

Clean photodecomposition of 1-methyl-4-phenyl-1*H*-tetrazole-5(4*H*)-thiones to carbodiimides proceeds *via* a biradical

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Theoretical calculations on the electronic properties **1b**

Ground state geometries

To gain insights into the electronic properties of **1b**, we performed DFT calculations employing 6-311+G*. The optimized ground state geometries of **1b** at B3LYP/6-311+G* and their corresponding bond lengths are shown in Figure S1. The molecule display C_1 symmetry. The dihedral angle between the tetrazolethione ring and the phenyl ring was 41.1°.

Frontier molecular orbitals

The electronic structure of **1b** was analyzed in the presence of cyclohexane, THF and acetonitrile. The isodensity plots of the frontier molecular orbitals obtained at B3LYP/6-311+G* in acetonitrile are depicted in Figure S3 and they all exhibit π -type symmetry. The HOMO-3 for **1b** exclusively localized over the aromatic ring while the HOMO-2 is delocalized over the entire molecule. The HOMO-1 is mainly localized on the tetrazolethione ring and has major contribution from the C₅-S π bond (Refer to Scheme S1 for the numbering of atoms). The HOMO is delocalized over the entire molecule showing bonding contributions from the aromatic ring.

The LUMOs exhibit a bonding character at the N₁-C₇, C₈-C₉ and C₁₁-C₁₂ bonds that supports the resonance structures **1b'** (Scheme S1). The LUMO+1 is mainly localized over the tetrazolethione ring, while the LUMO+2 is a π^* orbital exclusively localized over the aromatic ring. LUMO+3 is delocalized over the entire molecule.

Vertical excitation energies

In order to determine the nature of the electronic transitions that give rise to bands in the UV spectra of **1b**, time-dependent density functional calculations were carried out and thirty low lying singlet excited states were calculated. The vertical excitation energies, corresponding wavelengths, oscillator strengths, MO character and the transition type for the most intense transitions calculated at TDDFT/6-311+G* in cyclohexane, THF and MeCN are reported in Tables S1.

The analysis of TDDFT wave function indicates that λ_1 experimentally observed at 4.27, 4.35 and 4.41 eV in cyclohexane (Table 1), THF and MeCN corresponds to a transition from HOMO-1 or HOMO to the LUMO and is calculated at 4.07, 4.11 and 4.14 eV, respectively (Table S1). The band λ_2 experimentally found at 4.66, 4.69 and 4.77 eV in cyclohexane, THF and MeCN is comprised of transitions from HOMO-1/HOMO to LUMO+1. It is calculated at 4.67, 4.72 and 4.74 eV in the three solvents, respectively. λ_3 is predicted at 5.35, 5.31 and 5.34 eV and observed at 5.58, 5.55 and 5.61 eV in cyclohexane, THF and acetonitrile. This band is formed of many excited states consisting of transitions from several MOs of similar energy including HOMO-3→LUMO/LUMO+1, HOMO-2→LUMO+2, HOMO-1/HOMO→LUMO+3/LUMO+2 and HOMO→LUMO+2. λ_4 appears experimentally at 5.98 and 6.32 eV in cyclohexane and acetonitrile and is calculated at 6.01 and 6.05 eV, respectively, consisting of transitions from HOMO-3→LUMO+2.

Furthermore, the analyses of the MOs indicate that all bands observed in the UV spectra of **1b** are $\pi \rightarrow \pi^*$ in nature. λ_1 is accompanied by intramolecular charge transfer (CT) from the heterocycle to the phenyl ring; note that both HOMO-1 and HOMO are

localized on the tetrazolethione while LUMO is delocalized over the entire molecule and has bonding characteristics at the N₁-C₇, C₈-C₉ and C₁₁-C₁₂ bonds. Similarly, λ_2 and λ_3 correspond to a $\pi \rightarrow \pi^*$ transition, the latter is also associated with some degree of charge transfer within the molecule. λ_4 is a $\pi \rightarrow \pi^*$ transition localized on the phenyl ring. In accordance with the experimental observations, the calculated transitions show modest dependence on the polarity of the solvent.

Computational methods. All calculations were carried out with Gaussian 03 package of programs¹. B3LYP functional was used which combines Becke's three parameter exchange functional with the correlation functional of Lee, Yang, and Parr^{2, 3}. All calculations employed 6-311+G* basis sets. All the geometry optimizations were followed by vibrational analyses to ensure the positive sign of all eigenvalues of the Hessian matrix and to confirm that the stationary point found was a true minimum on the potential energy surface. Vertical excitation energies were computed using time dependent density functional theory (TDDFT)⁴ at optimized geometries. The solvent effects on the ground state geometries and excitation energies were considered using the integral equation formalism of the polarized continuum model (IEFPCM). The molecular orbitals were visualized using GaussView.

SCHEME S1. Resonance structures of 1b.

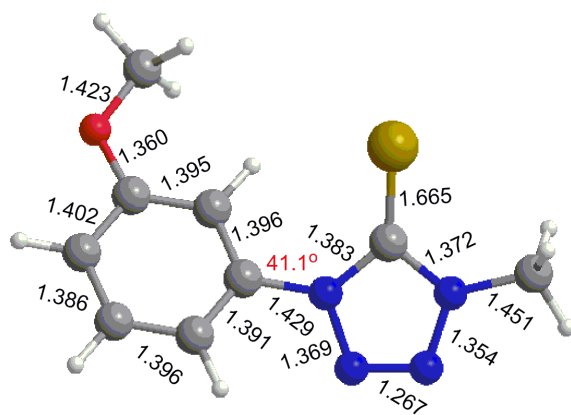
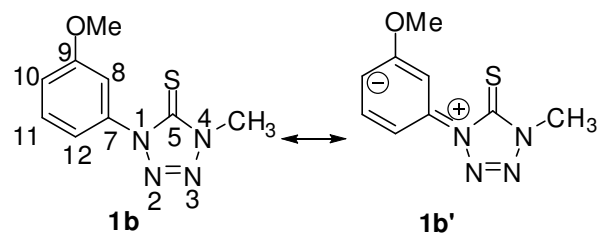


FIGURE S1. Ground state geometry of 1b.

