Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Novel Chromophores with Condensed 1,2,4-Triazine Simultaneously DIsplaying Thermally Activated Delayed Fluorescence and Crystallization-Induced Phosphorescence.

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Supporting Information

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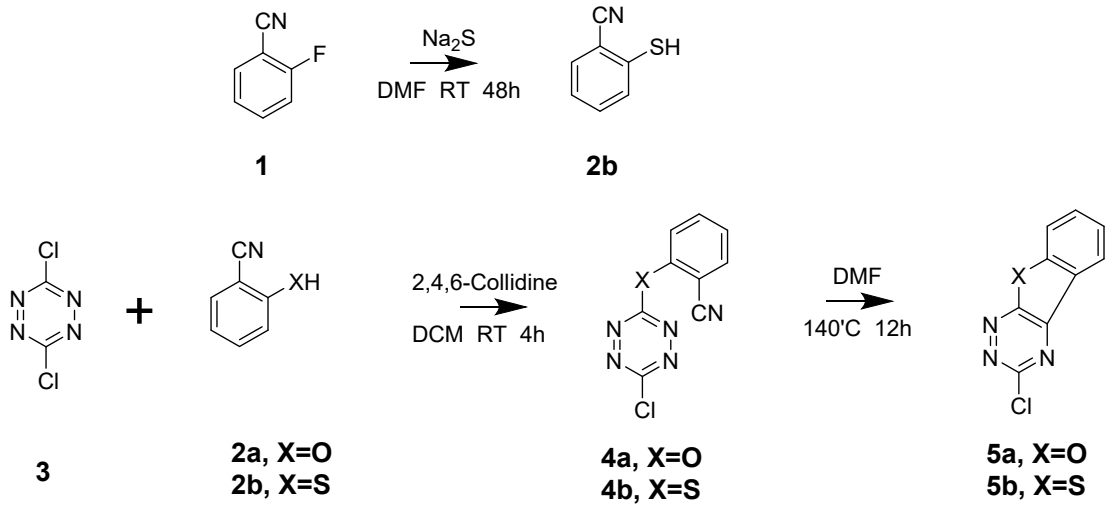
1. Materials and methods

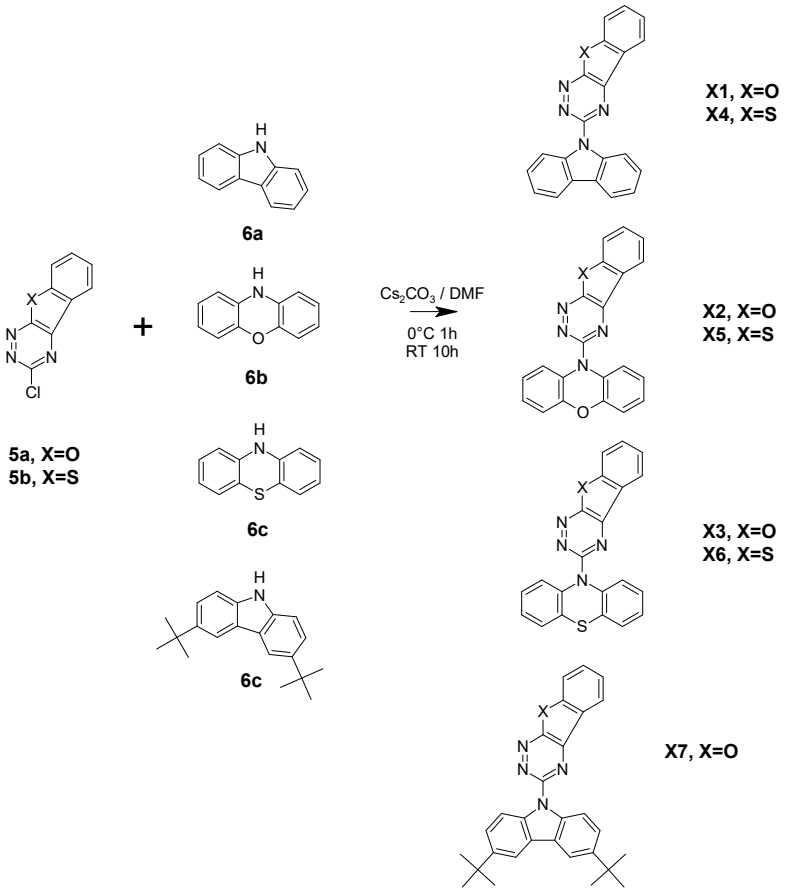
All chemicals were received from commercial sources and used without further purification. Thin layer chromatography (TLC) was performed on silica gel. Solvent for synthesis (Carlo Erba) were purified with a MB SPS80 from MBraun. Column chromatography was performed with SDS 0.040–0.063 mm silica gel. All mixtures of solvents are given in v/v ratio. NMR spectra were recorded on a JEOL ECS (400 MHz) spectrometer. ^{13}C NMR spectra were proton decoupled. HRMS spectra were measured either on an UPLC/ESI-HRMS device (an Acquity Waters UPLC system coupled to a Waters LCT Premier XE mass spectrometer equipped with an electrospray ion source), or a Q-TOF mass spectrometer (Q-TOF 6540, Agilent) equipped with an APPI ion source. TGA analysis were done with a Perkin Elmer Pyris 6.

2. Synthesis and characterization

The complete reaction scheme was as follows:



Scheme S1. Synthetic Route to the Electron Accepting Monomers 5a and 5b.
i) 2-fluorobenzonitrile, Na_2S, DMF, RT, 48h;
ii) 3,6-dichloro-1,2,4,5-tetrazine, **2a**/**2b**, 2,4,6-Collidine, DCM, RT, 4h;
iii) **4a**/**4b**, DMF, 140°C, 12h.



Scheme S2. Synthetic Route to the final compounds X1-X7.

5a/**5b**, **6a**/**6b**/**6c**/**6d**, Cs_2CO_3, DMF, 0 °C, 0.5h then RT, overnight.

2-Mercaptobenzonitrile (2b).[1] 2-Fluorobenzonitrile (6.0 g, 50 mmol), Na_2S (9.7 g 125 mmol), were added in 2-necked round bottom flask containing 30 mL of *N,N*-dimethylformamide. The mixture was stirred for 2 days at room temperature and the reaction was quenched with 1M NaOH aq (250 mL). The crude mixture was extracted with dichloromethane (2×75 mL). The aqueous layer was concentrated under vacuum, acidified with 1M HCl to pH≈1-2, extracted with dichloromethane (2×50 mL). The combined organic layers were dried under vacuum. 1M HCl (250mL) was added to the residue after evaporation and the mixture cooled with an ice bath. Zn (17.5 g) was added to the mixture and the reaction stirred for 1h. Ethyl acetate (500 mL) was added and the reaction stirred for another 0.5h. The organic layer was isolated, washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude oil was purified on by column chromatography (SiO_2; eluent: n-hexane/ethyl acetate 50/1). The pure product was collected as a brown oil (4.86 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.37-7.46 (m, 2H), 7.20-7.25 (m, 1H), 4.09 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.3, 133.5, 133.1, 129.5, 125.8, 117.5, 111.8.

2-((6-chloro-1,2,4,5-tetrazin-3-yl)oxy)benzonitrile (4a). 3,6-dichloro-1,2,4,5-tetrazine **3** (3.0 g, 20 mmol) and 2-hydroxybenzonitrile **2a** (2.4 g, 20 mmol) were added into the round flask containing dichloromethane (200 mL) purged with nitrogen. 2,4,6-Collidine was added after 5min of stirring. After stirring the mixture for 4h at room temperature, the solvent was evaporated and quickly purified by flash chromatography (SiO_2; eluent: n-hexane/ethyl acetate 5/1 v/v) to recover 3.95 g (85%) of the expected product. Considering its instability, the intermediate product was used as such in the next step.

2-((6-chloro-1,2,4,5-tetrazin-3-yl)thio)benzonitrile (4b). 3,6-dichloro-1,2,4,5-tetrazine **3** (3.0 g, 20 mmol) and 2-mercaptobenzonitrile **2b** (2.7 g, 20 mmol) were introduced in a round bottom flask containing dichloromethane (200 mL) purged with nitrogen. 2,4,6-Collidine was added after 5min of stirring. After stirring the mixture for 4h at room temperature, the solvent was evaporated and quickly purified by flash chromatography (SiO_2; eluent: n-hexane/ethyl acetate 5/1 v/v) to recover 1.64 g (33%) of the expected product. Considering its instability, the intermediate product was used as such in the next step.

3-chlorobenzofuro[3,2-e][1,2,4]triazine (5a). 4a (3.95 g, 17 mmol) was dissolved in a round bottom flask containing *N,N*-dimethylformamide (170 mL). The solution was stirred overnight at 140°C. After returning to TA, the solvent was evaporated under vacuum. The crude product was purified by column chromatography (SiO_2; eluent: n-hexane/ethyl acetate 10/1). The pure product was collected as yellow crystals (3.08 g, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.89 (td, *J* = 7.4, 1.3 Hz, 1H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.07, 160.37, 159.41, 145.65, 136.33, 136.02, 124.97, 118.32, 113.72.

3-chlorobenzo[4,5]thieno[3,2-e][1,2,4]triazine (5b). 4b (1.64 g, 6.6 mmol) was dissolved in a round bottom flask containing *N,N*-dimethylformamide (66 mL). Stirring overnight at 140 °C. The solution was stirred overnight at 140°C. After returning to TA, the solvent was evaporated under vacuum. The crude product was purified by column chromatography (SiO_2; eluent: n-hexane/ethyl acetate 10/1). The pure product was collected as yellow crystals (1.32 g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 7.9 Hz, 1H), 7.94 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.81 (td, *J* = 7.3 1.3 Hz, 1H), 7.63 (td, *J* = 7.4, 0.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.30, 161.14, 152.06, 142.75, 134.18, 128.77, 126.83, 126.52, 124.02.

General Procedure for the synthesis of X1-X7.

5 (1 mmol) and **6** (3 mmol) were introduced in a round bottom flask containing *N,N*-dimethylformamide (40 mL) purged with nitrogen. The mixture was cooled to 0°C under nitrogen flow. Cs_2CO_3 (0.65 g, 2 mmol) was added at once and the reaction stirred for 0.5h. The reaction was slowly brought back to room temperature and stirred for another 10h. The reaction was quenched by addition of H_2O and extracted twice with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. The crude product was purified by column chromatography (SiO_2; eluent: n-hexane/ethyl acetate 10/1) and recrystallization from dichloromethane/petroleum ether.

3-(9*H*-carbazol-9-yl)benzofuro[3,2-*e*][1,2,4]triazine (X1). This compound was prepared from **5a** (0.2 g, 1 mmol) and **6a** (0.5 g, 3 mmol) according to the general procedure. The product was collected as yellow needle-like crystals (0.15 g, 45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.4 Hz, 2H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 2H), 7.86 (td, *J* = 8.48, 1.3 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.58-7.51 (m, 3H), 7.39 (td, *J* = 7.6, 0.72 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.20, 158.17, 143.84, 139.00, 135.29, 126.94, 125.92, 125.31, 124.73, 122.76, 119.77, 119.49, 115.72, 113.58

MS (EI) calcd. for $C_{21}H_{13}N_4O$ 337.1083 ($M+H^+$), found 337.1083.

10-(benzofuro[3,2-e][1,2,4]triazin-3-yl)-10H-phenoxazine (X2). This compound was prepared from **5a** (0.2 g, 1 mmol) and **6b** (0.55 g, 3 mmol) according to the general procedure. The product was collected as yellow flaky crystals (0.11 g, 31%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.87-7.84 (m, 2H), 7.78 (td, *J* = 7.4, 1.4 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 8.3 Hz, 1H), 7.17-7.10 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.88, 159.22, 159.14, 151.02, 143.72, 134.82, 130.58, 126.10, 125.55, 124.87, 124.66, 123.15, 119.61, 116.92, 113.42.

MS (EI) calcd. for $C_{21}H_{13}N_4O_2$ 353.1033 ($M+H^+$), found 353.1039.

10-(benzofuro[3,2-e][1,2,4]triazin-3-yl)-10H-phenothiazine (X3). This compound was prepared from **5a** (0.2 g, 1 mmol) and **6c** (0.60 g, 3 mmol) according to the general procedure. The product was collected as yellow flaky crystals (0.02 g, 5%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.86 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.74 (td, *J* = 7.4, 1.4 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.44-7.37 (m, 3H), 7.26-7.22 (td, *J* = 7.5, 1.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.58, 159.07, 143.56, 139.94, 134.57, 133.36, 128.50, 128.19, 126.88, 126.46, 124.67, 119.72, 113.32.

MS (EI) calcd. for $C_{21}H_{13}N_4OS$ 369.0805 ($M+H^+$), found 369.0792.

3-(9H-carbazol-9-yl)benzo[4,5]thieno[3,2-e][1,2,4]triazine (X4). This compound was prepared from **5b** (0.22 g, 1 mmol) and **6a** (0.5 g, 3 mmol) according to the general procedure. The product was collected as yellow needle-like crystals (0.16 g, 45%).

^1H NMR (400 MHz, $CDCl_3$): δ 8.94 (d, *J* = 8.5 Hz, 2H), 8.65 (d, *J* = 7.7 Hz, 1H), 8.10 (d, *J* = 7.0 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 1H),7.80 (td, *J* = 8.3, 1.2 Hz, 1H), 7.66 (td, *J* = 8.0, 0.7 Hz, 1H), 7.57 (td, *J* = 7.2, 1.2 Hz, 2H), 7.42 (td, *J* = 7.8, 0.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.06, 157.25, 150.53, 142.63, 138.99, 133.40, 129.99, 127.00, 126.36, 126.18, 124.07, 122.92, 119.82, 116.20.

MS (EI) calcd. for $C_{21}H_{13}N_4S$ 353.0855 ($M+H^+$), found 353.0854.

10-(benzo[4,5]thieno[3,2-e][1,2,4]triazin-3-yl)-10H-phenoxazine (X5). This compound was prepared from **5b** (0.22 g, 1 mmol) and **6b** (0.55 g, 3 mmol) according to the general procedure. The product was collected as yellow flaky crystals (0.14 g, 38%).

^1H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.98-7.94 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.69 (td, *J* = 7.4 1.3 Hz, 1H), 7.51 (td, *J* = 7.9, 0.8 Hz, 1H), 7.20-7.13 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.68, 156.40, 151.27, 150.31, 142.55, 132.91, 130.15, 130.07, 126.29, 126.11, 125.93, 125.87, 123.86, 123.04, 116.94.

MS (EI) calcd. for $C_{21}H_{13}N_4OS$ 369.0805 ($M+H^+$), found 369.0808.

10-(benzo[4,5]thieno[3,2-e][1,2,4]triazin-3-yl)-10H-phenothiazine (X6). This compound was prepared from **5b** (0.22 g, 1 mmol) and **6c** (0.60 g, 3 mmol) according to the general procedure. The product was collected as yellow flaky crystals (0.13 g, 34%).

^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.66 (td, *J* = 7.3, 1.2 Hz,1H), 7.46 (td, *J* = 7.8, 1.2 Hz, 3H), 7.40 (td, *J* = 7.6, 1.4 Hz, 2H), 7.25 (td, *J* = 7.7, 1.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.02, 155.64, 150.32, 142.53, 129.52, 133.27, 132.74, 130.16, 128.47, 128.16, 126.75, 126.52, 125.91, 125.68, 123.78.

MS (EI) calcd. for $C_{21}H_{13}N_4S_2$ 385.0576 ($M+H^+$), found 385.0572.

3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzofuro[3,2-*e*][1,2,4]triazine (X7). This compound was prepared from **5a** (0.20 g, 1 mmol) and **6d** (0.84 g, 3 mmol) according to the general procedure. The product was collected as yellow needle-like crystals (0.12 g, 27%).

^1H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J*=8.8 Hz, 2 H), 8.33 (d, *J*=7.8 Hz, 1 H), 8.03 (d, *J*=1.7 Hz, 2 H), 7.74-7.85 (m, 1 H), 7.69 (d, *J*=8.6 Hz, 1 H), 7.45-7.61 (m, 3 H), 1.43 (s, 18 H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.12, 145.76, 143.69, 137.32, 135.05, 126.05, 125.17, 124.59, 124.47, 119.62, 115.76, 115.49, 113.54, 34.82, 31.87.

MS (EI) calcd. for $C_{29}H_{29}N_4O$ 449.2336 ($M+H^+$), found 449.2338.

3. Quantum chemical calculations

Ground state geometries were optimized at the PBE0/6-31+g(d,p) level of calculation followed by a frequency calculation. TDDFT on these geometries were done at the PBE0/6-311+g(d,p) level of theory looking for both singlets and triplets levels in vacuo and including toluene solvent effect with IEFPCM model. Then first singlet excited state geometries were optimized at the PBE0/6-31+g(d,p) level followed by a frequency calculation at the same level. Finally, a TDDFT calculation was done on these S1 optimized geometries at the PBE0/6-311+g(d,p) level of theory looking for both singlets and triplets levels in vacuo and including toluene solvent effect with IEFPCM model.

For all geometries frequency calculations gave only real values confirming that all structures are true minima. The excited states nature was attributed based on NTO analysis of the relevant transitions. All NTO account for at least 99.5% of the transition. All calculations were done with Gaussian 16 (Revision B.01) software.[2] Data were analyzed with GaussView 6.0 (molecular orbitals, NTO and density difference between excited state and ground state plots), PyMOL (The PyMOL Molecular Graphics System, Version 2.1.1 Schrödinger, LLC; molecular structures plots), Mercury 4.1.0 (angles measurements), GaussSum3.0[3] (energy levels of molecular orbitals) and Multiwfn3.7 (D end t indexes)[4] softwares.

4. Film processing

a) Doped PMMA films casting

All blends were obtained by drop-casting DCM solutions (0.1 g/L) of the compounds at room temperature on quartz slides followed by slow (1 night) evaporation in solvent saturated conditions. Concentration of the fluorophore in the film is reported in weight percentage (w/w) relative to the polymer mass in the solution. All blends formed clear, glassy, transparent solid films.

b) Neat films casting

All films were obtained by drop-casting DCM solutions at room temperature followed by slow (1 night) evaporation in solvent saturated conditions. The compounds **X2**, **X3**, **X5** and **X6** formed clear, glassy, transparent solid films; on the other hand, compounds **X1**, **X4**, and **X7** formed polycrystalline films.

c) polycrystalline powders

As synthesized powders were collected from PE/DCM solution and studied in a 1mm quartz cuvette.

5. Photophysical studies

Absorption spectra were collected using a Cary 4000 double beam spectrophotometer (Agilent). Luminescence spectra were collected on a FluoroLog3 fluorescence spectrometer (Horiba Jobin Yvon) The relative photoluminescence quantum yields in solution were determined from corrected emission spectra using quinine dication (Φ_{PL}= 0.59 in $HClO_4$[5]) as the standard.

Photoluminescence quantum yield of the films were measured by an absolute method with a barium sulphate-coated integrating sphere F-3018(Horiba) inserted into the spectrofluorimeter sample compartment.

Fluorescence (PF and DF) and phosphorescence spectra and decays in solid state (PMMA, neat film, polycrystalline powder) were recorded by nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using either third harmonics of a high-energy, pulsed Nd:YAG laser emitting at 355 nm (EKSPLA) or a N_2 laser emitting at 337 nm. Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) of subnanosecond resolution. PF/DF time-resolved measurements were performed by exponentially increasing gate and delay times. Lifetimes were extracted by a multi-exponential mathematical fit.

The **ns** fluorescence decay curves in solution, were obtained by the time-correlated single-photon counting (TCSPC) method with a femtosecond laser excitation composed of a Titanium Sapphire laser (Tsunami, Spectra-Physics) pumped by a doubled Nd:YVO_4 laser (Millennia Xs, Spectra-Physics). The fluorescence data were analyzed using the Globals software package developed at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana-Champaign, which includes reconvolution analysis and global non-linear least-squares minimization method. The quality of the fit was estimated by visual inspection of the weighted residuals and calculation of χ^2

The **µs** fluorescence decay curves in solution were obtained using an Edinburgh instrument LP920 laser flash photolysis spectrometer combined with an Nd:YAG laser (Continuum) tripled at 355 nm via non-linear crystals. The Levenberg Marquardt algorithm was used for non-linear least square fit (tail fit) as implemented in the L900 software (Edinburgh instrument). The quality of the fit was estimated by visual inspection of the weighted residuals and calculation of χ^2.

6. Supplementary data

Table S1 Thermal decomposition temperature (T_d) and melting points (mp) of the fused 1,2,4-triazines.

	T_d (°C)	mp (°C)
X1	306	228
X2	285	205
X3	298	257
X4	310	256
X5	288	223
X6	319	256
X7	321	307

Table S2 Calculated main angles for the ground state structures of the fused 1,2,4-triazines

	A (°)[a]	**D (°)[b]**	**A-D (°)[c]**	**A-D dihedral angle (°)**
X1	0.06	1.06	15.32	14.74
X2	0.22	35.39	45.88	9.60
X3	0.14	46.98	56.71	5.65
X4	0.31	1.13	16.40	15.53
X5	0.03	35.35	45.46	9.34
X6	0.07	46.90	56.31	5.44
X7	0.03	0.56	7.71	7.39

a) A angle refers to the calculated angle between the mean planes of the two rings of the fused 1,2,4-triazine acceptors; b) D angle refers to the calculated angle between the mean planes of the two phenyl rings of the Donor; c) A-D angle refers to the calculated angle between the mean planes of the Donor and the Acceptor.

