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Supporting Information

1,2,3-triazolyl bisphosphine with pyridyl functionality: Synthesis, copper(I) chemistry and application in click catalysis

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Crystal structure determination of complexes L, 2, and **3**.

Single crystals of all complexes were mounted on a Cryoloop with a drop of paratone oil and positioned in the cold nitrogen stream on a Bruker D8 Venture diffractometer. The data collections were performed at 100 K to 150 K using Bruker D8 Venture diffractometer with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å) with the ω-scan technique. The data were reduced using CrysalisPro Red 171.41_64.93a software.[1] The structures were solved using Olex2 1.5[2] with the ShelXT[3] structure solution program using intrinsic phasing and refined with SHELXL[3] refinement package using least-squares minimization. For ligand **L**, density associated with disordered and partially occupied solvent sites that were well-removed from the main molecule and was removed with Olex2.[2] A solvent mask was calculated and 188 electrons were found in a volume of 670 Å in 2 voids per unit cell. This is consistent with the presence of 1[$C_4H_{10}O$] per Formula Unit which account for 168 electrons per unit cell. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. The given chemical formula and other crystal data do not take into account the unknown solvent molecule(s). The reflections with error/esd more than 10 were excluded in order to avoid problems related to better refinement of the data. The data completeness is more than 99.8% in most of the cases, which is enough to guarantee a very good refinement of data. The details of X-ray structural determinations are given in Tables S1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 2236223-2236225.

Table S1 Crystallographic information of compounds **L** and **2–3.**

Identification code	**L**	**2·CH_2Cl_2**	**3·(2CH_3CN)**
Formula	$C_{42}H_{41}N_5OP_2$	$C_{39}H_{33}CuBrCl_2N_5P_2$	$C_{42}H_{37}Br_{0.18}CuI_{0.82}N_7P_2$
Formula weight	693.774	847.99	883.864
Temperature/K	150.00	150.00(10)	150.00
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	19.3688(18)	10.2611(3)	10.2428(10)
b/Å	12.3133(11)	25.5075(7)	26.910(2)
c/Å	16.7470(16)	13.8777(4)	14.2499(13)
α/°	90	90	90
β/°	115.162(3)	92.168(3)	95.008(3)
γ/°	90	90	90
Volume/$Å^3$	3615.1(6)	3629.68(18)	3912.8(6)
Z	4	4	4
$\rho_{calc}g/cm^3$	1.275	1.552	1.500
μ/mm^{-1}	0.161	1.975	1.510
F(000)	1465.6	1720.0	1788.9
Crystal size/mm^3	0.125 × 0.086 × 0.075	0.099 × 0.077 × 0.075	0.215 × 0.076 × 0.058
2θ range, deg	4.26 to 51	4.282 to 49.994	4.18 to 52
Total no of reflection	53250	63357	127660
Independent reflections	6703 [R_{int} = 0.0663]	6395 [Rint = 0.0797]	7709 [R_{int} = 0.0875]
Goodness-of-fit on F^2	1.0637	1.042	1.085
R_1 (I > 2σ(I))	0.0652	0.0393	0.0294
wR_2 (all data)	0.1672	0.0961	0.0697

Molecular orbitals, TD-DFT and NBO calculations

All DFT calculations were performed with the Gaussian09 (Rev. D.01) suite of programs.[4] Initially we optimized all of the structures (**1-3**) with different basic sets (using the hybrid density functional B3LYP with TZVP basic sets for C, H, N, P, Cl, Br, and SDD basic sets for Cu and I atoms with the relativistic electron core potential) and the results obtained are given below in Table S2. Frequency calculations were performed subsequently to confirm the presence of local minima (only positive frequencies). Vertical excitations (100 singlet excited

states) were calculated by TD-DFT method. Molecular orbitals were visualised using Chemcraft software with countor value: 0.030.

Table S2 Selected bond length and bond angles of **1-3** obtained from X-ray diffraction analysis and *DFT* calculation

	1 (X = Cl)	**2** (X = Br)		**3** (X = I)	
	DFT	**X-ray**	**DFT**	**X-ray**	**DFT**
Bond lengths (Å)					
Cu1–P1	2.26656	2.2267(9)	2.27335	2.2188(8)	2.22852
Cu1–P2	2.28629	2.2257(9)	2.29627	2.2325(8)	2.23787
Cu1–X	2.28696	2.4045(5)	2.41731	2.5865(11)	2.57585
Cu1–N1	2.23357	2.168(3)	2.24317	2.161(2)	2.16589
C1-N1	1.34321	1.348(4)	1.34341	1.351(4)	1.34078
C5–N1	1.34371	1.344(4)	1.34408	1.344(4)	1.36039
Bond angles (°)					
P1–Cu1–X	117.676	114.61(3)	115.804	115.03(3)	114.228
P2–Cu1–X	111.019	111.62(3)	111.443	111.38(3)	110.889
P1–Cu1–P2	130.128	132.02(4)	132.682	131.01(3)	133.286
N1–Cu1–X	107.711	109.52(7)	109.698	111.06(6)	108.227
P1-Cu1-N1	82.066	83.19(7)	83.814	83.14(6)	83.459
P2-Cu1-N1	93.398	93.25(7)	93.039	94.51(6)	93.472

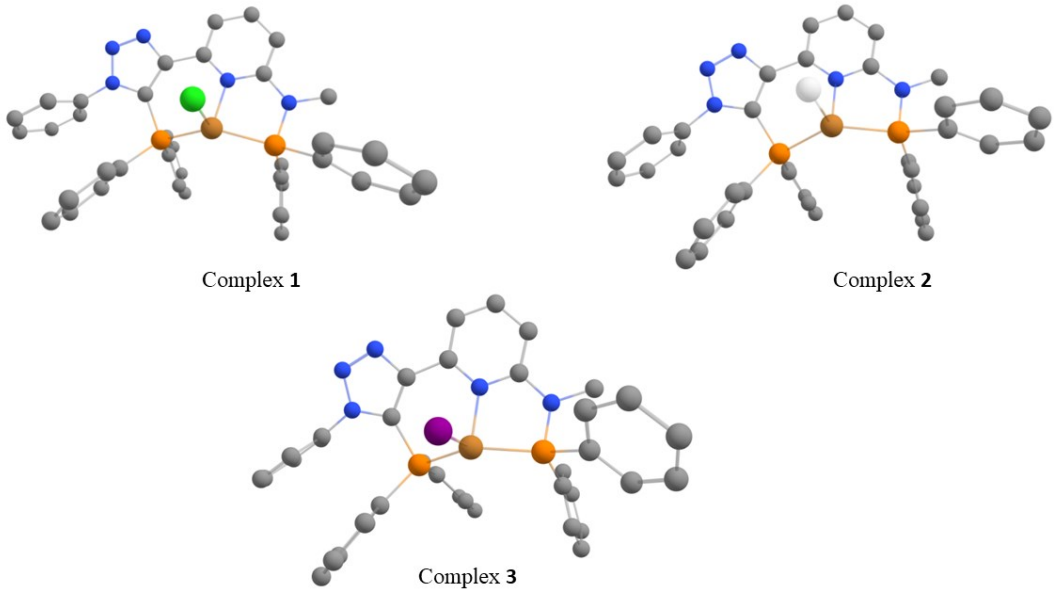


Fig. S1. Optimised structure based on the DFT calculations.

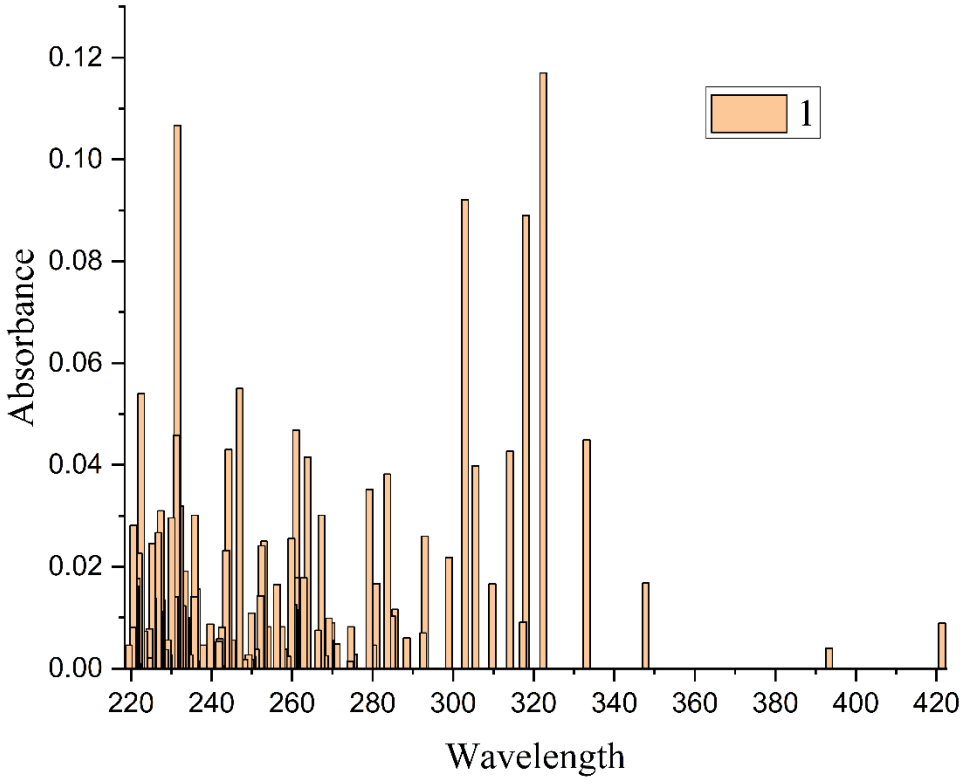


Fig. S2. Calculated absorption spectrum of **1** based on the TDDFT method.

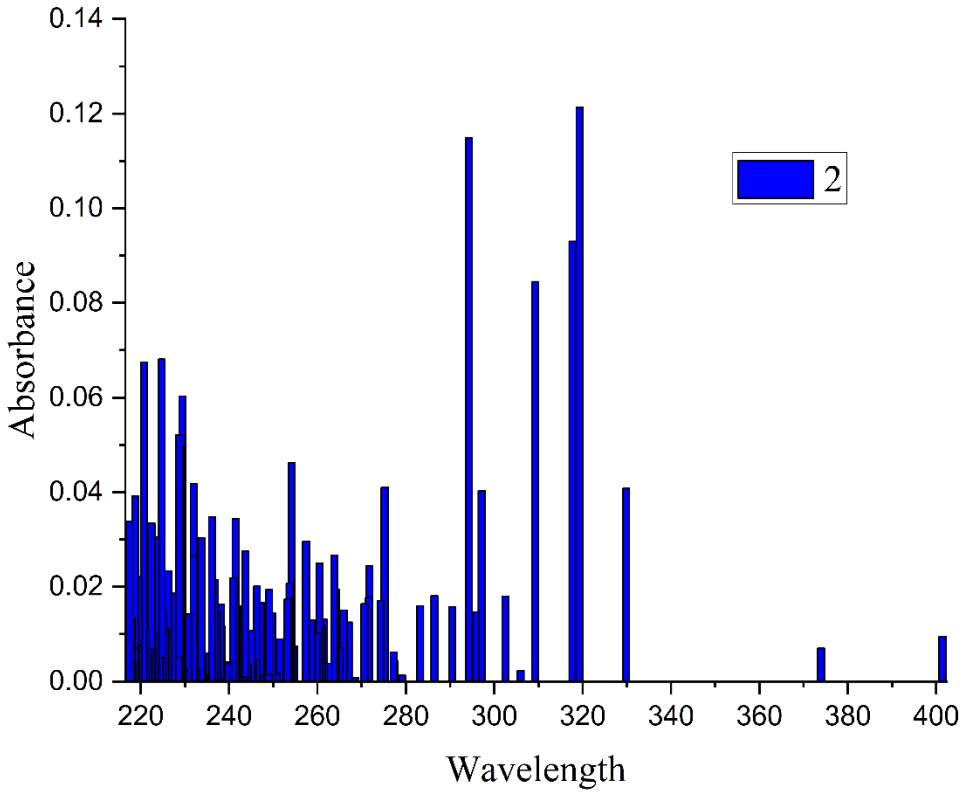


Fig. S3. Calculated absorption spectrum of **2** based on the TDDFT method.

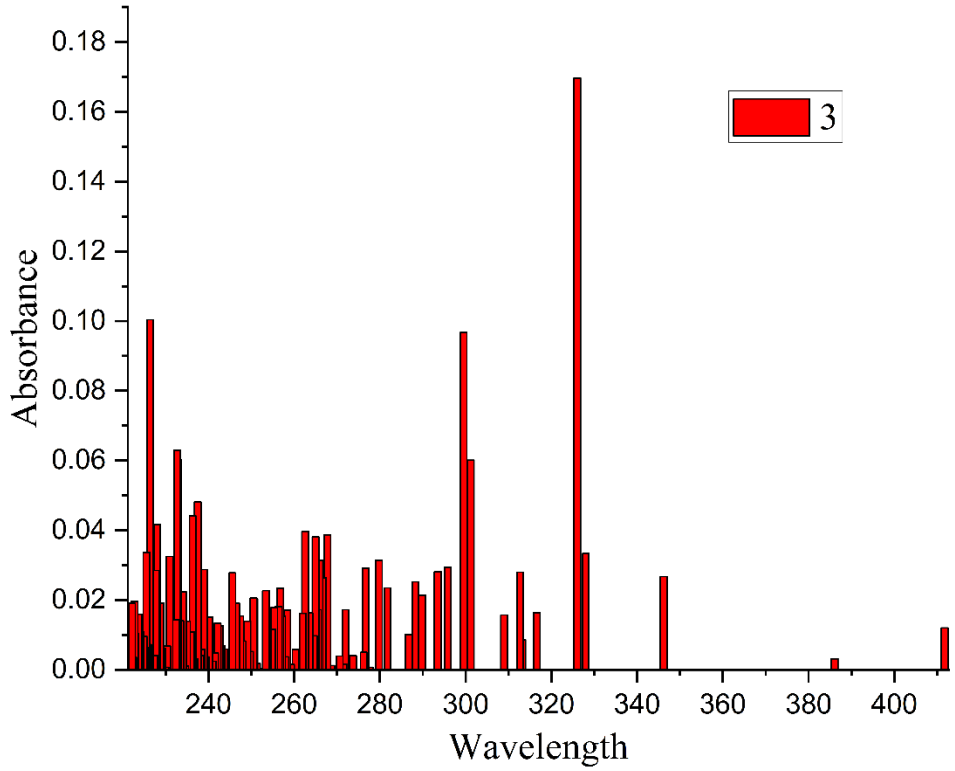


Fig. S4. Calculated absorption spectrum of **3** based on the TDDFT method.

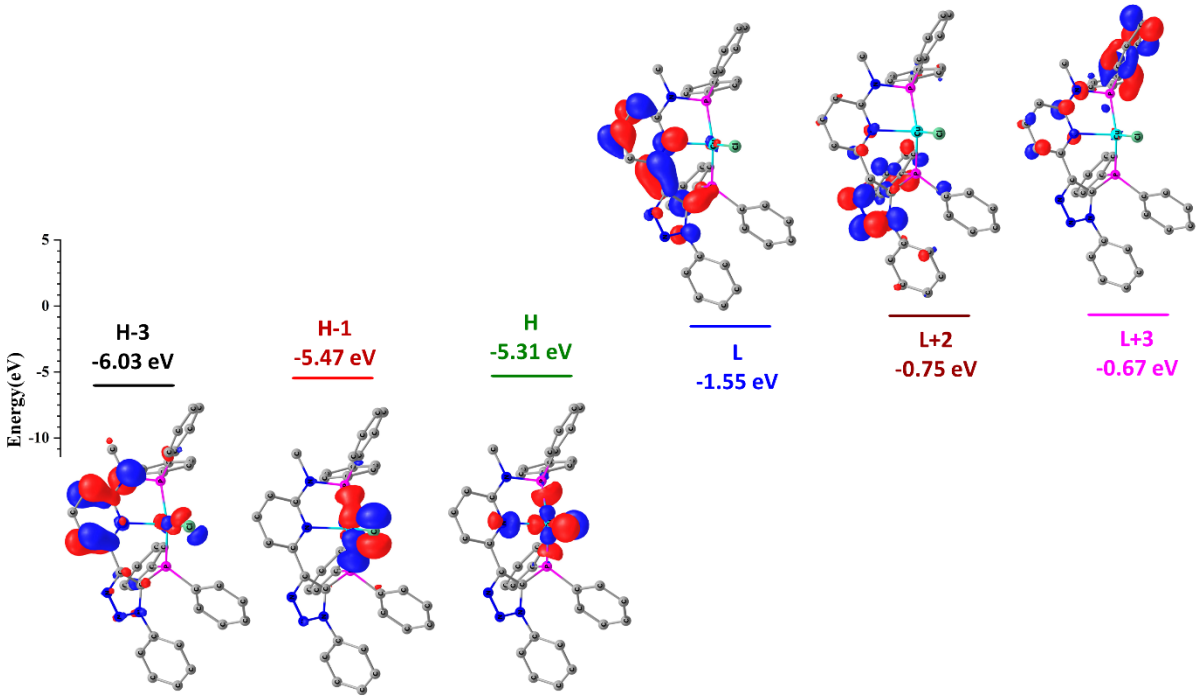


Fig. S5. Extended energy level plots for complex **1**.

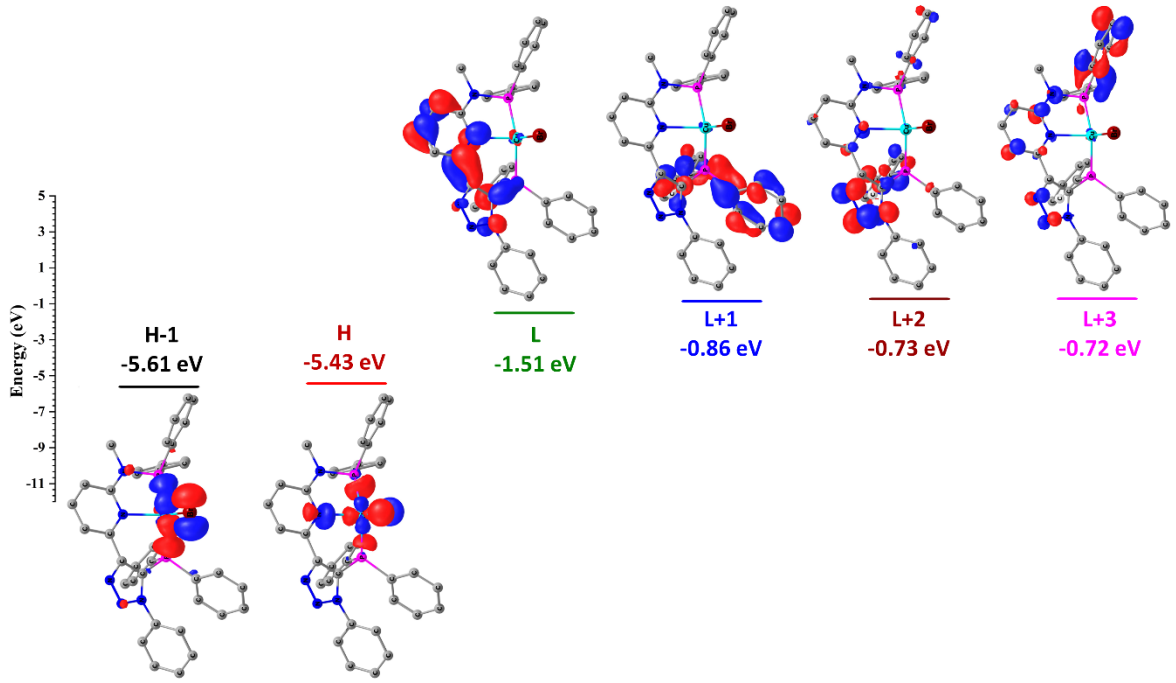


Fig. S6. Extended energy level plots for complex **2.**

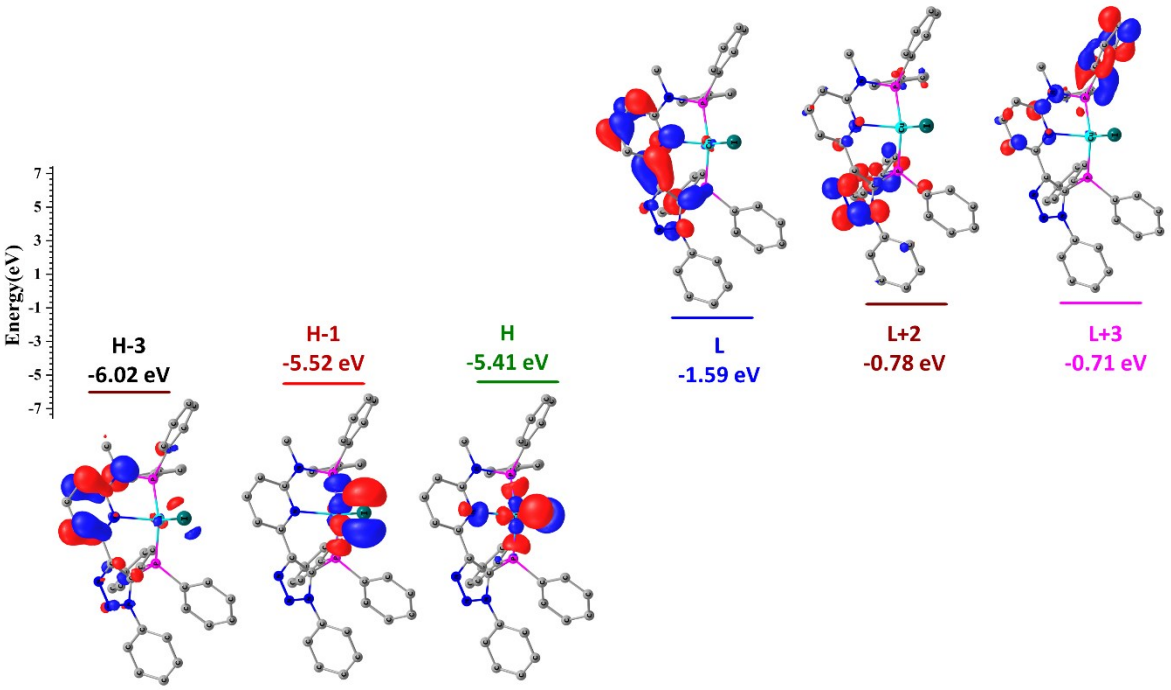


Fig. S7. Extended energy level plots for complex **3.**

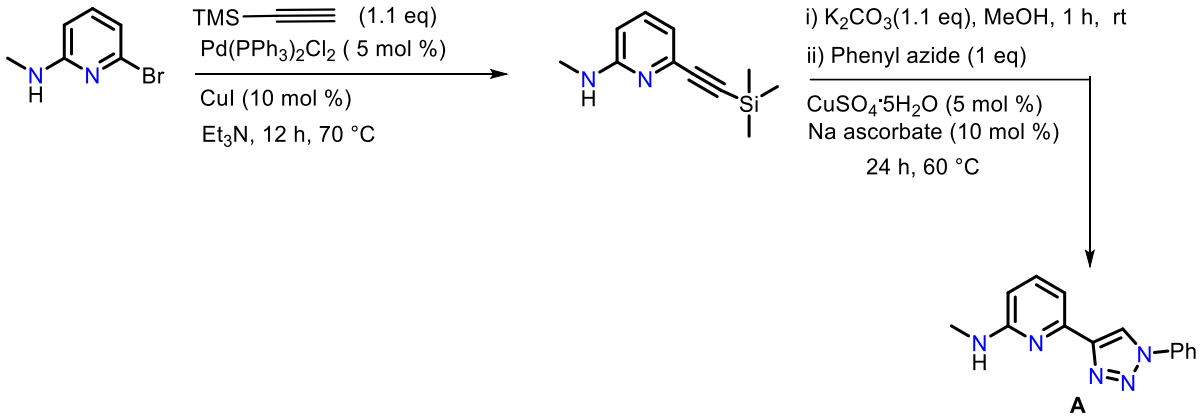
Table S3. TD-DFT data for complexes **1-3**

Comp	λ (nm)	E_{ex} (eV)	Oscillator strength *f*	Orbitals involved	
1	322	3.8460	0.1170	H-3 → L	(0.63)
				H → L+3	(0.20)
	318	3.8997	0.0890	H → L+2	(0.59)
				H → L+3	(0.27)
	303	4.0928	0.0921	H-1→ L+2	(0.55)
				H-1→ L+3	(0.38)
2	319	3.8831	0.0181	H-3→ L	(0.56)
				H-2→ L	(0.37)
	317	3.9026	0.0930	H-1→ L+1	(0.13)
				H → L+1	(0.66)
	294	3.2133	0.1149	H-1→ L+2	(0.42)
				H-1→ L+3	(0.37)

	326	3.8025	0.1697	H-3→ L	(0.67)
3	299	4.1391	0.0968	H-1→ L+2 H-1→ L+3	(0.56) (0.35)

Synthesis of [2,6-(Me)HNC$_6$H$_3$N(C$_2$HN$_3$C$_6$H$_5$)] (A)

Synthesis of compound **A** was achieved through a multistep process involving Sonagashira coupling of 6-bromo-N-methylpyridine-2-amine with trimethylsilyl acetylene in dry Et_3N to afford protected acetylene; which was deprotected by treatment with MeOH/K_2CO_3. Later acetylene derivative was treated with phenyl azide under click condition [$CuSO_4{\cdot}5H_2O$ and sodium ascorbate] to yield triazole derivative **A**.[5] The formation of **A** was confirmed by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. In the ^{1}H NMR spectrum of **A**, triazolic proton showed a singlet at 8.48 ppm and CH_3 protons appeared as a doublet at 2.95 ppm, possibly due to the coupling with NH proton ($^2J_{H\text{-}H}$ = 8 Hz).



Scheme 1. Synthesis of **A**.

Synthesis of compound [2,6-(Me)HNC$_6$H$_3$N(C$_2$HN$_3$C$_6$H$_5$)] (A)

Compound **A** was obtained by the combination of two-name reactions respectively. First 6-Bromo-N-methyl pyridine-2-amine (1000 mg, 5.34 mmol) was treated with trimethylsilyl acetylene (0.84ml, 5.88 mmol) in presence of $PdCl_2(PPh_3)_2$ (188 mg, 5 mol %) and CuI (102

mg, 10 mol %) in triethylamine at 60°C. The reaction mixture was stirred at room temperature for 12 h and after completion, the solution was passed through a neutral alumina pad. Then the solvent was evaporated using a rota-evaporator and the trimethylsilyl acetylene deprotected with the help of potassium carbonate in MeOH (20 mL). Deprotection was monitored with the help of TLC, after 1 h the deprotection was complete, added 20 mL H_2O. After that click reaction was performed with the help of phenyl azide (700 mg, 5.88 mmol), $CuSO_4.5H_2O$ (66.84 mg, 5 mmol%), and Na ascorbate (106 mg, 10 mmol%) respectively. The reaction mixture was stirred at 60°C for 24 h. Compound A was purified with help of column chromatography (1:1, pet ether: ethyl acetate). Yield 71% (953 mg). ^{1}H NMR (400 MHz, $CDCl_3$ δ 8.48 (s, 1H), 7.79 (d, J = 7.9 Hz, 2H), 7.52 (q, J = 7.2 Hz, 4H), 7.42 (t, J = 8.1 Hz, 1H), 6.38 (d, J = 7.3 Hz, 1H), 4.71 (br, 1H), 2.96 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.48, 149.63, 148.04, 138.38, 137.21, 129.82, 128.77, 120.56, 119.79, 109.58, 105.94, 29.17.

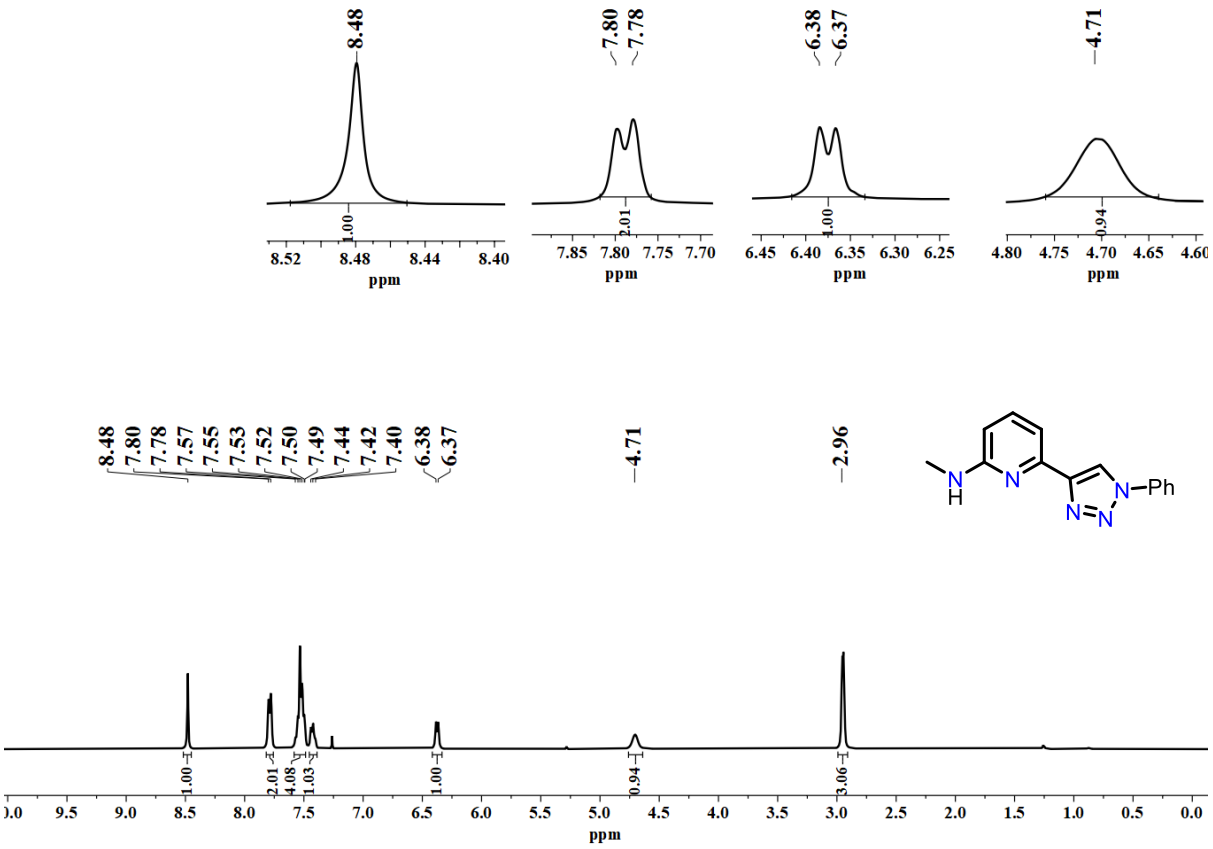


Fig. S8. ^{1}H NMR spectrum of **A** in $CDCl_3$ (400 MHz).

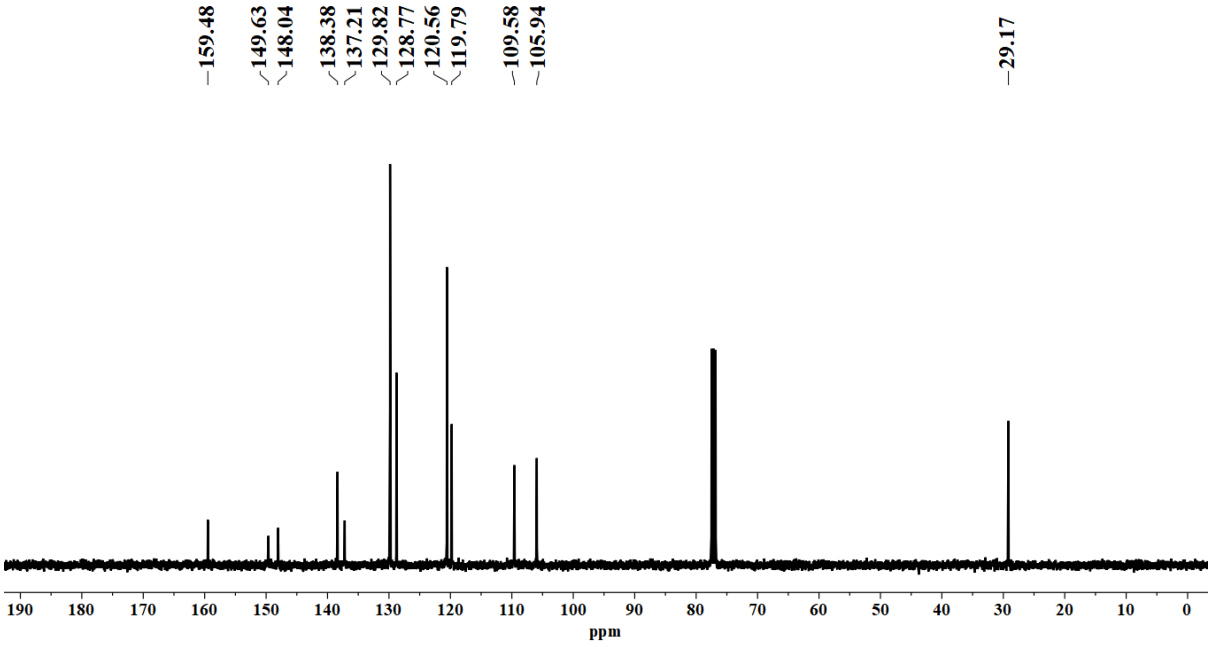


Fig. S9. $^{13}C\{^{1}H\}$ NMR spectrum of **A** in $CDCl_3$ (400 MHz).

