Supporting Information

Highly efficient click reaction on water catalyzed by ruthenium complex

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Table of Contents

Page

1. General Information

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. $RuH_2(CO)(PPh_3)_3$ were prepared according to literature methods.[1] Freshly distilled water was used as solvent. Alkynes and other chemicals were purchased from Aldrich. Mass spectra were collected on API QSTAR XLSystem (ESI) or GCT Premier^{TM} Mass Spectrometer (CI). ^1H, $^{13}C\{^1H\}$ NMR spectra were collected on Bruker AV 400 MHz NMR spectrometer. ^1H and ^{13}C NMR chemical shifts are relative to TMS or residue of deuterium solvents.

2. Experimental procedures

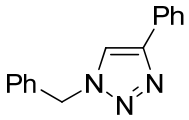
Typical procedure for the $RuH_2(CO)(PPh_3)_3$-catalyzed cycloaddition of various alkynes and organic azides on water with low catalyst loading.

Procedure: To a mixture of azide (0.5 mmol), alkyne (0.6 mmol), and H_2O (0.5 mL) were added catalyst $RuH_2(CO)(PPh_3)_3$ (0.001 mmol) and phase transformation catalyst (PTC) Bu_4NBr (0.025 mmol). The resulting solution was stirred at 80 °C for 2 h. Then the reaction mixture was extracted three times with 1 mL $CHCl_3$. The organic phases were combined, the solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography on silica gel to afford the desired product. All the compounds reported here are known, except for **3i** and **3r**.

Typical procedure for one-pot synthesis of 1,2,3-triazoles from bromides, sodium azide, and alkynes.

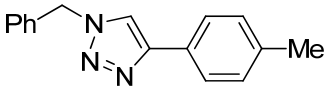
Procedure: To a mixture of bromide (0.5 mmol), sodium azide (0.55 mmol), alkyne (0.6 mmol) and H_2O (0.5 mL) were added catalyst $RuH_2(CO)(PPh_3)_3$ (0.01 mmol) and PTC Bu_4NI (0.025 mmol). The resulting solution was stirred at 80 °C for 2 h. Then the reaction mixture was extracted three times with 1 mL $CHCl_3$. The organic phases were combined, the solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography on silica gel to afford the desired product. All the compounds reported here are known, except for **3i** and **3r**.

3. Analytical data for products.



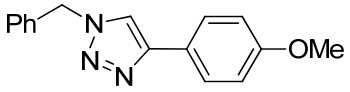
1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (**3a**)[2]

Mp: 124-126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.79-7.81 (m, 2H), 7.66 (s, 1H), 7.30-7.42 (m, 8H), 5.58 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 148.1, 134.6, 130.4, 129.1, 128.7, 128.1, 128.0, 125.6, 119.5, 54.1; MS (+CI) m/z (%) 236.13 ($M+H^+$, 100).



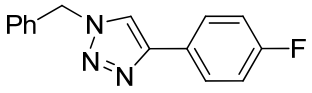
1-Benzyl-4-*p*-tolyl-1*H*-1,2,3-triazole (**3b**)[2]

Mp: 152-154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.67-7.69 (m, 2H), 7.62 (s, 1H), 7.36-7.41 (m, 3H), 7.30-7.32 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.58 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 148.1, 137.9, 134.7, 129.4, 129.0, 128.6, 127.9, 127.6, 125.5, 119.1, 54.0, 21.1; MS (+CI) m/z (%) 249.98 ($M+H^+$, 100).



1-Benzyl-4-(4-methoxy-phenyl)-1*H*-1,2,3-triazole (**3c**)[2]

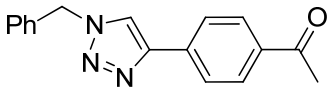
Mp: 141.9-144 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.70-7.74 (m, 2H), 7.58 (s, 1H), 7.37-7.39 (m, 3H), 7.30-7.32 (m, 2H), 6.92-6.94 (m, 2H), 5.57 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C) δ 159.2, 148.0, 134.7, 129.0, 128.6, 128.0, 126.9, 123.2, 118.7, 114.1, 55.2, 54.1; MS (+CI) m/z (%) 266.13 (M+H+, 100).



1-Benzyl-4-(4-fluoro-phenyl)-1*H*-1,2,3-triazole (**3d**)[2]

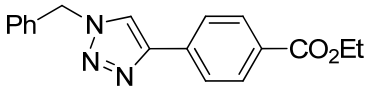
Mp: 107-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.75-7.78 (m, 2H), 7.62 (s, 1H), 7.30-7.40 (m, 5H), 7.07-7.11 (m, 2H), 5.58 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 163.7, 161.3, 147.2, 134.5, 129.0, 128.7, 127.9, 127.4, 127.3, 126.7, 119.3, 115.8, 115.5,

54.1; MS (+CI) m/z (%) 254.10 ($M+H^+$, 100).



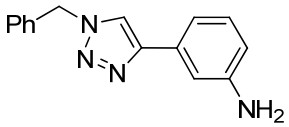
1-[4-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-phenyl]-ethanone (**3e**)[2]

Mp: 159-162 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ 8.00 (d, J = 8.5, 2H), 7.91(d, J = 8.5, 2H), 7.76 (d, 1H), 7.39-7.42 (m, 3H), 7.32-7.34 (m, 2H), 5.60 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 197.6, 147.1, 136.5, 135.0, 134.4, 129.3, 129.0, 128.9, 128.2, 125.6, 120.4, 54.4, 26.6; MS (+CI) m/z (%) 278.13 ($M+H^+$, 100).



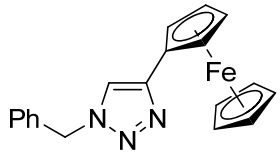
4- (1-Benzyl-1*H*-1,2,3-triazol-4-yl)-benzoic acid ethyl ester (**3f**)[2]

Mp: 124-126.3 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ 8.07 (d, J = 8.5, 2H), 7.87(d, J = 8.5, 2H), 7.74(s, 1H), 7.40-7.41 (m, 3H), 7.32-7.34 (m, 2H), 5.60 (s, 2H), 4.36-4.41(q, J = 7.1, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 166.3, 147.2, 134.7, 134.4, 130.2, 129.9, 129.3, 128.9, 128.2, 125.4, 120.4, 61.1, 54.4, 14.4; MS (+CI) m/z (%) 308.14 ($M+H^+$, 100).



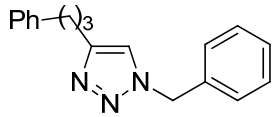
3-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-phenylamine (**3g**)[3]

Mp: 144.7-147 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ 7.61 (s, 1H), 7.36-7.40(m, 3H), 7.29-7.31(m, 2H), 7.24-7.25 (m, 1H), 7.15-7.19 (t, J = 7.7 Hz, 1H), 7.08-7.10 (m, 1H), 6.63-6.58 (m, 1H), 5.57 (s, 2H), 3.73 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 148.4, 147.0, 134.8, 131.5, 129.8, 129.2, 128.8, 128.1, 119.6, 116.0, 115.0, 112.2, 54.2; MS (EI) m/z (%) 250.12 (M^+, 100).



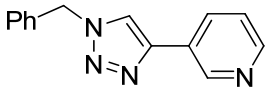
1-Benzyl-4-ferrocenyl-1*H*-1,2,3-triazole (**3h**)[2]

Mp: 151-152.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.29-7.40 (m, 6H), 5.55 (s, 2H), 4.68 (t, J = 1.8 Hz, 2H), 4.28 (t, J = 1.8 Hz, 2H), 4.05 (s, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 147.2, 134.9, 129.0, 128.6, 127.8, 118.7, 75.4, 69.5, 68.6, 66.6, 54.0; MS (+CI) m/z (%) 344.21 ($M+H^+$, 100).



