Supporting Information

A Robust and Recyclable Polyurea-Encapsulated Copper(I) Chloride for One-Pot Ring-Opening/Huisgen Cycloaddition/CO_2 Capture in Water

Yun Chen[a], Wei-Qiang Zhang[a], Bin-Xun Yu[a], Yu-Ming Zhao[a], Zi-Wei Gao*[a], Ya-Jun Jian[a], Li-Wen Xu*[a,b]

a. Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education (MOE) and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China. E-mail: liwenxu@hznu.edu.cn

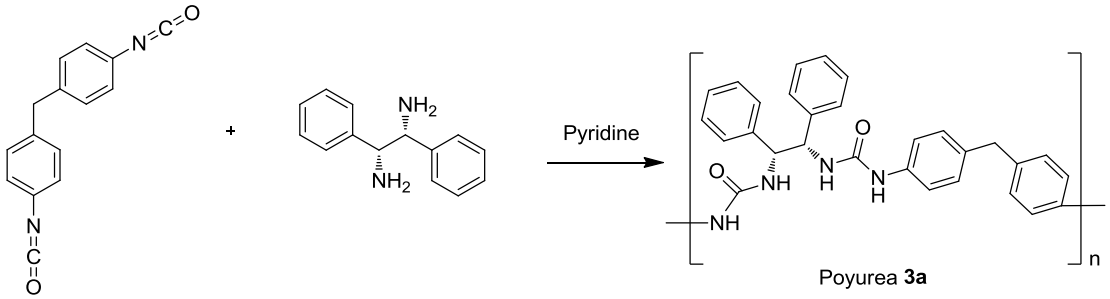
b. Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, No 1378, Wenyi West Road, Science Park of HZNU, Hangzhou 311121, P. R. China

Table of Contents

S-1. General information

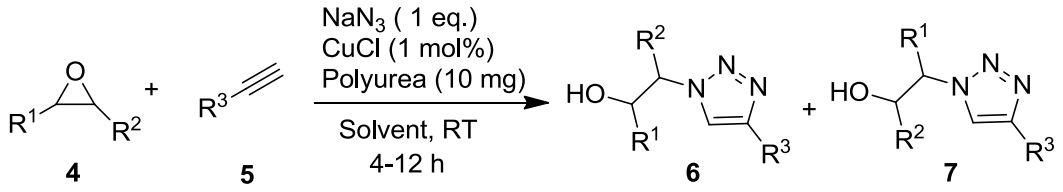
All reagents and solvents were dried and purified before use by the usual procedures. Reactions were monitored by thin layer chromatography using silica gel. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Scanning electron microscope (SEM) observation was carried out using a JEOL JSM-6500F instrument operated at an accelerating voltage of 30 kV. UV-vis absorption spectra were measured at room temperature with a JASCO V-570 spectrophotometer. Photo-luminescent spectra were taken on a HITACHI F-7000 fluorescence spectrophotometer in the setting of PMT voltage: 300 V (for DMSO solutions), and 350 V (for films), λ_{ex}: 263 nm, excitation band and fluorescence band: 5 nm, rate of scanning: 200 nm min^{-1}, and input range: 1 nm. ^{1}H NMR was recorded at 400 MHz or 500 MHz: chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm). ^{13}C NMR was recorded at 100 MHz or 126 MHz: chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm). The ESI - MS analysis of the samples was operated on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). high resolution mass spectral analyses (LRMS and HRMS) were performed at Chemical Instrument Center, Hangzhou Normal University (Bruker Daltonics MICROOTOF-QII). Tetrahydrofuran (with Na and benzophenone) were freshly distilled in prior to use.

S-2. Synthesis of Polyurea



A solution of 4,4'-diphenylmethane diisocyanate (2.5 g, 10 mmol) in pyridine (6 mL) was added dropwise in the solution of (1*R*,2*R*)-(+)-1,2-Diphenylethylenediamine (2.123 g, 10 mmol) dissolved in pyridine (10 mL). The solution was then stirred at room temperature for 0.5 h, and then at 60 ^{o}C for an additional 5 h to ensure the completion of the polymerization reaction. The resulting mixture was filtered and the residue was washed with water (20 mL×3) then dried under vacuum to afford a white solid (3.82 g, 90% yield).

S-3. Synthesis of Hydroxytriazoles



General Procedure for the Cu/Polyurea-Catalyzed Synthesis of *β*-Hydroxytriazoles from Epoxides in Water: NaN_3 (65 mg, 1.0 mmol), the epoxide (1 mmol), and the alkyne (1 mmol) were added to a suspension of CuCl (1 mg, 1 mol % Cu) and polyurea **3a** (10 mg,) in H_2O (2 mL) under the carbon dioxide atmosphere (balloon). After the completion of the reaction, as monitored by TLC using *n*-hexane/ethyl acetate (2:1), the mixture was diluted by H_2O (5 mL), then the whole reaction mixture was centrifuged and the supernatant was decanted to separate the heterogeneous catalyst, which was washed several times with EtOAc, diethyl ether or dichloromethane. The reaction vessel containing the heterogeneous catalyst was recharged with epoxide, alkyne, sodium azide and water for another reaction run. The combined

supernatant and organic washings were extracted with ethyl acetate (3×10 mL), the combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum, followed by purification on silica gel using hexane-ethyl acetate (4:1) as the eluent afforded the pure 2-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanol derivatives.

S-4-1. Characterization data of Products 3a-3d

3a: ^{1}H NMR (400 MHz, DMSO) δ = 8.63 – 8.42 (m, 3H), 7.23 (d, J = 8.4 Hz, 3H), 7.16 (d, J = 4.9 Hz, 5H), 7.06 (d, J = 6.7 Hz, 4H), 6.97 (d, J = 7.3 Hz, 3H), 4.99 (d, J = 4.4 Hz, 2H), 3.96 –3.55(m,3H), 3.34 (s, 3H), 2.60 – 2.35 (m, 1H).

IR (KBr) ν = 697, 756, 1028, 1453, 1493, 1601, 2922, 3025.

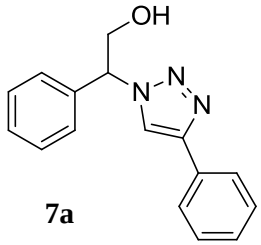
GPC: Mn = 27757, Mw = 29145.

3b: IR (KBr) ν = 640, 779, 808, 916, 1018, 1108, 1178, 1235, 1304, 1408, 1509, 1548, 1594, 1639, 3308.

3c: IR (KBr) ν = 641,779, 808, 916, 1018, 1233, 1305, 1409, 1509, 1547, 1595, 1640, 3002.

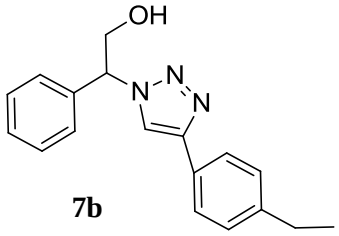
3d: IR (KBr) ν = 648, 699, 762, 1030, 1072, 1257, 1454, 1558, 1636, 2930, 3009.

S-4-2. Characterization data of Products 7a-7p



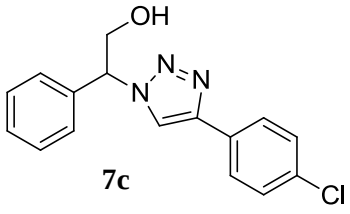
7a

2-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanol: White solid 95% yield; mp 153~155 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 – 7.74 (m, 2H), 7.69 (s, 1H), 7.43 – 7.36 (m, 5H), 7.35 – 7.29 (m, 1H), 7.29 – 7.25 (m, 2H), 5.68 (dd, *J* = 8.2, 3.7 Hz, 1H), 4.63 (dd, *J* = 12.4, 8.2 Hz, 1H), 4.23 (dd, *J* = 12.4, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.2 , 135.7, 130.2 , 129.2, 129.0, 128.8, 128.3, 127.1, 125.7, 120.3, 67.1, 65.1; HR-MS calculated for $C_{16}H_{15}N_3O$ $[M+H]^+$: 266.1288, found: 266.1287.



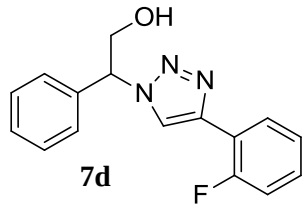
7b

2-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)-2-phenylethanol: White solid ; 85% yield; mp 150~153 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.69 (s, 3H), 7.38 (d, *J* = 5.6 Hz, 3H), 7.30 – 7.25 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.69 (dd, *J* = 8.2, 3.7 Hz, 1H), 4.63 (dd, *J* = 12.3, 8.4 Hz, 1H), 4.23 (dd, *J* = 12.4, 3.5 Hz, 1H), 3.72 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.8, 144.6, 136.2, 129.1, 129.0, 128.3, 127.6, 127.2, 125.70, 120.3, 67.3, 65.1, 28.7, 15.5; HR-MS calculated for $C_{18}H_{19}N_30$ $[M+Na]^+$: 316.1420, found: 316.1416.



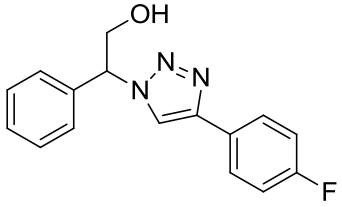
7c

2-(4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)-2-phenylethanol: White solid ; 85% yield; mp 127~130 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.74 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.27 (m, 2H), 5.81 – 5.60 (m, 1H), 4.62 (t, *J* = 9.0 Hz, 1H), 4.23 (d, *J* = 11.4 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.8, 144.1, 128.2, 127.7, 125.4, 119.5, 72.5, 67.3, 33.8, 31.5, 28.7, 24.8, 24.1, 15.6; HR-MS calculated for $C_{16}H_{14}ClN_3O$ $[M+Na]^+$: 322.0718, found: 322.0722.



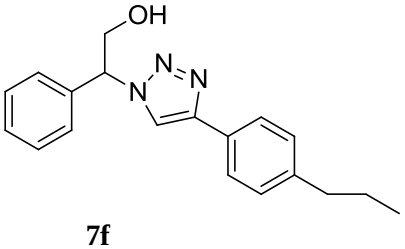
7d

2-(4-(2-fluorophenyl)-1H-1,2,3-triazol-1-yl)-2-phenylethanol: Yellow oil liquid ; 85% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.24 (t, *J* = 6.8 Hz, 1H), 7.92 (d, *J* = 3.3 Hz, 1H), 7.43 – 7.21 (m, 7H), 7.16 – 6.99 (m, 1H), 5.73 (dd, *J* = 8.0, 3.6 Hz, 1H), 4.66 (dd, *J* = 12.2, 8.5 Hz, 1H), 4.26 (dd, *J* = 12.3, 3.6 Hz, 1H), 3.59 (d, *J* = 126.8 Hz, 1H). ^{13}C NMR (126 MHz, None) δ = 159.2 (d, *J* = 248.3 Hz), 141.2, 136.0, 129.4 (d, *J* = 8.5 Hz), 129.1, 129.0, 127.6 (d, *J* = 3.3 Hz), 127.1, 124.6 (d, *J* = 3.1 Hz), 123.7 (d, *J* = 12.9 Hz), 118.2 (d, *J* = 12.9 Hz), 115.7 (d, *J* = 21.7 Hz), 67.4, 65.1; HR-MS calculated for $C_{16}H_{14}FN_3O$ $[M+Na]^+$: 306.1013, found: 306.1018.



7e

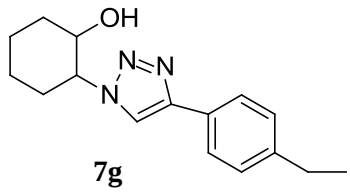
2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-2-phenylethanol: White solid; 87% yield; mp 130~132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.65 (m, 3H), 7.43 – 7.34 (m, 3H), 7.31 – 7.24 (m, 2H), 7.12 – 7.01 (m, 2H), 5.67 (dd, *J* = 8.3, 3.8 Hz, 1H), 4.63 (dd, *J* = 12.4, 8.3 Hz, 1H), 4.22 (dd, *J* = 12.4, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.7 (d, *J* = 247.6 Hz), 146.8, 136.0, 129.2, 129.0, 127.4 (d, *J* = 8.1 Hz), 127.2, 126.5 (d, *J* = 3.3 Hz), 120.3, 115.8 (d, *J* = 21.8 Hz), 67.4, 65.1; HR-MS calculated for $C_{16}H_{14}FN_3O$ $[M+Na]^+$: 306.1031, found: 306.1033.



7f

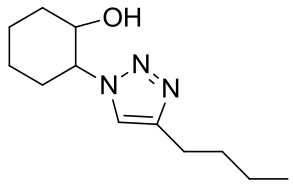
2-phenyl-2-(4-(4-propylphenyl)-1H-1,2,3-triazol-1-yl)ethanol: White solid ; 87% yield; mp 138~140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 – 7.61 (m, 3H), 7.44 – 7.32 (m, 3H), 7.28 – 7.24 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 5.67 (dd, *J* = 8.1, 3.6 Hz, 1H), 4.61 (dd, *J* = 12.3, 8.3 Hz, 1H), 4.22 (dd, *J* = 12.4, 3.7 Hz, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.54 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.8, 143.0, 136.2, 129.1, 129.0,

128.9, 127.7, 127.2, 125.6, 120.3, 67.3, 65.1, 37.8, 24.4, 13.7; HR-MS calculated for $C_{19}H_{21}N_3O$ $[M+H]^+$: 308.1757, found: 308.1741.



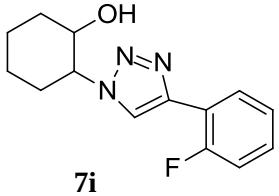
7g

2-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)cyclohexanol: White solid ; 80% yield; mp 188~190 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 1.1 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.3 Hz, 2H), 4.43 (s, 1H), 4.09 (t, *J* = 12.1 Hz, 2H), 2.79 – 2.47 (m, 2H), 2.30 – 2.07 (m, 2H), 2.00 (dd, *J* = 22.6, 10.8 Hz, 1H), 1.85 (d, *J* = 9.3 Hz, 2H), 1.55 – 1.34 (m, 3H), 1.25 (dd, *J* = 10.4, 7.6, 2.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.8, 144.1, 128.2, 127.7, 125.4, 119.5, 72.5, 67.3, 33.8, 31.5, 28.7, 24.9, 24.1, 15.6; HR-MS calculated for $C_{16}H_{21}N_3O$ $[M+Na]^+$: 294.1577, found: 294.1576.



7h

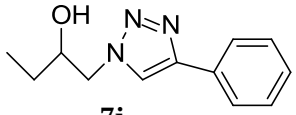
2-(4-butyl-1H-1,2,3-triazol-1-yl)cyclohexanol: White solid ; 60% yield; mp 90~93 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.31 (s, 1H), 4.15 – 4.03 (m, 2H), 3.98 (dt, *J* = 9.2, 4.5 Hz, 1H), 2.74 – 2.53 (m, 2H), 2.14 (dt, *J* = 32.4, 12.8 Hz, 2H), 1.94 – 1.78 (m, 3H), 1.59 (dt, *J* = 15.4, 7.6 Hz, 2H), 1.46 – 1.29 (m, 5H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.5, 120.5, 72.4, 66.7, 33.9, 31.7, 31.4, 25.3, 24.7, 24.1, 22.3, 13.8; HR-MS calculated for $C_{12}H_{21}N_3O$ $[M+Na]^+$: 246.1577, found: 246.1583.



7i

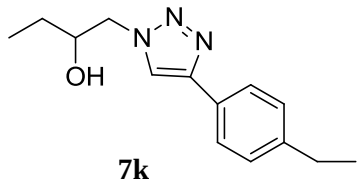
2-(4-(2-fluorophenyl)-1H-1,2,3-triazol-1-yl)cyclohexanol: White solid ; 87% yield; mp 153~155^oC; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.08 (t, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 3.7 Hz, 1H), 7.27 – 7.17 (m, 2H), 6.96 (dd, *J* = 11.1, 8.1 Hz, 1H), 4.15 (dd, *J* = 13.9, 9.6, 4.2 Hz, 2H), 2.32 – 2.12 (m, 2H), 2.05 (qd, *J* = 12.7, 3.5 Hz, 1H), 1.97 – 1.84 (m, 2H), 1.60 – 1.38 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.0 (d, *J* = 248.2 Hz),

140.2, 129.1 (d, *J* = 8.5 Hz), 127.2 (d, *J* = 3.5 Hz), 124.5 (d, *J* = 3.3 Hz), 123.0 (d, *J* = 13.5 Hz), 118.1 (d, *J* = 12.8 Hz), 115.5 (d, *J* = 21.8 Hz), 72.6, 67.4, 33.8, 31.5, 24.8, 24.1; HRMS calculated for $C_{14}H_{16}FN_3O$ $[M+Na]^+$: 284.1170, found: 284.1186.



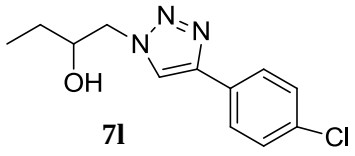
7j

1-(4-phenyl-1H-1,2,3-triazol-1-yl)butan-2-ol: White solid ; 73% yield; mp 148~150 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83 (s, 1H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 4.50 (dd, *J* = 13.9, 2.5 Hz, 1H), 4.30 – 4.20 (m, 1H), 4.12 – 4.04 (m, 1H), 3.43 (s, 1H), 1.59 (dt, *J* = 14.2, 7.1 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.3, 130.3, 128.8, 128.1, 125.5, 121.2, 71.8, 56.0, 27.5, 9.8; HRMS calculated for $C_{12}H_{15}N_3O$ $[M+Na]^+$: 240.1107, found: 240.1115.



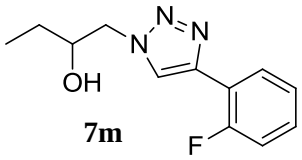
7k

1-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)butan-2-ol: White solid ; 85% yield; mp 125~128 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 3.2 Hz, 1H), 7.58 (dd, *J* = 7.2, 3.4 Hz, 2H), 7.18 (d, *J* = 6.9 Hz, 2H), 4.46 (dd, *J* = 13.8, 4.0, 2.7 Hz, 1H), 4.27 – 4.15 (m, 1H), 4.06 (s, 1H), 3.99 – 3.80 (m, 1H), 2.74 – 2.58 (m, 2H), 1.63 – 1.52 (m, 2H), 1.26 (td, *J* = 7.6, 3.5 Hz, 3H), 1.06 (td, *J* = 7.4, 3.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.3, 144.3, 128.2, 127.7, 125.5, 120.9, 71.7, 56.0, 28.7, 27.5, 15.5, 9.9; HRMS calculated for $C_{14}H_{19}N_3O$ $[M+H]^+$: 246.1601, found: 246.1610.



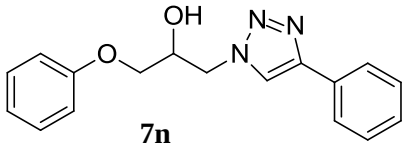
7l

1-(4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)butan-2-ol: White solid ;75% yield; mp 136~138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.82 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.30 (m, 2H), 4.50 (dd, *J* = 13.9, 2.7 Hz, 1H), 4.23 (dd, *J* = 13.9, 8.3 Hz, 1H), 4.08 (d, *J* = 7.3 Hz, 1H), 3.51 (s, 1H), 1.67 – 1.53 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.2, 133.9, 129.0, 128.8, 126.7, 121.3, 71.7, 56.0, 27.5, 9.8; HRMS calculated for $C_{12}H_{14}ClN_3O$ $[M+Na]^+$: 274.0718, found: 274.0727.



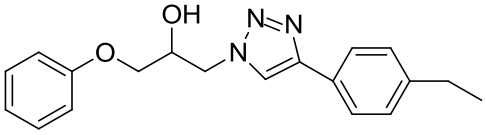
7m

1-(4-(2-fluorophenyl)-1H-1,2,3-triazol-1-yl)butan-2-ol: White solid ;80% yield; mp 100~104 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17 (td, *J* = 7.6, 1.3 Hz, 1H), 8.00 (d, *J* = 3.7 Hz, 1H), 7.31 – 7.20 (m, 2H), 7.04 (dd, *J* = 11.1, 8.2 Hz, 1H), 4.52 (dd, *J* = 13.8, 2.8 Hz, 1H), 4.28 (dd, *J* = 13.8, 8.2 Hz, 1H), 4.12 (dd, *J* = 8.0, 5.5, 2.8 Hz, 1H), 3.33 (s, 1H), 1.68 – 1.55 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.1 (d, *J* = 248.1 Hz), 140.8 (d, *J* = 2.4 Hz), 129.2 (d, *J* = 8.5 Hz), 127.4 (d, *J* = 3.5 Hz), 124.5 (d, *J* = 3.3 Hz), 124.2 (d, *J* = 13.1 Hz), 118.3 (d, *J* = 12.8 Hz), 115.6 (d, *J* = 21.8 Hz), 71.7, 56.0, 27.5, 9.8; HRMS calculated for $C_{12}H_{14}FN_3O$ $[M+Na]^+$: 258.1013, found: 258.1007.



7n

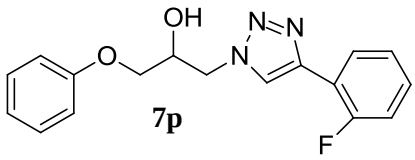
1-phenoxy-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol: White solid ;70% yield; mp 145~148 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (s, 1H), 7.71 (d, *J* = 6.3 Hz, 2H), 7.33 (dd, *J* = 25.0, 6.3 Hz, 5H), 7.07 – 6.85 (m, 3H), 4.72 (d, *J* = 9.3 Hz, 1H), 4.53 (d, *J* = 7.9 Hz, 2H), 4.03 (s, 2H), 3.82 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.8, 144.1, 128.2, 127.7, 125.4, 119.5, 72.5, 67.3, 33.8, 31.5, 28.7, 24.8, 24.1, 15.6. HRMS calculated for $C_{17}H_{17}N_3O_2$ $[M+Na]^+$: 318.1213, found: 318.1215.



7o

1-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)-3-phenoxypropan-2-ol: White solid ;70% yield; mp 128~130 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.00 (dd, *J* = 15.6, 8.3 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.73 (q, *J* = 6.3 Hz, 1H), 4.62 – 4.47 (m, 2H), 4.12 – 3.96 (m, 2H), 3.91 – 3.70 (m, 1H), 2.78 – 2.59 (m, 2H), 1.34 – 1.22 (m, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.8, 144.1, 128.2, 127.7, 125.4, 119.5, 72.5, 67.3, 33.8, 31.5, 28.7, 24.8, 24.1, 15.6;

HRMS calculated for $C_{19}H_{21}N_3O_2$ $[M+Na]^+$: 346.1526, found: 346.1532.

