Supporting information

Copper-Catalyzed Decarboxylative Regioselective Synthesis of 1,5-Disubstituted 1,2,3-Triazoles

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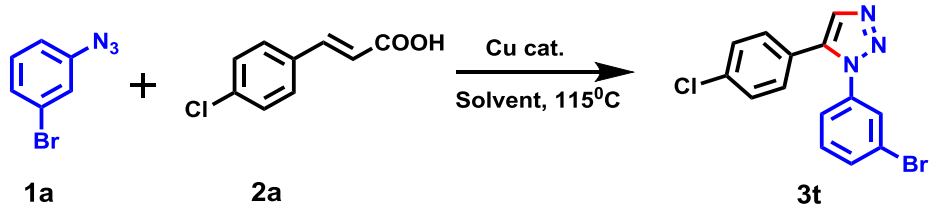
(1) General remarks:

All the reactions were carried out in oven-dried glassware. All the chemicals and reagents were purchased from commercial sources and were used without further purification. Reagents grade solvent DMF (Spectrochem) was used for reaction. TLC (Thin Layer Chromatography) was performed on Merck-percoated silica gel and 100-200 mesh silica gel was used for column chromatography. The chromatographic solvents are mentioned as v/v ratios. All the synthesized compounds were fully characterized by ^{1}H, ^{13}C NMR, IR, and further confirmed through ESI-MS and HRMS analyses. IR spectra were recorded on a Perkin-Elmer FT-IR RXI spectrophotometer and values reported in cm^{-1}. NMR spectra were recorded with 400 MHz spectrometers for ^{1}H NMR, 100 MHz for ^{13}C NMR respectively. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H), $CDCl_3$ and DMSO-d_6 (^{13}C) as internal standards. Integrals are in accordance with assignments; coupling constants are given in Hz. ESI-MS spectra were obtained on a LCQ Advantage Ion trap mass spectrometer (Finnigan thermo fischer scientific).

A good quality single crystal of size 0.22 x 0.22 x 0.07 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound 3t were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the monochromated Mo-Kα radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using ω-scans of 0.5^{o} steps at 293(2) K. Cell determination, data collection and data reduction was performed using the Rigaku Crystal Clear-SM Expert 2.1 b24[1] software. Structure solution and refinement were performed by using SHELX-97[2]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model. Crystal data are summarized in Table 2.

(2) Optimization studies

Optimization studies were started with the reaction of 1-azido-3-bromobenzene (1.2 mmol) **1a** with 4-chlorocinnamic acid (1.0 mmol) **2a** in the presence of copper(II)trifluoromethanesulfonate (20 mol %) catalyst and were taken in a 50 mL round bottom flask containing ascorbic acid/DMF (1:4, w/v) as a solvent under air condition. The reaction mixture was stirred at 115°C. A systematic optimization study, using $Cu(OTf)_2$ (20 mol %) and ascorbic acid/DMF (1:4, w/v) system works best for this reaction.



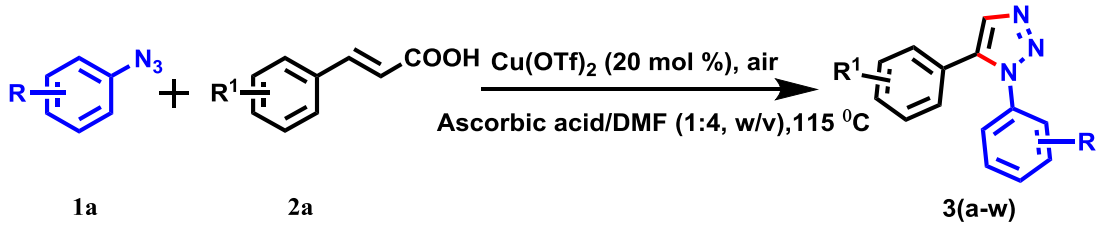
1a **2a** **3t**

Entry	Catalyst (mol %)	Solvent	time (h)	yield[b] (%)
1[c]	CuI (15)	Toluene	16	-
2	CuI (15)	MeOH	14	21
3	CuI (15)	DMF	15	25
4	CuI (15)	MeCN	15	20
5	CuI (15)	DMF/MeOH (1:4, w/v)	14	23
6	CuI (15)	DMF/MeCN (1:4, w/v)	15	18
7	CuCl (15)	DMF	16	15
8	CuBr (15)	DMF	15	20
9	CuI (20)	DMF	15	30
10	$Cu(OTf)_2$(15)	DMF	16	35
11	$Cu(OTf)_2$(15)	Ascorbic acid/DMF (1:4, w/v)	16	70
12	$Cu(OTf)_2$(20)	Ascorbic acid/DMF (1:4, w/v)	16	80
13	$Cu(OTf)_2$(15)	Isoascorbic acid/ DMF (1:4, w/v)	16	70
14	$Cu(OTf)_2$(20)	Isoascorbic acid/DMF (1:4, w/v)	16	75
15	CuI (20)	Ascorbic acid/DMF (1:4, w/v)	15	45
16[d]	$Cu(OTf)_2$(20)	Ascorbic acid/DMF (1:4, w/v)	16	12

[a]Reaction conditions: Organic azides (1.2 mmol), cinnamic acids (1.0 mmol) and $Cu(OTf)_2$ (20 mol%), air (1atm) in Ascorbic acid/DMF (1:4, w/v), 10-16 hrs. [b]Yields of isolated products.[c]No reaction takes place. [d]Under N_2 in 16 hrs.

Table1. Optimization by varying catalyst and solvent

(3) Representative experimental procedure for the synthesis of 1,5-disubstituted 1,2,3-triazole 3(a-w):



Organic azides (1.2 mmol) **1a**, cinnamic acids (1.0 mmol) **2a** and copper(II)trifluoromethanesulfonate (20 mol %) were taken in a 50 mL round bottom flask containing ascorbic acid/DMF (1:4, w/v) as a solvent under air condition, the reaction mixture was stirred at 115°C. The completion of reaction was monitored by TLC, the reaction mixture was allowed to cool at room temperature. Then reaction mixture was filtered through celite and washed 3-4 times by ethyl acetate and water. The extracted layer was dried over anhydrous sodium sulphate and concentrated *in vacuo*. The crude product was purified by 100-200 mesh silica gel by column chromatography with hexane:ethyl acetate (95:5) to afford 1,5-disubstituted 1,2,3-triazole derivatives.

(4) Characterization data of all the synthesized compounds:

1-(4-nitrophenyl)-5-phenyl-1*H*-1,2,3-triazole (3a):

Yellow solid; yield 69 %; **mp:** 164-165 °C; **^{1}H NMR (400 MHz; DMSO-d_6):** δ 8.31(app. dt, J_1=9.1 Hz and J_2=2.2 Hz, 2H), 7.90 (s, 1H), 7.60 (app. dt, J_1=9.1Hz and J_2=2.2 Hz, 2H), 7.49-7.41 (m, 3H), 7.28-7.25(m, 2H); **^{13}C NMR (100 MHz; DMSO-d_6)** δ 147.9, 141.4, 138.4, 134.3, 130.0, 129.5, 129.1, 126.8, 126.3, 125.4; **IR (KBr) max** 3400, 3019, 2400, 1529, 1384, 1215, 856, 758, 669; **ESI-MS (m/z)** = 267(M+H); Analysis cald. for **$C_{14}H_{10}N_4O_2$** C, 63.15; H, 3.89; N, 21.04; Found: C, 63.18; H, 3.91; N, 21.08; **ESI-HRMS** for cald. **$C_{14}H_{10}N_4O_2$; (M+H)**, 267.0879; found: m/z 267.0882.

1-(4-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole (3b):

Light brown solid; yield 75 %; **mp:** 88-89 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.13 (s, 1H), 7.61 (dt, J_1=8.1 Hz and J_2=2.1 Hz, 2H), 7.47-7.44 (m, 2H), 7.43-7.41(m, 3H),7.32-7.28 (m, 2H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 138.2, 135.5, 134.6, 133.7, 130.1, 129.8, 129.4, 129.0, 127.8, 126.5; **IR (KBr) max** 3400, 3019, 2400, 1529, 1384, 1215, 856, 758, 669, 528;

ESI-MS (m/z) = 256 (M+H); Analysis cald. for **$C_{14}H_{11}N_3Cl$:** C, 65.76; H, 3.94; N, 16.41; Found: C, 65.80; H, 3.98; N, 16.38; **ESI-HRMS** for cald. **$C_{14}H_{11}N_3Cl$**; **(M+H)**, 256.0636; found: m/z 256.0634.

1-(4-iodophenyl)-5-phenyl-1*H*-1,2,3-triazole (3c):

Brown solid; yield 71 %; **mp:** 114-116 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (s, 1H), 7.69 (dt, J_1= 8.6 Hz and J_2=2.0 Hz, 2H), 7.33-7.28 (m, 3H), 7.19-7.14 (m, 2H), 7.04 (dt, J_1=8.7 Hz and J_2=2.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.5, 137.6, 136.2, 133.6, 129.4, 129.0, 128.6, 126.6, 126.4, 94.6; **IR (KBr) max** 3389, 3019, 2499, 1629, 1402, 1215, 929, 757, 669; **ESI-MS (m/z**) = 348 (M+H); Analysis cald. for **$C_{14}H_{11}N_3I$:** C, 48.44; H, 2.90; N, 12.10; Found: C, 48.50; H, 2.86; N, 12.13; **ESI-HRMS** for cald. **$C_{14}H_{11}N_3I$; (M+H)**, 347.9992; found: m/z 347.9993.

1-(4-fluorophenyl)-5-phenyl-1*H*-1,2,3-triazole (3d):

Light yellow solid; yield 73 %; **mp:** 140-141 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (s, 1H), 7.41-7.36 (m, 5H), 7.25-7.23 (m, 2H), 7.17-7.13 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.9, 161.4, 137.8, 133.4, 132.7, 129.3, 128.9,128.6, 127.1, 127.0, 126.5, 116.5, 116.3; **IR (KBr) max** 3853, 3750, 3392, 3019, 2399,1622, 1402, 1215, 928, 757, 669; **ESI-MS (m/z**) = 240 (M+H); Analysis cald. for **$C_{14}H_{10}N_3F$**: C, 70.28; H, 4.21; N, 17.56; Found: C, 70.32; H, 4.24; N,17.59; **ESI-HRMS** for cald. **$C_{14}H_{10}N_3F$**; (**M+H),** 240.0932; found: m/z 240.0935.

1-(4-bromophenyl)-5-phenyl-1*H*-1,2,3-triazole (3e):

Yellow solid; yield 71 %; **mp**:151-152 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (s, 1H), 7.58 (dt, J_1=8.7 Hz and J_2=2.0 Hz, 2H), 7.42-7.37 (m, 3H), 7.28-7.23 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.7, 135.6, 132.6, 129.4, 129.0, 128.6, 126.5, 126.4, 123.2; **IR (KBr) max** 3392, 3019, 2399,1622, 1402, 1215, 928, 757, 669; **ESI-MS (m/z**) = 300 (M+H); Analysis cald. for **$C_{14}H_{10}N_3Br$:** C, 56.02; H, 3.36; N, 14.00; Found: C, 56.06; H, 3.39; N, 14.03; **ESI-HRMS** for cald. **$C_{14}H_{10}N_3Br$**; **(M+H)**, 300.0131; found: m/z 300.0134.

5-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (3f):

Light brown solid; yield 79 %; **mp:** 141-143 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (s, 1H), 7.37-7.25 (m, 9H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.3, 137.6, 134.1, 133.3, 129.9, 129.1, 128.8, 128.5, 126.9, 125.0, 21.2; **IR (KBr) max** 3400, 1637, 1403, 1217, 1069, 771, 669; **ESI-MS (m/z**) = 236 (M+H); Analysis cald. for **$C_{15}H_{13}N_3$**: C, 76.57; H, 5.57;

N,17.86; Found: C, 76.60; H, 5.61; N, 17.90; **ESI-HRMS** for cald. **$C_{15}H_{13}N_3$**; (**M+H),** 236.1211; found: m/z 236.1210.

1-(2-methyl-4-nitrophenyl)-5-phenyl-1*H*-1,2,3-triazole (3g):

Light yellow solid; yield 65 %; **mp:** 130-132 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (s, 1H), 8.18 (d, *J*=7.6 Hz, 1H), 7.9 (s, 1H), 7.47 (d, *J*=8.4 Hz, 1H), 7.37-7.17 (m, 5H), 2.12 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.3, 140.9, 138.9, 137.4, 132.6, 129.7, 129.2, 128.8, 127.7, 126.4, 125.9, 122.1, 18.0; **IR (KBr) max** 3400, 3019, 2399,1644, 1402, 1215, 928, 770, 669; **ESI-MS (m/z**) = 281 (M+H); Analysis cald. for **$C_{15}H_{12}N_4O_2$**: C, 64.28; H, 4.32; N, 19.99; Found: C, 64.32; H, 4.35; N, 19.95; **ESI-HRMS** for cald. **$C_{15}H_{12}N_4O_2$**; **(M+H)**, 281.1033; found: m/z 281.1036.

1-(3,4-dimethylphenyl)-5-phenyl-1*H*-1,2,3-triazole (3h):

Light yellow solid; yield 69 %; **mp:** 140-141 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (s, 1H), 7.29-7.25 (m, 3H), 7.17-7.15 (m, 3H), 7.06 (d, *J*=8.0 Hz, 1H), 6.90 (d, *J*=8.0 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.0, 137.9, 137.5, 134.3, 133.1, 130.2, 129.0, 128.7, 128.5, 126.9, 126.1, 122.4, 19.7, 19.4; **IR (KBr) max** 3394, 3019, 2400,1637, 1385, 1067, 669; **ESI-MS (m/z**) = 250 (M+H); Analysis cald. for **$C_{16}H_{15}N_3$**: C, 77.81; H, 6.06; N, 16.85; Found: C, 77.85; H,6.10; N, 16.90; **ESI-HRMS** for cald. **$C_{16}H_{15}N_3$**; (**M+H),** 250.1336; found: m/z 250.131

1-(3-bromophenyl)-5-phenyl-1*H*-1,2,3-triazole (3i):

Yellow solid; yield 79 %; **mp:** 132-133 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (s, 1H), 7.65 (t, *J*=2.0 Hz, 1H), 7.59 (d, *J*=2.0 Hz, 1H), 7.44-7.37 (m, 3H), 7.30 (d, *J*=8.1 Hz, 1H), 7.27-7.24 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.8, 137.6, 133.5, 132.3, 130.5, 129.5, 129.0, 128.6, 128.2, 126.3, 123.6, 122.8; **IR (KBr) max** 3385, 3019, 2399,1644, 1402, 1215, 770, 669; **ESI-MS (m/z**) = 300 (M+H); Analysis cald. for **$C_{14}H_{10}N_3Br$**: C, 56.02; H, 3.36; N, 14.00; Found: C, 56.07; H, 3.40; N, 14.03; **ESI-HRMS** for cald.**$C_{14}H_{10}N_3Br$**;**(M+H),** 300.0131; found: m/z 300.0136.

1,5-diphenyl-1*H*-1,2,3-triazole (3j):

Off-white solid; yield 75 %; **mp:** 113-114 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (s, 1H), 7.46-7.43 (m, 3H), 7.40-7.33 (m, 5H), 7.25-7.23 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.7, 136.6, 133.4, 129.3, 129.2, 128.8, 128.6, 126.7, 125.2; **IR (KBr) max** 3400, 3019,

2399,1637, 1403, 1155, 1068, 929, 769, 669; **ESI-MS (m/z**) = 222 (M+H); Analysis cald. for **$C_{14}H_{11}N_3$**: C, 76.00; H, 5.01; N, 18.99; Found: C, 76.03; H, 5.05; N, 18.95; **ESI-HRMS** for cald. **$C_{14}H_{11}N_3$**; (**M+H),** 222.1026; found: m/z 222.1027.

5-(4-methoxyphenyl)-1-(4-nitrophenyl)-1*H*-1,2,3-triazole (3k):

Yellow solid**;** yield 60 %**; mp:** 114-115 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J*=8.9 Hz, 2H), 7.84 (s, 1H), 7.61 (d, *J*=8.9 Hz, 2H), 7.17 (d, *J*=8.6 Hz, 2H), 6.94 (d, *J*=8.6 Hz, 2H), 3.8 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.8, 147.4, 141.4, 137.9, 133.7, 130.1, 125.3, 124.8, 118.0, 114.7, 55.4; **IR (KBr) max** 3392, 3019, 2399,1650, 1403, 1215, 1155, 928, 770, 669; **ESI-MS (m/z**) = 297 (M+H); Analysis cald. for **$C_{15}H_{12}N_4O_3$**: C, 60.81; H, 4.08; N 18.91; Found: C, 60.85; H, 4.12; N, 18.95; **ESI-HRMS** for cald. **$C_{15}H_{12}N_4O_3$**; (**M+H),** 297.0986; found: m/z 297.0992.