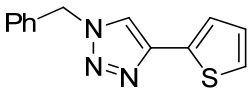
1-Benzyl-4-(3-phenyl-propyl)-1*H*-1,2,3-triazole (**3i**)

Mp: 60-62.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.34-7.37 (m, 3H), 7.24-7.26 (m, 4H), 7.15-7.19 (m, 4H), 5.49 (s, 2H), 2.64-2.74 (dt, 4H), 1.94-2.02 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 148.4, 141.9, 135.0, 129.1, 128.6, 128.5, 128.4, 128.0, 125.9, 120.7, 54.0, 35.4, 31.3, 25.3; HRMS (ESI, TOF) calcd for $C_{18}H_{20}N_3$ $[M+H]^+$ 278.1562, found 278.1567.



3-(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine (**3j**)[4]

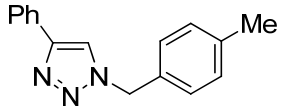
Mp: 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.96 (s broad, 1H), 8.57 (s broad, 1H), 8.19 (d, J = 7.96Hz, 1H), 7.75 (s, 1H), 7.32-7.43 (m, 6H), 5.61 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 149.3, 147.1, 145.2, 134.4, 133.0, 129.3, 129.0, 128.2, 126.7, 123.8, 119.9, 54.5; HRMS (EI, TOF) calcd for $C_{14}H_{12}N_4$ $[M]^+$ 236.1061, found 236.1063.



1-benzyl-4-(thiophen-2-yl)-1*H*-1,2,3-triazole (**3k**)[5]

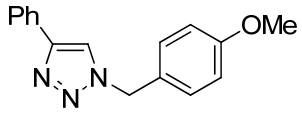
Mp: 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.57 (s, 1H), 7.37-7.40 (m, 3H), 7.27-7.35 (m, 4H), 7.05 (dd, J_1 = 3.6 Hz, J_2 = 5.08 Hz, 1H), 5.56 (s, 2H); ^{13}C NMR

(100.6 MHz, $CDCl_3$, 25 °C) δ 143.4, 134.6, 133.0, 129.3, 128.9, 128.2, 127.7, 125.1, 124.2, 119.0, 54.3; HRMS (EI, TOF) calcd for $C_{13}H_{11}N_3S$ $[M]^+$ 241.0674, found 241.0673.



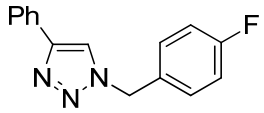
1-(4-Methyl-benzyl)-4-phenyl-1*H*-1,2,3-triazole (**3l**)[2]

Mp: 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) *δ* 7.78-7.80 (m, 2H), 7.63 (s, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.29-7.33 (m, 1H), 7.19-7.23 (m, 4H), 5.54 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 148.0, 138.6, 131.6, 130.5, 129.7, 128.7, 128.0, 125.6, 119.4, 53.9, 21.1; MS (ESI) m/z (%) 250.04 ($M + H^+$, 100)



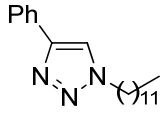
1-(4-Methoxy-benzyl)-4-phenyl-1*H*-1,2,3-triazole (**3m**)[6]

Mp: 125-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.62 (s, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.31-7.33 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.51 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 147.8, 140.0, 130.7, 129.1, 128.8, 128.6, 128.2, 126.6, 125.7, 118.5, 60.3, 21.4; MS (EI) m/z (%) 265.12 (M^+, 100).



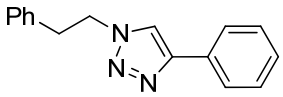
1-(4-Fluoro-benzyl)-4-phenyl-1*H*-1,2,3-triazole(**3n**)[7]

Mp: 129-131 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.80 (d, *J* = 7.1 Hz, 2H), 7.66 (s, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.29-7.34 (m, 3H), 7.08 (t, *J* = 8.6 Hz, 2H), 5.56 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 163.0 (J_{CF} = 247.5 Hz), 148.4, 130.6 (J_{CF} = 3.4 Hz), 130.5, 130.0 (J_{CF} = 8.5 Hz), 128.9, 128.3, 125.8, 119.4, 116.2 (J_{CF} = 21.8 Hz), 53.5; MS (EI) m/z (%) 253.10 (M^+, 100).



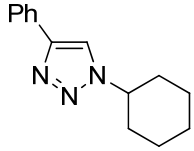
1-(*n*-Dodecyl)-4-(phenyl)-1*H*-1,2,3-triazole(**3o**)[2]

Mp: 90.8-91.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.83 (d, *J* = 7.1 Hz, 2H), 7.74 (s, 1H), 7.41-7.45 (m, 2H), 7.31-7.35 (m, 1H), 4.40 (t, *J* = 7.2 Hz, 2H), 1.91-1.98 (m, 2H), 1.25-1.35 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 147.7, 130.8, 128.8, 128.0, 125.7, 119.3, 50.5, 31.9, 30.4, 29.6, 29.5, 29.4, 29.3, 29.0, 26.5, 22.7, 14.1; MS (ESI) m/z (%) 314.26 ($M+H^+$, 100).



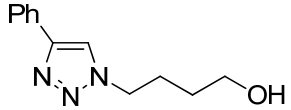
1-Phenethyl-4-phenyl-1H-1,2,3-triazole(**3p**)[8]

Mp: 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.76 (d, *J* = 7.0 Hz, 2H), 7.46 (s, 1H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.28-7.34 (m, 4H), 7.14 (d, *J* = 6.6 Hz, 2H), 4.64 (t, *J* = 7.2 Hz, 2H), 3.26 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 147.5, 137.1, 130.7, 128.91, 128.87, 128.8, 128.1, 127.2, 125.7, 120.0, 51.8, 36.9; MS (EI) m/z (%) 249.13 (M^+, 100).



1-Cyclohexyl-4-phenyl-1*H*-1,2,3-triazole (**3q**)[2]

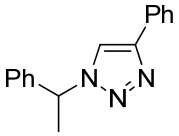
Mp: 104-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.83-7.84 (m, 2H), 7.77 (s, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 4.47-4.55 (m, 1H), 2.27 (dd, J_1 = 11.2 Hz, J_2 = 2.2 Hz, 2H), 1.93-1.98 (m, 2H), 1.75-1.85 (m, 3H), 1.44-1.56 (m, 2H), 1.26-1.36 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 147.2, 130.8, 128.7, 127.9, 125.5, 117.3, 60.0, 33.5, 25.1, 25.0; MS (+CI) m/z (%) 228.14 ($M+H^+$, 100).



4-(4-phenyl-1,2,3-triazol-1-yl)-butan-1-ol (**3r**)

Mp: 88-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) *δ* 7.82 (m, 2H), 7.78 (s, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 4.47 (t, *J* = 7.1 Hz, 2H), 3.71 (t, *J* = 6.1 Hz, 2H),

2.04-2.12 (m, 2H), 1.60-1.66 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C) δ 147.8, 130.6, 128.9, 128.2, 125.7, 119.6, 61.9, 50.2, 29.3, 27.0; HRMS (ESI, TOF) calcd for $C_{12}H_{15}N_3O$ $[M+H]^+$ 218.1288, found 218.1287.



4-Phenyl-1-(1-phenyl-ethyl)-1*H*-1,2,3-triazole (**3s**)[9]

Mp: 80-82 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.81-7.79 (m, 2H), 7.64 (s, 1H), 7.41-7.29 (m, 7H), 5.86 (q, J = 7.0 Hz, 1H), 2.02 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 160.0, 148.2, 130.7, 129.7, 128.9, 128.2, 126.7, 125.7, 119.3, 114.6, 55.4, 53.8; MS (EI) m/z (%) 249.13 (M^+, 100).