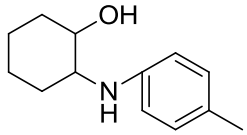


7p

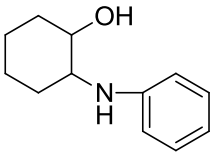
1-(4-(2-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-phenoxypropan-2-ol: White solid ; 70% yield; mp 135~138 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.19 (td, *J* = 7.6, 1.5 Hz, 1H), 8.06 (d, *J* = 3.6 Hz, 1H), 7.31 (dd, *J* = 16.2, 8.3 Hz, 3H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.06 (dd, *J* = 11.0, 8.3 Hz, 1H), 7.01 (dd, *J* = 13.3, 6.0 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.82 – 4.72 (m, 1H), 4.64 – 4.54 (m, 2H), 4.14 – 4.04 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 160.1, 158.2, 141.0 (d, *J* = 2.5 Hz), 129.6, 129.4 (d, *J* = 8.4 Hz), 127.5 (d, *J* = 3.4 Hz), 124.6 – 124.5 (m), 124.4, 121.5, 118.1 (d, *J* = 12.8 Hz), 115.7 (d, *J* = 21.7 Hz), 114.6, 68.9, 53.3; HR-MS calculated for $C_{17}H_{16}FN_3O_2$ $[M+Na]^+$: 336.1119, found: 336.1129.

S-5. Ring-opening reaction of epoxide with aromatic amines catalyzed by polyurea-encapsulated copper(I) chloride

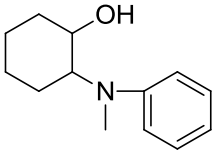
General Procedure for the Cu/Polyurea-Catalyzed Synthesis of *β*-Hydroxyamines from Epoxides in Water: epoxide (1 mmol), and arylamine (1 mmol) were added to a suspension of CuCl (1 mg, 1 mol % Cu) and polyurea **3a** (10 mg) in H_2O (2 mL). After the completion of the reaction, as monitored by TLC using *n*-hexane/ethyl acetate (5:1). The combined and organic washings were extracted with ethyl acetate (3×10 mL), the combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum, followed by purification on silica gel using hexane-ethyl acetate (10:1) to give the desired product **9** or **10**.



2-(p-tolylamino)cyclohexanol (9a): Red brown liquid; 85% yield ; ^{1}H NMR (400 MHz, CDCl3) δ = 6.89 (d, J = 8.1 Hz, 2H), 6.53 (d, J = 8.4 Hz, 2H), 3.26 – 3.16 (m, 1H), 2.96 (td, J = 11.3, 4.0 Hz, 3H), 2.15 (s, 3H), 1.99 (dt, J = 15.3, 8.5 Hz, 2H), 1.69 – 1.50 (m, 2H), 1.38 – 1.05 (m, 3H), 0.96 – 0.82 (m, 1H). ^{13}C NMR (101 MHz, CDCl3) δ = 145.5, 129.8, 127.8, 114.8, 74.4, 60.7, 33.3, 31.6, 25.1, 24.4, 20.4; HR-MS calculated for $C_{13}H_{19}NO$ $[M+H]^+$: 206.1539, found: 206.1581.

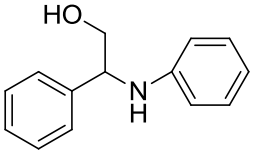


2-(phenylamino)cyclohexanol (9b): Red brown liquid; 90% yield ; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 – 7.13 (m, 2H), 6.81 – 6.67 (m, 3H), 3.35 (td, *J* = 10.0, 4.3 Hz, 1H), 3.14 (ddd, *J* = 11.2, 9.2, 4.0 Hz, 1H), 2.72 (s, 1H), 2.19 – 2.04 (m, 2H), 1.83 – 1.67 (m, 2H), 1.38 – 1.22 (m, 3H), 1.06 (ddd, *J* = 20.3, 12.8, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.0, 129.4, 118.3, 114.4, 74.5, 60.1, 33.3, 31.62, 25.0, 24.3; HR-MS calculated for $C_{12}H_{17}NO$ $[M+H]^+$: 192.1384, found:192.1388.



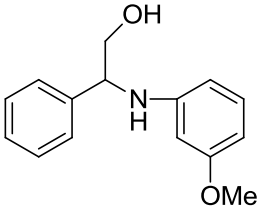
2-(methyl(phenyl)amino)cyclohexanol (9c): Red brown liquid; 83% yield;

^{1}H NMR (500 MHz, None) δ = 7.31 – 7.26 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 3.69 (td, *J* = 10.2, 4.5 Hz, 1H), 3.51 – 3.33 (m, 1H), 2.80 (s, 3H), 2.27 – 2.14 (m, 1H), 1.83 – 1.71 (m, 3H), 1.49 – 1.39 (m, 2H), 1.33 – 1.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.1, 137.6, 129.3, 128.6, 127.6, 127.2, 118.4, 114.8, 64.6, 61.8, 32.2; HR-MS calculated for $C_{13}H_{19}NO$ $[M+H]^+$: 206.1539, found: 206.1537.



2-phenyl-2-(phenylamino)ethanol (10a): red brown liquid; 87% yield;

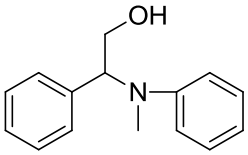
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 2H), 4.50 (dd, *J* = 7.0, 4.2 Hz, 1H), 3.93 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.75 (dd, *J* = 11.1, 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.4, 140.3, 129.3, 128.9, 127.6, 126.9, 118.0, 114.0, 67.3, 60.0; HR-MS calculated for $C_{14}H_{15}NO$ $[M+Na]^+$: 236.1046, found: 236.1051.



2-((3-methoxyphenyl)amino)-2-phenylethanol (10b):

Red brown liquid; 80% yield ; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 7.00 (t, *J* = 8.1 Hz, 1H), 6.28 – 6.17 (m, 2H), 6.12 (t, *J* = 2.3 Hz, 1H), 4.48 (dd, *J* = 6.9, 4.2 Hz, 1H),

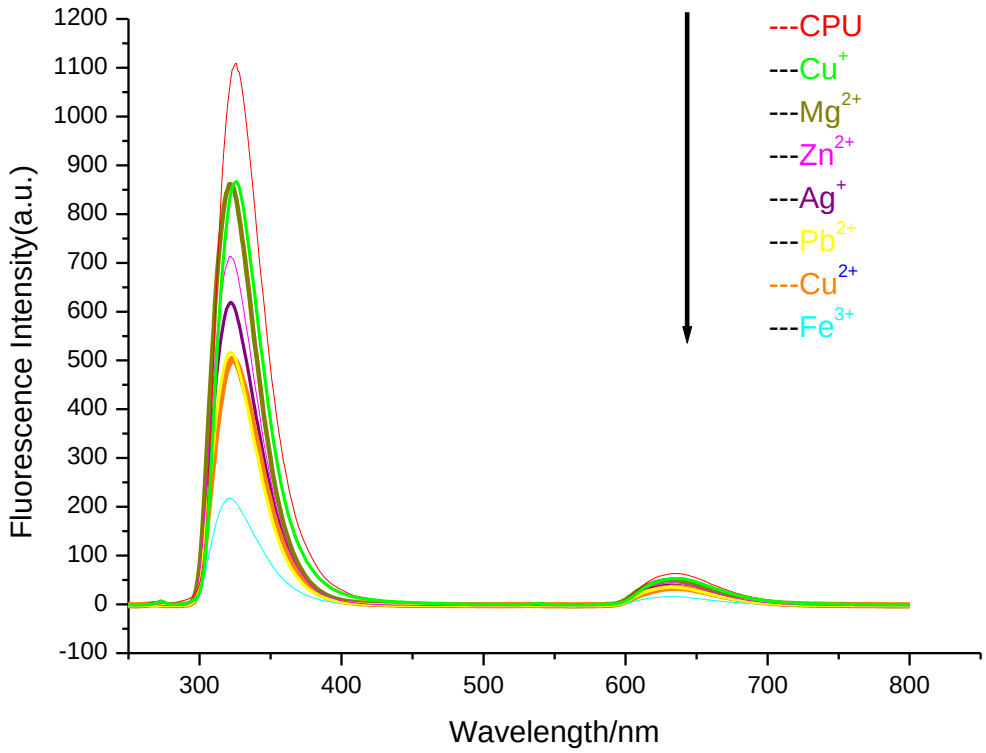
3.92 (dd, *J* = 11.2, 4.2 Hz, 1H), 3.75 (dd, *J* = 11.2, 7.0 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.3, 148.2, 139.5, 129.9, 128.8, 127.6, 126.7, 107.0, 103.2, 100.1, 67.2, 60.0, 55.0; HR-MS calculated for $C_{15}H_{17}NO_2$ $[M+H]^+$: 244.1332, found: 244.1329.



2-(methyl(phenyl)amino)-2-phenylethanol (10c): Red brown liquid; 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.20 (m, 5H), 7.16 – 7.08 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 5.07 (dd, *J* = 8.6, 6.1 Hz, 1H), 4.42 – 3.73 (m, 2H), 2.70 (s, 3H).

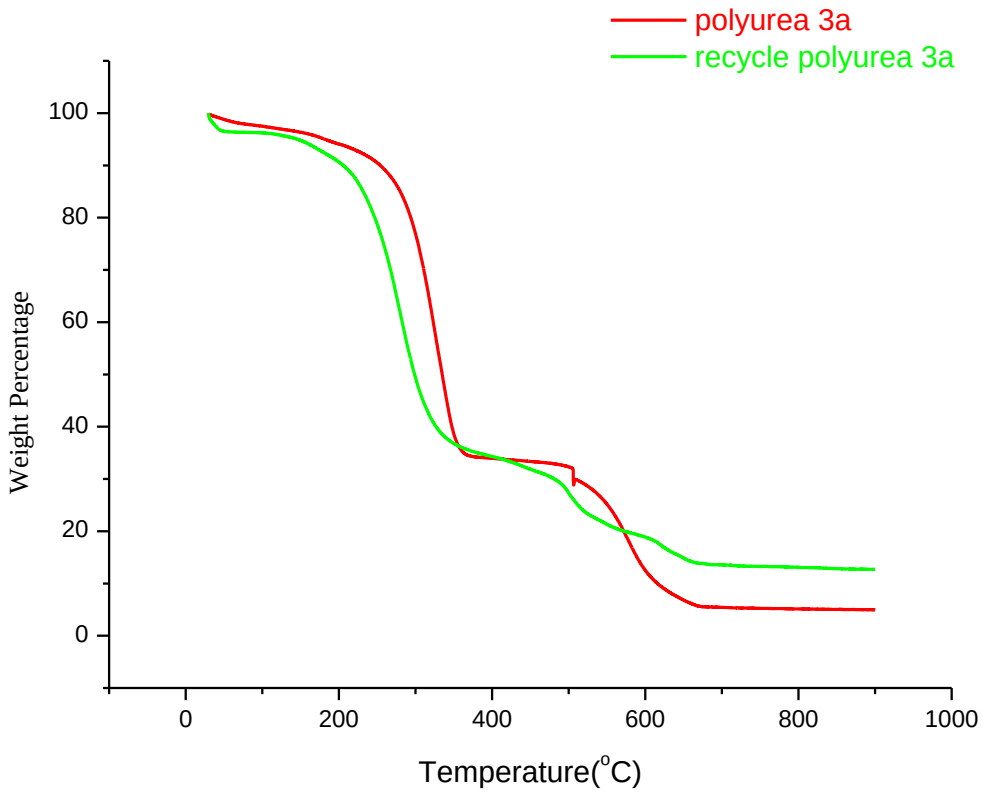
^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.1, 137.6, 129.3, 128.6, 127.6, 127.2, 118.4, 114.8, 64.6, 61.8, 32.2; HR-MS calculated for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1383, found: 228.1380.

Figure S1. Fluorescence response profiles of polyurea 3a in DMSO ($1x10^{-5}$) upon addition of different metal ions: A direct evidence for the good interaction between polyurea and CuCl.



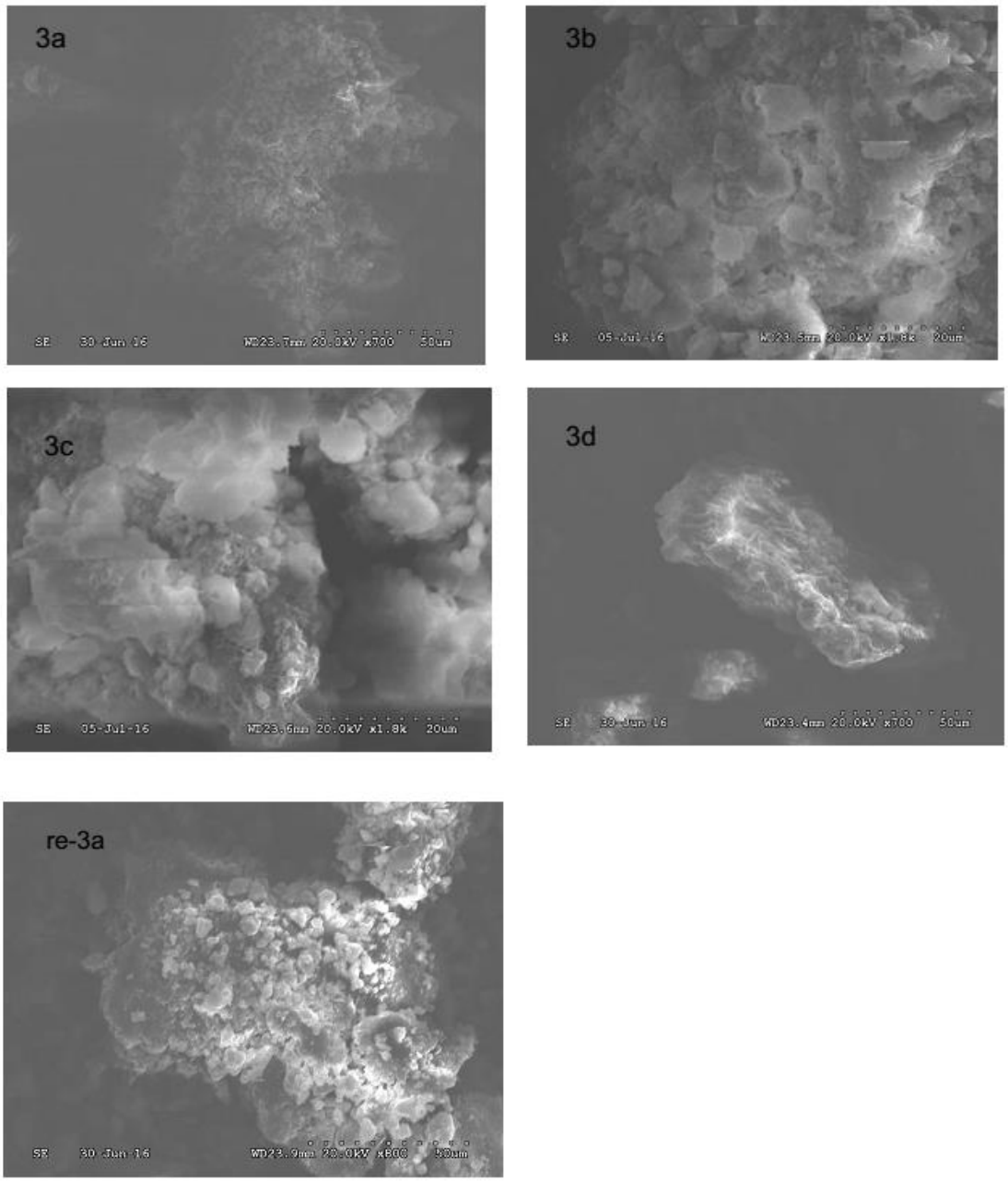
Note: The quenching of polyurea **3a** with CuCl is the less pronounced of the tested metal ions (chloride anion) in solution.

Figure S2. The TGA study of the polyurea 3a and the recycled polyurea 3a.



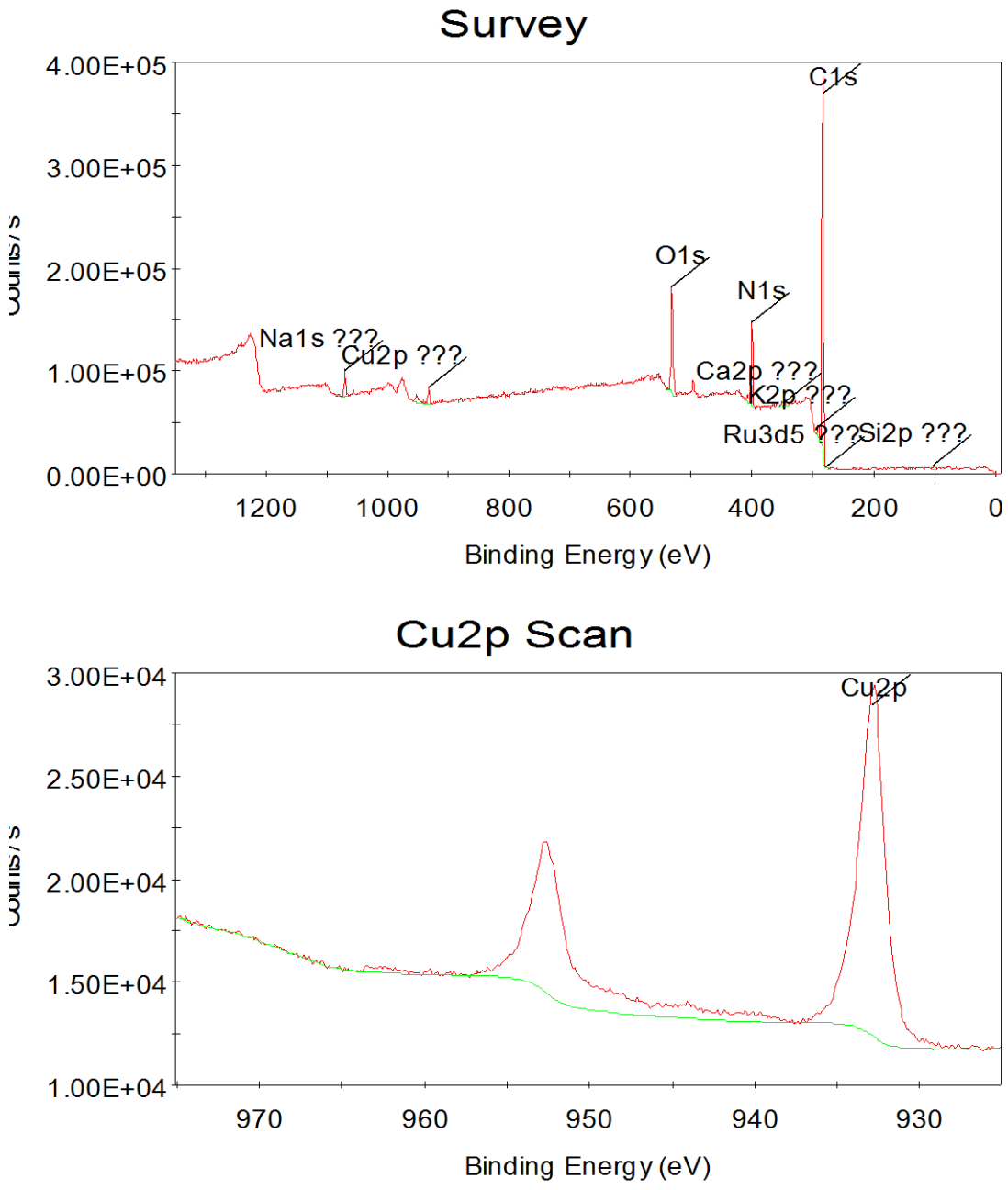
Note: There is no obvious difference for the polyurea **3a** and recycled polyurea **3a** – encapsulated CuCl catalyst before and after reaction respectively.

Figure S3. SEM images of polyurea 3a, 3b, 3c, 3d and the SEM image of recycled poyurea 3a.

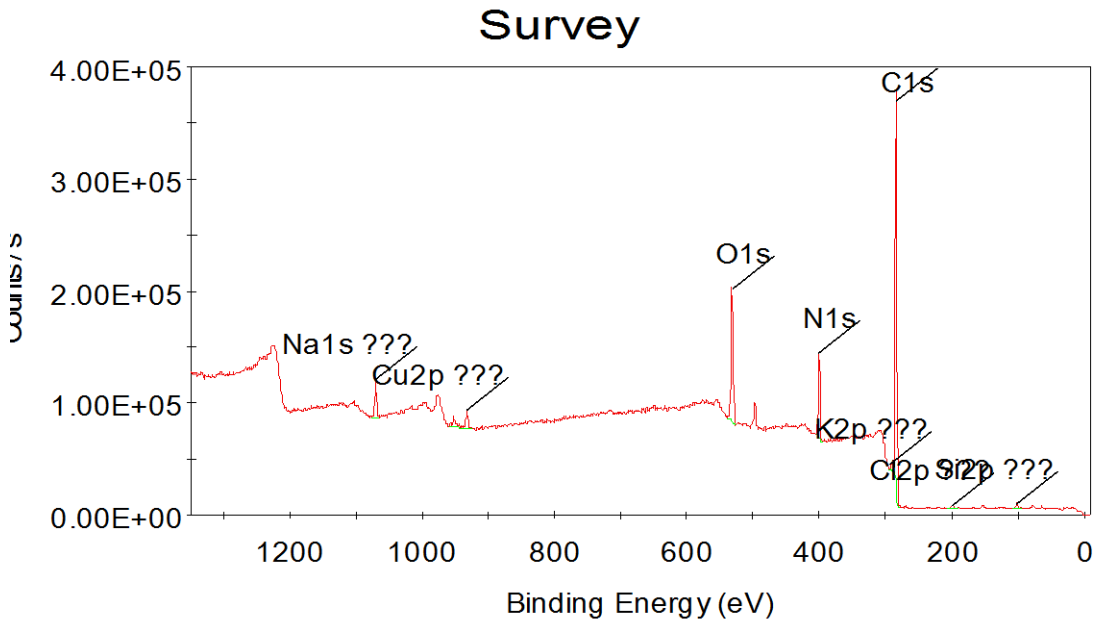


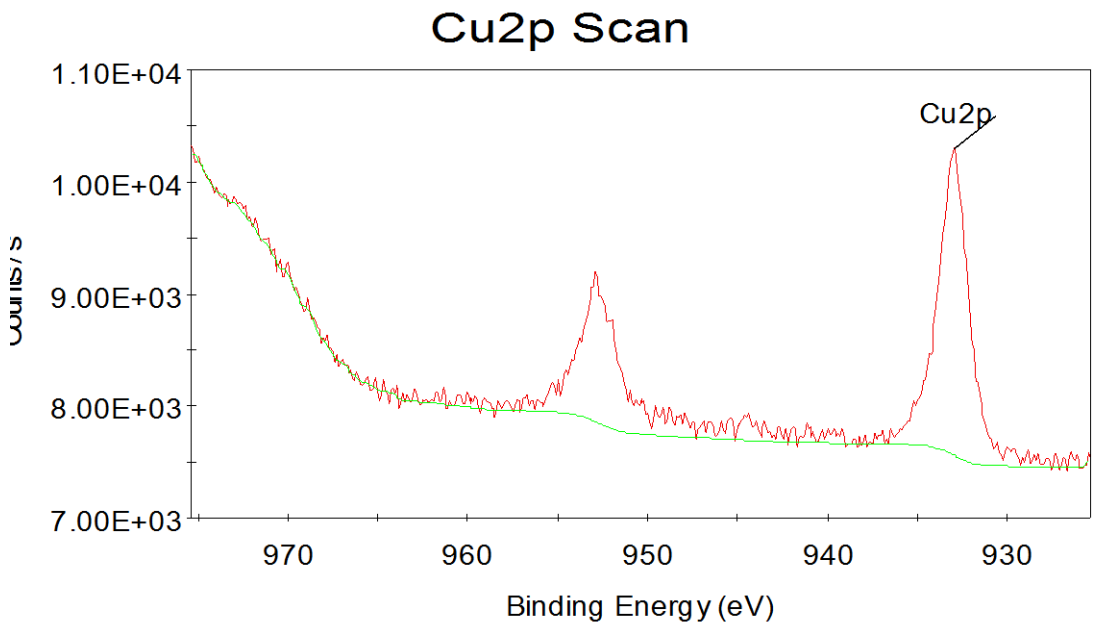
Note: There is no difference for the SEM images of polyurea **3a** and recycled polyurea **3a** –encapsulated CuCl catalyst before and after reaction respectively.