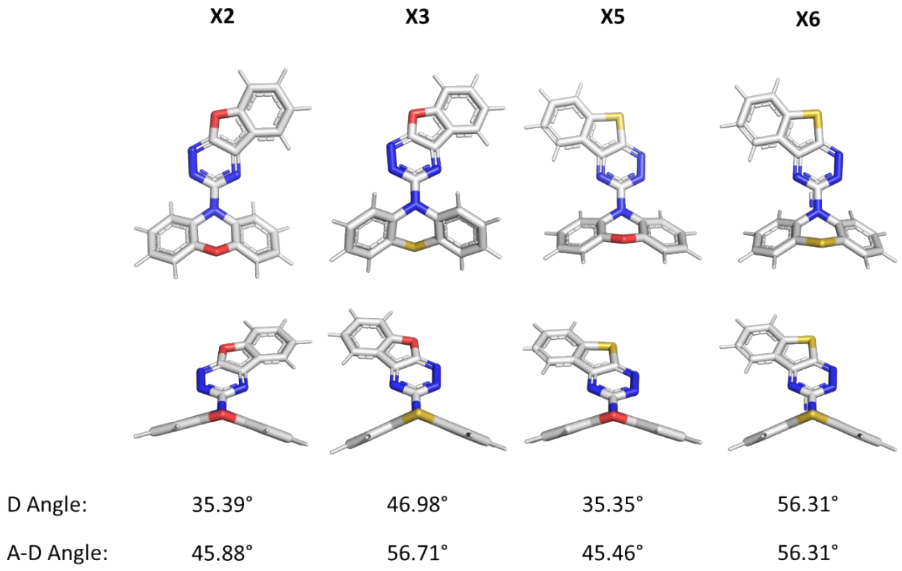


Fig. S1 Optimized ground state structures of, from left to right, **X2**, **X3**, **X5** and **X6**. D angle refers to the calculated angle between the mean planes of the two phenyl rings of the Donor; D-A angle refers to the calculated angle between the mean planes of the Donor and the Acceptor.

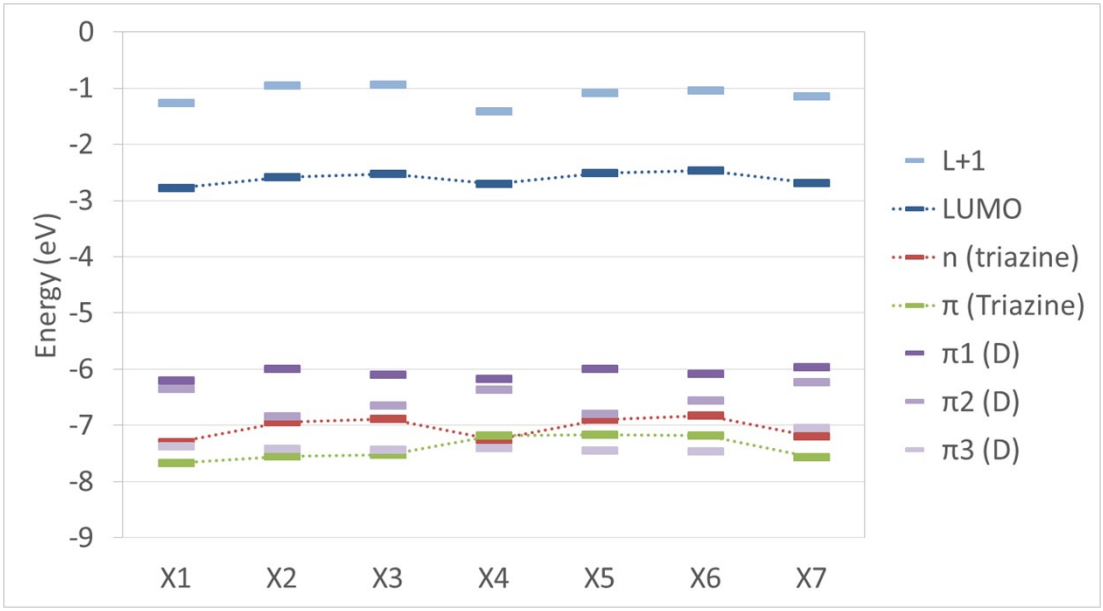


Fig. S2 Energy levels of the frontier molecular orbitals of the fused 1,2,4-triazines **X1-7**.

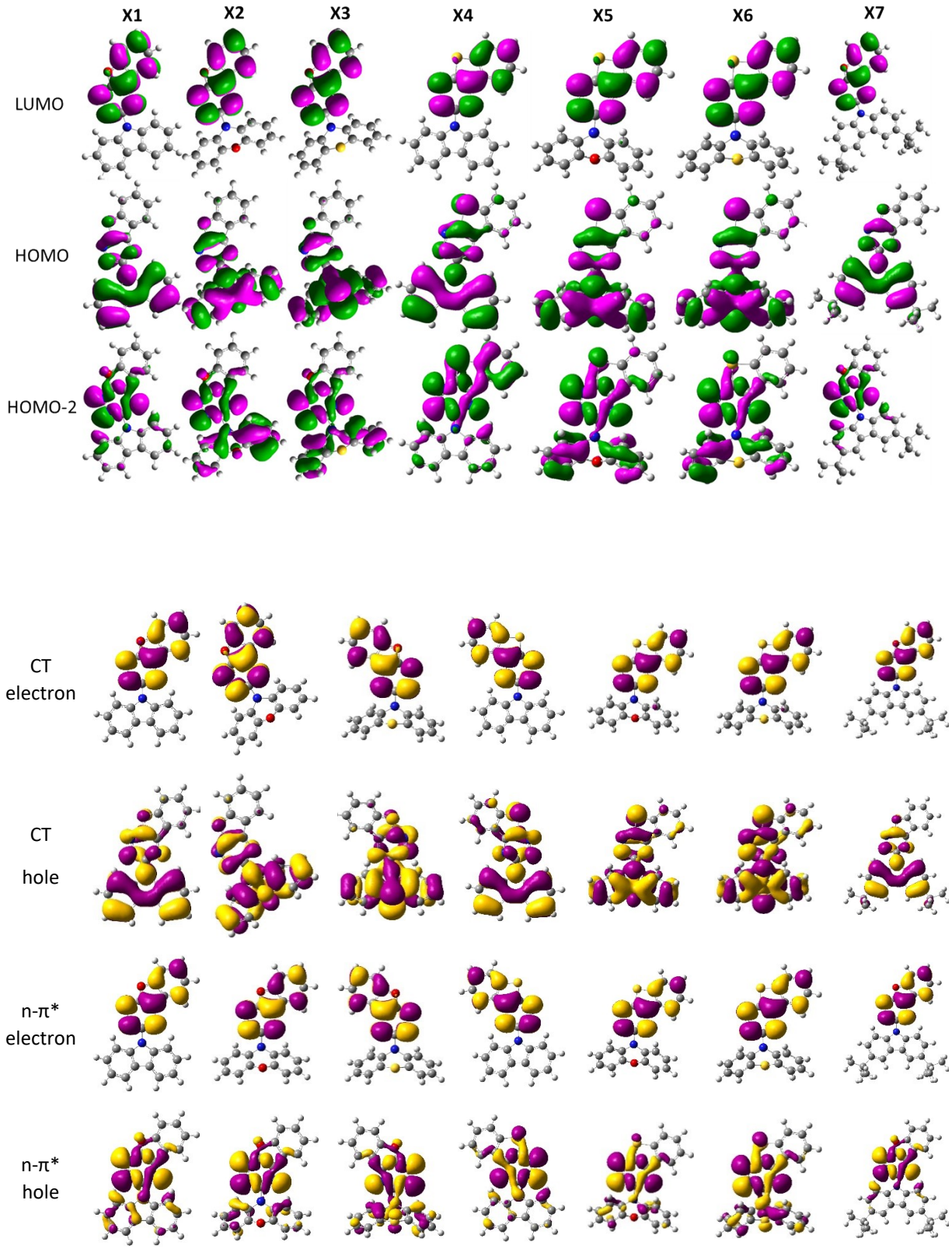


Fig. S3 top) Electron density distributions in molecular orbitals involved in the first two calculated transitions of D-A as-triazines. **Bottom)** NTO for the CT and n-π* transitions reported in Table S3.

Table S3 Calculated values of two lowest energy transitions and singlet – triplet energy differences at the ground state geometries for **X1-7** in vacuum and including toluene solvent effect.

	vacuum		toluene	
	λ_{calc} (nm)	ΔE_{S-T} (eV)	λ_{calc} (nm)	ΔE_{S-T} (eV)
X1	462 (CT) 411 (n-π*)	0.45	449 (CT) 402 (n-π*)	0.47
X2	467 (CT) 424 (n-π*)	0.50	462 (CT) 415 (n-π*)	0.50
X3	438 (CT) 423 (n-π*)	0.54	435 (CT) 415 (n-π*)	0.57
X4	454 (CT) 413 (n-π*)	0.50	445 (CT) 406 (n-π*)	0.50
X5	458 (CT) 424 (n-π*)	0.51	457 (CT) 418 (n-π*)	0.51
X6	434 (CT) 421 (n-π*)	0.55	433 (CT) 416 (n-π*)	0.60
X7	481 (CT) 426 (n-π*)	0.42	470 (CT) 406 (n-π*)	0.43

Charge transfer quantification.

Table S4 Calculated values of D and t indexes of the CT transition for the GS geometry as defined in the hole-electron formalism obtained with the Multiwfn 3.7 code[6]. (Values in parenthesis calculated on the S1 optimized states)

Compound	D index (Å)	t index (Å)
X1	4.226 (4.889)	2.072 (3.102)
X2	4.017 (4.817)	1.970 (3.265)
X3	3.985 (5.112)	1.895 (3.467)
X4	3.266 (4.692)	0.862 (2.900)
X5	3.384 (4.676)	1.143 (3.178)
X6	3.547 (4.977)	1.344 (3.384)
X7	4.576 (5.092)	2.384 (3.247)

Note D index refers to magnitude of CT length and t index is designed to measure separation degree of hole and electron.

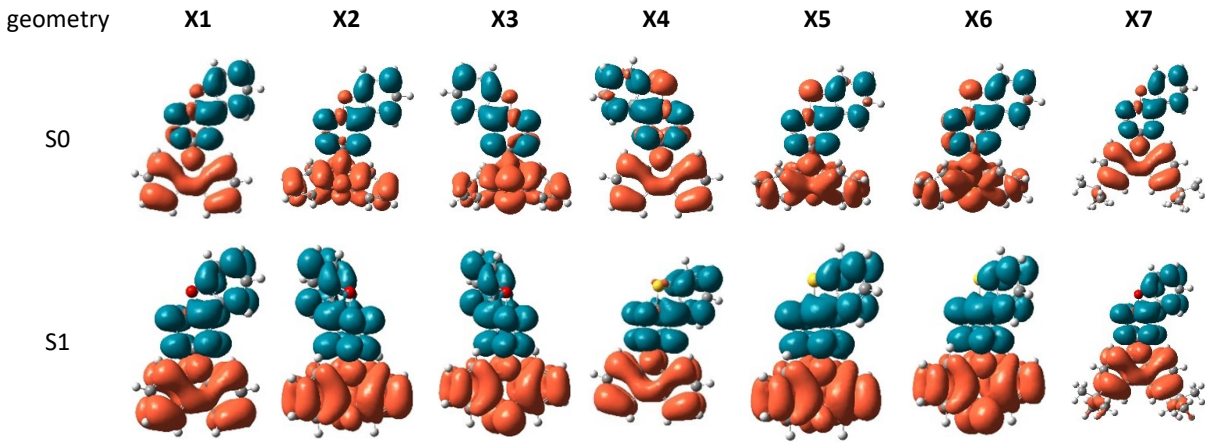


Fig. S4 Density difference between excited state and ground state for the first singlet excited state in the S0 and S1 optimized geometries (orange means density decrease and blue density increase)

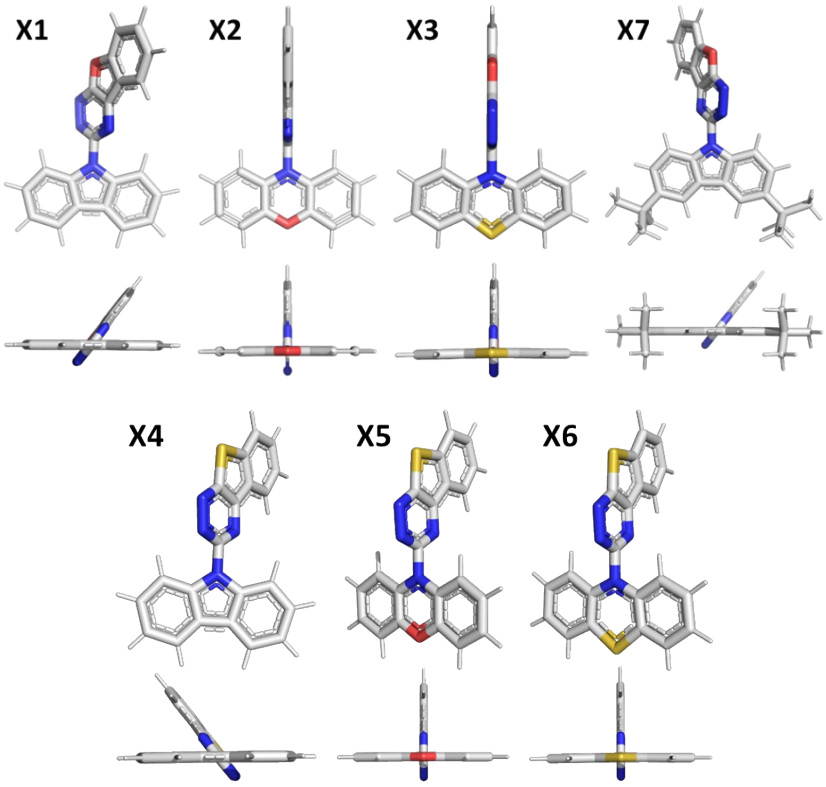


Fig. S5 Optimized molecular structures of the first excited states of the as-triazines

Table S5 Calculated D-A angles and ΔE_{S-T} in vacuo and including toluene solvent effect at the S1 geometry for **X1-7**.

	A-D (°)[a]	ΔE_{S-T} in vacuo (eV)	ΔE_{S-T} in toluene (eV)
X1	52.23	0.09	0.10
X2	89.99	0.02	0.02
X3	89.99	0.02	0.02
X4	52.03	0.10	0.11
X5	90.00	0.02	0.02
X6	89.98	0.02	0.02
X7	51.75	0.09	0.09

[a]A-D angle refers to the calculated angle between the mean planes of the Acceptor and the Donor.

Table S6

	λ_{exp} (nm)	λ_{calc} (nm) (toluene)	MAE (%)
X1	416	449	7.9
X2	429	462	7.7
X3	398	435	9.3
X4	419	445	6.2
X5	431	457	6.0
X6	422	433	2.6
X7	427	470	10.1

$$MAE = \frac{|\lambda_{exp} - \lambda_{calc}|}{\lambda_{exp}} \times 100$$

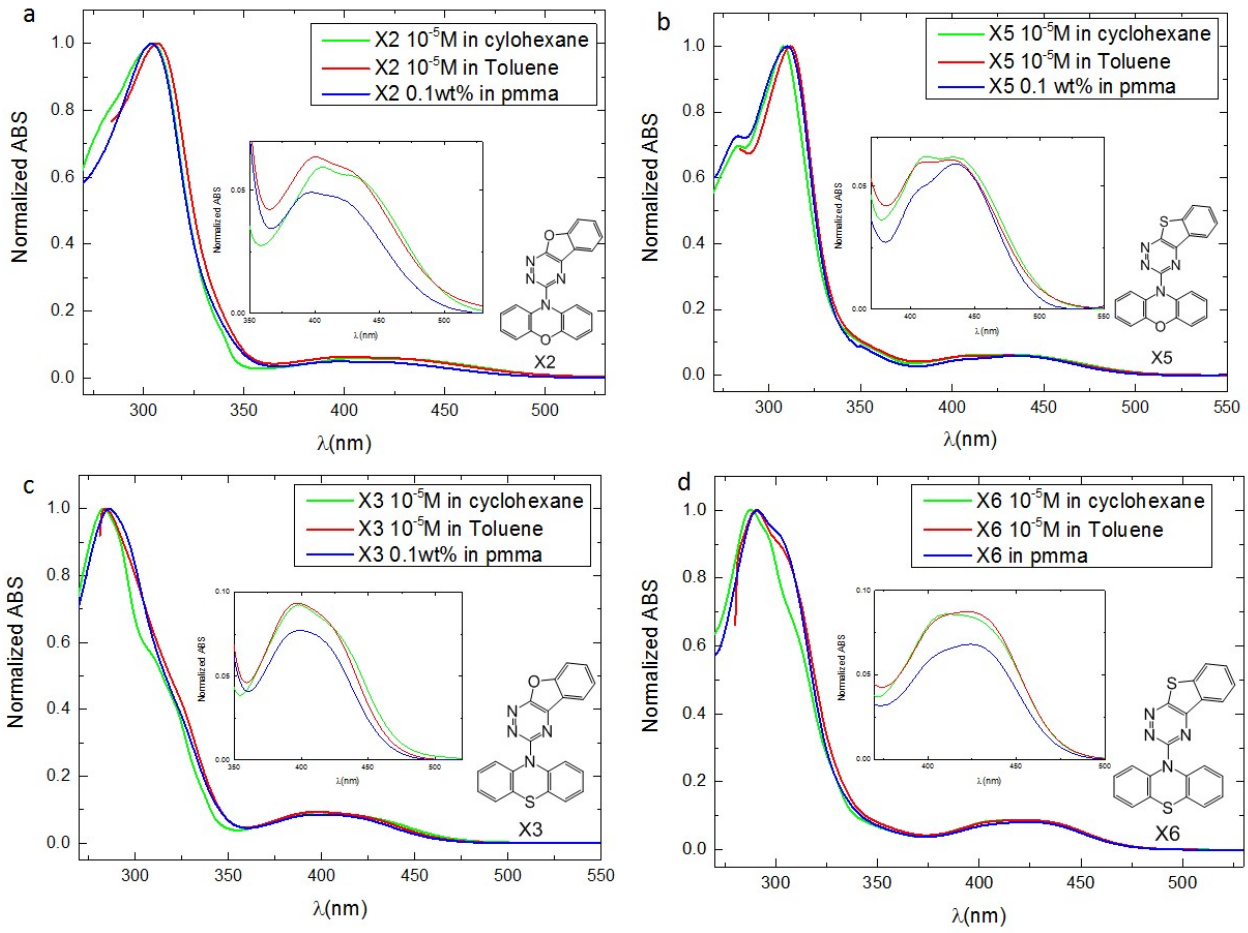


Fig. S6 Absorption spectra of (a) **X2**, (c) **X3**, (b) **X5** and (d) **X6** in cyclohexane (10^{-5} M, green), toluene (10^{-5} M, red), and PMMA (0.1wt%, blue). Inset: zoom of the low energy region between 350 nm and 550 nm.

Table S7 Maximum absorption and emission wavelengths for X1-X7 in cyclohexane, toluene and DCM.

MOLECULE	Absorption (nm)			Emission (nm)		
	Cyclohexane	Toluene	DCM	Cyclohexane	Toluene	DCM
X1	454(s), 432, 412, 393, 323, 309, 297(s), 288	416(s), 388, 325, 312, 298(s), 289	414(s), 381, 324, 311, 299(s), 289	548(s), 510, 477	556	609
X2	433(s), 405, 304, 283(s)	429(s), 401, 306	n.m.	388	385	n.e.
X3	397,310(s),283	398, 284	n.m.	566, 416	n.e.	n.e.
X4	454, 433,413(s), 397, 325, 311, 296, 287	419, 399, 327, 315, 296, 288	423, 392, 327, 314, 296, 289	547(s), 504,474	543	601
X5	432, 413, 308, 284	431, 412, 312, 284	n.m.	394	398	n.e.
X6	413, 308(s), 296(s), 288	422, 301(s), 290	n.m.	n.e.	n.e.	n.e.
X7	479(s), 450, 430, 400	427, 395, 383, 331, 317	426, 389, 330, 316, 301, 294	589(s), 544, 508	599	648

(s)=shoulder, n.e.= non-emissive, n.m.=not measured (as the solution was non-emissive).