Cartesian coordinates for the optimized 1b (B3LYP/6-311+G*)

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O,3.6352630818,1.0279999844,0.2821998276
C,3.1898298213,2.3258175696,0.6592921786
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N,-2.886014086,-1.3454126561,0.6940861909
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H,0.2662534901,-2.8891291571,-0.6096738797
H,0.9238434123,1.1880906058,0.547450015
H,4.087787637,2.9363180753,0.7304534832
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H,2.5176465909,2.7501492554,-0.0922915772
H,-5.0121215937,-0.0727346438,0.4860314433
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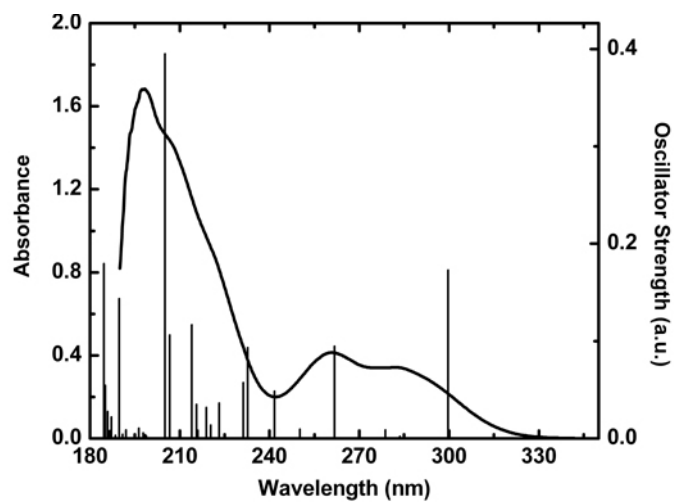
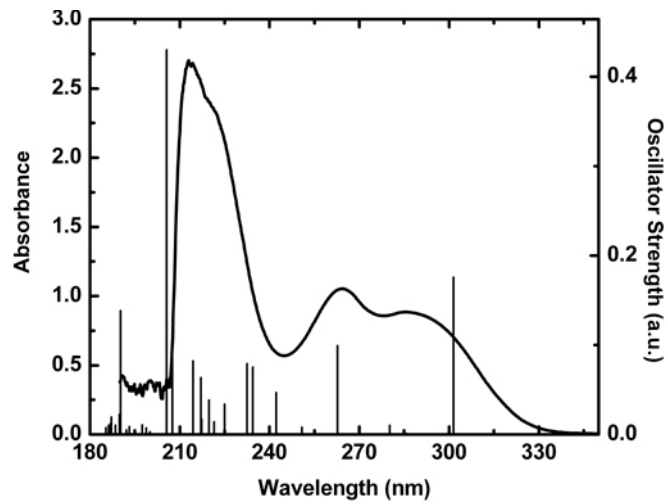
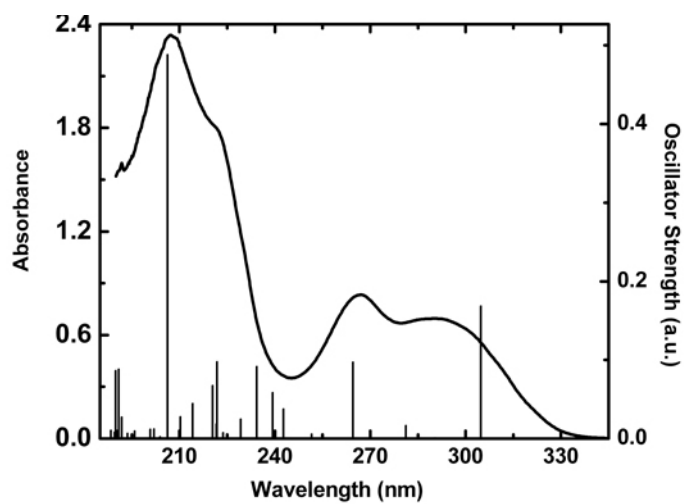


FIGURE S2. Experimental absorption spectra of **1b** in cyclohexane, tetrahydrofuran and acetonitrile. The vertical excitations calculated at TDDFT/6-311+G* are shown as stick spectra.

