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Supporting Information

Visible-light driven regioselective synthesis of 1*H*-tetrazoles from aldehydes through isocyanide-based [3+2] cycloaddition

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Characterization of reused catalyst:

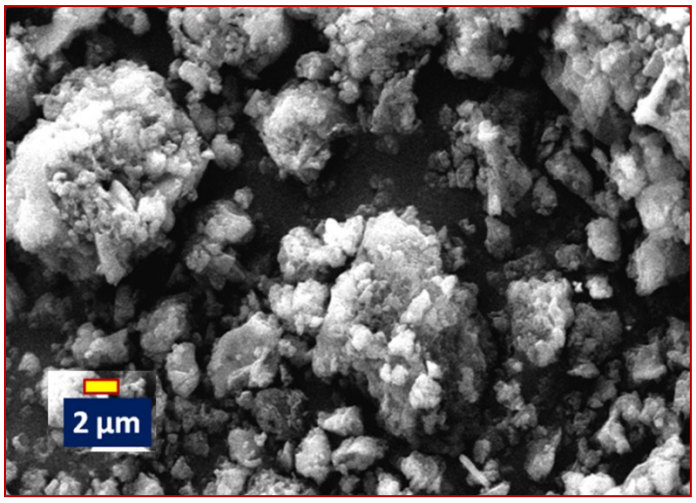


Figure 1. SEM image of $Co@C_3N_4$ after 5th cycles.

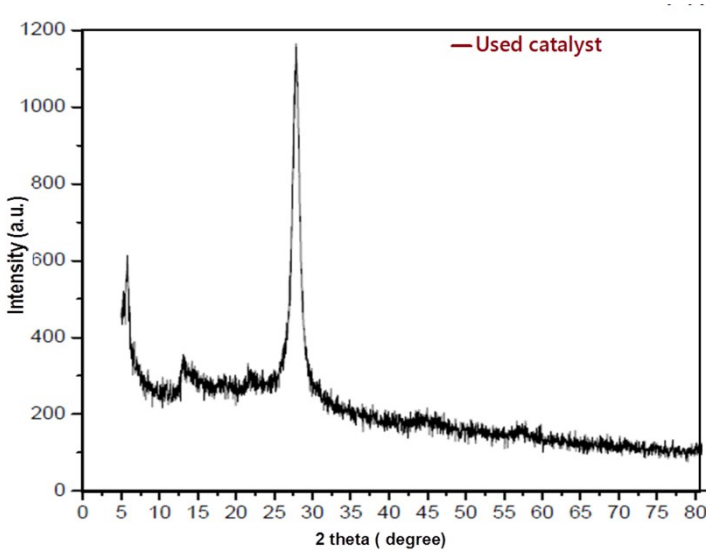


Figure 2. XRD spectra of $Co@C_3N_4$ after 5th cycles.

General information:

All chemicals were purchased from Aldrich, Sd-Fine and HI-MEDIA (India) and used as received, except all solvents which were used after distillation. All reactions were carried out with oven-dried glassware under air. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). ^{1}H NMR spectra were recorded on Bruker AV 400 MHz. The ^{1}H NMR chemical shifts are reported relative to the centre of solvent resonance ($CDCl_3$: 7.26 (^{1}H). Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), dd (double doublet), t (triplet), dt (doublet triplet), q (quartet), m (multiplet) and coupling constants *J* were given in Hz. ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ solution. Chemical shifts are expressed in parts per million (δ) and are referenced to $CDCl_3$ (δ = 77.16) as internal standard.

General procedure for synthesis of tetrazole 4:

A mixture of aldehyde **1** (1 mmol), sodium azide **2** (3 mmol), Co@g-C_3N_4 (10 mg) and MeOH (5 mL) in a hot air-dried round bottom flask was stirred at room temperature under the visible light. After completion of the reaction (as monitored by TLC), water was added to the reaction mixture to separate the remaining sodium azide in aqueous layer leaving target compound in organic residue. The catalyst was then simply filtered from reaction mixture and washed with water and ethanol, dried in under vacuum and was reused for further experiment. Then, the organic layer was washed with brine (2 x 10 mL) and water (2 x 10 mL), dried under vacuum evaporator to obtain the crude isolates as colourless solid. Finally, recrystalized of crude isolate in ethanol afforded the analytically pure sample of tetrazole **4** without any column chromatography. Structures of all the synthesized compounds were confirmed by their ^{1}H and ^{13}C NMR spectral analysis. Characterization data of the representative compounds are:

1-(4-chlorolphenyl)-1*H*-1,2,3,4-tetrazole (4a): Yield: 92%; mp: 156-158 °C; colourless solid. IR (KBr): (ν) 827, 997, 1087, 1173, 1204, 1214, 1384, 1505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.86 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 8.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 118.8, 123.8, 126.3, 131.5, 147.8; $C_7H_5ClN_4$ (180.59): calcd. C 46.55, H 2.79, N 31.02; found C 46.59, H 2.87, N 30.95.

1-(4-Boromophenyl)-1*H*-1,2,3,4-tetrazole (4b): Yield: 93%; mp: 182-184 °C; colourless solid; IR (KBr): (ν) 1480, 1575, 1660, 3152 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.83 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 8.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.7, 123.1, 125.1, 130.5, 148.0; $C_7H_5BrN_4$ (225.05): calcd. C 37.36, H 2.24, N 24.90; found C 37.59, H 2.59, N 25.15.

1-(4-Nitrophenyl)-1*H*-1,2,3,4-tetrazole (4c): Yield: 95%; solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 8.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.6, 125.5, 127.6, 138.7, 150.4; $C_7H_5N_5O_2$ (191.15): calcd. C 43.98, H 2.64, N 36.64; found C 43.79, H 2.89, N 36.99.

1-(4-methylphenyl)-1*H*-1,2,3,4-tetrazole (4d): Yield: 88%; mp: 93-95 °C; colourless solid. IR (KBr): (ν) 821, 997, 1046, 1095, 1177, 1205, 1215, 1393, 1466, 1518 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.75 (s, 3H), 6.73 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 8.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 116.7, 124.6, 128.0, 133.5, 145.7; $C_8H_8N_4$ (160.18): calcd. C 59.99, H 5.03, N 34.98; found C 59.89, H 5.31, N 35.05.

1-(4-methoxyphenyl)-1*H*-1,2,3,4-tetrazole (4e): Yield: 87%; solid. ^1H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 3H), 6.75 (d, J = 8.1Hz, 2H), 7.17 (d, J = 8.1Hz, 2H), 8.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 57.7, 115.5, 123.7, 128.5, 133.6, 150.7; $C_8H_8N_4O$ (176.18): calcd. C 54.54, H 4.48, N 31.80; found C 54.69, H 4.31, N 31.95.

1-(4-Acetylphenyl)-1*H*-tetrazole (4f): Yield: 90%; mp: 174-177 °C; yellow solid. IR (KBr): (ν) 977, 1057, 1244, 1501, 1530, 1574, 1602, 1633, 1677, 1713, 3025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.76 (s, 3H), 6.74 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 8.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.5, 118.4, 123.9, 130.3, 137.9, 147.6, 190.9; $C_8H_8N_4$ (160.18): calcd. C 59.99, H 5.03, N 34.98; found C 60.34, H 5.11, N 34.75.

1-phenyl-1*H*-1,2,3,4-tetrazole (4g): Yield: 89%; mp: 63-66 °C; pale yellow solid. IR (KBr): (ν) 1207, 1321, 1487, 1588, 1680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.77 (m, 5H), 9.05 (s,

1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.2, 129.5, 131.0, 133.1, 140.7; $C_7H_6N_4$ (146.15): calcd. C 57.53, H 4.14, N 38.34; found C 57.39, H 4.27, N 38.46.

1-(3-Chlorophenyl)-1*H*-1,2,3,4-tetrazole (4h): Yield: 89%; mp: 138-140 °C; colourless solid; IR (KBr): (ν) 1588, 1467, 1672, 3064 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 1H), 7.08 (d, J = 8.3 Hz, 2H), 7.24 (t, J = 8.3 Hz, 1H), 8.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.5, 119.2, 123.7, 130.4, 135.2, 146.1, 149.7; $C_7H_5ClN_4$ (180.59): calcd. C 46.55, H 2.79, N 31.02; found C 46.78, H 2.44, N 31.37.

1-(3-methylphenyl)-1*H*-1,2,3,4-tetrazole (4i): Yield: 87%; mp: 52-54 °C; pale yellow solid. IR (KBr): (ν) 1098, 1166, 1175, 1177, 1187, 1225, 1377, 1484, 1492 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 6.87-6.91 (m, 3H), 7.18-7.25 (m, 1H), 8.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 115.3, 119.4, 124.1, 129.2, 140.0, 145.4, 149.2; $C_8H_8N_4$ (160.18): calcd. C 59.99, H 5.03, N 34.98; found C 60.34, H 5.11, N 34.75.

1-(2-chlorolphenyl)-1*H*-1,2,3,4-tetrazole (4j): Yield: 90%; mp: 86-88 °C; colourless solid. IR (KBr): (ν) 762, 887, 994, 1091, 1175, 1205, 1462, 1495 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, J = 8.1 Hz, 1H), 7.25 (t, J = 8.3 Hz , 1H), 7.36 (t, J = 8.3 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 8.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.7, 124.9, 125.4, 130.4, 130.7, 134.9, 146.1; $C_7H_5ClN_4$ (180.59): calcd. C 46.55, H 2.79, N 31.02; found C 46.52, H 2.64, N 31.07.

1-(2-Methylphenyl)-1*H*-1,2,3,4-tetrazole (4k): Yield: 88%; mp: 152-154 °C; colourless solid; IR (KBr): (ν) 1487, 1591, 1667, 2872, 3016 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 7.00- 7.08 (m, 2H), 7.18-723 (m, 2H), 8.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 117.7, 123.9, 127.4, 128.7, 130.8, 144.1, 147.7; $C_8H_8N_4$ (160.18): calcd. C 59.99, H 5.03, N 34.98; found C 59.64, H 5.31, N 34.78.

1-(3-chloro-4-fluorophenyl)-1*H*-1,2,3,4-tetrazole (4l): Yield: 87%; mp: 95-97 °C; colourless solid. IR (KBr): (ν) 3018, 1655, 1506, 1461, 1524, 1214, 1087, 997 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.44 (m, 1H), 7.62-7.67 (m, 1H), 7.82-7.88 (m, 1H), 8.97 (s, 1H); ^{13}C NMR (100

MHz, $CDCl_3$): δ 118.1, 118.3, 121.1, 121.2, 123.1, 123.6, 124.0, 130.2, 140.4, 157.1, 160.0; $C_7H_4ClFN_4$ (198.58): calcd. C 42.34, H 2.03, N 28.21; found C 42.30, H 2.24, N 28.37.

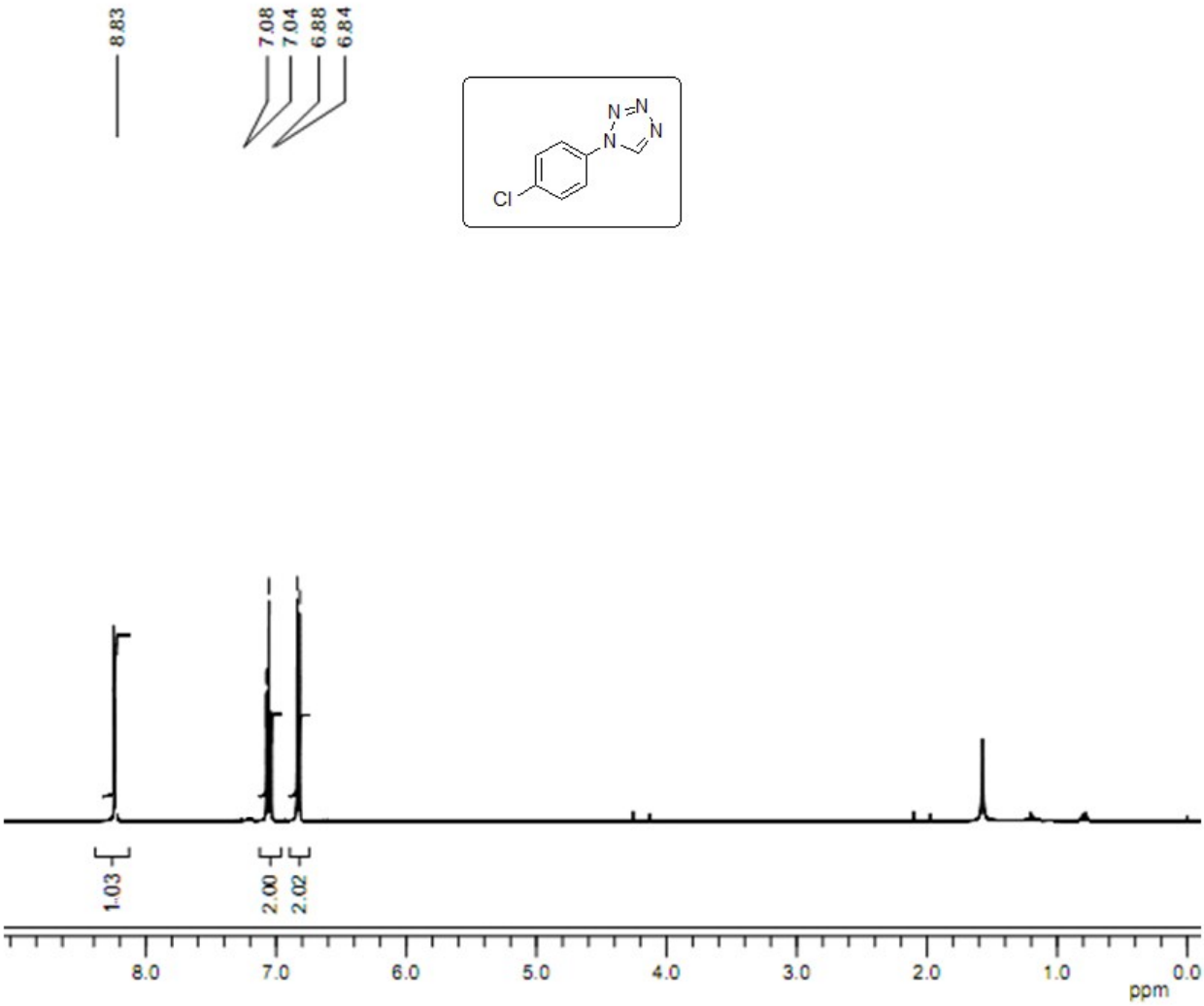
1-(4-isopropylphenyl)-1*H*-1,2,3,4-tetrazole (4m): Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (d, *J* = 6.9 Hz, 6H), 3.02 (sept, *J* = 6.9 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 8.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ23.5, 33.8, 121.5, 128.0, 131.2, 140.2, 151.5; $C_{10}H_{12}N_4$ (188.23): calcd. C 63.81, H 6.43, N 29.77; found C 63.98, H 6.36, N 29.65.

1-benzyl-1*H*-1,2,3,4-tetrazole (4n): Yield: 89%; mp: 57-59 °C; colourless solid. IR (KBr): (ν) 1105, 1164, 1243, 1421, 1434, 1455, 1477, 1495 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.28 (s, 2H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 8.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 26.7, 118.7, 124.8, 128.3, 138.0, 148.7; $C_8H_8N_4$ (160.18): calcd. C 59.99, H 5.03, N 34.98; found C 59.94, H 5.38, N 34.63.

1-(3-pyridine)-1*H*-1,2,3,4-tetrazole (4o): Yield: 86%; mp: 128-130 °C; colourless solid. IR (KBr): (ν) 1007, 1091, 1150, 1182, 1211, 1393, 1471, 1577, 1598 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.49-7.51 (m, 1H), 7.52-8.53 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 9.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 114.6, 123.6, 128.4, 135.5, 147.8, 153.8; $C_6H_5N_5$ (147.14): calcd. C 48.98, H 3.43, N 47.60; found C 48.91, H 3.39, N 47.63.

4-methyl-2-(1*H*-1,2,3,4-tetrazol-1-yl)pyridine (4p): Yield: 85%; mp: 130-131 °C; pink solid. IR (KBr): (ν) 837, 950, 997, 1092, 1175, 1237, 1451, 1477, 1618 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 3.19 (s, 3H), 6.84 (d, *J* = 8.2 Hz, 1H), 7.14 (s, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 9.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 23.6, 123.8, 128.5, 136.0, 147.9, 153.7; $C_7H_7N_5$ (161.16): calcd. C 52.17, H 4.38, N 43.45; found C 52.32, H 4.47, N 43.40.

