Supporting Information

Efficient Synthetic route to Aromatic Secondary Amines via Pd/RuPhos/TBAB Catalyzed Cross Coupling

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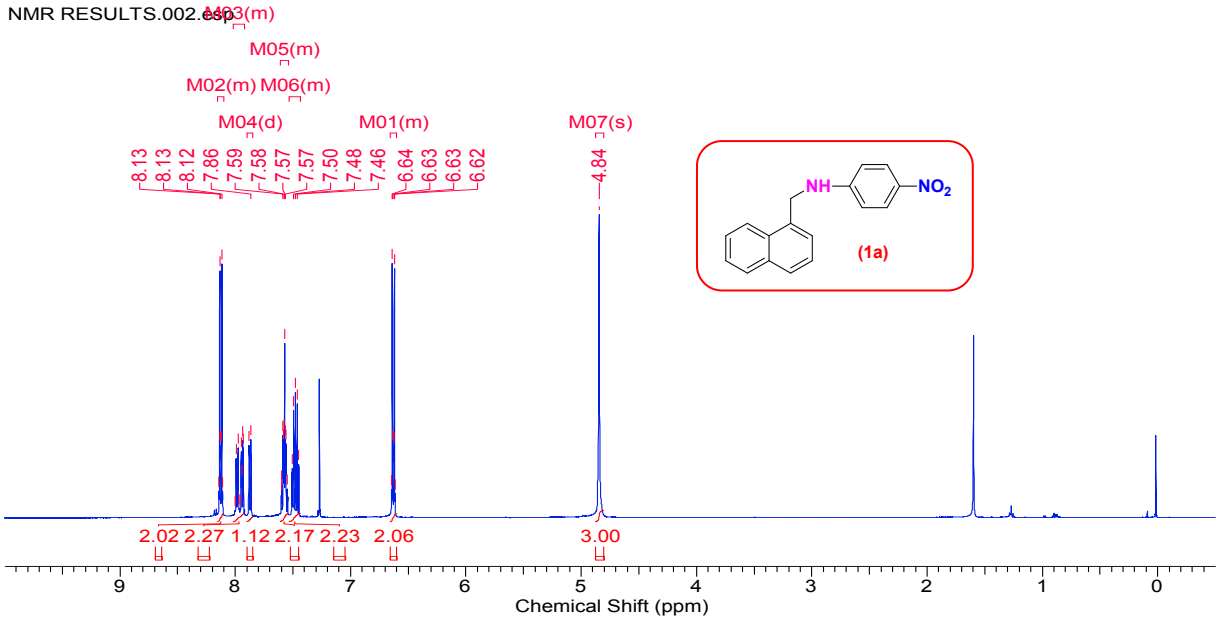
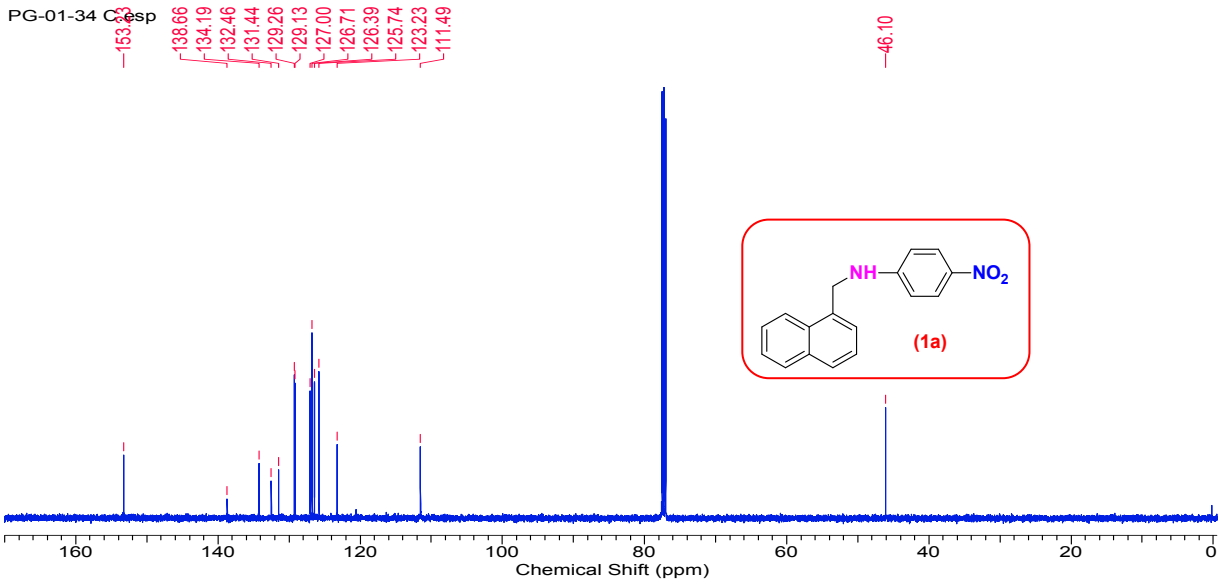
Contents:

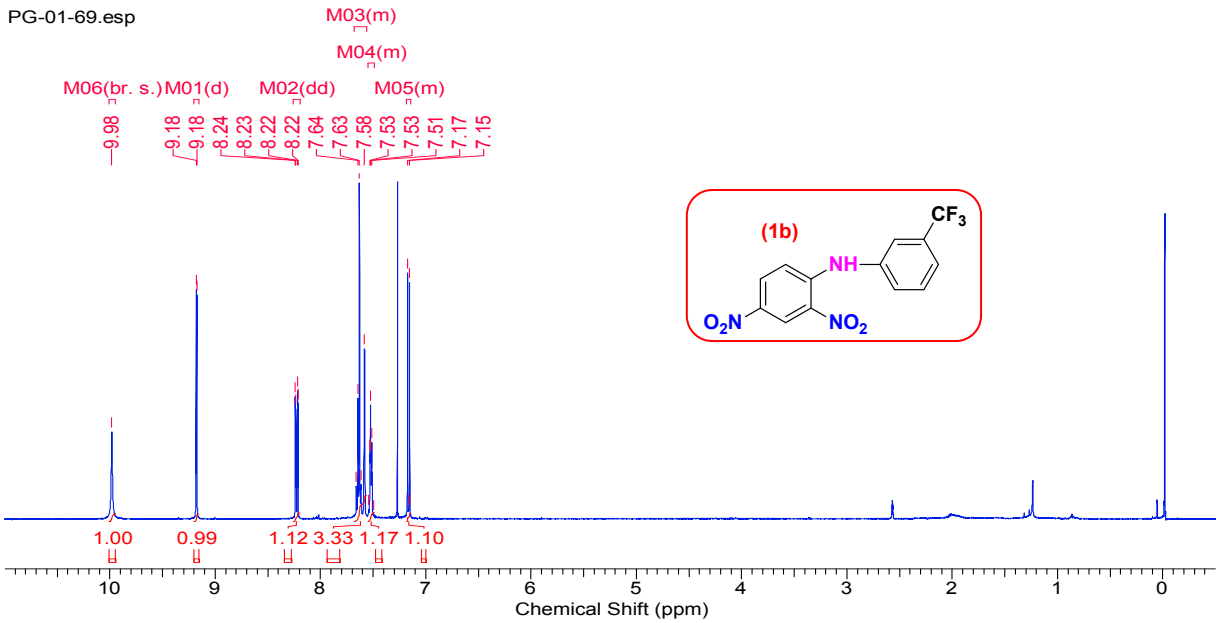
1. General Information:

All reactions were regulated under nitrogen atmosphere. Solvents: Hexane, ethyl acetate (EtOAc) for extraction and chromatography were purchased from spectrochem. All these compounds were recognized by the usual physical methods, that is IR (Bruker), ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, CHN spectra were measured in $CDCl_3$ (300, 500, 125, 376 MHz) on Bruker instrument. ^{1}H chemical shift are reported in ppm from an internal standard TMS or of residual chloroform (7.27 ppm). Following abreviations are used: m (multiplet), s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet of doublet), td (triplet of doublet), q (quadruplet), IR spectra measured are reported in wave numbers (cm-1). TLC was performed on precoated silica gel 60-F254 plates. Silica gel (100-200) mesh size was used for column chromatoghraphy. Melting points were recorded on a B-450 apparatus. Aryl/alkyl halides and aryl amines are commercially available compounds of Sigma Aldrich make.

^{1}H, ^{13}C and ^{19}F NMR Spectra:



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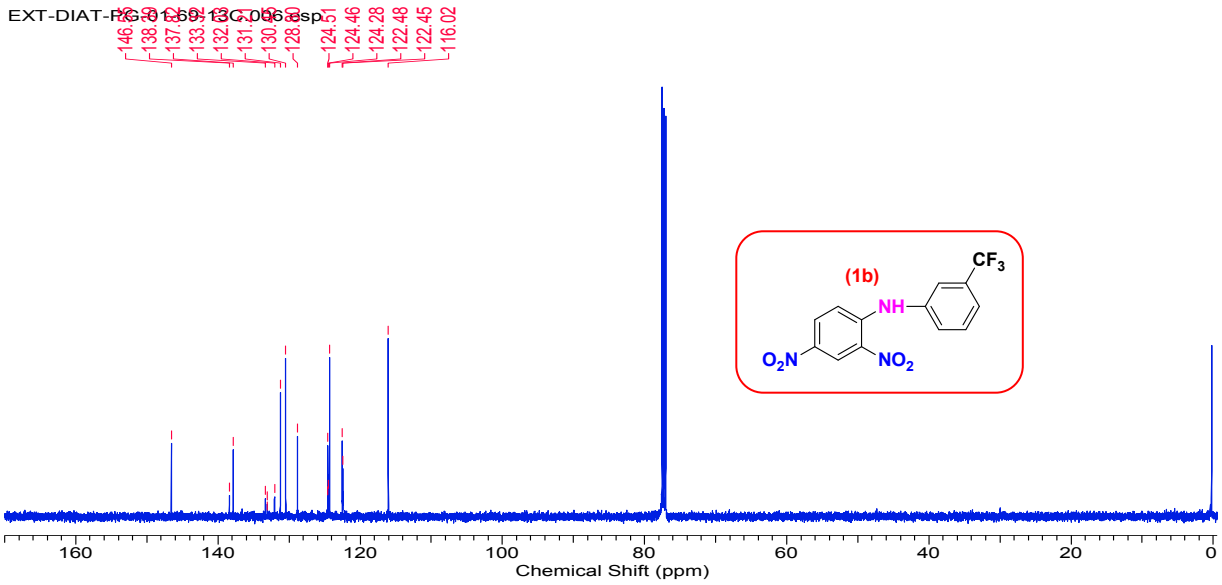
M04(m)
M06(br. s.)
M01(d)
M02(dd)
M05(m)
9.98
9.18
9.18
8.24
8.23
8.22
8.22
7.64
7.63
7.58
7.53
7.53
7.51
7.17
7.15
(1b)
CF3
NH
O2N
NO2
1.00
0.99
1.12
3.33
1.17
1.10
Chemical Shift (ppm)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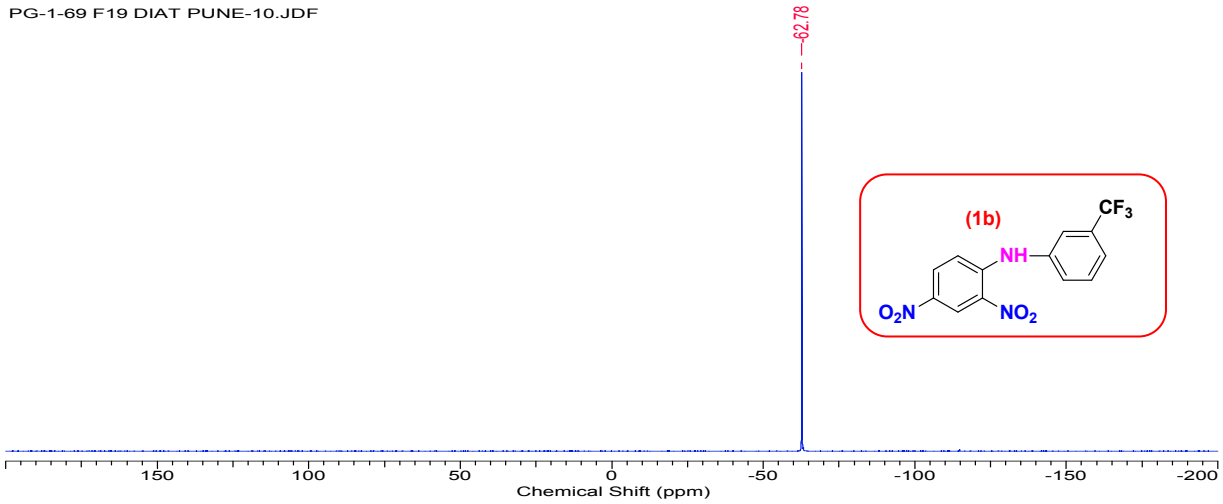
124.51
124.46
124.28
122.48
122.45
116.02
(1b)
CF3
NH
O2N
NO2
Chemical Shift (ppm)

