Supplementary Material (ESI) for Green Chemistry

Supporting Information

Solvent-free synthesis of 1,4-disubstituted 1,2,3-triazoles using a low amount of $Cu(PPh_3)_2NO_3$ complex

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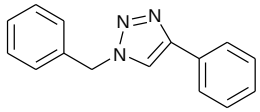
1. General Remarks:

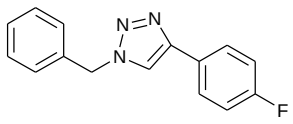
Flash column chromatography was performed using silica gel (300–400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR spectra were recorded on 300 or 400 MHz and ^{13}C NMR spectra were recorded on 75 or 100 MHz using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus. All new products were further characterized by ESI HRMS and IR; copies of ^{1}H NMR and ^{13}C NMR spectra are provided. Commercially available reagents were used without further purification.

2. Spectral data of the compounds:



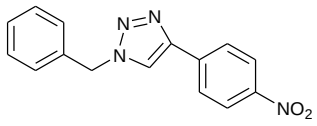
3a

1-benzyl-4-phenyl-1*H*-1,2,3-triazole (3a) [1] : 3a was isolated as a white solid (yield 96%). mp: 128-130°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.79(t, *J*=4.4 Hz, 2H), 7.66(s, 1H), 7.34-7.40(m, 5H), 7.25-7.31(m, 3H), 5.54(s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 148.15, 134.67, 130.52, 129.08, 128.74, 128.70, 128.09, 127.99, 125.65, 119.48, 54.15.



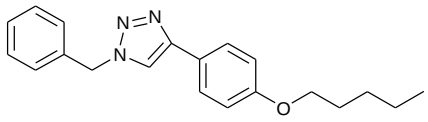
3b

1-benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole (3b) [1] : 3b was isolated as a white solid (yield 80%). mp: 113-115°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.73-7.78(m, 2H), 7.63(s, 1H), 7.35-7.38(m, 3H), 7.28-7.31(m, 2H), 7.04-7.10(m, 2H), 5.55(s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 164.21, 160.94, 147.28, 134.55, 129.10, 128.75, 128.00, 127.42, 127.31, 126.74, 119.25, 115.84, 115.55, 54.17.



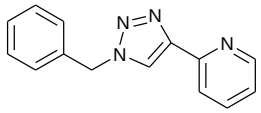
3c

1-benzyl-4-(4-nitrophenyl)-1*H*-1,2,3-triazole (3c) [2] : 3c was isolated as a yellow solid (yield 81%), mp: 168 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.24(d, *J*=8.8 Hz, 2H), 7.96(d, *J*=8.8 Hz, 2H), 7.81(s, 1H), 7.32-7.43(m, 5H), 5.60(s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.28, 145.96, 136.78, 134.16, 129.25, 129.00, 128.14, 126.09, 124.20, 120.97, 54.42.



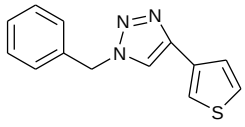
3d

1-benzyl-4-(4-(pentyloxy)phenyl)-1*H*-1,2,3-triazole (3d): 3d was isolated as a white solid (yield 81%), mp: 121-123 ^{o}C. IR (cm^{-1}): 3090.72, 2933.29, 2861.00, 1452.13, 1250.60, 1214.05, 1193.62, 1074.71, 1018.71, 824.00, 713.55, 577.17, 529.34.^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.69-7.71(m, 2H), 7.56(s, 1H), 7.34-7.38(m, 3H), 7.26-7.30(m, 2H), 6.91(d, *J*=9.0 Hz, 2H), 5.53(s, 2H), 3.96(t, *J*=6.5 Hz, 2H), 1.76-1.81(m, 2H), 1.37-1.46(m, 4H), 0.93(t, *J*=7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 159.16, 148.10, 134.77, 129.06, 128.66, 127.98, 126.92, 123.00, 118.62, 114.74, 68.01, 54.11, 28.90, 28.14, 22.41, 13.96. ESI HRMS: calcd. for $C_{20}H_{23}N_3O$ $[M+H]^+$: 322.1914, found: 322.1906.



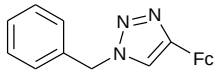
3e

2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine (3e) [2]: 3e was isolated as a white solid (yield 86%). mp: 114-115^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.51-8.53(m, 1H), 8.15-8.18(m, 1H), 8.06(s, 1H), 7.71-7.77(m, 1H), 7.29-7.38(m, 5H), 7.16-7.20(m, 1H), 5.56(s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 150.11, 149.18, 148.56, 136.75, 134.26, 129.00, 128.67, 128.15, 122.70, 121.84, 120.07, 54.20.



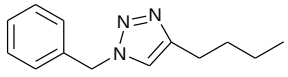
3f

1-benzyl-4-(thiophen-3-yl)-1*H*-1,2,3-triazole (3f) [3] : 3f was isolated as a white solid (yield 99%). mp: 140-142°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.62-7.63(m, 1H), 7.57(s, 1H), 7.37-7.41(m, 1H), 7.32-7.36(m, 4H), 7.25-7.32(m, 2H), 5.51(s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 144.23, 134.59, 131.69, 129.00, 128.62, 127.88, 126.18, 125.67, 120.95, 119.32, 53.99.



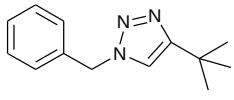
3g

1-benzyl-4-ferrocenyl-1*H*-1,2,3-triazole (3g) [4] : 3g was isolated as a golden yellow solid (yield 70%). mp: 145-147°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.36(d, *J*=8.1 Hz, 4H), 7.25(t, *J*=3.6 Hz, 2H), 5.51(s, 2H), 4.69(s, 2H), 4.27(s, 2H), 4.05(s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 147.11, 134.83, 128.98, 128.55, 127.75, 118.69, 75.41, 69.52, 68.61, 66.55, 53.90.



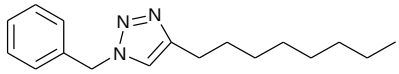
3h

1-benzyl-4-butyl-1*H*-1,2,3-triazole (3h) [5] : 3h was isolated as a white solid (yield 94%). mp: 62-63°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.33-7.38(m, 3H), 7.25(t, *J*=3.9 Hz, 2H), 7.20(s, 1H), 5.48(s, 2H), 2.68(t, *J*=7.8 Hz, 2H), 1.57-1.65(m, 2H), 1.32-1.39(m, 2H), 0.91(t, *J*=7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 148.80, 134.93, 128.92, 128.45, 127.82, 120.41, 53.82, 31.40, 25.29, 22.20, 13.70.



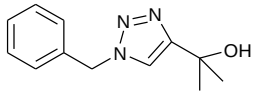
3i

1-benzyl-4-*tert*-butyl-1*H*-1,2,3-triazole (3i) [5] : 3i was isolated as a white solid (yield 95%). mp: 84-85 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.34-7.39(m, 3H), 7.25-7.27(m, 2H), 7.17(s, 1H), 5.48(s, 2H), 1.32(s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 158.05, 134.97, 128.94, 128.46, 127.92, 118.33, 53.83, 30.68, 30.26.



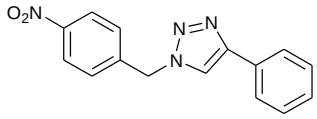
3j

1-benzyl-4-octyl-1*H*-1,2,3-triazole (3j) [1] : 3j was isolated as a white solid (yield 98%). mp: 70-71^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.33-7.38(m, 3H), 7.25(t, *J*=3.8 Hz, 2H), 7.20(s, 1H), 5.48(s, 2H), 2.68(t, *J*=7.8 Hz, 2H), 1.60-1.67(m, 2H), 1.25-1.30(m, 10H), 0.87(t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 148.82, 134.94, 128.89, 128.43, 127.80, 120.40, 53.81, 31.70, 29.28, 29.18, 29.13, 29.06, 25.61, 22.52, 13.97.



3k

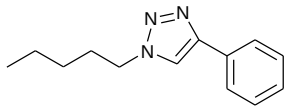
2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (3k) [6]: 3k was isolated as a white solid (yield 95%). mp: 78-80^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.41(s, 1H), 7.31-7.35(m, 3H), 7.23-7.27(m, 2H), 5.44(s, 2H), 3.61(s, 1H), 1.58(s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 156.00, 134.48, 128.84, 128.44, 127.89, 119.17, 68.19, 53.81, 30.24.



4a

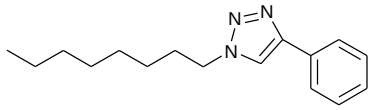
1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (4a) [7]: 4a was isolated as a yellow solid (yield 98%). mp: 84-86^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.19(d, *J*=8.8 Hz, 2H), 7.79-7.81(m, 3H), 7.38-7.43(m, 4H), 7.31-7.35(m, 1H), 5.68(s, 2H). ^{13}C NMR

(100 MHz, $CDCl_3$): δ_C 148.52, 147.93, 141.74, 130.04, 128.82, 128.47, 128.38, 125.64, 124.17, 119.81, 53.03.



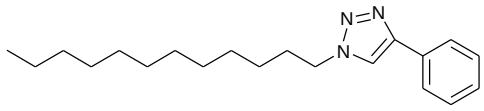
4b

1-pentyl-4-phenyl-1*H*-1,2,3-triazole (4b) : 4b was isolated as a white solid (yield 94%). mp: 70-71°C. IR (cm^{-1}): 3734.40, 3118.35, 2924.67, 1461.53, 1214.21, 1076.02, 839.23, 759.57, 693.33, 521.80. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.84(t, *J*=4.2 Hz, 2H), 7.75(s, 1H), 7.41(t, *J*=7.6 Hz, 2H), 7.27-7.34(m, 1H), 4.36(t, *J*=7.2 Hz, 2H), 1.89-1.96(m, 2H), 1.30-1.37(m, 4H), 0.89(t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.56, 130.65, 128.71, 127.94, 125.56, 119.38, 50.29, 29.93, 28.48, 21.99, 13.74. ESI HRMS: calcd. for $C_{13}H_{17}N_3$ $[M+H]^+$: 216.1495, found: 216.1499.



4c

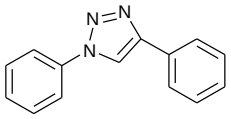
1-octyl-4-phenyl-1*H*-1,2,3-triazole (4c) [9]: 4c was isolated as a white solid (yield 99%). mp: 68-70°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83(d, *J*=7.2 Hz, 2H), 7.75(s, 1H), 7.41(t, *J*=7.6 Hz, 2H), 7.31(t, *J*=7.4 Hz, 1H), 4.36(t, *J*=7.2 Hz, 2H), 1.92(t, *J*=7.0 Hz, 2H), 1.25-1.32(m, 10H), 0.87(t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.53, 130.66, 128.69, 127.91, 125.54, 119.37, 50.29, 31.58, 30.22, 28.92, 28.85, 26.37, 22.47, 13.94.



4d

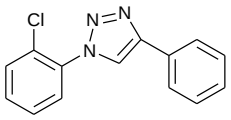
1-dodecyl-4-phenyl-1*H*-1,2,3-triazole (4d) [10] : 4d was isolated as a white solid (yield 90%). mp: 90-92°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83(d, *J*=7.2 Hz, 2H), 7.74(s, 1H), 7.42(t, *J*=7.6 Hz, 2H), 7.32(t, *J*=7.4 Hz, 1H), 4.38(t, *J*=7.2 Hz, 2H), 1.90-1.97(m, 2H), 1.25-1.34(m, 18H), 0.88(t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.70, 130.76, 128.78, 128.02, 125.67, 119.33, 50.40, 31.86, 30.32,

29.66, 29.56, 29.47, 29.35, 29.28, 28.98, 26.48, 22.64, 14.06.



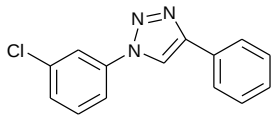
4e

1,4-diphenyl-1*H*-1,2,3-triazole (4e) [11] **: 4e** was isolated as a white solid (yield 98%). mp: 183-184°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.20(s, 1H), 7.92(d, *J*=7.2 Hz, 2H), 7.80(t, *J*=4.6 Hz, 2H), 7.52-7.56(m, 2H), 7.43-7.48(m, 3H), 7.36(t, *J*=7.4 Hz, 1H). ^{13}C NMR (100 MHz, d6-DMSO): δ_C 147.29, 136.62, 130.22, 129.87, 128.93, 128.66, 128.18, 125.32, 119.98, 119.55.



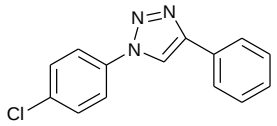
4f

1-(2-chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (4f) [8] **: 4f** was isolated as a brown solid (yield 98%). mp: 128-129°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.19(s, 1H), 7.92(t, *J*=4.2 Hz, 2H), 7.62-7.65(m, 1H), 7.55-7.58(m, 1H), 7.42-7.46(m, 4H), 7.35(t, *J*=7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.46, 134.77, 130.68, 130.66, 130.07, 128.80, 128.46, 128.29, 127.85, 127.63, 125.76, 121.53.



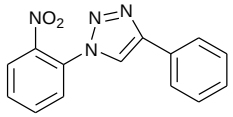
4g

1-(3-chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (4g) : 4g was isolated as a white solid (yield 99%). mp: 170-172°C. IR (cm^{-1}): 3418.49, 3096.39, 2920.14, 1587.21, 1453.81, 1226.61, 1074.03, 884.46, 764.29, 695.94. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.19(s, 1H), 7.91(t, *J*=4.2 Hz, 2H), 7.84(t, *J*=1.8 Hz, 1H), 7.71(d, *J*=8.0 Hz, 1H), 7.36-7.51(m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 148.66, 137.90, 135.63, 130.86, 129.93, 128.96, 128.80, 128.61, 125.89, 120.71, 118.45, 117.39. ESI HRMS: calcd. for $C_{14}H_{10}N_3Cl$ $[M+H]^+$: 256.0636, found: 256.0644.



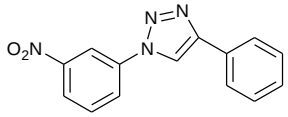
4h

1-(4-chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (4h) [12] **: 4h** was isolated as a yellow solid (yield 57%). mp: 224-226°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.16(s, 1H), 7.91(d, *J*=7.2 Hz, 2H), 7.76(d, *J*=8.8 Hz, 2H), 7.53(d, *J*=8.8 Hz, 2H), 7.47(t, *J*=7.4 Hz, 2H), 7.39(d, *J*=7.2 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 148.71, 135.60, 134.59, 130.05, 129.99, 128.97, 128.59, 125.91, 121.68, 117.40.



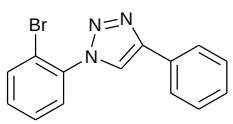
4i

1-(2-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (4i) [13] **: 4i** was isolated as a yellow solid (yield 45%). mp: 144-145°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.06(t, *J*=3.4 Hz, 2H), 7.89(d, *J*=7.2 Hz, 2H), 7.77-7.81(m, 1H), 7.65-7.71(m, 2H), 7.45(t, *J*=7.4 Hz, 2H), 7.37(t, *J*=7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 148.31, 144.34, 133.83, 130.73, 130.16, 129.69, 128.91, 128.61, 127.81, 125.92, 125.54, 120.98.



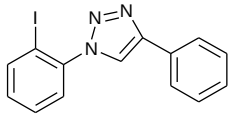
4j

1-(3-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (4j) [14] **: 4j** was isolated as a yellow solid (yield 81%). mp: 198-200°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.67(s, 1H),.8.26-8.34 (m, 3H), 7.90-7.94(m, 2H), 7.78(t, *J*=8.2 Hz, 1H), 7.43-7.51?(m, 2H), 7.36-7.41(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 149.20, 149.02, 131.02, 129.61, 129.04, 128.88, 128.72, 125.99, 125.92, 123.16, 117.26, 115.11.



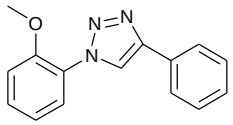
4k

1-(2-bromophenyl)-4-phenyl-1*H*-1,2,3-triazole (4k) : 4k was isolated as a yellow solid (yield 97%). mp: 100-101°C. IR (cm^{-1}): 3732.42, 3130.85, 1496.31, 1438.50, 1230.42, 1036.09, 765.04, 689.77, 514.21, 450.83. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.15(s, 1H), 7.92(t, *J*=4.2 Hz, 2H), 7.73-7.76(m, 1H), 7.56-7.58(m, 1H), 7.37-7.49(m, 3H), 7.25-7.37(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.44, 136.49, 133.85, 131.11, 130.14, 128.83, 128.44, 128.31, 128.09, 125.81, 121.61, 118.49. ESI HRMS: calcd. for $C_{14}H_{10}N_3Br$ $[M+H]^+$: 300.0131, found: 300.0140, 302.0117.



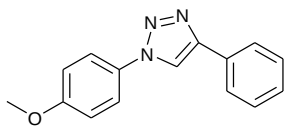
4l

1-(2-iodophenyl)-4-phenyl-1*H*-1,2,3-triazole (4l) : 4l was isolated as a white solid (yield 81%). mp: 156-158°C. IR (cm^{-1}): 3400.50, 3135.60, 3061.01, 1478.14, 1231.06, 1030.85, 761.58, 695.78. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.09(s, 1H), 8.08(t, *J*=4.4 Hz, 1H), 7.94(t, *J*=4.4 Hz, 2H), 7.45-7.56(m, 4H), 7.38(t, *J*=7.4 Hz, 1H), 7.24-7.29(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.64, 140.29, 140.10, 131.50, 130.21, 129.29, 128.93, 128.42, 127.87, 125.90, 121.53, 93.88. ESI HRMS: calcd. for $C_{14}H_{10}N_3I$ $[M+H]^+$: 347.9992, found: 347.9995.



4m

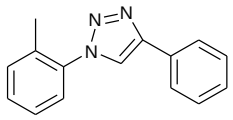
1-(2-methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (4m) [12]: 4m was isolated as a brown oil (yield 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.31(s, 1H), 7.91(t, *J*=4.2 Hz, 2H), 7.78-7.81(m, 1H), 7.37-7.44(m, 3H), 7.32(t, *J*=7.2 Hz, 1H), 7.05-7.10(m, 2H), 3.86(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 150.98, 147.06, 130.57, 130.00, 128.69, 127.94, 126.15, 125.67, 125.25, 121.70, 121.06, 112.19, 55.87.



4n

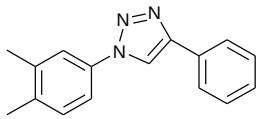
1-(4-methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (4n)[12] : 4n was isolated as a white

solid (yield 99%). mp: 164-165°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.10(s, 1H), 7.90(t, *J*=4.2 Hz, 2H), 7.65-7.68(m, 2H), 7.42-7.46(m, 2H), 7.35(t, *J*=3.6 Hz, 1H), 7.01(d, *J*=8.8 Hz, 2H), 3.85(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 159.82, 148.16, 130.50, 130.37, 128.84, 128.26, 125.78, 122.11, 117.81, 114.76, 55.59.



4o

4-phenyl-1-*o*-tolyl-1*H*-1,2,3-triazole (4o) [12]: 4o was isolated as a yellow solid (yield 85%). mp: 83-84°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96(s, 1H), 7.92(t, *J*=4.4 Hz, 2H), 7.25-7.47(m, 7H), 2.26(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.52, 136.43, 133.69, 131.45, 130.30, 129.82, 128.85, 128.25, 126.79, 125.89, 125.73, 121.09, 17.85.



4p

1-(3,4-dimethylphenyl)-4-phenyl-1*H*-1,2,3-triazole (4p): 4p was isolated as a white solid (yield 98%). mp: 140-141°C. IR (cm^{-1}): 3425.85, 3121.73, 2920.07, 1608.61, 1460.96, 1382.93, 1221.79, 1041.34, 1019.75, 813.22, 759.88, 687.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.13(s, 1H), 7.89(t, *J*=4.4 Hz, 2H), 7.54(d, *J*=1.5 Hz, 1H), 7.40-7.46(m, 3H), 7.33-7.36(m, 1H), 7.23(t, *J*=5.6 Hz, 1H), 2.31(s, 3H), 2.29(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 148.05, 138.25, 137.40, 134.86, 130.53, 130.33, 128.78, 128.19, 125.72, 121.51, 117.66, 117.60, 19.80, 19.36. ESI HRMS: calcd. for $C_{16}H_{15}N_3$ $[M+H]^+$: 250.1339, found: 250.1344.

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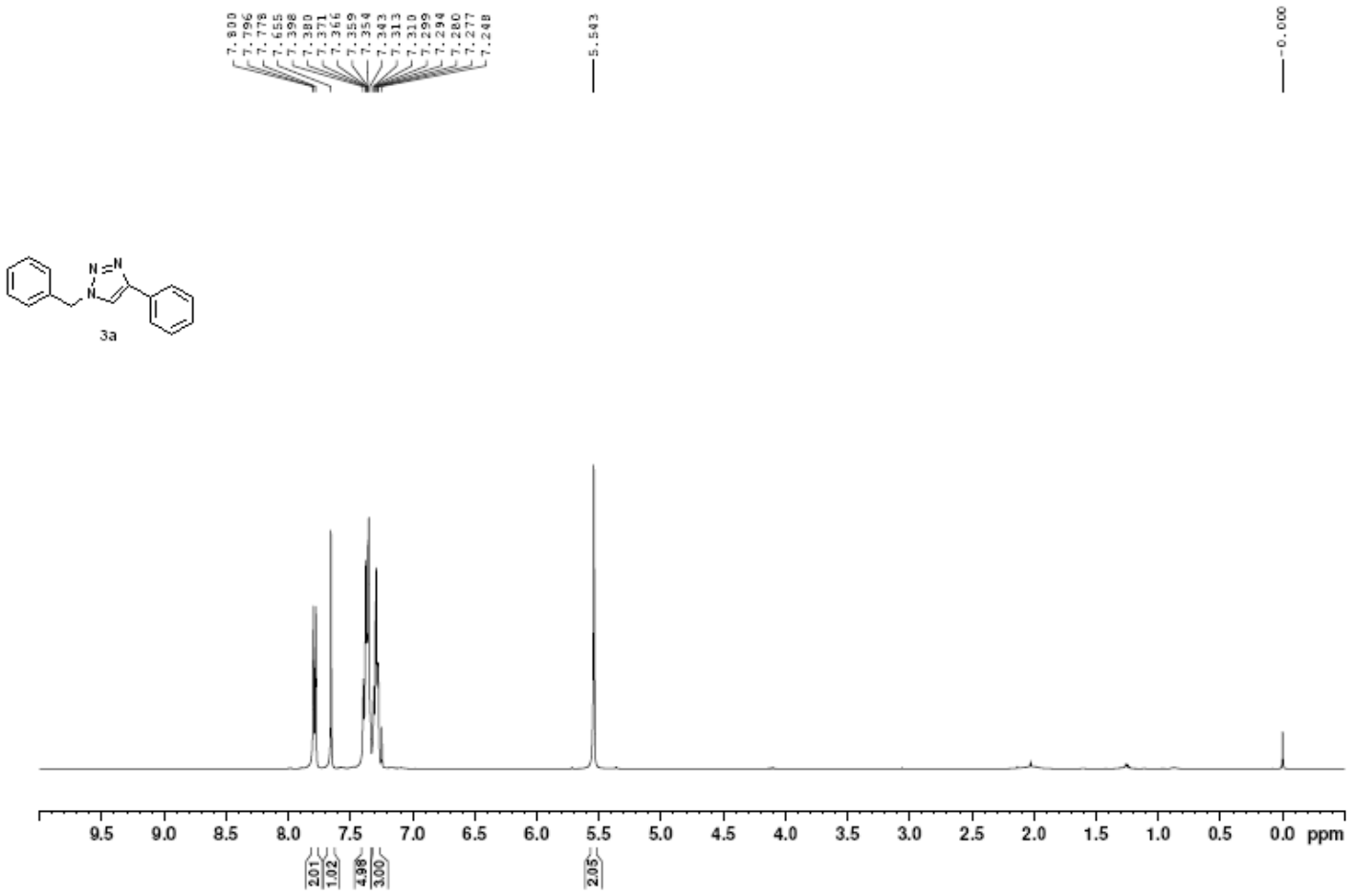
3a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7.294
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7.248
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8.0
7.5
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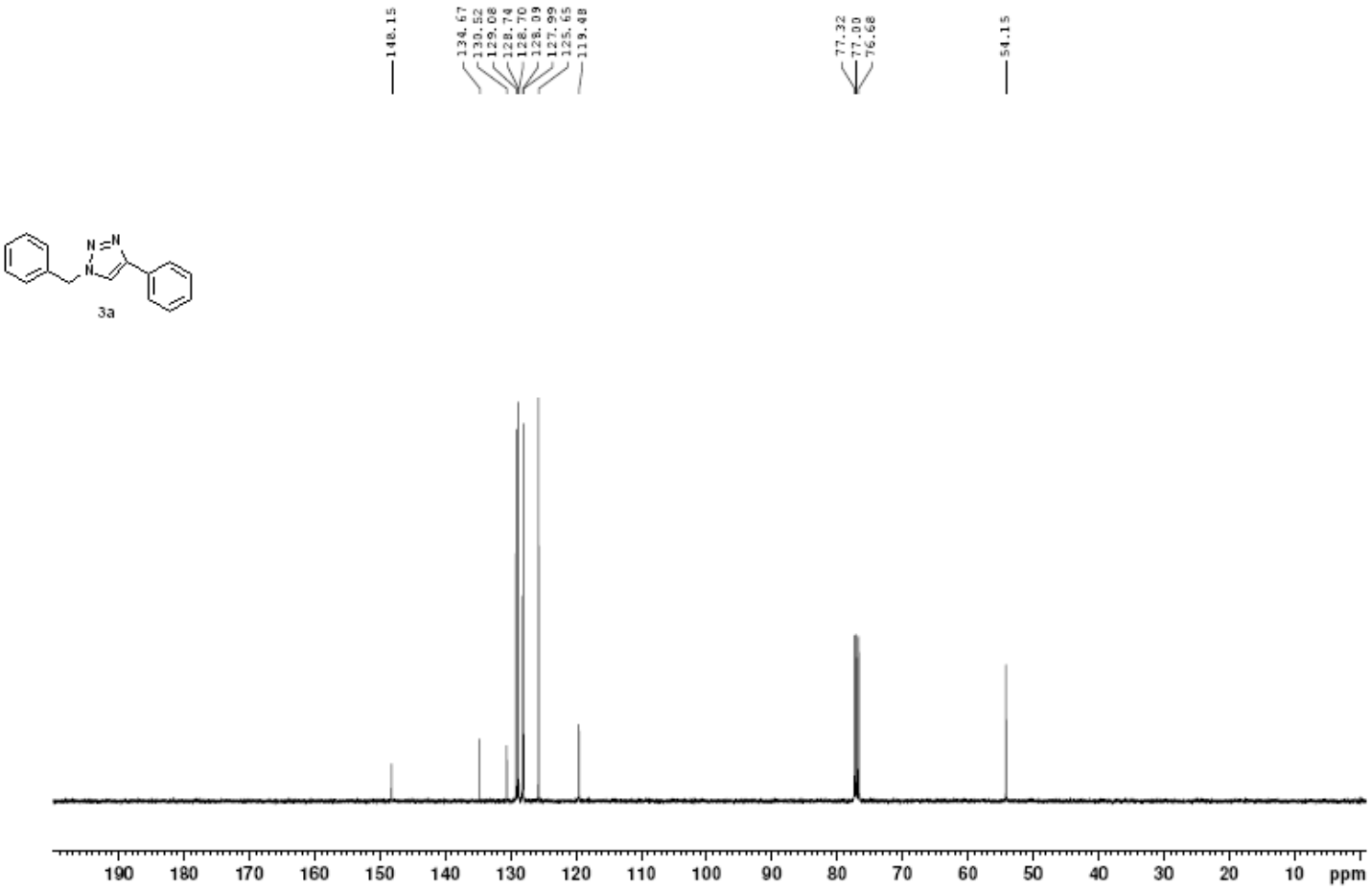

