Supporting Information for

Emissive Silver(I) Cyclic Trinuclear complexes with aromatic amine donor pyrazolate derivatives: way to efficiency

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1. Physical measurement and instrumentation

^{1}H, ^{19}F, and ^{13} C NMR measurements were carried out on Bruker Avance-III-500 spectrometer with CryoProbe Prodigy operating at 500.13 MHz. Infrared (IR) spectra were collected on a Shimadzu IRPrestige 21 FT-IR spectrometer using KBr pellets. The UV-vis spectra of solutions were measured on Cary 50.

Photoluminescence

The photoluminescence spectra of solid samples were recorded at 77 K and 298 K on the Horiba Jobin Yvon S.A.S. Fluorolog 3 instrument. The excitation source was a 450 W Xenon lamp with Czerny–Turner double monochromators the registration channel was equipped by R928 photomultiplier with Czerny–Turner double monochromators. 150 W pulsed Xenon lamp was used for phosphorescence decay curves and phosphorescence spectra measurements. The phosphorescence decay curves were analyzed using the FluoroEssence software for the calculation of the phosphorescence lifetime values.

Photoluminescence quantum yield was measured by absolute method for the solutions in moisture free degassed DCE at T = 298 K (optical density of the solution was not more than 0.1 for the maximum of the most intensive band in quarts cuvette of 1 cm pathlength in order to avoid self-absorption effect). Light of photoluminescence was collected by Quanta-φ F-3029- sphere linked with Fluorolog 3 by Fiber-Optics adaptor FL-3000 produced by Horiba Jobin Yvon. Fluorescence quantum yields were calculated by FluoroEssence software of Horiba.

Fluorescence decay curves were measured with a Horiba Jobin Yvon S.A.S. Fluorolog 3 instrument equipped with a FluoroHub with a NanoLED (368 nm) as an impulse light source (T = 298K). Fluorescence decay curves were analysed as monoexponential functions by the DAS 6.6 software for fluorescence lifetime decay fitting.

X-ray diffraction study

Single-crystal X-ray diffraction experiments of ^{TPA}PzH and **1** were carried out with a Bruker SMART APEX II diffractometer. X-ray diffraction experiment of ^{Carb}PzH wascarried out with a Bruker APEX-II diffractometer. The APEX II software [1] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling, and absorption correction. X-ray dataset for complex **2** was collected in Kurchatov Centre for Synchrotron Radiationand Nanotechnology using “Belok” beamline. The intensities of collected reflections were integrated, merged, and empirically corrected for absorption using XDS software. [2] The

structures were solved by dual-space algorithm and refined in anisotropic approximation for non-hydrogen atoms against F 2 (*hkl*). Hydrogen atoms of methyl, methylene and aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C-H and N-H bond lengths and equivalent displacement parameters (U eq (H) = 1.2U eq (X), X - cental atom of XH_2 group; U eq (H) = 1.5U eq (Y), Y - central atom of YH_3 group). All structures were solved with the ShelXT[3] program and refined with the ShelXL[4] program. Molecular graphics was drawn using OLEX2[5] program.

Table S 1. Crystal data, data collection, and structure refinement parameters for ^{TPA}PzH, ^{Carb}PzH and **1**-**2**.

Compound	^{TPA}PzH	**1**	^{Carb}PzH	**2**
Empirical formula	$C_{44}H_{32}F_6N_6$	$C_{67}H_{47}Ag_3Cl_2F_9N_9$	$C_{18}H_{14}F_3N_3$	$C_{54}H_{39}Ag_3F_9N_9$
Formula weight	758.75	1543.64	329.32	1308.55
Temperature/K	120	120.00	296.15	100.00
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	C2/c	P-1	P-1	$P2_12_12_1$
a/Å	25.971(2)	10.3233(13)	12.7238(5)	21.673(4)
b/Å	13.3722(12)	18.234(2)	12.8680(5)	10.194(2)
c/Å	24.747(3)	18.299(2)	18.9788(8)	21.619(4)
α/°	90	76.795(3)	89.672(2)	90
β/°	120.356(2)	83.404(3)	82.532(2)	90
γ/°	90	75.108(3)	89.798(2)	90
Volume/Å^3	7416.1(13)	3235.1(7)	3081.0(2)	4776.4(16)
Z	8	2	8	4
ρ_{calc} g/cm^3	1.359	1.585	1.420	1.820
μ/mm^{-1}	0.103	1.056	0.111	1.467
F(000)	3136.0	1536.0	1360.0	2592.0
Crystal	0.29 × 0.17 ×	0.22 × 0.14 ×	0.12 × 0.08 × 0.03	0.1 × 0.08 × 0.02

size/mm^3	0.12	0.08		
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	synchrotron (λ = 0.745)
2Θ range for data collection/°	3.546 to 51.996	2.93 to 52	3.646 to 52	4.63 to 62.102
Index ranges	-31 ≤ h ≤ 32, -16 ≤ k ≤ 16, -30 ≤ l ≤ 21	-12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -22 ≤ l ≤ 21	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -23 ≤ l ≤ 19	-26 ≤ h ≤ 29, -14 ≤ k ≤ 13, -28 ≤ l ≤ 27
Reflections collected	22942	30612	30934	31159
Independent reflections	7283 [R_{int} = 0.0601, R_{sigma} = 0.1262]	12659 [R_{int} = 0.0559, R_{sigma} = 0.0987]	12075 [R_{int} = 0.0422, R_{sigma} = 0.0610]	12624 [R_{int} = 0.0744, R_{sigma} = 0.0874]
Data/restraints/parameters	7283/0/513	12659/0/811	12075/0/885	12624/361/745
Goodness-of-fit on F^2	1.053	0.916	1.090	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0680, wR_2 = 0.1698	R_1 = 0.0459, wR_2 = 0.1049	R_1 = 0.0957, wR_2 = 0.2288	R_1 = 0.0799, wR_2 = 0.1657

MALDI-TOF Mass Spectrometry

Mass spectra were obtained at Axima Confidence (Shimadzu Biotech) spectrometer using MALDI ionization (laser wavelength 337 nm) and Time-of-Flight (ToF) sensors. Positive ions were scanned in the m/z range from 0 to 2000 Da with pyrene used as a matrix. The sample was dissolved in THF at a concentration of 0.1 mg/ml. Then, 2 µl of the solution was applied to a steel MALDI-MS target plate, the solvent was allowed to evaporate, and 2 µl of the matrix solution (20 mg/ml in acetonitrile) was applied. After the complete evaporation of the solvent, the analysis was performed.

2. Experimental section

General procedure for pyrazole synthesis was adopted from [6].

N,N-diphenyl-4-(3-(trifluoromethyl)-1H-pyrazol-5-yl)aniline (^{TPA}PzH). The product was purified by column chromatography using mixture of EtOAc/petroleum ether =1/7 as an eluent. Yellowish solid. Yeild = 73%. ^{1}H NMR (400 MHz, Acetone-d_6): δ 13.11 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.33 (t, J = 7.8 Hz, 4H), 7.15 – 7.04 (m, 8H), 6.97 (s, 1H) ppm. ^{19}F NMR (282 MHz, Acetone-d_6): δ - 62.43 ppm. ^{13}C NMR (101 MHz, Acetone-d_6): δ 149.2, 148.1, 145.2, 144.1 (q, J^{2}_{C-F} = 36.9 Hz), 130.7, 127.5, 125.7, 124.6, 123.5, 122.7, 121.1(q, J^{1}_{C-F} = 268.7 Hz), 100.8 ppm. Elemental analysis (Found./Calc.): C: 69.45/69.65; H: 4.37/4.29; N: 11.17/12.76. IR (KBr, cm^{-1}): 3164 (ν NH^{Pz}), 2965, 2392, 1943, 1614, 1590, 1545, 1488, 1435, 1404, 1330, 1316, 1253, 1009, 898, 752, 730, 798, 644, 635.

9-ethyl-2-(3-(trifluoromethyl)-1H-pyrazol-5-yl)-9H-carbazole (^{Carb}PzH). The product was purified by column chromatography using mixture of EtOAc/$CHCl_3$=1/9 as an eluent. Yellow solid. Yield = 79%. ^{1}H NMR (400 MHz, Acetone-d_6): δ 13.13 (br.s, 1H, NH), 8.67 (s., 1H), 8.20 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 8.5, 1.6 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.51 (t, J = 8.2 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 7.09 (s, 1H), 4.52 (q, J = 7.2 Hz, 2H, CH_2), 1.42 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, Acetone-d_6): δ 145.8, 140.5, 140.1, 126.3, 123.5, 123.2, 122.6, 120.3, 119.3, 119.5 (q, J^{1}_{C-F} = 221.1 Hz), 117.8, 115.4, 109.4, 109.1, 99.8, 37.3, 13.2 ppm. ^{19}F NMR (282 MHz, Acetone-d_6): δ - 62.43 ppm. Elemental analysis (Found./Calc.): C: 65.23/65.65; H: 4.73/4.29; N: 12.38/12.76. IR (KBr, cm^{-1}): 3188 (ν NH^{Pz}), 3046, 2957, 2876, 1600, 1489, 1257, 1121.

General procedure for synthesis of complexes 1 and 2. In a Schlenk vessel equipped with a magnetic stir and a reflux condenser, 1 mmol of silver(I) oxide and 1.8 mmol of the corresponding pyrazole were dissolved in 15 ml of freshly distilled toluene. The solution was refluxed under an argon atmosphere and then cooled to ambient temperature. The resulting suspension was filtered under argon atmosphere trough a celite pad.

Complex 1. Colorless crystals were obtained by slow evaporation of DCM/hexane solution of the complex at 5ºC. Yield = 52%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.56 (d, J = 7.8 Hz, 2H), 7.26 (t, J = 7.4 Hz, 4H), 7.16 – 6.98 (m, 8H), 6.83 (s, 1H) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ - 60.26 ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 148.9, 147.9, 145.0 (q, J^{2}_{C-F} = 35.1 Hz), 129.9, 127.8, 126.3, 125.3, 123.9, 122.9, 121.8 (q, J^{1}_{C-F} = 270.1 Hz) 102.1, 100.6 ppm. Elemental analysis (Found./Calc.): C: 55.36/54.34; H: 3.70/3.11; N: 8.29/8.64. IR (KBr, cm^{-1}): 3060, 3035, 1590, 1543, 1517, 1489, 1436, 1332, 1315, 1282, 1249, 1151, 1126, 1008, 839, 794, 752, 697, 622, 528.

Complex 2. Yellow crystals were obtained by slow evaporation of DCE/hexane solution of the complex at 5ºC. Yield = 61%. ^{1}H NMR (300 MHz, Benzene-d_6): δ 8.59 – 8.10 (m, 6H), 7.96 –

7.67 (m., 3H), 7.61 – 7.21 (m, 8H), 6.91 (s, 6H), 6.51 – 6.26 (m, 1H), 3.82 (s, 3H), 3.29 (s, 3H), 1.04 (s, 4H), 0.68 (s, 5H) ppm. ^{19}F NMR (282 MHz,): δ - 59.15 (br. s), -59.90 (br. s) ppm. DEPT ^{13}C NMR (101 MHz, CD_2Cl_2): δ 154.7, 144.02, 140.0, 126.1, 124.6, 123.1, 122.5, 120.5, 120.4, 119.0, 118.2, 108.9, 101.4, 37.1, 13.3 ppm. Elemental analysis (Found./Calc.): C: 46.71/49.57; H: 3.14/3.00; N: 9.18/9.63. IR (KBr, cm^{-1}): 3053, 2975, 2930, 1901, 1488, 1474, 1419, 1329, 1247, 1230, 1147, 1124, 1008, 977, 792, 745, 629.

3. Computational details

The TDF computations performed with ORCA 5.03 package[7, 8] applying ωB97X-D3 functional [9, 10] and def2-TZVP[11] basis set with ZORA relativistic Hamiltonian. Basis set for silver atoms was the relativistic SARC-ZORA-TZVP.[12] Ground states of pyrazoles and their silver complexes were fully optimized without any contrains. Additionally ground states of free pyrazoles were optimized with constrained to 0 dihedral angle between pyrazole ring and substituent ring ($D_{R\text{-}Pz}$). RIJCOSX procedure was used in order to speedup calculations. 20 lowest energy exited states were considered under Tamm-Dancoff approximation (TDA). Spin-orbit coupling (SOC) matrix was obtained by SOMF(1X) method.[13] Optimization of excited states were done in the TD-DFT formalizm for first singlets, and with unrestricted DFT approach for the triplet state. Modeling of the absorbance, fluorescence and phosphorescence spectra was done with the ORCA exited states dynamics (ESD) module.[14] The negative frequencies which appears in the constrained ground state (^{D0}GS) were removed. The quantitative analysis of excitations (natural transition orbitals, fragment impacts) was performed with the Multiwfn v3.7 program.[15]

