Electronic Supporting information for:

Click 1,2,3-triazole derived fluorescent scaffold by mesoionic carbene-nitrene cyclization: an experimental and theoretical study

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Contents

SI 1. *Crystal Structure Report for 5a*

A specimen of $C_{16}H_{14}N_4$, approximate dimensions 0.057 mm x 0.168 mm x 0.251 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.
The total exposure time was 39.43 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 116902 reflections to a maximum θ angle of 34.53° (0.63 Å resolution), of which 5211 were independent (average redundancy 22.434, completeness = 93.7%, R_{int} = 8.74%, R_{sig} = 6.36%) and 2938 (56.38%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.3021(12) Å, b = 8.0165(6) Å, c = 20.5586(14) Å, β = 103.284(4)°, volume = 2614.8(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9642 reflections above 20 σ(I) with 5.774° < 2θ< 45.56°. Data were corrected for absorption effects using the Numerical Mu From Formula method (SADABS). The ratio of minimum to maximum apparent transmission was 0.944. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9790 and 0.9950.

The final anisotropic full-matrix least-squares refinement on F^2 with 182 variables converged at R1 = 5.01%, for the observed data and wR2 = 12.90% for all data. The goodness-of-fit was 1.002. The largest peak in the final difference electron density synthesis was 0.249 $e^-/Å^3$ and the largest hole was -0.239 $e^-/Å^3$ with an RMS deviation of 0.049 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.333 g/cm^3 and F(000), 1104 e^-.

Table S1. Sample and crystal data for **5a.**

Chemical formula	$C_{16}H_{14}N_4$
Formula weight	262.31 g/mol
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal size	0.057 x 0.168 x 0.251 mm
Crystal system	monoclinic
Space group	C 1 2/c 1
Unit cell dimensions	a = 16.3021(12) Å
	b = 8.0165(6) Å α = 90°
	c = 20.5586(14) Å β = 103.284(4)°
Volume	2614.8(3) $Å^3$ γ = 90°
Z	8
Density (calculated)	1.333 g/cm^3
Absorption coefficient	0.083 mm^{-1}
F(000)	1104

Table S2. Data collection and structure refinement for **5a**

Theta range for data collection	3.63 to 34.53°
Index ranges	-25<=h<=25, -12<=k<=12, -31<=l<=31
Reflections collected	116902
Independent reflections	5211 [R(int) = 0.0874]
Coverage of independent reflections	93.7%
Absorption correction	Numerical Mu From Formula
Max. and min. transmission	0.9950 and 0.9790
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5211 / 0 / 182
Goodness-of-fit on F^2	1.002
Final R indices	2938 data; I>2σ(I) R1 = 0.0501, wR2 = 0.1030
	all data R1 = 0.1235, wR2 = 0.1290
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0519P)^2+1.1356P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.249 and -0.239 $eÅ^{-3}$
R.M.S. deviation from mean	0.049 $eÅ^{-3}$

The packing of **5a** in the solid phase is depicted hereafter. Besides bond distances and angles described in the main text, the crystallographic analysis reveals that the crystal packing relies on short p-p contacts between equivalent molecules of **5a**. In particular, there is a rather short

separation (3.377 Å) between the centroids of 1,2,3-triazole ring of a molecule and the imidazole ring of its neighbor.

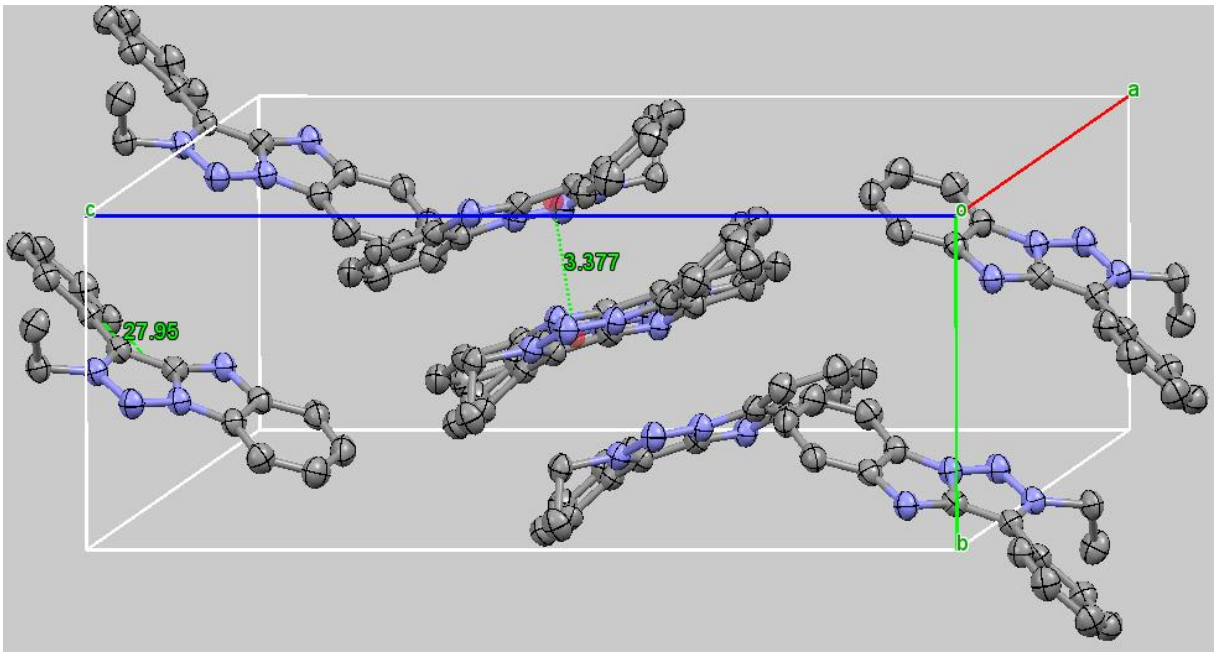

Fig. S1 view of the packing in the X-ray crystal structure of **5a.** Hydrogen atoms omitted for the sake of clarity.

SI 2. *Computation of the infrared spectra of 5a,b,d*

The FT-IR of the three compounds were recorded in the wavenumber region of 4000-700 cm^{-1}. The experimental and calculated IR spectra of **5a**, **5b** and **5d** are shown in Fig. S2. The analysis for modes of vibration with B3LYP level is mentioned in Table S3. None of the predicted vibrational spectra have any imaginary frequency prove that optimized geometry is located at the lowest point on the potential energy surface. The calculated values are globally in good agreement with the experimental data. The wavenumbers for ν(C-H) aromatic stretching has been calculated at 3205, 3206 and 3209 cm^{-1} for **5a**, **5b** and **5d** respectively in good agreement with the experimental. The ν(C-H) alkyl stretching vibrations of the three compounds appearing as a broadened and intense peak in the range of 3052-3128 cm^{-1} .The wavenumber for $\nu(C\text{-}H)_{pr\text{-}alc}$ was computed at 2991 cm^{-1} for **5d**. The peak at 1533, 1584 and 1593 cm^{-1} are due to ν(C-C) stretching vibrations of phenyl ring for **5a**, **5b** and **5d** respectively and of heteroaromatic ring for **5d**. The B3LYP method with 6-31+G (d,p) basis set has good ability to predict the IR spectra of the set of compounds.

Table S3 Experimental and calculated vibrational frequencies (cm^{-1}) with B3LYP level for **5a**, **5b** and **5d**.

	Vibrational wavenumbers (cm^{-1})		Assignments
	Experimental	B3LYP/ 6-31G+ (d, p)	
5a	739	744	δC-H_{Ph} (wag)
	1215	1242	ν_{as} C-N, β C-H_{Ph}
	1393	1431	ν_{s} C-N, β C-H_{Ph}, β NNC (scis)
	1442	1472	ν_{s} C-C
	1585	1593	$\nu_{as}Ring_{Ph}$, ν_{as} C-N , β C-H_{Ph}
	2984	3052	ν_{s} C-H_{alk}
	-	3126	ν_{s} C-H_{alk}
	-	3205	ν_{as} C-H_{Ph}
5b	759	769	δC-H_{Ph} (wag)
	1220	1241	ν_{as} C-N, β C-H_{Ph}
	1394	1381	ν_{s} C-N, β C-H_{Ph}
	1425	1430	ν_{s} C-N, β C-H_{Ph}, β NNC (scis)
	1581	1584	$\nu_{as}Ring_{Ph}$, ν_{as} C-N , β C-H_{Ph}
	2979	3053	ν_{s} C-H_{alk}
	-	3126	ν_{s} C-H_{alk}
	-	3206	ν_{as} C-H_{Ph}
5d	739	744	δC-H_{Ph} (wag)
	1220	1234	ν_{as} C-N, β C-H_{Ph}
	1393	1385	ν_{s} C-N, β C-H_{Ph}, β NNC (scis)
	1425	1476	ν_{s} C-C, β C-H_{Ph}
	1540	1533	$\nu_{as}Ring_{Ph}$, ν_{as} C-N, β C-H_{Ph}
	2927	2991	ν_{s} C-$H_{pr\text{-}alc}$
	-	3055	ν_{s} C-H_{alk}
	-	3128	ν_{as} C-H_{alk}
	3215	3209	ν_{as} C-H_{Ph}

ν: stretching, β: in plane bending, δ out of plane bending, s:symmetric, as:asymmytric, Ph : phenyl, Alk: alkyne,pr-alc: primary alcohol, wag : wagging, scis : scissoring

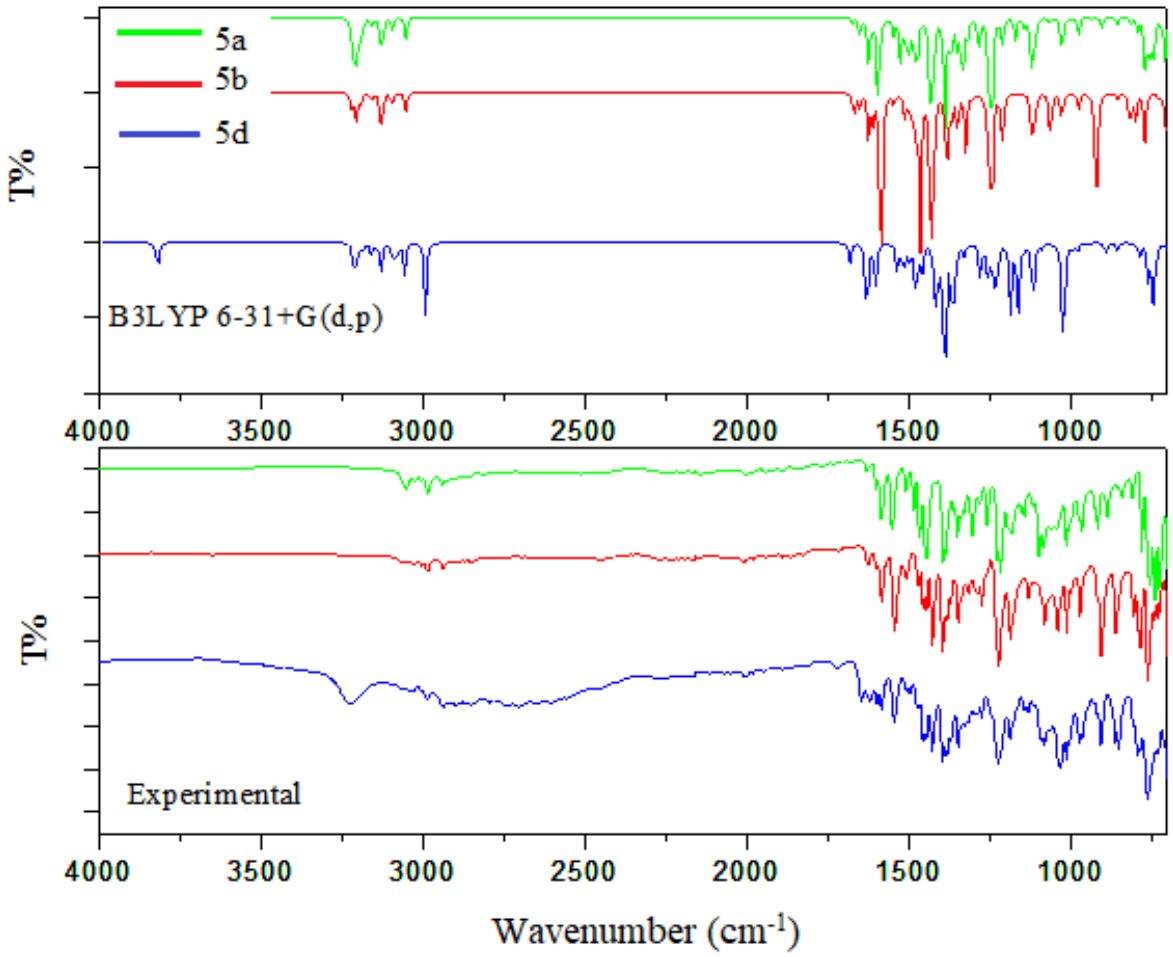

Fig. S2. Experimental and calculated FT-IR spectra with B3LYP level in the range 4000–700cm^{-1} of **5a**, **5b** and **5d** .

