Supporting Information

Gold and Palladium Combined for Sonogashira-type Cross-coupling of Arenediazonium Salts

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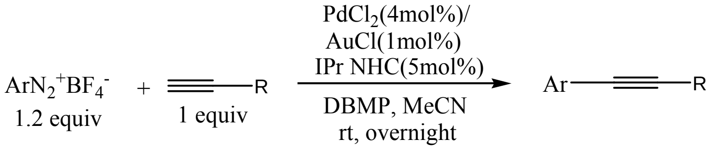
General

^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz or 400 and 100 MHz, respectively. 2,6-Lutidine, Et_3N, 1,4-dioxane, CH_3CN were distilled from CaH_2 and stored over 4 Å activated molecular sieves under an argon atmosphere. Every time THF and hexane were freshly dried over sodium and benzophenone. $BF_3.OEt_2$ was distilled from CaH_2 everytime before reaction. CH_2Cl_2 was distilled from P_2O_5 and stored over 4 Å activated molecular sieves under an argon atmosphere. 2,6-Di-tert-butyl-4-methylpyridine(DBMP) was obtained from Aldrich. $PdCl_2$(Arora metthey, kolkata,India) was stored in the presence of anhydrous calcium chloride in a bench-top desiccator at room temperature and weighed under argon atmosphere. AuCl (Aldrich) was weighed under argon atmosphere.

General Procedure for the Preparation of Arenenediazonium Tetrafluoroborate Salts:[1]

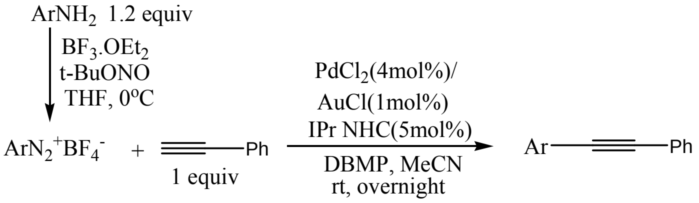
To a solution of the appropriately substituted aniline (10 mmol, 1.0 equiv.) in 100 mL of CH_2Cl_2 at 0 °C was added $BF_3{\cdot}OEt_2$ (15 mmol, 1.5 equiv.) followed by tert-butyl nitrite (12 mmol, 1.2 equiv.). The resulting reaction mixture was stirred for 1h at that temperature and then it was allowed to warm to room temperature. Dry hexane (80 ml) was added to it and the slurry was stirred at this temperature for 10 min and filtered. The crude product was washed with 25 mL of dry CH_2Cl_2 and dried under vacuum to give the benzenediazonium tetrafluoroborate salt in >95% yield.

General procedure for Sonogashira coupling:



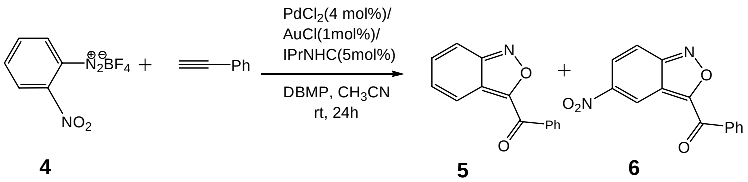
A flame-dried two-necked flask, equipped with gas inlet/outlet, and rubber septum, was evacuated and backfilled with argon (the cycle was performed twice) and then charged under a positive pressure of argon with 2,6-di-tert-butyl-4-methylpyridine(3 mmol), dry CH_3CN (5ml), $PdCl_2$(0.04mmol), AuCl (0.01mmol), (IPr NHC).HCl (0.05 mmol) and the mixture was stirred for 1h at room temperature. Then acetylenes (1 mmol) was added to it and stirring was continued for 5 min. After that a solution of arenediazonium salts (1.2 mmol) in 10 ml CH_3CN was added dropwise over 30 min at 0°C and stirring was continued again for 30 min at that temperature. Then it was warmed to room temperature and monitored by TLC. After completion of reaction it was concentrated, diluted with dichloromethane (10 ml) and poured into aqueous $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (10 ml x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, then the filtrate was evaporated under reduced pressure. The product and base were isolated by chromatography on a silica gel column.

General in situ procedure for Sonogashira coupling:



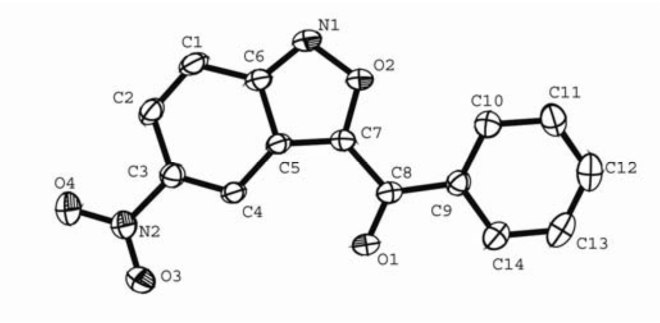
A flame-dried two-necked flask, equipped with gas inlet/outlet , and rubber septum, was evacuated and backfilled with argon (the cycle was performed twice) and then charged under a positive pressure of argon at 0°C with anilines (1.2 mmol), dry THF (5 ml) followed by $BF_3.OEt_2$ (1.8 mmol) and stirred for 15 min. To the solution was added tert-butyl nitrite (1.44 mmol) diluted with 2 ml THF and stirring was continued for 1h at 0ºC. Then $PdCl_2$(0.04mmol), AuCl(0.01mmol), (IPr NHC).HCl (0.05 mmol) followed by a mixture of 2,6-di-tert-butyl-4-methylpyridine(3 mmol), terminal acetylene (1 mmol) in CH_3CN (8 ml) was added dropwise and stirring was continued for 30 min at that temperature. The reaction mixture was warmed to room temperature and monitored by TLC. After completion of reaction it was concentrated, then diluted with dichloromethane (10 ml) and poured into aqueous $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (10ml x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, then the filtrate was evaporated under reduced pressure. The product and base were isolated by chromatography on a silica gel column.

Tandem reaction of 2-nitrobenzenediazonium tetrafluoroborate:



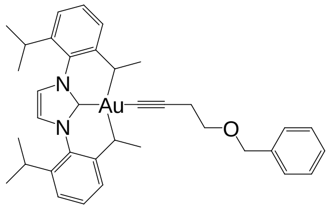
A flame-dried two-necked flask, equipped with gas inlet/outlet, and rubber septum, was evacuated and backfilled with argon (the cycle was performed twice) and then charged under a positive pressure of argon with 2,6-di-tert-butyl-4-methylpyridine (615 mg, 3 mmol), dry CH_3CN (5 ml), $PdCl_2$(7 mg, 0.04 mmol), AuCl (3 mg, 0.01mmol), (IPr NHC).HCl (14 mg, 0.05 mmol) and the mixture stirred for 1h at room temperature. Then phenylacetylene (102 mg, 0.011ml, 1 mmol) was added to it and stirring was continued for 5 min. After that a solution of 2-nitrobenzenediazonium tetrafluoroborate (285 mg, 1.2 mmol) in 10 ml CH_3CN was added dropwise over 30 min at 0°C and stirring was continued again for 30 min at that temperature. Then it was warmed to room temperature and strring was continued for 24 h. After completion of reaction it was concentrated, then diluted with dichloromethane (10 ml) and poured into water and the aqueous layer was extracted with dichloromethane (10 ml x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, then the filtrate was evaporated under reduced pressure. The products **5** (65 mg, 29%) and **6** (88 mg, 33%) were isolated by chromatographic purification on a silica gel column.

Crystal data of compound **6**: $C_{14}H_8N_2O_4$, M_r- 268.22, T-293 K, monoclinic, space group I 2/a, a = 13.0640(10), b = 12.9928(10), c = 14.0524(11)Å, V =2375.2(3)A^3, Z = 7, Final indices R_1 = 0.0552, wR_2=0.1114. **CCDC** 753368.



ORTEP diagram of compound **6**

Preparation of gold-acetylide complex(8):

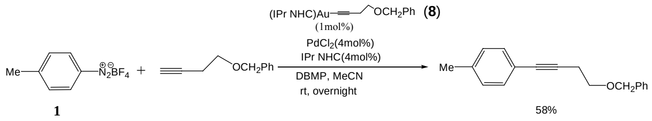


8

A solution of NaOH (1.5 mg, 0.0375 mmol) in 2 ml methanol was added to the mixture of (IPr NHC)AuCl(10 mg, 0.0156 mmol) and but-3-ynyloxymethyl-benzene(5 mg, 0.0312 mmol) in dry methanol (3 ml). Then the flask was covered by a black paper and the mixture was allowed to stir at room temperature under argon overnight. The solvent was removed under reduced pressure. Then the crude product was diluted by diethyl ether and filtered through a small Celite bed (to remove the salts) and the filtrate was dried in vacuum. The solid material was washed by dry hexane (1ml) twice (to remove the excess but-3-ynyloxymethyl-benzene) and the solid was dried under vacuum yielding 10 mg (86%) of gold-acetylid **8**.

1H NMR (200 MHz, CDCl3): δ 7.50-7.42(d, *J* = 7.6, 2H), 7.27-7.24(m, 9H), 7.07(s, 2H), 4.44(s, 2H), 3.48(t, J = 7.6, 2H), 2.63-2.40(m, 3H), 1.35(s, 3H), 1.32(s, 3H), 1.20(s, 3H), 1.16(s, 3H); HRMS(ES+) calculated for $C_{38}H_{48}N_2OAu$(M+H)+ m/z 745.3432, found 745.3425 and for $C_{38}H_{47}N_2OAuNa$ (M+Na)+ calculated 767.3252, found 767.3244.

Sonogashira coupling using preformed alkynylgold as catalyst:

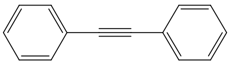


A flame-dried two-necked flask, equipped with gas inlet/outlet, and rubber septum, was evacuated and backfilled with argon (the cycle was performed twice) and then charged under a positive pressure of argon with 2,6-di-tert-butyl-4-methyl pyridine(410 mg, 3 mmol), dry CH_3CN (5 ml), $PdCl_2$(7 mg, 0.04 mmol), gold-acetylide complex **8**(7 mg, 0.01mmol), (IPr NHC).HCl (10 mg, 0.04 mmol) and the mixture stirred for 1h at room temperature. Then but-3-ynyloxymethyl-benzene (60 mg, 1 mmol) was added to it and stirring was continued for 15 min. After that a solution of 4-methylbenzenediazonium salt **1**(247 mg, 1.2 mmol) in 6 ml CH_3CN was added dropwise over 30 min at 0 °C and stirring was continued again for 30 min at that temperature. Then it was warmed to room temperature and stirred overnight. After completion of reaction it was concentrated, then diluted with dichloromethane (10 ml) and poured into aqueous

$NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (10 ml x 3). The combined organic layer was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The product and base were isolated by chromatography on a silica gel column: yield of the product was 93 mg (58%), accompanied with 390 mg, 95% recovery of base (DBMP).

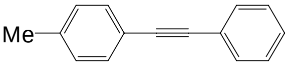
Proton and carbon NMR spectral data:

Diphenylacetylene[2]



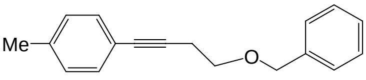
^{1}H NMR (200 MHz, $CDCl_3$) δ 7.64-7.59 (m, 4H), 7.41-7.38 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 131.76, 128.49, 128.39, 123.45, 89.58.

Phenyl-p-tolyl-acetylene[3]



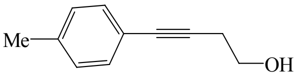
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55-7.50 (m, 2H), 7.43 (d, J= 8Hz, 2H) , 7.37-7.32 (m, 3H), 7.16 (d, J= 7.8Hz, 2H), 2.37 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.34, 131.48, 131.43, 129.06, 128.26, 128.02, 123.37, 120.08, 89.47, 88.63, 21.48.

1-(4-Benzyloxy-but-1-ynyl)-4-methyl-benzene



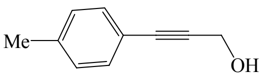
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.37-7.29 (m, 7H), 7.10 (d, 2H), 4.61 (s, 2H), 3.69 (t, 2H), 2.74 (t, 2H), 2.34 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 138.37,137.85, 131.64, 129.09, 128.56, 127.83, 127.80, 120.76, 86.09, 81.75, 73.14, 68.72, 21.53, 21.04; HRMS(FAB) calculated for $C_{18}H_{19}O(M+H)^+$ m/z 251.1436, found 251.1435.

4-p-Tolyl-but-3-yn-1-ol[4]



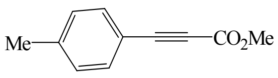
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.30 (d, J= 6.4Hz, 2H), 7.09 (d, J= 7.8Hz, 2H), 3.79 (dd, J= 12, 6Hz, 2H), 2.68 (t, J= 6.3Hz, 2H), 2.33(s, 3H), 1.93 (t, J= 6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ137.97, 131.52, 129.00, 120.22,85.47, 82.57, 61.20, 23.84, 21.39.

3-p-Tolyl-prop-2-yn-1-ol[5]



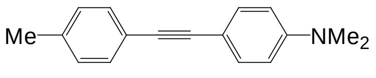
^{1}H NMR (200 MHz, CDCl3): δ 7.33 (d, J= 8.2Hz, 2H), 7.11 (d, J= 7.8Hz, 2H), 4.49(s, 2H) 2.34 (s, 3H), 2.02 (brs,1H); ^{13}C NMR (50 MHz, CDCl3): δ 138.76, 131.72, 129.20, 119.60, 86.69, 85.95, 51.78, 21.57.

p-Tolyl-propynoic acid methyl ester[6]



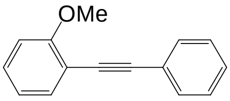
^{1}H NMR (200 MHz, CDCl3): δ 7.48 (d, J= 8Hz, 2H), 7.18 (d, J= 8Hz, 2H), 3.83 (s, 3H) 2.38 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.82, 141.56, 133.21, 129.57, 116.63, 87.28, 80.22, 52.92, 21.91.

Dimethyl-(4-p-tolylethynyl-phenyl)-amine[7]



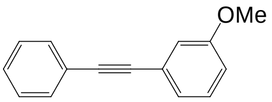
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.39-7.35(m, 4H), 7.09(d, J =7.8, 2H), 6.63(d, J =8, 2H); ^{13}C NMR (50 MHz, CDCl3): δ 150.23, 137.68, 132.85, 131.40, 129.22, 121.28, 112.10, 110.59, 90.02, 87.64, 40.45, 21.66.

1-Methoxy-2-phenylethynyl-benzene[2]



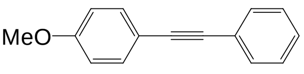
^{1}H NMR (200 MHz, CDCl3): δ 7.57-7.48 (m, 3H), 7.37-7.27 (m, 4H), 6.98-6.89 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (50 MHz, CDCl3): δ 160.00, 133.61, 131.70, 129.78, 128.27, 128.13, 123.64, 120.53, 112.55, 110.80, 93.47, 85.79, 55.88.

1-(2-(3-Methoxyphenyl)ethynyl)benzene[3]



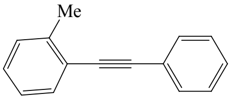
^{1}H NMR (200 MHz, CDCl3) δ 7.54-7.52 (m, 2H), 7.36-7.30 (m, 3H), 7.24 (d, J = 8Hz, 1H), 7.13 (d, J= 8Hz, 1H), 7.06 (m, 1H), 6.92-6.88 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (50 MHz, CDCl3) δ 159.40, 131.67, 129.44, 128.38, 128.34, 124.31, 124.23, 123.23, 116.39, 114.99, 89.34, 89.23, 55.33.

4-Phenylethynylanisole[2]



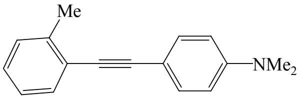
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.54-7.45 (m, 4H), 7.36-7.31 (m, 3H), 6.91-6.85 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 159.79, 133.21, 131.61, 128.47, 128.09, 123.77, 115.55, 114.17, 89.56, 88.24, 55.43.

1-Methyl-2-phenylethynyl-benzene[2]



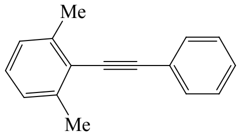
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.65-7.57 (m, 3H), 7.45-7.39 (m, 3H), 7.31-7.21 (m, 3H), 2.60 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.37, 132.05, 131.71, 129.66, 128.55, 128.50, 128.36, 125.79, 123.78, 123.25, 93.57, 88.57, 20.93.

Dimethyl-(4-o-tolylethynyl-phenyl)-amine



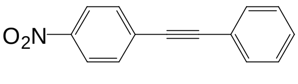
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.48-7.39(m, 3H), 7.21-7.12(m, 3H), 6.69-6.65(m, 2H), 2.99(s, 6H), 2.50(s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.27, 139.89, 132.77, 131.62, 129.49, 127.66, 125.64, 124.06, 112.07, 110.63, 94.74, 86.45, 40.43, 20.96.

2,6-Dimethylphenyl phenyl acetylene[3]



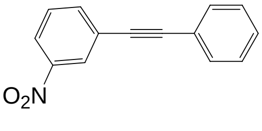
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.69-7.64 (m, 2H), 7.48-7.43 (m, 3H), 7.28-7.14 (m, 3H), 2.64 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.32, 131.49, 128.45, 128.17, 127.87, 126.81, 123.96, 123.08, 97.98, 87.28, 21.21.

1-Nitro-4-phenylethynyl-benzene[2]



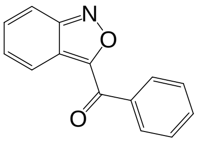
^{1}H NMR (200 MHz, $CDCl_3$): δ 8.24-8.20(m, 2H), 7.68-7.64(m, 2H), 7.58-7.54(m,2H), 7.40-7.37(m,3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 147.04, 132.28, 131.86, 130.29, 129.28, 128.55, 123.65, 122.15, 94.72, 87.56.

1-Nitro-3-phenylethynyl-benzene[8]



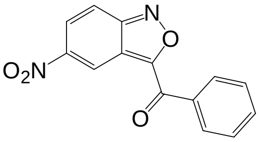
^{1}H NMR (200 MHz, CDCl$_3$): δ 8.32(s, 1H), 8.18-8.09(m, 1H), 7.82-7.75(m,1H), 7.55-7.38(m,3H), 7.36-7.32(m, 3H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 148.12, 137.22, 131.79, 129.38, 129.08, 128.52, 126.35, 125.12, 122.87, 122.19, 91.95, 86.91.

Benzo[c]isoxazol-3-yl-phenyl-methanone[9]



^{1}H NMR (400 MHz, CDCl$_3$): δ 8.31-8.29(m, 2H), 8.15(d, J =8.8,1H), 7.77(d, J =9.2,1H), 7.71-7.67(m, 1H), 7.61-7.57(m, 2H), 7.46-7.42(m, 1H), 7.32-7.29(m,1H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 181.54, 160.47, 157.35, 136.11, 133.84, 131.39, 130.16, 128.79, 128.51, 121.74, 121.68, 115.94

(5-Nitro-benzo[c]isoxazol-3-yl)-phenyl-methanone 6



^{1}H NMR (400 MHz, CDCl$_3$): δ 9.16(s, 1H), 8.32(d, J = 7.6, 2H), 8.21-8.19(m, 1H), 7.907(d, J = 9.6, 1H), 7.75-7.71(m, 1H), 7.63-7.60(m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 180.58, 164.74, 156.83, 147.51, 135.05, 134.73, 130.31, 129.08, 125.43, 121.15, 119.92, 117.71; HRMS(FAB) calcd. for $C_{14}H_9O_4N_2(M+H)^+$ m/z 269.0562, found 269.0557.