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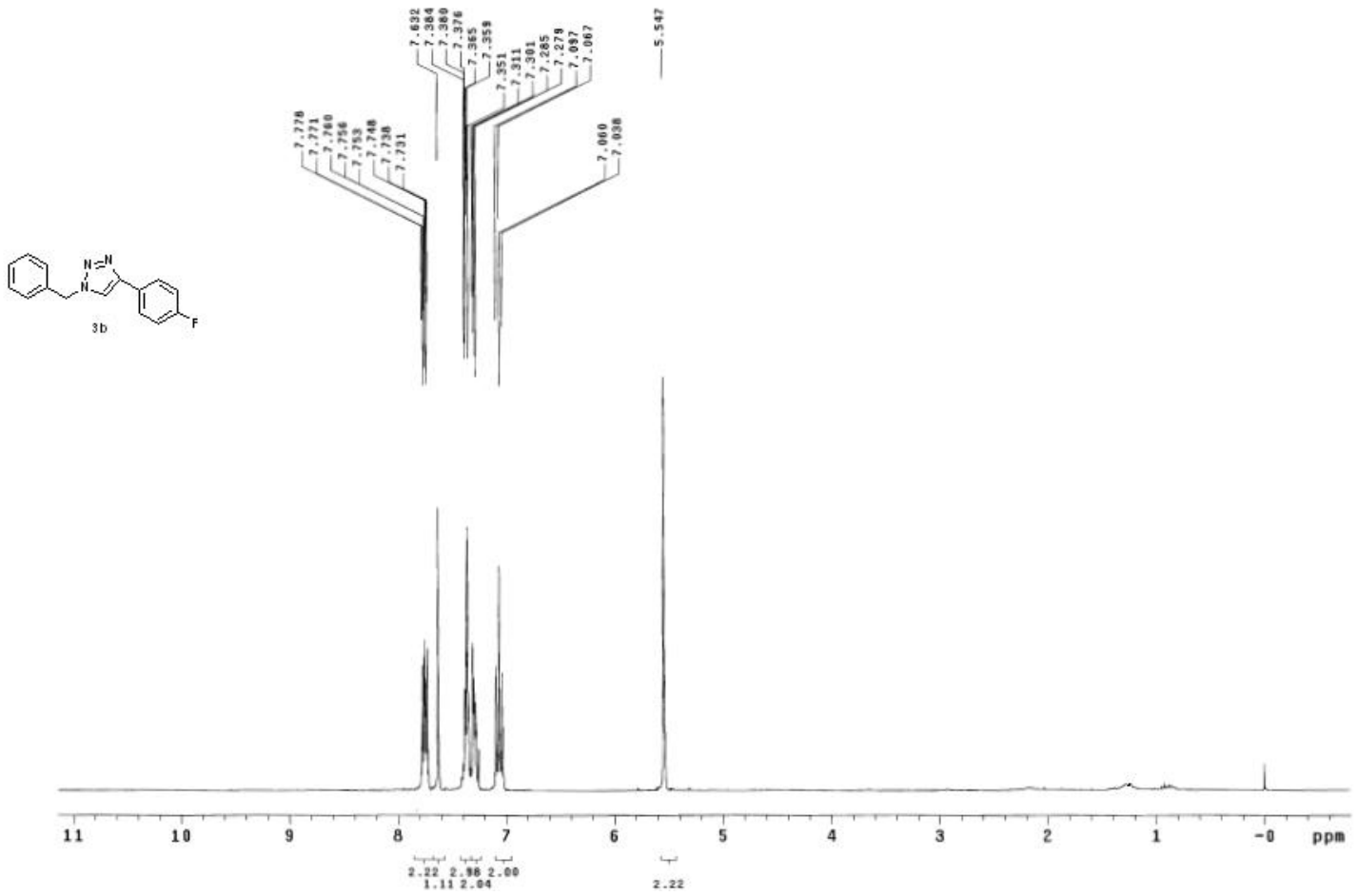
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7.038
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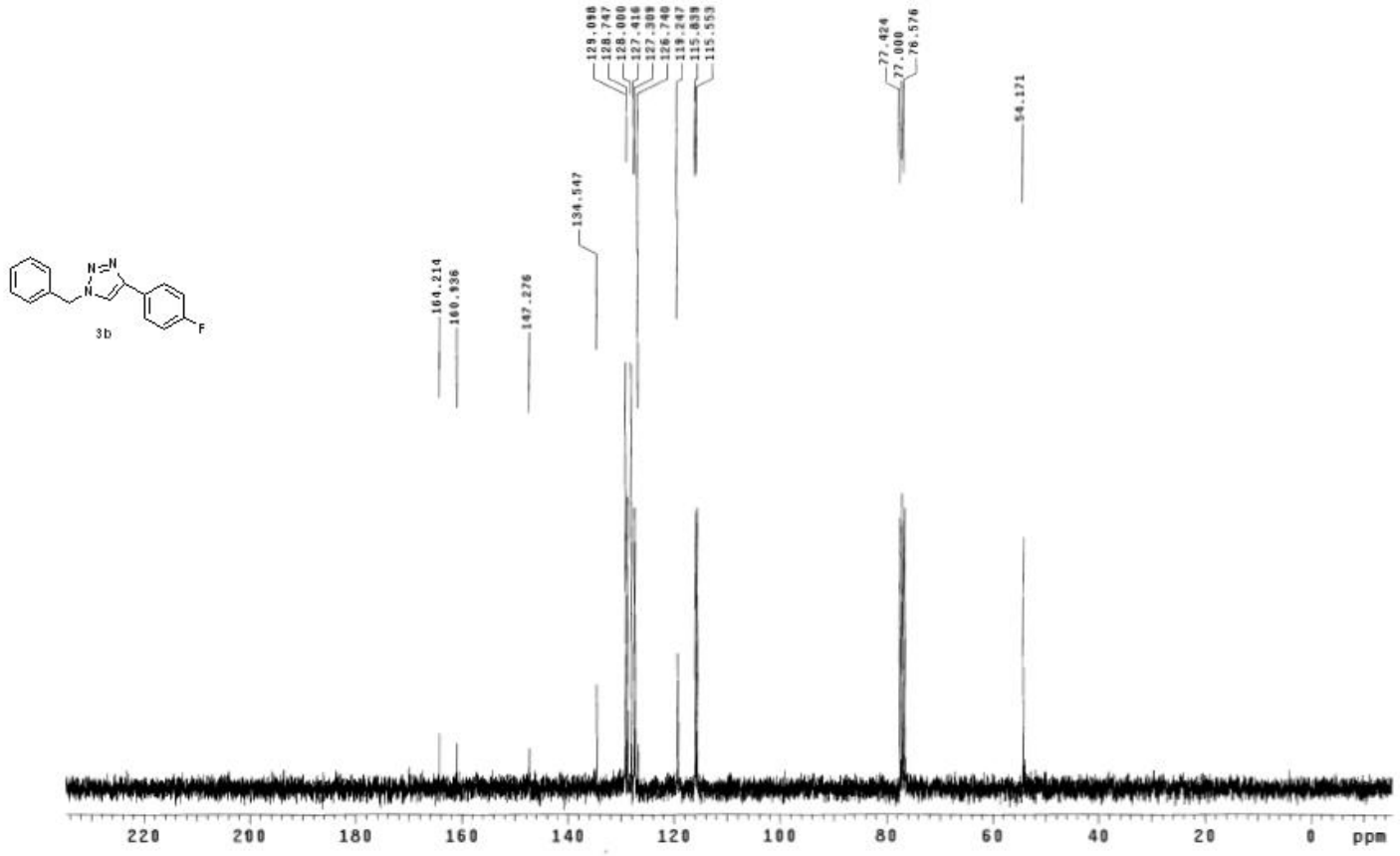

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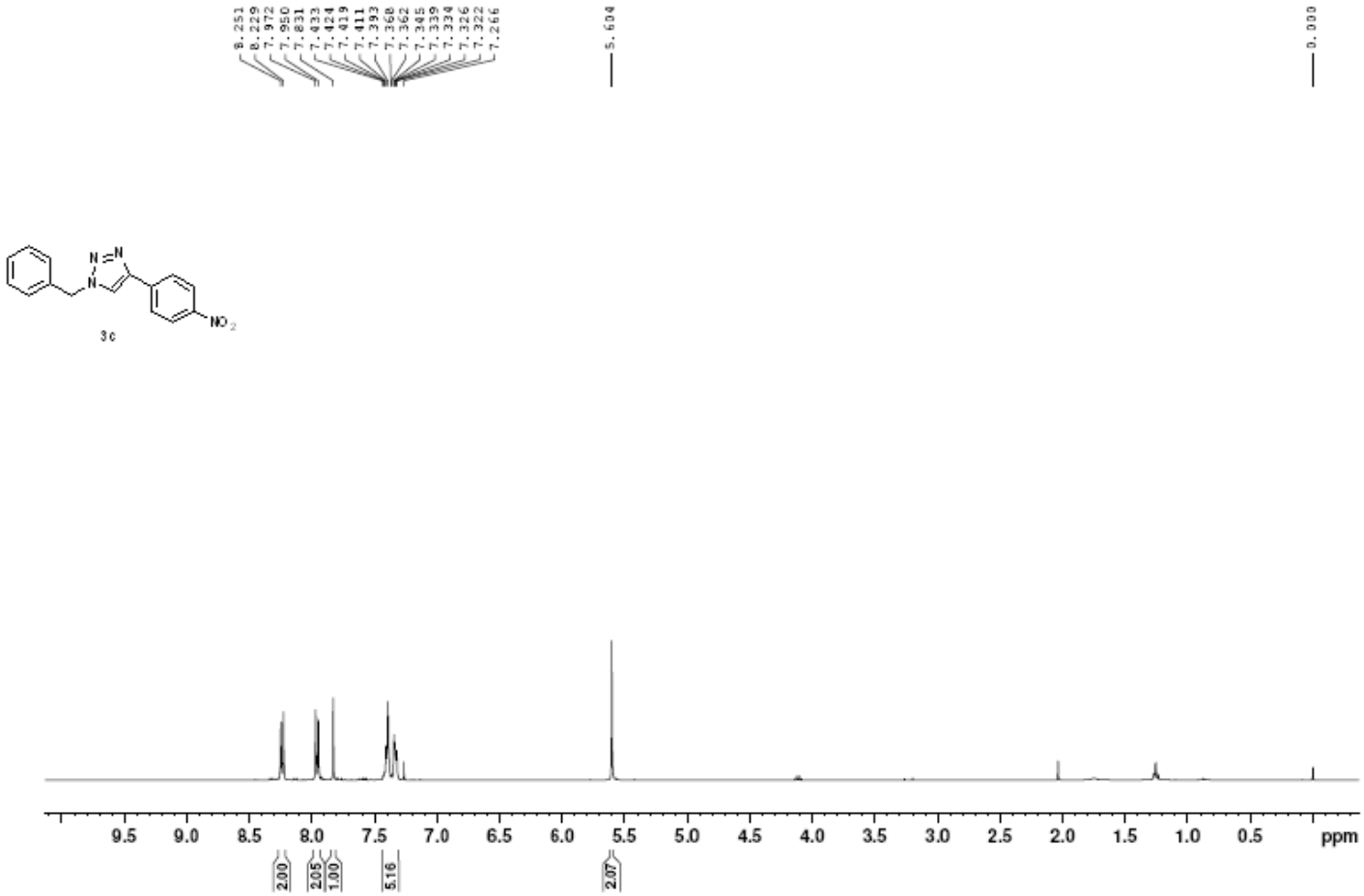
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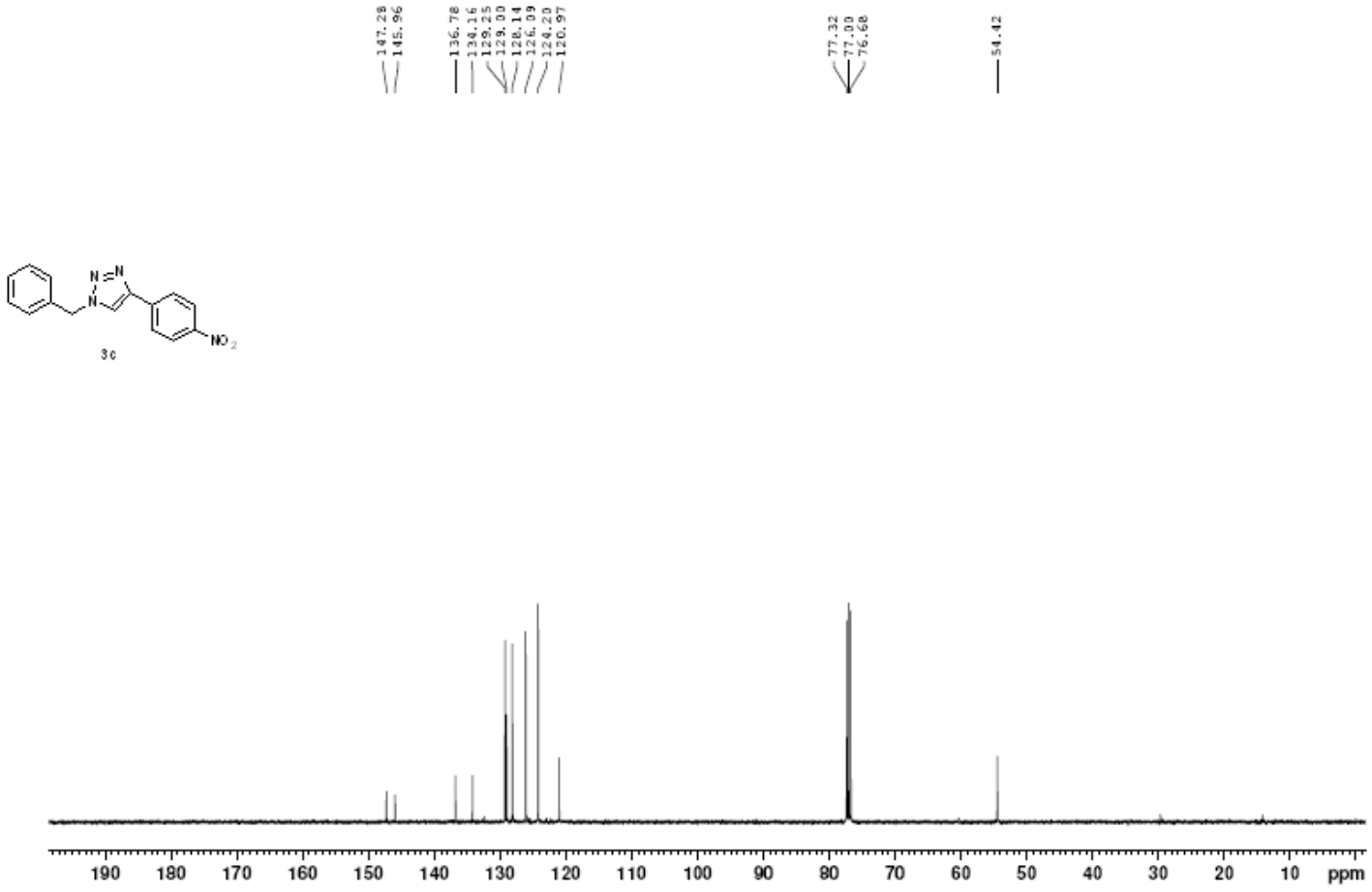
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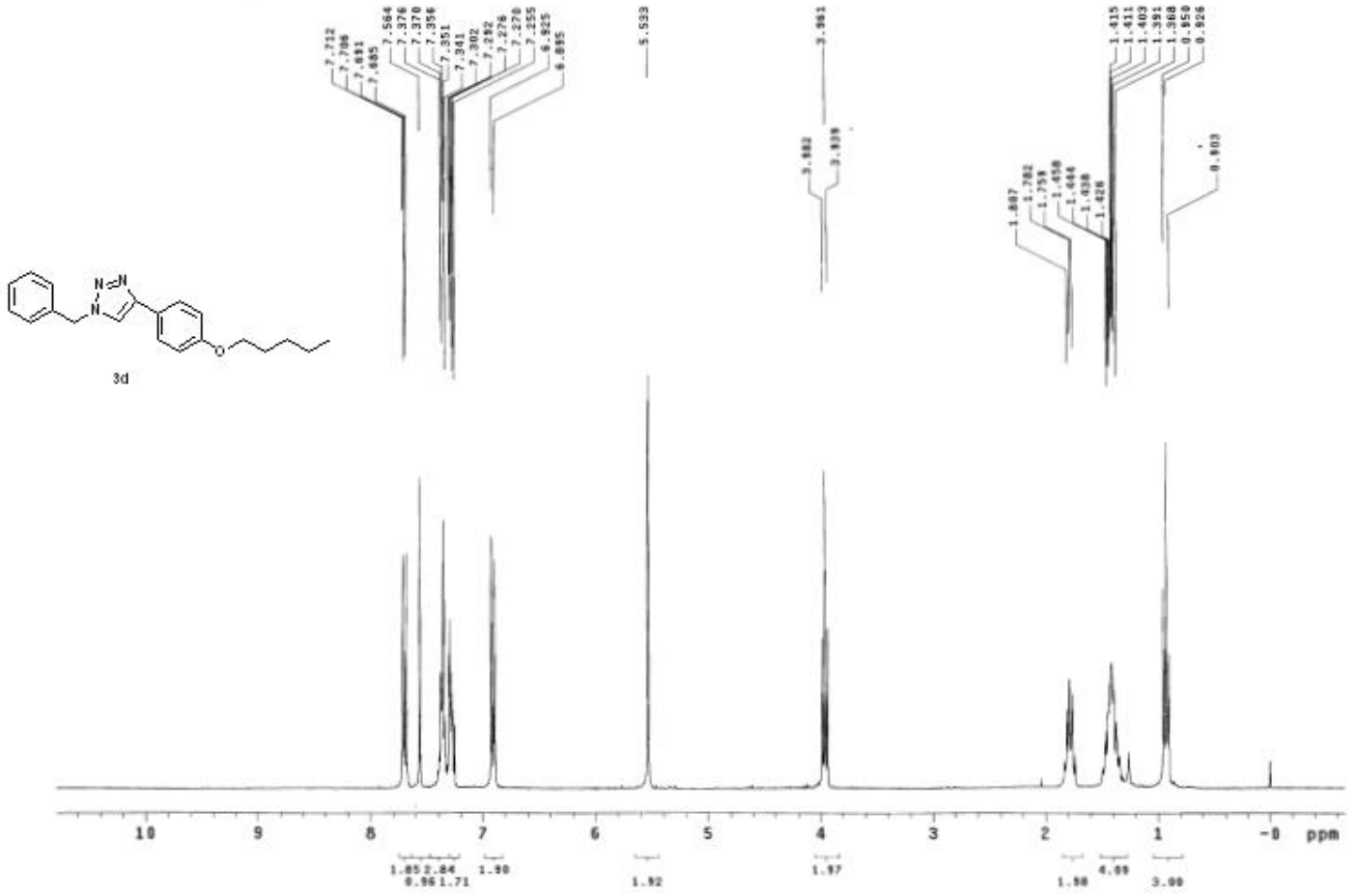
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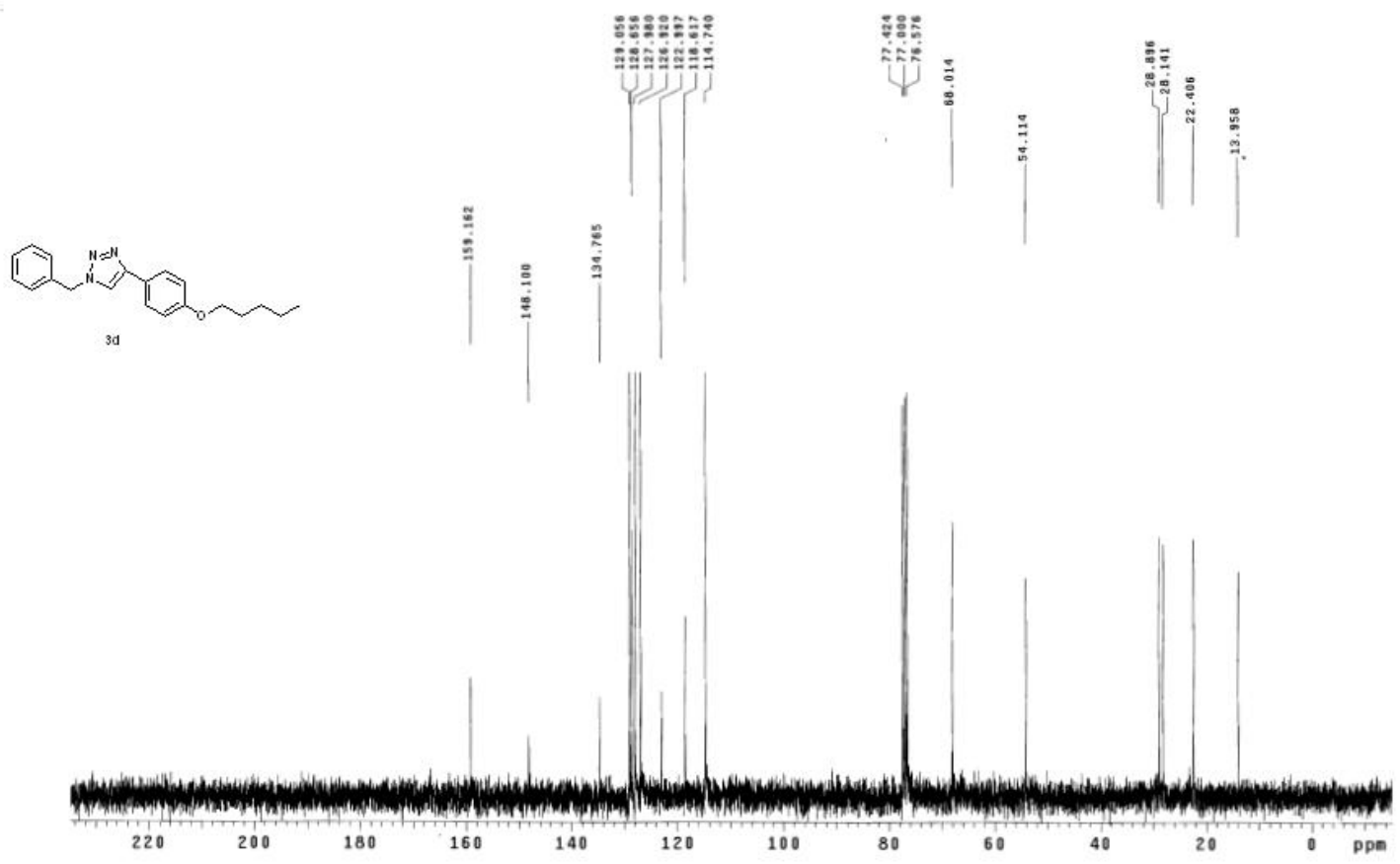

