Convenient One-Pot Synthesis of 1,2,3,4-Thiatriazoles Towards a Novel Electron Acceptor for Highly-Efficient Thermally-Activated Delayed-Fluorescence Emitters

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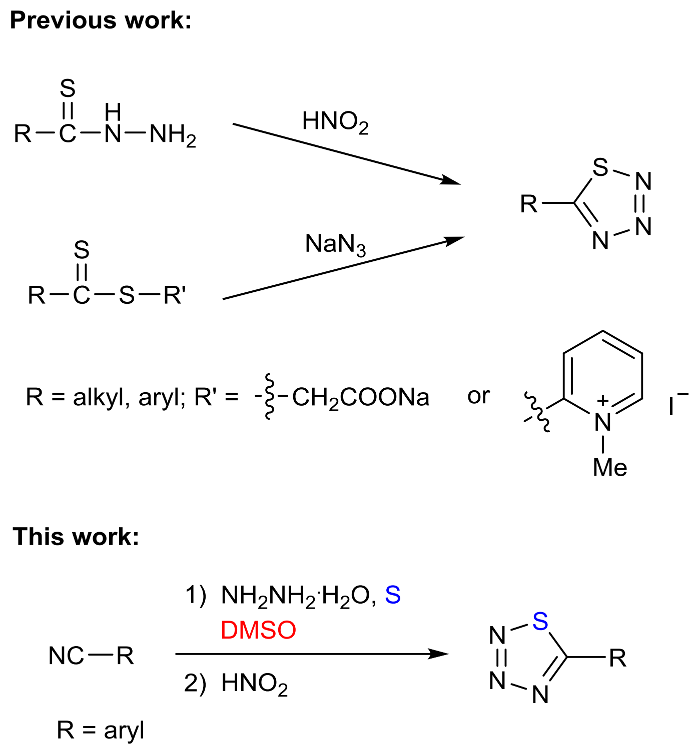
Abstract: A novel and unexpected convenient one-pot synthesis of 1,2,3,4-thiatriazoles has been discovered meanwhile investigating on the classical tetrazine “Pinner synthesis”. The synthetic route starts from commercially-available nitrile derivatives and gives good to high yields (51%-80%) with no need to isolate any thioacylating agents. The crucial impact of the solvent on the outcome of the modified “Pinner synthesis” is moreover examined and discussed. Using this new synthetic route a novel donor-acceptor thiatriazole derivative has been prepared which exhibits prominent thermally activated delayed fluorescence (TADF) in both solution and film. The photoluminescence quantum yield (PLQY) in methylcyclohexane (MCH) and Zeonex in oxygen-free conditions were determined to be 76% and 99%, respectively. This work provides an efficient and practical synthetic approach to functionalized 1,2,3,4-thiatriazole derivatives, and will noticeably facilitate the application of 1,2,3,4-thiatriazole as an electron acceptor in organic electronics.

1,2,3,4-thiatriazole heterocycle was first reported in 1896 by Freund and co-workers.[1] Its structural assignment was firmly established in the 1950s by Lieber and co-workers.[2] A number of 1,2,3,4-thiatriazoles were then prepared and studied during that period.[3] The chemistry of 1,2,3,4-thiatriazoles has been unfortunately almost forgotten for many decades thereafter. As a strong electron-deficient heterocycle, 1,2,3,4-thiatriazole is however potentially an excellent electron acceptor in organic donor-acceptor materials. Due to charge-transfer (CT) states introduced in the donor-acceptor system, these molecules can exhibit interesting photophysical and electrochemical properties, and therefore are of interest in organic electronics.[4,5] though strangely, no related applications have been reported so far. Thermally activated delayed fluorescence (TADF) molecules have recently received significant attention since the first efficient TADF organic light emitting diodes (OLEDs) reported in 2012 by Adachi [6] In TADF molecules, the triplet excitons can be converted to the emissive singlet excitons via efficient reverse intersystem crossing (RISC) from the lowest triplet excited state (T1) to the lowest singlet excited state (S1), when their energy difference (ΔEST) is small enough.[5] Most of the TADF molecules were therefore designed by coupling various electron donors and acceptors with a large twisting angle, to separate the spatial distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), The aim is harvesting 100% of triplet exciton.[7] The use of purely organic TADF emitters however goes far beyond their use in electroluminescent devices. They can supersede metal-complex emitters by acting as triplet sensitizers,[8] or bio-imaging dyes.[9] These molecules with efficient

RISC [10] count also among mechanochromic materials with switchable parameters, such as emission color,[11] on/off TADF[12] or interplay between TADF and prompt fluorescence.[13] Therefore, exploration of novel electron acceptors for TADF emitters is of clear interest to this community.



Scheme 1. Overview of synthetic approaches to 1,2,3,4-thiatriazoles.

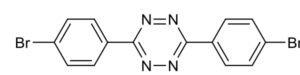
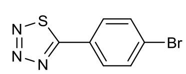
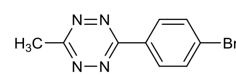
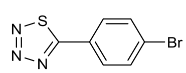
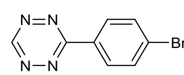
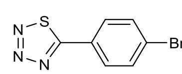
1,2,3,4-thiatriazoles have been previously prepared by diazotization of thiohydrazides, or reaction of dithioates with azide ion, in high yields (Scheme 1).[3] However, both methods require preparation of starting thioacylating agents, which are often difficult to obtain. This increases the synthetic complexity of 1,2,3,4-thiatriazole derivatives, especially for those with complex functional groups. As a result, no 1,2,3,4-thiatriazole derivatives with complex functional groups have been reported so far. Therefore, developing practical and convenient synthetic approaches for preparing functionalized 1,2,3,4-thiatriazole derivatives is quite desirable.

In this study, we report a novel convenient one-pot synthesis of 1,2,3,4-thiatriazoles directly from commercially available nitriles in high yields (51%-80%), with no need of isolating any thioacylating agents (Scheme 1). The access to the 1,2,3,4-thiatriazoles can therefore be significantly improved because oft he large availability of commercially available nitriles. Through this approach we have designed and synthesized an example of a donor-acceptor thiatriazole derivative using phenoxazine as a donor, in high yield (70%). This molecule exhibits excellent TADF characteristics in both solution and film. To the best of our knowledge, this is the first example of a highly efficient TADF emitter using a 1,2,3,4-thiatriazole as acceptor.

Having a long experience in 1,2,4,5-tetrazine chemistry,[14,15] we had already noticed that the solvent nature can play an important role in the tetrazine forming reaction called “Pinner synthesis”.[16] For example, we have recently found that dichloromethane (DCM) can serve as a novel reagent in the synthesis of 3-monosubstituted unsymmetrical 1,2,4,5-tetrazines.[15] In this work a comprehensive study of solvent effect in the modified “Pinner synthesis” was performed, and we found out that the products of the reaction are significantly influenced by the solvent employed.

The traditional “Pinner synthesis” is a two-step procedure starting from the formal addition of hydrazine to nitrile precursors in ethanol, followed by oxidation of the intermediate 1,2-dihydrotetrazine to afford 1,2,4,5-tetrazines.[16] It has been demonstrated later that addition of sulfur helps accelerating the reaction.[17] Here we used 4-bromobenzonitrile as a standard nitrile precursor to survey the effect of a range of solvents on this reaction. The results are summarized in Table 1. When our optimized reaction conditions for tetrazine synthesis (hydrazine hydrate, sulfur and heating at 90° for 1 hour in a sealed tube with microwave irradiation followed by oxidation), with ethanol as a solvent in the first step, was used, the 3,6-disubstituted symmetrical tetrazine T1 was obtained in good yield (43%) as expected. However, when the polar protic solvent ethanol was replaced by a non-polar (e.g., toluene, chloroform) or a slightly polar aprotic solvent (e.g., tetrahydrofuran (THF)), no reaction was observed and the starting nitrile agent was fully recovered.

Table 1. Survey of solvents and outcomes in the modified “Pinner synthesis”(a).

Solvent		Dielectric Constant	Products(b)
Polar protic solvent	Ethanol	25	 **T1, 43%**
Non-polar solvent	Toluene	2.3	SN(c)
	Chloroform	4.8	SN
Polar aprotic solvent	THF	7.5	SN
	Acetonitrile	37	 **TT1, 9%** +  **T2, 16%**
	DMF	38	 **TT1, 41%** +  **T3, 8%**[18]
	DMSO	47	 **TT1, 74%**

(a) All reactions were carried out on a 0.5 mmol scale in 2 ml solvent. MW = microwave. (b) Yields (isolated) based on the nitrile precursor. (c) SN = Starting Nitrile precursor

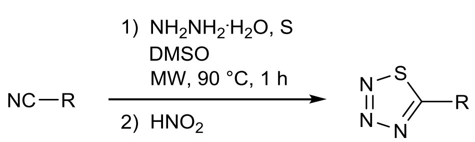
When the highly polar aprotic solvent acetonitrile was used, we isolated 16% of unsymmetrical 3-(4-bromophenyl)-6-methyl-1,2,4,5-tetrazine T2 because acetonitrile acts as both solvent and second nitrile precursor in the reaction. In addition to the tetrazine, the unusual 1,2,3,4-thiatriazole TT1 was also obtained with a 9% yield. More interestingly, when using dimethylformamide (DMF) as a solvent, the yield of TT1 significantly increased to 41%.[18] And remarkably, when the even more polar solvent dimethyl sulfoxide (DMSO) was employed, the yield was optimized to as high as 74%. These findings are remarkably interesting because this is the first time that the 1,2,3,4-thiatriazole has been isolated using “Pinner synthesis". All the reactions were performed in a one-pot procedure without isolating any thioacylating agents. It is worth noting that in the case of all three polar solvents (acetonitrile, DMF and DMSO) only a trace amount (yield below 1%) of symmetrical tetrazine T1 could also be observed.

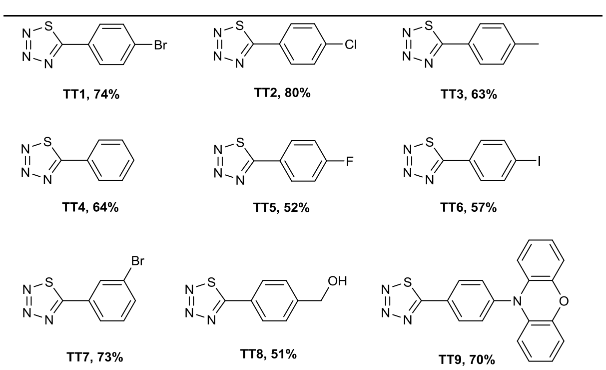
Formation of 1,2,3,4-thiatriazole in this reaction is assumed to process through diazotization of a thiohydrazide intermediate, formed in the first step, by the nitrous acid used in the second step. However, the detailed mechanism of formation of these thiohydrazide intermediates is still under investigation and it is not clear if small amounts of hydrogen sulfide are formed or not.

The reaction with DMSO as a solvent became the most interesting to us because it provides a novel, convenient pathway to 1,2,3,4-thiatriazoles directly from commercially available nitrile reagents in an excellent yield. The reaction conditions were optimized by changing the amount of sulfur and reaction temperature. Probably acting both as an inducer and reactant in the reaction, the amount of sulfur is crucial in this reaction. Theoretically, one equivalent of sulfur should be enough to obtain the thiatriazole product. In those conditions the reaction already led to a reasonable yield (53%, Table S1), while slight excesses (1.3 equiv.) of sulfur could still improve the yield and 1.5 equiv. of sulfur gave the best yield (74%). The reaction temperature and time were optimized to 90 °C for 1 hour because decreasing the reaction temperature only resulted in prolonged reaction times to reach similar yields (Table S2). We used microwave heating throughout, but we have verified that running the reaction in a sealed tube with conventional heating worked fine as well, resulting in a similar yield (72%).

To extend the scope of this synthetic approach, we engaged a series of nitrile substrates in our new one-pot synthetic approach. Thus, a series of 5-aryl-1,2,3,4-thiatriazoles were successfully prepared in good to high yields (51%-80%, Table 2), among which many were previously complicated to prepare.[3] The reactions are simple and efficient, and the nitrile substrate can contain different functional groups such as halogens and hydroxyl groups. Although the reaction is versatile, unfortunately, preparation of 5-alkyl-1,2,3,4-thiatriazoles using benzyl cyanide or tert-butyl cyanide was not successful, probably due to instability of the thioacylating intermediates which have been described previously.[3]

Table 2. Synthesis of 5-aryl-1,2,3,4-thiatriazoles TT1-TT9(a).





(a) Reactions were carried out on a 0.5 mmol scale in 2 ml DMSO. Yields (isolated) based on the starting nitrile.

With our convenient one-pot synthetic approach in hand, we hypothesized that it could be used to prepare donor-acceptor type thiatriazole derivatives using an appropriate nitrile precursor. More importantly, we also believed that 1,2,3,4-thiatriazole could act as a novel electron acceptor for efficient TADF emitters. Indeed one-pot or multicomponent synthesis of functional chromophores has received considerable interest both in academia and industry.[19] To our delight, donor-acceptor thiatriazole derivative using phenoxazine as a donor motif TT9 was easily prepared in a high yield (70%) using our approach. TT9 easily forms yellow crystals, which are stable and could be stored at room temperature for several months without noticeable degradation. The single crystal structure (Figure 1) shows a large twisting angle (67°) between the planes of donor and acceptor, which is desired to achieve small HOMO-LUMO overlap and to realize a small ΔEST, and therefore efficient TADF characteristics.[4]

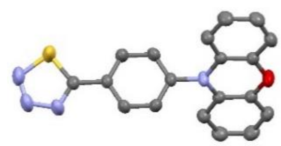


Figure 1. Crystal structure of TT9. Hydrogen atoms are omitted for clarity.

TT9 was further characterized by electrochemistry (Figure S8). The cyclic voltamogram in DCM display a reversible oxidation wave for the phenoxazine, an irreversible reduction one corresponding to the thiatriazole. The HOMO and LUMO energies were determined to be 5.35 eV and 3.41 eV from the onset of the respective waves.

DFT based calculations were also performed on TT9. The ground state structure of the molecule shows an almost perpendicular twist between the phenoxazine and the thiatriazole-phenyl moieties and complete spatial separation of the HOMO and LUMO (Figure 2) which is an ideal situation to reach a small singlet-triplet energy difference. Optimization in the first singlet excited state gave a very similar geometry where the main difference is a flattening of the phenoxazine moiety (Figure S10). The computed ΔEST on this excited state optimized structure is 0.005 eV which is excellent to get efficient TADF.