6-Methyl-2-(1*H*-1,2,3,4-tetrazol-1-yl)pyridine (4q): Yield: 84%; mp: 105-107 °C; colourless solid. IR (KBr): (ν) 998, 1085, 1216, 1478, 1507, 1540, 1572, 1613, 3017 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.61 (s, 3H), 7.28-7.32 (m, 1H), 7.81-7.91 (m, 2H), 9.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 110.9, 124.8, 139.1, 139.2, 146.0, 158.8; $C_7H_7N_5$ (161.16): calcd. C 52.17, H 4.38, N 43.45; found C 52.34, H 4.41, N 43.48.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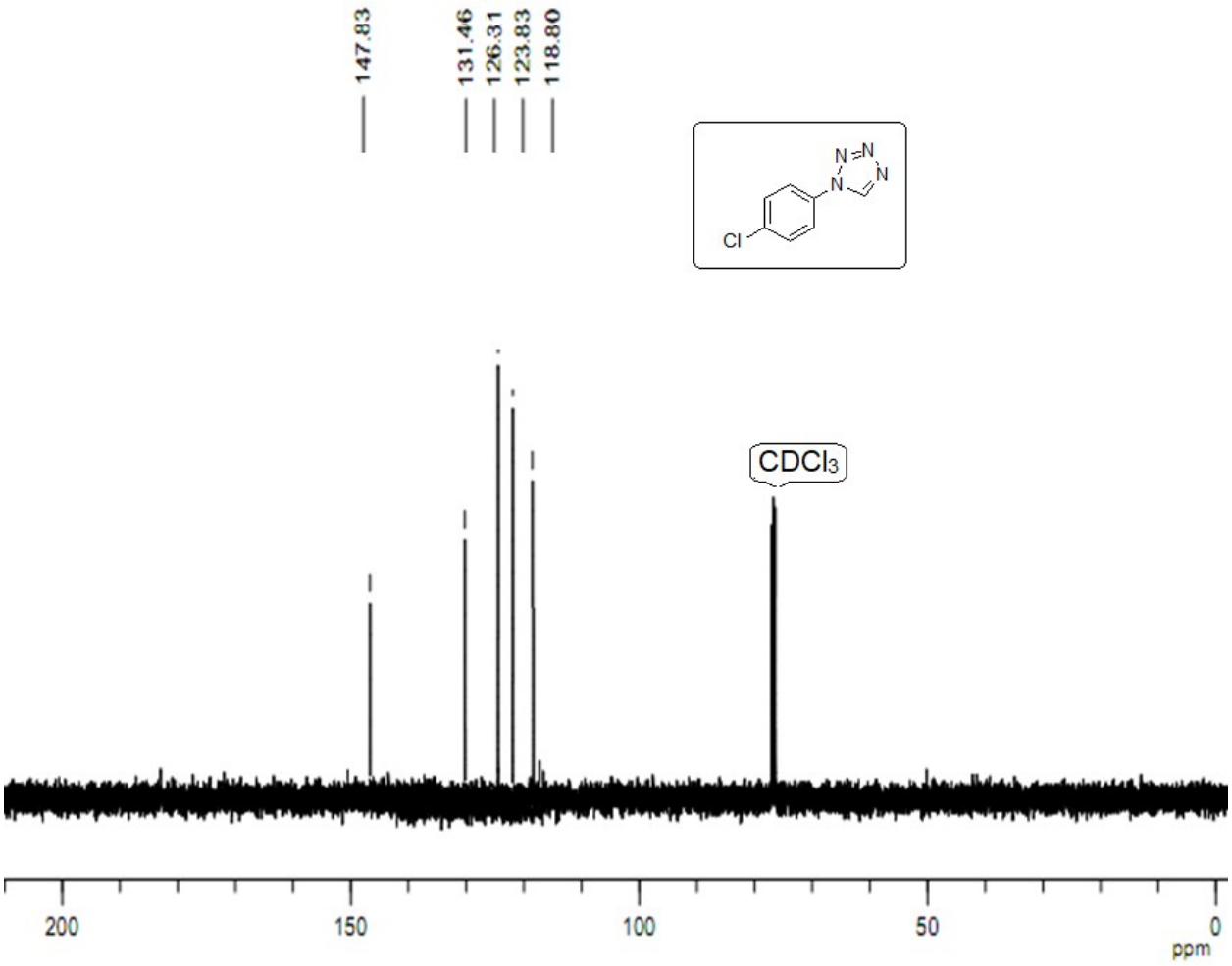
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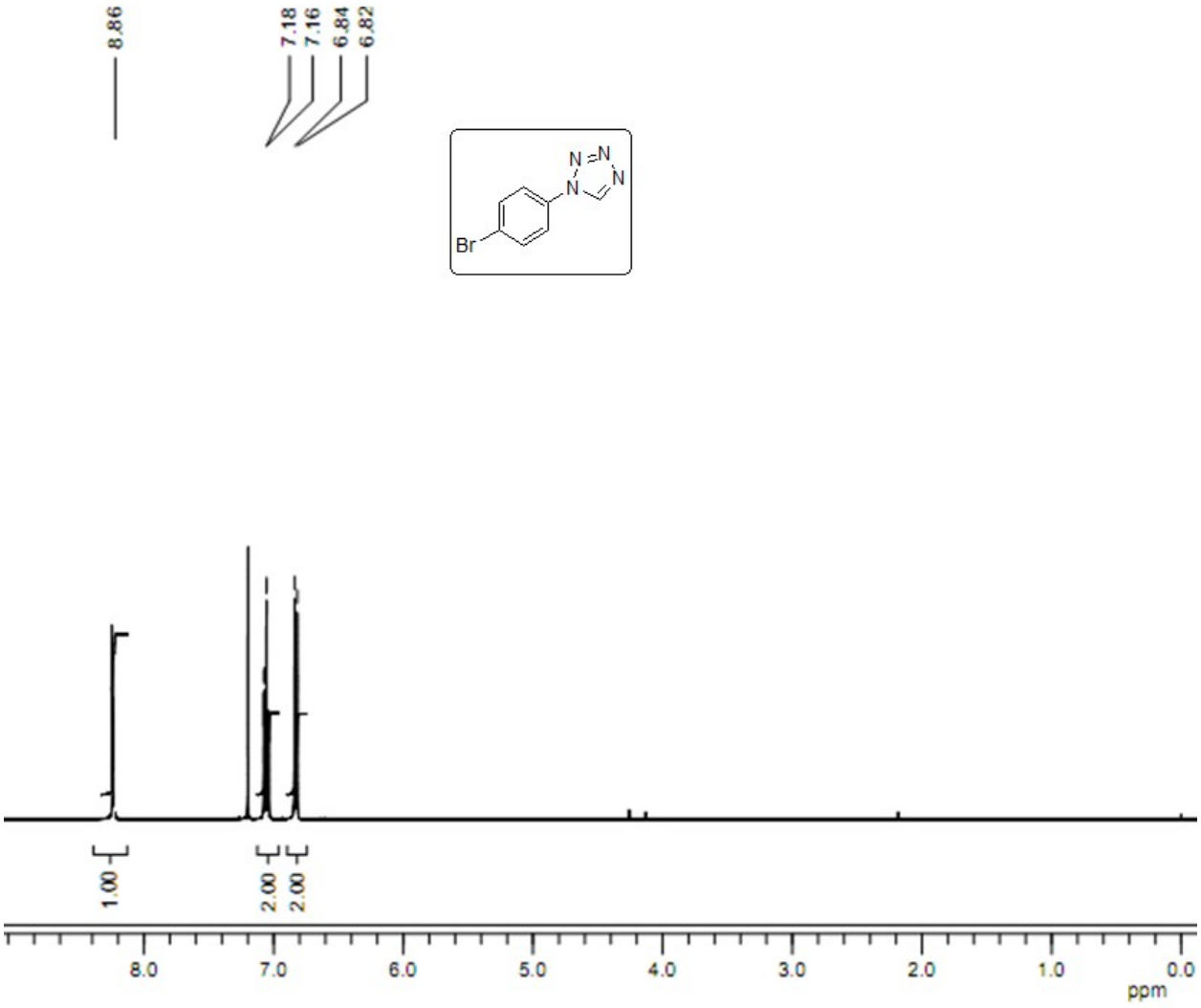
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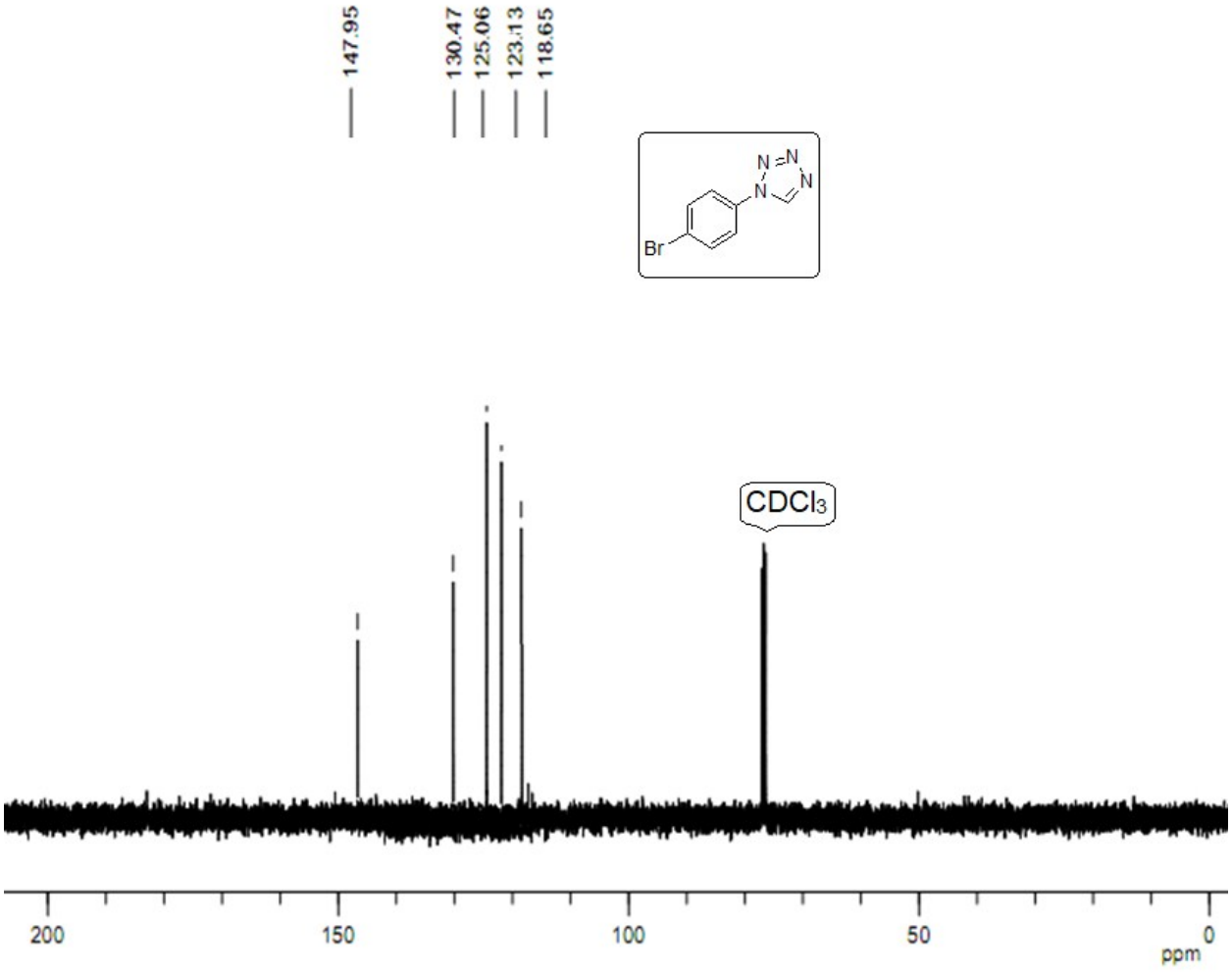