5-(4-methoxyphenyl)-1-(*p*-tolyl)-1*H*-1,2,3-triazole (3l):

White solid; yield 62 %; **mp:** 135-136 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (s, 1H), 7.27-7.23 (m, 4H), 7.18-7.16 (m, 2H), 6.89-6.87 (m, 2H), 3.83 (s, 3H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.2, 139.2, 137.5, 134.2, 132.8, 129.9, 125.0, 119.0, 114.2, 55.3, 21.2; **IR (KBr) max** 3390, 3019, 1639, 1402, 1215, 1067, 770, 669; **ESI-MS (m/z**) = 266 (M+H); Analysis cald. for **$C_{16}H_{15}ON_3$**: C, 72.43; H, 5.70; N, 15.84; Found: C, 72.46; H, 5.73; N, 15.87; **ESI-HRMS** for cald. **$C_{16}H_{15}ON_3$**; (**M+H),** 266.1283; found: m/z 266.1278.

5-(4-chlorophenyl)-1-(4-iodophenyl)-1*H*-1,2,3-triazole (3m):

Light yellow solid; yield 70 %; **mp:**140-142 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (s, 1H), 7.71 (d, *J*=8.5 Hz, 2H), 7.29 (d, *J*=8.5 Hz, 2H), 7.09 (d, *J*=8.5 Hz, 2H), 7.03 (d, *J*=8.5 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.7, 136.6, 136.0, 135.8, 133.6, 129.8, 129.4, 128.8, 126.6, 124.9, 94.9; **IR (KBr) max** 3676, 3019, 2399,1650, 1403, 1215, 1065, 928, 770, 669; **ESI-MS (m/z**) = 381 (M+H); Analysis cald. for **$C_{14}H_9N_3ClI$**: C, 44.07; H, 2.38; N, 11.01; Found: C, 44.4; H, 2.40; N, 11.05; **ESI-HRMS** for cald. **$C_{14}H_9N_3ClI$**; (**M+H),** 381.9602; found: m/z 381.9601.

5-(4-chlorophenyl)-1-(2-methyl-4-nitrophenyl)-1H-1,2,3-triazole (3n):

Yellow solid; yield 69 %; **mp:**121-123 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 (s, 1H), 8.20 (d, *J*=8.4 Hz, 1H), 7.98 (s, 1H), 7.47 (d, *J*=8.4 Hz, 1H), 7.34 (d, *J*=7.4 Hz, 2H), 7.11 (d, *J*=7.6 Hz, 2H) 2.13 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.5, 140.6, 137.9, 137.3, 136.0,

132.7, 129.6, 128.9, 128.7, 126.5, 124.3, 122.2, 18.0; **IR (KBr) max** 3847, 3740, 3395,1639, 1402, 1067, 770; **ESI-MS (m/z**) = 315 (M+H); Analysis cald. for **$C_{15}H_{11}ClN_4O_2$**: C, 57.24; H, 3.52; N, 17.80; Found: C, 57.27, H, 3.55, N, 17.84; **ESI-HRMS** for cald. **$C_{15}H_{11}ClN_4O_2$**; (**M+H),** 315.0645; found: m/z 315.0650.

5-(4-chlorophenyl)-1-(3,4-dimethylphenyl)-1*H*-1,2,3-triazole (3o):

White solid; yield 75 %; **mp:** 117-118 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (s, 1H), 7.24 (d, *J*=8.0 Hz, 2H), 7.13 (s, 1H), 7.10-7.09 (m, 3H), 6.89 (d, *J*=7.9 Hz, 1H), 2.23 (s, 3H), 2.20 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.3, 138.2, 136.5, 135.2, 134.0, 133.2, 130.3, 129.1, 126.2, 125.4, 122.4, 19.7, 19.5; **IR (KBr) max** 3390, 3019, 2399,1637, 1507, 1385, 1067, 928, 669; **ESI-MS (m/z**) = 284 (M+H); Analysis cald. for **$C_{16}H_{14}N_3Cl$**: C, 67.73; H, 4.97; N, 14.81; Found: C, 67.76; H, 4.93; N, 14.84; **ESI-HRMS** for cald. **$C_{16}H_{14}N_3Cl$**; (**M+H),** 284.1010; found: m/z 284.1014.

5-(4-chlorophenyl)-1-(4-nitrophenyl)-1*H*-1,2,3-triazole (3p):

Yellow solid; yield 70 %; **mp:**115-117 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.34 (d, *J*=8.8 Hz, 2H), 7.90 (s, 1H), 7.60 (d, *J*=8.7 Hz, 2H), 7.42 (d, *J*=8.1 Hz, 2H), 7.20 (d, *J*=8.2 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.7, 141.0, 136.9, 136.3, 134.2, 129.9, 129.6, 125.3, 125.0, 124.5; **IR (KBr) max** 3019, 1639, 1530, 1402, 1215, 1067, 770, 669; **ESI-MS (m/z**) = 301 (M+H); Analysis cald. for **$C_{14}H_9ClN_4O_2$**: C, 55.92; H, 3.02; N, 18.63; Found: C, 55.96; H, 3.05; N, 18.66; **ESI-HRMS** for cald. **$C_{14}H_9ClN_4O_2$**; (**M+H),** 301.0487; found: m/z 301.0484.

5-(4-chlorophenyl)-1-(*p*-tolyl)-1*H*-1,2,3-triazole (3q):

Light yellow solid; yield 75 %; **mp:**139-141 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (s, 1H), 7.33 (d, *J*=8.4 Hz, 2H), 7.28-7.22 (m, 4H), 7.17 (d, *J*=8.4 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.6, 136.6, 135.3, 133.9, 133.3, 130.0, 129.8, 129.1, 125.3,125.0, 21.2; **IR (KBr) max** 3400, 3019, 2399, 1639, 1530, 1402, 1215, 1067, 770, 669, 626; **ESI-MS (m/z**) = 270 (M+H); Analysis cald. for **$C_{15}H_{12}ClN_3$**: C,66.79; H,4.48; N,15.58; Found: C, 66.82; H, 4.51; N, 15.63; **ESI-HRMS** for cald. **$C_{15}H_{12}ClN_3$**; (**M+H),** 270.0809; found: m/z 270.0813.

5-(4-chlorophenyl)-1-phenyl-1*H*-1,2,3-triazole (3r):

White solid; yield 76 %; **mp:** 105-107 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (s, 1H), 7.48-7.46 (m, 3H), 7.38-7.33 (m, 4H), 7.19-7.17 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 136.6, 136.3, 135.5, 133.4, 129.8, 129.5, 129.2, 125.2; **IR (KBr) max** 3401, 3019, 1639, 1530, 1402, 1215, 1067, 770, 669; **ESI-MS (m/z**) = 256 (M+H); Analysis cald. for **$C_{14}H_{10}ClN_3$**: C, 65.76; H, 3.94; N, 16.43; Found: C, 65.80; H, 3.91; N, 16.48; **ESI-HRMS** for cald. **$C_{14}H_{10}ClN_3$**; (**M+H),** 256.0644; found: m/z 256.0649.

5-(4-chlorophenyl)-1-(3-fluorophenyl)-1*H*-1,2,3-triazole (3s):

Off-white solid; yield 79 %; **mp**: 142-143 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (s, 1H), 7.46-7.36 (m, 3H), 7.20-7.12 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.8, 161.4, 136.7, 135.8, 133.6, 130.8, 130.8, 129.8, 129.3, 124.8, 120.8, 120.8, 116.6, 116.4, 112.9, 112.7; **IR (KBr) max** 3400, 3018, 1609, 1403, 1216, 1070, 669; **ESI-MS (m/z**) = 274 (M+H); Analysis cald. for **$C_{14}H_9N_3ClF$**: C, 61.44; H, 3.31; N, 15.35; Found: C, 61.49; H, 3.35; N, 15.38; **ESI-HRMS** for cald. **$C_{14}H_9N_3ClF$**; (**M+H),** 274.0539; found: m/z 274.0533.

1-(3-bromophenyl)-5-(4-chlorophenyl)-1*H*-1,2,3-triazole (3t):

White solid; yield 80 %; **mp:** 133-134 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (s, 1H), 7.65 (d, *J*=8.5 Hz, 2H), 7.38-7.32 (m, 3H), 7.20 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.3, 136.7, 135.8, 133.6, 132.5, 130.6, 129.8, 129.4, 128.2, 124.7, 123.6, 123.0; **IR (KBr) max** 3660, 3399, 3018, 1644, 1482, 1403, 1070, 826, 668; **ESI-MS (m/z**) = 333 (M+H); Analysis cald. for **$C_{14}H_9N_3ClBr$**: C, 50.26; H, 2.71; N, 12.56; Found: C, 50.31; H, 2.76; N, 12.60; **ESI-HRMS** for cald. **$C_{14}H_9N_3ClBr$**; (**M+H),** 333.9741; found: m/z 333.9739.

1-(3,4-dimethylphenyl)-5-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole(3u):

White solid; yield 65 %; **mp:** 147-149 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.99-697 (m, 1H), 2.34 (s, 3H), 2.30 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.5, 138.4, 136.2, 133.9, 133.6, 131.2, 130.8, 130.5, 130.4, 128.7, 126.2, 125.8, 125.8, 125.7, 125.7, 125.0, 122.5, 19.7, 19.5; **IR (KBr) max** 3853, 3750, 3392, 3019, 2399, 1325, 1215, 928, 757, 669; **ESI-MS (m/z**) = 318 (M+H); Analysis cald. for **$C_{17}H_{14}N_3F_3$**: C, 64.35; H, 4.45; N, 13.24; Found: C, 64.32; H, 4.40; N,13.27; **ESI-HRMS** for cald. **$C_{17}H_{14}N_3F_3$**; (**M+H),** 318.1213; found: m/z 318.1211.

1-(3,4-dimethylphenyl)-5-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole(3v):

Yellow oil; yield 61 %; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.55 (s, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.21-7.18 (m, 2H), 6.99 (d, *J* = 7.4 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.5, 138.3, 136.2, 133.8, 133.4, 131.6, 131.5, 131.2, 130.4, 129.3, 127.8, 126.1, 125.7, 125.2, 122.4, 19.7, 19.5; **IR (KBr) max** 3853, 3750, 3392, 2399,1622, 1402, 1215, 928, 757, 669; **ESI-MS (m/z**) = 318 (M+H); Analysis cald. for **$C_{17}H_{14}N_3F_3$**: C, 64.35; H, 4.45; N, 13.24; Found: C, 64.32; H, 4.49; N,13.28; **ESI-HRMS** for cald. **$C_{17}H_{14}N_3F_3$**; (**M+H),** 318.1213; found: m/z 318.1231.

1-(*p*-tolyl)-5-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (3w):

Light yellow oil; yield 60 %; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.54 (s, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.28-7.22 (m, 4H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.9, 136.2, 133.6, 133.5, 131.7, 131.6, 131.2, 130.1, 129.4, 127.8, 125.8, 125.3, 125.2, 125.0, 124.8, 21.1; **IR (KBr) max** 3853, 3750, 3019, 2399,1622, 1402, 1215, 928, 669; **ESI-MS (m/z**) = 304 (M+H); Analysis cald. for **$C_{16}H_{12}N_3F_3$**: C, 63.36; H, 3.99; N, 13.86; Found: C, 63.40; H, 4.02; N,13.89; **ESI-HRMS** for cald. **$C_{16}H_{12}N_3F_3$**; (**M+H),** 304.1061; found: m/z 304.1065.

(5) NMR-Spectra of Compounds

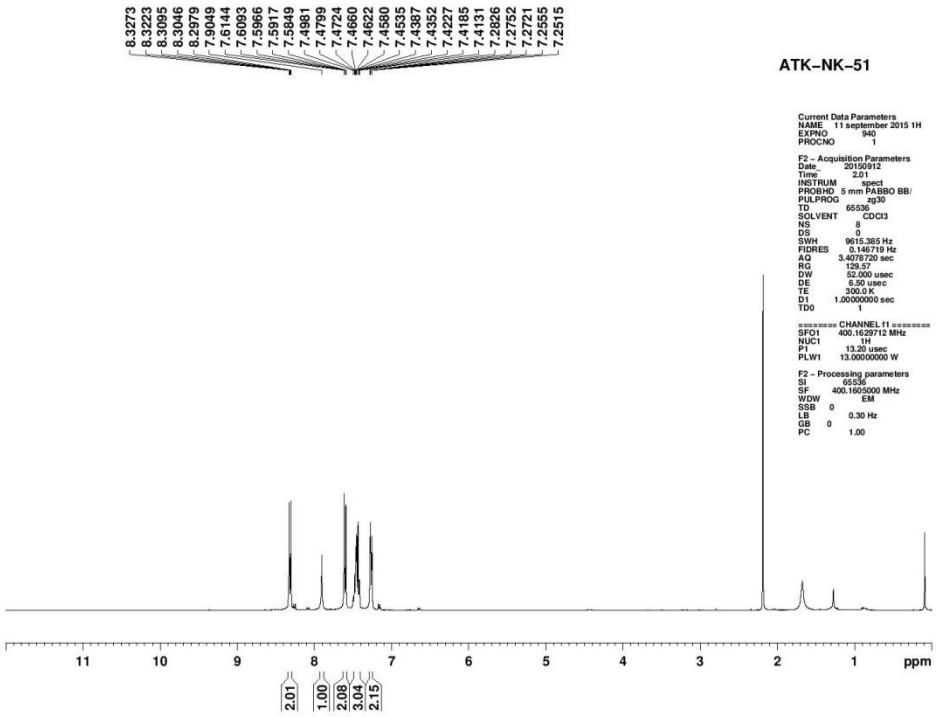


Figure1: ^{1}H NMR of compound (3a)

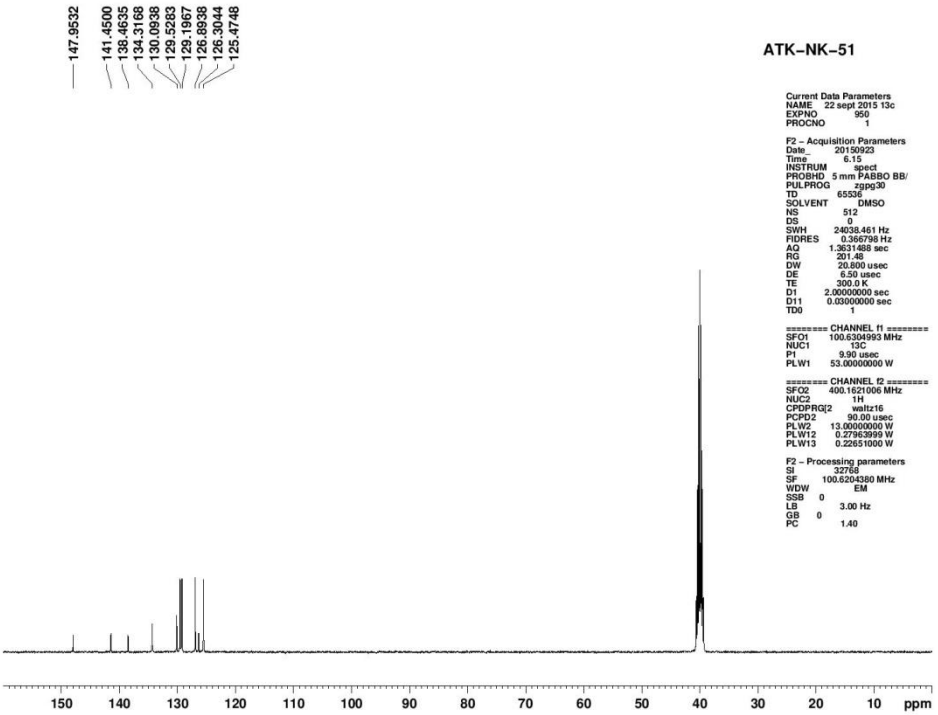


Figure2: ^{13}C NMR of compound (3a)

