Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information 1

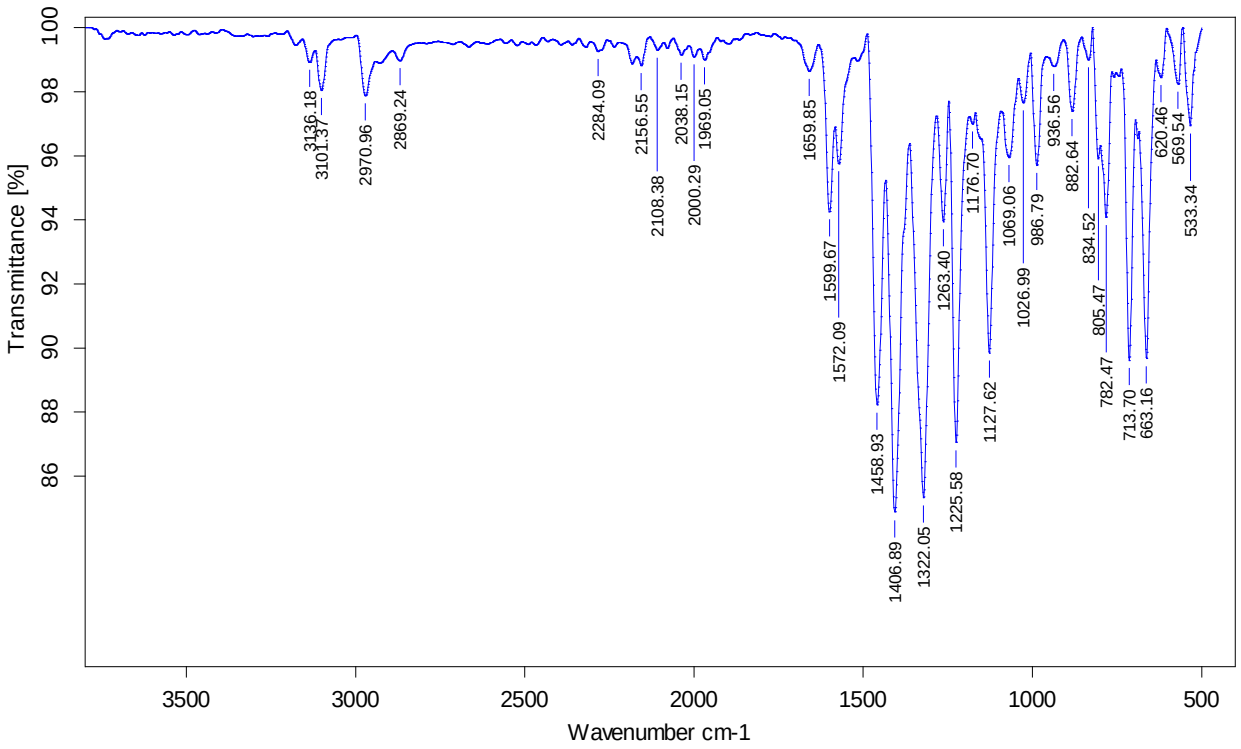



**Fig. S1**. Neat FT-IR spectrum of **Bptp** at room temperature.

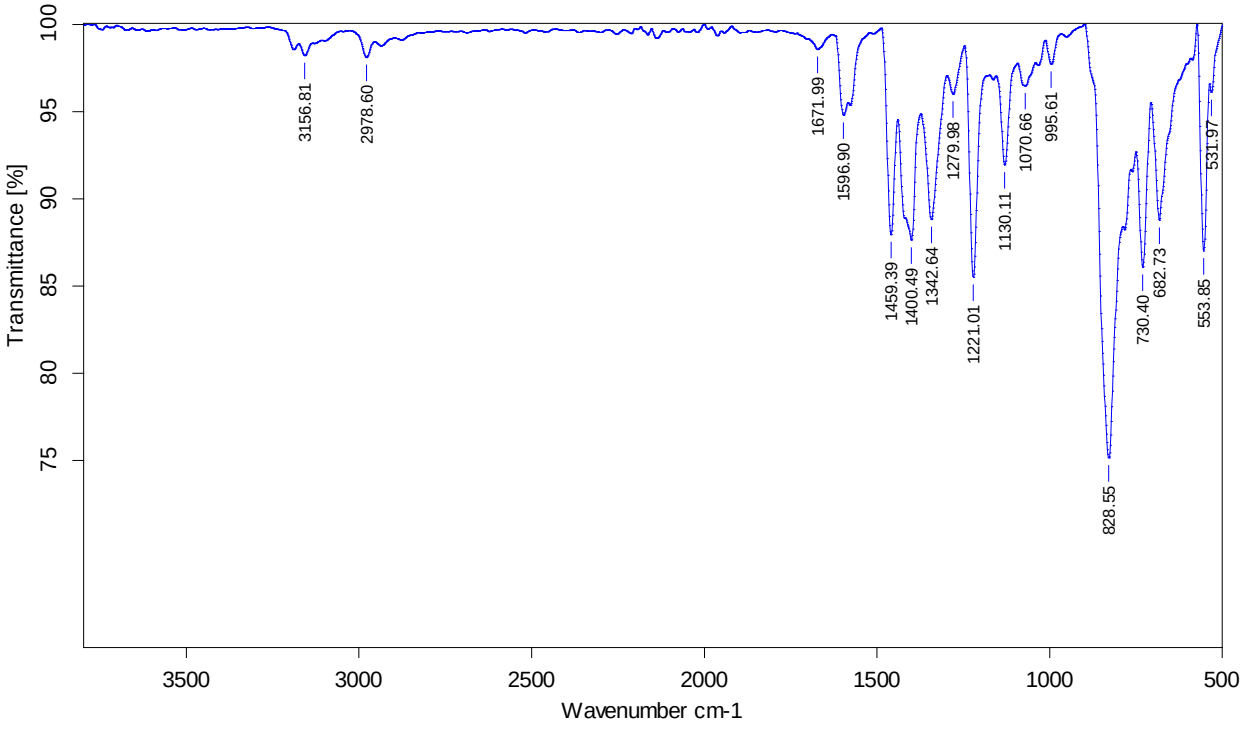



**Fig. S2**. Neat FT-IR spectrum of **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$ (1)** at room temperature.

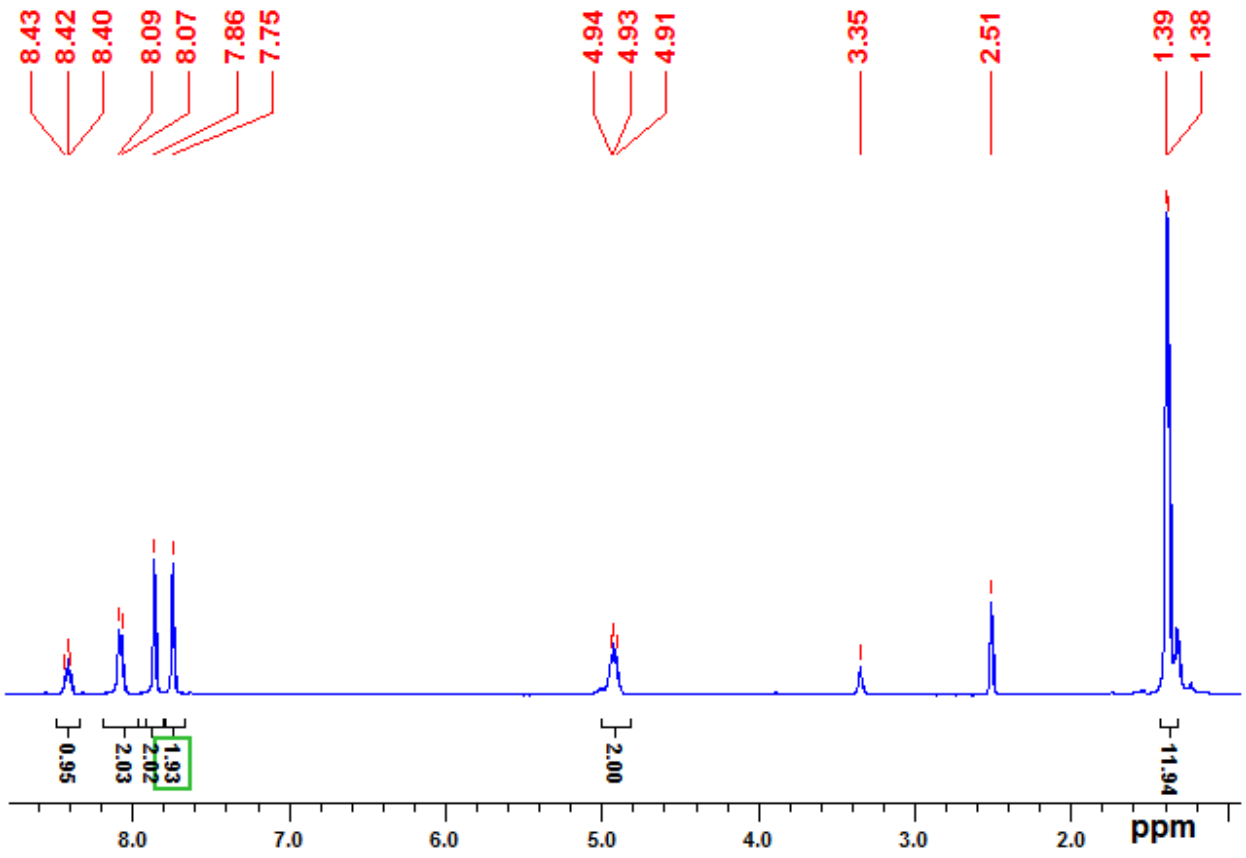



**Fig. S3**. $^{1}$H NMR spectrum of **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$** in DMSO-$d_6$ at room temperature.

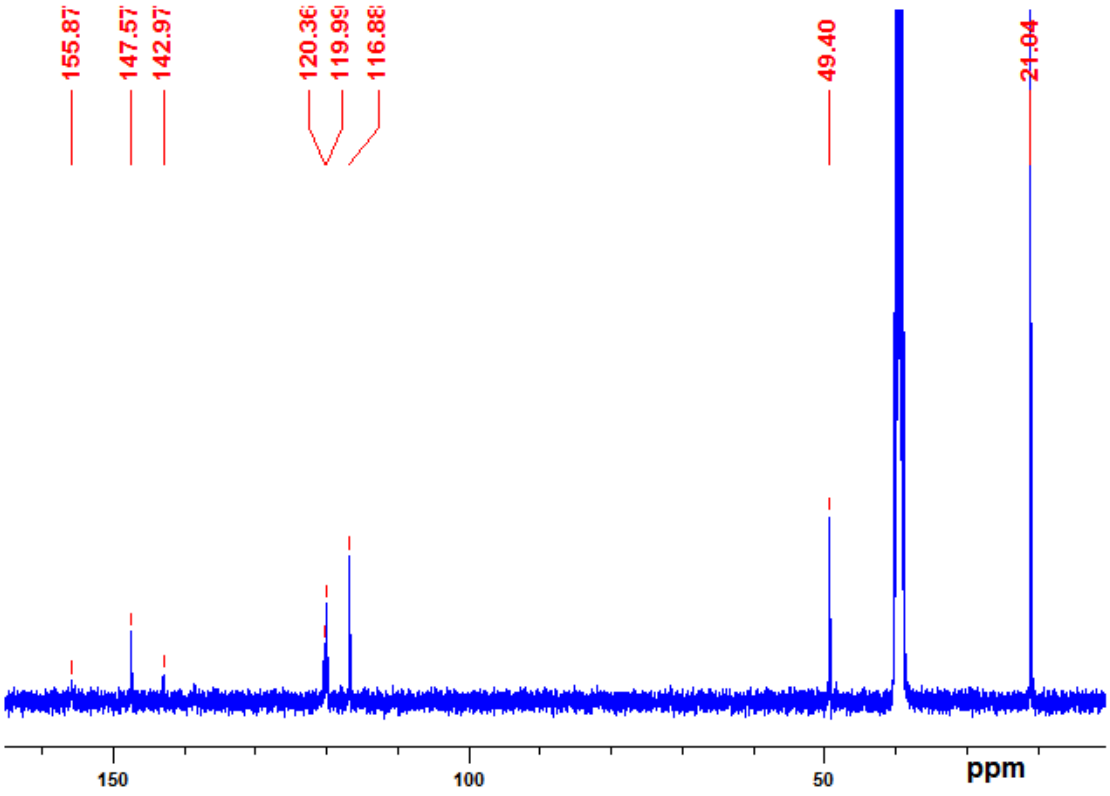



**Fig. S4**. $^{13}$C NMR spectrum of **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$** in DMSO-$d_6$ at room temperature.

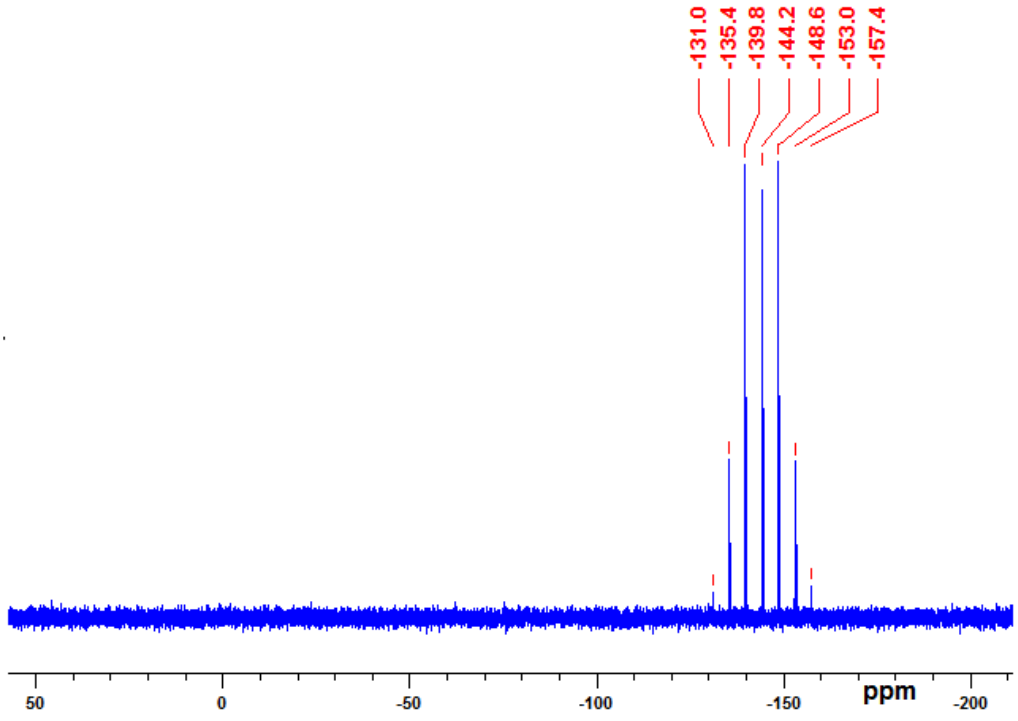



**Fig. S5**. $^{31}$P NMR spectrum of **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$** in DMSO-$d_6$ at room temperature.

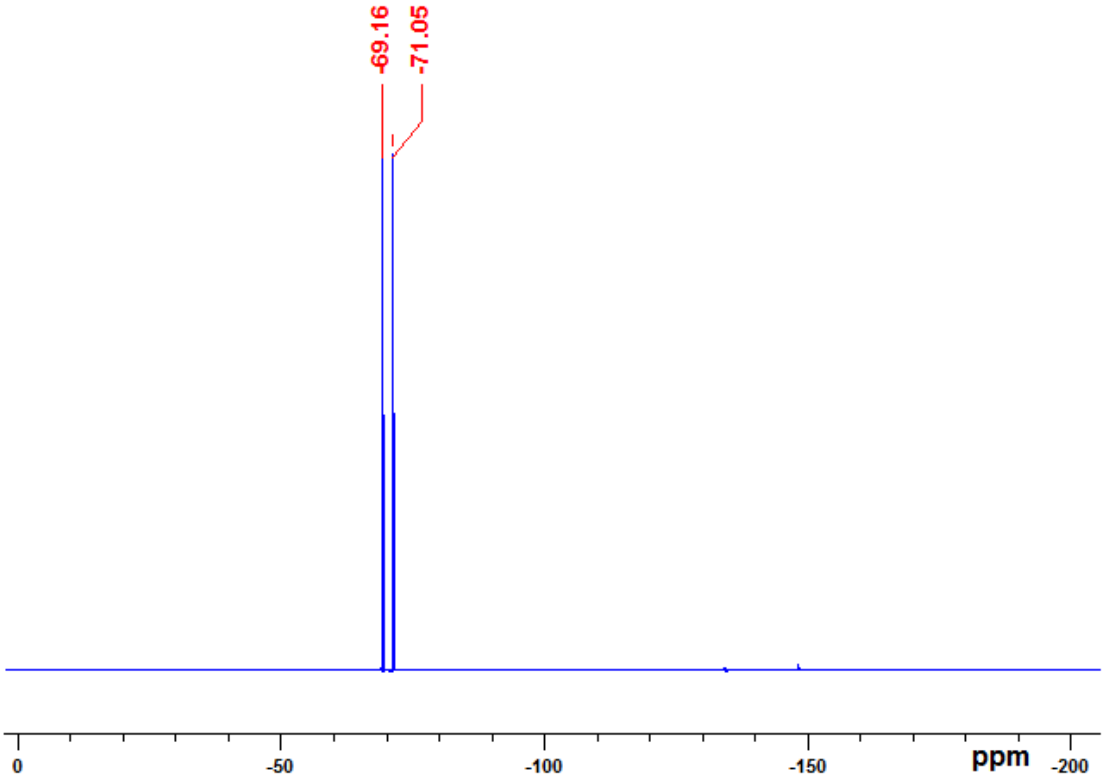



**Fig. S6**. $^{19}$F NMR spectrum of **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$** in DMSO-$d_6$ at room temperature.

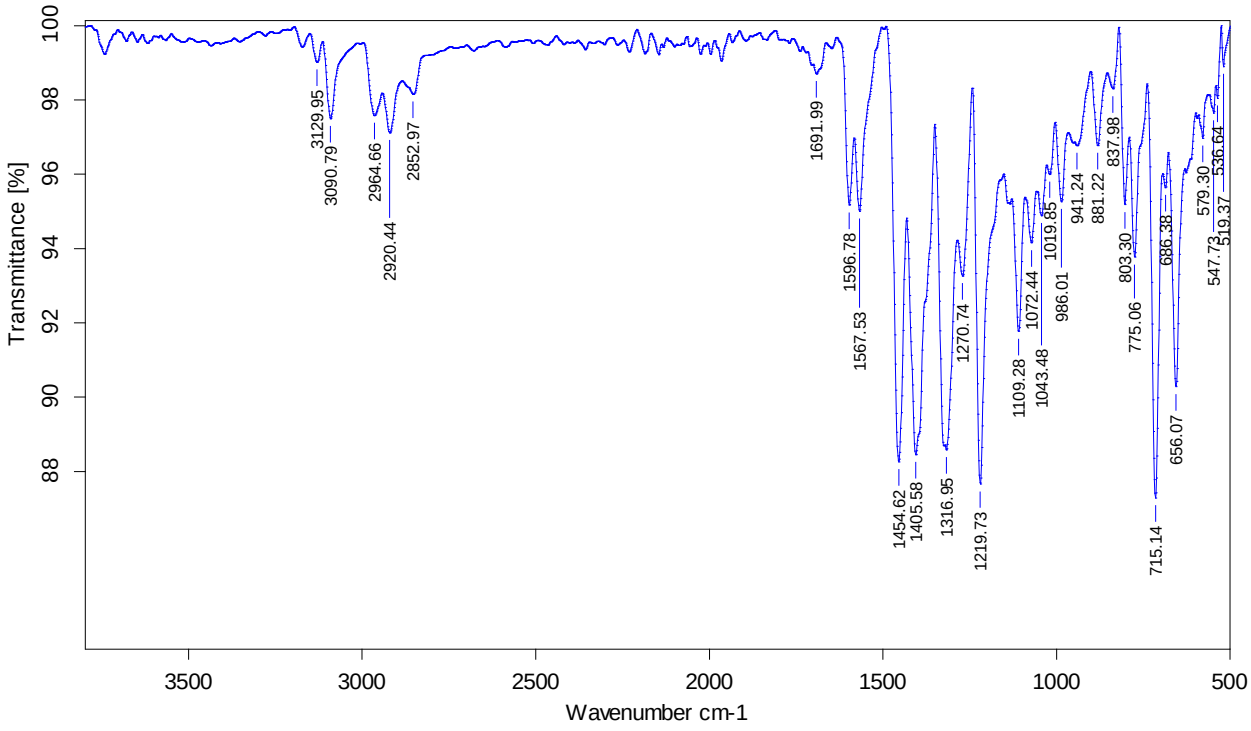



**Fig. S7**. Neat FT-IR spectrum of **Bpsp** at room temperature.

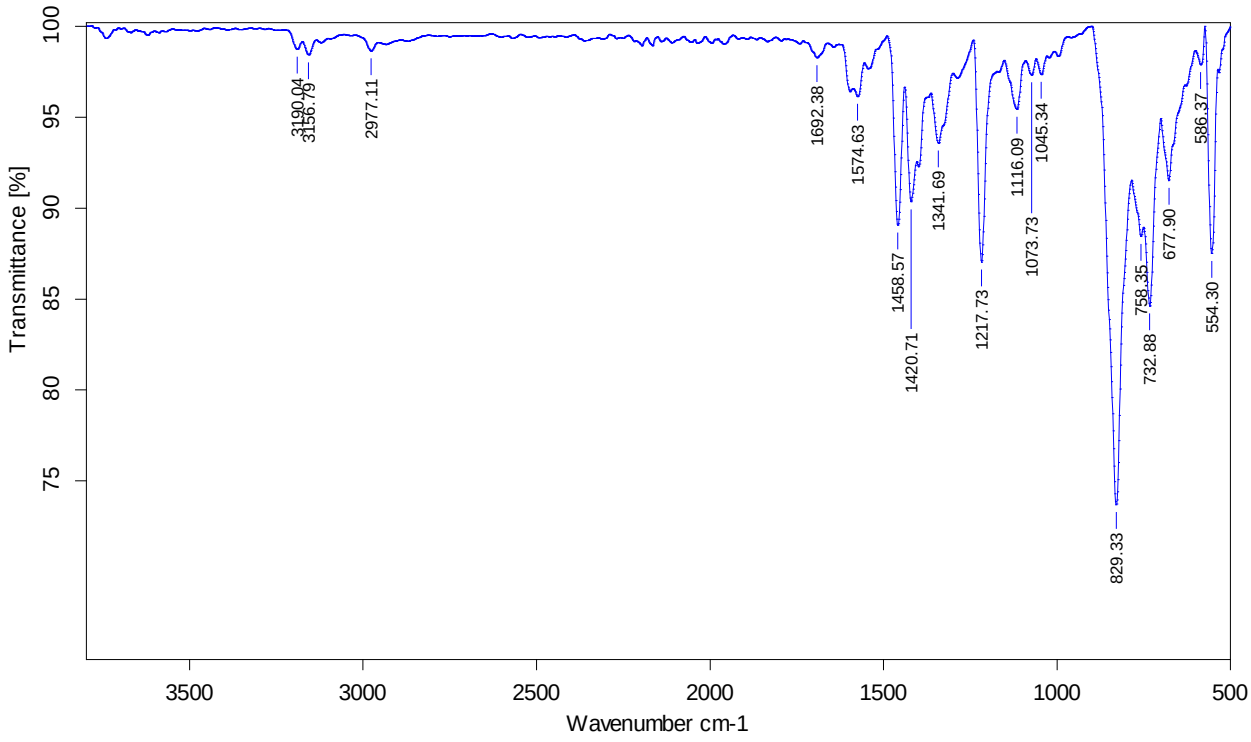



**Fig. S8**. Neat FT-IR spectrum of **{(Bpsp)$_{12}$Cu$_8$}(PF$_6$)$_8$ (2)** at room temperature.

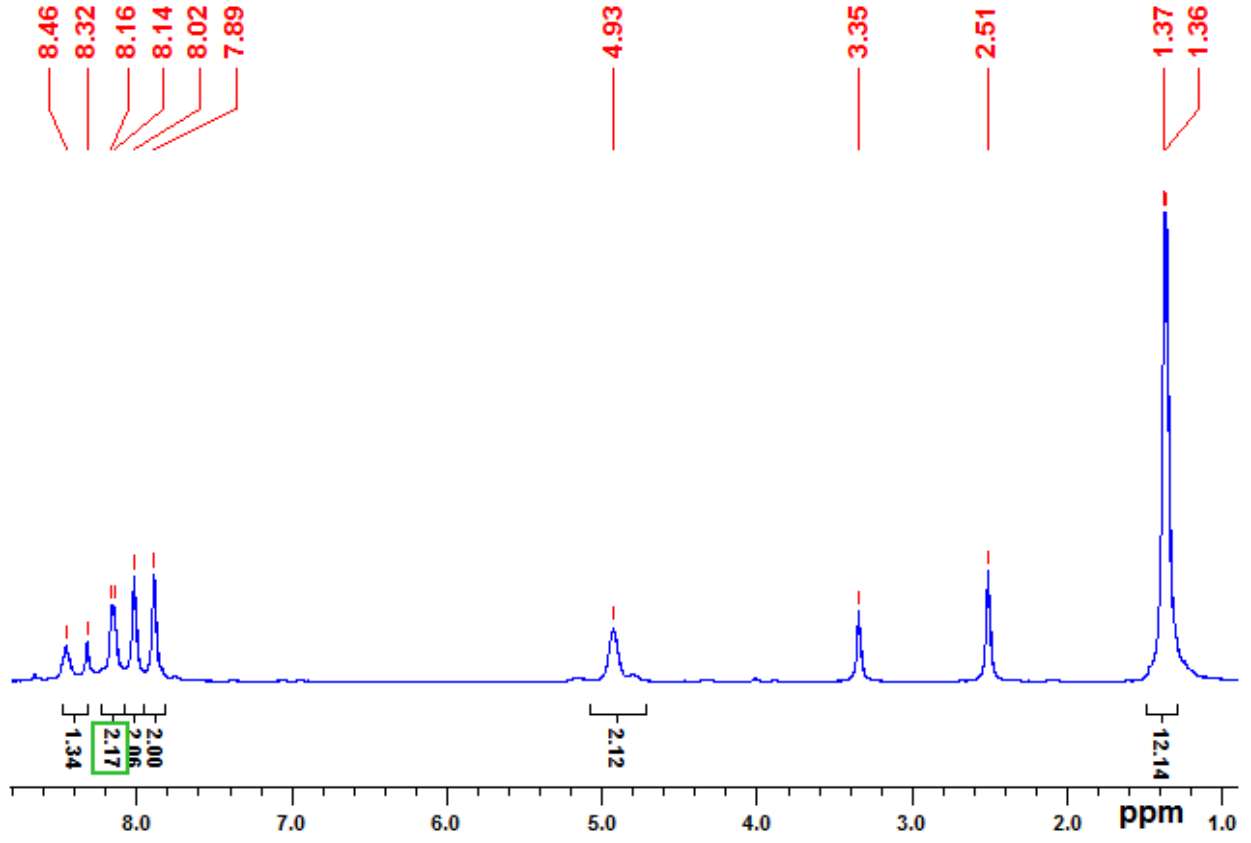


**Fig. S9**. $^{1}$H NMR spectrum of **{(Bpsp)$_{12}$Cu$_8$}(PF$_6$)$_8$** in DMSO-$d_6$ at room temperature.

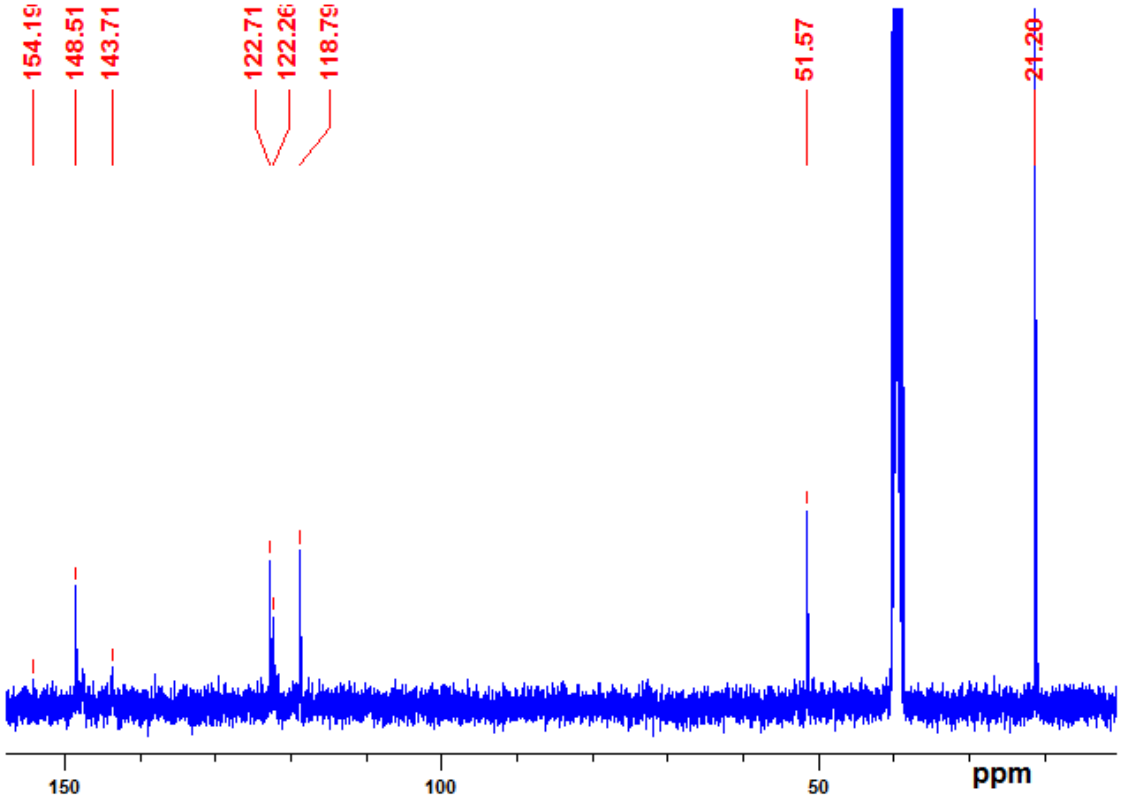



**Fig. S10**. $^{13}$C NMR spectrum of **{(Bpsp)$_{12}$Cu$_8$}(PF$_6$)$_8$** in DMSO-$d_6$ at room temperature.

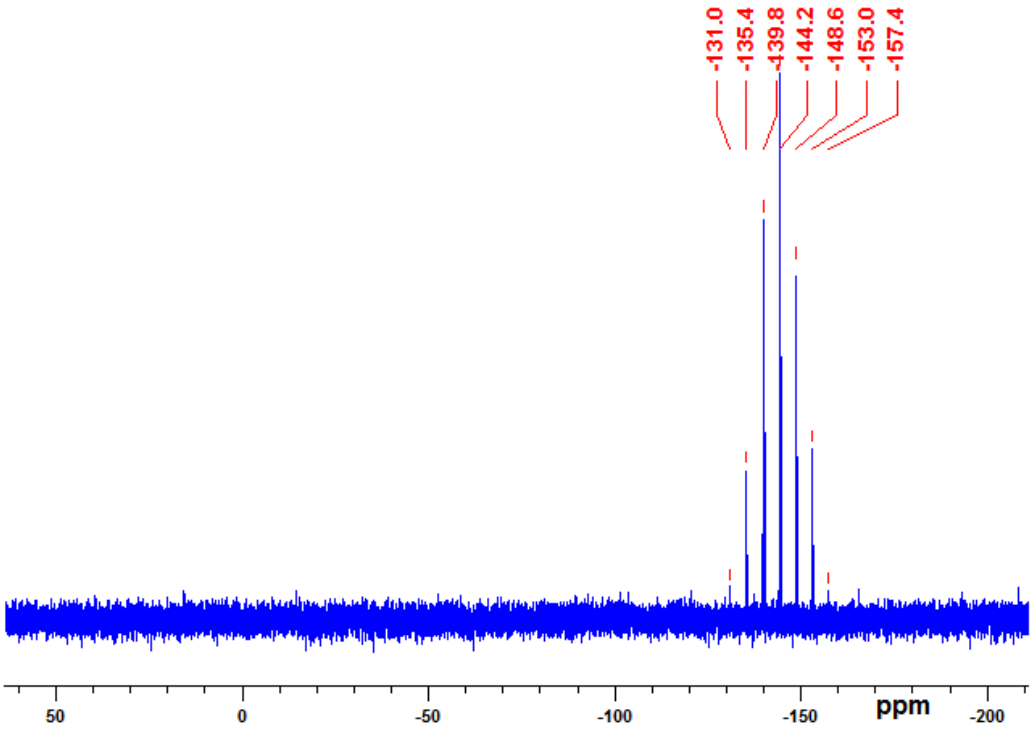



**Fig. S11**. $^{31}$P NMR spectrum of **{(Bpsp)$_{12}$Cu$_8$}(PF$_6$)$_8$** in DMSO-$d_6$ at room temperature.

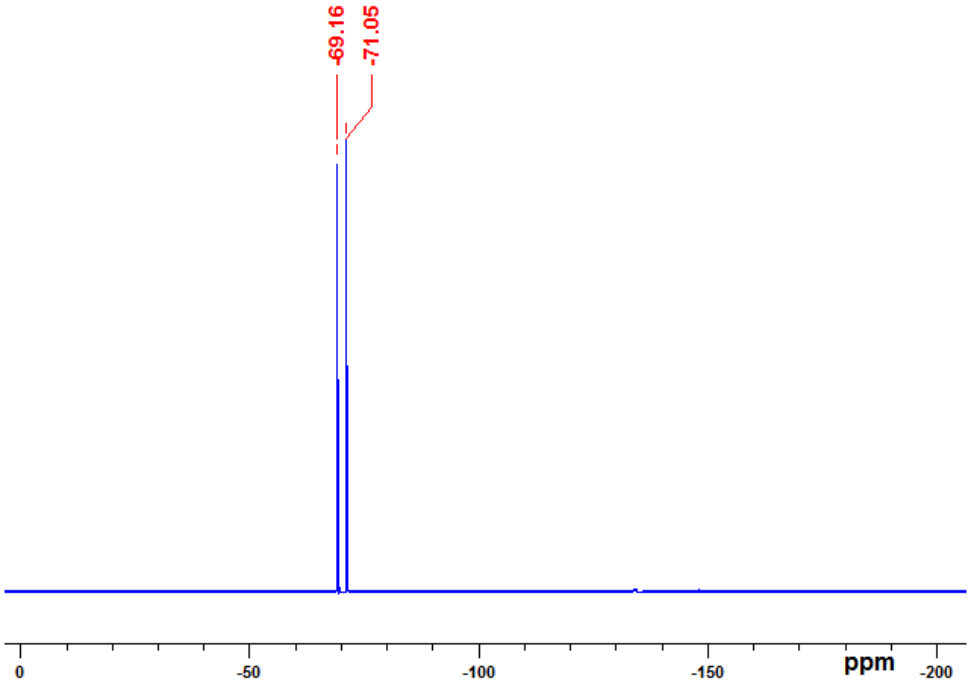



**Fig. S12**. $^{19}$F NMR spectrum of **{(Bpsp)$_{12}$Cu$_8$}(PF$_6$)$_8$** in DMSO-$d_6$ at room temperature.

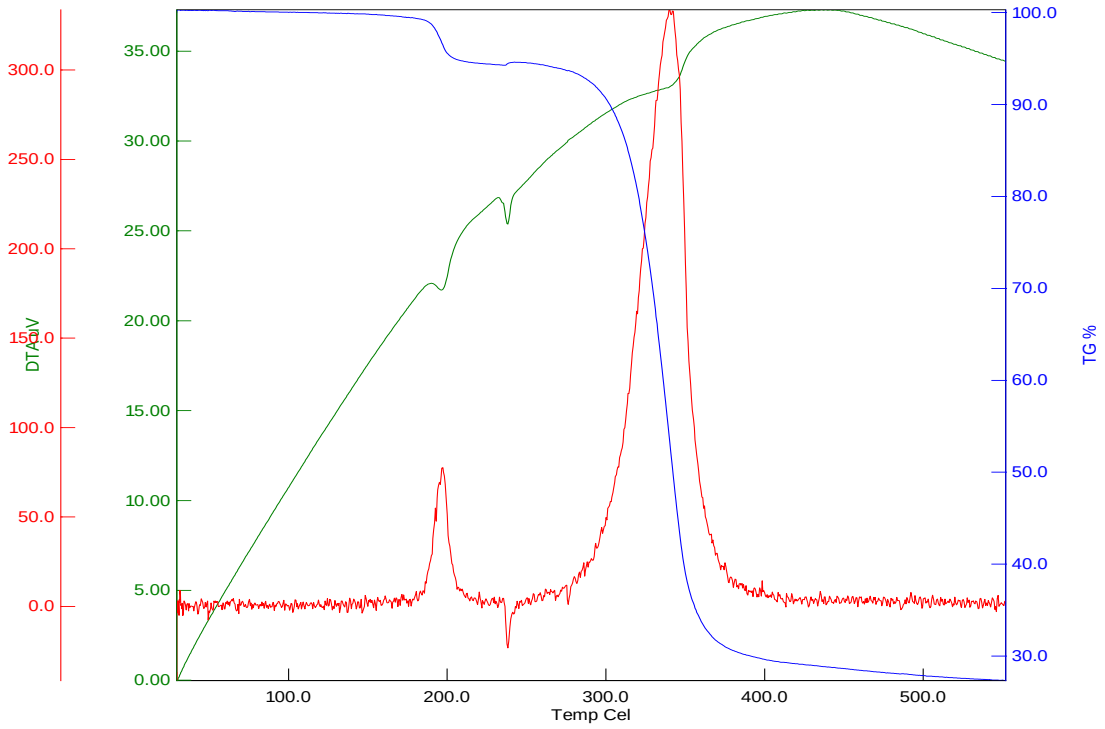



**Fig. S13**. TG-DTA plots for **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$** from room temperature to 550 $^{o}$C.

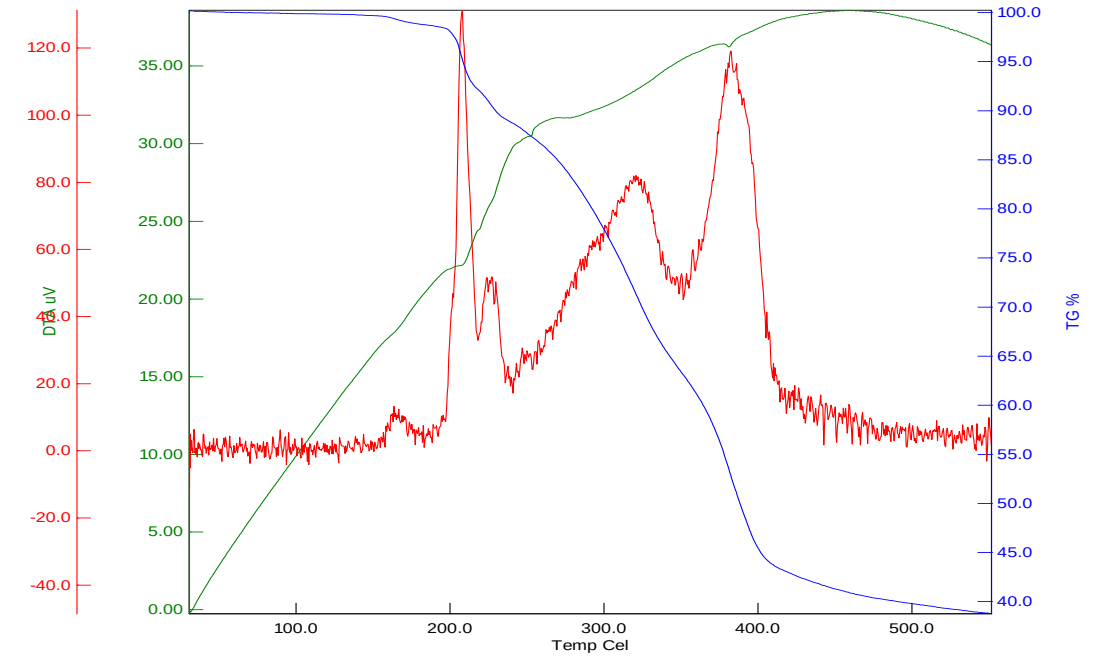
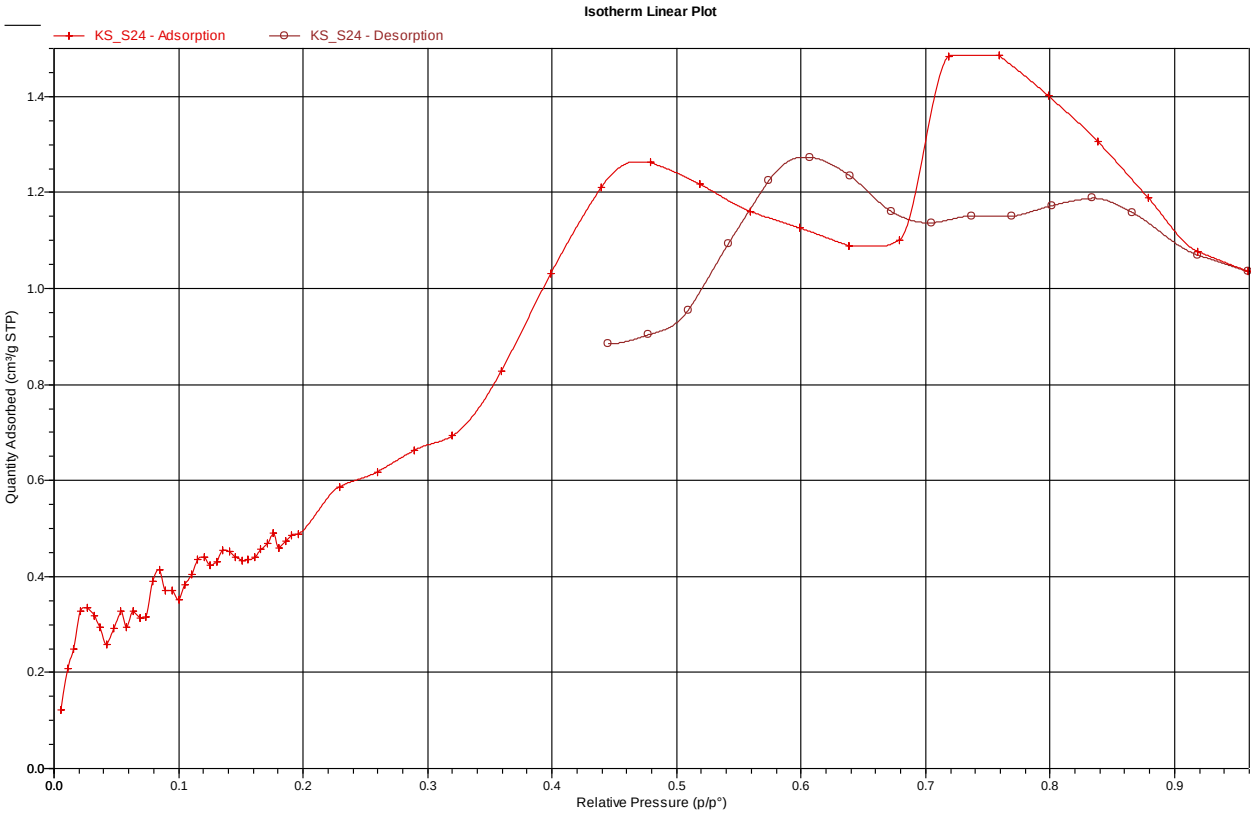



**Fig. S14**. TG-DTA plots for **{(Bpsp)$_{12}$Cu$_8$}(PF$_6$)$_8$** from room temperature to 550 $^{o}$C.

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3Flex 3.01 | 3Flex Version 3.01 Serial # 387 Unit 1 Port 1 | Page 1

Sample: KS_S24
Operator: Raghav
Submitter: Raghav
File: D:\Dropbox\RUB characterizations\...\KS_S24_N2_77K.SMP

**Summary Report**

**Surface Area**

Single point surface area at p/p° = 0.300000000: 2.0515 m²/g

BET Surface Area: 1.2395 m²/g

**BET Report**

| | |
|---|---|
| BET surface area: | 1.2395 ± 0.0913 m²/g |
| Slope: | 3.514942 ± 0.258222 g/cm³ STP |
| Y-intercept: | -0.003399 ± 0.012309 g/cm³ STP |
| C: | -1033.222384 |
| Qm: | 0.2848 cm³/g STP |
| Correlation coefficient: | 0.9790870 |
| Molecular cross-sectional area: | 0.1620 nm² |

| Relative Pressure (p/p°) | Quantity Adsorbed (cm³/g STP) | 1/[Q(p°/p - 1)] |
|---|---|---|
| 0.021303849 | 0.3280 | 0.066363 |
| 0.026627860 | 0.3349 | 0.081677 |
| 0.031975046 | 0.3192 | 0.103474 |
| 0.037268006 | 0.2940 | 0.131647 |
| 0.042533615 | 0.2588 | 0.171664 |
| 0.047826782 | 0.2915 | 0.172335 |
| 0.053203114 | 0.3266 | 0.172054 |
| 0.058478394 | 0.2944 | 0.210950 |
| 0.063673808 | 0.3271 | 0.207886 |
| 0.068897001 | 0.3136 | 0.235972 |

**Langmuir Report**

Langmuir surface area: 6.9844 ± 0.4274 m²/g
Slope: 0.623184 ± 0.038137 g/cm³ STP
Y-intercept: 17.9972 ± 1.4480 kPa·g/cm³ STP
b: 0.03463 1/kPa
Qm: 1.6047 cm³/g STP
Correlation coefficient: 0.909195
Molecular cross-sectional area: 0.1620 nm²

| Pressure (kPa) | Quantity Adsorbed (cm³/g STP) | p/Q (kPa·g/cm³ STP) |
|---|---|---|
| 0.5368823 | 0.1223 | 4.3894 |
| 1.0715618 | 0.2080 | 5.1509 |
| 1.6060565 | 0.2497 | 6.4309 |
| 2.1381649 | 0.3280 | 6.5186 |
| 2.6728996 | 0.3349 | 7.9804 |
| 3.2096723 | 0.3192 | 10.0546 |
| 3.7402440 | 0.2940 | 12.7198 |
| 4.2690082 | 0.2588 | 16.4968 |
| 4.8002091 | 0.2915 | 16.4694 |
| 5.3393250 | 0.3266 | 16.3483 |
| 5.8684452 | 0.2944 | 19.9313 |
| 6.3890131 | 0.3271 | 19.5310 |
| 6.9146022 | 0.3136 | 22.0508 |
| 7.4368530 | 0.3167 | 23.4811 |
| 7.9626547 | 0.3909 | 20.3720 |
| 8.4898052 | 0.4132 | 20.5447 |
| 9.0096737 | 0.3711 | 24.2767 |
| 9.5324377 | 0.3701 | 25.7575 |
| 10.0491973 | 0.3520 | 28.5488 |
| 10.5654818 | 0.3831 | 27.5804 |
| 11.0782399 | 0.4034 | 27.4648 |
| 11.5876260 | 0.4342 | 26.6853 |
| 12.0993526 | 0.4395 | 27.5316 |
| 12.6098820 | 0.4234 | 29.7817 |
| 13.1215131 | 0.4318 | 30.3903 |
| 13.6334919 | 0.4557 | 29.9148 |
| 14.1342006 | 0.4515 | 31.3044 |
| 14.6371084 | 0.4412 | 33.1736 |
| 15.1384660 | 0.4339 | 34.8909 |
| 15.6499780 | 0.4351 | 35.9706 |
| 16.1516174 | 0.4392 | 36.7769 |
| 16.6633175 | 0.4558 | 36.5623 |
| 17.1645734 | 0.4688 | 36.6109 |
| 17.6686540 | 0.4903 | 36.0373 |

**Fig. S15**. Neat BET surface area analysis on **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$**.

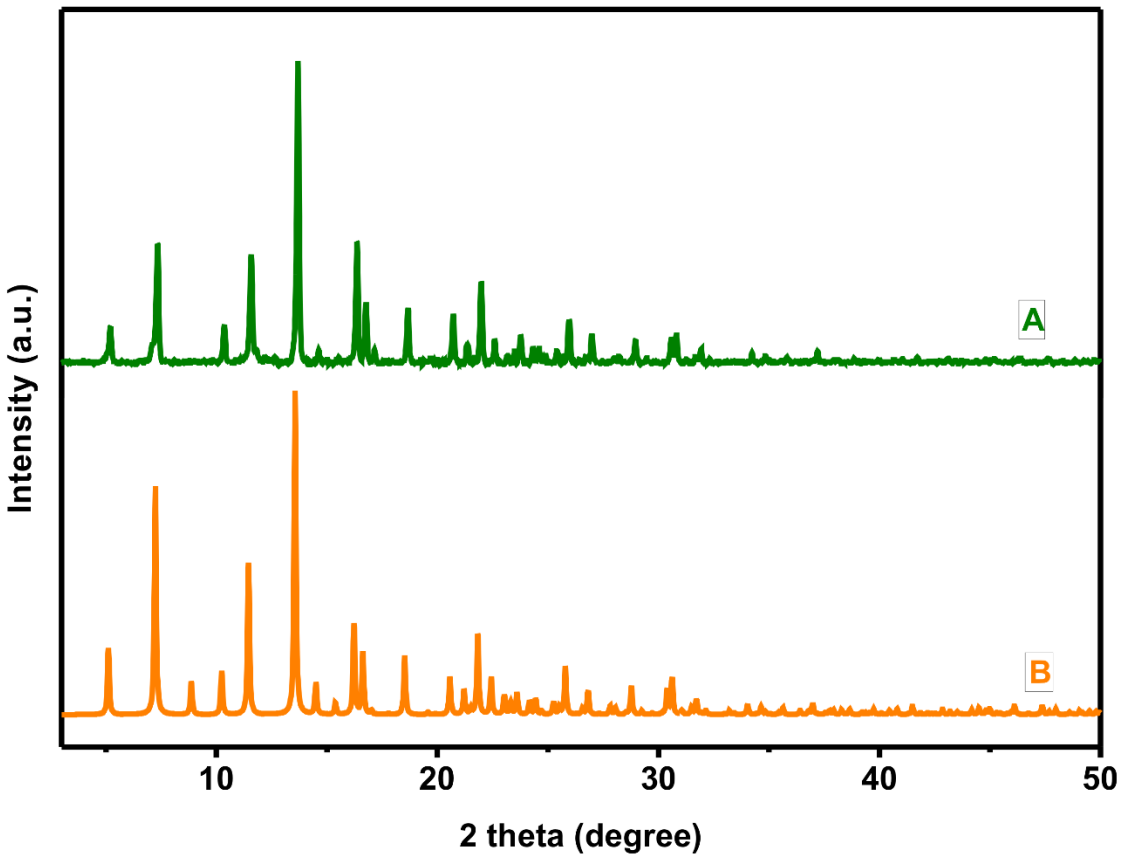



**Fig. S16**. Experimental powder X-ray diffraction pattern (A) of **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$** vs. simulated powder pattern (B) for **{(Bptp)$_{12}$Cu$_8$}(PF$_6$)$_8$**.

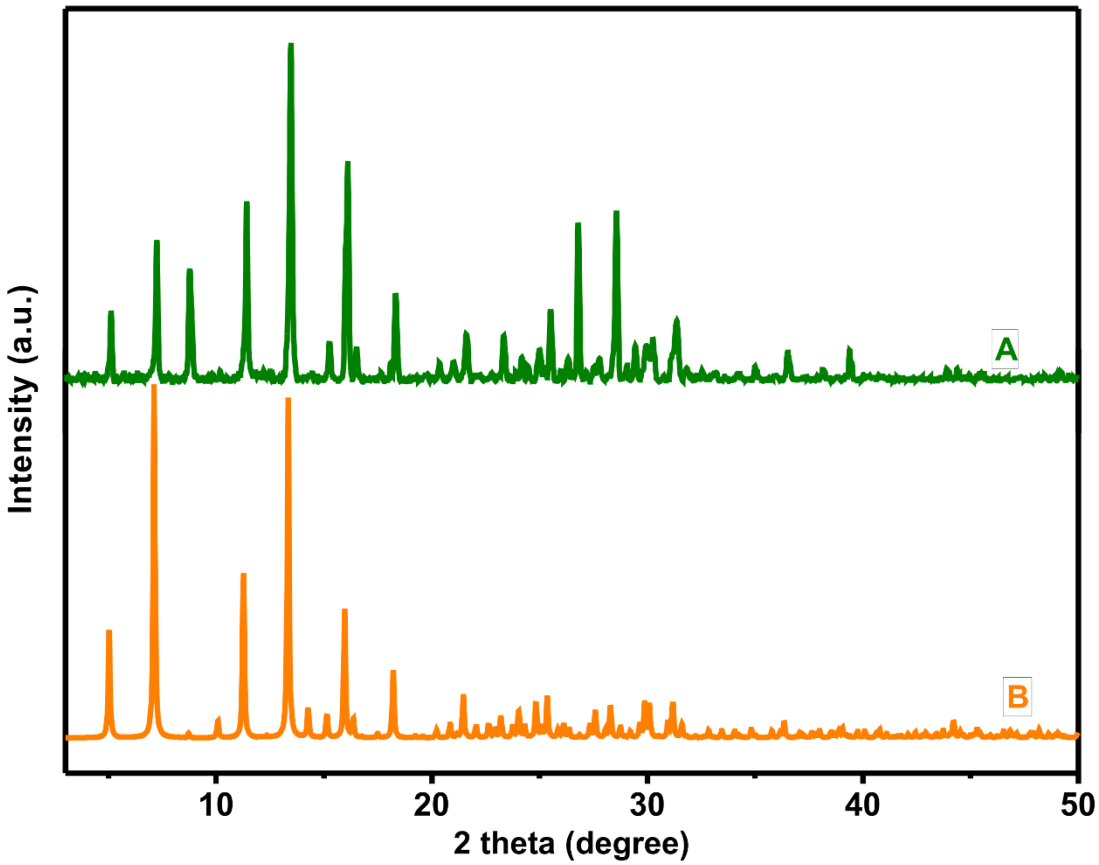



**Fig. S17**. Experimental powder X-ray diffraction pattern (A) of **{(Bpsp)$_{12}$Cu$_8$}(PF$_6$)$_8$** vs. simulated powder pattern (B) for **{(Bpsp)$_{12}$Cu$_8$}(PF$_6$)$_8$**.

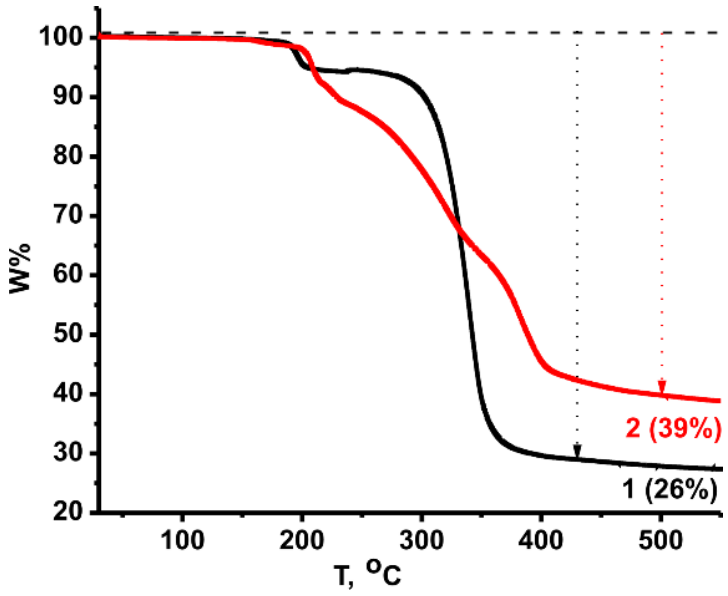


**Fig. S18.** TGA curves of **1** and **2** from 30 to 550 °C under a nitrogen atmosphere with a heating rate of 10 °C $min^{-1}$. For 1: residual wt 26%, calc. wt 23%; For 2: residual wt 39%, calc. wt 40%.

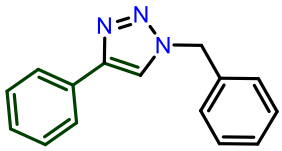
**Table S1.** Structural parameters of compounds **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{72}H_{88}N_{24}F_{48}P_8S_{24}Cu_8$ | $C_{72}H_{88}N_{24}F_{24}P_{16}Cu_8Se_{16}$ |
| Formula weight | 5837.38 | 6817.85 |
| Temperature (K) | 298 | 298 |
| Crystal system | cubic | cubic |
| Space group | *Pn-3n* | *Pn-3n* |
| *a*/Å | 24.4090(3) | 24.82051(14) |
| *b*/Å | 24.4090(3) | 24.82051(14) |
| *c*/Å | 24.4090(3) | 24.82051(14) |
| α/° | 90 | 90 |
| *β*/° | 90 | 90 |
| *γ*/° | 90 | 90 |
| Volume (Å$^3$) | 14542.9(3) | 15290.87(15) |
| *Z* | 2 | 2 |
| $\rho_{calc}$/mg mm$^{-3}$ | 1.3329 | 14807 |
| Absorption coefficient ($\mu$/mm$^{-1}$) | 3.301 | 4.785 |
| *F*(000) | 5995.9 | 6666.0 |
| Reflections collected | 10421 | 12189 |
| $R_{int}$ | 0.0266 | 0.0288 |
| GOF on $F^2$ | 1.005 | 1.011 |
| $R_1$ ($I>2\sigma(I)$) | 0.0410 | 0.0359 |
| w$R_2$ ($I>2\sigma(I)$) | 0.1338 | 0.0893 |
| $R_1$ values (all data) | 0.0496 | 0.0478 |
| $R_2$ values (all data) | 0.1432 | 0.0979 |

# Supporting Information 2

**Cu(I) catalysts catalyzed azide–alkyne cycloaddition reactions (CuAAC).** Catalyst **1** or **2** (1 mol%), azide (1 mmol) and terminal alkyne (1.2 mmol) were placed in an oven dried schlenk flask. The reaction mixture was then allowed to stir at room temperature and the progress of the reaction was monitored by thin layer chromatography. The solid mass obtained was dissolved in ethyl acetate and passed through silica gel column. The solvent has been removed by rotary evaporator and the residue washed several times with n-hexane yielded pure desired products. All the isolated products were well characterized by $^{1}$H and $^{13}$C NMR and few products (**Ia**, **Ib**, **IIa** and **IIb**) were also characterized by single crystal X-ray diffraction analysis.

**1. 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (Ia)**




$^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.80-7.89 (d, 2H), 7.66 (s, 1H), 7.40-7.35 (m, 5H), 7.31-7.28 (m, 3H), 5.54 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.23, 134.72, 130.55, 129.17, 128.83, 128.80, 128.19, 128.07, 125.71, 119.59, 54.22 ppm.

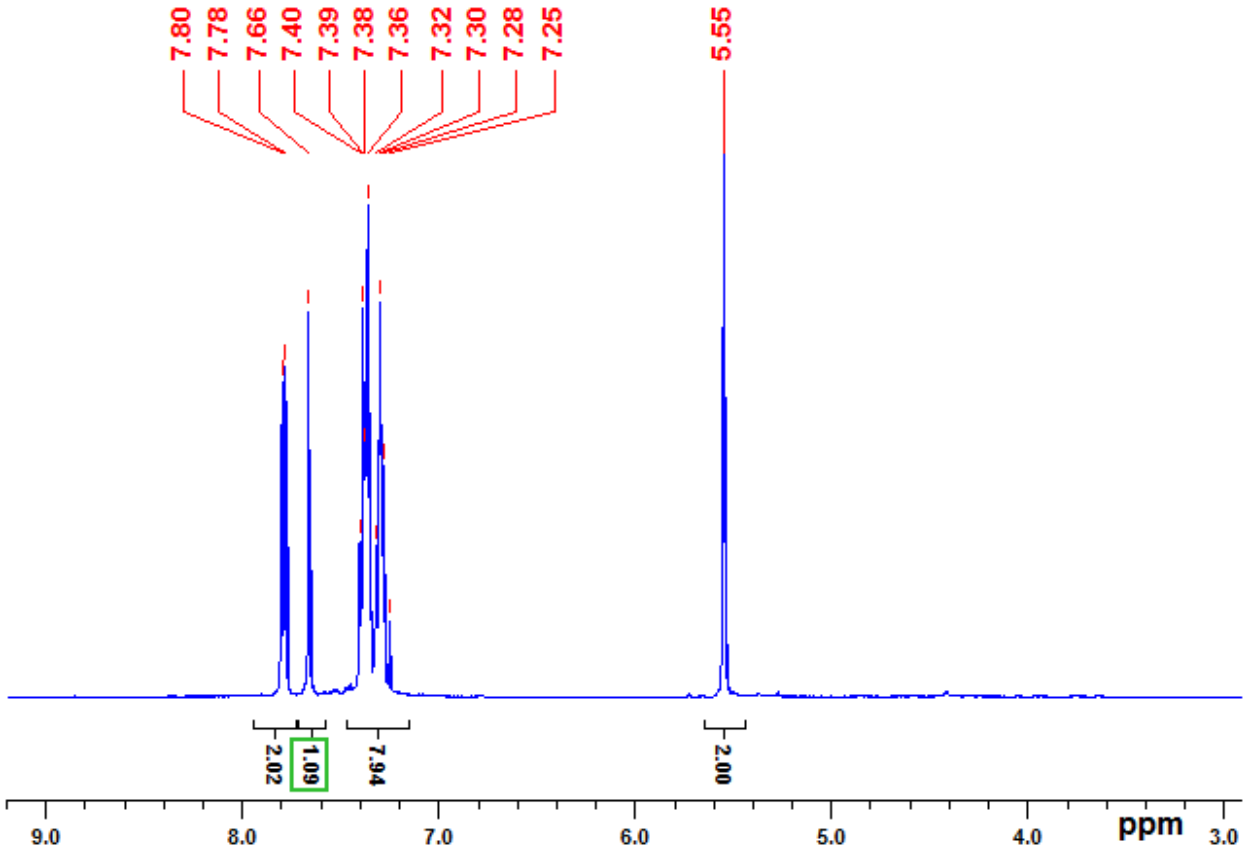



**Fig. S1**. $^{1}H$ NMR spectrum of **1a** in $CDCl_3$ at room temperature.

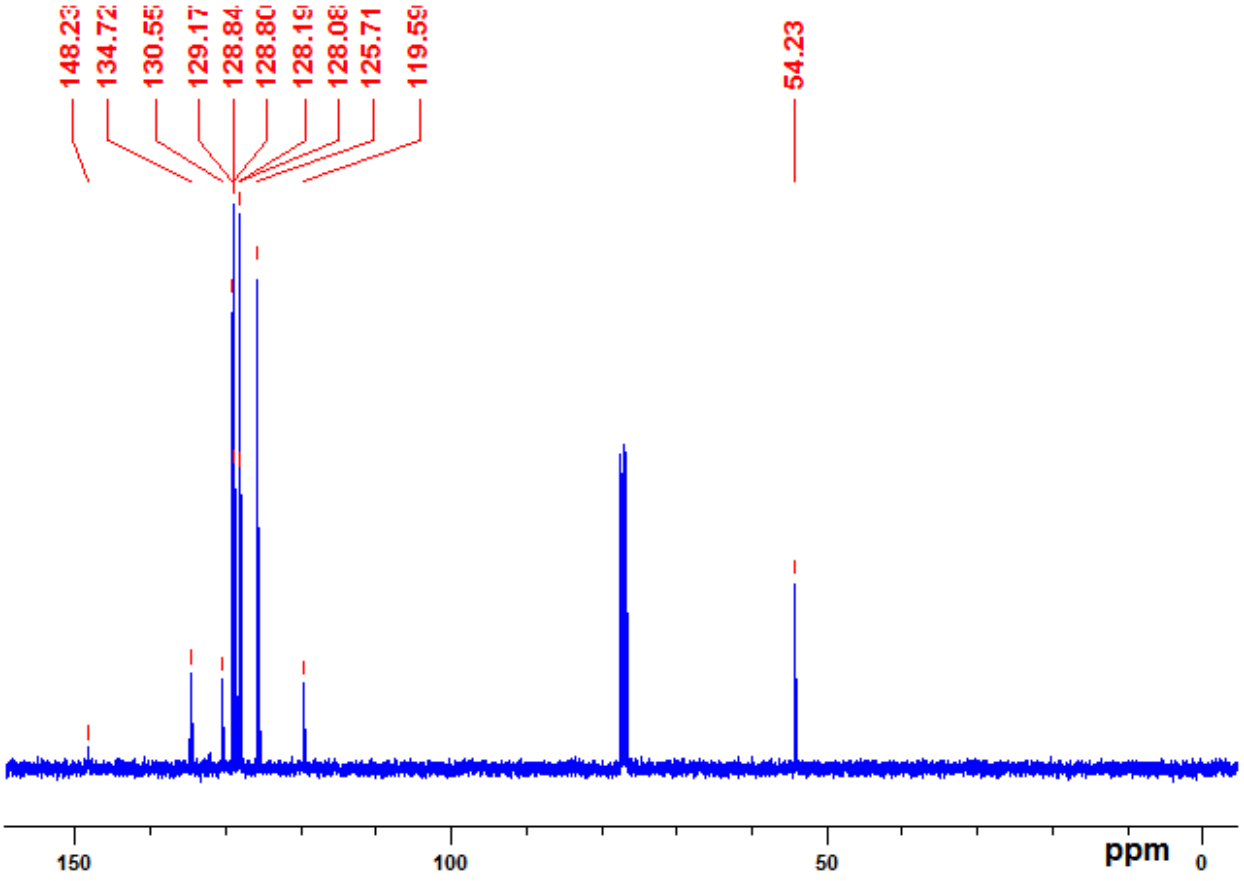
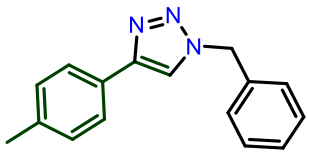



**Fig. S2**. $^{13}$C NMR spectrum of **Ia** in $CDCl_3$ at room temperature.

**2. 1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (Ib)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.68-7.66 (d, 2H), 7.61 (s, 1H), 7.37-7.36 (t, 3H), 7.30-7.28 (m, 2H), 7.20-7.18 (d, 2H), 5.54 (s, 2H), 2.35 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.34, 138.02, 134.77, 129.50, 129.15, 128.76, 128.07, 127.73, 125.61, 119.21, 54.20, 21.31 ppm.

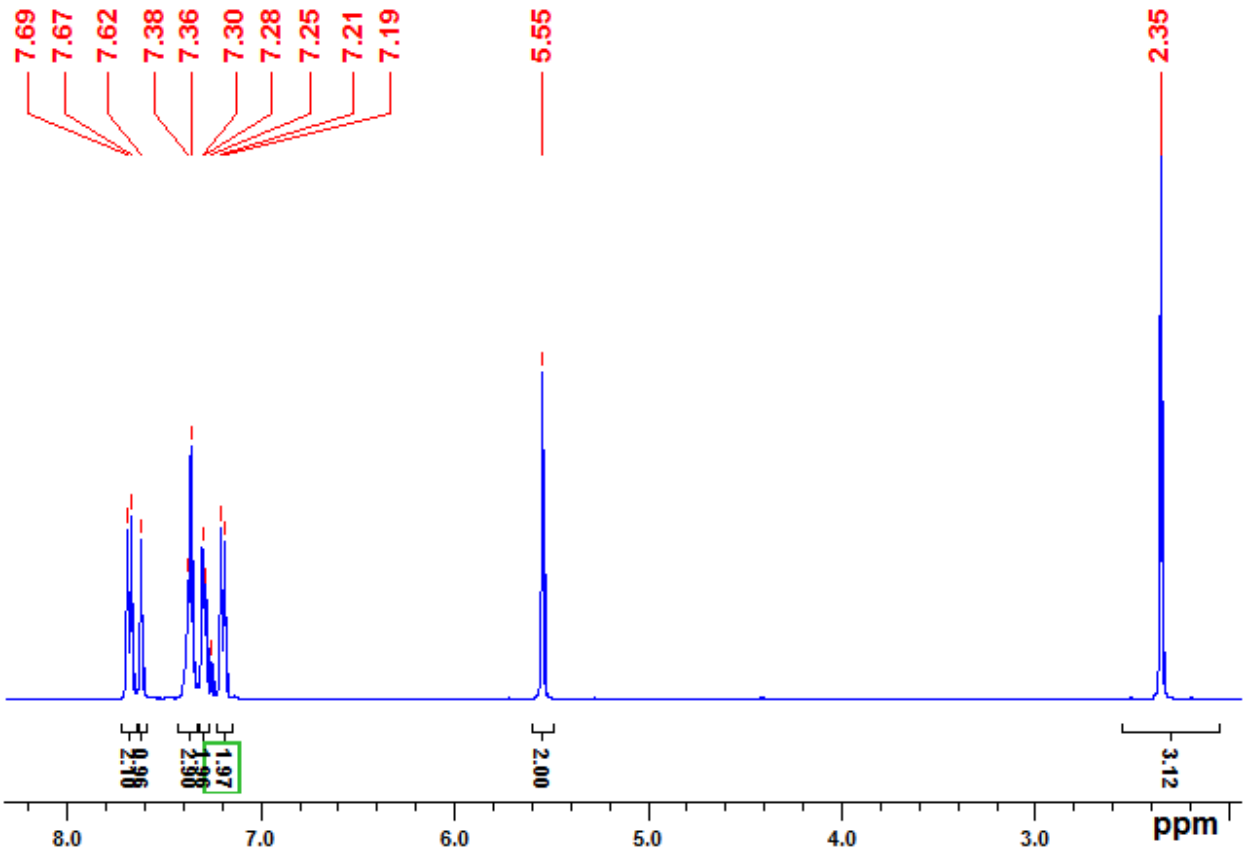



**Fig. S3**. $^{1}$H NMR spectrum of **Ib** in $CDCl_3$ at room temperature.

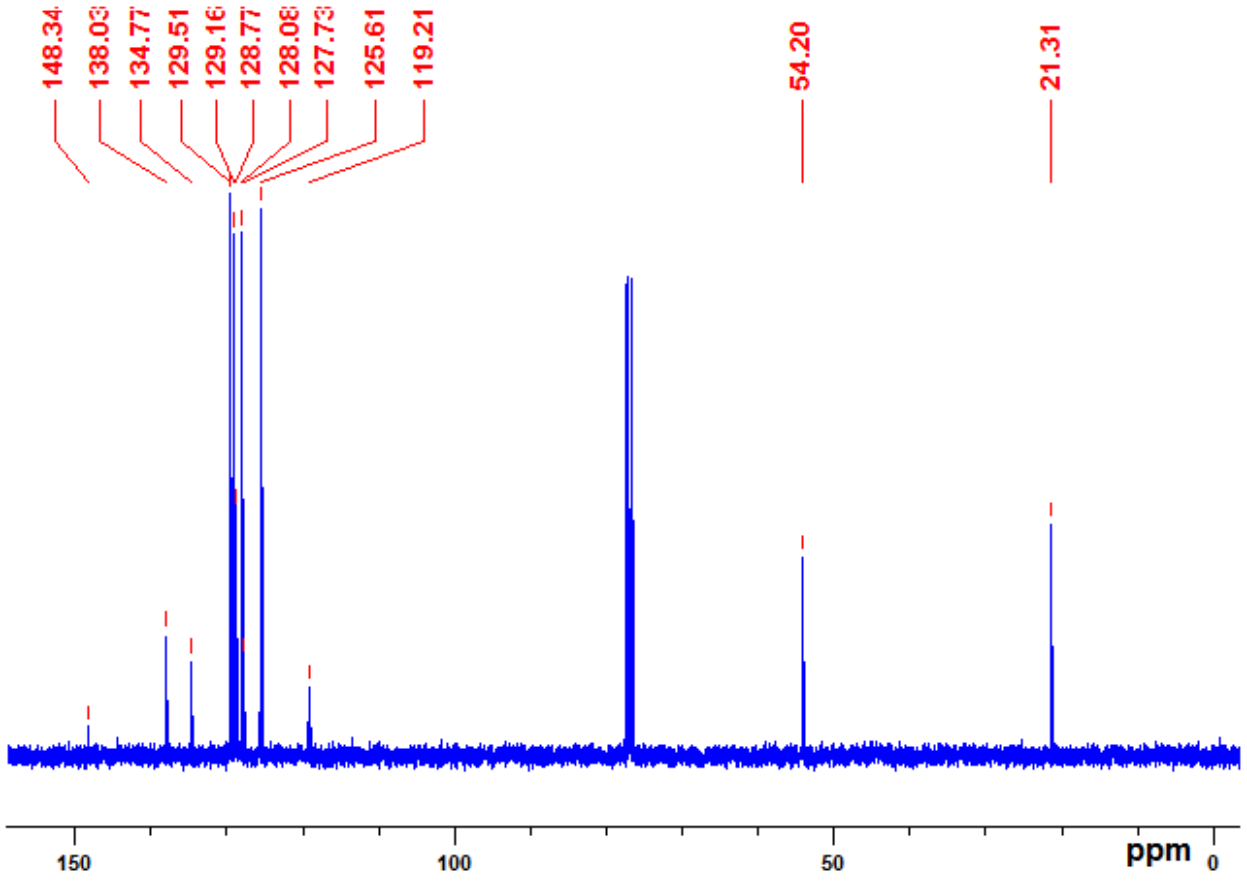
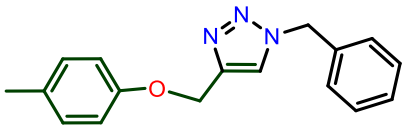



**Fig. S4**. $^{13}$C NMR spectrum of **Ib** in $CDCl_3$ at room temperature.

**3. 1-benzyl-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (Ic)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.51 (s, 1H), 7.34-7.37 (m, 3H), 7.24-7.26 (t, 2H), 7.05-7.07 (d, 2H), 6.83-6.86 (d, 2H), 5.50 (s, 2H), 5.13 (s, 2H), 2.26 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.11, 134.52, 130.53, 129.98, 129.15, 128.81, 128.14, 122.65, 114.65, 62.21, 54.23, 20.51 ppm..