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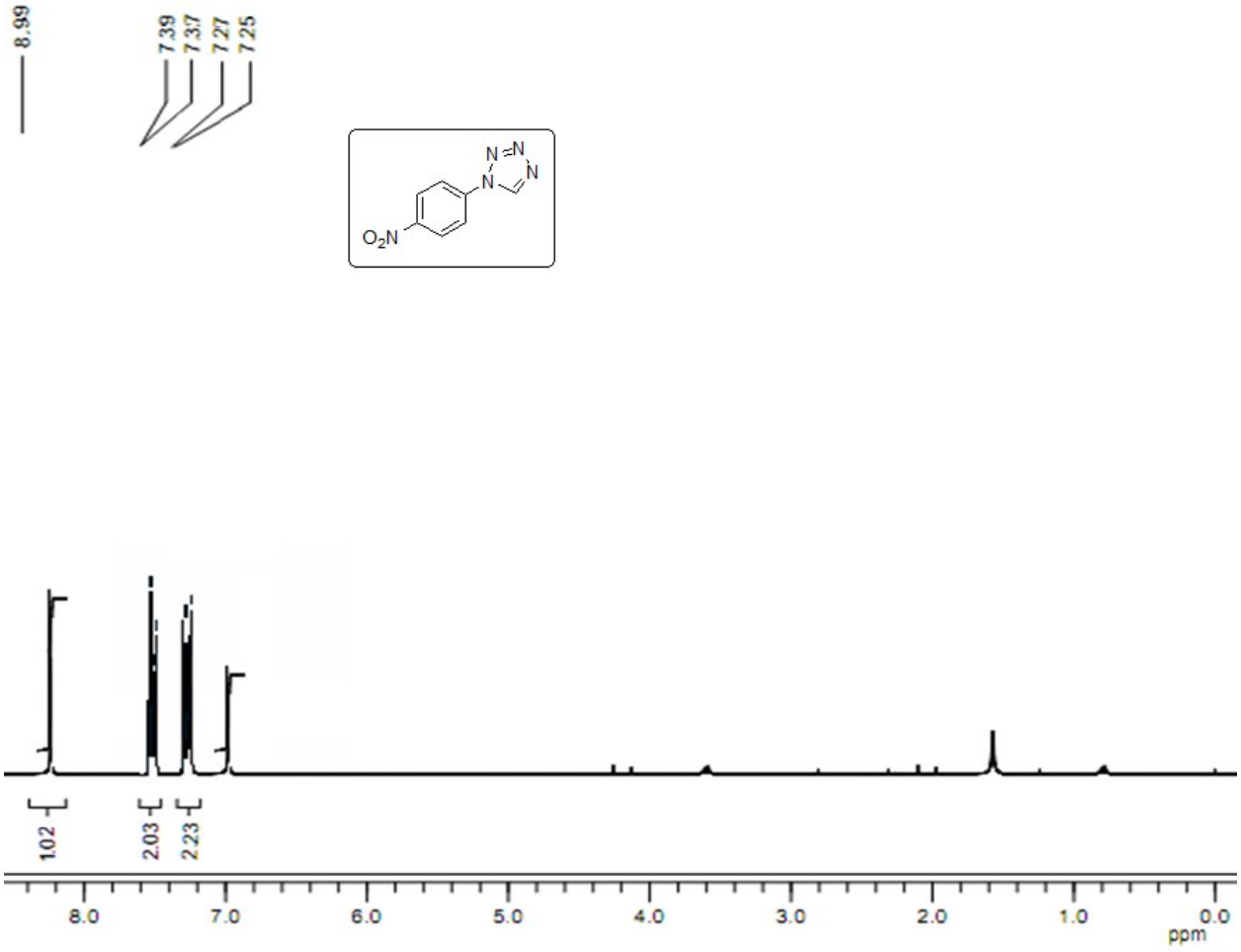
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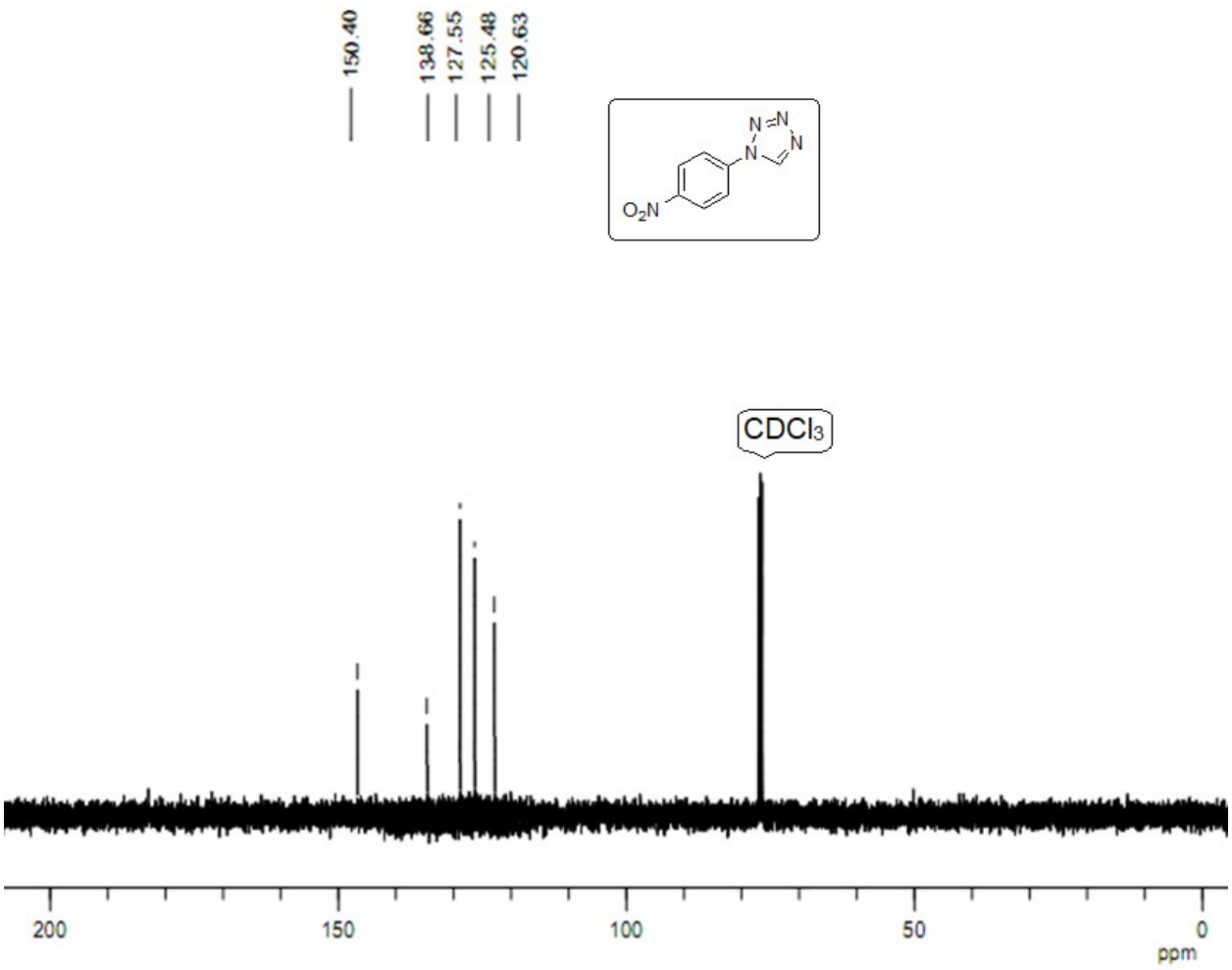
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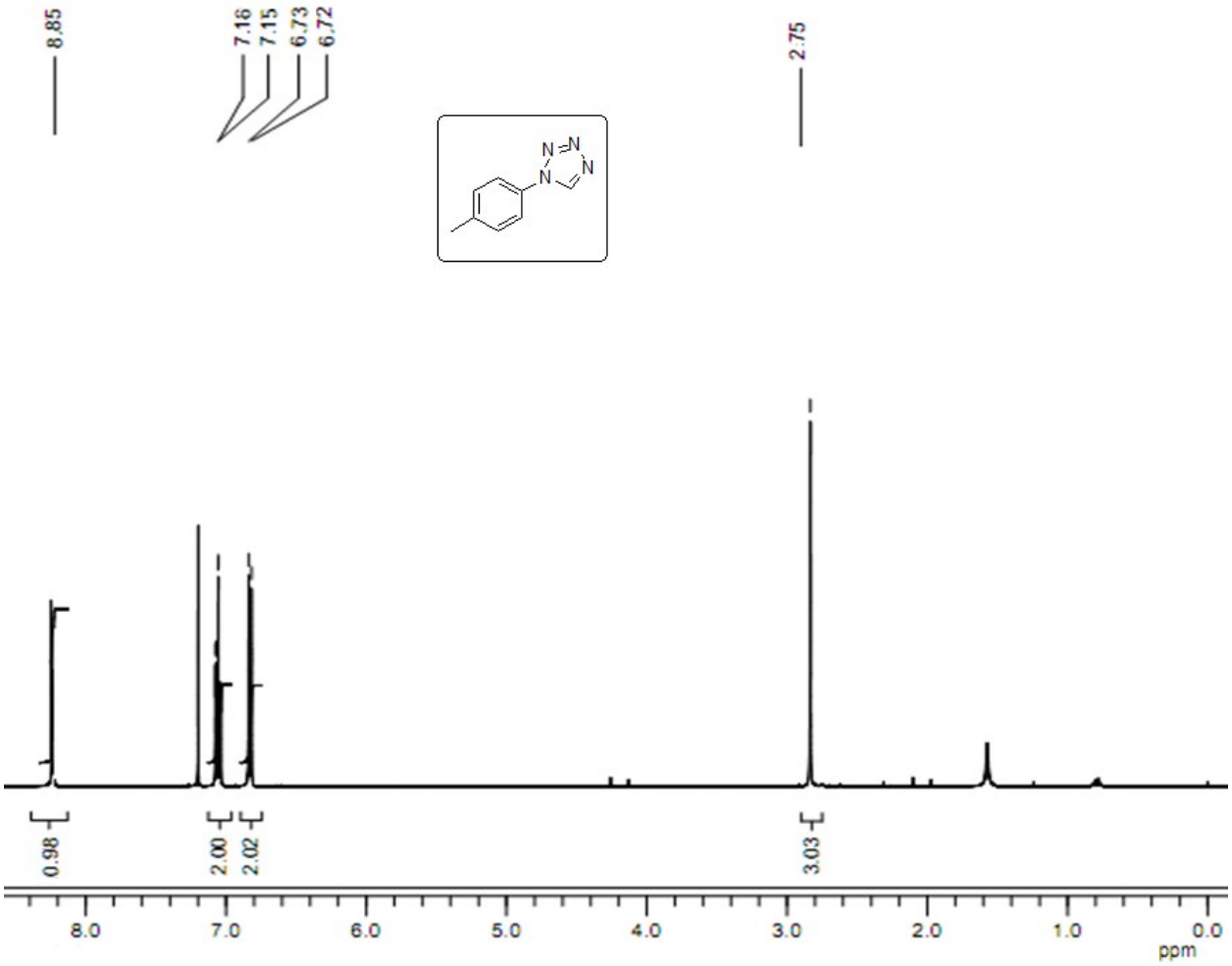
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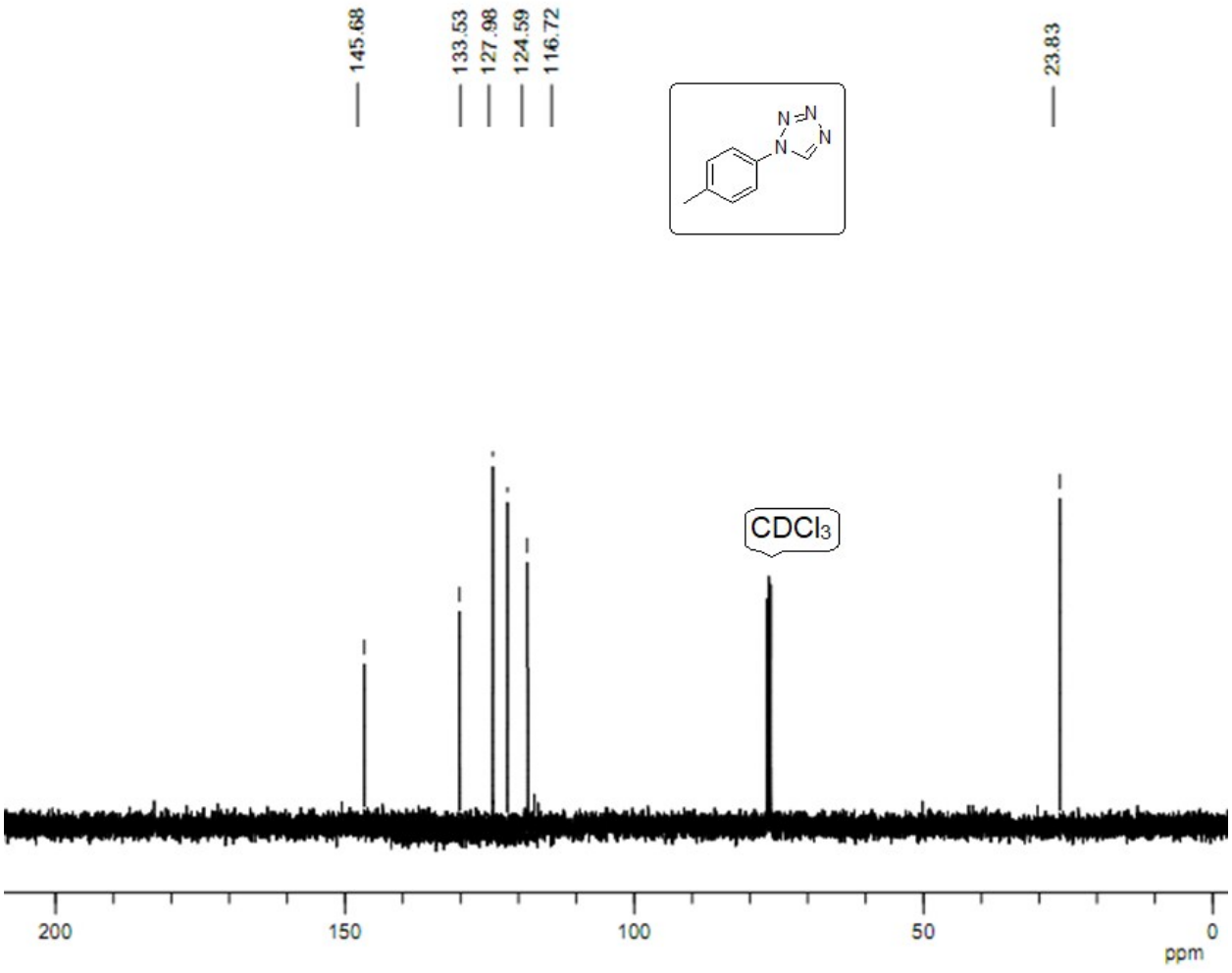
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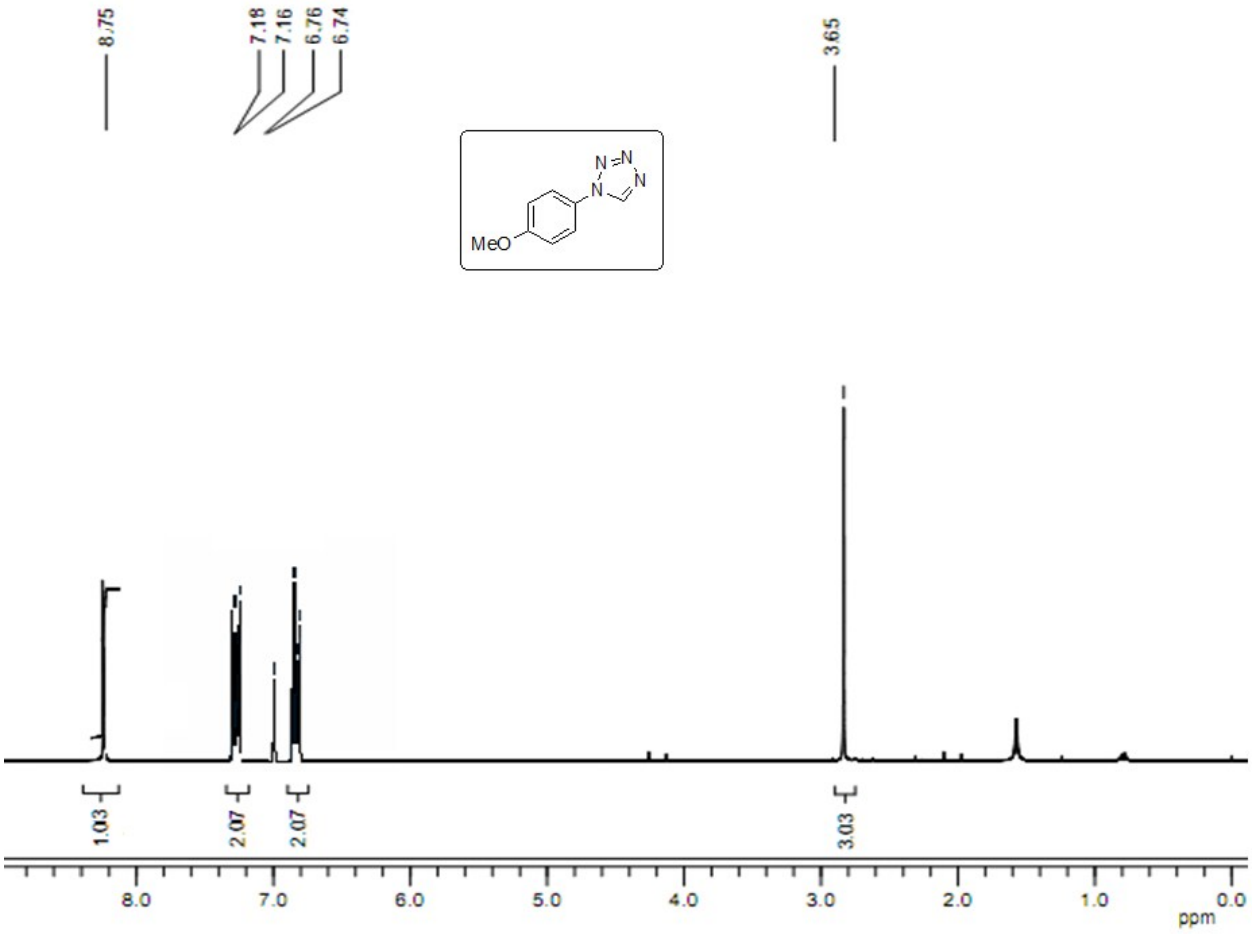
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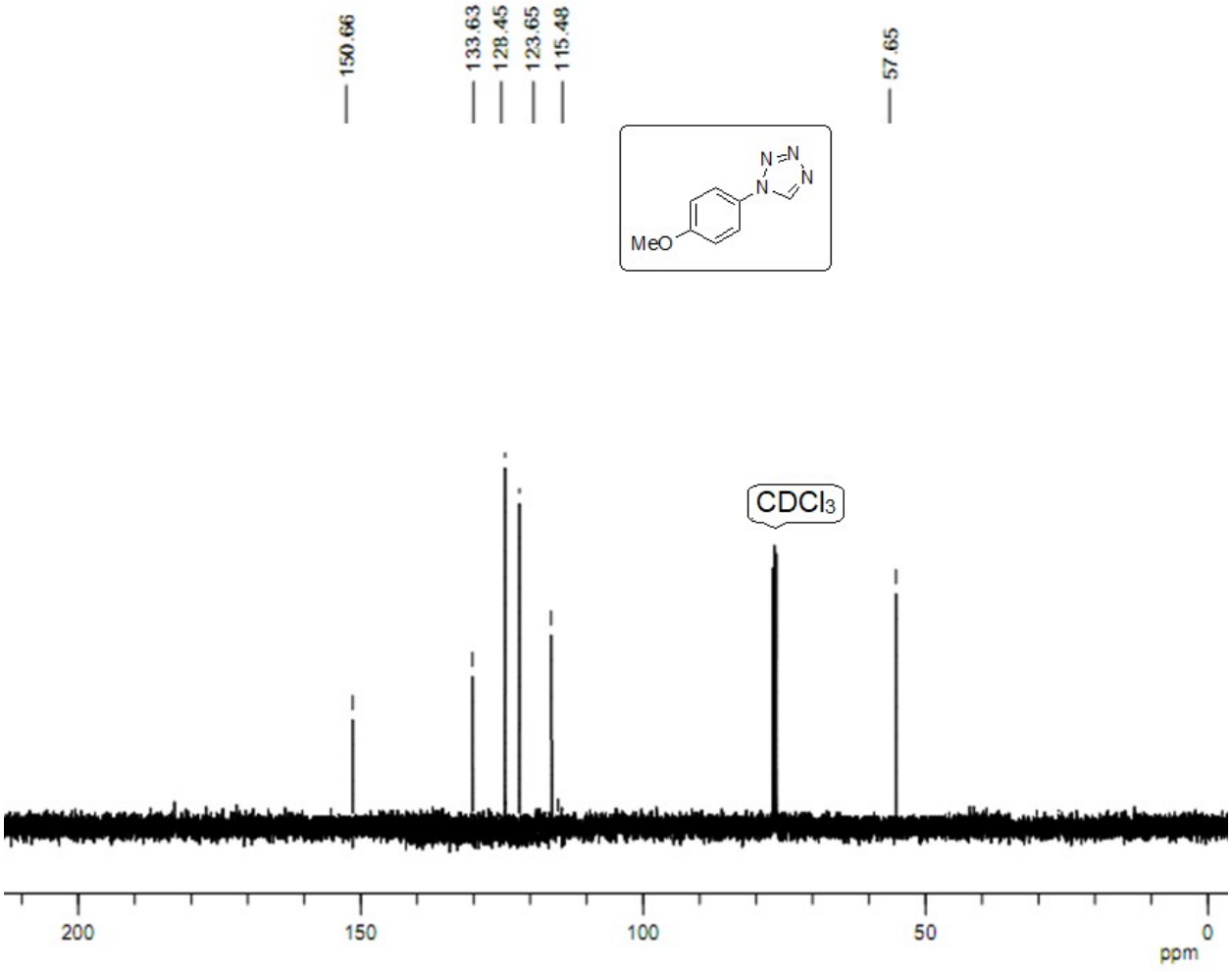
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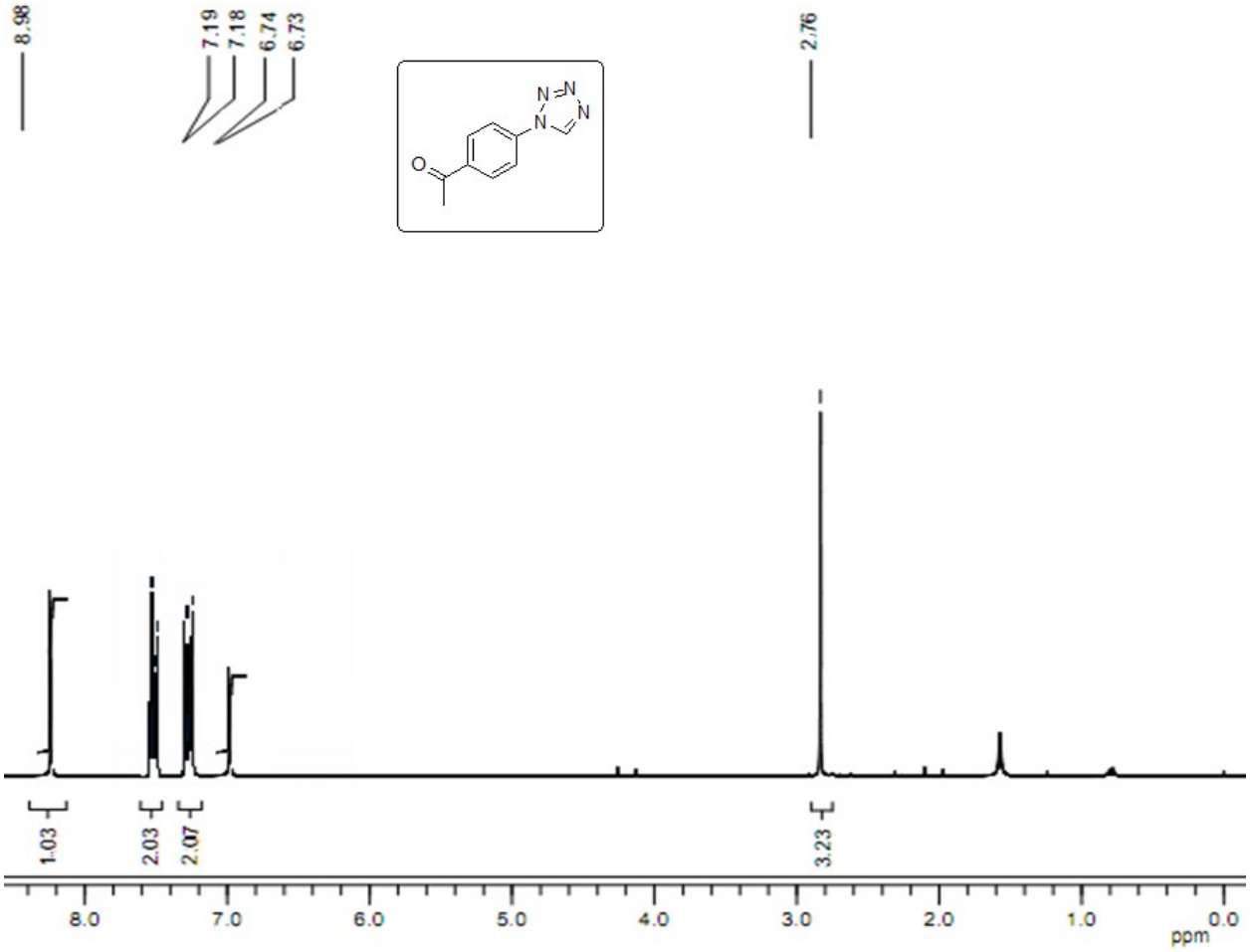
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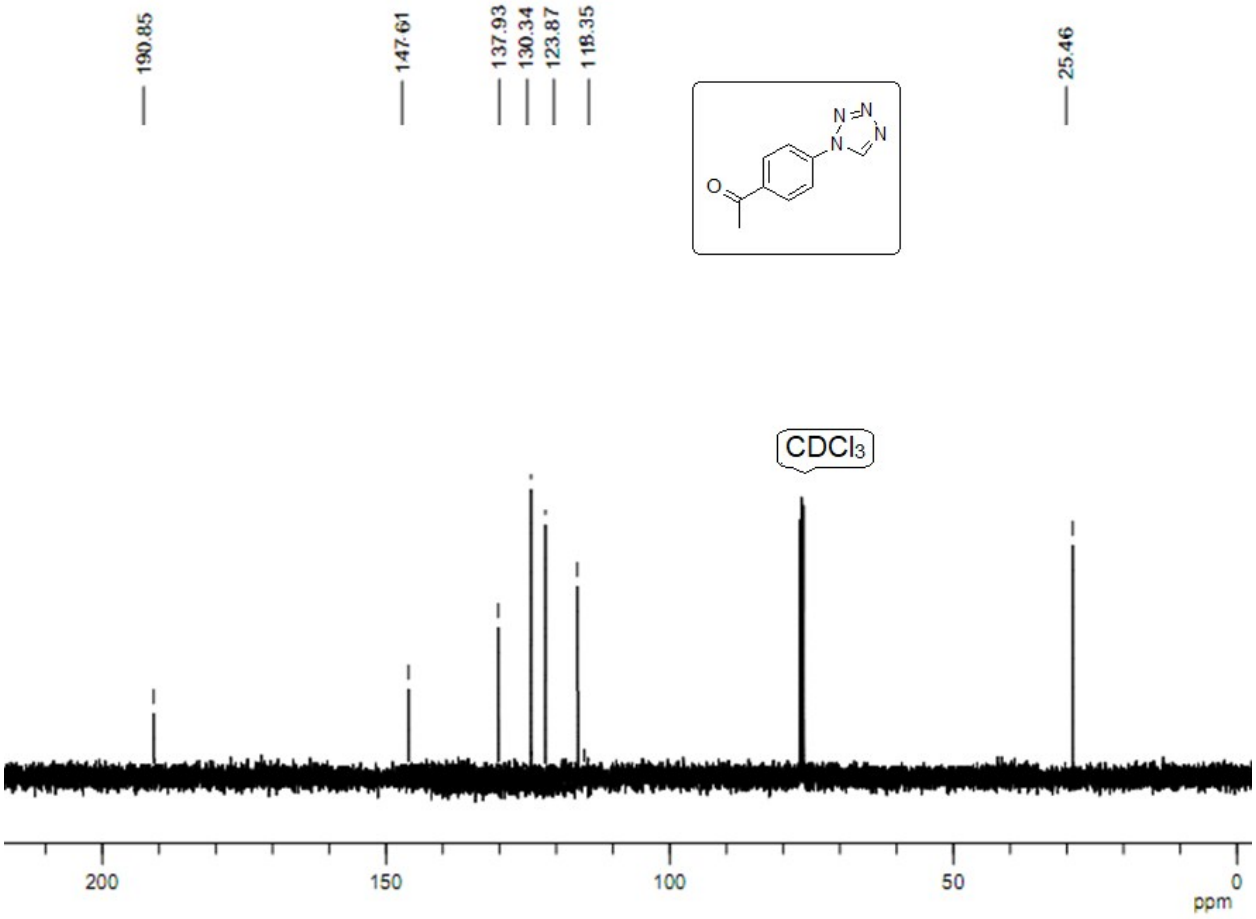
