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Enhanced Synthesis of oxo-Verdazyl Radicals Bearing Sterically-and Electronically-Diverse C3-Substitents

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Supporting Information

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I. X-ray Crystallography

Table S1. Single crystal X-ray crystallographic data for **1b**, **2b**, **7b, 9b** and **9c**. All data are collected at *T* = 100 K on a XtaLAB Synergy diffractometer using Cu *K*α radiation.

	1b	**2b**	**7b**	**9b**	**9c**
Chemical formula	$C_{19}H_{22}N_4O_3$	$C_{19}H_{22}N_4O_3$	$C_{19}H_{22}N_4O$	$C_{15}H_{16}N_6O$	$C_9H_{13}N_5O$
M_r	354.40	354.40	322.40	296.34	207.24
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, *Pbca*	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
Temperature (K)	100	100	100	100	100
a, *b*, *c* (Å)	8.5045 (3), 9.7970 (4), 11.9453 (5)	10.9788 (1), 14.7369 (1), 22.0879 (2)	7.5570 (2), 9.8051 (3), 12.9529 (3)	11.4529 (3), 10.4903 (3), 12.3136 (3)	19.7981 (3), 7.6021 (1), 16.1604 (3)
α, *β*, γ (°)	108.084 (4), 100.023 (3), 101.754 (3)	90, 90, 90	103.486 (2), 91.205 (2), 111.252 (2)	90 98.940 (2), 90	90, 124.601 (2), 90
V (Å^3)	895.65 (7)	3573.68 (5)	863.92 (4)	1461.44 (7)	2002.05 (7)
Z	2	8	2	4	8
Radiation type	Cu *K*α	Cu *K*α	Cu *K*α	Cu *K*α	Cu *K*α
μ (mm^{-1})	0.74	0.75	0.63	0.74	0.79
Crystal	Clear, colourless block	Clear, colourless block	Clear, colourless plate	Clear, colourless block	Clear, colourless block
Crystal size (mm)	0.16 × 0.09 × 0.06	0.19 × 0.16 × 0.13	0.12 × 0.06 × 0.04	0.21 × 0.19 × 0.08	0.19 × 0.17 × 0.11
Diffractometer	XtaLab Synergy S	XtaLab Synergy S	XtaLab Synergy S	XtaLab Synergy S	XtaLab Synergy S
Absorption correction	Multi-scan (CrysAlis Pro)	Gaussian (CrysAlis Pro)	Multi-scan (CrysAlis Pro)	Multi-scan (CrysAlis Pro)	Multi-scan (CrysAlis Pro)
T_{min}, T_{max}	0.498, 1.000	0.804, 1.000	0.806, 1.000	0.538, 0.681	0.683, 1.000
No. of measured, independent and observed reflections	31657, 3558, 2984	31632, 3642, 3296	30689, 3408, 2965	25448, 2957, 2593	28970, 2042, 1937
R_{int}	0.126	0.042	0.043	0.101	0.064
θ_{max}	73.0	75.6	74.7	74.7	74.0
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.628	0.628	0.627	0.630	0.628
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.067, 0.201, 1.07	0.033, 0.085, 1.06	0.039, 0.097, 1.05	0.065, 0.210, 1.12	0.039, 0.105, 1.08
No. of reflections	3558	3642	3408	2957	2042
No. of parameters	239	0	221	202	139
No. of restraints	0.067, 0.201, 1.07	0	0	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, -0.48	0.19, −0.21	0.19, -0.18	0.41, -0.42	0.28, -0.28

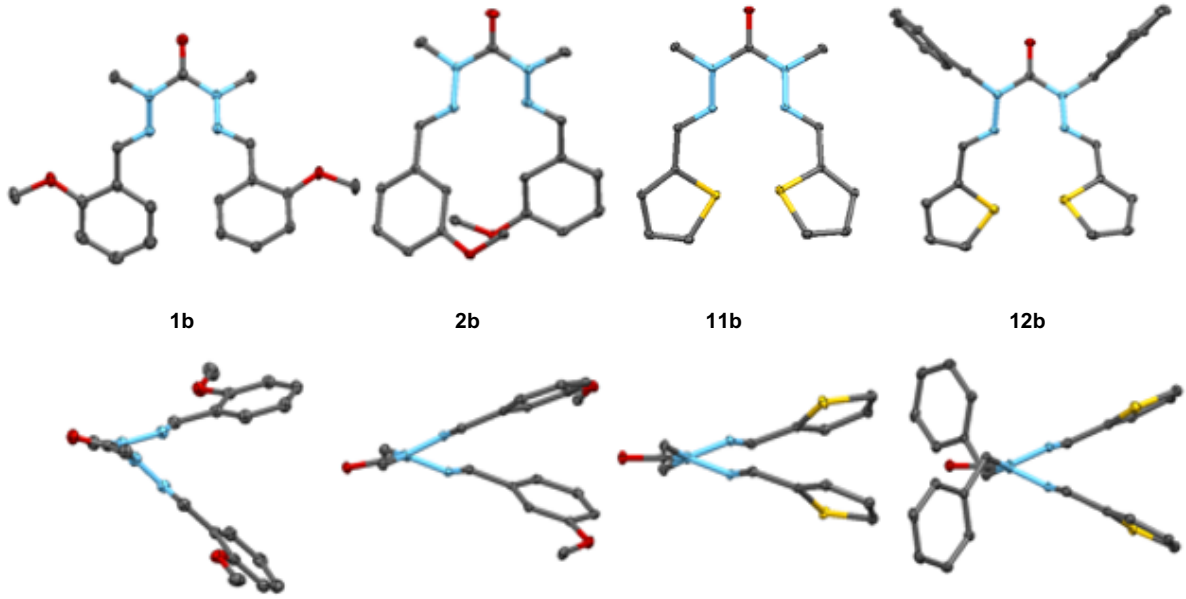
Computer programs: *CrysAlis PRO* 1.171.41.104a (Rigaku OD, 2021), SHELXT 2018/2 (Sheldrick, 2018), *SHELXL* 2018/3 (Sheldrick, 2015), Olex2 1.5 (Dolomanov *et al.*, 2009).

Table S2. Single crystal X-ray crystallographic data for 1**1b**, 1**2b**, **12c** and **13c**. All data are collected at *T* = 100 K on a XtaLAB Synergy diffractometer using Cu *K*α radiation.

	11b	**12b**	**12c**	**13c**
Chemical formula	$C_{13}H_{14}N_4OS_2$	$C_{25}H_{22}N_4OS_2$	$C_{20}H_{22}N_4OS{\cdot}H_2O$	$C_8H_{11}N_5O_3S$
M_r	306.40	458.58	382.49	257.28
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Orthorhombic, *Pnma*	Monoclinic, $P2_1/c$
Temperature (K)	100	100	100	100
a, *b*, *c* (Å)	7.3232 (1), 19.6029 (2), 10.4905 (2)	18.9089 (3), 11.6130 (2), 10.5619 (2)	4.9308 (1), 19.1358 (5), 20.4329 (5)	8.7388 (1), 8.7377 (1), 15.3935 (3)
α, *β*, γ (°)	90, 107.845 (2), 90	90, 90.812 (2), 90	90, 90, 90	90, 105.809 (2), 90
V (Å^3)	1433.52 (4)	2319.05 (7)	1927.94 (8)	1130.94 (3)
Z	4	4	4	4
Radiation type	Cu *K*α	Cu *K*α	Cu *K*α	Cu *K*α
μ (mm^{-1})	3.38	2.28	1.68	2.64
Crystal	Clear, colourless block	Clear, colourless block	Clear, colourless needle	Clear, colourless block
Crystal size (mm)	0.26 × 0.12 × 0.09	0.35 × 0.24 × 0.18	0.29 × 0.05 × 0.03	0.03 × 0.03 × 0.03
Diffractometer	XtaLab Synergy S	XtaLab Synergy S	XtaLab Synergy S	XtaLab Synergy S
Absorption correction	Multi-scan (CrysAlis Pro)	Multi-scan (CrysAlis Pro)	Multi-scan (CrysAlis Pro)	Multi-scan (CrysAlis Pro)
T_{min}, T_{max}	0.644, 1.000	0.797, 1.000	0.850, 1.000	0.950, 1.000
No. of measured, independent and observed reflections	21491, 1468, 1426	10618, 2302, 2154	13320, 1736, 1534	20676, 2293, 2078
R_{int}	0.075	0.030	0.070	0.053
θ_{max}	75.1	74.9	67.3	73.1
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.628	0.628	0.598	0.627
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.032, 0.123, 1.14	0.033, 0.094, 1.06	0.136, 0.265, 1.28	0.050, 0.134, 1.09
No. of reflections	1468	2302	1736	2293
No. of parameters	93	146	121	156
No. of restraints	0	0	30	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, -0.39	0.32, −0.26	0.58, −0.40	0.89, -0.80

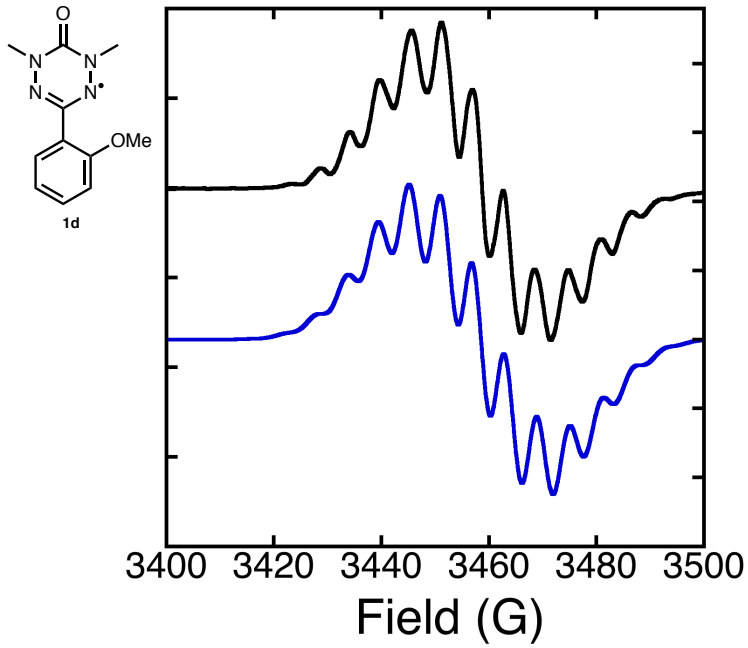
Computer programs: *CrysAlis PRO* 1.171.41.104a (Rigaku OD, 2021), SHELXT 2018/2 (Sheldrick, 2018), *SHELXL* 2018/3 (Sheldrick, 2015), Olex2 1.5 (Dolomanov *et al.*, 2009).

Fig. S1: Structural representations of **1b**, **2b**, **11b** and **12b**. Thermal ellipsoids are set to 30 % probability. Nitrogen (blue); oxygen (red), carbon (grey) For clarity, hydrogen atoms and lattice solvent are omitted. Displacement of the ring systems are highlighted when looking side on to the N1-C6-N5 plane (lower). Centroids have been used to measure the distance from the ring system to the N1-C6-N5 plane. **1b** 2.425 Å and 2.108 Å; **2b** 0.661 Å and 2.348 Å; **9b** 2.285 Å and 1.525 Å (Fig. 6); **11b** 1.322 Å and 1.322 Å; **12b** 1.487 Å and 1.844 Å. Values are given for the orientation shown below, with the above the plane distance is reported first.



II. EPR spectra

Fig. S2: The first derivative X-band (CW) EPR spectrum (ν =9.696 GHz) of 1,5-dimethyl-3-(2-methoxyphenyl)-6-oxoverdazyl (**1d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 10 mW (18 dB attenuation) was used. The spectroscopic data matched previously reported [1]



[1] F. A. Neugebauer, H. Fischer and R. Siegel Chem. Ber. 121 815-822 1988

Fig. S3: The first derivative X-band (CW) EPR spectrum (ν =9.691 GHz) of 1,5-dimethyl-3-(3-methoxyphenyl)-6-oxoverdazyl (**2d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 10 mW (18 dB attenuation) was used.

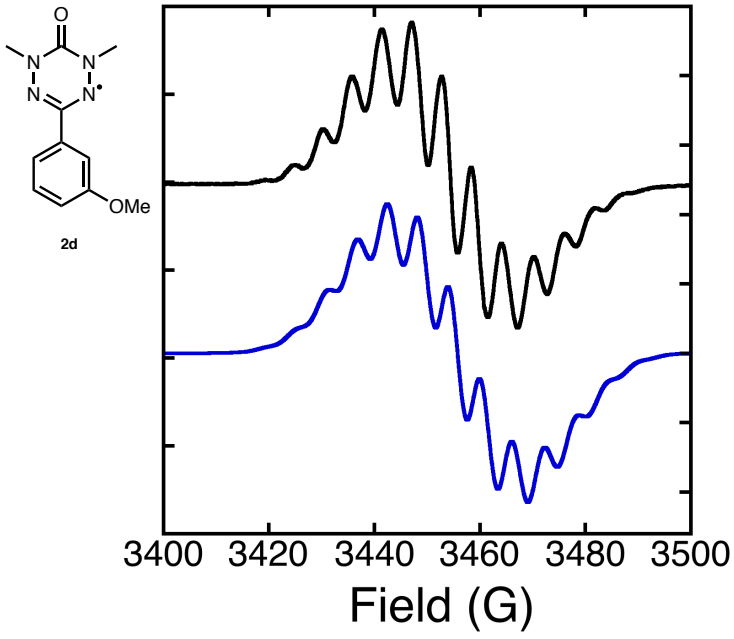
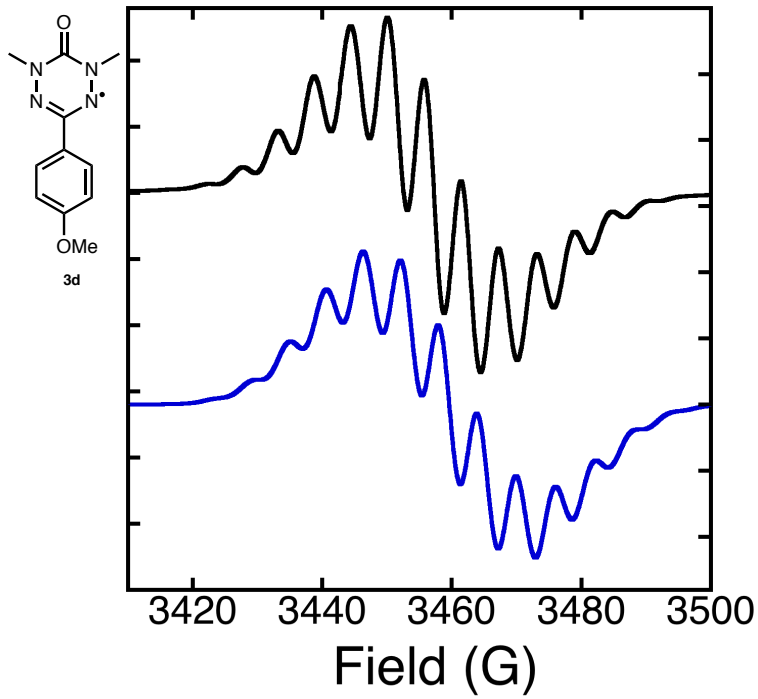


Fig. S4: The first derivative X-band (CW) EPR spectrum (ν =9.699 GHz) of 1,5-dimethyl-3-(4-methoxyphenyl)-6-oxoverdazyl (**3d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 10 mW (12 dB attenuation) was used. Matched previously reported spectra [2].



[2] F. A. Neugebauer, H. Fischer, R. Siegel and C. Krieger, Chem. Ber. ***116,*** *3461-3481 (1983);*

Fig. S5: The first derivative X-band (CW) EPR spectrum (ν =9.688 GHz) of 1,5-dimethyl-3-(2-trifluoromethylphenyl)-6-oxoverdazyl (**4d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 3 mW (18 dB attenuation) was used.

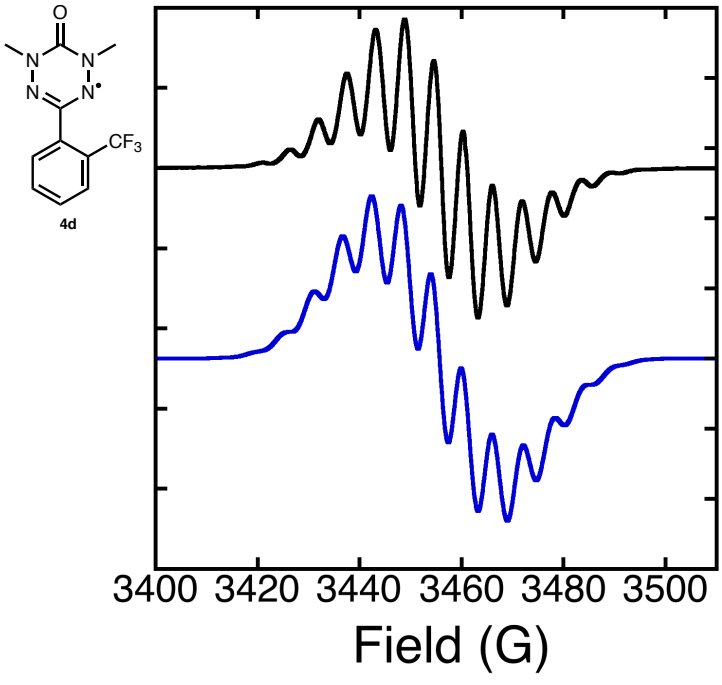


Fig. S6: he first derivative X-band (CW) EPR spectrum (ν =9.682 GHz) of 1,5-dimethyl-3-(3-trifluoromethylphenyl)-6-oxoverdazyl (**5d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 6 mW (12 dB attenuation) was used.

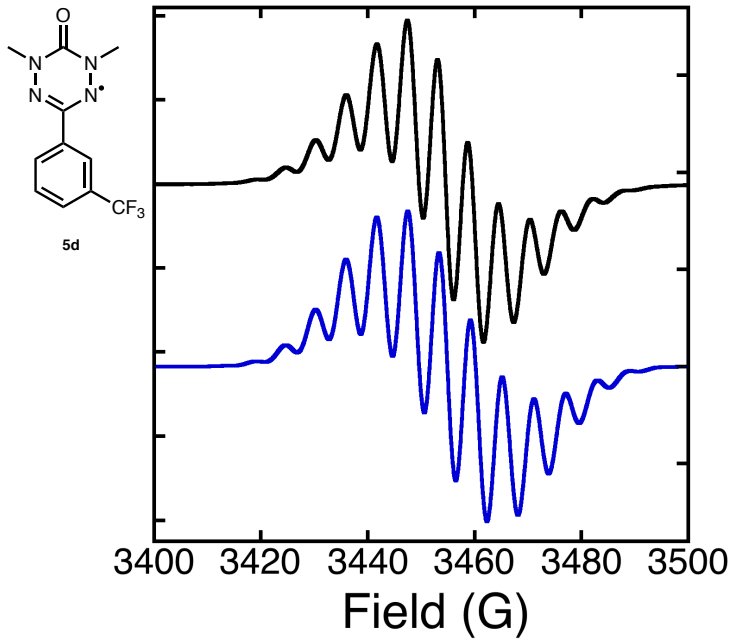


Fig. S7: The first derivative X-band (CW) EPR spectrum (ν =9.695 GHz) of 1,5-dimethyl-3-(4-trifluoromethylphenyl)-6-oxoverdazyl (**6d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 6 mW (12 dB attenuation) was used.

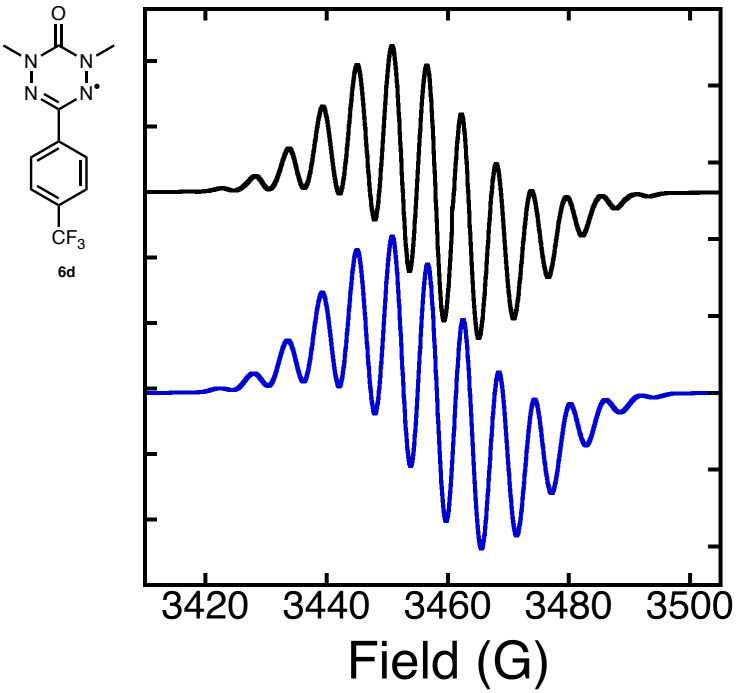


Fig. S8: The first derivative X-band (CW) EPR spectrum (ν =9.687 GHz) of 1,5-dimethyl-3-(2-methylphenyl)-6-oxoverdazyl (**7d**) in degassed chloroform at 298 K (blue trace) together with simulation (black trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 10 mW (18 dB attenuation) was used. Matched previously reported spectra [2].

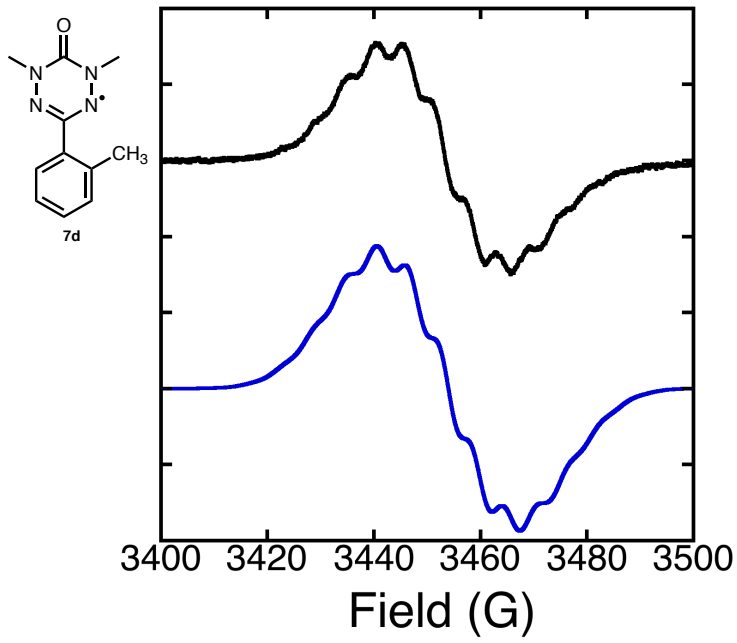


Fig. S9: The first derivative X-band (CW) EPR spectrum (ν =9.669 GHz) of 1,5-dimethyl-3-(2-nitrobenzyl)-6-oxoverdazyl (**8d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 8 mW (18 dB attenuation) was used.

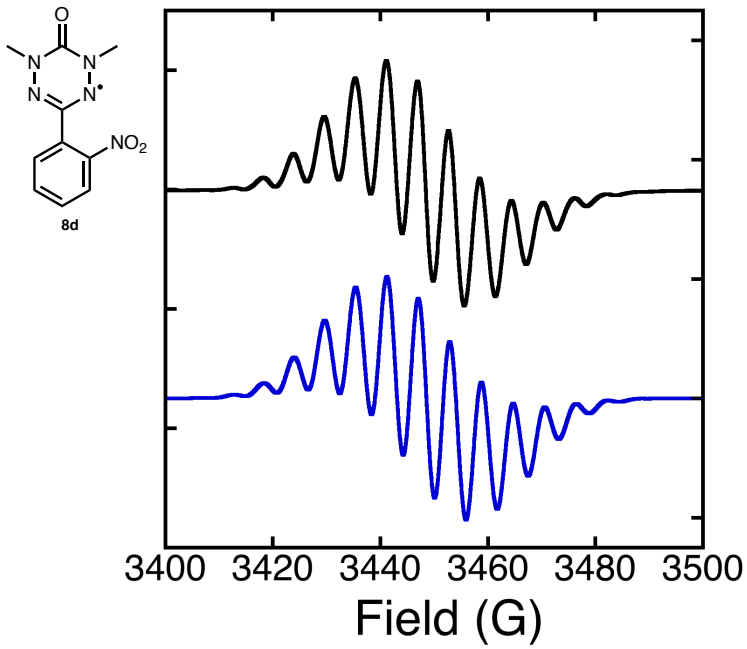
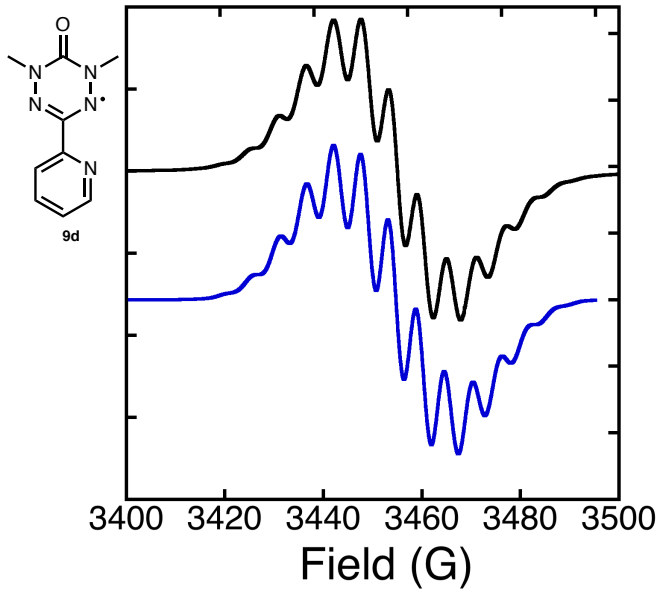


Fig. S10: The first derivative X-band (CW) EPR spectrum (ν =9.693 GHz) of 1,5-dimethyl-3-(2-pyridine)-6-oxoverdazyl (**9d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 6 mW (12 dB attenuation) was used. The spectroscopic data matched previously reported [3].



[3] C. L. Barr., P. A. Chase, R. G. Hicks, M. T. Lemaire and C. L. Stevens, *J. Org. Chem.,* **1999,** *64,* 8893-8897.

Fig. S11: The first derivative X-band (CW) EPR spectrum (ν =9.691 GHz) of 1,5-dimethyl-3-(2-methoxy-4-trifluoromethylphenyl)-6-oxoverdazyl (**10d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 10 mW (18 dB attenuation) was used.

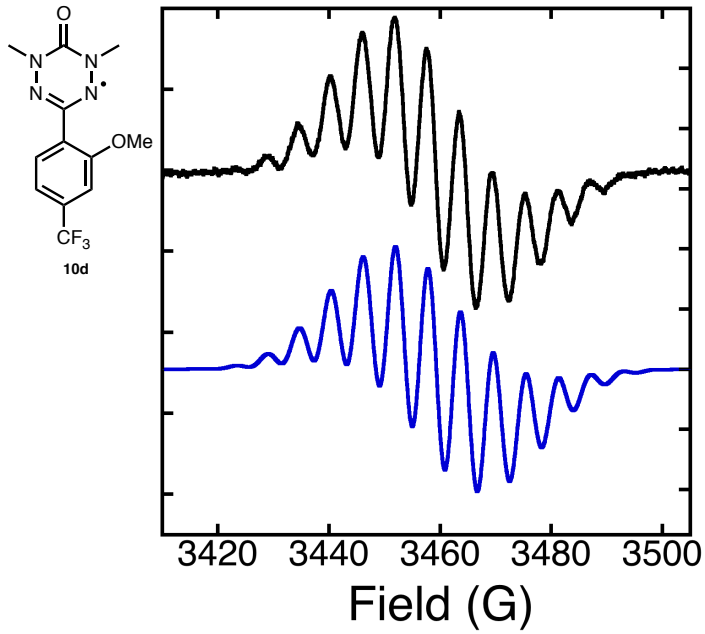


Fig. S12: The first derivative X-band (CW) EPR spectrum (ν =9.686 GHz) of 1,5-dimethyl-3-(2-thiophene)-6-oxoverdazyl (**11d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 2 G and power of 6 mW (12 dB attenuation) was used.

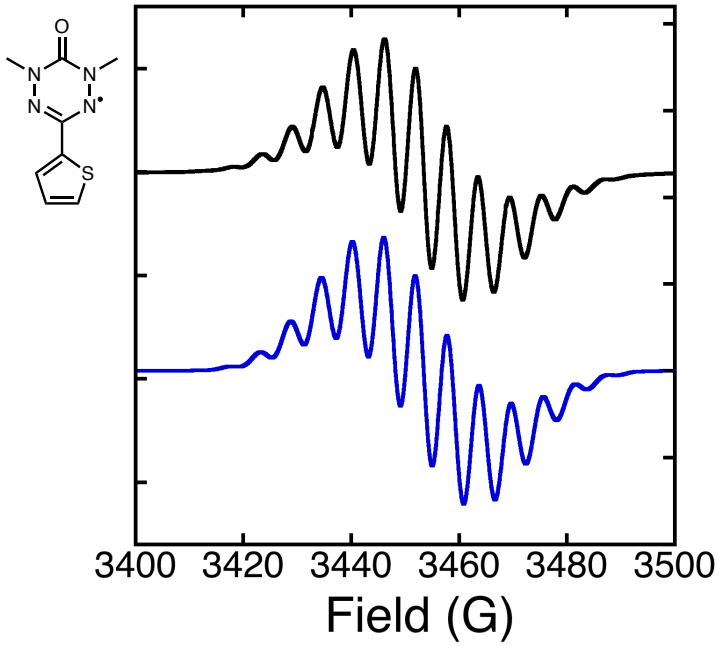


Table S3. Linewidths (lw) and g -value (g) for the EPR simulations shown in Fig. S2-S12. Spectra were recorded with a modulation amplitude of 2 G. Simulations used hyperfine coupling constants $a(N_{2,4})$ = 6.5 G (18.2 MHz); $a(N_{1,5})$ = 5.3 G (14.9 MHz); $a(H_{CH})$ = 5.3 G (14.9 MHz) from the hyperfine coupling of the unpaired electron with four nitrogen atoms of the verdazyl ring (^{14}N, I=1 abundance 99.6 %) with six hydrogen atoms (^{1}H, I=1/2, Natural abundance=99.98 %) on the methyl groups.

Entry	g	lw (G)	ν (GHz)
1d	2.0023	0.51	9.696
2d	2.0036	0.52	9.691
3d	2.0044	0.46	9.699
4d	2.0028	0.43	9.688
5d	2.0022	0.43	9.682
6d	2.0031	0.38	9.695
7d	2.0038	0.52	9.687
8d	2.0032	0.40	9.669
9d	2.0043	0.49	9.693
10d	2.0021	0.40	9.694
11d	2.0037	0.44	9.686

Fig. S13: The first derivative X-band (CW) EPR spectrum (ν =9.686 GHz) of 1,5-dimethyl-3-(2-methoxyphenyl)-6-oxoverdazyl (**9d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 0.1 G was used.

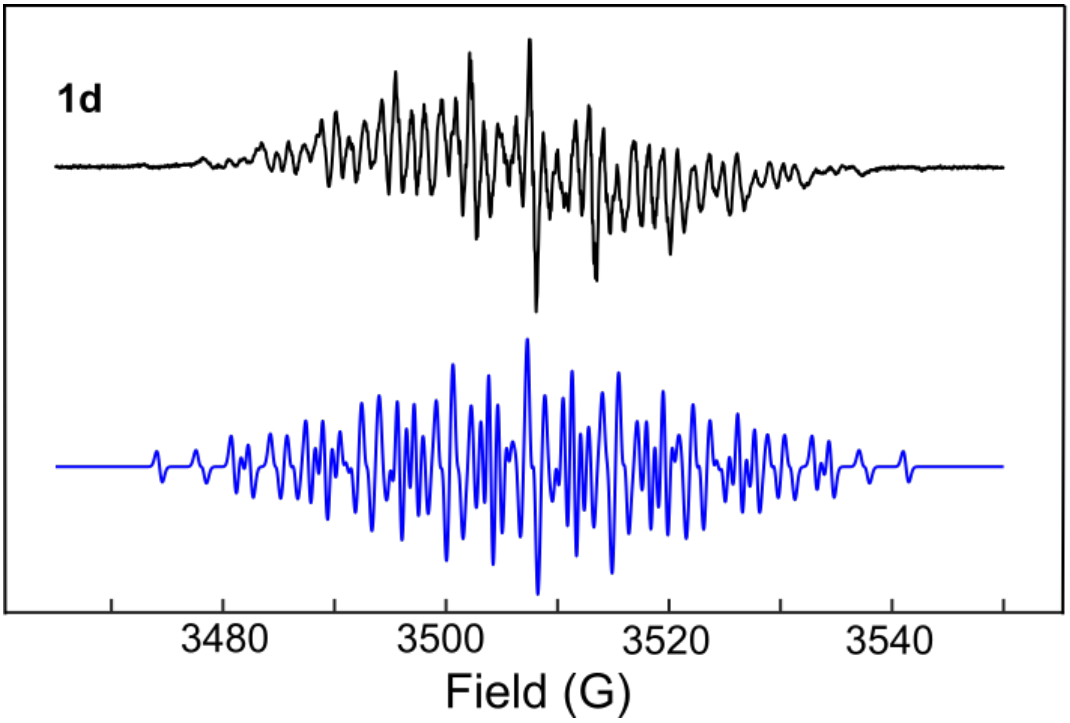


Fig. S14: The first derivative X-band (CW) EPR spectrum (ν =9.686 GHz) of 1,5-dimethyl-3-(2-pyridine)-6-oxoverdazyl (**9d**) in degassed chloroform at 298 K (black trace) together with simulation (blue trace) using EasySpin garlic package in MATLAB. A field modulation of 0.1 G was used.

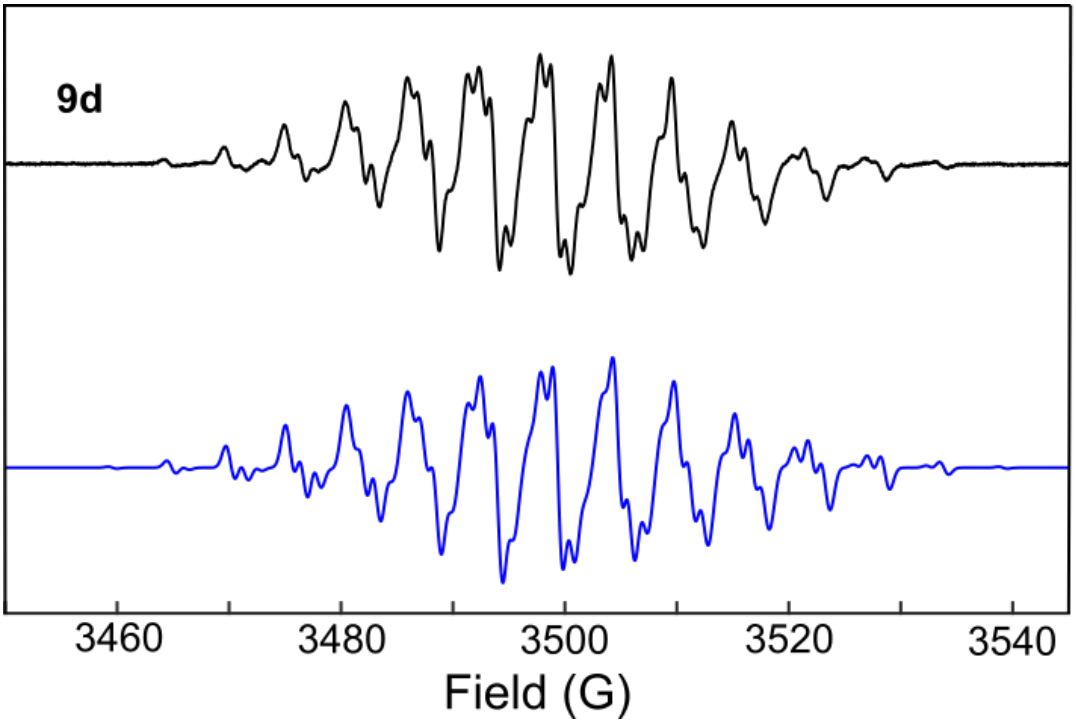


Table S4. Hyperfine (a) and linewidth (lw) fitting parameters for EPR simulations of spectra of **1d, 9d** and **11d,** which were measured degassed with N_2 in chloroform, and recorded with a modulation amplitude of 0.1 G to resolve the narrow features of the hyperfine. (lower) table is reproduced with hyperfine values given in SI units.

	Hyperfine (G)					*lw (G)*
	$a(N_{2,4})$	$a(N_{1,5})$	$a(H_{CH})$	$a(H_{CH})$	$a(H_{CH})$	
1d	6.6	5.3	3.0	-	-	0.6
9d	6.5	5.6	5.2			0.8
11d	6.5	5.3	5.3	5.1	5.0	0.2

	Hyperfine (MHz)					*lw (G)*
	$a(N_{2,4})$	$a(N_{1,5})$	$a(H_{CH})$	$a(H_{CH})$	$a(H_{CH})$	
1d	18.6	14.8	8.4	-	-	0.6
9d	18.2	15.7	14.6			0.8
11d	18.2	14.8	14.9	14.3	14.0	0.2

Table S5. Thin layer Chromatography Rf analysis of the verdazyl and leucoverdazyl compounds. The eluent used in most cases is 100% EtOAc. One exception is compound **9d**, the radical did not elute in 100 % EtOAc, and 1% MeOH in EtOAc was used instead.

	Rf		**Rf**
1d	0.85	**leuco-1d**	0.79
2d	0.82	**leuco-2d**	0.66
3d	0.79	**leuco-3d**	0.68
4d	0.86	**leuco-4d**	0.70
5d	0.86	**leuco-5d**	0.77
6d	0.86	**leuco-6d**	0.78
7d	0.83	**leuco-7d**	0.68
8d	0.86	**leuco-8d**	0.76
9d	0.73	**leuco-9d**	0.63
10d	0.83	**leuco-10d**	0.70
11d	0.85	**leuco-11d**	0.79

