

Supporting Information

for

N-2-Selective gold-catalyzed alkylation of 1-sulfonyl-1,2,3-triazoles

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1. General considerations

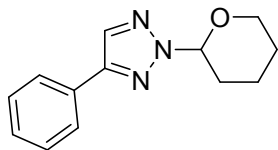
All reactions were performed using Schlenk tubes, septa, and syringes without protection of nitrogen. THF, toluene and DCM, DCE were freshly distilled over sodium/benzophenone and calcium hydride, respectively. Commercial reagents were used as supplied or were purified by standard techniques where necessary. Column chromatography was performed using Qingdao Haiyang Chemical Co., Ltd silica gel (200–300 mesh) with the appropriate solvent system, as determined by TLC analysis (Qingdao Haiyang Chemical Co., Ltd, silica gel F254) using UV light and KMnO_4 stain to visualize the reaction components. Melting points were determined using a WRS-1B digital melting point instrument. IR spectra were recorded on a Nicoletisso FTIR spectrometer using KBr disks. Unless otherwise noted, nuclear magnetic resonance spectra were recorded at room temperature on an Agilent 400 MHz spectrometer using CDCl_3 as the solvent and TMS as the internal reference. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million relative to tetramethylsilane using the central peak of deuteriochloroform (77.0 ppm) as the internal standard. HRMS was performed using a Bruker Daltonics Bio TOF mass spectrometer.

1-Sulfonyl-1,2,3-trizoles **1a-1n** were prepared according to the published methods.¹ Vinyl ethers were obtained commercially and used without further purification.

General procedure for N-2-Selective gold-catalyzed alkylation of 4-phenyl-1-sulfonyl-1,2,3-trizole **1a with vinyl ether **2a**.**

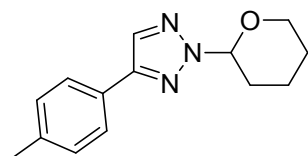
To a Schlenk tube charged with nitrogen was added IPrAuCl/AgNTf_2 (5 mol%) in dry DCE (3 mL). After three minutes, 4-phenyl-1-sulfonyl-1,2,3-trizole **1a** (0.5 mmol), vinyl ether **2a** (2.5 mmol) and H_2O (1.0 mmol) were added to the reaction. Then the reaction mixture was stirred at 80 °C for 6 h until complete consumption of starting material as monitored by TLC. Concentration of the reaction mixture in vacuo followed by purification through flash chromatography on silica gel column (hexane/EtOAc = 30/1) afforded **3a** (112.8 mg, 98% yield) as yellow oil liquid.

2. Analytical Data



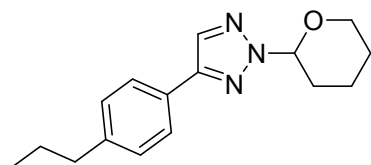
4-phenyl-2-(tetrahydro-2H-pyran-2-yl)-2H-1,2,3-triazole (**3a**)

Yellow oil liquid; yield, 98%; IR (neat) 3475, 2951, 1611, 1391, 1063 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.82 (d, $J = 7.2$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 5.75 (dd, $J = 9.1, 2.6$ Hz, 1H), 4.07 (dt, $J = 7.1, 3.0$ Hz, 1H), 3.79 – 3.73 (m, 1H), 2.52 – 2.45 (m, 1H), 2.17 – 2.09 (m, 2H), 1.78 – 1.72 (m, 2H), 1.68 – 1.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 131.59, 130.13, 128.79, 128.57, 126.10, 109.99, 89.13, 67.50, 29.40, 24.78, 21.85. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{16}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 230.1288; found, 230.1287.



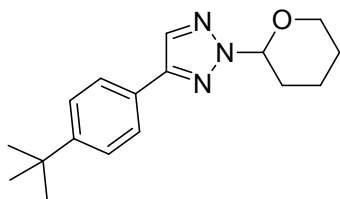
2-(tetrahydro-2H-pyran-2-yl)-4-(*p*-tolyl)-2H-1,2,3-triazole (**3b**)

Colorless oil liquid; yield, 74%; IR (neat) 3466, 2955, 1645, 1398, 1070 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (s, 1H), 7.71 (d, $J = 7.9$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 5.73 (dd, $J = 9.1, 1.8$ Hz, 1H), 4.08 – 4.05 (m, 1H), 3.78 – 3.72 (m, 1H), 2.51 – 2.43 (m, 1H), 2.37 (s, 3H), 2.16 – 2.06 (m, 2H), 1.77 – 1.68 (m, 2H), 1.67 – 1.61 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.11, 138.38, 131.32, 129.39, 127.21, 125.91, 89.00, 67.43, 29.33, 24.71, 21.81, 21.23. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 244.1444; found, 244.1443.



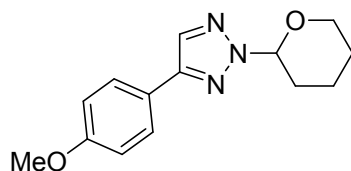
4-(4-propylphenyl)-2-(tetrahydro-2H-pyran-2-yl)-2H-1,2,3-triazole (**3c**)

Yellow oil liquid; yield, 84%; IR (neat) 3463, 2954, 1645, 1382, 1057 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.73 (d, $J = 7.6$ Hz, 2H), 7.23 (d, $J = 7.7$ Hz, 2H), 5.74 (d, $J = 8.5$ Hz, 1H), 4.07 (d, $J = 11.5$ Hz, 1H), 3.76 (t, $J = 10.4$ Hz, 1H), 2.61 (t, $J = 7.6$ Hz, 2H), 2.52 – 2.44 (m, 1H), 2.16 – 2.09 (m, 2H), 1.78 – 1.71 (m, 2H), 1.69 – 1.63 (m, 3H), 0.95 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.29, 131.43, 128.89, 127.55, 126.00, 109.99, 89.07, 67.47, 37.81, 29.40, 24.79, 24.44, 21.86, 13.77. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{22}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 272.1757; found, 272.1758.



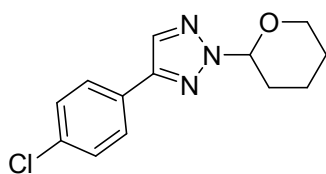
4-(4-(*tert*-butyl)phenyl)-2-(tetrahydro-2*H*-pyran-2-yl)-2*H*-1,2,3-triazole (**3d**)

Colorless oil liquid; yield, 86%; IR (neat) 3470, 2970, 1644, 1490, 1092 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.74 (d, $J = 7.9$ Hz, 2H), 7.44 (d, $J = 7.9$ Hz, 2H), 5.74 (d, $J = 9.1$ Hz, 1H), 4.08 – 4.05 (m, 1H), 3.78 – 3.73 (m, 1H), 2.53 – 2.44 (m, 1H), 2.14 – 2.08 (m, 2H), 1.74 – 1.71 (m, 2H), 1.66 – 1.64 (m, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.62, 148.06, 131.43, 127.29, 125.80, 125.65, 89.00, 67.37, 34.62, 31.20, 29.35, 24.75, 21.79. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{24}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 286.1914; found, 286.1914.



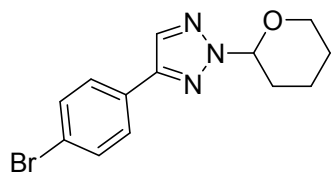
4-(4-methoxyphenyl)-2-(tetrahydro-2*H*-pyran-2-yl)-2*H*-1,2,3-triazole (**3e**)

Yellow oil liquid; yield, 91%; IR (neat) 3467, 2954, 1631, 1396, 1058 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.75 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 5.72 (d, $J = 8.6$ Hz, 1H), 4.09 – 4.06 (m, 1H), 3.84 (s, 3H), 3.78 – 3.73 (m, 1H), 2.52 – 2.44 (m, 1H), 2.15 – 2.08 (m, 2H), 1.76 – 1.72 (m, 2H), 1.66 – 1.65 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.88, 148.00, 131.08, 127.41, 122.81, 114.17, 89.04, 67.49, 55.28, 29.40, 24.78, 21.89. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$ 260.1394; found, 260.1394.



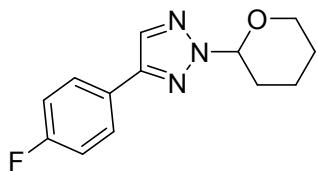
4-(4-chlorophenyl)-2-(tetrahydro-2*H*-pyran-2-yl)-2*H*-1,2,3-triazole (**3f**)

Yellow oil liquid; yield, 77%; IR (neat) 3475, 2971, 1645, 1393, 1093 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.75 (d, $J = 8.1$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 5.74 (d, $J = 9.3$ Hz, 1H), 4.07 (d, $J = 11.4$ Hz, 1H), 3.76 (t, $J = 9.9$ Hz, 1H), 2.51 – 2.53 (m, 1H), 2.14 – 2.08 (m, 2H), 1.75 – 1.712 (m, 2H), 1.69 – 1.65 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.04, 134.30, 131.41, 128.94, 128.60, 127.27, 89.12, 67.43, 29.31, 24.69, 21.73. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{ClN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 264.0898; found, 264.0898.



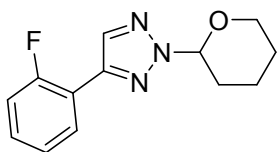
4-(4-bromophenyl)-2-(tetrahydro-2H-pyran-2-yl)-2H-1,2,3-triazole (**3g**)

Colorless oil liquid; yield, 57%; IR (neat) 3470, 2948, 1645, 1387, 1066 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 5.74 (dd, J = 9.1, 2.6 Hz, 1H), 4.10 – 4.04 (m, 1H), 3.80 – 3.73 (m, 1H), 2.51 – 2.42 (m, 1H), 2.16 – 2.08 (m, 2H), 1.78 – 1.71 (m, 2H), 1.68 – 1.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.09, 131.92, 131.44, 129.09, 127.57, 122.53, 89.16, 67.46, 29.34, 24.72, 21.75. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{BrN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 308.0393; found, 308.0393.



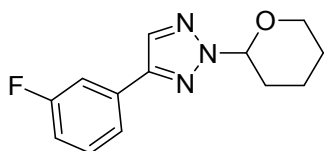
4-(4-fluorophenyl)-2-(tetrahydro-2H-pyran-2-yl)-2H-1,2,3-triazole (**3h**)

Colorless oil liquid; yield, 99%; IR (neat) 3477, 2959, 1617, 1397, 1094 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.79 (dd, J = 8.0, 5.6 Hz, 2H), 7.11 (t, J = 8.5 Hz, 2H), 5.76 – 5.70 (m, 1H), 4.07 (d, J = 11.8 Hz, 1H), 3.78 – 3.73 (m, 1H), 2.51 – 2.42 (m, 1H), 2.16 – 2.07 (m, 2H), 1.78 – 1.71 (m, 2H), 1.70 – 1.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.81 (d, J = 246.5 Hz), 147.19, 131.22, 127.77 (d, J = 8.2 Hz), 126.28 (d, J = 3.2 Hz), 115.71 (d, J = 21.6 Hz), 89.05, 67.42, 29.29, 24.67, 21.75. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{FN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 248.1194; found, 248.1194.



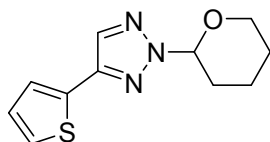
4-(2-fluorophenyl)-2-(tetrahydro-2H-pyran-2-yl)-2H-1,2,3-triazole (**3i**)

Colorless oil liquid; yield, 73%; IR (neat) 3466, 2955, 1645, 1390, 1071 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 6.8 Hz, 2H), 7.37 – 7.28 (m, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.18 – 7.10 (m, 1H), 5.77 (d, J = 8.7 Hz, 1H), 4.08 (d, J = 11.3 Hz, 1H), 3.77 (t, J = 10.4 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.13 (t, J = 11.2 Hz, 2H), 1.75 (s, 2H), 1.69 – 1.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.00 (d, J = 248.4 Hz), 142.65, 134.30 (d, J = 11.8 Hz), 129.86 (d, J = 8.4 Hz), 128.52 (d, J = 3.6 Hz), 124.40 (d, J = 3.4 Hz), 118.12 (d, J = 12.3 Hz), 115.94 (d, J = 21.5 Hz), 89.10, 67.40, 29.35, 24.74, 21.73. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{FN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 248.1194; found, 248.1193.