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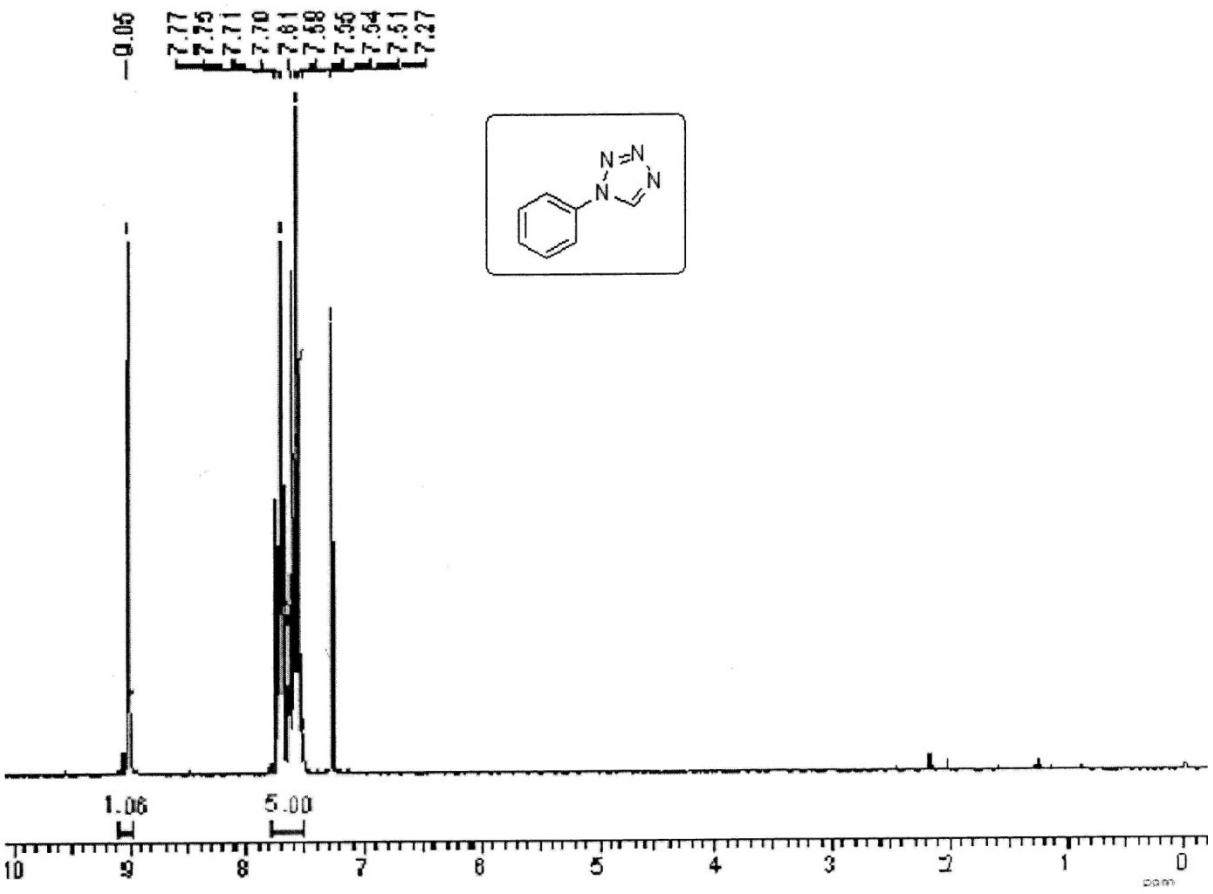
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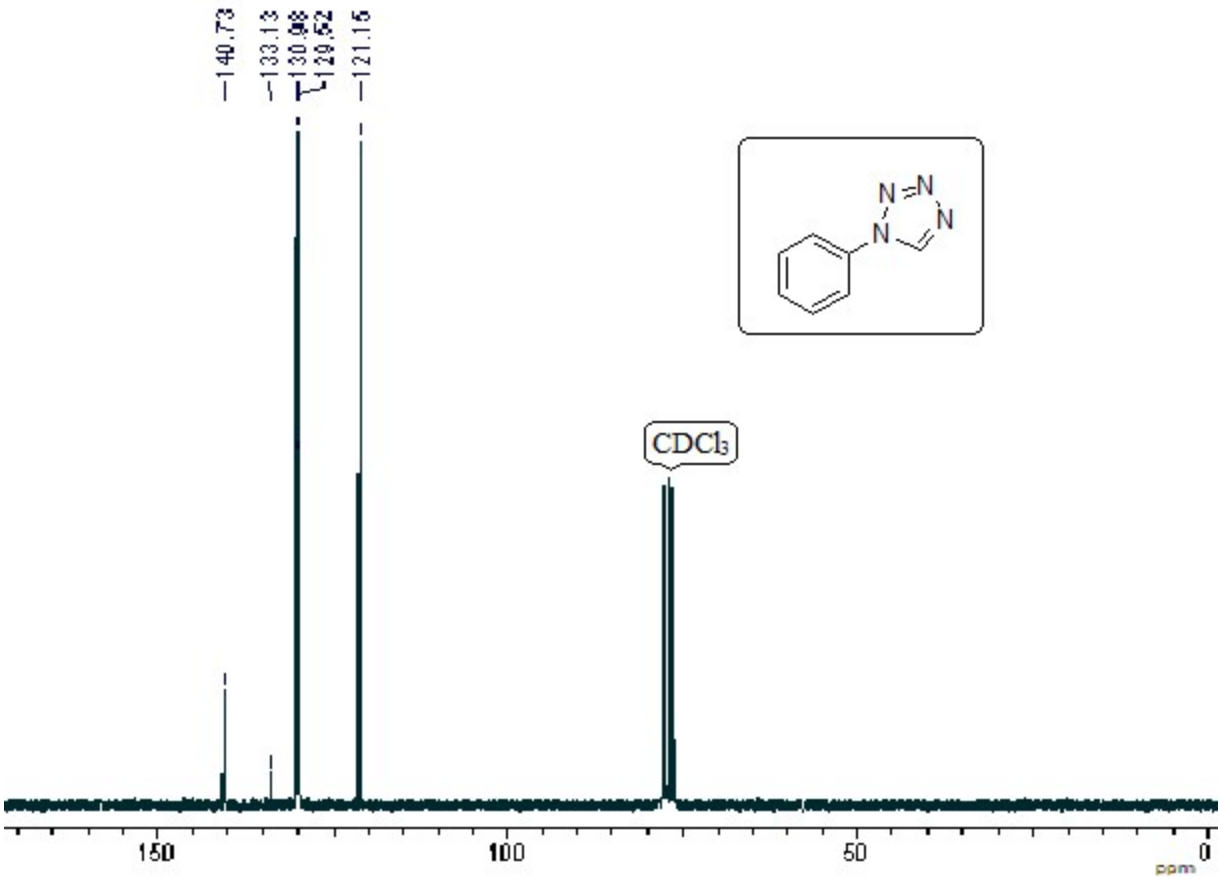
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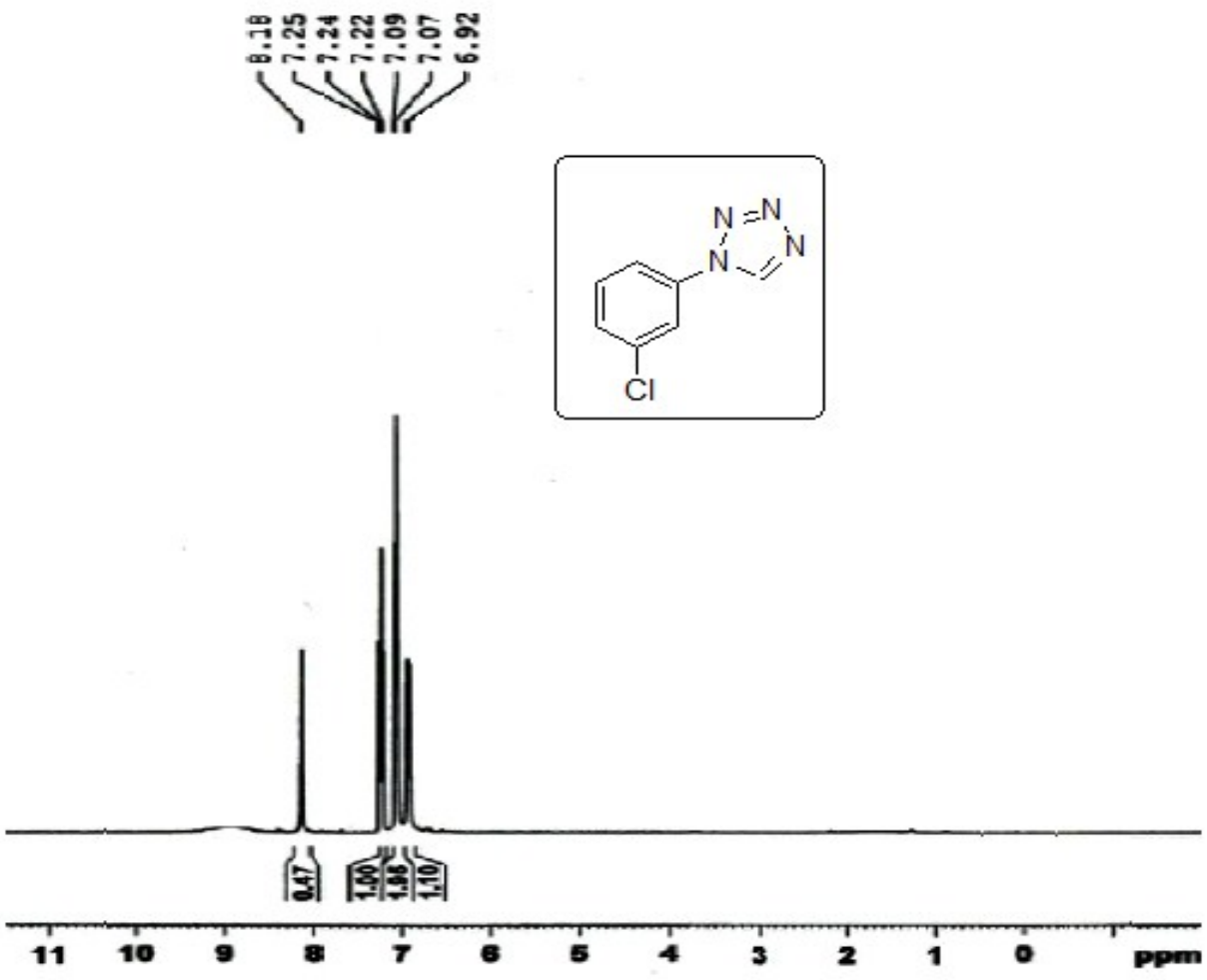
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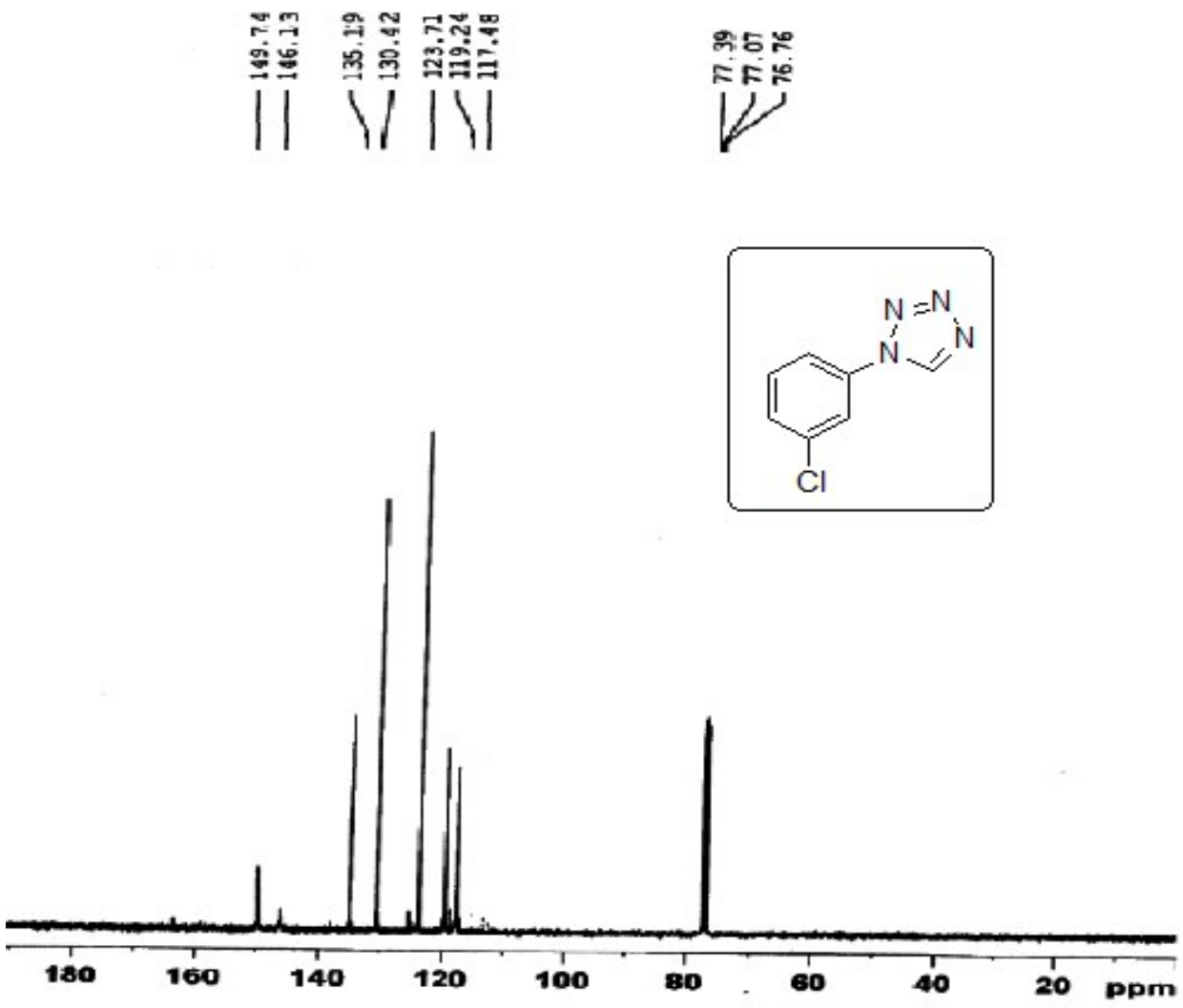
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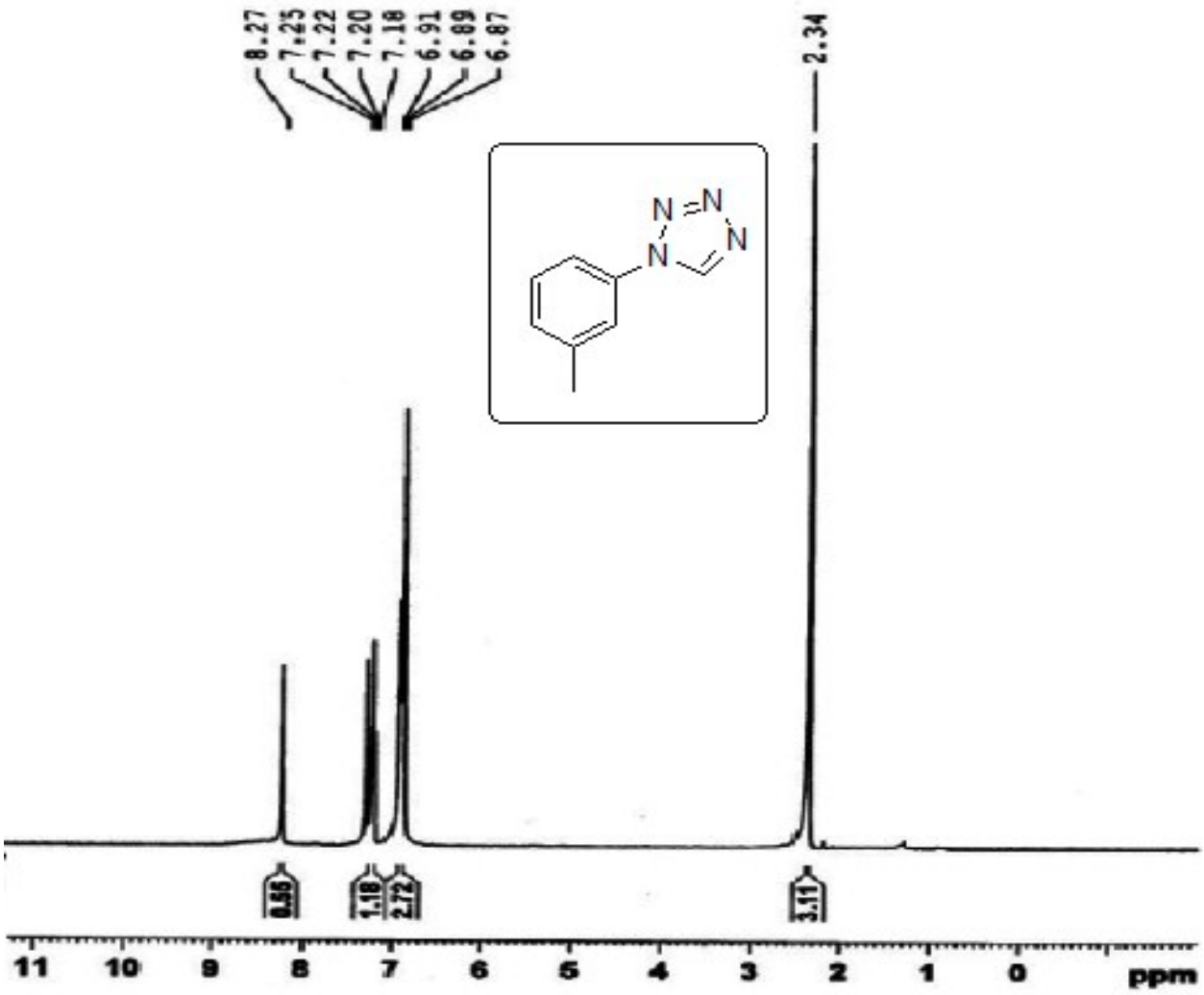
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3.11
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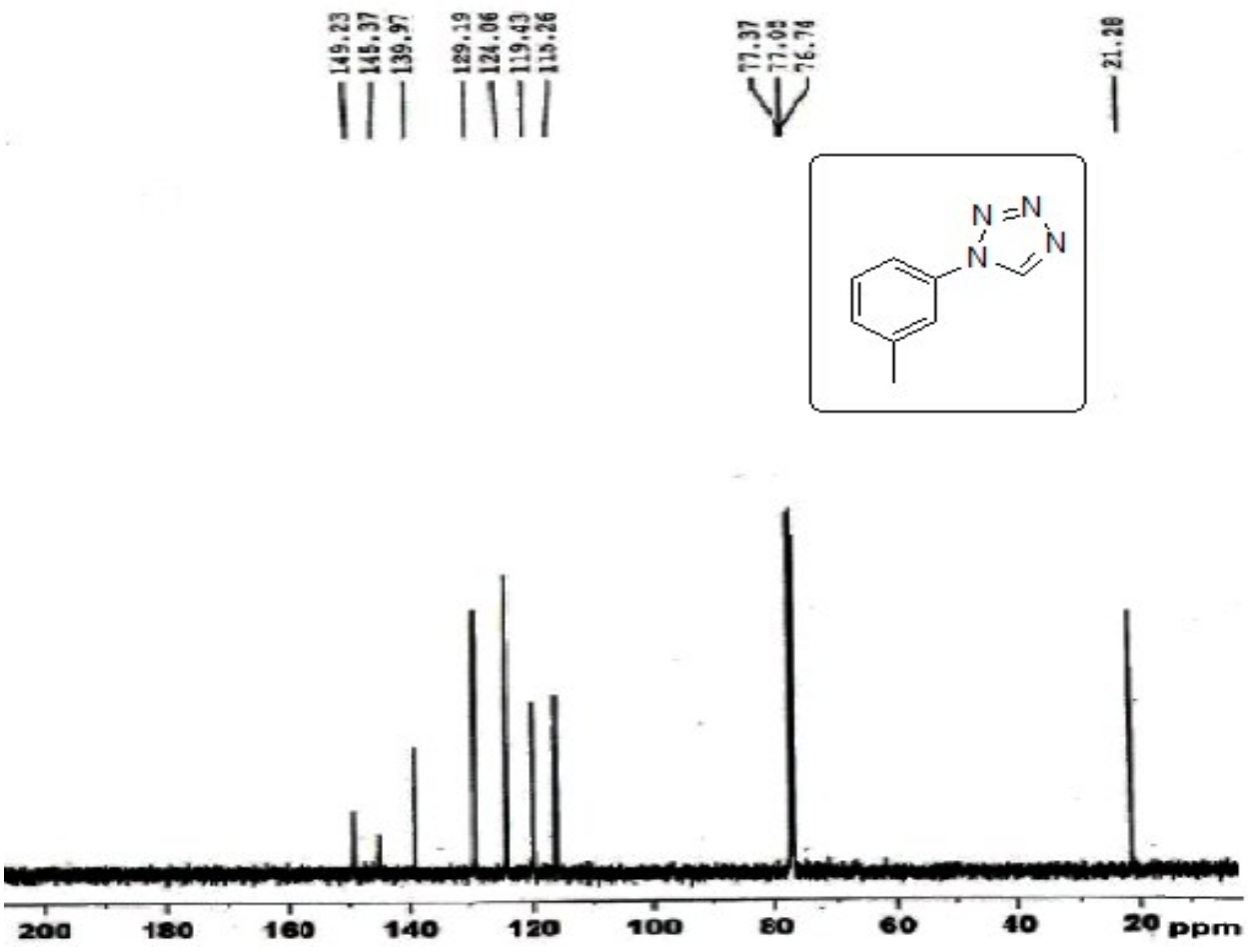
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119.43