SI 3. *Electronic spectra: impact of the dilution on the absorption properties of a solution of 5d*

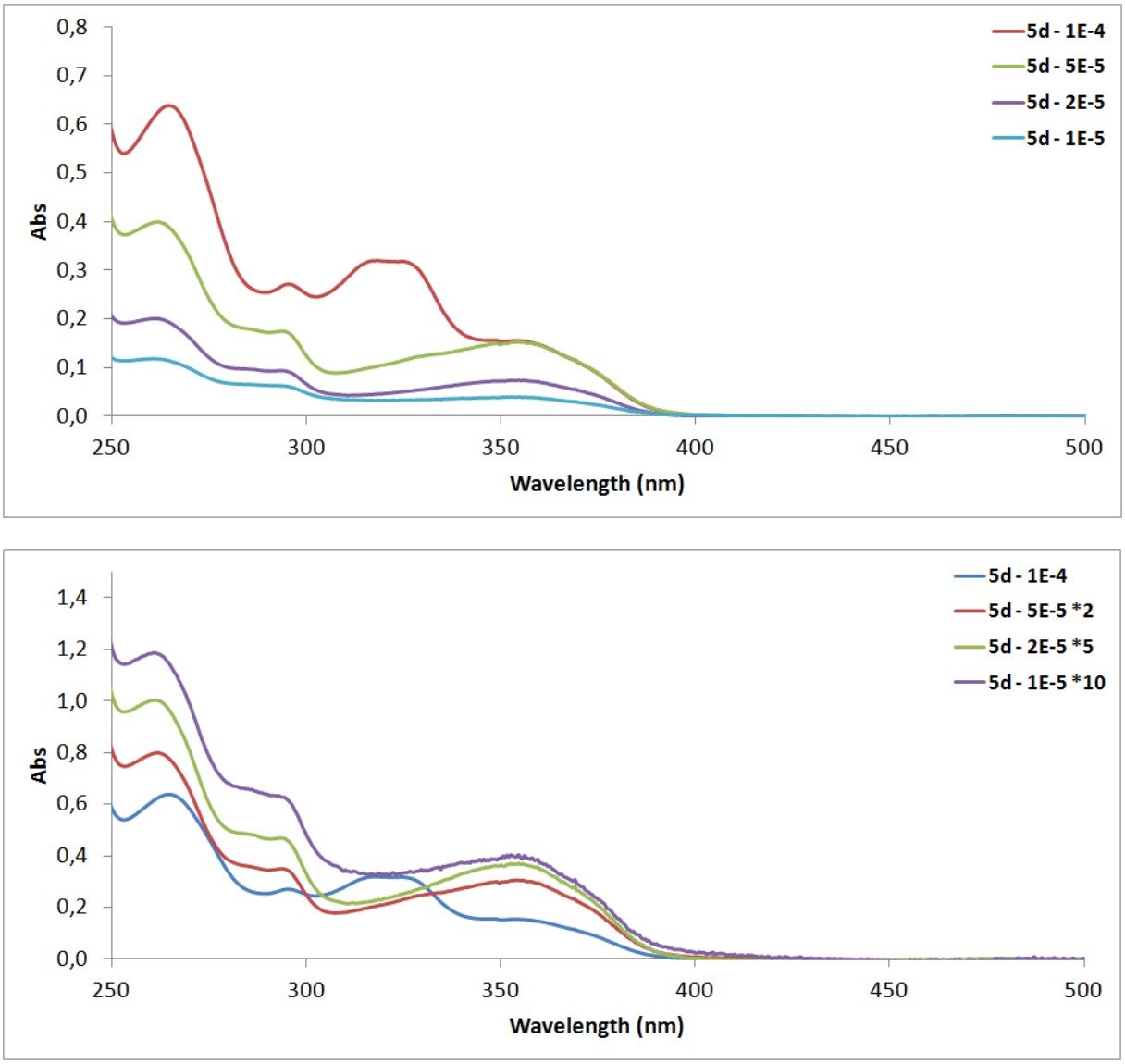

Fig. S3 Experimental spectra recorded upon dilution of a solution of **5d** in methanol. Top: raw data, bottom: data multiplied by the dilution factor. Concentration in mol L^{-1} given for each spectra within the figures.

SI 4. *Additional fluorescence spectra of 5a,b,d*

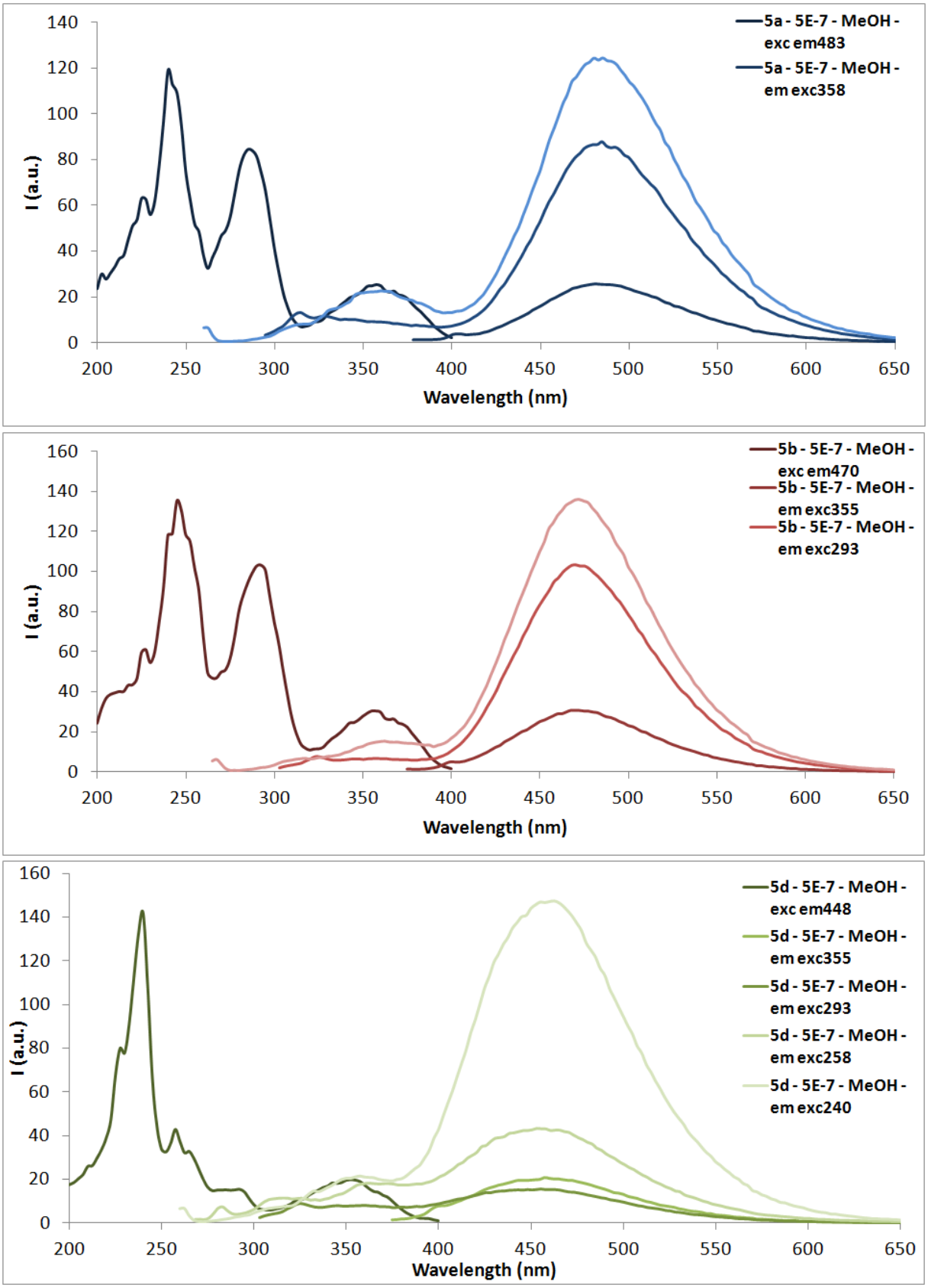

Fig. S4 Supplementary fluorescence spectra of **5a,b,d**. Excitation (exc) spectra at a fixed emission wavelength or emission (em) spectra at a fixed excitation wavelength.

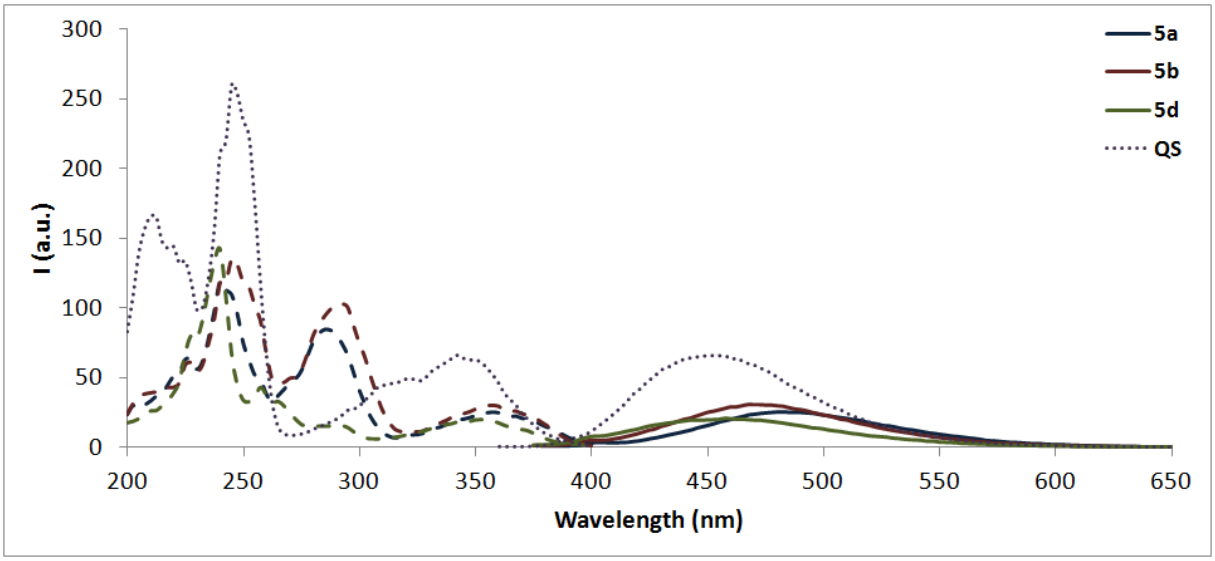

Fig. S5 Experimental fluorescence spectra of **5a**, **5b** and **5d** compounds in methanol. Excitation spectra (dashed) recorded for maximum emission wavelengths. Emission spectra (plain) recorded for maximum excitation wavelengths (Table 3). Concentration: 5×10^{-7} mol L^{-1} superimposed to quinine excitation and emission spectra (dotted) recorded in 0.5 M H_2SO_4 for quantum yield determination with the same instrumental parameters.

SI 5. *Complete depiction of computational data on emission properties*

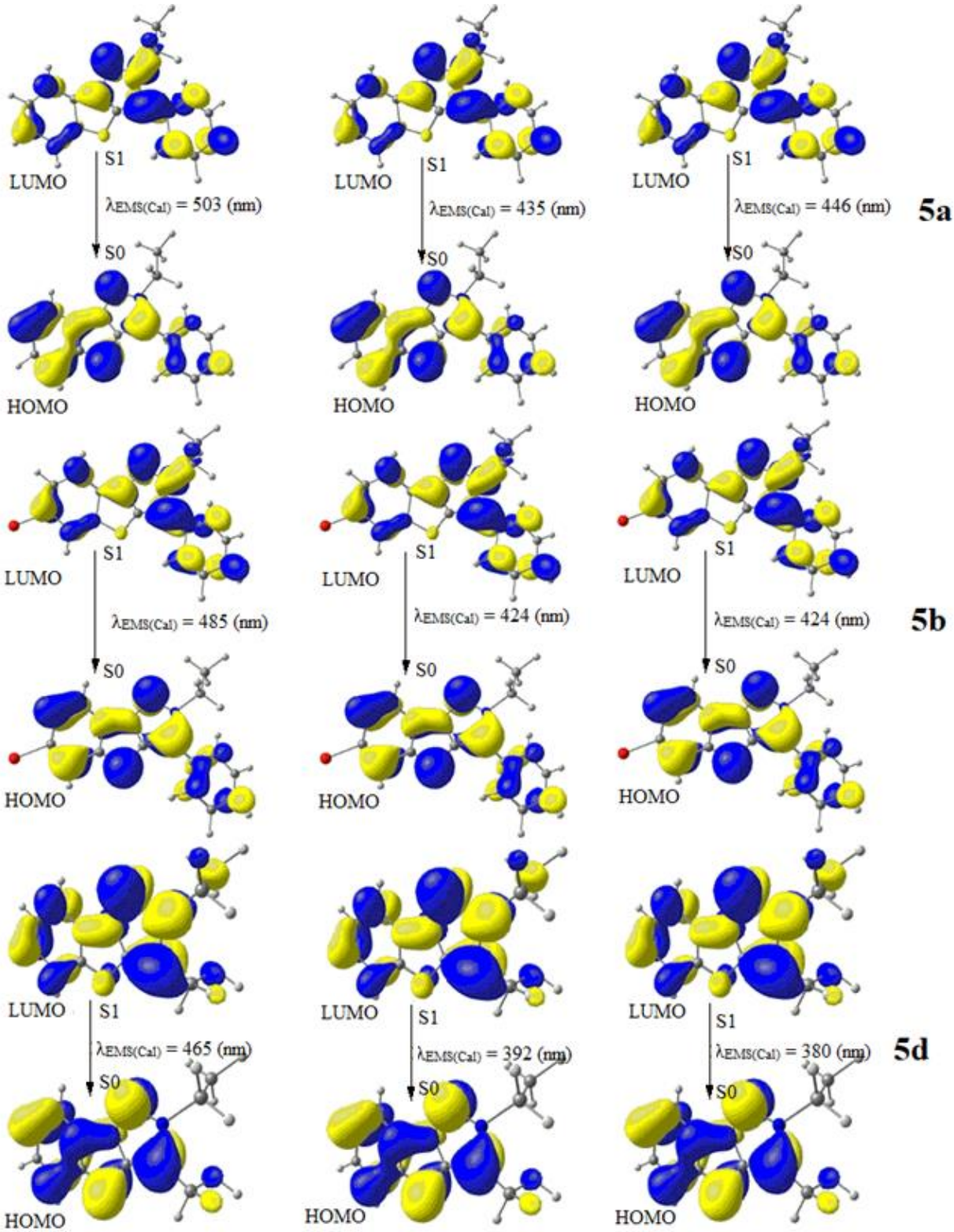

Fig. S6 Difference density for the emission of **5a**, **5b** and **5d** compounds by the TD-DFT method

