Synthesis of Heterogeneous Ru(II)-1,2,3-Triazole catalyst supported over SBA-15; Application to the Transfer Hydrogen reaction and unusual highly selective 1-4-disbustituted traizole formation via Multicomponent Click Reaction

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[#]Equal Contribution

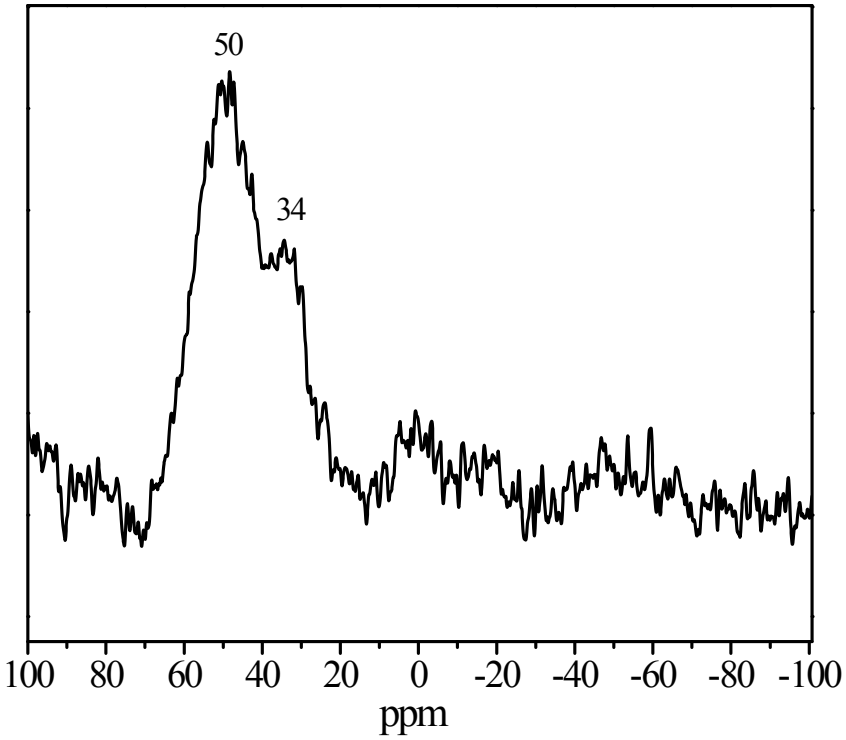


Figure S1: ^{31}P NMR of catalyst SBA-15-Tz-Ru(II)TPP.

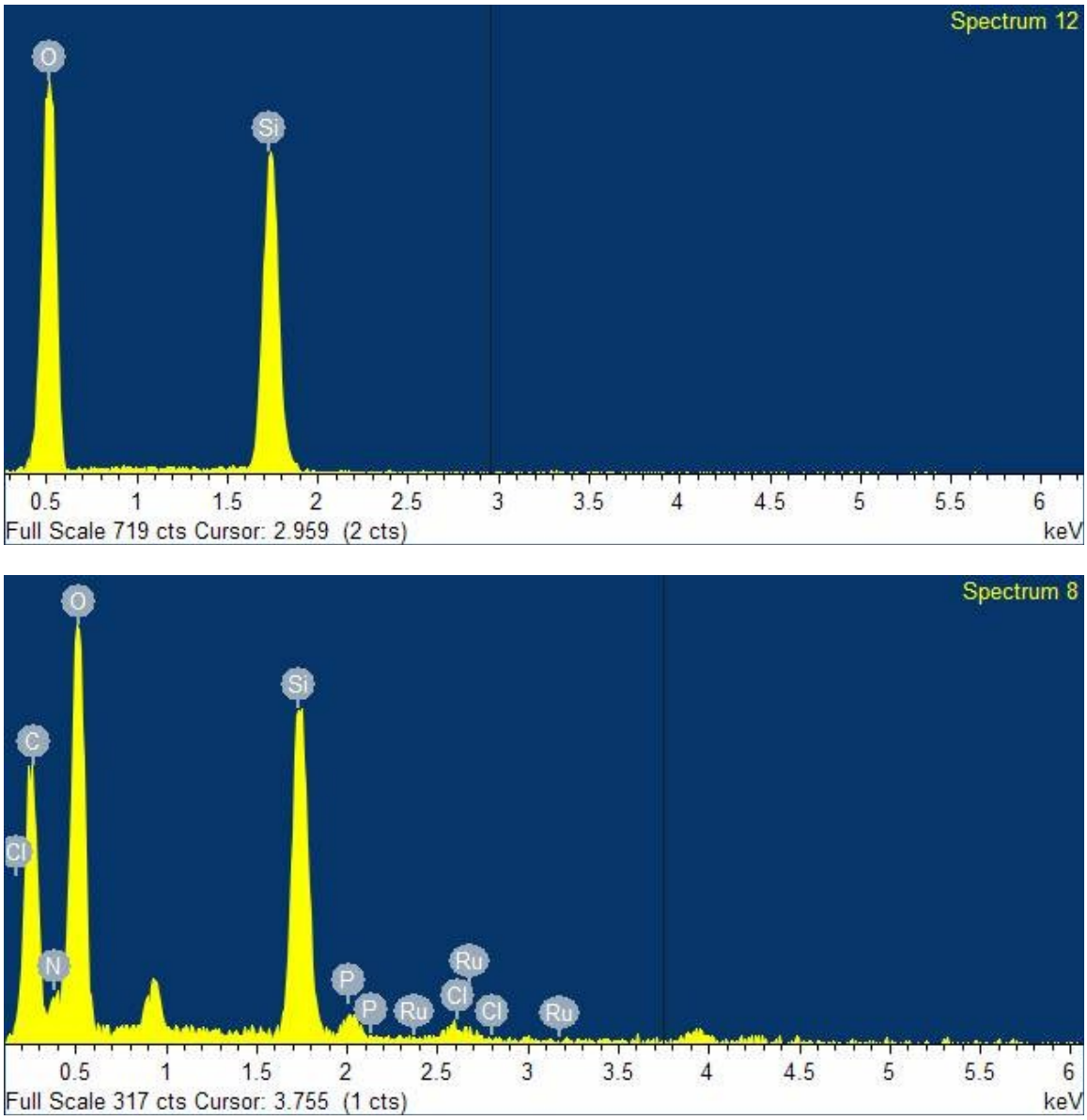


Figure S2: SEM-EDX analysis of (a) calcined SBA-15, (b) SBA-15-Tz-Ru(II)TPP.

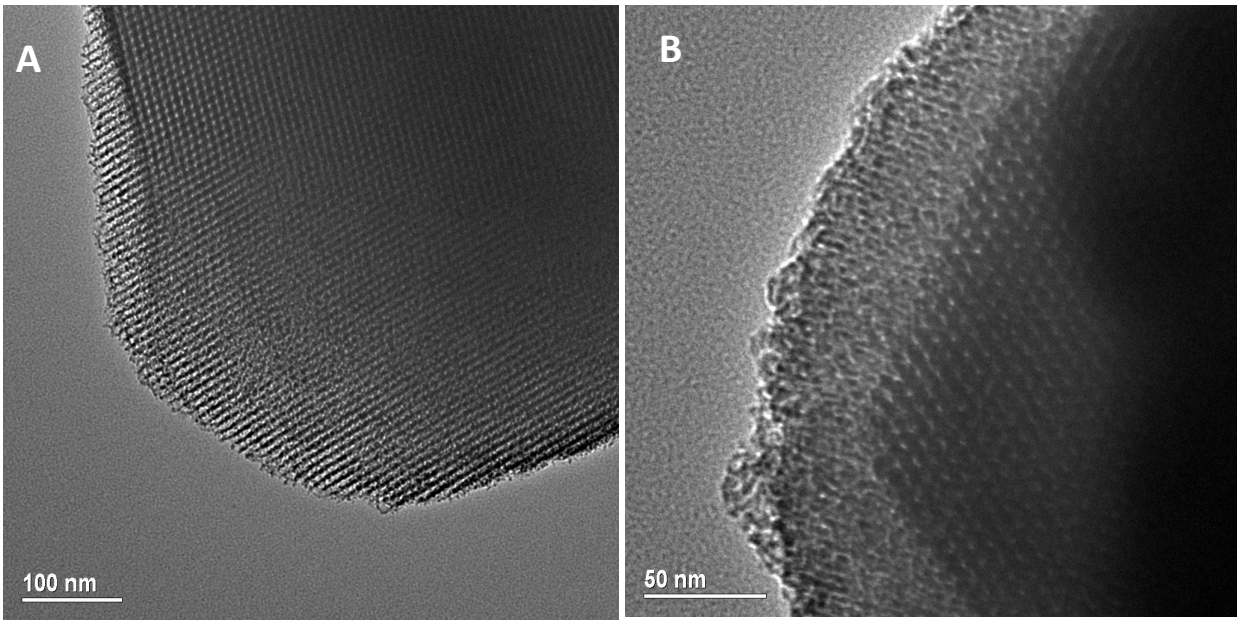


Figure S3: TEM images of calcined SBA-15 at different magnification (A) 100 nm, (B) 50 nm.

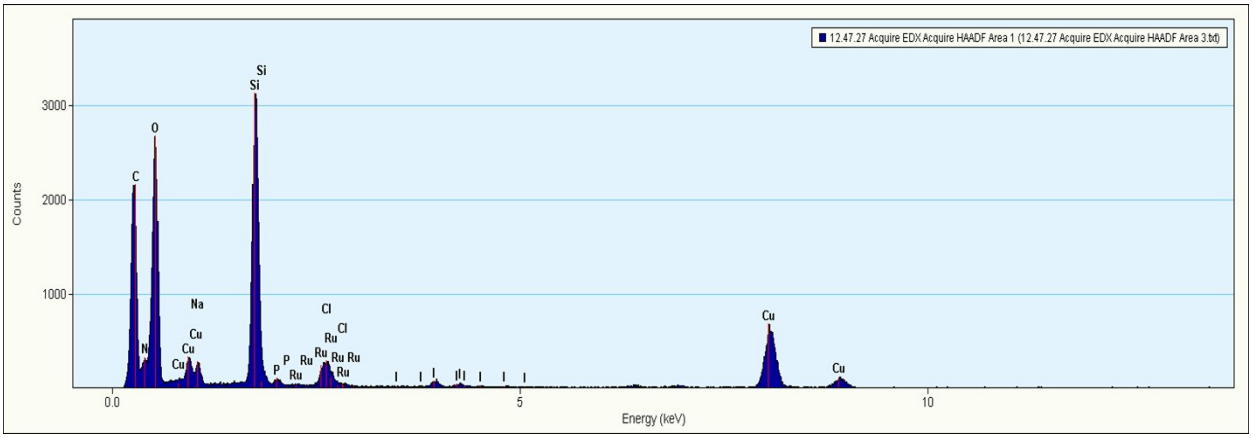


Figure S4: TEM-EDX analysis of SBA-15-Tz-Ru(II)TPP catalyst.

Sample 3 S4

Peak	Type	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
Cu 2p	Reg	930.000	2.011	1810.8	5.321	63.549	0.48	1.93
I 3d	Reg	616.600	1.543	4957.1	10.343	126.904	0.78	6.27
O 1s	Reg	530.100	1.970	10329.5	0.780	15.999	22.07	22.26
N 1s	Reg	397.900	2.699	2745.3	0.477	14.007	9.72	8.58
Ru 3d	Reg	279.400	1.508	1024.8	4.273	101.069	0.40	2.56
C 1s	Reg	282.700	2.272	9812.5	0.278	12.011	59.21	44.82
Cl 2p	Reg	195.800	2.504	620.3	0.891	35.460	1.17	2.62
P 2p	Reg	128.700	1.368	103.3	0.486	30.974	0.36	0.70
Si 2p	Reg	100.900	1.799	1131.2	0.328	28.086	5.79	10.25

Figure S5: XPS result of the SBA-15-Tz-Ru(II)TPP catalyst.

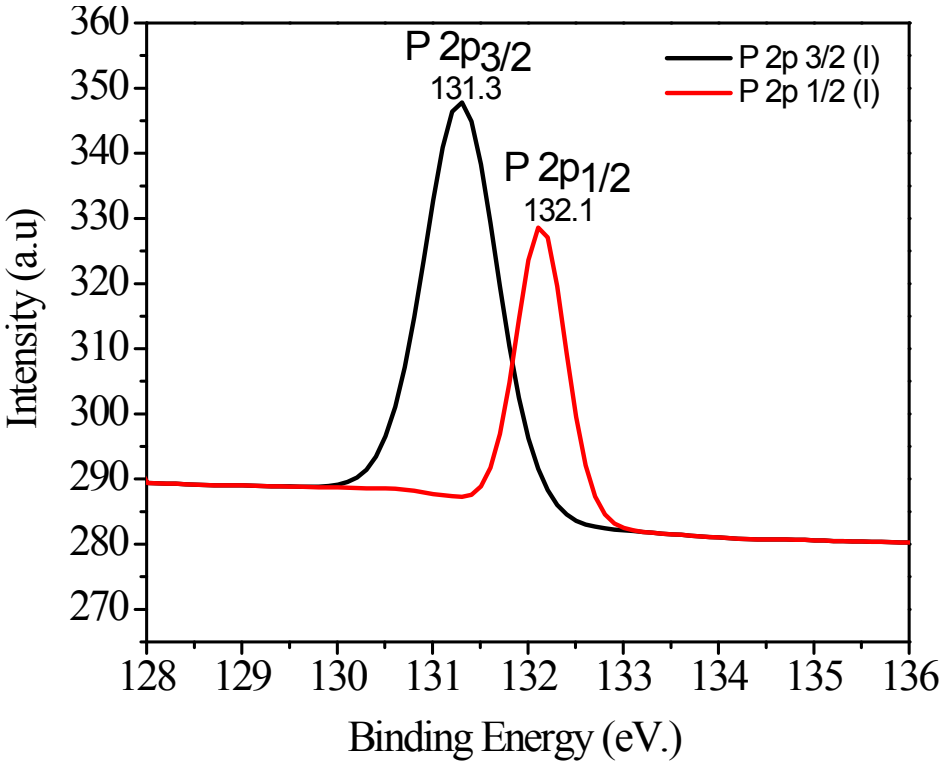


Figure S6. P XPS spectrum of SBA-15-Tz-Ru(II)TPP.