4. Supplementary Figures and Tables

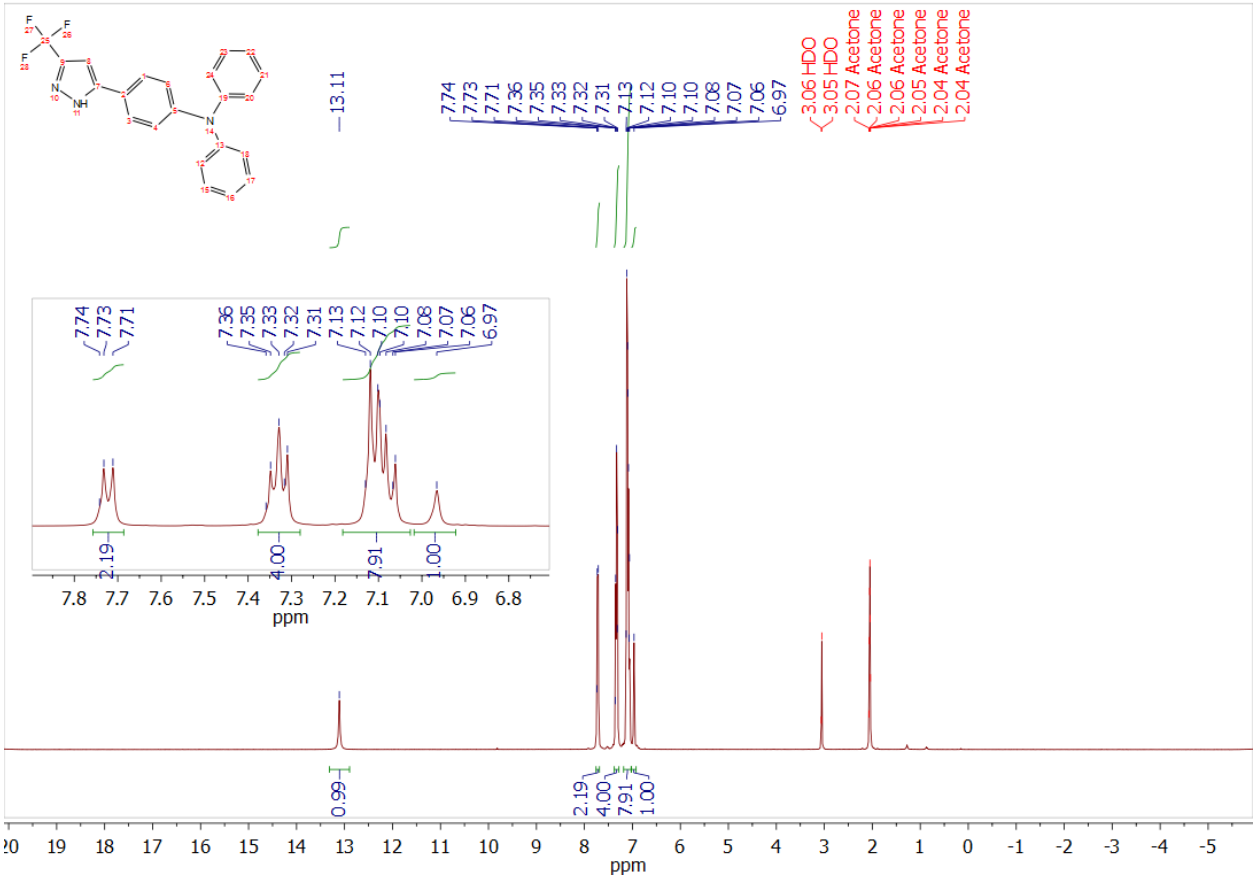


Figure S1. ^{1}H NMR (acetone d-6) spectrum for ^{TPA}PzH

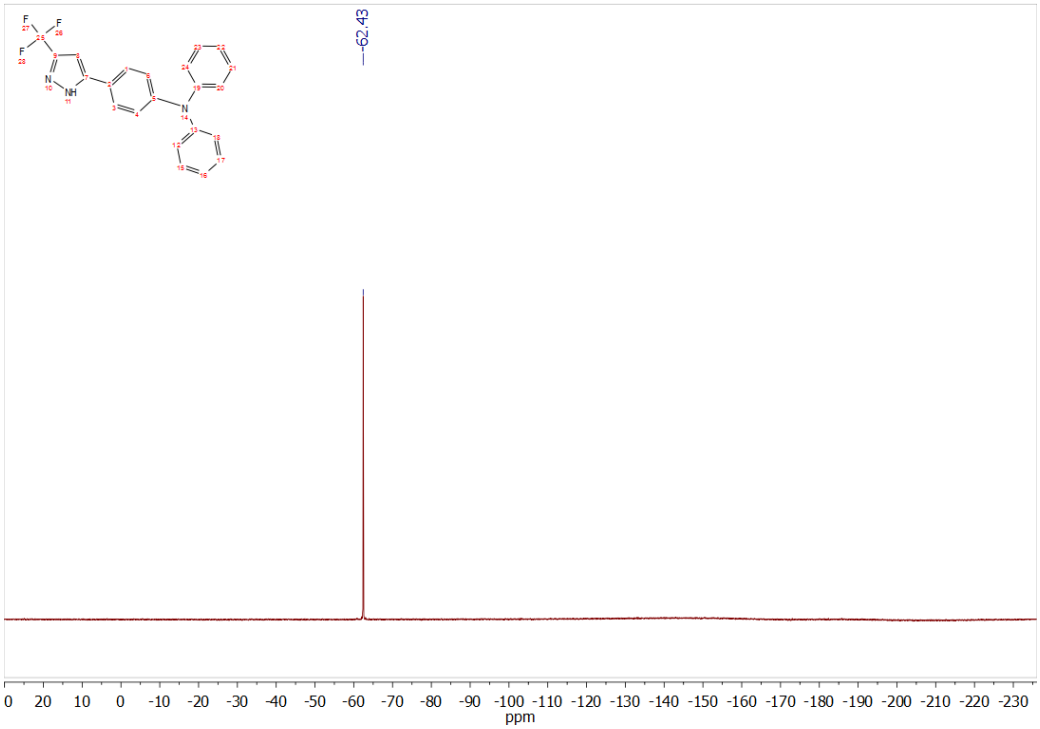


Figure S2. ^{1}F NMR (acetone d-6) spectrum for ^{TPA}PzH

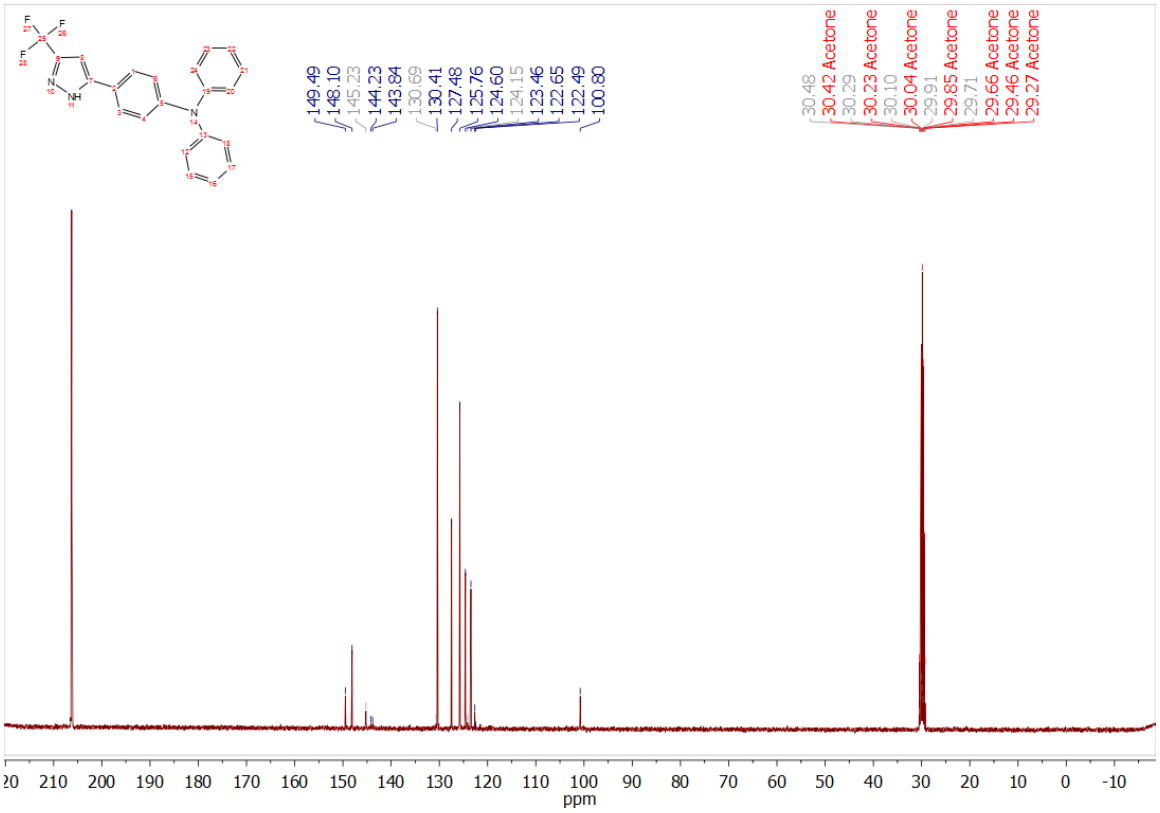


Figure S3. ^{13}C NMR (acetone d-6) spectrum for ^{TPA}PzH

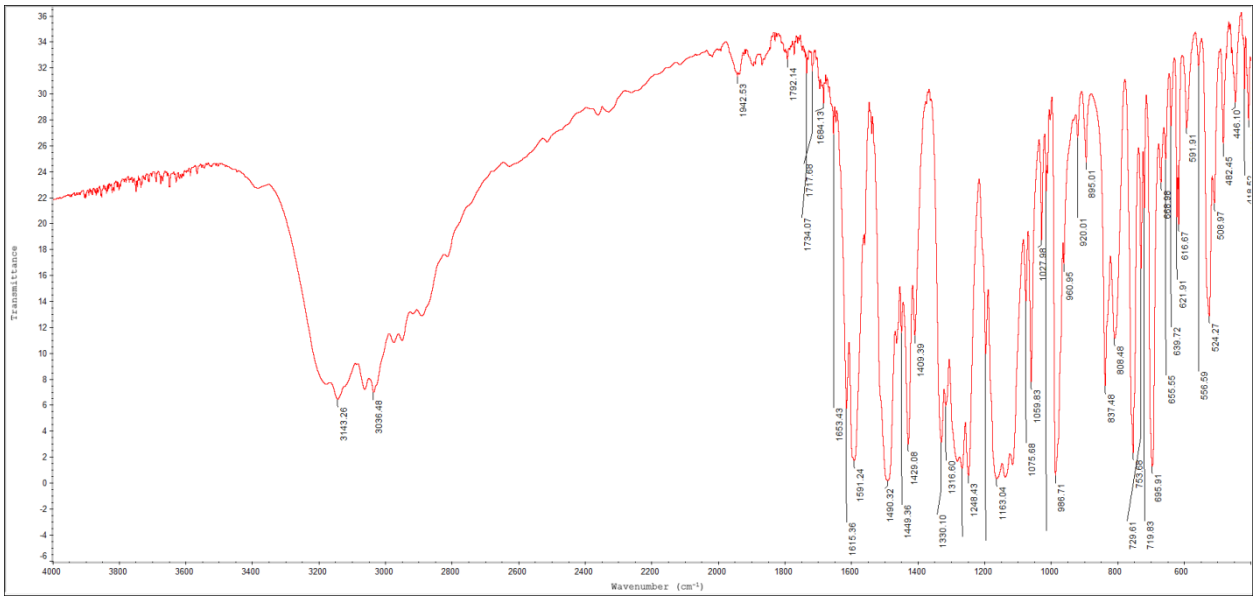


Figure S4. IR spectrum for ^{TPA}PzH (KBr).

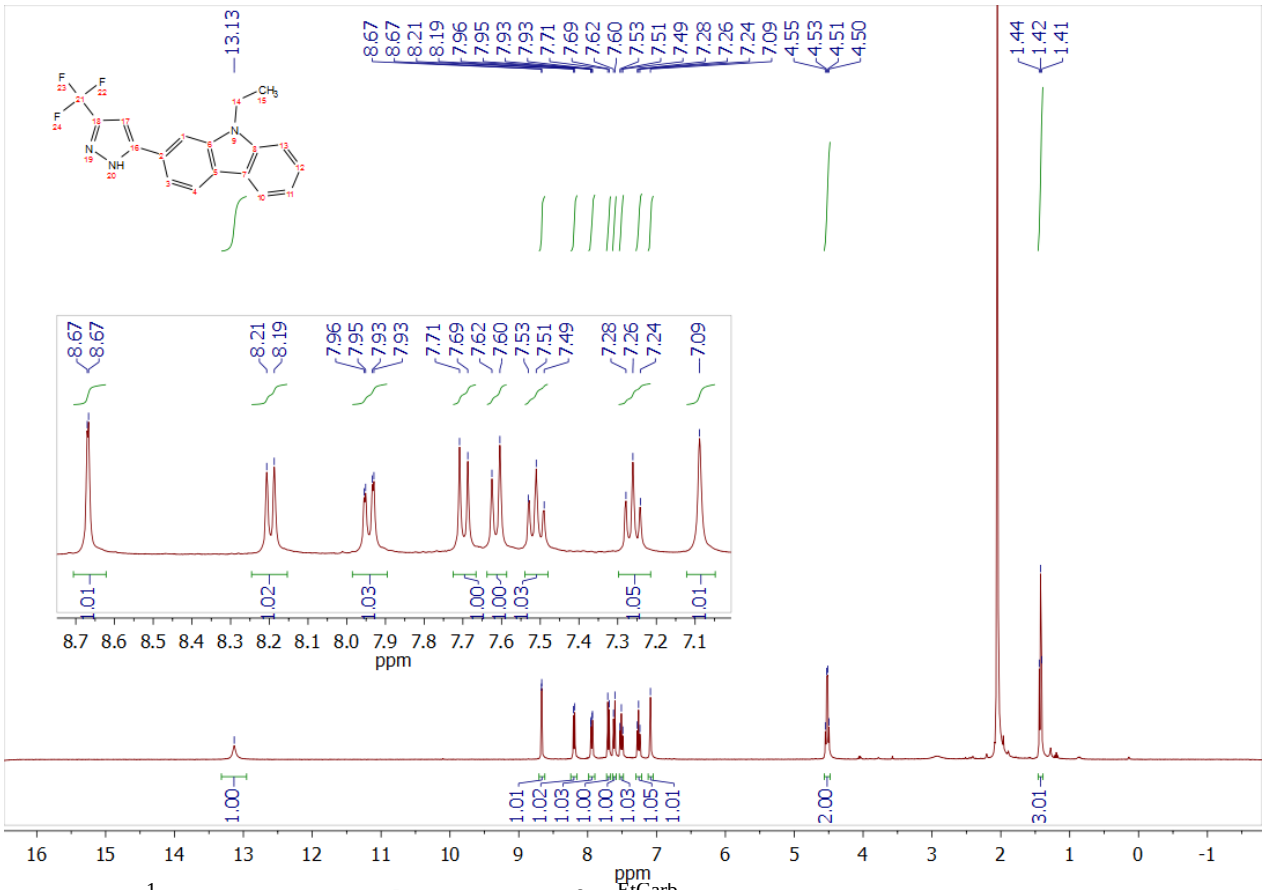


Figure S5. ^{1}H NMR (acetone d-6) spectrum for ^{EtCarb}PzH

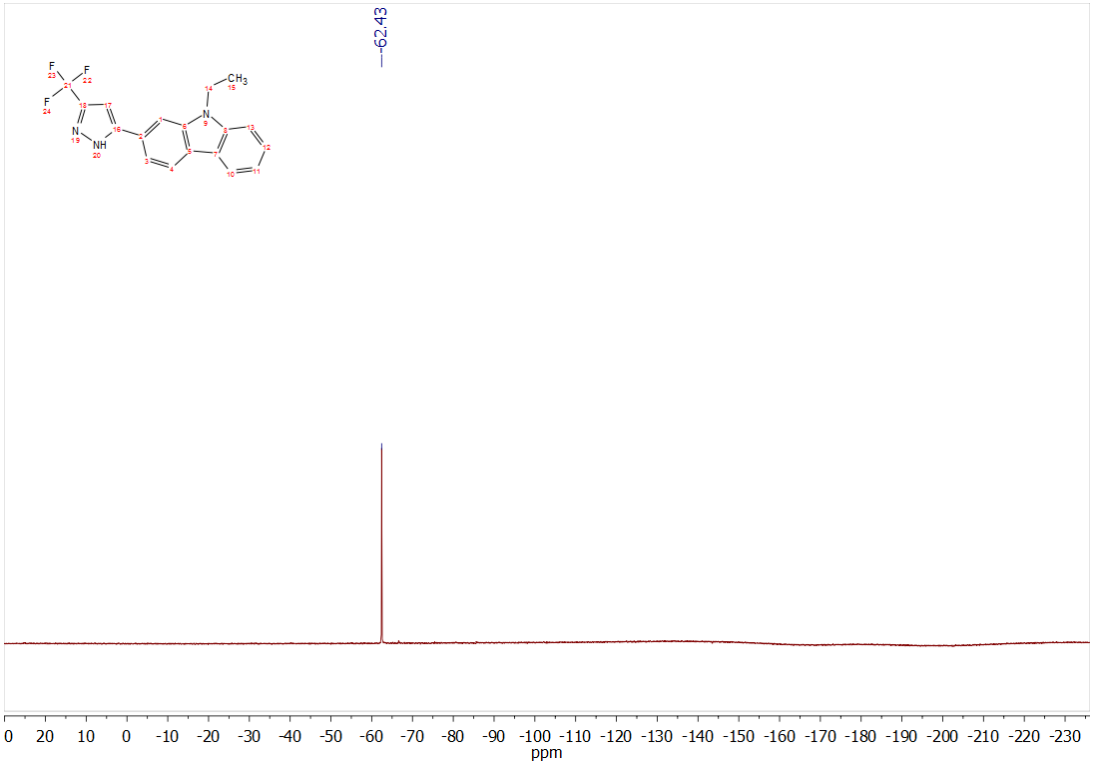


Figure S6. ^{19}F NMR (acetone d-6) spectrum for ^{EtCarb}PzH

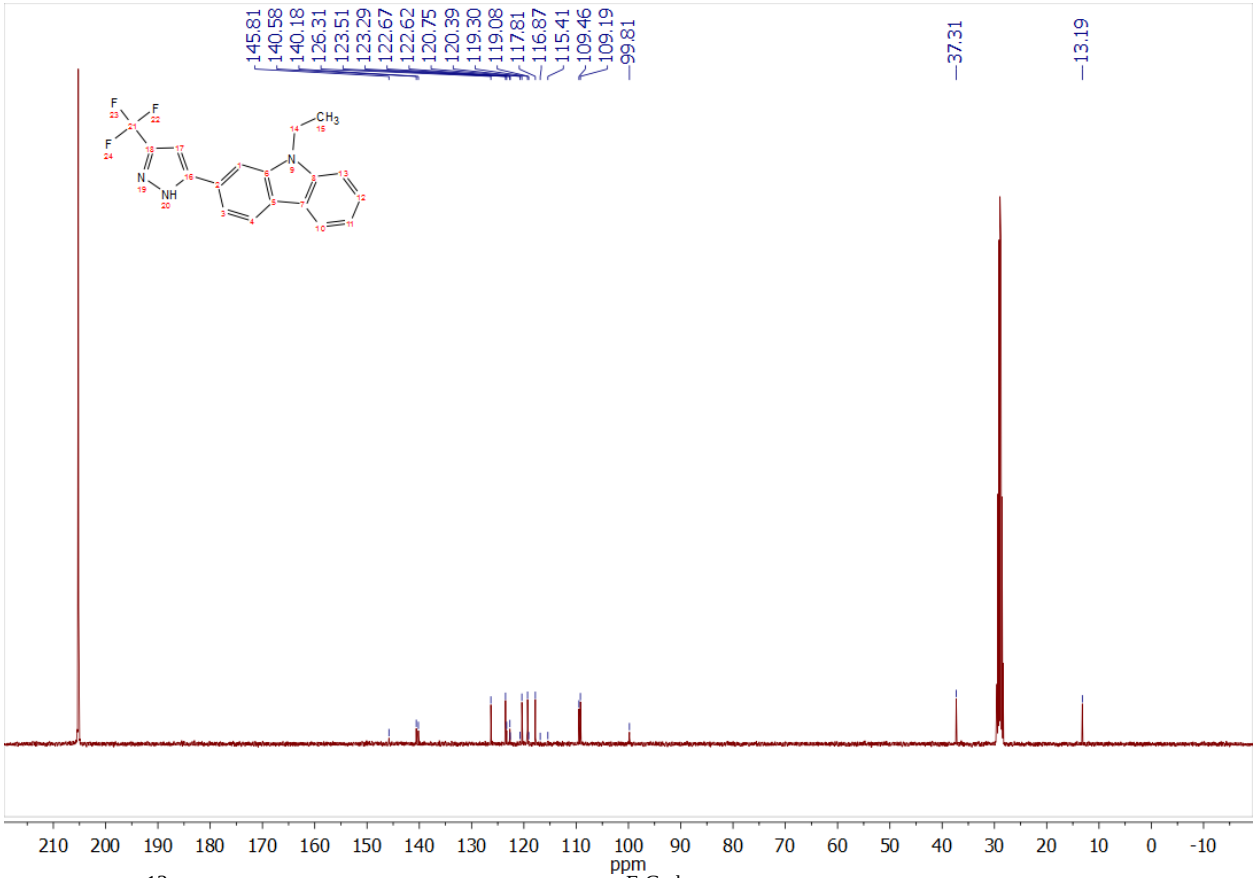


Figure S7. ^{13}C NMR (acetone d-6) spectrum for ^{EtCarb}PzH

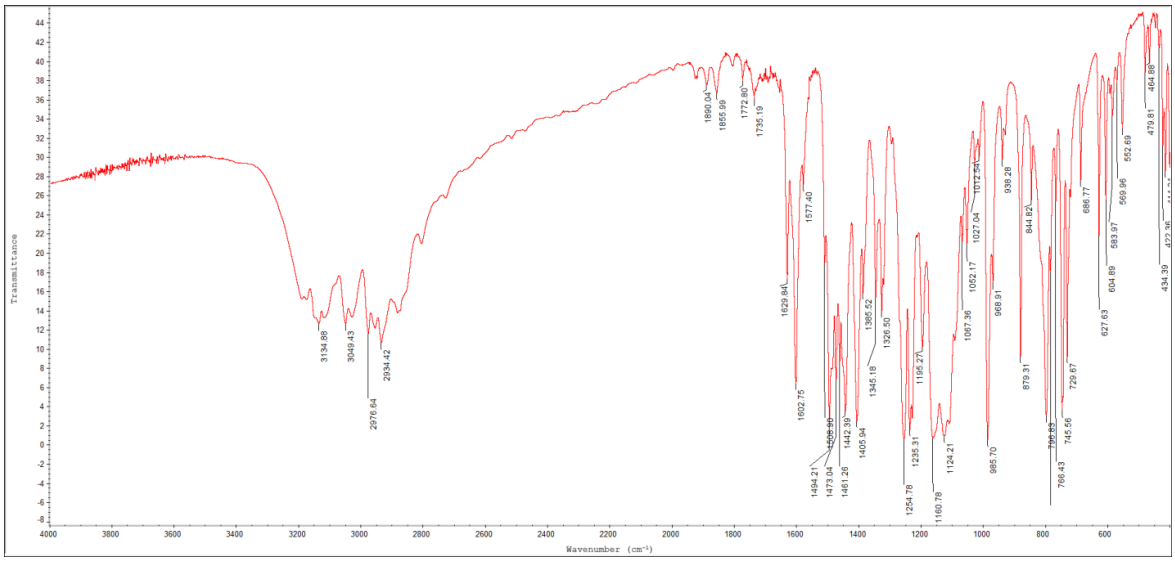


Figure S8. IR spectrum for ^{EtCarb}PzH (KBr).

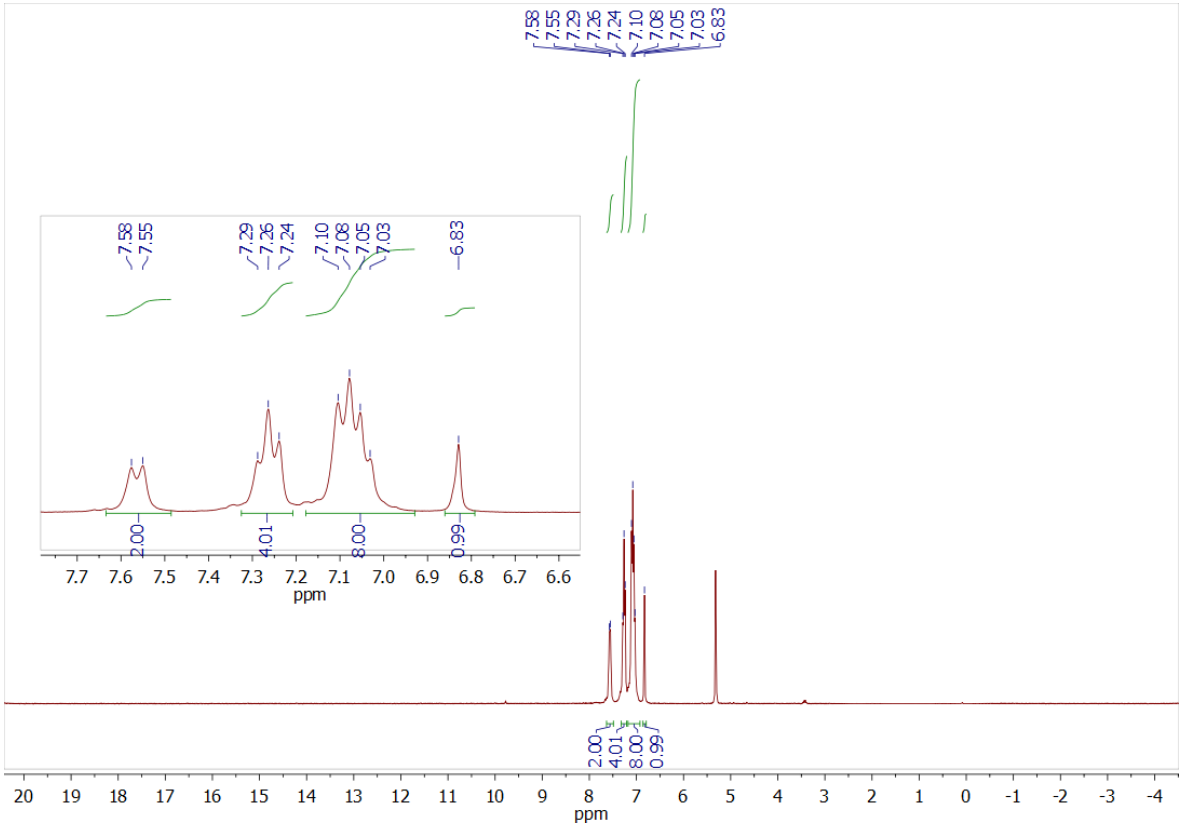


Figure S9. ^{1}H NMR (CD_2Cl_2) spectrum for complex 1.