SI 6. *^{1}H and ^{13}C NMR spectrum of synthesized compounds*

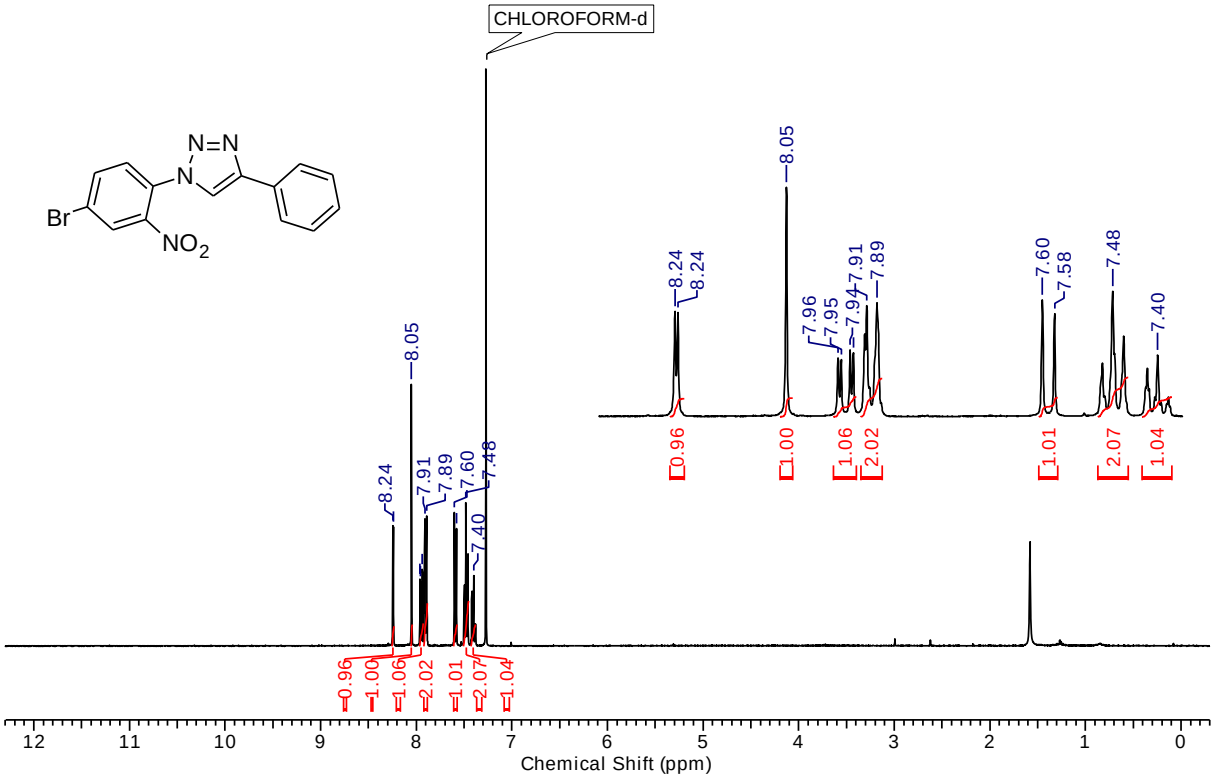

Fig. S7 ^{1}H NMR spectrum of **1b**

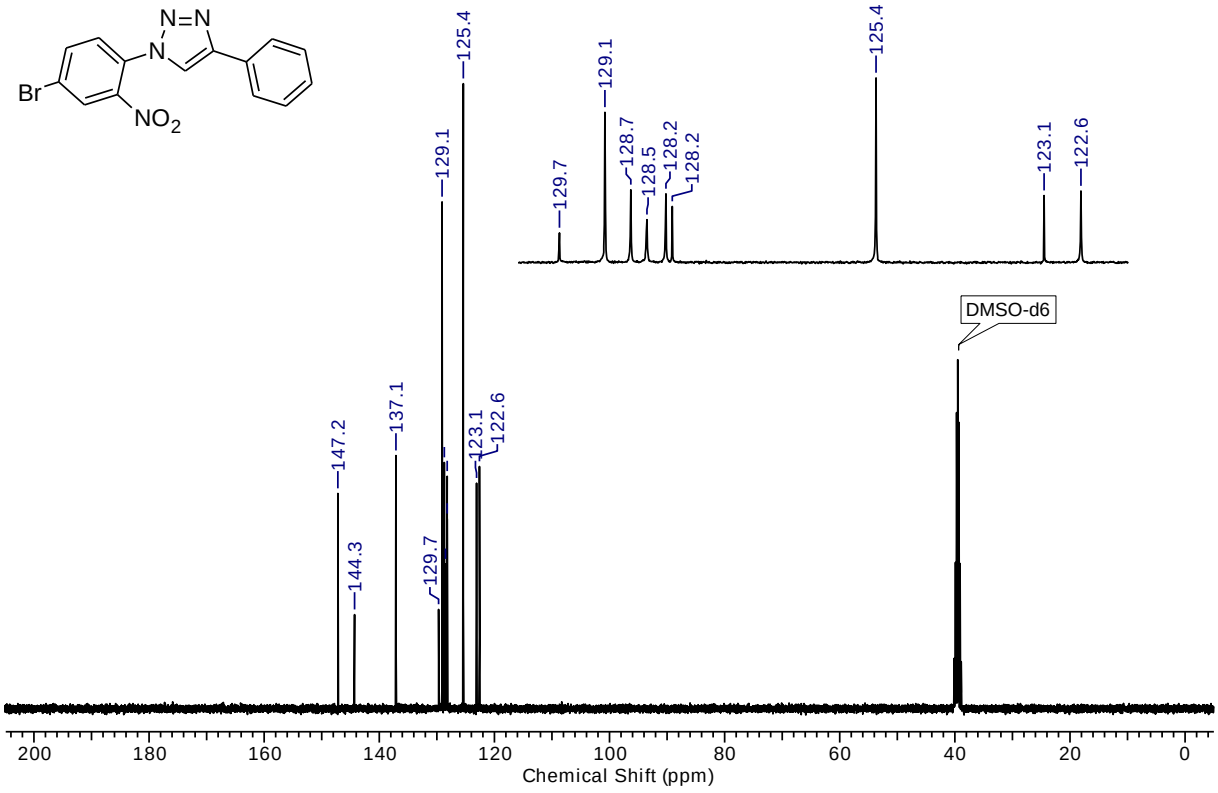

Fig. S8 ^{13}C NMR spectrum of **1b**

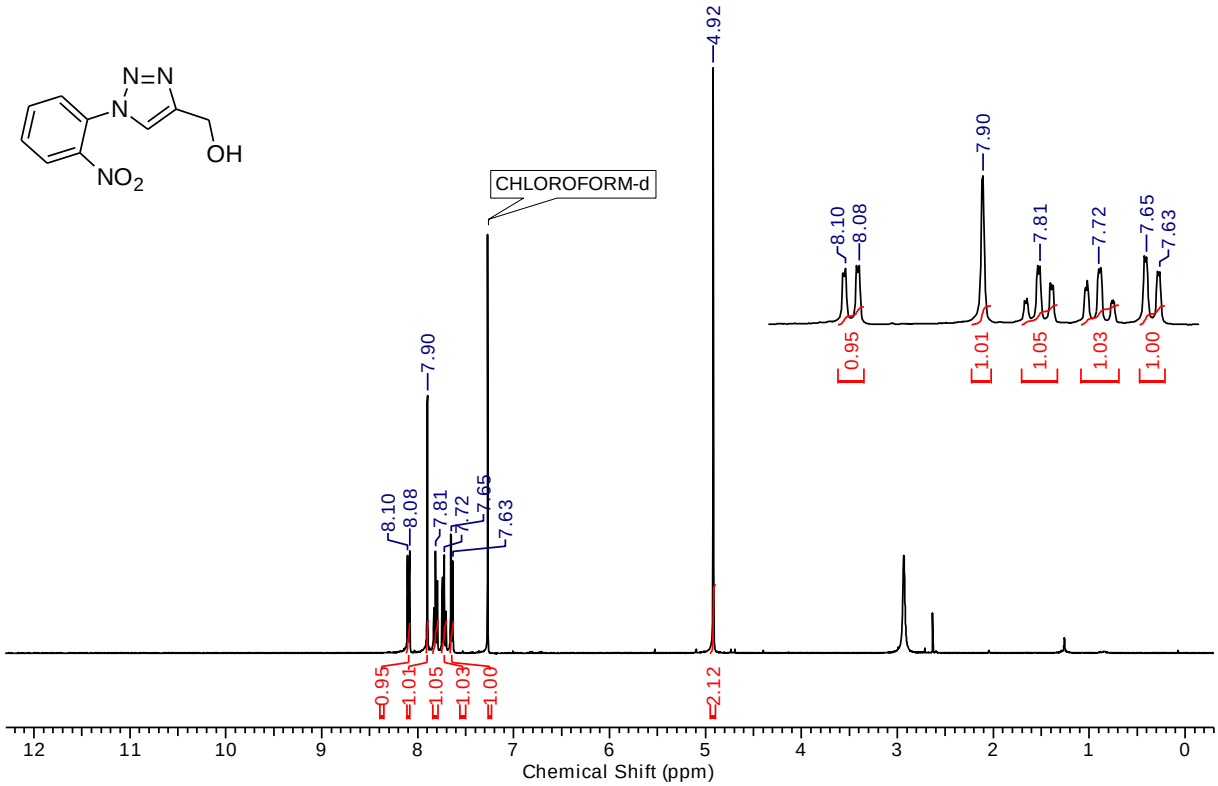

Fig. S9 ^{1}H NMR spectrum of **1d**

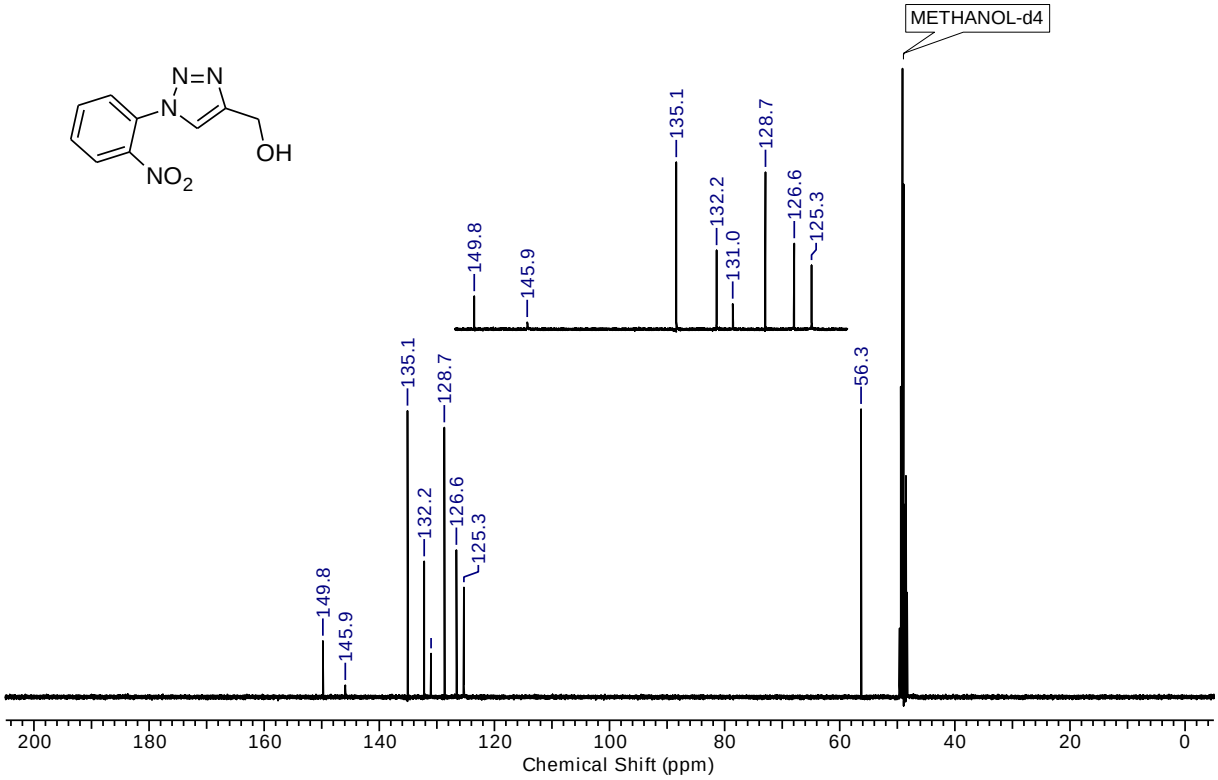

Fig. S10 ^{13}C NMR spectrum of **1d**

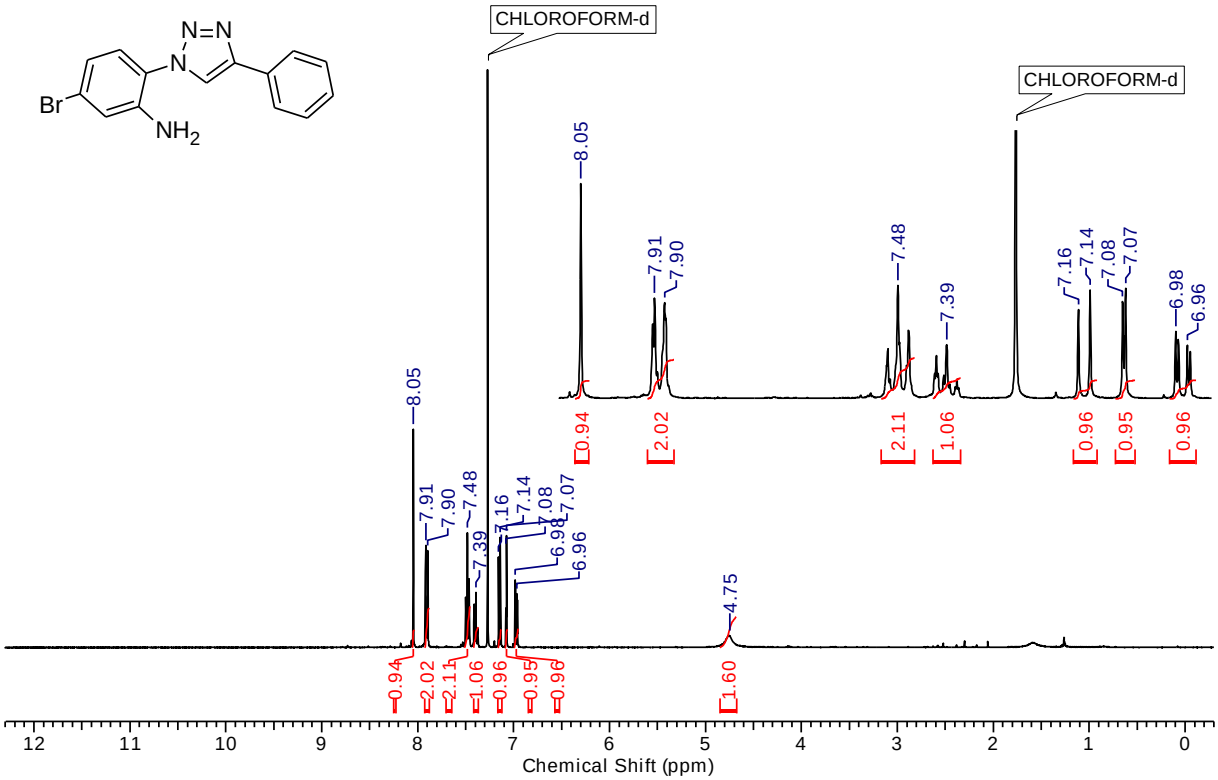

Fig. S11 ^{1}H NMR spectrum of **2b**

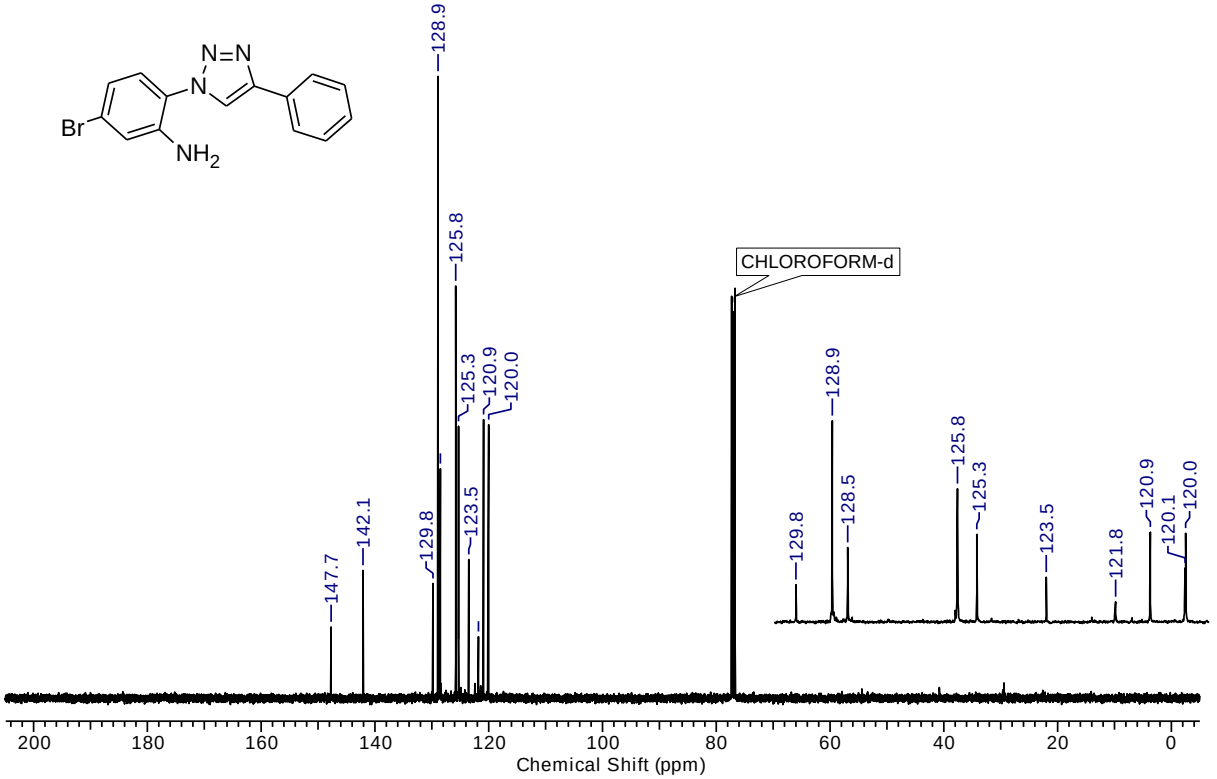

Fig. S12 ^{13}C NMR spectrum of **2b**

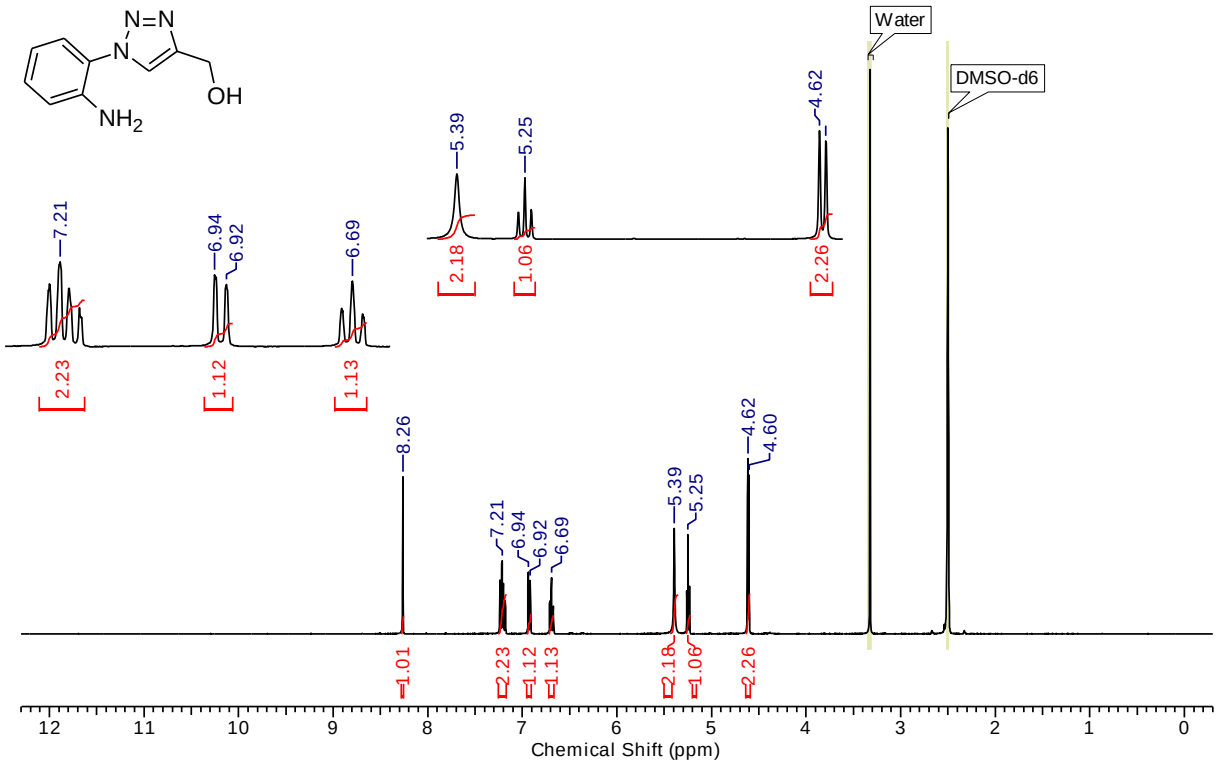

Fig. S13 ^{1}H NMR spectrum of **2d**

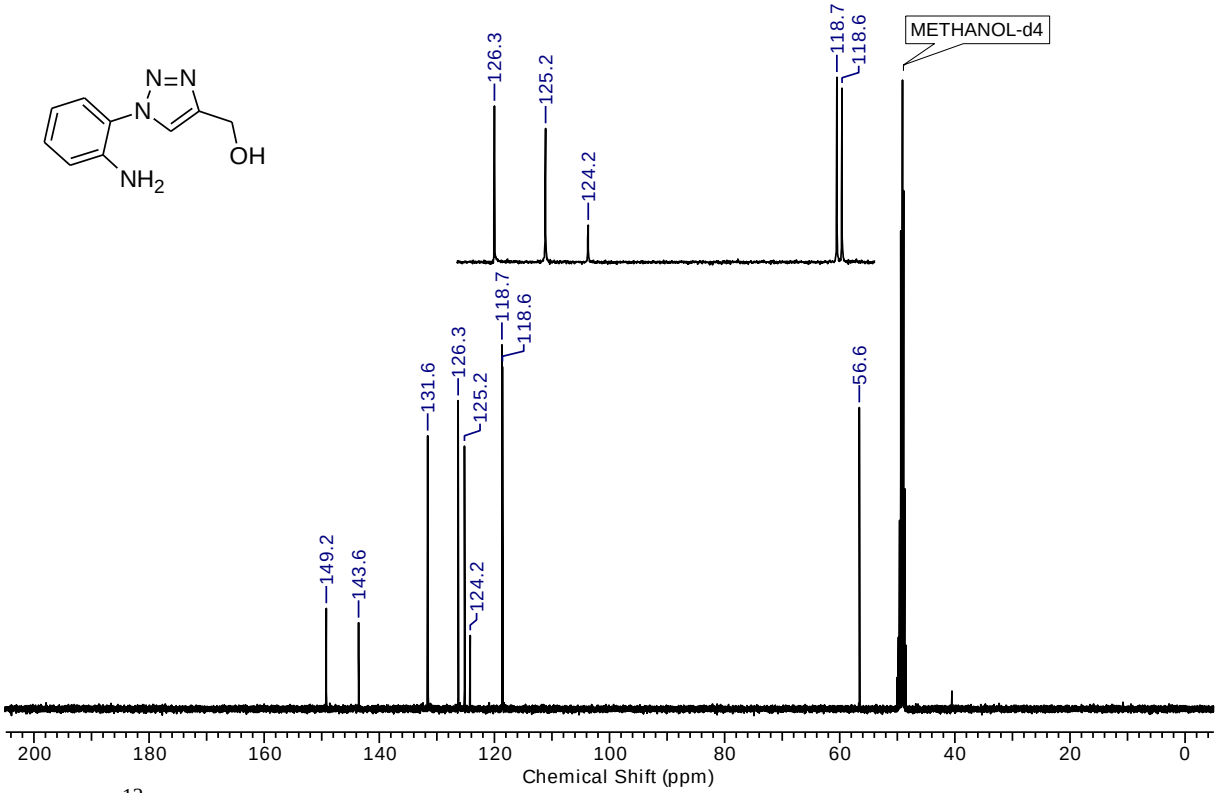

Fig. S14 ^{13}C NMR spectrum of **2d**

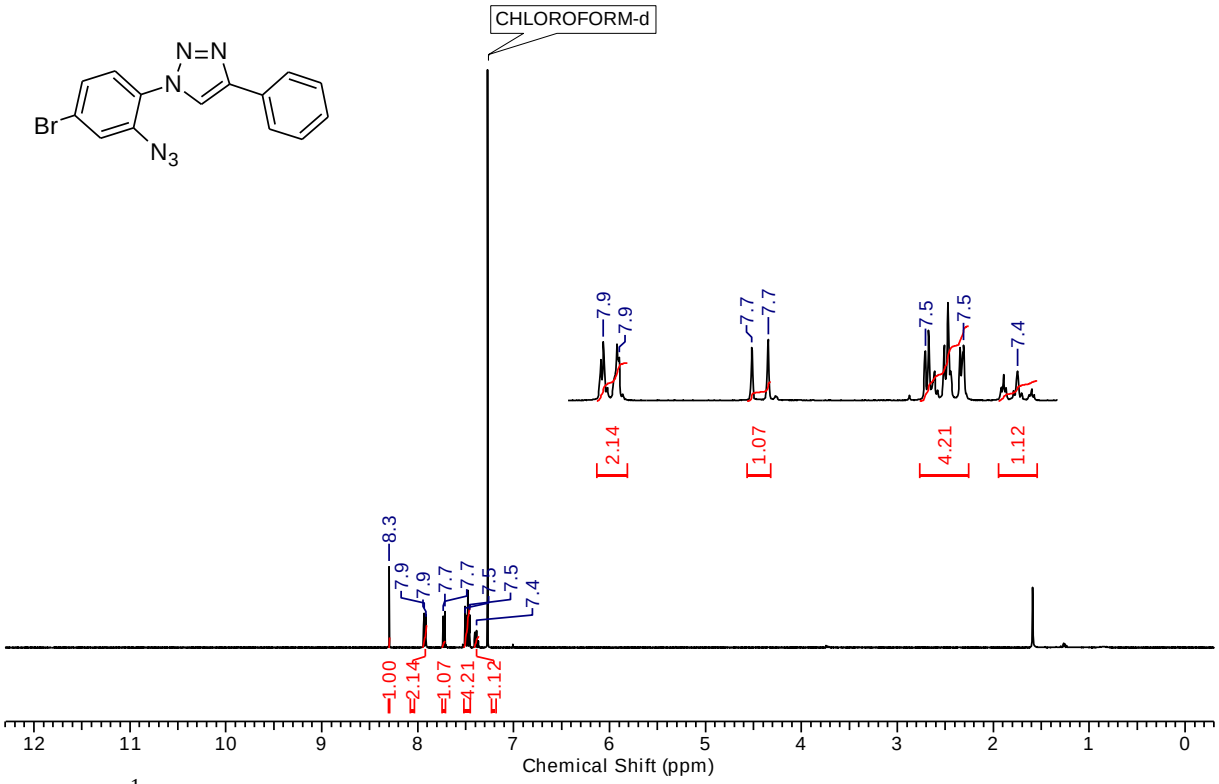

Fig. S15 ^{1}H NMR spectrum of **3b**

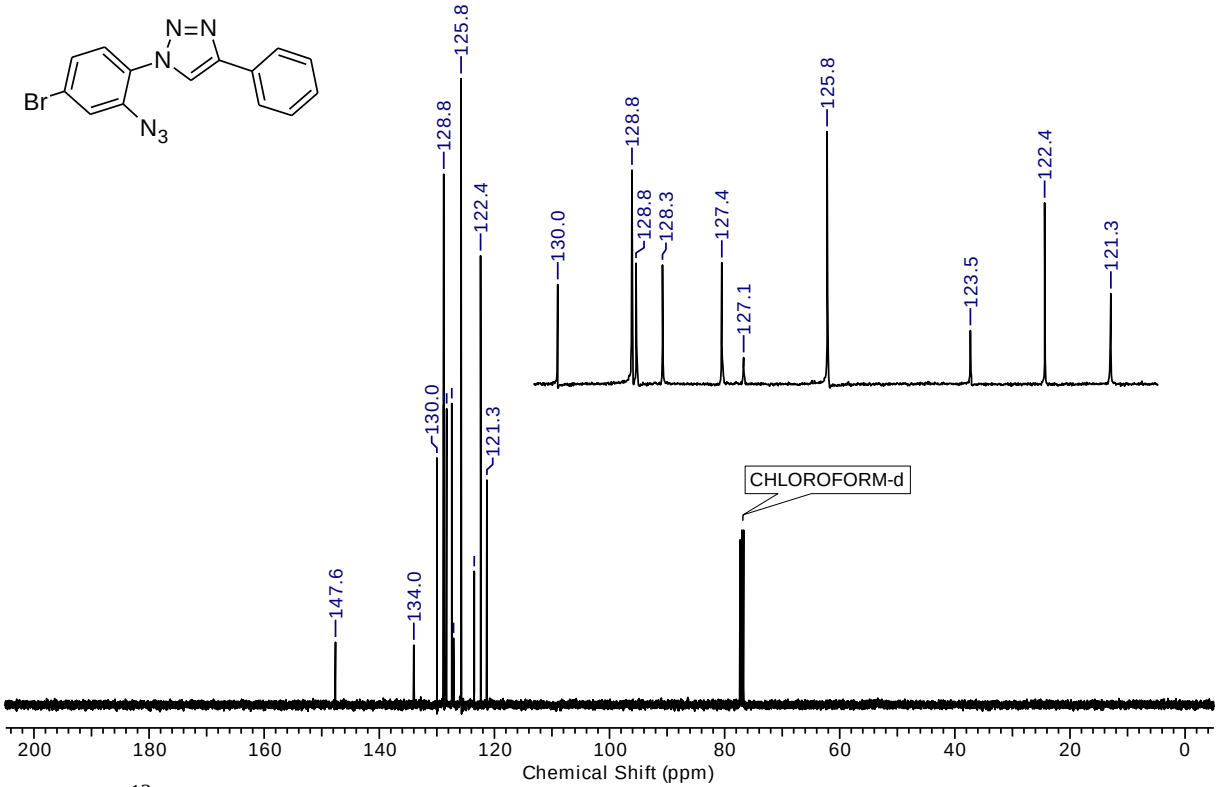

Fig. S16 ^{13}C NMR spectrum of 3**b**

