Supporting information

Nickel nanoparticles supported reduced graphene oxide sheets: A phosphine free, magnetically recoverable and cost effective catalyst for Sonogashira cross-coupling reaction

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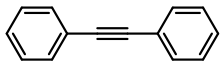
General procedure for the Sonogashira cross-coupling reaction:

A mixture of aryl halide (1 mmol), phenyl acetylene (1.5 mmol), K_2CO_3 (3 mmol) and CuI (0.08 mmol) was taken in round bottom flask. A suspension of Ni NPs-rGO (25 mg, 0.15 mmol Ni) N-methyl-2-pyrrolidone (5 mL) was added to it. The whole reaction mixture was stirred at 120 ^oC for 4 h. After completion of the reaction (monitored by TLC), the catalyst was separated from the reaction mixture by using an external magnet and the reaction mixture was poured into water. The organic product was recovered by extracting with ethyl acetate (3x10 mL). Then the organic phase were dried over Na_2SO_4 and concentrated in vacuum. The products were purified by column chromatography using silica gel (60-120 mesh) with EtOAc/hexanes as eluent to obtain the desired Sonogashira cross-coupling product.

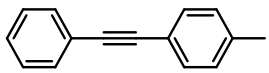
Analytical data:

Biphenylacetylene, 3a: [1]



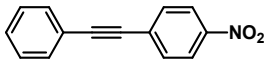
[White solid; mp 58-61^oC; Yield = 95% (107 mg); R_f = 0.66 (Hexane)]; ^1H NMR (500 MHz, $CDCl_3$): δ 7.51-7.54 (m, 4H), 7.32-7.34 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.5, 128.3, 128.2, 123.2, 89.3; IR ($CHCl_3$): 3308, 2914, 1214, 742, 670 cm^{-1}.

1-methyl-4-(phenylethynyl)benzene, 3b: [2]



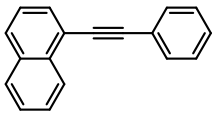
[Light yellow solid; mp 68-71^oC; Yield = 94% (146 mg); R_f = 0.62 (Hexane)]; ^1H NMR (500 MHz, $CDCl_3$): δ 7.49-7.52 (m, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.29-7.32 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 131.54, 129.1, 128.2, 128.0, 123.4, 120.1, 89.5, 88.6, 21.4. IR ($CHCl_3$): 2922, 2199, 1600, 1511, 747, 484 cm^{-1}.

1-nitro-4-(phenylethynyl)benzene, 3c: [2, 3]



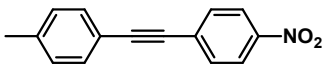
[Light yellow solid; mp 108-110 ^{o}C; Yield = 93% (102 mg); R_f = 0.65 (10% EtOAc in hexanes)]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, *J* = 9 Hz, 2H), 7.65-7.68 (m, 2H), 7.55-7.57(m, 2H), 7.38-7.41 (m, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.2, 132.3, 131.8, 130.3, 129.3, 128.5, 123.6, 122.1, 94.7, 87.5; IR ($CHCl_3$): 3305, 2930, 2197, 1502.16, 855, 759, 513 cm^{-1}

1-(phenylethynyl)naphthalene, 3d: [1]



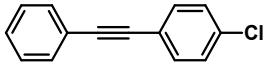
[Light yellow colour liquid; Yield = 93% (102 mg); R_f = 0.42 (Hexane)]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43-8.45 (m, 1H), 7.75-7.87 (m, 3H), 7.23-7.69 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.1, 131.6, 130.3, 128.7, 128.3, 128.3, 128.2, 126.7, 126.3, 126.1, 125.2, 120.8, 94.2, 87.4; IR ($CHCl_3$): 3111, 2012, 1251.21, 744, 544, 519 cm^{-1}

1-methyl-4-((4-nitrophenyl)ethynyl)benzene, 3e: [6]



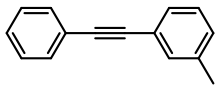
[yellow solid; mp = 120-122 ^{o}C; yield = 88 % (102 mg); R_f = 0.58 (10% EtOAc in hexanes)]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J*= 9 Hz, 2H), 7.65 (d, *J*= 9 Hz, 2H), 7.45 (d, *J* = 8 Hz, 2H), 7.19 (d, *J* = 8 Hz, 2H), 2.39(s, 3H; ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.5, 132.0, 132.2, 131.65, 129.2, 123.0, 118.1, 94.9, 87.2, 21.4 ; IR ($CHCl_3$): 3158, 2943, 2029, 152, 814, 540 cm^{-1}

1-chloro-4-(phenylethynyl)benzene, 3f: [4]



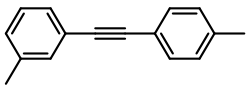
[White solid; mp 83-84 ^{o}C; Yield = 91% (101 mg)]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.58 (m, 2H), 7.46 (d, *J* = 8.3, 2H) 7.31-7.39 (m, 5H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.2, 132.7, 131.5, 128.6, 128.4, 128.2, 122.9, 121.7, 90.2, 88.2; IR ($CHCl_3$): 3494, 2310, 1464, 810, 499 cm^{-1}

1-methyl-3-(phenylethynyl)benzene, 3g: [5]



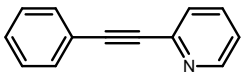
[White solid; mp 69-70 ^{o}C; Yield = 93% (105 mg); R_f = 0.68 (Hexane)]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.53 (m, 2H), 7.30-7.40 (m, 5H), 7.21 (d, *J* =7.5 Hz, 1H), 7.12 (d, *J* =7 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 132.2, 131.6, 129.1, 128.7, 128.3, 128.2, 128.1, 123.3, 123.0, 89.5, 89.0, 21.2; IR ($CHCl_3$): 3312, 2925, 2132, 1483, 892, 591 cm^{-1}.