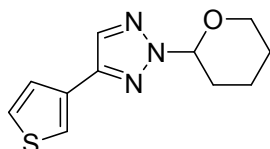
4-(3-fluorophenyl)-2-(tetrahydro-2H-pyran-2-yl)-2H-1,2,3-triazole (**3j**)

Colorless oil liquid; yield, 87%; IR (neat) 3484, 2957, 1595, 1399, 1063 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.58 (d, $J = 7.7$ Hz, 1H), 7.54 (d, $J = 9.7$ Hz, 1H), 7.41 – 7.35 (m, 1H), 7.04 (td, $J = 8.5, 1.5$ Hz, 1H), 5.77 – 5.73 (m, 1H), 4.08 – 4.05 (m, 1H), 3.79 – 3.74 (m, 1H), 2.51 – 2.43 (m, 1H), 2.16 – 2.08 (m, 2H), 1.78 – 1.73 (m, 2H), 1.70 – 1.66 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.06 (d, $J = 244.5$ Hz), 146.96, 132.28 (d, $J = 8.4$ Hz), 131.65, 130.35 (d, $J = 8.4$ Hz), 121.67 (d, $J = 2.9$ Hz), 115.37 (d, $J = 21.1$ Hz), 112.99 (d, $J = 22.8$ Hz), 89.16, 67.41, 29.33, 24.72, 21.71. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{FN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 248.1194; found, 248.1193.



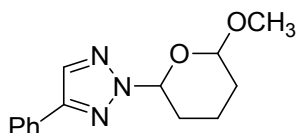
2-(tetrahydro-2H-pyran-2-yl)-4-(thiophen-2-yl)-2H-1,2,3-triazole (**3k**)

Yellow oil liquid; yield, 63%; IR (neat) 3470, 2951, 1648, 1392, 1075 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.42 – 7.38 (m, 1H), 7.32 (d, $J = 4.7$ Hz, 1H), 7.08 (t, $J = 3.7$ Hz, 1H), 5.72 (d, $J = 9.3$ Hz, 1H), 4.08 – 4.05 (m, 1H), 3.78 – 3.73 (m, 1H), 2.49–2.42 (m, 1H), 2.14 – 2.08 (m, 2H), 1.76 – 1.71 (m, 2H), 1.68 – 1.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 132.39, 131.33, 127.57, 125.74, 125.06, 109.99, 89.08, 76.68, 67.48, 29.37, 24.74, 21.80. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_3\text{OS}^+$ $[\text{M}+\text{H}]^+$ 236.0852; found, 236.0851.



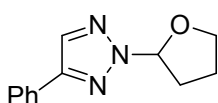
2-(tetrahydro-2H-pyran-2-yl)-4-(thiophen-3-yl)-2H-1,2,3-triazole (**3l**)

Yellow oil liquid; yield, 70%; IR (neat) 3466, 2953, 1648, 1368, 1067 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.66 – 7.65 (m, 1H), 7.48 (d, $J = 5.0$ Hz, 1H), 7.40 – 7.36 (m, 1H), 5.74 – 5.71 (m, 1H), 4.08 – 4.05 (m, 1H), 3.78 – 3.73 (m, 1H), 2.51 – 2.43 (m, 1H), 2.15 – 2.11 (m, 2H), 1.76 – 1.71 (m, 2H), 1.67 – 1.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.28, 131.68, 131.41, 126.29, 125.96, 121.95, 89.02, 67.45, 29.36, 24.72, 21.80. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_3\text{OS}^+$ $[\text{M}+\text{H}]^+$ 236.0852; found, 236.0852.



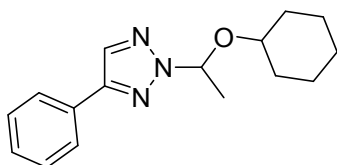
2-(6-methoxytetrahydro-2H-pyran-2-yl)-4-phenyl-2H-1,2,3-triazole (**4b**)

Colorless oil liquid; yield, 81%; IR (neat) 3466, 2960, 1648, 1374, 1009 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.82 (d, $J = 7.5$ Hz, 2H), 7.43 (t, $J = 7.3$ Hz, 2H), 7.38 – 7.33 (m, 1H), 6.08 (d, $J = 10.7$ Hz, 1H), 4.94 (s, 1H), 3.52 (s, 3H), 2.56 – 2.46 (m, 1H), 2.09 – 2.02 (m, 2H), 1.90 – 1.85 (m, 2H), 1.79 – 1.76 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.28, 131.74, 130.13, 128.78, 128.58, 126.12, 100.34, 83.75, 55.28, 29.44, 28.74, 17.65. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$ 260.1394; found, 260.1393.



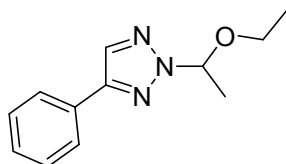
4-phenyl-2-(tetrahydrofuran-2-yl)-2H-1,2,3-triazole (**4c**)

Colorless oil liquid; yield, 94%; IR (neat) 3474, 2979, 1645, 1381, 1074 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.80 (d, $J = 7.9$ Hz, 2H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 1H), 6.34 (d, $J = 4.8$ Hz, 1H), 4.22 – 4.17 (m, 1H), 4.08 – 4.03 (m, 1H), 2.72 – 2.66 (m, 1H), 2.48 – 2.39 (m, 2H), 2.13 – 2.07 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.99, 131.36, 130.25, 128.77, 128.45, 125.96, 92.26, 69.53, 31.30, 24.44. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{14}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 216.1131; found 216.1130.



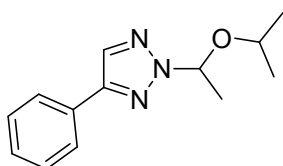
2-(1-(cyclohexyloxy)ethyl)-4-phenyl-2H-1,2,3-triazole (**4d**)

Colorless oil liquid; yield, 51%; IR (neat) 3465, 2948, 1644, 1383, 1102 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.83 (d, $J = 7.5$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 1H), 5.97 – 5.93 (m, 1H), 3.41 – 3.37 (m, 1H), 2.02 – 1.99 (m, 1H), 1.81 (d, $J = 5.9$ Hz, 3H), 1.74 – 1.72 (m, 2H), 1.64 – 1.58 (m, 1H), 1.47 – 1.40 (m, 2H), 1.26 – 1.78 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.67, 131.09, 130.38, 128.80, 128.44, 125.99, 87.19, 76.17, 32.64, 31.36, 25.48, 23.99, 23.91, 21.42. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{22}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 272.1757; found, 272.1758.



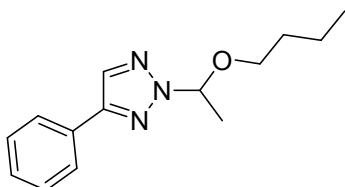
2-(1-ethoxyethyl)-4-phenyl-2H-1,2,3-triazole (**4e**)

Colorless oil liquid; yield, 64%; IR (neat) 3466, 3001, 1650, 1357, 1125 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.83 (d, $J = 7.4$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.36 (t, $J = 7.3$ Hz, 1H), 5.81 (q, $J = 6.0$ Hz, 1H), 3.60 – 3.53 (m, 1H), 3.43 – 3.36 (m, 1H), 1.84 (d, $J = 6.0$ Hz, 3H), 1.16 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.82, 131.26, 130.26, 128.82, 128.51, 125.99, 89.44, 64.57, 20.88, 14.72. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 218.1288; found 218.1285.



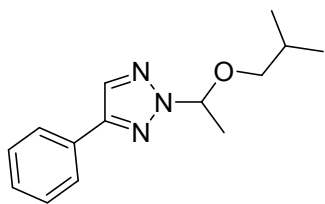
2-(1-isopropoxyethyl)-4-phenyl-2H-1,2,3-triazole (**4f**)

Colorless oil liquid; yield, 56%; IR (neat) 3473, 2972, 1649, 1375, 1118 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.83 (d, $J = 7.8$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 2H), 7.35 (t, $J = 7.2$ Hz, 1H), 5.91 (q, $J = 5.8$ Hz, 1H), 3.73 - 3.67 (m, 1H), 1.81 (d, $J = 5.9$ Hz, 3H), 1.24 (d, $J = 6.0$ Hz, 3H), 0.95 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.70, 131.15, 130.31, 128.81, 128.47, 125.98, 87.41, 70.40, 22.62, 21.37. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 232.1444; found, 232.1444.



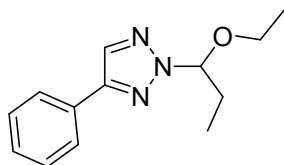
2-(1-butoxyethyl)-4-phenyl-2H-1,2,3-triazole (**4g**)

Colorless oil liquid; yield, 75%; IR (neat) 3475, 2956, 1634, 1381, 1129 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.83 (d, $J = 7.7$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 5.79 (q, $J = 5.9$ Hz, 1H), 3.53 - 3.47 (m, 1H), 3.35 – 3.30 (m, 1H), 1.83 (d, $J = 6.0$ Hz, 3H), 1.54 – 1.47 (m, 2H), 1.35 – 1.26 (m, 2H), 0.85 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.75, 131.21, 130.29, 128.79, 128.46, 125.97, 89.64, 68.82, 31.21, 20.80, 19.04, 13.68. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 246.1601; found 246.1601.



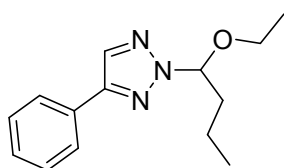
2-(1-isobutoxyethyl)-4-phenyl-2H-1,2,3-triazole (**4h**)

Colorless oil liquid; yield, 70%; IR (neat) 3468, 2959, 1648, 1381, 1126 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.83 (d, $J = 7.8$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.36 (t, $J = 7.1$ Hz, 1H), 5.77 (q, $J = 5.9$ Hz, 1H), 3.30 – 3.25 (m, 1H), 3.12 – 3.07 (m, 1H), 1.84 (d, $J = 5.9$ Hz, 3H), 1.82 – 1.74 (m, 1H), 0.87 (d, $J = 6.6$ Hz, 3H), 0.82 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.72, 131.20, 130.33, 128.81, 128.47, 125.98, 89.85, 75.78, 28.13, 20.74, 19.19, 19.06. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 246.1601; found, 246.1601.



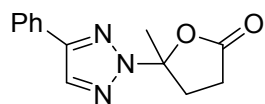
2-(1-ethoxypropyl)-4-phenyl-2H-1,2,3-triazole (**4i**)

Colorless oil liquid; yield, 79%; IR (neat) 3465, 2963, 1650, 1381, 1107 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.82 (d, $J = 7.4$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 1H), 5.52 (t, $J = 6.6$ Hz, 1H), 3.47 – 3.59 (m, 1H), 3.43 – 3.35 (m, 1H), 2.25 – 2.17 (m, 2H), 1.15 (t, $J = 7.0$ Hz, 3H), 0.88 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.82, 131.28, 130.26, 128.79, 128.47, 125.96, 94.45, 64.71, 28.00, 14.67, 9.05. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$ 232.1450; found, 232.1443.