Figure S4. XPS fully scanned spectrum and XPS spectrum of Cu 2p of the polyurea-encapsulated copper catalyst.

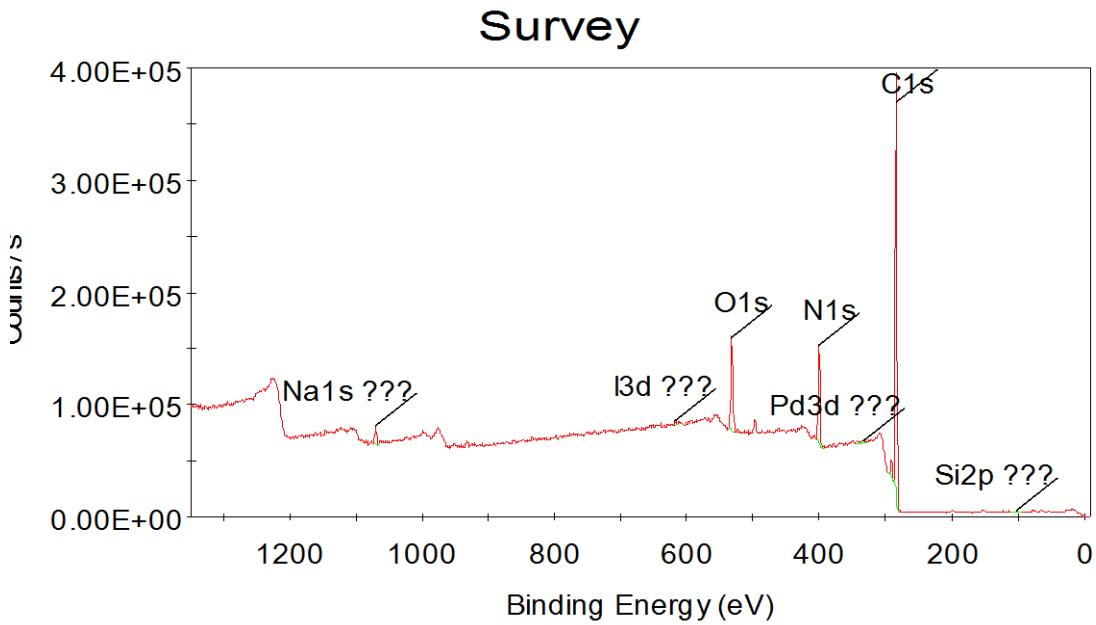


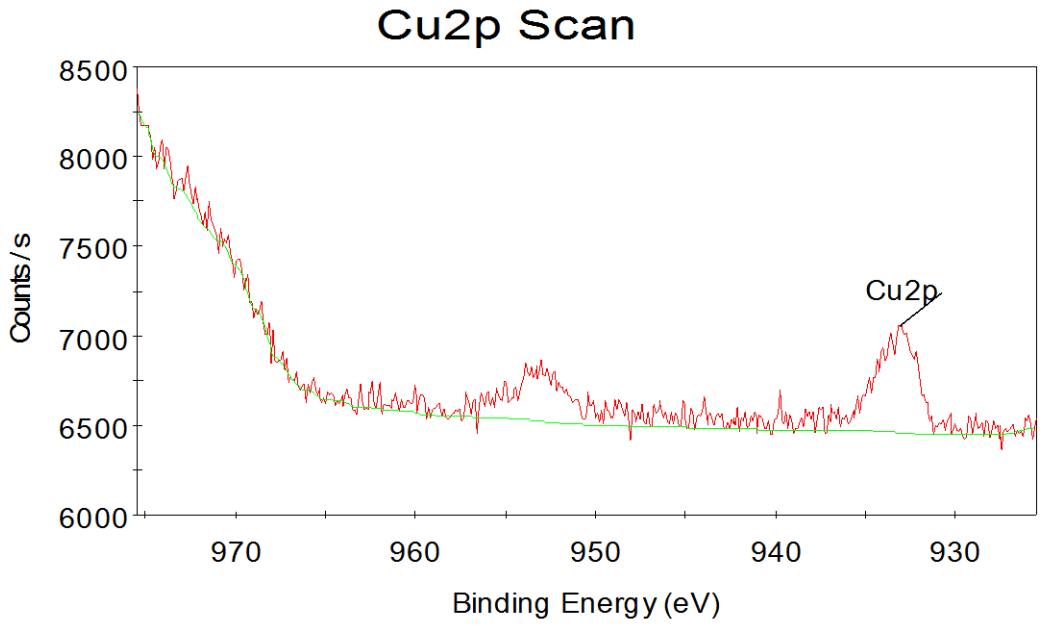
(a) For the reused polyurea-encapsulated copper catalyst of run 2. The measured binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are equal to 933.08 and 953.08.





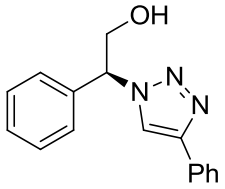
(b) For the reused polyurea-encapsulated copper catalyst of run 4. The measured binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are equal to 933.08 and 953.08.



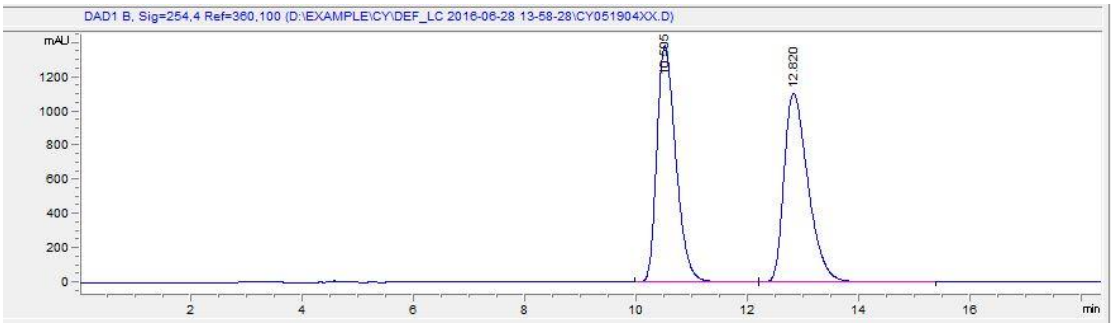


(c) For the reused polyurea-encapsulated copper catalyst of run 6. The measured binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are equal to 933.08 and 953.08.

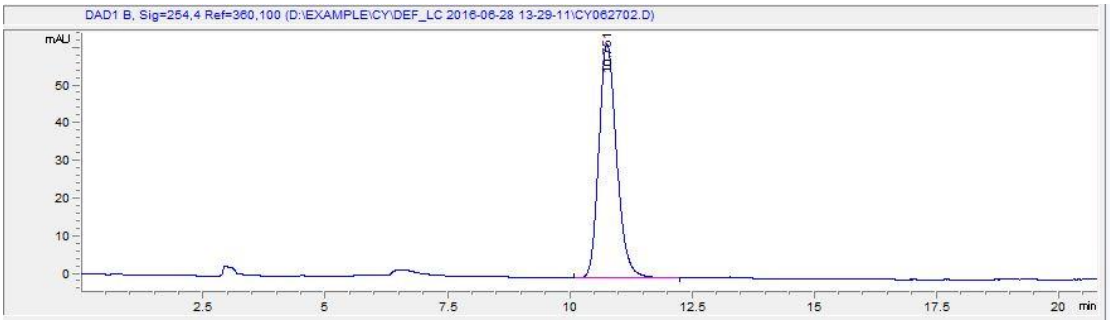
S-6. HPLC spectra of product (s)-7a~7f



(*S*)-**7a**
95% yield
100% *ee*

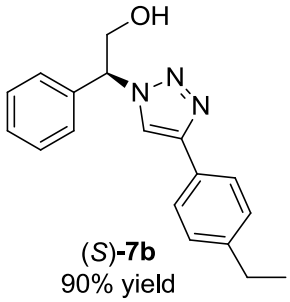


#	Time	Area	Height	Width	Symmetry	Area%
1	10.509	41612.2	1568.1	0.4216	0.68	48.562
2	12.823	44076.2	1366.6	0.5003	0.613	51.438

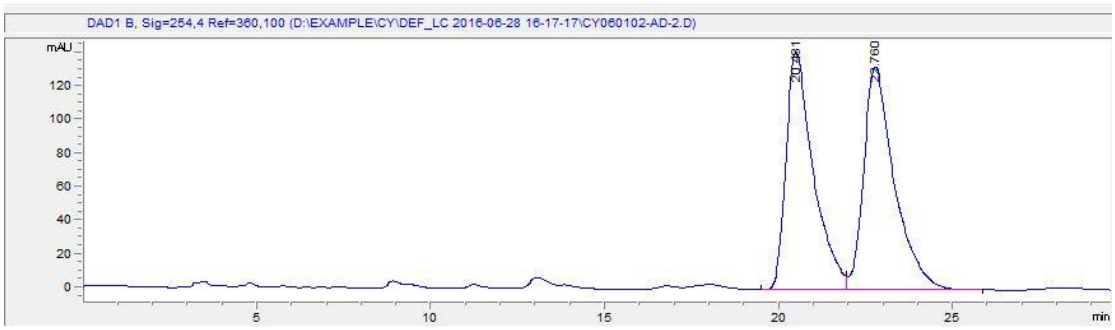


#	Time	Area	Height	Width	Symmetry	Area%
1	10.751	1576.5	62.1	0.3884	0.782	100.000

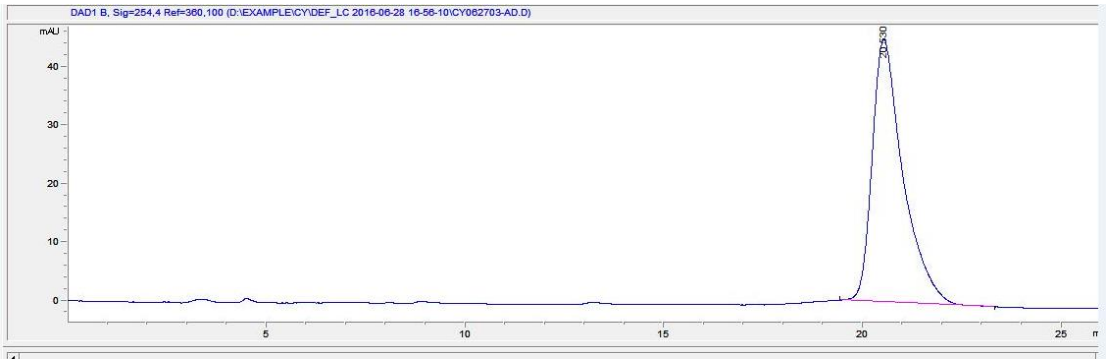
(HPLC conditions: chiralcel OD-H, n-hexane/2-propanol = 80/20, 1 mL/min)



(*S*)-**7b**
90% yield
100% *ee*

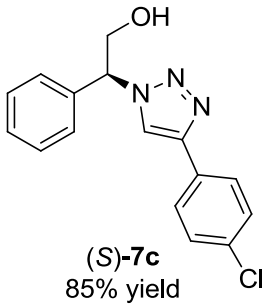


#	Time	Area	Height	Width	Symmetry	Area%
1	20.481	7749.4	141.4	0.8056	0.532	48.905
2	22.76	8096.4	132.8	0.895	0.565	51.095

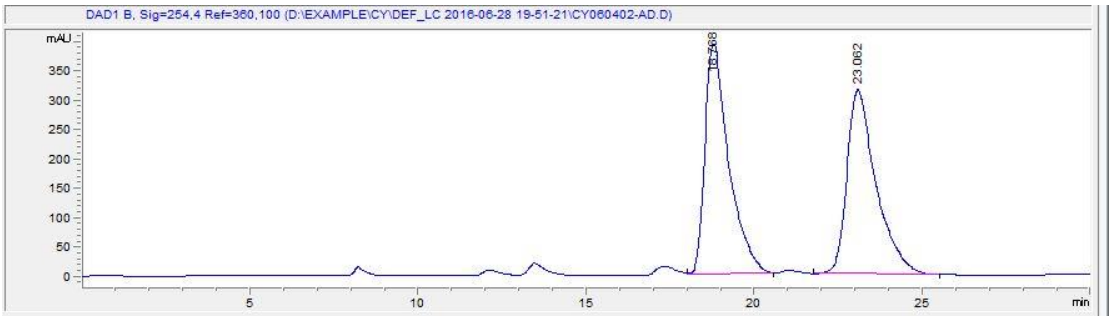


#	Time	Area	Height	Width	Symmetry	Area%
1	20.53	2426.8	44.9	0.7848	0.556	100.000

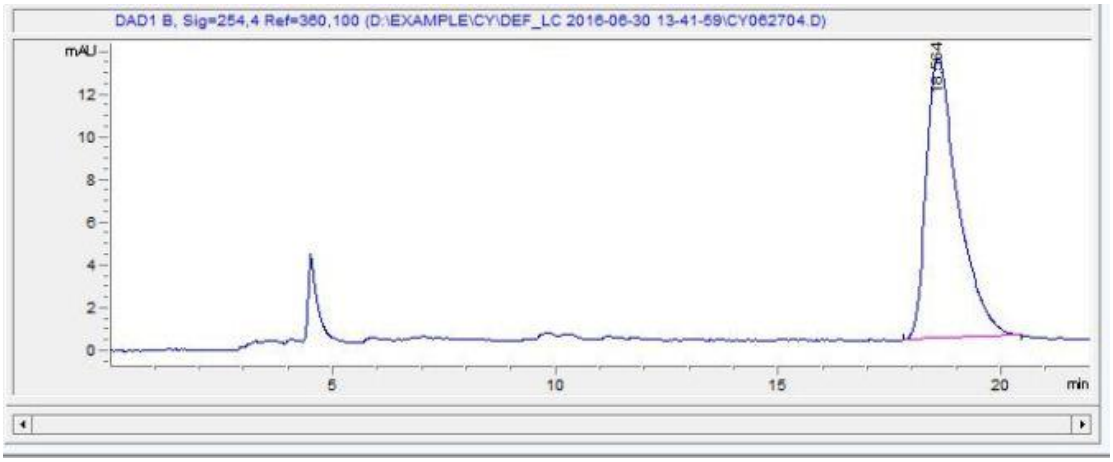
(HPLC conditions: chiralcel AD-H, n-hexane/2-propanol = 80/20, 1 mL/min)



(*S*)-**7c**
85% yield
100% *ee*

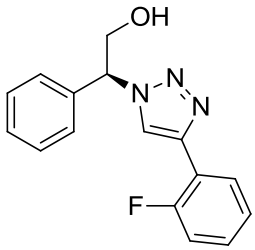


#	Time	Area	Height	Width	Symmetry	Area%
1	18.768	19313.2	392.3	0.7223	0.518	50.550
2	23.062	18893.3	314.4	0.8852	0.557	49.450

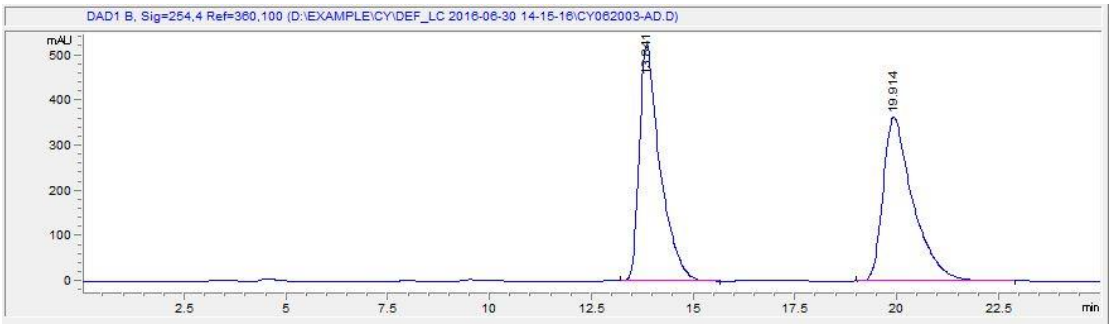


#	Time	Area	Height	Width	Symmetry	Area%
1	18.564	652.6	13.2	0.6965	0.526	100.000

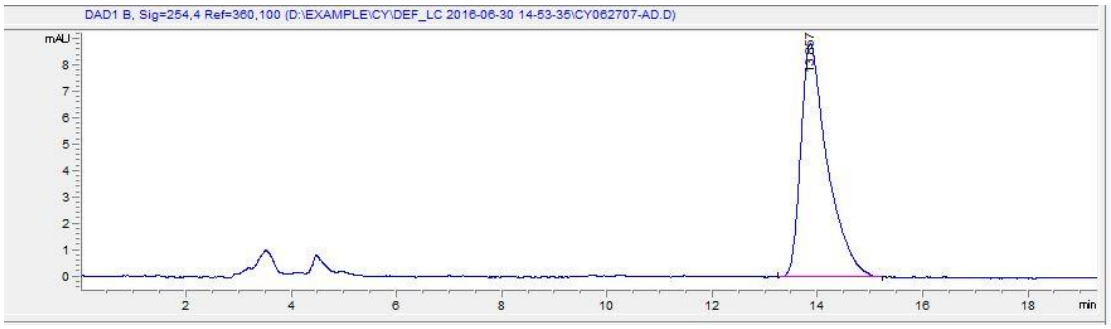
(HPLC conditions: chiralcel AD-H, n-hexane/2-propanol = 80/20, 1 mL/min)



(*S*)-**7d**
85% yield
100% *ee*

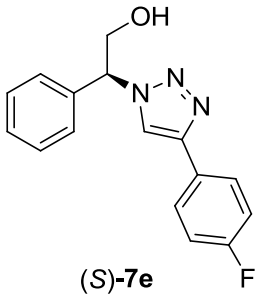


#	Time	Area	Height	Width	Symmetry	Area%
1	13.841	18524.8	521.2	0.5167	0.501	50.113
2	19.914	18441	362.3	0.7418	0.521	49.887

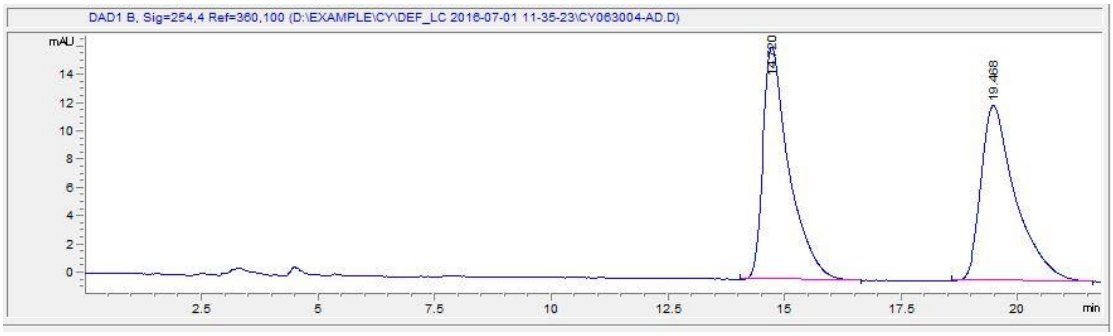


#	Time	Area	Height	Width	Symmetry	Area%
1	13.857	310.1	8.8	0.4931	0.528	100.000

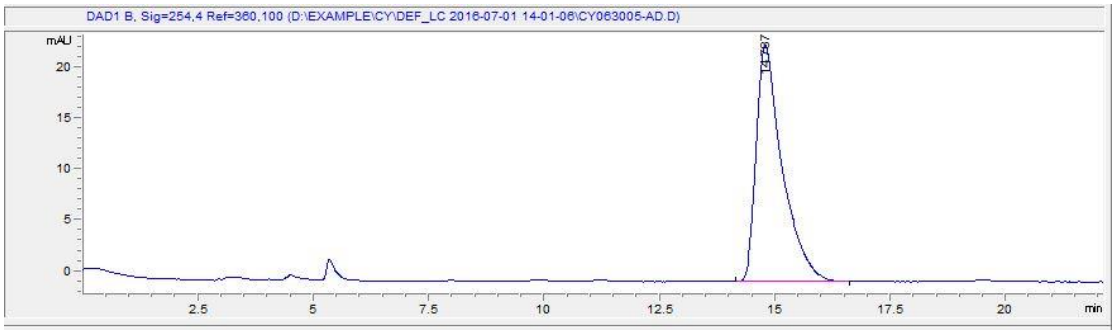
(HPLC conditions: chiralcel AD-H, n-hexane/2-propanol = 80/20, 1 mL/min)



