Supplementary Material (ESI) for Green Chemistry

Supporting Information

(Part I: Experimental procedures, Analytical data)

Cu_2O acting as a robust catalyst in CuAAC reactions: Water is the required medium

Kai Wang, Xihe Bi,* Shuangxi Xing, Peiqiu Liao, Zhongxue Fang, Xianyu Meng, Qian Zhang,* Qun Liu, Yu Ji

Department of Chemistry, Northeast Normal University, Changchun 130024, China

E-mail: bixh507@nenu.edu.cn; zhangq651@nenu.edu.cn

Contents

I. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 25ºC on a Varian 500 MHz and 125 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

II. Procedure for the reactions 'in water'

Sulfonyl azide (1.0 mmol) , alkyne (1.2 mmol),[1] Cu_2O (0.1 mmol) , water (1.0 mL) were added to a flask with a stir bar, and the mixture was stirred at room temperature (25°C) without exclusion of air. After the reaction was completed, monitored by TLC, the reaction mixture was diluted by adding CH_2Cl_2 (2 mL) and aqueous NH_4Cl solution (3 mL). The mixture was stirred for an additional 30 minutes and two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The crude product was purified on a short silica gel column with an appropriate eluting solvent (using EtOAc/ petroleum ether) to get a pure *N*-sulfonyl-1,2,3-triazoles.

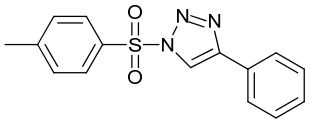
III. Procedure for the reactions under neat conditions

Sufonyl azide (0.5 mmol) , alkyne (0.6 mmol) , Cu_2O (1 *ul* , 0.05 M in THF) were added into a flask with a stir bar and 100 *ul* H_2O as the additive.[2] The mixture was stirred at 50°C without exclusion of air. After most of the starting azide was consumed, monitorde by TLC, the reaction mixture was washed by small amount of ether, then collected *N*-sulfonyl-1,2,3-triazoles by the filtration.

[1] Solid alkynes **1f**, **1g** or solid azides **2o**, **2p** was pre-dissolved in 0.2 mL ethyl acetate.
[2] Using the Dragon® MicroPette to transfer the micro amount of reagents.

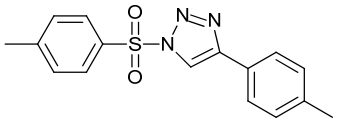
IV. Analytical data of compounds [3]

3a (1-(4-Methylbenzenesulfonyl)-4-phenyl-1,2,3-triazole)



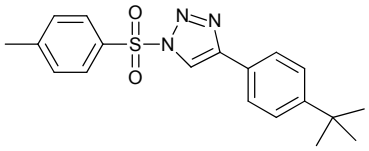
White solid, m.p. 108-109 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.44-7.35 (m, 5H), 2.44 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.32, 147.31, 133.08, 130.43, 129.05, 128.95, 128.84, 128.66, 126.04, 118.90, 21.78; **MALDI-TOF/TOF-MS**: (m/z): 300.1 $[M + 1]^+$.

3b (1-(4-Methylbenzenesulfonyl)-4-(4-methylphenyl)-1,2,3-triazole)



White solid, m.p. 158-159 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.43, 147.23, 139.06, 133.13, 130.39, 129.62, 128.63, 125.93, 118.47, 21.78, 21.28; **MALDI-TOF/TOF-MS**: (m/z): 314.1 $[M + 1]^+$.

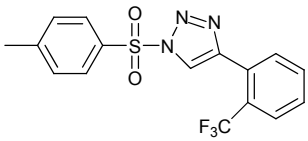
3c (1-(4-Methylbenzenesulfonyl)-4-(4-tert-butylphenyl)-1,2,3-triazole)



White solid, m.p. 171-172 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.33 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 152.27, 147.34, 147.24, 133.04, 130.39, 128.58, 125.92, 125.86, 125.75, 118.57, 34.69, 31.16, 21.78; **MALDI-TOF/TOF-MS**: (m/z): 356.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{19}H_{22}N_3O_2S$ $[M+1]^+$: 356.1427, found: 356.1426.

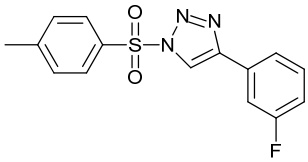
[3] Compounds **3a, 3b, 3h, 3j, 3m, 3q, 3r** have been previously reported in the reference of E. J. Yoo, M. Ahlquist, S. H. Kim, I. Bae, V. V. Fokin, K. B. Sharpless, S. Chang, *Angew. Chem. Int. Ed.*, 2007, **46**, 1730.

3d (1-(4-Methylbenzenesulfonyl)-4-(2-trifluoromethylphenyl)-1,2,3-triazole)



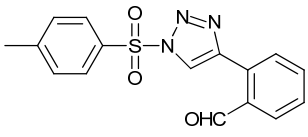
White solid, m.p. 108-109 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.76 (d, J = 8.0 Hz), 7.64-7.61 (m, 1H), 7.54-7.51 (m, 1H), 7.41 (d, *J* = 7.5 Hz), 2.45 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 147.51, 143.77, 132.81, 132.08, 131.76, 130.50, 129.07, 128.63, 127.58, 127.47, 126.28, 126.23, 124.88, 122.71, 122.36, 122.31, 21.80; **MALDI-TOF/TOF-MS**: (m/z): 368.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{16}H_{13}F_3N_3O_2S$ $[M+1]^+$:368.0675, found: 368.0674.

3e (1-(4-Methylbenzenesulfonyl)-4-(3-fluorophenyl)-1,2,3-triazole)



White solid, m.p. 140-141 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.59-7.54 (m, 2H), 7.42-7.39 (m, 3H), 7.07-7.05 (m, 1H), 2.45 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 164.32, 161.86, 147.50, 146.21, 132.91, 131.03, 130.6,7 130.59, 130.49, 128.74, 121.68, 119.35, 116.05, 115.84, 113.18, 112.95, 25.80, 21.82; **MALDI-TOF/TOF-MS**: (m/z): 318.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{15}H_{13}FN_3O_2S$ $[M+1]^+$:318.0707, found: 318.0704.

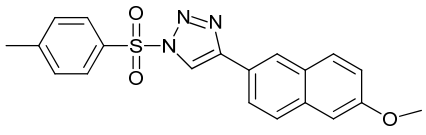
3f (1-(4-Methylbenzenesulfonyl)-4-(2-aldehydephenyl)-1,2,3-triazole)



White solid, m.p. 107-108 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.28 (s, 1H), 8.45 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.68-7.65 (m, 1H), 7.58-7.55 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 191.67, 147.69, 144.32, 133.96, 133.83, 132.77, 130.95, 130.59, 130.31, 129.69, 129.45, 128.86, 122.65, 21.87;

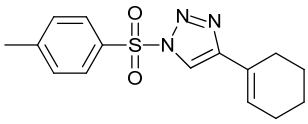
MALDI-TOF/TOF-MS: (m/z): 328.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{16}H_{14}N_3O_3S$ $[M+1]^+$:328.0751, found: 328.0751.

3g (1-(4-Methylbenzenesulfonyl)-4-(6-methoxynaphthalen)-1,2,3-triazole)



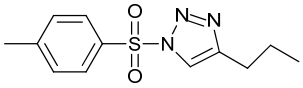
White solid, m.p. 166-167 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.27 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.84-7.82 (m, 1H), 7.78-7.75 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 3.92 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 158.27, 147.59, 147.28, 134.75, 133.09, 130.43, 129.77, 128.74, 128.64, 127.54, 125.10, 124.13, 123.94, 119.54, 118.68, 105.74, 55.32, 21.80; **MALDI-TOF/TOF-MS**: (m/z): 380.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{20}H_{18}N_3O_3S$ $[M+1]^+$: 380.1063, found: 380.1052.

3h (4-(Cyclohex-1-enyl)- 1-(4-Methylbenzenesulfonyl)- 1,2,3-triazole)



White solid, m.p. 102-103 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.89 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.65 (t, *J* = 3.5 Hz, 1H), 2.43 (s, 3H), 2.31-2.29 (m, 2H), 2.20-2.18 (m, 2H), 1.76-1.72 (m, 2H), 1.67-1.62 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 148.92, 147.01, 133.33, 130.31, 128.50, 127.64, 125.77, 117.34, 26.14, 25.24, 22.21, 21.94, 21.76; **MALDI-TOF/TOF-MS**: (m/z): 304.1 $[M + 1]^+$.

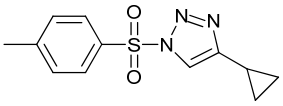
3i (4-Propyl-1-(4-Methylbenzenesulfonyl)- 1,2,3-triazole)



Colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz), 7.84 (s, 1H), 7.37 (d, *J* = 8.0 Hz), 2.70-2.66 (m, 2H), 2.44 (s, 3H), 1.69-1.66 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.04, 147.01, 133.29, 130.31, 128.48, 120.27, 27.29, 22.13, 21.73, 13.57; **MALDI-TOF/TOF -MS**: (m/z): 266.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{12}H_{16}N_3O_3S$

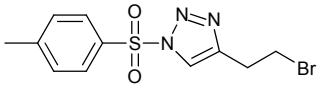
$[M+1]^+$: 266.0958, found: 266.0961.

3j (4-Cyclopropyl-1-(4-Methylbenzenesulfonyl)- 1,2,3-triazole)



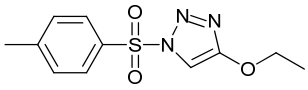
White solid, m.p. 105-106 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz), 7.80 (s, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 2.43 (s, 3H), 1.94-1.91 (m, 1H), 0.99-0.95 (m, 2H), 0.88-0.84 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 150.06, 147.01, 133.25, 130.30, 128.48, 119.19, 21.72, 7.90, 6.39; **MALDI-TOF/TOF-MS**: (m/z): 264.1 $[M + 1]^+$.

3k (4-(Bromomethyl)- 1-(4-Methylbenzenesulfonyl)- 1,2,3-triazole)



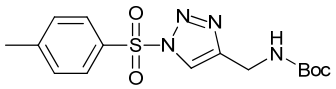
White solid, m.p. 104-106 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 3.62 (t, *J* = 7.0 Hz, 2H), 3.30 (t, *J* = 7.0 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 147.33, 144.57, 132.94, 130.44, 128.64, 121.50, 30.49, 29.02, 21.85; **MALDI-TOF/TOF-MS**: (m/z): 330.0$[M + 1]^+$.

3l (4-Ethyloxy-1-(4-Methylbenzenesulfonyl)- 1,2,3-triazole)



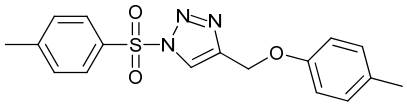
White solid, m.p. 88-89 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 160.07, 147.16, 132.87, 130.32, 128.48, 104.75, 66.98, 21.73, 14.55; **MALDI-TOF/TOF-MS**: (m/z): 268.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{11}H_{14}N_3O_3S$ $[M+1]^+$:268.0751, found: 268.0750.

3m (4-(Tert-Butyloxycarbamidomethyl)-1-(4-methylbenzenesulfonyl)-1,2,3-triazol)



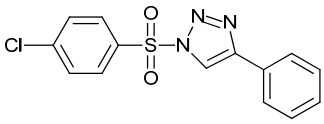
White solid, m.p. 118-119 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 5.17 (br, 1H), 4.39 (d, *J* = 4.5 Hz, 2H), 2.45 (s, 3H), 1.42 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.71, 147.31, 145.38, 132.95, 130.40, 128.64, 121.75, 35.76, 28.26, 21.77; **MALDI-TOF/TOF-MS**: (m/z): 353.1 $[M + 1]^+$.

3n (4-(p-Tolyloxymethyl)- 1-(4-Methylbenzenesulfonyl)- 1,2,3-triazole)



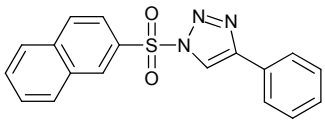
White solid, m.p. 135-136 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.16 (s, 2H), 2.45 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.79, 147.40, 144.34, 132.94, 130.93, 130.44, 130.04, 128.77, 122.39, 114.57, 61.76, 21.82, 20.45; **MALDI-TOF/TOF-MS**: (m/z): 344.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{17}H_{18}N_3O_3S$ $[M+1]^+$: 344.1064, found: 344.1067.

3o (1-(4-Chlorobenzenesulfonyl)-4-phenyl-1,2,3-triazole)



White solid, m.p. 133-134 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.09 (d, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.45-7.38 (m, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 147.54, 142.81, 134.42, 130.23, 130.03, 129.24, 129.01, 128.56, 126.08, 118.90; **MALDI-TOF/TOF-MS**: (m/z): 320.0 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{14}H_{11}ClN_3O_2S$ $[M+1]^+$: 320.0255, found: 320.0263.

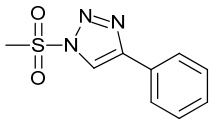
3p (1-(Naphthalenyl-2-sulfonyl)- 4-phenyl-1,2,3-triazole)



White solid, m.p. 143-144 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.38 (s, 1H), 8.05-8.00 (m, 3H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.83-7.81 (m, 2H), 7.74-7.71 (m, 1H), 7.74-7.71 (m, 1H),

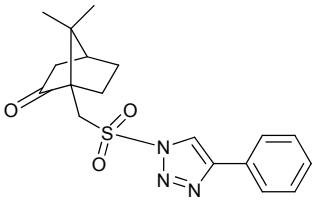
7.71-7.65 (m, 1H), 7.43-7.40 (m, 2H), 7.36 (d, J = 7.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 147.40, 135.98, 132.68, 131.84, 131.23, 130.50, 130.31, 129.77, 129.10, 128.96, 128.71, 128.29, 128.08, 126.04, 122.15, 119.01; **MALDI-TOF/TOF-MS**: (m/z): 336.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{18}H_{14}N_3O_2S$ $[M+1]^+$: 336.0801, found: 336.0809.

3q (1-(Methylsulfonyl)-4-phenyl-1,2,3-triazole)



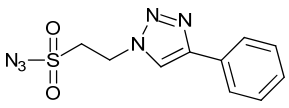
White solid, m.p. 89-90 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.86 (d, J = 7.0 Hz, 2H), 7.48-7.40 (m, 3H), 3.57 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.41, 129.24, 129.03, 128.56, 126.10, 118.91, 42.63; **MALDI-TOF/TOF-MS**: (m/z): 224.0 $[M + 1]^+$.

3r (1-[(7,7-Dimethylbicyclo[2.2.1]heptan-1-yl)methanesulfonyl]-4-phenyl-1,2,3-triazole)



Yellow solid, m.p. 101-102 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.47-7.44 (m, 2H), 7.39-7.37 (m, 1H), 3.99 (d, J = 15.0 Hz, 1H), 3.64 (d, J = 15.0 Hz, 1H), 2.41-2.31 (m, 2H), 2.17-2.15 (m, 1H), 2.11-2.05 (m, 1H), 1.90-1.85 (m, 1H), 1.51-1.46 (m, 1H), 1.12 (s, 3H), 0.89 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 212.99, 147.13, 129.02, 128.90, 128.64, 126.00, 119.39, 58.69, 53.54, 48.36, 42.58, 42.18, 26.81, 25.05, 19.48; **MALDI-TOF/TOF-MS**: (m/z): 360.1 $[M + 1]^+$.

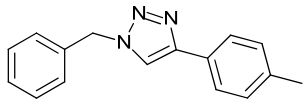
4a (1-[Ethanesulfonyl azide]-4-phenyl-1,2,3-triazole)



Yellow solid, m.p. 173-174 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.83 (d, J = 6.0 Hz, 2H), 7.44-7.37 (m, 3H), 4.93 (t, J = 7.5 Hz, 2H), 4.04 (t, J = 7.5 Hz, 2H); **^{13}C NMR** (125 MHz, DMSO) δ 147.09, 131.07, 129.57, 128.60, 125.70, 122.45, 54.55, 44.57; MALDI-TOF/TOF-MS:

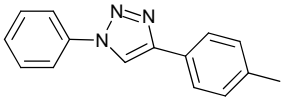
(m/z): 279.1 $[M + 1]^+$. **HRMS** (ESI) m/z calculated for $C_{10}H_{10}N_6O_2S$ $[M+1]^+$: 279.0659, found: 279.0658.

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



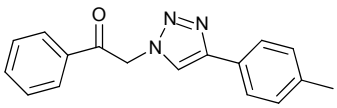
White solid, m.p. 179-180 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.62 (s, 1H), 7.39-7.36 (m, 3H), 7.31 (d, *J* = 6.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.56 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 148.27, 137.97, 134.69, 129.44, 129.11, 128.72, 128.03, 127.66, 125.55, 119.09, 54.16, 21.25. **HRMS** (ESI) m/z calculated for $C_{16}H_{16}N_3$ $[M+1]^+$: 250.1339, found: 250.1336.

4c (1-Phenyl-4-*p*-tolyl-1,2,3-triazole)



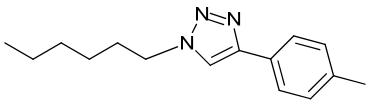
White solid, m.p. 173-174 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.81-7.78 (m, 4H), 7.56-7.53 (m, 2H), 7.46-7.44 (m, 1H), 7.27 (d, *J* = 6.5 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 148.47, 138.31, 137.09, 129.75, 129.59, 128.69, 127.38, 125.73, 120.49, 117.21, 21.32. **HRMS** (ESI) m/z calculated for $C_{15}H_{13}N_3$ $[M+1]^+$: 236.1182, found: 236.1192.

4d (1-Phenylethaneone-4-*p*-tolyl-1,2,3-triazole)



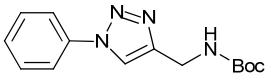
White solid, m.p. 182-183 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.89 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.68-7.66 (m, 1H), 7.24 (d, *J* = 7.5 Hz, 2H), 5.86 (s, 2H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 190.31, 148.20, 137.99, 134.56, 133.86, 129.46, 129.12, 128.12, 127.62, 125.65, 121.14, 55.42, 21.27. **HRMS** (ESI) m/z calculated for $C_{17}H_{16}N_3O$ $[M+1]^+$: 236.1288, found: 236.1290.

4e (1-Hexyl-4-*p*-tolyl-1,2,3-triazole)



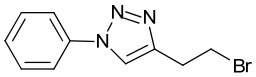
White solid, m.p. 76-77 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.31 (t, *J* = 7.5 Hz, 2H), 2.35 (s, 3H), 1.89-1.86 (m, 2H), 1.26-1.29 (m, 6H), 0.86 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 147.40, 137.53, 129.23, 127.72, 125.28, 119.03, 50.08, 30.92, 30.06, 25.90, 22.18, 21.02, 13.72. **HRMS** (ESI) m/z calculated for $C_{15}H_{22}N_3$ $[M+1]^+$: 244.1808, found: 244.1810.

4f (1-Phenyl-4-(tert-Butyloxycarbamidomethyl)- 1,2,3-triazole)



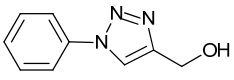
White solid, m.p. 131-132 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.53-7.49 (m, 2H), 7.45-7.41 (m, 1H), 5.37 (br, 1H), 4.49 (d, *J* = 6.0 Hz, 2H), 1.45 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.85, 146.14, 136.90, 129.64, 128.65, 120.40, 120.17, 79.66, 35.97, 28.29. **HRMS** (ESI) m/z calculated for $C_{14}H_{19}N_4O_2$ $[M+1]^+$: 275.1503, found: 275.1501.

4g (1-Phenyl-4-(Bromomethyl)- 1,2,3-triazole)



White solid, m.p. 106-107 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.52-7.49 (m, 2H), 7.45-7.43 (m, 1H), 3.72 (t, *J* = 6.0 Hz, 2H), 3.38 (t, *J* = 6.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 145.43, 136.93, 129.65, 128.61, 120.38, 119.88, 31.36, 29.33. **HRMS** (ESI) m/z calculated for $C_{10}H_{11}BrN_3$ $[M+1]^+$: 252.0131, found: 252.0130.

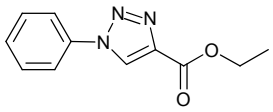
4h (1-Phenyl-4-[4-hydroxymethyl]- 1,2,3-triazole)



White solid, m.p. 122-123 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.69 (d, *J* = 8.0 Hz,

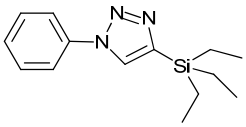
2H), 7.50-7.47 (m, 2H), 7.43-7.40 (m, 1H), 4.89 (s, 2H), 4.27 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 148.32, 136.83, 129.66, 128.73, 120.44, 120.23, 56.06. **HRMS** (ESI) m/z calculated for $C_9H_{10}N_3O$ $[M+1]^+$: 176.0819, found: 176.0818.

4i (Ethyl 1-phenyl-1,2,3-triazole-4-caboxylate)



White solid, m.p. 107-108 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.57-7.54 (m, 2H), 7.51-7.48 (m, 1H), 4.46 (dd, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 160.47, 140.64, 136.17, 129.78, 129.36, 125.44, 120.62, 61.32, 14.18. **HRMS** (ESI) m/z calculated for $C_{11}H_{11}N_3O_2Na$ $[M+Na]^+$: 240.0743, found: 240.0736.

4j (1-Phenyl-4-triethylsilyl-1,2,3-triazole)



Colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.50-7.47 (m, 2H), 7.40-7.37 (m, 1H), 1.03 (t, *J* = 8.0 Hz, 9H), 0.88 (t, *J* = 8.0 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 144.35, 136.88, 129.47, 128.22, 127.51, 120.46, 7.19, 3.30. **HRMS** (ESI) m/z calculated for $C_{14}H_{22}N_3Si$ $[M+1]^+$: 260.1578, found: 260.1581.