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77.37
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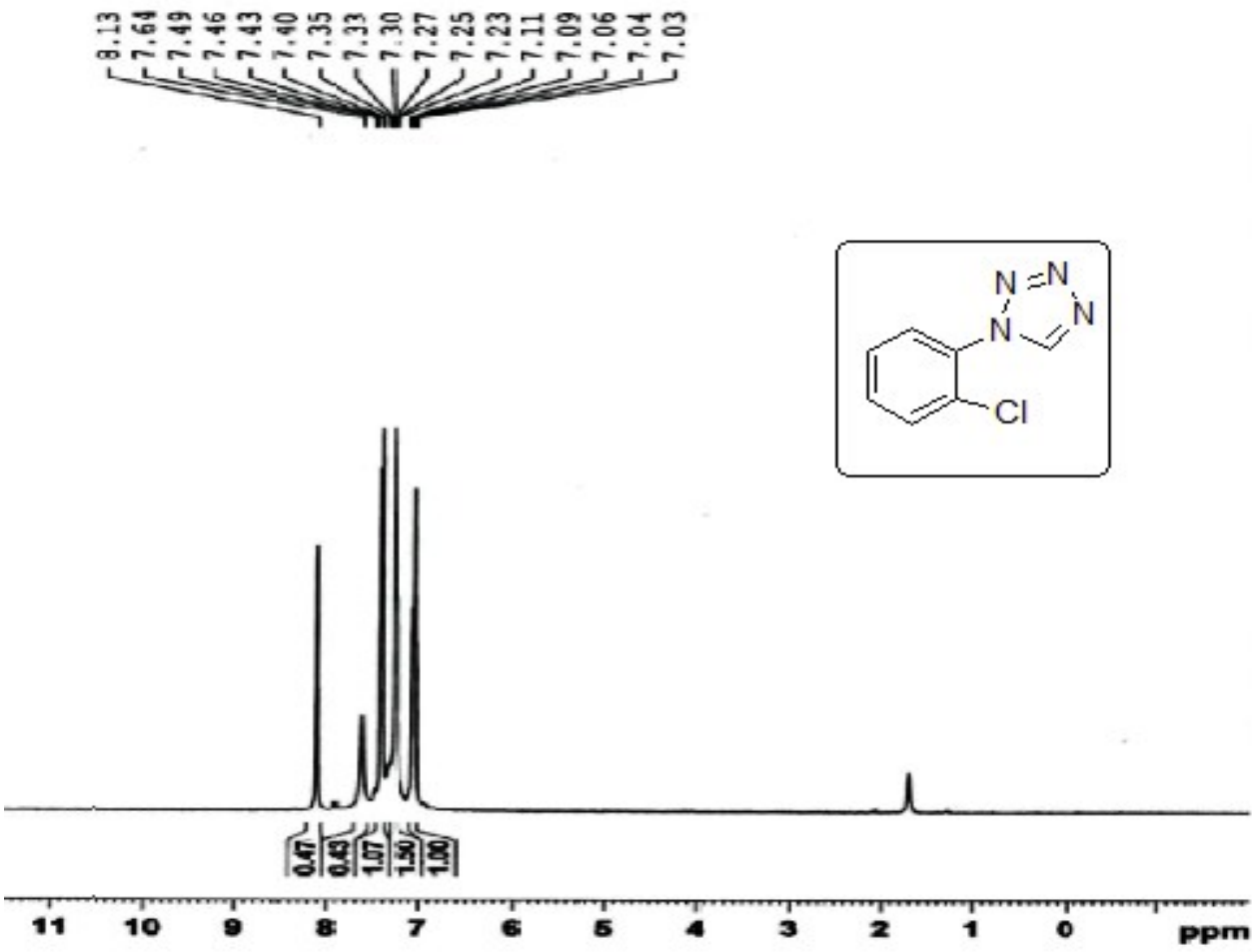
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7.33
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7.27
7.25
7.23
7.11
7.09
7.06
7.04
7.03
N
N
N
N
Cl
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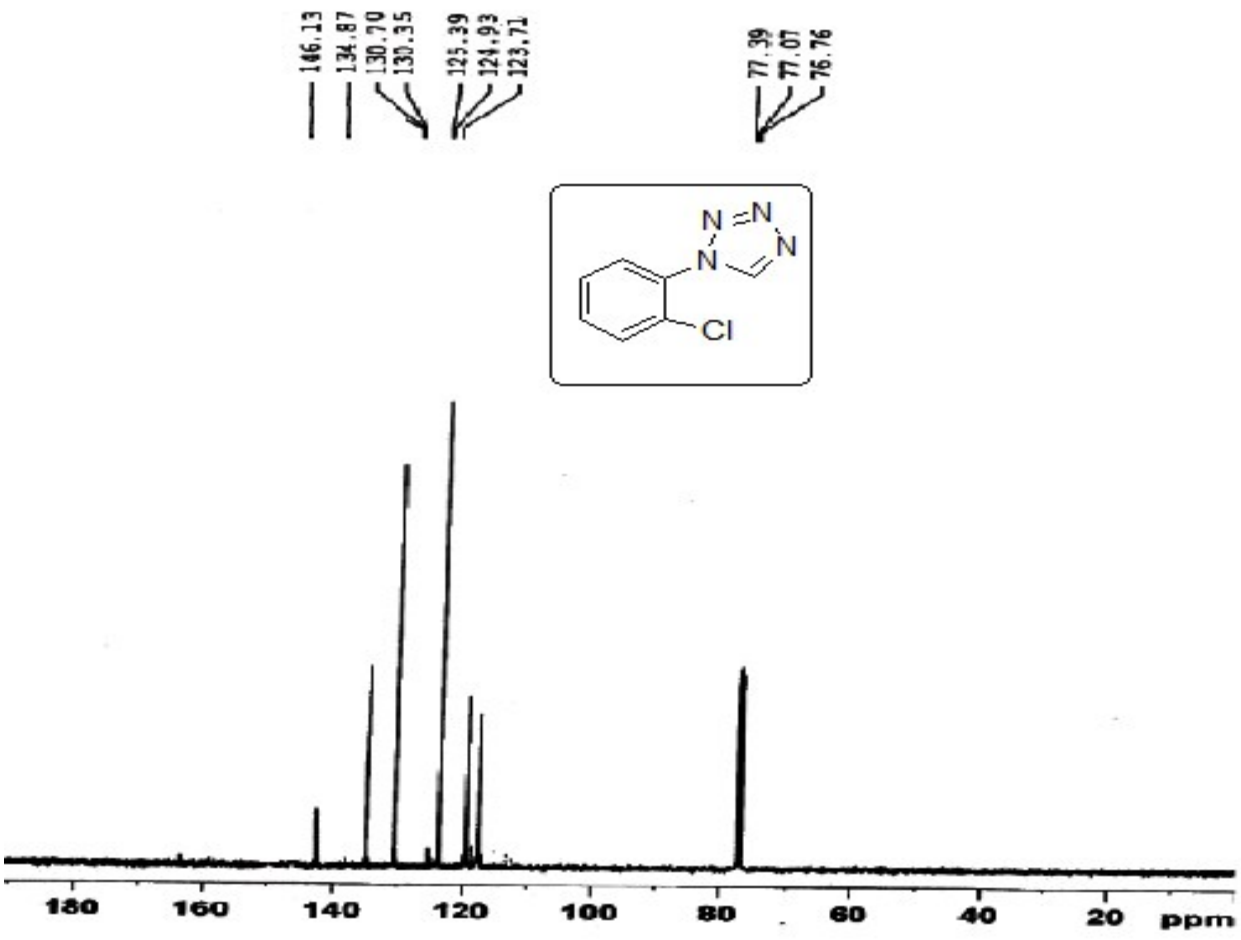
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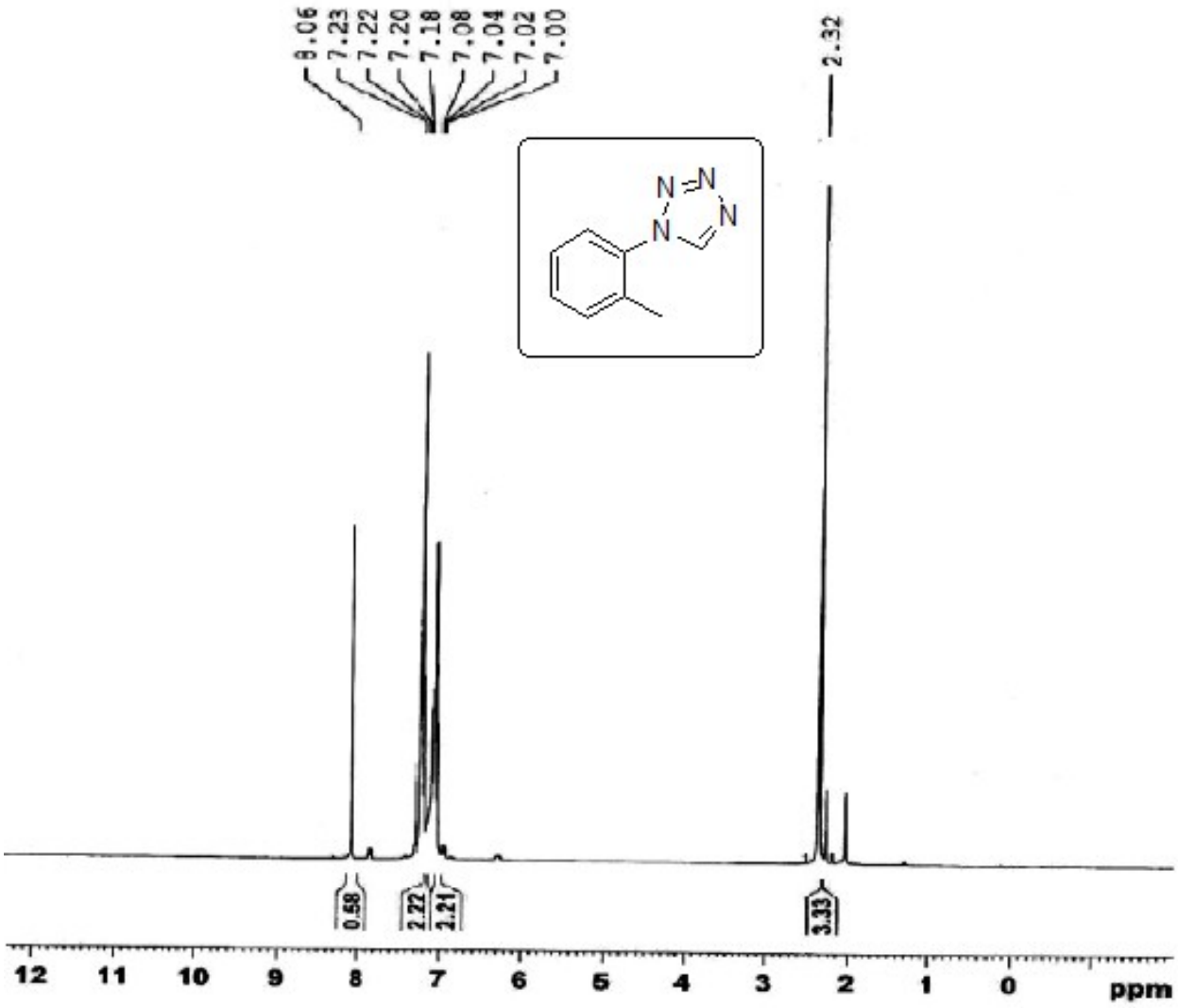
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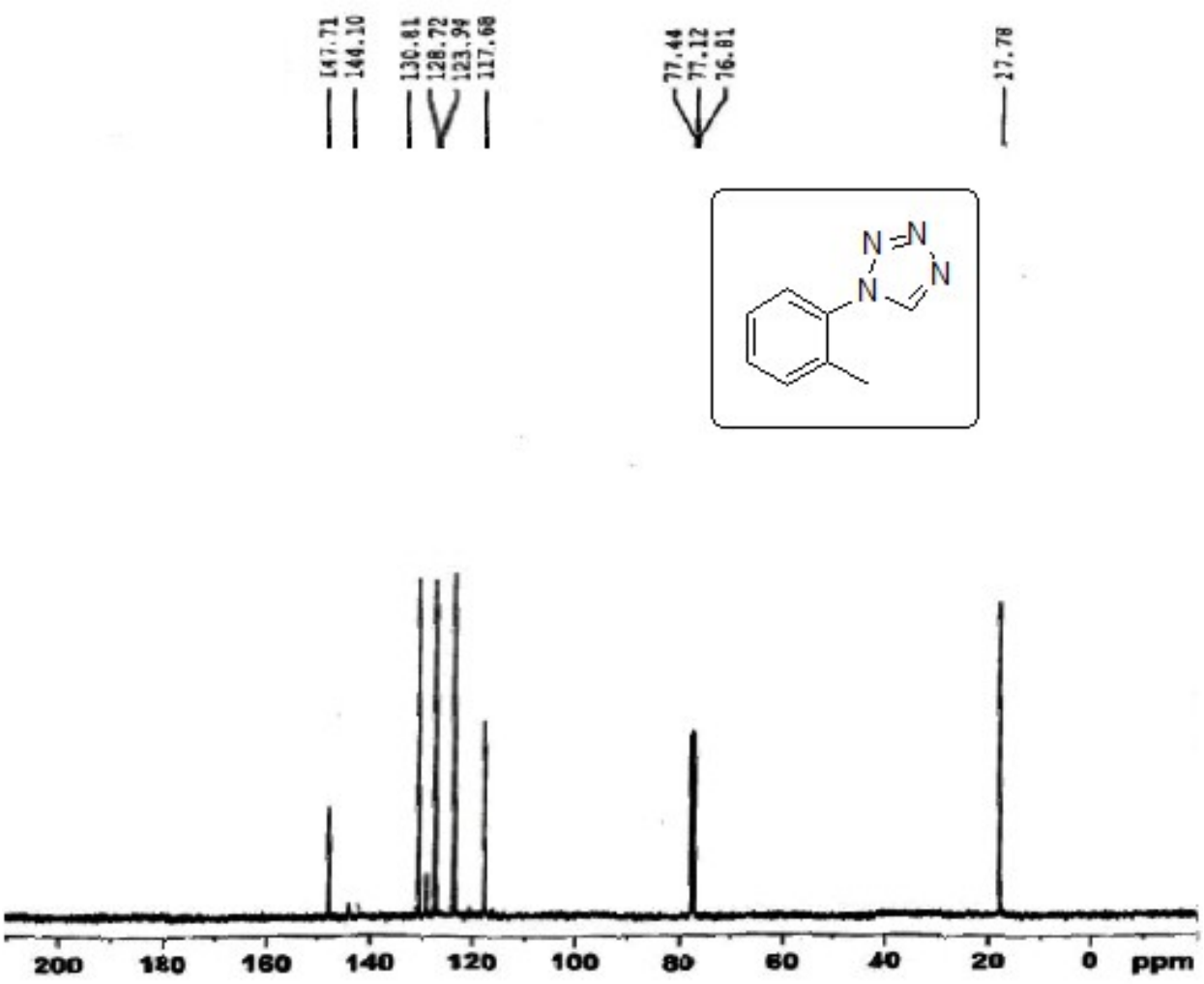
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144.10
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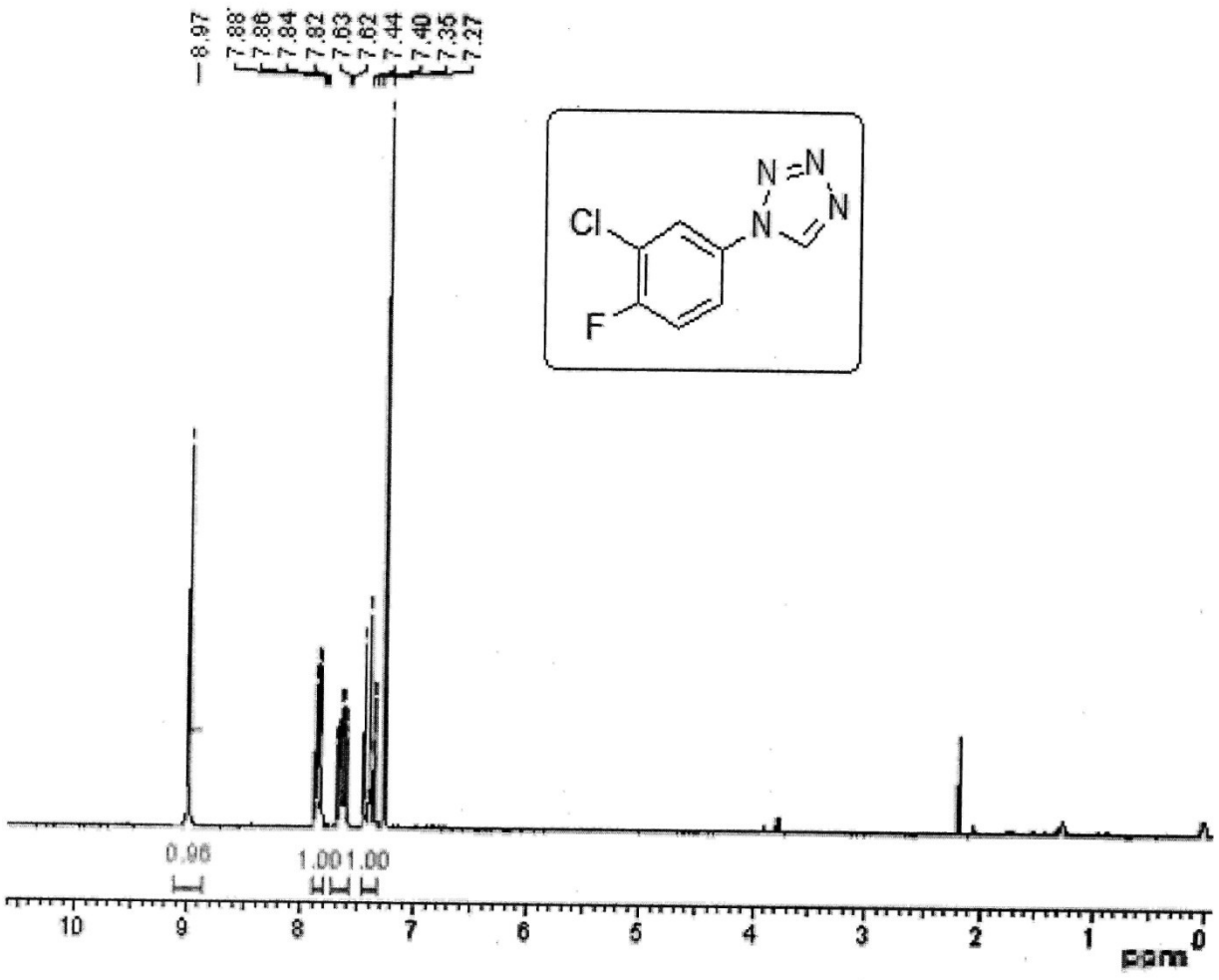