NMR and HRMS spectra of compound L, and 1-3

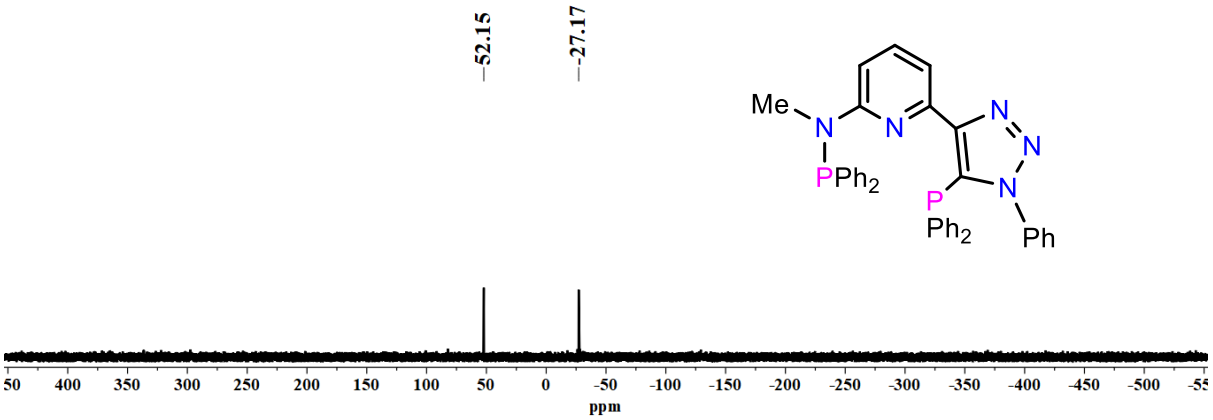


Fig. S10. $^{31}P\{^{1}H\}$ NMR spectrum of **L** in C_6D_6 (162 MHz).

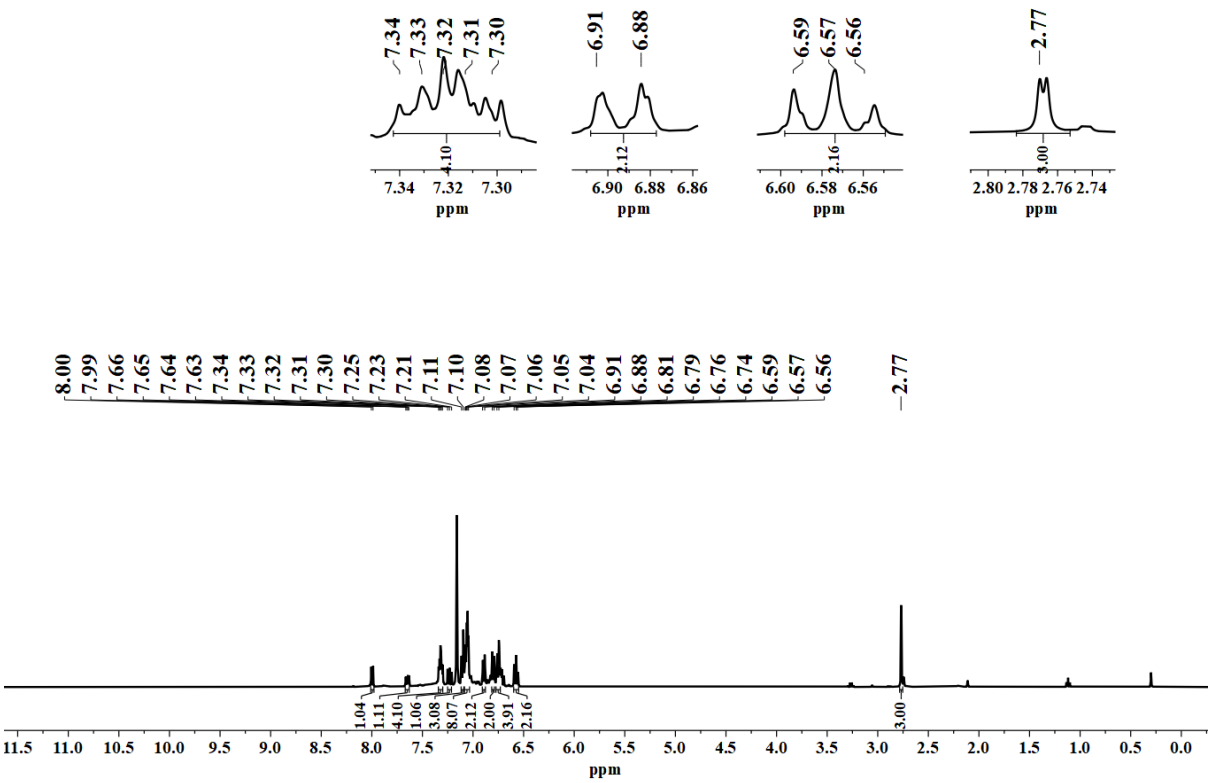


Fig. S11. ^{1}H NMR spectrum of **L** in C_6D_6 (400 MHz).

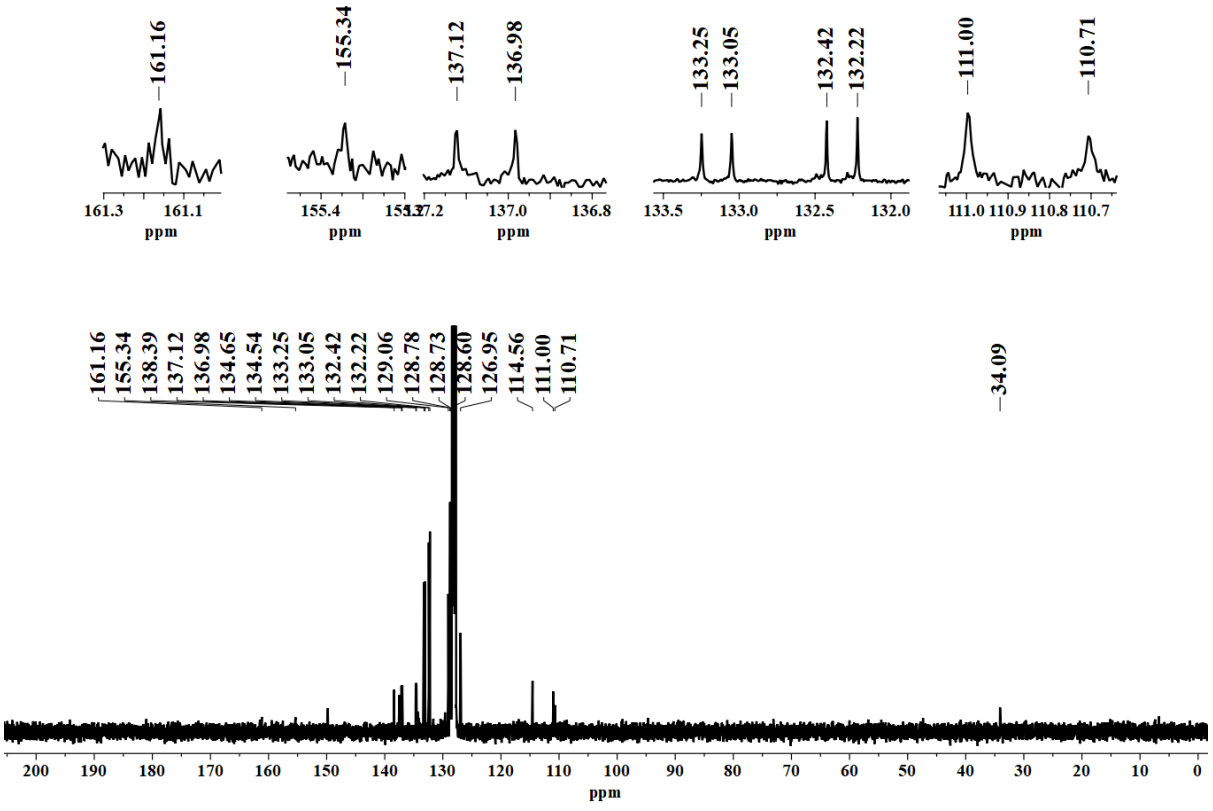


Fig. S12. ^{13}C{^{1}H} NMR spectrum of **L** in C_6D_6 (400 MHz).

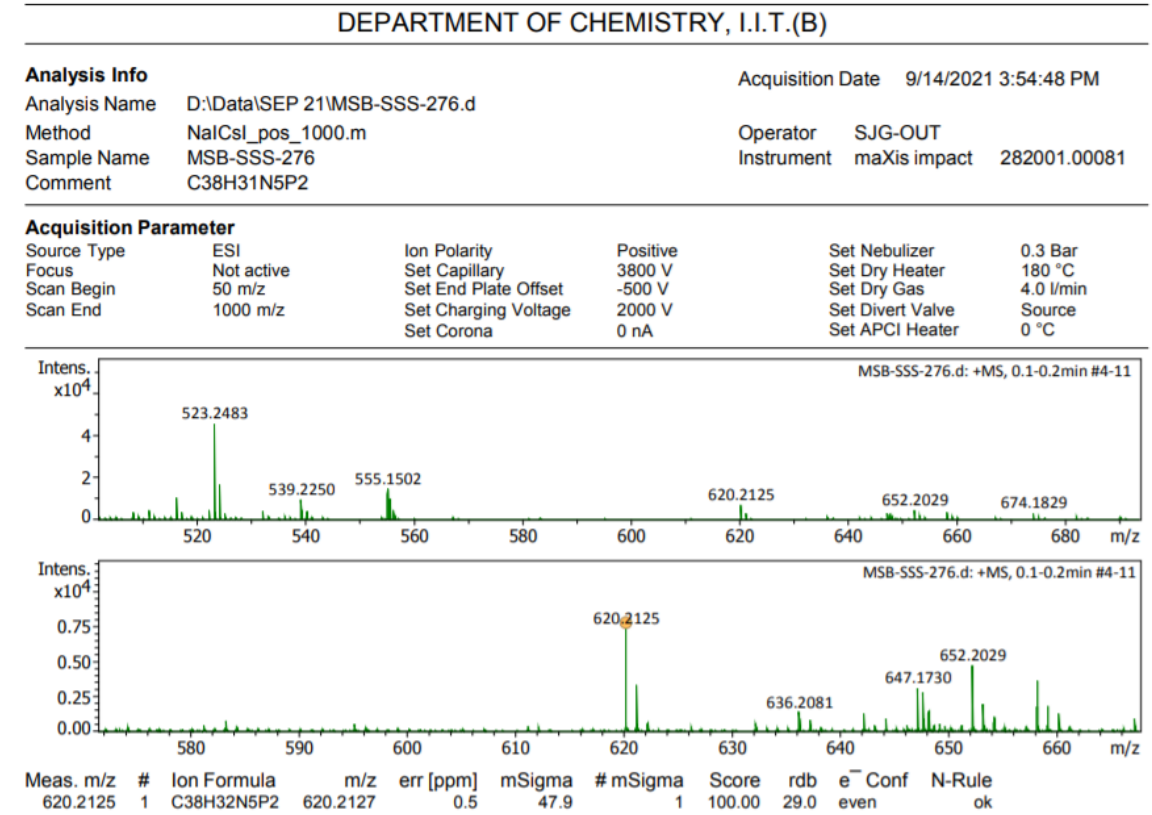


Fig. S13. HRMS spectrum of **L**.

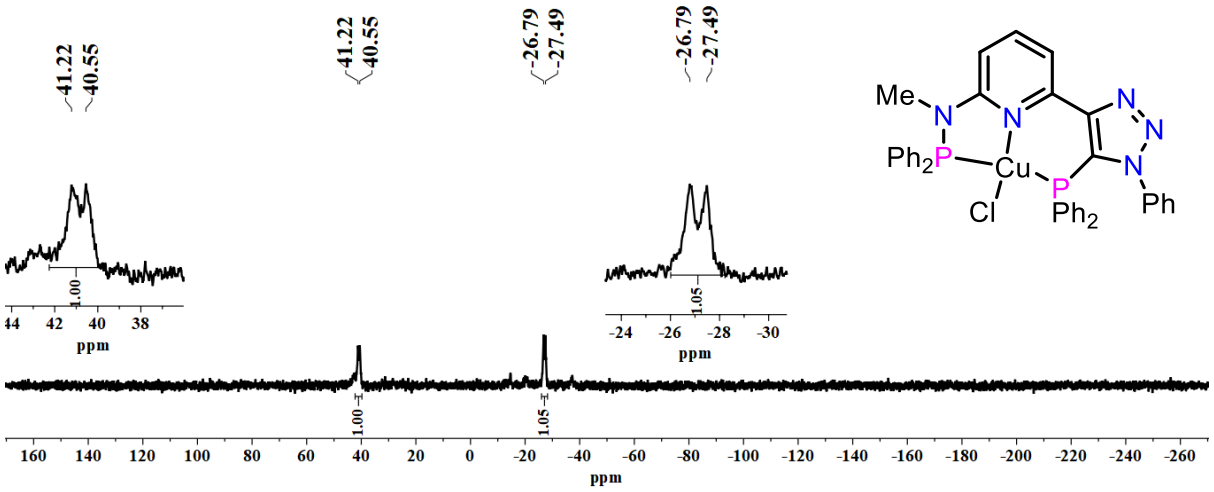


Fig. S14. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ (162 MHz).

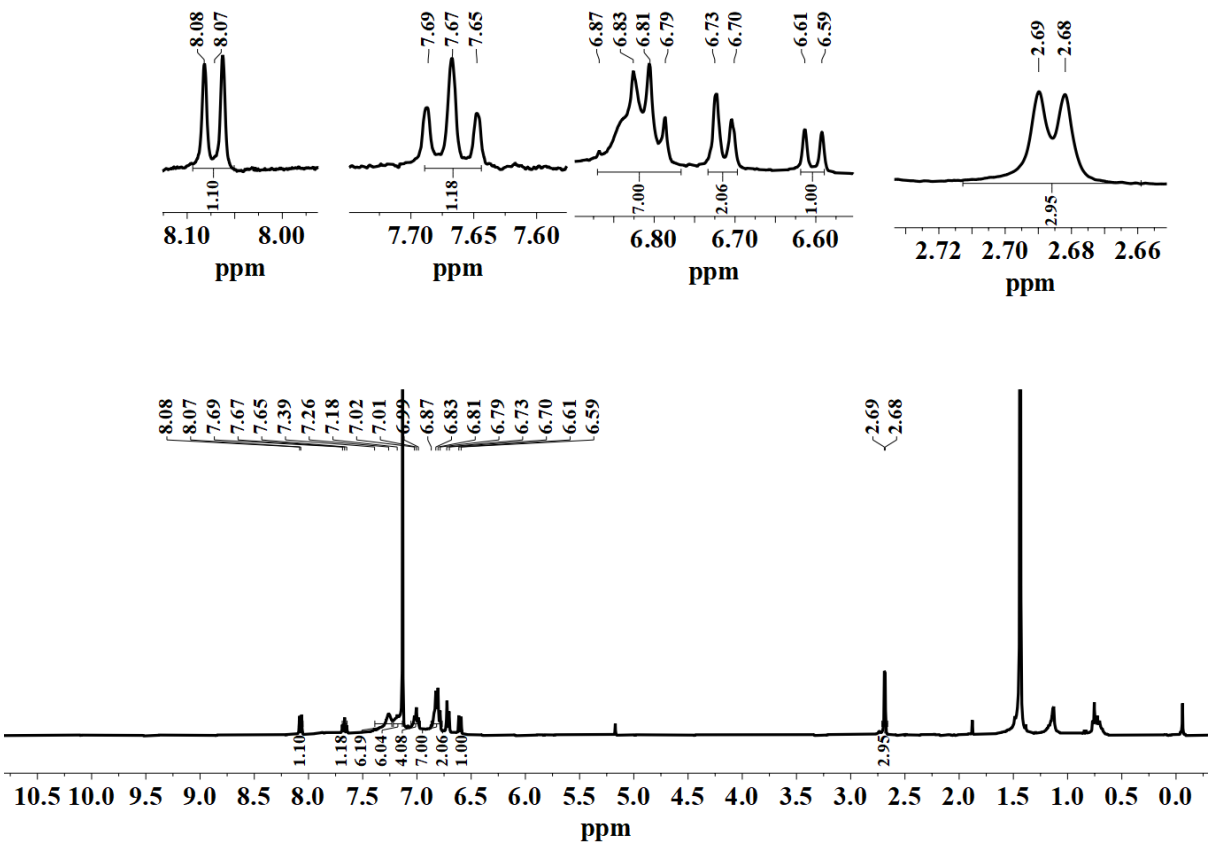


Fig. S15. ^{1}H NMR spectrum of **1** in $CDCl_3$ (400 MHz).

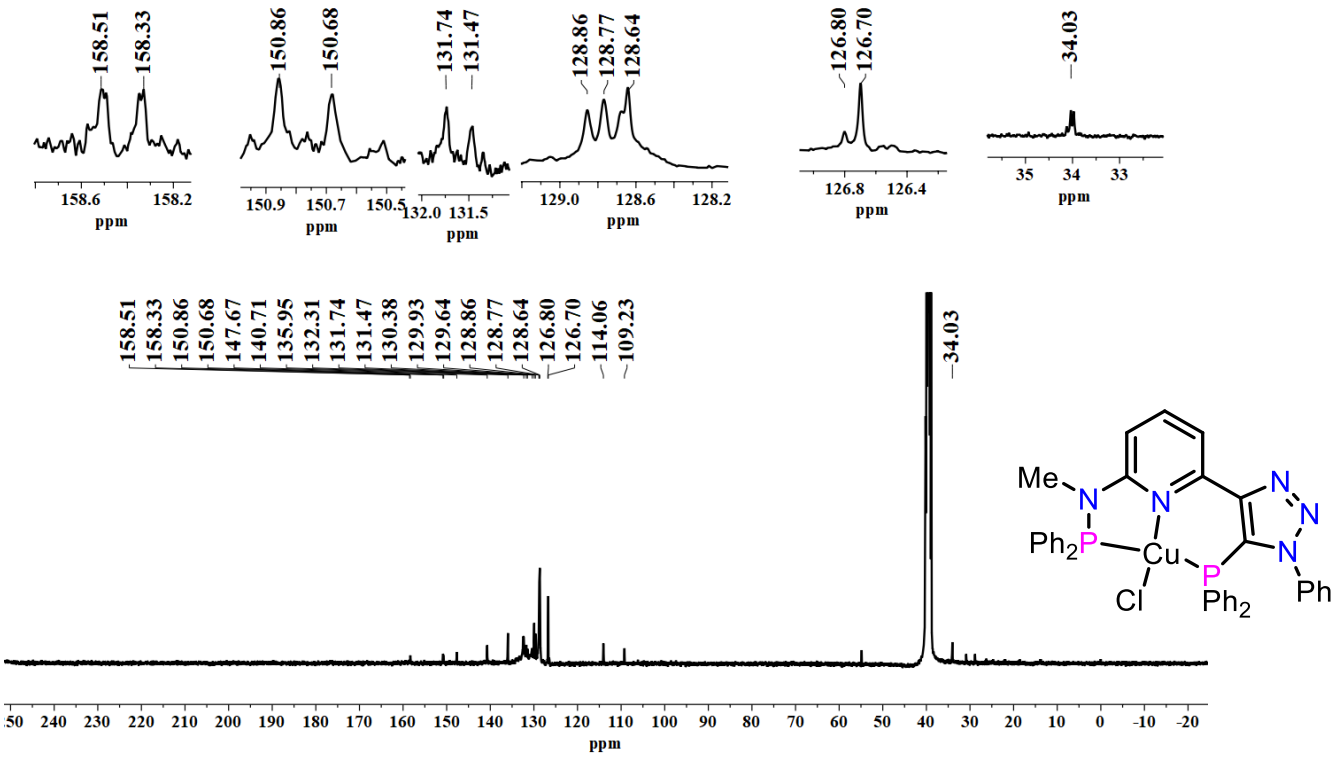


Fig. S16. ^{13}C {^{1}H} NMR spectrum of **1** in DMSO-d_6 (101 MHz).

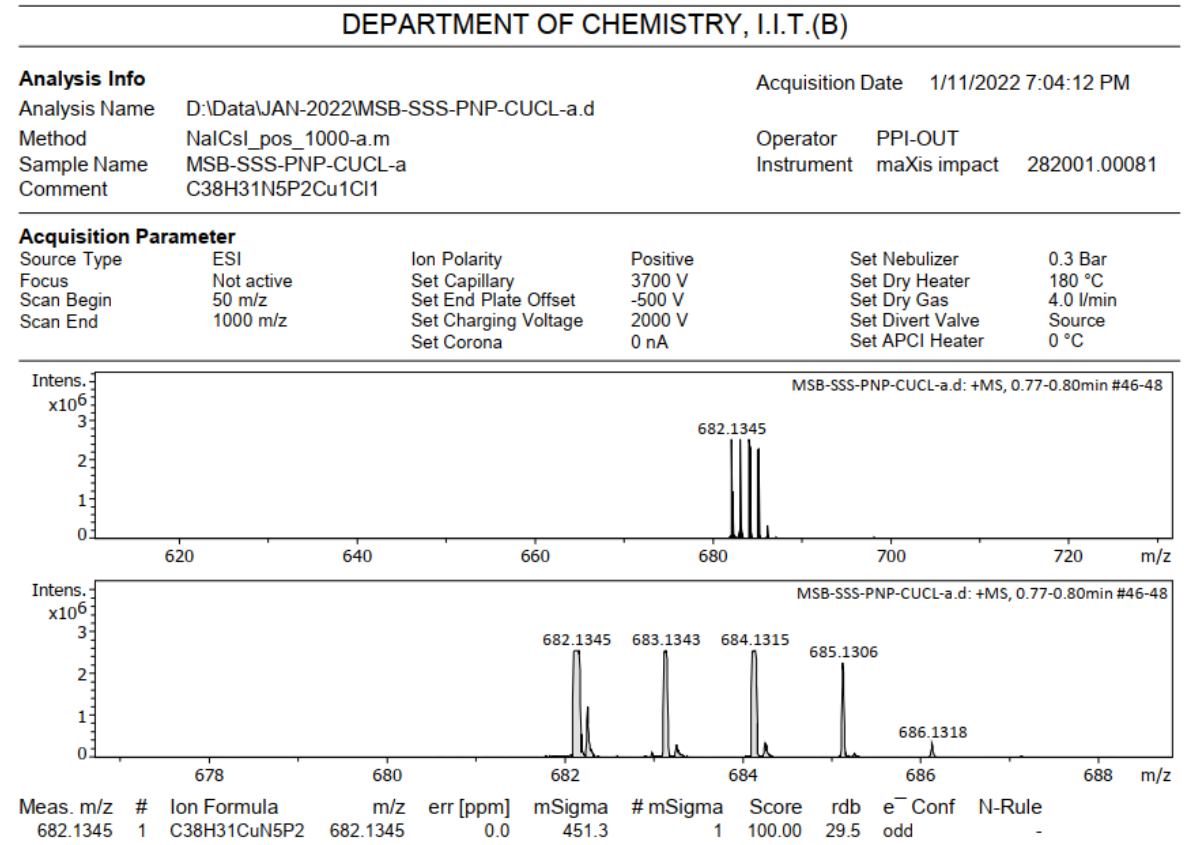


Fig. S17. HRMS spectrum of **1**.

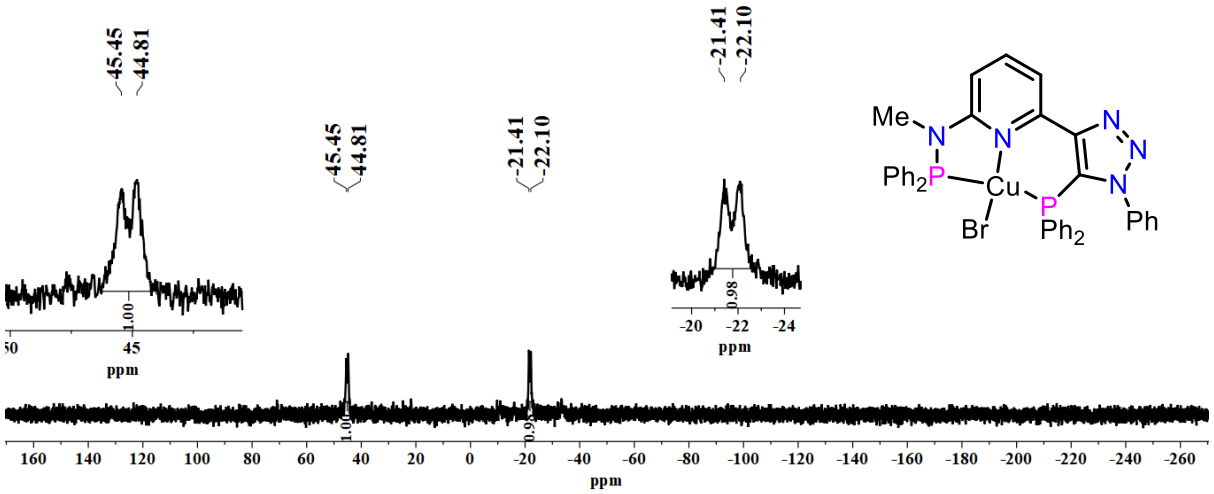


Fig. S18. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ (162 MHz).

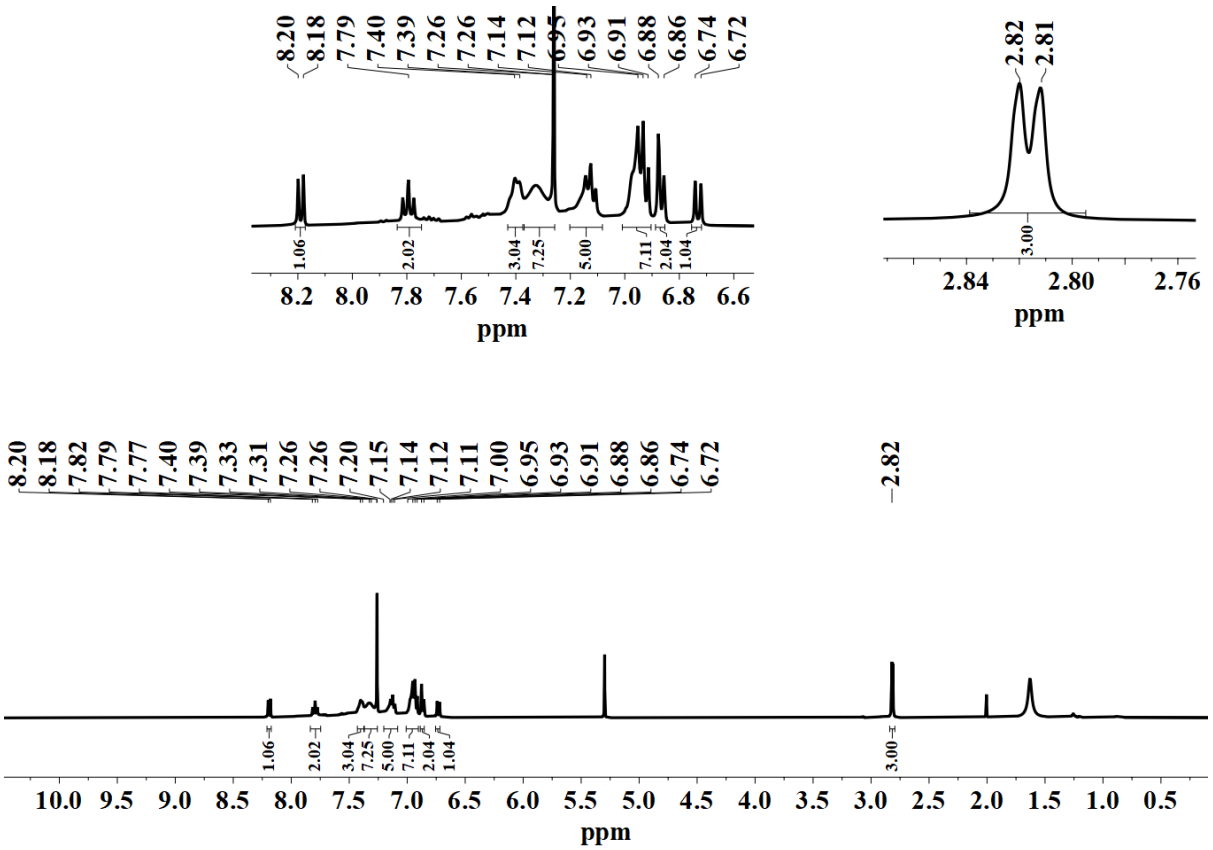


Fig. S19. ^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz).

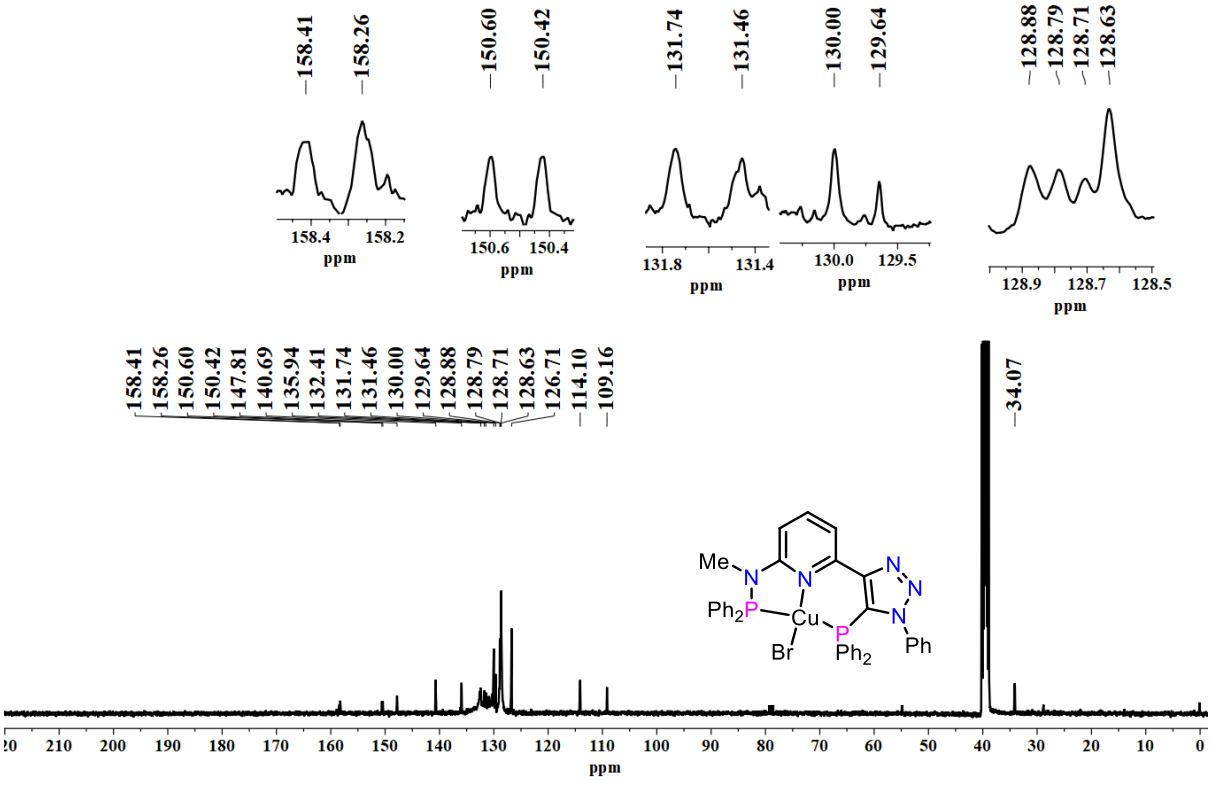


Fig. S20. ^{13}C {^{1}H} NMR spectrum of **2** in DMSO-d_6 (101 MHz).