4. References

(1) N. Ahmad; J. J. Levison; S. D. Robinson; M. F. Uttley; E. R. Wonchoba and G. W. Parshall, *Inorg. Synth.*, 1974, **15**, 45.

(2) P. N. Liu, H. X. Siyang, L. Zhang, S. K. S. Tse and G. Jia, *J. Org. Chem.*, 2012, **77**, 5844.

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(4) S. Díez-González and S. P. Nolan, *Angew. Chem. Int. Ed.*, 2008, **47**, 8881.

(5) K. Lőrincz, P. Kele and Z. Novák, *Synthesis*, 2009, 3527.

(6) K. Asano and S. Matsubara, *Org. Lett.*, 2010, **12**, 4988.

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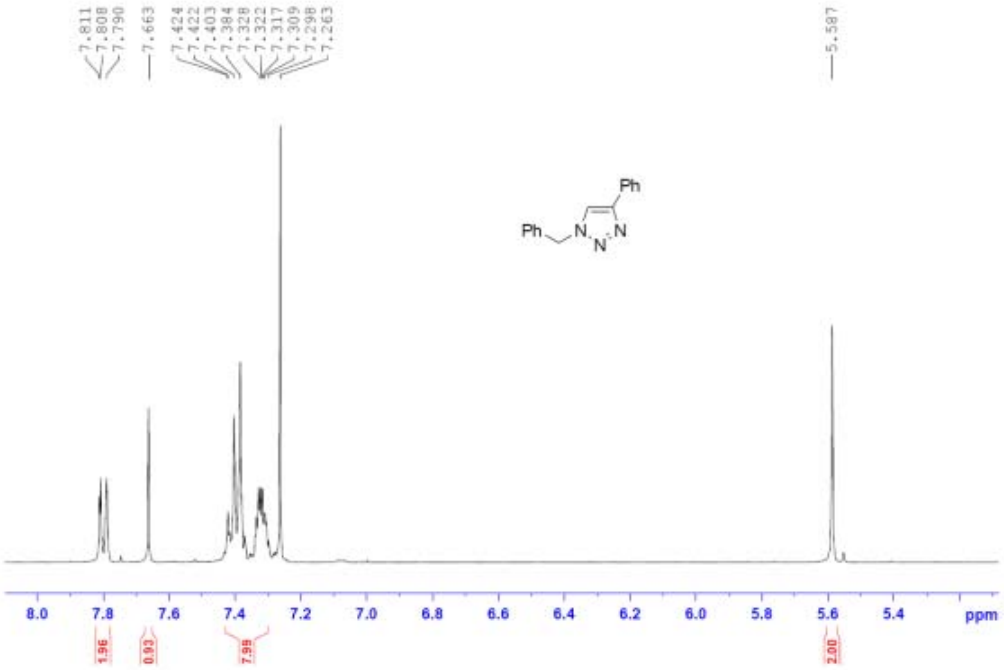
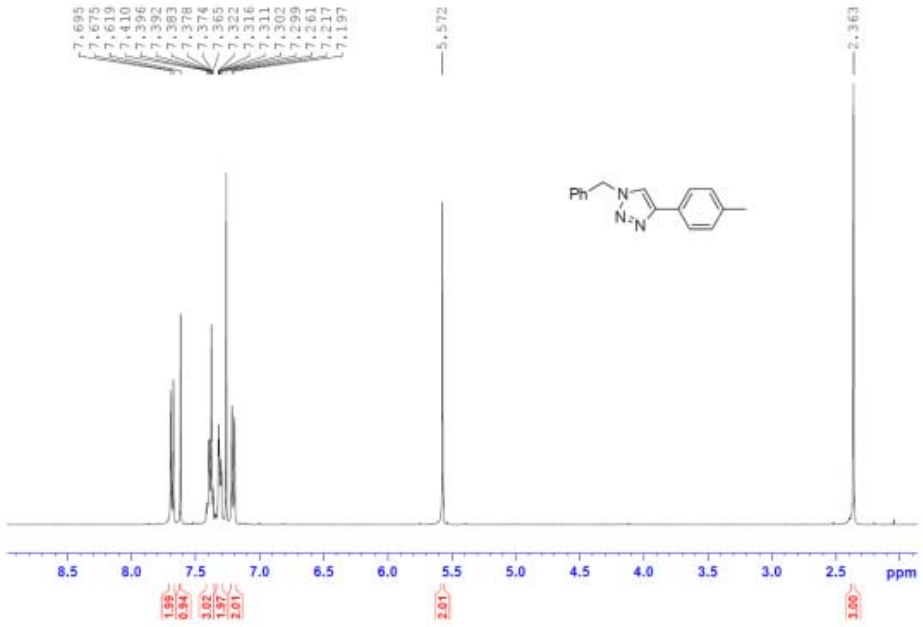
5. Copies of ^{1}H and ^{13}C NMR spectra

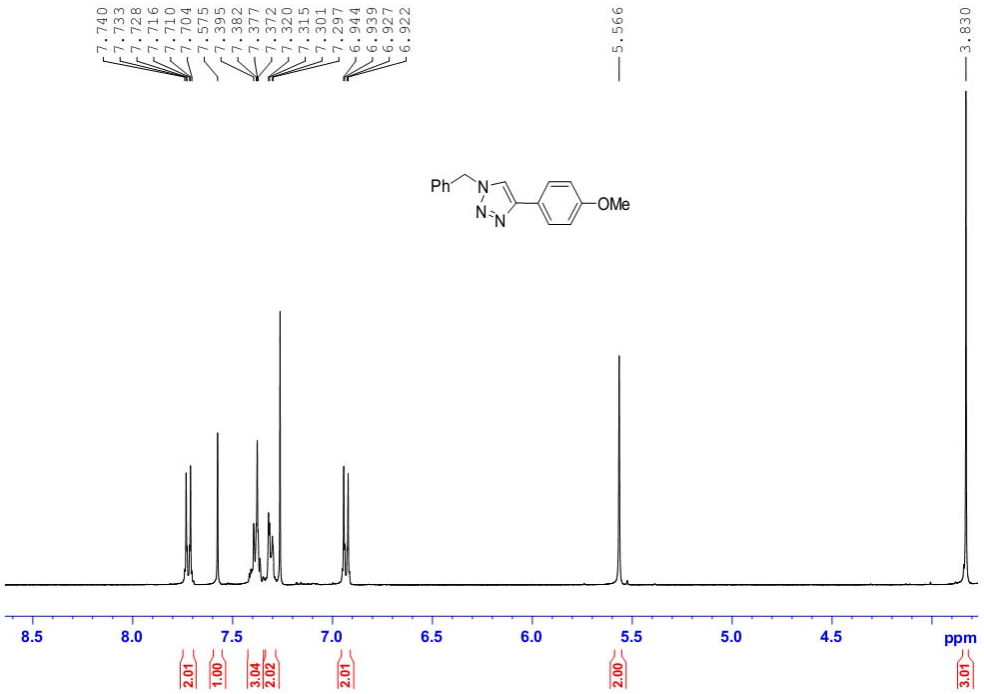
^{1}H NMR of phenzyl-4-phenyl-1*H*-1,2,3-triazole (**3a**)



