	-4.21362	1.81482	-0.95779
62	C	-6.49769	0.65748	1.8964
63	H	-6.56775	-0.40574	1.64366
64	H	-7.50222	1.01715	2.13555
65	H	-5.89179	0.72916	2.80577
66	C	-2.96394	1.40844	-1.69271
67	H	-3.13233	0.52664	-2.32079
68	H	-2.14943	1.16095	-1.00446
69	H	-2.62344	2.21719	-2.34507
70	C	-6.72436	4.69056	-1.0964
71	H	-6.566	4.91047	-2.15637
72	H	-6.33045	5.54021	-0.52487
73	H	-7.80153	4.64555	-0.90977

Table S26. Atomic coordinates for the ground state (S_0) of compound **FR1TM** at the SMD(acetonitrile)/mPW1PW91/6-31+G(d) level of theory.

		Energy (Hartree)	Imaginary frequencies
Vacuum	**FR1**	-945.107595	0
	FR2TP	-1456.409608	0
	FR1TP	-1417.099744	0
	FR1TM	-1535.021972	0
Toluene	**FR1**	-945.131480	0
	FR2TP	-1456.445047	0
	FR1TP	-1417.133509	0
	FR1TM	-1535.056876	0
DCM	**FR1**	-945.138311	0
	FR2TP	-1456.457419	0
	FR1TP	-1417.144952	0
	FR1TM	-1535.068553	0
ACN	**FR1**	-945.136764	0
	FR2TP	-1456.455695	0
	FR1TP	-1417.143357	0
	FR1TM	-1535.066463	0

Table S27. Computed energies for optimized geometries at the ground state and imaginary frequencies for all derivatives under study at the mPW1PW91/6-31+G(d) level of theory, with and without considering solvent effects (*vide supra*).

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