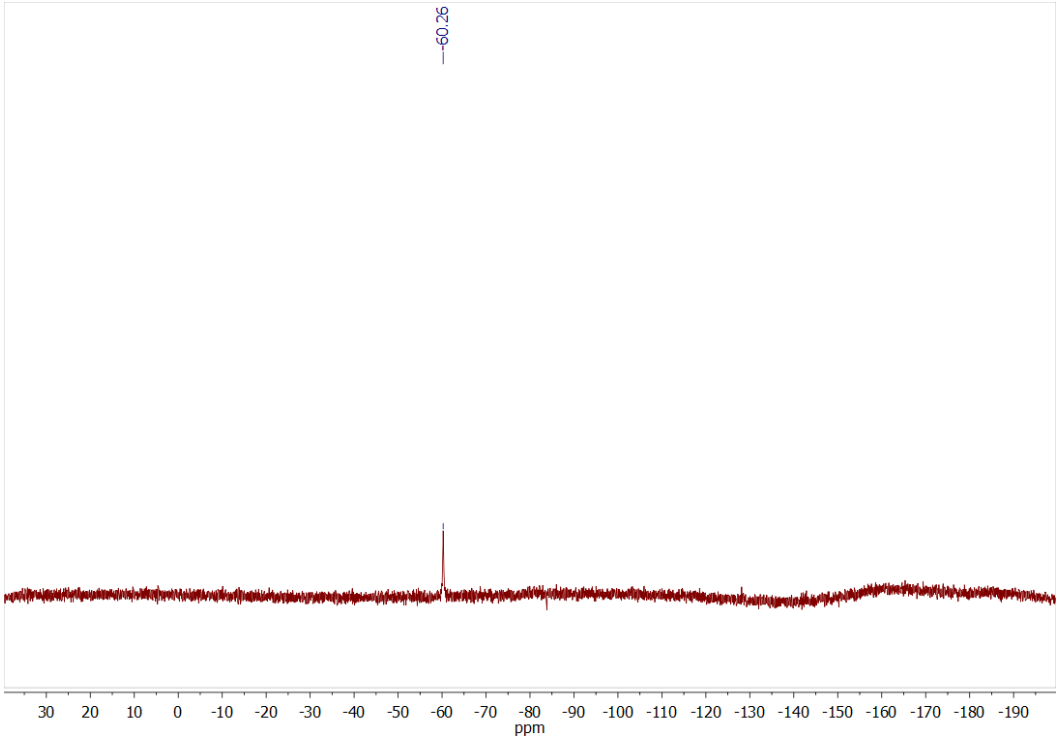


Figure S10. ^{1}F NMR (CD_2Cl_2) spectrum for complex 1.

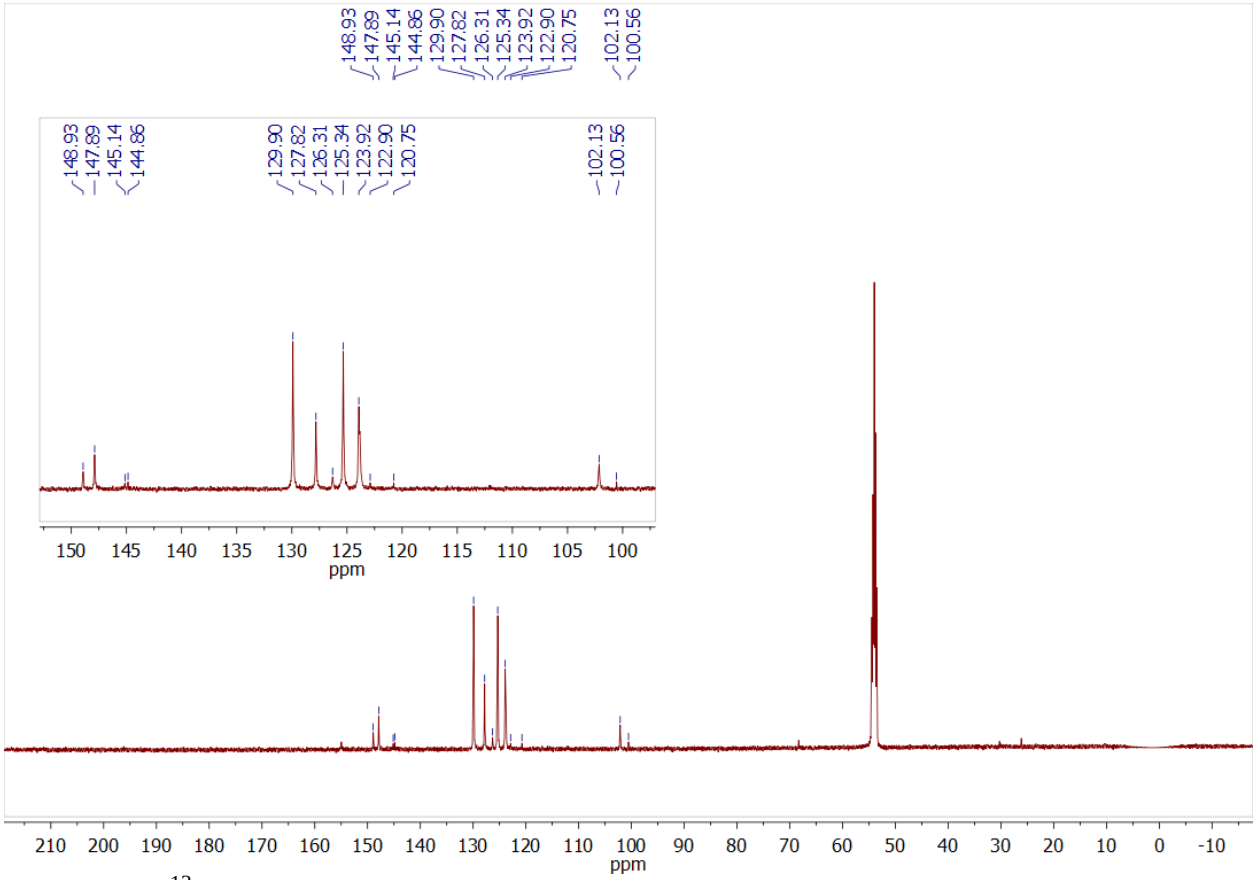


Figure S11. ^{13}C NMR (CD_2Cl_2) spectrum for complex 1.

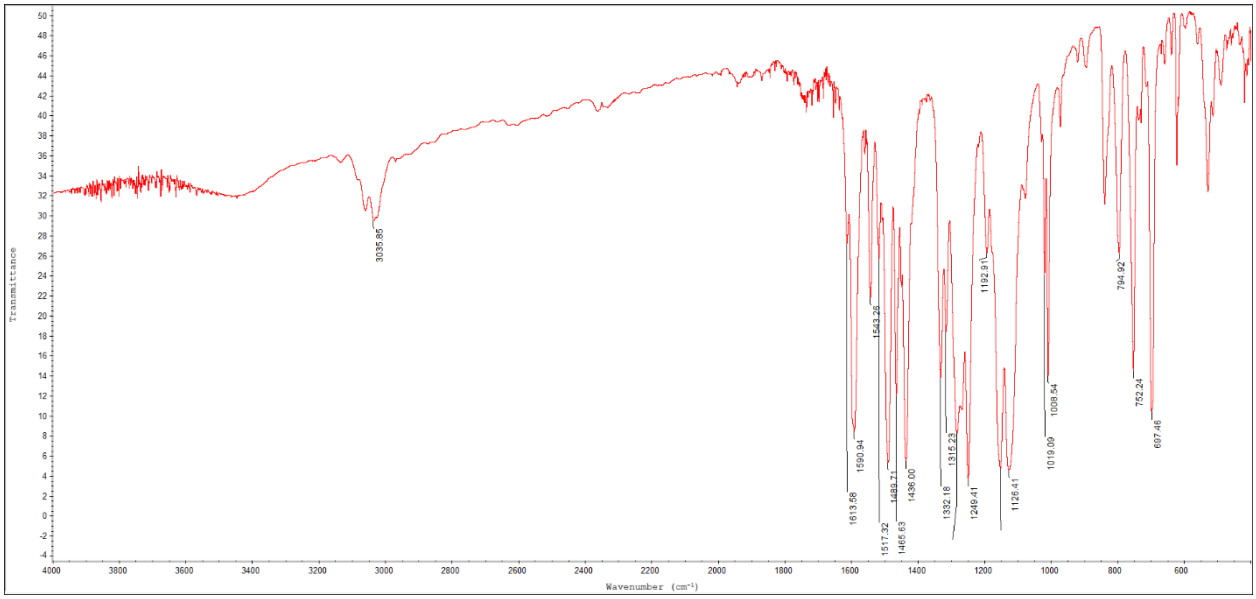


Figure S12. IR spectrum for complex 1 (KBr).

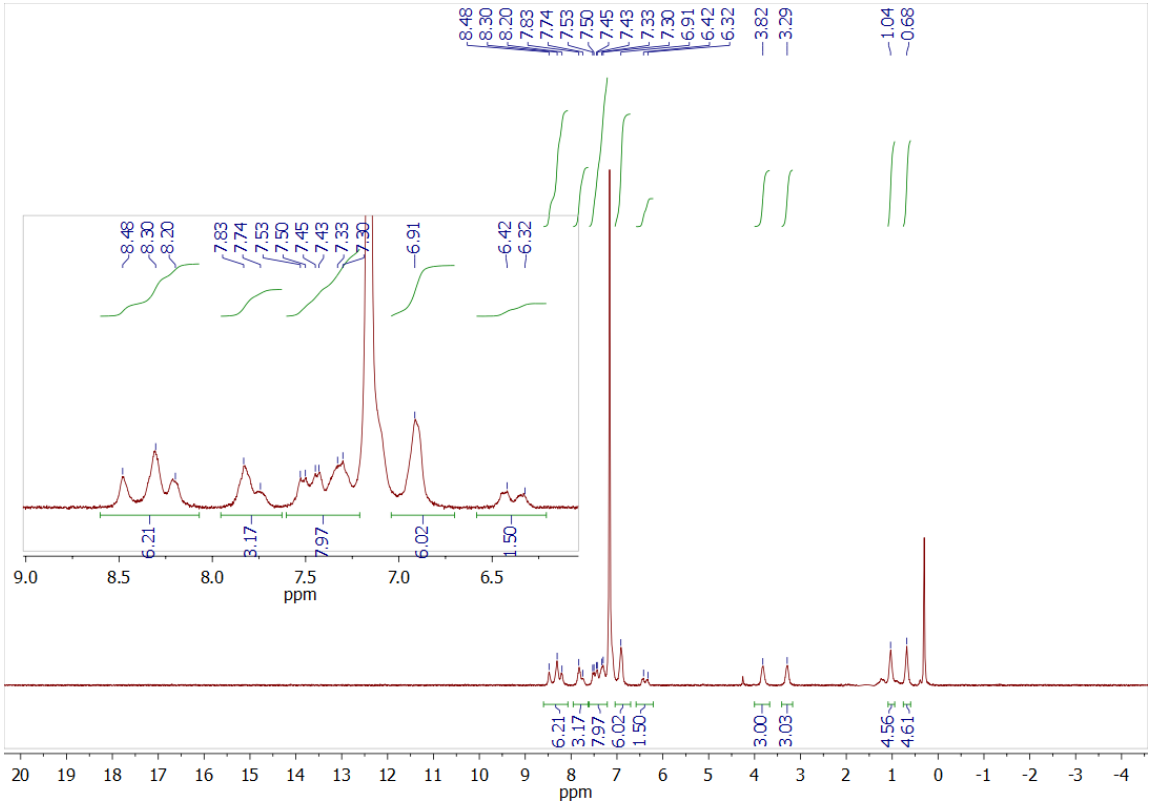


Figure S13. ^{1}H NMR (C_6D_6) spectrum for complex 2.

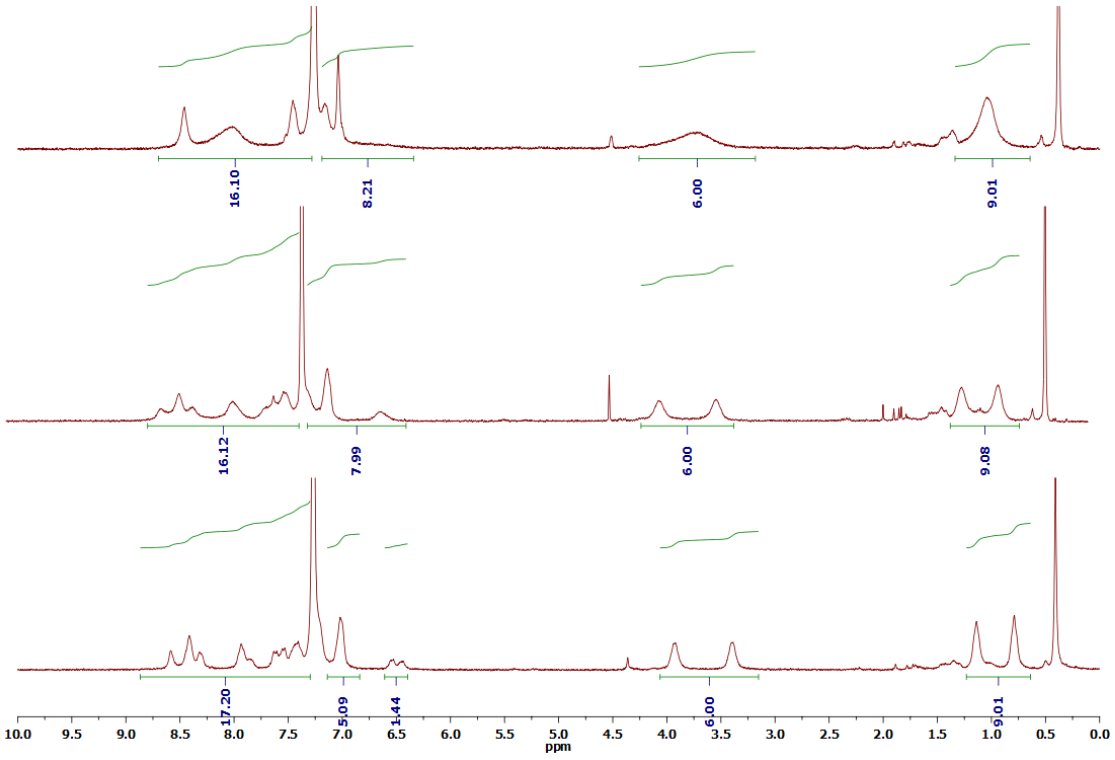


Figure S14. ^{1}H NMR (C_6D_6) spectra for complex 2 at 293 K (bottom), 313 K (middle) and 343 K (top).

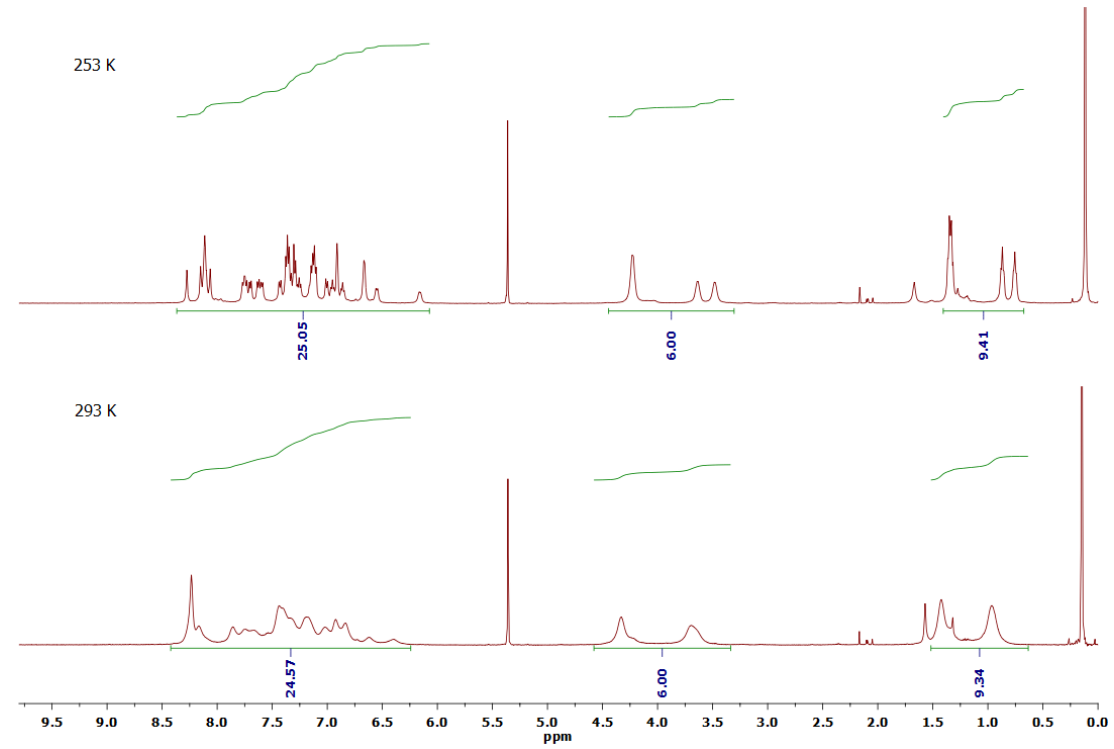


Figure S15. ^{1}H NMR (CD_2Cl_2) spectra for complex 2 at 293 K (bottom) and 253 K (top)

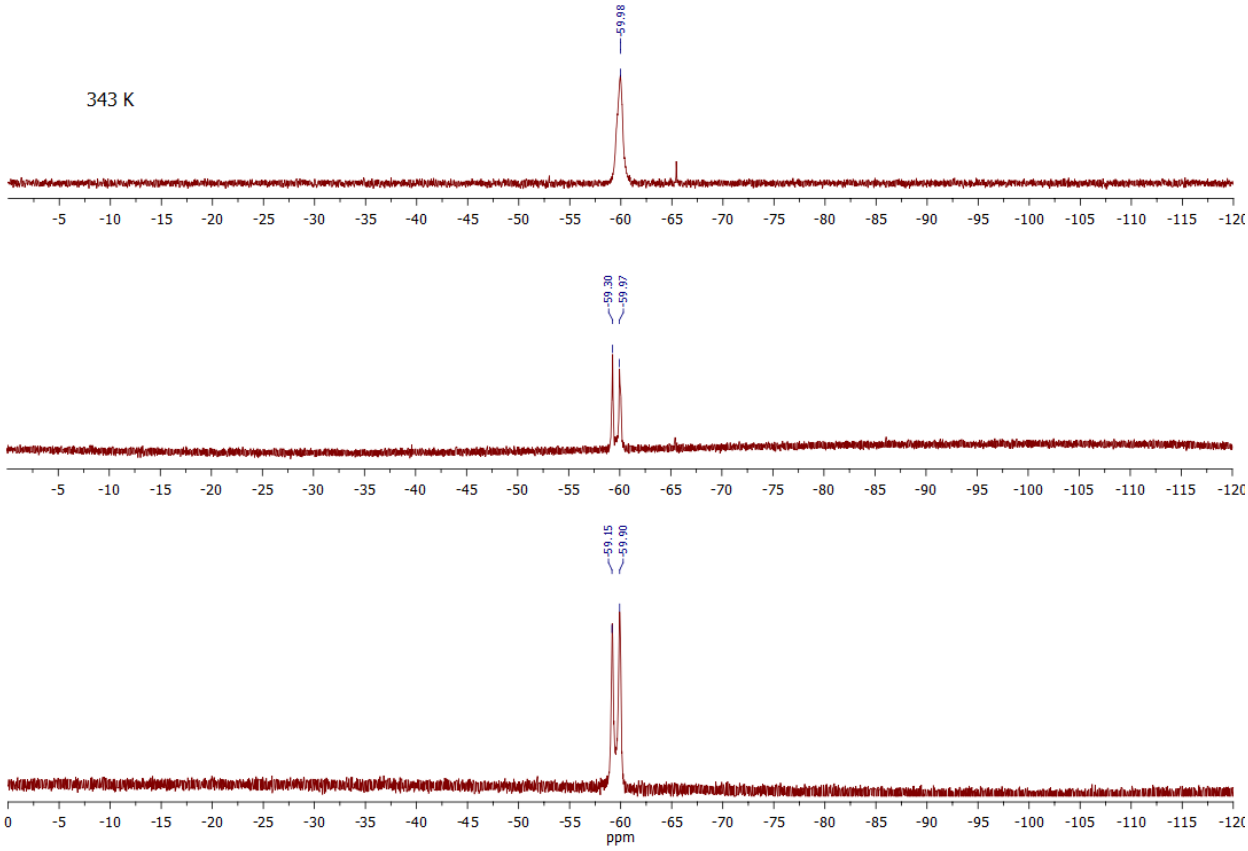


Figure S16. ^{19}F NMR (C_6D_6) of complex 2 at 293 K (bottom), 313 K (middle) and 343 K (top).