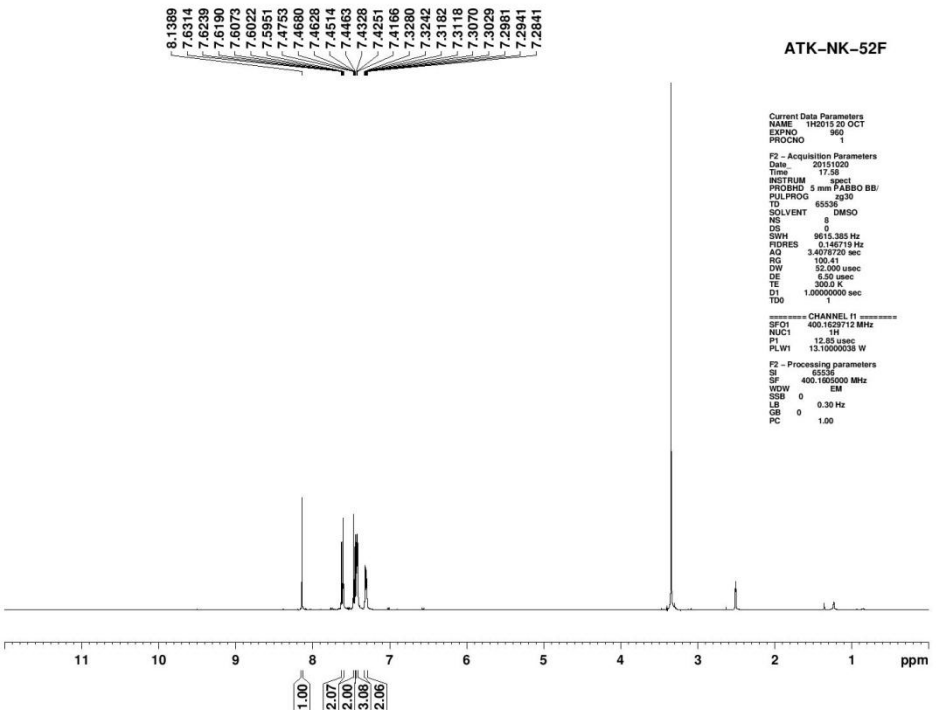


Figure 3: ^{1}H NMR of compound (3b)

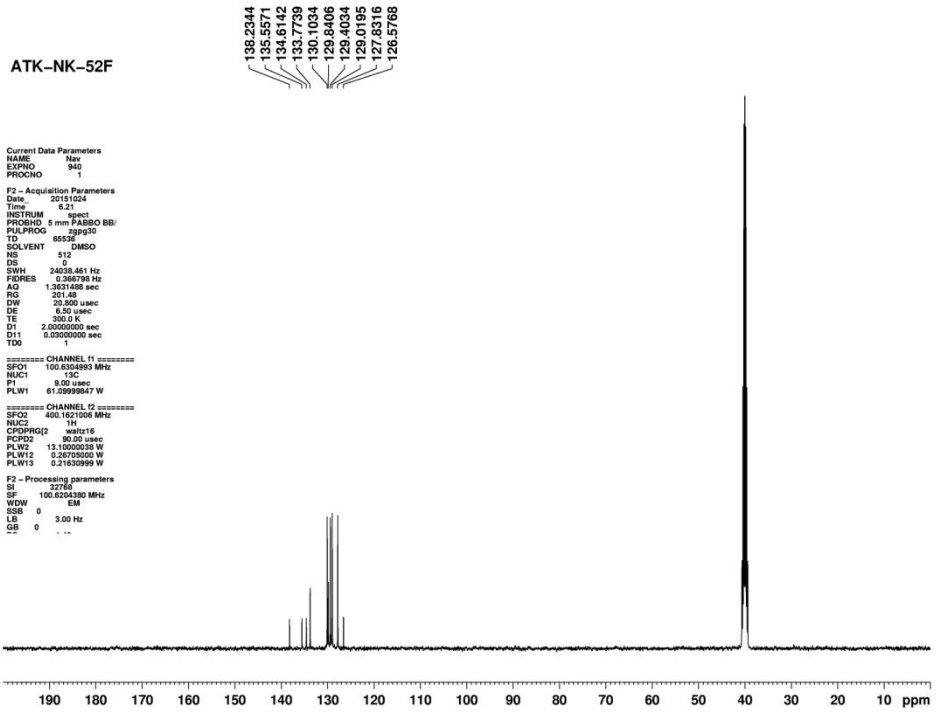


Figure 4: ^{13}C NMR of compound (3b)

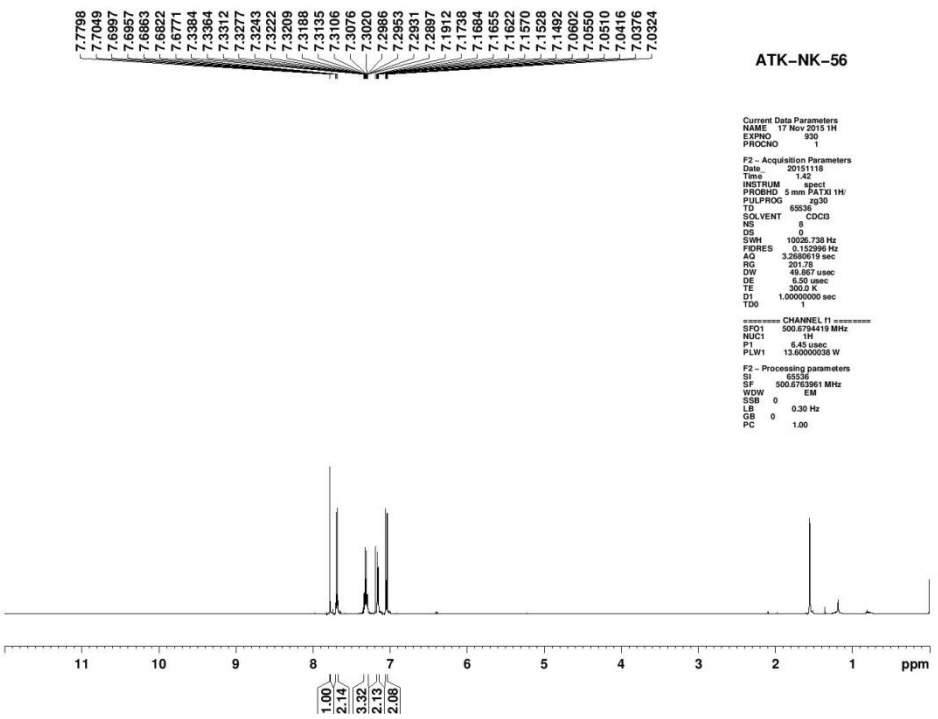


Figure 5: ^{1}H NMR of compound (3c)

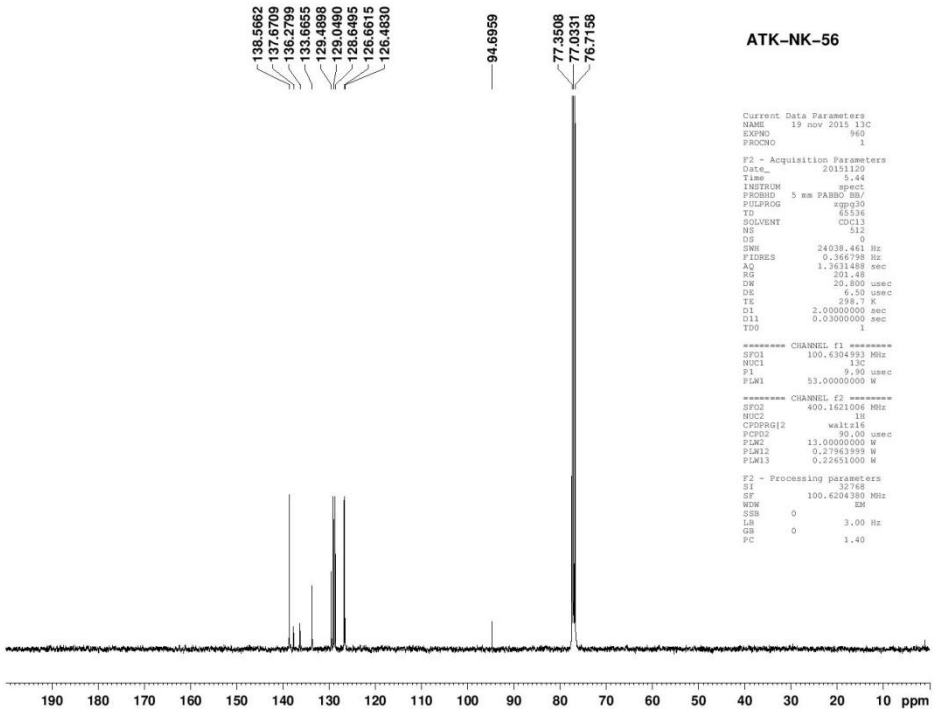


Figure 6: ^{13}C NMR of compound (3c)

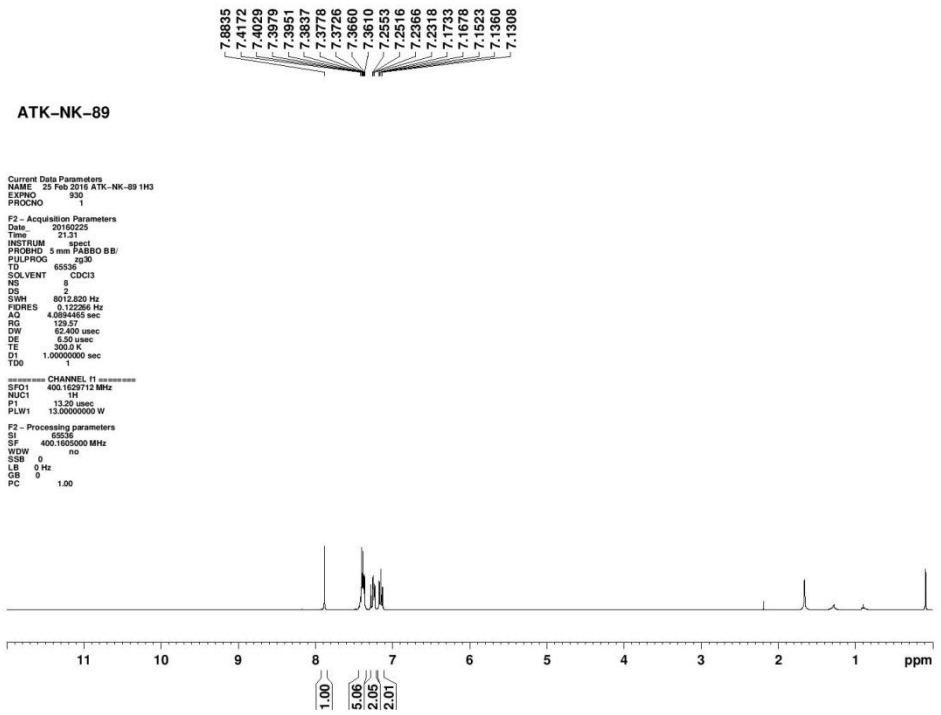


Figure 7: ^{1}H NMR of compound (3d)

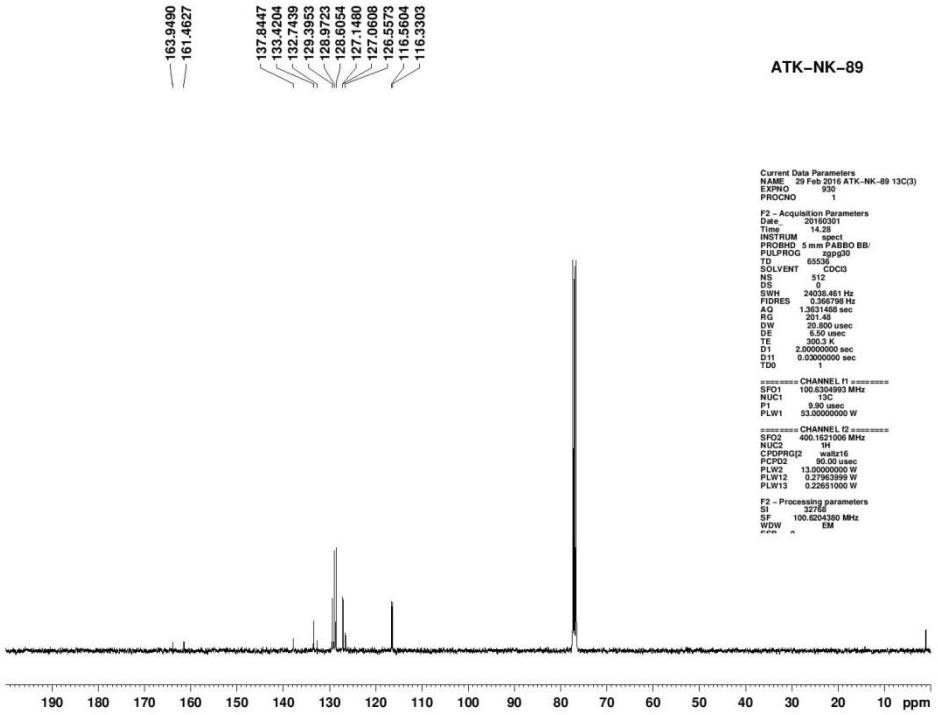


Figure 8: ^{13}C NMR of compound (3d)

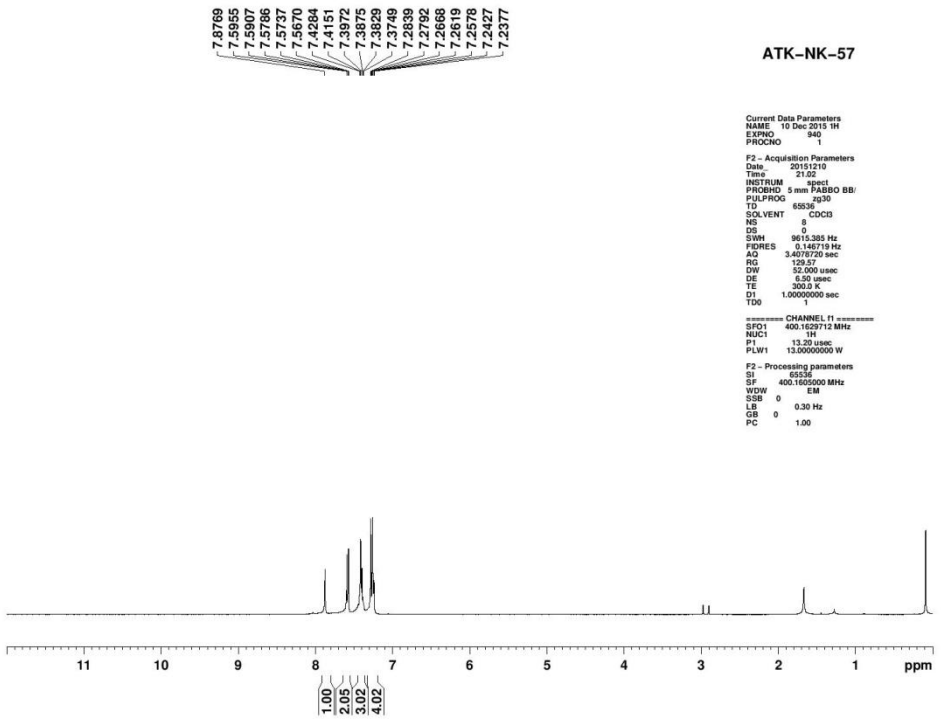


Figure 9: ^{1}H NMR of compound (3e)

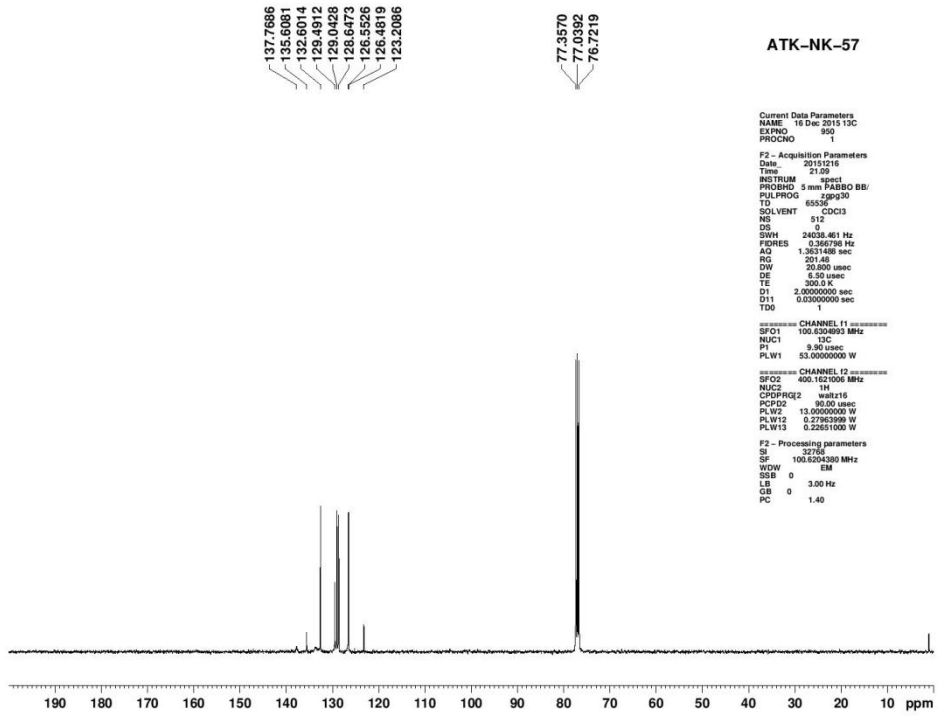


Figure 10:^{13}C NMR of compound (3e)