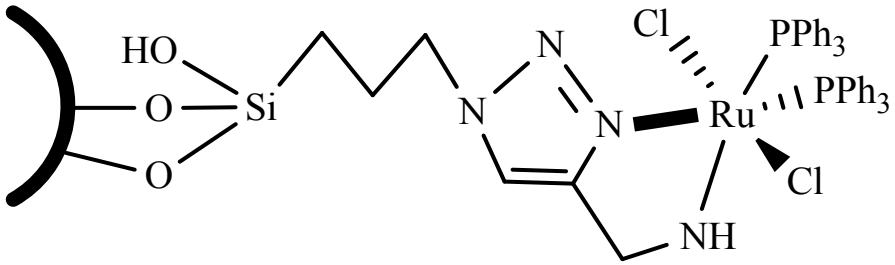
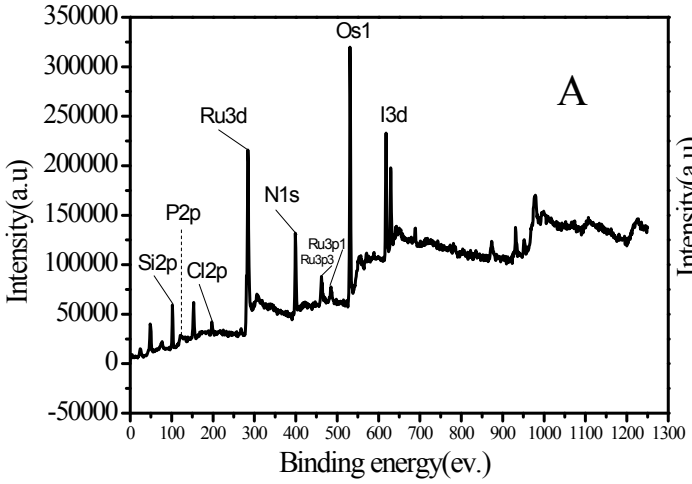
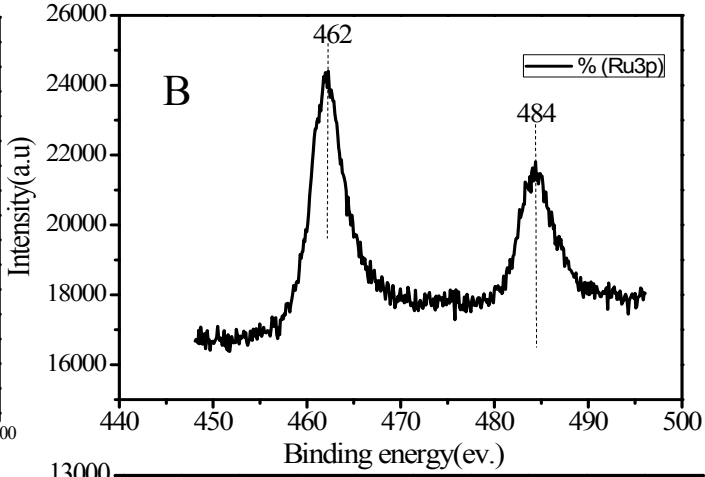
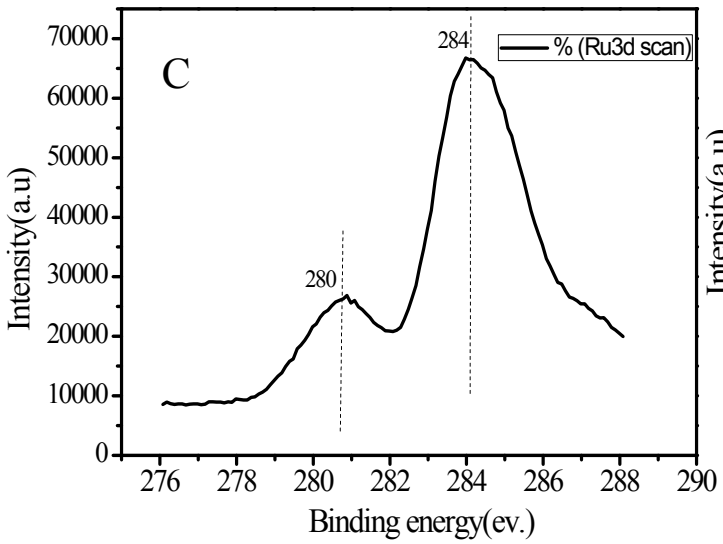
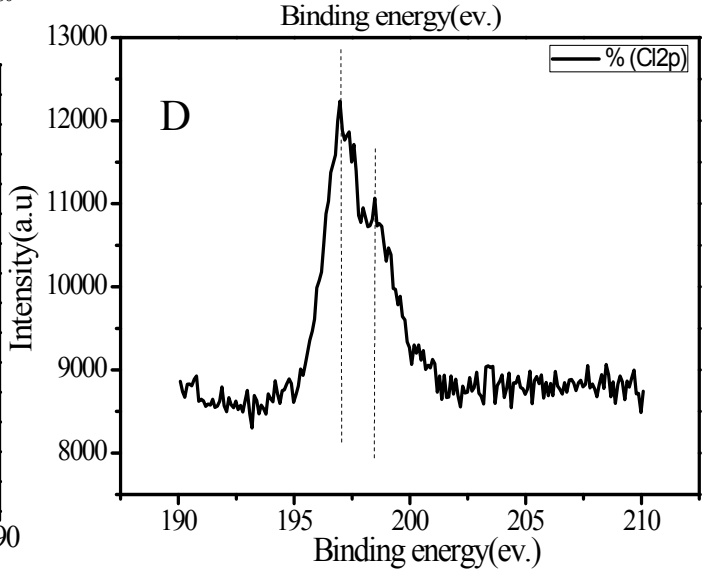


Figure S7: Other possible structure for methoxy group anchoring to Si with surface OH group.


A
Os1
Ru3d
I3d
N1s
P2p
Si2p
Cl2p
Ru3p1
Ru3p3
Intensity(a.u)
Binding energy(ev.)


B
462
484
% (Ru3p)
Intensity(a.u)
Binding energy(ev.)


C
284
280
% (Ru3d scan)
Intensity(a.u)
Binding energy(ev.)


D
% (Cl2p)
Intensity(a.u)
Binding energy(ev.)

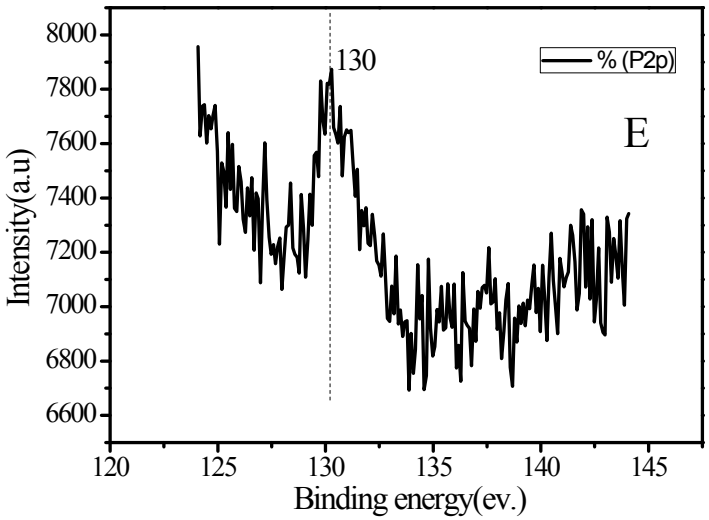

E
130
% (P2p)
Intensity(a.u)
Binding energy(ev.)

Figure S8: HR-XPS of (A) Full scan of SBA-15-Tz-Ru(II)TPP, (B) of Ru3p, (C) of Ru3d, (D) Cl2p, (E) of P2p.

	Sample	Ru
		mg/l
Fresh Catalyst	JBR-04	21.078
V^{th} Recycle catalyst	JBR-05	17.09

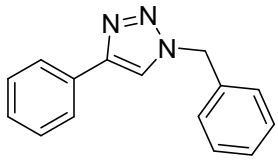
S 9: ICP Analysis

Heterogeneous catalyst SBA-15-Tz-Ru(II)TPP (0.70 gm) weight dissolvend in HF solution drop by drop to make clear solution with constant stirring. Finally milipore water is added to homogeneous solution is made up to 10 ML solution for further ICP characterization.

Table for ICP analysis Ru content.

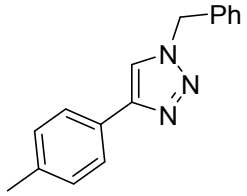
S10: Analytical Data

1-benzyl-4-phenyl-1H-1,2,3-triazole (4a).[1]



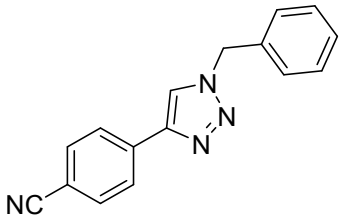
White solid, M.P. 126-128 ^{o}C, ^{1}H NMR (400MHz, CHLOROFORM-d) δ = 7.81 (d, J = 7.3 Hz, 2 H), 7.68 (s, 1 H), 7.47 - 7.28 (m, 8 H), 5.57 (s, 2 H); ^{13}C NMR (101MHz, CHLOROFORM-d) δ = 148.1, 134.6, 130.5, 129.1, 128.7, 128.7, 128.1, 128.0, 125.6, 119.5, 54.2; MS (EI) m/z = 235.1 [M^{+}].

1-benzyl-4-(p-tolyl)-1H-1,2,3-triazole (4b).[1]



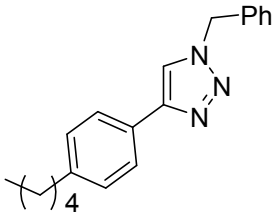
White solid, M.P. 142-144 ^{o}C, ^{1}H NMR (400 MHz, CHLOROFORM-d): δ = 2.37 (s, 3H,), 5.56 (s, 2H,), 7.17 - 7.26 (m, J=7.9 Hz, 2H), 7.30 (br. s., 1H,), 7.31 - 7.35 (m, 1H,), 7.35 - 7.43 (m, 3H,), 7.64 (s, 1H,), 7.66 - 7.77 (m, J=7.9 Hz, 2H) ppm; ^{13}C NMR (101 MHz, CHLOROFORM-d): δ = 21.2, 54.1 , 119.1, 125.5, 127.6, 128.0, 128.7, 129.1, 129.4, 134.7, 137.9, 148.2; MS (EI) m/z = 249.2 [M^{+}].

4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzonitrile (4c).[2]



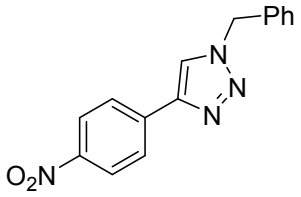
White solid, M.P. 140-142 °C, ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 7.83 - 8.01 (m, J=8.0 Hz, 2 H), 7.77 (s, 1 H), 7.53 - 7.73 (m, J=8.0 Hz, 2 H), 7.40 (br. s., 3 H), 7.28 - 7.37 (m, 2 H), 5.60 ppm (s, 2 H); ^{13}C NMR (126MHz, CHLOROFORM-d,): δ = 146.3, 134.9, 134.2, 132.6, 129.2, 129.0, 128.1, 126.0, 120.6, 118.7, 111.5, 54.4; MS (EI) m/z = 260.1 [M^{+}].

1-benzyl-4-(4-pentylphenyl)-1H-1,2,3-triazole (4d).[3]



White solid, M.P. 92-94 °C, ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 0.90 (t, J=6.9 Hz, 3H), 1.29 - 1.43 (m, 4H), 1.63 (quin, J=7.3 Hz, 2H), 2.62 (t, J=7.6 Hz, 2H), 5.57 (s, 2H), 7.17 - 7.26 (m, J=8.0 Hz, 2H), 7.30 (br. s., 1H), 7.30 - 7.34 (m, 1H), 7.34 - 7.41 (m, 3H), 7.64 (s, 1H), 7.67 - 7.78 (m, J=8.0 Hz, 2H); ^{13}C NMR (126 MHz, CHLOROFORM-d): δ = 14.0, 22.5, 31.0, 31.4, 35.6, 54.1, 119.1, 125.6, 127.9, 128.0, 128.7, 128.8, 129.1, 134.7, 143.1, 148.3; MS (EI) m/z = 263.2 [M^{+}].

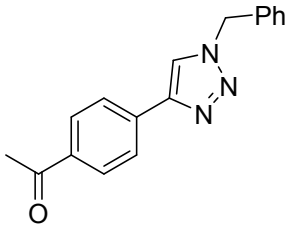
1-benzyl-4-(4-nitrophenyl)-1H-1,2,3-triazole (4e).[1]



Light yellow solid, M.P. 166-168 °C, ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 5.61 (s, 2H), 7.29 - 7.52 (m, 5H), 7.83 (s, 1H), 7.91 - 8.06 (m, J=8.8 Hz, 2H), 8.18 - 8.35 (mJ=8.8 Hz, , 2H); ^{13}C NMR (126 MHz,

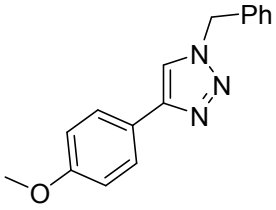
CHLOROFORM-d): δ = 54.4, 121.0, 124.2, 126.1, 128.2, 129.0, 129.3, 134.1, 136.8, 146.0, 147.3; MS (EI) m/z = 280.1 [M+].

1-(4-(1-benzyl-1H-1,2,3-triazol-4-yl)phenyl)ethan-1-one (4f).[6]



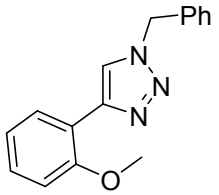
White solid, M.P. 160-162 °C, ^{1}H NMR (400 MHz, CHLOROFORM-d): δ = 2.61 (s, 3H), 5.59 (s, 2H), 7.33 (d, J=6.7 Hz, 2H), 7.36 - 7.51 (m, 3H), 7.77 (s, 1H), 7.85 - 7.94 (m, J=7.9 Hz, 2H), 7.94 - 8.09 (m, J=8.5 Hz, 2H); ^{13}C NMR (101 MHz, CHLOROFORM-d): δ = 26.6, 54.3, 120.4, 125.6, 128.1, 128.9, 129.2, 134.4, 134.9, 136.4, 147.0, 197.5, 209.0; MS (EI) m/z = 277.2 [M+].