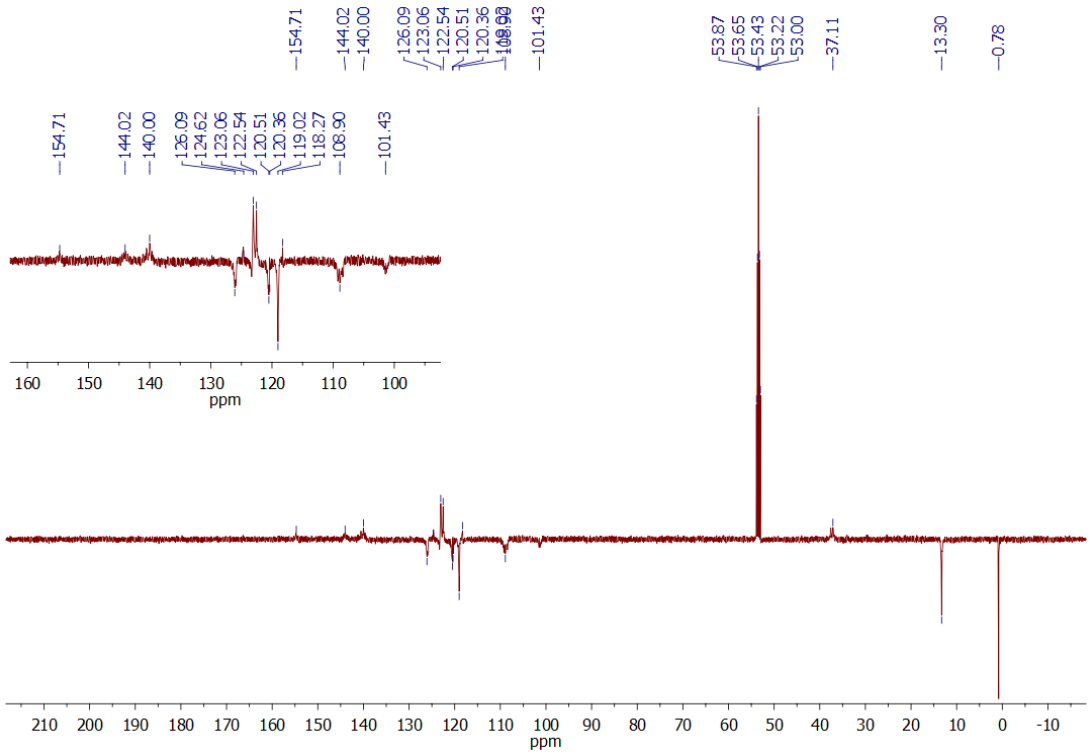


Figure S17. DEPT ^{13}C NMR (CD_2Cl_2) spectrum for complex 2.

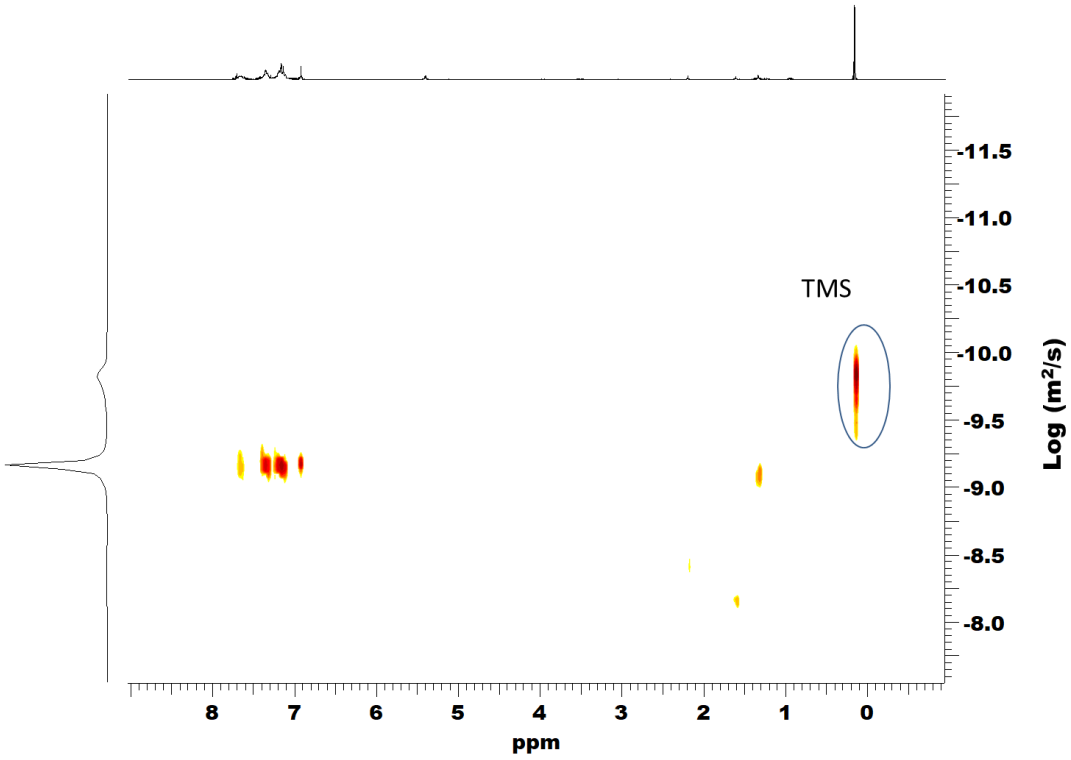


Figure S18. NMR DOSY spectrum for complex 1 (C= 10^{-4}M, CD_2Cl_2, D= $7.85 \cdot 10^{-10}$ m^2/s).

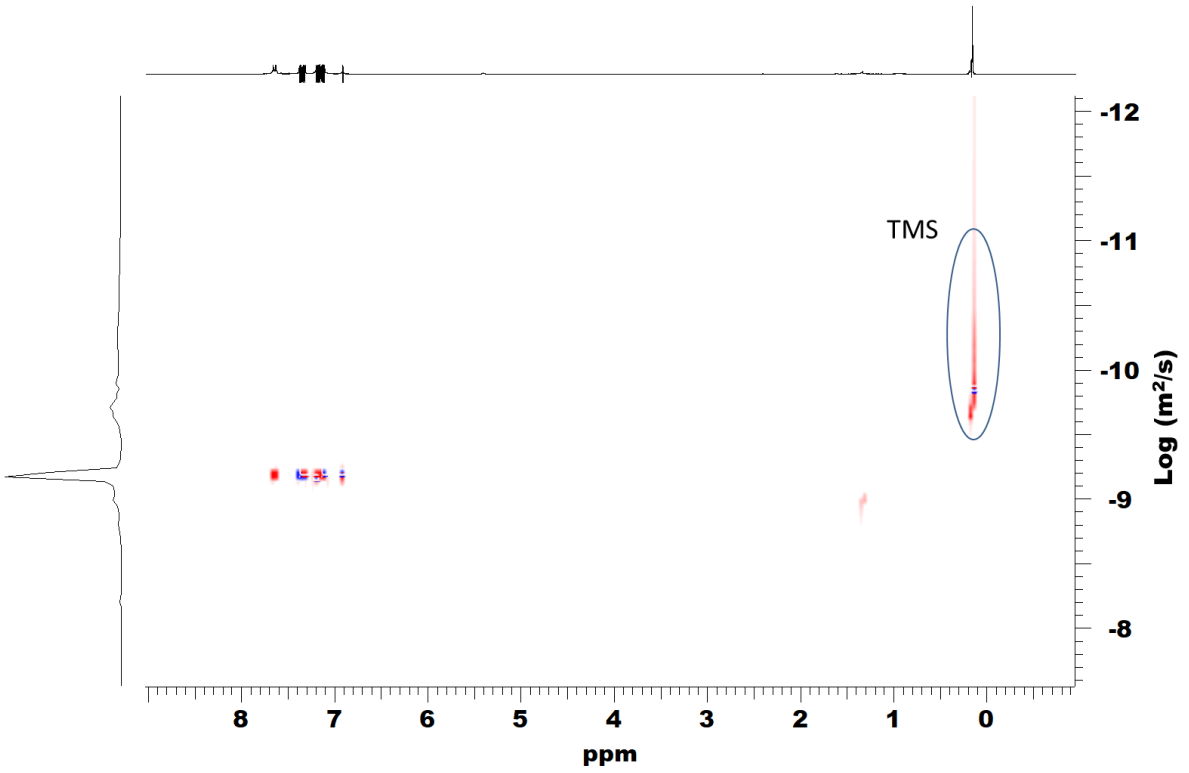


Figure S19. NMR DOSY spectrum for complex 1 (C=10^{-2} M, CD_2Cl_2, D= $7.32 \cdot 10^{-10}$ m^2/s).

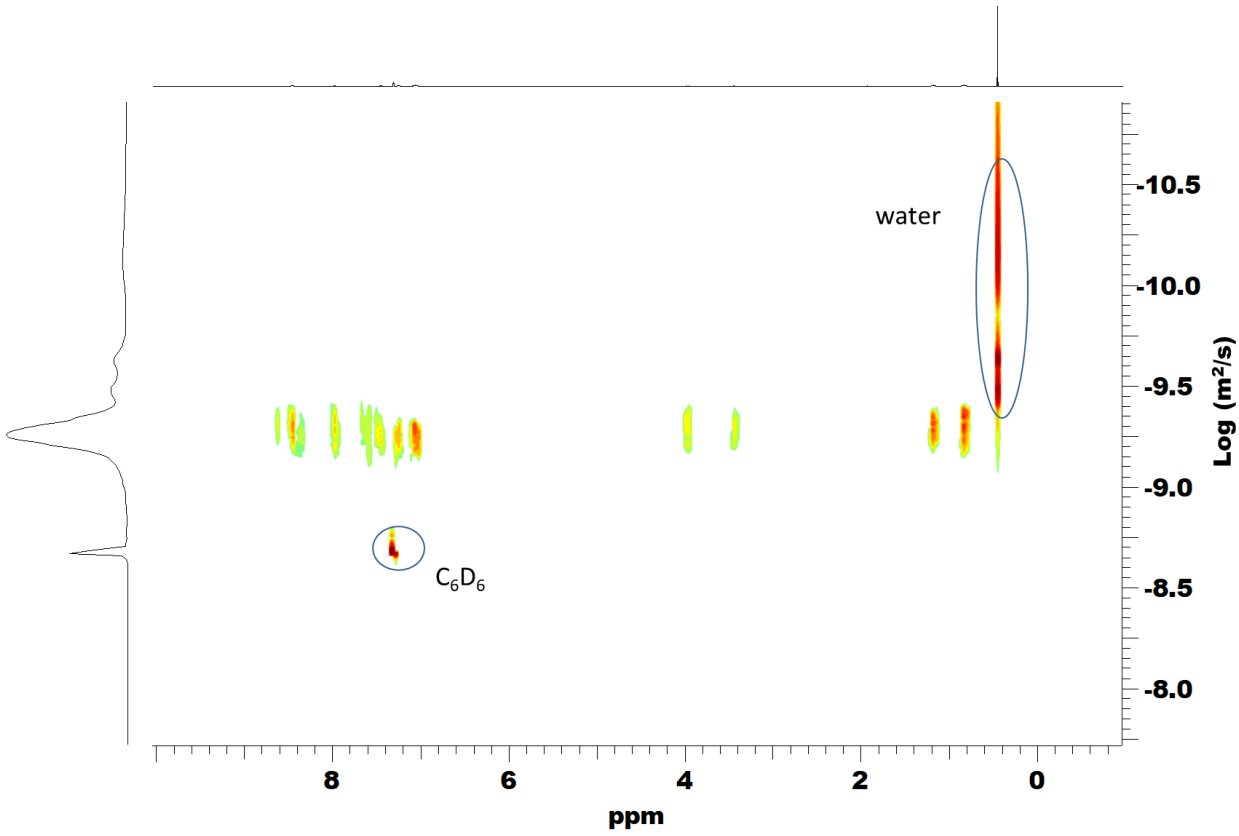


Figure S 20. NMR DOSY spectrum for complex 2 (C=10^{-4} M, C_6D_6, D= $5.29 \cdot 10^{-10}$ m^2/s).

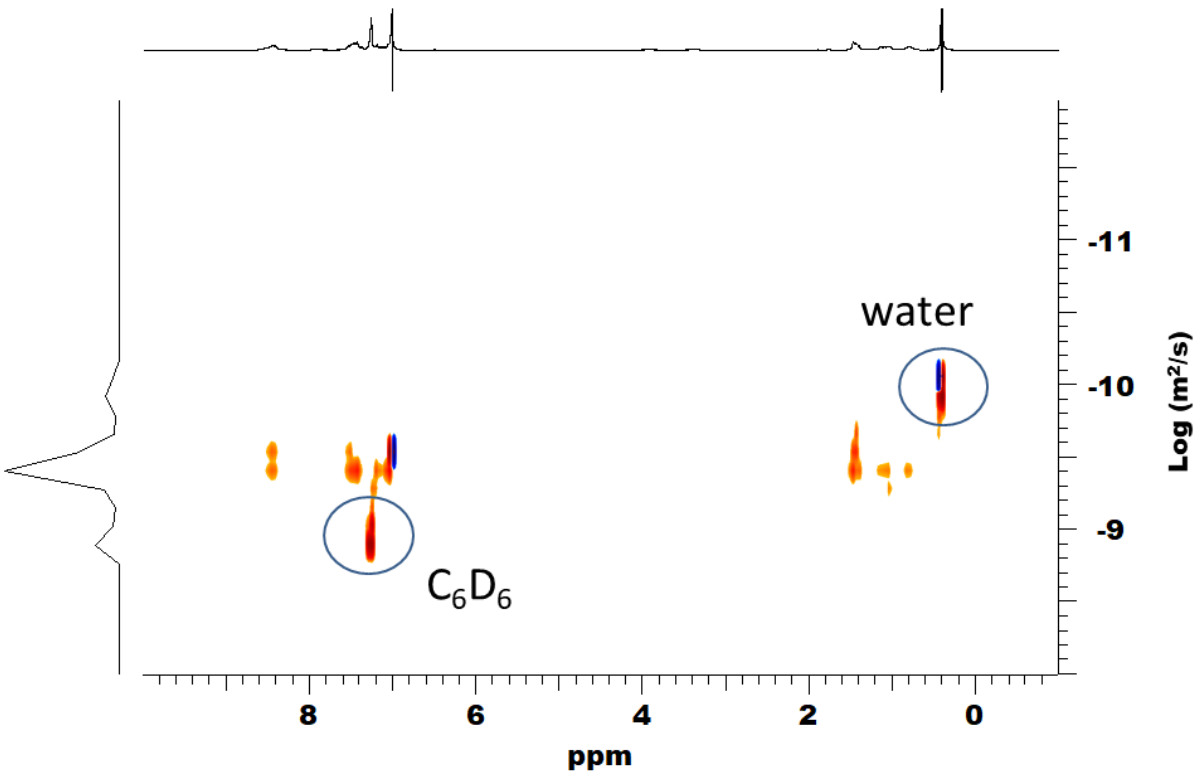


Figure S21. NMR DOSY spectrum for complex 2 (C=10^{-2} M, C_6D_6, D= $4.52 \cdot 10^{-10}$ m^2/s).

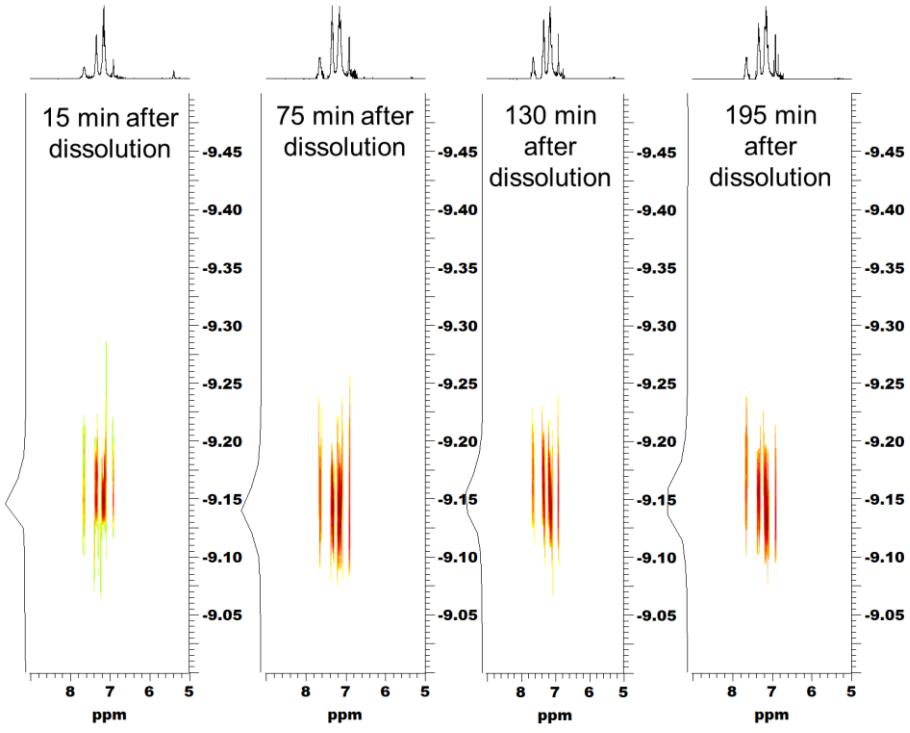


Figure S22. NMR DOSY spectrum for complex 1 for a time of 195 min (C=10^{-4} M, CD_2Cl_2).