PG-1-69 F19 DIAT PUNE-10.JDF



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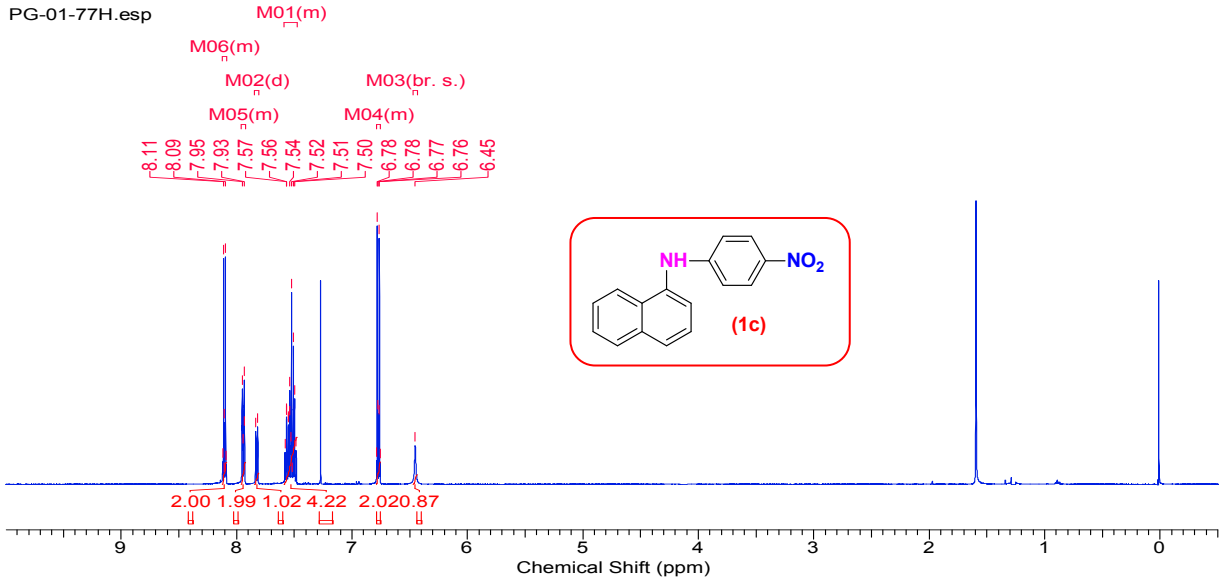

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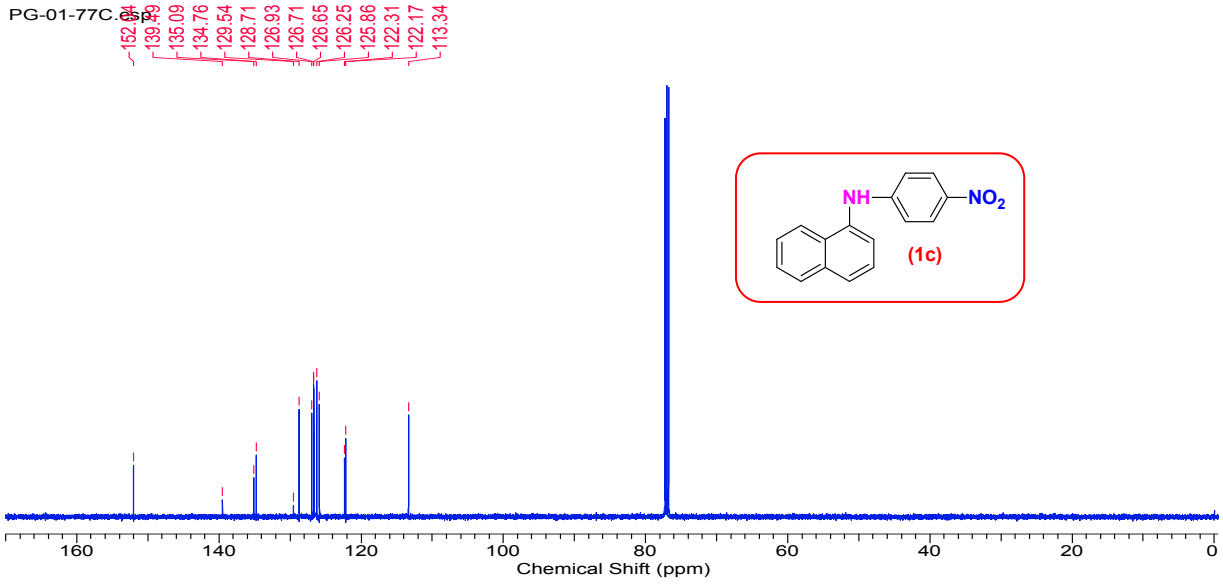