1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (4g).[1]



White solid, M.P. 138-140 °C, ^{1}H NMR (400MHz, CHLOROFORM-d) δ = 7.80 - 7.67 (m, J = 8.5 Hz, 2 H), 7.58 (s, 1 H), 7.47 - 7.35 (m, 3 H), 7.31 (d, J = 6.7 Hz, 2 H), 7.00 - 6.85 (m, J = 8.5 Hz, 2 H), 5.56 (s, 2 H), 3.83 (s, 3 H); ^{13}C NMR (101MHz ,CHLOROFORM-d) d = 159.6, 148.1, 134.7, 129.1, 128.7, 128.0, 127.0, 123.2, 118.7, 114.2, 55.3, 54.2; MS (EI) m/z = 265.1 [M+].

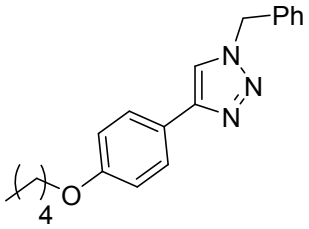
1-benzyl-4-(2-methoxyphenyl)-1H-1,2,3-triazole (4h).[5]



White solid, M.P. 168-170 °C, ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 3.85 (s, 3H), 5.55 (s, 2H), 6.92 (d, J=8.4 Hz, 1H), 7.05 (t, J=7.4 Hz, 1H), 7.21 - 7.40 (m, 6H), 7.96 (s, 1H), 8.34 (d, J=7.6 Hz, 1H); ^{13}C NMR (126

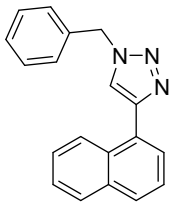
MHz, CHLOROFORM-d) δ = 53.9, 55.3, 110.7, 119.3, 120.9, 123.0, 127.6, 127.7, 128.4, 128.8, 128.9, 135.1, 143.5, 155.5; MS (EI) m/z = 265.1 [M^+].

1-benzyl-4-(4-(pentyloxy)phenyl)-1H-1,2,3-triazole (4i).[4]



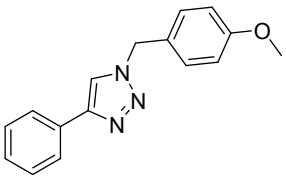
White solid, M.P. 116-118 °C, ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 7.65 - 7.82 (m, J=8.8 Hz, 2 H), 7.57 (s, 1 H), 7.35 - 7.50 (m, 3 H), 7.32 (d, J=6.5 Hz, 2 H), 6.83 - 7.06 (m, J=8.4 Hz, 2 H), 5.57 (s, 2 H), 3.98 (t, J=6.5 Hz, 2 H), 1.80 (quin, J=6.9 Hz, 2 H), 1.32 - 1.52 (m, 4 H), 0.94 ppm (t, J=7.1 Hz, 3 H); ^{13}C NMR (126MHz, CHLOROFORM-d): δ = 159.2, 148.2, 134.8, 129.1, 128.7, 128.0, 127.0, 123.0, 118.6, 114.8, 68.1, 54.2, 28.9, 28.2, 22.5, 14.0; MS (EI) m/z = 265.1 [M^+].

1-benzyl-4-(naphthalen-1-yl)-1H-1,2,3-triazole (4j).[7]



White solid, M.P. 74-76 °C, ^{1}H NMR (400MHz, CHLOROFORM-d) : δ = 8.38 (dd, J=5.8, 3.4 Hz, 1 H), 7.82 - 7.99 (m, 2 H), 7.73 (s, 1 H), 7.70 (d, J=6.7 Hz, 1 H), 7.47 - 7.59 (m, 3 H), 7.31 - 7.44 (m, 4 H), 5.67 ppm (s, 2 H); ^{13}C NMR (101MHz, CHLOROFORM-d): δ = 147.3, 134.6, 133.8, 131.0, 129.2, 128.9, 128.8, 128.4, 128.1, 128.0, 127.2, 126.6, 125.9, 125.4, 125.3, 122.4, 54.3; MS (EI) m/z = 285.1 [M^+].

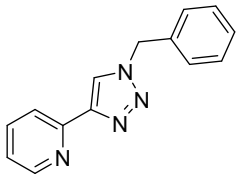
1-(4-methoxybenzyl)-4-phenyl-1H-1,2,3-triazole[8] (4k)



White solid, M.P. 134-136 °C; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.81 - 7.77 (m, 2 H), 7.64 (s, 1 H), 7.42 - 7.36 (m, 2 H), 7.31 (d, *J* = 7.2 Hz, 1 H), 7.25 (s, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 5.49 (s, 2 H),

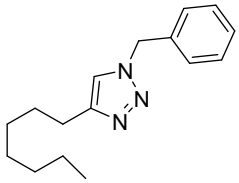
3.80 (s, 3 H): ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 159.9, 148.0, 130.5, 129.6, 128.7, 128.0, 126.6, 125.6, 119.3, 114.4, 55.3, 53.7

2-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine [9] (4l)



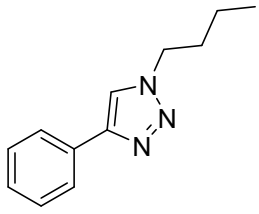
White solid, M.P. 114-116 °C; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 8.54 (d, *J* = 4.2 Hz, 1 H), 8.18 (d, *J* = 8.0 Hz, 1 H), 8.06 (s, 1 H), 7.77 (dt, *J* = 1.7, 7.7 Hz, 1 H), 7.43 - 7.32 (m, 5 H), 7.21 (ddd, *J* = 1.0, 5.5, 6.9 Hz, 1 H), 5.59 (s, 2 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 150.2, 149.3, 148.7, 136.9, 134.3, 129.2, 128.8, 128.3, 122.8, 121.9, 120.2, 54.4.

1-benzyl-4-heptyl-1H-1,2,3-triazole [8] (4m)



White solid, M.P. 66-68 °C; ^{1}H NMR (400MHz ,CHLOROFORM-d) d = 7.20 - 7.09 (m, 3 H), 7.04 (d, *J* = 7.9 Hz, 2 H), 6.99 - 6.90 (m, 1 H), 5.28 (s, 2 H), 2.47 (t, *J* = 7.9 Hz, 2 H), 1.42 (quin, *J* = 7.3 Hz, 2 H), 1.13 - 0.99 (m, 10 H), 0.66 (t, *J* = 6.7 Hz, 3 H); ^{13}C NMR (101MHz ,CHLOROFORM-d) d = 149.0, 135.0, 129.0, 128.9, 128.5, 127.9, 120.4, 53.9, 31.8, 29.4, 29.3, 29.2, 29.2, 29.0, 25.7, 22.6, 14.1;

1-butyl-4-phenyl-1H-1,2,3-triazole[10] (4n)



Colorless thick liquid; ^{1}H NMR (400MHz ,CHLOROFORM-d) d = 7.83 (d, *J* = 7.3 Hz, 2 H), 7.75 (s, 1 H), 7.46 - 7.37 (m, 2 H), 7.33 (d, *J* = 7.3 Hz, 1 H), 4.39 (t, *J* = 7.3 Hz, 2 H), 1.99 - 1.88 (m, 2 H), 1.47 - 1.31 (m, 2 H), 0.97 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (101MHz ,CHLOROFORM-d) d = 147.6, 130.7, 128.7, 128.0, 125.6, 119.4, 50.0, 32.2, 19.6, 13.4

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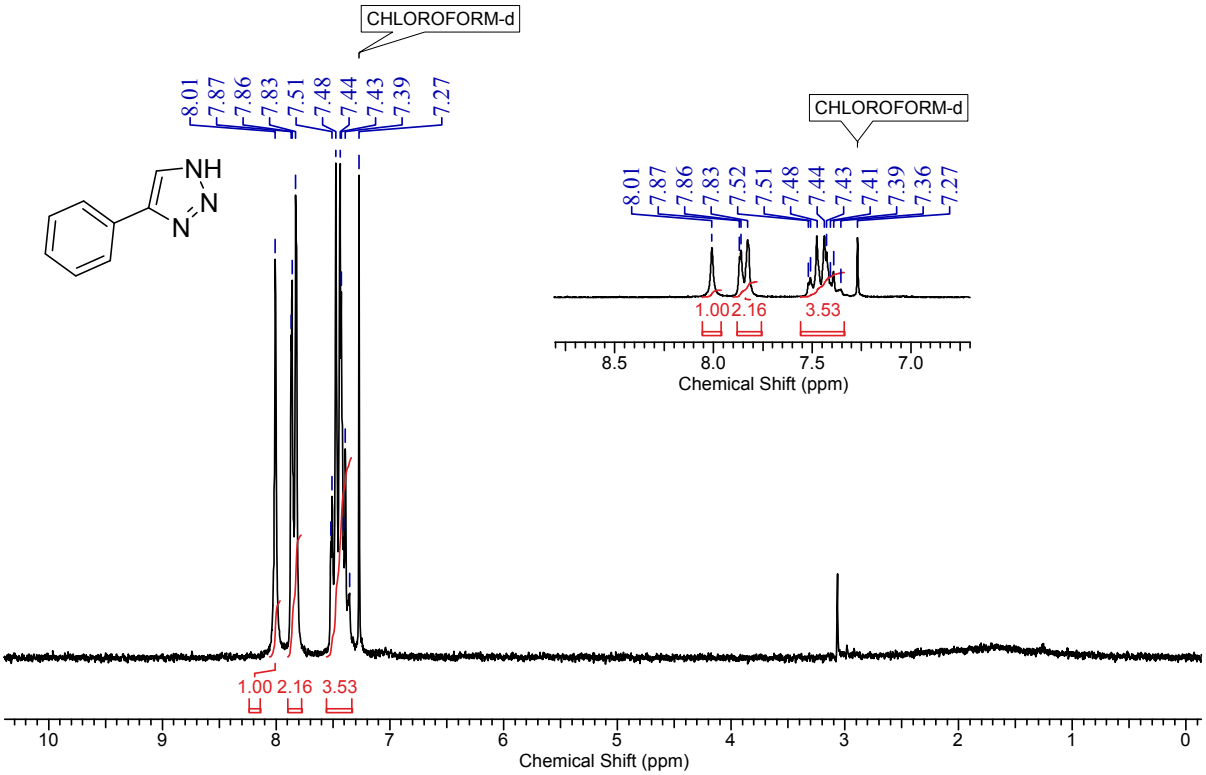
Figure S11 a : ^{1}H NMR of Intermediate 4-phenyl-1H-1,2,3-triazole



NMR in $CDCl_3$

NMR in DMSO

Figure S11 b: ^1H NMR of Intermediate 4-phenyl-1H-1,2,3-triazole

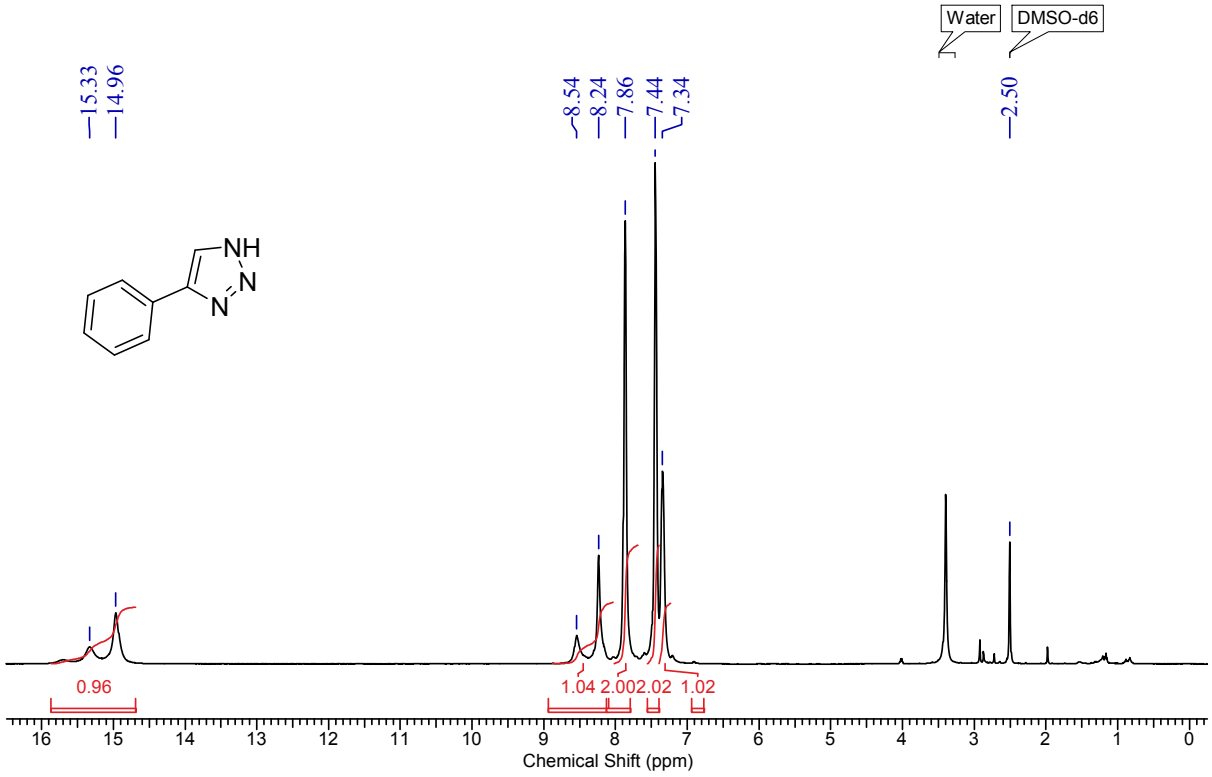
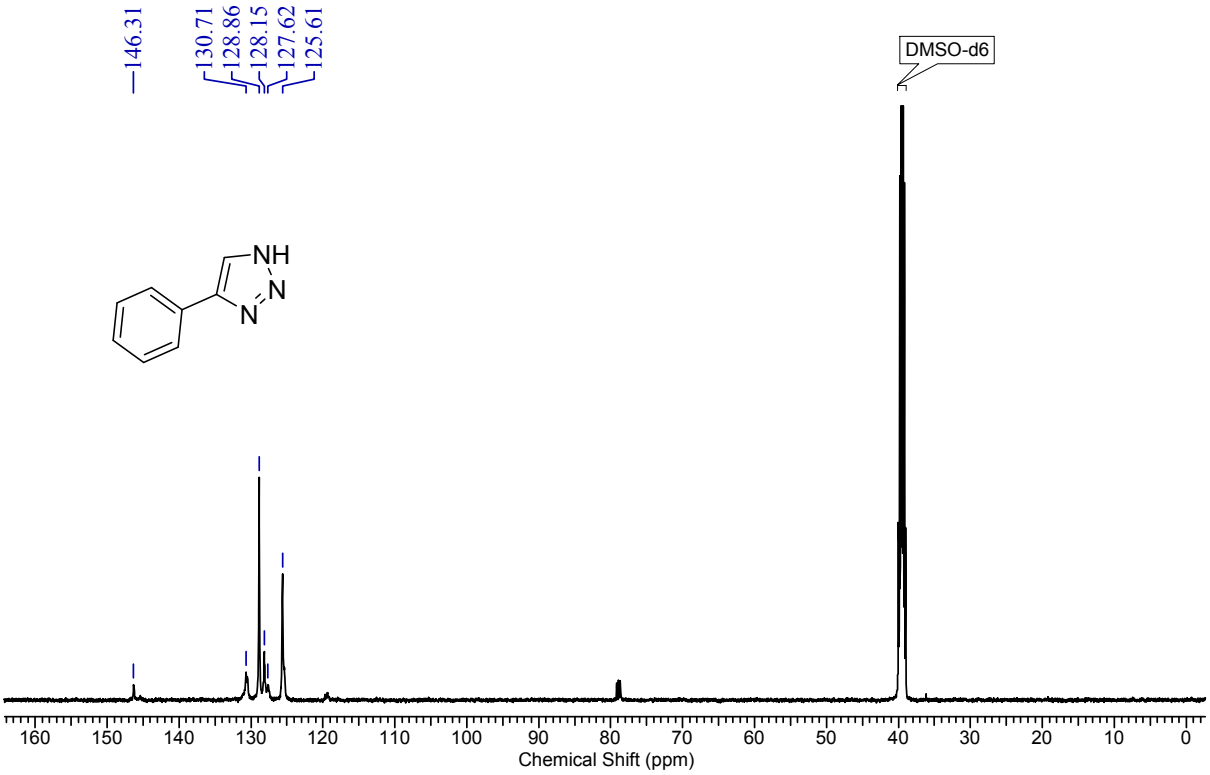
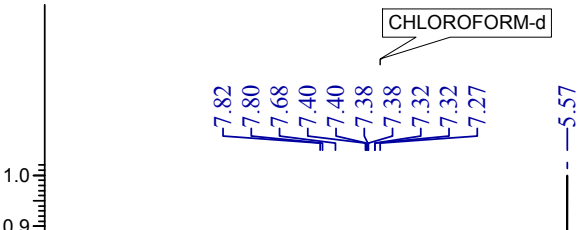


