Synthesis of Fused 1,2,3-Triazoles through Carbocation-Mediated Intramolecular [3+2] Cycloaddition of Azido-Propargyl Alcohols

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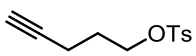
Supporting Information

General information

^{1}H and ^{13}C NMR were recorded on a JEOL JNM-ECP500 spectrometer (500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR). Chemical shifts are reported as δ values in ppm and calibrated by residual solvent peak ($CDCl_3$, δ 7.26 for 1H NMR, δ 77.00 for ^{13}C NMR; CD_3OD, δ 3.31 for ^{1}H NMR, δ 49.00 for ^{13}C NMR; CD_2Cl_2, δ 5.32 for ^{1}H NMR, δ 53.8 for ^{13}C NMR) or tetramethylsilane (δ 0 for ^{1}H NMR). Abbreviations are following: s (singlet), d (doublet), t (triplet), q (quartet), br (broad peak), m (complex multiplet). Inflared spectra were measured on a JASCO FT/IR-4200 spectrometer. Mass spectra were recorded on a JEOL JMS-700 MStaion [EI (70 eV), CI, FAB and ESI]. Flush column chromatography was performed by MERCK Silica gel 60. The progress of reactions was monitored by silica gel thin layer chromatographyplates (MERCKTLC Silicagel 60 F_{254}). Phosphomolybdic acid ethanol solution, ninhydrin-acetic acid butanol solution and anisaldehyde-acetic acid-sulfuric acid ethanol solution were used as TLC stain. All reagents were purchased from Sigma-Aldrich, Wako pure chemical industries, Ltd, TCI (Tokyo Chemical Industry, Co. Ltd), Kanto Chemical Co. Inc., and Nakalai Tesque. Used Dehydrated solvents —tetrahydrofuran, dichloromethane and toluene— were purchased from Kanto Chemical, Wako pure chemical industries, Ltd, and Nakalai Tesque. Sodium azide purchased from Nakalai Tesque was carefully handled, and transferred with plastic spatulas.

Experimental Procedure of Tosylate compound pent-4-yn-1-yl 4-methylbenzenesulfonate



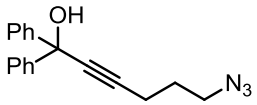
To a stirred solution of 4-pentyn-1-ol **1** (100.0 mg, 1.19 mmol) and TsCl (249.3 mg, 1.31 mmol) in dichloromethane (12 ml) was added dropwise triethylamine (0.2 mL, 1.43 mmol) at 0 ℃, then reaction mixture was allowed to warm up to ambient temperature. After 2 h, the mixture was diluted with ethyl acetate and was washed with water and brine. Drying collected organic layer over $MgSO_4$ followed by silica

gel column chromatography (ethyl acetate / hexane = 1/10) gave tosylate compound (220 mg, 77.7%) as a colorless oil.
Colorless oil; R_f value 0.53(ethyl acetate / hexane = 1/3);IR (NaCl, neat) ν_{max} = 3291, 2962, 1598, 1360, 1176 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, 2H, *J* = 8.5 Hz), 7.35 (d, 2H, *J* = 8.5 Hz), 4.14 (t, 2H, *J* = 6.0 Hz), 2.45 (s, 3H), 2.25 (td, 2H, *J* = 6.5, 2.5 Hz), 1.88 (t, 1H, *J* = 2.5 Hz), 1.86 (tt, 2H, *J* = 6.5, 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 132.9, 129.8, 127.9, 82.1, 69.4, 68.7, 27.7, 21.6, 14.7; HRMS (ESI) calcd for $C_{12}H_{14}O_3SNa$ $[M+Na]^+$ 261.0561, found 261.0561.

General Experimental Procedure of propargyl alcohols

To a stirred solution of tosylate compound in dry THF under an atmosphere of nitrogen was added dropwise *n*-BuLi at -78 ℃ and the mixture was stirred for 10 min. Benzaldehyde was then added at same temperature. After 4h, the reaction was quenched with water. The mixture was diluted with ethyl acetate and was washed with water and brine. Drying collected organic layer over $MgSO_4$. The crude product can be used to the next step without further purification.
To a stirred solution of benzyl alcohols in DMF was added sodium azide at room temperature and the reaction mixture was heated to 50 ℃. After 20 min, the reaction mixture was diluted with ether and was washed with water and brined. Drying collected organic layer over $MgSO_4$ followed by silica gel column chromatography gave azide as colorless oil.

6-azido-1,1-diphenylhex-2-yn-1-ol (1a)



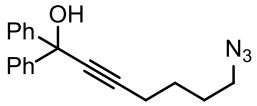
1a

The reaction with tosylate (0.543 g, 2.15 mmol), *n*-BuLi (1.58 M in hexane, 1.46 mL, 2.30 mmol) and ketone (0.28 g, 1.54 mmol) in THF (15 mL) followed by followed by collected the organic layer under vacuum affording the product 2.2 g. [silica gel purification (ethyl acetate / hexane = 1 / 8 to 1/4)].
Colorless oil; R_f value 0.25(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3502, 3060, 3029, 2958, 1598, 1491, 1449, 1360, 1175 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.75(d, 2H, *J* = 7.5 Hz), 7.53(m, 4H), 7.23–7.32(m, 8H), 4.15(t, 2H, *J* = 6.0 Hz), 2.76(s, 1H), 2.43(t, 2H, *J* = 6.5 Hz), 2.39(s, 3H), 1.90(tt, 2H, *J* = 6.5, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.1, 144.8, 132.8, 129.9, 128.2, 127.9, 127.6, 125.9, 85.5, 84.4, 74.3, 68.8, 27.7, 21.6, 15.2; LRMS (EI) 420(M^+, 0.8%), 403(5), 343(100), 220(53), 105(71); HRMS (EI) calcd for $C_{25}H_{24}O_4S$ (M^+) 420.1395, found 420.1397.

Then the crude benzyl alcohol with sodium azide (0.124 g, 1.9 mmol) in DMF (5 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/10 to 1/5) gave azide **1a** (0.32 g, 70%) as a colorless oil.
Colorless oil; R_f value 0.50(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3426, 2933, 2099, 1490, 1449 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.59(m, 4H), 7.31(m, 4H),

7.27(m, 2H), 3.43(t, 2H, *J* = 6.5 Hz), 2.75(s, 1H), 2.48(t, 2H, *J* = 7.0 Hz), 1.85(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.2, 128.2, 127.6, 125.9, 86.2, 84.2, 74.4, 50.2, 27.7, 16.2; HRMS (CI) calcd for $C_{18}H_{18}N_3O$ $[M+H]^+$ 292.1450, found 292.1455.

7-azido-1,1-diphenylhept-2-yn-1-ol(1b)



1b

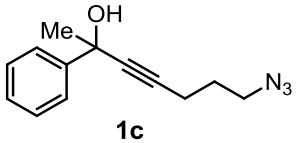
The reaction with tosylate compound(0.255 g, 1.07 mmol), *n*-BuLi (1.55 M in hexane, 0.729 mL, 1.15 mmol) and ketone (0.15 g, 0.823 mmol) in THF (8 mL) followed by followed by collected the organic layer under vacuum affording the product 0.45 g. [silica gel purification (ethyl acetate / hexane = 1 / 8 to 1/3)].

Colorless solid; R_f value 0.28(ethyl acetate/hexane = 1/3); m.p. 102.8–103.2 ℃;IR (NaCl, neat) ν_{max} 3477, 1644, 1174, 933 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.78(d, 2H, *J* = 8.0 Hz), 7.60–7.57(m, 4H), 7.38–7.31(m, 6H), 7.28–7.25(m, 2H), 4.06(t, 2H, *J* = 6.5 Hz), 2.92(s, 1H, OH), 2.44(s, 3H), 2.34(t, 2H, *J* = 7.0 Hz), 1.82(tt, 2H, *J* = 6.5, 6.5 Hz), 1.63(tt, 2H, *J* = 6.5, 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.4, 144.8, 132.9, 129.9, 128.2, 127.8, 127.5, 125.9, 86.9, 83.9, 74.4, 69.9, 28.0, 24.3, 21.6, 18.3; HRMS (ESI) calcd for $C_{26}H_{26}O_4SNa$ $[M+Na]^+$457.14495, found 457.14440.

Then the crude benzyl alcohol with sodium azide (83.47 mg, 1.28 mmol) in DMF (20 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/10 to 1/5) gave azide **1b** (0.108 g, 43%) as a colorless oil.

Colorless oil; R_f value 0.47(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3421, 2935, 2096, 1489, 1449 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.60(m, 4H), 7.33(dd, 4H, *J* = 6.5, 6.5 Hz), 7.27(m, 2H), 3.31(t, 2H, *J* = 6.5 Hz), 2.76(s, 1H, OH), 2.40(t, 2H, *J* = 7.0 Hz), 1.66–1.76(m, 4H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.3, 128.2, 127.6, 125.9, 87.2, 83.7, 74.4, 50.9, 28.0, 25.6, 18.5,; HRMS (ESI) calcd for $C_{19}H_{19}N_3ONa$ $[M+Na]^+$ 328.1426, found 328.1424.

7-azido-2-phenylhept-3-yn-2-ol(1c)



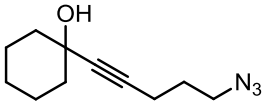
1c

The reaction with tosylate compound (1.40 g, 6.24 mmol), *n*-BuLi (1.55 M in hexane, 4.43 mL, 6.87 mmol) and ketone (0. 5 g, 4.16 mmol) in THF (42 mL) followed by followed by collected the organic layer under vacuum affording the crude product 0.95 g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol with sodium azide (446.2 mg, 6.86mmol) in DMF (20 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 20 to

1/10 to 1/5) gave azide **1c** (0.872 g, 91 %) as a colorless oil.
Colorless oil; R_f value 0.19(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3393, 2982, 2094, 1446 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.65(d, 2H, *J* = 6.5 Hz), 7.37(dd, 2H, *J* = 7.5, 7.5 Hz), 7.29(dd, 1H, *J* = 7.5, 7.5 Hz), 3.43(t, 2H, *J* = 6.5 Hz), 2.42(t, 2H, *J* = 6.5 Hz), 2.31(s, 1H, OH), 1.83(tt, 2H, *J* = 6.5, 6.5 Hz), 1.75(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.9, 128.3, 127.6, 124.8, 85.0, 83.7, 70.0, 50.2, 33.4, 27.8, 16.1; HRMS (ESI) calcd for $C_{13}H_{15}N_3ONa$ $[M+Na]^+$ 252.11128, found 252.11129.

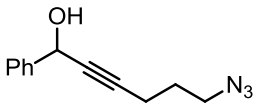
1-(5-azidopent-1-yn-1-yl)cyclohexan-1-ol(1d)



1d

The reaction with tosylate compound (1.37 g, 6.11 mmol), *n*-BuLi (1.55 M in hexane, 3.62 mL, 5.60 mmol) and ketone (0.5 g, 5.09 mmol) in THF (50 mL) followed by followed by collected the organic layer under vacuum affording the crude product 1.71 g. The crude product can be used to the next step without further purification.
Then the crude benzyl alcohol with sodium azide (1.71 g, 5.08 mmol) in DMF (20 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/10 to 1/5) gave azide **1d** (0.97 g, 85%) as a colorless oil.
Colorless oil; R_f value 0.58(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3383, 2933, 2856, 2097 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 3.42(t, 2H, *J* = 6.0 Hz), 2.35(t, 2H, *J* = 6.5 Hz), 1.80–1.89(m, 3H including OH), 1.78(tt, 2H, *J* = 6.5, 6.0 Hz), 1.68(m, 2H), 1.47–1.59(m, 6H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 85.1, 82.7, 68.7, 50.2, 40.1, 27.9, 25.1, 23.4, 16.0; HRMS (ESI) calcd for $C_{11}H_{17}N_3ONa$ $[M+Na]^+$ 230.1269, found 230.1273.

6-azido-1-phenylhex-2-yn-1-yl acetate (1e)

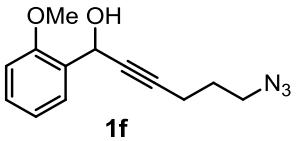


1e

The reaction with tosylate compound (146 mg, 0.612 mmol), *n*-BuLi (1.6 M in hexane, 0.44 mL, 0.706 mmol) and benzaldehyde (47.6 μL, 0.471 mmol) in TH F (4.8 mL) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1 / 5) gave tosylate benzyl alcohol **1e'** (148 mg, 91% based on benzaldehyde) as a colorless oil.
Colorless oil; R_f value 0.15(ethyl acetate / hexane = 1/3);IR (NaCl, neat) ν_{max} = 3524, 2960, 1598, 1189, 1175, 930 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, 2H, *J* = 8.0 Hz), 7.48 (d, 2H, *J* = 8.0 Hz), 7.30 – 7.38 (m, 3H), 5.36 (br, 1H), 4.14 (t, 2H, *J* = 6.5 Hz), 2.42 (s, 3H), 2.35 (td, 2H, *J* = 7.0, 2.0 Hz), 1.87 (tt, 2H, *J* = 7.0, 6.5 Hz) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 140.9, 132.8, 129.8, 128.5, 128.2, 127.8, 126.5, 84.2, 81.3, 68.9, 64.5, 27.6, 21.6, 15.1; HRMS (ESI) calcd for $C_{19}H_{20}O_4SNa$ $[M+Na]^+$ 367.0980, found 367.09800.

To a stirred solution of tosylate benzyl alcohol (780 mg, 2.02 mmol) in DMF (20 mL) was added sodium azide (170.6 mg, 2.62 mmol) at room temperature and the reaction mixture was heated to 50 ℃. After 20 min, the reaction mixture was diluted with ether and was washed with water and brined. Drying collected organic layer over $MgSO_4$ followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 3) gave azide **1e** (487.9 mg, 94%) as a colorless oil.
Colorless oil; R_f value 0.45(ethyl acetate / hexane = 1/2); IR (NaCl, neat) ν_{max} = 2931, 2098, 1739, 1227 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, 2H, *J* = 7.0 Hz), 7.38 (m, 3H), 6.45 (br, 1H), 3.40 (t, 2H, *J* = 7.0 Hz), 2.40 (td, 2H, *J* = 2.0, 6.5 Hz), 2.10 (s, 3H), 1.80 (tt, 2H, *J* = 6.5, 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 137.2, 128.7, 128.5, 127.5, 86.1, 77.9, 65.7, 49.9, 27.4, 20.9, 16.0; HRMS (ESI) calcd for $C_{14}H_{15}N_3O_2Na$ $[M+Na]^+$ 280.1062, found 280.1061.

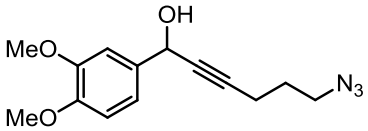
6-azido-1-(2-methoxyphenyl)hex-2-yn-1-ol(1f)



1f

The reaction with tosylate compound (3.94 g, 16.5 mmol), *n*-BuLi (1.55 M in hexane, 12.77 mL, 19.8 mmol) and benzaldehyde (1.5 g, 11.02 mmol) in THF (110 mL) followed by collected the organic layer under vacuum affording the crude product 3.12 g. The crude product can be used to the next step without further purification.
Then the crude tosylate benzyl alcohol (3.12 g, 8.33 mmol) with sodium azide (0.65 g, 10 mmol) in DMF (8 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 2) gave azide **1f** (1.98 g, 97%) as a colorless oil.
Colorless oil; R_f value 0.36(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3417, 2938, 2098, 1244 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.56(dd, 1H, *J* = 7.5, 2.0 Hz), 7.31(ddd, 1H, *J* = 7.5, 7.5, 2.0 Hz), 6.99(dd, 1H, *J* = 7.5, 7.5 Hz), 6.92(d, 1H, *J* = 7.5 Hz), 5.70(td, 1H, *J* = 6.0, 2.0 Hz), 3.90(s, 3H), 3.43(t, 2H, *J* = 6.5 Hz), 3.00(d, 1H, OH, *J* = 6.0 Hz), 2.41(td, 2H, *J* = 7.0, 2.0 Hz), 1.82(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 156.7, 129.6, 128.9, 127.7, 120.8, 110.7, 85.0, 80.4, 61.2, 55.5, 50.2, 27.7, 16.2; HRMS (ESI) calcd for $C_{13}H_{15}N_3O_2Na$ $[M+Na]^+$ 268.1062, found 268.1061.

6-azido-1-(3,4-dimethoxyphenyl)hex-2-yn-1-ol(1g)

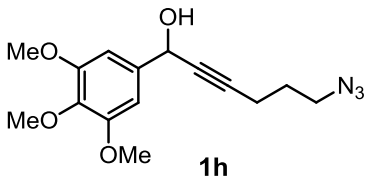


1g

The reaction with tosylate compound (2.15 g, 9.03 mmol), *n*-BuLi (1.55 M in hexane, 6.41 mL, 9.93 mmol) and benzaldehyde (1 g, 6.02 mmol) in THF (60 mL) followed by collected the organic layer under vacuum affording the crude product 2.97g. The crude product can be used to the next step without further purification.
Then the crude tosylate benzyl alcohol (2.87g, 7.15 mmol) with sodium azide (0.511g,

7.86mmol) in DMF (25ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 5 to 1/2) gave azide **1g** (1.81 g, 92%) as a colorless oil.
Colorless oil; R_f value 0.34 (ethyl acetate / hexane = 1/2); IR (NaCl, neat) ν_{max} 3433, 2938, 2098, 1593, 1125 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.07(m, 2H), 6.86(d, 1H, *J* = 8.5 Hz), 5.41(m, 1H), 3.91(s, 3H), 3.89(s, 3H), 3.42(t, 2H, *J* = 7.0 Hz), 2.42(td, 2H, *J* = 6.5, 2.0 Hz), 2.18(d, 1H, OH, *J* = 5.5 Hz), 1.82(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 149.1, 133.7, 118.9, 110.9, 109.8, 85.4, 81.2, 64.6, 55.93, 55.86, 50.2, 27.7, 16.1; HRMS (ESI) calcd for $C_{14}H_{17}N_3O_3Na$ $[M+Na]^+$ 298.1168, found 298.1166.

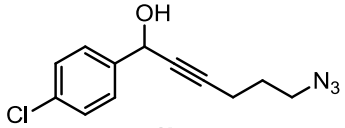
6-azido-1-(3,4,5-trimethoxyphenyl)hex-2-yn-1-ol(1h)



1h

The reaction with tosylate compound (1.09 g, 4.59 mmol), *n*-BuLi (1.55 M in hexane, 3.26 mL, 5.05 mmol) and benzaldehyde (1 g, 3.06 mmol) in THF (31 mL) followed by collected the organic layer under vacuum affording the crude product 1.32g. The crude product can be used to the next step without further purification.
Then the crude tosylate benzyl alcohol (1.32 g, 3.04 mmol) with sodium azide (0.217 g, 3.34 mmol) in DMF (15 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1/1) gave azide **1h** (0.897 g, 96%) as a colorless oil.
Colorless oil; R_f value 0.48(ethyl acetate/hexane = 1/1); IR (NaCl, neat) ν_{max} 3433, 2999, 2099, 1594, 1125 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.73(s, 2H), 5.34(t, 1H, *J* = 2.0 Hz), 3.84(s, 6H), 3.80(s, 3H), 3.39(t, 2H, *J* = 6.5 Hz), 2.37(td, 2H, *J* = 7.0, 2.0 Hz), 1.78(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 153.1, 137.6, 136.7, 103.4, 85.2, 81.1, 64.6, 60.7, 56.0, 50.0, 27.6, 16.0; HRMS (ESI) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1273, found 328.1273.