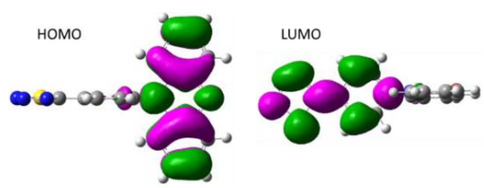


Figure 2. Calculated spatial distributions of the HOMO (left) and LUMO (right) of TT9.

Photophysical studies demonstrated that TT9 indeed exhibits prominent thermally activated delayed fluorescence (TADF) characteristics both in solution and film. Relevant photophysical properties of TT9 are displayed in Figure 3 and Table 3. Like other donor-acceptor molecules, TT9 shows a clear solvatochromic effect (Figure 3a). It is highly emissive in non-polar media such as methylcyclohexane (MCH), Toluene (Tol) and Zeonex, while however very weakly emissive or non-emissive in more polar solvents (Figure S1) as is typical for strong charge transfer (CT) excited state systems.[20] Photoluminescence (PL) intensity of TT9 in MCH increases 6.3-fold in degassed solution relatively to the air-equilibrated (Figure S2), indicating that oxygen largely influences the PL of this material. Comparison of PL decays of TT9 in air-equilibrated and degassed MCH (Figure S3) shows that in the latter case, a longer lifetime indicative of TADF, as well as a longer prompt fluorescence lifetime than in the presence of oxygen is observed. Thus oxygen apparently not only quenches the triplet state but also the singlet one. The ratio of the delayed fluorescence component to the prompt fluorescence one (DF/PF) was determined to be 2.65 from the PL decay of TT9 in degassed MCH (Table 3). PLQY of TT9 in MCH and Zeonex in air were determined to be 12% and 65%, respectively. The PLQY in degassed MCH increased to 76%, and the PLQY in Zeonex under nitrogen reached 99%. This is remarkable since many CT molecules suffer from a small radiative decay rate due to the spatial separation of HOMO and LUMO originating from the molecular design.[4] TT9 exhibits prominent TADF characteristic not only in MCH but also in Zeonex (Figure 3c, 3d) with a DF/PF ratio in the latter equal to 2.37. Temperature dependence of delayed fluorescence recorded in Zeonex (Figure 3c) is typical of TADF molecules showing clearly the thermal activation of the process.[5] Interestingly, at 80 K the intensity of TADF is still substantial and thus phosphorescence is hardly distinguishable from delayed fluorescence (Figure 3b). This gives a clear indication for a ΔEST approaching zero. It is also noteworthy that the prompt fluorescence is completely unaffected by temperature change which indicates that it has almost no effect of the non-radiative decay rate of the singlet excited state. This also contributes to the high PLQY of the molecule. Power dependence of delayed fluorescence of TT9 is linear in both MCH and Zeonex confirming the TADF mechanism (Figure S6, S7).

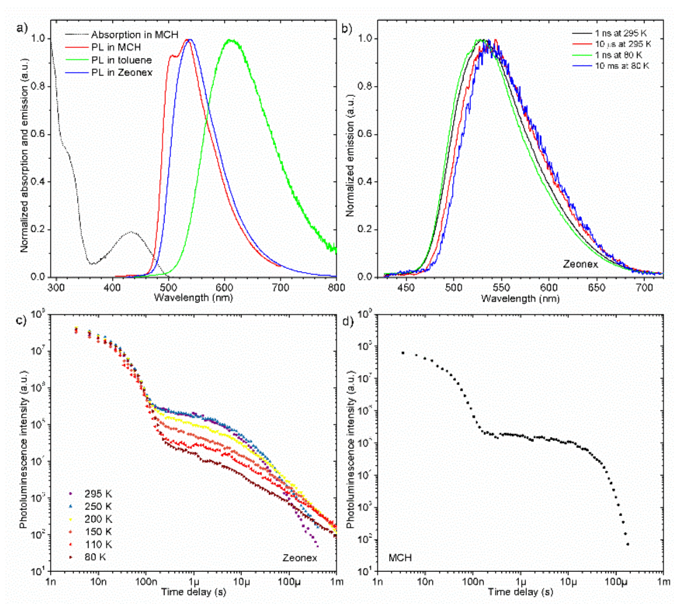


Figure 3. (a) Normalized fluorescence spectra of TT9 in MCH, Tol and Zeonex 1% (w/w) and normalized absorption spectrum in MCH. (b) Time-resolved spectra of TT9 in Zeonex. (c) PL decays of TT9 in Zeonex 1% (w/w) at various temperatures. (d) PL decay of TT9 in degassed MCH at room temperature.

In conclusion, we have examined and proved that the solvent plays an important role in the "Pinner synthesis" outcome. We have discovered a novel, convenient one-pot synthesis of 1,2,3,4-thiatriazoles directly from nitrile substrates in high yields (51%-80%), with no need for isolating the thioacylating agents. We believe that our work significantly improves access to differently functionalized 1,2,3,4-thiatriazoles. Using this new one-pot approach a peculiar donor-acceptor thiatriazole derivative has been synthesized which proved to be quite an efficient TADF emitter. This is the first example of 1,2,3,4-thiatriazole use as an electron acceptor for TADF emitters. Our new approach opens possibility to further develop 1,2,3,4-

thiatriazole derivatives as new families of molecules for applications in organic electronics and other related fields. One-pot synthesis and high reaction yields are two key factors to reduce costs in large scale synthesis and correlatively possible industrial applications.

Table 3. Photophysical properties of TT9.

Sample	λ_{PL} (nm)[(a)]	$\Phi_{PL}^{air}/\Phi_{PL}^{deg}$ (%)	τ_{PF} (ns)[(d)]	τ_{DF} (µs)[(e)]	DF/PF[(f)]
Zeonex film	539	65/99[(b)]	20.4 ± 0.7	5.5 ± 0.28, 28.0 ± 1.7	2.37
MCH Solution	505,532	12/76[(c)]	18.6 ± 0.6	22.2 ± 1.2	2.65

(a) Emission maxima. (b) PLQY in air and N2 atmosphere. (c) PLQY in air-equilibrated and degassed MCH solution. (d) Prompt fluorescence lifetime determined from PL decay (Figure S4, S5). (e) Delayed fluorescence lifetime determined from PL decay (Figure S4, S5). (f) Ratio of delayed fluorescence component to prompt fluorescence one.

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Keywords: delayed fluorescence • one-pot synthesis • Pinner synthesis • tetrazines • thiatriazoles

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[19] a) L. Levia, T. J. J. Müller, Chem. Soc. Rev. 2016, 45, 2825–2846; b) F. de Moliner, N. Kielland, R. Lavilla, M. Vendrell, Angew. Chem. Int. Ed. 2017, 56, 3758–3769.
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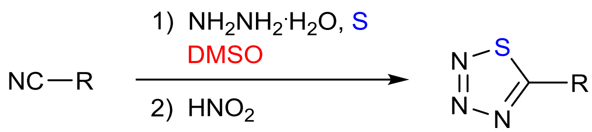
COMMUNICATION



- ✓ One-pot synthesis
- ✓ Novel acceptor for efficient TADF emitters

A novel and unexpected convenient one-pot synthesis of 1,2,3,4-thiatriazoles has been discovered meanwhile investigating on the classical tetrazine "Pinner synthesis". The synthetic route starts from commercially-available nitrile derivatives and gives good to high yields (51%-80%) with no need to isolate any thioacylating agents. Using this new synthetic route a novel donor-acceptor thiatriazole derivative has been prepared which exhibits prominent thermally activated delayed fluorescence (TADF).

Y. Qu, P. Pander, A. Bucinskas, M. Vasylieva, Y. Tian, F. Miomandre, F. B. Dias, G. Clavier, P. Data, P. Audebert**

Convenient One-Pot Synthesis of 1,2,3,4-Thiatriazoles Towards a Novel Electron Acceptor for Highly Efficient Thermally Activated Delayed Fluorescence Emitters

Convenient One-Pot Synthesis of 1,2,3,4-Thiatriazoles Towards a Novel Electron Acceptor for Highly Efficient Thermally Activated Delayed Fluorescence Emitters

Yangyang Qu,[a] Piotr Pander,[b] Audrius Bucinskas,[c] Marharyta Vasylieva,[d] Yayang Tian,[a] Fabien Miomandre,[a] Fernando B. Dias,[b] Gilles Clavier,*[a] Przemyslaw Data[b,d] and Pierre Audebert*[a]

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1. Experimental details

General Methods:

Synthesis. All chemicals were received from commercial sources and used without further purification. Microwave reaction was performed on a microwave synthesis reactor (Anton Paar Monowave 300). Thin layer chromatography (TLC) was performed on silica gel. Flash column chromatography purification was performed on a CombiFlash-Rf system with a variable wavelength UV detector. 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.

*All the 1,2,3,4-thiatriazole samples were analyzed in both ESI and APPI HRMS, but only **TT9** gave good result in ESI, and a loss of N_2 was observed for all the 1,2,3,4-thiatriazole samples in APPI which is in accordance to the literature description on the stability of 1,2,3,4-thiatriazoles.[1] Nevertheless, **TT9** was confirmed by both ESI HRMS and single crystal XRD measurements. And the NMR spectra of **TT2-TT4** are in accordance to the literature values.[2] The signals shown between 177 and 180 ppm in ^{13}C NMR for all the 1,2,3,4-thiatriazole samples **TT1-TT9** are characteristic signals for C=N of 1,2,3,4-thiatriazoles.

The single crystal of compound **TT9** was obtained from slow evaporation of the mixture of solvents (Petroleum ether:CH_2Cl_2 = 1:1). The yellow colour single crystal was mounted on the glass capillary using glue. The crystallographic analysis was performed employing XtaLAB mini diffractometer (Rigaku) with graphite monochromated Mo Kα (λ = 0.71075 Å) X-ray source. The measurements were performed at the temperature of 293 K. The crystallographic data is summarized in **Table S3**. Packing along a-axis is presented in **Figure S9**. The crystallographic data for structure **TT9** reported in this paper have been deposited in Cambridge Crystallographic Data Centre with CCDC no 1873600. The copies of data can be obtained free of charge on application to CCDC. (The Cambridge Structural Database (CSD)- The Cambridge Crystallographic Data Centre (CCDC), (http://www.ccdc.cam.ac.uk/solutions/csd-system/components/csd/). Calculations/visualizations were performed using the OLEX2[3] crystallographic software package except for refinement, which was performed using SHELXL.[4] Anisotropic thermal parameters were assigned to all nonhydrogen atoms. The hydrogens were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically.

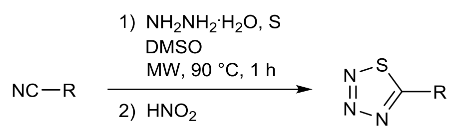
Photophysics. Zeonex ® 480 blends were prepared from toluene solutions by the drop-cast method and dried in a vacuum (Zeonex ® 480 is a type of Cyclo Olefin Polymer (COP) developed by ZEON CORPORATION[5]). All solutions were investigated at 10^{-5} mol dm^{-3} concentration and were degassed using five freeze/pump cycles. Absorption and emission spectra were collected using a UV-3600 double beam spectrophotometer (Shimadzu), and a Fluoromax fluorescence spectrometer (Jobin Yvon) or QePro fluorescence spectrometer (Ocean Optics). Photoluminescence quantum yield was recorded using an integrating sphere (Labsphere) coupled with a 365 nm LED light source (Ocean Optics) and a QePro fluorescence spectrometer (Ocean Optics).

Phosphorescence, prompt fluorescence (PF), and delayed fluorescence (DF) spectra and decays were recorded using 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 N2 laser emitting at 337 nm. Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) of sub-nanosecond resolution. PF/DF time-resolved measurements were performed by exponentially increasing gate and delay times.

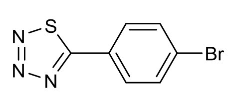
Electrochemistry. The electrochemical cell comprised of platinum electrode with a 1 mm diameter of working area as a working electrode, an Ag electrode as a reference electrode and a platinum coil as an auxiliary electrode. Cyclic voltammetry measurements were conducted at room temperature at a potential rate of 50 mV/s and were calibrated against ferrocene/ferrocenium redox couple. Electrochemical measurements were conducted in 1.0 mM concentrations for all cyclic voltammetry measurements. Electrochemical studies were undertaken in 0.1 M solutions of Bu_4NPF_6, 99% in DCM at room temperature.

DFT calculations. Ground state geometry optimization was done at the B3LYP/6-31+G(d,p) and excited state one at the M06-2X/6-31+G(d,p) level of theory. Frequency calculations were done at the same levels of theory to confirm that a true minimum was obtained. TDDFT calculations were done on the first excited state optimized structure (M06-2X/6-311++G(d,p)) to compute the energies of the relaxed first singlet and triplet excited states. Solvent effect (cyclohexane) was included throughout the process. All calculations have been done with Gaussian 09 (Revision D.01).[6] Spatial distributions of the molecular orbitals were generated with GaussView 5.0 and the overlay of the two optimized geometries with PyMOL.[7]

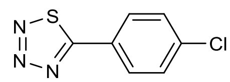
General procedure for synthesis of TT1-TT8 ("Pinner Synthesis" using DMSO as solvent)



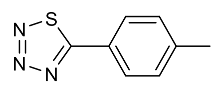
Nitrile substrate (0.5 mmol), sulfur (0.75 mmol, 24 mg) and DMSO (2 ml) were mixed together in a 30 ml microwave reaction tube. Hydrazine monohydrate (5 mmol, 0.25 ml) was added with stirring afterwards. The vessel was sealed and the reaction mixture was heated to 90 °C for 1 hour. (Caution should be exercised due to the elevated pressure in the sealed reaction vessel when heating, particularly attempting scale up). Then 5 ml of CH_2Cl_2 and sodium nitrite (5 mmol, 0.35 g) in 10 ml of H_2O were added to the mixture. Excess acetic acid (20 mmol, 1.14 ml) was then added slowly at 0 °C. The reaction mixture was allowed to stir for another 1 hour at room temperature, and then extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified using flash column chromatography.



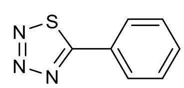
TT1: A white crystalline solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 4:1) (90 mg, yield: 74%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.92 (d, J = 8.60 Hz, 2H), 7.71 (d, J = 8.60 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 178.24, 133.24, 131.11, 128.21, 125.42 ppm; HRMS-APPI $[M-N_2]^+$ m/z calcd. for $[C_7H_4BrNS]^+$ 212.9248, found 212.9246.



