Supporting Information

Visible light assisted photocatalytic [3+2] azide-alkyne "Click" reaction for the synthesis of 1,4 substituted 1, 2, 3, triazoles using a novel bimetallic Ru-Mn complex

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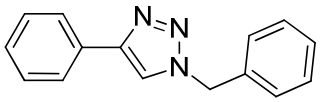
1. Synthesis of substituted azides [1]

Some of substituted azides was synthesized by reaction of Alkyl halide (10 mmol) and NaN_3 (11 mmol) in DMF by irradiating the samples in microwave at 100 ^{o}C for 10-60 min. The progress of reaction was monitored by TLC. After the completion of reaction, diethyl ether was added to reaction mixture and washed with water, Brine and dried over Na_2SO_4. The solvent was removed at room temperature and atmospheric pressure (Note: small azides are explosive and sensitive to vacuum). The confirmation of synthesized azide was done with IR and ^{1}H NMR Fig S10. Azides gave strong peak due to –N=N=N stretch around 2080-2100 cm^{-1} in IR spectra Fig S9.

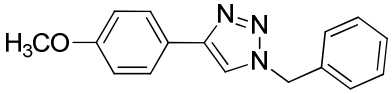
2. Synthesis of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole



In a round bottom flask having 10 mL ethanol, Phenyl acetyne(1mmol), Benzyl azide(1.5 mmol), Cu(II)sulphate (0.5 mmol), triethyl amine (0.5 mL) and catalyst (5 mol%) was added. The RB was sealed with a septum and irradiated with stirring in visible light by using a 20 Watt white

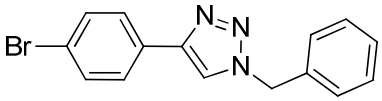
cold LED (Model - HP-FL-20W-F-Hope LED Opto-Electric Co., Ltd) for desired time period. After completion of reaction, monitored by TLC, the reaction mixture was filtered and product was extracted using DCM and washed with water, brine and dried over Na_2SO_4. Solvent was removed by rota-vapour and product having some catalyst was isolated. For purifying the product was dissolved in minimum amount of DCM and hexane was added to precipitate the catalyst. Filter the solution and dried over vacuum to getting crude product. Further purification was done by using column chromatography on silica gel. The product was identified with FT-IR Fig S9. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.50 (s, 2H), 7.20 – 7.50 (m, 8H), 7.65 (s, 1H), 7.80 (d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 54.20, 119.53, 125.6, 127.4, 127.8, 128.5, 128.6, 128.8, 130.4, 134.6, 148.2 ppm, Fig. S9-Fig. S12.

3. Synthesis of 1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole



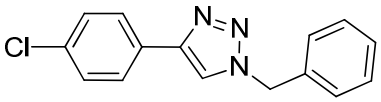
^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.90 (s, 3H), 5.50 (s, 2H), 7.05–7.60 (m, 9H), 7.70 (s, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 54.3, 55.2, 114.1, 123.2, 126.9, 128.0, 128.4, 128.7, 129.1, 134.7, 149.0, 159.0 ppm, Fig. S13-Fig. S15

4. Synthesis of 1-benzyl-4-(4-bromophenyl)-1*H*-1,2,3-triazole



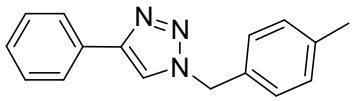
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.50 (s, 2H), 7.25–7.55 (m, 7H), 7.60 (s, 1H), 7.75 (d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 53.3, 118.5, 125.8, 126.79, 127.7, 127.9, 128.1, 132.8, 133.4, 138.2, 146.1 ppm, Fig. S16-Fig. S18.

5. Synthesis of 1-benzyl-4-(4-chlorophenyl)-1*H*-1,2,3-triazole



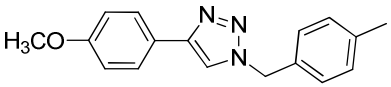
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.48 (s, 2H), 7.25–7.60 (m, 7H), 7.65 (s, 1H), 7.85 (d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 53.4, 118.5, 125.9, 126.7, 127.8, 127.9, 128.1, 132.8, 133.4, 138.2, 146.1 ppm, Fig. S19-Fig. S21.

6. Synthesis of 1-(4-methylbenzyl)-4-phenyl-1H-1,2,3-triazole



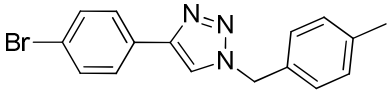
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 5.53 (s, 2H), 7.19 – 7.39 (m, 7H), 7.63 (s, 1H), 7.78 (d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 21.1, 54.0, 119.3, 125.6, 128.1, 128.7, 129.8, 130.5, 131.6, 138.7, 148.1 ppm, Fig. S22-Fig. S24.

7. Synthesis of 4-(4-methoxyphenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole



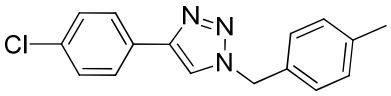
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 3.80 (s, 3H), 5.48 (s, 2H), 6.9–7.20 (m, 6H), 7.40 (d, 2H), 7.52 (s, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 21.1, 55.1, 60.3, 114.1, 123.2, 126.9, 128.0, 129.7, 131.7, 133.5, 138.5, 147.9, 159.8 ppm, Fig. S25-Fig. S26.

8. Synthesis of 4-(4-bromophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole



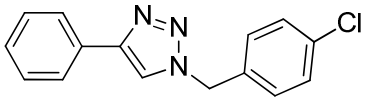
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 5.53 (s, 2H), 7.20 (s, 4H), 7.50 (d, 2H) 7.62 (s, 1H), 7.65 (d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 21.1, 54.1, 119.4, 121.9, 127.1, 128.2, 129.5, 129.8, 131.4, 131.9, 138.8, 147.1 ppm, Fig. S27-Fig. S29.

9. Synthesis of 4-(4-chlorophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole



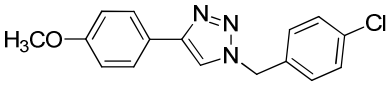
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 5.53 (s, 2H), 7.20 (s, 4H), 7.35 (d, 2H) 7.61 (s, 1H), 7.71(d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 21.1, 54.1, 119.3, 126.9, 128.1, 128.9, 129.0, 129.8, 131.4, 133.8, 138.8, 147.1 ppm, Fig. S30-Fig. S32.

10. Synthesis of 1-(4-chlorobenzyl)-4-phenyl-1H-1,2,3-triazole



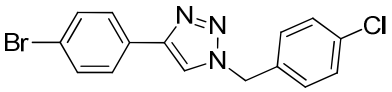
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.55 (s, 2H), 7.24–7.42 (m, 7H), 7.66 (s, 1H), 7.79 (d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 53.4, 119.4, 125.6, 128.2, 128.8, 129.3, 130.3, 133.1, 134.8, 148.4 ppm, Fig S33-Fig. S35.

11. Synthesis of 1-(4-chlorobenzyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazole



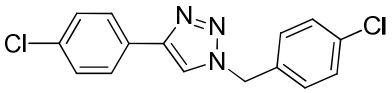
^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 5.52 (s, 2H), 6.83–7.43 (m, 8H), 7.60 (s, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 53.6, 56.1, 113.6, 121.4, 127.7, 128.2, 130.4, 131.2, 134.6, 147.9, 159.6 ppm, Fig. S36.

12. Synthesis of 4-(4-bromophenyl)-1-(4-chlorobenzyl)-1H-1,2,3-triazole



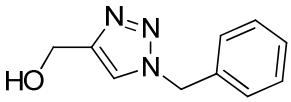
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.55 (s, 2H), 7.20–7.55 (m, 6H), 7.67 (s, 1H), 7.70 (d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 53.2, 122.8, 126.9, 129.0, 129.1, 131.3, 131.7, 132.6, 133.2, 134.7, 147.1 ppm, Fig. S37-Fig. S38.

13. Synthesis of 1-(4-chlorobenzyl)-4-(4-chlorophenyl)-1H-1,2,3-triazole



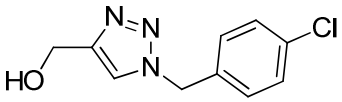
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.55 (s, 2H), 7.25–7.40 (m, 6H), 7.67 (s, 1H), 7.75 (d, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 53.5, 119.4, 126.9, 128.4, 129.0, 129.4, 132.9, 134.0, 134.9, 147.3 ppm, Fig. S39-Fig. S40

14. Synthesis of (1-benzyl-1H-1,2,3-triazol-4-yl)methanol



^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.71 (s, 1H), 4.79 (s, 2H), 5.50 (s, 2H), 7.25–7.39 (m, 5H), 7.55 (s, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 54.1, 56.2, 121.9, 128.1, 128.8, 129.1, 134.4, 148.0 ppm, Fig. S41-Fig. S43.

15. Synthesis of (1-(4-chlorobenzyl)-1H-1,2,3-triazol-4-yl)methanol



^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.6 (s, 1H –OH), 4.78 (s, 2H), 5.50 (s, 2H), 7.20–7.35 (m, 4H), 7.50 (s, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 53.4, 56.1, 121.7, 129.4, 132.9, 134.8, 148.3 ppm, Fig. S44-Fig. S45.