6-azido-1-(4-chlorophenyl)hex-2-yn-1-ol(1i)

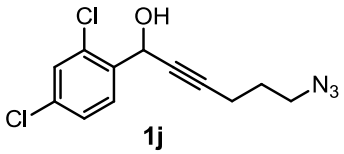


1i

The reaction with tosylate compound (1.53 g, 6.40 mmol), *n*-BuLi (1.55 M in hexane, 4.54 mL, 7.04 mmol) and benzaldehyde (0.6 g, 4.27 mmol) in THF (42 mL) followed by collected the organic layer under vacuum affording the crude product 1.6g. The crude product can be used to the next step without further purification.
Then the crude tosylate benzyl alcohol (1.6 g, 6.40 mmol) with sodium azide (0.499 g, 7.68mmol) in DMF (32 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1/3) gave azide **1i** (1.08 g, 99%) as a colorless oil.
Colorless oil; R_f value 0.52(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3388, 2936, 2099, 1488, 1255, 1089 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.45(m, 2H),

7.34(m, 2H), 5.41(s, 1H), 3.40(t, 2H, *J* = 6.0 Hz), 2.43(br, 1H, OH), 2.39(td, 2H, *J* = 7.0, 2.0 Hz), 1.80(tt, 2H, *J* = 7.0, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 139.5, 134.0, 128.7, 127.9, 85.9, 80.7, 63.9, 50.1, 27.6, 16.1; HRMS (ESI) calcd for $C_{12}H_{12}ClN_3ONa$ $[M+Na]^+$ 272.0567, found 272.0566.

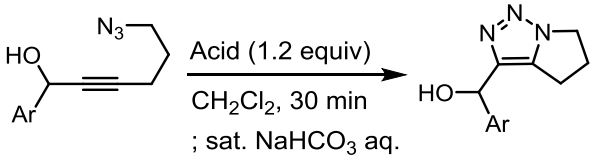
6-azido-1-(2,4-dichlorophenyl)hex-2-yn-1-ol(1j)



1j

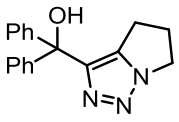
The reaction with tosylate compound (787.0 g, 1.7 mmol), *n*-BuLi (1.55 M in hexane, 2.27 mL, 1.85 mmol) and benzaldehyde (0.34 g, 1.94 mmol) in THF (20 mL) followed by collected the organic layer under vacuum affording the crude product 0.880 g. The crude product can be used to the next step without further purification.
Then the crude tosylate benzyl alcohol (0.880 g, 2.13 mmol) with sodium azide (0.166 g, 2.55 mmol) in DMF (10 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 5) gave azide **1j** (0.461 g, 87%) as a colorless oil.
Colorless oil; R_f value 0.38(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3346, 2932, 2098, 1469, 1254 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.67(d, 1H, *J* = 8.5 Hz), 7.39(d, 1H, *J* = 1.5 Hz), 7.30(dd, 1H, *J* = 8.5, 1.5 Hz), 5.75(br, 1H), 3.40(t, 2H, *J* = 6.5 Hz), 2.40(br, 1H), 2.39(td, 2H, *J* = 7.0, 2.0 Hz), 1.80(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 136.9, 134.8, 133.2, 129.5, 129.0, 127.5, 85.9, 79.6, 61.5, 50.1, 27.6, 16.1; LRMS (EI) 255($[M-N_2]^+$, 5%), 220(86), 175(64), 110(100); HRMS (EI) calcd for $C_{12}H_{11}Cl_2NO$ $[M-N_2]^+$ 255.0218, found 255.0188.

General Experimental Procedure of triazolations



To the mixture of propargyl alcohol (1.0 equiv) in dichloromethane (0.1 M to alcohols) under nitrogen atmosphere, TsOH H_2O (1.2 equiv) was added at ambient temperature. After 30 minutes, the reaction was quenched with saturated sodium bicarbonate aqueous solution, and was washed with brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography afforded triazole.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)dip henylmethanol(2a)

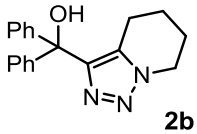


2a

The reaction with propargyl alcohol **1a** (42.0 mg, 0.144 mmol) and TsOH H_2O (38.5 mg, 0.173 mmol) in dichloromethane (2 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/4 to 1/1) afforded triazole **2a** (41.8 mg, 99%).

White crystal; R_f value 0.24(ethyl acetate/hexane = 1/1); m.p. 113–114 ℃; IR (NaCl, neat) ν_{max} 3378, 3059, 1491, 1448, 1316, 1168, 1021 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.25–7.34(m, 10H), 4.24(t, 2H, *J* = 7.5 Hz), 4.19(br-s, 1H, OH), 2.56(tt, 2H, *J* = 7.5, 7.5 Hz), 2.07(t, 2H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.5, 145.1, 140.2, 127.8, 127.34, 127.29, 76.6, 46.2, 27.9, 20.8; HRMS (ESI) calcd for $C_{18}H_{17}N_3ONa$ $[M+Na]^+$ 314.1269, found 314.1267.

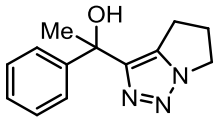
diphenyl(4,5,6,7-tetrahydro-[1,2,3]triazolo[1,5-a]pyridin-3-yl)methanol(2b)



2b

The reaction with propargyl alcohol **1b** (62.0 mg, 0.203 mmol) and TsOH ·H_2O (54.2 mg, 0.244 mmol) in dichloromethane (2 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to 1/1) afforded triazole **2b** (55.6mg, 90%).
Colorless oil; R_f value 0.11(ethyl acetate/hexane = 1/3); IR (NaCl, neat) ν_{max} 3376, 2953, 1490, 1447, 1016, 759, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.28–7.31(m, 10H), 4.34(t, 2H, *J* = 6.0 Hz), 4.28(br, 1H, OH), 2.00(t, 2H, *J* = 7.0 Hz), 1.93(m, 2H), 1.67(m, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 147.7, 145.2, 131.0, 127.9, 127.7, 127.5, 77.4, 46.6, 22.2, 20.6, 19.9; HRMS (ESI) calcd for $C_{19}H_{19}N_3ONa$ $[M+Na]^+$ 328.1426, found 328.1426.

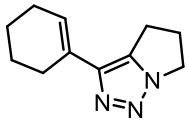
1-(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)-1-phenylethan-1-ol(2c)



2c

The reaction with propargyl alcohol **1c** (154 mg, 0.671 mmol) and TsOH ·H_2O (153 mg, 0.806 mmol) in dichloromethane (6.7 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/5 to 1/2 to 1/1 to 2/1) afforded triazole **2c** (114.0 mg, 74%).
Colorless oil; R_f value 0.28(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3362, 2980, 1446, 1066, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.48(d, 2H, *J* = 8.0 Hz), 7.33(dd, 2H, *J* = 8.0, 7.5 Hz), 7.25(dd, 1H, *J* = 7.0, 6.5 Hz), 4.25(t, 2H, *J* = 7.5 Hz), 3.26(s, 1H, OH), 2.66(m, 2H), 2.49(m, 2H), 1.99(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 146.4, 146.2, 138.6, 128.1, 127.0, 125.2, 71.9, 46.2, 30.0, 28.1, 21.2,; HRMS (ESI) calcd for $C_{13}H_{15}N_3O$ $[M+Na]^+$ 252.1113, found 252.1118.

3-(cyclohex-1-en-1-yl)-5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazole (2d')



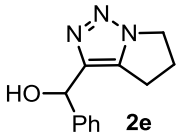
2d'

The reaction with propargyl alcohol **1d** (100 mg, 0.482 mmol) and TsOH ·H_2O (110 mg, 0.579 mmol) in dichloromethane (4.8 ml) followed by silica gel column

purification (ethyl acetate/hexane = 1/10 to 1/4 to 1/2 to 1/1) afforded triazole **2d'** (45.7 mg, 50%) along with dehydrate propargyl alcohol **1d** (30.1 mg, 30%).

Colorless oil; R_f value 0.13(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 2926, 1558 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.19(m, 1H), 4.30(t, 2H, *J* = 7.5 Hz), 2.96(t, 2H, *J* = 8.0 Hz), 2.80 (tt, 2H, *J* = 8.0, 7.5 Hz), 2.21-2.18(m, 2H), 1.78-1.73(m, 2H), 1.68-1.63(m, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 141.4, 137.2, 128.6, 124.2, 46.0, 28.3, 26.0, 25.3, 22.5, 22.2, 22.0; HRMS (ESI) calcd for $C_{11}H_{16}N_3$ $[M+H]^+$ 190.1344, found 190.1338.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(phenyl)methanol (2e)

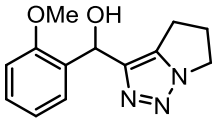


2e

The reaction with propargyl alcohol **1e** (50 mg, 0.232 mmol) and TsOH·H_2O (53.0 mg, 0.278 mmol) in dichloromethane (2.3 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to ethyl acetate) afforded triazole **2e** (31.8 mg, 63%).

Colorless oil; R_f value 0.15(dichloromethane/mechanol = 20/1); IR (NaCl, neat) ν_{max} 3250, 1228, 1487, 1087, 1013, 805 cm^{-1}; cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.43(d, 2H, *J* = 7.0 Hz), 7.34(dd, 1H, *J* = 7.0, 7.5 Hz), 7.28(t, 2H, *J* = 7.5 Hz), 6.01(sd, 1H, *J* = 2.5 Hz), 4.20(t, 2H, *J* = 7.0 Hz), 4.12(sd, 1H, *J* = 3.0 Hz), 2.65-2.55(m, 2H), 2.48-2.42(m, 1H), 2.28-2.22(m, 1H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 143.0, 141.8, 139.4, 128.3, 127.6, 126.1, 68.6, 46.2, 28.0, 20.6; HRMS (ESI) calcd for $C_{12}H_{11}NONa$ $[M+Na]^+$ 238.0956, found 238.0955.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(2-methoxyphenyl)methanol (2f)

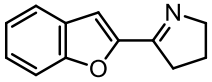


2f

The reaction with propargyl alcohol **1f** (80 mg, 0.326 mmol) and TsOH·H_2O (74.5 mg, 0.19 mmol) in dichloromethane (3 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to 1/1 to 2/1) afforded triazole **2f** (56.1 mg, 70%), along with imine **2f'** (3.5mg, 6%).

White solid; R_f value 0.43(methaol/dichloromethane = 1/10); m.p. 119.1–119.4 ℃; IR (NaCl, neat) ν_{max} 3340, 1490, 1240, 1028 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.47(dd, 1H, *J* = 7.5, 2.0 Hz), 7.27(ddd, 1H, *J* = 8.0, 7.5, 2.0 Hz), 6.98(dd, 1H, *J* = 8.0, 8.0 Hz), 6.87(d, 1H, *J* = 8.0 Hz), 6.23(d, 1H, *J* = 5.0 Hz), 4.23(t, 2H, *J* = 7.0 Hz), 3.80(s, 3H), 3.69(d, 1H, OH, *J* = 5.0 Hz), 2.63(tt, 2H, *J* = 7.5, 7.5 Hz), 2.38(td, 1H, *J* = 15.0, 7.5 Hz), 2.38(td, 1H, *J* = 15.0, 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 156.2, 142.1, 139.2, 129.9, 128.7, 127.2, 120.7, 110.3, 64.7, 55.4, 46.1, 28.0, 20.6; HRMS (ESI) calcd for $C_{13}H_{15}N_3O_2$ $[M+Na]^+$ 268.1062, found 268.1062.

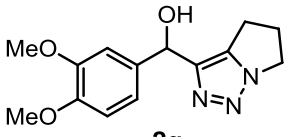
5-(benzofuran-2-yl)-3,4-dihydro-2H-pyrrole(2f')



2f'

Colorless oil; R_f value 0.48 (methanol/dichloromethane = 1/10); IR (NaCl, neat) ν_{max} 3423, 1630, 824, 599 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.62(d, 1H, *J* = 8.0 Hz), 7.56(d, 1H, *J* = 7.5 Hz), 7.35(dd, 1H, *J* = 8.0, 7.5 Hz), 7.26(dd, 1H, *J* = 7.5, 7.5 Hz), 7.10(s, 1H), 4.14(t, 2H, *J* = 8.0 Hz), 2.97(t, 2H, *J* = 8.0 Hz), 2.07(tt, 2H, *J* = 8.0, 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 164.7, 155.4, 151.3, 127.8, 126.2, 123.2, 121.9, 111.9, 109.2, 62.0, 35.0, 22.5; HRMS (ESI) calcd for $C_{12}H_{12}NO$ $[M+H]^+$ 186.0919, found 186.0918.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(3,4-dimethoxyphenyl)methanol (2g)

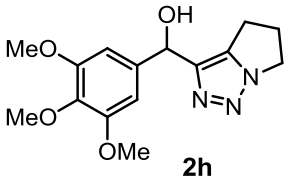


2g

The reaction with propargyl alcohol **1g** (150 mg, 0.545 mmol) and TsOH ·H_2O (124.4 mg, 0.654 mmol) in dichloromethane (5 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to ethyl acetate) afforded triazole **2g** (106.7 mg, 71%).

White solid; R_f value 0.10(ethyl acetate/hexane = 1/1); m.p. 125.4–125.7 ℃; IR (NaCl, neat) ν_{max} 3433, 1644, 1514, 1234, 1137 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.01(d, 1H, *J* = 2.0 Hz), 6.94(dd, 1H, *J* = 8.0, 2.0 Hz), 6.84(d, 1H, *J* = 8.0 Hz), 5.95(s, 1H), 4.24(t, 2H, *J* = 7.5 Hz), 2.77(br, 1H, OH), 2.63(m, 2H), 2.47(ddd, 1H, *J* = 15.1, 8.5, 6.0 Hz), 2.33(ddd, 1H, *J* = 15.1, 8.0, 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 149.0, 148.5, 143.0, 139.2, 134.4, 118.4, 110.8, 109.3, 68.6, 55.9, 46.2, 28.0, 20.7; HRMS (ESI) calcd for $C_{14}H_{17}N_3O_3Na$ $[M+Na]^+$ 298.1168, found 298.1170.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(3,4,5-trimethoxyphenyl)methanol(2h)



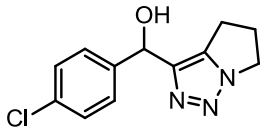
2h

The reaction with propargyl alcohol **1h** (200 mg, 0.655 mmol) and TsOH ·H_2O (149.5 mg, 0.786 mmol) in dichloromethane (6.6 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to 1/1 to ethyl acetate then methanol/dichloromethane = 30/1 to 20/1) afforded triazole **2h** (168.2 mg, 84%).

White crystal; R_f value 0.22(dichloromethane/mechanol = 20/1); m.p. 137.8–138.2 ℃;

IR (NaCl, neat) ν_{max} 3433, 1233, 1124 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.66(s, 2H), 5.91(s, 1H), 4.17(t, 2H, *J* = 7.5 Hz), 3.78 (s, 6H), 3.77(s, 3H), 2.48–2.64(m, 3H), 2.29(ddd, 1H, *J* = 16.0, 9.5, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 153.0, 143.0, 139.2, 137.7, 137.0, 102.8, 68.3, 60.7, 56.0, 46.1, 27.9, 20.7; HRMS (ESI) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1273, found 328.1276.

(4-chlorophenyl)(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)methanol(2i)

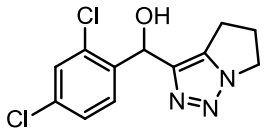


2i

The reaction with propargyl alcohol **1i** (200 mg, 0.801 mmol) and TsOH·H_2O (182.8 mg, 0.961 mmol) in dichloromethane (8 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/10 to 1/5 to 1/2 to 1/1 to 2/1) afforded triazole **2i** (121.7 mg, 61%).

White crystal; R_f value 0.2(ethyl acetate/hexane = 1/2); m.p. 142.8–142.9 ℃; IR (NaCl, neat) ν_{max} 3250, 1228, 1487, 1087, 1013, 805 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.38(d, 2H, *J* = 8.5 Hz), 7.32(d, 2H, *J* = 8.5 Hz), 6.00(s, 1H), 4.23(t, 2H, *J* = 7.5 Hz), 2.64(m, 2H), 2.47(ddd, 1H, *J* = 15.0, 8.5, 6.5 Hz), 2.29(ddd, 1H, *J* = 15.0, 9.0, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 142.6, 140.3, 139.3, 133.4, 128.5, 127.6, 68.0, 46.3, 28.0, 20.7; HRMS (ESI) calcd for $C_{12}H_{12}ClN_3ONa$ $[M+Na]^+$ 272.0567, found 272.0570.

(2,4-dichlorophenyl)(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)methanol(2j)

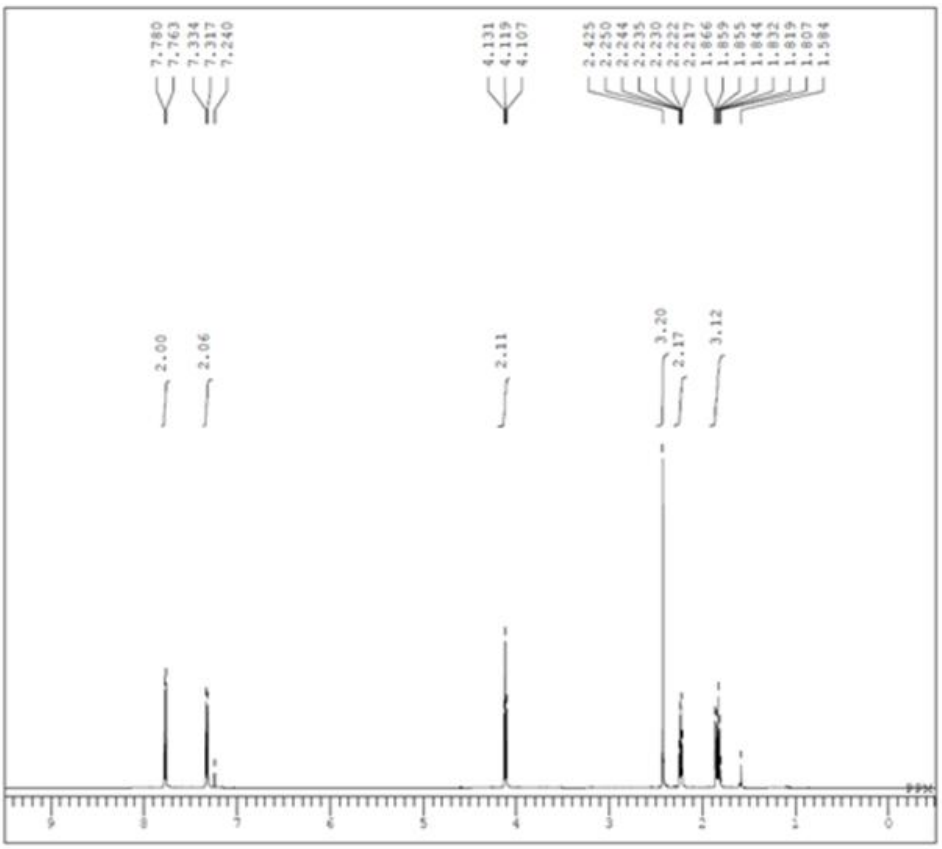


2j

The reaction with propargyl alcohol **1j** (150 mg, 0.528 mmol) and TsOH·H_2O (120.5 mg, 0.633 mmol) in dichloromethane (5 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/5 to 1/2 to 1/1 to 2/1 to ethyl acetate then methanol / dichloromethane = 20/1) afforded triazole **2j** (66.3 mg, 44%).

White crystal; R_f value 0.1(ethyl acetate/hexane = 1/2); m.p. 176.8–170.0 ℃; IR (NaCl, neat) ν_{max} 3224, 2879, 1589, 1035, 858 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.76(d, 1H, *J* = 8.5 Hz), 7.36(d, 1H, *J* = 1.0 Hz), 7.33(dd, 1H, *J* = 8.5, 1.0 Hz), 6.30(s, 1H), 4.43(br, 1H, OH), 4.25(t, 2H, *J* = 7.0 Hz), 2.65(tdd, 2H, *J* = 8.0, 7.5, 7.0 Hz), 2.37(td, 1H, *J* = 16.0, 7.5 Hz), 2.30(td, 1H, *J* = 16.0, 8.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 141.0, 139.3, 137.9, 133.9, 132.6, 129.0, 128.9, 127.4, 64.9, 46.3, 28.0, 20.5; HRMS (ESI) calcd for $C_{12}H_{11}Cl_2N_3ONa$ $[M+Na]^+$ 306.0177, found 306.0177.