References:

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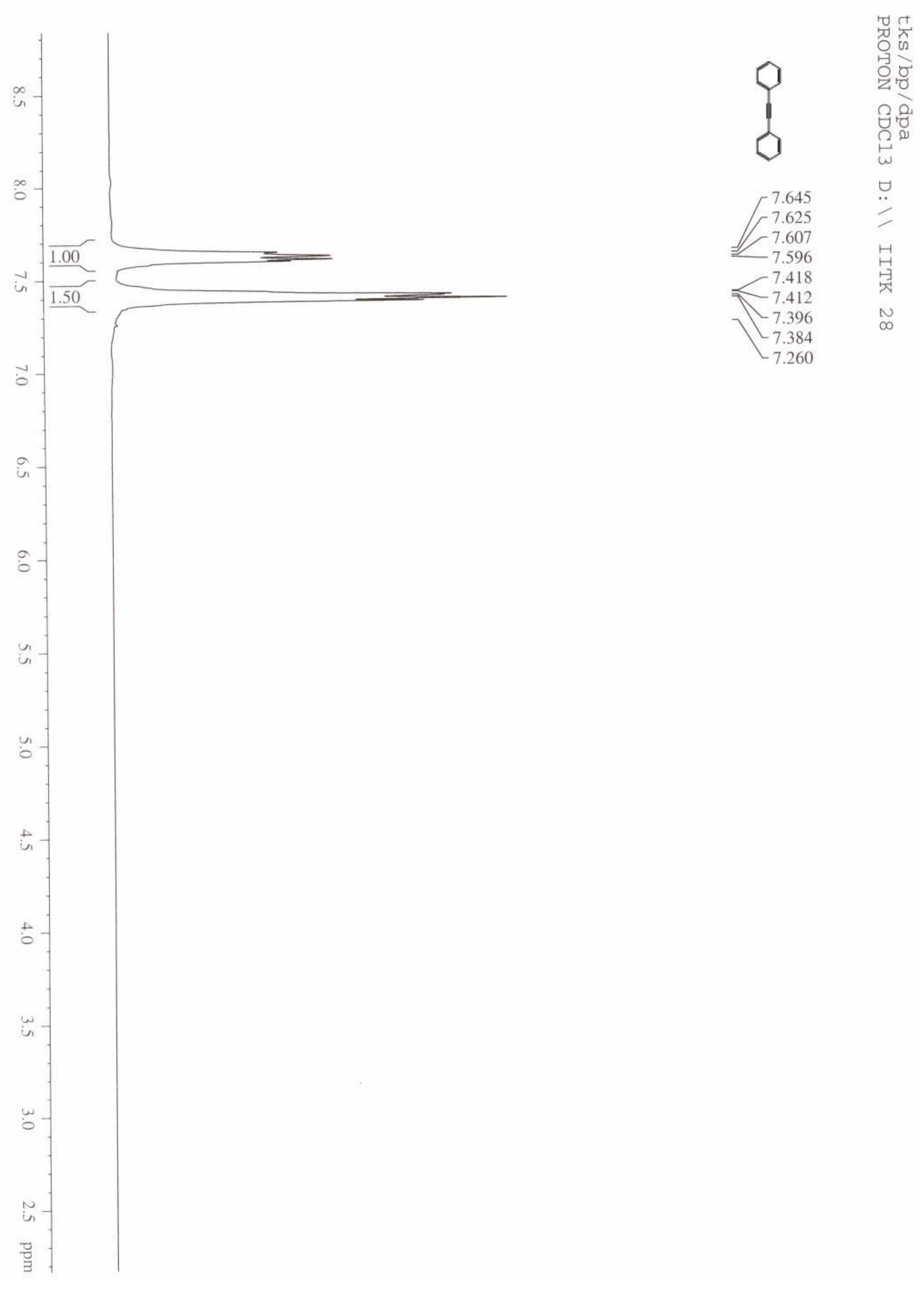
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7.625
7.607
7.596
7.418
7.412
7.396
7.384
7.260
1.00
1.50
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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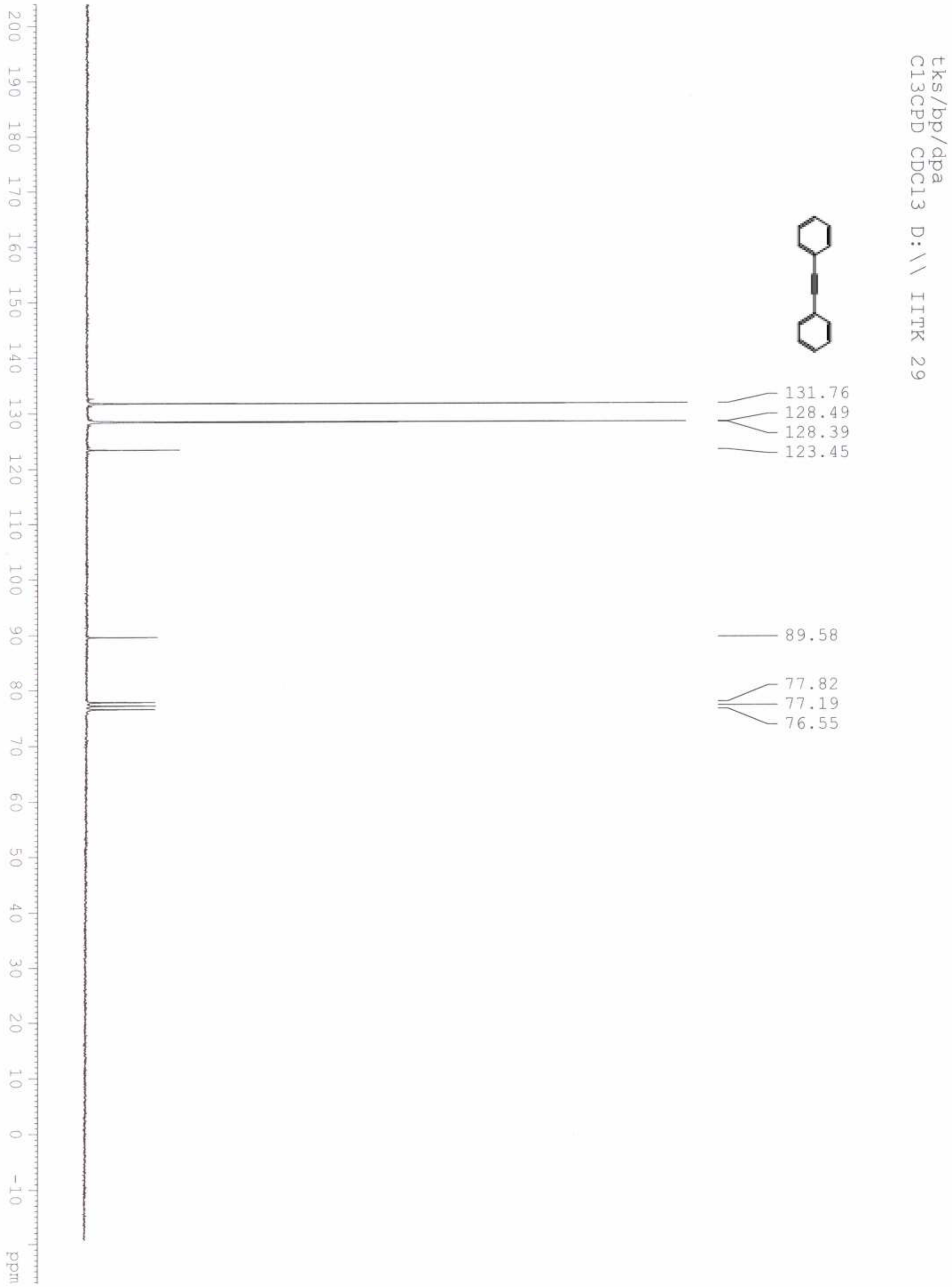
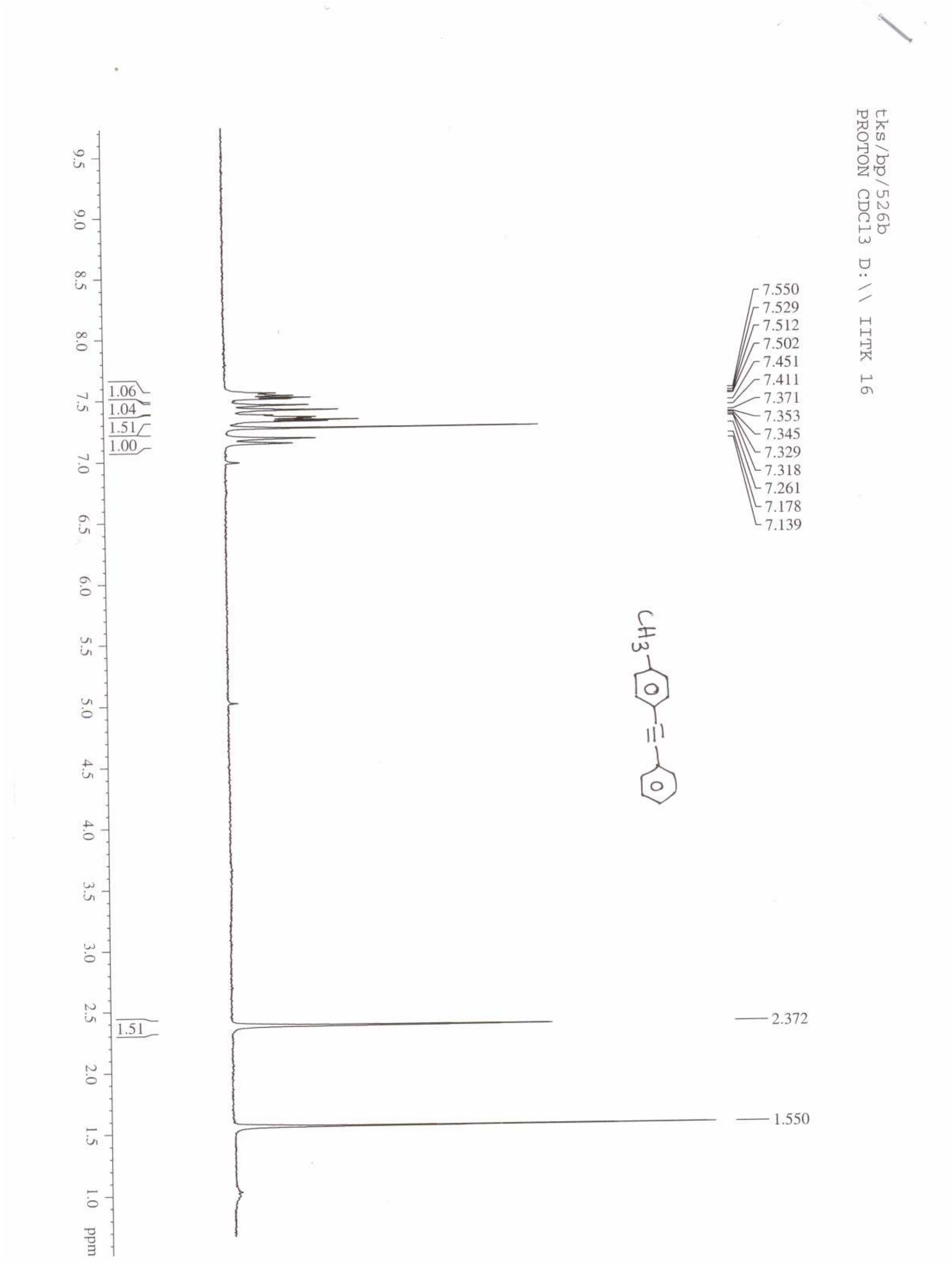
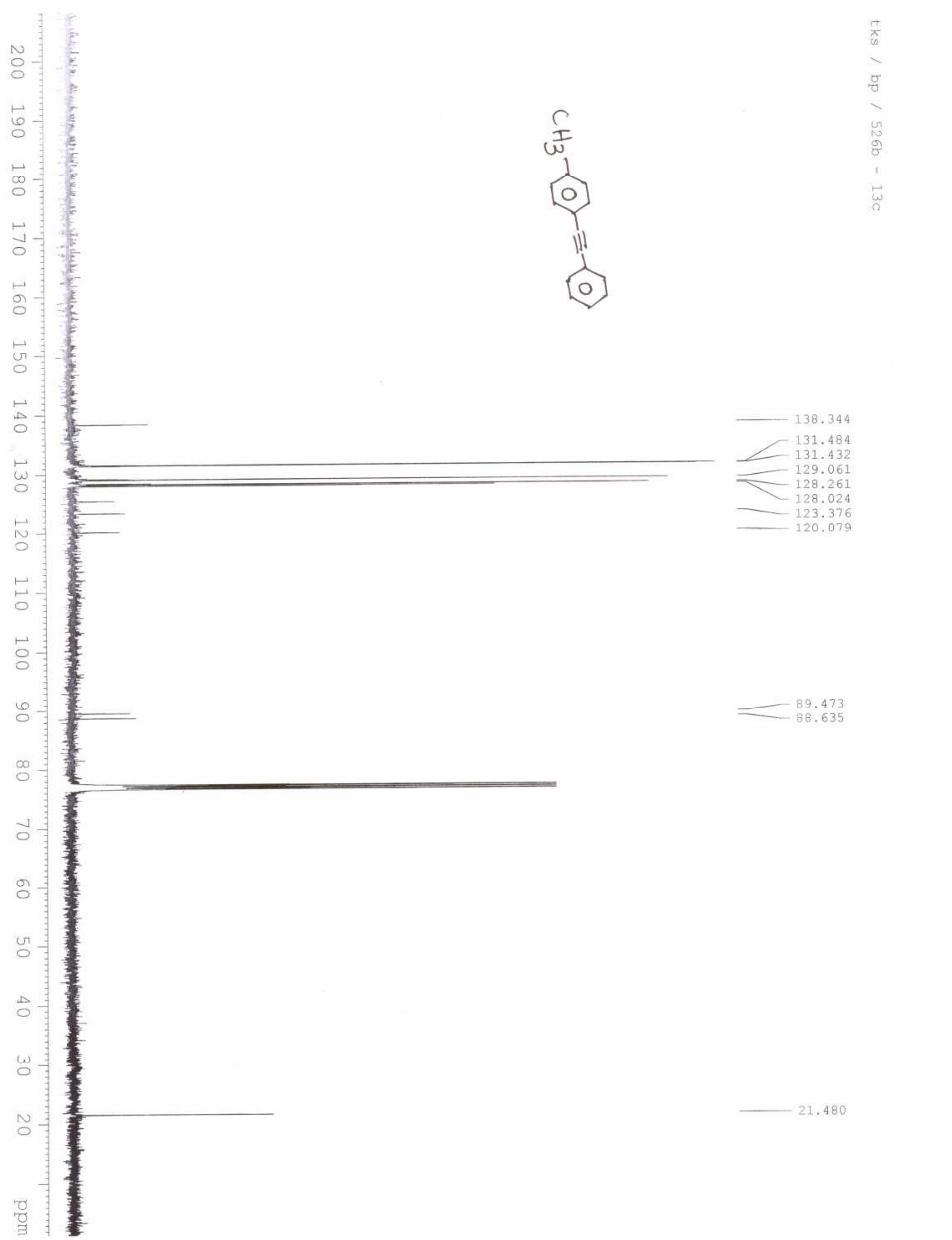
4.0
3.5
3.0
2.5
ppm


tks/bp/dpa
C13CPD CDCl3 D:\\ IITK 29
131.76
128.49
128.39
123.45
89.58
77.82
77.19
76.55
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


tks/bp/526b
PROTON CDCl3 D:\\ IITK 16
7.550
7.529
7.512
7.502
7.451
7.411
7.371
7.353
7.345
7.329
7.318
7.261
7.178
7.139
2.372
1.550
1.06
1.04
1.51
1.00
1.51
CH3
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
ppm


tks / bp / 526b - 13c
CH3
138.344
131.484
131.432
129.061
128.261
128.024
123.376
120.079
89.473
88.635
21.480
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

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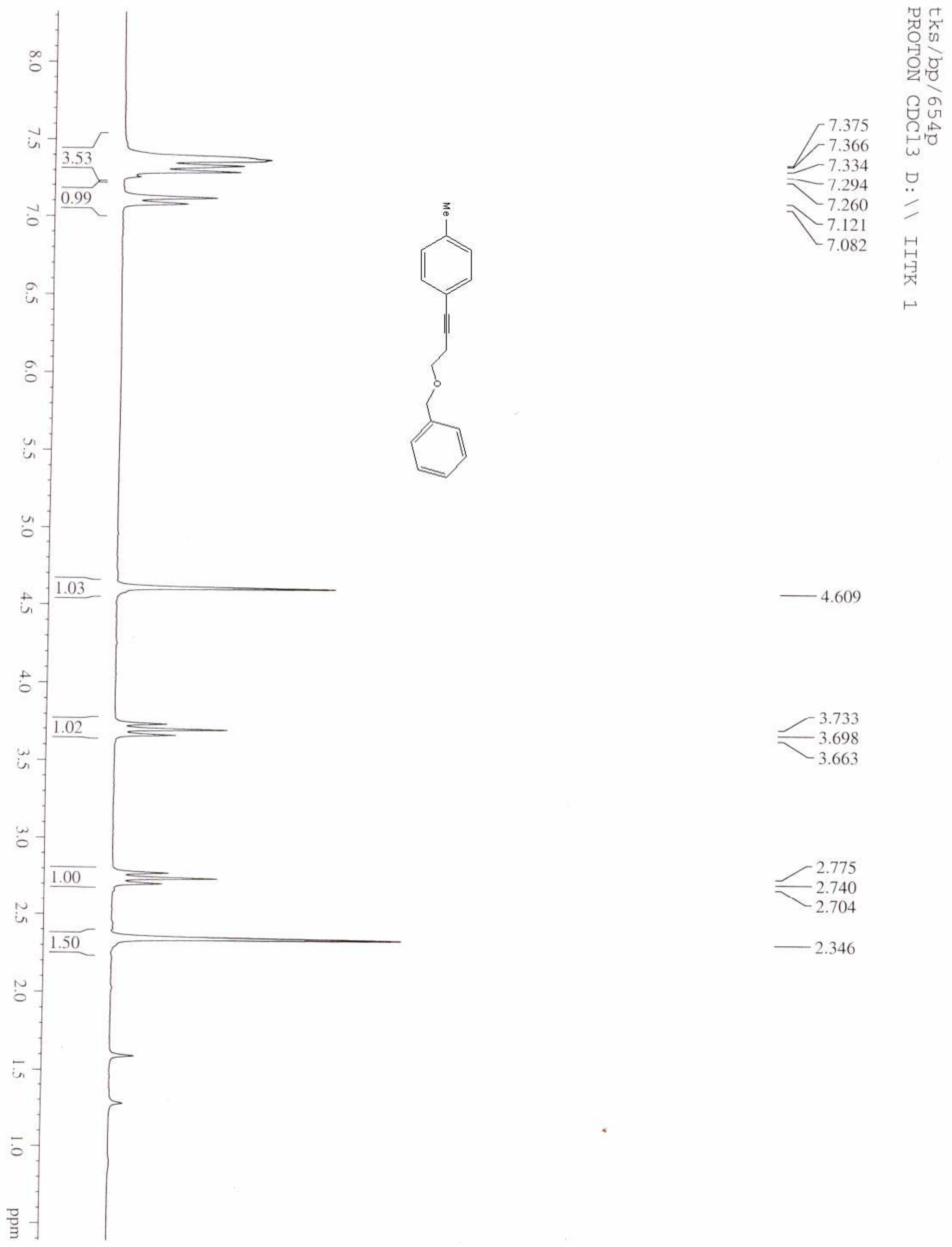