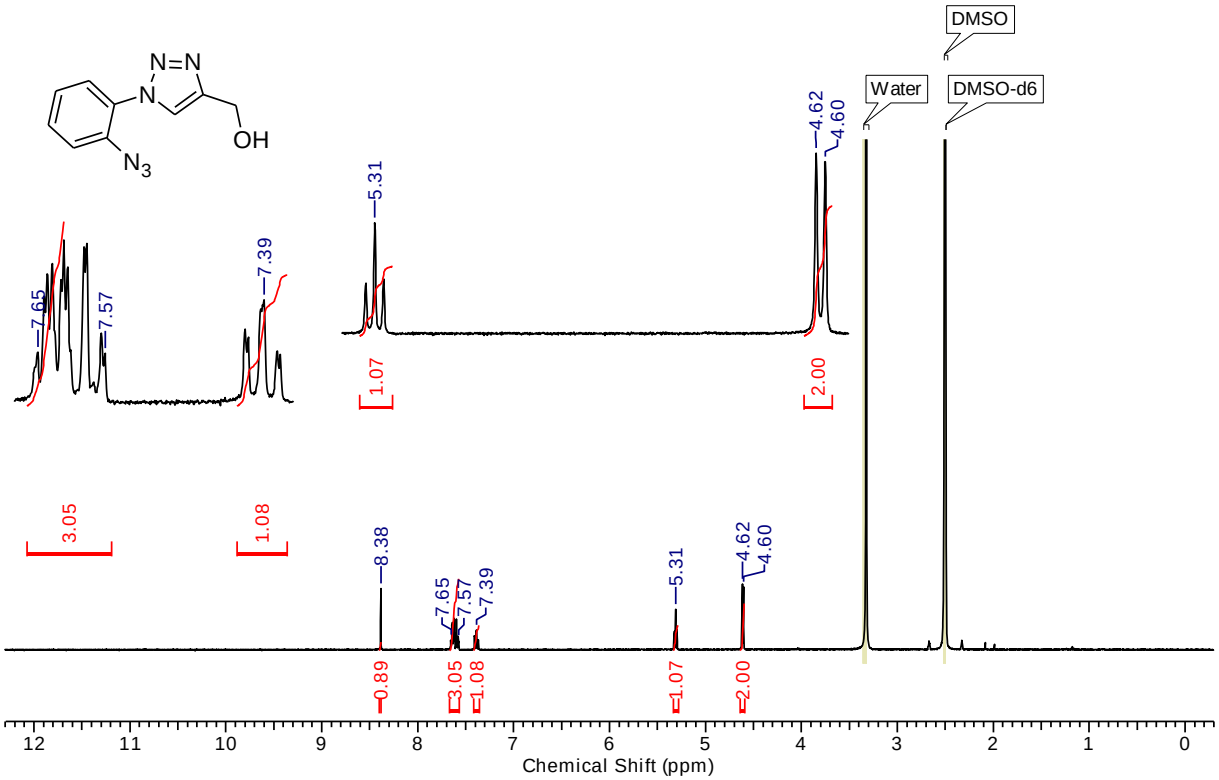

Fig. S17 ^{1}H NMR spectrum of **3d**

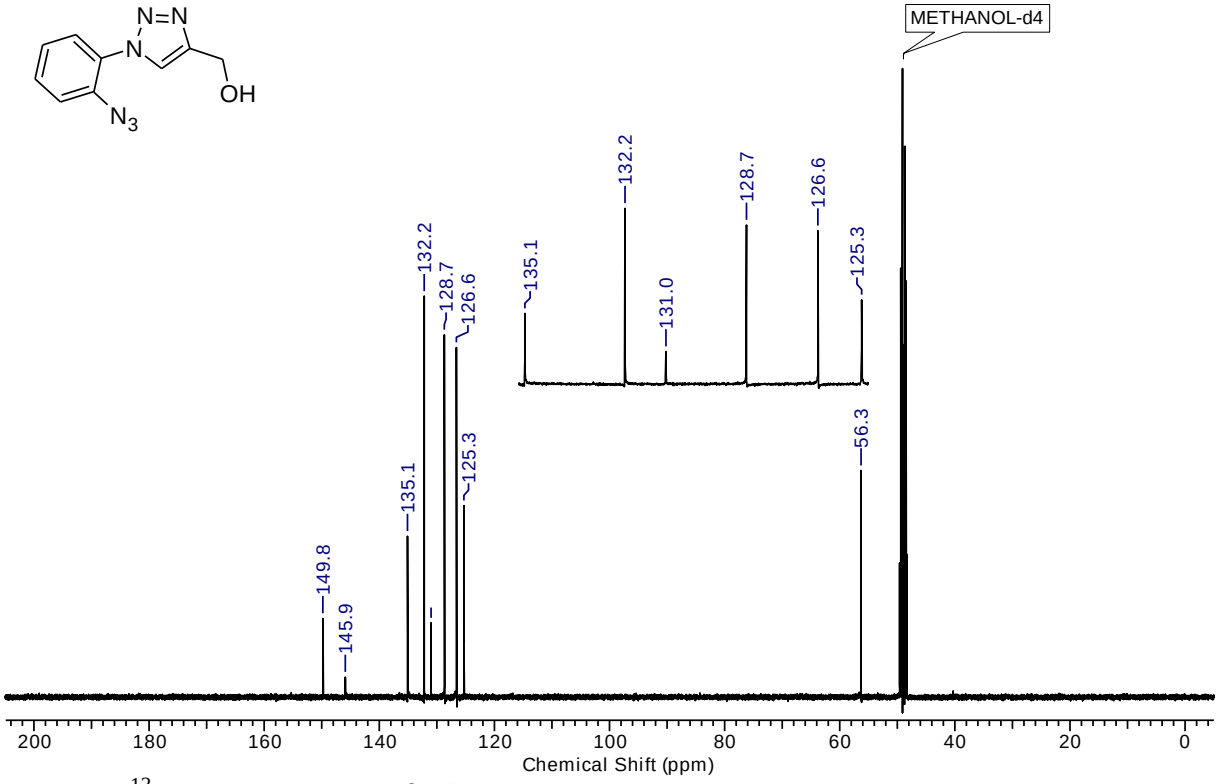

Fig. S18 ^{13}C NMR spectrum of **3d**

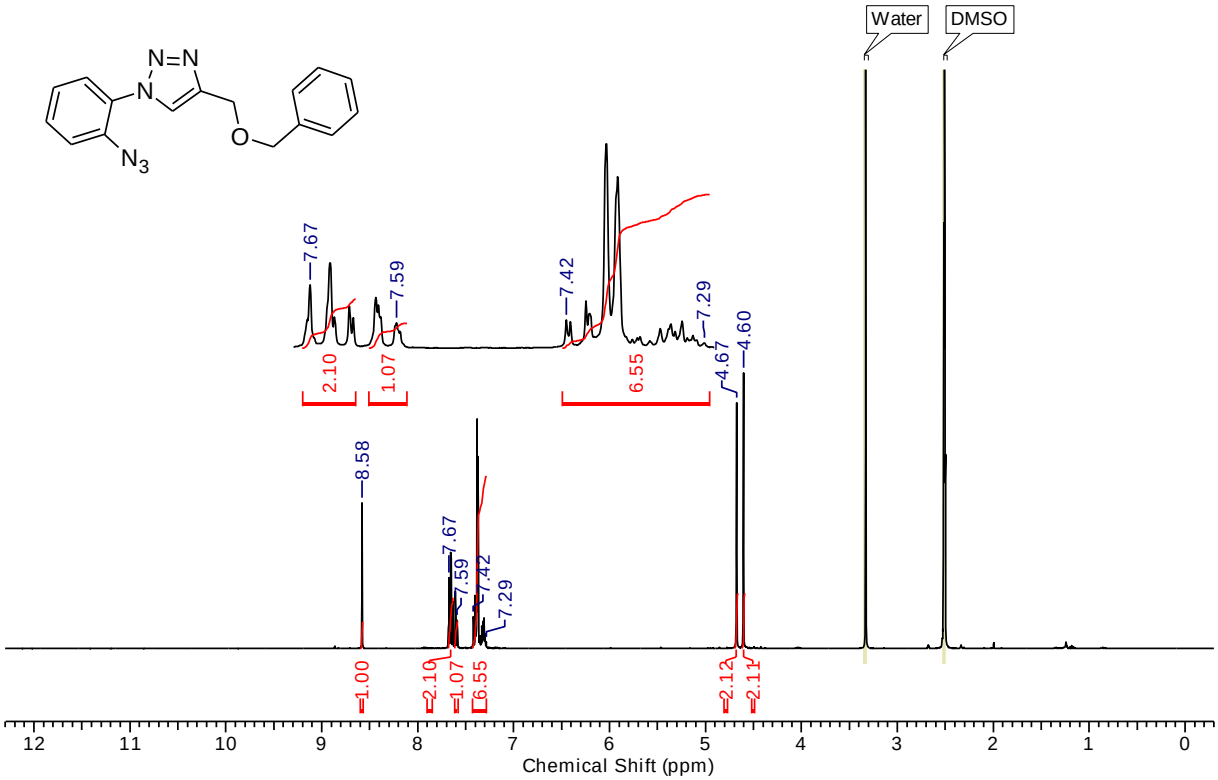

Fig. S19 ^{1}H NMR spectrum of **3c**

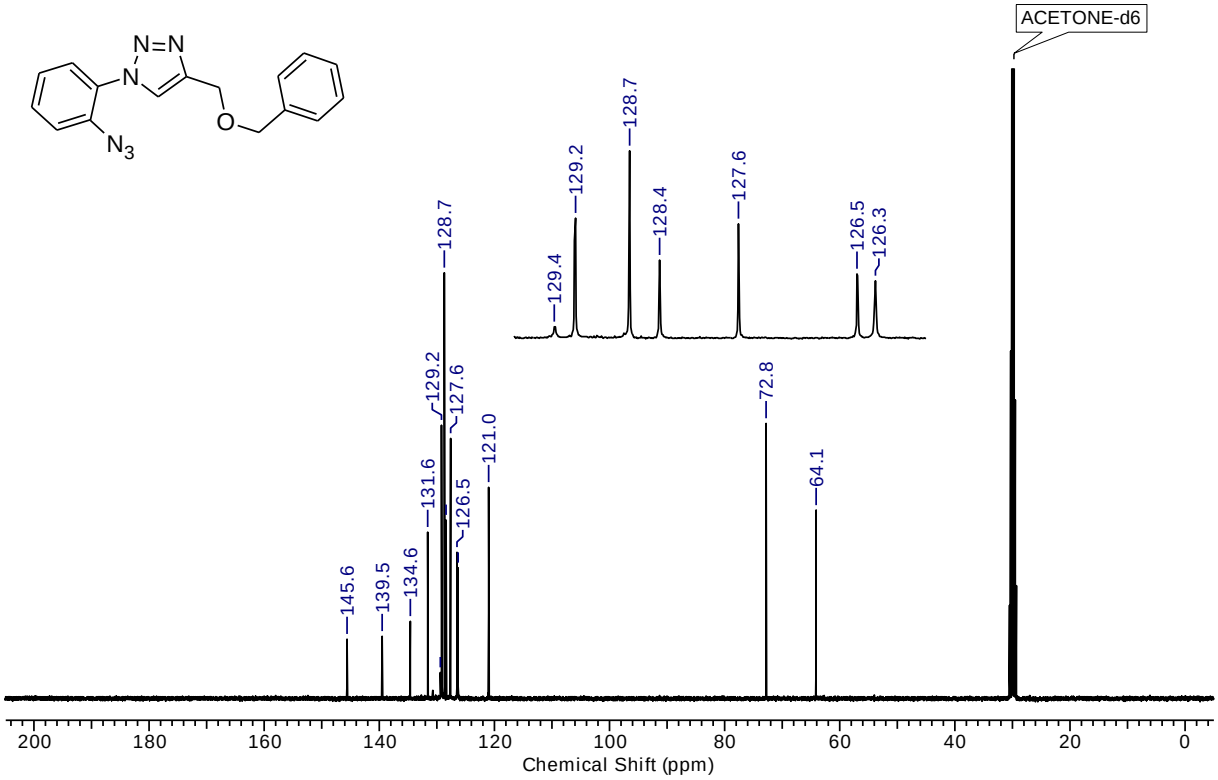

Fig. S20 ^{13}C NMR spectrum of **3c**

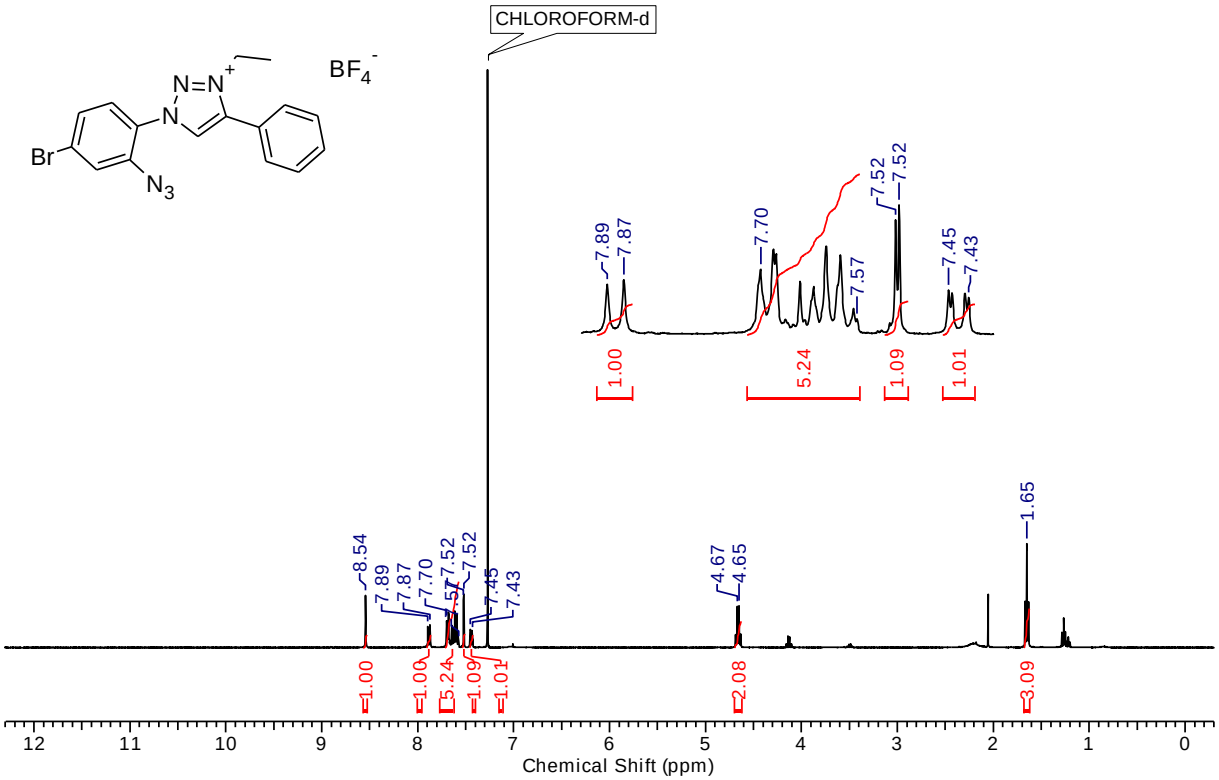

Fig. S21 ^{1}H NMR spectrum of **4b**

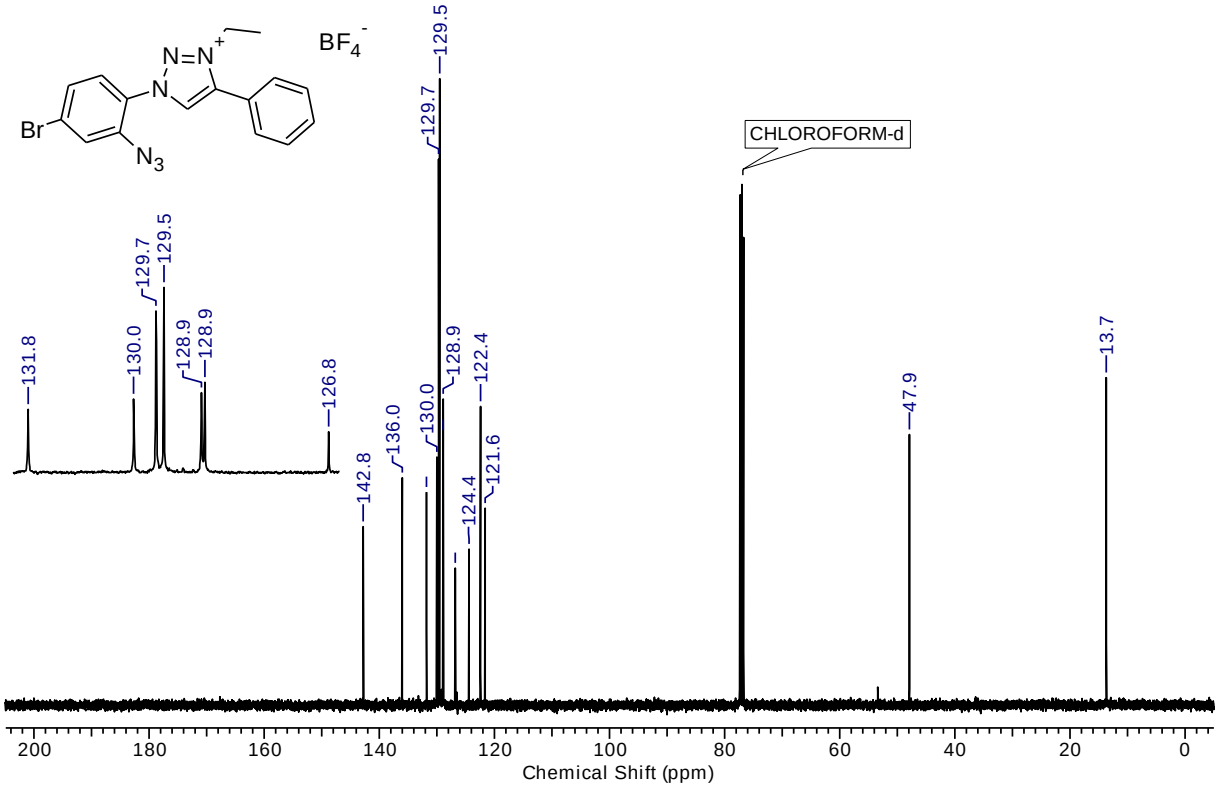

Fig. S22 ^{13}C NMR spectrum of **4b**

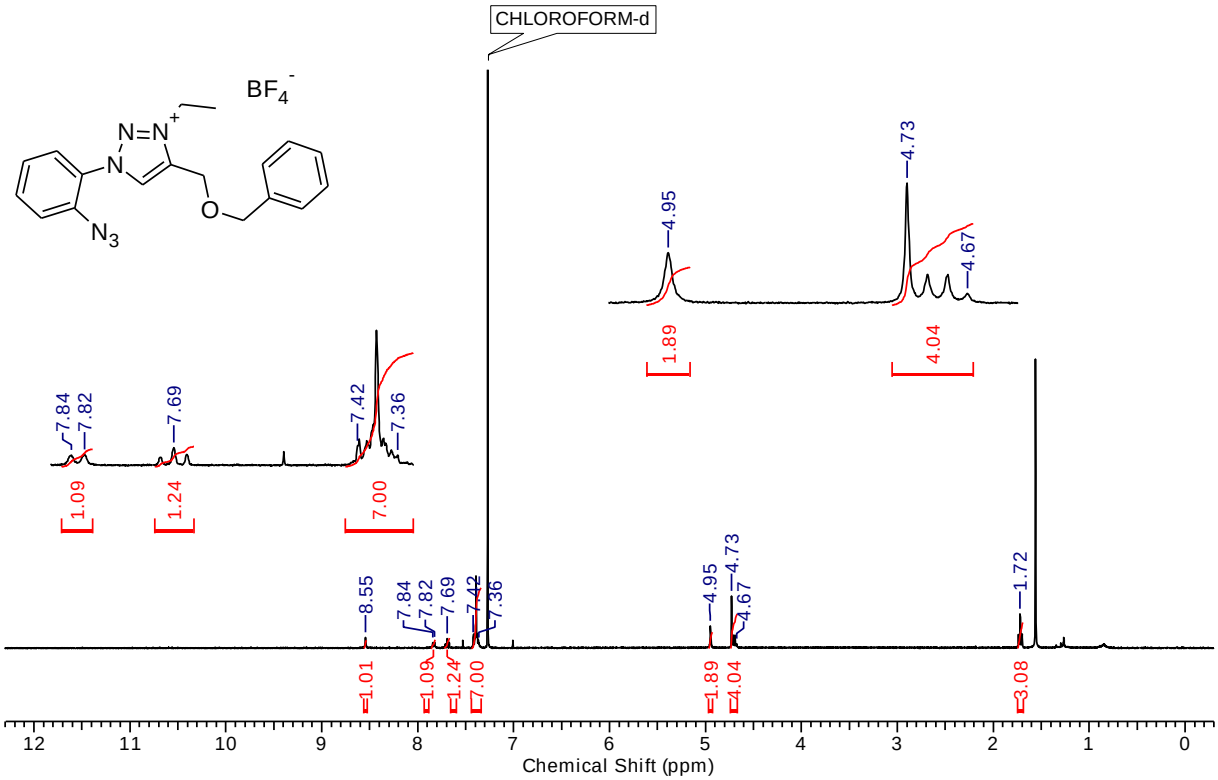

Fig. S23 ^{1}H NMR spectrum of **4c**

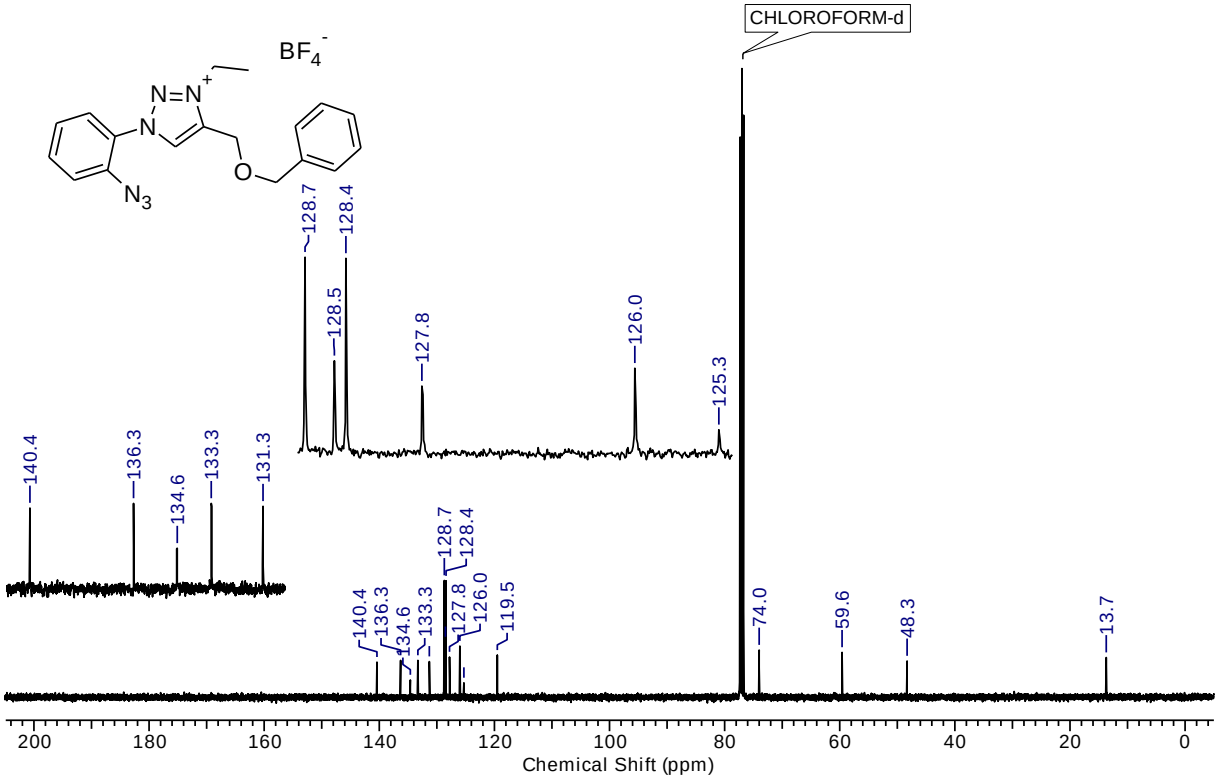

Fig. S24 ^{13}C NMR spectrum of **4c**

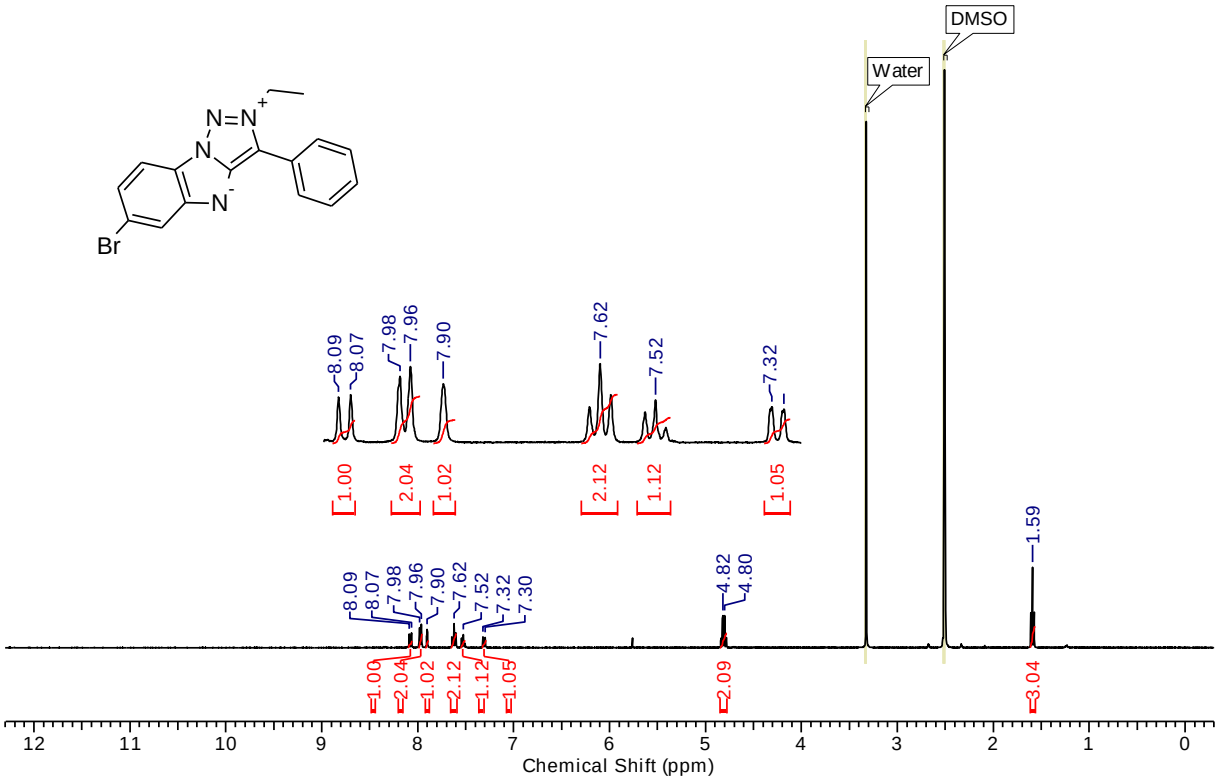

Fig. S25 ^{1}H NMR spectrum of **5b**

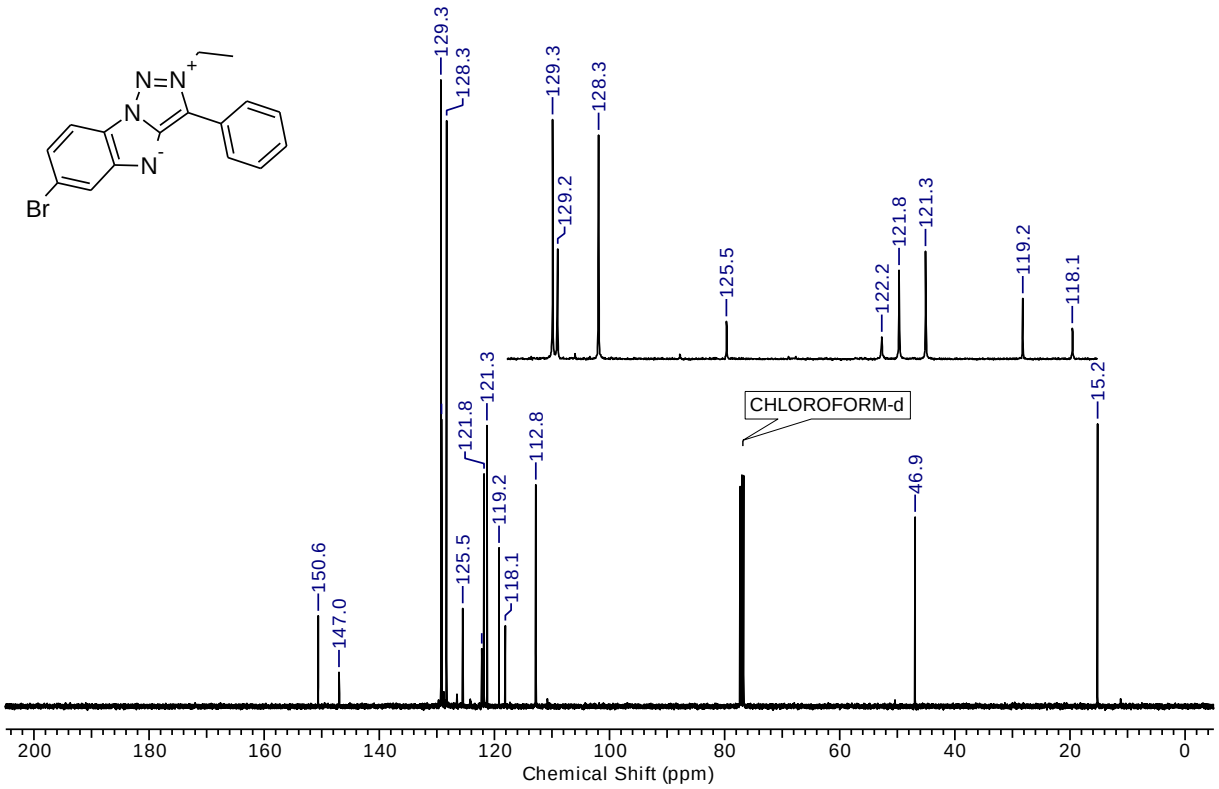

Fig. S26 ^{13}C NMR spectrum of **5b**

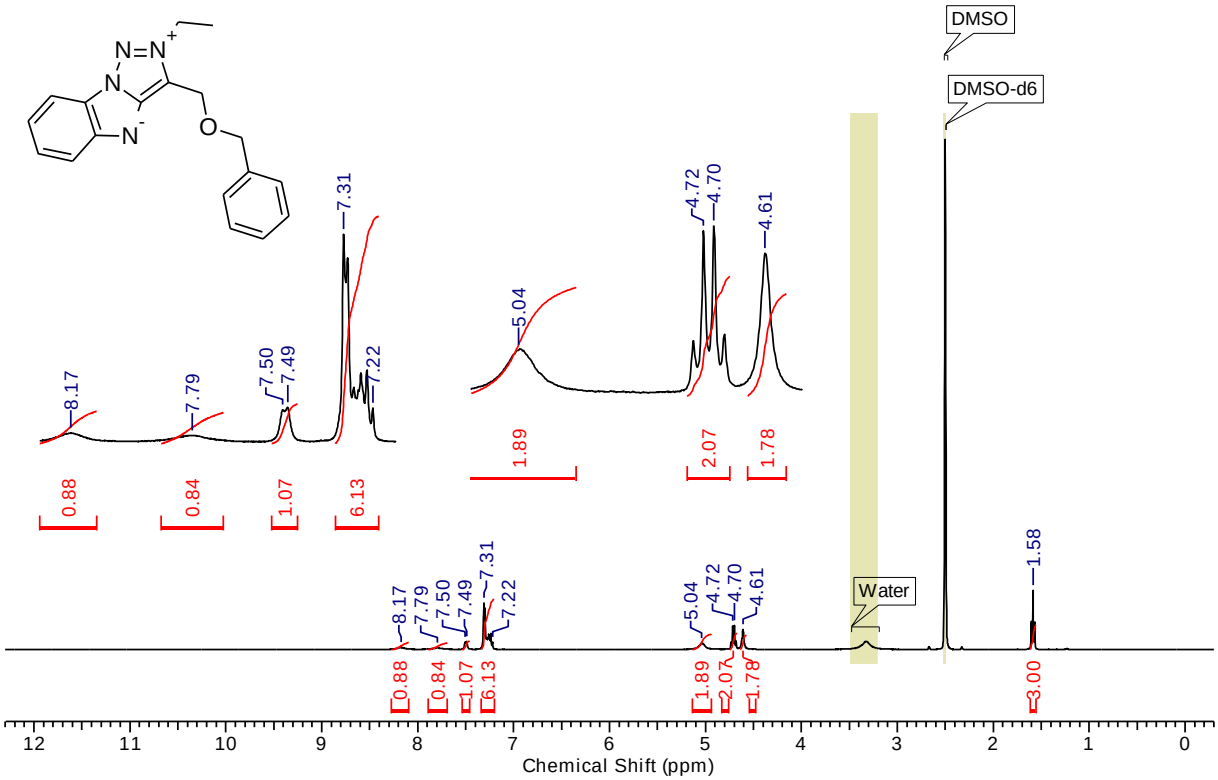