OTs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2.222
2.217
1.666
1.659
1.655
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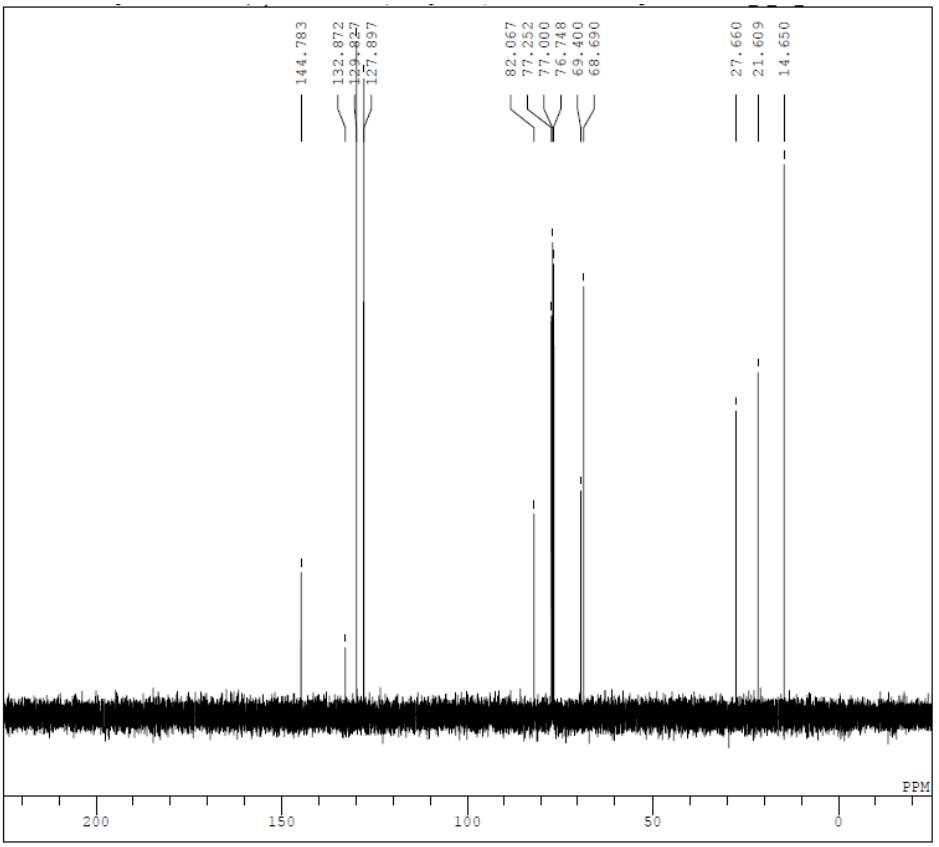
2.06
2.11
3.20
2.17
3.12
PPM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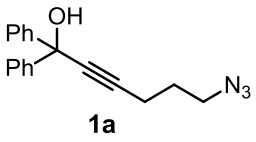
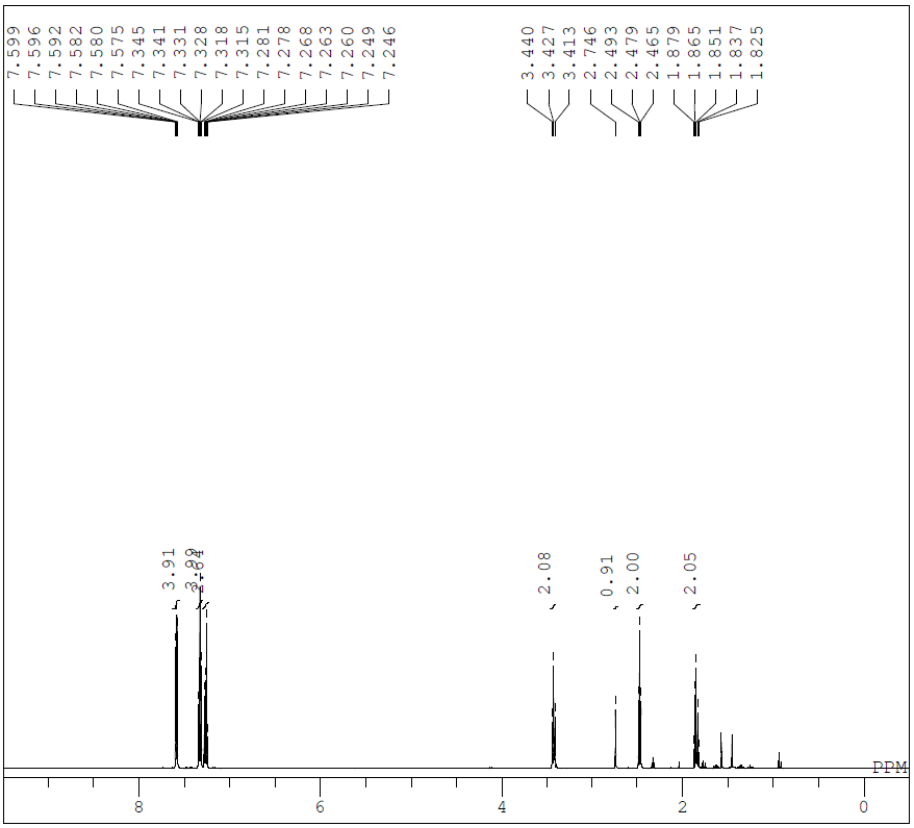

OH
Ph
Ph
N3

1a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7.281
7.278
7.268
7.263
7.260
7.249
7.246
3.440
3.427
3.413
2.746
2.493
2.479
2.465
1.879
1.865
1.851
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3.89
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0.91
2.00
2.05
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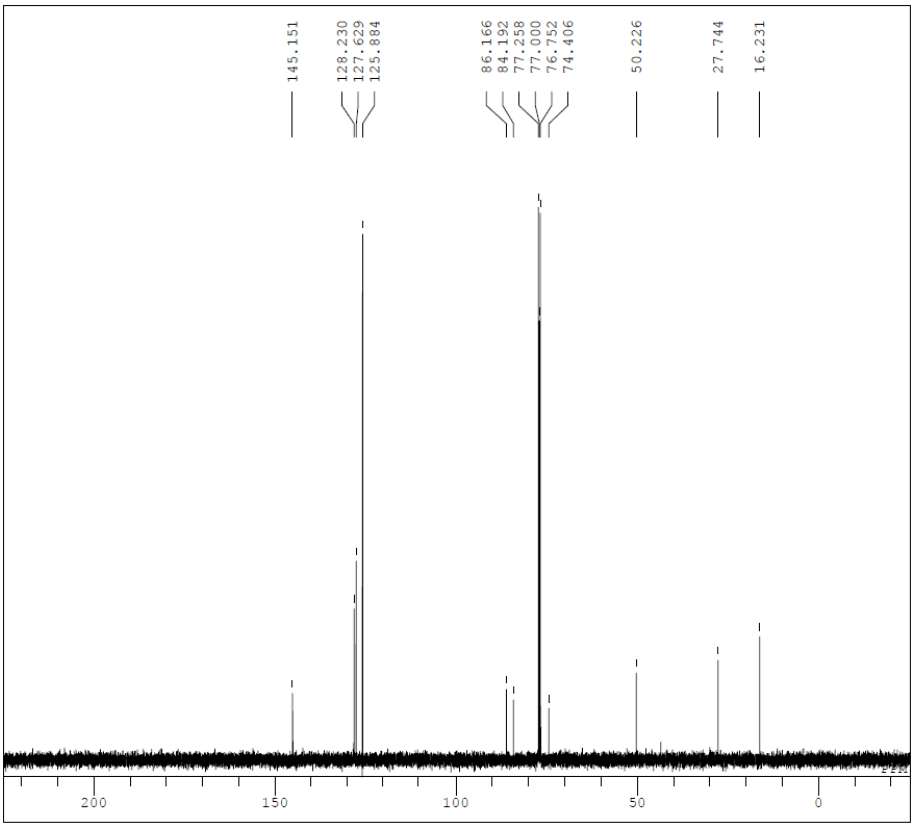
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127.629
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16.231
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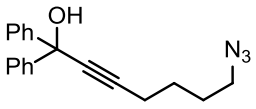
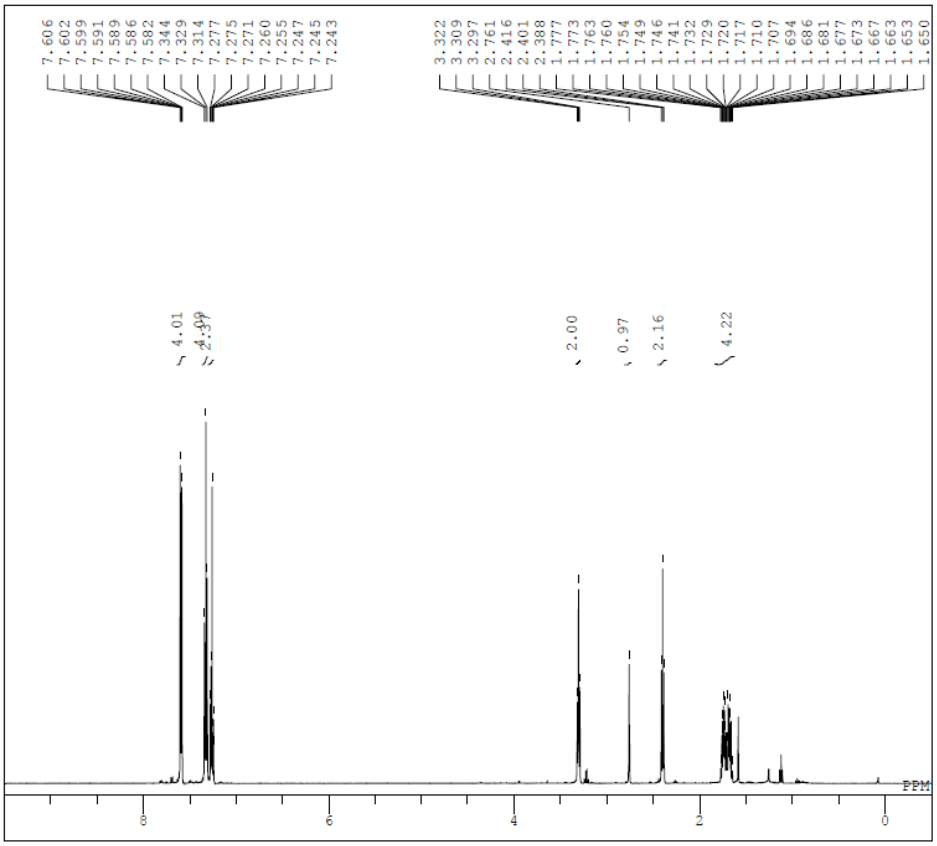

OH
Ph
Ph
N3

1b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7.271
7.260
7.255
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7.245
7.243
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3.309
3.297
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1.686
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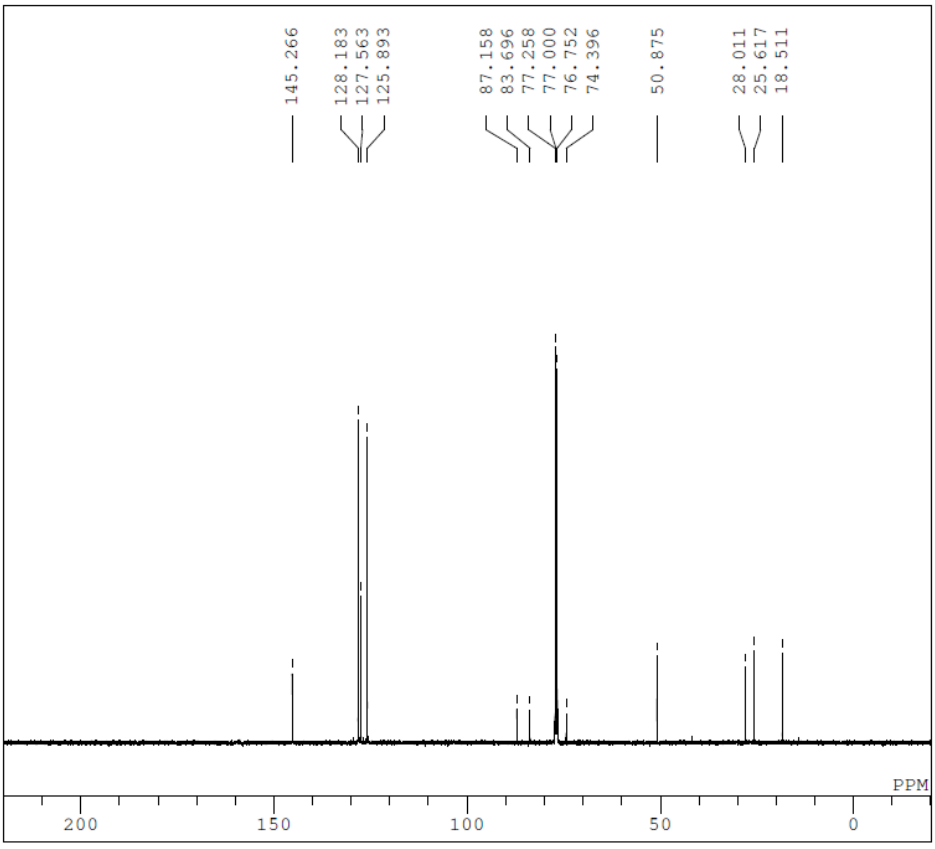
PPM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18.511
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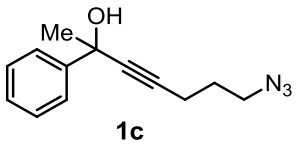
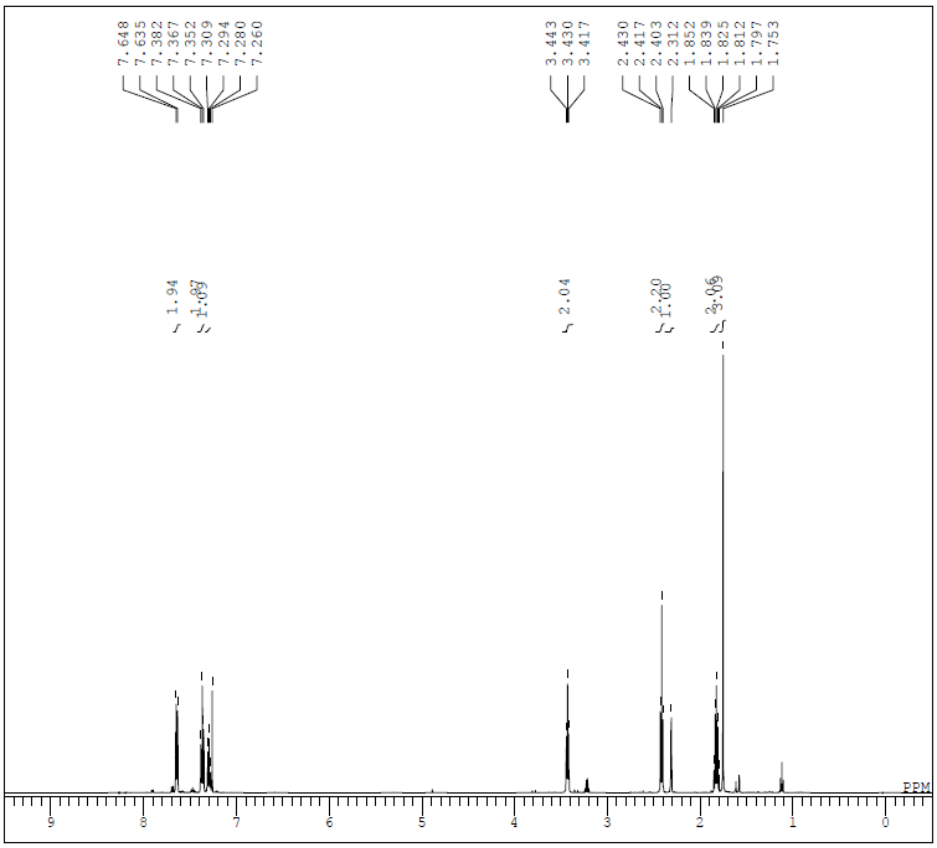

OH
Me
N3

1c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3.417
2.430
2.417
2.403
2.312
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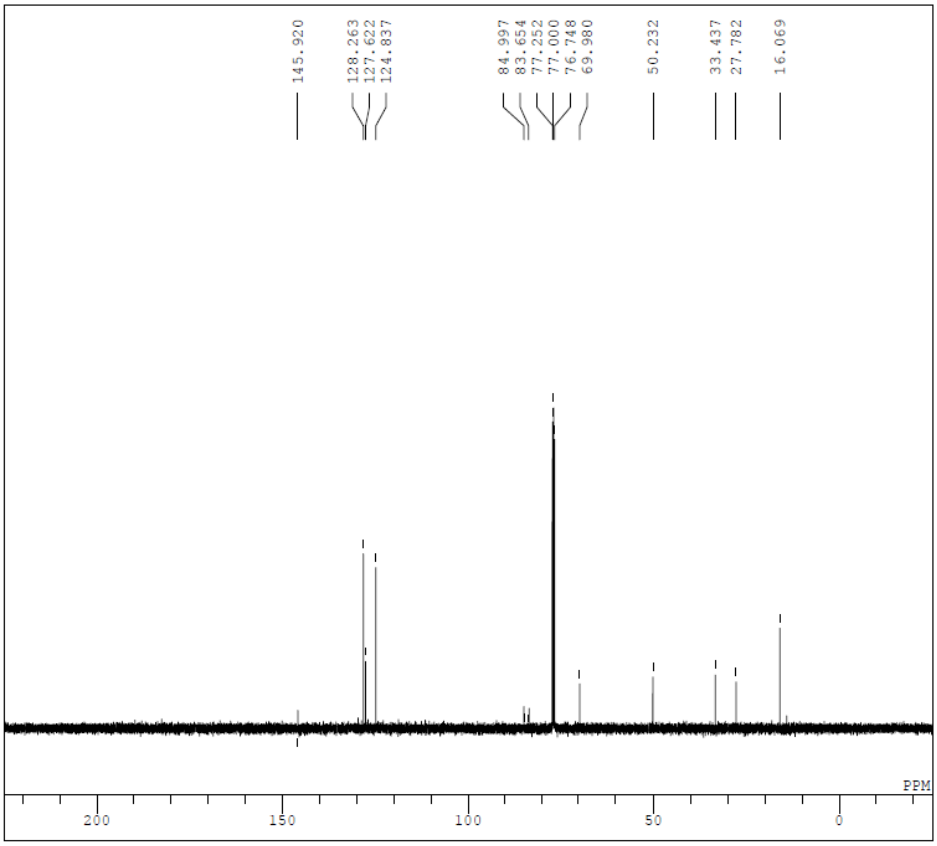
PPM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77.000
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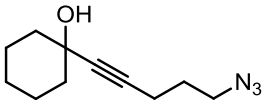
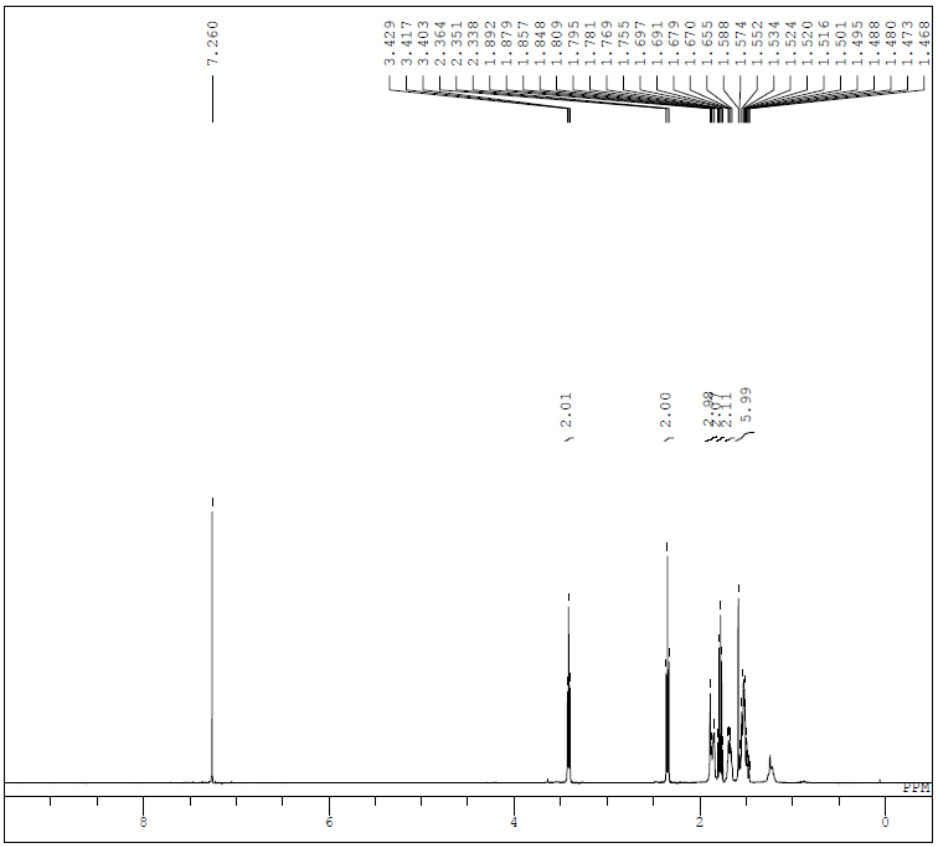
PPM