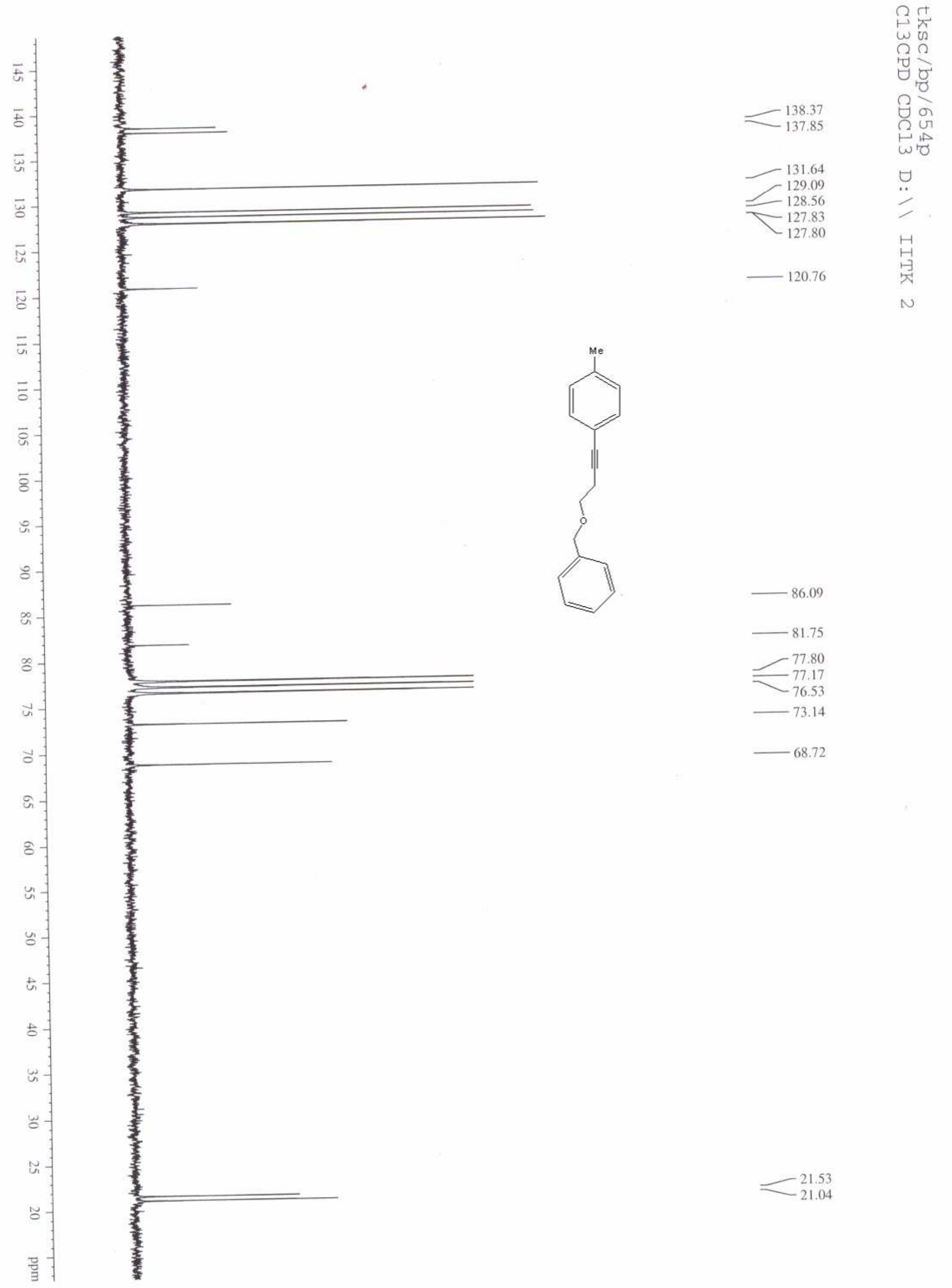
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C13CPD CDCl3 D:\\ IITK 2
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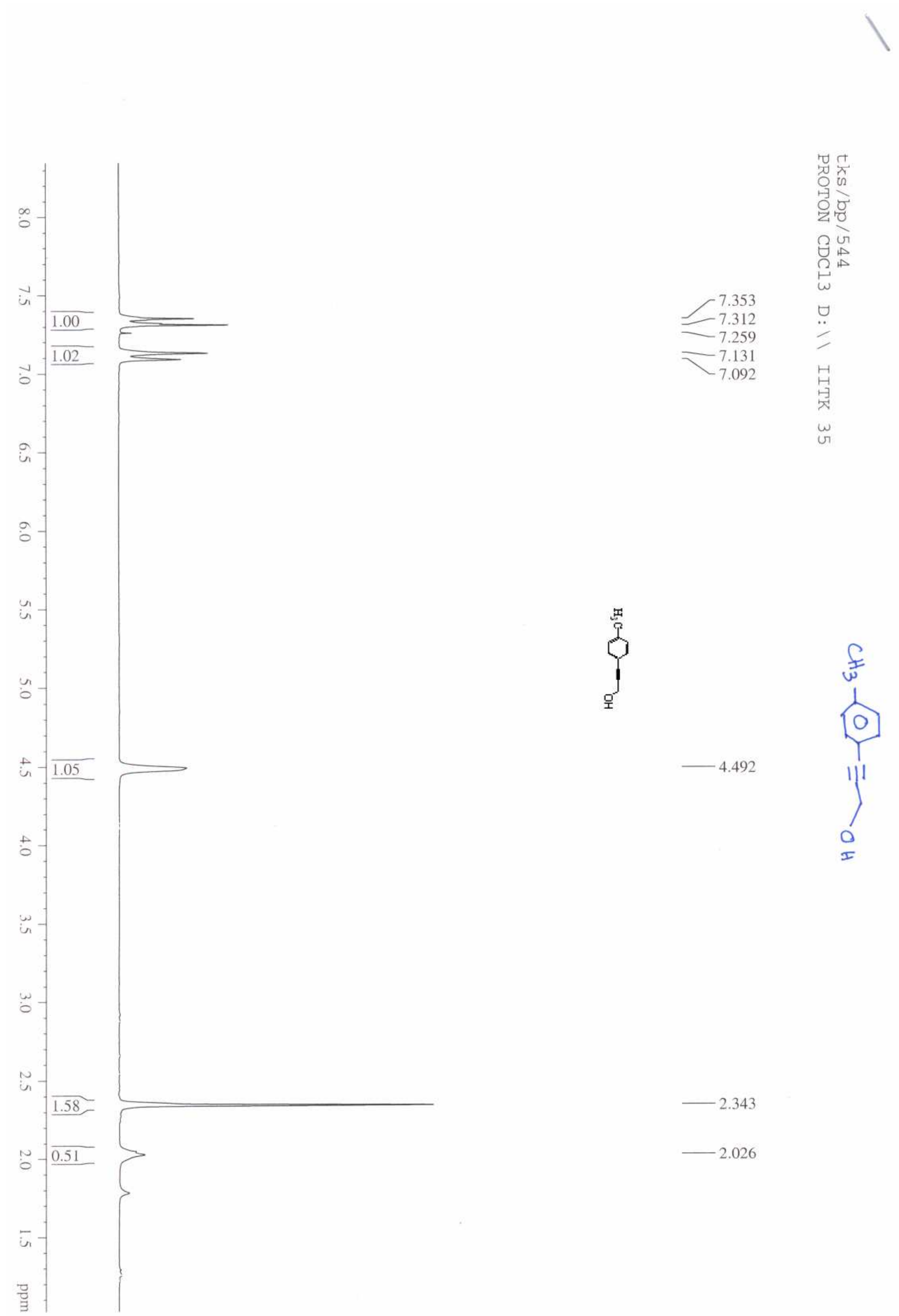
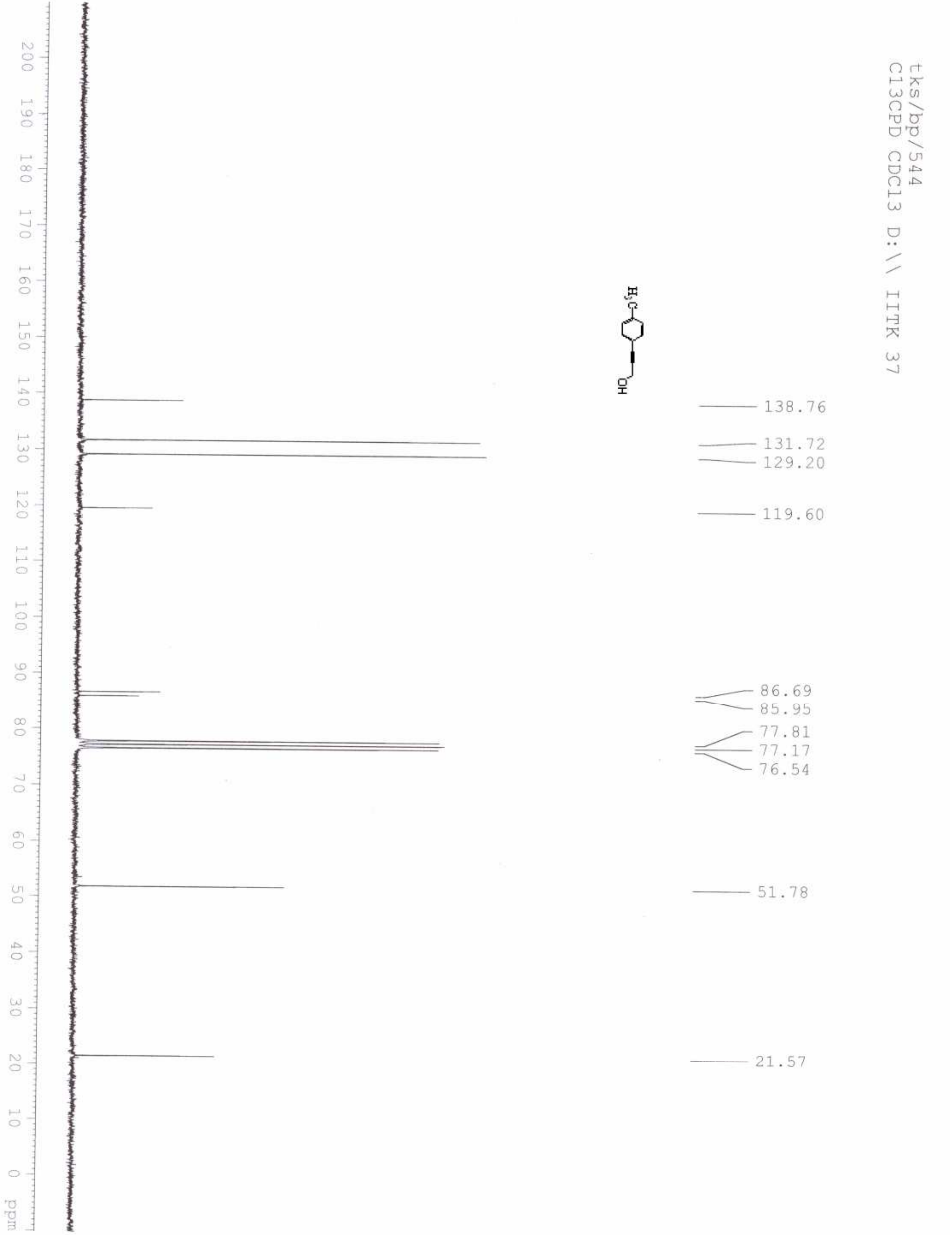
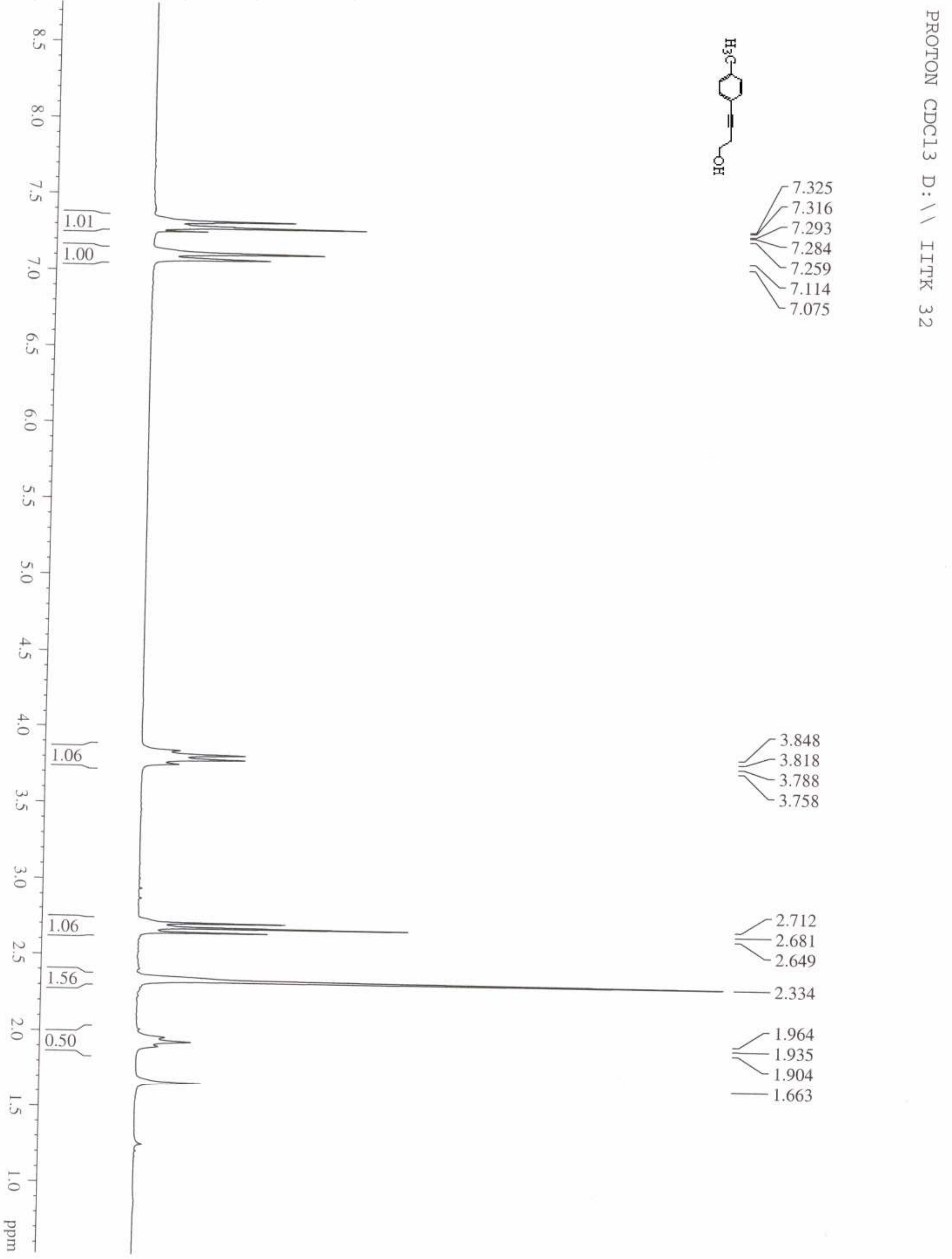
137.85
131.64
129.09
128.56
127.83
127.80
120.76
86.09
81.75
77.80
77.17
76.53
73.14
68.72
21.53
21.04
Me
O
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
ppm


tks/bp/544
PROTON CDCl3 D:\\ IITK 35
7.353
7.312
7.259
7.131
7.092
4.492
2.343
2.026
1.00
1.02
1.05
1.58
0.51
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
ppm
H3C
OH
CH3
OH