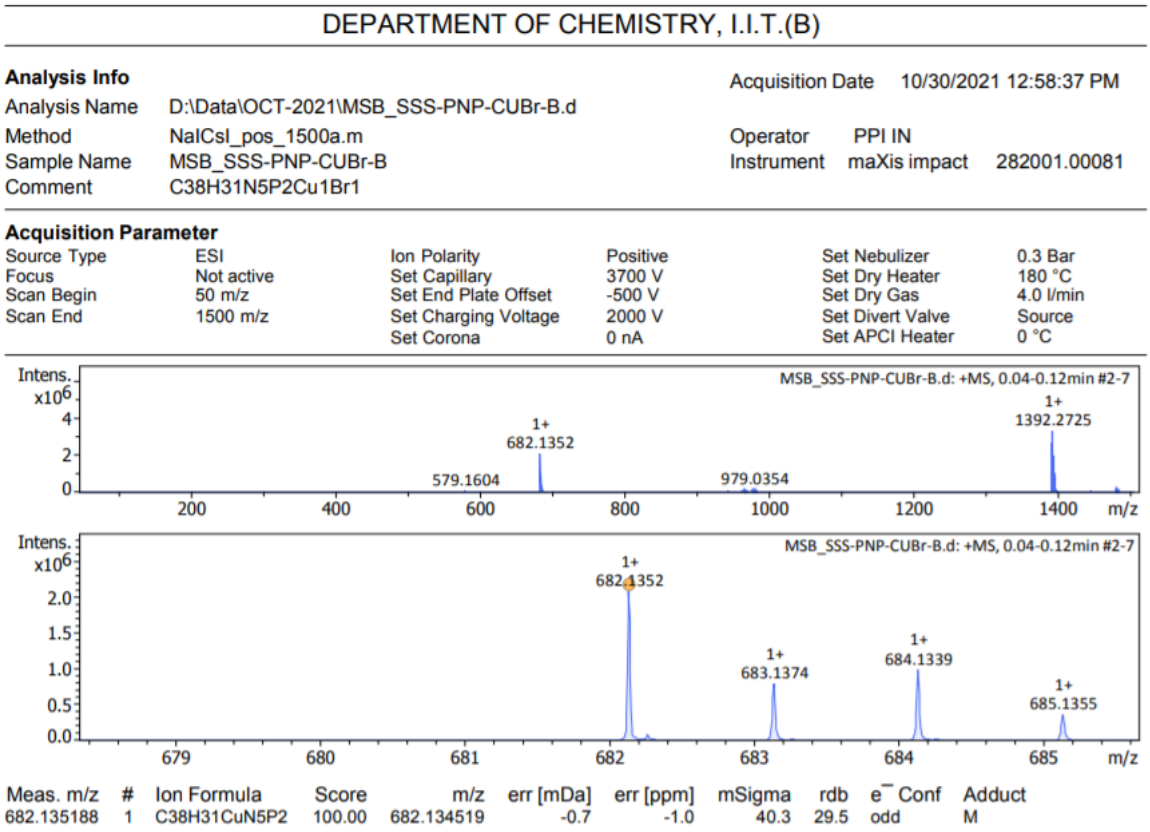


Fig. S21. HRMS spectrum of **2**.

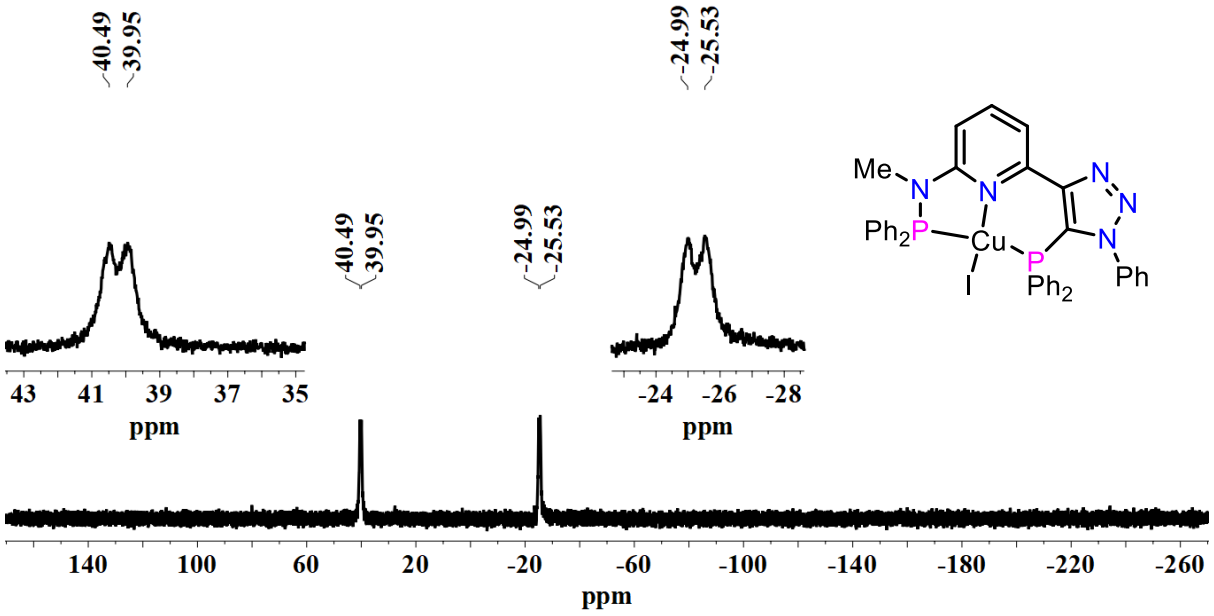


Fig. S22. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in DMSO-d_6 (162 MHz).

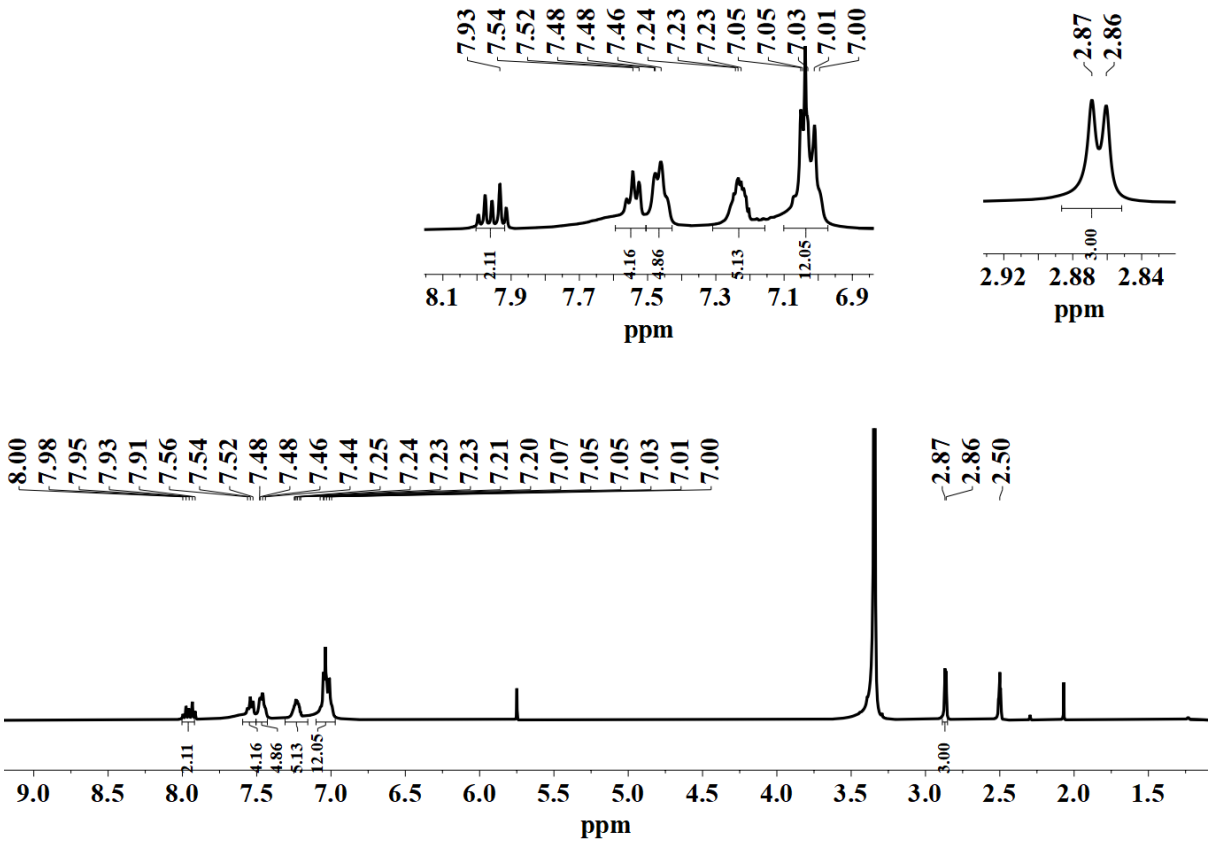


Fig. S23. ^{1}H NMR spectrum of **3** in DMSO-d_6 (400 MHz).

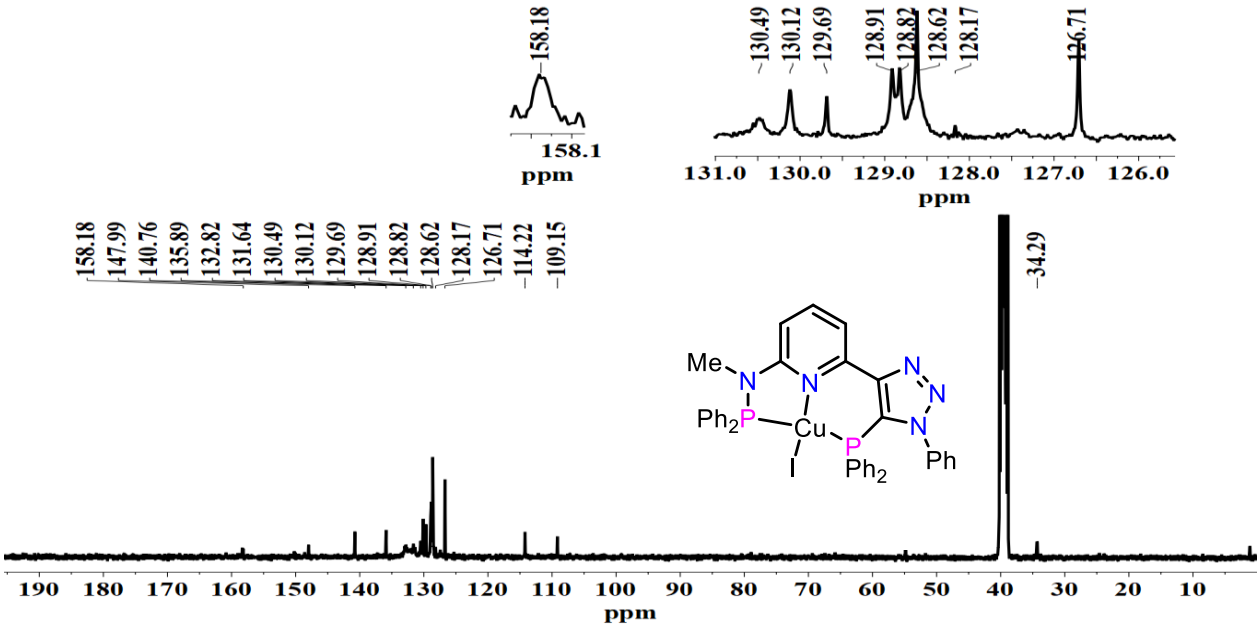


Fig. S24. ^{13}C {^{1}H} NMR spectrum of **3** in DMSO-d_6 (101 MHz).

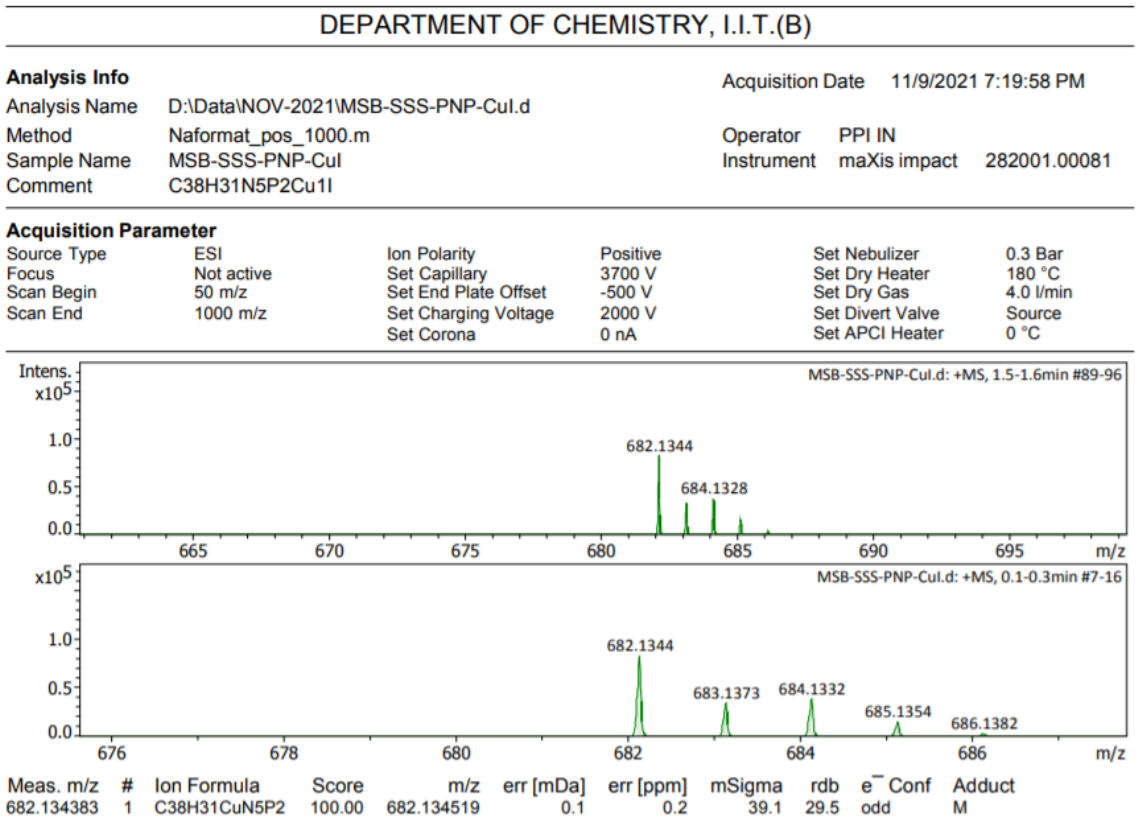
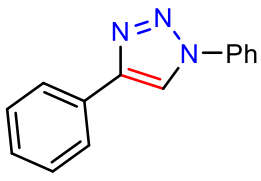


Fig. S25. HRMS spectrum of **3**.

General procedure for CuAAC

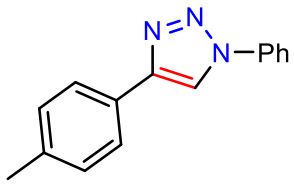
Acetylene (1 eq.) and azide (1 eq) derivatives were taken in a 10 ml catalytic tube: catalyst (0.2 mol%) loaded in CH_2Cl_2 (1 mL) as a solvent. The reaction mixture was stirred at room temperature for 4 h, the corresponding product was isolated through the column chromatography technique.

NMR spectral data of catalytic products

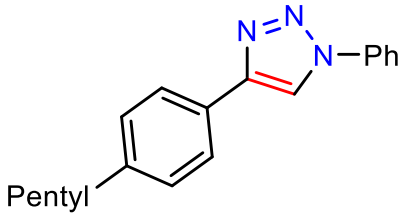


1,4-diphenyl-1H-1,2,3-triazole (**I**).[6] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 97 % (108 mg) yielded a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.92 (d, J = 7.9 Hz, 2H), 7.80 (d, J = 7.9 Hz,

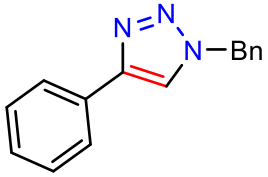
2H), 7.58 – 7.53 (m, 2H), 7.50 – 7.43 (m, 3H), 7.38 (t, J = 7.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 148.57, 137.23, 130.40, 129.93, 129.07, 128.93, 128.58, 126.01, 120.69, 117.73.



1-phenyl-4-(p-tolyl)-1H-1,2,3-triazole (**II**).[7] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 94 % (111 mg) yielded a white solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.89 – 7.71 (m, 4H), 7.65 – 7.40 (m, 4H), 7.31 (d, J = 15.7 Hz, 1H), 2.44 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 148.63, 138.47, 137.27, 129.90, 129.74, 128.84, 127.57, 125.91, 120.66, 117.37, 21.46.

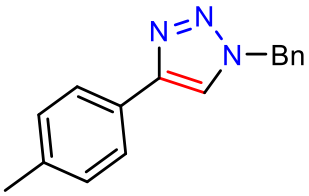


4-(4-pentylphenyl)-1-phenyl-1H-1,2,3-triazole (**III**).[8] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 95 % (138 mg) yielded a white solid .^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.81 (t, J = 9.0 Hz, 4H), 7.55 (t, J = 7.9 Hz, 2H), 7.46 (d, J = 7.3 Hz, 1H), 7.26 (d, J = 3.5 Hz, 2H), 2.65 (t, J = 7.8 Hz, 2H), 1.65 (t, J = 7.7 Hz, 2H), 1.38 – 1.30 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 148.73, 143.57, 132.16, 129.90, 129.10, 128.84, 127.79, 125.92, 120.65, 117.34, 35.92, 31.67, 31.23, 22.69, 14.19.

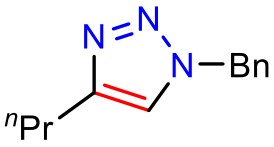


1-hexyl-4-phenyl-1H-1,2,3-triazole (**IV**).[9] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 96 % (113 mg) yielded a white solid

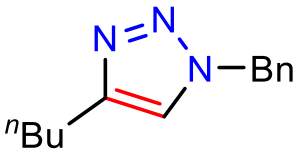
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.78 (s, 1H), 7.65 (s, 1H), 7.39 (d, J = 16.6 Hz, 5H), 7.34 – 7.28 (m, 3H), 5.57 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.37, 134.82, 130.67, 129.29, 128.93, 128.30, 128.19, 125.83, 119.61, 54.36.



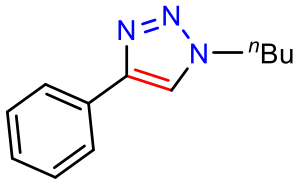
1-hexyl-4-(p-tolyl)-1H-1,2,3-triazole (**V**).[6] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 94 % (117 mg) yielded a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.68 (s, 1H), 7.62 (s, 1H), 7.41 – 7.36 (m, 3H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.57 (s, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.46, 138.15, 134.88, 129.61, 129.28, 128.89, 128.20, 127.85, 125.74, 119.26, 54.35, 21.41.



1-hexyl-4-propyl-1H-1,2,3-triazole (**VI**).[10] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 75 % (75 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.26 (s, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.16 (s, 2H), 5.40 (s, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.59 (h, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.55, 134.99, 128.92, 128.45, 127.82, 120.62, 53.80, 27.61, 22.56, 13.68.

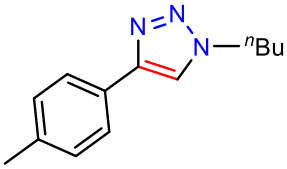


4-butyl-1-hexyl-1H-1,2,3-triazole (**VII**).[6] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 77 % (83 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.33 (s, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.18 (s, 1H), 5.47 (s, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.33 (dt, *J* = 14.7, 7.3 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.98, 135.09, 129.09, 128.63, 128.00, 120.56, 54.00, 31.57, 25.47, 22.38, 13.87.

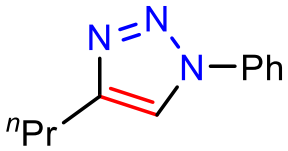


1-butyl-4-phenyl-1H-1,2,3-triazole (**VIII**).[11] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 85 % (85 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.80 (s, 1H), 7.74 (s, 1H), 7.44

– 7.35 (m, 2H), 7.31 (d, J = 7.5 Hz, 1H), 4.36 (t, J = 7.2 Hz, 2H), 1.94 – 1.83 (m, 2H), 1.41 – 1.29 (m, 2H), 1.01 – 0.88 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.71, 130.80, 128.86, 128.09, 125.70, 119.54, 50.16, 32.34, 19.75, 13.51.

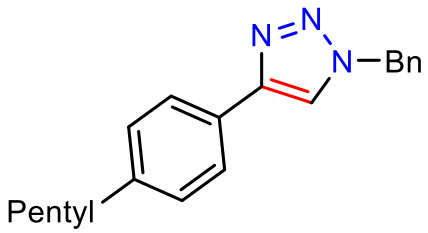


1-butyl-4-(p-tolyl)-1H-1,2,3-triazole (**IX**).[12] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 81 % (87 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.70 (s, 2H), 7.22 (d, J = 8.2 Hz, 2H), 4.38 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.96 – 1.88 (m, 2H), 1.39 (q, J = 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.91, 138.01, 129.61, 128.01, 125.70, 119.18, 50.22, 32.44, 21.40, 19.85, 13.60.

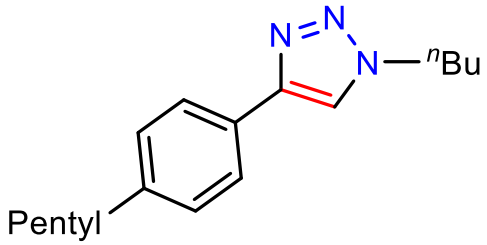


1-phenyl-4-propyl-1H-1,2,3-triazole (**X**).[13] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 74 % (69 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 7.8 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 2.53 (t, J = 7.6 Hz, 2H), 1.53 (h, J = 7.4 Hz, 2H), 0.77 (t, J = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.37, 136.74, 129.22, 127.94, 119.79, 118.69, 27.16, 22.19, 13.37.

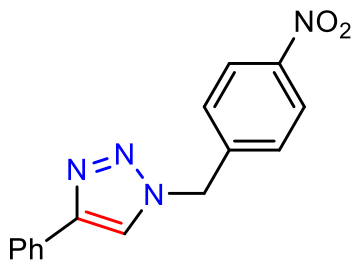
4-butyl-1-phenyl-1H-1,2,3-triazole (**XI**).[14] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 70% (71 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.54 – 7.46 (m, 2H), 7.26 (t, J = 8.8 Hz, 2H), 7.16 (q, J = 8.5 Hz, 1H), 2.56 (t, J = 7.5 Hz, 2H), 1.55 – 1.44 (m, 2H), 1.19 (h, J = 7.3 Hz, 2H), 0.76 – 0.68 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.70, 136.87, 129.33, 128.03, 119.89, 118.68, 31.14, 24.97, 21.93, 13.51.



1-hexyl-4-(4-pentylphenyl)-1H-1,2,3-triazole (**XII**).[9] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 85 % (122 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.69 (s, 1H), 7.62 (s, 1H), 7.38 (d, *J* = 6.9 Hz, 3H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.56 (s, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.65 – 1.59 (m, 2H), 1.35 – 1.28 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.49, 143.25, 134.91, 129.26, 128.98, 128.87, 128.16, 128.04, 125.74, 119.29, 54.32, 35.83, 31.58, 31.20, 22.66, 14.16.

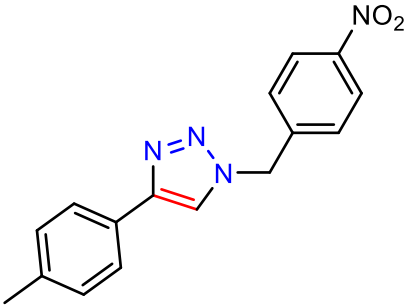


1-butyl-4-(4-pentylphenyl)-1H-1,2,3-triazole (**XIII**). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 82 % (105 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.74 (s, 1H), 7.71 (s, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 4.40 (t, *J* = 7.2 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.98 – 1.90 (m, 2H), 1.67 – 1.62 (m, 2H), 1.44 – 1.39 (m, 2H), 1.34 (d, *J* = 6.9 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.98, 143.15, 129.00, 128.23, 125.74, 119.18, 50.24, 35.85, 32.46, 31.61, 31.23, 22.68, 19.86, 14.17, 13.61.

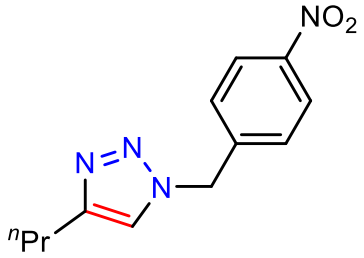


1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (**XIV**).[15] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 94 % (150 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 7.4 Hz, 2H), 7.76 (s, 1H), 7.47 –

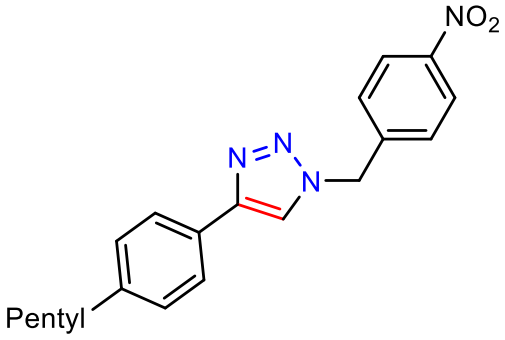
7.39 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 5.69 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.84, 148.21, 141.88, 130.21, 129.04, 128.68, 128.63, 125.87, 124.47, 119.83, 53.31.



1-(4-nitrobenzyl)-4-(p-tolyl)-1H-1,2,3-triazole (**XV**).[16] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 93 % (137 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.8 Hz, 2H), 7.74 – 7.66 (m, 3H), 7.44 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 5.69 (s, 2H), 2.37 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.97, 148.23, 141.94, 138.56, 129.73, 128.68, 127.40, 125.79, 124.49, 119.44, 53.30, 21.44.

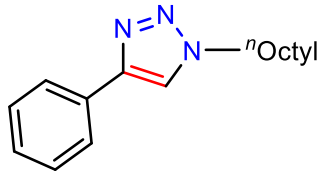


1-(4-nitrobenzyl)-4-propyl-1H-1,2,3-triazole (**XVI**). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 86 % (106 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 6.7 Hz, 2H), 7.28 (s, 2H), 5.52 (s, 2H), 2.55 (t, J = 7.6 Hz, 2H), 1.54 (h, J = 7.3 Hz, 2H), 0.80 (t, J = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.94, 147.67, 142.30, 128.38, 124.00, 121.13, 52.72, 27.48, 22.44, 13.61.

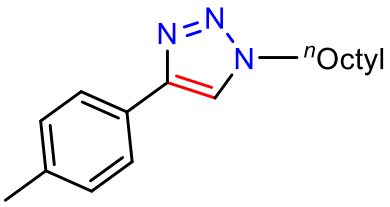


1-(4-nitrobenzyl)-4-(4-pentylphenyl)-1H-1,2,3-triazole (**XVII**). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 81 % (116 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.18 (m, 2H), 7.75 – 7.66 (m, 3H), 7.46 – 7.38 (m, 2H), 7.23 (dd, J = 8.3, 2.4 Hz, 2H), 5.68 (d, J = 3.9 Hz, 2H), 2.62 (t, J = 8.8 Hz, 2H),

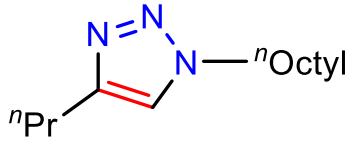
1.62 (t, J = 6.7 Hz, 2H), 1.36 – 1.25 (m, 4H), 0.94 – 0.83 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.98, 148.16, 143.64, 141.97, 129.09, 128.64, 127.57, 125.78, 124.42, 119.48, 53.27, 35.83, 31.57, 31.18, 22.65, 14.15.



1-octyl-4-phenyl-1H-1,2,3-triazole (**XVIII**).[17] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 79 % (102 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.7 Hz, 2H), 7.74 (s, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 4.39 (t, J = 7.3 Hz, 2H), 1.93 (q, J = 7.3 Hz, 2H), 1.38 – 1.25 (m, 10H), 0.90 – 0.84 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.89, 130.86, 128.95, 128.20, 125.82, 119.52, 50.58, 31.84, 30.49, 29.18, 29.11, 26.63, 22.73, 14.19.

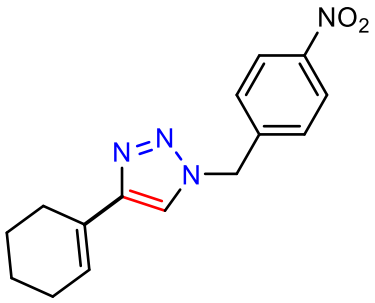


1-octyl-4-(p-tolyl)-1H-1,2,3-triazole (**XIX**).[18] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 72 % (98 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 3H), 7.30 – 7.23 (m, 2H), 4.40 (t, J = 7.3 Hz, 2H), 2.40 (s, 3H), 2.01 – 1.90 (m, 2H), 1.38 – 1.26 (m, 10H), 0.89 (t, J = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.94, 138.02, 129.62, 128.04, 125.72, 119.18, 50.55, 31.84, 30.49, 29.18, 29.11, 26.64, 22.72, 21.41, 14.19.

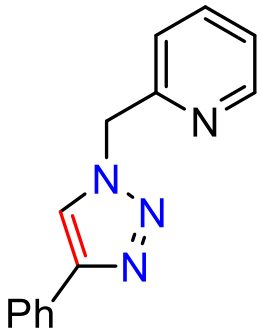


1-octyl-4-propyl-1H-1,2,3-triazole (**XX**).[19] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 74 % (100 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.70 (s, 1H), 7.23 (d, J = 7.9 Hz, 2H), 4.38 (t, J = 7.3 Hz, 2H), 2.62 (t, J = 7.7 Hz, 2H), 1.93 (d, J = 7.8 Hz, 2H), 1.62 (q, J = 7.5 Hz, 4H), 1.37 – 1.29 (m, 12H), 0.88 (d, J = 7.9 Hz, 6H).

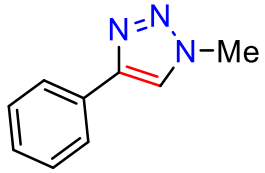
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.16, 139.67, 129.01, 128.23, 125.74, 119.21, 50.56, 35.85, 31.85, 31.61, 31.23, 30.50, 29.84, 29.19, 26.65, 22.74, 22.68, 14.20, 14.18.



4-(cyclohex-1-en-1-yl)-1-(4-nitrobenzyl)-1H-1,2,3-triazole (**XXI**).[15] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 85 % (121 mg) yielded a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 11.3 Hz, 3H), 6.53 (s, 1H), 5.63 (s, 2H), 2.33 (s, 2H), 2.19 (s, 2H), 1.76 – 1.63 (m, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 150.56, 148.13, 142.17, 128.55, 127.05, 125.94, 124.38, 118.61, 53.12, 26.45, 25.39, 22.50, 22.24.



2-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)pyridine (**XXIV**).[20] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 79 % (92 mg) yielded a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (dt, *J* = 4.9, 1.3 Hz, 1H), 7.96 (s, 1H), 7.85 (d, *J* = 7.0 Hz, 2H), 7.71 (t, *J* = 8.6 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.23 (m, 2H), 5.72 (s, 2H).$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ δ 154.65, 149.91, 148.36, 137.50, 130.66, 128.92, 128.29, 125.85, 123.56, 122.57, 120.30, 55.85.



1-methyl-4-phenyl-1H-1,2,3-triazole (**XXV**).[21] Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 85 % (66 mg) yielded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.73 (s, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 4.12 (s, 3H).$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.16, 130.72, 128.95, 128.25, 125.83, 120.69, 36.85.