III. NMR spectra

Fig. S15: ^{1}H NMR of **1a**

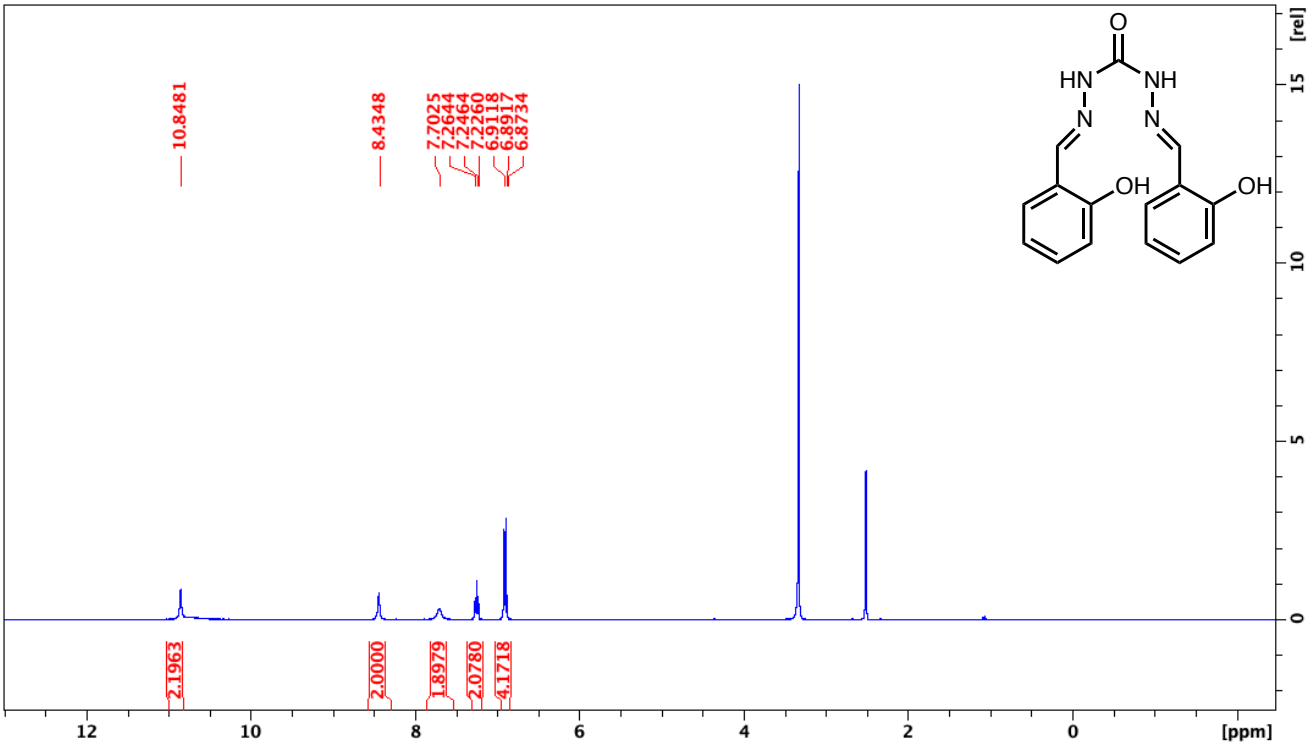


Fig. S16: ^{13}C NMR of **1a**

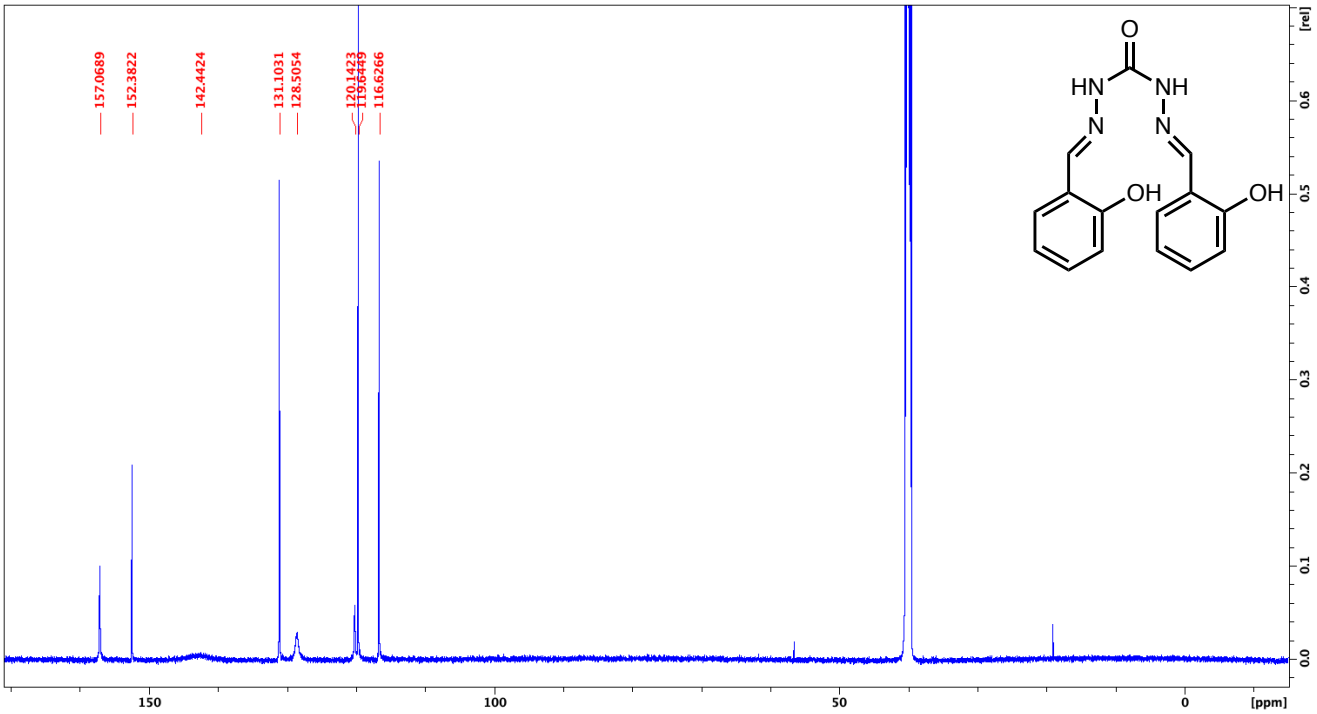


Fig. S17: ^{1}H NMR of **1b**

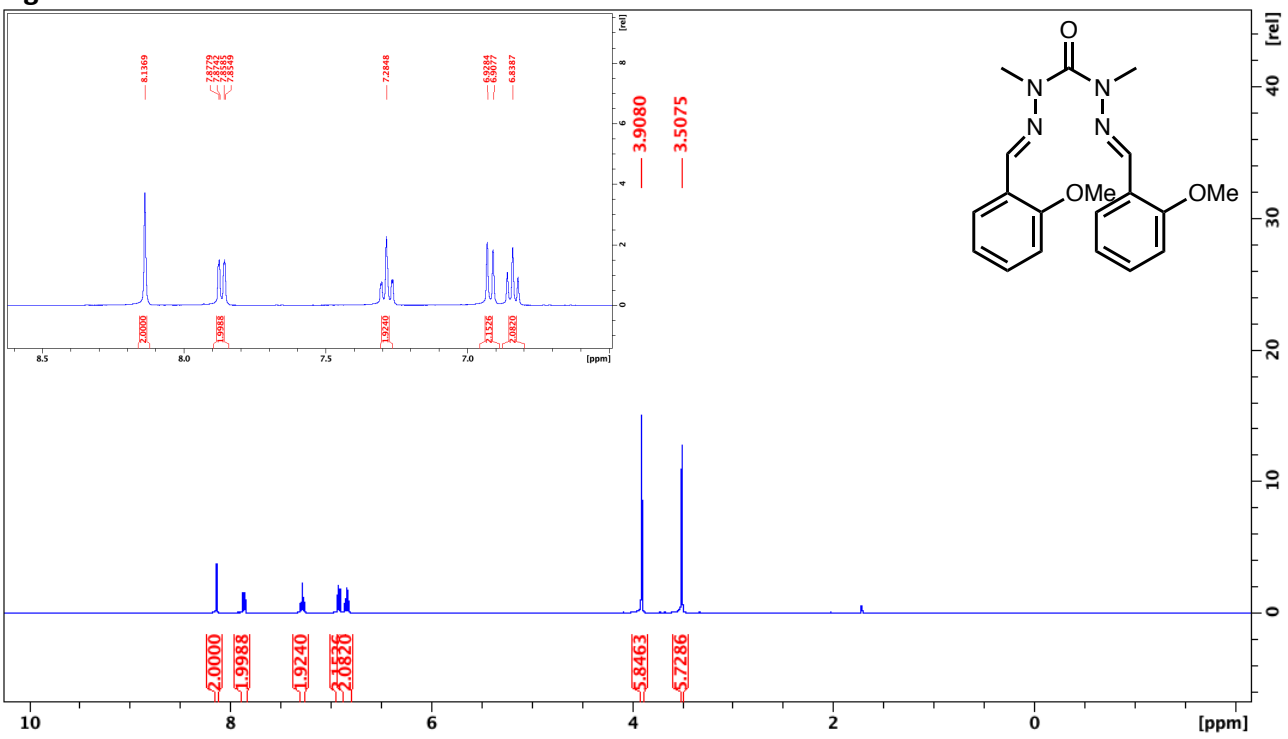


Fig. S18: ^{13}C NMR of **1b**

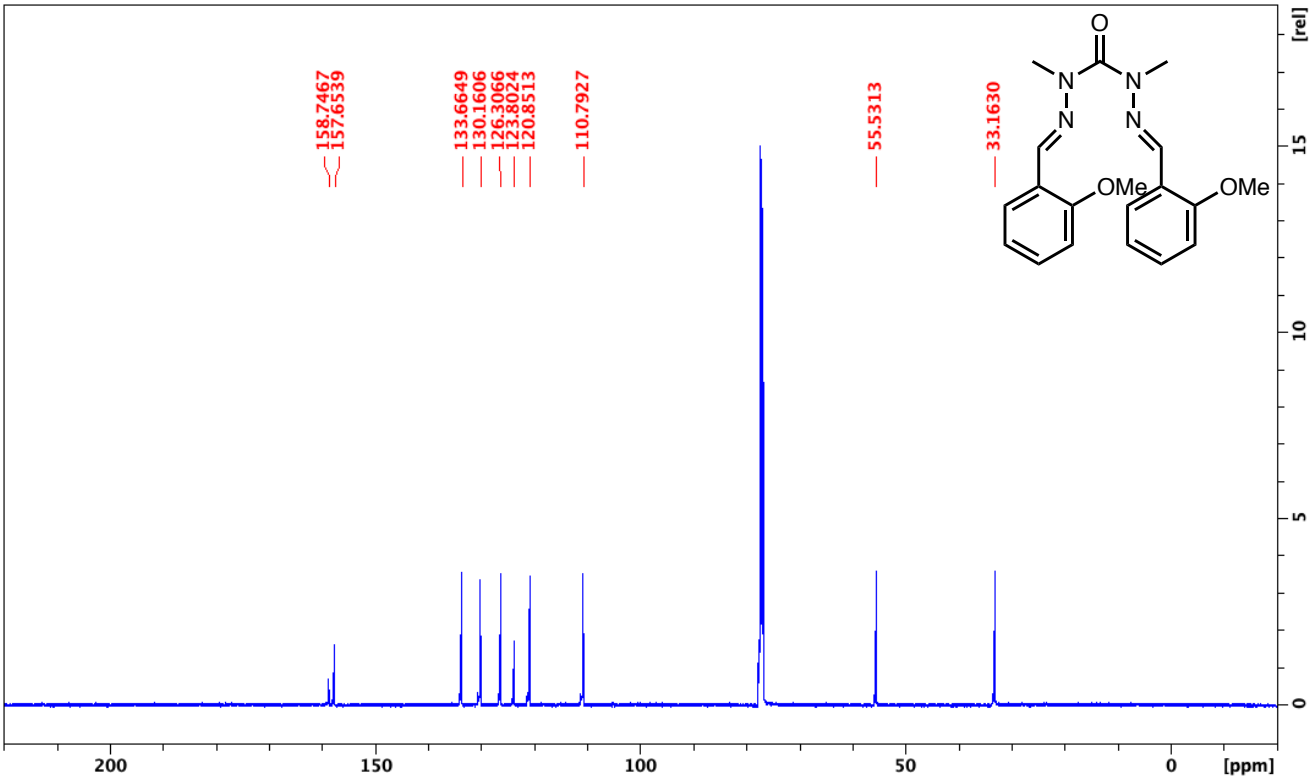
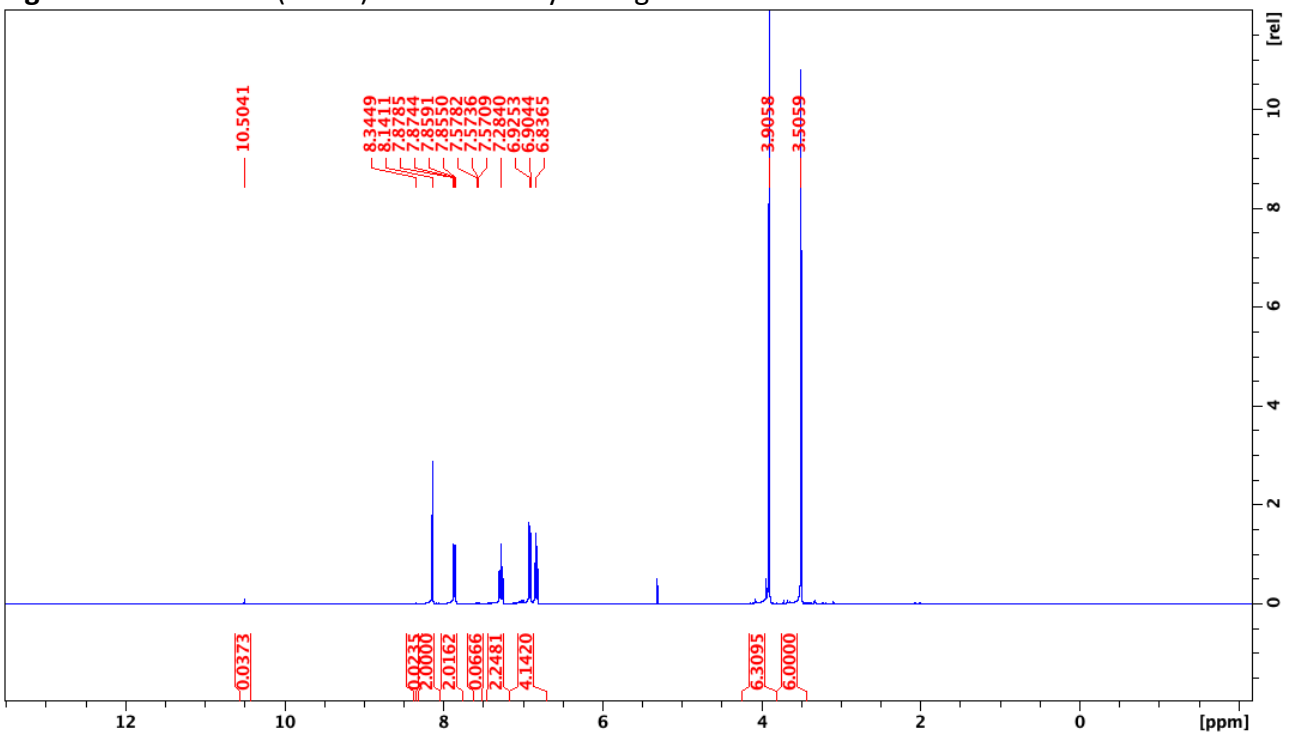
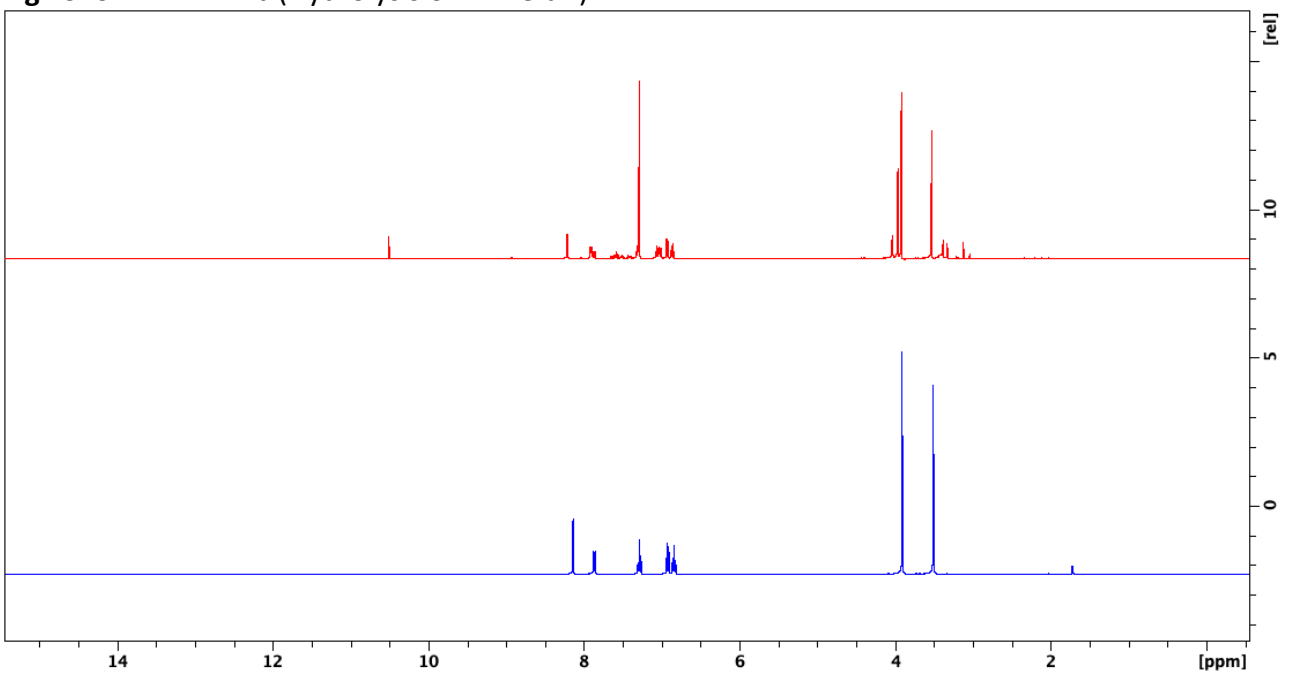


Fig. S19: ^{1}H NMR **1b** (crude) - used directly in ring closure



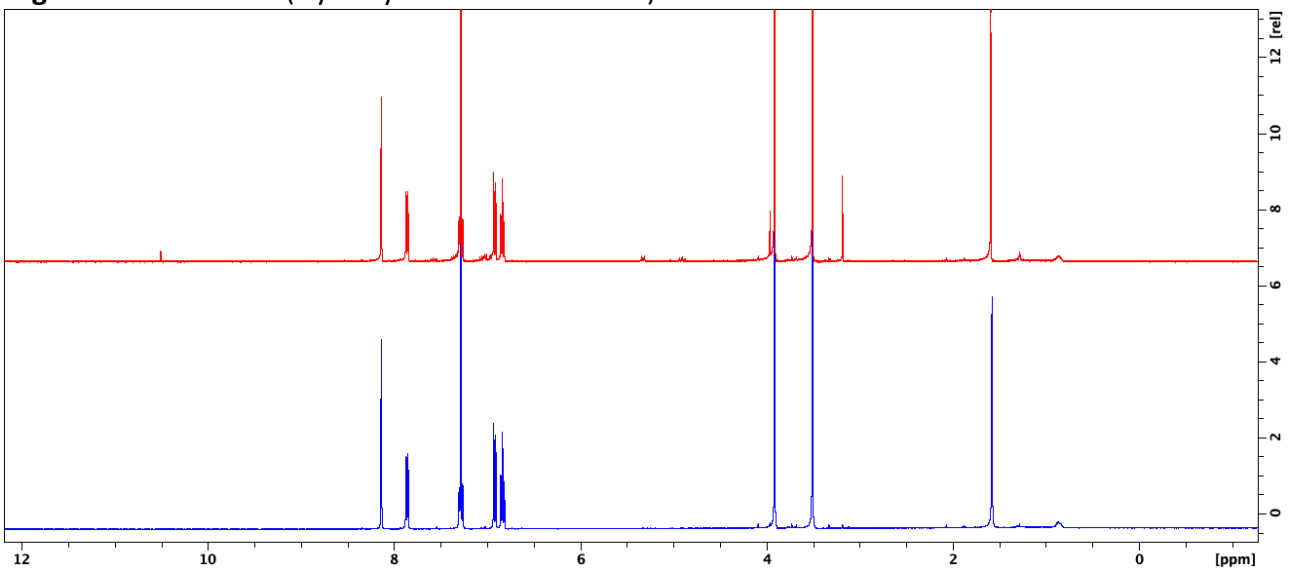
*The crude **1b** contains a small amount of the monomethylated product and can be used directly in the synthesis of **1c** with little impact on the yield.*

Fig. S20: ^{1}H NMR **1b** (Hydrolysis of imine-air)



*Spectrum of **1b** crystals (lower trace) on the day of collection; (upper trace) crystals two months later after storage in air.*

Fig. S21: ^{1}H NMR **1b** (Hydrolysis of imine-solvent)



*Spectrum of in wet $CDCl_3$ **1b** (lower trace) and remeasured after 3 days **1b** (lower trace) ;*

Fig. S22: ^{1}H NMR of **1c**

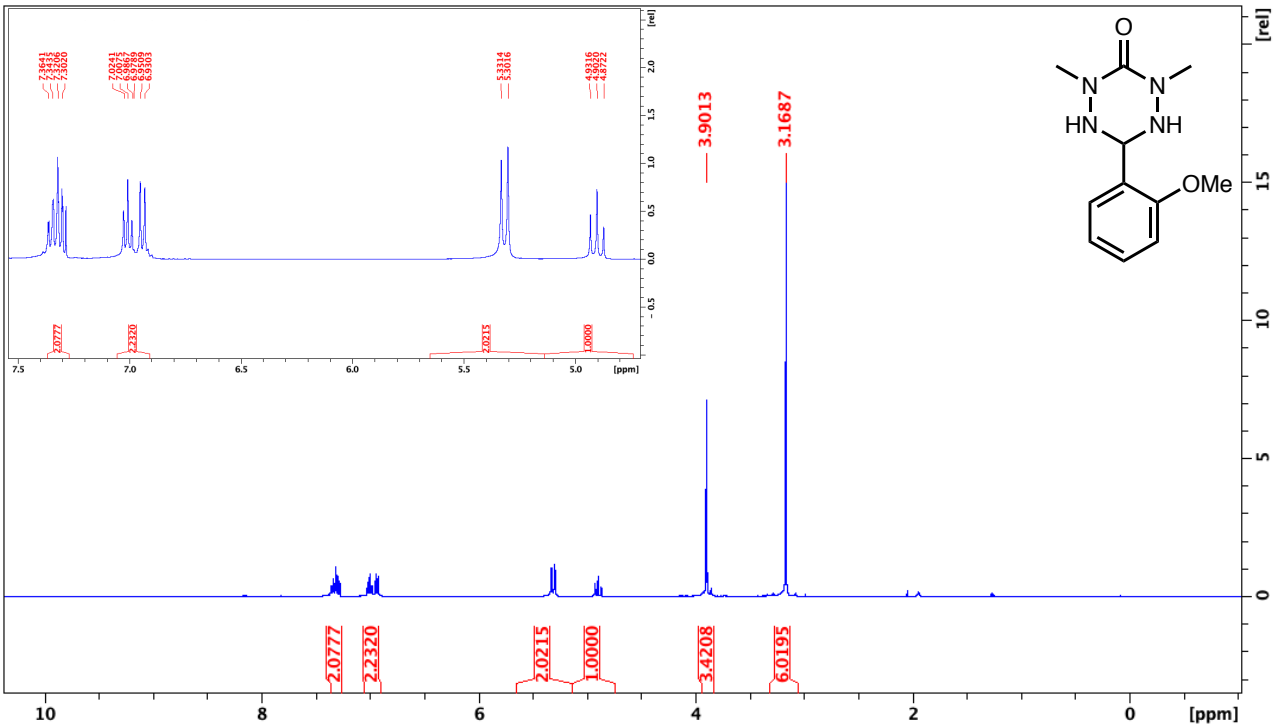


Fig. S23: ^{13}C NMR of **1c**

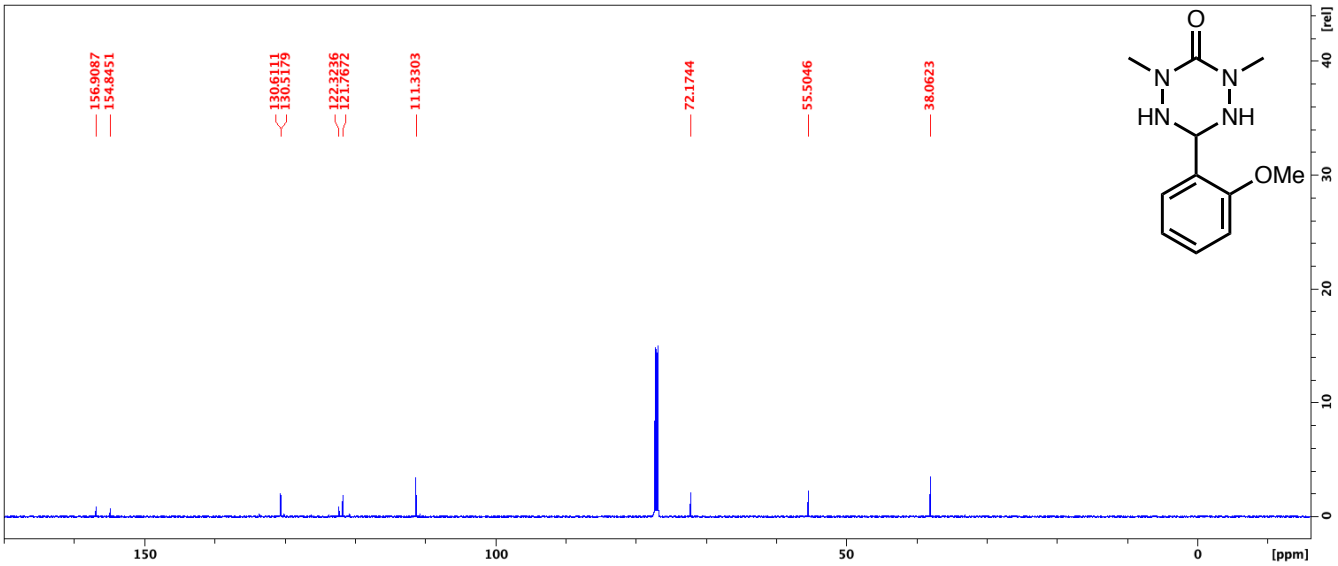


Fig. S24: ^{1}H NMR of **2a**

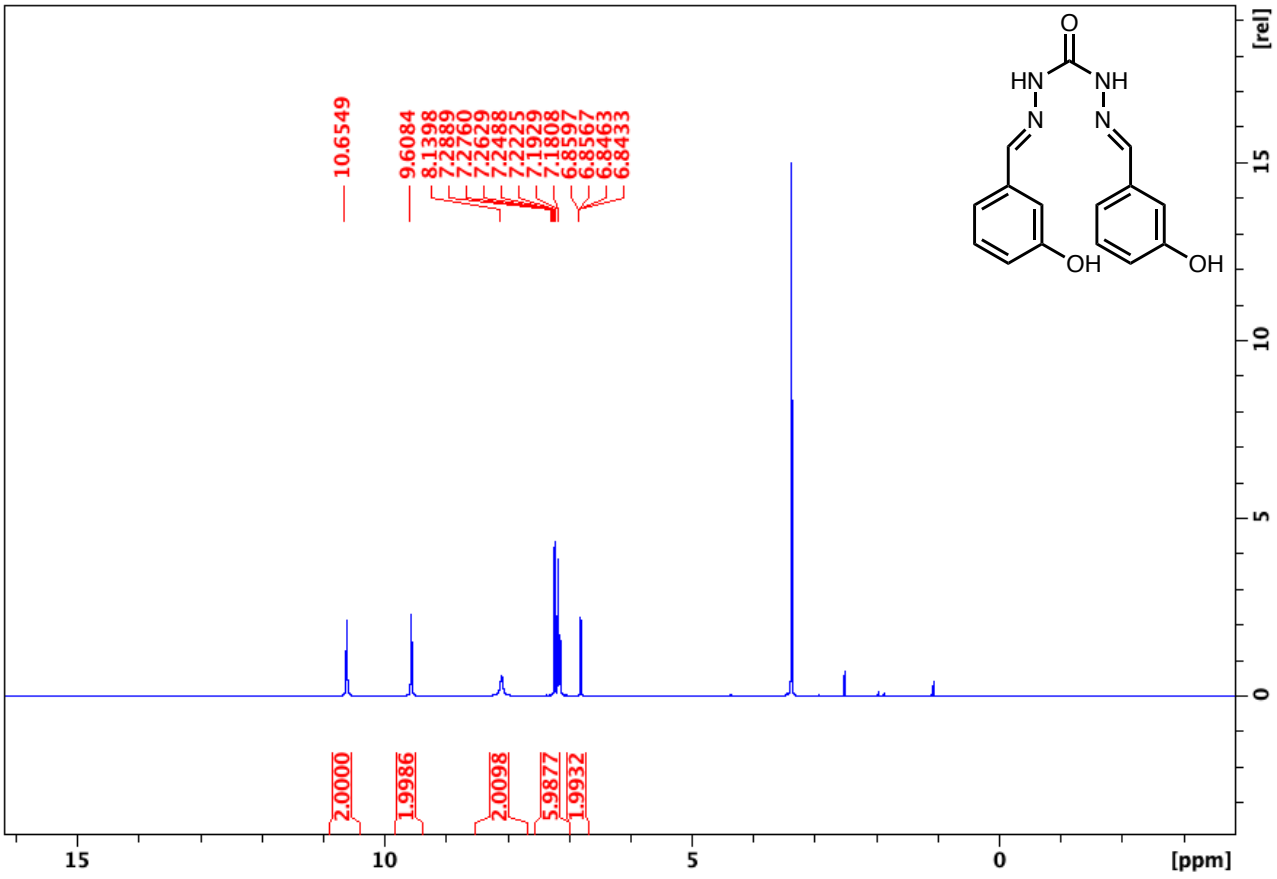


Fig. S25: ^{13}C NMR of **2a**

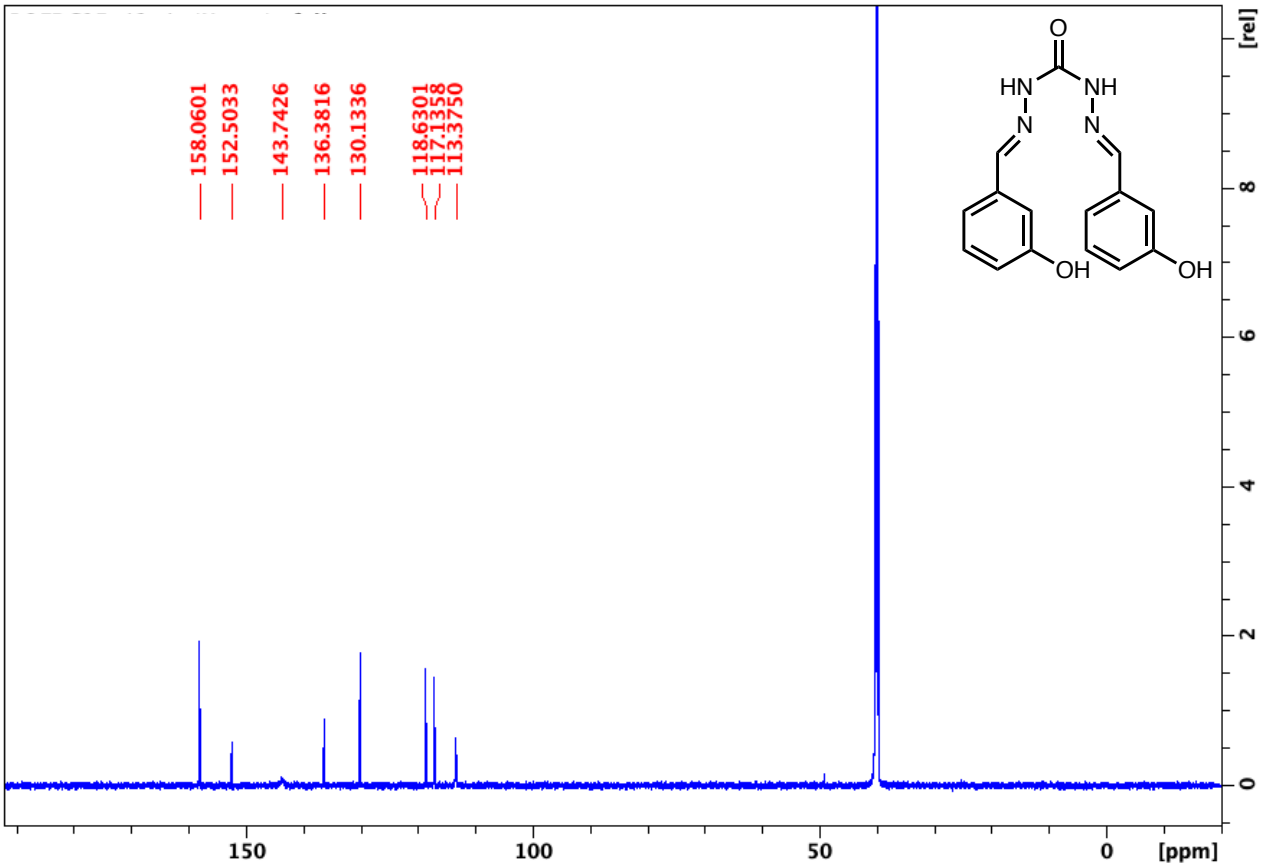


Fig. S26: ^{1}H NMR of **2b**

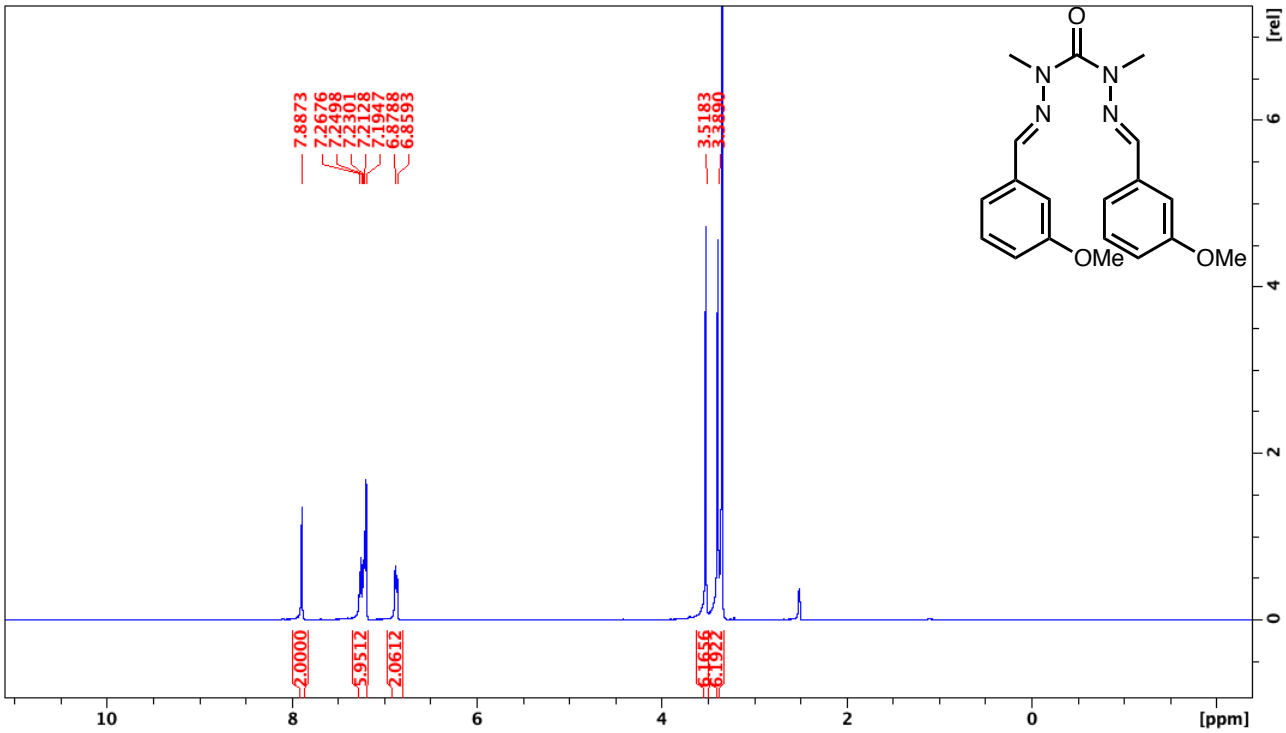


Fig. S27: ^{13}C NMR of **2b**

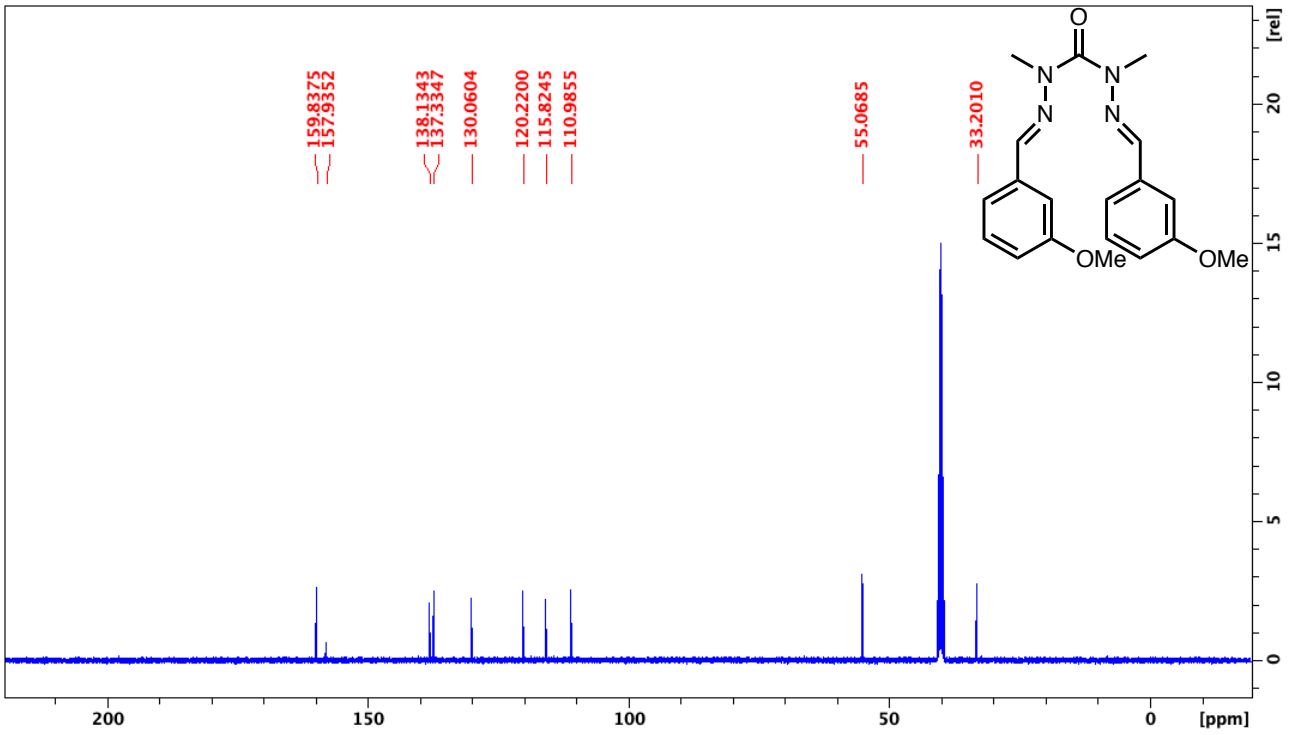


Fig. S28: ^{1}H NMR of **2c**

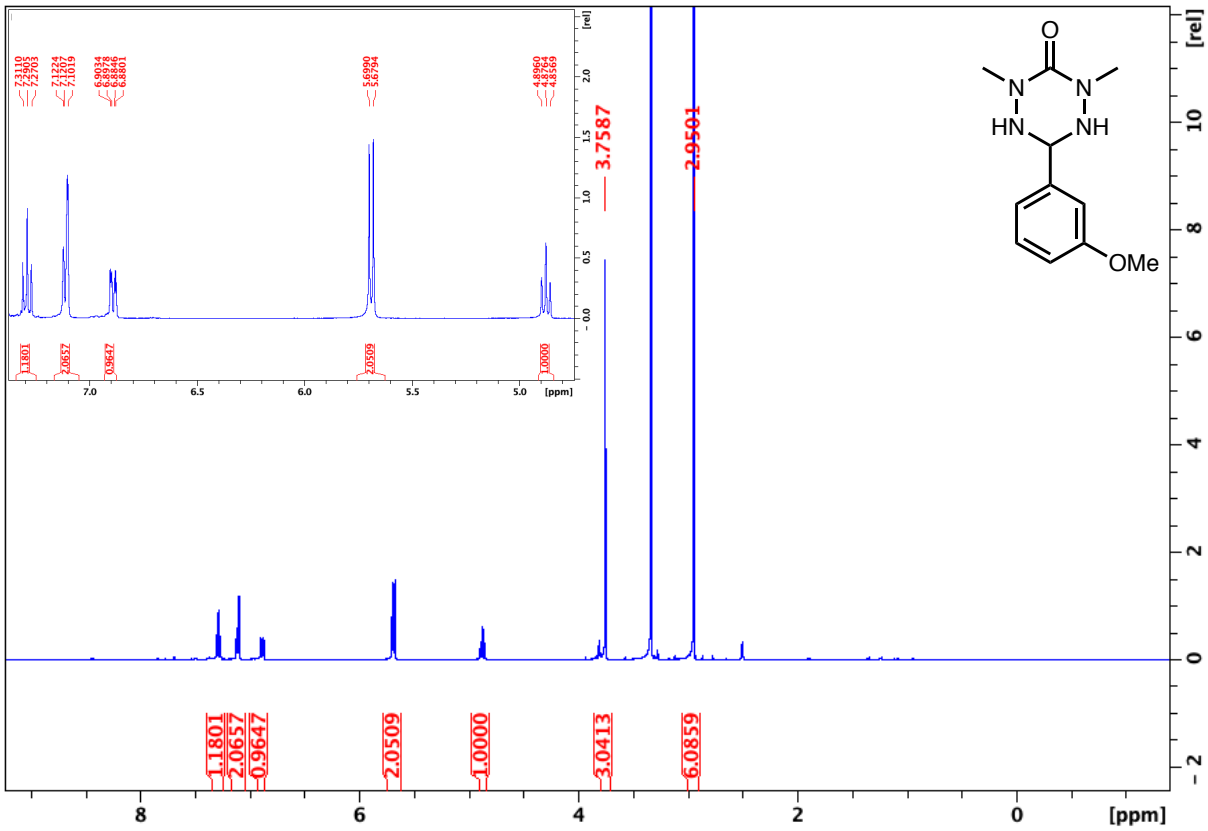


Fig. S29: ^{1}H NMR of **3a**

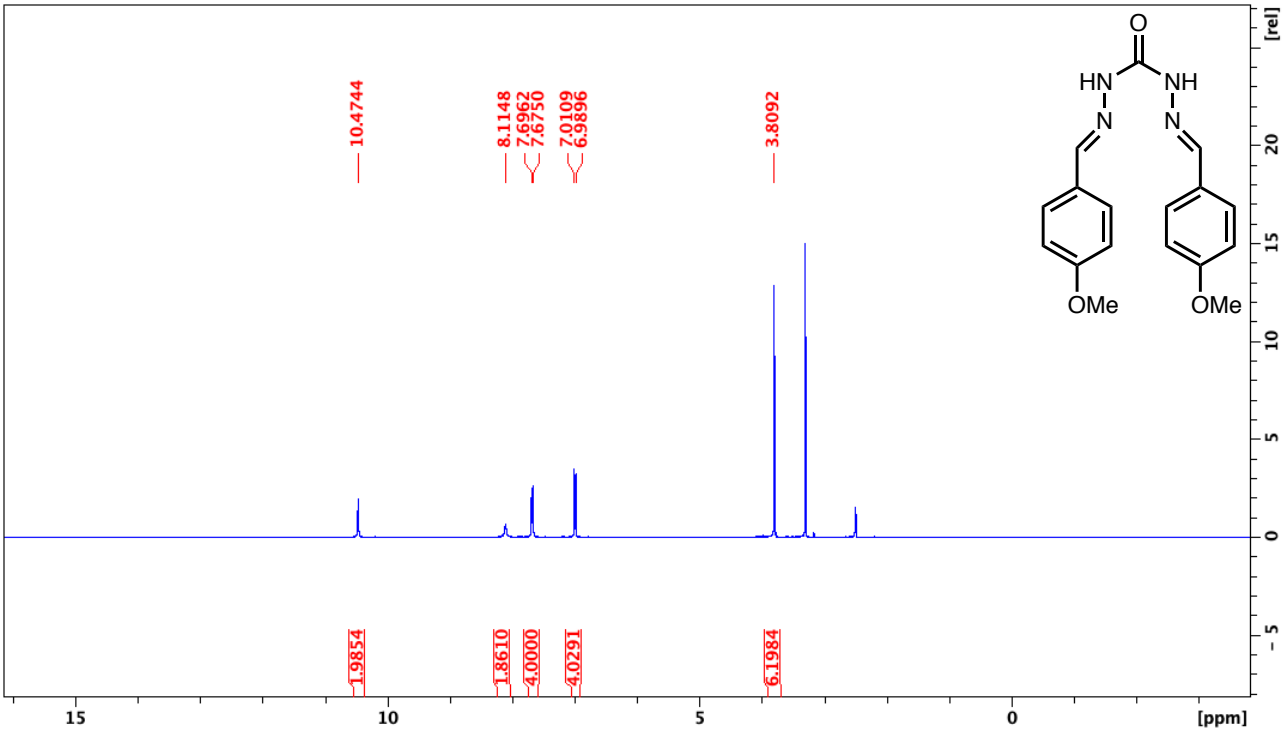


Fig. S30: ^{13}C NMR of **3a**

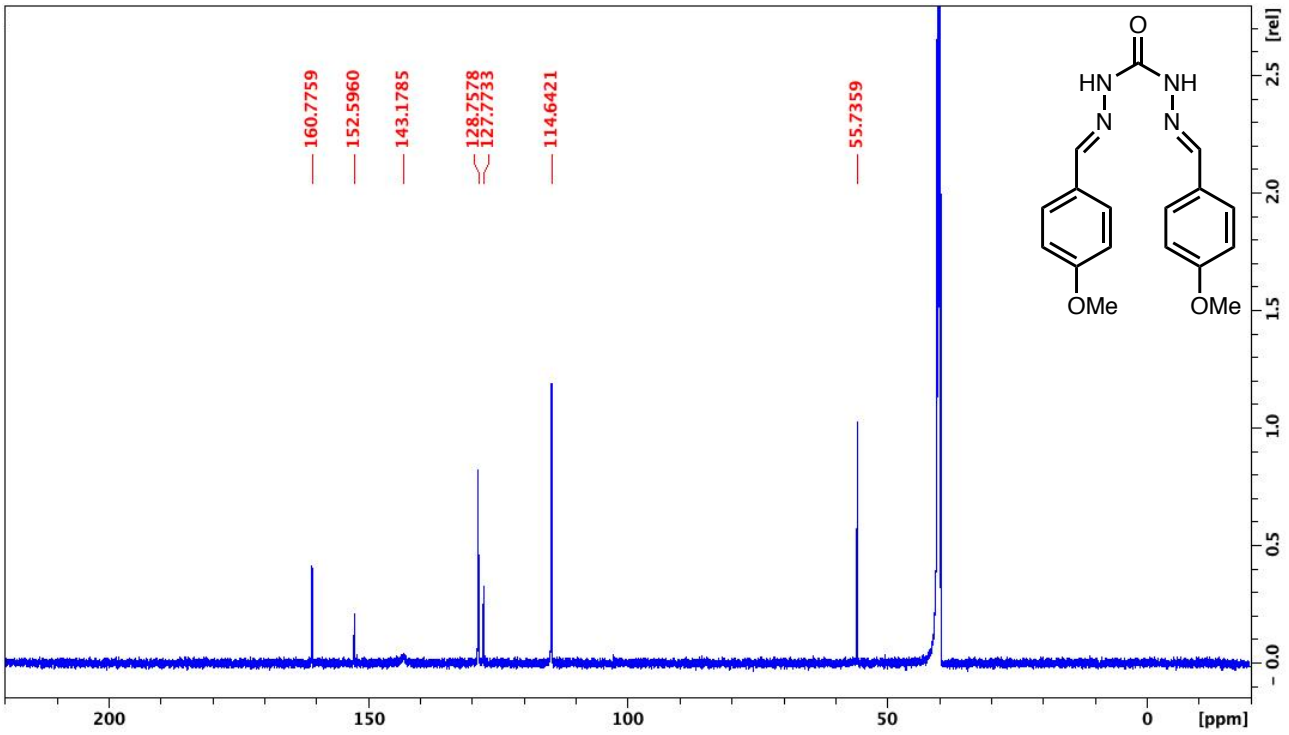


Fig. S31: ^{1}H NMR of **3b**

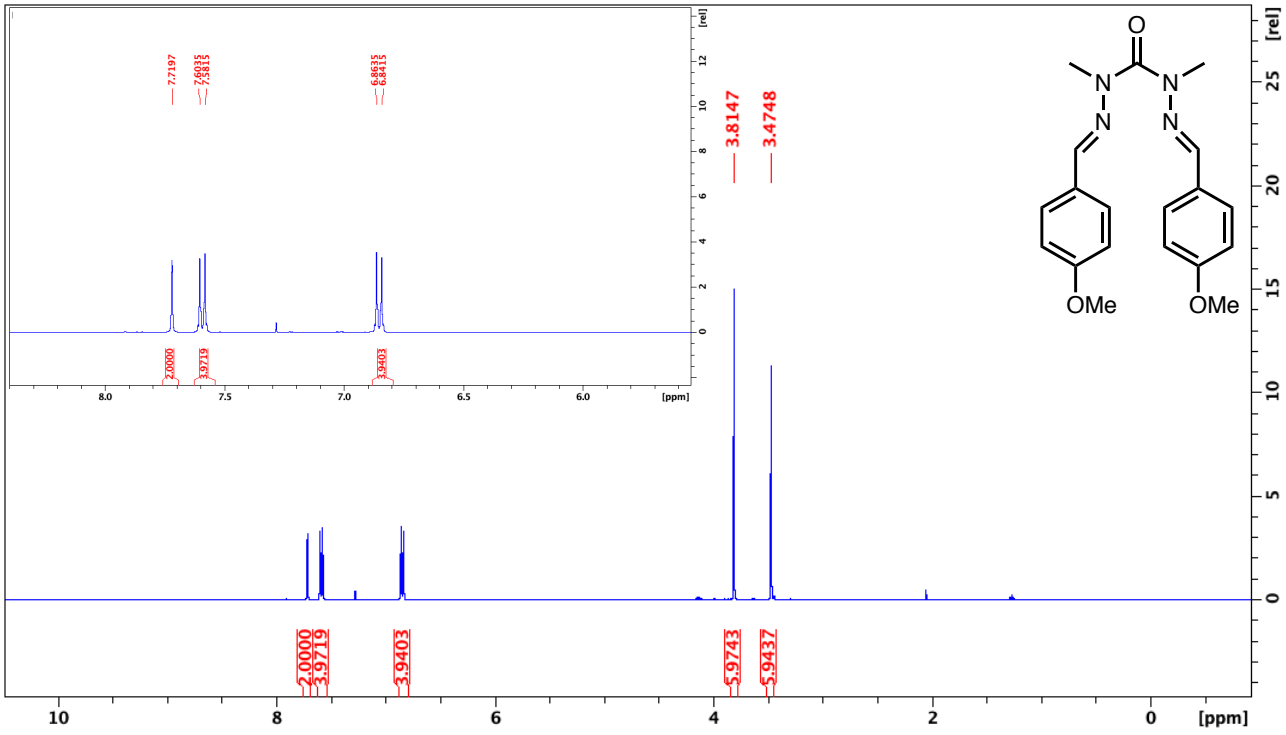


Fig. S32: ^{13}C NMR of **3b**

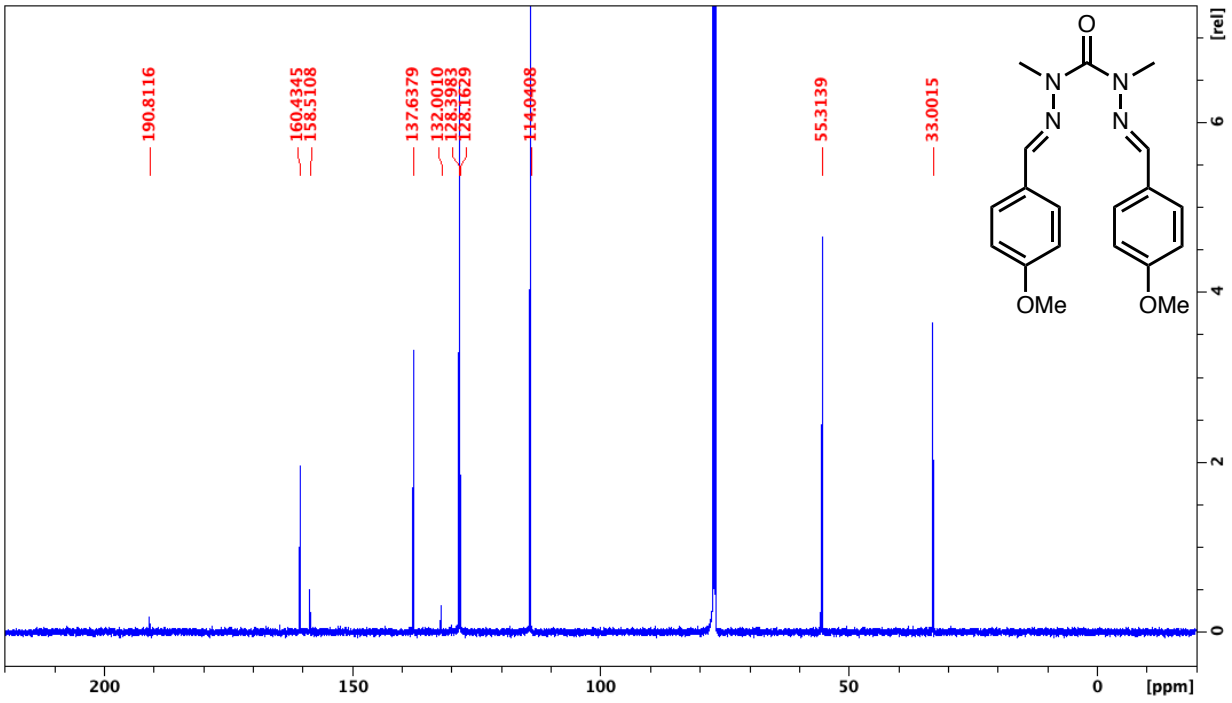
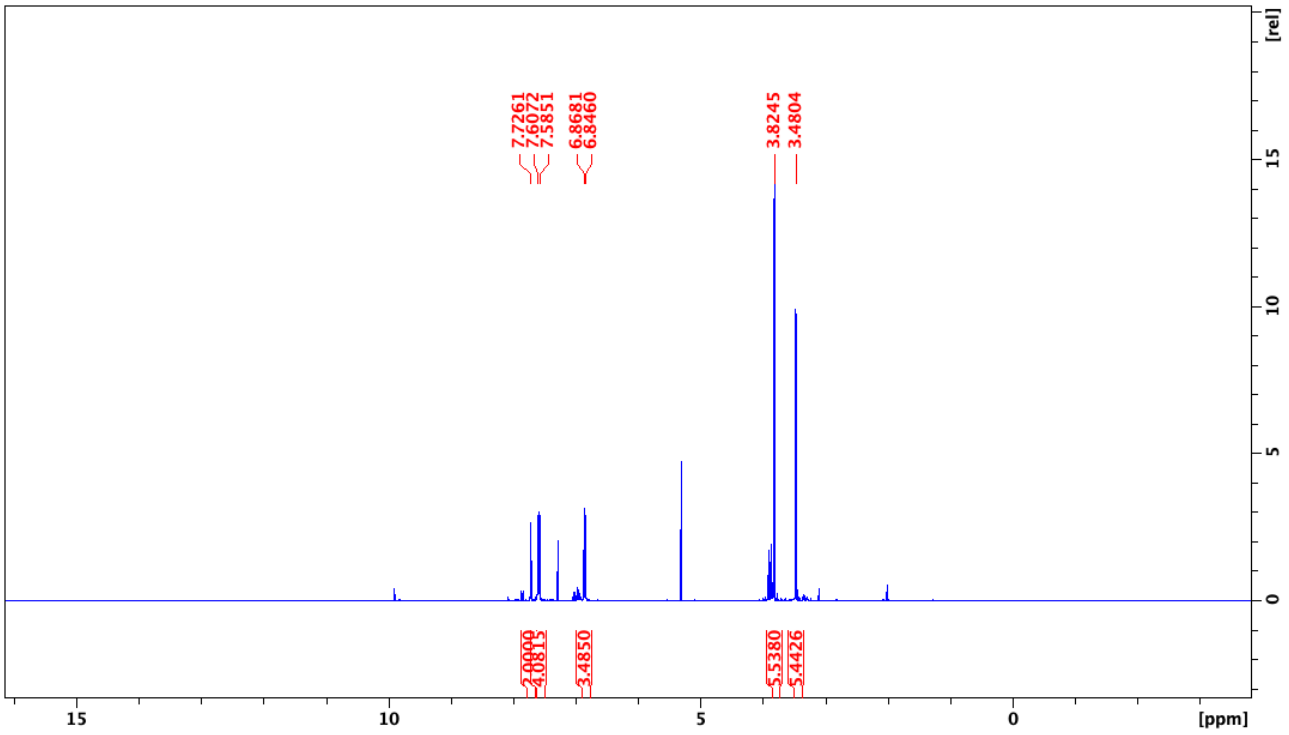