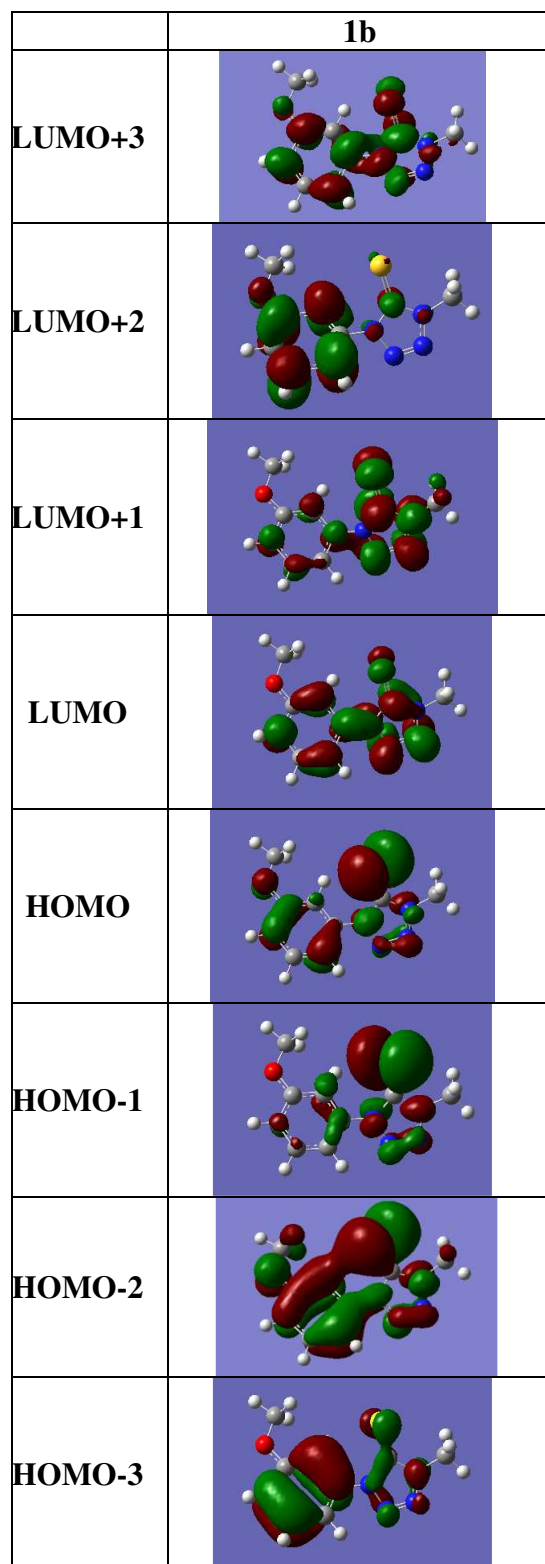


FIGURE S3. Molecular orbitals for B3LYP/6-311+G* optimized geometries of **1b** in acetonitrile.

Table S1. TDDFT/6-311+G* vertical excitation energies ($E(\lambda)$ / eV (nm)), oscillator strengths (f), MO character and transition type of **1b** in cyclohexane, tetrahydrofuran and acetonitrile.

State	$E(\lambda)$	f	MO Character	Type
Cyclohexane				
λ_1	2 4.07 (304.8)	0.168	H-1 \rightarrow L; H \rightarrow L	$\pi \rightarrow \pi^*$ / CT
λ_2	5 4.67 (264.5)	0.097	H \rightarrow L+1; H-1 \rightarrow L+1	$\pi \rightarrow \pi^*$
λ_3	8 5.18 (239.3)	0.058	H-1 \rightarrow L+2	$\pi \rightarrow \pi^*$
	9 5.29 (234.3)	0.091	H-3 \rightarrow L; H \rightarrow L+2; H-1 \rightarrow L+2; H-1 \rightarrow L+3	$\pi \rightarrow \pi^*$ / CT
	12 5.58 (221.8)	0.098	H-3 \rightarrow L+1; H-1 \rightarrow L+2; H-2 \rightarrow L+2	$\pi \rightarrow \pi^*$
λ_4	17 6.01 (206.2)	0.488	H-2 \rightarrow L+3	$\pi \rightarrow \pi^*$
Tetrahydrofuran				
λ_1	2 4.11 (301.5)	0.175	H-1 \rightarrow L; H \rightarrow L	$\pi \rightarrow \pi^*$ / CT
λ_2	5 4.72 (262.7)	0.099	H \rightarrow L+1; H-1 \rightarrow L+1	$\pi \rightarrow \pi^*$
λ_3	8 5.29 (234.4)	0.075	H-1 \rightarrow L+2; H-1 \rightarrow L+3; H \rightarrow L+2	$\pi \rightarrow \pi^*$
	9 5.33 (232.5)	0.079	H-3 \rightarrow L; H-1 \rightarrow L+2; H \rightarrow L+2	$\pi \rightarrow \pi^*$ / CT
λ_4^a	17 6.03 (206.0)	0.430	H-2 \rightarrow L+3	$\pi \rightarrow \pi^*$
Acetonitrile				
λ_1	2 4.14 (300.0)	0.173	H-1 \rightarrow L; H \rightarrow L	$\pi \rightarrow \pi^*$ / CT
λ_2	5 4.74 (261.7)	0.094	H \rightarrow L+1; H-1 \rightarrow L+1	$\pi \rightarrow \pi^*$
λ_3	8 5.33 (232.6)	0.093	H-1 \rightarrow L+2; H-1 \rightarrow L+3; H \rightarrow L+2	$\pi \rightarrow \pi^*$
	9 5.36 (231.2)	0.057	H-3 \rightarrow L; H-1 \rightarrow L+2; H \rightarrow L+2	$\pi \rightarrow \pi^*$ / CT
λ_4	17 6.05 (205.0)	0.395	H-2 \rightarrow L+3	$\pi \rightarrow \pi^*$

^a experimentally not observed.