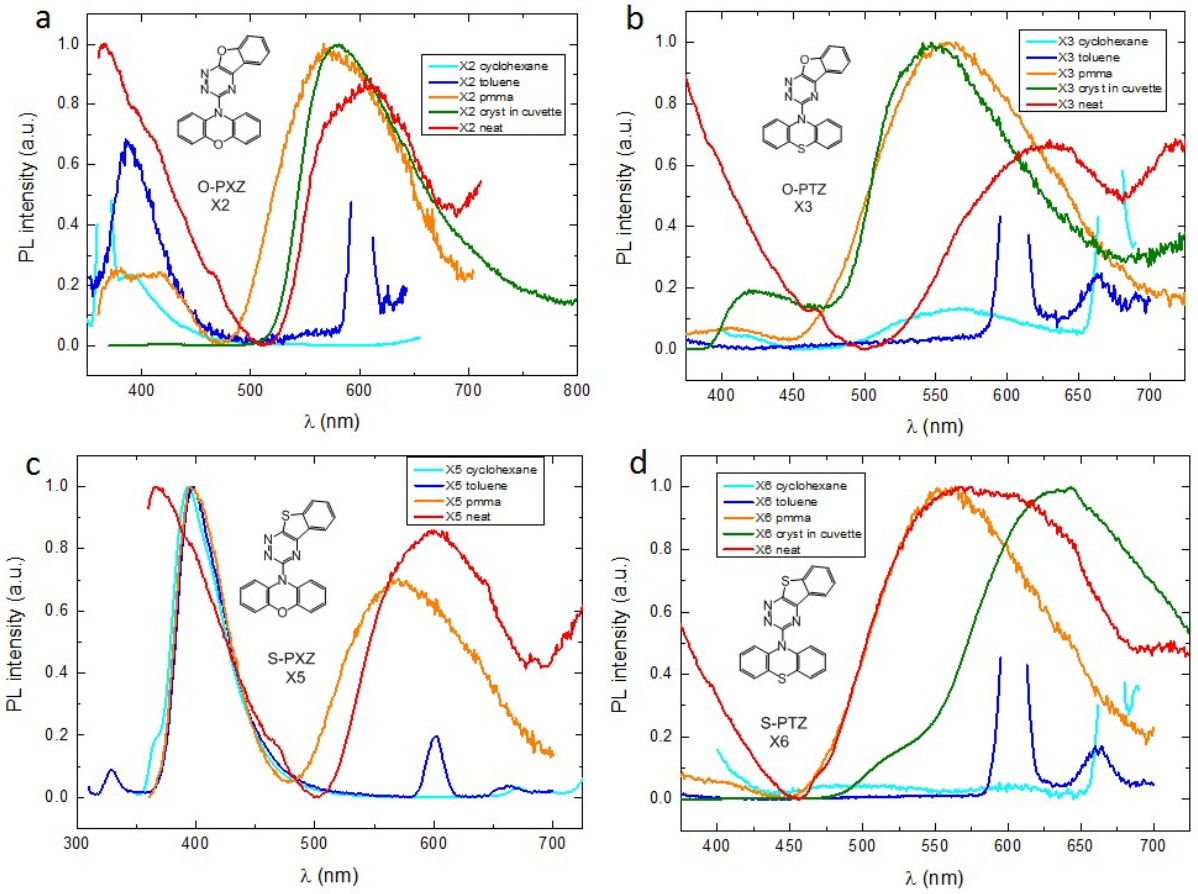


Fig. S7 Emission spectra of (a) **X2**, (b) **X3**, (c) **X5** and (d) **X6** in cyclohexane (10^{-5} M, cyan), toluene (10^{-5} M, blue), PMMA (0.1wt%, orange), crystalline powder in cuvette (green, except c, no emission) and neat film (red). λ_{exc} = between 300-350 nm.

Table S8: QYs and decay times of **X2**, **X3, X5** and **X6** in solid state.

	QY PMMA	**QY cryst. powd.**	**$\tau_{1,av.}$ (ns) PMMA**	**$\tau_{2,av.}$ (µs) PMMA**	**$\tau_{1,av.}$ (ns) cryst. powd.**	**$\tau_{2,av.}$ (µs) cryst. powd.**
X2	§	0.5%	1.29	9.29	2.34	0.2
X3	0.2%	§	1.20	21.10	n.m.	n.m.
X5	§	n.e.	1.07	11.16	n.e.	n.e.
X6	0.2%	0.5%	0.62	14.45	2.44	0.84

§ = less than 0.05%

n.e= not emissive

n.m. = not measured

Table S9: Maximum absorption wavelengths for **X1-X7** in PMMA

MOLECULE	Absorption wavelength (nm)
X1	412(s), 380, 324, 311, 297(s), 289
X2	425(s), 398,304
X3	398, 286
X4	423,392, 327, 313, 295(s), 290
X5	436, 409(s), 310, 283
X6	424, 301(s), 291
X7	414, 383, 330, 316, 303, 293

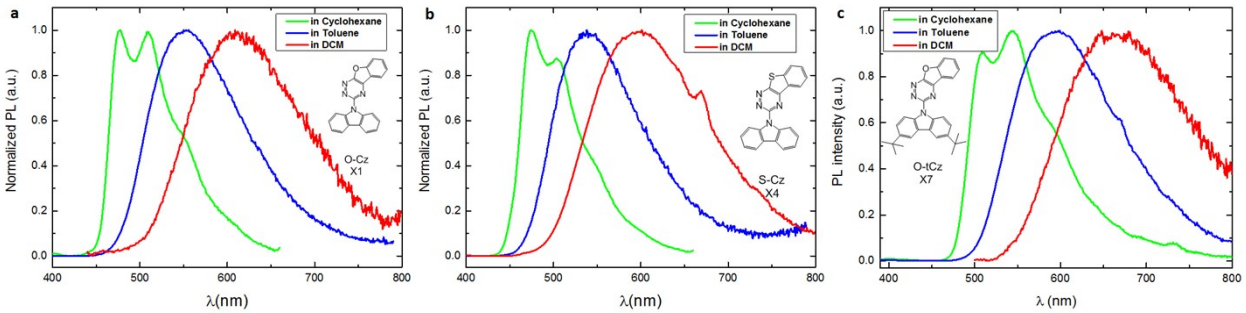


Fig. S8 Photoluminescence spectra of **X1** (a), **X4** (b) and **X7** (c) in cyclohexane (10^{-5} M, green), toluene (10^{-5} M, blue) and dichloromethane (10^{-5} M, red). λ_{exc} = between 325-330 nm.

Table S10: Spectroscopic properties of **X1**, **X4** and **X7** in cyclohexane.

Cyclohexane	QY (air)	QY(deg)	$\tau_{1,av.}$ (ns)	$\tau_{2,av.}$ (μs)
X1	0.20%	0.20%	0.4	1.85
X4	0.08%	0.09%	0.26	1.64
X7	0.60%	0.60%	1.70	6.97

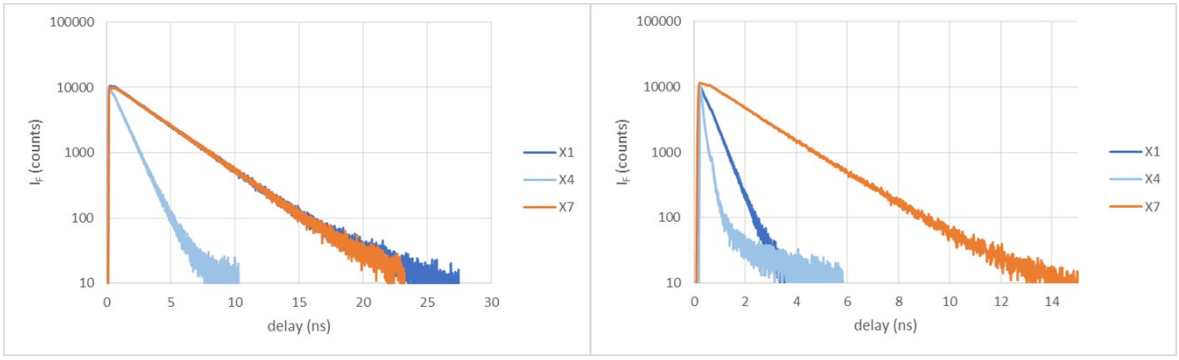


Fig. S9 Fluorescence decays (ns regime) of **X1**(dark blue), **X4** (light blue) and **X7** (orange) in toluene (left) and cyclohexane (right).

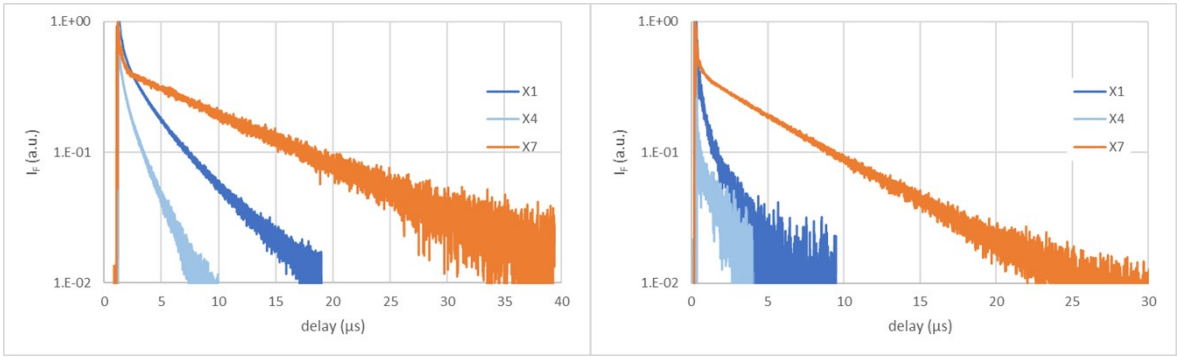


Fig. S10 Fluorescence decays (µs regime) of **X1**(dark blue), **X4** (light blue) and **X7** (orange) in toluene (left) and cyclohexane (right). Decays were recorded in the absence of oxygen.

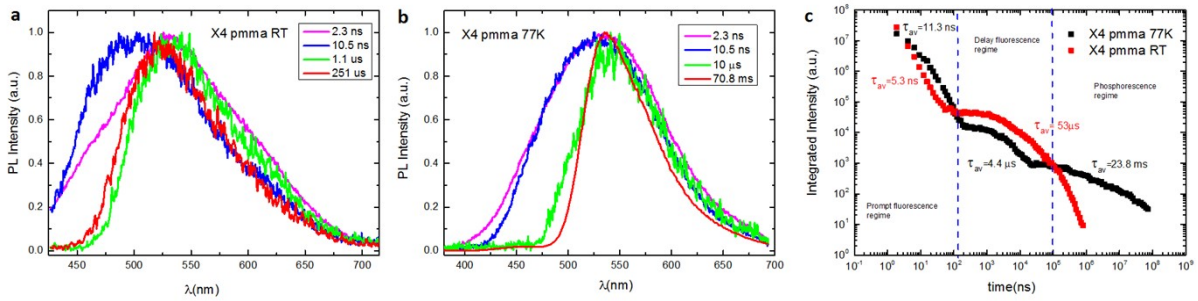


Fig. S11 Time-resolved emission spectra at increasing delay times for **X4** at 0.1wt% PMMA films at 77K (left) and room temperature (center) and corresponding decay curves at room temperature and 77K (right).

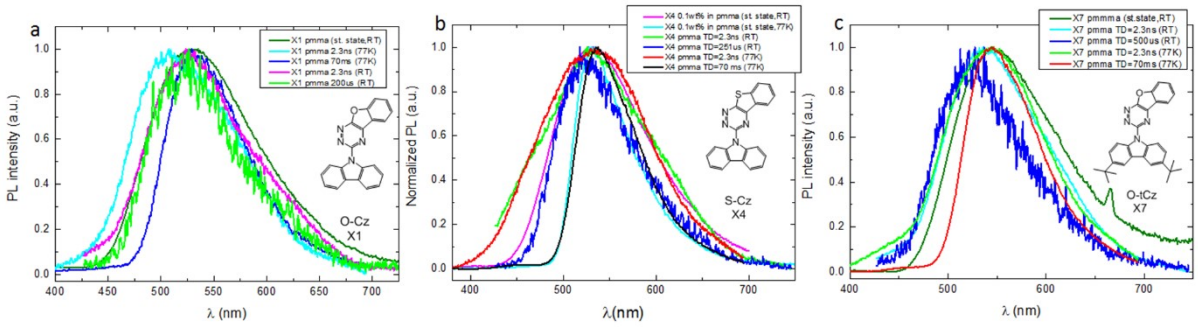


Fig. S12: PMMA steady state (st) and time-resolved emission spectra of **X1** (a), **X4** (b) and **X7** (c) at room temperature and 77K and at various delay times after excitation.

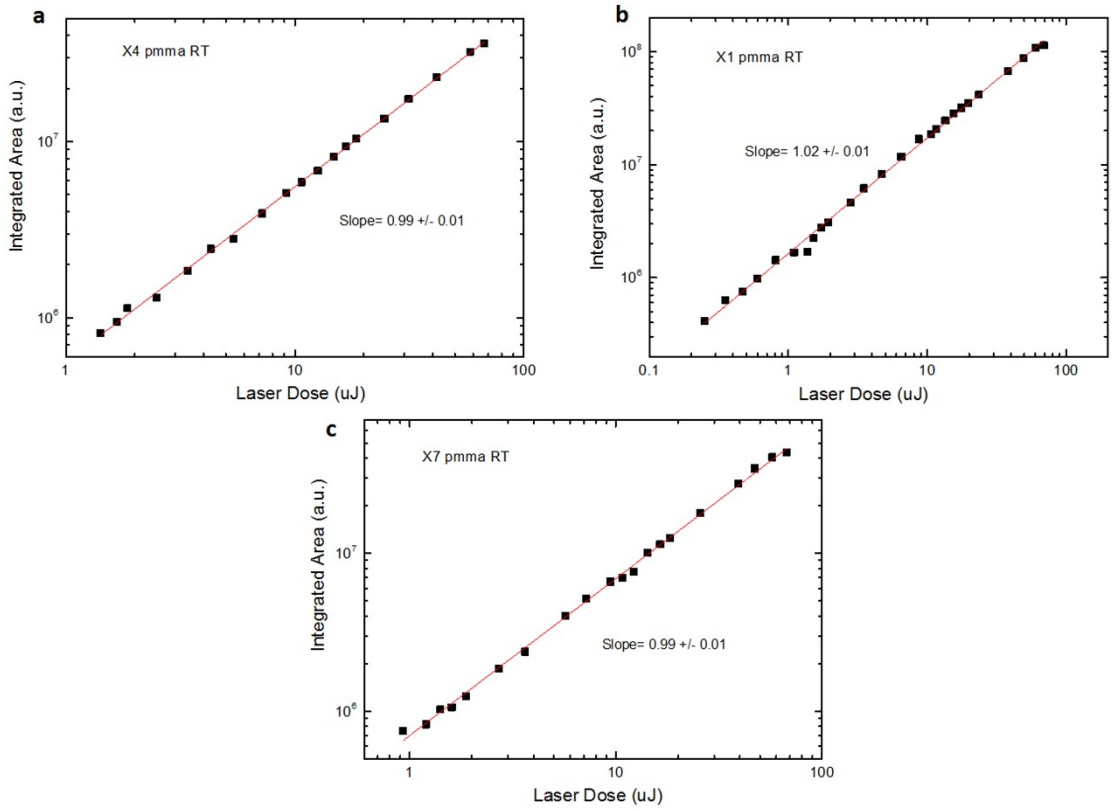


Fig. S13 Power dependence of the integrated delayed fluorescence in PMMA thin films of **X1** (a), **X4** (b) and **X7** (c) at RT.

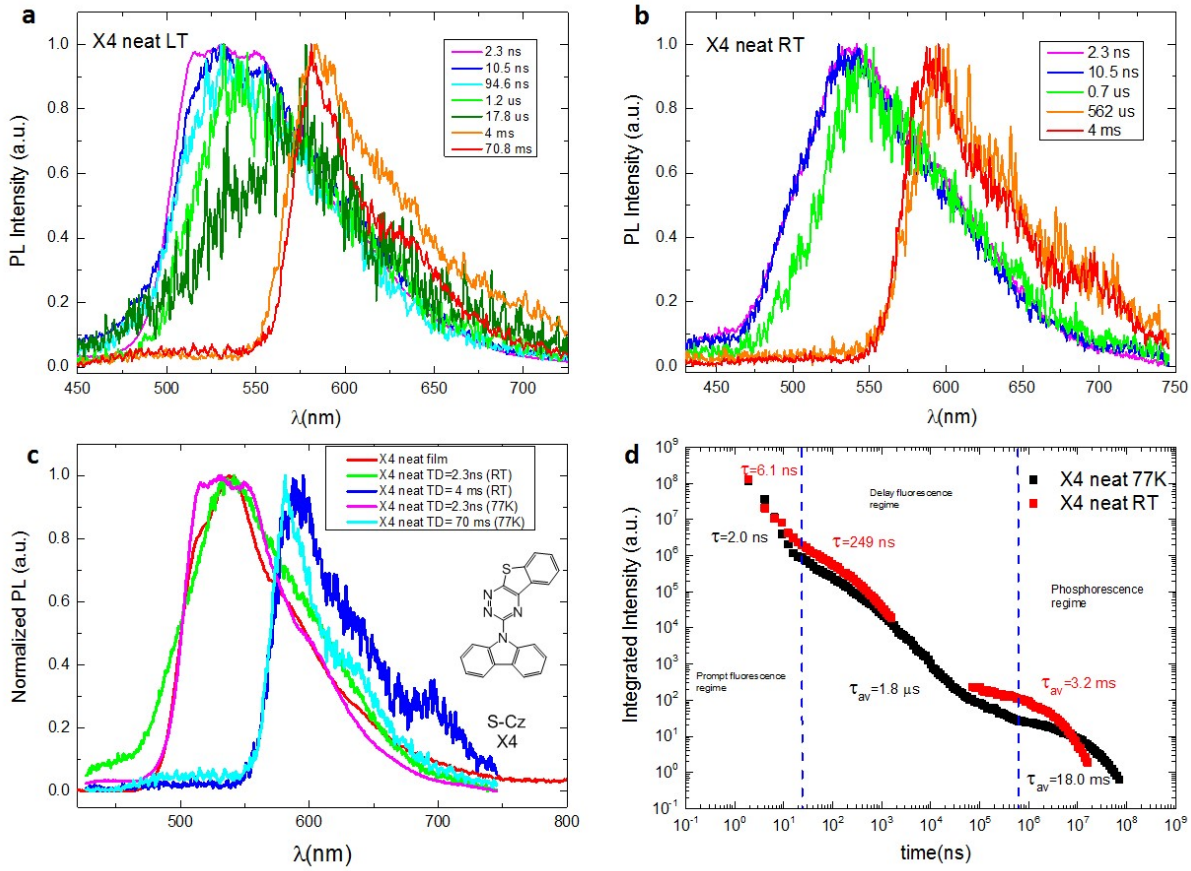


Fig. S14 Time-resolved emission spectra and decay of **X4** in neat films: (a) 77K time-resolved spectra at increasing delay times, (b) room temperature time-resolved spectra at increasing delay times, (c) comparison of steady state (st) and time-resolved emission spectra at 77K and room temperature, and (d) decay curves at room temperature and 77K.

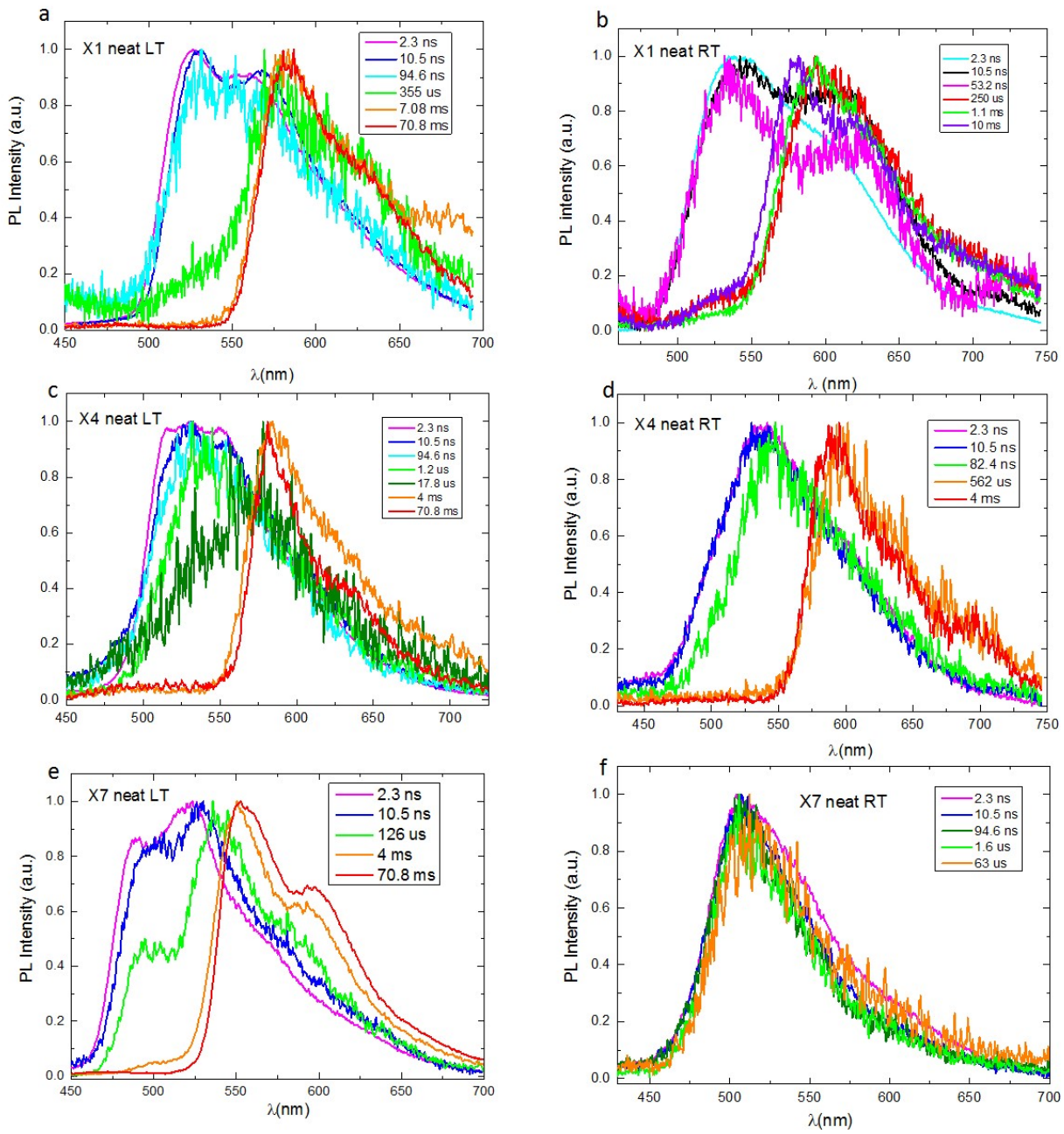


Fig. S15 Time-resolved emission spectra at increasing delay times for **X1** (a,b), **X4** (c,d) and **X7** (e,f) in neat films at 77K (LT, left) and room temperature (RT, right).