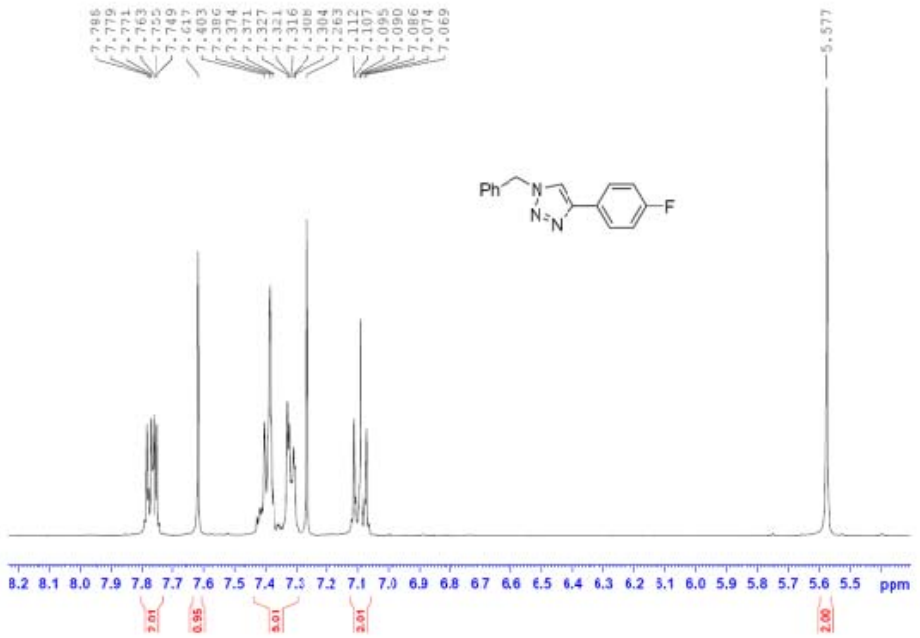
^{1}H NMR of 1-Benzyl-4-*p*-tolyl-1*H*-1,2,3-triazole (**3b**)



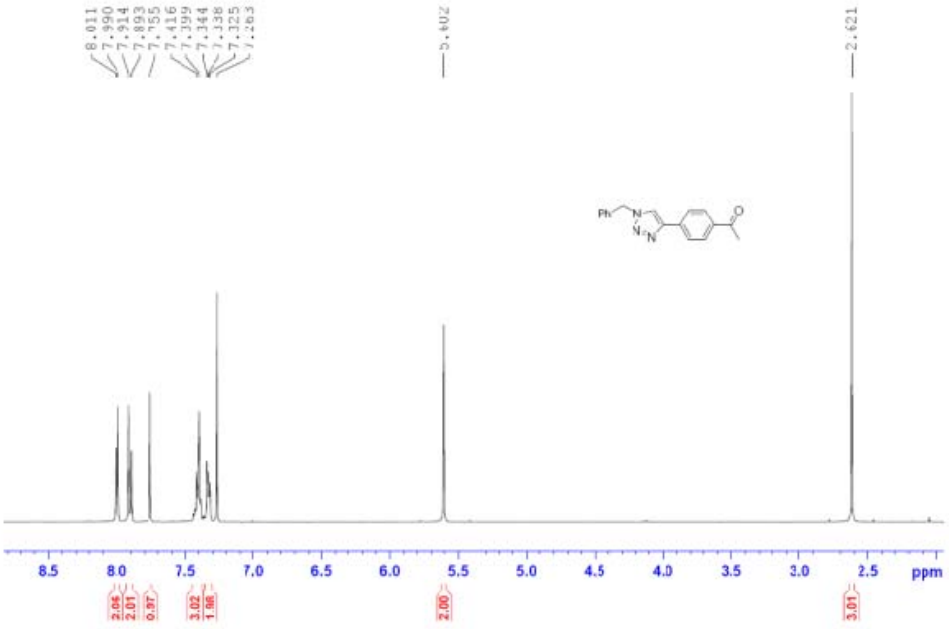
^{1}H NMR of 1-Benzyl-4-(4-methoxy-phenyl)-1*H*-1,2,3-triazole (**3c**)



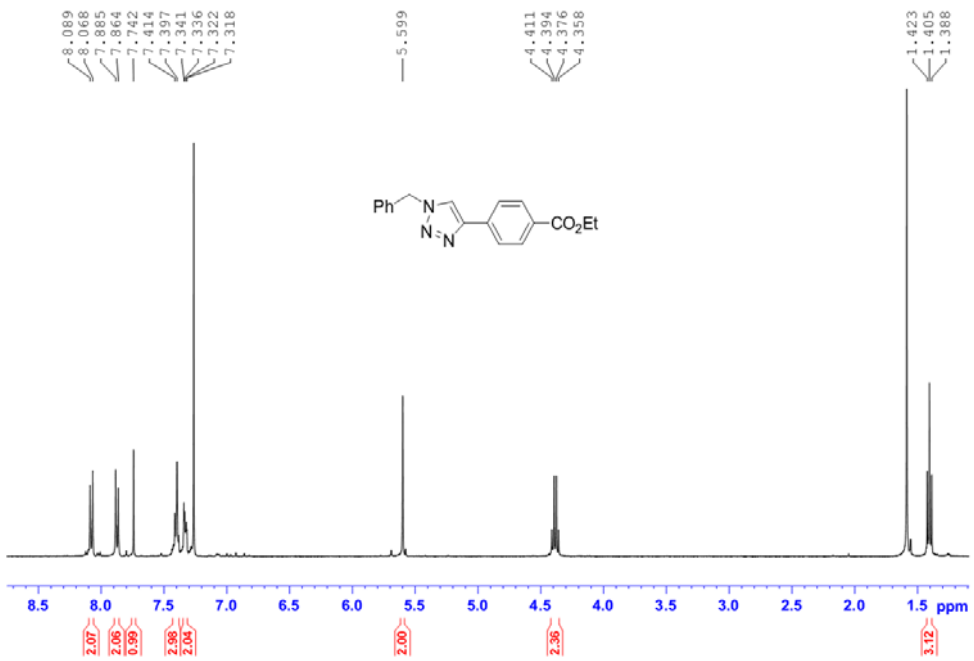
^{1}H NMR of 1-Benzyl-4-(4-fluoro-phenyl)-1*H*-1,2,3-triazole (**3d**)



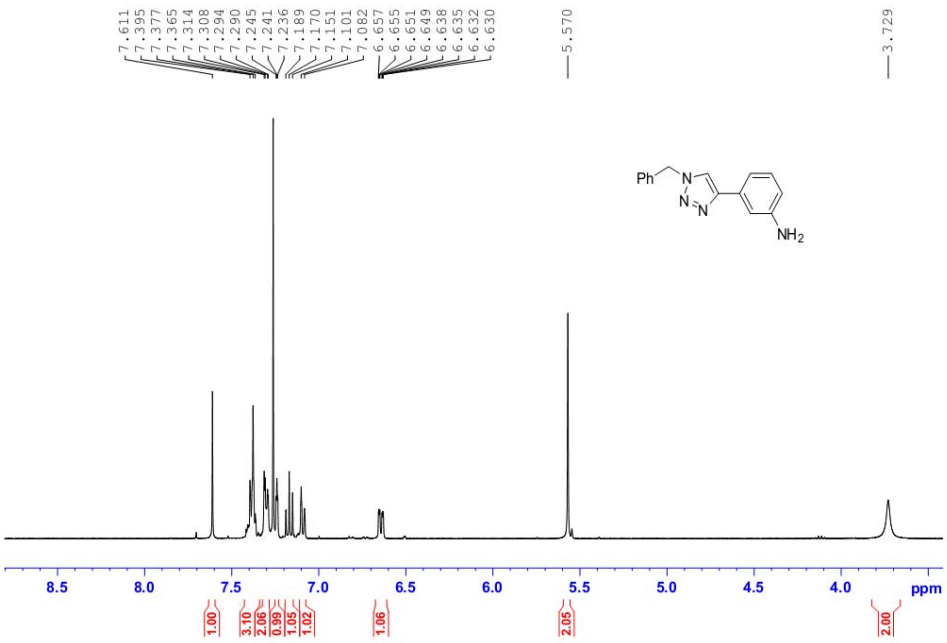
^{1}H NMR of 1-[4-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-phenyl]-ethanone (**3e**)