Fig. S33: ^{1}H NMR **3b** (crude) – used directly in ring closure



*The crude **3b** contains a small amount of the monomethylated product and can be used directly in the synthesis of **3c** with little impact on the yield.*

Fig. S34: ^{1}H NMR of **3c**

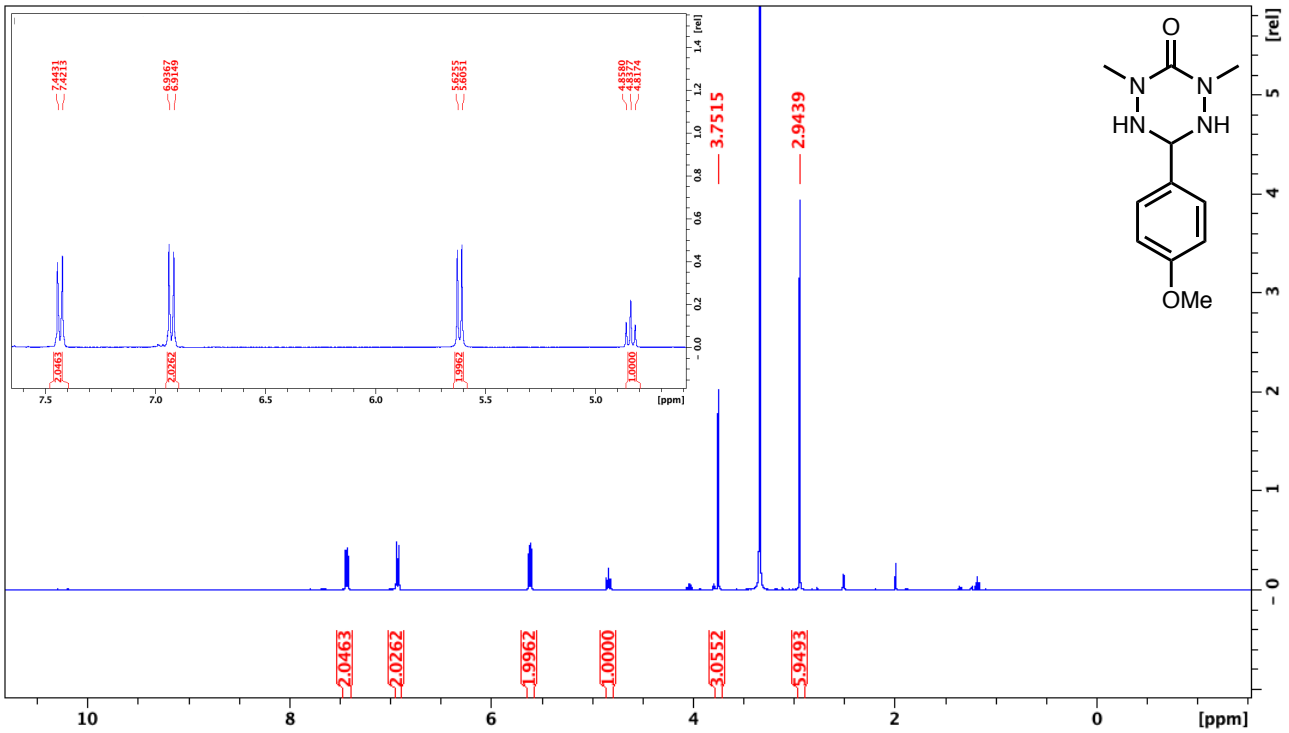


Fig. S35: ^{13}C NMR of **3c**

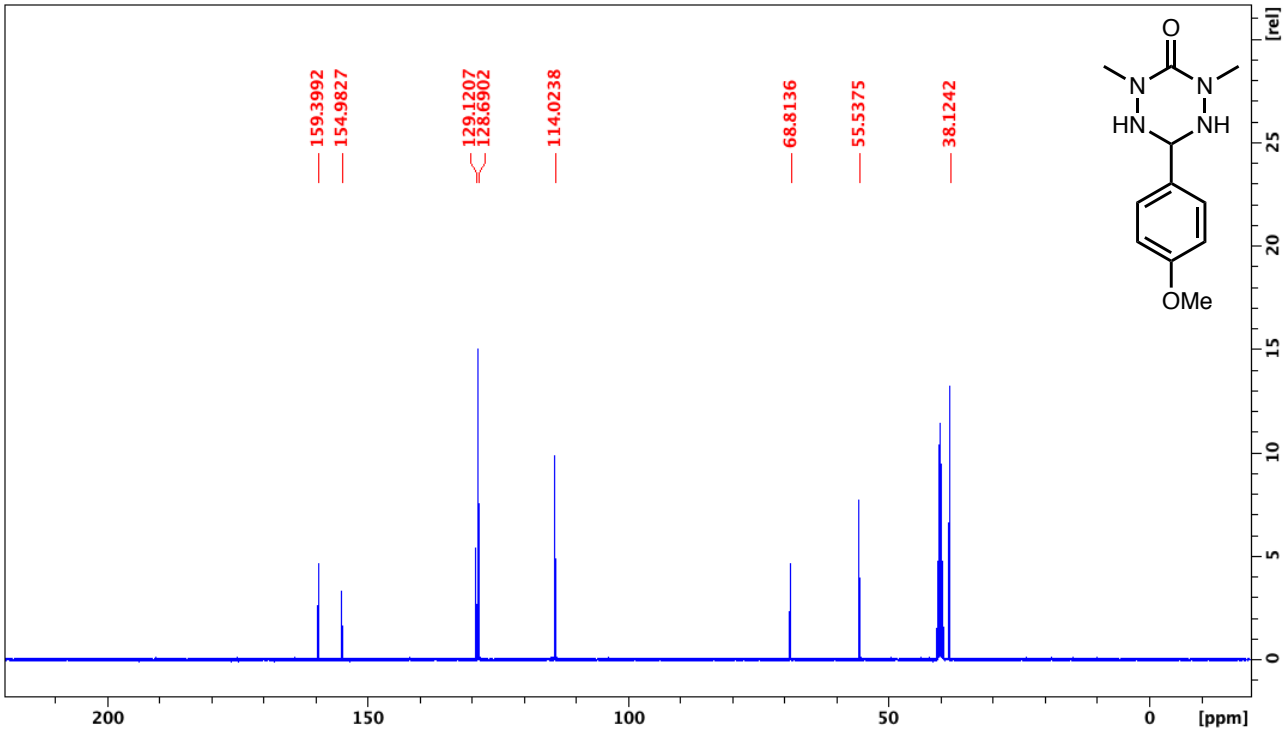


Fig. S36: ^{1}H NMR of **4a**

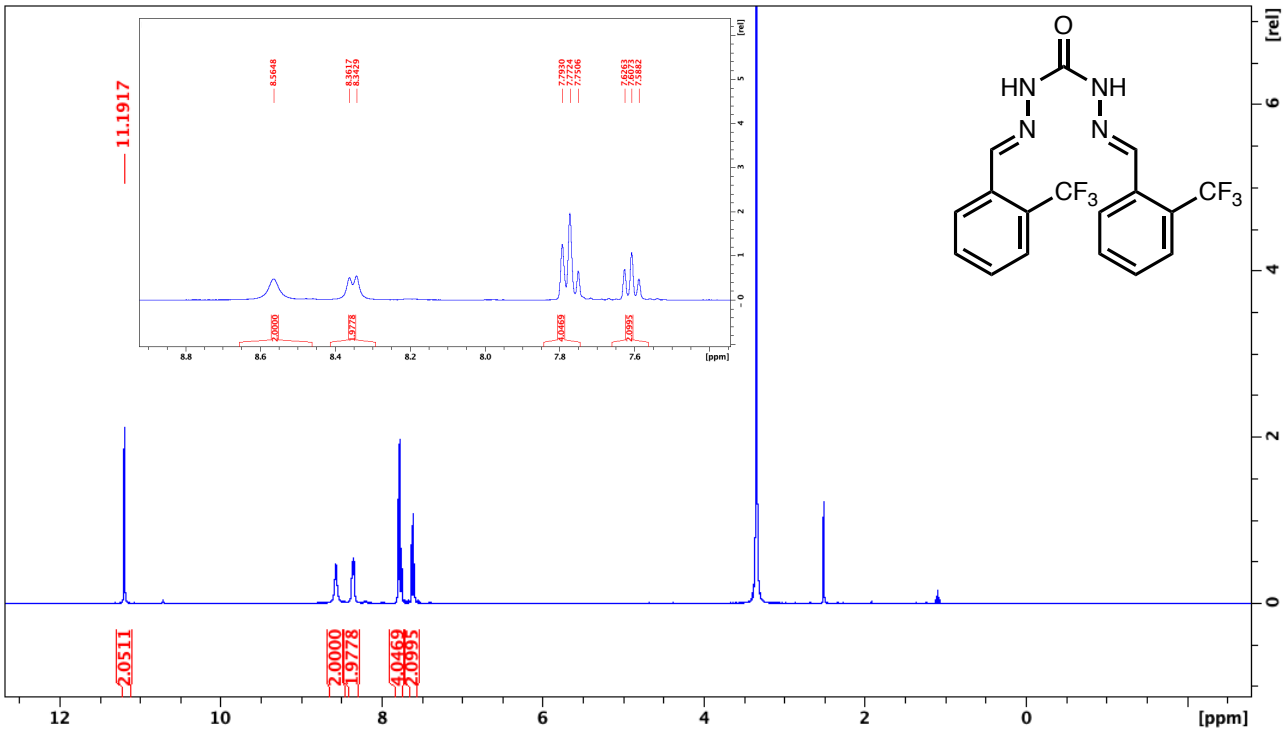


Fig. S37: ^{13}C NMR of **4a**

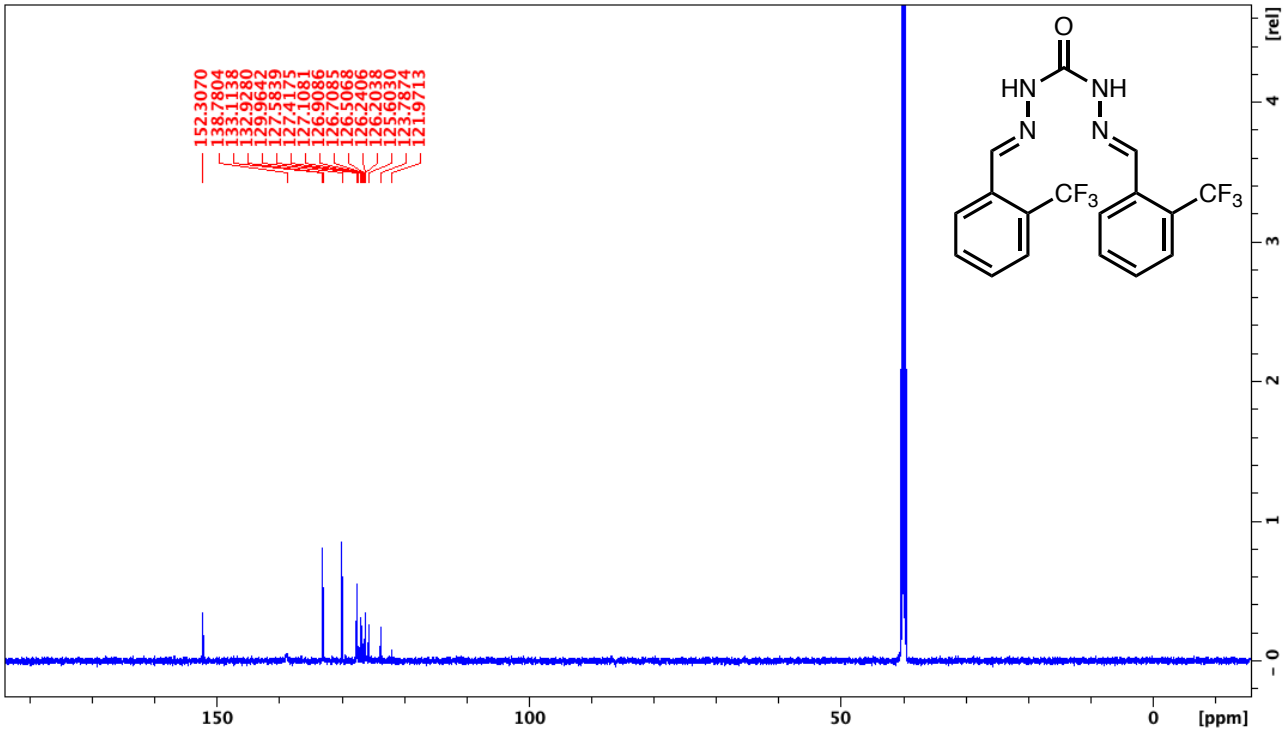


Fig. S38: ^{19}F NMR of **4a**

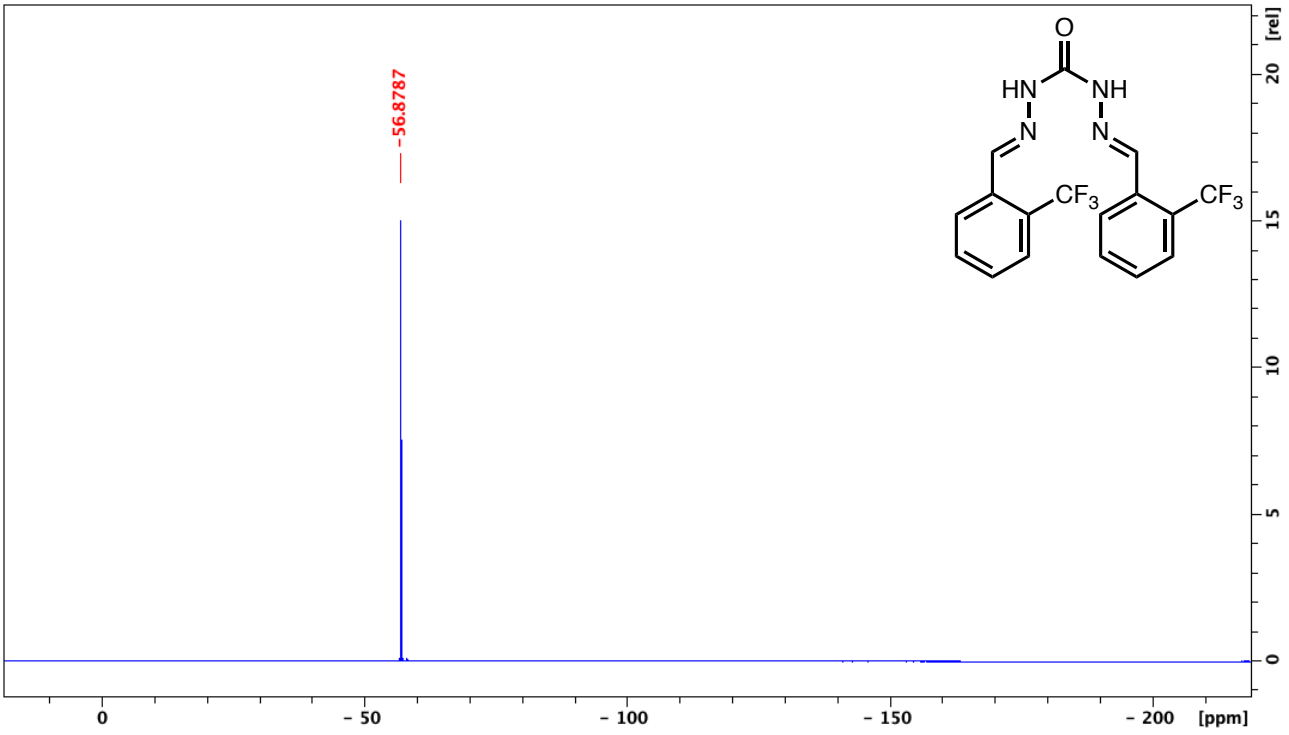


Fig. S39: ^{1}H NMR of **4b**

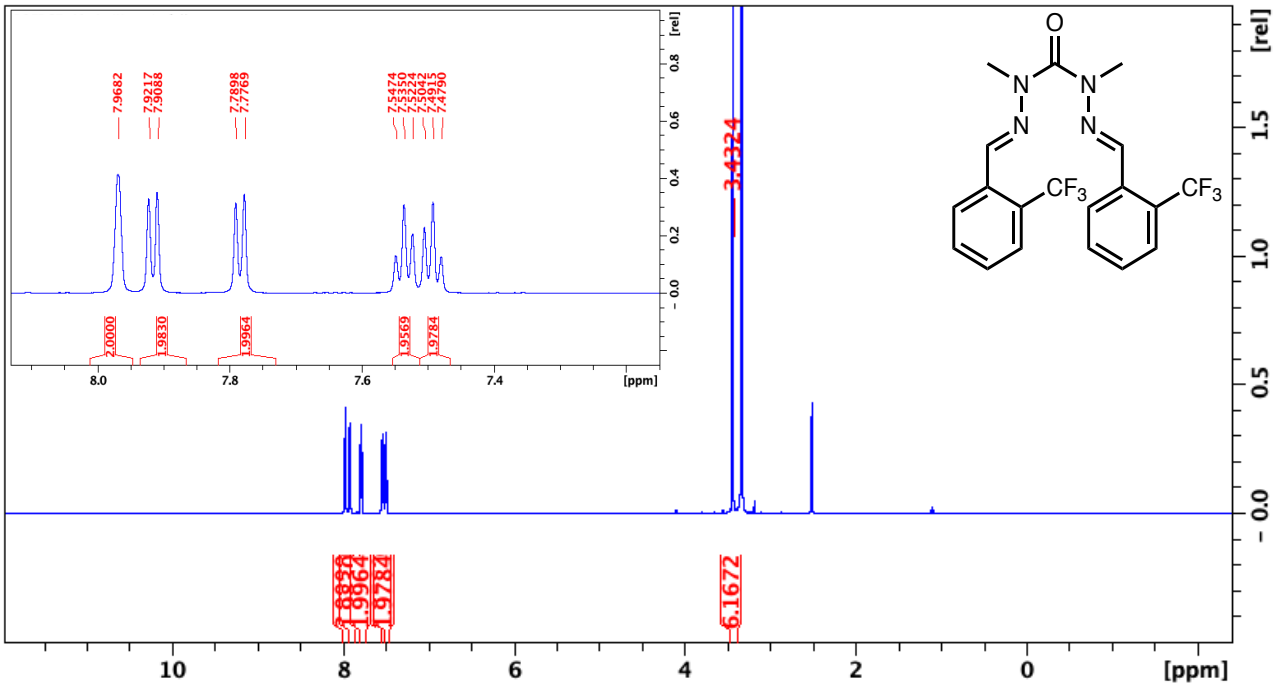


Fig. S40: ^{13}C NMR of **4b**

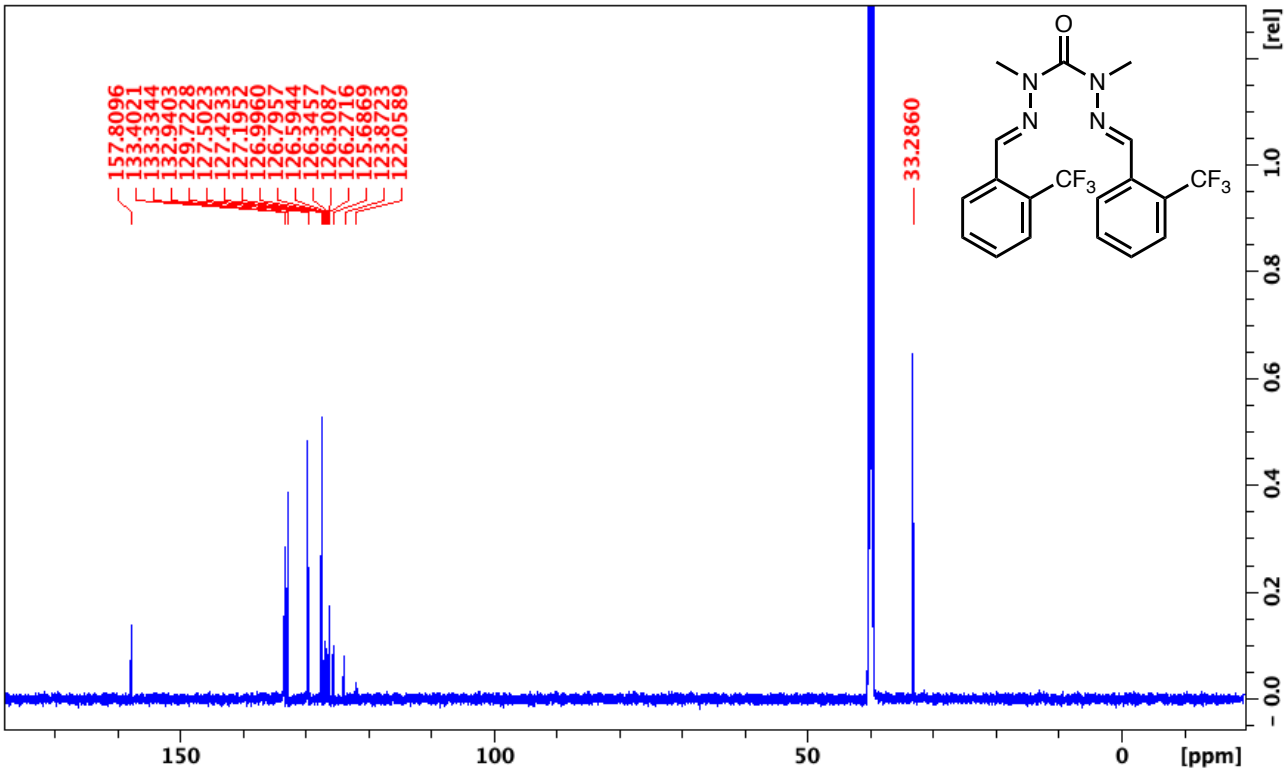


Fig. S41: ^{19}F NMR of **4b**

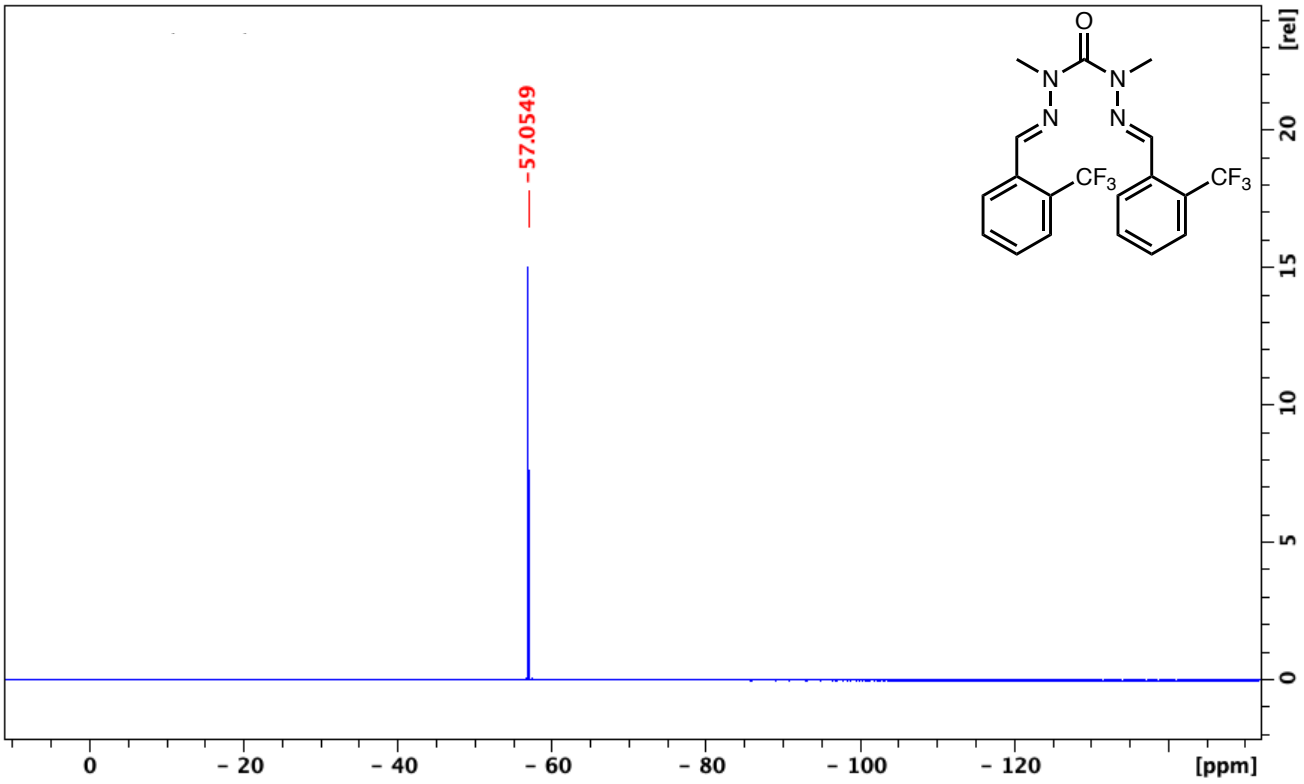


Fig. S42: ^{1}H NMR of **4c**

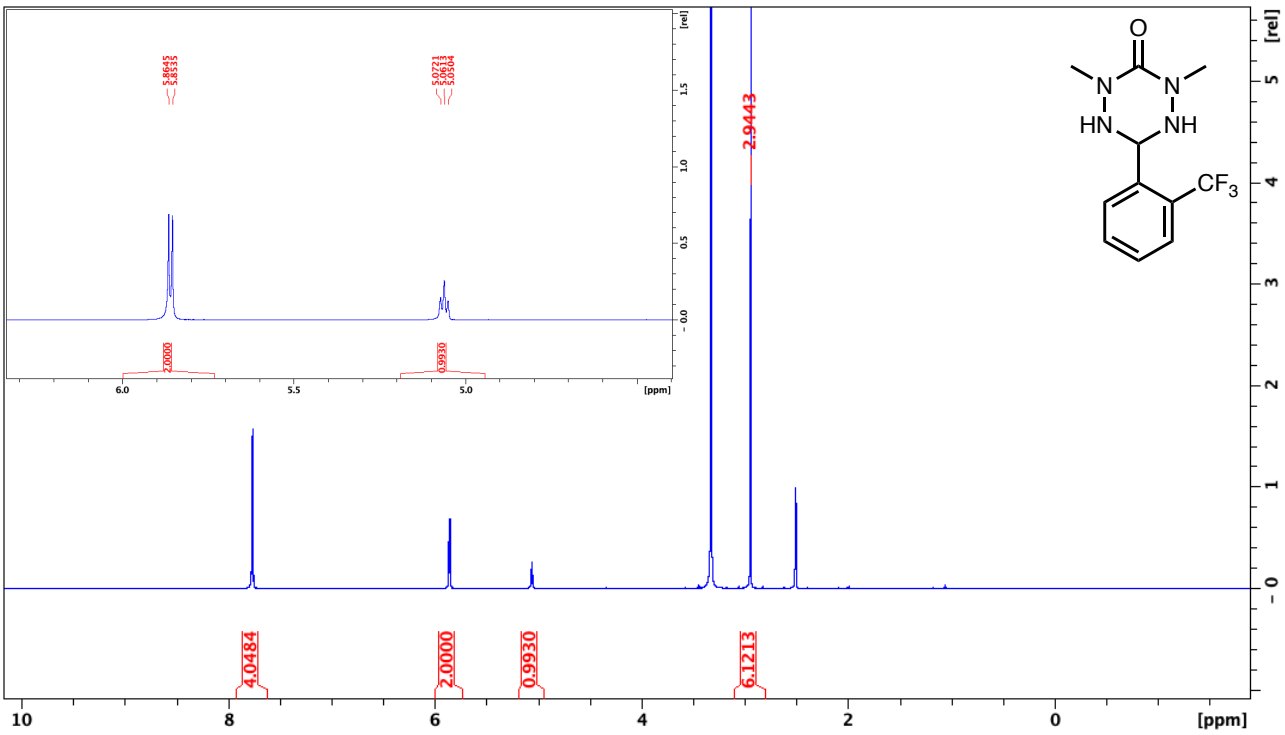


Fig. S43: ^{13}C NMR of **4c**

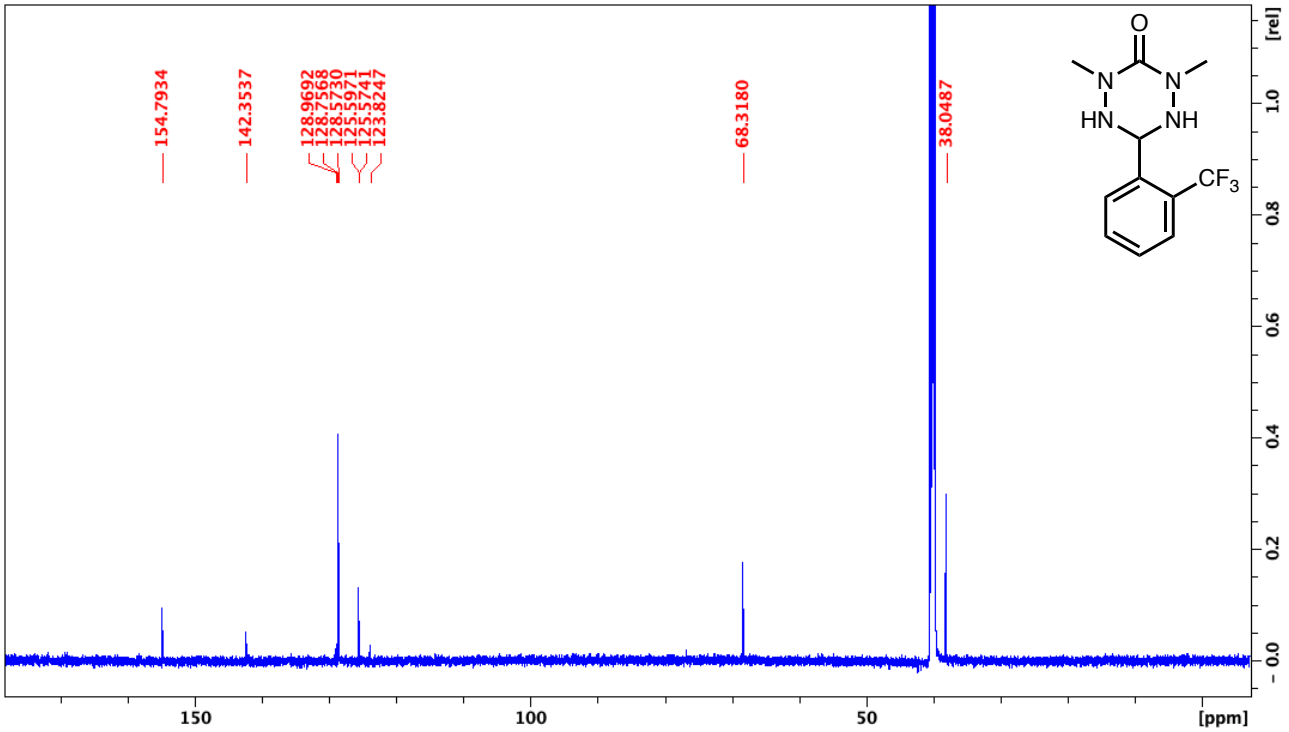


Fig. S44: ^{19}F NMR of **4c**

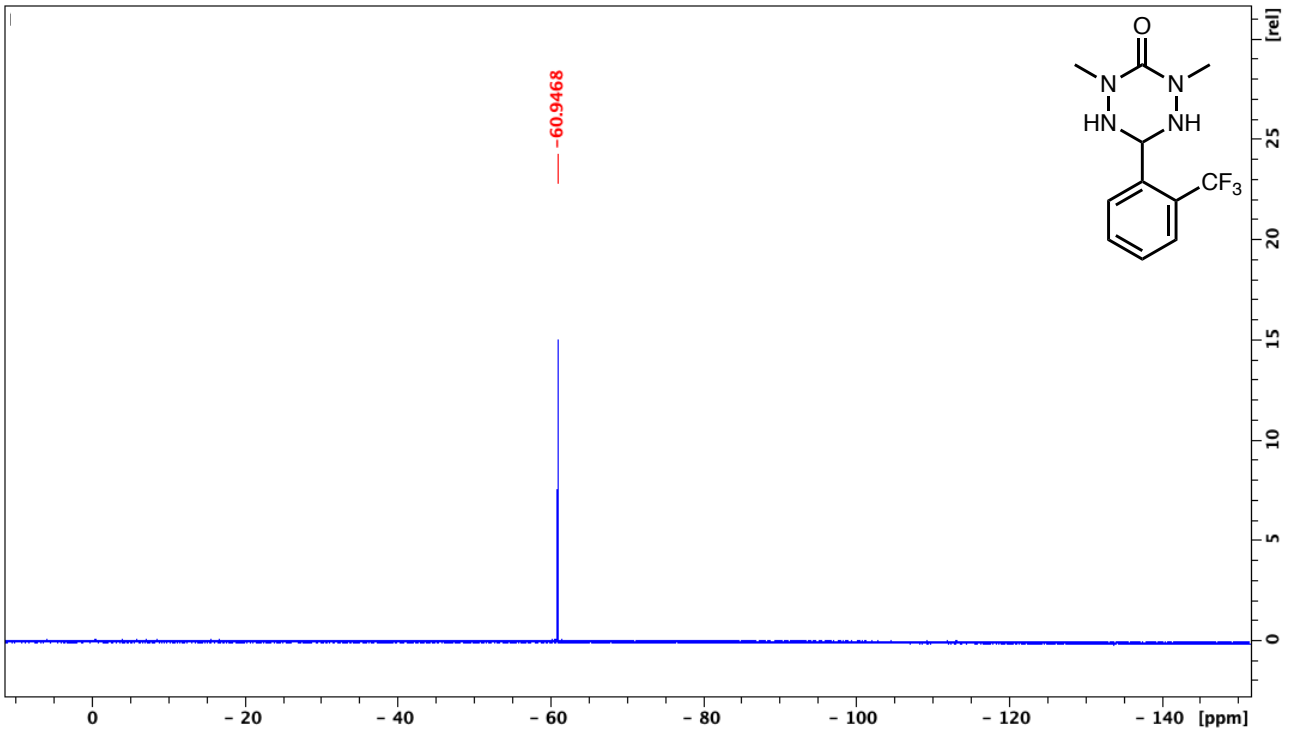


Fig. S45: ^{1}H NMR of **5a**

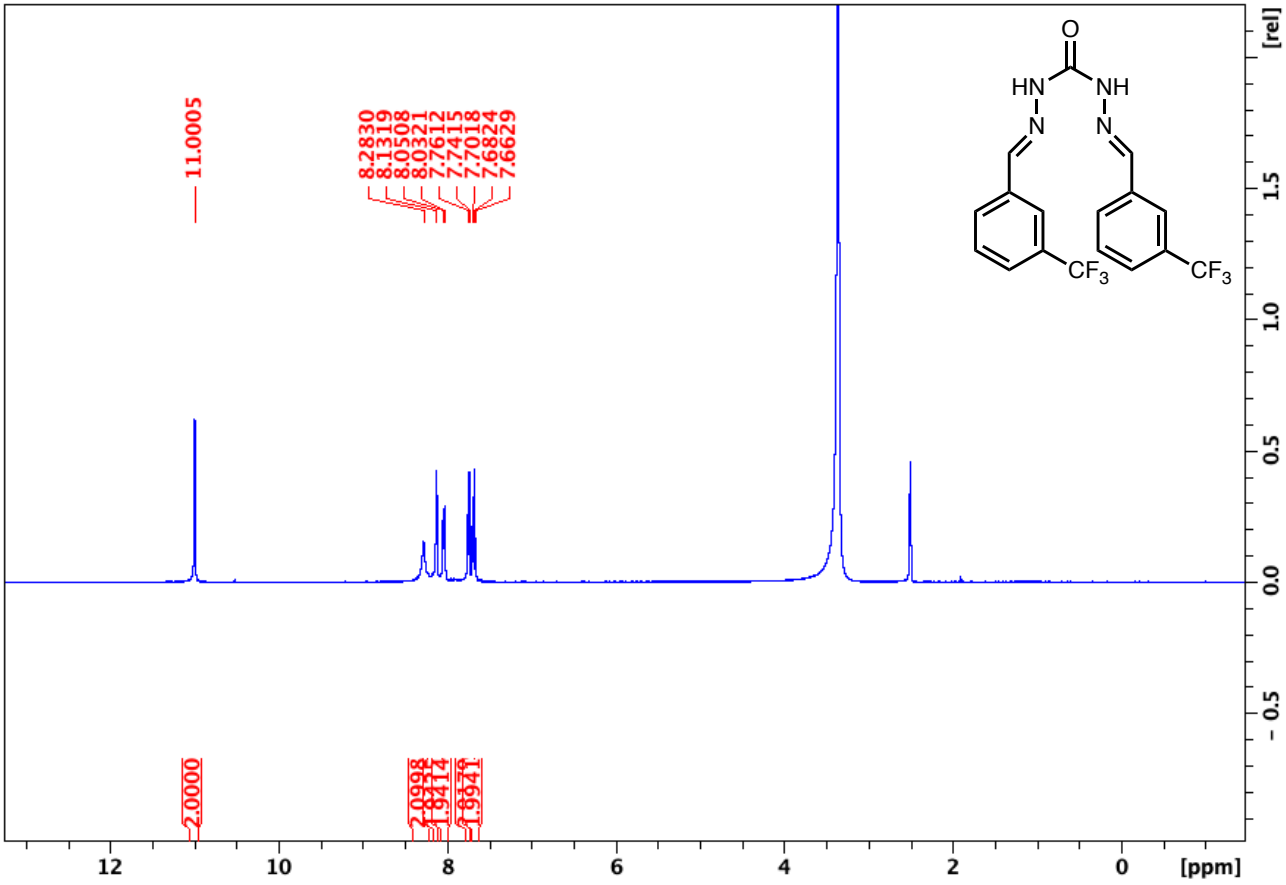


Fig. S46: ^{13}C NMR of **5a**

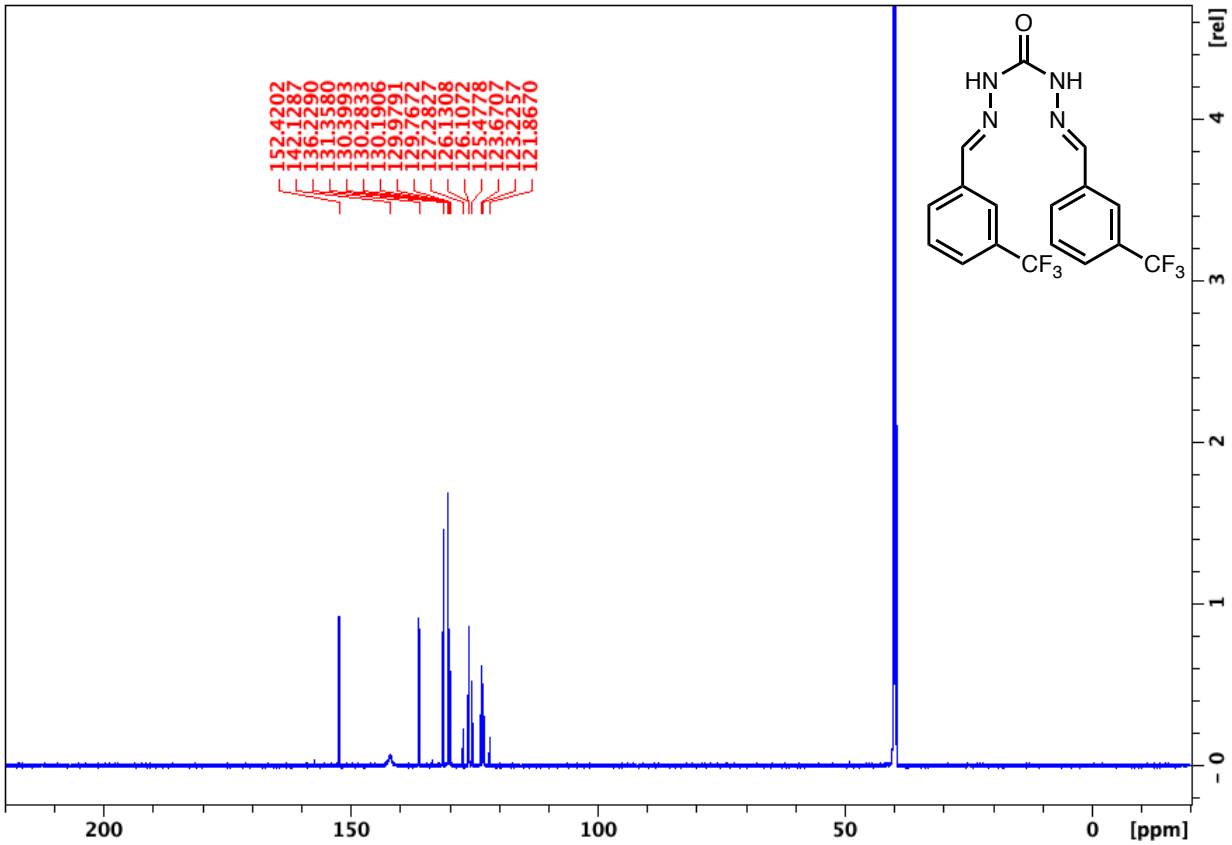


Fig. S47: ^{19}F NMR of **5a**

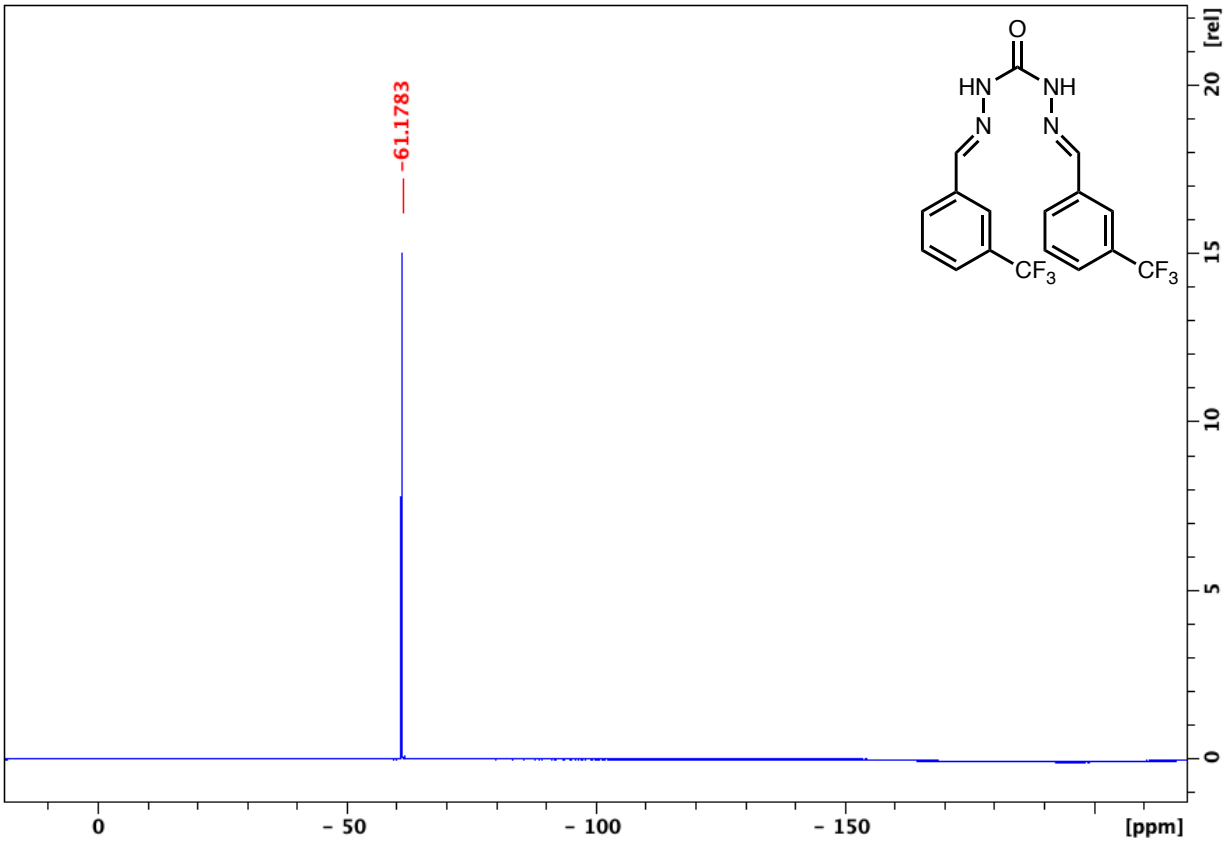


Fig. S48: ^{1}H NMR of **5b**

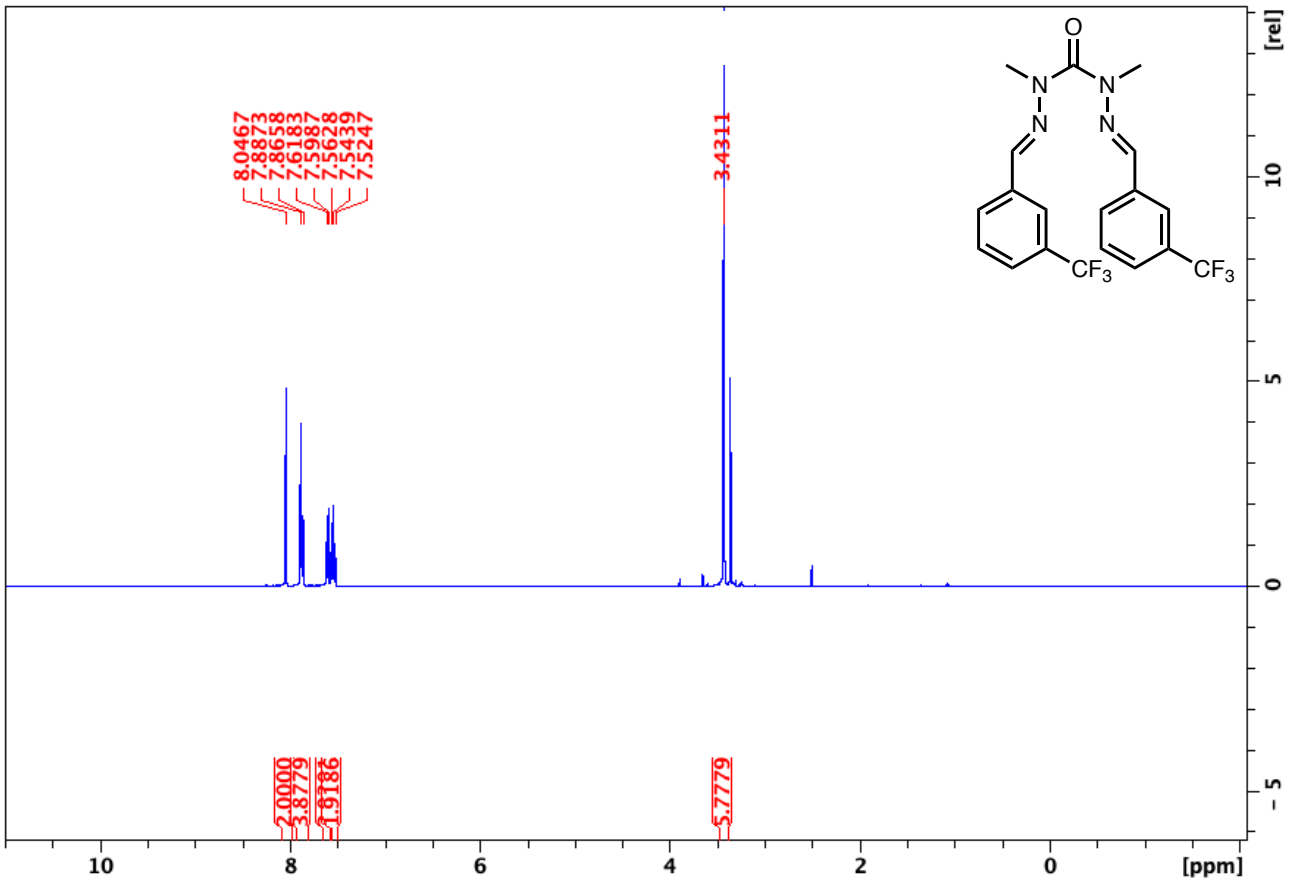


Fig. S49: ^{13}C NMR of **5b**