2-(1-ethoxybutyl)-4-phenyl-2H-1,2,3-triazole (**4j**)

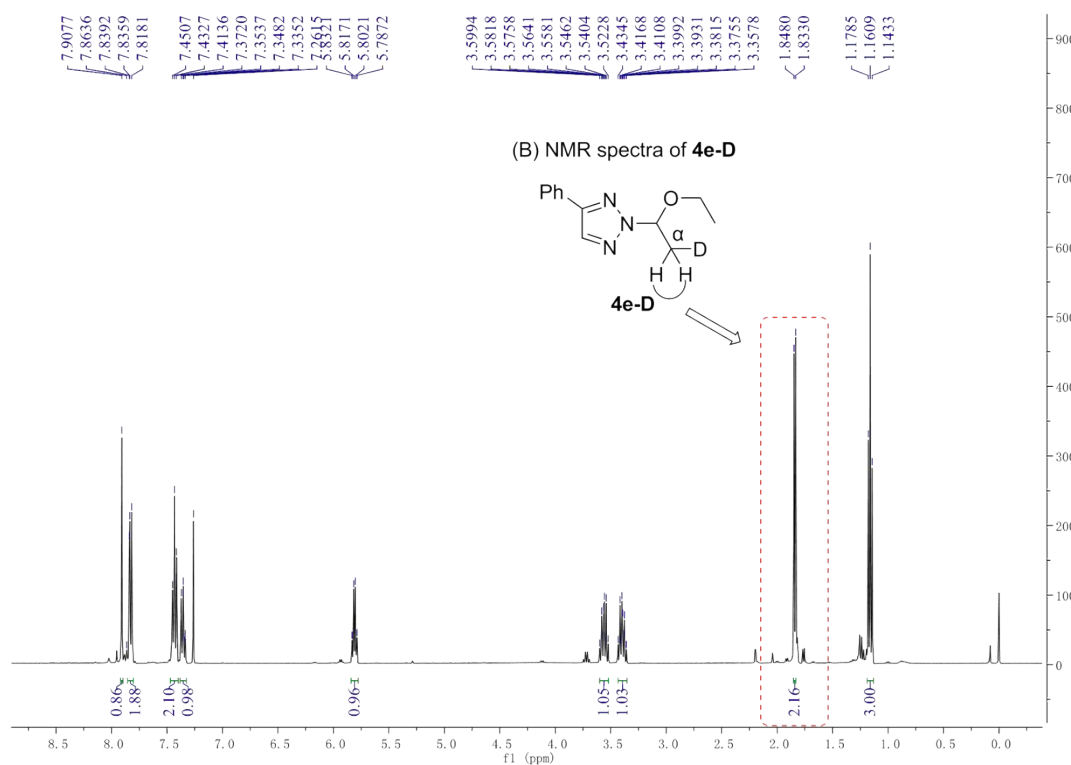
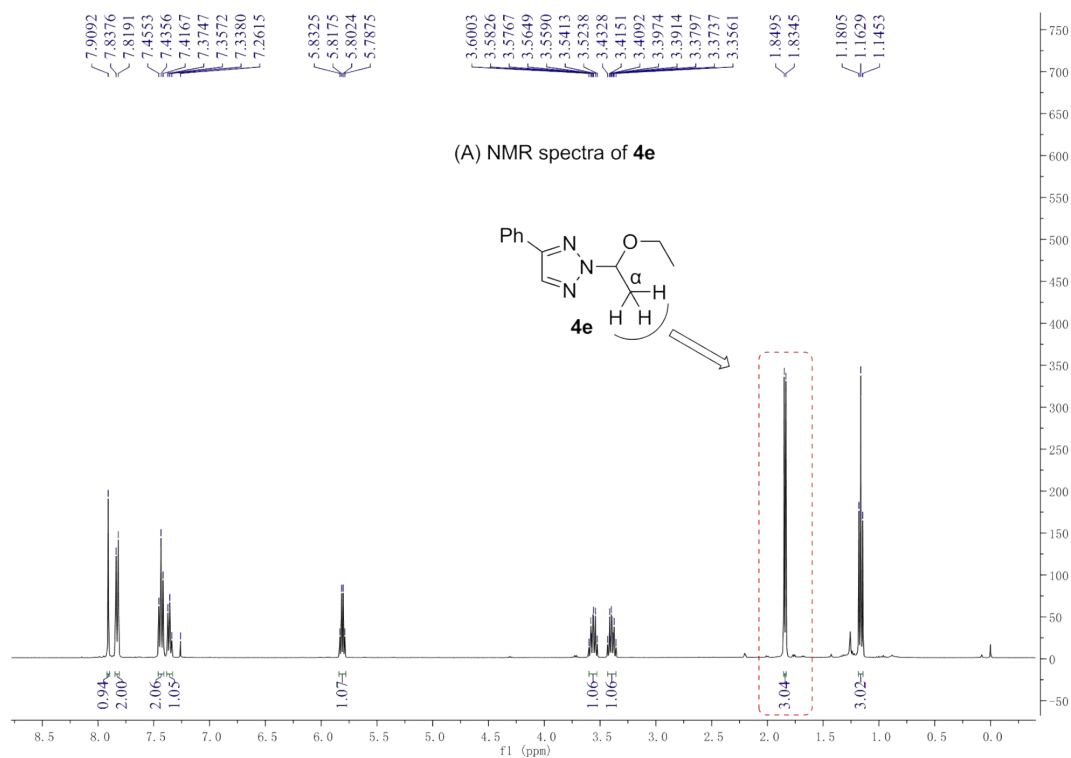
Colorless oil liquid; yield, 90%; IR (neat) 3469, 2962, 1647, 1381, 1112 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.83 (d, $J = 7.6$ Hz, 2H), 7.43 (t, $J = 7.3$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 5.62 (t, $J = 6.6$ Hz, 1H), 3.58 – 3.50 (m, 1H), 3.45 – 3.37 (m, 1H), 2.22 – 2.16 (m, 2H), 1.47 – 1.37 (m, 1H), 1.27 – 1.21 (m, 1H), 1.16 (t, $J = 7.0$ Hz, 3H), 0.94 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.78, 131.22, 130.26, 128.77, 128.45, 125.96, 92.96, 64.65, 36.62, 17.94, 14.66, 13.50. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$ 246.1601; found, 246.1600.



5-methyl-5-(4-phenyl-2H-1,2,3-triazol-2-yl)dihydrofuran-2(3H)-one (**4k**)²

¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 1H), 3.33 – 3.15 (m, 2H), 2.80 – 2.71 (m, 1H), 2.54 (dt, *J* = 13.2, 9.9 Hz, 1H), 2.25 (s, 3H);
¹³C NMR (100 MHz, CDCl₃) δ 175.39, 148.70, 132.09, 129.68, 128.91, 128.87, 126.12, 109.97, 97.30, 34.28, 29.21, 25.39.

3. Deuterium-Labeling Experiment Result

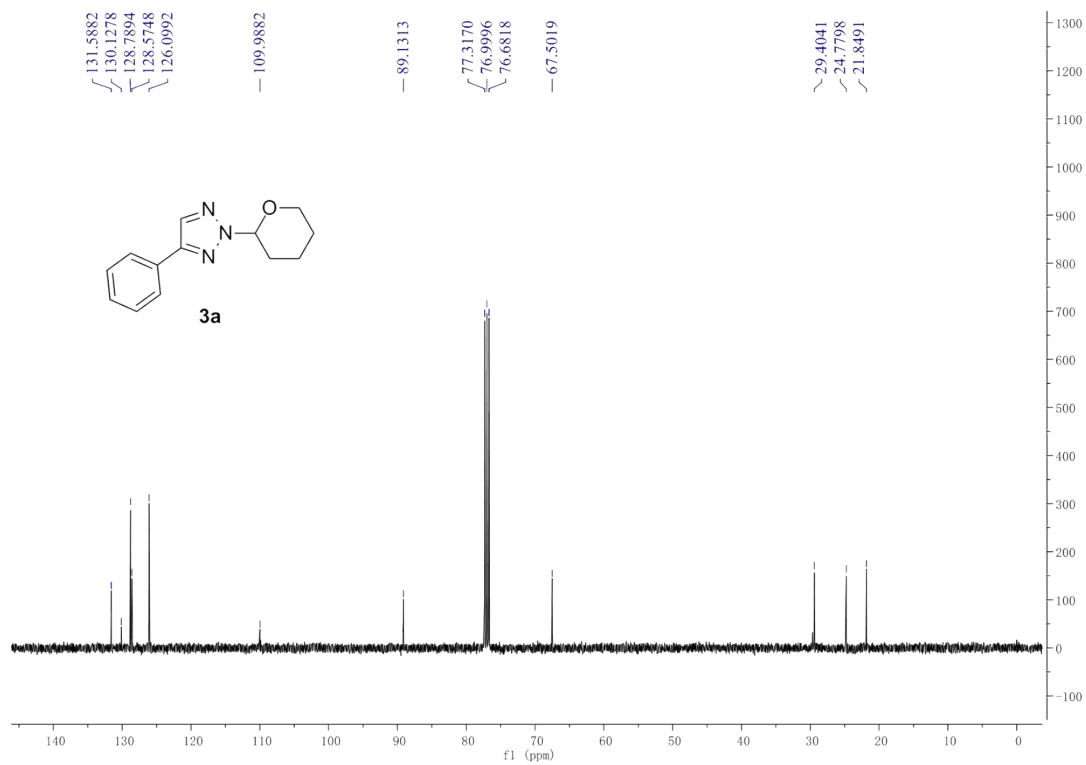
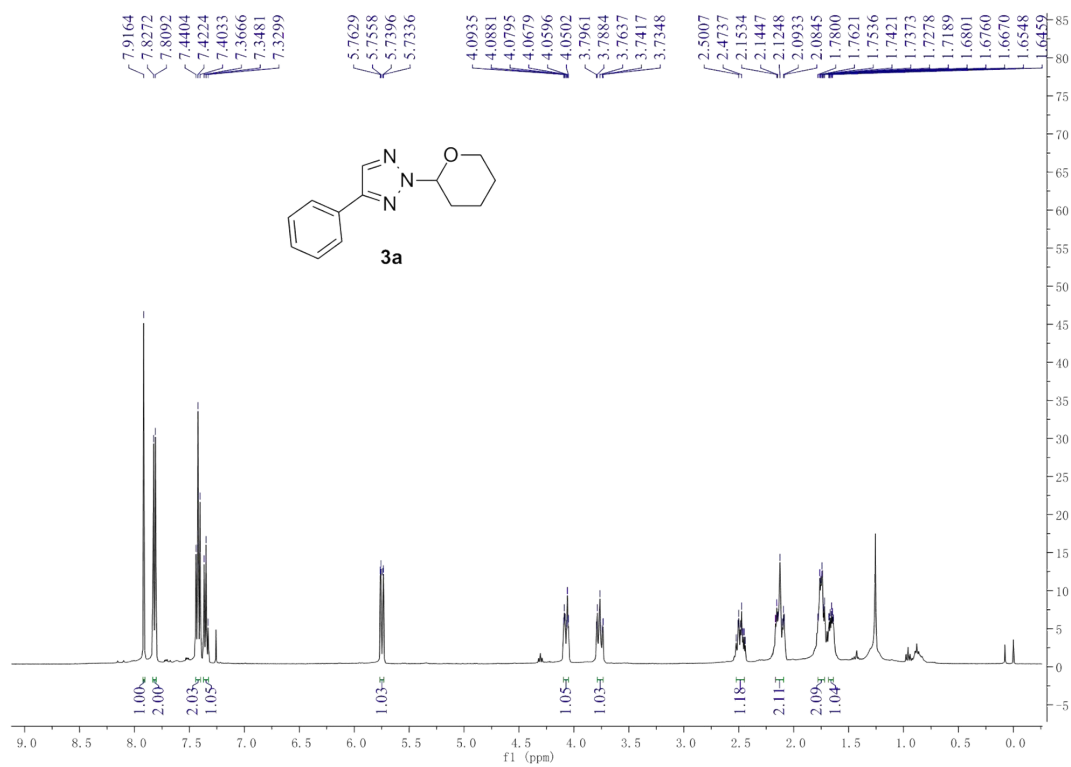