tks/bp/544
C13CPD CDCl3 D:\\ IITK 37
H3C
OH
138.76
131.72
129.20
119.60
86.69
85.95
77.81
77.17
76.54
51.78
21.57
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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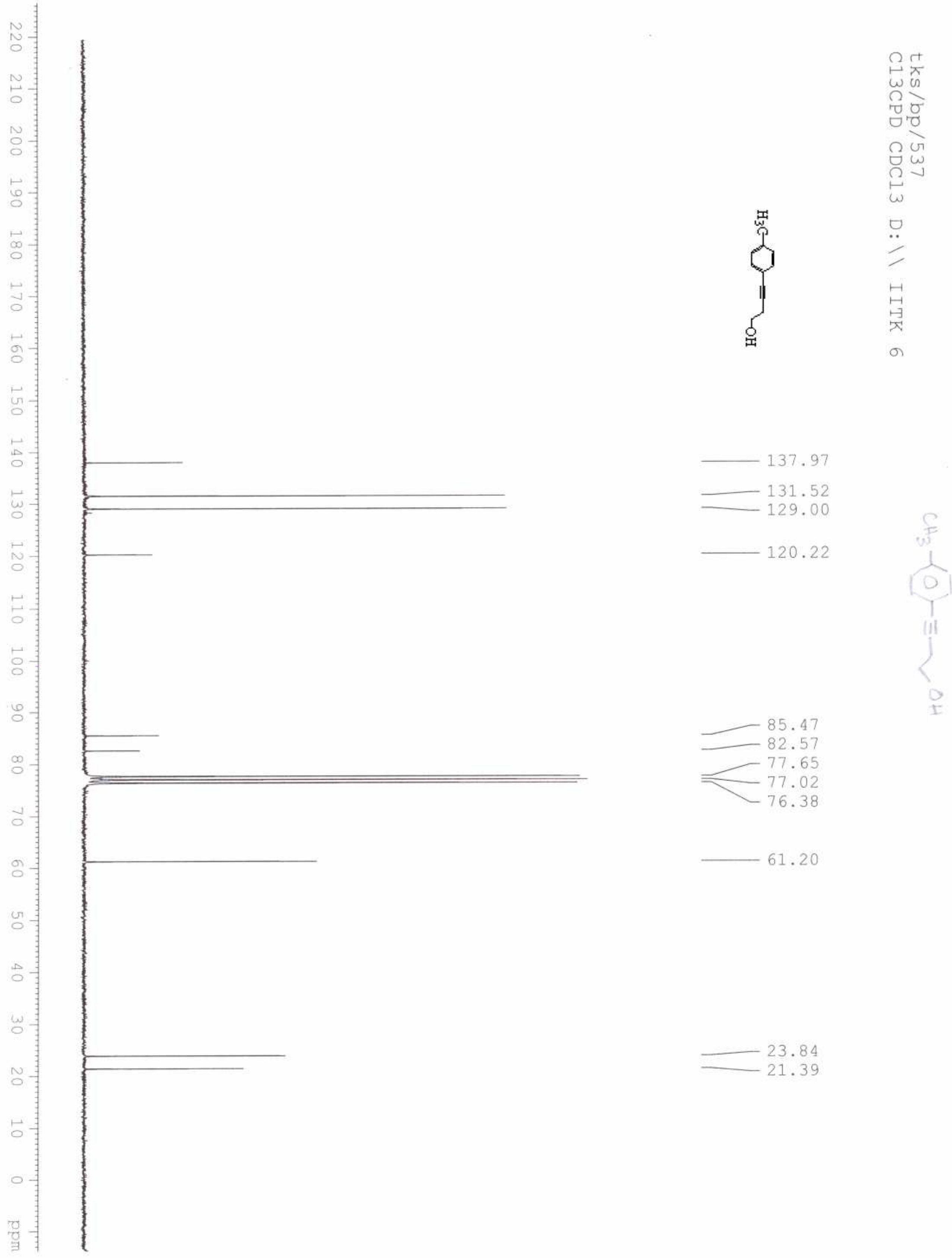
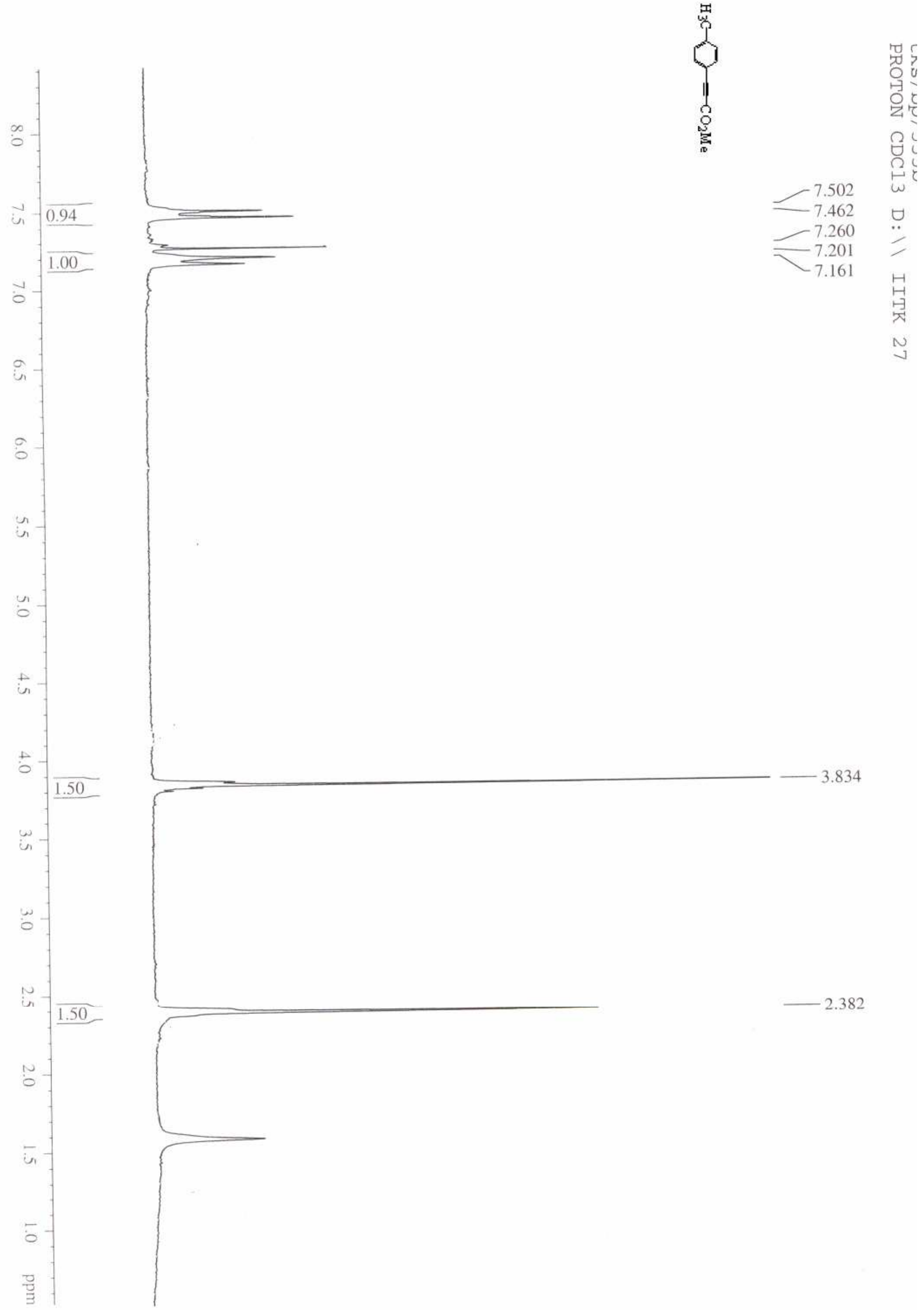
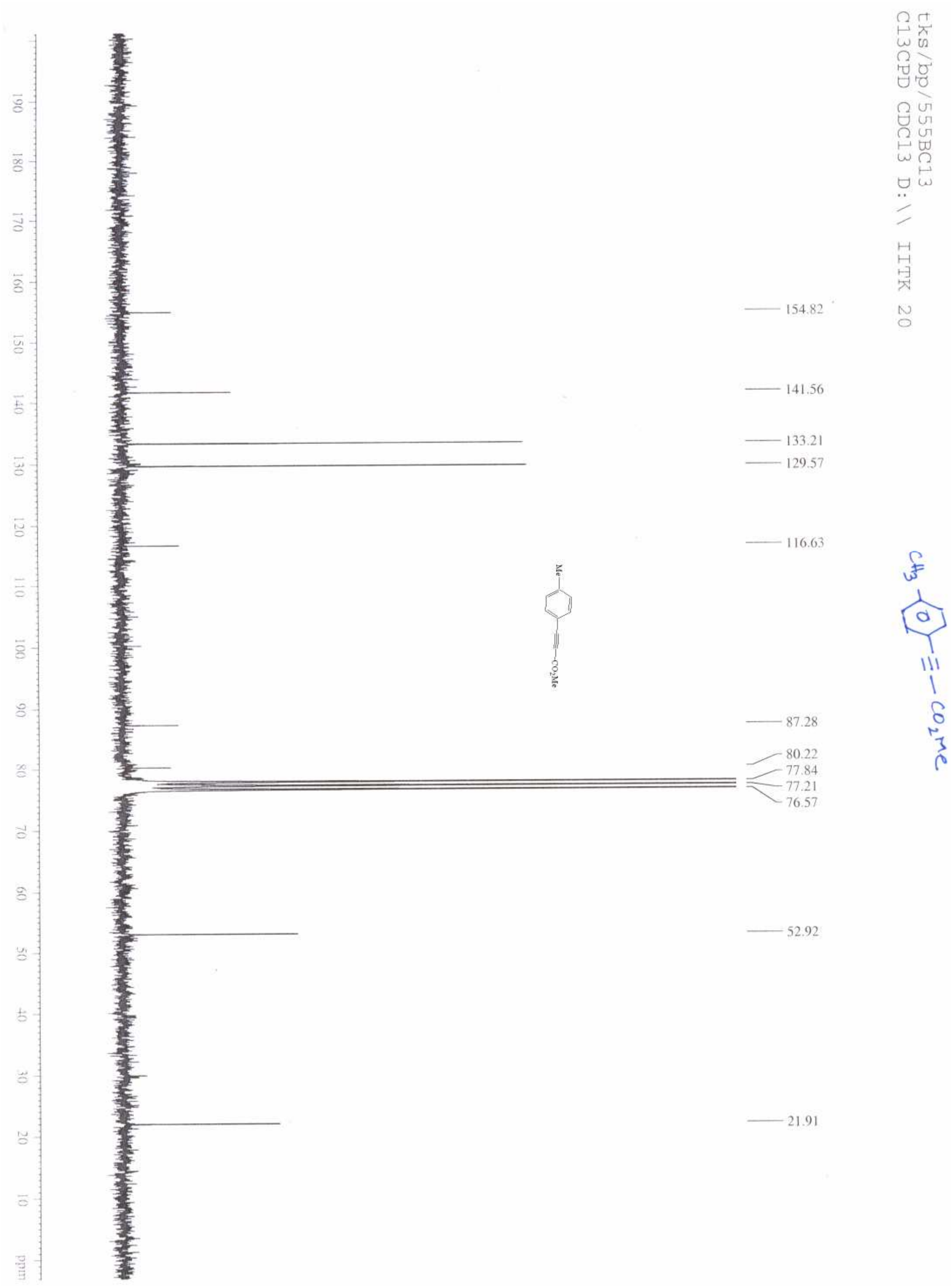
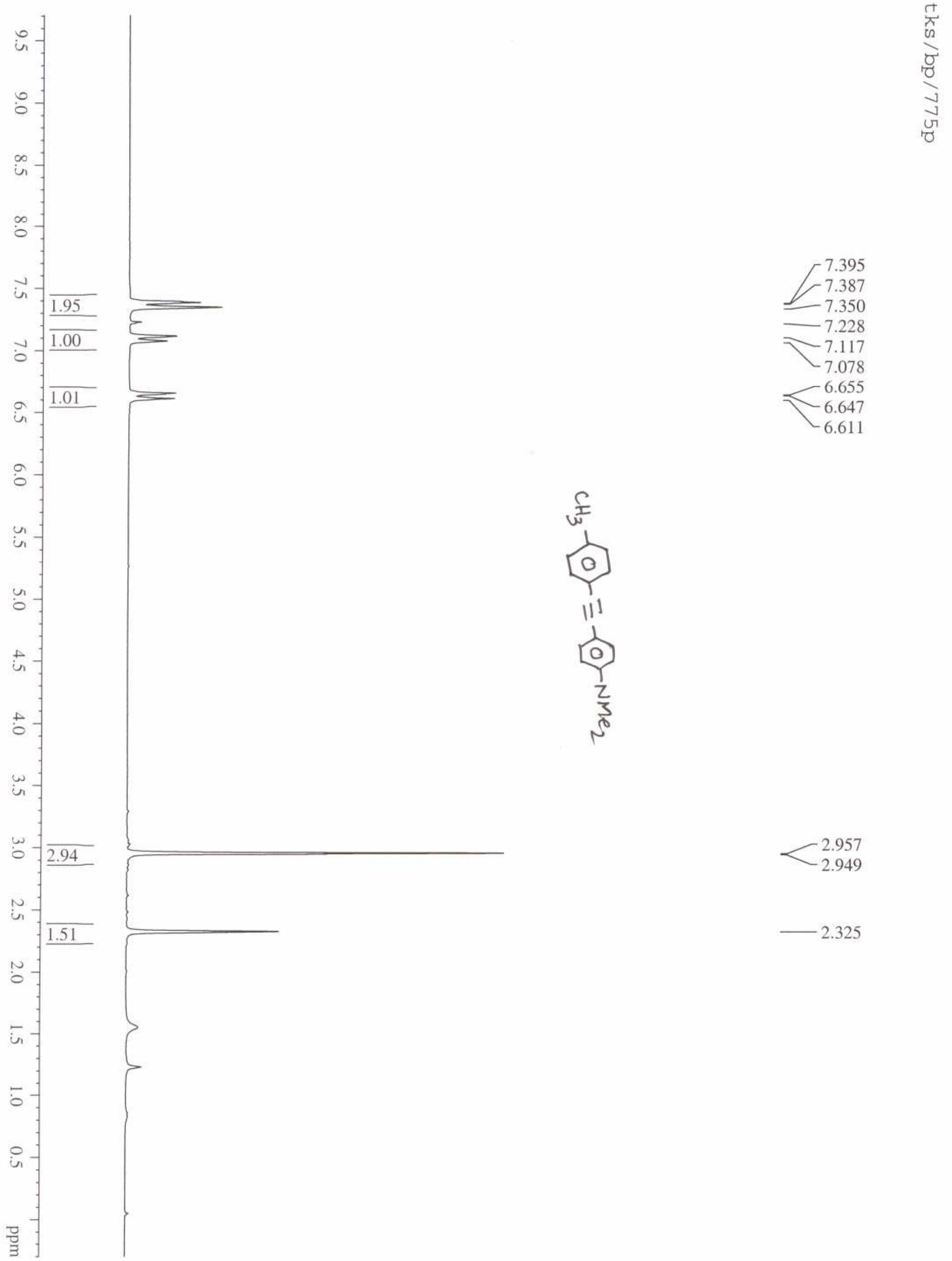
H3C
OH
7.325
7.316
7.293
7.284
7.259
7.114
7.075
3.848
3.818
3.788
3.758
2.712
2.681
2.649
2.334
1.964
1.935
1.904
1.663
1.01
1.00
1.06
1.06
1.56
0.50
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


tks/bp/537
C13CPD CDCl3 D:\\ IITK 6
H3C
OH
137.97
131.52
129.00
120.22
85.47
82.57
77.65
77.02
76.38
61.20
23.84
21.39
CH3
OH
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


PROTON CDCl3 D:\\ IITK 27
H3C
CO2Me
7.502
7.462
7.260
7.201
7.161
3.834
2.382
0.94
1.00
1.50
1.50
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
ppm


tks/bp/555BC13
C13CPD CDCl3 D:\\ IITK 20
154.82
141.56
133.21
129.57
116.63
87.28
80.22
77.84
77.21
76.57
52.92
21.91
Me
CO$_2$Me
CH$_3$
CO$_2$Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


tks/bp/775p
7.395
7.387
7.350
7.228
7.117
7.078
6.655
6.647
6.611
2.957
2.949
2.325
1.95
1.00
1.01
2.94
1.51
CH3
NMe2
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
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ppm