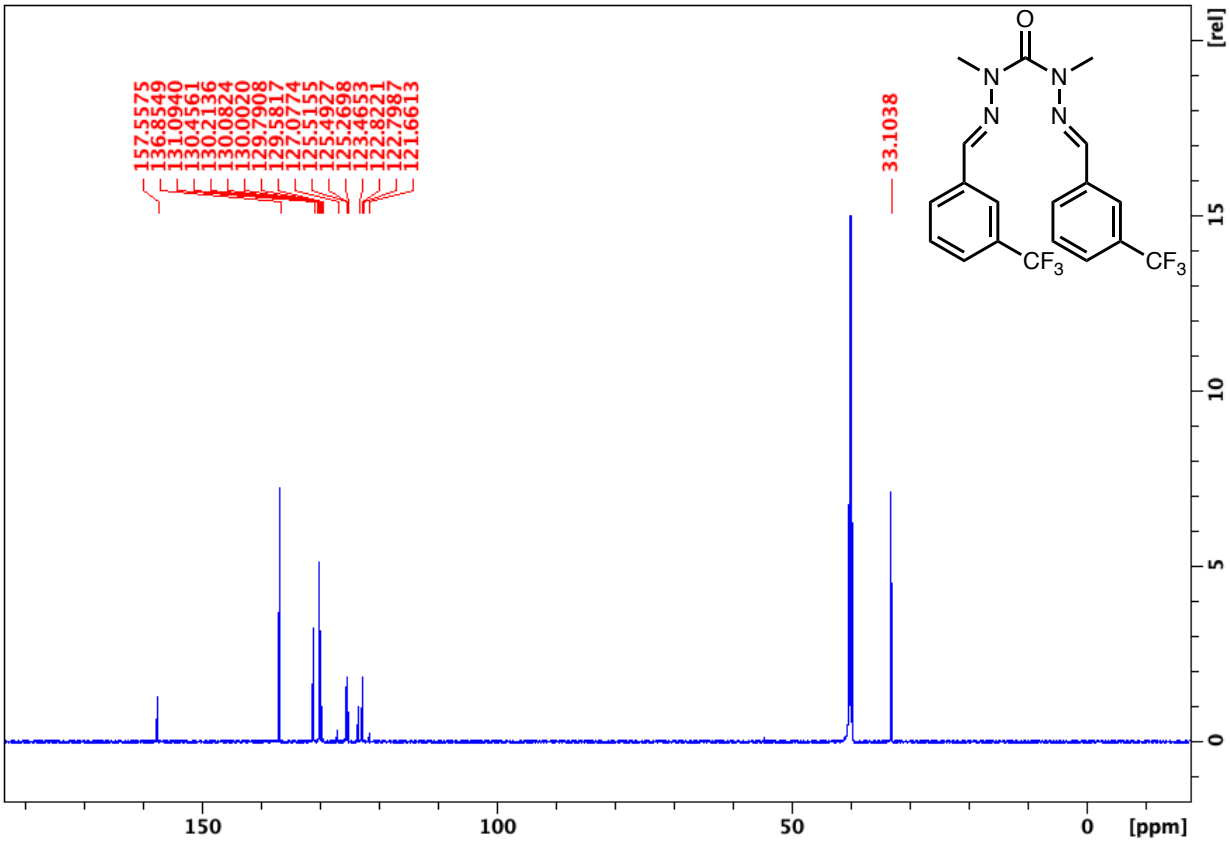


Fig. S50: ^{19}F NMR of **5b**

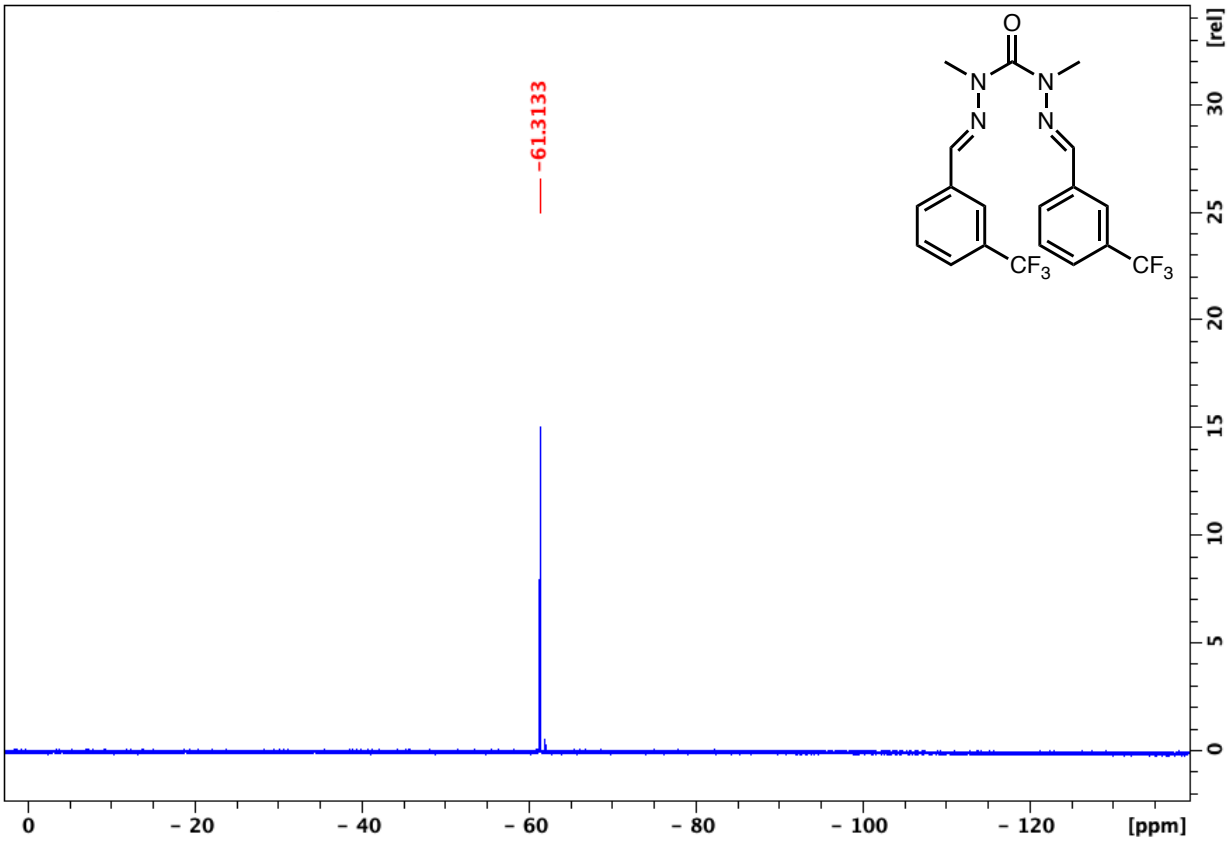


Fig. S51: ^{1}H NMR of **5c**

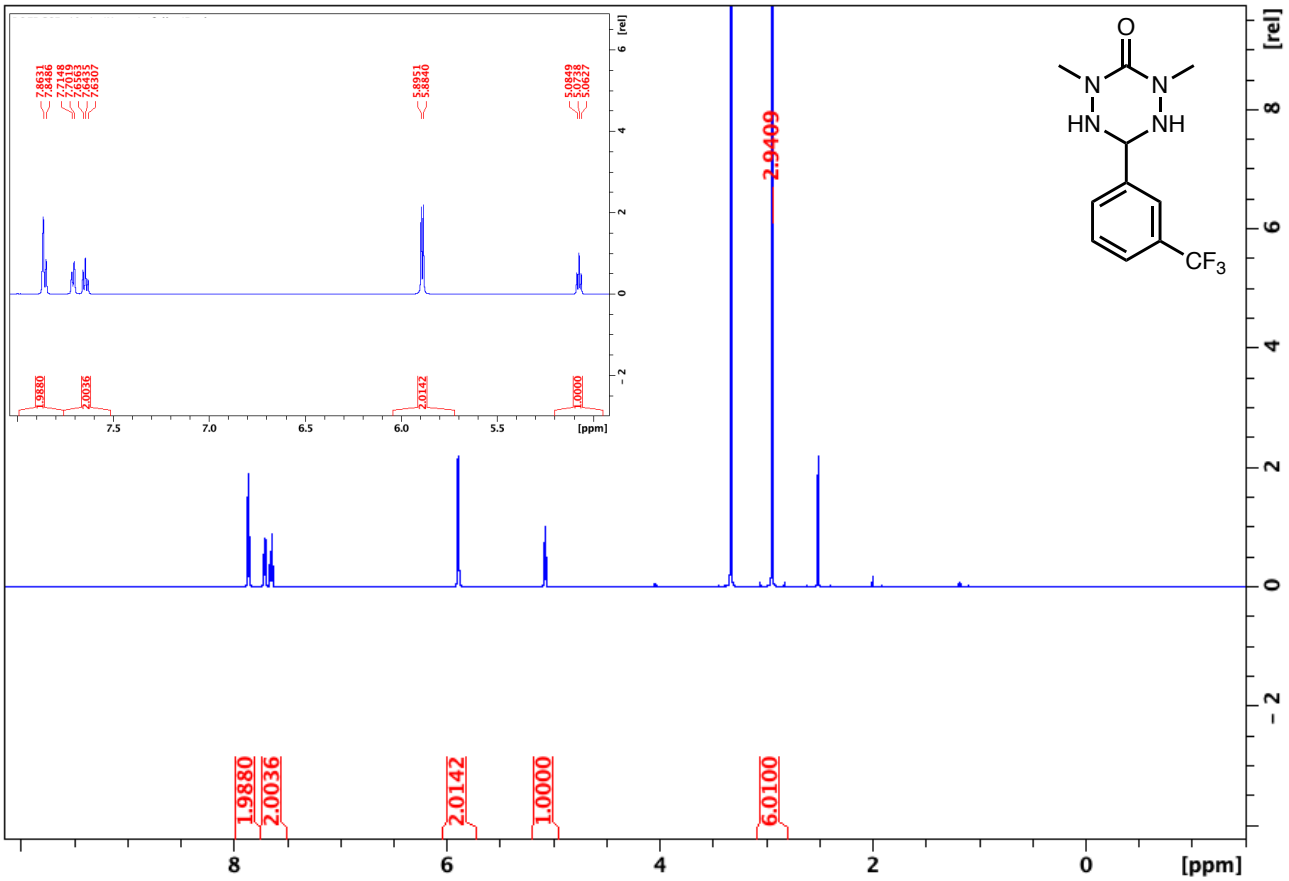


Fig. S52: ^{13}C NMR of **5c**

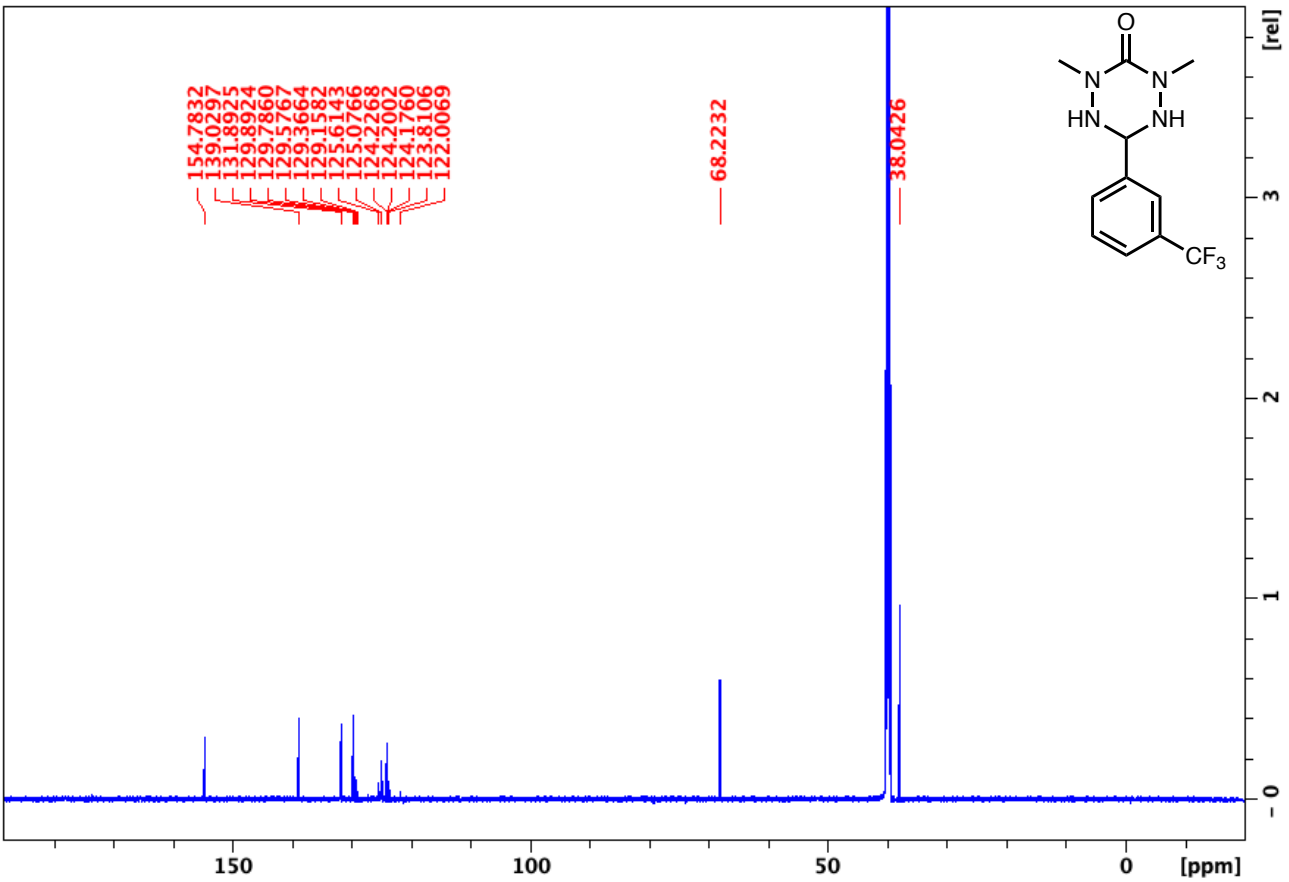


Fig. S53: ^{1}H NMR of **6a**

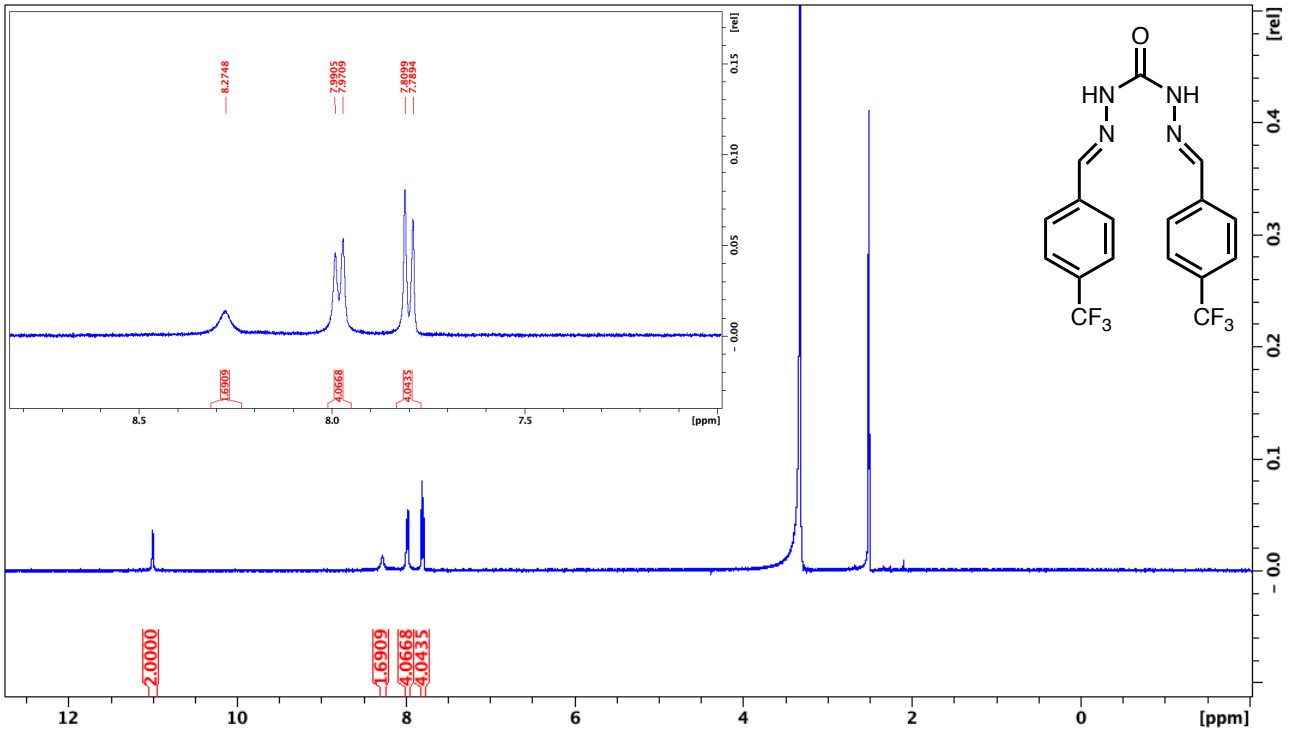


Fig. S54: ^{13}C NMR of **6a**

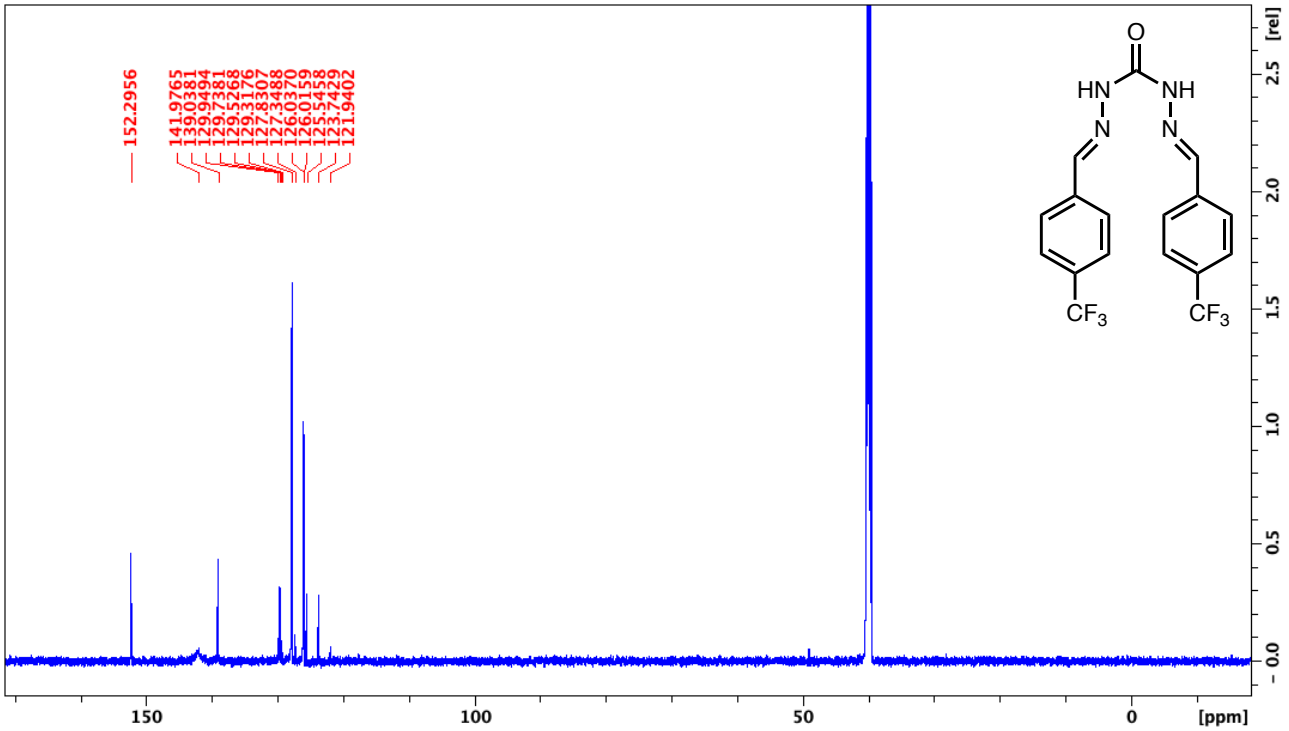


Fig. S55: ^{19}F NMR of **6a**

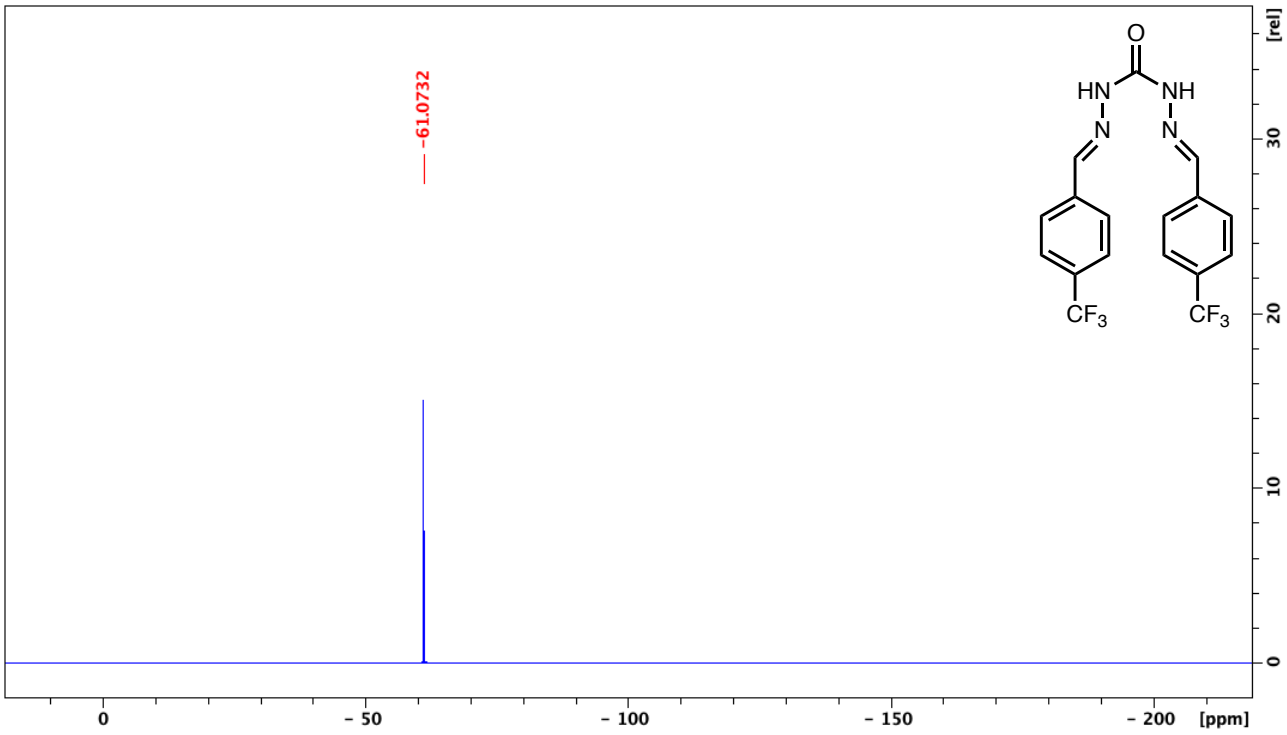


Fig. S56: ^{1}H NMR of **6b**

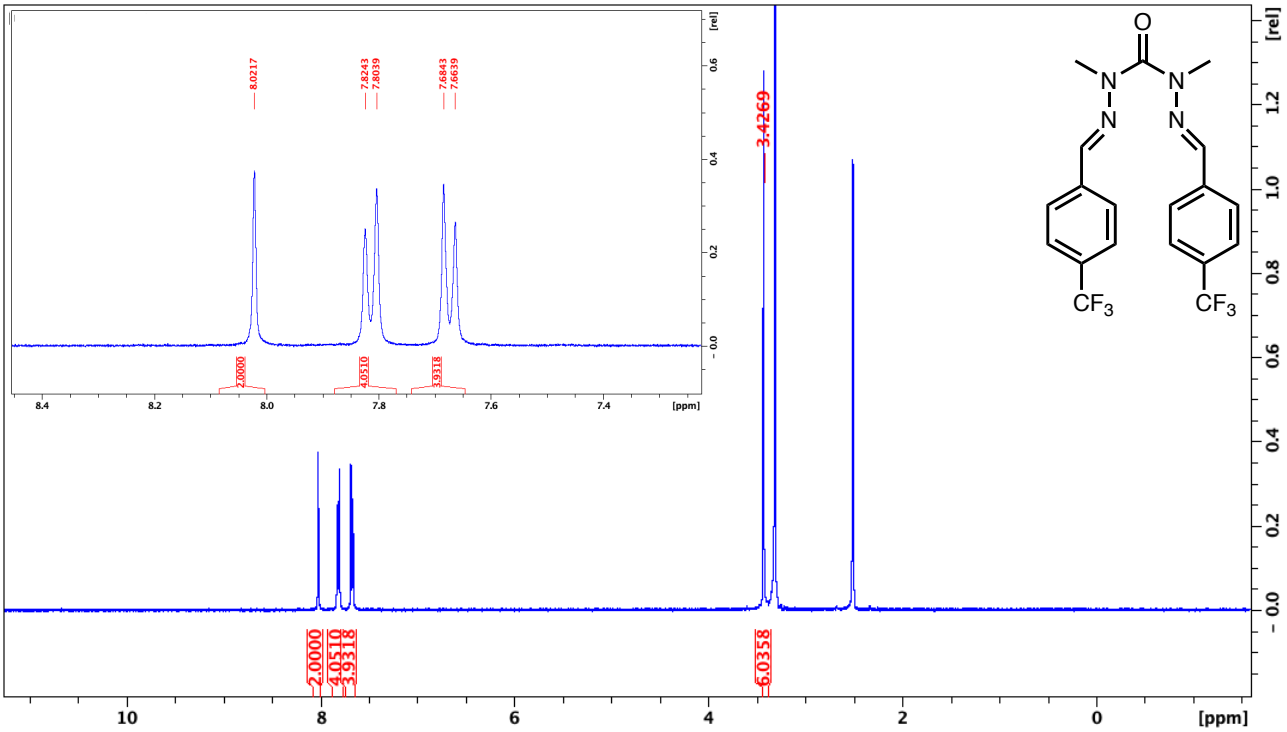


Fig. S57: ^{13}C NMR of **6b**

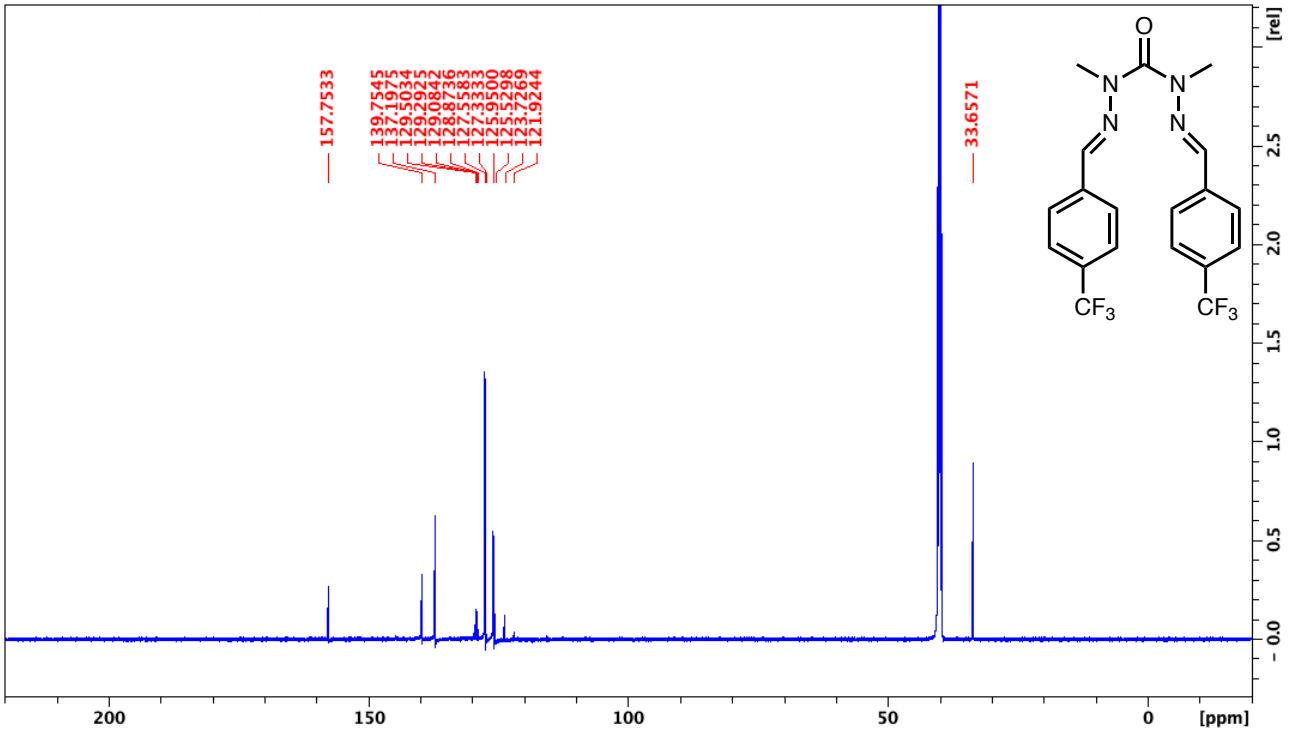


Fig. S58: ^{19}F NMR of **6b**

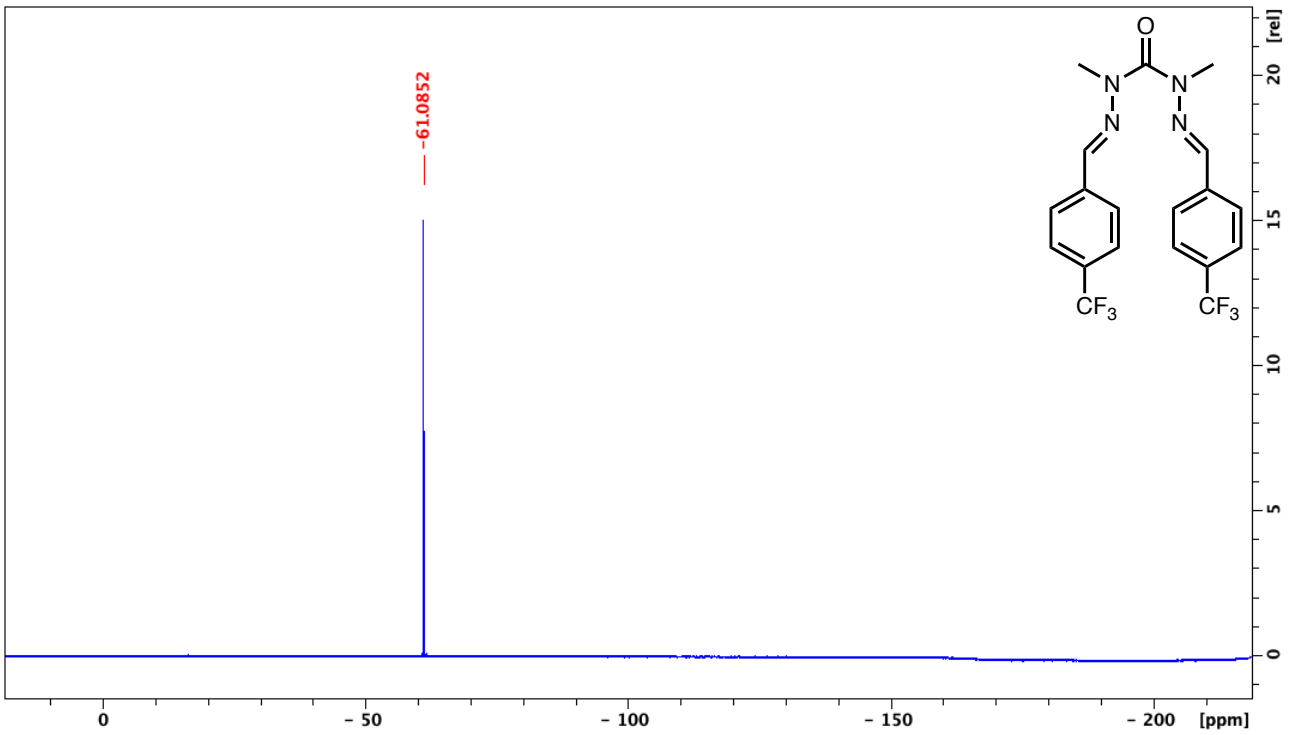


Fig. S59: ^{1}H NMR of **6c**

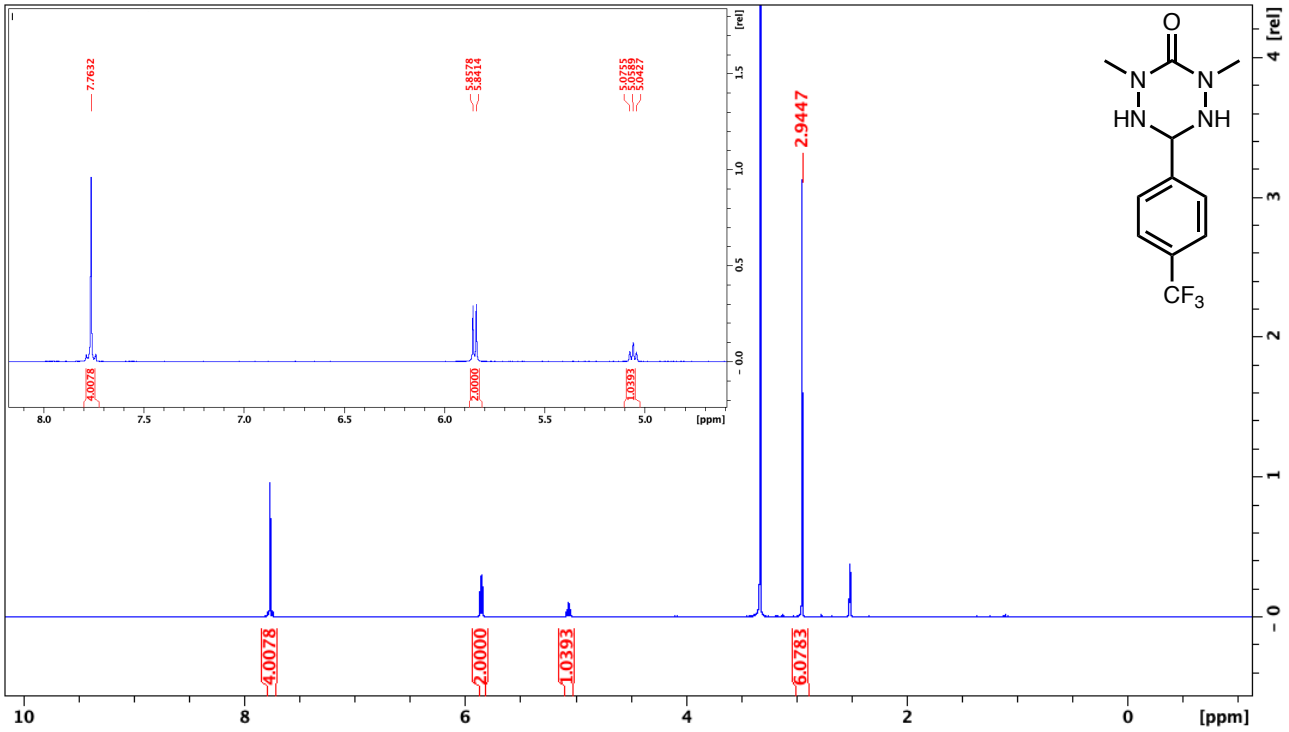


Fig. S60: ^{13}C NMR of **6c**

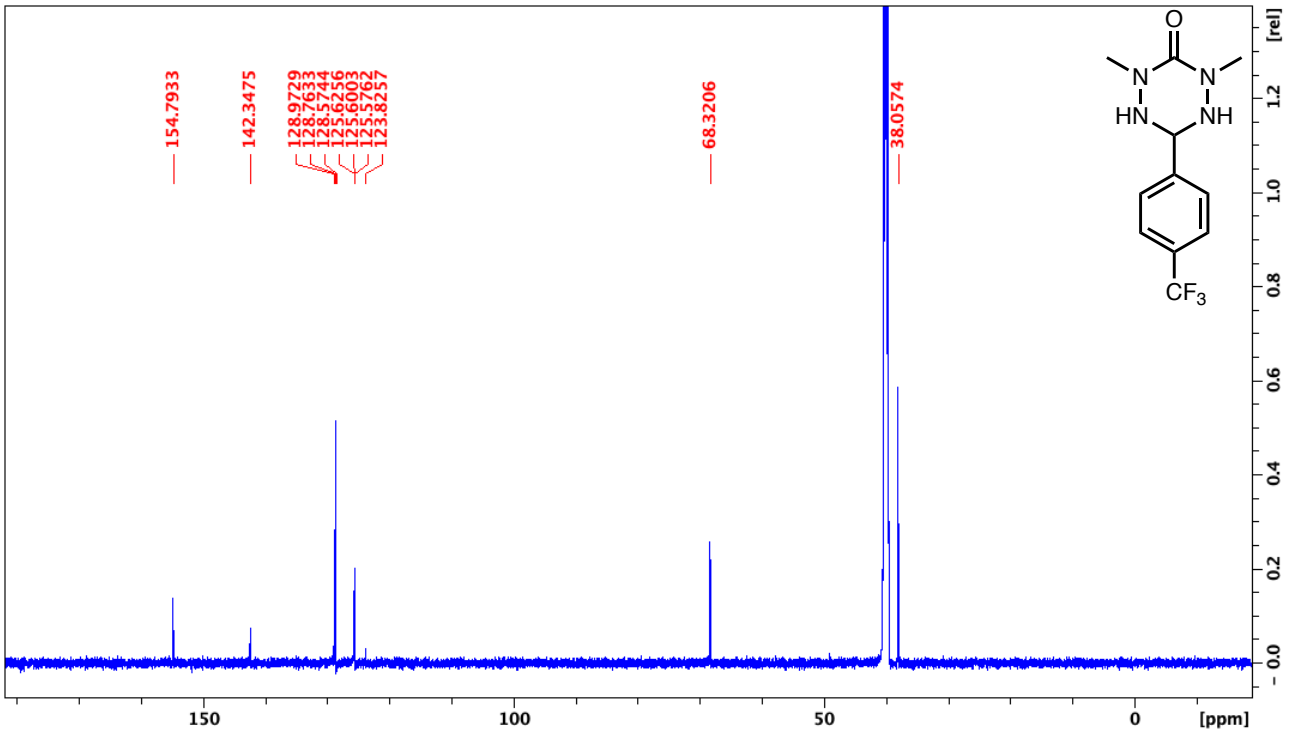


Fig. S61: ^{19}F NMR of **6c**

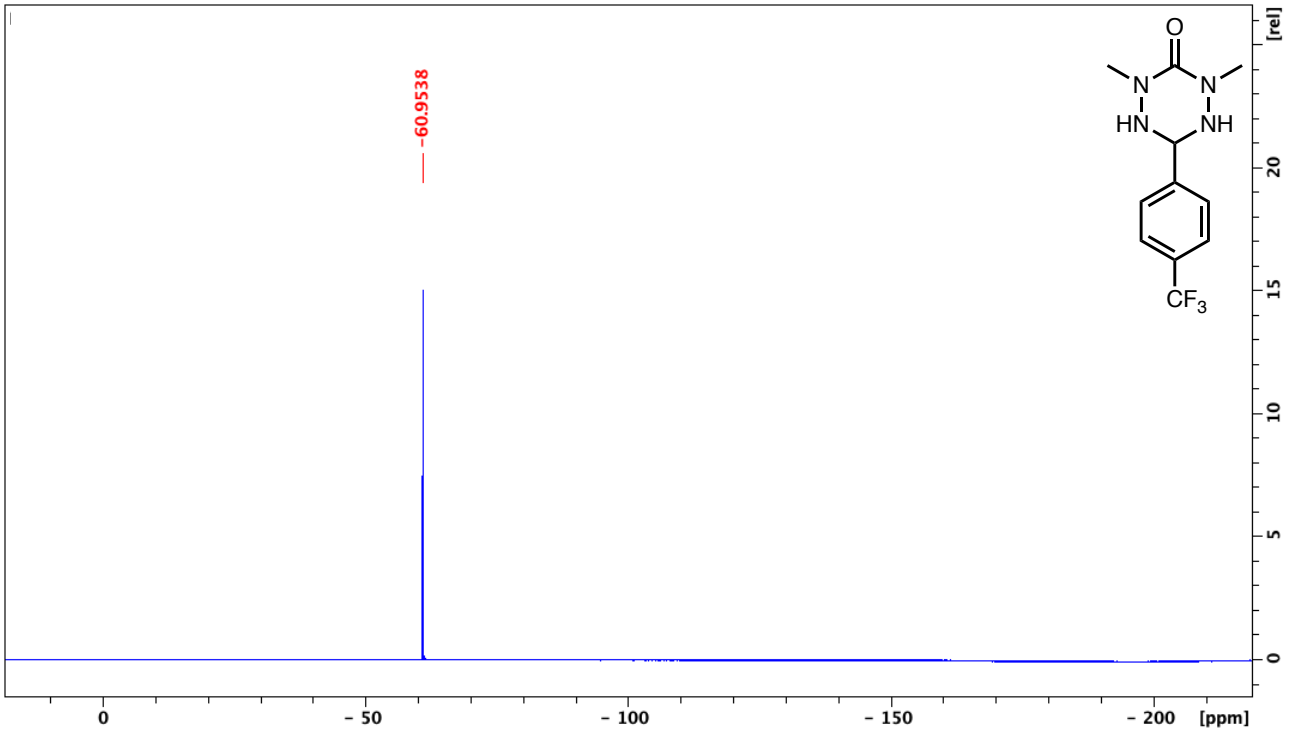


Fig. S62: ^{1}H NMR of **7a**

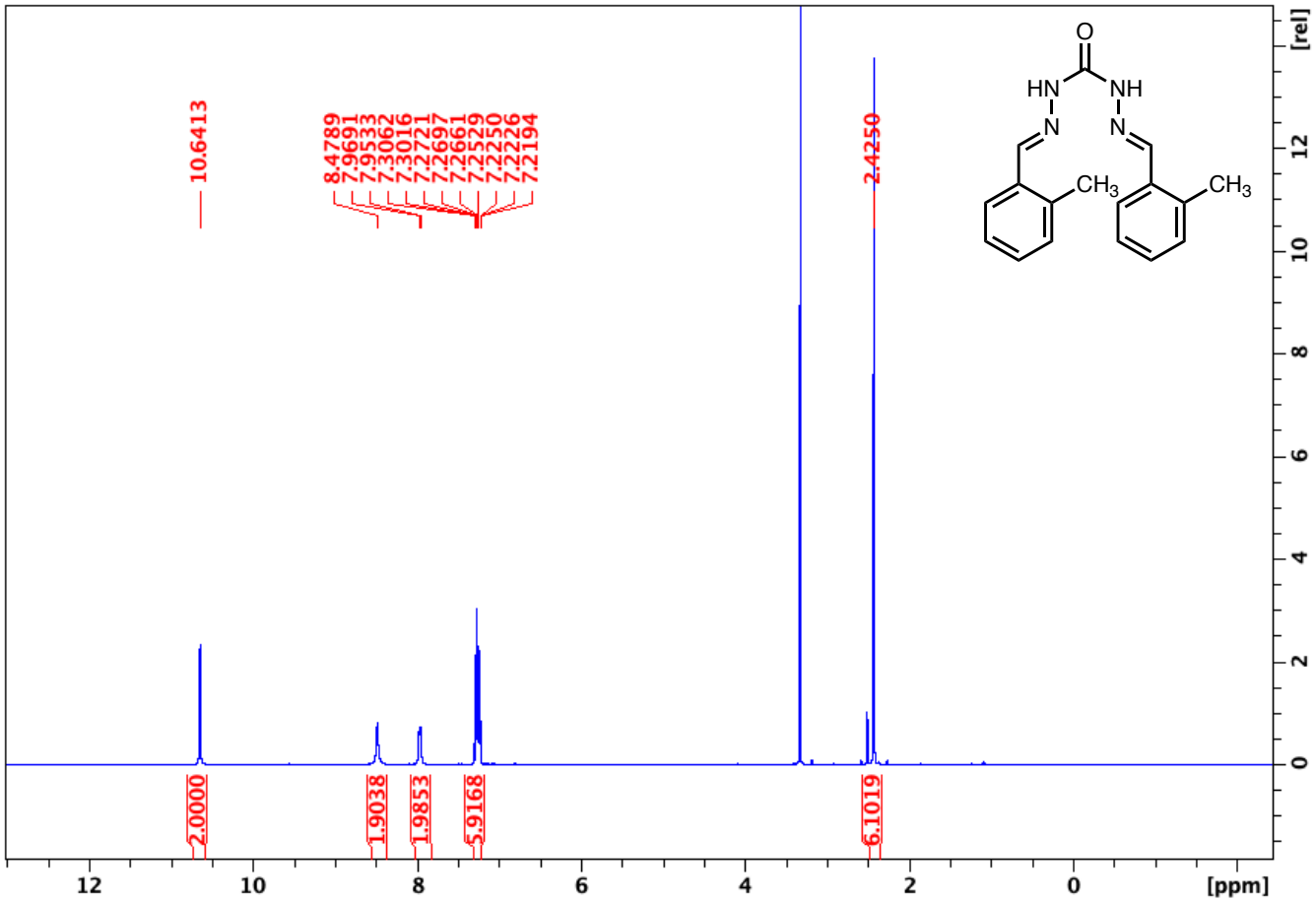


Fig. S63: ^{13}C NMR of **7a**

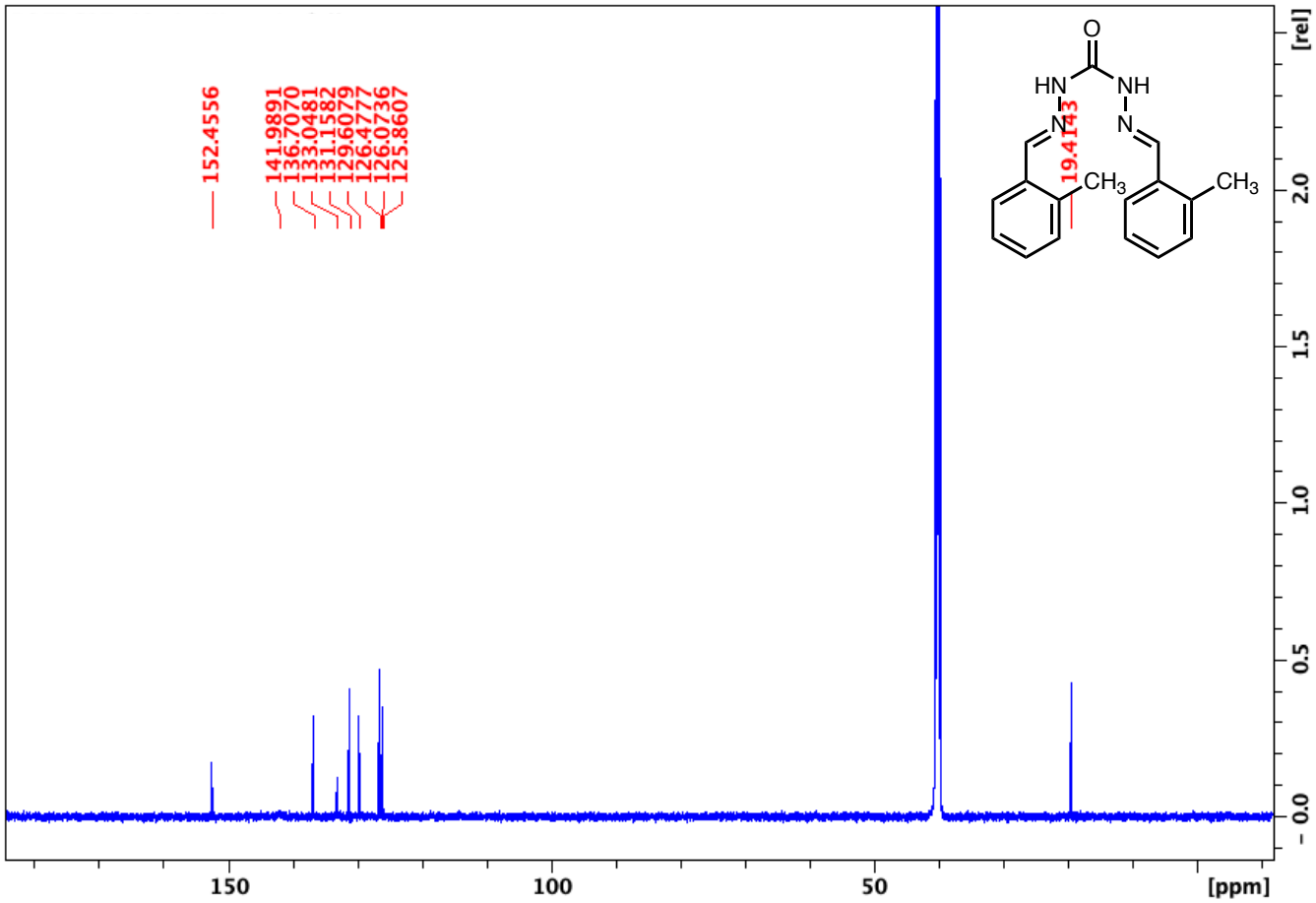


Fig. S64: ^{1}H NMR of **7b**

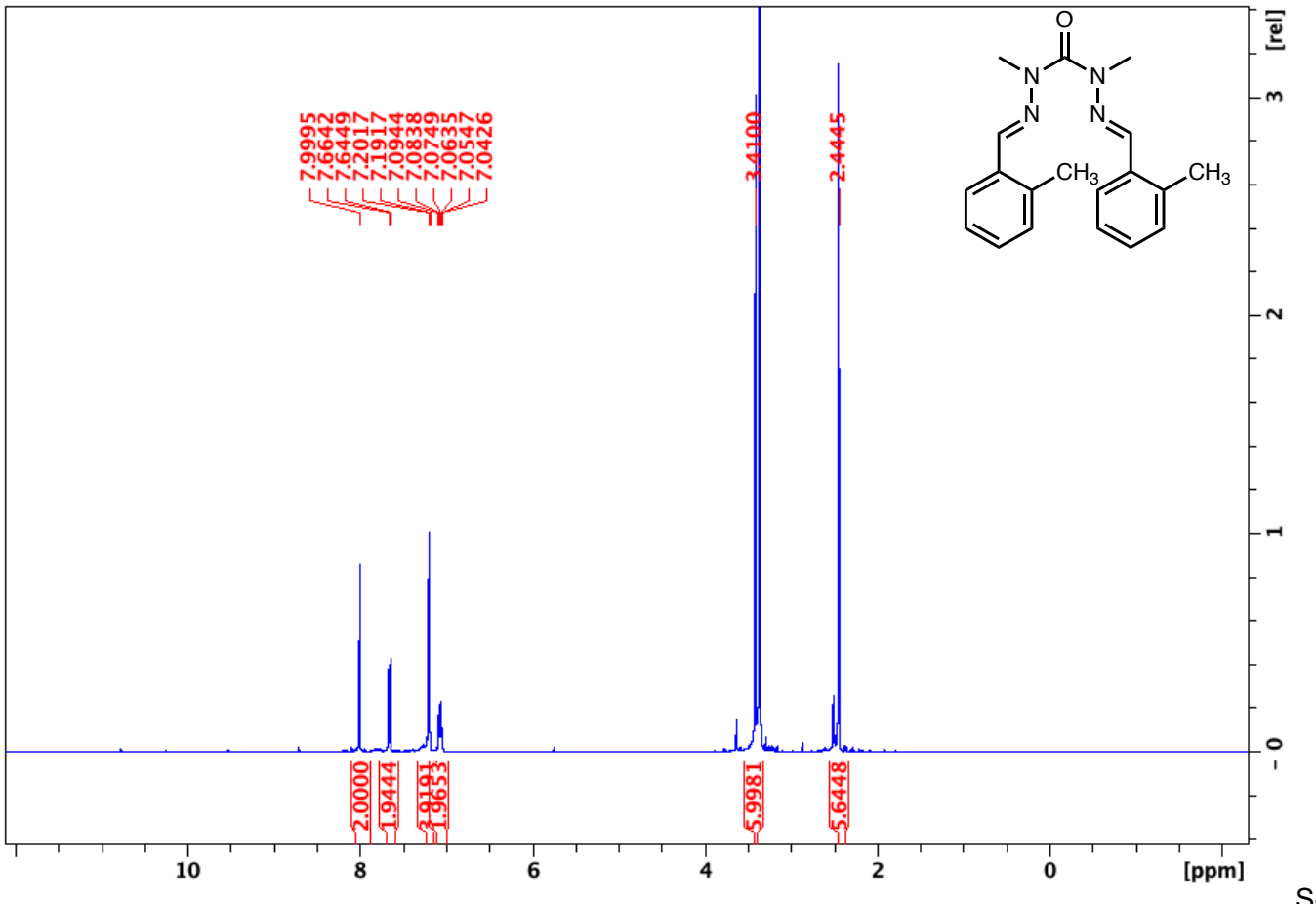


Fig. S65: ^{13}C NMR of **7b**

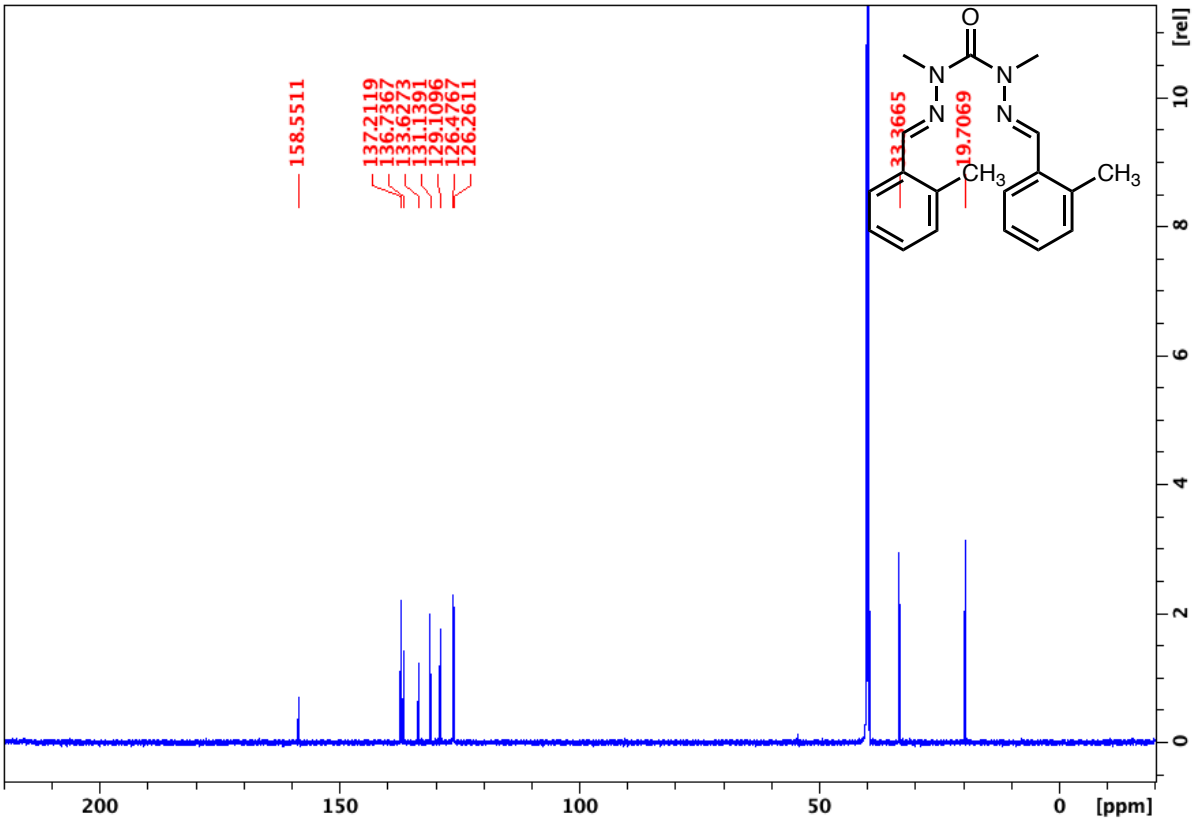


Fig. S66: ^{1}H NMR of **7c**

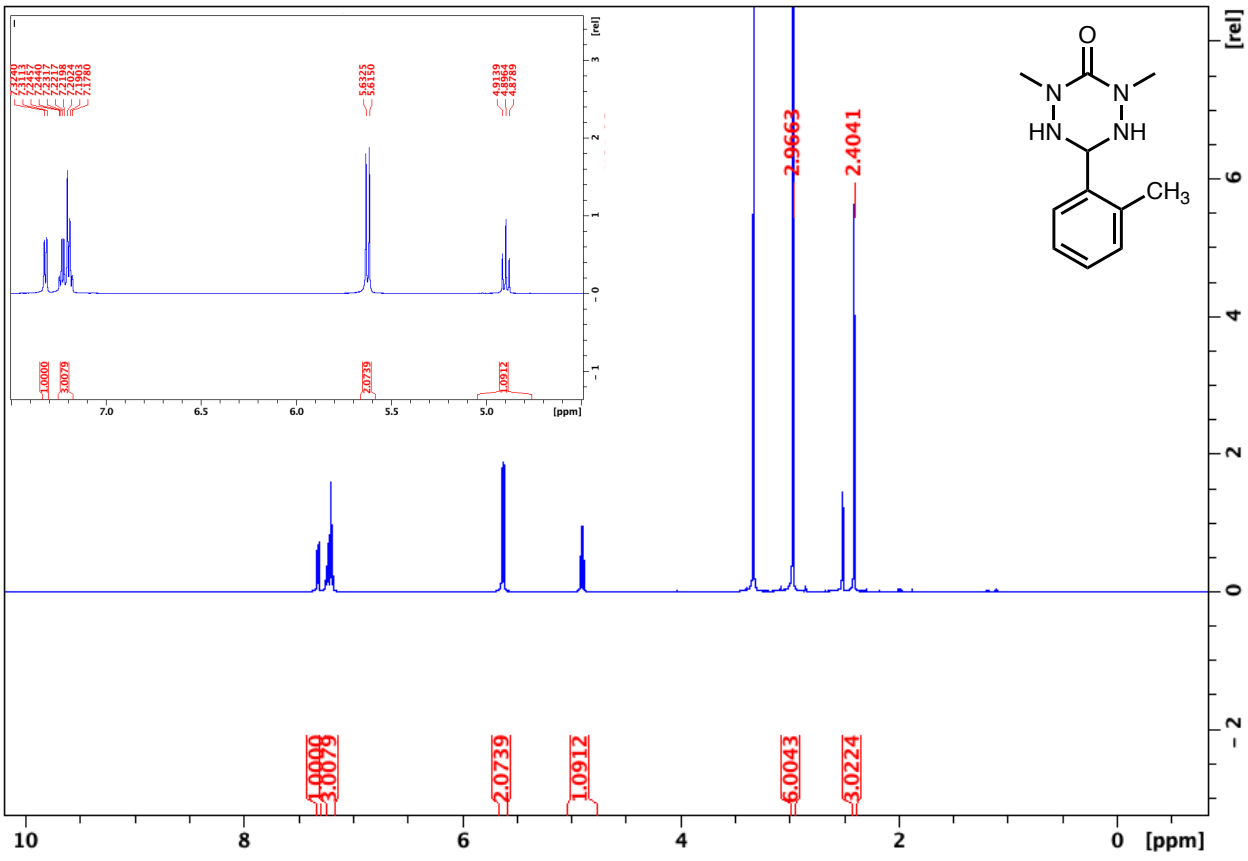


Fig. S67: ^{13}C NMR of **7c**

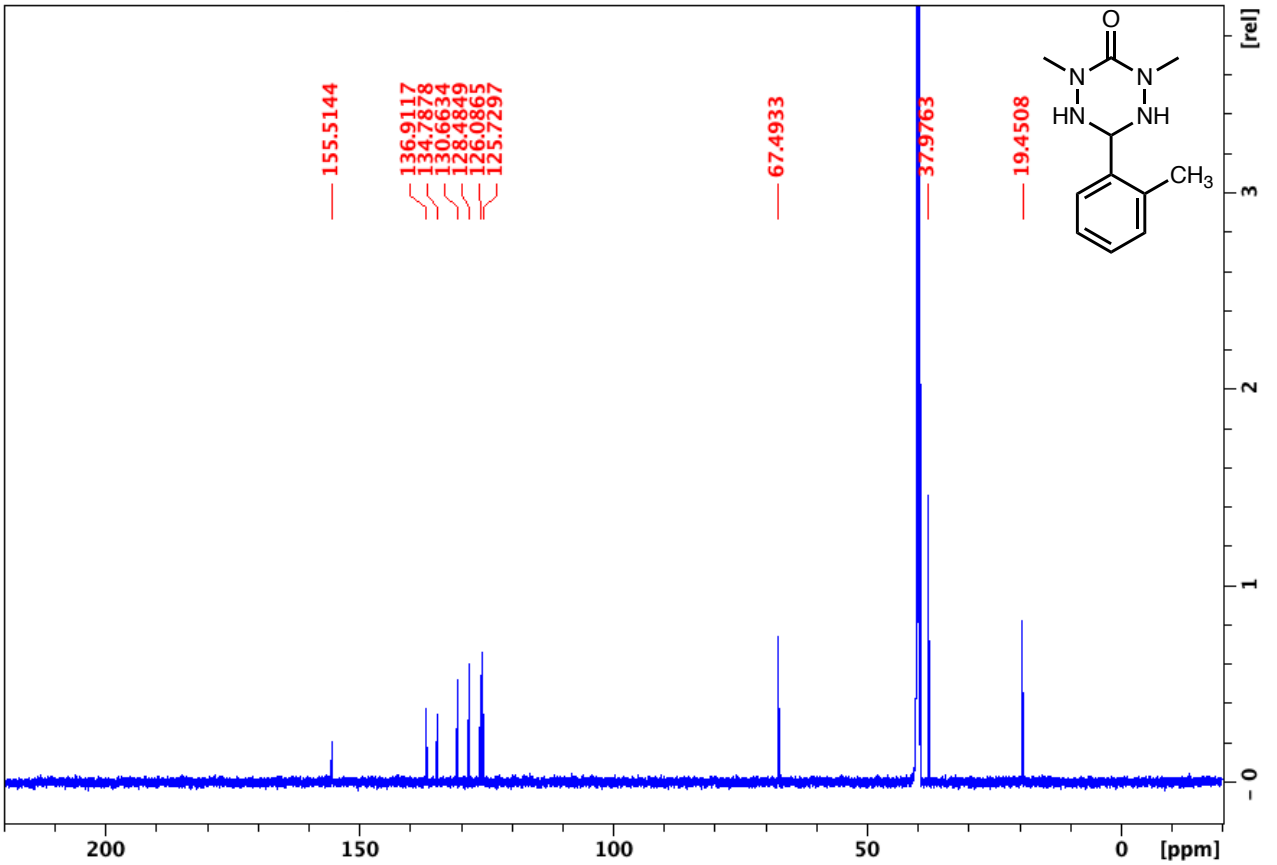