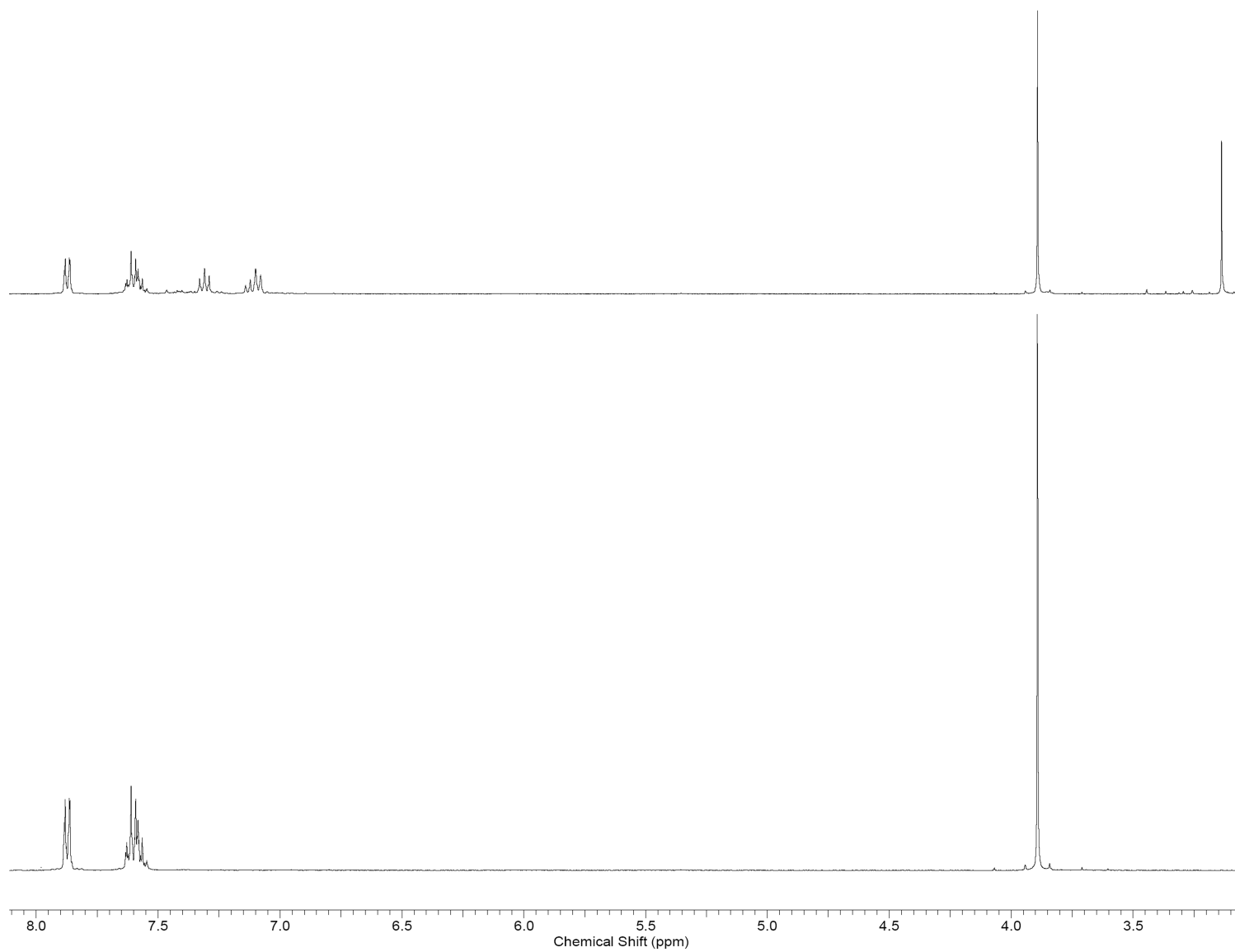


FIGURE S4. NMR spectra of **1a** taken at 0 min (bottom) and at 15 min (top) of irradiation at 254 nm