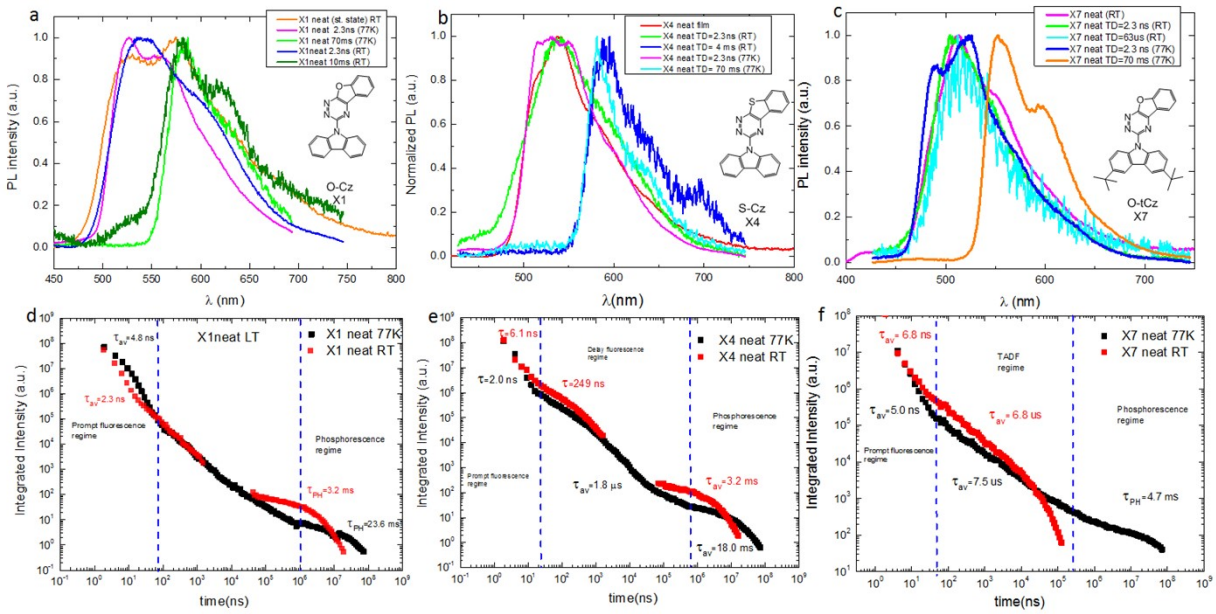


Figure S16: Top: steady state (st) and time-resolved emission spectra in crystalline films at room temperature and 77K and at various delayed time after excitation of **X1** (a), **X4** (b) and **X7** (c). Bottom: corresponding decay curves at room temperature and 77K.

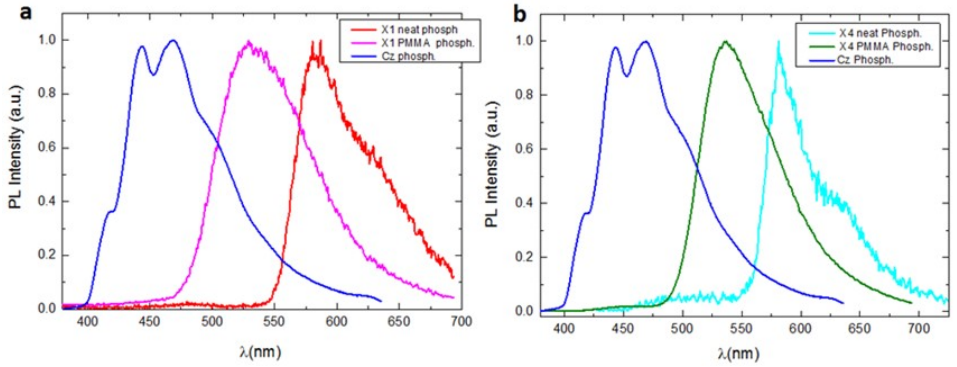
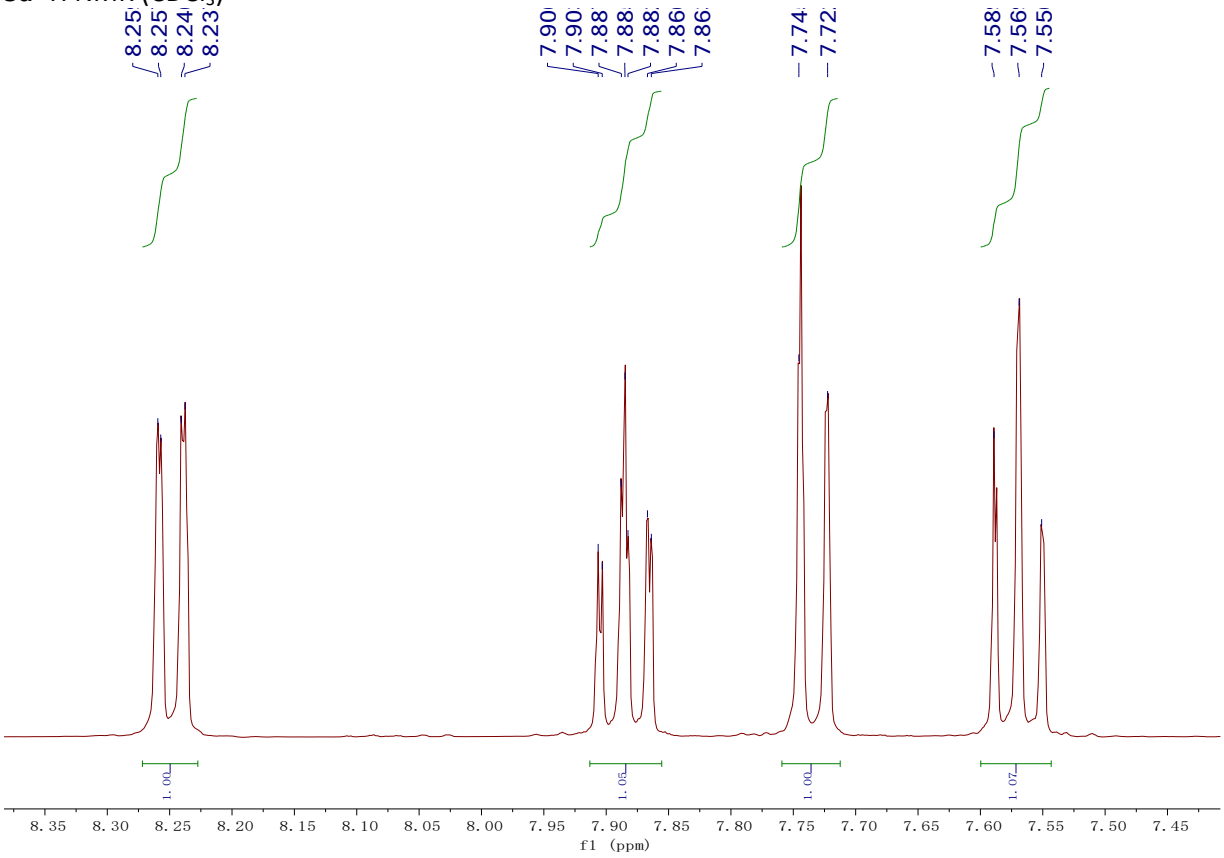


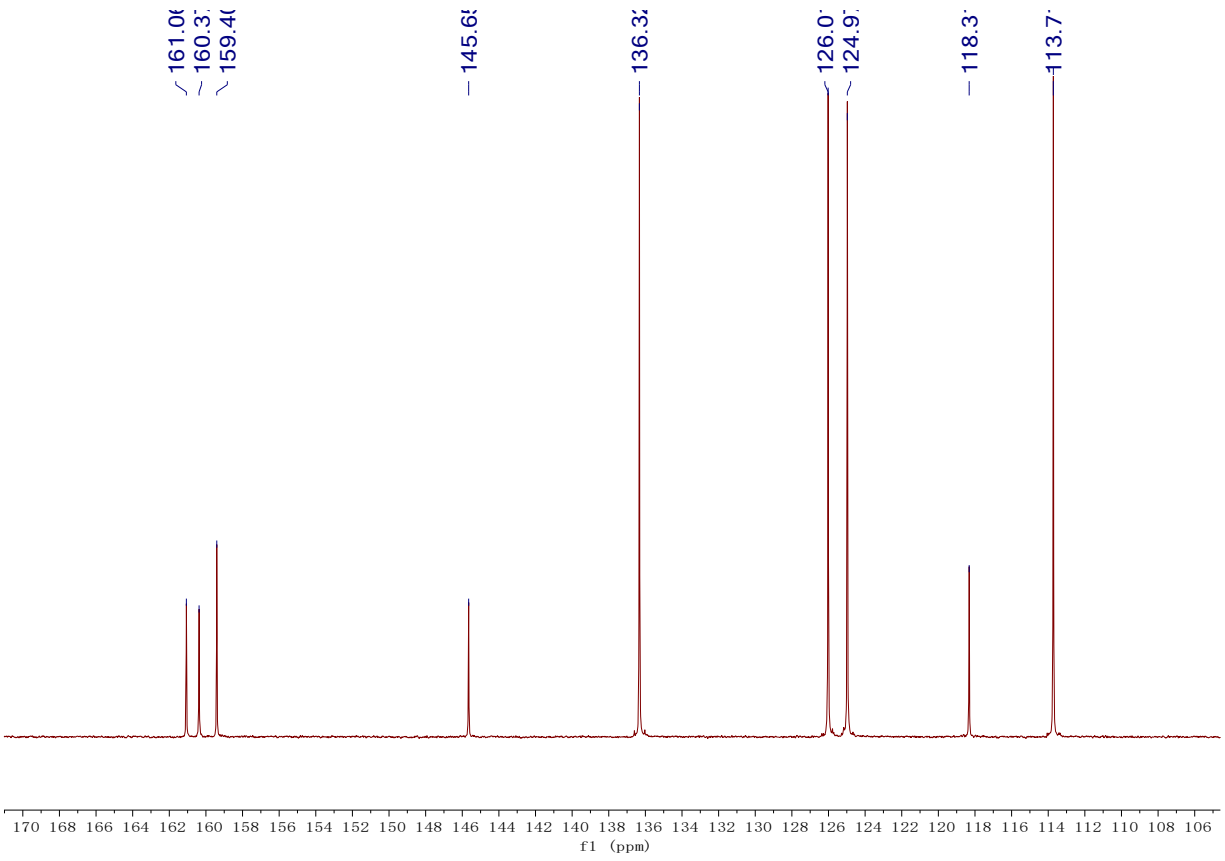
Figure S17: Comparison of Phosphorescence (77K) spectra in neat film and PMMA with the phosphorescence of carbazole of X1 (a) and X4 (b).

7. NMR and MS spectra

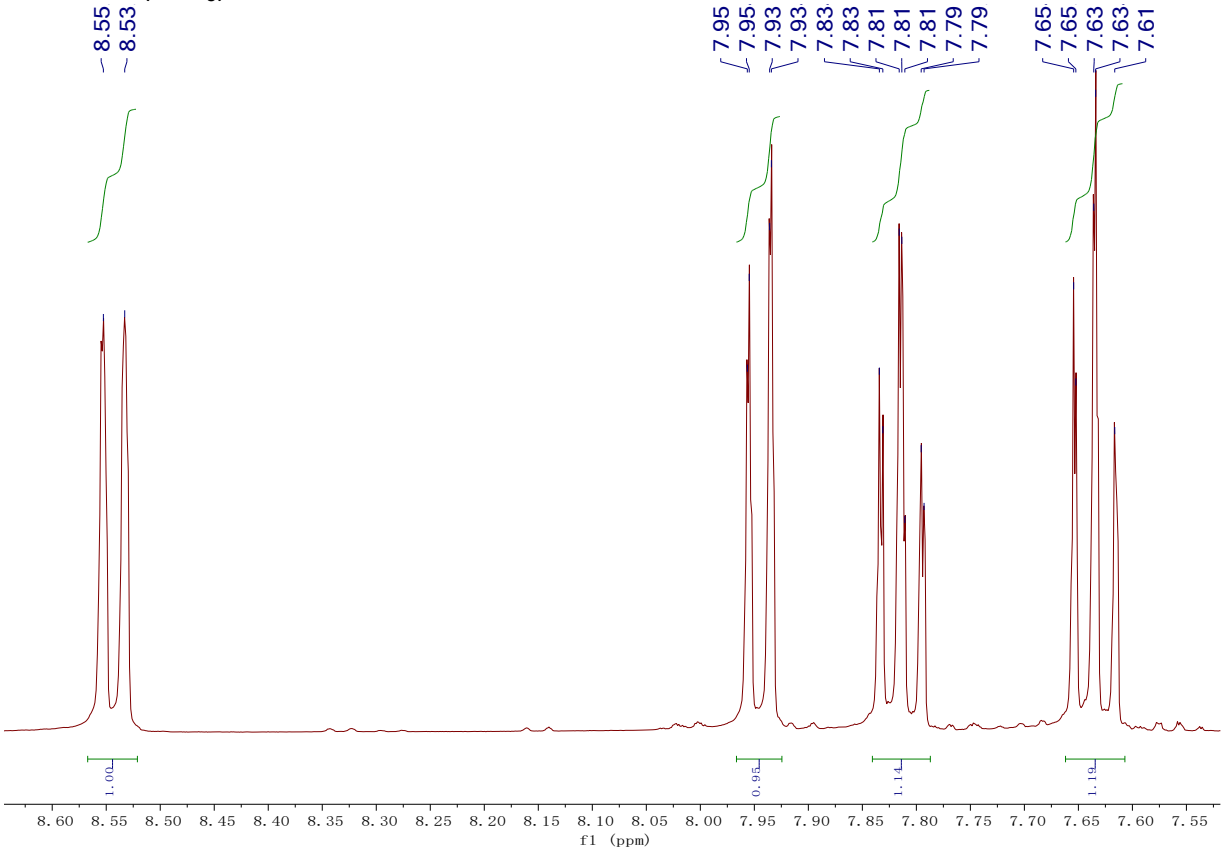
5a ^{1}H NMR ($CDCl_3$)



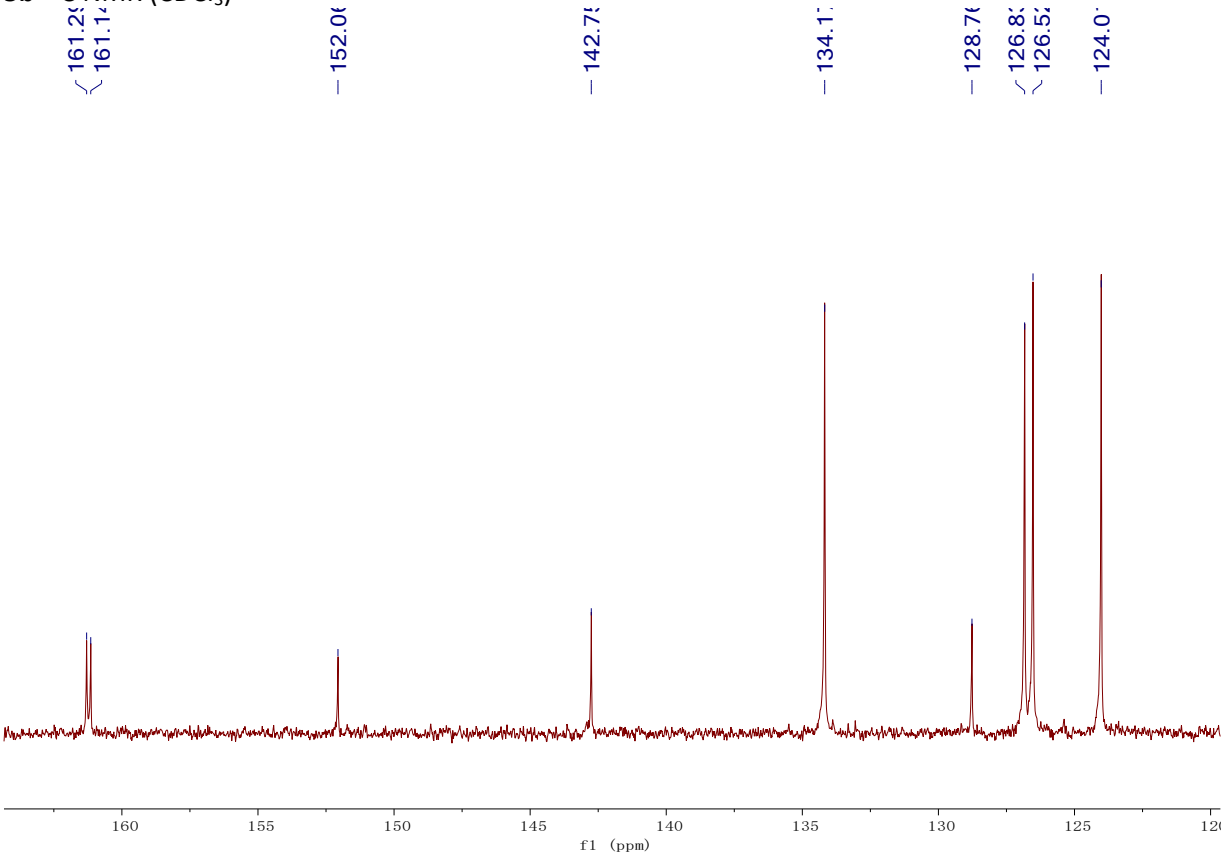
5a ^{13}C NMR ($CDCl_3$)



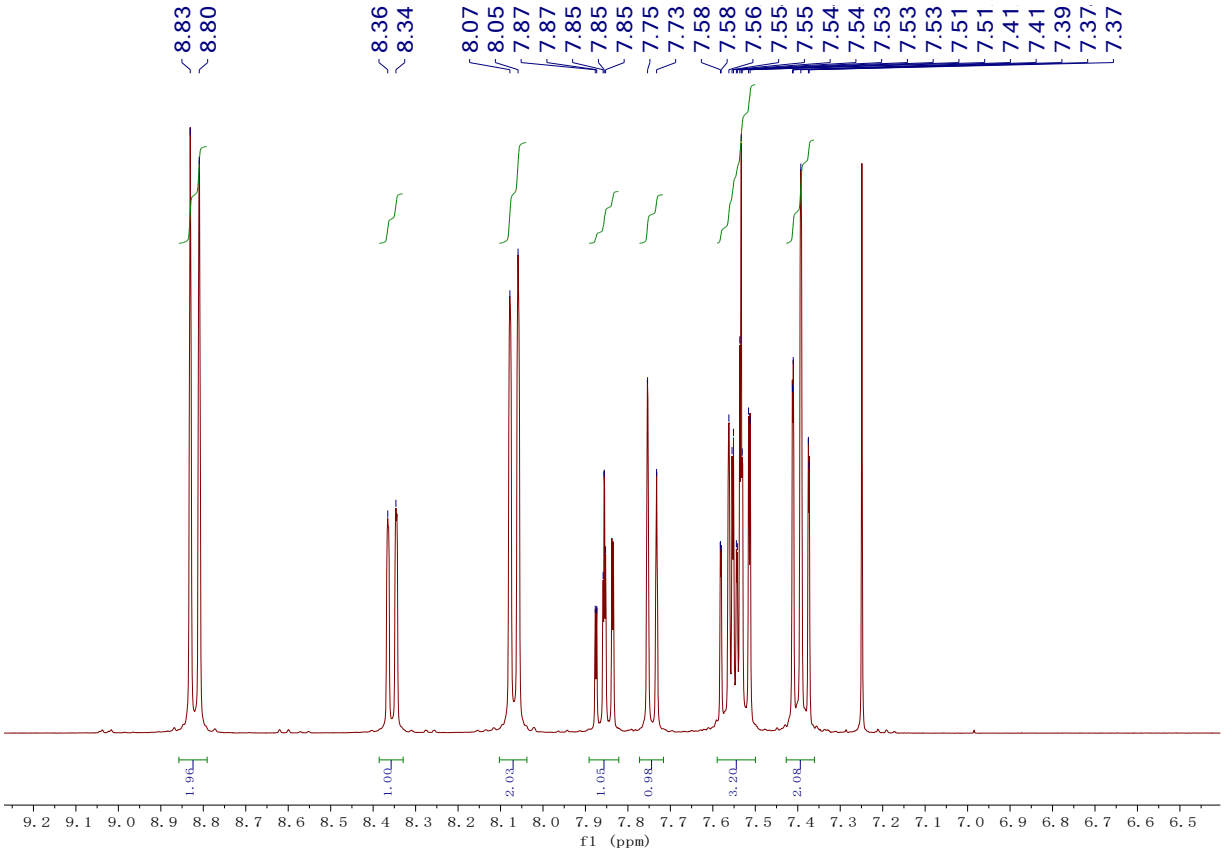
5b ^{1}H NMR ($CDCl_3$)