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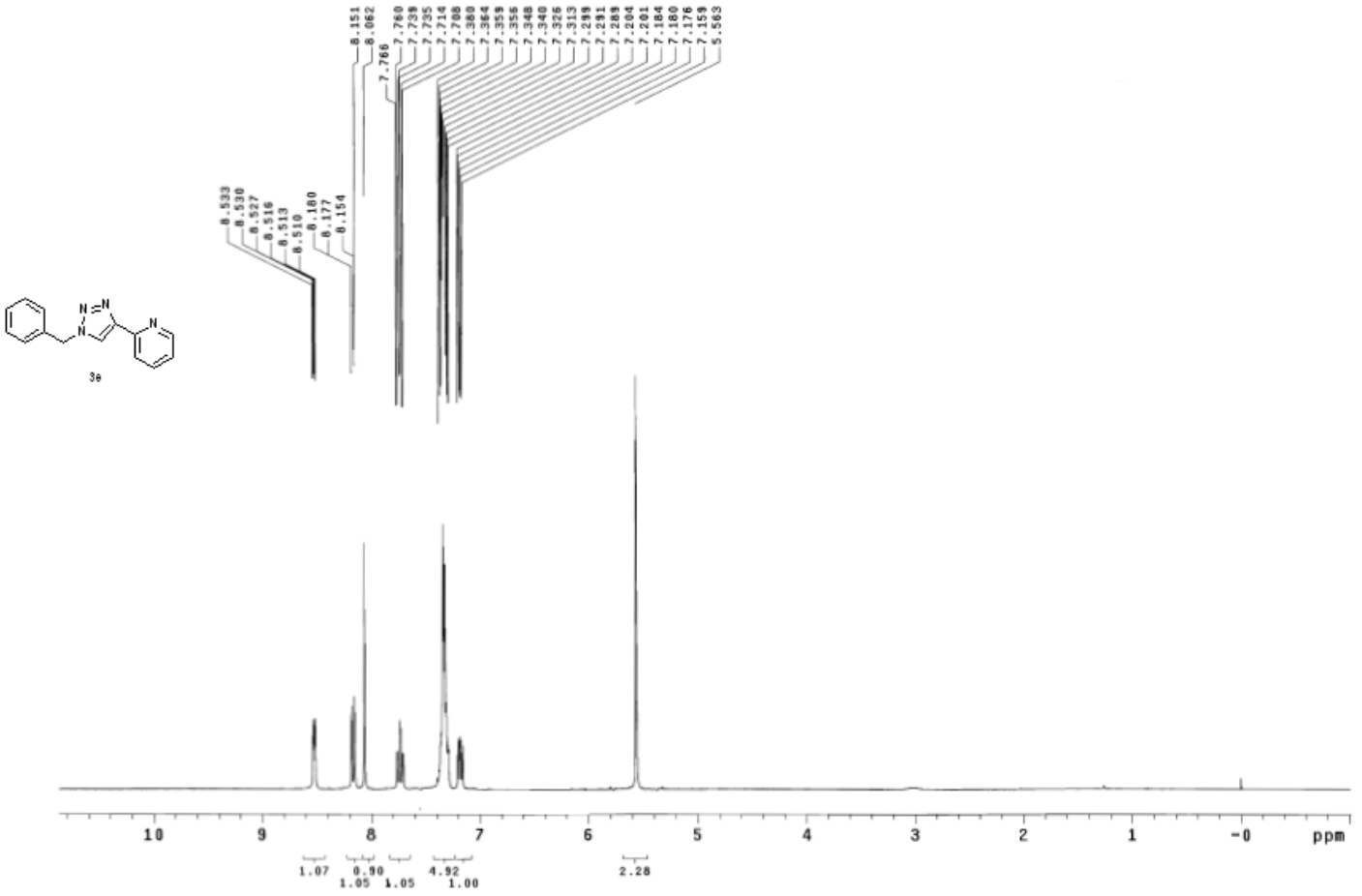
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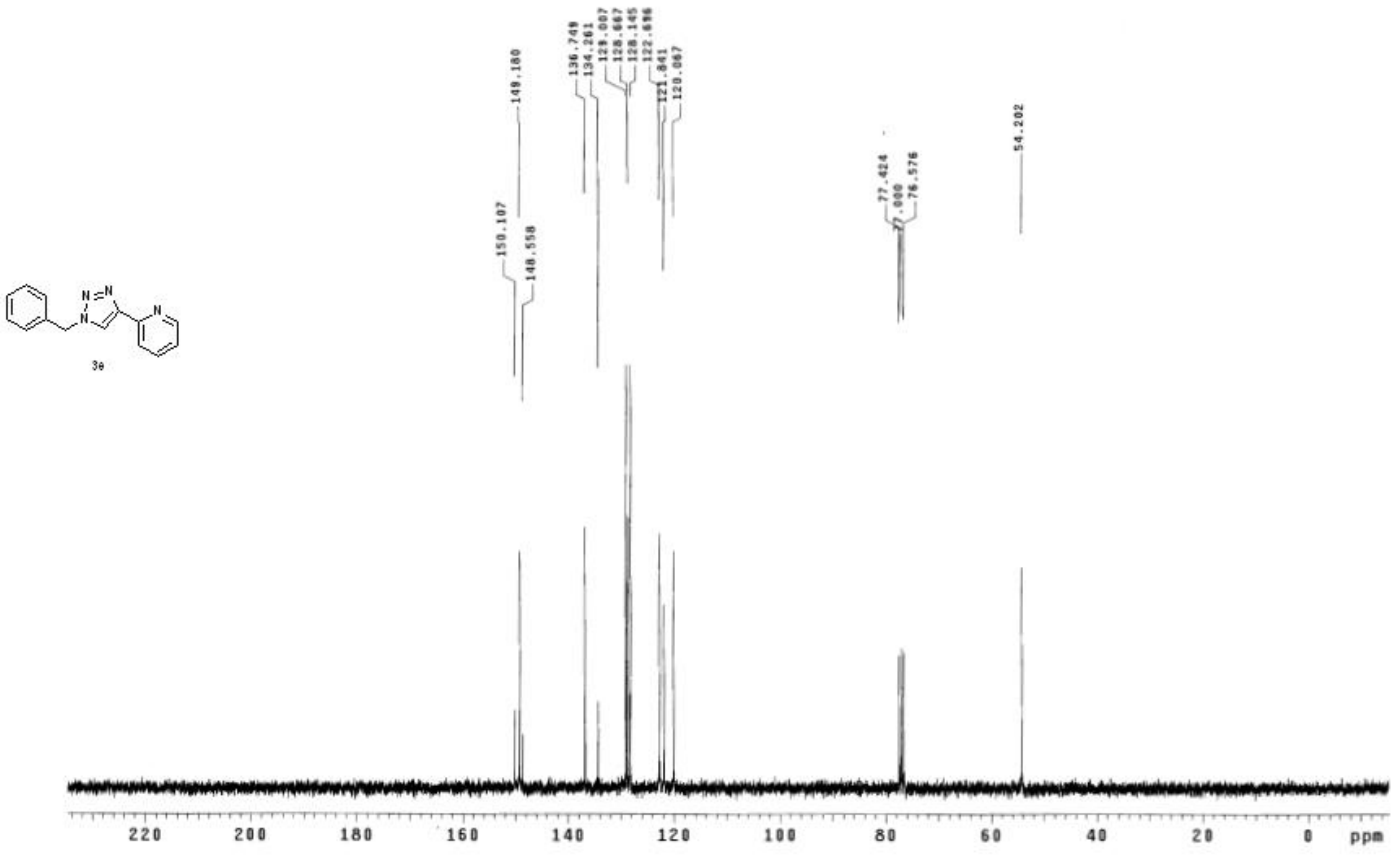

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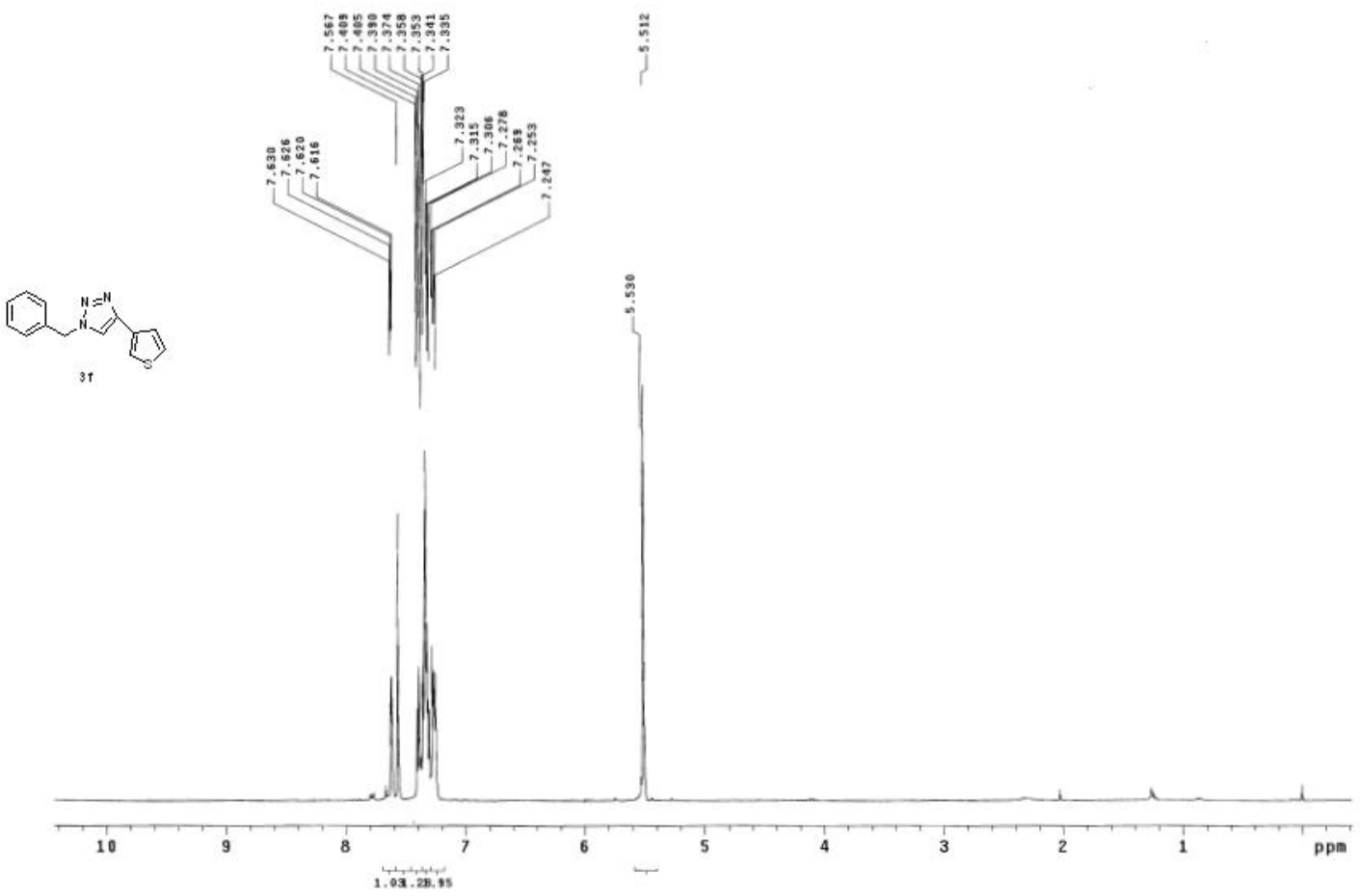
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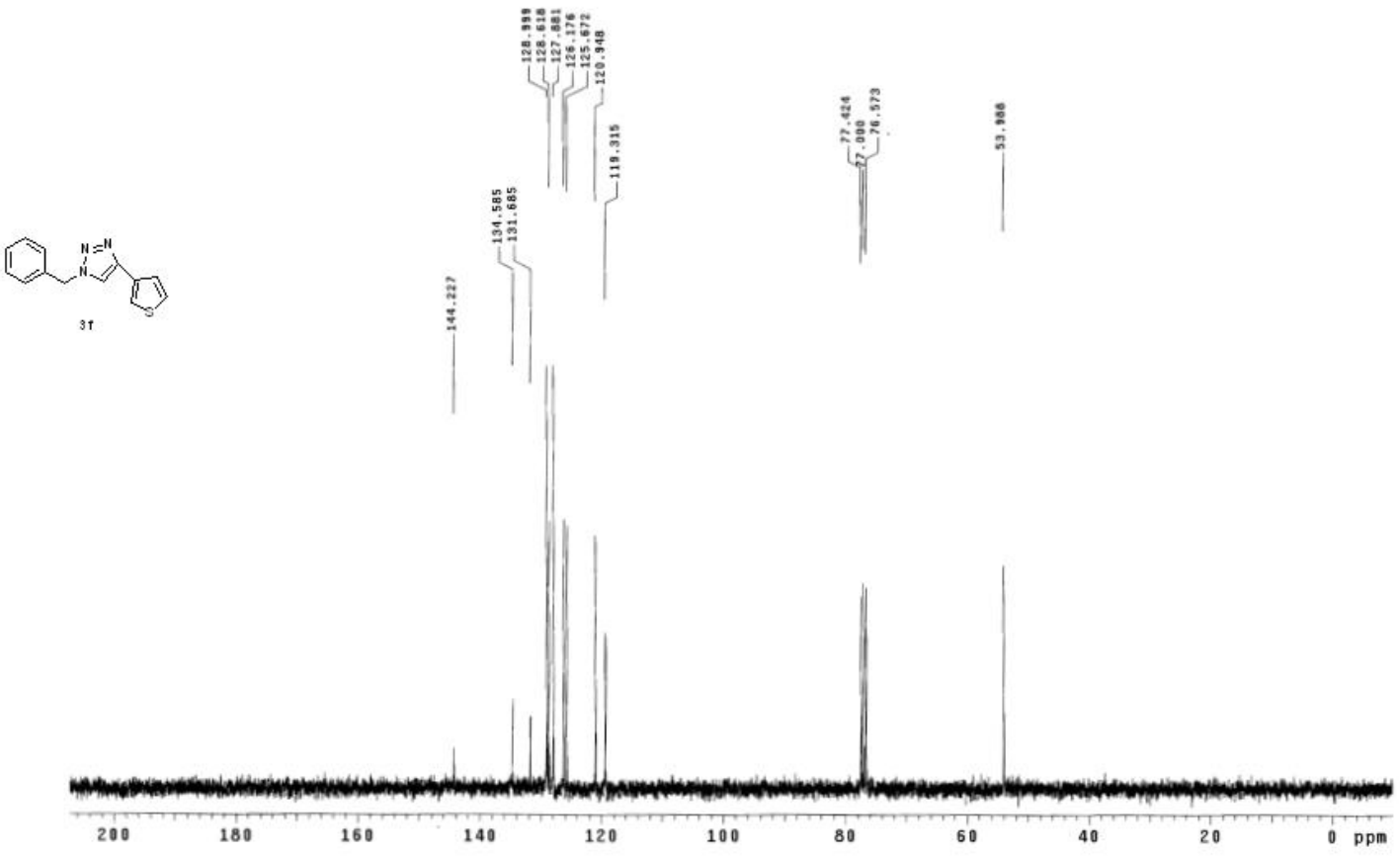

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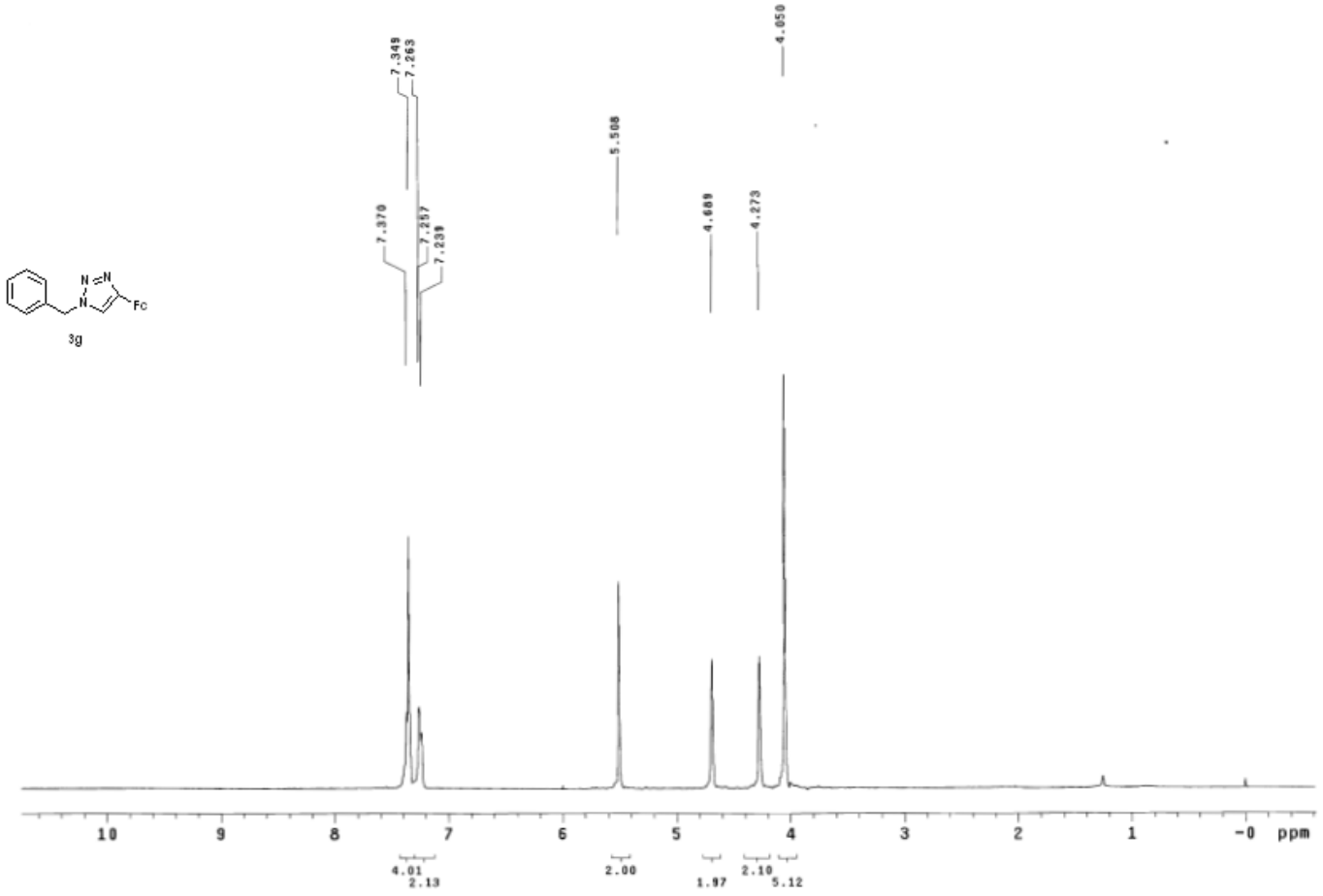
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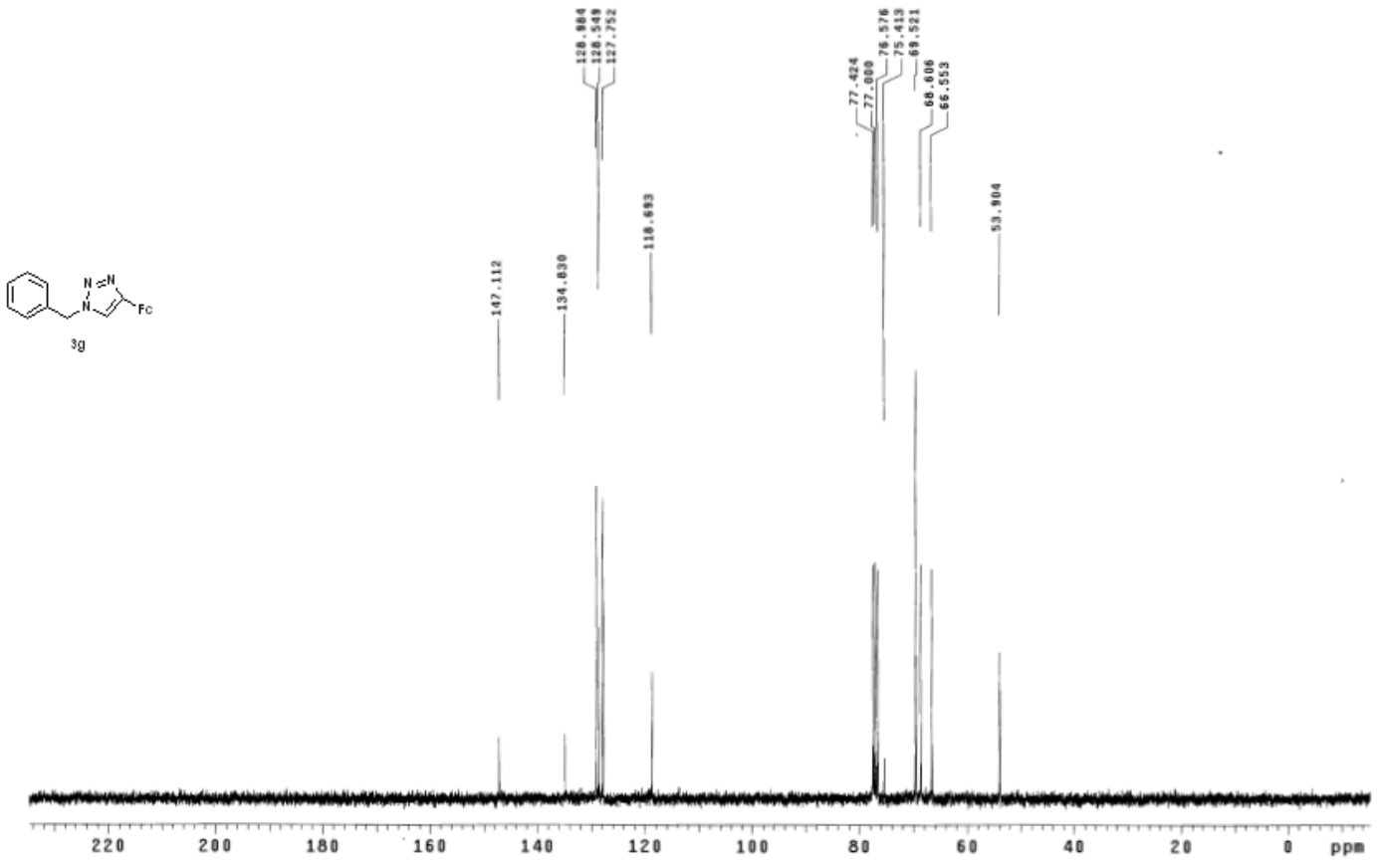

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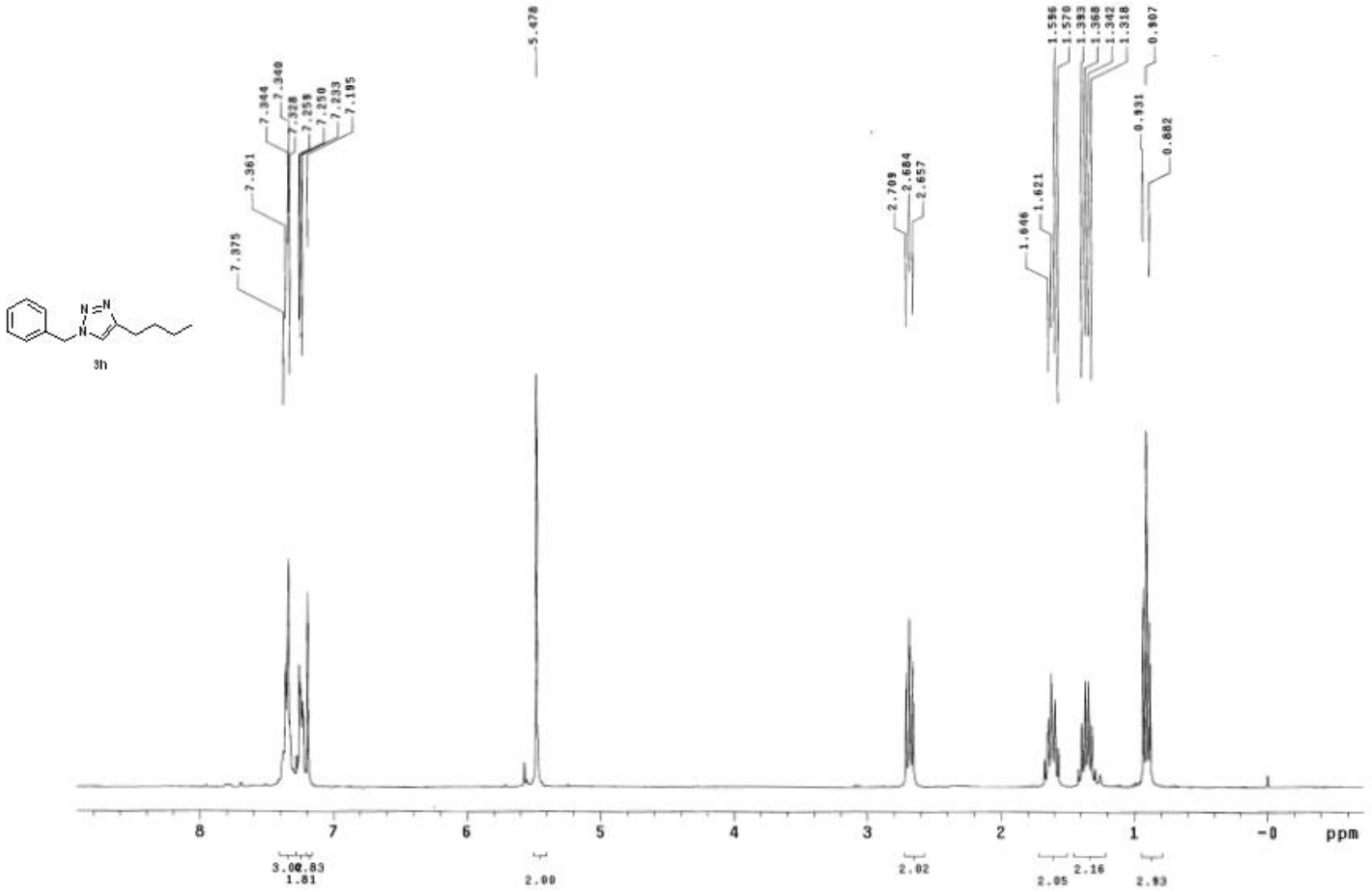
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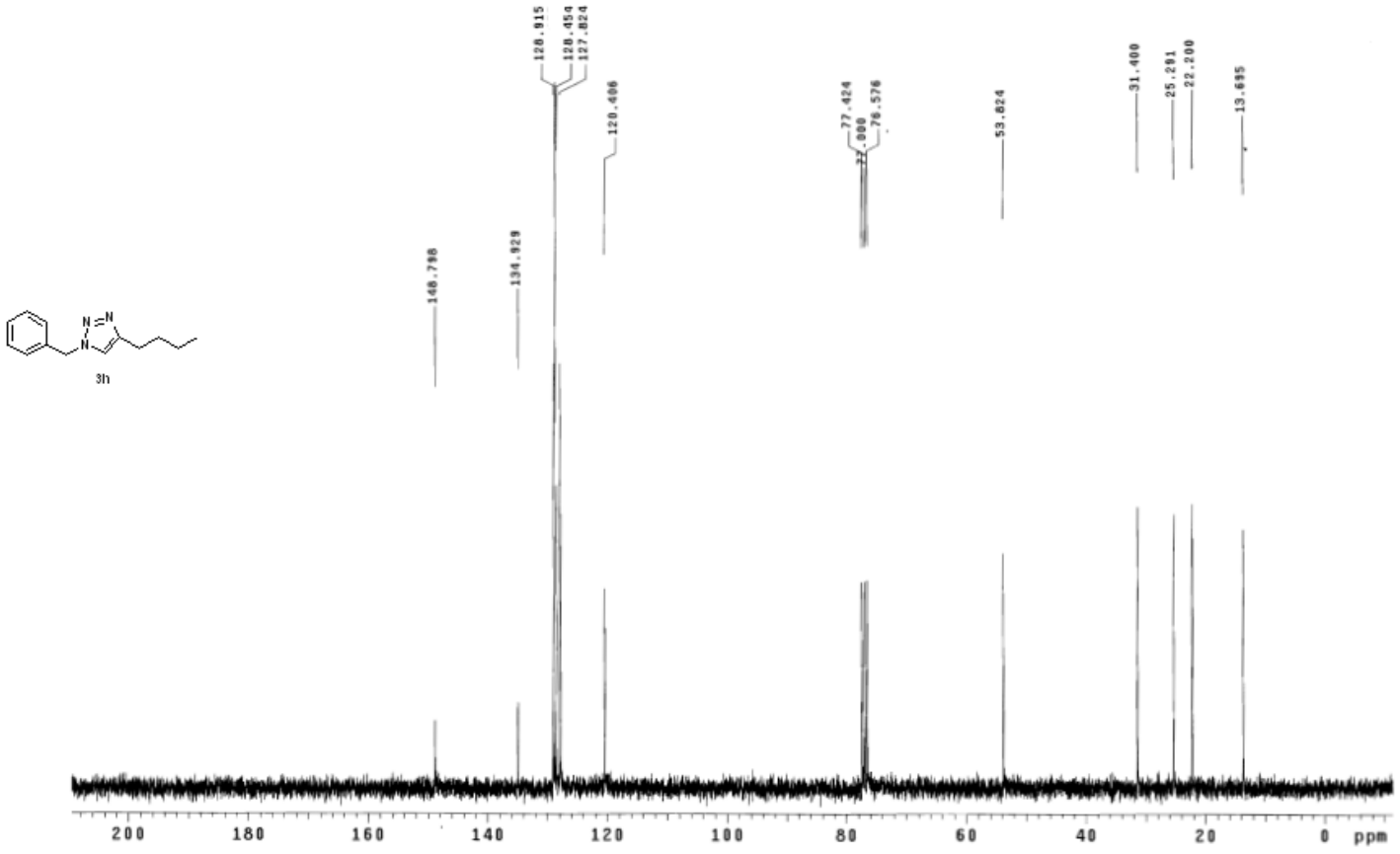