1-methyl-3-(p-tolylethynyl)benzene, 3h: [5]



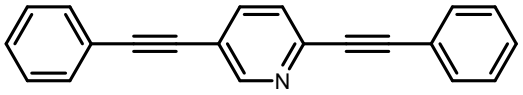
[Pale yellow solid; mp = 81-84 ^{o}C; Yield = 93% (112 mg); R_f = 0.54 (Hexane)]; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.42(d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.10-7.24 (m, 4H), 2.35(s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139, 138.1, 132.2, 131.4, 129.1, 129.0, 128.9, 128.5, 123.1, 120.2, 89.1, 88.8, 21.5, 21.4.; IR ($CHCl_3$): 3309, 2926, 2121, 1484, 800, 516 cm^{-1}

2-(phenylethynyl)pyridine, 3i:[5]



[yellow solid; mp = 39 ^{o}C; Yield = 86% (145 mg); R_f = 0.25 (10% EtOAc in hexanes]; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.62-8.63(m, 1H), 7.66-7.71 (m, 5H), 7.36-7.61(m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 143.5, 136.1, 132.0, 128.9, 128.4, 127.2, 122.7, 122.3, 89.3, 88.6; IR ($CHCl_3$): 3387, 2154, 1423, 795, 648 cm^{-1}

2,5-bis(2-phenylethynyl)pyridine, 3j:[7]



[Brown solid; mp = 168-170 ^{o}C; Yield = 91% (252 mg); R_f = 0.29 (10% EtOAc in hexanes]; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.76(m, 1H), 7.73-7.85 (m, 1H), 7.58-7.63(m, 2H), 7.52-7.57 (m, 2H), 7.48-750 (m, 1H), 7.32-7.42 (m, 6H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.3,141.8, 138.3, 132.0, 131.6, 129.1, 128.9, 128.4, 128.3, 126.3, 122.3, 122.0, 119.3, 94.2, 91.2, 88.4, 85.9; IR ($CHCl_3$): 3403, 2193, 1500, 2121, 1498, 760, 512 cm^{-1}

References:

1. M. Shunmughanathan, P. Puthiaraj and K. Pitchumani, *ChemCatChem,* 2015, **7**, 666-673.
2. F. Farjadian and B. Tamami, *ChemPlusChem*, 2014, **79**, 1767 – 1773.
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4. M. Gholinejad and J. Ahmadi, *ChemPlusChem.*, 2015, **80**, 973-979.
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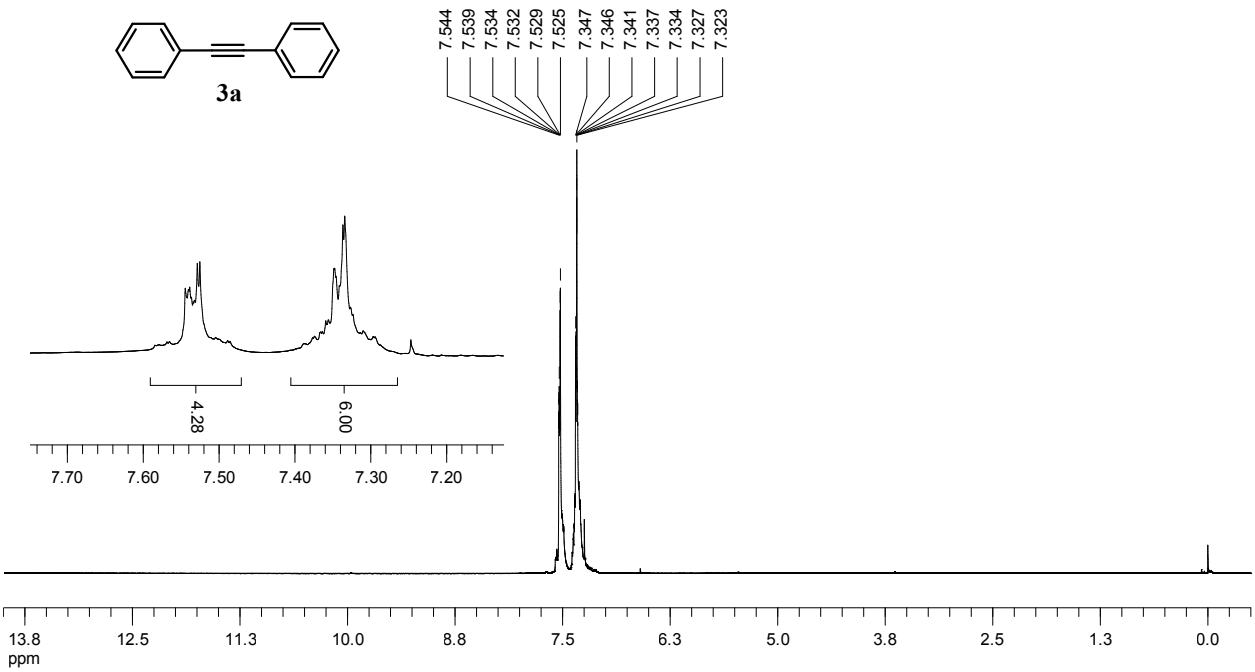
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7.323
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6.00
7.70
7.60
7.50
7.40
7.30
7.20
13.8
12.5
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7.5
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3.8
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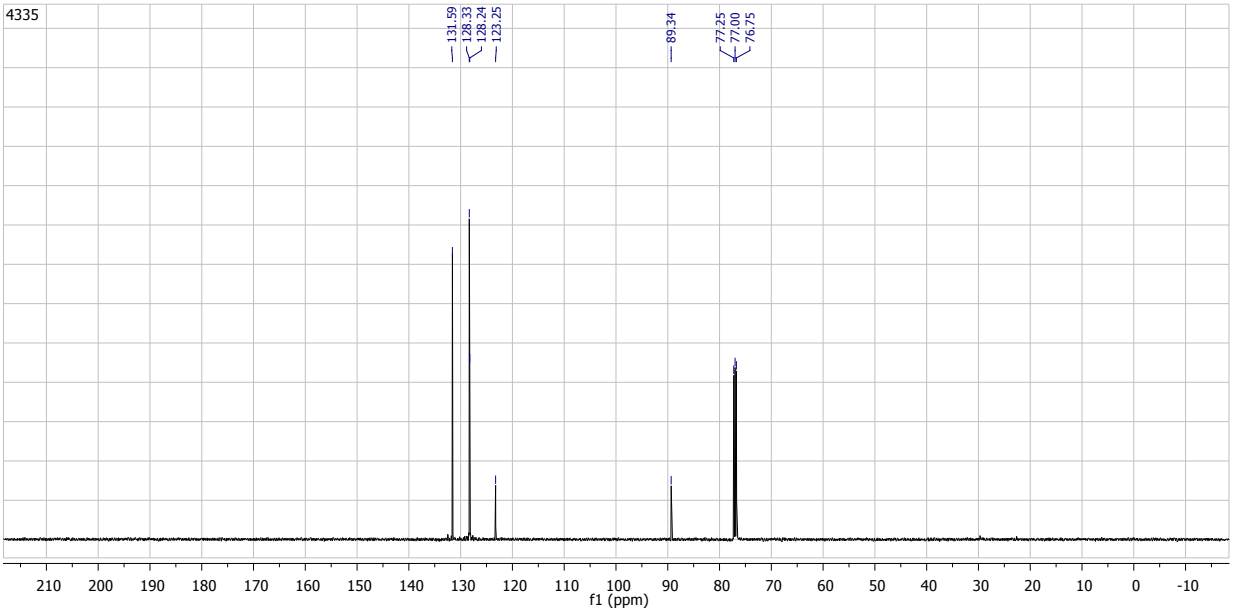
ppm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89.34
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77.00
76.75