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7.44
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7.35
7.27
Cl
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6
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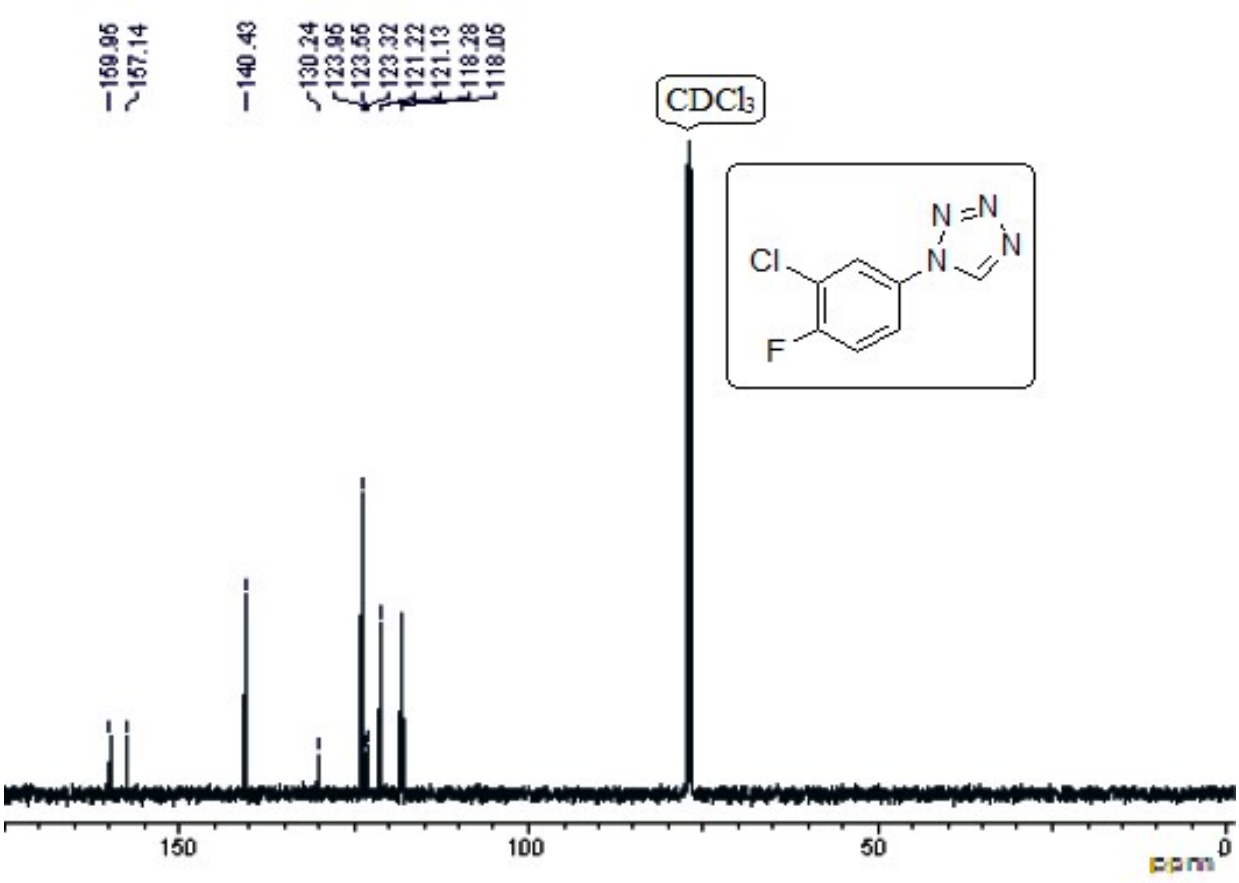
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Cl
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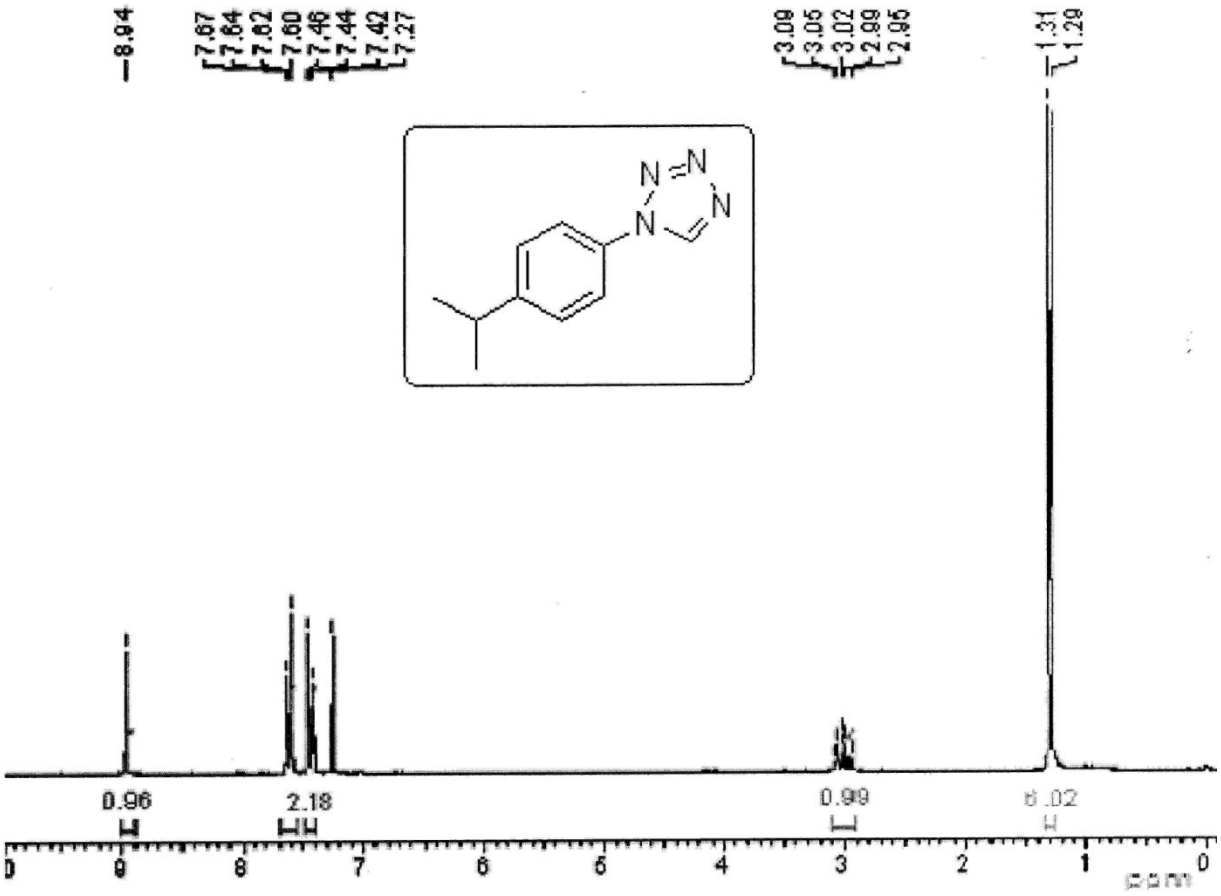
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7.46
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7.42
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3.09
3.05
3.02
2.99
2.95
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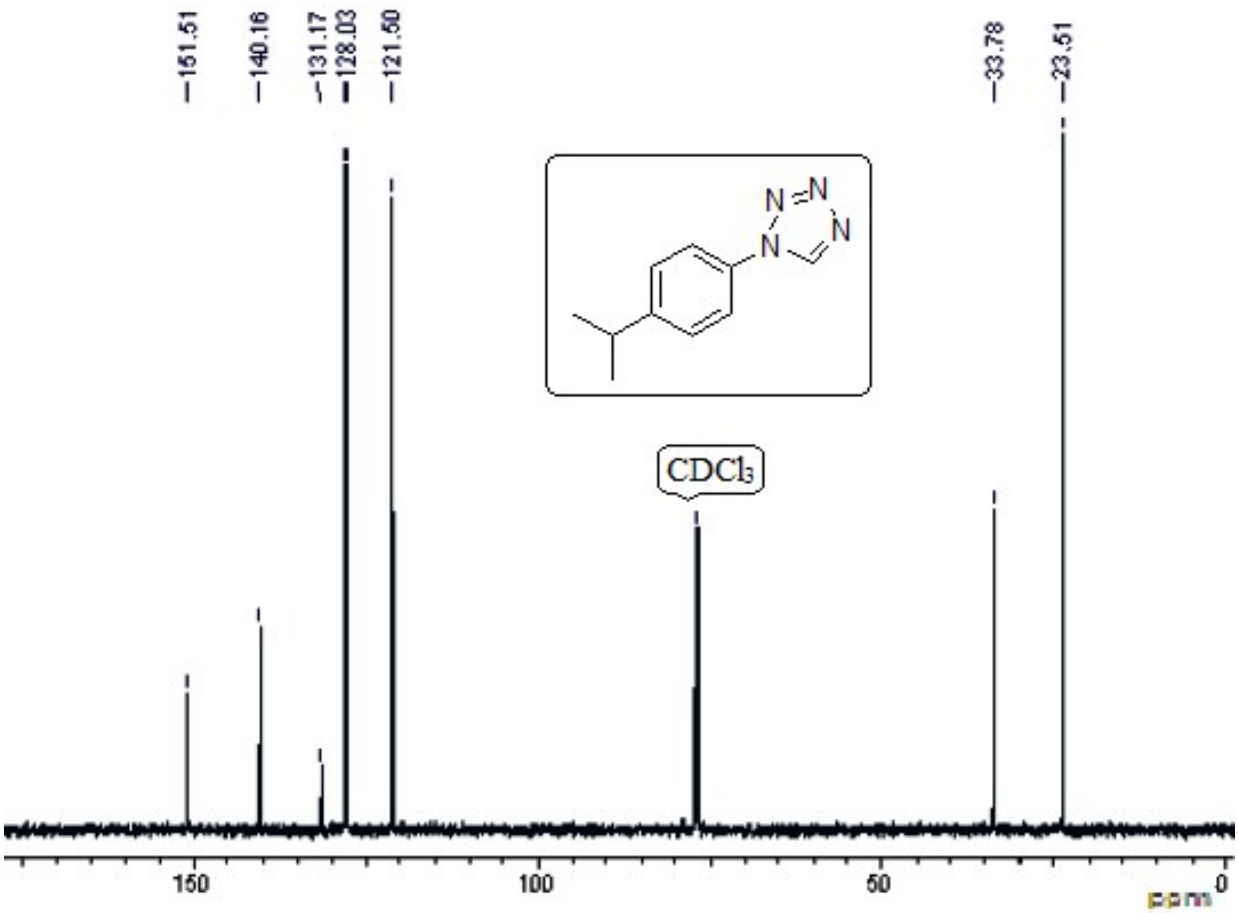