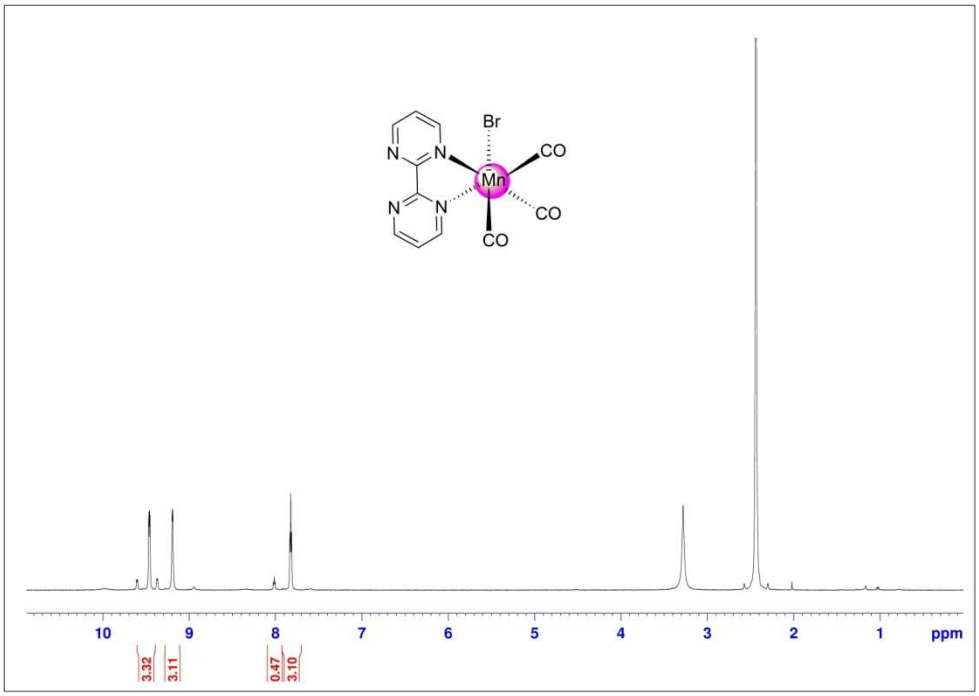


Fig. S1 ^{1}HNMR of Mn(bpm)(CO)$_3$Br

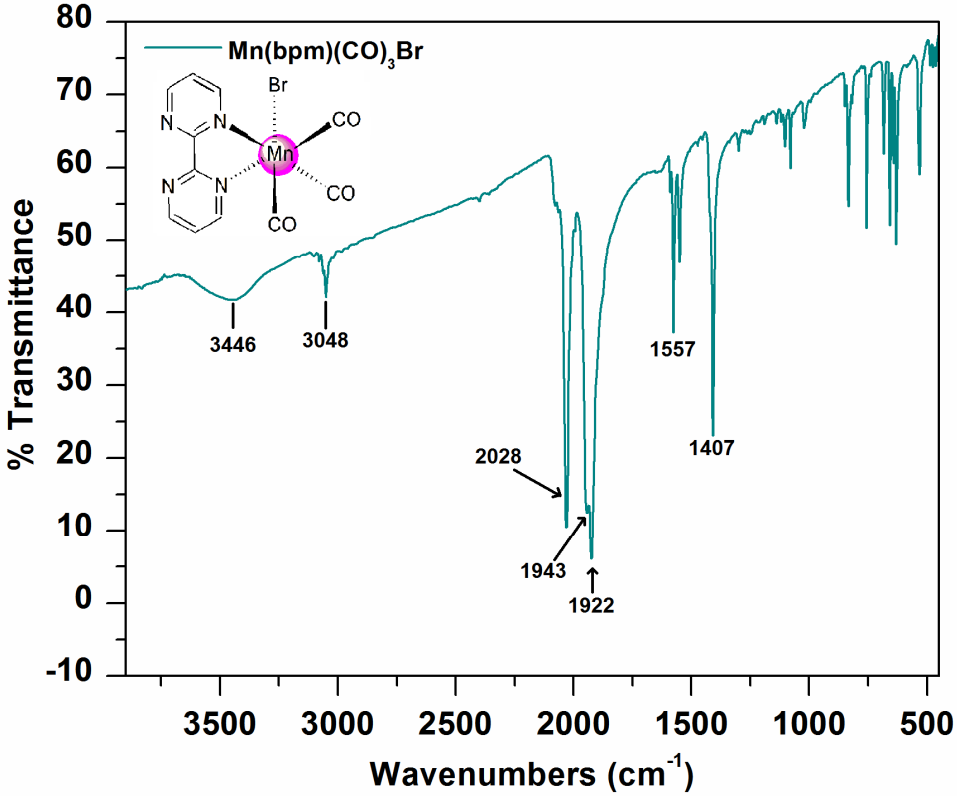


Fig. S2 FTIR of Mn(bpm)(CO)$_3$Br

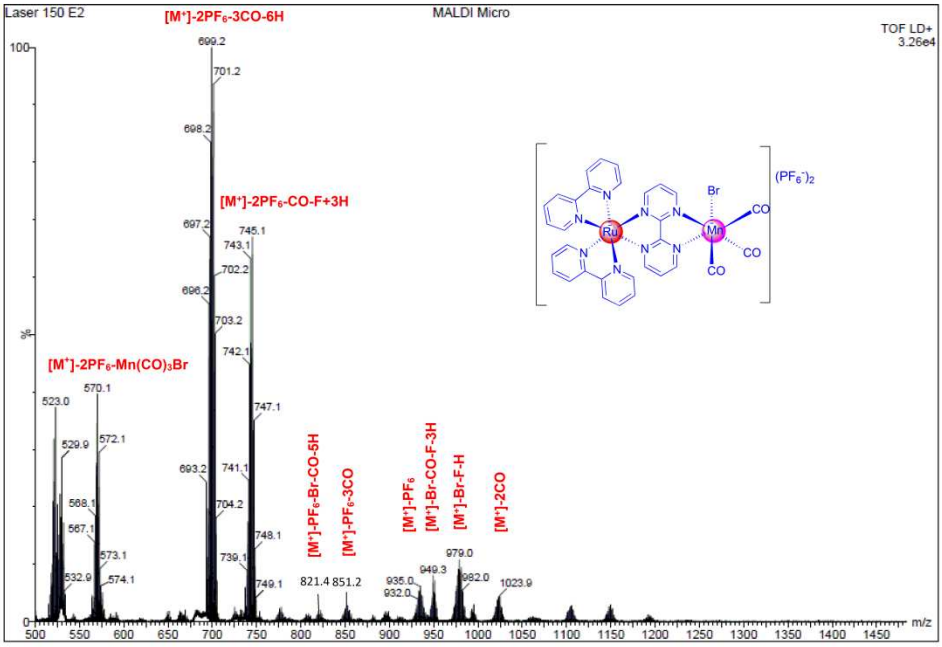


Fig. S3MALDI-TOF MS spectra of Ru-Mn complex

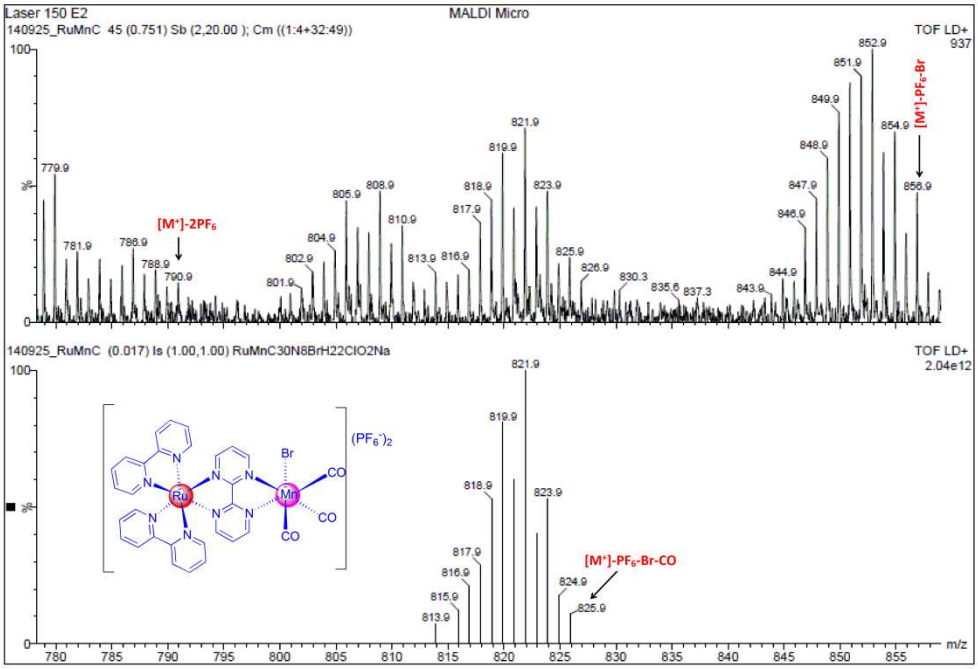


Fig. S4 MALDI-TOF MS spectra of Ru-Mn complex (extended between m/e 780-860)

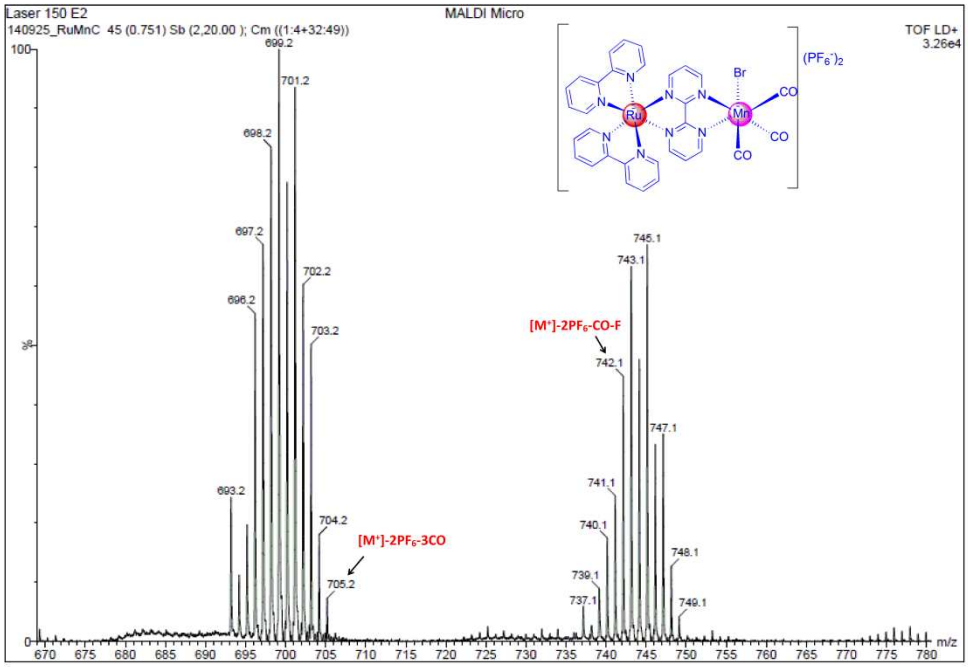


Fig. S5 MALDI-TOF MS spectra of Ru-Mn complex (extended between m/e 670-780)

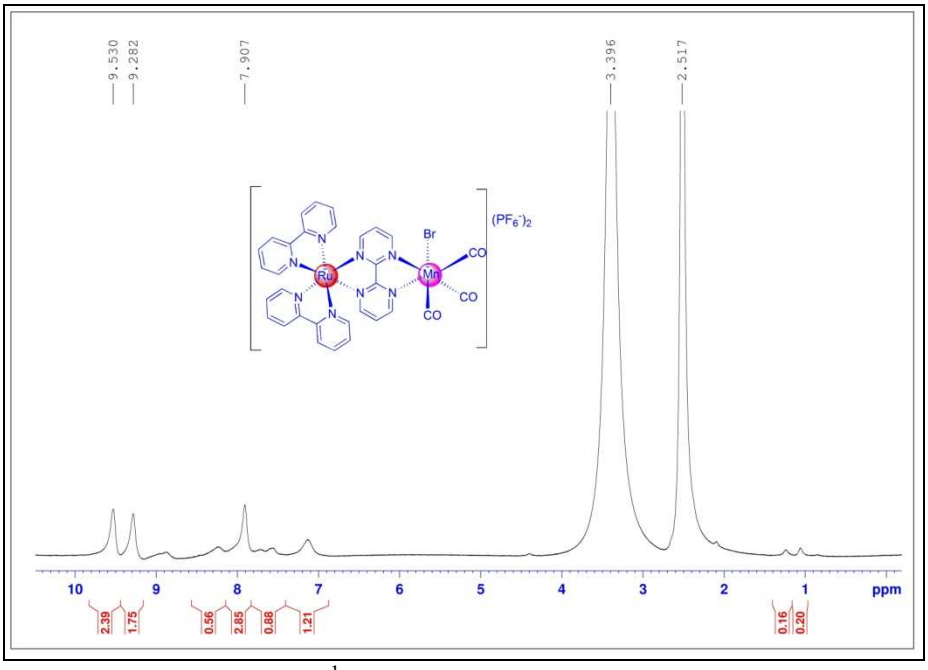


Fig. S6 ^{1}H NMR of Ru-Mn complex

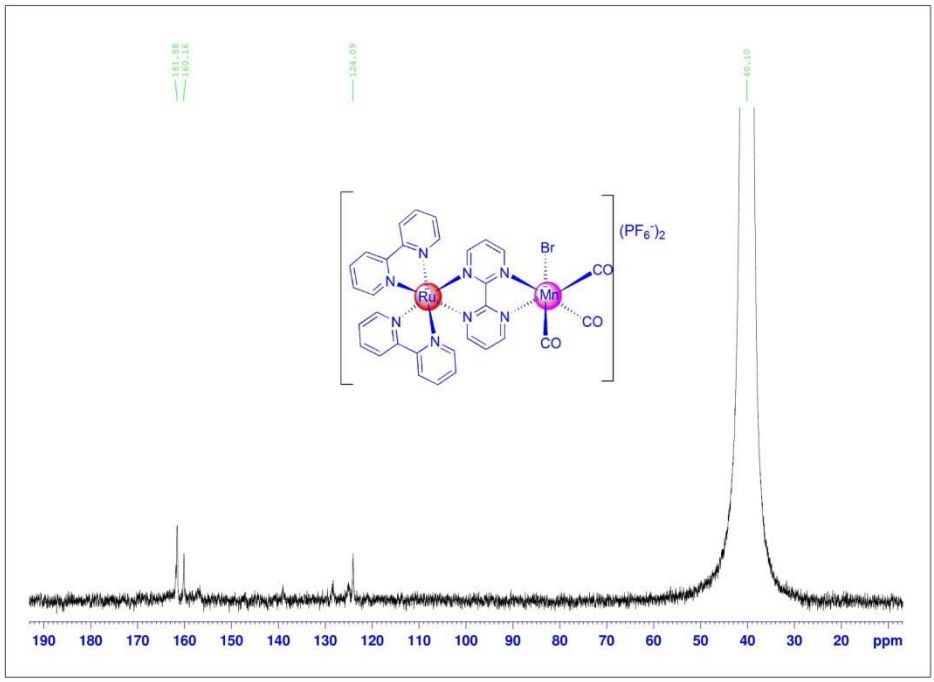


Fig. S7 ^{13}C NMR of Ru-Mn complex

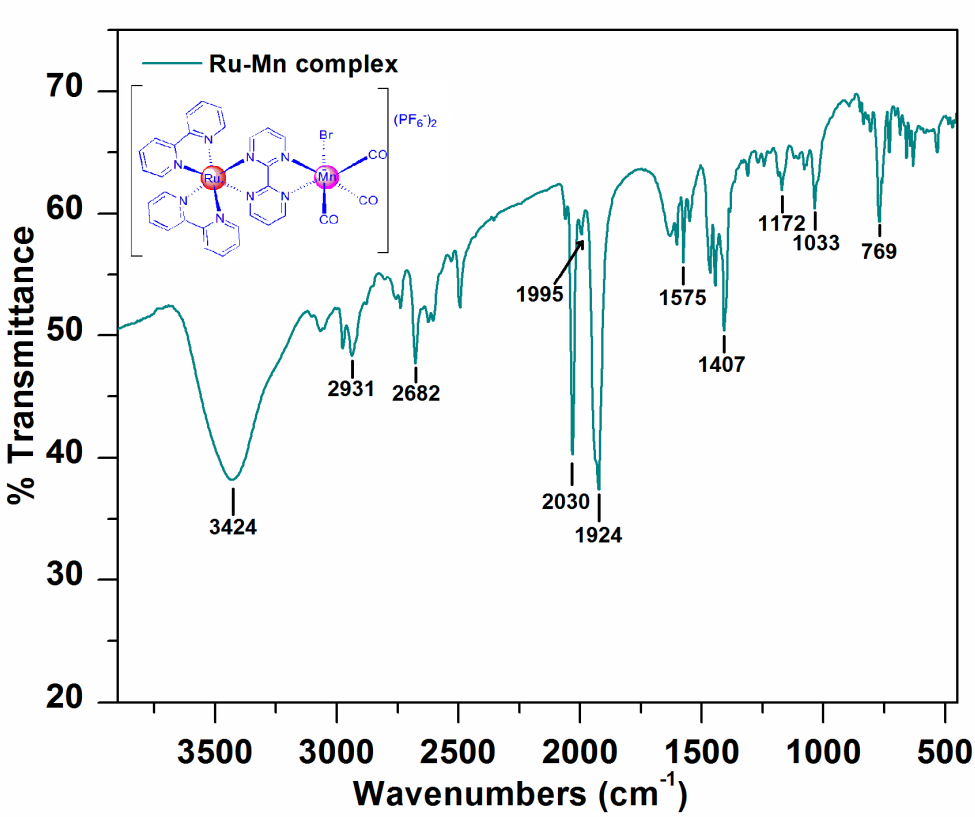


Fig. S8 FTIR of Ru-Mn complex

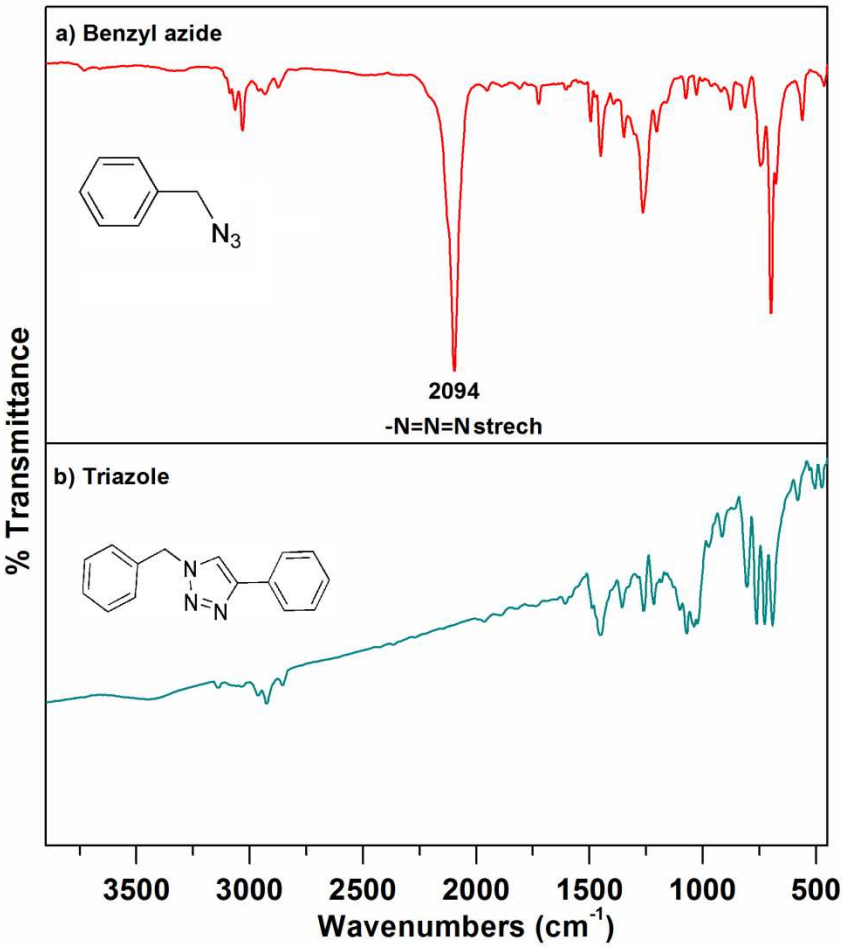


Fig. S9 FT-IR spectra of a) Benzyl azide showing –N=N=N stretch b) 1-benzyl-4-phenyl-1*H*-1,2,3-triazole showing disappearance of azide peak