Supplementary Material (ESI) for Green Chemistry

Supporting Information

(Part II: Spectra Copies)

Cu_2O acting as a robust catalyst in CuAAC reactions: Water is the required medium

Kai Wang, Xihe Bi,* Shuangxi Xing, Peiqiu Liao, Zhongxue Fang, Xianyu Meng, Qian Zhang,* Qun Liu, Yu Ji

Department of Chemistry, Northeast Normal University, Changchun 130024, China
E-mail: bixh507@nenu.edu.cn; zhangq651@nenu.edu.cn

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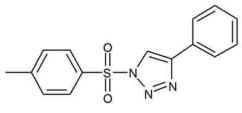

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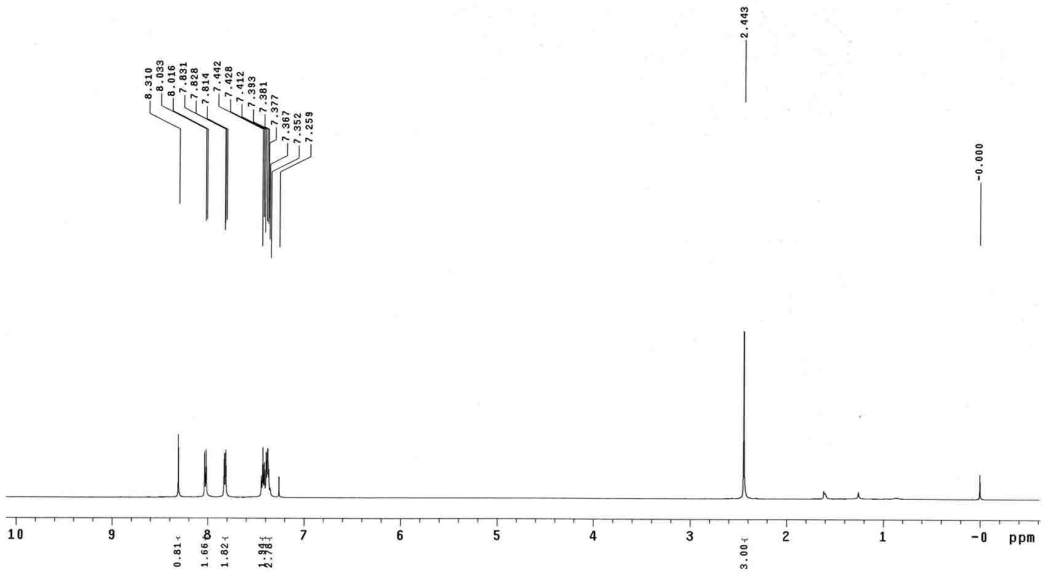
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9
7
6
5
4
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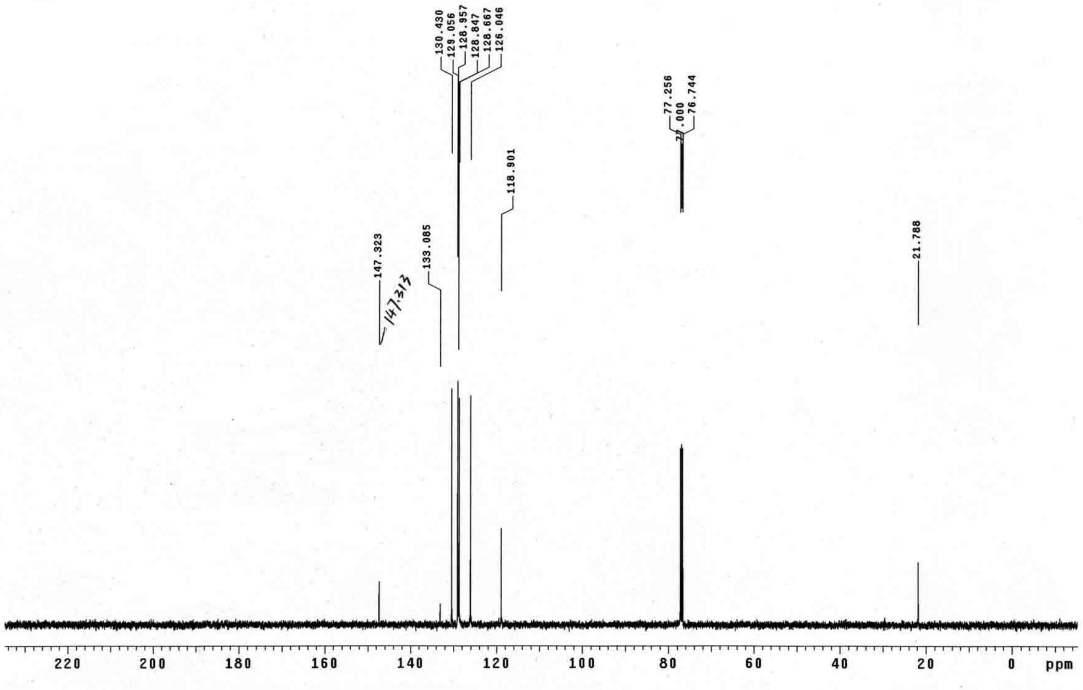
3.00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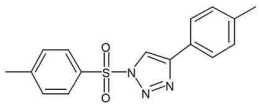

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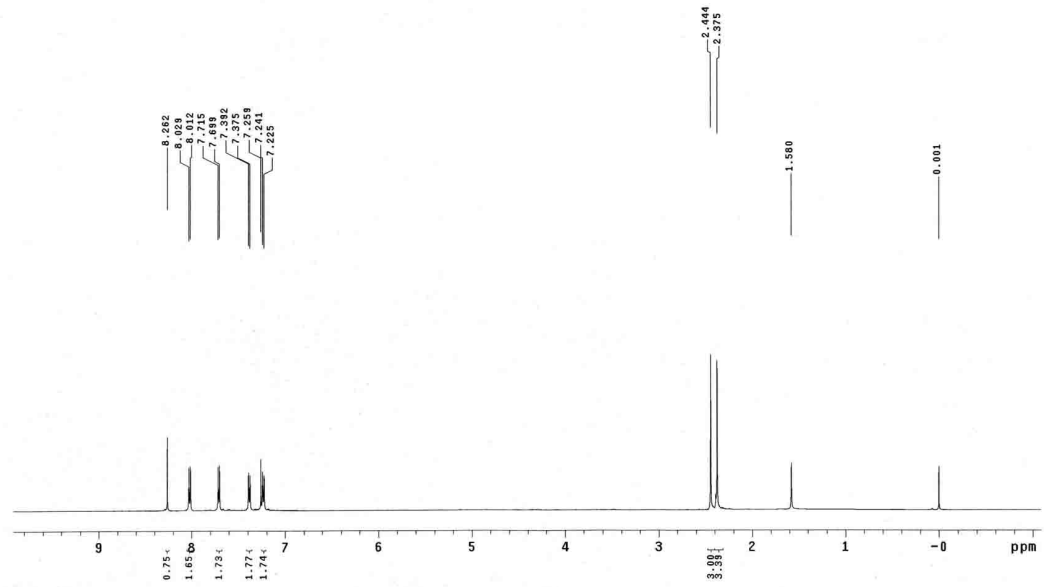
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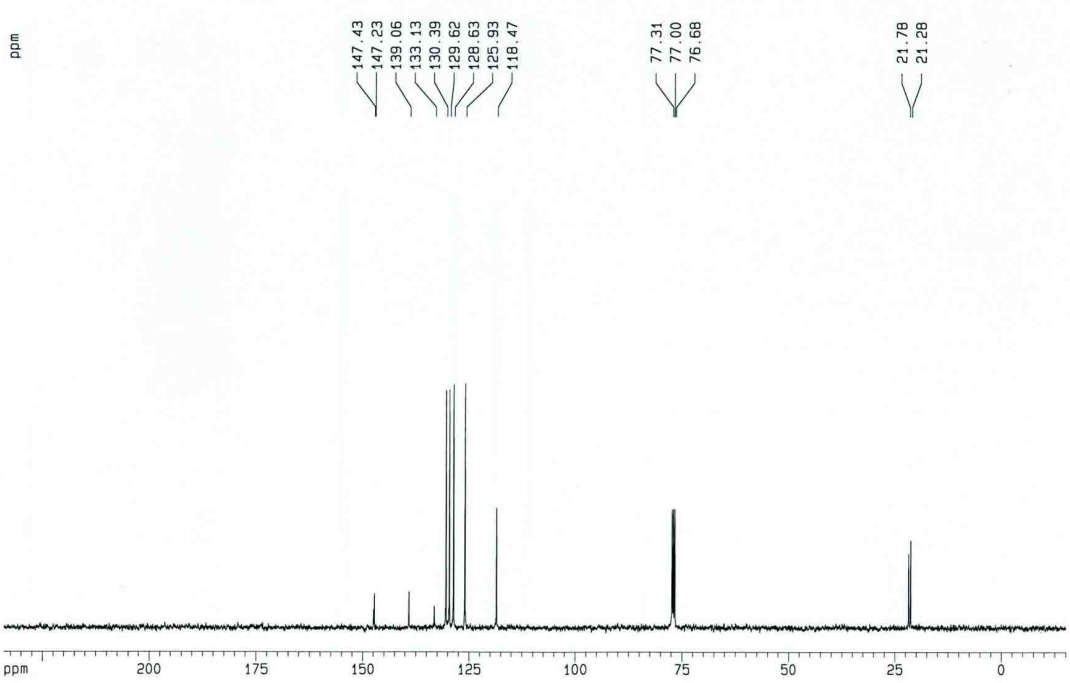
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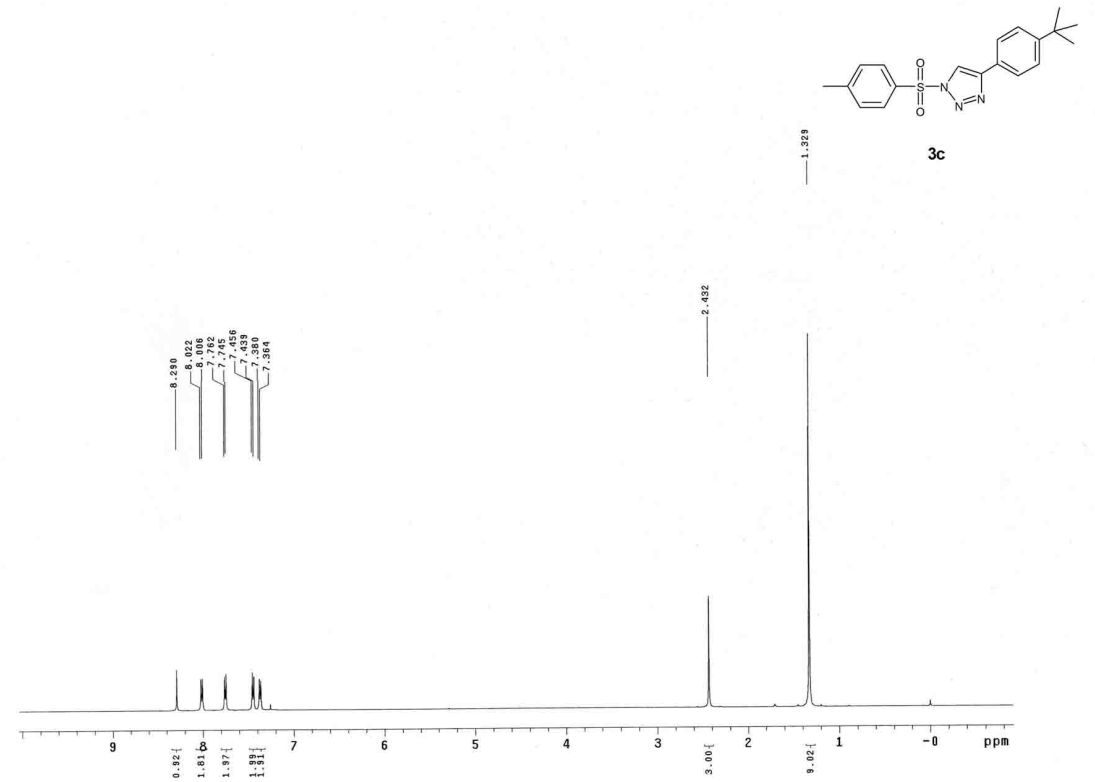
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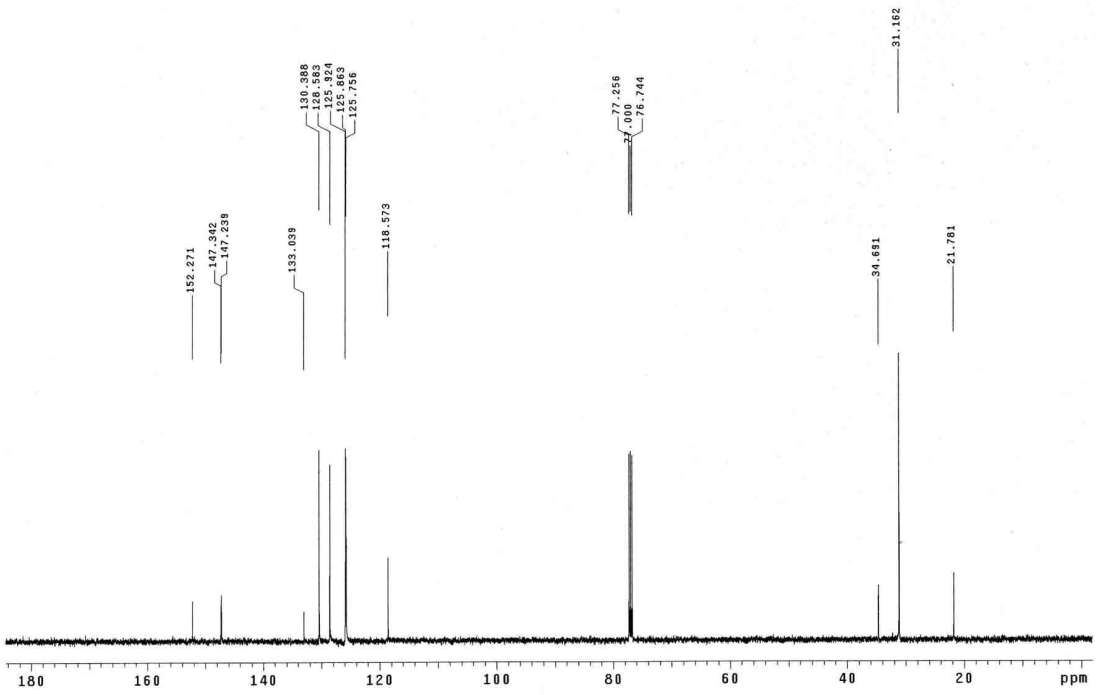
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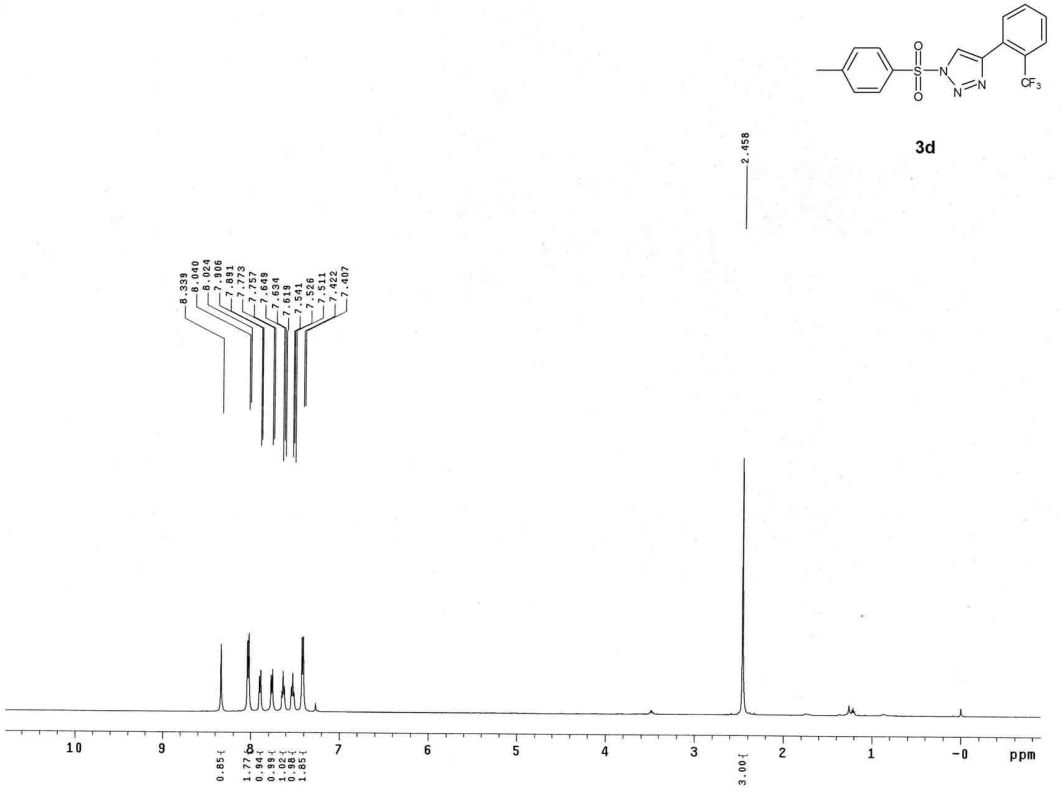
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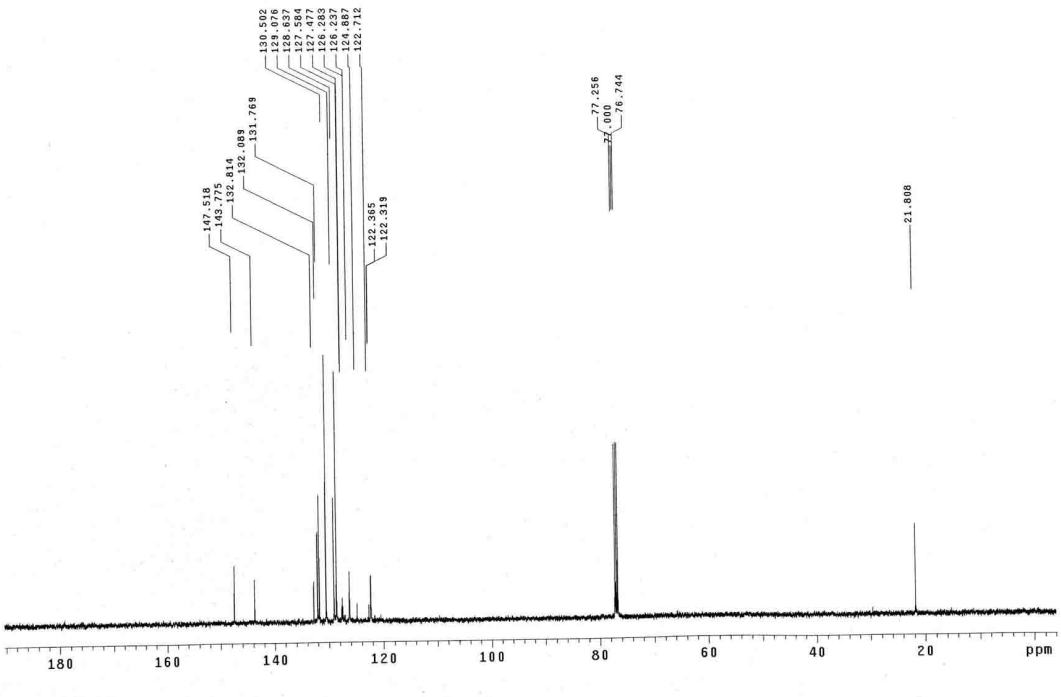
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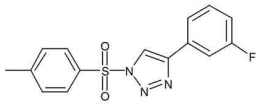