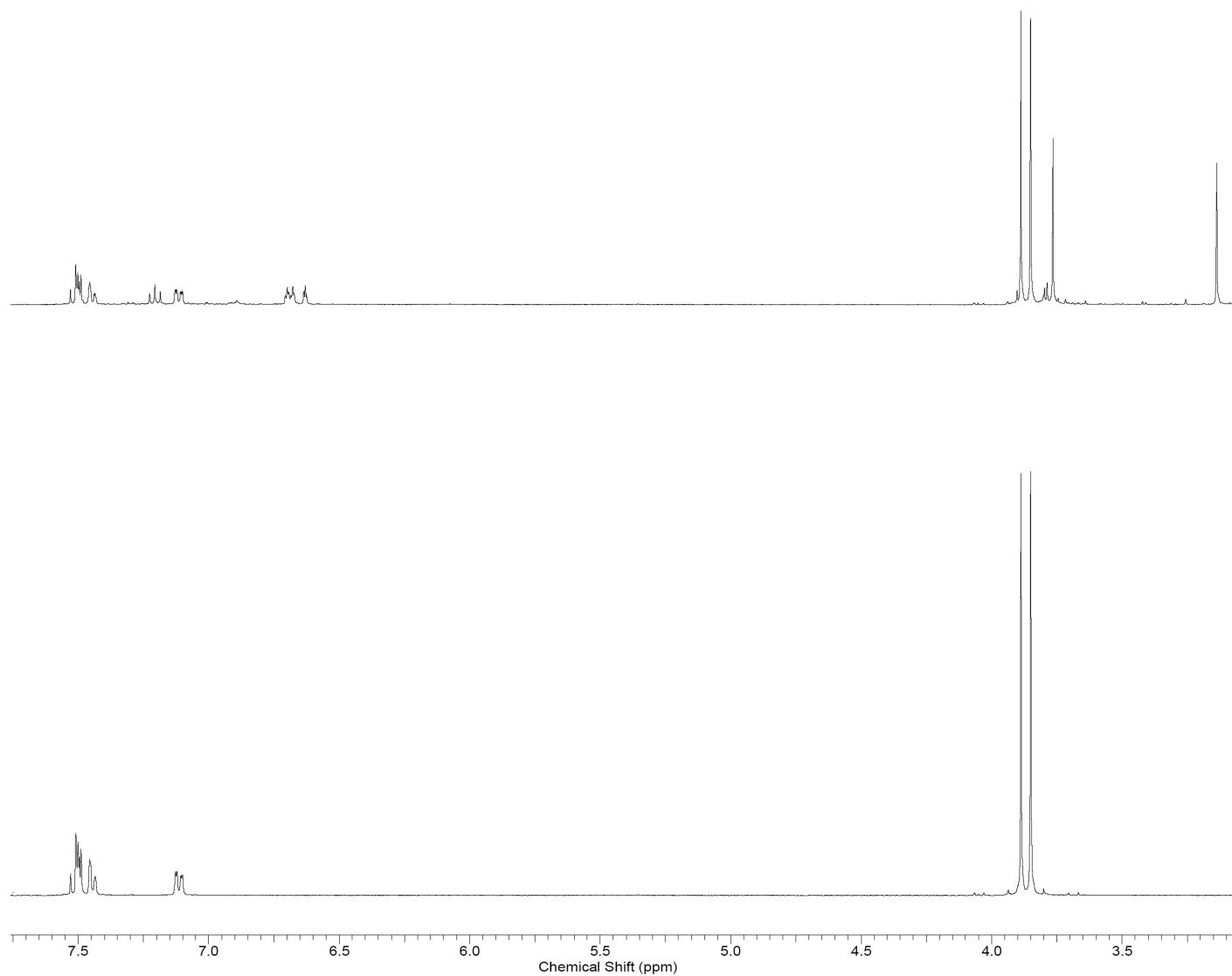
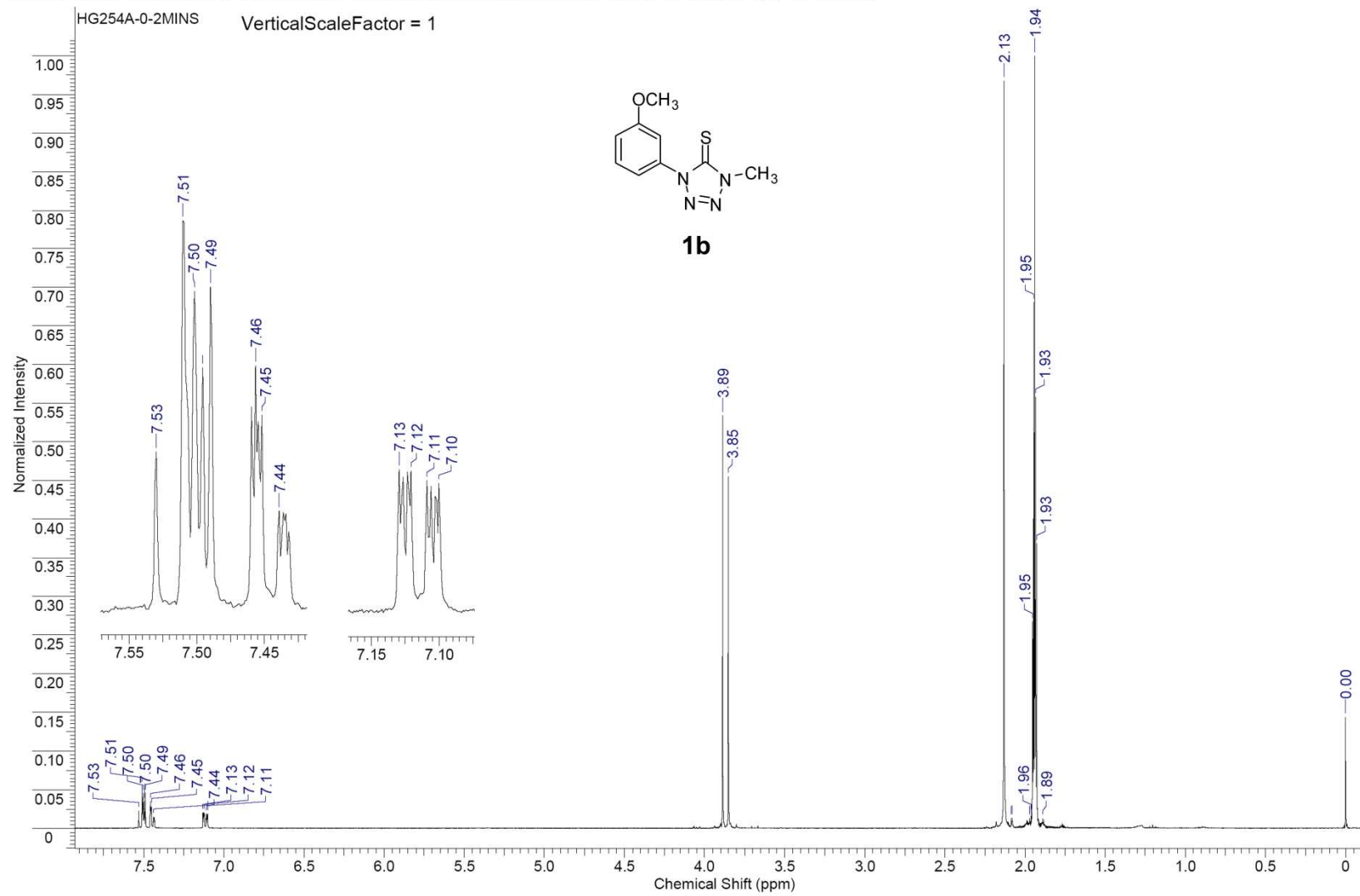