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200
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180
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160
150
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80
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60
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40
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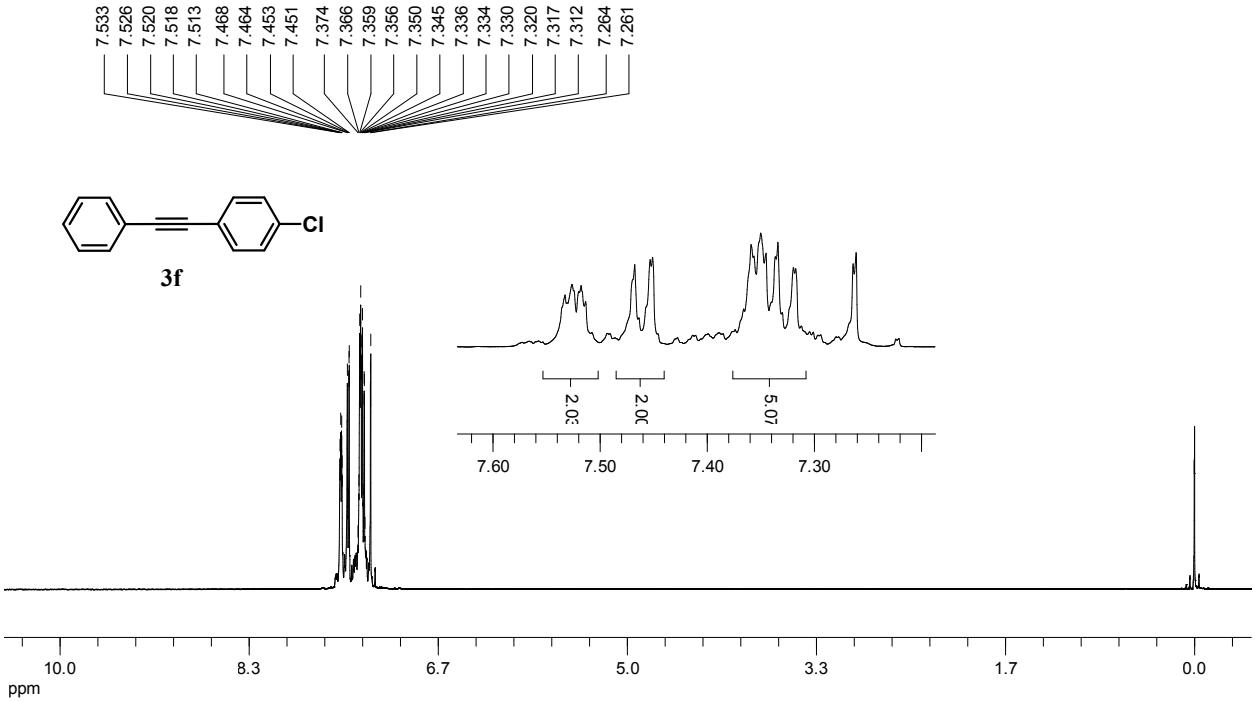
0
-10
f1 (ppm)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7.356
7.350
7.345
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7.334
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7.320
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7.312
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7.261
Cl
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3.3
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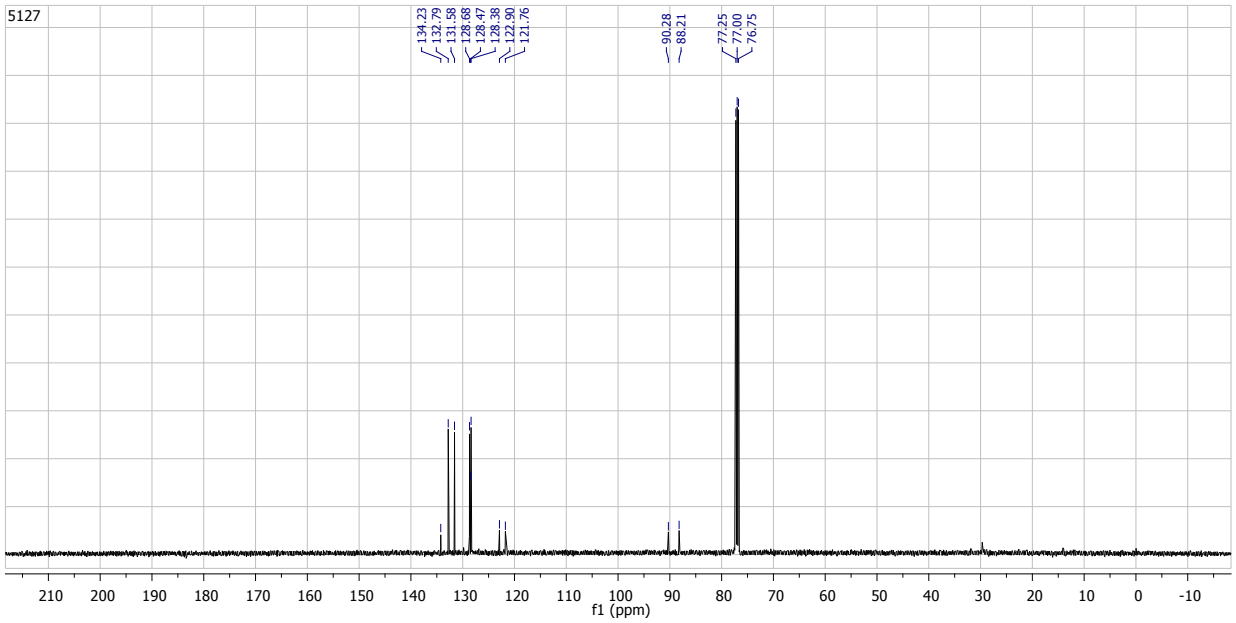
ppm