Fig. S27 ^{1}H NMR spectrum of **5c**

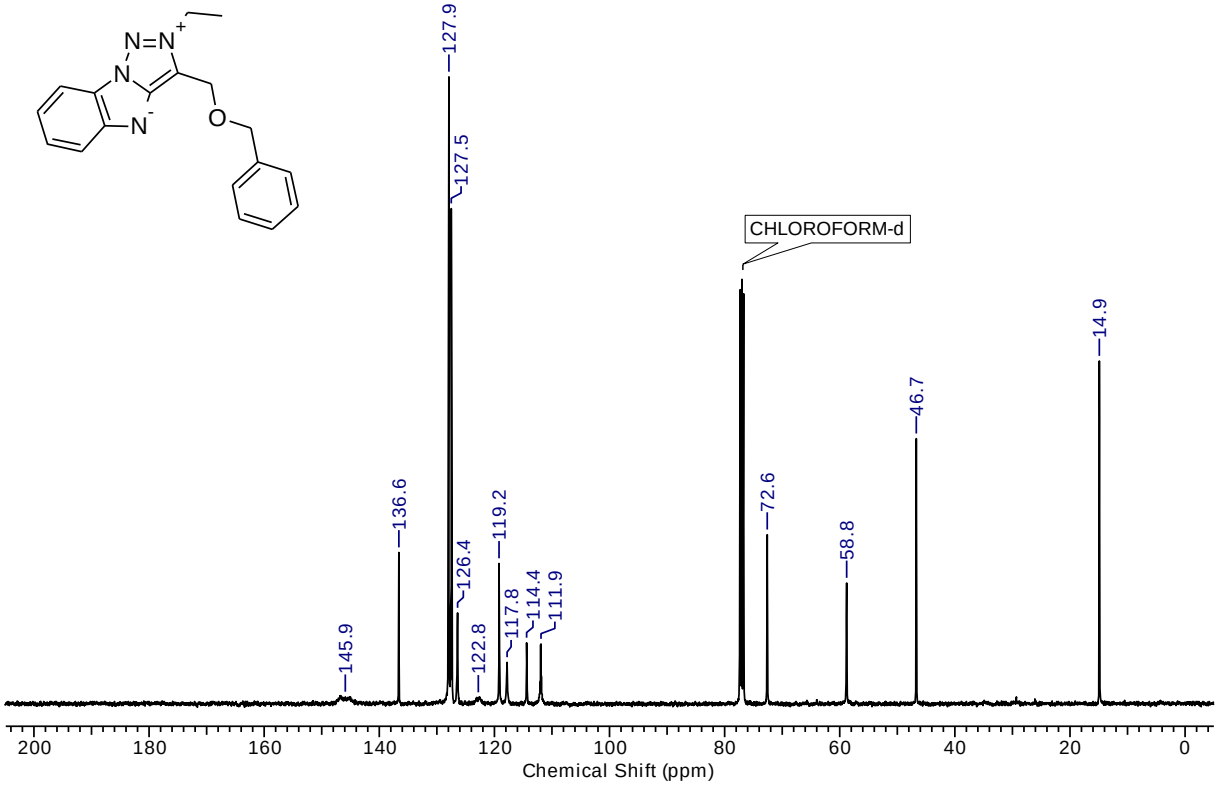

Fig. S28 ^{13}C NMR spectrum of **5c**

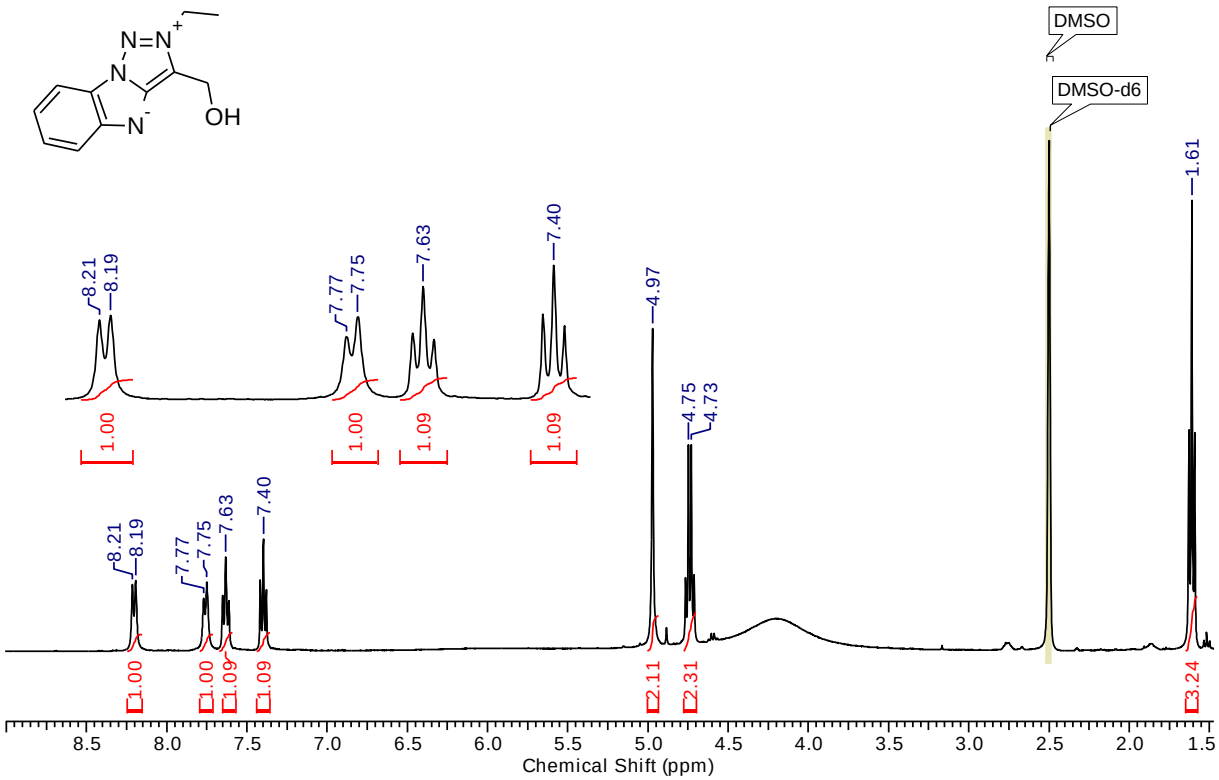

Fig. S29 ^{1}H NMR spectrum of **5d**

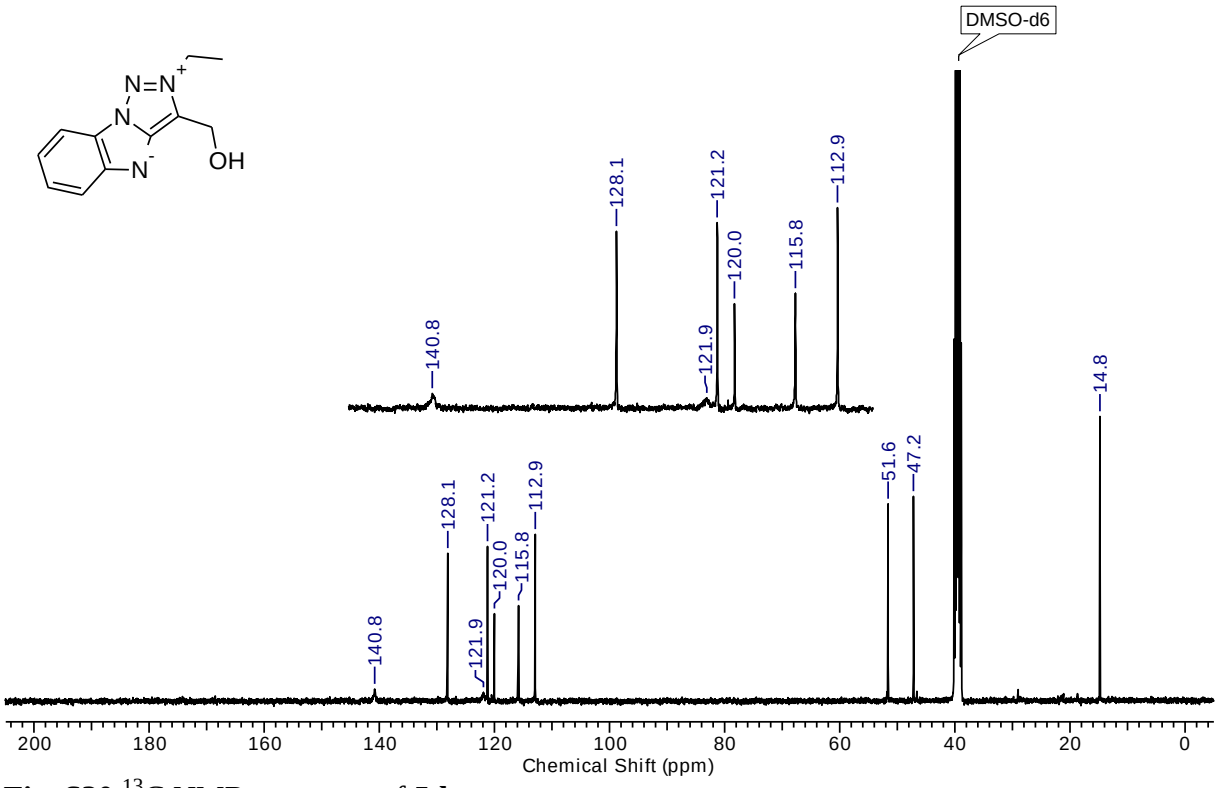

Fig. S30 ^{13}C NMR spectrum of **5d**

SI 7. *xyz coordinates for 5a,b,d*

5a

	X	Y	Z
1N	1.310121	0.758025	-0.149530
2N	-0.608840	1.563249	-0.321280
3N	0.684279	1.923952	-0.349561
4N	1.097539	-1.489377	0.172386
5H	-2.487807	2.171555	-0.948272
6H	-1.144771	3.219975	-1.418231
7H	-2.221422	2.975652	1.464800
8H	-2.525970	4.325220	0.353976
9H	-0.880497	4.009393	0.940022
10C	-1.569429	2.641213	-0.594591
11C	-1.813167	3.538083	0.619682
12C	-0.837847	0.224404	-0.112268
13C	0.456673	-0.336225	-0.008741
14C	-2.120914	-0.475044	-0.045391
15C	2.607602	0.290850	-0.049267
16C	2.426500	-1.116746	0.150959
17C	3.576545	-1.917456	0.294626