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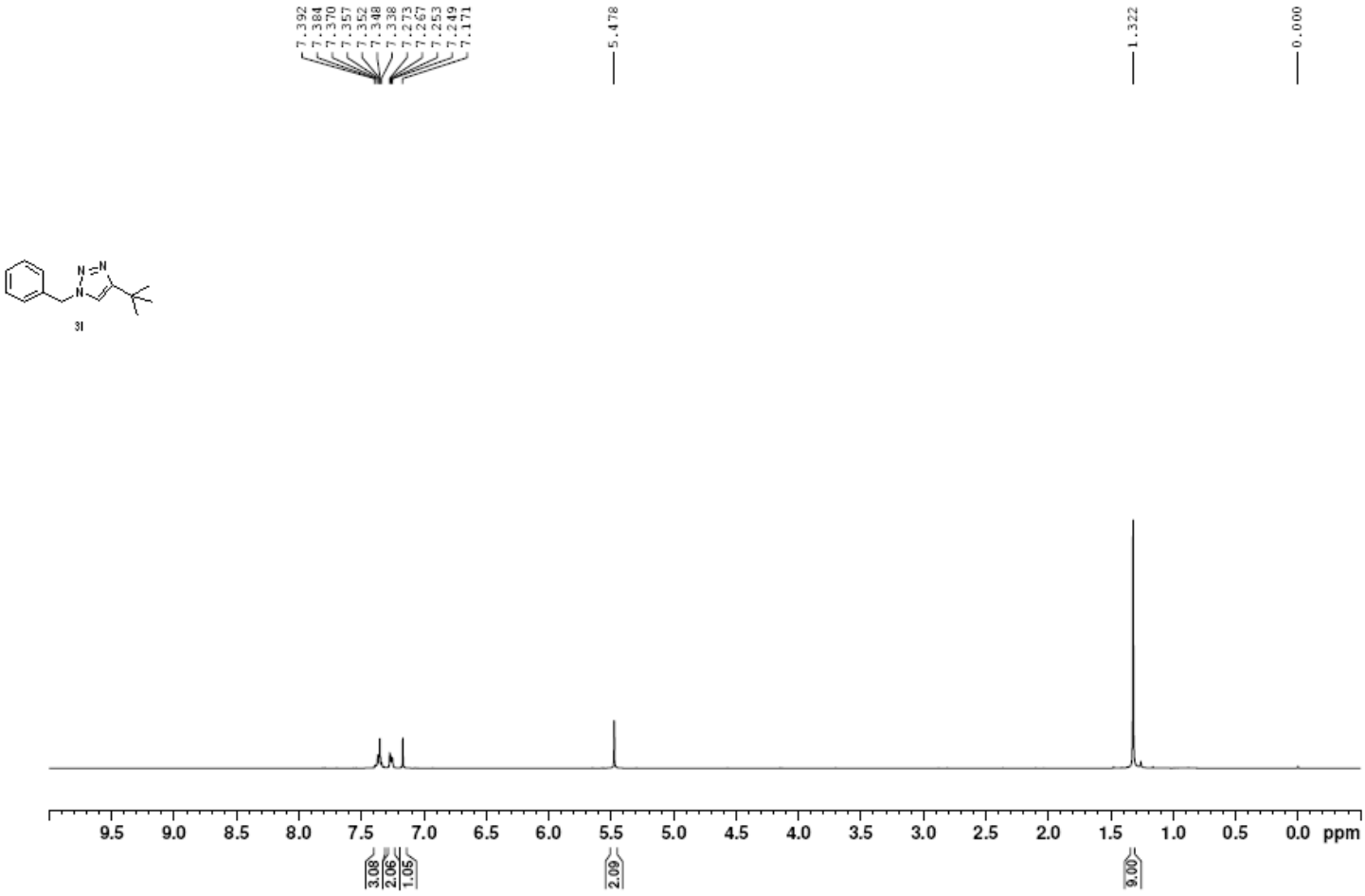
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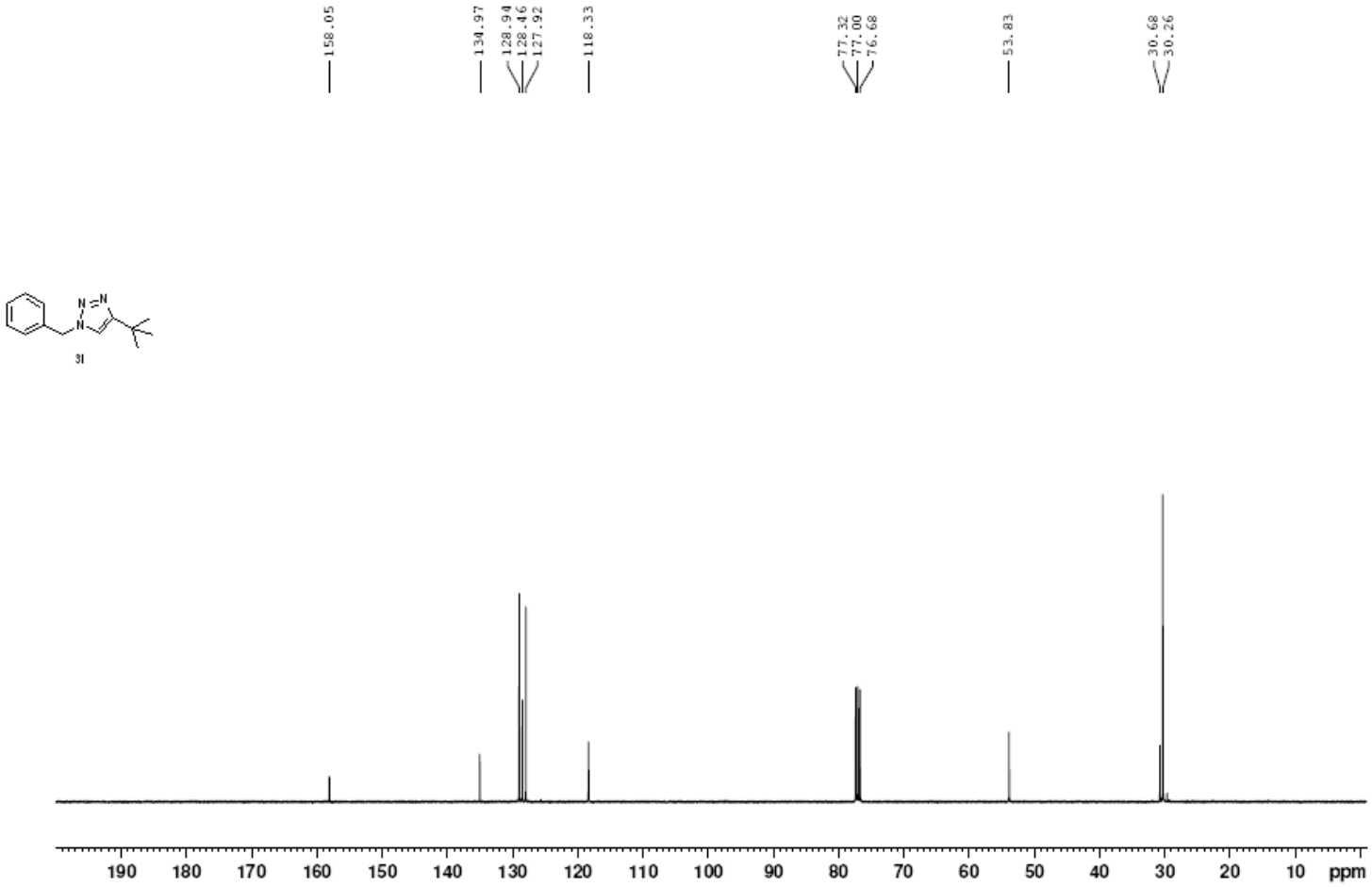

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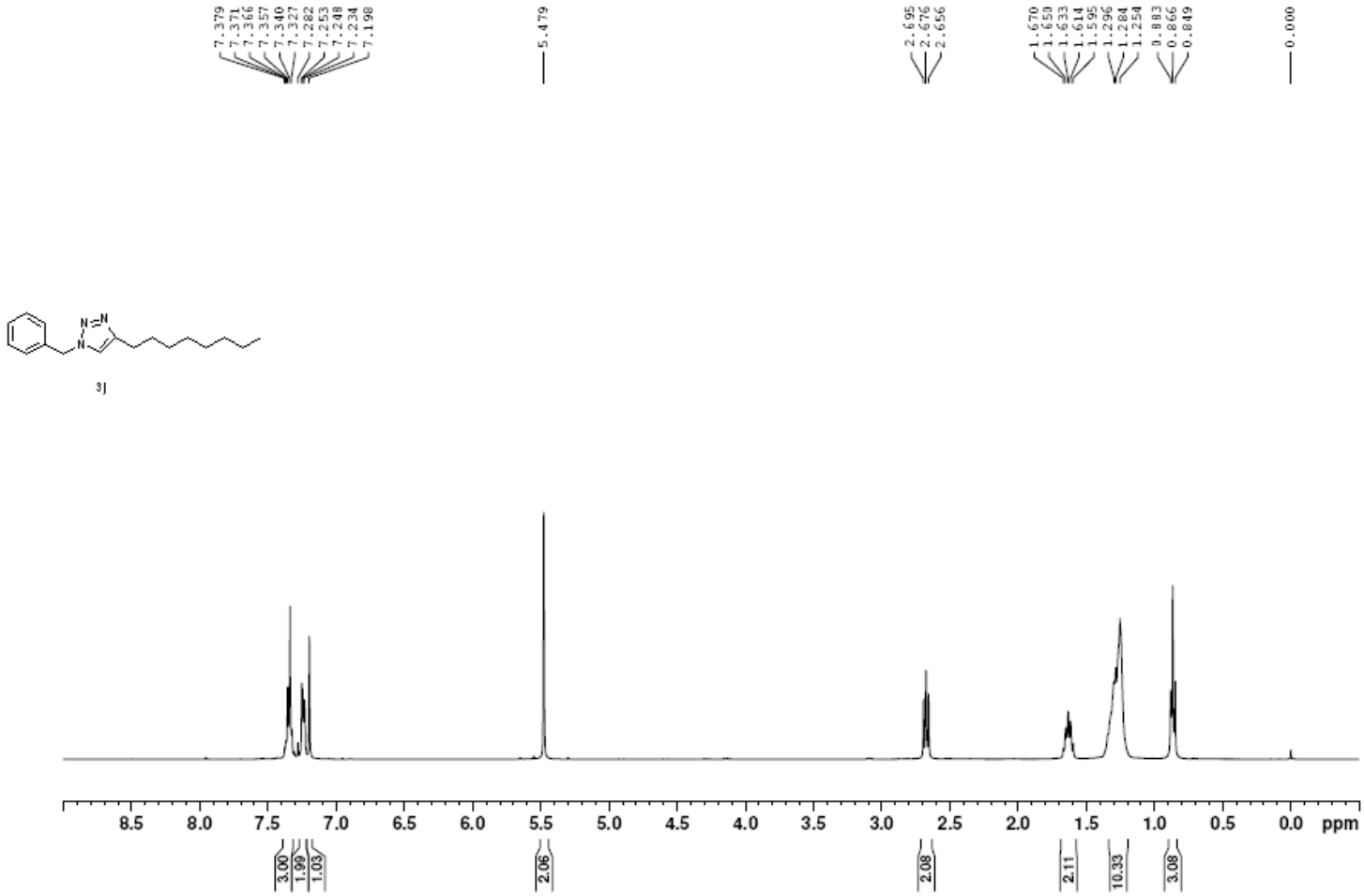
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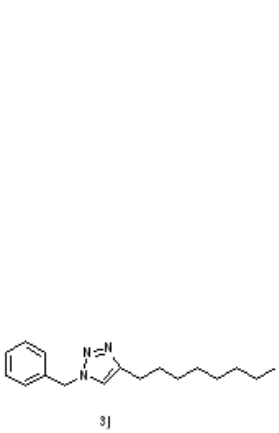
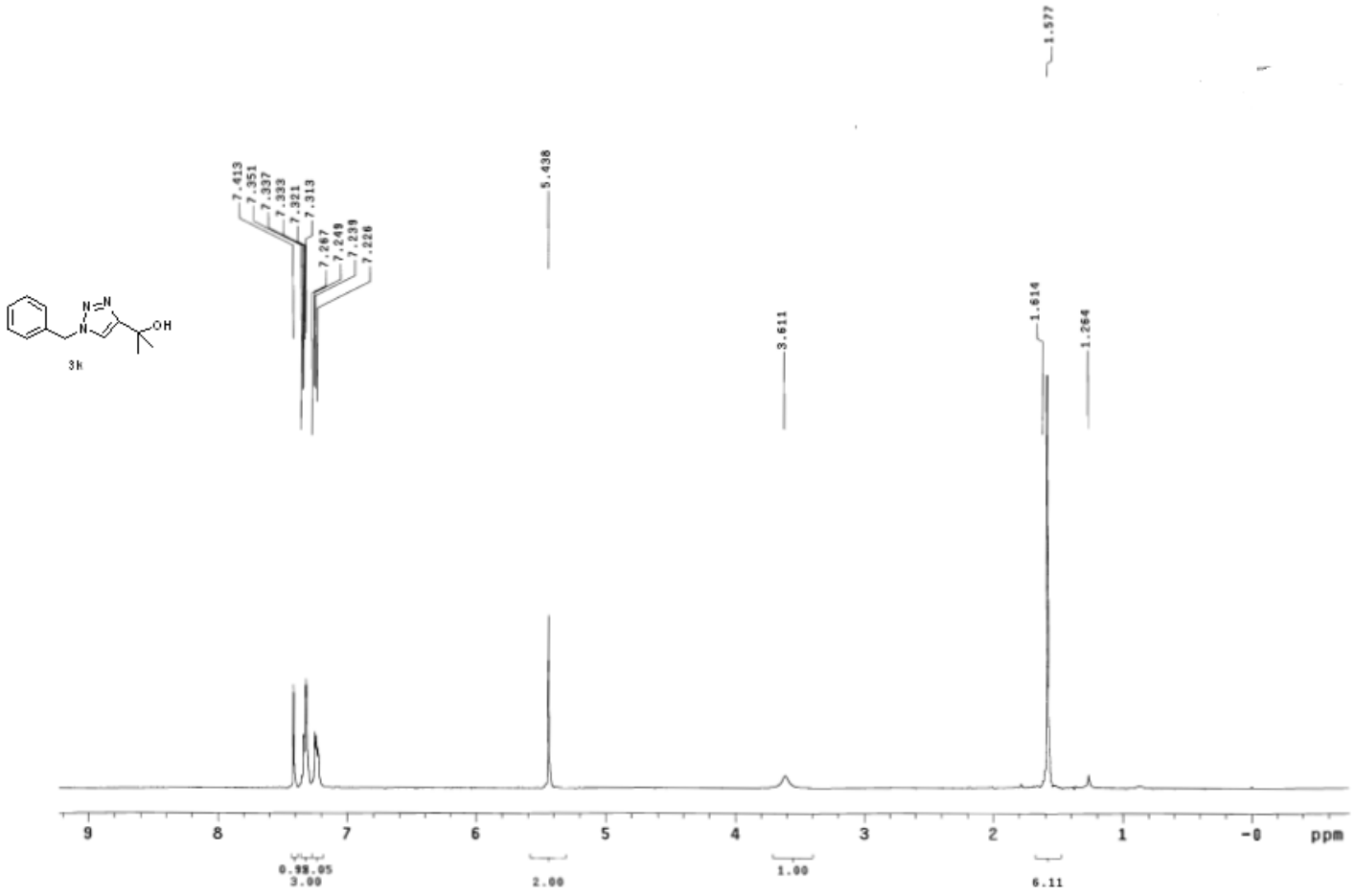
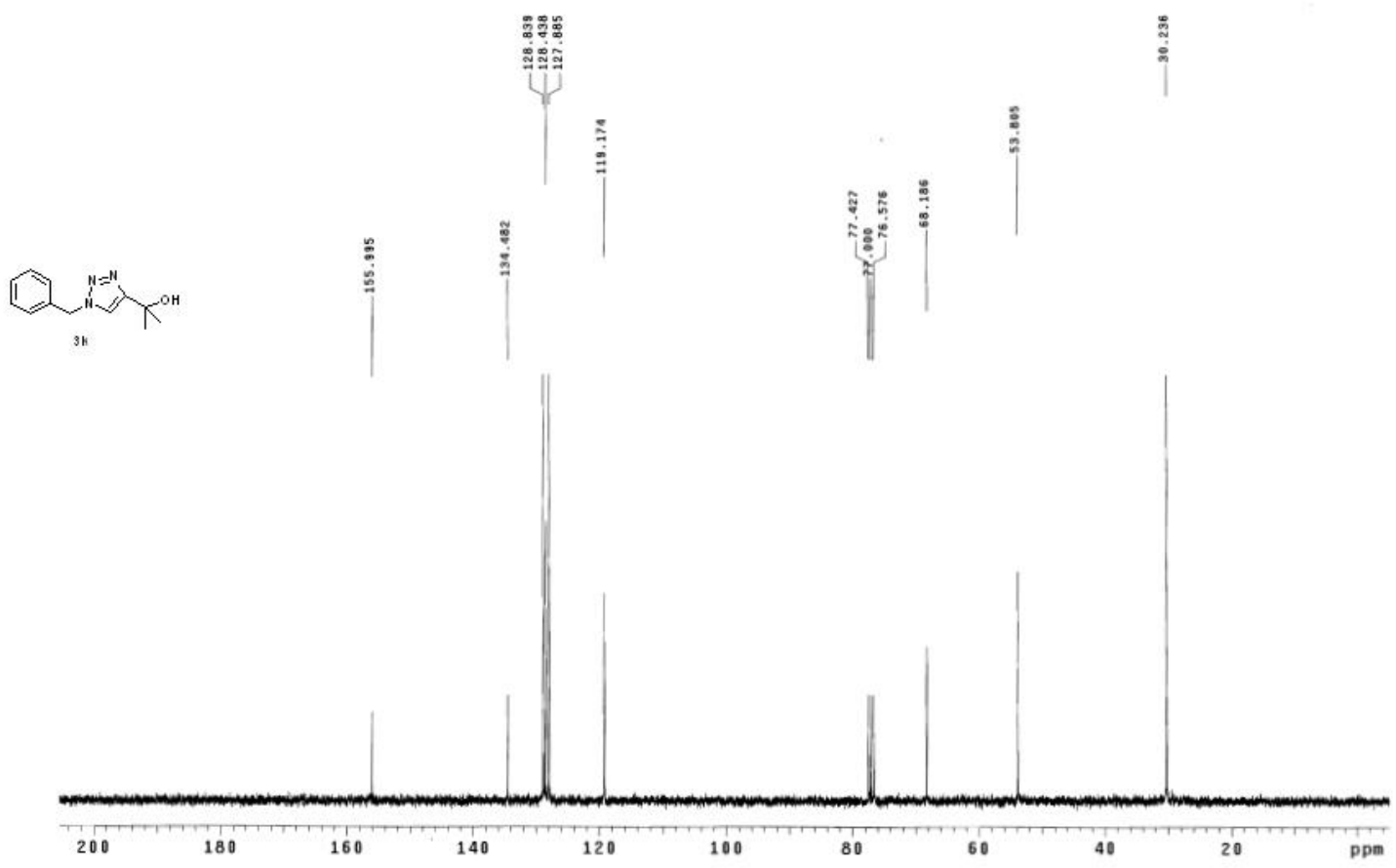
3.08

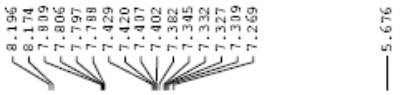


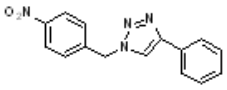
3k


7.413
7.351
7.337
7.333
7.321
7.313
7.267
7.249
7.239
7.226
5.438
3.611
1.614
1.577
1.264
OH
3k
9
8
7
6
5
4
3
2
1
-0
ppm
3.00
2.00
1.00
6.11

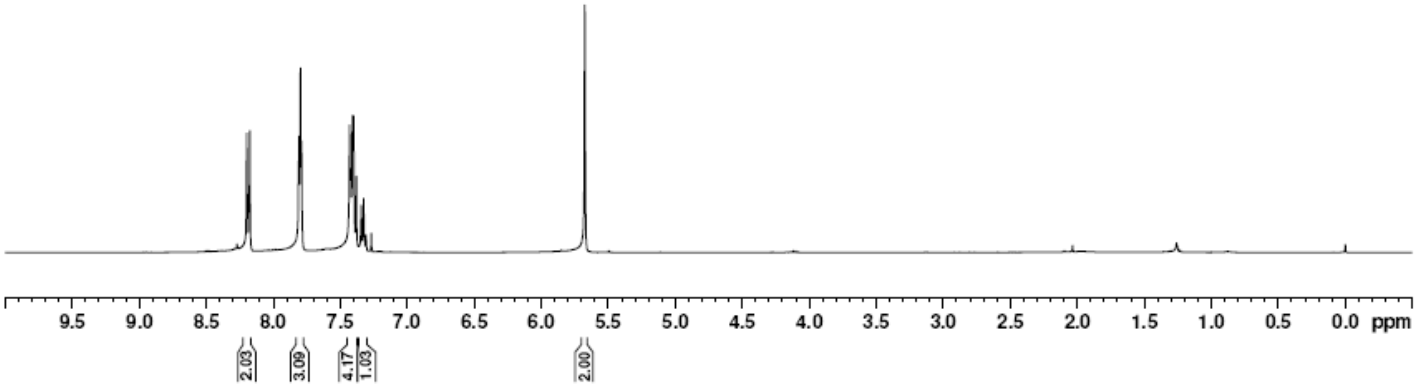


4a


8.196
8.174
7.809
7.806
7.797
7.788
7.429
7.420
7.407
7.402
7.382
7.345
7.332
7.327
7.309
7.269
5.676



4a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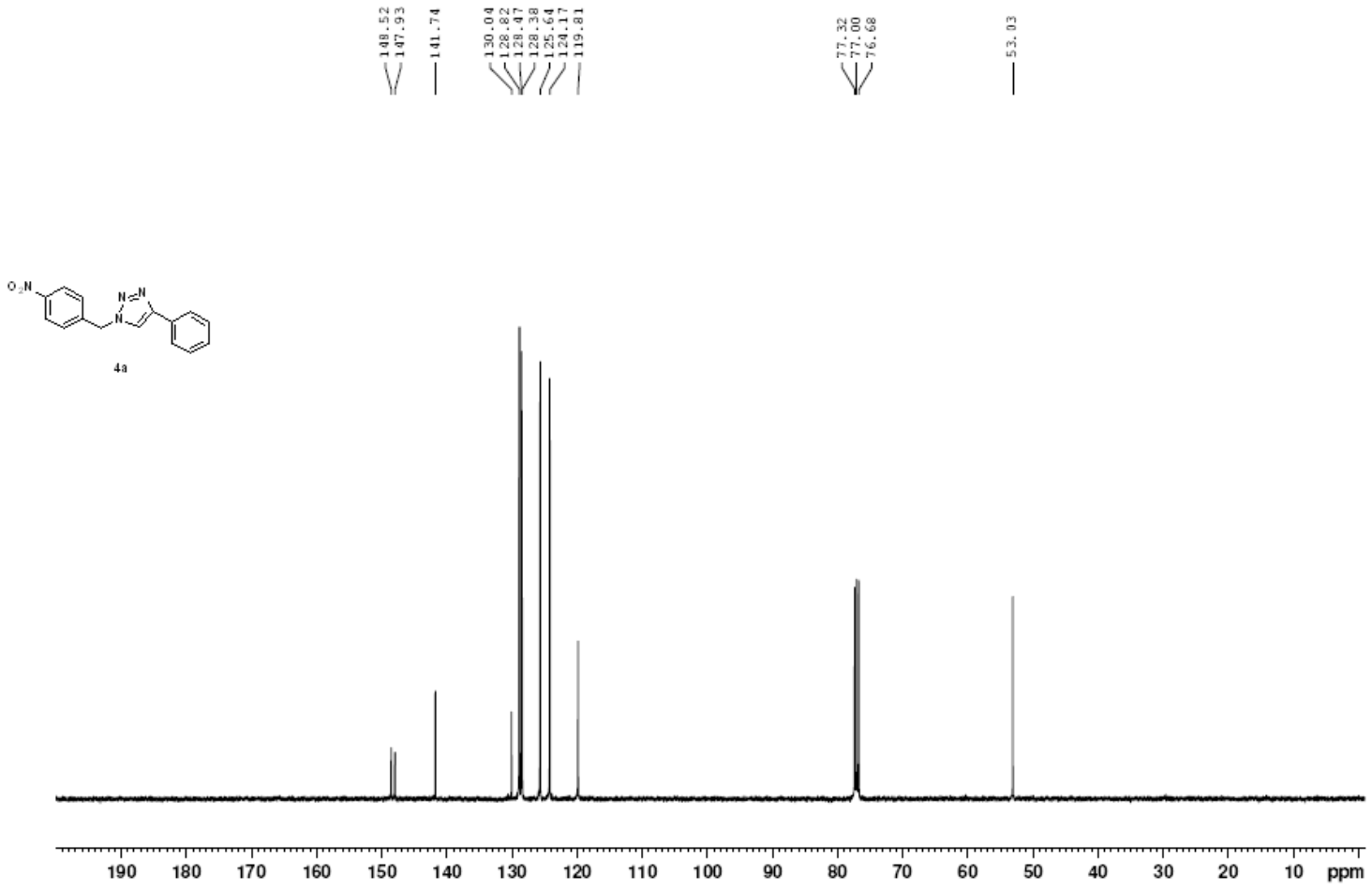
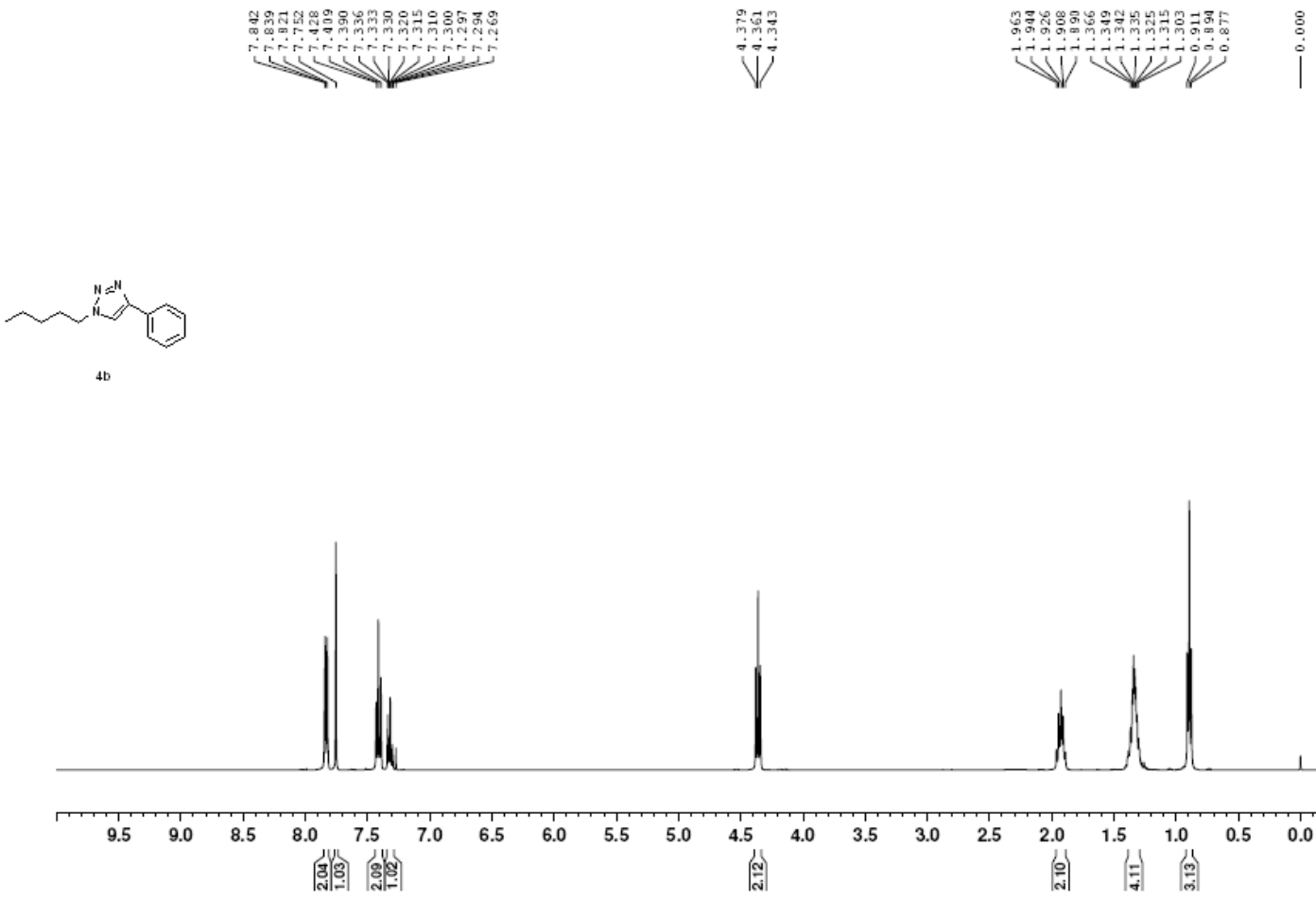
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.03
3.09
4.17
1.03
2.00