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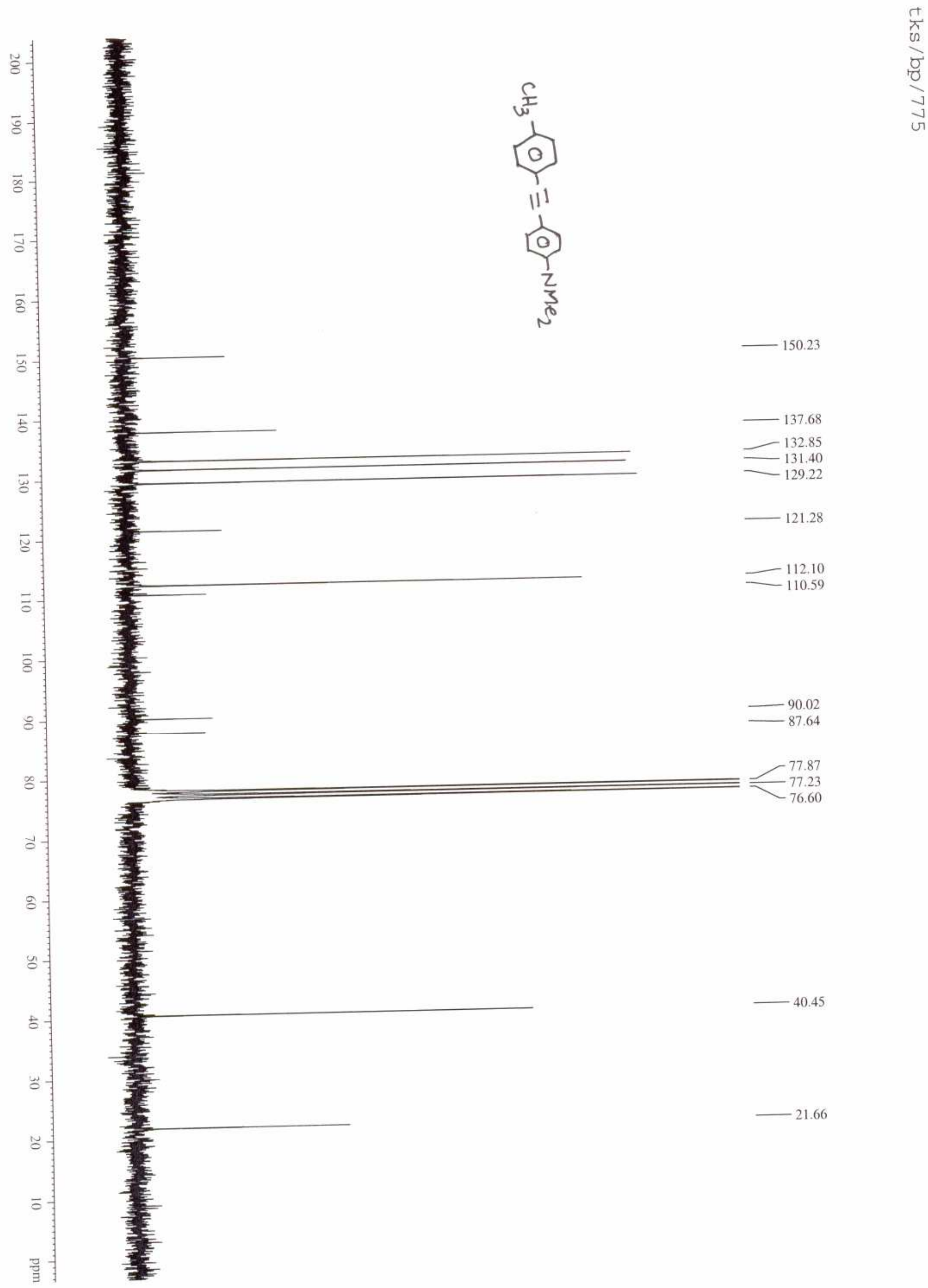
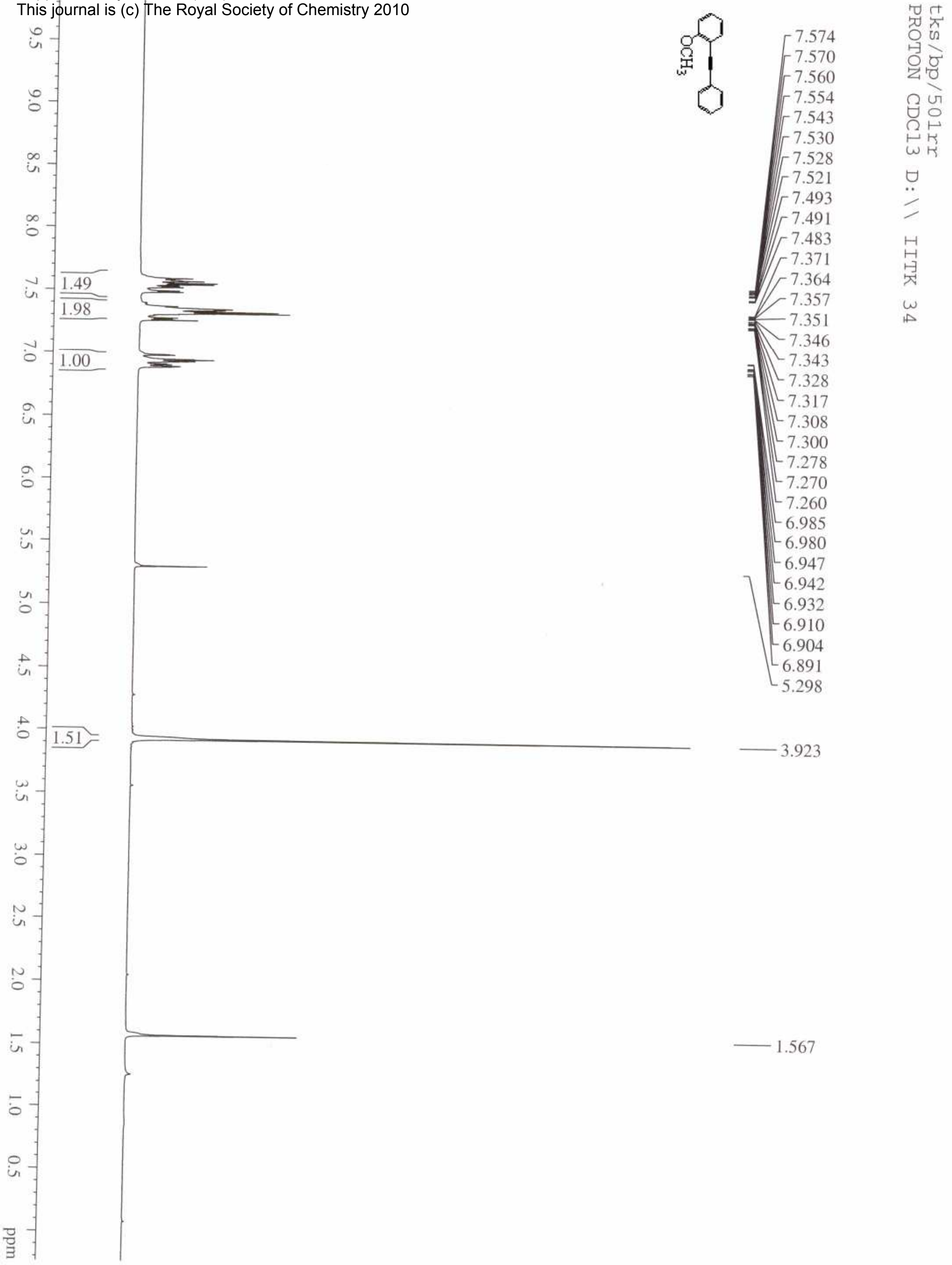
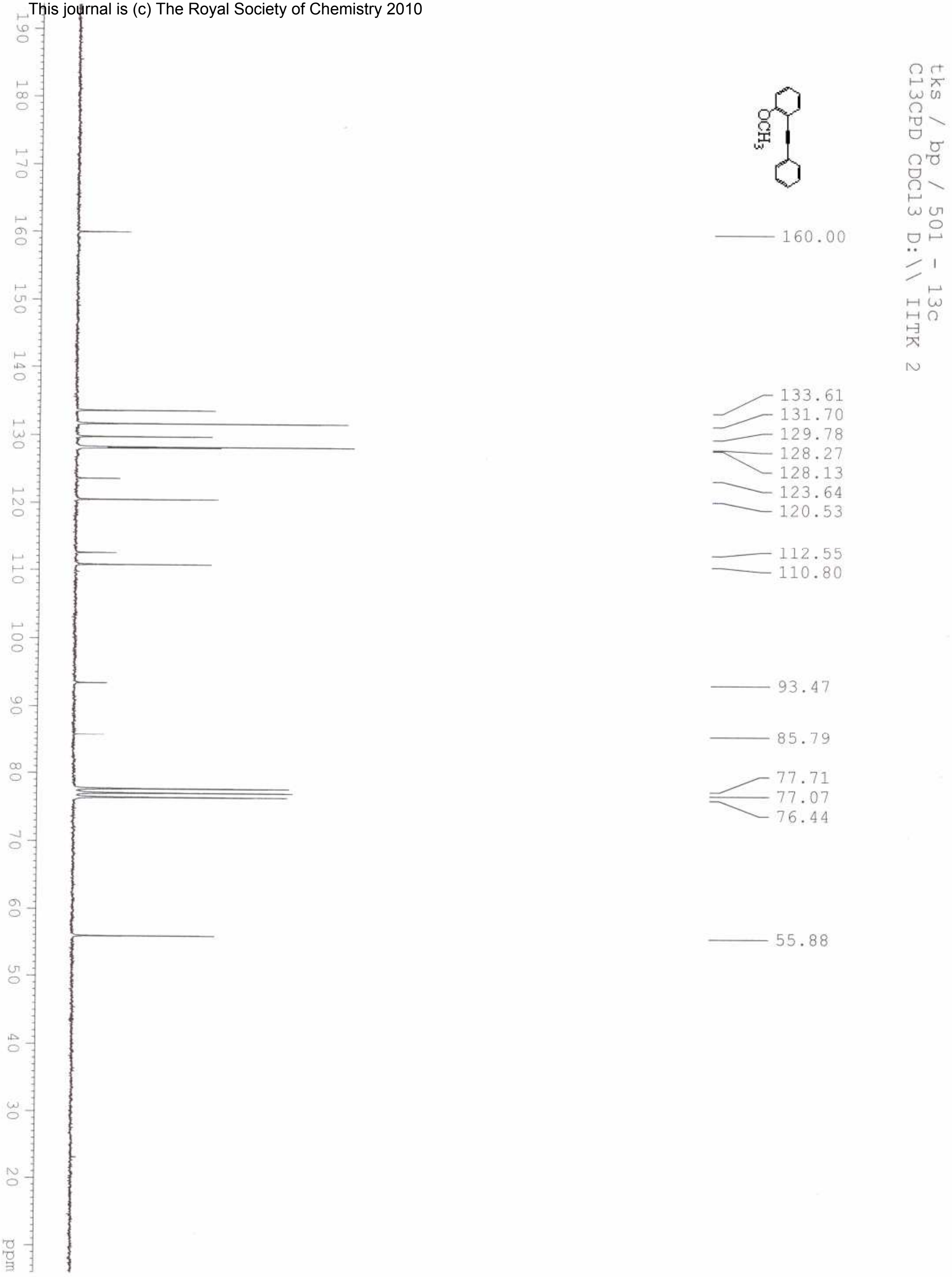
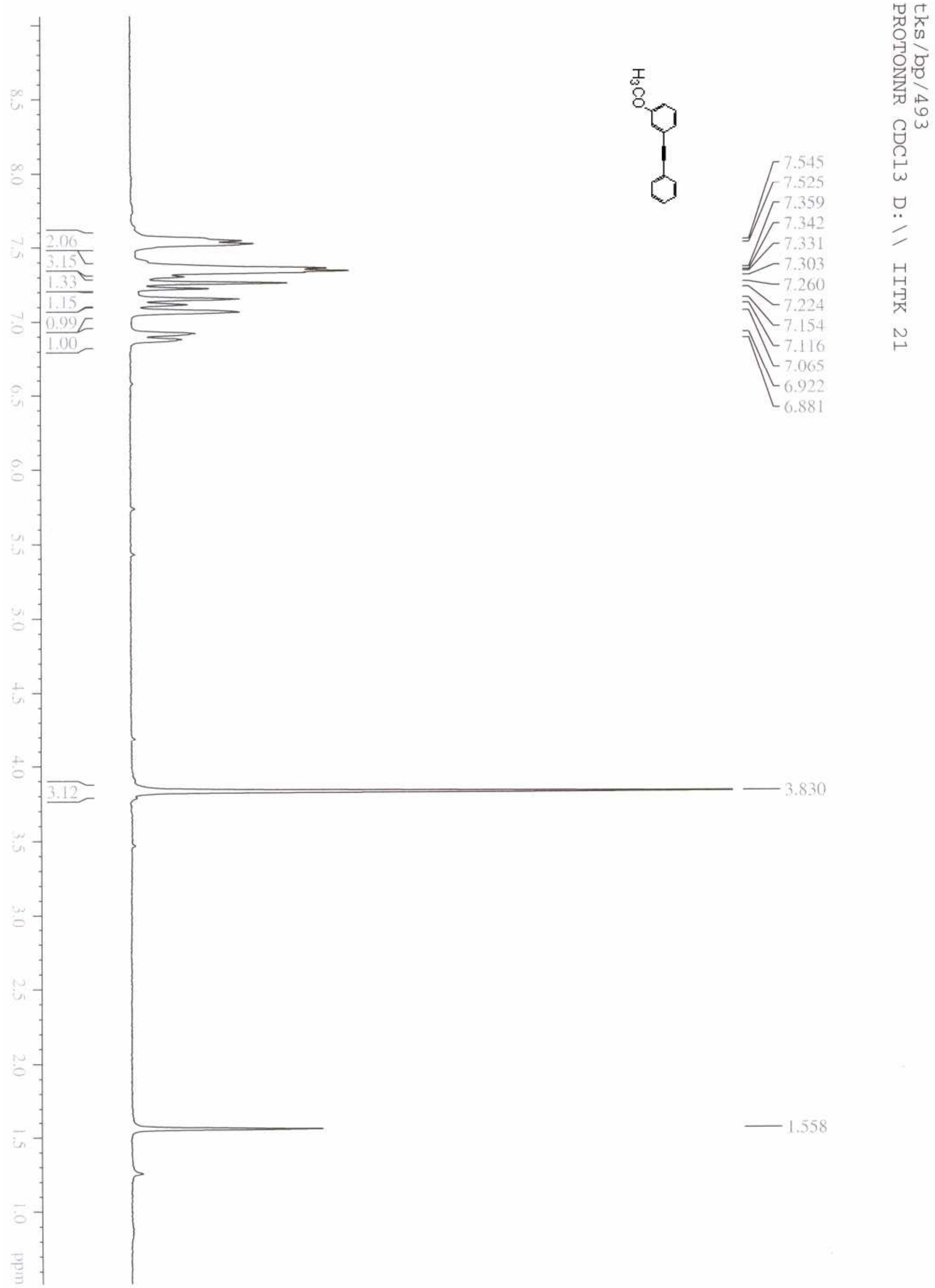
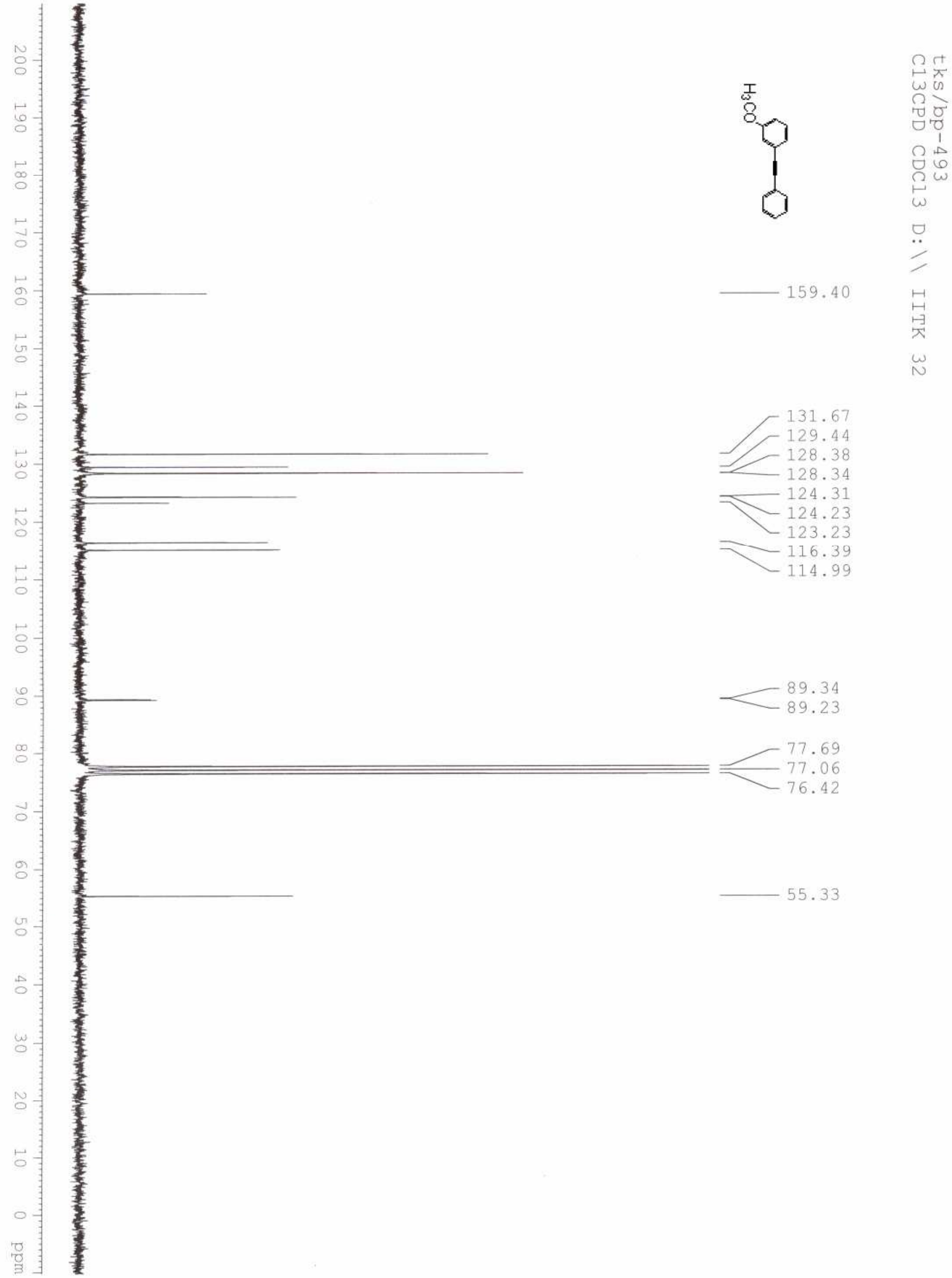
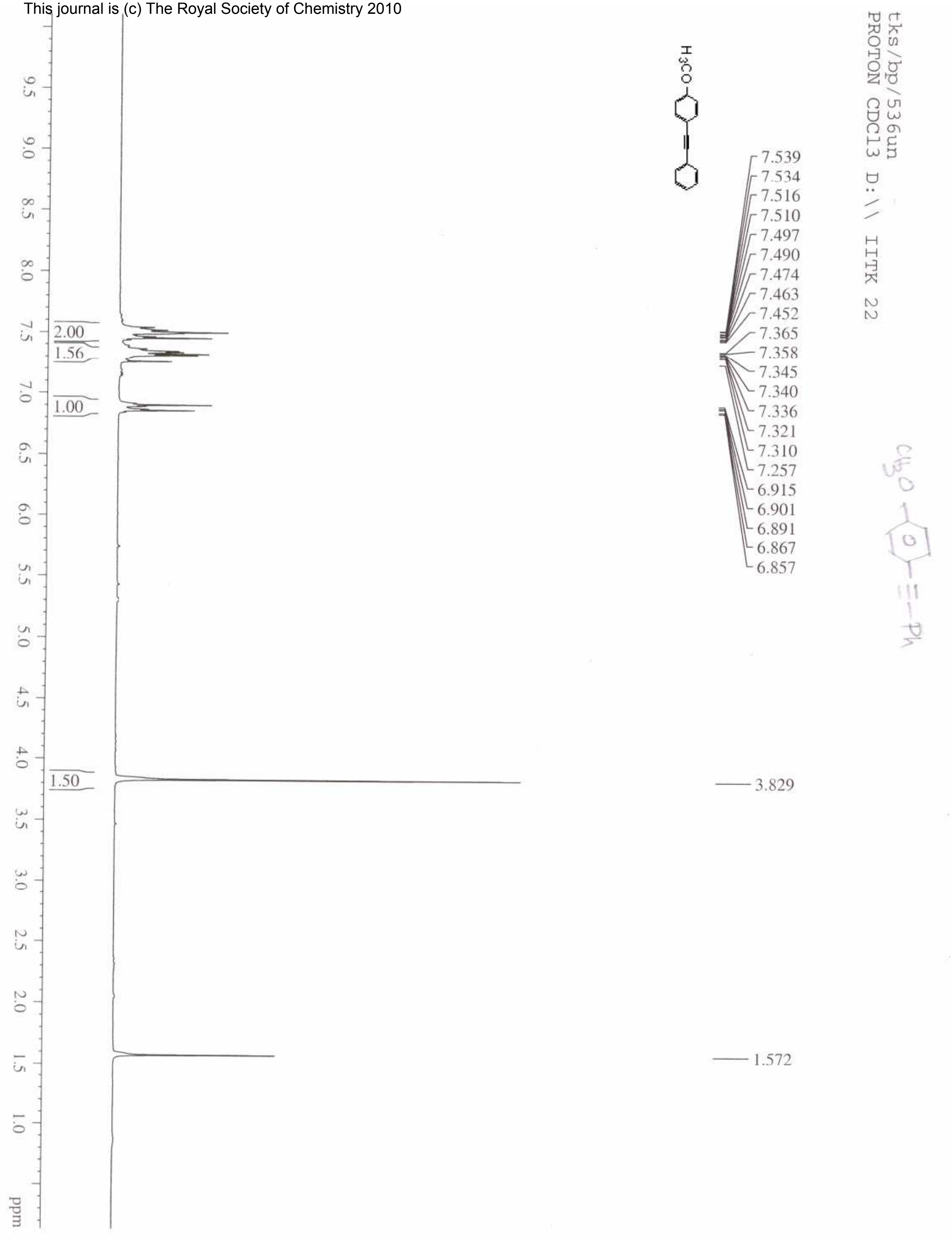


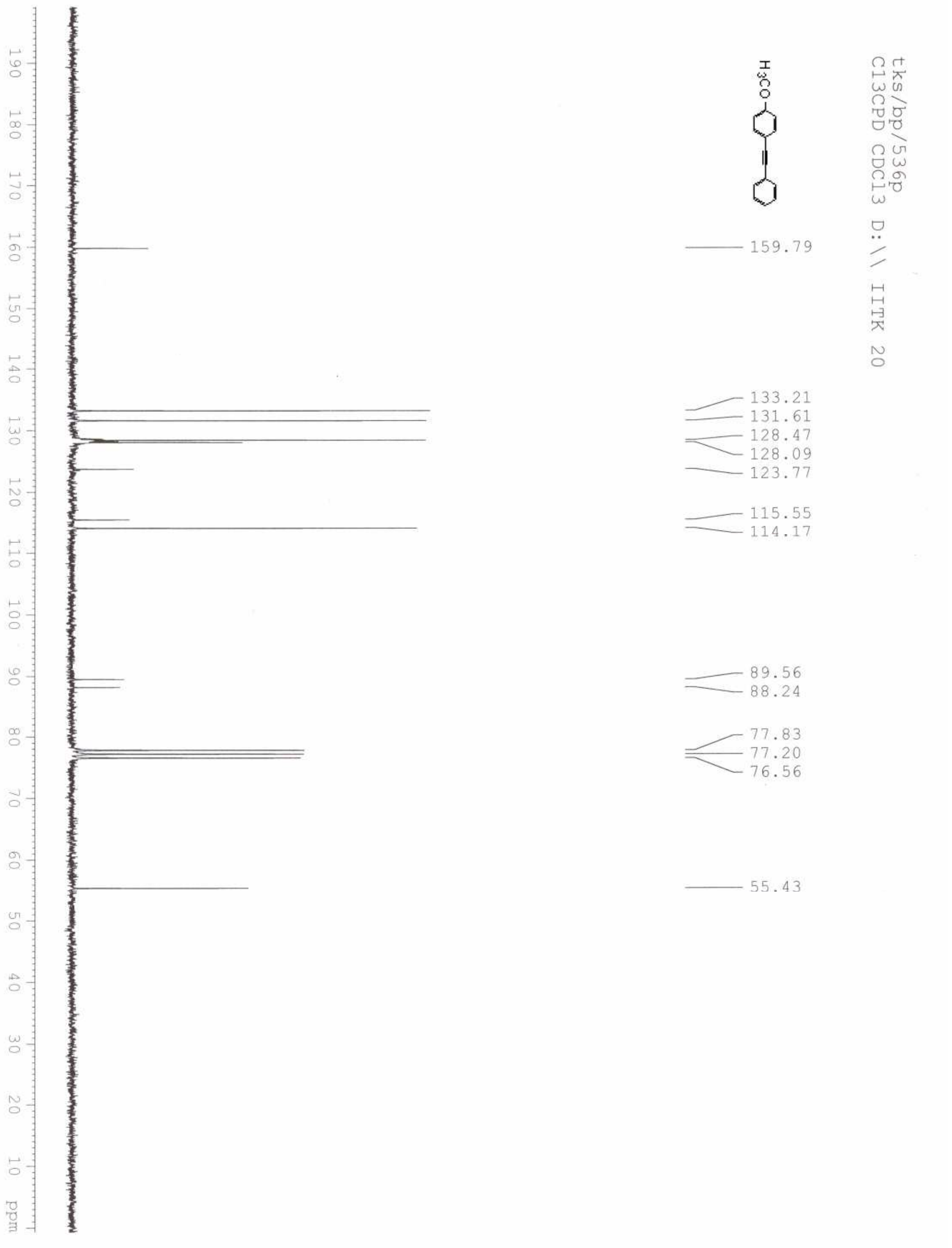

tks/bp/501rr
PROTON CDCl3 D:\\ IITK 34
OCH3
7.574
7.570
7.560
7.554
7.543
7.530
7.528
7.521
7.493
7.491
7.483
7.371
7.364
7.357
7.351
7.346
7.343
7.328
7.317
7.308
7.300
7.278
7.270
7.260
6.985
6.980
6.947
6.942
6.932
6.910
6.904
6.891
5.298
3.923
1.567
1.49
1.98
1.00
1.51
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