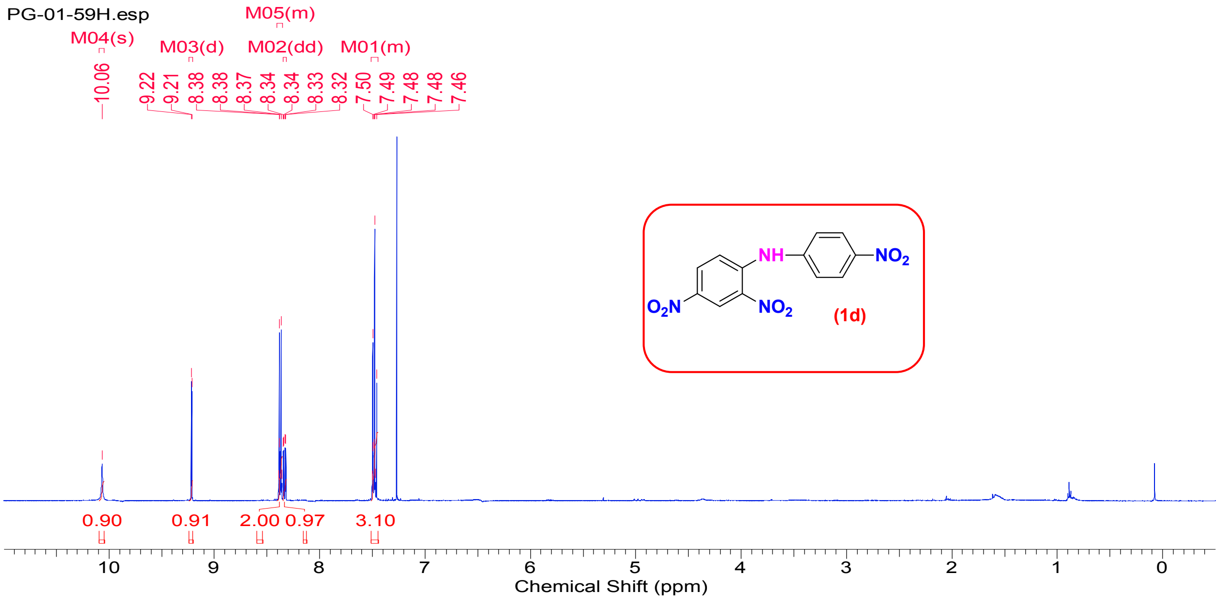
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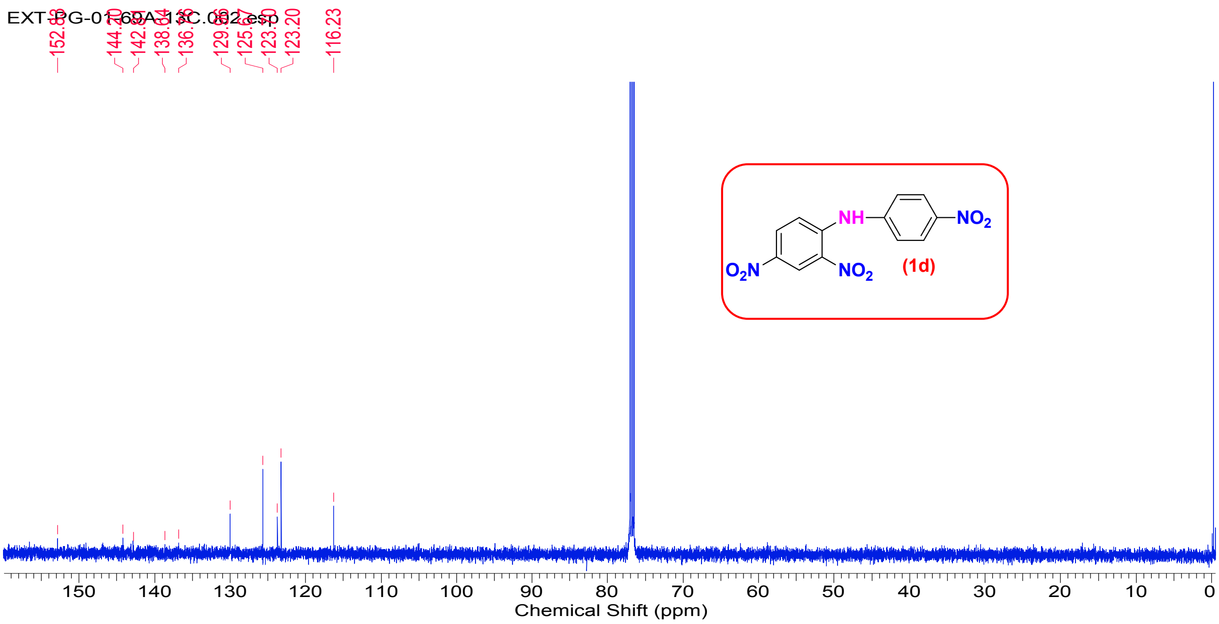
M04(s)
M03(d)
M02(dd)
M01(m)
10.06
9.22
9.21
8.38
8.38
8.37
8.34
8.34
8.33
8.32
7.50
7.49
7.48
7.48
7.46
NH
NO_2
O_2N
NO_2
(1d)
0.90
0.91
2.00
0.97
3.10
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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123.20
NH
NO_2
O_2N
NO_2
(1d)
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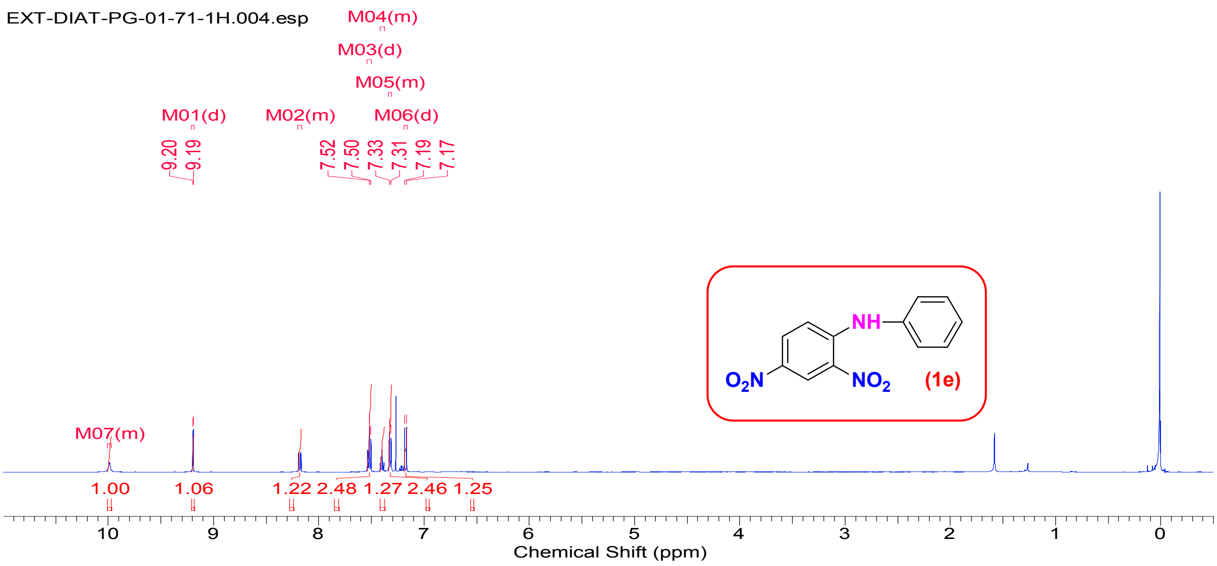
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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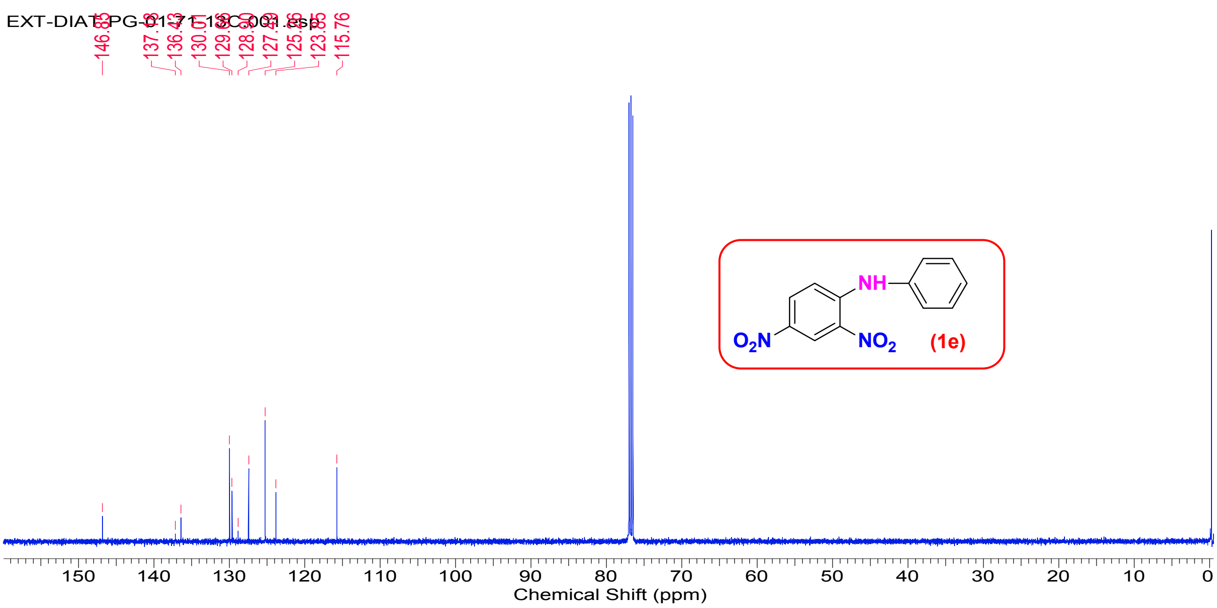
M03(d)
M05(m)
M01(d)
M02(m)
M06(d)
9.20
9.19
7.52
7.50
7.33
7.31
7.19
7.17
M07(m)
NH
O_2N
NO_2
(1e)
1.00
1.06
1.22
2.48
1.27
2.46
1.25
Chemical Shift (ppm)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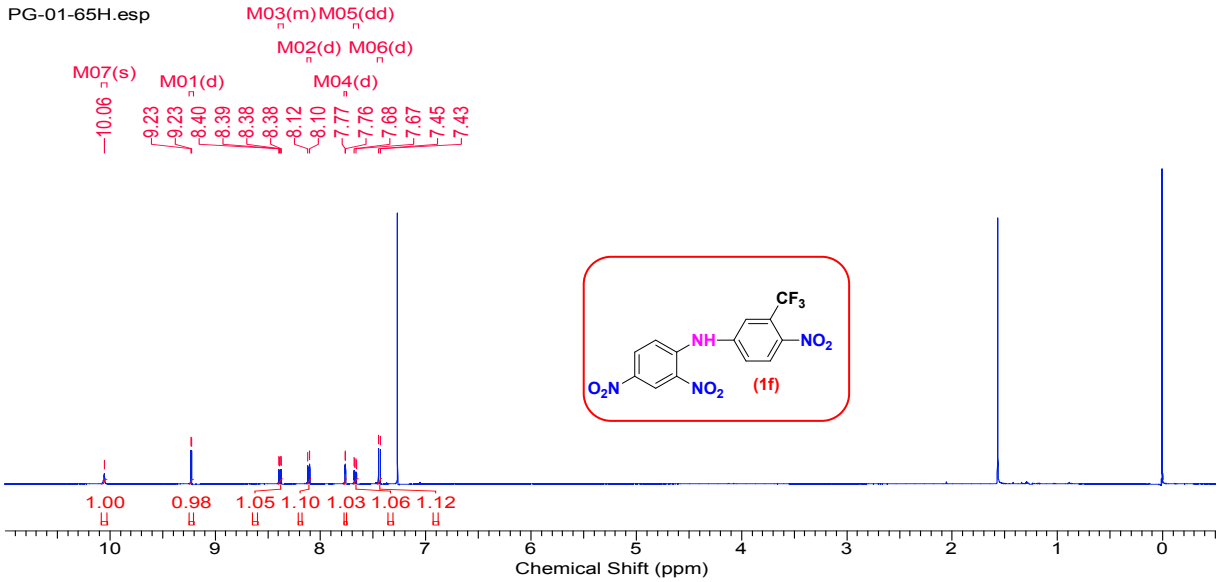
137.18
136.43
130.11
129.88
128.30
127.49
125.35
123.85
115.76
NH
O_2N
NO_2
(1e)
Chemical Shift (ppm)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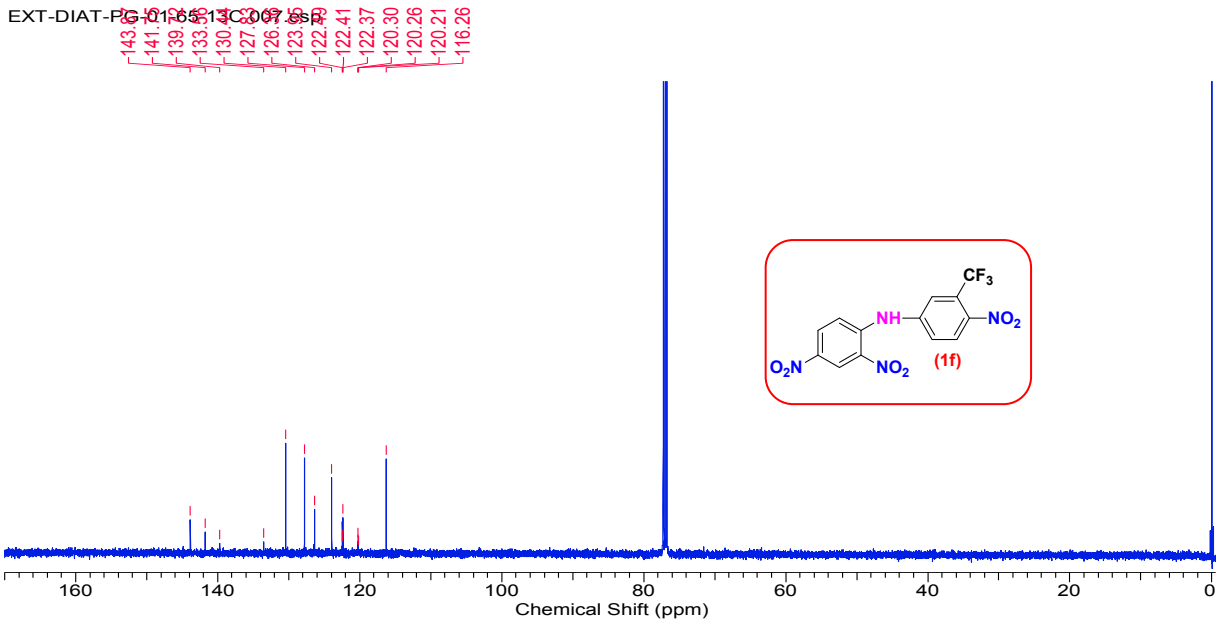
M03(m) M05(dd)
M02(d) M06(d)
M07(s)
M01(d)
M04(d)
10.06
9.23
9.23
8.40
8.39
8.38
8.38
8.12
8.10
7.77
7.76
7.68
7.67
7.45
7.43
1.00
0.98
1.05 1.10 1.03 1.06 1.12
CF3
NH
NO2
O2N
NO2
(1f)
Chemical Shift (ppm)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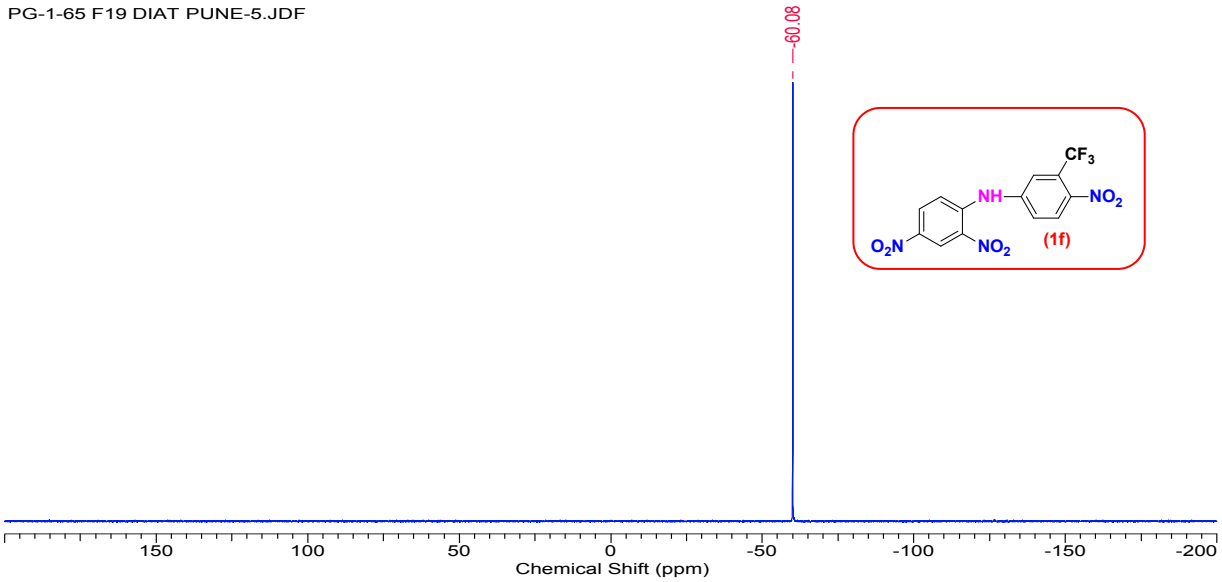
143.
141.
139.
133.
130.
127.
126.
123.
122.
122.41
122.37
120.30
120.26
120.21
116.26
CF3
NH
NO2
O2N
NO2
(1f)
Chemical Shift (ppm)