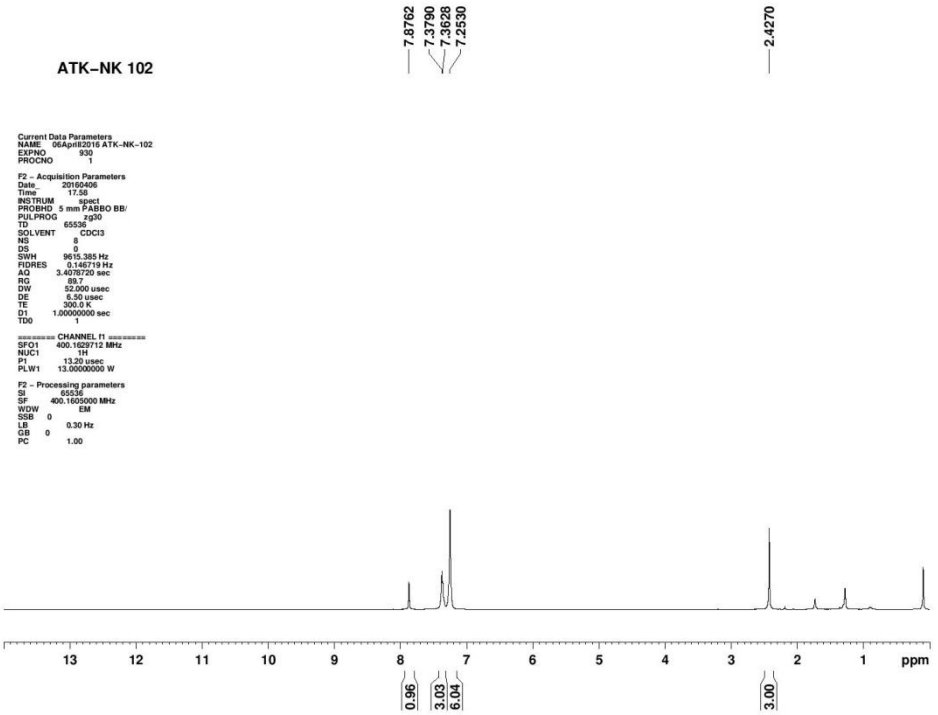


Figure 11: ^{1}H NMR of compound (3f)

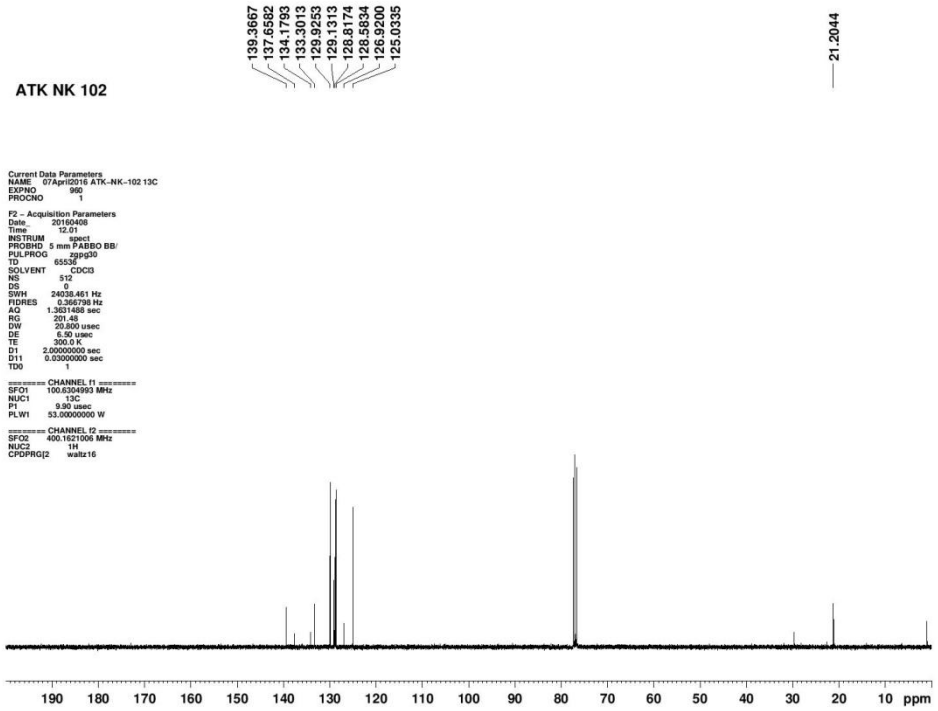


Figure 12: ^{13}C NMR of compound (3f)

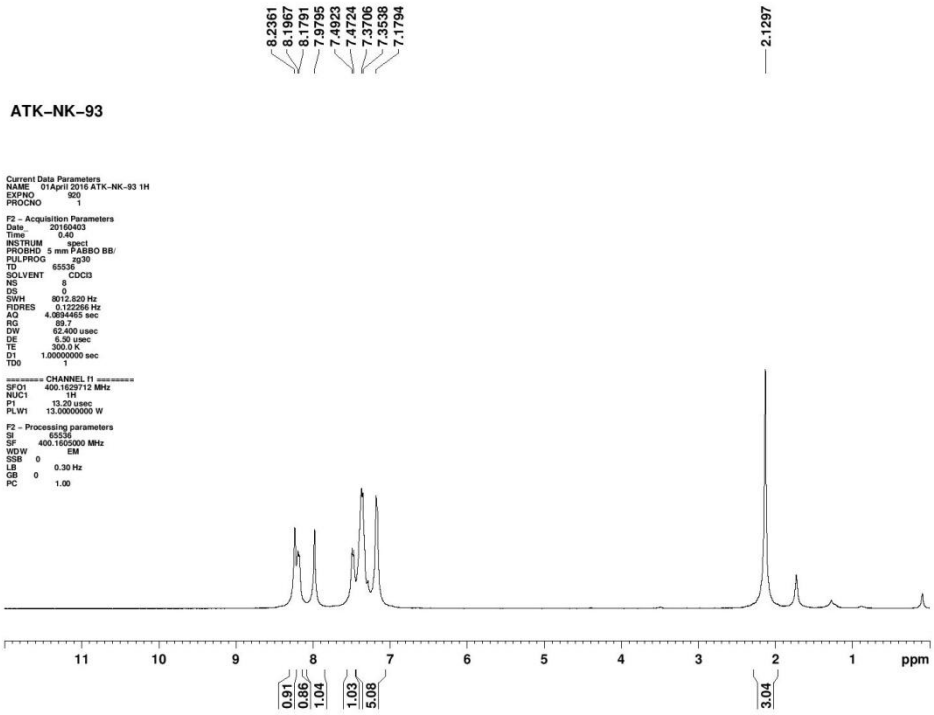


Figure 13: ^{1}H NMR of compound (3g)

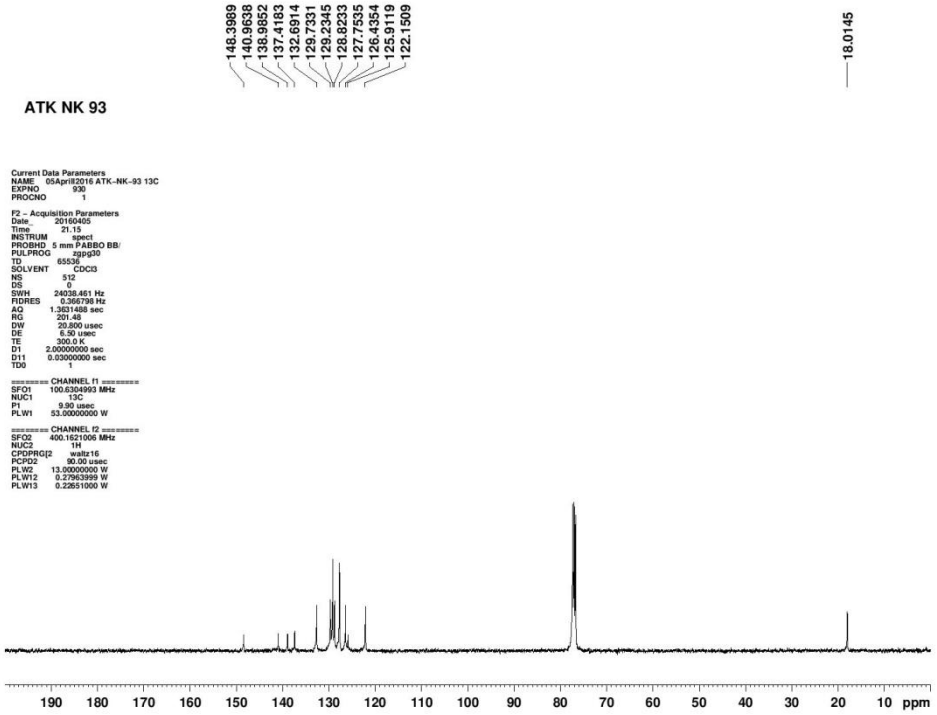


Figure 14: ^{13}C NMR of compound (3g)

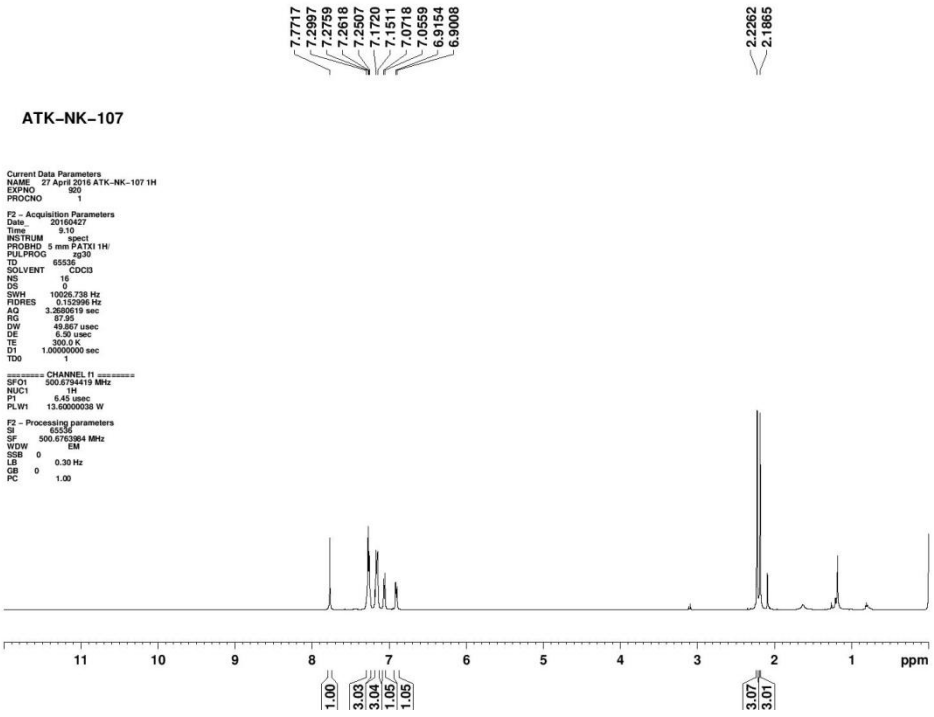


Figure 15: ^{1}H NMR of compound (3h)

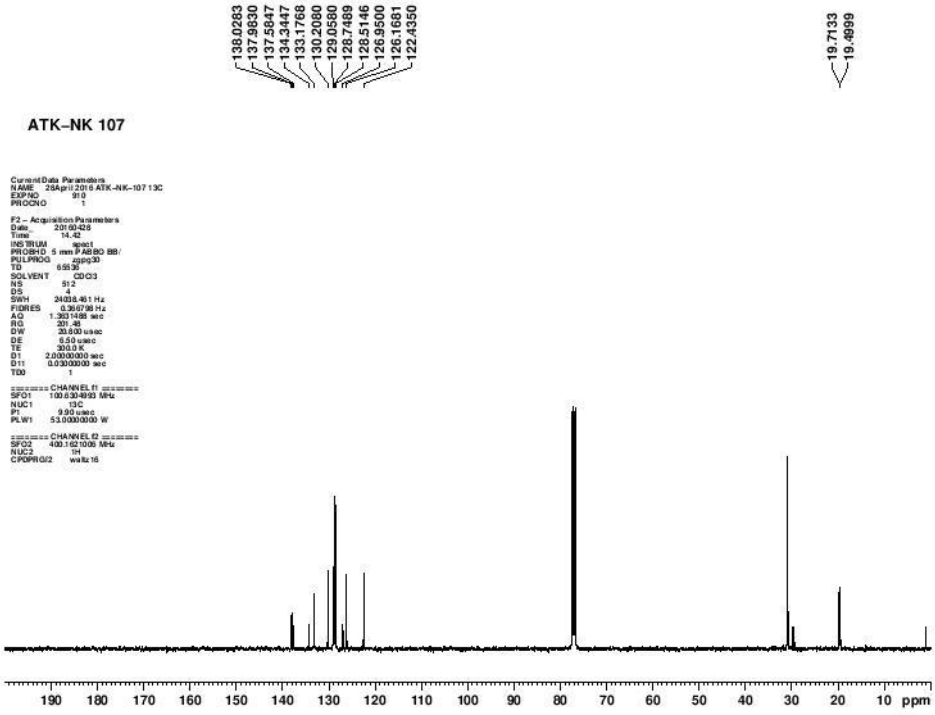


Figure 16: ^{13}C NMR of compound (3h)

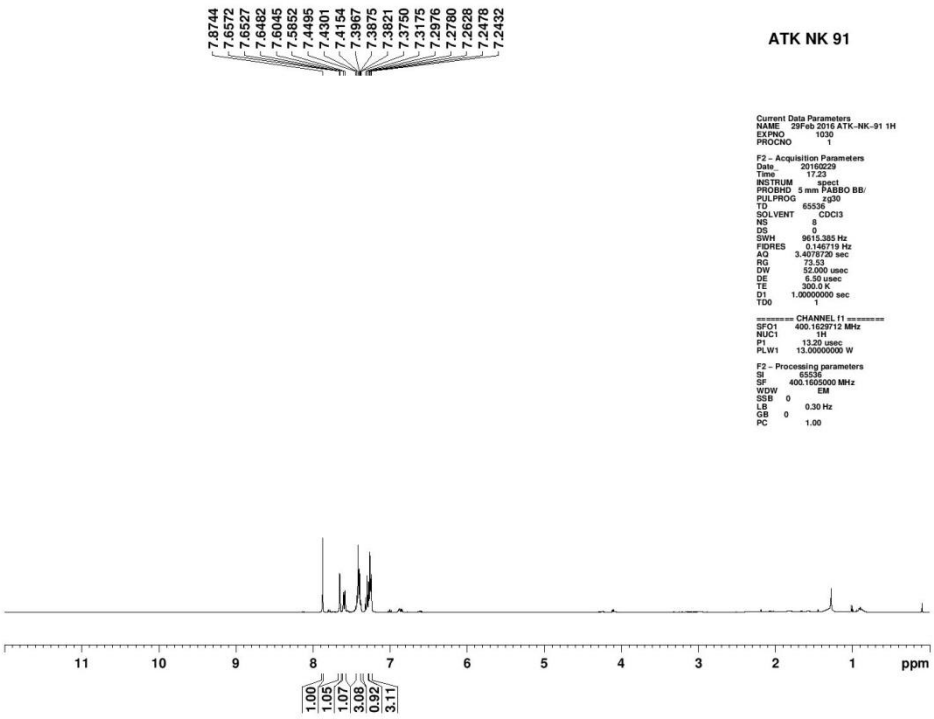


Figure 17: ^{1}H NMR of compound (3i)