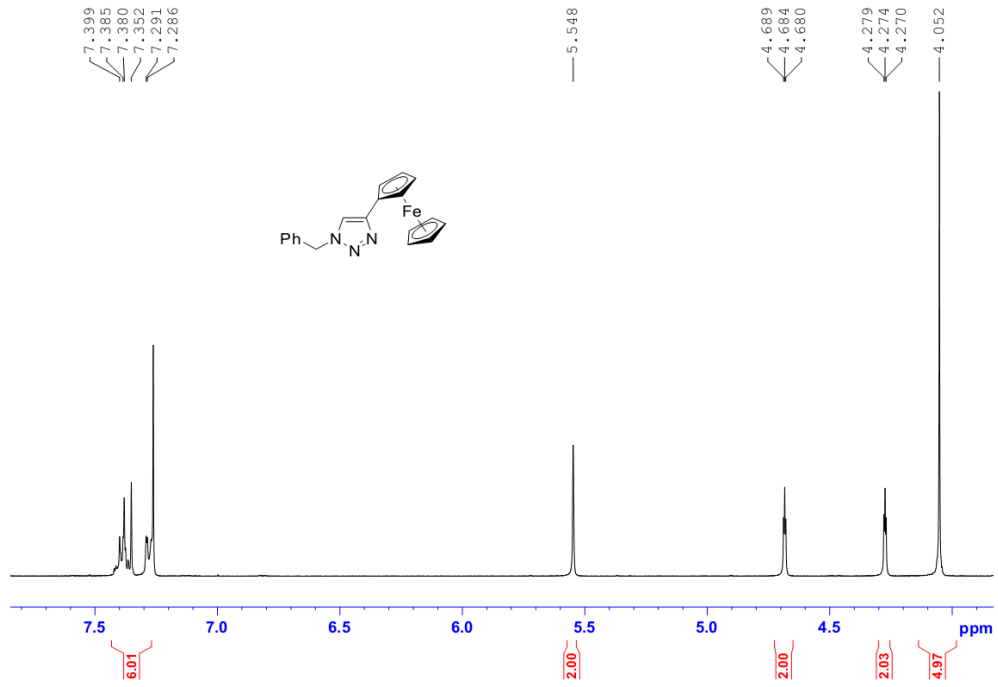
^{1}H NMR of 4- (1-Benzyl-1*H*-1,2,3-triazol-4-yl)-benzoic acid ethyl ester (**3f**)



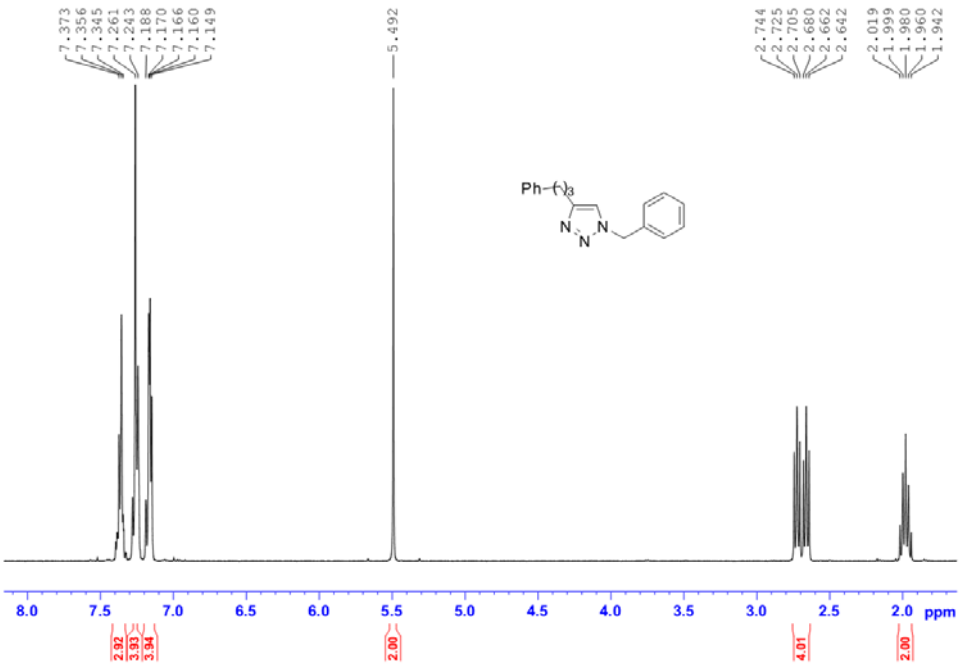
^{1}H NMR of 3-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-phenylamine (**3g**)



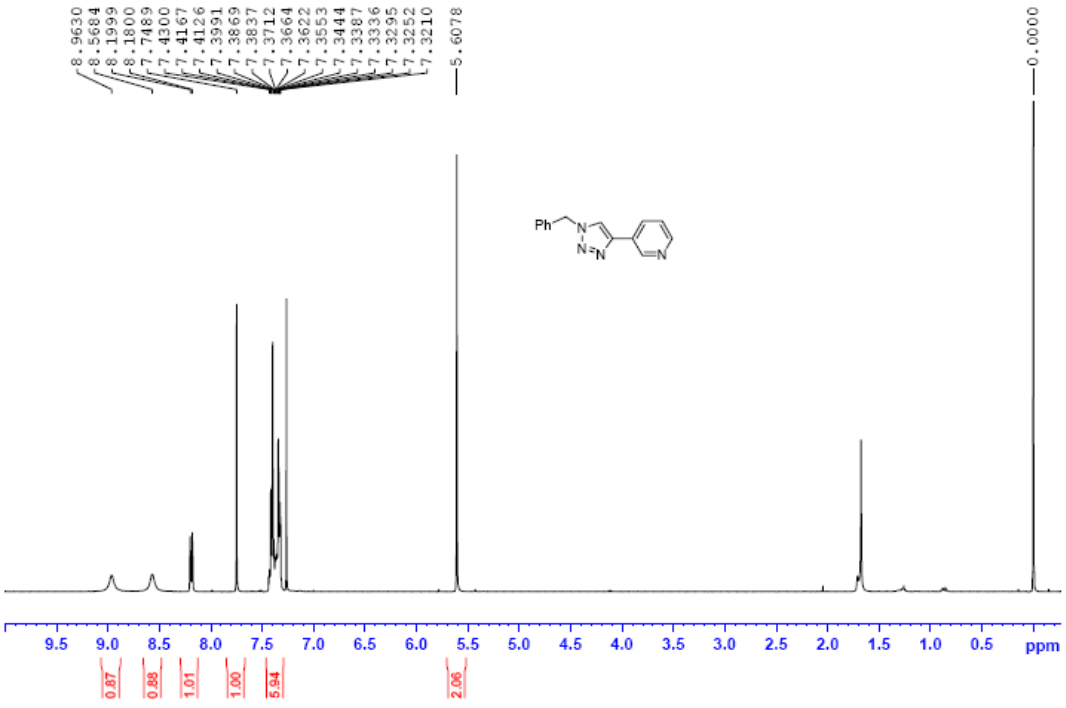
^{1}H NMR of 1-Benzyl-4-ferrocenyl-1*H*-1,2,3-triazole (**3h**)