Fig. S68: ^{1}H NMR of **8a**

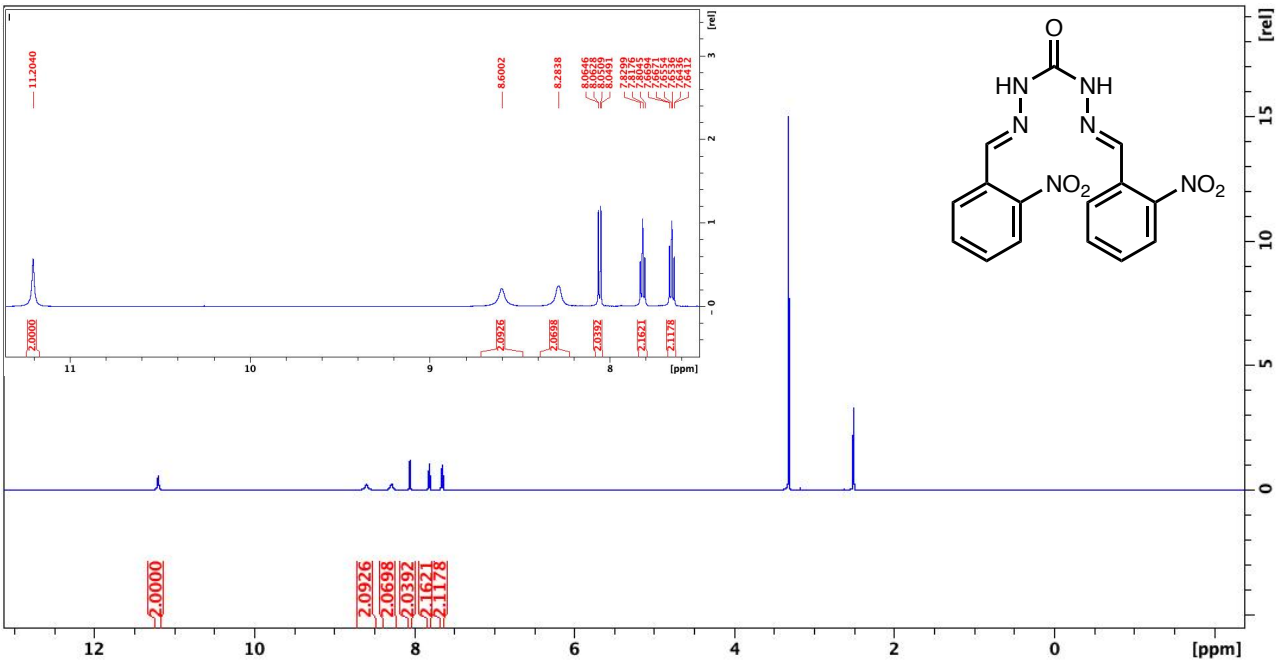


Fig. S69: ^{13}C NMR of **8a**

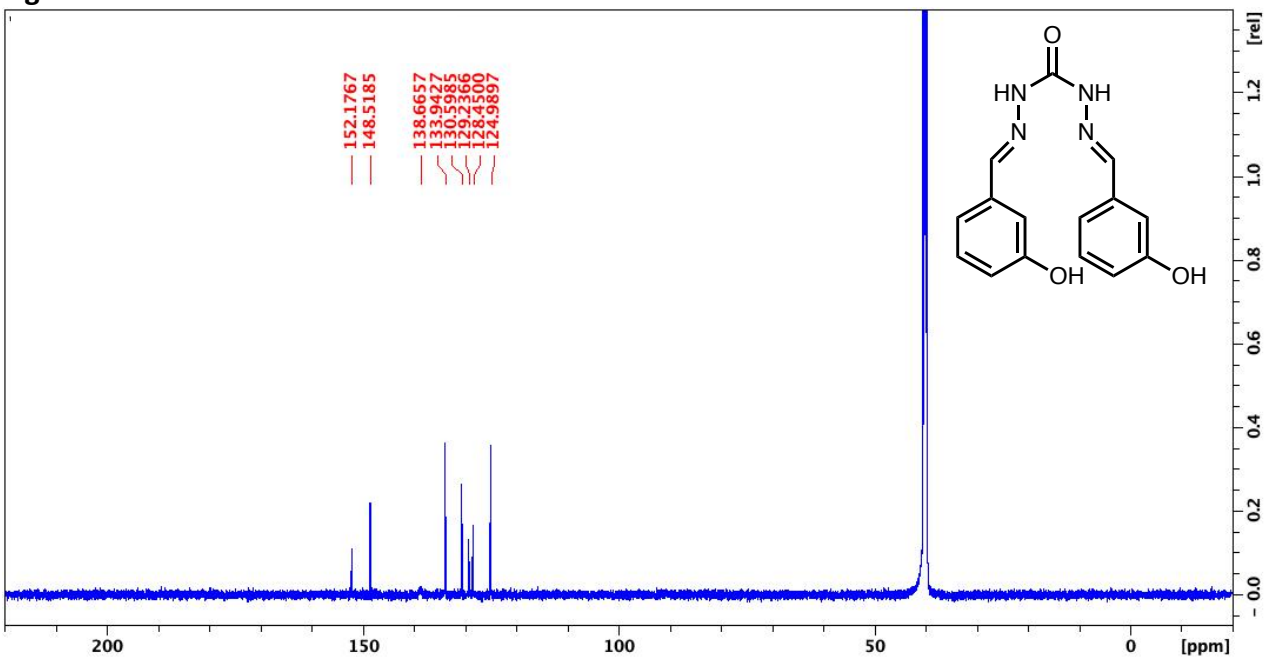


Fig. S70: ^{1}H NMR of **8b**

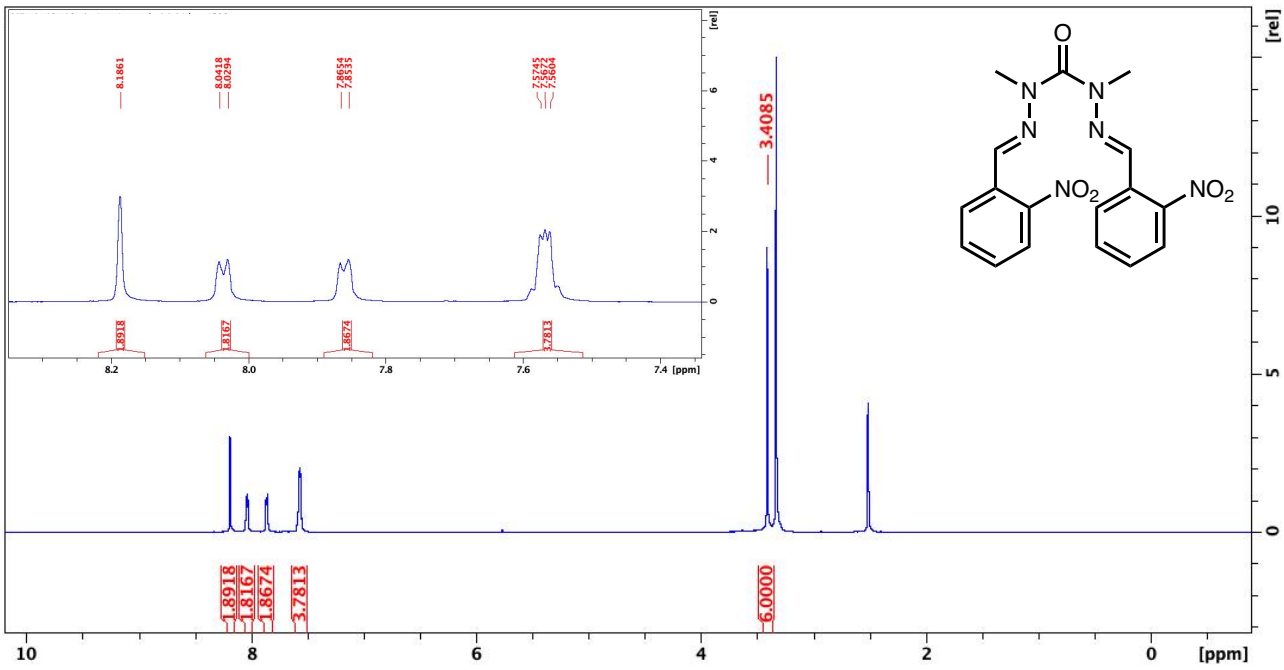


Fig. S71: ^{13}C NMR of **8b**

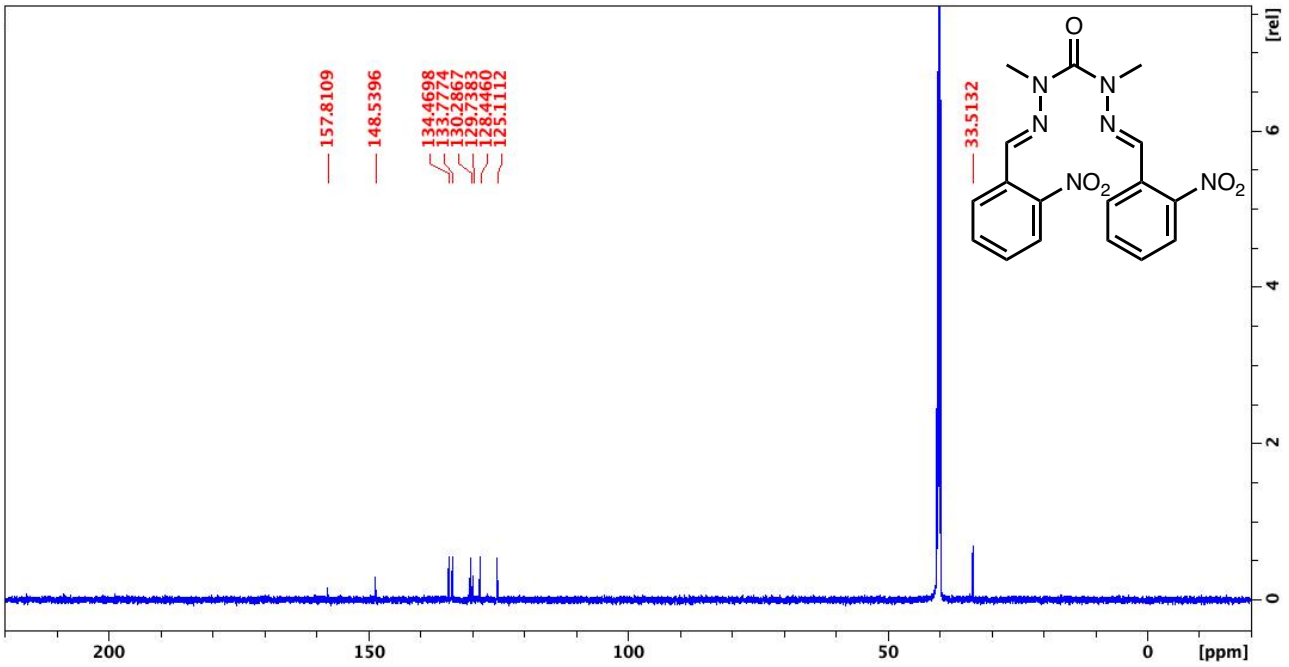


Fig. S72: ^{1}H NMR of **8c**

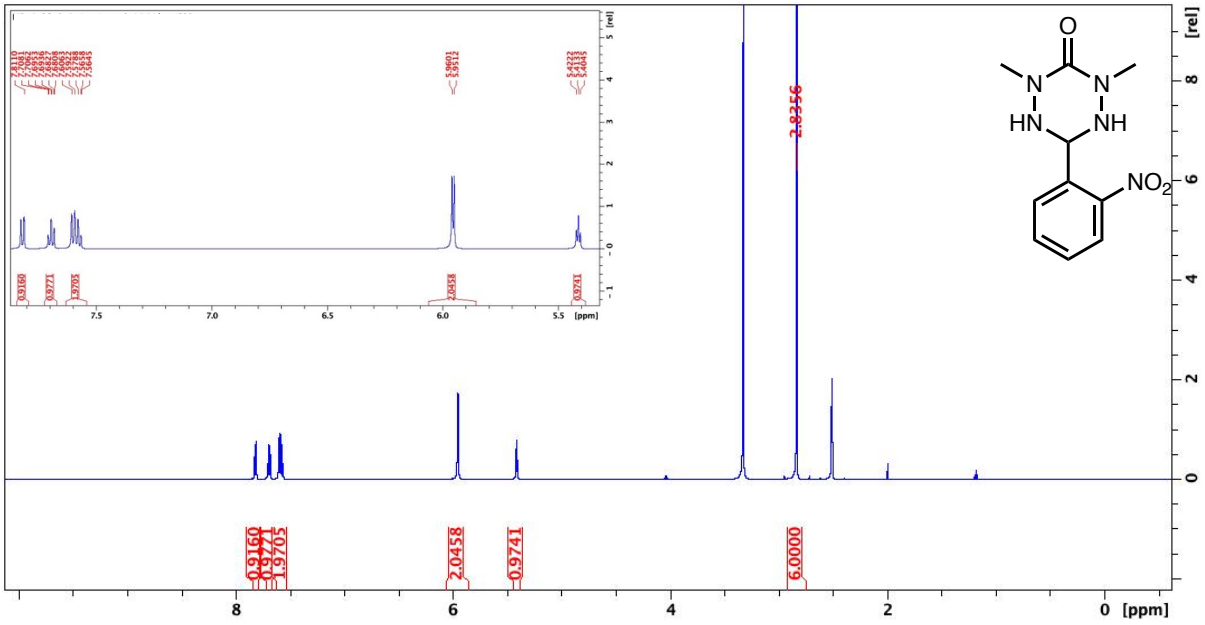


Fig. S73: ^{13}C NMR of **8c**

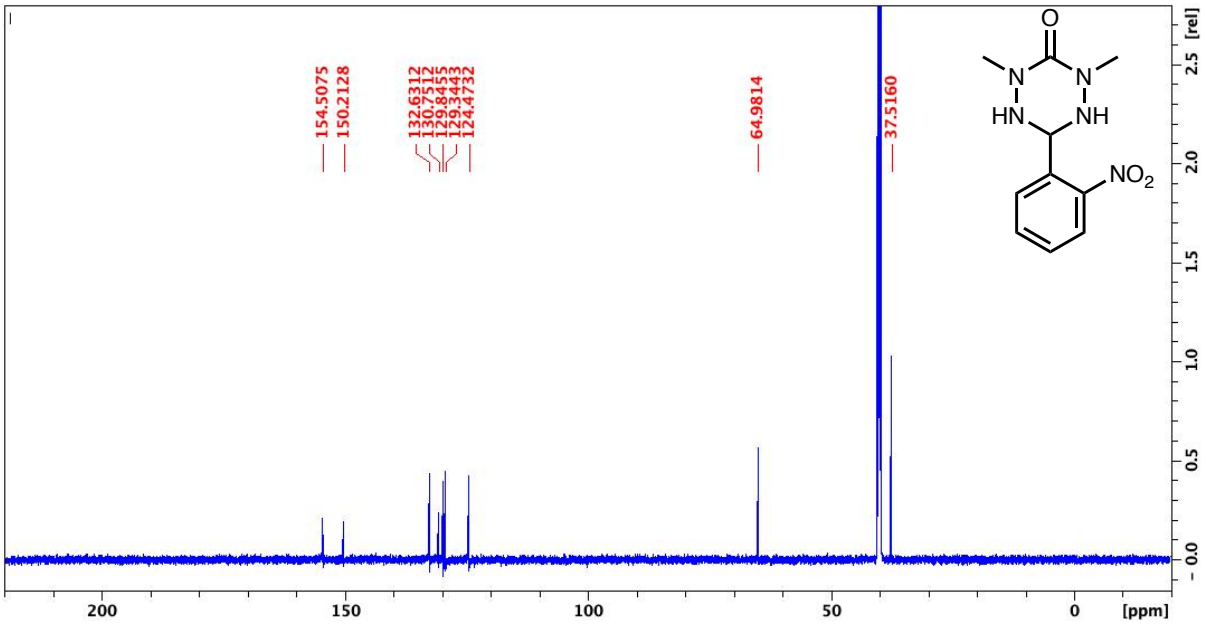


Fig. S74: ^{1}H NMR of **9a**

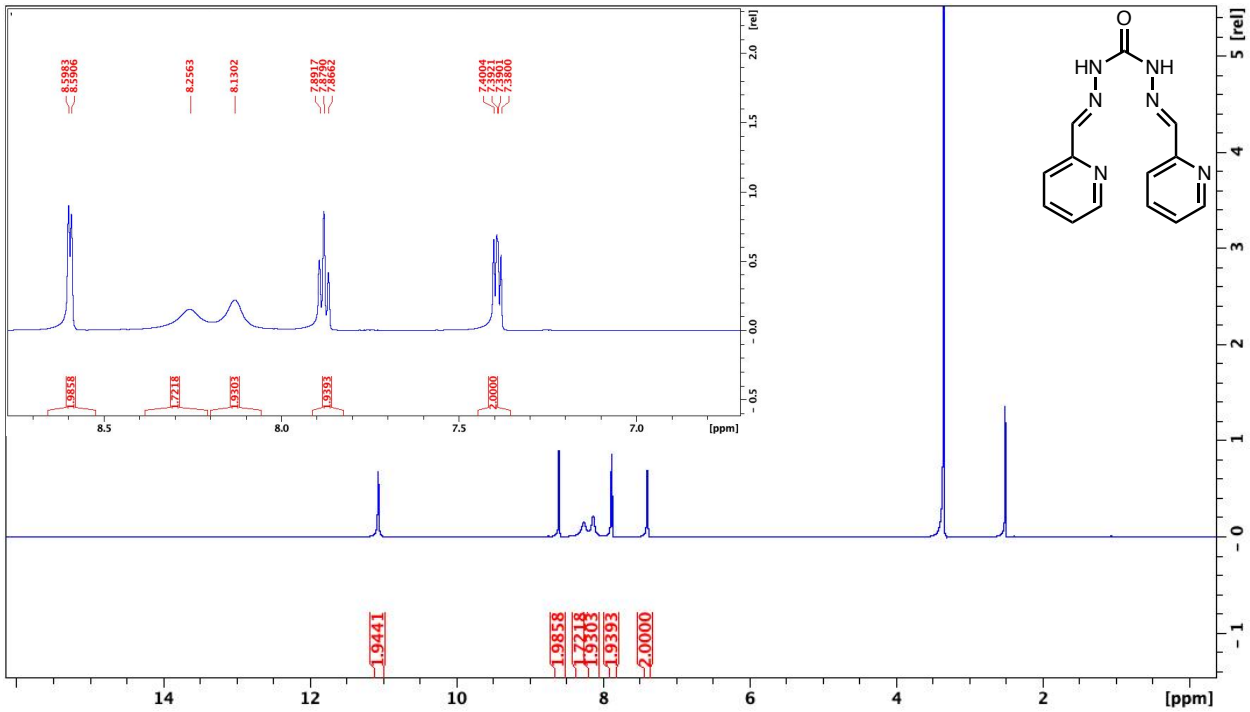


Fig. S75: ^{13}C NMR of **9a**

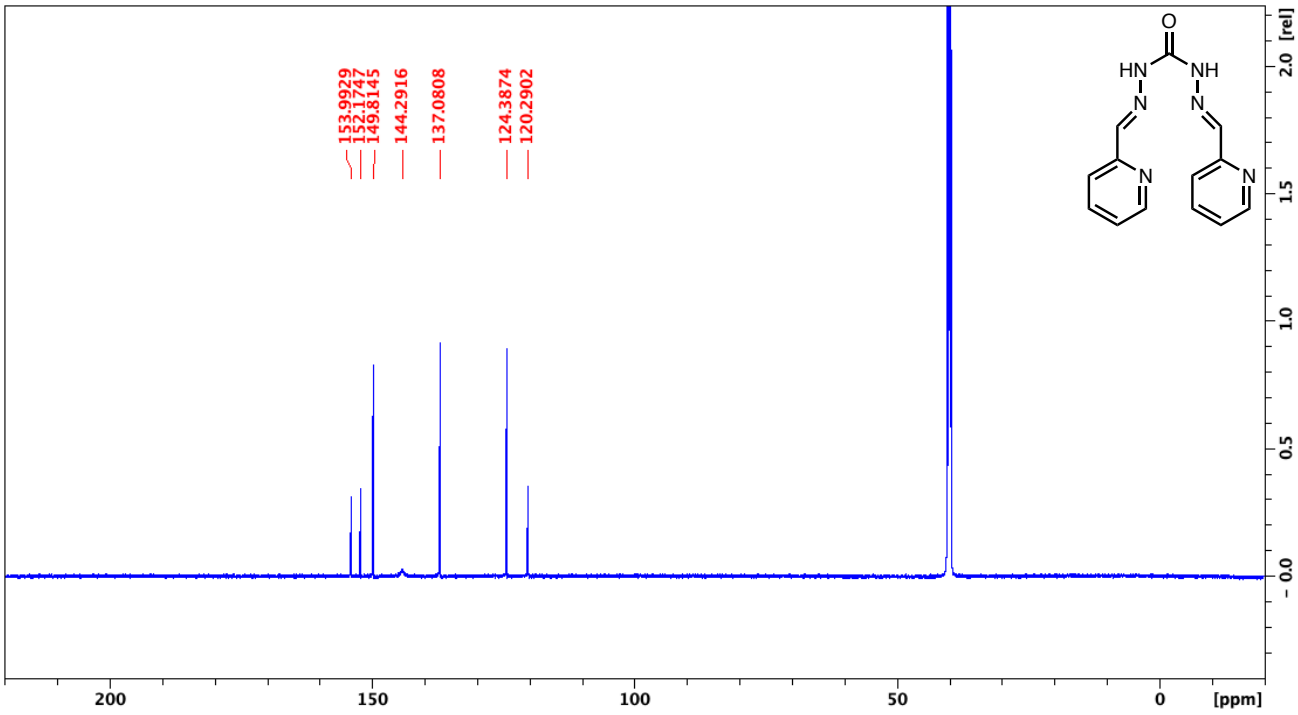


Fig. S76: ^{1}H NMR of **9b**

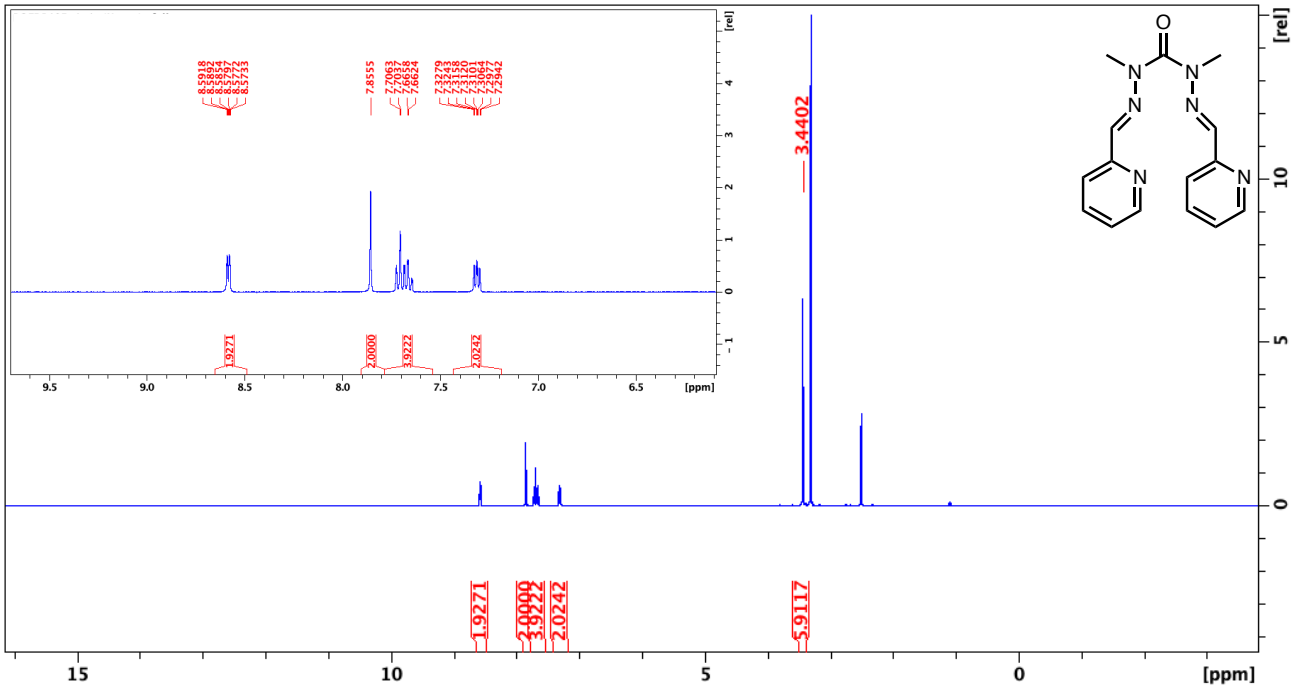


Fig. S77: ^{13}C NMR of **9b**

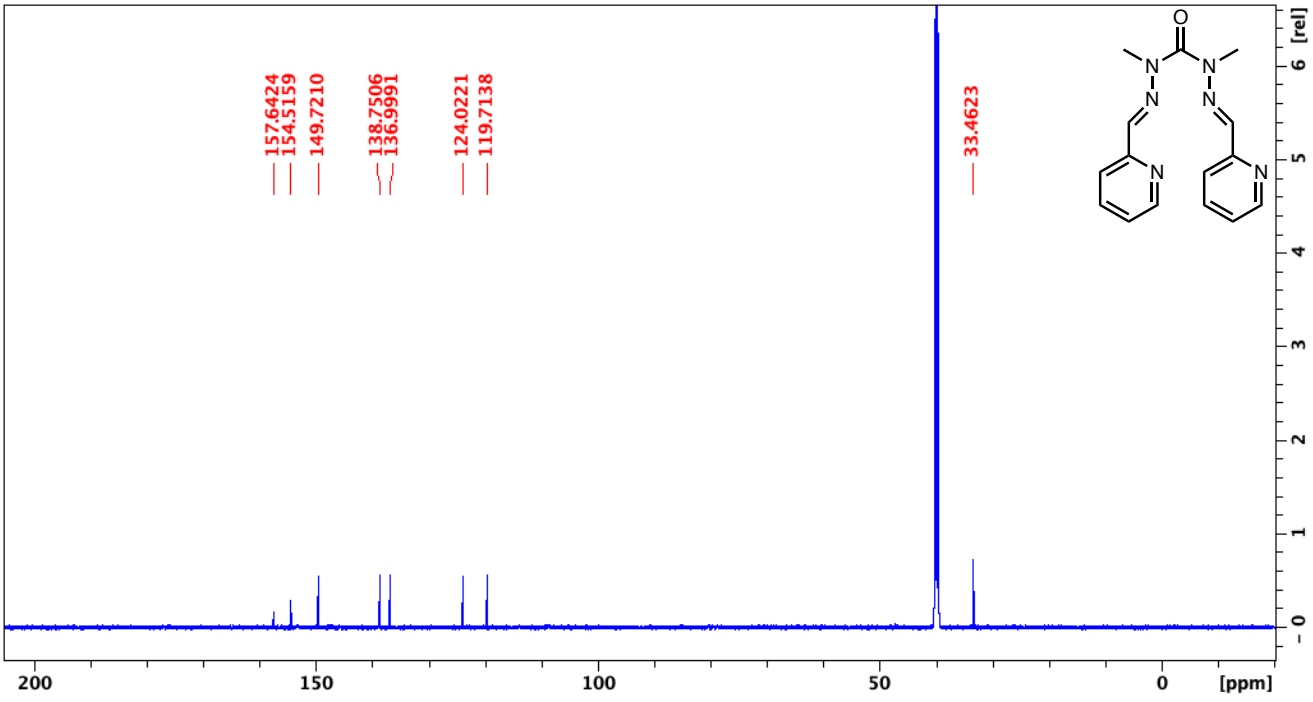


Fig. S78: ^{1}H NMR of **9b** decomposition

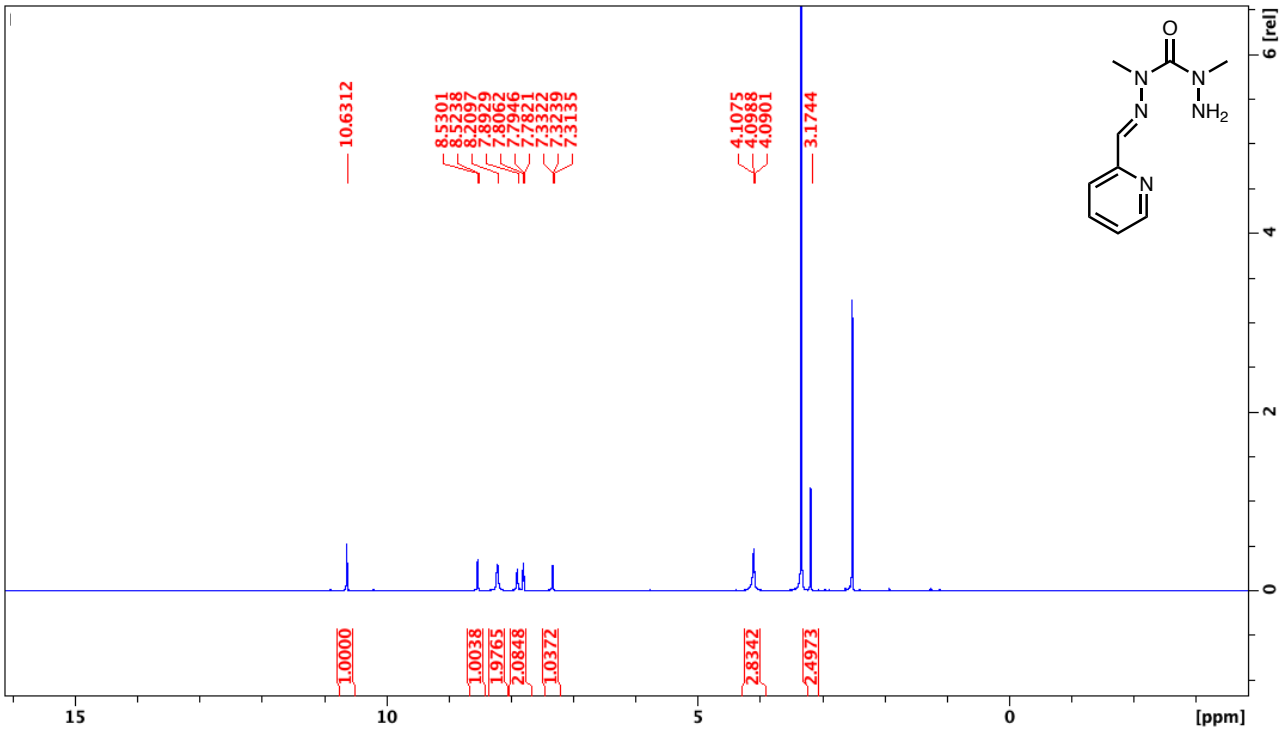


Fig. S79: ^{13}C NMR of **9b** decomposition

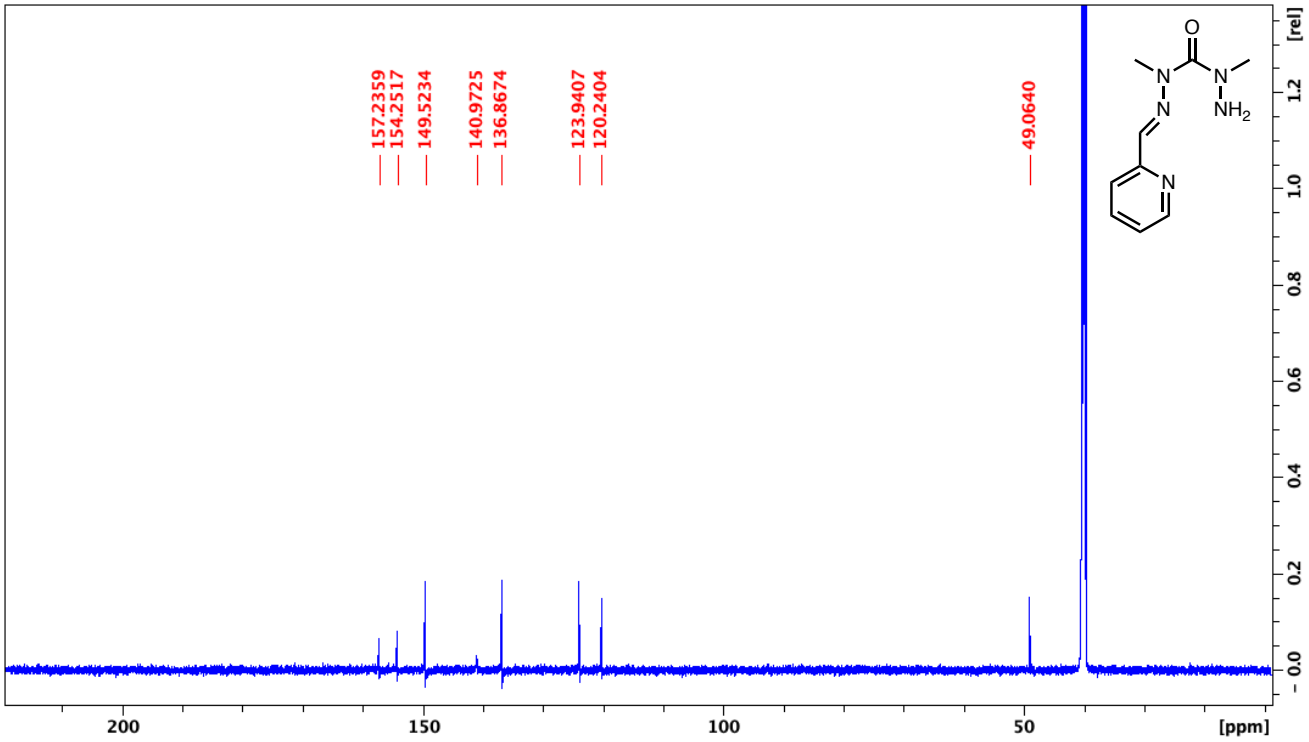


Fig. S80: ^{1}H NMR of **9c**

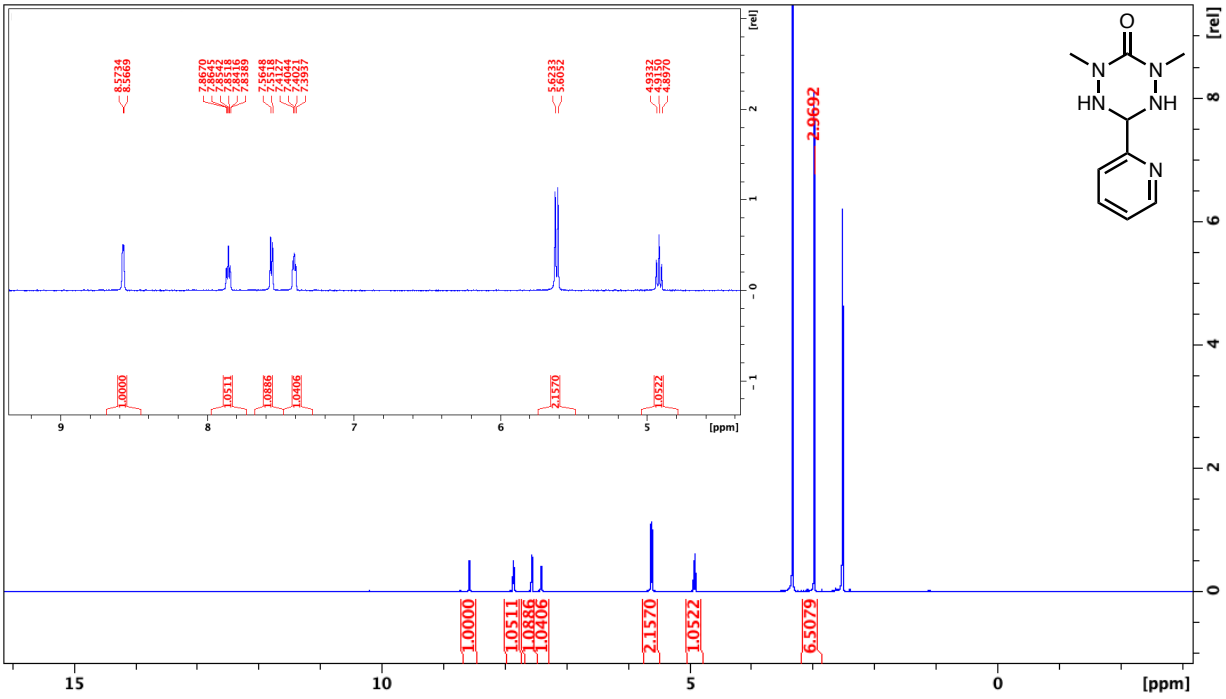


Fig. S81: ^{13}C NMR of **9c**

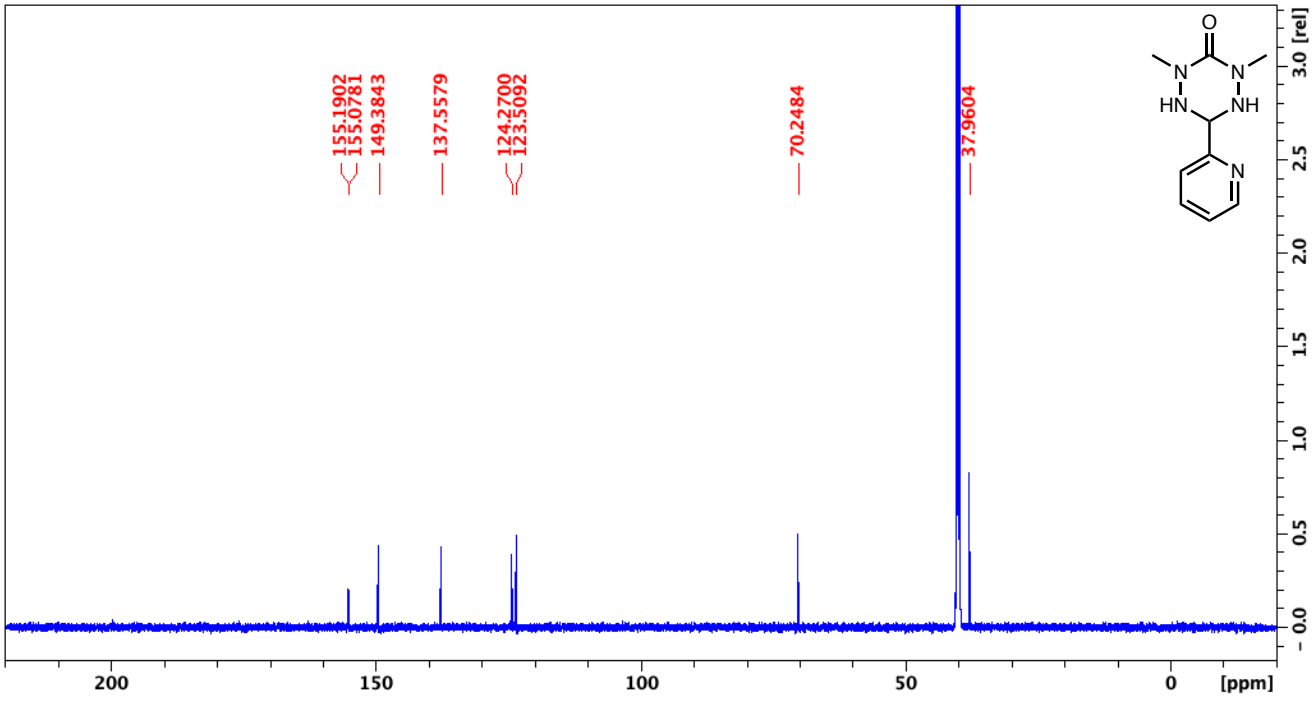


Fig. S82: ^{1}H NMR of **10a**

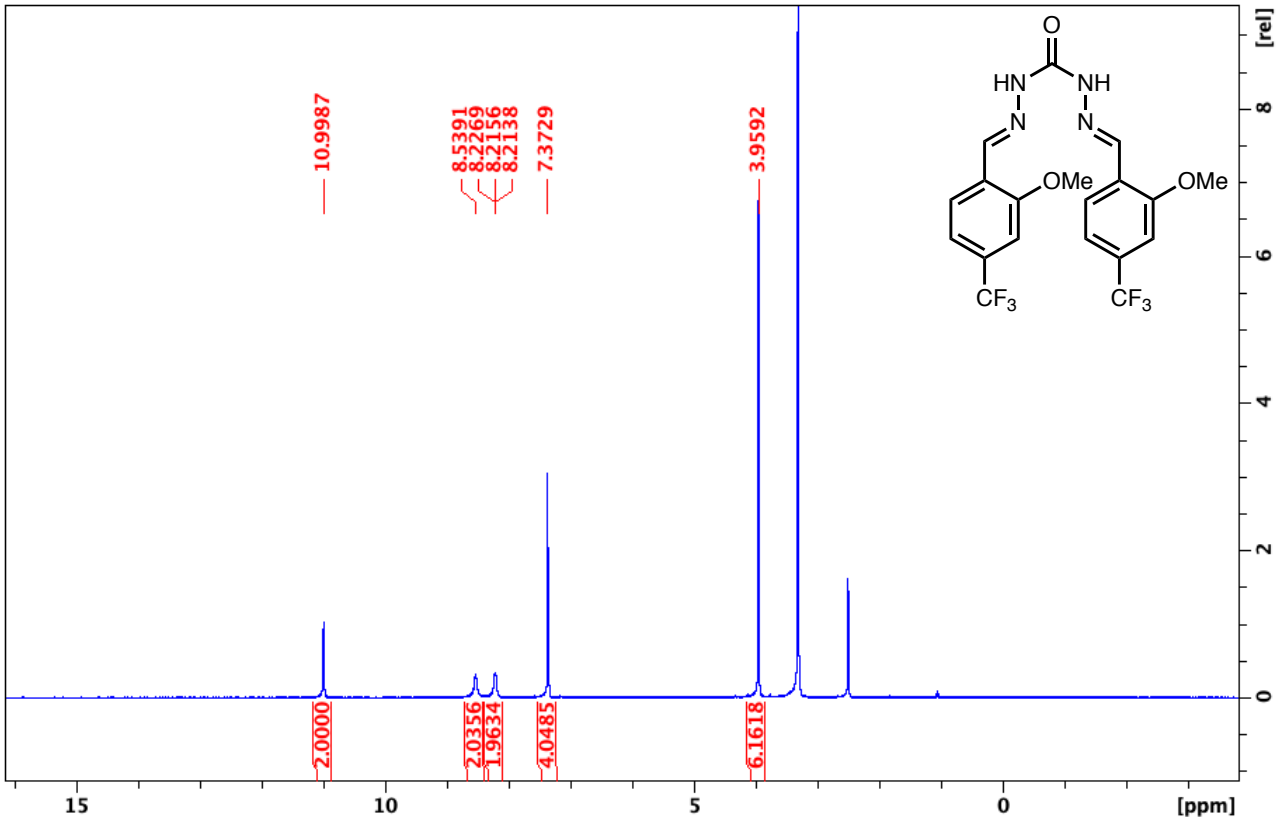


Fig. S83: ^{13}C NMR of **10a**

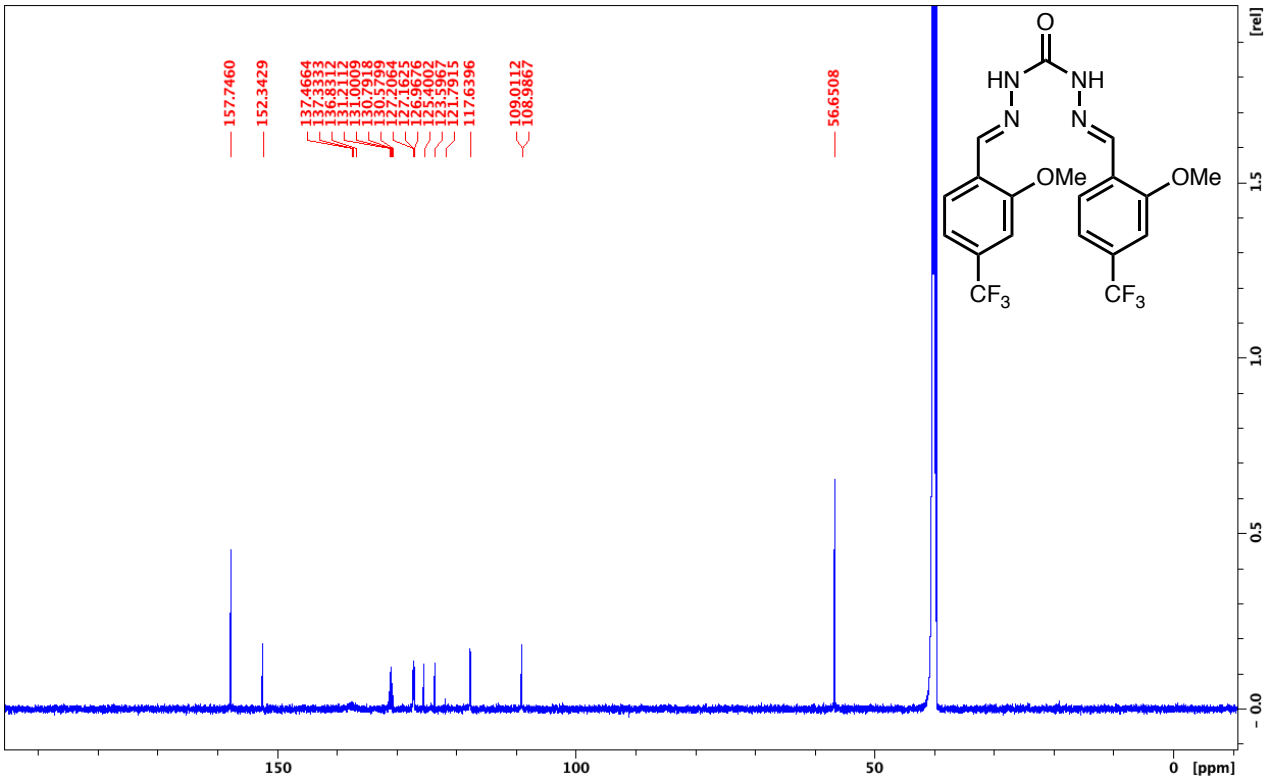


Fig. S84: ^{19}F NMR of **10a**

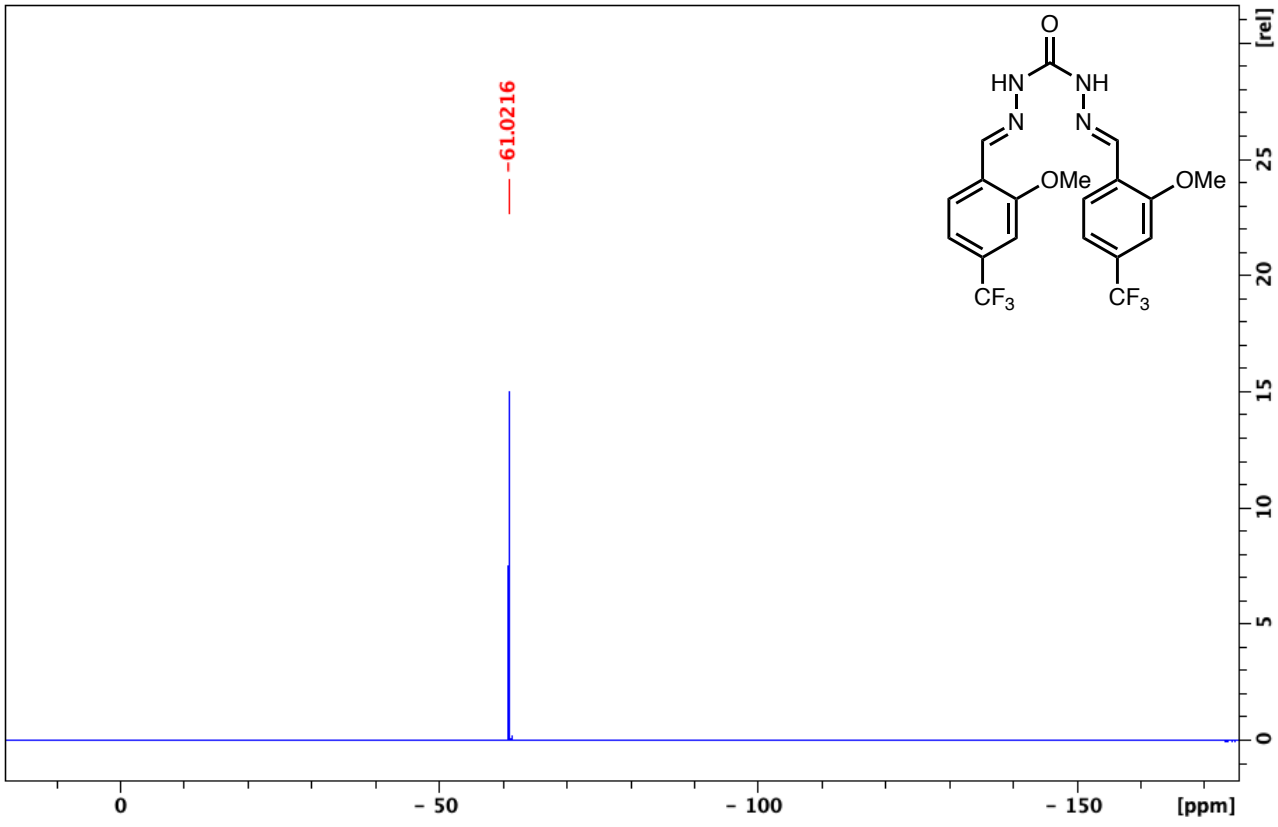


Fig. S85: ^{1}H NMR of **10b**

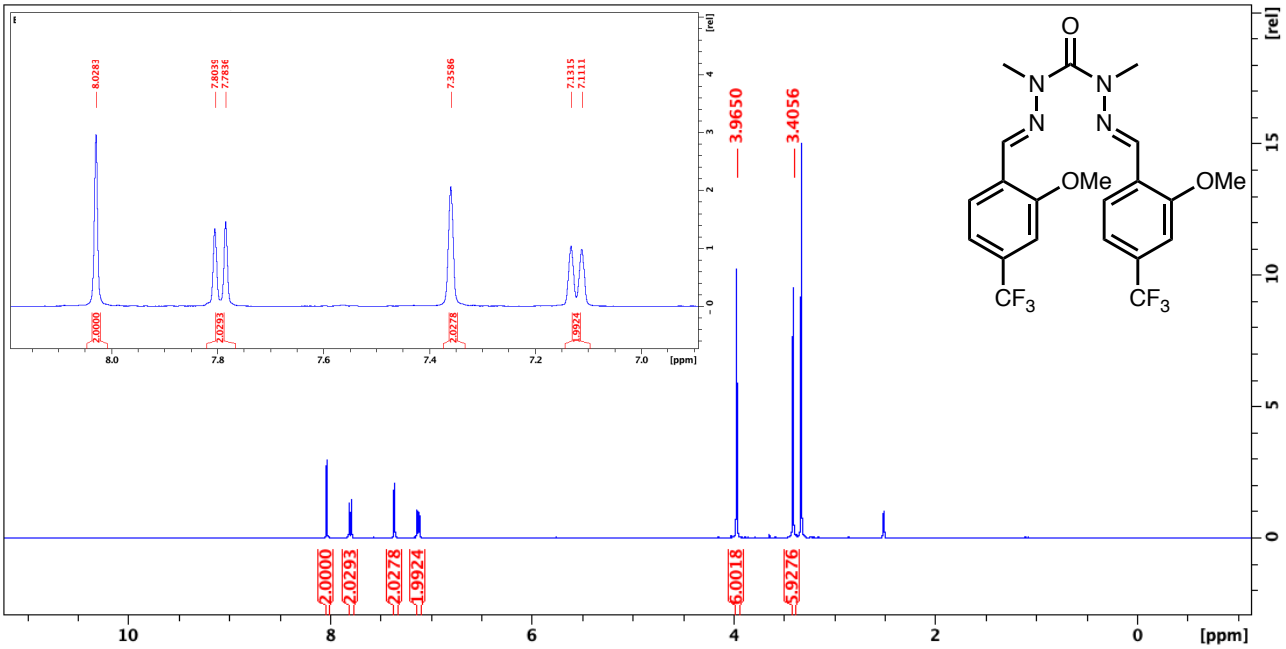