4b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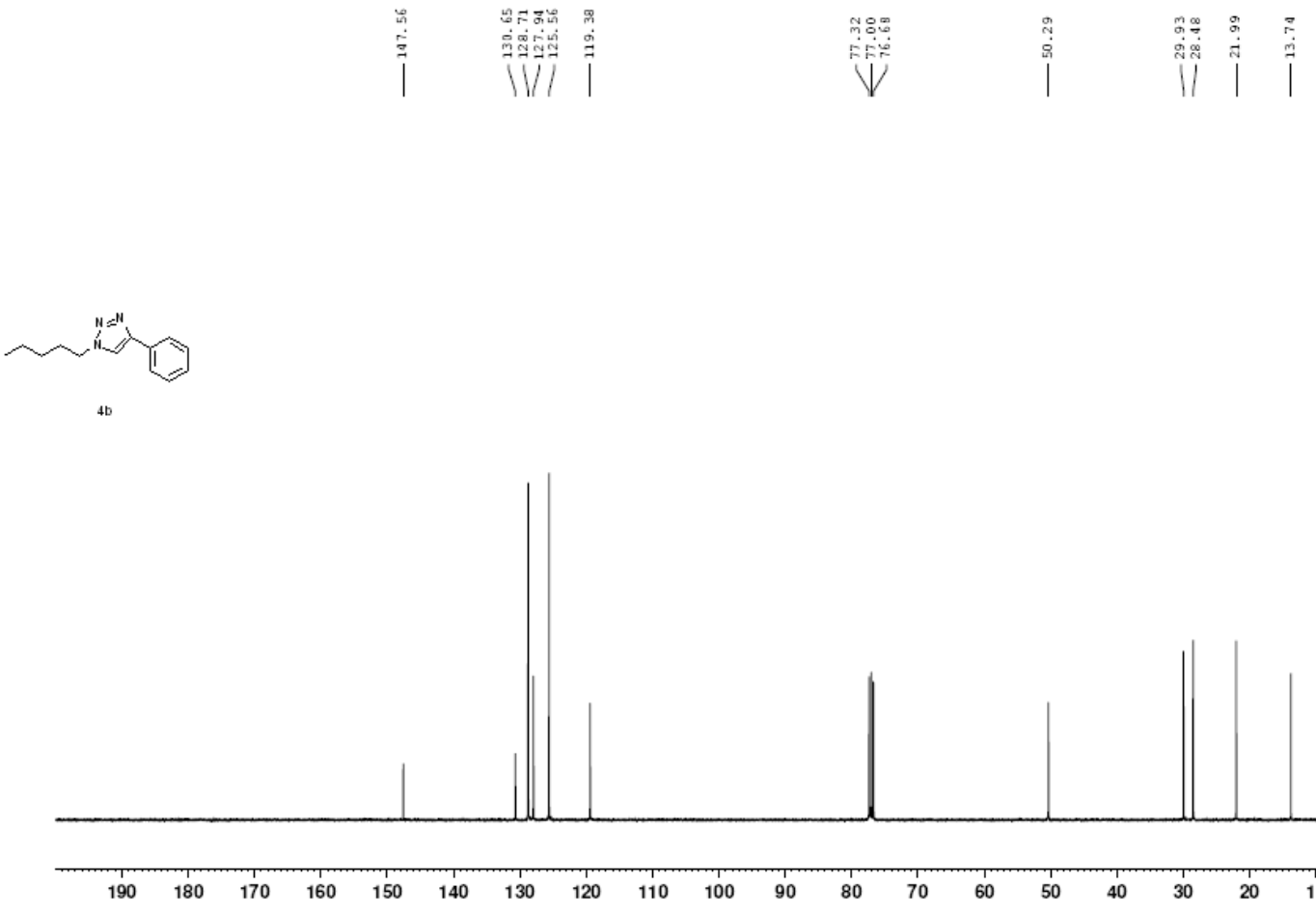
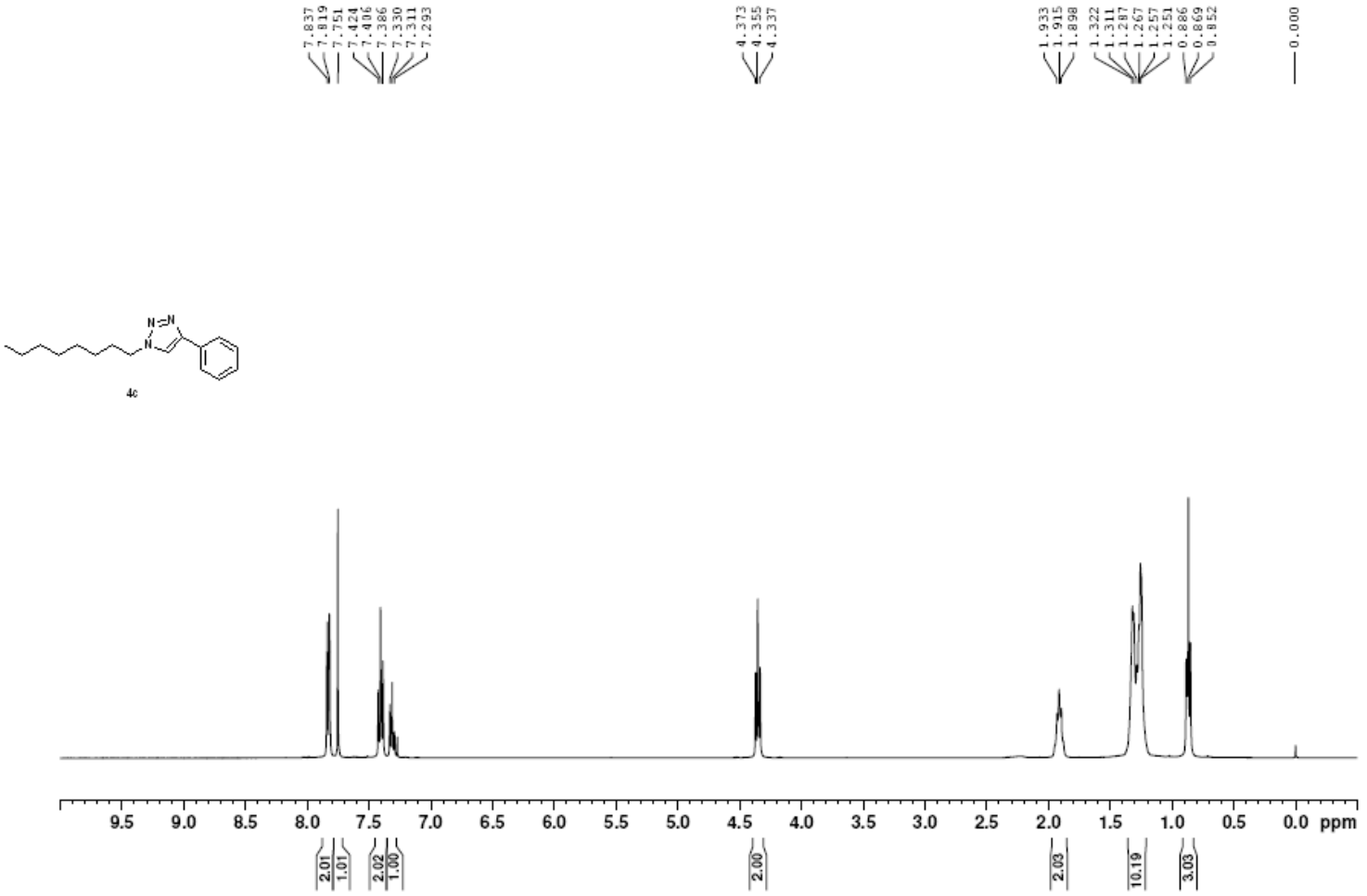
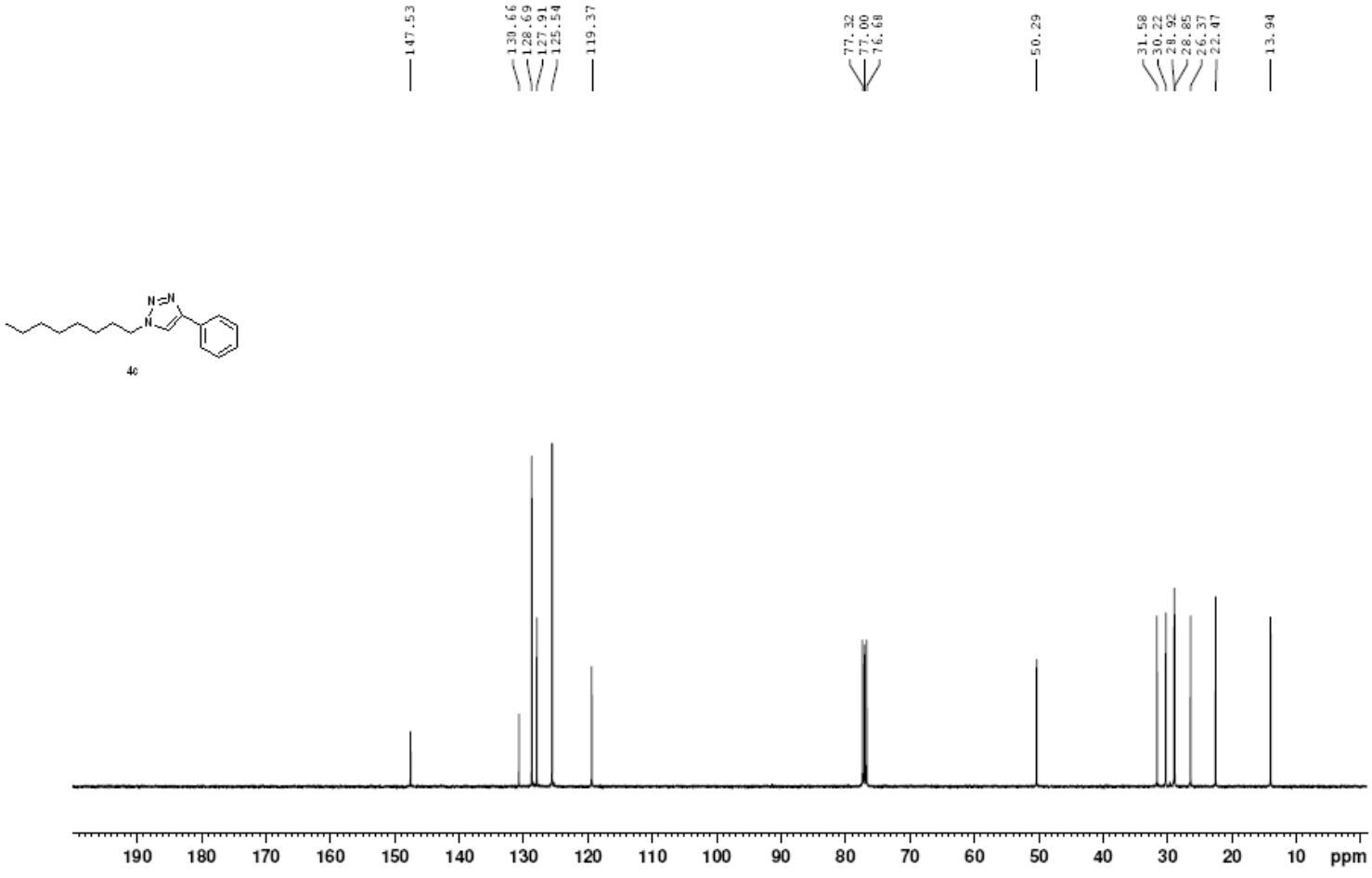
7.839
7.821
7.752
7.428
7.409
7.390
7.336
7.333
7.330
7.320
7.315
7.310
7.300
7.297
7.294
7.269
4.379
4.361
4.343
1.963
1.944
1.926
1.908
1.890
1.366
1.349
1.342
1.335
1.325
1.315
1.303
0.911
0.894
0.877
0.000
4b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
2.04
1.03
2.09
1.02
2.12
2.10
4.11
3.13



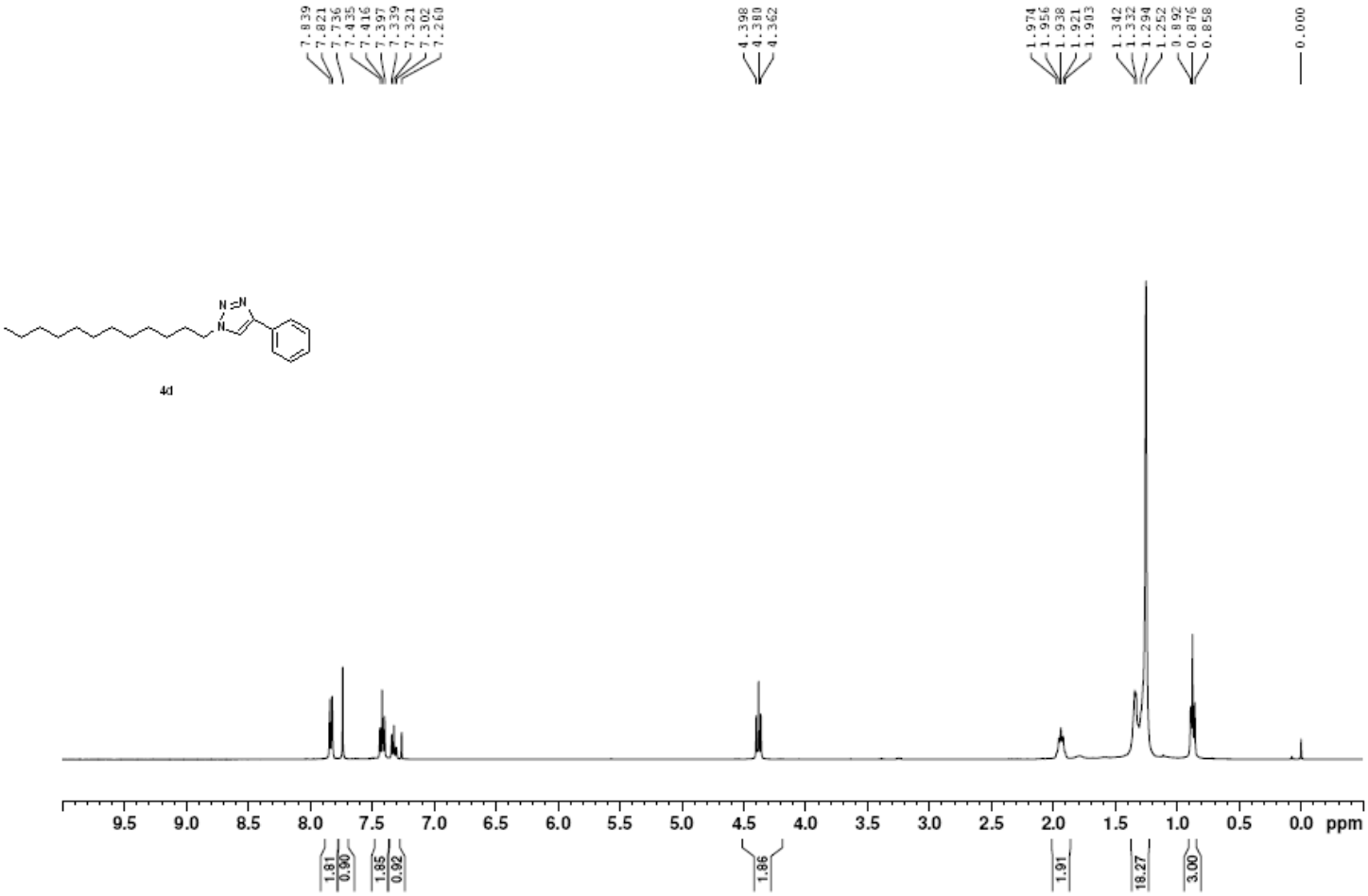
4b

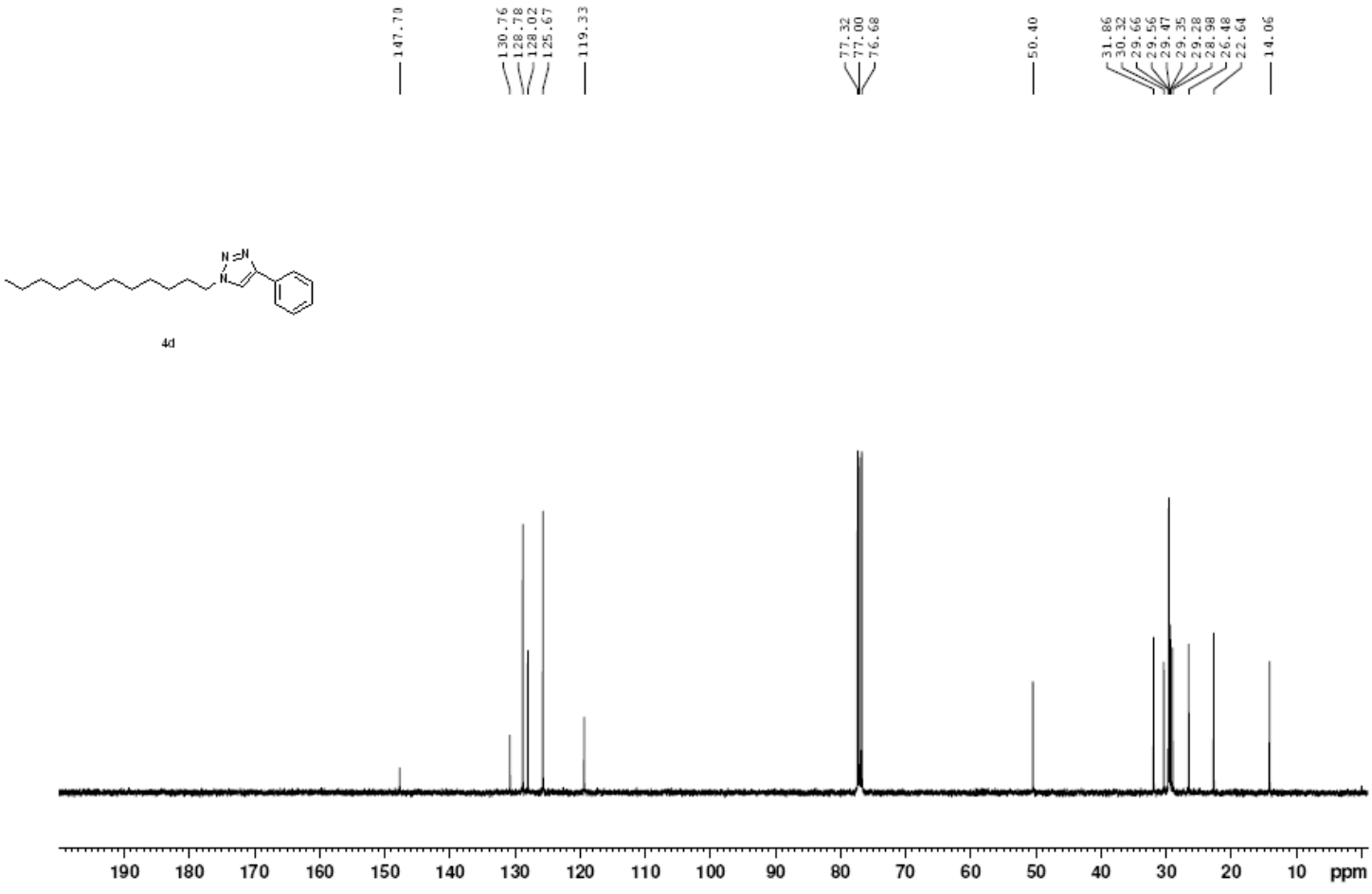
4c


7.837
7.819
7.751
7.424
7.406
7.386
7.330
7.311
7.293
4.373
4.355
4.337
1.933
1.915
1.898
1.322
1.311
1.287
1.267
1.257
1.251
0.886
0.869
0.852
0.000
4c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
1.01
2.02
1.00
2.00
2.03
10.19
3.03

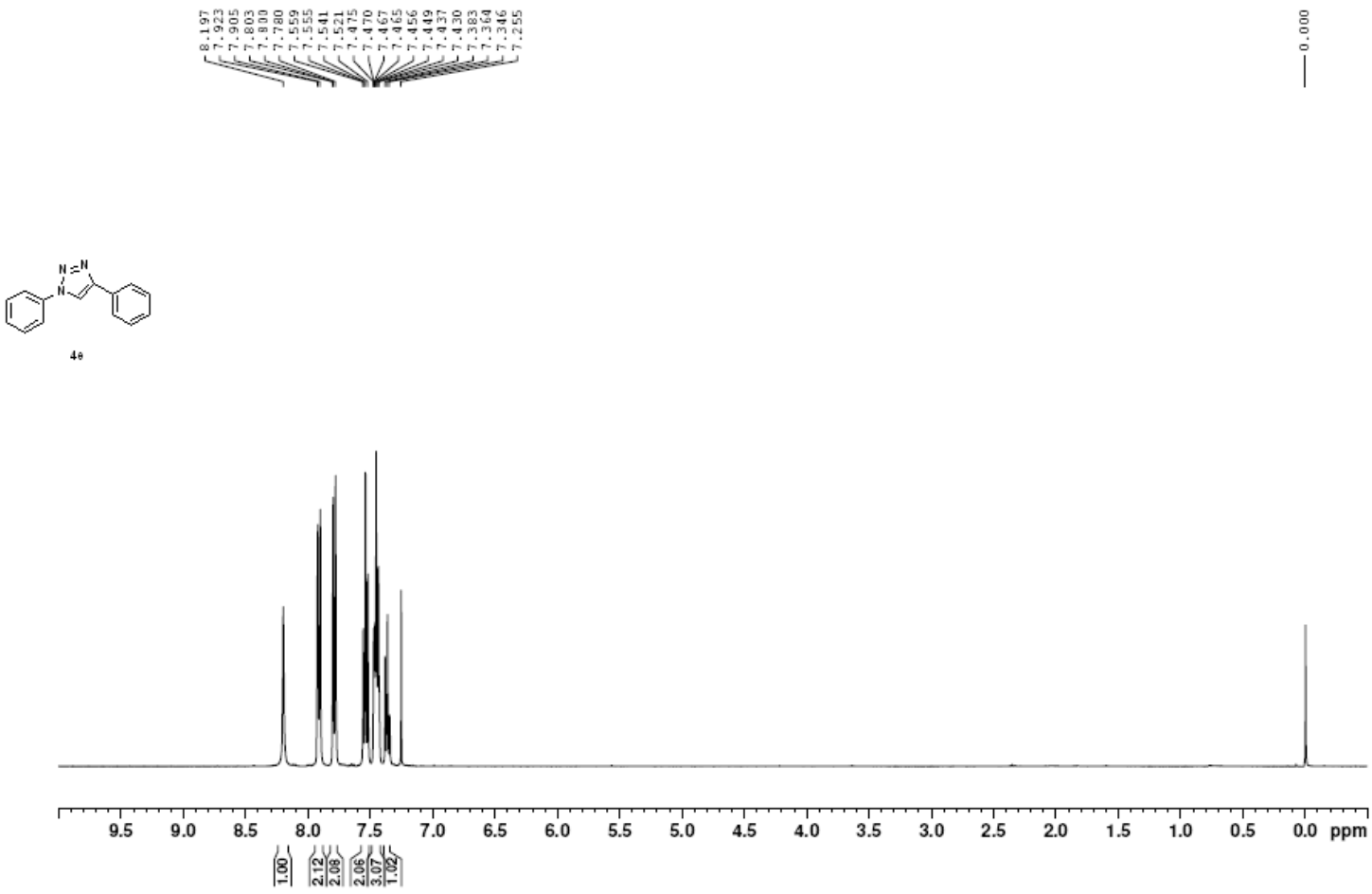


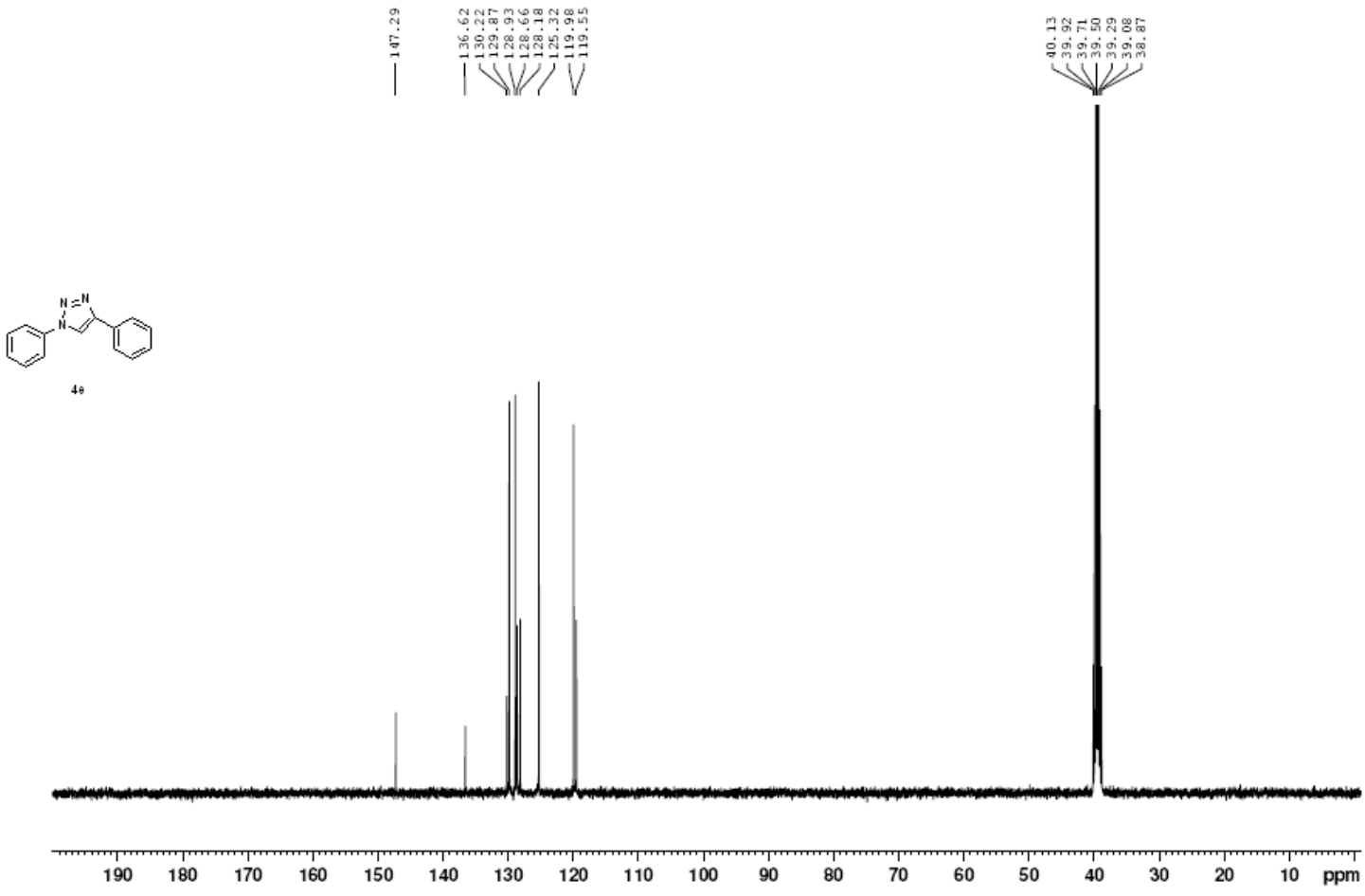
4d


7.839
7.821
7.736
7.435
7.416
7.397
7.339
7.321
7.302
7.260
4.398
4.380
4.362
1.974
1.956
1.938
1.921
1.903
1.342
1.332
1.294
1.252
0.892
0.876
0.858
0.000
4d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.81
0.90
1.85
0.92
1.86
1.91
18.27
3.00