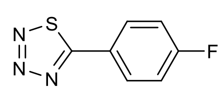
TT2[2]**:** A white solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 4:1) (79 mg, yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.00 (d, J = 8.60 Hz, 2H), 7.54 (d, J = 8.60 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 178.12, 139.72, 131.01, 130.25, 124.96 ppm; HRMS-APPI $[M-N_2]^+$ m/z calcd. for $[C_7H_4ClNS]^+$ 168.9753, found 168.9748.



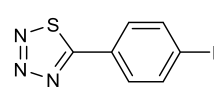
TT3[2]**:** A white solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 3:1) (56 mg, yield: 63%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.94 (d, J = 8.20 Hz, 2H), 7.54 (d, J = 8.20 Hz, 2H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 179.34, 144.30, 130.57, 129.82, 123.81, 21.87 ppm; HRMS-APPI $[M-N_2]^+$ m/z calcd. for $[C_8H_7NS]^+$ 149.0299, found 149.0292.



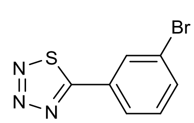
TT4[2]**:** A white solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 4:1) (52 mg, yield: 64%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.07–8.01 (m, 2H), 7.66–7.51 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 179.32, 133.31, 129.86, 129.82, 126.45 ppm; HRMS-APPI $[M-N_2]^+$ m/z calcd. for $[C_7H_5NS]^+$ 135.0143, found 135.0135.



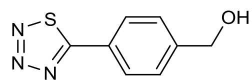
TT5: A white solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 3:1) (47 mg, yield: 52%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.10–8.01 (m, 2H), 7.29–7.20 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 178.05 (s), 165.66 (d, $^1J_{CF}$ = 256.03 Hz), 132.15 (d, $^3J_{CF}$ = 8.98 Hz), 122.88 (d, $^4J_{CF}$ = 3.10 Hz), 117.29 (d, $^2J_{CF}$ = 22.33 Hz) ppm; HRMS-APPI $[M-N_2]^+$ m/z calcd. for $[C_7H_4FNS]^+$ 153.0048, found 153.0045.



TT6: A white solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 4:1) (82 mg, yield: 57%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.92 (d, J = 8.60 Hz, 2H), 7.77 (d, J = 8.60 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 178.48, 139.17, 130.98, 125.90, 100.58 ppm; HRMS-APPI $[M-N_2]^+$ m/z calcd. for $[C_7H_4INS]^+$ 260.9109, found 260.9108.

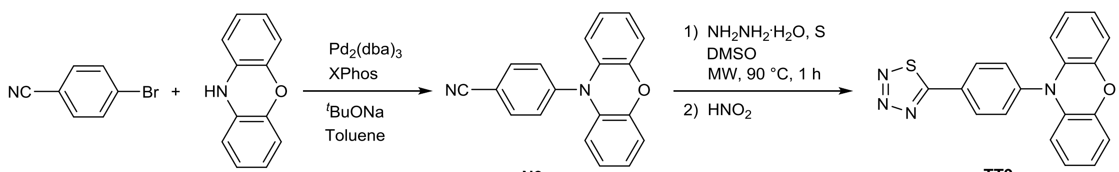


TT7: A white solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 3:1) (88 mg, yield: 73%). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.22 (t, *J* = 1.70 Hz, 1H), 7.97 (d, *J* = 7.80 Hz, 1H), 7.74 (d, *J* = 7.80 Hz, 1H), 7.44 (t, *J* = 7.80 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 177.79, 136.16, 132.36, 131.35, 128.47, 128.20, 123.80 ppm; HRMS-APPI $[M\text{-}N_2]^+$ m/z calcd. for $[C_7H_4BrNS]^+$ 212.9248, found 212.9247.



TT8: A white solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 5:2) (49 mg, yield: 51%). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.04 (d, *J* = 8.20 Hz, 2H), 7.56 (d, *J* = 8.20 Hz, 2H), 4.83 (s, 2H), 1.97 (s, br, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 179.08, 146.62, 130.04, 127.85, 125.55, 64.56 ppm; HRMS-APPI $[M\text{-}N_2]^+$ m/z calcd. for $[C_8H_7NOS]^+$ 165.0248, found 165.0246.

Synthesis of TT9



N9 TT9

To a 250 mL two-neck round bottom flask equipped with a stir bar, 4-bromobenzonitrile (5 mmol, 0.91 g), phenoxazine (5.5 mmol, 1.0 g), Sodium *tert*-butoxide (5.5 mmol, 0.53 g) and 100 ml of anhydrous toluene were added. The reaction mixture was degassed by bubbling through nitrogen for 15 min under vigorous stirring. Then $Pd_2(dba)_3$ (0.1 mmol, 92 mg) and XPhos (0.25 mmol, 119 mg) were added and degassed for another 15 min. The reaction mixture was heated to 110 °C under a nitrogen atmosphere for 15 h. The reaction mixture was then cooled down to room temperature, extracted with dichloromethane, and dried over anhydrous magnesium sulfate ($MgSO_4$). The product was purified using flash column chromatography (Petroleum ether:CH_2Cl_2= 9:1) to give 1.03 g of **N9** (yield: 73%). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.89 (d, *J* = 8.20 Hz, 2H), 7.50 (d, *J* = 8.20 Hz, 2H), 6.76–6.56 (m, 6H), 5.91 (d, *J* = 7.80 Hz, 2H) ppm.[8]

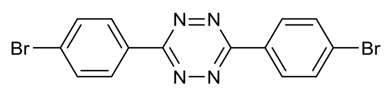
N9 (0.5 mmol, 142 mg), sulfur (0.75 mmol, 24 mg) and DMSO (2 ml) were mixed together in a 30 ml microwave reaction tube. Hydrazine monohydrate (5 mmol, 0.25 ml) was added with stirring afterwards. The vessel was sealed and the reaction mixture was heated to 90 °C for 1 hour. (Caution should be exercised due to the elevated pressure in the sealed reaction vessel when heating, particularly attempting scale up). Then 5 ml of CH_2Cl_2 and sodium nitrite (5 mmol, 0.35 g) in 10 ml of H_2O were added to the mixture. Excess acetic acid (20 mmol, 1.14 ml) was then added slowly at 0 °C. The reaction mixture was allowed to stir for another 1 hour at room temperature, and then extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified using flash column chromatography.

TT9: A yellow crystalline solid was obtained after flash column chromatography (Petroleum ether:CH_2Cl_2 = 3:2) (120 mg, yield: 70%). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.29 (d, *J* = 8.20 Hz, 2H), 7.59 (d, *J* = 8.20 Hz, 2H), 6.78–6.59 (m, 6H), 6.01 (d, *J* = 7.80 Hz, 2H) ppm; ^{13}C NMR (100

MHz, $CDCl_3$, δ): 178.17, 144.20, 144.02, 133.57, 132.55, 132.43, 126.34, 123.49, 122.30, 116.04, 113.50 ppm; HRMS-APPI $[M+H-N_2]^+$ m/z calcd. for $[C_{19}H_{13}N_2OS]^+$ 317.0749, found 317.0738; HRMS-ESI $[M]^+$ m/z calcd. for $[C_{19}H_{12}N_4OS]^+$ 344.0732, found 344.0745.

"Pinner Synthesis" using ethanol as solvent

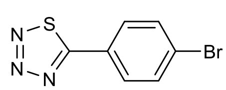
4-Bromobenzonitrile (0.5 mmol, 91 mg), sulfur (0.75 mmol, 24 mg) and ethanol (2 ml) were mixed together in a 30 ml microwave reaction tube. Hydrazine monohydrate (5 mmol, 0.25 ml) was added with stirring afterwards. The vessel was sealed and the reaction mixture was heated to 90 °C for 1 hour. (Caution should be exercised due to the elevated pressure in the sealed reaction vessel when heating, particularly attempting scale up). Then 5 ml of CH_2Cl_2 and sodium nitrite (5 mmol, 0.35 g) in 10 ml of H_2O were added to the mixture. Excess acetic acid (20 mmol, 1.14 ml) was then added slowly at 0 °C. The reaction mixture was allowed to stir for another 1 hour at room temperature, and then extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified using flash column chromatography (CH_2Cl_2) to give **T1** as a pink solid (42 mg, yield: 43%).



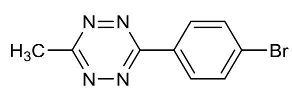
T1[9]**:** ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.98 (d, J = 8.60 Hz, 4H), 7.81 (d, J = 8.60 Hz, 4H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, δ): 167.13, 132.60, 129.59, 128.60, 125.08 ppm.

"Pinner Synthesis" using acetonitrile as solvent

4-Bromobenzonitrile (0.5 mmol, 91 mg), sulfur (0.75 mmol, 24 mg) and acetonitrile (2 ml) were mixed together in a 30 ml microwave reaction tube. Hydrazine monohydrate (5 mmol, 0.25 ml) was added with stirring afterwards. The vessel was sealed and the reaction mixture was heated to 90 °C for 1 hour. (Caution should be exercised due to the elevated pressure in the sealed reaction vessel when heating, particularly attempting scale up). Then 5 ml of CH_2Cl_2 and sodium nitrite (5 mmol, 0.35 g) in 10 ml of H_2O were added to the mixture. Excess acetic acid (20 mmol, 1.14 ml) was then added slowly at 0 °C. The reaction mixture was allowed to stir for another 1 hour at room temperature, and then extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified using flash column chromatography.



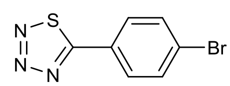
TT1: Petroleum ether:CH_2Cl_2 = 4:1 (11 mg, yield: 9%), obtained as a white crystalline solid.



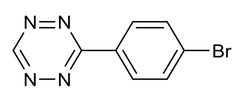
T2[10]**:** Petroleum ether:CH_2Cl_2 = 3:1 (20 mg, yield: 16%), obtained as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.46 (d, *J* = 8.60 Hz, 2H), 7.73 (d, *J* = 8.60 Hz, 2H), 3.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.60, 163.72, 132.72, 130.83, 129.46, 127.87, 21.36 ppm.

"Pinner Synthesis" using DMF as solvent

4-Bromobenzonitrile (0.5 mmol, 91 mg), sulfur (0.75 mmol, 24 mg) and DMF (2 ml) were mixed together in a 30 ml microwave reaction tube. Hydrazine monohydrate (5 mmol, 0.25 ml) was added with stirring afterwards. The vessel was sealed and the reaction mixture was heated to 90 °C for 1 hour. (Caution should be exercised due to the elevated pressure in the sealed reaction vessel when heating, particularly attempting scale up). Then 5 ml of CH_2Cl_2 and sodium nitrite (5 mmol, 0.35 g) in 10 ml of H_2O were added to the mixture. Excess acetic acid (20 mmol, 1.14 ml) was then added slowly at 0 °C. The reaction mixture was allowed to stir for another 1 hour at room temperature, and then extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified using flash column chromatography.



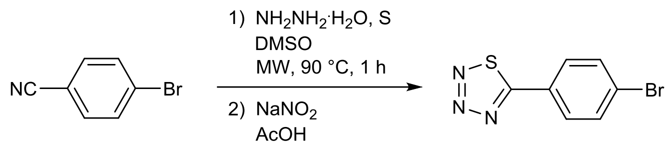
TT1: Petroleum ether:CH_2Cl_2 = 4:1 (50 mg, yield: 41%), obtained as a white crystalline solid.



T3[11]**:** Petroleum ether:CH_2Cl_2 = 3:1 (10 mg, yield: 8%), obtained as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.25 (s, 1H), 8.51 (d, *J* = 8.70 Hz, 2H), 7.76 (d, *J* = 8.70 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.12, 158.04, 132.89, 130.62, 129.82, 128.64 ppm.

2. Supporting experimental results

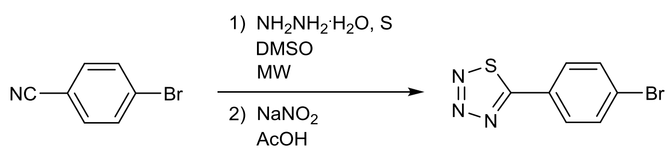
Table S1: Survey of sulfur amounts in the modified "pinner synthesis"(a).



Entry	**S**	**Yield (%)(b)**
1	1 equiv.	53
2	1.3 equiv.	72
3	1.5 equiv.	74
4	2 equiv.	71

(a) All reactions were carried out on a 0.5 mmol scale in 2 ml DMSO. MW = microwave. (b) Yields (isolated) based on the nitrile precursor.

Table S2: Survey of reaction temperature and time in the modified "pinner synthesis"(a).



Entry	**Temp., time**	**Yield (%)(b)**
1	90 °C, 1 h	74
2	80 °C, 1 h	59
3	80 °C, 3 h	72
4	70 °C, 6 h	74
5	60 °C, 24 h	69

(a) All reactions were carried out on a 0.5 mmol scale in 2 ml DMSO. MW = microwave. (b) Yields (isolated) based on the nitrile precursor.

Table S3*.* Summary of crystal data and intensity collection parameters for compound **TT9**.

	TT9
Empirical formula	$C_{19}H_{12}N_4OS$

Mol wt	342.67
Crystal system	Triclinic
Shape	Yellow block
Space group	P -1
a / Å	7.8935(9)
b / Å	9.7239(11)
c / Å	11.0347(14)
α / º	111.205(11)
β / º	95.584(10)
γ / º	91.415(9)
V / Å^3	784.24(17)
Z	3
D / g cm^{-3}	1.458
Temperature / K	293

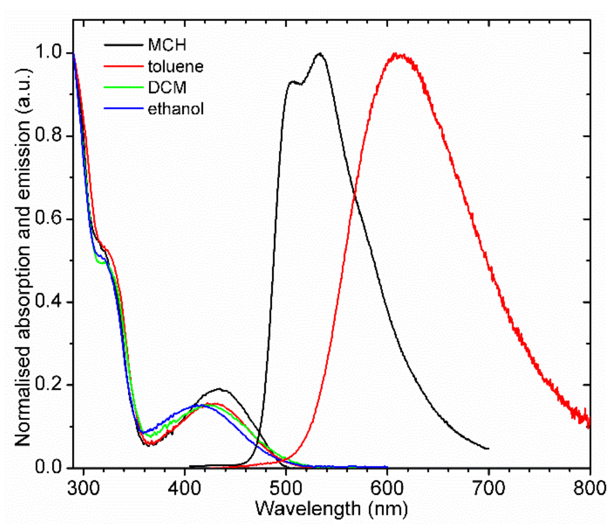


Figure S1: Absorption and photoluminescence spectra of **TT9** in various solvents at room temperature. A characteristic behavior of the 350-500 nm absorption band indicates its charge transfer (CT) origin. Note: DCM and ethanol solutions are virtually non-emissive.