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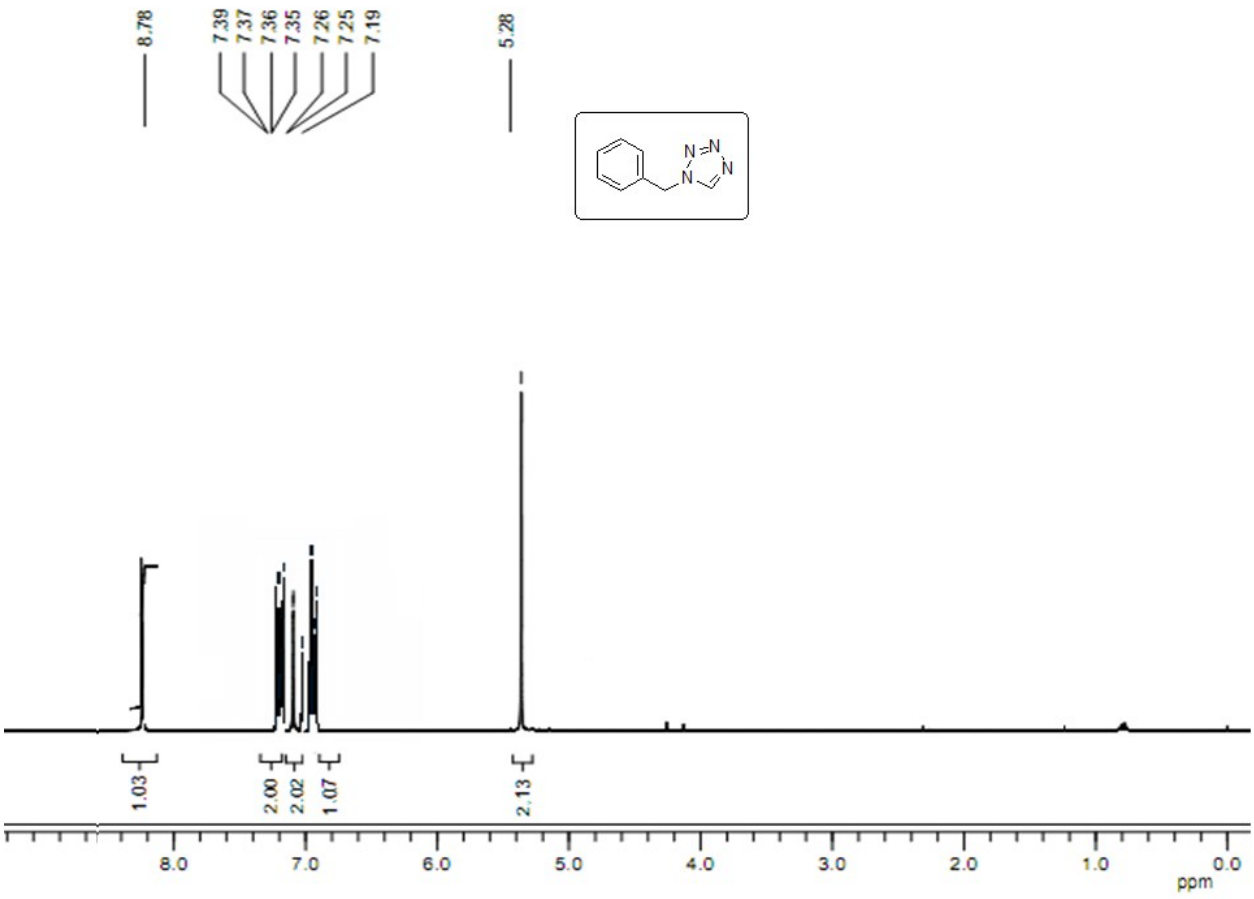
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7.26
7.25
7.19
5.28
1.03
2.00
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3.0
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1.0
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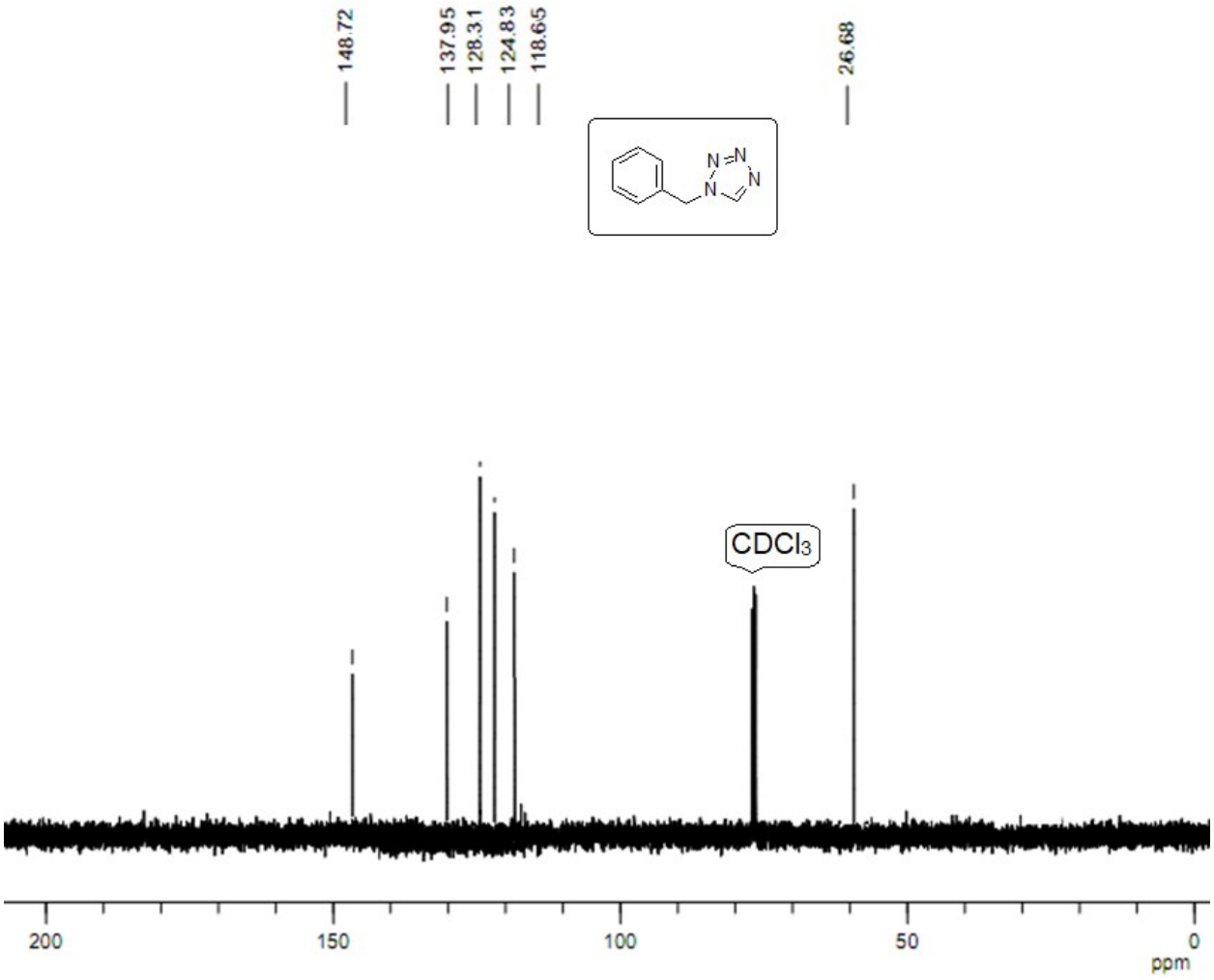
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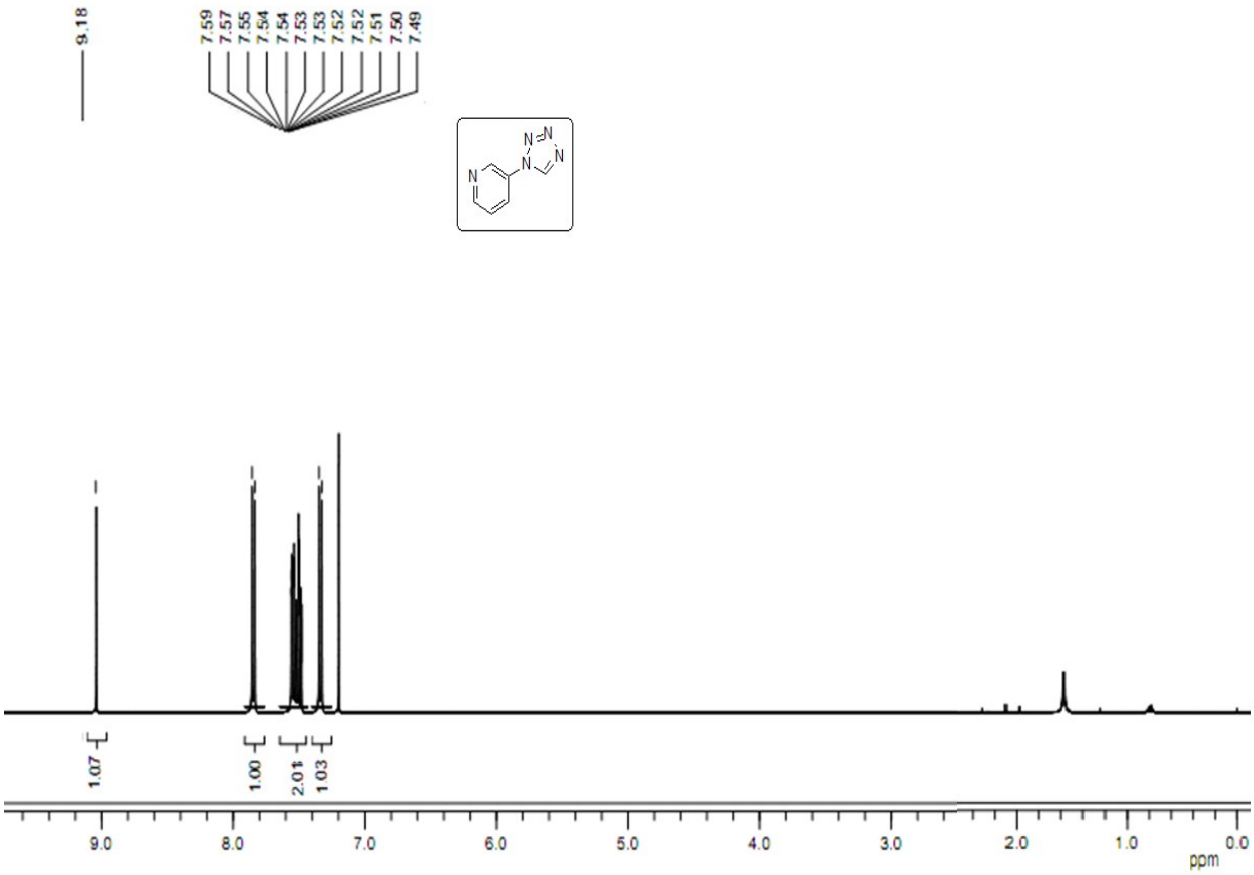
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1.00
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1.0
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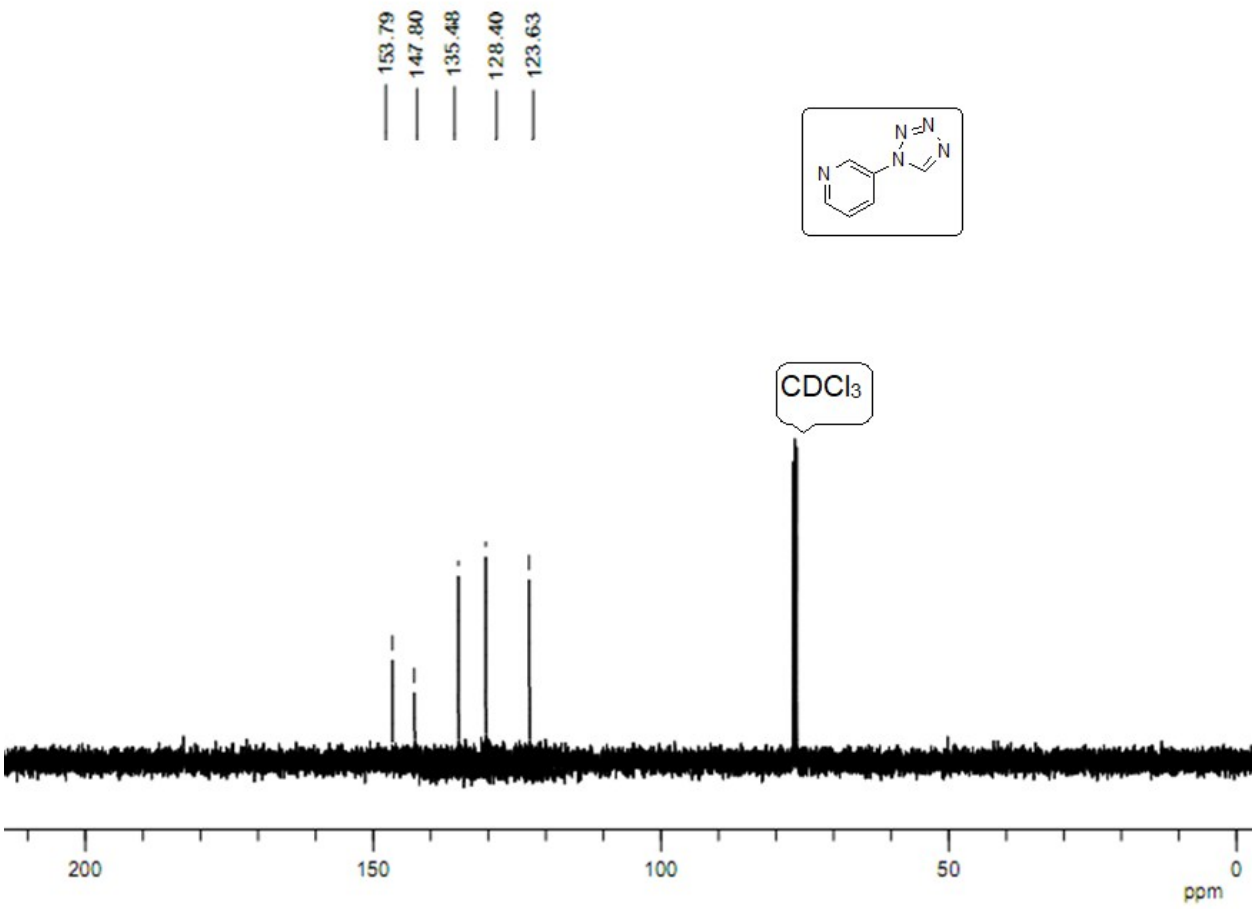
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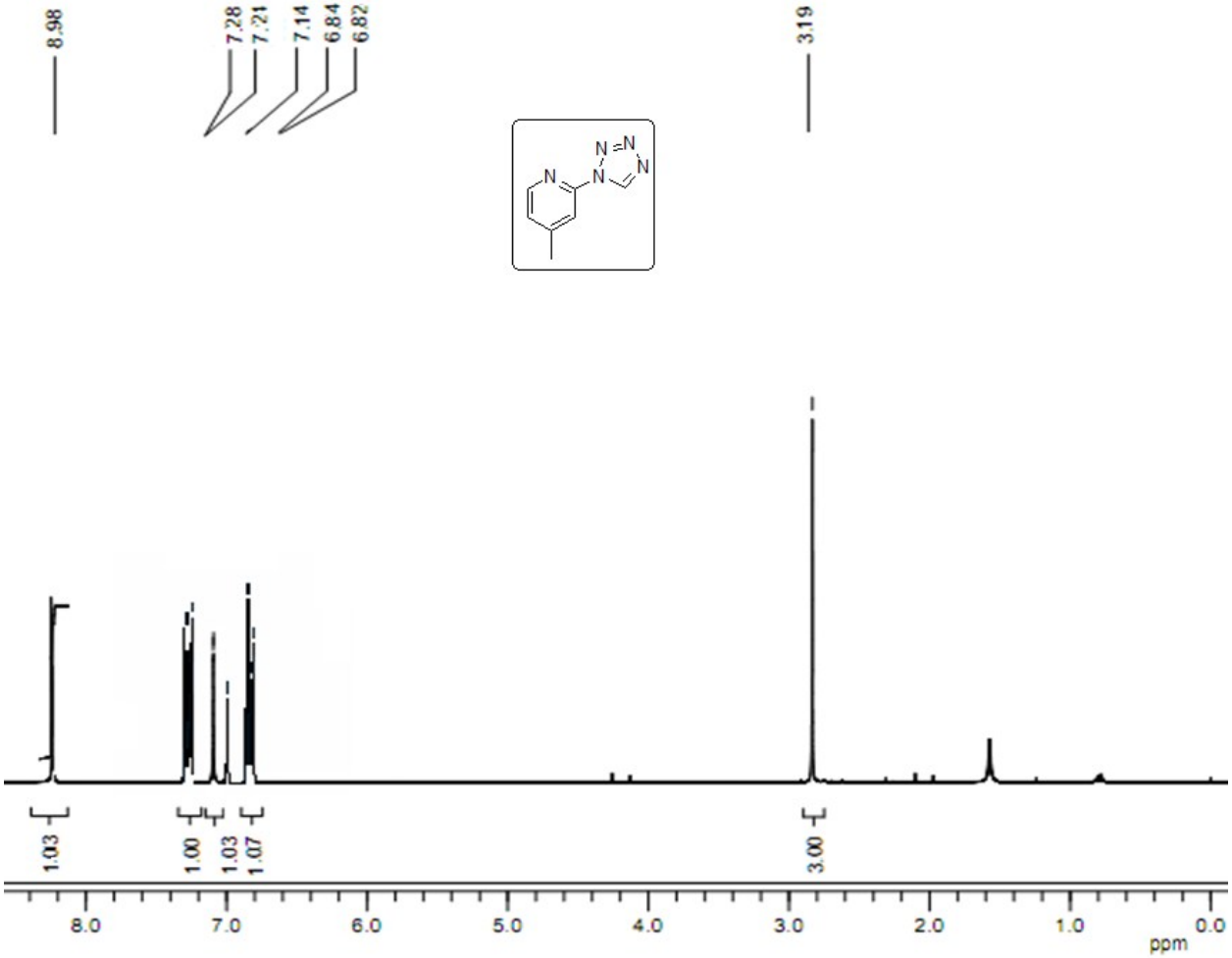