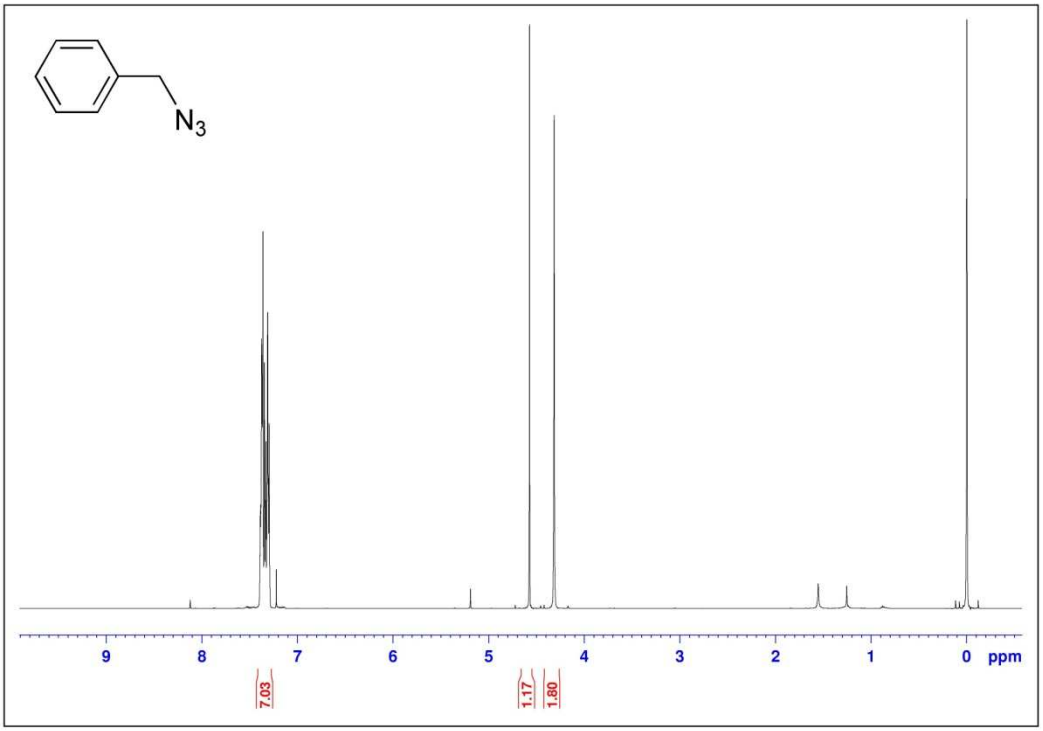


Fig. S10 ^{1}H NMR of Benzyl Azide

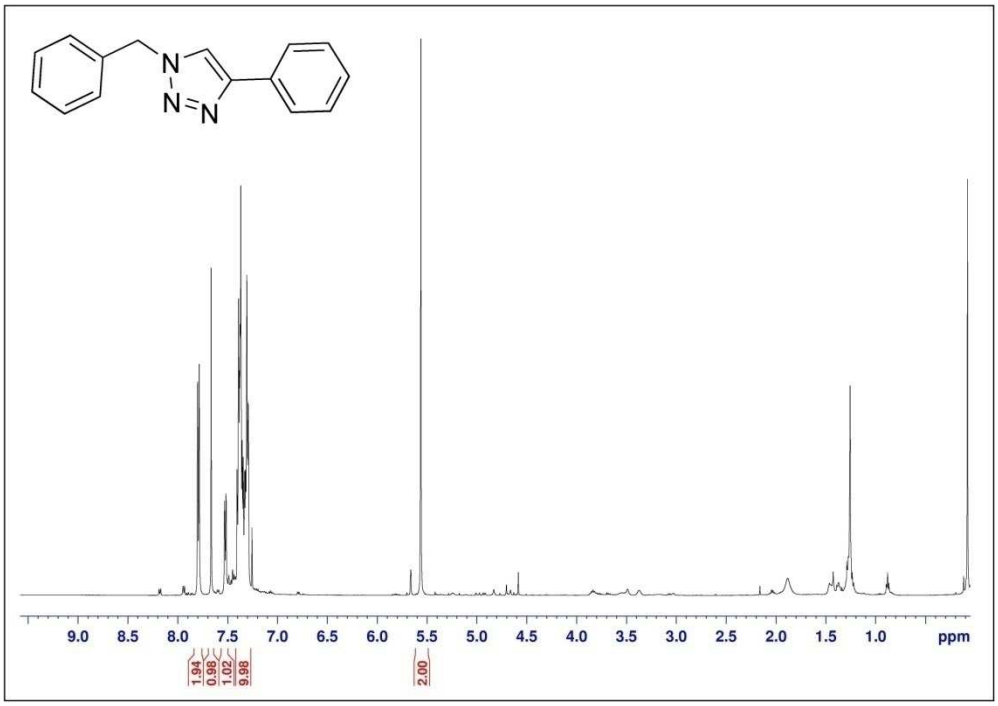


Fig. S11 ^{1}H NMR of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole

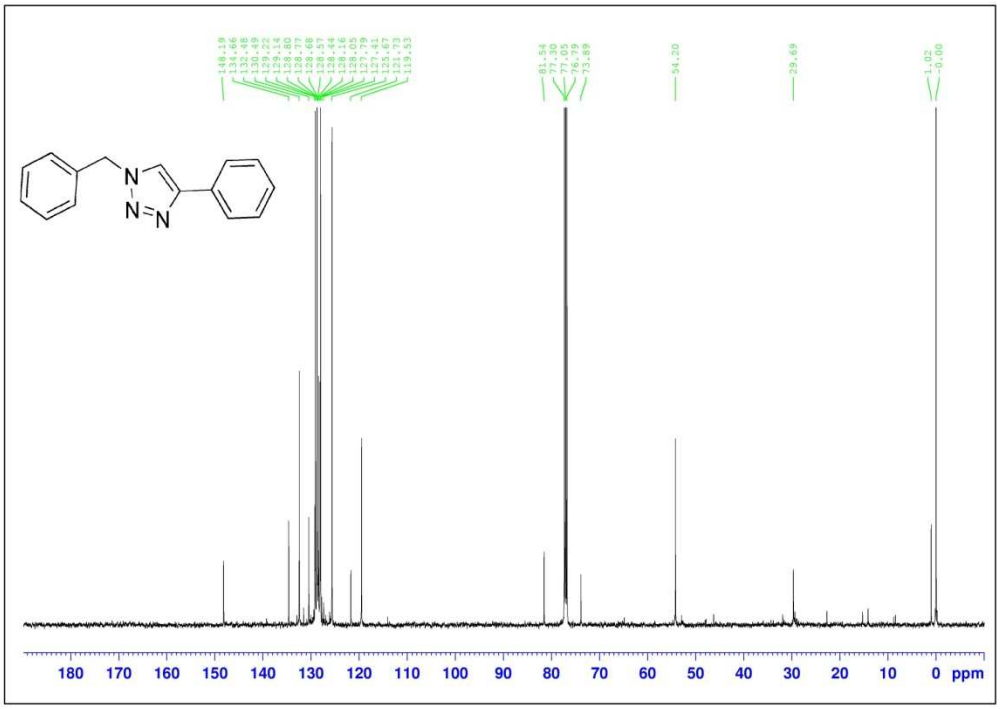


Fig. S12 ^{13}C NMR of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole

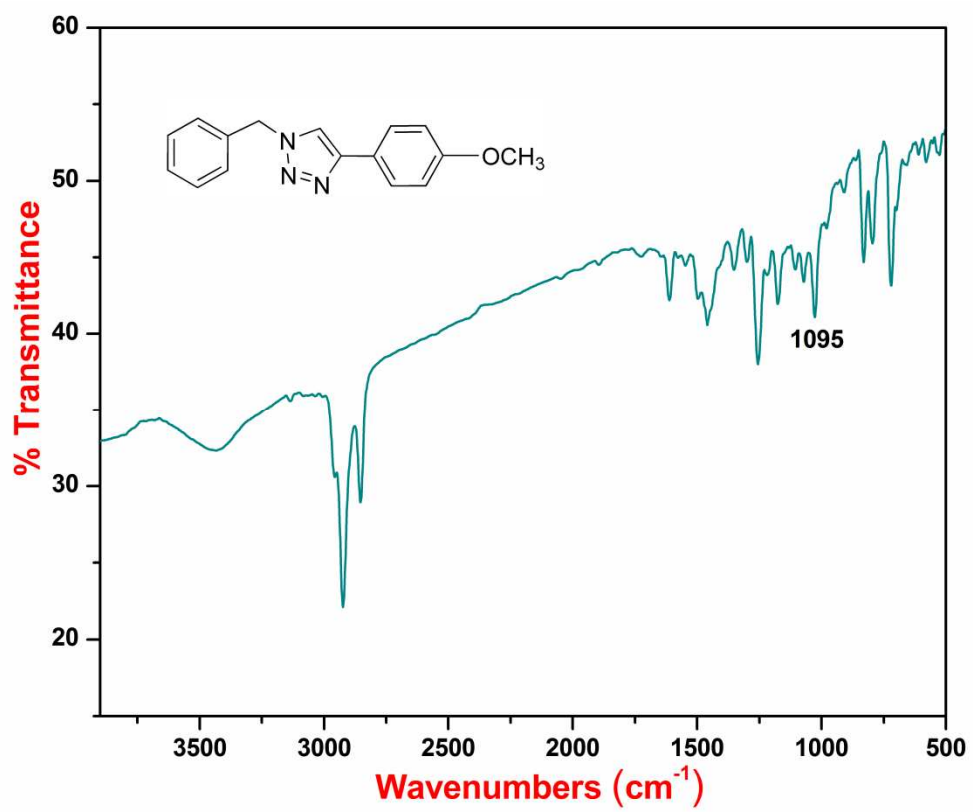


Fig. S13 FTIR spectra of 1-benzyl-4-methoxy phenyl-1*H*-1,2,3-triazole

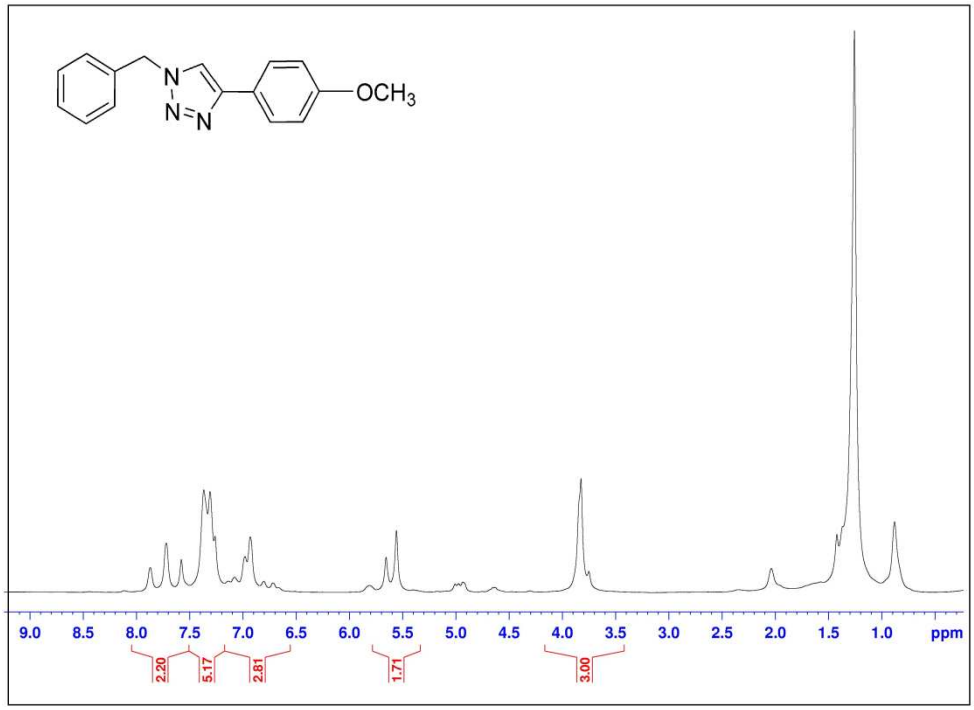


Fig. S14 ^{1}H NMR of 1-benzyl-4-methoxy phenyl-1*H*-1,2,3-triazole

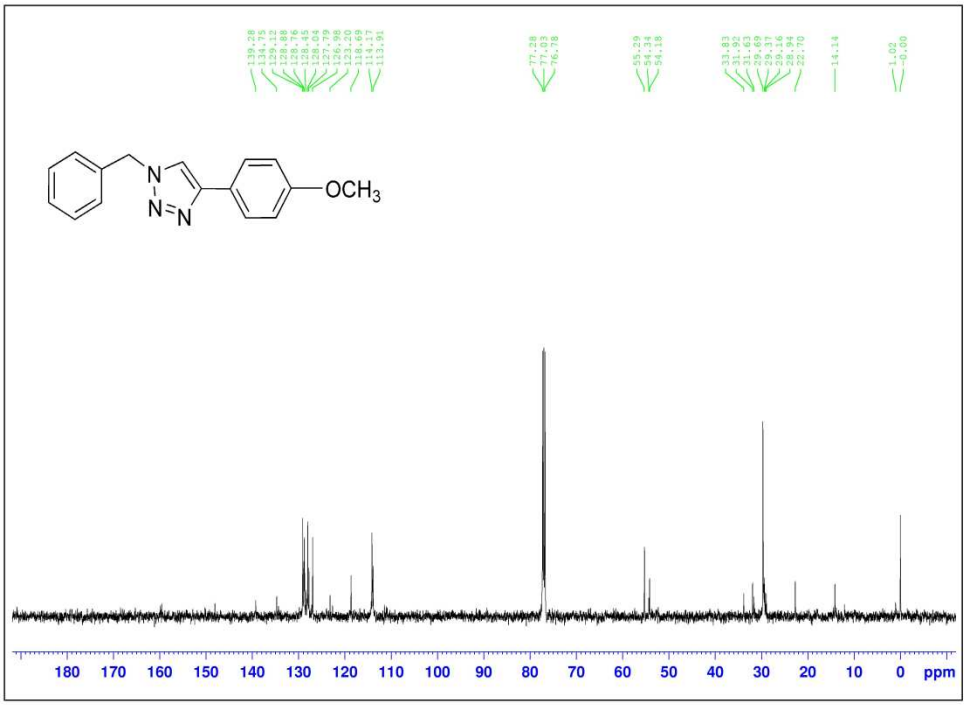


Fig. S15 ^{13}C NMR of FTIR spectra of 1-benzyl-4-methoxyphenyl-1*H*-1,2,3-triazole