3f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200
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180
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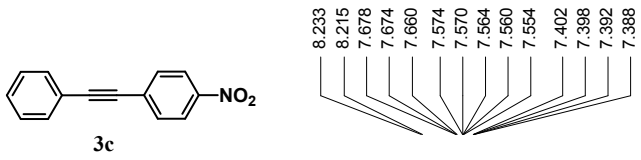
0
-10
f1 (ppm)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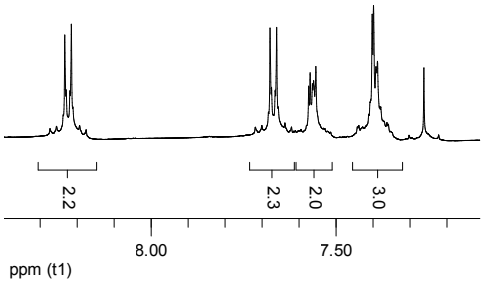
NO2

3c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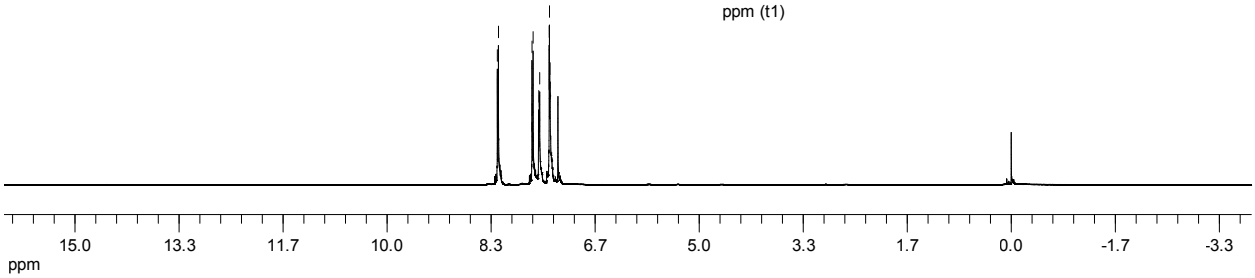
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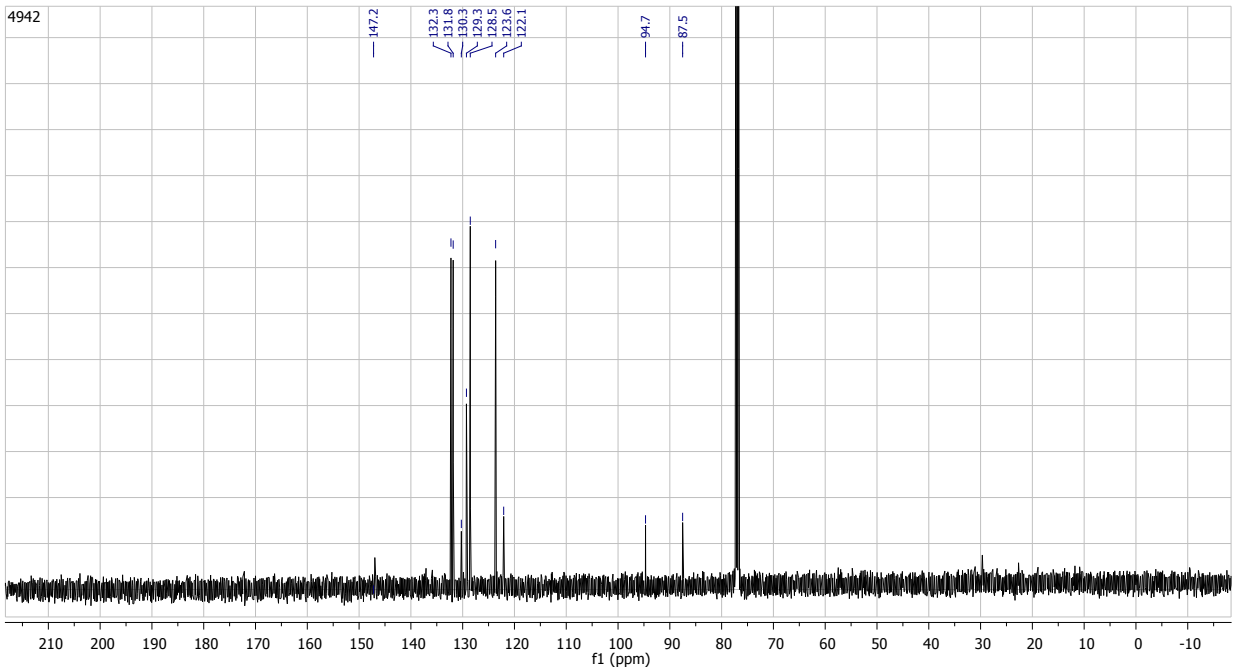
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180
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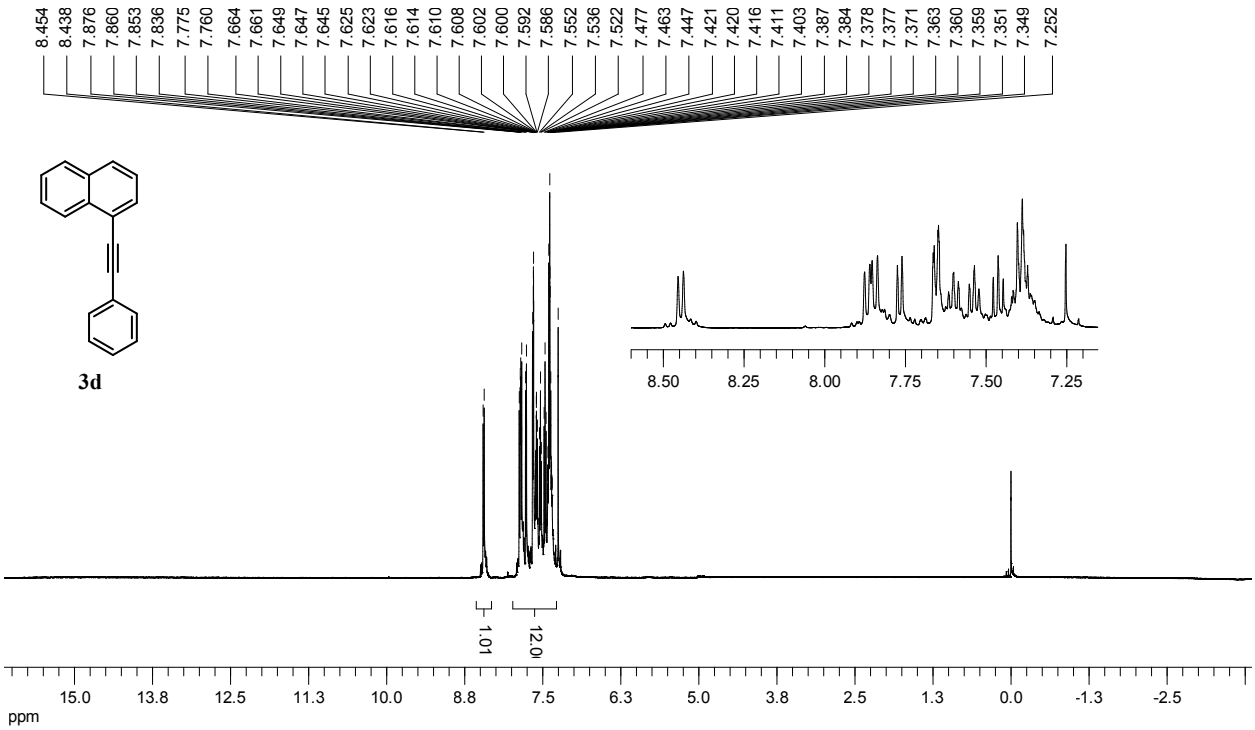