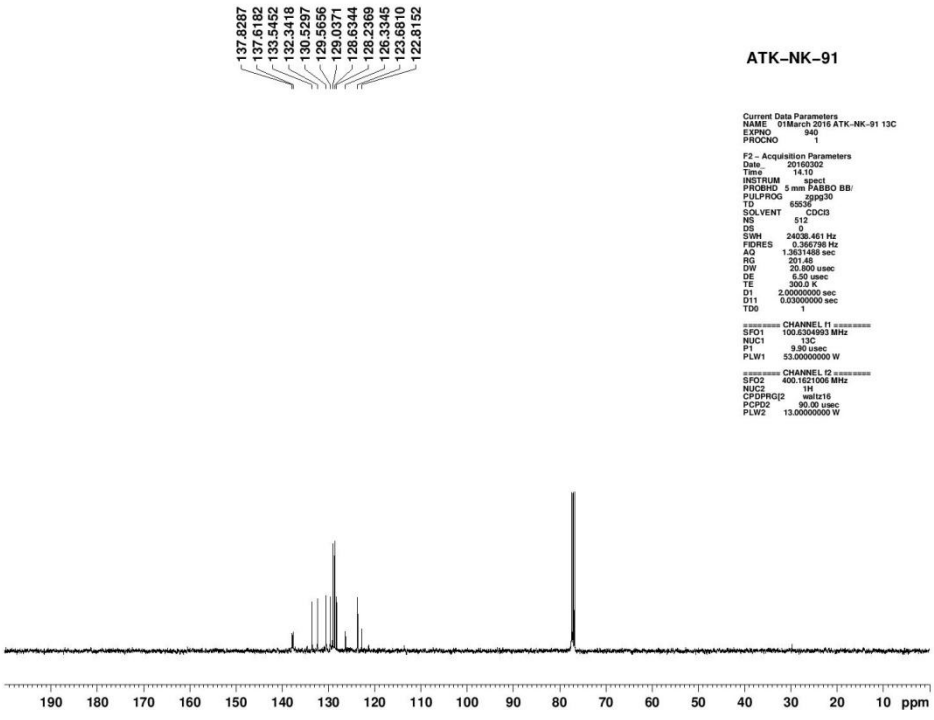


Figure 18: ^{13}C NMR of compound (3i)

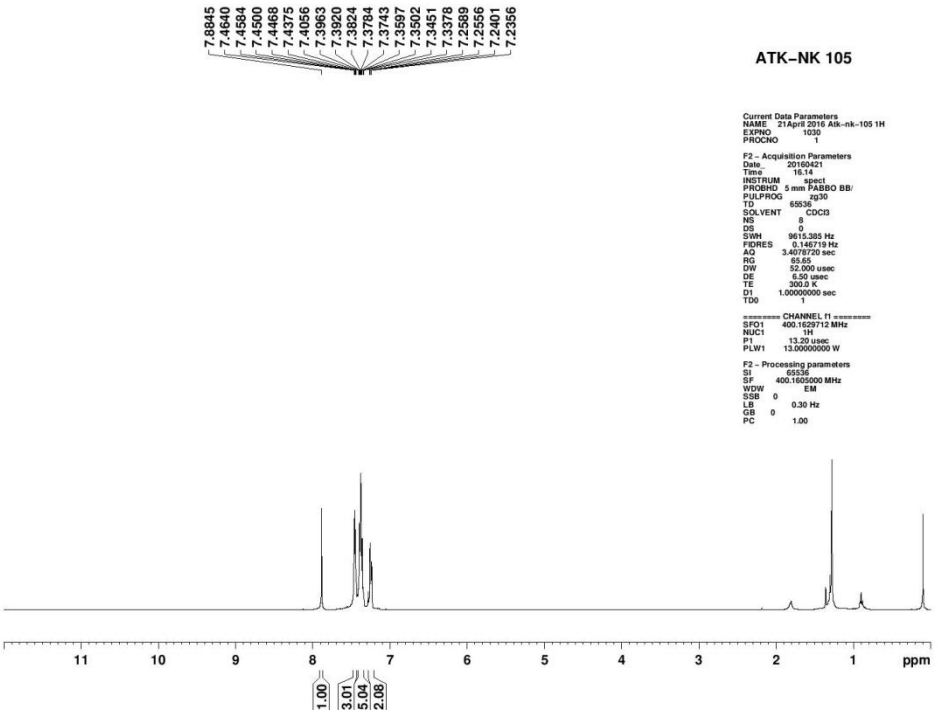


Figure 19: ^{1}H NMR of compound (3j)

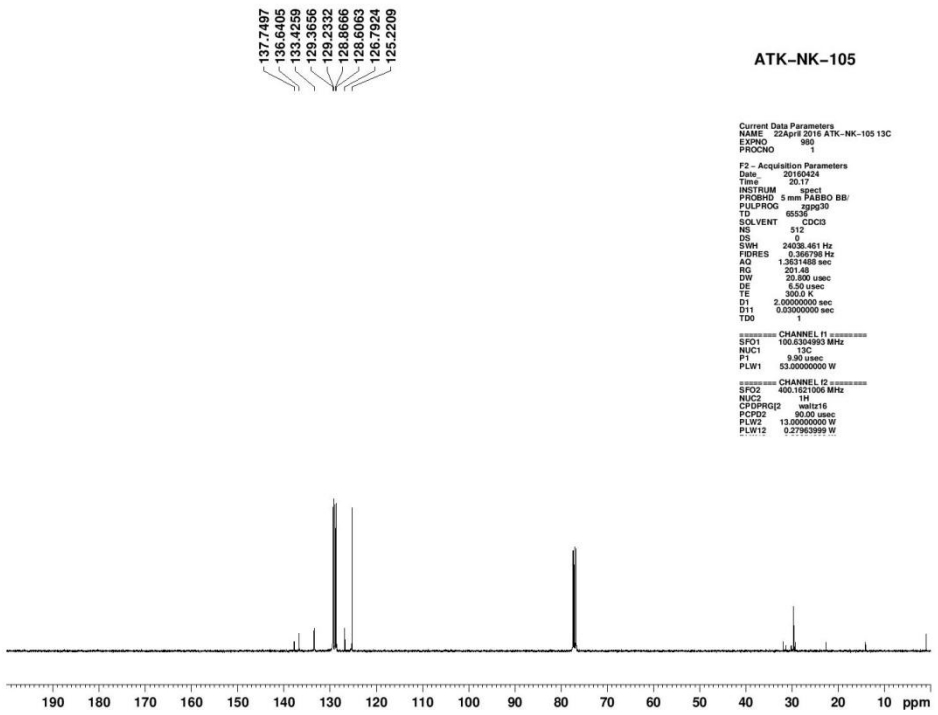


Figure 20: ^{13}C NMR of compound (3j)

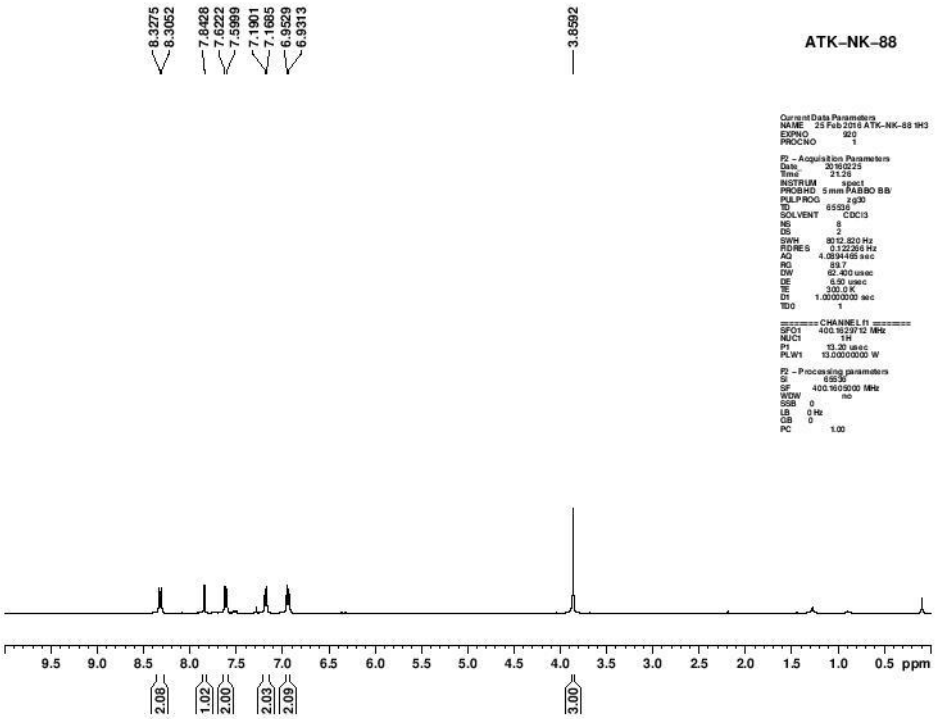


Figure 21: ^{1}H NMR of compound (3k)

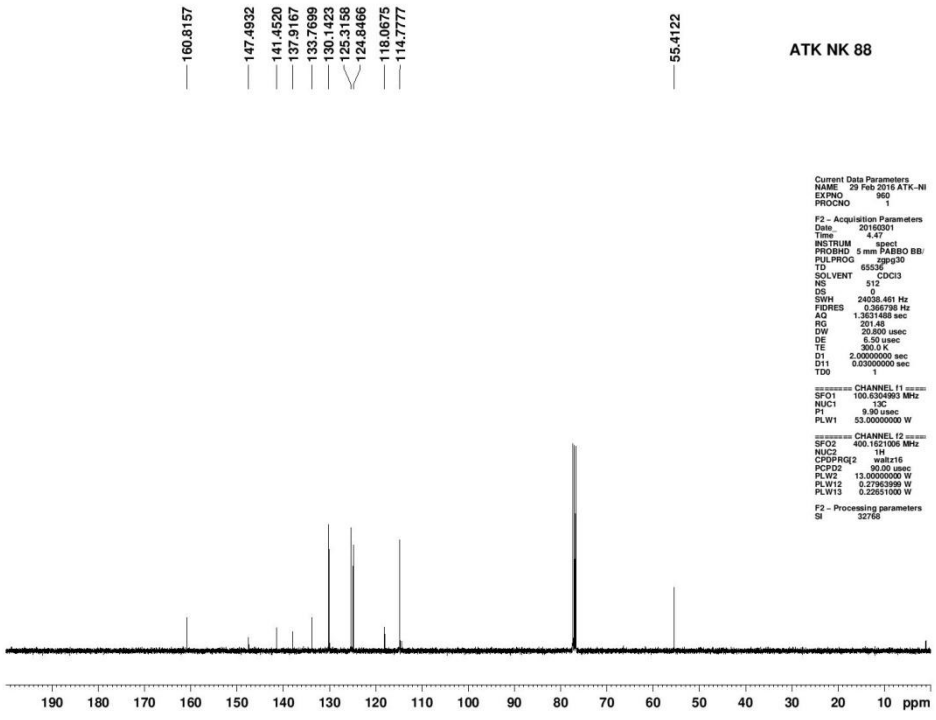


Figure 22: ^{13}C NMR of compound (3k)

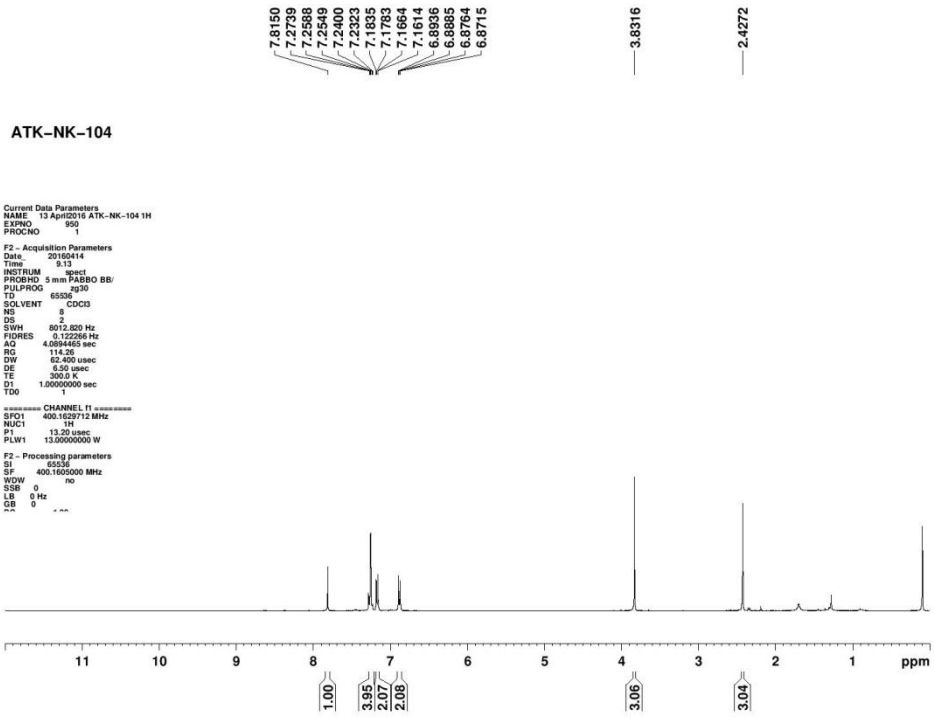


Figure 23: ^{1}H NMR of compound (3l)

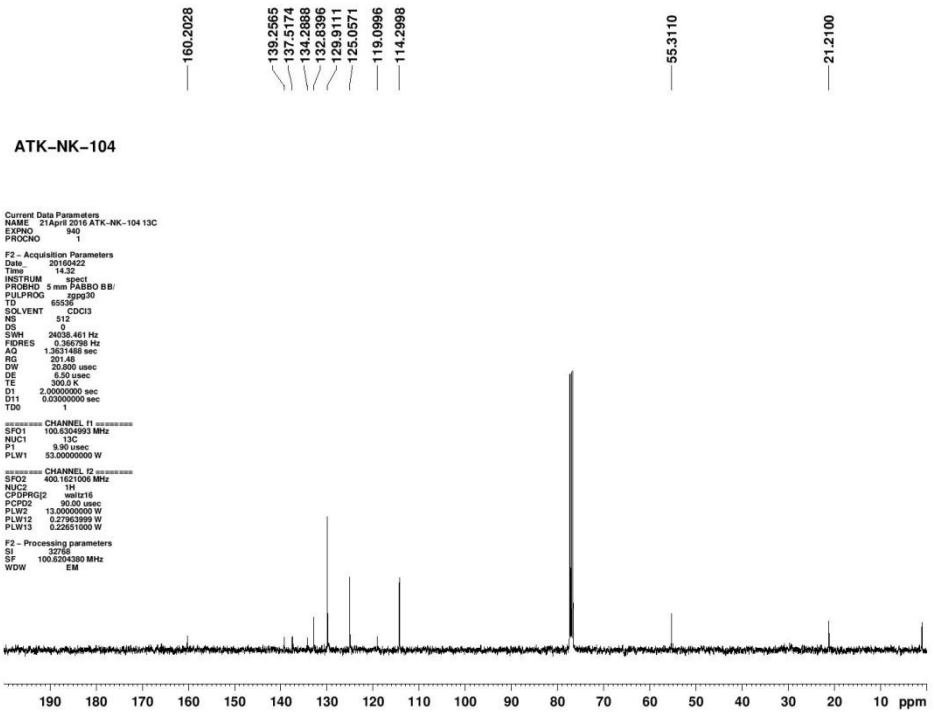


Figure 24: ^{13}C NMR of compound (3l)

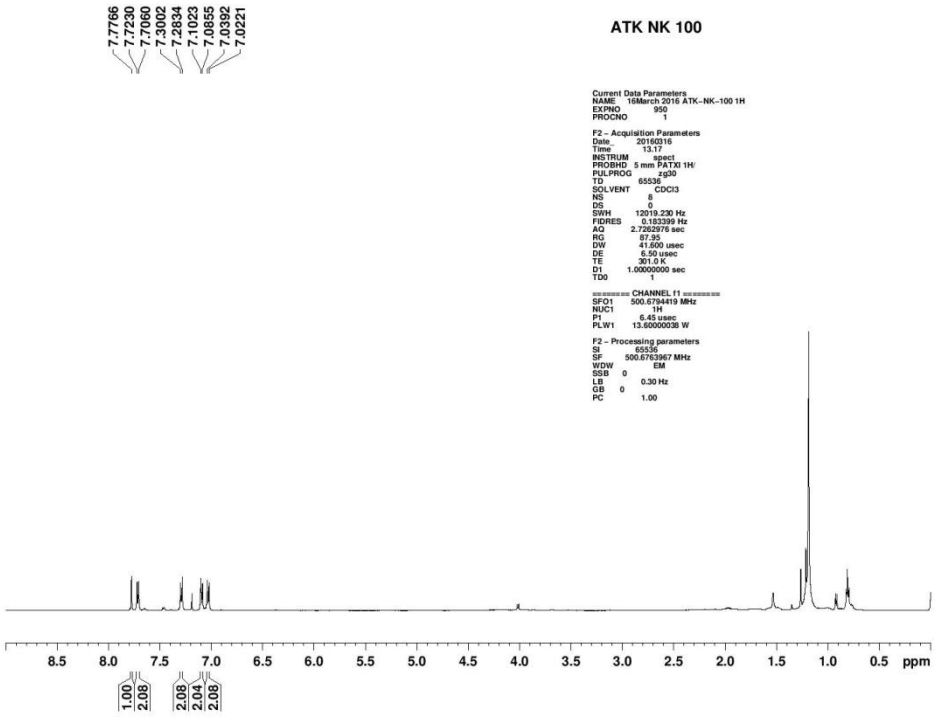


Figure 25: ^{1}H NMR of compound (3m)