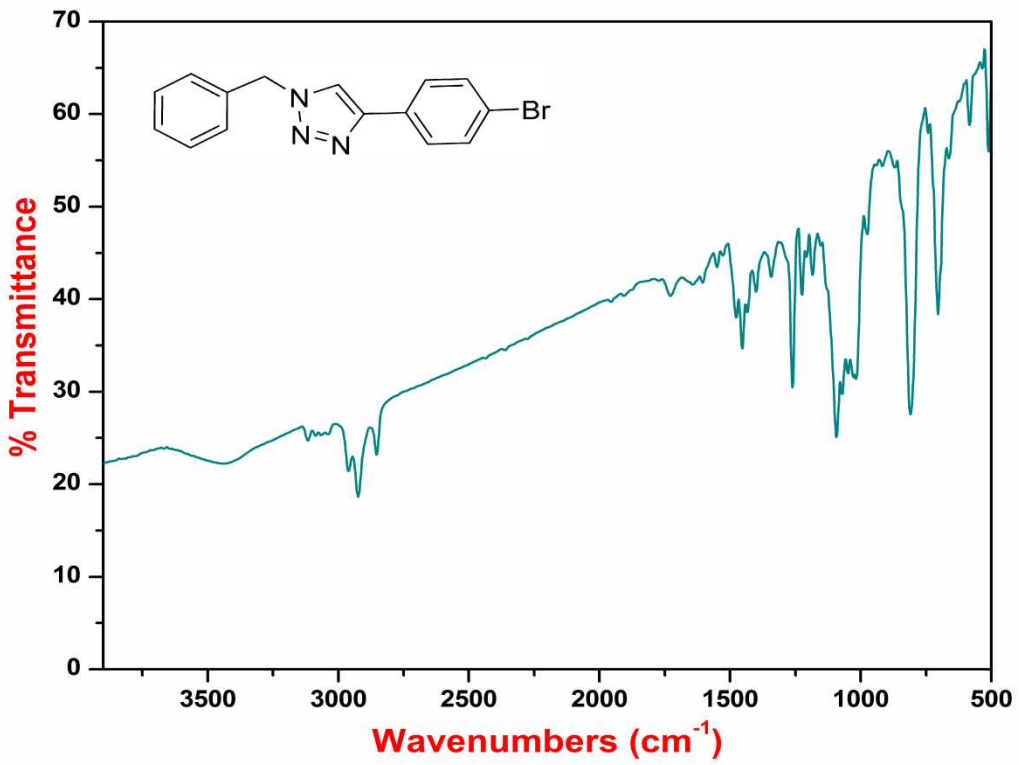


Fig. S16 FTIR spectra of 1-benzyl-4-Bromophenyl-1*H*-1,2,3-triazole

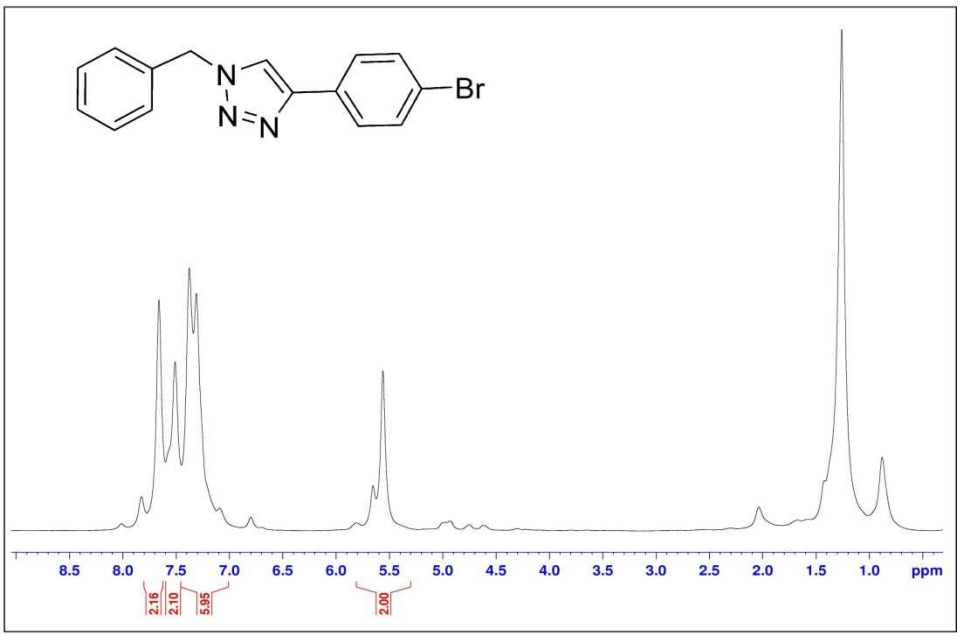


Fig. S17 ^{1}H NMR of 1-benzyl-4-bromophenyl-1*H*-1,2,3-triazole

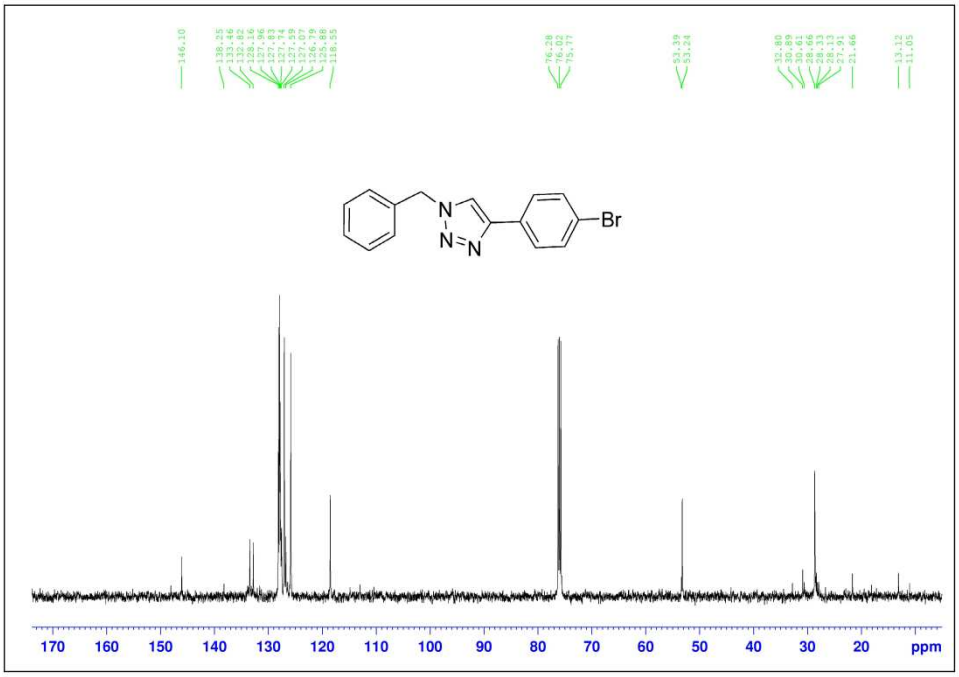


Fig. S18 ^{13}C NMR of 1-benzyl-4-bromophenyl-1*H*-1,2,3-triazole

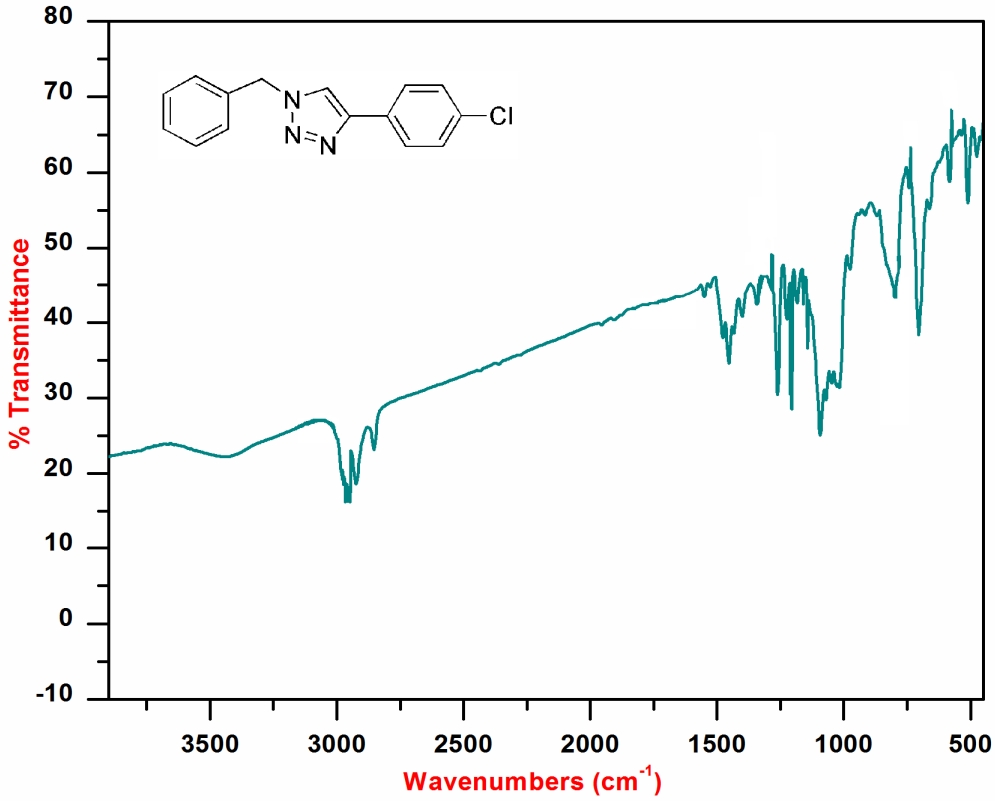


Fig. S19 FTIR of 1-benzyl-4-Chlorophenyl-1*H*-1,2,3-triazole

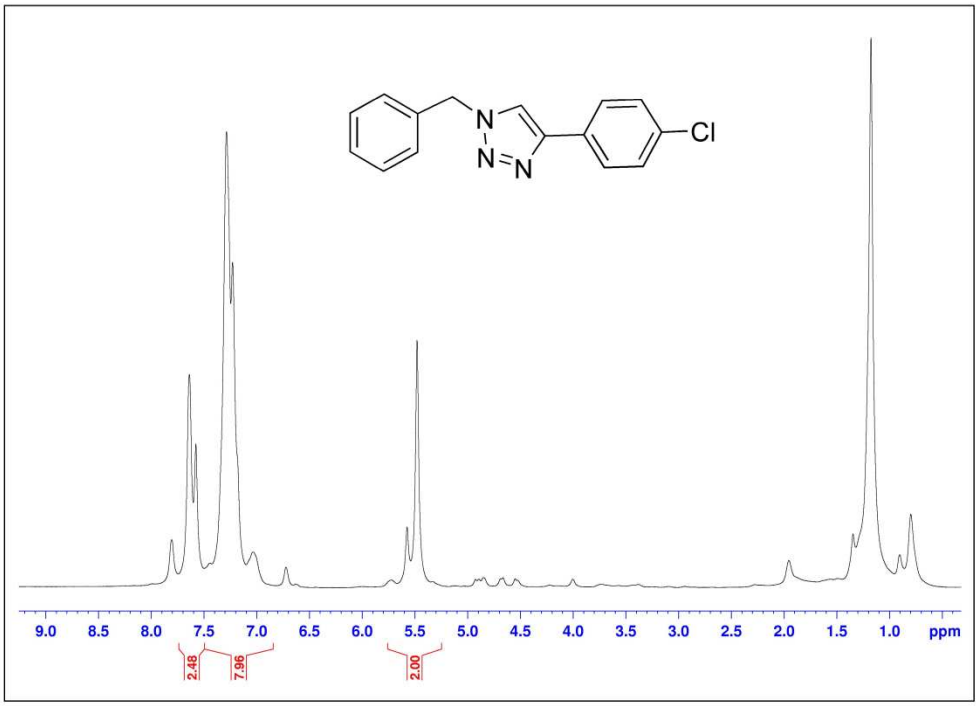


Fig. S20 ^{1}H NMR of 1-benzyl-4-chlorophenyl-1*H*-1,2,3-triazole

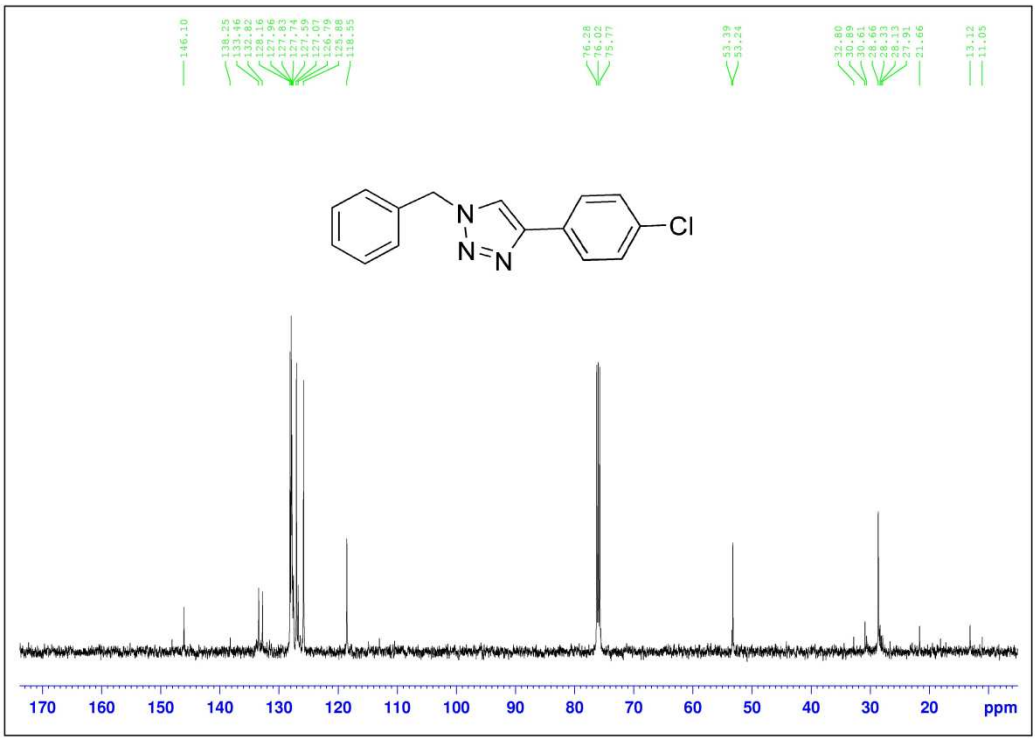


Fig. S21 ^{13}C NMR of 1-benzyl-4-chlorophenyl-1*H*-1,2,3-triazole