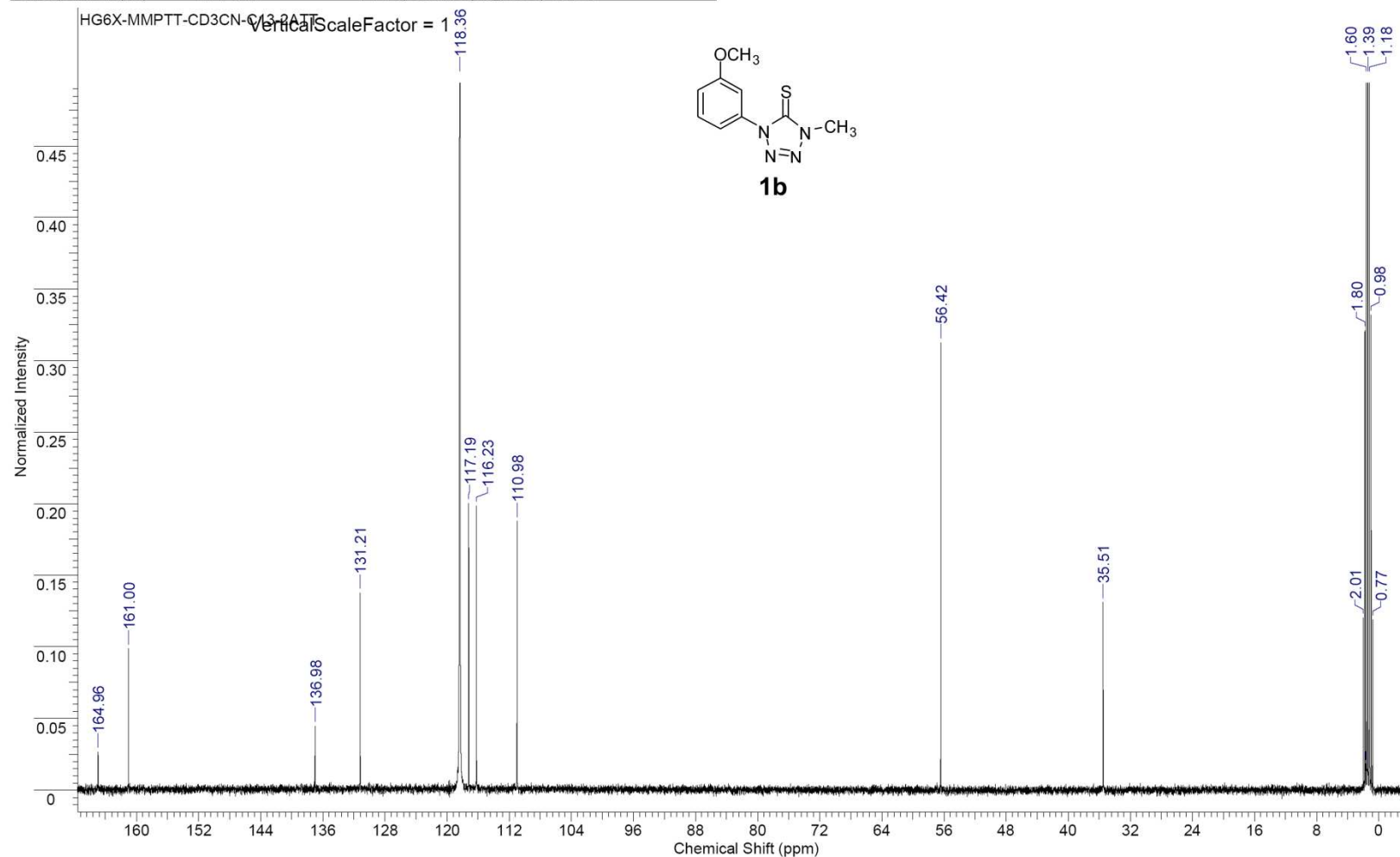