PG-1-65 F19 DIAT PUNE-5.JDF



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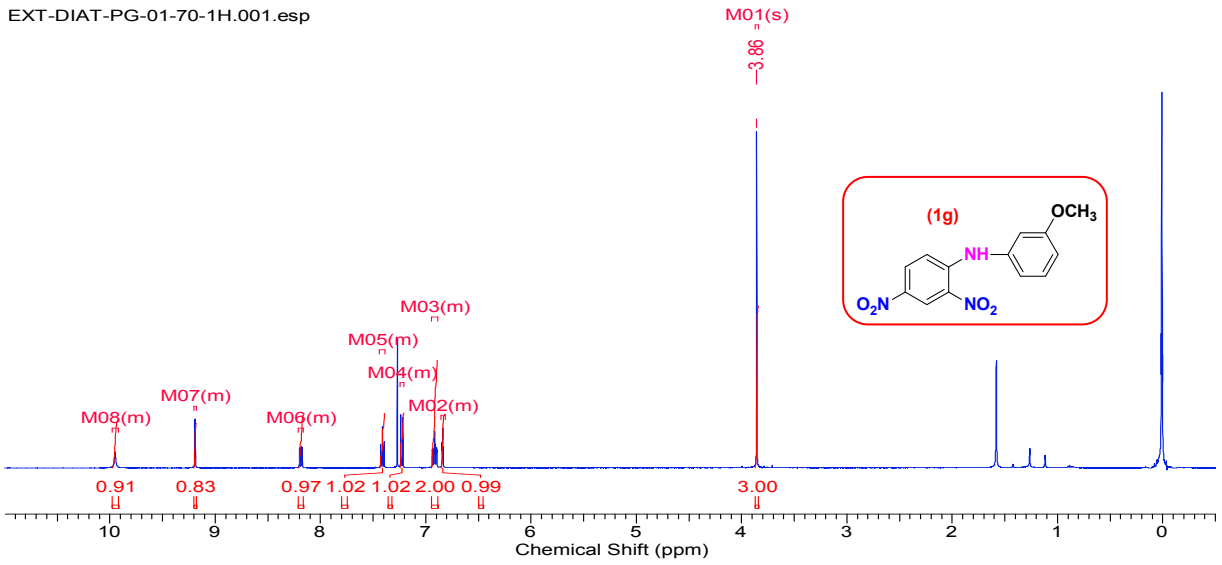