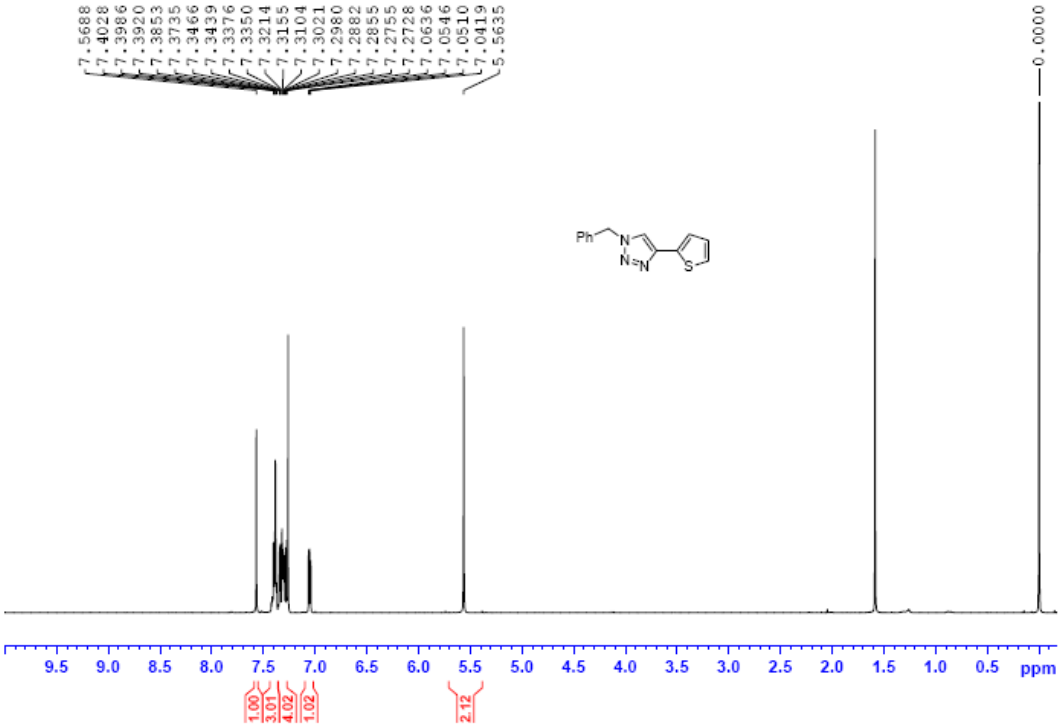
^{1}H NMR of 1-Benzyl-4-(3-phenyl-propyl)-1*H*-1,2,3-triazole (**3i**)



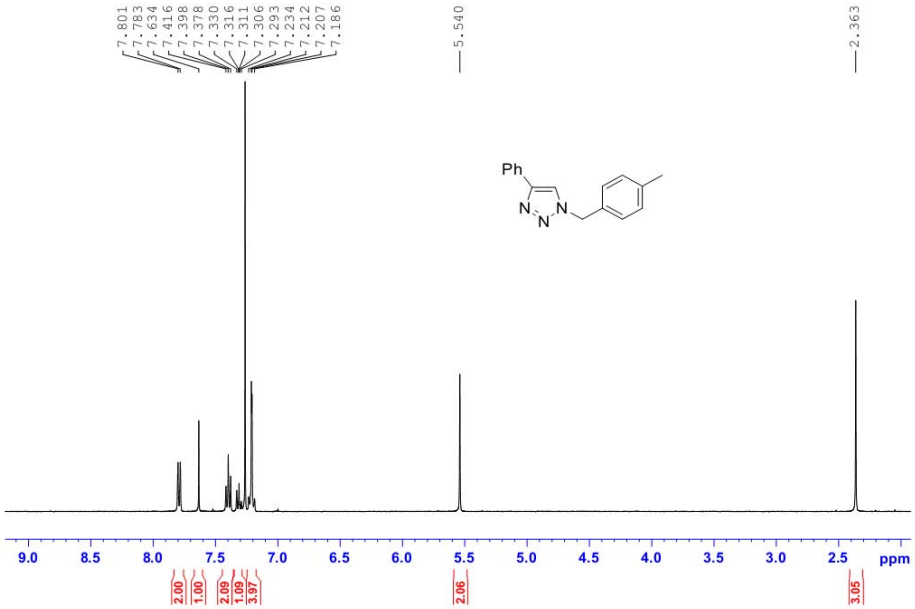
^{1}H NMR of 3-(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine (**3j**)



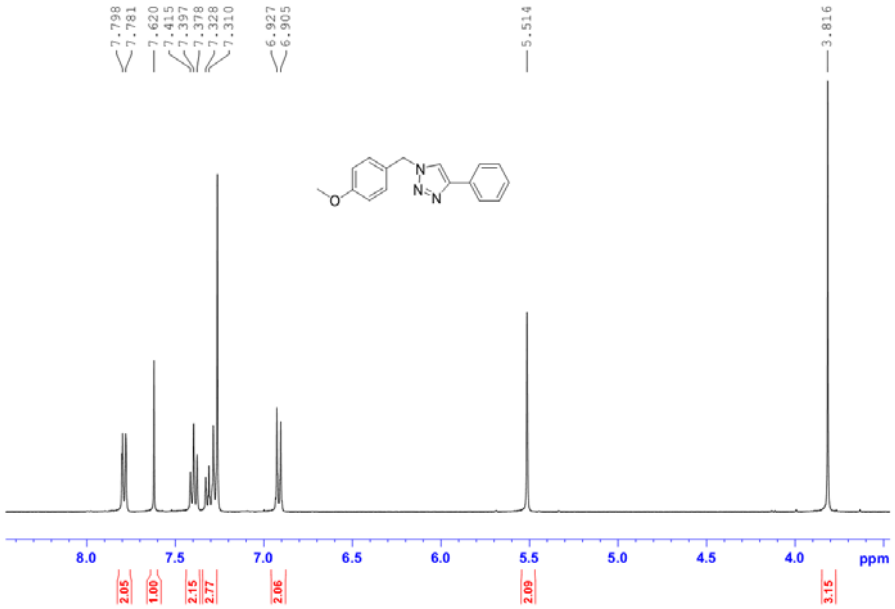
^{1}H NMR of 1-benzyl-4-(thiophen-2-yl)-1*H*-1,2,3-triazole (**3k**)



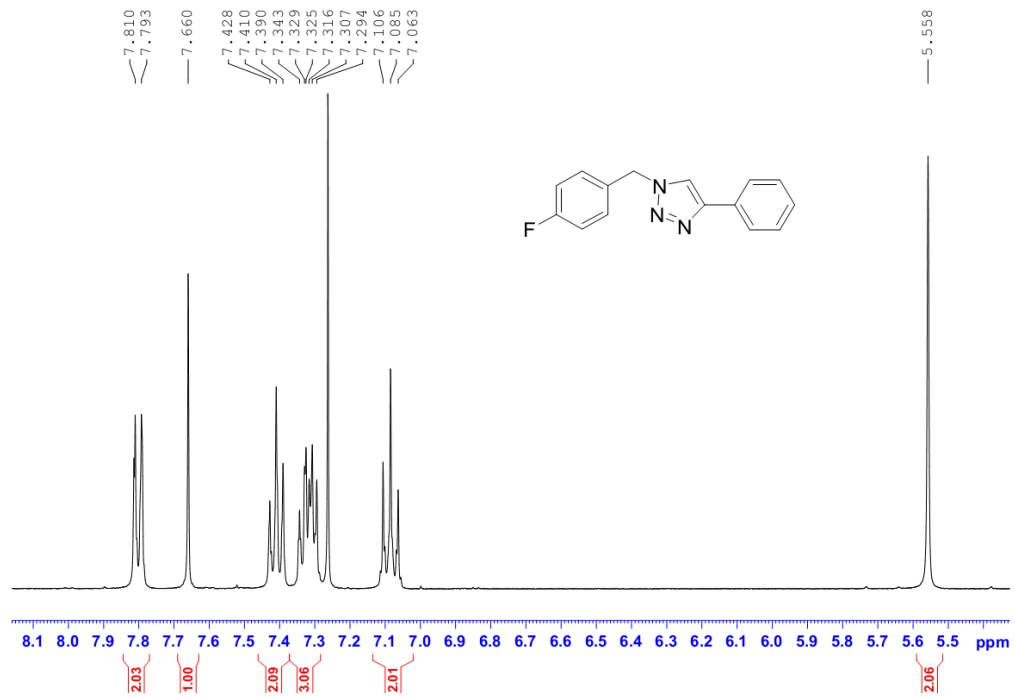
^{1}H NMR of 1-(4-Methyl-benzyl)-4-phenyl-1*H*-1,2,3-triazole (**3l**)