FIGURE S5. NMR spectra of **1b** taken at 0 min (bottom) and at 15 min (top) of irradiation at 254 nm

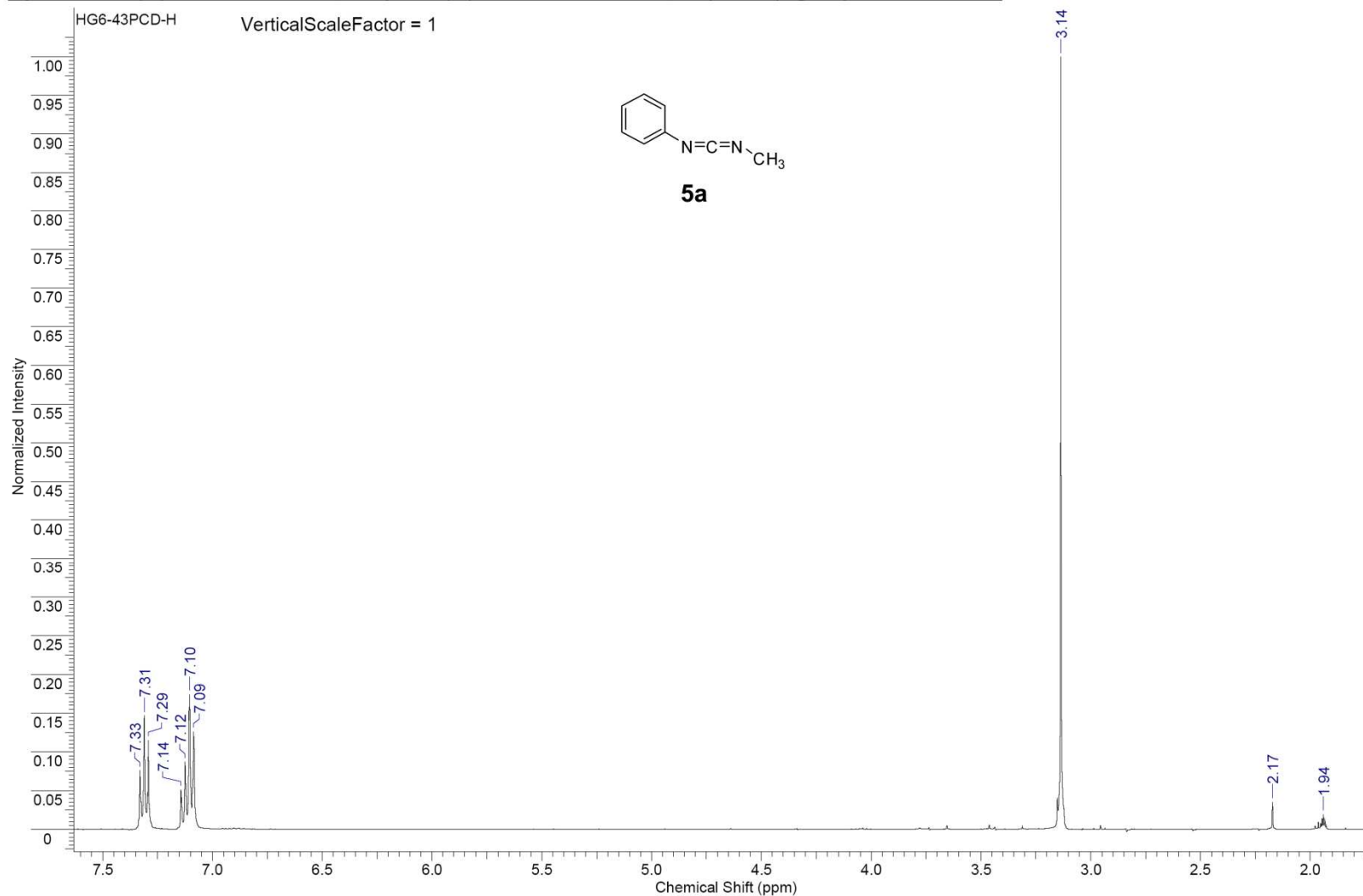
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Nucleus	1H	Number of Transients	32	Original Points Count	13103	Points Count	16384
Pulse Sequence	s2pul	Receiver Gain	56.00	Solvent	ACETONITRILE-d3		
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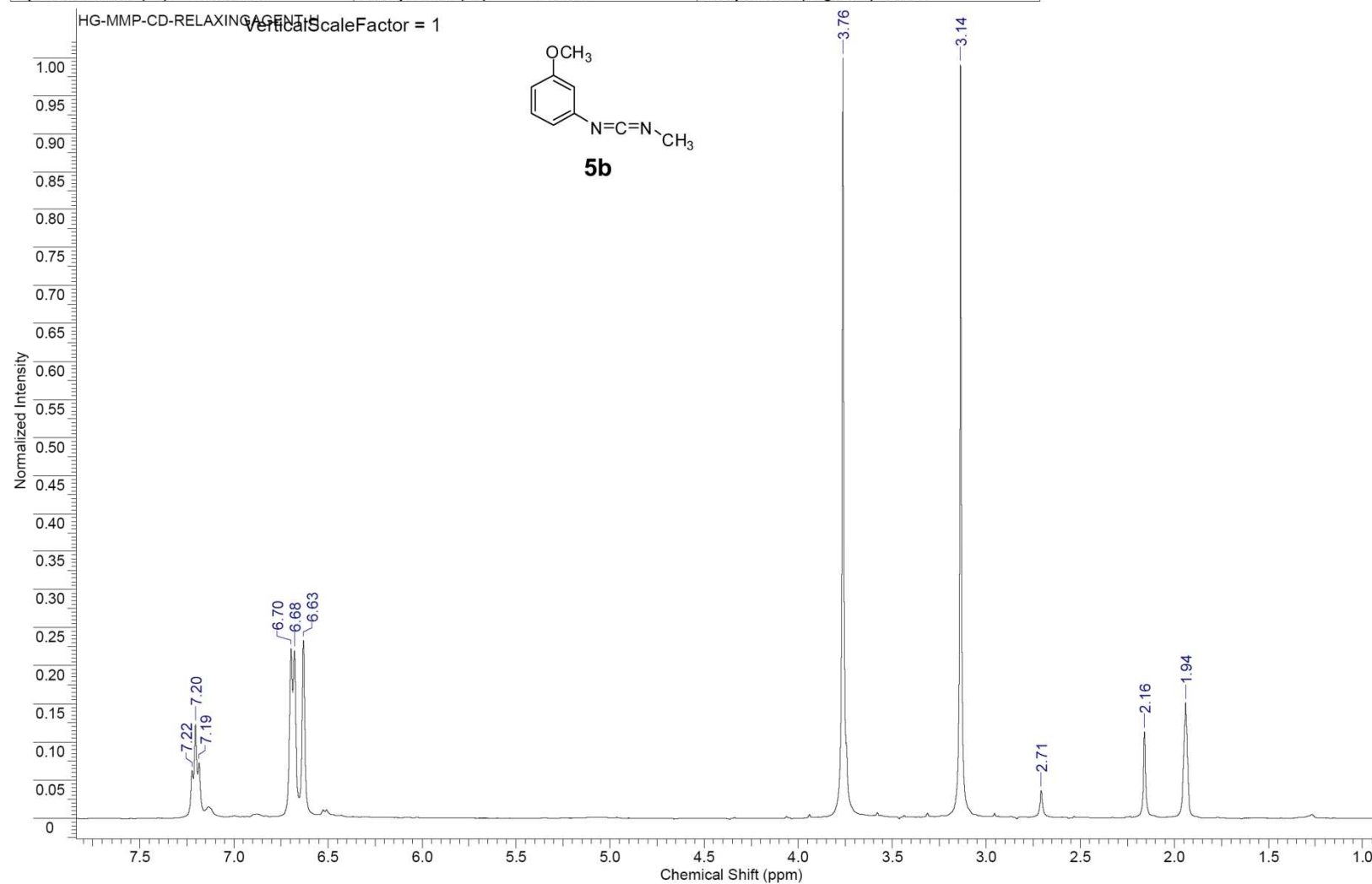