OH
N3

1d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1.879
1.857
1.848
1.809
1.795
1.781
1.769
1.755
1.697
1.691
1.679
1.670
1.655
1.588
1.574
1.552
1.534
1.524
1.520
1.516
1.501
1.495
1.488
1.480
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2.08
2.07
2.11
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2
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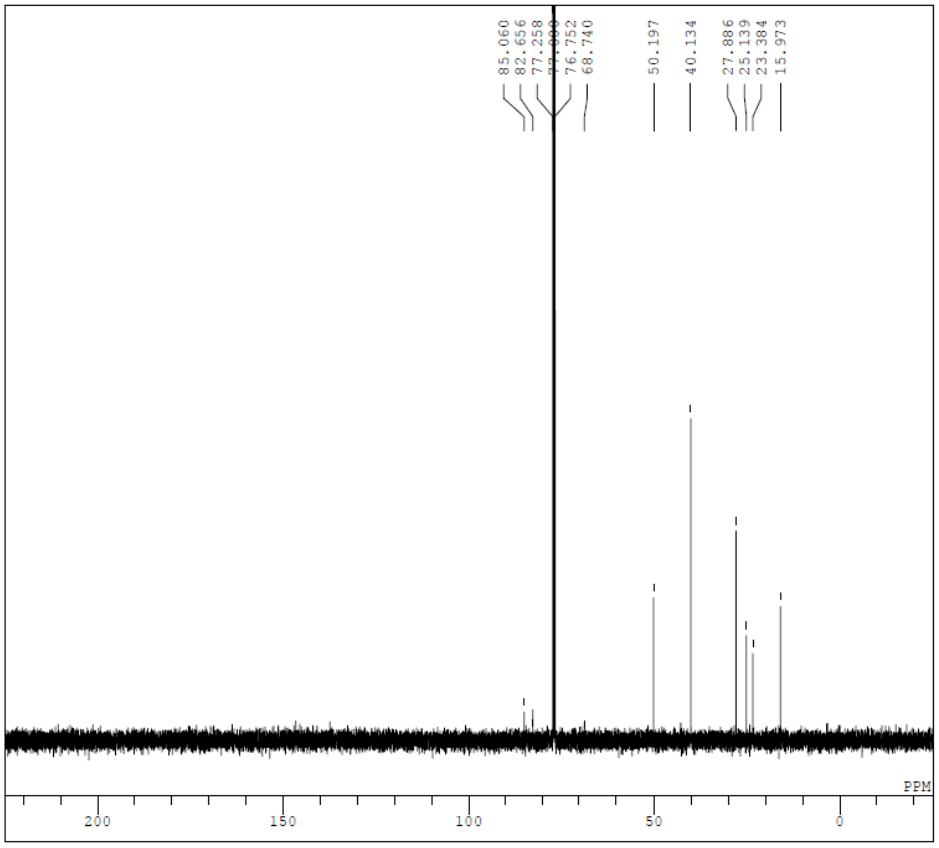
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40.134
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25.139
23.384
15.973
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50
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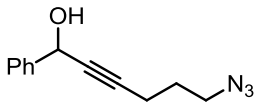
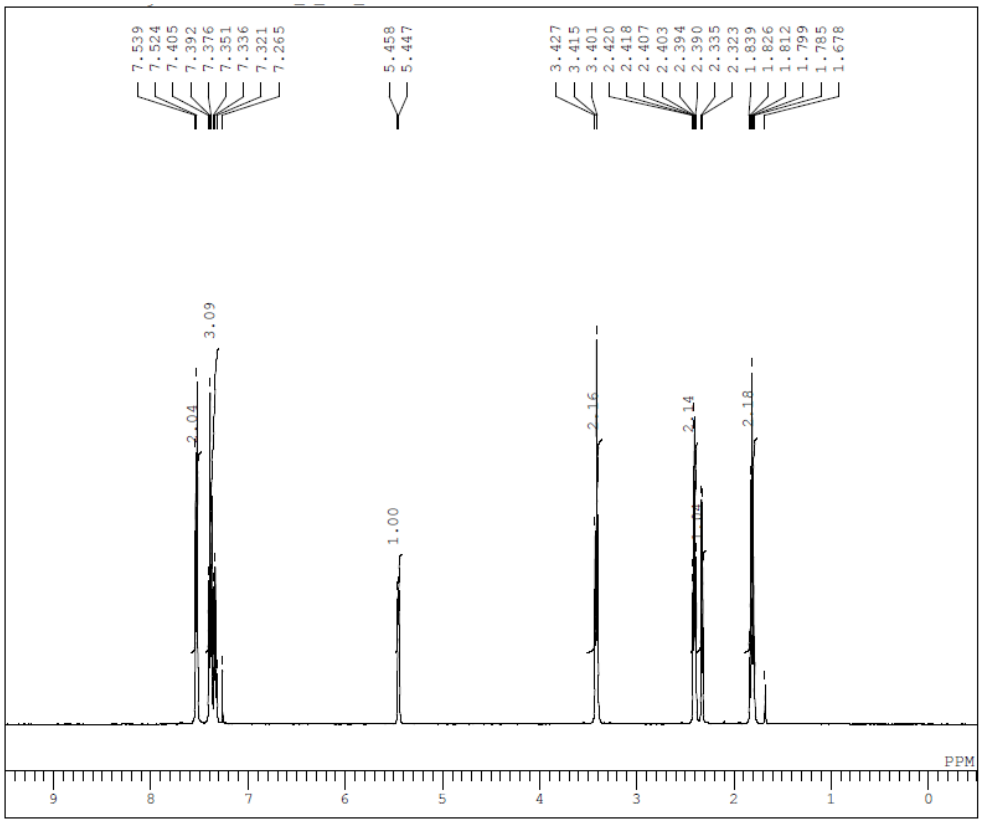

OH
Ph
N3

1e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7.321
7.265
5.458
5.447
3.427
3.415
3.401
2.420
2.418
2.407
2.403
2.394
2.390
2.335
2.323
1.839
1.826
1.812
1.799
1.785
1.678
3.09
2.04
1.00
2.16
2.14
2.18
PPM
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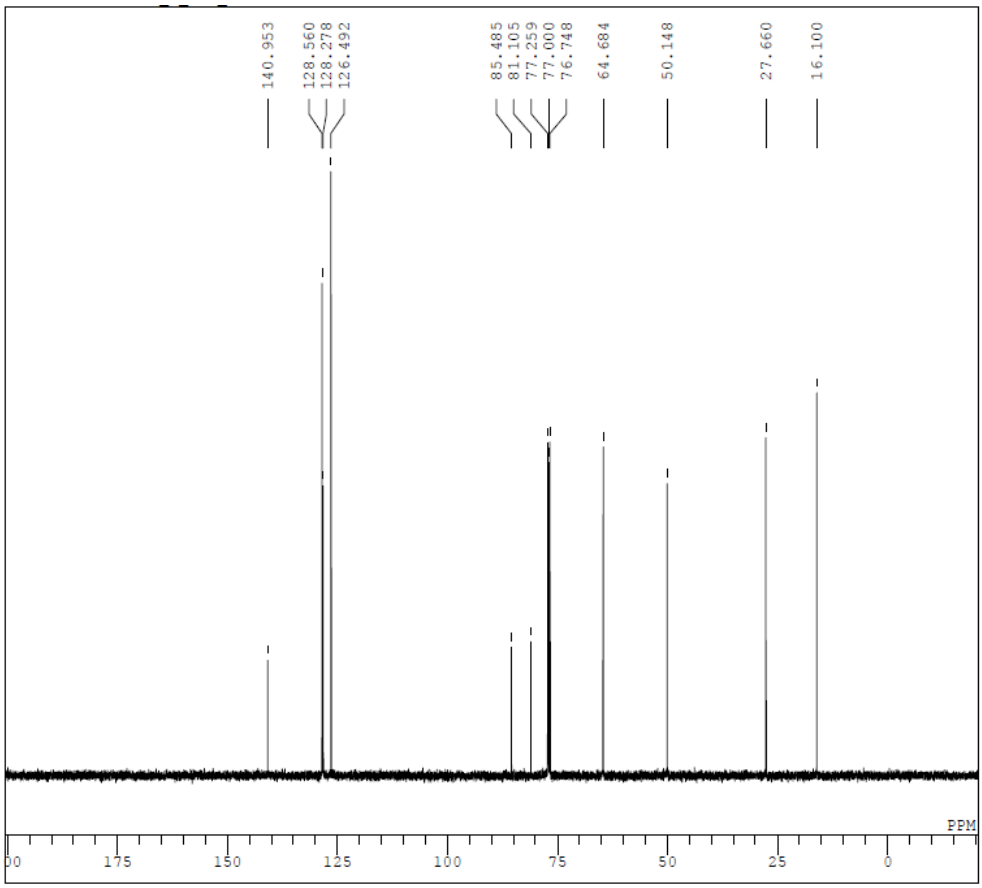
8
7
6
5
4
3
2
1
0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126.492
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81.105
77.259
77.000
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50.148
27.660
16.100
PPM
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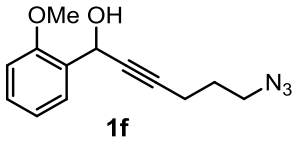
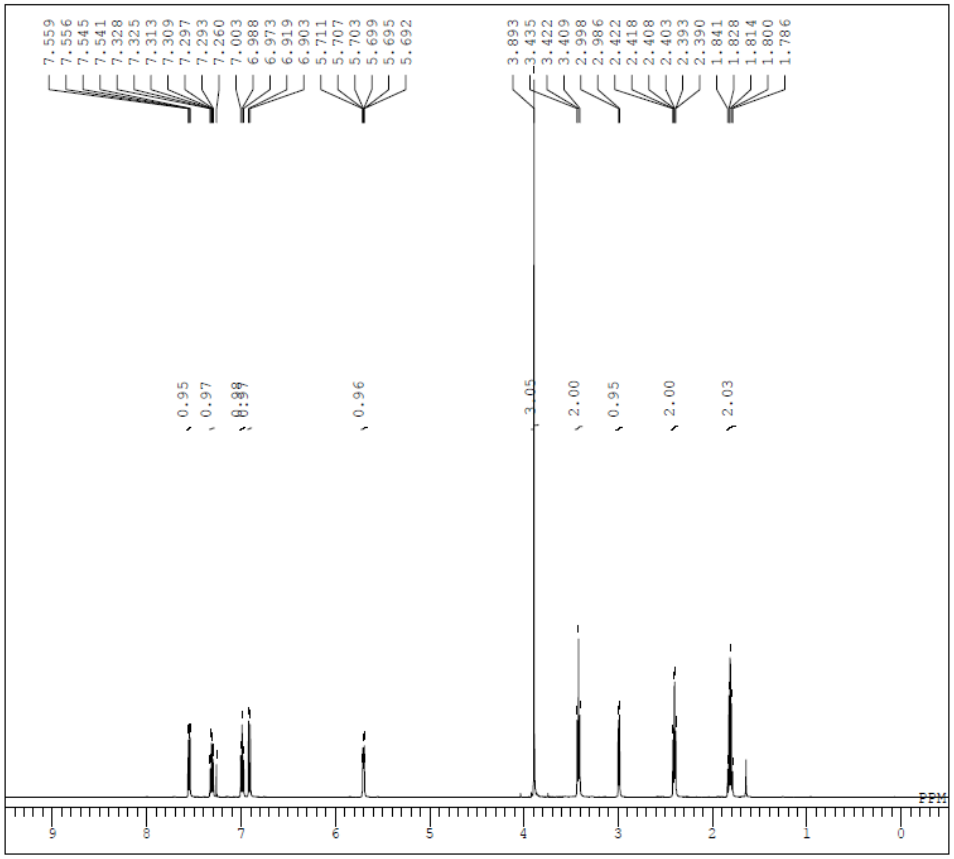
175
150
125
100
75
50
25
0


OMe
OH
N3

1f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7.325
7.313
7.309
7.297
7.293
7.260
7.003
6.988
6.973
6.919
6.903
5.711
5.707
5.703
5.699
5.695
5.692
3.893
3.435
3.422
3.409
2.998
2.986
2.422
2.418
2.408
2.403
2.393
2.390
1.841
1.828
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1.800
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0.97
0.96
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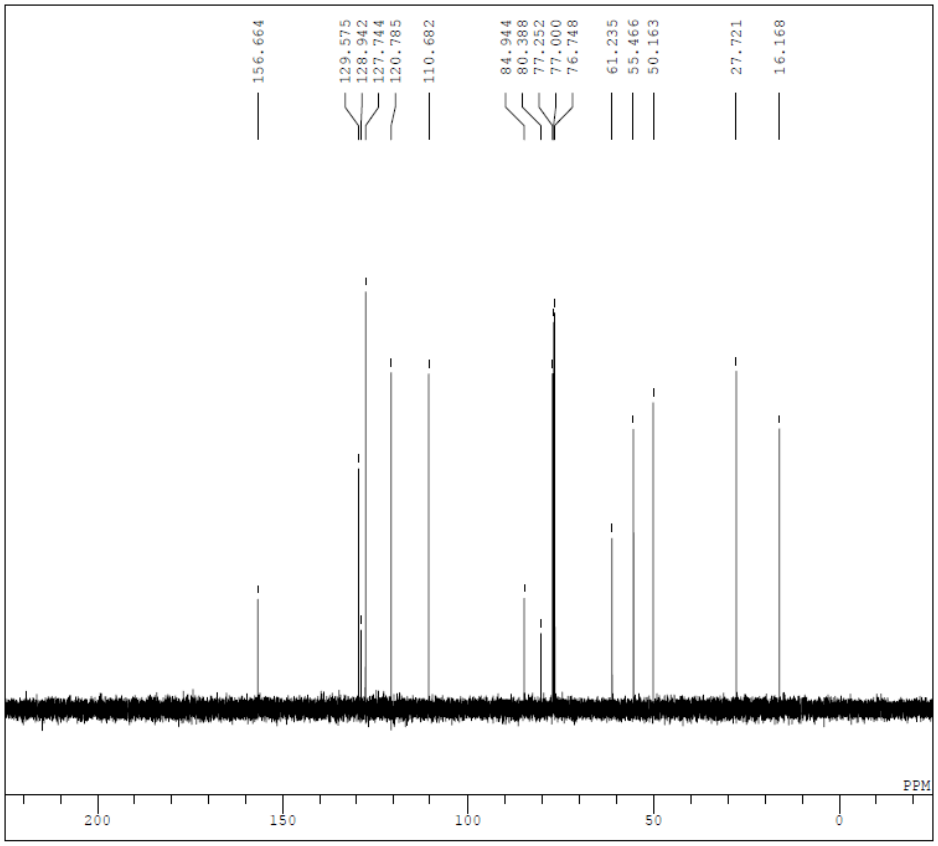
2.00
0.95
2.00
2.03
PPM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127.744
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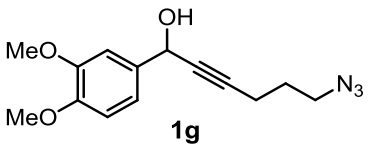
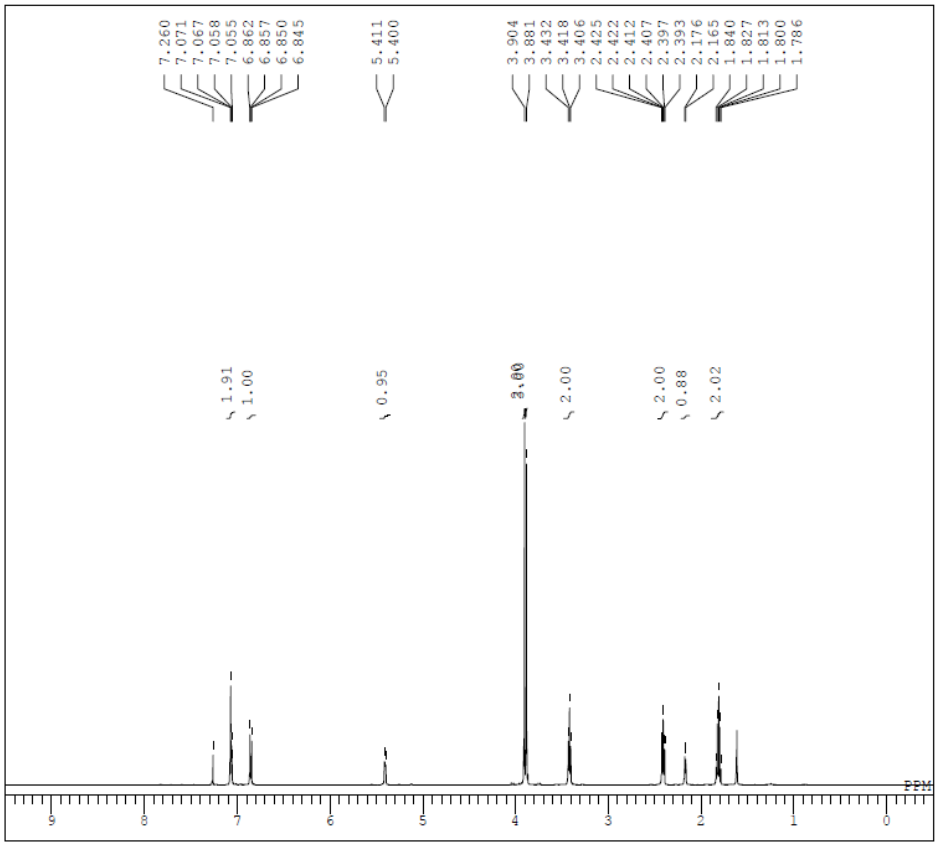
PPM