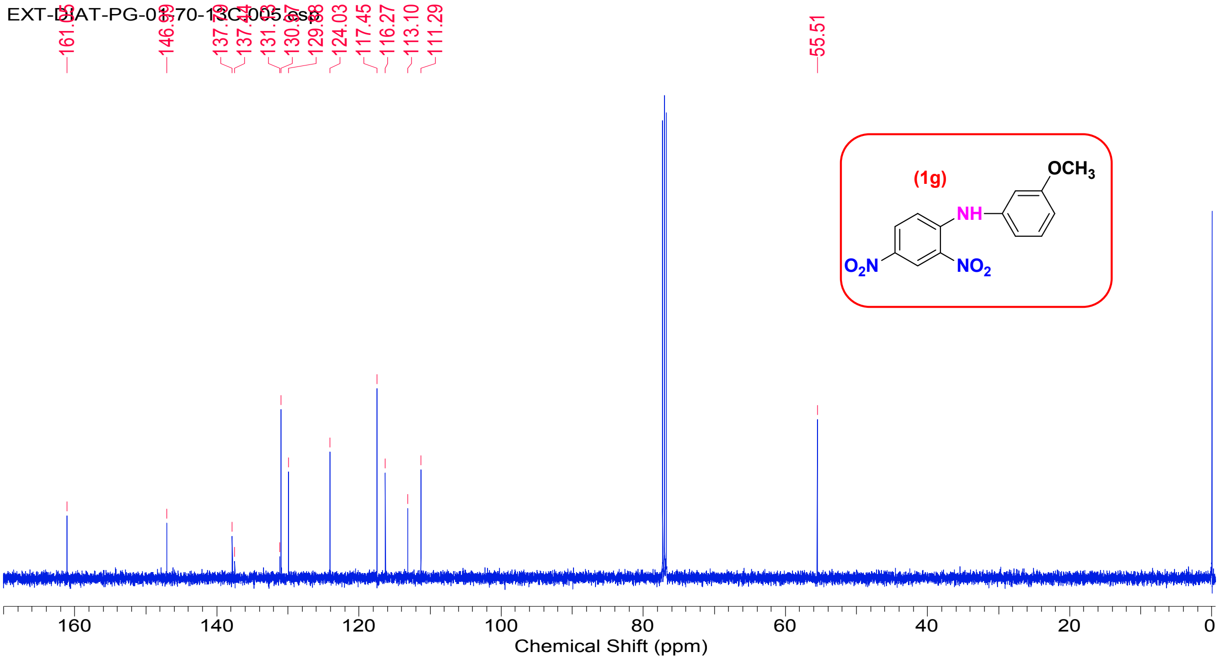
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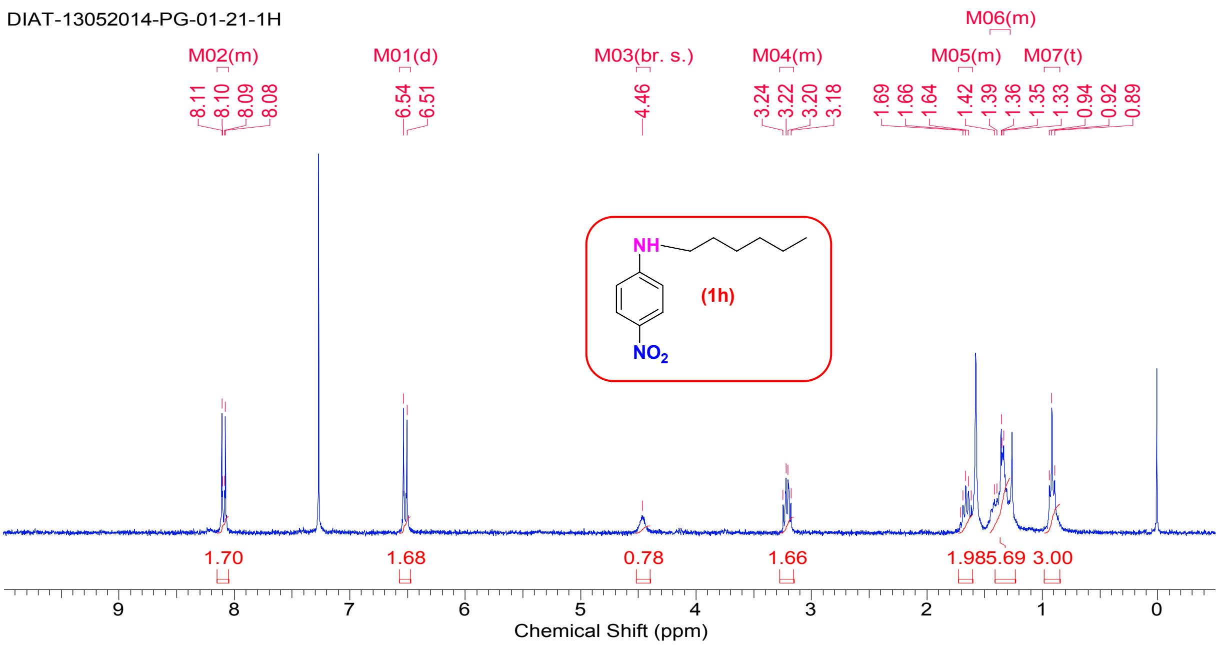
137.70
137.41
131.13
130.07
129.68
124.03
117.45
116.27
113.10
111.29
55.51
(1g)
OCH3
NH
O2N
NO2
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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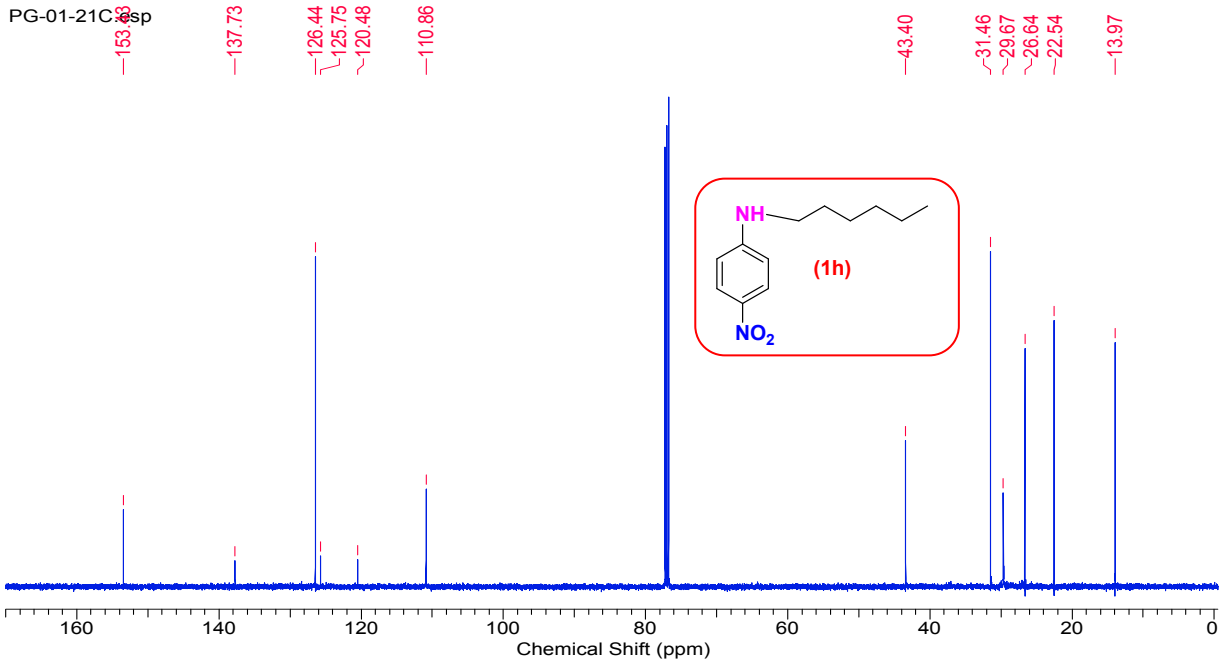
M02(m)
M01(d)
M03(br. s.)
M04(m)
M06(m)
M05(m)
M07(t)
8.11
8.10
8.09
8.08
6.54
6.51
4.46
3.24
3.22
3.20
3.18
1.69
1.66
1.64
1.42
1.39
1.36
1.35
1.33
0.94
0.92
0.89
NH
(1h)
NO2
1.70
1.68
0.78
1.66
1.98
5.69
3.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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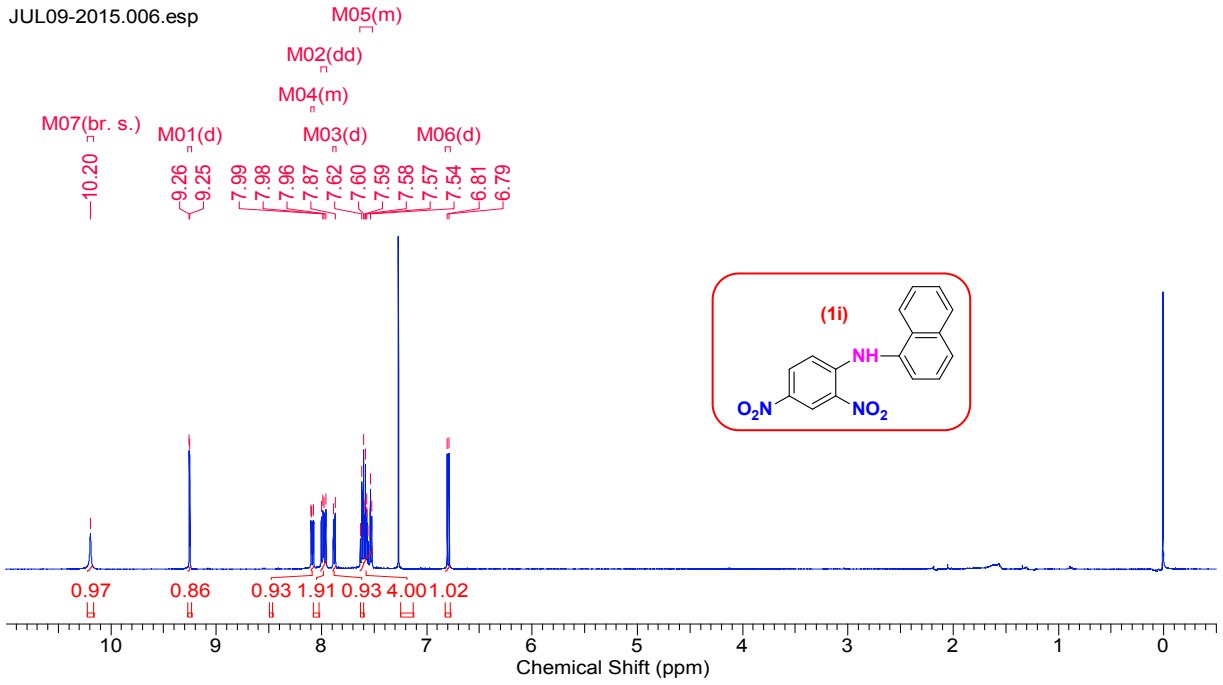
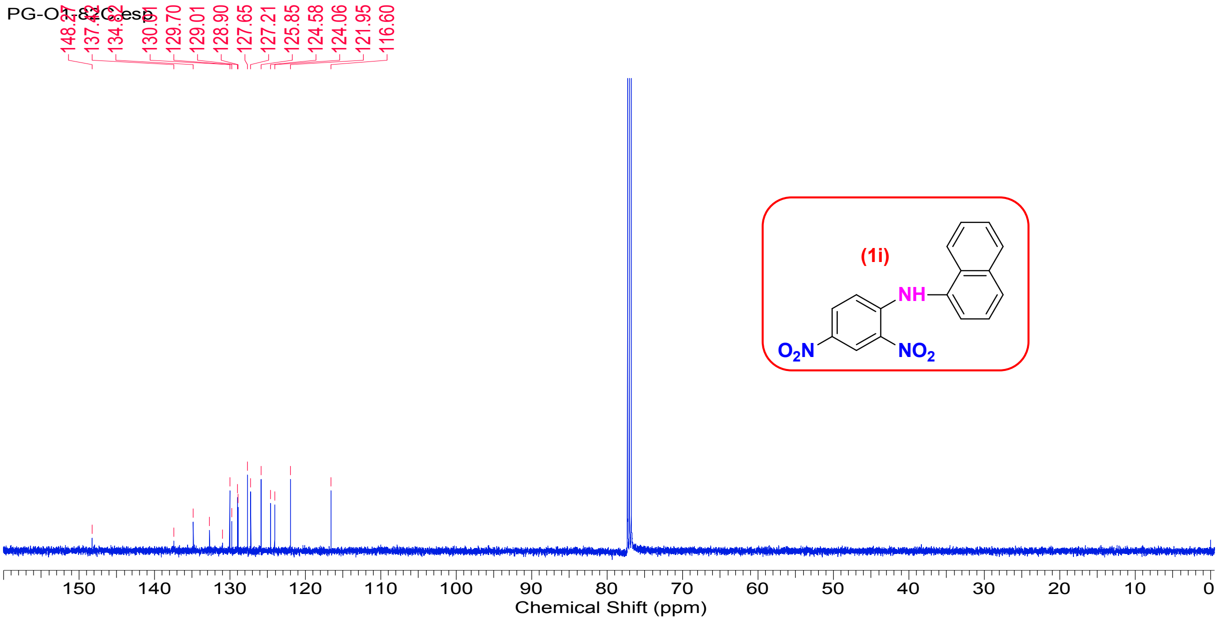
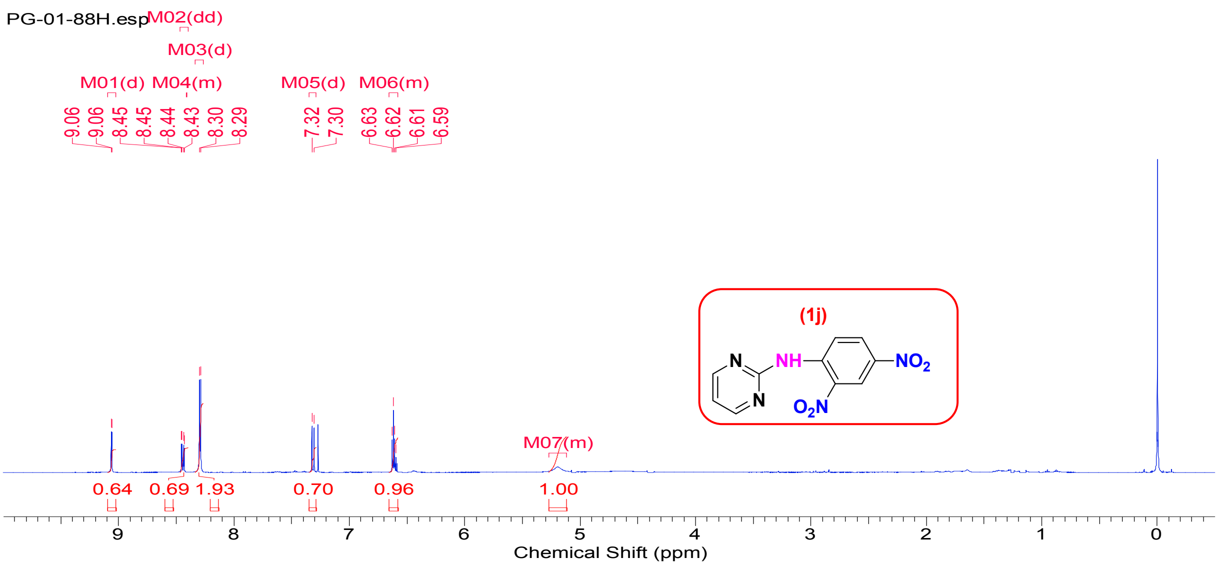
153.83
137.73
126.44
125.75
120.48
110.86
43.40
31.46
29.67
26.64
22.54
13.97
NH
(1h)
NO2
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