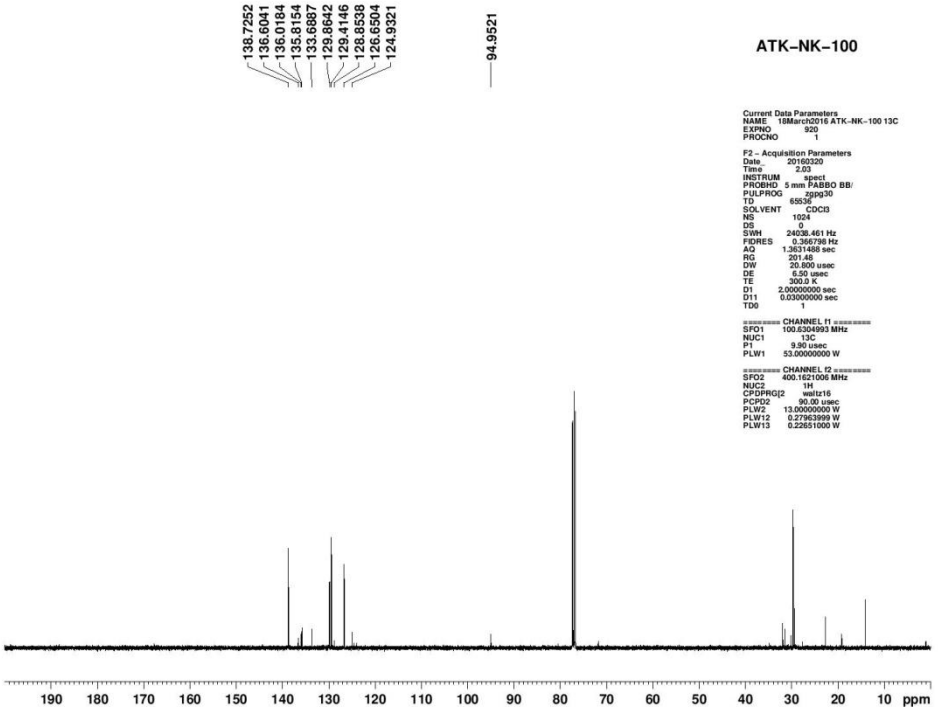


Figure 26: ^{13}C NMR of compound (3m)

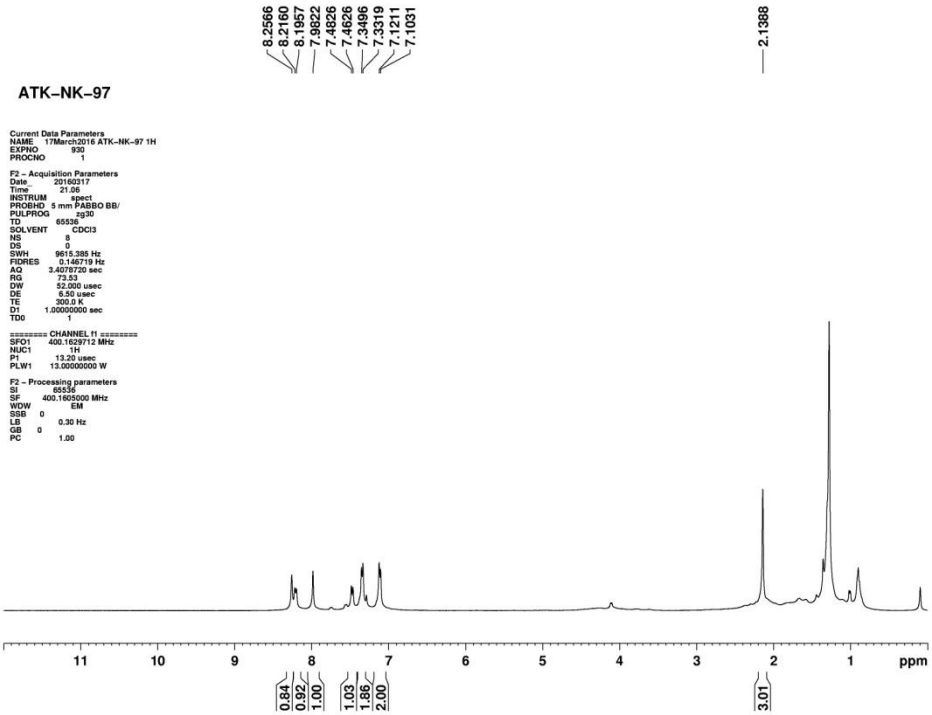


Figure 27: ^{1}H NMR of compound (3n)

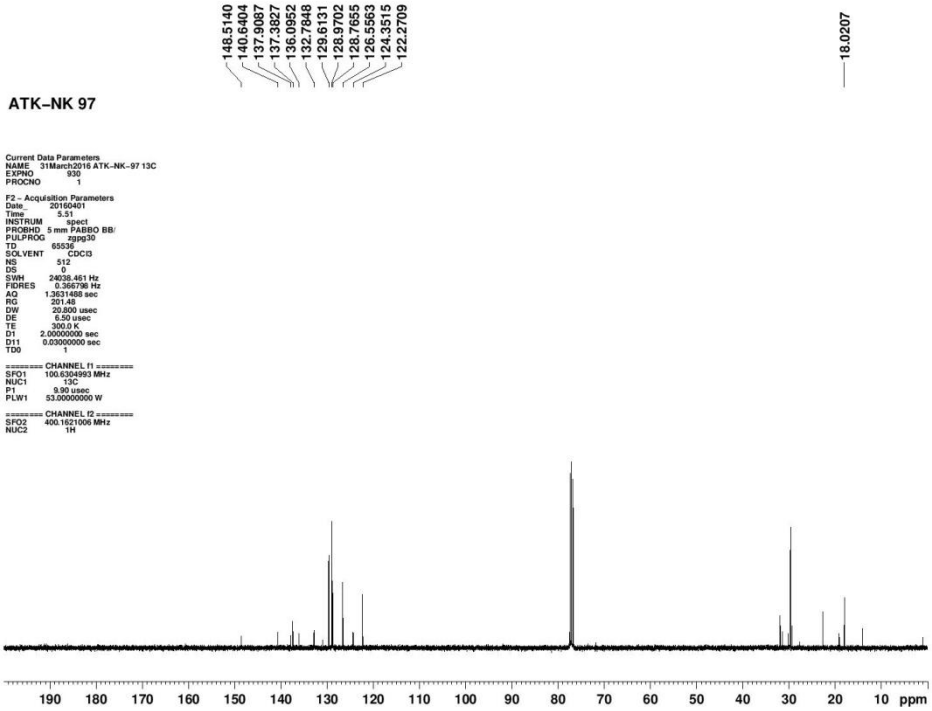


Figure 28: ^{13}C NMR of compound (3n)

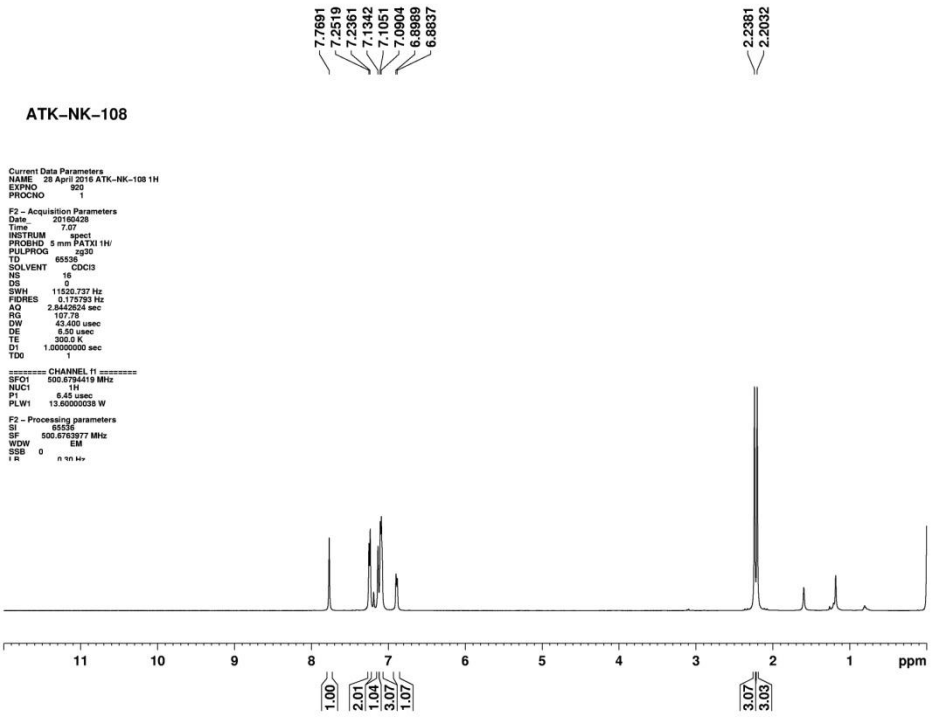


Figure 29: ^{1}H NMR of compound (3o)

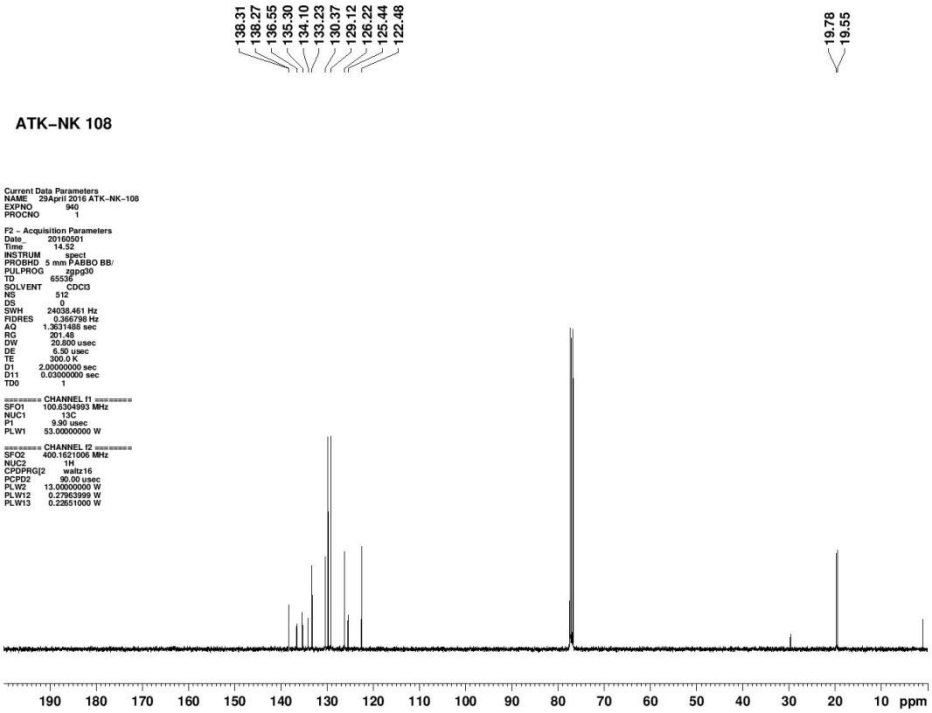


Figure 30: ^{13}C NMR of compound (3o)

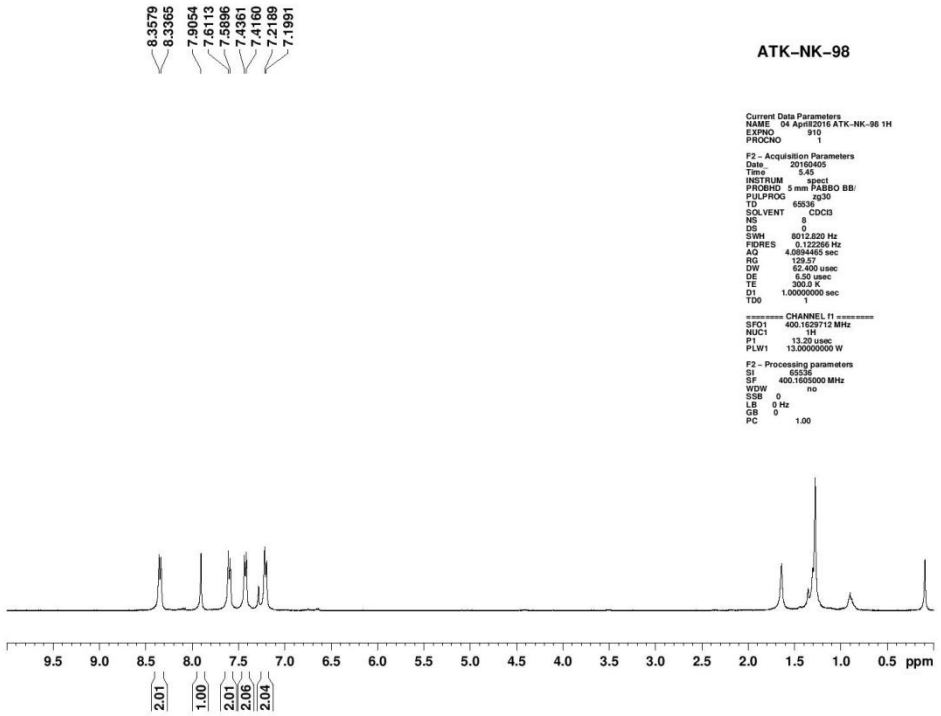


Figure 31: ^{1}H NMR of compound (3p)

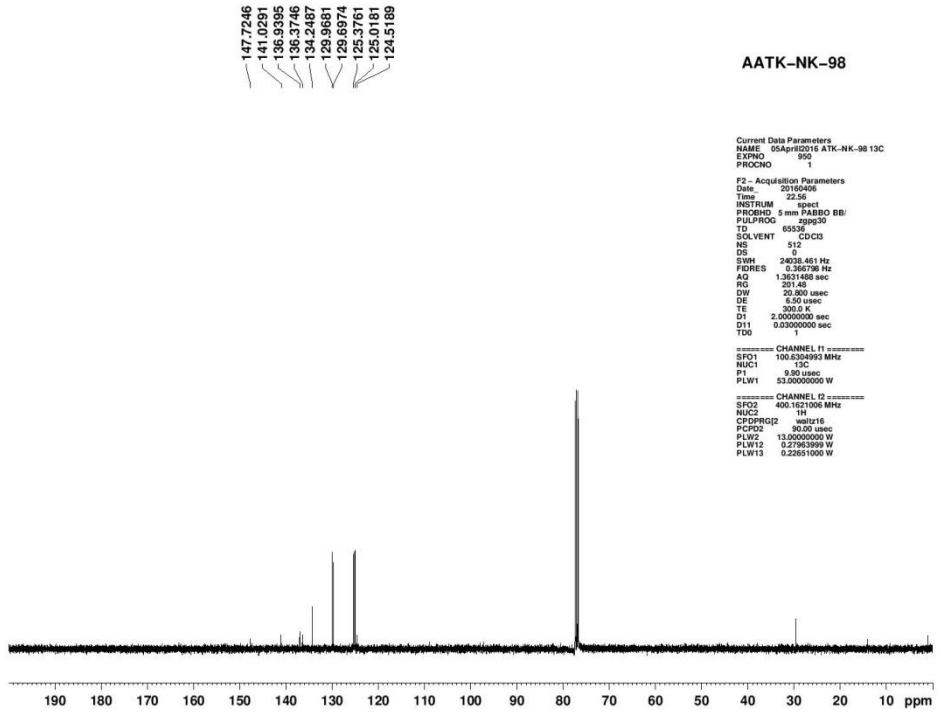


Figure 32: ^{13}C NMR of compound (3p)