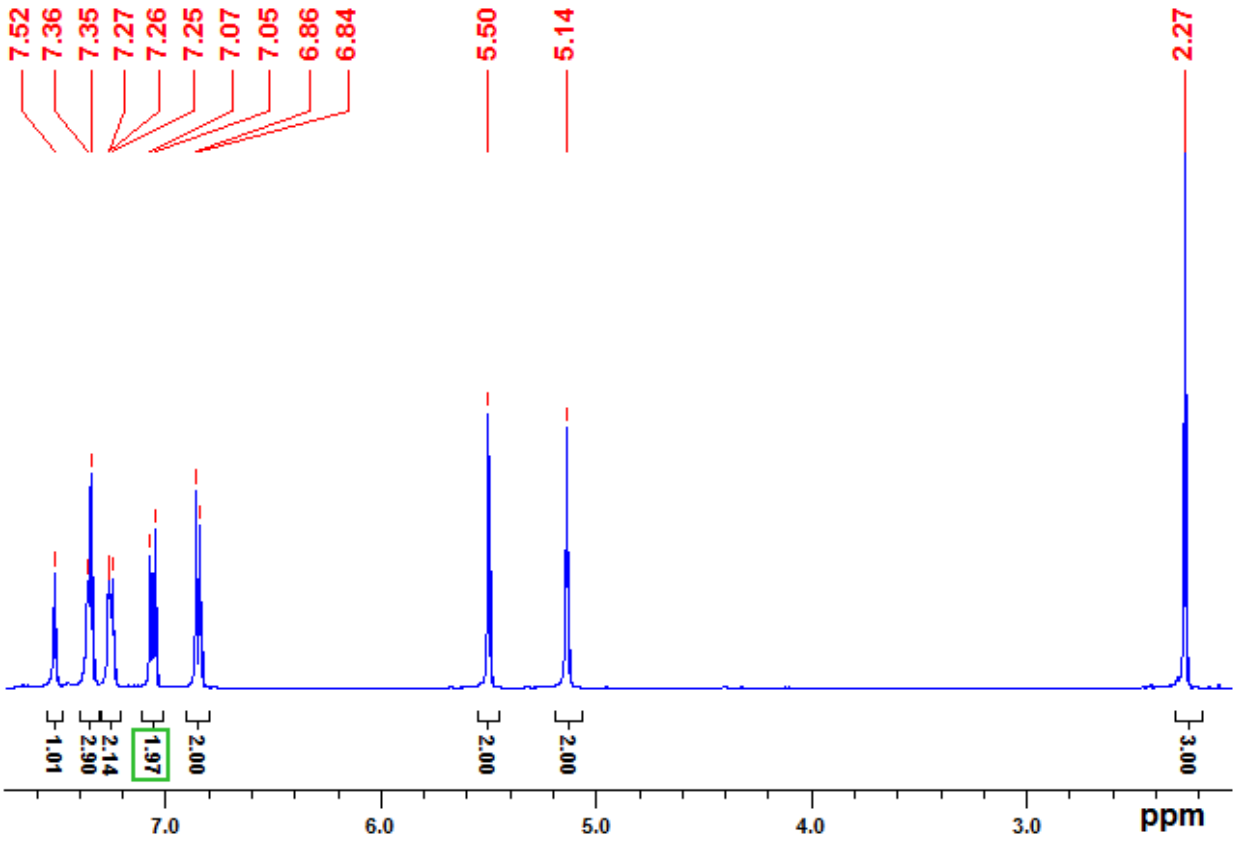



**Fig. S5**. $^{1}$H NMR spectrum of **Ic** in $CDCl_3$ at room temperature.

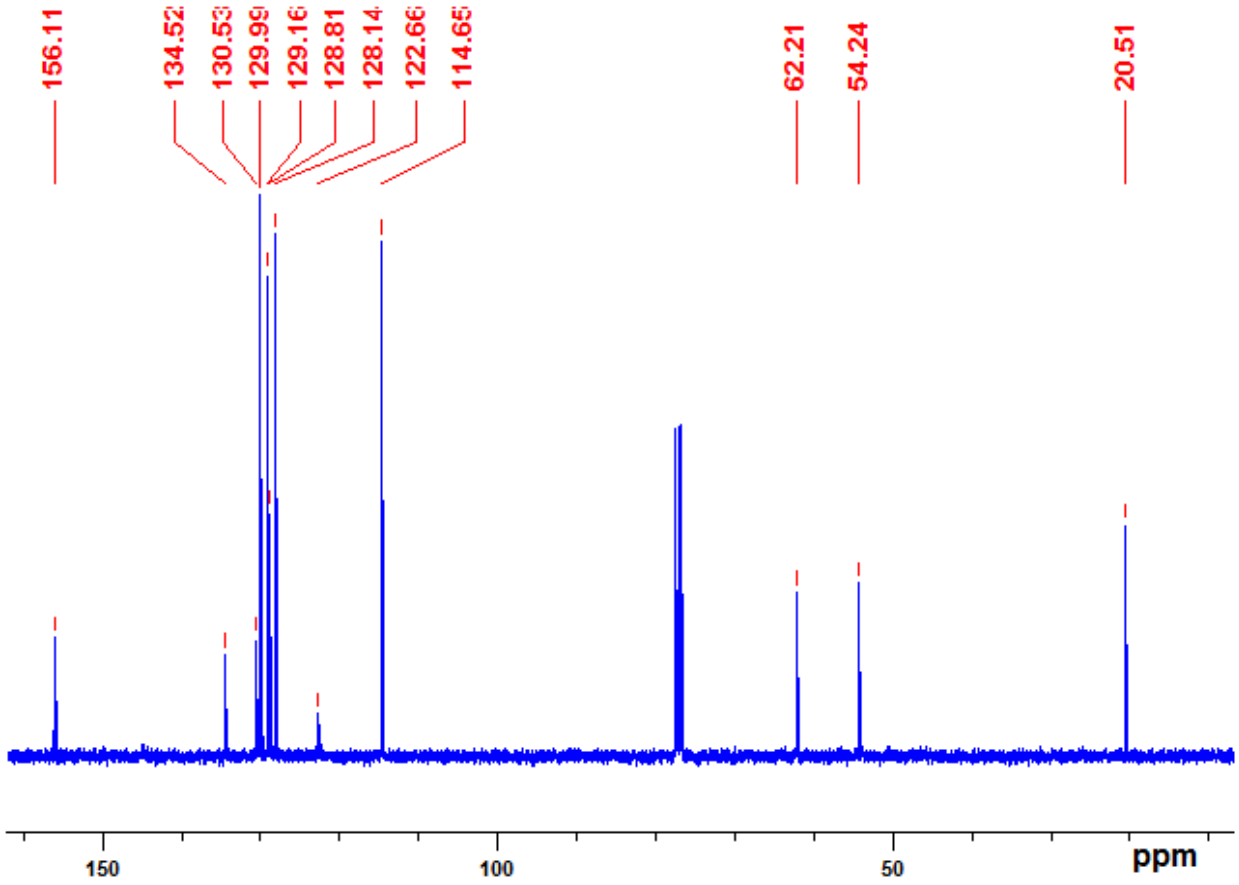
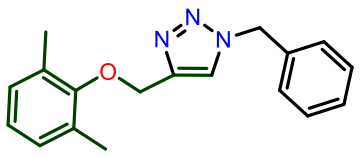



**Fig. S6**. $^{13}$C NMR spectrum of **Ic** in $CDCl_3$ at room temperature.

**4. 1-benzyl-4-((2,6-dimethylphenoxy)methyl)-1*H*-1,2,3-triazole (Id)**



$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.55 (s, 1H), 7.27-7.37 (m, 5H), 6.90-7.00 (m, 3H), 5.53 (s, 2H), 4.94 (s, 2H), 2.25 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.30, 145.08, 134.61, 132.05, 131.07, 129.16, 128.91, 128.11, 124.27, 122.65, 65.60, 54.21, 16.40 ppm.

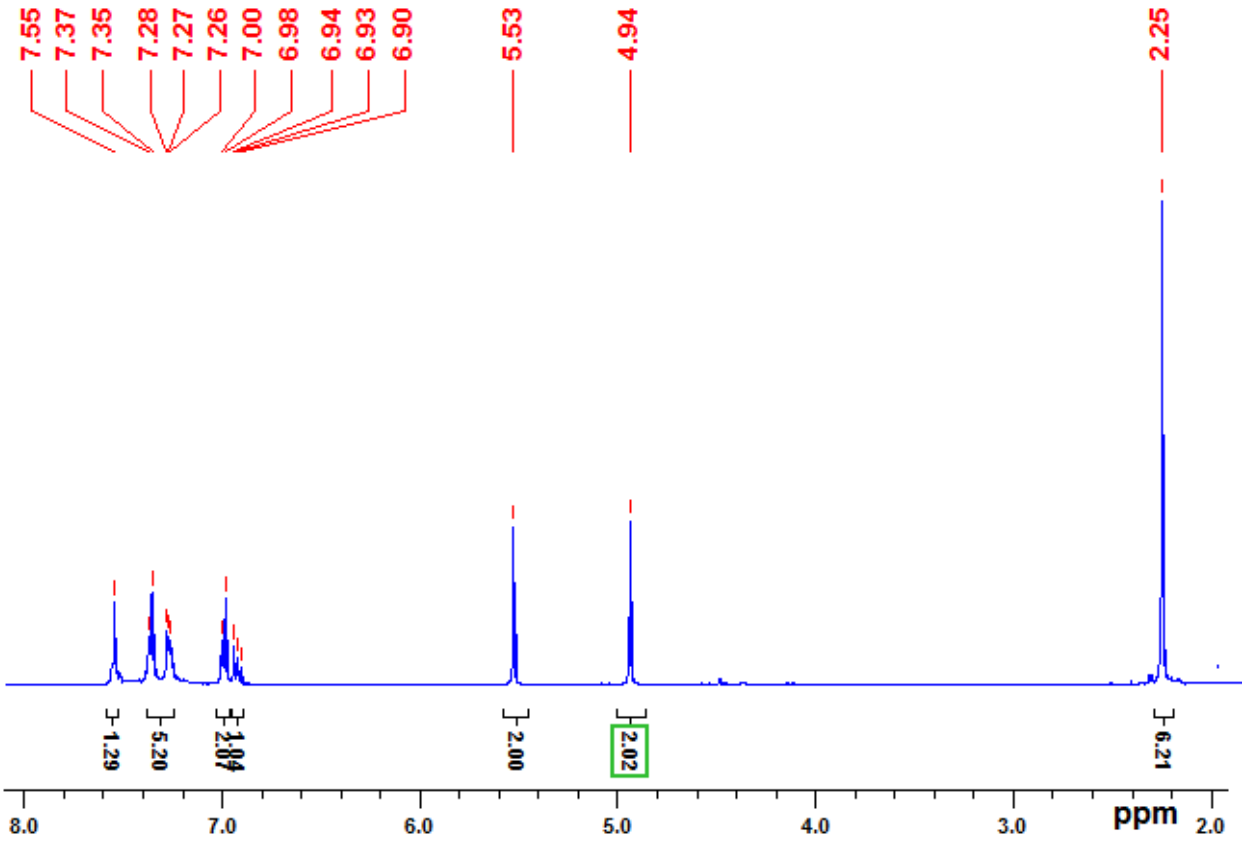



**Fig. S7**. $^{1}$H NMR spectrum of **Id** in $CDCl_3$ at room temperature.

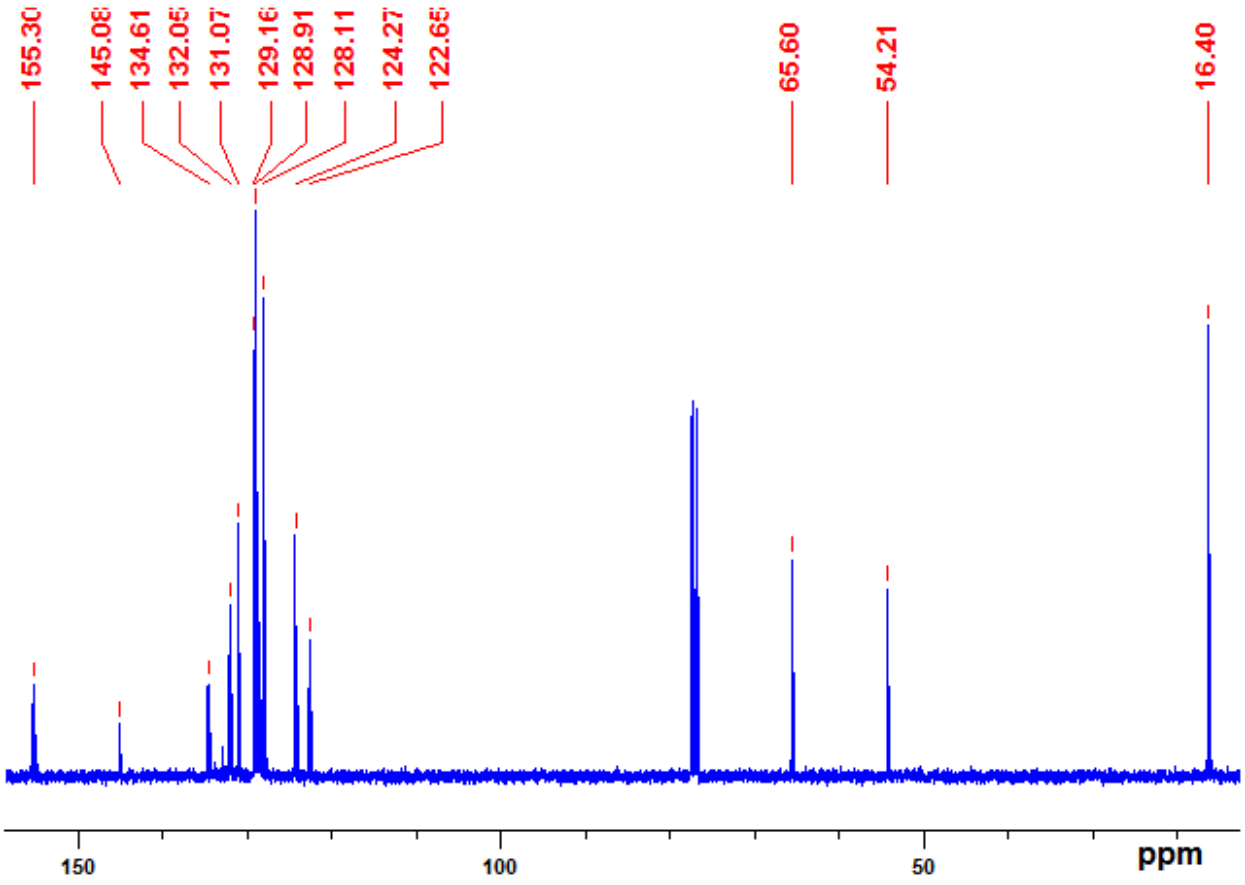
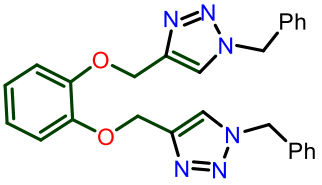



**Fig. S8**. $^{13}$C NMR spectrum of **Id** in $CDCl_3$ at room temperature.

**5. 1,2-bis((1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)benzene (Ie)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.43-7.68 (m, 4H), 7.23-7.34 (m, 8H), 6.88-7.01 (m, 4H), 5.47 (s, 4H), 5.18 (s, 4H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.43, 134.58, 132.15, 132.05, 132.01, 129.10, 128.74, 128.61, 128.49, 128.10, 123.20, 122.23, 115.60, 63.51, 54.15 ppm.

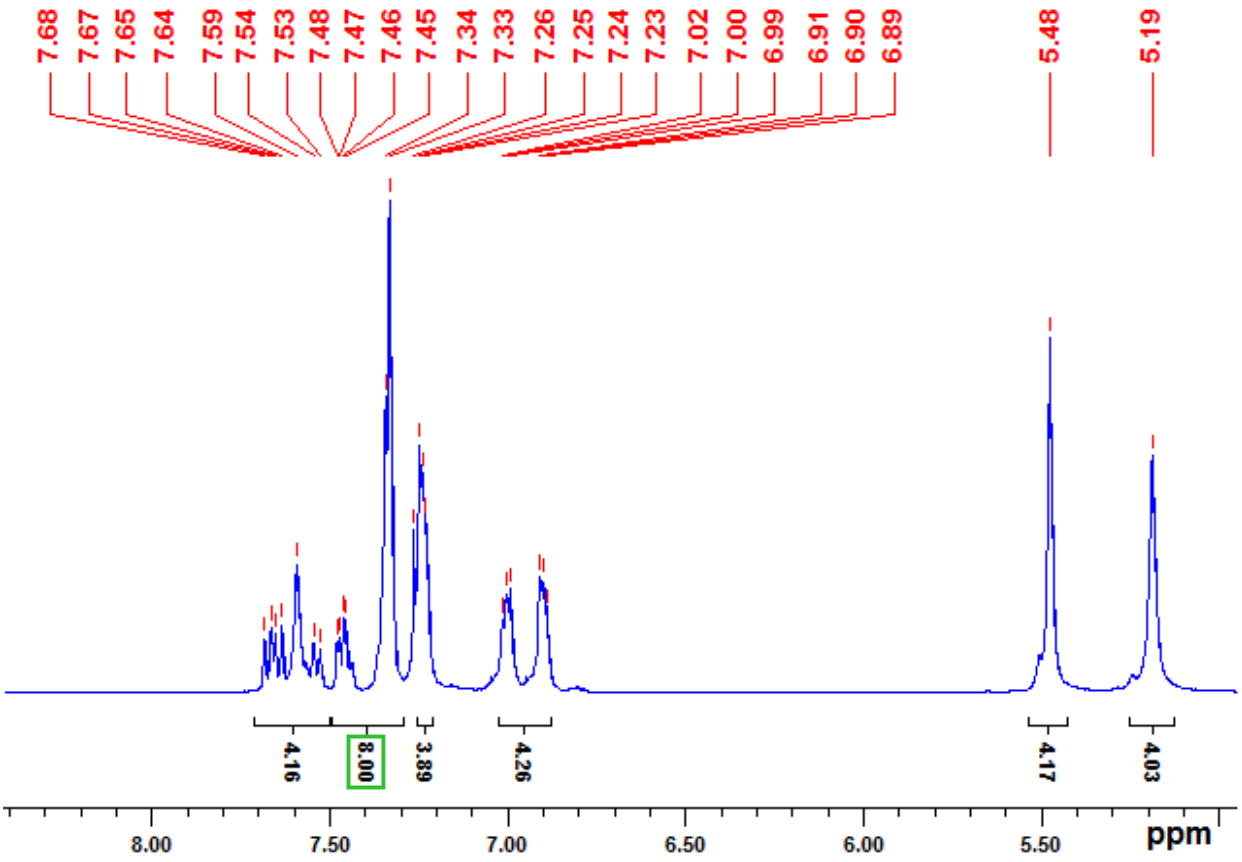



**Fig. S9**. $^{1}$H NMR spectrum of **Ie** in $CDCl_3$ at room temperature.

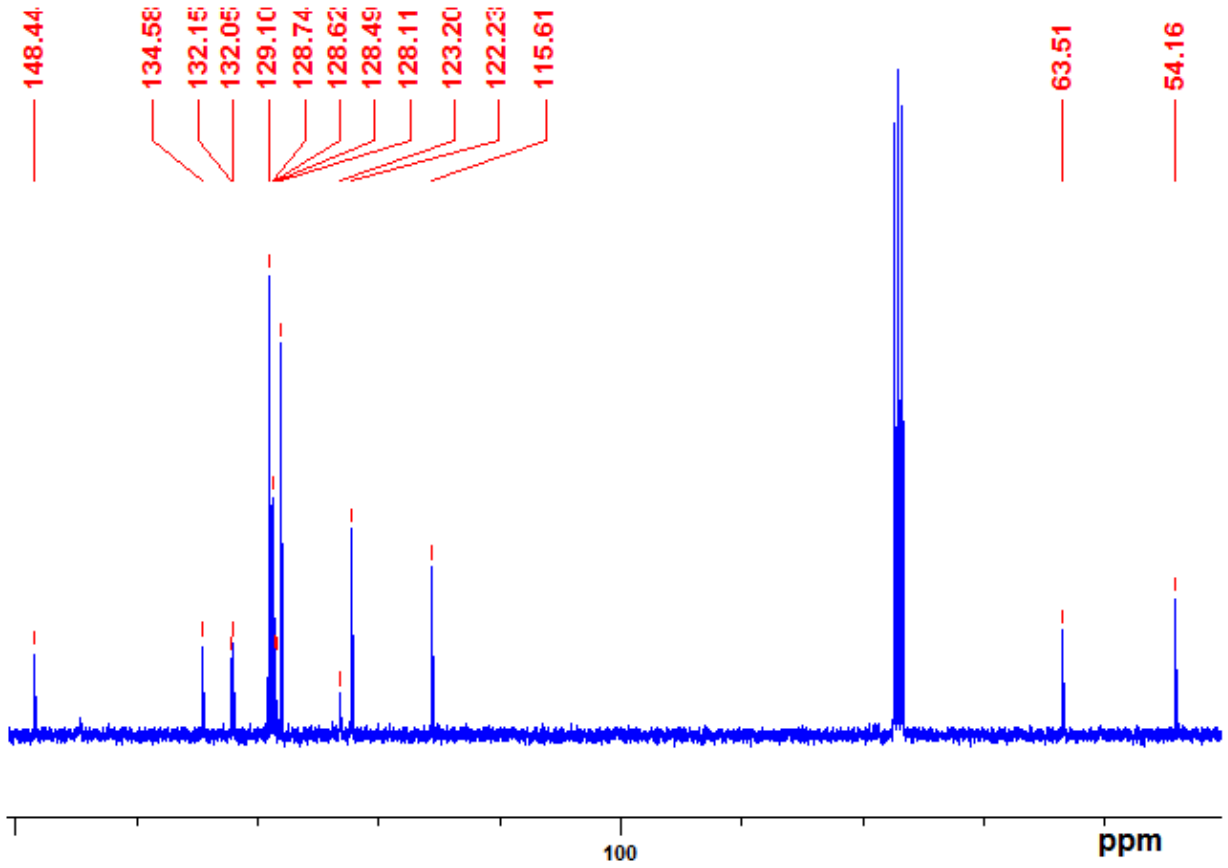
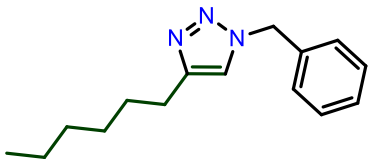



**Fig. S10**. $^{13}$C NMR spectrum of **Ie** in $CDCl_3$ at room temperature.

**6. 1–benzyl–4–hexyl–1H–1,2,3–triazole (If)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.33-7.36 (m, 3H), 7.23-7.27 (m, 2H), 7.19 (2, 1H), 5.48 (s, 2H), 2.65-2.69 (t, 2H), 1.58-1.64 (m, 2H), 1.25-1.34 (m, 6H), 0.84-0.87 (t, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 135.01, 129.04, 128.59, 128.47, 127.94, 120.55, 53.96, 31.54, 29.37, 29.37, 25.73, 22.54, 14.06 ppm.

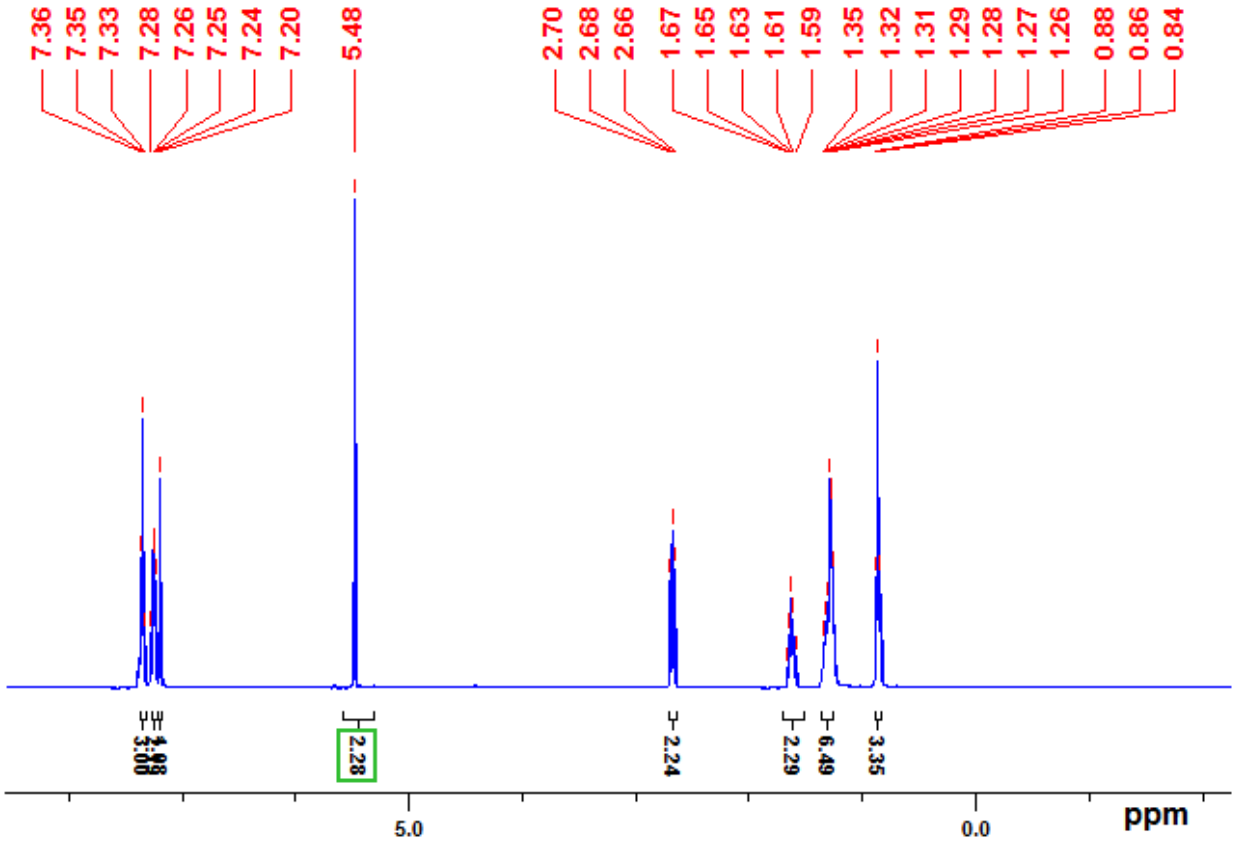



**Fig. S11**. $^{1}$H NMR spectrum of **If** in $CDCl_3$ at room temperature.

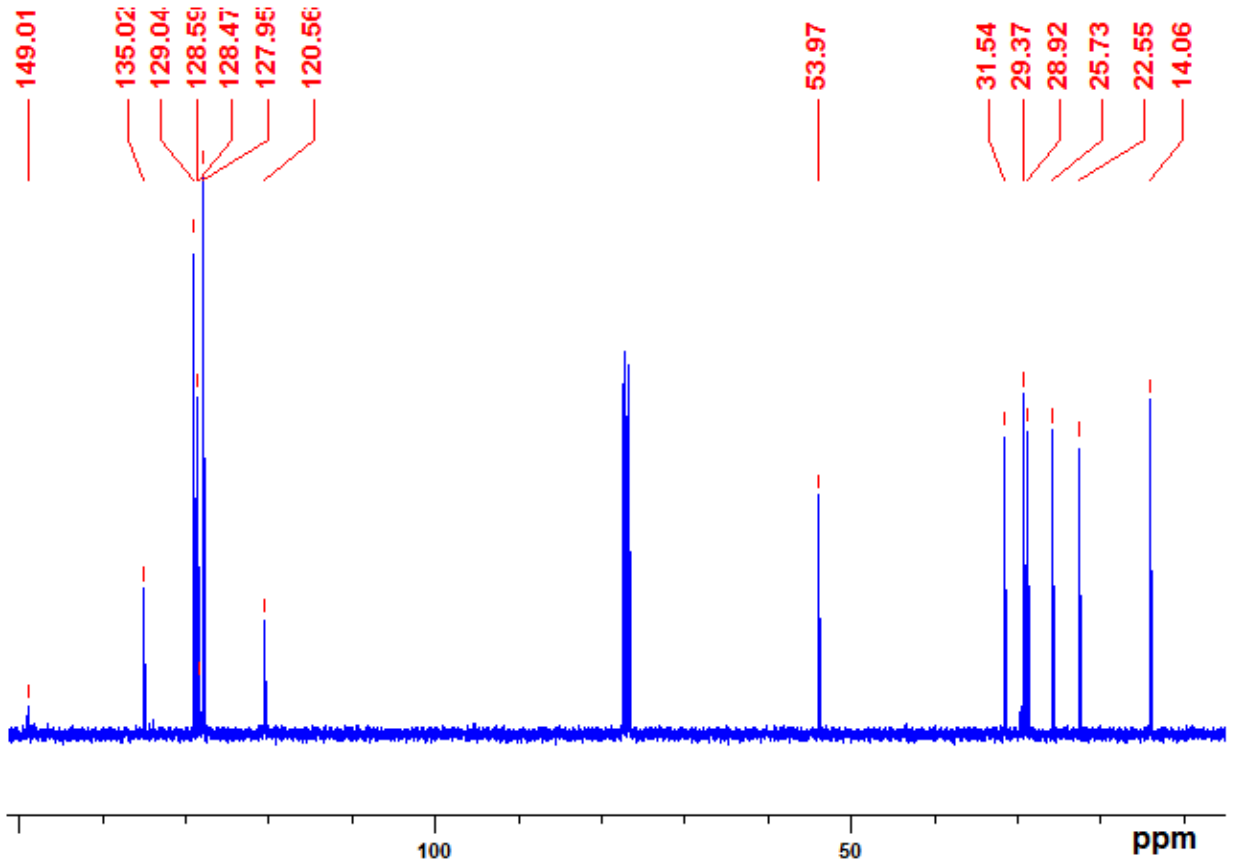
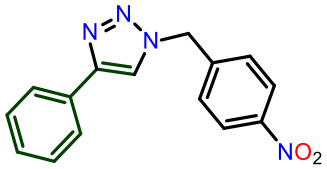



**Fig. S12**. $^{13}$C NMR spectrum of **If** in $CDCl_3$ at room temperature.

**7. 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (IIa)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.19-8.22 (d, 2H), 7.78-7.81 (m, 3H), 7.44-7.33 (m, 5H), 5.69 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.68, 148.04, 141.81, 130.10, 128.93, 128.57, 128.51, 125.74, 124.33, 119.84, 53.17 ppm.

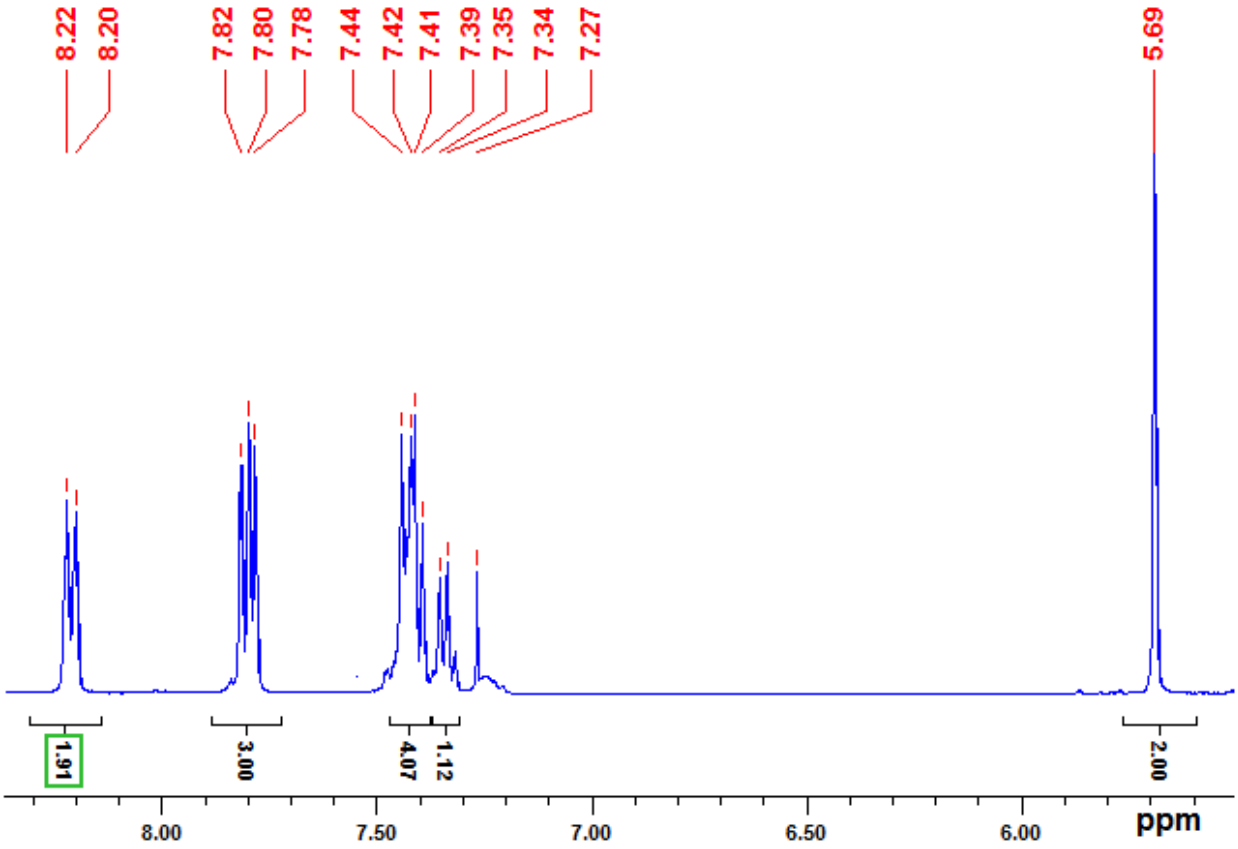



**Fig. S13**. $^{1}$H NMR spectrum of **IIa** in $CDCl_3$ at room temperature.

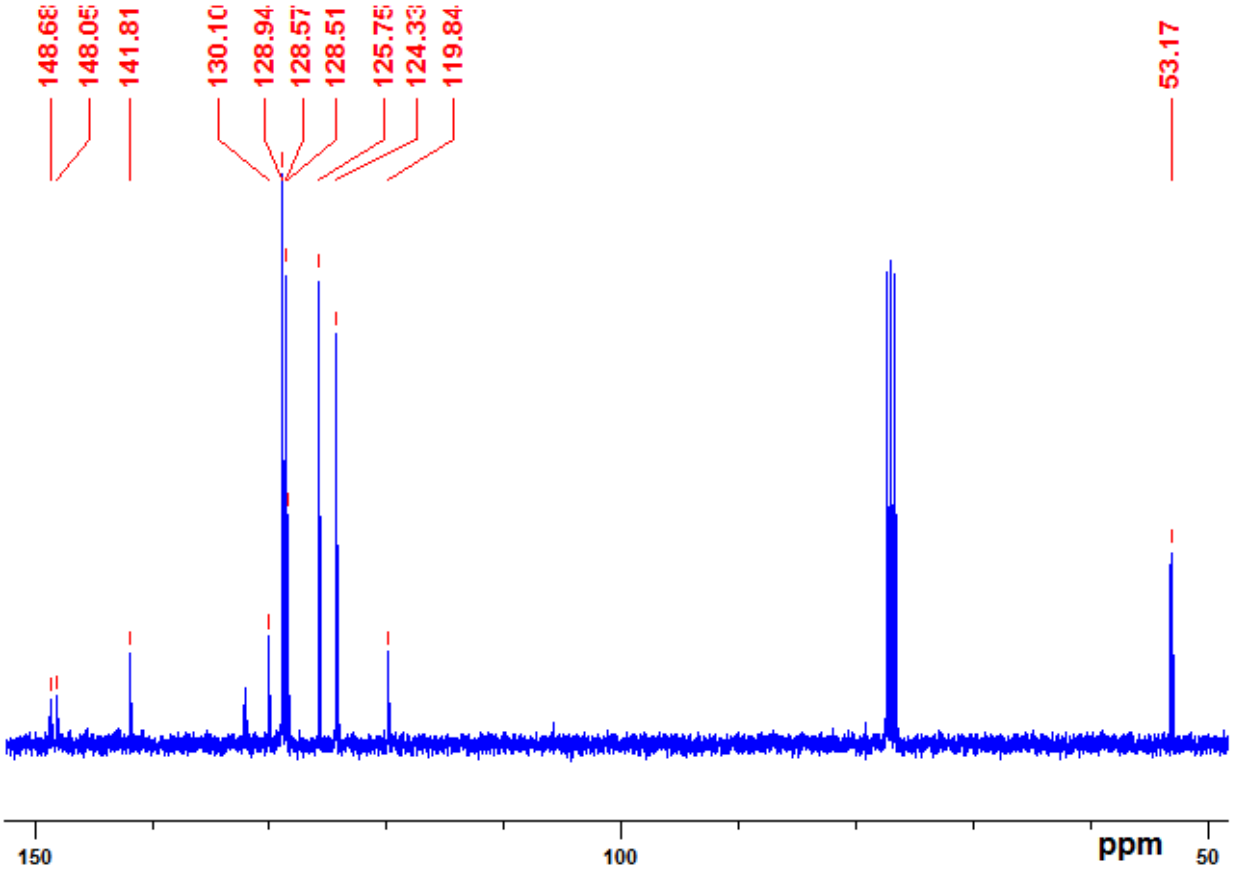
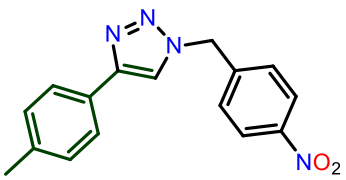



**Fig. S14**. $^{13}$C NMR spectrum of **IIa** in $CDCl_3$ at room temperature.

**8. 1-(4-nitrobenzyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IIb)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.19-8.21 (d, 2H), 7.67-7.73 (m, 3H), 7.41-7.43 (d, 2H), 7.20-7.22 (d, 2H), 5.67 (s, 2H), 2.36 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.75, 148.02, 141.88, 138.42, 129.60, 128.56, 127.27, 125.65, 124.30, 119.50, 53.13, 21.31 ppm.

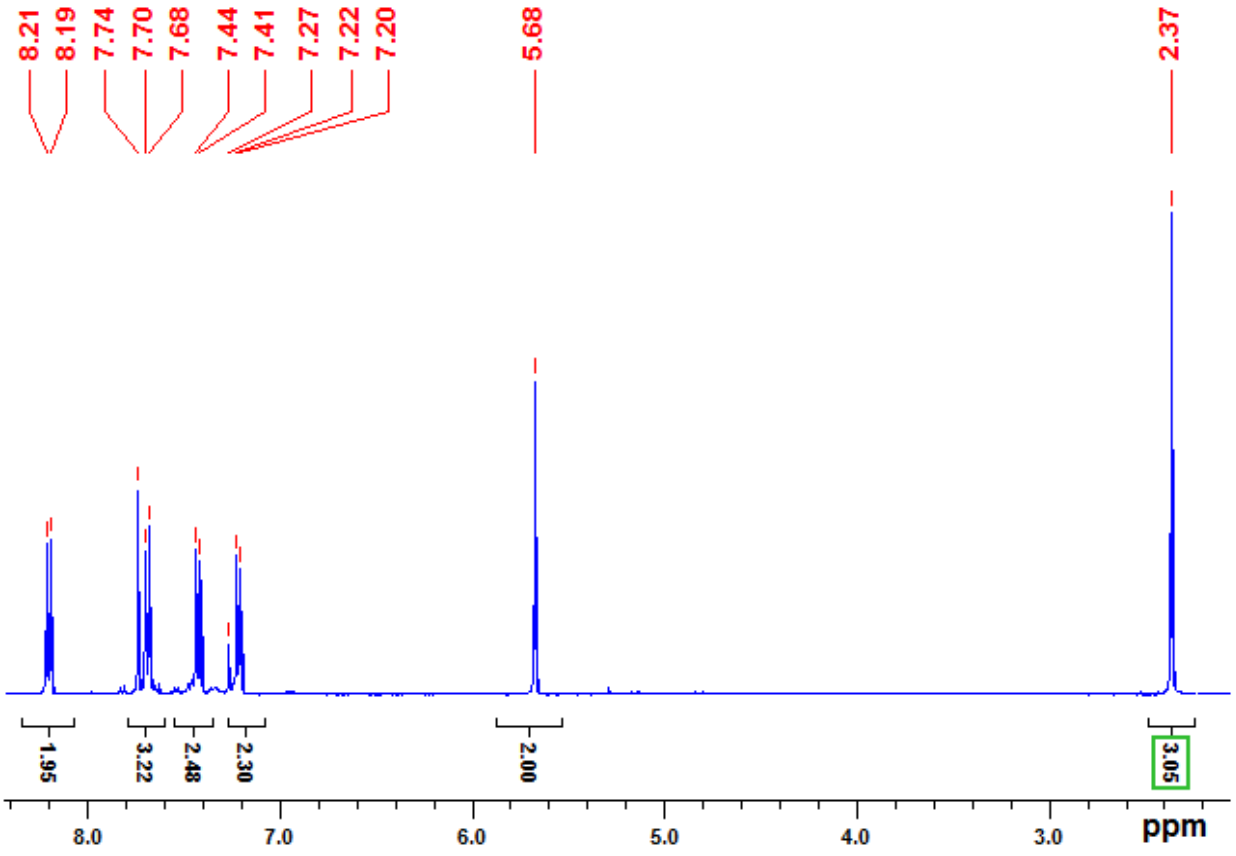



**Fig. S15**. $^{1}$H NMR spectrum of **IIb** in $CDCl_3$ at room temperature.

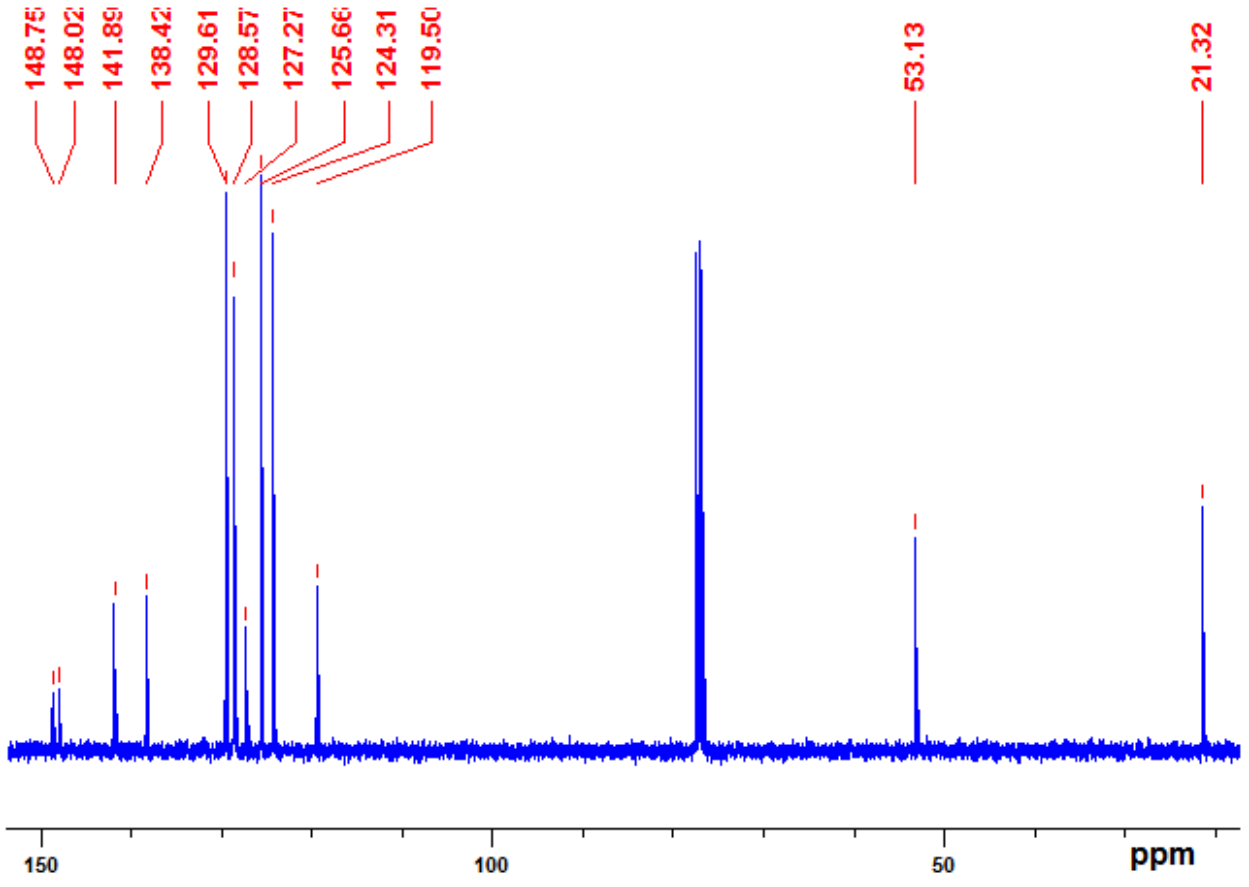
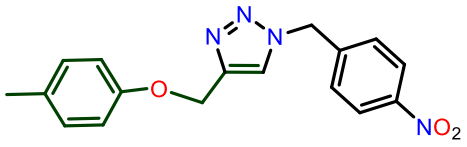



**Fig. S16**. $^{13}$C NMR spectrum of **IIb** in $CDCl_3$ at room temperature.

**9. 1-(4-nitrobenzyl)-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (IIc)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.19-8.22 (d, 2H), 7.62 (s, 1H), 7.38-7.40 (d, 2H), 7.06-7.08 (d, 2H), 6.83-6.86 (d, 2H), 5.64 (s, 2H), 5.18 (s, 2H), 2.27 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.94, 148.06, 141.58, 130.72, 130.02, 128.70, 128.62, 124.32, 122.95, 114.61, 62.08, 53.17, 20.49 ppm.

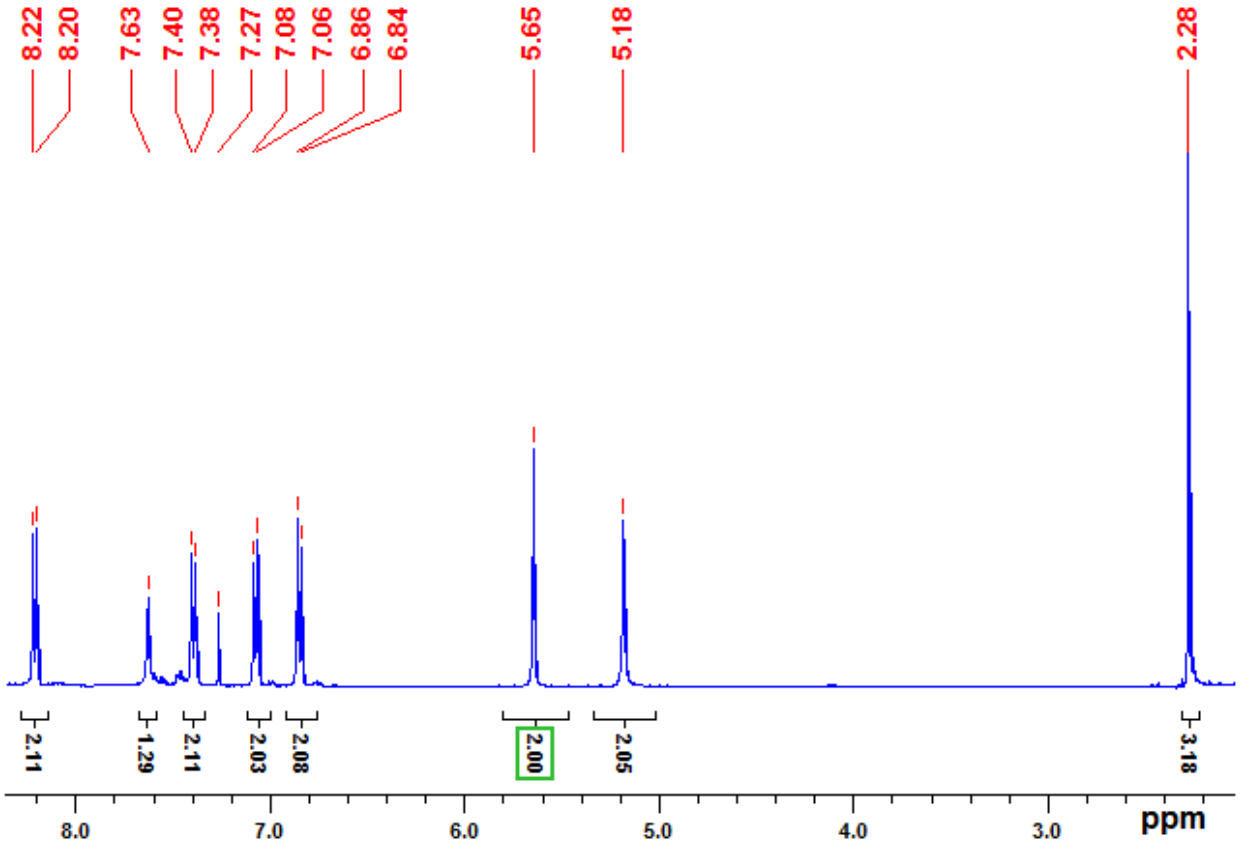



**Fig. S17**. $^{1}$H NMR spectrum of **IIc** in $CDCl_3$ at room temperature.

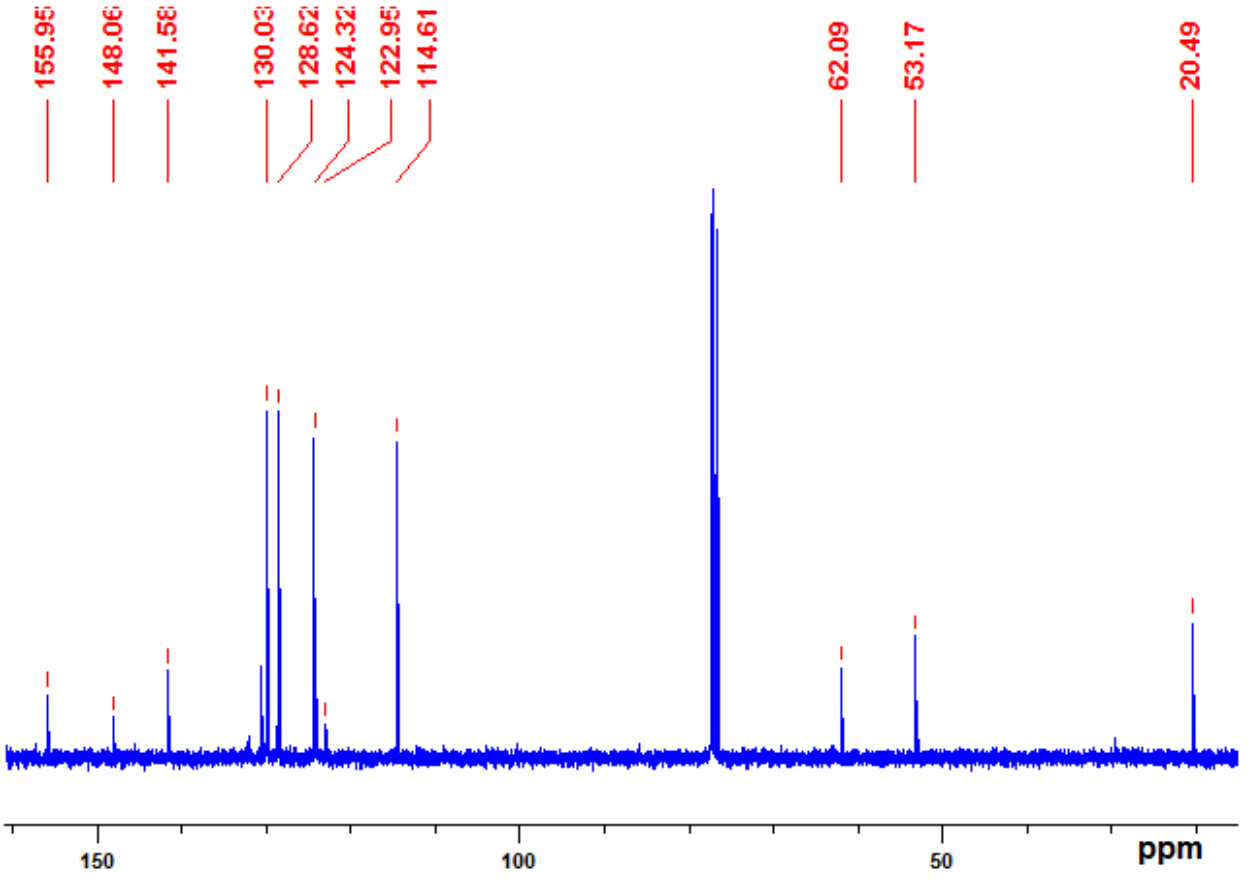
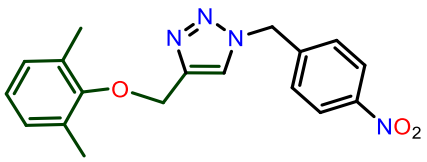



**Fig. S18**. $^{13}$C NMR spectrum of **IIc** in $CDCl_3$ at room temperature.

**10. 4-((2,6-dimethylphenoxy)methyl)-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (IId)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.16-8.18 (d, 2H), 7.74 (s, 1H), 7.39-7.41 (m, 2H), 6.93-7.00 (m, 3H), 5.67 (s, 2H), 4.97 (s, 2H), 2.25 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.18, 147.93, 141.90, 130.96, 128.95, 128.64, 124.37, 124.22, 123.26, 65.39, 53.07, 16.37 ppm.

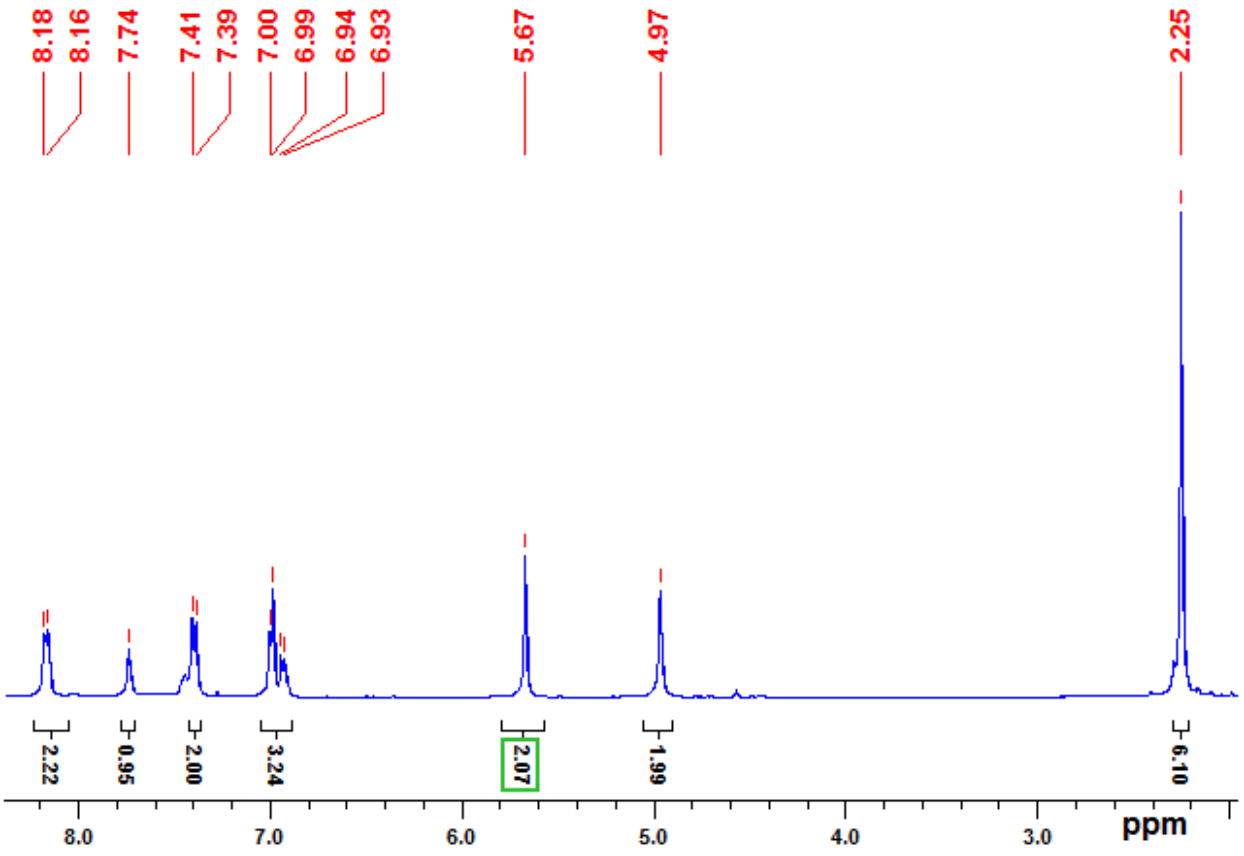



**Fig. S19**. $^{1}$H NMR spectrum of **IId** in $CDCl_3$ at room temperature.

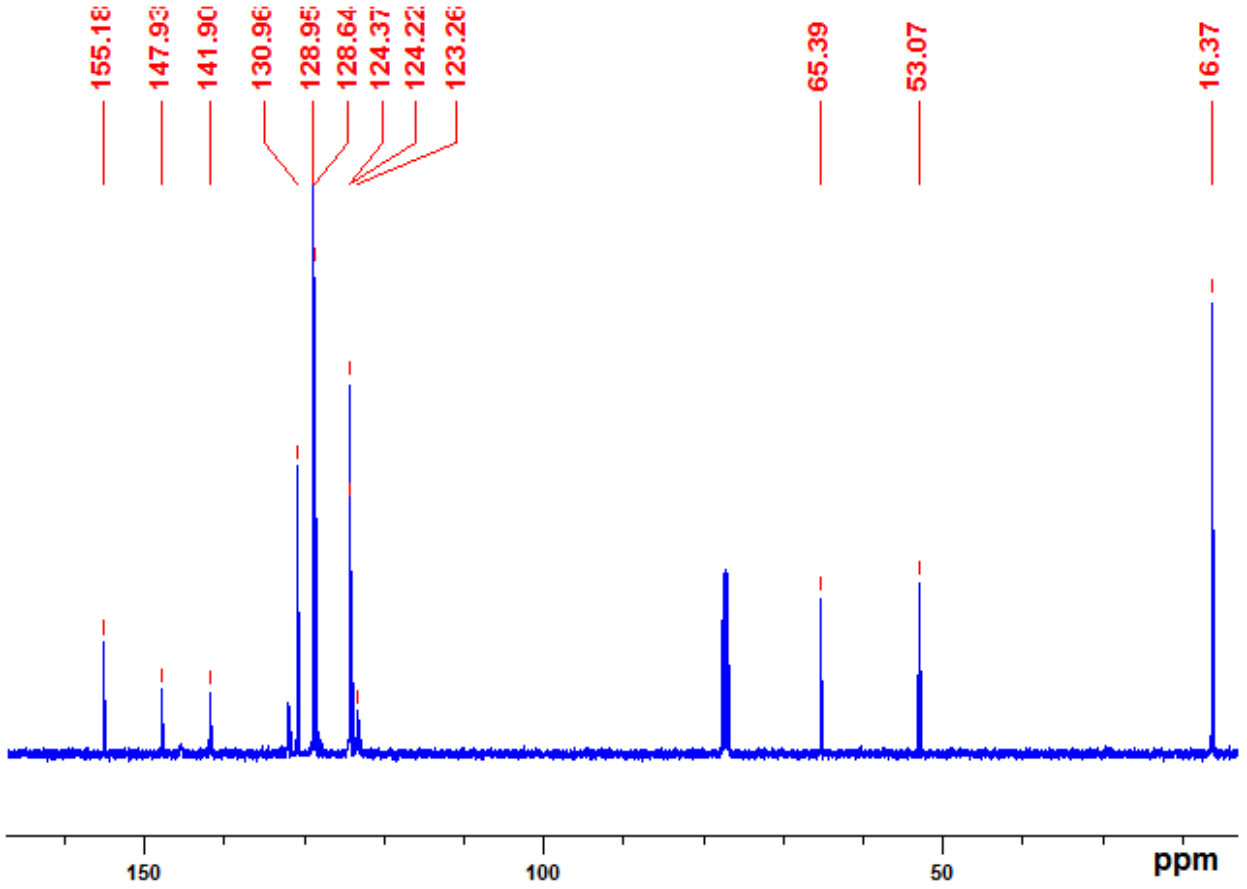
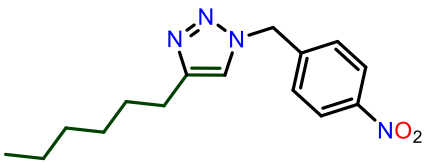



**Fig. S20**. $^{13}$C NMR spectrum of **IId** in $CDCl_3$ at room temperature.

**11. 4-hexyl-1-(4-nitrobenzyl)-1H-1,2,3-triazole (IIe)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.17-8.19 (d, 1H), 7.39-7.64 (m, 2H), 5.65 (s, 2H), 2.71 (t, 2H), 1.65 (m, 2H), 1.28-1.33 (m, 6H), 0.85 (t, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 135.01, 129.04, 128.59, 128.47, 127.94, 120.55, 53.96, 31.54, 29.37, 29.37, 25.73, 22.54, 14.06 ppm.

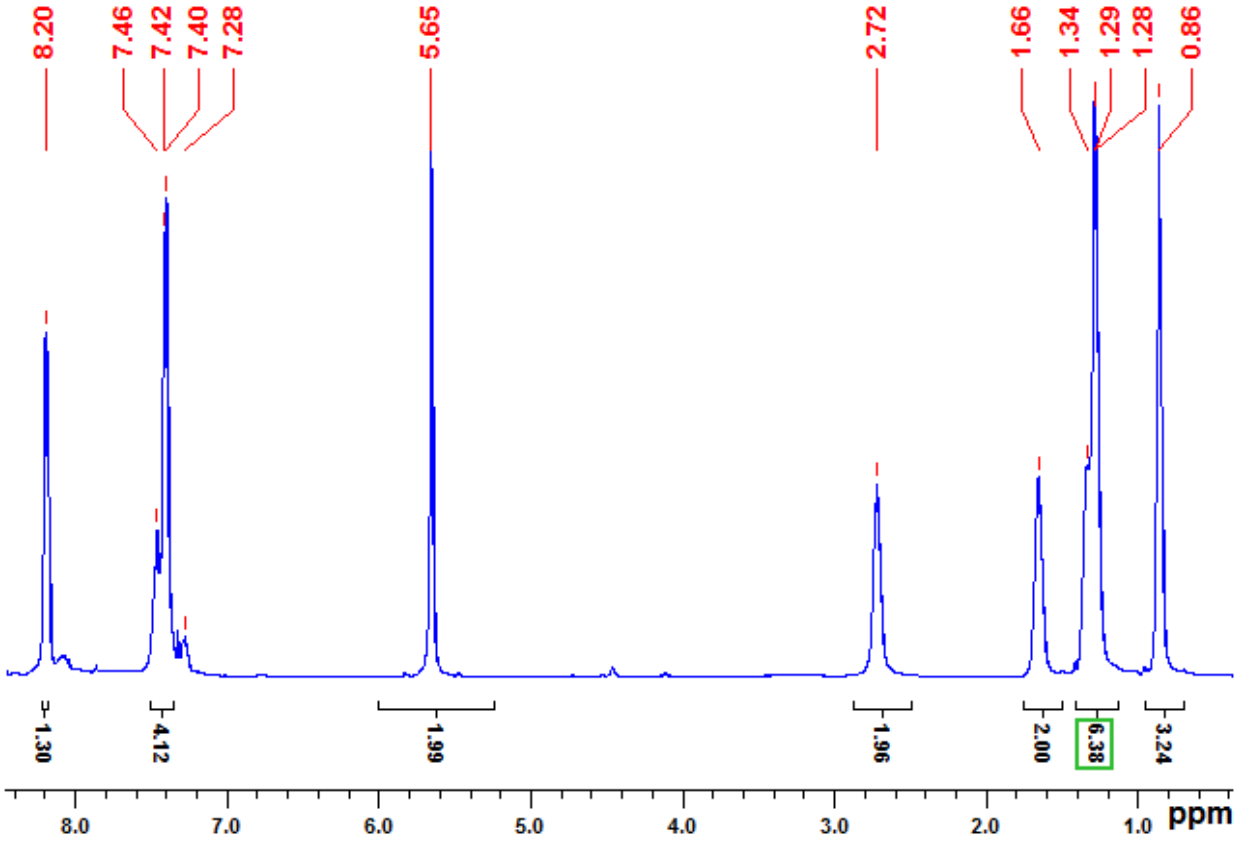



**Fig. S21**. $^{1}$H NMR spectrum of **IIe** in $CDCl_3$ at room temperature.

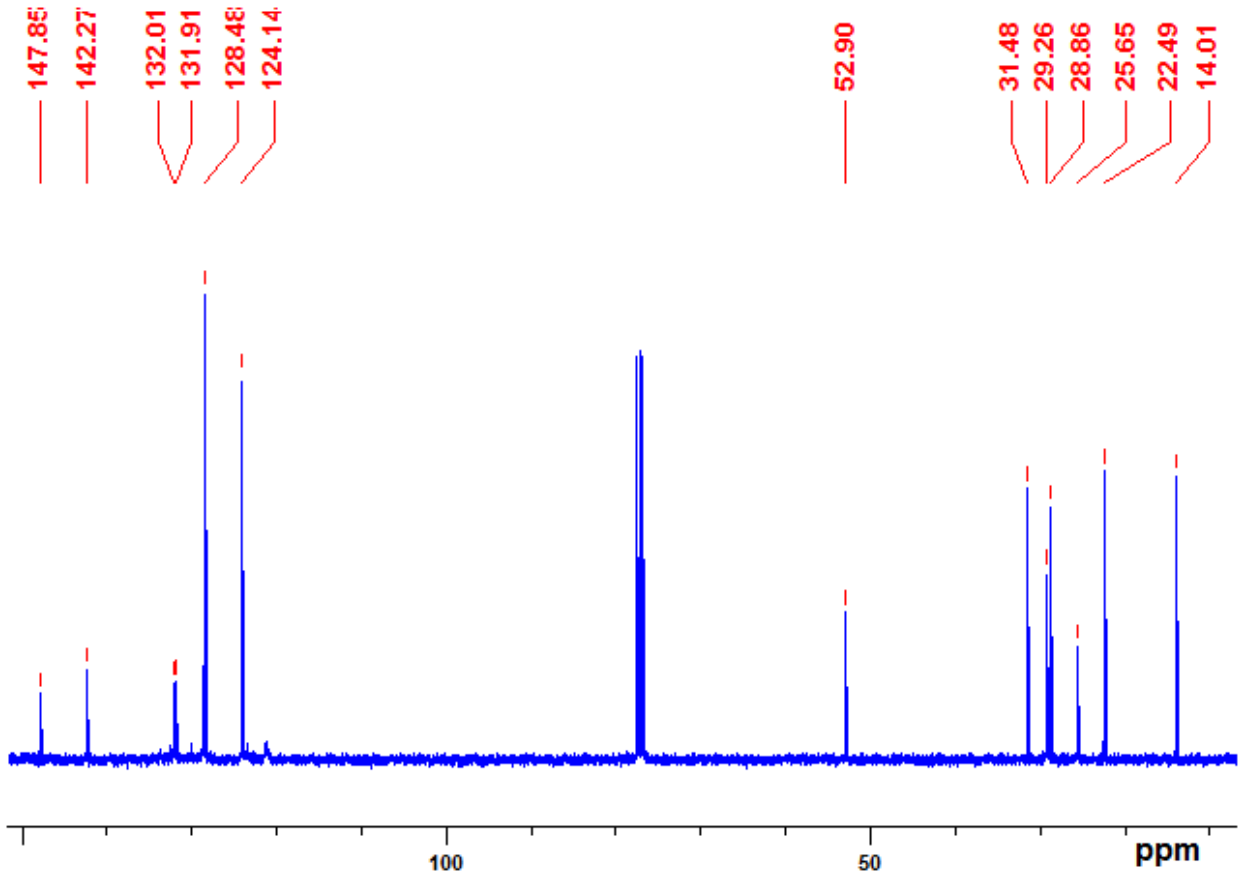
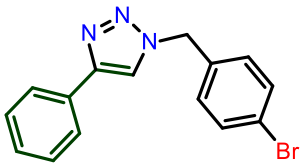



**Fig. S22**. $^{13}$C NMR spectrum of **IIe** in $CDCl_3$ at room temperature.

**12. 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (IIIa)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.15-7.80 (m, 10H), 5.50 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.39, 133.75, 132.32, 130.38, 129.66, 128.87, 128.30, 125.72, 122.94, 119.53, 53.51 ppm.