f1 (ppm)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7.600
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15.0
13.8
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3.8
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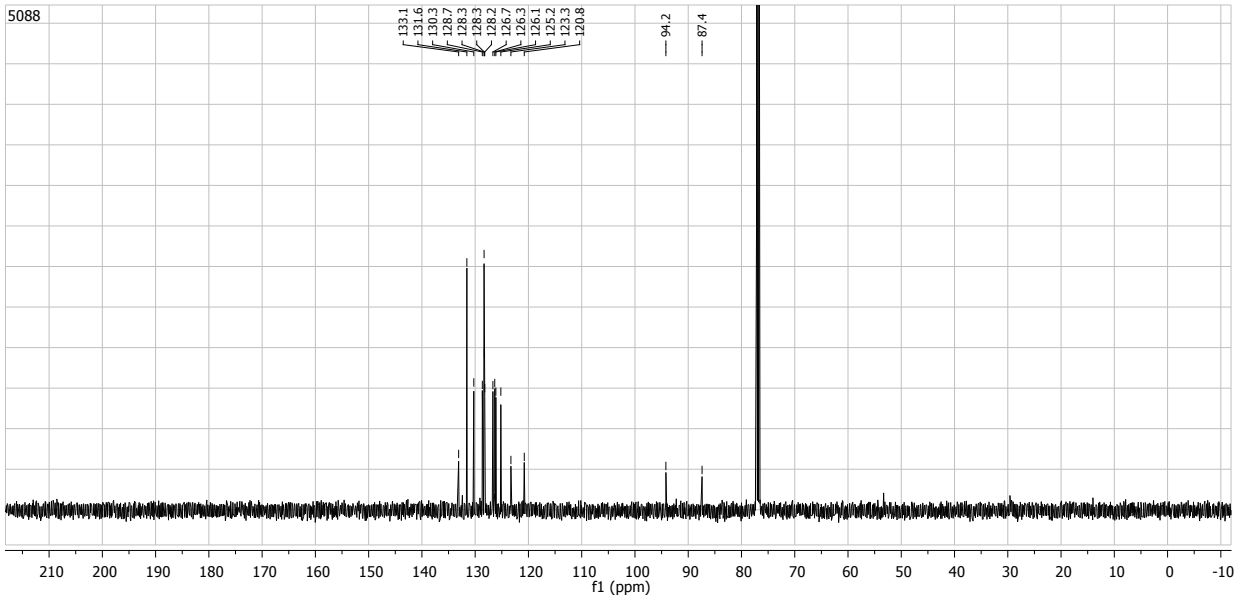
ppm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128.3
128.2
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123.3
120.8
94.2
87.4
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170
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0
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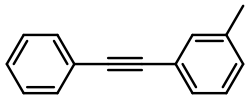
f1 (ppm)