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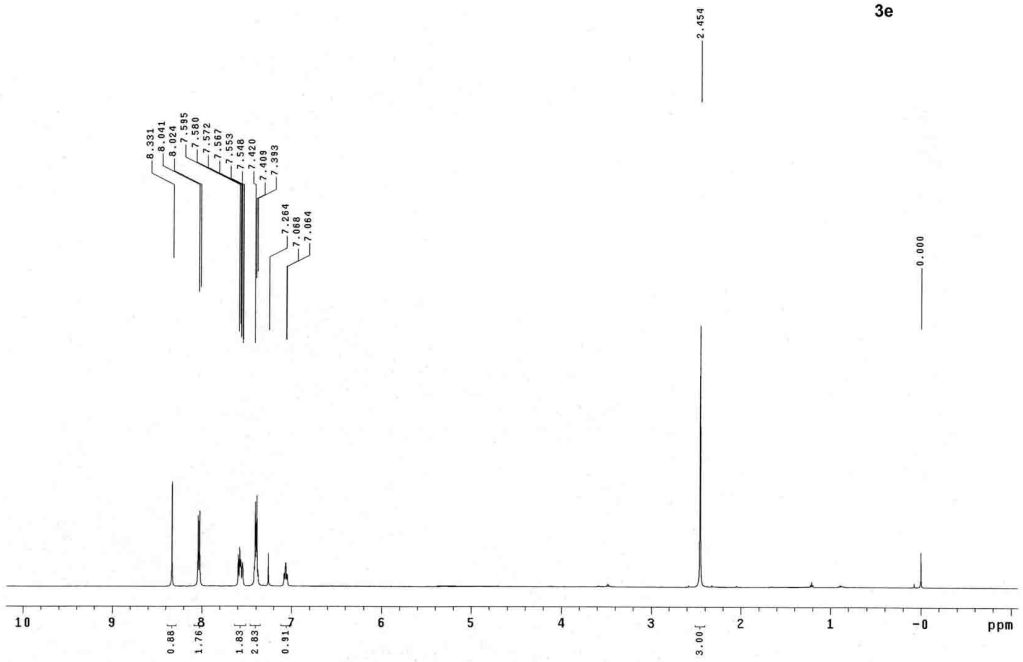
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7.420
7.409
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7.264
7.088
7.084
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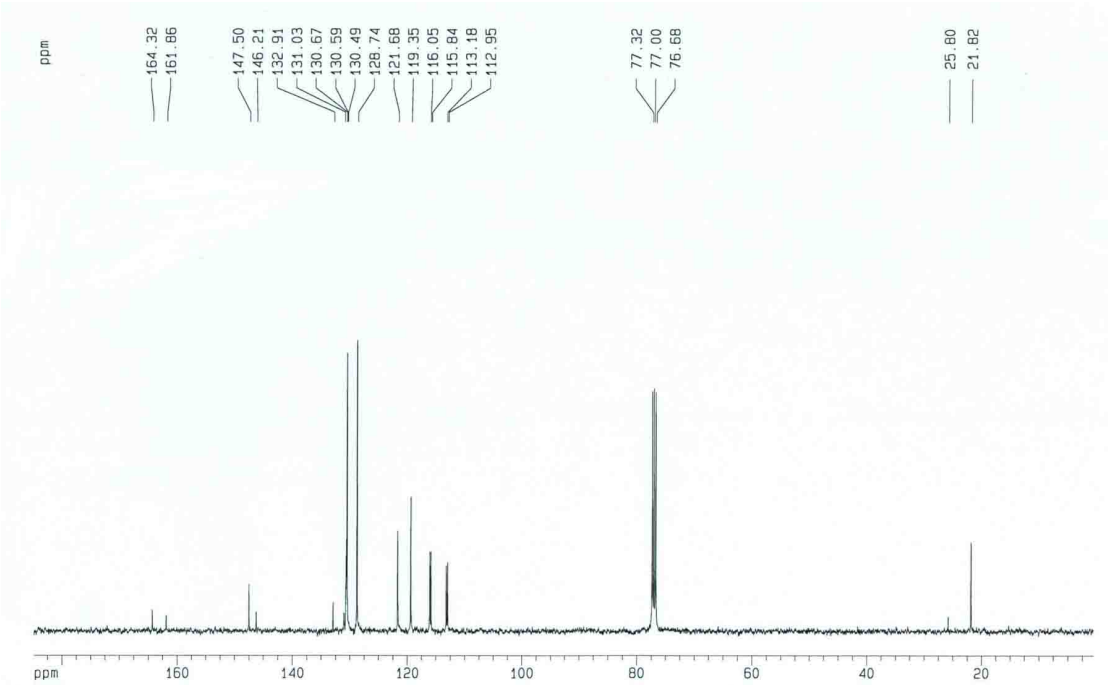
0.91
3.00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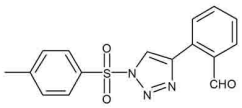
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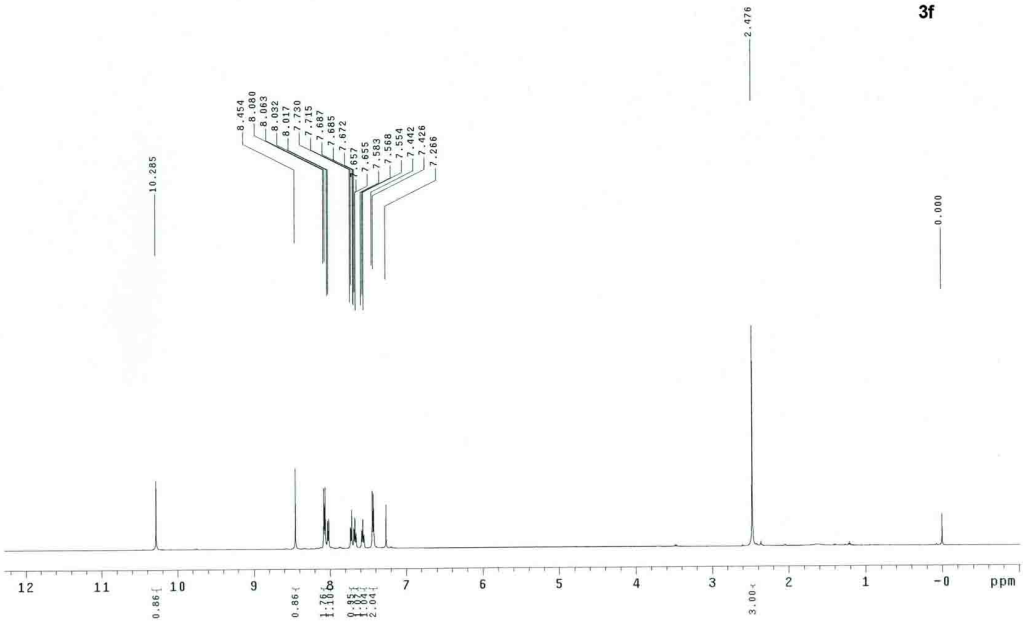
N
N
N
CHO

3f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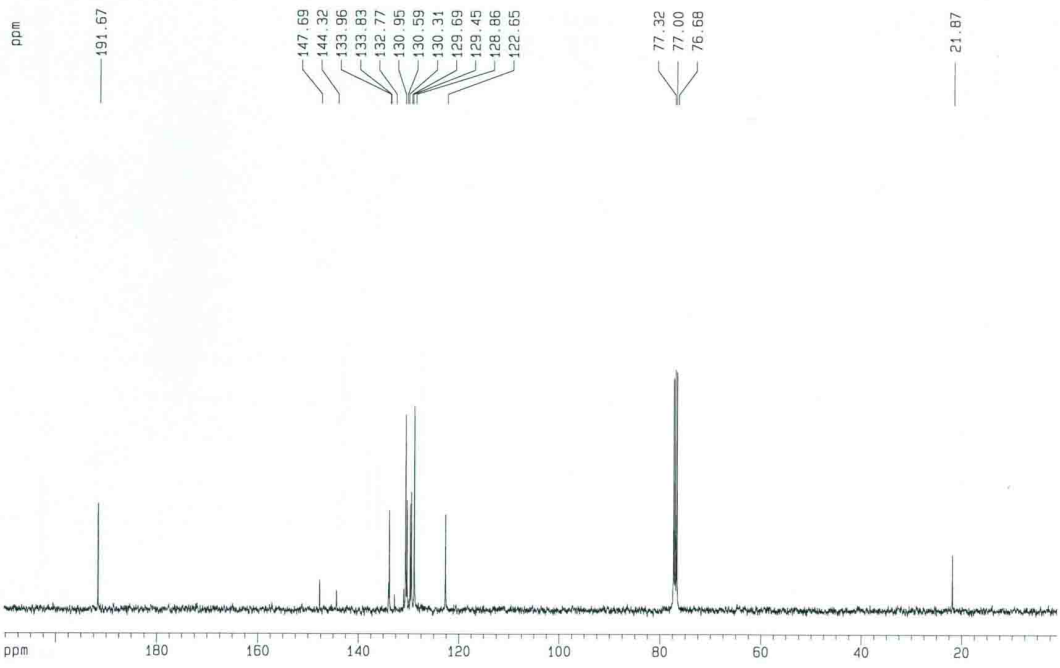
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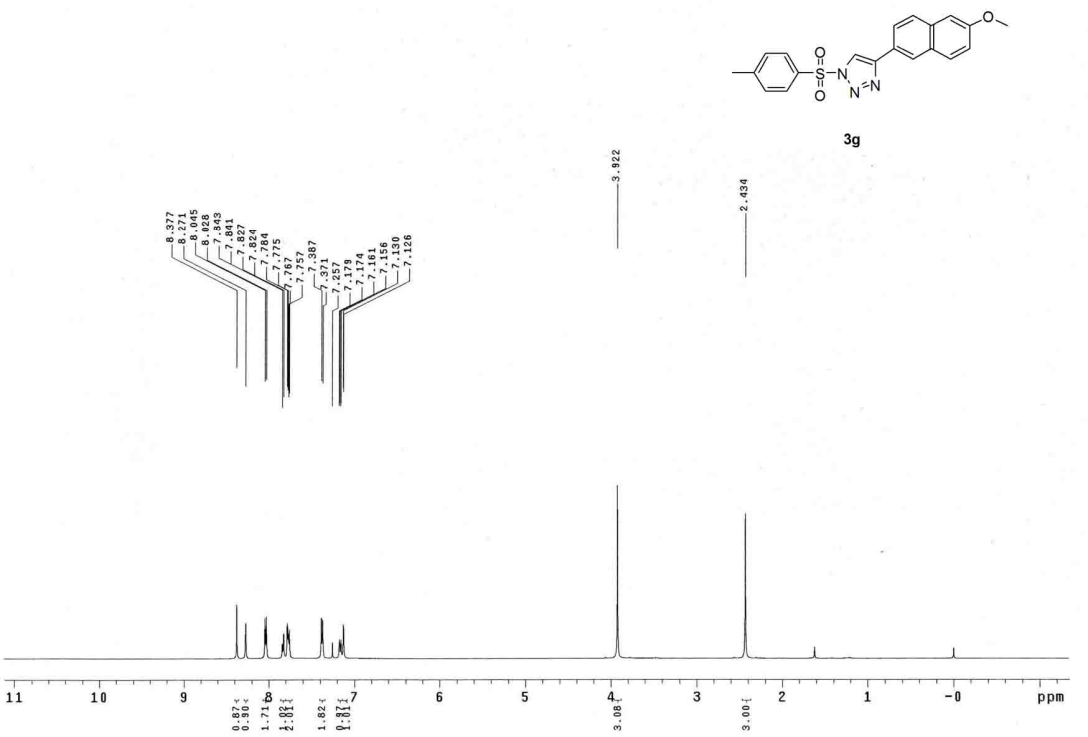
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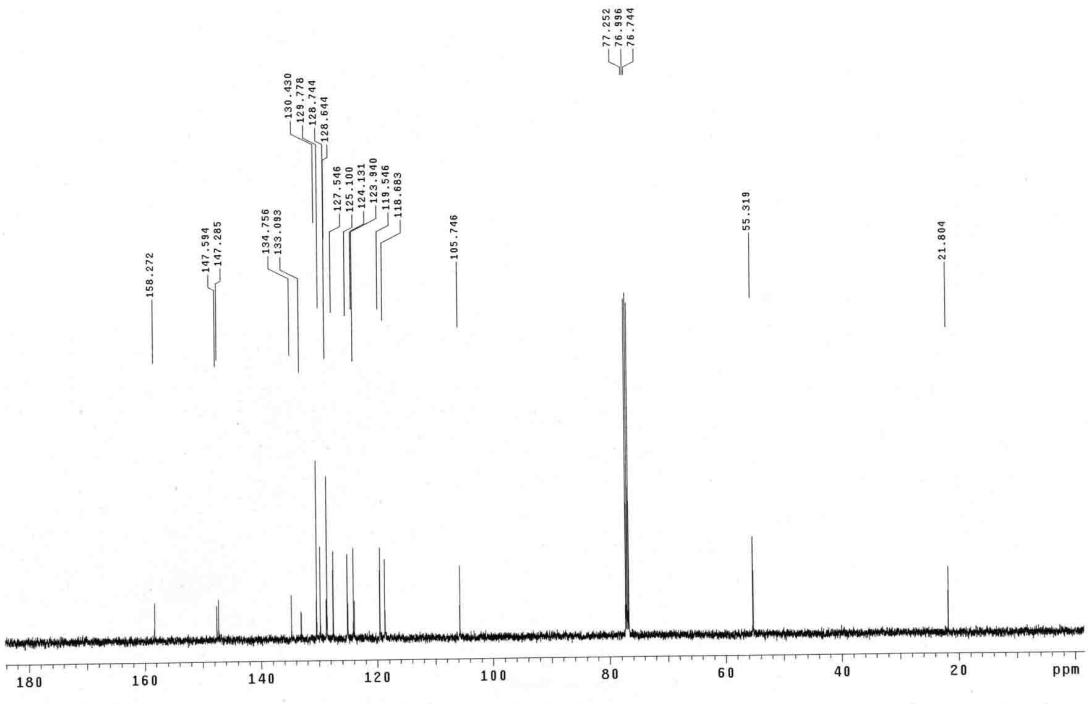
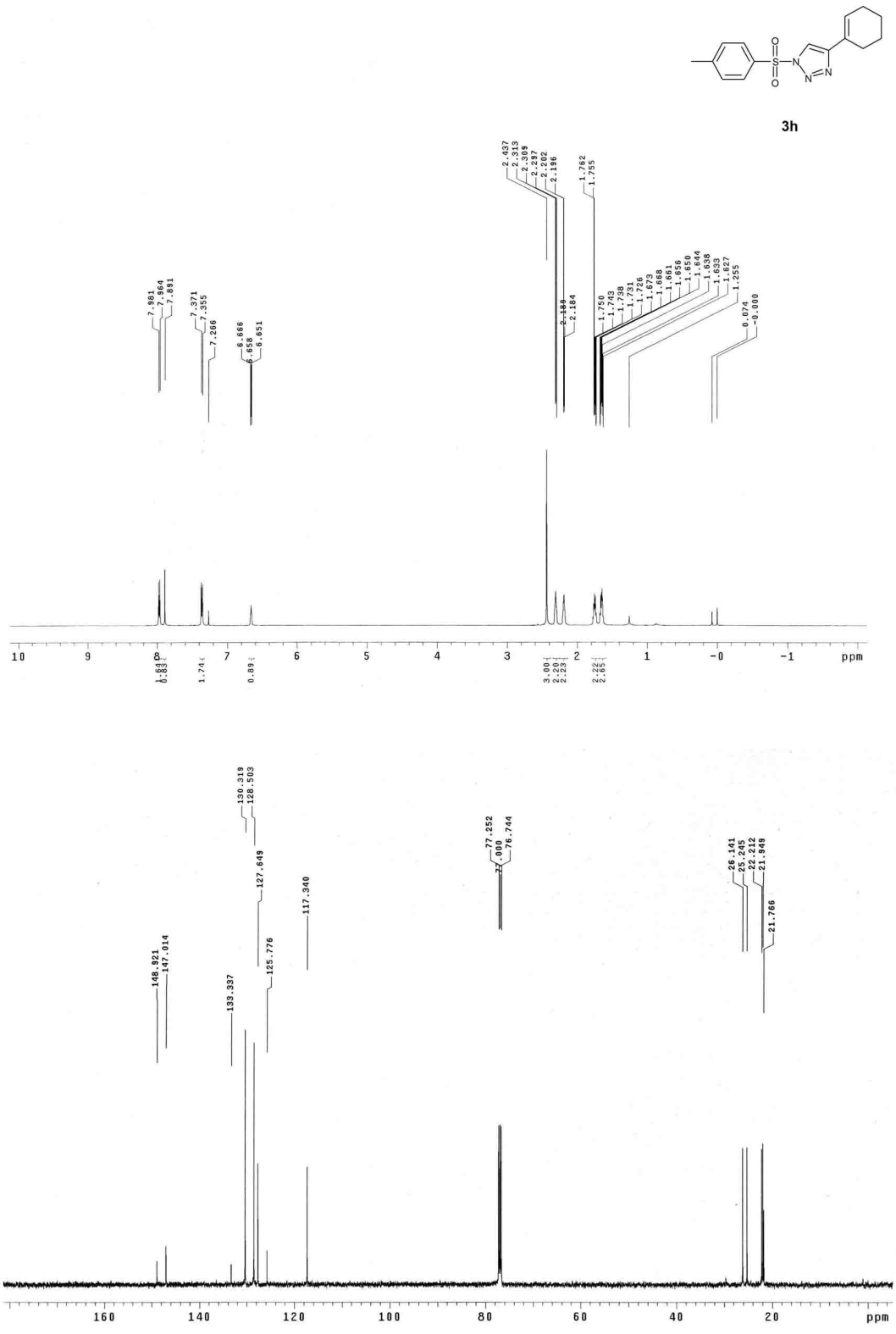
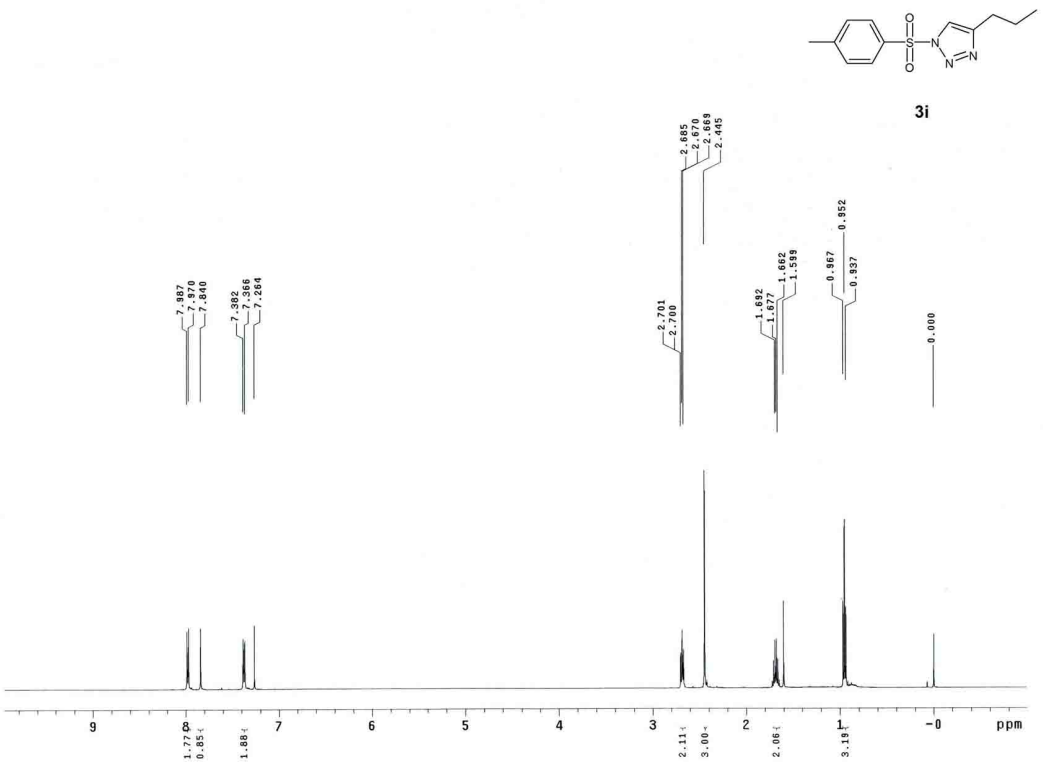
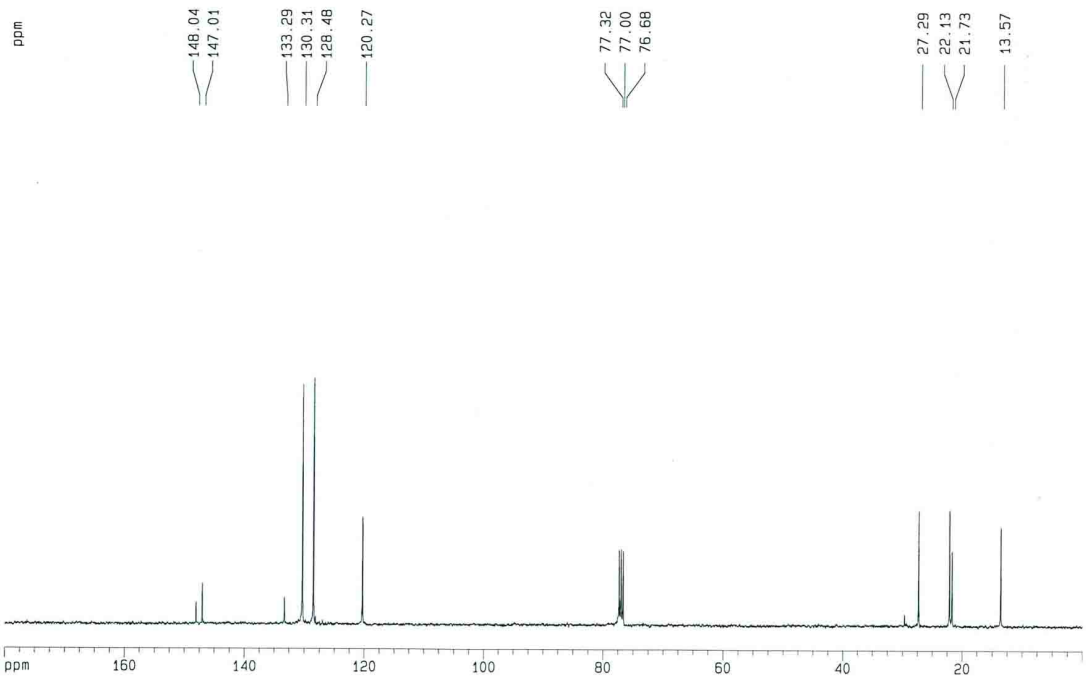
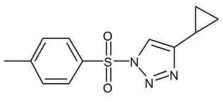
7.130
7.126
3.922
2.434
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.87
0.90
1.71
2.00
1.82
1.00
3.08
3.00


158.272
147.594
147.285
134.756
133.093
130.430
129.778
128.744
128.644
127.546
125.100
124.153
123.340
119.546
118.683
105.746
77.252
76.986
76.744
55.319
21.804
180
160
140
120
100
80
60
40
20
ppm