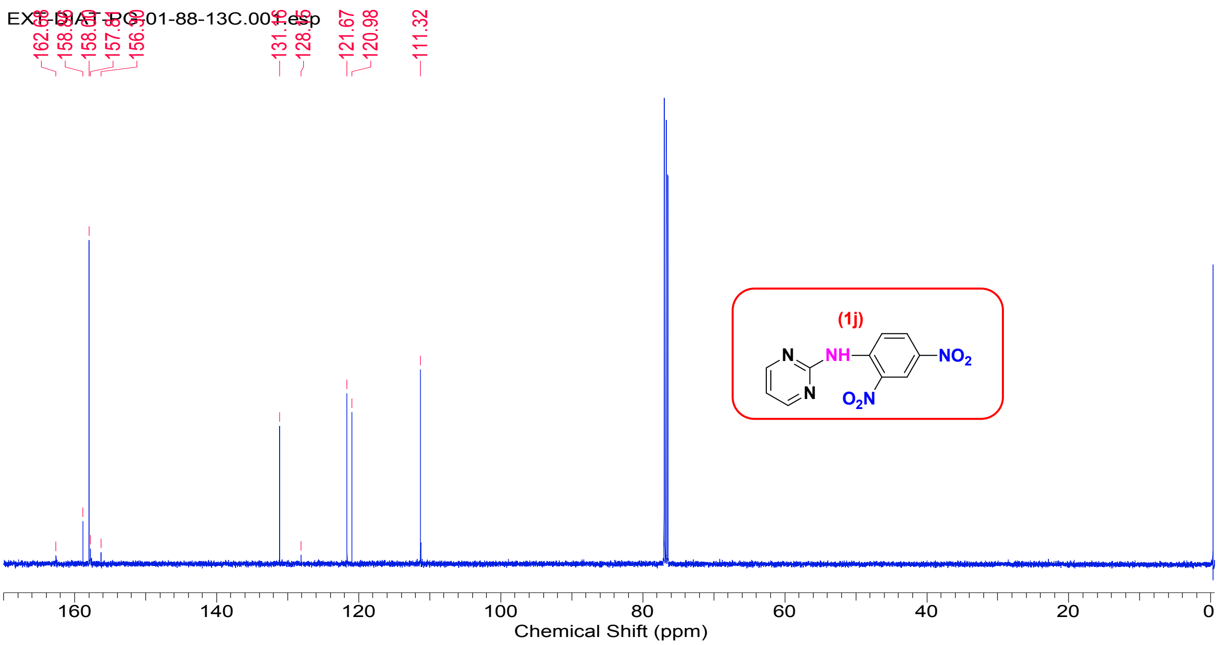

JUL09-2015.006.esp
M05(m)
M02(dd)
M04(m)
M07(br. s.)
M01(d)
M03(d)
M06(d)
10.20
9.26
9.25
7.99
7.98
7.96
7.87
7.62
7.60
7.59
7.58
7.57
7.54
6.81
6.79
(1i)
NH
O2N
NO2
0.97
0.86
0.93
1.91
0.93
4.00
1.02
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



129.70
129.01
128.90
127.65
127.21
125.85
124.58
124.06
121.95
116.60
(1i)
NH
O_2N
NO_2
Chemical Shift (ppm)



PG-01-88H.esp
M02(dd)
M03(d)
M01(d) M04(m)
M05(d) M06(m)
9.06
9.06
8.45
8.45
8.44
8.43
8.30
8.29
7.32
7.30
6.63
6.62
6.61
6.59
(1j)
N
NH
N
NO_2
O_2N
M07(m)
0.64 0.69 1.93 0.70 0.96 1.00
Chemical Shift (ppm)



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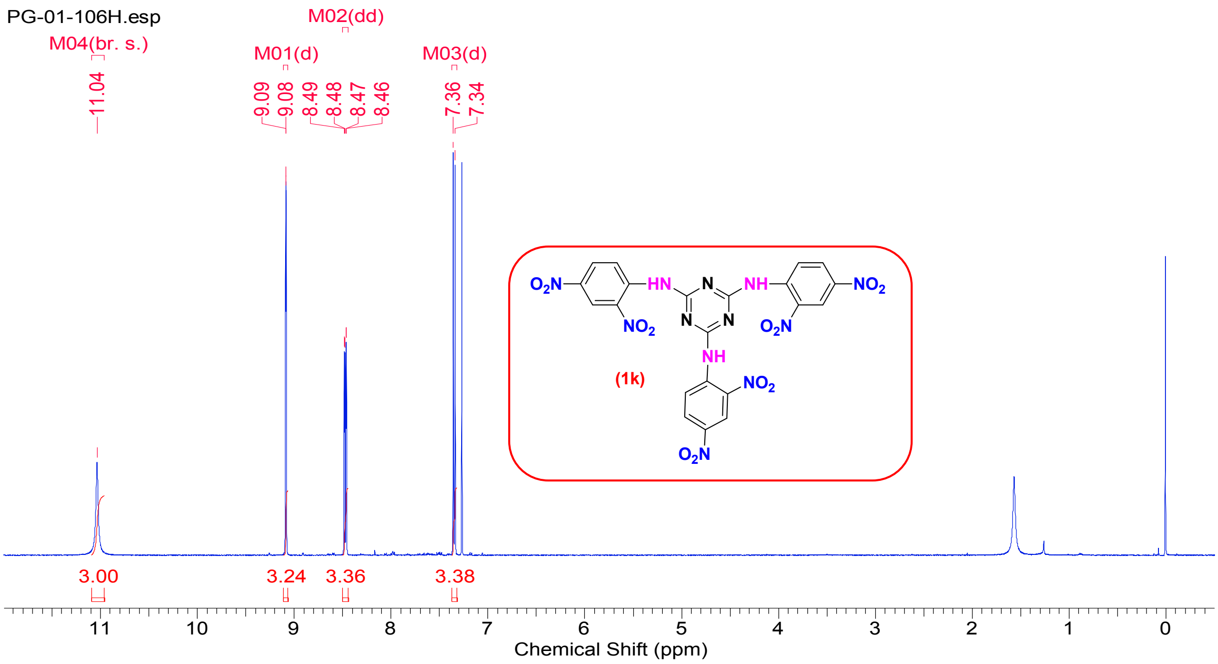
162.
158.
158.
157.
156.
131.
128.
121.67
120.98
111.32
(1j)
N
NH
NO2
N
O2N
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