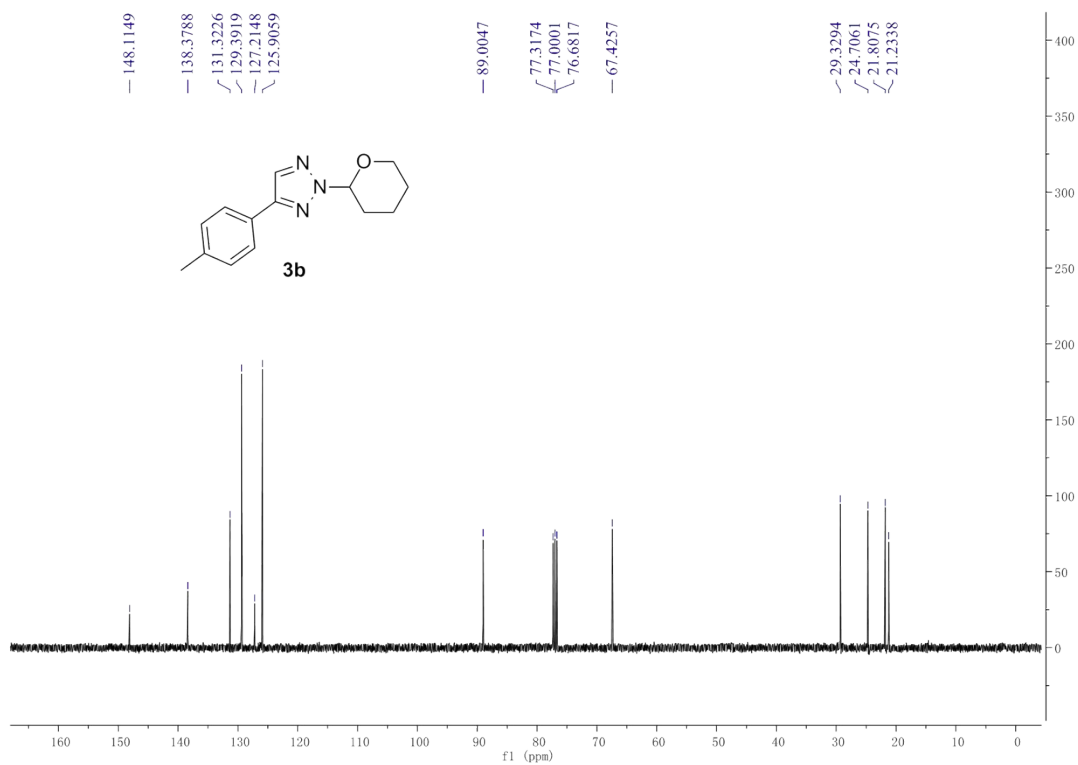
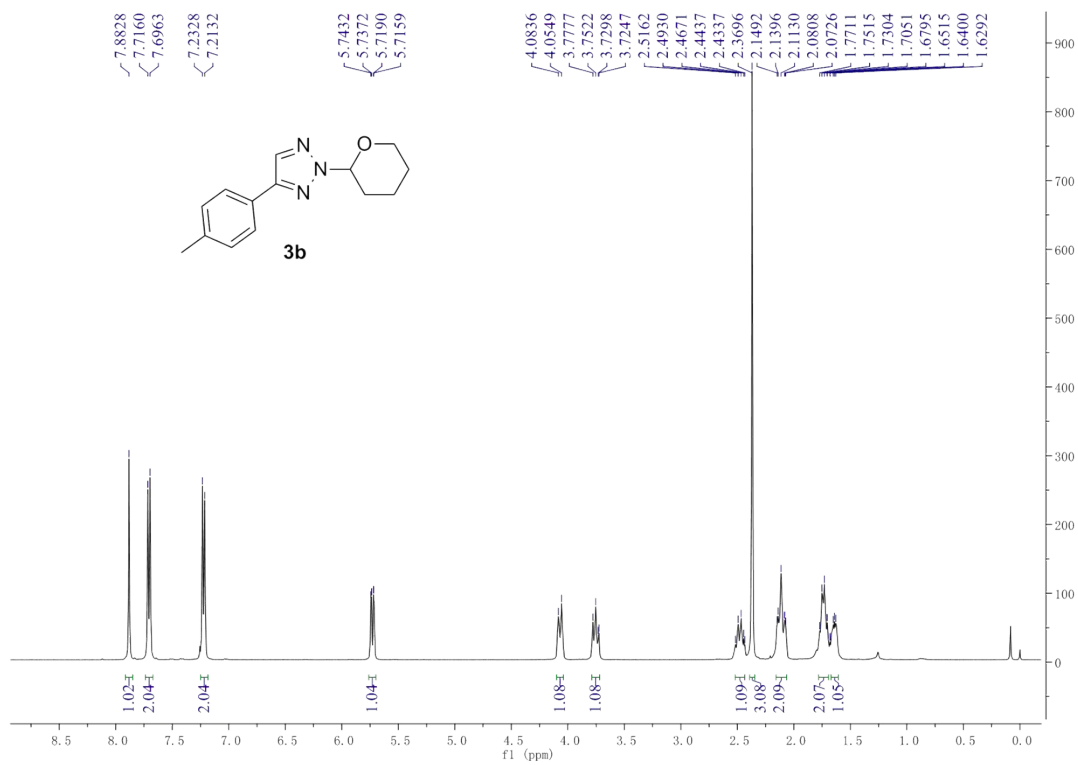
The incorporation of deuterium at the α -position ($f1 = 1.84$ ppm) of **4e** is $(3.04-2.16)/3.04 \times 100\% = 28\%$.

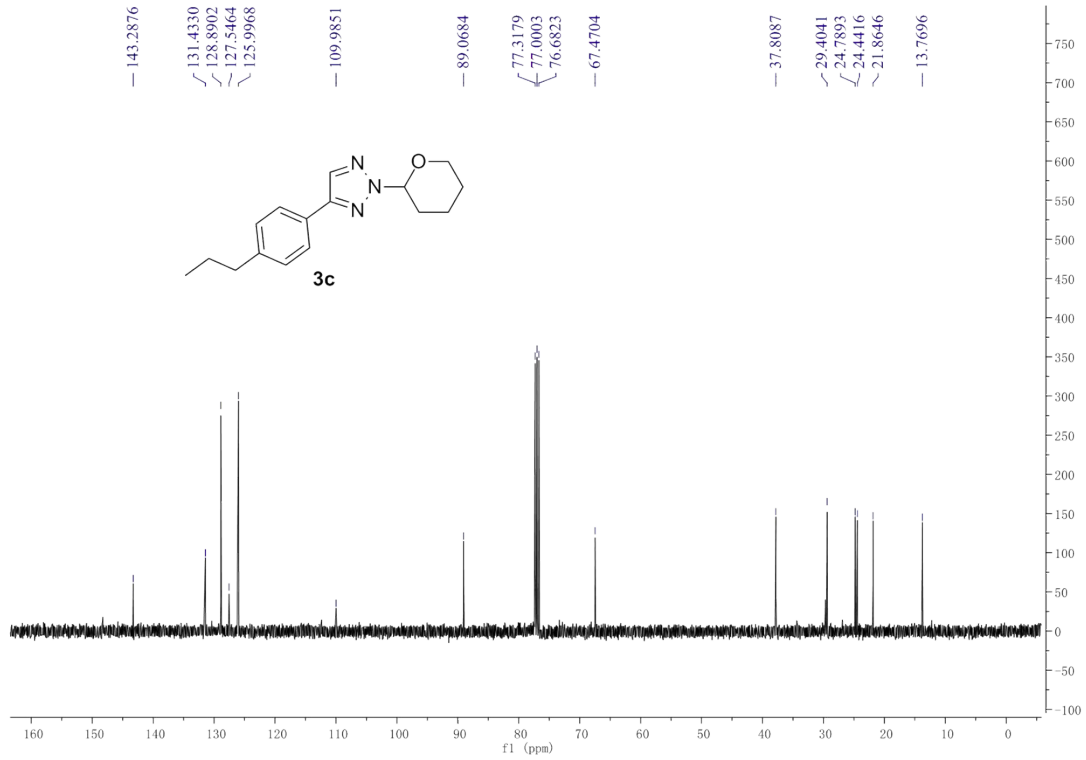
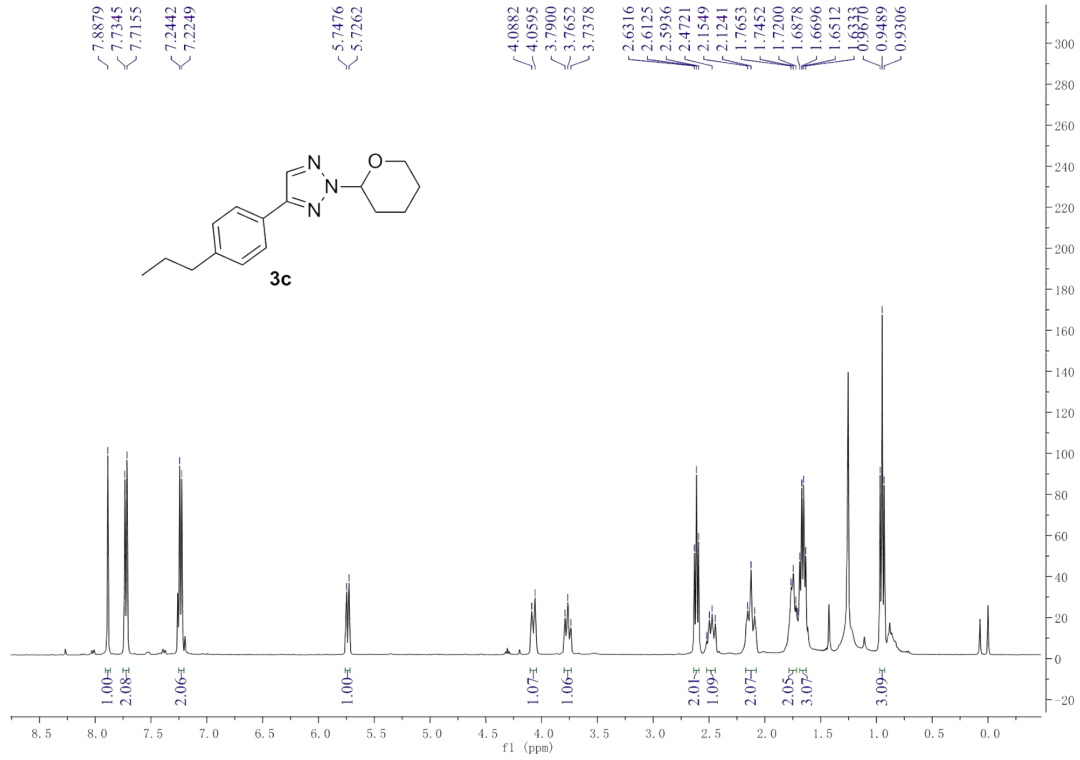
4. References