Fig. S86: ^{13}C NMR of **10b**

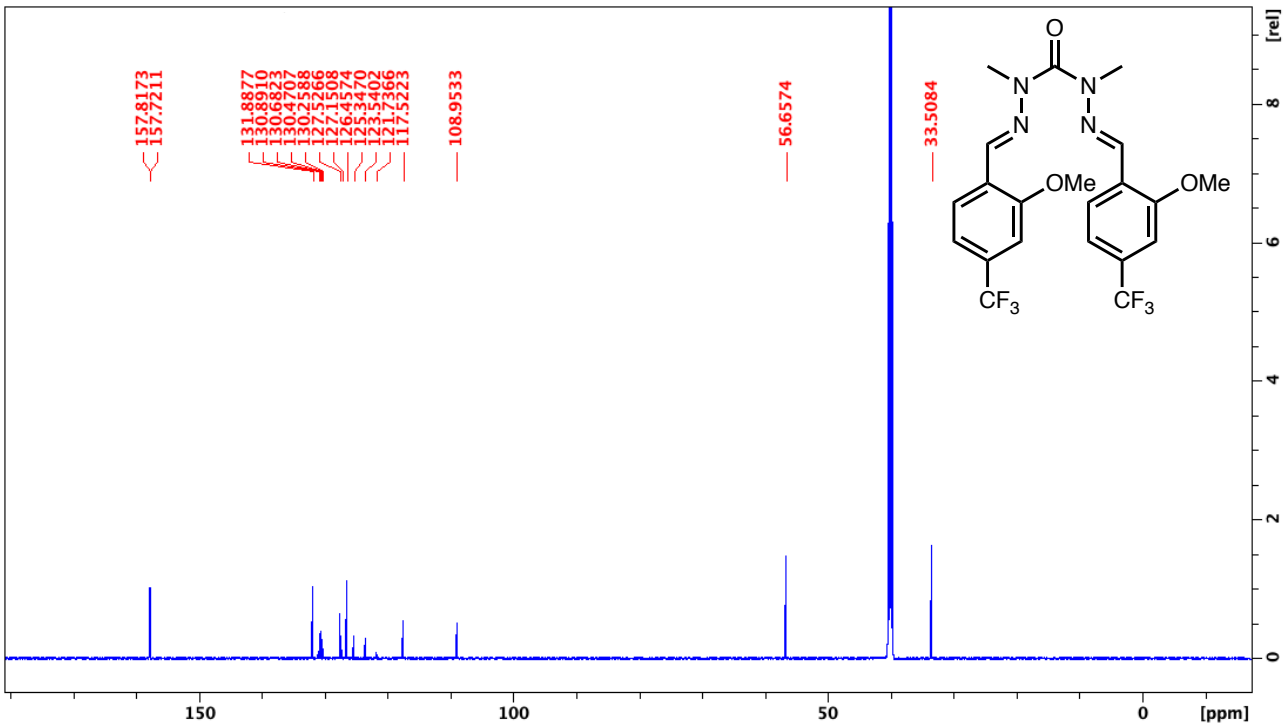


Fig. S87: ^{19}F NMR of **10b**

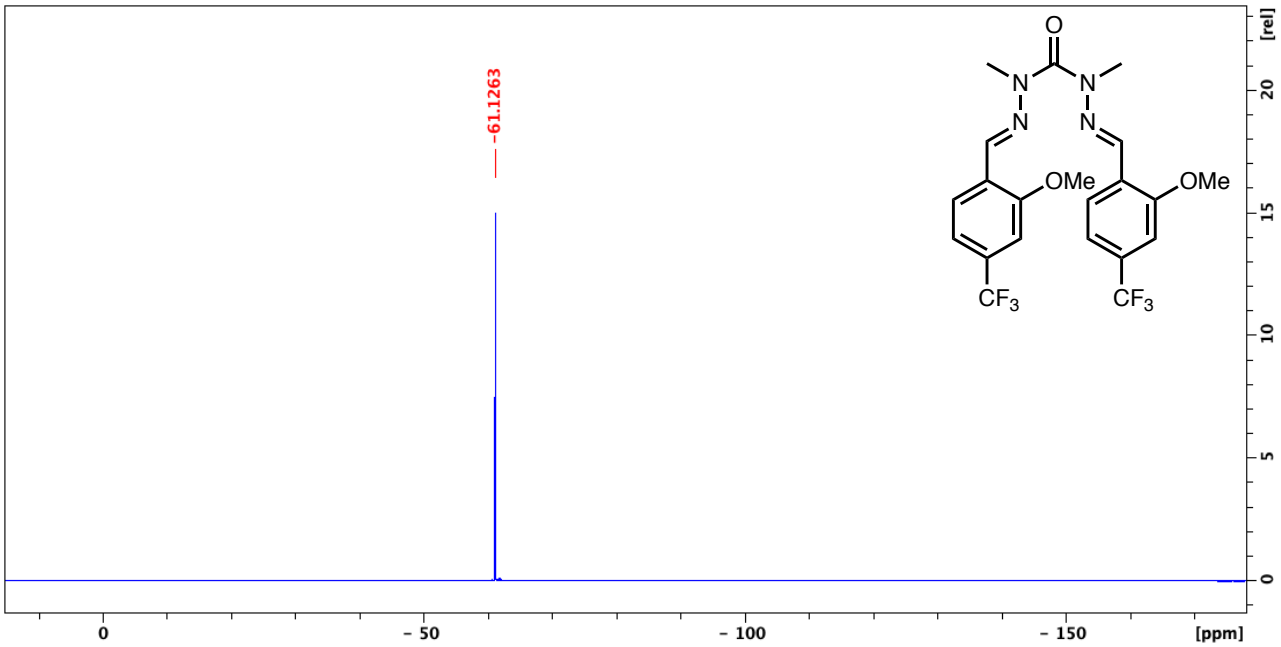


Fig. S88: ^{1}H NMR of **10c**

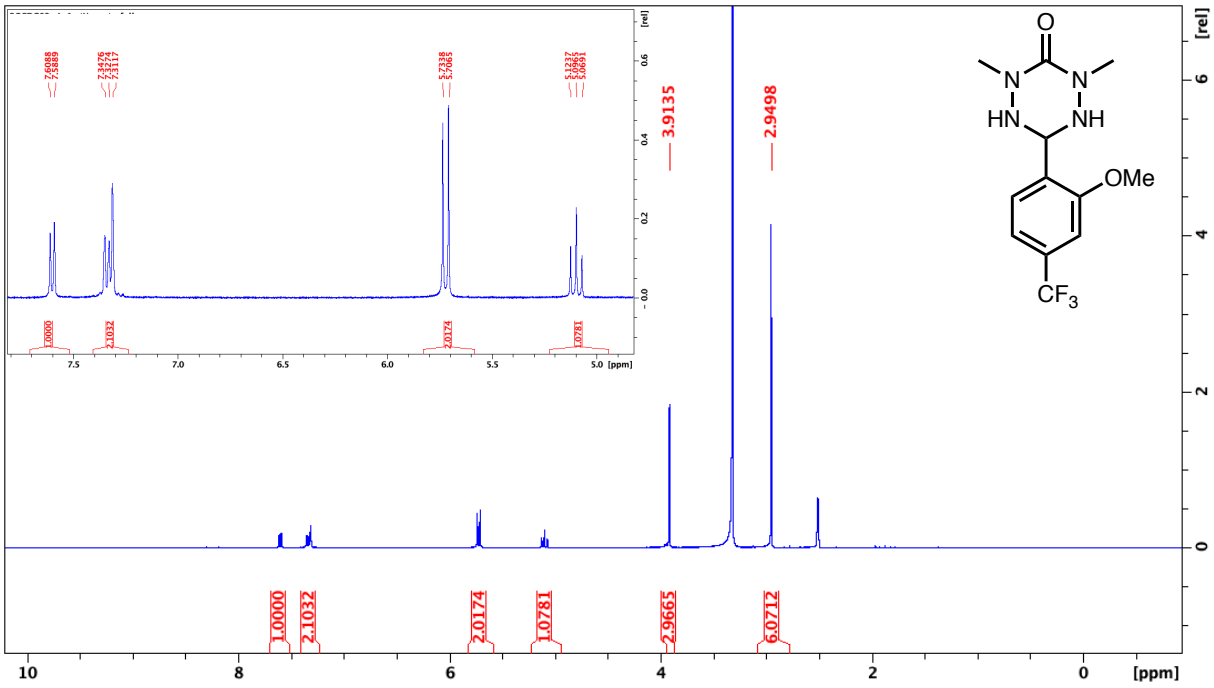


Fig. S89: ^{13}C NMR of **10c**

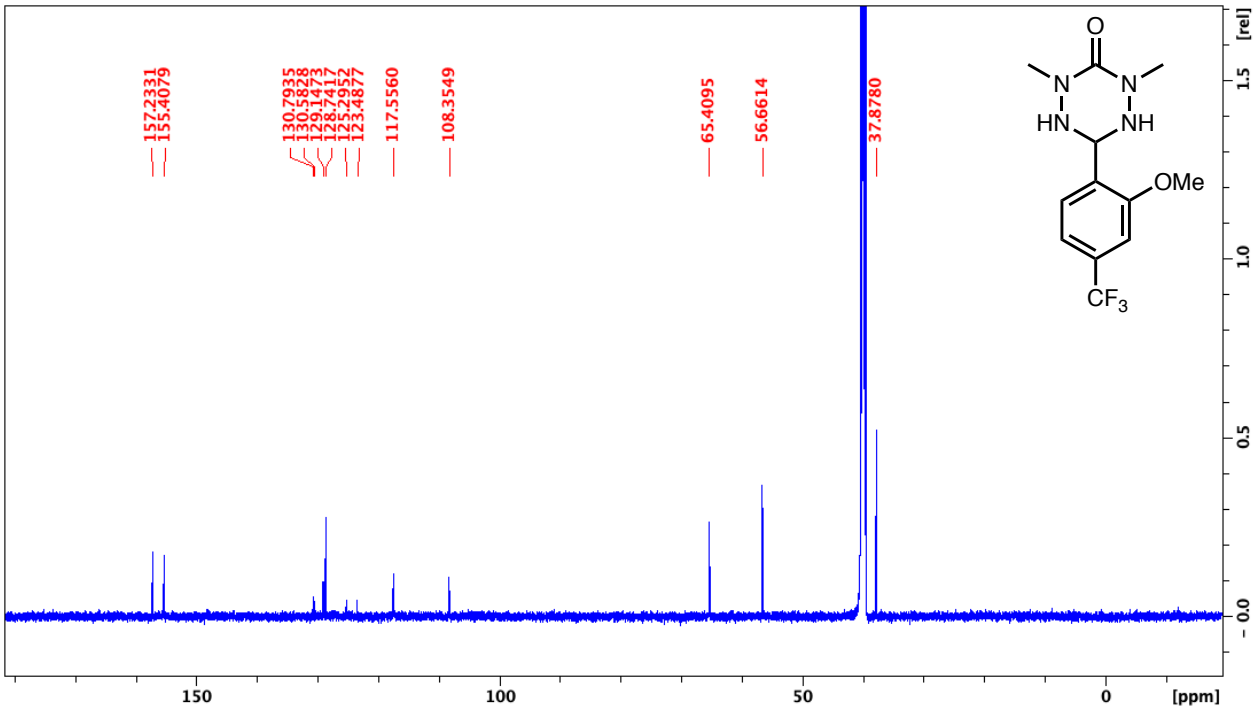


Fig. S90: ^{19}F NMR of **10c**

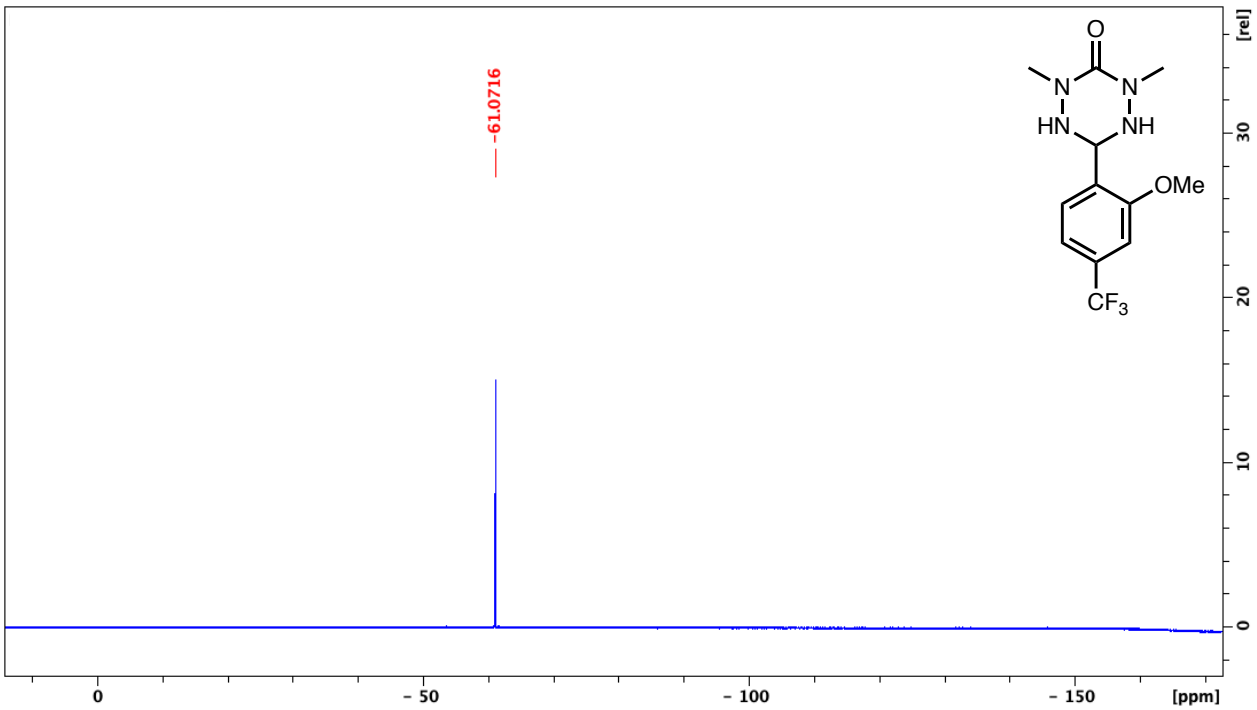


Fig. S91: ^{1}H NMR of **11a**

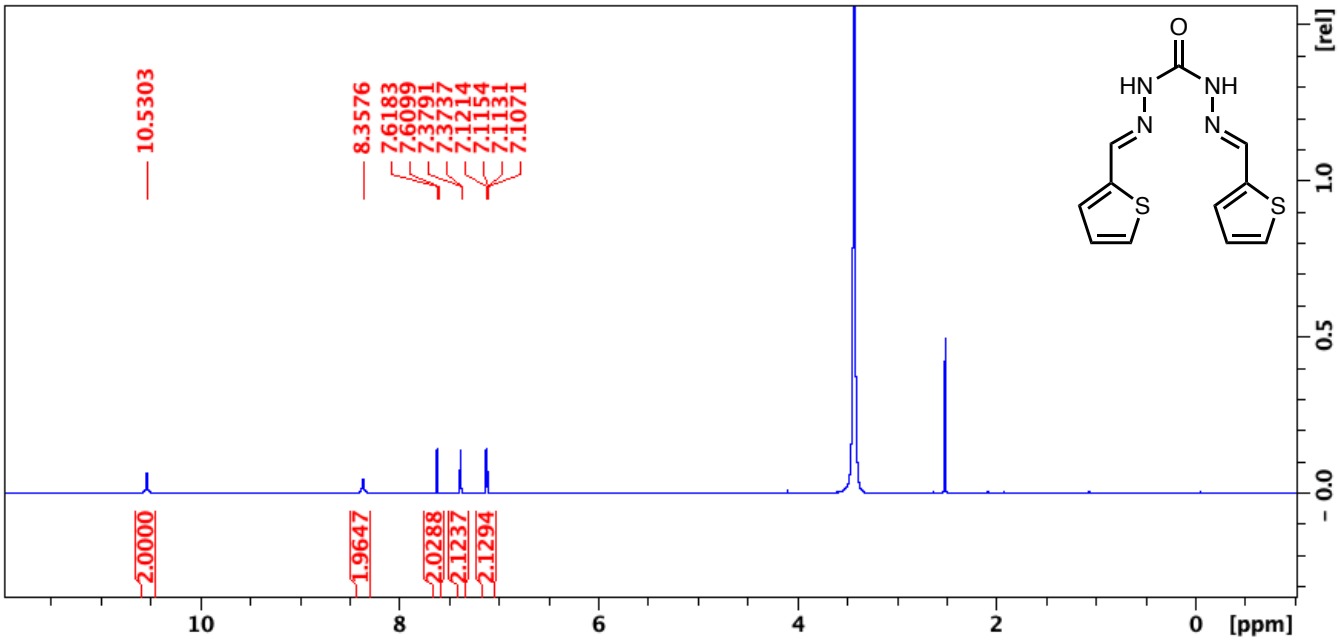


Fig. S92: ^{13}C NMR of **11a**

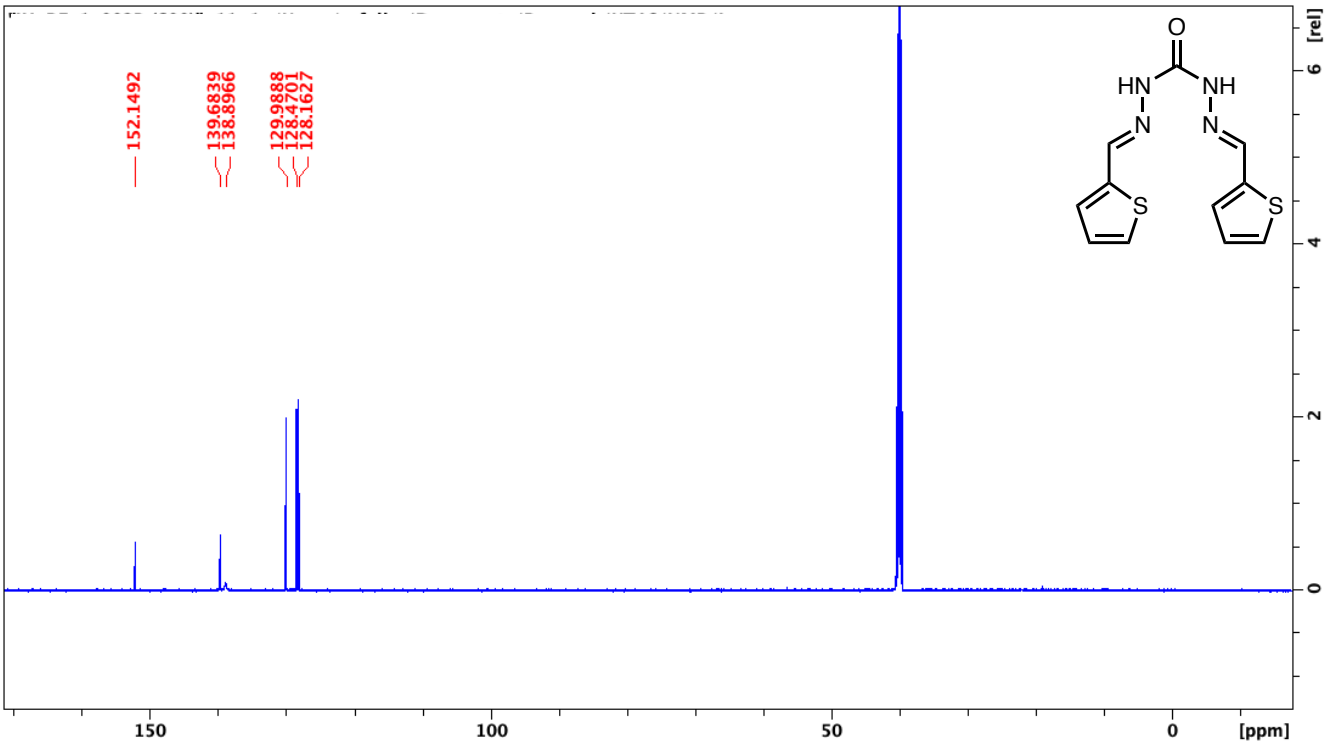


Fig. S93: ^{1}H NMR of **11b**

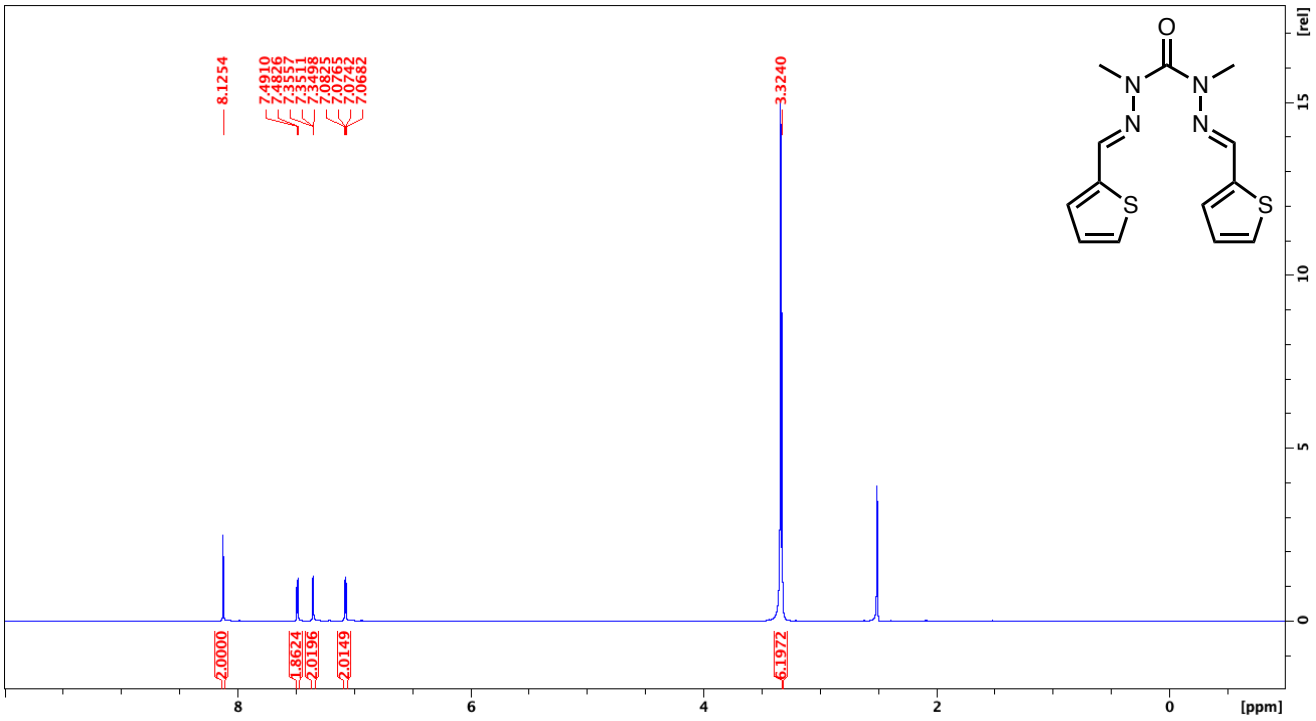


Fig. S94: ^{13}C NMR of **11b**

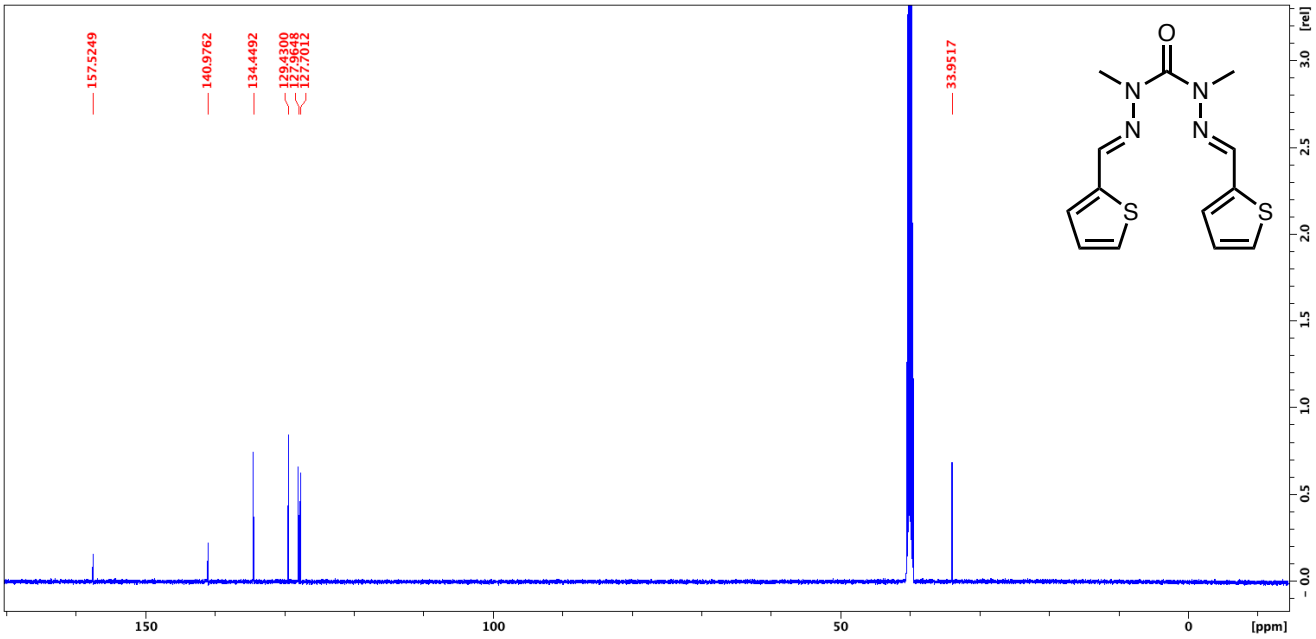


Fig. S95: ^{1}H NMR of **11c**

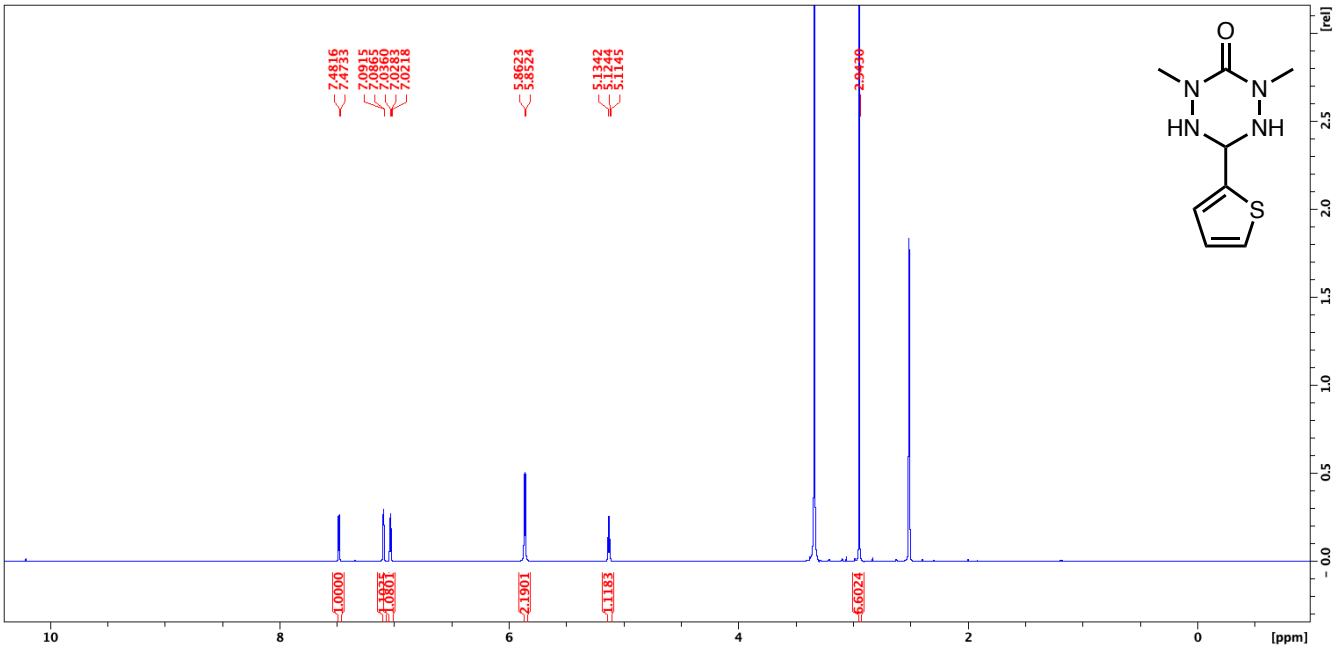


Fig. S96: ^{13}C NMR of **11c**

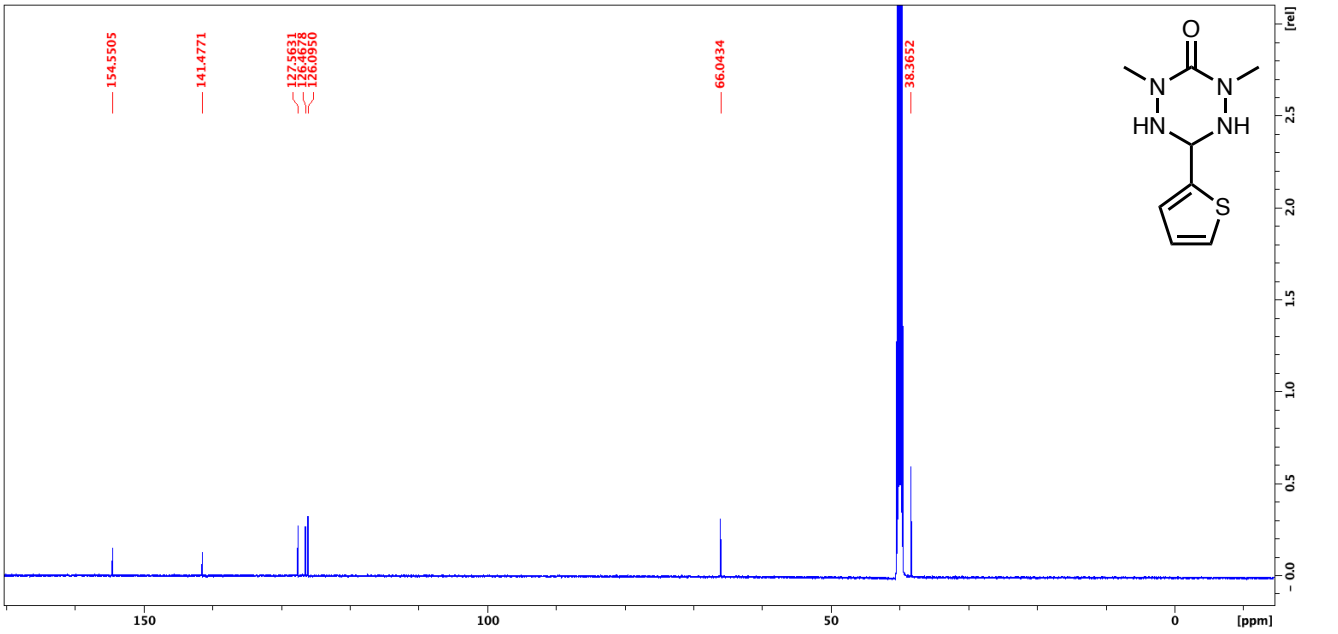
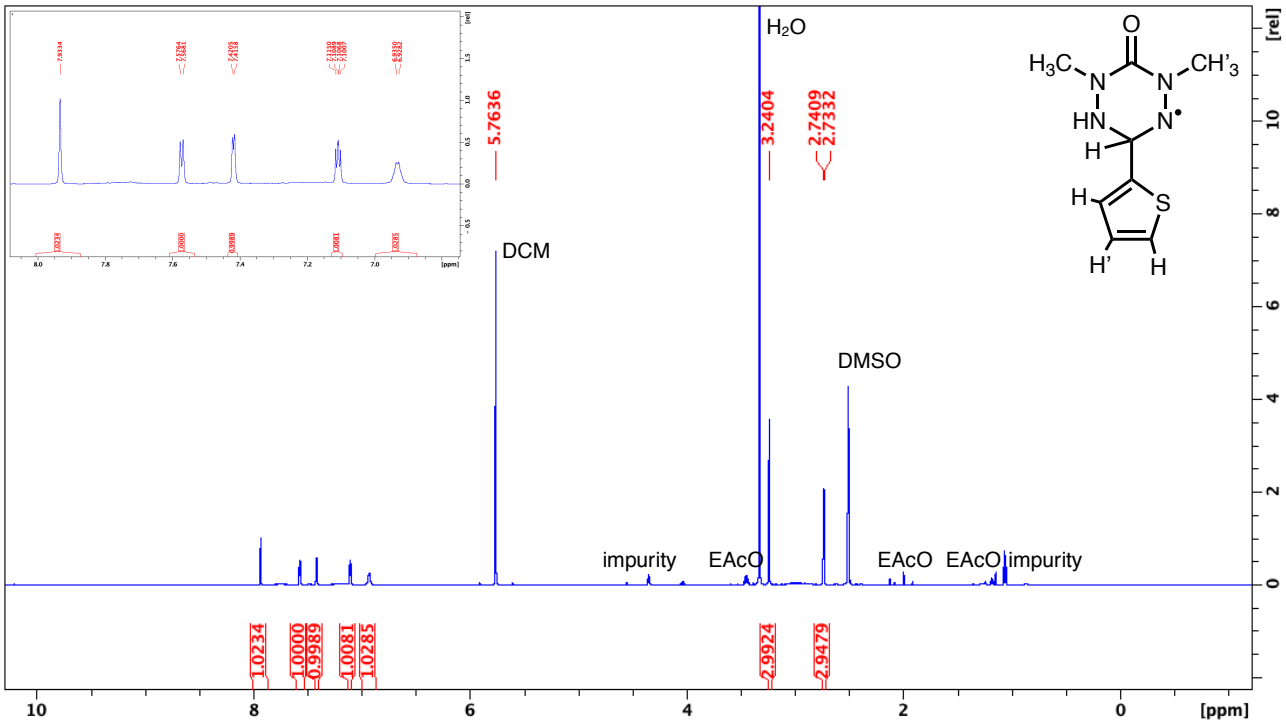
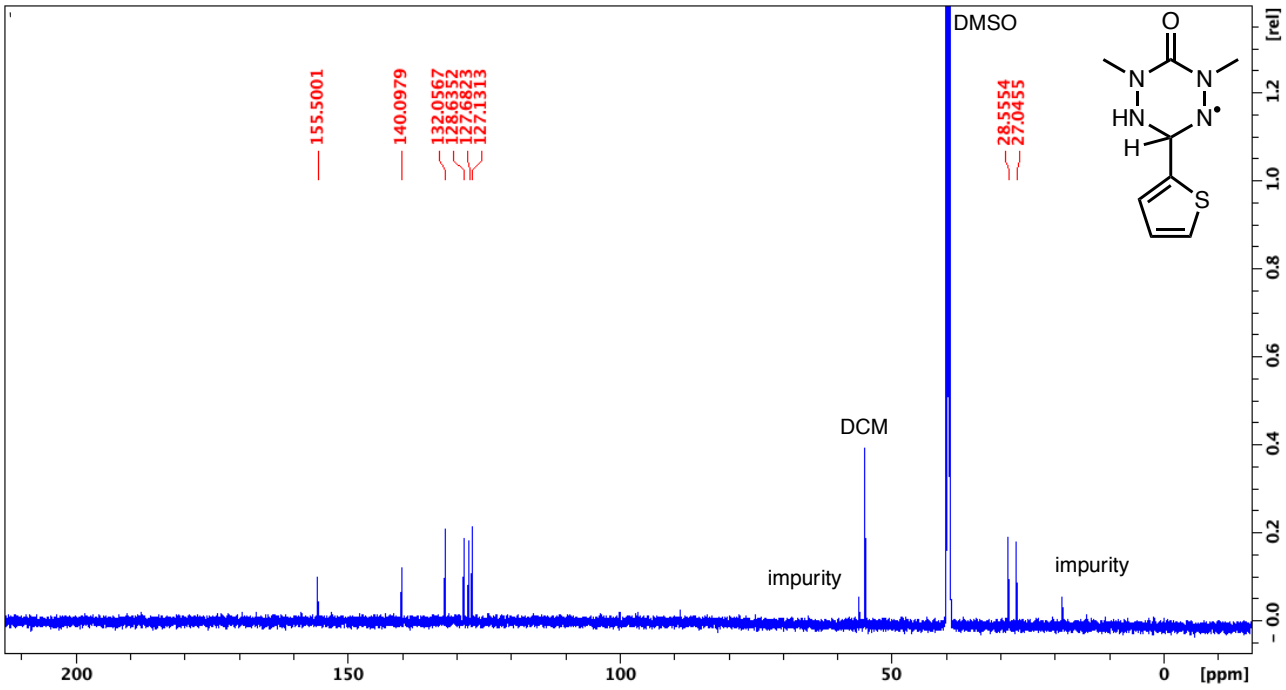


Fig. S97: ^{1}H NMR 1,5-dimethyl-3-(2-thiophene)-6-oxo-leucoverdazyl



^{1}H NMR (δ / ppm, DMSO-d_6): 7.93 (s, 1H NH), 7.52 (d, 1H J=4.97 Hz, ArH), 7.41(d, 1H, J= 2.83 Hz ArH), 7.11(t, 1H, J= 2.85 Hz ArH'), 6.93(d, br J=4.05 Hz CH), 3.24(s, 3H, CH'_3) 2.74(d, 3H, J=4.65 Hz, CH_3).

Fig. S98:^{13}C HMR 1,5-dimethyl-3-(2-thiophene)-6-oxo-leucoverdazyl



^{13}C NMR (δ / ppm, DMSO-d_6): 155.5(C=O), 140.1(C), 132.1(CH), 128.6(ArCH), 127.7(ArCH), 127.1(ArCH), 28.5(CH_3), 27.0(CH_3).