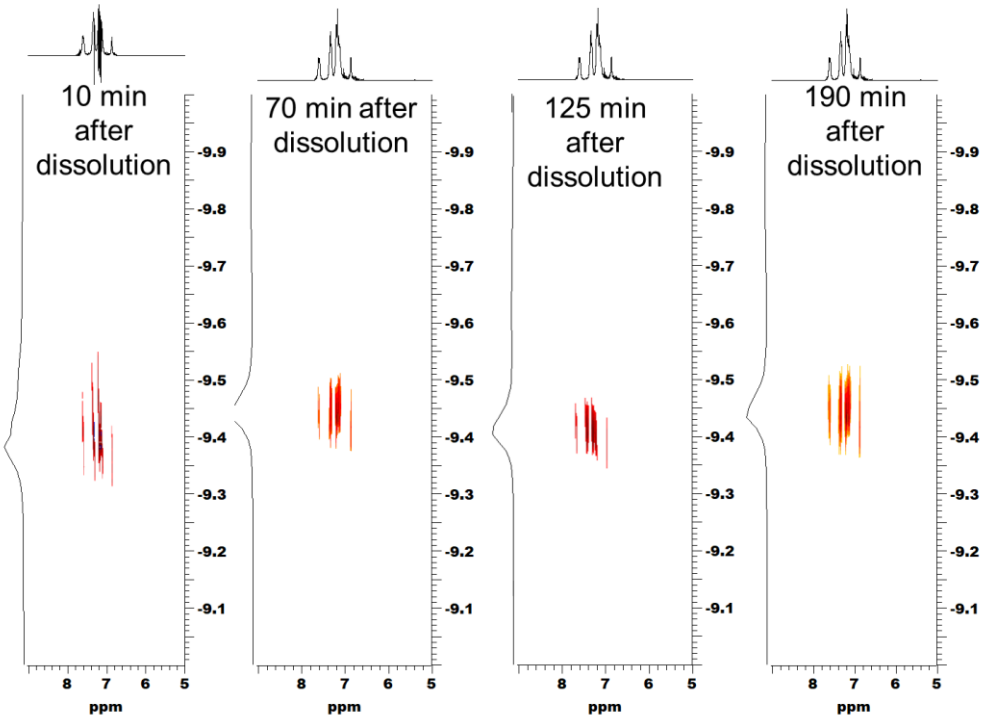


Figure S23. NMR DOSY spectrum for complex 1 for a time of 190 min (C=10^{-2} M, CD_2Cl_2/CCl_4).

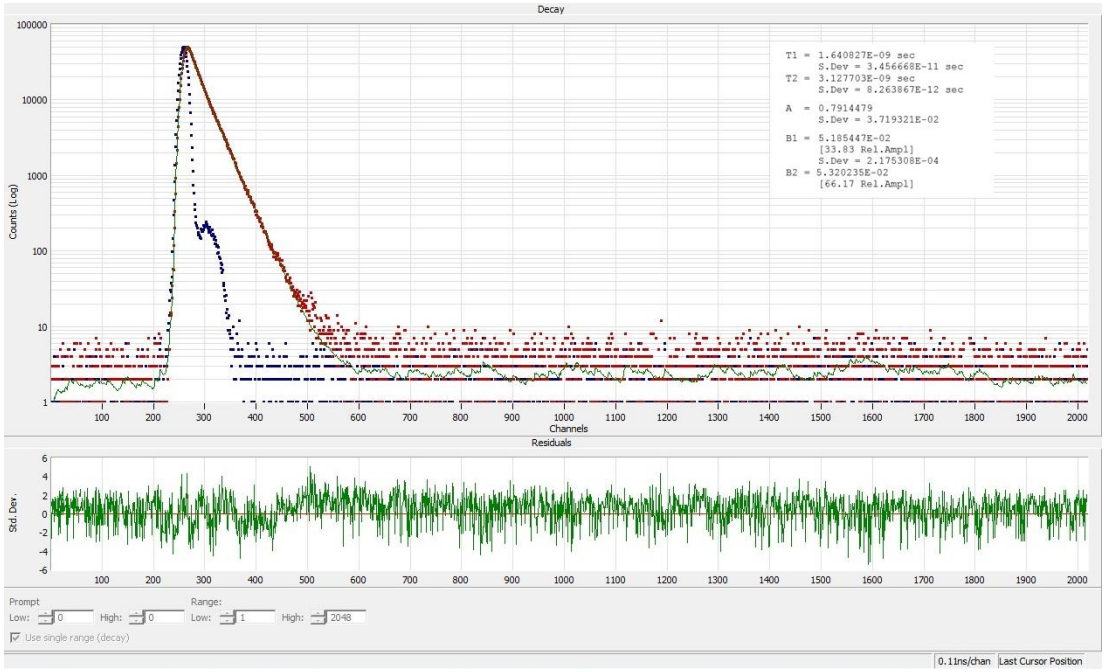


Figure S24. Fluorescence decay of ^{TPA}PzH (λ^{em} = 410 nm) in the degassed DCE solution at 298 K. Brown – sample, blue –prompt.

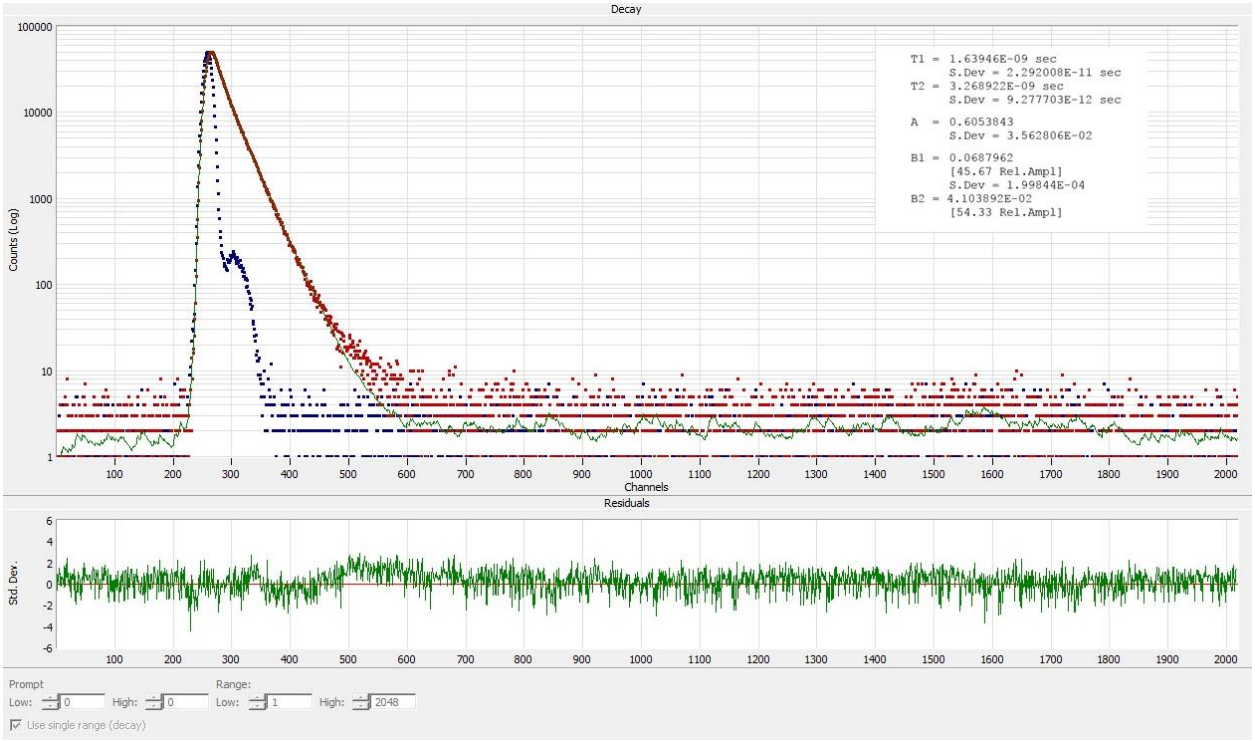


Figure S25. Fluorescence decay of **1** (λ^{em} = 410 nm) in the degassed DCE solution at 298 K. Brown – sample, blue –prompt.

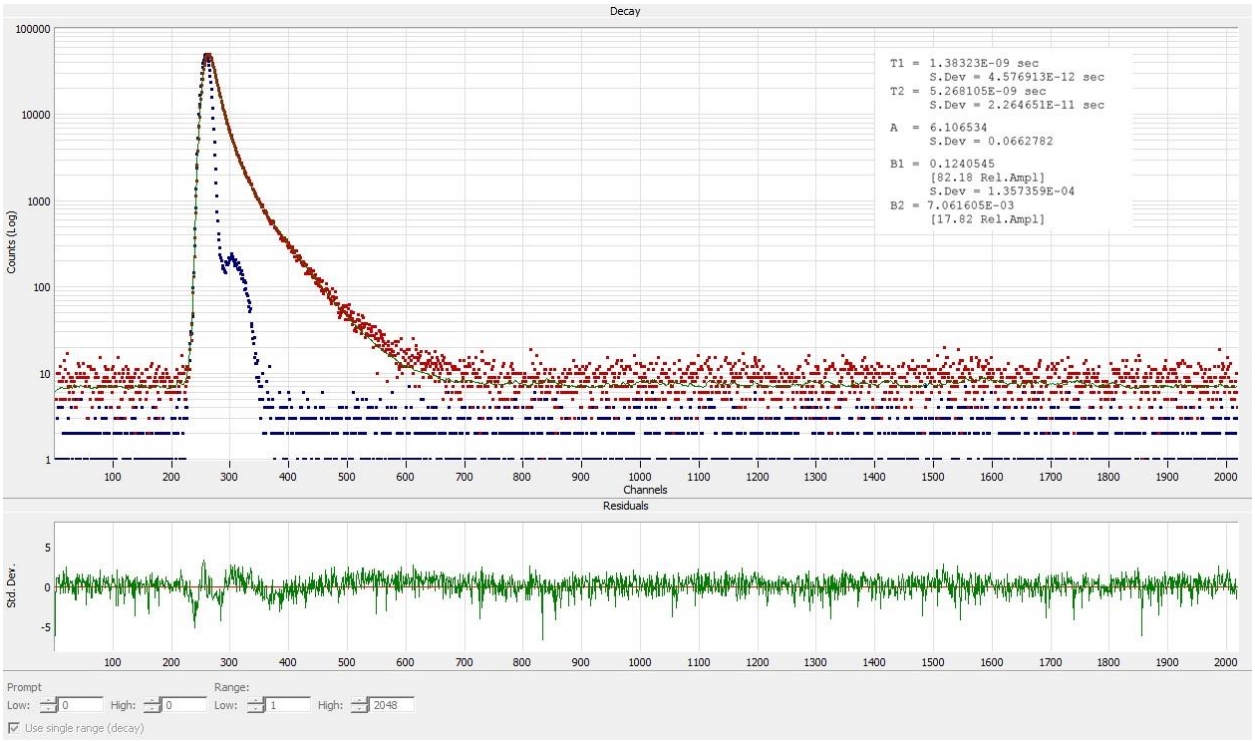


Figure S26. Fluorescence decay of ^{Carb}PzH (λ^{em} = 410 nm) in the degassed DCE solution at 298 K. Brown – sample, blue –prompt.

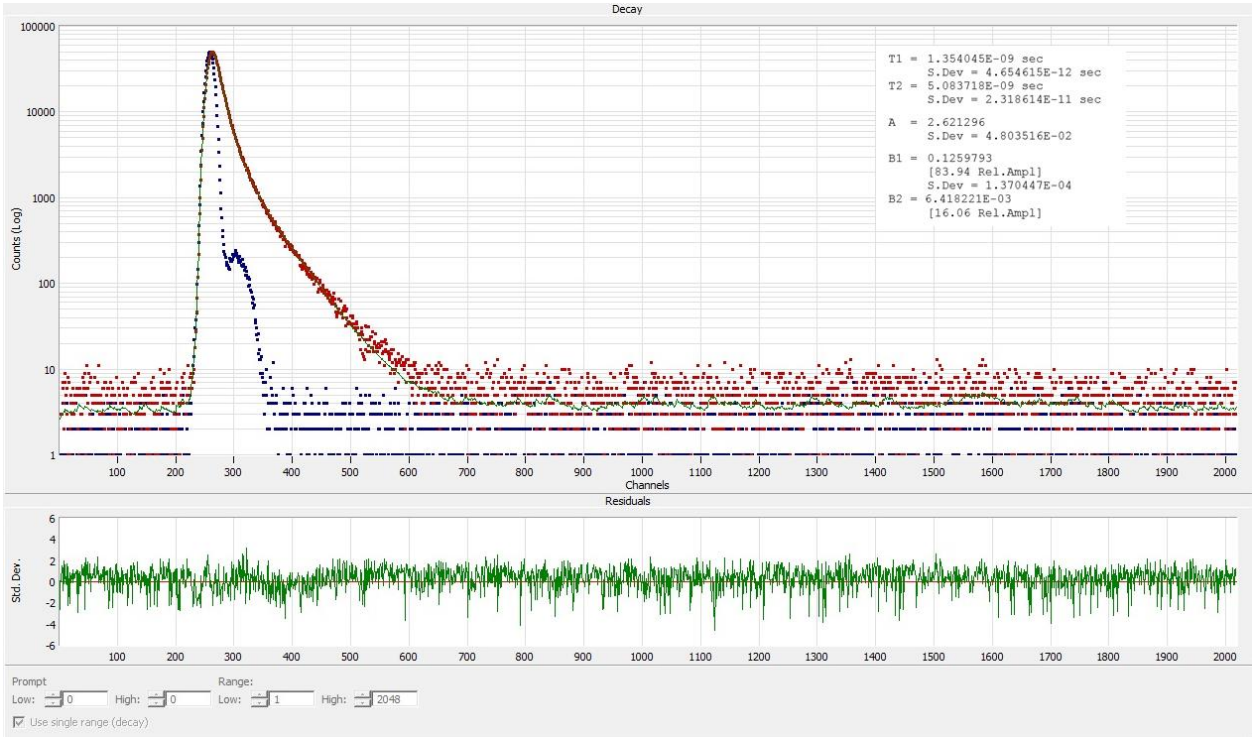


Figure S27. Fluorescence decay of **2** (λ^{em} = 410 nm) in the degassed DCE solution at 298 K. Brown – sample, blue –prompt.

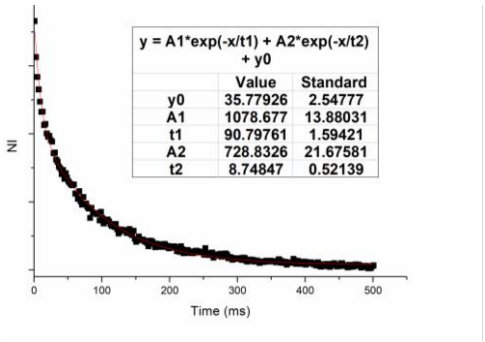
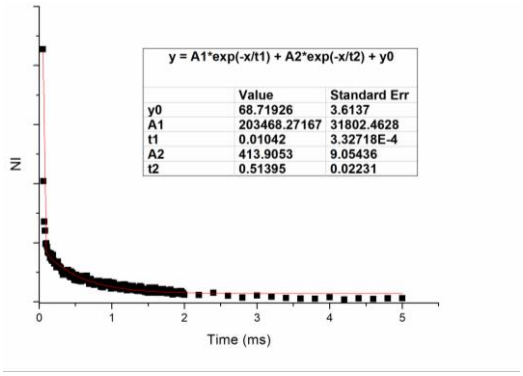
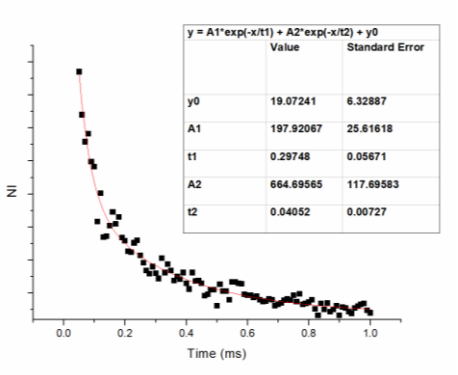
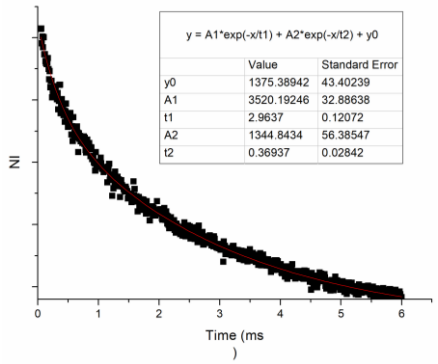
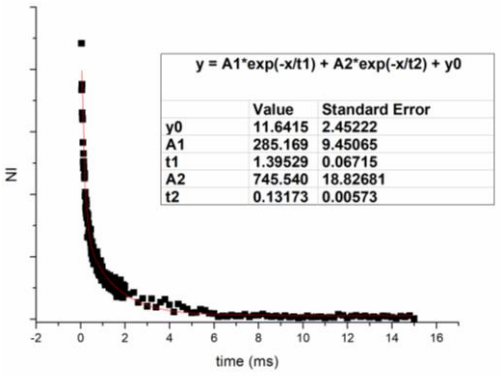
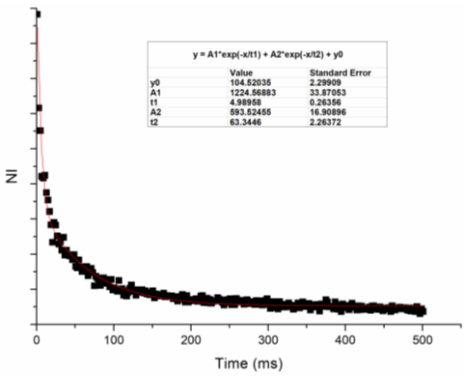
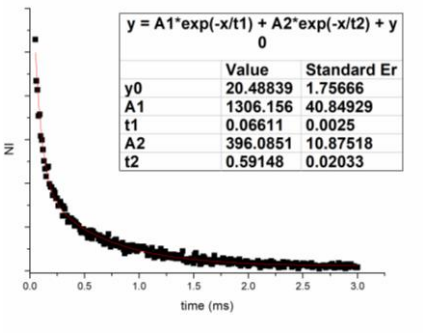
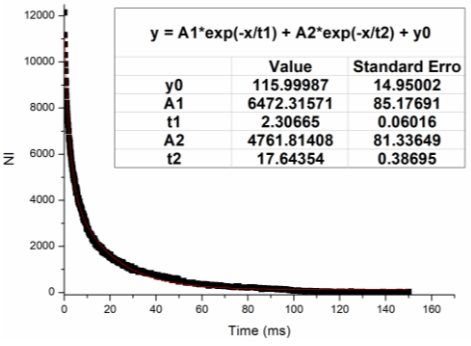
	298 K	77 K
^{TPA}PzH		
1		
^{Carb}PzH		
2		

Figure S28. Phosphorescence decays of compounds obtained in the solid state at 298 K and 77 K.