18H	3.474232	-2.986845	0.448708
19C	4.823308	-1.307486	0.235843
20H	5.716481	-1.915856	0.346733
21C	4.969194	0.086733	0.035949
22H	5.964189	0.518927	-0.003302
23C	3.858009	0.910454	-0.110246
24H	3.954526	1.980164	-0.264189
25C	-2.146458	-1.828522	-0.443870

26H	-1.228244	-2.298073	-0.780721
27C	-3.330506	-2.560851	-0.392523
28H	-3.327868	-3.600505	-0.706498
29C	-4.513218	-1.967355	0.059445
30H	-5.434875	-2.540225	0.097625
31C	-4.495028	-0.635097	0.478869
32H	-5.400728	-0.170030	0.857340
33C	-3.311744	0.103365	0.436557
34H	-3.316057	1.117791	0.817705

5b

	X	Y	Z
1N	-0.231747	1.215217	-0.197959
2N	-2.283679	1.584470	-0.292504
3N	-1.102248	2.220169	-0.345546
4N	0.063218	-1.031347	0.061861
5H	-4.271009	1.780024	-0.845365
6H	-3.206254	3.105234	-1.328199
7H	-4.099371	2.577201	1.579646
8H	-4.730112	3.848032	0.514450
9H	-3.035412	3.888582	1.040249