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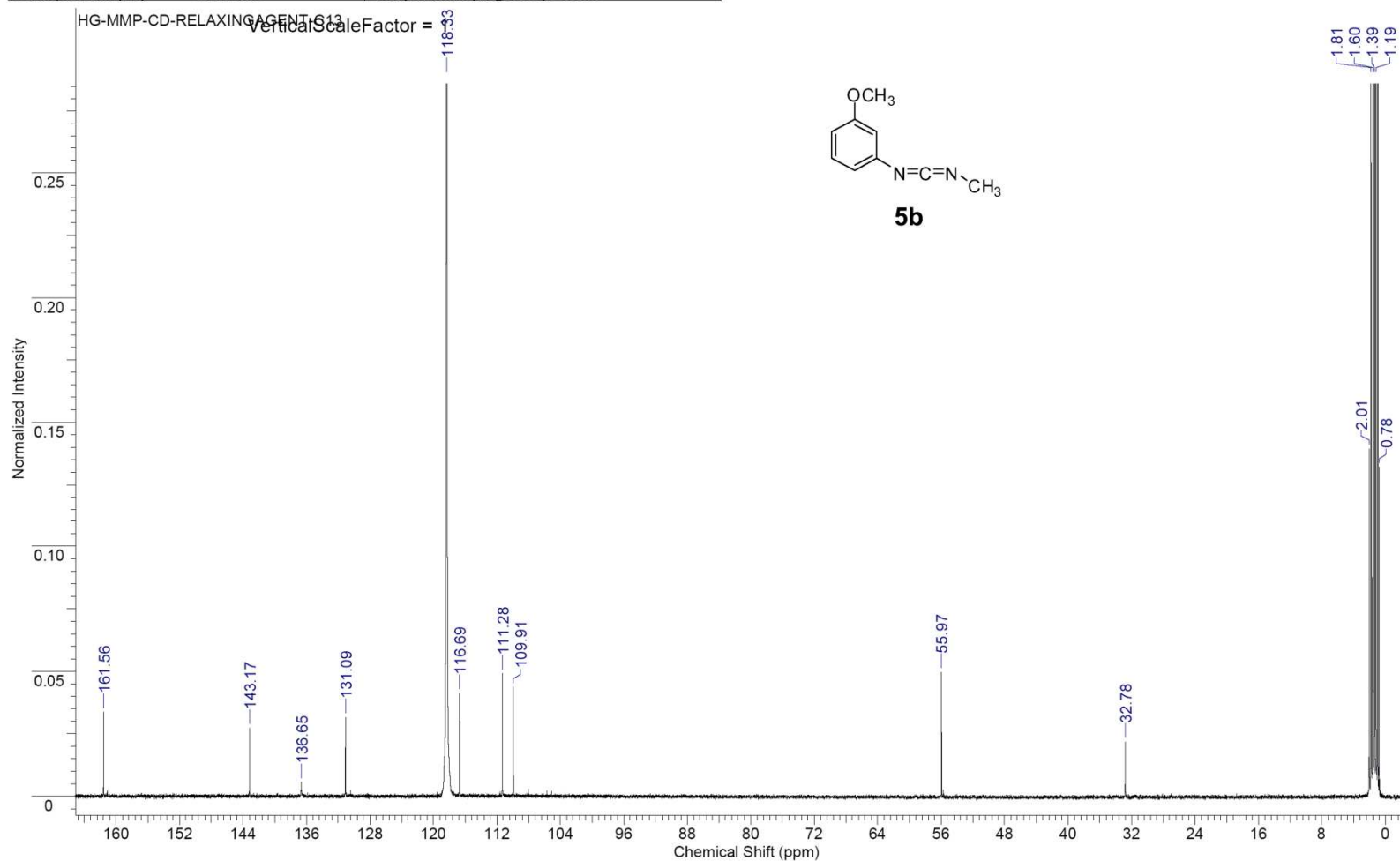
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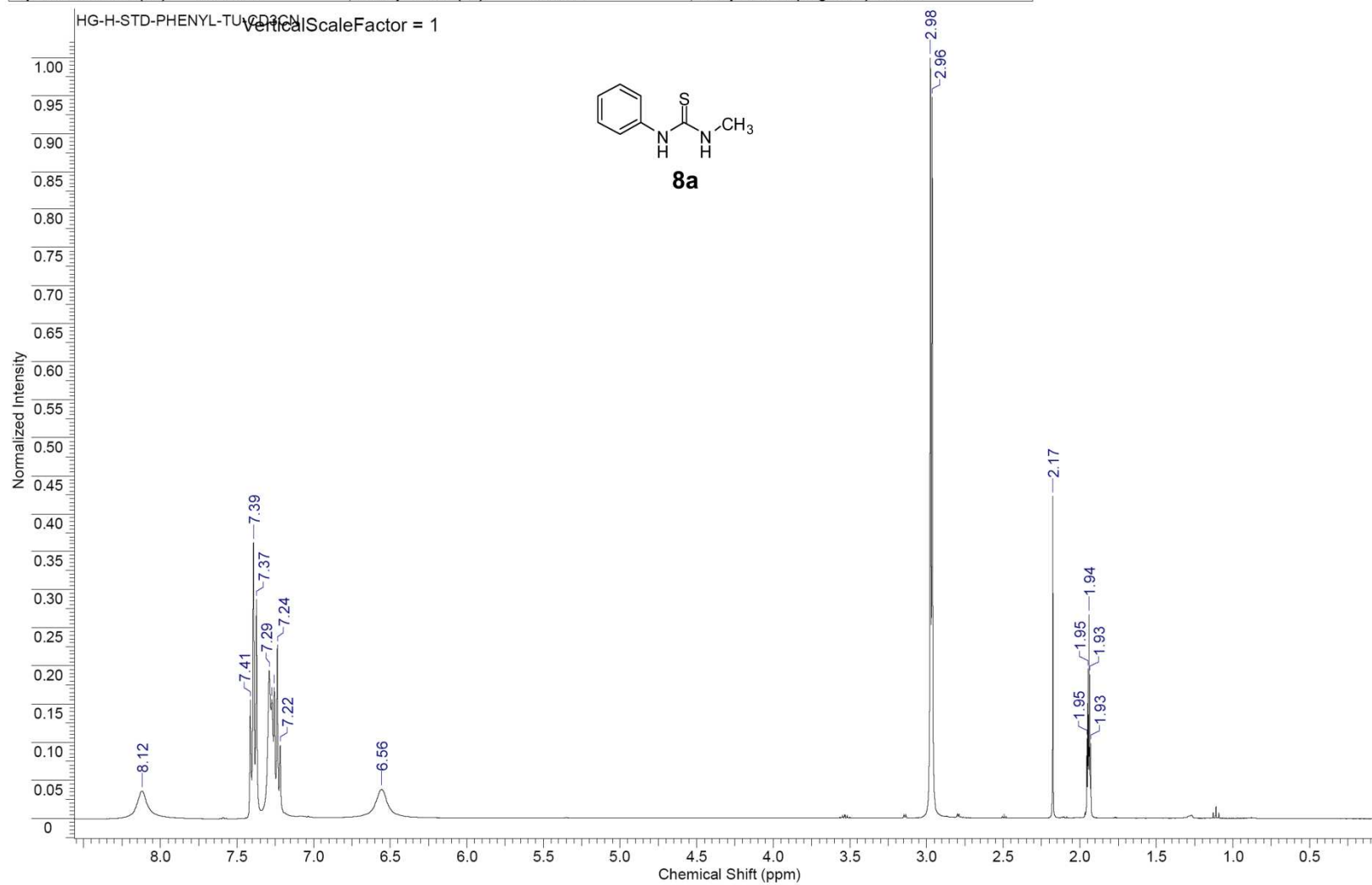
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Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	36.00	Solvent	ACETONITRILE-d3
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Spectrum Offset (Hz)	1798.7549	Sweep Width (Hz)	4399.71	Temperature (degree C)	30.000		



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