OH
MeO
MeO
N3

1g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7.067
7.058
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6.850
6.845
5.411
5.400
3.904
3.881
3.432
3.418
3.406
2.425
2.422
2.412
2.407
2.397
2.393
2.176
2.165
1.840
1.827
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2.00
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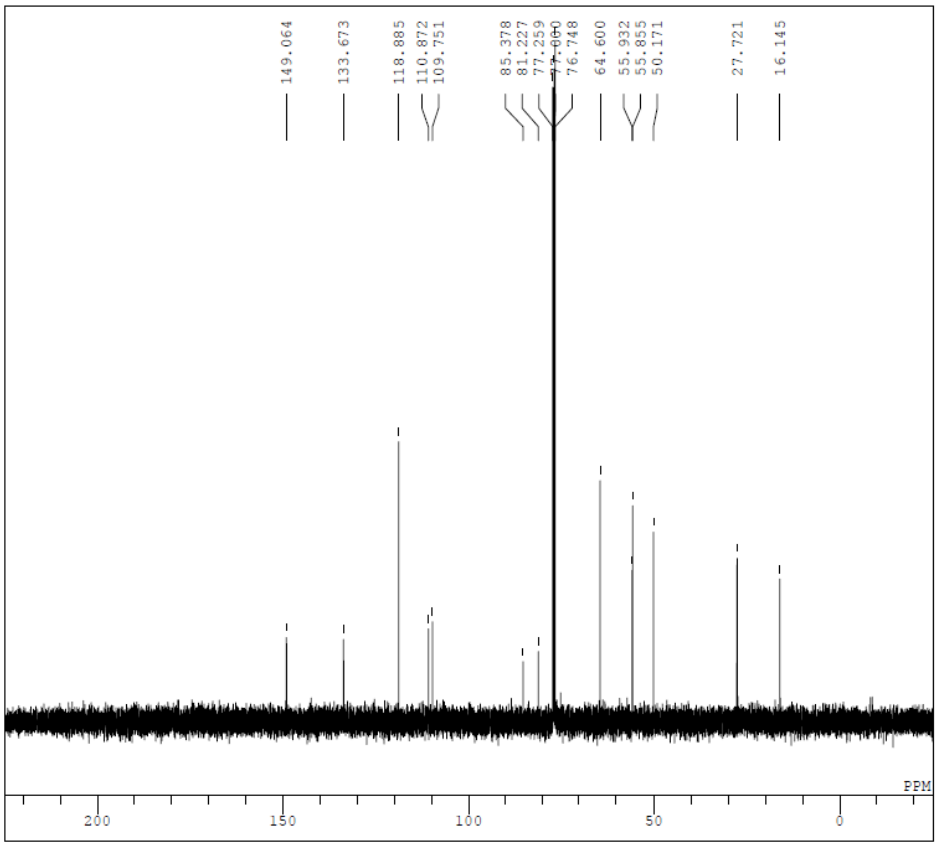
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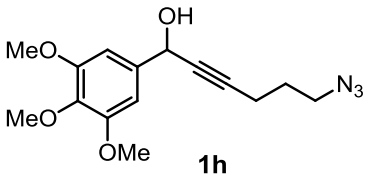
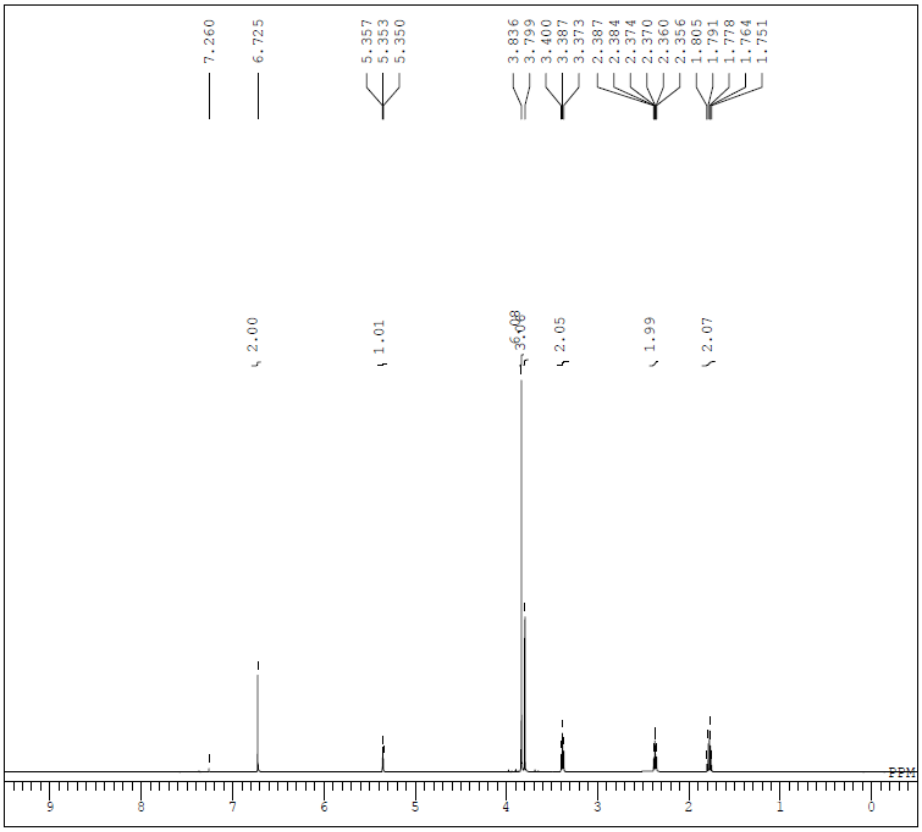

OH
MeO
MeO
OMe
N3

1h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3.400
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3.373
2.387
2.384
2.374
2.370
2.360
2.356
1.805
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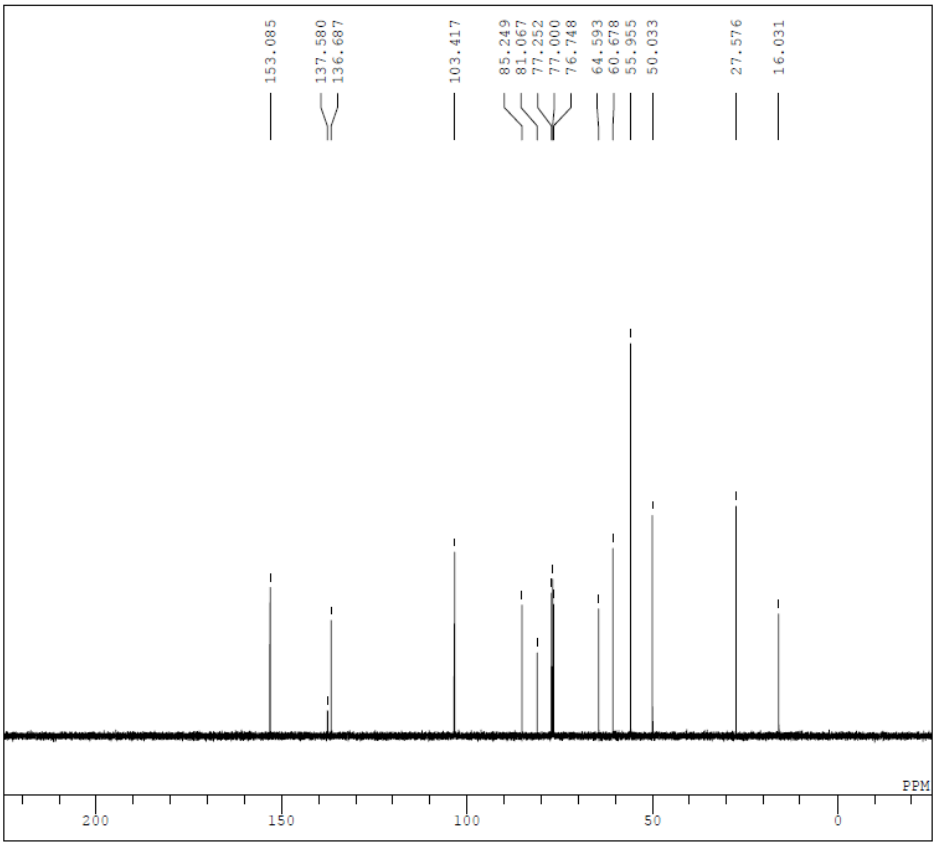
1.01
6.08
5.00
2.05
1.99
2.07
PPM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103.417
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77.000
76.748
64.593
60.678
55.955
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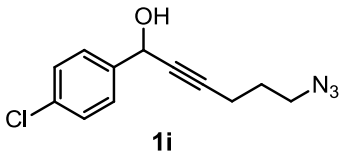
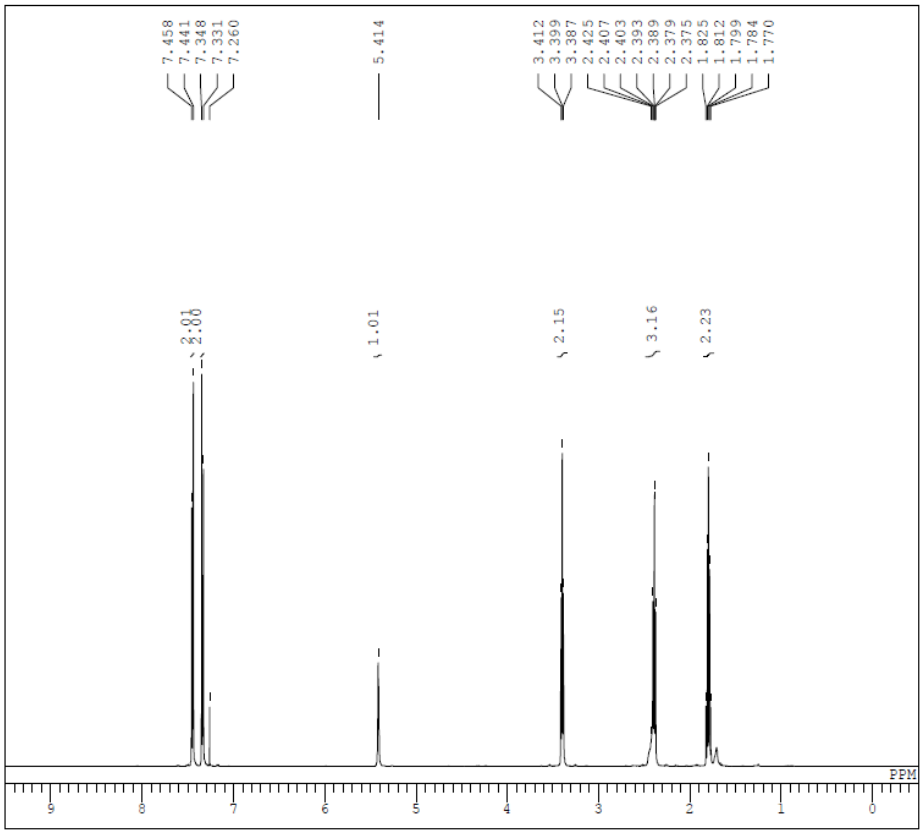
16.031
PPM


OH
Cl
N_3

1i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7.260
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3.387
2.425
2.407
2.403
2.393
2.389
2.379
2.375
1.825
1.812
1.799
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2.01
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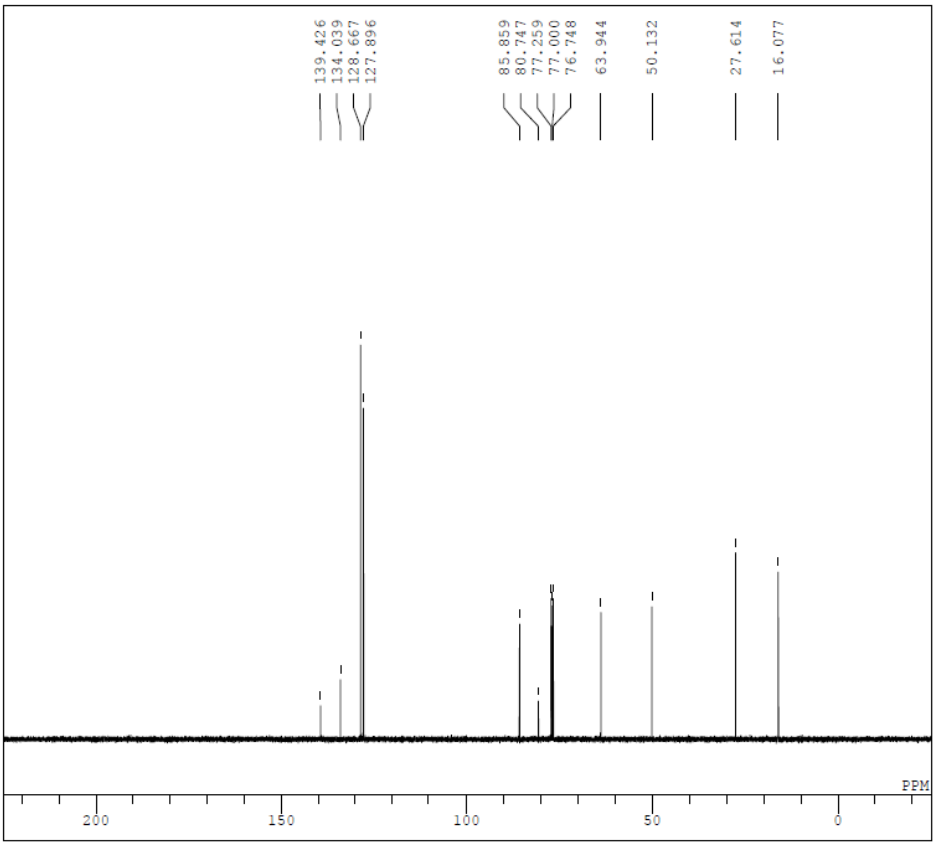
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16.077
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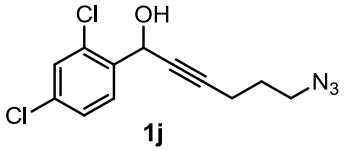
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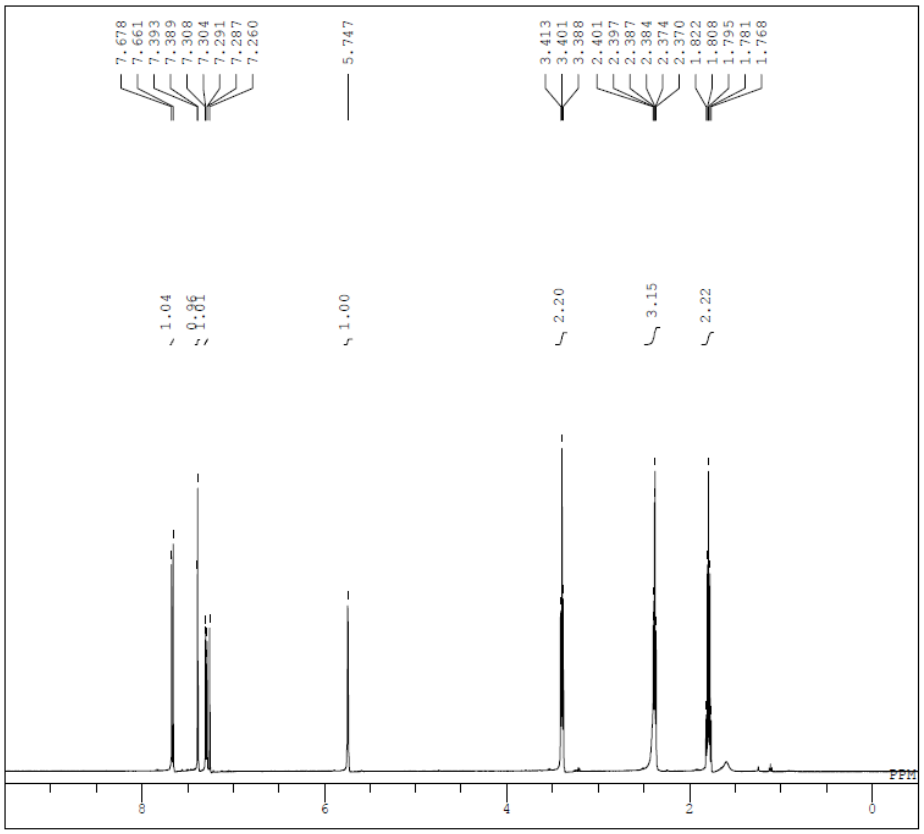
OH
Cl
N3

1j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3.388
2.401
2.397
2.387
2.384
2.374
2.370
1.822
1.808
1.795
1.781
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2.22
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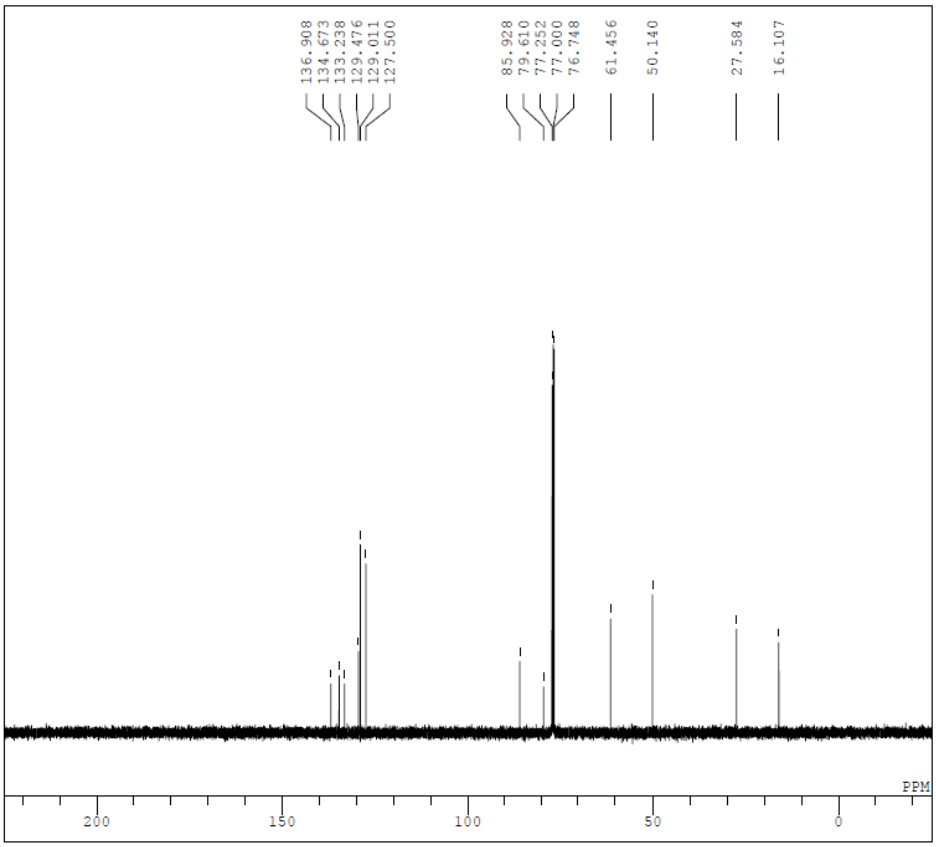
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50.140
27.584
16.107
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50
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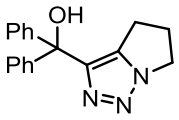
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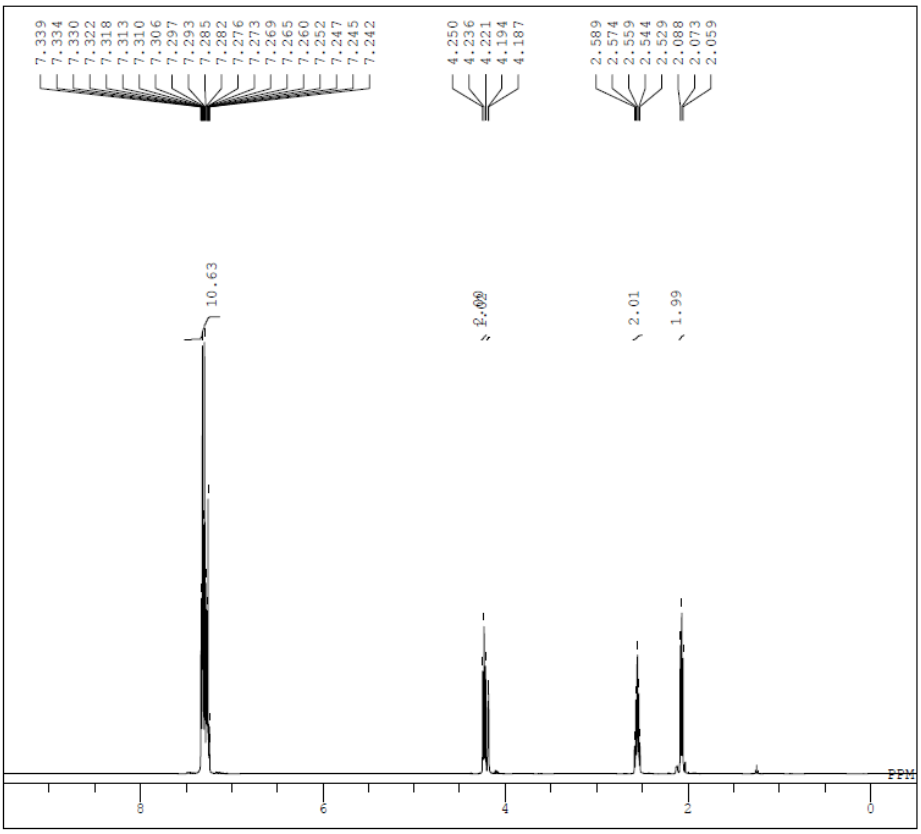
OH
Ph
N
N=N