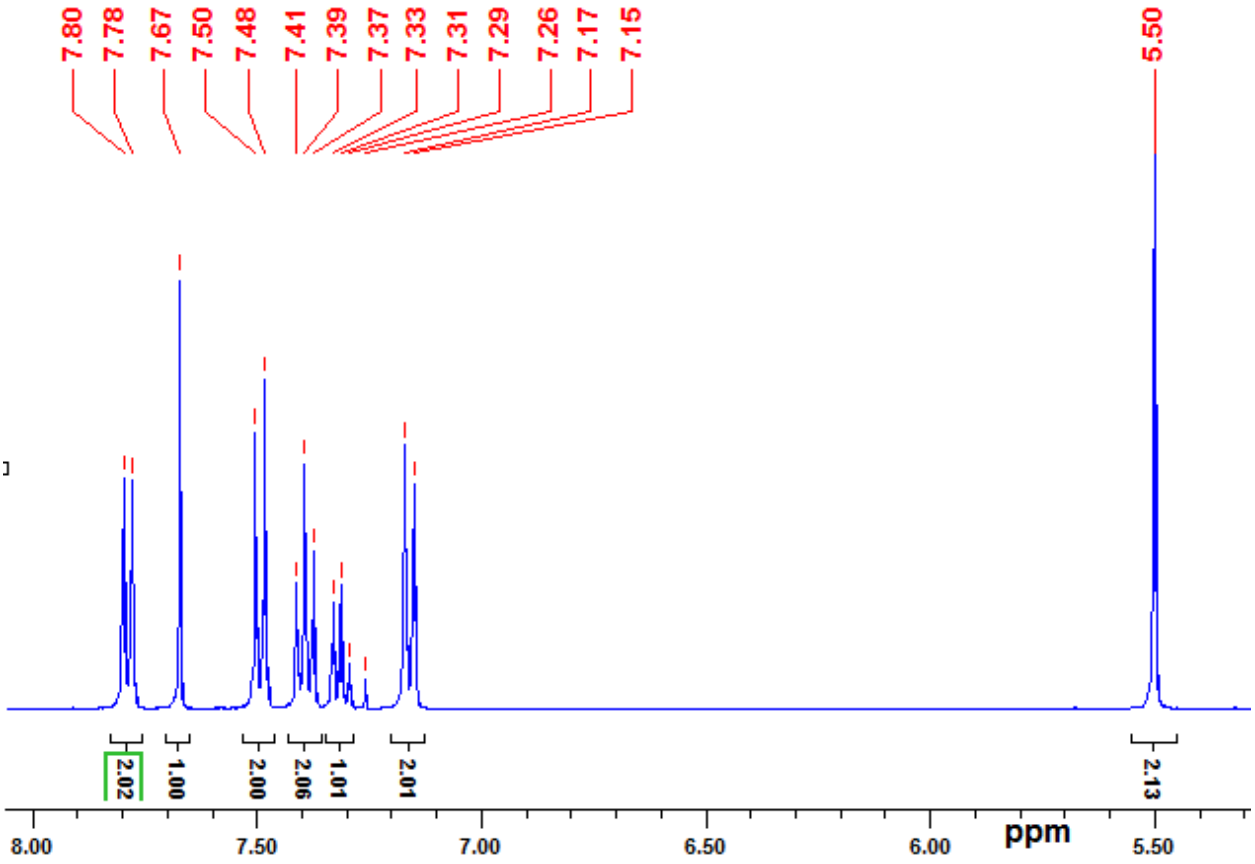



**Fig. S23**. $^{1}$H NMR spectrum of **IIIa** in $CDCl_3$ at room temperature.

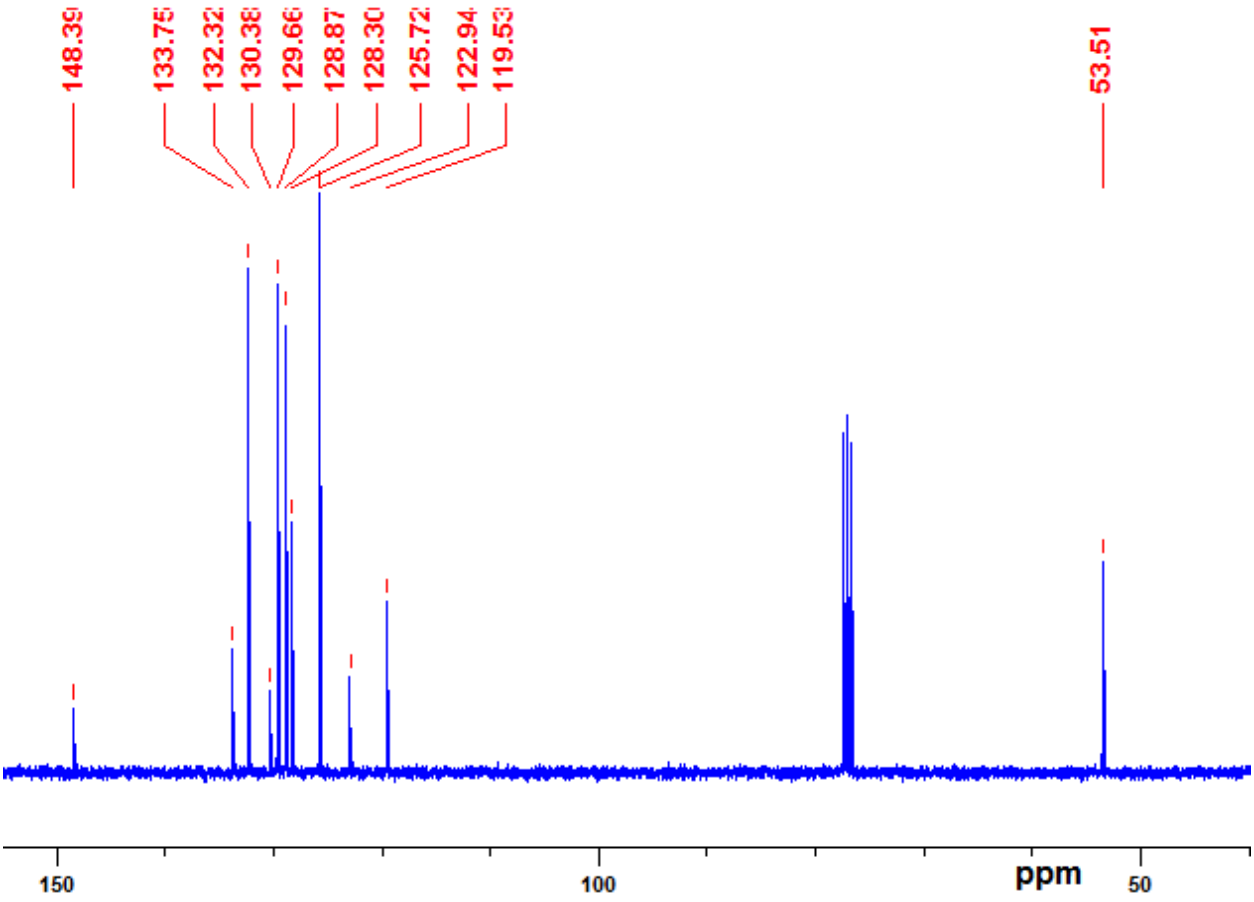
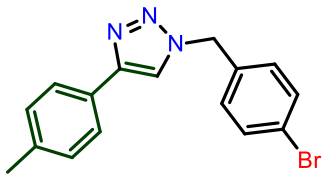



**Fig. S24**. $^{13}$C NMR spectrum of **IIIa** in $CDCl_3$ at room temperature.

**13. 1-(4-nitrobenzyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IIIb)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62-7.69 (m, 3H), 7.49-7.51 (m, 2H), 7.15-7.21 (m, 4H), 5.50 (s, 2H), 2.36 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.48, 138.16, 133.80, 132.31, 129.66, 128.53, 127.57, 125.63, 122.91, 119.13, 53.48, 21.30 ppm.

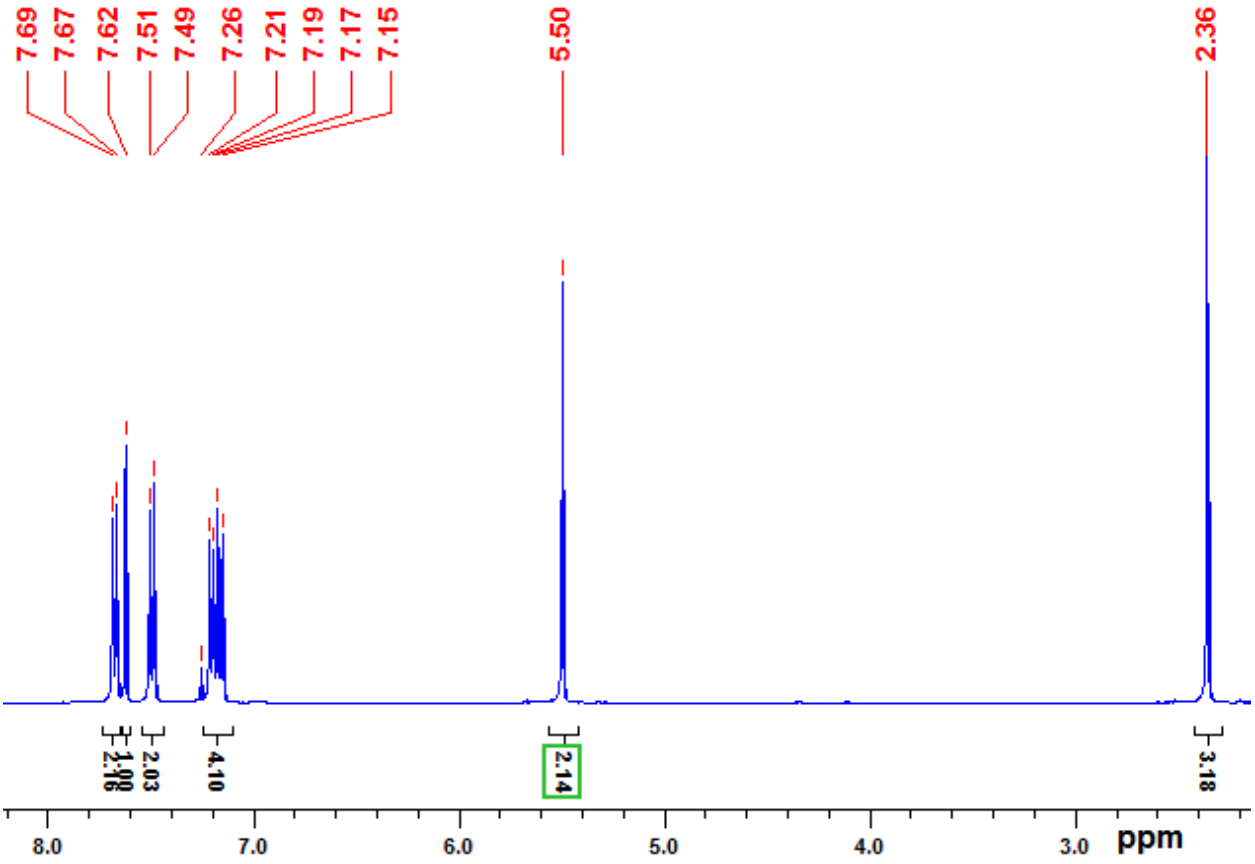



**Fig. S25**. $^{1}$H NMR spectrum of **IIIb** in $CDCl_3$ at room temperature.

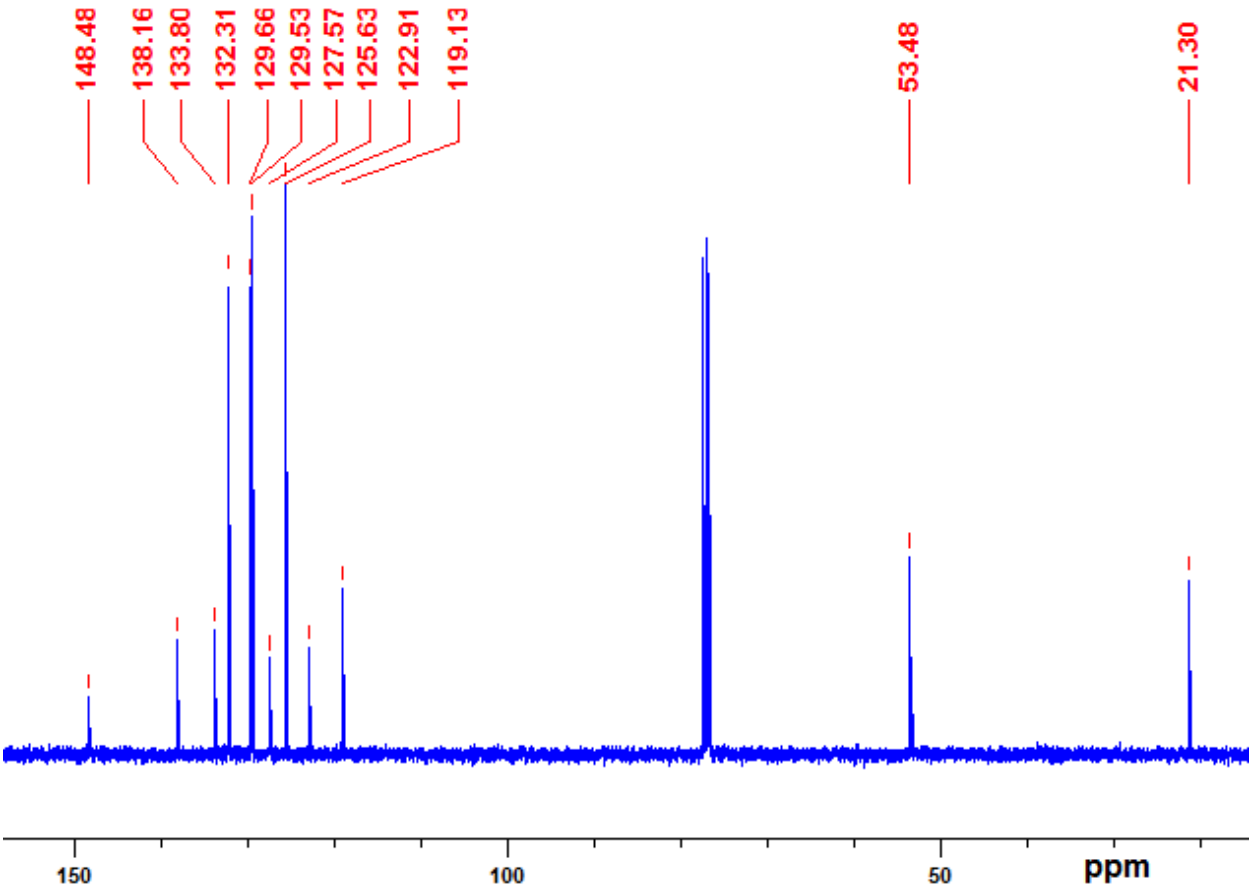
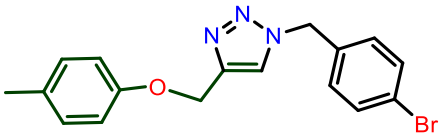



**Fig. S26**. $^{13}$C NMR spectrum of **IIIb** in $CDCl_3$ at room temperature.

**14. 1-(4-nitrobenzyl)-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (IIIc)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.48-7.52 (m, 3H), 7.06-7.14 (m, 4H), 6.84-6.86 (m, 2H), 5.47 (s, 2H), 5.15 (s, 2H), 2.28 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.06, 145.13, 133.54, 132.32, 130.60, 129.99, 129.71, 122.98, 122.52, 114.65, 62.21, 53.52, 20.49 ppm.

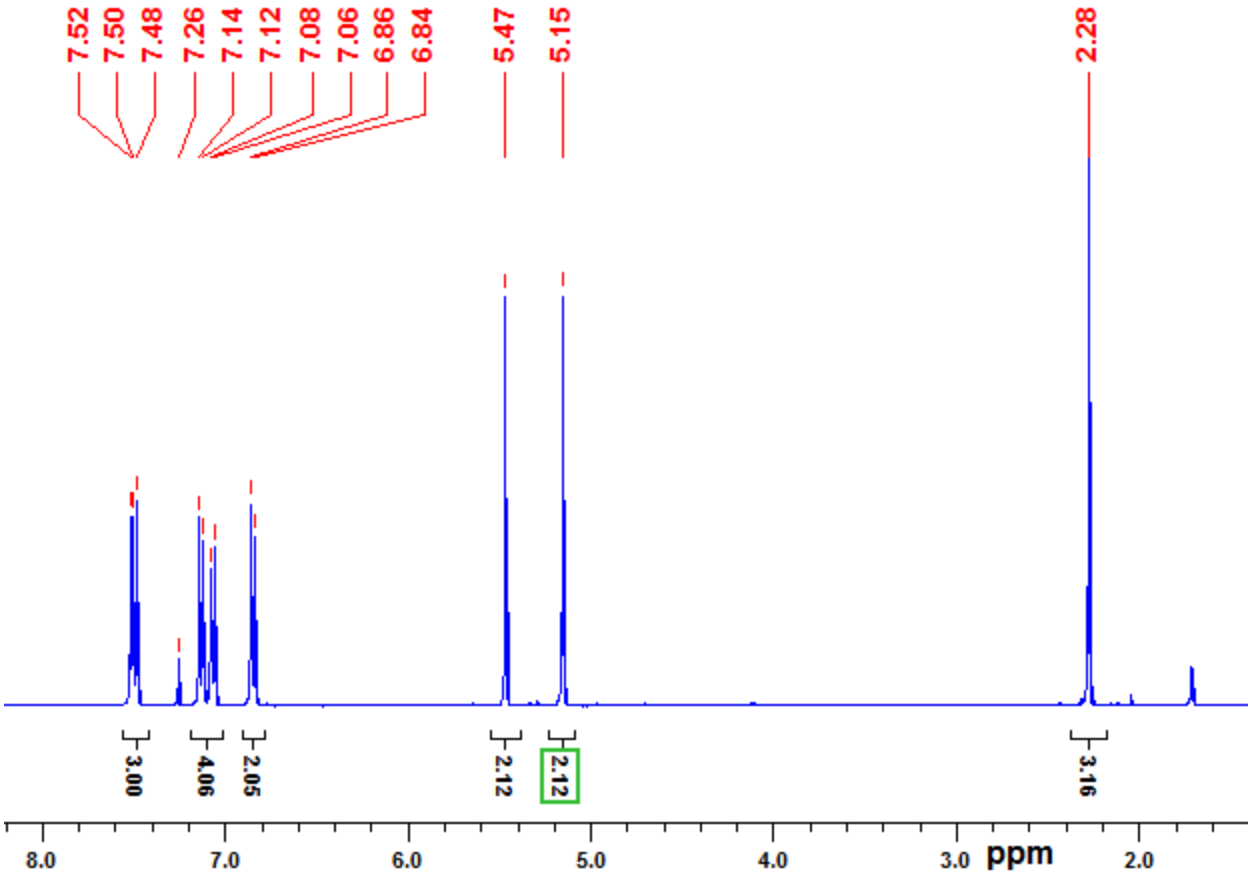



**Fig. S27**. $^{1}$H NMR spectrum of **IIIc** in $CDCl_3$ at room temperature.

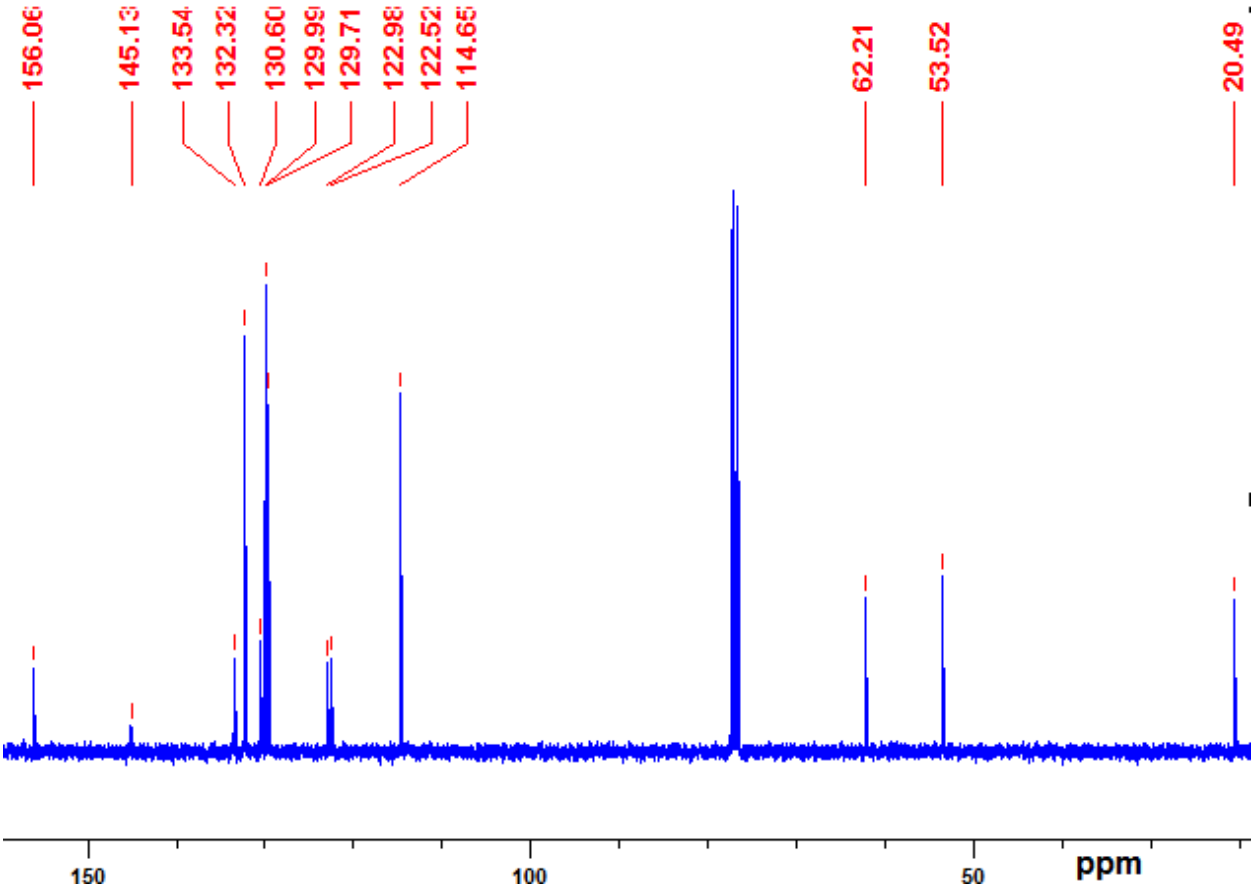
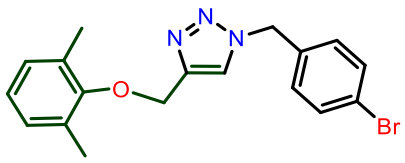



**Fig. S28**. $^{13}$C NMR spectrum of **IIIc** in $CDCl_3$ at room temperature.

**15. 4-((2,6-dimethylphenoxy)methyl)-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (IIId)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.50-7.54 (m, 3H), 7.15-7.17 (m, 2H), 6.92-7.02 (m, 3H), 5.50 (s, 2H), 4.95 (s, 2H), 2.26 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.24, 145.35, 133.61, 132.34, 131.02, 129.69, 128.91, 124.29, 122.99, 122.47, 65.56, 53.53, 16.36 ppm.

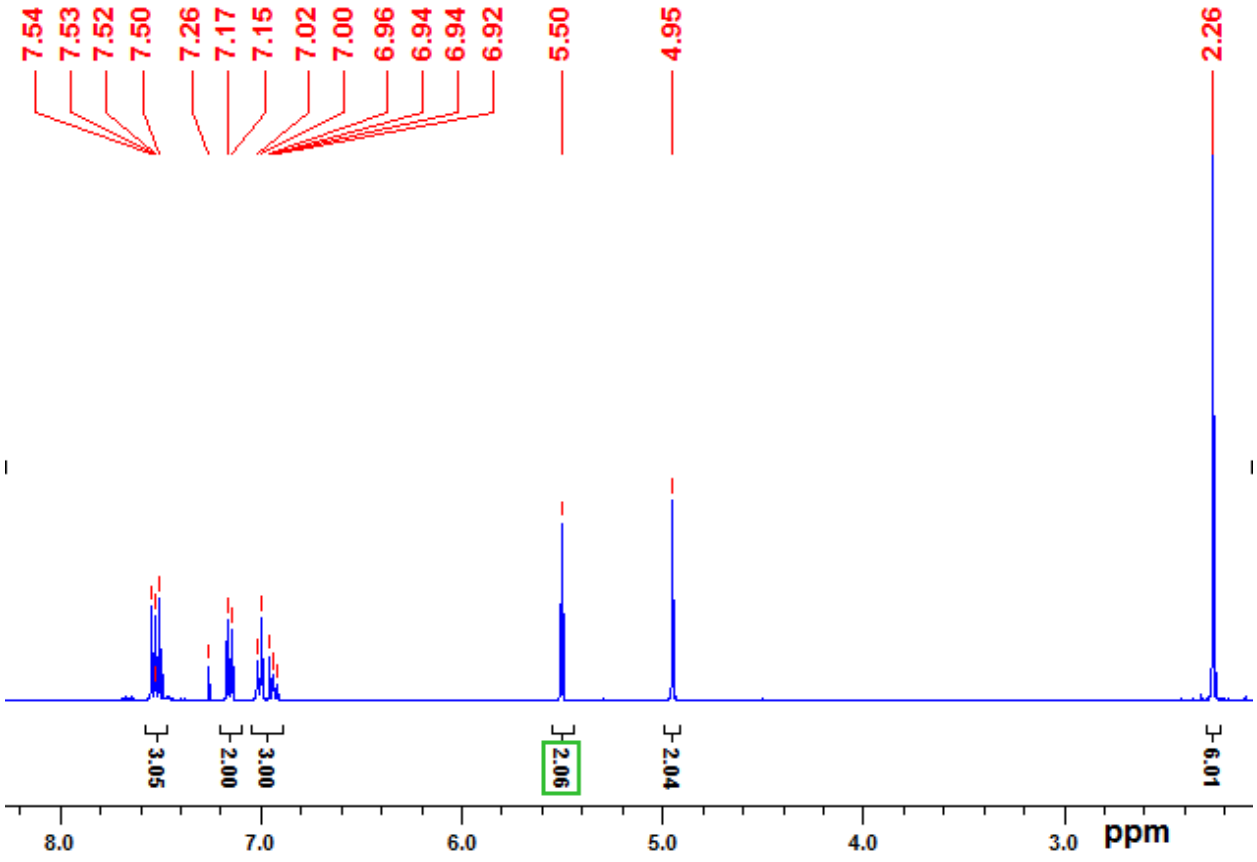



**Fig. S29**. $^{1}$H NMR spectrum of **IIId** in $CDCl_3$ at room temperature.

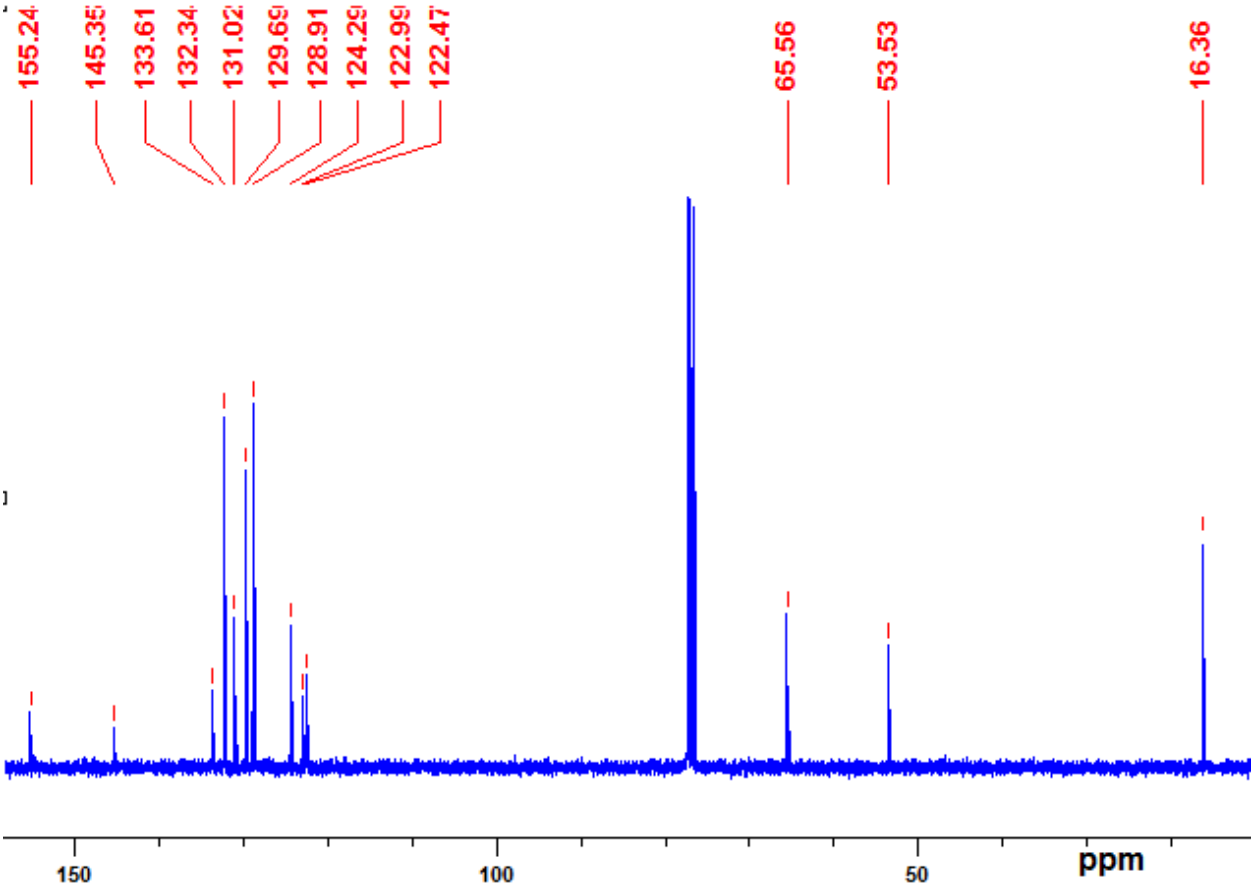
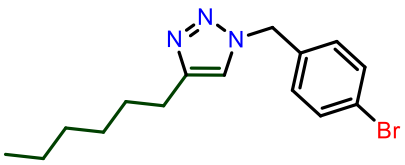



**Fig. S30**. $^{13}$C NMR spectrum of **IIId** in $CDCl_3$ at room temperature.

**16. 4-hexyl-1-(4-nitrobenzyl)-1H-1,2,3-triazole (IIIe)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.48-7.50 (m, 2H), 7.11-7.19 (m, 3H), 5.44 (s, 2H), 2.67-2.71 (t, 2H), 1.59-1.67 (m, 2H), 1.26-1.37 (m, 6H), 0.85-0.88 (t, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 149.23, 134.05, 132.22, 129.56, 122.74, 120.47, 53.28, 31.53, 29.34, 28.91, 25.72, 22.53, 14.04 ppm.

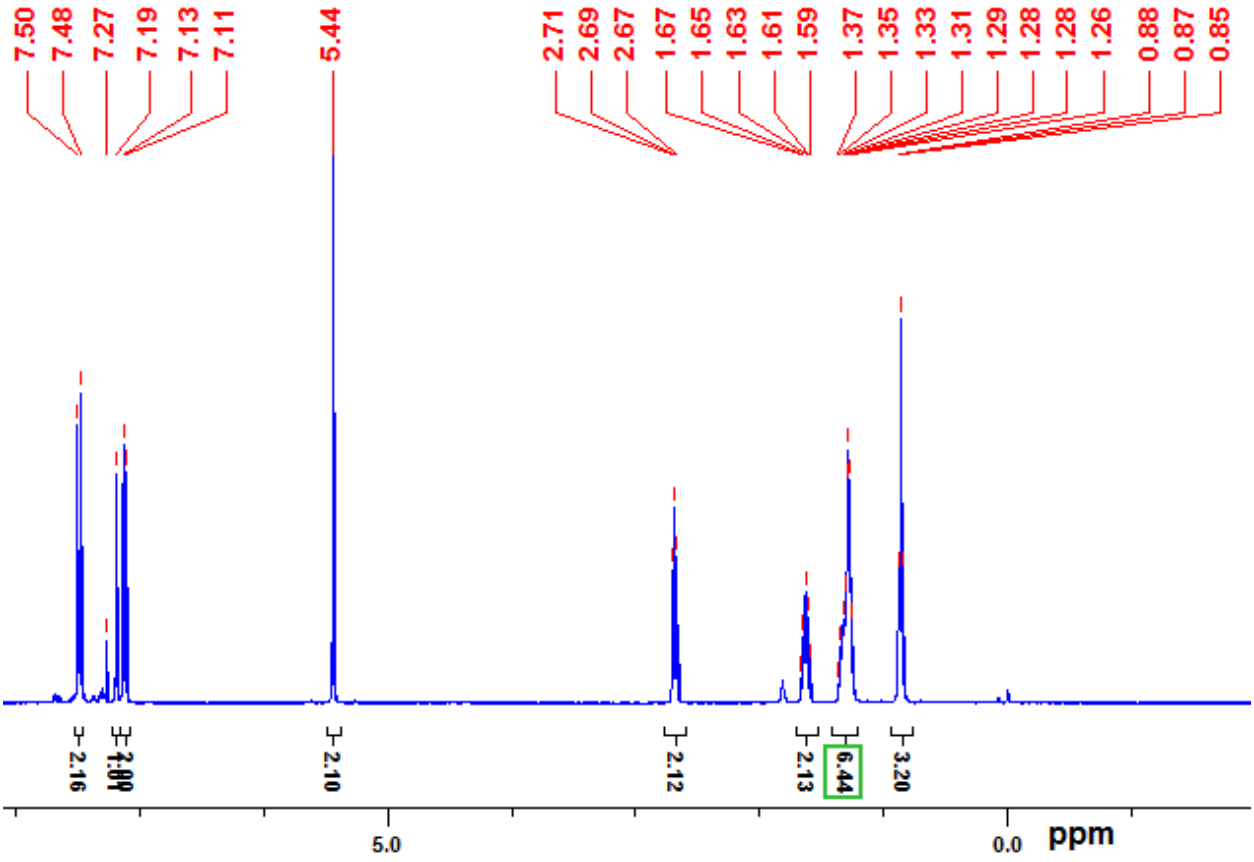



**Fig. S31**. $^{1}$H NMR spectrum of **IIIe** in $CDCl_3$ at room temperature.

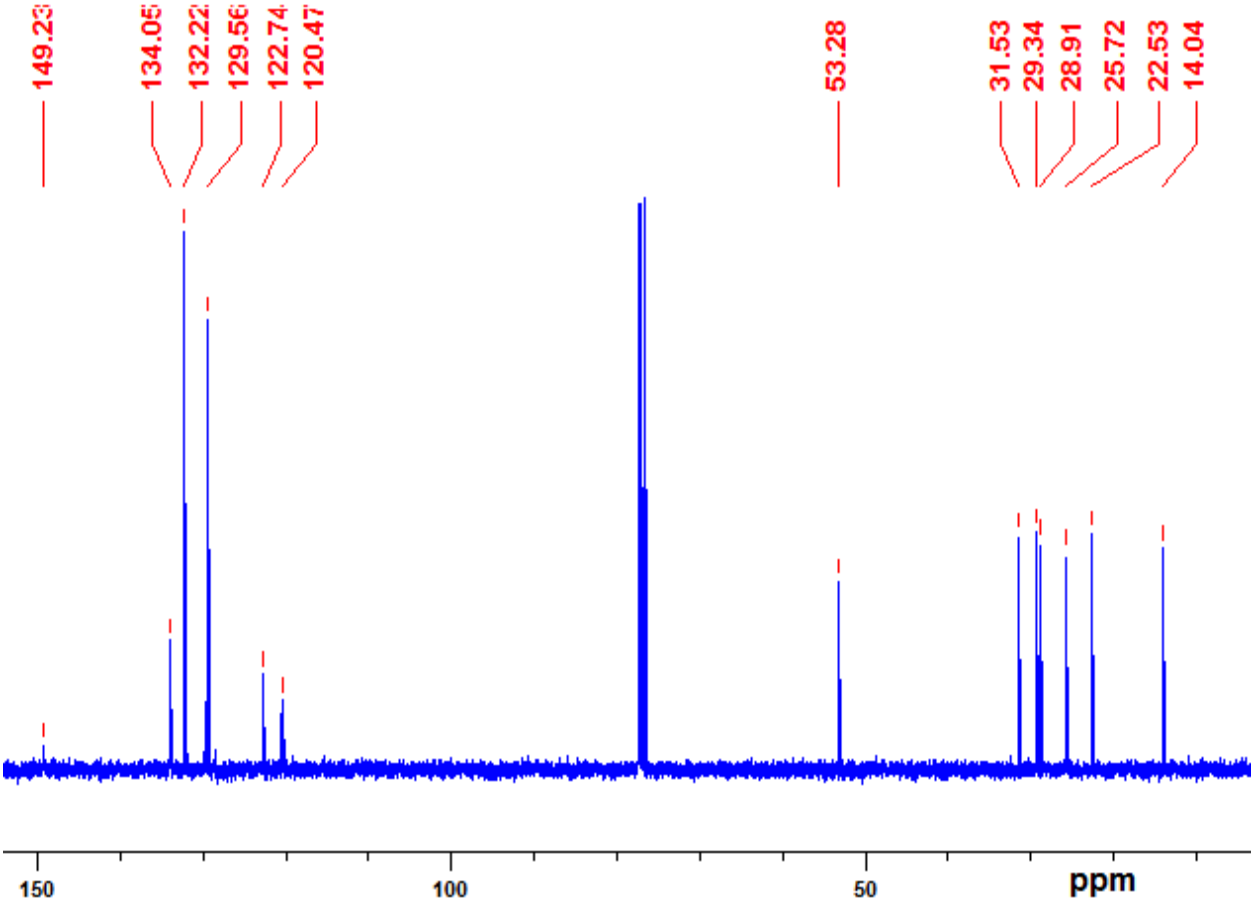
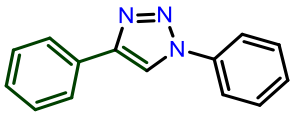



**Fig. S32**. $^{13}$C NMR spectrum of **IIIe** in $CDCl_3$ at room temperature.

**17. 1,4-diphenyl-1*H*-1,2,3-triazole (IVa)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.20 (s, 1H), 7.90-7.92 (d, 2H), 7.78-7.80 (d, 2H), 7.52-7.56 (t, 2H), 7.43-7.48 (m, 3H), 7.35-7.39 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.43, 137.08, 130.25, 129.81, 128.95, 128.80, 128.45, 125.87, 120.55, 117.63 ppm.

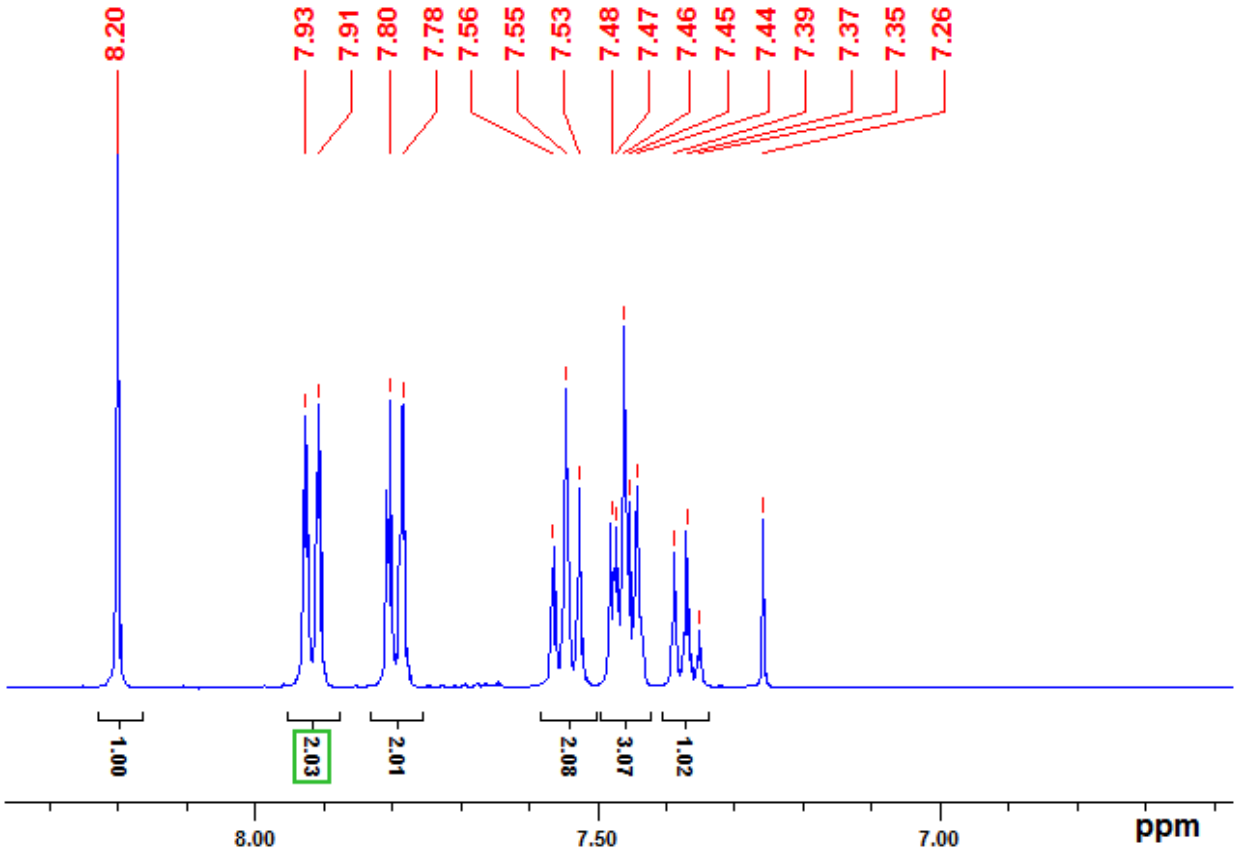



**Fig. S33**. $^{1}$H NMR spectrum of **IVa** in $CDCl_3$ at room temperature.

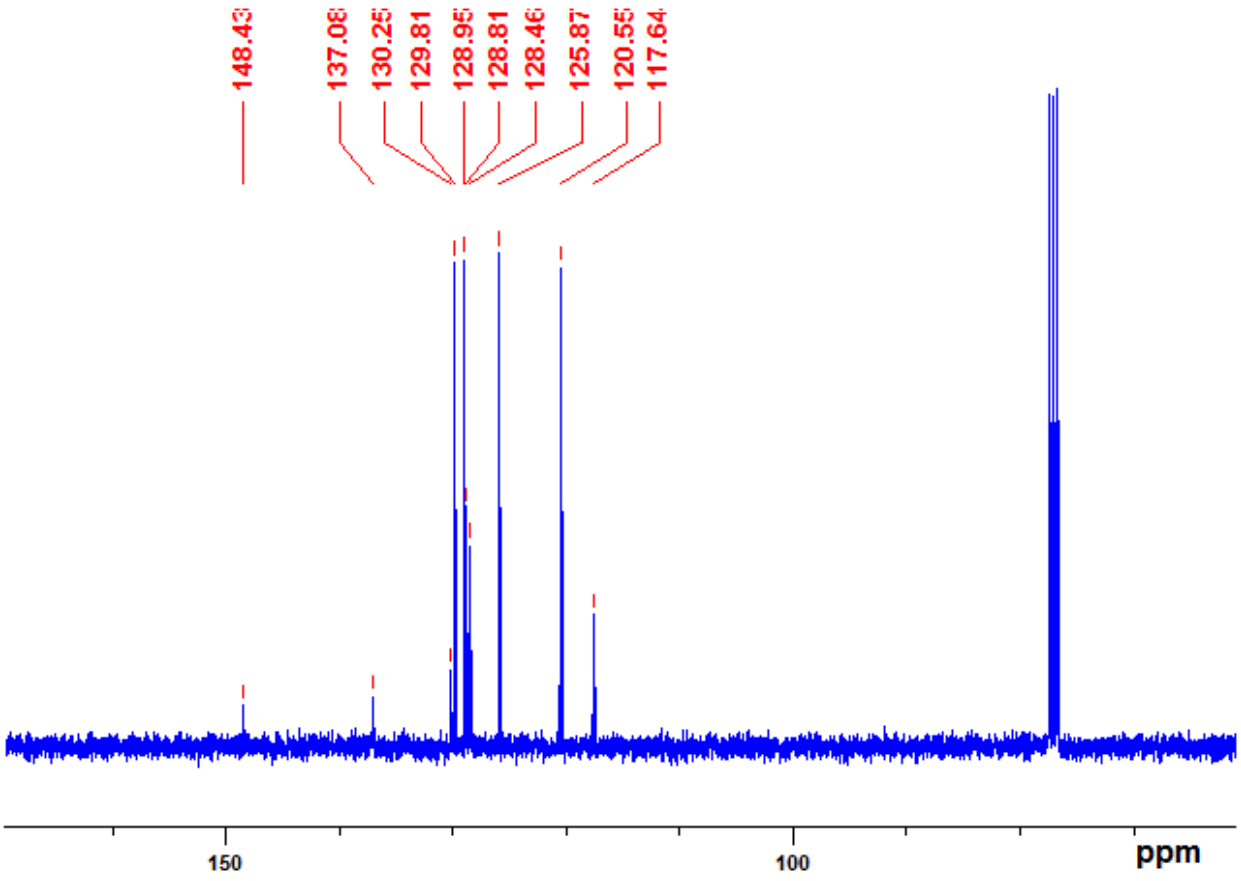
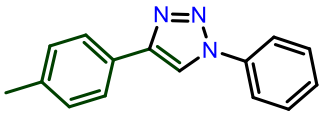



**Fig. S34**. $^{13}$C NMR spectrum of **IVa** in $CDCl_3$ at room temperature.

**18. 1-phenyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IVb)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.15 (s, 1H), 7.76-7.80 (t, 4H), 7.50-7.54 (t, 2H), 7.41-7.45 (t, 1H), 7.24-7.25 (m, 2H), 2.38 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.50, 138.34, 137.10, 129.77, 129.62, 128.71, 127.42, 125.77, 120.50, 117.29, 21.36 ppm.

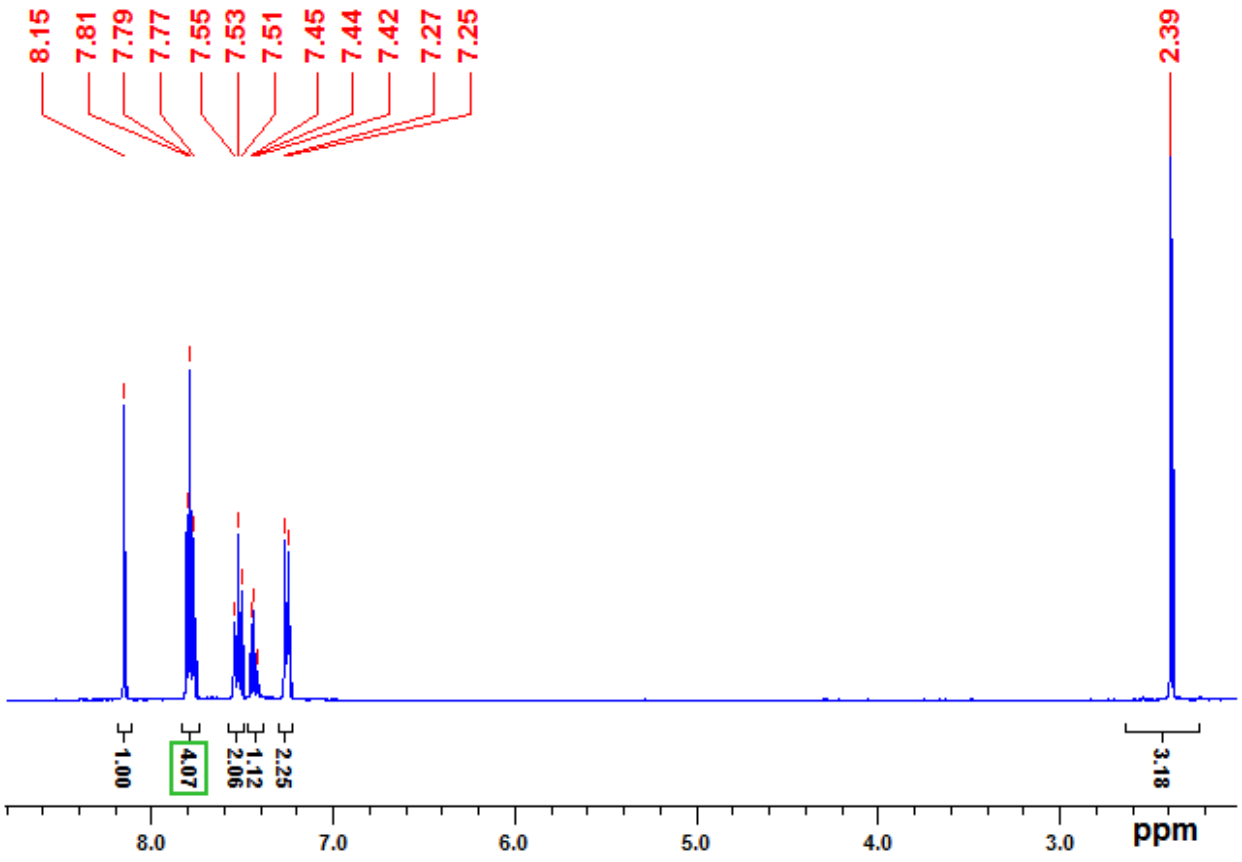



**Fig. S35**. $^{1}$H NMR spectrum of **IVb** in $CDCl_3$ at room temperature.

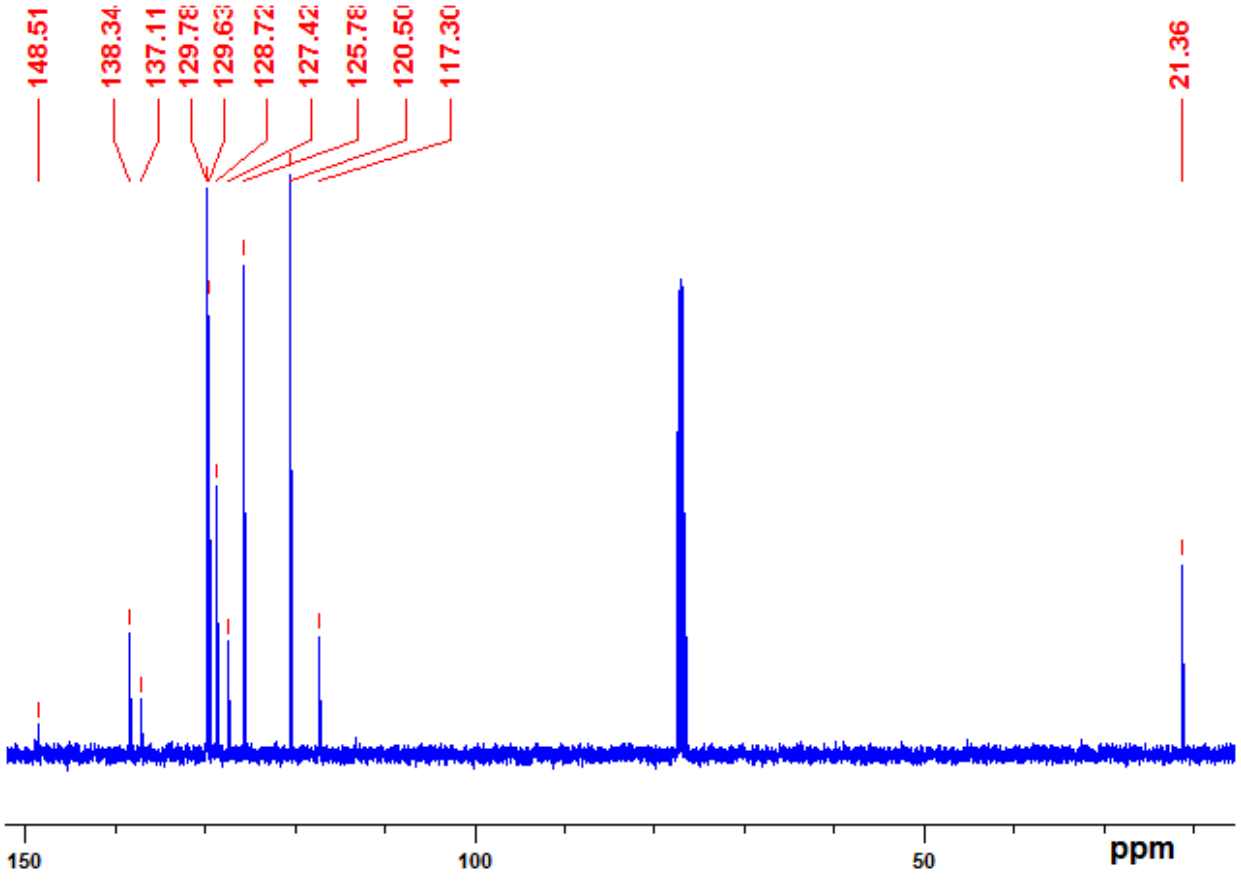
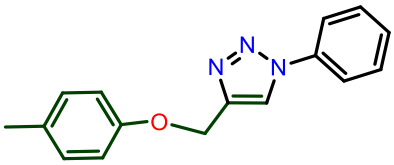



**Fig. S36**. $^{13}$C NMR spectrum of **IVb** in $CDCl_3$ at room temperature.

**19. 1-phenyl-4-((*p*-tolyloxy)methyl)-1*H*-1.2.3-triazole (IVc)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.04 (s, 1H), 7.71-7.73 (d, 2H), 7.49-7.53 (t, 2H), 7.41-7.45 (t, 1H), 7.09-7.11 (d, 2H), 6.90-6.93 (m, 2H), 5.26 (s, 2H), 2.28 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.07, 145.22, 137.00, 130.65, 130.06, 129.79, 128.87, 120.90, 120.61, 114.64, 62.13, 20.51 ppm.

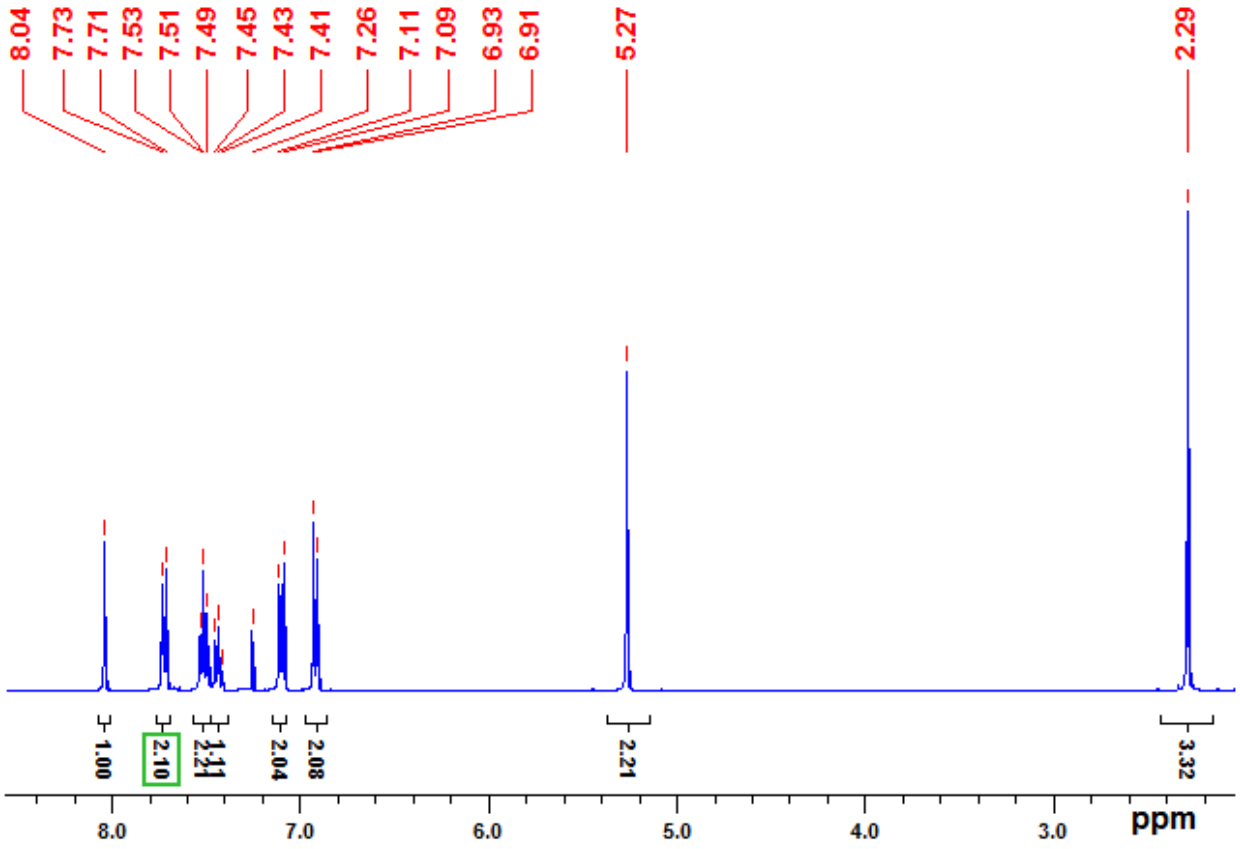



**Fig. S37**. $^{1}$H NMR spectrum of **IVc** in $CDCl_3$ at room temperature.

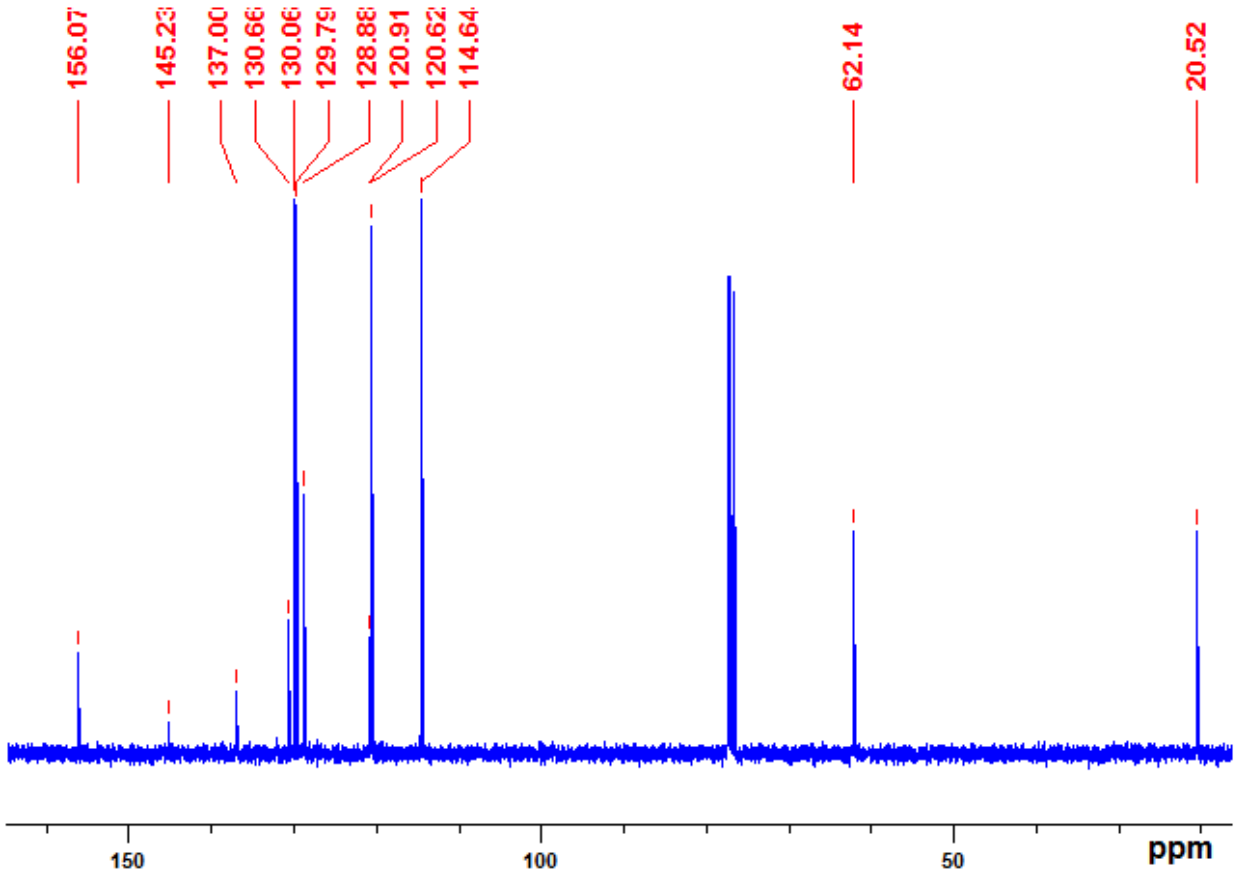
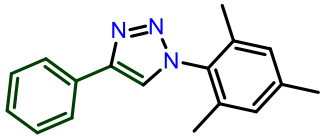



**Fig. S38**. $^{13}$C NMR spectrum of **IVc** in $CDCl_3$ at room temperature.

**20. 1-mesityl-4-phenyl-1*H*-1,2,3-triazole (Va)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.92-7.94 (d, 2H), 7.84 (s, 1H), 7.34-7.48 (m, 3H), 7.01 (s, 2H), 2.36 (s, 3H), 2.01 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 147.58, 140.11, 135.13, 133.51, 130.50, 129.13, 128.95, 128.30, 125.76, 121.52, 21.18, 17.37 ppm.

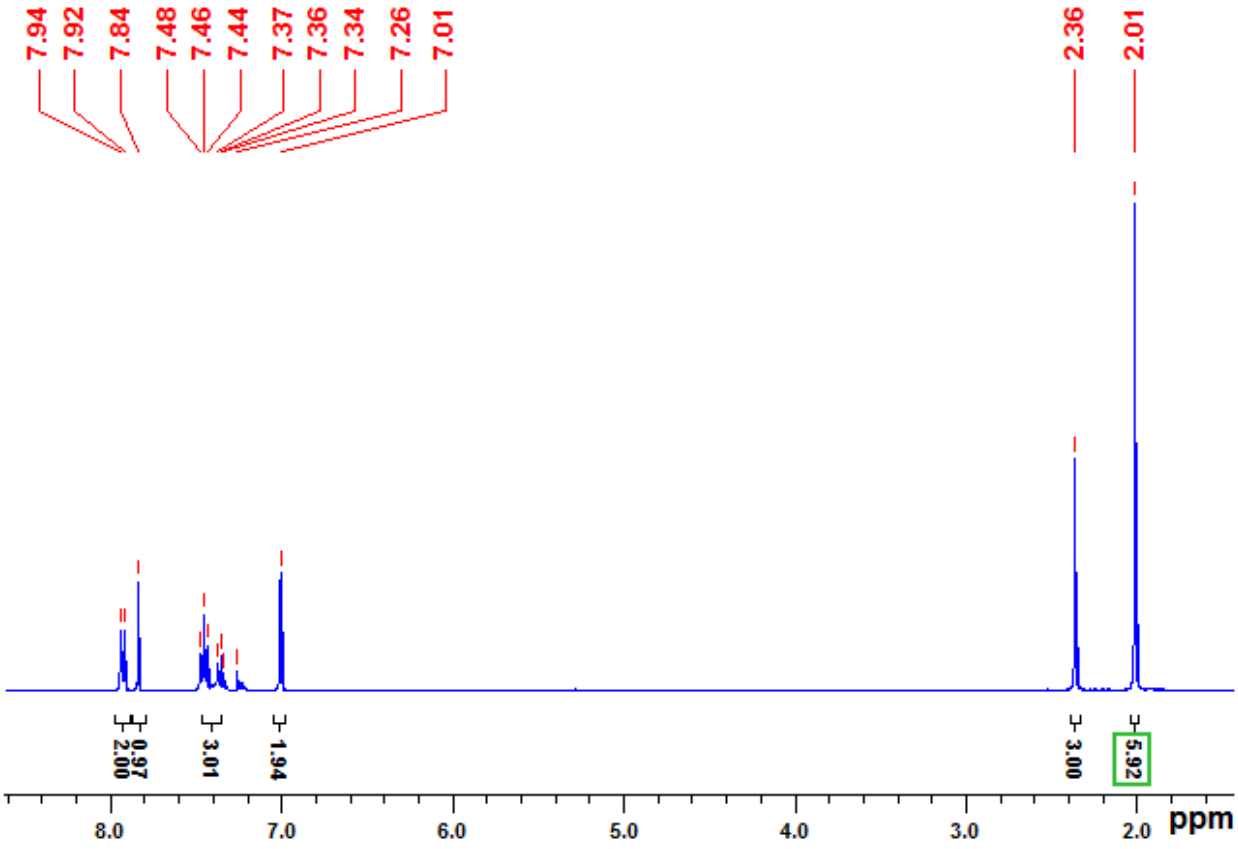



**Fig. S39**. $^{1}$H NMR spectrum of **Va** in $CDCl_3$ at room temperature.

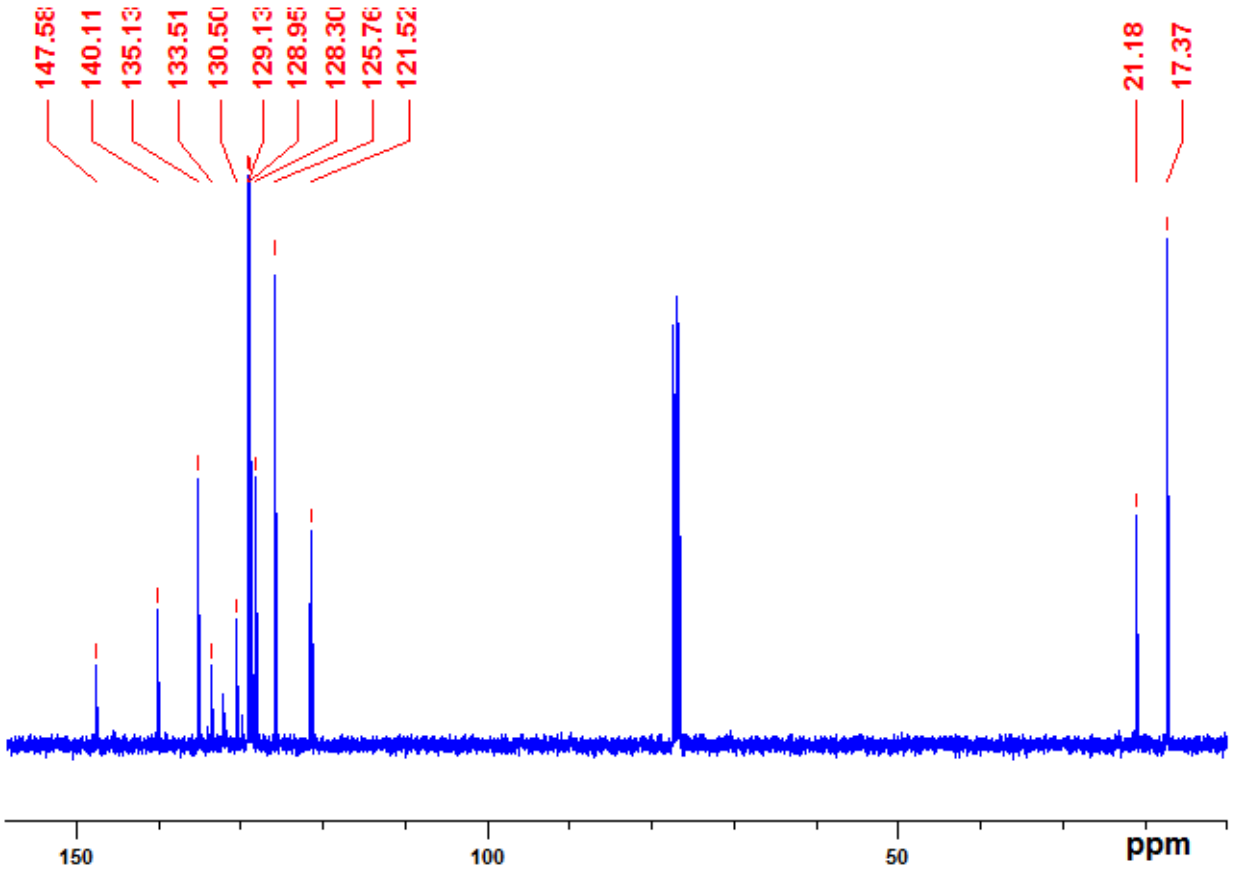
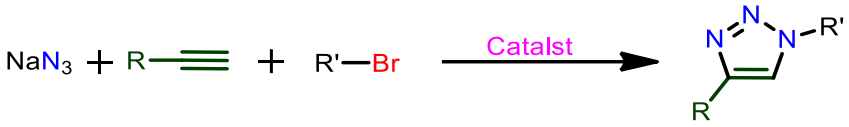


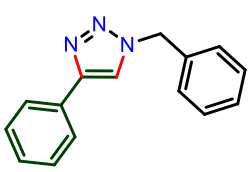

**Fig. S40**. $^{13}C$ NMR spectrum of **Va** in $CDCl_3$ at room temperature.

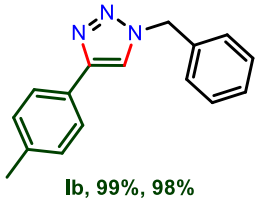
**Table S1.** Structural parameters of compounds **Ia, Ib, IIa** and **IIb**.

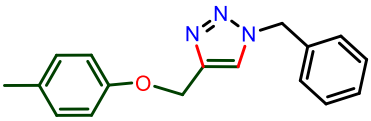
| | **Ia** | **Ib** | **IIa** | **IIb** |
|---|---|---|---|---|
| Empirical formula | $C_{15}H_{13}N_3$ | $C_{16}H_{14}N_3$ | $C_{15}H_{12}N_4O_2$ | $C_{16}H_{14}N_4O_2$ |
| Formula weight | 235.29 | 249.32 | 280.29 | 294.32 |
| Temperature (K) | 298 | 298 | 298 | 298 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1$ | $P2_12_12_1$ | $P2_1/c$ |
| $a$/Å | 6.0383(13) | 8.0688(12) | 5.7169(7) | 9.5421(9) |
| $b$/Å | 8.0923(17) | 5.8237(6) | 13.9426(17) | 5.7049(4) |
| $c$/Å | 25.709(8) | 14.4259(17) | 17.101(3) | 27.128(3) |
| α/° | 90 | 90 | 90 | 90 |
| $\beta$/° | 93.516(19) | 100.683(13) | 90 | 98.745(10) |
| $\gamma$/° | 90 | 90 | 90 | 90 |
| Volume (Å$^3$) | 1253.9(5) | 666.13(15) | 1363.1(3) | 1459.6(2) |
| $Z$ | 4 | 2 | 4 | 4 |
| $\rho_{calc}$/mg mm$^{-3}$ | 1.2463 | 1.2429 | 1.3657 | 1.3392 |
| Absorption coefficient ($\mu$/mm$^{-1}$) | 0.076 | 0.076 | 0.095 | 0.092 |
| $F$(000) | 496.2 | 264.1 | 584.3 | 616.3 |
| Reflections collected | 10726 | 2967 | 3974 | 6410 |
| $R_{int}$ | 0.0743 | 0.0457 | 0.0430 | 0.0333 |
| GOF on $F^2$ | 1.040 | 1.035 | 1.066 | 1.069 |
| $R_1$ ($I>2\sigma(I)$) | 0.0688 | 0.0736 | 0.0884 | 0.0688 |
| w$R_2$ ($I>2\sigma(I)$) | 0.1682 | 0.1638 | 0.2247 | 0.1538 |
| $R_1$ values (all data) | 0.1497 | 0.1494 | 0.1699 | 0.1375 |
| $R_2$ values (all data) | 0.2335 | 0.2281 | 0.2989 | 0.1999 |

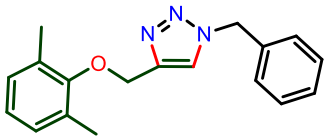
**Chart S1.** Complex **1** and/or **2** catalyzed [3 + 2] cycloaddition of aliphatic azide with alkyne[a]

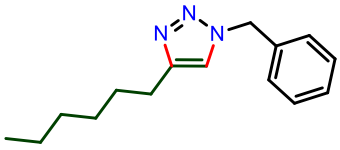


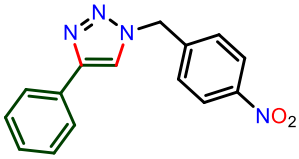


**Ia, 99%, 96%**

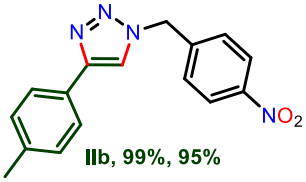

**Ib, 99%, 98%**

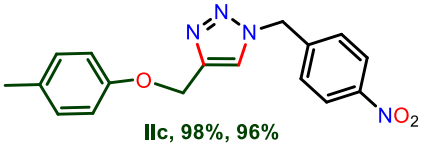

**Ic, 99%, 95%**

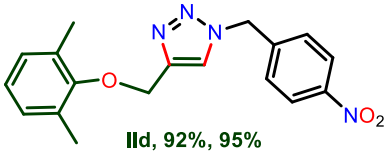

**Id, 98%, 96%**

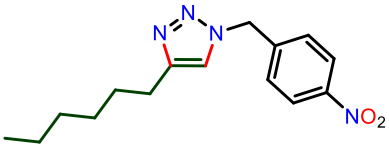

**If, 95%, 98%**

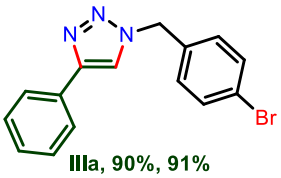

**IIa, 98%, 99%**

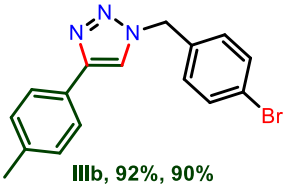

**IIb, 99%, 95%**

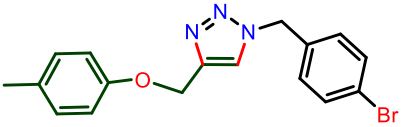

**IIc, 98%, 96%**

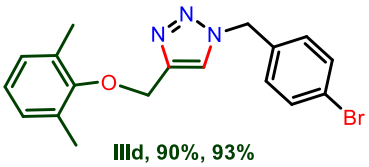

**IId, 92%, 95%**

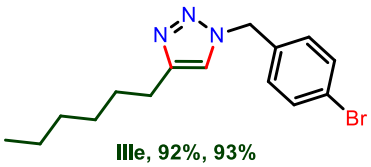

**IIe, 94%, 98%**


**IIIa, 90%, 91%**


**IIIb, 92%, 90%**


**IIIc, 94%, 91%**


**IIId, 90%, 93%**

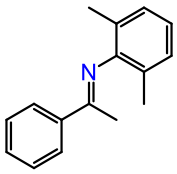

**IIIe, 92%, 93%**

[a]Reaction conditions: alkyne (1.2 mmol), azide (1 mmol), Catalyst **1** and/or **2** (1 mol%), neat, isolated yield.

**Copper(I) catalysts mediated hydroamination of terminal alkynes with substituted anilines:**

Catalysts **1** or **2** (1 mol %) and $AgBF_4$ (1 mol %) were placed together in an oven dried schlenk flask. The schlenk flask was then evacuated and refilled with nitrogen two to three times. Subsequently, 1 mL of acetonitrile was added to the mixture and was allowed to stir at room temperature for 5-10 minutes. After which, the corresponding arylamine (0.6 mmol) and terminal alkyne (0.50 mmol) were added successively. The resulting mixture was allowed to stir at 70 ºC for the appropriate time and the progression of the reactions were determined by thin layer chromatography.