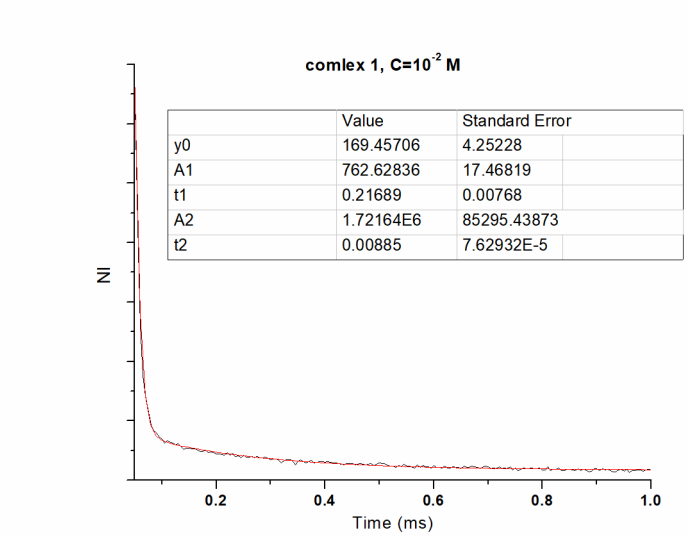


Figure S29. Phosphorescence decays of complex **1** (λ^{em} = 515 nm) at high concentration (c = $1 \cdot 10^{-2}$ M) in the degased DCE solution at 298 K.

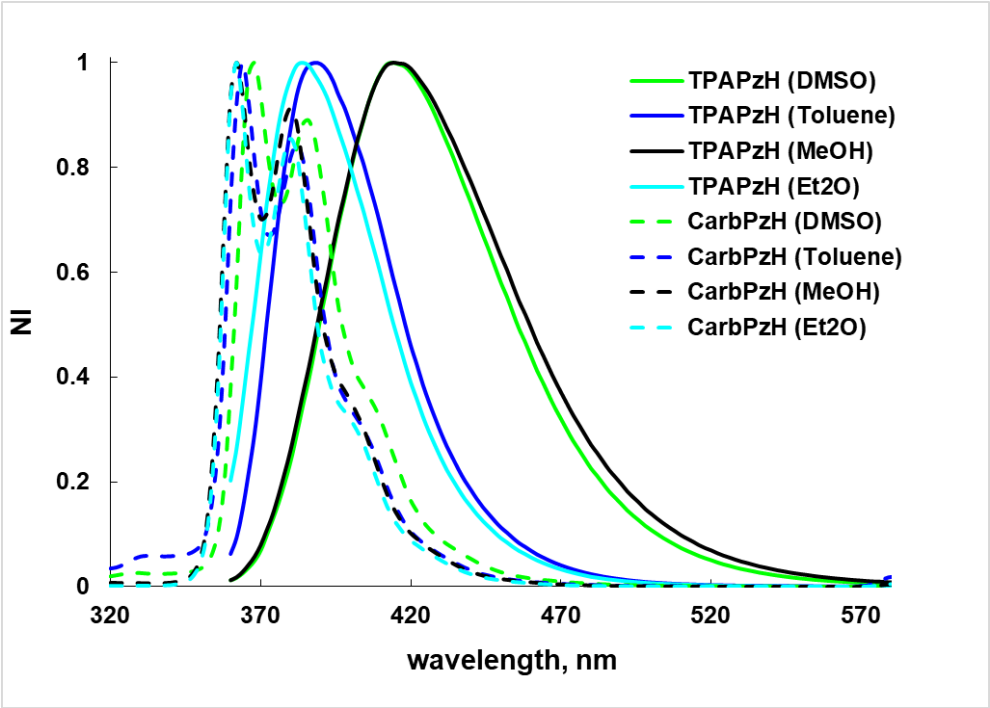


Figure S30. PL spectra of initial pyrazoles in different solvents.

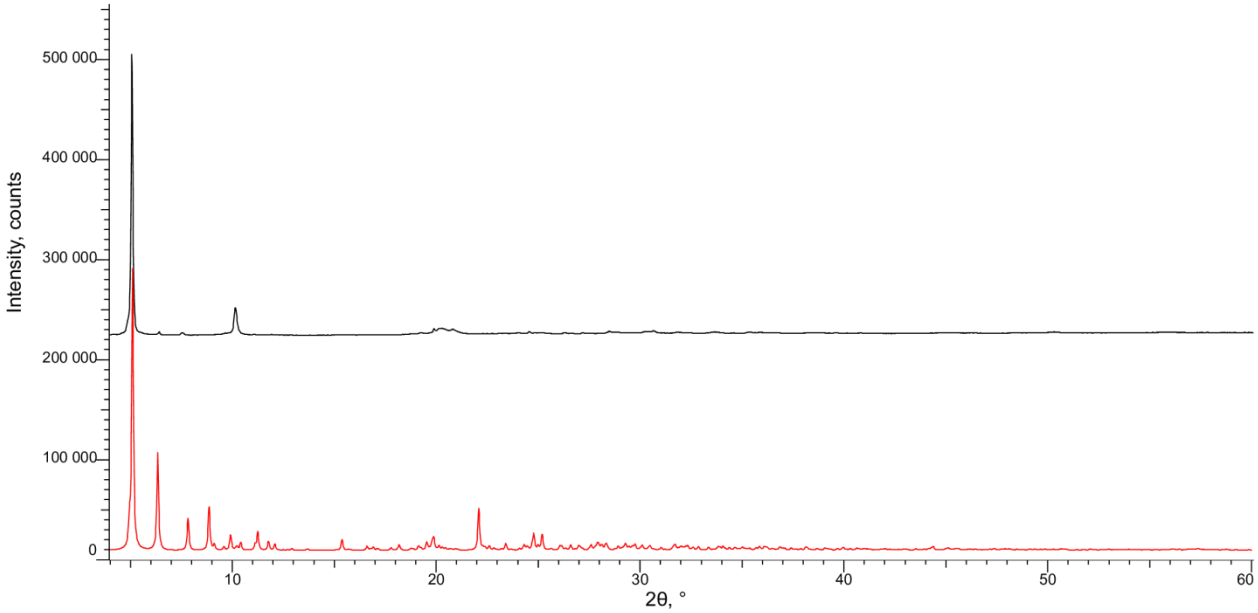


Figure S31. XRPD data for complex 1: measured (black), calculated (red).

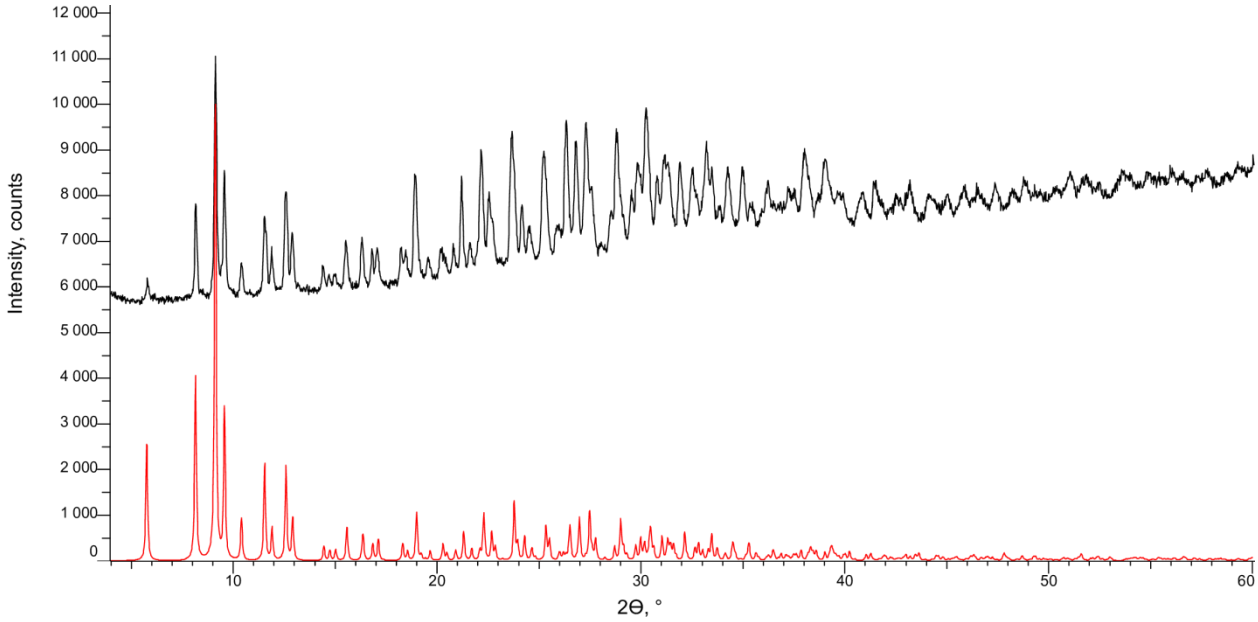


Figure S32. XRPD data for complex 2: measured (black), calculated (red).

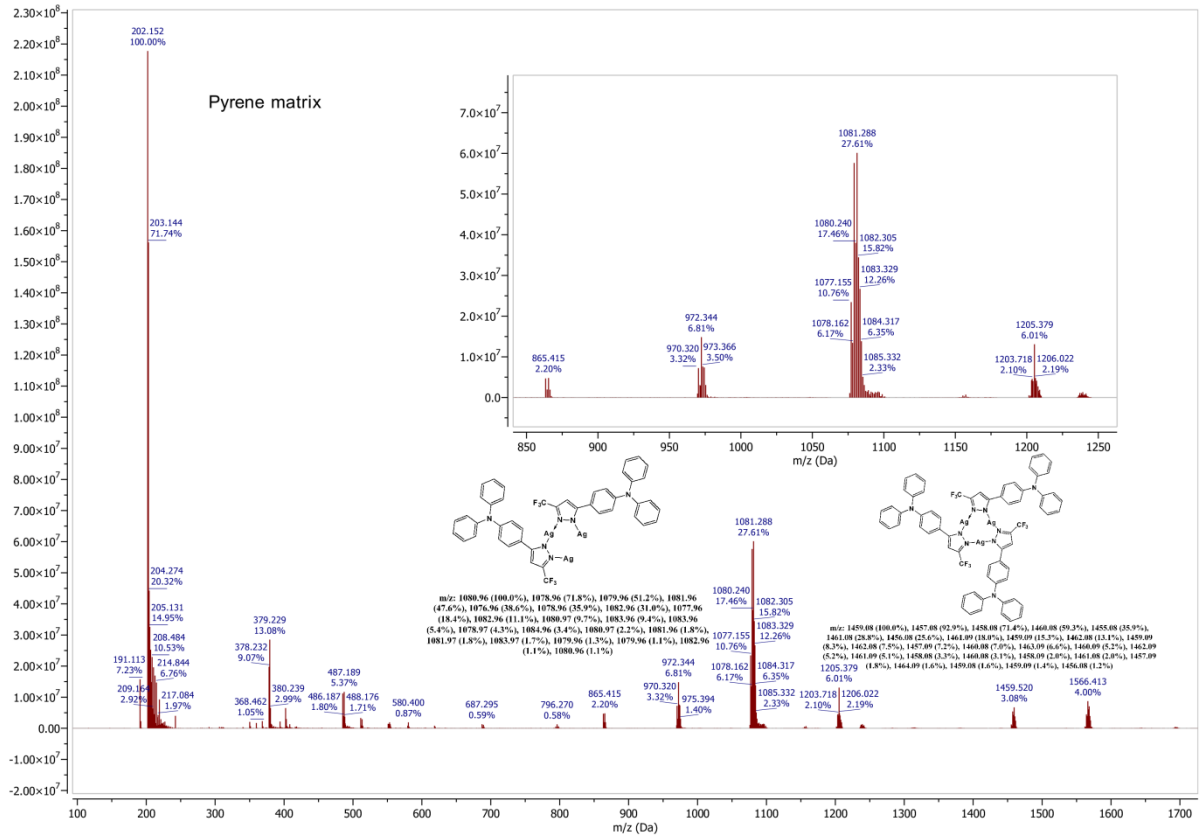


Figure S33. Mass Spectrum (MALDI-TOF) for 1 on pyrene matrix.

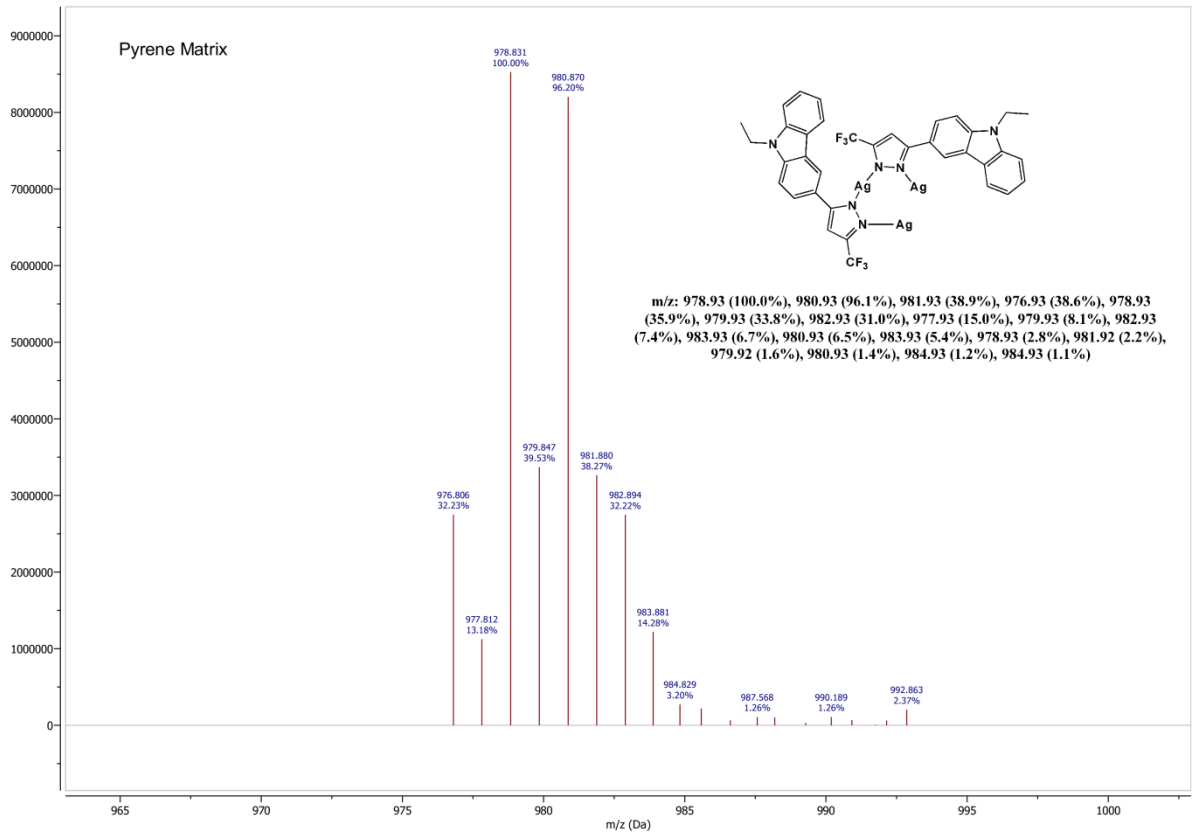
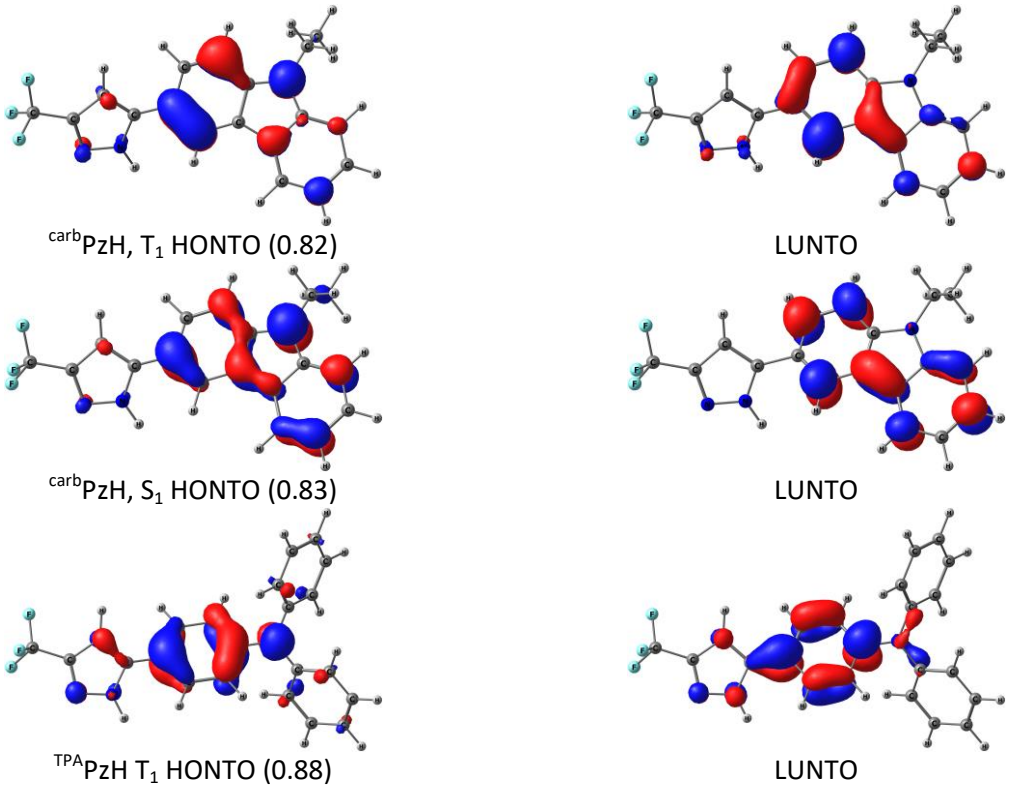


Figure S 34. Mass Spectrum (MALDI-TOF) for 2 on pyrene matrix.