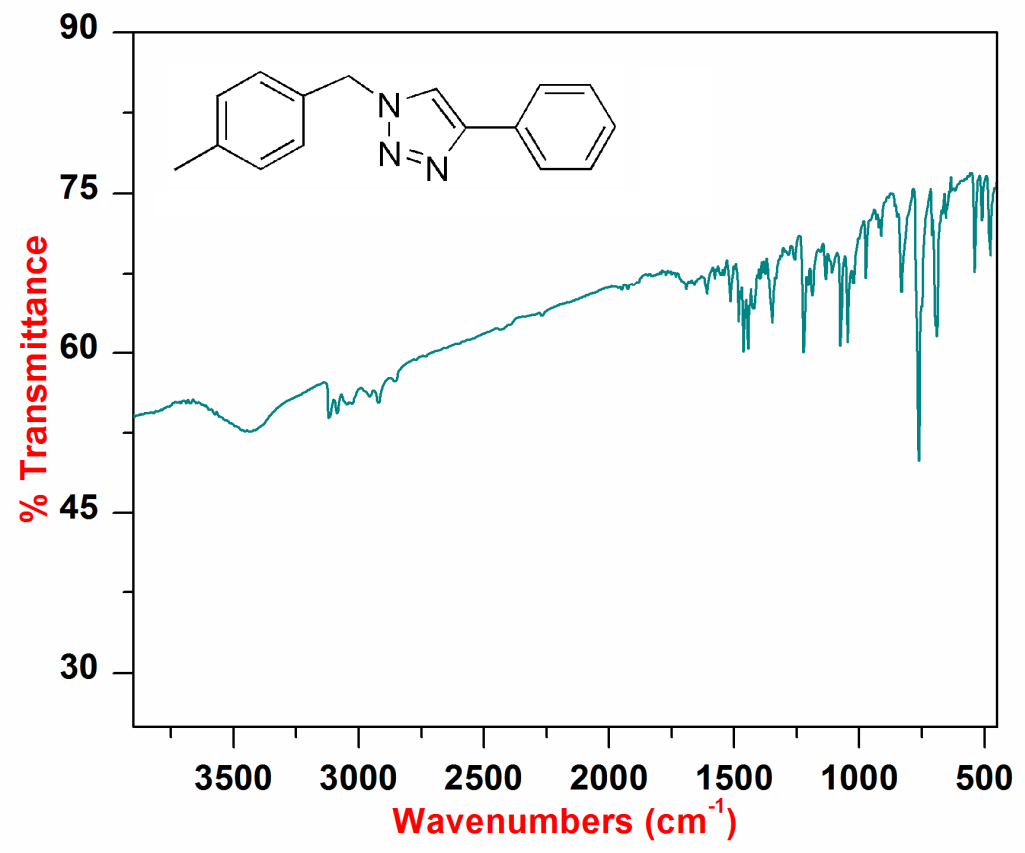


Fig. S22 FTIR of 1-(4-methylbenzyl)-4-phenyl-1H-1,2,3-triazole

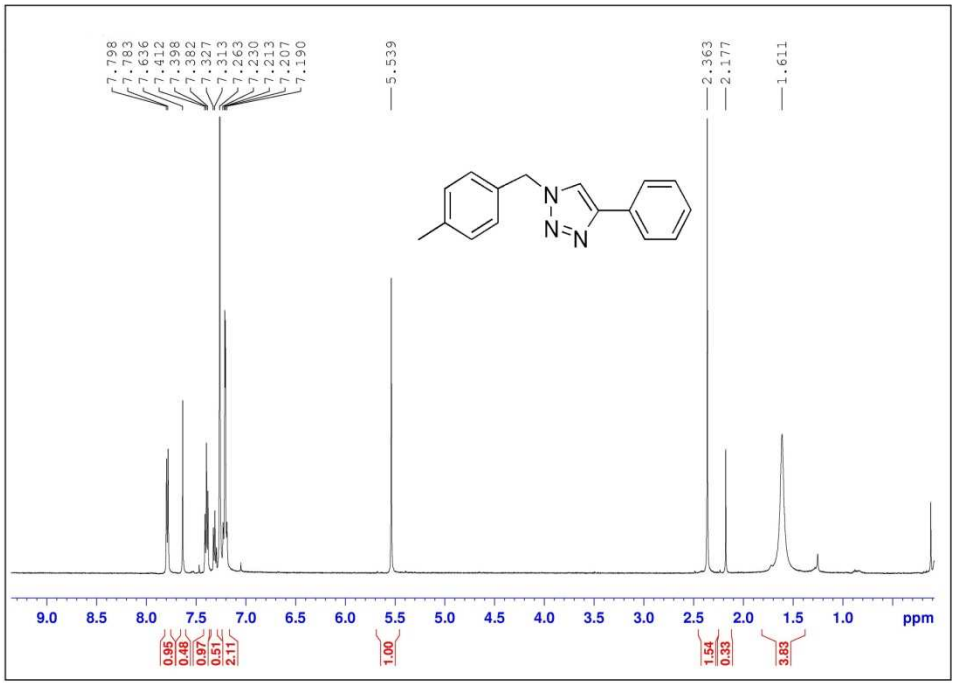


Fig. S23 ^{1}H NMR of 1-(4-methylbenzyl)-4-phenyl-1H-1,2,3-triazole

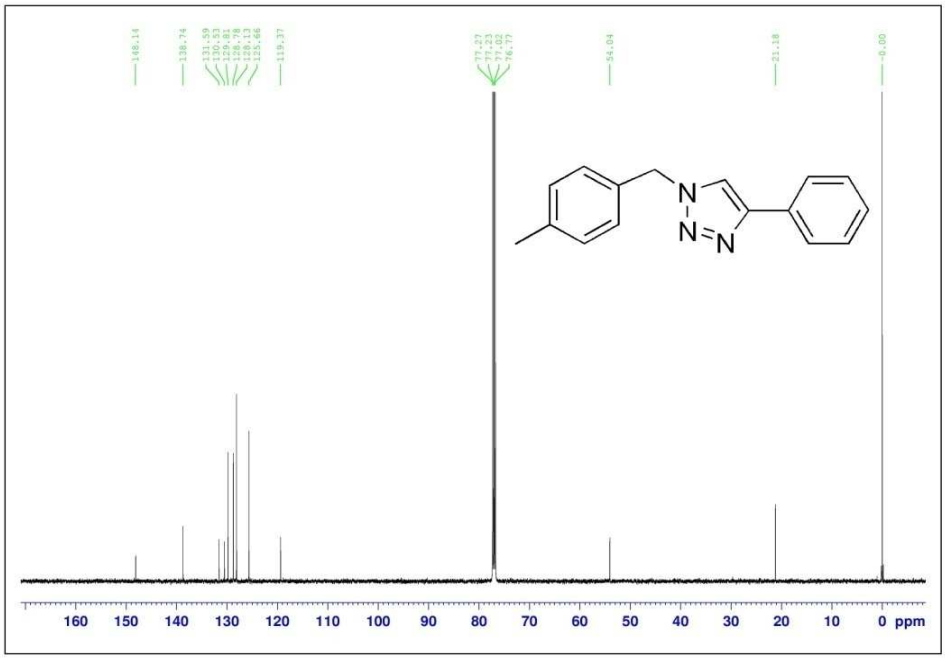


Fig. S24 ^{13}C NMR of 1-(4-methylbenzyl)-4-phenyl-1H-1,2,3-triazole

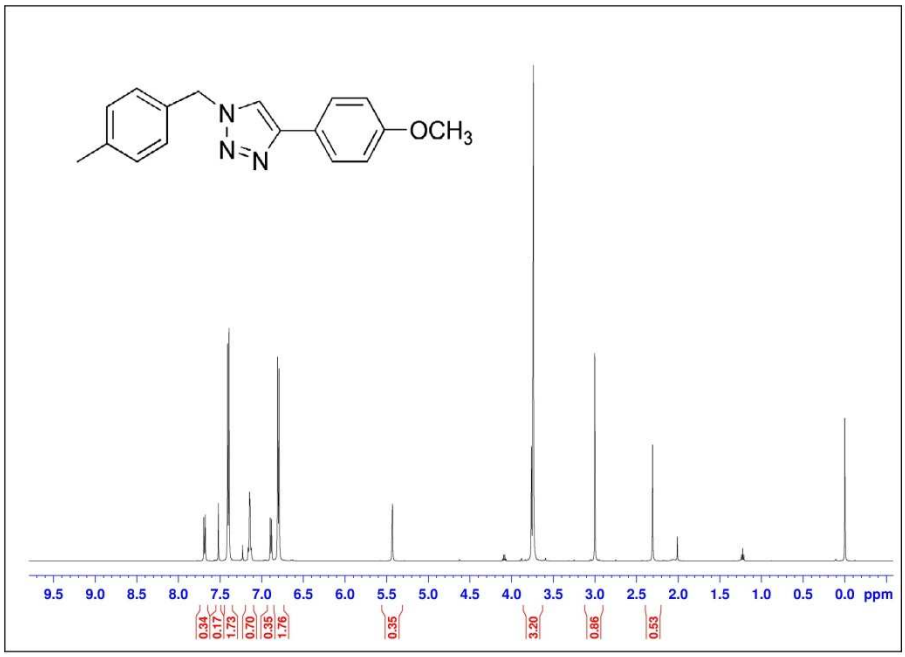


Fig. S25 ^{1}H NMR of 4-(4-methoxyphenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

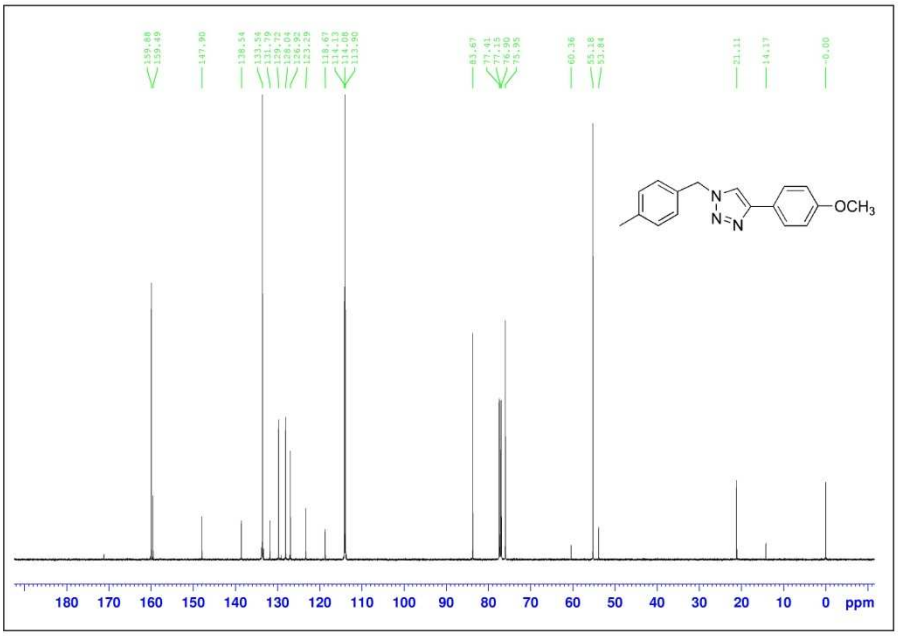


Fig. S26 ^{13}C NMR of 4-(4-methoxyphenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