147.70
130.76
128.78
128.02
125.67
119.33
77.32
77.00
76.68
50.40
31.86
30.32
29.66
29.56
29.47
29.35
29.28
28.98
26.48
22.64
14.06
4d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

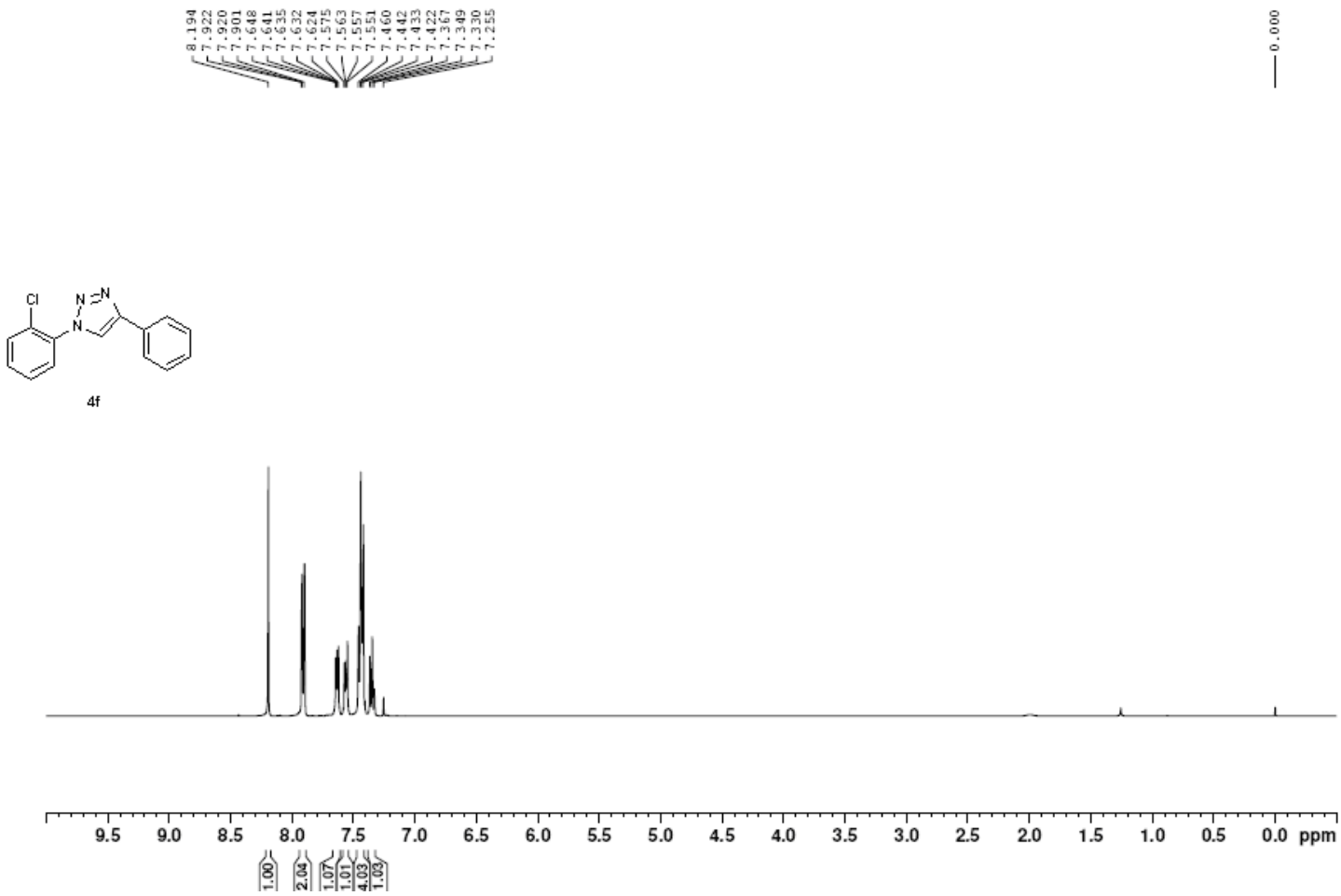
4e

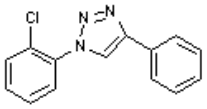

8.197
7.923
7.905
7.803
7.800
7.780
7.559
7.555
7.541
7.521
7.475
7.470
7.467
7.465
7.456
7.449
7.437
7.430
7.383
7.364
7.346
7.255
0.000
4e
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.12
2.08
2.06
3.07
1.02



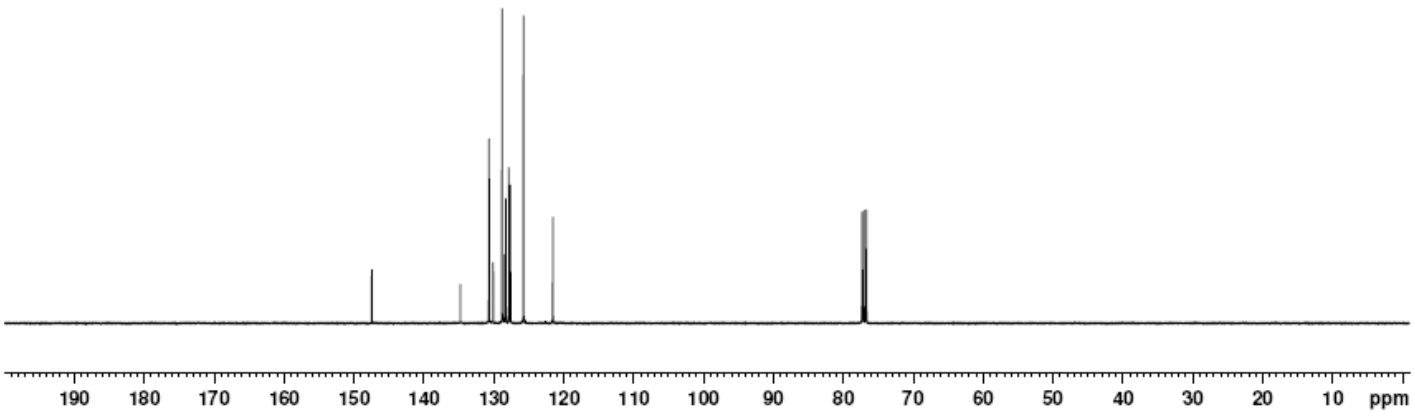
4e

4f

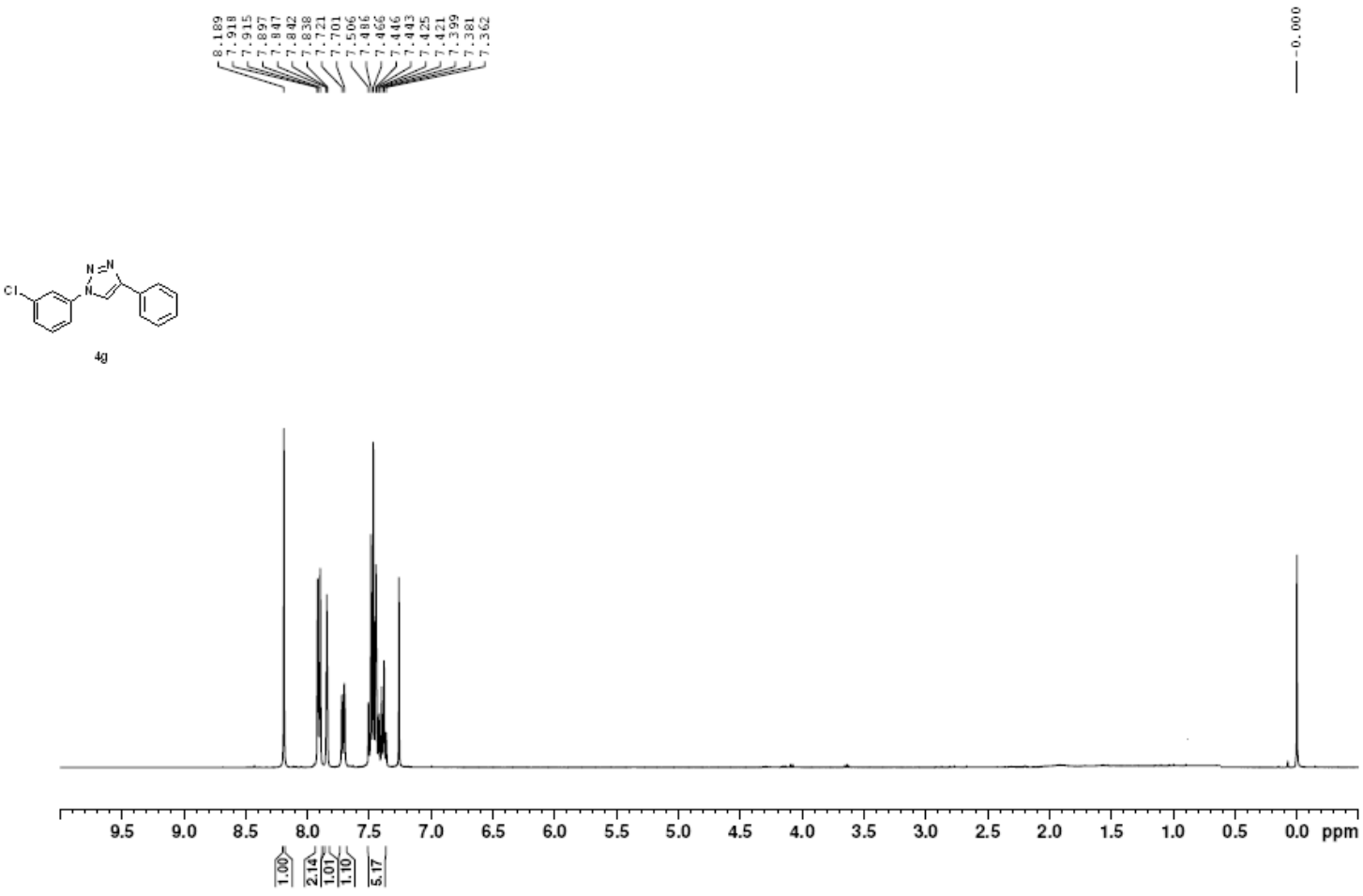

8.194
7.922
7.920
7.901
7.648
7.641
7.635
7.632
7.624
7.575
7.563
7.557
7.551
7.460
7.442
7.433
7.422
7.367
7.349
7.330
7.255
0.000
Cl
N
N
4f
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.00
2.04
1.07
1.01
4.03
1.03

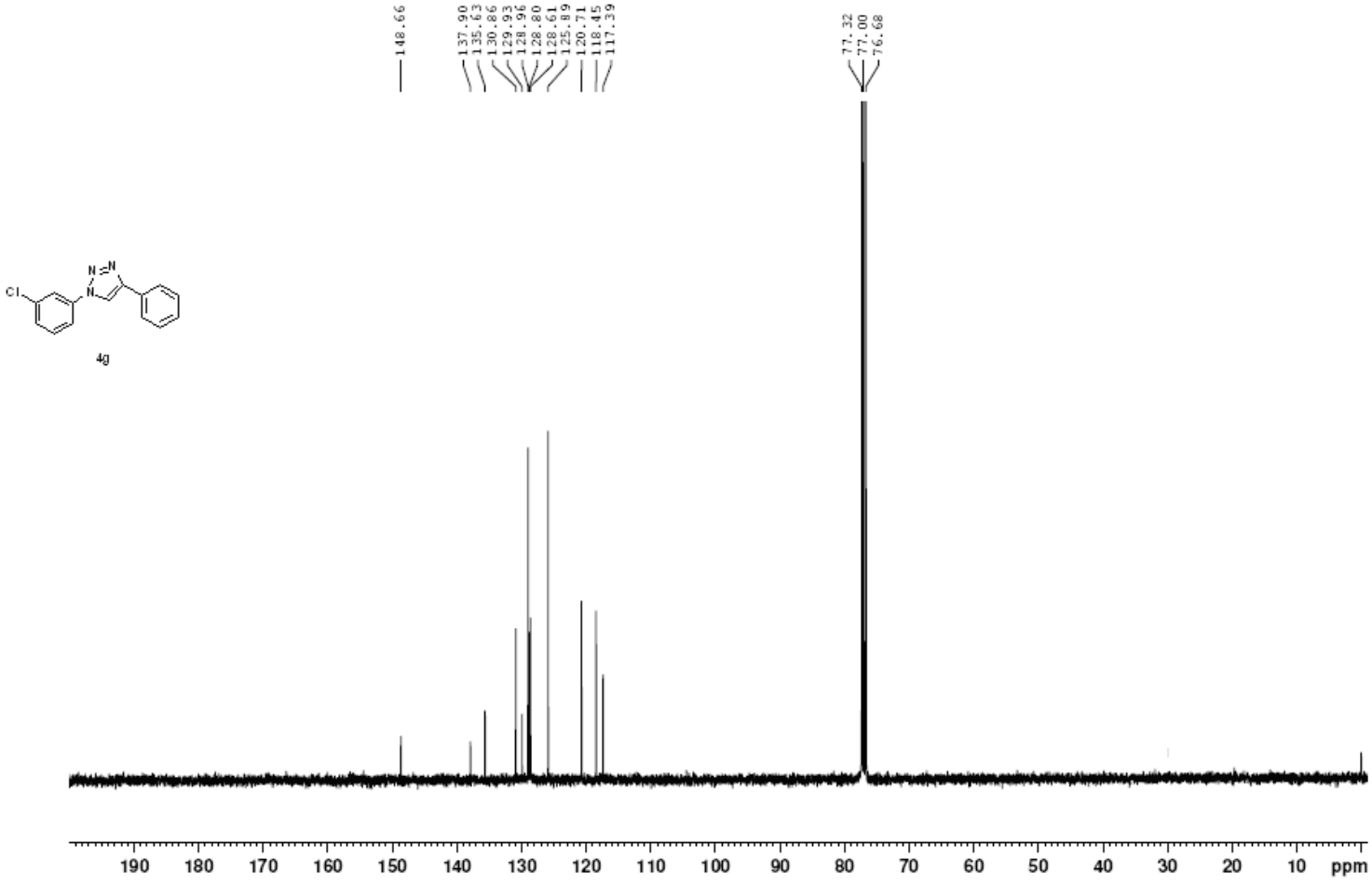


4f

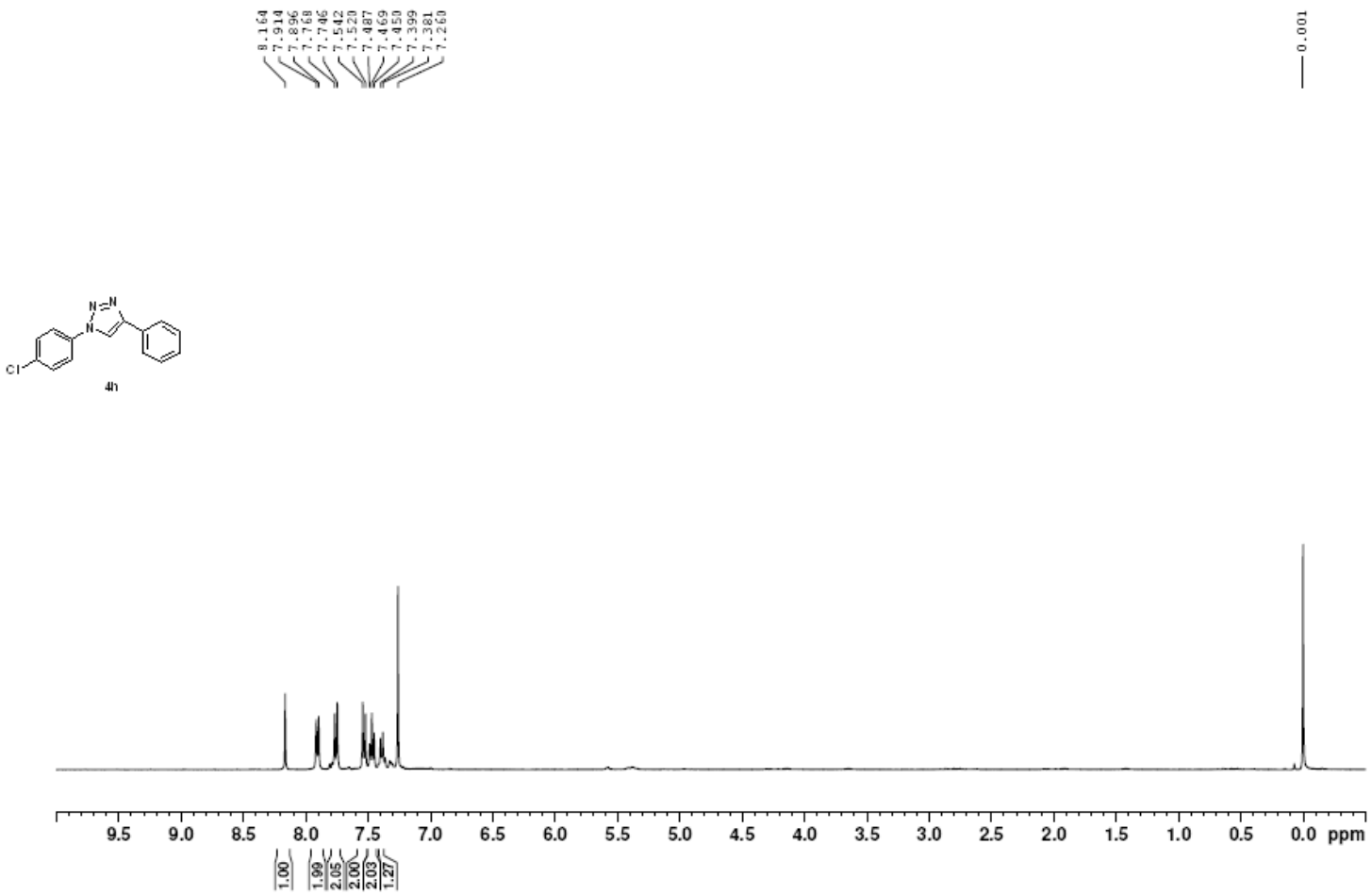


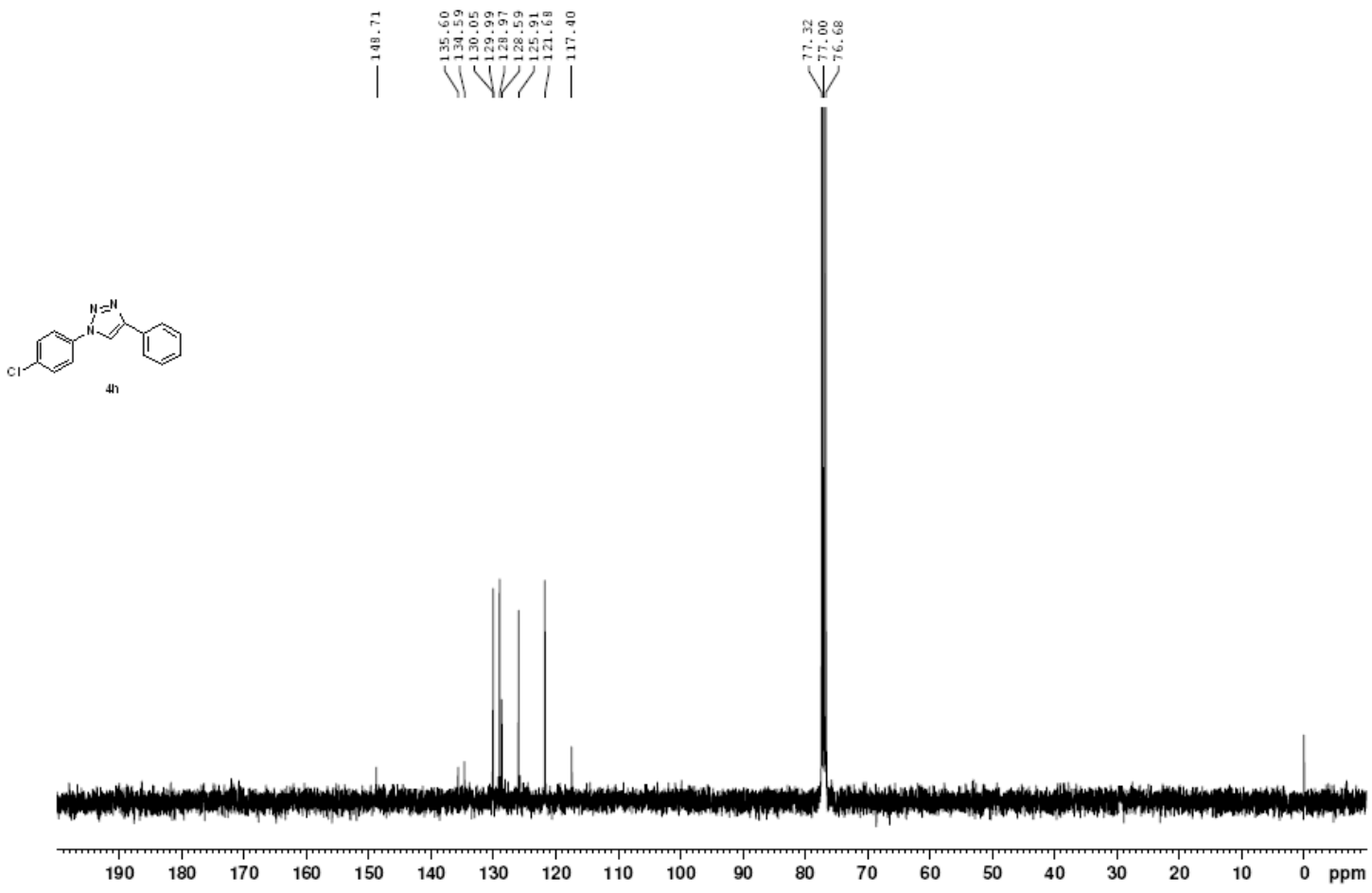
4g


8.189
7.918
7.915
7.897
7.847
7.842
7.838
7.721
7.701
7.506
7.486
7.466
7.446
7.443
7.425
7.421
7.399
7.381
7.362
0.000
Cl
4g
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.00
2.14
1.01
1.10
5.17



4h

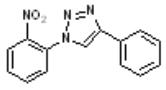

8.164
7.914
7.896
7.768
7.746
7.542
7.520
7.487
7.469
7.459
7.399
7.381
7.260
0.001
Cl
4h
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.00
1.99
2.05
2.00
2.03
1.27