10C	-3.465350	2.432336	-0.507439
11C	-3.854001	3.230849	0.737230
12C	-2.208311	0.223766	-0.116800
13C	-0.820504	-0.041329	-0.066129
14C	-3.304925	-0.741323	-0.036734
15C	1.137869	1.040573	-0.148467
16C	1.273900	-0.376604	0.013954
17C	2.570862	-0.918860	0.103923

18H	2.714065	-1.985369	0.229559
19C	3.638721	-0.040139	0.027601
20Br	5.414948	-0.742644	0.147780
21C	3.491696	1.355784	-0.134481
22H	4.371392	1.985882	-0.186937
23C	2.222130	1.914916	-0.224406
24H	2.085874	2.983956	-0.348071
25C	-3.048832	-2.055599	-0.481329
26H	-2.063100	-2.303923	-0.860313
27C	-4.043149	-3.029741	-0.423417
28H	-3.825883	-4.034557	-0.773333
29C	-5.310115	-2.720917	0.080970
30H	-6.083633	-3.481747	0.123816
31C	-5.567503	-1.429446	0.546739
32H	-6.539002	-1.184488	0.966073
33C	-4.574853	-0.449876	0.498636
34H	-4.785353	0.527823	0.916052

5d

	X	Y	Z
1N	-0.352234	-0.526464	-0.179346