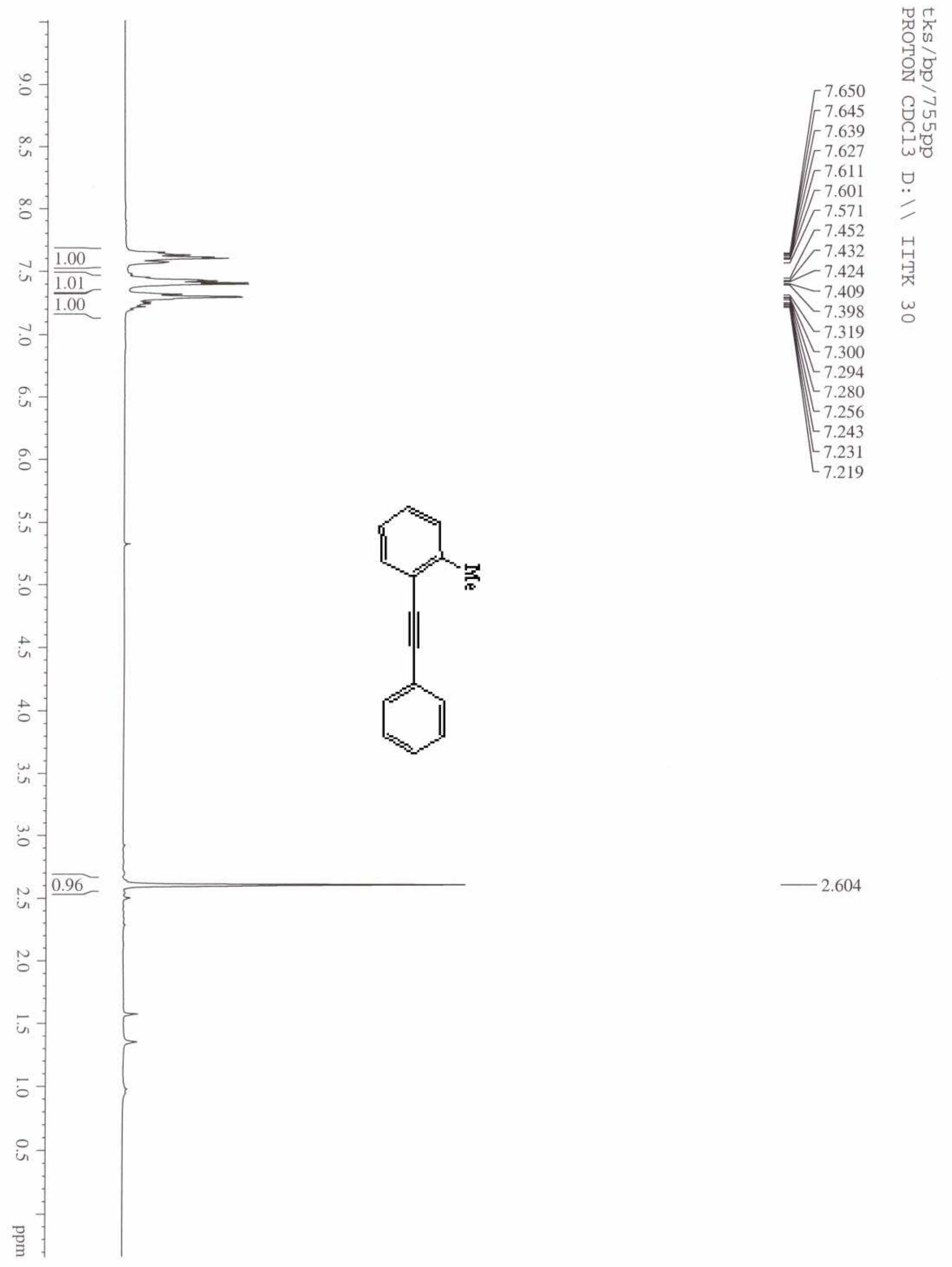

tks / bp / 501 - 13c
C13CPD CDCl3 D:\\ IITK 2
OCH3
160.00
133.61
131.70
129.78
128.27
128.13
123.64
120.53
112.55
110.80
93.47
85.79
77.71
77.07
76.44
55.88
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


tks/bp/493
PROTONNR CDCl3 D:\\ IITK 21
H3CO
7.545
7.525
7.359
7.342
7.331
7.303
7.260
7.224
7.154
7.116
7.065
6.922
6.881
3.830
1.558
2.06
3.15
1.33
1.15
0.99
1.00
3.12
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
ppm


tks/bp-493
C13CPD CDCl3 D:\\ IITK 32
H_3CO
159.40
131.67
129.44
128.38
128.34
124.31
124.23
123.23
116.39
114.99
89.34
89.23
77.69
77.06
76.42
55.33
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


tks/bp/536un
PROTON CDCl3 D:\\ IITK 22
H3CO
7.539
7.534
7.516
7.510
7.497
7.490
7.474
7.463
7.452
7.365
7.358
7.345
7.340
7.336
7.321
7.310
7.257
6.915
6.901
6.891
6.867
6.857
3.829
1.572
2.00
1.56
1.00
1.50
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
ppm
CH3O
Ph


tks/bp/536p
C13CPD CDCl3 D:\\ IITK 20
H3CO
159.79
133.21
131.61
128.47
128.09
123.77
115.55
114.17
89.56
88.24
77.83
77.20
76.56
55.43
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


tks/bp/755pp
PROTON CDCl3 D:\\ IITK 30
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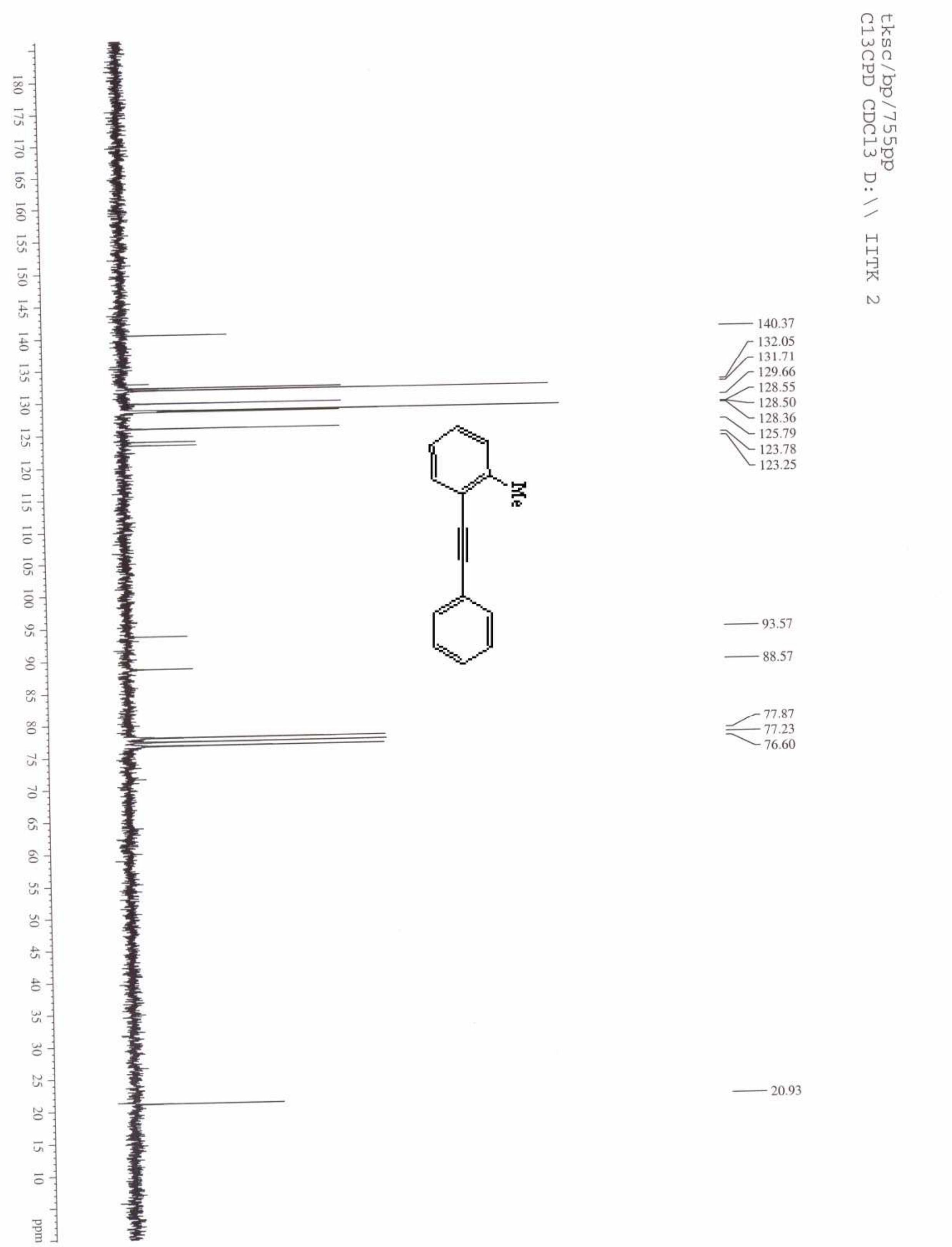
7.645
7.639
7.627
7.611
7.601
7.571
7.452
7.432
7.424
7.409
7.398
7.319
7.300
7.294
7.280
7.256
7.243
7.231
7.219
2.604
1.00
1.01
1.00
0.96
Me
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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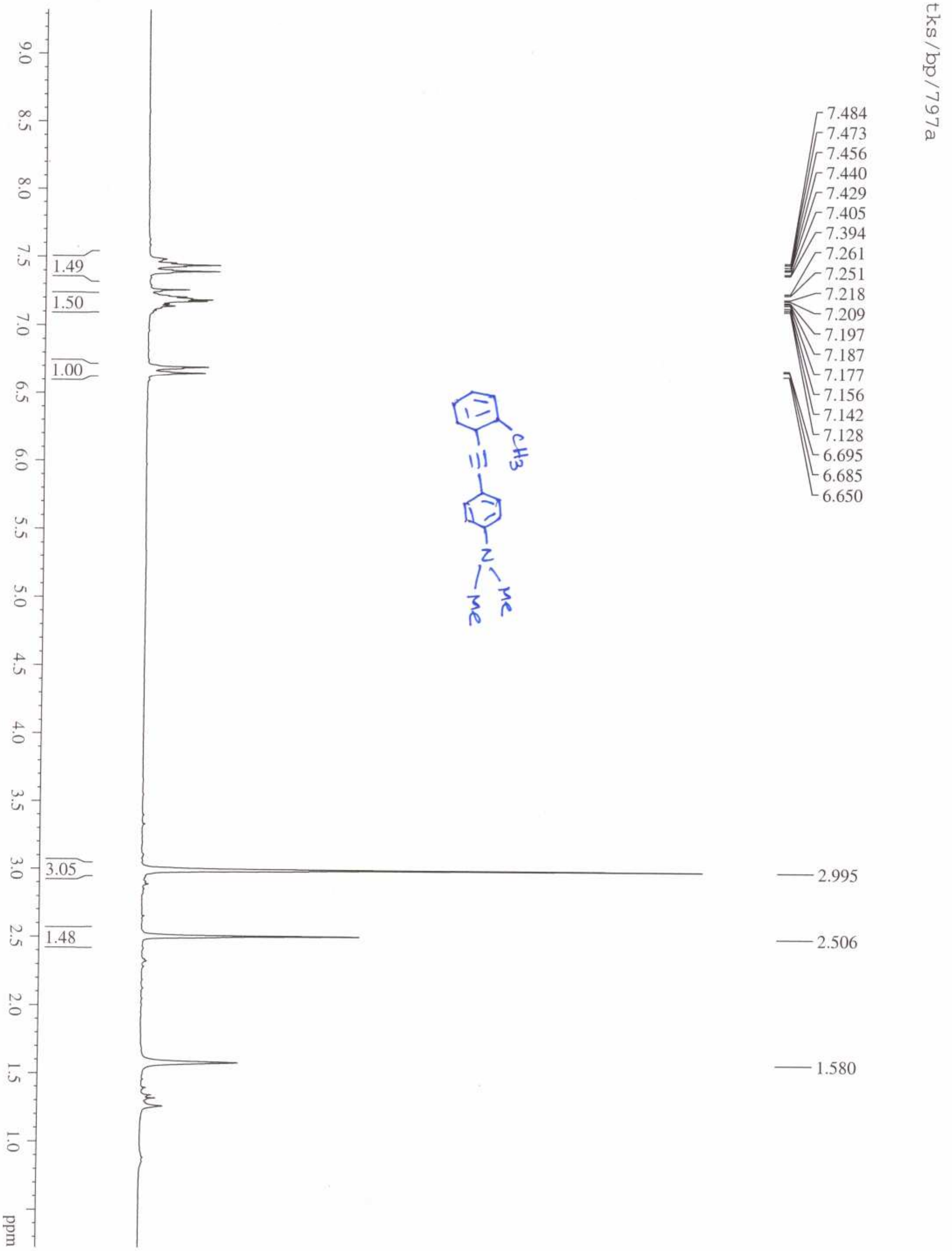
140.37
132.05
131.71
129.66
128.55
128.50
128.36
125.79
123.78
123.25
93.57
88.57
77.87
77.23
76.60
20.93
Me
180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 ppm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7.429
7.405
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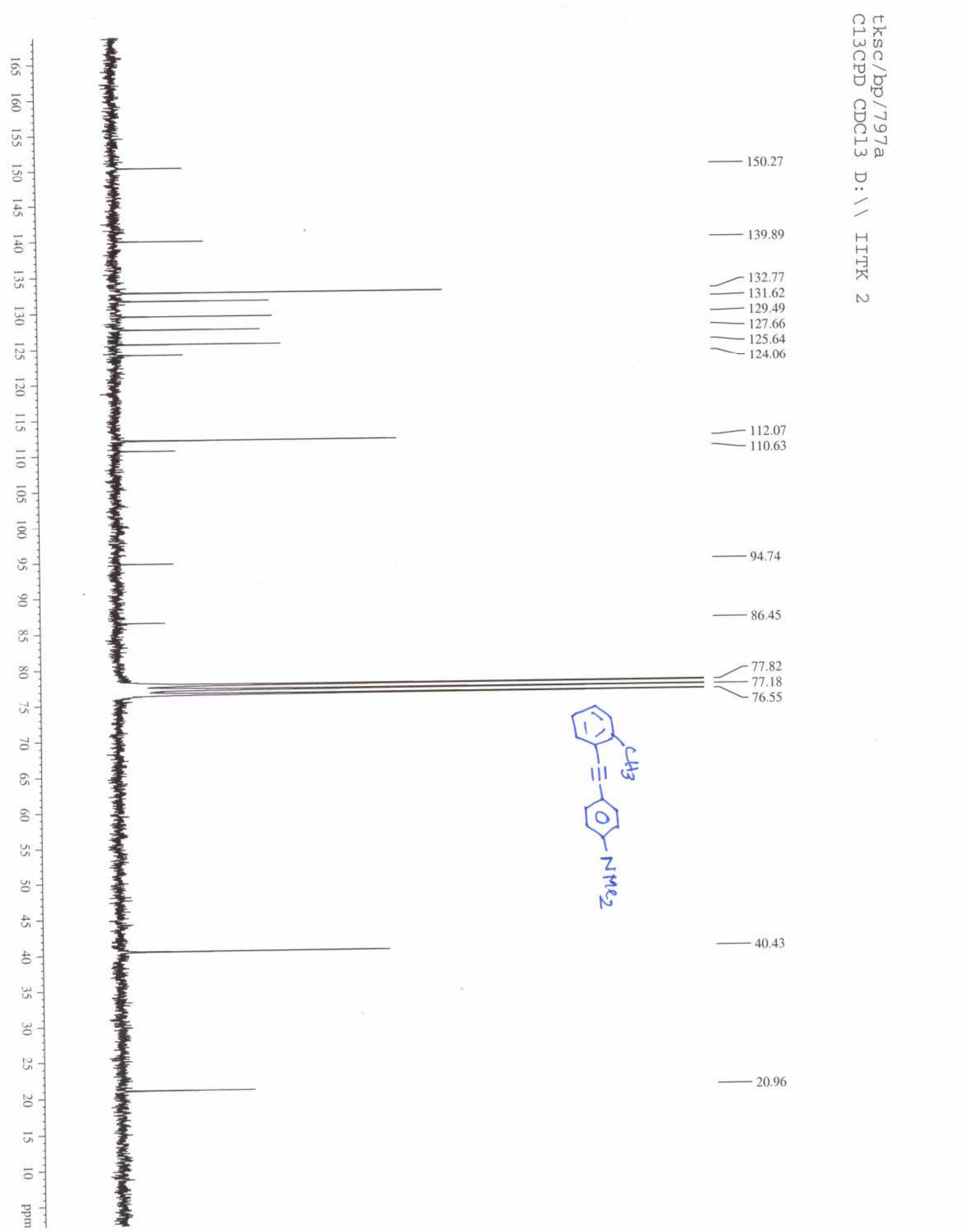
7.261
7.251
7.218
7.209
7.197
7.187
7.177
7.156
7.142
7.128
6.695
6.685
6.650
2.995
2.506
1.580
CH3
N
Me
Me
1.49
1.50
1.00
3.05
1.48
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