NMR spectra of catalytic products

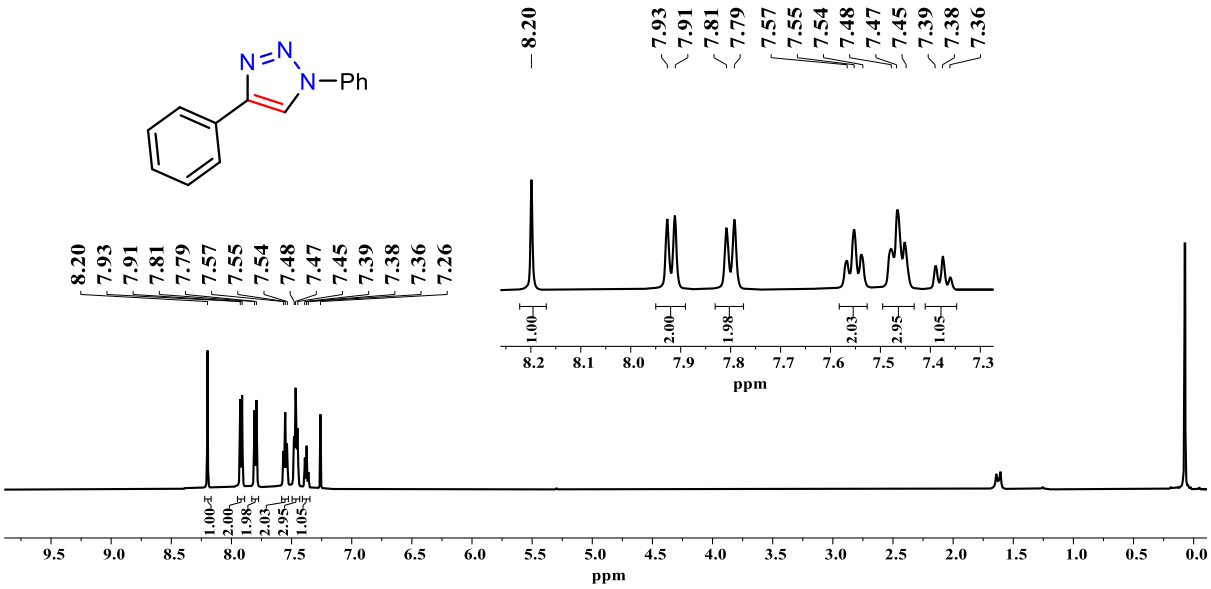


Fig. S26. ^{1}H NMR spectrum of **I** in $CDCl_3$ (500 MHz)

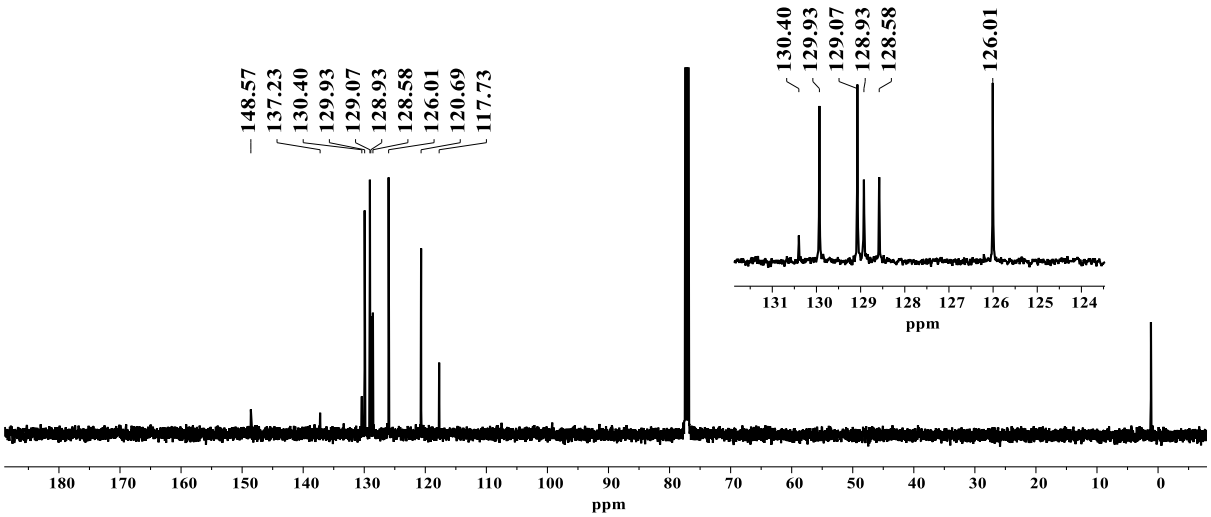


Fig. S27. $^{13}C\{^{1}H\}$ NMR spectrum of **I** in $CDCl_3$ (126 MHz)

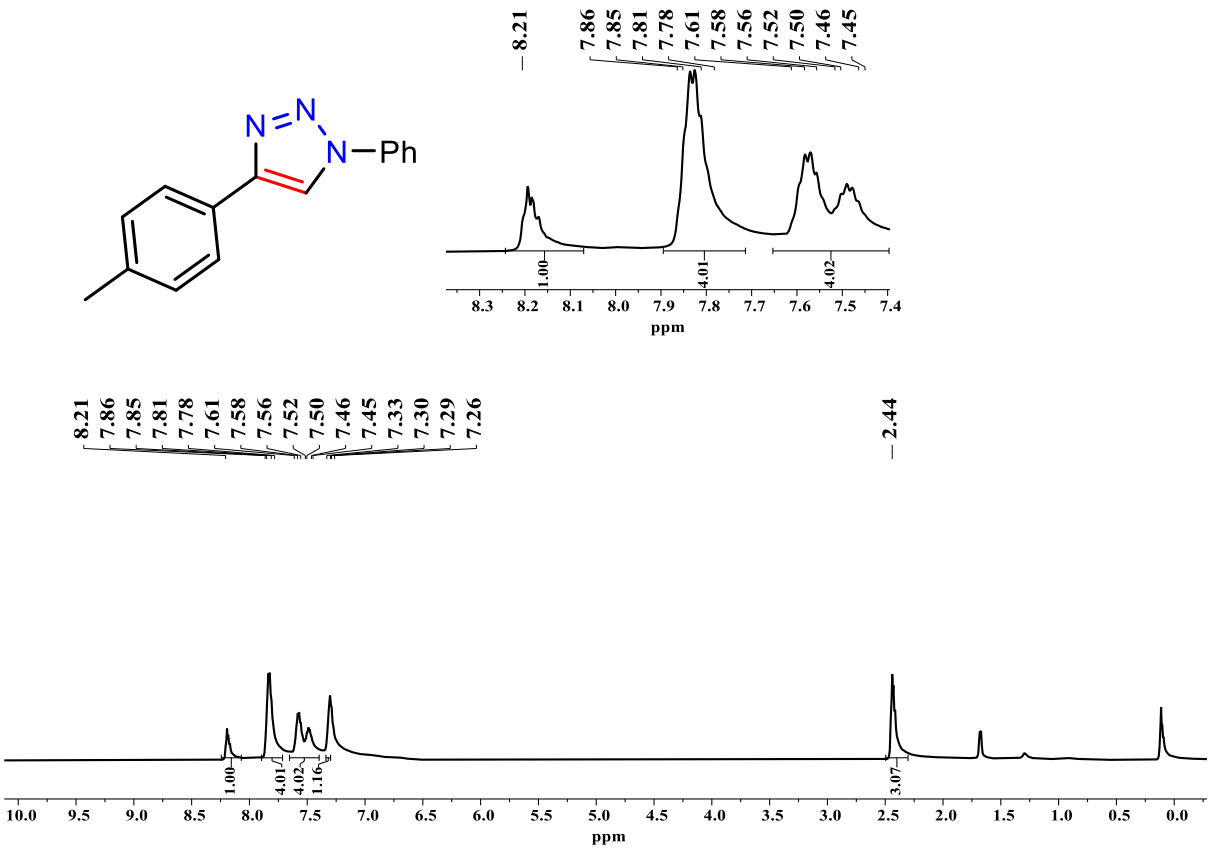


Fig. S28. ^{1}H NMR spectrum of **II** in $CDCl_3$ (500 MHz)

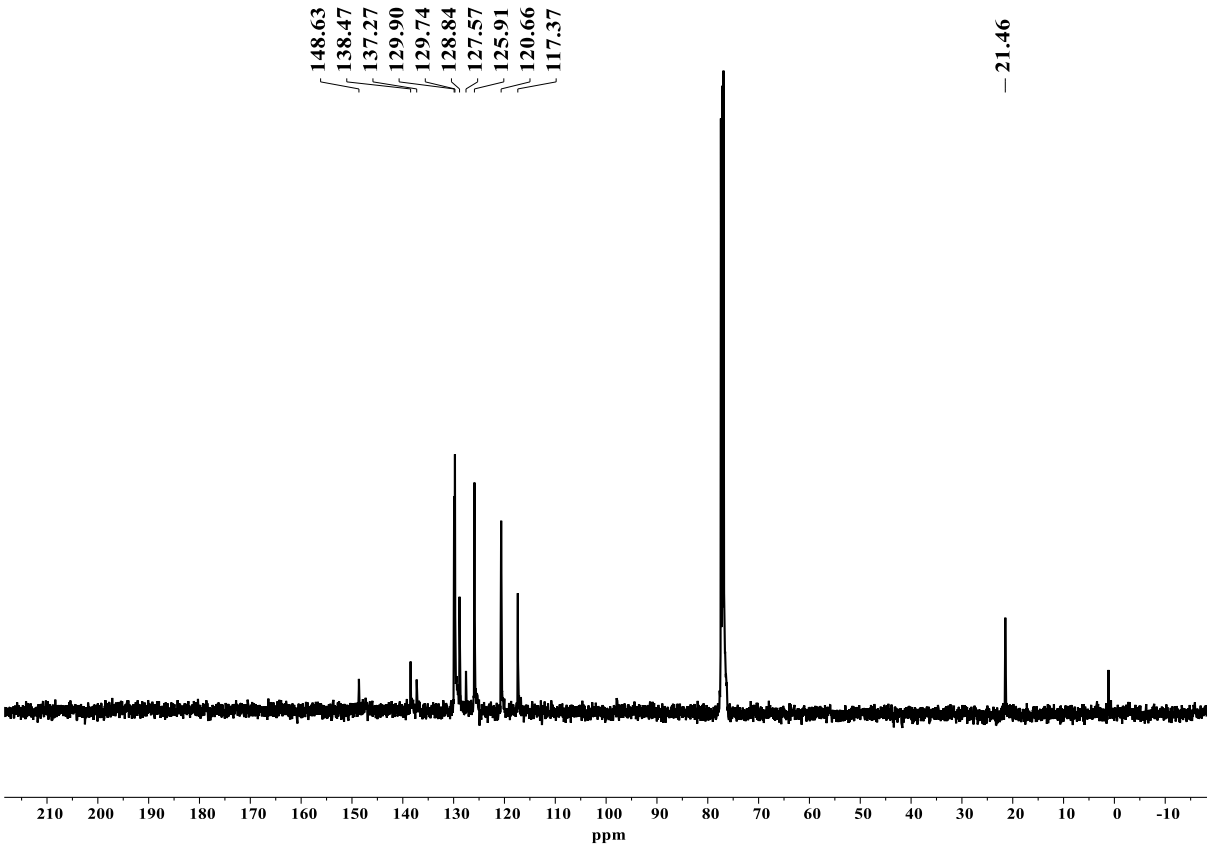


Fig. S29. $^{13}C\{^{1}H\}$ NMR spectrum of **II** in $CDCl_3$ (126 MHz)

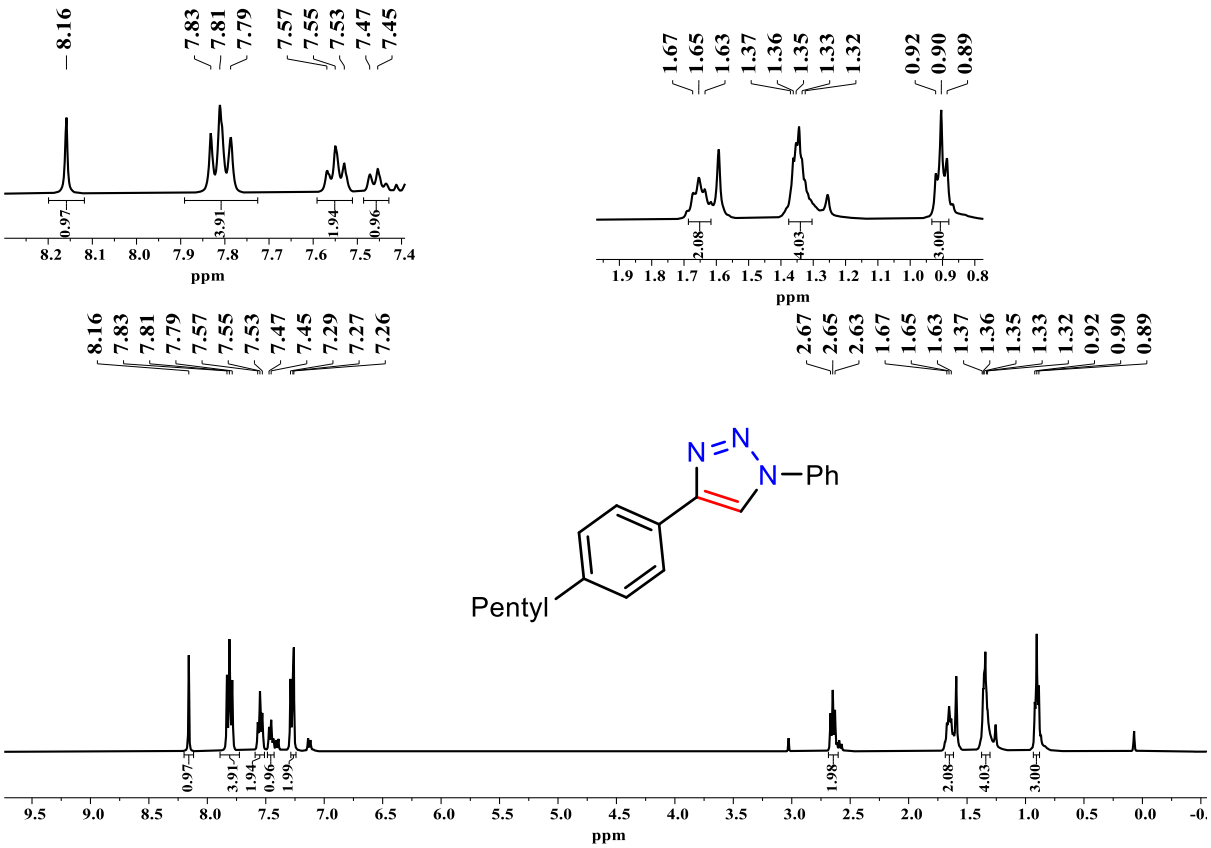


Fig. S30. ^{1}H NMR spectrum of **III** in $CDCl_3$ (400 MHz)

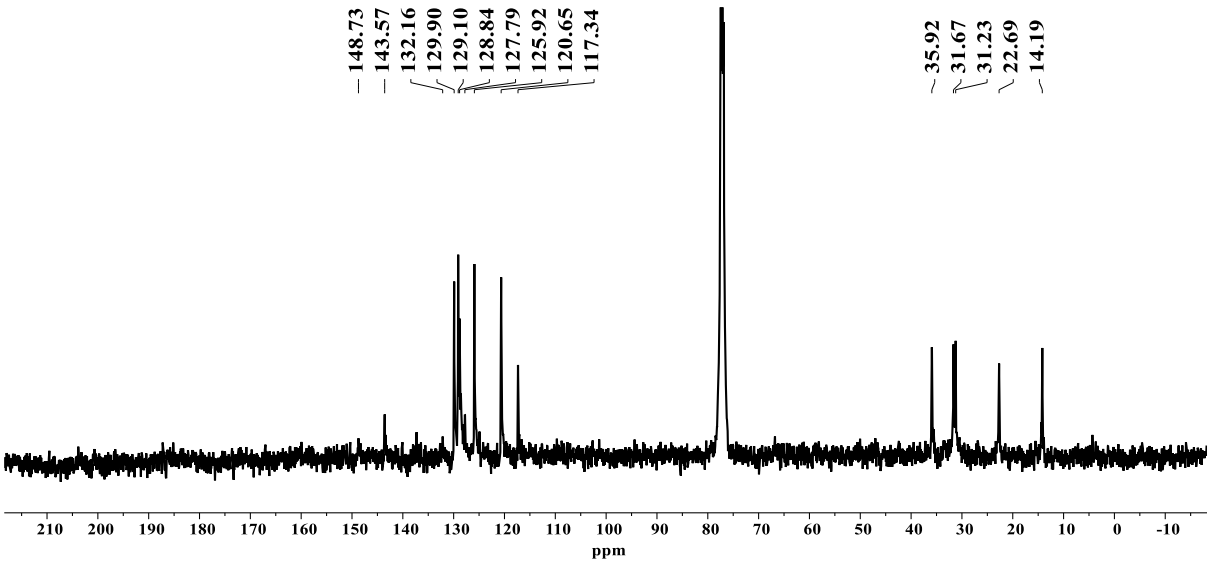


Fig. S31. $^{13}C\{^{1}H\}$ NMR spectrum of **III** in $CDCl_3$ (126 MHz)

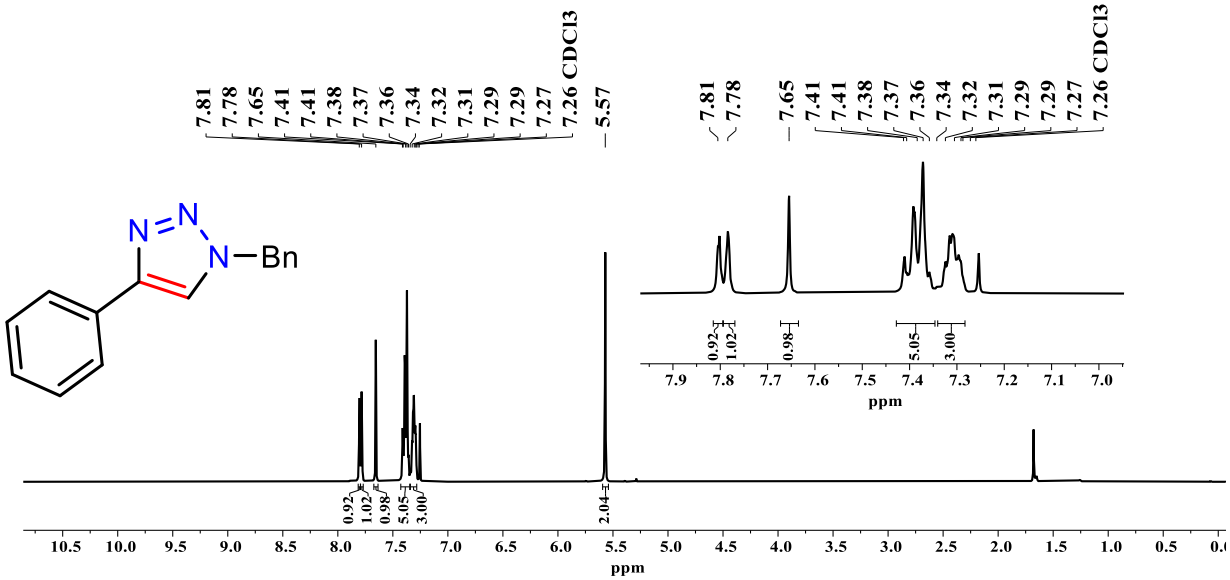


Fig. S32. ^{1}H NMR spectrum of **IV** in $CDCl_3$ (400 MHz)

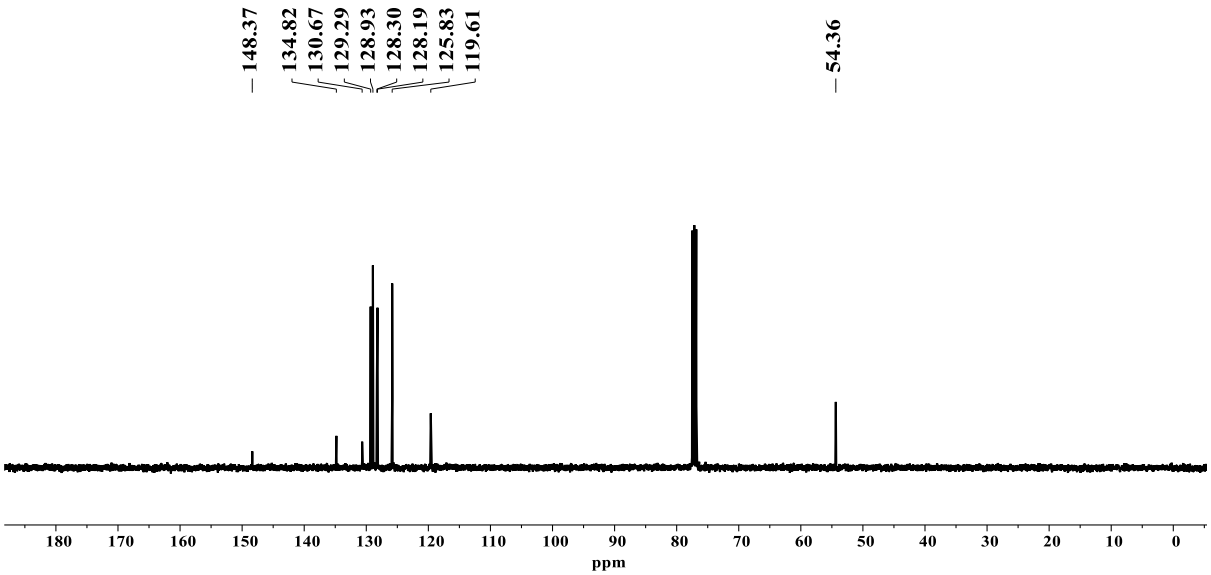


Fig. S33. $^{13}C\{^{1}H\}$ NMR spectrum of **IV** in $CDCl_3$ (101 MHz)

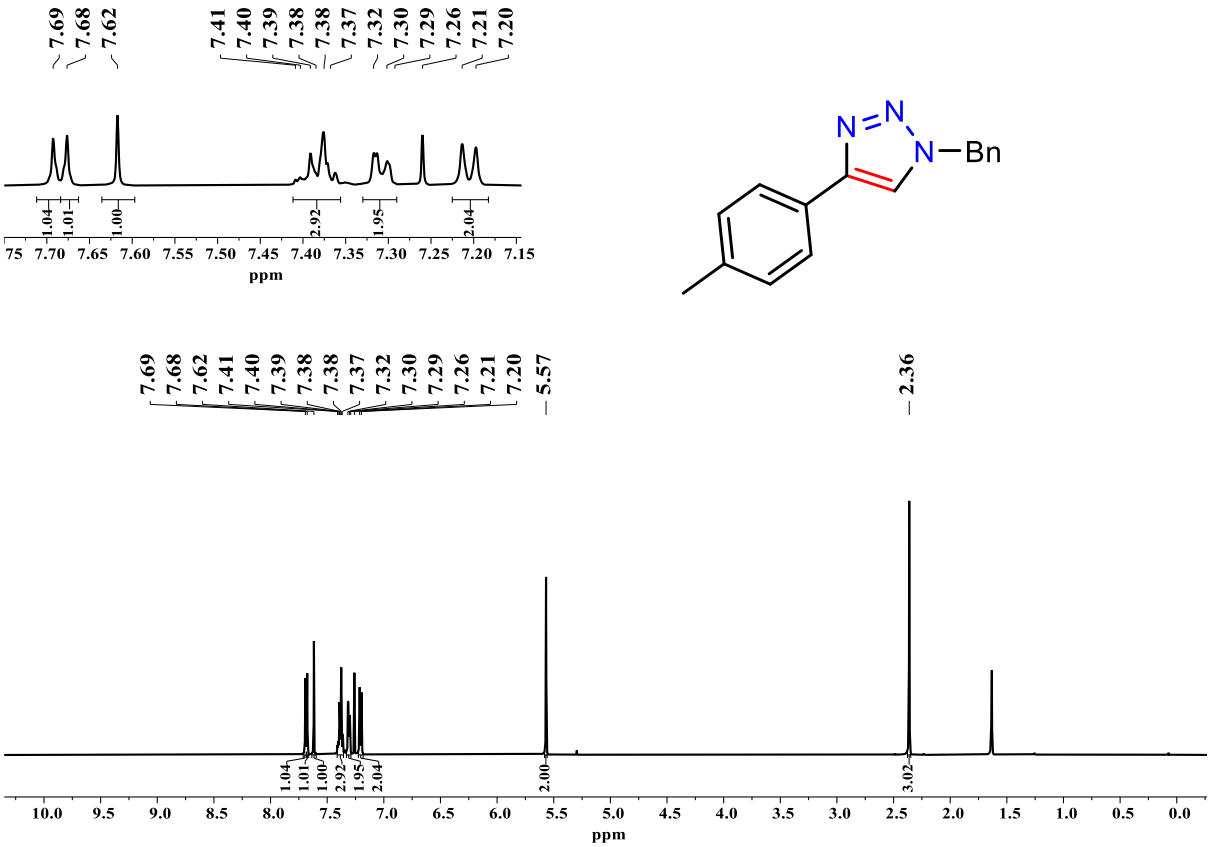


Fig. S34. ^{1}H NMR spectrum of **V** in $CDCl_3$ (500 MHz)

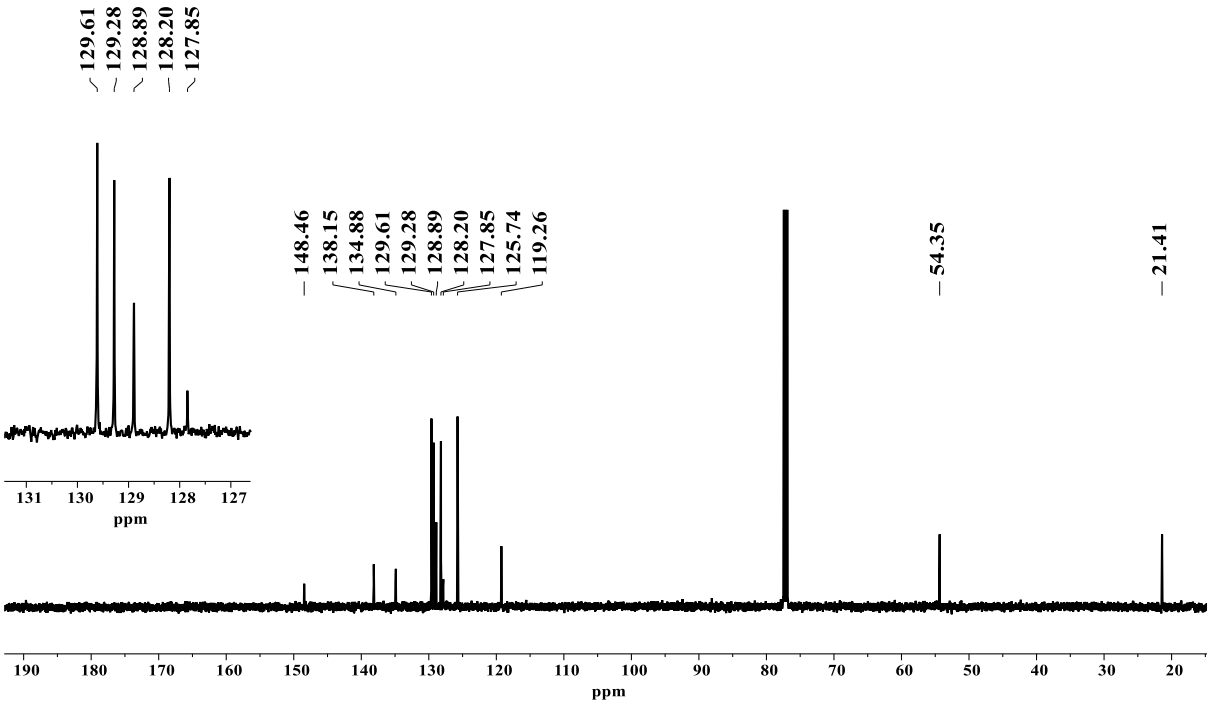


Fig. S35. ^{13}C{^{1}H} NMR spectrum of **V** in $CDCl_3$ (126 MHz)

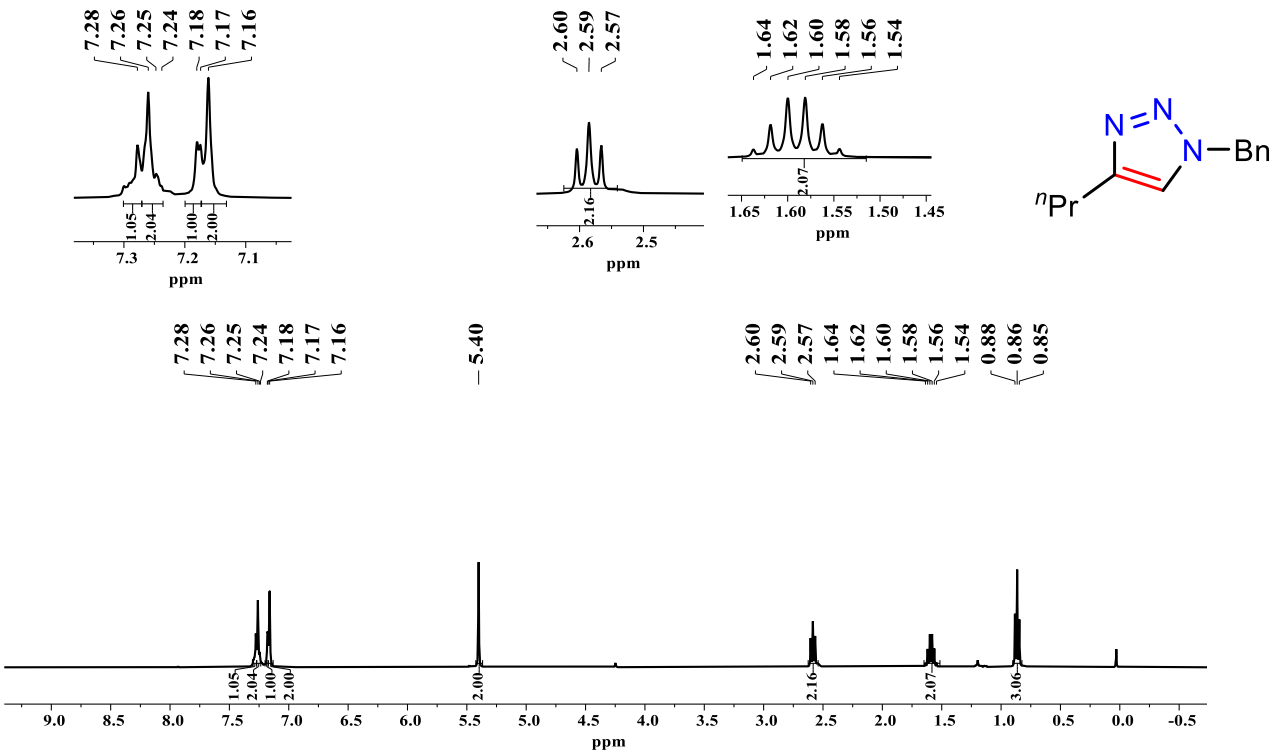


Fig. S36. ^{1}H NMR spectrum of **VI** in $CDCl_3$ (400 MHz)

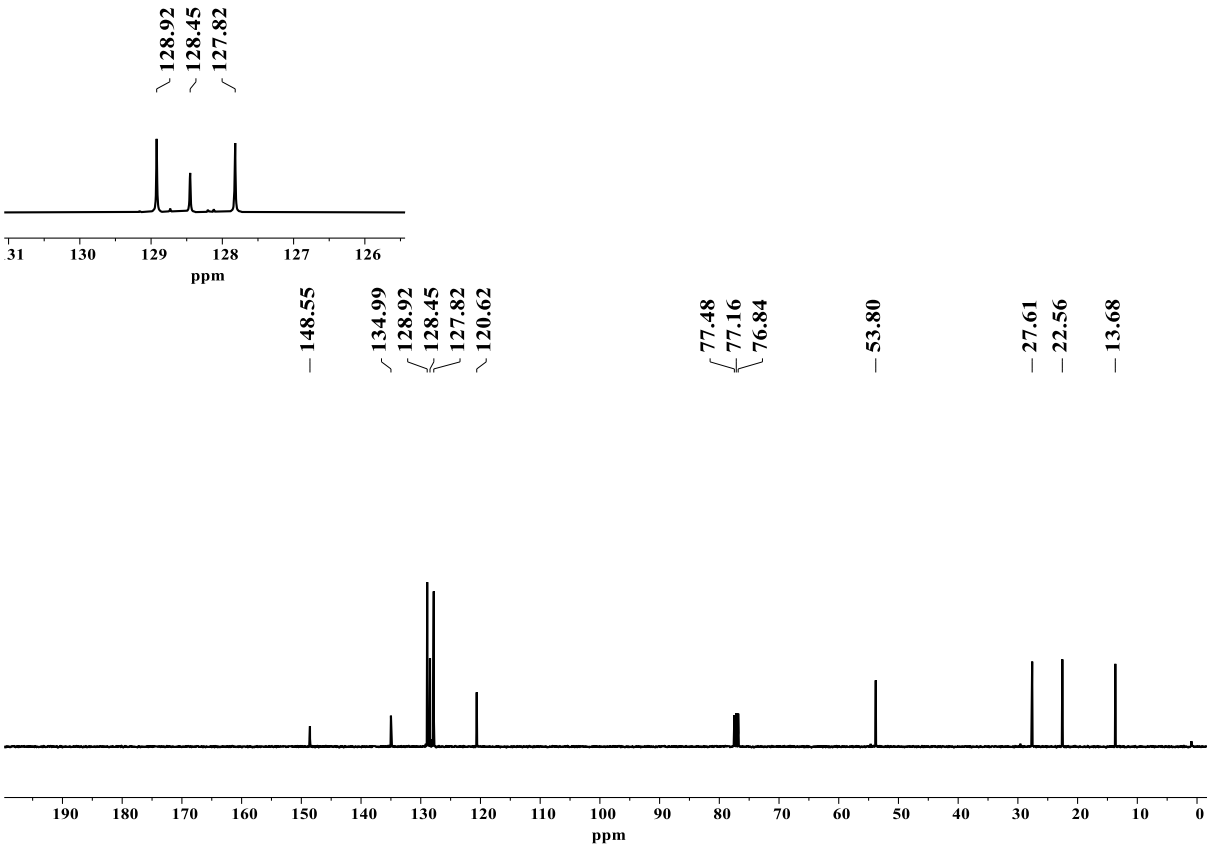


Fig. S37. $^{13}C\{^{1}H\}$ NMR spectrum of **VI** in $CDCl_3$ (101 MHz)