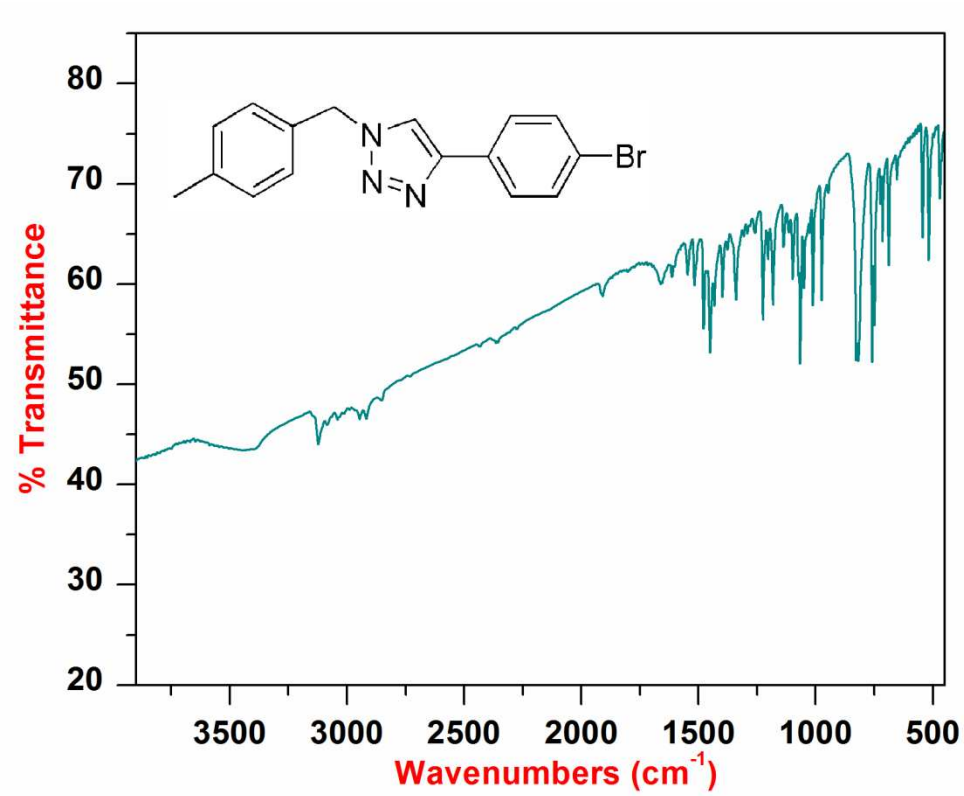


Fig. S27 FTIR of 4-(4-bromophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

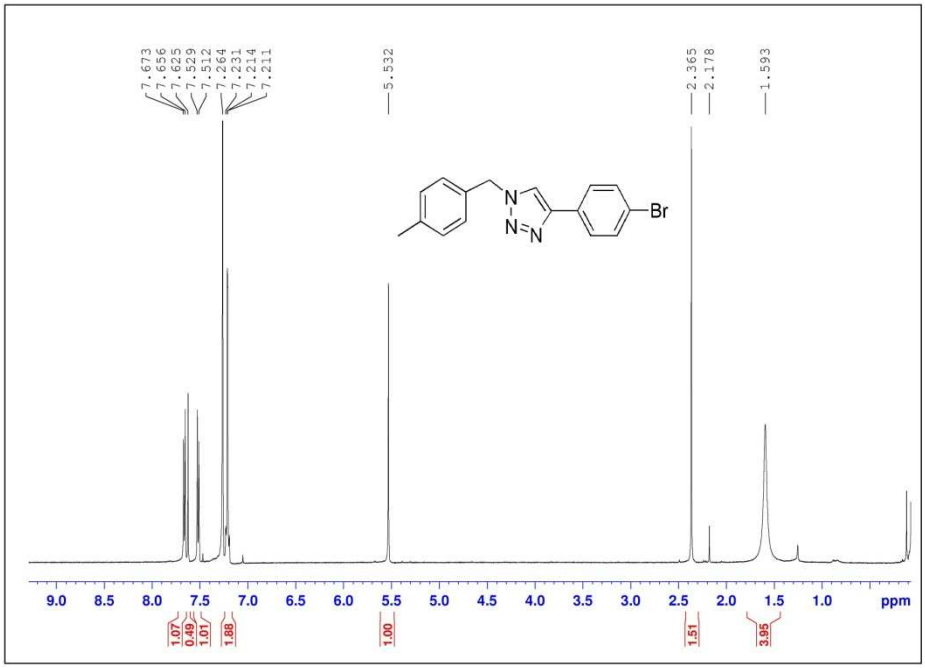


Fig. S28 ^{1}H NMR of 4-(4-bromophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

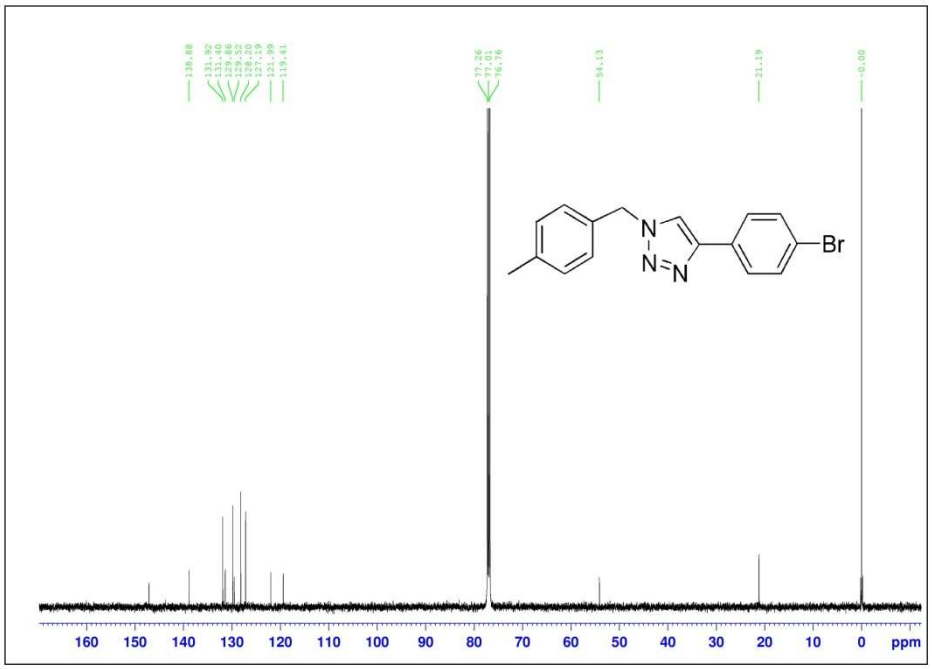


Fig. S29 ^{13}C NMR of 4-(4-bromophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

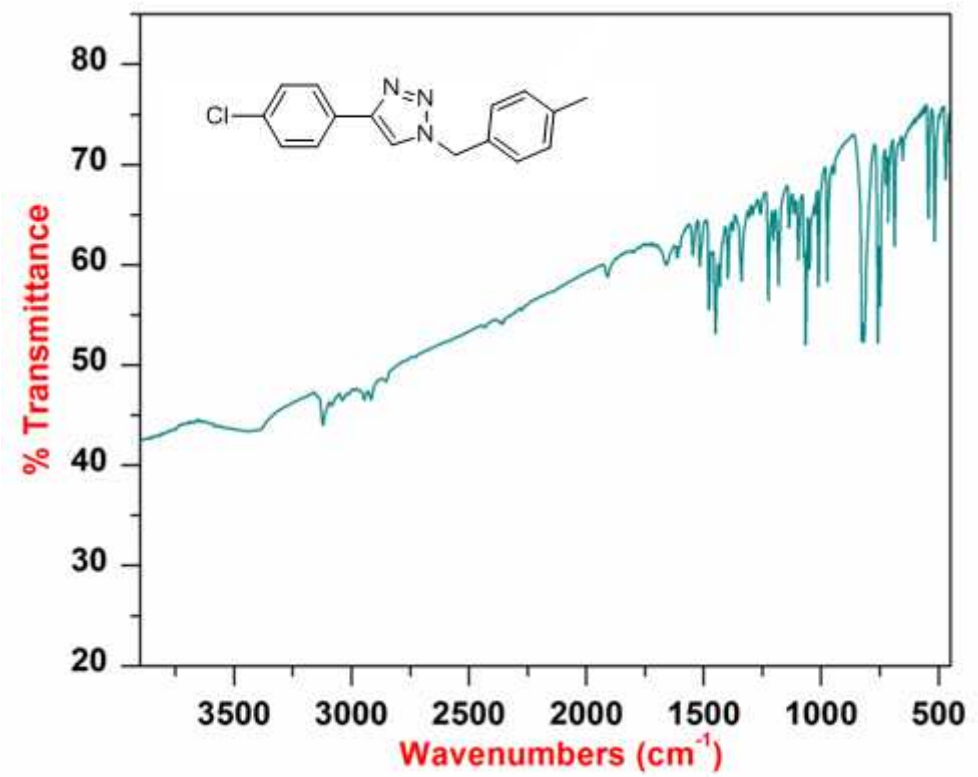


Fig. S30 FTIR of 4-(4-chlorophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

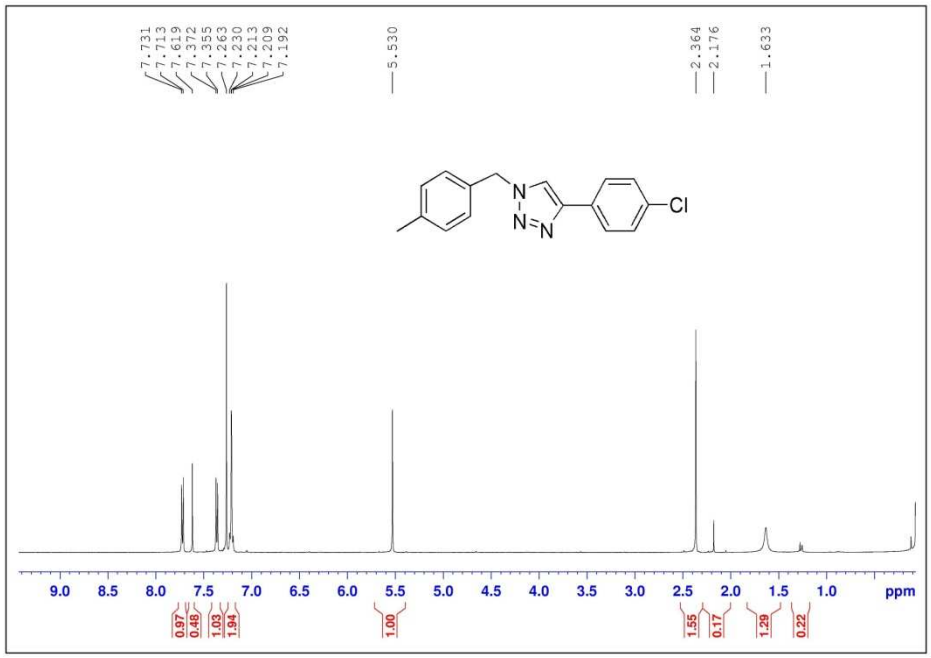


Fig. S31 ^{1}H NMR of 4-(4-chlorophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

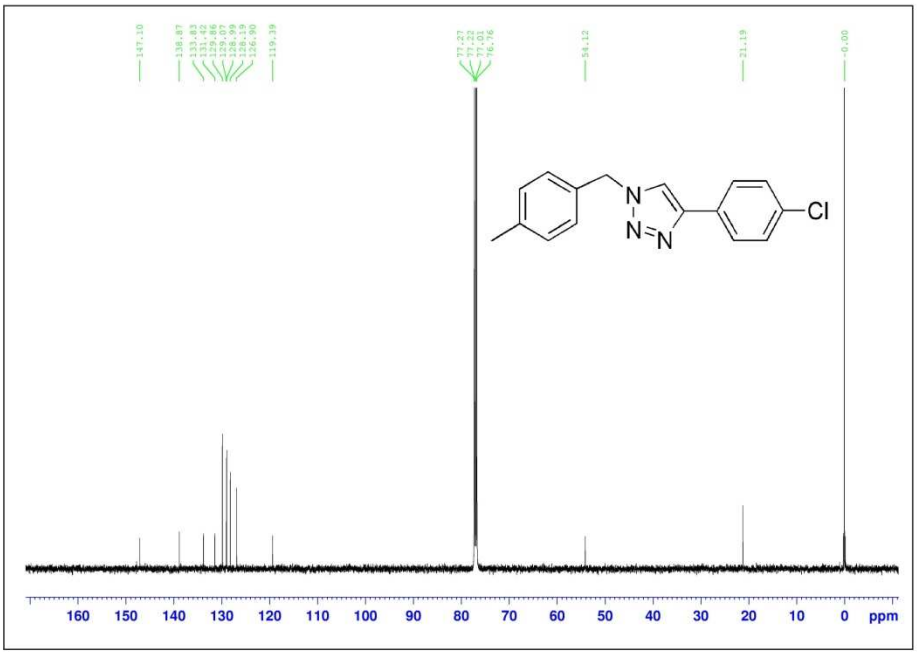


Fig. S32 ^{13}C NMR of 4-(4-chlorophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

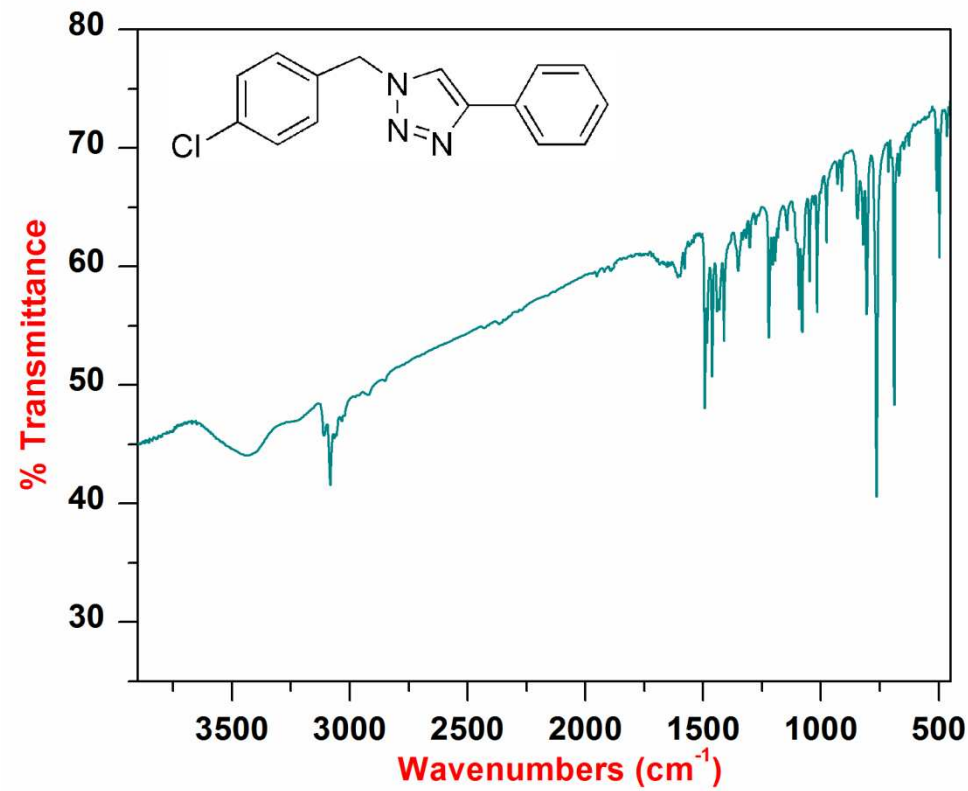


Fig. S33 FTIR of 4-(4-chlorophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