**21. 2,6-dimethyl-*N*-(1-phenylethylidene)aniline (VIa)**




$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.04-8.07 (m, 2H), 7.47-7.50 (m, 3H), 7.07-7.09 (d, 2H), 6.92-6.94 (t, 1H), 2.09 (s, 3H), 2.05 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 165.2, 149.0, 139.1, 130.4, 128.4, 127.8, 127.1, 125.7, 122.7, 18.0, 17.5.

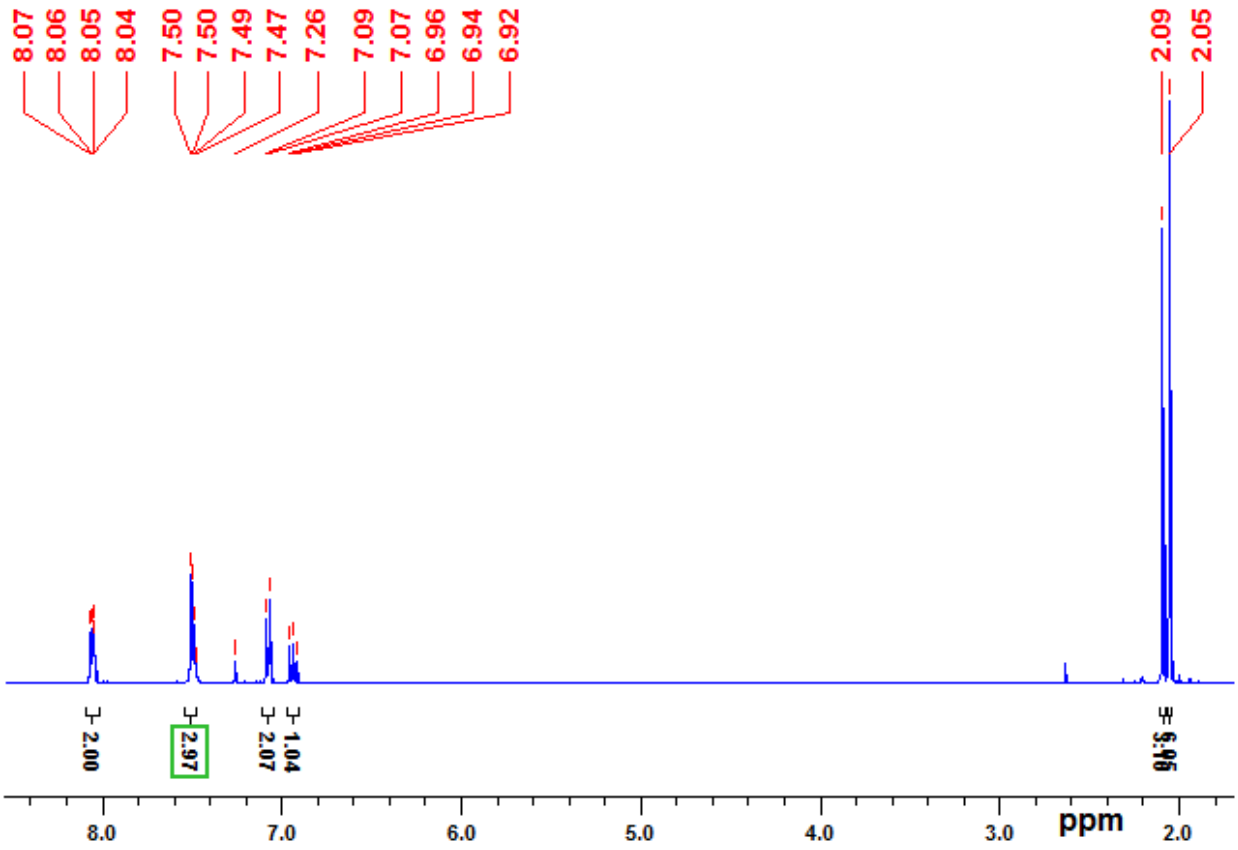



**Fig. S41**. $^{1}$H NMR spectrum of **VIa** in $CDCl_3$ at room temperature.

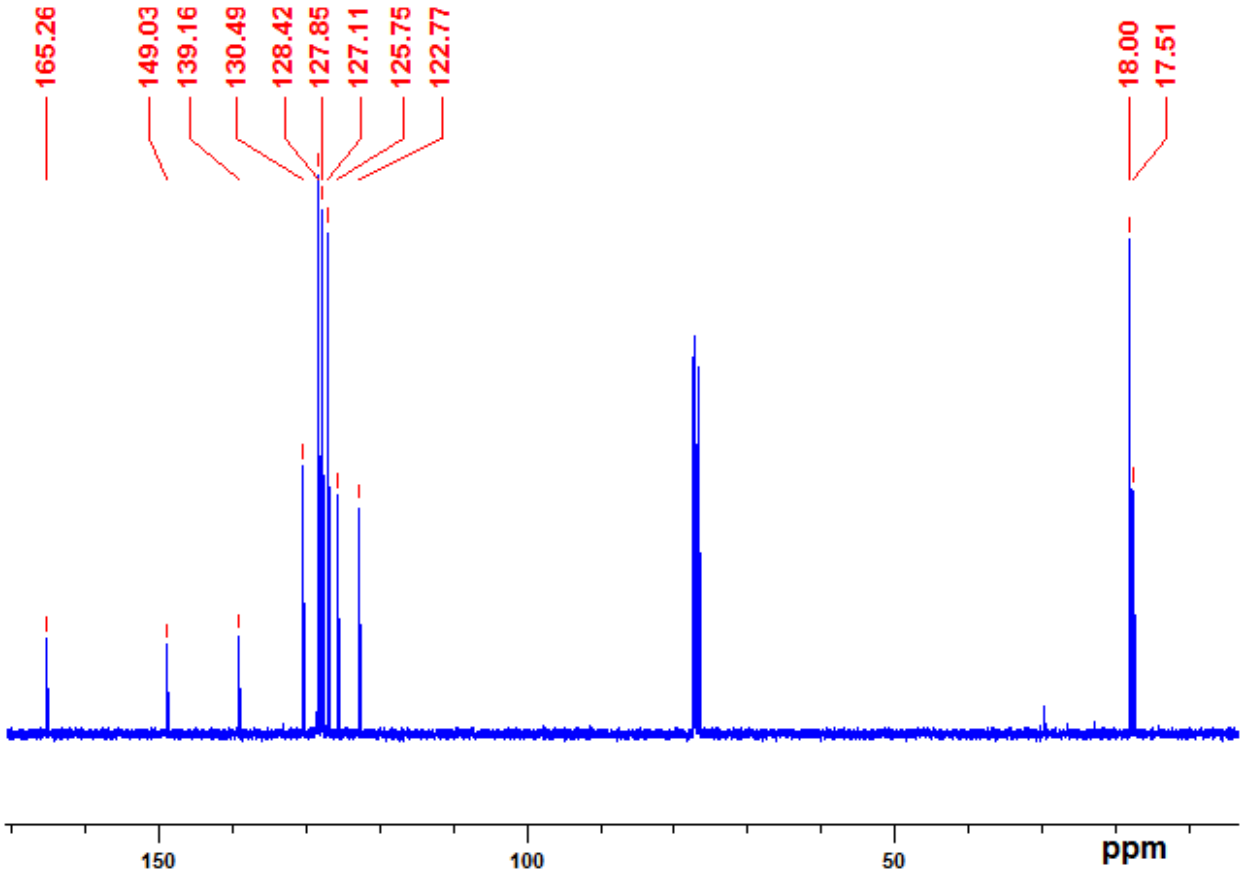
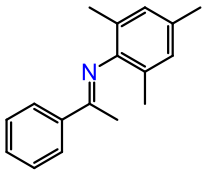



**Fig. S42**. $^{13}$C NMR spectrum of **VIa** in $CDCl_3$ at room temperature.

**22. 2,4,6-trimethyl-*N*-(1-phenylethylidene)aniline (VIb)**




$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.08-8.09 (d, 2H), 7.51-7.53 (d, 3H), 6.94 (s, 2H), 2.35 (s, 3H), 2.12 (s, 6H), 2.06 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 165.4, 146.5, 139.3, 133.1, 131.9, 130.4, 128.5, 128.4, 127.1, 125.6, 20.8, 17.9, 17.4.

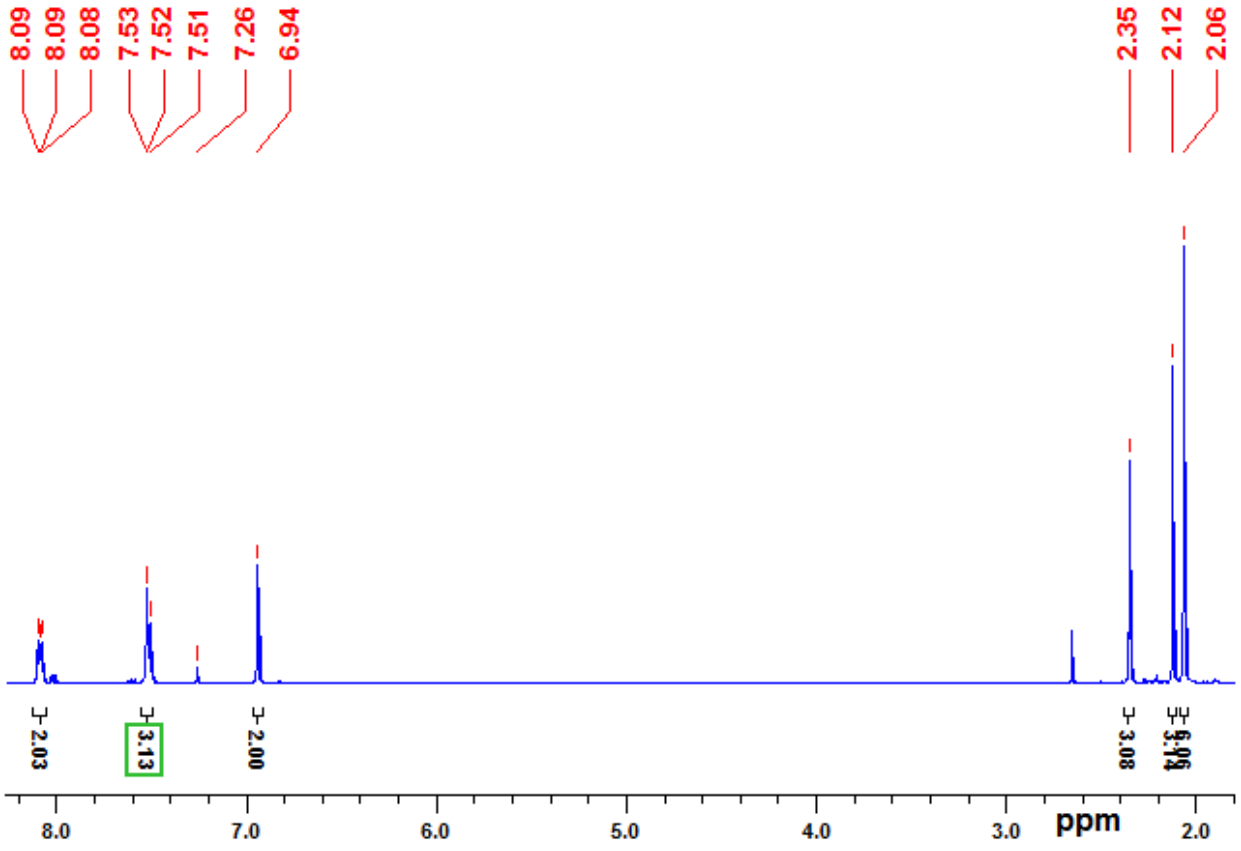



**Fig. S43**. $^{1}$H NMR spectrum of **VIb** in $CDCl_3$ at room temperature.

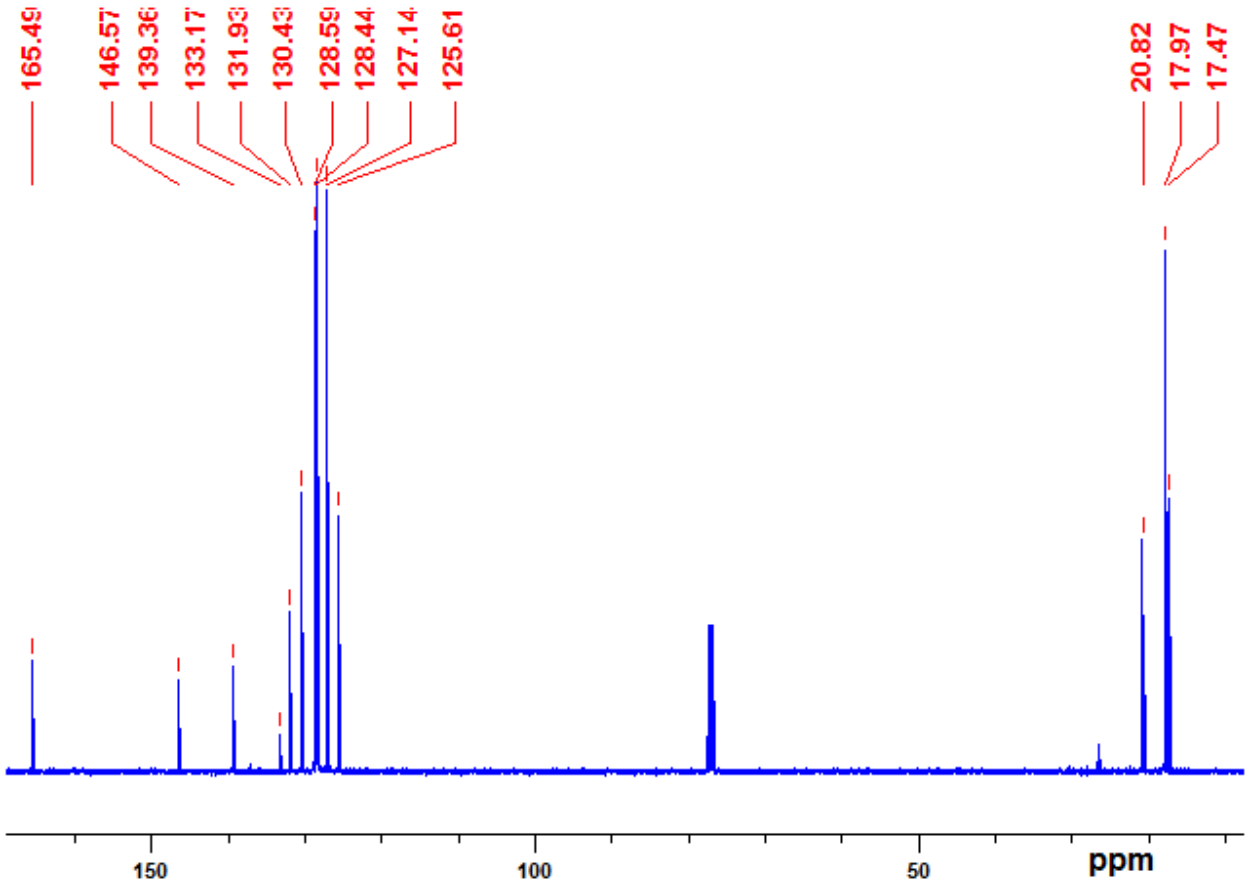
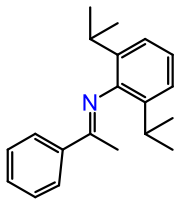



**Fig. S44**. $^{13}$C NMR spectrum of **VIb** in $CDCl_3$ at room temperature.

### 23. 2,6-diisopropyl-*N*-(1-phenylethylidene)aniline (VIc)

$^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.07-8.09 (d, 2H), 7.51-7.52 (t, 3H), 7.07-7.20 (m, 3H), 2.75-2.85 (sept, 2H), 2.14 (s, 3H), 2.00 (s, 3H), 1.17-1.20 (d, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 164.8, 146.7, 139.0, 136.0, 130.0, 128.3, 127.1, 123.2, 122.9, 28.1, 23.2, 22.9, 22.4. 18.0.



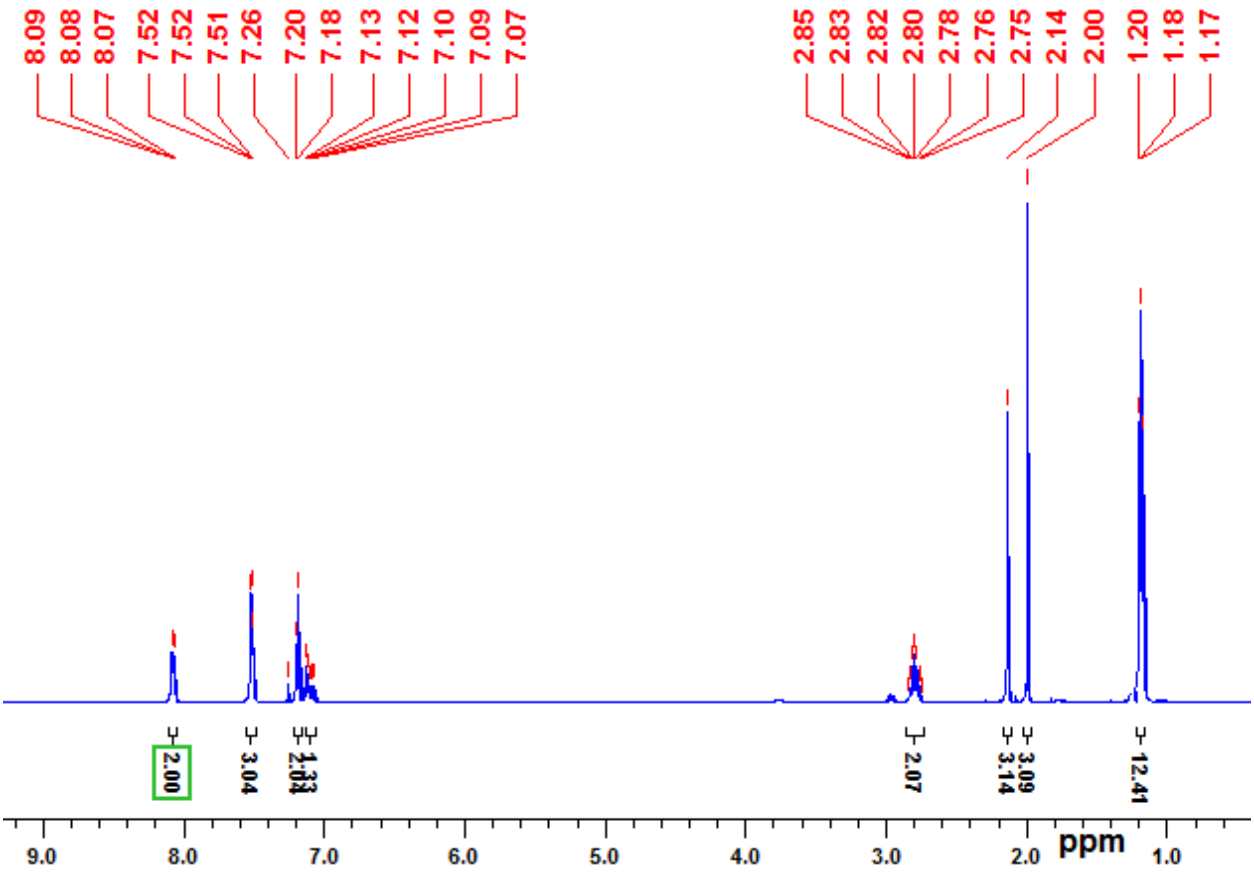



**Fig. S45**. $^{1}$H NMR spectrum of **VIc** in $CDCl_3$ at room temperature.

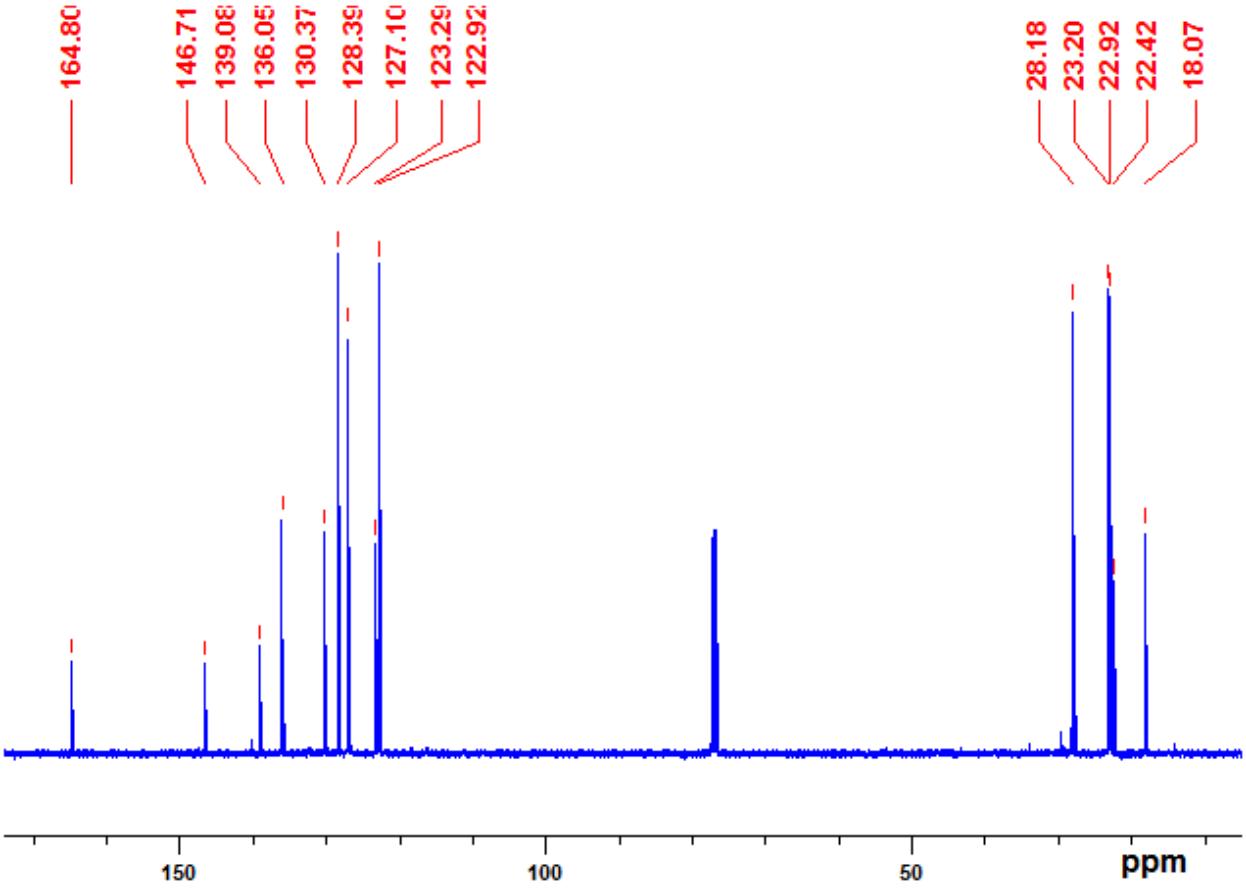
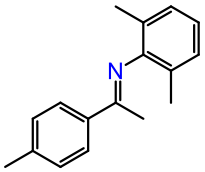



**Fig. S46**. $^{13}$C NMR spectrum of **VIc** in $CDCl_3$ at room temperature.

### 24. 2,6-dimethyl-*N*-(1-(*p*-tolyl)ethylidene)aniline (VIIa)

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.92-7.94 (d, 2H), 7.23-7.28 (d, 2H), 7.03-7.05 (d, 2H), 6.88-6.92 (t, 1H), 2.42 (s, 3H), 2.02-2.04 (d, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 165.0, 149.1, 140.7, 136.4, 129.1, 127.8, 127.1, 125.8, 122.6, 21.4, 18.0, 17.4.



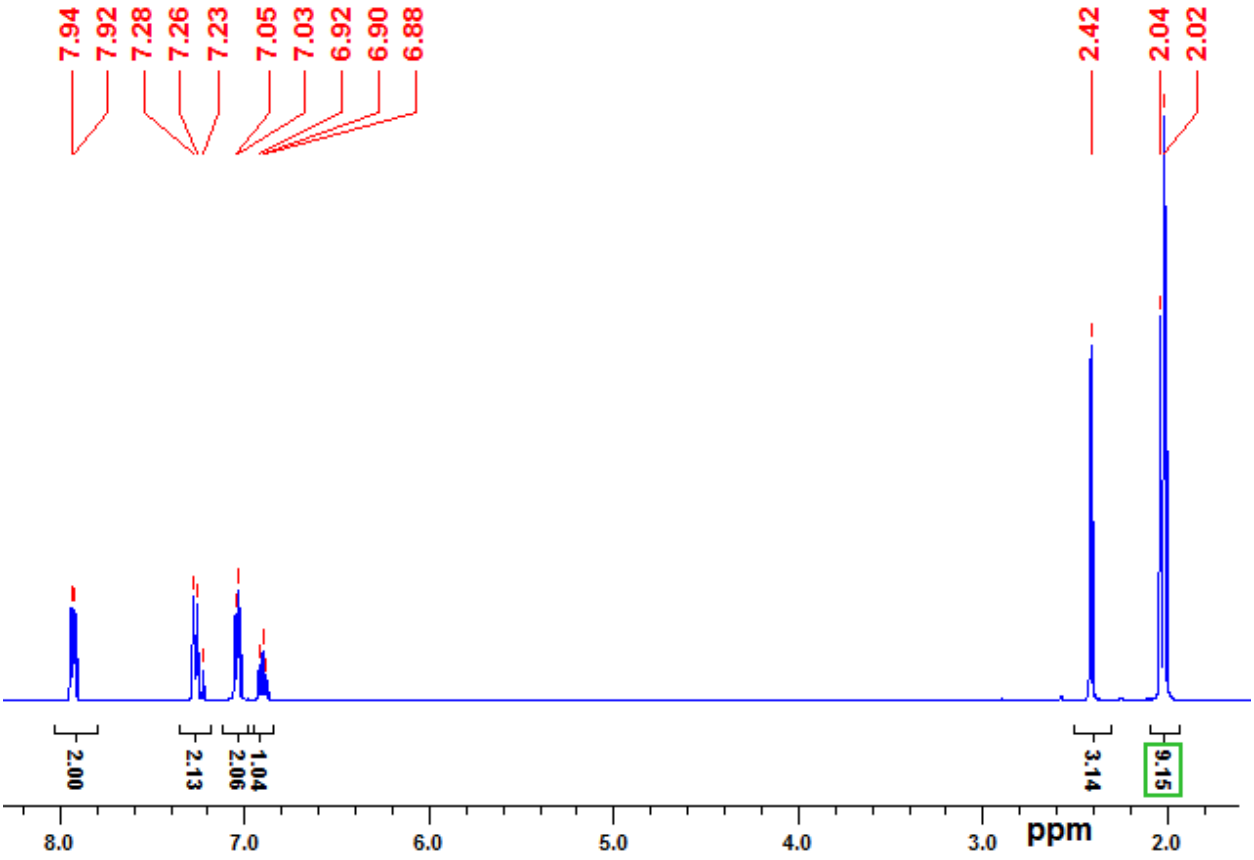



**Fig. S47**. $^{1}H$ NMR spectrum of **VIIa** in $CDCl_3$ at room temperature.

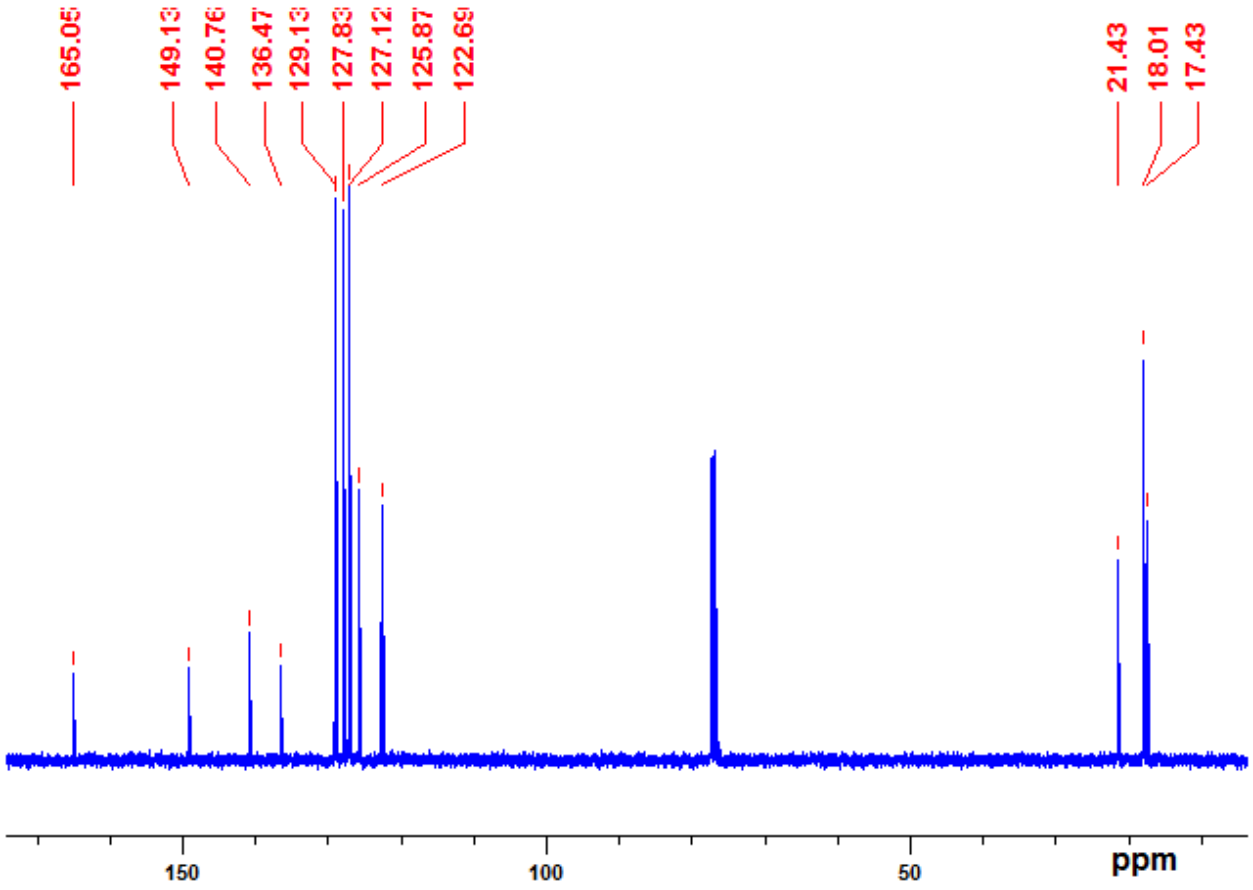
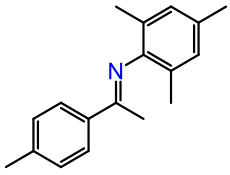



**Fig. S48**. $^{13}$C NMR spectrum of **VIIa** in $CDCl_3$ at room temperature.

### 25. 2,4,6-trimethyl-*N*-(1-(*p*-tolyl)ethylidene)aniline (VIIb)

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.91-7.93 (d, 2H), 7.23-7.27 (d, 2H), 6.86 (s, 2H), 2.41 (s, 3H), 2.28 (s, 3H), 2.03 (s, 3H), 1.98 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 165.2, 146.5, 140.6, 136.6, 131.8, 129.0, 128.5, 127.0, 125.7, 21.4, 20.7, 17.9, 17.3.



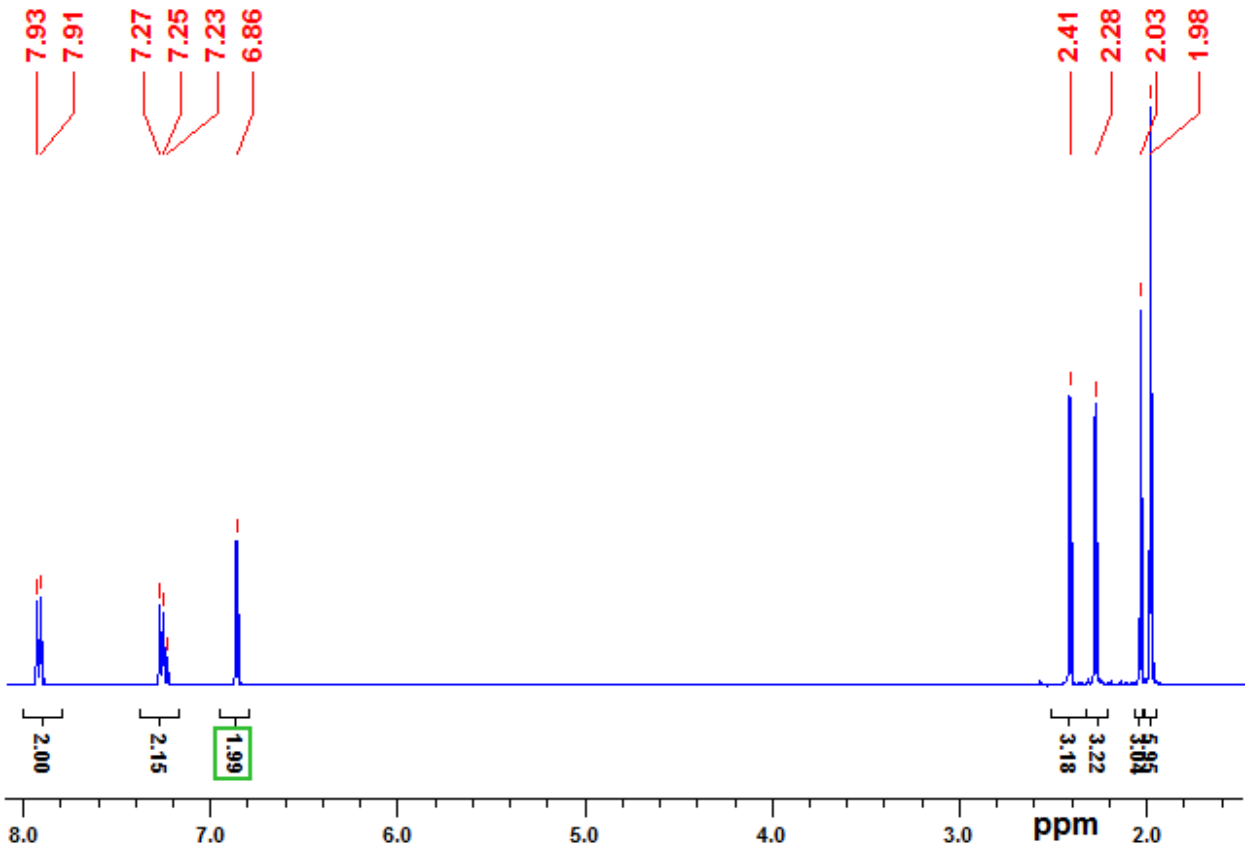



**Fig. S49**. $^{1}H$ NMR spectrum of **VIIb** in $CDCl_3$ at room temperature.

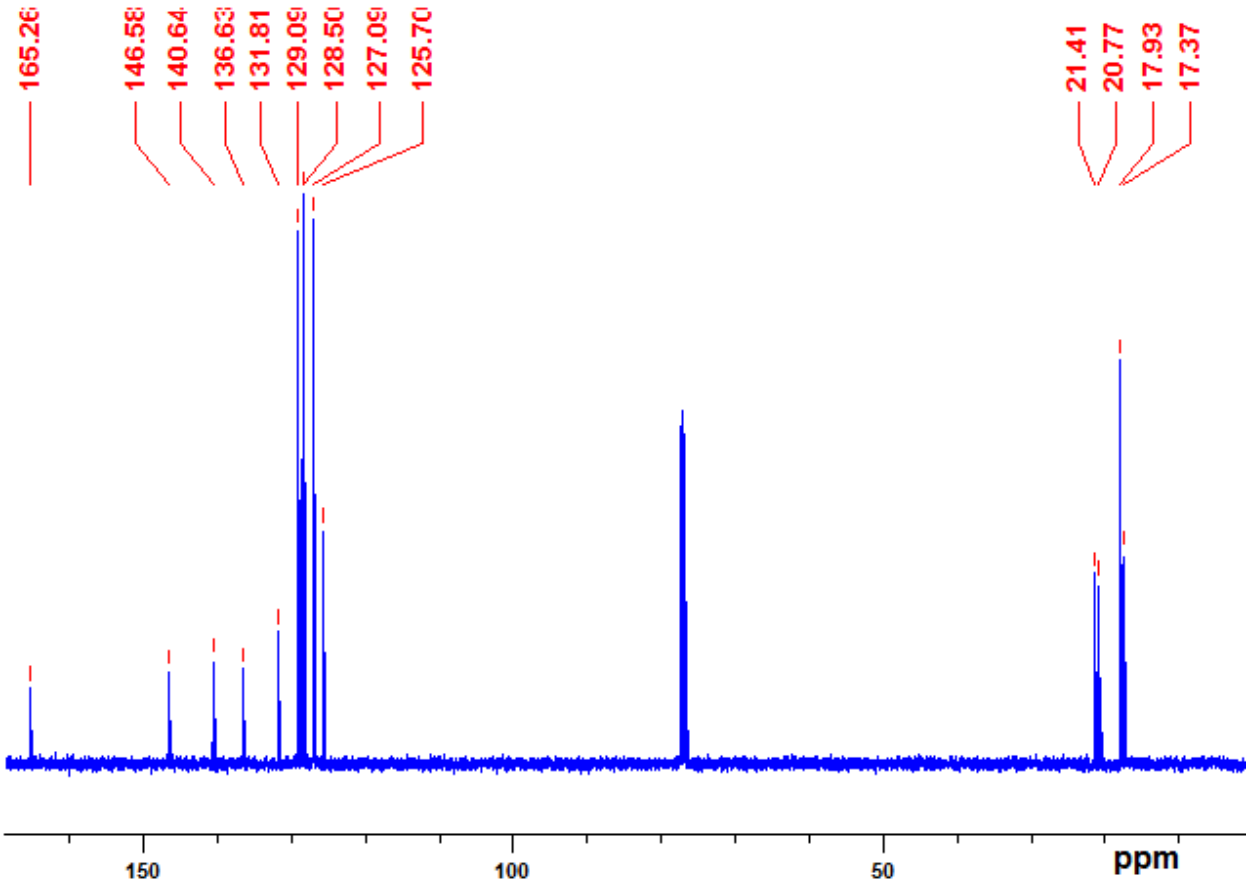
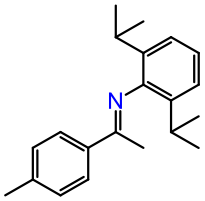



**Fig. S50**. $^{13}$C NMR spectrum of **VIIb** in $CDCl_3$ at room temperature.

**26. 2,6-diisopropyl-*N*-(1-(*p*-tolyl)ethylidene)aniline (VIIc)**

$^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.93-7.95 (d, 2H), 7.27-7.30 (d, 2H), 7.13-7.15 (m, 2H), 7.05-7.09 (m, 1H), 2.70-2.80 (sept, 2H), 2.43 (s, 3H), 2.08 (s, 3H), 1.11-1.15 (d, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 164.5, 146.8, 140.7, 136.4, 136.2, 129.1, 127.1, 123.2, 122.9, 28.2, 23.2, 22.9, 21.4. 18.0.



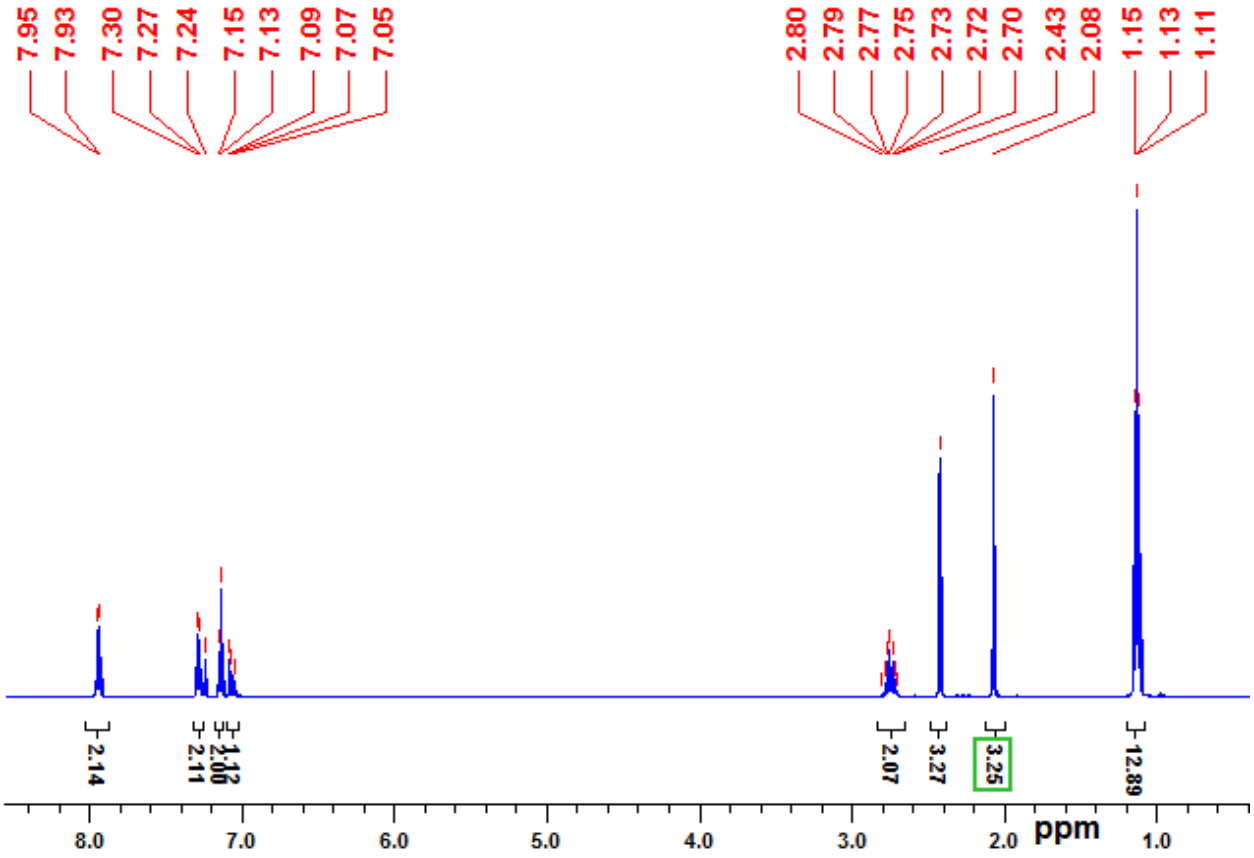



**Fig. S51**. $^{13}C$ NMR spectrum of **VIIc** in $CDCl_3$ at room temperature.

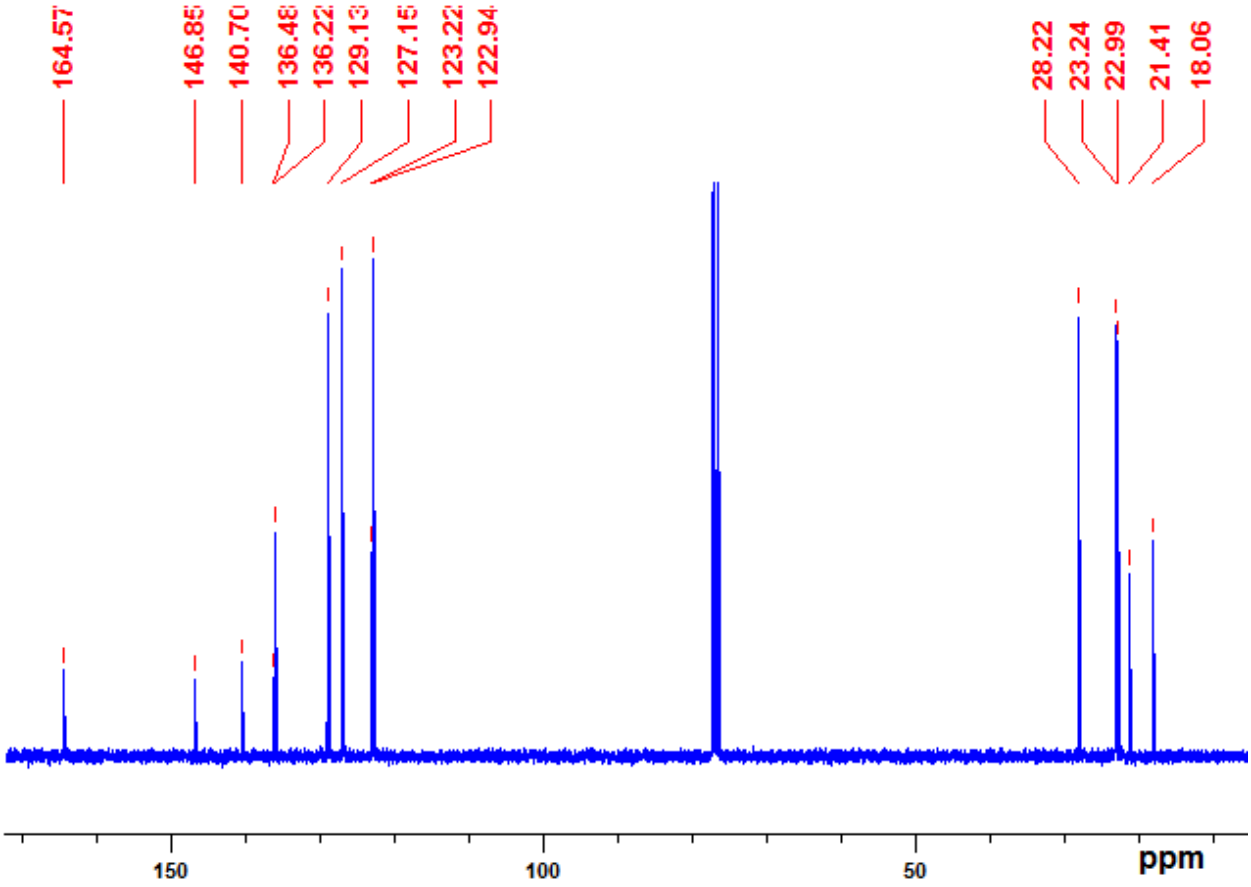
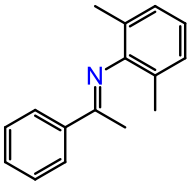
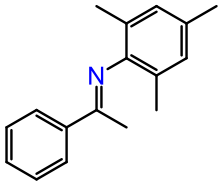



**Fig. S52**. $^{13}C$ NMR spectrum of **VIIc** in $CDCl_3$ at room temperature.

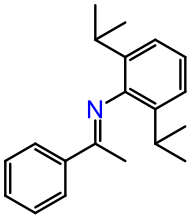
**Chart S2.** Isolated products of hydroamination reaction catalyzed by copper(I) catalysts **1** and **2**.[a]



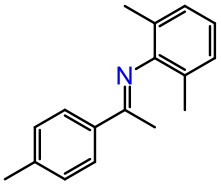
**VIa**, 98%, 96%



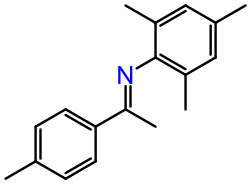
**VIb**, 95%, 97%



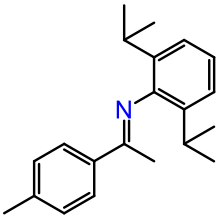
**VIc**, 99%, 95%



**VIIc**, 94%, 96%



**VIIc**, 98%, 97%



**VIIc**, 92%, 96%

[a]Reaction conditions: alkyne (0.5 mmol), substituted aniline (0.6 mmol) and solvent (2 mL).

**Note 1:**

**Trans Metallation reaction with Molecule 1.**

Molecule **1** (0.01g, 1 equiv) and an excess (dms)AuCl (0.07g, 16 equiv) were mixed together and evacuated for 10 minutes, after which 1 mL of acetonitrile was added under argon flow and allowed to stir at room temperature for 12h. $^{1}$H NMR (DMSO-$d_6$, 400 MHz): 1.39 (s, 2((C$H_3$)$_2$CH), 12H), 4.98 (m, 2(CH$_3$)$_2$C*H*, 2H), 7.65-7.73 (m, imidazole, 4H), 8.27 (m, pyridine, 3H) ppm.

**Observations:**

The compound **1** and (dms)AuCl were dissolved completely in acetonitrile and was colorless in the beginning, after 10 minutes the reaction mixture turns violet in color and then after 30 minutes the reaction mixture contains blue precipitate in a colorless solution. After which the reaction mixture was dried in *vacuo* and subjected to NMR measurements. The $^{1}$H NMR measurement supports the presence of ligand (**Bptp**) moiety in the crude product of trans-metallation reaction.

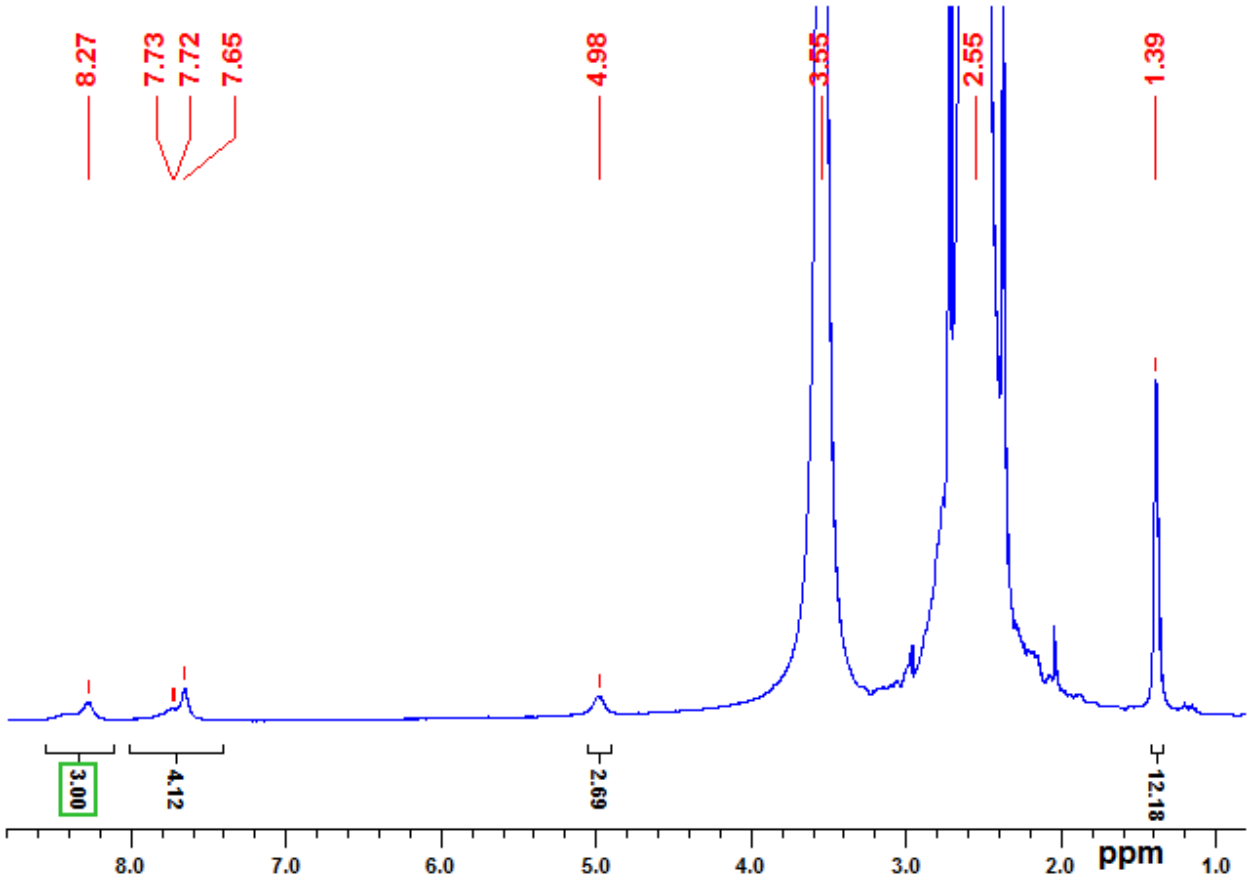



**Fig. S53.** $^{1}$H NMR spectrum of trans-metalation reaction mixture in DMSO-d$_6$ at room temperature.

**Note 2:**

**Host-Guest interactions on Molecule 1 with Perylene.**

**1@Perylene:** Molecule **1** (0.01g, 1 equiv) and an excess perylene (0.03g, 8 equiv) were mixed together and evacuated for 10 minutes, after which 1 mL of acetonitrile was added under argon flow and was allowed to stir at reflux for 4h. $^{1}$H NMR (DMSO-$d_6$, 400 MHz): 1.39-1.41 (d, 2((C$H_3$)$_2$CH), 12H), 4.93-5.02 (m, 2(CH$_3$)$_2$C$H$, 2H), 7.53-7.57 (t, perylene, 2H), 7.73 (d, imidazole, 2H), 7.79-7.81 (d, perylene, 2H), 7.86 (d, imidazole, 2H), 8.18-8.20 (d, pyridine, 2H), 8.35-8.42 (m, perylene, 2H and pyridine 1H) ppm.

**Observations:**

The compound **1** and perylene were not dissolved completely in acetonitrile and has a yellow turbid solution in the beginning and was allowed to stir at 85 $^{o}$C, the reaction mixture forms a yellow crystalline solid in a clear colorless solution after 4h, and then the reaction mixture was dried in vacuo and subjected to spectroscopic measurements, which evidently displays the existence of 1@perylene molecule.

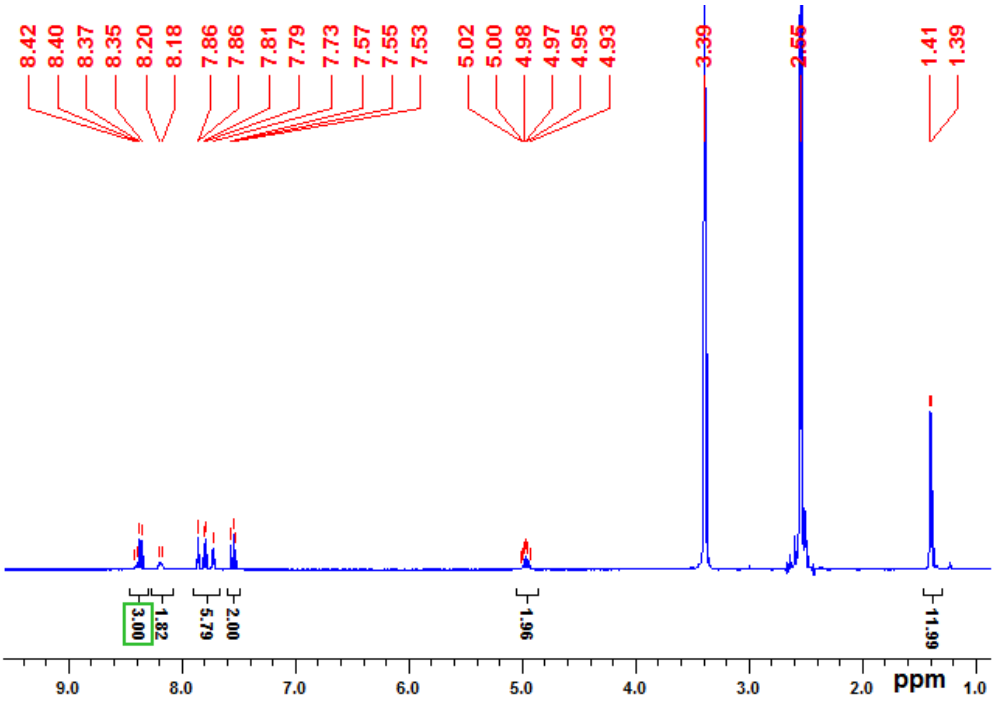



**Fig. S54**. $^{1}$H NMR spectrum of **1**@perylene in DMSO-d$_6$ at RT.

Moreover, (Figure S56) the reaction mixture of **1** and perylene represents the mixed absorption bands in solution UV-vis spectra up to 2h, while almost complete reaction noticed after 3h is due to the association of pyrene with molecule 1, and the reaction mixtures after 3h and 4h represent the identical absorption spectra suggesting no further incorporation/association and as noticed for pyrene reaction, the reaction mixture of perylene is also legitimately altered from the molecule 1.

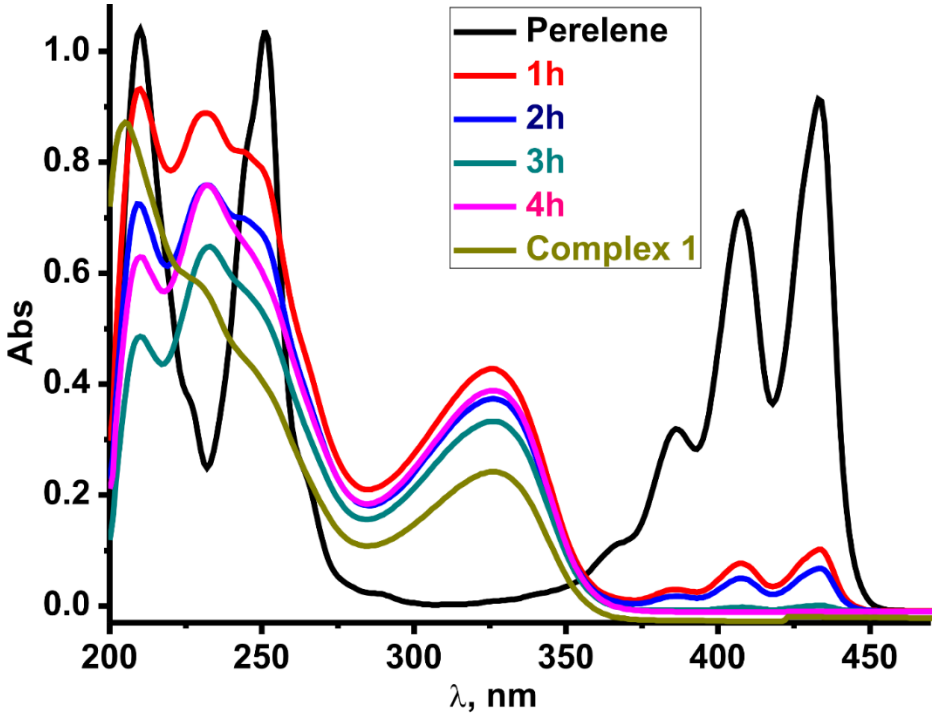



**Fig. S55**. Solution state UV-visible spectral analysis of **1** and the reaction mixture of **1**@perylene in acetonitrile at elevated temperature with 1h interval, measured at 298K with 2.8 x $10^{-5}$ M acetonitrile solution.

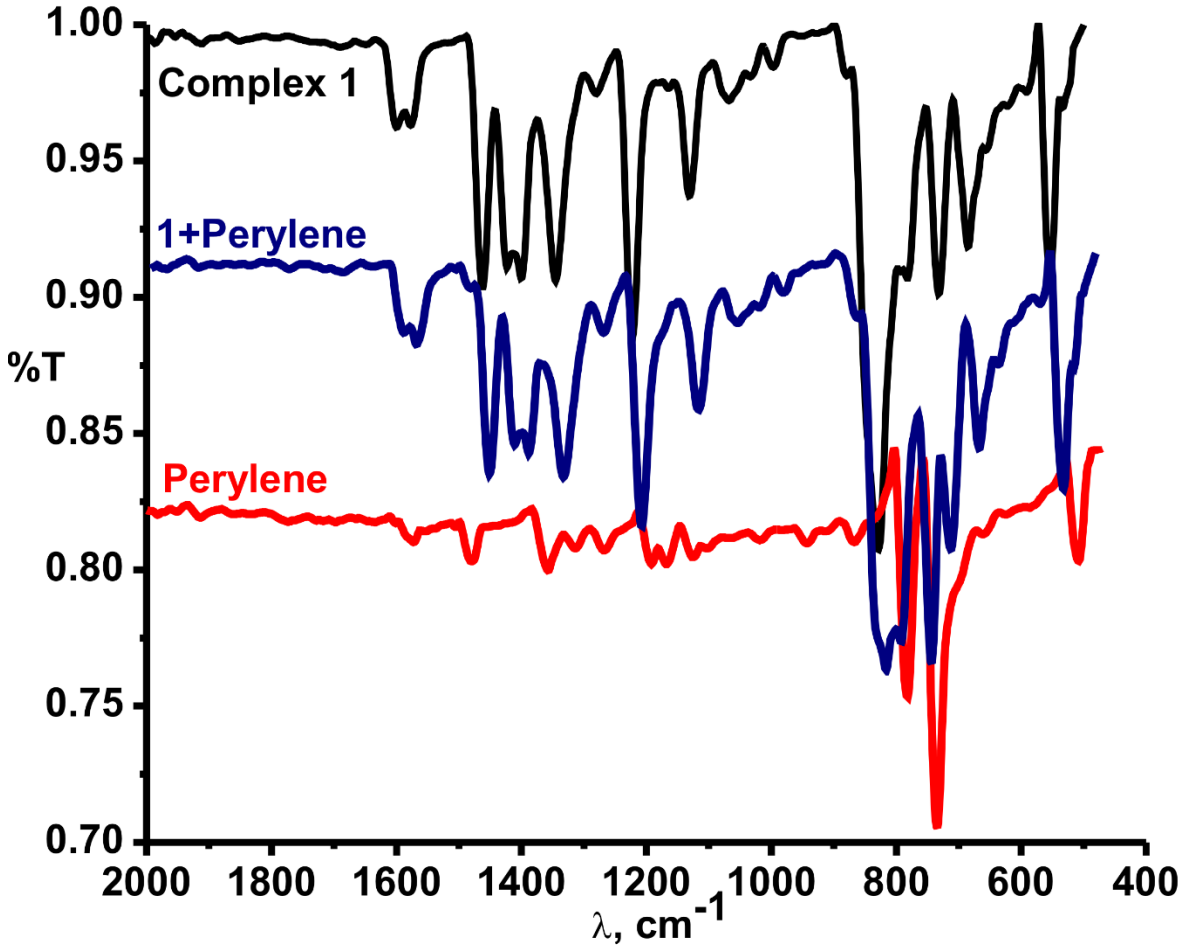
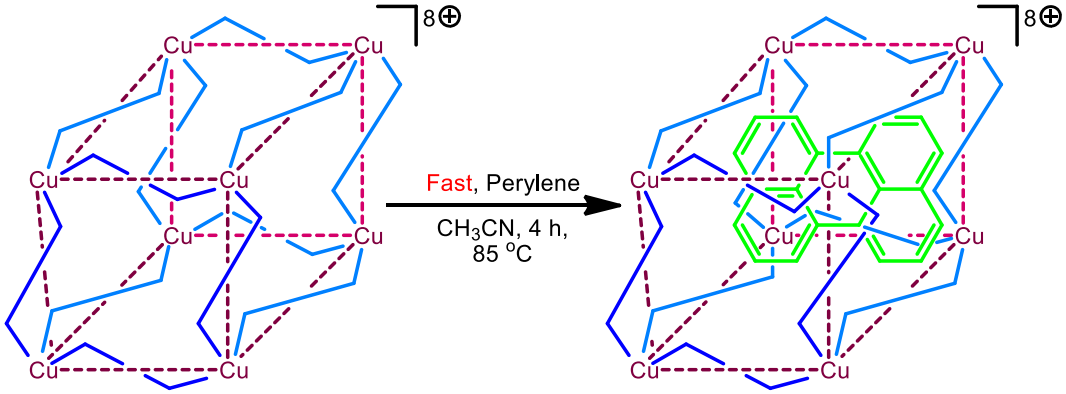



**Fig. S56**. Neat FT-IR spectrum of **1** (Black), a reaction mixture of **1** and perylene (Blue) and perylene (Red) after 4h in acetonitrile.




**Scheme S1**. Synthesis of 1@Perylene molecule by host-guest interactions.

**Host-Guest interactions on Molecule 1 with Pyrene.**

**1@Pyrene:** Molecule **1** (0.01g, 1 equiv) and an excess pyrene (0.03g, 8 equiv) were mixed together and evacuated for 10 minutes, after which 1 mL of acetonitrile was added under argon flow and was allowed to stir at reflux for 4h. $^{1}$H NMR (DMSO-$d_6$, 400 MHz): 1.39-1.41 (d, 2((C$H_3$)$_2$CH), 12H), 4.95-4.98 (m, 2(CH$_3$)$_2$C$H$, 2H), 7.74 (d, imidazole, 2H), 7.87 (d, imidazole, 2H), 8.07-8.30 (m, pyrene, 10H), 8.32-8.40 (m, pyrene, 3H) ppm.

**Observations:**

The compound **1** and pyrene were not dissolved completely in acetonitrile and was a little yellow turbid solution in the beginning, after 10 minutes at 85 $^{o}$C, the reaction mixture turns as clear yellow solution after 4h, and the reaction mixture was dried in vacuo and subjected to spectroscopic measurements, which clearly shows the existence of 1@pyrene molecule.

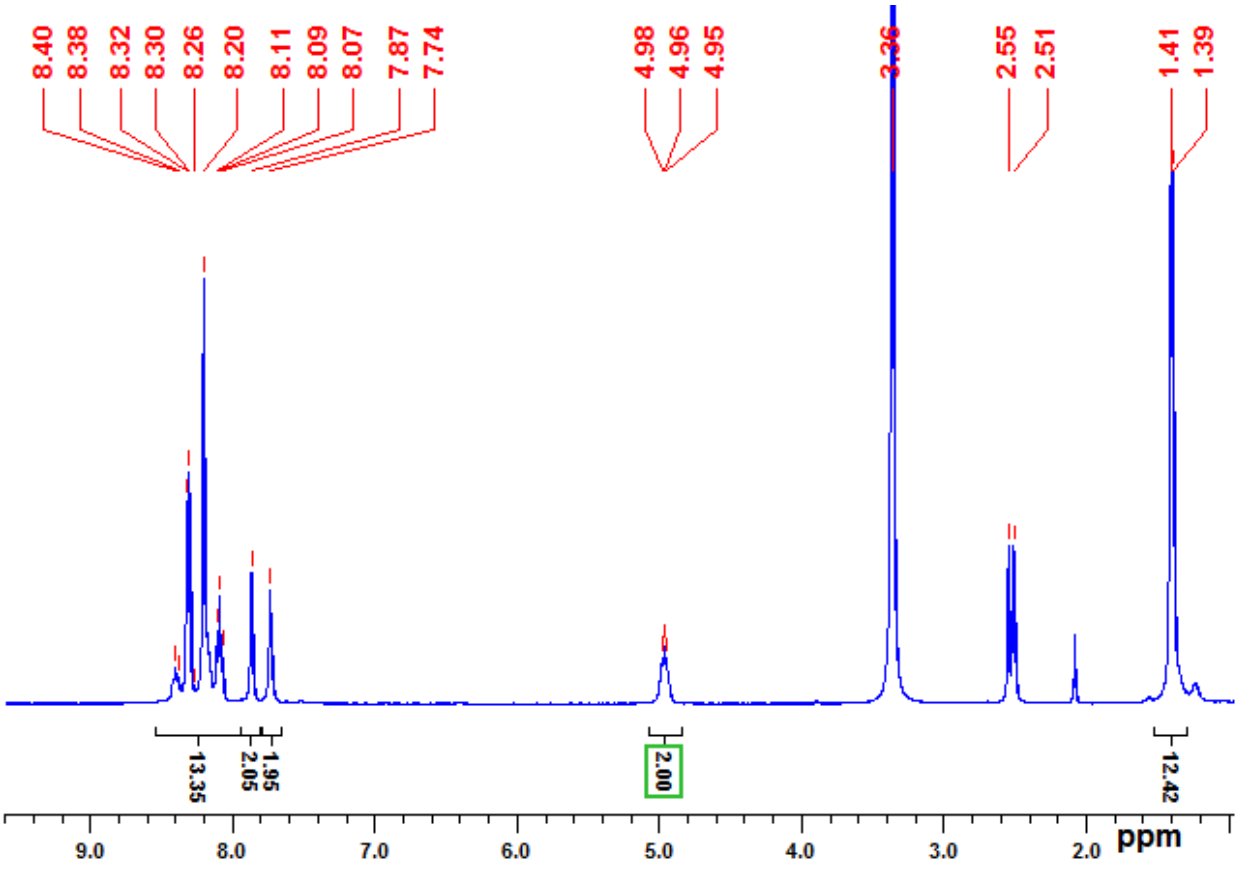



**Fig. S57**. $^{1}$H NMR spectrum of pyrene and molecule **1** reaction mixture (1@pyrene) in DMSO-$d_6$ at RT.

As presented in figure S59, the reaction mixture represents only pyrene absorption spectra in solution UV-vis spectroscopy up to 2h, while broadening of the absorption bands noticed after 3h is due to the association of pyrene with molecule **1**, and the final (4h) absorption spectra of the reaction mixture is fairly altered from the molecule **1** alone, suggesting the complete incorporation/association of pyrene into the molecule **1**.

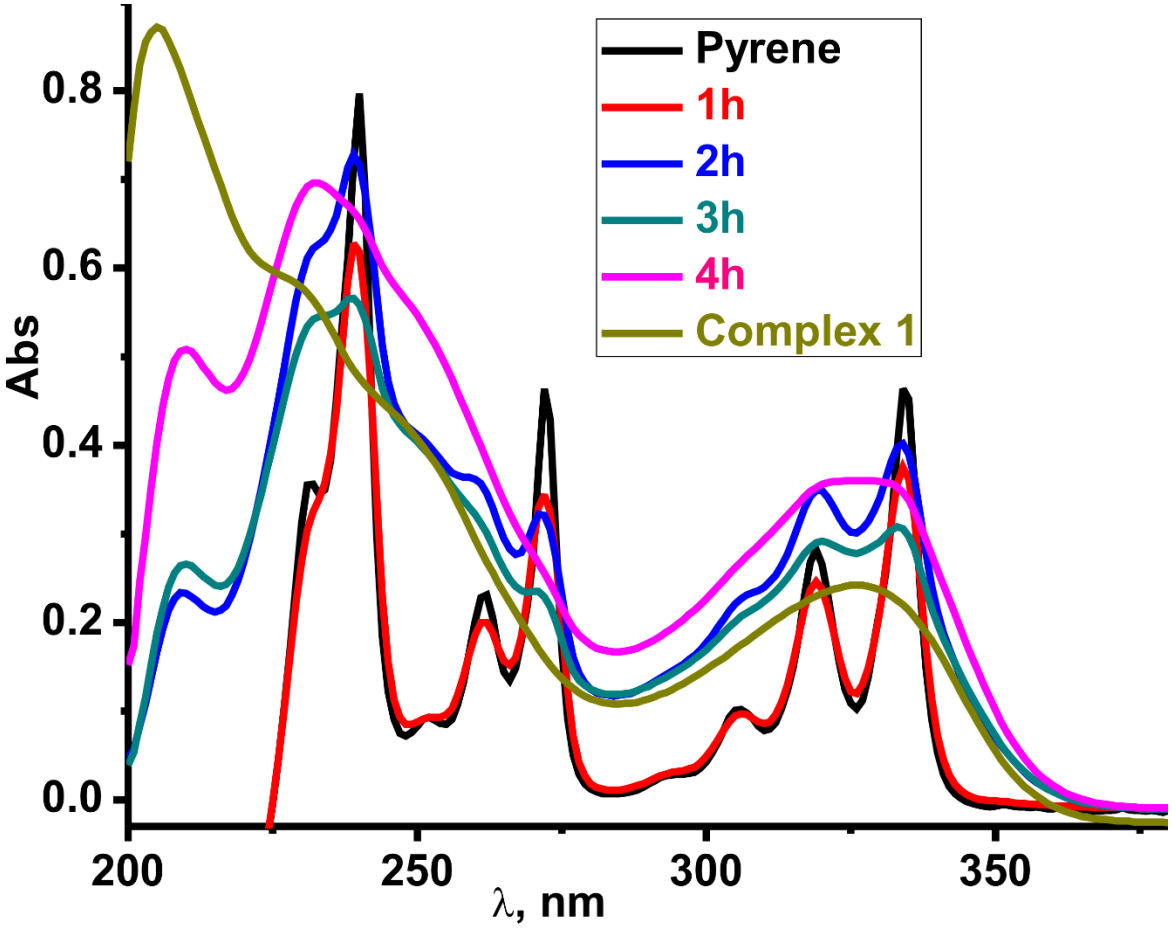



**Fig. S58**. Solution state UV-visible spectral analysis of **1** and the reaction mixture of **1** and pyrene in acetonitrile at elevated temperature with 1h interval, measured at 298K with 2.8 x $10^{-5}$ M acetonitrile solution.