(*S*)-**7e**
80% yield
100% *ee*

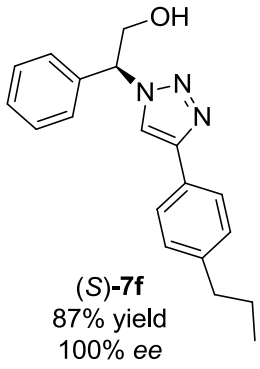


#	Time	Area	Height	Width	Symmetry	Area%
1	14.72	648.7	16.5	0.5607	0.494	50.492
2	19.468	636.1	12.4	0.7209	0.522	49.508

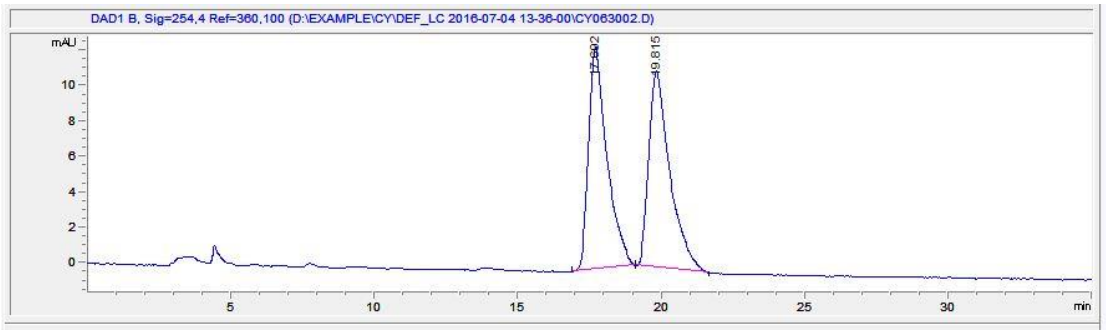


#	Time	Area	Height	Width	Symmetry	Area%
1	14.784	901.7	23.1	0.5569	0.5	100.000

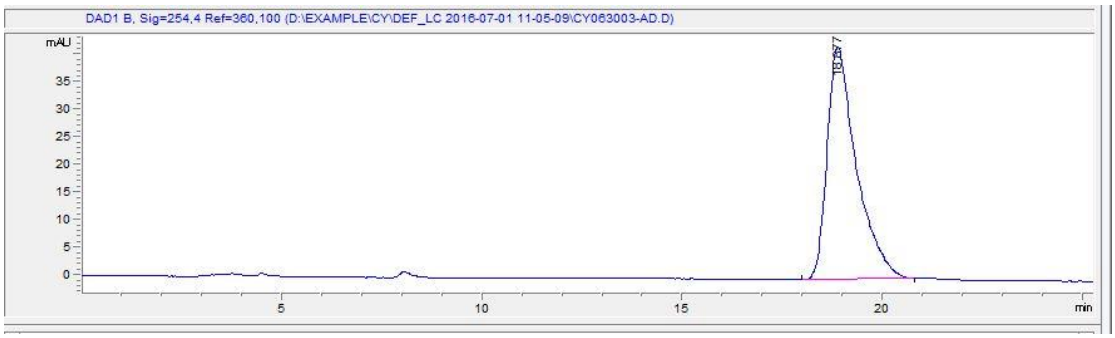
(HPLC conditions: chiralcel AD-H, n-hexane/2-propanol = 80/20, 1 mL/min)



(*S*)-**7f**
87% yield
100% *ee*



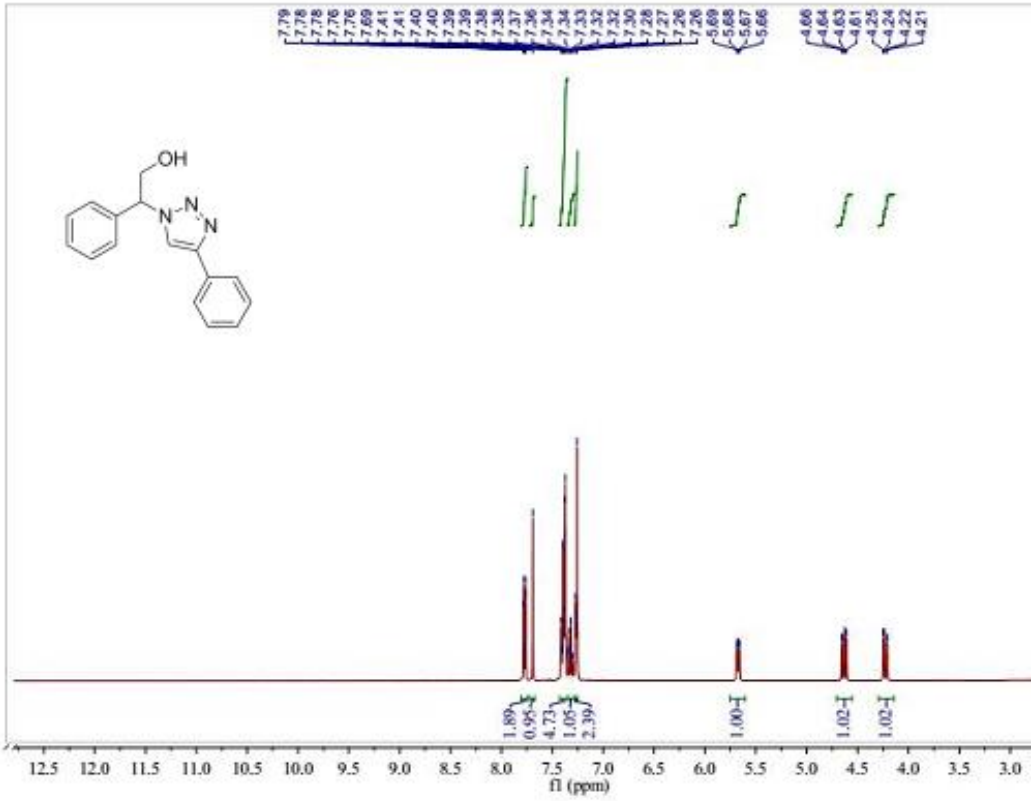
#	Time	Area	Height	Width	Symmetry	Area%
1	17.692	562.8	12.5	0.6386	0.554	49.809
2	19.815	567.1	11.1	0.718	0.533	50.191

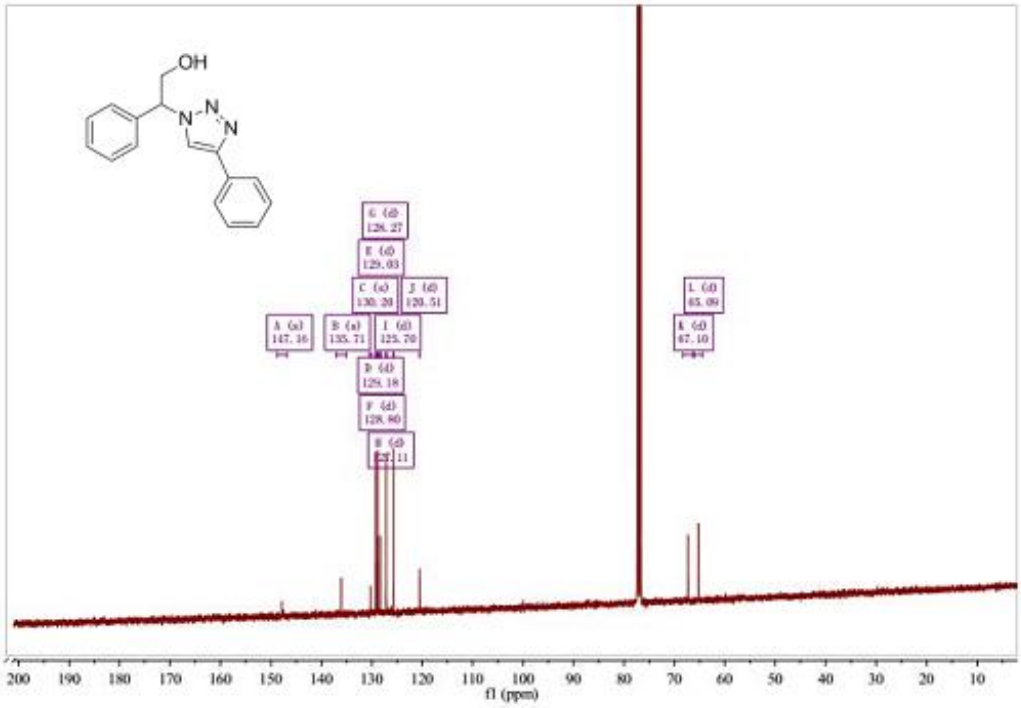


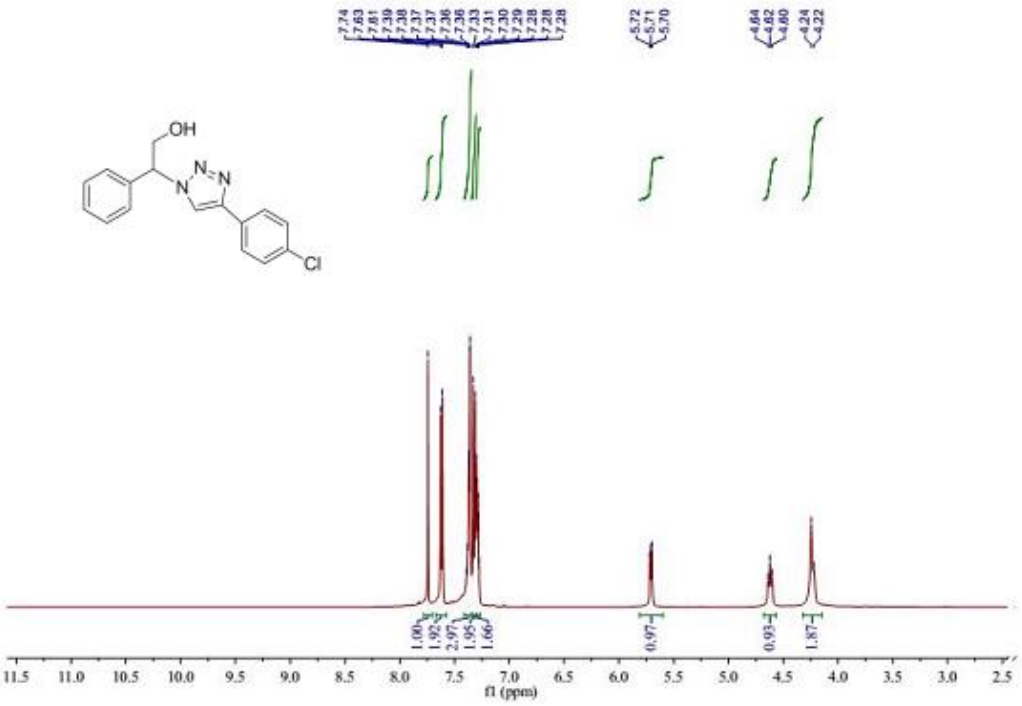
#	Time	Area	Height	Width	Symmetry	Area%
1	18.887	2139.8	42	0.7405	0.538	100.000

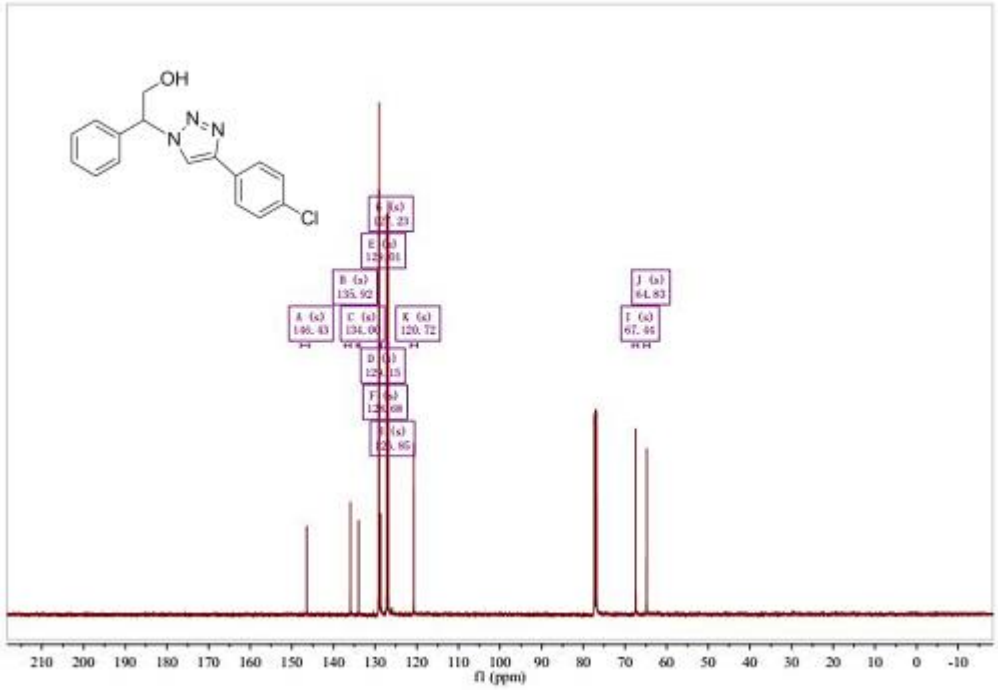
(HPLC conditions: chiralcel AD-H, n-hexane/2-propanol = 80/20, 1 mL/min)

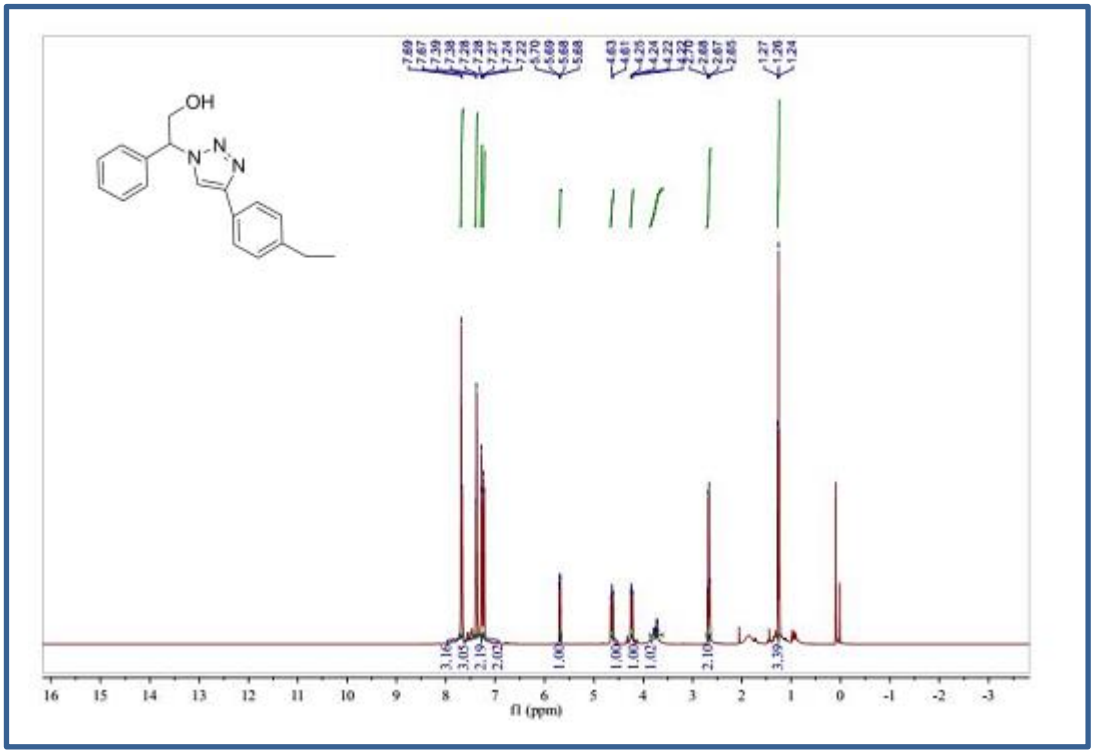
S-7. NMR Spectrum

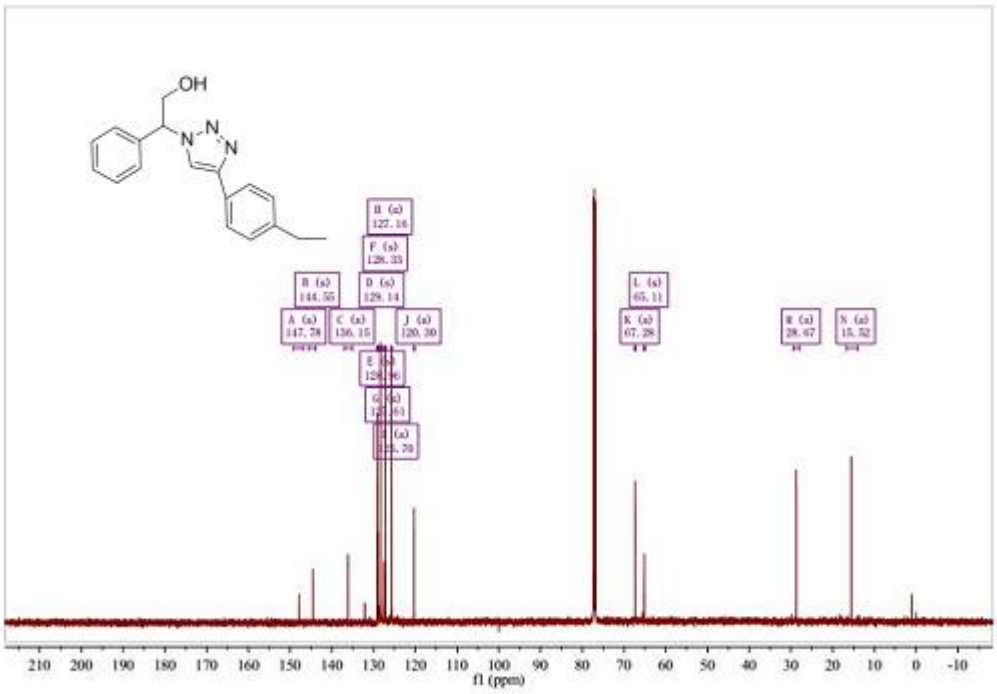


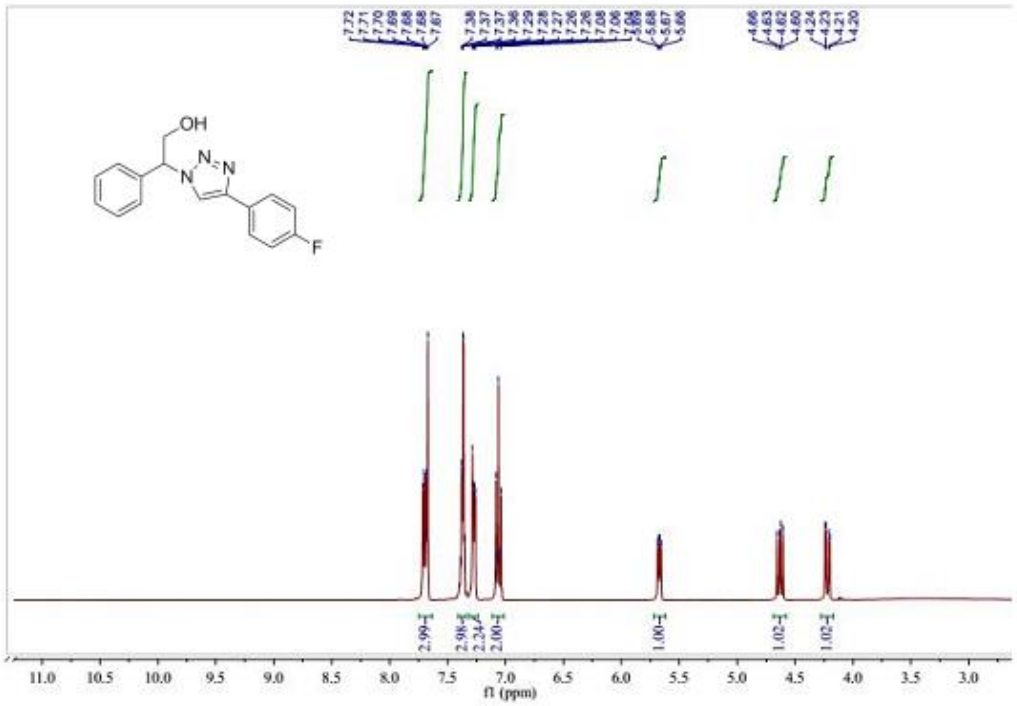


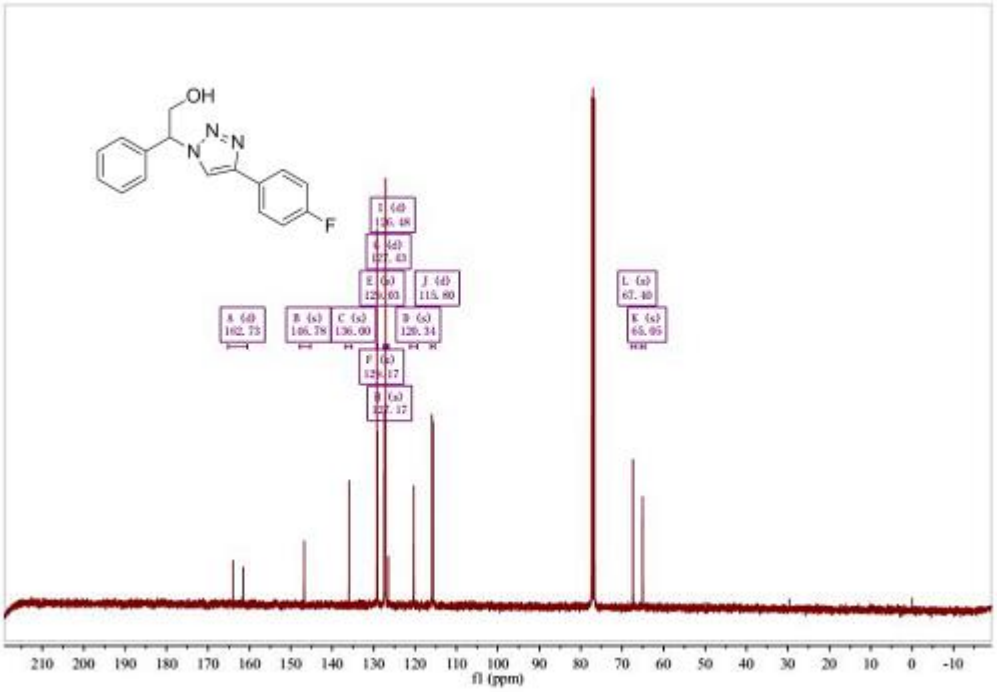

OH
N
N
N
Cl
7.74
7.63
7.61
7.39
7.38
7.37
7.37
7.36
7.36
7.33
7.31
7.30
7.29
7.28
7.28
7.28
5.72
5.71
5.70
4.64
4.62
4.60
4.24
4.22
1.00
1.92
2.97
1.95
1.66
0.97
0.93
1.87
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
f1 (ppm)