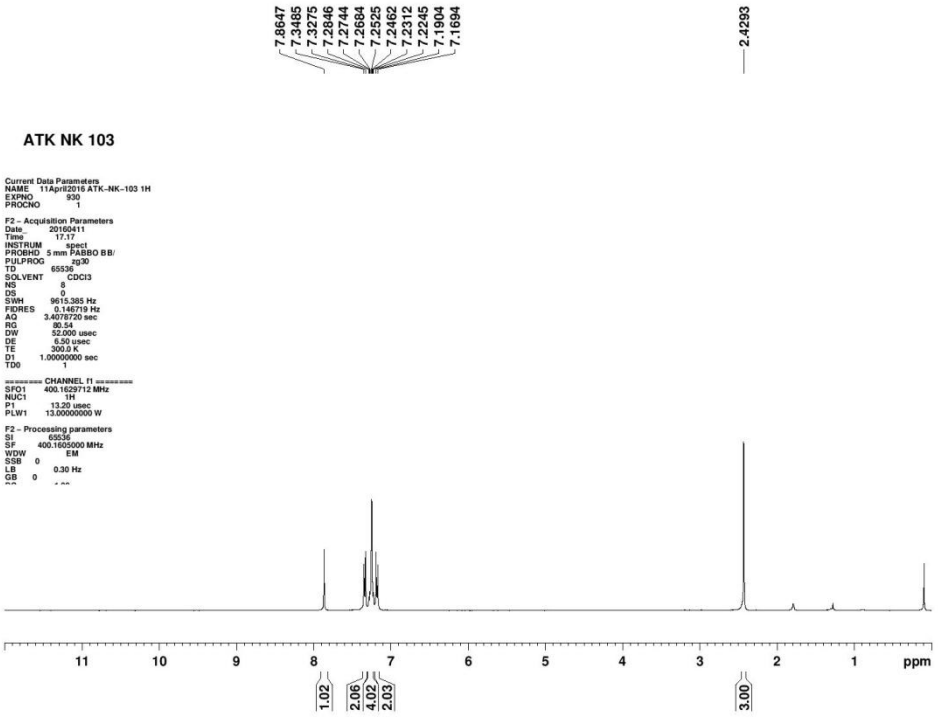


Figure 33: ^{1}H NMR of compound (3q)

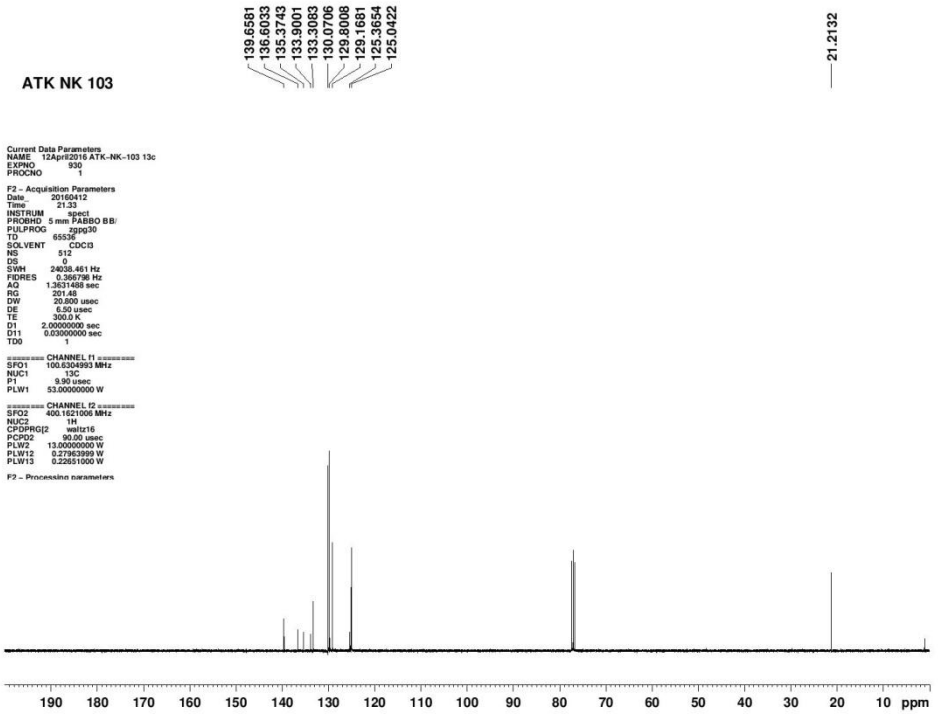


Figure 34: ^{13}C NMR of compound (3q)

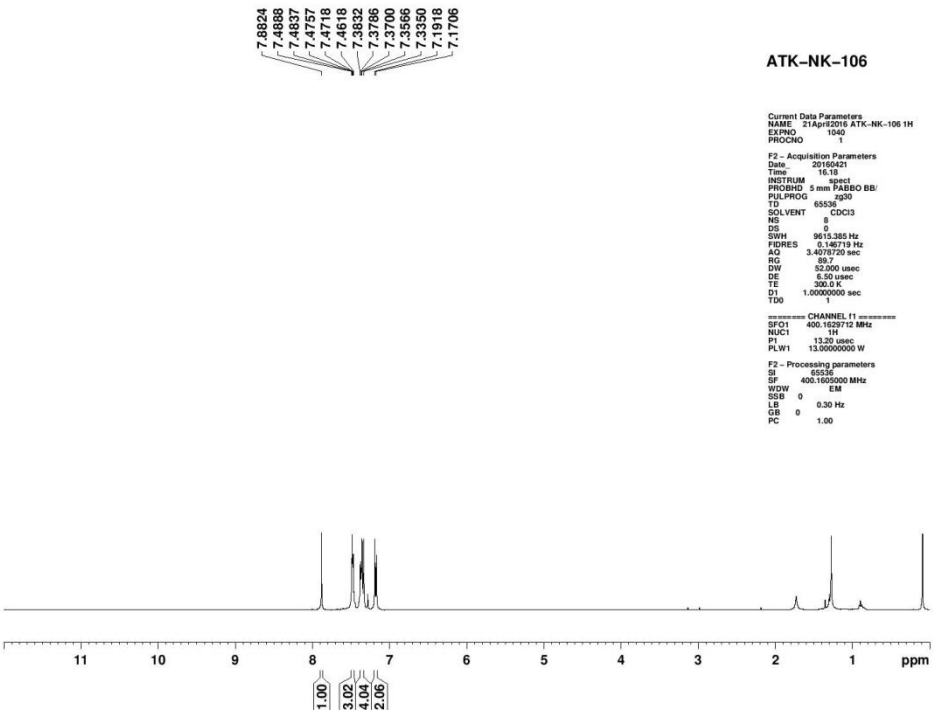


Figure 35: ^{1}H NMR of compound (3r)

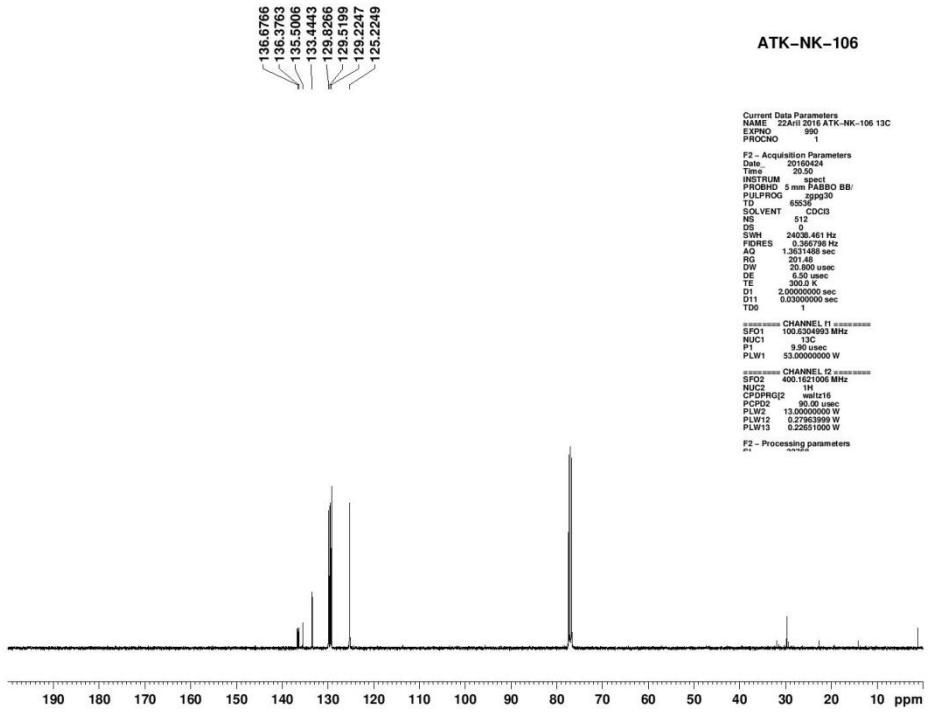


Figure 36: ^{13}C NMR of compound (3r)

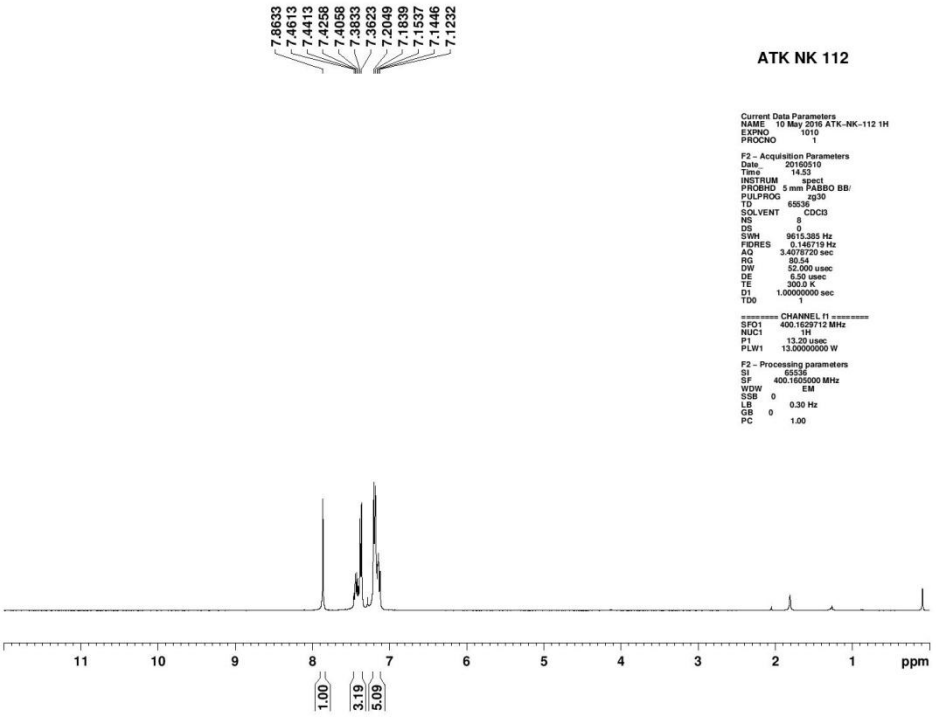


Figure 37: ^{1}H NMR of compound (3s)

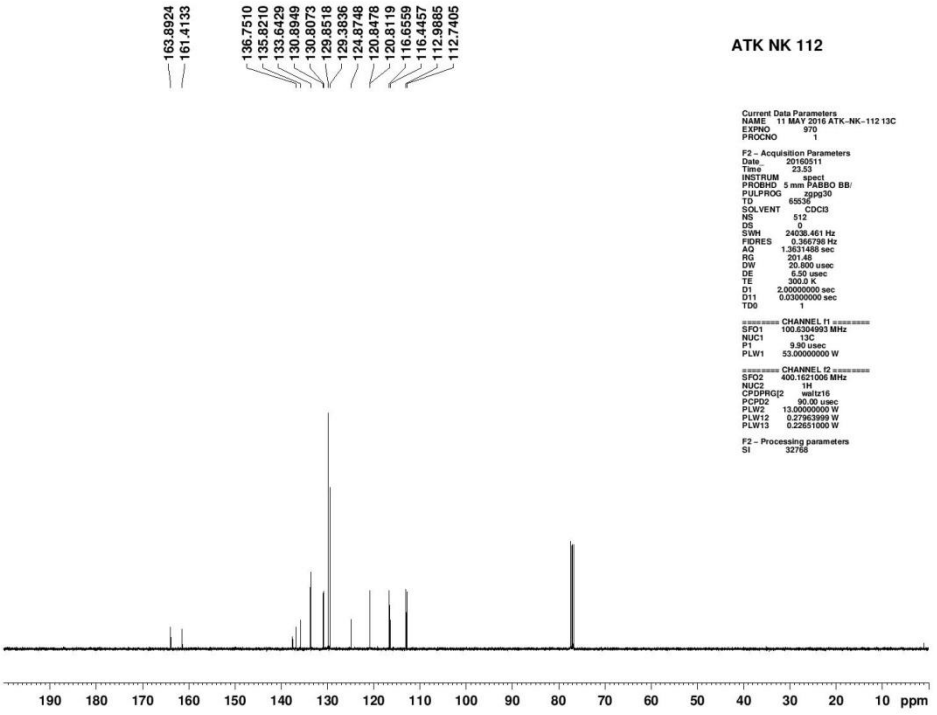


Figure 38: ^{13}C NMR of compound (3s)

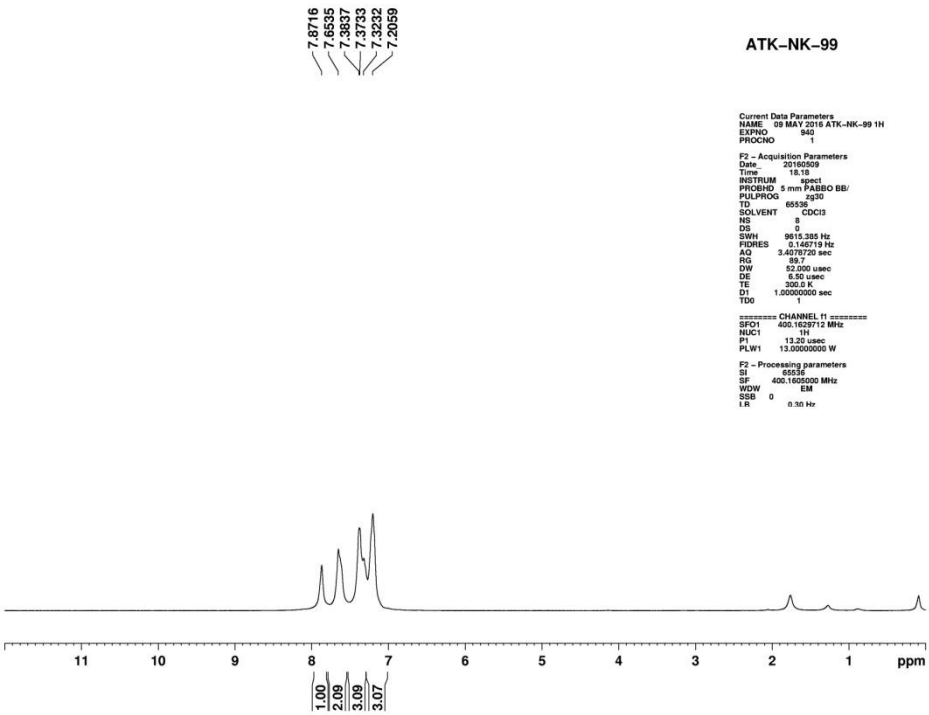


Figure 39: ^{1}H NMR of compound (3t)

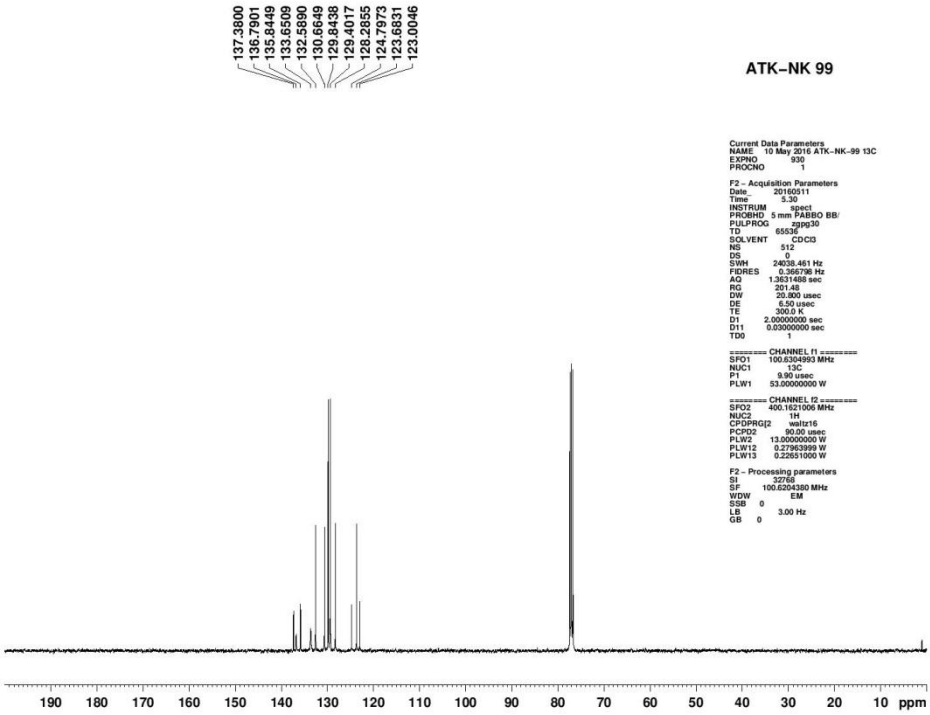


Figure 40: ^{13}C NMR of compound (3t)