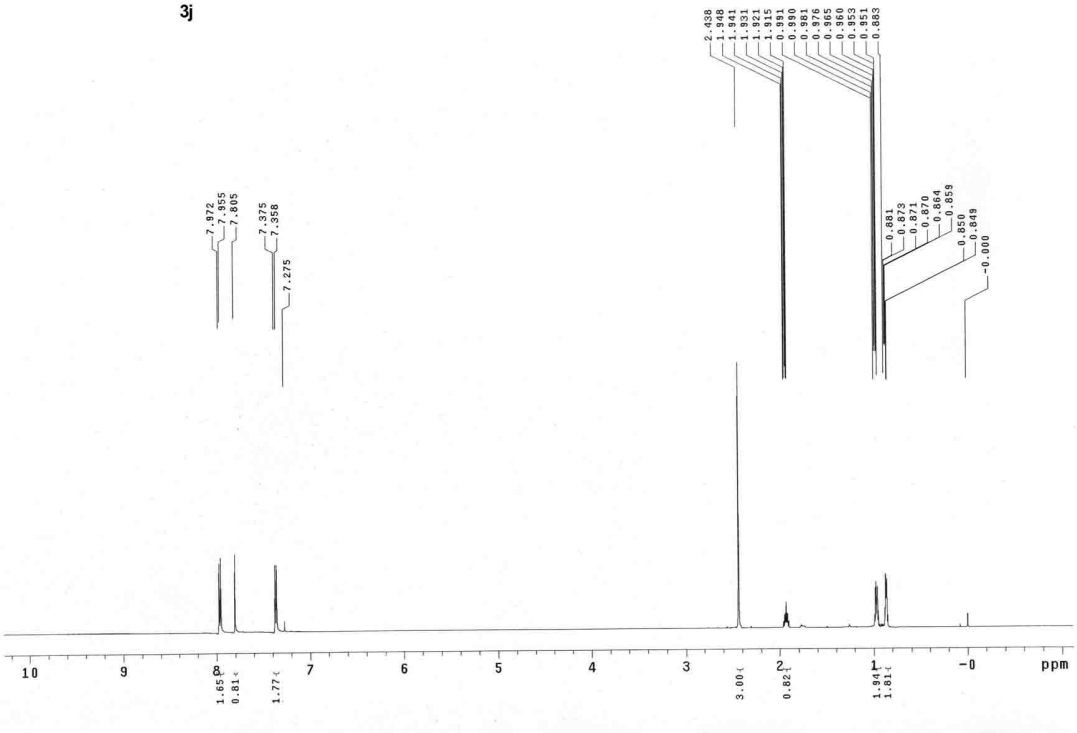

3h
7.981
7.964
7.891
7.371
7.355
7.266
6.666
6.651
2.437
2.313
2.309
2.202
2.196
2.189
2.184
1.762
1.755
1.750
1.743
1.738
1.731
1.726
1.673
1.668
1.661
1.656
1.650
1.644
1.638
1.633
1.627
1.255
0.074
-0.000
ppm
148.921
147.014
133.337
130.319
128.503
127.649
125.776
117.340
77.252
77.070
76.744
26.141
25.245
22.212
21.949
21.766
ppm

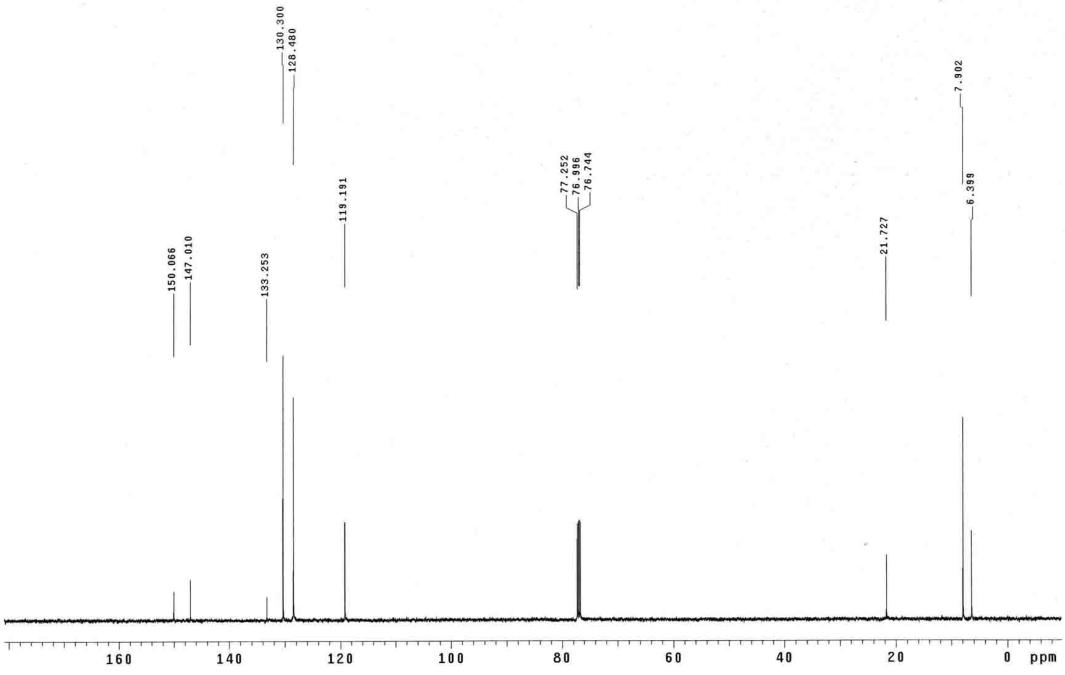

3i
7.987
7.970
7.840
7.382
7.366
7.264
2.701
2.700
2.685
2.670
2.654
2.445
1.692
1.677
1.662
1.599
0.967
0.952
0.937
0.000
ppm

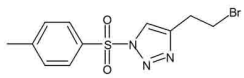

ppm
148.04
147.01
133.29
130.31
128.48
120.27
77.32
77.00
76.68
27.29
22.13
21.73
13.57
ppm



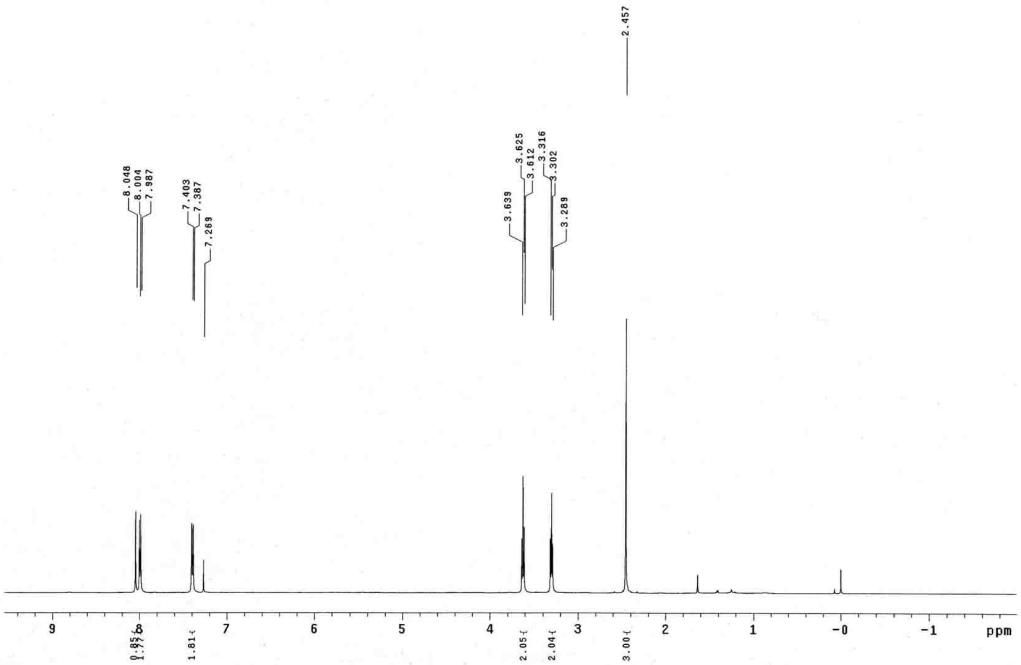
3j

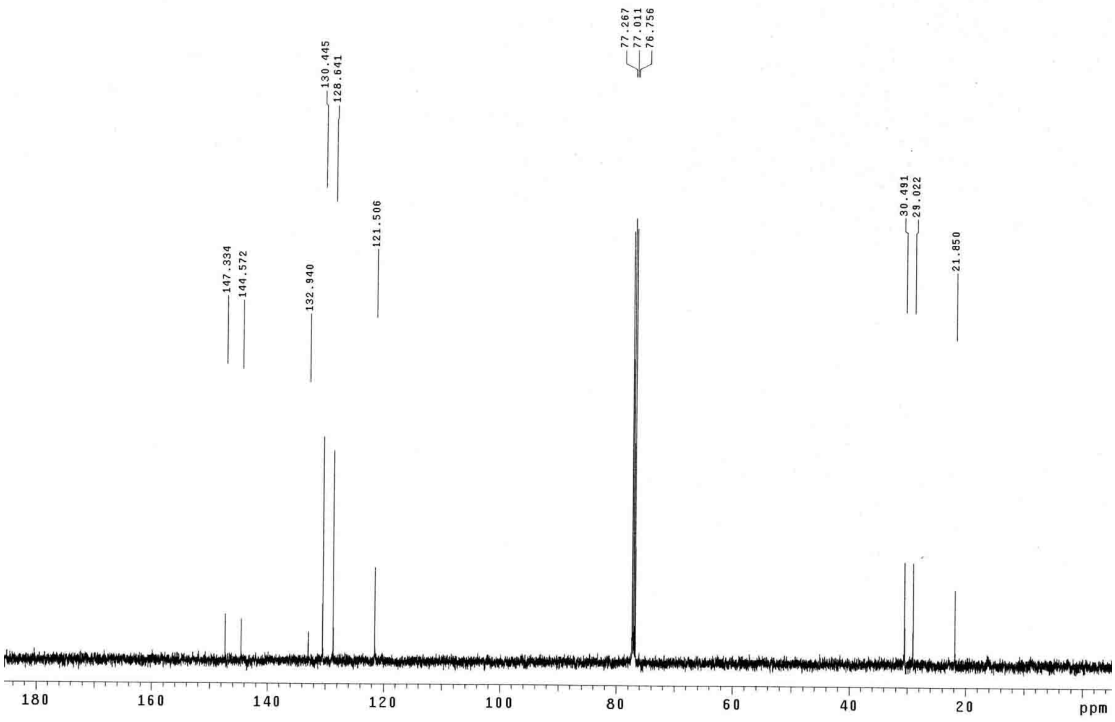

2.438
1.948
1.941
1.931
1.921
1.915
1.891
0.990
0.981
0.976
0.965
0.960
0.953
0.951
0.883
7.972
7.955
7.805
7.375
7.358
7.275
0.881
0.873
0.871
0.670
0.864
0.853
0.850
0.849
-0.000
10
9
8
7
6
5
4
3
2
1
-0
ppm

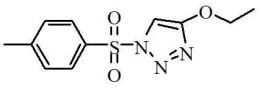

130.300
128.480
119.191
77.252
76.998
76.744
7.902
6.389
150.066
147.010
133.253
21.727
160
140
120
100
80
60
40
20
0
ppm


Br

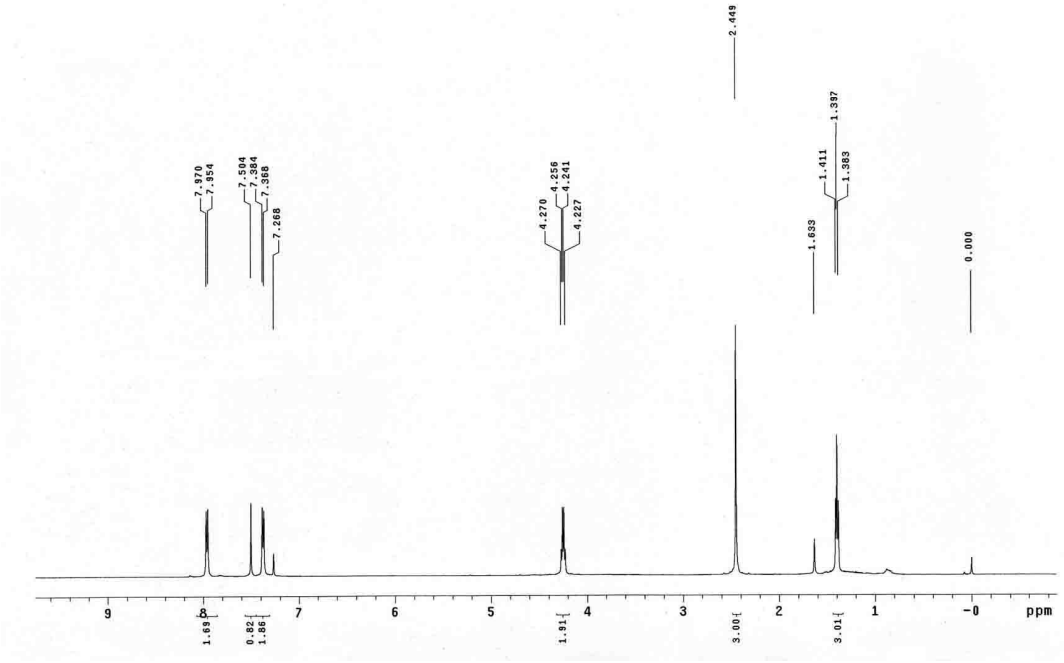
3k

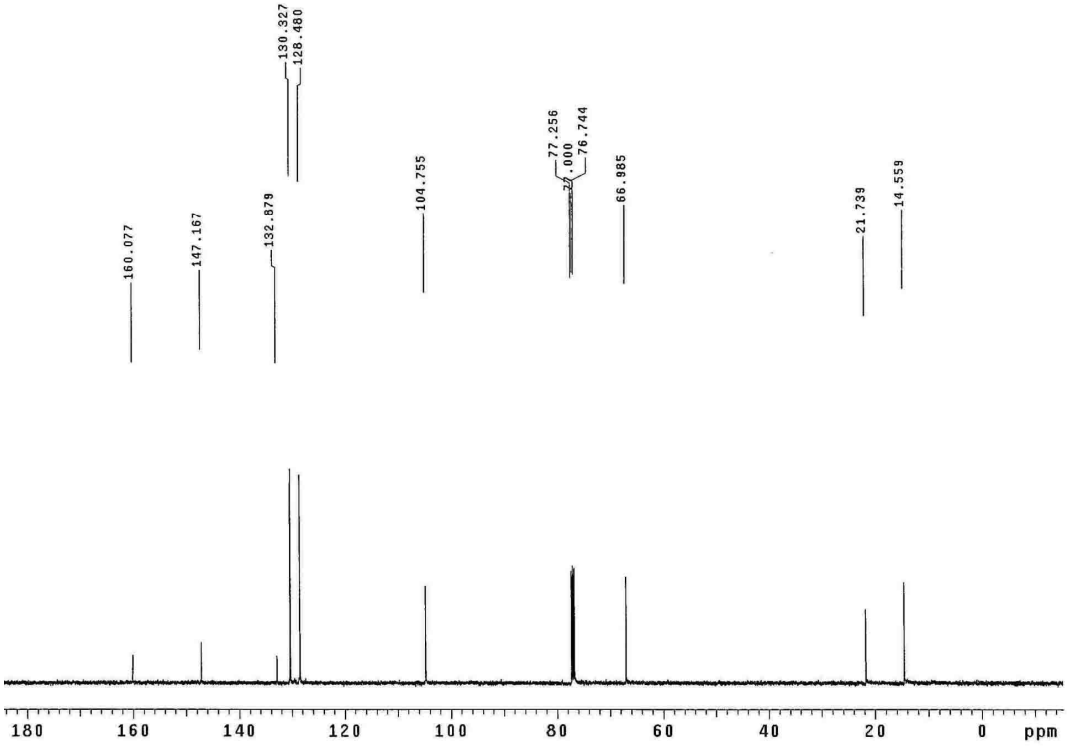

8.048
8.004
7.987
7.409
7.387
7.269
3.639
3.625
3.612
3.316
3.302
3.269
2.457
ppm

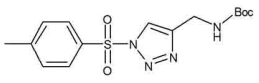

147.334
144.572
132.940
130.445
128.641
121.506
77.267
77.011
76.756
30.491
29.022
21.850
ppm



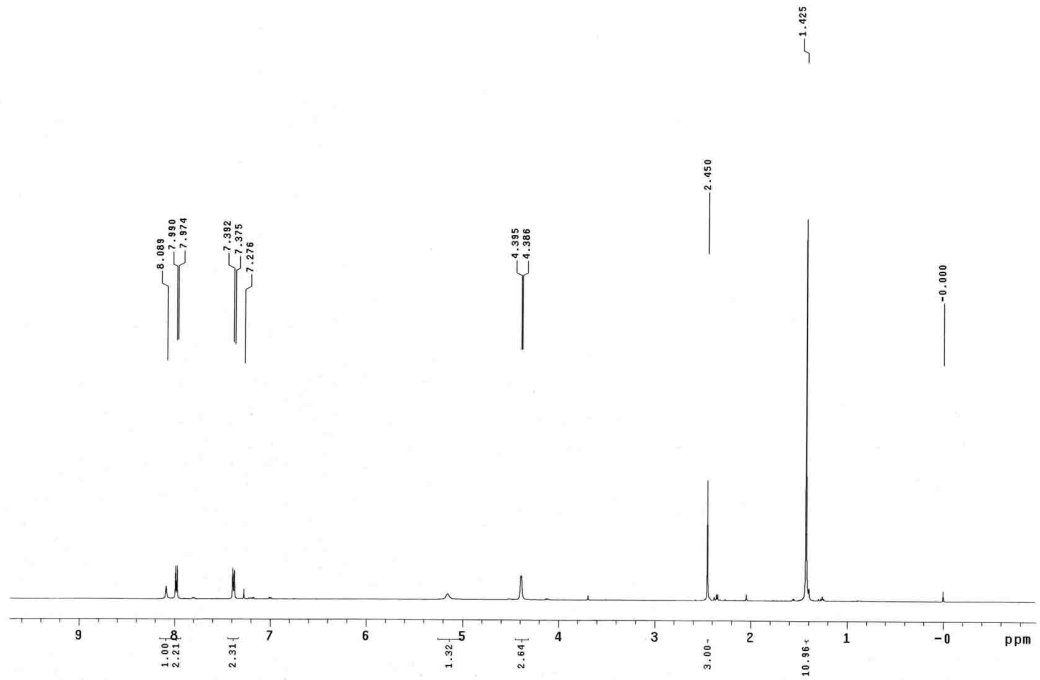
31

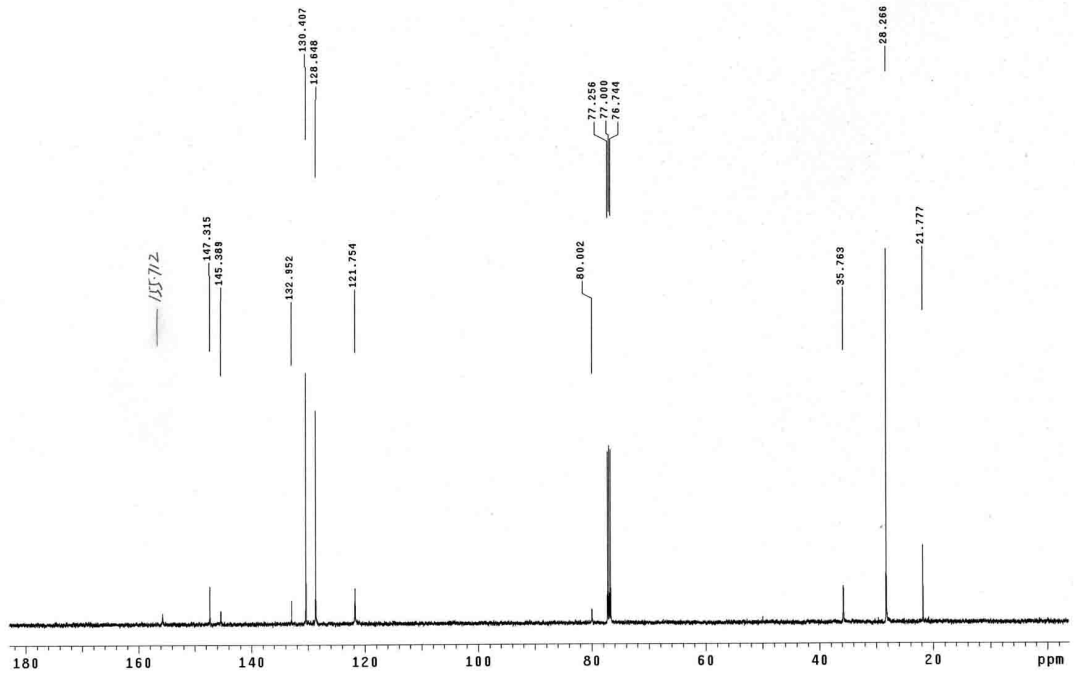

7.970
7.954
7.504
7.384
7.366
7.266
4.270
4.256
4.241
4.227
2.449
1.633
1.411
1.397
1.383
0.000
ppm

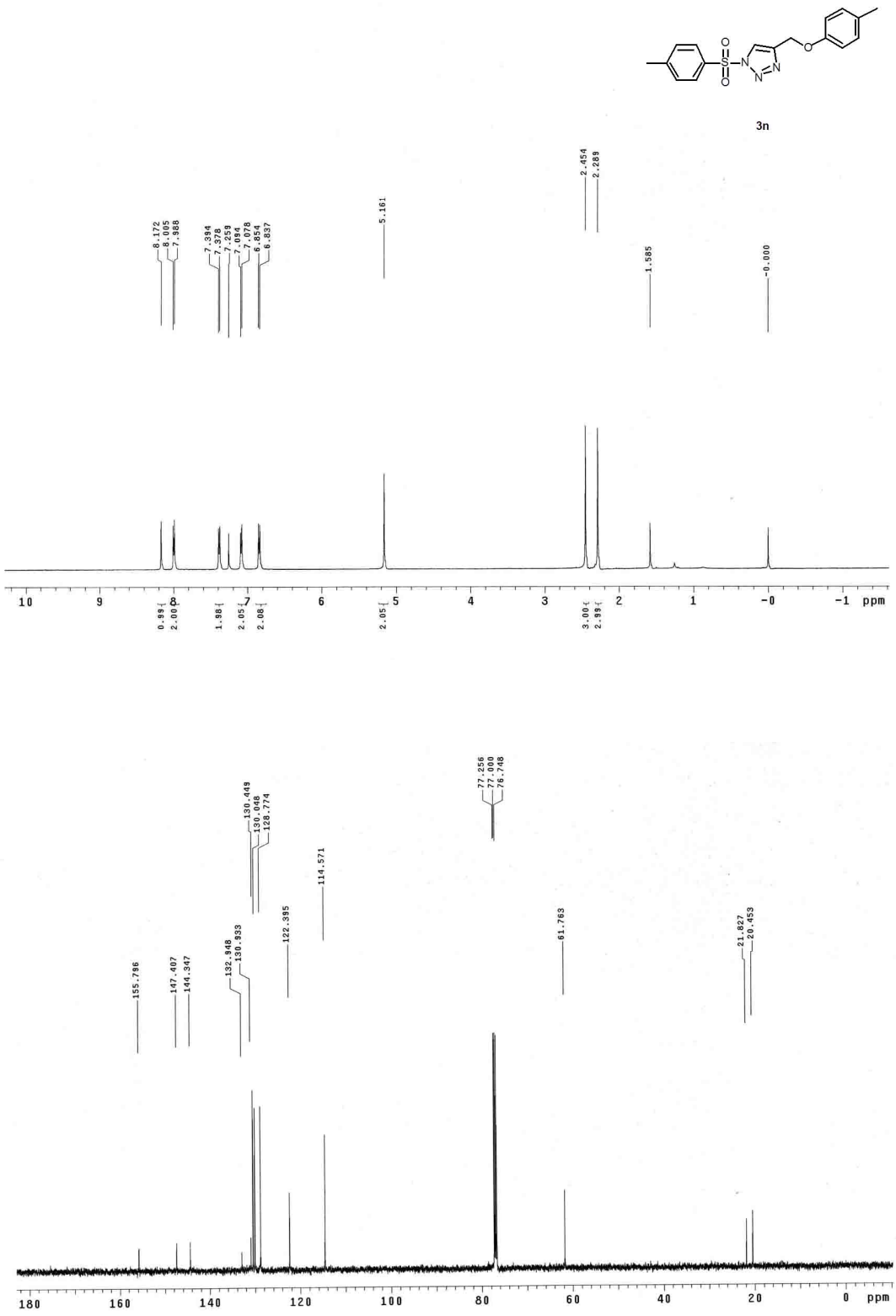

160.077
147.167
132.879
130.327
128.480
104.755
77.256
77.000
76.744
66.985
21.739
14.559
ppm