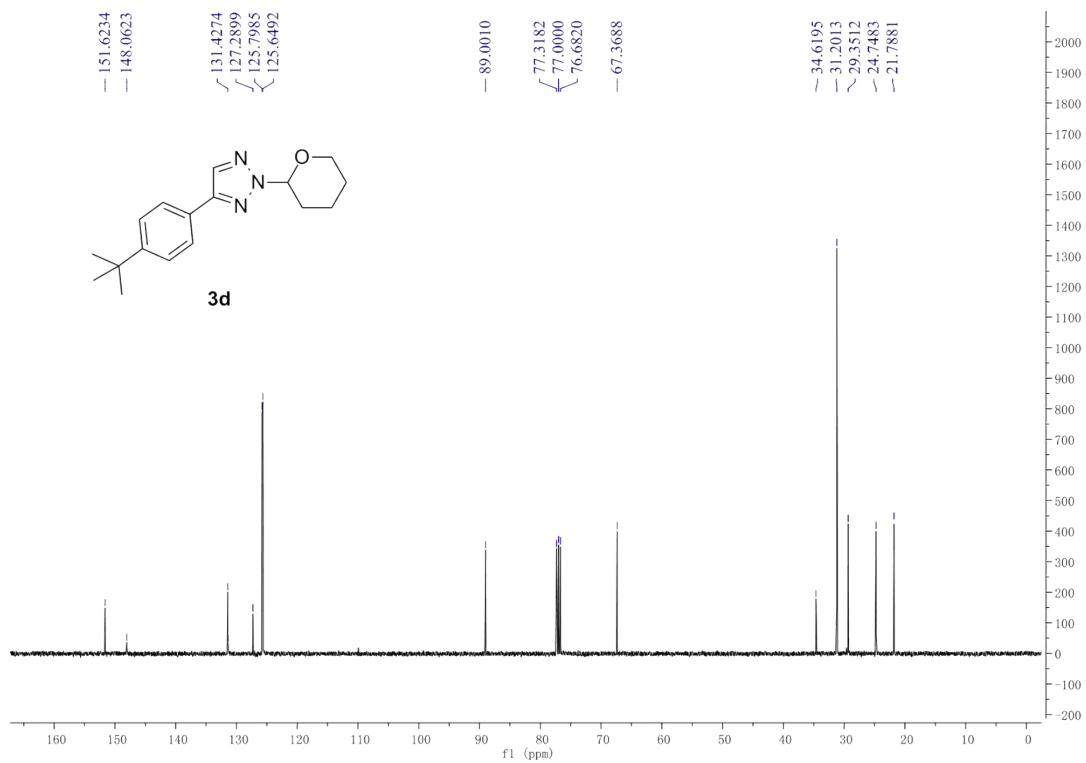
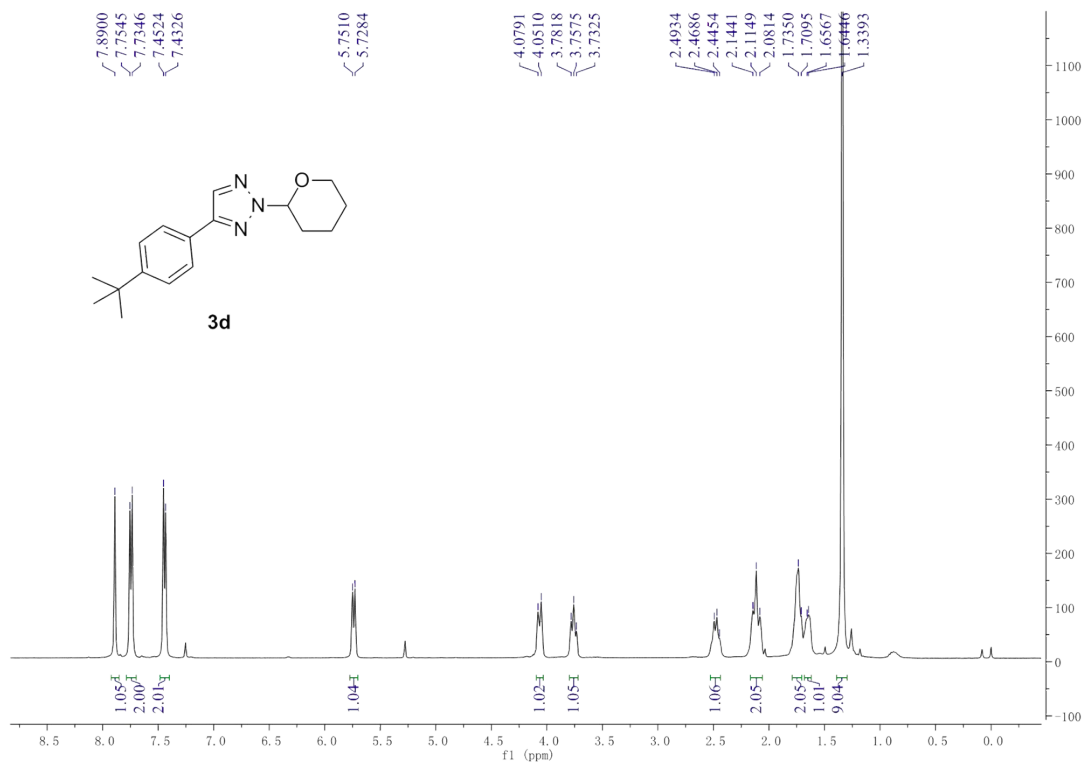
1. Yoo, E. J.; Ahlquist, M.; Kim, S. H.; Bae, I.; Fokin, V. V.; Sharpless, K. B.; Chang, S., *Angew. Chem. Int. Ed.*, **2007**, *46* (10), 1730-1733.
2. J. W. Shi, L. L. Zhu, J. Wen and Z. L. Chen, *Chinese. J. Catal.*, 2016, **37**, 1222-1226.

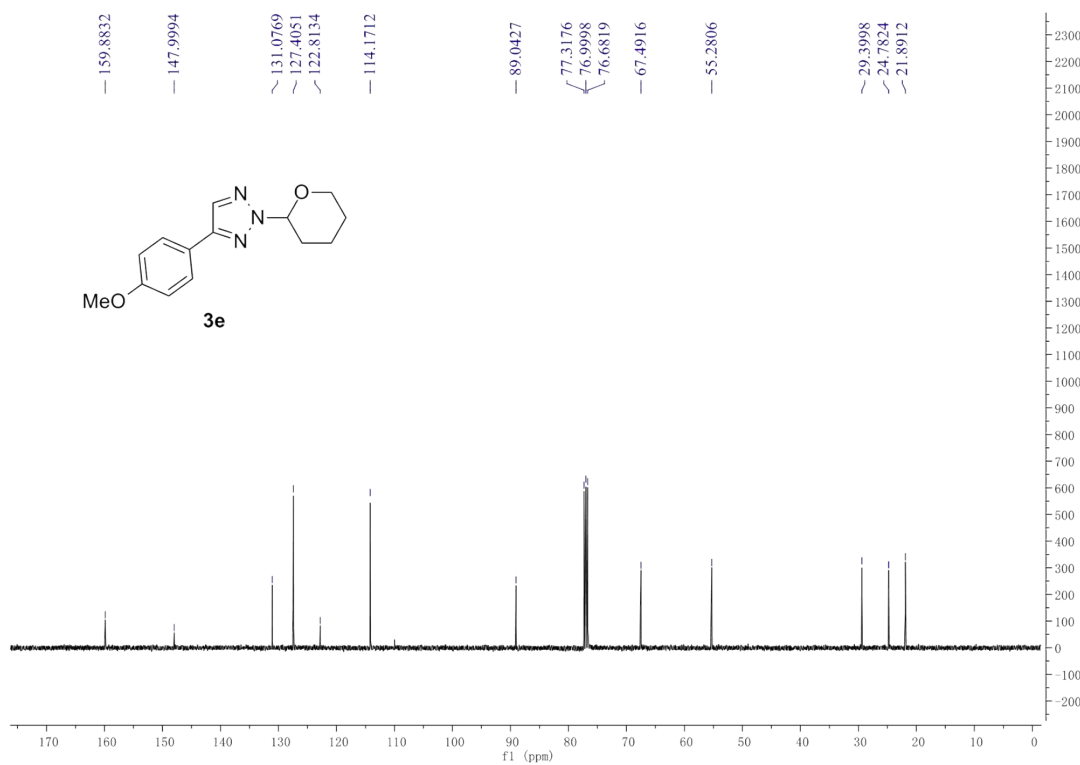
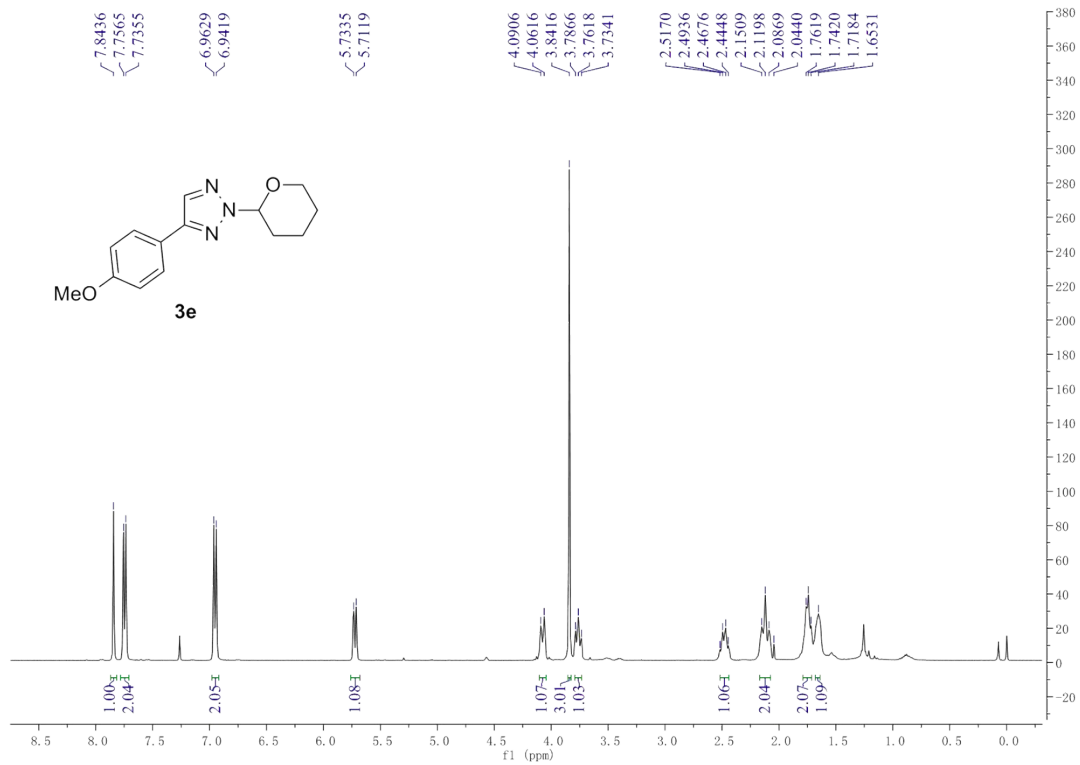
5. NMR Spectra of 3a-3I