tksc/bp/797a
C13CPD CDCl3 D:\\ IITK 2
150.27
139.89
132.77
131.62
129.49
127.66
125.64
124.06
112.07
110.63
94.74
86.45
77.82
77.18
76.55
40.43
20.96
CH3
NMe2
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
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85
80
75
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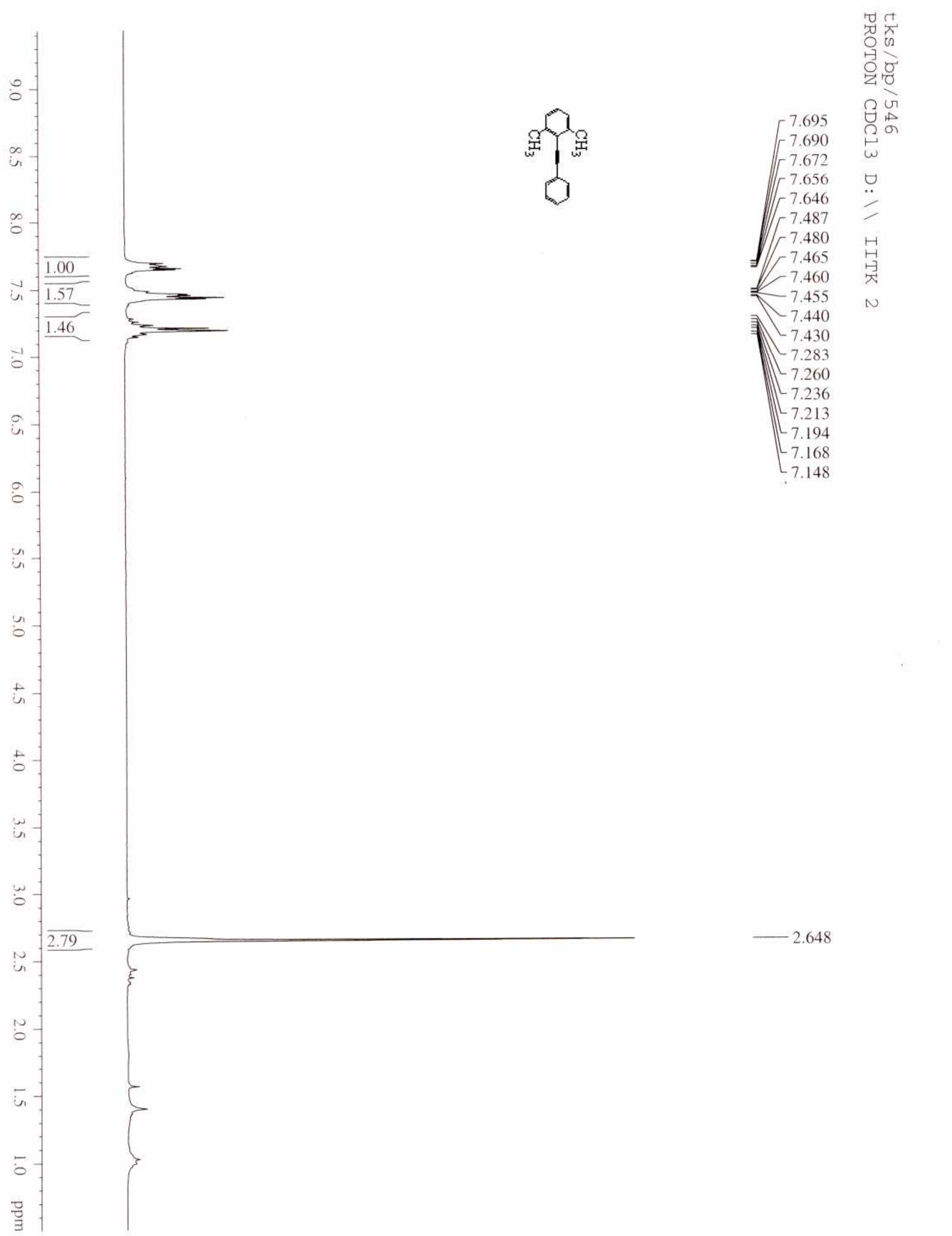
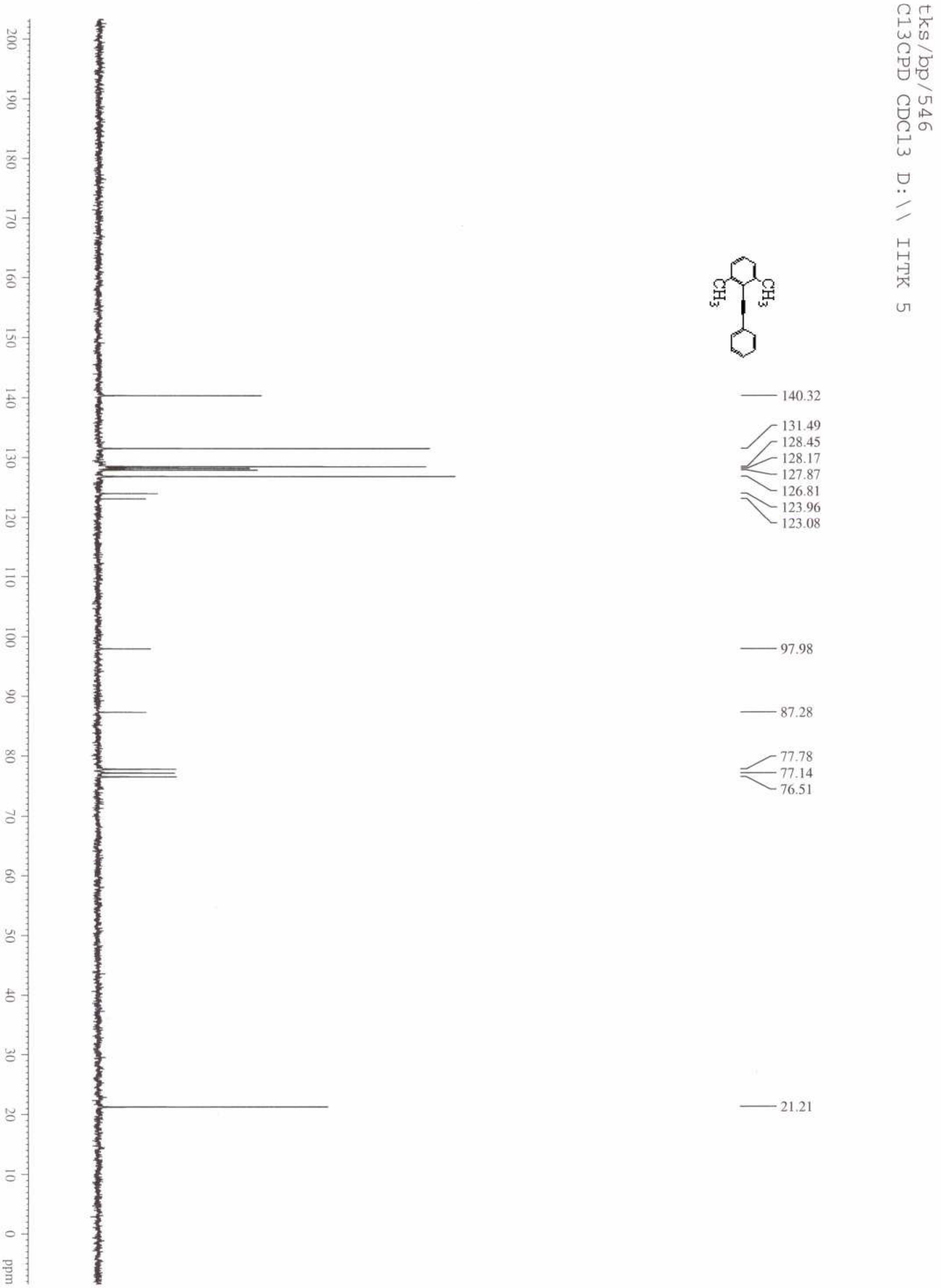
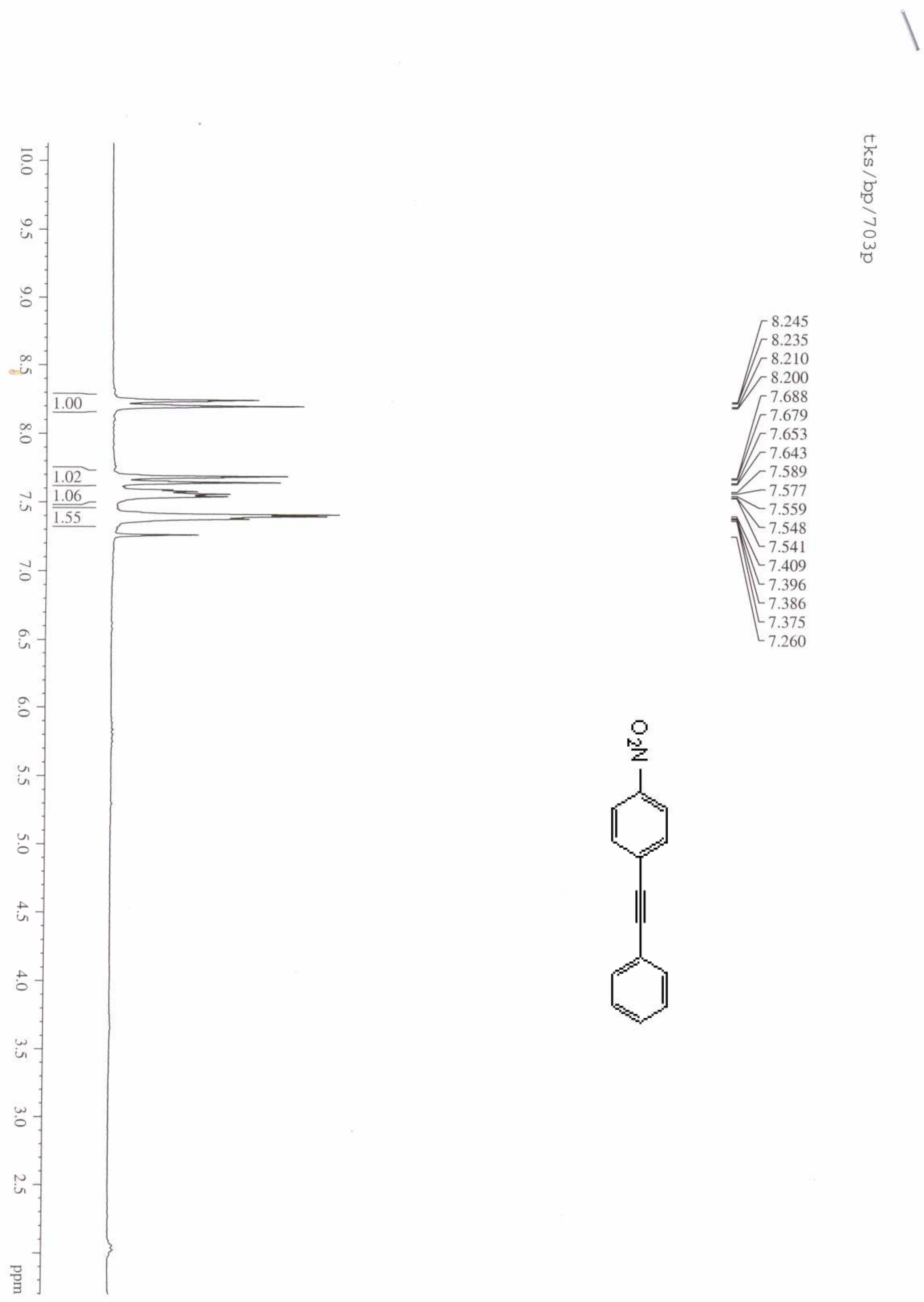
65
60
55
50
45
40
35
30
25
20
15
10
ppm


tks/bp/546
PROTON CDCl3 D:\\ IITK 2
CH3
CH3
7.695
7.690
7.672
7.656
7.646
7.487
7.480
7.465
7.460
7.455
7.440
7.430
7.283
7.260
7.236
7.213
7.194
7.168
7.148
2.648
1.00
1.57
1.46
2.79
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
ppm


tks/bp/546
C13CPD CDCl3 D:\\ IITK 5
CH3
CH3
140.32
131.49
128.45
128.17
127.87
126.81
123.96
123.08
97.98
87.28
77.78
77.14
76.51
21.21
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


tks/bp/703p
8.245
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8.210
8.200
7.688
7.679
7.653
7.643
7.589
7.577
7.559
7.548
7.541
7.409
7.396
7.386
7.375
7.260
1.00
1.02
1.06
1.55
10.0
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
ppm
O2N

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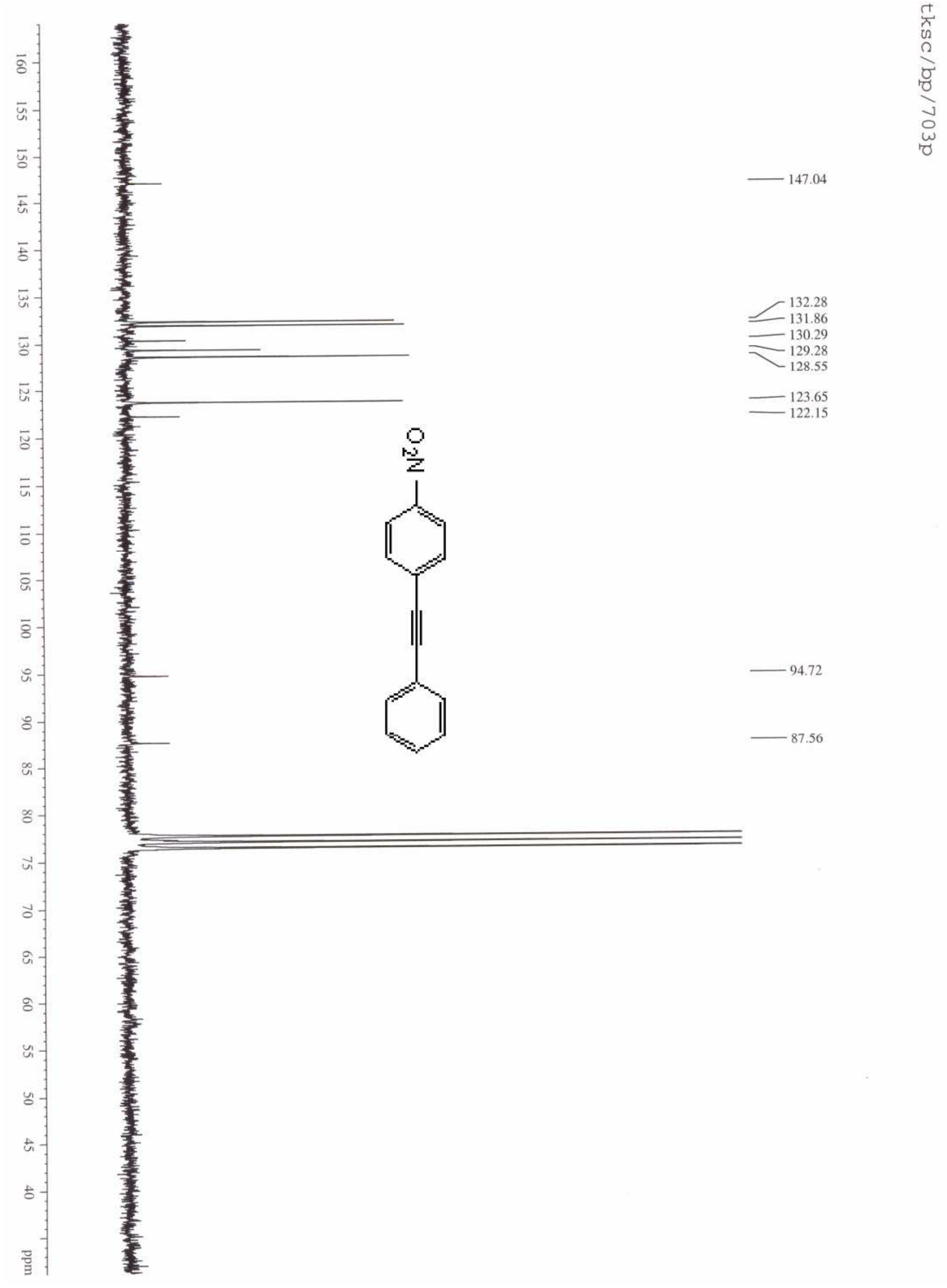