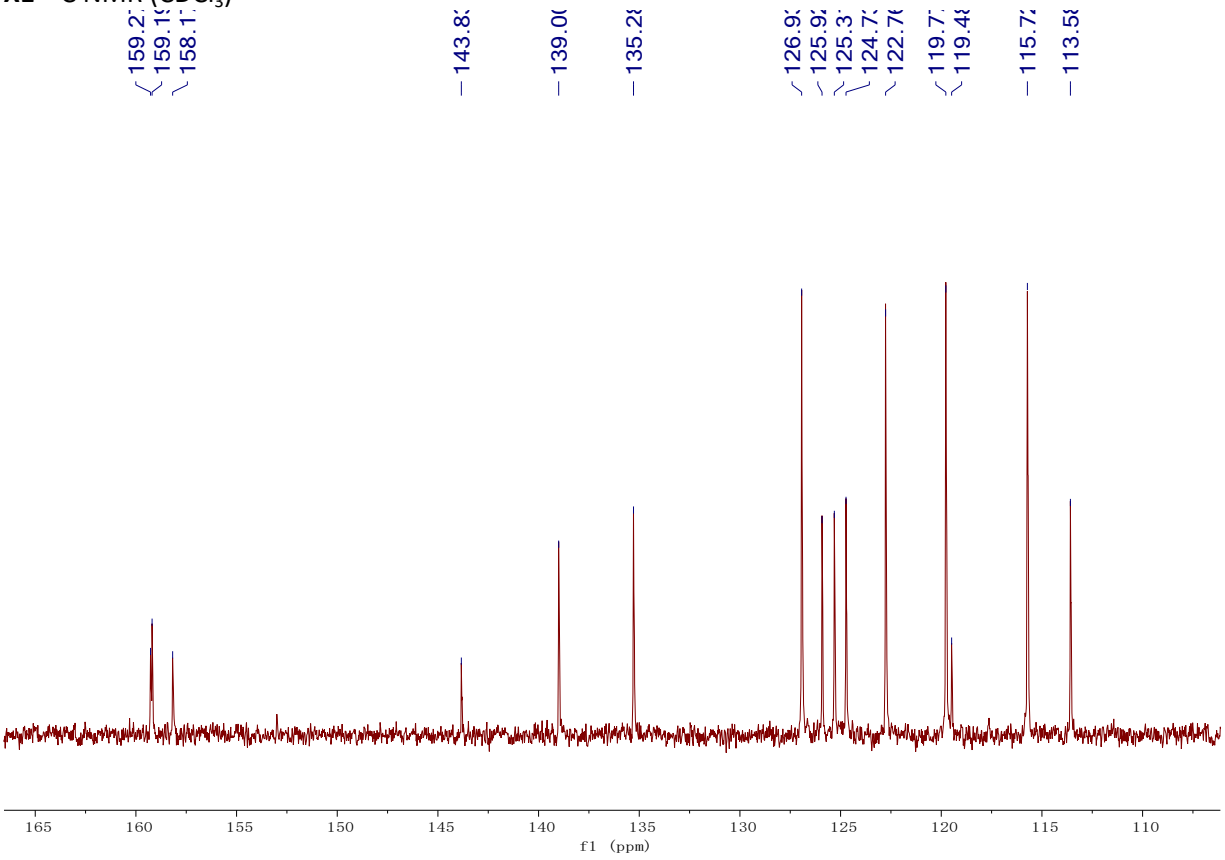
5b ^{13}C NMR ($CDCl_3$)



X1 ^{1}H NMR ($CDCl_3$)

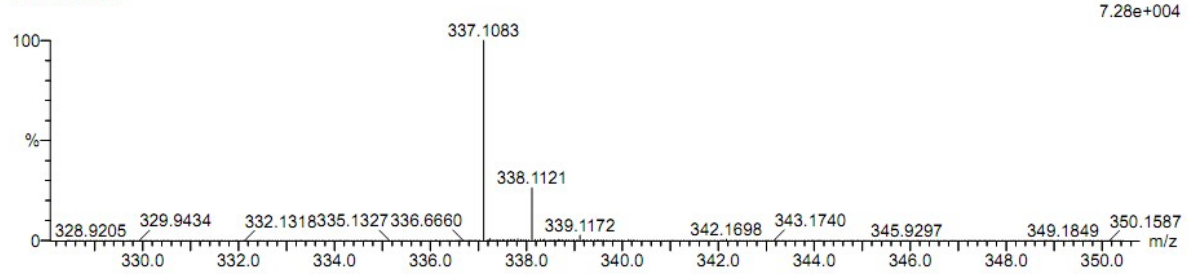


X1 ^{13}C NMR ($CDCl_3$)



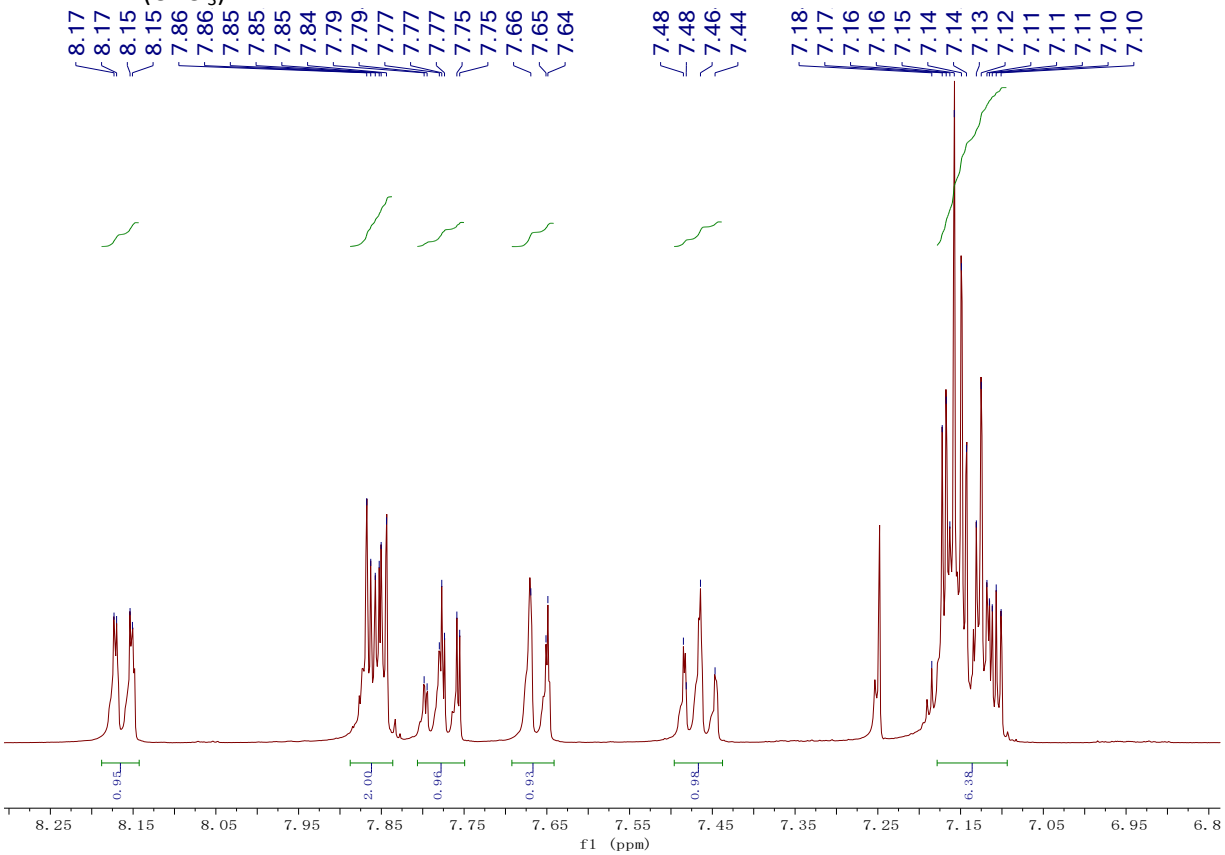
X1 EI HRMS

Monoisotopic Mass, Even Electron Ions
422 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-120 H: 1-150 N: 0-10 O: 0-10
PPSM_X1 21 (0.572) Cm (17:30)
1: TOF MS ES+

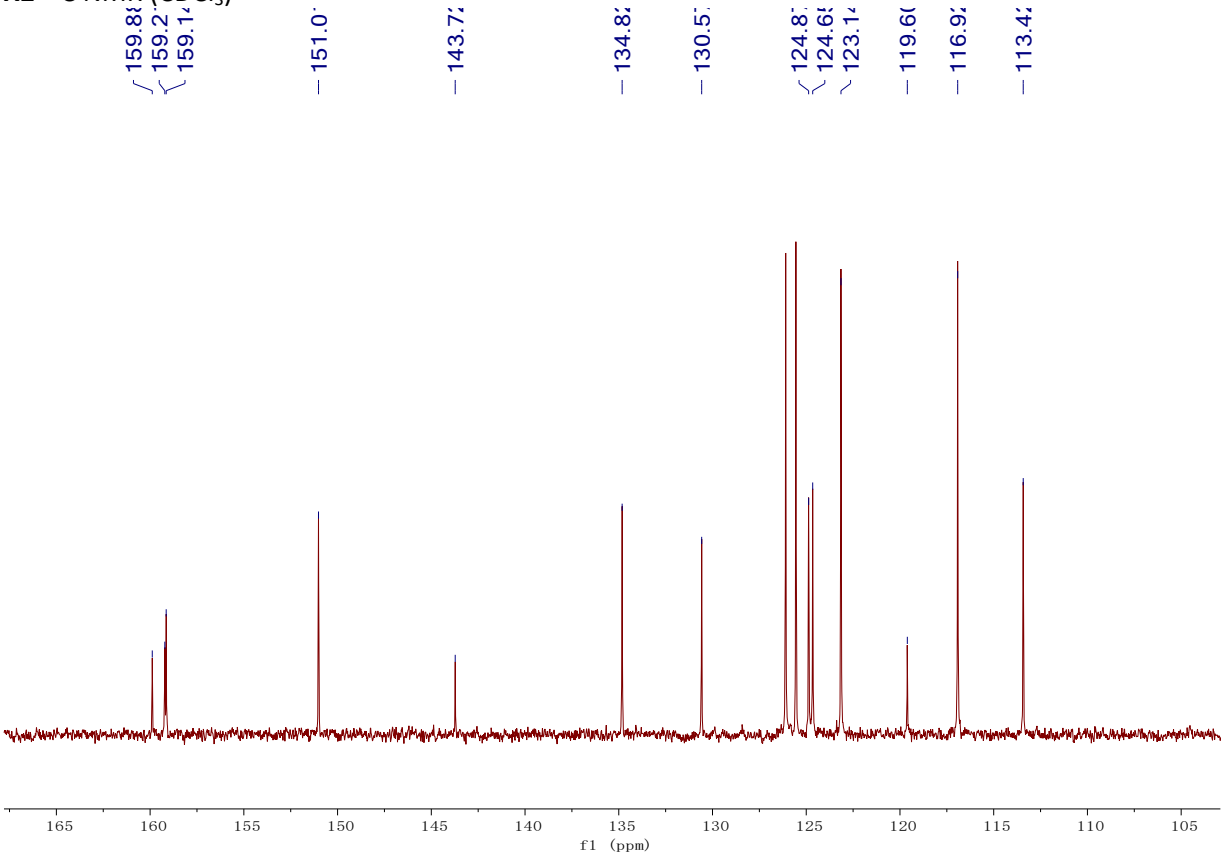


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
337.1083	337.1089	-0.6	-1.8	17.5	1365.1	0.1	C21 H13 N4 O
	337.1076	0.7	2.1	12.5	1367.5	2.4	C20 H17 O5
	337.1068	1.5	4.4	0.5	1379.8	14.7	C4 H17 N8 O10

X2 ^{1}H NMR ($CDCl_3$)



X2 ^{13}C NMR ($CDCl_3$)



X2 EI HRMS

Monoisotopic Mass, Even Electron Ions
446 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
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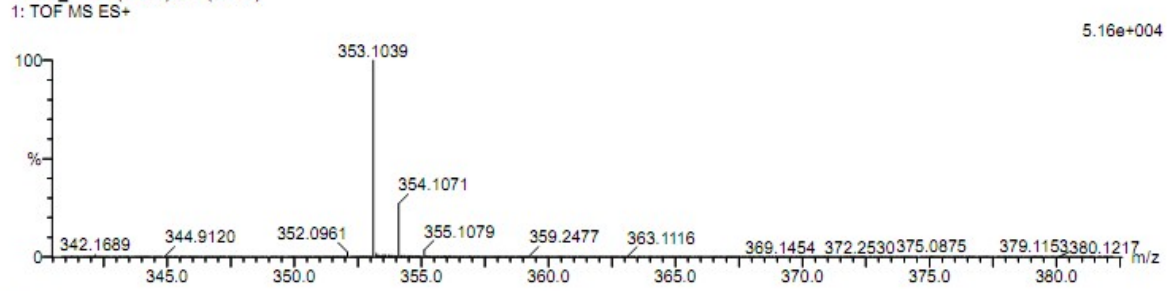
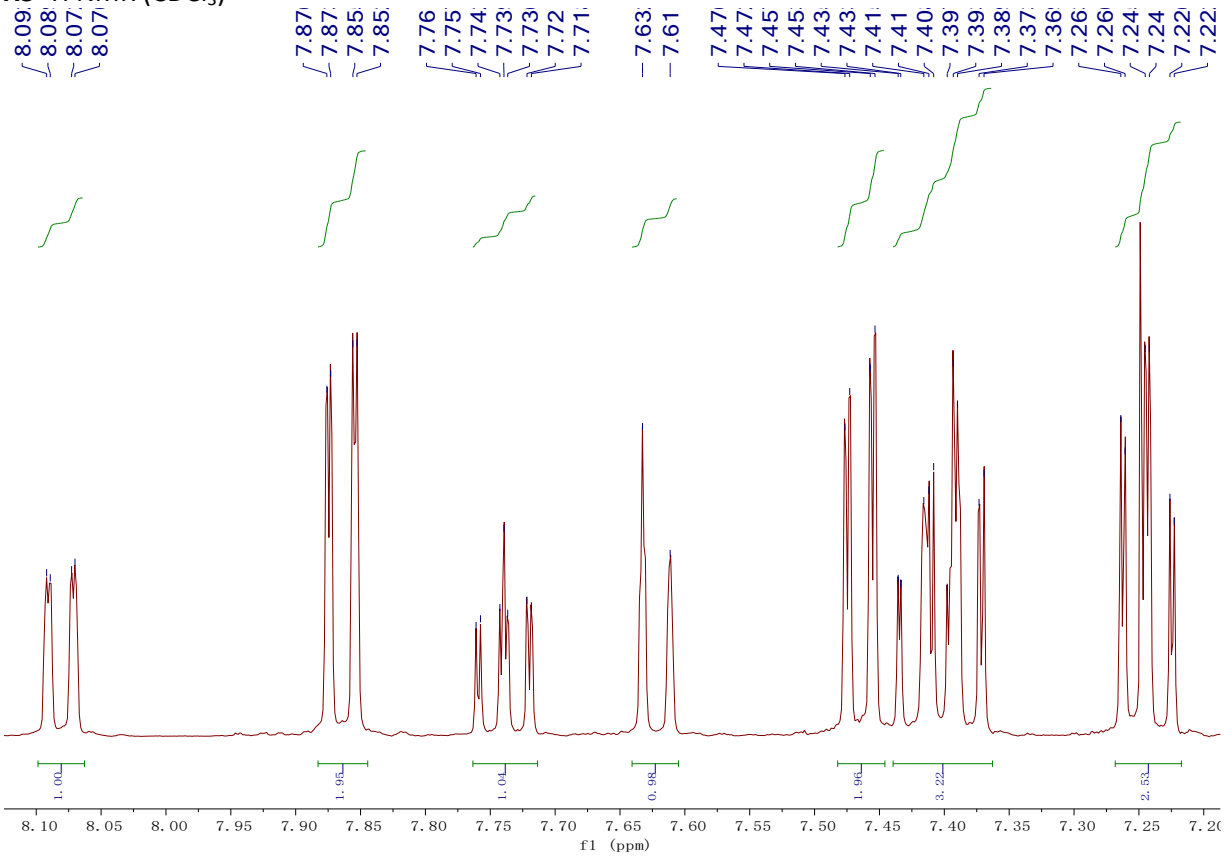
PPSM_X2 37 (0.934) Cm (37:49)
1: TOF MS ES+

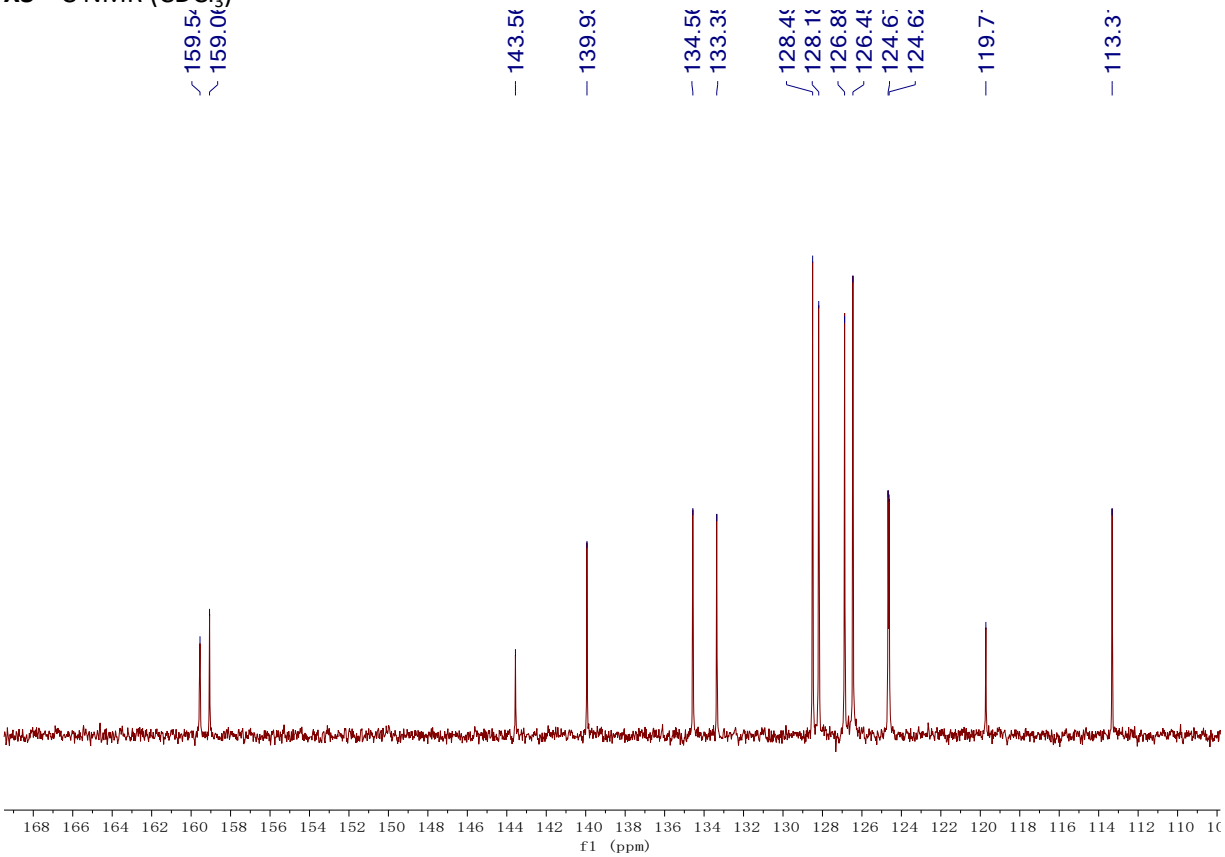


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
353.1039	353.1039	0.0	0.0	17.5	1199.2	0.0	C21 H13 N4 O2
	353.1025	1.4	4.0	12.5	1204.3	5.1	C20 H17 O6

X3 ^{1}H NMR ($CDCl_3$)



X3 ^{13}C NMR ($CDCl_3$)