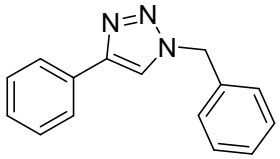
Figure S11 C : ^{13}C NMR of Intermediate 4-phenyl-1H-1,2,3-triazole



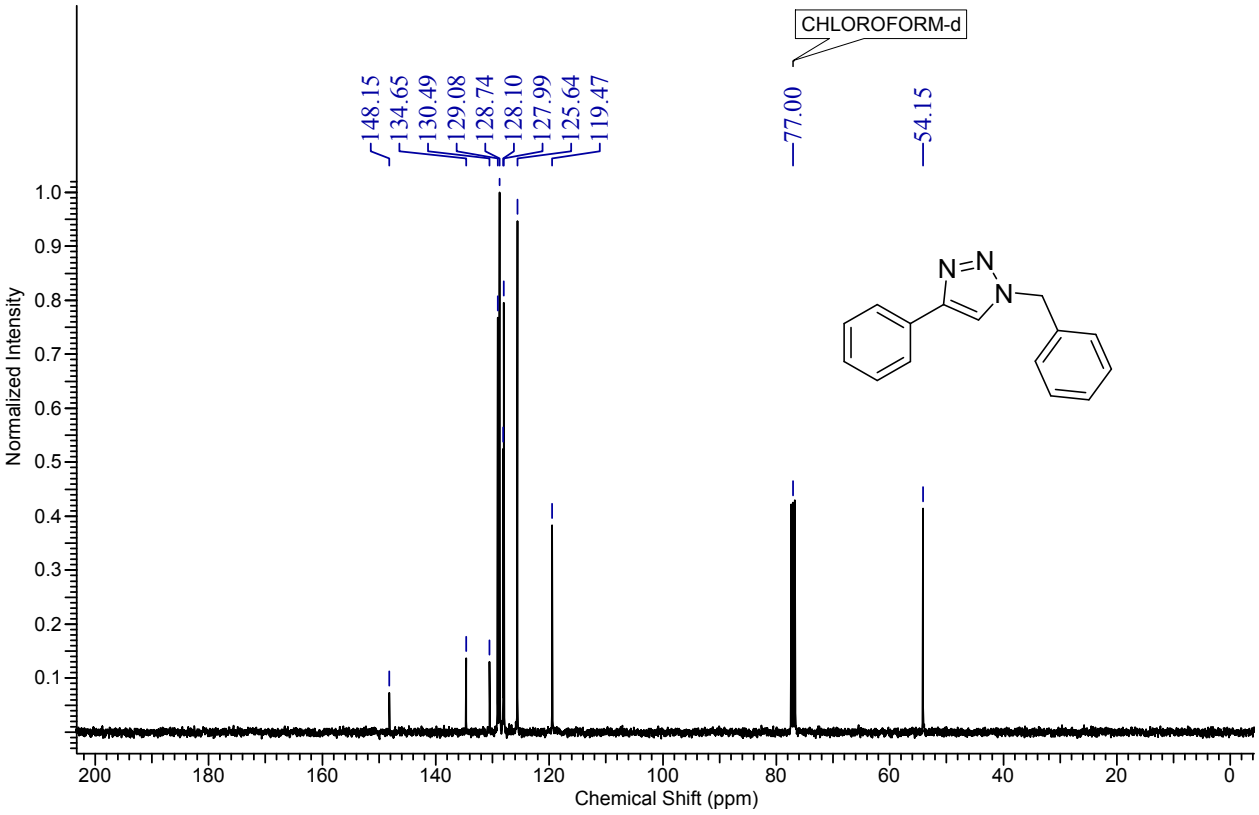
[redacted]

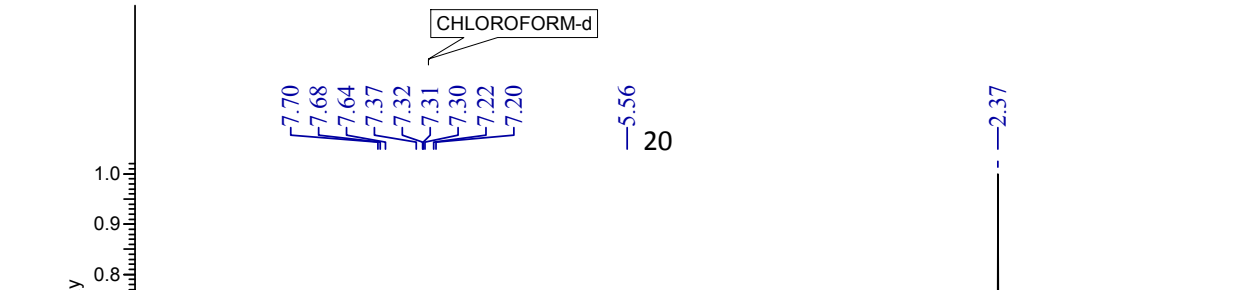
^{1}H 1-benzyl-4-phenyl-1H-1,2,3-triazole (4a)

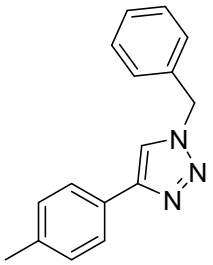




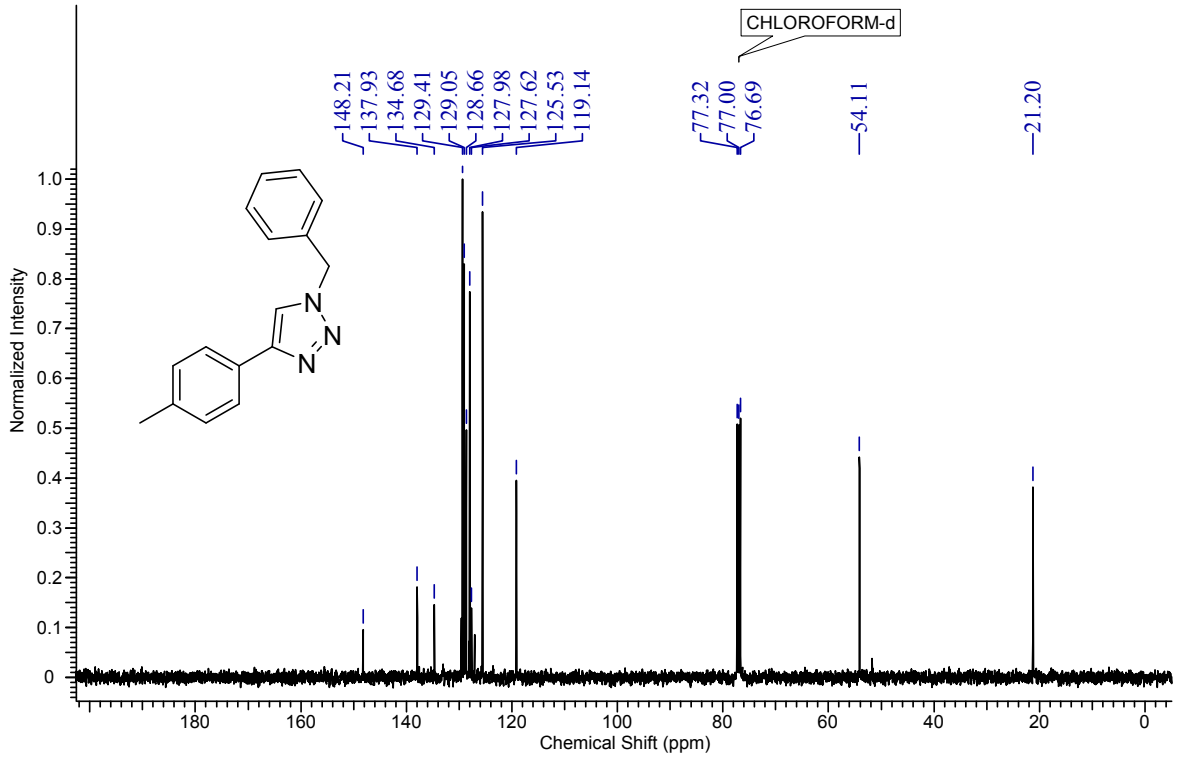
^{13}C 1-benzyl-4-phenyl-1H-1,2,3-triazole (4a).



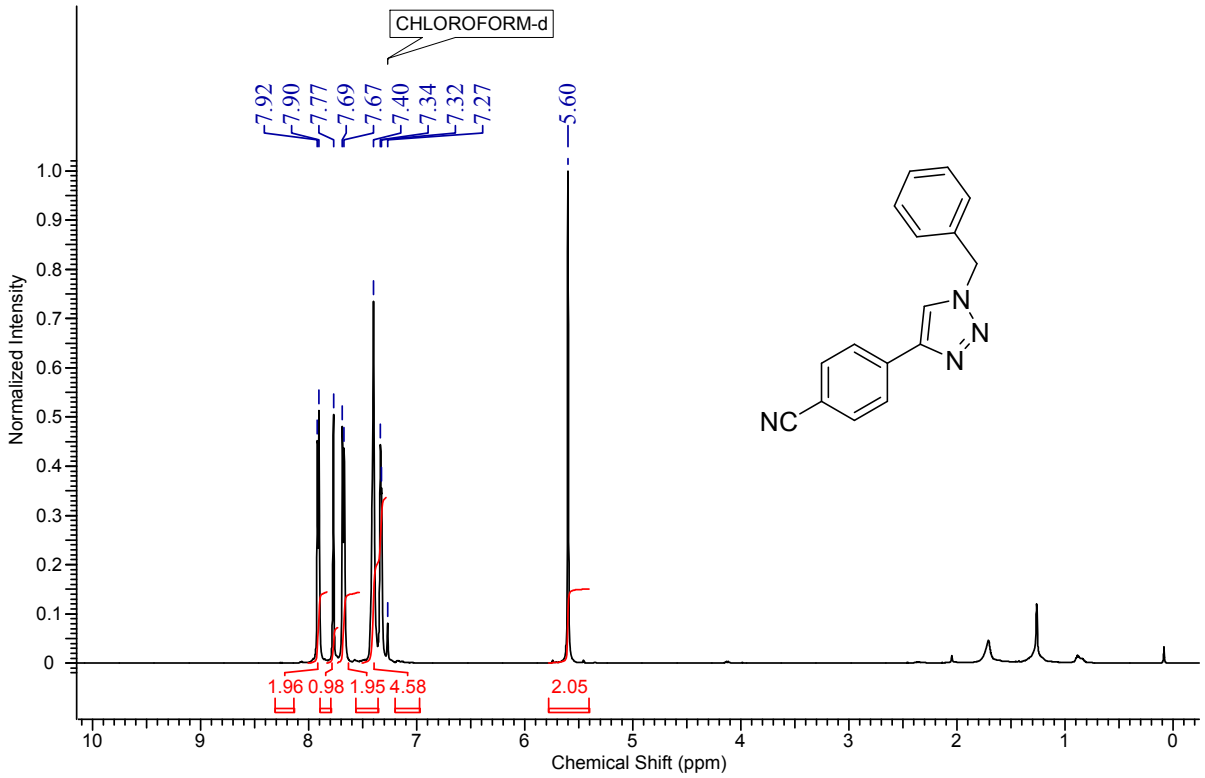




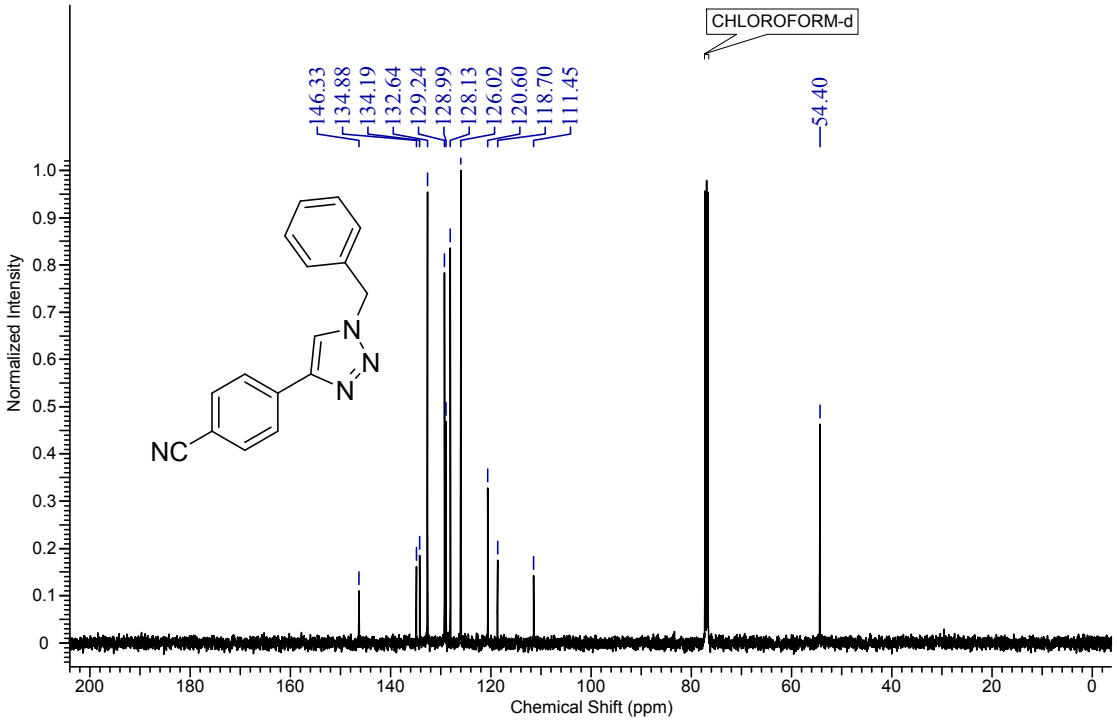
^{13} C 1-benzyl-4-(p-tolyl)-1H-1,2,3-triazole (4b).