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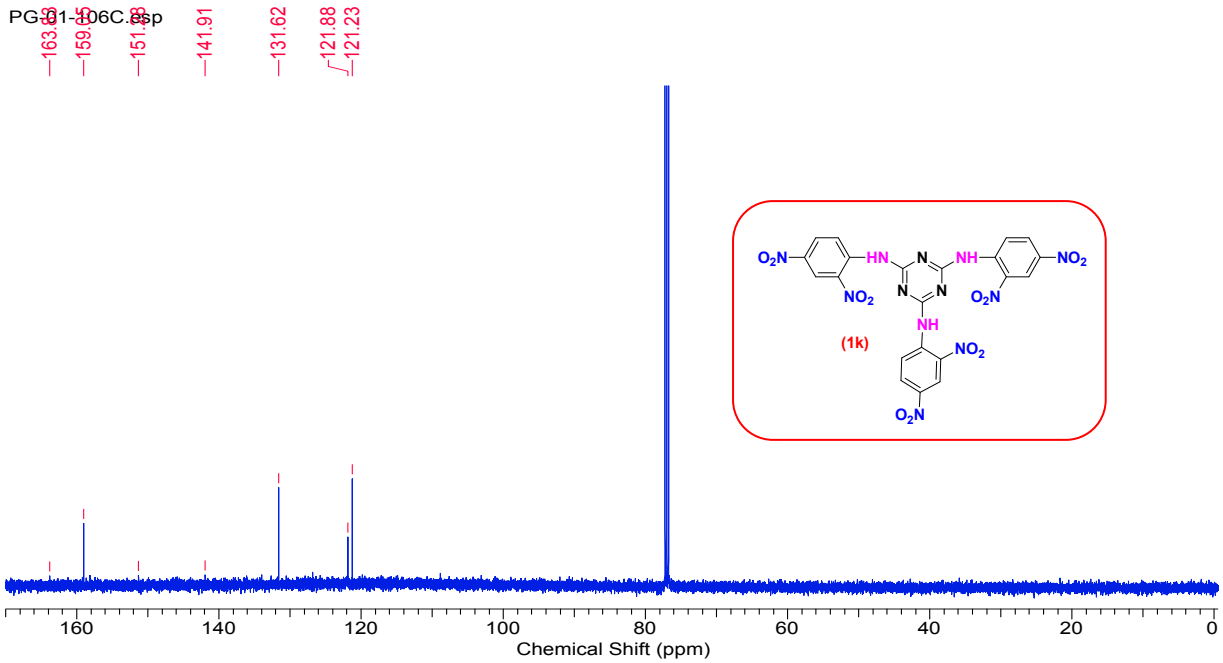
M04(br. s.)
M01(d)
M03(d)
11.04
9.09
9.08
8.49
8.48
8.47
8.46
7.36
7.34
O2N
HN
N
NH
NO2
NO2
N
N
O2N
NH
(1k)
NO2
O2N
3.00
3.24
3.36
3.38
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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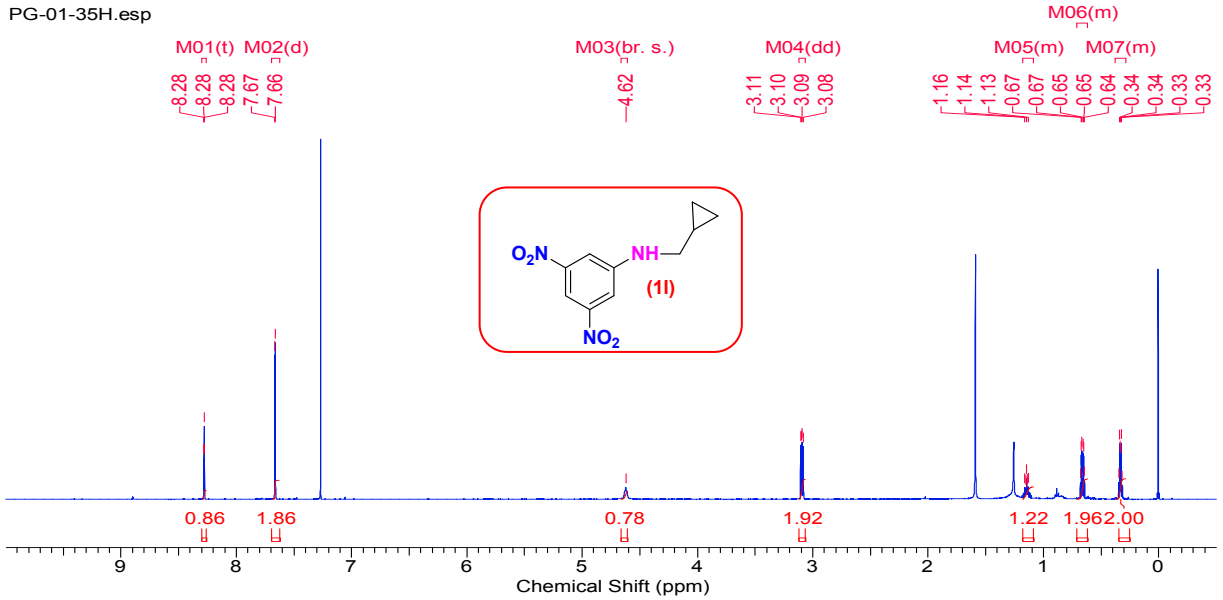
159.45
151.88
141.91
131.62
121.88
121.23
(1k)
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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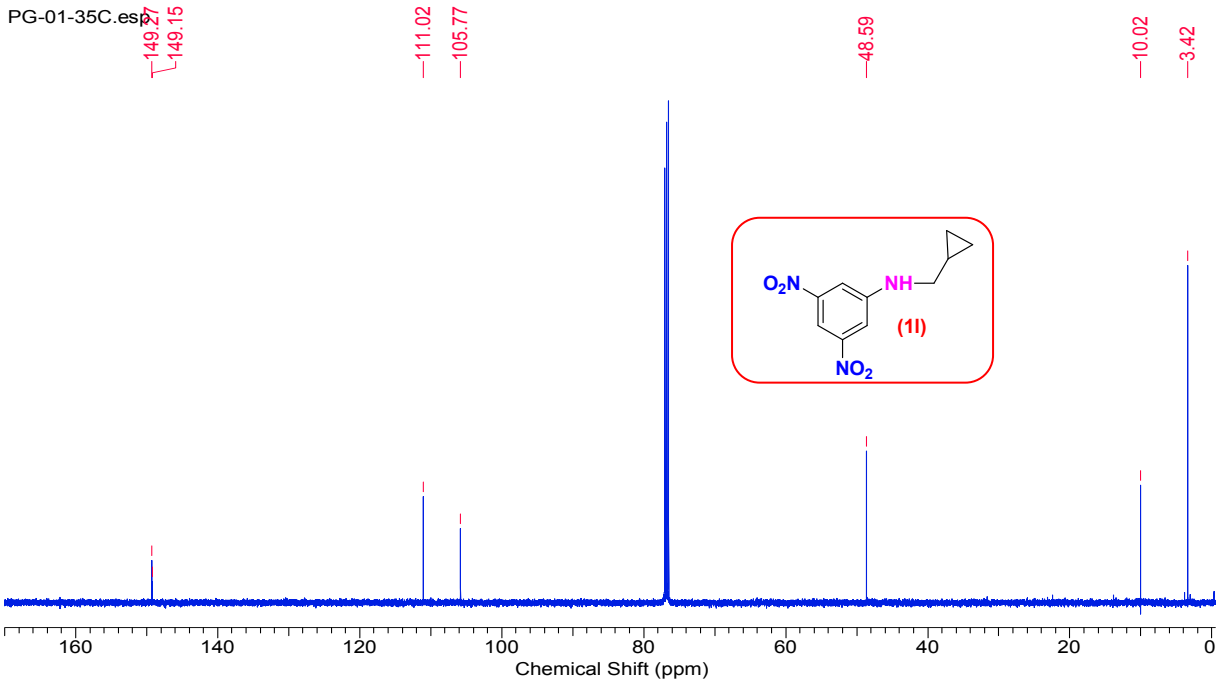
M01(t)
M02(d)
M03(br. s.)
M04(dd)
M05(m)
M06(m)
M07(m)
8.28
8.28
8.28
7.67
7.66
4.62
3.11
3.10
3.09
3.08
1.16
1.14
1.13
0.67
0.67
0.65
0.65
0.64
0.34
0.34
0.33
0.33
(1l)
0.86
1.86
0.78
1.92
1.22
1.96
2.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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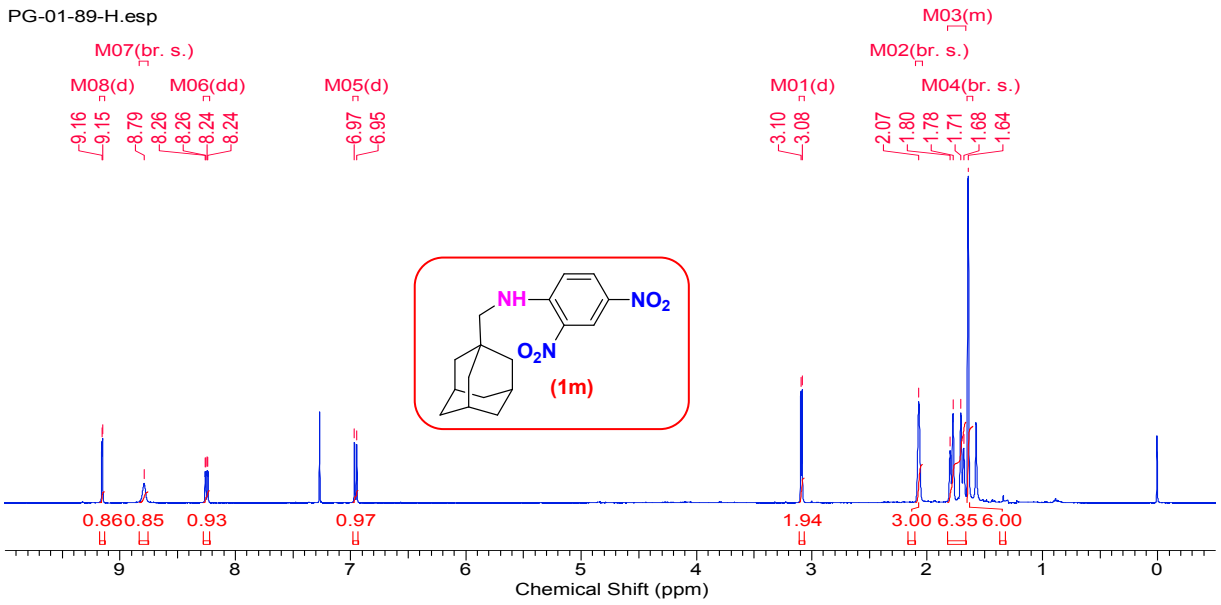
149.27
149.15
111.02
105.77
48.59
10.02
3.42
O2N
NH
NO2
(1l)
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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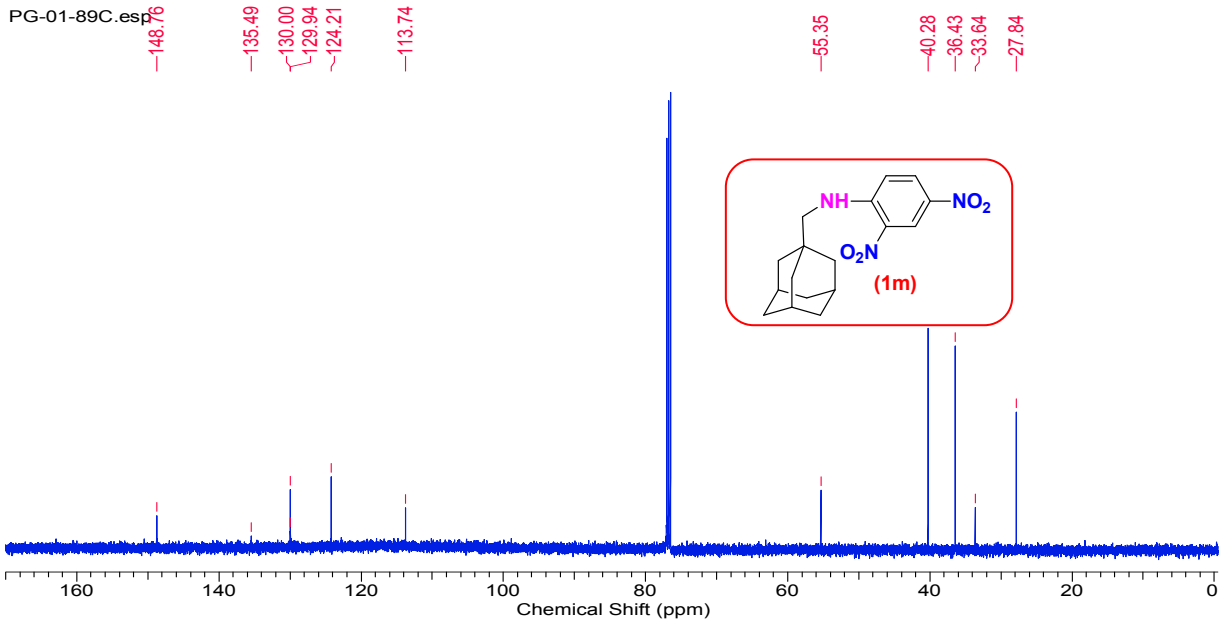
M07(br. s.)
M08(d)
M06(dd)
M05(d)
M01(d)
M03(m)
M02(br. s.)
M04(br. s.)
9.16
9.15
8.79
8.26
8.26
8.24
8.24
6.97
6.95
3.10
3.08
2.07
1.80
1.78
1.71
1.68
1.64
NH
NO2
O2N
(1m)
0.86
0.85
0.93
0.97
1.94
3.00
6.35