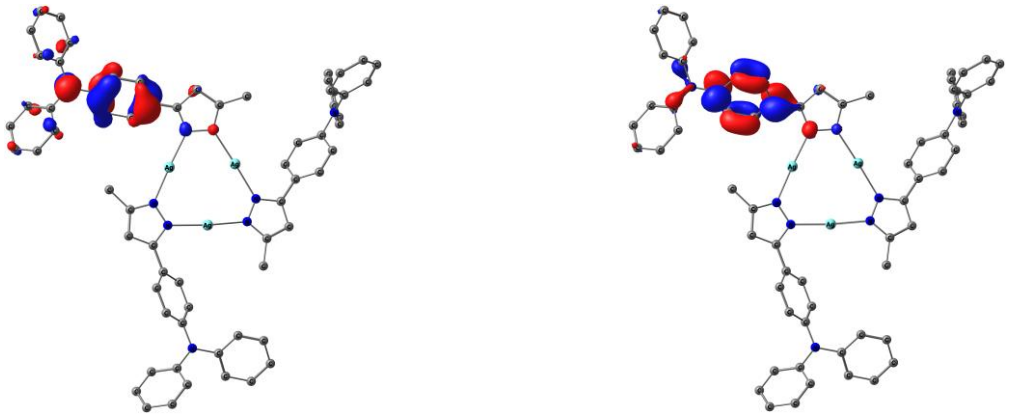


^{TPA}PzH S_1 HONTO (0.95)

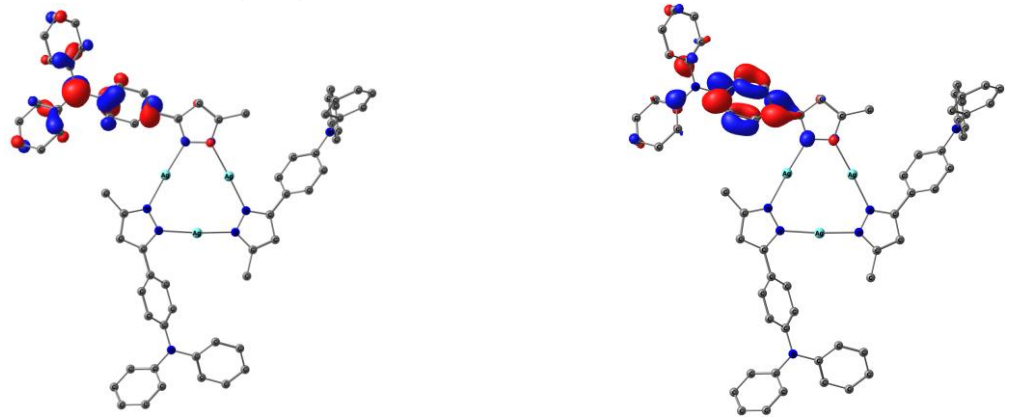
^{carb}PzH, S_3 HONTO[a]

[a] represented as sum of HONTO (0.61) and HONTO-1 (0.35); and LUNTO,LUNTO-1

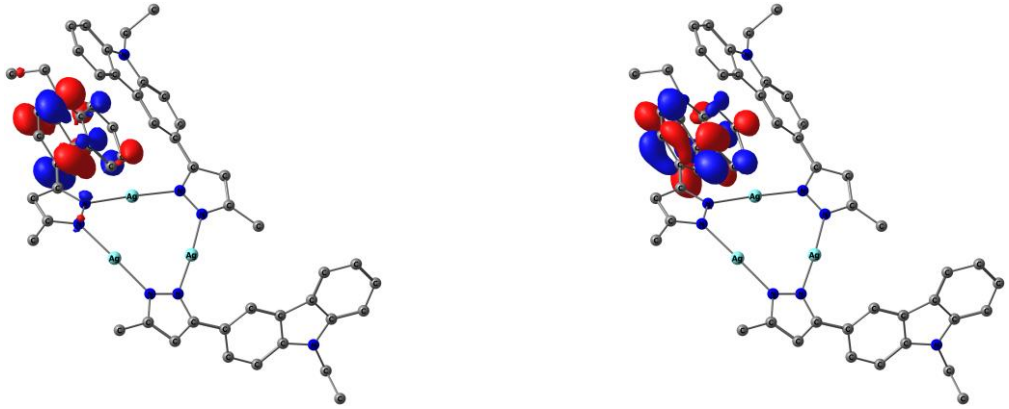
Figure S35. HONTOs-LUNTOs for ^{TPA}PzH and ^{Carb}PzH.



1, T_1 HONTO (0.86)



1, S_1 HONTO (0.72)



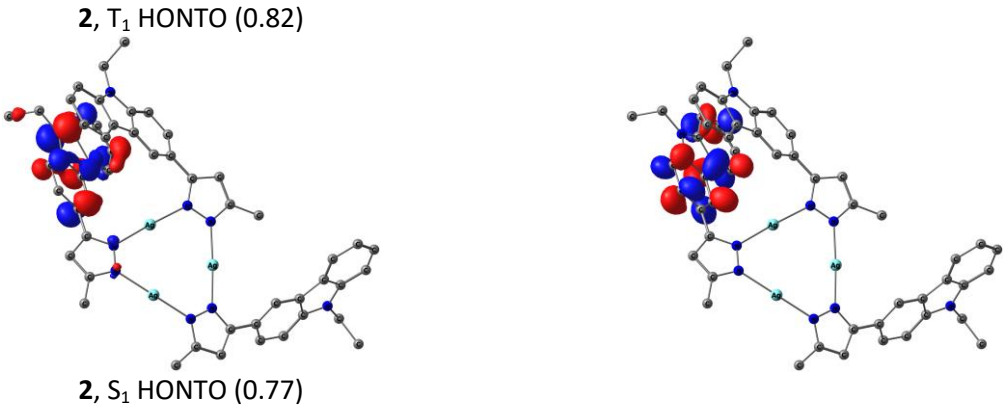


Figure S36. HONTOs-LUNTOs for 1 and 2.

Table S2. Characteristics of 10 lowest energy vertical singlet transition for ^{TPA}PzH, with participation of fragments atoms in the transitions.

				Ground state		Excited state	
	E, eV	E, nm	f	Pz	TPA	Pz	TPA
S1	4.27	290.5	0.909	8.2	91.8	14.3	85.7
S2	4.42	280.3	0.040	3.6	96.4	1.3	98.8
S3	4.69	264.6	0.351	1.6	98.4	0.0	100.0
S4	5.02	247.2	0.044	3.9	96.1	2.1	98.0
S5	5.15	240.7	0.033	0.9	99.2	0.2	99.8
S6	5.77	214.7	0.216	29.8	70.2	32.7	67.3
S7	6.01	206.2	0.138	0.9	99.2	6.8	93.2
S8	6.22	199.3	0.070	3.4	96.6	4.4	95.6
S9	6.28	197.4	0.173	17.9	82.1	15.8	84.2
S10	6.31	196.5	0.056	4.3	95.7	3.2	96.8

Table S3. Characteristics of 10 lowest energy vertical triplet transition for ^{TPA}PzH, with participation of fragments atoms in the transitions.

			Ground state		Excited state	
	E, eV	E, nm	Pz	TPA	Pz	TPA
T1	3.32	373.1	13.5	86.5	17.0	83.0
T2	3.73	332.3	1.0	99.0	0.0	100.0
T3	3.90	318.2	4.7	95.4	0.8	99.2
T4	4.11	301.9	11.3	88.7	10.8	89.2
T5	4.34	285.5	3.6	96.4	0.9	99.1
T6	4.49	276.4	1.1	98.9	0.7	99.4
T7	4.56	271.8	58.9	41.1	60.6	39.4
T8	4.66	265.9	0.3	99.7	1.3	98.7
T9	4.68	264.8	0.1	99.9	0.0	100.0
T10	4.84	256.2	7.4	92.6	8.1	92.0

Table S4. Characteristics of 10 lowest energy vertical singlet transition for ^{carb}PzH, with participation of fragments atoms in the transitions.

	E, eV	E, nm	f	Ground state		Excited state	
				Pz	carbazole	Pz	carbazole
S1	4.35	284.8	0.054	5.0	95.0	2.6	97.4
S2	4.79	258.7	0.026	4.3	95.7	7.3	92.7
S3	5.05	245.5	1.692	15.5	84.5	21.3	78.7
S4	5.67	218.5	0.279	4.6	95.4	11.6	88.4

S5	5.83	212.5	0.414	7.9	92.1	13.0	87.0
S6	6.08	204.1	0.779	7.0	93.0	9.7	90.3
S7	6.44	192.7	0.010	61.6	38.4	69.1	30.9
S8	6.64	186.8	0.089	32.9	67.1	20.8	79.2
S9	6.70	185.1	0.116	9.6	90.4	7.9	92.1
S10	6.83	181.6	0.029	14.6	85.4	14.1	85.9

Table S5. Characteristics of 10 lowest energy vertical triplet transition for ^{carb}PzH, with participation of fragments atoms in the transitions.

	E, eV	E, nm	Ground state		Excited state	
			Pz	carbazole	Pz	carbazole
T1	3.56	348.4	9.2	90.8	9.1	90.9
T2	3.61	343.4	4.2	95.8	2.3	97.7
T3	3.93	315.8	18.8	81.2	21.7	78.3
T4	4.32	287.0	9.6	90.4	8.0	92.0
T5	4.68	265.0	44.0	56.1	45.5	54.5
T6	4.71	263.3	5.5	94.5	12.3	87.7
T7	4.79	259.1	14.2	85.8	14.2	85.8
T8	4.99	248.6	1.2	98.8	7.1	92.9
T9	5.37	230.7	96.7	3.3	88.6	11.4
T10	5.43	228.1	4.2	95.8	5.4	94.6

Table S6. Characteristics of 9 lowest energy vertical singlet transition for **1**, with participation of fragments atoms in the transitions.

				Ground state			Excited state		
	E, eV	E, nm	f	Ag	Pz	TPA	Ag	Pz	TPA
S1	4.35	284.8	1.249	0.4	6.8	92.9	0.5	10.5	89.1
S2	4.37	283.4	0.714	0.3	6.0	93.7	0.5	9.5	90.1
S3	4.41	281.5	0.055	0.1	2.6	97.2	1.0	0.8	98.3
S4	4.41	281.0	0.041	0.4	3.3	96.3	1.1	1.1	97.8
S5	4.42	280.7	0.266	0.2	3.6	96.2	0.3	5.1	94.6
S6	4.44	279.0	0.199	0.1	2.6	97.3	0.4	3.6	96.0
S7	4.65	266.5	0.305	0.1	1.2	98.7	0.0	0.0	100.0
S8	4.66	266.1	0.409	0.1	1.0	98.9	0.1	0.1	99.9
S9	4.66	266.0	0.394	0.1	0.9	99.1	0.2	0.1	99.8

Table S7. Characteristics of 9 lowest energy vertical triplet transition for **1**, with participation of fragments atoms in the transitions.

			Ground state			Excited state		
	E, eV	E, nm	Ag	Pz	TPA	Ag	Pz	TPA
T1	3.44	360.2	0.5	8.7	90.9	0.3	10.6	89.2
T2	3.46	358.1	0.5	8.7	90.9	0.9	10.3	88.9
T3	3.53	351.4	0.5	5.2	94.3	0.0	7.1	92.9
T4	3.70	335.1	0.1	0.4	99.5	0.1	0.0	99.9
T5	3.71	334.4	0.1	0.8	99.2	0.0	0.0	100.0
T6	3.71	334.3	0.1	0.7	99.3	0.0	0.0	100.0
T7	3.88	319.4	0.2	3.3	96.5	1.3	0.5	98.2
T8	3.89	318.8	0.1	3.3	96.6	1.3	0.1	98.6

T9	3.92	316.5	0.2	2.4	97.4	0.6	0.9	98.5

Table S8. Characteristics of 9 lowest energy vertical singlet transition for **2**, with participation of fragments atoms in the transitions.

				Ground state			Excited state		
	E, eV	E, nm	f	Ag	Pz	carbazole	Ag	Pz	carbazole
S1	4.30	288.3	0.040	0.3	4.7	95.0	2.2	1.9	95.9
S2	4.32	286.9	0.031	0.4	5.4	94.2	1.5	2.1	96.4
S3	4.38	282.8	0.077	0.4	2.9	96.7	0.8	0.9	98.3
S4	4.77	260.1	0.074	0.4	2.4	97.2	2.0	4.1	93.9
S5	4.78	259.4	0.116	0.2	2.7	97.1	1.6	4.1	94.3
S6	4.84	256.0	0.221	0.3	1.6	98.2	0.8	1.8	97.4
S7	5.02	246.8	0.750	1.8	17.3	80.9	4.5	21.2	74.3
S8	5.04	246.0	1.231	1.3	14.5	84.2	3.3	17.6	79.2
S9	5.28	235.0	1.112	2.4	9.4	88.2	3.6	10.7	85.7

Table S9. Characteristics of 9 lowest energy vertical triplet transition for **2**, with participation of fragments atoms in the transitions.

			Ground state			Excited state		
	E, eV	E, nm	Ag	Pz	carbazole	Ag	Pz	carbazole
T1	3.53	350.9	0.6	5.6	93.8	1.6	2.8	95.6
T2	3.55	348.8	0.5	5.8	93.7	1.2	2.4	96.5
T3	3.60	344.6	0.4	2.8	96.8	0.5	2.9	96.6
T4	3.61	343.9	0.2	2.7	97.2	0.5	2.1	97.4
T5	3.61	343.6	0.2	2.4	97.4	0.3	0.4	99.4
T6	3.64	340.8	0.0	1.1	98.9	0.4	0.8	98.8
T7	3.99	310.9	0.6	16.7	82.7	1.9	17.4	80.7
T8	3.99	310.5	0.9	14.8	84.3	1.7	15.7	82.6
T9	4.15	298.9	0.2	5.9	93.9	0.9	6.0	93.2

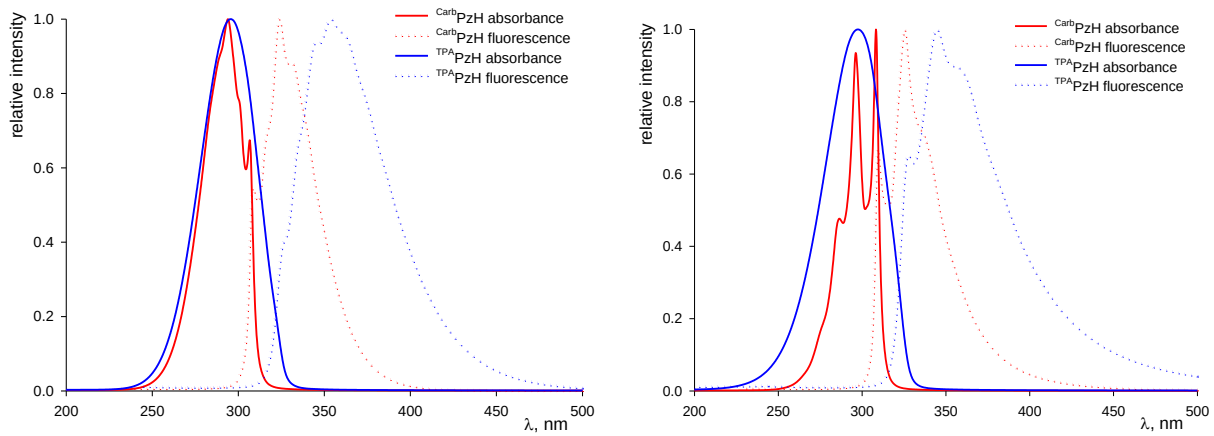


Figure S37. Modeling of electronic spectra of substituted pyrazoles assuming optimized ground state (left) and constrained flattened ground state (right).

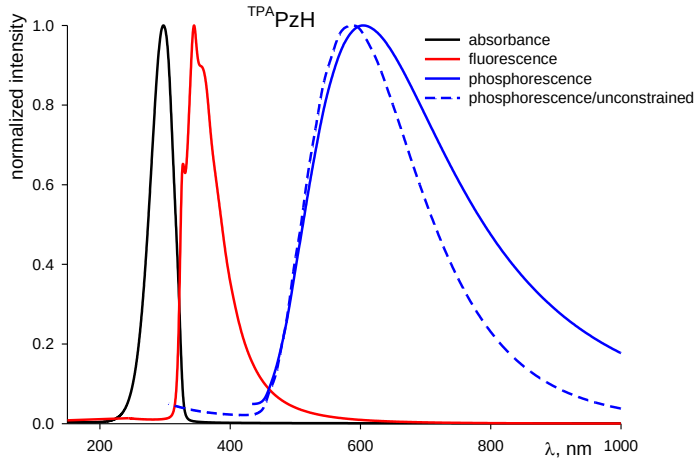


Figure S 38. Modeling of absorption, fluorescence and phosphorescence spectra of ^{TPA}PzH assuming constrained flattened ground state, and phosphorescence to the optimized (unconstrained) ground state.

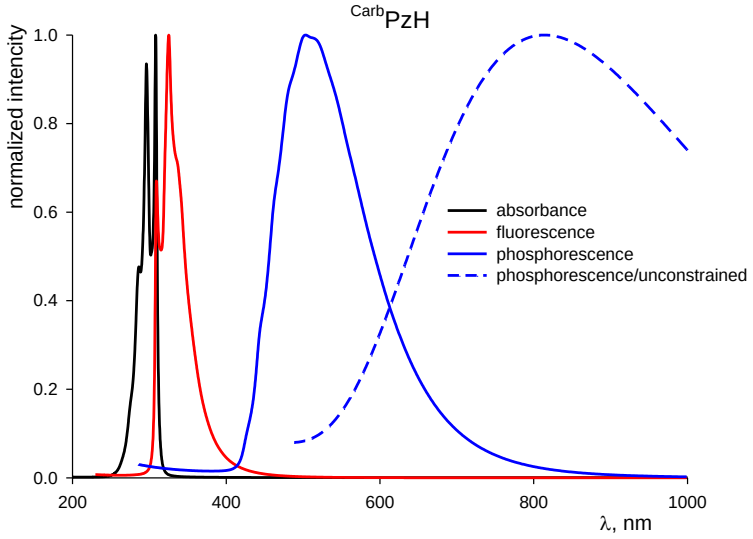


Figure S39. Modeling of absorption, fluorescence and phosphorescence spectra of ^{Carb}PzH assuming constrained flattened ground state, and phosphorescence to the optimized (unconstrained) ground state.

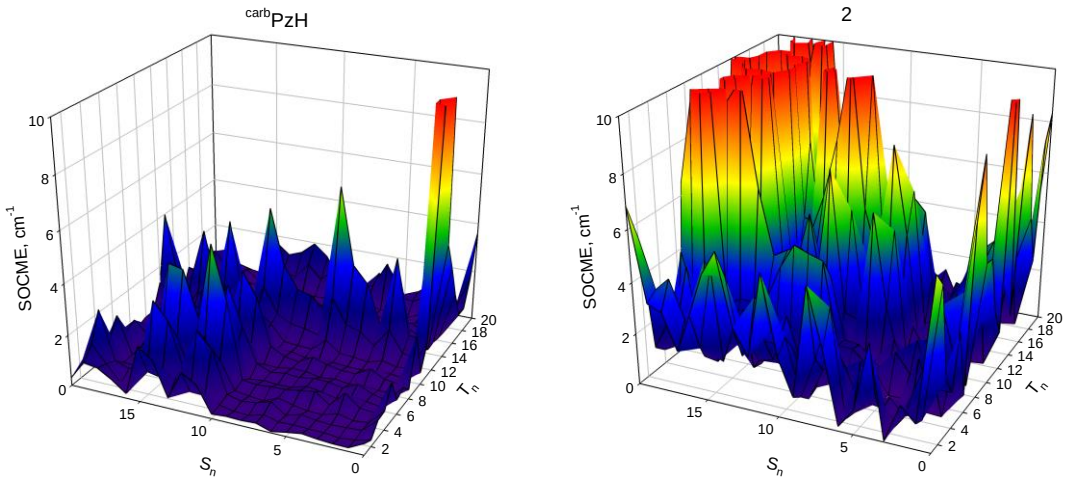


Figure S40. Representation of SOCME matrix elements for free ^{carb}PzH (left) and its silver complex **2** (right).

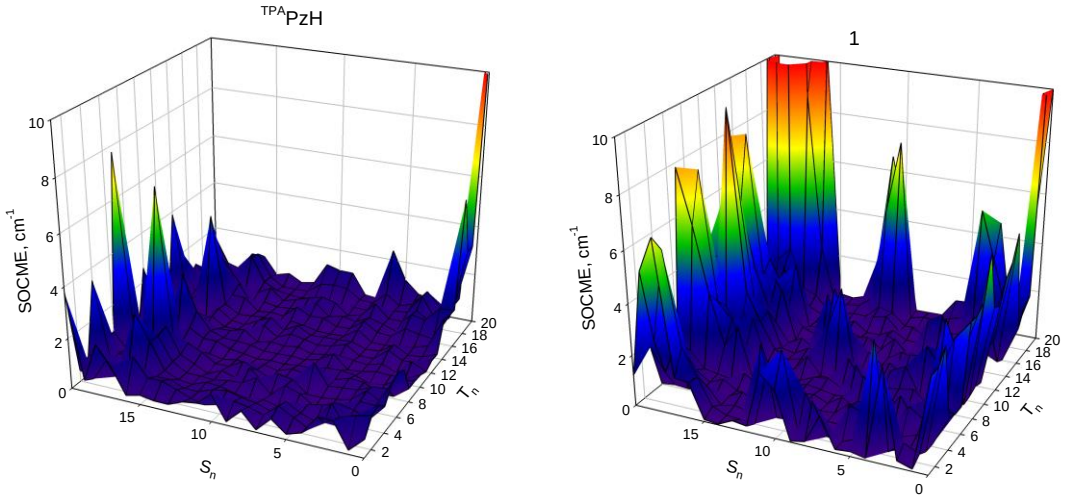


Figure S41. Representation of SOCME matrix elements for free ^{TPA}PzH (left) and its silver complex **1** (right).