3g

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7.50
7.40
7.30
7.20
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5.0
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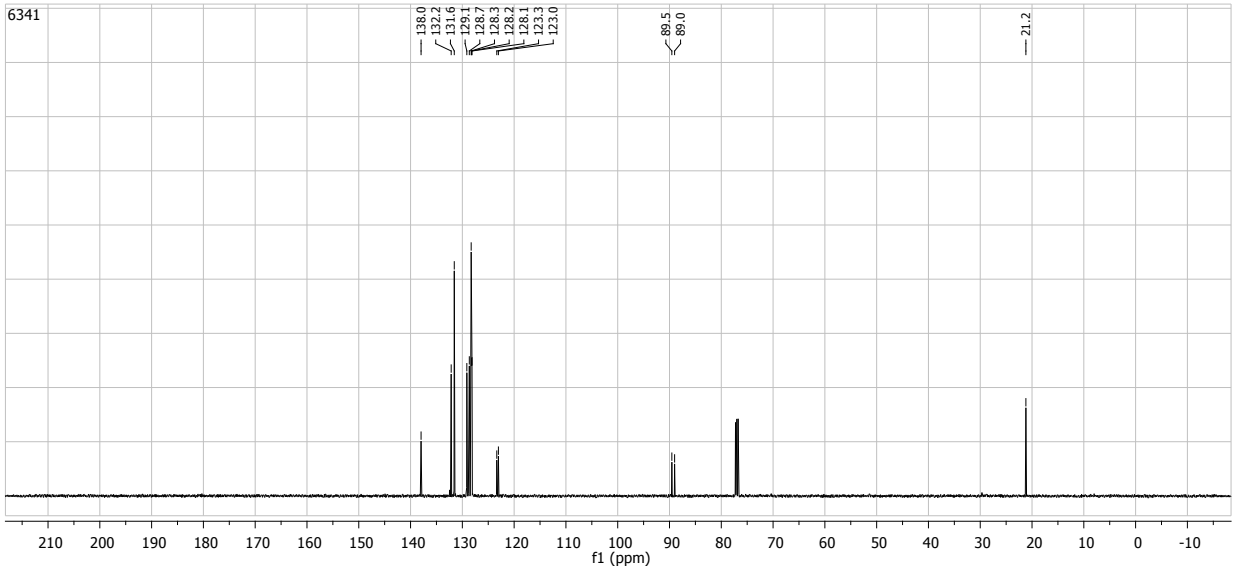
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21.2
210
200
190
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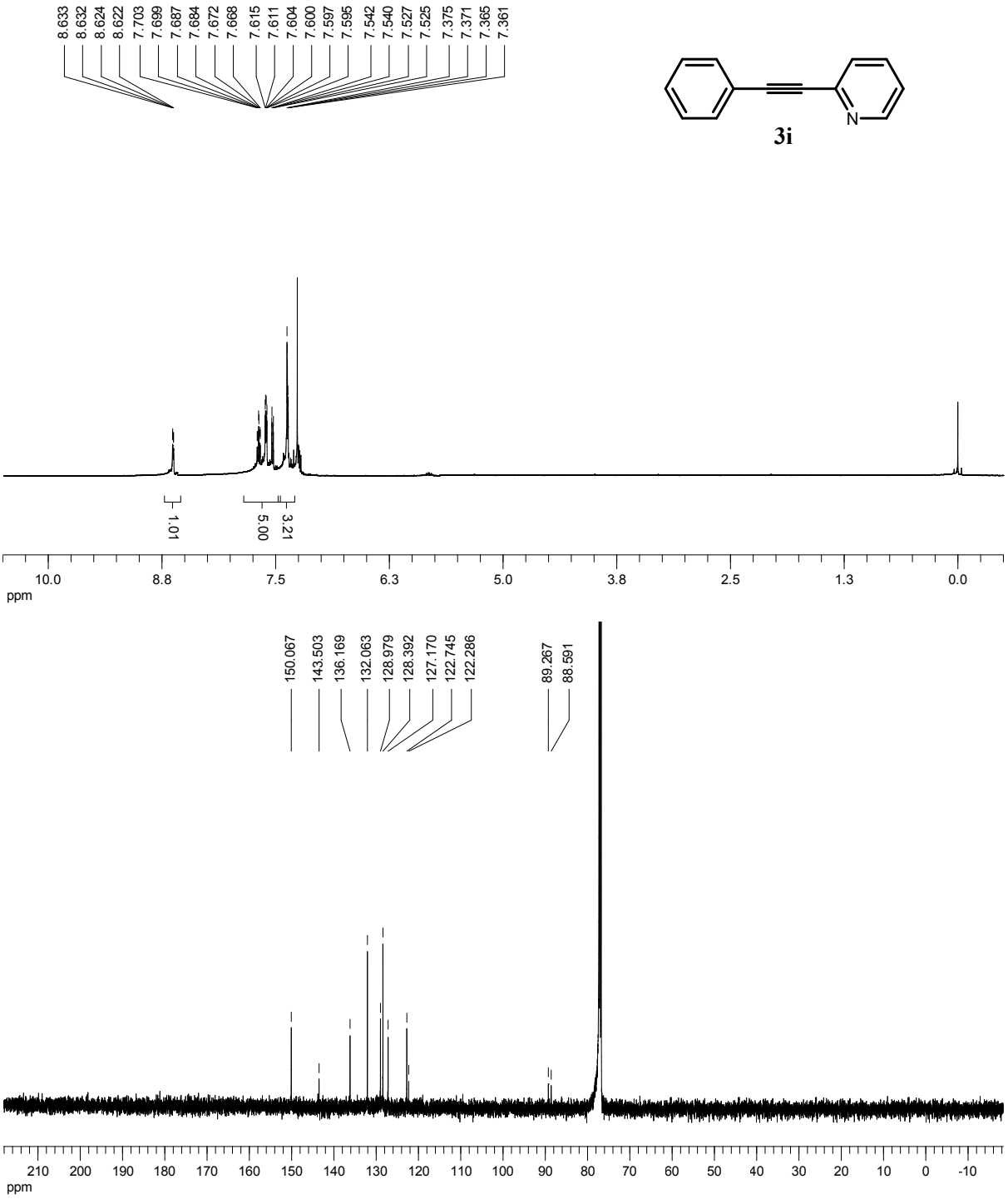
f1 (ppm)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7.365
7.361
N
3i
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1.3