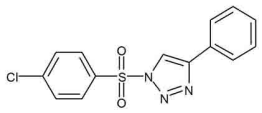

Boc
N
H
O
S
O
N
N
N

3m

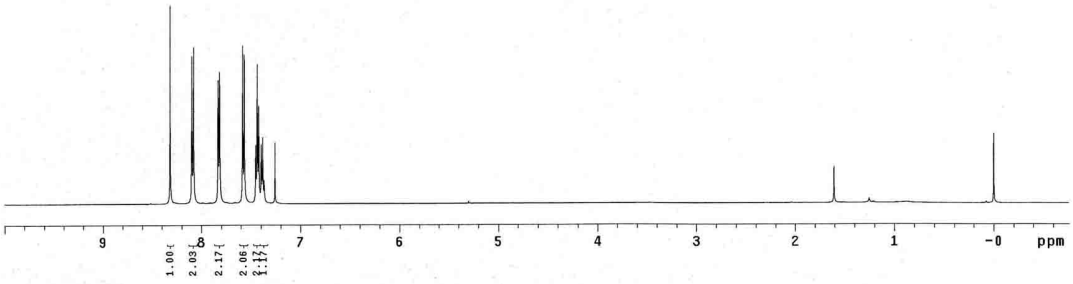

1.425
2.450
8.088
7.980
7.974
7.382
7.375
7.276
4.395
4.386
0.000
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
2.21
2.31
1.32
2.64
3.00
10.96

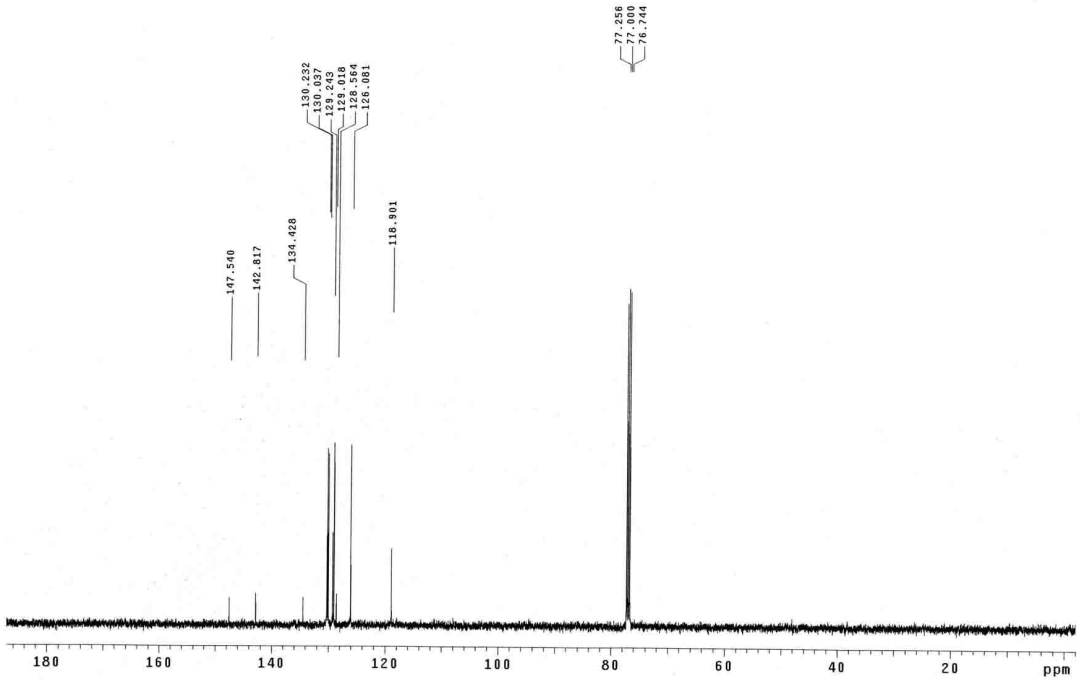

130.407
128.648
77.256
77.000
76.744
28.266
147.315
145.389
132.852
121.754
80.002
35.763
21.777
180
160
140
120
100
80
60
40
20
ppm

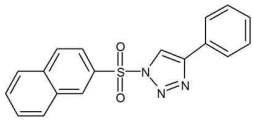

3n
8.172
8.165
7.388
7.394
7.378
7.259
7.084
7.078
6.854
6.837
5.161
2.454
2.289
1.585
-0.000
0.99
2.00
1.98
2.05
2.08
2.05
3.00
2.99
ppm
155.796
147.407
144.347
132.948
130.933
130.449
130.048
128.774
122.395
114.571
77.256
77.000
76.748
61.763
21.827
20.453
ppm



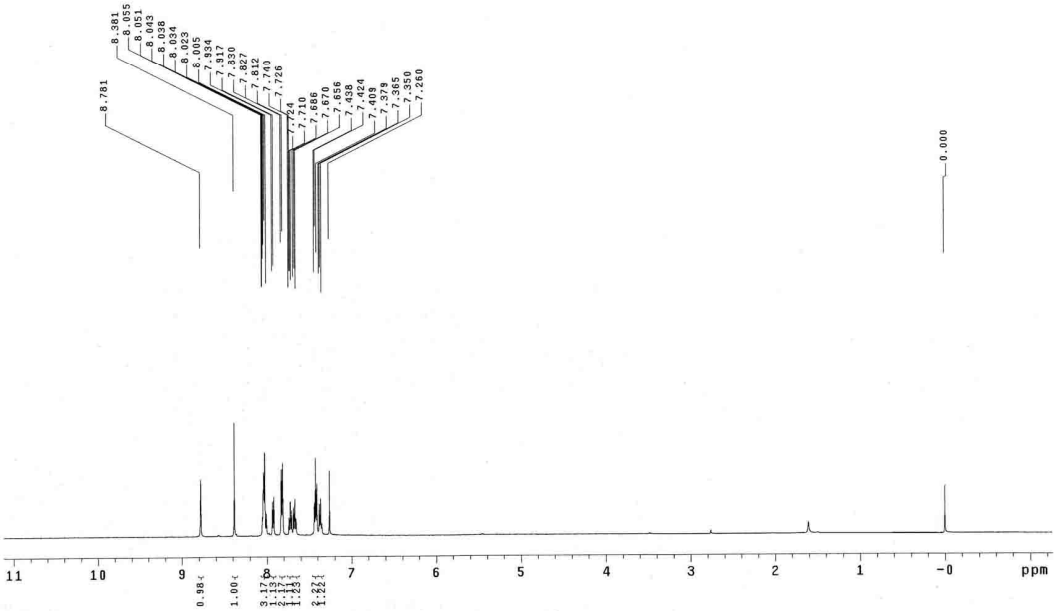
3o

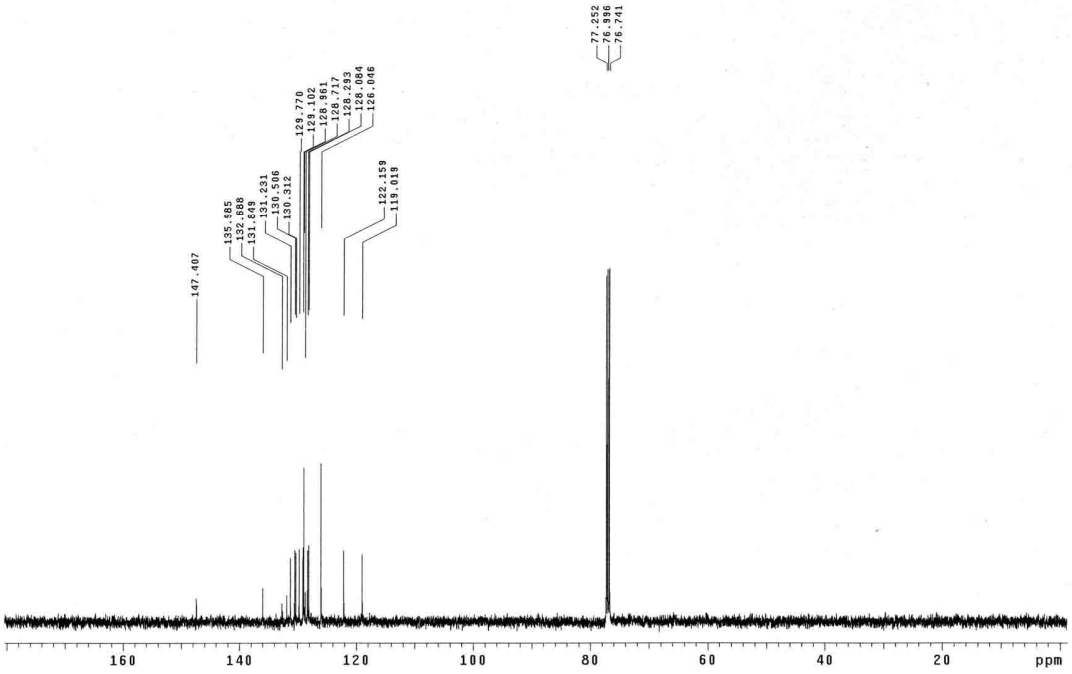

9
8
7
6
5
4
3
2
1
-0
ppm
1.00
2.03
2.17
2.06

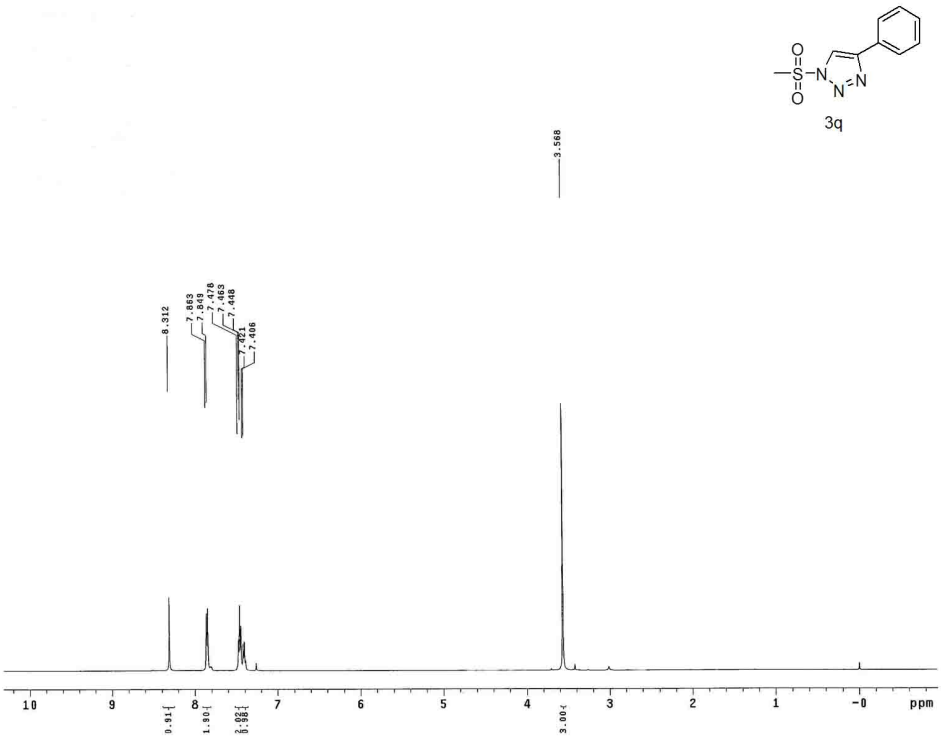

77.256
77.000
76.744
130.232
130.037
129.243
128.516
126.081
147.540
142.817
134.428
118.901
180
160
140
120
100
80
60
40
20
ppm

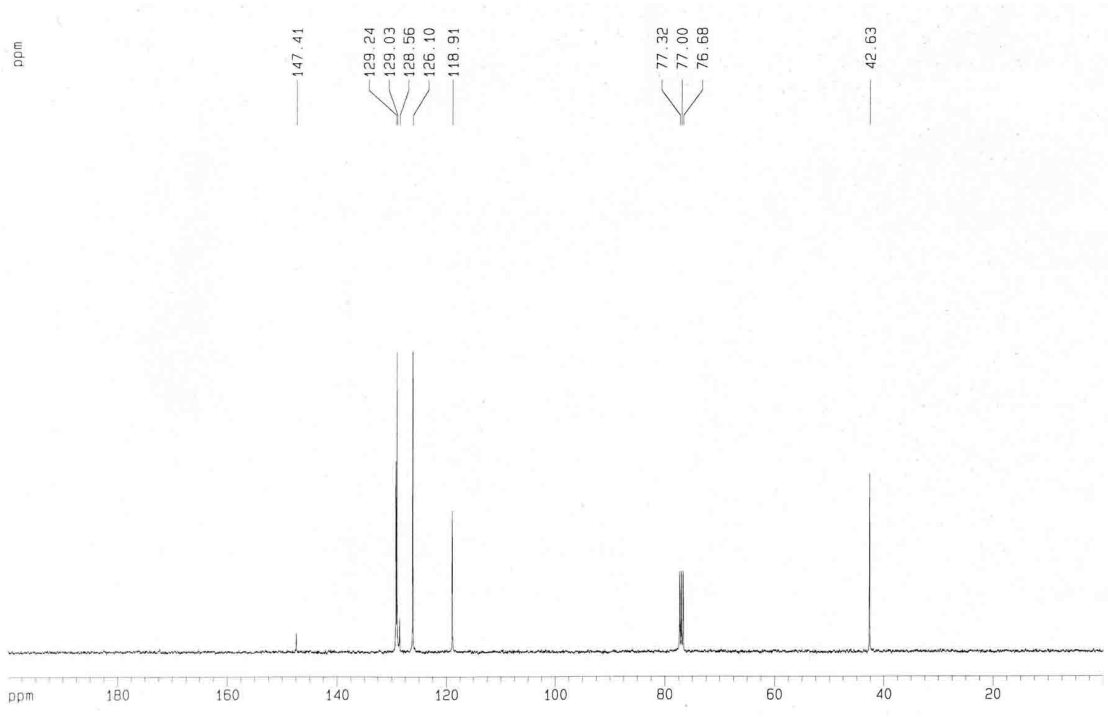


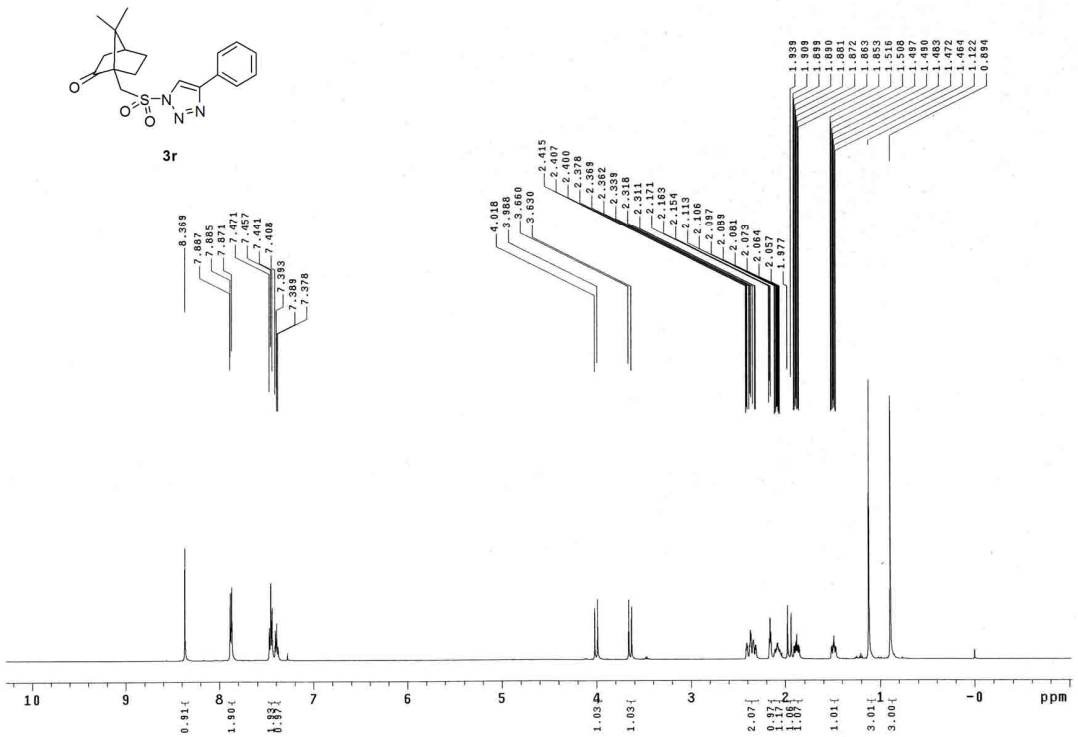
3p

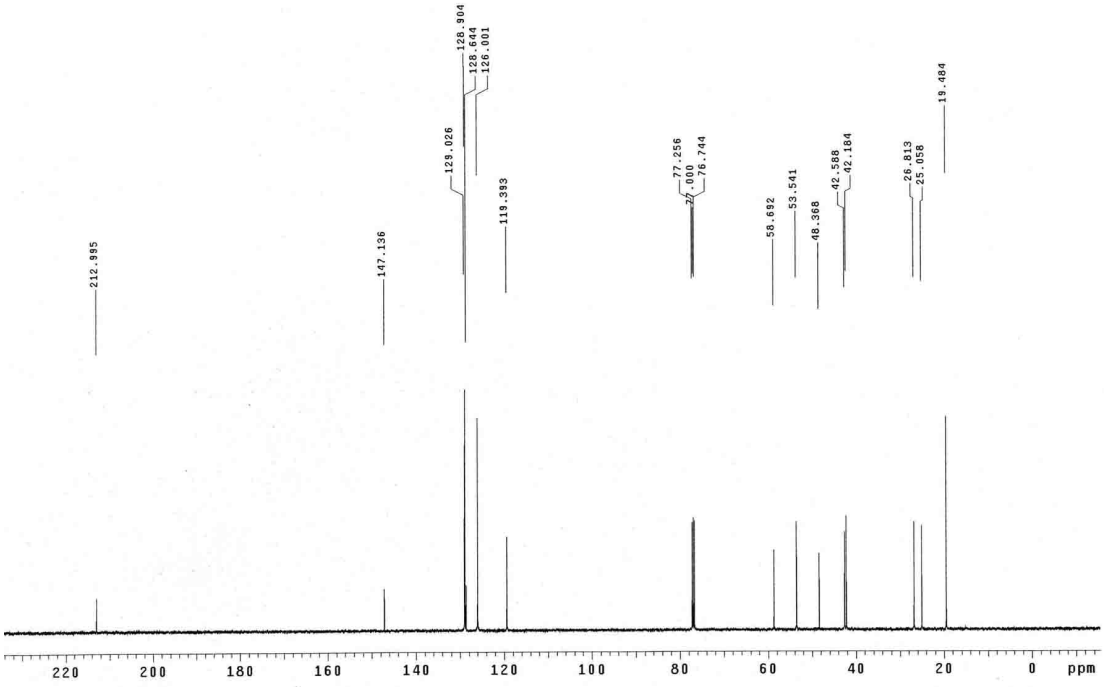

8.781
8.381
8.055
8.051
8.043
8.038
8.034
8.023
8.005
7.934
7.917
7.830
7.827
7.812
7.810
7.726
7.724
7.710
7.686
7.670
7.655
7.438
7.424
7.409
7.379
7.365
7.355
7.260
0.000
11
10
9
8
7
6
5
4
3
2
1
-0
ppm