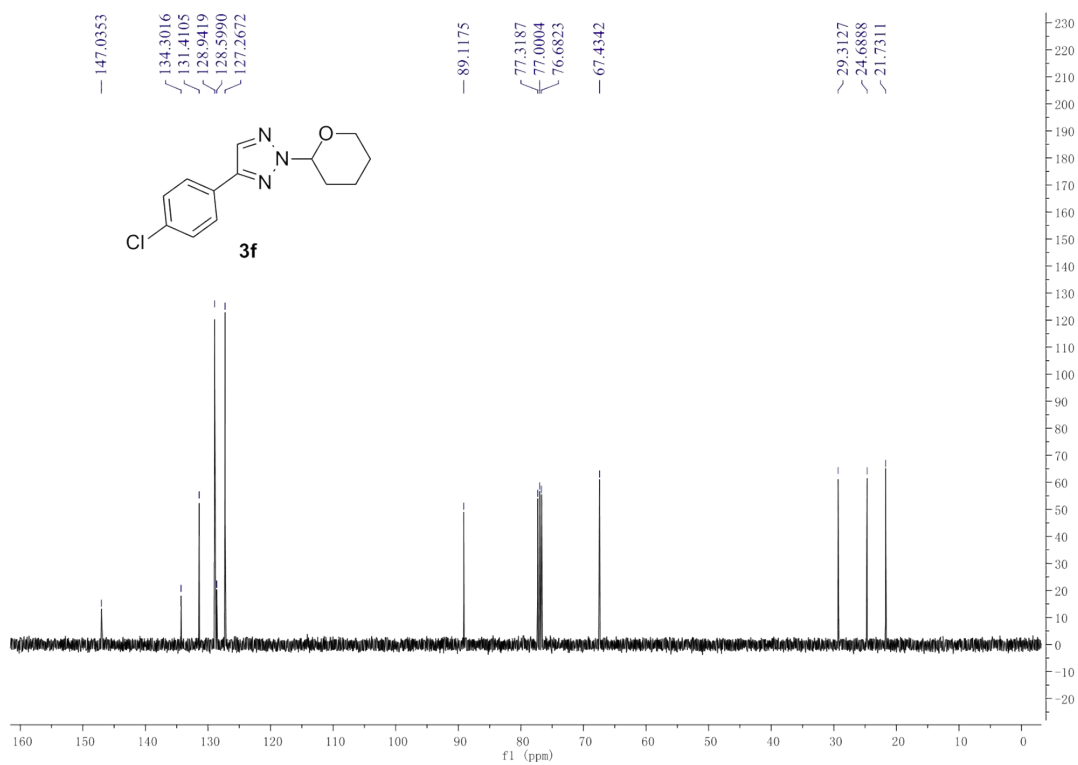
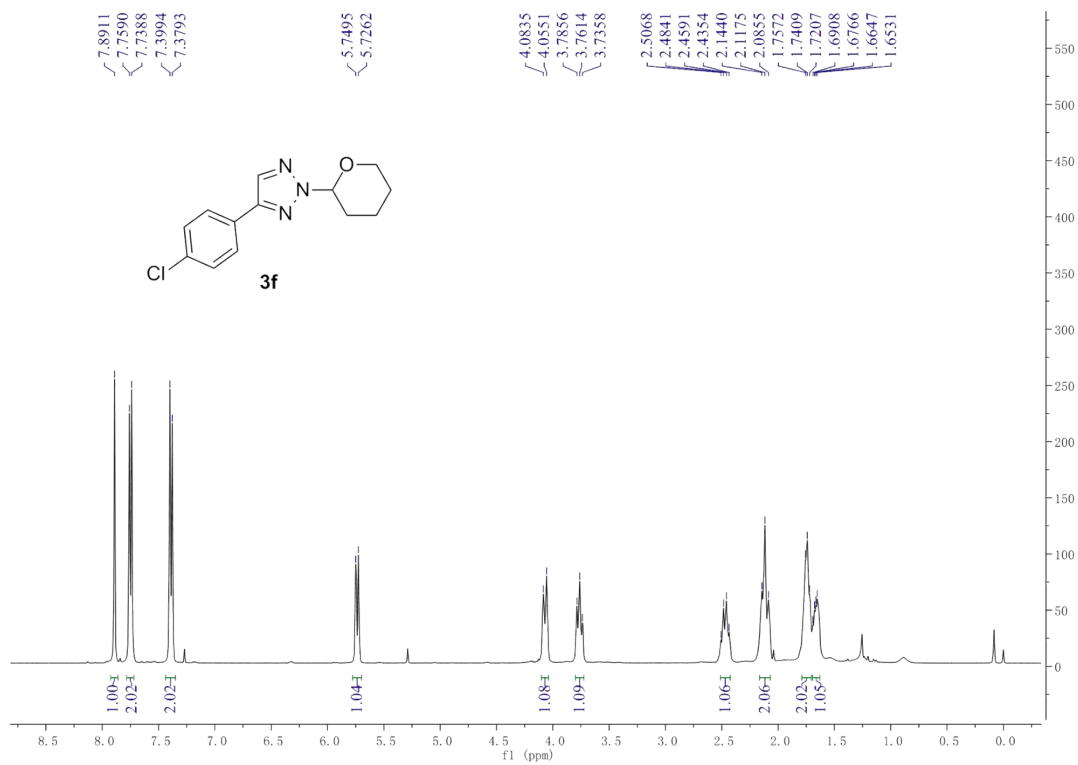


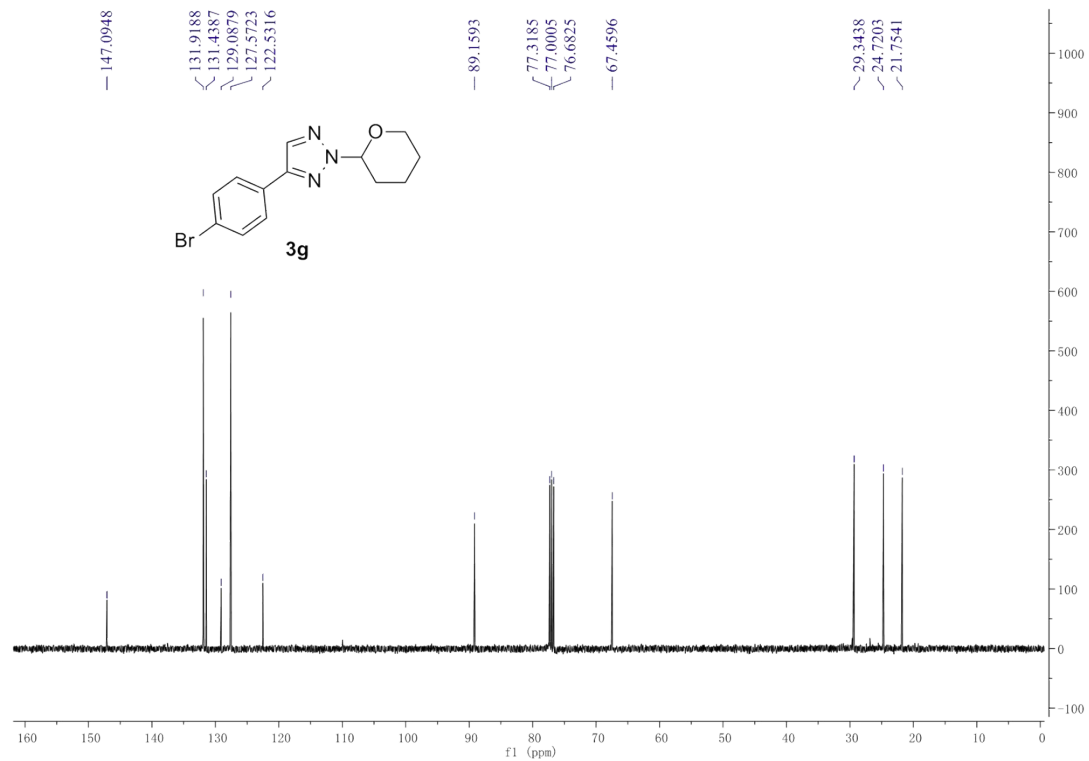
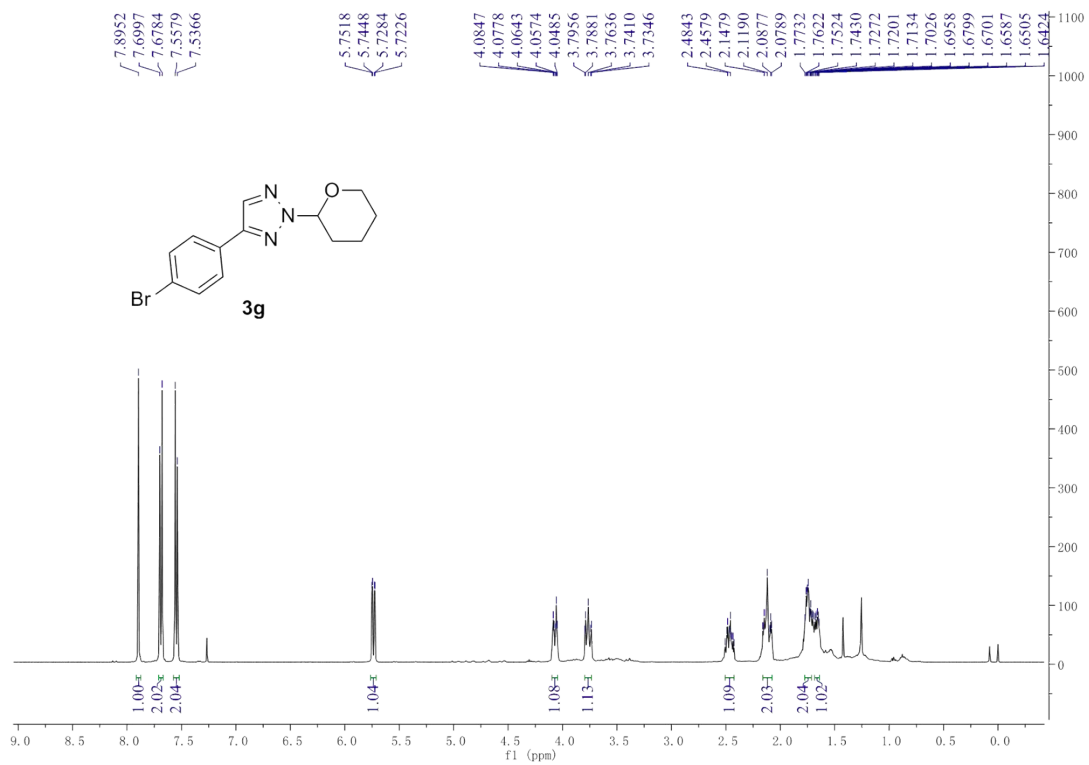


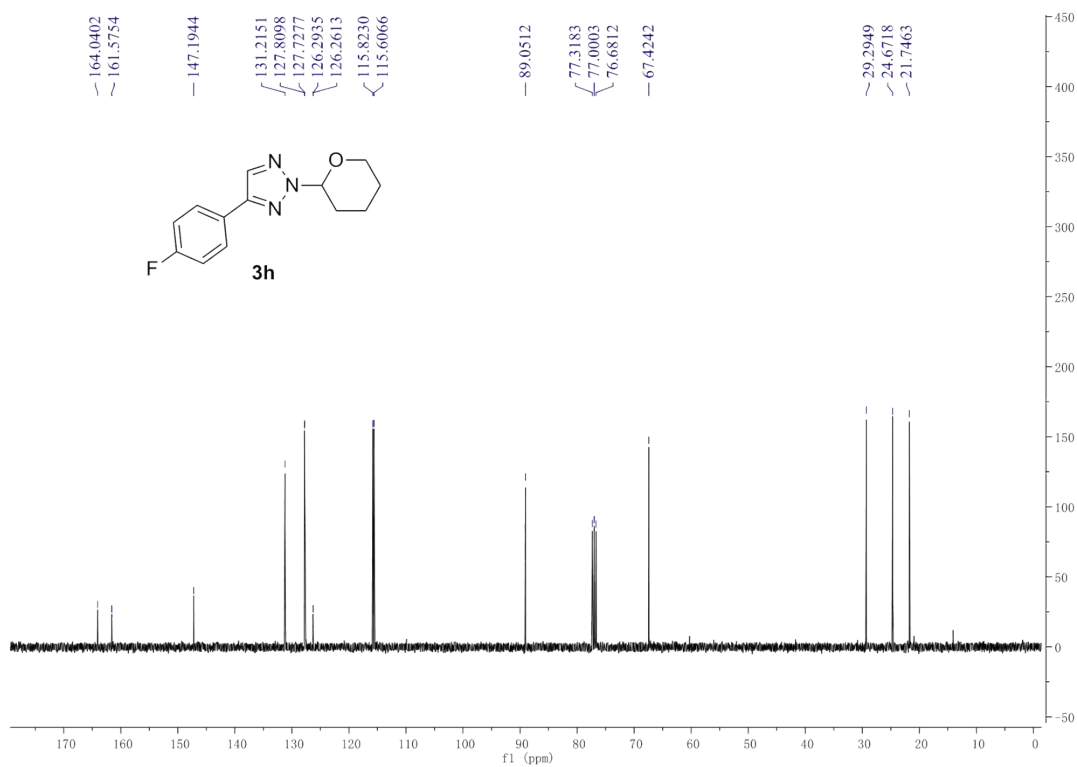
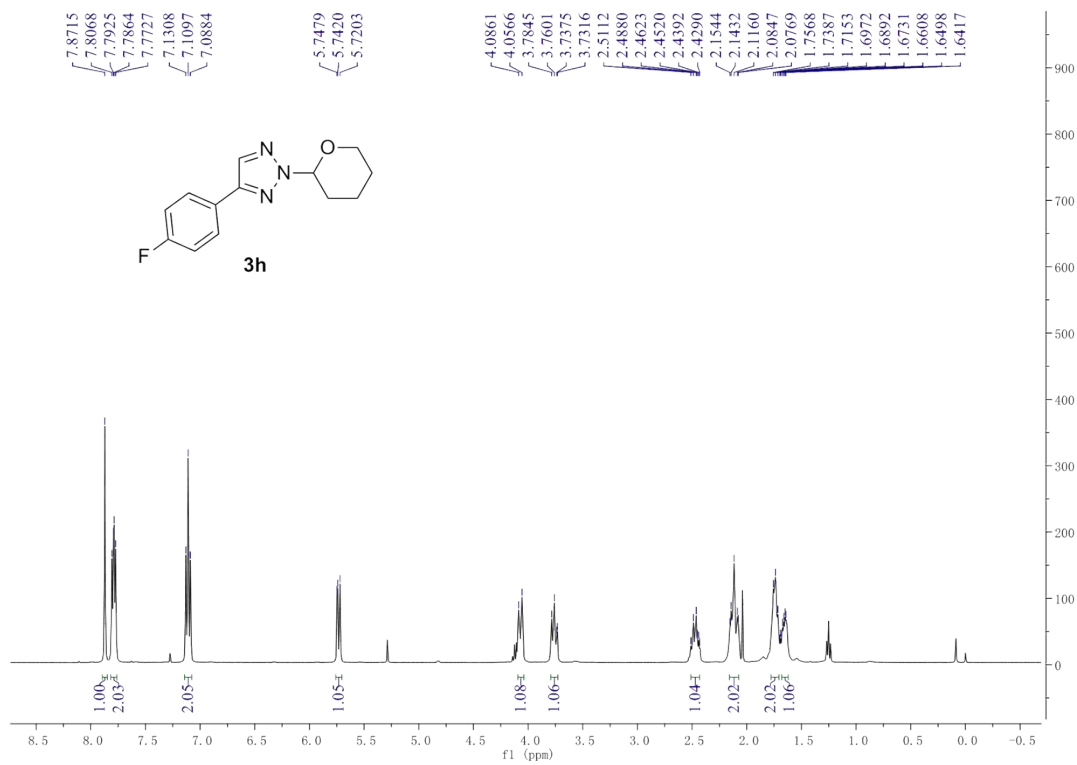