Fig. S99: ^{1}H NMR of **12b**

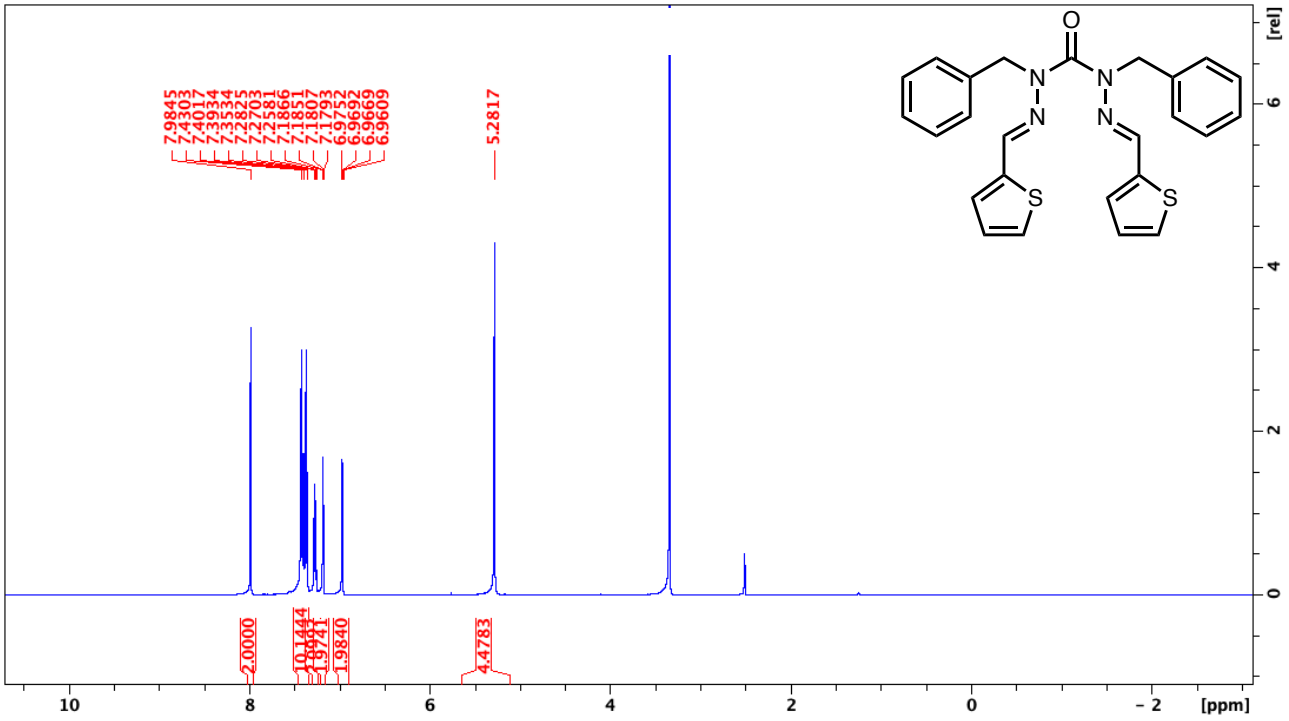


Fig. S100: ^{13}C HMR **12b**

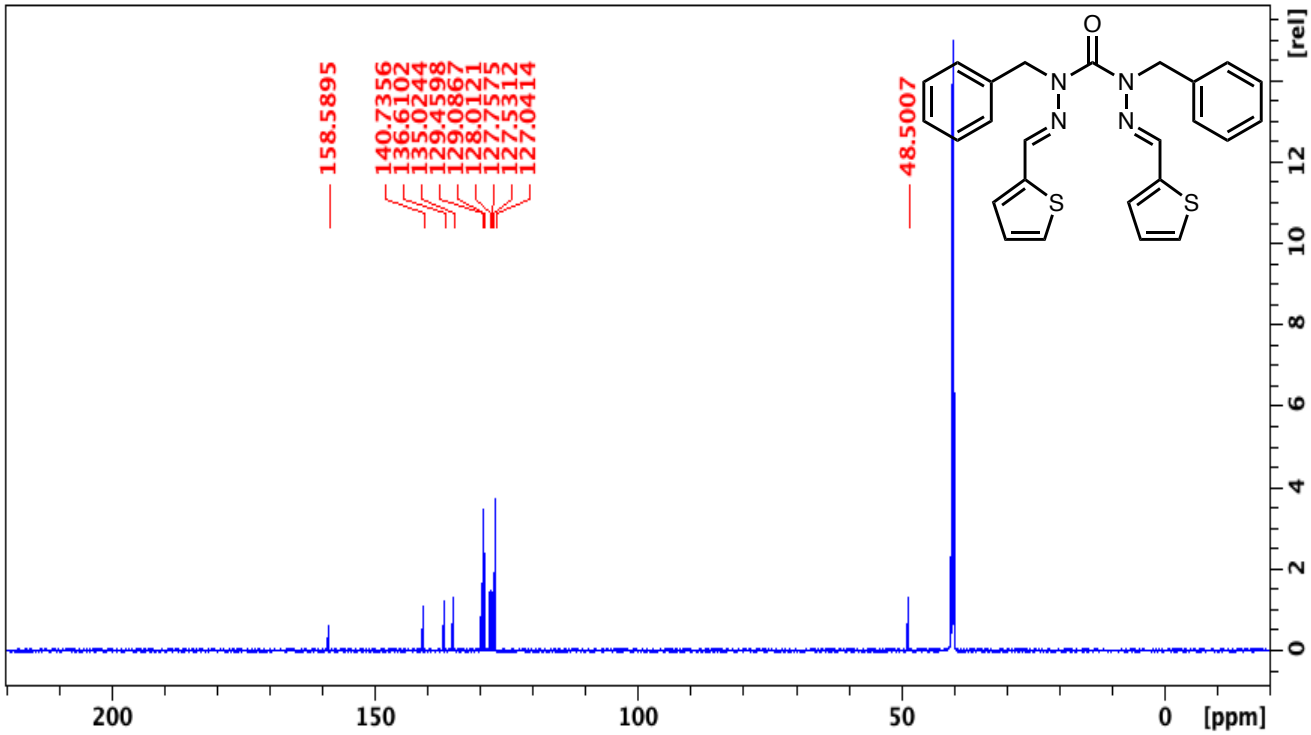


Fig. S101: ^{1}H NMR of **12c**

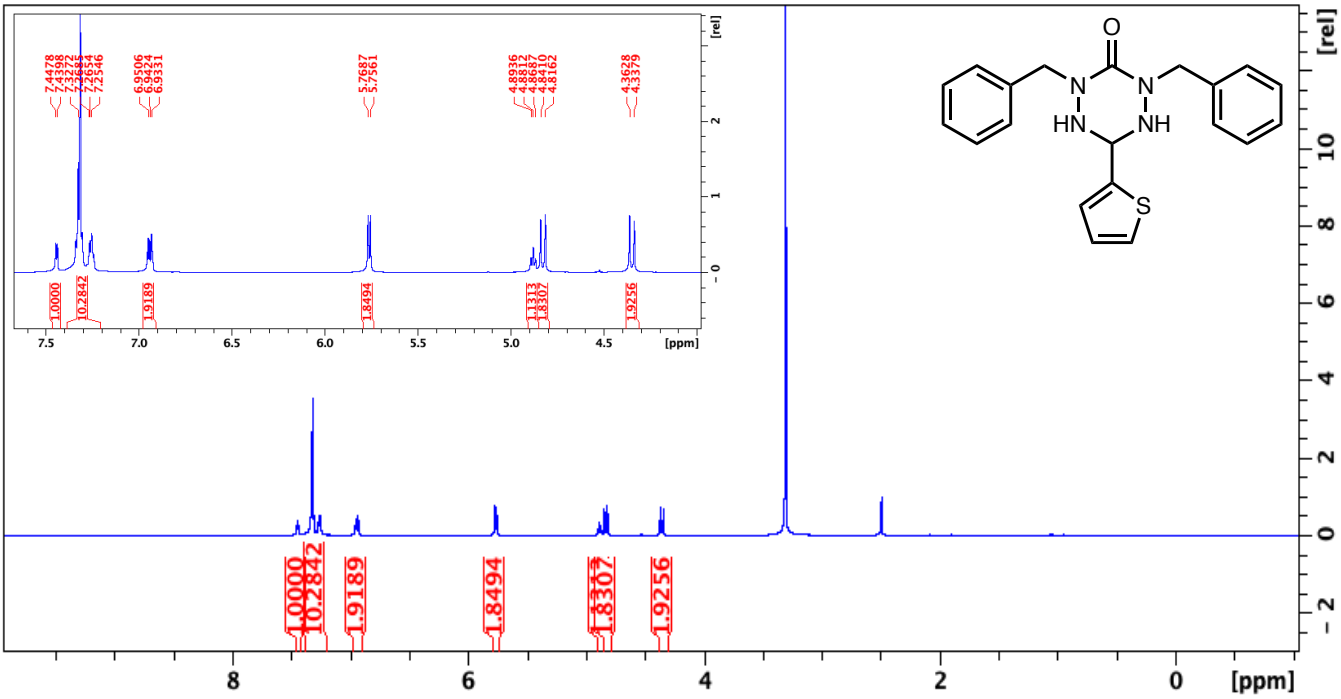


Fig. S102: ^{13}C NMR of **12c**

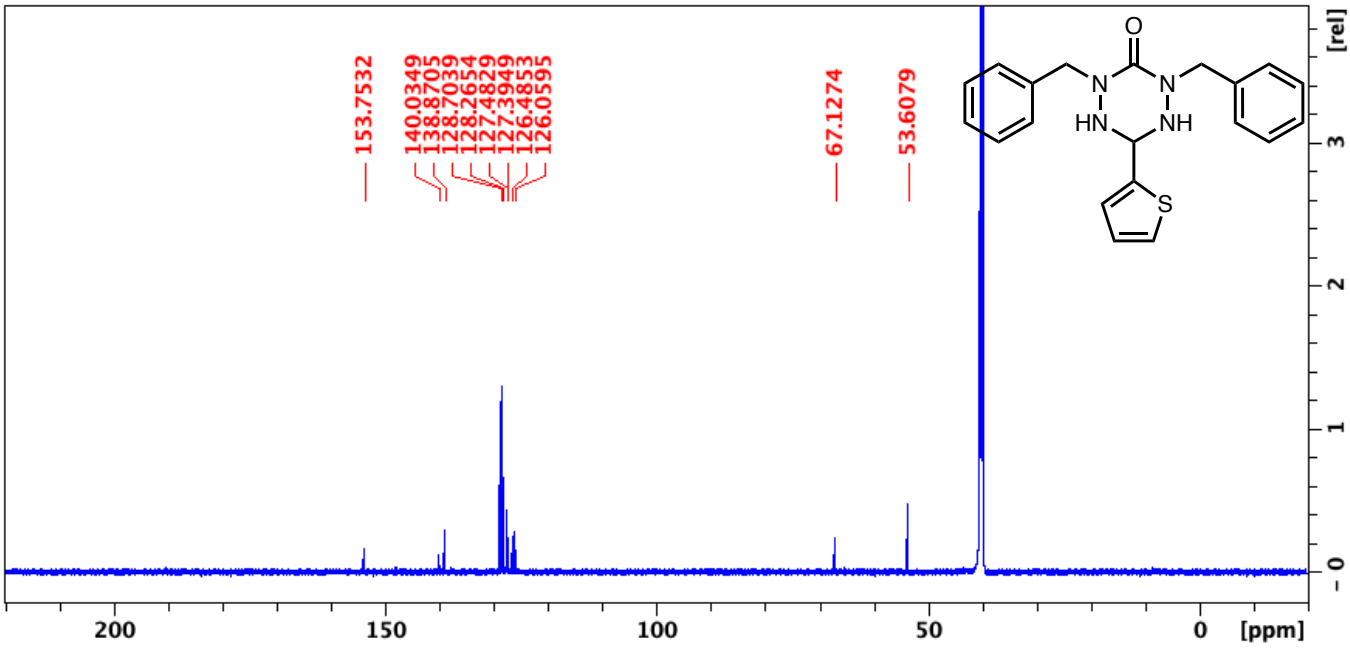


Fig. S103: ^{1}H NMR of **13a**

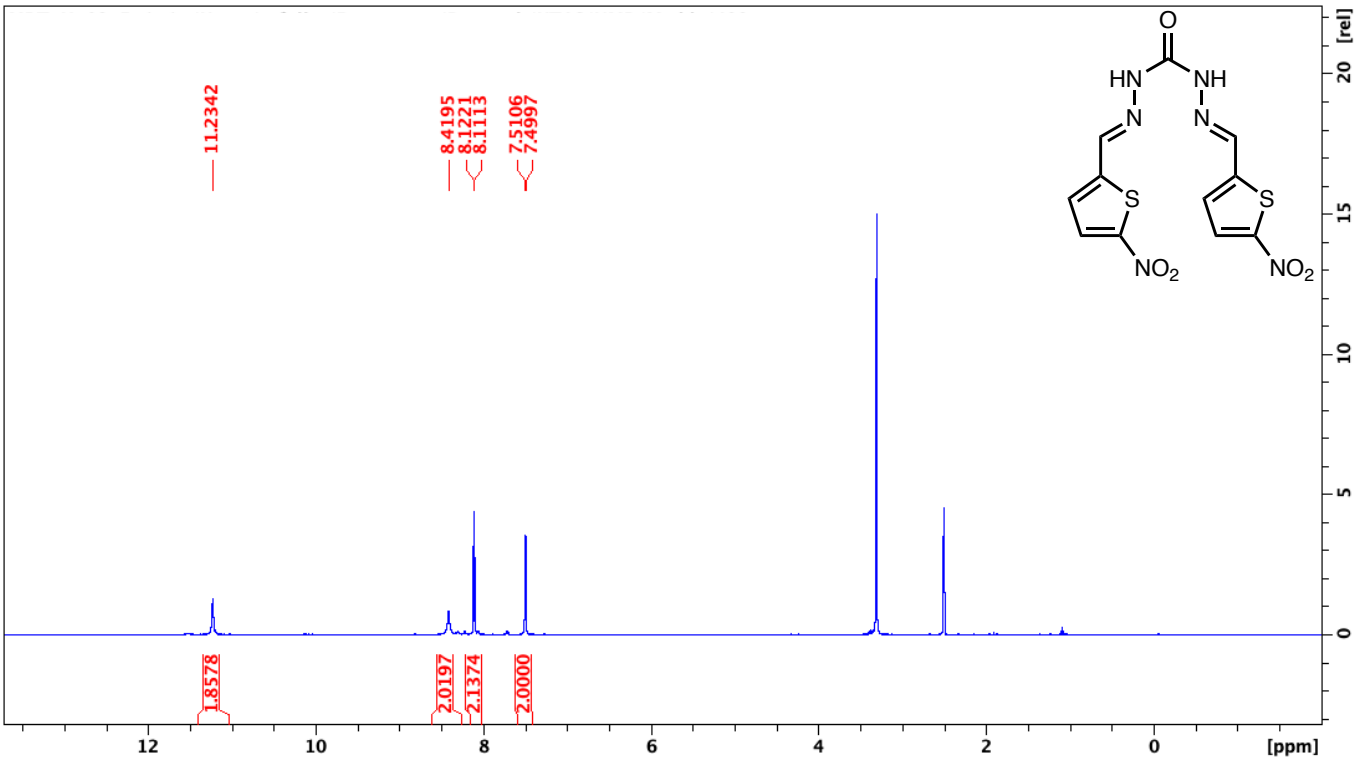


Fig. S104: ^{13}C NMR of **13a**

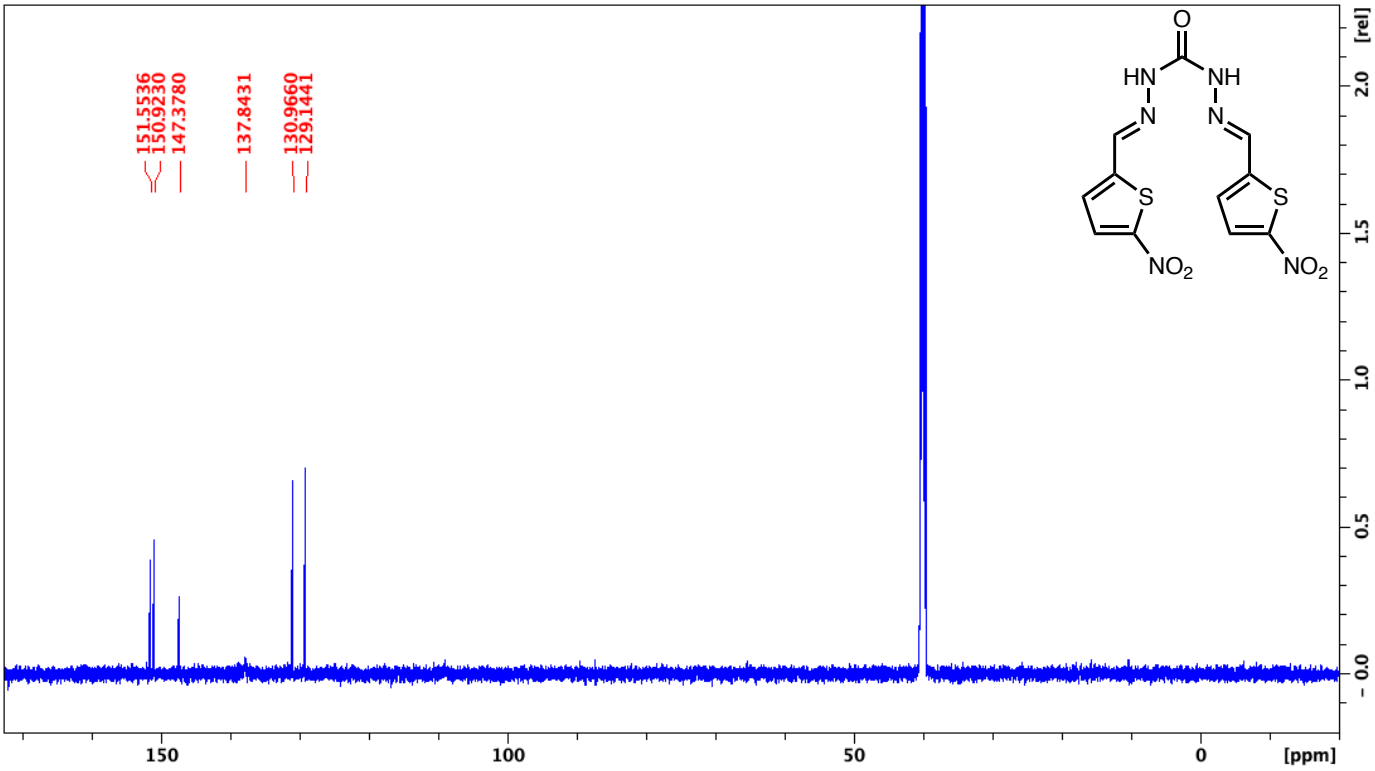


Fig. S105: ^{1}H NMR of **13b**

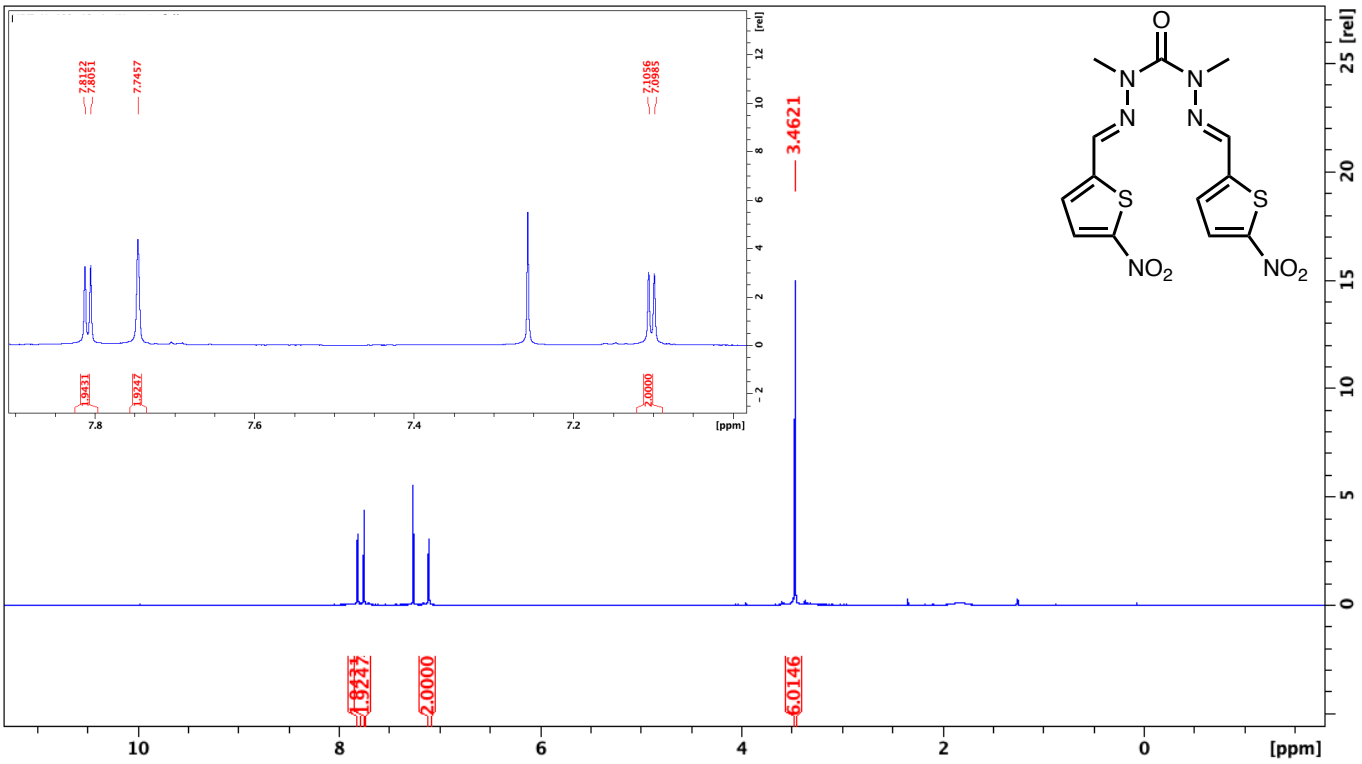


Fig. S106: ^{13}C NMR of **13b**

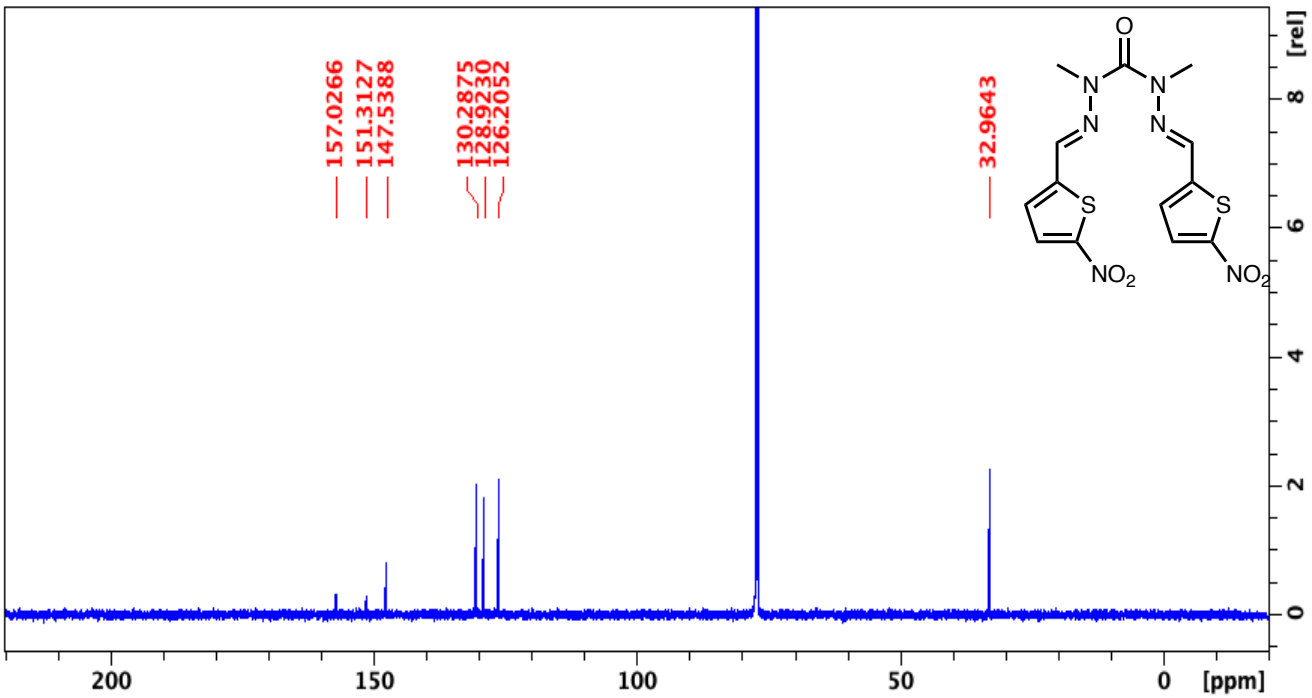


Fig. S107: ^{1}H NMR of **13c**

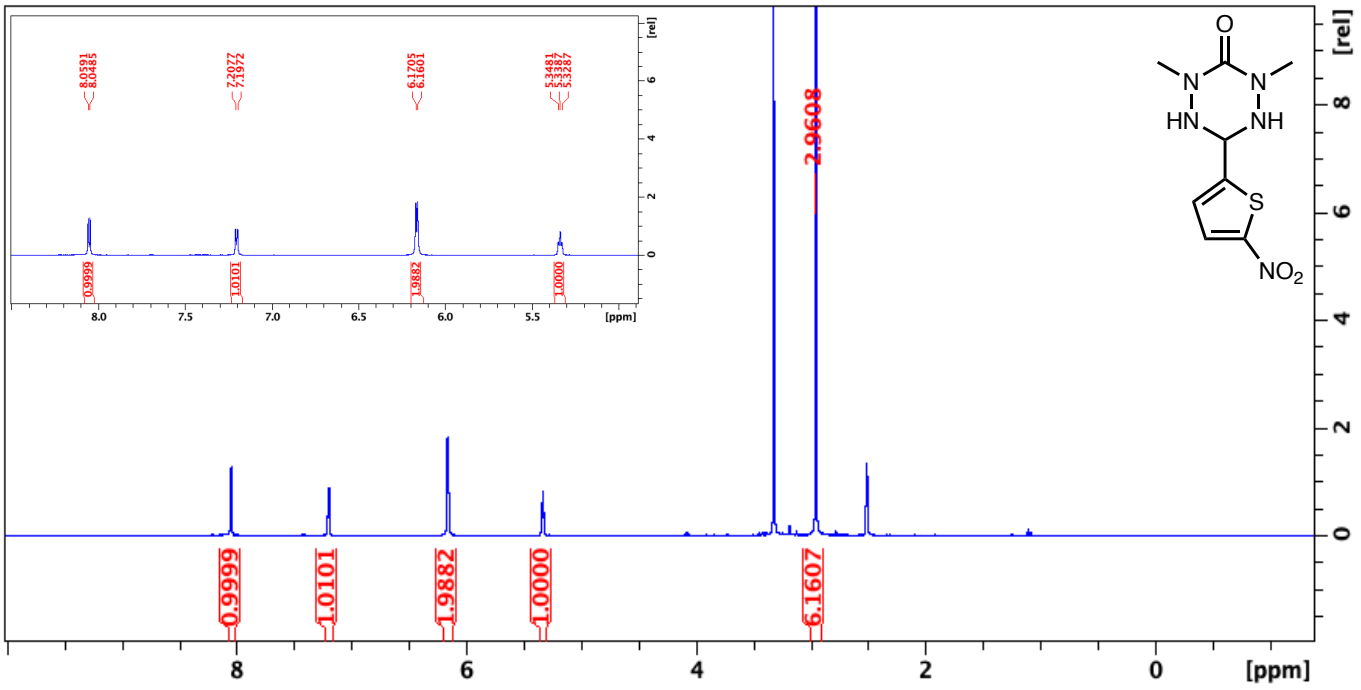


Fig. S108: ^{13}C NMR of **13c**

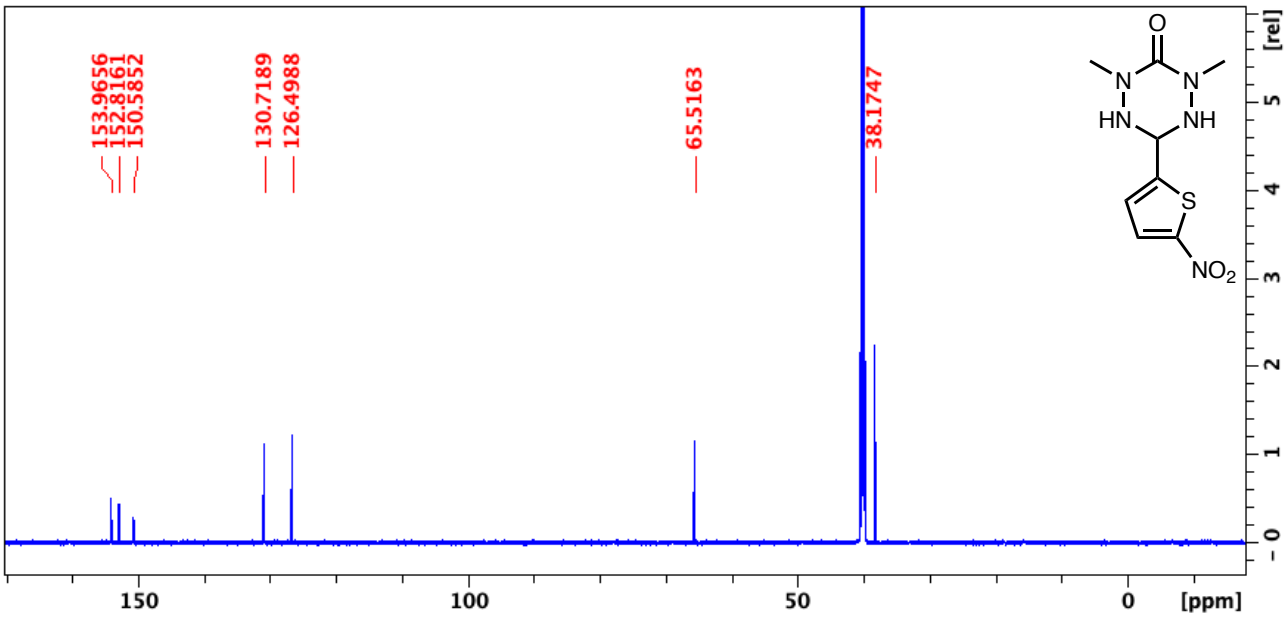


Fig. S109: ^{1}H NMR of **14b**

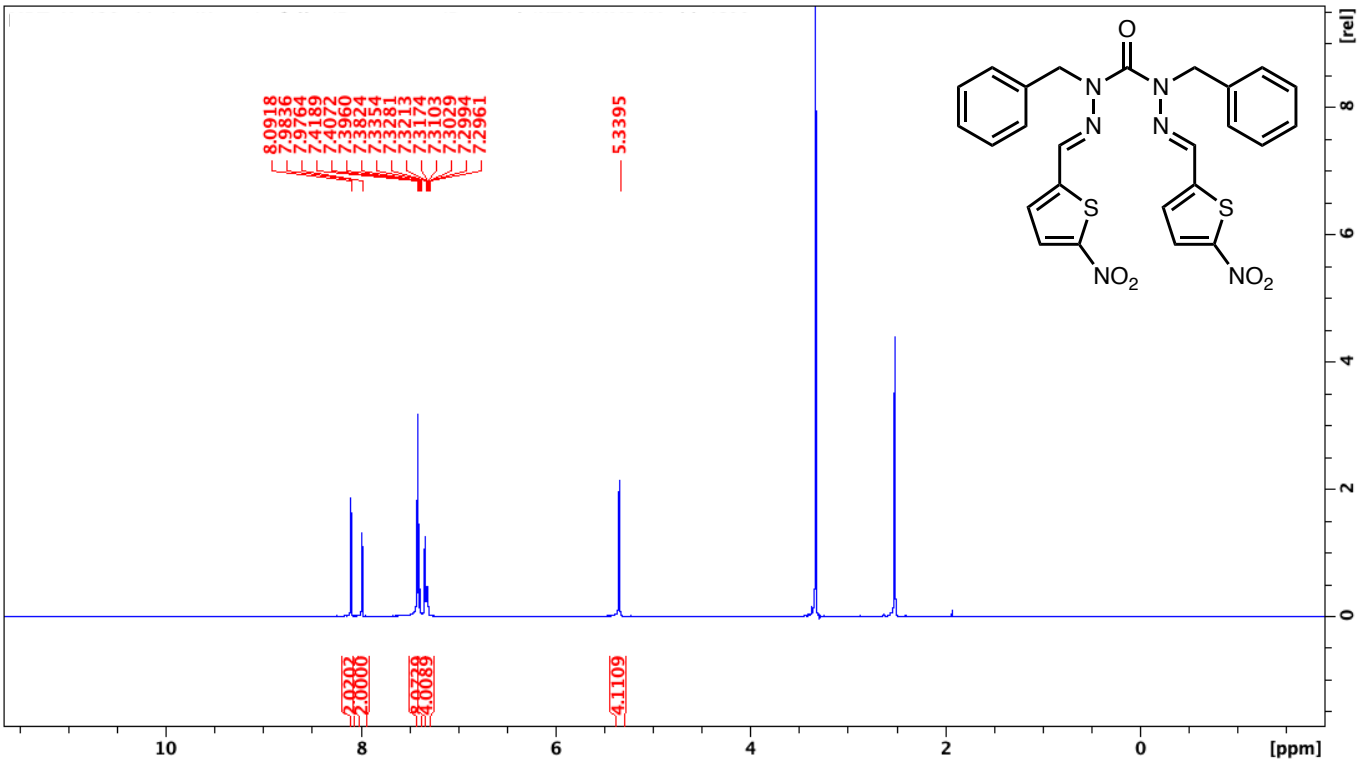


Fig. S110: ^{13}C NMR of **14b**

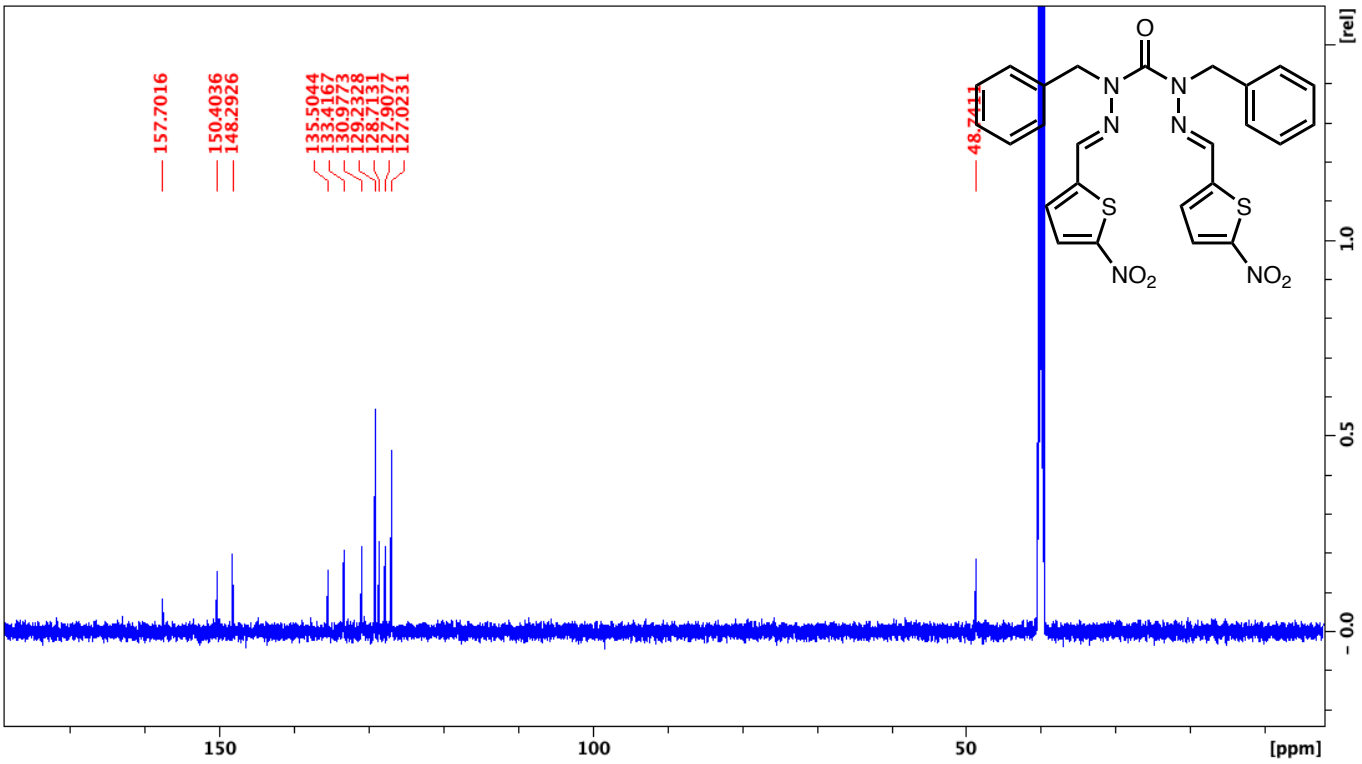


Fig. S111: ^{1}H NMR of **14c**

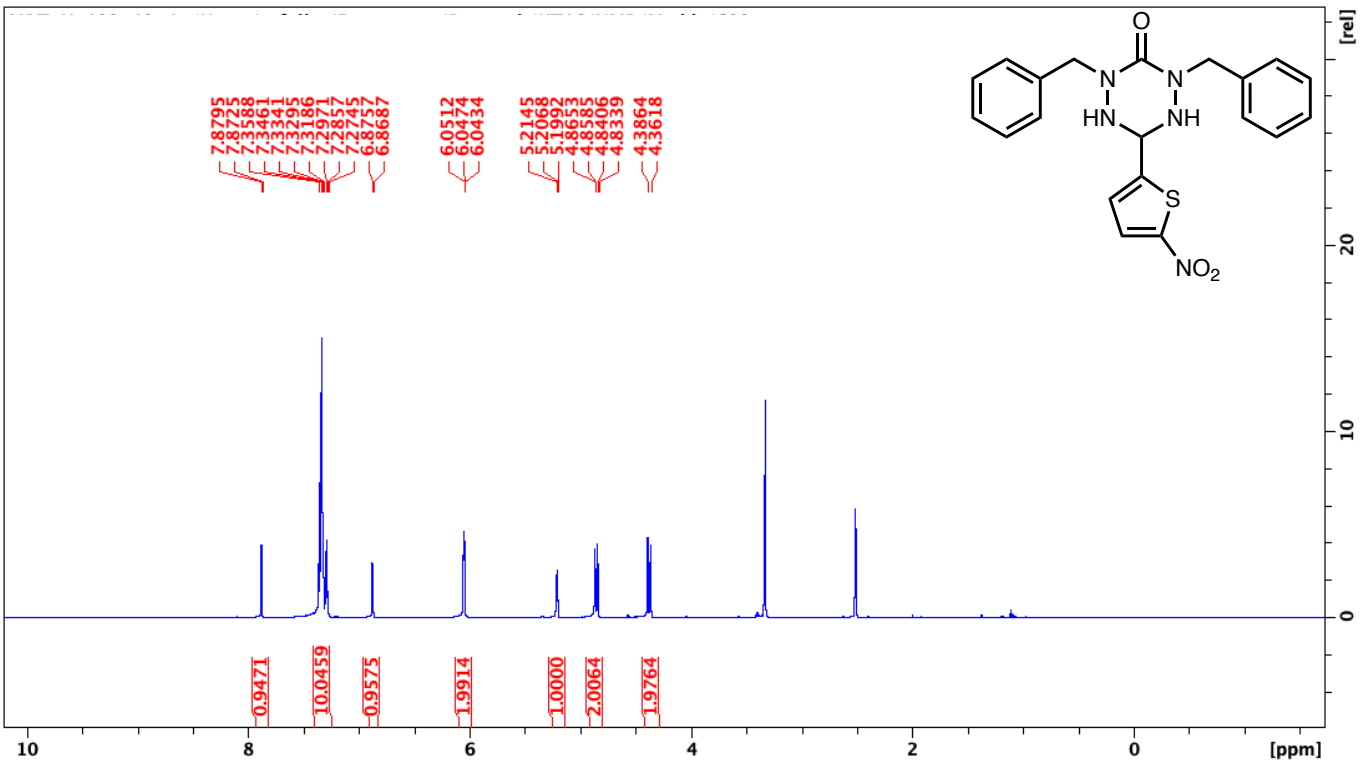
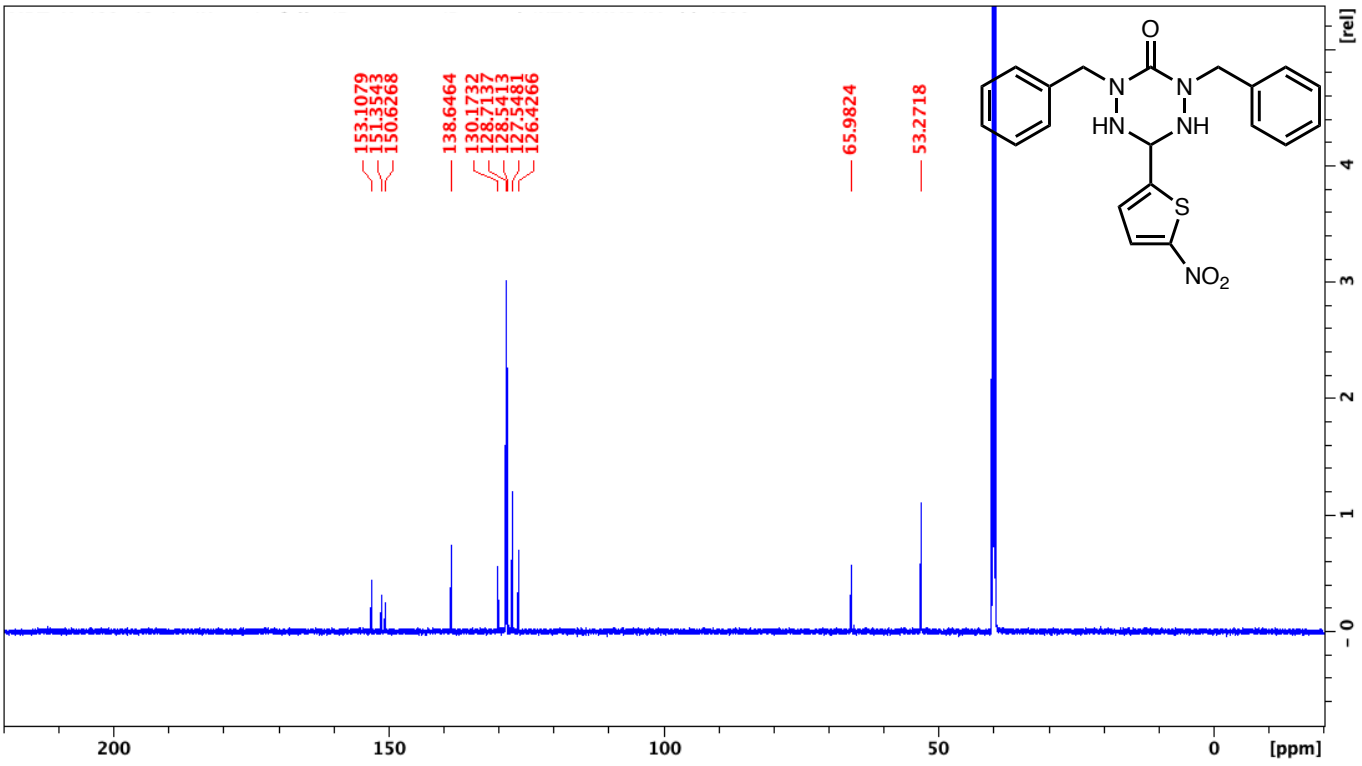
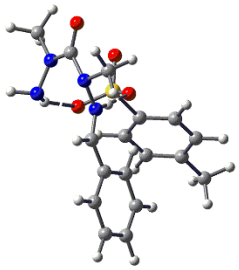


Fig. S112: ^{13}C NMR of **14c**

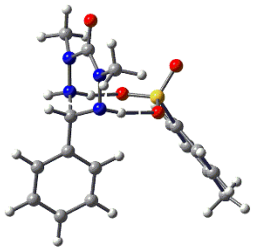


IV. Computational Details

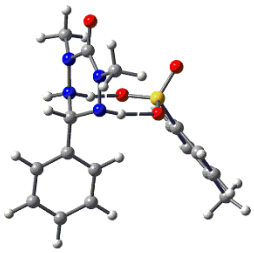
Fig. S113: Gaussview diagrams and Energy parameters and Cartesian coordinates for calculated species



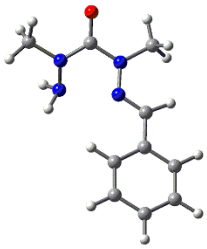
Va



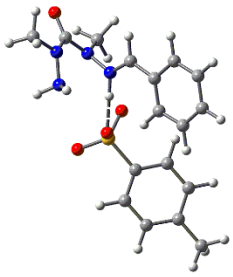
TS-Va/VI.p-TsO



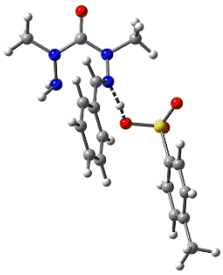
VI.p-TsO



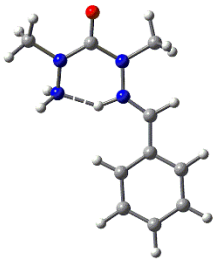
VII



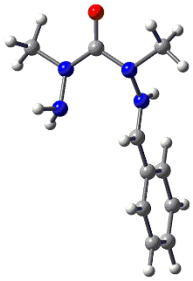
Vb



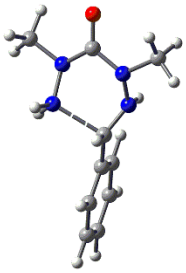
TS for deprotonation of Vb to give VII



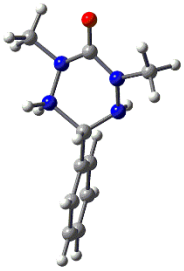
VIII



IX



TS-VI/IX



VI

Energy parameters and Cartesian coordinates for calculated species

All calculations related to thermodynamic effects are obtained using B3LYP/BS1; single-point data, listed immediately after BS1 data and before coordinates, are calculated using BS2 and M06-2X incorporating Grimme's D3 computation as discussed in the manuscript.

Va

E(RB3LYP) = -1579.04154272
Zero-point correction= 0.385986 (Hartree/Particle)
Thermal correction to Energy= 0.412851
Thermal correction to Enthalpy= 0.413795
Thermal correction to Gibbs Free Energy= 0.323830
Sum of electronic and zero-point Energies= -1578.655557
Sum of electronic and thermal Energies= -1578.628692
Sum of electronic and thermal Enthalpies= -1578.627748
Sum of electronic and thermal Free Energies= -1578.717712
E(RM062X) = -684.024151901

C -0.45977 -5.24439 2.40165
C 0.82502 -5.75219 2.58147
C 1.88685 -4.87826 2.82703
C 1.67183 -3.49179 2.88187

C 0.39574 -2.97501 2.69778
C -0.68428 -3.85123 2.46877
H -1.28944 -5.91475 2.21558
H 0.99892 -6.81932 2.53421
H 2.8921 -5.27256 2.96958
H 2.50514 -2.81987 3.05869
H 0.23374 -1.90123 2.73445
C -2.04991 -3.41022 2.30377
H -1.84429 -1.34109 2.47344
N -2.47893 -2.17554 2.402
C -4.21622 -1.86806 0.67282
O -5.26241 -1.26787 0.42394
C -4.45632 -0.99845 2.97902
H -3.98171 -0.00934 3.00009
H -5.49598 -0.89226 2.67085
H -4.40826 -1.44929 3.97215
C -3.96675 -2.34897 -1.69256
H -3.77138 -3.26284 -2.26101
H -5.03093 -2.12218 -1.73098
H -3.40034 -1.52103 -2.14237
N -3.78952 -1.89398 2.02756
N -3.55372 -2.56912 -0.3053
N -2.25011 -3.09427 -0.13456
H -1.56759 -2.36159 -0.35669
H -2.14704 -3.87367 -0.78569
C 1.61475 0.46408 -0.53728
C 1.04598 0.68598 0.71889
C 1.85552 1.03067 1.80045
C 3.23394 1.1453 1.62386
C 3.82727 0.92283 0.37163
C 2.99523 0.58316 -0.70501
H 0.98241 0.19112 -1.37561
H 1.41042 1.19633 2.77609
H 3.85948 1.41165 2.47245
H 3.43308 0.40726 -1.68461
C 5.32456 1.01873 0.19602
H 5.80934 0.06011 0.42405
H 5.5906 1.2812 -0.83295
H 5.75862 1.76837 0.8658
S -0.73856 0.61225 0.91194
O -1.23085 -0.34654 -0.12371
O -0.95121 0.09182 2.31877
O -1.25487 1.99296 0.74581
H -2.81997 -4.15448 2.13389

Vb

E(RB3LYP) = -1579.03833913
Zero-point correction= 0.385463 (Hartree/Particle)
Thermal correction to Energy= 0.412623
Thermal correction to Enthalpy= 0.413567
Thermal correction to Gibbs Free Energy= 0.321736
Sum of electronic and zero-point Energies= -1578.652876
Sum of electronic and thermal Energies= -1578.625716
Sum of electronic and thermal Enthalpies= -1578.624772
Sum of electronic and thermal Free Energies= -1578.716603
E(RM062X) = -1578.96660998

C 0.03248 -3.05909 2.85982
C 1.3571 -3.40976 3.1052
C 2.29379 -3.34371 2.06862
C 1.90723 -2.93427 0.7858
C 0.58646 -2.58657 0.52981
C -0.36425 -2.63699 1.57125
H -0.69682 -3.10178 3.66191
H 1.66108 -3.73107 4.09704
H 3.32957 -3.6127 2.25545
H 2.6387 -2.89186 -0.01306
H 0.29111 -2.27346 -0.4669
C -1.75243 -2.26323 1.40282
H -1.88785 -1.60177 -0.56505
N -2.33001 -1.82449 0.32648
C -4.62918 -2.55073 0.76626
O -5.67721 -2.2405 1.32632
C -4.03645 -0.15826 0.67967

H -3.38596 0.47615 0.0739
H -5.0804 0.01615 0.40839
H -3.89274 0.07304 1.74295
C -5.25663 -4.90276 0.82577
H -4.71537 -5.8444 0.94989
H -5.75 -4.64309 1.76762
H -6.02222 -5.02669 0.04989
N -3.71309 -1.56 0.38142
N -4.29428 -3.86116 0.474
N -3.45261 -4.09948 -0.63344
H -4.02136 -4.40989 -1.42199
H -2.82263 -4.86163 -0.39246
C 0.96253 -0.28967 -4.07968
C 0.50272 0.04855 -2.80966
C 1.40183 0.42915 -1.8074
C 2.76934 0.45582 -2.08716
C 3.2598 0.11043 -3.35925
C 2.33353 -0.25735 -4.34626
H 0.25618 -0.57173 -4.85427
H 1.03944 0.70785 -0.82749
H 3.46746 0.75034 -1.31184
H 2.6922 -0.52861 -5.33903
C 4.73502 0.1676 -3.66126
H 5.01842 -0.56666 -4.422
H 5.02257 1.15729 -4.03991
H 5.33746 -0.02627 -2.76539
S -1.25404 -0.04599 -2.42912
O -1.44387 -1.43631 -1.80785
O -1.52843 1.01264 -1.41723
O -1.97239 0.0897 -3.7138
H -2.3926 -2.36633 2.28434

VI
E(RB3LYP) = -684.099370935
Zero-point correction= 0.257129 (Hartree/Particle)
Thermal correction to Energy= 0.271229
Thermal correction to Enthalpy= 0.272173
Thermal correction to Gibbs Free Energy= 0.215410
Sum of electronic and zero-point Energies= -683.842242
Sum of electronic and thermal Energies= -683.828142
Sum of electronic and thermal Enthalpies= -683.827198
Sum of electronic and thermal Free Energies= -683.883961
E(RM062X) = -684.031413942

C -0.46514 -5.18833 2.52142
C 0.85523 -5.58826 2.76774
C 1.88836 -4.65169 2.7058
C 1.60309 -3.31377 2.41356
C 0.28664 -2.91326 2.16089
C -0.7542 -3.84991 2.20715
H -1.26553 -5.91882 2.57625
H 1.06438 -6.62447 3.00986
H 2.91203 -4.96158 2.89136
H 2.4021 -2.5839 2.36985
H 0.09997 -1.87008 1.91528
C -2.19366 -3.48421 1.93803
H -1.96637 -1.47249 2.31203
N -2.61559 -2.24742 2.49409
C -4.1118 -1.68279 0.74885
O -5.03716 -1.03268 0.2861
C -4.79497 -1.31903 3.08386
H -4.49447 -0.28485 3.28324
H -5.81691 -1.33002 2.71253
H -4.72741 -1.90755 3.99998
C -3.25337 -2.06022 -1.53999
H -3.98868 -2.76448 -1.94841
H -3.58798 -1.0387 -1.72455
H -2.28374 -2.21338 -2.02197
N -3.92745 -1.94258 2.08386
N -3.09269 -2.20689 -0.08188
N -2.47551 -3.43014 0.33761
H -1.59425 -3.54512 -0.16796
H -3.06218 -4.26585 0.16624
H -2.89332 -4.27214 2.25923

VI.p-TsO
E(RB3LYP) = -1579.04878569
Zero-point correction= 0.389073 (Hartree/Particle)
Thermal correction to Energy= 0.414914
Thermal correction to Enthalpy= 0.415858
Thermal correction to Gibbs Free Energy= 0.327784
Sum of electronic and zero-point Energies= -1578.659712
Sum of electronic and thermal Energies= -1578.633872
Sum of electronic and thermal Enthalpies= -1578.632928
Sum of electronic and thermal Free Energies= -1578.721001
E(RM062X) = -1578.98415492

C -0.76977 -5.33777 2.39045
C 0.45748 -5.92008 2.70937
C 1.58269 -5.11464 2.89788
C 1.47646 -3.72756 2.76653
C 0.25237 -3.14003 2.44363
C -0.87995 -3.94678 2.25555
H -1.64591 -5.96561 2.25068
H 0.53127 -6.99838 2.81435
H 2.5386 -5.56555 3.14854
H 2.34887 -3.09783 2.91429
H 0.18577 -2.0607 2.34824
C -2.22889 -3.3696 1.89989
H -1.92085 -1.42542 2.47419
N -2.59533 -2.1913 2.61463
C -4.32669 -1.79201 0.92717
O -5.38397 -1.29088 0.55377
C -4.66835 -1.11401 3.27056
H -4.1958 -0.18466 3.60832
H -5.65719 -0.89164 2.87305
H -4.74754 -1.80379 4.11539
C -3.71258 -2.335 -1.41961
H -3.58175 -3.27788 -1.95858
H -4.72055 -1.96241 -1.58692
H -2.97858 -1.59988 -1.76797
N -3.87822 -1.73631 2.21724
N -3.58125 -2.57834 0.01913
N -2.26428 -3.02007 0.39409
H -1.54509 -2.26359 0.1551
H -2.05415 -3.85882 -0.16119
C 1.96651 0.50312 -0.81367
C 1.26839 0.60707 0.39455
C 1.9217 1.03573 1.55018
C 3.28009 1.35603 1.49409
C 4.00068 1.25702 0.29695
C 3.32045 0.82595 -0.85442
H 1.45804 0.16258 -1.71008
H 1.37404 1.10954 2.48336
H 3.7861 1.68735 2.39744
H 3.86026 0.74079 -1.79448
C 5.47413 1.58483 0.24199
H 6.07748 0.67286 0.14599
H 5.70968 2.21718 -0.6215
H 5.80184 2.10558 1.14677
S -0.49181 0.25944 0.43304
O -0.65361 -1.00528 -0.38366
O -0.835 0.02598 1.87312
O -1.18783 1.41825 -0.17148
H -3.01441 -4.11914 2.01292

VII
E(RB3LYP) = -683.662036318
Zero-point correction= 0.240051 (Hartree/Particle)
Thermal correction to Energy= 0.254918
Thermal correction to Enthalpy= 0.255862
Thermal correction to Gibbs Free Energy= 0.197270
Sum of electronic and zero-point Energies= -683.421985
Sum of electronic and thermal Energies= -683.407118
Sum of electronic and thermal Enthalpies= -683.406174
Sum of electronic and thermal Free Energies= -683.464766
E(RM062X) = -683.598954138

C 0.45048 -2.03299 -0.21007
C 1.83648 -1.94411 -0.19517
C 2.46306 -0.71393 0.04527
C 1.69823 0.43291 0.2707
C 0.30848 0.35272 0.25739
C -0.33109 -0.8809 0.02076
H -0.01429 -2.99384 -0.4078
H 2.4335 -2.83249 -0.37493
H 3.54713 -0.65297 0.05265
H 2.18224 1.38668 0.45477
H -0.29005 1.2419 0.43268
C -1.77918 -0.87869 0.03543
H -2.28579 0.06983 0.16926
N -2.51077 -1.94425 -0.097
C -4.59202 -3.17807 0.15554
O -5.79795 -3.099 0.34921
C -4.60565 -0.72046 -0.19973
H -4.50457 -0.16837 0.74206
H -4.22976 -0.11755 -1.03102