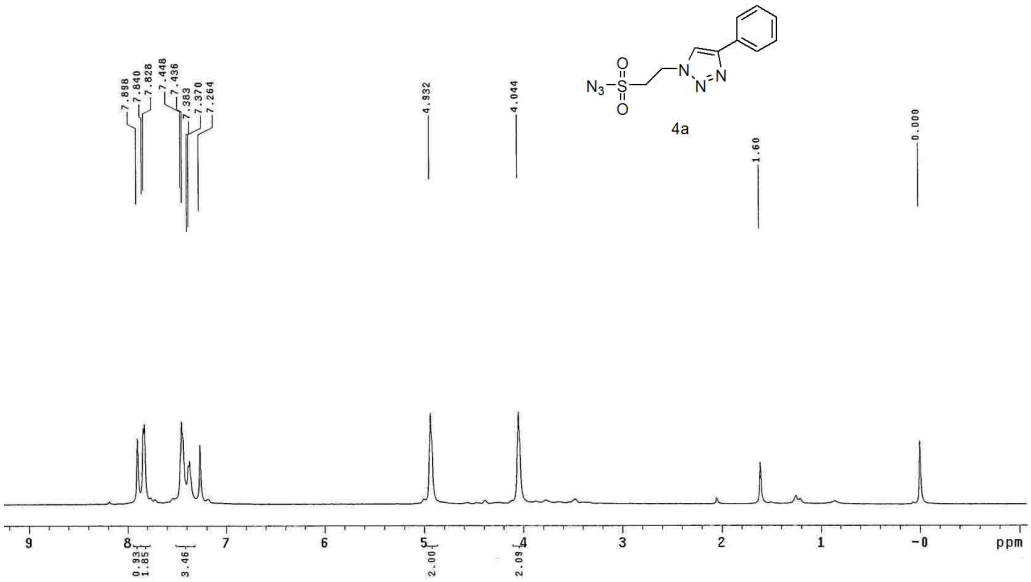

147.407
135.585
132.688
131.649
131.231
130.506
130.312
129.770
129.102
128.961
128.717
128.293
128.084
126.046
122.159
119.019
77.252
76.996
76.741
160
140
120
100
80
60
40
20
ppm

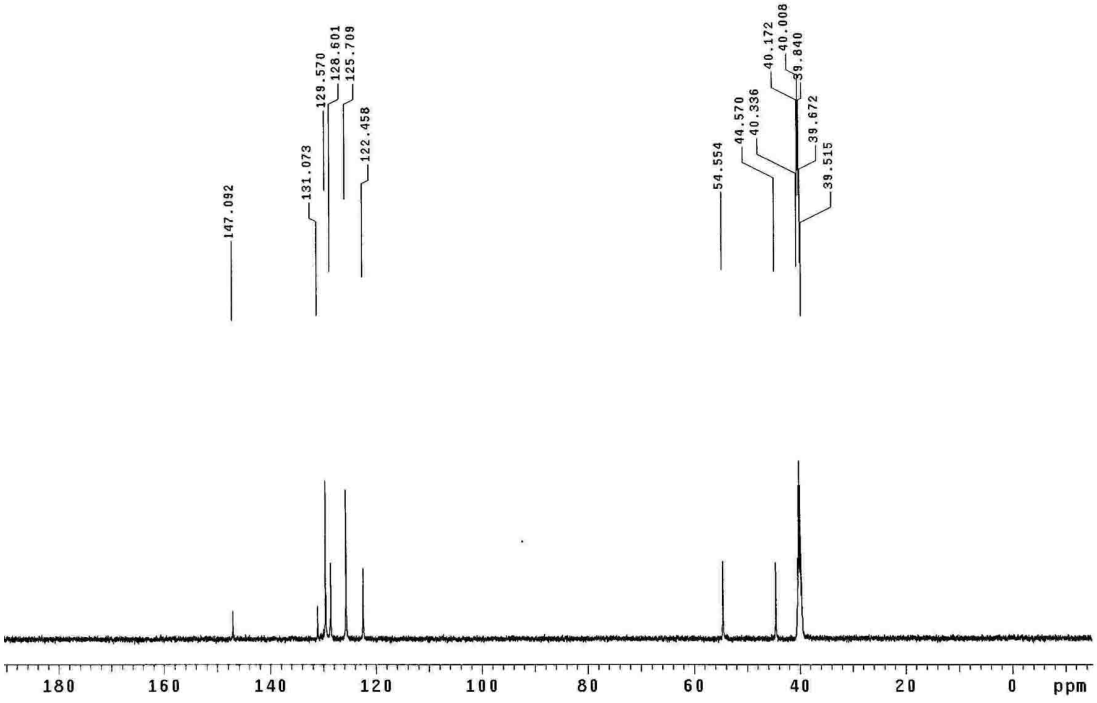

3q
3.568
8.312
7.863
7.858
7.478
7.463
7.448
7.406
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.91
1.90
3.00

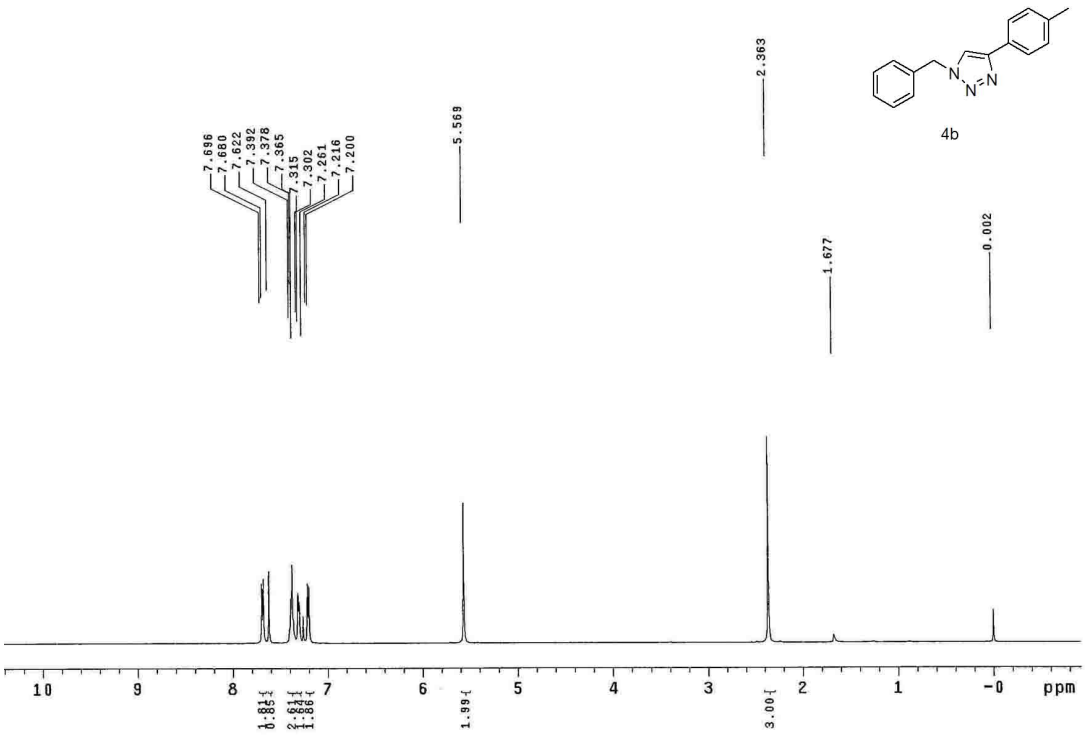

ppm
147.41
129.24
129.03
128.56
126.10
118.91
77.32
77.00
76.68
42.63
ppm
180
160
140
120
100
80
60
40
20

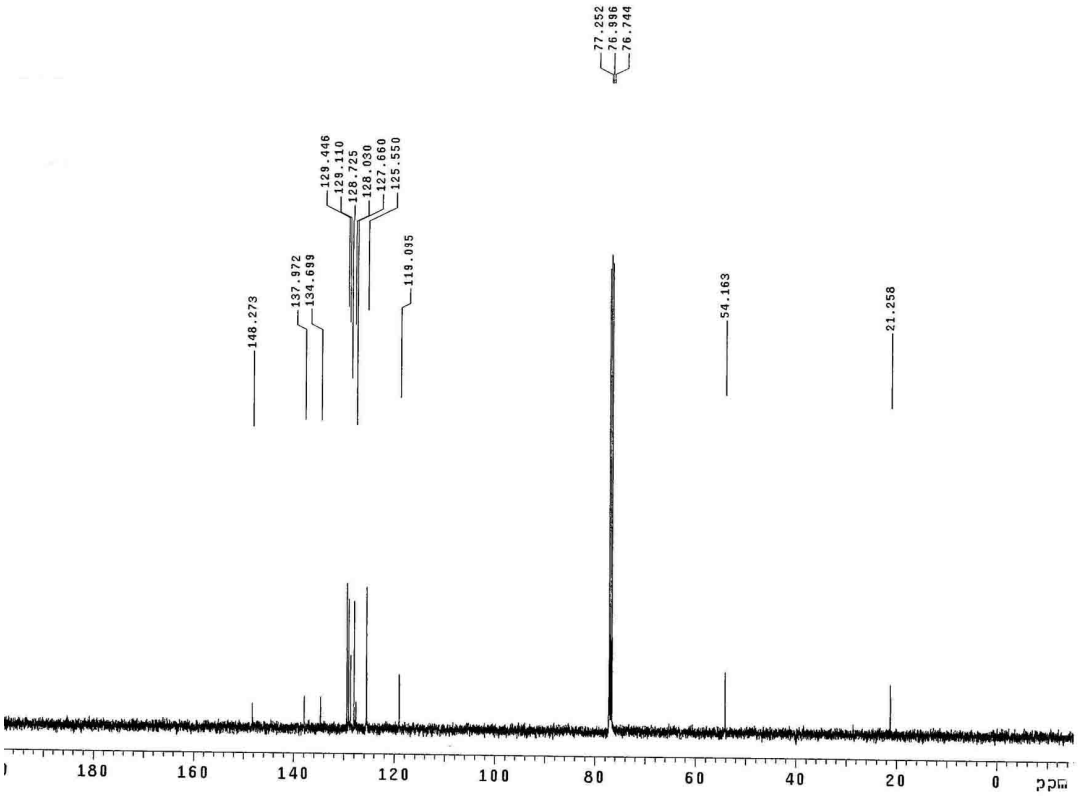

3r
8.389
7.887
7.885
7.871
7.471
7.457
7.441
7.404
7.393
7.389
7.378
4.018
3.988
3.660
3.630
2.415
2.407
2.400
2.376
2.368
2.362
2.339
2.318
2.311
2.171
2.163
2.154
2.113
2.106
2.097
2.089
2.081
2.073
2.064
2.057
1.977
1.939
1.909
1.888
1.880
1.881
1.872
1.863
1.853
1.516
1.508
1.497
1.490
1.483
1.472
1.464
1.122
0.894
ppm

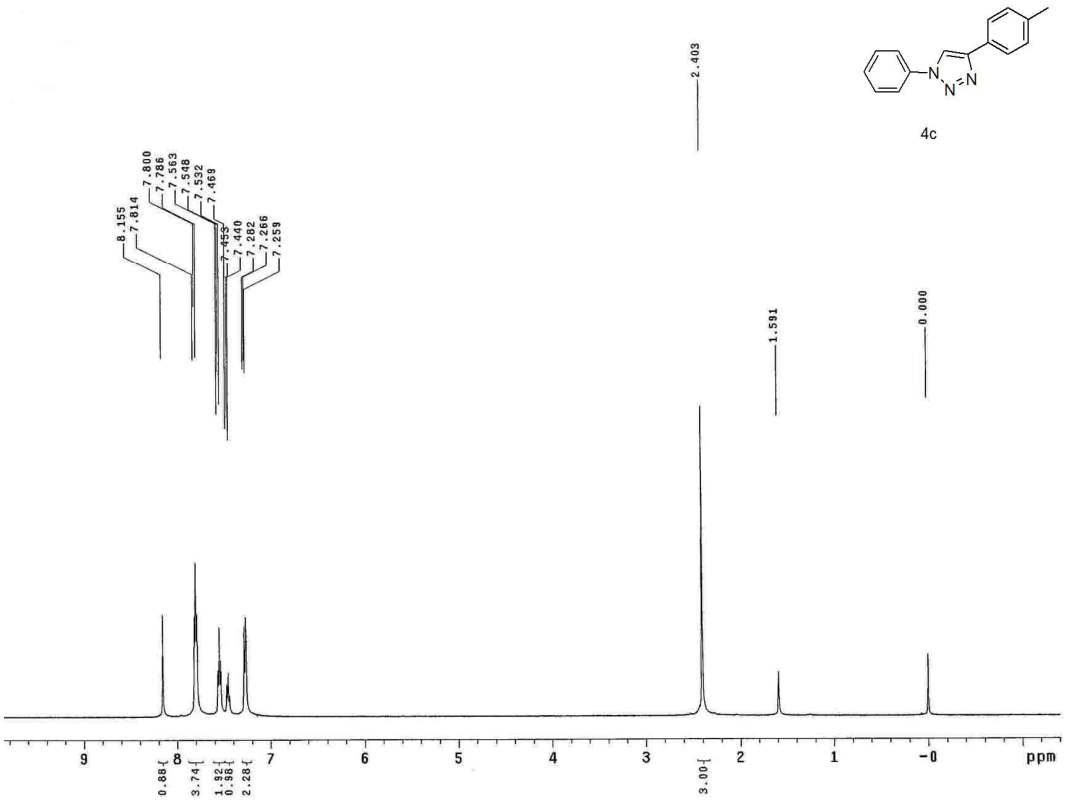

212.995
147.136
129.026
128.904
128.644
126.001
119.383
77.256
77.000
76.744
58.692
53.541
48.368
42.588
42.184
26.813
25.058
19.484
ppm

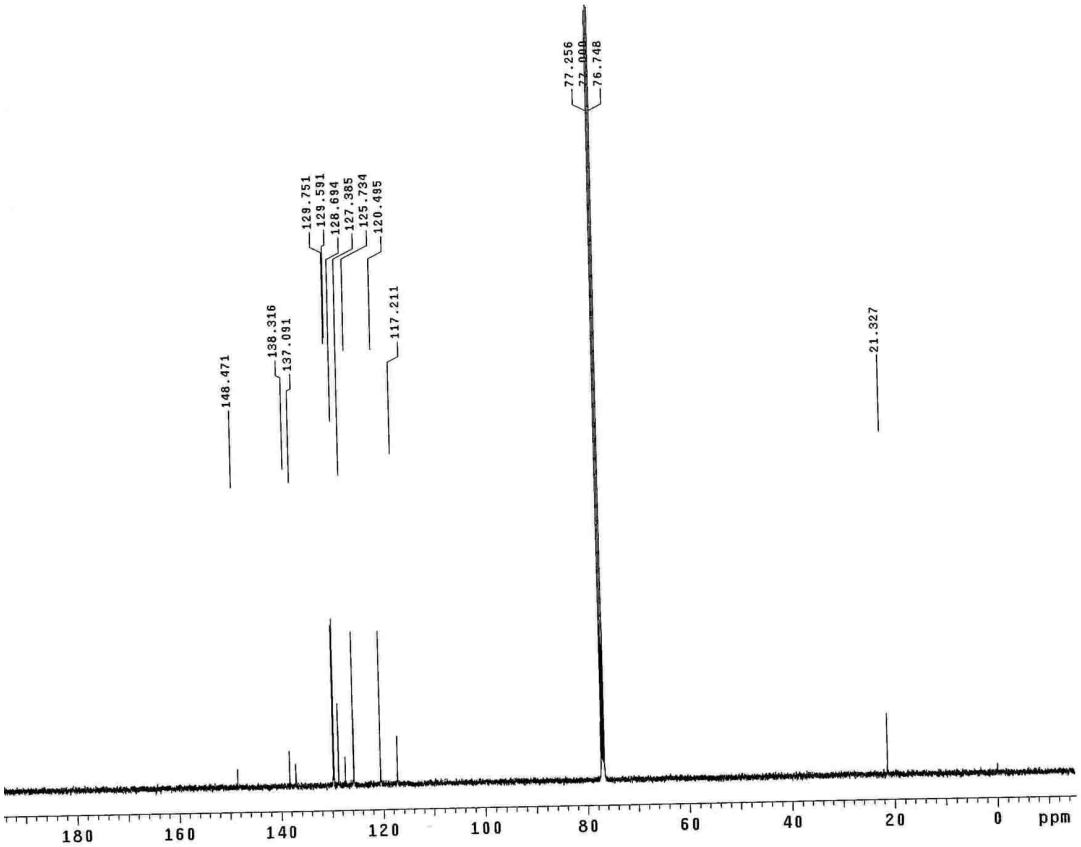

7.898
7.840
7.828
7.448
7.436
7.383
7.370
7.264
4.932
4.044
1.60
0.000
4a
9
8
7
6
5
4
3
2
1
-0
ppm
0.93
1.85
3.46
2.00
2.09

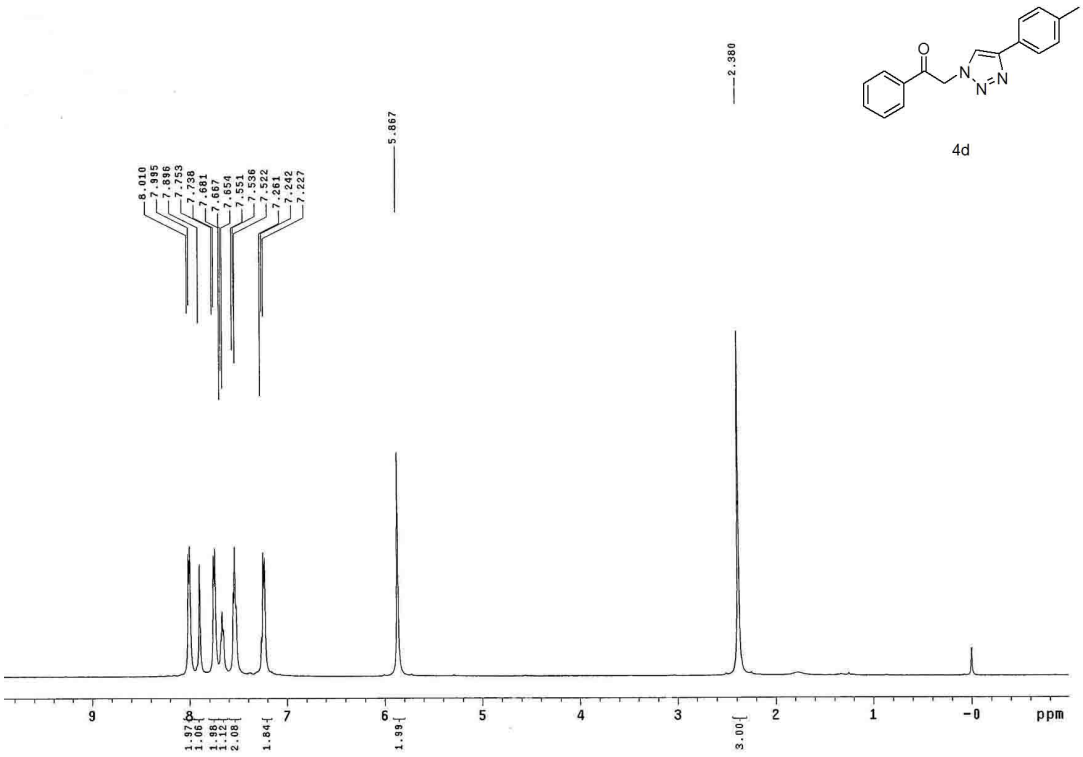

147.092
131.073
129.570
128.601
125.709
122.458
54.554
44.570
40.336
40.172
40.008
39.840
39.672
39.515
180
160
140
120
100
80
60
40
20
0
ppm

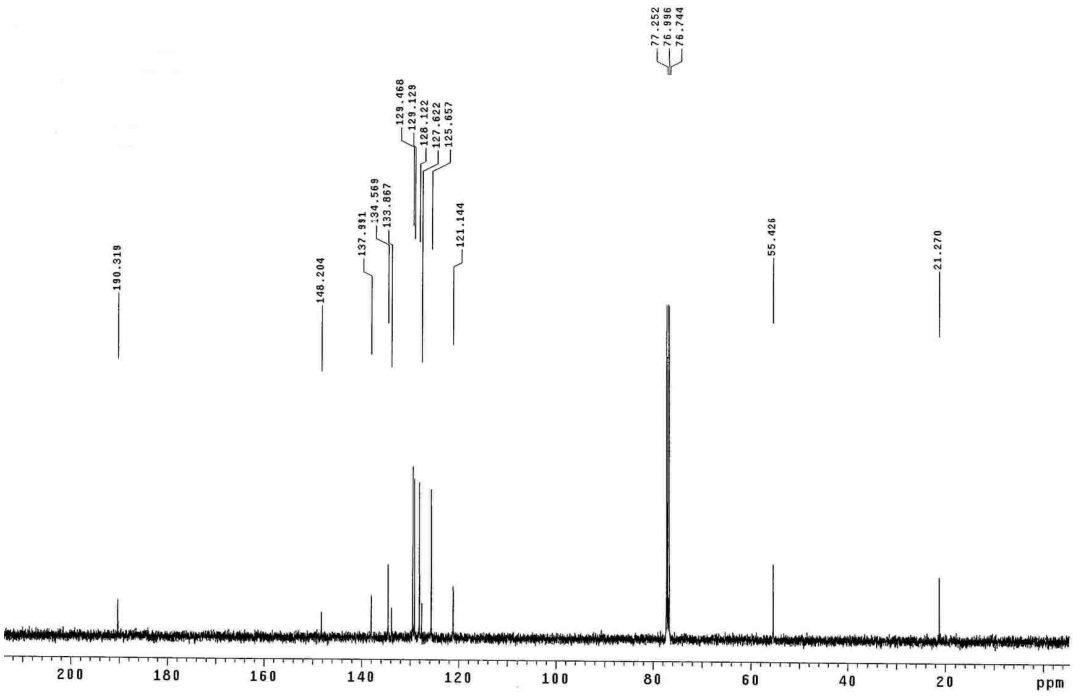

4b
7.696
7.680
7.622
7.392
7.376
7.365
7.315
7.302
7.261
7.216
7.200
5.569
2.363
1.677
0.002
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.81
0.85
2.61
1.80
1.99
3.00