Table S10. XYZ coordinates of all computes species.

^{TPA}PzH, optimized GS, E=-1311.912471406135

9	-6.500560000	1.572850000	-0.672182000
9	-7.272451000	-0.434361000	-0.897477000
9	-7.062058000	0.426888000	1.066407000
7	-4.884371000	-1.478286000	0.135249000
7	-3.562426000	-1.596908000	0.199534000
7	2.757942000	0.031365000	0.057413000
6	-5.083889000	-0.185907000	-0.059773000
6	-3.884397000	0.533580000	-0.121259000
1	-3.750319000	1.593704000	-0.254767000
6	-2.904361000	-0.425870000	0.050303000
6	-6.479125000	0.340563000	-0.144064000
6	-1.442747000	-0.317090000	0.070487000
6	-0.811783000	0.725590000	-0.606292000
1	-1.404219000	1.443378000	-1.161430000
6	0.564499000	0.840922000	-0.613006000
1	1.031940000	1.650257000	-1.159559000
6	1.359326000	-0.083915000	0.067679000
6	0.730120000	-1.120690000	0.758879000
1	1.325593000	-1.836775000	1.311104000
6	-0.647430000	-1.234068000	0.756215000
1	-1.103687000	-2.038217000	1.322426000
6	3.361807000	1.314379000	0.036204000
6	2.958796000	2.294824000	0.938711000
1	2.183573000	2.069100000	1.661310000
6	3.545875000	3.549917000	0.911122000
1	3.223757000	4.304575000	1.618927000
6	4.551658000	3.835078000	-0.002635000
1	5.014241000	4.814450000	-0.018143000
6	4.961583000	2.854143000	-0.895167000
1	5.742243000	3.066465000	-1.616119000
6	4.366460000	1.602239000	-0.883533000
1	4.678805000	0.841489000	-1.589056000
6	3.583004000	-1.117204000	0.015383000

6	4.743844000	-1.169491000	0.784471000
1	4.998687000	-0.334022000	1.425495000
6	5.570425000	-2.280463000	0.726504000
1	6.471629000	-2.304561000	1.327875000
6	5.244456000	-3.359588000	-0.083567000
1	5.888112000	-4.229906000	-0.122315000
6	4.084234000	-3.311920000	-0.844672000
1	3.820691000	-4.143275000	-1.488062000
6	3.262305000	-2.196799000	-0.805642000
1	2.367669000	-2.159973000	-1.415399000
1	-3.158882000	-2.513871000	0.305542000

^{TPA}PzH, ^{D0}GS, E=-1311.911678206654

9	-6.443454000	1.213140000	-1.317553000
9	-7.224836000	-0.747998000	-0.854329000
9	-7.111781000	0.753898000	0.683363000
7	-4.904346000	-1.292426000	0.671934000
7	-3.584803000	-1.390344000	0.796352000
7	2.762696000	0.038947000	0.028039000
6	-5.080741000	-0.197899000	-0.047346000
6	-3.870068000	0.414257000	-0.388207000
1	-3.725940000	1.311192000	-0.965780000
6	-2.904454000	-0.397425000	0.179503000
6	-6.464770000	0.251183000	-0.383767000
6	-1.441102000	-0.297537000	0.164545000
6	-0.823986000	0.757485000	-0.507347000
1	-1.424797000	1.501154000	-1.016565000
6	0.551177000	0.867823000	-0.557428000
1	1.003222000	1.691181000	-1.095994000
6	1.364244000	-0.073639000	0.076342000
6	0.752424000	-1.124771000	0.759322000
1	1.361005000	-1.861249000	1.268676000
6	-0.624687000	-1.234729000	0.796021000
1	-1.051498000	-2.066895000	1.342757000
6	3.371677000	1.317953000	0.059348000
6	2.960728000	2.268993000	0.989864000
1	2.175685000	2.022212000	1.694674000
6	3.551673000	3.522039000	1.012902000
1	3.222046000	4.253251000	1.741583000
6	4.570023000	3.835381000	0.122832000
1	5.035699000	4.813089000	0.146677000
6	4.989037000	2.883428000	-0.796377000
1	5.780010000	3.117102000	-1.499280000
6	4.389844000	1.634215000	-0.836234000
1	4.709444000	0.897171000	-1.563317000
6	3.577720000	-1.114232000	-0.062214000
6	4.740078000	-1.210476000	0.699711000
1	5.006992000	-0.403796000	1.371899000
6	5.551265000	-2.329537000	0.596766000
1	6.453833000	-2.388677000	1.193564000
6	5.208297000	-3.372530000	-0.252473000
1	5.840289000	-4.249122000	-0.326154000
6	4.046724000	-3.280712000	-1.007325000
1	3.770358000	-4.083065000	-1.681436000
6	3.240136000	-2.157095000	-0.922761000
1	2.343055000	-2.084900000	-1.525839000
1	-3.207547000	-2.173443000	1.304171000

^{TPA}PzH, S_1, E=-1311.770203365512

9	-6.407697000	0.982879000	-1.472639000
9	-7.164878000	-0.898542000	-0.725901000
9	-7.043592000	0.807252000	0.582299000
7	-4.833196000	-1.214368000	0.833263000
7	-3.504568000	-1.291343000	0.965101000
7	2.785960000	0.067685000	-0.005120000
6	-5.014966000	-0.226506000	-0.031430000
6	-3.822399000	0.347589000	-0.460947000
1	-3.695285000	1.148347000	-1.169234000
6	-2.818314000	-0.376296000	0.211445000
6	-6.404845000	0.161889000	-0.411783000
6	-1.406341000	-0.274183000	0.168633000
6	-0.777012000	0.780229000	-0.568023000
1	-1.393062000	1.493154000	-1.102641000
6	0.574087000	0.910641000	-0.614307000
1	1.028584000	1.704281000	-1.194119000
6	1.415257000	-0.043370000	0.049153000
6	0.798773000	-1.113781000	0.773305000
1	1.422887000	-1.822533000	1.303256000
6	-0.554780000	-1.209329000	0.842321000
1	-0.982449000	-2.021471000	1.417908000
6	3.394985000	1.334235000	0.084427000
6	2.836956000	2.307897000	0.920465000
1	1.976415000	2.059083000	1.528290000
6	3.412311000	3.563647000	0.987233000
1	2.987800000	4.308552000	1.649329000
6	4.530073000	3.867856000	0.220613000
1	4.972764000	4.854818000	0.273208000
6	5.075308000	2.900929000	-0.621004000
1	5.939402000	3.137164000	-1.230090000
6	4.514906000	1.641594000	-0.697781000
1	4.922925000	0.896907000	-1.369743000
6	3.576613000	-1.091568000	-0.135896000
6	4.767190000	-1.224365000	0.588350000
1	5.095057000	-0.421469000	1.236569000
6	5.499626000	-2.390823000	0.487403000
1	6.415752000	-2.495597000	1.055808000
6	5.060971000	-3.434173000	-0.323807000
1	5.639763000	-4.346822000	-0.394637000
6	3.875055000	-3.302222000	-1.036049000
1	3.530609000	-4.107680000	-1.673357000
6	3.127556000	-2.142488000	-0.943074000
1	2.210437000	-2.026526000	-1.506630000
1	-3.124069000	-1.968573000	1.602955000

^{TPA}PzH, T_1, E= -1311.808002651403

9	-6.447235000	1.283969000	-1.111977000
9	-6.872432000	-0.799837000	-1.488330000
9	-7.298960000	0.048414000	0.441854000
7	-4.845456000	-1.382578000	0.622076000
7	-3.529360000	-1.429988000	0.822786000
7	2.757608000	0.096211000	0.090134000
6	-5.028828000	-0.287172000	-0.110809000
6	-3.845862000	0.380639000	-0.390308000
1	-3.717751000	1.283627000	-0.961911000
6	-2.840959000	-0.391652000	0.237360000
6	-6.410054000	0.061555000	-0.562964000
6	-1.456173000	-0.227943000	0.291351000
6	-0.807855000	0.903749000	-0.374833000
1	-1.423738000	1.648221000	-0.863045000
6	0.529915000	1.016809000	-0.412434000
1	0.988894000	1.845609000	-0.937849000
6	1.383649000	0.021827000	0.201304000
6	0.758268000	-1.060484000	0.919480000
1	1.389625000	-1.763783000	1.449789000
6	-0.579350000	-1.178603000	0.984817000
1	-1.007792000	-1.980171000	1.572602000
6	3.409153000	1.353522000	0.075380000
6	3.023525000	2.345292000	0.973438000
1	2.243189000	2.136675000	1.695333000
6	3.649745000	3.581380000	0.947113000
1	3.348576000	4.346058000	1.652963000
6	4.665486000	3.834304000	0.035777000
1	5.155657000	4.800070000	0.019853000
6	5.051514000	2.841164000	-0.855929000
1	5.838057000	3.032783000	-1.575957000
6	4.426655000	1.606163000	-0.843022000
1	4.717159000	0.837368000	-1.548548000
6	3.526936000	-1.084521000	-0.046639000
6	4.727486000	-1.228184000	0.646981000
1	5.069345000	-0.433748000	1.299169000
6	5.470486000	-2.387276000	0.504088000
1	6.401740000	-2.492841000	1.047576000
6	5.024414000	-3.413144000	-0.320265000
1	5.608808000	-4.318893000	-0.426388000
6	3.826941000	-3.269353000	-1.006751000
1	3.476261000	-4.058586000	-1.660963000
6	3.079530000	-2.110082000	-0.876493000
1	2.154398000	-1.985811000	-1.426064000
1	-3.150645000	-2.188162000	1.363377000

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^{carb}PzH, optimized GS, E=-1158.304658158122

9	6.352982000	0.165505000	0.942658000
9	6.183083000	-1.005451000	-0.855087000
9	5.837563000	1.126315000	-0.921330000
7	3.797108000	-1.222834000	0.806934000
7	2.472800000	-1.116557000	0.846048000
7	-3.477255000	1.059290000	-0.288910000
6	5.636747000	0.023865000	-0.185484000
6	4.182945000	-0.183872000	0.086105000
6	1.993677000	-0.045192000	0.176006000
6	3.102906000	0.597793000	-0.339492000
6	-2.110502000	0.969895000	-0.165667000
6	-1.738506000	-0.383292000	-0.041848000
6	-0.398207000	-0.728606000	0.068054000
6	-2.965625000	-1.148379000	-0.075346000
6	-1.153087000	1.982413000	-0.161090000
6	0.564639000	0.272538000	0.071940000
6	0.171304000	1.617124000	-0.041143000
6	-3.258316000	-2.507168000	0.003901000
6	-4.008257000	-0.213504000	-0.218090000
6	-4.579315000	-2.910899000	-0.056366000
6	-5.340925000	-0.614952000	-0.274721000
6	-5.606262000	-1.969609000	-0.193462000
1	-0.114012000	-1.773538000	0.127327000
1	-1.429031000	3.026561000	-0.237885000
1	0.930111000	2.390268000	-0.020476000
1	-2.462970000	-3.235649000	0.114238000
1	-6.145328000	0.102919000	-0.377111000
1	-4.825658000	-3.963960000	0.004687000
1	-6.634686000	-2.309073000	-0.234775000
1	3.121848000	1.484773000	-0.949835000
6	-4.243366000	2.287289000	-0.359429000
1	-3.641466000	3.026942000	-0.888958000
1	-5.120187000	2.098126000	-0.980730000
6	-4.655366000	2.806310000	1.009531000
1	-3.778312000	3.017685000	1.623777000
1	-5.272990000	2.074555000	1.533315000
1	-5.230516000	3.727513000	0.904799000
1	1.943525000	-1.787442000	1.379509000

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^{carb}PzH, ^{D0}GS, E=-1158.304036715289

9	6.169075000	0.006678000	1.344764000
9	6.361386000	-0.615019000	-0.706577000
9	5.852131000	1.434736000	-0.242429000
7	3.793768000	-1.424846000	0.220740000
7	2.466415000	-1.357521000	0.173897000
7	-3.491677000	1.037476000	-0.326147000
6	5.640291000	0.160548000	0.117235000
6	4.184151000	-0.169750000	0.084044000
6	1.987897000	-0.103501000	0.009641000
6	3.105212000	0.710483000	-0.050954000
6	-2.122186000	0.937547000	-0.254724000
6	-1.758223000	-0.411097000	-0.075418000
6	-0.418978000	-0.765598000	0.010952000
6	-2.992999000	-1.162607000	-0.018993000
6	-1.153252000	1.935830000	-0.338426000
6	0.557811000	0.219130000	-0.074592000
6	0.170285000	1.559898000	-0.249012000
6	-3.294098000	-2.512185000	0.144424000
6	-4.032125000	-0.224165000	-0.168318000
6	-4.620136000	-2.904192000	0.157741000
6	-5.369648000	-0.613689000	-0.150363000
6	-5.643443000	-1.959773000	0.012156000
1	-0.160915000	-1.809527000	0.147549000
1	-1.418142000	2.977745000	-0.466450000
1	0.931106000	2.327499000	-0.316217000
1	-2.501408000	-3.242479000	0.261712000
1	-6.171193000	0.106587000	-0.257956000
1	-4.872905000	-3.949798000	0.284522000
1	-6.675569000	-2.289852000	0.028341000
1	3.141630000	1.778918000	-0.176634000
6	-4.242578000	2.274349000	-0.411205000
1	-3.665158000	2.972719000	-1.018598000
1	-5.162968000	2.070868000	-0.960334000
6	-4.548845000	2.873005000	0.953820000
1	-3.627436000	3.085299000	1.498998000
1	-5.152349000	2.188311000	1.552464000
1	-5.102246000	3.806286000	0.839567000
1	1.938409000	-2.210607000	0.252375000

^{carb}PzH, S_1, E=-1158.151373226206

9	6.151901000	0.083478000	1.366313000
9	6.338203000	-0.616253000	-0.660636000
9	5.837020000	1.450032000	-0.276591000
7	3.766166000	-1.364886000	0.415532000
7	2.445562000	-1.310607000	0.327550000
7	-3.460174000	1.020657000	-0.292268000
6	5.622542000	0.192889000	0.135566000
6	4.165353000	-0.134274000	0.119425000
6	1.969598000	-0.084038000	-0.006037000
6	3.097078000	0.716928000	-0.154603000
6	-2.113888000	0.918321000	-0.266211000
6	-1.762132000	-0.467465000	-0.134144000
6	-0.408661000	-0.825624000	-0.083591000
6	-2.986824000	-1.193128000	-0.067744000
6	-1.161333000	1.942743000	-0.351165000
6	0.558363000	0.213618000	-0.139549000
6	0.179604000	1.562978000	-0.279797000
6	-3.316957000	-2.545937000	0.062054000
6	-4.043229000	-0.246232000	-0.156644000
6	-4.670740000	-2.903712000	0.108943000
6	-5.368616000	-0.585987000	-0.103976000
6	-5.684087000	-1.958333000	0.032111000
1	-0.123039000	-1.865942000	-0.012050000
1	-1.445064000	2.982443000	-0.438110000
1	0.945306000	2.326209000	-0.307697000
1	-2.546242000	-3.304512000	0.128380000
1	-6.152509000	0.159258000	-0.161483000
1	-4.932478000	-3.950999000	0.209052000
1	-6.720865000	-2.265587000	0.073850000
1	3.137284000	1.757111000	-0.428249000
6	-4.206132000	2.261958000	-0.387205000
1	-3.629837000	2.949548000	-1.005433000
1	-5.133698000	2.046958000	-0.917450000
6	-4.485493000	2.862604000	0.982828000
1	-3.552750000	3.088808000	1.501831000
1	-5.068964000	2.175377000	1.596867000
1	-5.050518000	3.787643000	0.865191000
1	1.911337000	-2.138336000	0.536735000

^{carb}PzH, T_1, E= -1158.190232711473

9	6.130983000	0.020344000	1.403075000
9	6.357330000	-0.568931000	-0.654939000
9	5.849713000	1.475168000	-0.166631000
7	3.780364000	-1.401416000	0.254546000
7	2.453294000	-1.352487000	0.174709000
7	-3.472791000	1.020581000	-0.321581000
6	5.625944000	0.197184000	0.169001000
6	4.169522000	-0.129476000	0.105896000
6	1.953390000	-0.077951000	-0.020337000
6	3.116561000	0.742881000	-0.066550000
6	-2.117324000	0.894362000	-0.274353000
6	-1.756432000	-0.456000000	-0.103496000
6	-0.436356000	-0.846241000	-0.040297000
6	-3.009736000	-1.186176000	-0.031525000
6	-1.119458000	1.941157000	-0.396524000
6	0.608496000	0.219550000	-0.132559000
6	0.177472000	1.593701000	-0.327373000
6	-3.328340000	-2.529681000	0.132798000
6	-4.040209000	-0.236438000	-0.162157000
6	-4.662598000	-2.900183000	0.164037000
6	-5.380829000	-0.599229000	-0.127072000
6	-5.674554000	-1.943202000	0.035702000
1	-0.165270000	-1.886647000	0.066468000
1	-1.409897000	2.974131000	-0.537338000
1	0.935948000	2.361298000	-0.416365000
1	-2.546524000	-3.273207000	0.237592000
1	-6.171857000	0.134244000	-0.222513000
1	-4.928425000	-3.942602000	0.291224000
1	-6.710913000	-2.257941000	0.064819000
1	3.161948000	1.809241000	-0.205819000
6	-4.214963000	2.266893000	-0.389089000
1	-3.638468000	2.967029000	-0.993317000
1	-5.141517000	2.072572000	-0.930117000
6	-4.500979000	2.847807000	0.987755000
1	-3.570759000	3.054125000	1.519905000
1	-5.096022000	2.157118000	1.587603000
1	-5.055818000	3.781778000	0.889273000
1	1.930166000	-2.205649000	0.267147000

1, E=-20077.467033585515

47	-1.264728000	-1.608506000	-0.337334000
47	-0.478024000	1.788238000	-0.258867000
47	2.147622000	-0.633380000	-0.178288000
9	-3.903448000	-2.357456000	-1.980945000
9	-4.982517000	-2.250124000	-0.118467000
9	-5.838160000	-1.399651000	-1.906251000
9	0.331146000	4.706644000	-1.336509000
9	0.700587000	5.078027000	0.753137000
9	2.060375000	5.854207000	-0.732594000
9	4.232108000	-3.056557000	-1.317041000
9	4.253710000	-5.045973000	-0.468909000
9	4.350953000	-3.314913000	0.817235000
7	-2.757785000	-0.156538000	-0.624809000
7	-2.480894000	1.139879000	-0.397860000
7	1.555372000	2.350536000	-0.242316000
7	2.540311000	1.439086000	-0.152318000
7	1.595188000	-2.670260000	-0.191053000
7	0.295522000	-2.994275000	-0.090819000
7	-3.771135000	7.496728000	0.163762000
7	8.661044000	-0.744007000	0.060947000
7	-5.044722000	-6.562434000	0.229600000
6	-4.050254000	-0.244354000	-0.946115000
6	-4.638531000	1.007911000	-0.926115000
1	-5.667016000	1.260025000	-1.123210000
6	-3.599015000	1.862060000	-0.566494000
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