6.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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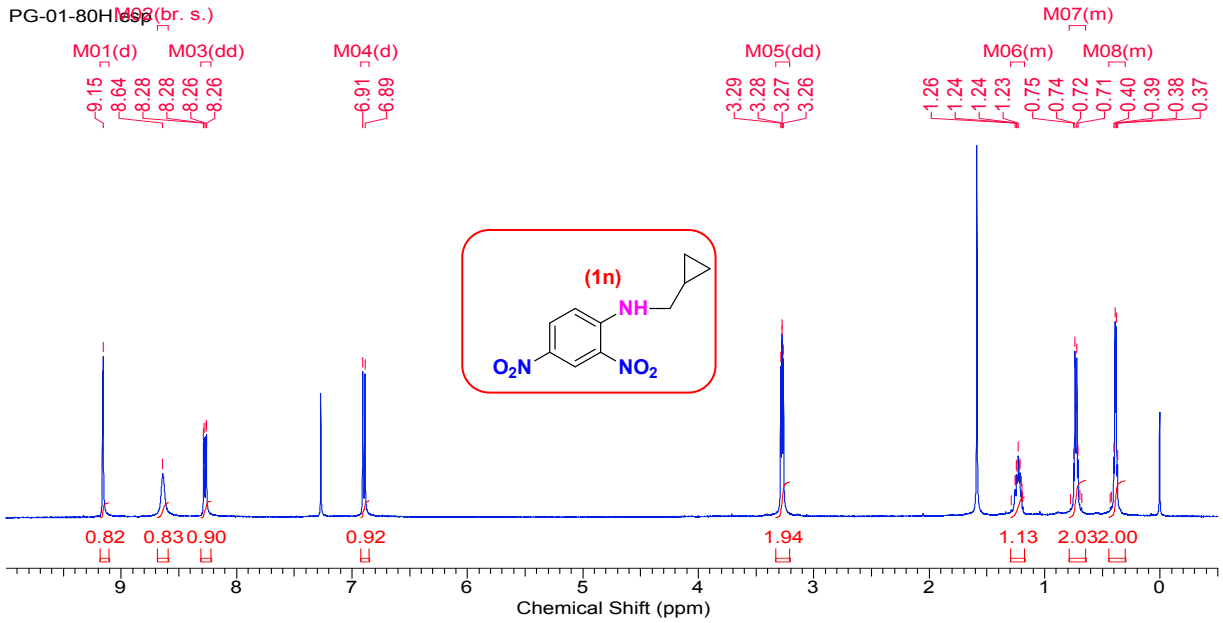
148.76
135.49
130.00
129.94
124.21
113.74
55.35
40.28
36.43
33.64
27.84
NH
NO2
O2N
(1m)
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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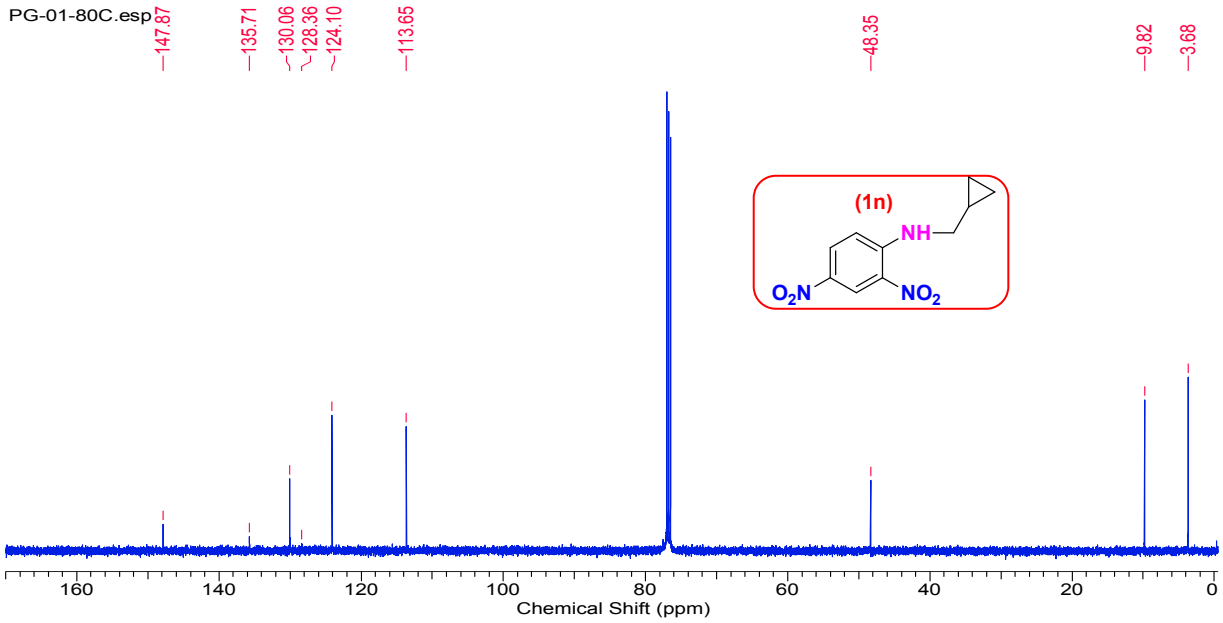
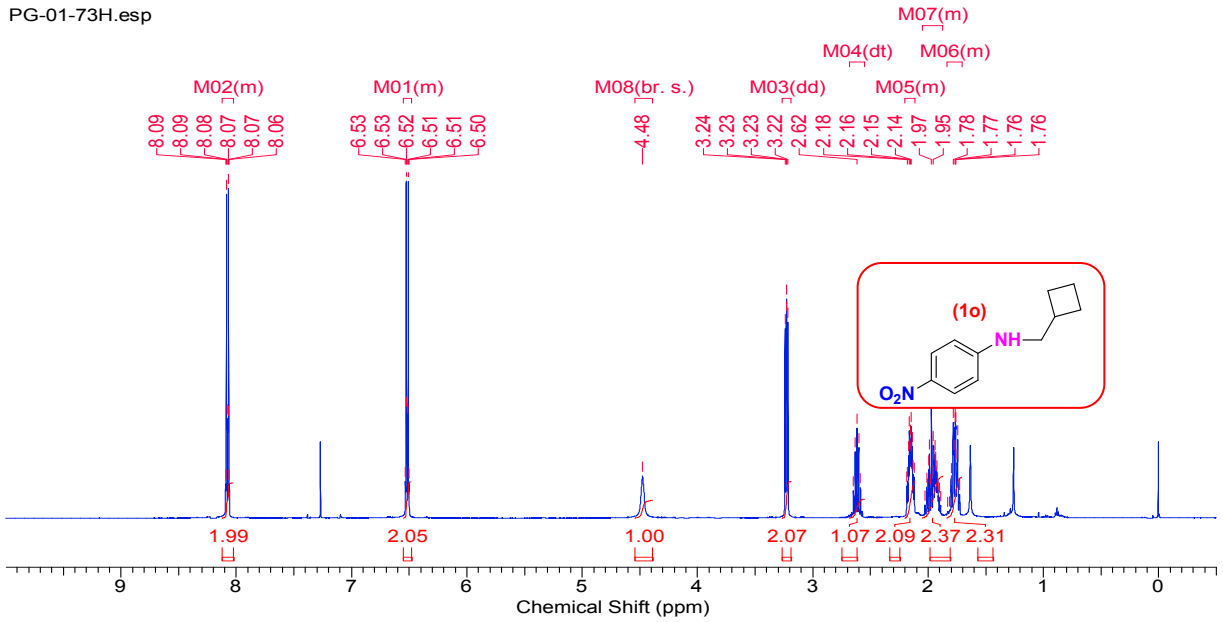
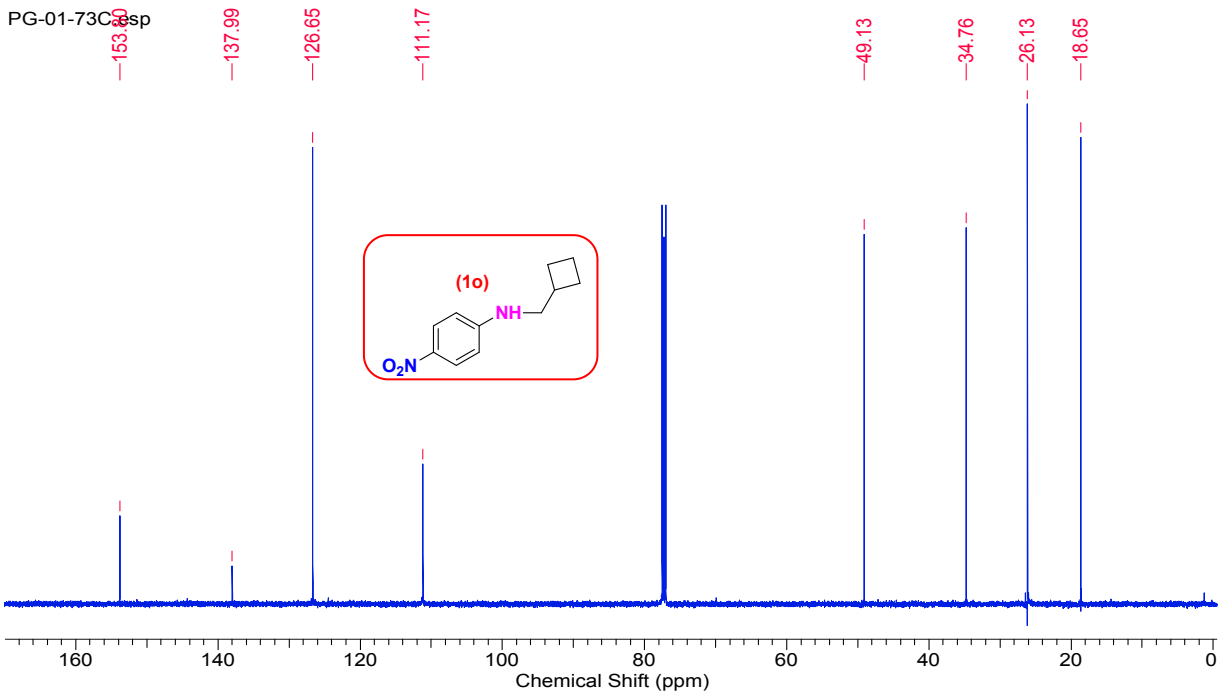
M02(br. s.)
M07(m)
M01(d)
M03(dd)
M04(d)
M05(dd)
M06(m)
M08(m)
9.15
8.64
8.28
8.28
8.26
8.26
6.91
6.89
3.29
3.28
3.27
3.26
1.26
1.24
1.24
1.23
0.75
0.74
0.72
0.71
0.40
0.39
0.38
0.37
(1n)
NH
O2N
NO2
0.82
0.83
0.90
0.92
1.94
1.13
2.03
2.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


PG-01-80C.esp
147.87
135.71
130.06
128.36
124.10
113.65
48.35
9.82
3.68
(1n)
NH
O2N
NO2
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


PG-01-73H.esp
M07(m)
M04(dt)
M06(m)
M02(m)
M01(m)
M08(br. s.)
M03(dd)
M05(m)
8.09
8.09
8.08
8.07
8.07
8.06
6.53
6.53
6.52
6.51
6.51
6.50
4.48
3.24
3.23
3.23
3.22
2.62
2.18
2.16
2.15
2.14
1.97
1.95
1.78
1.77
1.76
1.76
(1o)
NH
O2N
1.99
2.05
1.00
2.07
1.07
2.09
2.37
2.31
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


PG-01-73C.esp
153.80
137.99
126.65
111.17
49.13
34.76
26.13
18.65
(1o)
NH
O2N
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)