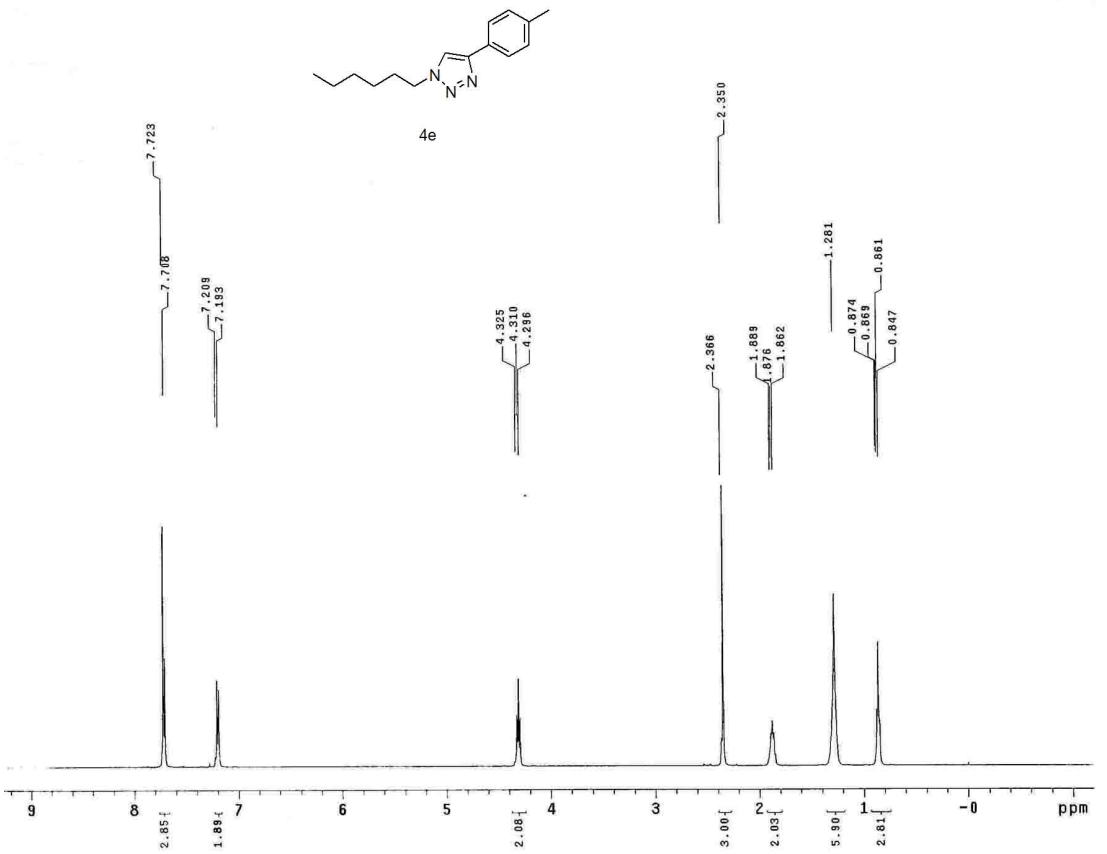

77.252
76.996
76.744
129.446
129.110
128.725
128.030
127.660
125.550
119.035
148.273
137.872
134.699
54.163
21.258
180
160
140
120
100
80
60
40
20
0
ppm

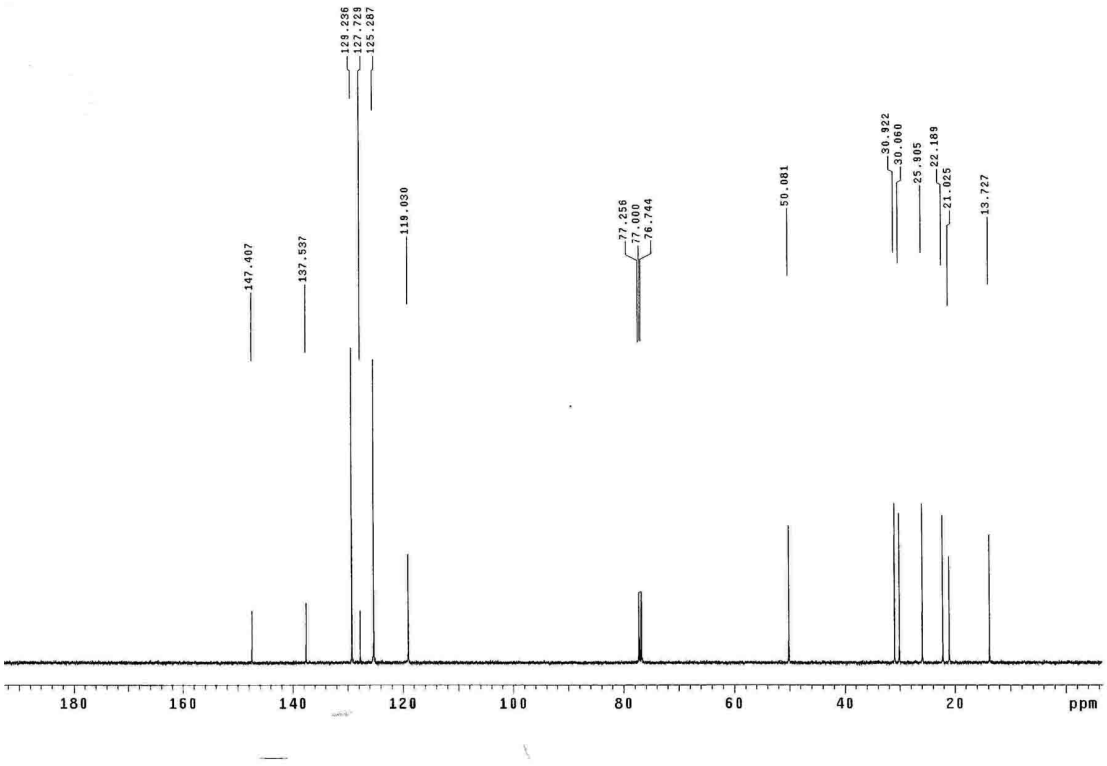

4c
8.155
7.814
7.800
7.786
7.563
7.548
7.532
7.469
7.455
7.440
7.282
7.266
7.259
2.403
1.591
0.000
ppm
0.88
3.74
1.82
0.98
2.28
3.00

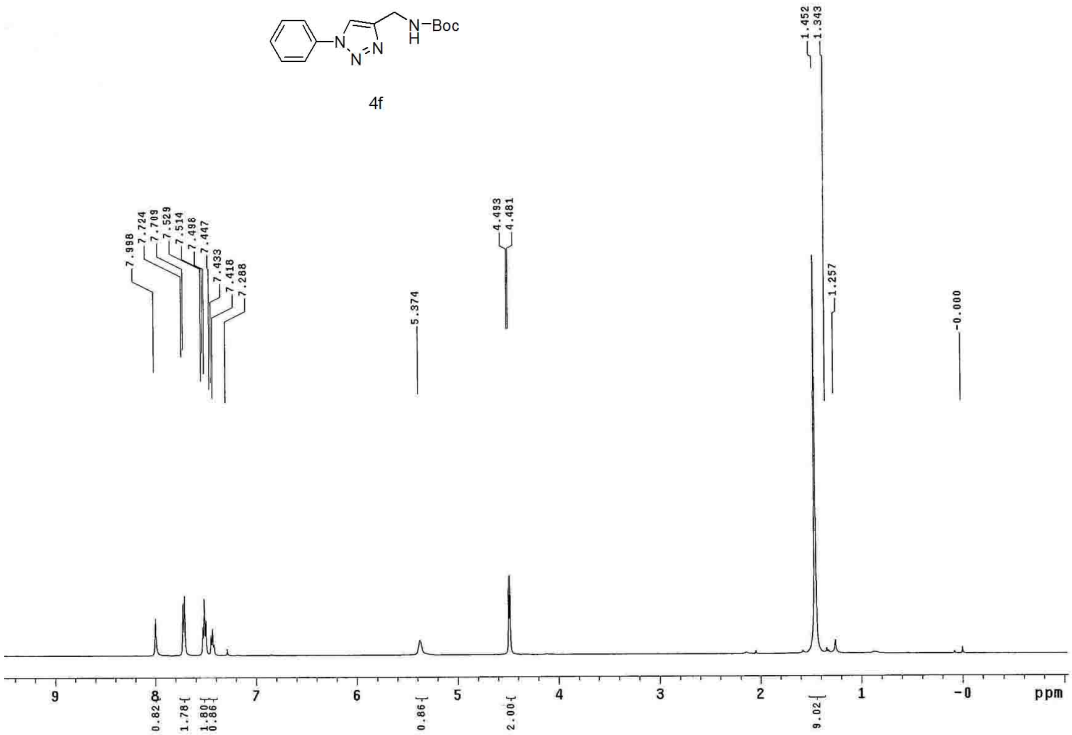

148.471
138.316
137.091
129.751
129.591
128.694
127.385
125.734
120.485
117.211
77.256
77.000
76.748
21.327
ppm

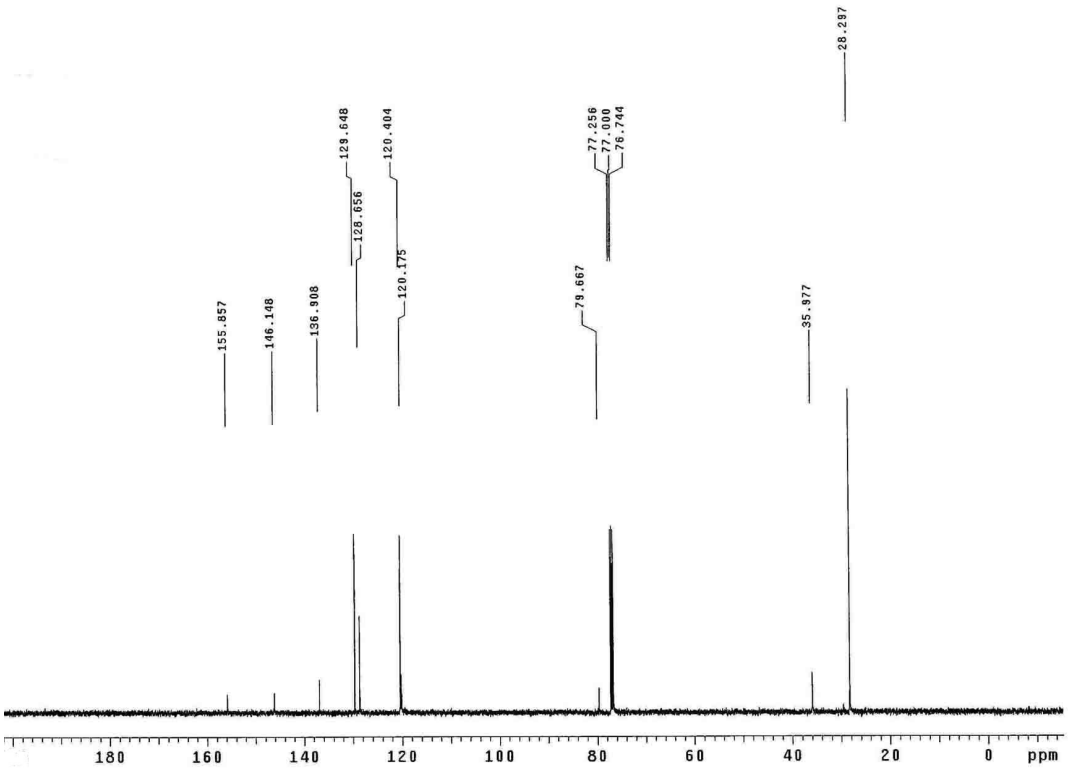

8.010
7.995
7.896
7.753
7.738
7.681
7.667
7.654
7.551
7.536
7.522
7.261
7.242
7.227
5.867
2.380
4d
1.97
1.06
1.12
1.08
2.08
1.84
1.99
3.00
ppm

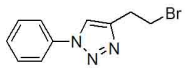

190.319
148.204
137.931
134.569
133.867
129.468
129.128
128.122
127.822
125.867
121.144
77.252
76.996
76.744
55.426
21.270
ppm


4e
7.723
7.708
7.209
7.193
4.325
4.310
4.296
2.366
2.350
1.889
1.876
1.862
1.281
0.874
0.869
0.861
0.847
ppm

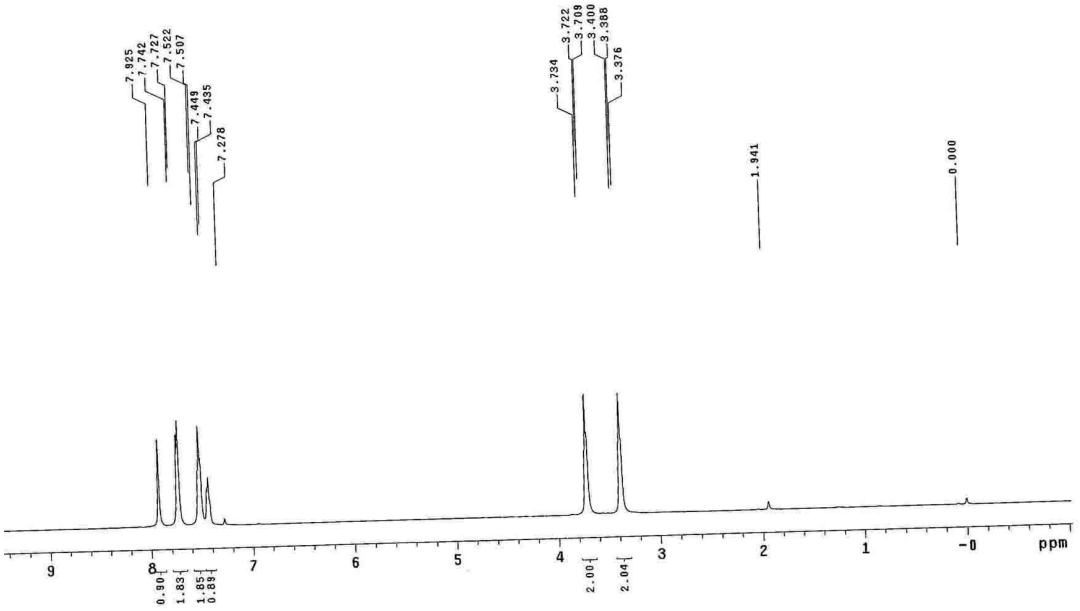

147.407
137.537
129.236
127.729
125.287
119.030
77.256
77.000
76.744
50.081
30.922
30.060
25.905
22.189
21.025
13.727
ppm

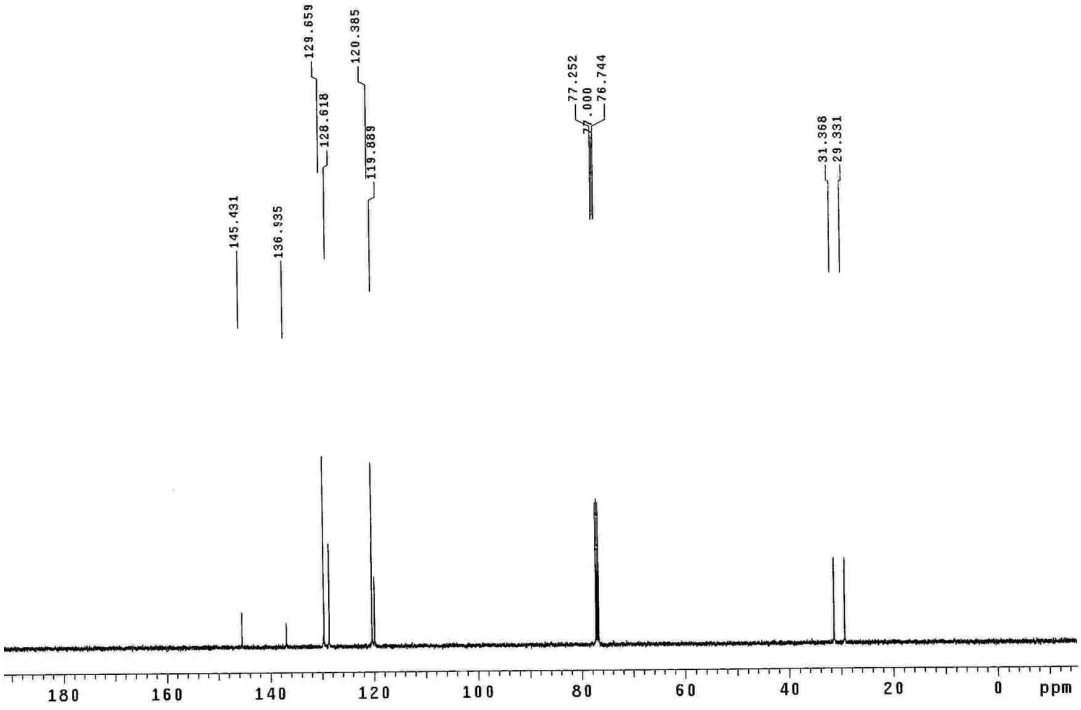

N–Boc
H
4f
7.988
7.714
7.709
7.529
7.514
7.498
7.447
7.433
7.418
7.288
5.374
4.493
4.481
1.452
1.343
1.257
0.000
ppm

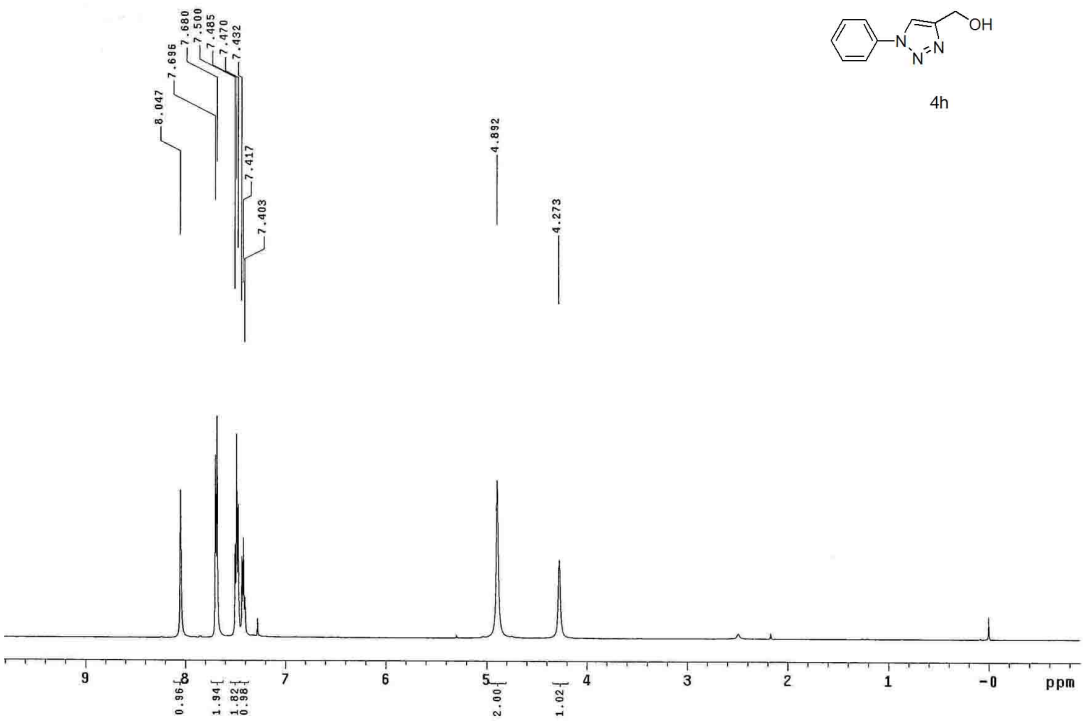

155.857
146.148
136.908
129.648
128.656
120.404
120.175
79.667
77.256
77.000
76.744
35.977
28.287
ppm