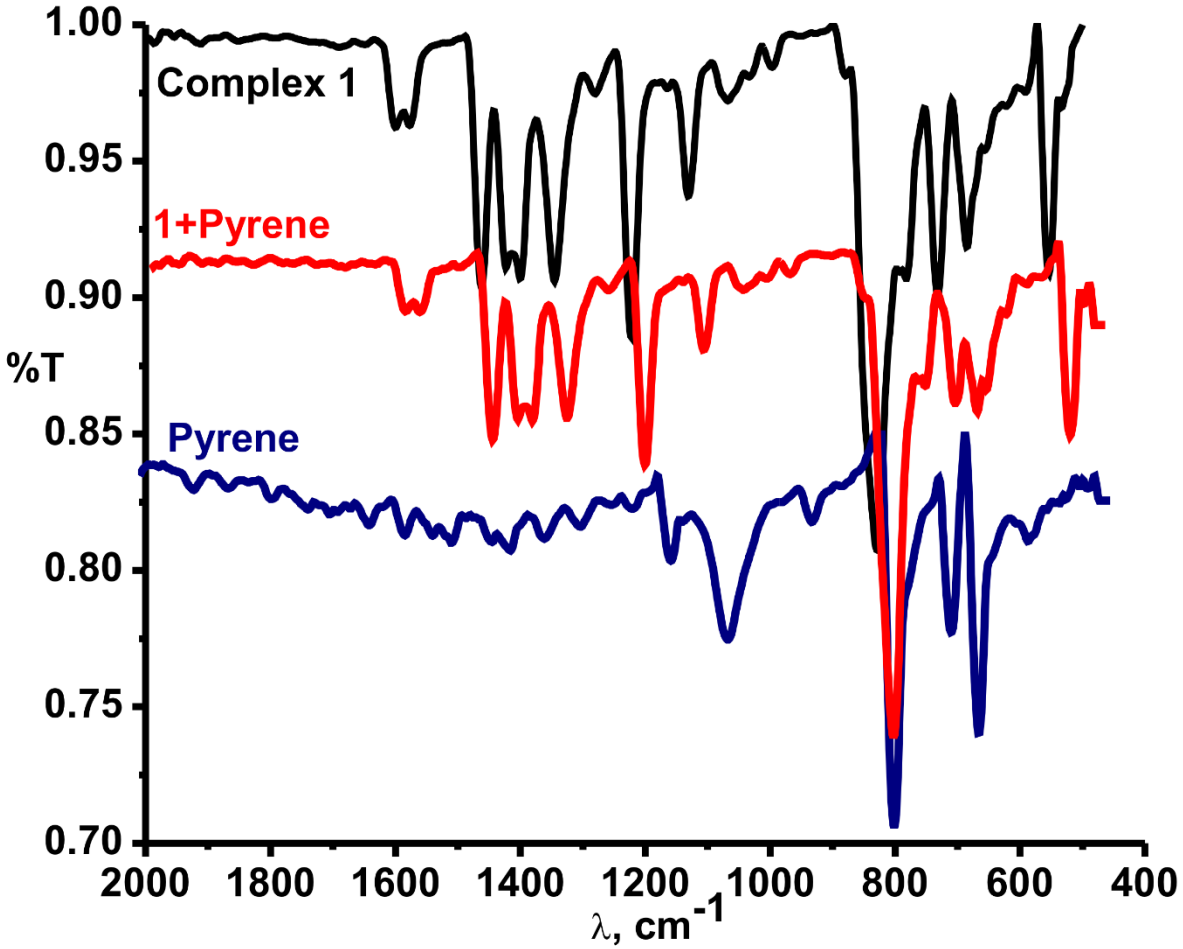
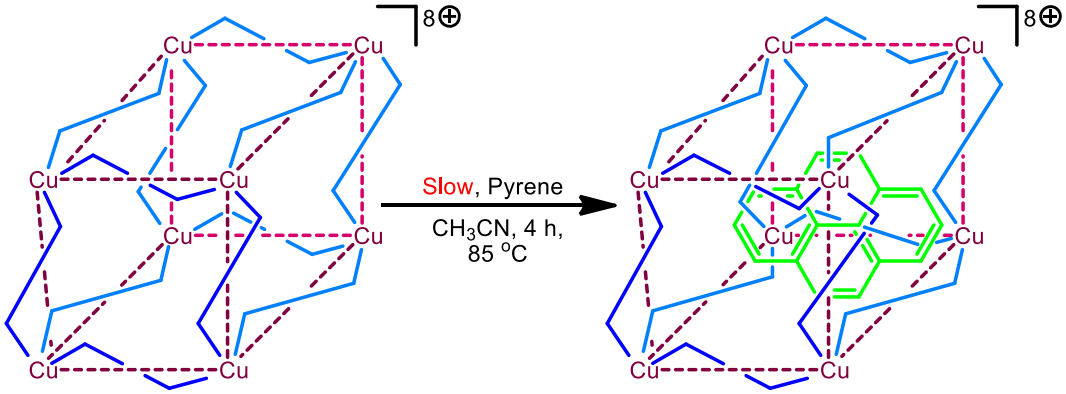



**Fig. S59**. Neat FT-IR spectrum of **1** (Black), a reaction mixture of **1** and pyrene (Red) and pyrene (Blue) after 4h in acetonitrile.




**Scheme S2**. Synthesis of 1@Pyrene molecule by host-guest interactions.

# Host-Guest interactions on Molecule 1 with $C_{60}$ molecule.

Molecule **1** (0.014g, 1 equiv) and $C_{60}$ (0.02g, 1 equiv) were mixed together under argon flow in an NMR tube and was dissolved in DMF-$d_7$ (0.5 mL), then it was subjected to NMR measurement at time 0 minutes. After which it was allowed to stay at 85 $^oC$ and then $^1H$ NMR was measured every day to investigate the incorporation/association of $C_{60}$ into the cavity of molecule **1**. $^1H$ NMR (DMF-$d_7$, 400 MHz): 1.47-1.49 (d, 2((C$H_3$)$_2$CH), 12H), 5.01-5.08 (m, 2(C$H_3$)$_2$C$H$, 2H), 7.78-7.79 (d, imidazole, 2H), 7.95 (d, imidazole, 2H), 8.27-8.29 (m, pyridine, 2H), 8.46-8.50 (m, pyridine, 1H) ppm.

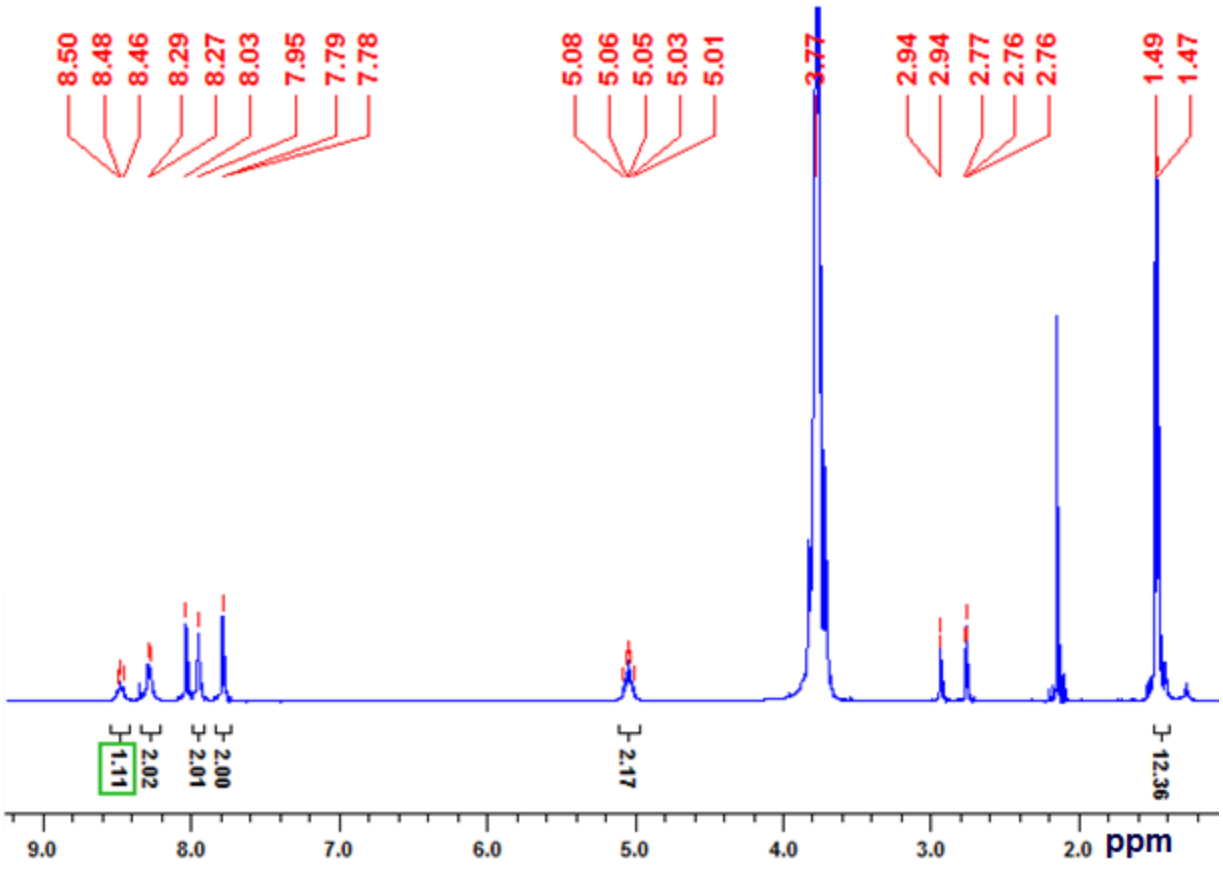



**Fig. S60**. $^1H$ NMR spectrum of comple **1** with $C_{60}$ at time 0 minutes in DMF-$d_7$ at RT.

**Observations:**

It was observed that the addition of $C_{60}$ to the molecule **1** led to slight deviation in the chemical shift of all the protons in **1**. However, the reaction at 85 $^oC$ for prolonged time does not produce any further alteration in chemical shift of protons in **1**. Which suggest the non existance of host-guest interactions between $C_{60}$ and molecule **1**.

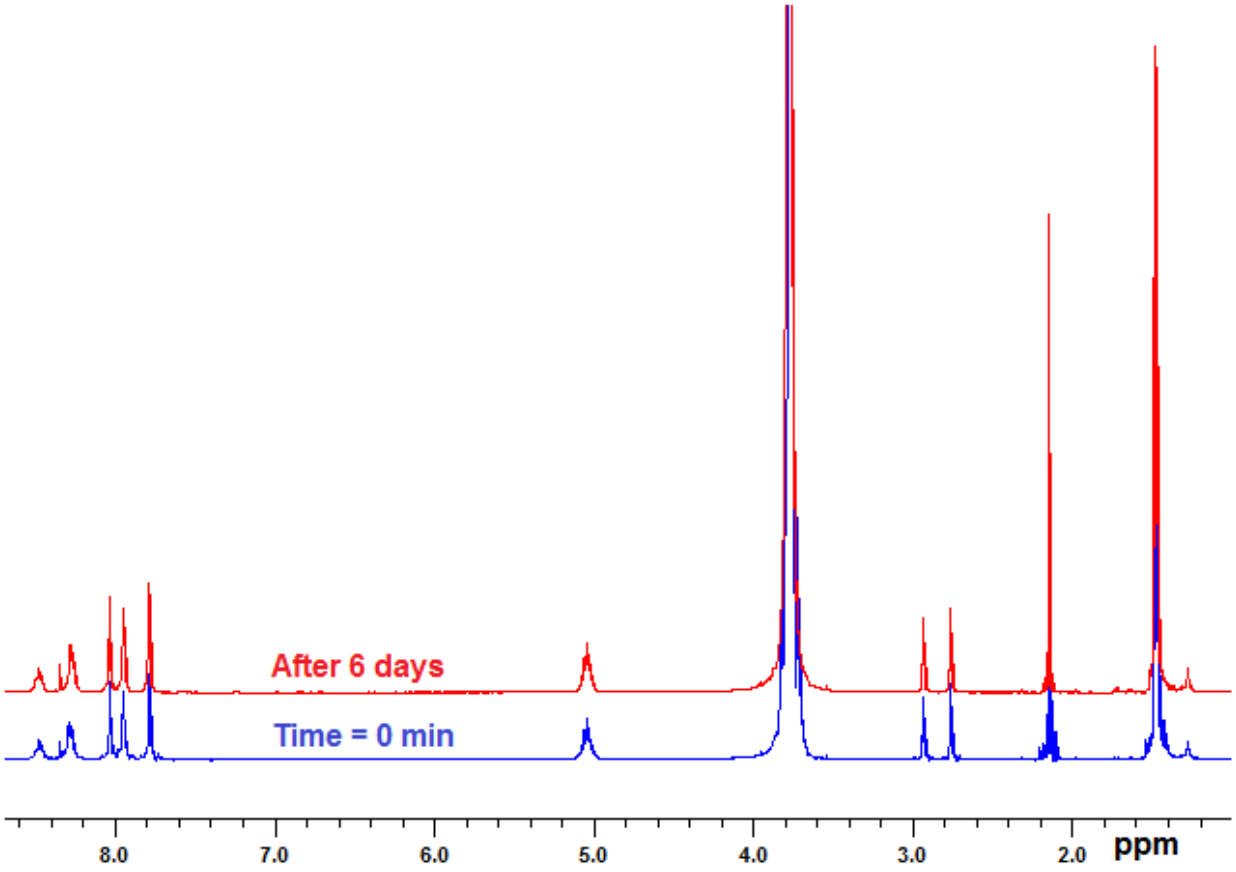
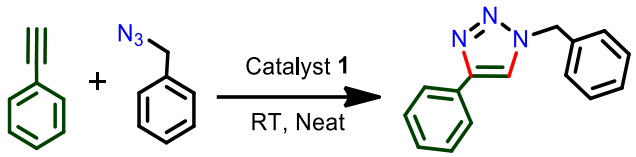



**Fig. S61**. $^{1}$H NMR comparison of molecule **1**@$C_{60}$ host-guest interactions in DMF-$d_7$ at RT.

Therefore, the host-guest interactions on molecule **1** with both pyrene and perylene signifying the prominence of the size of the guest. Although the perylene is bigger in size than pyrene, the pore size in molecule **1** accepts perylene more rapidly than pyrene when performed the experiment individually with molecule **1**. Besides, the $C_{60}$ incorporation into the cavity was not promising.

**Note 3:**

In order to investigate the changes in catalysts during the catalysis, we have subjected the crude sample for powder XRD measurements. Since the reaction is very fast, the crude sample was collected after 15 minutes and characterized by FT-IR, $^{1}$H NMR and PXRD techniques. As observed, the catalyst undergoes a minor structural/face changes after the catalytic cycle. However, the complete decomposition of catalyst was not observed. Attempt to isolate the single crystal X-ray structure of catalyst was no successful yet.




**Scheme 3**. Click reaction used in this study.

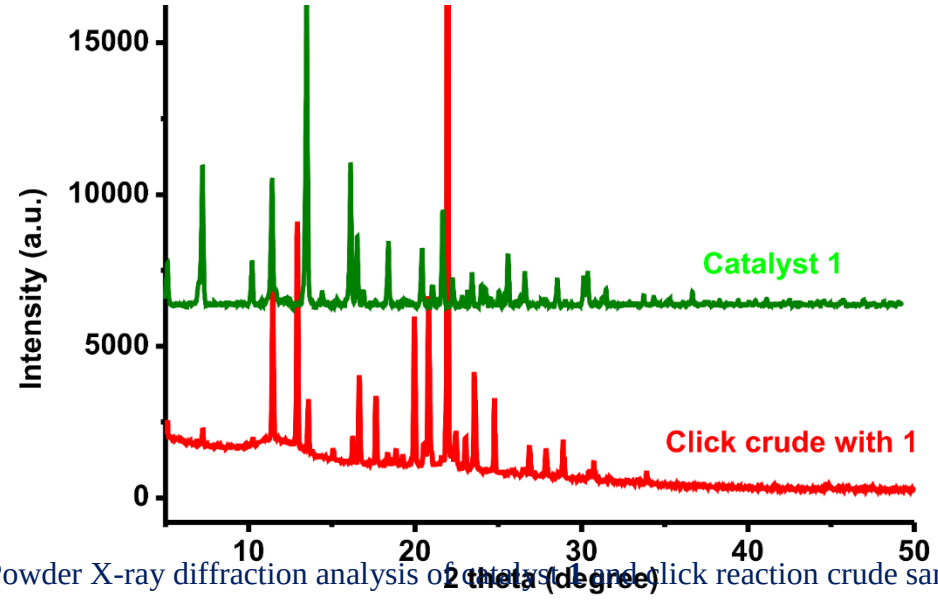



**Fig. S62**. Powder X-ray diffraction analysis of catalyst **1** and click reaction crude sample with **1**.

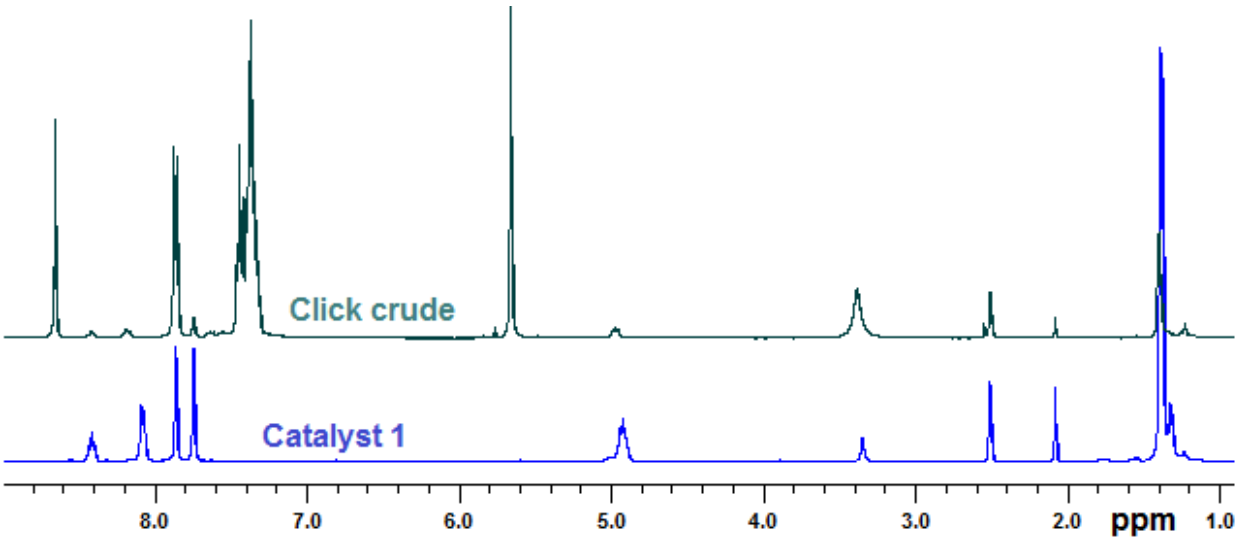


**Fig. S63**. $^{1}$H NMR comparison of catalyst **1** and click reaction crude sample with **1**.

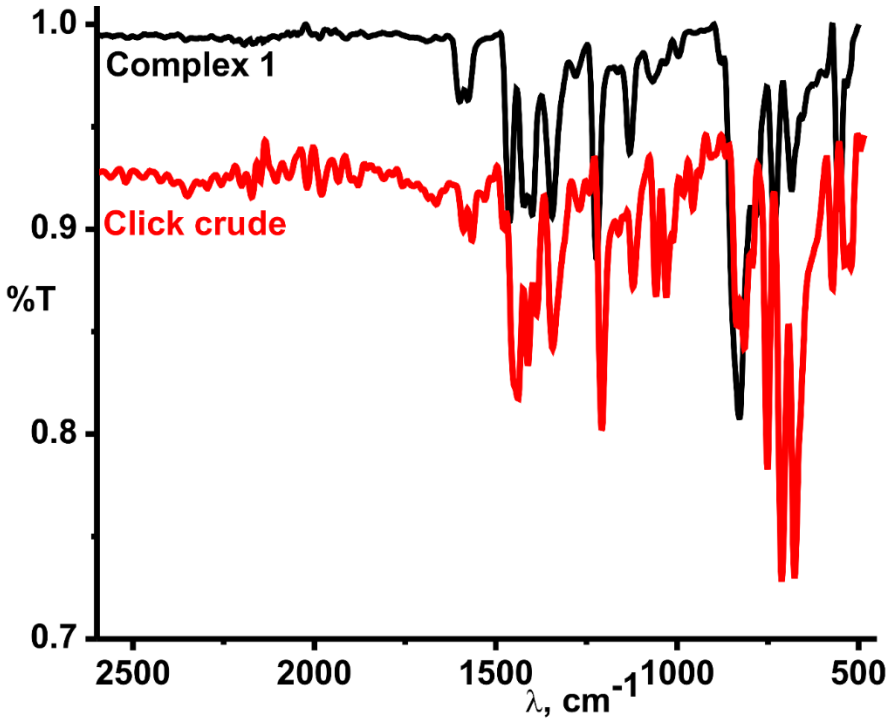
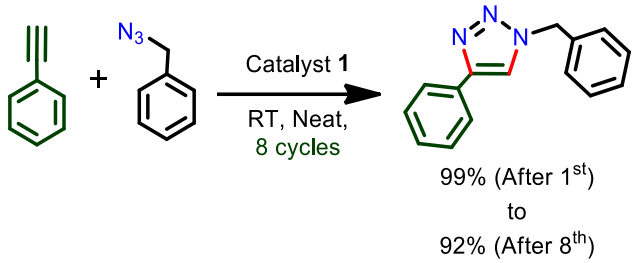



**Fig. S64**. Neat FT-IR comparison of catalyst **1** and click reaction crude sample with **1**.

the catalyst can be reusable for 8 times without any considerable decrease in the product formation.




**Scheme 4**. Catalyst **1** mediated click reaction.

For example, one of the catalysts (**1**) was studied for the prolonged existence and efficiency in click catalysis up to eight successive cycles without any significant loss of reactivity using 1 mol% catalyst **1** with benzyl azide (0.1 g, 0.75 mmol) and phenyl acetylene (0.092 g, 0.90 mmol) in neat conditions at room temperature. The catalyst **1** was recovered by *n*-hexane and ethyl acetate wash. Subsequently, the fresh batch of substrates such as benzyl azide (0.1 g, 0.75 mmol) and phenyl acetylene (0.092 g, 0.90 mmol) were added for the next cycle. This process was continued for eight repeated catalytic cycles and found to be an efficient enough. Besides it was noticed that the quantitative yield was isolated from first 3 catalytic cycles. After third catalytic cycle the reaction time (20 minutes) was increased to get appreciable yield (92% in 8$^{th}$ cycle).

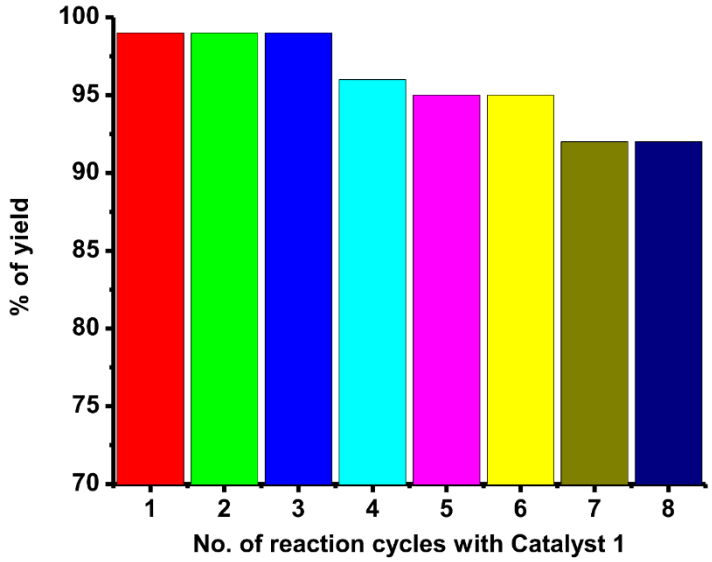



**Fig. S64**. % of isolated yield in 1-8 reaction cycles using catalyst **1**.

To investigate the aggregates after the catalysis, we have subjected the reused catalyst (for 8 times) to powder x-ray diffraction techniques, $^{1}$H NMR spectroscopy. As observed, the molecule remains intact than mononuclear subunits during/after the catalysis.

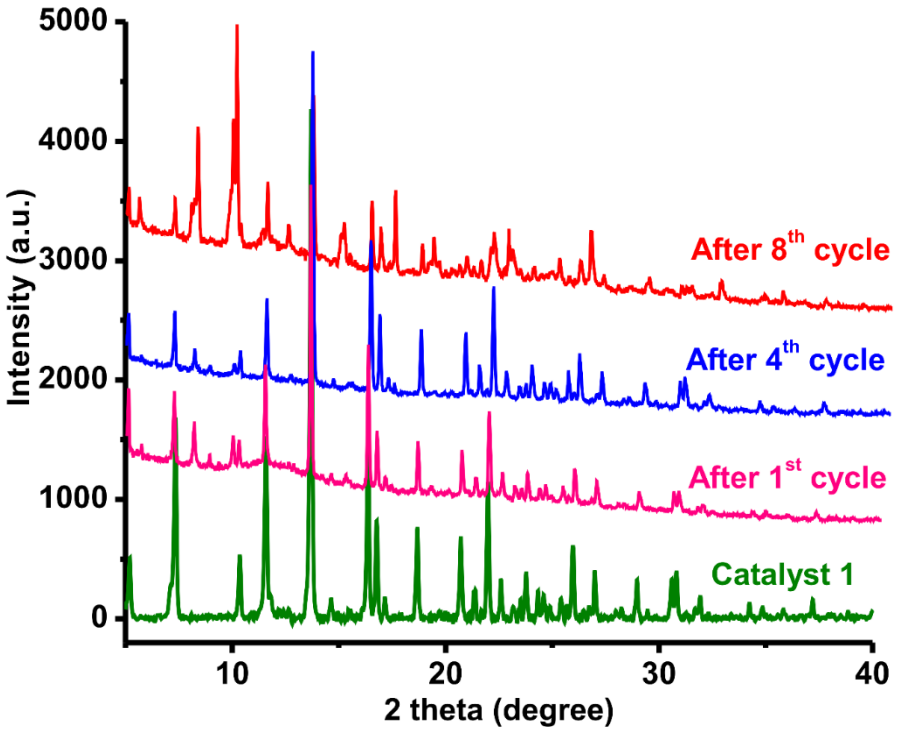



**Fig. S65**. Powder XRD patterns of reused catalyst **1** for 8 reaction cycles.

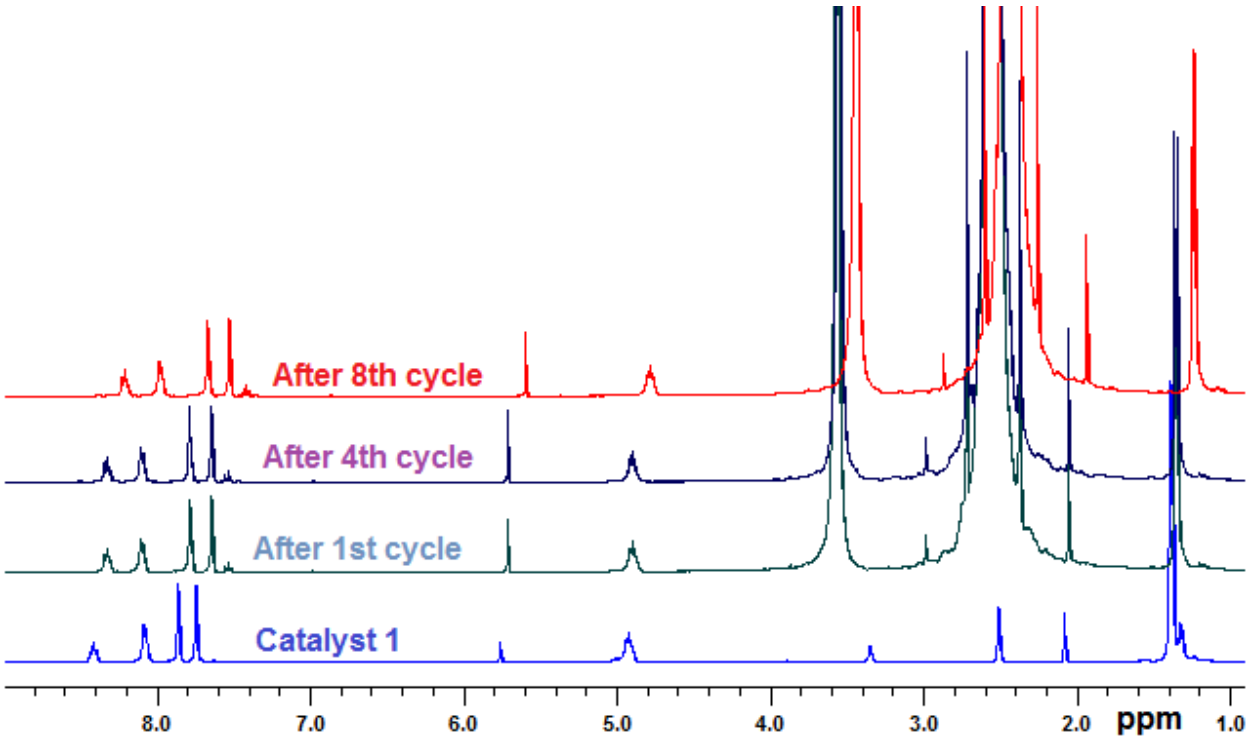
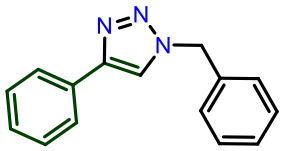



**Fig. S66**. $^{1}$H NMR spectra of catalyst **1** during the prolonged existence studies.

**Cu(I) catalysts catalyzed azide–alkyne cycloaddition reactions (CuAAC).** Catalyst **1** or **2** (1 mol%), azide (1 mmol) and terminal alkyne (1.2 mmol) were placed in an oven dried schlenk flask. The reaction mixture was then allowed to stir at room temperature and the progress of the reaction was monitored by thin layer chromatography. The solid mass obtained was dissolved in ethyl acetate and passed through silica gel column. The solvent has been removed by rotary evaporator and the residue washed several times with n-hexane yielded pure desired products. All the isolated products were well characterized by $^{1}$H and $^{13}$C NMR and few products (**Ia**, **Ib**, **IIa** and **IIb**) were also characterized by single crystal X-ray diffraction analysis.

**1. 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (Ia)**




$^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.80-7.89 (d, 2H), 7.66 (s, 1H), 7.40-7.35 (m, 5H), 7.31-7.28 (m, 3H), 5.54 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.23, 134.72, 130.55, 129.17, 128.83, 128.80, 128.19, 128.07, 125.71, 119.59, 54.22 ppm.

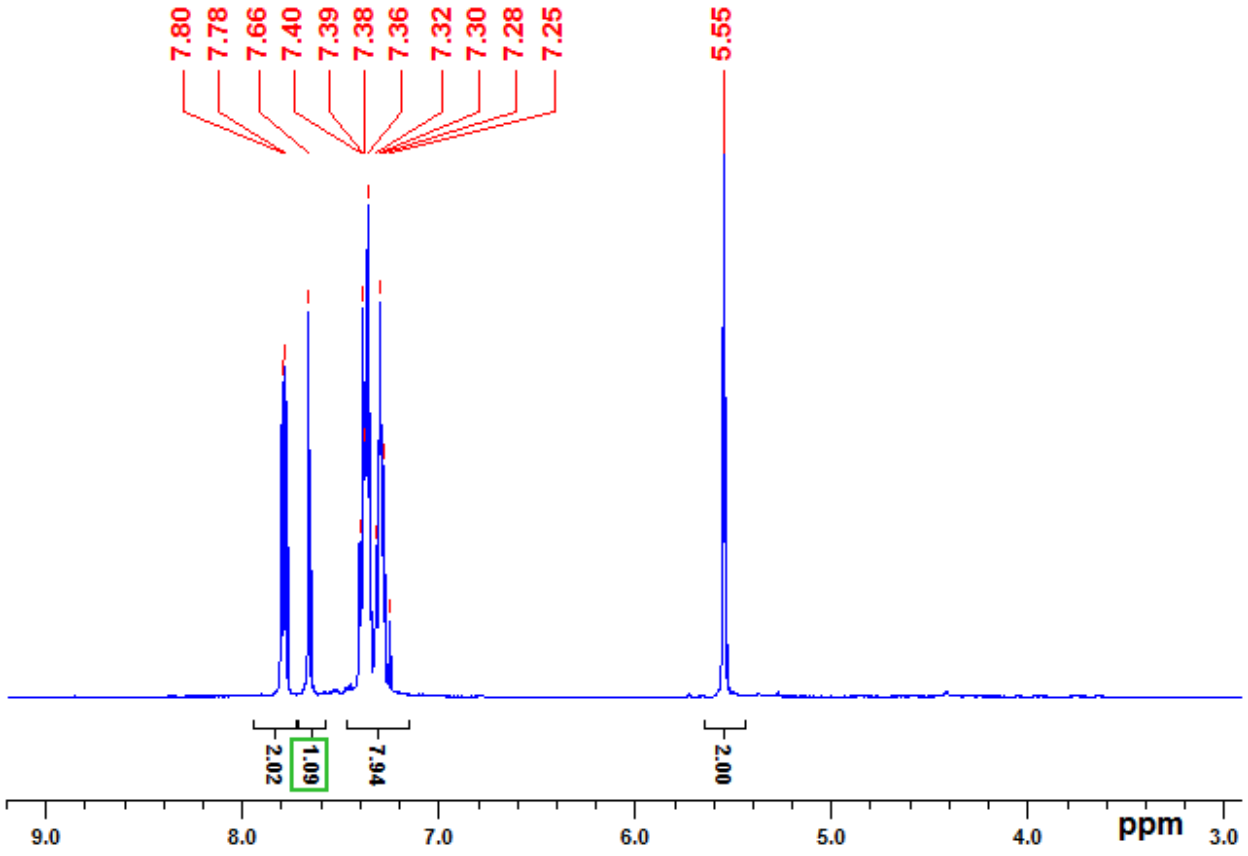



**Fig. S1**. $^{1}H$ NMR spectrum of **1a** in $CDCl_3$ at room temperature.

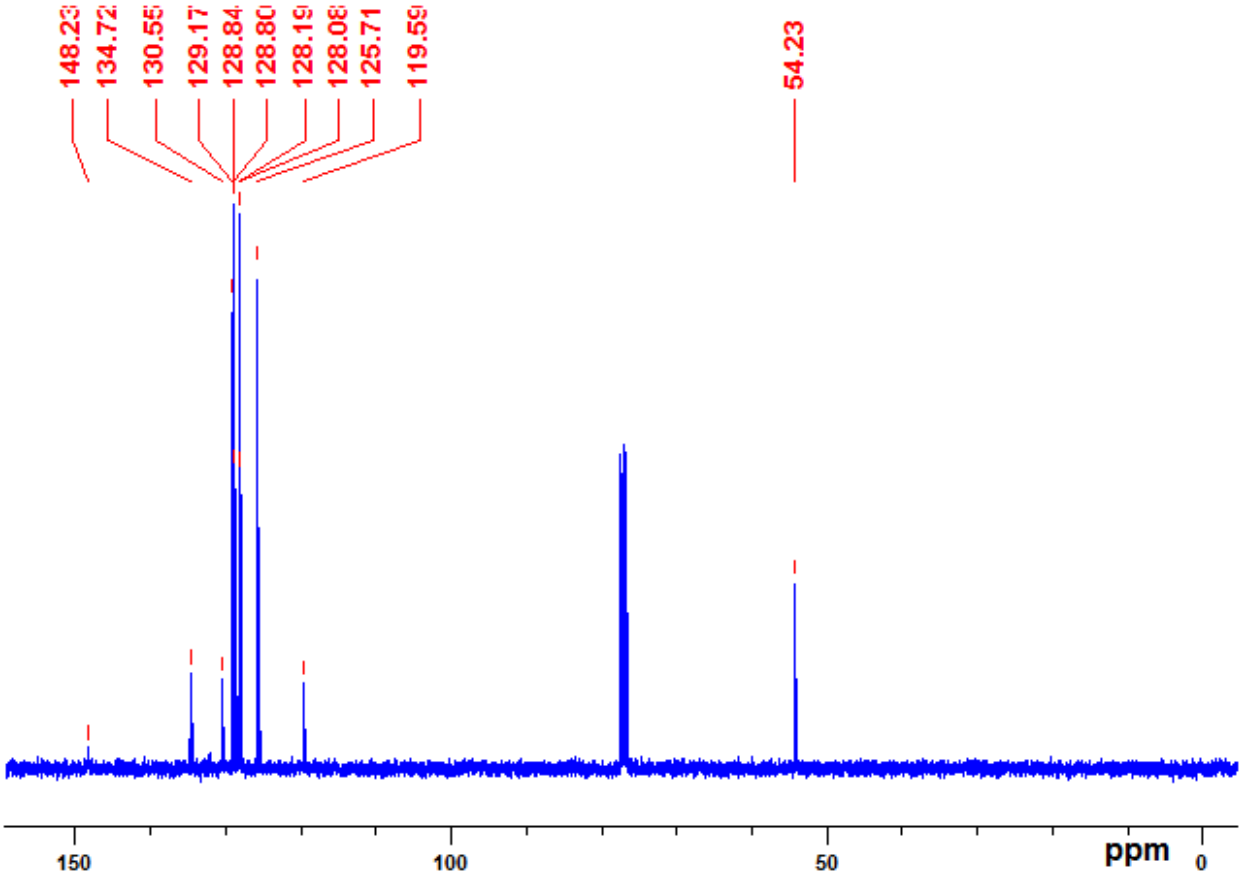
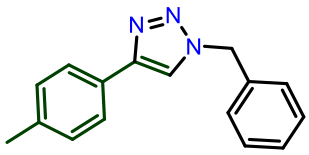



**Fig. S2**. $^{13}$C NMR spectrum of **Ia** in $CDCl_3$ at room temperature.

**2. 1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (Ib)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.68-7.66 (d, 2H), 7.61 (s, 1H), 7.37-7.36 (t, 3H), 7.30-7.28 (m, 2H), 7.20-7.18 (d, 2H), 5.54 (s, 2H), 2.35 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.34, 138.02, 134.77, 129.50, 129.15, 128.76, 128.07, 127.73, 125.61, 119.21, 54.20, 21.31 ppm.

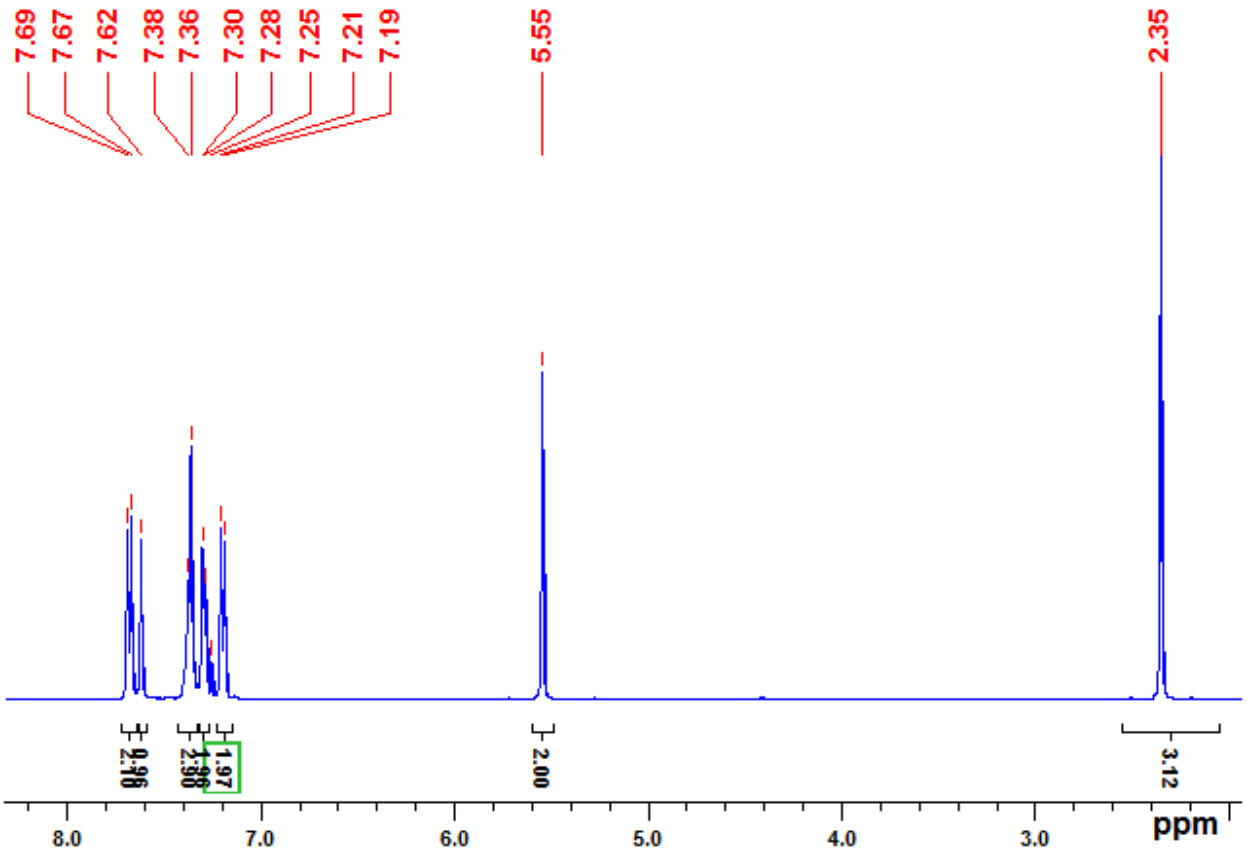



**Fig. S3**. $^{1}$H NMR spectrum of **Ib** in $CDCl_3$ at room temperature.

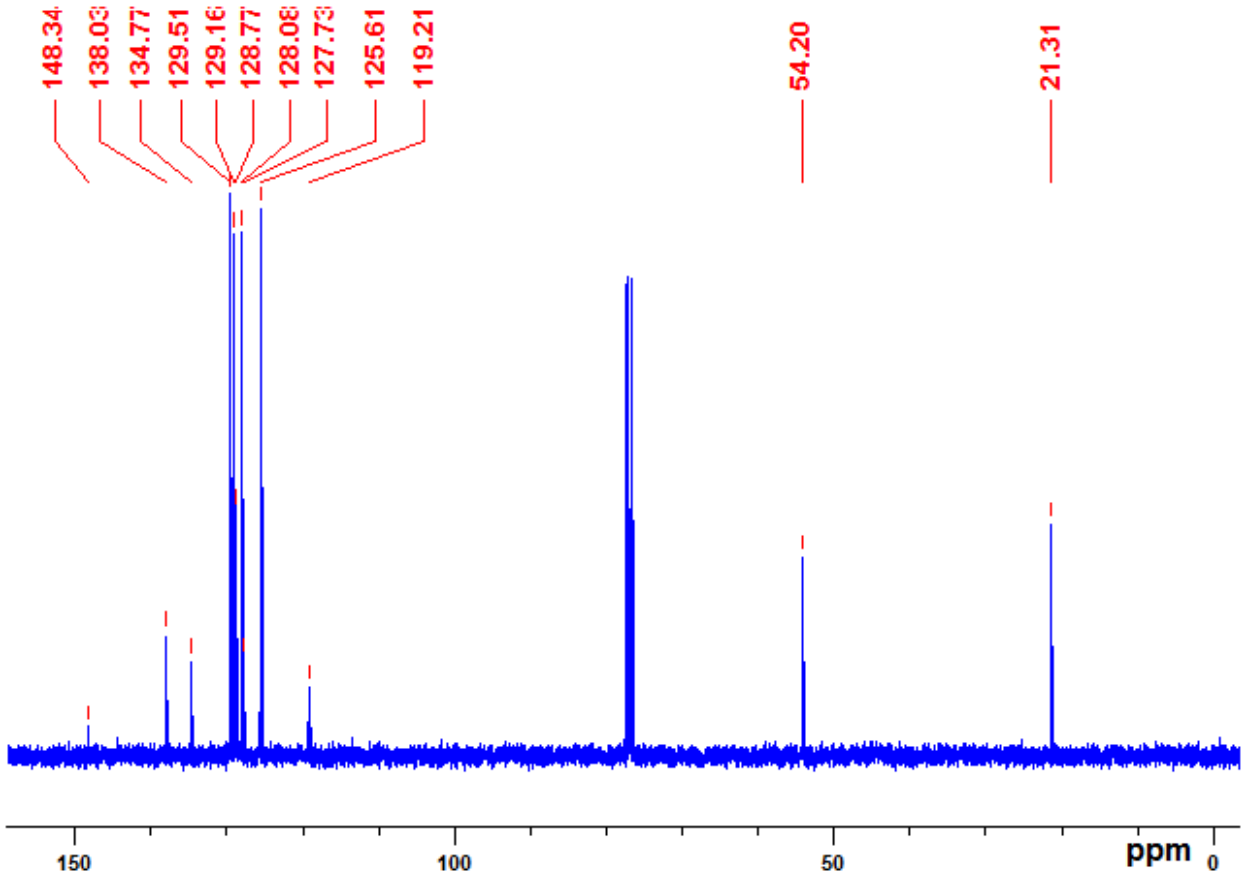
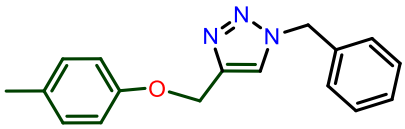



**Fig. S4**. $^{13}$C NMR spectrum of **Ib** in $CDCl_3$ at room temperature.

**3. 1-benzyl-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (Ic)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.51 (s, 1H), 7.34-7.37 (m, 3H), 7.24-7.26 (t, 2H), 7.05-7.07 (d, 2H), 6.83-6.86 (d, 2H), 5.50 (s, 2H), 5.13 (s, 2H), 2.26 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.11, 134.52, 130.53, 129.98, 129.15, 128.81, 128.14, 122.65, 114.65, 62.21, 54.23, 20.51 ppm..

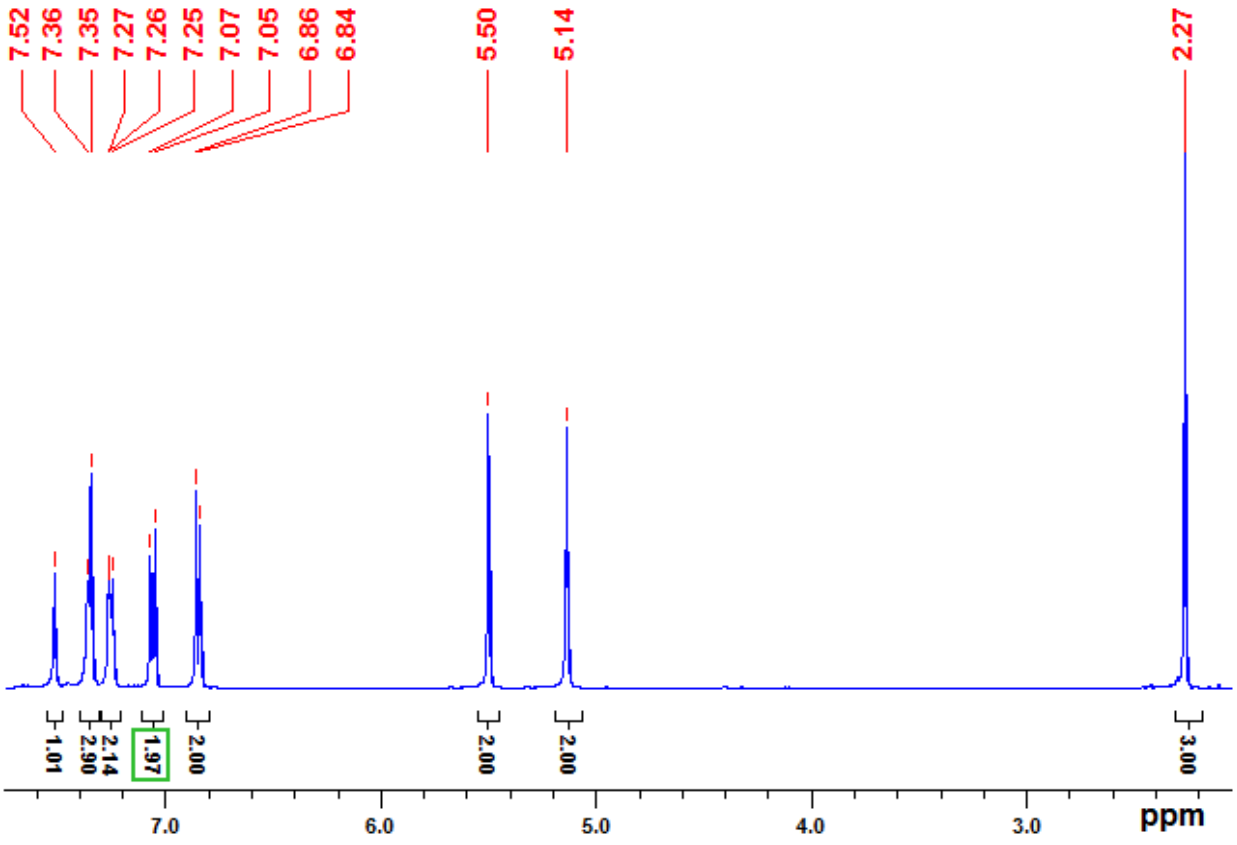



**Fig. S5**. $^{1}$H NMR spectrum of **Ic** in $CDCl_3$ at room temperature.

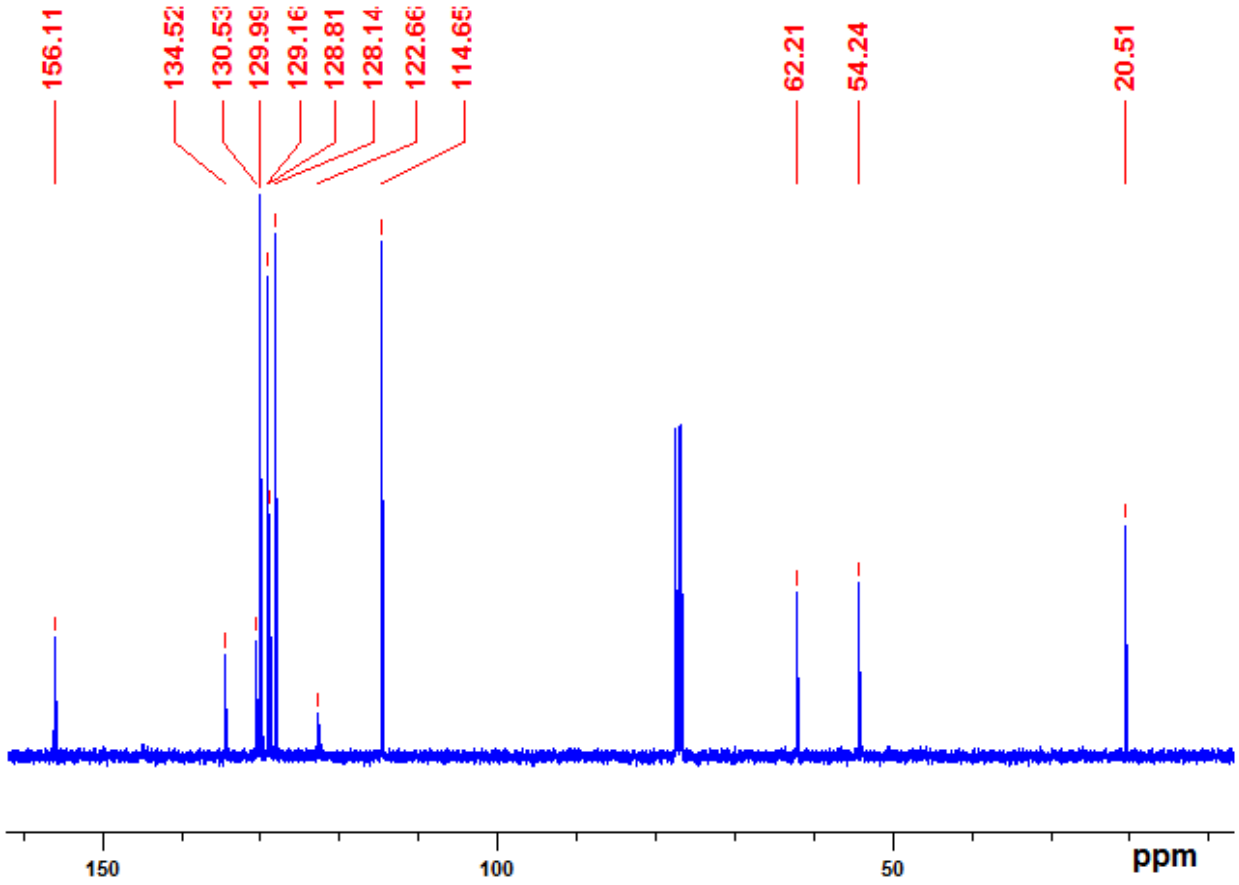
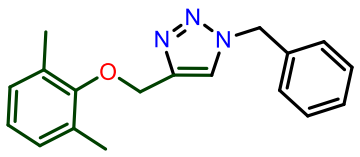



**Fig. S6**. $^{13}$C NMR spectrum of **Ic** in $CDCl_3$ at room temperature.

**4. 1-benzyl-4-((2,6-dimethylphenoxy)methyl)-1*H*-1,2,3-triazole (Id)**



$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.55 (s, 1H), 7.27-7.37 (m, 5H), 6.90-7.00 (m, 3H), 5.53 (s, 2H), 4.94 (s, 2H), 2.25 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.30, 145.08, 134.61, 132.05, 131.07, 129.16, 128.91, 128.11, 124.27, 122.65, 65.60, 54.21, 16.40 ppm.

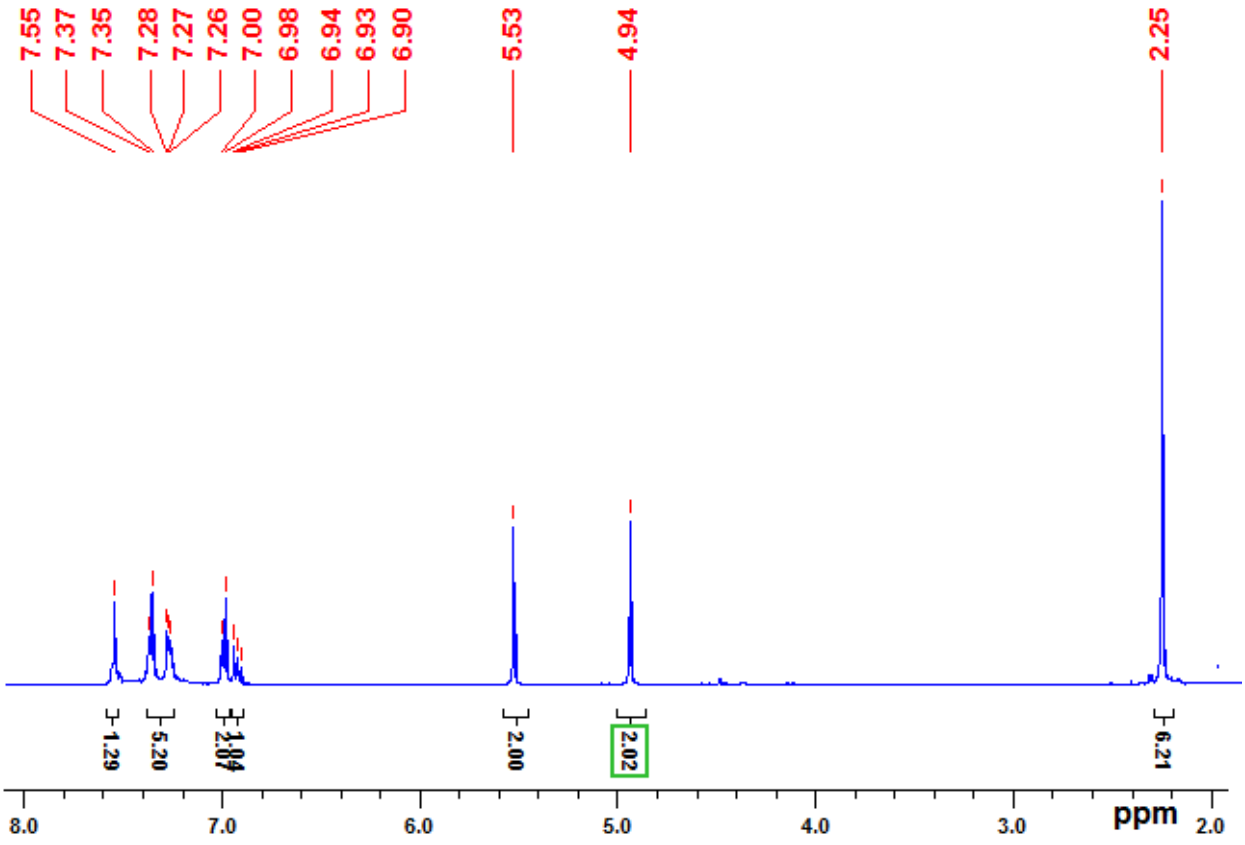



**Fig. S7**. $^{1}$H NMR spectrum of **Id** in $CDCl_3$ at room temperature.

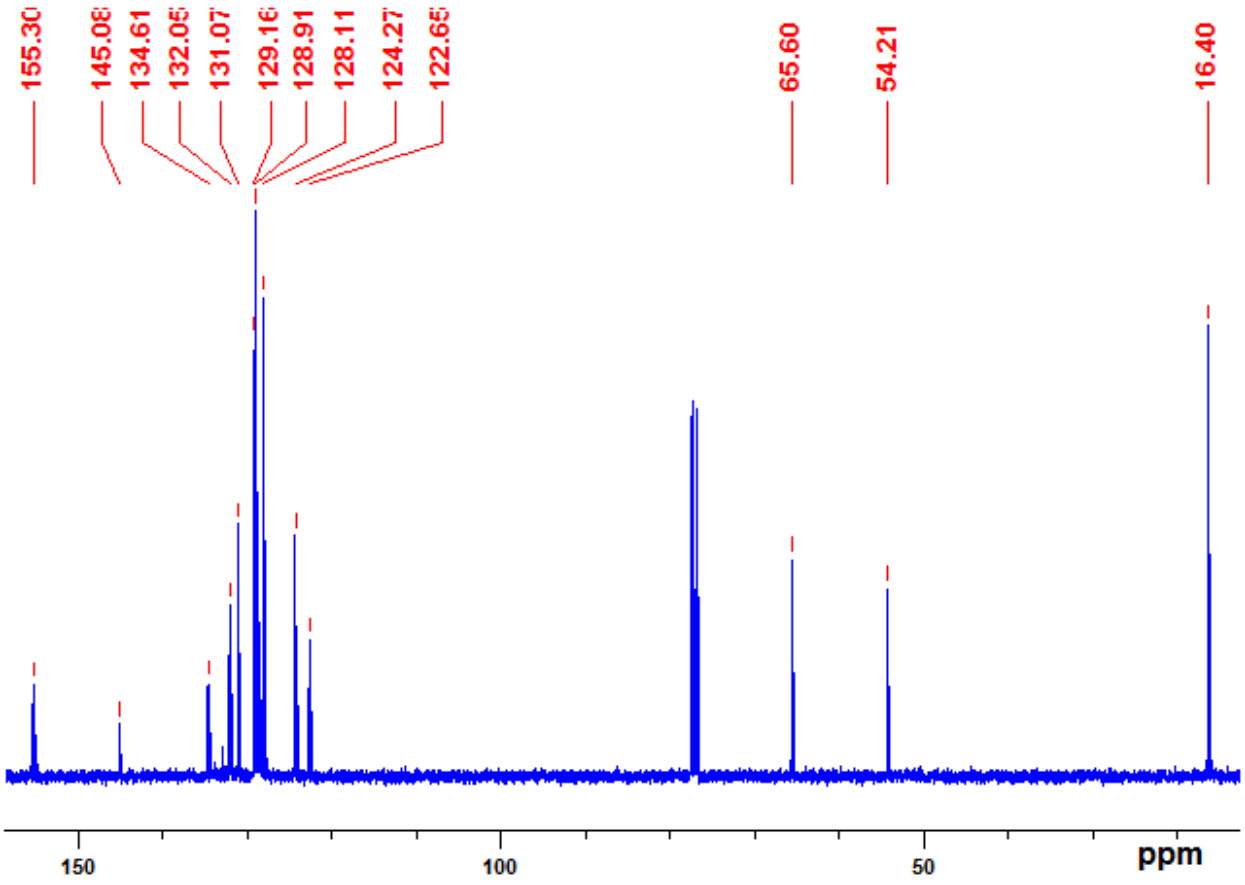
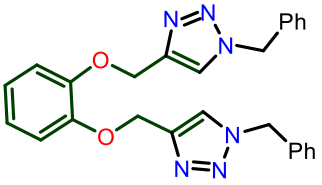



**Fig. S8**. $^{13}$C NMR spectrum of **Id** in $CDCl_3$ at room temperature.

**5. 1,2-bis((1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)benzene (Ie)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.43-7.68 (m, 4H), 7.23-7.34 (m, 8H), 6.88-7.01 (m, 4H), 5.47 (s, 4H), 5.18 (s, 4H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.43, 134.58, 132.15, 132.05, 132.01, 129.10, 128.74, 128.61, 128.49, 128.10, 123.20, 122.23, 115.60, 63.51, 54.15 ppm.

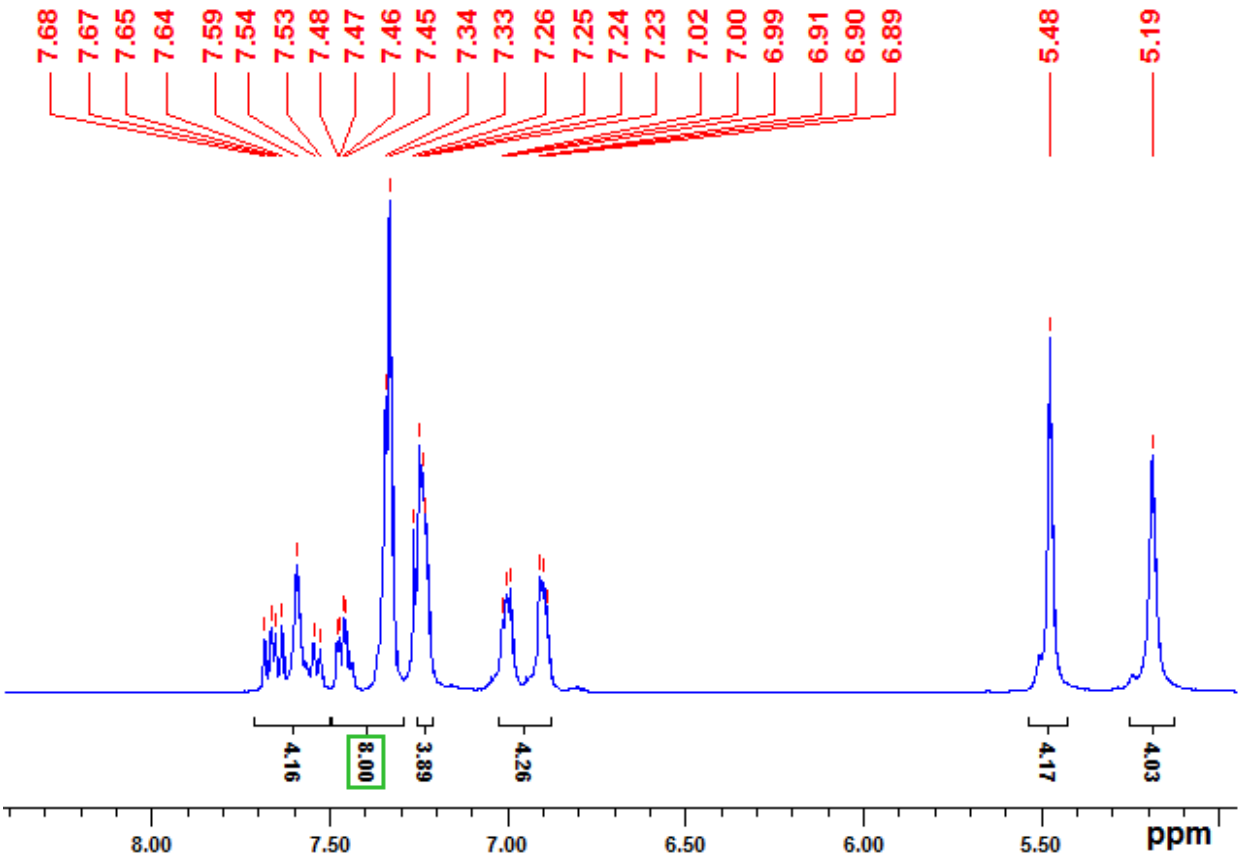



**Fig. S9**. $^{1}$H NMR spectrum of **Ie** in $CDCl_3$ at room temperature.

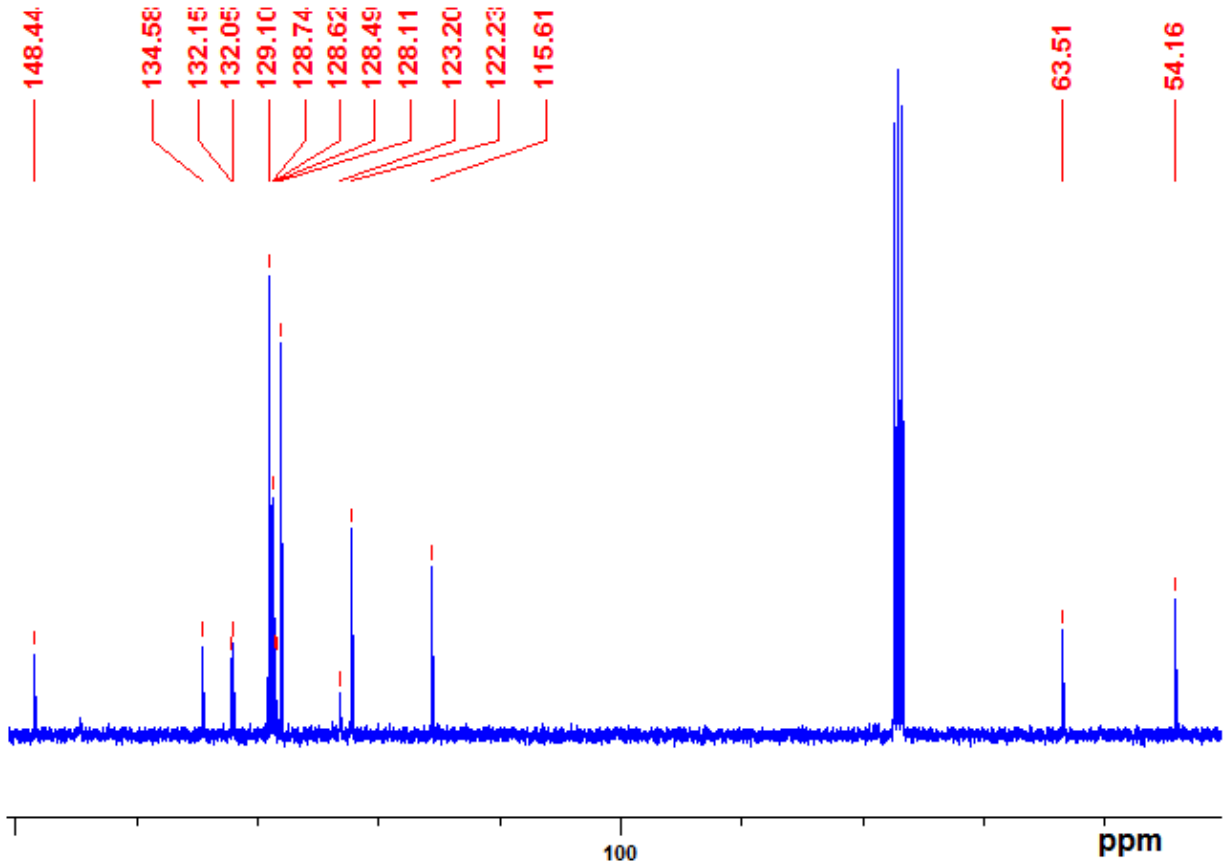
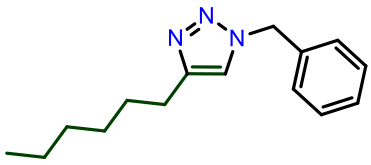



**Fig. S10**. $^{13}$C NMR spectrum of **Ie** in $CDCl_3$ at room temperature.

**6. 1–benzyl–4–hexyl–1H–1,2,3–triazole (If)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.33-7.36 (m, 3H), 7.23-7.27 (m, 2H), 7.19 (2, 1H), 5.48 (s, 2H), 2.65-2.69 (t, 2H), 1.58-1.64 (m, 2H), 1.25-1.34 (m, 6H), 0.84-0.87 (t, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 135.01, 129.04, 128.59, 128.47, 127.94, 120.55, 53.96, 31.54, 29.37, 29.37, 25.73, 22.54, 14.06 ppm.

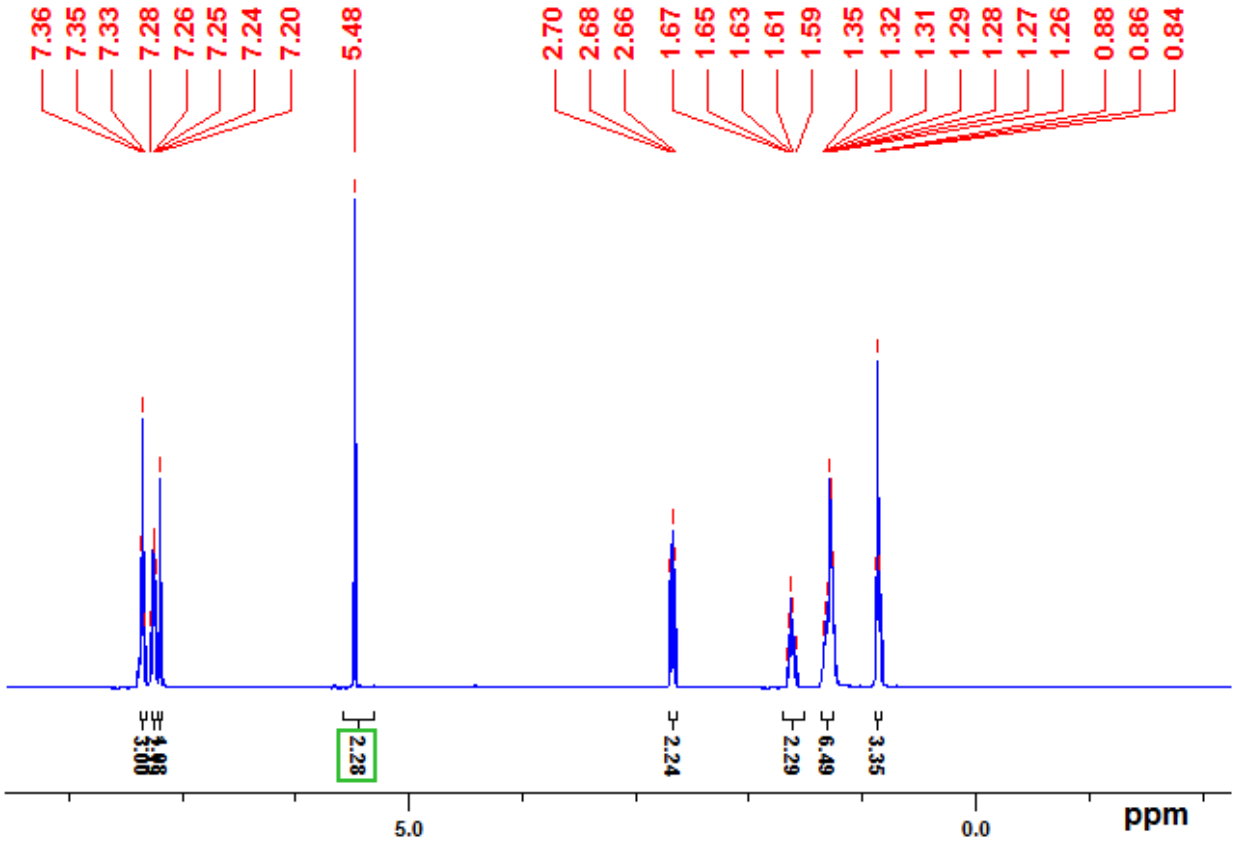



**Fig. S11**. $^{1}$H NMR spectrum of **If** in $CDCl_3$ at room temperature.

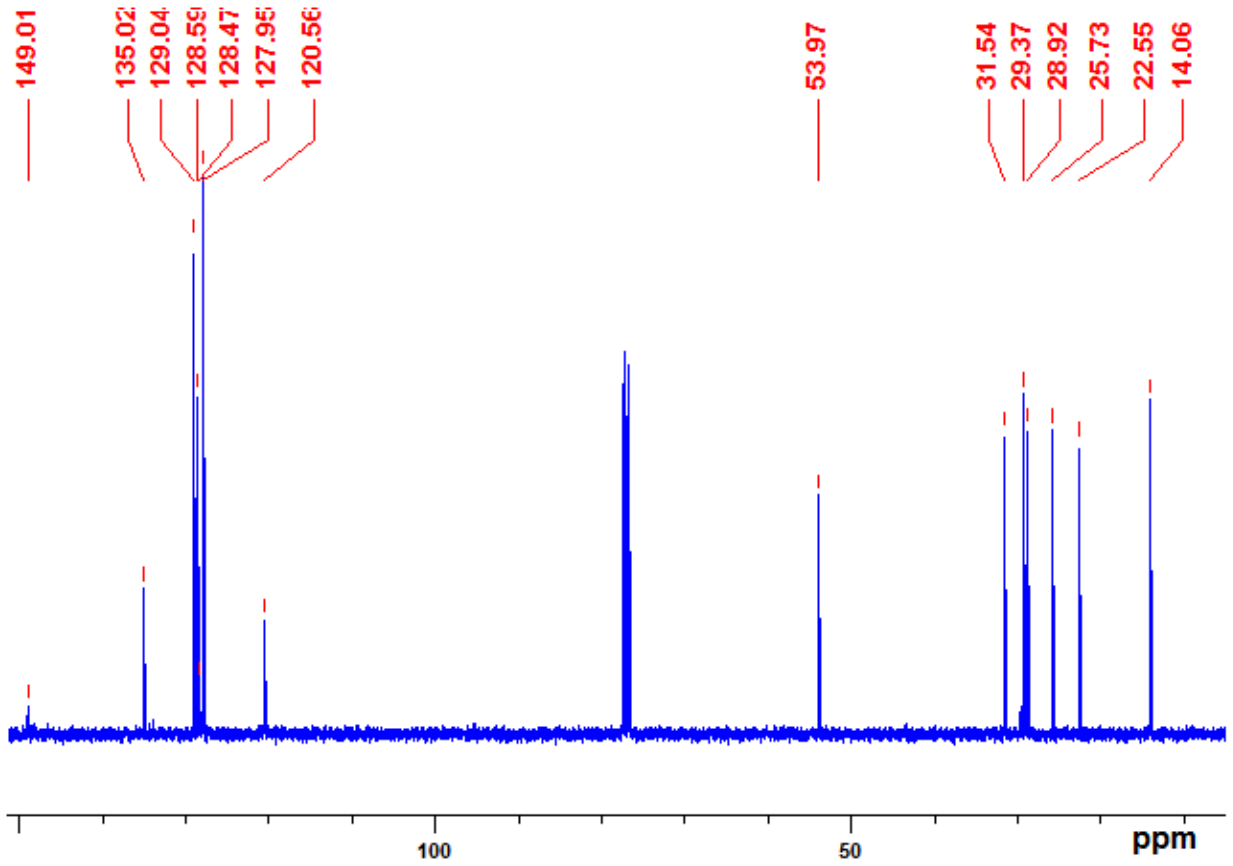
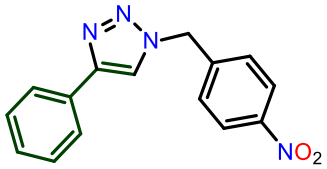



**Fig. S12**. $^{13}$C NMR spectrum of **If** in $CDCl_3$ at room temperature.

**7. 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (IIa)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.19-8.22 (d, 2H), 7.78-7.81 (m, 3H), 7.44-7.33 (m, 5H), 5.69 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.68, 148.04, 141.81, 130.10, 128.93, 128.57, 128.51, 125.74, 124.33, 119.84, 53.17 ppm.