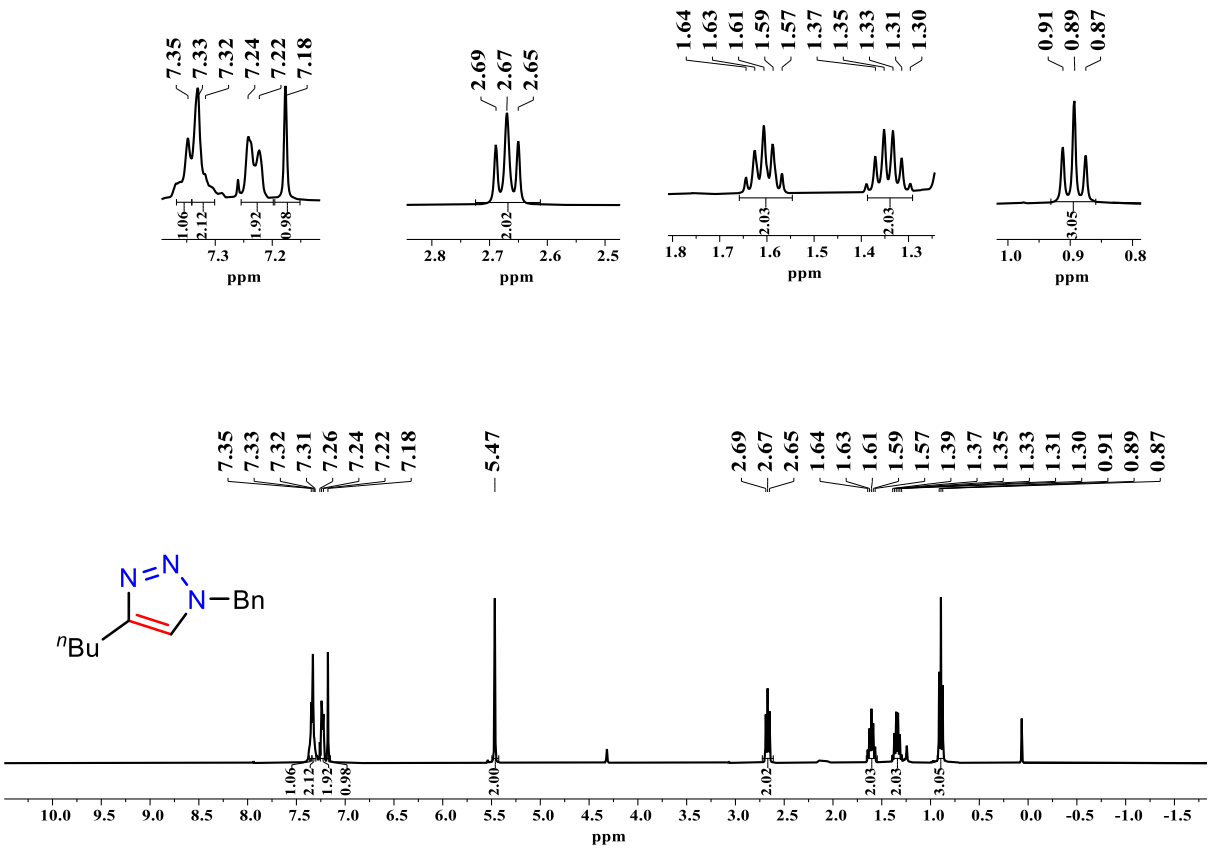


Fig. S38. ^{1}H NMR spectrum of **VII** in $CDCl_3$ (400 MHz)

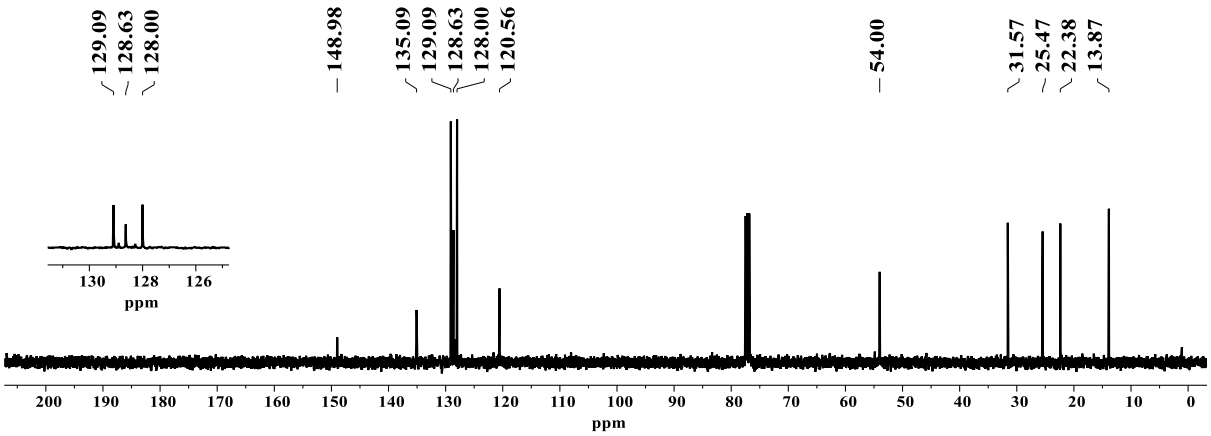


Fig. S39. $^{13}C\{^{1}H\}$ NMR spectrum of **VII** in $CDCl_3$ (101 MHz)

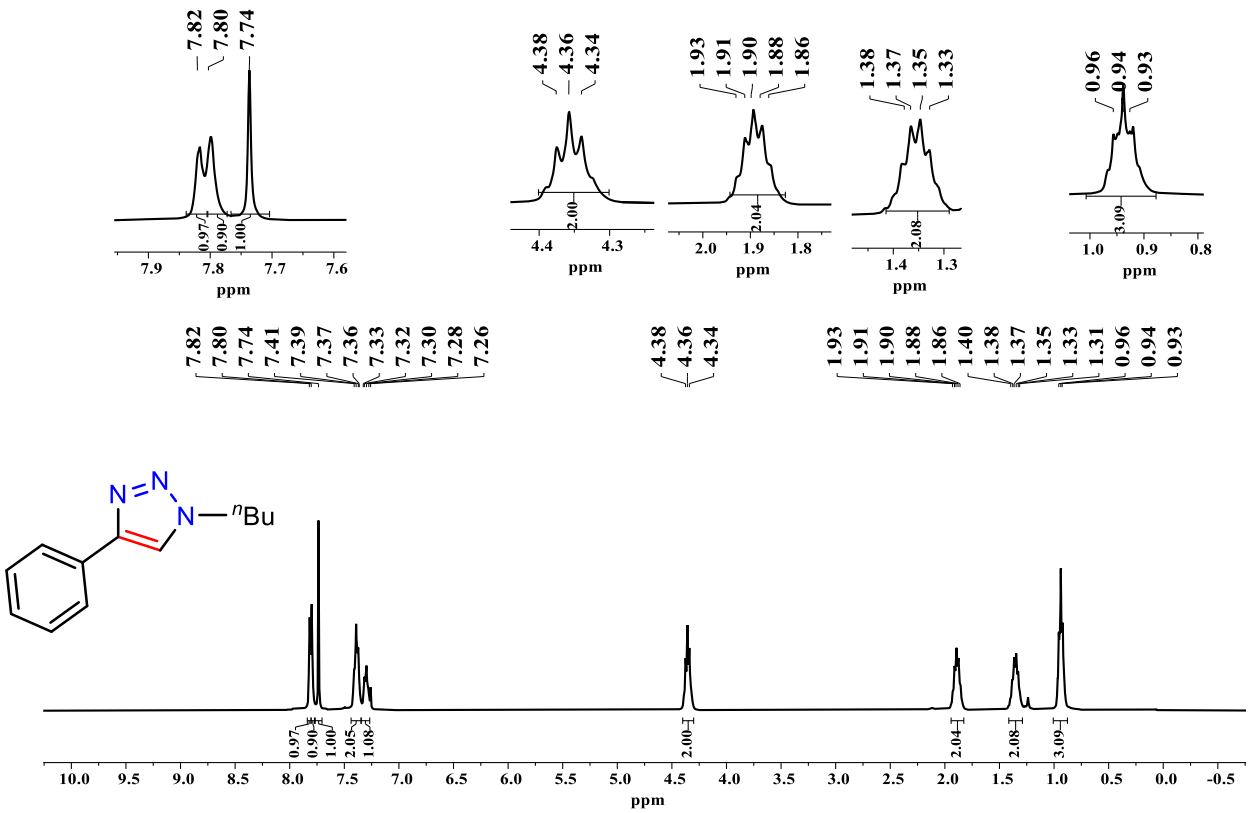


Fig. S40. ^{1}H NMR spectrum of **VIII** in $CDCl_3$ (400 MHz)

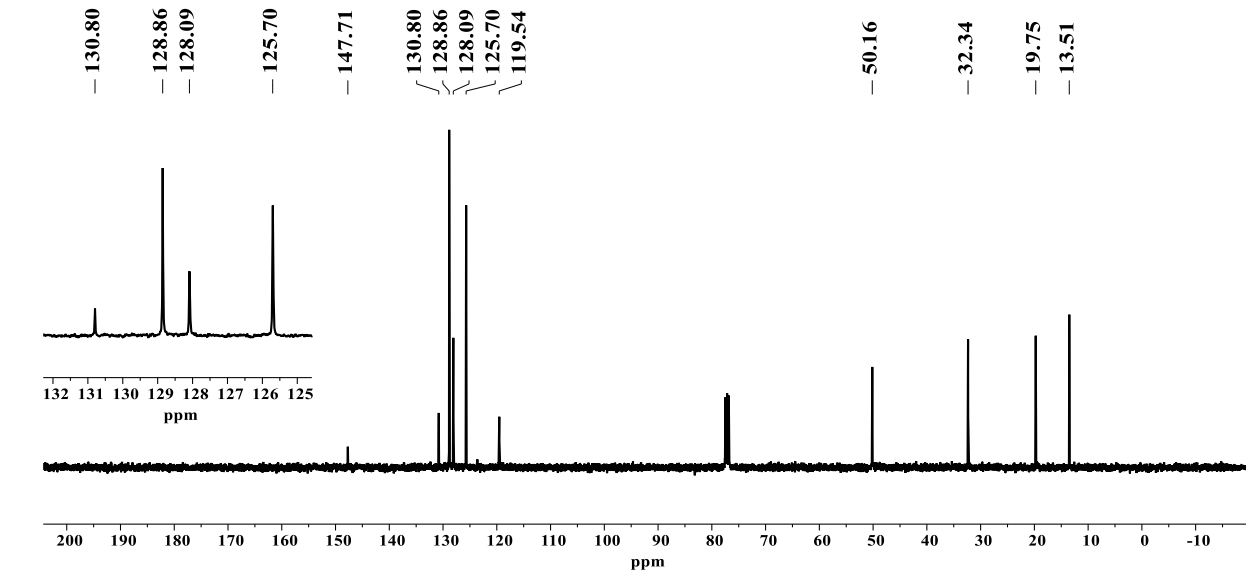


Fig. S41. $^{13}C\{^{1}H\}$ NMR spectrum of **VIII** in $CDCl_3$ (101 MHz)

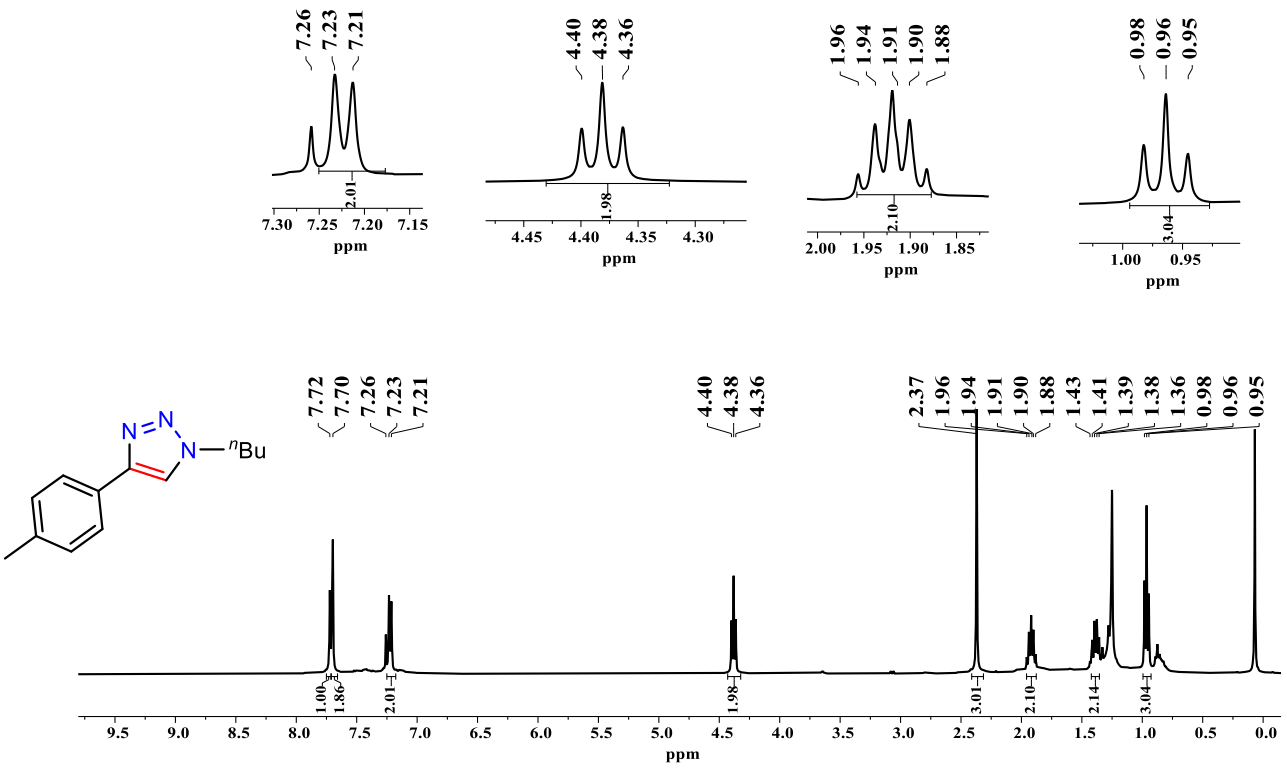


Fig. S42. ^{1}H NMR spectrum of **IX** in $CDCl_3$ (400 MHz)

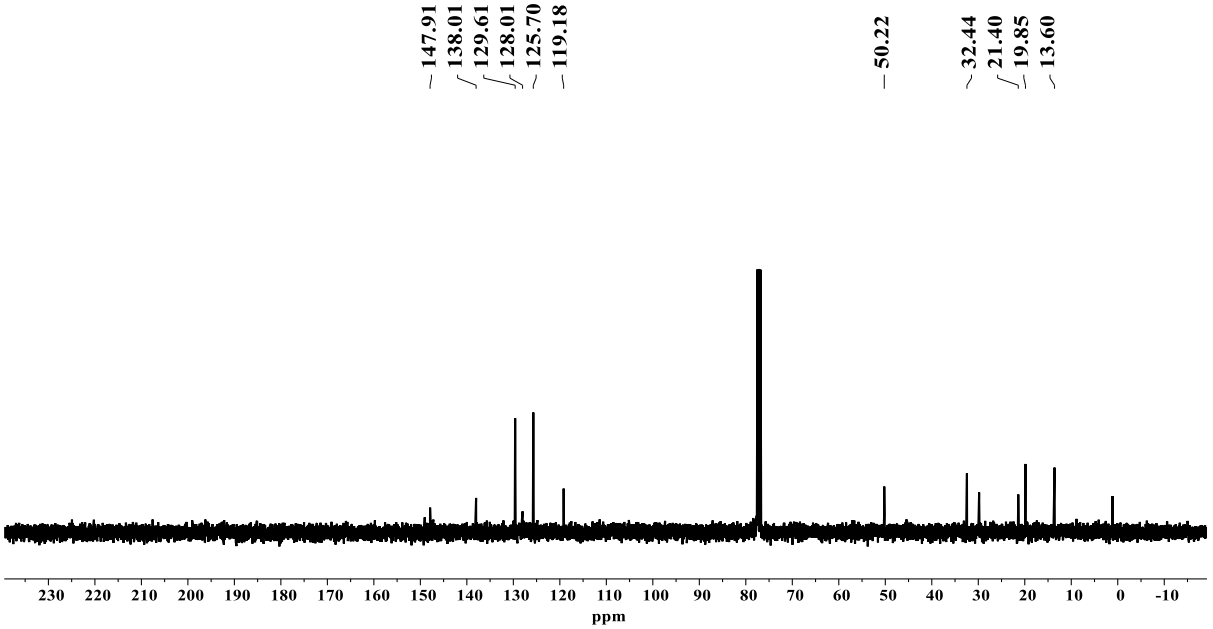


Fig. S43. ^{13}C{^{1}H} NMR spectrum of **IX** in $CDCl_3$ (101 MHz)

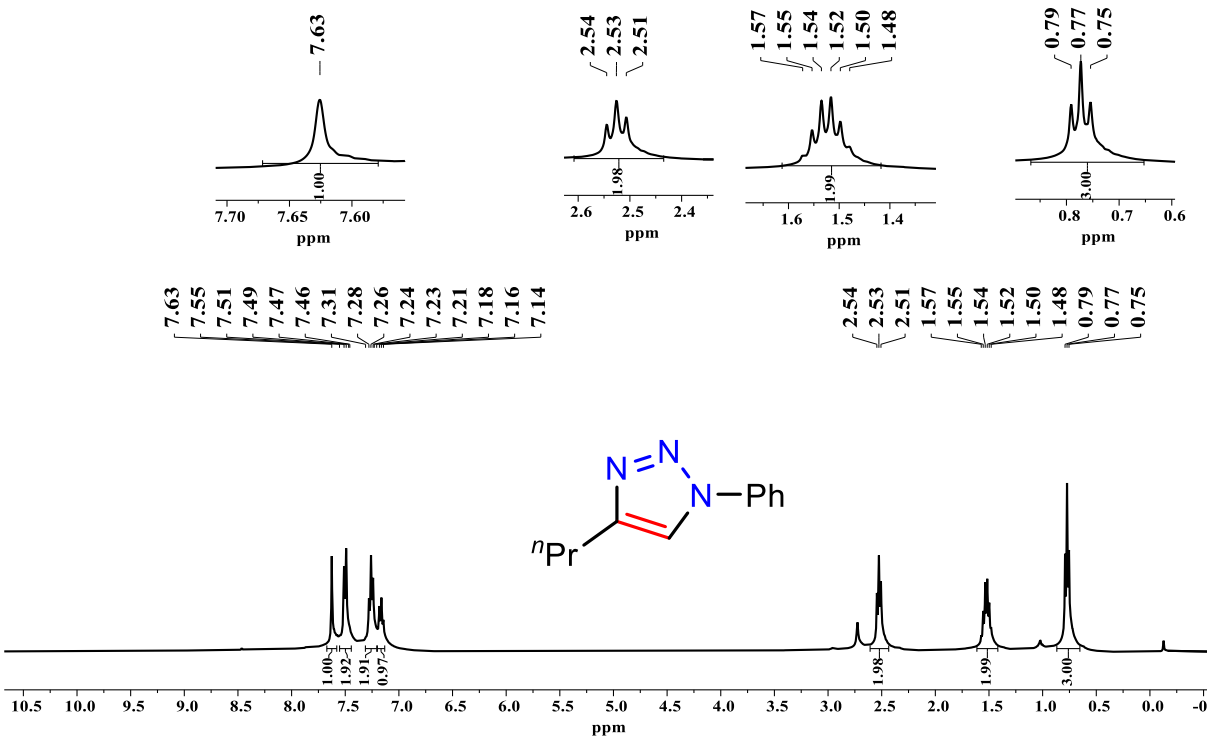


Fig. S44. ^{1}H NMR spectrum of **X** in $CDCl_3$ (400 MHz)

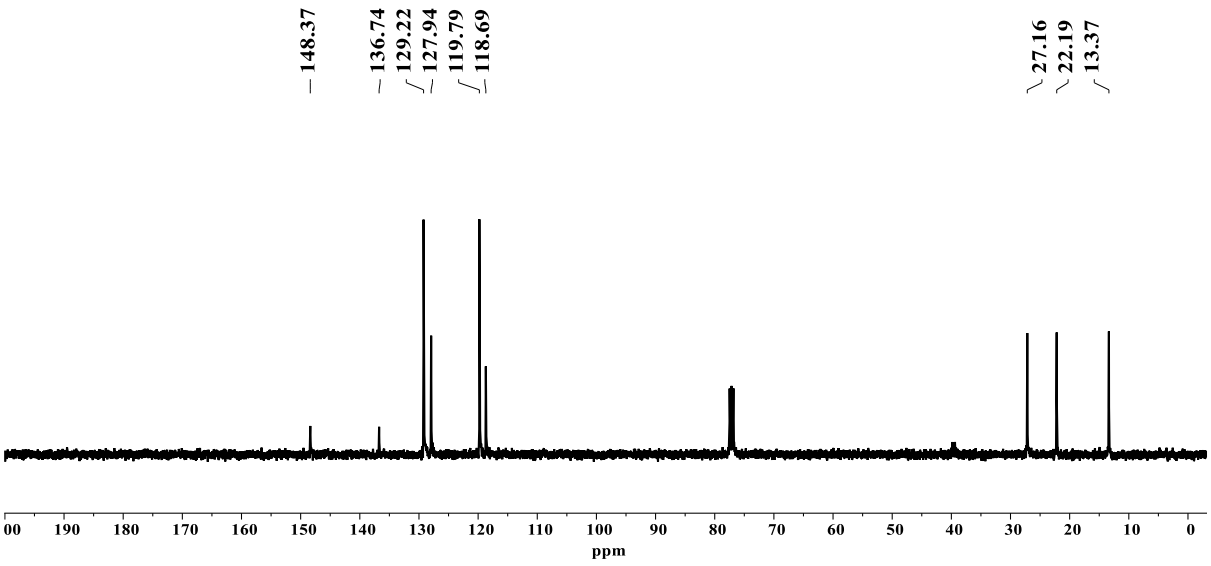


Fig. S45. $^{13}C\{^{1}H\}$ NMR spectrum of **X** in $CDCl_3$ (101 MHz)

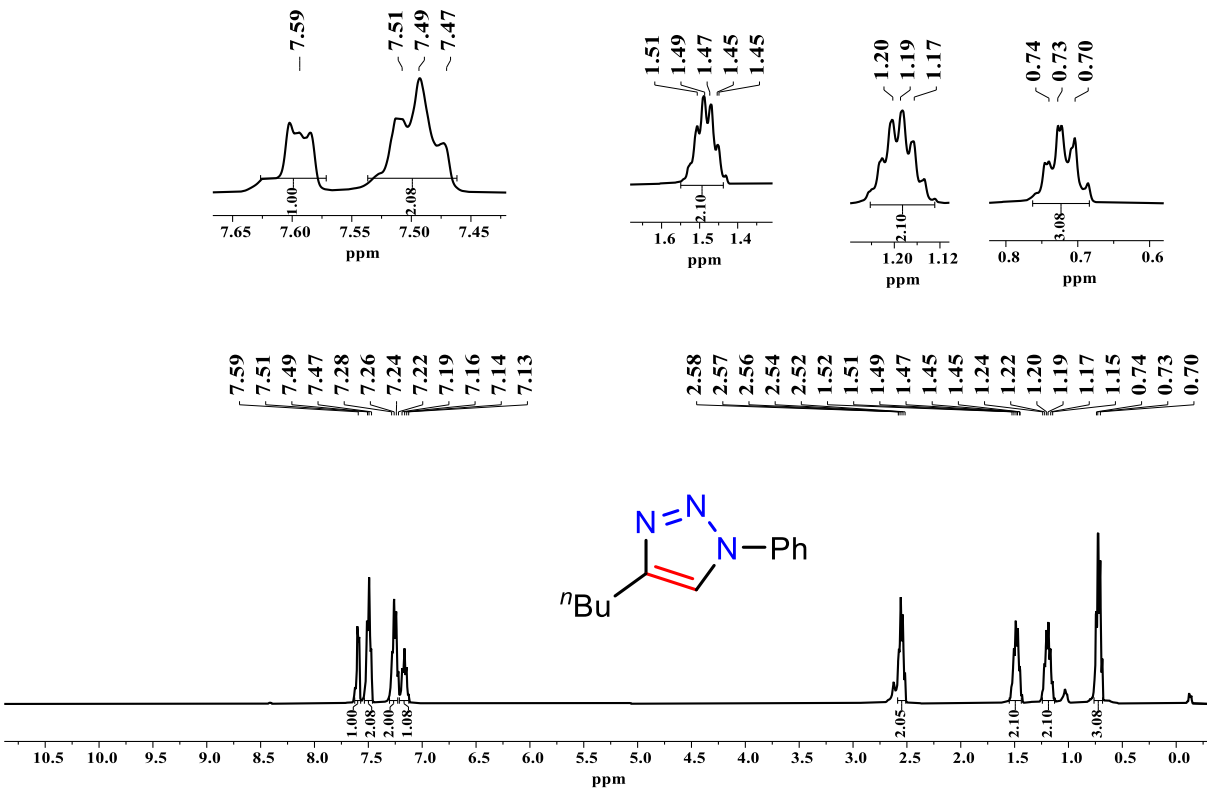


Fig. S46. ^{1}H NMR spectrum of **XI** in $CDCl_3$ (400 MHz)

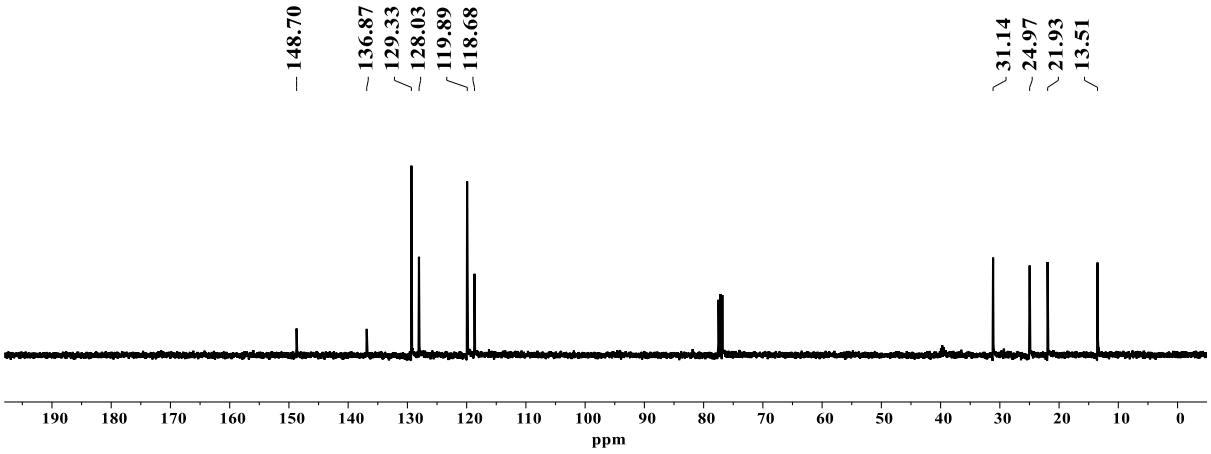


Fig. S47. $^{13}C\{^{1}H\}$ NMR spectrum of **XI** in $CDCl_3$ (101 MHz)

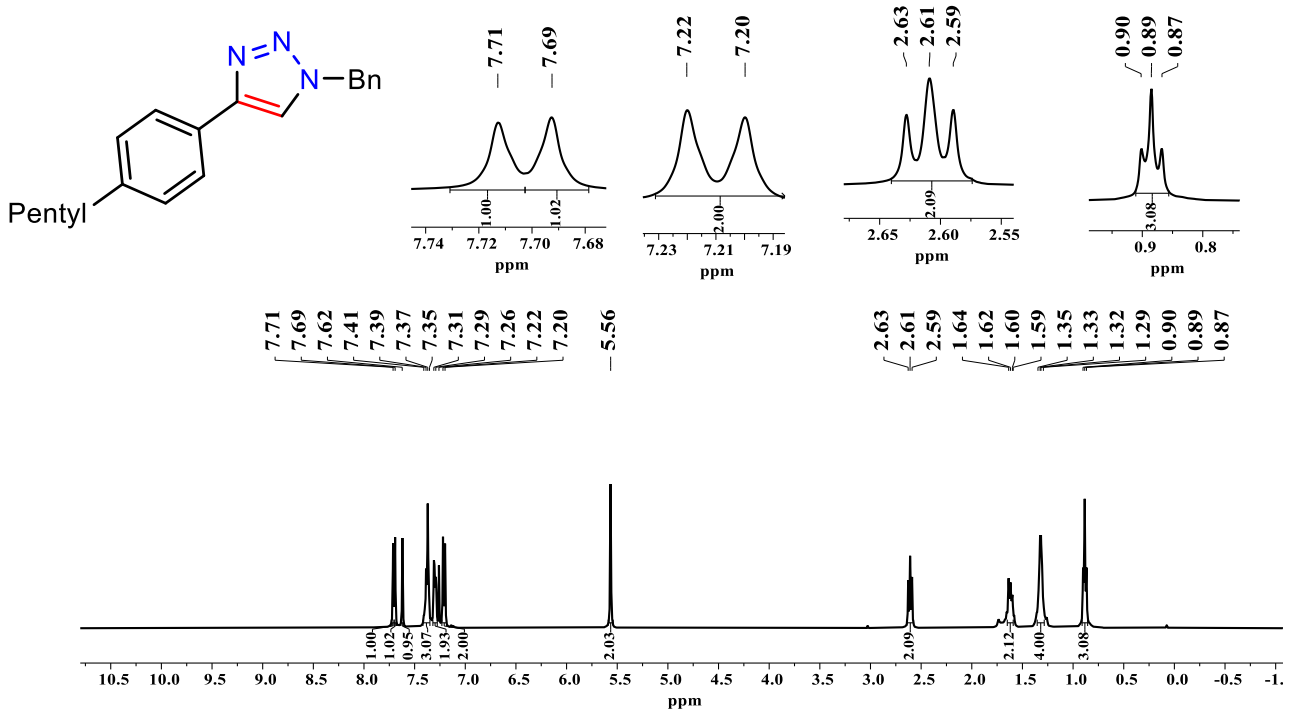


Fig. S48. ^{1}H NMR spectrum of **XII** in $CDCl_3$ (400 MHz)

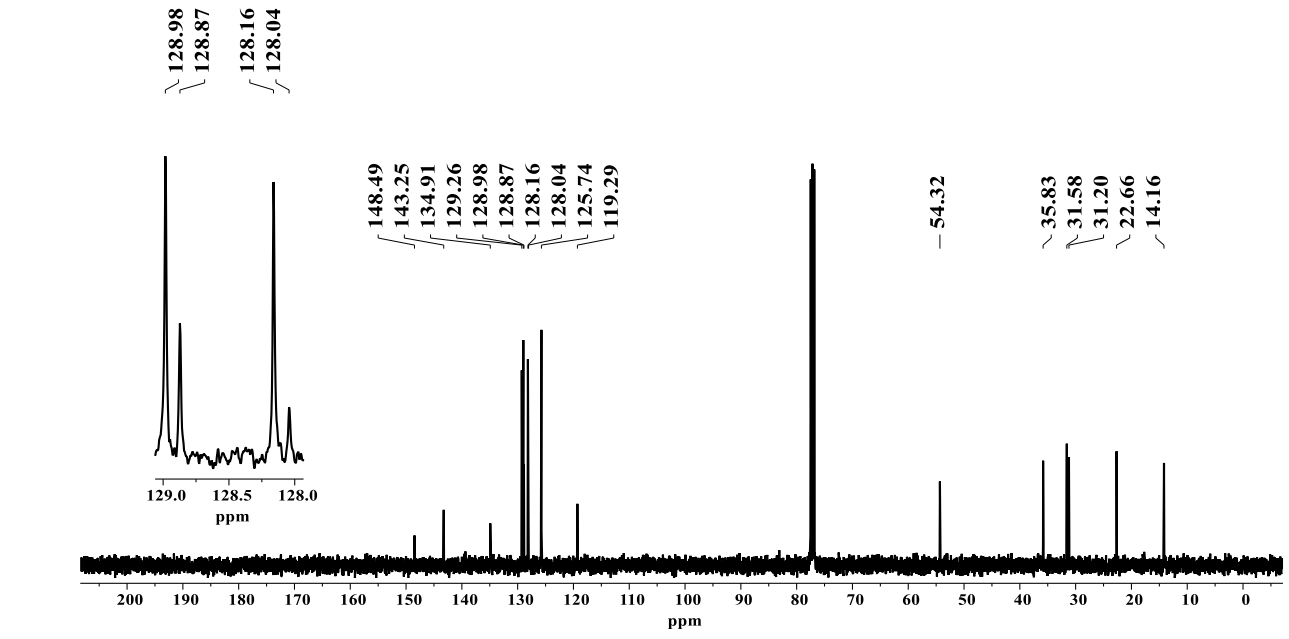


Fig. S49. $^{13}C\{^{1}H\}$ NMR spectrum of **XII** in $CDCl_3$ (101 MHz)