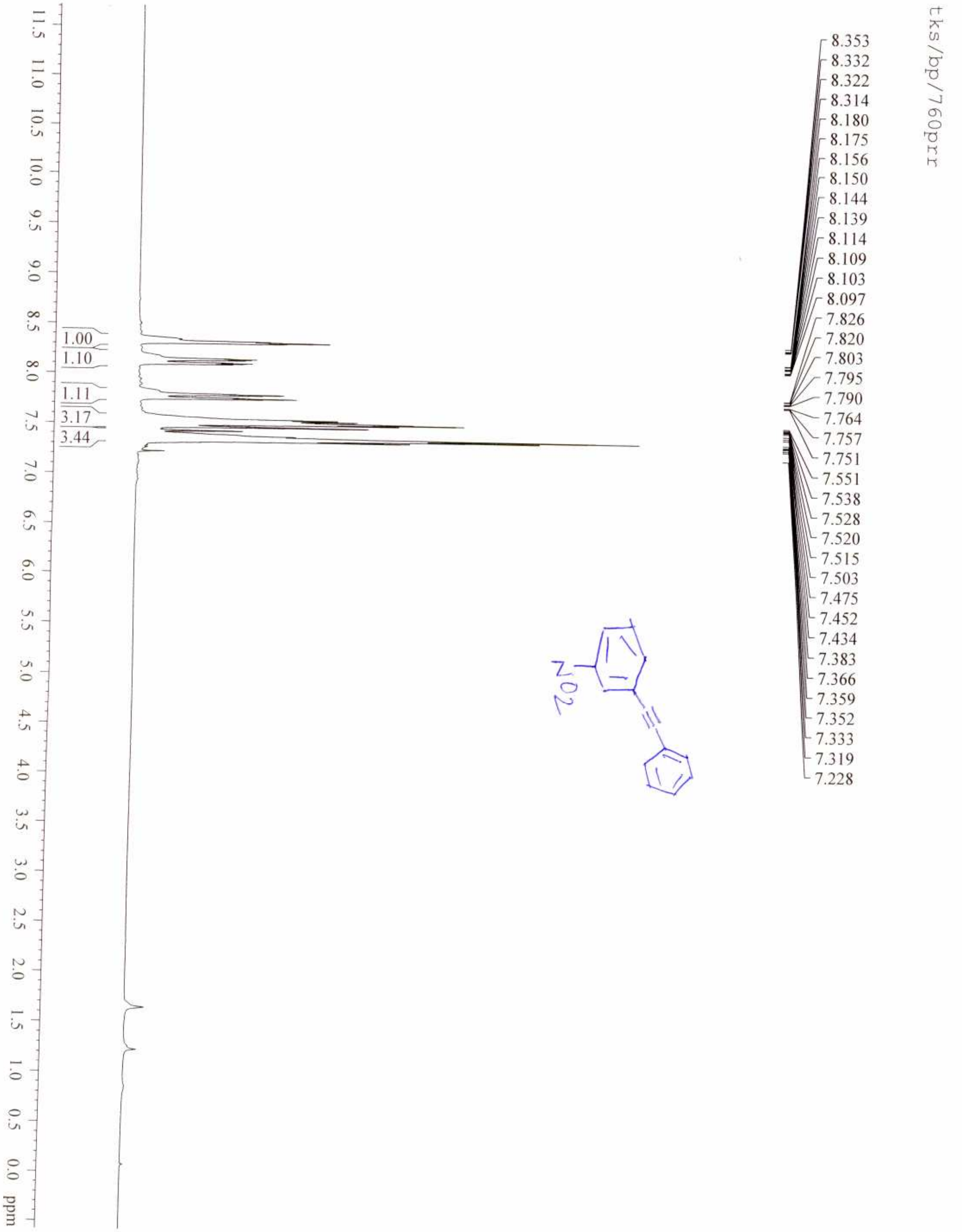
tks/bp/760prr
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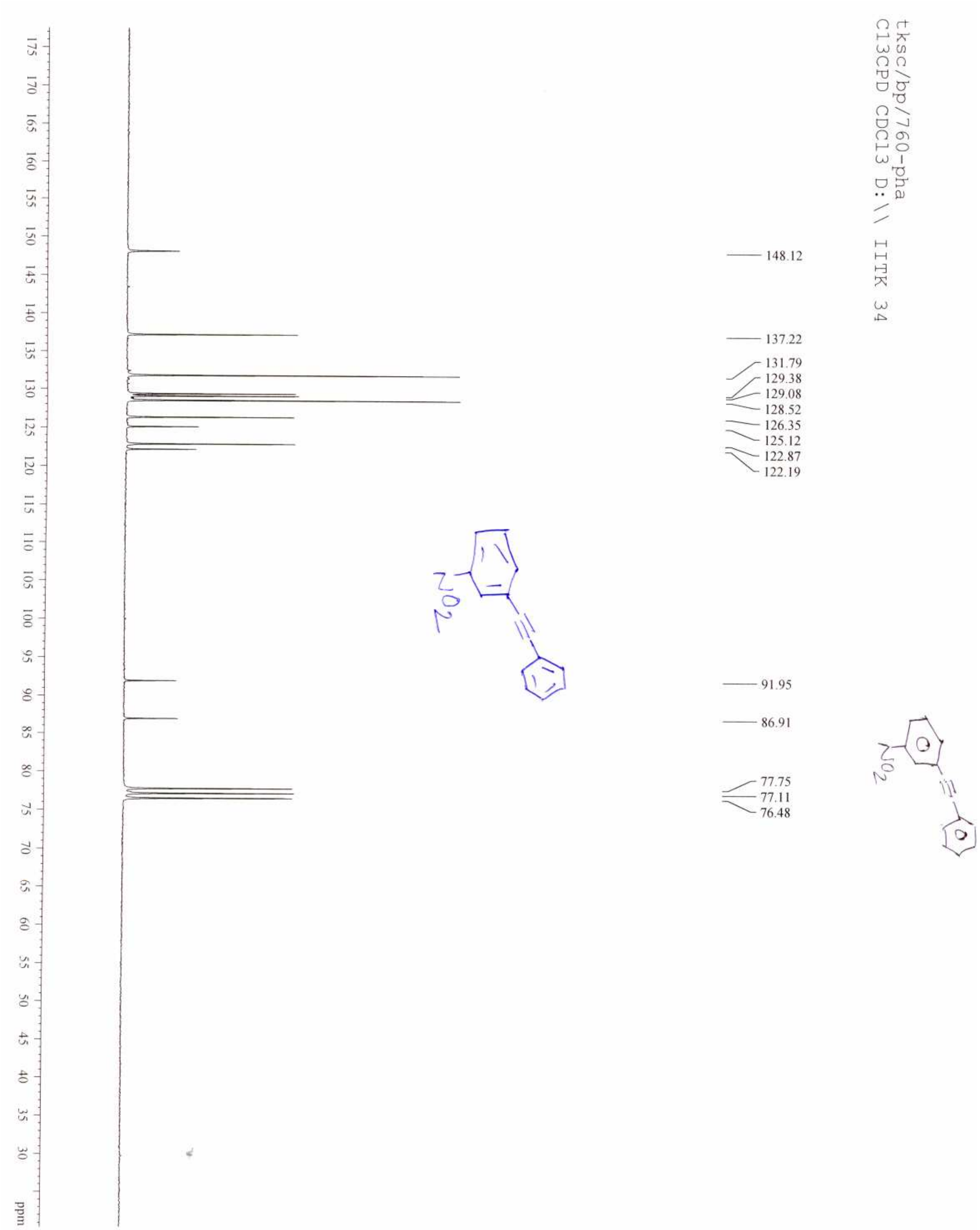
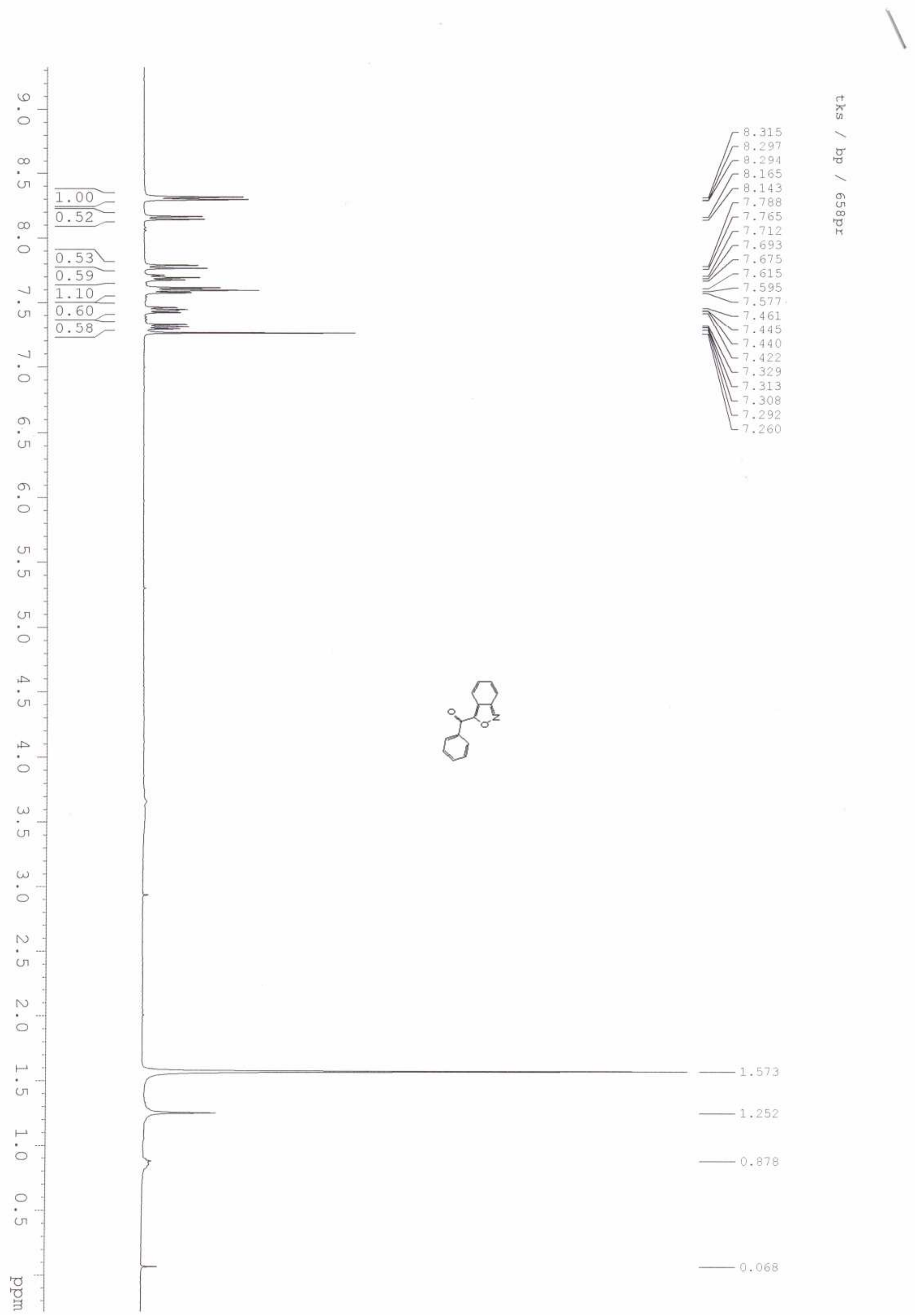
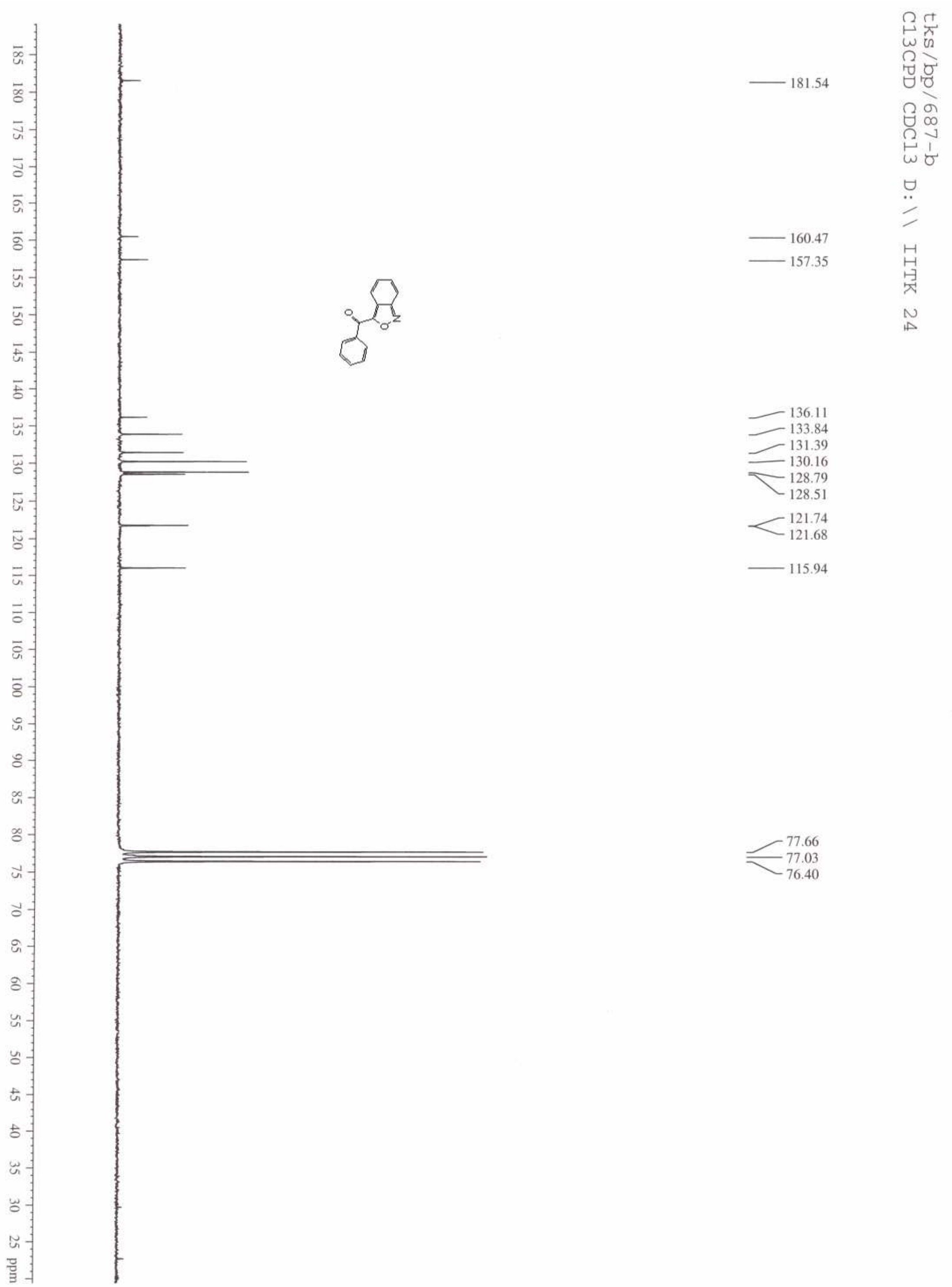
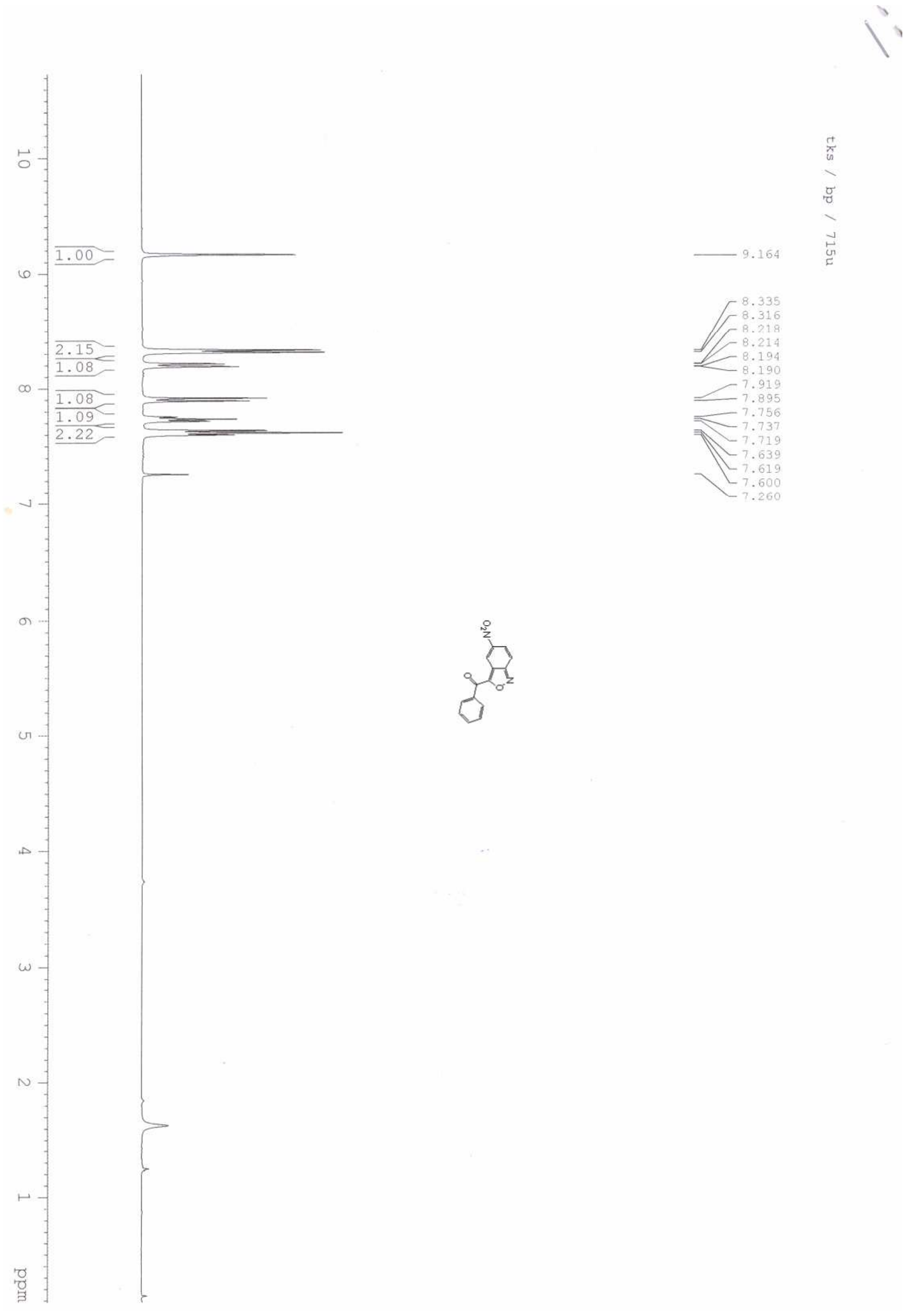
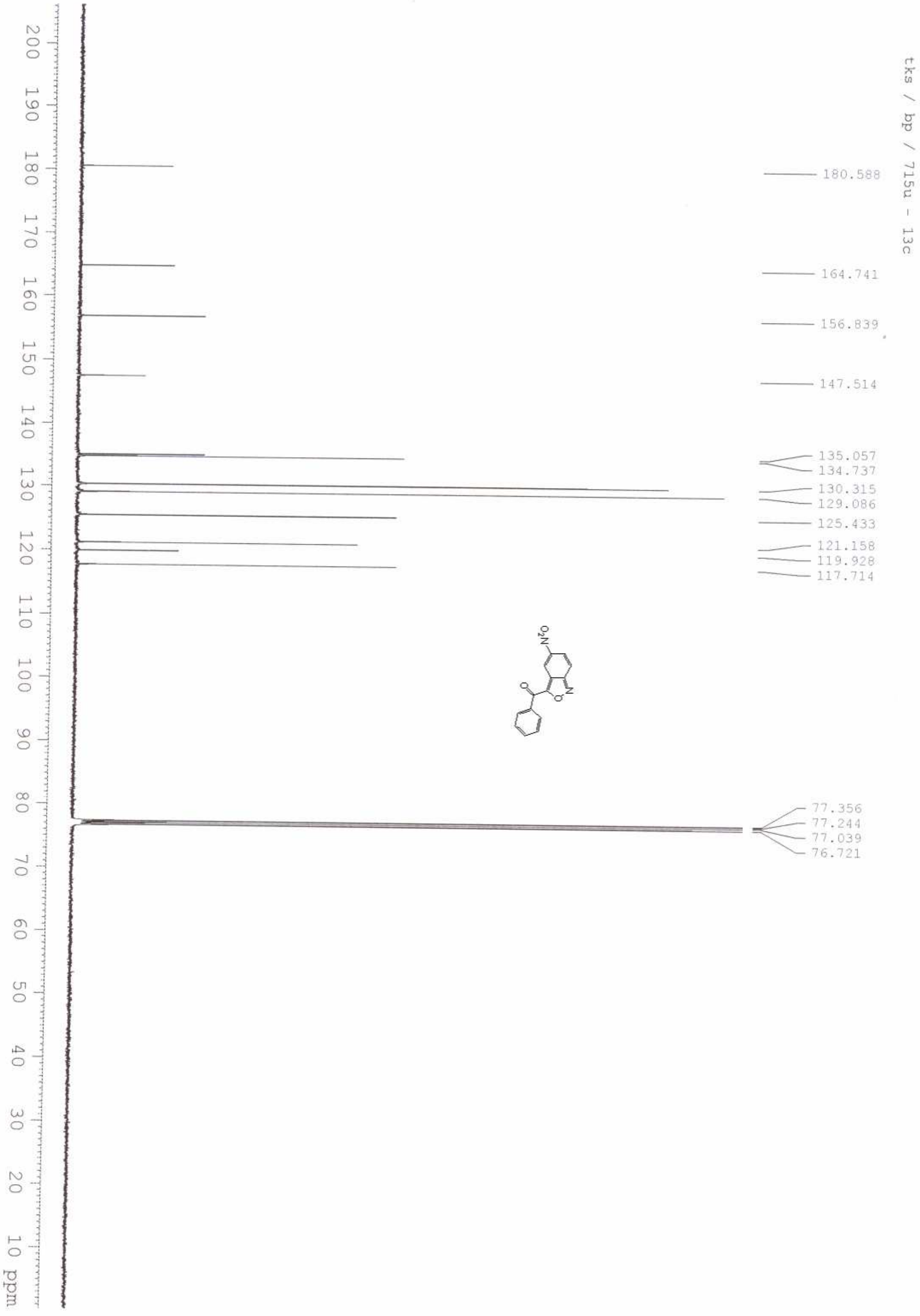
8.322
8.314
8.180
8.175
8.156
8.150
8.144
8.139
8.114
8.109
8.103
8.097
7.826
7.820
7.803
7.795
7.790
7.764
7.757
7.751
7.551
7.538
7.528
7.520
7.515
7.503
7.475
7.452
7.434
7.383
7.366
7.359
7.352
7.333
7.319
7.228
1.00
1.10
1.11
3.17
3.44
NO2
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

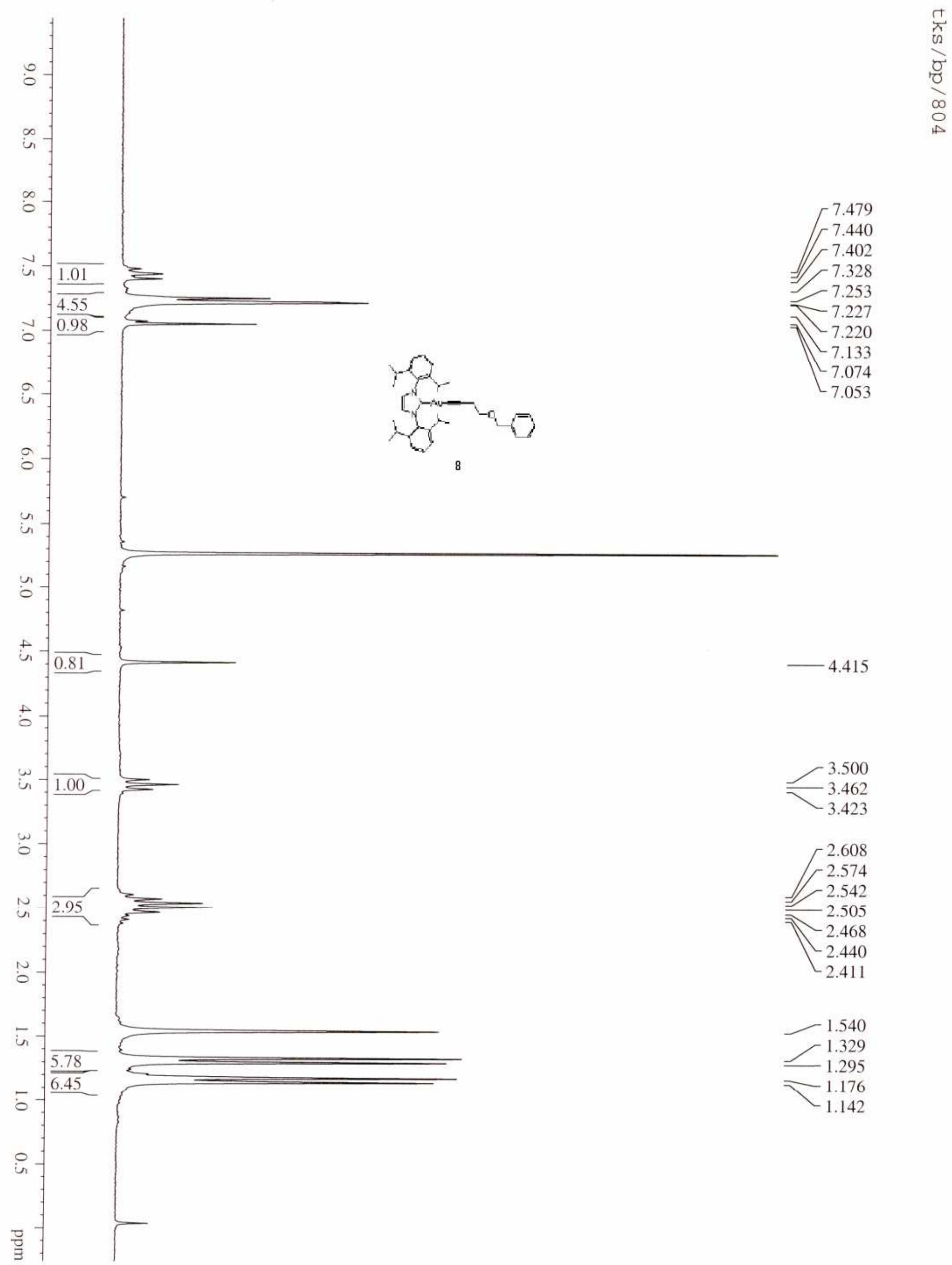

tksc/bp/760-pha
C13CPD CDCl3 D:\\ IITK 34
148.12
137.22
131.79
129.38
129.08
128.52
126.35
125.12
122.87
122.19
91.95
86.91
77.75
77.11
76.48
NO2
NO2
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
ppm


tks / bp / 658pr
8.315
8.297
8.294
8.165
8.143
7.788
7.765
7.712
7.693
7.675
7.615
7.595
7.577
7.461
7.445
7.440
7.422
7.329
7.313
7.308
7.292
7.260
1.573
1.252
0.878
0.068
1.00
0.52
0.53
0.59
1.10
0.60
0.58
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
ppm
O
N


tks/bp/687-b
C13CPD CDCl3 D:\\ IITK 24
181.54
160.47
157.35
136.11
133.84
131.39
130.16
128.79
128.51
121.74
121.68
115.94
77.66
77.03
76.40
O
N
O
185
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25 ppm


tks / bp / 715u
9.164
8.335
8.316
8.218
8.214
8.194
8.190
7.919
7.895
7.756
7.737
7.719
7.639
7.619
7.600
7.260
1.00
2.15
1.08
1.08
1.09
2.22
10
9
8
7
6
5
4
3
2
1
ppm
O₂N
O
N
O


tks / bp / 715u - 13c
180.588
164.741
156.839
147.514
135.057
134.737
130.315
129.086
125.433
121.158
119.928
117.714
77.356
77.244
77.039
76.721
O_2N
N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


tks/bp/804
8
7.479
7.440
7.402
7.328
7.253
7.227
7.220
7.133
7.074
7.053
4.415
3.500
3.462
3.423
2.608
2.574
2.542
2.505
2.468
2.440
2.411
1.540
1.329
1.295
1.176
1.142
1.01
4.55
0.98
0.81
1.00
2.95
5.78
6.45
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
ppm