2N	1.715276	-0.648130	-0.411330
3N	0.630398	-1.426531	-0.322808
4N	-0.906258	1.685693	-0.035576
5H	3.706200	-0.611251	-0.974608
6H	2.874383	-2.162973	-1.191582
7H	3.686548	-0.928670	1.513518
8H	4.503088	-2.288036	0.711734
9H	2.843834	-2.487491	1.309756

10C	3.017557	-1.320205	-0.511247
11C	3.541236	-1.783100	0.848598
12C	1.474923	0.694094	-0.319362
13C	0.082587	0.804024	-0.164233
14C	2.507550	1.760590	-0.398720
15C	-1.728608	-0.512791	-0.048072
16C	-2.028915	0.887232	0.039470
17C	-3.379135	1.264261	0.182785
18H	-3.641203	2.315115	0.252263
19C	-4.347085	0.269225	0.231413
20H	-5.390646	0.550585	0.341362
21C	-4.017971	-1.105198	0.142471
22H	-4.808834	-1.847476	0.185804
23C	-2.697340	-1.517883	0.001017
24H	-2.429830	-2.567159	-0.068271
25H	3.051335	1.712244	-1.354939
26H	1.979143	2.719639	-0.356735
27H	4.020028	2.388108	0.700489
28O	3.430861	1.621738	0.693738