X3 EI HRMS

Monoisotopic Mass, Even Electron Ions
422 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
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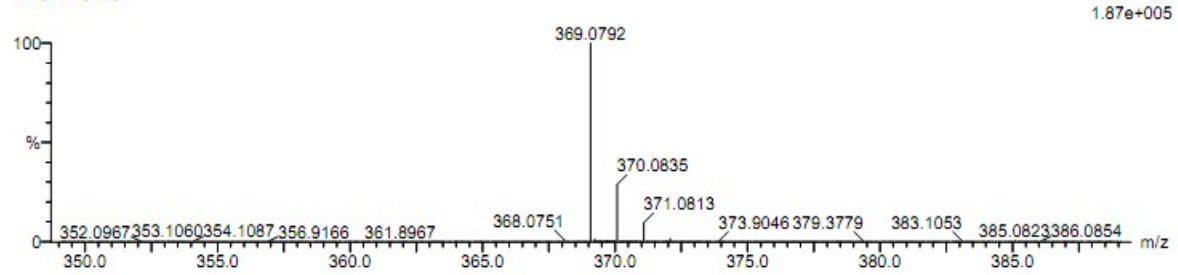
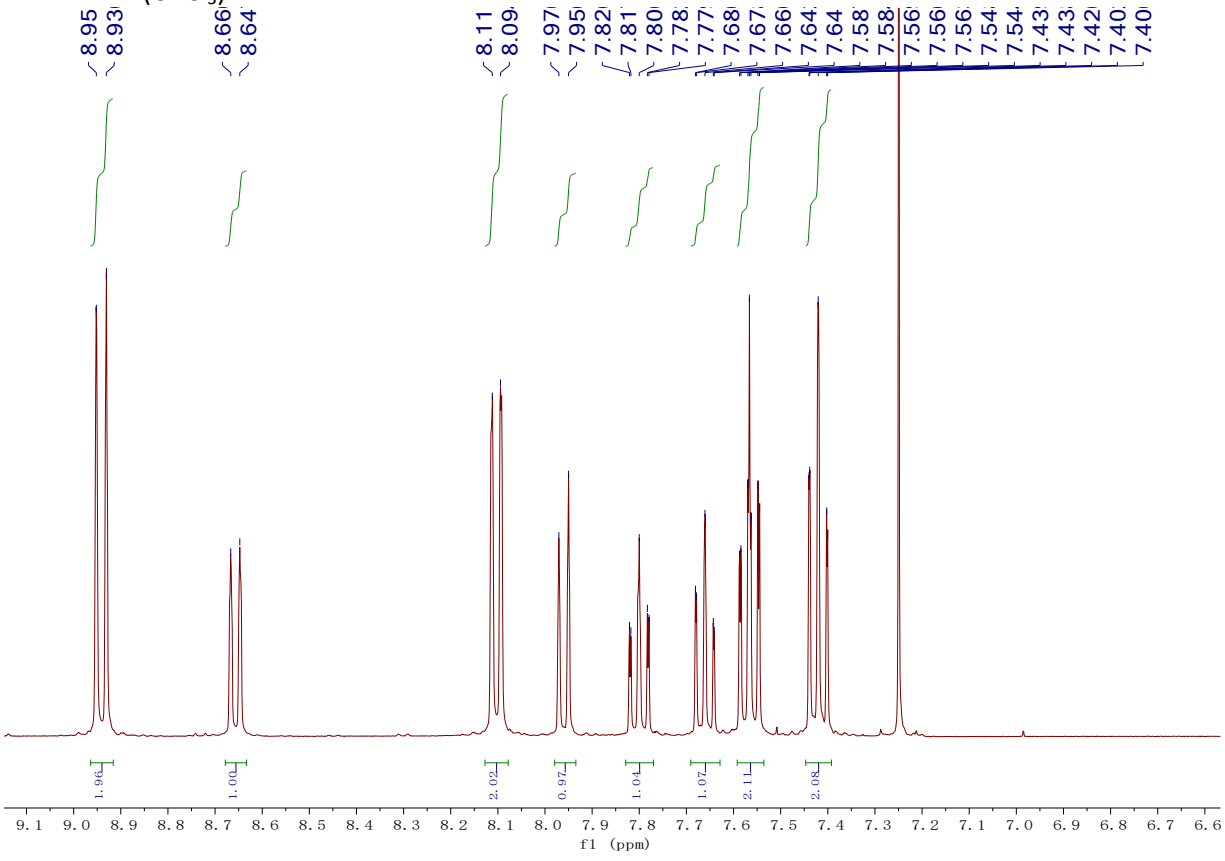
PPSM_X3 21 (0.572) Cm (19:26)
1: TOF MS ES+

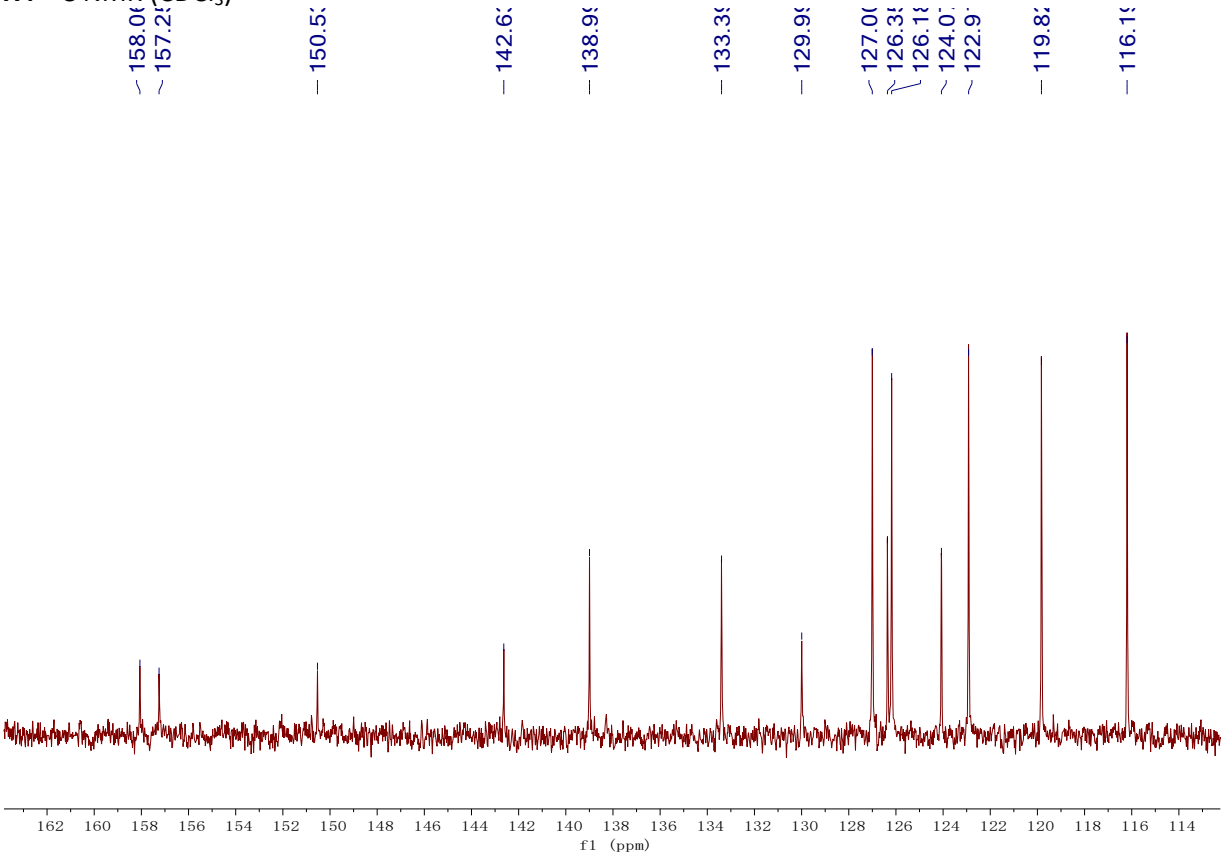


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
369.0792	369.0810	-1.8	-4.9	17.5	1449.4	0.1	C21 H13 N4 O S
	369.0797	-0.5	-1.4	12.5	1451.7	2.4	C20 H17 O5 S
	369.0788	0.4	1.1	0.5	1469.3	20.0	C4 H17 N8 O10 S

X4 ^{1}H NMR ($CDCl_3$)

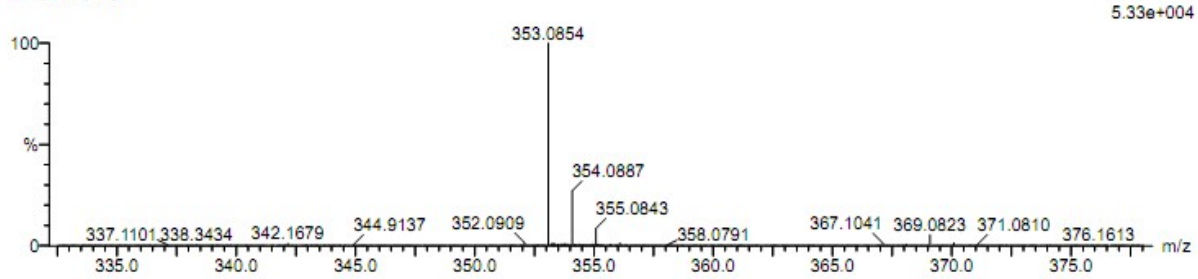


X4 ^{13}C NMR ($CDCl_3$)



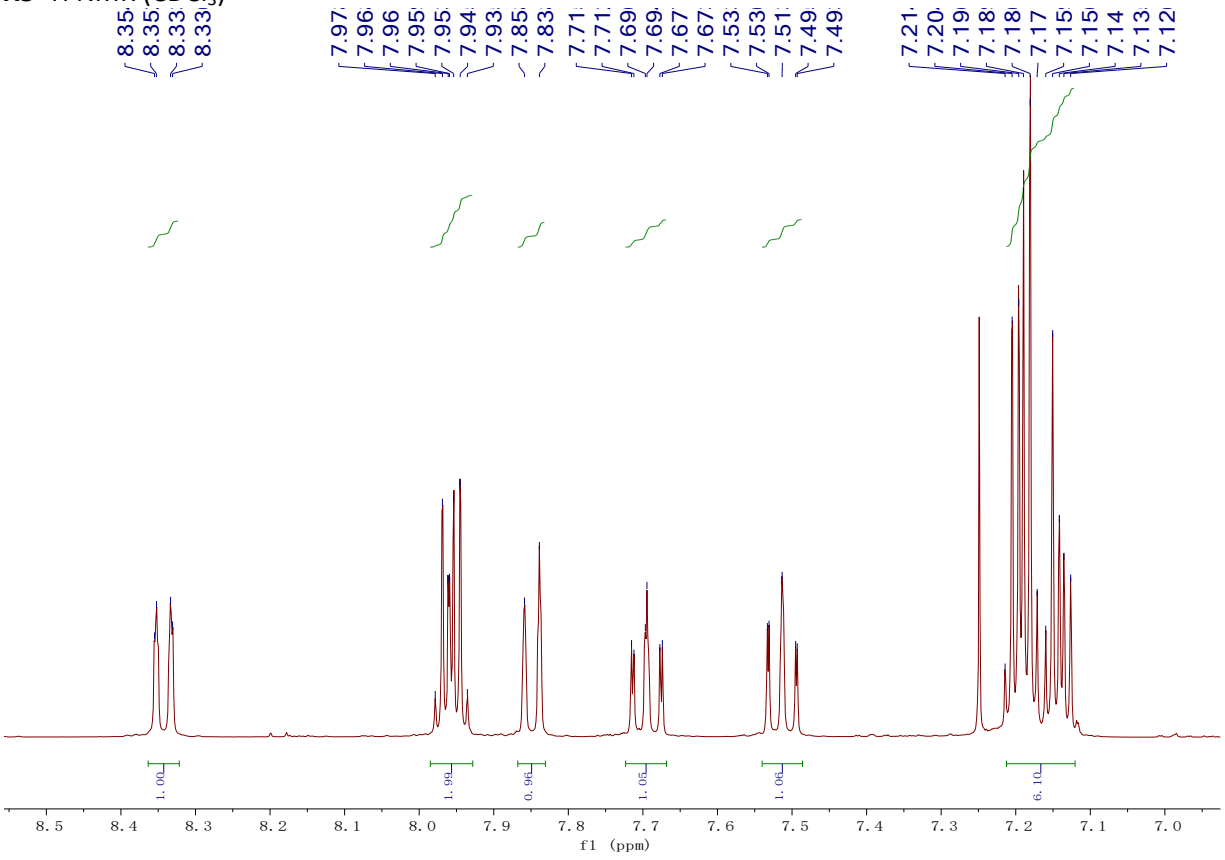
X4 EI HRMS

Monoisotopic Mass, Even Electron Ions
396 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-120 H: 1-150 N: 0-10 O: 0-10 S: 1-1
PPSM_X4 22 (0.589) Cm (18:30)
1: TOF MS ES+

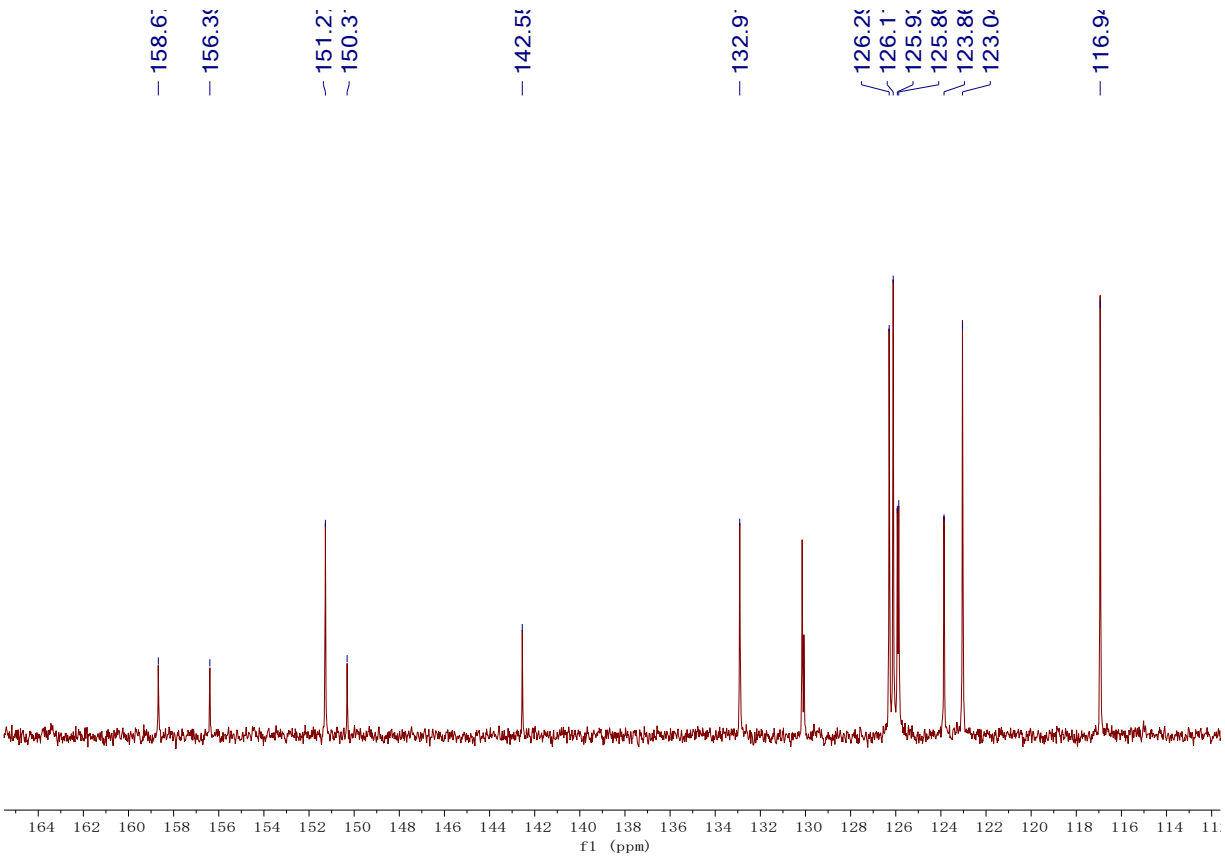


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
353.0854	353.0861	-0.7	-2.0	17.5	1271.5	0.0	C21 H13 N4 S
	353.0848	0.6	1.7	12.5	1276.3	4.9	C20 H17 O4 S
	353.0839	1.5	4.2	0.5	1292.6	21.1	C4 H17 N8 O9 S

X5 ^{1}H NMR ($CDCl_3$)



X5 ^{13}C NMR ($CDCl_3$)



X5 EI HRMS

Monoisotopic Mass, Even Electron Ions
422 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
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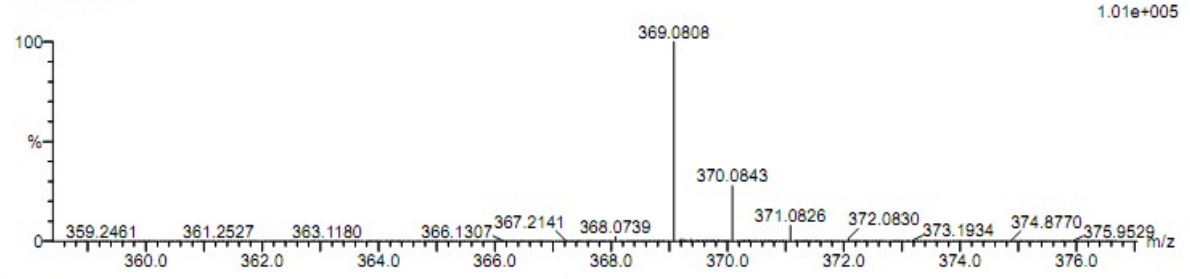
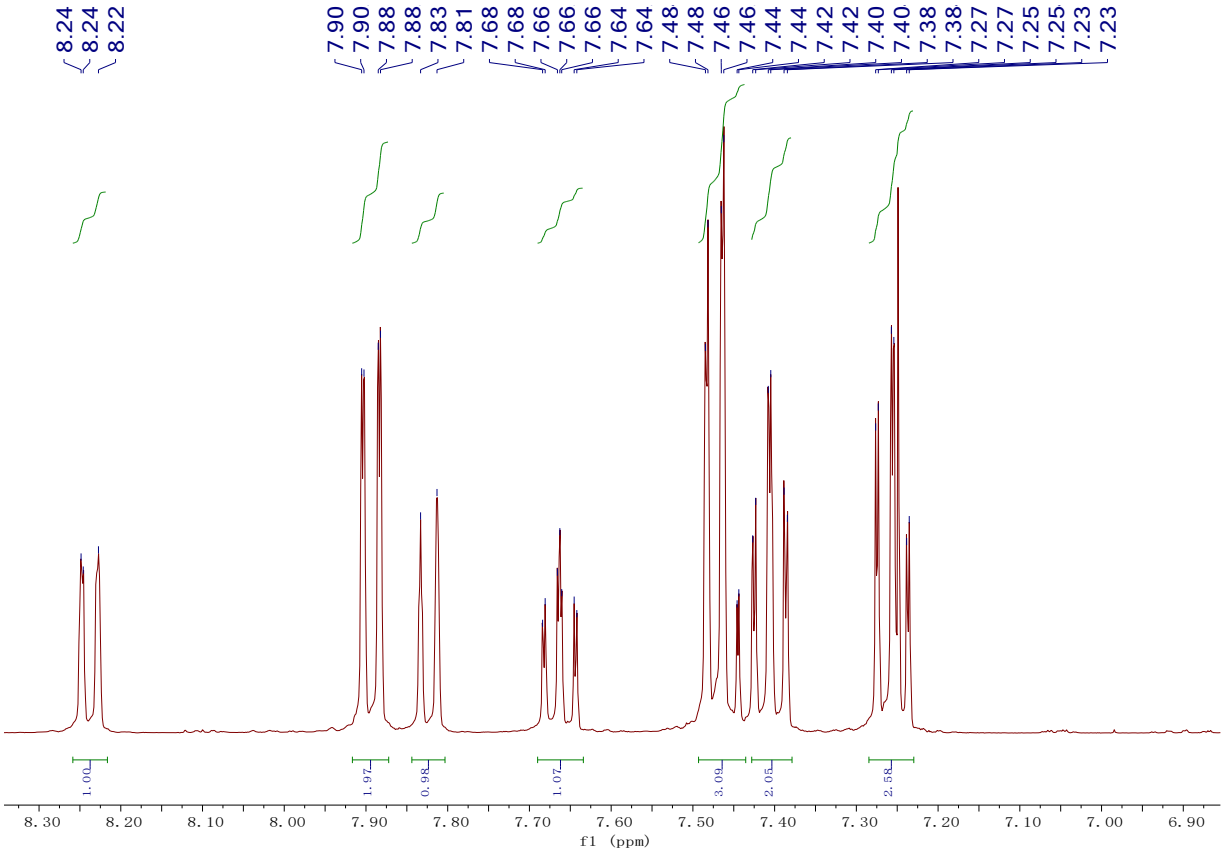
PPSM_X5 25 (0.663) Cm (20:27)
1: TOF MS ES+



Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
369.0808	369.0810	-0.2	-0.5	17.5	1274.3	0.0	C21 H13 N4 O S
	369.0797	1.1	3.0	12.5	1279.5	5.2	C20 H17 O5 S

X6 ^{1}H NMR ($CDCl_3$)