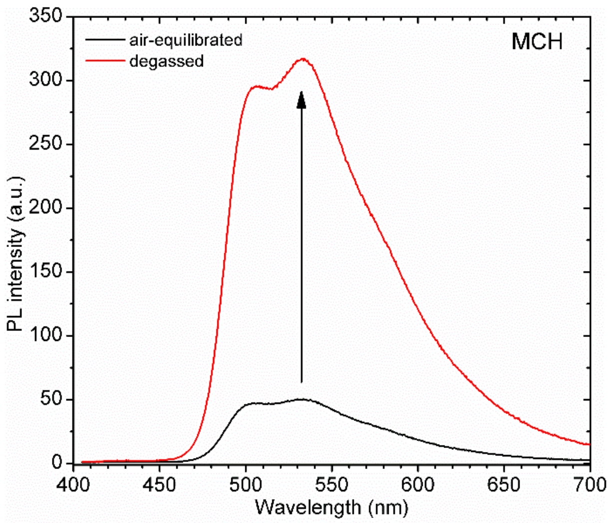


Figure S2: PL spectra of **TT9** in degassed and air-equilibrated MCH at room temperature.

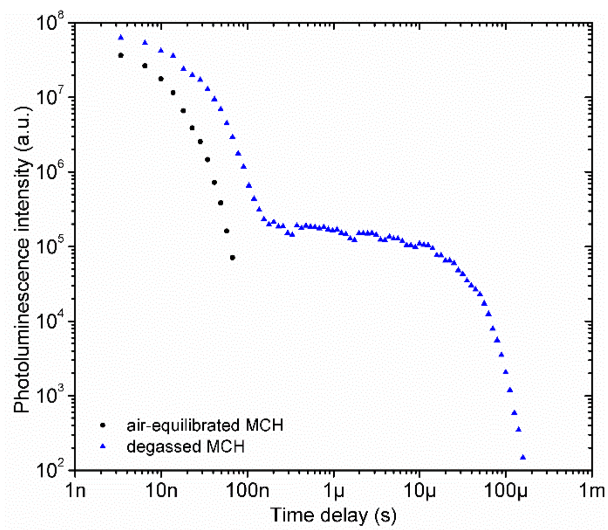


Figure S3: PL decay of **TT9** in degassed and air-equilibrated MCH at room temperature.

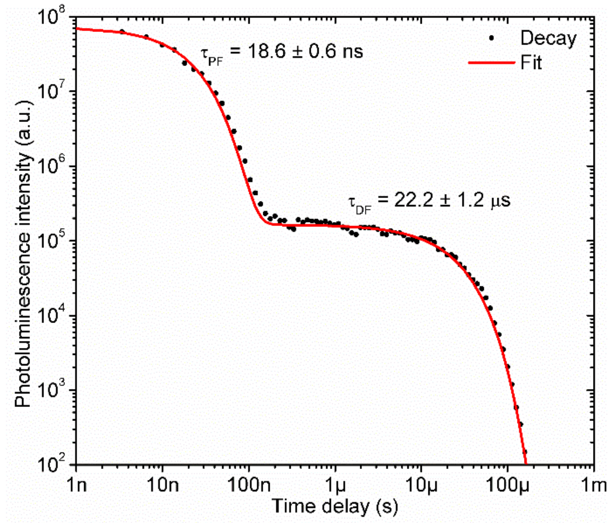


Figure S4: Fitted PL decay of **TT9** in degassed MCH at room temperature.

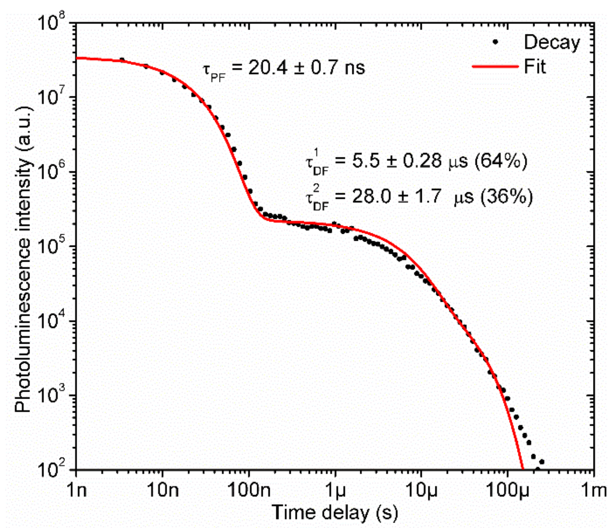


Figure S5: Fitted PL decay of **TT9** in Zeonex in vacuum at room temperature.

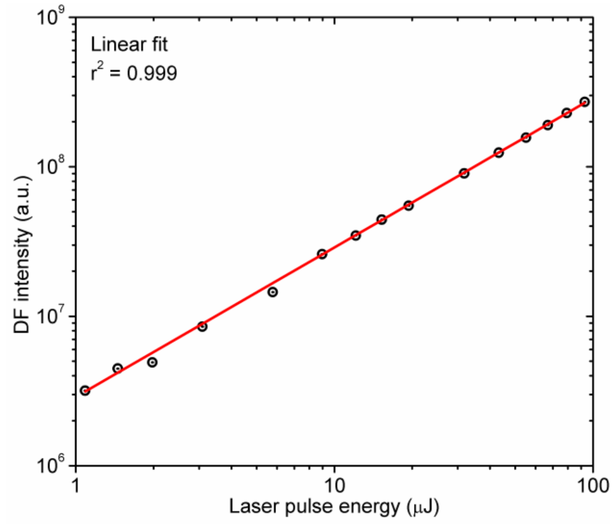


Figure S6: Power dependence of delayed fluorescence of **TT9** in degassed MCH at room temperature.

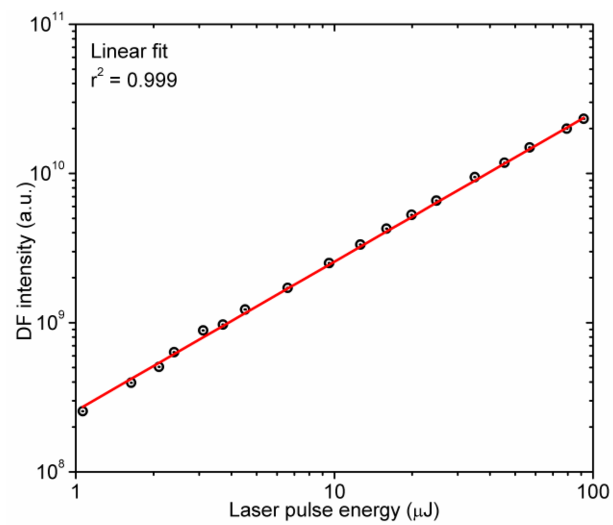


Figure S7: Power dependence of delayed fluorescence of **TT9** in Zeonex in vacuum at room temperature.

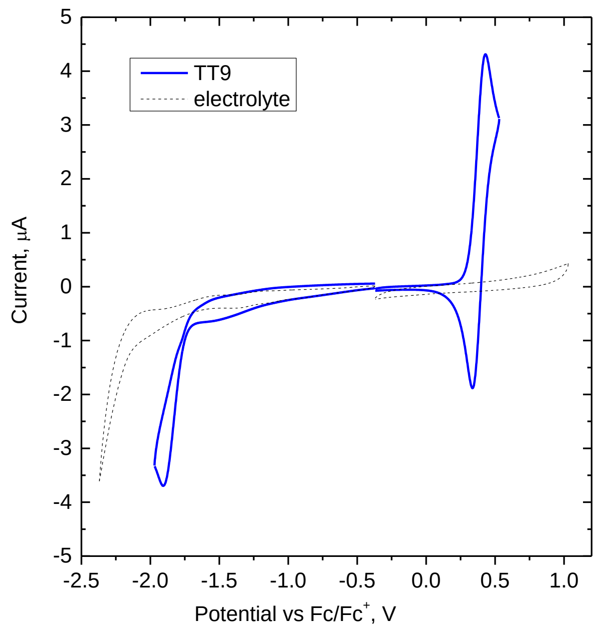


Figure S8: Cyclic voltammetry of **TT9** in DCM at room temperature.

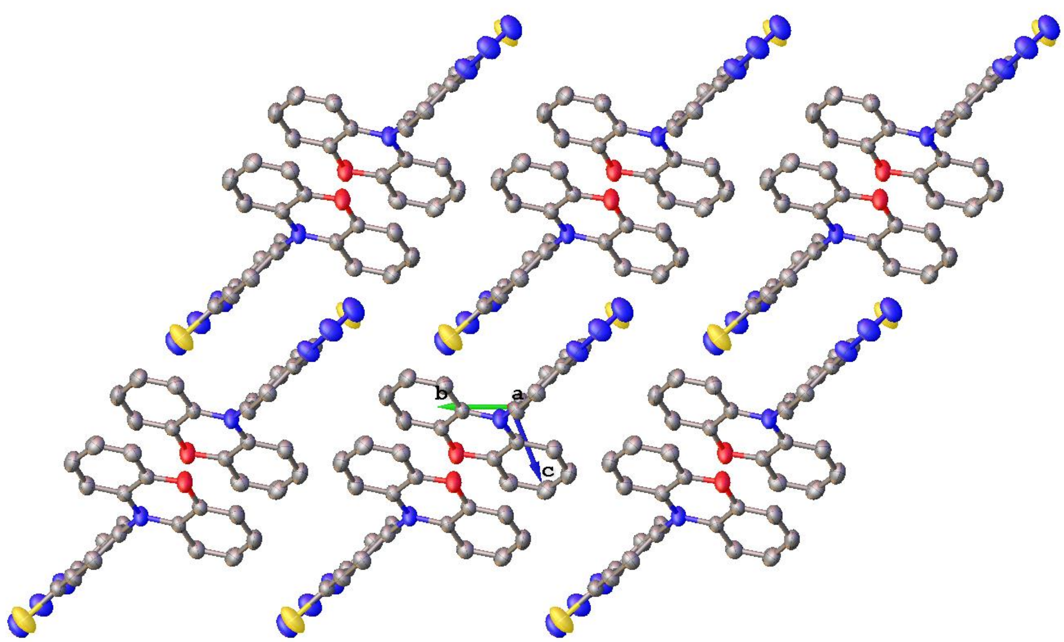


Figure S9. Packing in the crystal structure of compound **TT9**, viewed along the *a*-axis.

Figure S10. Overlay of the ground state (orange) and first singlet excited state (gray) optimized geometries.