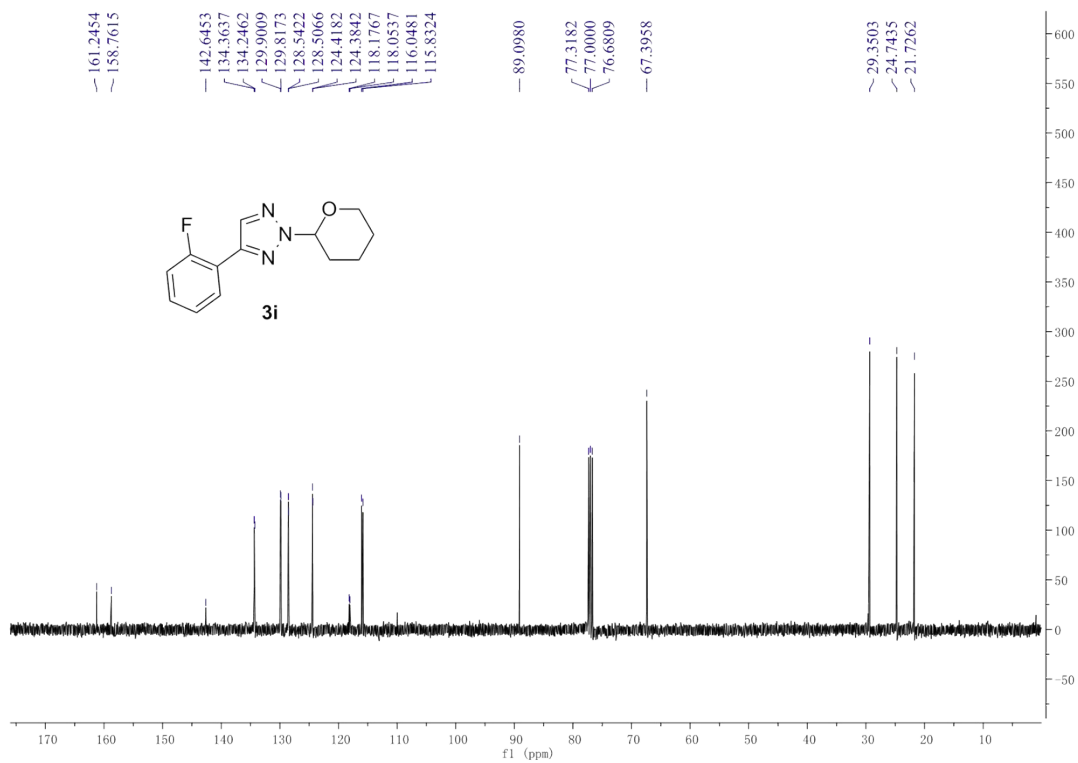
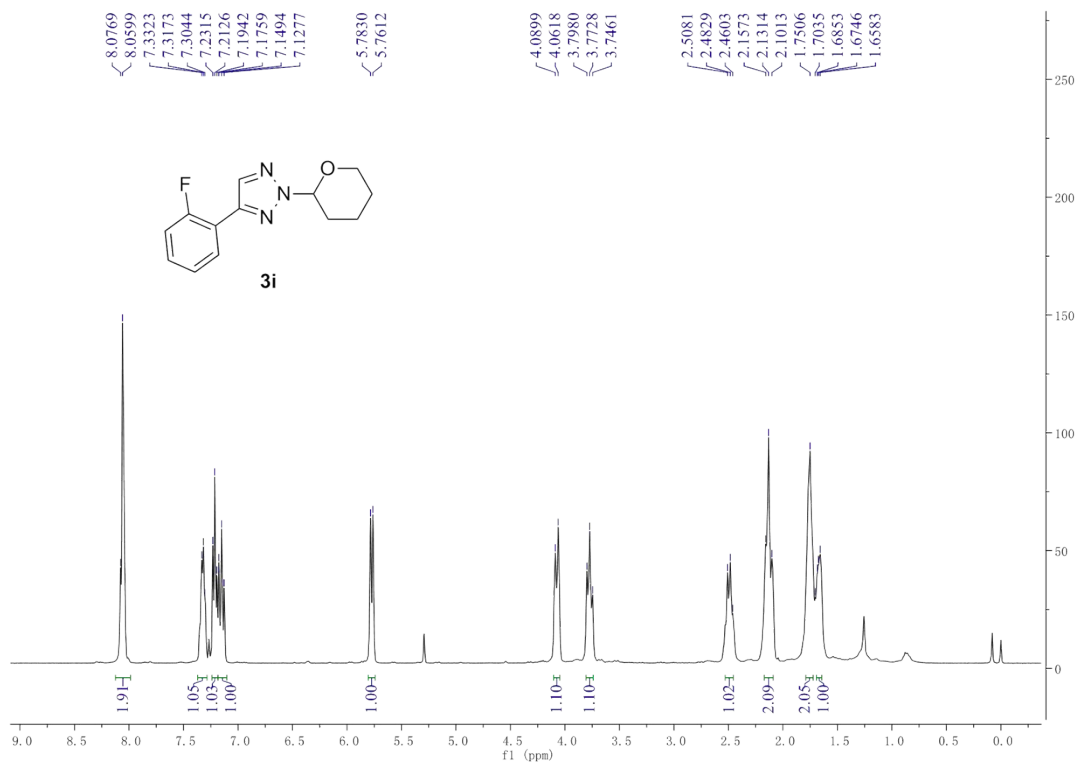


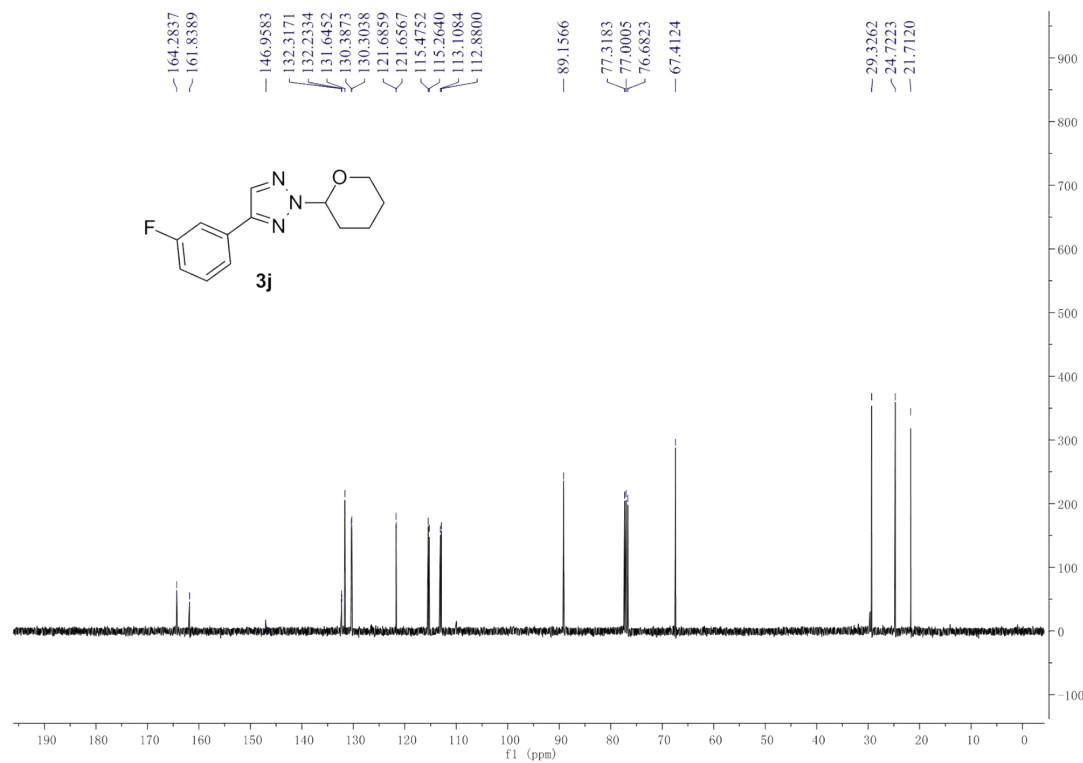
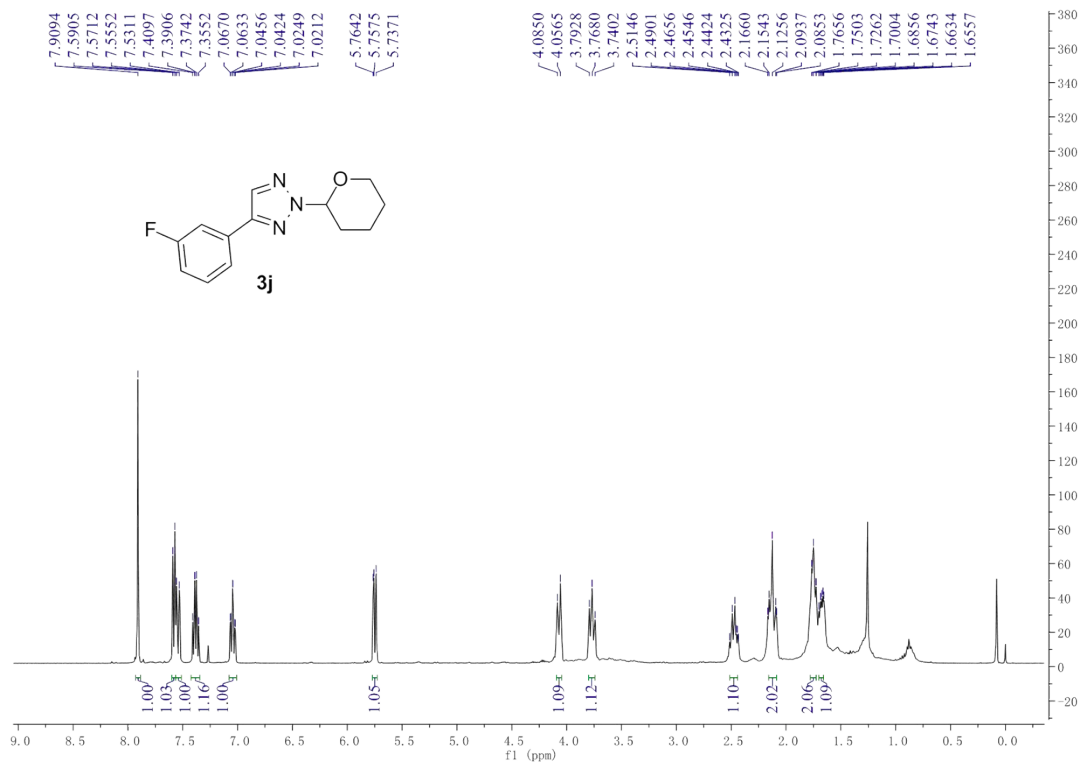