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8.0
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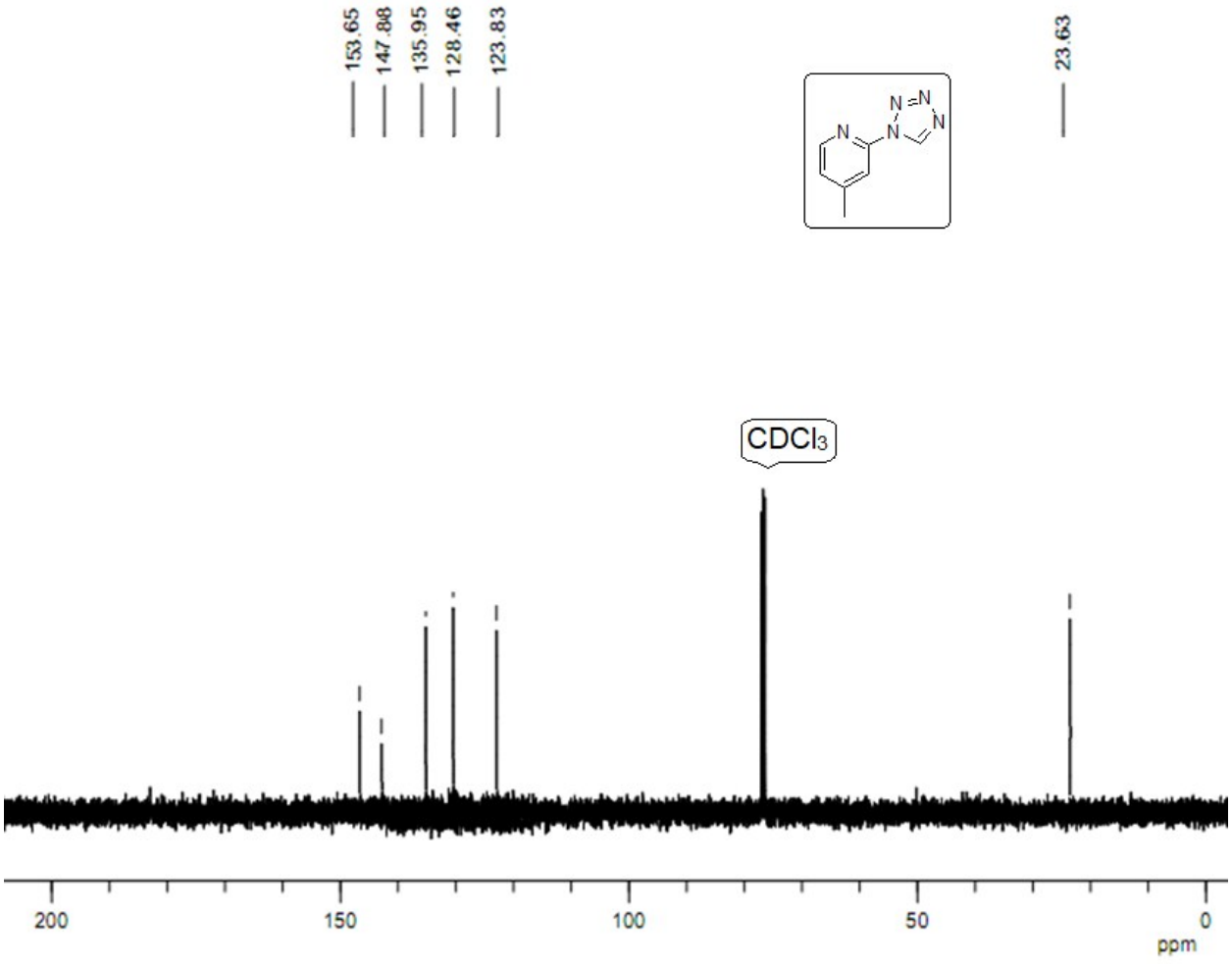
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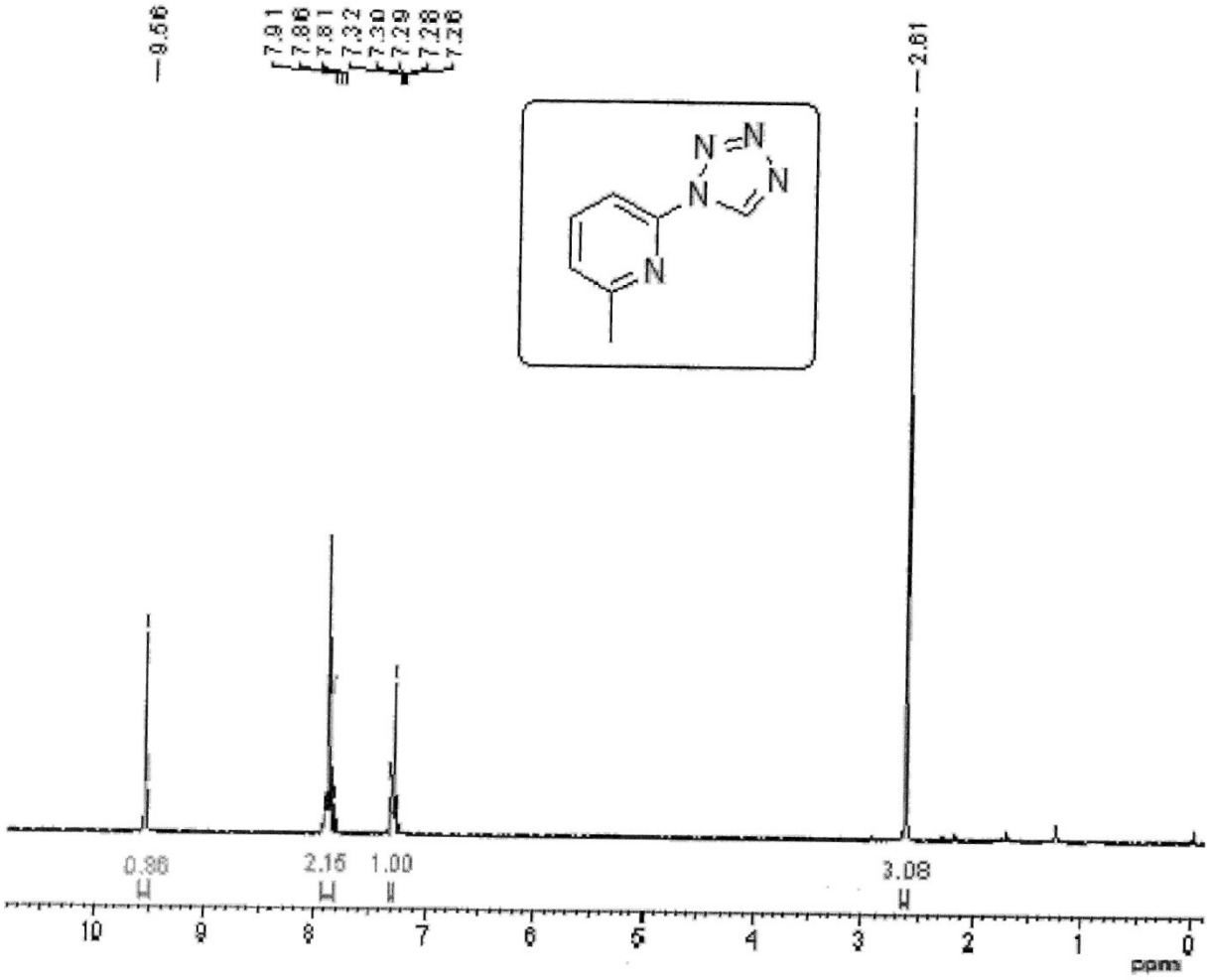
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7.32
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7.29
7.28
7.26
2.61
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N
N
N
0.86
H
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H
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H
3.08
H
10
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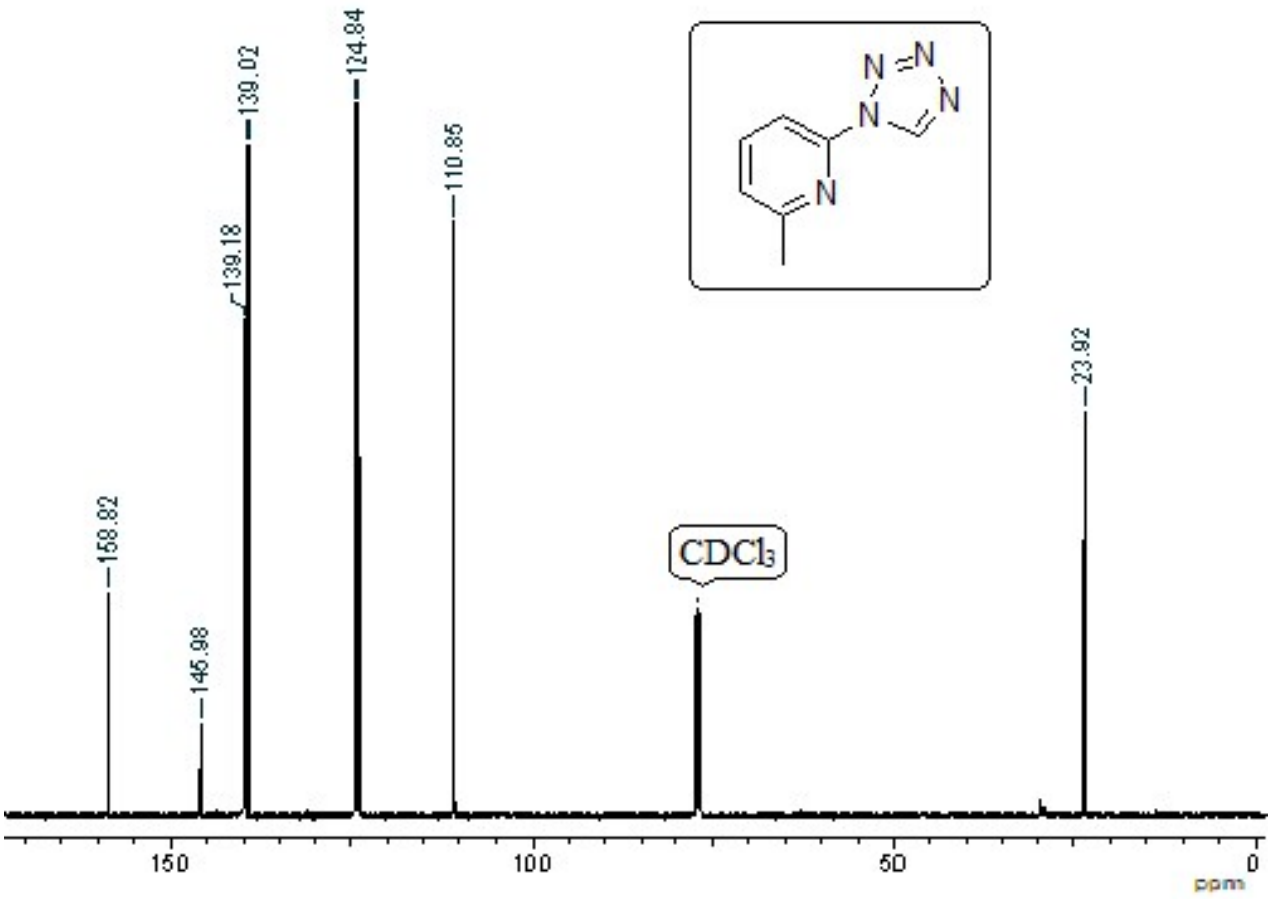
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