2a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7.310
7.306
7.297
7.293
7.285
7.282
7.276
7.273
7.269
7.265
7.260
7.252
7.247
7.245
7.242
4.250
4.236
4.221
4.194
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2.589
2.574
2.559
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1.99
PPM
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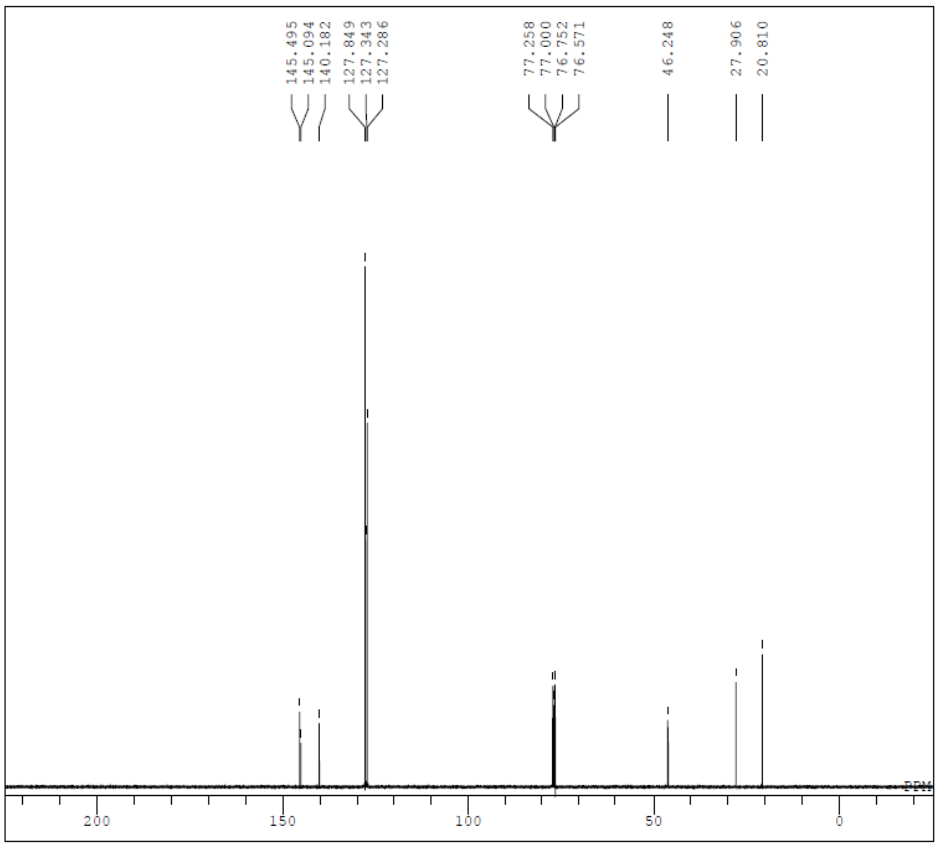
0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76.571
46.248
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20.810
PPM
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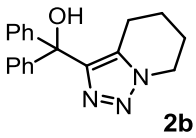
150
100
50
0


Ph
OH
Ph
N
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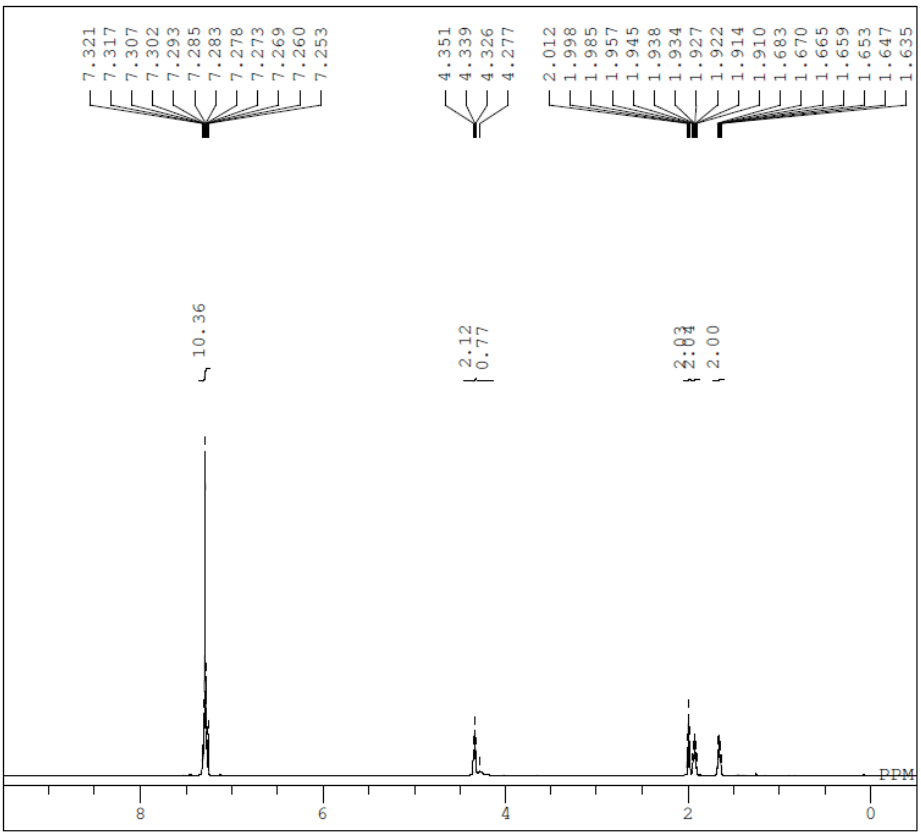
2b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7.269
7.260
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4.326
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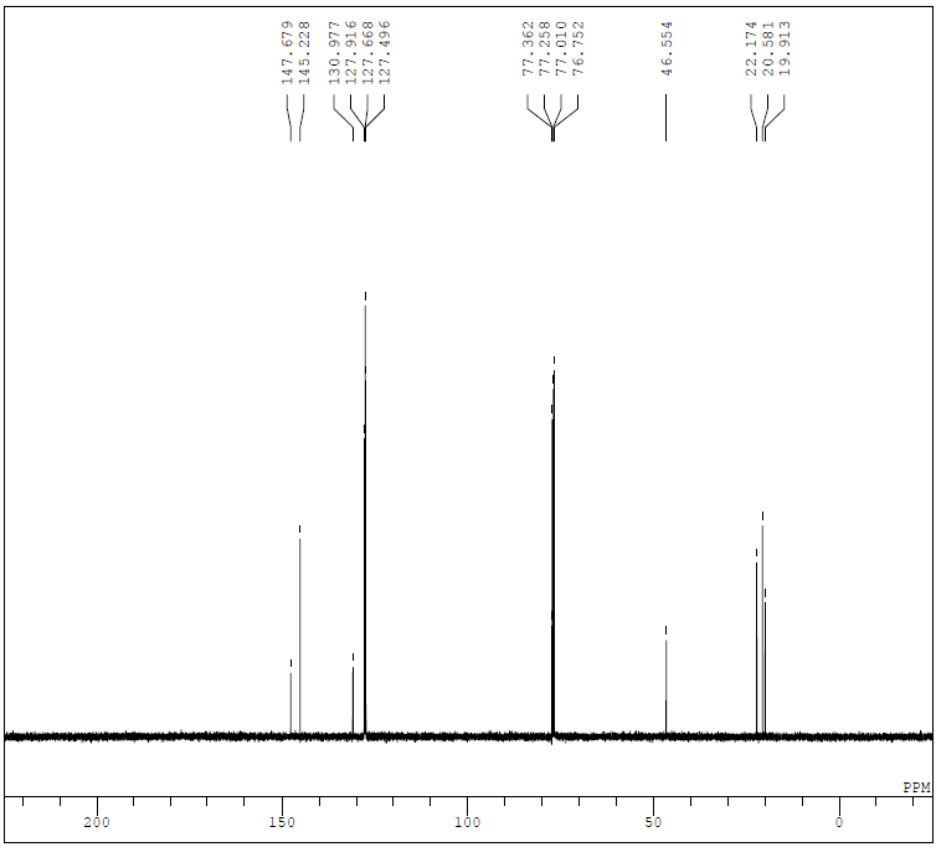
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145.228
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127.668
127.496
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76.752
46.554
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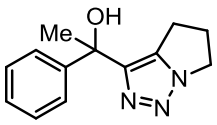
Me
OH
N
N=N

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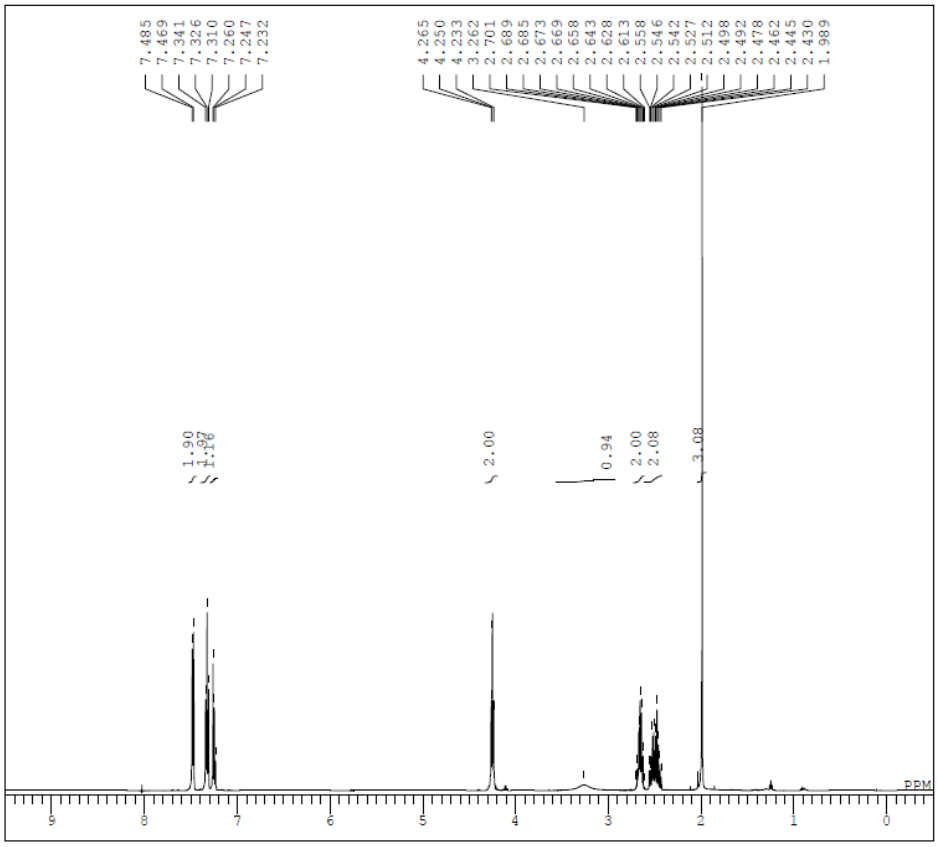
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7.232
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4.250
4.233
3.262
2.701
2.689
2.685
2.673
2.669
2.658
2.643
2.628
2.613
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2.546
2.542
2.527
2.512
2.498
2.492
2.478
2.462
2.445
2.430
1.989
1.90
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3.08
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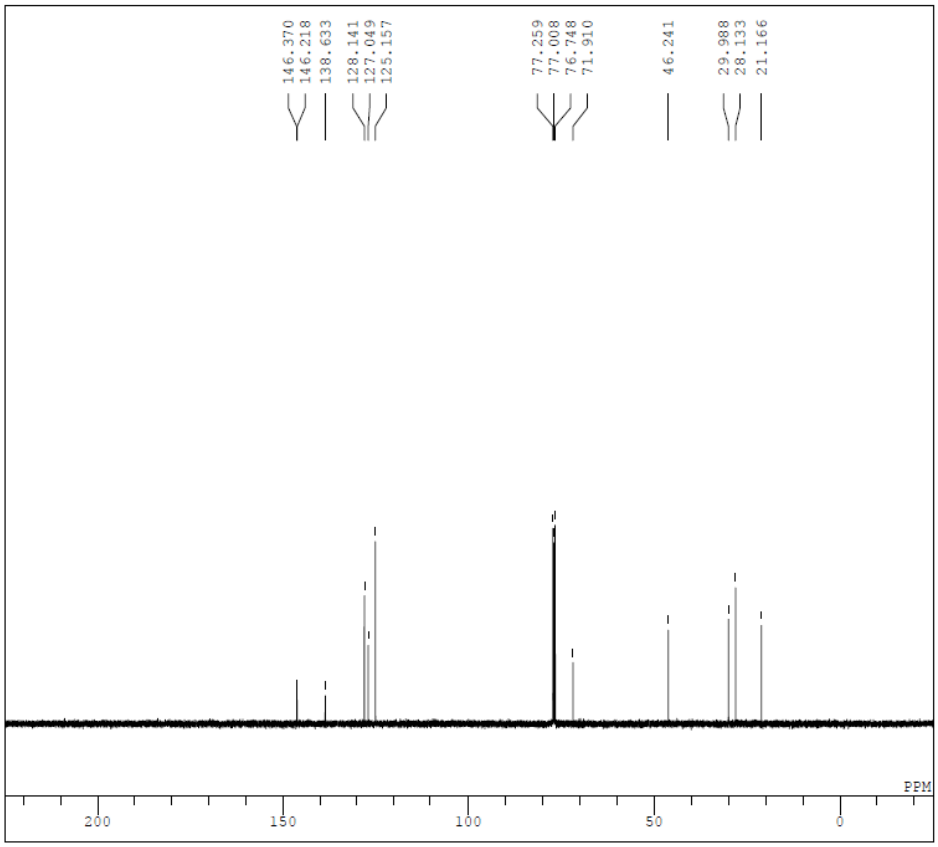
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21.166
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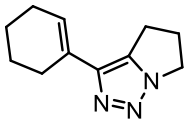

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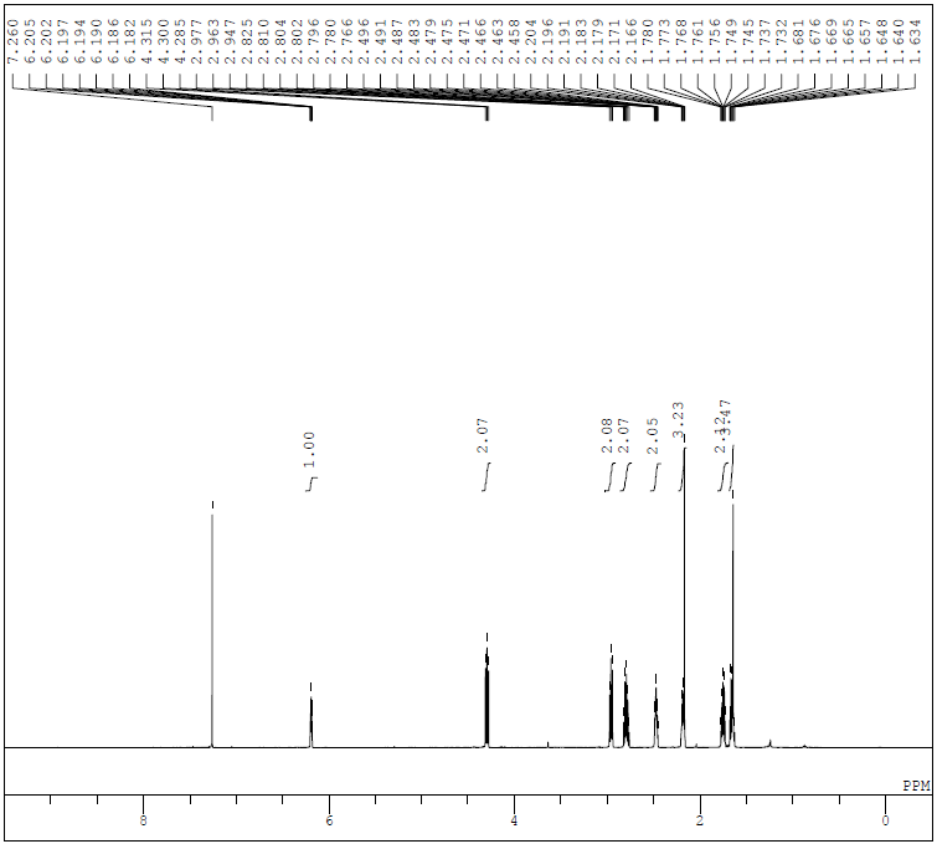
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6.202
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6.194
6.190
6.186
6.182
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4.300
4.285
2.977
2.963
2.947
2.825
2.810
2.804
2.802
2.796
2.780
2.766
2.496
2.491
2.487
2.483
2.479
2.475
2.471
2.466
2.463
2.458
2.204
2.196
2.191
2.183
2.179
2.171
2.166
1.780
1.773
1.768
1.761
1.756
1.749
1.745
1.737
1.732
1.681
1.676
1.669
1.665
1.657
1.648
1.640
1.634
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2.08
2.07
2.05
3.23
2.12
3.47
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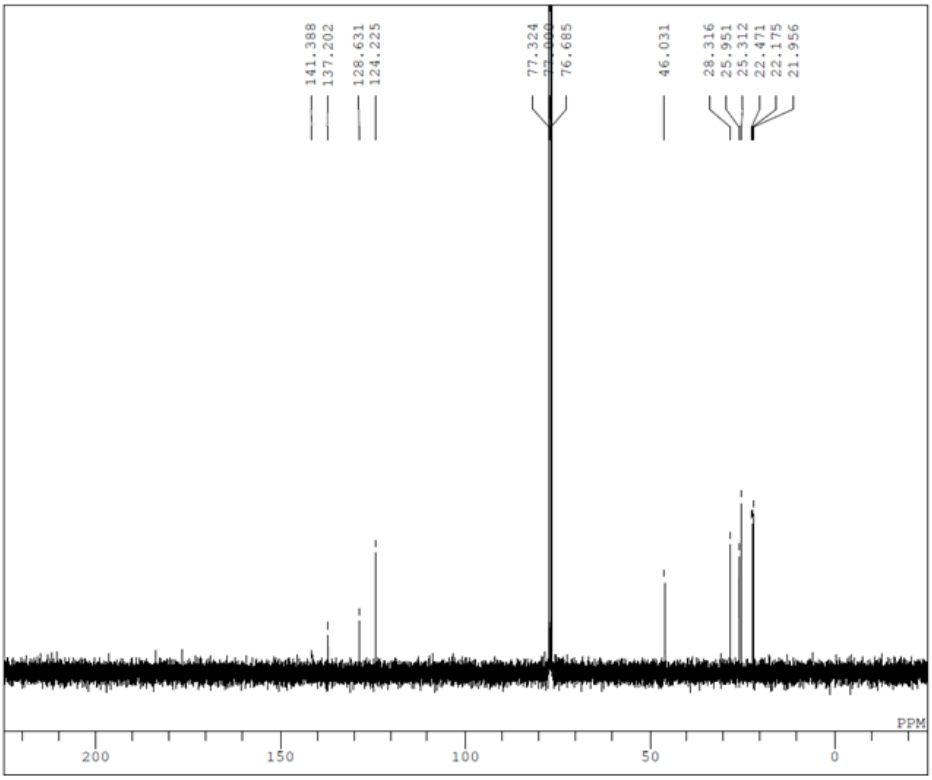
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124.225
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77.000
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46.031
28.316
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25.312
22.471
22.175
21.956
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100
50
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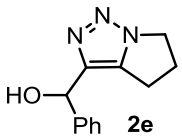
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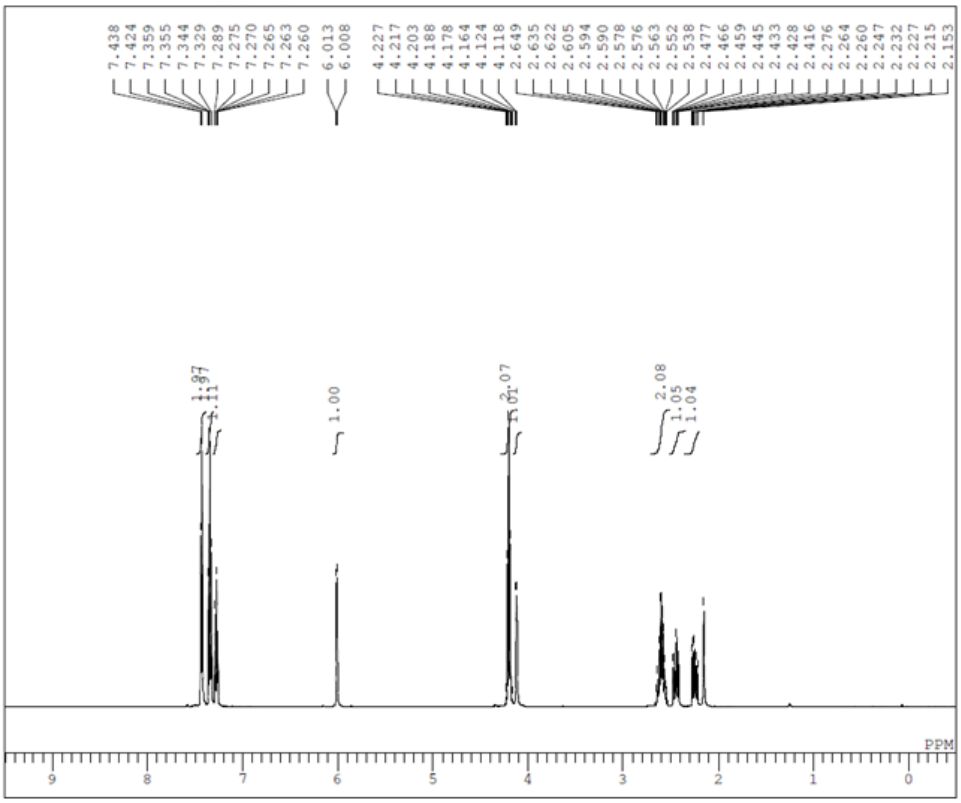
N
N
HO
Ph