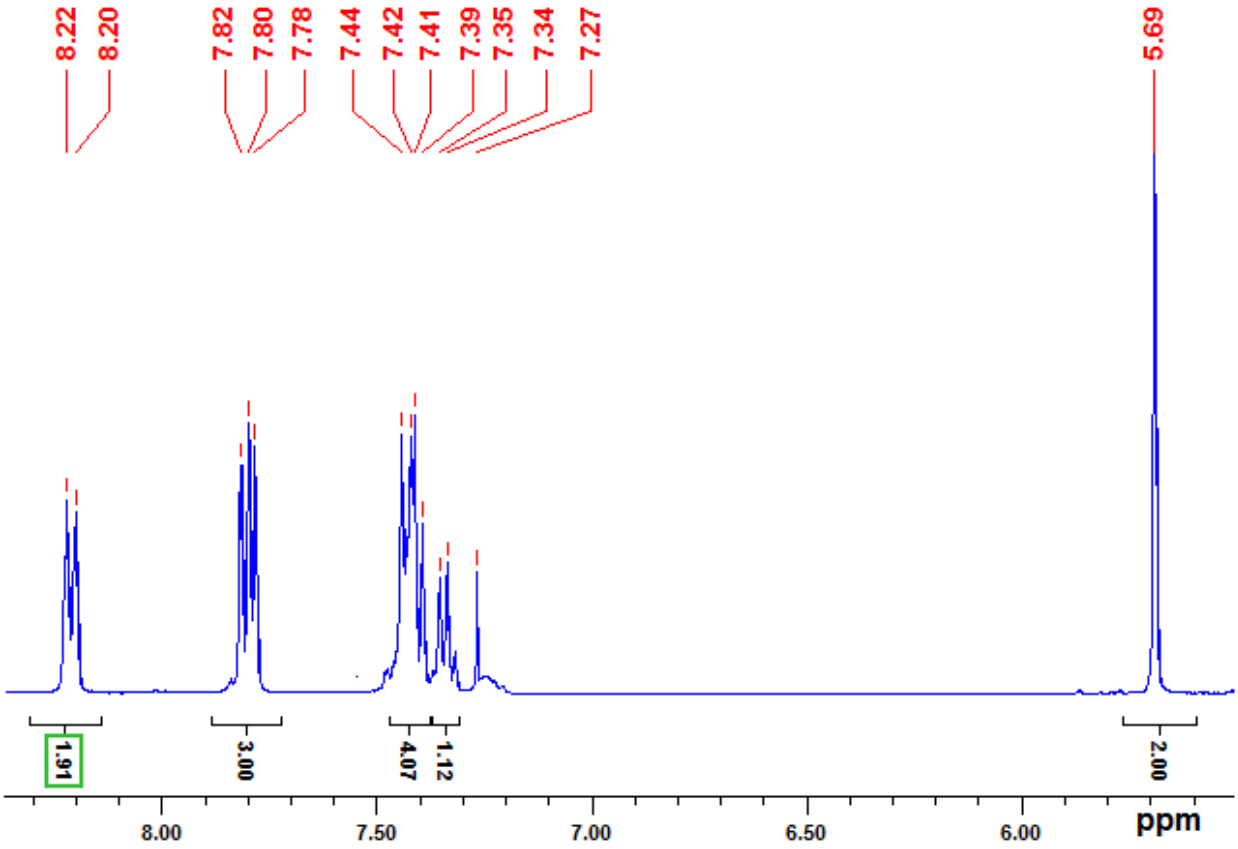



**Fig. S13**. $^{1}$H NMR spectrum of **IIa** in $CDCl_3$ at room temperature.

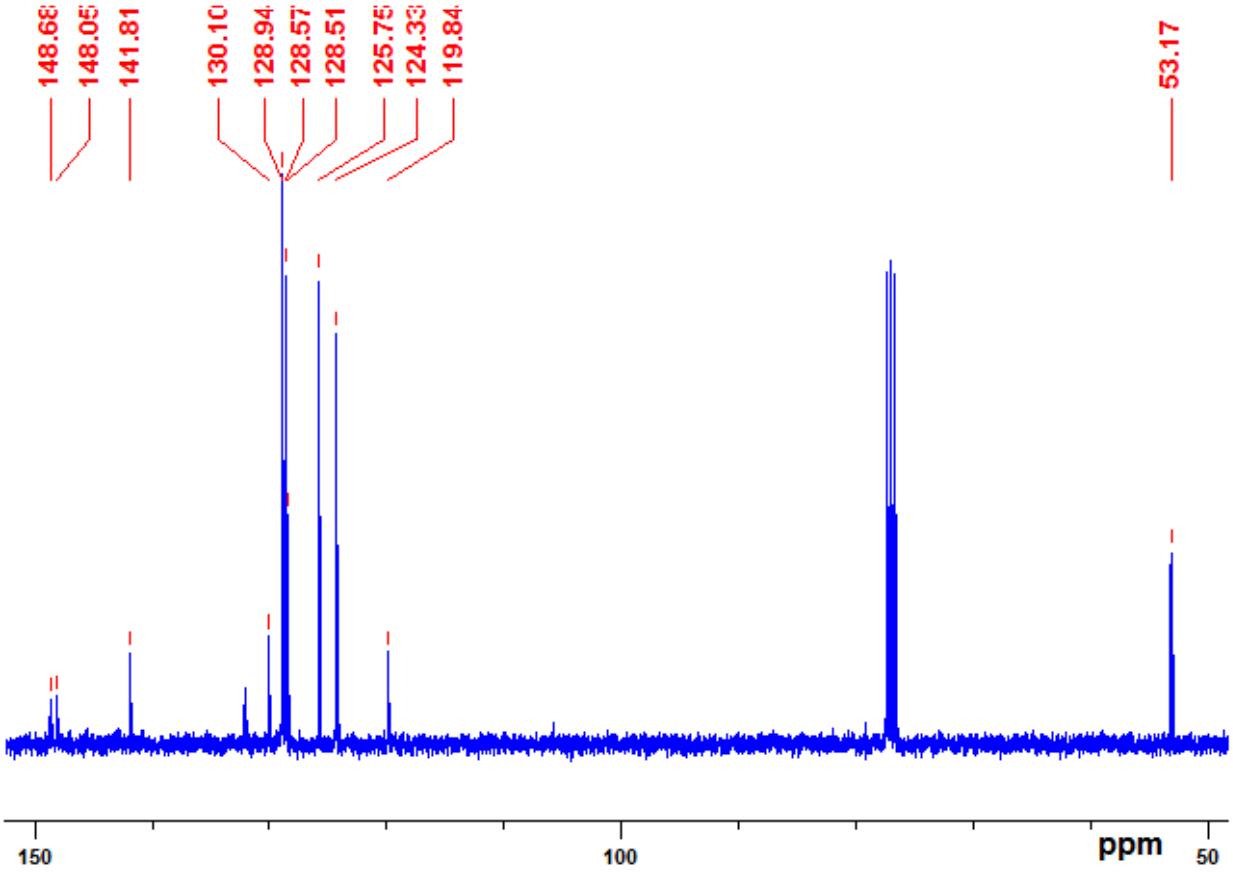
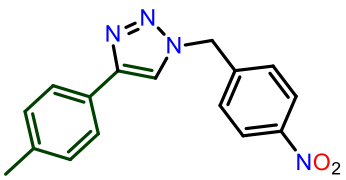



**Fig. S14**. $^{13}$C NMR spectrum of **IIa** in $CDCl_3$ at room temperature.

**8. 1-(4-nitrobenzyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IIb)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.19-8.21 (d, 2H), 7.67-7.73 (m, 3H), 7.41-7.43 (d, 2H), 7.20-7.22 (d, 2H), 5.67 (s, 2H), 2.36 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.75, 148.02, 141.88, 138.42, 129.60, 128.56, 127.27, 125.65, 124.30, 119.50, 53.13, 21.31 ppm.

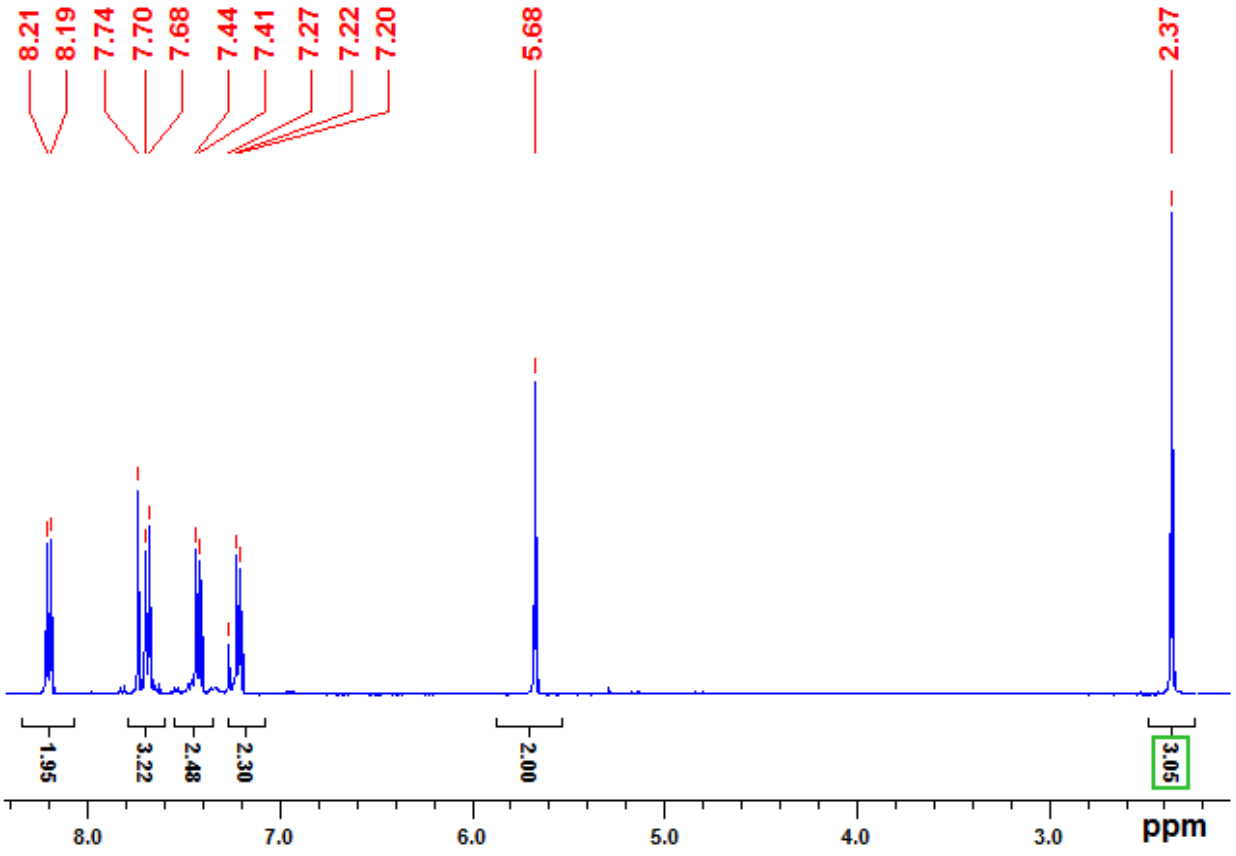



**Fig. S15**. $^{1}$H NMR spectrum of **IIb** in $CDCl_3$ at room temperature.

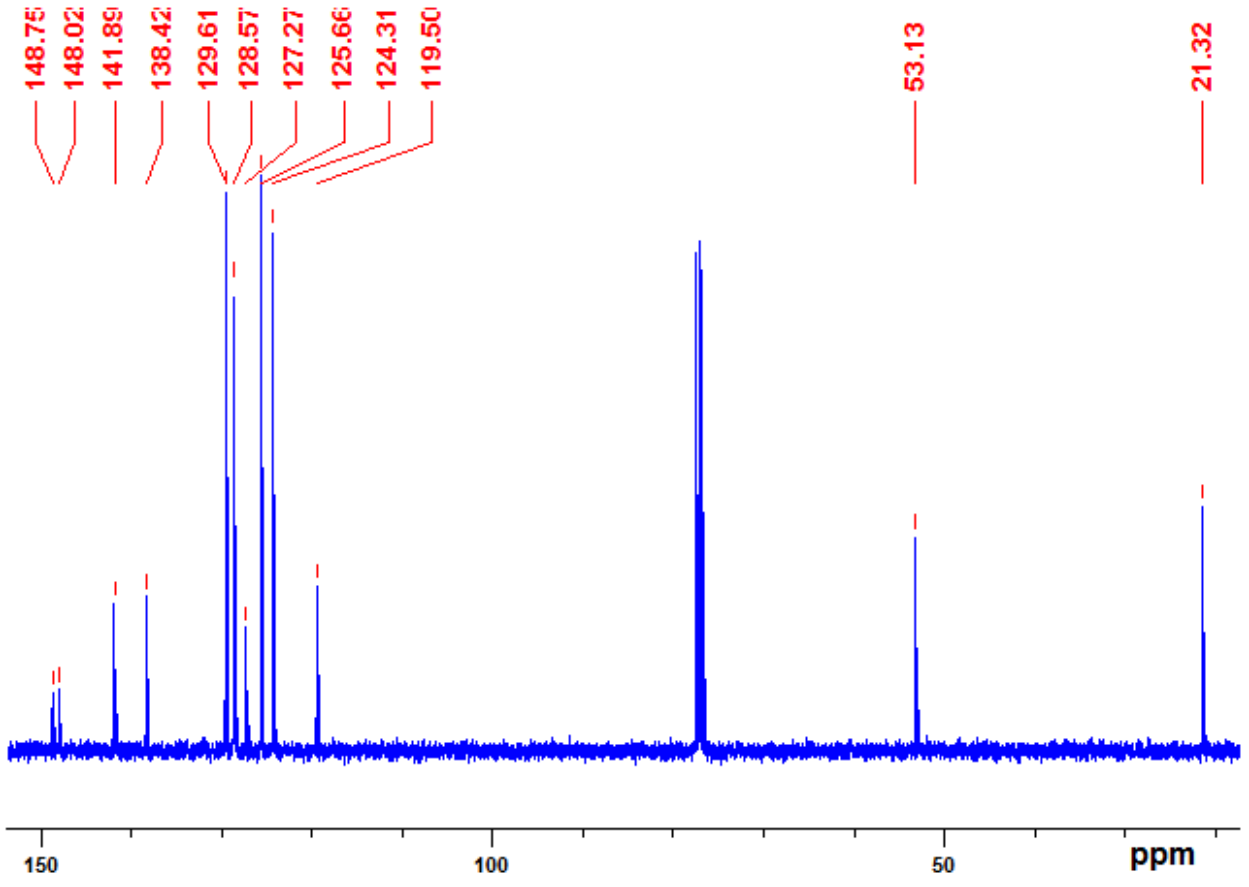
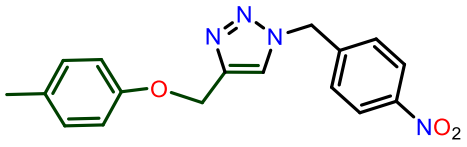



**Fig. S16**. $^{13}$C NMR spectrum of **IIb** in $CDCl_3$ at room temperature.

**9. 1-(4-nitrobenzyl)-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (IIc)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.19-8.22 (d, 2H), 7.62 (s, 1H), 7.38-7.40 (d, 2H), 7.06-7.08 (d, 2H), 6.83-6.86 (d, 2H), 5.64 (s, 2H), 5.18 (s, 2H), 2.27 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.94, 148.06, 141.58, 130.72, 130.02, 128.70, 128.62, 124.32, 122.95, 114.61, 62.08, 53.17, 20.49 ppm.

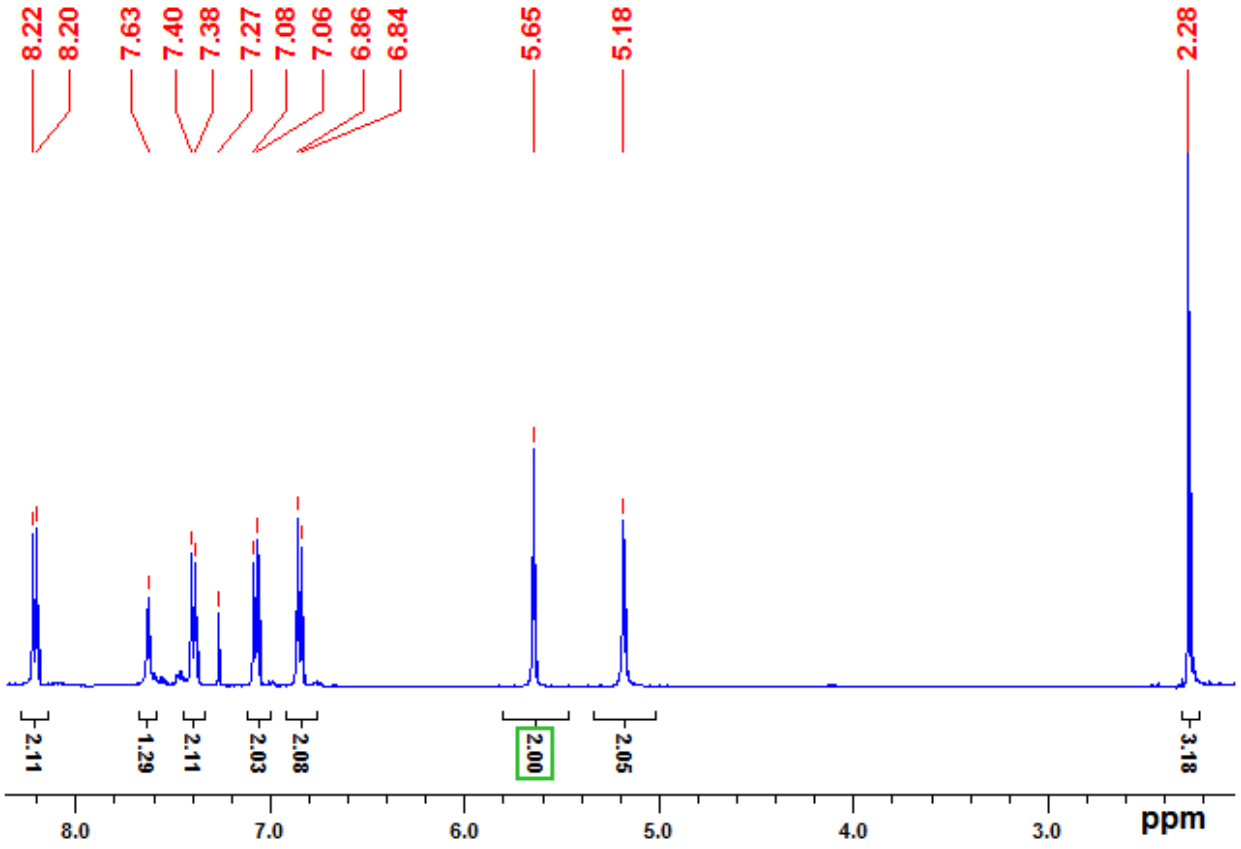



**Fig. S17**. $^{1}$H NMR spectrum of **IIc** in $CDCl_3$ at room temperature.

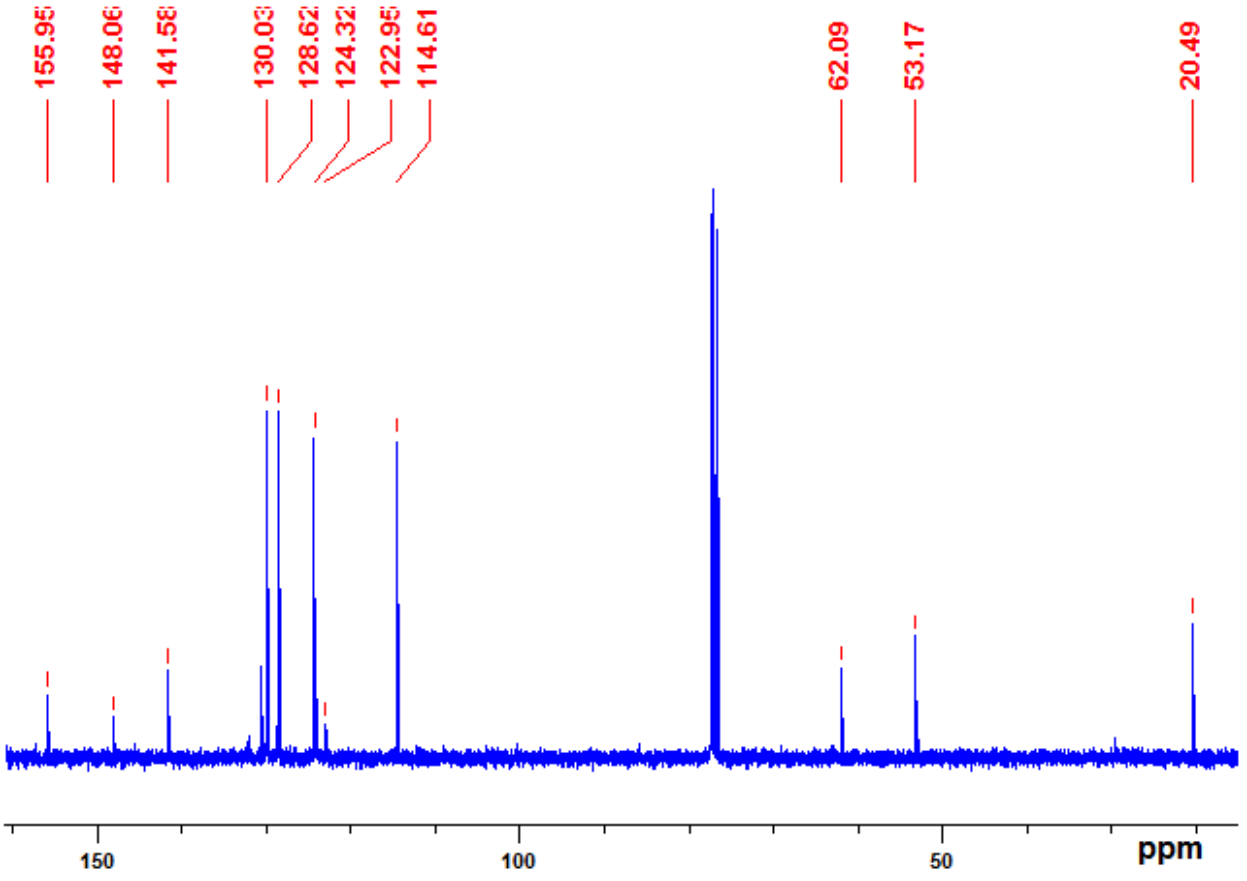
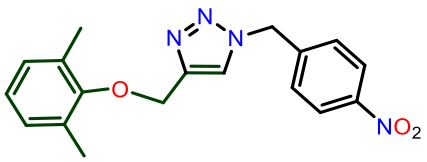



**Fig. S18**. $^{13}$C NMR spectrum of **IIc** in $CDCl_3$ at room temperature.

**10. 4-((2,6-dimethylphenoxy)methyl)-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (IId)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.16-8.18 (d, 2H), 7.74 (s, 1H), 7.39-7.41 (m, 2H), 6.93-7.00 (m, 3H), 5.67 (s, 2H), 4.97 (s, 2H), 2.25 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.18, 147.93, 141.90, 130.96, 128.95, 128.64, 124.37, 124.22, 123.26, 65.39, 53.07, 16.37 ppm.

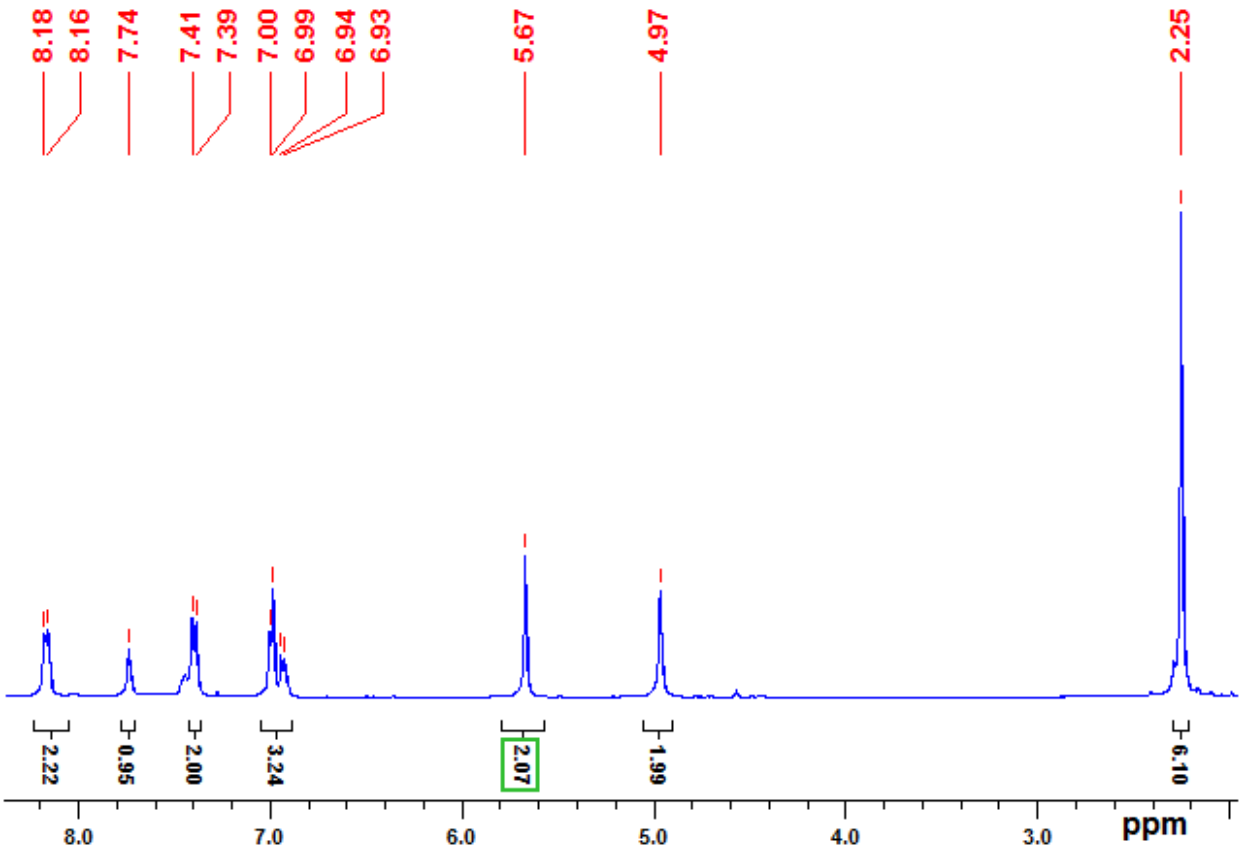



**Fig. S19**. $^{1}$H NMR spectrum of **IId** in $CDCl_3$ at room temperature.

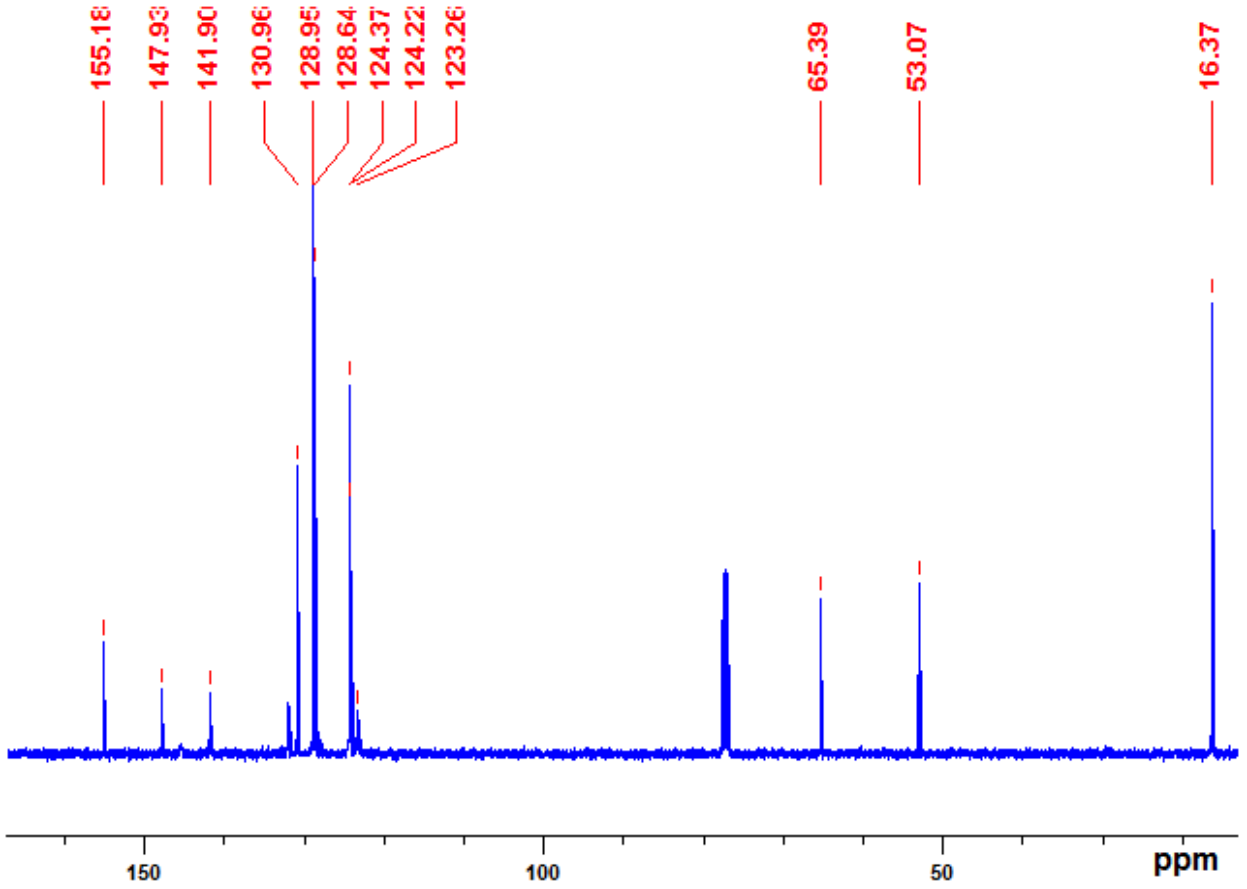
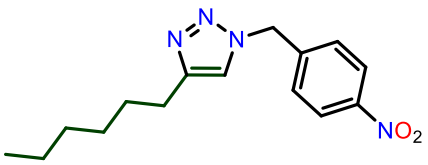



**Fig. S20**. $^{13}$C NMR spectrum of **IId** in $CDCl_3$ at room temperature.

**11. 4-hexyl-1-(4-nitrobenzyl)-1H-1,2,3-triazole (IIe)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.17-8.19 (d, 1H), 7.39-7.64 (m, 2H), 5.65 (s, 2H), 2.71 (t, 2H), 1.65 (m, 2H), 1.28-1.33 (m, 6H), 0.85 (t, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 135.01, 129.04, 128.59, 128.47, 127.94, 120.55, 53.96, 31.54, 29.37, 29.37, 25.73, 22.54, 14.06 ppm.

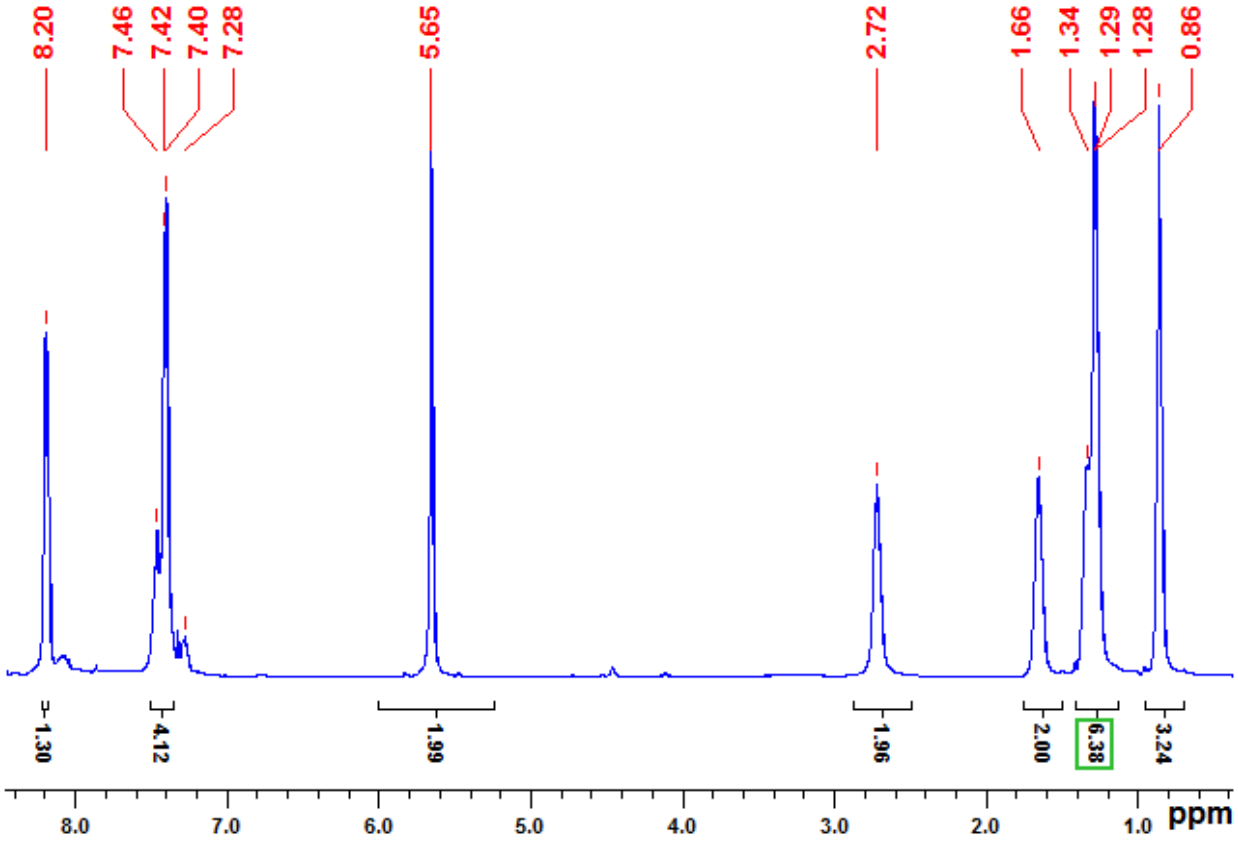



**Fig. S21**. $^{1}$H NMR spectrum of **IIe** in $CDCl_3$ at room temperature.

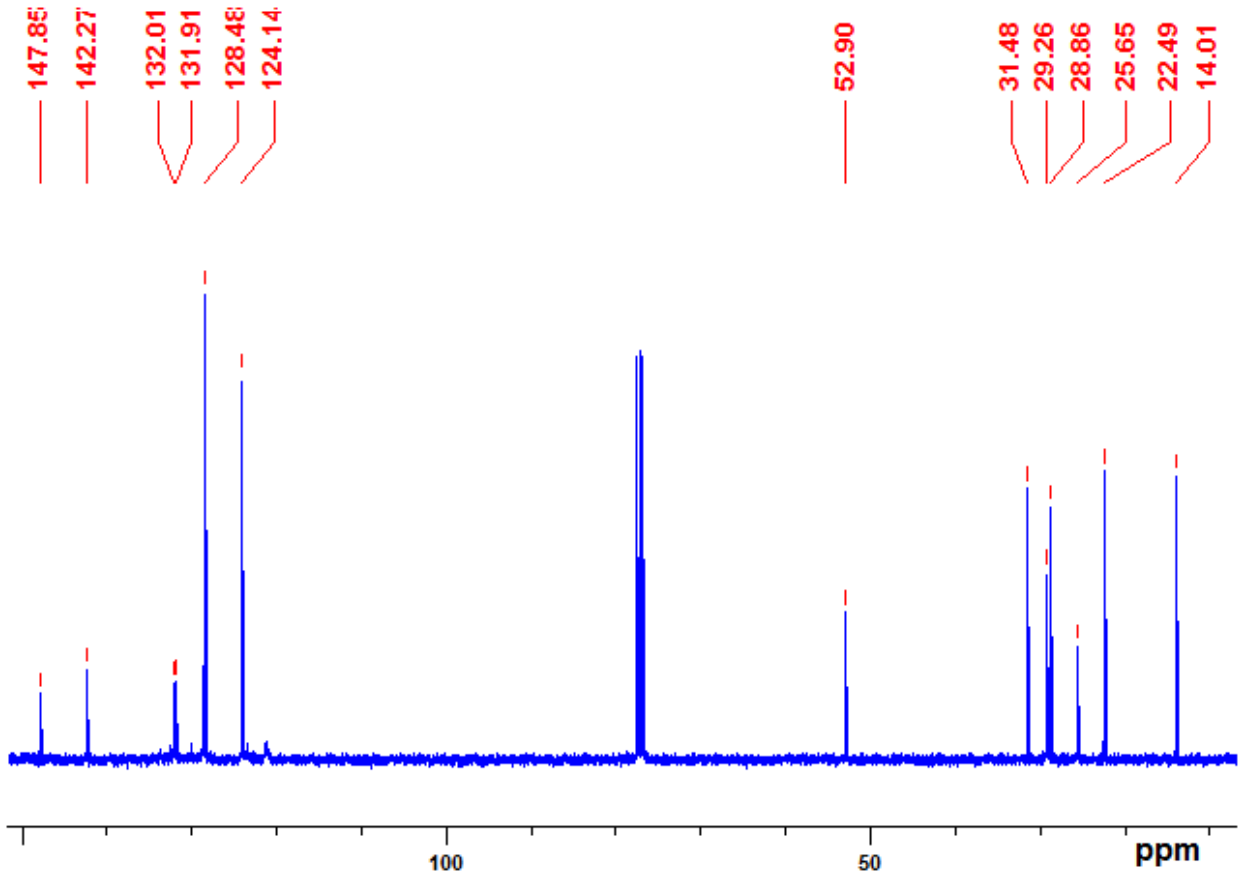
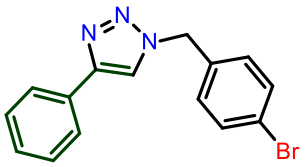



**Fig. S22**. $^{13}$C NMR spectrum of **IIe** in $CDCl_3$ at room temperature.

**12. 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (IIIa)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.15-7.80 (m, 10H), 5.50 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.39, 133.75, 132.32, 130.38, 129.66, 128.87, 128.30, 125.72, 122.94, 119.53, 53.51 ppm.

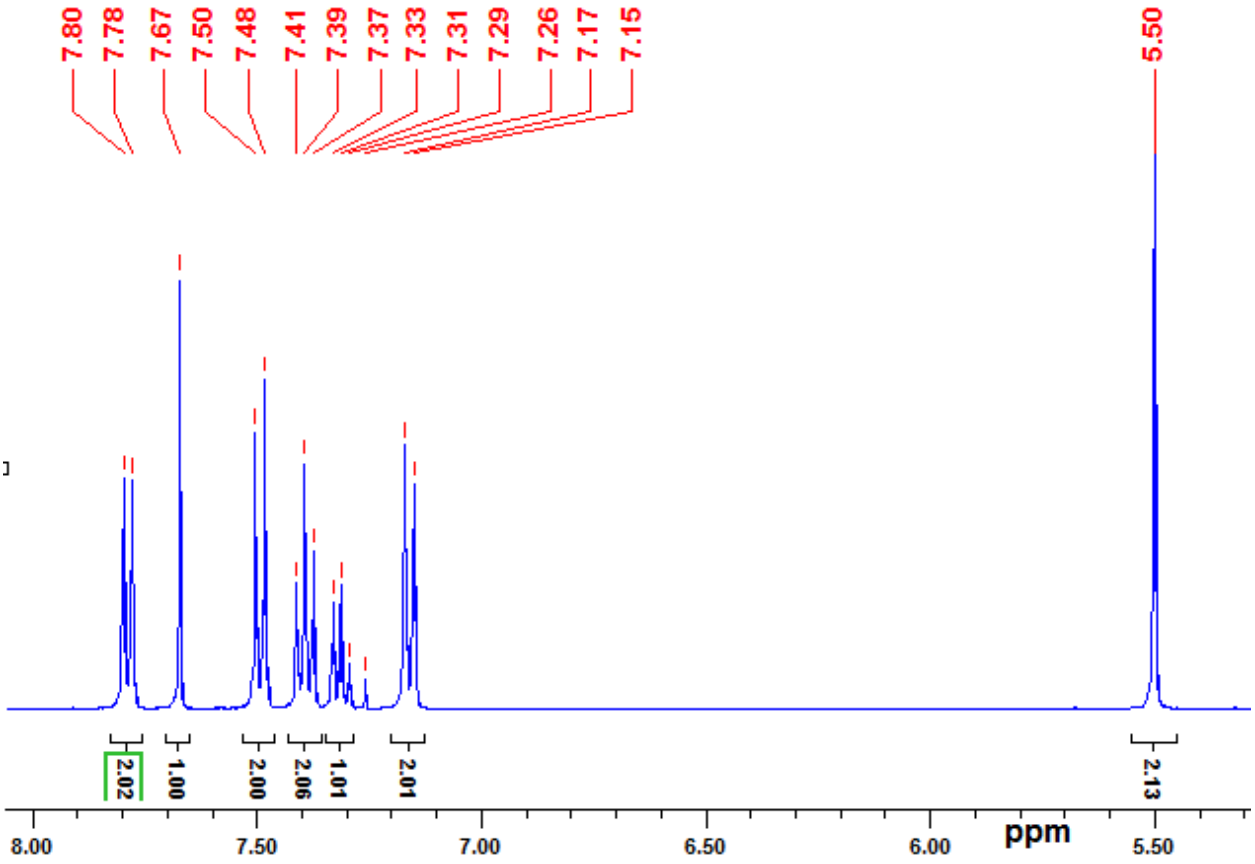



**Fig. S23**. $^{1}$H NMR spectrum of **IIIa** in $CDCl_3$ at room temperature.

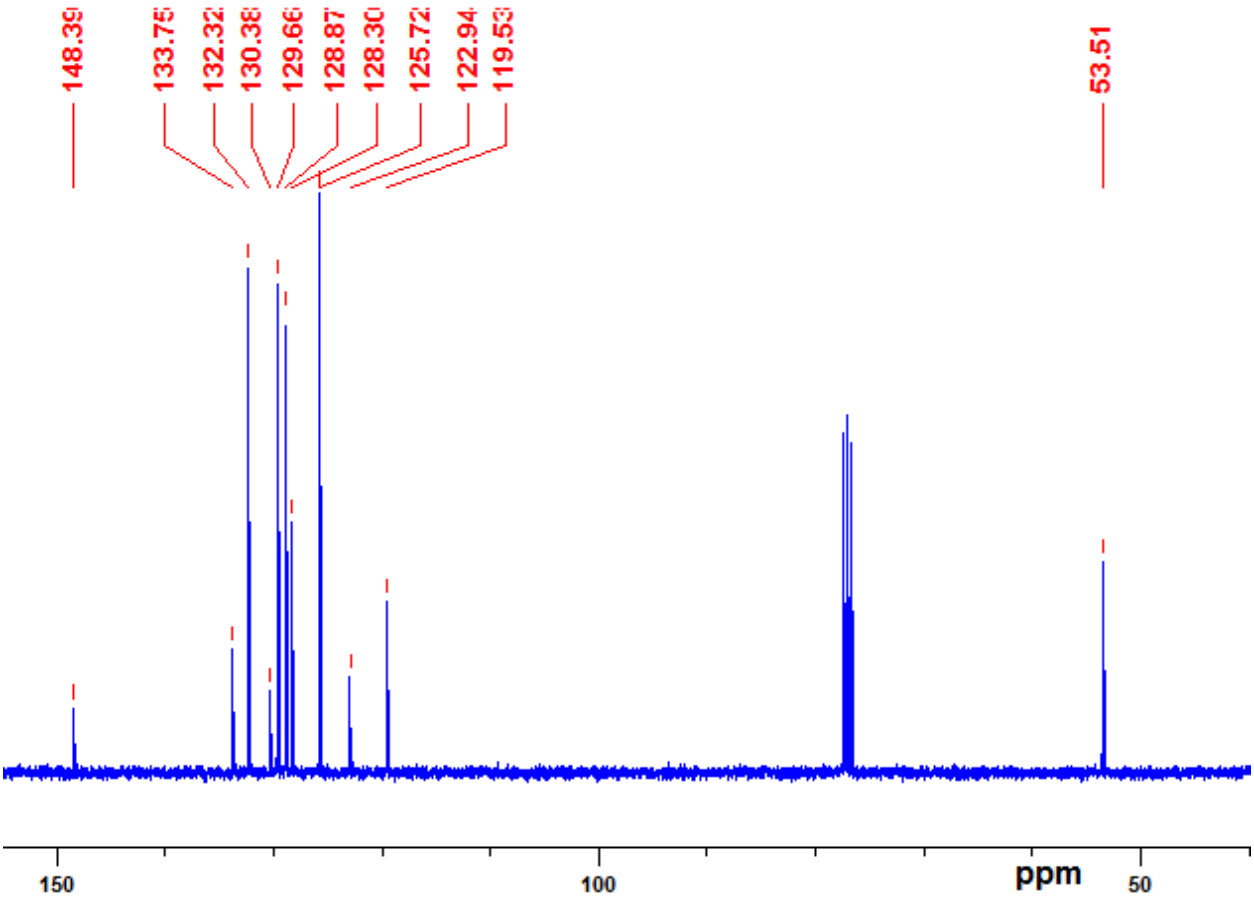
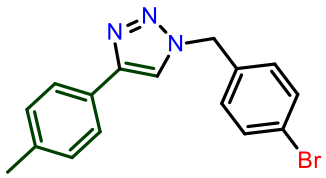



**Fig. S24**. $^{13}$C NMR spectrum of **IIIa** in $CDCl_3$ at room temperature.

**13. 1-(4-nitrobenzyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IIIb)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62-7.69 (m, 3H), 7.49-7.51 (m, 2H), 7.15-7.21 (m, 4H), 5.50 (s, 2H), 2.36 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.48, 138.16, 133.80, 132.31, 129.66, 128.53, 127.57, 125.63, 122.91, 119.13, 53.48, 21.30 ppm.

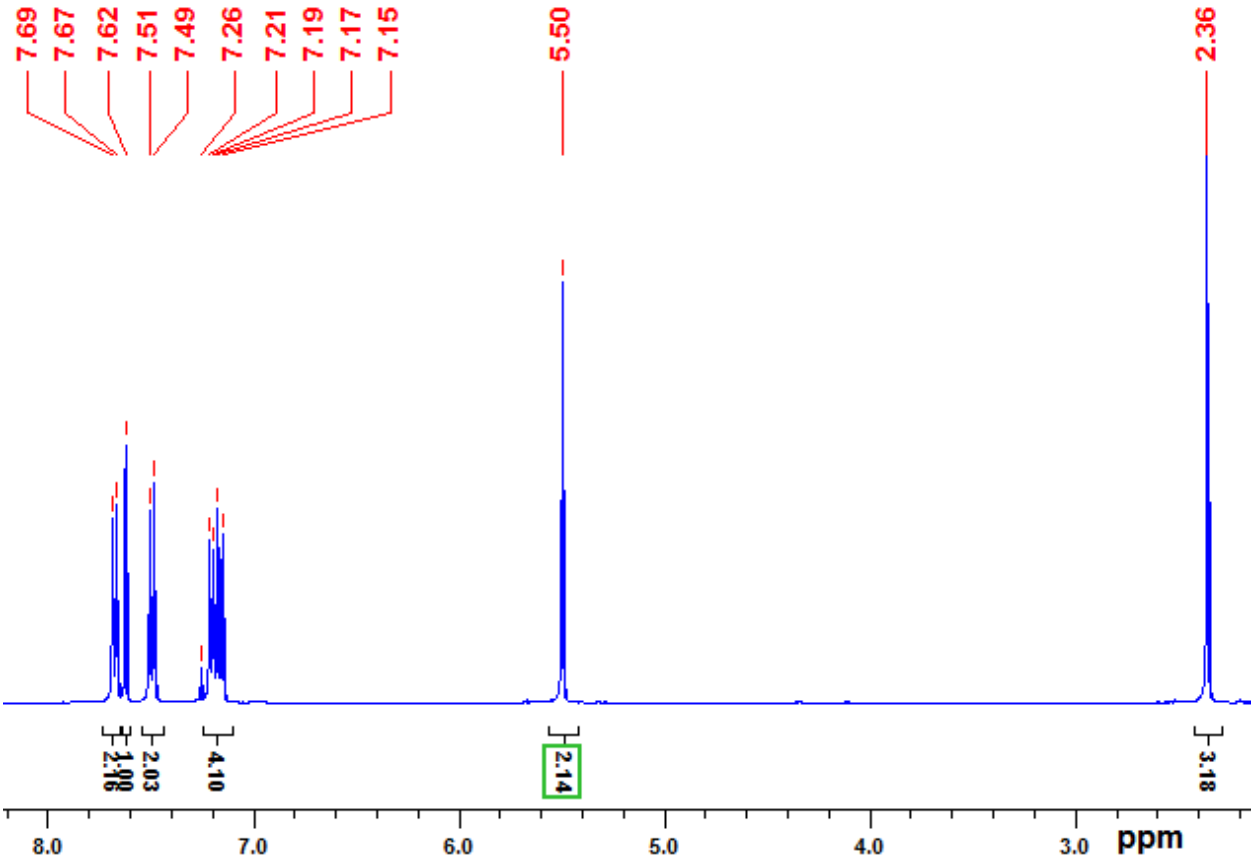



**Fig. S25**. $^{1}$H NMR spectrum of **IIIb** in $CDCl_3$ at room temperature.

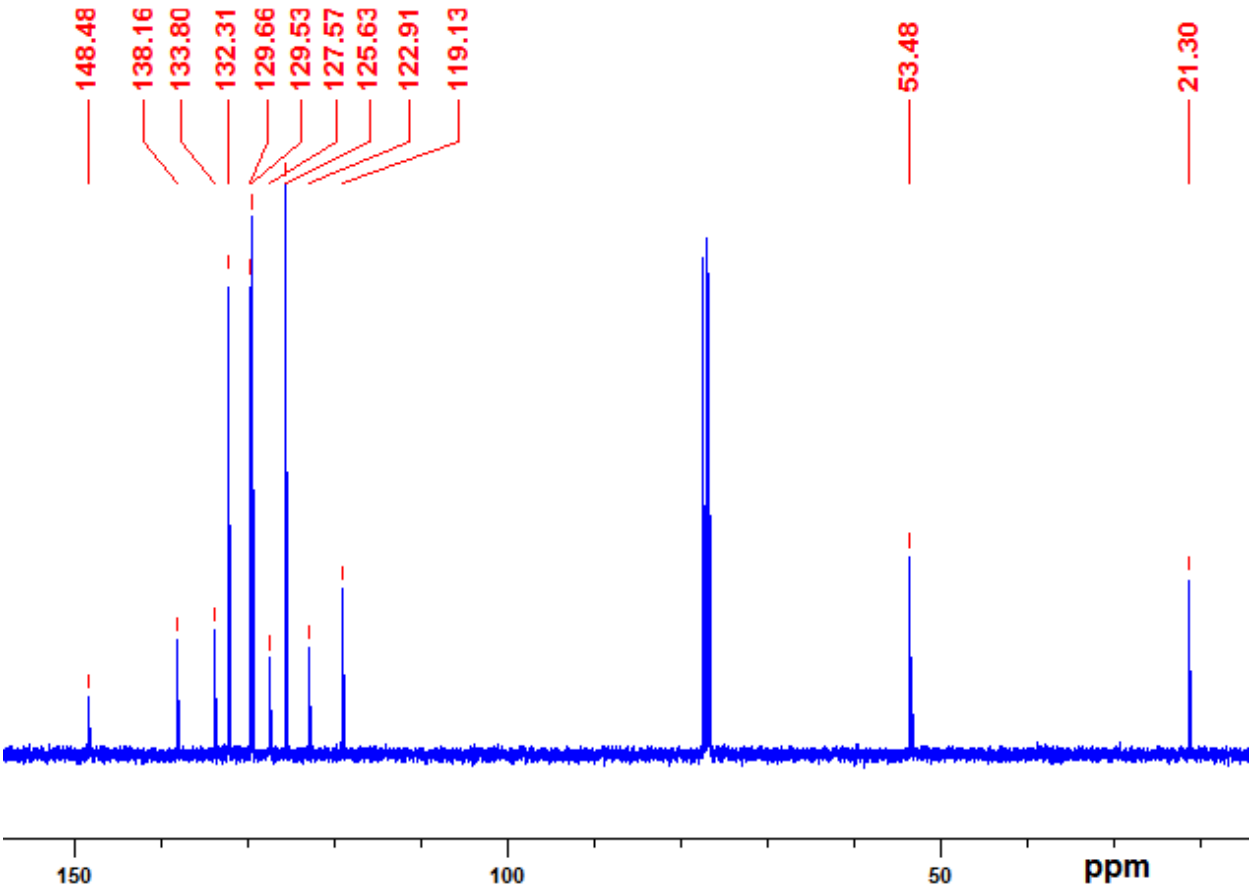
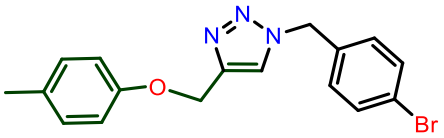



**Fig. S26**. $^{13}$C NMR spectrum of **IIIb** in $CDCl_3$ at room temperature.

**14. 1-(4-nitrobenzyl)-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (IIIc)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.48-7.52 (m, 3H), 7.06-7.14 (m, 4H), 6.84-6.86 (m, 2H), 5.47 (s, 2H), 5.15 (s, 2H), 2.28 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.06, 145.13, 133.54, 132.32, 130.60, 129.99, 129.71, 122.98, 122.52, 114.65, 62.21, 53.52, 20.49 ppm.

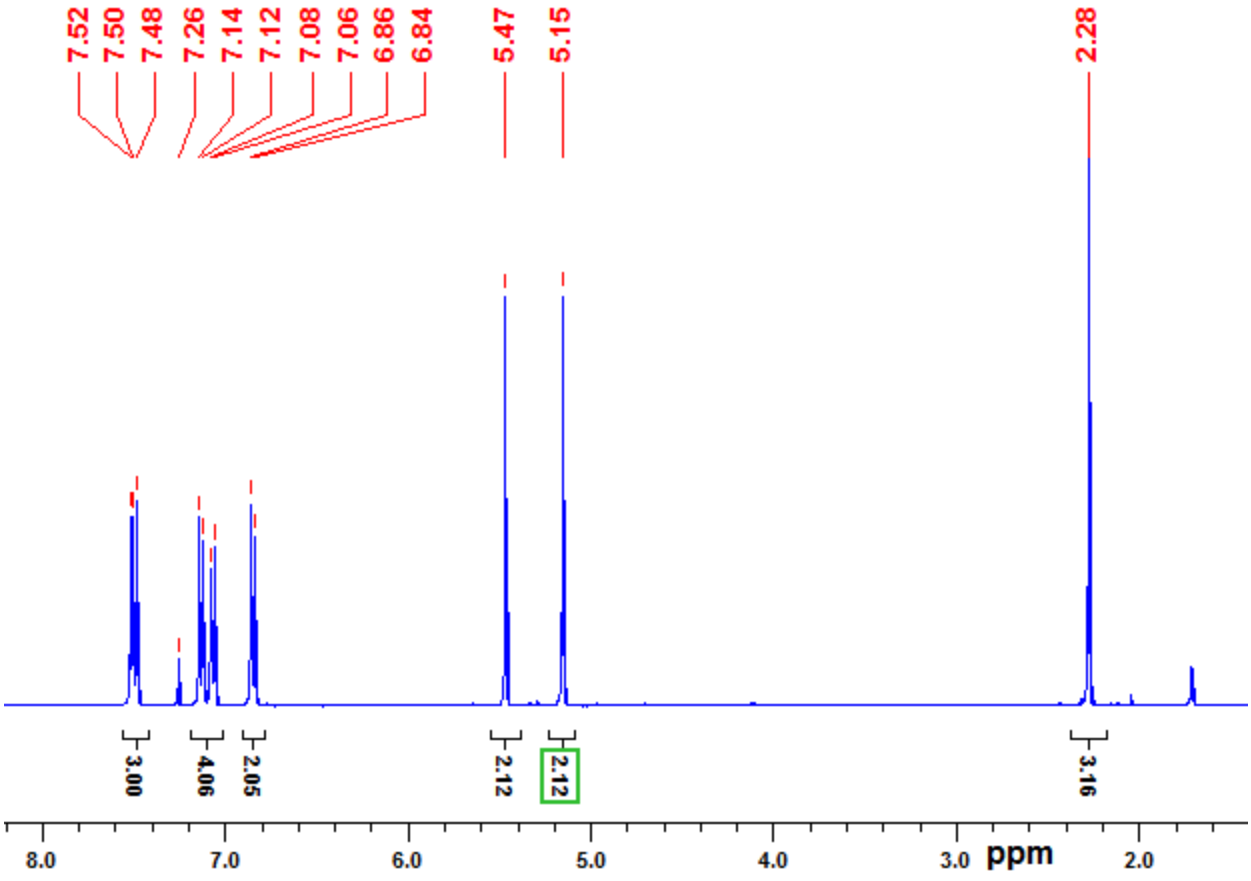



**Fig. S27**. $^{1}$H NMR spectrum of **IIIc** in $CDCl_3$ at room temperature.

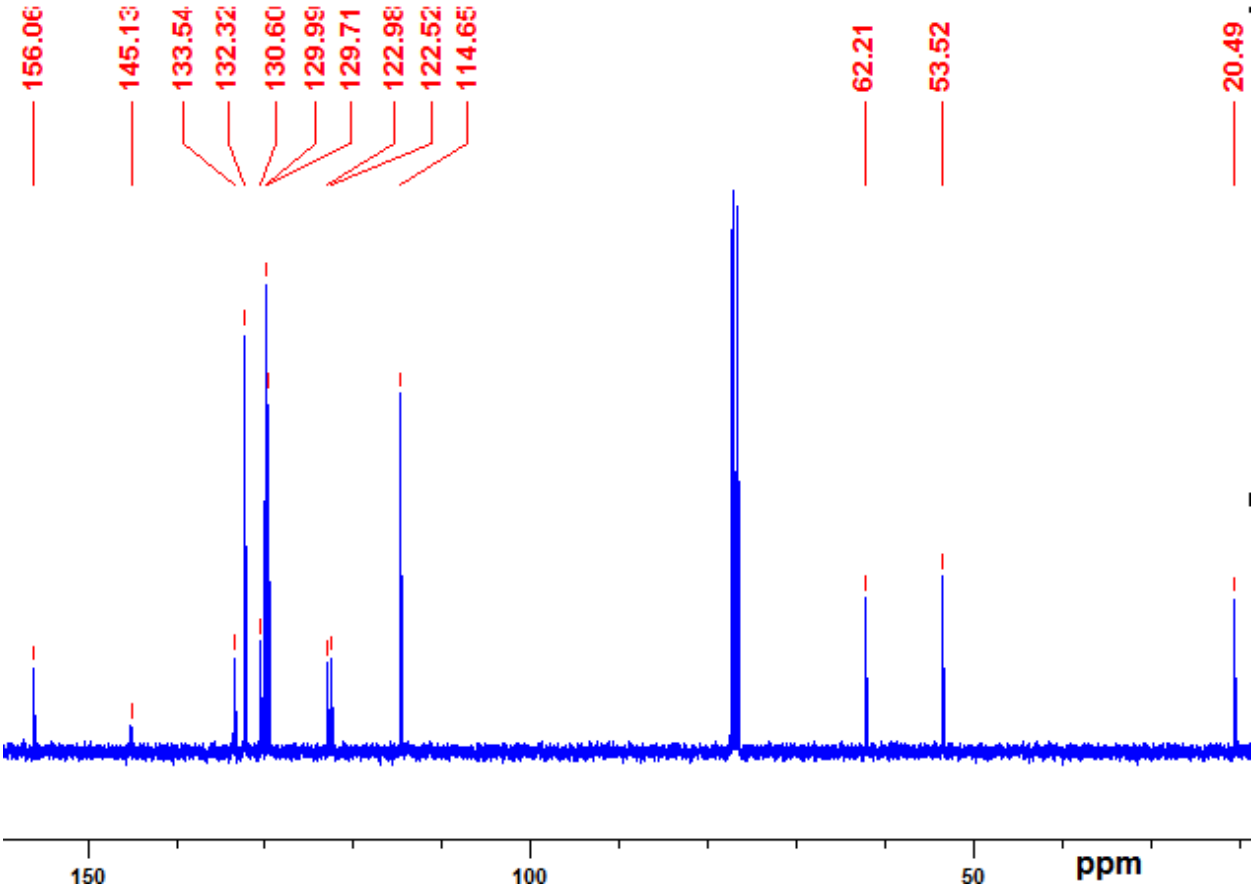
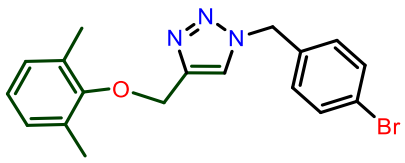



**Fig. S28**. $^{13}$C NMR spectrum of **IIIc** in $CDCl_3$ at room temperature.

**15. 4-((2,6-dimethylphenoxy)methyl)-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (IIId)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.50-7.54 (m, 3H), 7.15-7.17 (m, 2H), 6.92-7.02 (m, 3H), 5.50 (s, 2H), 4.95 (s, 2H), 2.26 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.24, 145.35, 133.61, 132.34, 131.02, 129.69, 128.91, 124.29, 122.99, 122.47, 65.56, 53.53, 16.36 ppm.

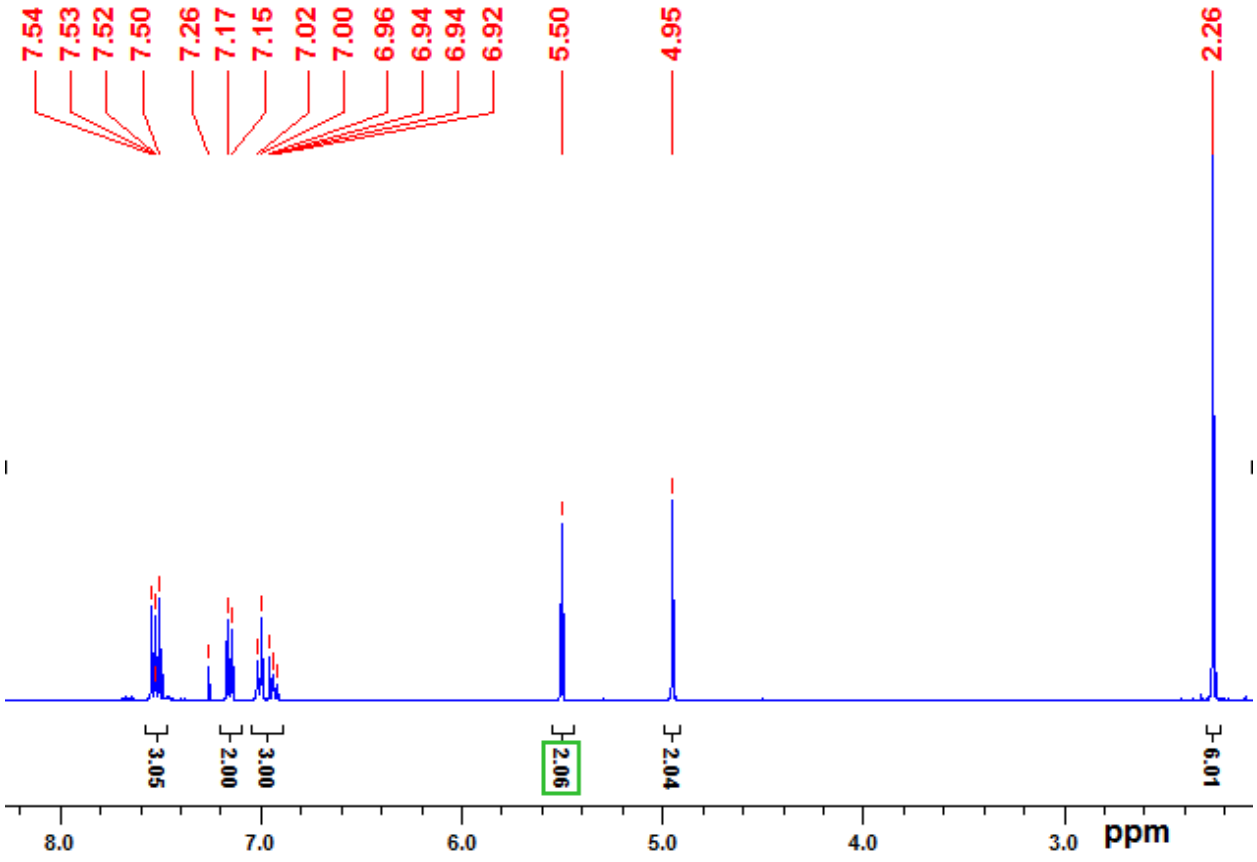



**Fig. S29**. $^{1}$H NMR spectrum of **IIId** in $CDCl_3$ at room temperature.

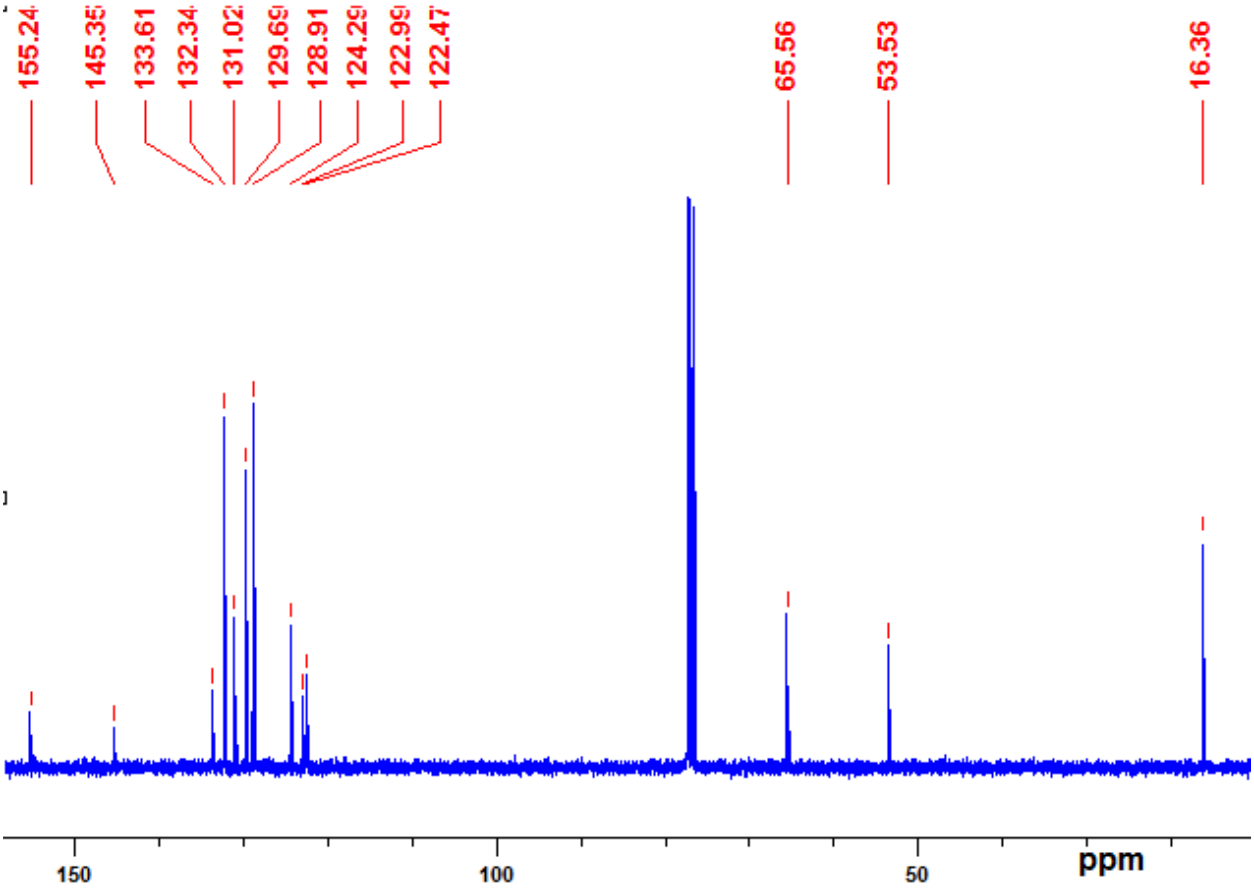
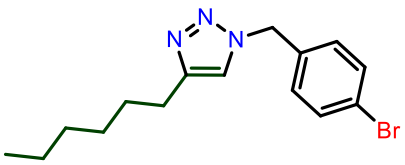



**Fig. S30**. $^{13}$C NMR spectrum of **IIId** in $CDCl_3$ at room temperature.

**16. 4-hexyl-1-(4-nitrobenzyl)-1H-1,2,3-triazole (IIIe)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.48-7.50 (m, 2H), 7.11-7.19 (m, 3H), 5.44 (s, 2H), 2.67-2.71 (t, 2H), 1.59-1.67 (m, 2H), 1.26-1.37 (m, 6H), 0.85-0.88 (t, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 149.23, 134.05, 132.22, 129.56, 122.74, 120.47, 53.28, 31.53, 29.34, 28.91, 25.72, 22.53, 14.04 ppm.