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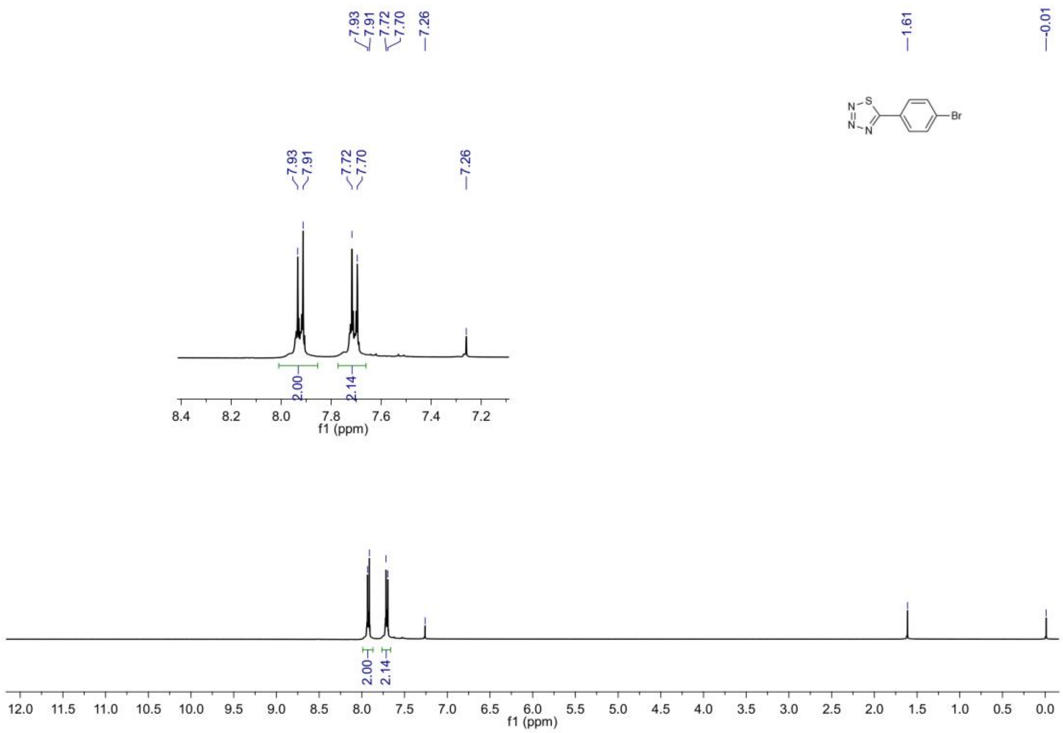
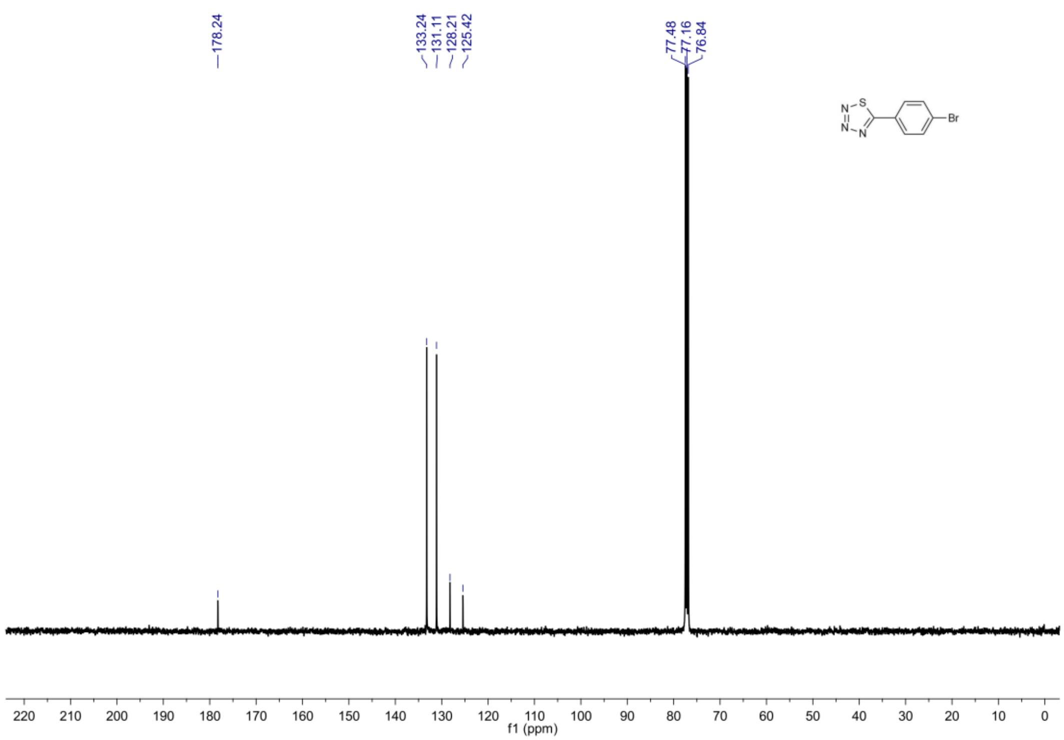
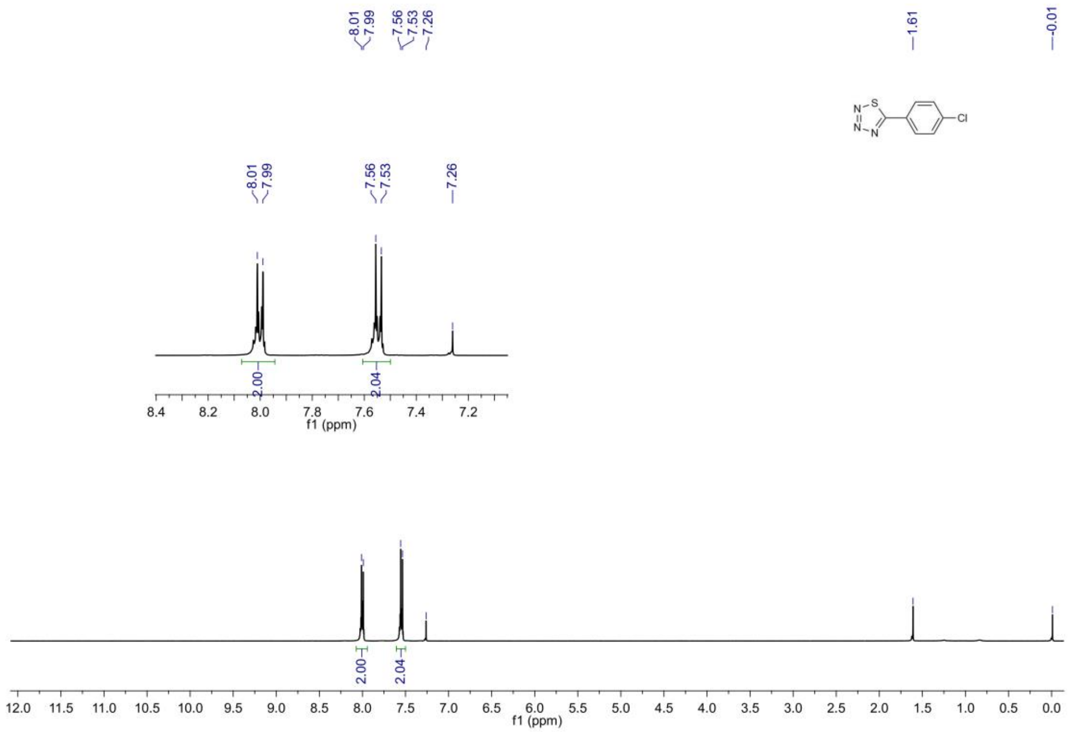
3. NMR Spectra



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2.00
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8.4
8.2
8.0
7.8
7.6
7.4
7.2
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2.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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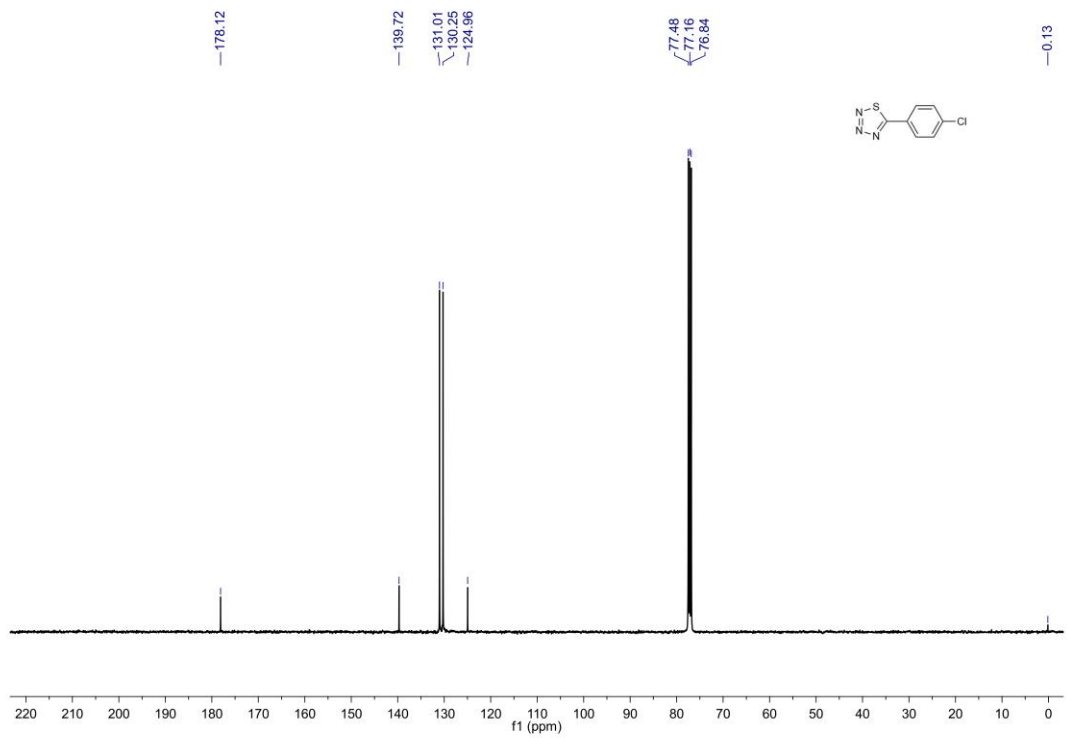
f1 (ppm)
Cl
N
S
N
N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S
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N
220
210
200
190
180
170
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130
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110
100
90
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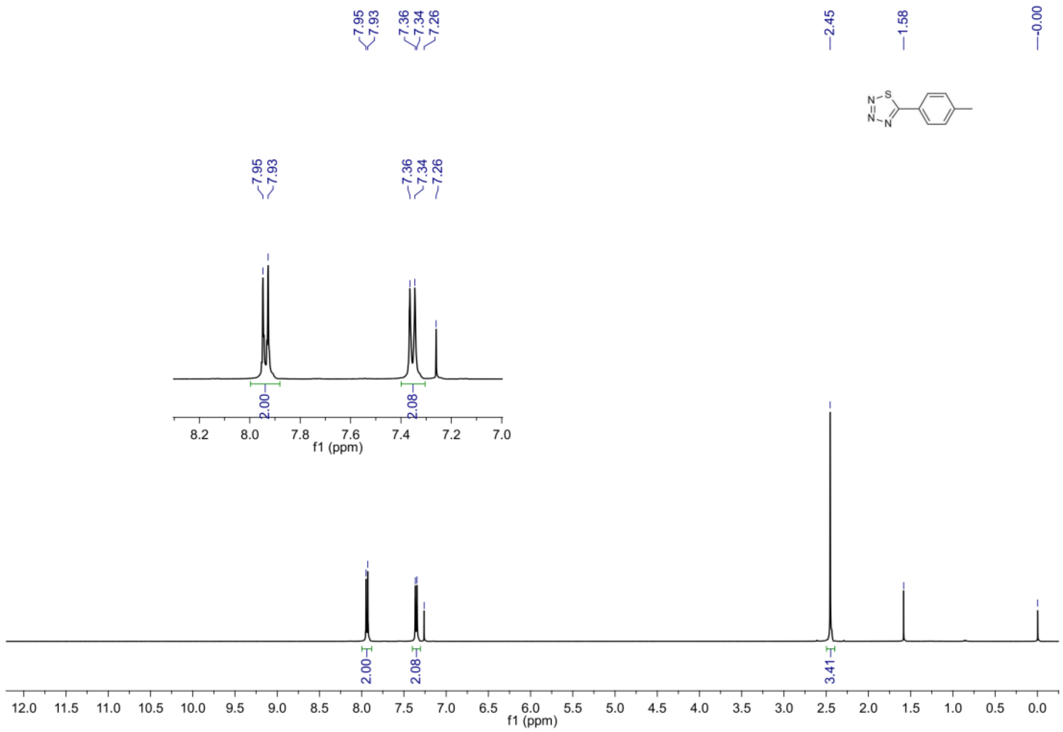
50
40
30
20
10
0
f1 (ppm)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f1 (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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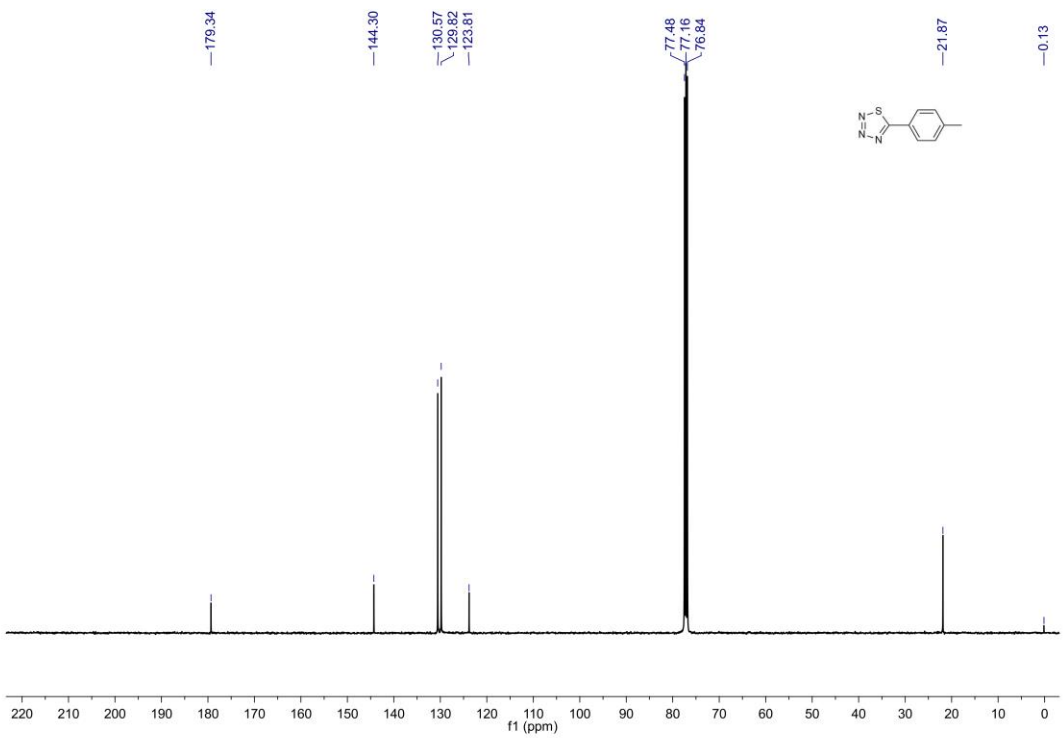
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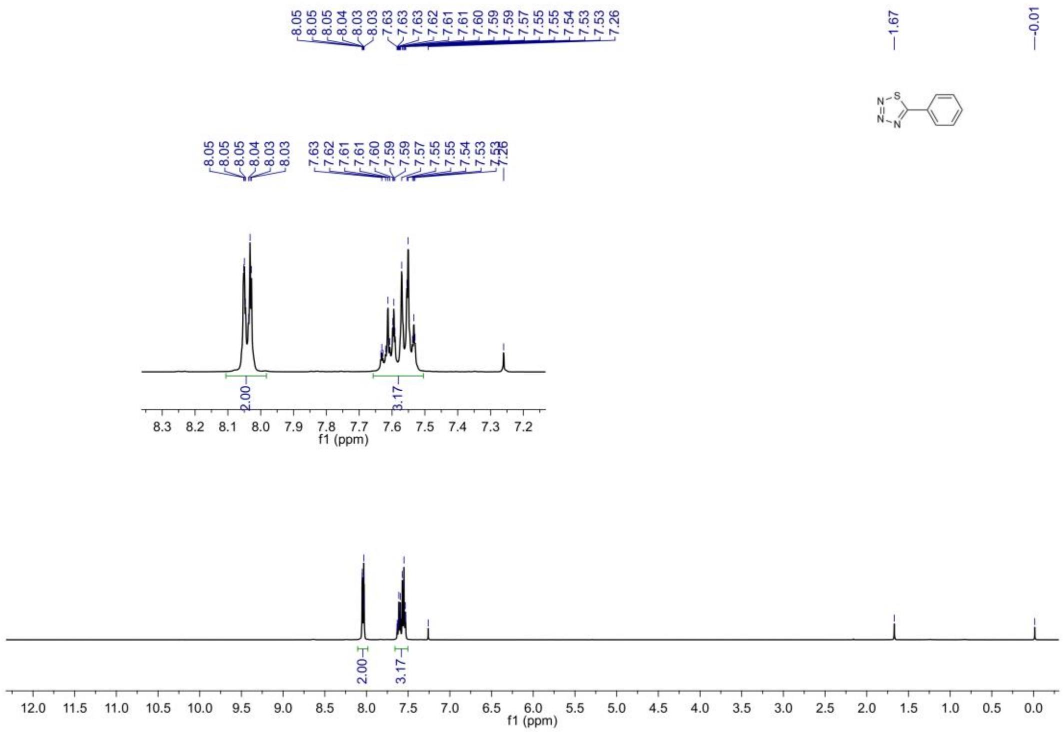
f1 (ppm)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7.59
7.59
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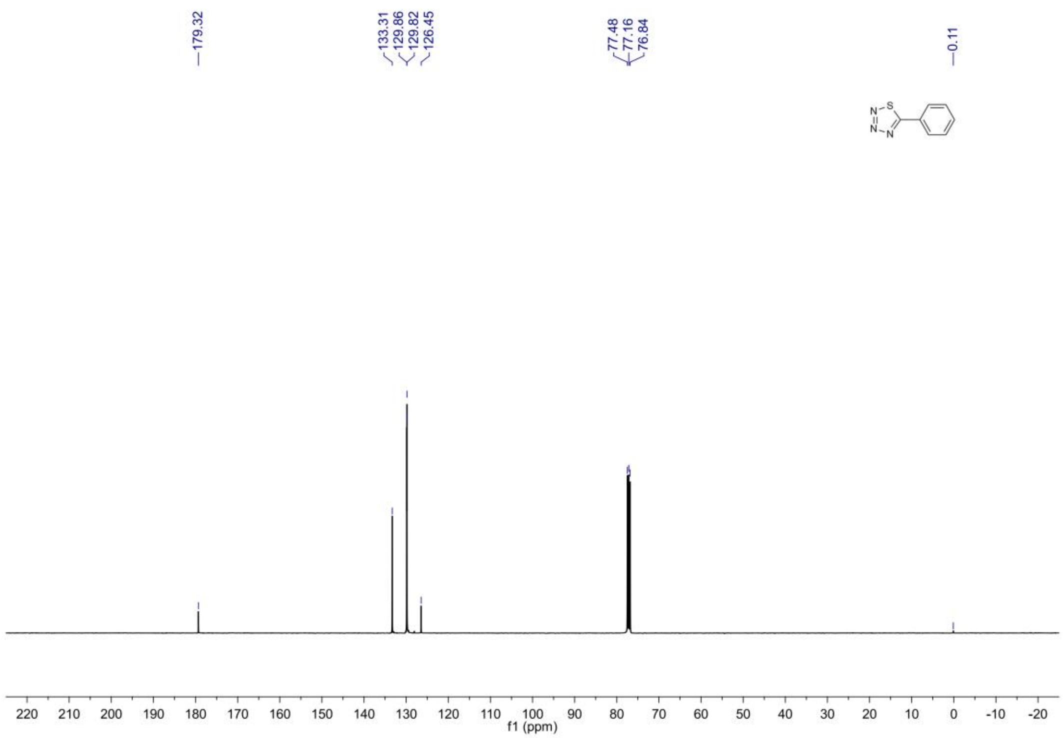
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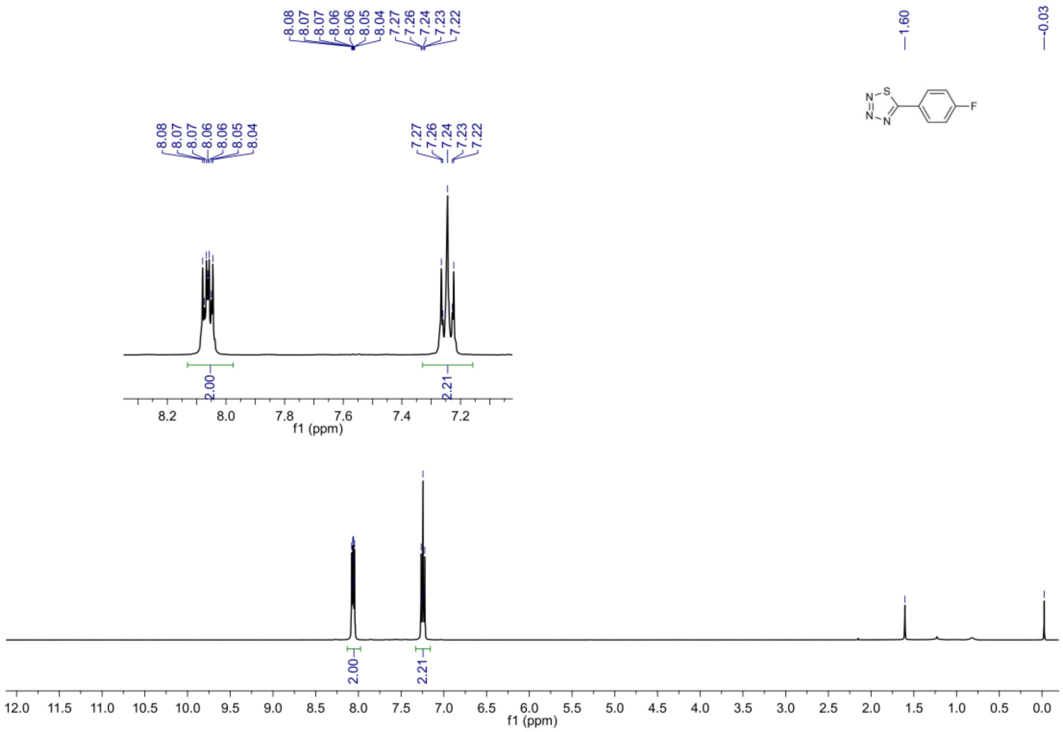