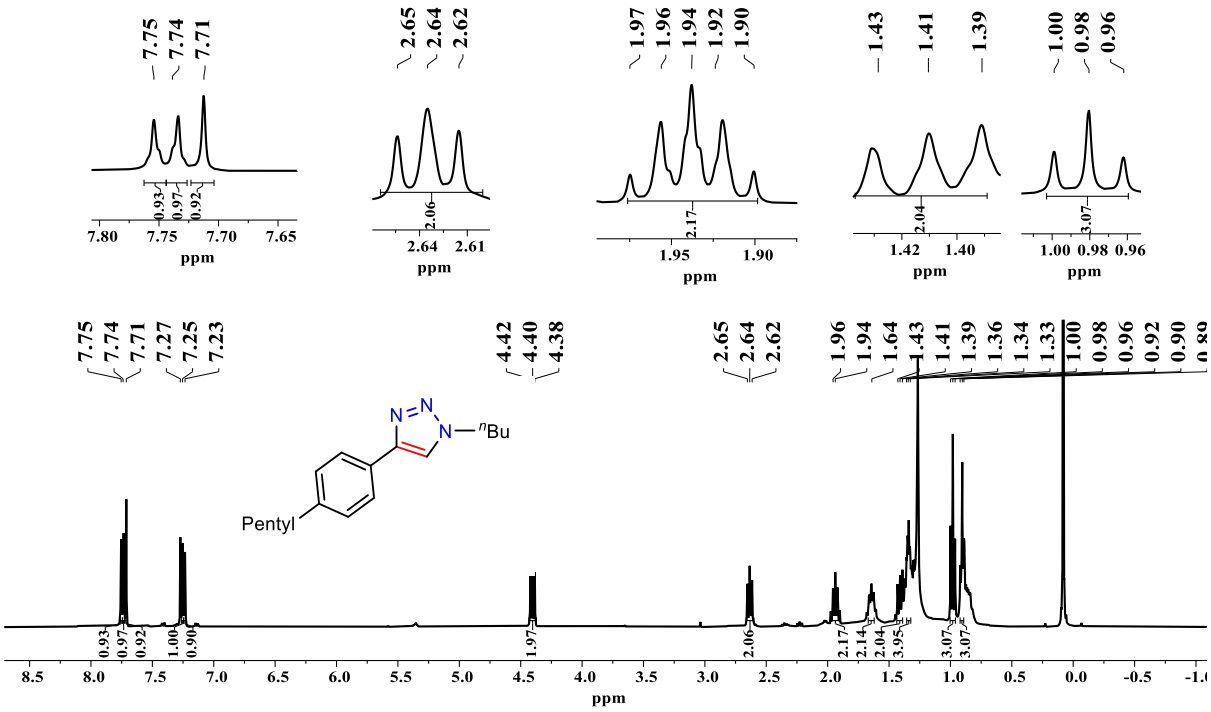


Fig. S50. ^{1}H NMR spectrum of **XIII** in $CDCl_3$ (400 MHz)

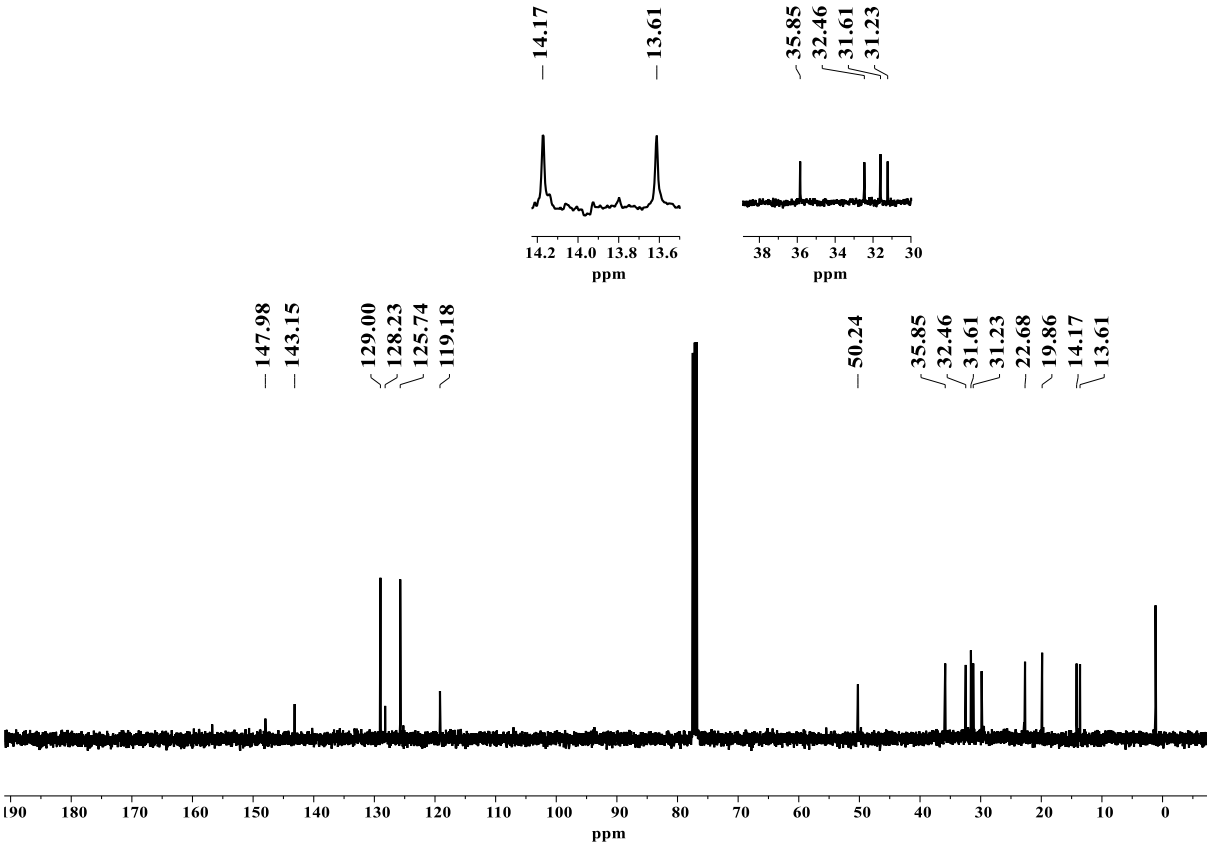


Fig. S51. ^{13}C{^{1}H} NMR spectrum of **XIII** in $CDCl_3$ (101 MHz)

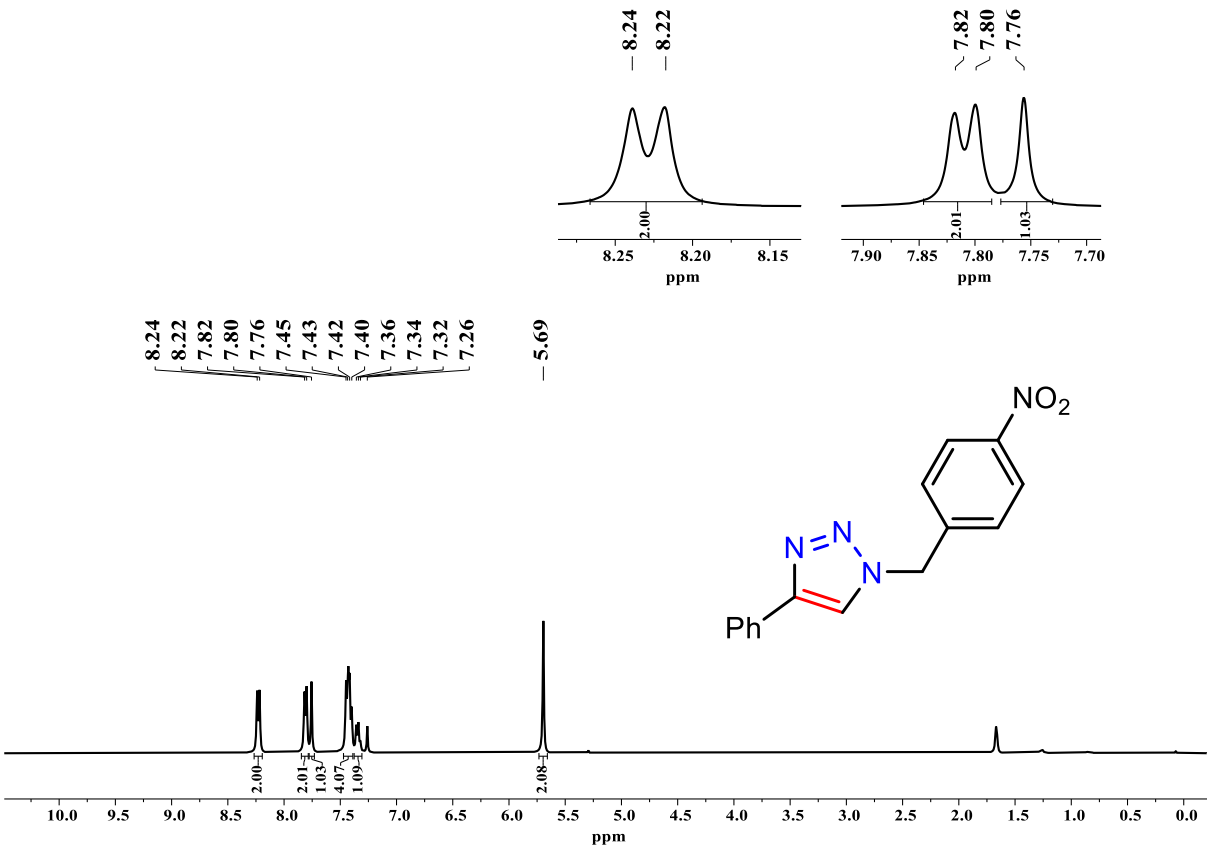


Fig. S52. ^{1}H NMR spectrum of **XIV** in $CDCl_3$ (400 MHz)

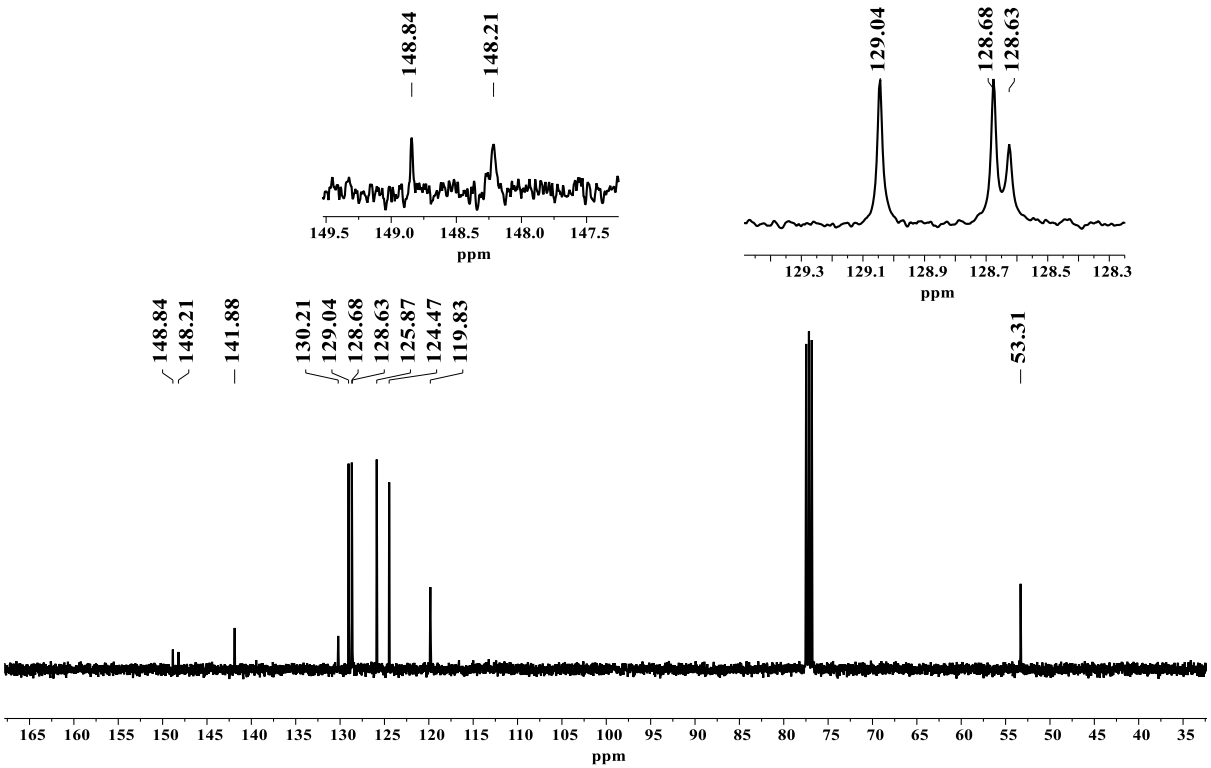


Fig. S53. ^{13}C{^{1}H} NMR spectrum of **XIV** in $CDCl_3$ (101 MHz)

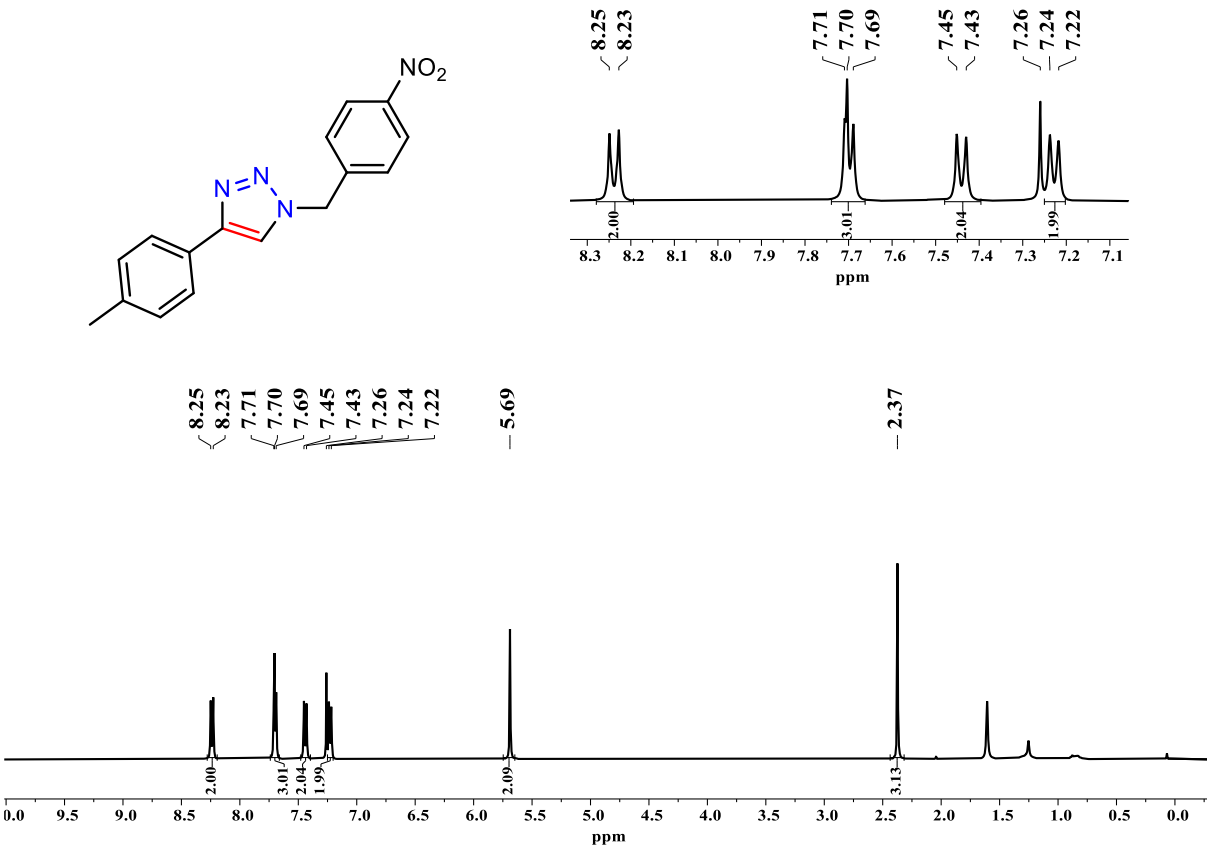


Fig. S54. ^{1}H NMR spectrum of **XV** in $CDCl_3$ (400 MHz)

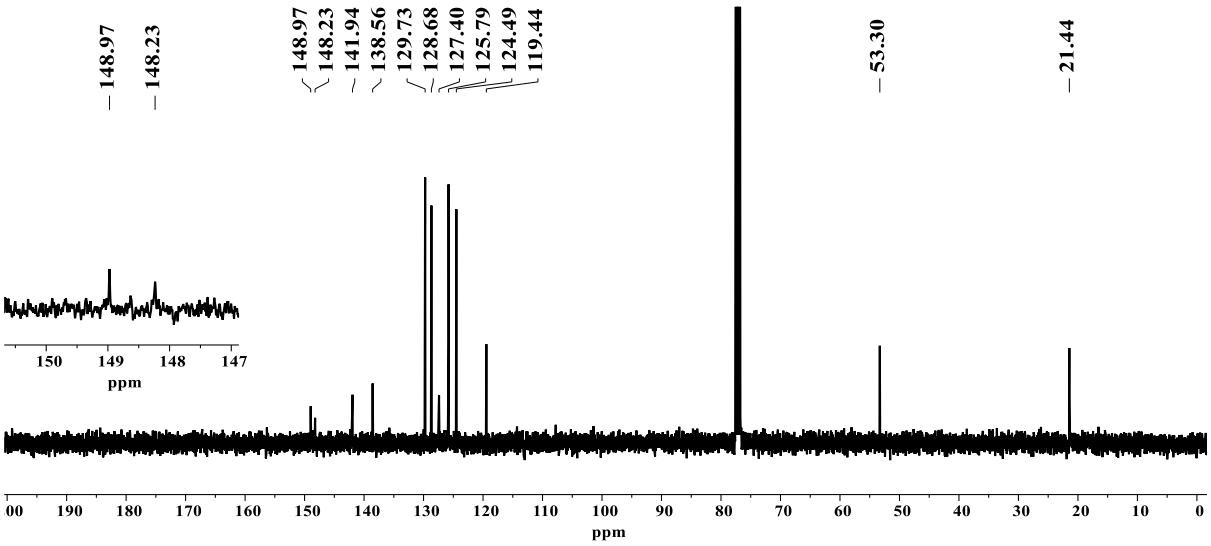


Fig. S55. $^{13}C\{^{1}H\}$ NMR spectrum of **XV** in $CDCl_3$ (101 MHz)

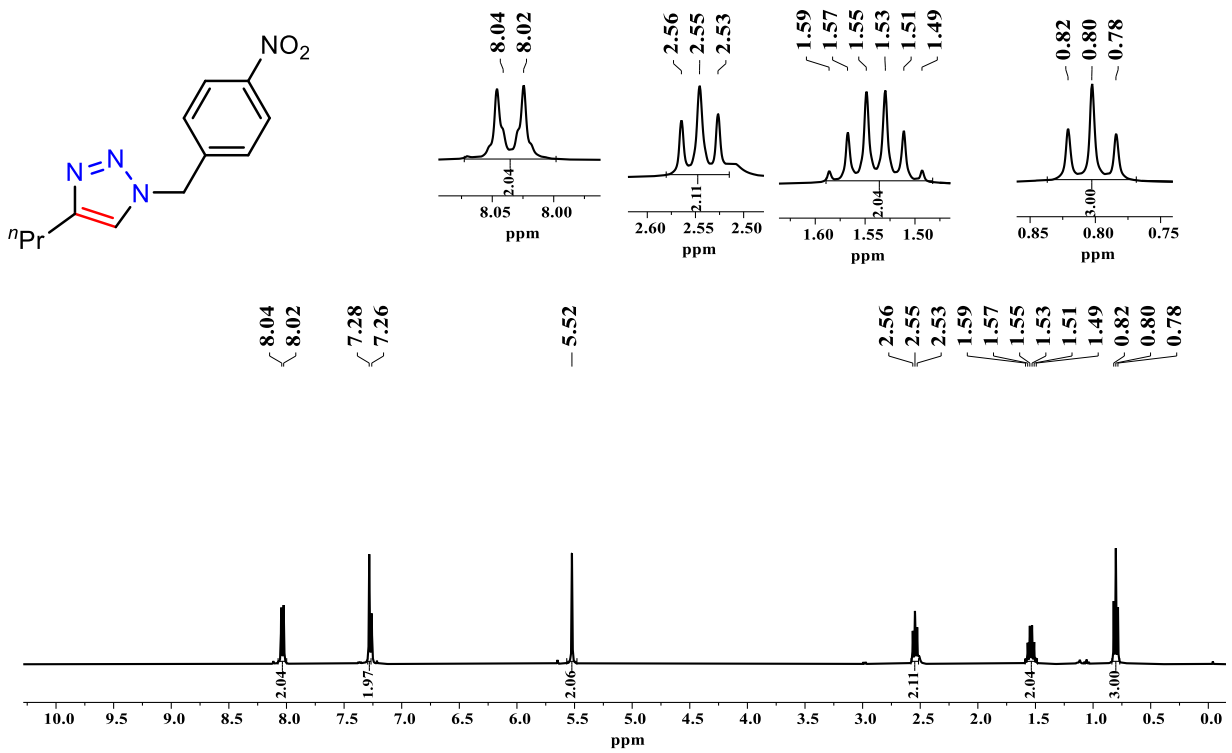


Fig. S56. ^{1}H NMR spectrum of **XVI** in $CDCl_3$ (400 MHz)

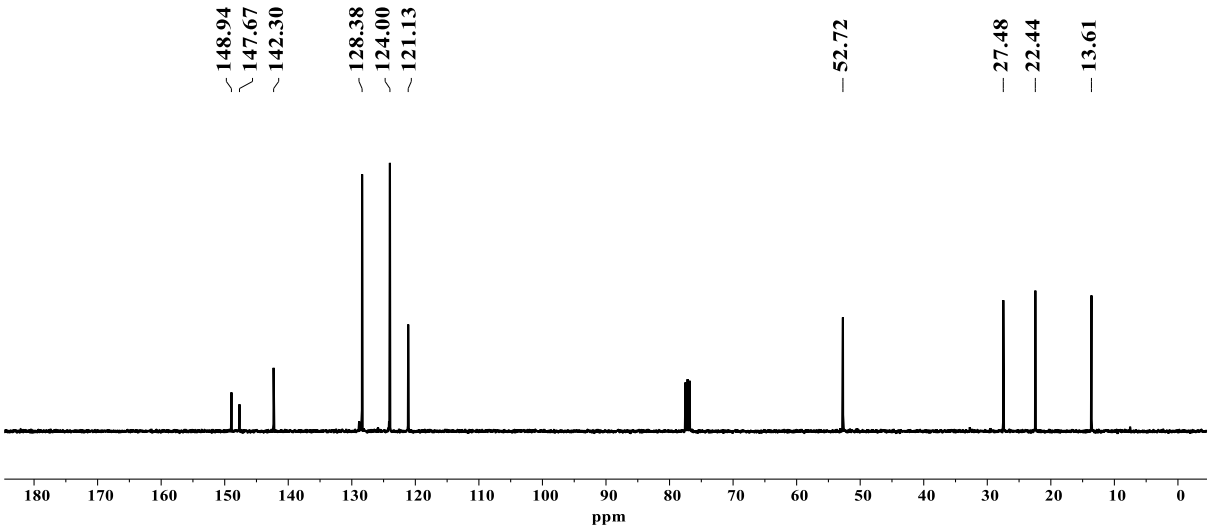


Fig. S57. $^{13}C\{^{1}H\}$ NMR spectrum of **XVI** in $CDCl_3$ (101 MHz)

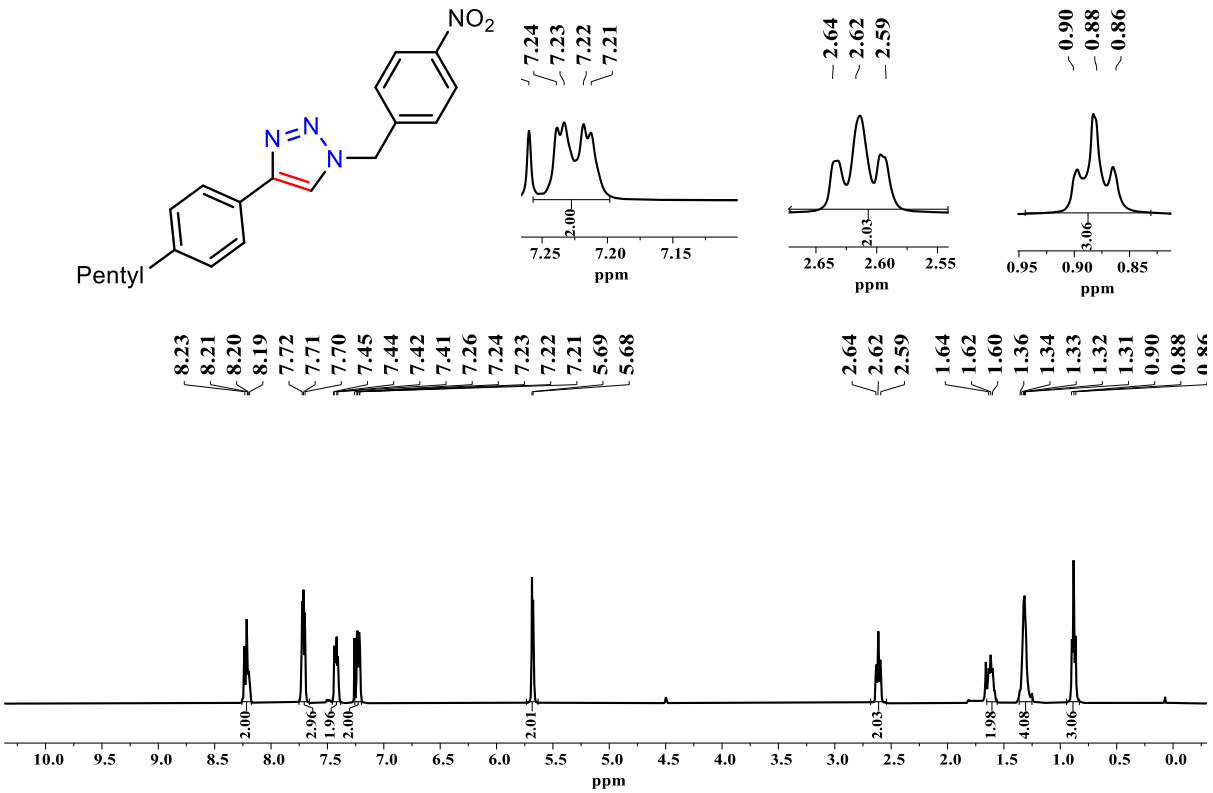


Fig. S58. ^{1}H NMR spectrum of **XVII** in $CDCl_3$ (400 MHz)

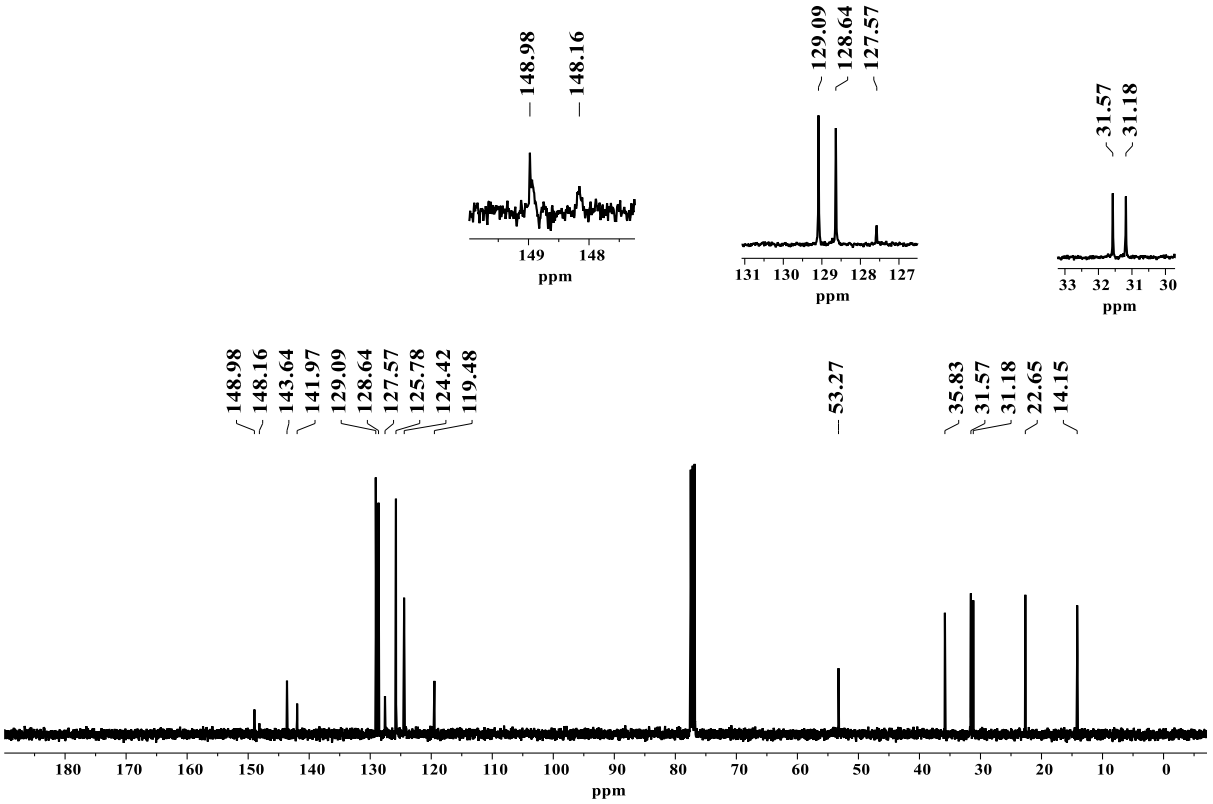


Fig. S59. $^{13}C\{^{1}H\}$ NMR spectrum of **XVII** in $CDCl_3$ (101 MHz)

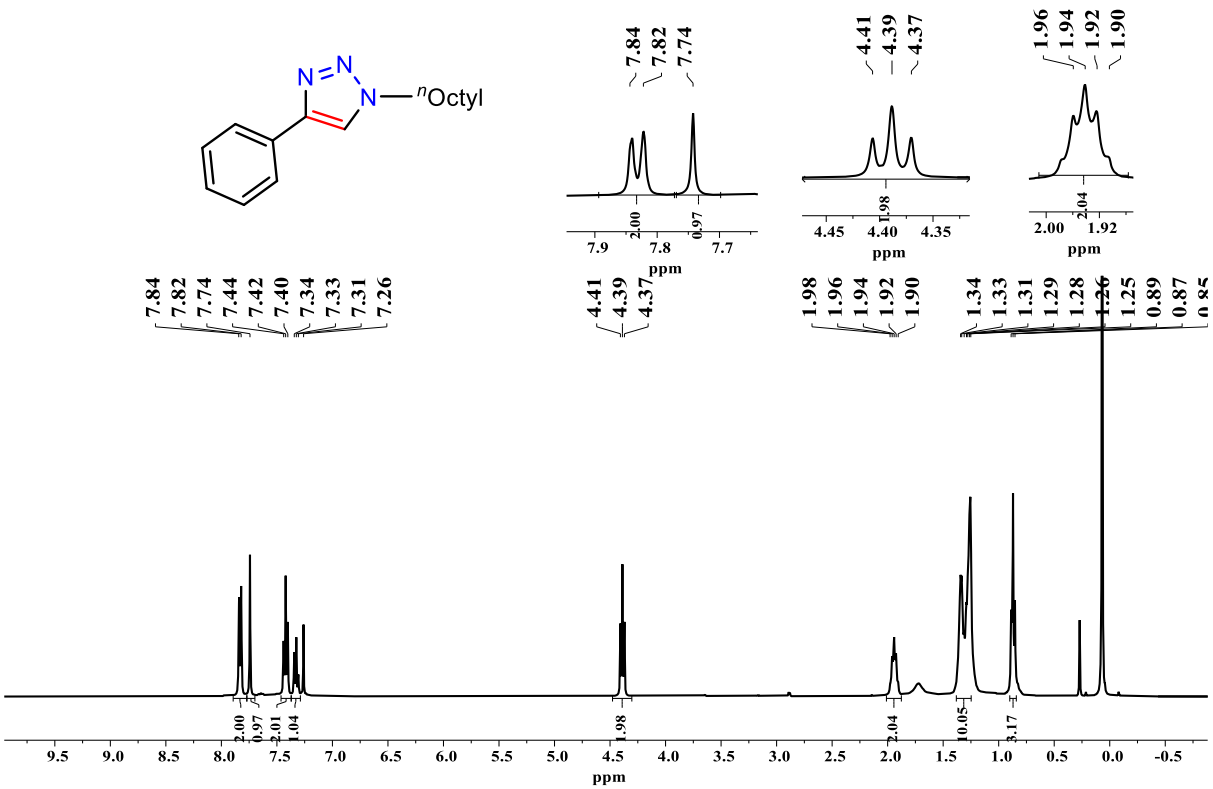


Fig. S60. ^{1}H NMR spectrum of **XVIII** in $CDCl_3$ (400 MHz)