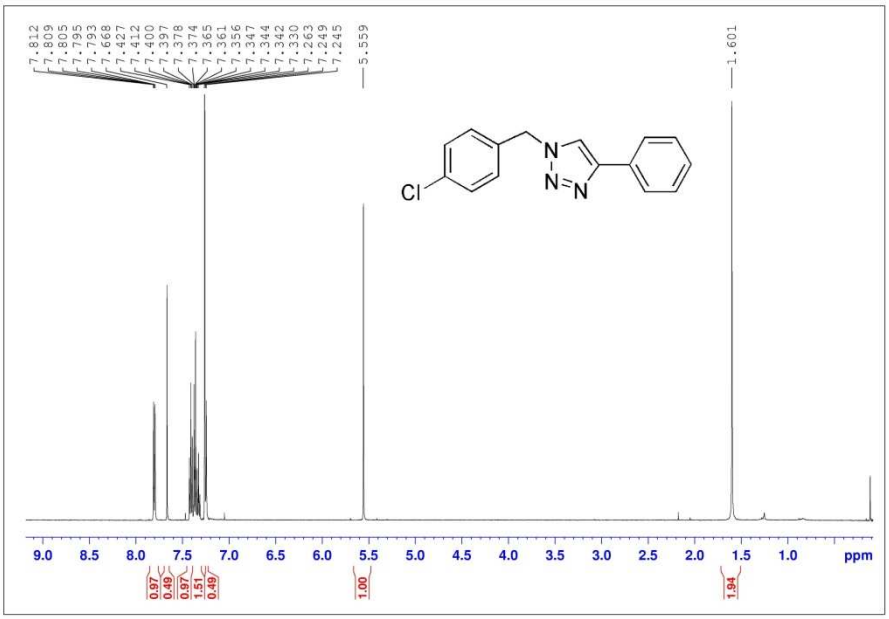


Fig. S34 ^{1}H NMR of 4-(4-chlorophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

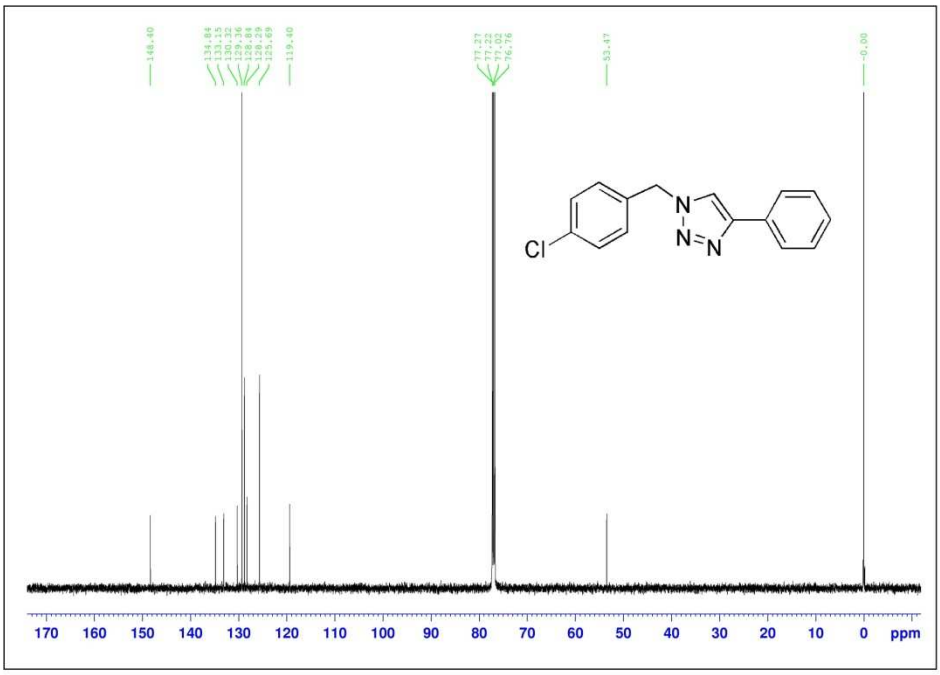


Fig. S35 ^{13}C NMR of 4-(4-chlorophenyl)-1-(4-methylbenzyl)-1H-1,2,3-triazole

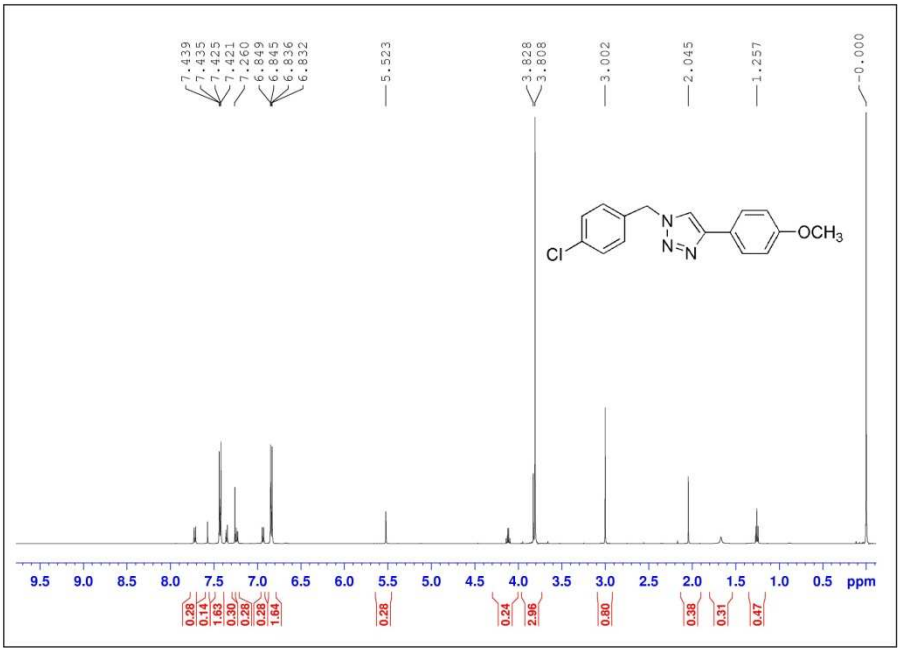


Fig. S36 ^{1}H NMR of 1-(4-chlorobenzyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazole