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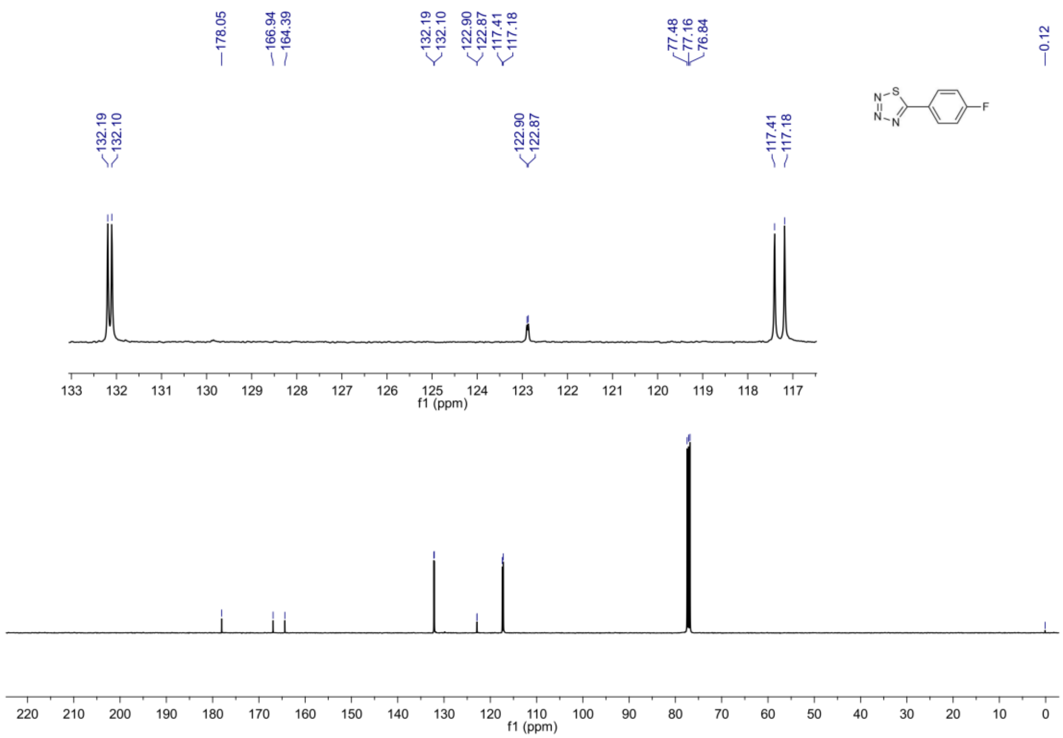

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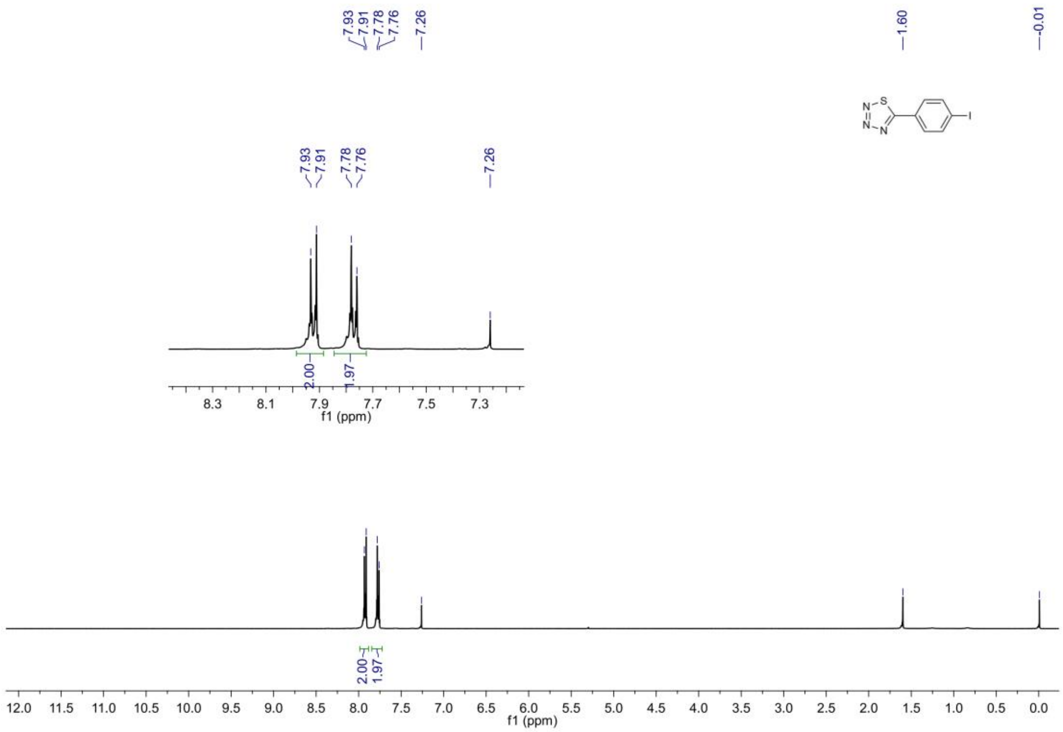

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1.97
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f1 (ppm)
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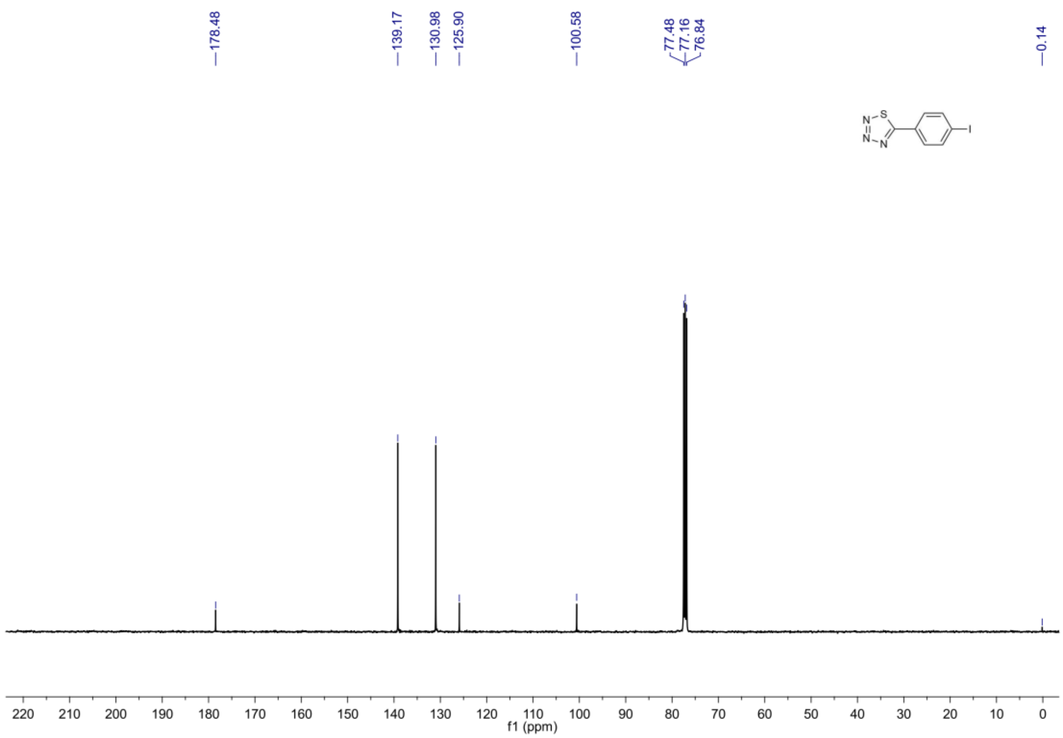