8.24
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7.88
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7.46
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7.25
7.23
7.23
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1.97
0.98
1.07
3.09
2.05
2.58
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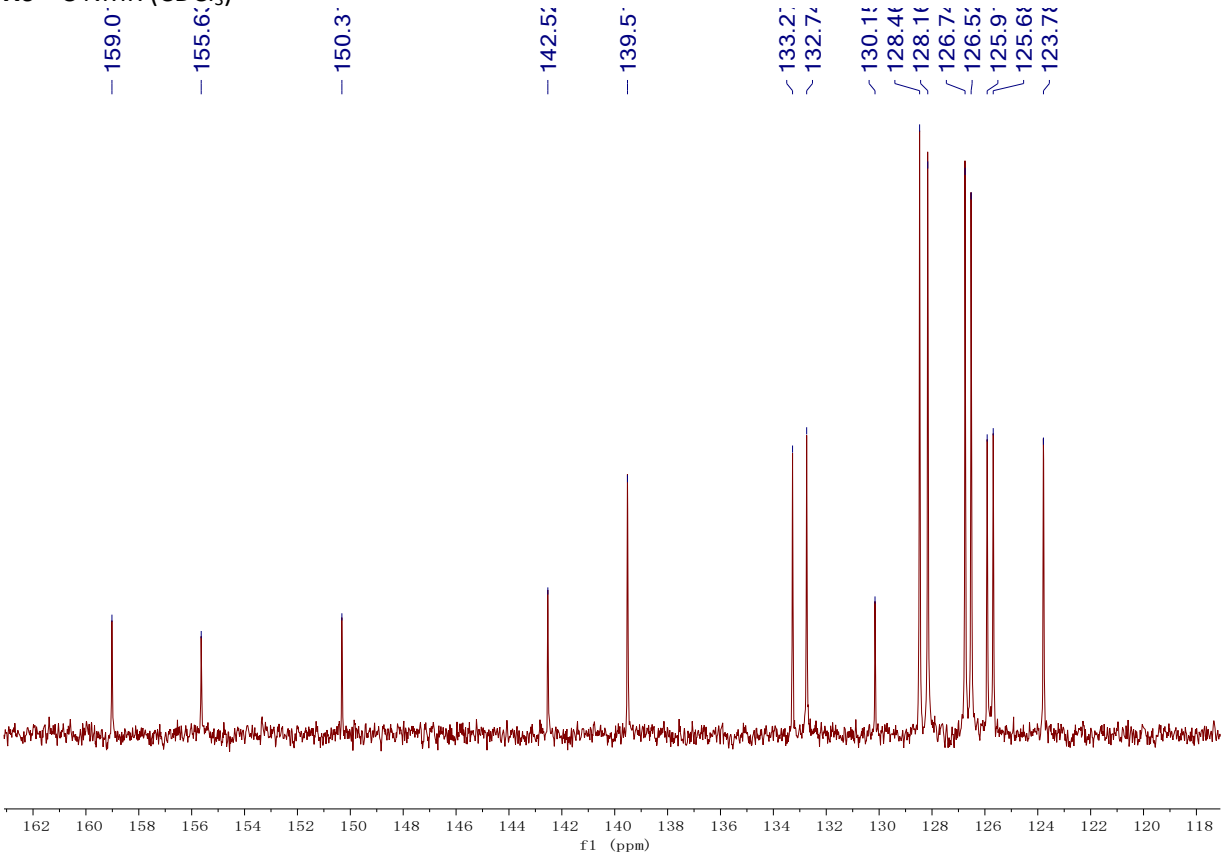
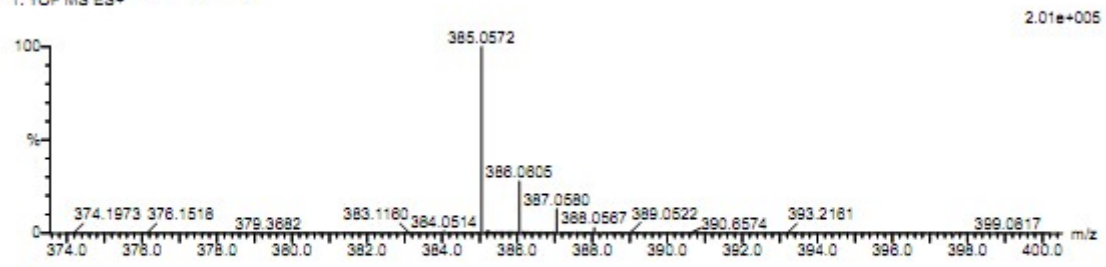
8.20
8.10
8.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
f1 (ppm)

X6 ^{13}C NMR ($CDCl_3$)



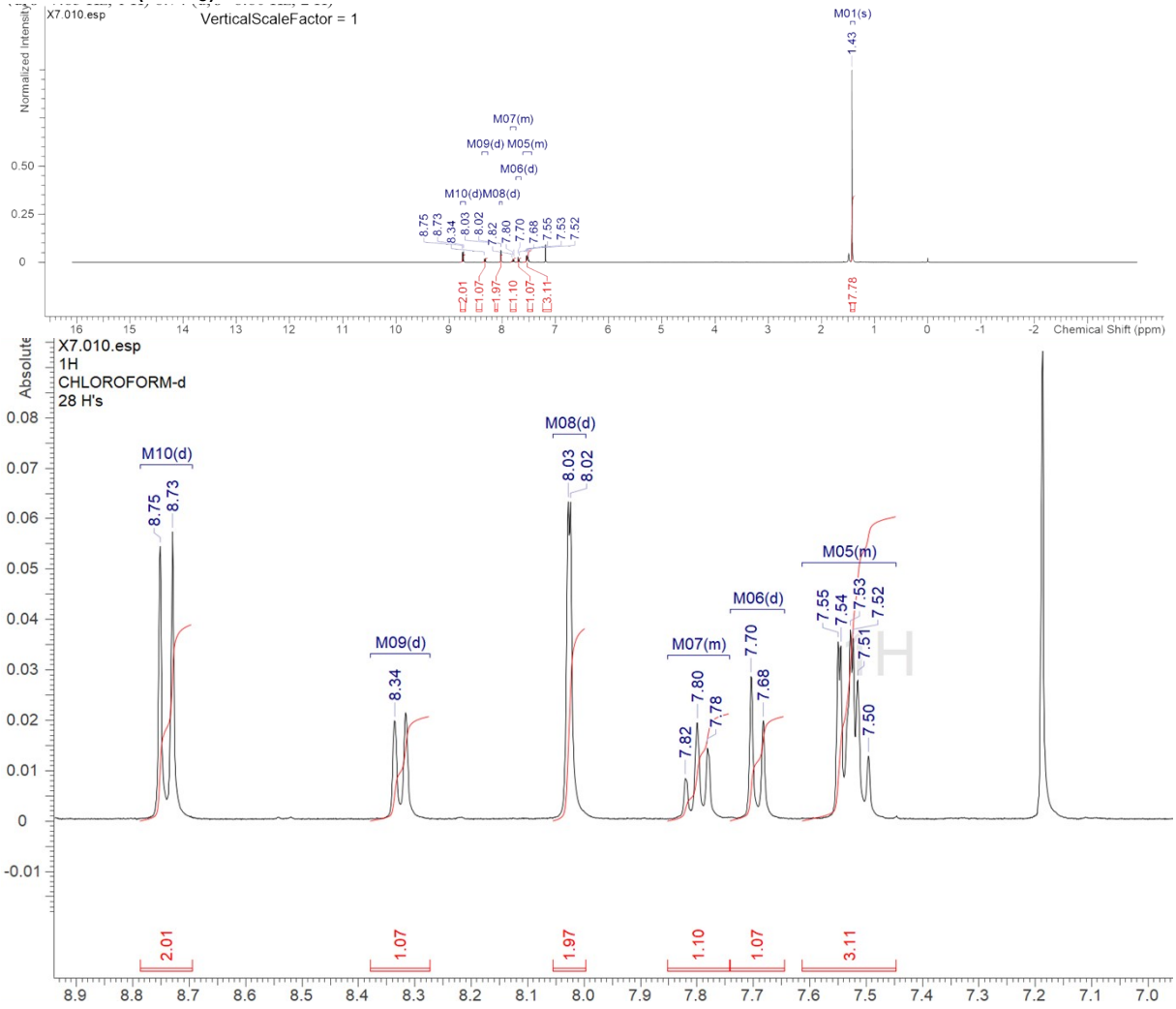
X6 EI HRMS

Monoisotopic Mass, Even Electron Ions
396 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-120 H: 1-150 N: 0-10 O: 0-10 S: 2-2
PPSM X8 19 (0.517) Cm (17:28)
1: TOF MS ES+

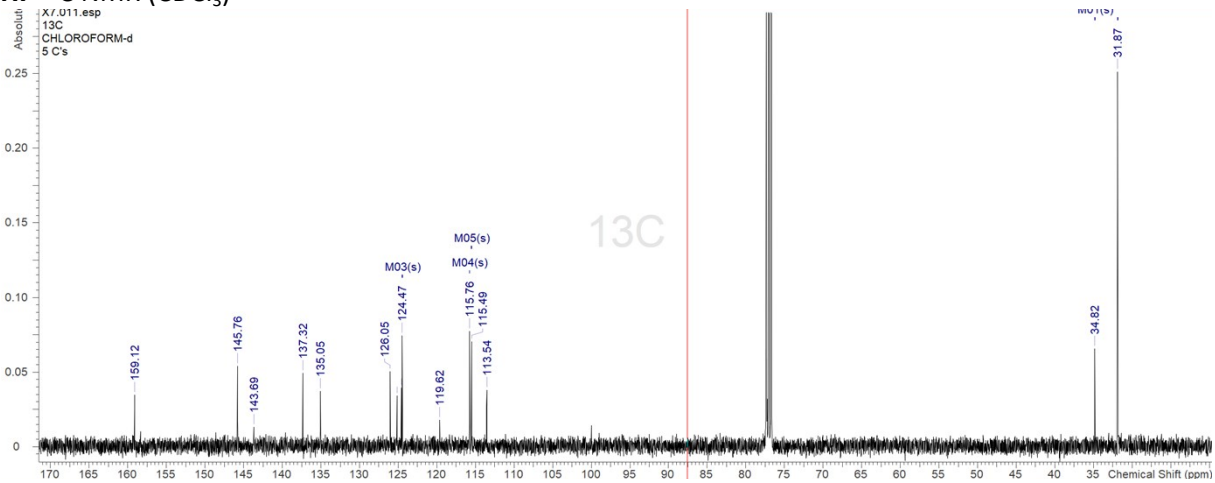


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
385.0572	385.0592	-1.0	-2.6	17.5	1573.8	0.0	C21 H13 N4 S2
	385.0569	0.4	1.0	12.5	1582.6	8.8	C20 H17 O4 S2
	385.0560	1.2	3.1	0.5	1601.2	27.4	C4 H17 N8 O9 S2

X7 ^{1}H NMR ($CDCl_3$)

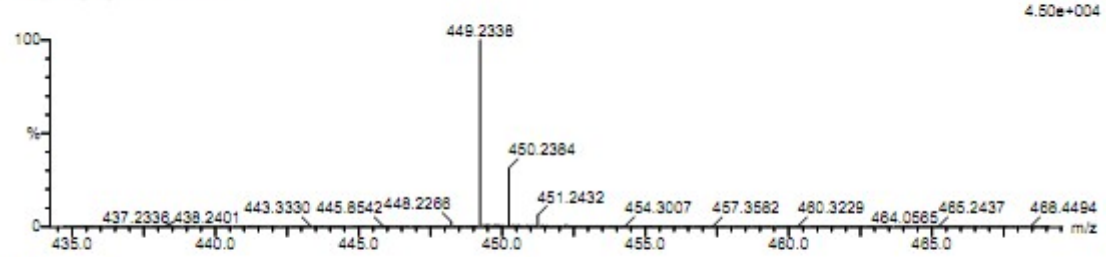


X7 ^{13}C NMR ($CDCl_3$)



X7 EI HRMS

Monoisotopic Mass, Even Electron Ions
583 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-120 H: 1-150 N: 0-10 O: 0-10
PPSM X7 30 (0.771) Cm (30:41)
1: TOF MS ES+



Minimum:				-1.5						
Maximum:		5.0	5.0	100.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
449.2338	449.2328	1.0	2.2	12.5	1140.3	0.0	C28	H33	O5	
	449.2341	-0.3	-0.7	17.5	1143.7	3.5	C29	H29	N4	O
	449.2360	-2.2	-4.9	4.5	1155.3	15.1	C17	H33	N6	O8
	449.2320	1.8	4.0	0.5	1161.1	20.9	C12	H33	N8	O10

8. Geometries of the calculated compounds

X1 ground state

Label	Atom	X	Y	Z
1	C	0.090549	-0.601409	-0.151868
2	C	-2.10656	-0.198777	-0.010199
3	C	-2.295356	-1.570487	-0.293268
4	N	-1.321102	-2.419089	-0.497902
5	N	-0.085225	-1.911168	-0.436392
6	N	-0.885889	0.306799	0.072791
7	C	-4.300679	-0.735007	-0.062145
8	C	-5.683105	-0.620277	0.001224
9	C	-3.431217	0.357022	0.145264
10	C	-6.190019	0.649631	0.286007
11	H	-6.328365	-1.477004	-0.162455
12	C	-3.960008	1.62317	0.431702
13	C	-5.344218	1.756786	0.499222
14	H	-7.266381	0.785604	0.345369
15	H	-3.302006	2.470801	0.59765
16	H	-5.782159	2.725882	0.719619
17	O	-3.62169	-1.909136	-0.32875
18	N	1.409661	-0.159895	-0.082927
19	C	2.564501	-0.982505	0.056673
20	C	1.836947	1.196428	-0.120814
21	C	2.694007	-2.372842	0.159743
22	C	3.702365	-0.1446	0.118771
23	C	1.111854	2.383554	-0.280337
24	C	3.246794	1.223946	-0.004975
25	C	3.977155	-2.898351	0.330098
26	H	1.833397	-3.021532	0.093344
27	C	4.978838	-0.692826	0.282934
28	C	1.821491	3.58648	-0.317567
29	H	0.035514	2.377013	-0.361854
30	C	3.93722	2.439925	-0.038101
31	C	5.112526	-2.075293	0.389282
32	H	4.091405	-3.976293	0.410036
33	H	5.851457	-0.04634	0.329685
34	C	3.218893	3.623468	-0.193992
35	H	1.269314	4.514574	-0.441555
36	H	5.02043	2.457432	0.05091
37	H	6.096608	-2.518212	0.517059
38	H	3.740328	4.57642	-0.222719

X1 first singlet excited state (S1)

Label	Atom	X	Y	Z
1	C	0.046162	-0.448008	-0.413664
2	C	-2.081293	-0.10014	-0.014296
3	C	-2.29193	-1.170709	-0.906574
4	N	-1.383206	-1.870641	-1.540346
5	N	-0.090221	-1.442736	-1.251088
6	N	-0.798344	0.309735	0.265528
7	C	-4.273412	-0.526629	-0.248493
8	C	-5.640042	-0.445918	-0.103616
9	C	-3.3617	0.324326	0.421569
10	C	-6.128004	0.542222	0.763902
11	H	-6.301874	-1.120054	-0.638498
12	C	-3.872422	1.305929	1.288068
13	C	-5.252149	1.398879	1.444623
14	H	-7.199946	0.641212	0.90876
15	H	-3.200574	1.970938	1.822526
16	H	-5.662072	2.152771	2.112268
17	O	-3.617108	-1.43195	-1.051774
18	N	1.453746	-0.112641	-0.175433
19	C	2.422294	-1.001866	0.18735
20	C	1.991019	1.144893	-0.279997
21	C	2.308141	-2.386406	0.397205
22	C	3.656707	-0.307966	0.342819
23	C	1.3557	2.339324	-0.640935
24	C	3.375183	1.085114	0.033387
25	C	3.457489	-3.06565	0.782564
26	H	1.363456	-2.889032	0.233768
27	C	4.784004	-1.006959	0.721658
28	C	2.141522	3.488269	-0.684483
29	H	0.294681	2.356616	-0.854253
30	C	4.133449	2.238084	-0.014339
31	C	4.67423	-2.394219	0.943185
32	H	3.410685	-4.13665	0.952271
33	H	5.74121	-0.509177	0.849167
34	C	3.503448	3.44398	-0.377597
35	H	1.684435	4.433897	-0.958539
36	H	5.194382	2.225982	0.219704
37	H	5.557072	-2.952558	1.240512
38	H	4.091195	4.356347	-0.418144

X2 ground state

Label	Atom	X	Y	Z
1	C	-0.093148	-0.623289	0.315815
2	C	2.105609	-0.291982	0.073318
3	C	2.233619	-1.698429	0.03332
4	N	1.230492	-2.52968	0.148612
5	N	0.023956	-1.972725	0.298868
6	N	0.917661	0.271744	0.22047
7	C	4.262166	-0.916279	-0.188657
8	C	5.639902	-0.844711	-0.350773
9	C	3.44555	0.229147	-0.074018
10	C	6.196685	0.43539	-0.397256
11	H	6.24472	-1.741377	-0.43703
12	C	4.023384	1.505028	-0.124207
13	C	5.403464	1.595211	-0.286239
14	H	7.27108	0.537935	-0.523363
15	H	3.403892	2.392976	-0.040968
16	H	5.878906	2.570819	-0.329442
17	O	3.539439	-2.091176	-0.122907
18	N	-1.384249	-0.117573	0.450975
19	C	-2.54952	-0.929312	0.240008
20	C	-1.641922	1.289999	0.384816
21	C	-3.502078	-0.437816	-0.662506
22	C	-2.801289	-2.137881	0.897017
23	C	-2.62078	1.715561	-0.521262
24	C	-1.01069	2.239666	1.193903
25	C	-4.661275	-1.151154	-0.955851
26	O	-3.312328	0.788448	-1.276861
27	C	-3.959383	-2.861266	0.605661
28	H	-2.075009	-2.522297	1.601095
29	C	-2.932358	3.064979	-0.67218
30	H	-0.268257	1.916657	1.91405
31	C	-1.312603	3.594436	1.047141
32	C	-4.88177	-2.377503	-0.327169
33	H	-5.36918	-0.734517	-1.665847
34	H	-4.134794	-3.809065	1.106455
35	H	-3.695075	3.351042	-1.389971
36	C	-2.261835	4.008987	0.106642
37	H	-0.804724	4.325897	1.669441
38	H	-5.779466	-2.945372	-0.555614
39	H	-2.494375	5.064071	-0.008277

X2 first singlet excited state (S1)

Label	Atom	X	Y	Z
1	C	-0.003156	-0.000095	0.589922
2	C	2.112364	-0.000026	0.017562
3	C	2.353803	-0.000252	1.404232
4	N	1.464606	-0.000398	2.370682
5	N	0.161779	-0.000306	1.887996
6	N	0.816886	0.000063	-0.448687
7	C	4.317025	-0.000119	0.445696
8	C	5.681622	-0.000107	0.25975
9	C	3.381363	0.000063	-0.616448
10	C	6.140546	0.000099	-1.065024
11	H	6.363051	-0.000251	1.104926
12	C	3.863172	0.000264	-1.936354
13	C	5.239904	0.000276	-2.139205
14	H	7.209491	0.000115	-1.258142
15	H	3.171499	0.000407	-2.773488
16	H	5.628083	0.000431	-3.154817
17	O	3.687336	-0.000309	1.669306
18	N	-1.426111	-0.000019	0.214651
19	C	-2.081719	-1.187568	0.037041
20	C	-2.081622	1.187606	0.037174
21	C	-3.442332	-1.170536	-0.350716
22	C	-1.455739	-2.433814	0.226604
23	C	-3.442231	1.170727	-0.350592
24	C	-1.455543	2.433778	0.226879
25	C	-4.160126	-2.344507	-0.548253
26	O	-4.095709	0.000132	-0.544654
27	C	-2.171512	-3.59583	0.02933
28	H	-0.41739	-2.460456	0.530104
29	C	-4.159928	2.344776	-0.548015
30	H	-0.417192	2.460312	0.530382
31	C	-2.17122	3.595876	0.029728
32	C	-3.522857	-3.558683	-0.358237
33	H	-5.201753	-2.277689	-0.845409
34	H	-1.680708	-4.552251	0.178926
35	H	-5.20156	2.278082	-0.845187
36	C	-3.522563	3.55888	-0.357864
37	H	-1.680337	4.552239	0.179425
38	H	-4.071097	-4.483475	-0.508069
39	H	-4.070725	4.483731	-0.507615