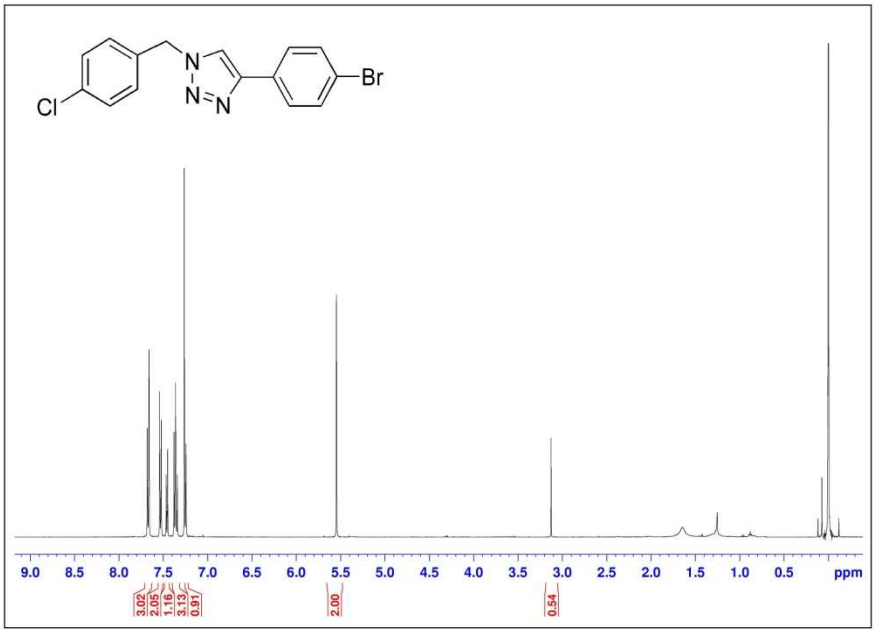


Fig. S37 ^{1}H NMR 4-(4-bromophenyl)-1-(4-chlorobenzyl)-1H-1,2,3-triazole

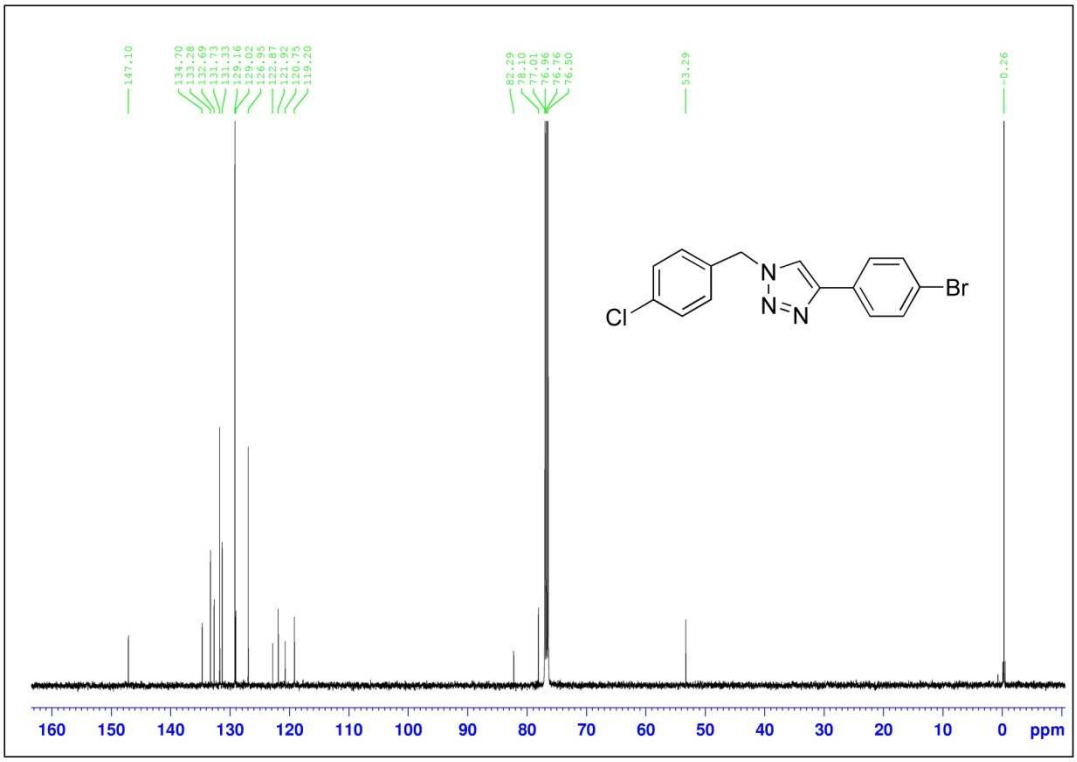


Fig. S38 ^{13}C NMR 4-(4-bromophenyl)-1-(4-chlorobenzyl)-1H-1,2,3-triazole

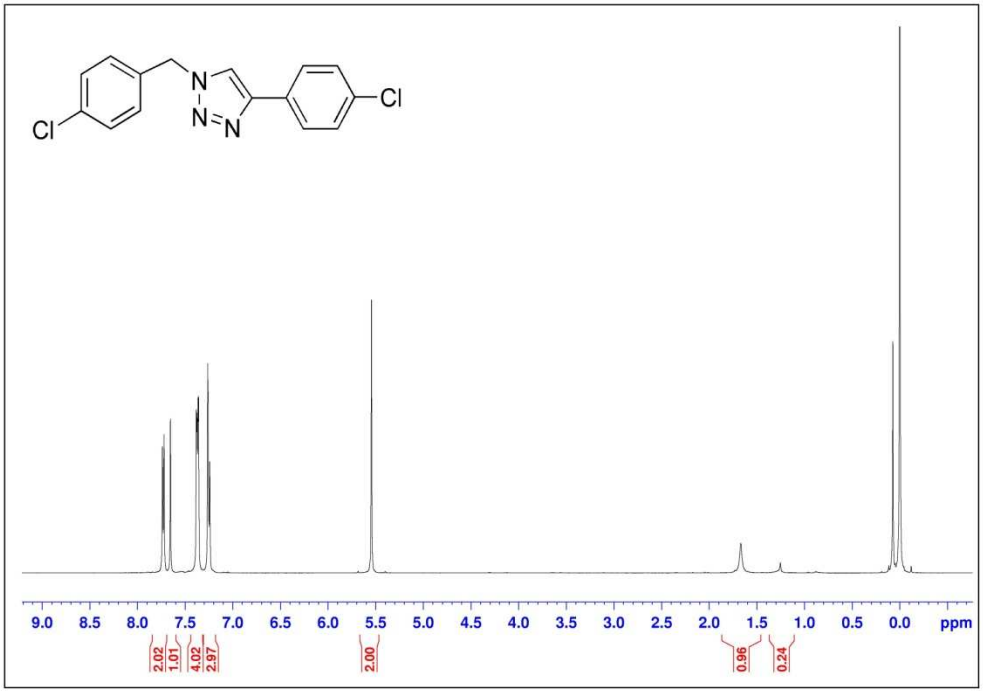


Fig. S39 ^{1}H NMR 1-(4-chlorobenzyl)-4-(4-chlorophenyl)-1H-1,2,3-triazole

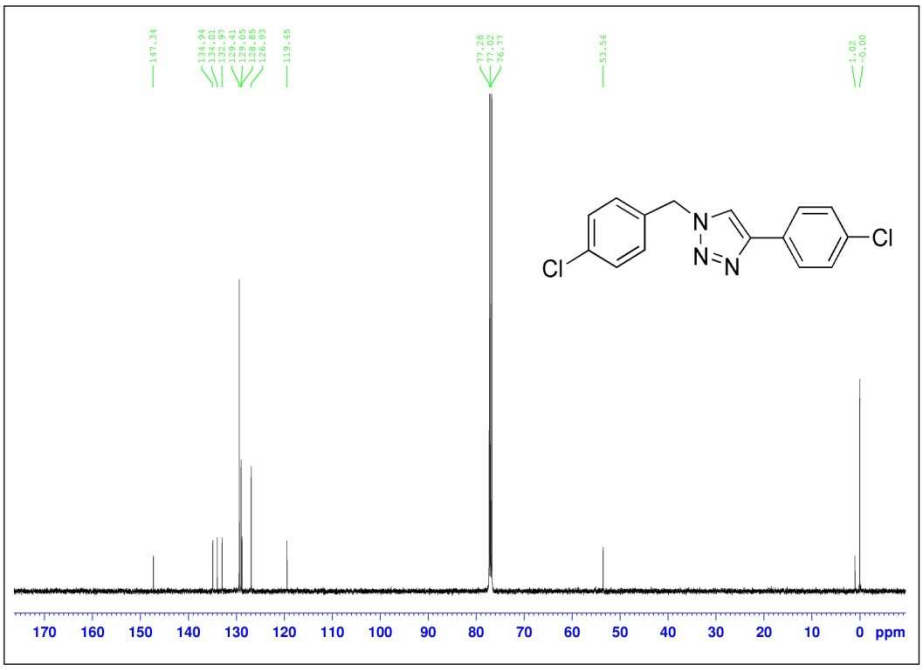


Fig. S40 ^{1}H NMR 1-(4-chlorobenzyl)-4-(4-chlorophenyl)-1H-1,2,3-triazole

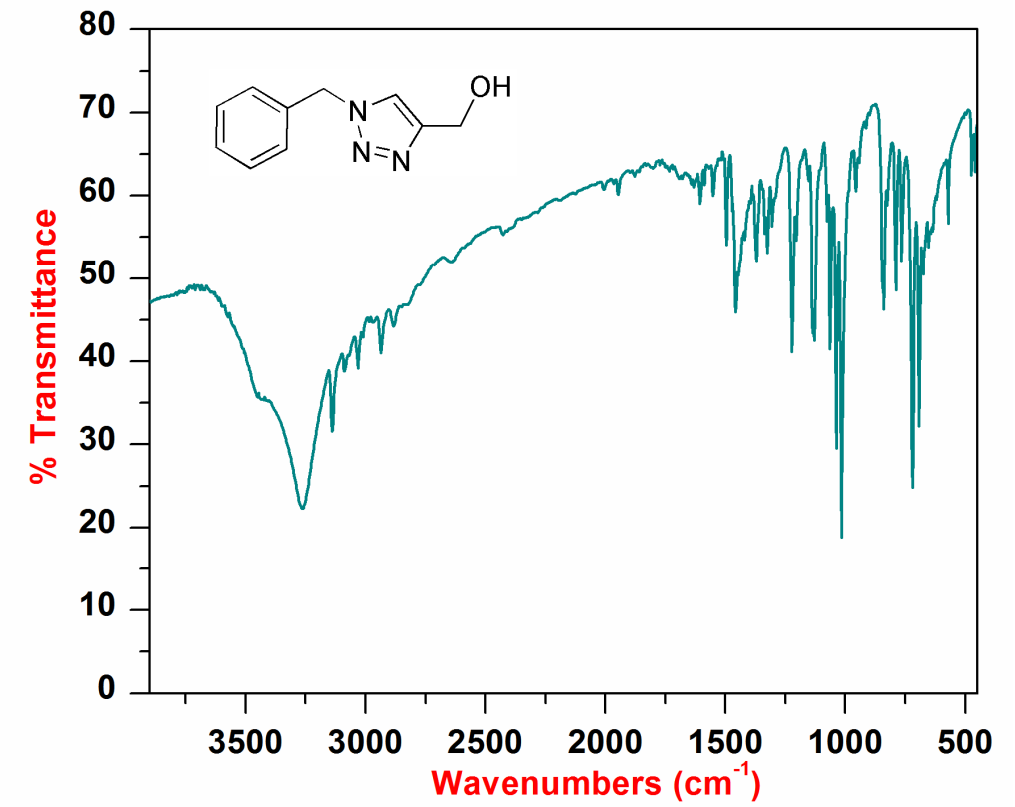


Fig. S41 FTIR of (1-benzyl-1H-1,2,3-triazol-4-yl)methanol

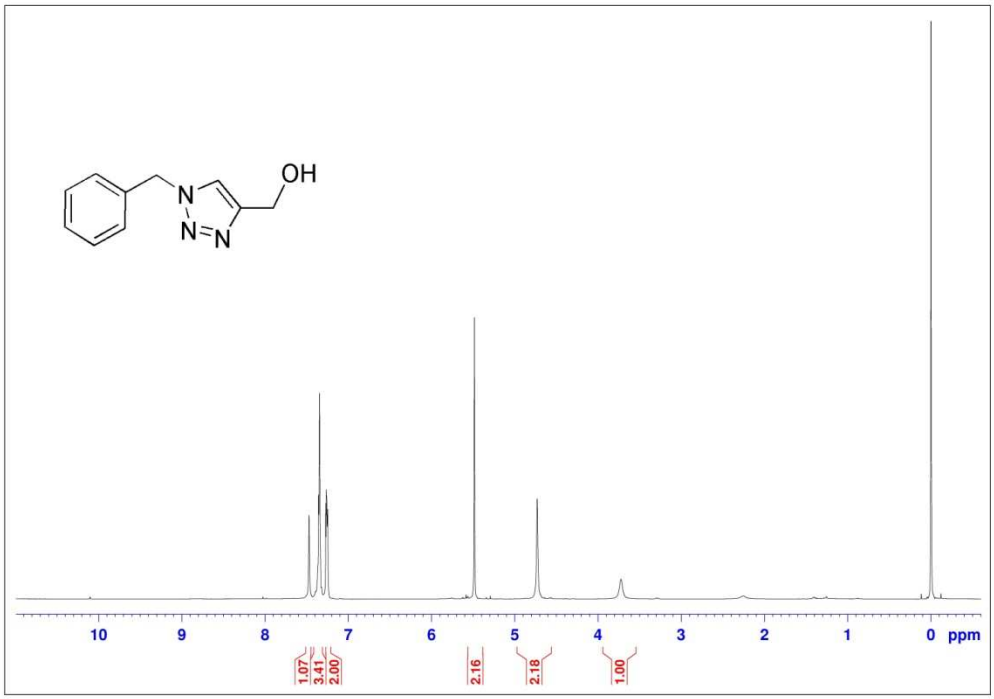


Fig. S42 ^{1}H NMR of (1-benzyl-1H-1,2,3-triazol-4-yl)methanol

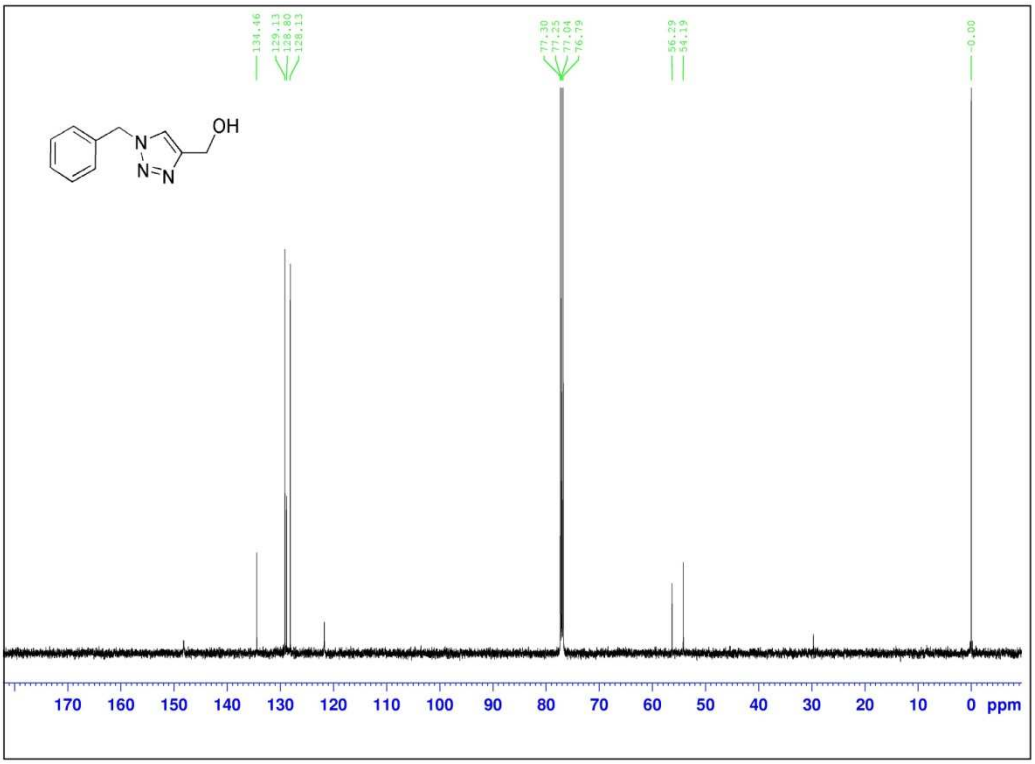


Fig. S43 ^{13}C NMR of (1-benzyl-1H-1,2,3-triazol-4-yl)methanol

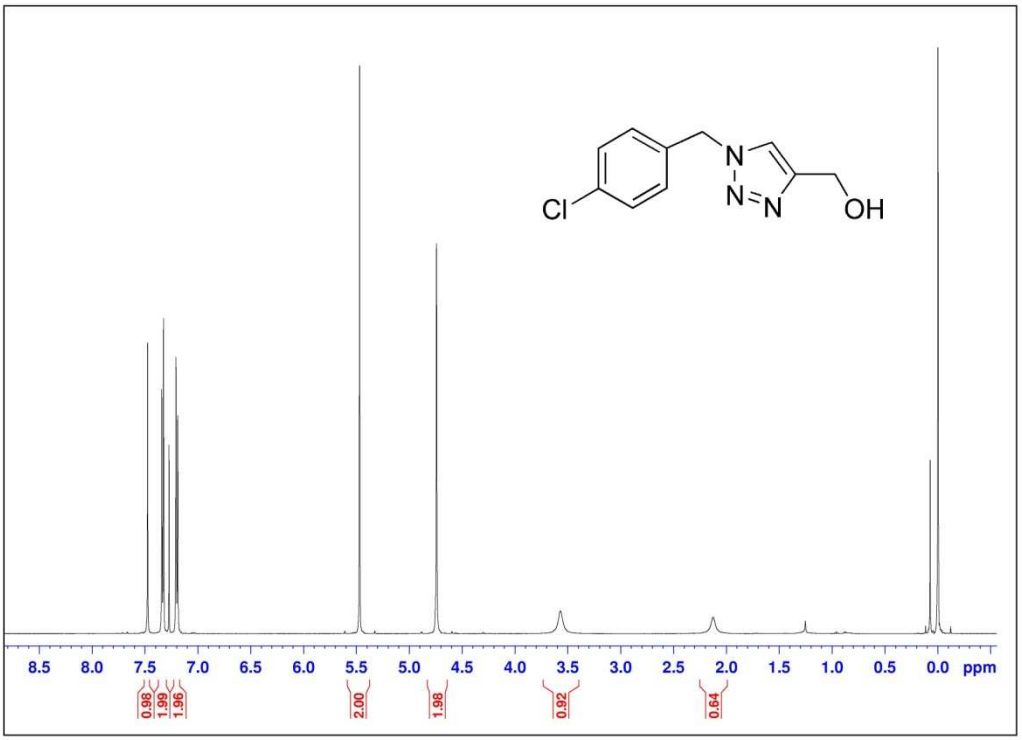


Fig. S44 ^{1}H NMR of (1-(4-chlorobenzyl)-1H-1,2,3-triazol-4-yl)methanol

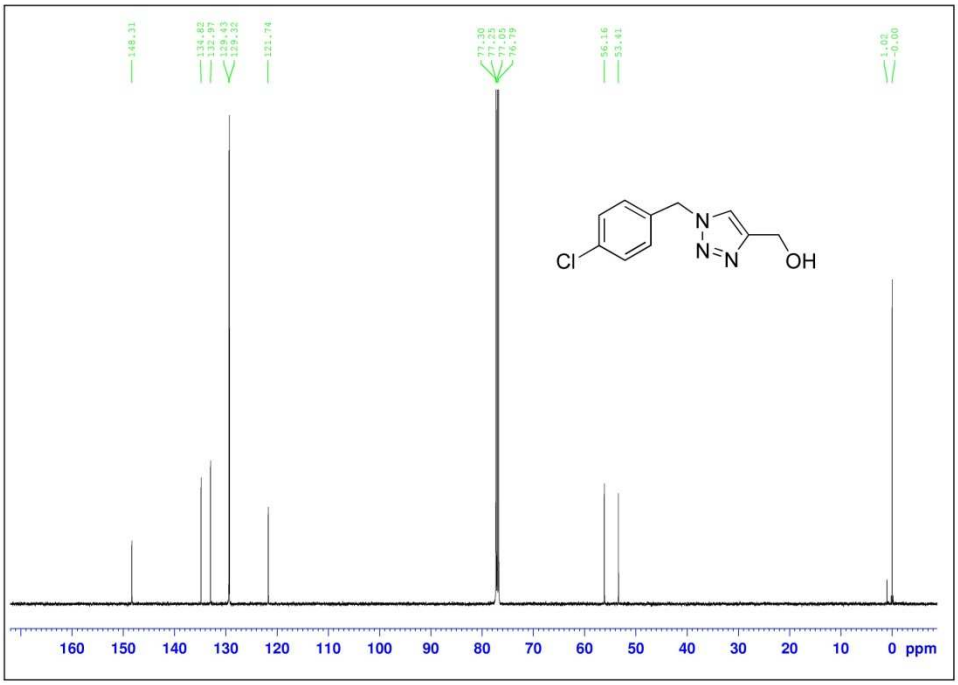


Fig. S45 ^{1}H NMR of (1-(4-chlorobenzyl)-1H-1,2,3-triazol-4-yl)methanol

References:

[1] Wilkening, I.; Signore, G. D.; Hackenberger, C. P. R. Synthesis of phosphonamidate peptides by Staudinger reactions of silylated phosphinic acids and esters. *Chem. Commun.,* **2011**, *47*, 349-351.