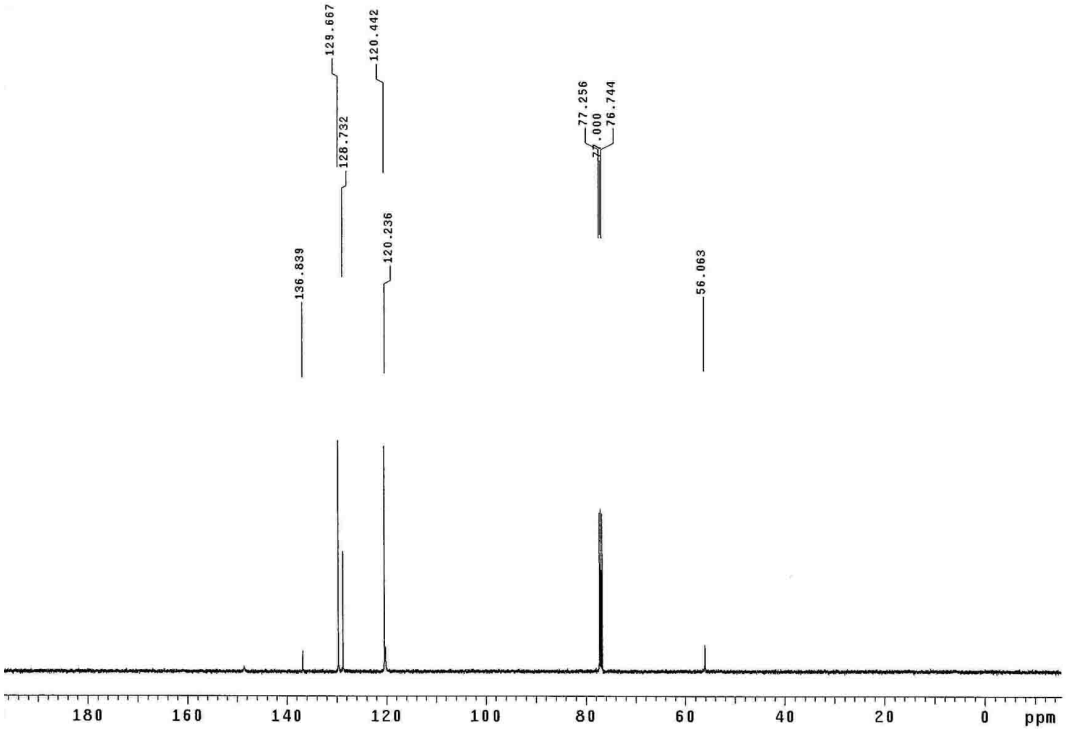

Br
N
N
N

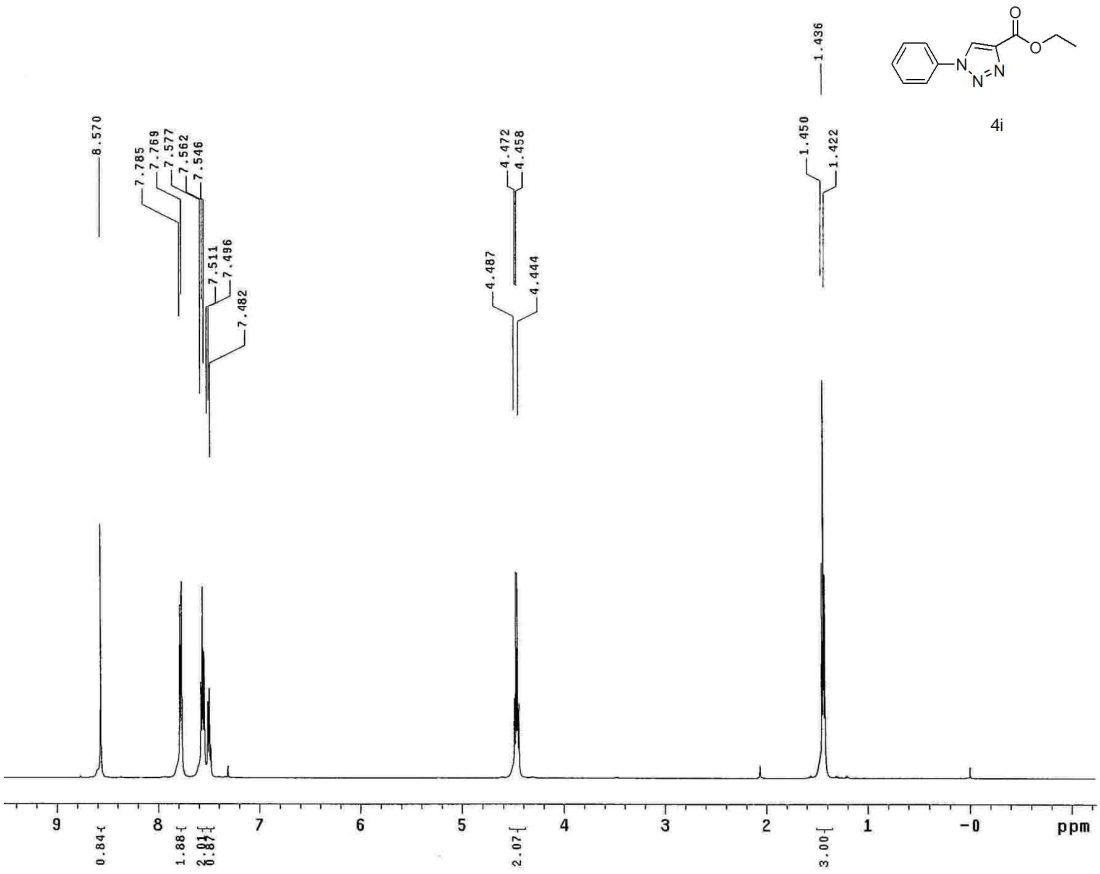
4g

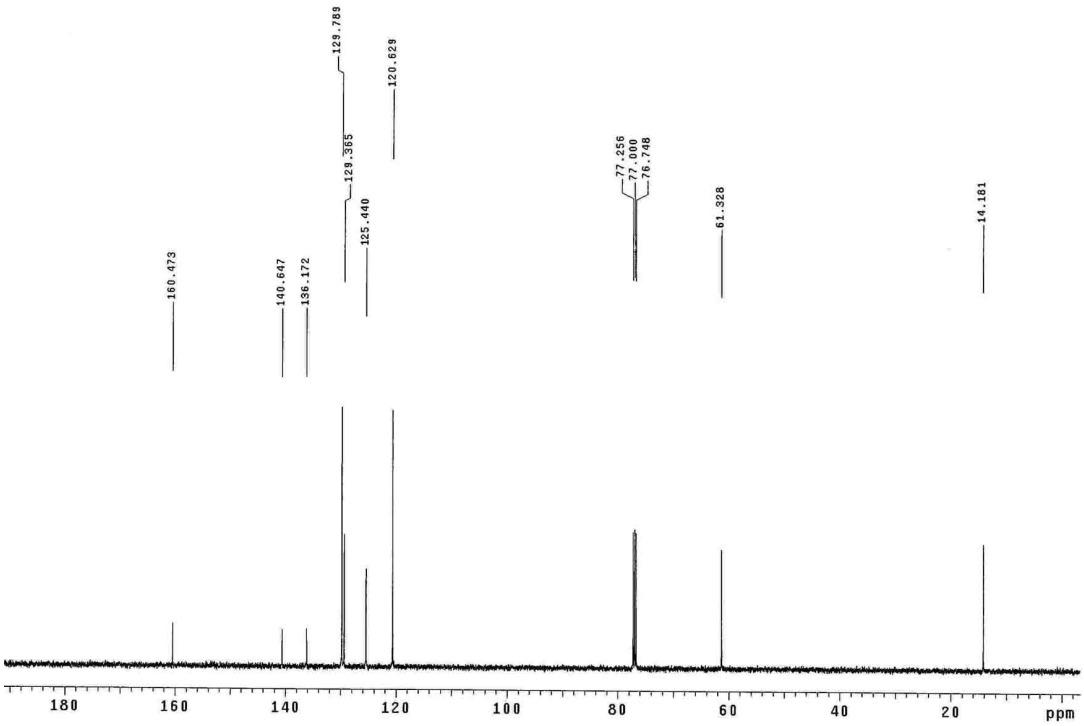

7.905
7.742
7.727
7.522
7.507
7.449
7.435
7.278
3.734
3.722
3.709
3.400
3.388
3.376
1.941
0.000
9
8
7
6
5
4
3
2
1
-0
ppm
0.90
1.83
1.85
0.89
2.00
2.04

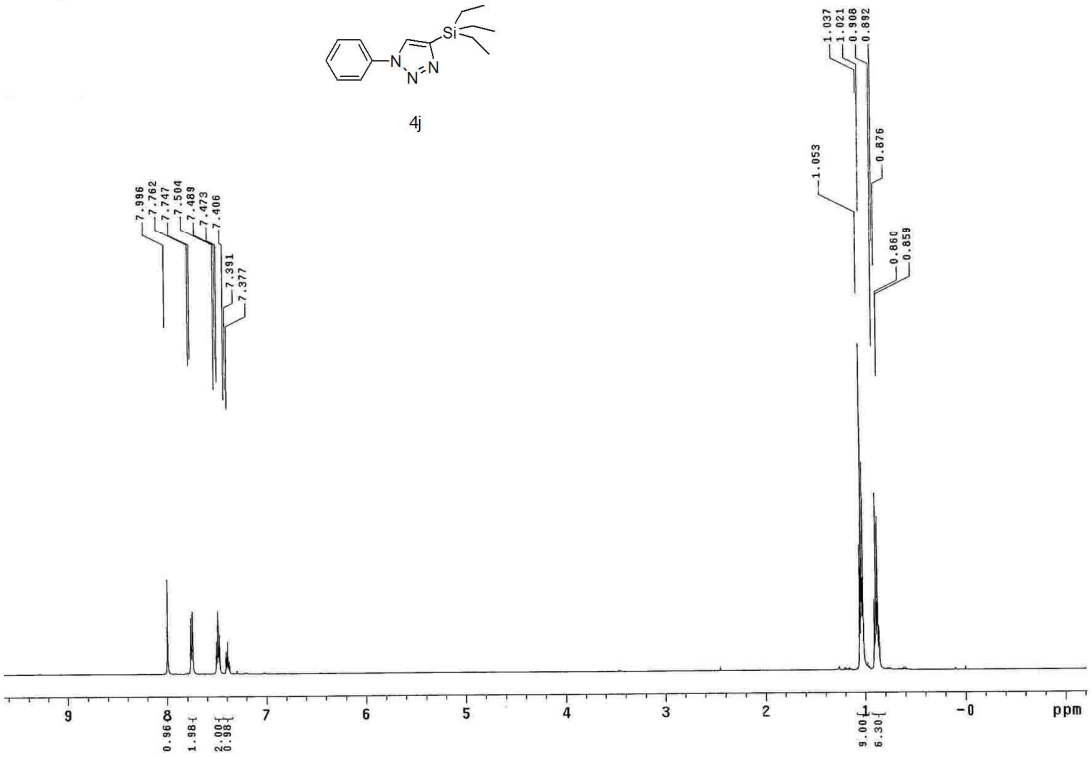

145.431
136.935
129.659
128.618
120.385
119.889
77.252
77.000
76.744
31.368
29.331
180
160
140
120
100
80
60
40
20
0
ppm

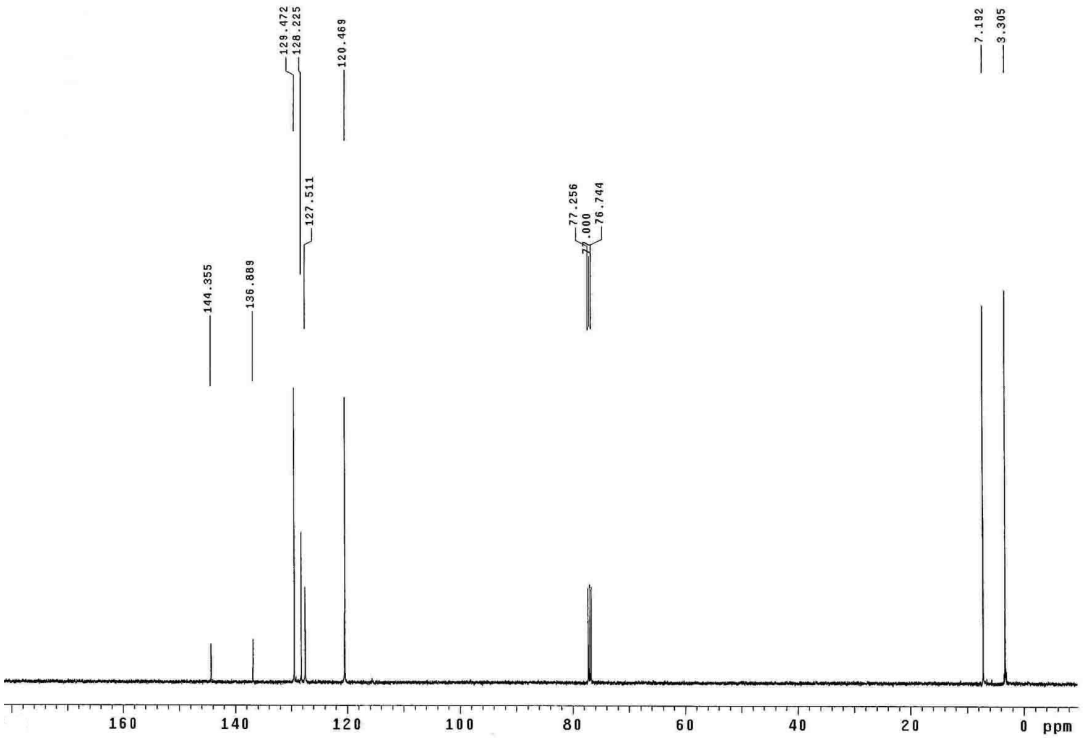

8.047
7.695
7.680
7.500
7.485
7.470
7.432
7.417
7.403
4.892
4.273
OH
N
N
N
4h
9
8
7
6
5
4
3
2
1
-0
ppm
0.96
1.94
1.82
0.98
2.00
1.02


129.667
128.732
120.442
120.236
136.839
77.256
77.000
76.744
56.063
180
160
140
120
100
80
60
40
20
0
ppm

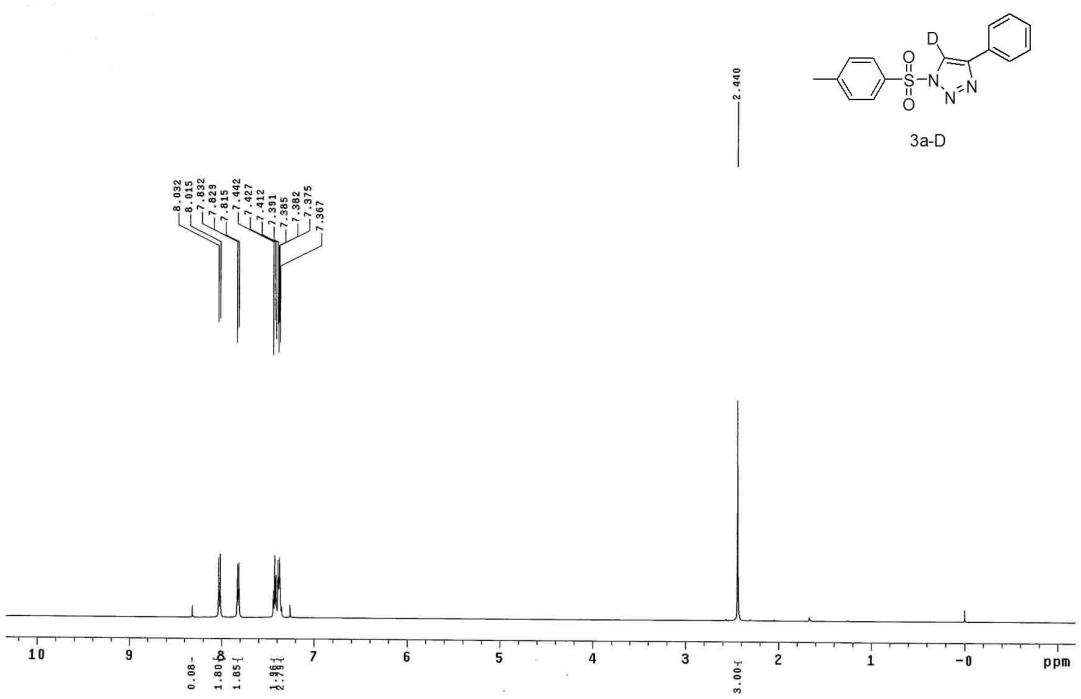

4i
8.570
7.785
7.769
7.577
7.562
7.546
7.511
7.496
7.482
4.487
4.472
4.458
4.444
1.450
1.436
1.422
0.84
1.88
2.07
3.00
ppm


160.473
140.647
136.172
129.789
129.365
125.440
120.629
77.256
77.000
76.748
61.328
14.161
ppm

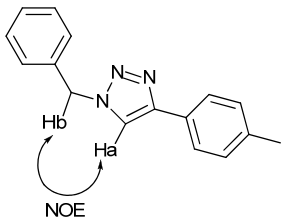

4j
7.996
7.762
7.747
7.504
7.489
7.473
7.406
7.391
7.377
1.037
1.021
0.908
0.892
1.053
0.876
0.860
0.859
ppm

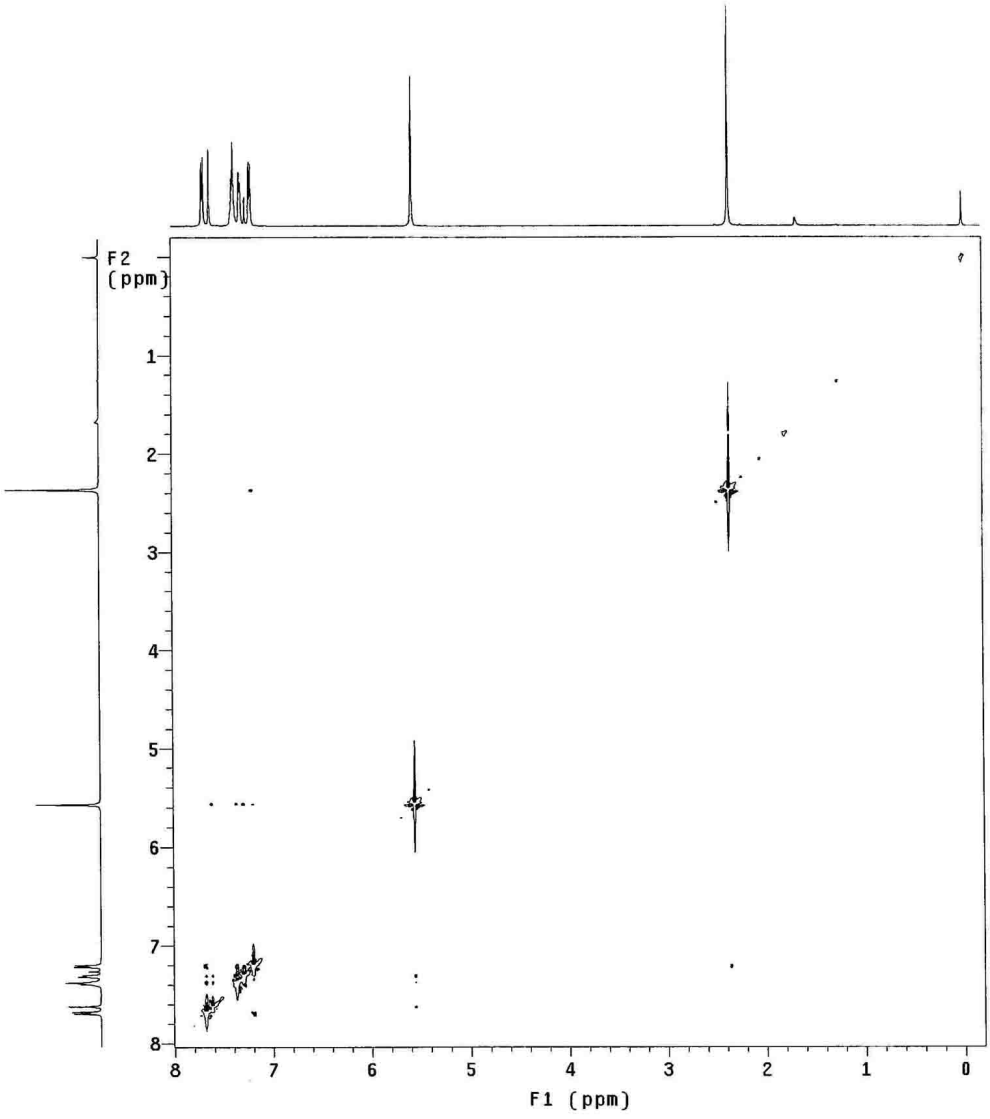

129.472
128.225
120.469
127.511
144.355
136.889
77.256
77.000
76.744
7.192
3.305
ppm

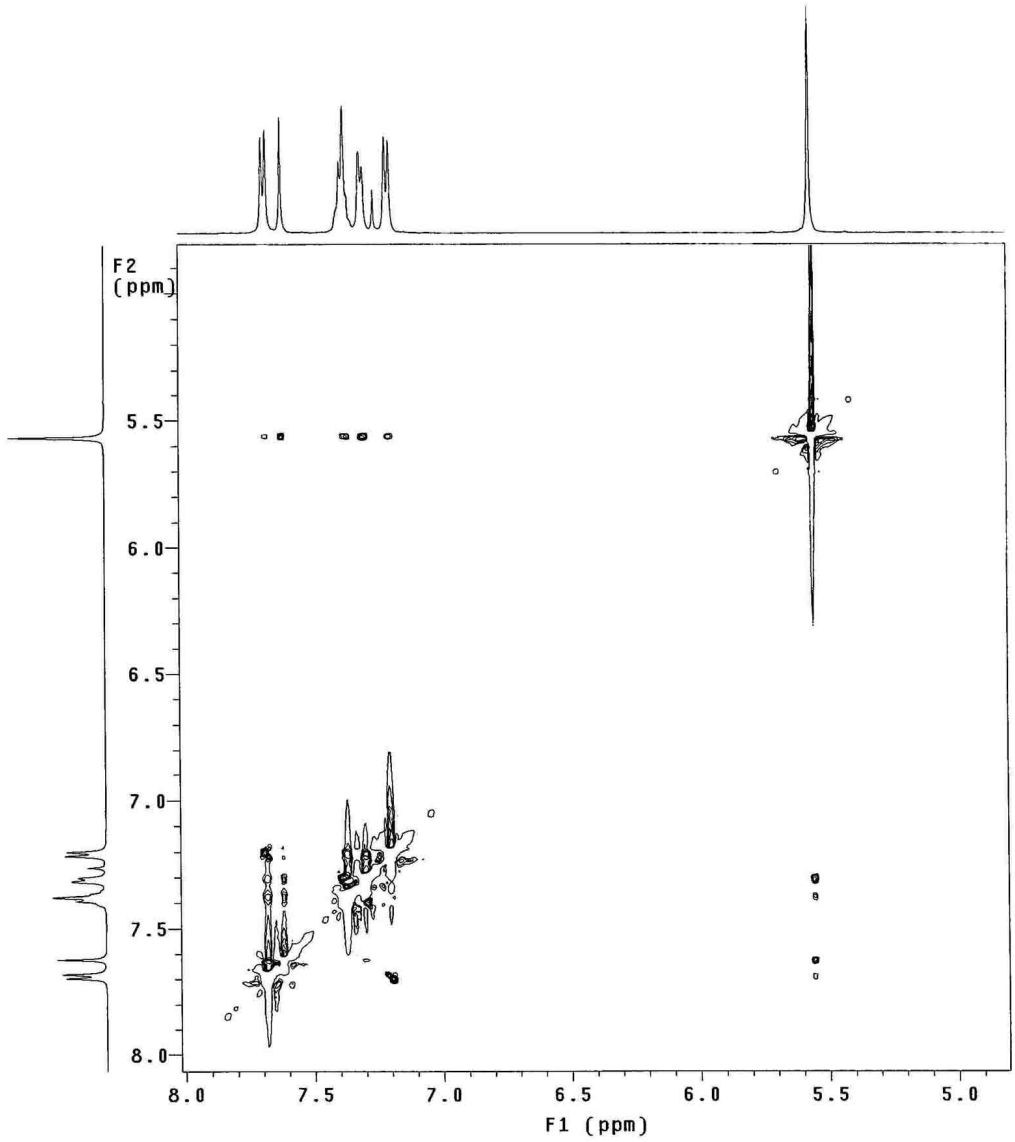
^{1}H NMR spectrum of **3a-D**



NOE spectrum of **4b**






F2
(ppm)
5.5
6.0
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
F1 (ppm)