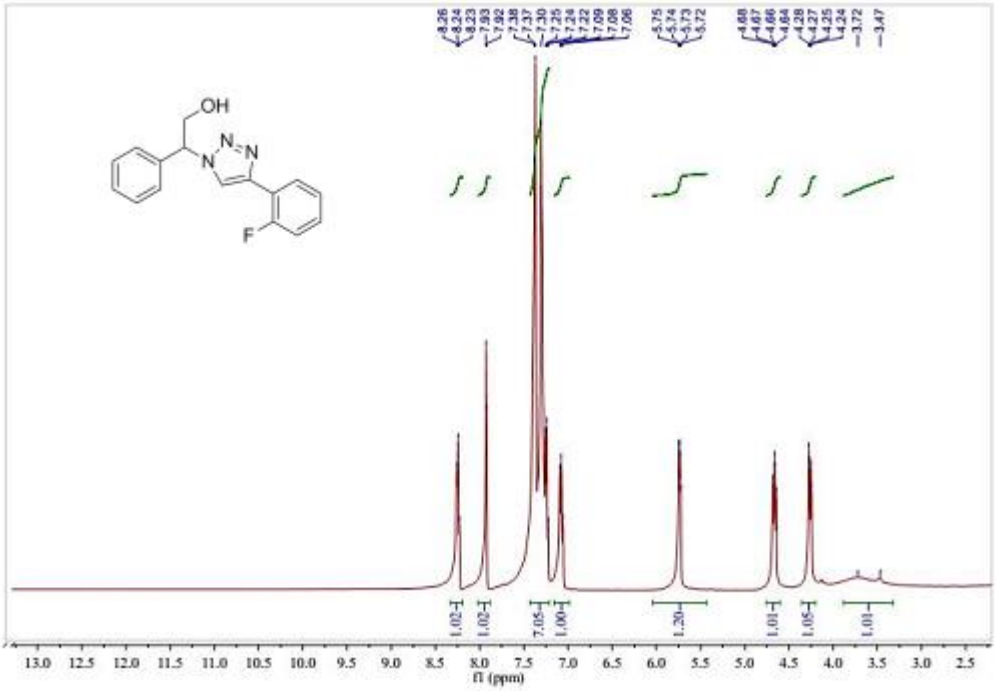

OH
N
N
N
Cl
A (s)
146.43
B (s)
135.92
C (s)
134.00
K (s)
120.72
J (s)
64.83
I (s)
67.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

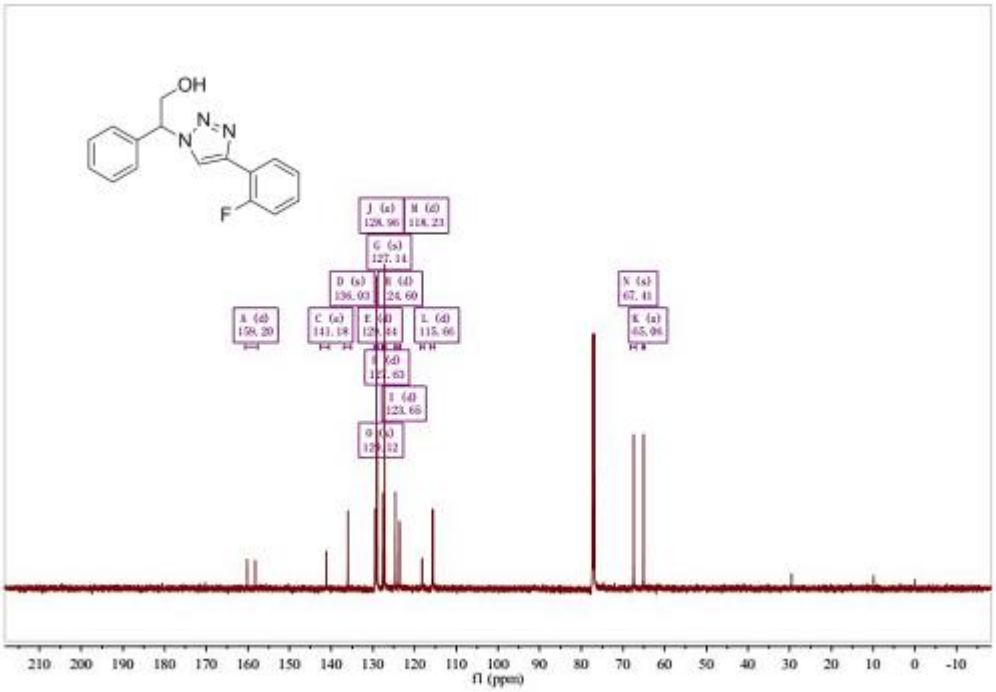

OH
N
N
N
fl (ppm)

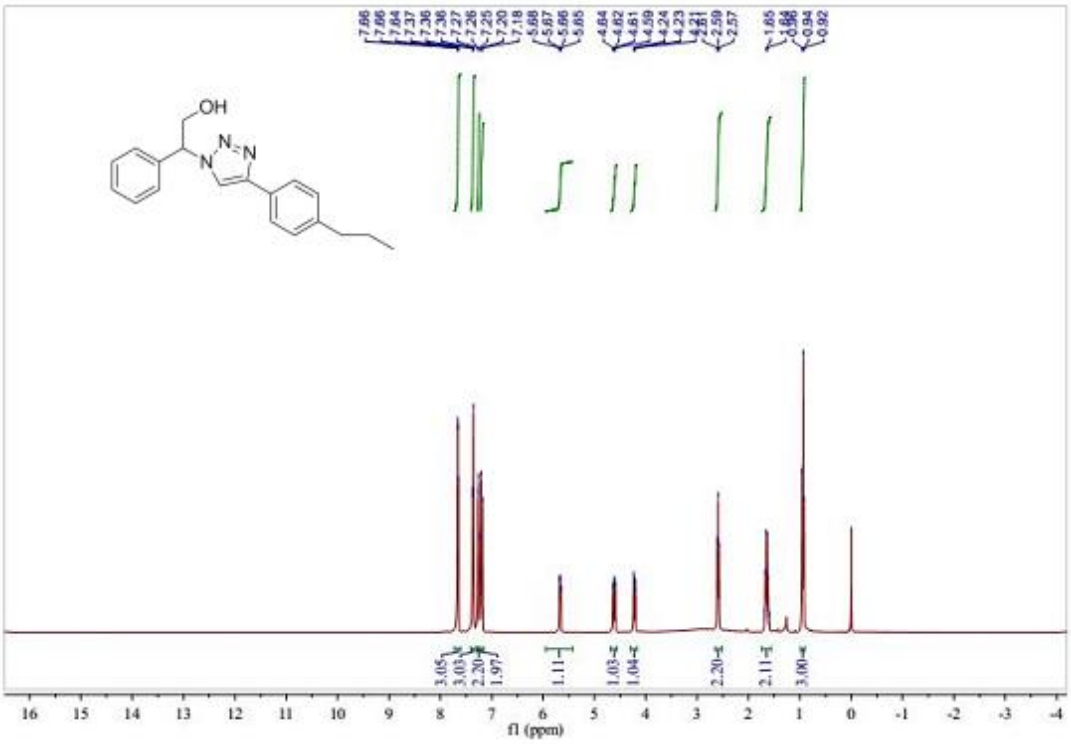

OH
N
N
N
fl (ppm)

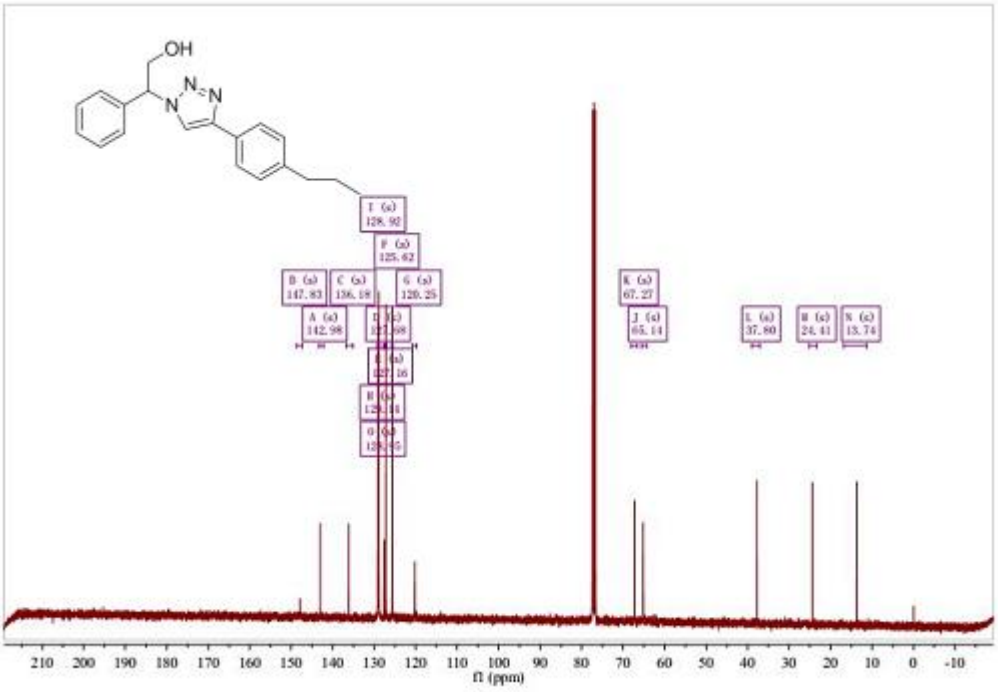

OH
N
N
N
F
2.99
2.98
2.24
2.00
1.00
1.02
1.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
f1 (ppm)

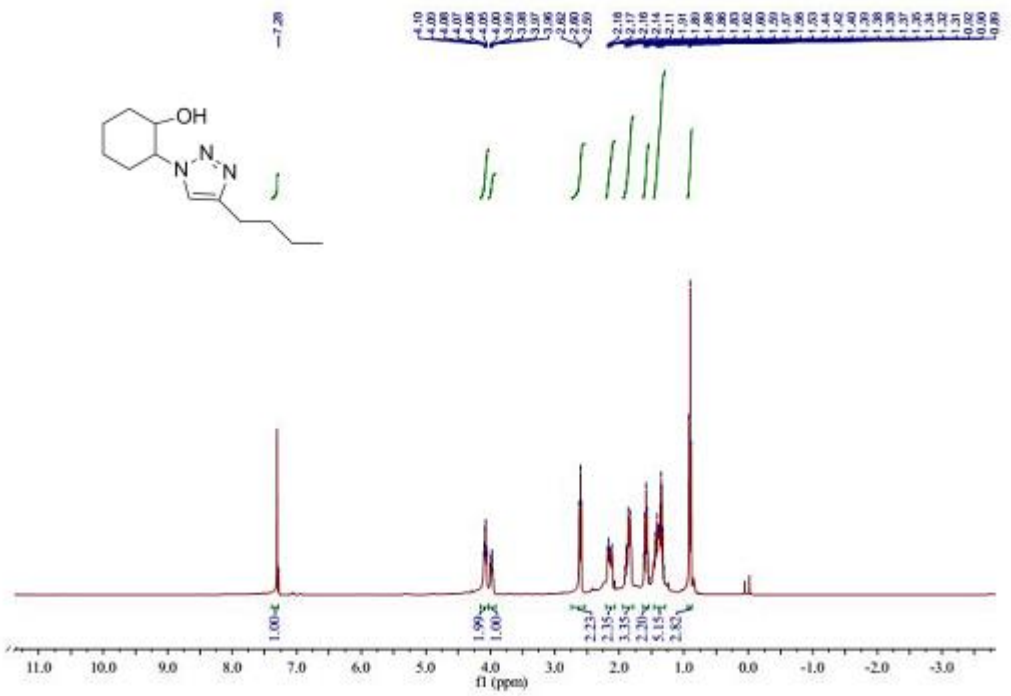

OH
N
N
N
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

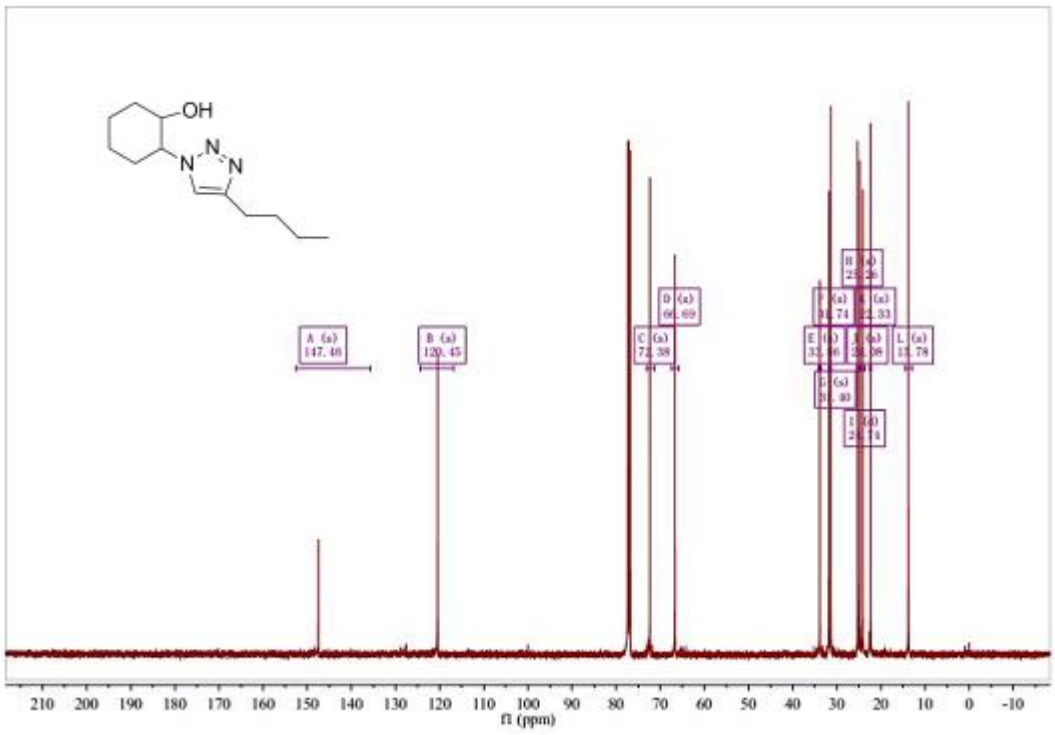

OH
N
N
N
F
8.26
8.24
8.23
7.93
7.92
7.38
7.37
7.30
7.26
7.24
7.22
7.09
7.08
7.06
5.75
5.74
5.73
5.72
4.68
4.67
4.66
4.64
4.28
4.27
4.25
4.24
3.72
3.47
1.02
1.02
7.05
1.00
1.20
1.01
1.05
1.01
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
f1 (ppm)

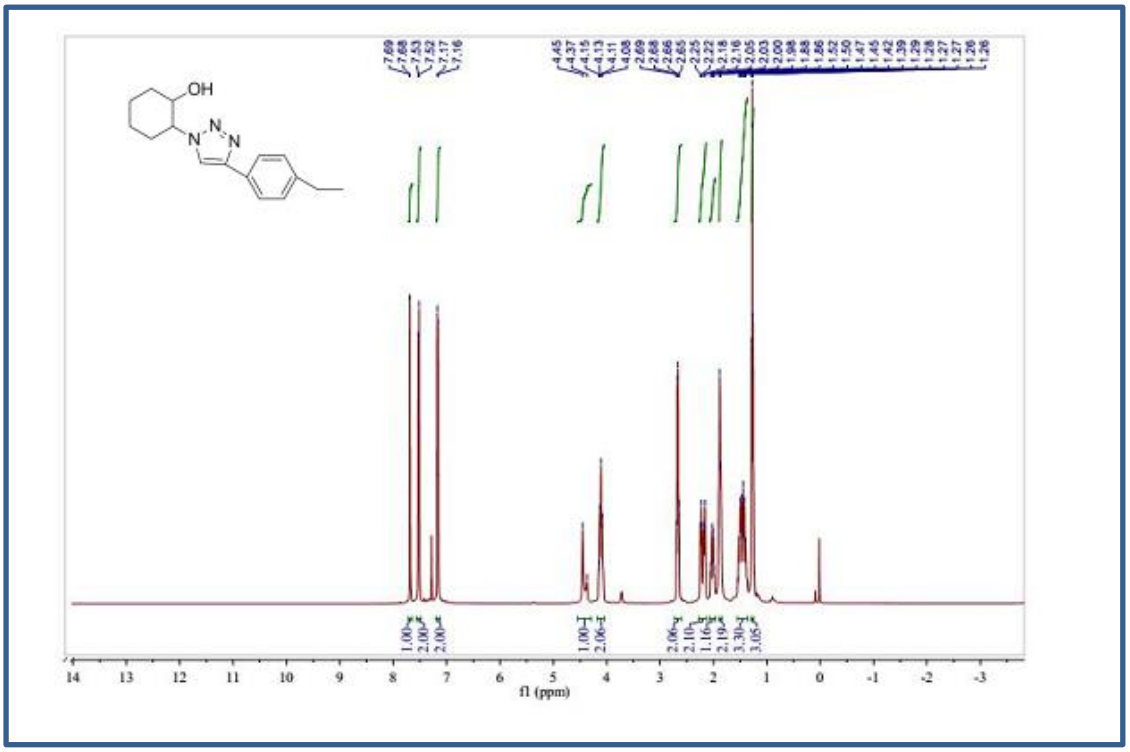

OH
N
N
N
F
J (s) 128.96
M (d) 118.23
G (s) 127.14
D (s) 136.03
H (d) 24.60
A (d) 159.20
C (s) 141.18
E (d) 129.84
L (d) 115.66
F (d) 121.63
I (d) 123.65
B (d) 129.12
N (t) 67.41
K (s) 65.96
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

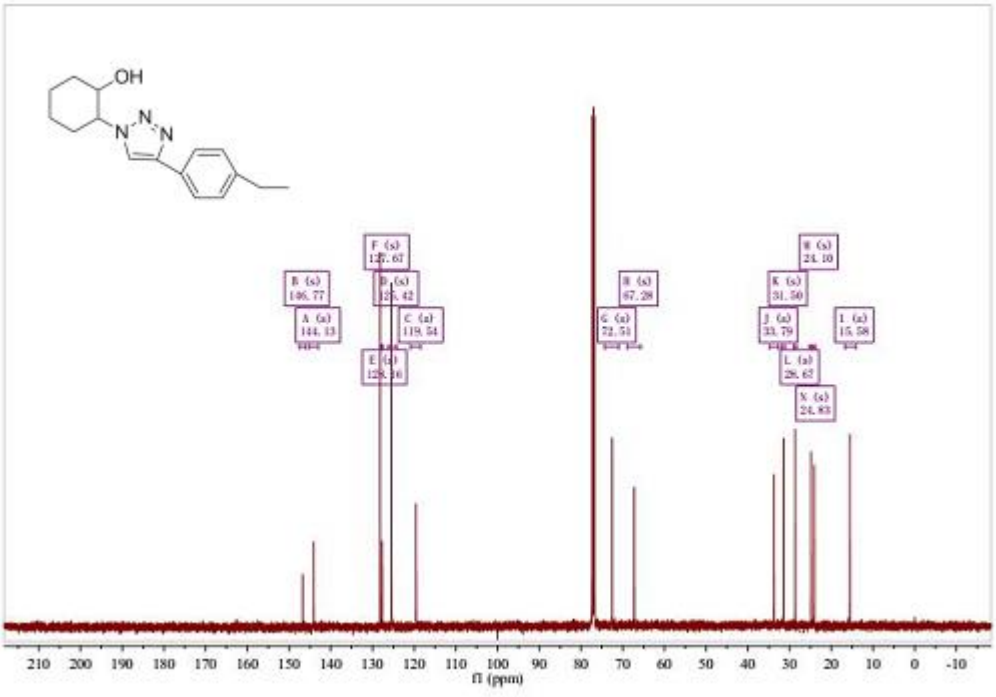

OH
N
N
N
f1 (ppm)

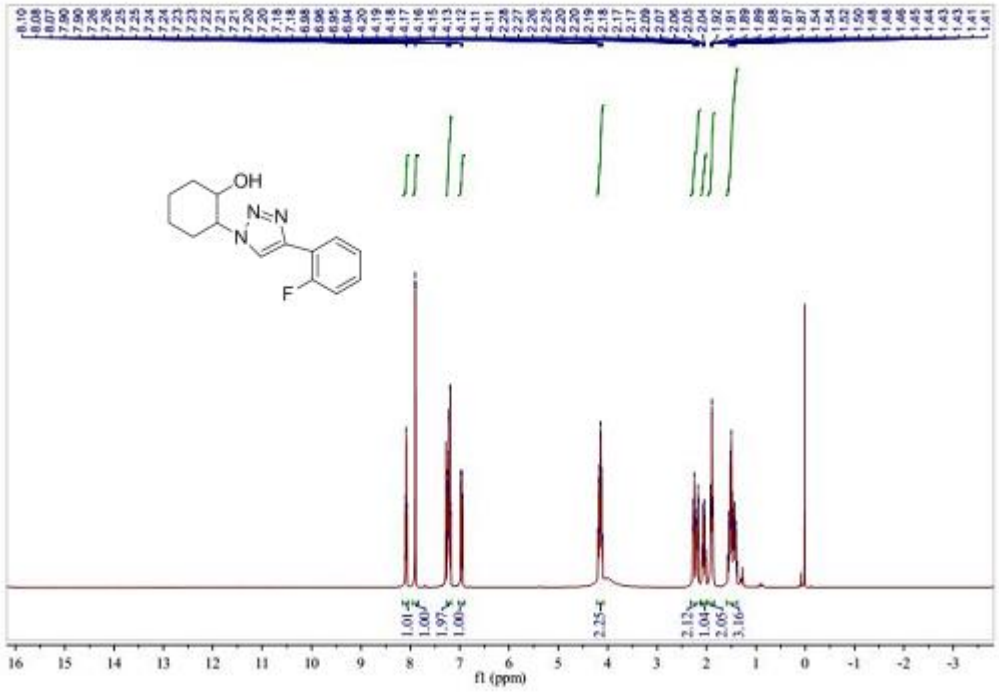

OH
N
N
N
f1 (ppm)