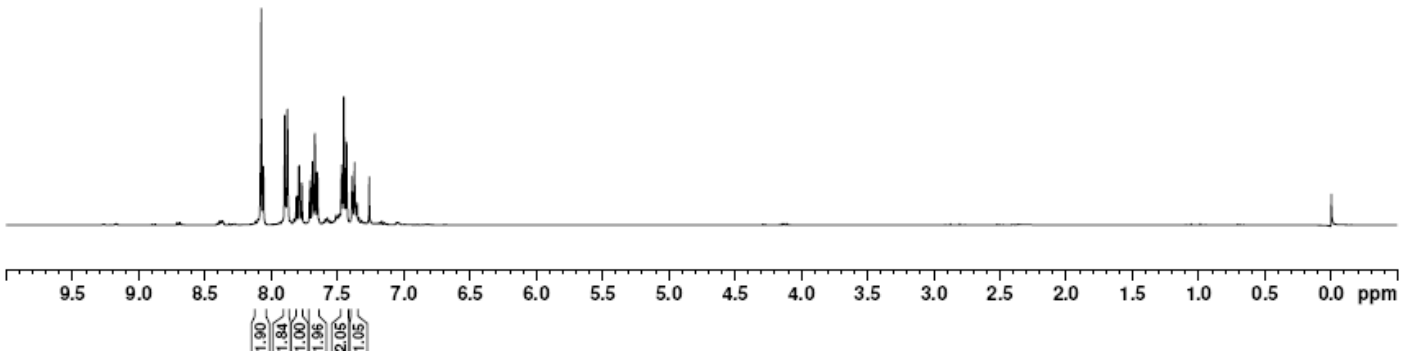
4i

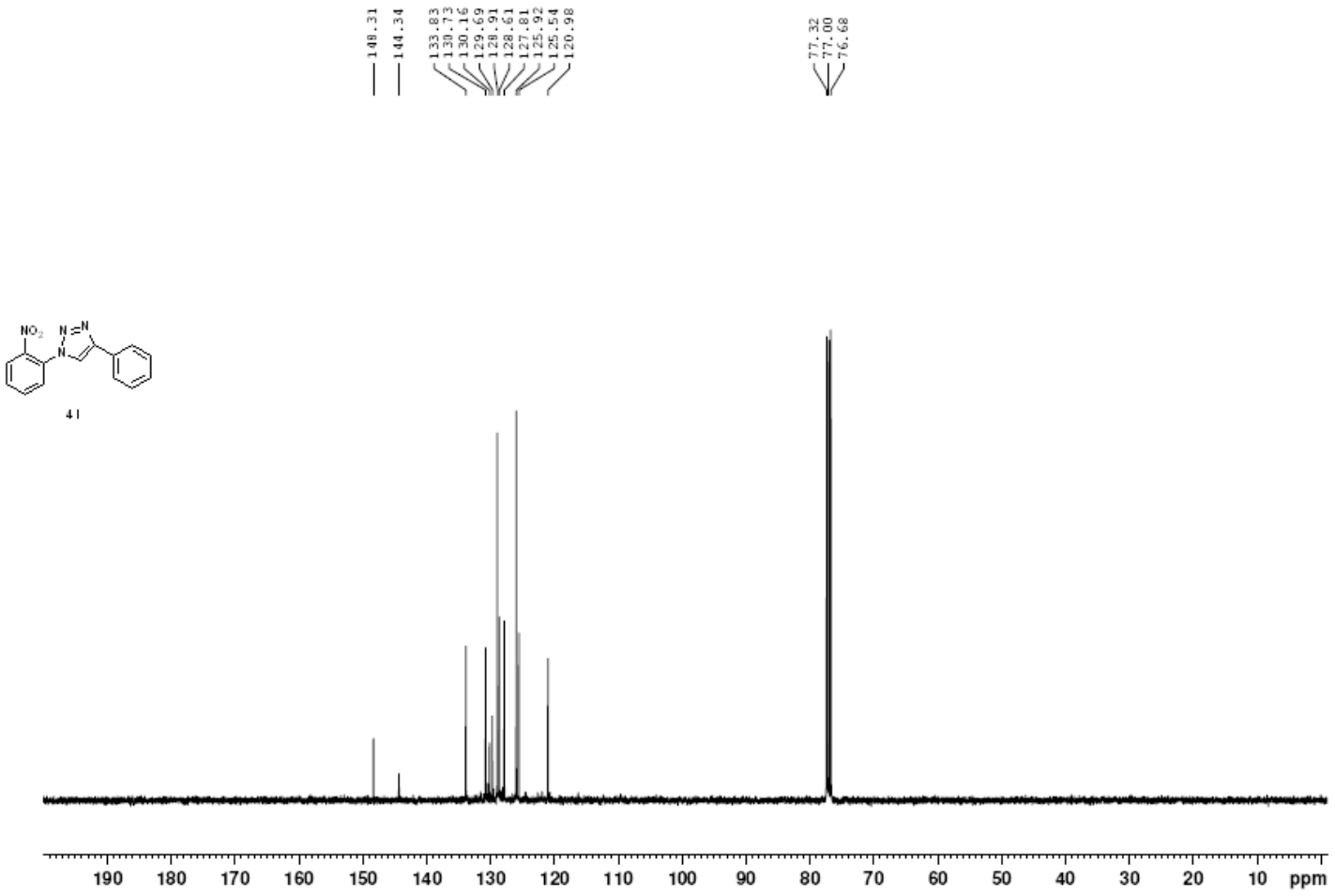

8.075
8.061
8.058
7.896
7.878
7.809
7.806
7.790
7.787
7.771
7.768
7.709
7.706
7.686
7.671
7.652
7.649
7.468
7.450
7.431
7.388
7.370
7.351
7.260


0.000

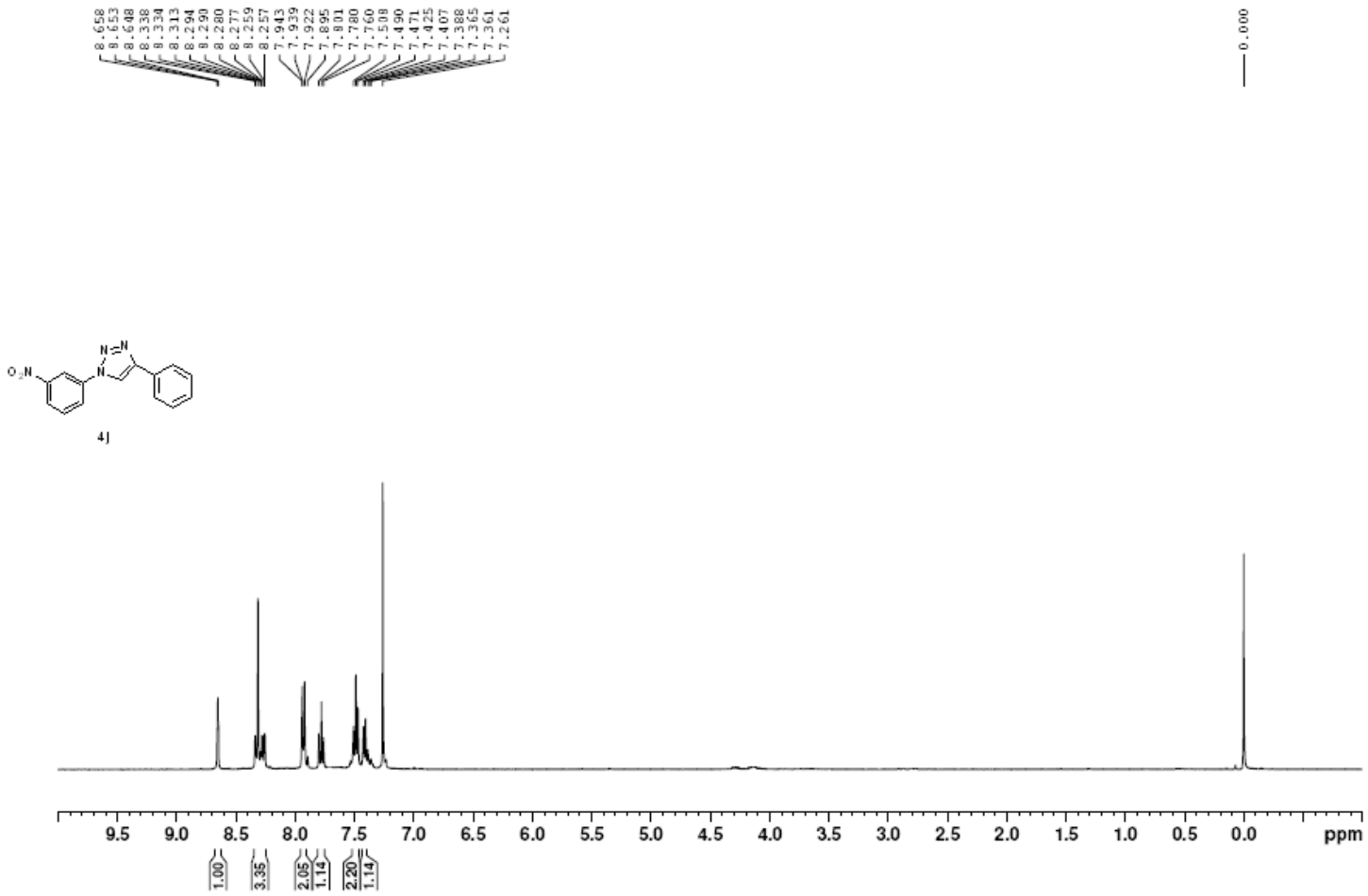

NO2
N
N

4 i


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.90
1.84
1.00
1.96
2.05
1.05



4j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8.653
8.648
8.338
8.334
8.313
8.294
8.290
8.280
8.277
8.259
8.257
7.943
7.939
7.922
7.895
7.801
7.780
7.760
7.508
7.490
7.471
7.425
7.407
7.388
7.365
7.361
7.261
0.000
4j
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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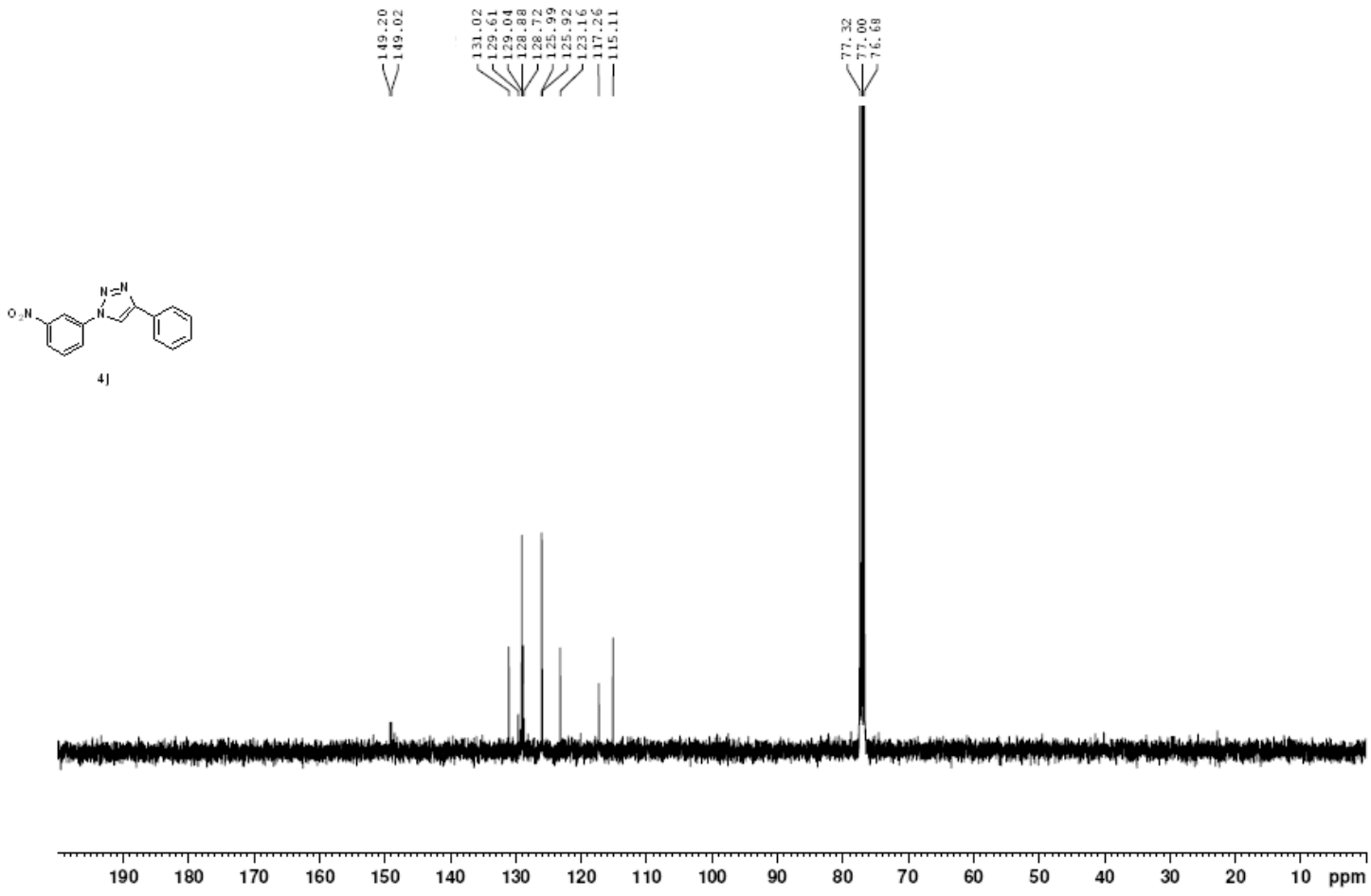
3.35
2.05
1.14
2.20
1.14

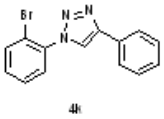


4j

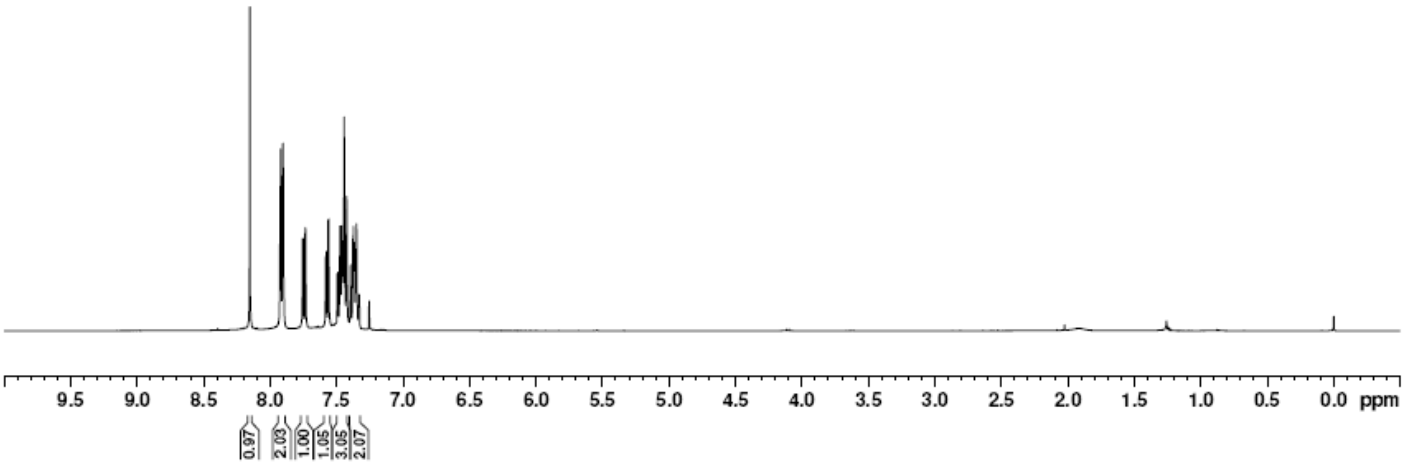
4k

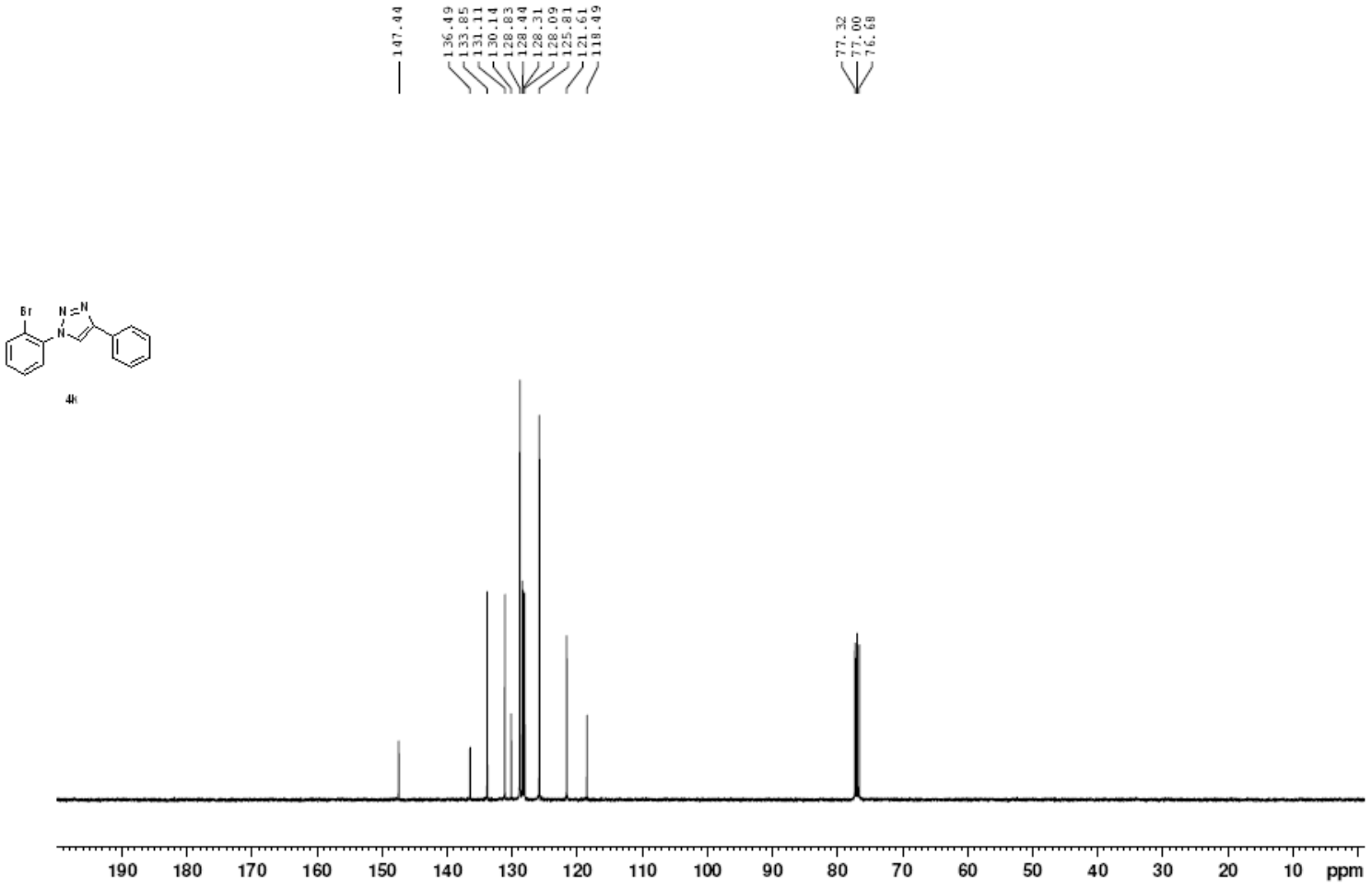

8.153
7.924
7.921
7.903
7.755
7.753
7.736
7.733
7.582
7.578
7.562
7.558
7.494
7.491
7.475
7.472
7.461
7.456
7.453
7.443
7.424
7.397
7.393
7.377
7.373
7.368
7.358
7.354
7.350
7.331
7.254


0.000

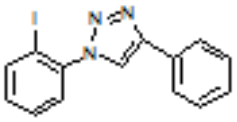

Br
N
N

4k

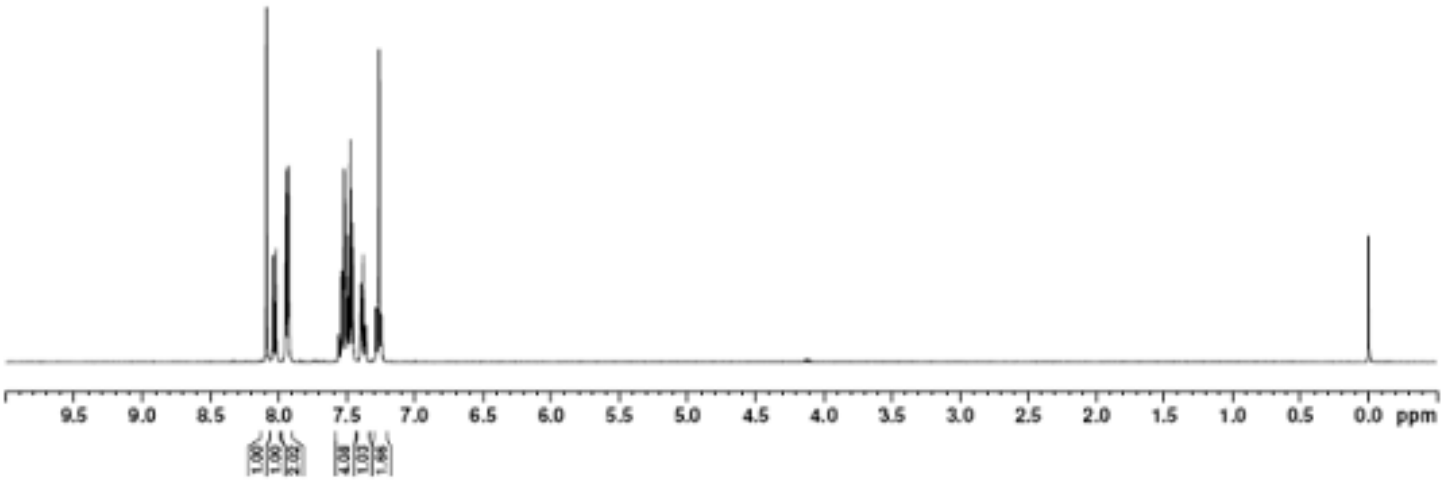

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
0.97
2.03
1.00
1.05
3.05
2.07

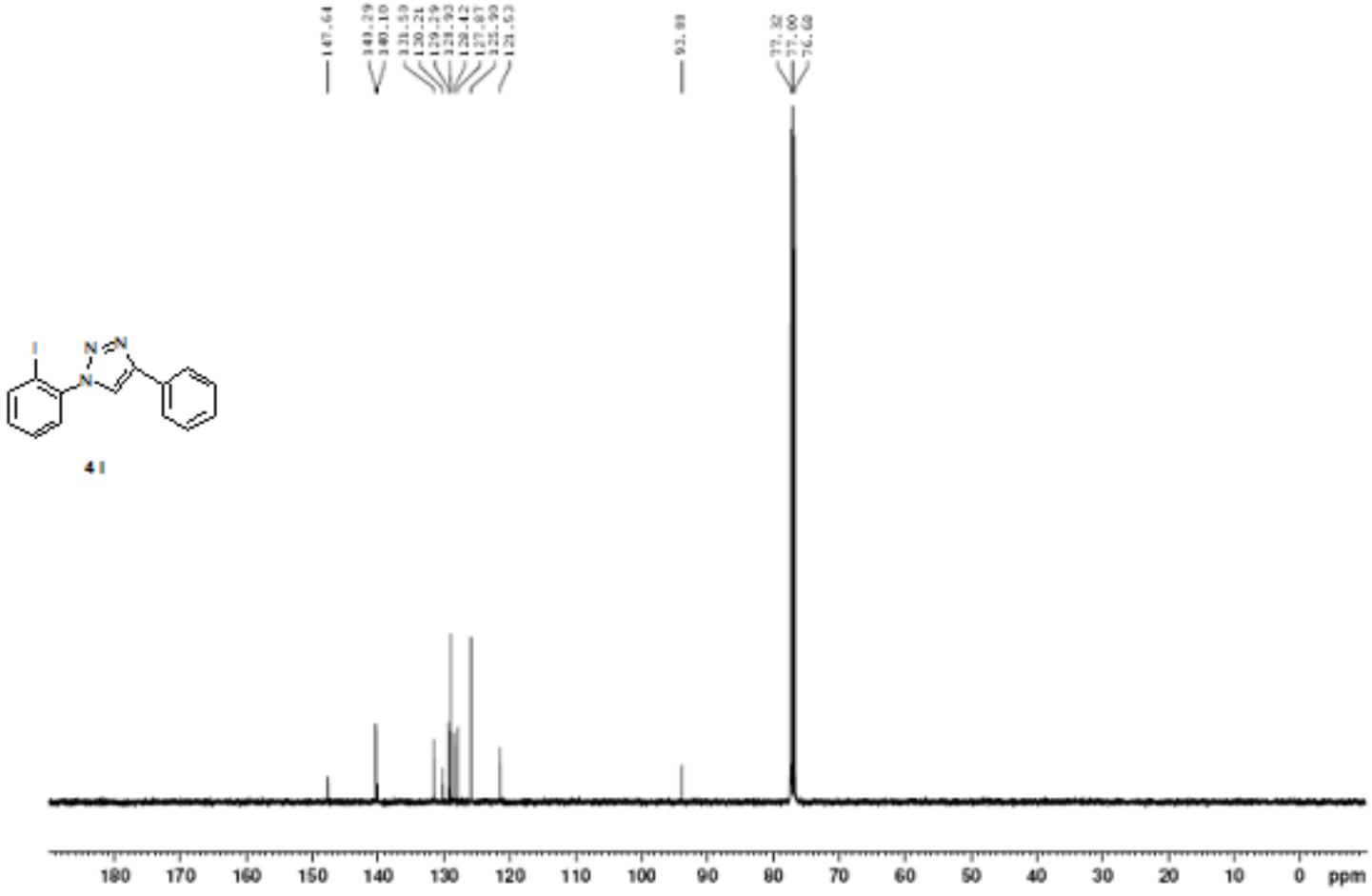

147.44
136.49
133.85
131.11
130.14
128.83
128.44
128.31
128.09
125.81
121.61
118.49
77.32
77.00
76.68
Br
N
N
4k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4l