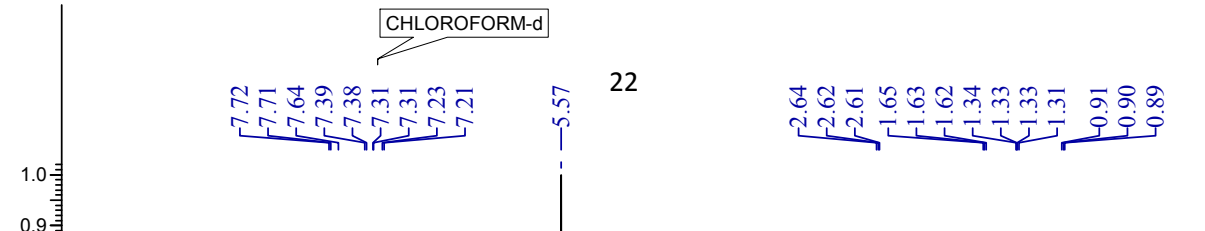
4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzonitrile (4c).

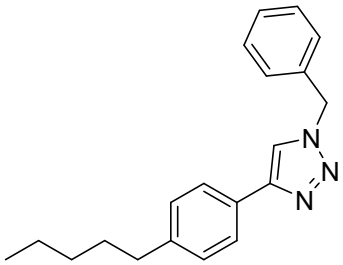


4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzonitrile (4c).

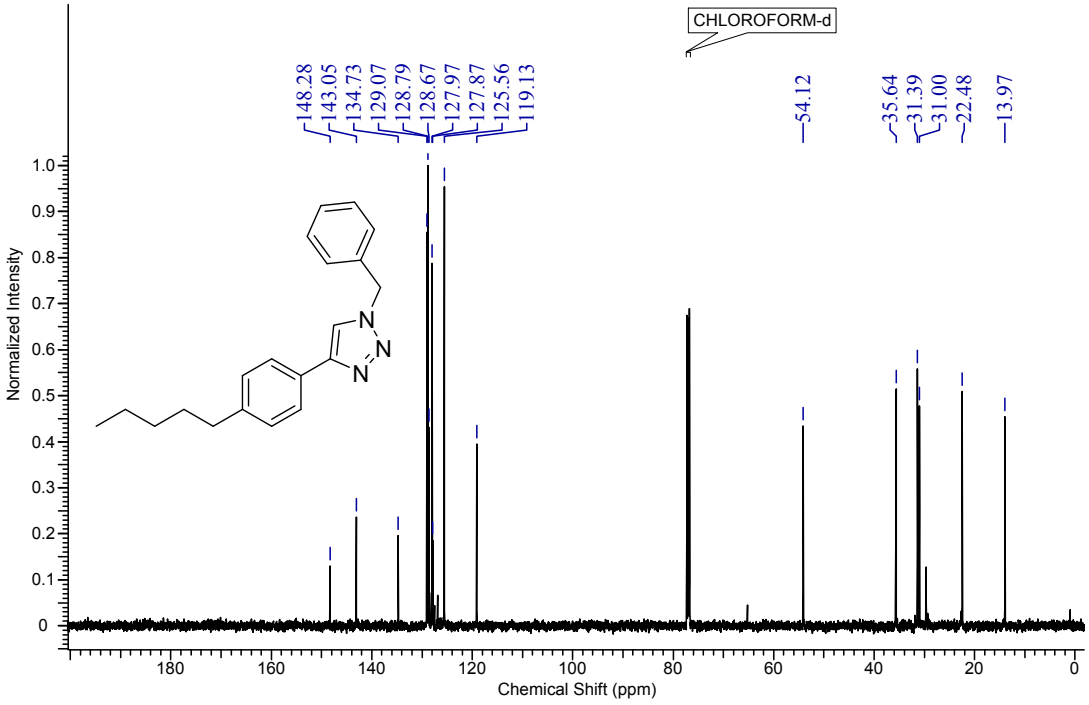


^{1}H 1-benzyl-4-(4-pentylphenyl)-1H-1,2,3-triazole (4d).

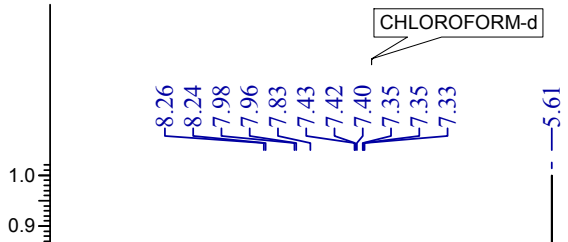


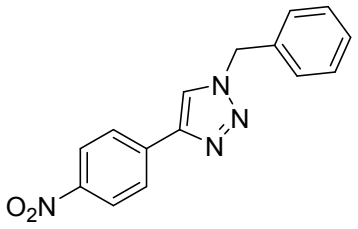


^{13}C 1-benzyl-4-(4-pentylphenyl)-1H-1,2,3-triazole (4d).



^{1}H 1-benzyl-4-(4-nitrophenyl)-1H-1,2,3-triazole (4e).





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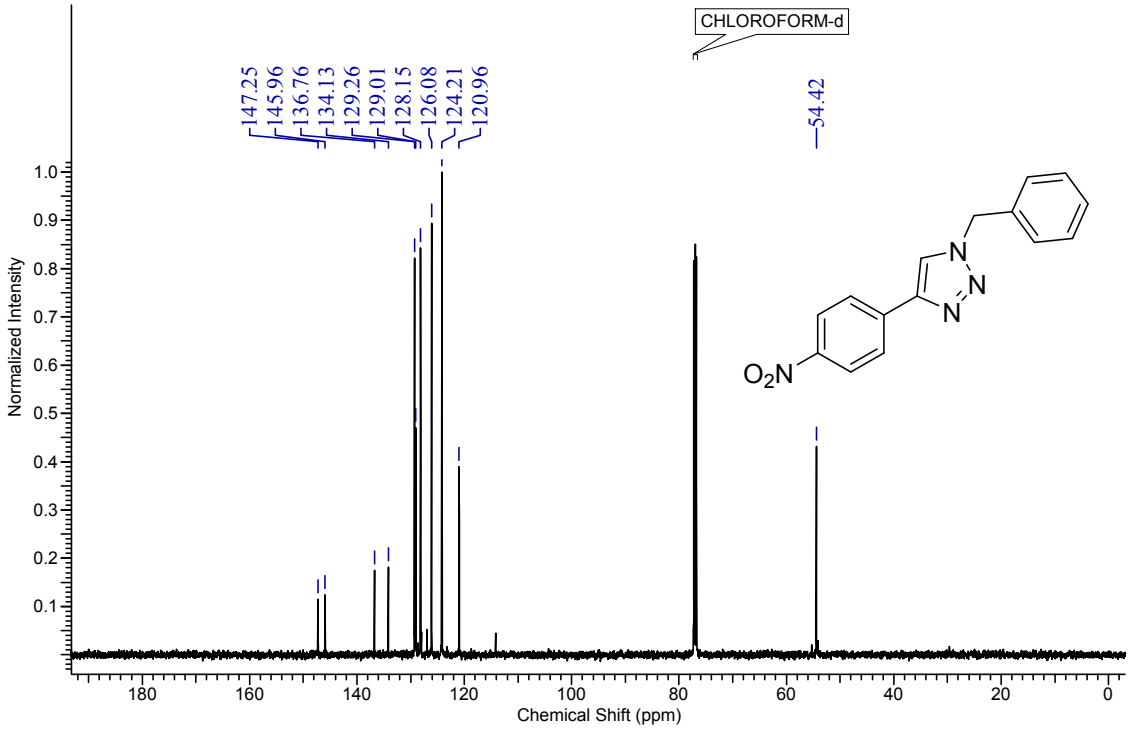
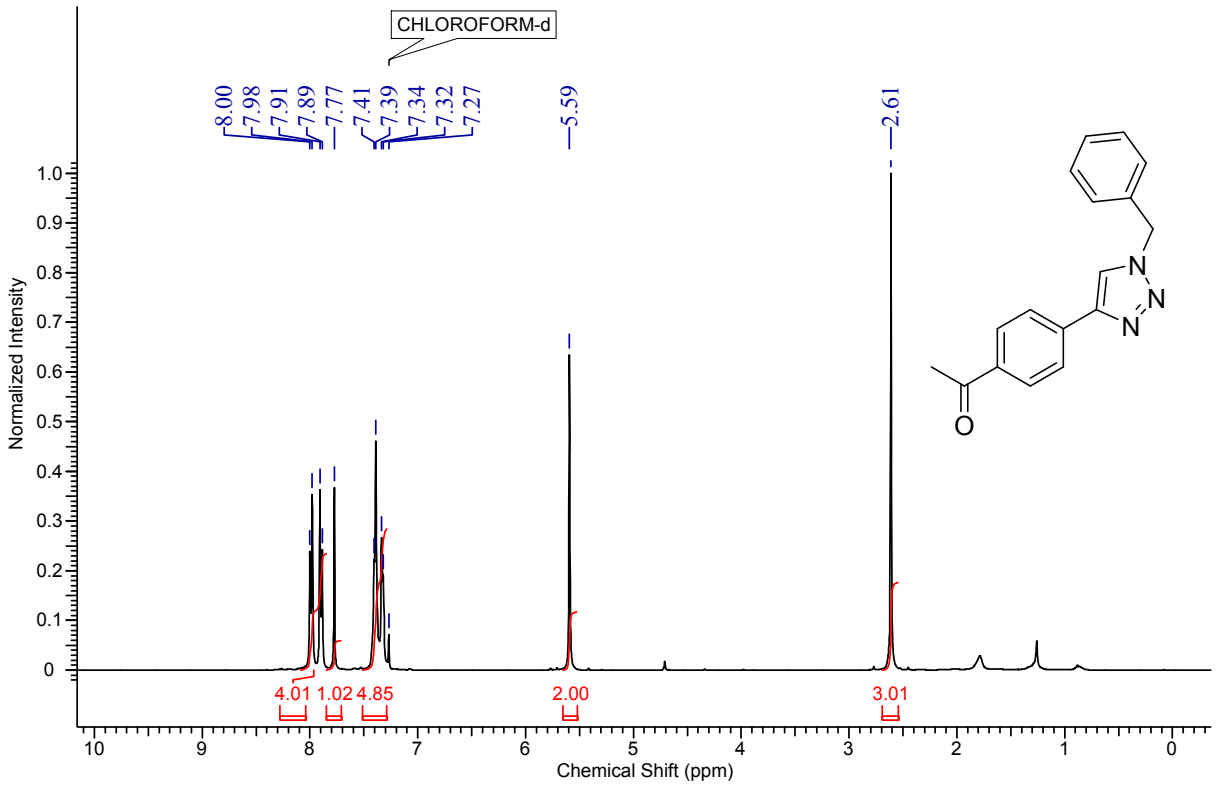
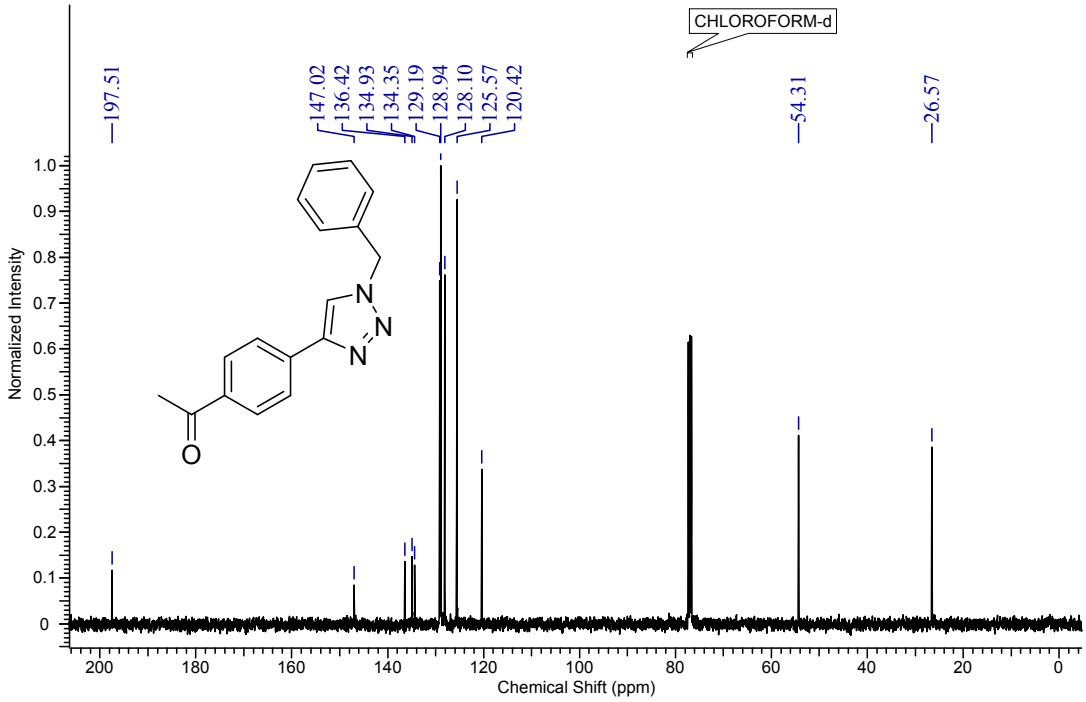