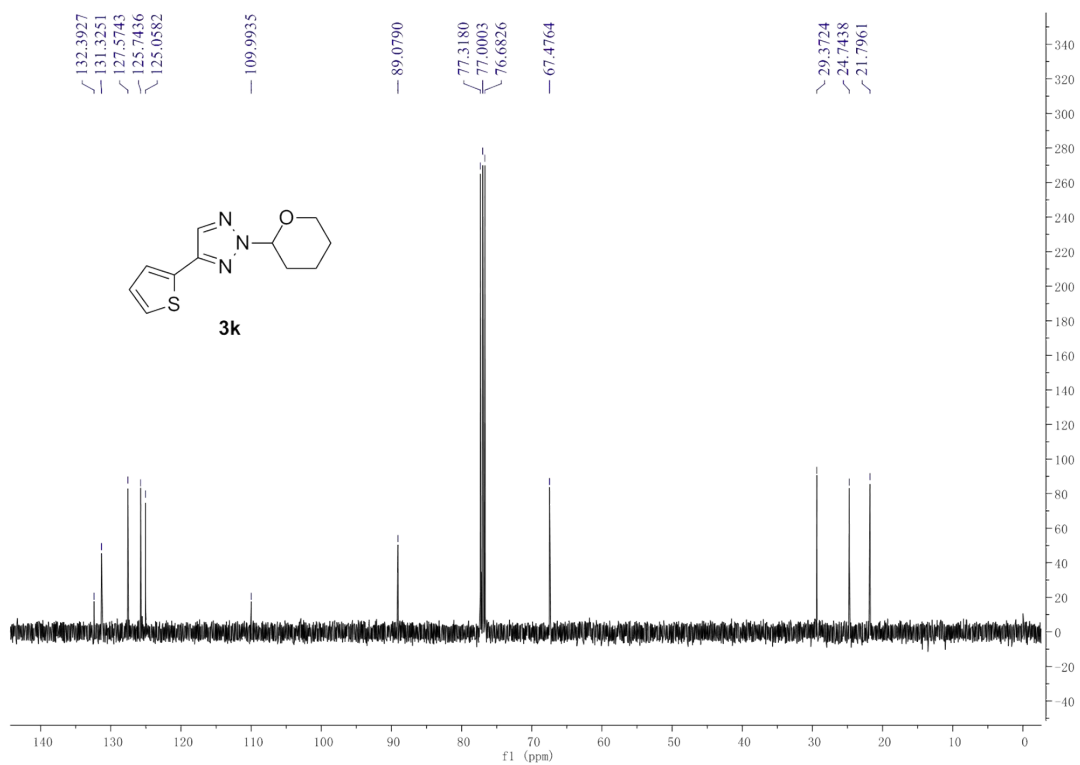
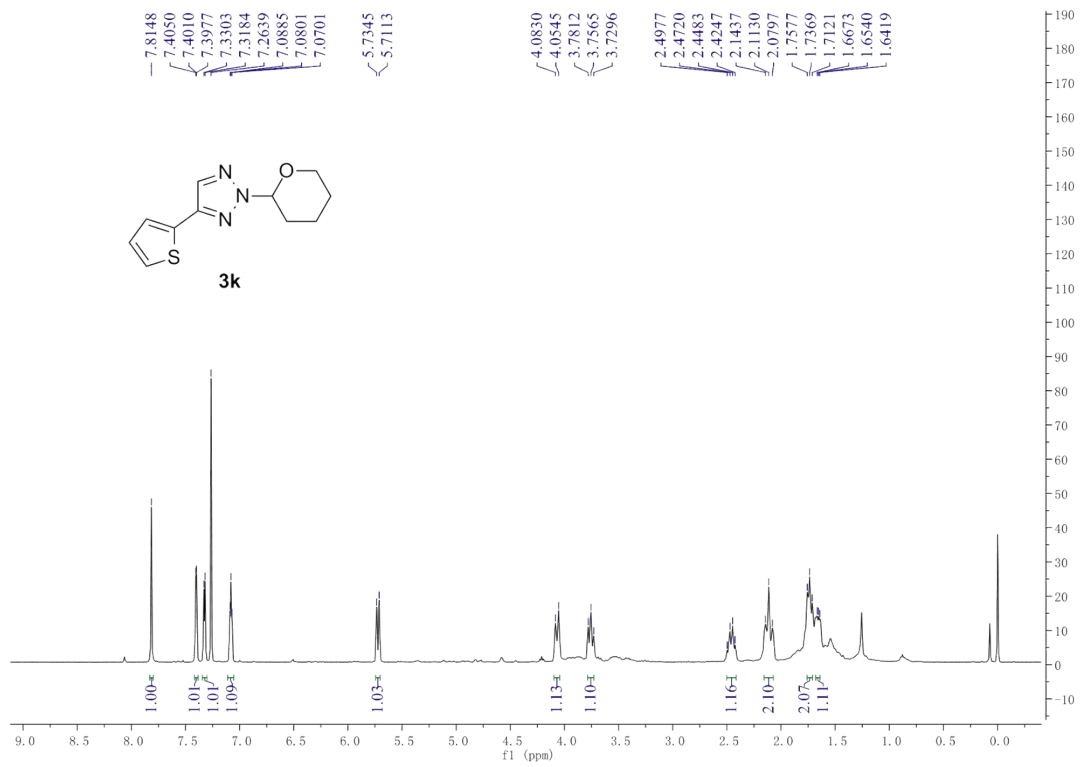


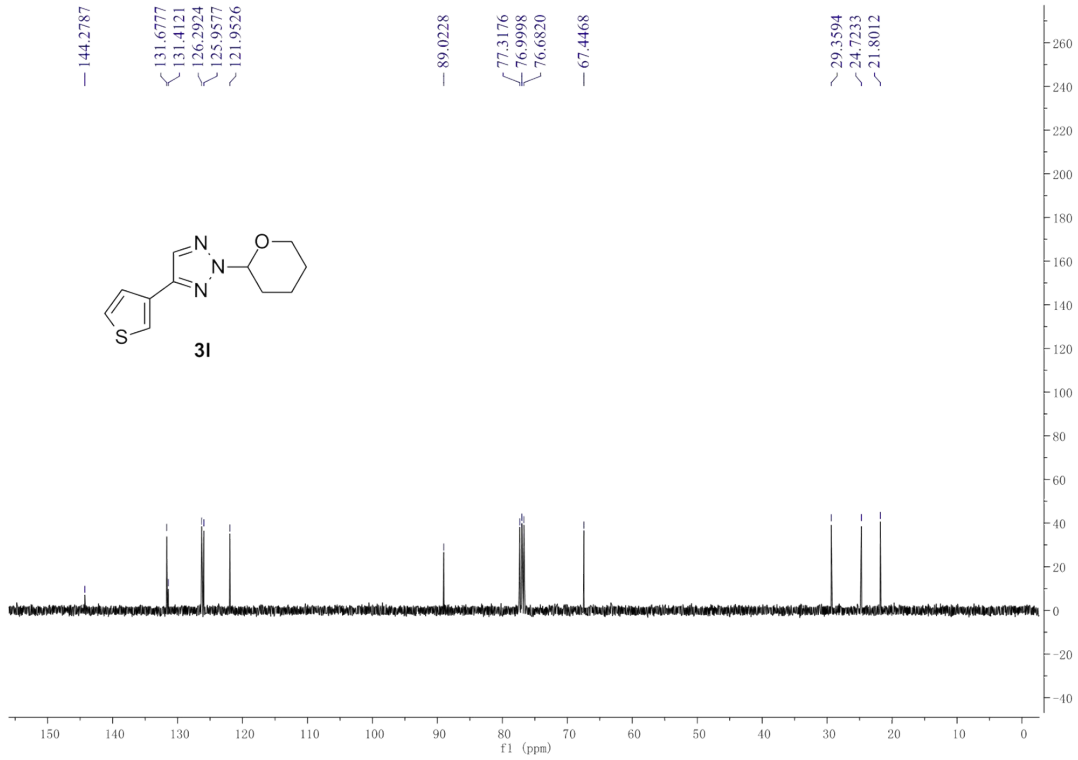
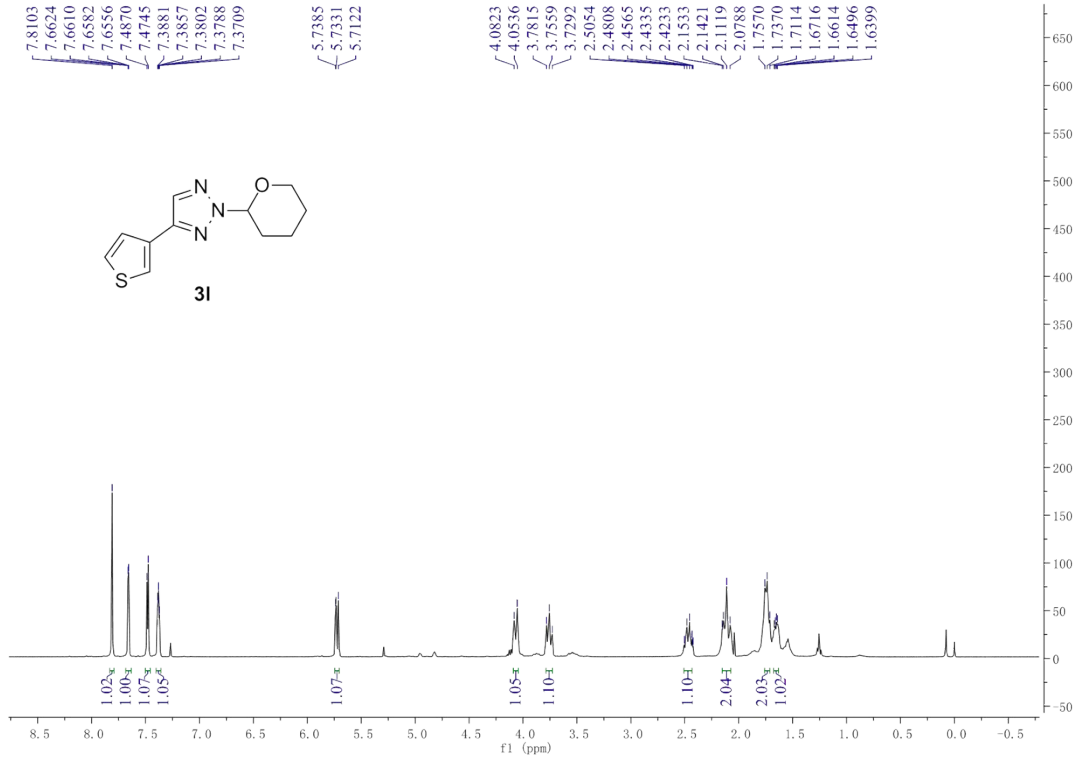












6. NMR Spectra of 4b-4k