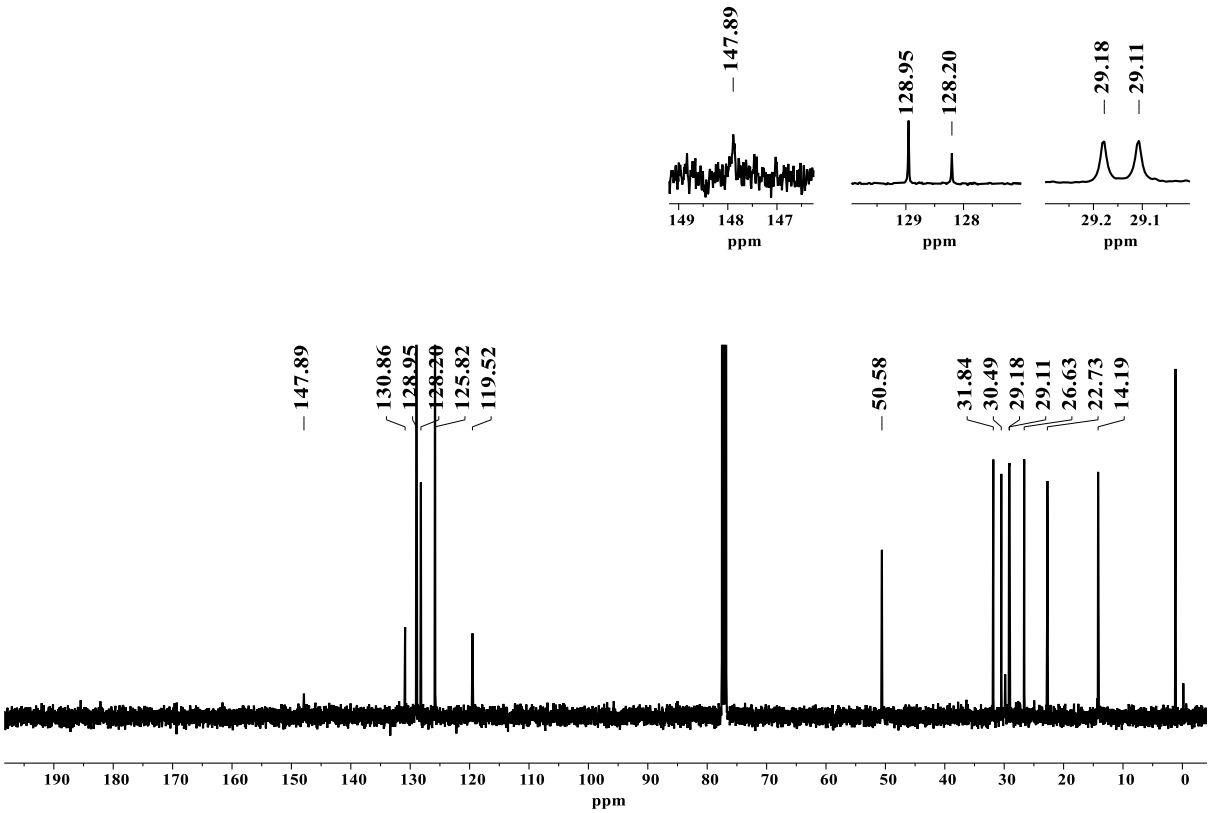


Fig. S61. ^{13}C{^{1}H} NMR spectrum of **XVIII** in $CDCl_3$ (101 MHz)

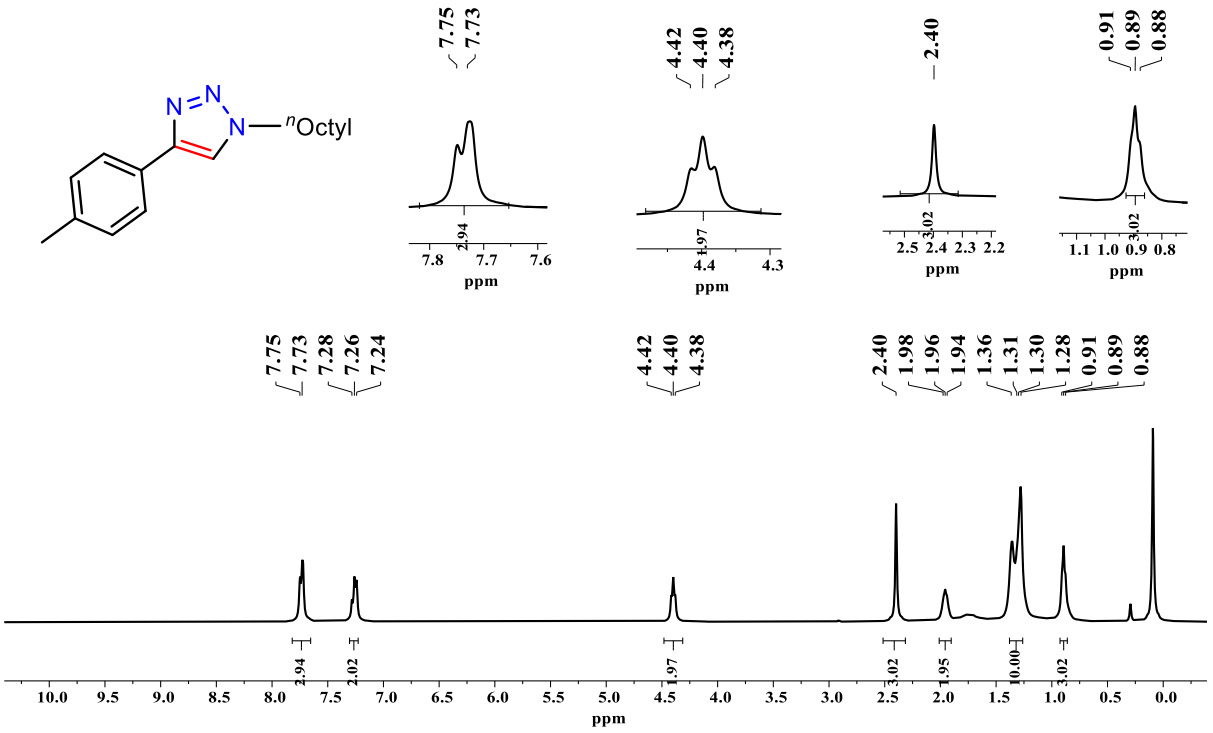


Fig. S62. ^{1}H NMR spectrum of **XIX** in $CDCl_3$ (400 MHz)

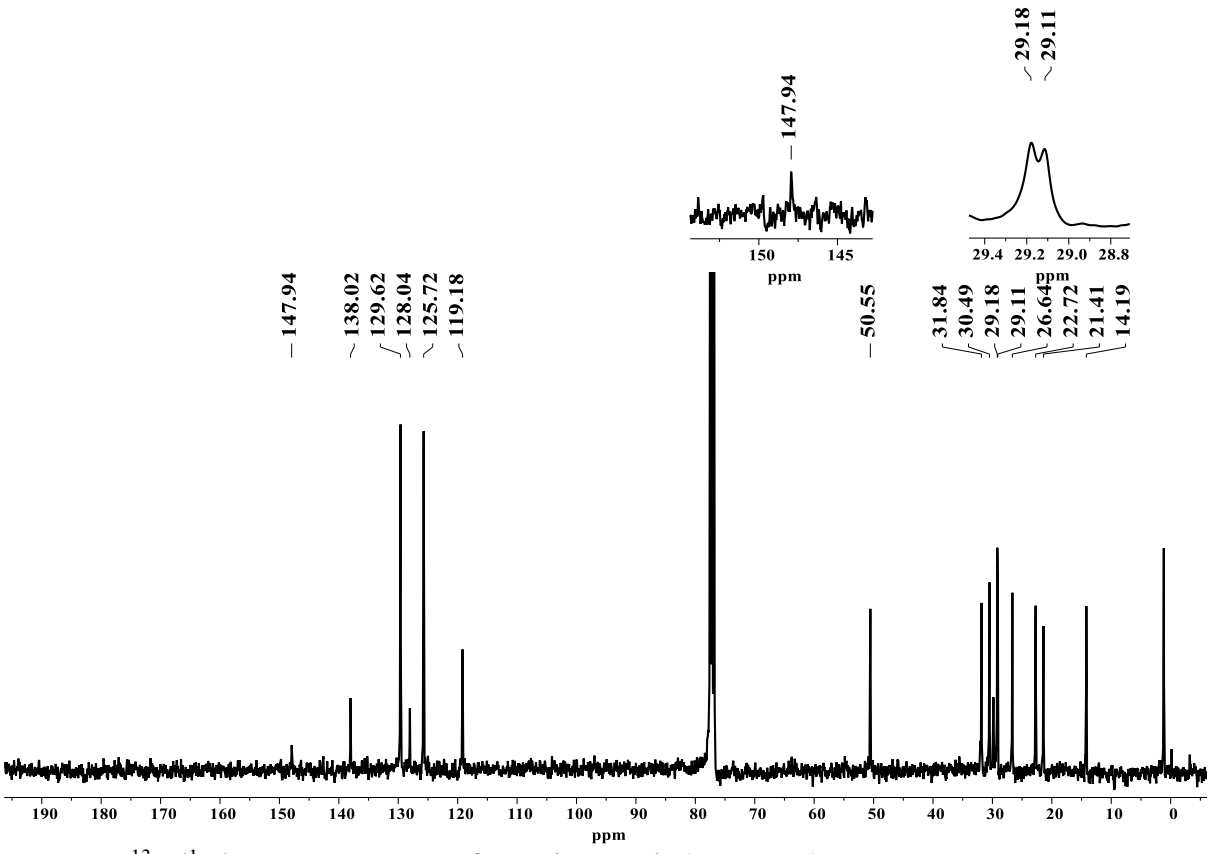


Fig. S63. ^{13}C{^{1}H} NMR spectrum of **XIX** in $CDCl_3$ (101 MHz)

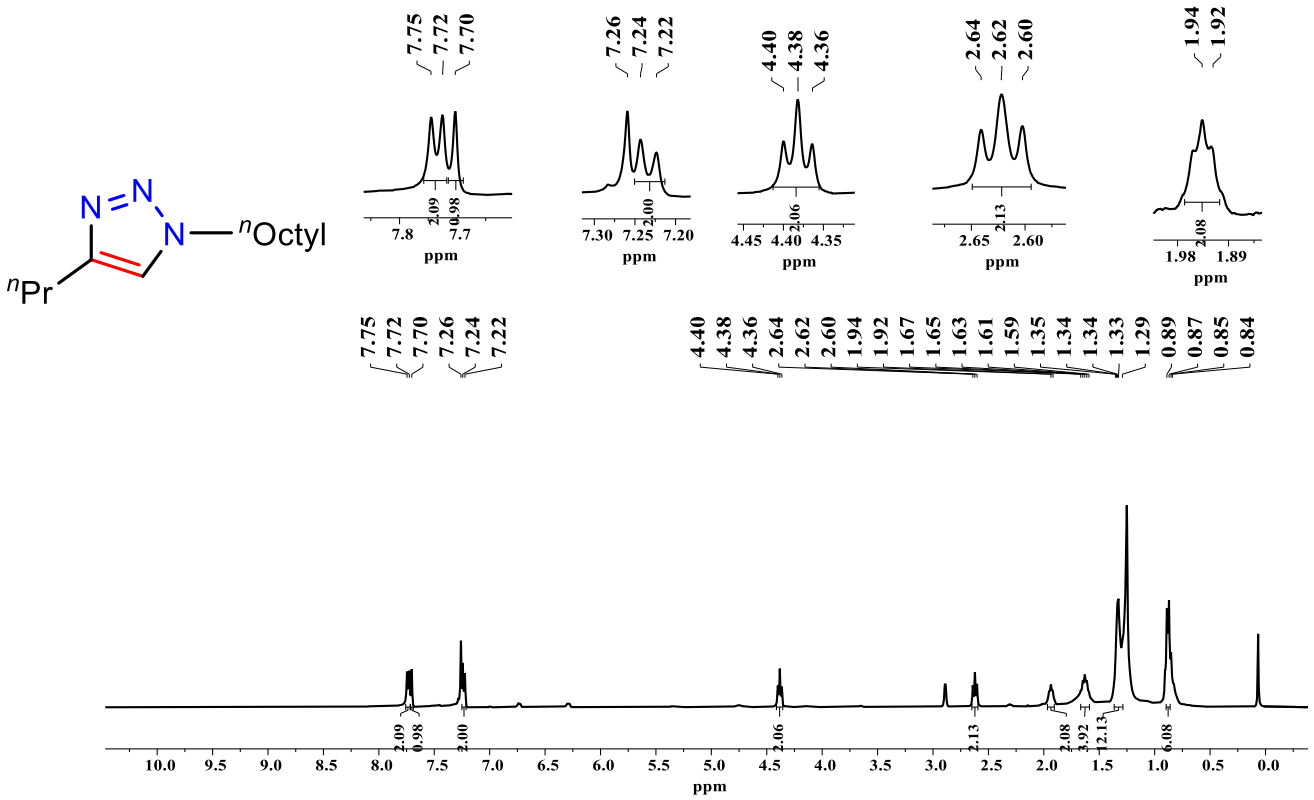


Fig. S64. ^{1}H NMR spectrum of **XX** in $CDCl_3$ (400 MHz)

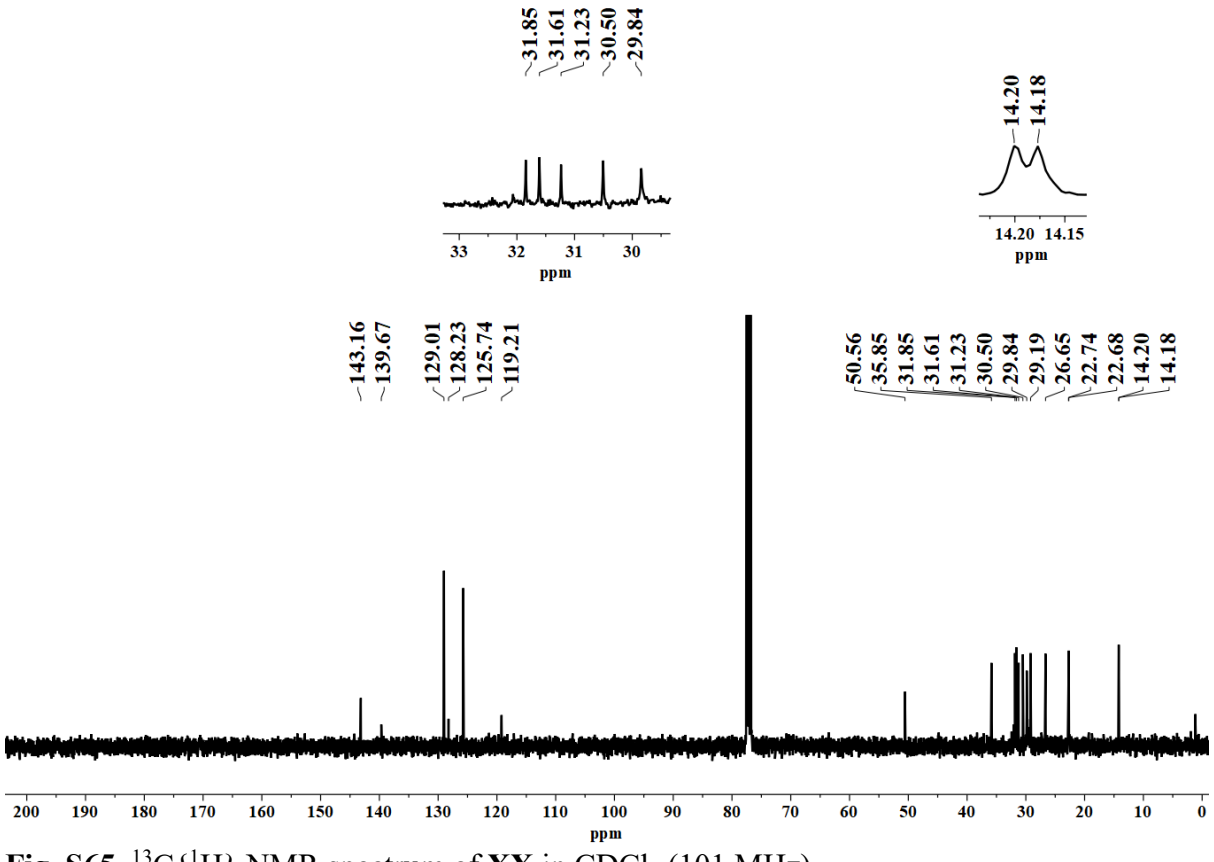


Fig. S65. ^{13}C{^{1}H} NMR spectrum of **XX** in $CDCl_3$ (101 MHz)

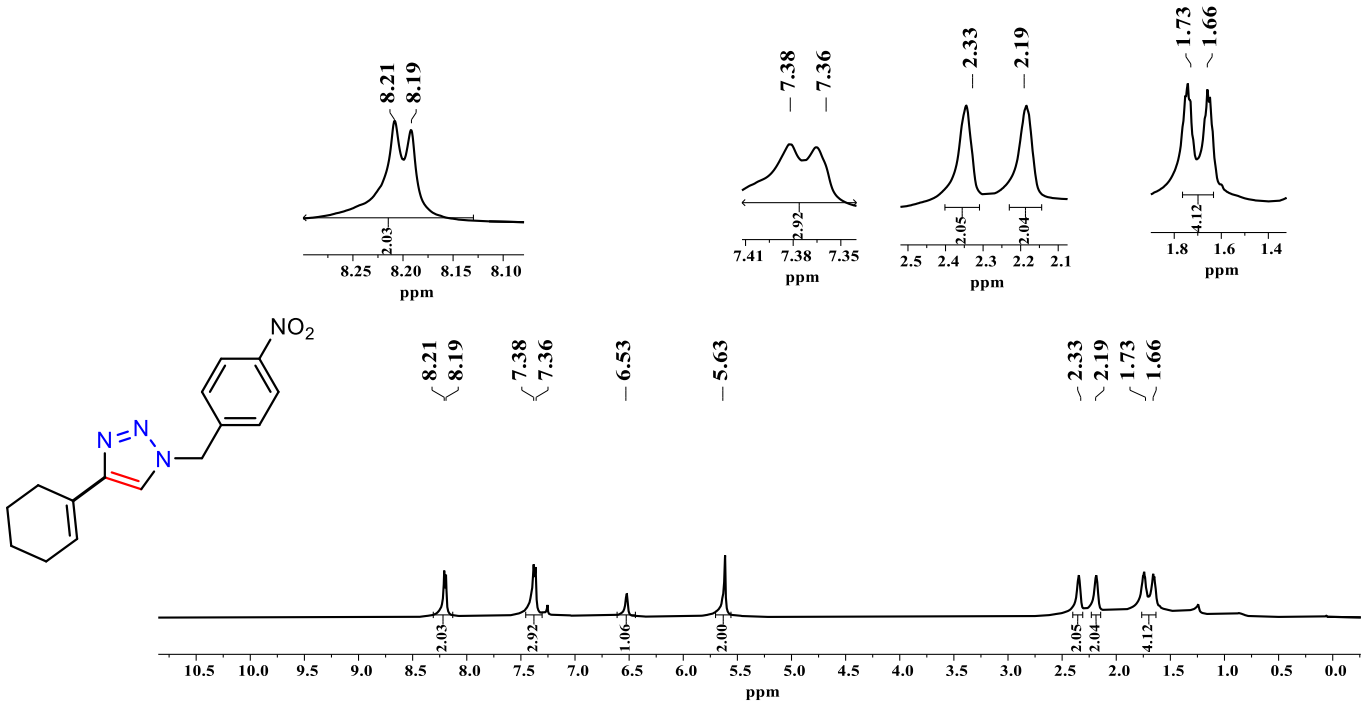


Fig. S66. ^{1}H NMR spectrum of **XXI** in $CDCl_3$ (400 MHz)

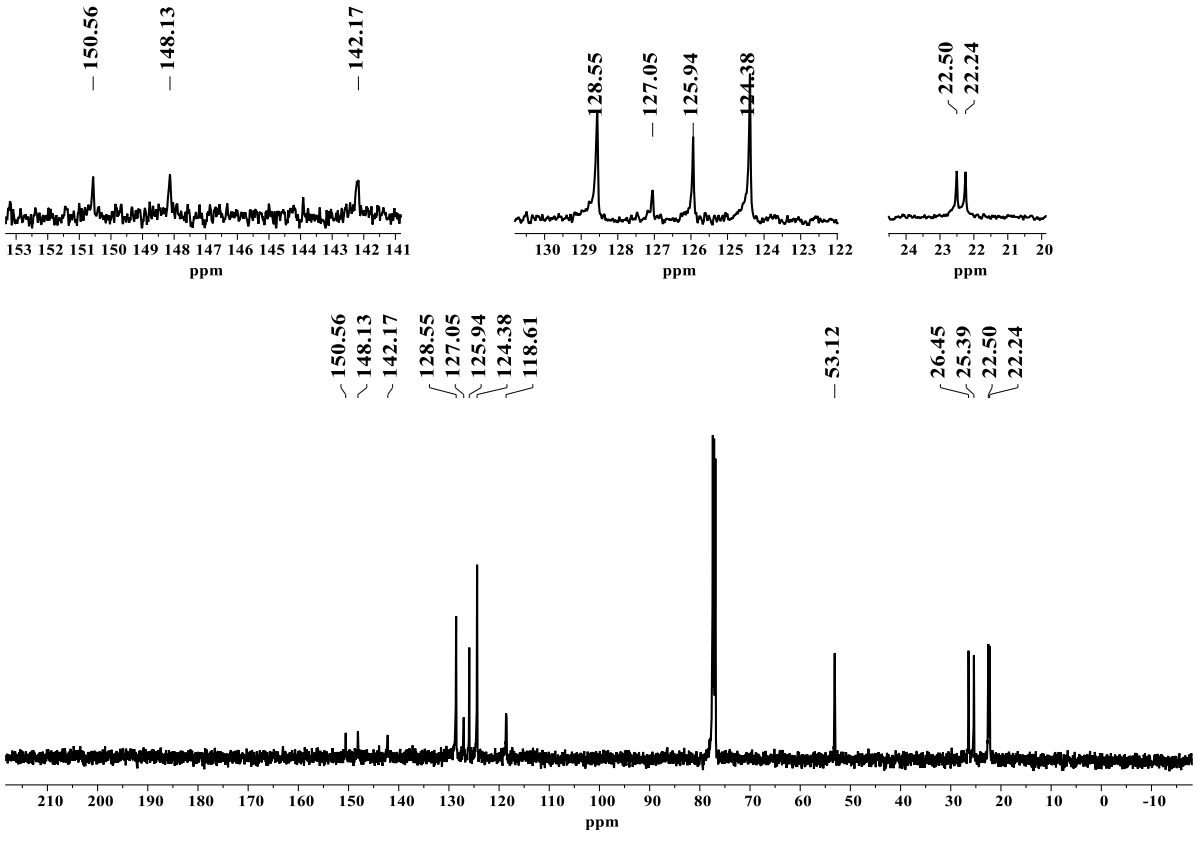


Fig. S67. $^{13}C\{^{1}H\}$ NMR spectrum of **XXI** in $CDCl_3$ (101 MHz)

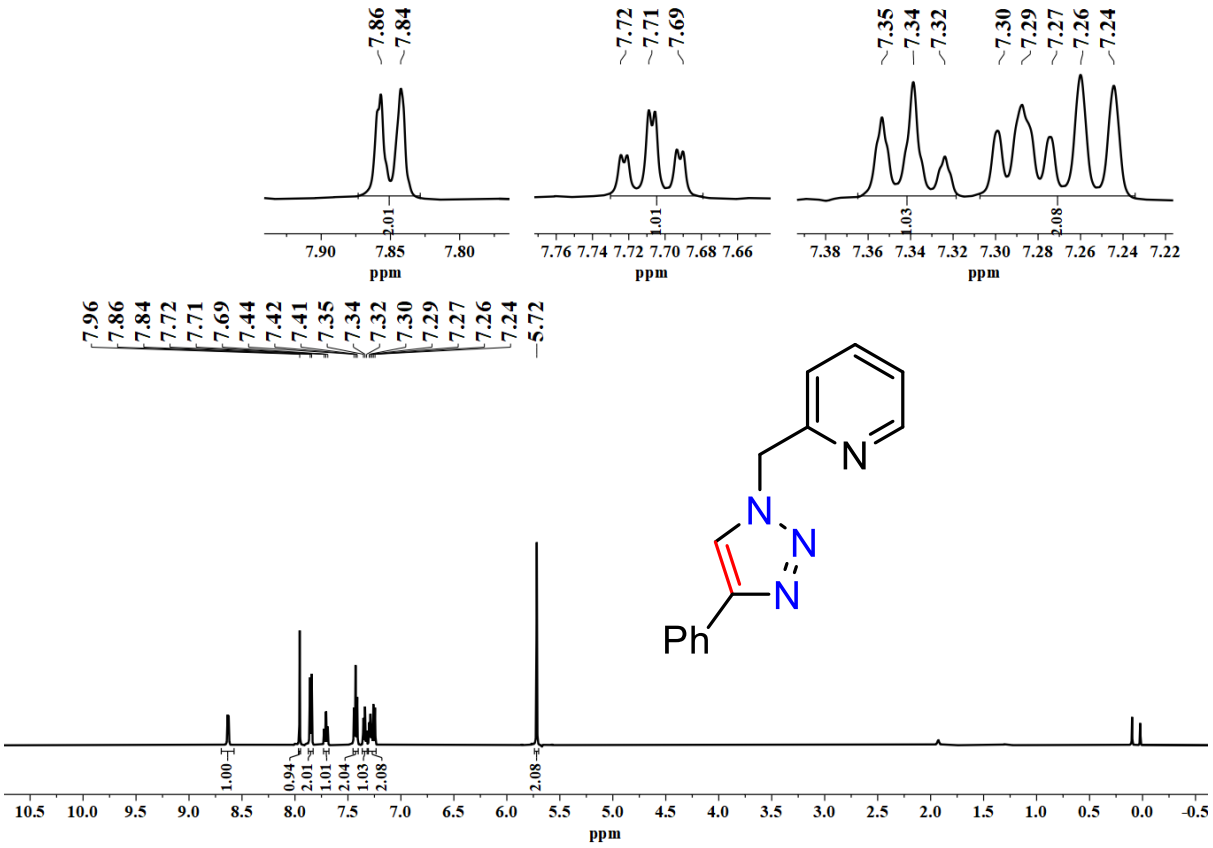


Fig. S68. ^{1}H NMR spectrum of **XXIV** in $CDCl_3$ (500 MHz)

.

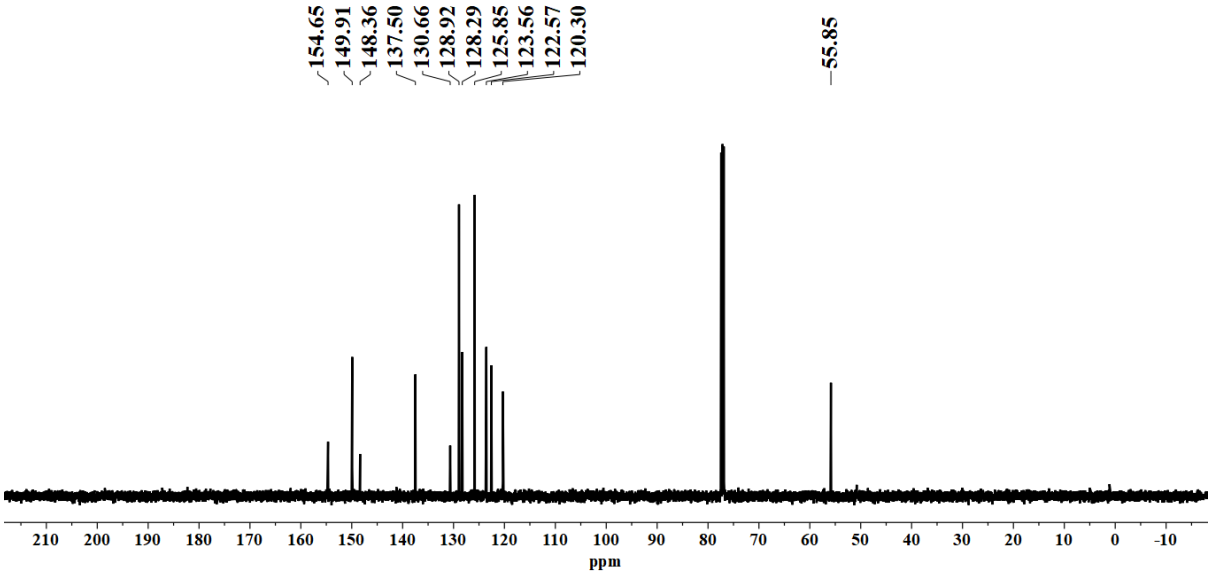


Fig. S69. $^{13}C\{^{1}H\}$ NMR spectrum of **XXIV** in $CDCl_3$ (126 MHz)

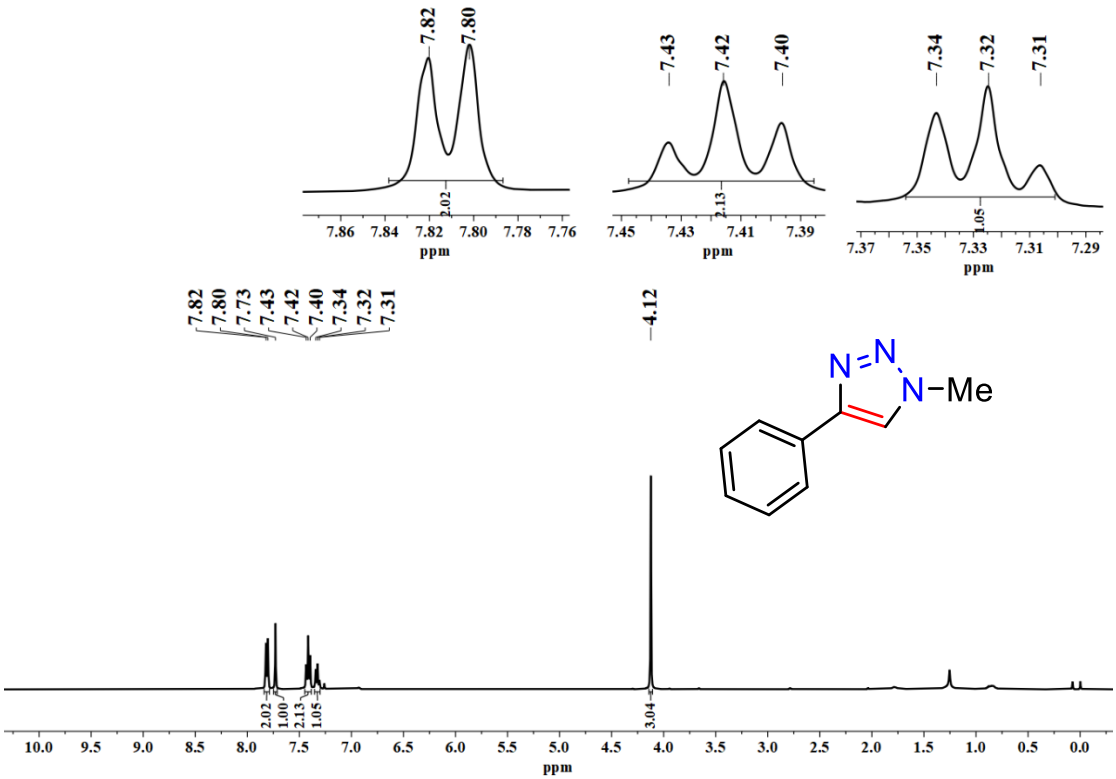


Fig. S70. ^{1}H NMR spectrum of **XXV** in $CDCl_3$ (400 MHz)