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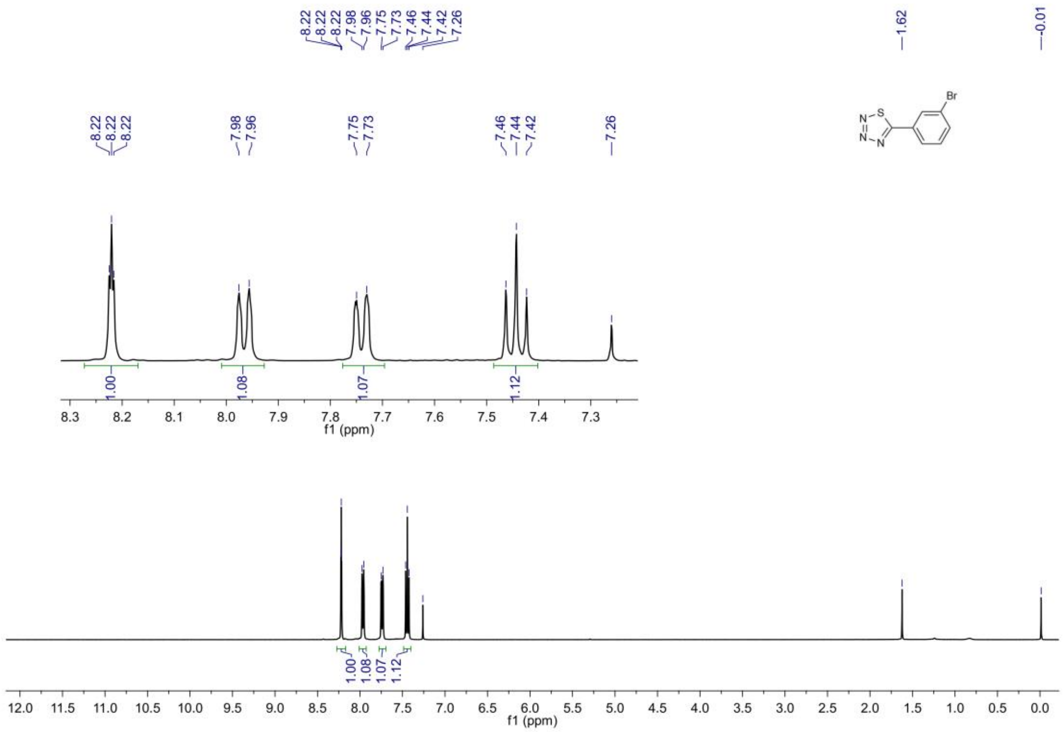
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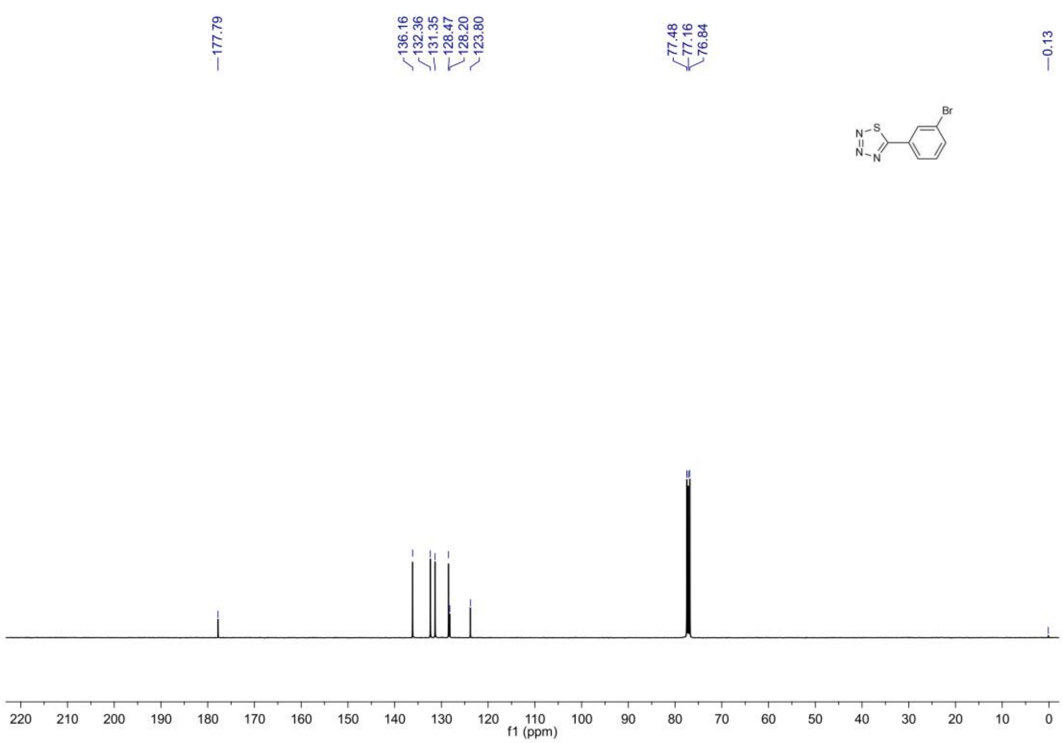
f1 (ppm)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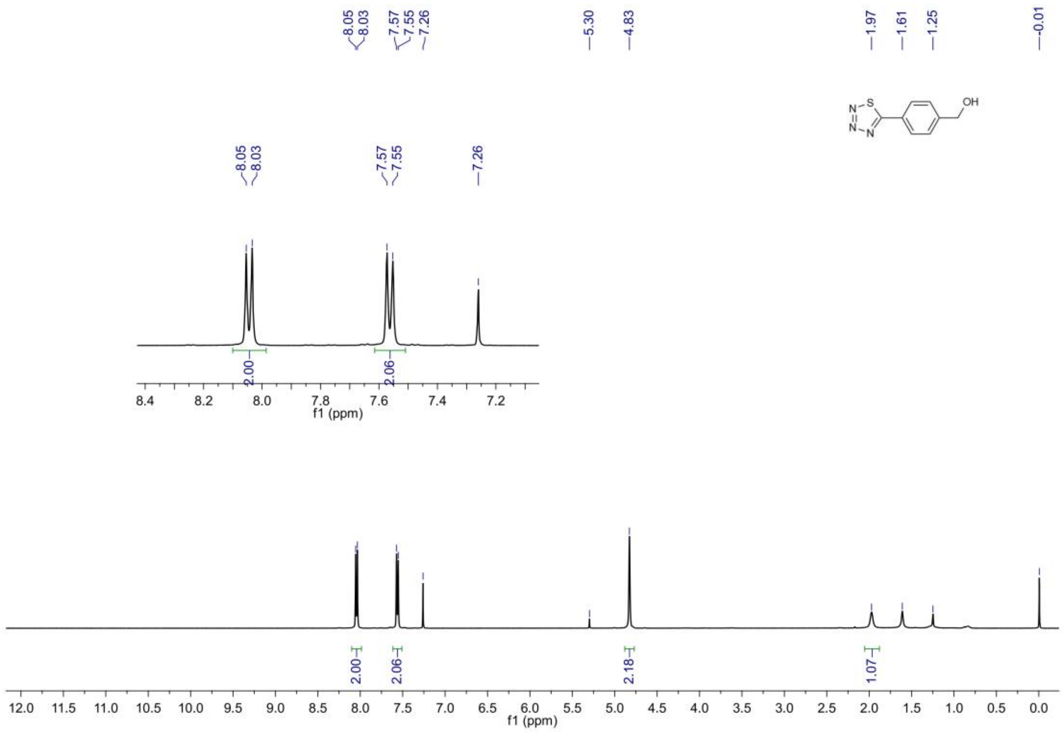
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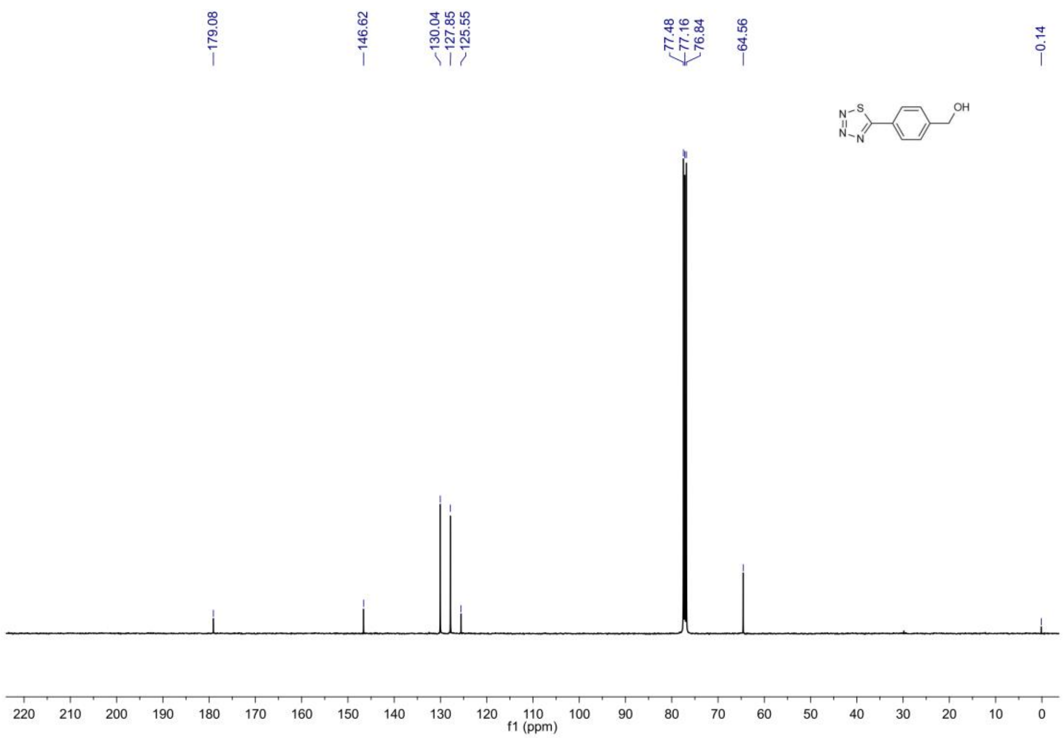
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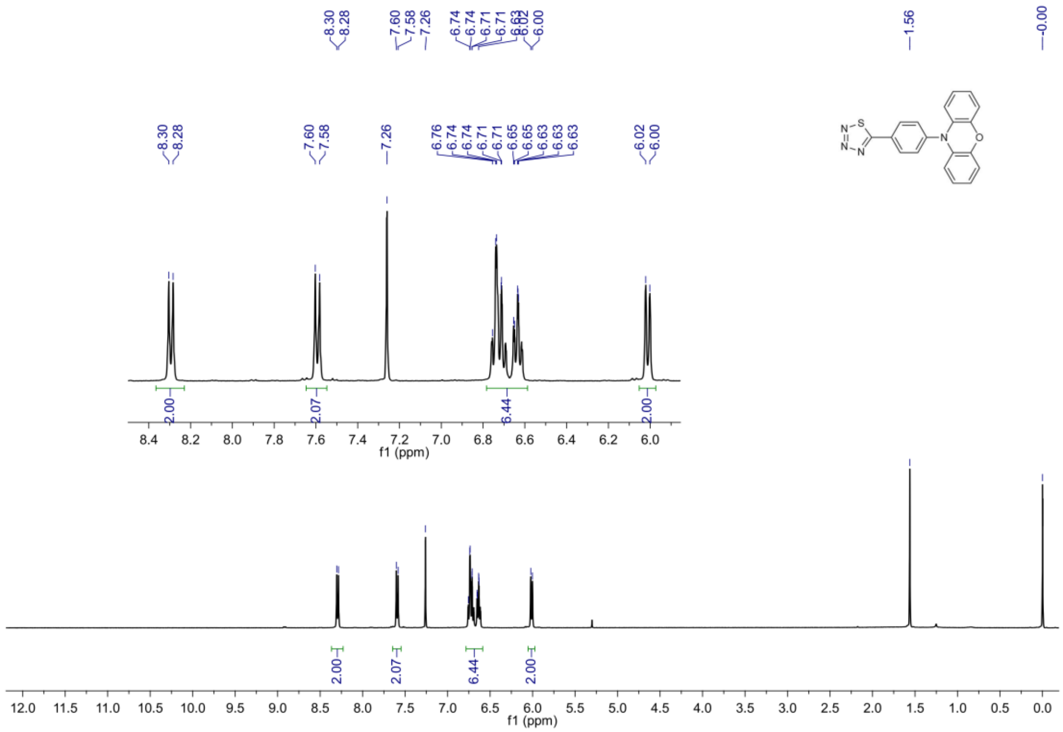

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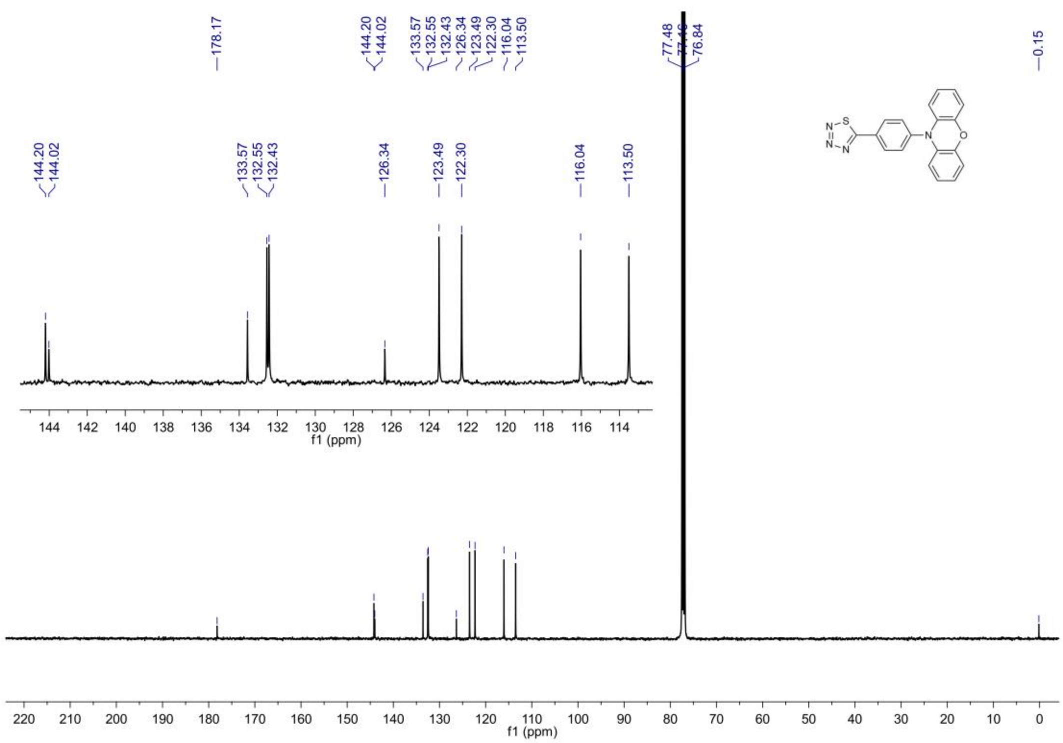
N
S
O