H -5.65306 -0.95846 -0.36107
C -4.69039 -5.59531 0.47986
H -4.05501 -6.30499 1.01579
H -5.56041 -5.35351 1.08719
H -5.01878 -6.04348 -0.46598
N -3.88089 -1.98642 -0.16002
N -3.9178 -4.37379 0.24399
N -2.62829 -4.52696 -0.32052
H -2.69541 -4.98666 -1.23218
H -2.07643 -5.1233 0.29656

VIII

E(RB3LYP) = -684.108729219
Zero-point correction= 0.254162 (Hartree/Particle)
Thermal correction to Energy= 0.268910
Thermal correction to Enthalpy= 0.269854
Thermal correction to Gibbs Free Energy= 0.211485
Sum of electronic and zero-point Energies= -683.854568
Sum of electronic and thermal Energies= -683.839819
Sum of electronic and thermal Enthalpies= -683.838875
Sum of electronic and thermal Free Energies= -683.897245
E(RM062X) = -684.029882824

C 0.40917 -2.02128 0.
C 1.80433 -2.02128 0.
C 2.50186 -0.81353 0.
C 1.80421 0.39498 -0.0012
C 0.40938 0.39491 -0.00168
C -0.28822 -0.8133 -0.00068
H -0.14059 -2.97359 0.00045
H 2.35383 -2.97379 0.00132
H 3.60154 -0.81345 0.00063
H 2.35441 1.34713 -0.00126
H -0.14074 1.34719 -0.00263
C -1.82822 -0.81304 -0.00093
H -2.36122 0.11277 -0.06166
H -1.9777 -2.9066 0.14474
N -2.51067 -1.98137 0.07549
C -4.73307 -3.15027 0.13943
O -6.16004 -3.13723 0.23149
C -4.81769 -0.6503 -0.03666
H -4.7304 -0.11837 0.88763
H -4.40583 -0.05984 -0.82826
H -5.84979 -0.84747 -0.23861
C -4.65956 -5.66024 0.2039
H -3.97005 -6.47815 0.18194
H -5.2174 -5.68841 1.11655
H -5.33007 -5.7366 -0.62645
N -4.05062 -1.98194 0.06301
N -3.97711 -4.49191 0.12747
N -2.44037 -4.50595 0.02833
H -2.04655 -4.45042 -0.75667
H -1.93964 -5.35974 0.17082

IX

E(RB3LYP) = -684.098583939
Zero-point correction= 0.253779 (Hartree/Particle)
Thermal correction to Energy= 0.268935
Thermal correction to Enthalpy= 0.269879
Thermal correction to Gibbs Free Energy= 0.210581
Sum of electronic and zero-point Energies= -683.844805
Sum of electronic and thermal Energies= -683.829649
Sum of electronic and thermal Enthalpies= -683.828705
Sum of electronic and thermal Free Energies= -683.888003
E(RM062X) = -684.024151901

C -0.43454 -5.19853 2.63362
C 0.88583 -5.60866 2.76774
C 1.91896 -4.67209 2.665
C 1.63369 -3.32397 2.41356
C 0.31724 -2.90306 2.28329
C -0.7338 -3.83971 2.41115
H -1.24513 -5.91882 2.70885
H 1.11538 -6.65507 2.94866
H 2.95283 -4.99218 2.76896
H 2.4429 -2.6043 2.31885
H 0.11017 -1.85988 2.06828
C -2.12226 -3.47401 2.33583
H -1.96637 -1.44189 2.47523
N -2.59519 -2.24742 2.44309
C -4.1016 -1.71339 0.68765
O -5.02696 -0.99188 0.3371
C -4.74397 -1.32923 3.04306
H -4.43327 -0.28485 3.18124
H -5.77611 -1.35042 2.69213
H -4.66621 -1.86675 3.98978
C -3.36557 -1.90723 -1.63179
H -4.12128 -2.55028 -2.10141
H -3.66958 -0.8653 -1.72455
H -2.40614 -2.05018 -2.13417
N -3.91725 -2.02418 2.05326
N -3.18449 -2.23749 -0.21448
N -2.58771 -3.49134 0.05201
H -1.69625 -3.53492 -0.44336
H -3.18458 -4.25565 -0.28256
H -2.88312 -4.25174 2.36123

p-TsO$^-$
E(RB3LYP) = -894.914558301
Zero-point correction= 0.131088 (Hartree/Particle)
Thermal correction to Energy= 0.141189
Thermal correction to Enthalpy= 0.142133
Thermal correction to Gibbs Free Energy= 0.093379
Sum of electronic and zero-point Energies= -894.783470
Sum of electronic and thermal Energies= -894.773370
Sum of electronic and thermal Enthalpies= -894.772426
Sum of electronic and thermal Free Energies= -894.821179
E(RM062X) = -894.918341257

C 2.11538 0.71497 0.31235
C 1.16756 1.0075 1.29923
C 1.50528 0.92429 2.6499
C 2.7987 0.54218 3.01222
C 3.76419 0.24038 2.04328
C 3.40034 0.33394 0.68921
H 1.84776 0.77459 -0.73777
H 0.76212 1.15138 3.40653
H 3.05881 0.47745 4.06571
H 4.13439 0.10411 -0.07923
C 5.15579 -0.19546 2.4364
H 5.28945 -1.27311 2.27572
H 5.9179 0.31527 1.83722
H 5.35598 0.0095 3.49239
S -0.46561 1.57656 0.82782
O -0.89153 0.62844 -0.31863
O -1.33851 1.42324 2.01298
O -0.32518 2.94526 0.28932

p-TsOH

E(RB3LYP) = -895.358735877
Zero-point correction= 0.142395 (Hartree/Particle)
Thermal correction to Energy= 0.153138
Thermal correction to Enthalpy= 0.154082
Thermal correction to Gibbs Free Energy= 0.103997
Sum of electronic and zero-point Energies= -895.216341
Sum of electronic and thermal Energies= -895.205598
Sum of electronic and thermal Enthalpies= -895.204654
Sum of electronic and thermal Free Energies= -895.254739
E(RM062X) = -895.351074943

H -1.61259 -0.51779 0.12538
C 2.11538 0.71497 0.31235
C 1.16756 1.0075 1.29923
C 1.50528 0.92429 2.6499
C 2.7987 0.54218 3.01222
C 3.76419 0.24038 2.04328
C 3.40034 0.33394 0.68921
H 1.84776 0.77459 -0.73777
H 0.76212 1.15138 3.40653
H 3.05881 0.47745 4.06571
H 4.13439 0.10411 -0.07923
C 5.15579 -0.19546 2.4364
H 5.28945 -1.27311 2.27572
H 5.9179 0.31527 1.83722
H 5.35598 0.0095 3.49239
S -0.46561 1.57656 0.82782
O -0.89153 0.62844 -0.31863
O -1.33851 1.42324 2.01298
O -0.32518 2.94526 0.28932

TS-Va/VI.p-TsO
E(RB3LYP) = -1579.03548109
Zero-point correction= 0.386175 (Hartree/Particle)
Thermal correction to Energy= 0.412220
Thermal correction to Enthalpy= 0.413164
Thermal correction to Gibbs Free Energy= 0.324615
Sum of electronic and zero-point Energies= -1578.649306
Sum of electronic and thermal Energies= -1578.623261
Sum of electronic and thermal Enthalpies= -1578.622317
Sum of electronic and thermal Free Energies= -1578.710866
E(RM062X) = -1578.96264713

C -0.46764 -5.24002 2.34511
C 0.80842 -5.7469 2.57477
C 1.86558 -4.87206 2.84082
C 1.6453 -3.49031 2.87574
C 0.3733 -2.97441 2.6465
C -0.69743 -3.85154 2.38284
H -1.29269 -5.91565 2.13781
H 0.97817 -6.81866 2.54718
H 2.86196 -5.26566 3.01951
H 2.4693 -2.81313 3.07849
H 0.21538 -1.90071 2.66829
C -2.06338 -3.39782 2.159
H -1.85392 -1.36441 2.49428
N -2.49719 -2.18573 2.44246
C -4.21174 -1.85771 0.70527
O -5.25647 -1.27722 0.41167
C -4.4842 -0.99199 3.00309
H -4.00013 -0.00951 3.06435
H -5.51237 -0.8687 2.67232
H -4.46096 -1.47172 3.98388
C -3.89696 -2.39659 -1.65221
H -3.65997 -3.3104 -2.20436
H -4.96463 -2.20061 -1.7187
H -3.33925 -1.55679 -2.08537
N -3.79528 -1.86063 2.04684
N -3.53223 -2.59922 -0.24671
N -2.21231 -3.06176 -0.02513
H -1.54518 -2.30465 -0.22572
H -2.04895 -3.86489 -0.63044
C 1.61561 0.4614 -0.54229
C 1.04574 0.68436 0.71318

C 1.85423 1.03078 1.79968
C 3.23271 1.14609 1.624
C 3.82714 0.92261 0.37247
C 2.99614 0.58121 -0.70442
H 0.98408 0.1871 -1.38079
H 1.40829 1.19725 2.77479
H 3.85743 1.41379 2.47277
H 3.43484 0.4045 -1.68349
C 5.3245 1.01935 0.19787
H 5.80982 0.06148 0.4279
H 5.59115 1.28031 -0.83131
H 5.75745 1.77044 0.86674
S -0.73893 0.60964 0.90955
O -1.22515 -0.35992 -0.12055
O -0.95222 0.09985 2.31688
O -1.26061 1.98522 0.72325
H -2.83316 -4.15171 2.04108

TS-VI/IX
E(RB3LYP) = -684.094787739
Zero-point correction= 0.254615 (Hartree/Particle)
Thermal correction to Energy= 0.268580
Thermal correction to Enthalpy= 0.269525
Thermal correction to Gibbs Free Energy= 0.213187
Sum of electronic and zero-point Energies= -683.840173
Sum of electronic and thermal Energies= -683.826207
Sum of electronic and thermal Enthalpies= -683.825263
Sum of electronic and thermal Free Energies= -683.881601
E(RM062X) = -684.019209276

C -0.4293 -5.19948 2.62741
C 0.89047 -5.60754 2.79713
C 1.9234 -4.66988 2.71369
C 1.63971 -3.32249 2.45695
C 0.32439 -2.90675 2.28791
C -0.72436 -3.84429 2.38218
H -1.23703 -5.92279 2.69073
H 1.11335 -6.65157 2.99172
H 2.95362 -4.98792 2.84247
H 2.44644 -2.60045 2.38327
H 0.1239 -1.86265 2.0676
C -2.12369 -3.48233 2.24674
H -1.96128 -1.45142 2.42522
N -2.58818 -2.25486 2.43262
C -4.10716 -1.70829 0.69259
O -5.02665 -0.98482 0.33717
C -4.73327 -1.33245 3.04865
H -4.42498 -0.28865 3.1843
H -5.76863 -1.35728 2.71197
H -4.64007 -1.87263 3.99188
C -3.38153 -1.93952 -1.62971
H -4.14092 -2.58797 -2.08384
H -3.68865 -0.89965 -1.73046
H -2.42622 -2.08565 -2.14017
N -3.91229 -2.02161 2.04947
N -3.19271 -2.24232 -0.20783
N -2.58153 -3.487 0.08862
H -1.69706 -3.53741 -0.41683
H -3.17291 -4.26567 -0.21798
H -2.86901 -4.26292 2.32703

TS for deprotonation of Vb to give VII
E(RB3LYP) = -1579.02904653
Zero-point correction= 0.381161 (Hartree/Particle)
Thermal correction to Energy= 0.407774
Thermal correction to Enthalpy= 0.408719
Thermal correction to Gibbs Free Energy= 0.318770
Sum of electronic and zero-point Energies= -1578.647885
Sum of electronic and thermal Energies= -1578.621272
Sum of electronic and thermal Enthalpies= -1578.620328
Sum of electronic and thermal Free Energies= -1578.710277
E(RM062X) = -1578.96306489

C 0.0702 -3.1793 2.84113

C 1.40313 -3.53298 3.04045
C 2.31269 -3.43621 1.9847
C 1.88546 -2.98747 0.72881
C 0.5563 -2.63163 0.52404
C -0.36716 -2.7183 1.58496
H -0.63964 -3.25467 3.66056
H 1.73001 -3.88472 4.01424
H 3.35191 -3.71352 2.13616
H 2.59223 -2.91747 -0.09262
H 0.2325 -2.29868 -0.45522
C -1.77339 -2.35003 1.46283
H -1.79017 -1.50417 -0.90093
N -2.30994 -1.80137 0.42647
C -4.63294 -2.53813 0.81632
O -5.69787 -2.23719 1.35761
C -4.03403 -0.15512 0.74082
H -3.37699 0.46387 0.12633
H -5.07343 0.01438 0.45998
H -3.90024 0.11176 1.79805
C -5.28931 -4.88382 0.809
H -4.76182 -5.83809 0.89779
H -5.77347 -4.64754 1.75652
H -6.06063 -4.97433 0.03041
N -3.70027 -1.55578 0.49107
N -4.31501 -3.84604 0.48578
N -3.48874 -4.06174 -0.64075
H -4.0753 -4.36131 -1.42319
H -2.85427 -4.83014 -0.42697
C 0.97161 -0.20265 -4.07358
C 0.51349 0.12147 -2.79469
C 1.40866 0.45854 -1.77602
C 2.77552 0.46601 -2.04842
C 3.26442 0.14454 -3.32432
C 2.34229 -0.18989 -4.32754
H 0.26573 -0.45358 -4.85786
H 1.04113 0.71886 -0.78911
H 3.47345 0.72951 -1.25804
H 2.70081 -0.44203 -5.3221
C 4.74482 0.18708 -3.61755
H 5.0144 -0.51133 -4.41599
H 5.04812 1.19038 -3.94459
H 5.33554 -0.05772 -2.72911
S -1.2378 0.07513 -2.44734
O -1.47675 -1.40916 -1.94731
O -1.51815 1.01534 -1.34744
O -1.95768 0.25225 -3.71564
H -2.4062 -2.56651 2.32541