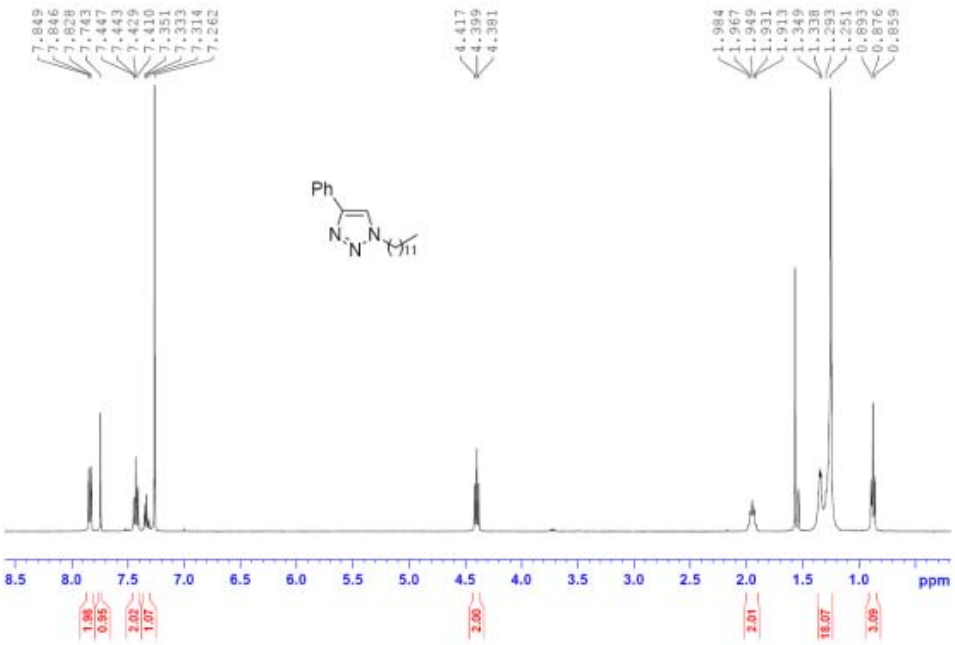
^{1}H NMR of 1-(4-Methoxy-benzyl)-4-phenyl-1*H*-1,2,3-triazole (**3m**)



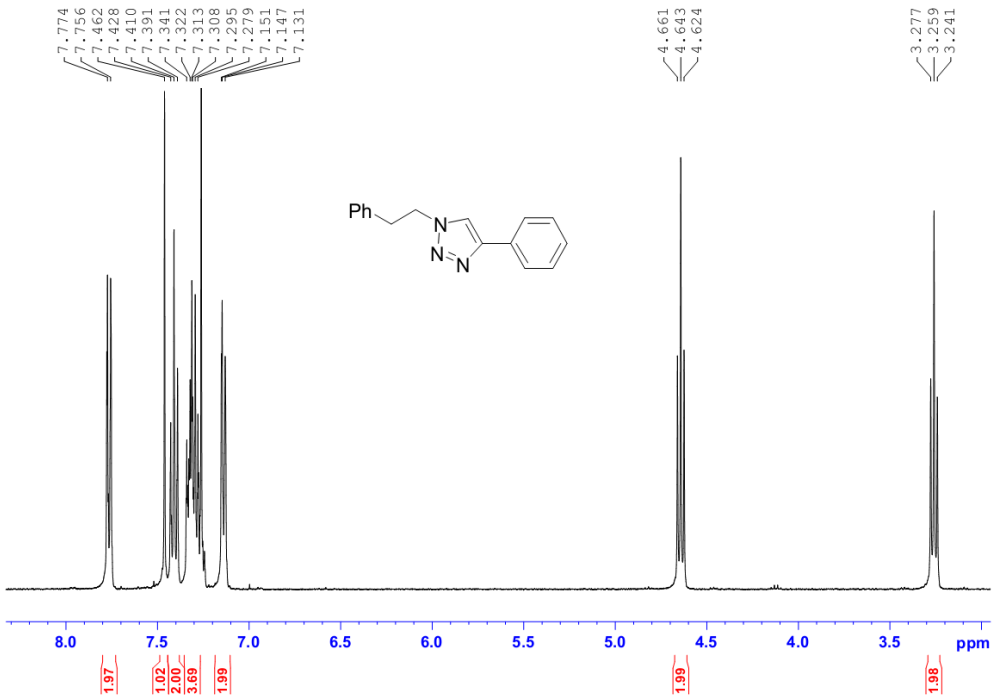
^{1}H NMR of 1-(4-Fluoro-benzyl)-4-phenyl-1*H*-1,2,3-triazole (**3n**)



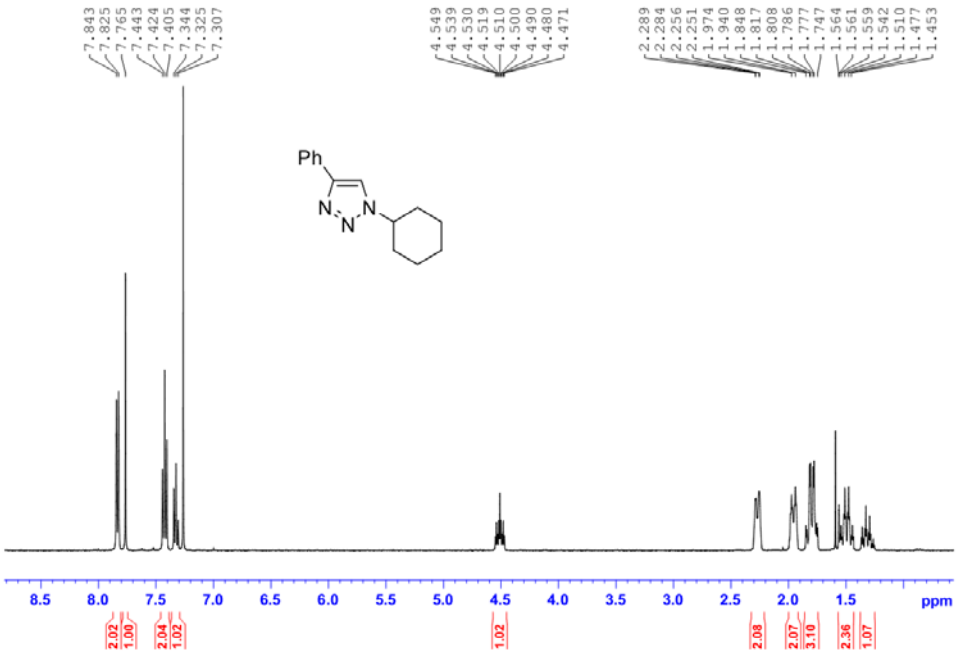
^{1}H NMR of 1-(*n*-Dodecyl)-4-(phenyl)-1*H*-1,2,3-triazole (**3o**)