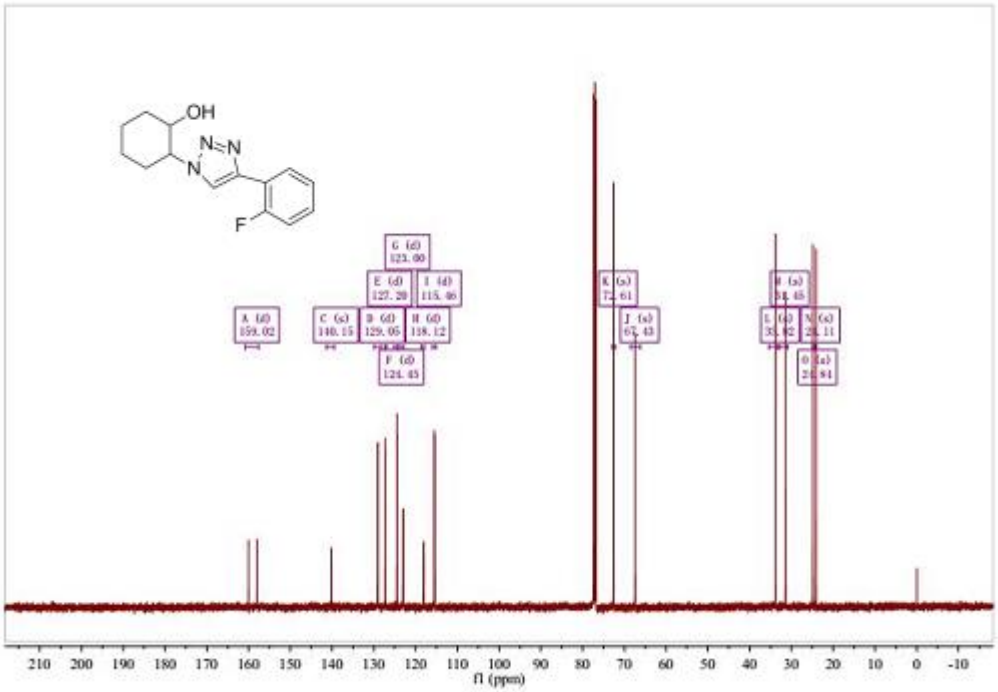

OH
N
N
N
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
f1 (ppm)

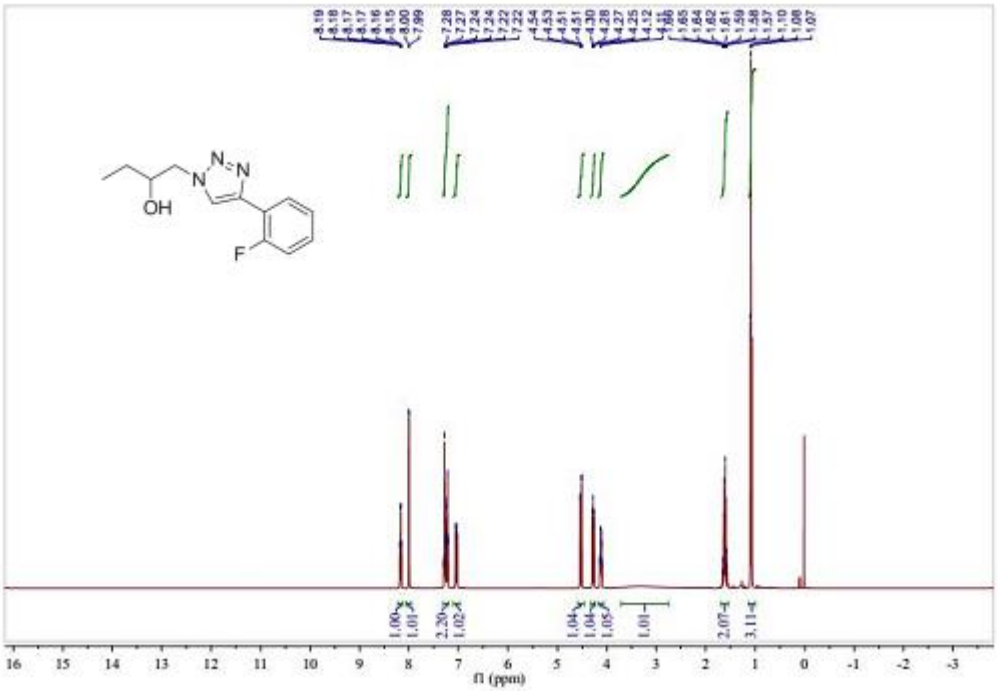

OH
N
N
N
A (s)
147.46
B (s)
120.45
C (s)
72.38
D (s)
66.69
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

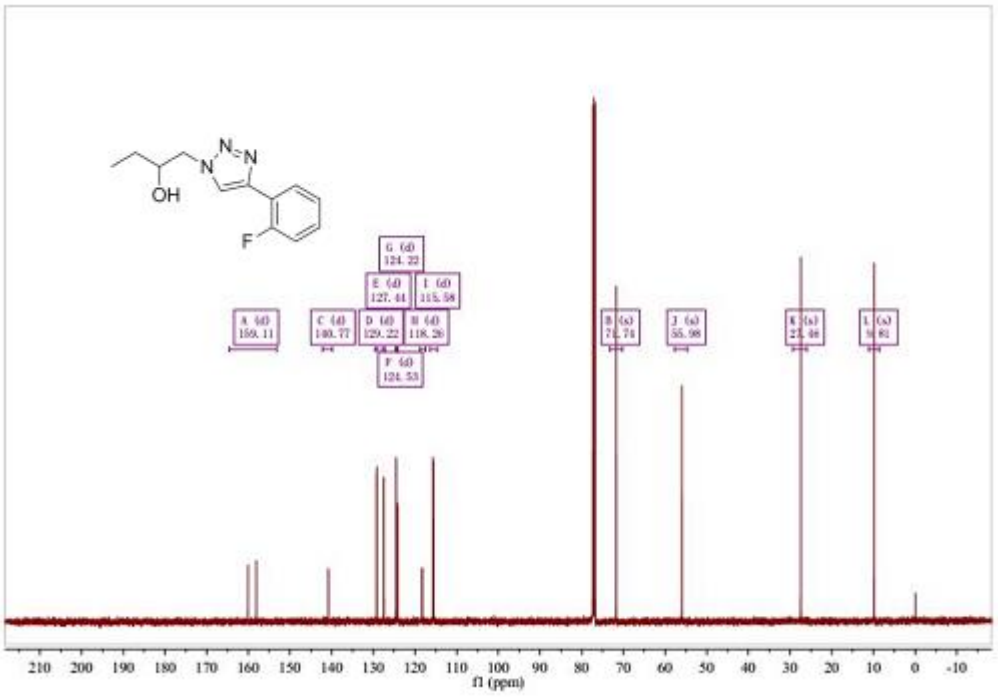

OH
N
N
N
7.69
7.68
7.53
7.52
7.17
7.16
4.45
4.37
4.15
4.13
4.11
4.08
2.69
2.68
2.66
2.65
2.25
2.22
2.18
2.16
2.05
2.03
2.00
1.98
1.88
1.86
1.52
1.50
1.47
1.45
1.42
1.39
1.28
1.27
1.27
1.26
1.26
1.00
2.00
2.00
1.00
2.06
2.06
2.10
1.16
2.19
3.30
3.05
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

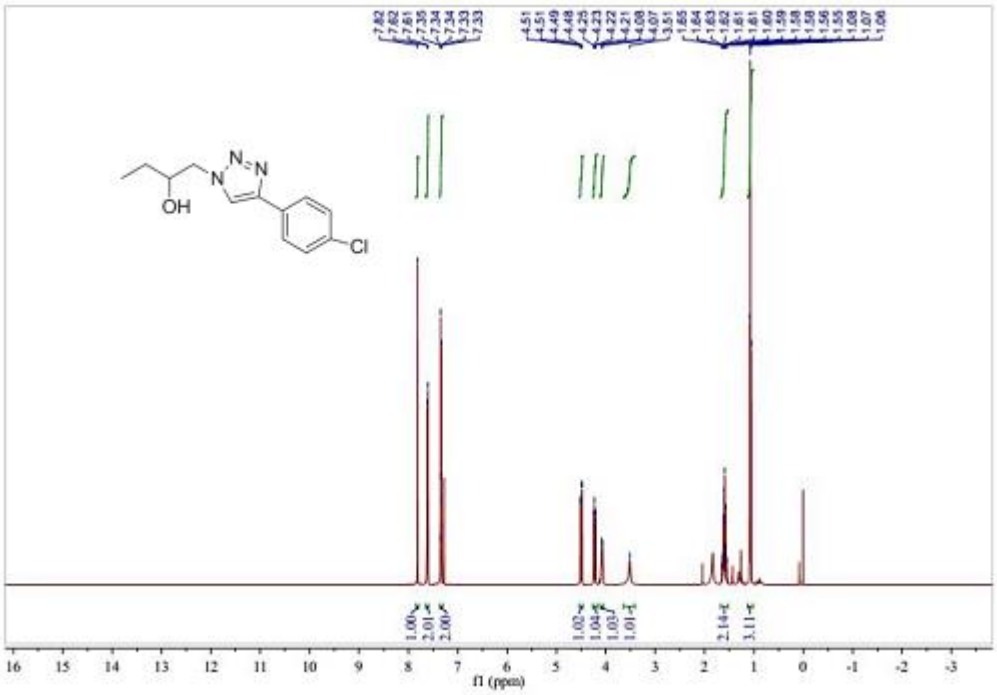

OH
N
N
N
B (s)
146.77
A (s)
144.13
F (s)
129.67
D (s)
129.42
C (s)
119.54
E (s)
128.16
H (s)
67.28
G (s)
22.51
R (s)
24.10
K (s)
31.50
J (s)
33.79
I (s)
15.58
L (s)
28.67
N (s)
24.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

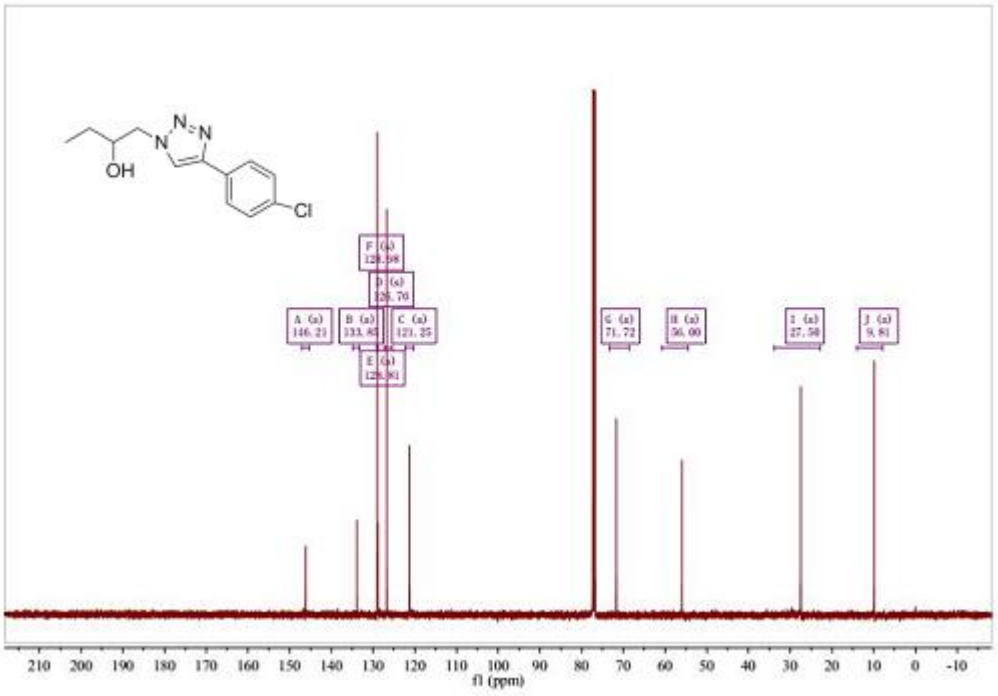

OH
N
N
N
F
f1 (ppm)

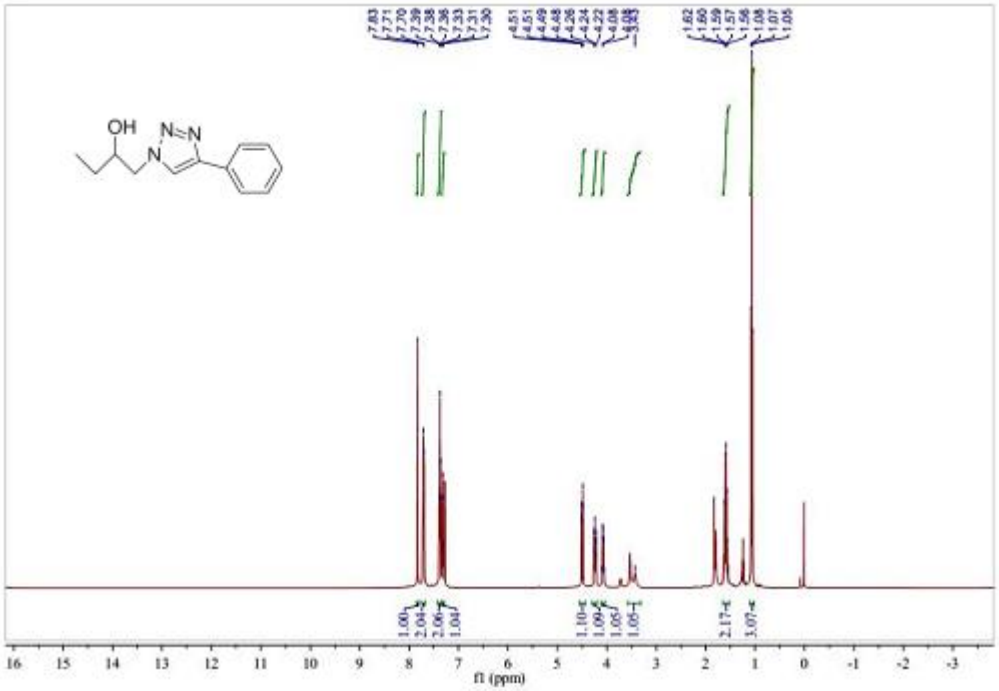

OH
N
N
N
F
f1 (ppm)

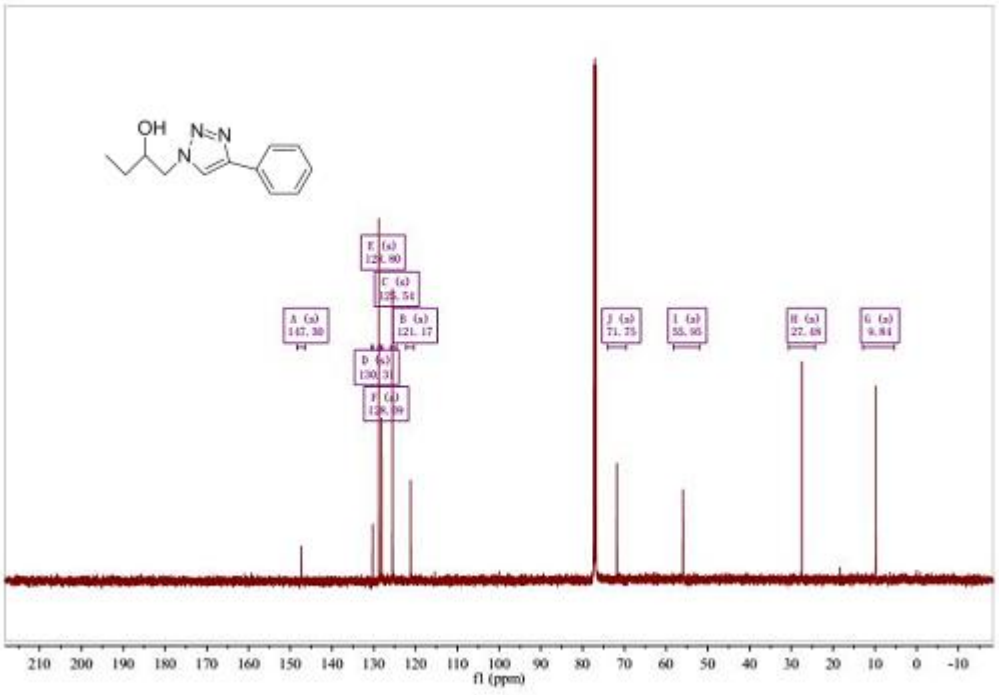

OH
F
f1 (ppm)

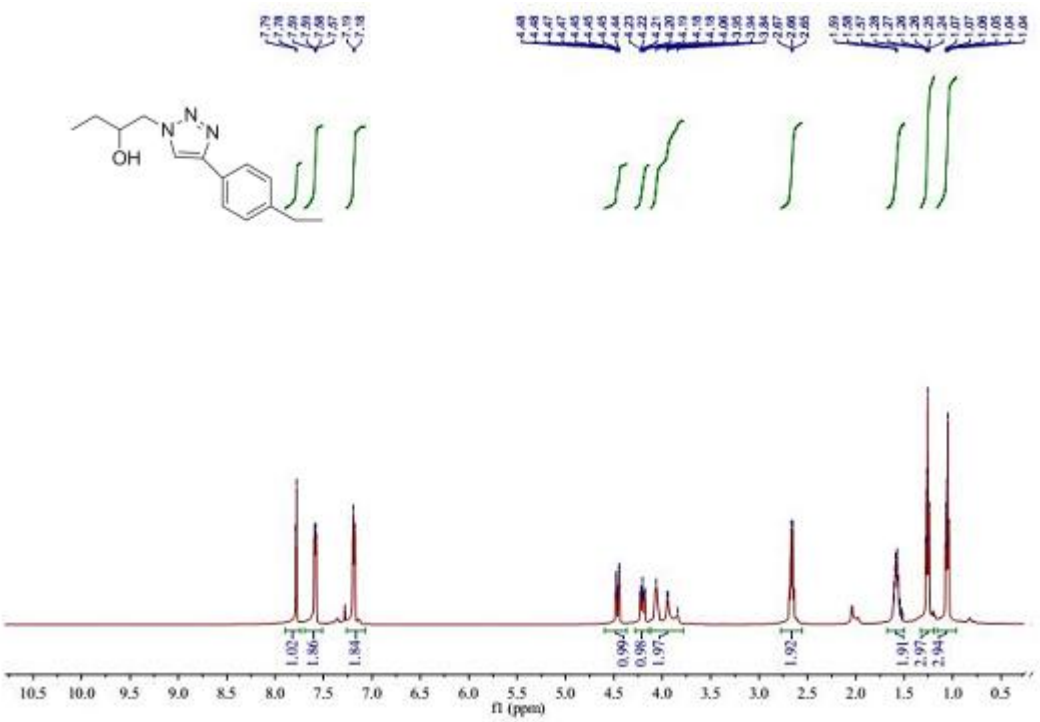

OH
F
f1 (ppm)

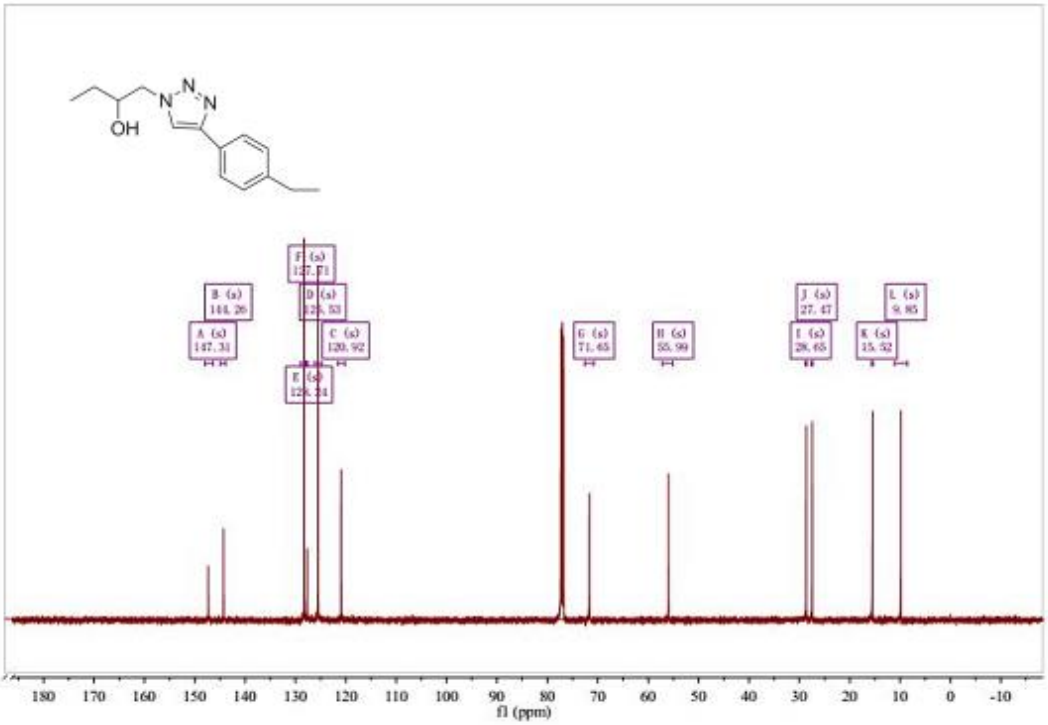

OH
Cl
f1 (ppm)