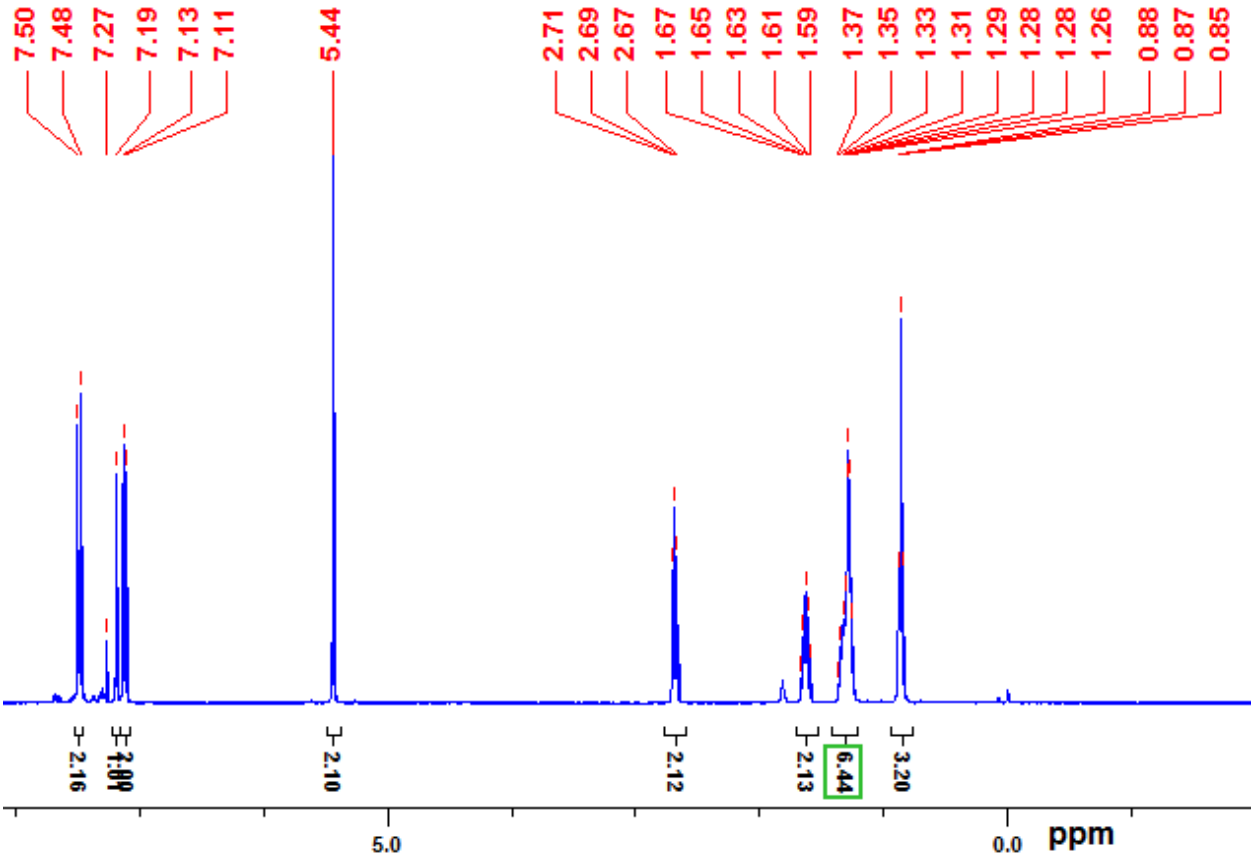



**Fig. S31**. $^{1}$H NMR spectrum of **IIIe** in $CDCl_3$ at room temperature.

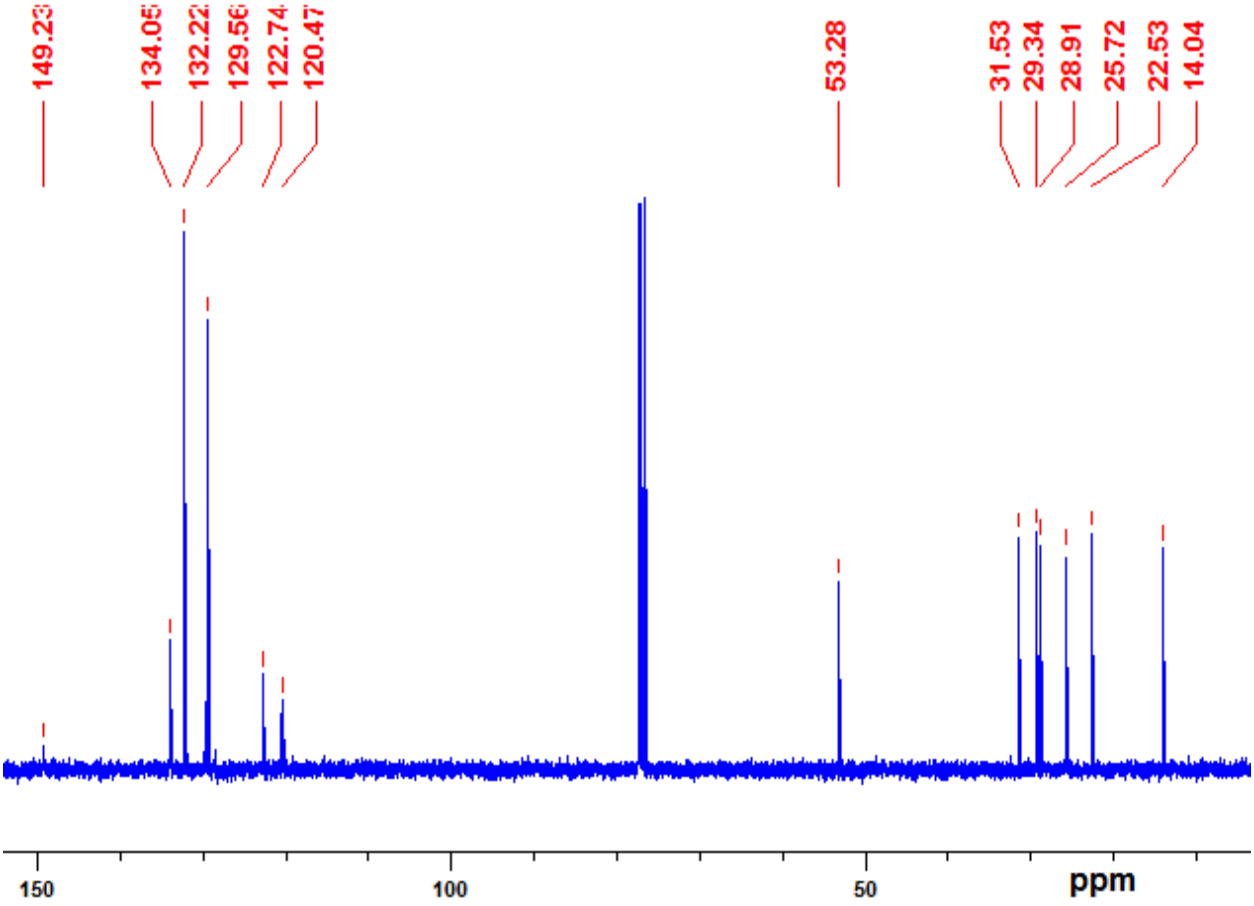
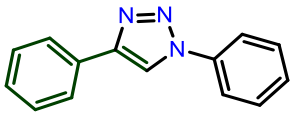



**Fig. S32**. $^{13}$C NMR spectrum of **IIIe** in $CDCl_3$ at room temperature.

**17. 1,4-diphenyl-1*H*-1,2,3-triazole (IVa)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.20 (s, 1H), 7.90-7.92 (d, 2H), 7.78-7.80 (d, 2H), 7.52-7.56 (t, 2H), 7.43-7.48 (m, 3H), 7.35-7.39 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.43, 137.08, 130.25, 129.81, 128.95, 128.80, 128.45, 125.87, 120.55, 117.63 ppm.

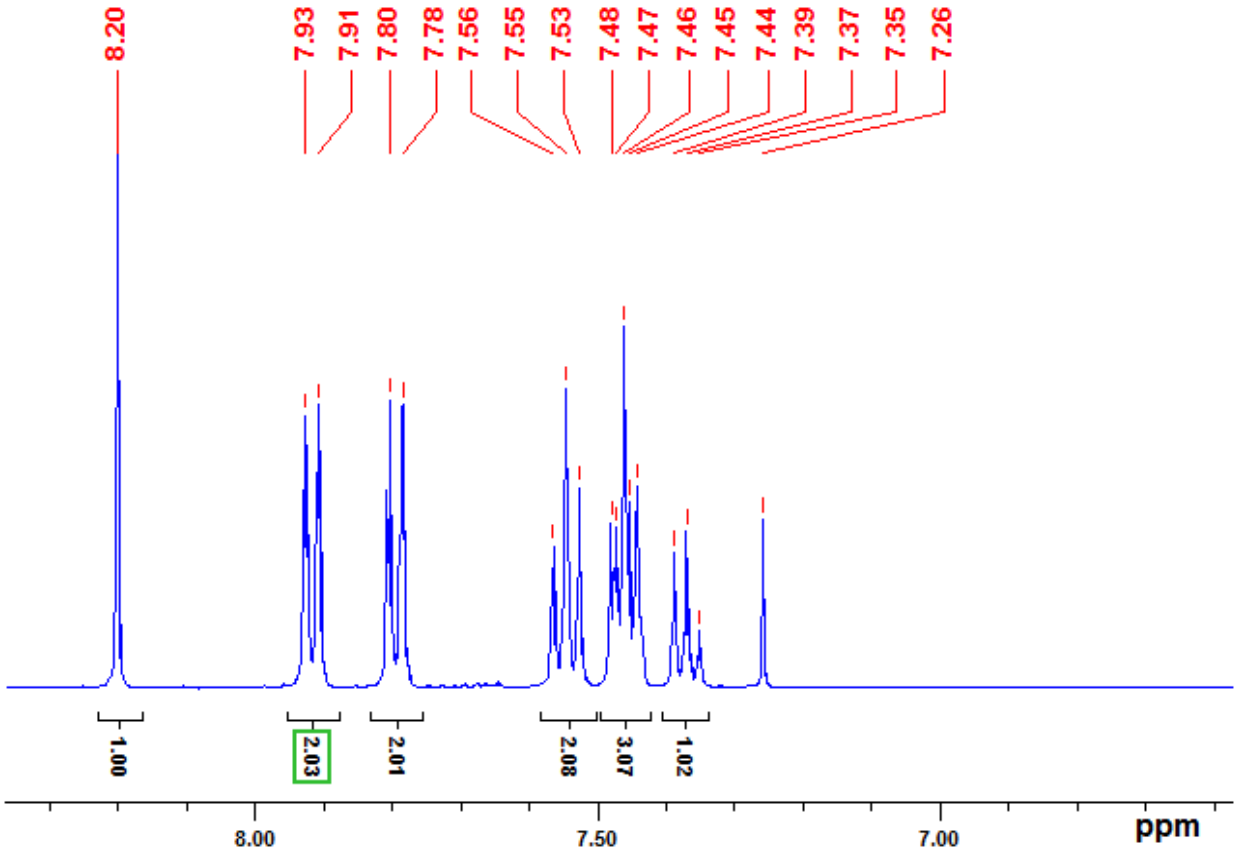



**Fig. S33**. $^{1}$H NMR spectrum of **IVa** in $CDCl_3$ at room temperature.

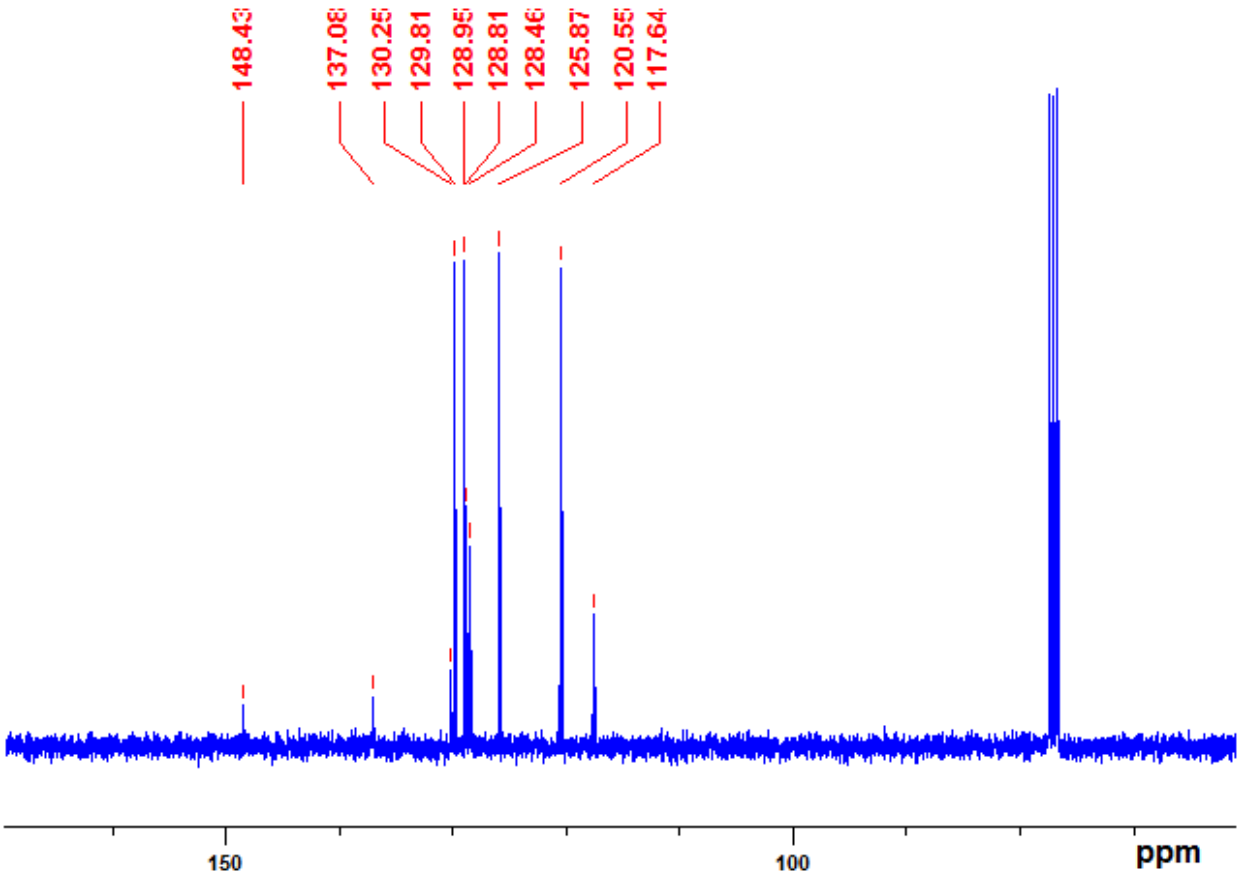
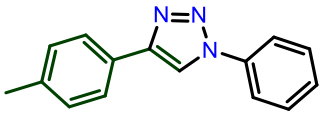



**Fig. S34**. $^{13}$C NMR spectrum of **IVa** in $CDCl_3$ at room temperature.

**18. 1-phenyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IVb)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.15 (s, 1H), 7.76-7.80 (t, 4H), 7.50-7.54 (t, 2H), 7.41-7.45 (t, 1H), 7.24-7.25 (m, 2H), 2.38 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.50, 138.34, 137.10, 129.77, 129.62, 128.71, 127.42, 125.77, 120.50, 117.29, 21.36 ppm.

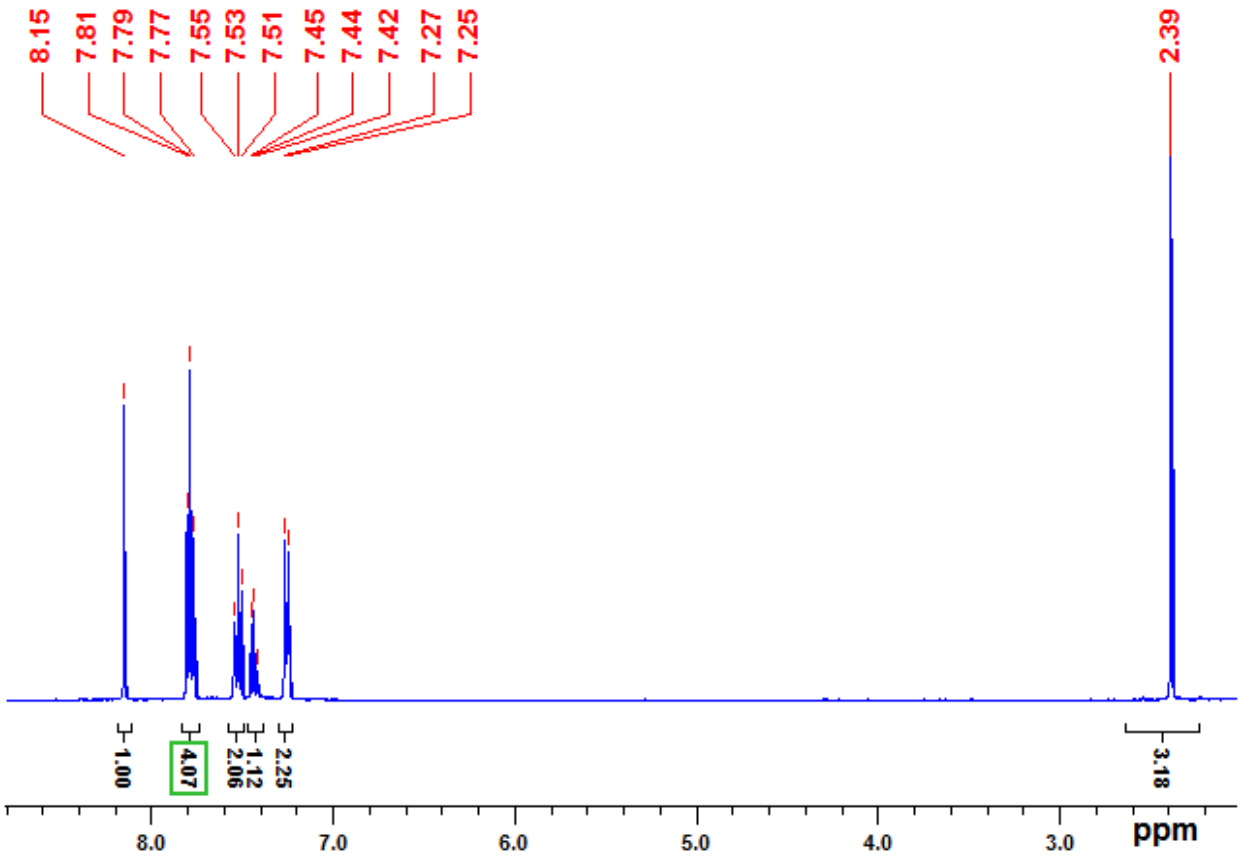



**Fig. S35**. $^{1}$H NMR spectrum of **IVb** in $CDCl_3$ at room temperature.

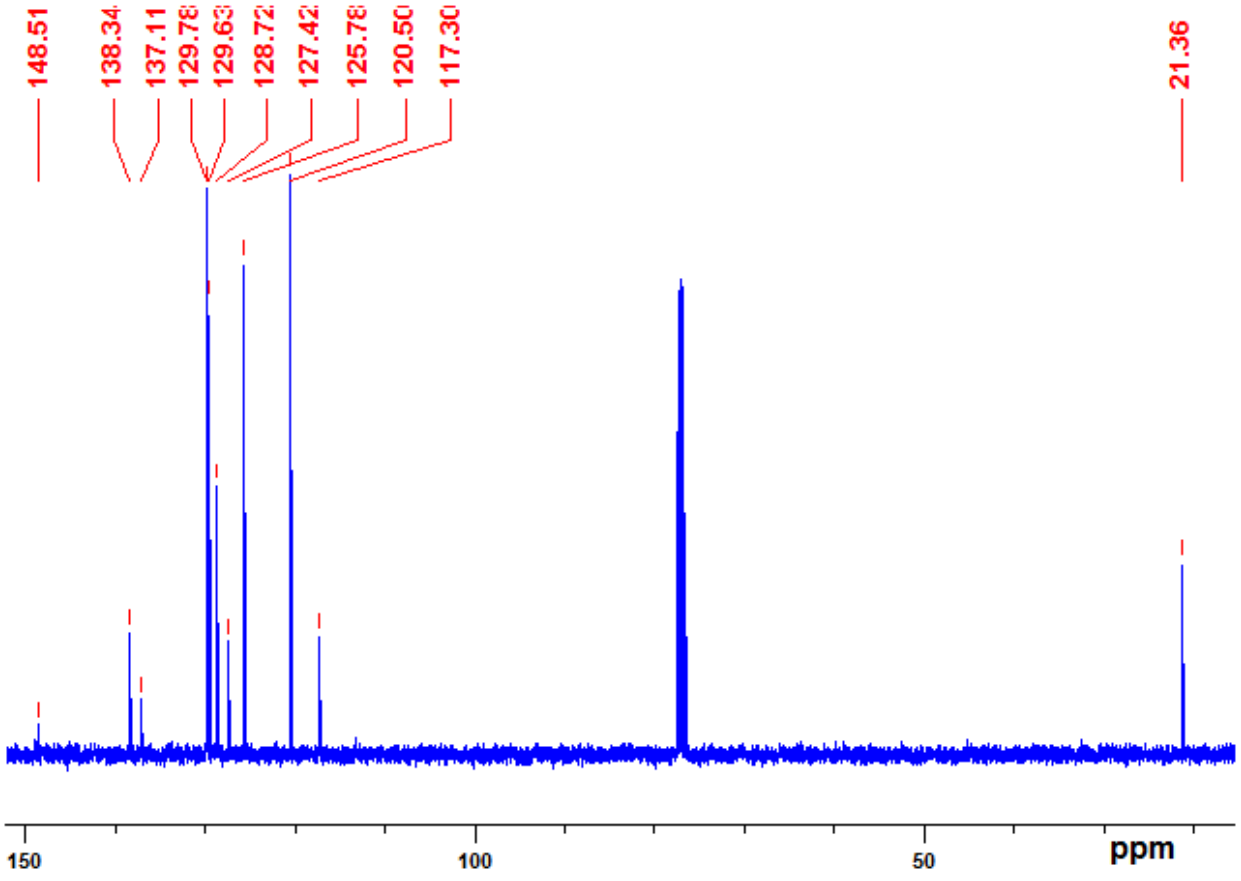
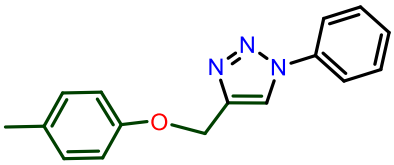



**Fig. S36**. $^{13}$C NMR spectrum of **IVb** in $CDCl_3$ at room temperature.

**19. 1-phenyl-4-((*p*-tolyloxy)methyl)-1*H*-1.2.3-triazole (IVc)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.04 (s, 1H), 7.71-7.73 (d, 2H), 7.49-7.53 (t, 2H), 7.41-7.45 (t, 1H), 7.09-7.11 (d, 2H), 6.90-6.93 (m, 2H), 5.26 (s, 2H), 2.28 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.07, 145.22, 137.00, 130.65, 130.06, 129.79, 128.87, 120.90, 120.61, 114.64, 62.13, 20.51 ppm.

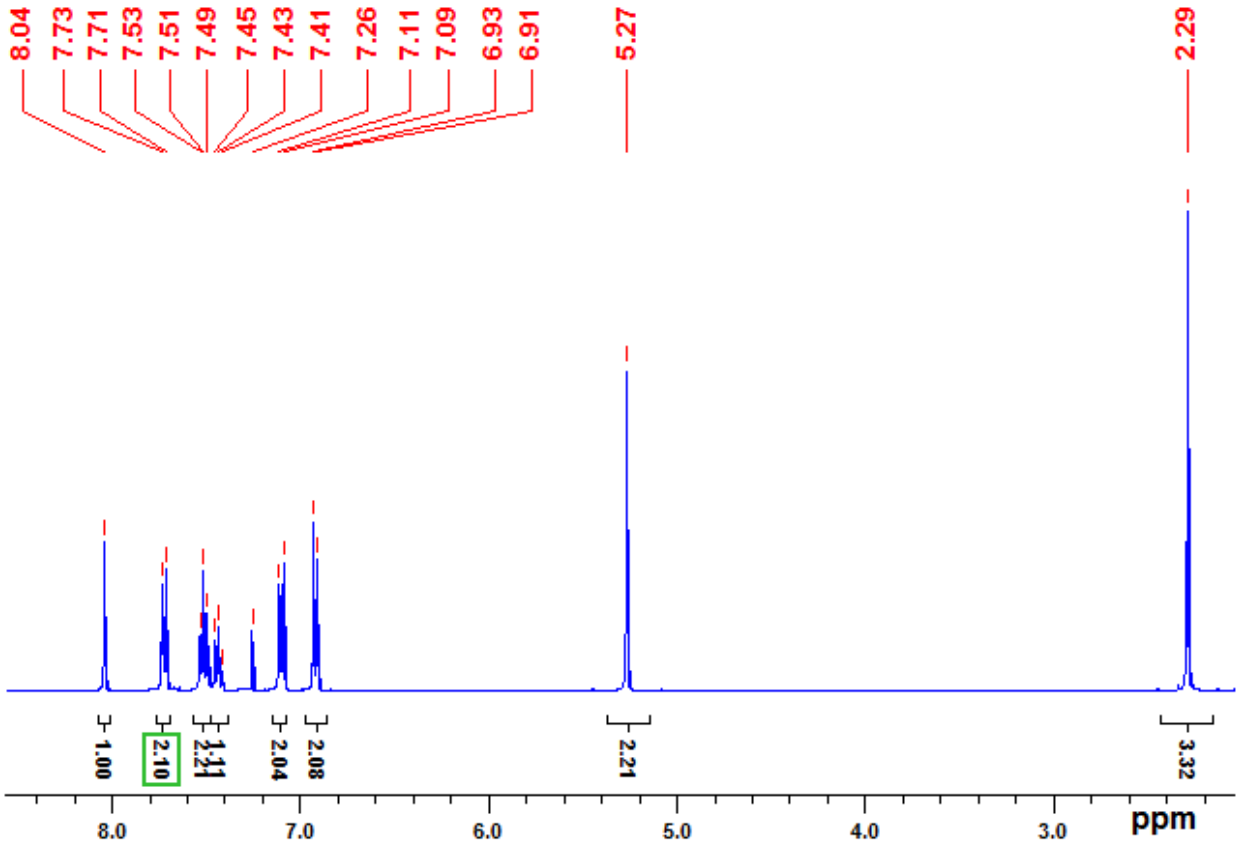



**Fig. S37**. $^{1}$H NMR spectrum of **IVc** in $CDCl_3$ at room temperature.

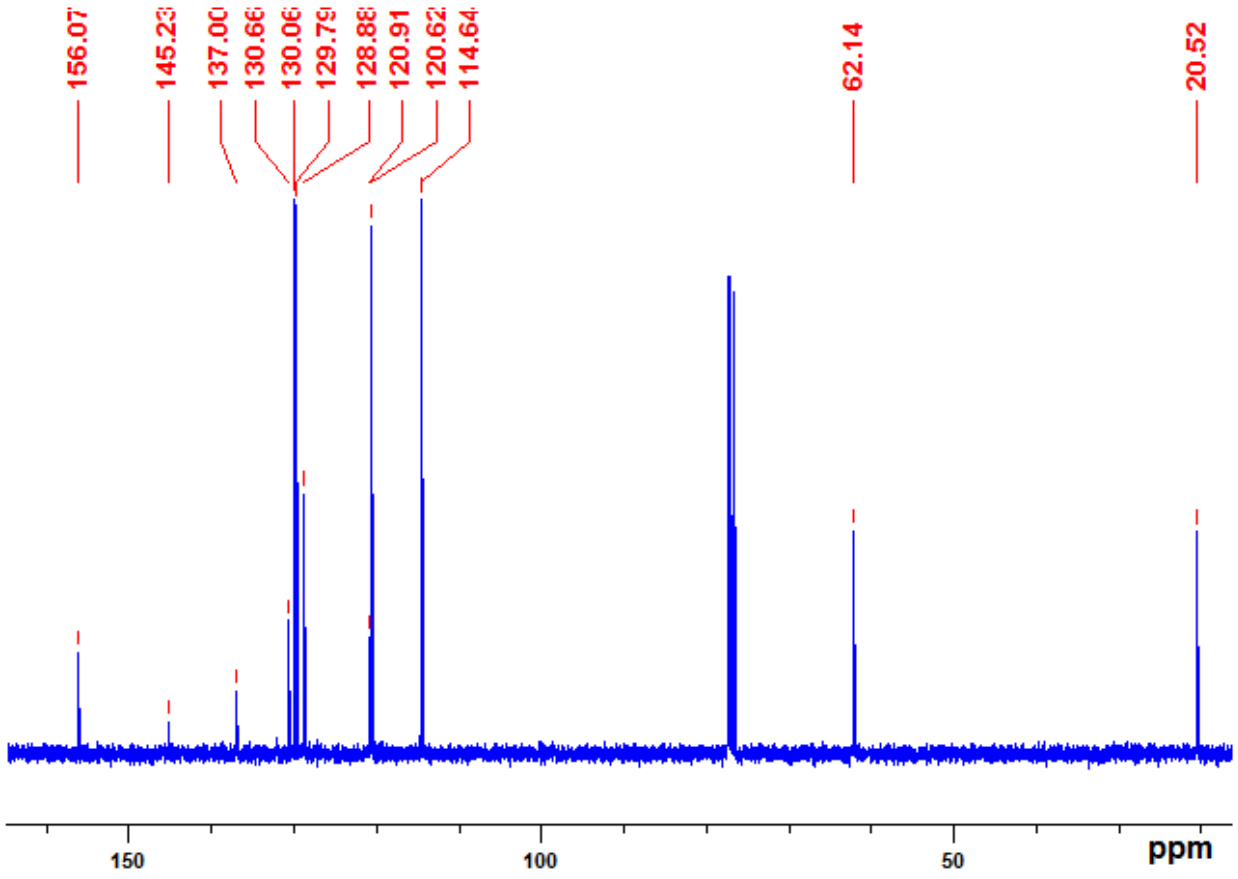
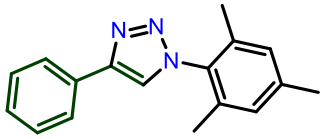



**Fig. S38**. $^{13}$C NMR spectrum of **IVc** in $CDCl_3$ at room temperature.

**20. 1-mesityl-4-phenyl-1*H*-1,2,3-triazole (Va)**




$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.92-7.94 (d, 2H), 7.84 (s, 1H), 7.34-7.48 (m, 3H), 7.01 (s, 2H), 2.36 (s, 3H), 2.01 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 147.58, 140.11, 135.13, 133.51, 130.50, 129.13, 128.95, 128.30, 125.76, 121.52, 21.18, 17.37 ppm.

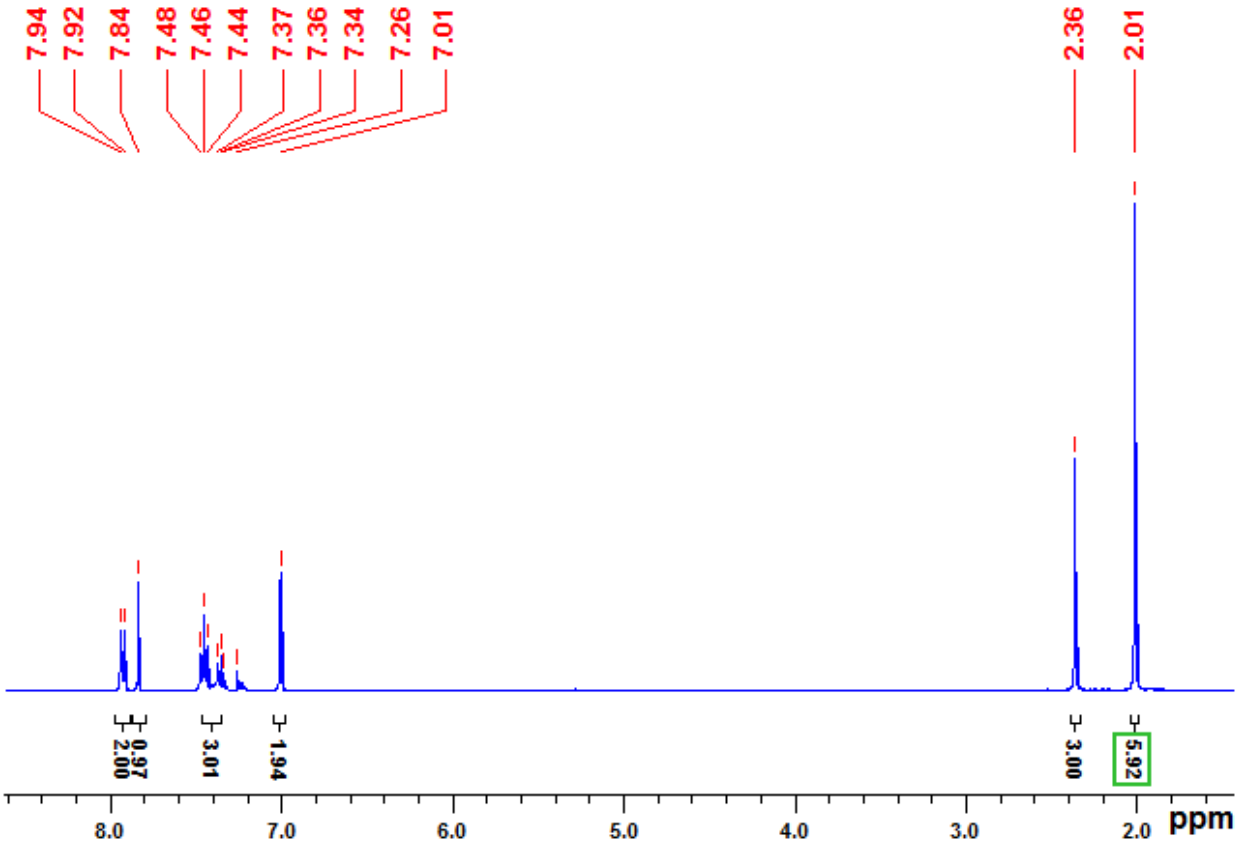



**Fig. S39**. $^{1}$H NMR spectrum of **Va** in $CDCl_3$ at room temperature.

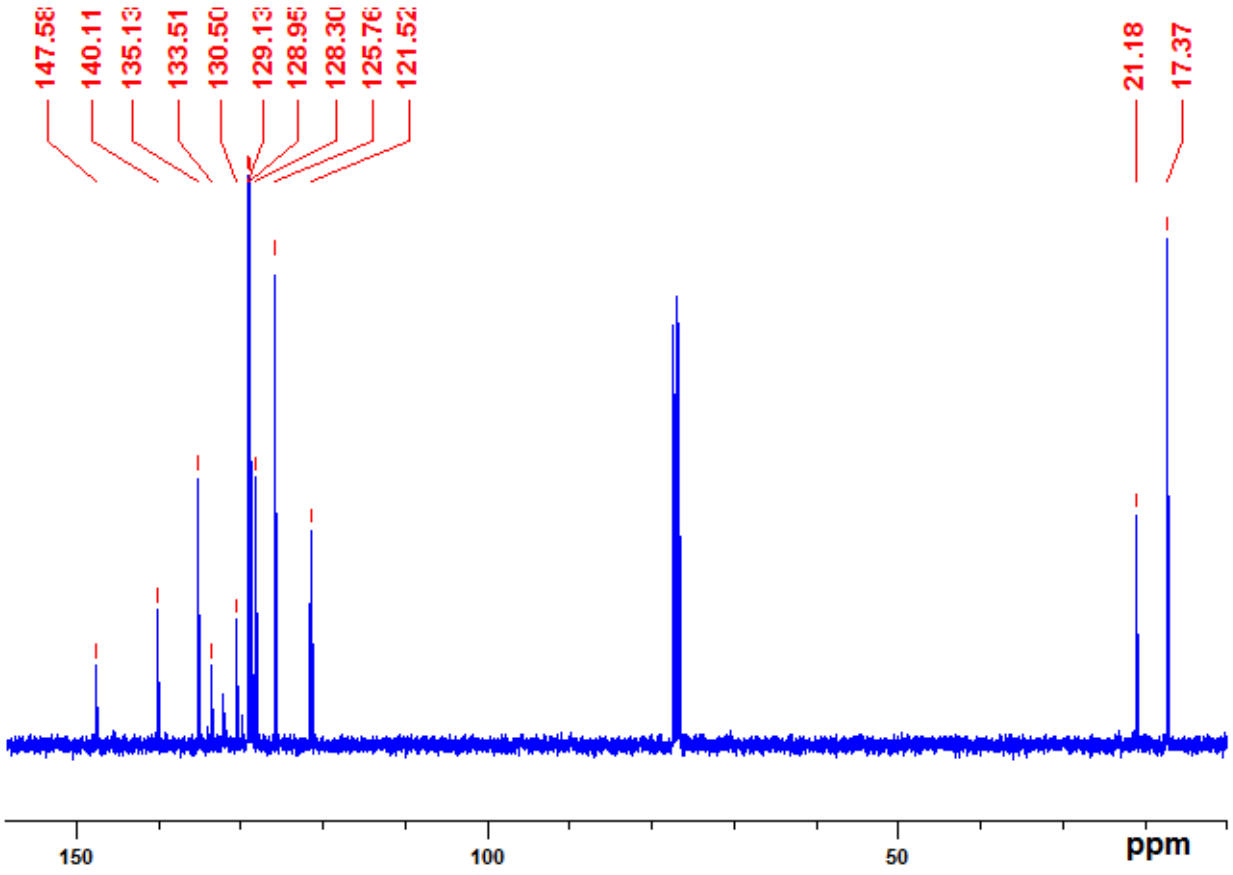
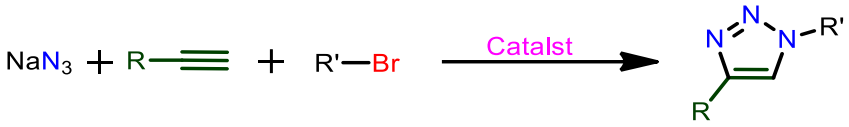


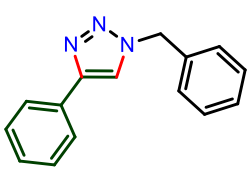

**Fig. S40**. $^{13}C$ NMR spectrum of **Va** in $CDCl_3$ at room temperature.

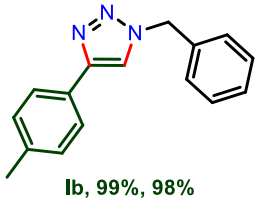
**Table S1.** Structural parameters of compounds **Ia, Ib, IIa** and **IIb**.

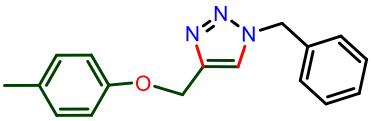
| | **Ia** | **Ib** | **IIa** | **IIb** |
|---|---|---|---|---|
| Empirical formula | $C_{15}H_{13}N_3$ | $C_{16}H_{14}N_3$ | $C_{15}H_{12}N_4O_2$ | $C_{16}H_{14}N_4O_2$ |
| Formula weight | 235.29 | 249.32 | 280.29 | 294.32 |
| Temperature (K) | 298 | 298 | 298 | 298 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1$ | $P2_12_12_1$ | $P2_1/c$ |
| $a$/Å | 6.0383(13) | 8.0688(12) | 5.7169(7) | 9.5421(9) |
| $b$/Å | 8.0923(17) | 5.8237(6) | 13.9426(17) | 5.7049(4) |
| $c$/Å | 25.709(8) | 14.4259(17) | 17.101(3) | 27.128(3) |
| α/° | 90 | 90 | 90 | 90 |
| $\beta$/° | 93.516(19) | 100.683(13) | 90 | 98.745(10) |
| $\gamma$/° | 90 | 90 | 90 | 90 |
| Volume (Å$^3$) | 1253.9(5) | 666.13(15) | 1363.1(3) | 1459.6(2) |
| $Z$ | 4 | 2 | 4 | 4 |
| $\rho_{calc}$/mg mm$^{-3}$ | 1.2463 | 1.2429 | 1.3657 | 1.3392 |
| Absorption coefficient ($\mu$/mm$^{-1}$) | 0.076 | 0.076 | 0.095 | 0.092 |
| $F$(000) | 496.2 | 264.1 | 584.3 | 616.3 |
| Reflections collected | 10726 | 2967 | 3974 | 6410 |
| $R_{int}$ | 0.0743 | 0.0457 | 0.0430 | 0.0333 |
| GOF on $F^2$ | 1.040 | 1.035 | 1.066 | 1.069 |
| $R_1$ ($I>2\sigma(I)$) | 0.0688 | 0.0736 | 0.0884 | 0.0688 |
| w$R_2$ ($I>2\sigma(I)$) | 0.1682 | 0.1638 | 0.2247 | 0.1538 |
| $R_1$ values (all data) | 0.1497 | 0.1494 | 0.1699 | 0.1375 |
| $R_2$ values (all data) | 0.2335 | 0.2281 | 0.2989 | 0.1999 |

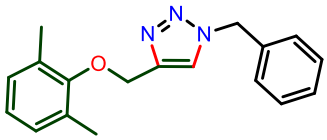
**Chart S1.** Complex **1** and/or **2** catalyzed [3 + 2] cycloaddition of aliphatic azide with alkyne[a]

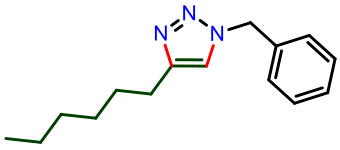


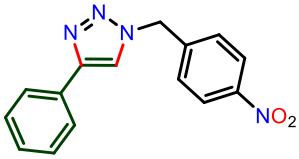


**Ia, 99%, 96%**

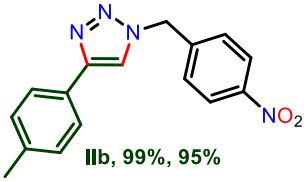

**Ib, 99%, 98%**

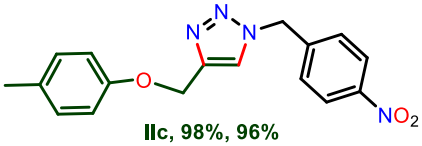

**Ic, 99%, 95%**

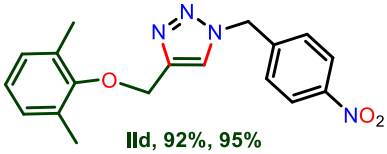

**Id, 98%, 96%**

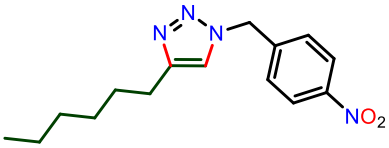

**If, 95%, 98%**

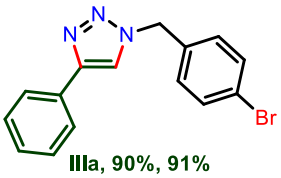

**IIa, 98%, 99%**

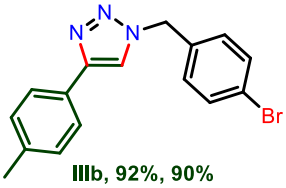

**IIb, 99%, 95%**

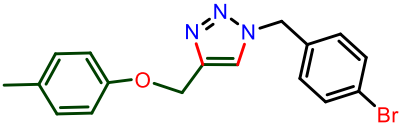

**IIc, 98%, 96%**

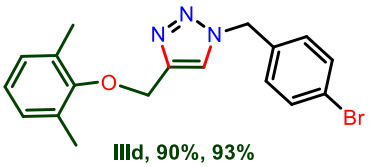

**IId, 92%, 95%**

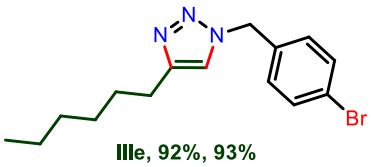

**IIe, 94%, 98%**


**IIIa, 90%, 91%**


**IIIb, 92%, 90%**


**IIIc, 94%, 91%**


**IIId, 90%, 93%**

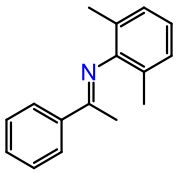

**IIIe, 92%, 93%**

[a]Reaction conditions: alkyne (1.2 mmol), azide (1 mmol), Catalyst **1** and/or **2** (1 mol%), neat, isolated yield.

**Copper(I) catalysts mediated hydroamination of terminal alkynes with substituted anilines:**

Catalysts **1** or **2** (1 mol %) and $AgBF_4$ (1 mol %) were placed together in an oven dried schlenk flask. The schlenk flask was then evacuated and refilled with nitrogen two to three times. Subsequently, 1 mL of acetonitrile was added to the mixture and was allowed to stir at room temperature for 5-10 minutes. After which, the corresponding arylamine (0.6 mmol) and terminal alkyne (0.50 mmol) were added successively. The resulting mixture was allowed to stir at 70 ºC for the appropriate time and the progression of the reactions were determined by thin layer chromatography.

**21. 2,6-dimethyl-*N*-(1-phenylethylidene)aniline (VIa)**




$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.04-8.07 (m, 2H), 7.47-7.50 (m, 3H), 7.07-7.09 (d, 2H), 6.92-6.94 (t, 1H), 2.09 (s, 3H), 2.05 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 165.2, 149.0, 139.1, 130.4, 128.4, 127.8, 127.1, 125.7, 122.7, 18.0, 17.5.

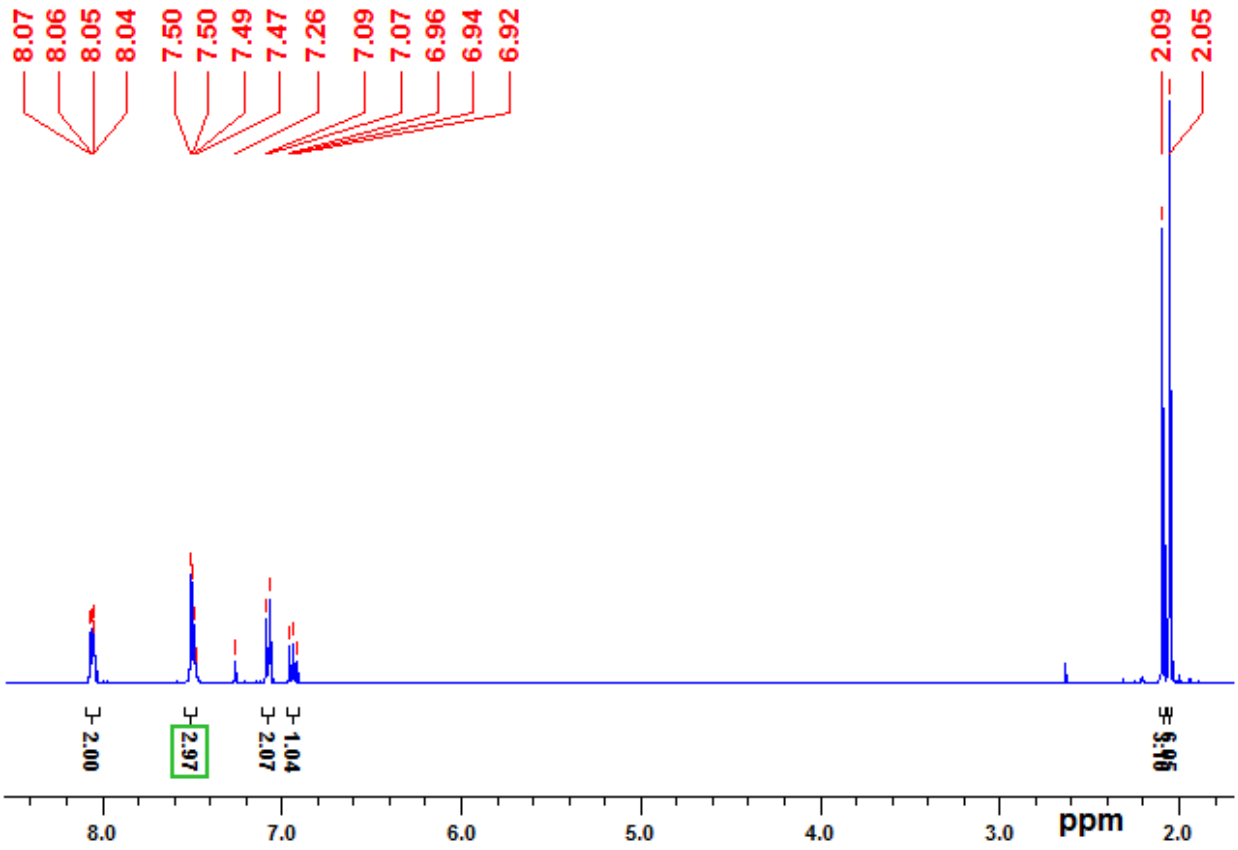



**Fig. S41**. $^{1}$H NMR spectrum of **VIa** in $CDCl_3$ at room temperature.

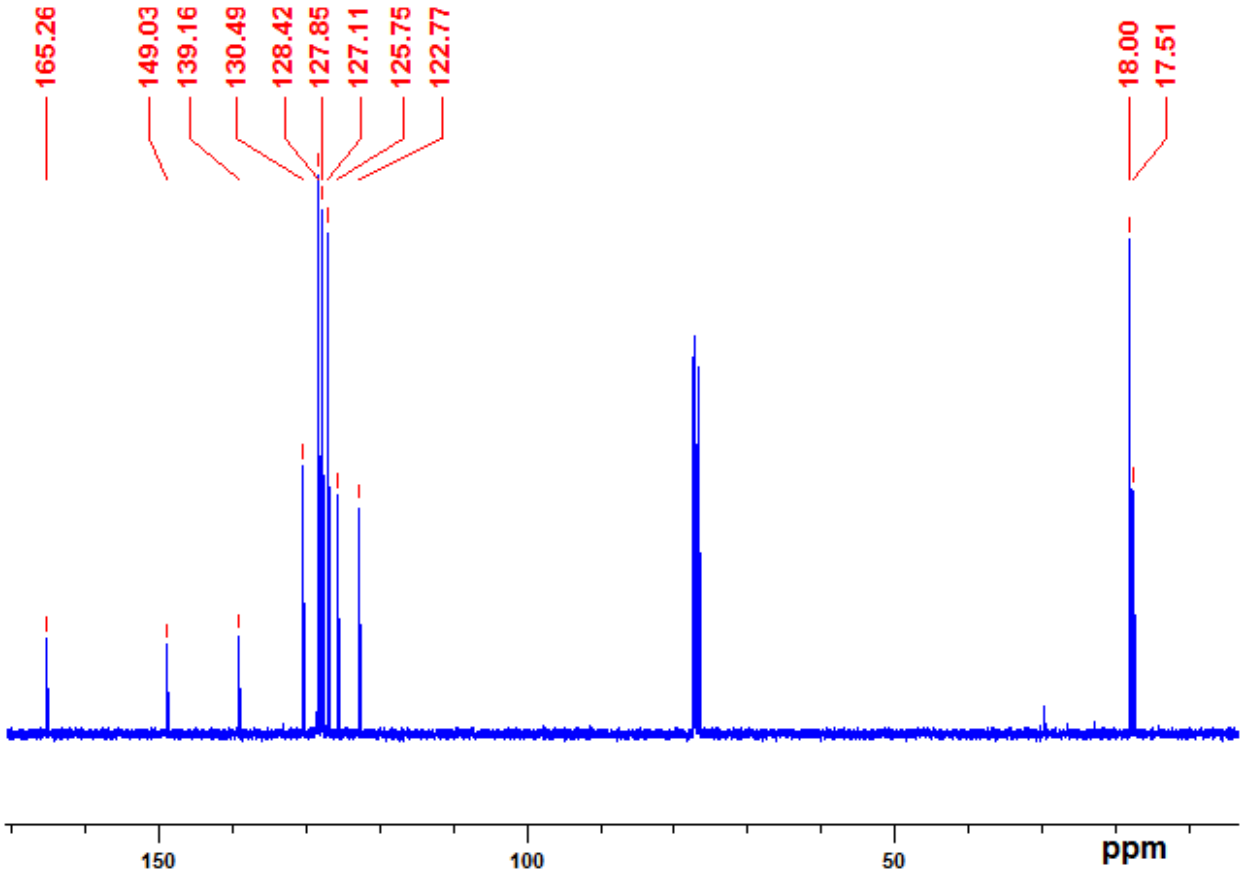
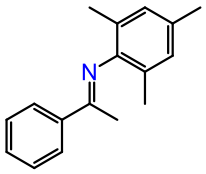



**Fig. S42**. $^{13}$C NMR spectrum of **VIa** in $CDCl_3$ at room temperature.

**22. 2,4,6-trimethyl-*N*-(1-phenylethylidene)aniline (VIb)**




$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.08-8.09 (d, 2H), 7.51-7.53 (d, 3H), 6.94 (s, 2H), 2.35 (s, 3H), 2.12 (s, 6H), 2.06 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 165.4, 146.5, 139.3, 133.1, 131.9, 130.4, 128.5, 128.4, 127.1, 125.6, 20.8, 17.9, 17.4.

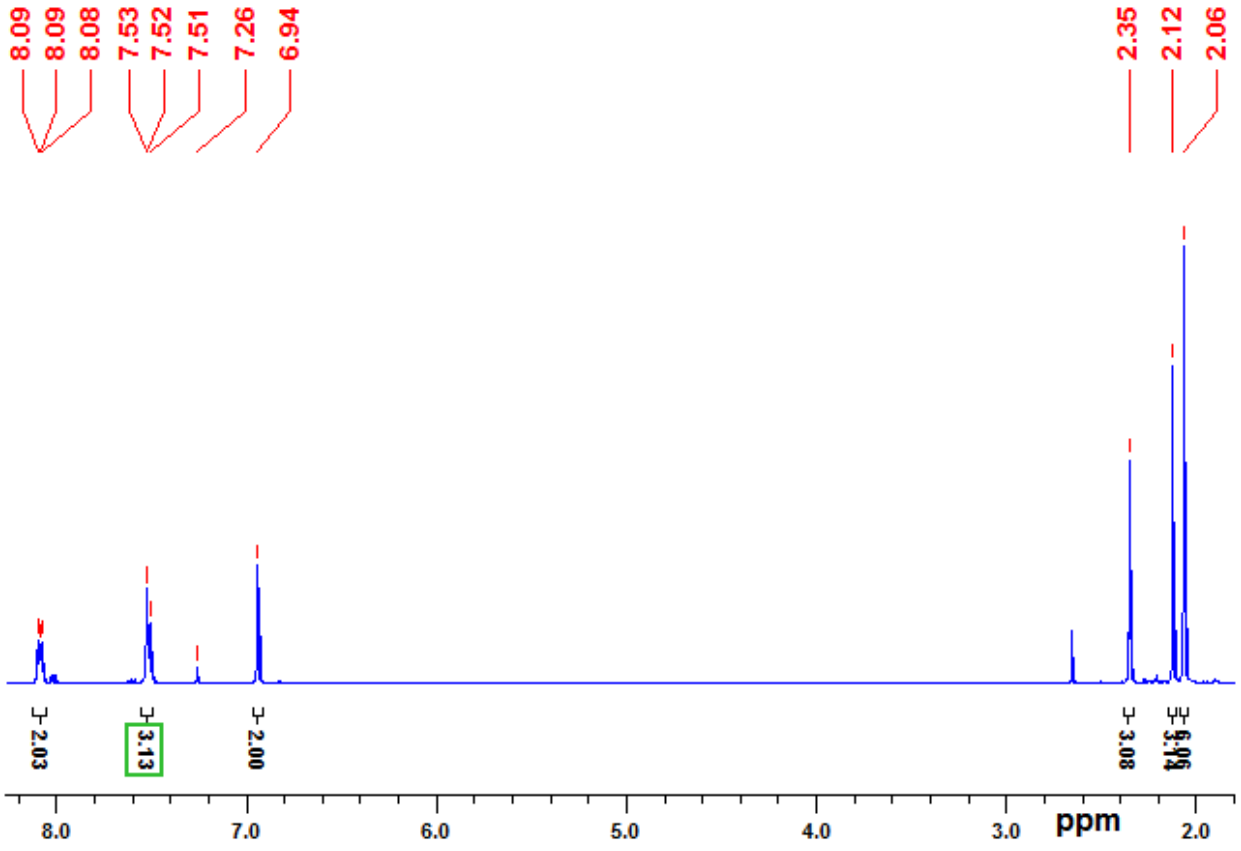



**Fig. S43**. $^{1}$H NMR spectrum of **VIb** in $CDCl_3$ at room temperature.

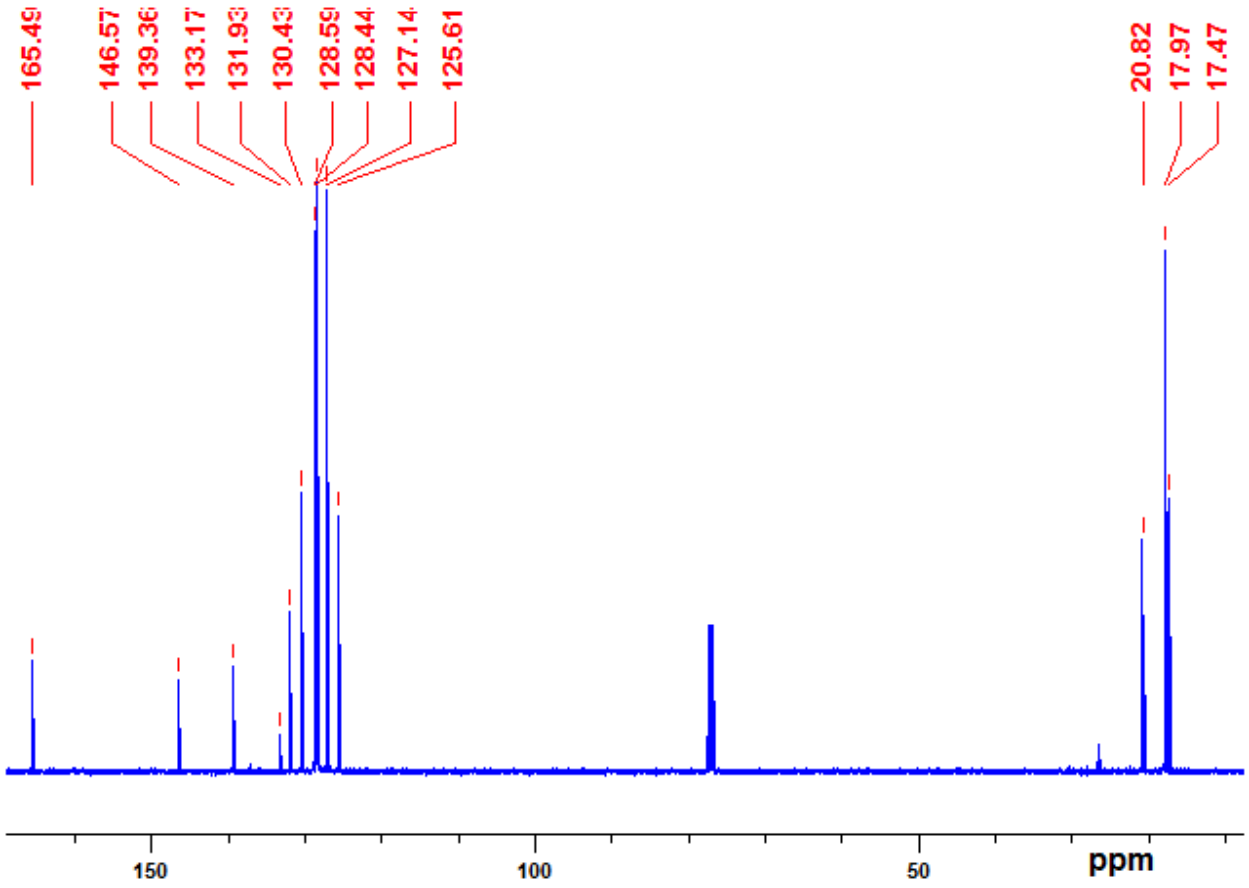
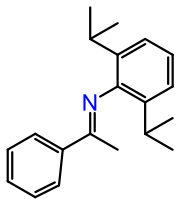



**Fig. S44**. $^{13}$C NMR spectrum of **VIb** in $CDCl_3$ at room temperature.

### 23. 2,6-diisopropyl-*N*-(1-phenylethylidene)aniline (VIc)

$^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.07-8.09 (d, 2H), 7.51-7.52 (t, 3H), 7.07-7.20 (m, 3H), 2.75-2.85 (sept, 2H), 2.14 (s, 3H), 2.00 (s, 3H), 1.17-1.20 (d, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 164.8, 146.7, 139.0, 136.0, 130.0, 128.3, 127.1, 123.2, 122.9, 28.1, 23.2, 22.9, 22.4. 18.0.



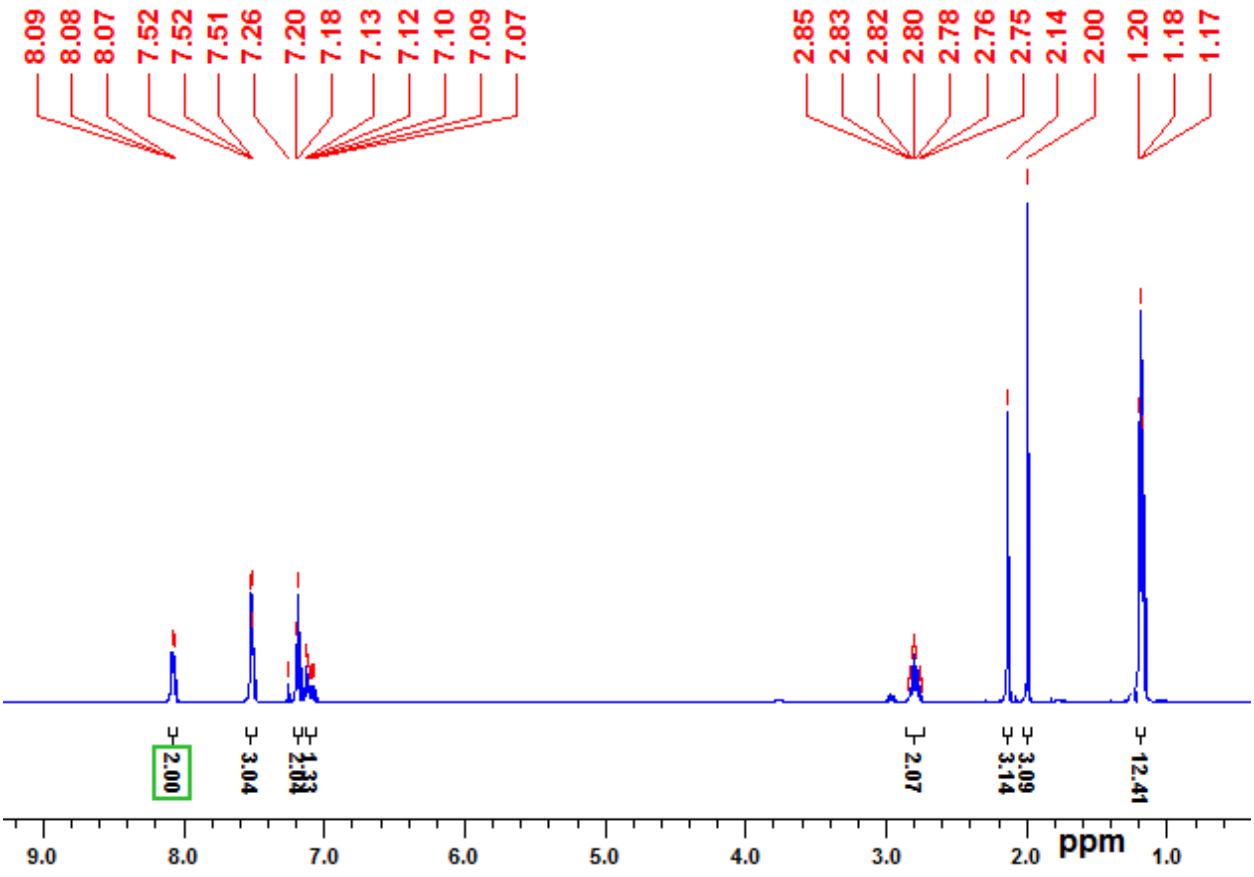



**Fig. S45**. $^{1}$H NMR spectrum of **VIc** in $CDCl_3$ at room temperature.

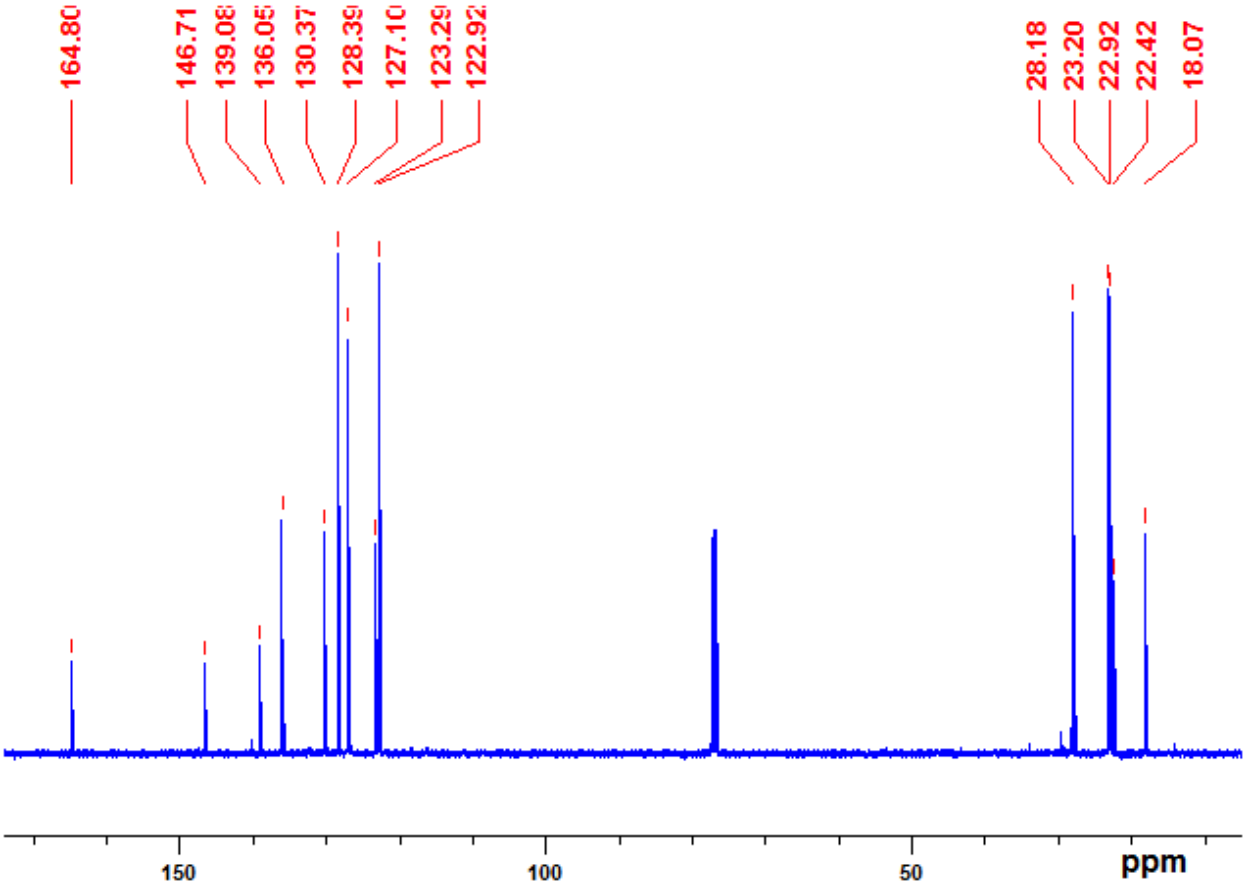
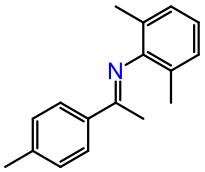



**Fig. S46**. $^{13}$C NMR spectrum of **VIc** in $CDCl_3$ at room temperature.

### 24. 2,6-dimethyl-*N*-(1-(*p*-tolyl)ethylidene)aniline (VIIa)

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.92-7.94 (d, 2H), 7.23-7.28 (d, 2H), 7.03-7.05 (d, 2H), 6.88-6.92 (t, 1H), 2.42 (s, 3H), 2.02-2.04 (d, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 165.0, 149.1, 140.7, 136.4, 129.1, 127.8, 127.1, 125.8, 122.6, 21.4, 18.0, 17.4.



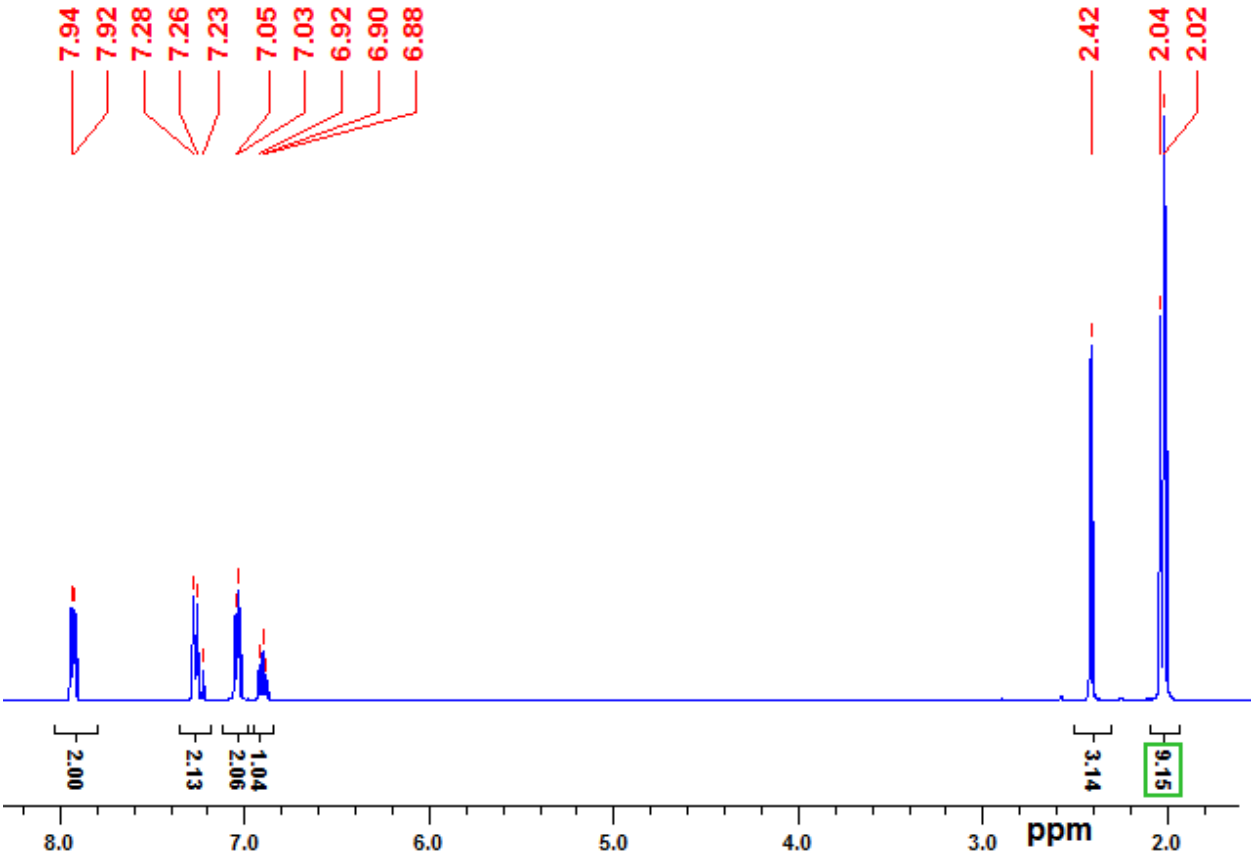



**Fig. S47**. $^{1}H$ NMR spectrum of **VIIa** in $CDCl_3$ at room temperature.

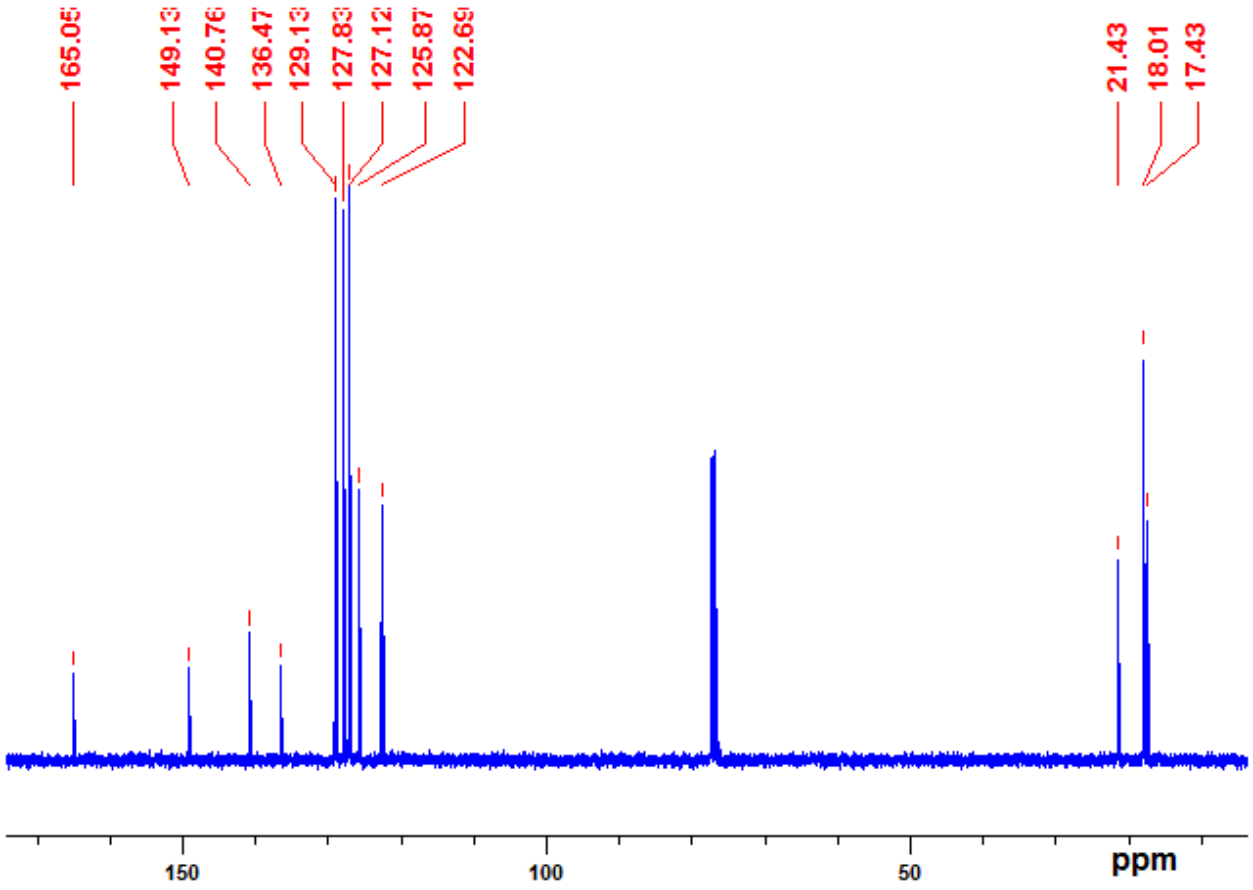
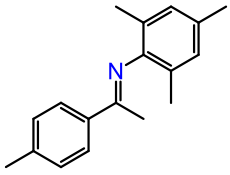



**Fig. S48**. $^{13}$C NMR spectrum of **VIIa** in $CDCl_3$ at room temperature.

### 25. 2,4,6-trimethyl-*N*-(1-(*p*-tolyl)ethylidene)aniline (VIIb)

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.91-7.93 (d, 2H), 7.23-7.27 (d, 2H), 6.86 (s, 2H), 2.41 (s, 3H), 2.28 (s, 3H), 2.03 (s, 3H), 1.98 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 165.2, 146.5, 140.6, 136.6, 131.8, 129.0, 128.5, 127.0, 125.7, 21.4, 20.7, 17.9, 17.3.