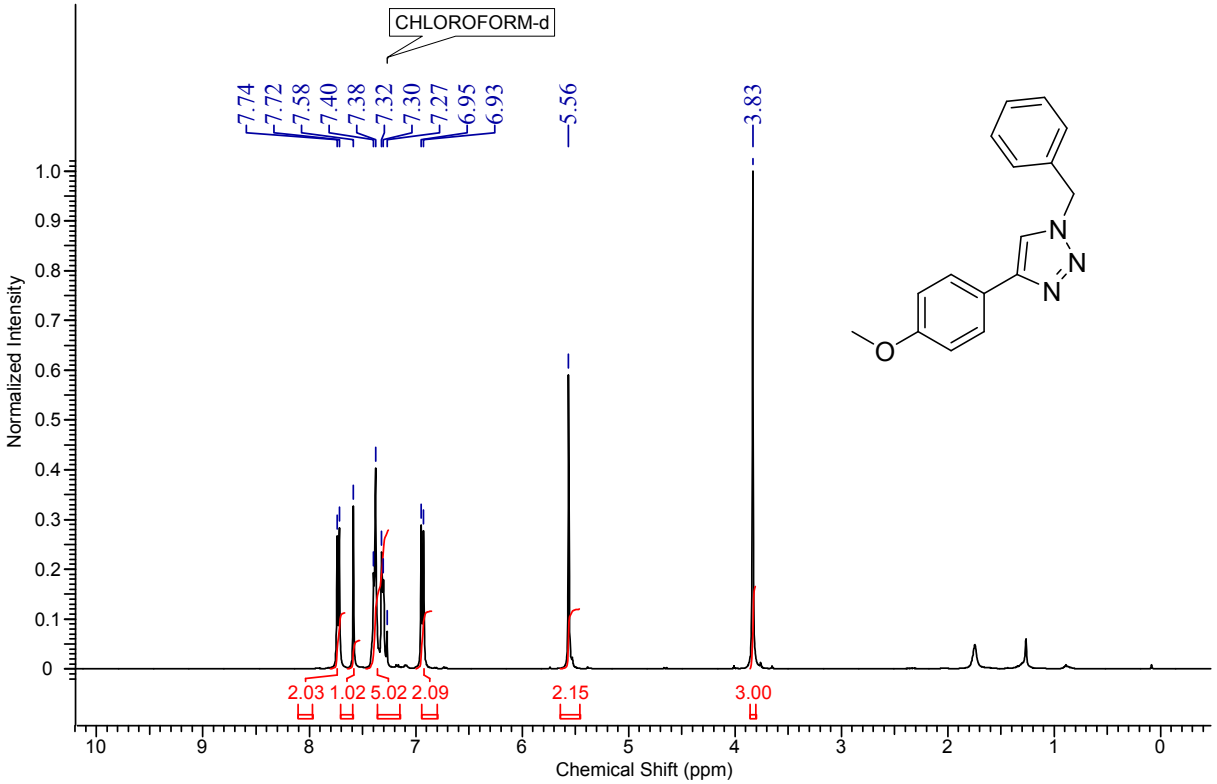
^{1}H 1-(4-(1-benzyl-1H-1,2,3-triazol-4-yl)phenyl)ethan-1-one (4f).



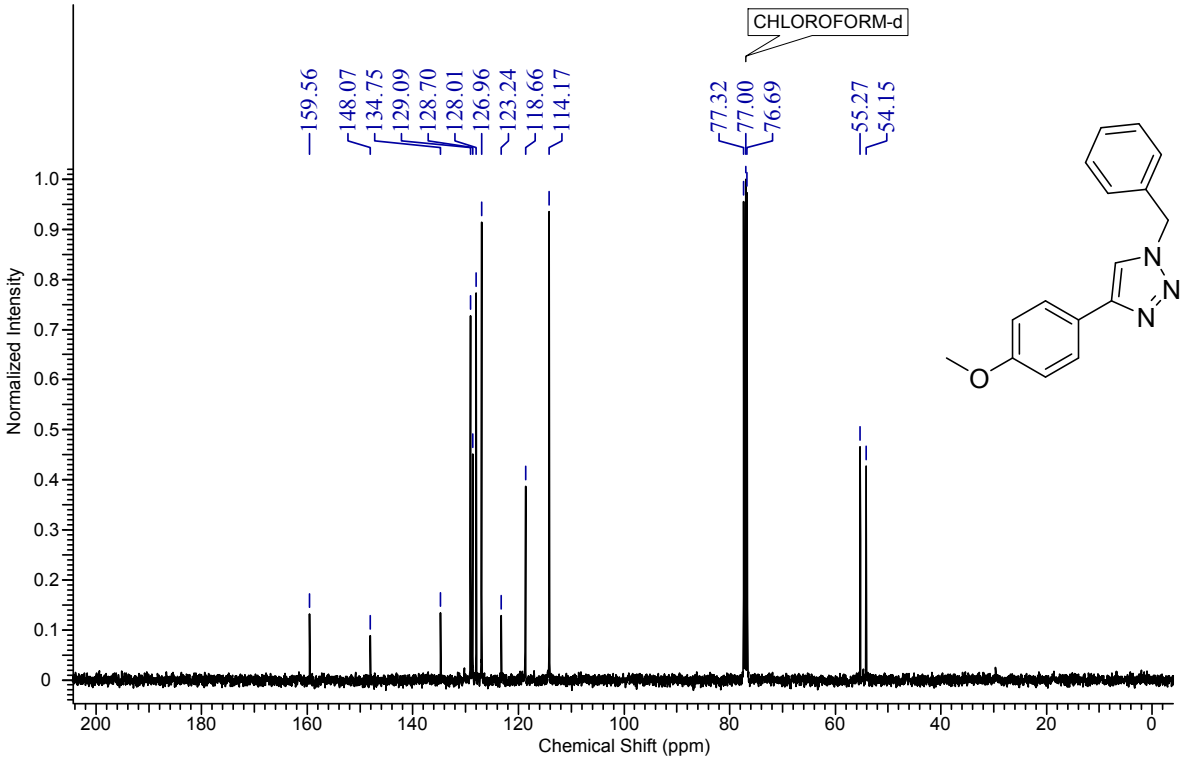
^{13}C 1-(4-(1-benzyl-1H-1,2,3-triazol-4-yl)phenyl)ethan-1-one (4f).



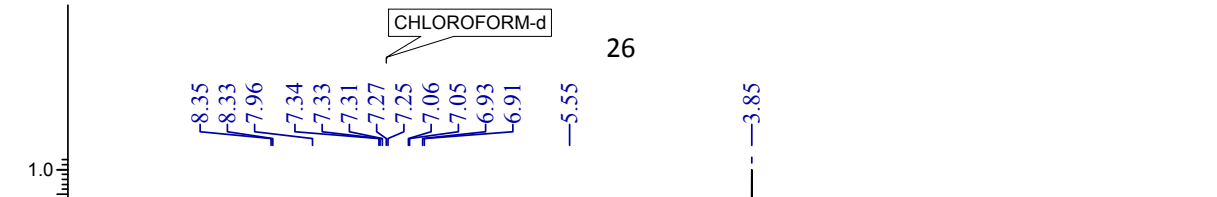
^{1}H 1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (4g).

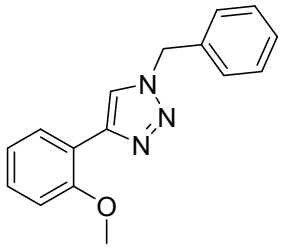


^{13}C 1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (4g).

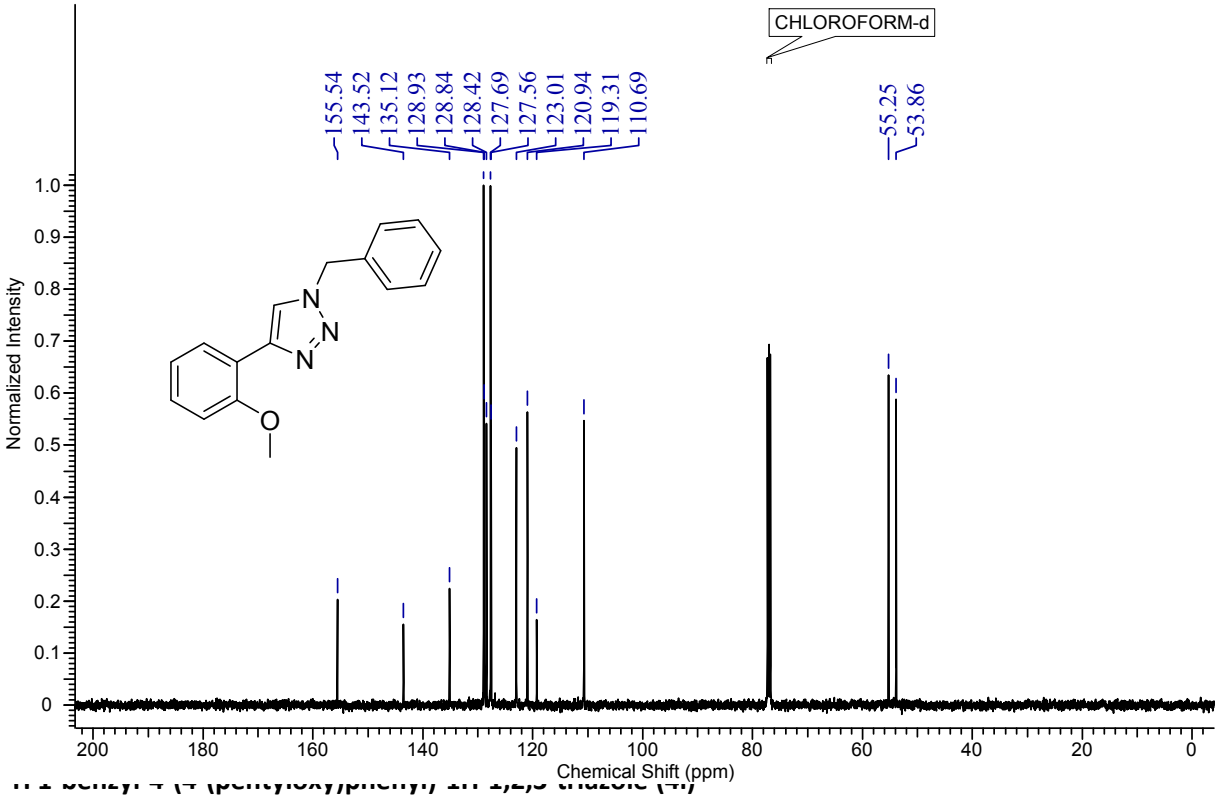


^{1}H1-benzyl-4-(2-methoxyphenyl)-1H-1,2,3-triazole (4h).