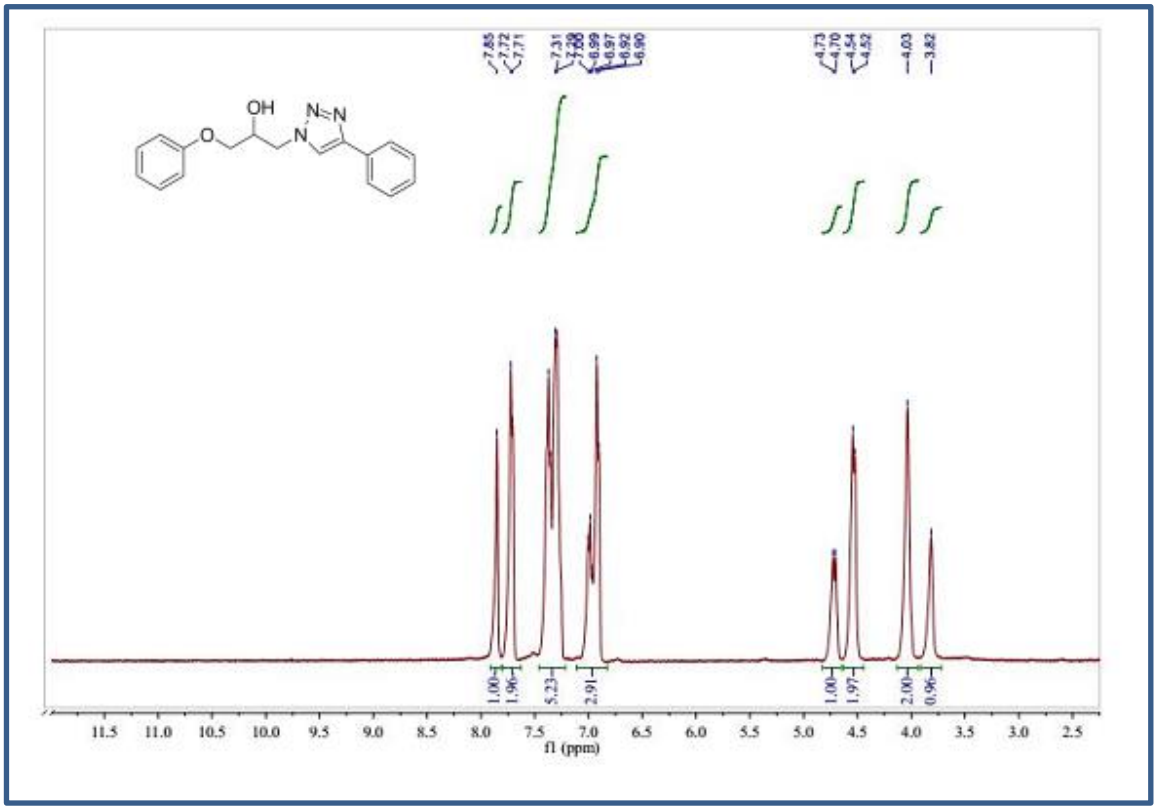

OH
Cl
f1 (ppm)

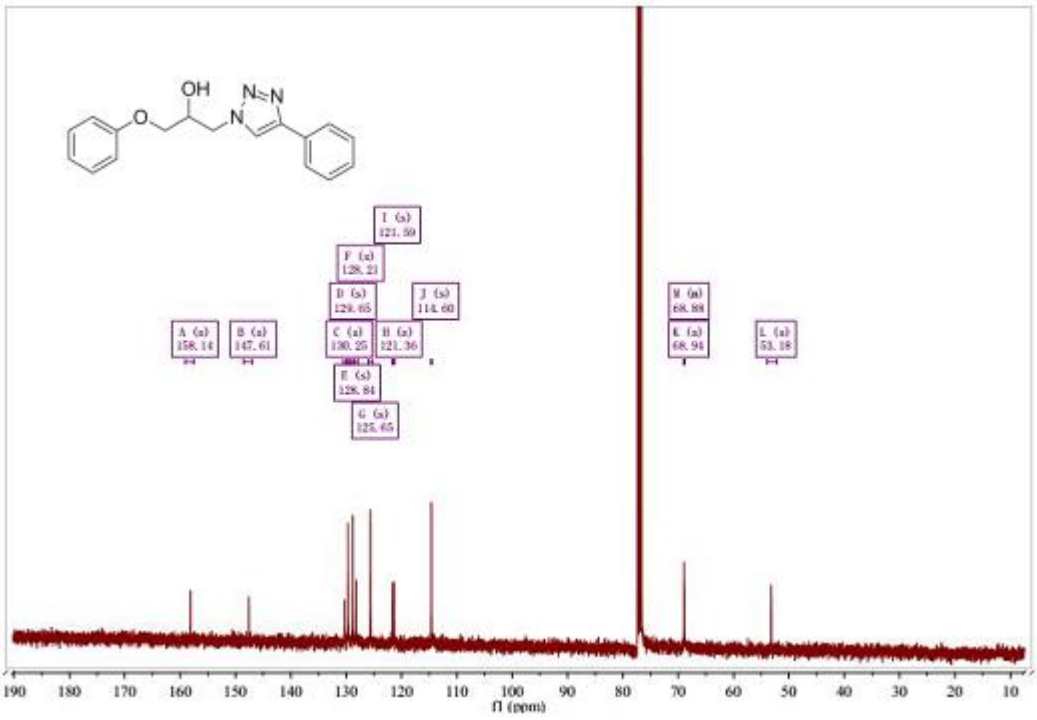

OH
N=N
N
f1 (ppm)

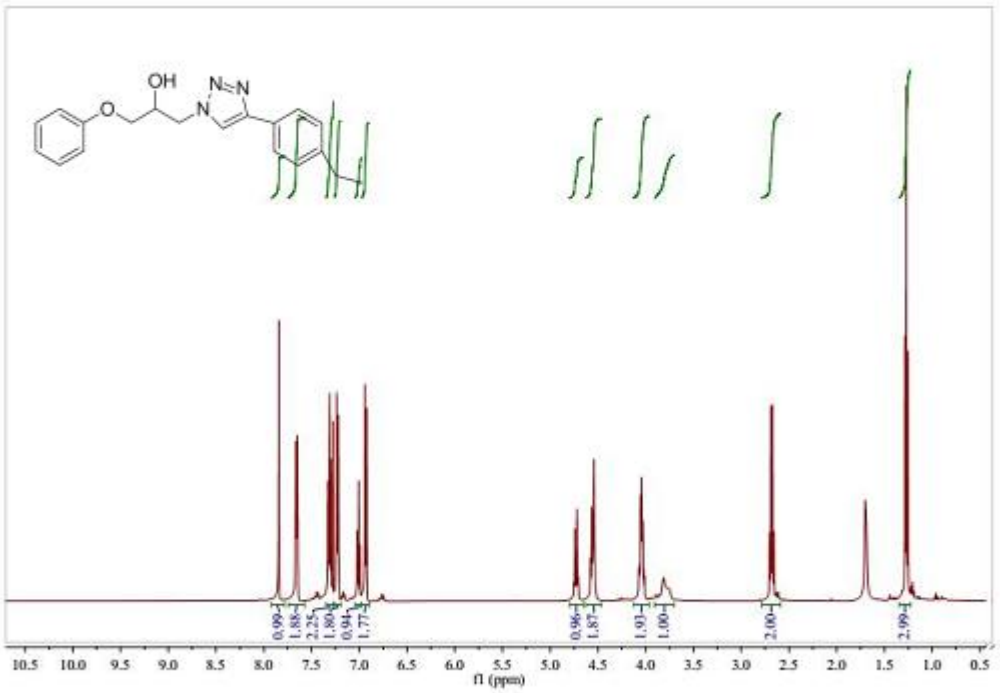

OH
N=N
N
f1 (ppm)

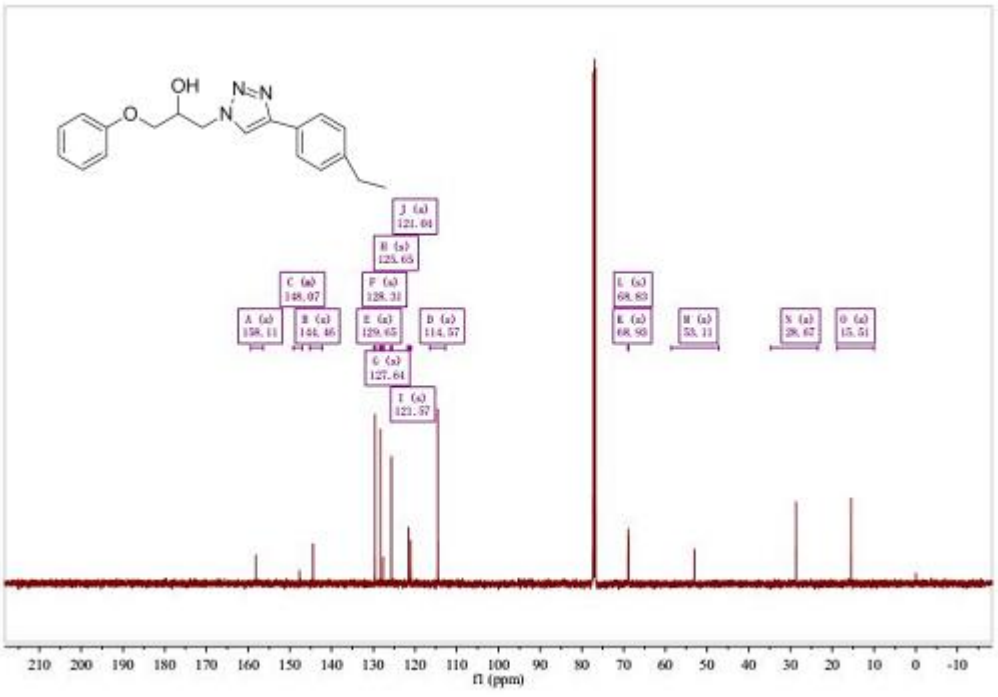

OH
1.02
1.86
1.84
0.99
0.98
1.97
1.92
1.91
2.97
2.94
f1 (ppm)

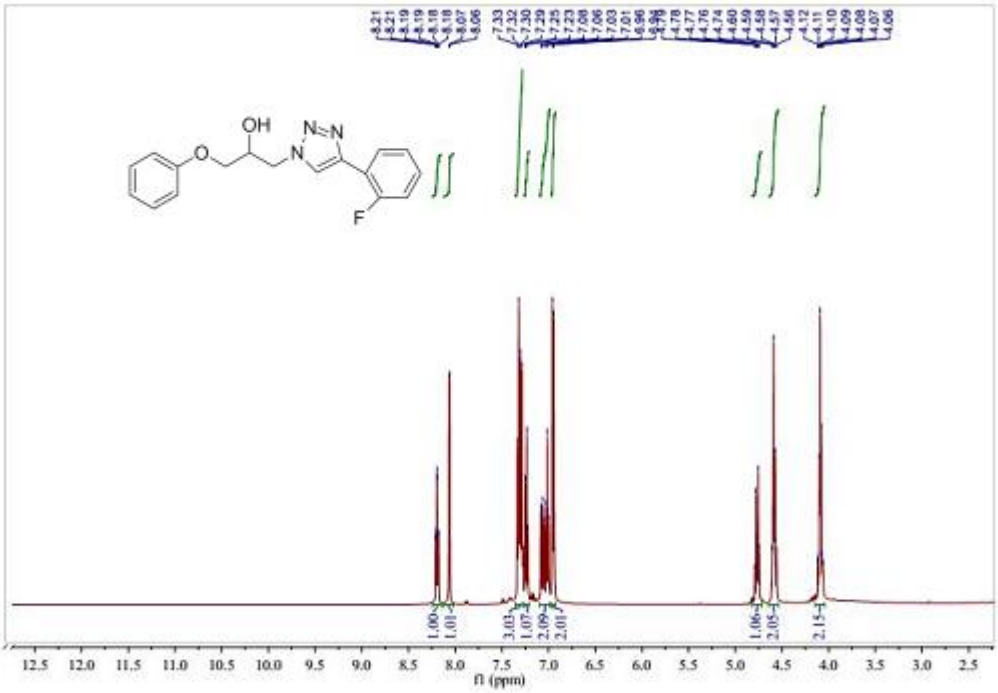

OH
A (s) 147.31
B (s) 144.26
C (s) 120.92
D (s) 129.53
E (s) 129.34
F (s) 127.71
G (s) 71.65
H (s) 55.99
I (s) 28.65
J (s) 27.47
K (s) 15.52
L (s) 9.85
f1 (ppm)

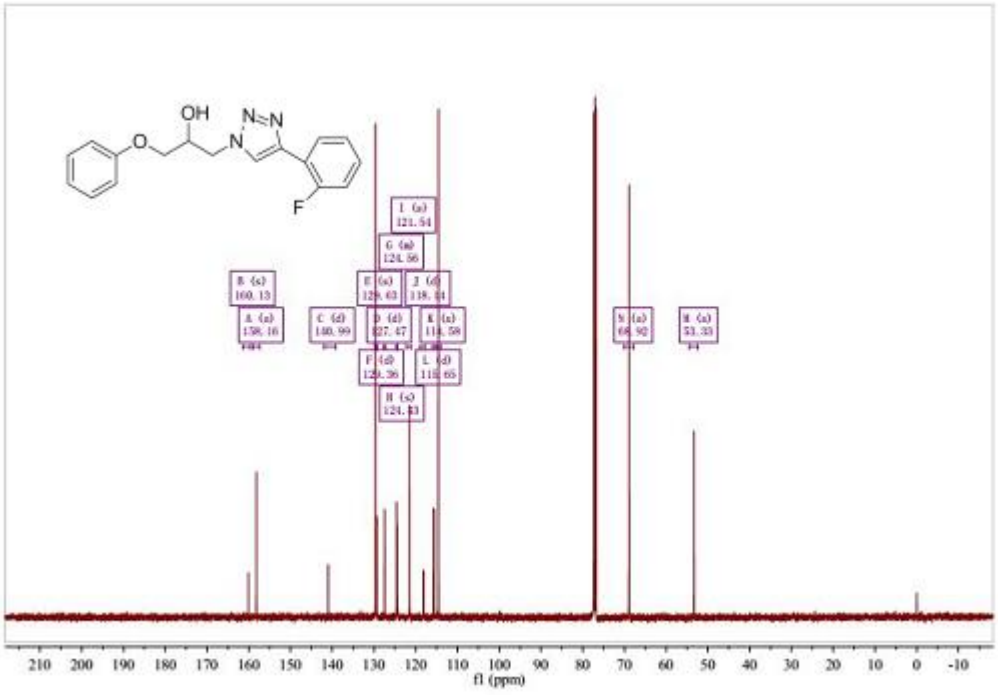

OH
N
N
O
7.85
7.72
7.71
7.31
7.30
7.28
6.99
6.97
6.92
6.90
4.73
4.70
4.54
4.52
4.03
3.82
1.00
1.96
5.23
2.91
1.00
1.97
2.00
0.96
f1 (ppm)

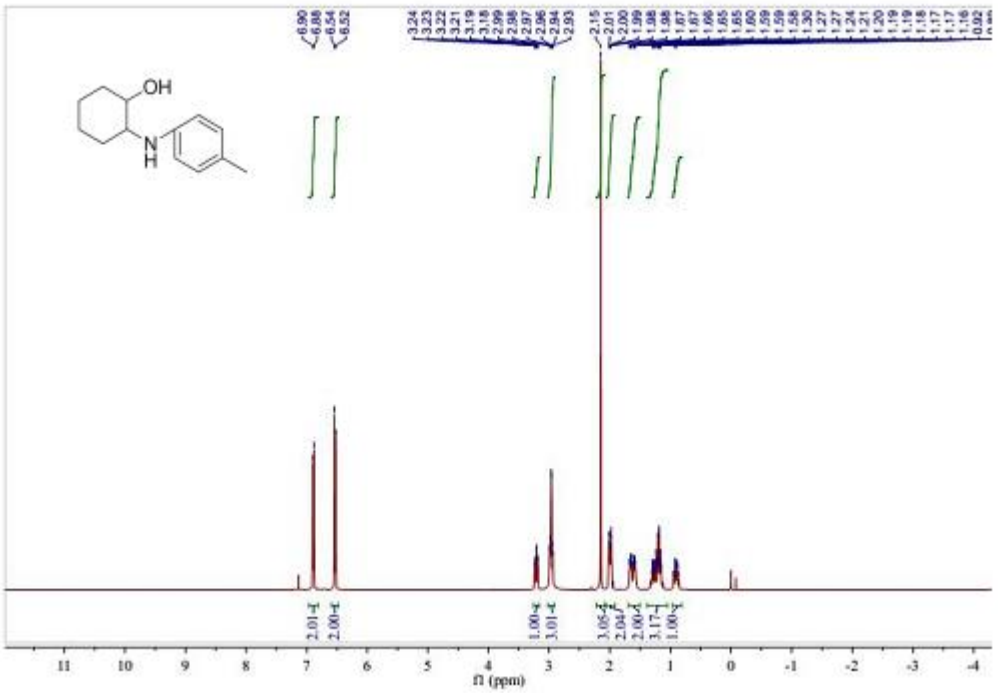

OH
N
N
O
I (s) 121.59
F (s) 128.23
D (s) 129.65
J (s) 114.60
A (s) 158.14
B (s) 147.61
C (s) 130.25
H (s) 121.36
E (s) 128.84
G (s) 125.65
M (s) 68.88
K (s) 68.94
L (s) 53.18
f1 (ppm)

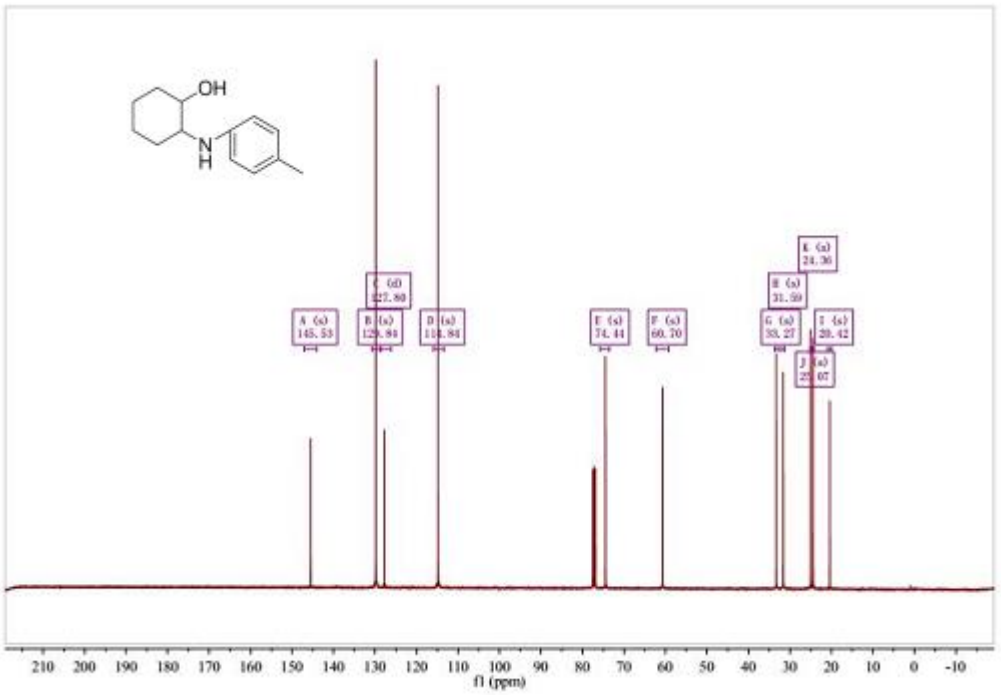

OH
N=N
N
O
0.99
1.88
2.25
1.80
0.94
1.77
0.96
1.87
1.93
1.00
2.00
2.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

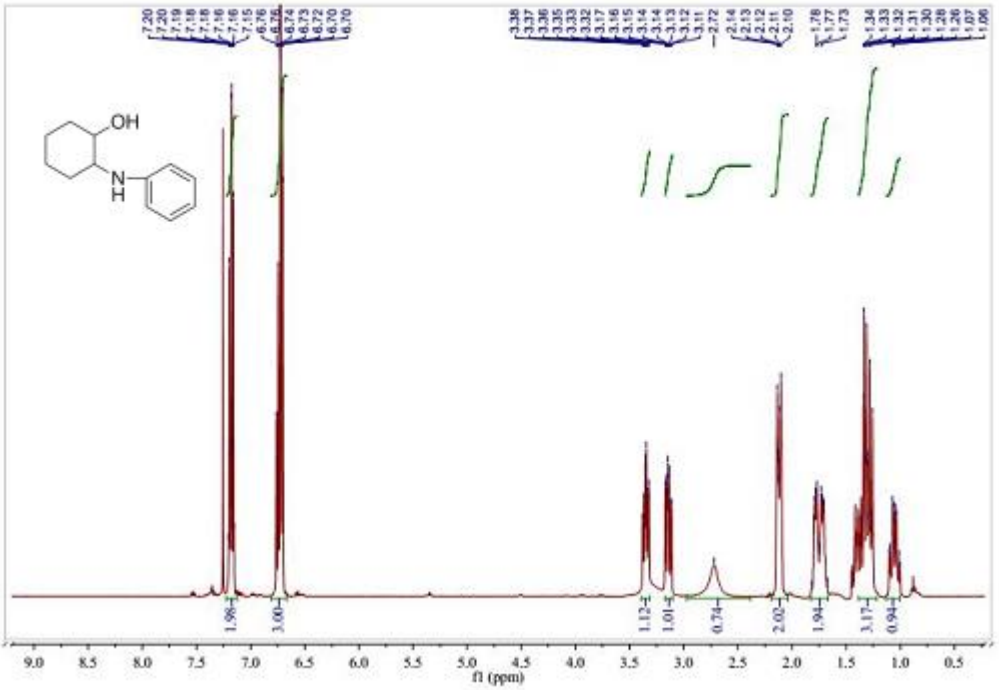

OH
N=N
N
O
J (s) 121.04
H (s) 125.65
C (s) 148.07
F (s) 128.31
A (s) 158.11
B (s) 144.46
E (s) 129.65
D (s) 114.57
G (s) 127.64
I (s) 121.57
L (s) 69.83
K (s) 68.98
M (s) 53.11
N (s) 28.67
O (s) 15.51
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