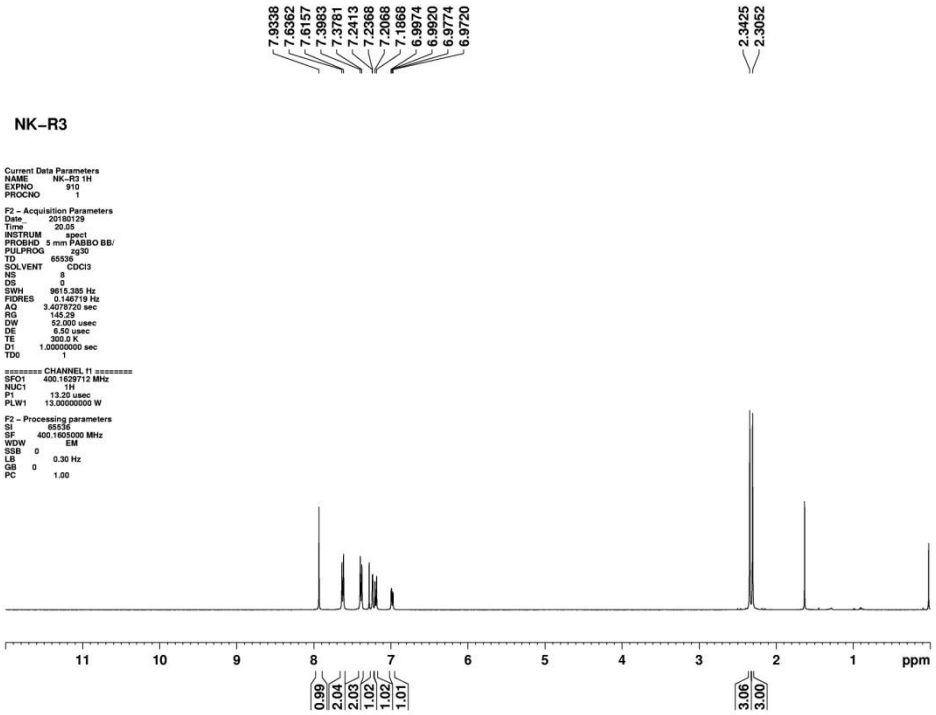


Figure 41: ^{1}H NMR of compound (3u)

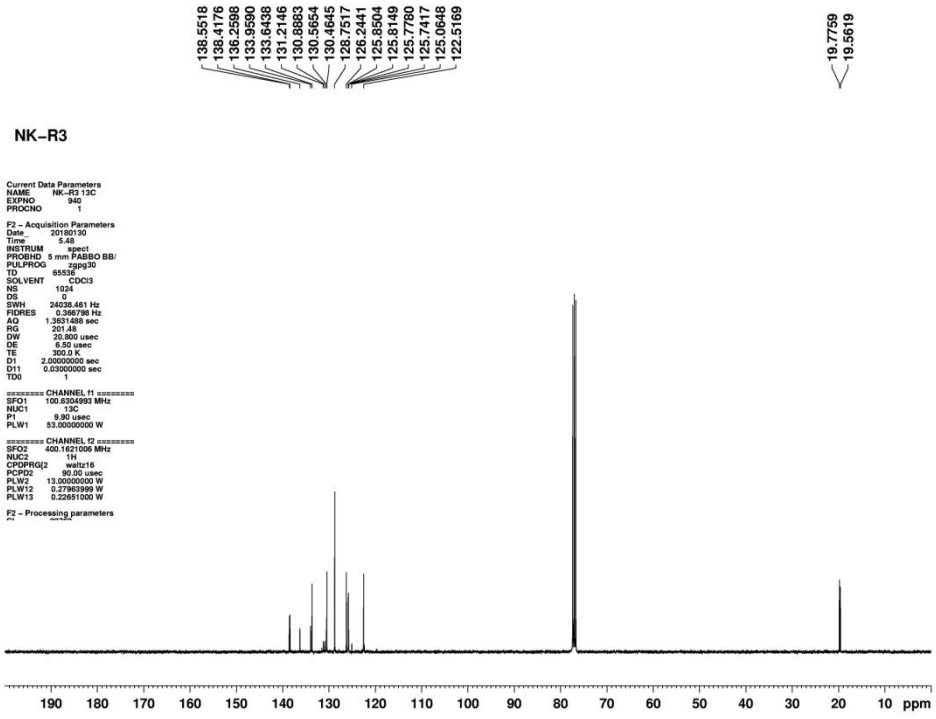


Figure 42: ^{13}C NMR of compound (3u)

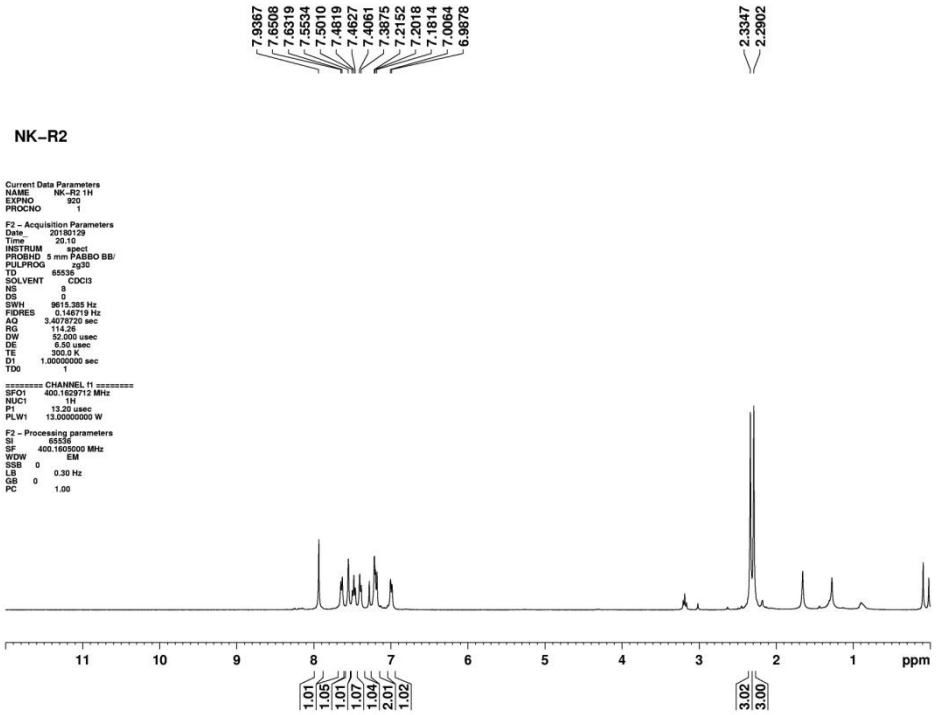


Figure 43: ^{1}H NMR of compound (3v)

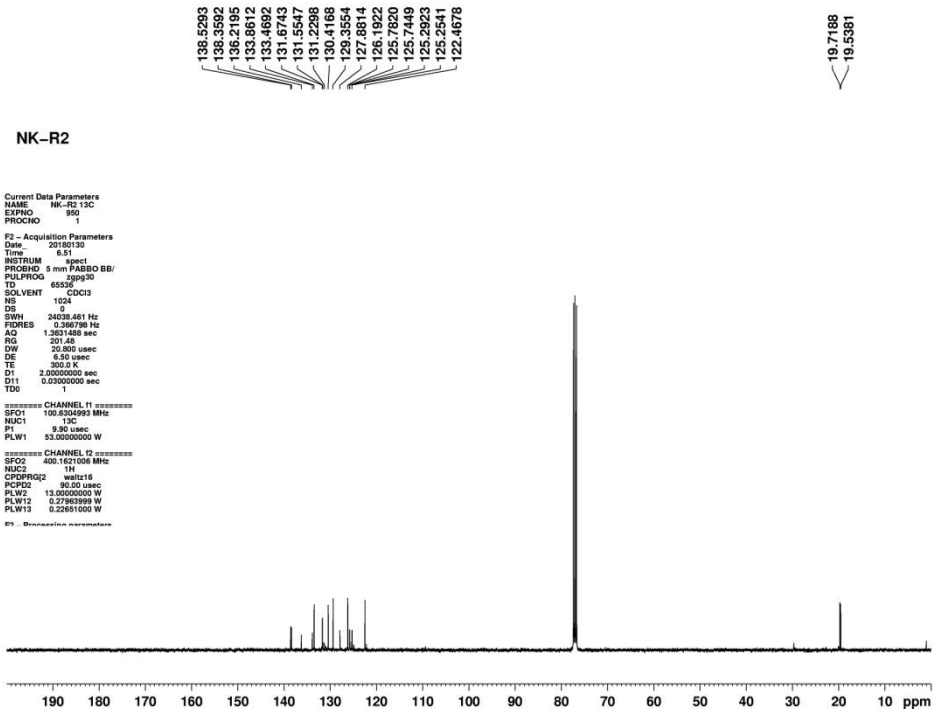


Figure 44: ^{13}C NMR of compound (3v)

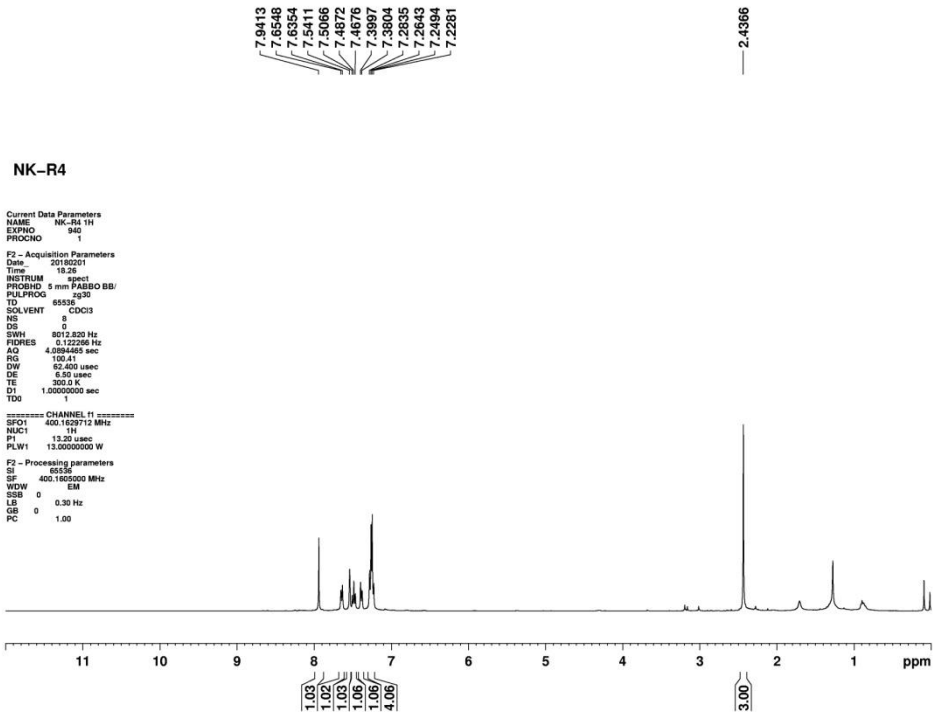


Figure 45: ^{1}H NMR of compound (3w)

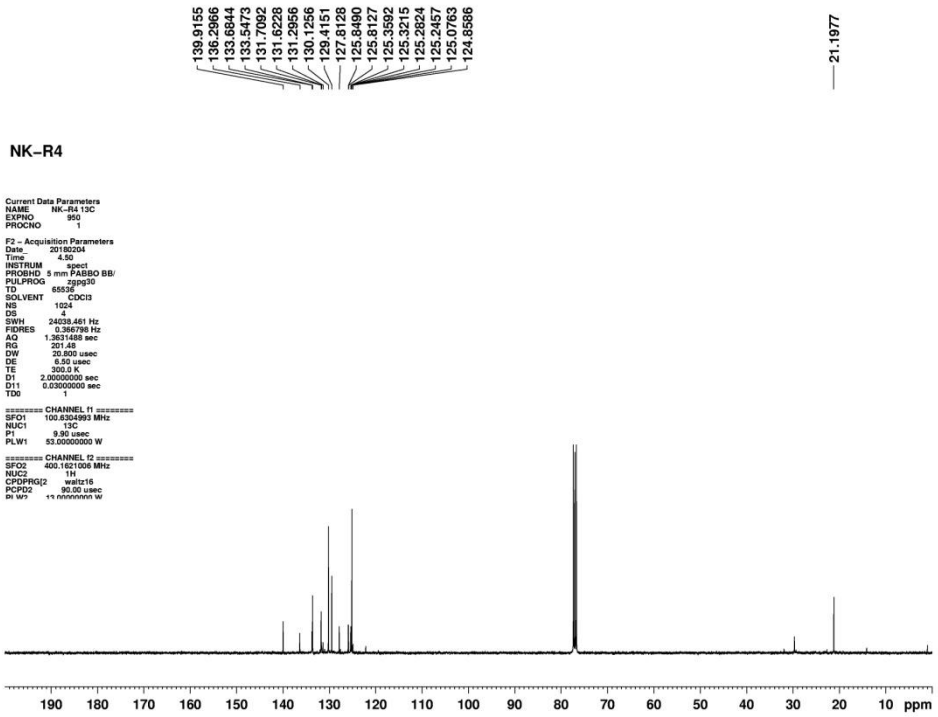
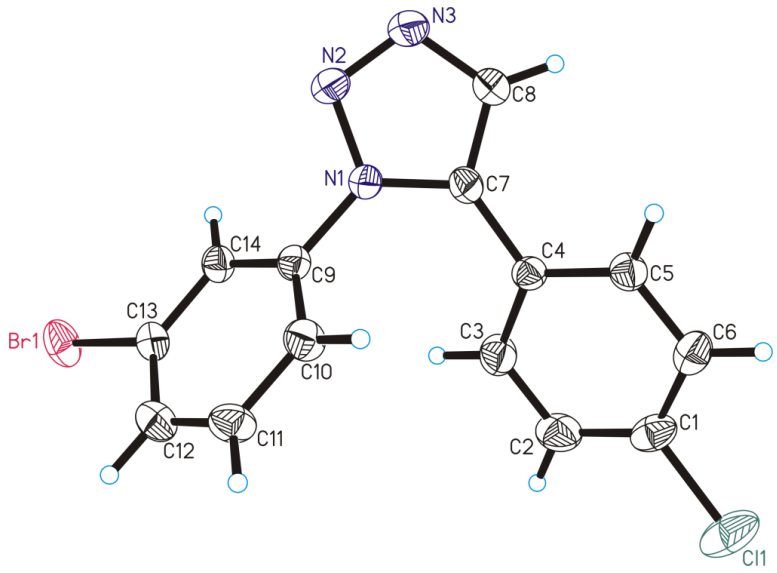


Figure 46: ^{13}C NMR of compound (3w)

(6) X-Ray Data for compound (3t)



ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound 3t determined at 293 K.

X-Ray Data Collection and Structure Refinement Details:

A good quality single crystal of size 0.22 x 0.22 x 0.07 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **3t** were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the monochromated Mo-Kα radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using ω-scans of 0.5^{o} steps at 293(2) K. Cell determination, data collection and data reduction was performed using the Rigaku CrystalClear-SM Expert 2.1 b24[1] software. Structure solution and refinement were performed by using SHELX-97[2]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model. Crystal data are summarized in Table 2.

1. CrystalClear 2.1, Rigaku Corporation, Tokyo, Japan
2. Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112–122.

Supplementary:

Table 2. Crystal data and structure refinement details for 3t

Compound	**3t**
Empirical formula	C_{14} H_9 Br CL N_3
Formula weight	334.60
Crystal System	Orthorhombic
Space group	*P* 2_1 2_1 2_1
a (Å)	7.656(2)
b (Å)	9.850(3)
c (Å)	18.330(5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	1382.3(7)
Z	4
D_c (g/cm^3)	1.608
F_{000}	664
μ (mm^{-1})	3.155
θ_{max} (°)	25.38
Total reflections	9574
Unique reflections	2525
Reflections [$I > 2\sigma(I)$]	1999
Parameters	173
R_{int}	0.0571
Goodness-of-fit	0.987
R [$F^2 > 2\sigma(F^2)$]	0.0367
wR (F^2, all data)	0.0768
CCDC No.	1571573