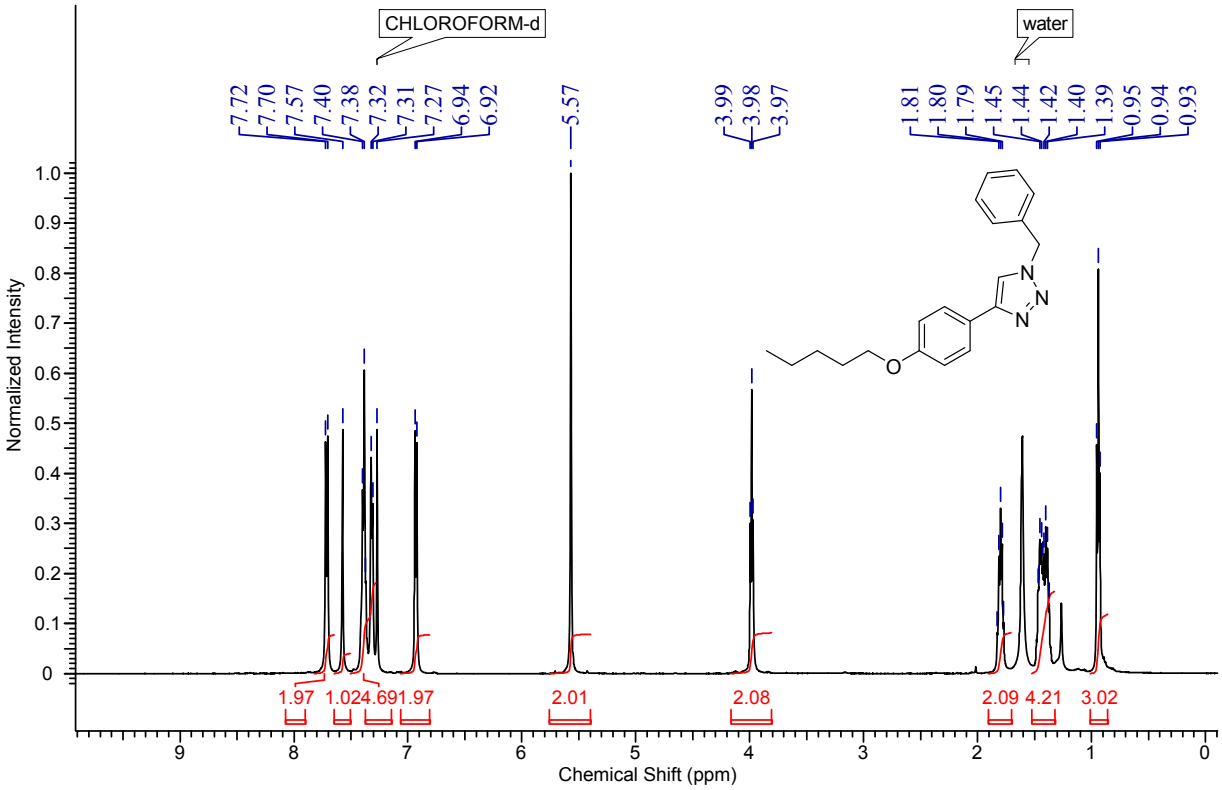




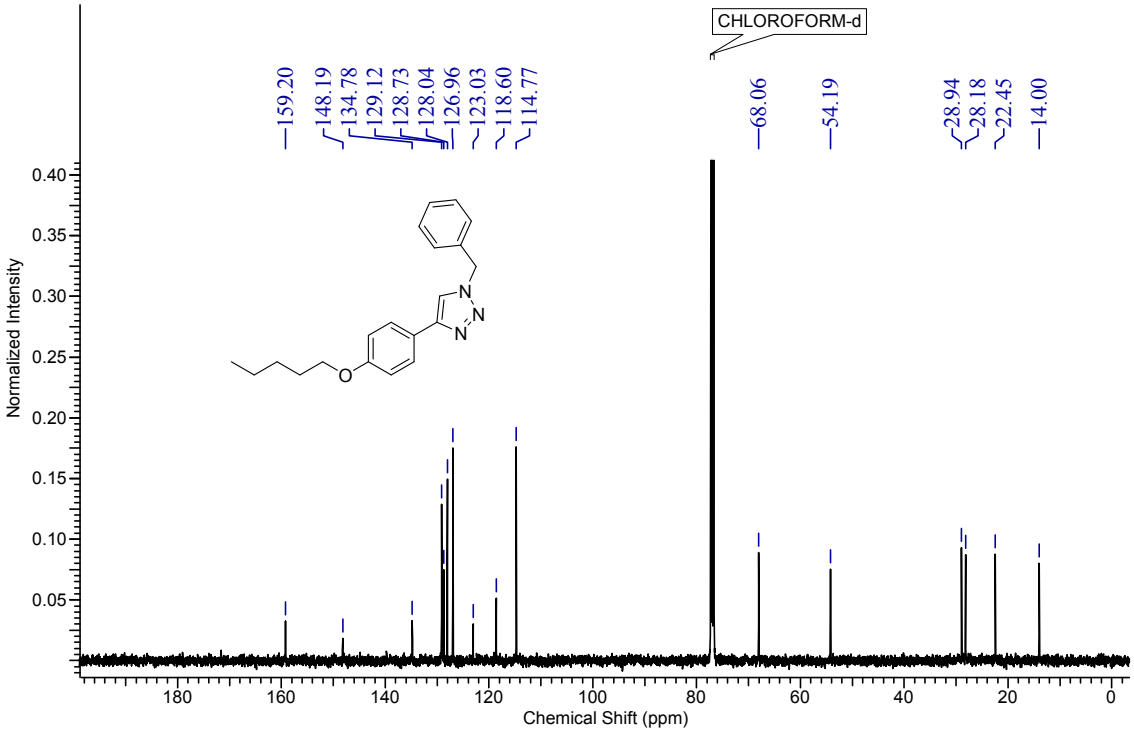
^{13}C1-benzyl-4-(2-methoxyphenyl)-1H-1,2,3-triazole (4h).



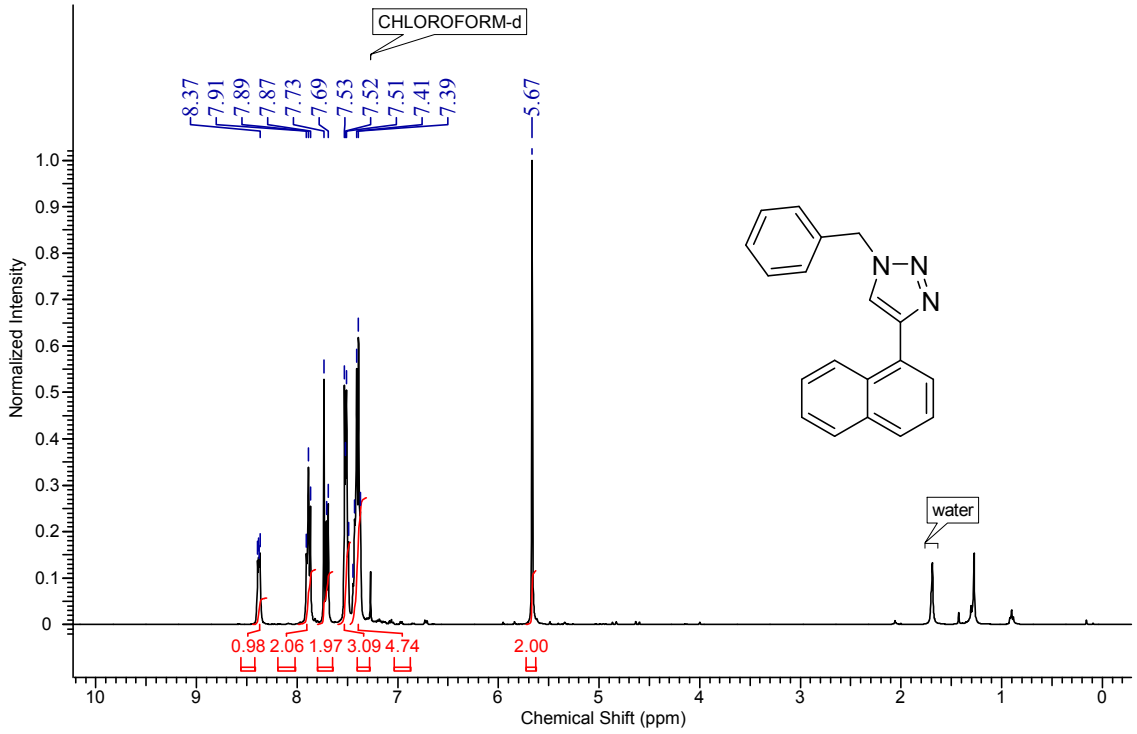
1-1-benzyl-4-(4-(pentyloxy)phenyl)-1H-1,2,3-triazole (4i)



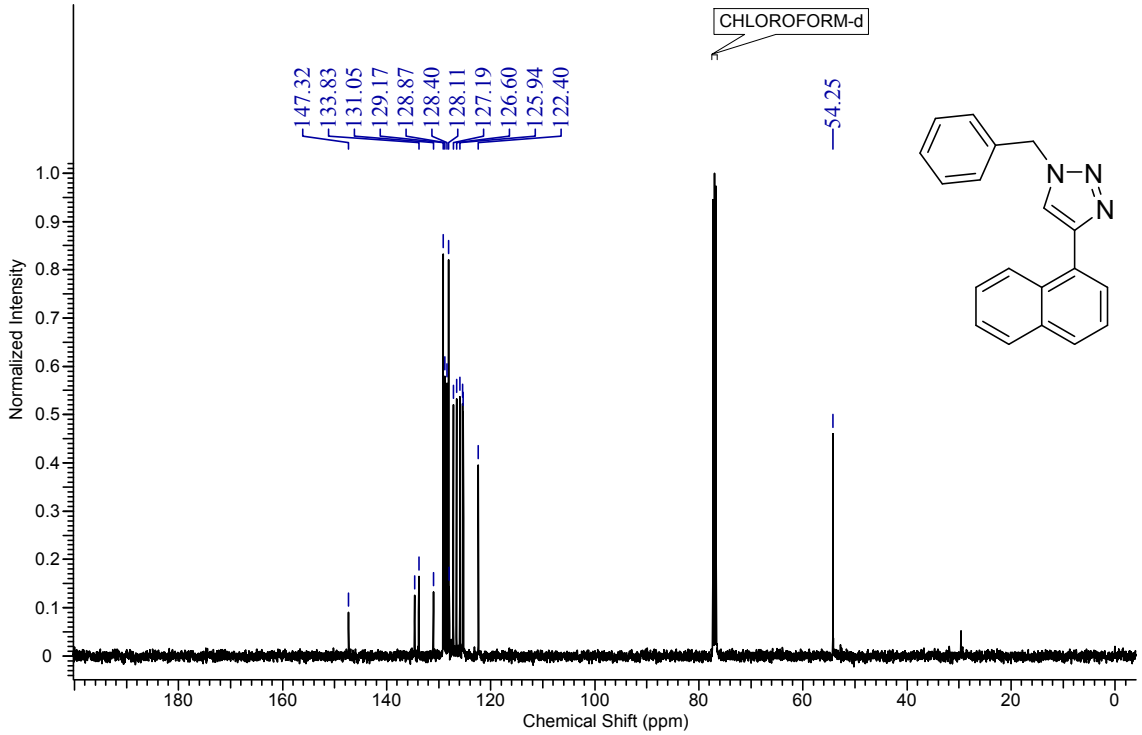
^{13}C 1-benzyl-4-(4-(pentyloxy)phenyl)-1H-1,2,3-triazole (4i)



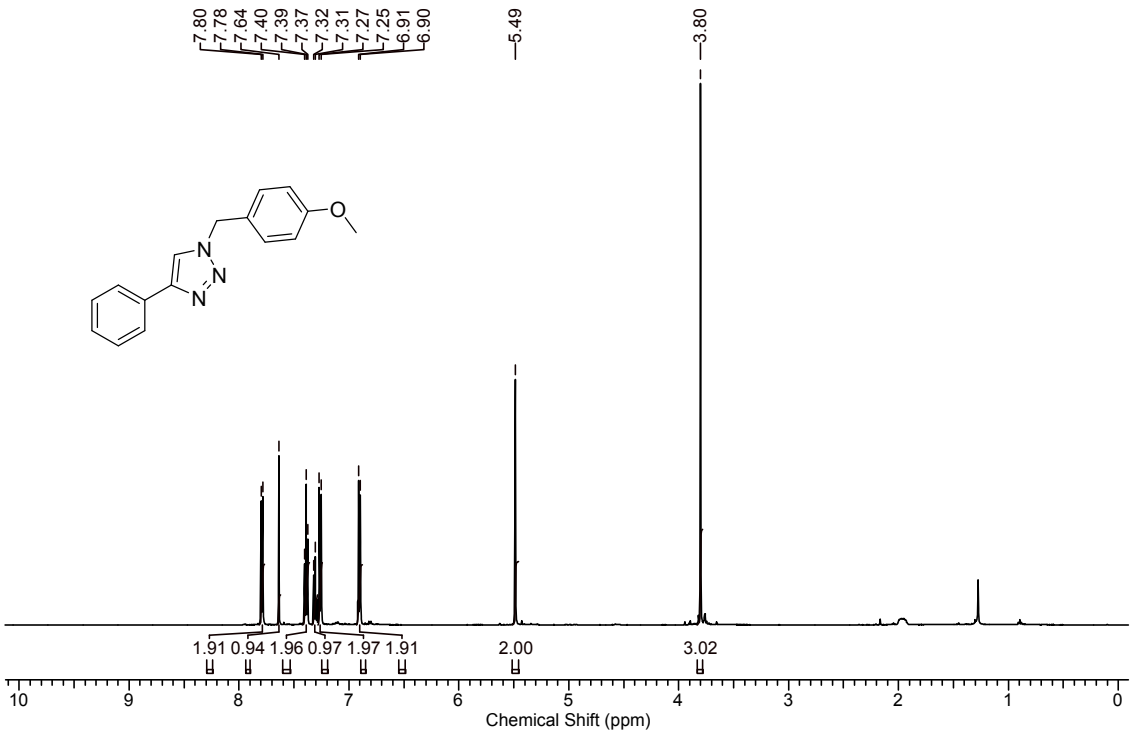
^{1}H NMR 1-benzyl-4-(naphthalen-1-yl)-1H-1,2,3-triazole (4j).



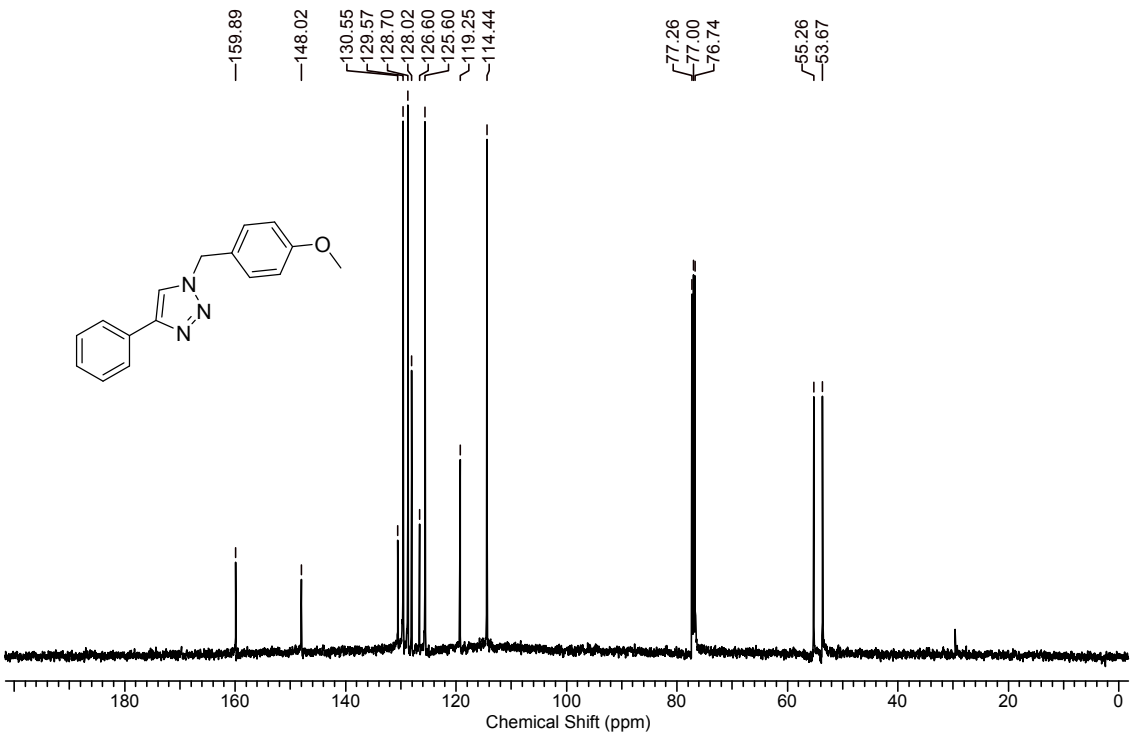
^{13}C NMR 1-benzyl-4-(naphthalen-1-yl)-1H-1,2,3-triazole (4j).