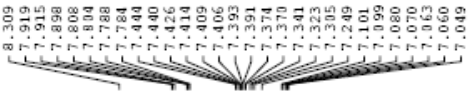


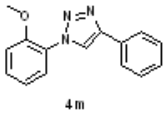
4 l

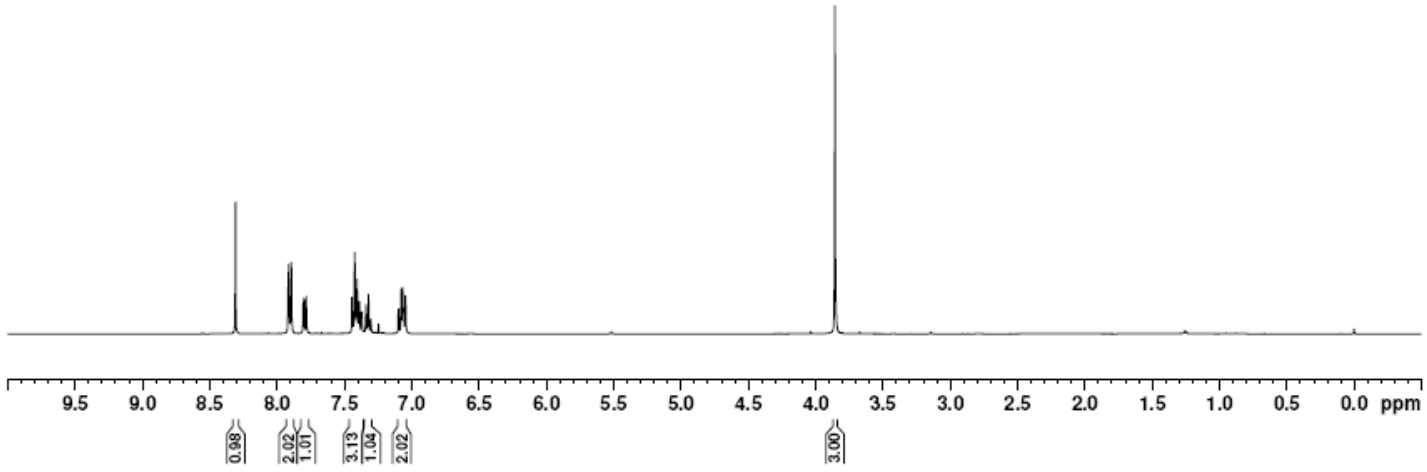


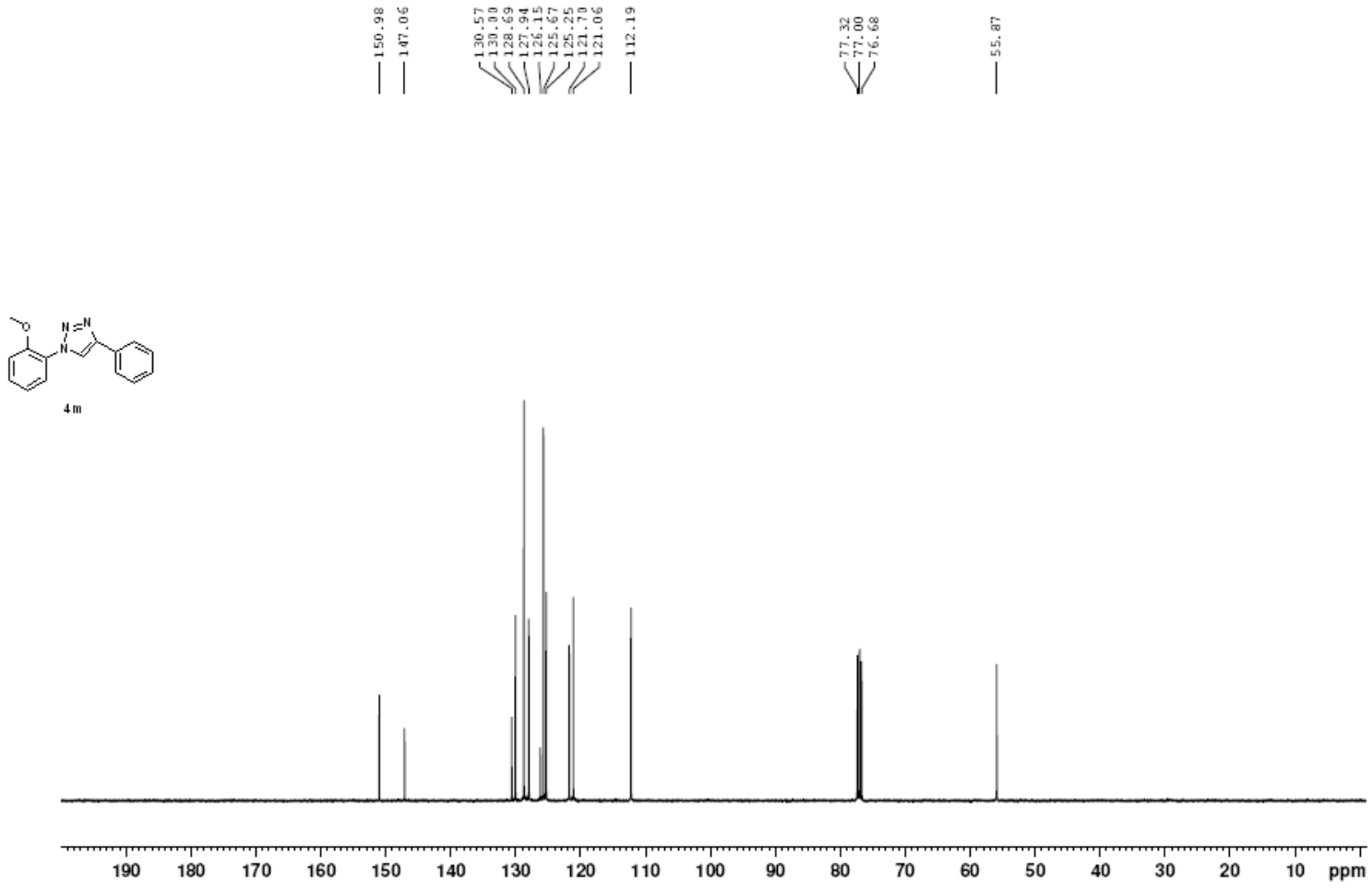


4m

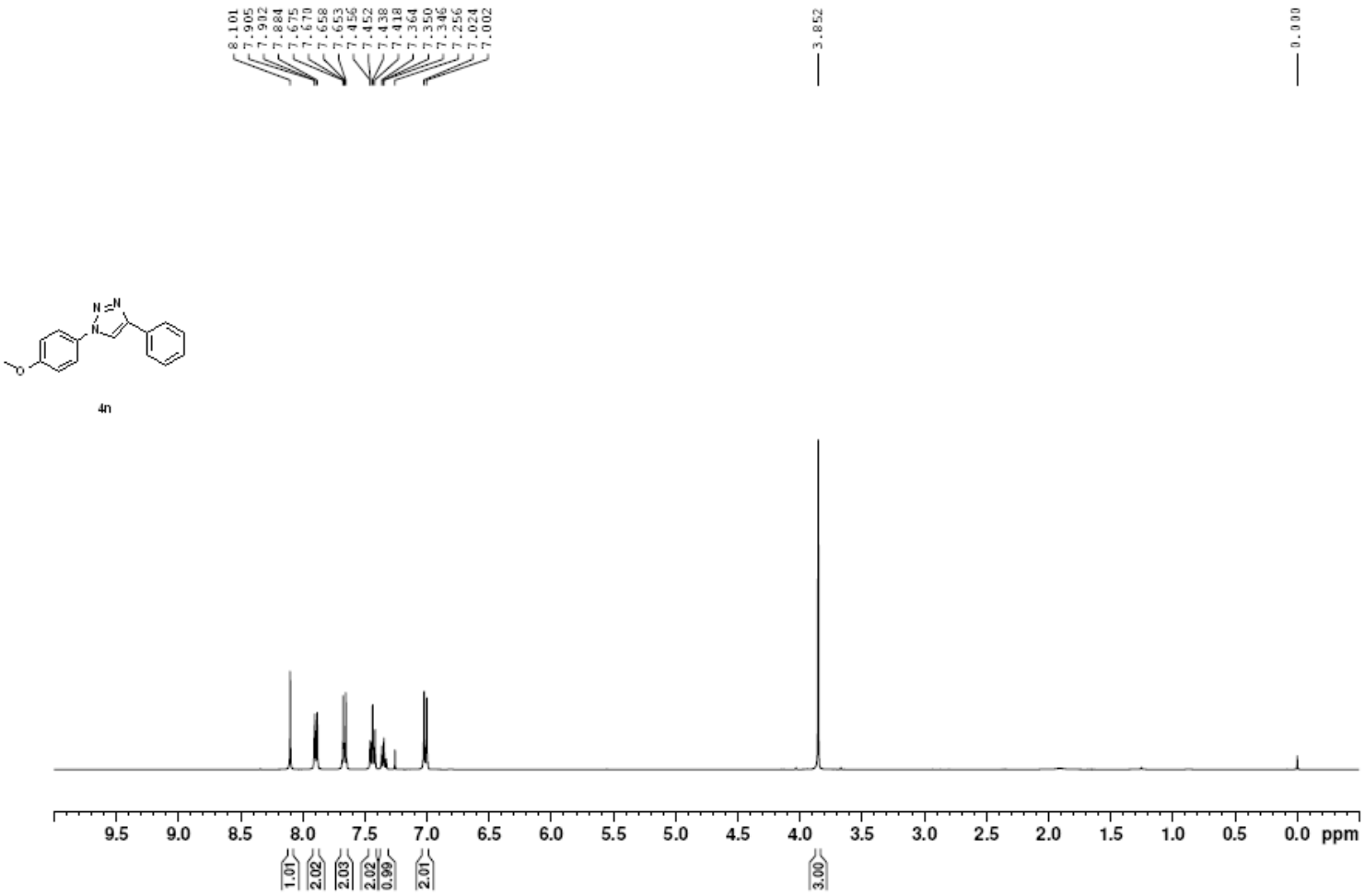

8.309
7.919
7.915
7.898
7.808
7.804
7.788
7.784
7.444
7.440
7.426
7.414
7.409
7.406
7.393
7.391
7.374
7.370
7.341
7.323
7.305
7.249
7.101
7.099
7.080
7.070
7.063
7.060
7.049
3.857
0.000

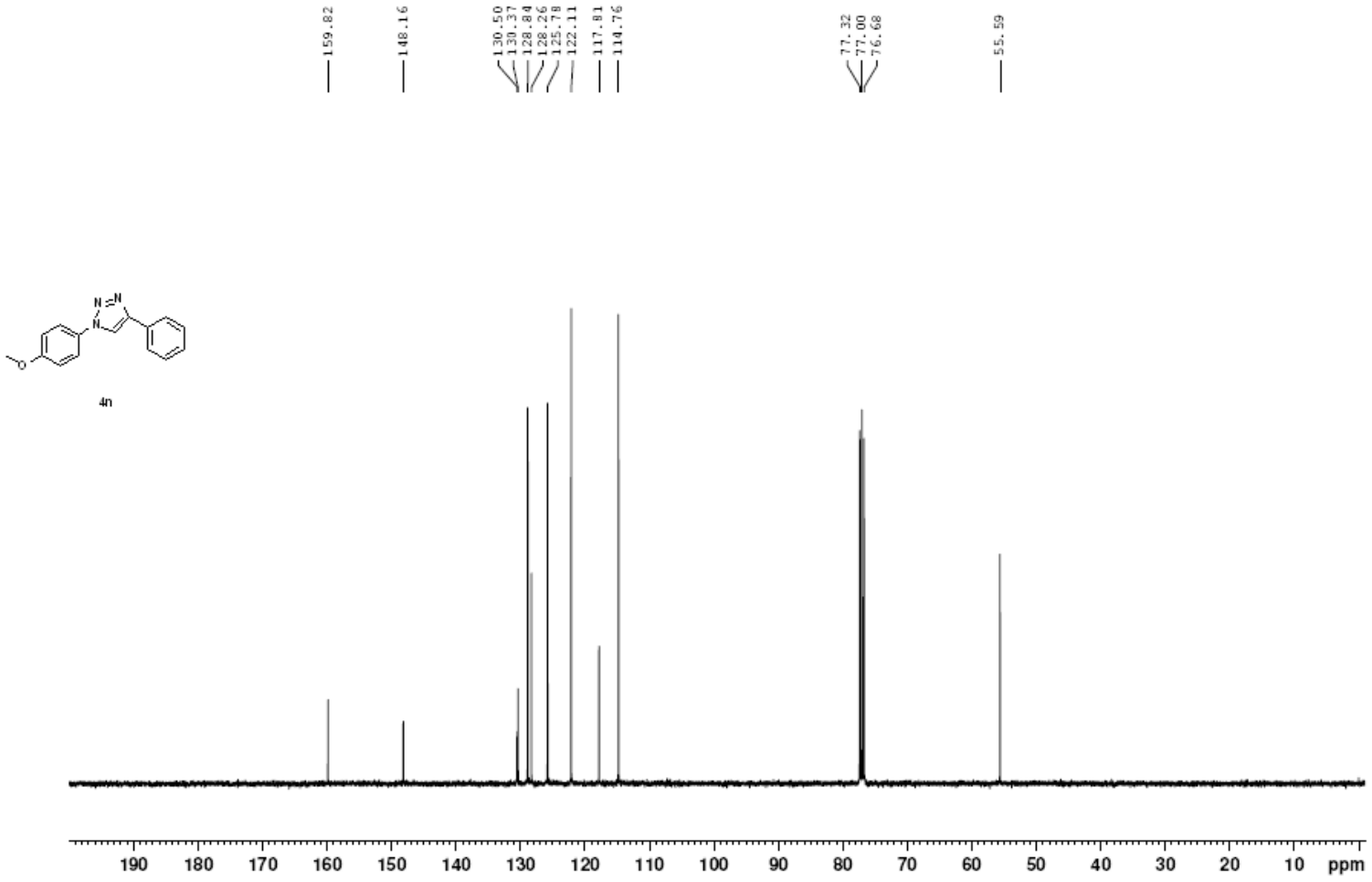

4m


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
0.98
2.02
1.01
3.13
1.04
2.02
3.00

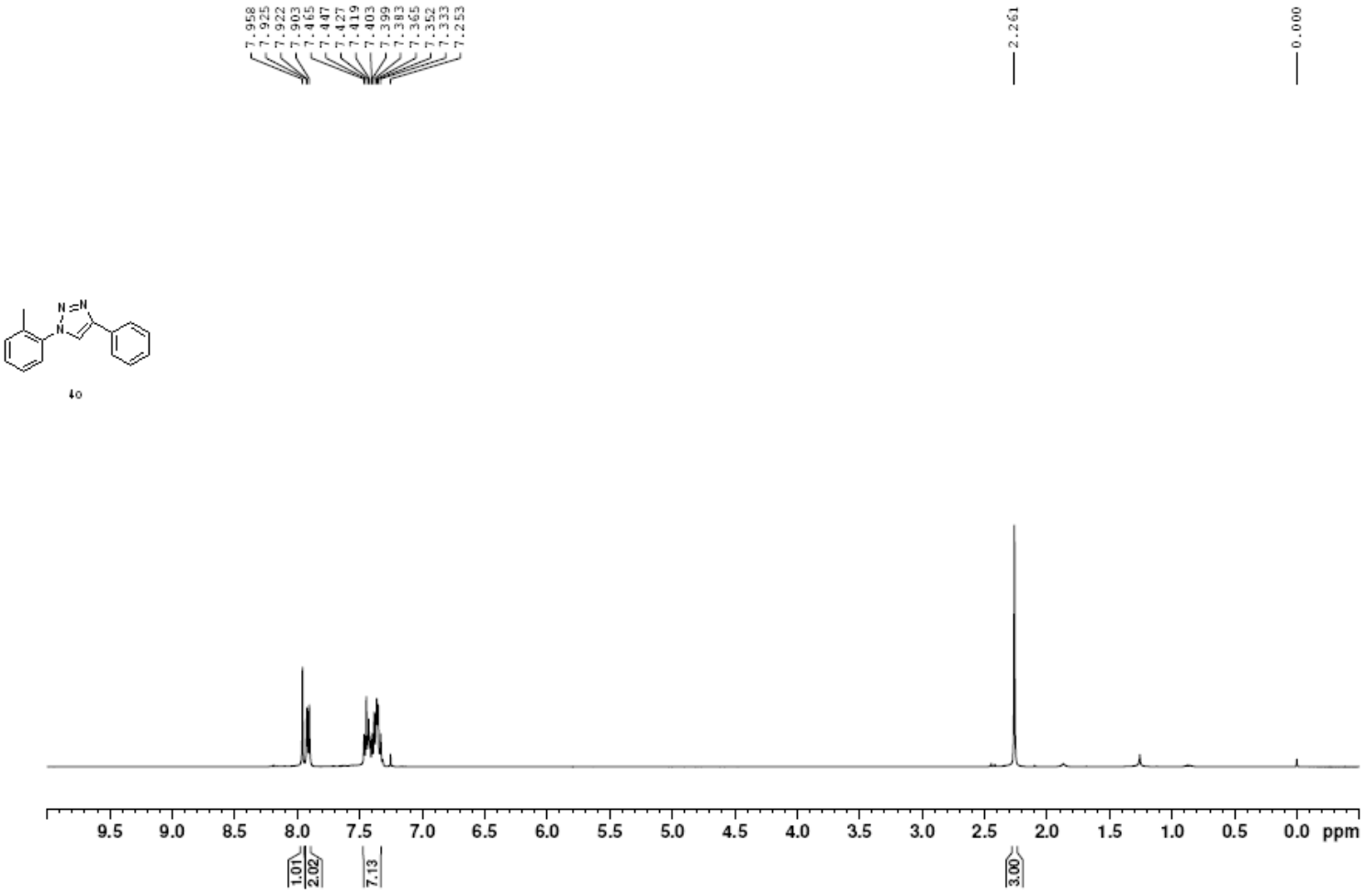


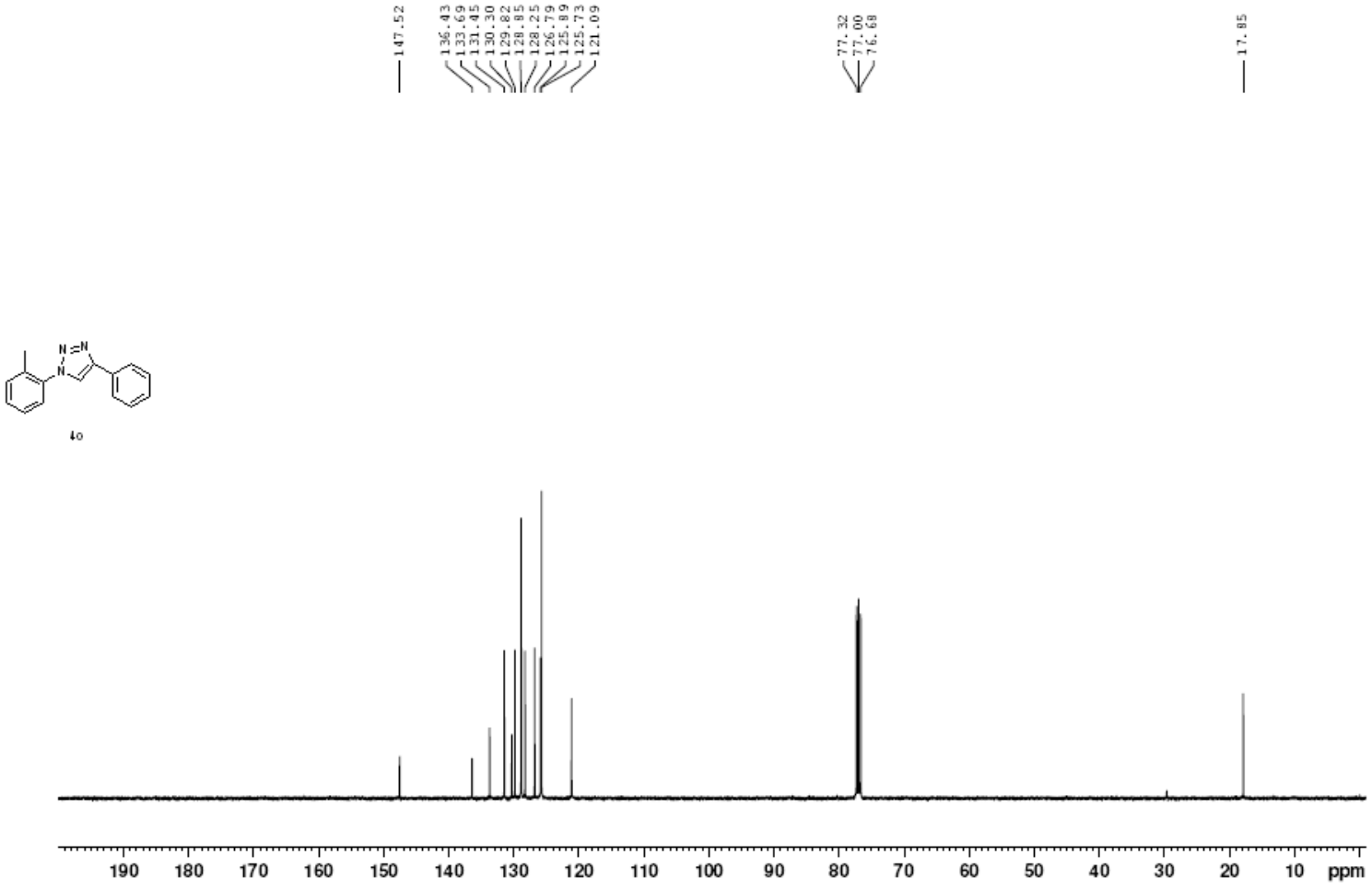
4n


8.101
7.905
7.902
7.884
7.675
7.670
7.658
7.653
7.456
7.452
7.438
7.418
7.364
7.350
7.346
7.256
7.024
7.002
3.852
0.000
4n
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.01
2.02
2.03
2.02
0.99
2.01
3.00

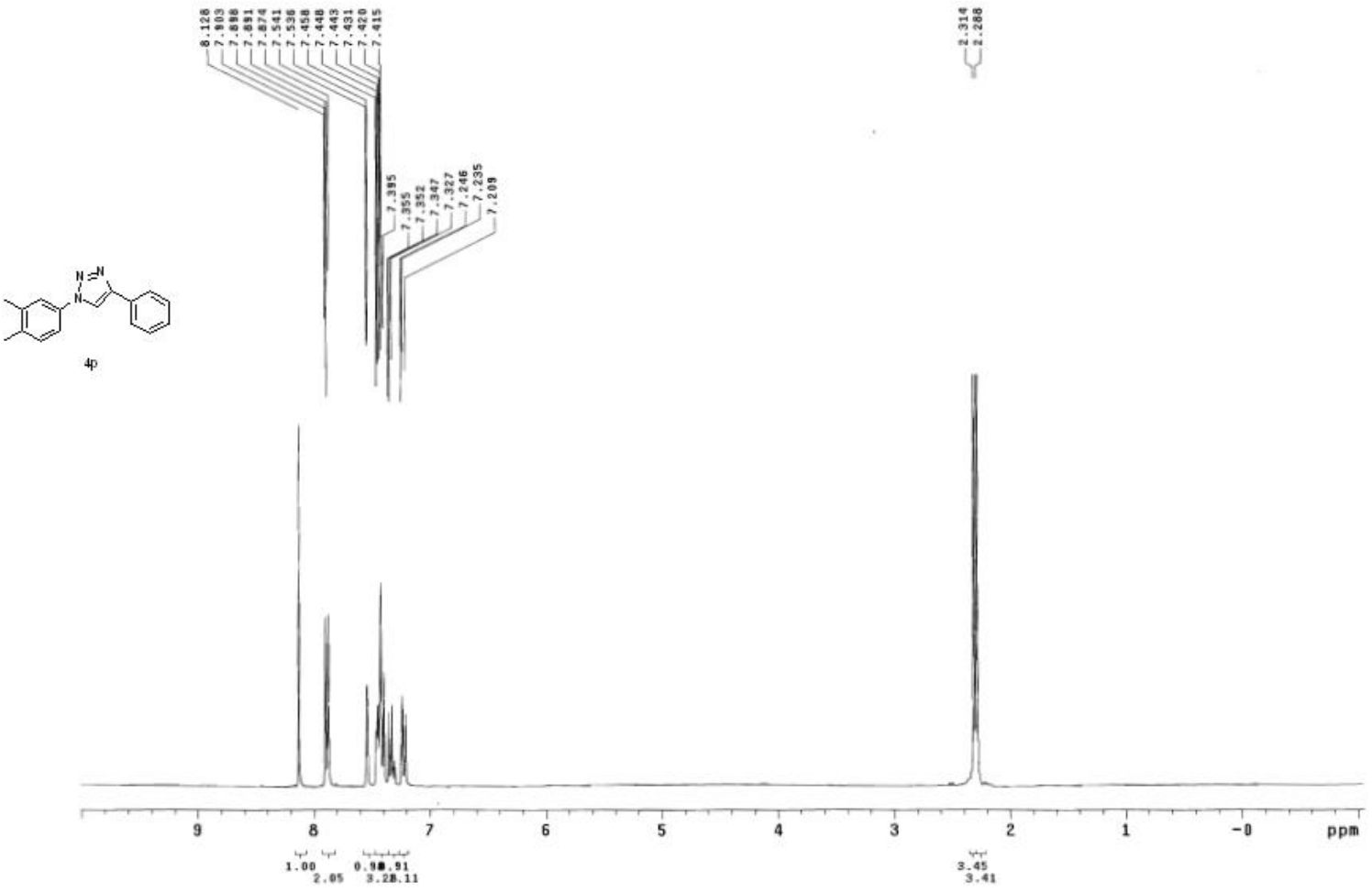


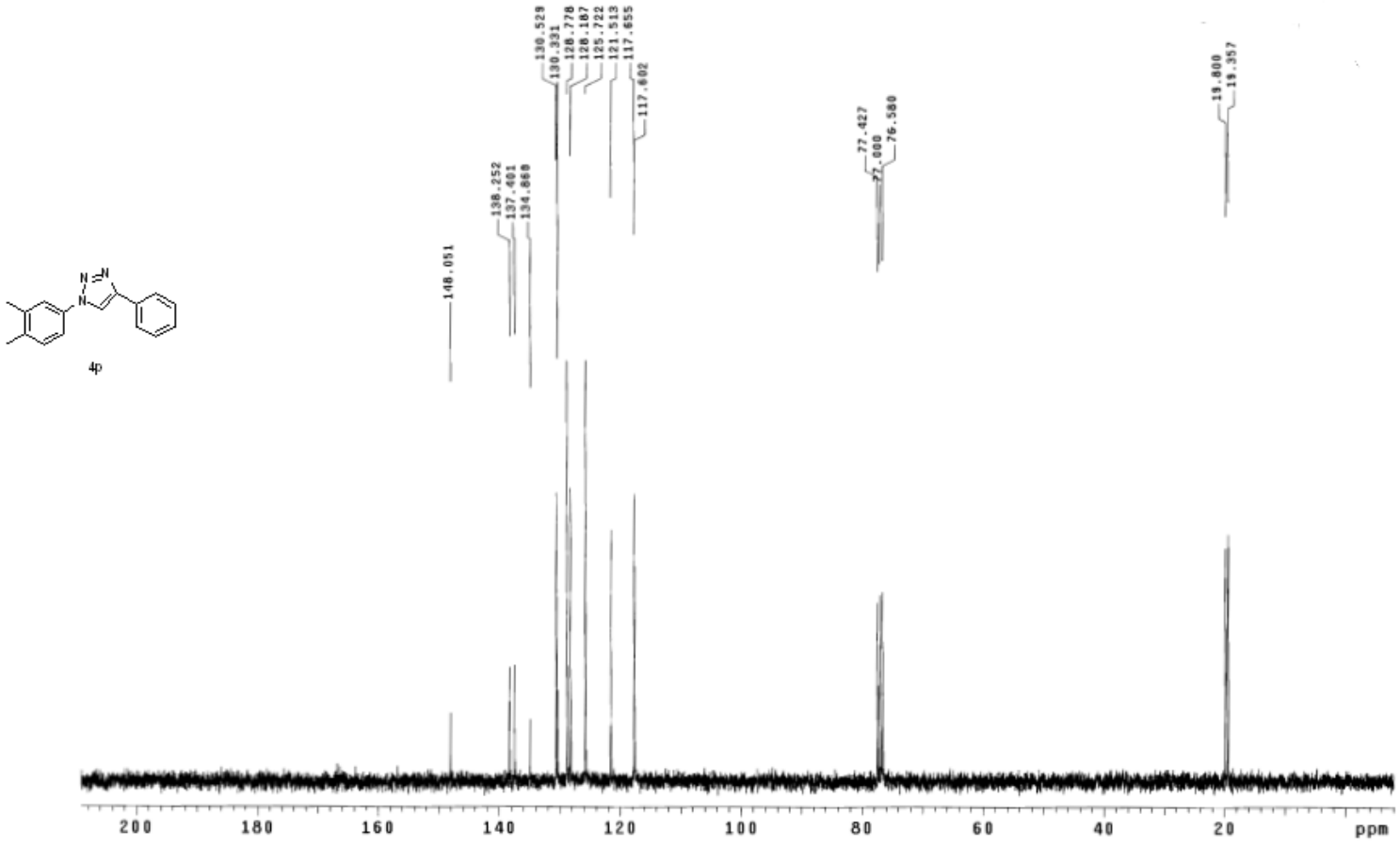
4o


7.958
7.925
7.922
7.903
7.465
7.447
7.427
7.419
7.403
7.399
7.383
7.365
7.352
7.333
7.253
2.261
0.000
4o
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.01
2.02
7.13
3.00


147.52
136.43
133.69
131.45
130.30
129.82
128.85
128.25
126.79
125.89
125.73
121.09
77.32
77.00
76.68
17.85
4o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4p


8.128
7.903
7.898
7.891
7.874
7.541
7.536
7.458
7.448
7.443
7.431
7.420
7.415
7.395
7.355
7.352
7.347
7.327
7.246
7.235
7.209
2.314
2.288
4p
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
2.05
3.45
3.41



4p