X3 ground state

Label	Atom	X	Y	Z
1	C	0.015965	-0.636131	-0.300017
2	C	2.215457	-0.308334	-0.070308
3	C	2.333542	-1.712057	0.03419
4	N	1.324595	-2.541317	-0.04021
5	N	0.121435	-1.984612	-0.213916
6	N	1.031473	0.256754	-0.245212
7	C	4.367911	-0.935053	0.219521
8	C	5.746363	-0.865502	0.376892
9	C	3.559161	0.209542	0.052552
10	C	6.31224	0.411388	0.362955
11	H	6.345055	-1.761406	0.504188
12	C	4.146035	1.482212	0.042142
13	C	5.526957	1.570259	0.198441
14	H	7.387512	0.512116	0.483041
15	H	3.532523	2.369462	-0.08258
16	H	6.009236	2.543481	0.195104
17	O	3.637155	-2.106399	0.208749
18	N	-1.269524	-0.130215	-0.460383
19	C	-1.511316	1.283107	-0.465718
20	C	-2.428617	-0.96944	-0.341945
21	C	-2.355971	1.823115	0.515189
22	C	-0.967055	2.118494	-1.446455
23	C	-3.372547	-0.665261	0.649926
24	C	-2.65929	-2.039446	-1.212208
25	C	-2.622329	3.197726	0.534043
26	S	-3.090666	0.734264	1.723691
27	C	-1.217046	3.489936	-1.414311
28	H	-0.331699	1.690498	-2.214572
29	C	-4.524496	-1.448765	0.789423
30	H	-1.929839	-2.26464	-1.981923
31	C	-3.796856	-2.83063	-1.058722
32	C	-2.037666	4.031842	-0.418749
33	H	-3.291347	3.603671	1.287807
34	H	-0.778185	4.134082	-2.171373
35	H	-5.256877	-1.194876	1.550762
36	C	-4.726101	-2.541322	-0.053574
37	H	-3.958121	-3.672715	-1.725927
38	H	-2.240825	5.099184	-0.397574
39	H	-5.615914	-3.154232	0.062422

X3 first singlet excited state (S1)

Label	Atom	X	Y	Z
1	C	-0.125537	-0.000124	0.609121
2	C	-2.237206	-0.000019	0.012286
3	C	-2.496204	-0.000461	1.395905
4	N	-1.618476	-0.000731	2.372013
5	N	-0.309014	-0.000535	1.905278
6	N	-0.936345	0.000163	-0.437051
7	C	-4.447401	-0.000183	0.412776
8	C	-5.80946	-0.000148	0.209382
9	C	-3.498174	0.000149	-0.637454
10	C	-6.251596	0.000236	-1.121266
11	H	-6.501639	-0.000411	1.045787
12	C	-3.963256	0.00053	-1.963478
13	C	-5.337285	0.000563	-2.183848
14	H	-7.318001	0.000278	-1.327953
15	H	-3.260837	0.000791	-2.791608
16	H	-5.712497	0.000855	-3.204338
17	O	-3.833395	-0.00055	1.644386
18	N	1.303631	-0.000009	0.246779
19	C	1.913124	1.220885	0.086666
20	C	1.913205	-1.220831	0.086461
21	C	3.266947	1.355445	-0.314522
22	C	1.182805	2.407234	0.325848
23	C	3.267027	-1.35523	-0.314743
24	C	1.182965	-2.407284	0.325412
25	C	3.851114	2.621696	-0.469088
26	S	4.288889	0.000165	-0.651458
27	C	1.770782	3.64167	0.16886
28	H	0.152114	2.334565	0.643041
29	C	3.851312	-2.621412	-0.469539
30	H	0.152275	-2.334779	0.642647
31	C	1.771035	-3.641638	0.168179
32	C	3.112221	3.761515	-0.231143
33	H	4.891349	2.690717	-0.777114
34	H	1.182208	4.533144	0.362499
35	H	4.891555	-2.690268	-0.777571
36	C	3.112495	-3.761323	-0.231834
37	H	1.182523	-4.533198	0.36162
38	H	3.566761	4.739949	-0.350462
39	H	3.567078	-4.739717	-0.351316

X4 ground state

Label	Atom	X	Y	Z
1	C	-0.259832	-0.625036	-0.148811
2	C	1.955788	-0.240501	-0.013173
3	C	2.144186	-1.619904	-0.283331
4	N	1.129114	-2.446927	-0.471295
5	N	-0.098711	-1.942468	-0.414236
6	N	0.729269	0.262514	0.061317
7	S	3.842385	-2.092517	-0.337641
8	C	4.310087	-0.416976	0.012081
9	C	5.620607	0.053332	0.140371
10	C	3.209536	0.459625	0.163814
11	C	5.816295	1.404504	0.423297
12	H	6.468209	-0.615902	0.023944
13	C	3.425006	1.816189	0.451811
14	C	4.728103	2.28295	0.579946
15	H	6.829776	1.783181	0.526095
16	H	2.573693	2.479355	0.574735
17	H	4.91003	3.330202	0.803419
18	N	-1.571806	-0.165214	-0.087412
19	C	-1.980542	1.194925	-0.158753
20	C	-2.736856	-0.967603	0.082136
21	C	-1.239475	2.365067	-0.361874
22	C	-3.388639	1.246074	-0.031932
23	C	-2.883607	-2.3527	0.223102
24	C	-3.862371	-0.112436	0.13142
25	C	-1.931223	3.577079	-0.428107
26	H	-0.164358	2.338507	-0.456337
27	C	-4.061115	2.470935	-0.094411
28	C	-4.17227	-2.856112	0.41676
29	H	-2.032081	-3.014429	0.16687
30	C	-5.144654	-0.638781	0.320163
31	C	-3.32661	3.638417	-0.291524
32	H	-1.3671	4.492699	-0.586243
33	H	-5.143116	2.507743	0.002934
34	C	-5.295858	-2.016152	0.463383
35	H	-4.300579	-3.929914	0.525651
36	H	-6.00813	0.020442	0.35746
37	H	-3.834199	4.597822	-0.343546
38	H	-6.284701	-2.442136	0.61045

X4 first singlet excited state (S1)

Label	Atom	X	Y	Z
1	C	-0.213338	-0.507934	-0.403268
2	C	1.936441	-0.144924	-0.04232
3	C	2.139008	-1.288476	-0.844606
4	N	1.193869	-2.020556	-1.407127
5	N	-0.095354	-1.570863	-1.155986
6	N	0.648428	0.287056	0.198711
7	S	3.842285	-1.664294	-1.020533
8	C	4.281759	-0.287834	-0.015326
9	C	5.56849	0.099321	0.330442
10	C	3.142934	0.429507	0.437396
11	C	5.736189	1.22183	1.145306
12	H	6.430954	-0.459376	-0.024066
13	C	3.333909	1.555505	1.260129
14	C	4.622258	1.939106	1.604033
15	H	6.737884	1.536362	1.424841
16	H	2.468054	2.105335	1.618321
17	H	4.771544	2.807782	2.240775
18	N	-1.612476	-0.133356	-0.178972
19	C	-2.131837	1.120547	-0.376458
20	C	-2.590914	-0.976654	0.260906
21	C	-1.483306	2.272312	-0.838704
22	C	-3.51308	1.107361	-0.045182
23	C	-2.495799	-2.342191	0.576641
24	C	-3.812373	-0.252845	0.374178
25	C	-2.252205	3.426663	-0.963615
26	H	-0.425321	2.255422	-1.066915
27	C	-4.254445	2.265055	-0.175351
28	C	-3.651371	-2.970619	1.025089
29	H	-1.56084	-2.871272	0.443083
30	C	-4.946165	-0.901763	0.81777
31	C	-3.610779	3.428453	-0.638899
32	H	-1.784486	4.340189	-1.317142
33	H	-5.312632	2.288089	0.070074
34	C	-4.855588	-2.269098	1.145367
35	H	-3.619204	-4.025882	1.277017
36	H	-5.893855	-0.379659	0.915808
37	H	-4.185165	4.344071	-0.745042
38	H	-5.743482	-2.788256	1.494237

X5 ground state

Label	Atom	X	Y	Z
1	C	0.256311	-0.636292	0.310552
2	C	-1.961466	-0.329852	0.072454
3	C	-2.085821	-1.7414	0.027753
4	N	-1.04055	-2.544126	0.139563
5	N	0.156922	-1.988859	0.287419
6	N	-0.768683	0.232326	0.219531
7	S	-3.754223	-2.286985	-0.167735
8	C	-4.293099	-0.597006	-0.195879
9	C	-5.615391	-0.164335	-0.337253
10	C	-3.239045	0.337185	-0.059321
11	C	-5.868973	1.20677	-0.341292
12	H	-6.428107	-0.877394	-0.442419
13	C	-3.511492	1.713718	-0.068174
14	C	-4.826416	2.142784	-0.208703
15	H	-6.892303	1.556204	-0.450697
16	H	-2.692101	2.419972	0.030699
17	H	-5.052916	3.20515	-0.218338
18	N	1.53818	-0.112168	0.446375
19	C	1.775183	1.299146	0.383923
20	C	2.716749	-0.906202	0.241405
21	C	2.751554	1.740201	-0.51744
22	C	1.126298	2.237886	1.191804
23	C	3.666148	-0.399454	-0.655894
24	C	2.983329	-2.110999	0.899347
25	C	3.042885	3.094428	-0.665862
26	O	3.460847	0.824427	-1.270164
27	C	1.408645	3.597262	1.047969
28	H	0.387106	1.902399	1.909553
29	C	4.837494	-1.094954	-0.943768
30	H	2.259613	-2.506666	1.599878
31	C	4.153721	-2.816472	0.613445
32	C	2.354963	4.027161	0.111357
33	H	3.804134	3.392966	-1.380105
34	H	0.888434	4.320234	1.67004
35	H	5.542679	-0.667168	-1.649808
36	C	5.073291	-2.318168	-0.314556
37	H	4.341185	-3.761646	1.114805
38	H	2.572059	5.085765	-0.001335
39	H	5.980716	-2.872127	-0.538614

X5 first singlet excited state (S1)

Label	Atom	X	Y	Z
1	C	-0.162974	-0.000129	-0.627093
2	C	1.975368	-0.000043	-0.074635
3	C	2.207782	-0.000324	-1.464561
4	N	1.280328	-0.000502	-2.410985
5	N	-0.017503	-0.000391	-1.927125
6	N	0.675277	0.00007	0.391858
7	S	3.921838	-0.000418	-1.837612
8	C	4.325157	-0.00008	-0.125166
9	C	5.602063	0.000015	0.419105
10	C	3.168011	0.000098	0.697352
11	C	5.739269	0.000285	1.808871
12	H	6.478824	-0.000124	-0.222182
13	C	3.328335	0.000376	2.095414
14	C	4.606312	0.000469	2.6351
15	H	6.731837	0.000361	2.248918
16	H	2.44744	0.000513	2.729937
17	H	4.732922	0.000684	3.714264
18	N	-1.579286	-0.000033	-0.226619
19	C	-2.231832	1.187708	-0.039812
20	C	-2.231946	-1.18767	-0.039586
21	C	-3.58745	1.17088	0.364555
22	C	-1.606719	2.433332	-0.235956
23	C	-3.587567	-1.170633	0.364774
24	C	-1.606953	-2.433396	-0.235495
25	C	-4.301996	2.345119	0.571328
26	O	-4.238813	0.000172	0.565596
27	C	-2.319468	3.595402	-0.029431
28	H	-0.57232	2.458444	-0.55134
29	C	-4.302228	-2.344766	0.571756
30	H	-0.572558	-2.458654	-0.550877
31	C	-2.319815	-3.595356	-0.028756
32	C	-3.665989	3.558709	0.374175
33	H	-5.339317	2.278501	0.880756
34	H	-1.830212	4.551093	-0.183887
35	H	-5.339544	-2.277985	0.881165
36	C	-3.666337	-3.558454	0.37483
37	H	-1.830655	-4.551123	-0.183035
38	H	-4.21137	4.483266	0.530981
39	H	-4.21181	-4.48293	0.531794

X6 ground state

Label	Atom	X	Y	Z
1	C	-0.14554	-0.649029	-0.299093
2	C	2.072384	-0.346015	-0.068839
3	C	2.188112	-1.755363	0.02885
4	N	1.138189	-2.556177	-0.05079
5	N	-0.056403	-2.00072	-0.218387
6	N	0.883157	0.217798	-0.239433
7	S	3.85366	-2.302907	0.246675
8	C	4.402617	-0.616516	0.209652
9	C	5.727457	-0.186287	0.333937
10	C	3.353993	0.317888	0.037625
11	C	5.98897	1.182475	0.285104
12	H	6.536126	-0.899445	0.466275
13	C	3.634343	1.692108	-0.007342
14	C	4.951791	2.118692	0.116406
15	H	7.014356	1.529955	0.380826
16	H	2.818728	2.398223	-0.134508
17	H	5.184528	3.179304	0.084685
18	N	-1.422194	-0.124544	-0.456963
19	C	-1.642478	1.292376	-0.460818
20	C	-2.594461	-0.946562	-0.346094
21	C	-2.48266	1.843128	0.51788
22	C	-1.081343	2.120676	-1.438023
23	C	-3.538152	-0.629453	0.642046
24	C	-2.837302	-2.011058	-1.219699
25	C	-2.727286	3.221775	0.538552
26	S	-3.23981	0.763219	1.720286
27	C	-1.310348	3.495797	-1.404211
28	H	-0.450627	1.683893	-2.204999
29	C	-4.702705	-1.395238	0.774315
30	H	-2.108085	-2.24565	-1.986796
31	C	-3.987818	-2.784743	-1.073164
32	C	-2.125851	4.048461	-0.410271
33	H	-3.392893	3.636718	1.290416
34	H	-0.859429	4.134487	-2.158829
35	H	-5.434777	-1.131567	1.532606
36	C	-4.917119	-2.482976	-0.071823
37	H	-4.159007	-3.622873	-1.742853
38	H	-2.312446	5.118797	-0.387807
39	H	-5.816923	-3.082155	0.038667

X6 first singlet excited state (S1)

Label	Atom	X	Y	Z
1	C	0.033308	-0.000214	-0.645177
2	C	-2.101956	-0.000077	-0.069741
3	C	-2.350708	-0.000495	-1.457111
4	N	-1.433723	-0.000764	-2.412736
5	N	-0.129661	-0.000612	-1.943735
6	N	-0.796811	0.000095	0.380706
7	S	-4.069508	-0.000639	-1.810093
8	C	-4.452501	-0.00013	-0.092802
9	C	-5.722788	0.000004	0.466501
10	C	-3.28552	0.000133	0.715948
11	C	-5.843679	0.00041	1.857941
12	H	-6.607071	-0.000211	-0.164388
13	C	-3.429448	0.000543	2.115946
14	C	-4.70096	0.000681	2.670653
15	H	-6.830983	0.000514	2.309674
16	H	-2.540989	0.000751	2.739823
17	H	-4.814768	0.000998	3.751259
18	N	1.455862	-0.000059	-0.256937
19	C	2.062239	1.220984	-0.087852
20	C	2.06244	-1.220965	-0.087457
21	C	3.413277	1.355807	0.321747
22	C	1.330286	2.406495	-0.326114
23	C	3.41355	-1.355422	0.322018
24	C	1.330653	-2.406676	-0.325221
25	C	3.99405	2.622545	0.484449
26	S	4.436381	0.000334	0.655155
27	C	1.915153	3.641097	-0.16112
28	H	0.301364	2.331911	-0.647394
29	C	3.994609	-2.622002	0.484906
30	H	0.301647	-2.332371	-0.646287
31	C	1.915789	-3.641125	-0.16001
32	C	3.254161	3.761564	0.246519
33	H	5.031669	2.69243	0.798524
34	H	1.326213	4.531754	-0.353676
35	H	5.032294	-2.691609	0.798824
36	C	3.254904	-3.761226	0.247365
37	H	1.326973	-4.531944	-0.352192
38	H	3.705936	4.73972	0.372242
39	H	3.706915	-4.739256	0.373206

X7 ground state

Label	Atom	X	Y	Z
1	C	-1.428148	-0.981617	-0.131828
2	C	-3.632972	-0.610679	-0.007127
3	C	-3.799092	-1.997957	-0.214547
4	N	-2.810408	-2.839613	-0.374852
5	N	-1.583677	-2.310069	-0.340329
6	N	-2.421578	-0.079435	0.042442
7	C	-5.818367	-1.186076	-0.024768
8	C	-7.202614	-1.091039	0.035124
9	C	-4.967228	-0.069622	0.119751
10	C	-7.730979	0.183866	0.24987
11	H	-7.833349	-1.966391	-0.079392
12	C	-5.517542	1.201286	0.335501
13	C	-6.903805	1.315298	0.398634
14	H	-8.809438	0.304661	0.304071
15	H	-4.874159	2.068332	0.450952
16	H	-7.357716	2.28785	0.565057
17	O	-5.120425	-2.361118	-0.228009
18	N	-0.119766	-0.515548	-0.093685
19	C	1.060735	-1.316347	-0.056579
20	C	0.281295	0.851524	-0.075763
21	C	1.245171	-2.700372	-0.04279
22	C	2.182545	-0.458892	-0.007853
23	C	-0.454049	2.037773	-0.119272
24	C	1.692751	0.905734	-0.027309
25	C	2.553288	-3.193346	0.021925
26	H	0.407161	-3.379042	-0.09121
27	C	3.47578	-0.978711	0.052492
28	C	0.241026	3.252545	-0.11141
29	H	-1.532616	2.030588	-0.1518
30	C	2.35945	2.130923	-0.0163
31	C	3.690169	-2.364216	0.069028
32	H	2.671394	-4.271175	0.030669
33	H	4.316332	-0.290697	0.088591
34	C	1.645051	3.336939	-0.057782
35	H	-0.352406	4.159536	-0.146166
36	H	3.445588	2.135703	0.021545
37	C	5.126636	-2.918709	0.135461
38	C	2.401931	4.679345	-0.044186
39	C	5.928133	-2.429819	-1.095726
40	C	5.817313	-2.414591	1.426216
41	C	5.164012	-4.459683	0.146528
42	C	3.241351	4.787377	1.252298
43	C	3.344941	4.755091	-1.269832
44	C	1.452389	5.892415	-0.098866
45	H	5.465527	-2.776921	-2.027289

46	H	5.984159	-1.3365	-1.138298
47	H	6.955278	-2.815277	-1.060608
48	H	5.274766	-2.750948	2.31775
49	H	6.843406	-2.799806	1.485769
50	H	5.869927	-1.320821	1.460586
51	H	6.204884	-4.80106	0.195159
52	H	4.640013	-4.876034	1.015033
53	H	4.719428	-4.886923	-0.760105
54	H	2.598928	4.743305	2.139828
55	H	3.975396	3.978036	1.331554
56	H	3.789375	5.738148	1.274628
57	H	2.777479	4.687546	-2.205647
58	H	3.893732	5.705656	-1.271428
59	H	4.082495	3.945102	-1.267911
60	H	2.039192	6.818588	-0.087877
61	H	0.846472	5.897628	-1.012783
62	H	0.775121	5.921882	0.763032

X7 first singlet excited state (S1)

Label	Atom	X	Y	Z
1	C	-1.472964	-0.628483	-0.572794
2	C	-3.58077	-0.38166	-0.01683
3	C	-3.827899	-1.322369	-1.036544
4	N	-2.947624	-1.909379	-1.80839
5	N	-1.645486	-1.499292	-1.533539
6	N	-2.289566	0.009009	0.249469
7	C	-5.777804	-0.813386	-0.191187
8	C	-7.135096	-0.77932	0.03634
9	C	-4.840085	-0.045594	0.540827
10	C	-7.58603	0.070739	1.057075
11	H	-7.817688	-1.385989	-0.550761
12	C	-5.313562	0.797466	1.560839
13	C	-6.68364	0.841971	1.80204
14	H	-8.64943	0.128491	1.271033
15	H	-4.620664	1.395239	2.145535
16	H	-7.064546	1.489065	2.588464
17	O	-5.156909	-1.586873	-1.145792
18	N	-0.060615	-0.302313	-0.364686
19	C	0.939905	-1.214039	-0.188483
20	C	0.455344	0.965517	-0.312598
21	C	0.875365	-2.613135	-0.176577
22	C	2.17135	-0.527457	-0.000339
23	C	-0.195304	2.194081	-0.45556
24	C	1.855226	0.891284	-0.086824
25	C	2.058323	-3.308984	0.042077
26	H	-0.062916	-3.121589	-0.359781
27	C	3.327159	-1.245615	0.208724
28	C	0.580351	3.34642	-0.370961
29	H	-1.266497	2.237749	-0.606704
30	C	2.596388	2.049822	-0.004473
31	C	3.292215	-2.664496	0.236653
32	H	2.013602	-4.391721	0.05039
33	H	4.269976	-0.724845	0.351989
34	C	1.966201	3.312333	-0.146968
35	H	0.079564	4.301345	-0.479988
36	H	3.667798	1.99567	0.168665
37	C	4.589927	-3.430649	0.469211
38	C	2.814091	4.577255	-0.052041
39	C	5.590015	-3.081163	-0.648519
40	C	5.181307	-3.020665	1.830741
41	C	4.384866	-4.947825	0.472532
42	C	3.496895	4.626545	1.327099
43	C	3.889224	4.548885	-1.153871
44	C	1.986039	5.853644	-0.222748
45	H	5.195243	-3.360632	-1.631647

46	H	5.828087	-2.012304	-0.672125
47	H	6.528188	-3.626064	-0.490231
48	H	4.490432	-3.257355	2.647609
49	H	6.116886	-3.564362	2.007283
50	H	5.406691	-1.949898	1.879242
51	H	5.346415	-5.44325	0.645883
52	H	3.70311	-5.268567	1.26856
53	H	3.997027	-5.312279	-0.485562
54	H	2.755037	4.646416	2.133246
55	H	4.153811	3.76624	1.494811
56	H	4.110462	5.531828	1.405972
57	H	3.432263	4.513322	-2.149148
58	H	4.506607	5.453048	-1.094296
59	H	4.556649	3.685604	-1.058549
60	H	2.644114	6.72608	-0.145563
61	H	1.49711	5.898286	-1.202713
62	H	1.218755	5.952536	0.553681

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