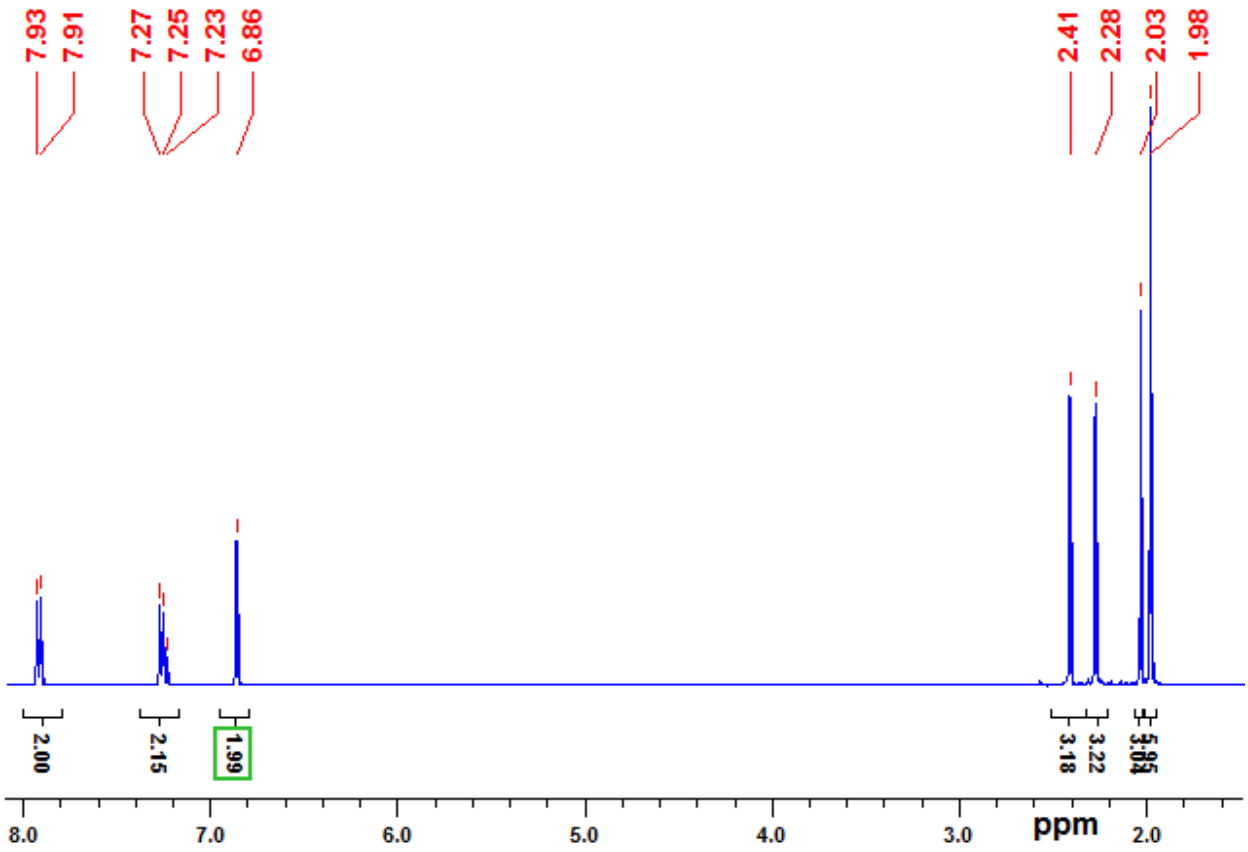



**Fig. S49**. $^{1}H$ NMR spectrum of **VIIb** in $CDCl_3$ at room temperature.

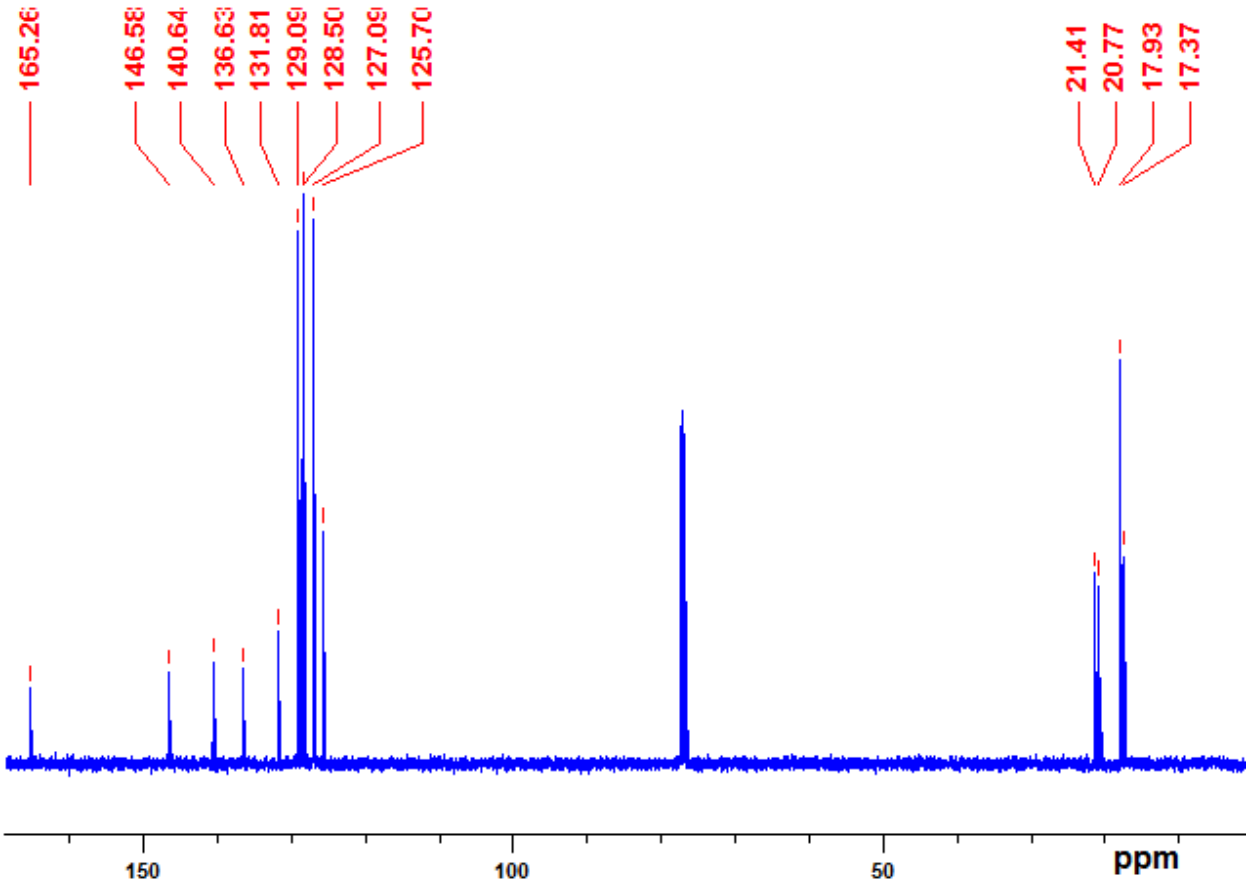
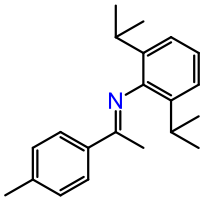



**Fig. S50**. $^{13}$C NMR spectrum of **VIIb** in $CDCl_3$ at room temperature.

**26. 2,6-diisopropyl-*N*-(1-(*p*-tolyl)ethylidene)aniline (VIIc)**

$^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.93-7.95 (d, 2H), 7.27-7.30 (d, 2H), 7.13-7.15 (m, 2H), 7.05-7.09 (m, 1H), 2.70-2.80 (sept, 2H), 2.43 (s, 3H), 2.08 (s, 3H), 1.11-1.15 (d, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 164.5, 146.8, 140.7, 136.4, 136.2, 129.1, 127.1, 123.2, 122.9, 28.2, 23.2, 22.9, 21.4. 18.0.



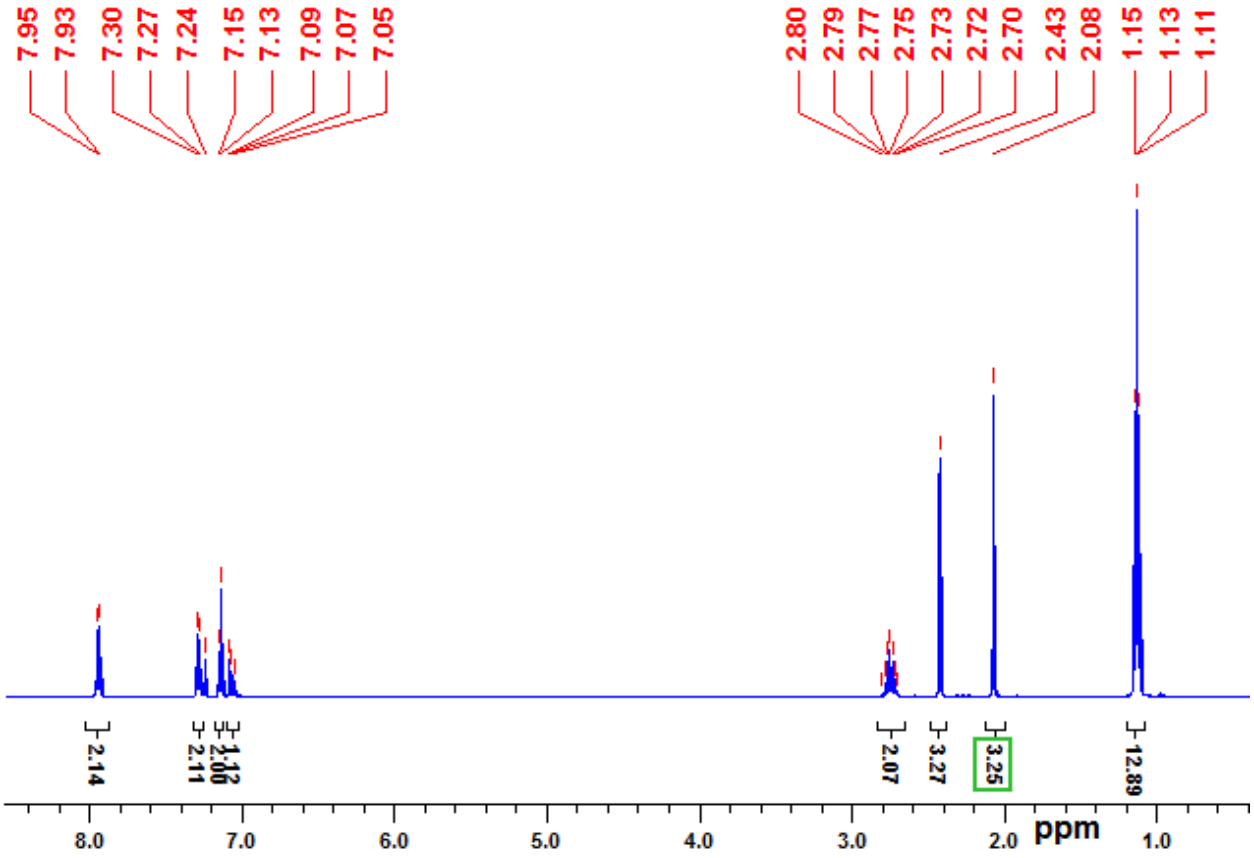



**Fig. S51**. $^{13}C$ NMR spectrum of **VIIc** in $CDCl_3$ at room temperature.

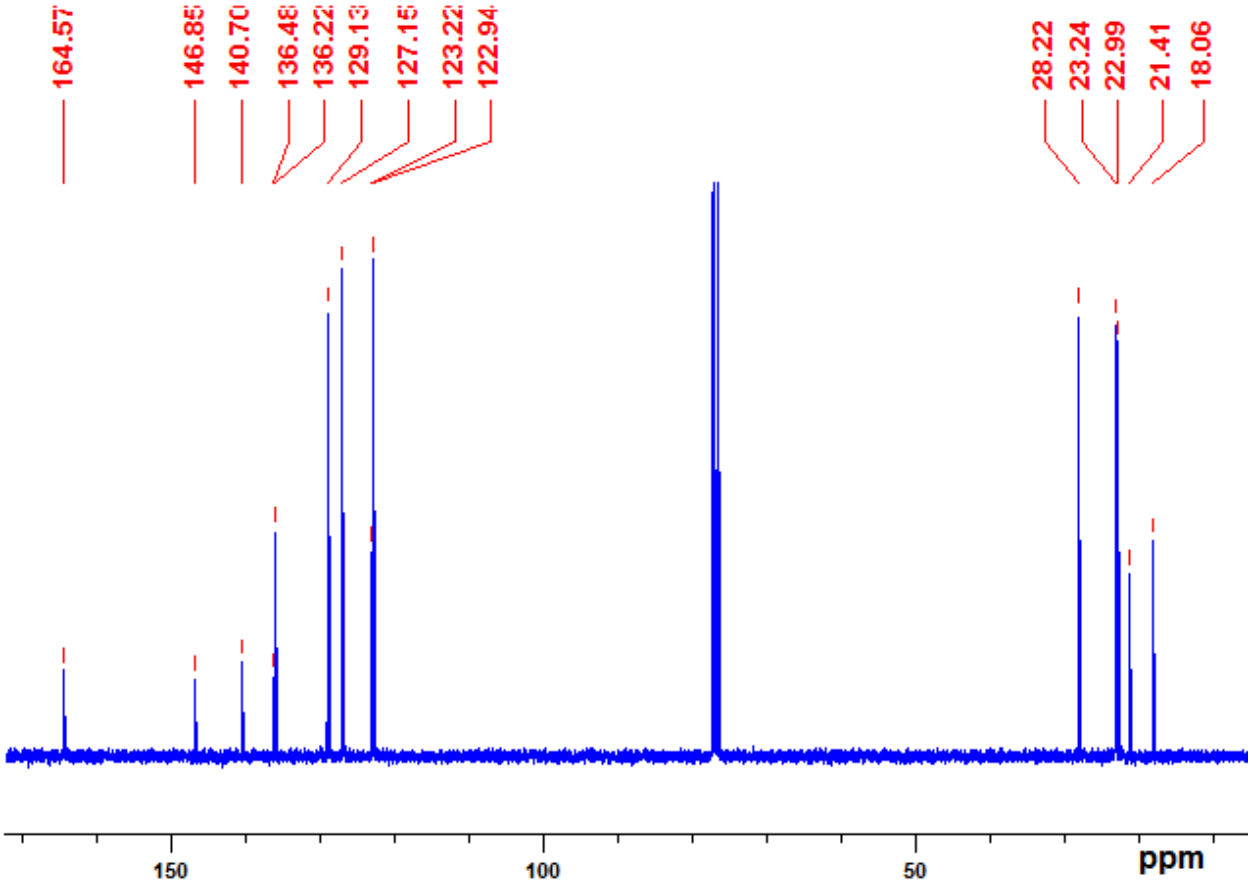
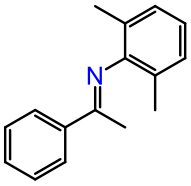
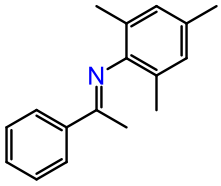



**Fig. S52**. $^{13}C$ NMR spectrum of **VIIc** in $CDCl_3$ at room temperature.

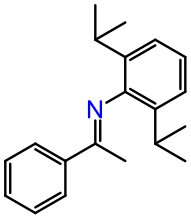
**Chart S2.** Isolated products of hydroamination reaction catalyzed by copper(I) catalysts **1** and **2**.[a]



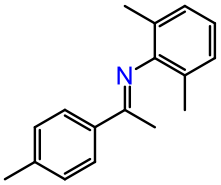
**VIa**, 98%, 96%



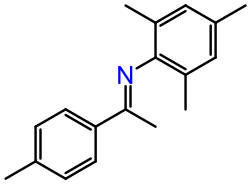
**VIb**, 95%, 97%



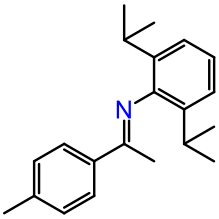
**VIc**, 99%, 95%



**VIIc**, 94%, 96%



**VIIc**, 98%, 97%



**VIIc**, 92%, 96%

[a]Reaction conditions: alkyne (0.5 mmol), substituted aniline (0.6 mmol) and solvent (2 mL).

**Note 1:**

**Trans Metallation reaction with Molecule 1.**

Molecule **1** (0.01g, 1 equiv) and an excess (dms)AuCl (0.07g, 16 equiv) were mixed together and evacuated for 10 minutes, after which 1 mL of acetonitrile was added under argon flow and allowed to stir at room temperature for 12h. $^{1}$H NMR (DMSO-$d_6$, 400 MHz): 1.39 (s, 2((C$H_3$)$_2$CH), 12H), 4.98 (m, 2(CH$_3$)$_2$C*H*, 2H), 7.65-7.73 (m, imidazole, 4H), 8.27 (m, pyridine, 3H) ppm.

**Observations:**

The compound **1** and (dms)AuCl were dissolved completely in acetonitrile and was colorless in the beginning, after 10 minutes the reaction mixture turns violet in color and then after 30 minutes the reaction mixture contains blue precipitate in a colorless solution. After which the reaction mixture was dried in *vacuo* and subjected to NMR measurements. The $^{1}$H NMR measurement supports the presence of ligand (**Bptp**) moiety in the crude product of trans-metallation reaction.

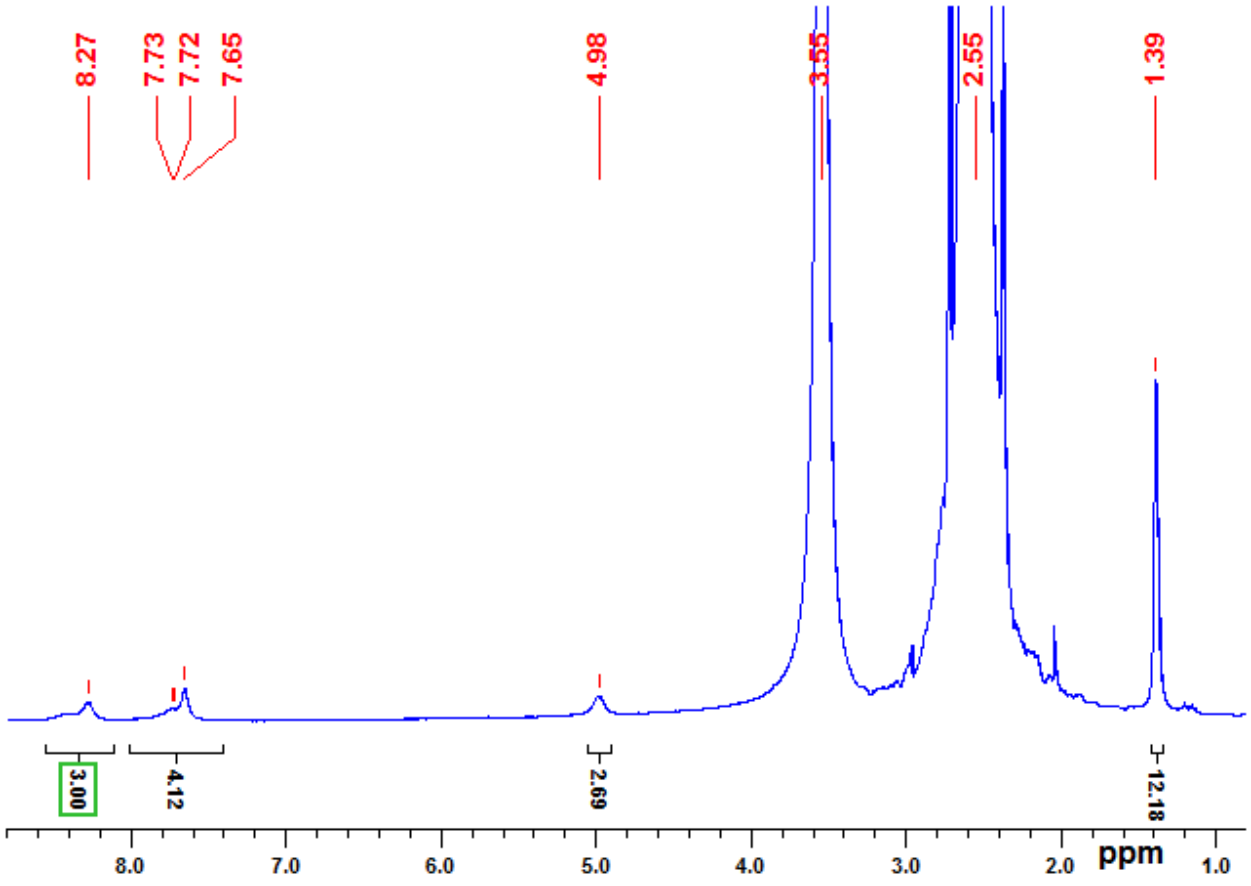



**Fig. S53.** $^{1}$H NMR spectrum of trans-metalation reaction mixture in DMSO-d$_6$ at room temperature.

**Note 2:**

**Host-Guest interactions on Molecule 1 with Perylene.**

**1@Perylene:** Molecule **1** (0.01g, 1 equiv) and an excess perylene (0.03g, 8 equiv) were mixed together and evacuated for 10 minutes, after which 1 mL of acetonitrile was added under argon flow and was allowed to stir at reflux for 4h. $^{1}$H NMR (DMSO-$d_6$, 400 MHz): 1.39-1.41 (d, 2((C$H_3$)$_2$CH), 12H), 4.93-5.02 (m, 2(CH$_3$)$_2$C$H$, 2H), 7.53-7.57 (t, perylene, 2H), 7.73 (d, imidazole, 2H), 7.79-7.81 (d, perylene, 2H), 7.86 (d, imidazole, 2H), 8.18-8.20 (d, pyridine, 2H), 8.35-8.42 (m, perylene, 2H and pyridine 1H) ppm.

**Observations:**

The compound **1** and perylene were not dissolved completely in acetonitrile and has a yellow turbid solution in the beginning and was allowed to stir at 85 $^{o}$C, the reaction mixture forms a yellow crystalline solid in a clear colorless solution after 4h, and then the reaction mixture was dried in vacuo and subjected to spectroscopic measurements, which evidently displays the existence of 1@perylene molecule.

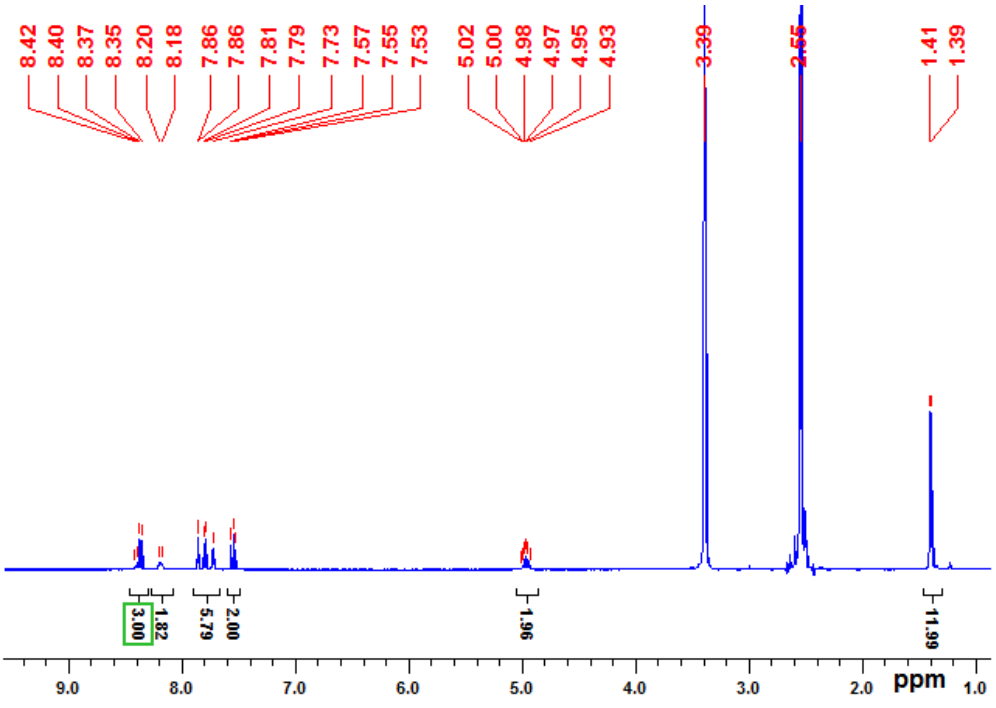



**Fig. S54**. $^{1}$H NMR spectrum of **1**@perylene in DMSO-d$_6$ at RT.

Moreover, (Figure S56) the reaction mixture of **1** and perylene represents the mixed absorption bands in solution UV-vis spectra up to 2h, while almost complete reaction noticed after 3h is due to the association of pyrene with molecule 1, and the reaction mixtures after 3h and 4h represent the identical absorption spectra suggesting no further incorporation/association and as noticed for pyrene reaction, the reaction mixture of perylene is also legitimately altered from the molecule 1.

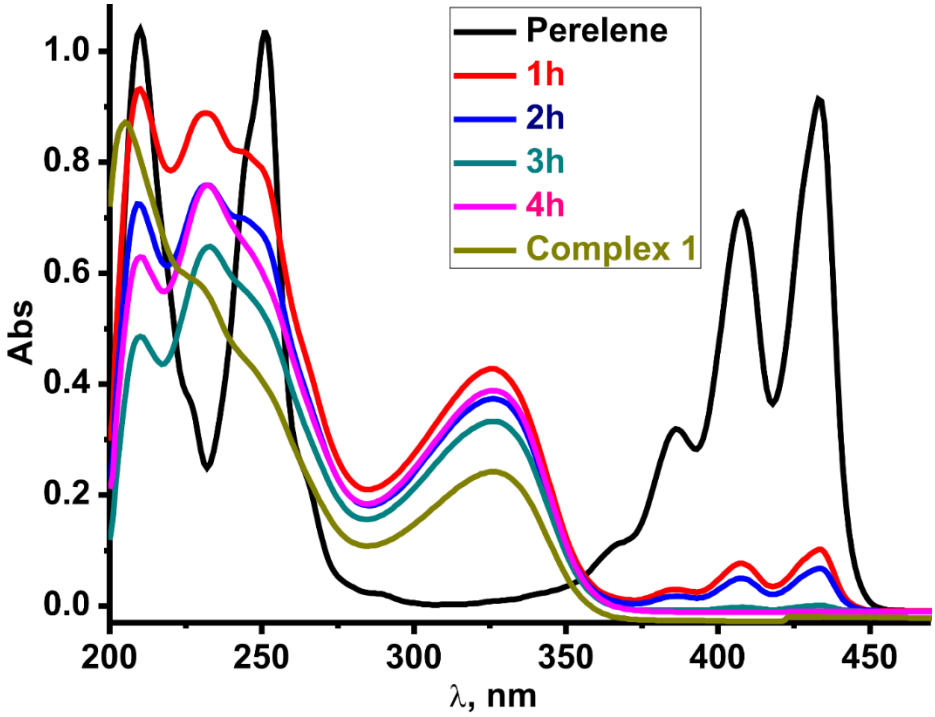



**Fig. S55**. Solution state UV-visible spectral analysis of **1** and the reaction mixture of **1**@perylene in acetonitrile at elevated temperature with 1h interval, measured at 298K with 2.8 x $10^{-5}$ M acetonitrile solution.

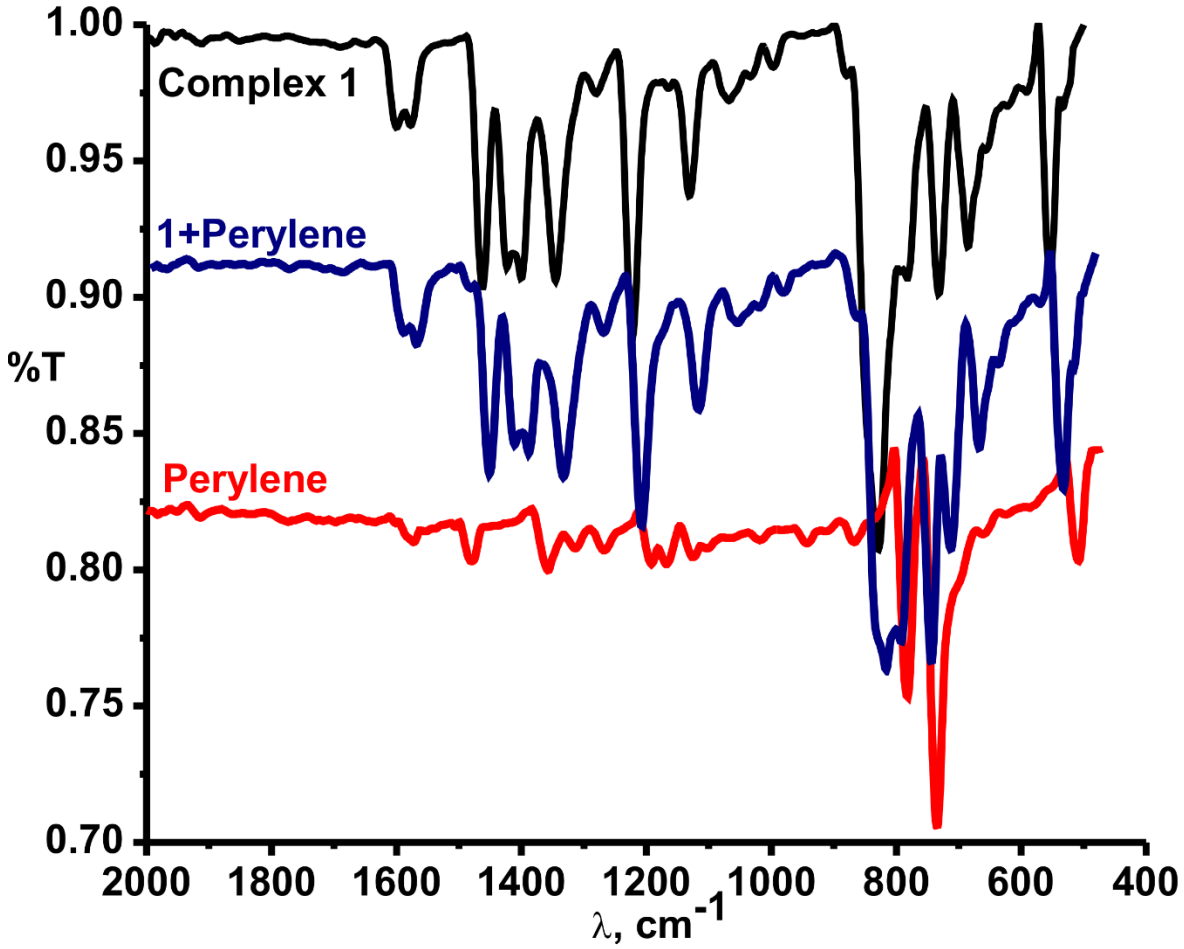
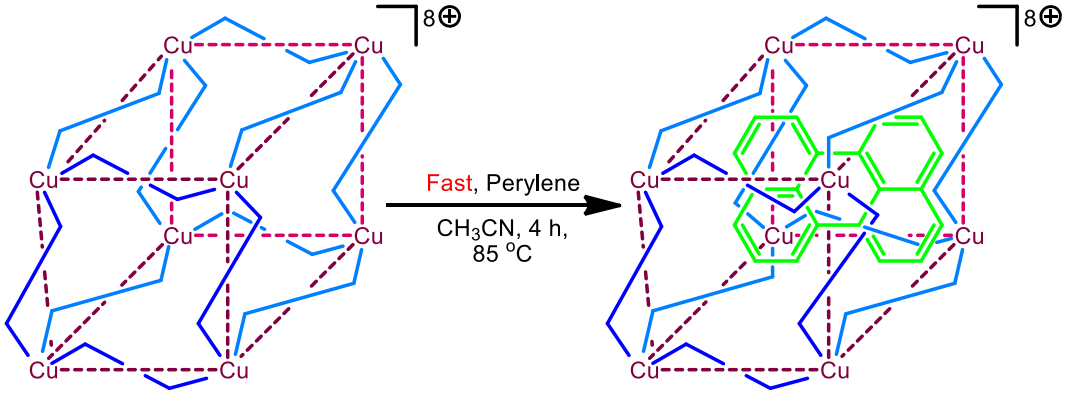



**Fig. S56**. Neat FT-IR spectrum of **1** (Black), a reaction mixture of **1** and perylene (Blue) and perylene (Red) after 4h in acetonitrile.




**Scheme S1**. Synthesis of 1@Perylene molecule by host-guest interactions.

**Host-Guest interactions on Molecule 1 with Pyrene.**

**1@Pyrene:** Molecule **1** (0.01g, 1 equiv) and an excess pyrene (0.03g, 8 equiv) were mixed together and evacuated for 10 minutes, after which 1 mL of acetonitrile was added under argon flow and was allowed to stir at reflux for 4h. $^{1}$H NMR (DMSO-$d_6$, 400 MHz): 1.39-1.41 (d, 2((C$H_3$)$_2$CH), 12H), 4.95-4.98 (m, 2(CH$_3$)$_2$C$H$, 2H), 7.74 (d, imidazole, 2H), 7.87 (d, imidazole, 2H), 8.07-8.30 (m, pyrene, 10H), 8.32-8.40 (m, pyrene, 3H) ppm.

**Observations:**

The compound **1** and pyrene were not dissolved completely in acetonitrile and was a little yellow turbid solution in the beginning, after 10 minutes at 85 $^{o}$C, the reaction mixture turns as clear yellow solution after 4h, and the reaction mixture was dried in vacuo and subjected to spectroscopic measurements, which clearly shows the existence of 1@pyrene molecule.

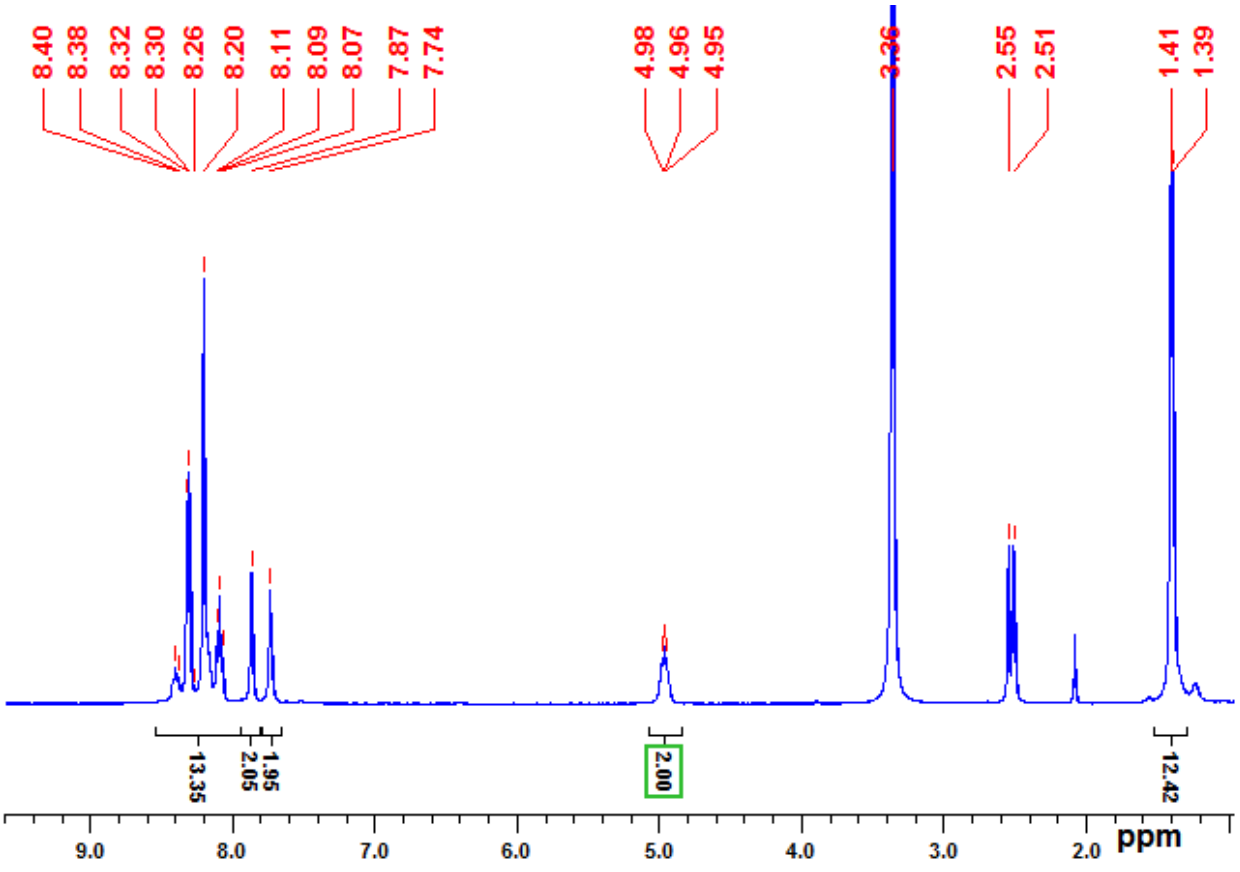



**Fig. S57**. $^{1}$H NMR spectrum of pyrene and molecule **1** reaction mixture (1@pyrene) in DMSO-$d_6$ at RT.

As presented in figure S59, the reaction mixture represents only pyrene absorption spectra in solution UV-vis spectroscopy up to 2h, while broadening of the absorption bands noticed after 3h is due to the association of pyrene with molecule **1**, and the final (4h) absorption spectra of the reaction mixture is fairly altered from the molecule **1** alone, suggesting the complete incorporation/association of pyrene into the molecule **1**.

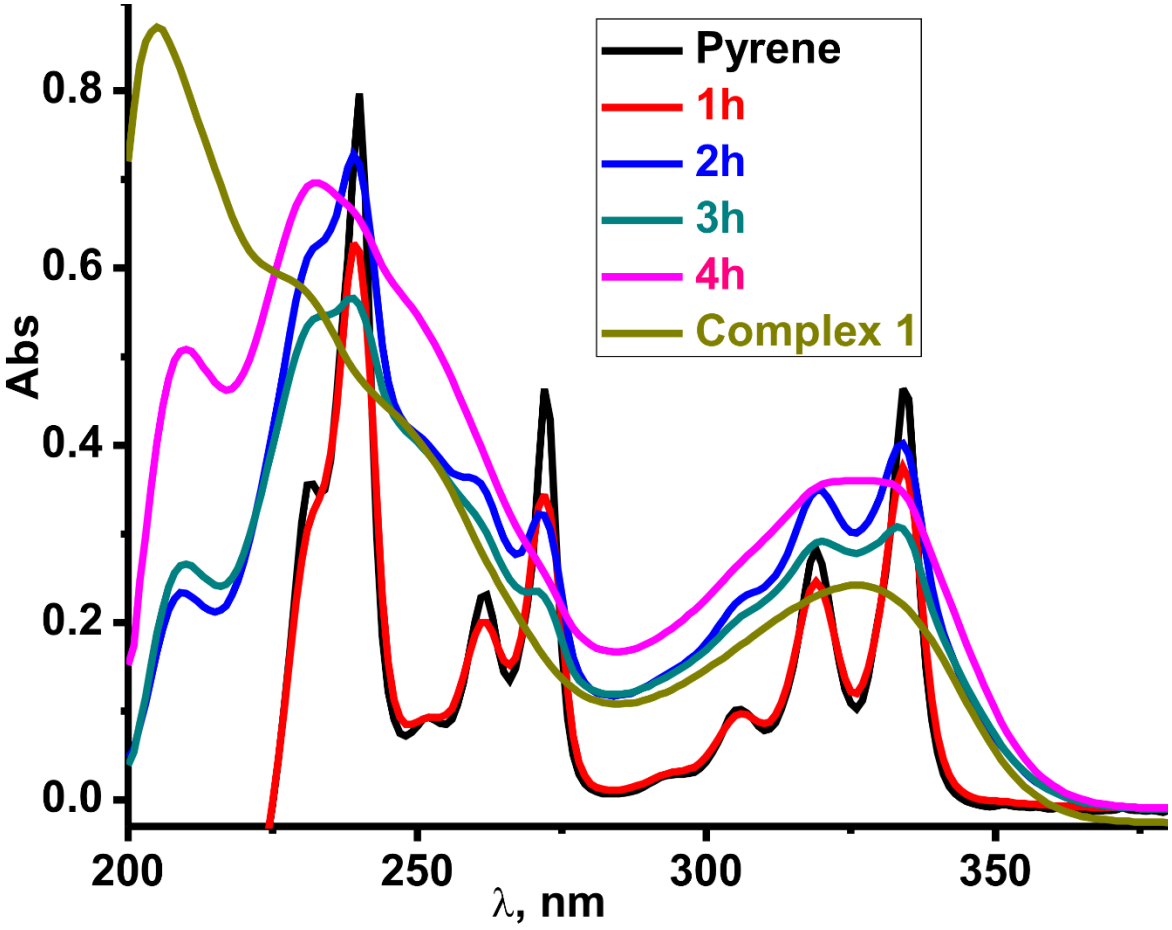



**Fig. S58**. Solution state UV-visible spectral analysis of **1** and the reaction mixture of **1** and pyrene in acetonitrile at elevated temperature with 1h interval, measured at 298K with 2.8 x $10^{-5}$ M acetonitrile solution.

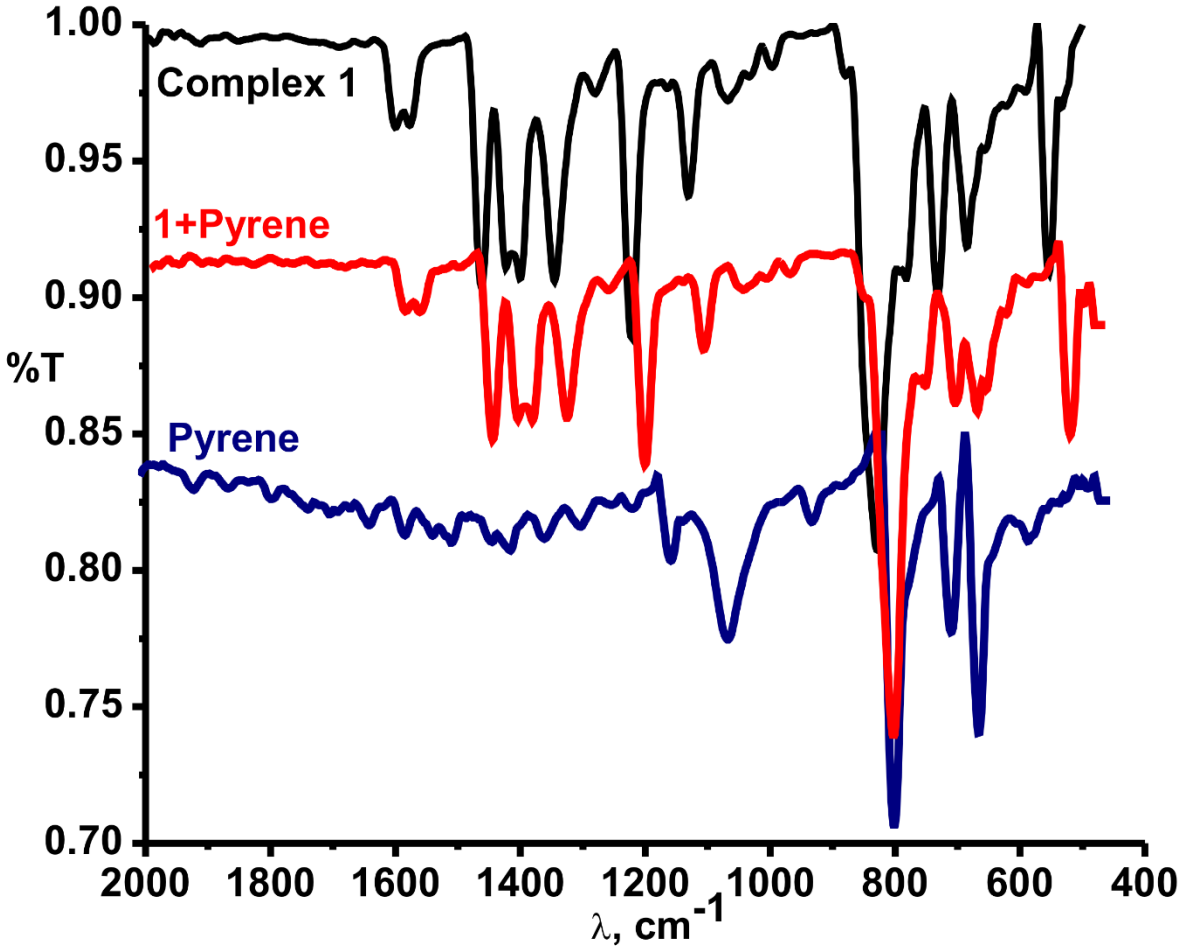
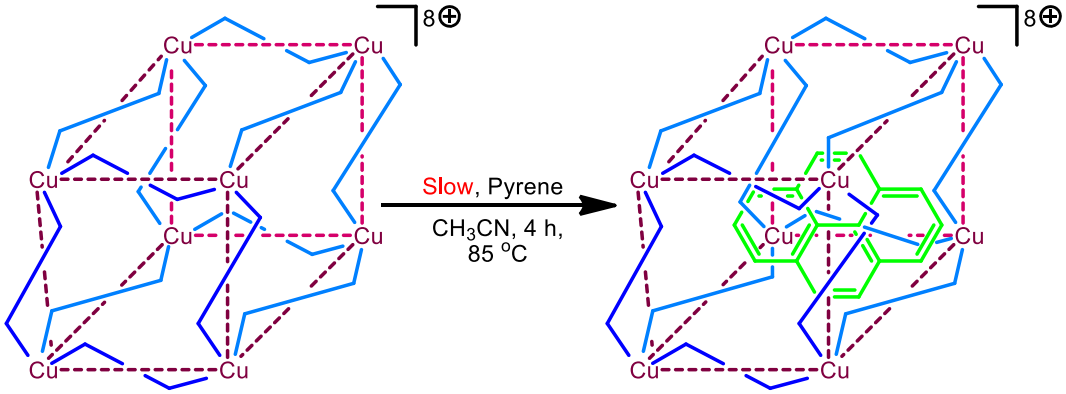



**Fig. S59**. Neat FT-IR spectrum of **1** (Black), a reaction mixture of **1** and pyrene (Red) and pyrene (Blue) after 4h in acetonitrile.




**Scheme S2**. Synthesis of 1@Pyrene molecule by host-guest interactions.

# Host-Guest interactions on Molecule 1 with $C_{60}$ molecule.

Molecule **1** (0.014g, 1 equiv) and $C_{60}$ (0.02g, 1 equiv) were mixed together under argon flow in an NMR tube and was dissolved in DMF-$d_7$ (0.5 mL), then it was subjected to NMR measurement at time 0 minutes. After which it was allowed to stay at 85 $^oC$ and then $^1H$ NMR was measured every day to investigate the incorporation/association of $C_{60}$ into the cavity of molecule **1**. $^1H$ NMR (DMF-$d_7$, 400 MHz): 1.47-1.49 (d, 2((C$H_3$)$_2$CH), 12H), 5.01-5.08 (m, 2(C$H_3$)$_2$C$H$, 2H), 7.78-7.79 (d, imidazole, 2H), 7.95 (d, imidazole, 2H), 8.27-8.29 (m, pyridine, 2H), 8.46-8.50 (m, pyridine, 1H) ppm.

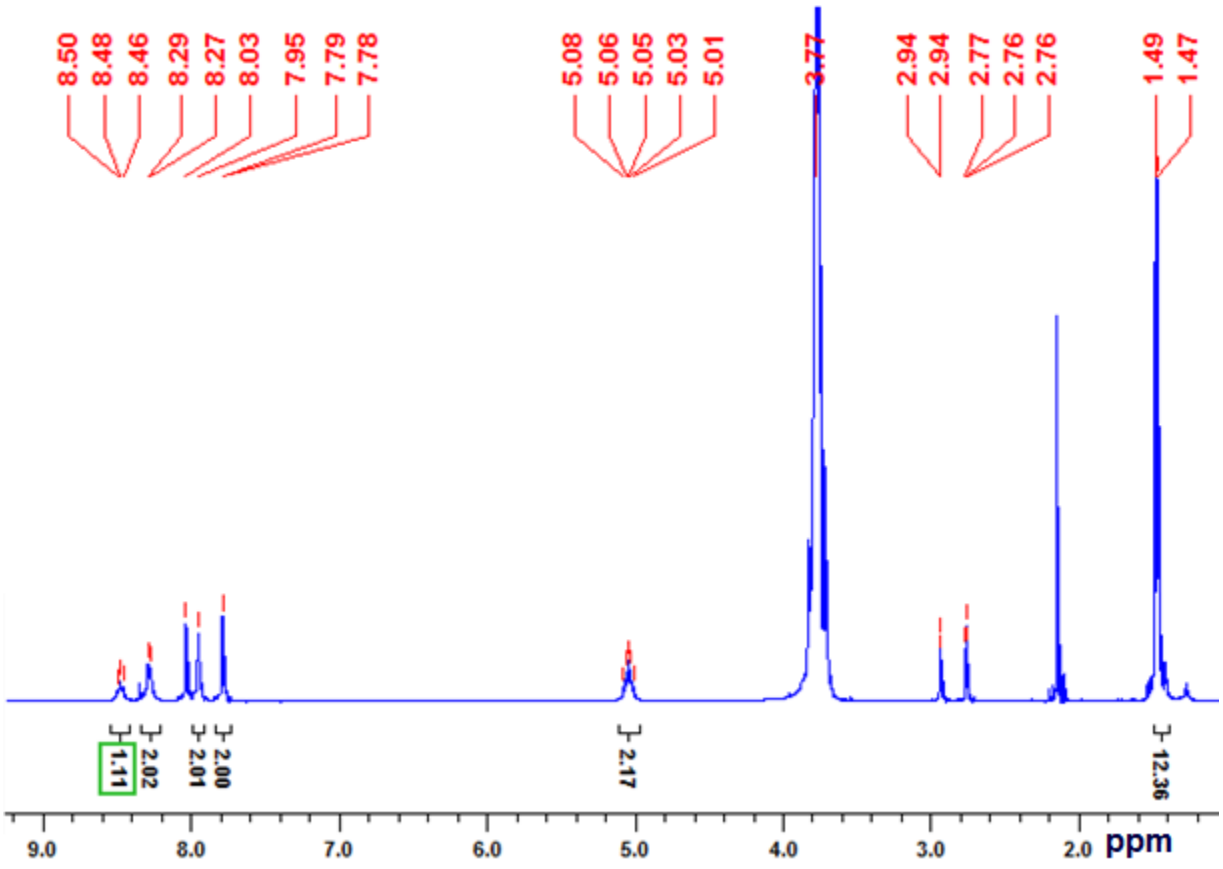



**Fig. S60**. $^1H$ NMR spectrum of comple **1** with $C_{60}$ at time 0 minutes in DMF-$d_7$ at RT.

**Observations:**

It was observed that the addition of $C_{60}$ to the molecule **1** led to slight deviation in the chemical shift of all the protons in **1**. However, the reaction at 85 $^oC$ for prolonged time does not produce any further alteration in chemical shift of protons in **1**. Which suggest the non existance of host-guest interactions between $C_{60}$ and molecule **1**.

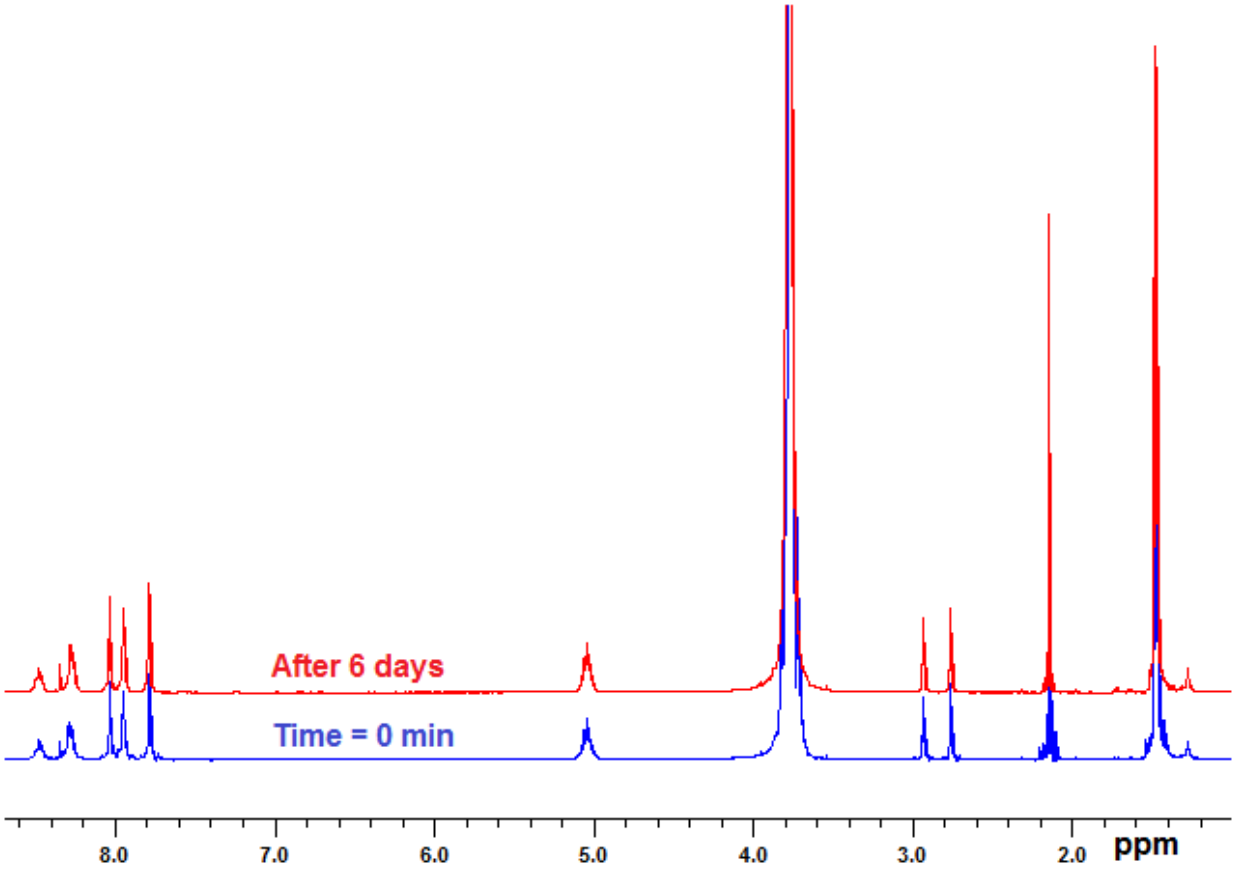
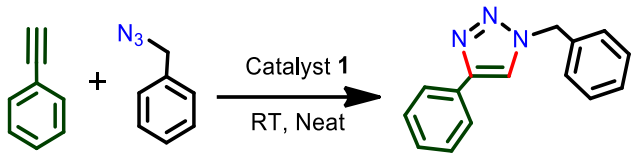



**Fig. S61**. $^{1}$H NMR comparison of molecule **1**@$C_{60}$ host-guest interactions in DMF-$d_7$ at RT.

Therefore, the host-guest interactions on molecule **1** with both pyrene and perylene signifying the prominence of the size of the guest. Although the perylene is bigger in size than pyrene, the pore size in molecule **1** accepts perylene more rapidly than pyrene when performed the experiment individually with molecule **1**. Besides, the $C_{60}$ incorporation into the cavity was not promising.

**Note 3:**

In order to investigate the changes in catalysts during the catalysis, we have subjected the crude sample for powder XRD measurements. Since the reaction is very fast, the crude sample was collected after 15 minutes and characterized by FT-IR, $^{1}$H NMR and PXRD techniques. As observed, the catalyst undergoes a minor structural/face changes after the catalytic cycle. However, the complete decomposition of catalyst was not observed. Attempt to isolate the single crystal X-ray structure of catalyst was no successful yet.




**Scheme 3**. Click reaction used in this study.

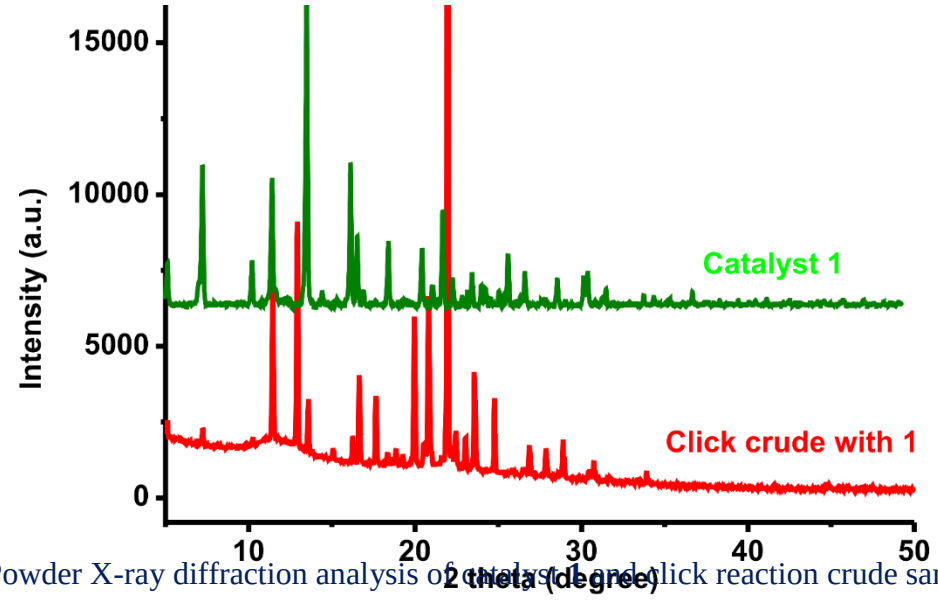



**Fig. S62**. Powder X-ray diffraction analysis of catalyst **1** and click reaction crude sample with **1**.

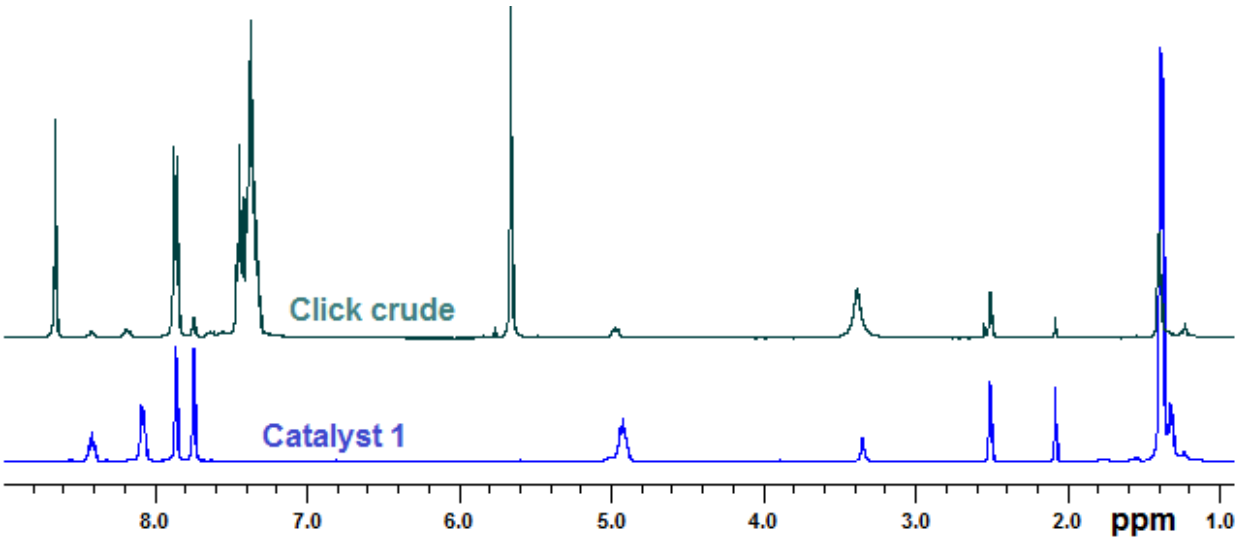


**Fig. S63**. $^{1}$H NMR comparison of catalyst **1** and click reaction crude sample with **1**.

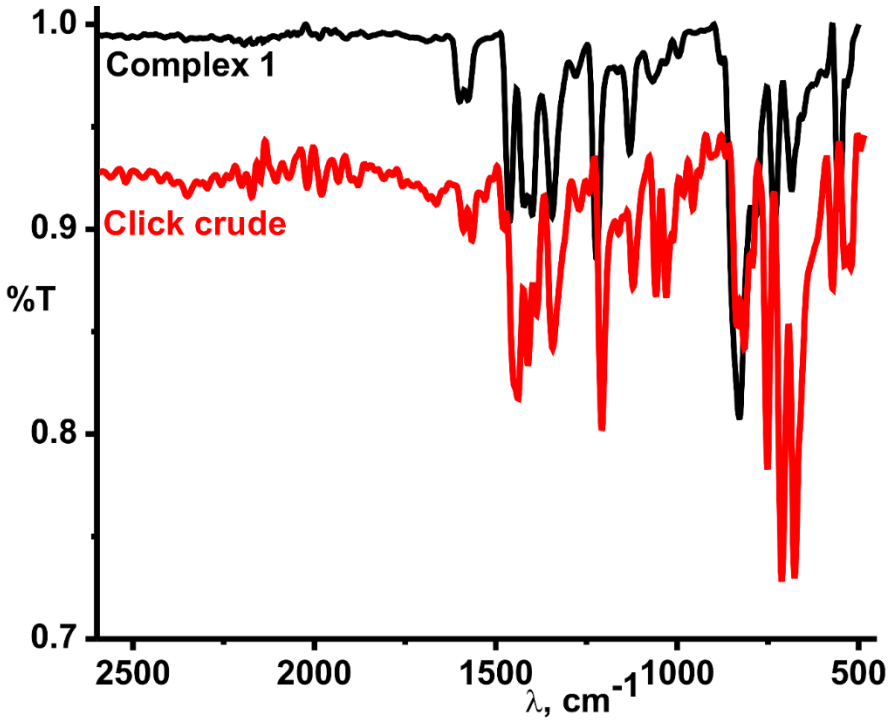
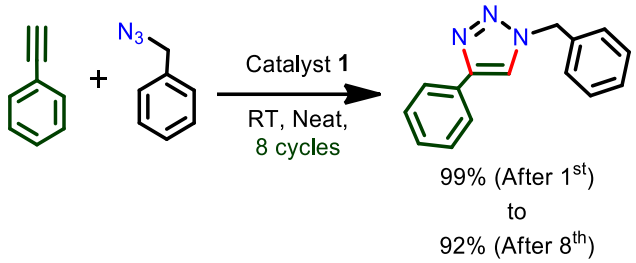



**Fig. S64**. Neat FT-IR comparison of catalyst **1** and click reaction crude sample with **1**.

the catalyst can be reusable for 8 times without any considerable decrease in the product formation.




**Scheme 4**. Catalyst **1** mediated click reaction.

For example, one of the catalysts (**1**) was studied for the prolonged existence and efficiency in click catalysis up to eight successive cycles without any significant loss of reactivity using 1 mol% catalyst **1** with benzyl azide (0.1 g, 0.75 mmol) and phenyl acetylene (0.092 g, 0.90 mmol) in neat conditions at room temperature. The catalyst **1** was recovered by *n*-hexane and ethyl acetate wash. Subsequently, the fresh batch of substrates such as benzyl azide (0.1 g, 0.75 mmol) and phenyl acetylene (0.092 g, 0.90 mmol) were added for the next cycle. This process was continued for eight repeated catalytic cycles and found to be an efficient enough. Besides it was noticed that the quantitative yield was isolated from first 3 catalytic cycles. After third catalytic cycle the reaction time (20 minutes) was increased to get appreciable yield (92% in 8$^{th}$ cycle).

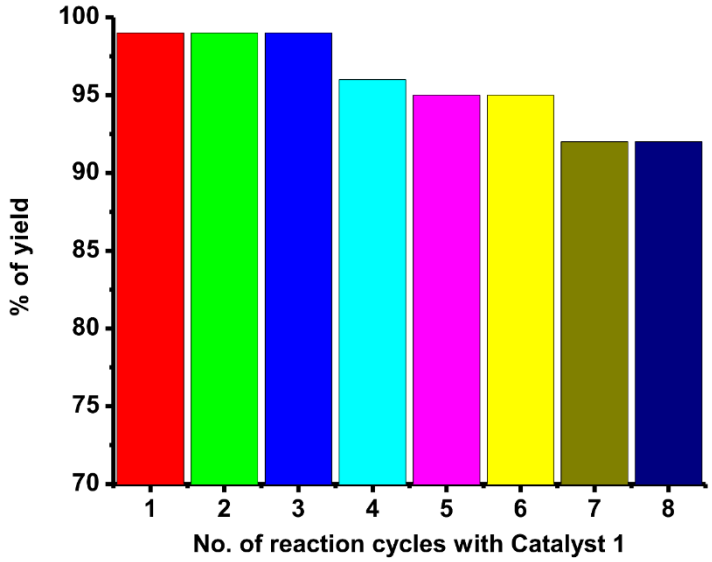



**Fig. S64**. % of isolated yield in 1-8 reaction cycles using catalyst **1**.

To investigate the aggregates after the catalysis, we have subjected the reused catalyst (for 8 times) to powder x-ray diffraction techniques, $^{1}$H NMR spectroscopy. As observed, the molecule remains intact than mononuclear subunits during/after the catalysis.

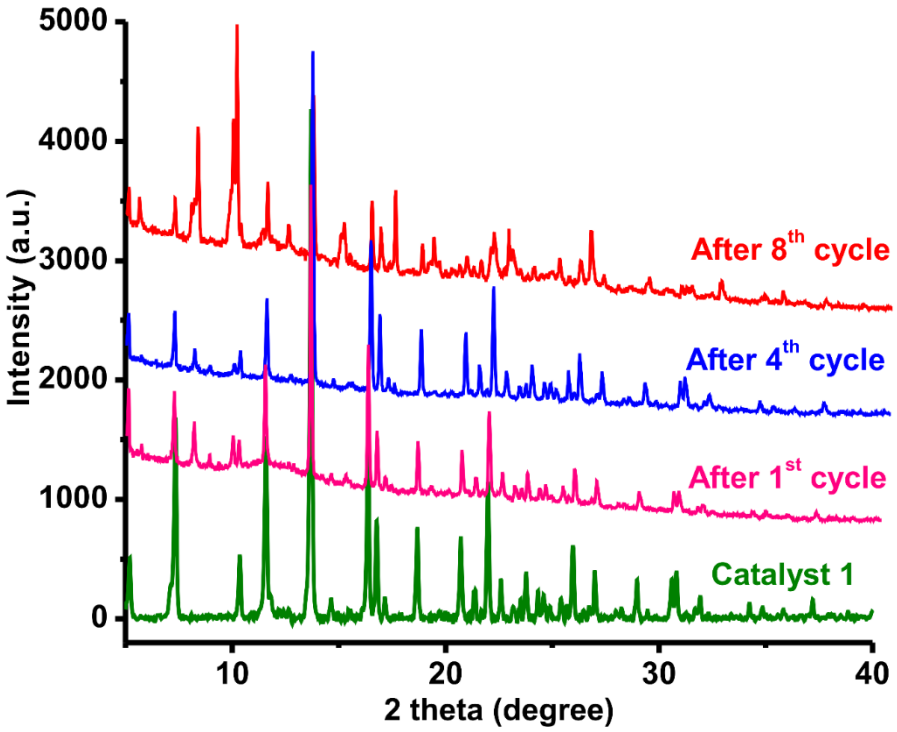



**Fig. S65**. Powder XRD patterns of reused catalyst **1** for 8 reaction cycles.

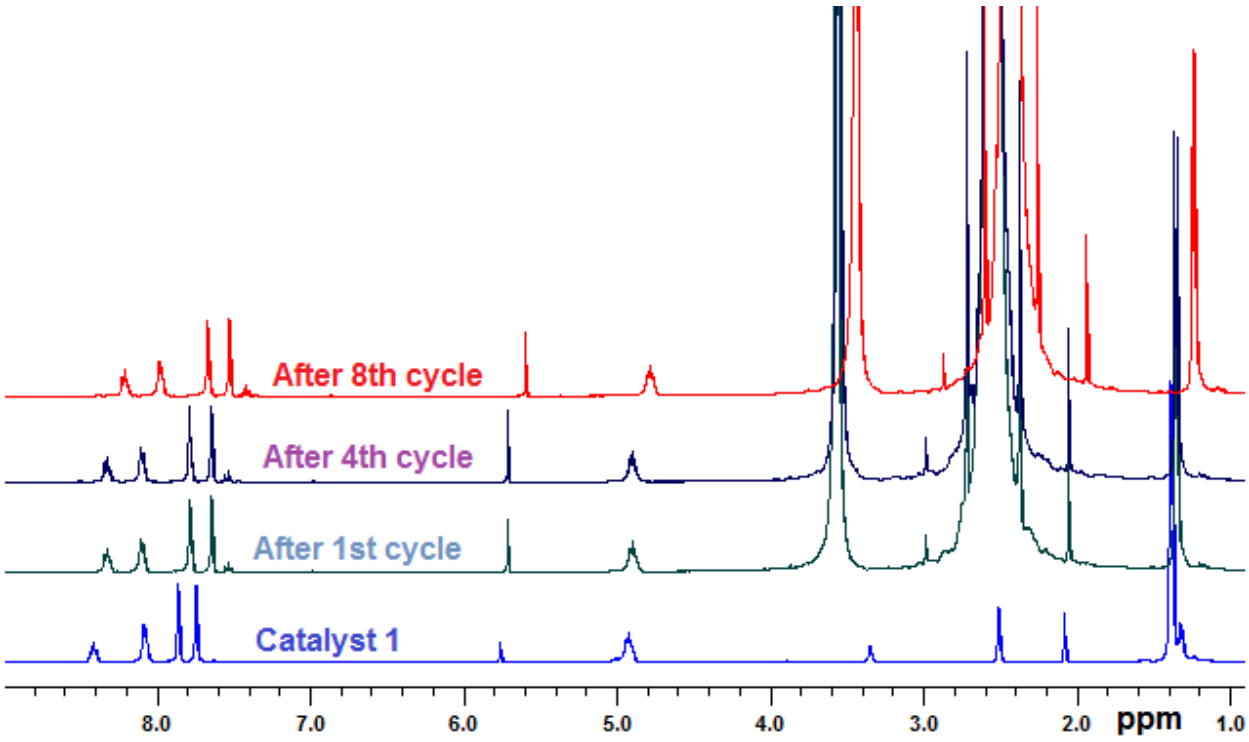



**Fig. S66**. $^{1}$H NMR spectra of catalyst **1** during the prolonged existence studies.