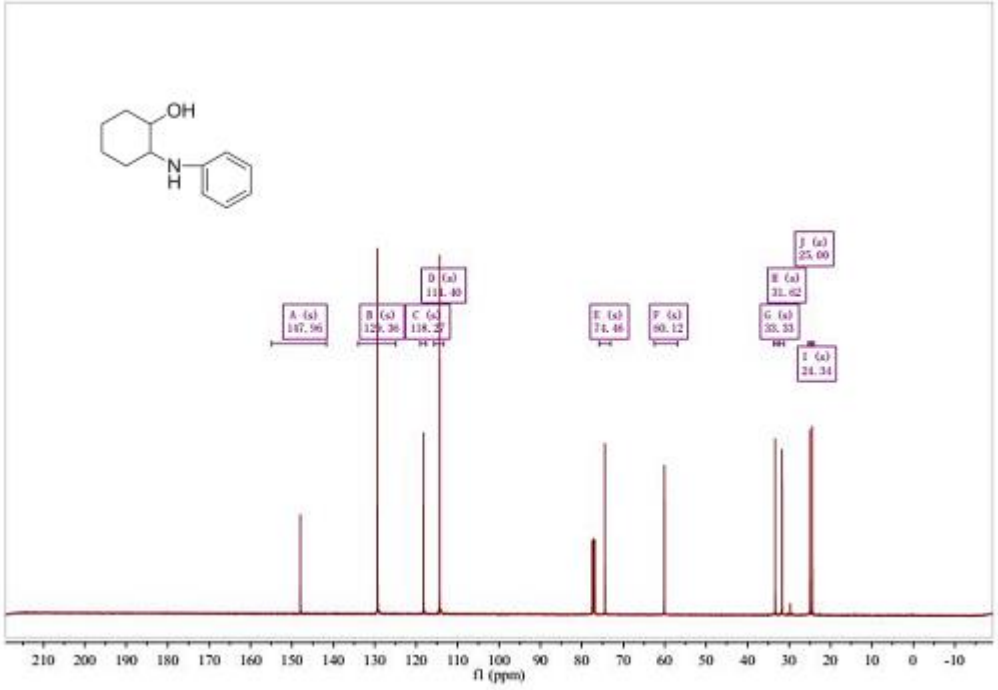

OH
N=N
N
O
F
1.00
1.01
3.03
1.07
2.09
2.01
1.06
2.05
2.15
f1 (ppm)

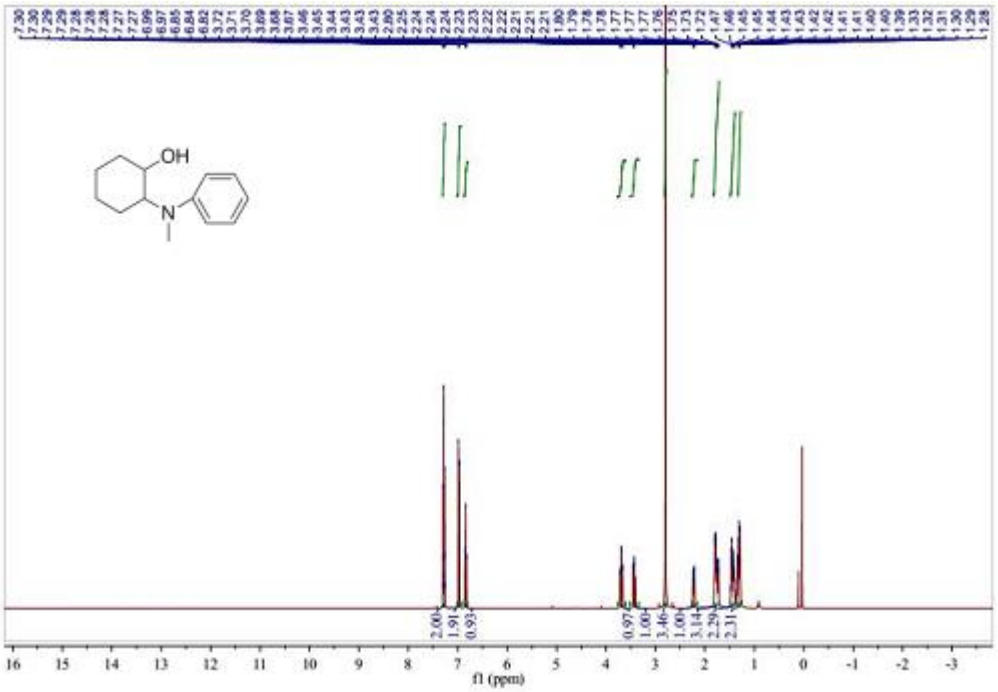

OH
N=N
N
O
F
f1 (ppm)

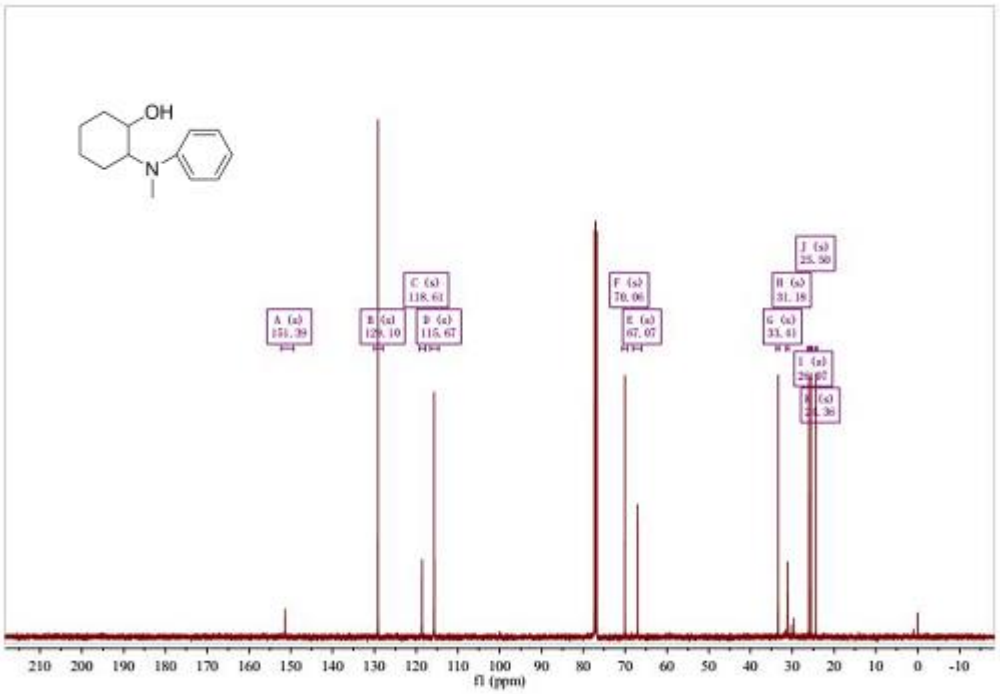

OH
N
H
f1 (ppm)

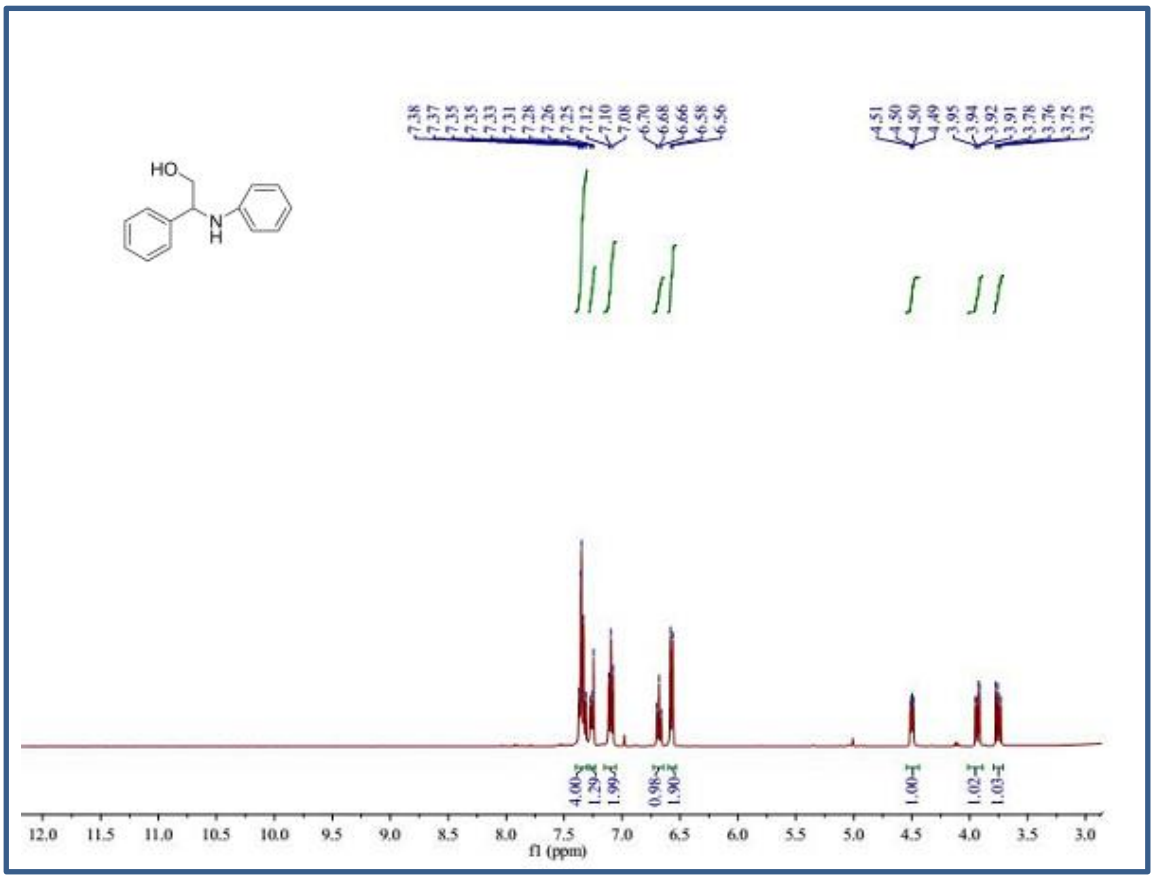

OH
N
H
f1 (ppm)

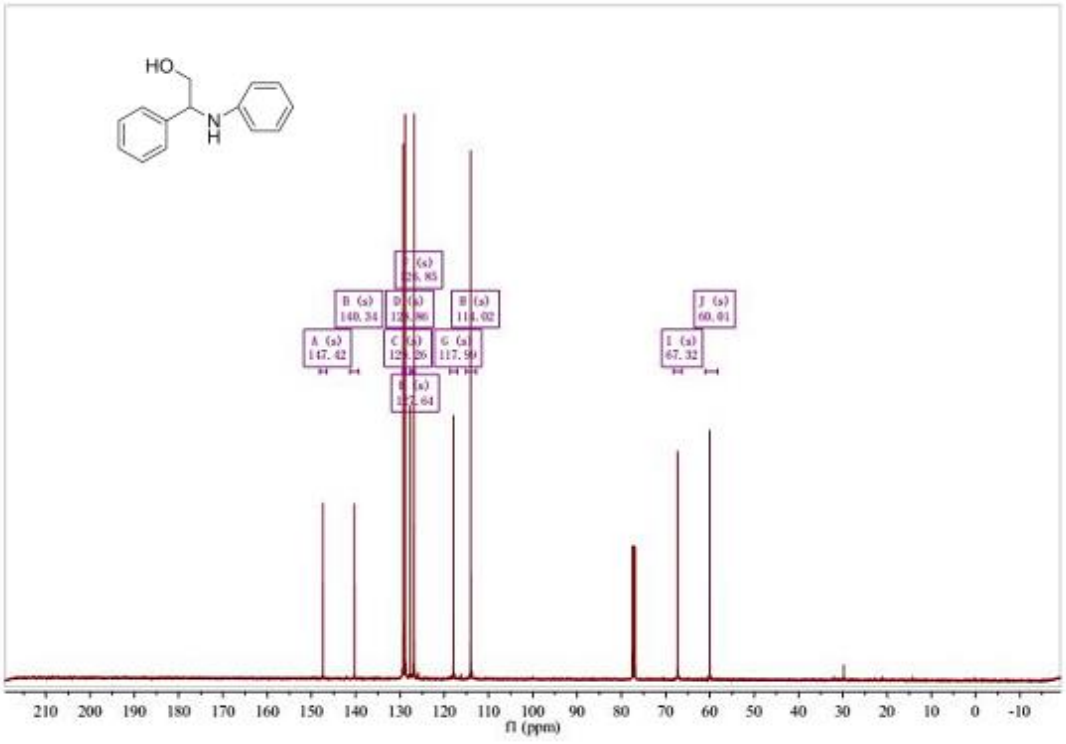

OH
N
H
f1 (ppm)

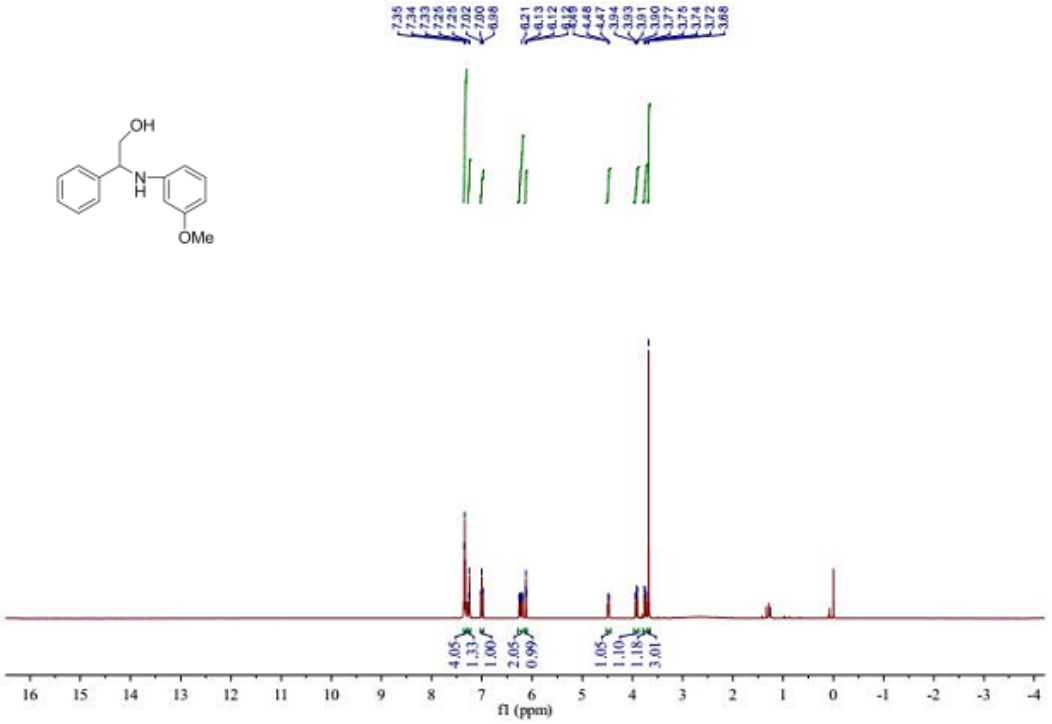

OH
N
H
f1 (ppm)

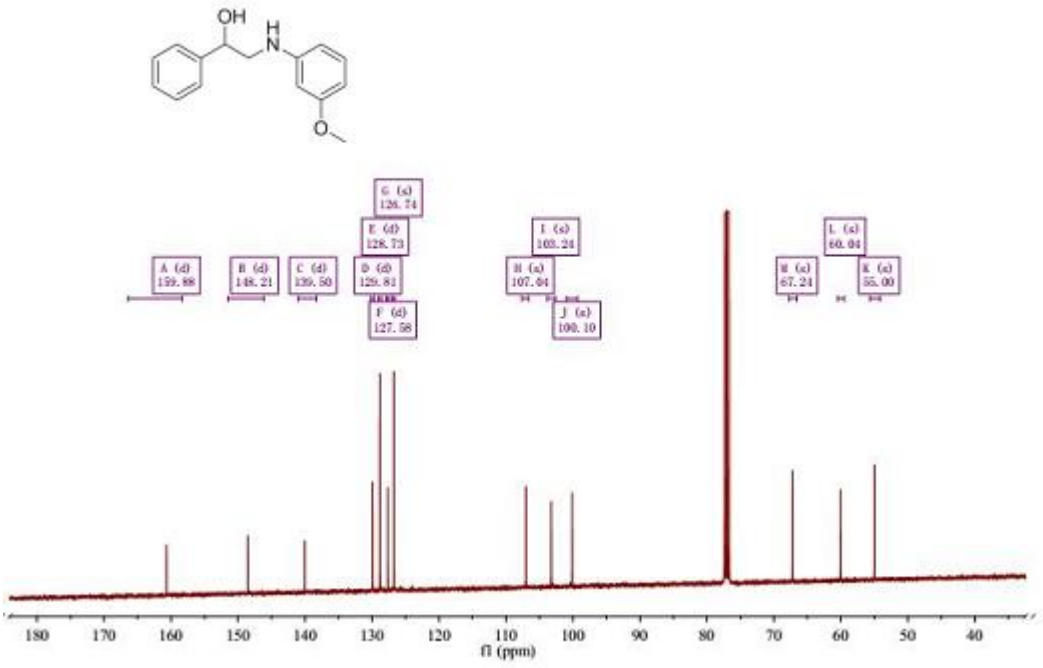

OH
N
f1 (ppm)

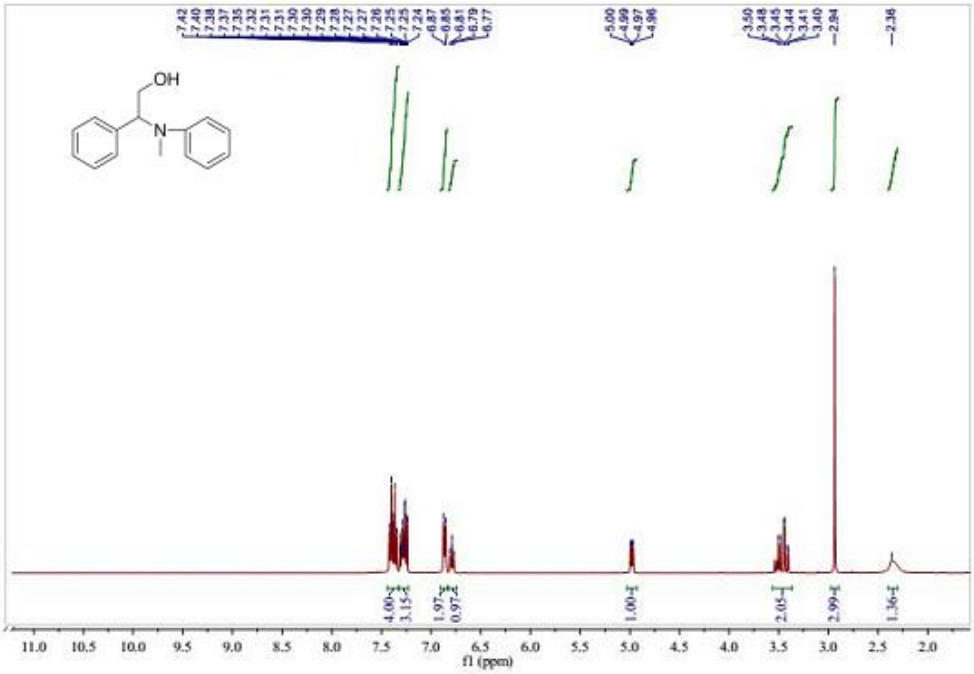

OH
N
f1 (ppm)

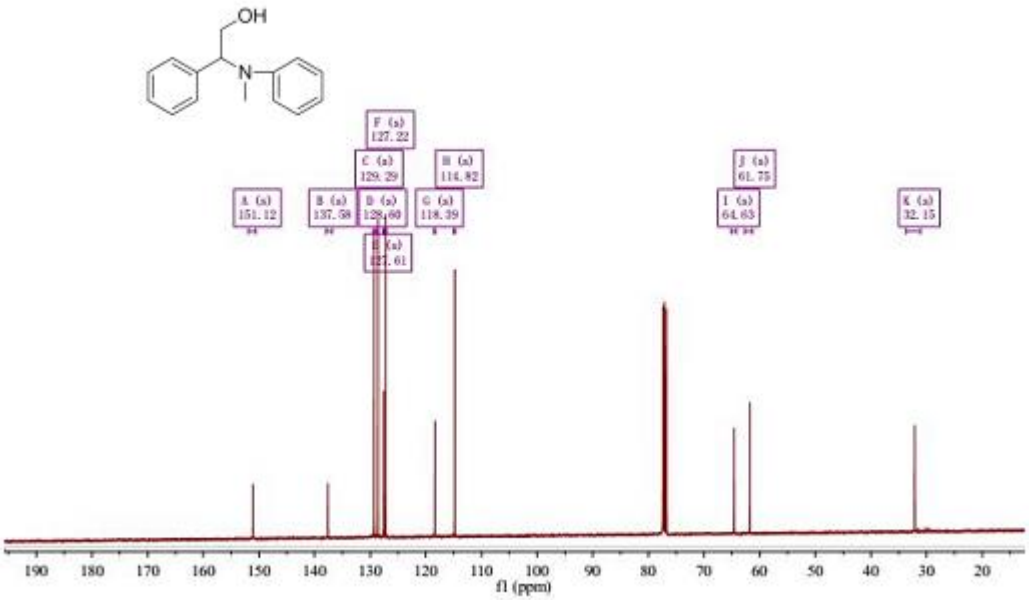

HO
N
H
7.38
7.37
7.35
7.35
7.33
7.31
7.28
7.26
7.25
7.12
7.10
7.08
6.70
6.68
6.66
6.58
6.56
4.51
4.50
4.50
4.49
3.95
3.94
3.92
3.91
3.78
3.76
3.75
3.73
4.00
1.29
1.99
0.98
1.90
1.00
1.02
1.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
f1 (ppm)


HO
N
H
A (s)
147.42
B (s)
140.34
D (s)
129.06
C (s)
129.26
E (s)
127.64
G (s)
117.96
H (s)
113.02
I (s)
67.32
J (s)
60.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
N
H
OMe
7.35
7.34
7.33
7.26
7.25
7.02
7.00
6.98
6.21
6.13
6.12
4.48
4.47
3.94
3.93
3.91
3.90
3.77
3.75
3.74
3.72
3.68
4.05
1.33
1.00
2.05
0.99
1.05
1.10
1.18
3.01
f1 (ppm)


OH
H
N
O
A (d) 159.88
B (d) 148.21
C (d) 139.50
D (d) 129.81
E (d) 128.73
F (d) 127.58
G (s) 126.74
H (s) 107.04
I (s) 103.24
J (s) 100.10
K (s) 67.24
L (s) 60.04
M (s) 55.00
f1 (ppm)


OH
N
7.42
7.40
7.38
7.37
7.35
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.24
6.87
6.85
6.81
6.79
6.77
5.00
4.99
4.97
4.96
3.50
3.48
3.45
3.44
3.41
3.40
2.84
2.36
4.00
3.15
1.97
0.97
1.00
2.05
2.99
1.36
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)


OH
N
A (s) 151.12
B (s) 137.58
D (s) 128.60
F (s) 127.22
C (s) 129.29
E (s) 127.61
G (s) 118.39
H (s) 114.82
I (s) 64.63
J (s) 61.75
K (s) 32.15
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)