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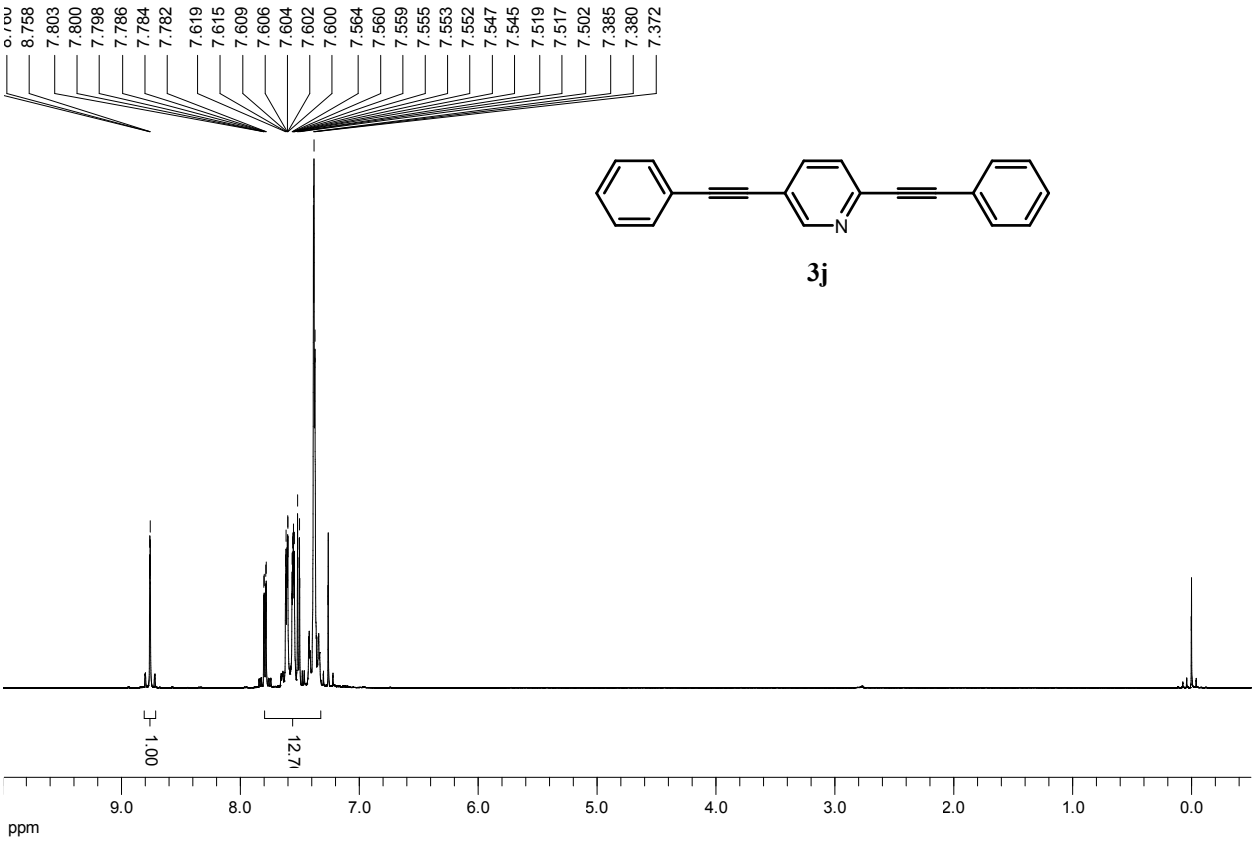
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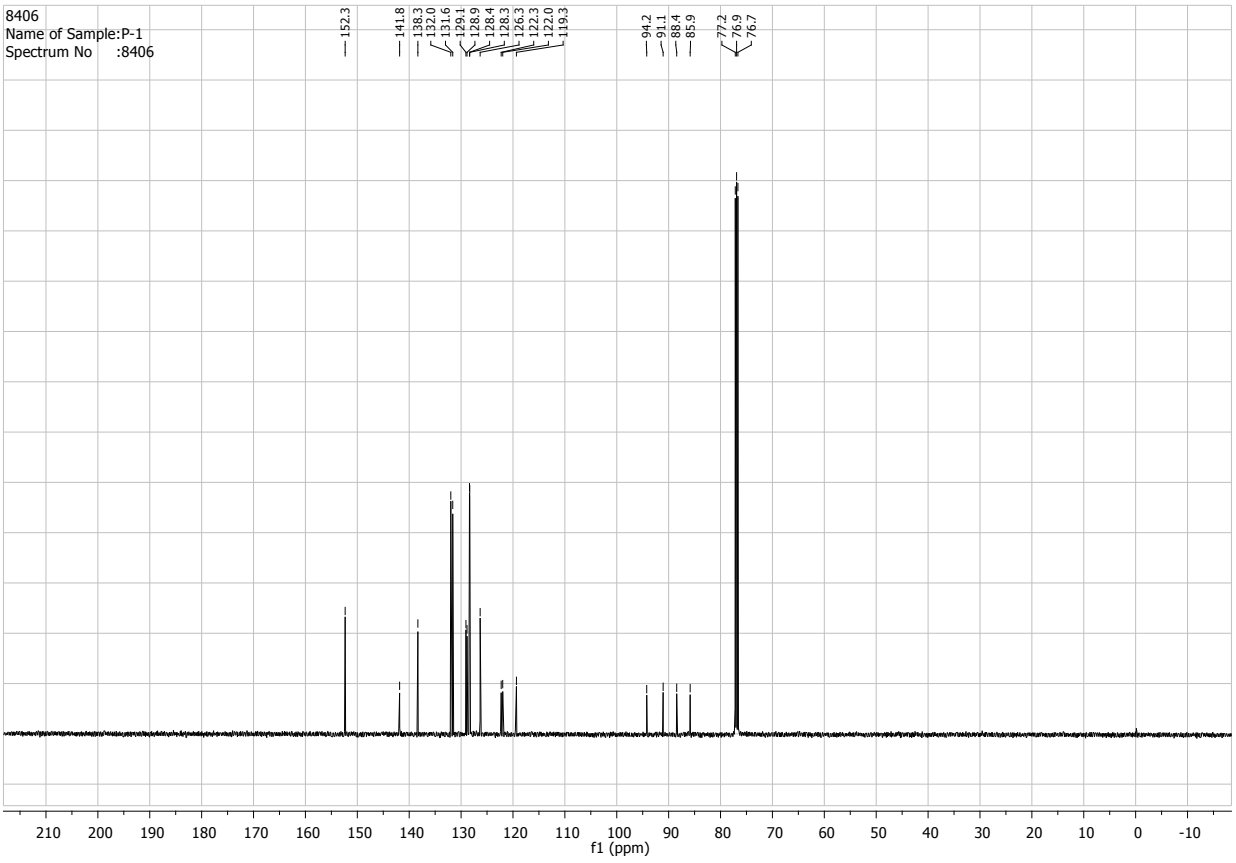
7.555
7.553
7.552
7.547
7.545
7.519
7.517
7.502
7.385
7.380
7.372
N
1.00
12.71
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

3j


8406
Name of Sample:P-1
Spectrum No :8406
152.3
141.8
138.3
132.0
131.6
129.1
128.9
128.4
128.3
126.3
122.3
122.0
119.3
94.2
91.1
88.4
85.9
77.2
76.9
76.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)