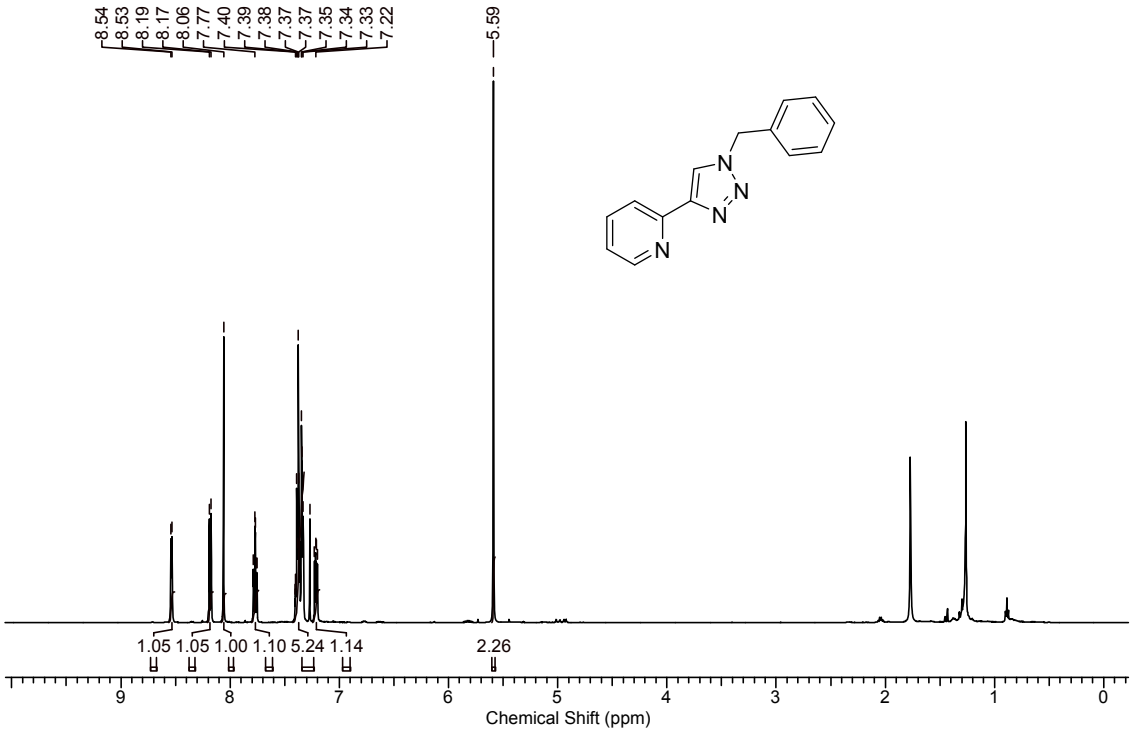
^{1}H NMR 1-(4-methoxybenzyl)-4-phenyl-1H-1,2,3-triazole (4k)



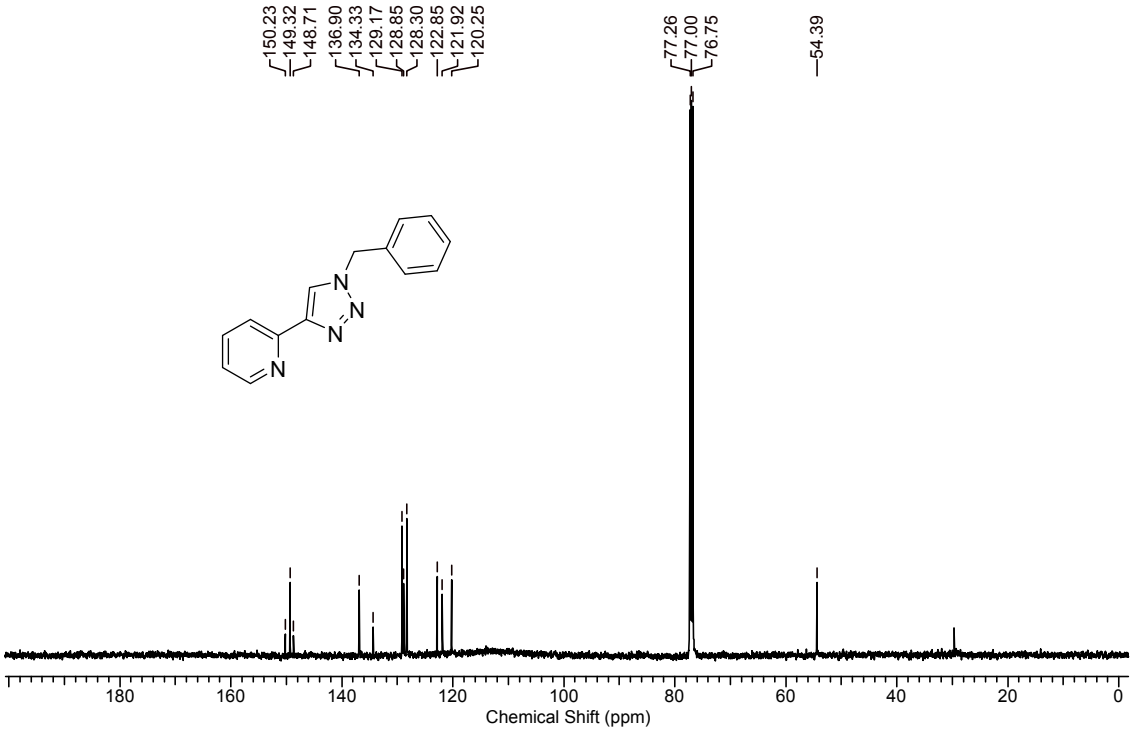
^{13}C NMR 1-(4-methoxybenzyl)-4-phenyl-1H-1,2,3-triazole (4k)



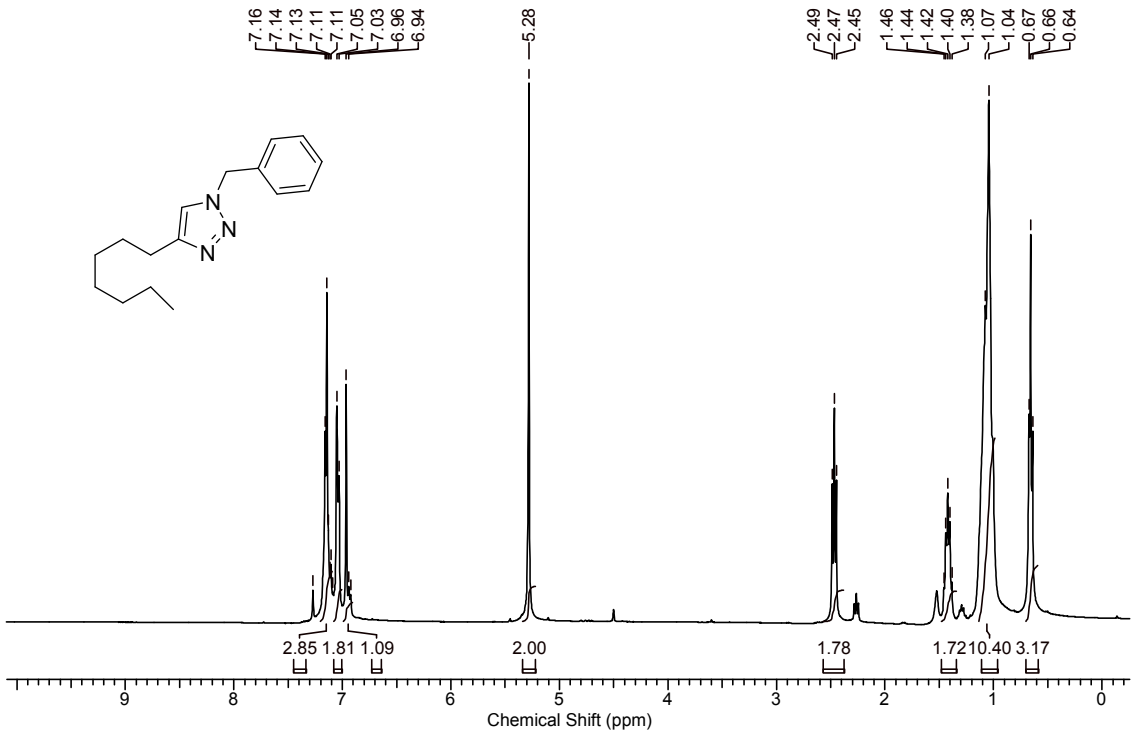
^{1}H NMR 2-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (4l)



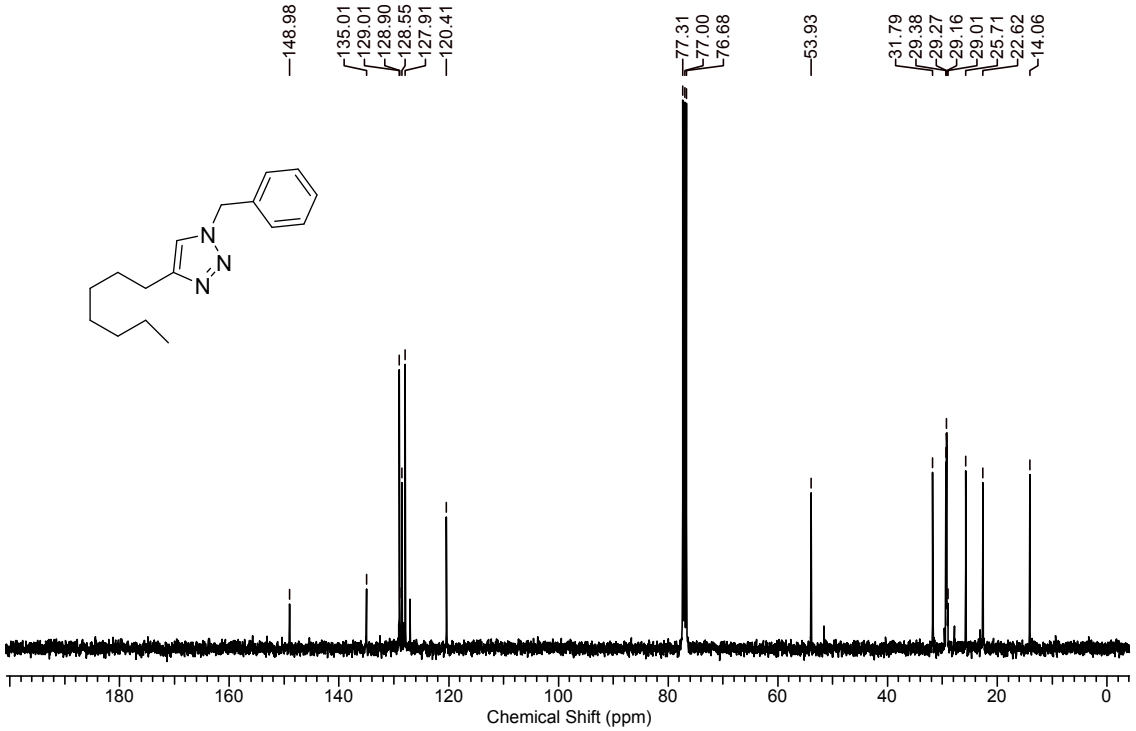
^{13}C NMR 2-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (4l)



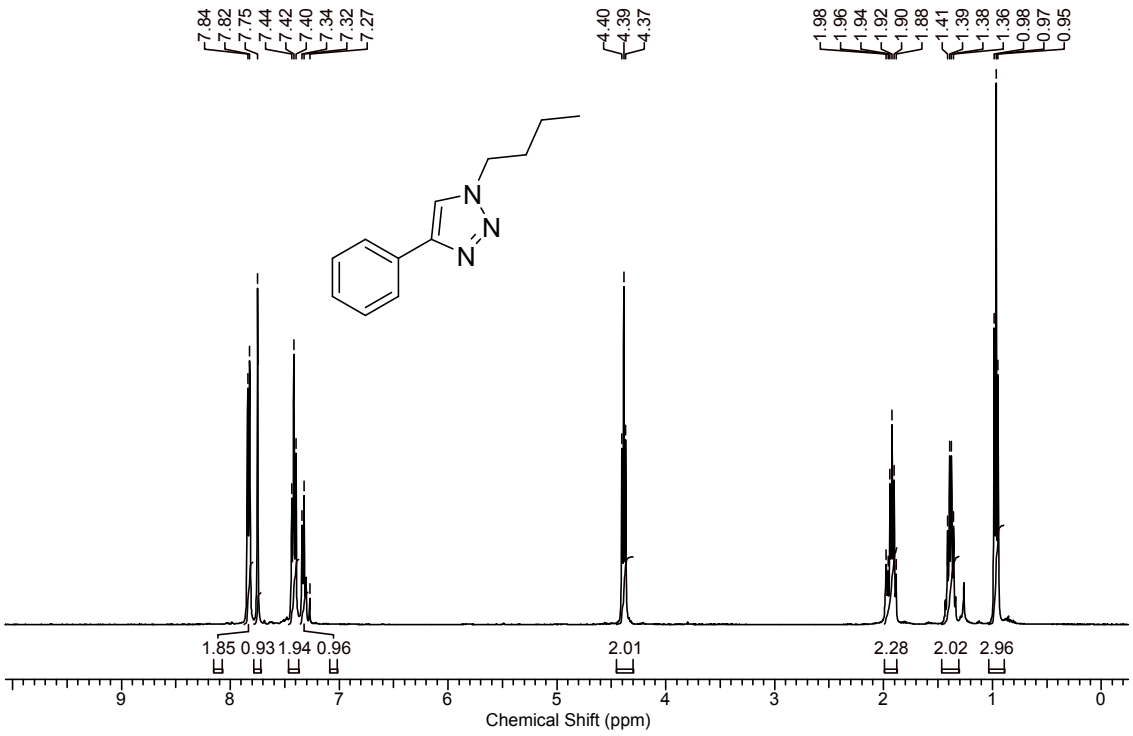
^{1}H NMR 1-benzyl-4-heptyl-1H-1,2,3-triazole (4m)



^{13}C NMR 1-benzyl-4-heptyl-1H-1,2,3-triazole (4m)



^{1}H NMR 1-butyl-4-phenyl-1H-1,2,3-triazole (4n)



^{13}C NMR 1-butyl-4-phenyl-1H-1,2,3-triazole (4n)