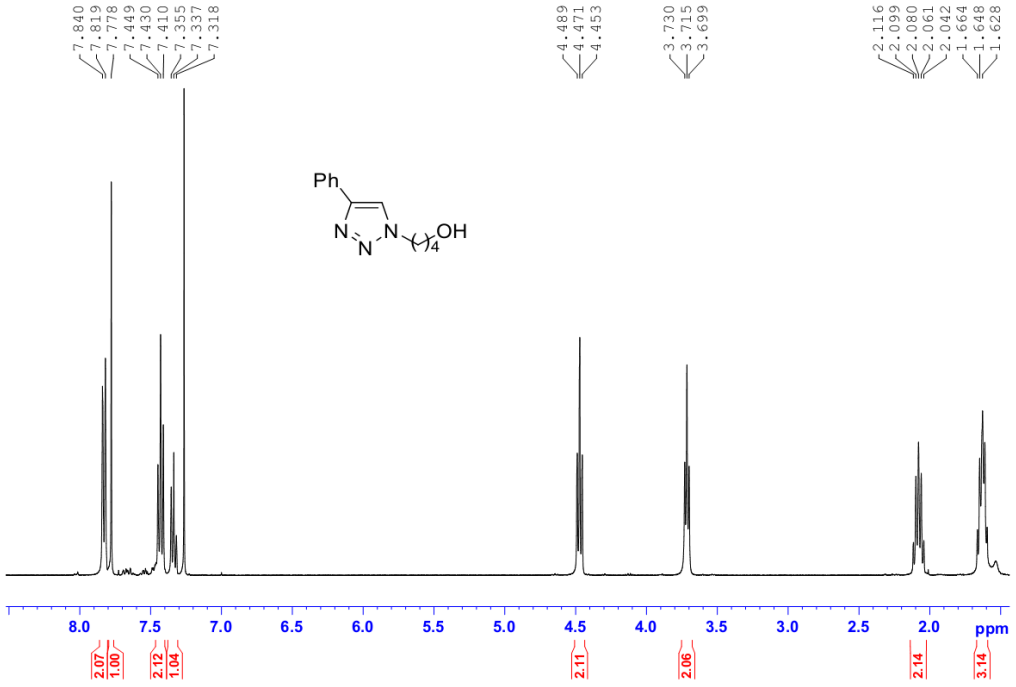
^{1}H NMR of 1-Phenethyl-4-phenyl-1*H*-1,2,3-triazole (**3p**)



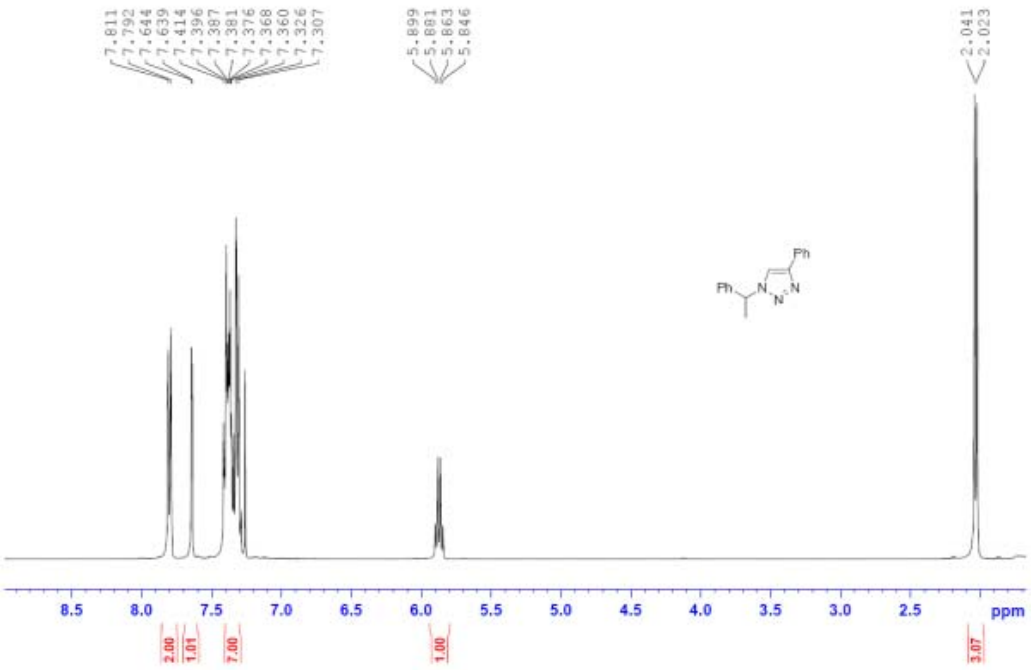
^{1}H NMR of 1-Cyclohexyl-4-phenyl-1*H*-1,2,3-triazole (**3q**)



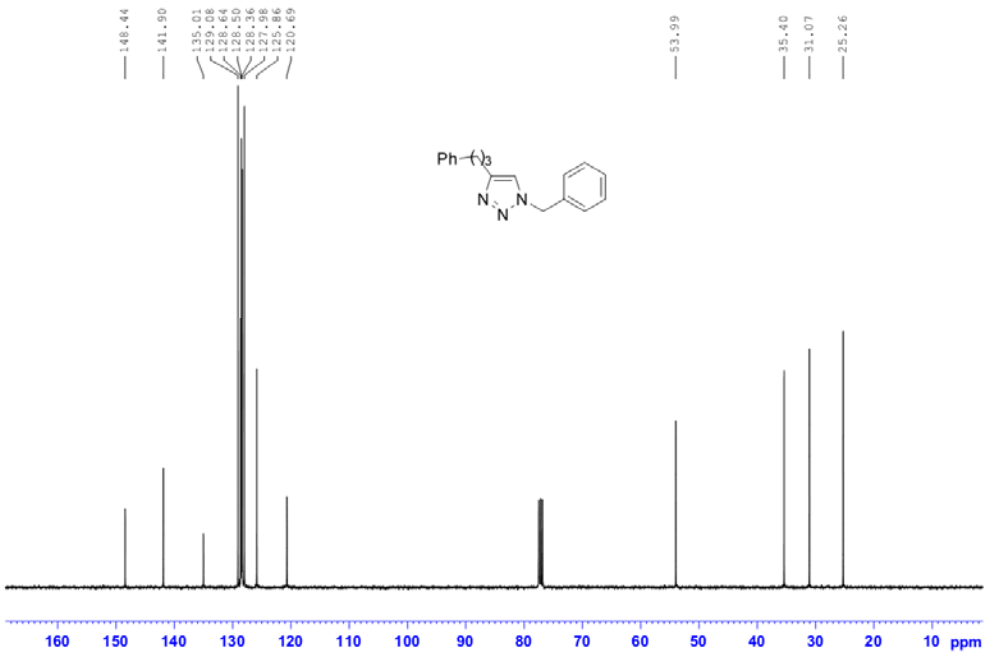
^{1}H NMR of 4-(4-phenyl-1,2,3-triazol-1-yl)-butan-1-ol (**3r**)



^{1}H NMR of 4-Phenyl-1-(1-phenyl-ethyl)-1*H*-1,2,3-triazole (**3s**)



^{13}C NMR of 1-Benzyl-4-(3-phenyl-propyl)-1*H*-1,2,3-triazole (**3i**)



^{13}C NMR of 4-(4-phenyl-1,2,3-triazol-1-yl)-butan-1-ol (**3r**)