2e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7.289
7.275
7.270
7.265
7.263
7.260
6.013
6.008
4.227
4.217
4.203
4.188
4.178
4.164
4.124
4.118
2.649
2.635
2.622
2.605
2.594
2.590
2.578
2.576
2.563
2.552
2.538
2.477
2.466
2.459
2.445
2.433
2.428
2.416
2.276
2.264
2.260
2.247
2.232
2.227
2.215
2.153
1.97
2.11
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2.08
1.05
1.04
PPM
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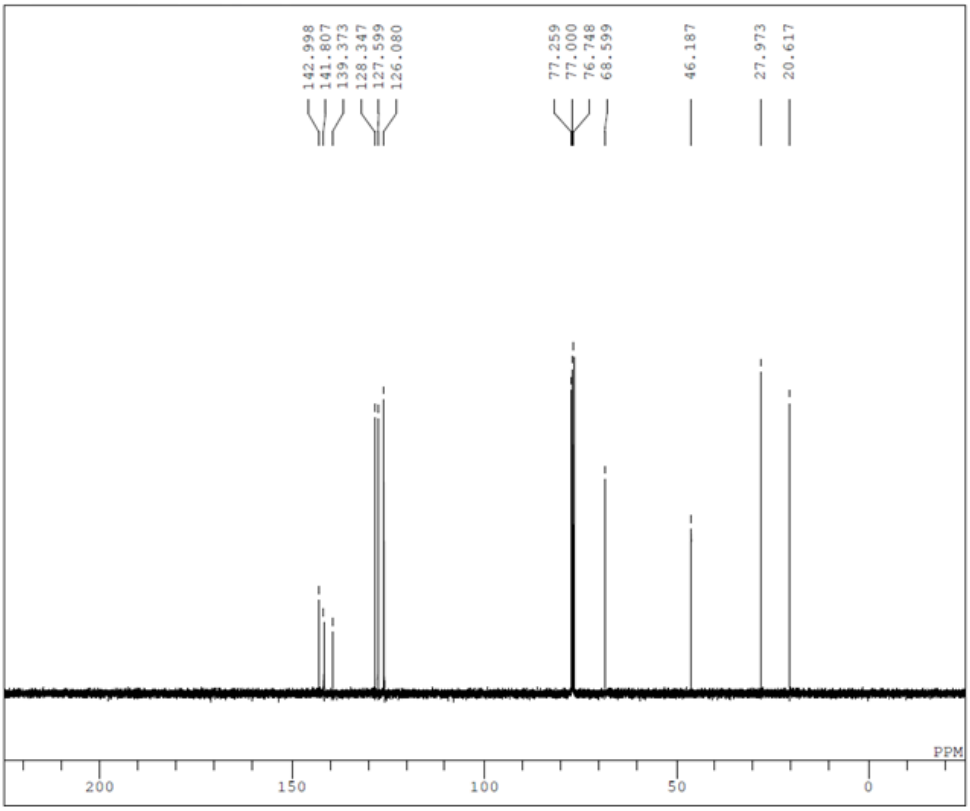
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141.807
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77.000
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68.599
46.187
27.973
20.617
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200
150
100
50
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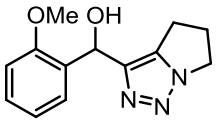
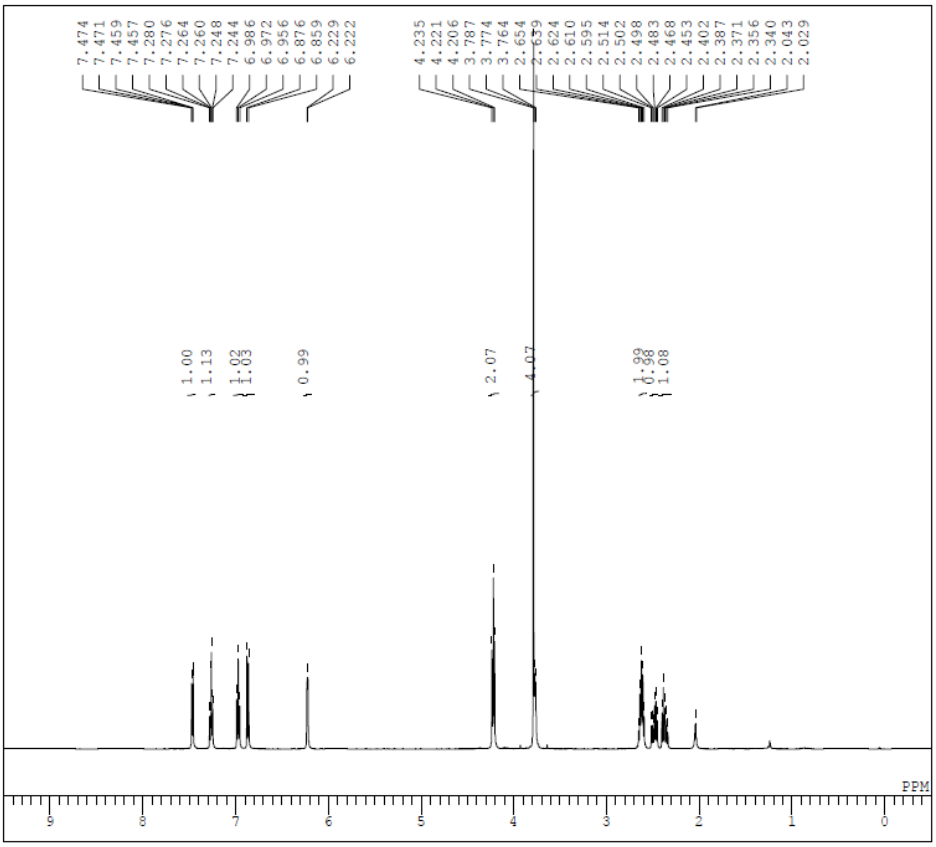

OMe OH
N
N=N

2f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7.457
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7.276
7.264
7.260
7.248
7.244
6.986
6.972
6.956
6.876
6.859
6.229
6.222
4.235
4.221
4.206
3.787
3.774
3.764
3.654
2.639
2.624
2.610
2.595
2.514
2.502
2.498
2.483
2.468
2.453
2.402
2.387
2.371
2.356
2.340
2.043
2.029
1.00
1.13
1.02
1.03
0.99
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4.07
1.98
0.98
1.08
PPM
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7
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3
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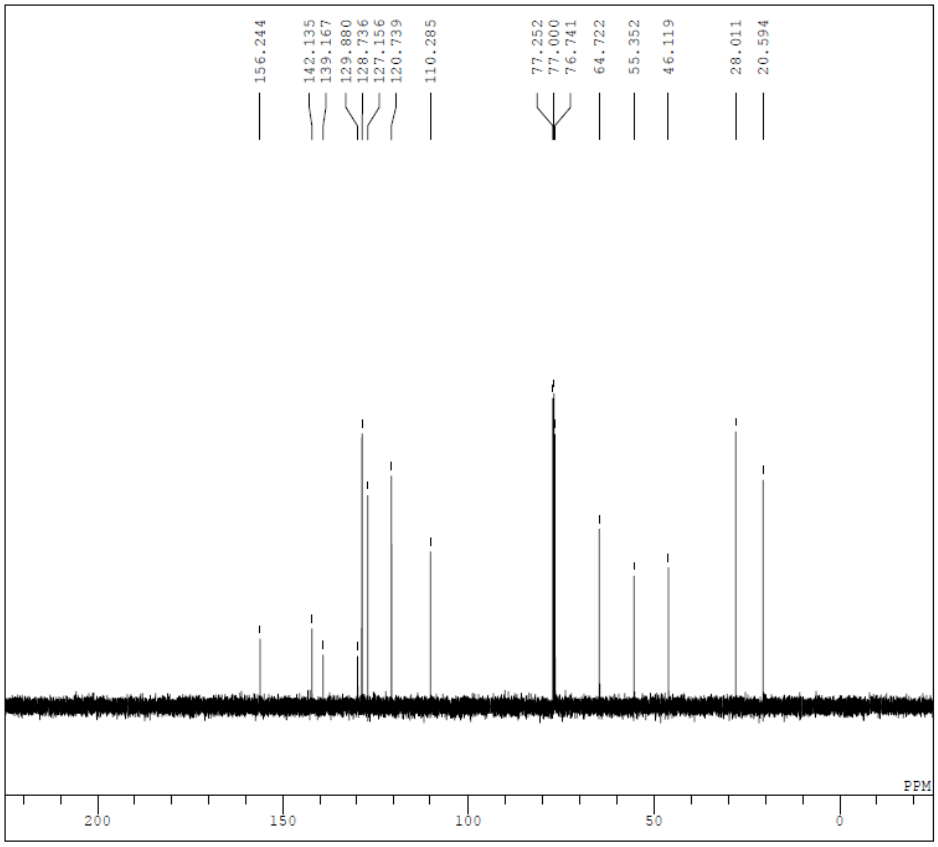
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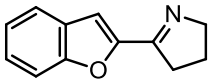
139.167
129.880
128.736
127.156
120.739
110.285
77.252
77.000
76.741
64.722
55.352
46.119
28.011
20.594
PPM
200
150
100
50
0



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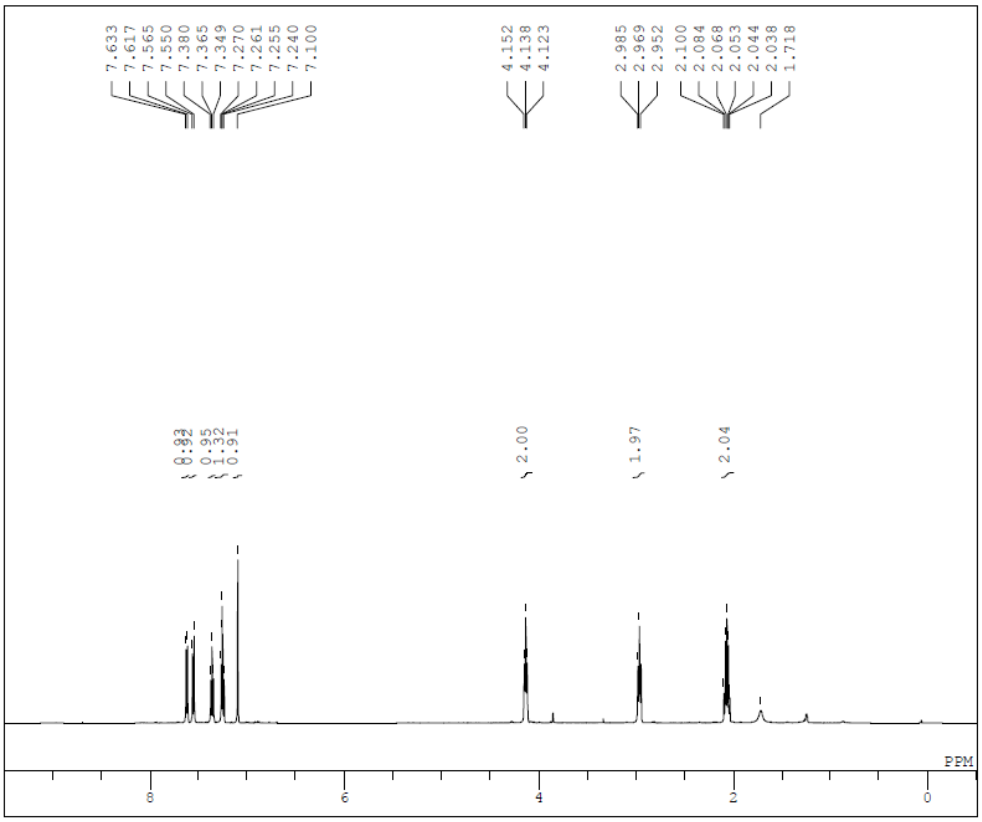
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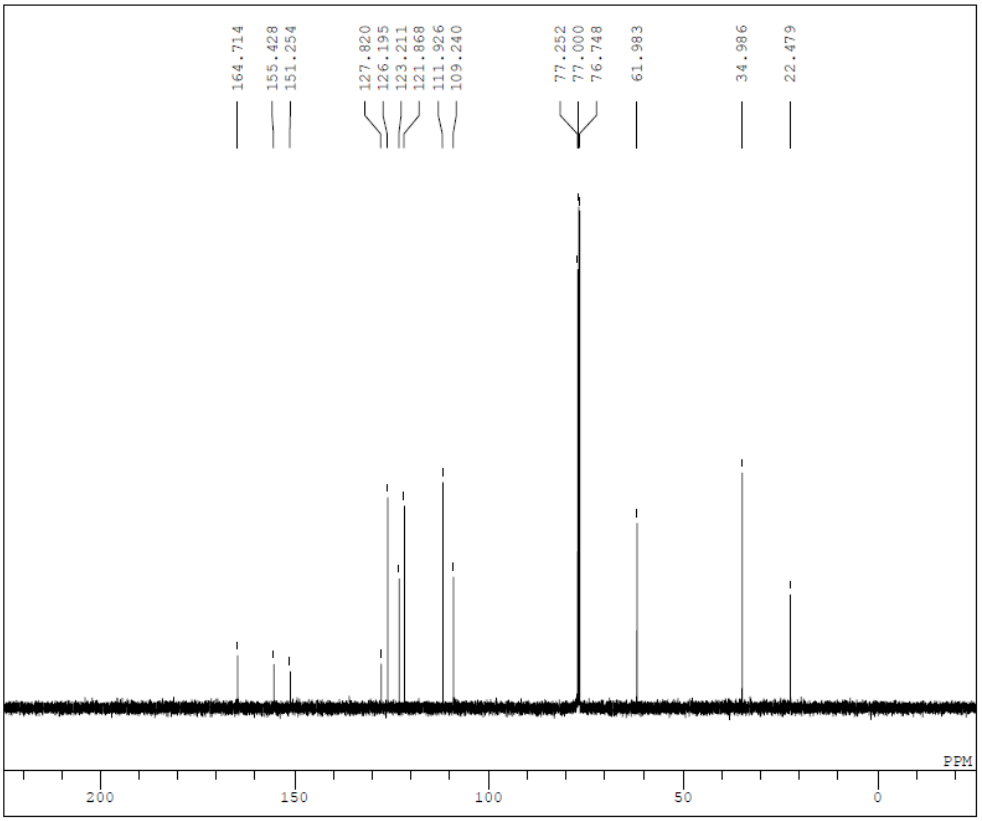
7.565
7.550
7.380
7.365
7.349
7.270
7.261
7.255
7.240
7.100
4.152
4.138
4.123
2.985
2.969
2.952
2.100
2.084
2.068
2.053
2.044
2.038
1.718
0.95
1.32
0.91
2.00
1.97
2.04
PPM
8
6
4
2
0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151.254
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123.211
121.868
111.926
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77.000
76.748
61.983
34.986
22.479
PPM
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150
100
50
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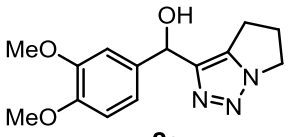
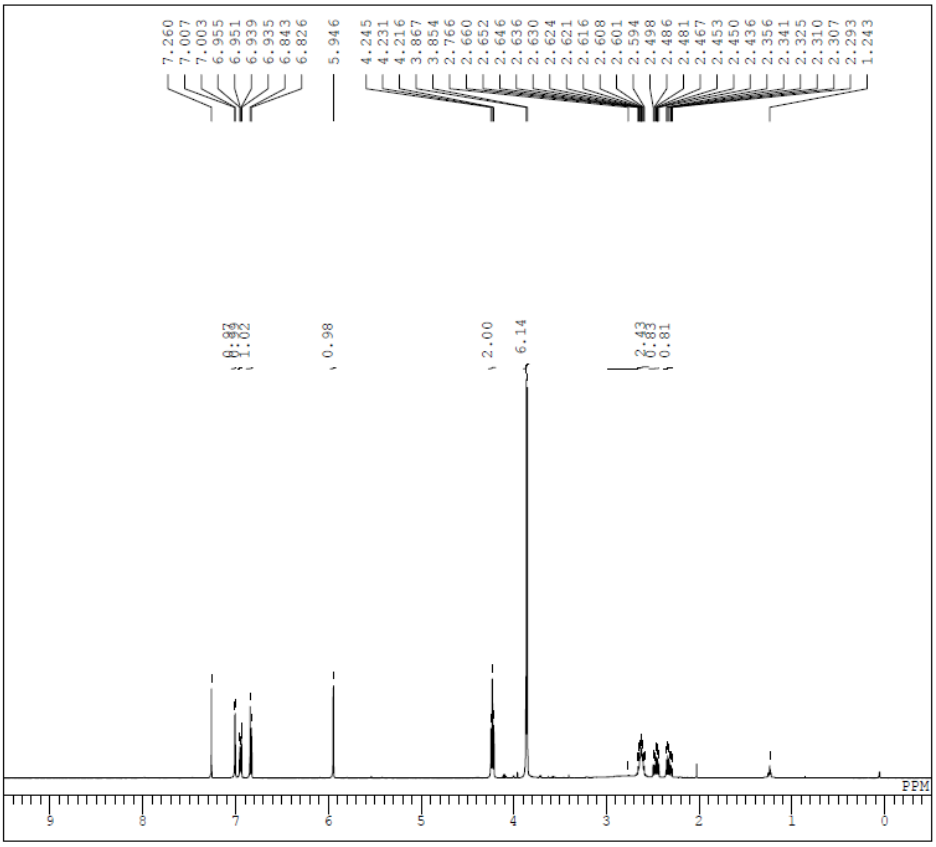