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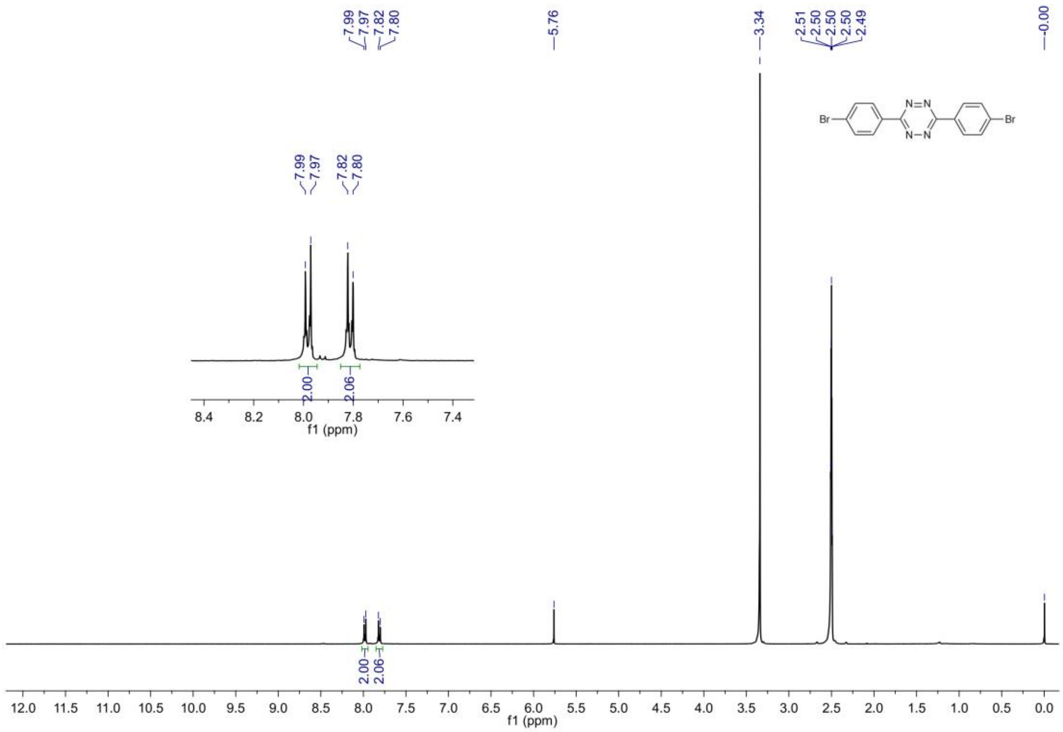
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N–N
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2.00
2.06
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f1 (ppm)
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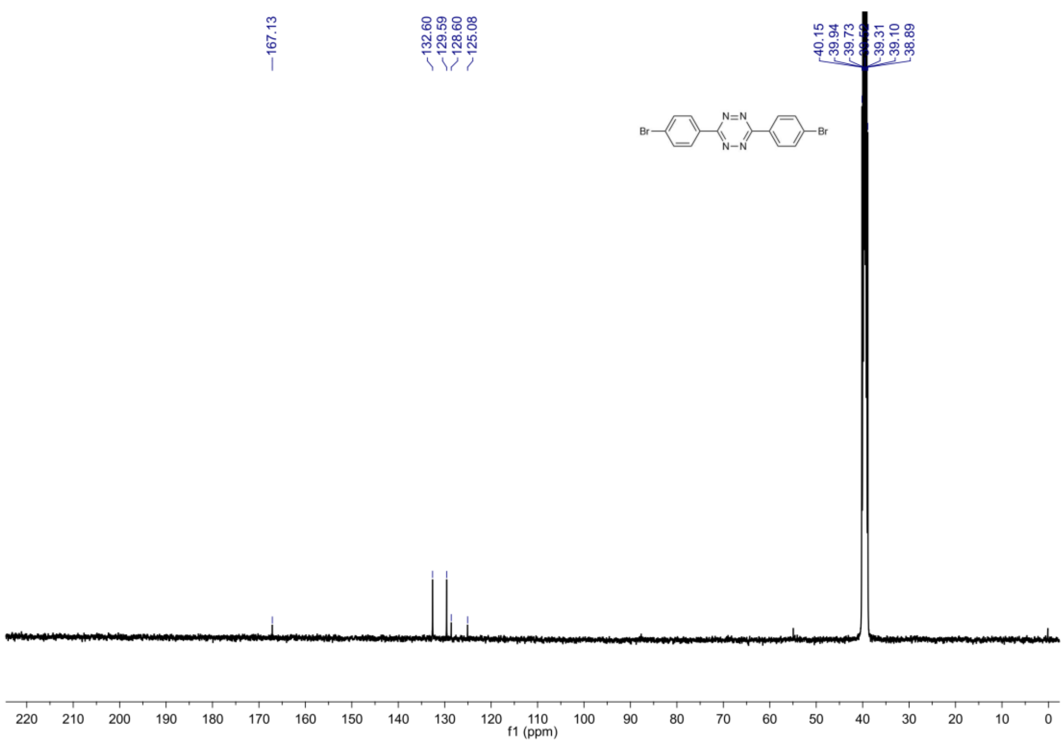
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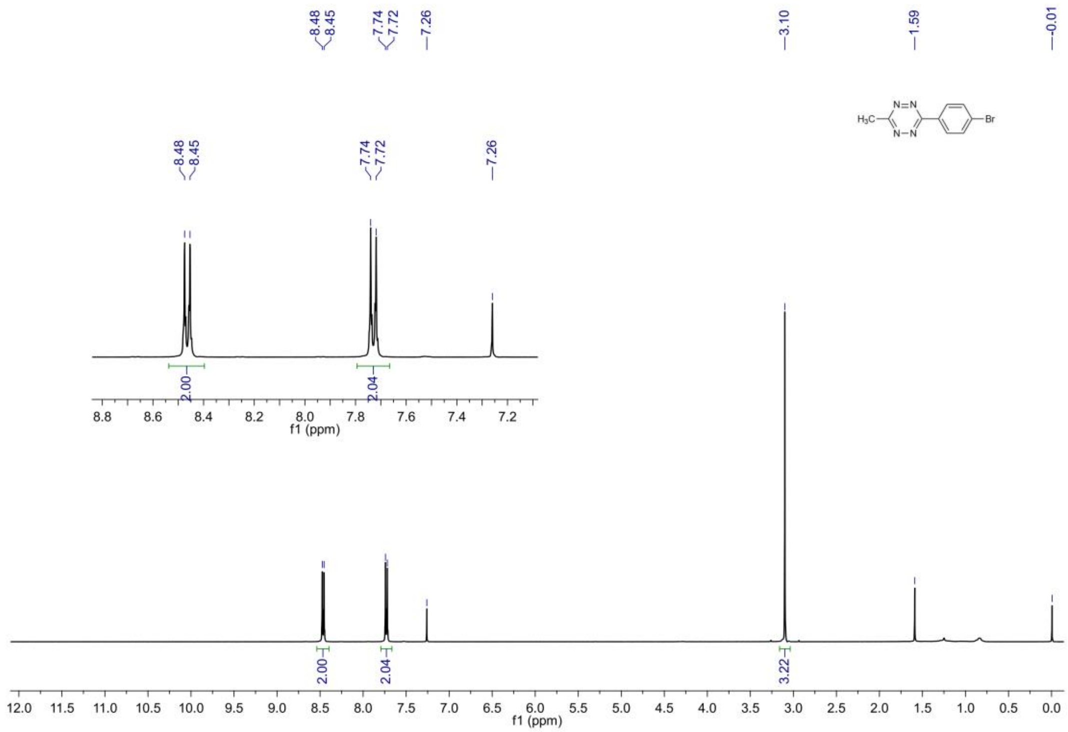

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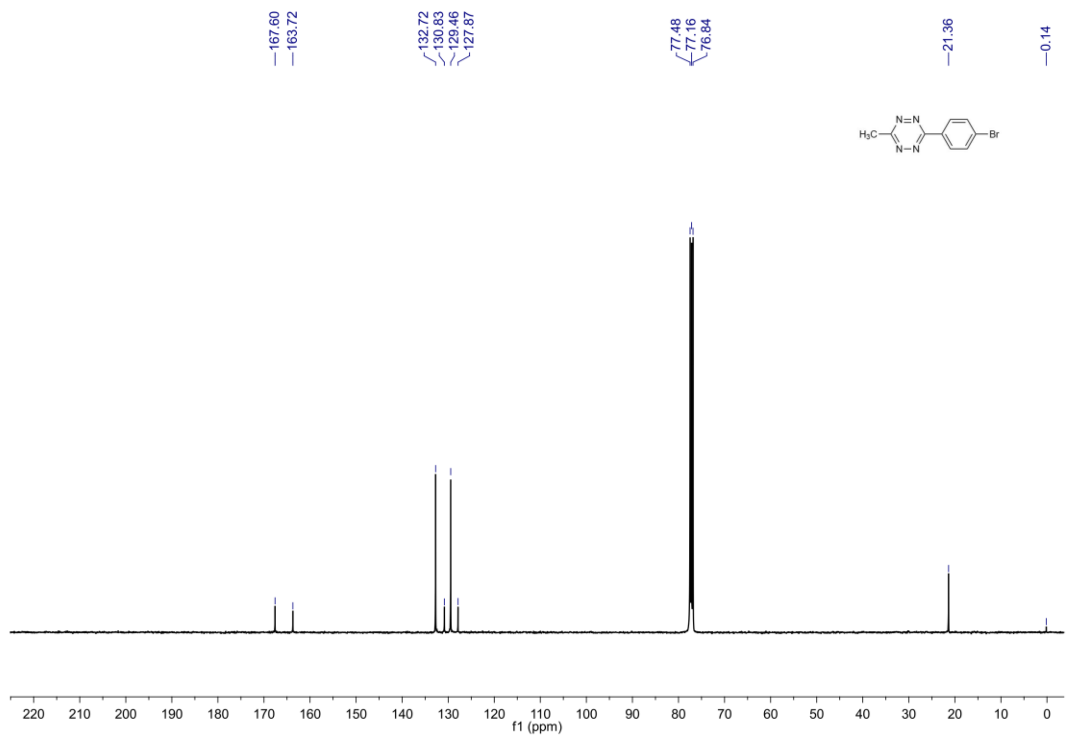

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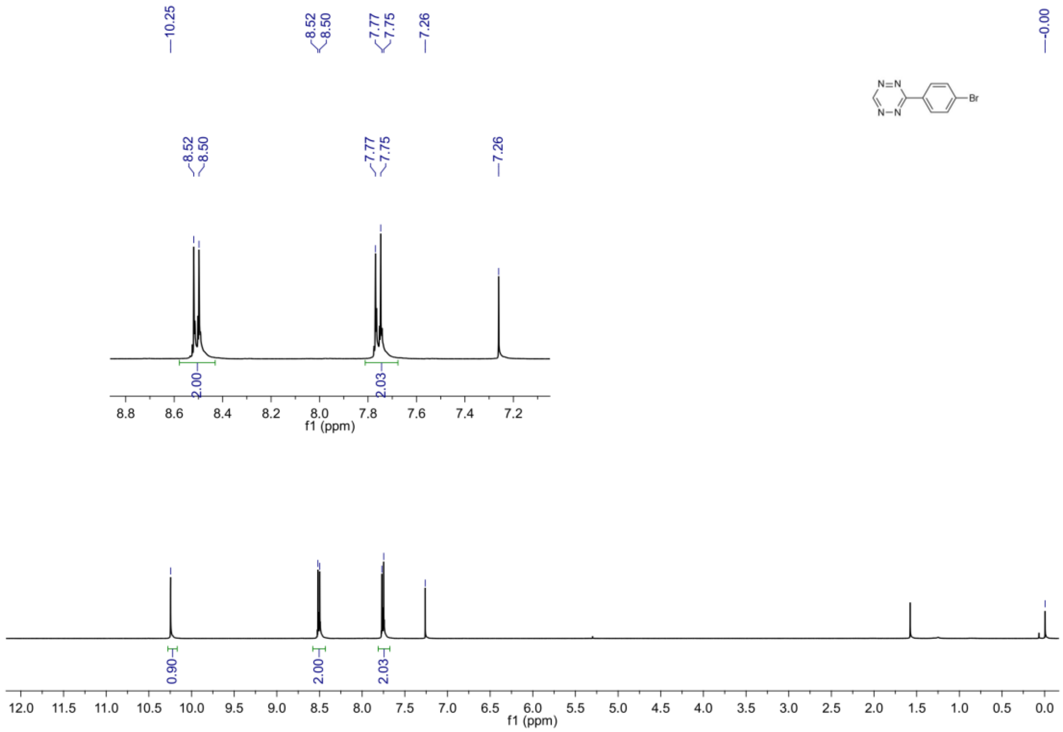
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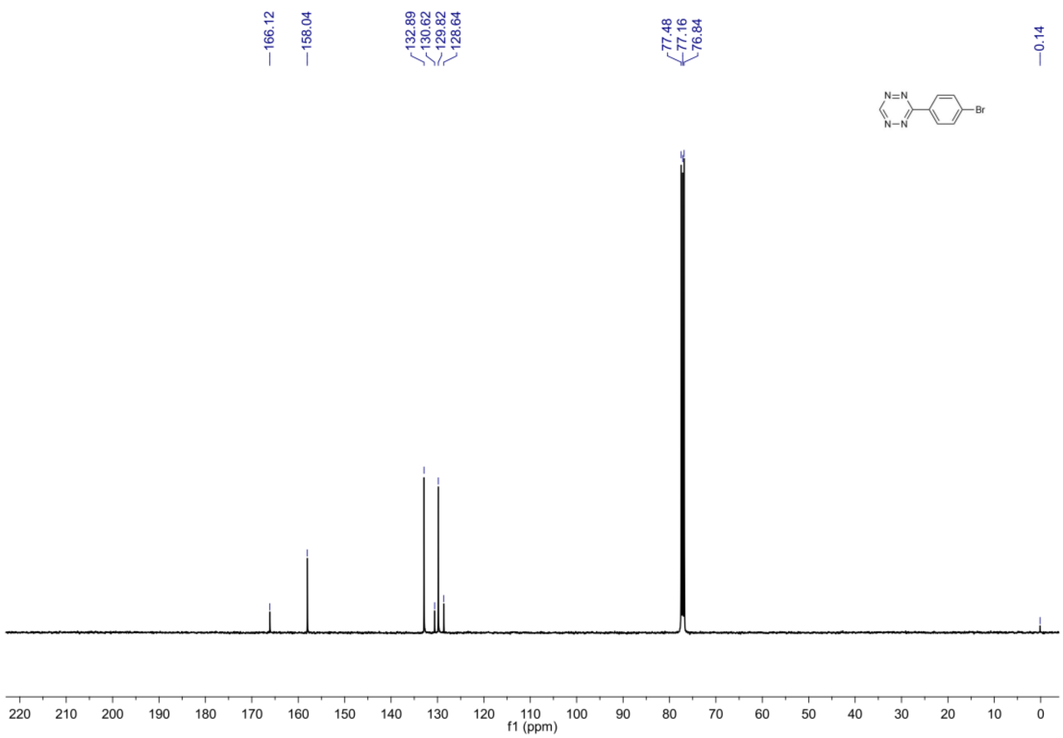
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