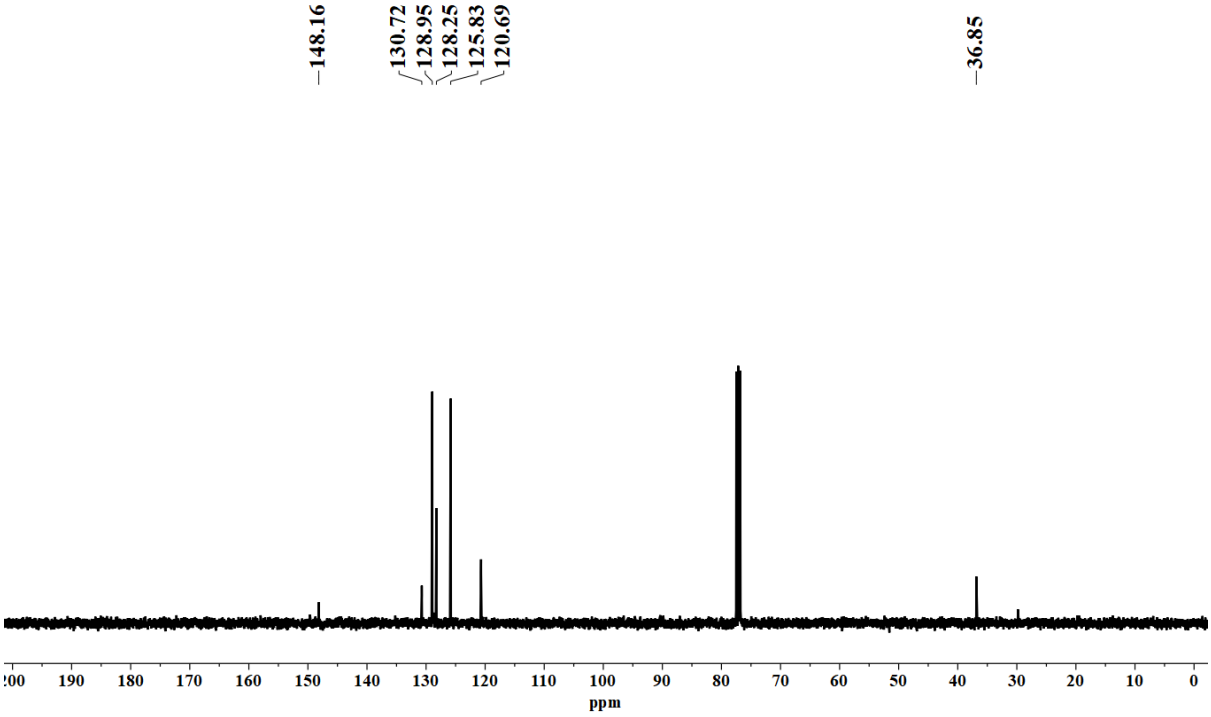
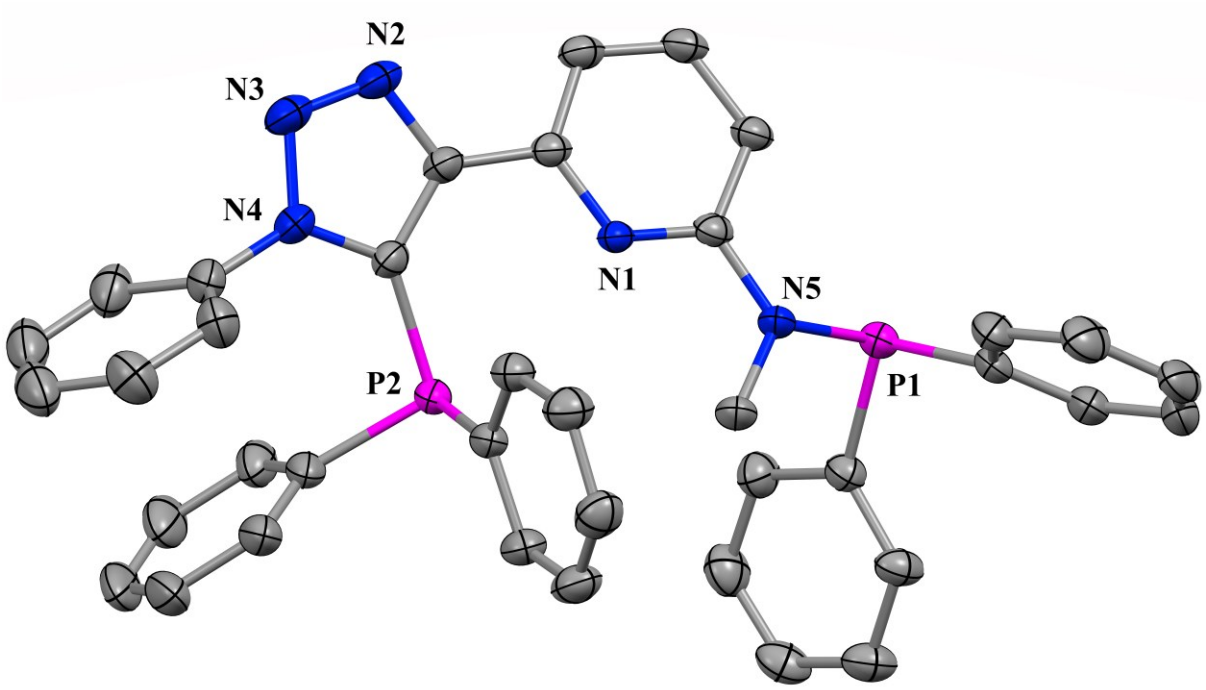
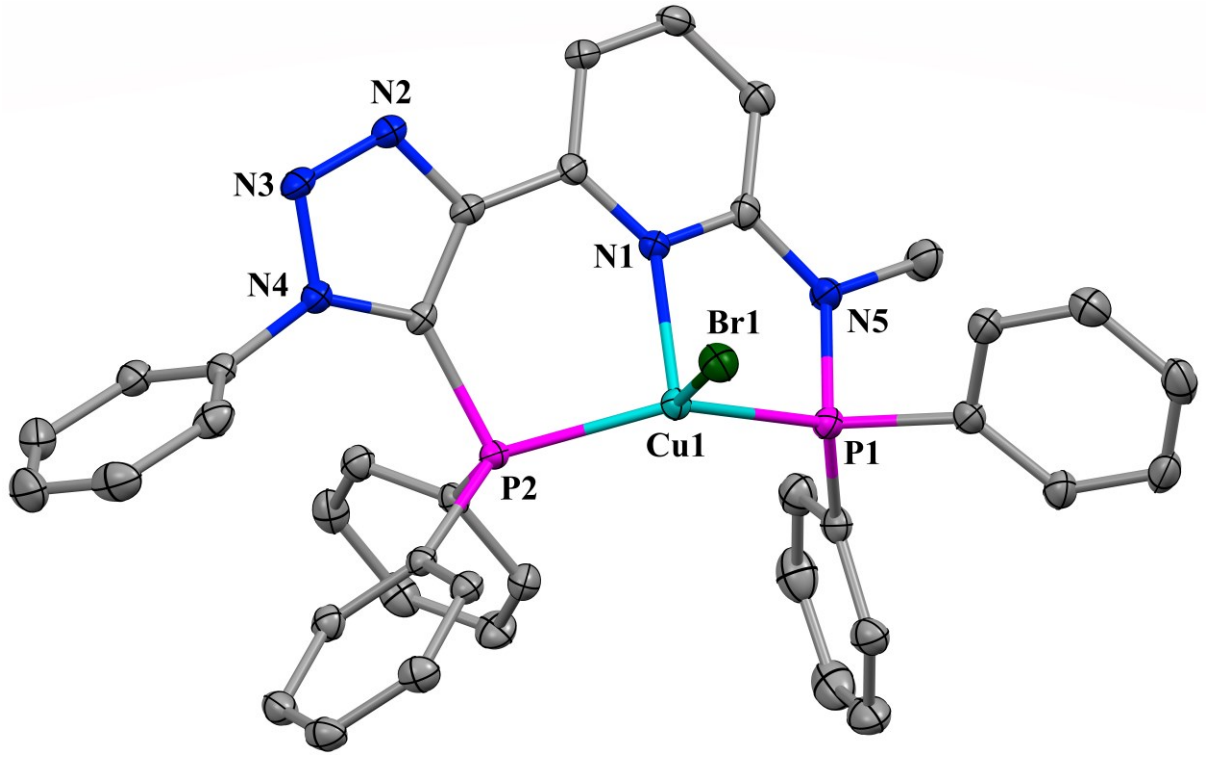


Fig. S71. $^{13}C\{^{1}H\}$ NMR spectrum of **XXV** in $CDCl_3$ (101 MHz)



L



2

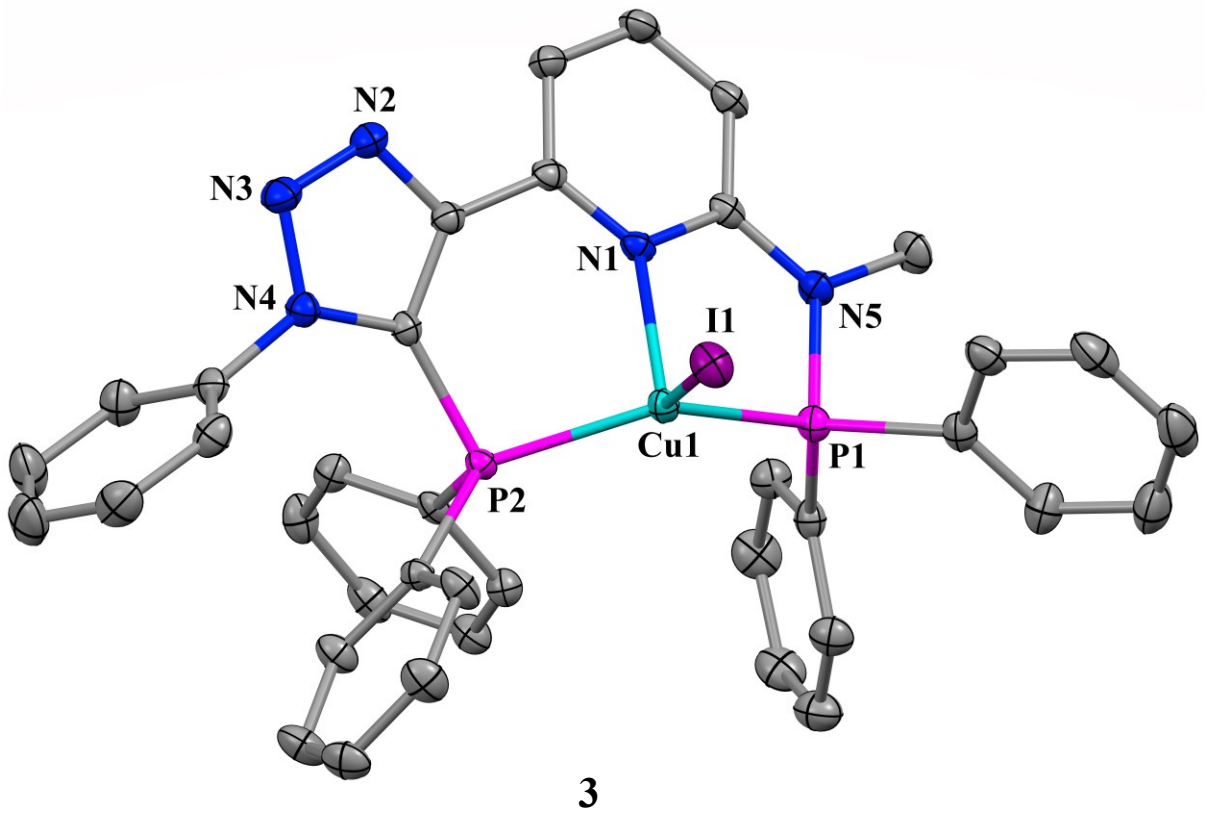


Fig. S72. Molecular structures of compounds **L**, **2** and **3**. All hydrogen atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 40% probability level.

Table S4 Hydrogen-bond geometry (Å, °) for **2** and **3**.

Cg1 is the centroid of the C33–C38 phenyl ring and Cg2 is the centroid of the C14–C19 phenyl ring.

	D–H···*A*	*D*–H	H···*A*	D···*A*	*D*–H···*A*
Comp-2	C9–H9···Br1^{i}	0.95	3.005	3.756	137
	C22–H22···Br1^{i}	0.95	3.000	3.754	137
	C23–H23···N2^{i}	0.95	2.673	3.481	143
	C32–H32···Cg1^{ii}	0.95	2.603	3.435	147
Comp-3	C16–H16···N2^{iii}	0.95	2.730	3.655	165
	C39–H39B···N7^{iv}	0.98	2.479	3.376	152
	C31–H31···Cg2^{v}	0.95	3.022	3.848	146

(i) -1/2+x, 1/2-y, 1/2+z; (ii) 1-x, 1-y, 1-z; (iii) 1/2+x, 1.5-y, 1/2+z; (iv) x,y,z; (v) 1-x, 2-y, 1-z.

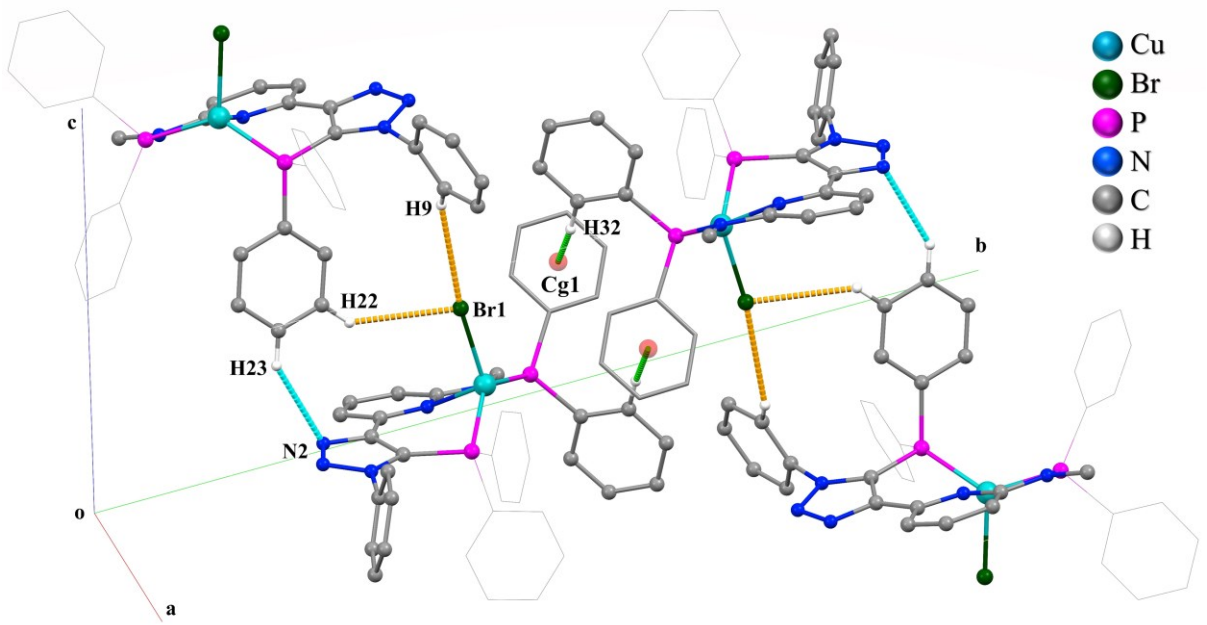


Fig. S73. Packing diagrams showing the two-dimensional arrangement of complex **2** involving: (i) intermolecular C–H···Br interactions (orange dotted lines) and (ii) C–H···N interactions (light blue dotted lines) and (iii) C–H···π(ring) interactions (green dotted lines).

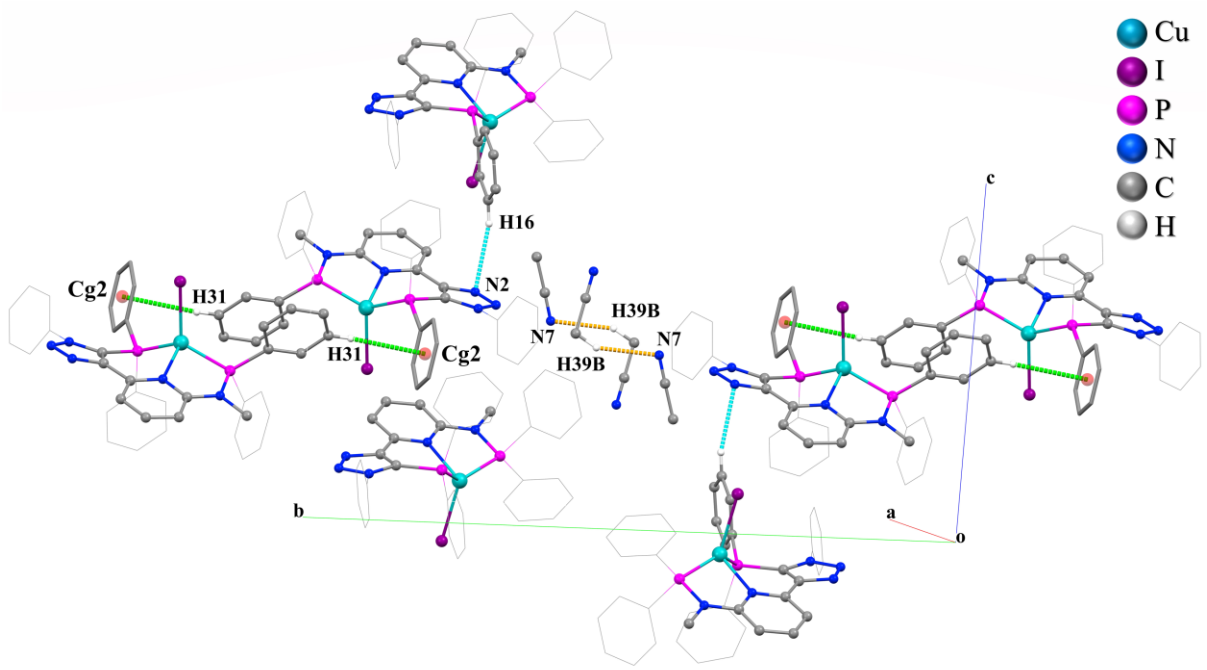


Fig. S74. Packing diagrams showing the two-dimensional arrangement of complex **2** involving: (i) C–H···N interactions (orange and light blue dotted lines) and (ii) C–H···π(ring) interactions (green dotted lines).

Optimised Coordinates for complexes **1-3**

Complex **1**

Cu	-0.718556000	-0.767329000	0.538620000
P	1.310135000	0.232415000	0.203918000
P	-2.812663000	0.019103000	0.173210000
N	3.424790000	-1.345370000	-1.028163000
N	2.425208000	-2.648299000	-2.392948000
N	-0.913336000	-1.389970000	-1.597549000
N	3.588453000	-2.343655000	-1.931588000
C	2.101486000	-1.015378000	-0.900807000
C	2.403149000	0.456242000	1.680830000
N	-3.158808000	-0.737790000	-1.373612000
C	4.605785000	-0.835117000	-0.389293000
C	-4.220554000	-0.520046000	1.245618000
C	-2.514465000	-2.321802000	-3.111911000
H	-3.534880000	-2.434564000	-3.440534000
C	2.200070000	-0.421201000	2.752401000
H	1.463101000	-1.213998000	2.672800000
C	3.328328000	1.495323000	1.808677000
H	3.491395000	2.186102000	0.992589000
C	1.468782000	-1.875786000	-1.799227000
C	-2.182152000	-1.494067000	-2.025905000
C	-3.272993000	2.679288000	0.937003000
H	-3.245990000	2.292222000	1.948977000
C	2.932630000	-0.267296000	3.924659000
H	2.768021000	-0.952089000	4.747728000
C	0.070032000	-2.048480000	-2.233863000
C	1.472657000	1.810926000	-0.750292000
C	-0.187273000	-2.876865000	-3.327028000

H	0.628009000	-3.393536000	-3.808668000
C	0.975998000	2.979220000	-0.159494000
H	0.568017000	2.947472000	0.843915000
C	-3.162217000	1.805489000	-0.151625000
C	1.957476000	1.873857000	-2.057661000
H	2.318345000	0.979074000	-2.547781000
C	-4.020769000	-1.682071000	1.999982000
H	-3.064742000	-2.195026000	1.964551000
C	4.046354000	1.650728000	2.988863000
H	4.760410000	2.460486000	3.078259000
C	1.498062000	4.240811000	-2.146671000
H	1.509866000	5.180322000	-2.685386000
C	-3.175904000	2.334805000	-1.443204000
H	-3.063379000	1.677577000	-2.295751000
C	3.852691000	0.768765000	4.047748000
H	4.412203000	0.893490000	4.967141000
C	-5.443238000	0.154295000	1.336103000
H	-5.607899000	1.066043000	0.775933000
C	5.272104000	0.246023000	-0.952193000
H	4.869449000	0.727767000	-1.832815000
C	5.114726000	-1.491530000	0.724385000
H	4.583801000	-2.339961000	1.134702000
C	-6.453825000	-0.331416000	2.157678000
H	-7.396196000	0.199291000	2.222286000
C	1.969650000	3.081843000	-2.750841000
H	2.348116000	3.111845000	-3.765574000
C	-5.039296000	-2.166706000	2.814859000
H	-4.872397000	-3.064786000	3.396701000
C	6.301214000	-1.043650000	1.291770000
H	6.701689000	-1.547840000	2.161918000

C	-6.254477000	-1.495278000	2.895544000
H	-7.042840000	-1.871860000	3.536282000
C	6.458897000	0.687972000	-0.378717000
H	6.985026000	1.528140000	-0.814239000
C	0.999681000	4.184839000	-0.847281000
H	0.616421000	5.079618000	-0.372470000
C	-3.426564000	4.044837000	0.733926000
H	-3.520380000	4.706453000	1.586692000
C	-1.499512000	-3.013422000	-3.749128000
H	-1.736560000	-3.662759000	-4.583167000
C	-4.522252000	-0.767095000	-1.900174000
H	-4.997147000	-1.741669000	-1.753199000
H	-4.529738000	-0.526490000	-2.965765000
H	-5.122865000	-0.021456000	-1.388528000
C	-3.327194000	3.703832000	-1.644720000
H	-3.340127000	4.097852000	-2.653728000
C	-3.457437000	4.561860000	-0.559048000
H	-3.578346000	5.626572000	-0.716912000
C	6.972798000	0.044559000	0.742277000
H	7.899840000	0.387214000	1.185121000
Cl	-0.500766000	-2.663293000	1.798800000

Complex **2** coordinates

Br	0.461685000	-3.046707000	-1.044689000
Cu	0.701675000	-0.763779000	-0.287051000
P	-1.325950000	0.310804000	-0.204329000
P	2.788234000	0.125250000	-0.132082000
N	0.883454000	-0.763453000	1.948743000
N	-3.441636000	-0.958174000	1.352803000
N	-2.440742000	-1.834610000	3.023380000

N	-3.601335000	-1.689970000	2.484593000
N	3.121584000	-0.157325000	1.569336000
C	2.147291000	-0.713539000	2.401470000
C	-2.430933000	0.231743000	-1.686960000
C	-2.123679000	-0.639915000	1.160644000
C	-1.490432000	-1.221228000	2.259580000
C	-2.241900000	-0.838973000	-2.567938000
H	-1.511889000	-1.608063000	-2.338802000
C	-4.623477000	-0.662610000	0.591645000
C	2.478229000	-1.189022000	3.682029000
H	3.495498000	-1.180954000	4.038334000
C	-1.461271000	2.064958000	0.376468000
C	-3.353738000	1.230179000	-2.008369000
H	-3.504601000	2.068683000	-1.342172000
C	3.086833000	1.941031000	-0.318707000
C	4.236306000	-0.647026000	-0.987972000
C	-0.096937000	-1.233083000	2.739202000
C	0.158622000	-1.708735000	4.025885000
H	-0.654534000	-2.083649000	4.627499000
C	4.093968000	-1.982687000	-1.380532000
H	3.155002000	-2.500340000	-1.214263000
C	-0.905073000	3.057751000	-0.438806000
H	-0.455896000	2.790225000	-1.388153000
C	-5.358347000	0.477315000	0.892710000
H	-5.007915000	1.157341000	1.657624000
C	-2.003670000	2.432712000	1.608830000
H	-2.417504000	1.681222000	2.268278000
C	-5.063701000	-1.569456000	-0.364060000
H	-4.481124000	-2.457844000	-0.568185000
C	-1.476328000	4.748320000	1.182171000

H	-1.484781000	5.785958000	1.492725000
C	-0.923016000	4.388878000	-0.044366000
H	-0.492379000	5.144162000	-0.690066000
C	3.200200000	2.477839000	-1.607295000
H	3.201944000	1.822937000	-2.470989000
C	5.439691000	0.017588000	-1.248975000
H	5.562800000	1.056649000	-0.971077000
C	3.063472000	2.810871000	0.772706000
H	2.946960000	2.416221000	1.773658000
C	-4.083872000	1.154814000	-3.188788000
H	-4.796831000	1.934540000	-3.428079000
C	1.466591000	-1.691212000	4.481383000
H	1.702927000	-2.069300000	5.468648000
C	-2.984058000	-0.913735000	-3.741804000
H	-2.829811000	-1.747605000	-4.415798000
C	-2.009558000	3.766835000	2.008795000
H	-2.433460000	4.035214000	2.969045000
C	5.147160000	-2.642584000	-2.006061000
H	5.022946000	-3.675377000	-2.307568000
C	4.474831000	-0.002274000	2.100736000
H	4.968365000	-0.967127000	2.251072000
H	4.456940000	0.537866000	3.050227000
H	5.073864000	0.573875000	1.402695000
C	-3.902559000	0.082467000	-4.056857000
H	-4.471101000	0.027292000	-4.977543000
C	6.342608000	-1.977719000	-2.256877000
H	7.158461000	-2.492322000	-2.750195000
C	-6.545344000	0.721502000	0.211481000
H	-7.125063000	1.606260000	0.443066000
C	6.485959000	-0.645090000	-1.880487000

H	7.412461000	-0.119821000	-2.079441000
C	3.315936000	4.708037000	-0.696422000
H	3.411638000	5.777114000	-0.841821000
C	-6.250171000	-1.317187000	-1.041853000
H	-6.597538000	-2.017343000	-1.790761000
C	3.320868000	3.849298000	-1.793123000
H	3.417338000	4.248016000	-2.795842000
C	3.182587000	4.185049000	0.584433000
H	3.167111000	4.845998000	1.442598000
C	-6.990374000	-0.174016000	-0.755467000
H	-7.917179000	0.015835000	-1.282647000

Coordinates for complex **3**

I	0.685027000	-2.793040000	-1.320540000
Cu	0.692583000	-0.450155000	-0.250095000
P	-1.382901000	0.377717000	-0.127331000
P	2.716118000	0.465493000	-0.067855000
N	-3.390573000	-1.136902000	1.320816000
N	-2.303685000	-2.182332000	2.844412000
N	0.877821000	-0.685985000	1.894930000
N	-3.499470000	-2.014083000	2.333714000
C	-2.107686000	-0.709698000	1.153474000
C	-2.558136000	0.403503000	-1.513911000
N	3.011065000	0.215104000	1.604950000
C	-4.624721000	-0.759230000	0.677883000
C	4.160755000	-0.419177000	-0.769929000
C	2.511121000	-1.086762000	3.603299000
H	3.389312000	-0.949414000	3.939239000
C	-2.377728000	-0.505931000	-2.576859000
H	-1.694425000	-1.162878000	-2.530869000

C	-3.555369000	1.376023000	-1.631471000
H	-3.664340000	2.020515000	-0.943310000
C	-1.412031000	-1.408513000	2.142756000
C	2.118330000	-0.532533000	2.379978000
C	3.219526000	2.770500000	-1.551334000
H	3.280427000	2.188195000	-2.301020000
C	-3.198493000	-0.438270000	-3.681340000
H	-3.077117000	-1.064870000	-4.385998000
C	-0.021889000	-1.377330000	2.645417000
C	-1.493286000	2.071785000	0.504628000
C	0.323421000	-1.981733000	3.826358000
H	-0.314633000	-2.498721000	4.304790000
C	-0.651523000	3.001594000	-0.152385000
H	-0.025253000	2.696916000	-0.798193000
C	3.021586000	2.245836000	-0.286491000
C	-2.385094000	2.541928000	1.464670000
H	-2.958014000	1.931782000	1.915401000
C	4.223495000	-1.772286000	-0.438863000
H	3.539090000	-2.161316000	0.094356000
C	-4.391117000	1.415340000	-2.744306000
H	-5.095230000	2.050931000	-2.786806000
C	-1.645182000	4.797297000	1.089899000
H	-1.713619000	5.726466000	1.272858000
C	2.910116000	3.128103000	0.790443000
H	2.750998000	2.782591000	1.662661000
C	-4.194384000	0.520009000	-3.794524000
H	-4.736161000	0.563411000	-4.574048000
C	5.163278000	0.138883000	-1.573472000
H	5.132476000	1.059958000	-1.800907000
C	-5.438052000	0.153510000	1.314319000

H	-5.151095000	0.571838000	2.116239000
C	-5.043242000	-1.400421000	-0.488985000
H	-4.489413000	-2.045051000	-0.911548000
C	6.192333000	-0.656344000	-2.031517000
H	6.861548000	-0.281083000	-2.594012000
C	-2.445179000	3.889478000	1.765170000
H	-3.038829000	4.197431000	2.440011000
C	5.281136000	-2.553163000	-0.882546000
H	5.338294000	-3.471026000	-0.642941000
C	-6.268145000	-1.080548000	-1.010170000
H	-6.553805000	-1.483858000	-1.821721000
C	6.259811000	-1.971469000	-1.688216000
H	6.984656000	-2.499489000	-2.001793000
C	-6.685464000	0.454889000	0.773970000
H	-7.253328000	1.091431000	1.191244000
C	-0.731061000	4.329373000	0.131736000
H	-0.165703000	4.944017000	-0.320305000
C	3.330788000	4.142407000	-1.735597000
H	3.456757000	4.490221000	-2.610464000
C	1.591747000	-1.834528000	4.309017000
H	1.840765000	-2.245769000	5.128270000
C	4.344082000	0.487364000	2.172248000
H	4.819860000	-0.359246000	2.308569000
H	4.245066000	0.947688000	3.031658000
H	4.853506000	1.052709000	1.554323000
C	3.024354000	4.479723000	0.612477000
H	2.944186000	5.069803000	1.353504000
C	3.262766000	4.990991000	-0.685620000
H	3.372427000	5.923954000	-0.817413000
C	-7.077347000	-0.186964000	-0.378804000

H -7.935216000 -0.002083000 -0.742730000

References

1. Z. Li, C. Brouwer and C. He, *Chem. Rev.*, 2008, **108**, 3239-3265.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
3. G. Sheldrick, *Acta Crystallographica Section A*, 2015, **71**, 3-8.
4. , M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, revision D.01, Gaussian, Inc., Wallingford, CT, 2013. .
5. L. Radhakrishna, B. S. Kote, H. S. Kunchur, M. K. Pandey, D. Mondal and M. S. Balakrishna, *Dalton Trans.*, 2022, **51**, 5480-5493.
6. M. González-Lainez, M. Gallegos, J. Munarriz, R. Azpiroz, V. Passarelli, M. V. Jiménez and J. J. Pérez-Torrente, *Organometallics*, 2022, **41**, 2154-2169.
7. R. Ray and J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2021, **60**, 8203-8211.
8. Z. Chen, Q. Yan, Z. Liu, Y. Xu and Y. Zhang, *Angew. Chem. Int. Ed.*, 2013, **52**, 13324-13328.
9. S. Sun, R. Bai and Y. Gu, *Chem. Eur. J.*, 2014, **20**, 549-558.
10. Y. Monguchi, K. Nozaki, T. Maejima, Y. Shimoda, Y. Sawama, Y. Kitamura, Y. Kitade and H. Sajiki, *Green Chem.*, 2013, **15**, 490-495.
11. E. Loukopoulos, A. Abdul-Sada, G. Csire, C. Kállay, A. Brookfield, G. J. Tizzard, S. J. Coles, I. N. Lykakis and G. E. Kostakis, *Dalton Trans.*, 2018, **47**, 10491-10508.
12. Q. Zhou, Z. Fu, L. Yu and J. Wang, *Asian J. Org. Chem.*, 2019, **8**, 646-649.
13. D. Drelinkiewicz and R. J. Whitby, *RSC Adv.*, 2022, **12**, 28910-28915.
14. Y. D. Bidal, M. Lesieur, M. Melaimi, F. Nahra, D. B. Cordes, K. S. Athukorala Arachchige, A. M. Z. Slawin, G. Bertrand and C. S. J. Cazin, *Adv. Synth. Catal.*, 2015, **357**, 3155-3161.
15. S. Díez-González, A. Correa, L. Cavallo and S. P. Nolan, *Eur. J. Chem.*, 2006, **12**, 7558-7564.
16. S. Katam and P. Ganesan, *Dalton Trans.*, 2017, **46**, 16615-16622.
17. J. H. Kim and S. Kim, *RSC Adv.*, 2014, **4**, 26516-26523.
18. A. Punzi, N. Zappimbulso and G. M. Farinola, *Eur. J. Org. Chem.*, 2020, **2020**, 3229-3234.
19. M. M. Obadia, B. P. Mudraboyina, A. Serghei, T. N. T. Phan, D. Gigmes and E. Drockenmuller, *ACS Macro Lett.*, 2014, **3**, 658-662.
20. L. Zheng, Y. Wang, X. Meng and Y. Chen, *Catal. Commun.*, 2021, **148**, 106165.
21. Á. Beltrán, I. Gata, C. Maya, J. Avó, J. C. Lima, C. A. T. Laia, R. Peloso, M. Outis and M. C. Nicasio, *Inorg. Chem.*, 2020, **59**, 10894-10906.