OH
MeO
MeO
N
N=N

2g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5.946
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4.231
4.216
3.867
3.854
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2.660
2.652
2.646
2.636
2.630
2.624
2.621
2.616
2.608
2.601
2.594
2.498
2.486
2.481
2.467
2.453
2.450
2.436
2.356
2.341
2.325
2.310
2.307
2.293
1.243
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0.83
0.81
PPM
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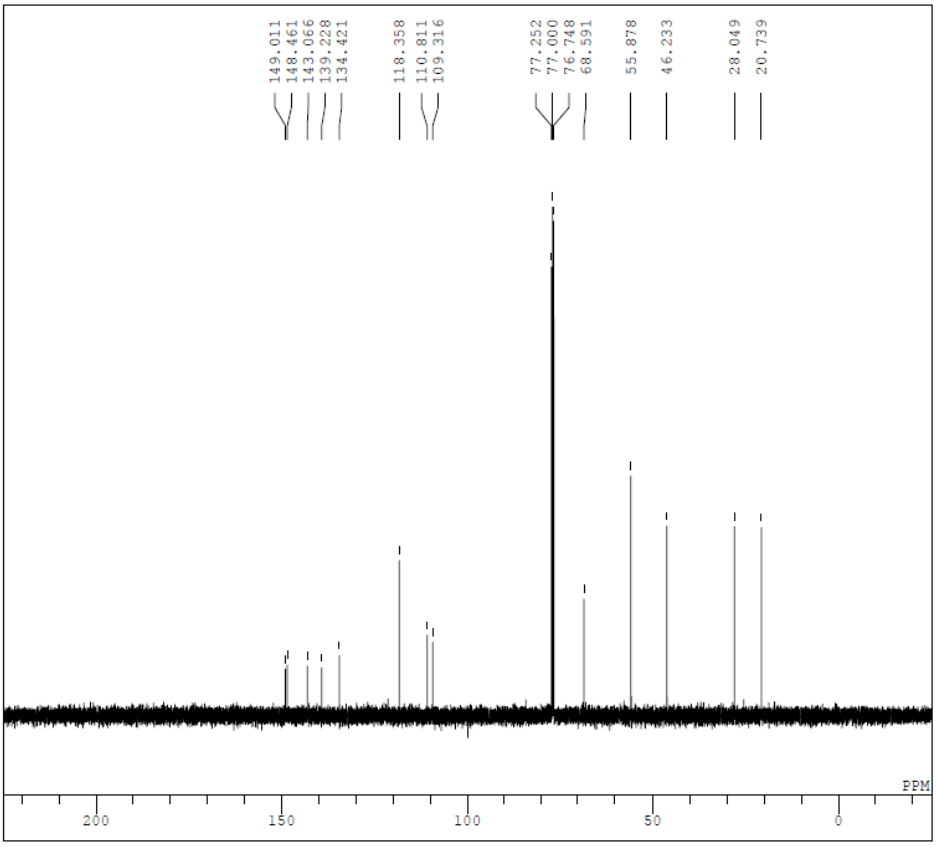
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118.358
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109.316
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20.739
PPM
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150
100
50
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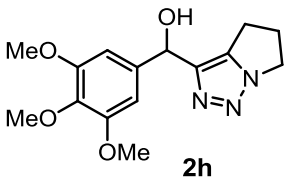
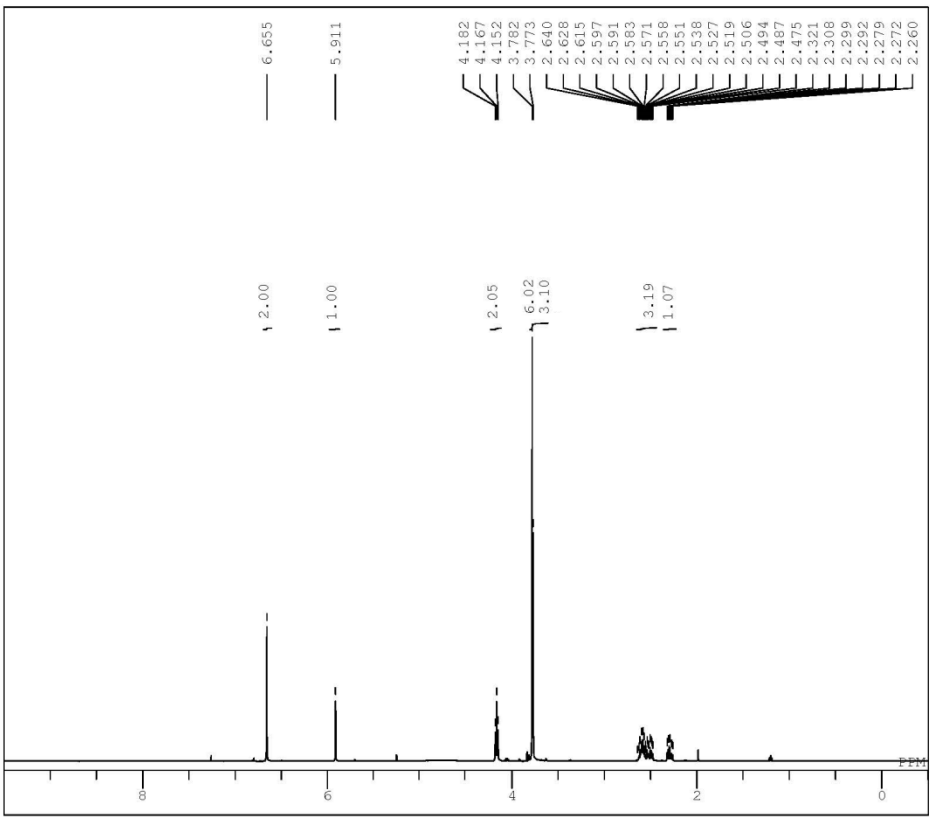

OH
MeO
MeO
OMe
N
N=N

2h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2.615
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2.591
2.583
2.571
2.558
2.551
2.538
2.527
2.519
2.506
2.494
2.487
2.475
2.321
2.308
2.299
2.292
2.279
2.272
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1.00
2.05
6.02
3.10
3.19
1.07
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6
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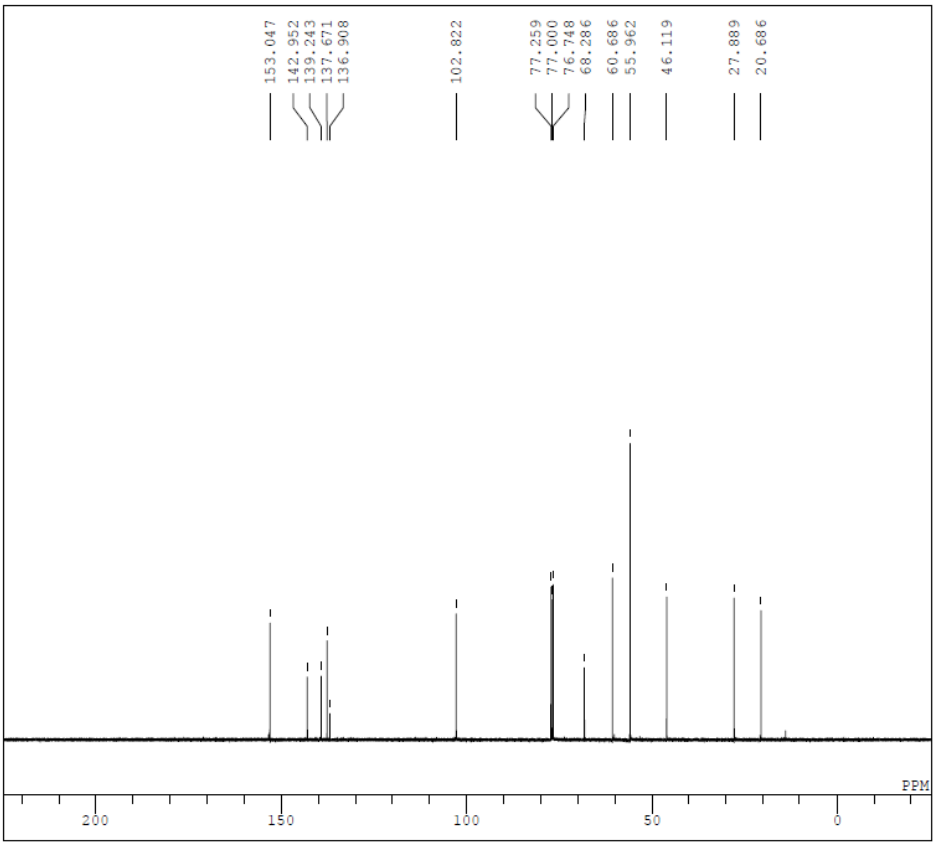
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102.822
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77.000
76.748
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46.119
27.889
20.686
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150
100
50
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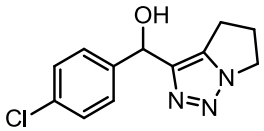
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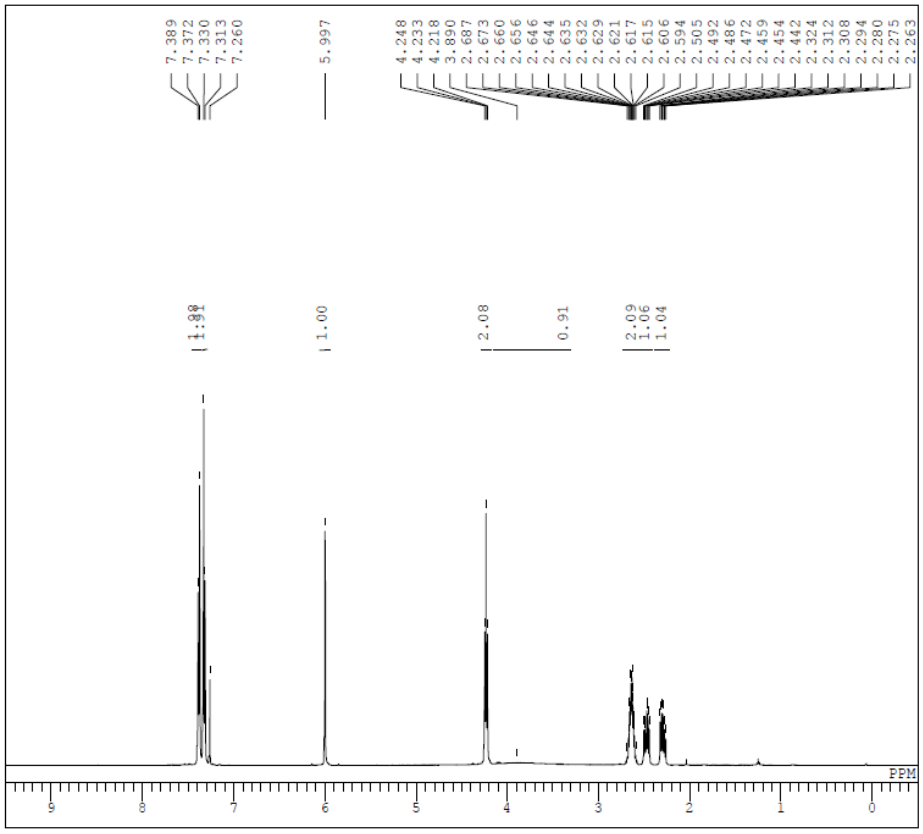
Cl
N
N=N

2i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4.218
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2.660
2.656
2.646
2.644
2.635
2.632
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2.606
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2.486
2.472
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2.454
2.442
2.324
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2.308
2.294
2.280
2.275
2.263
1.00
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1.06
1.04
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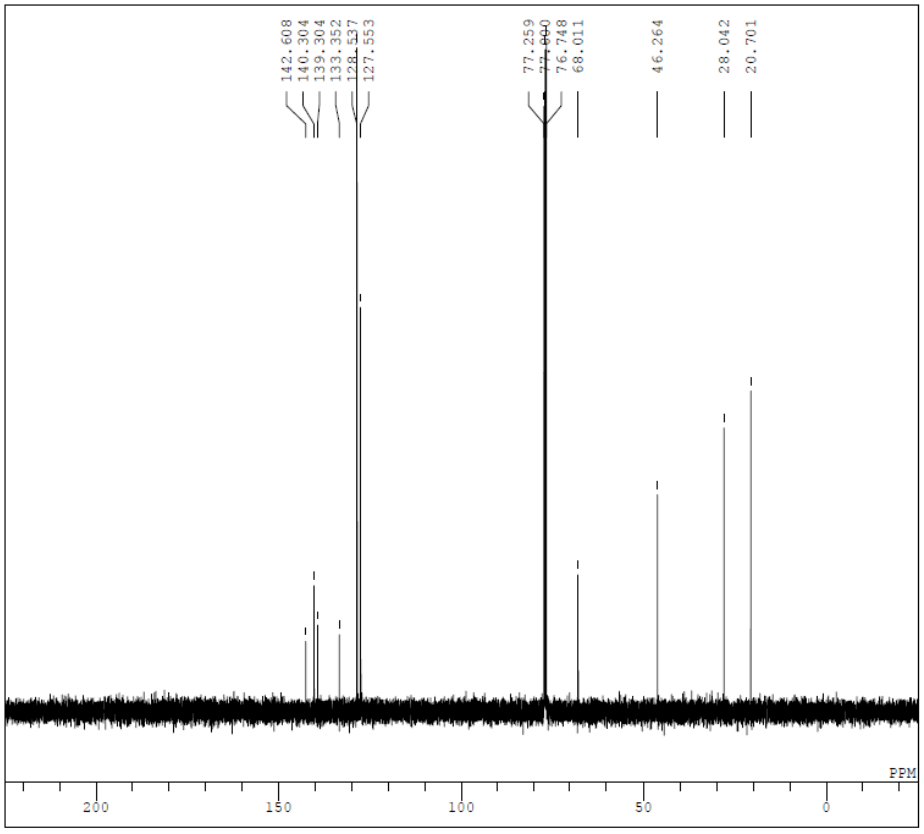
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20.701
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100
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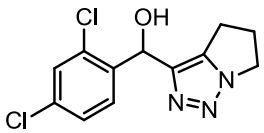
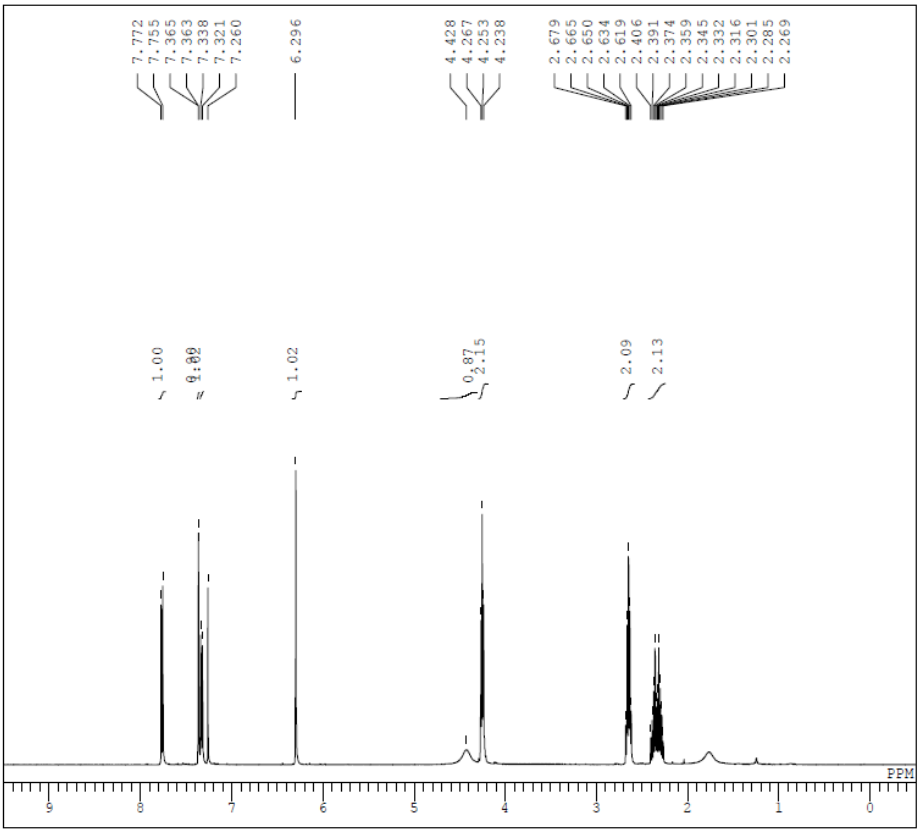

Cl
OH
N
N=N
Cl

2j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4.267
4.253
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2.665
2.650
2.634
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2.406
2.391
2.374
2.359
2.345
2.332
2.316
2.301
2.285
2.269
1.00
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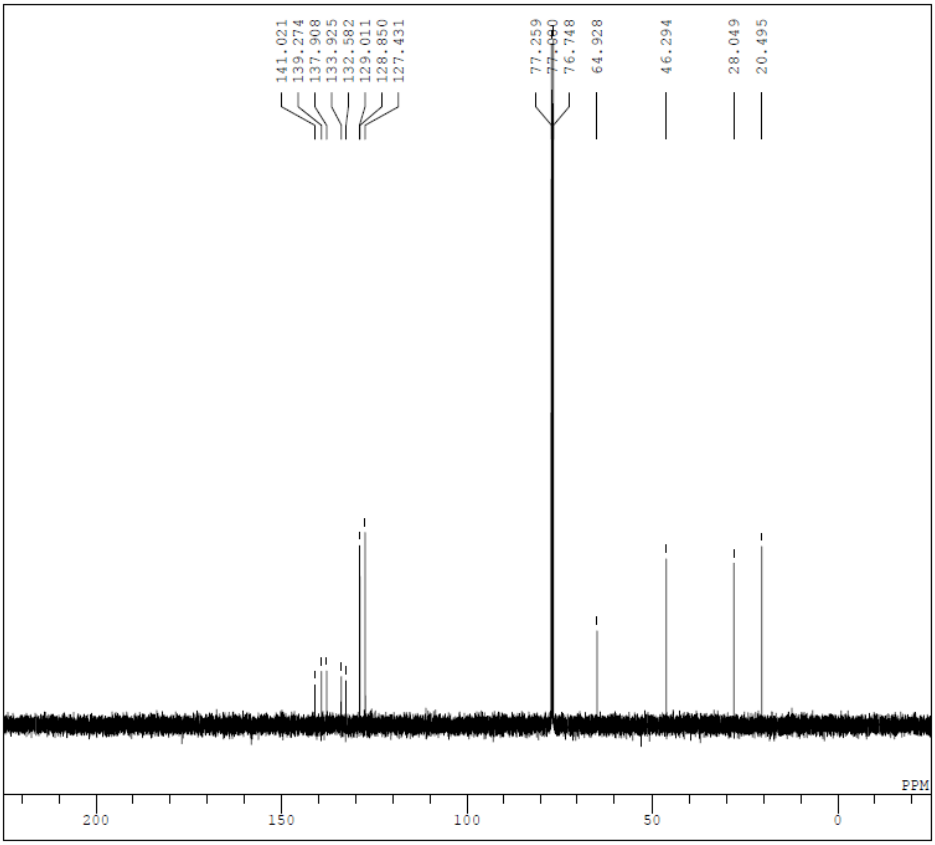
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77.080
76.748
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28.049
20.495
PPM
200
150
100
50
0