Supporting Information

Nano tetraimine Pd(0) complex: synthesis, characterization, computational studies and catalytic applications in the Heck-Mizoroki reaction in water

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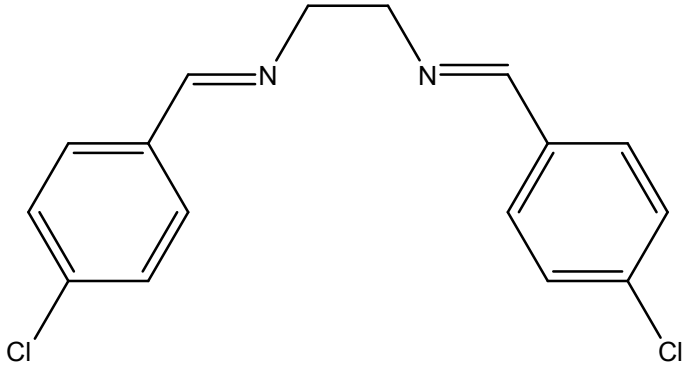
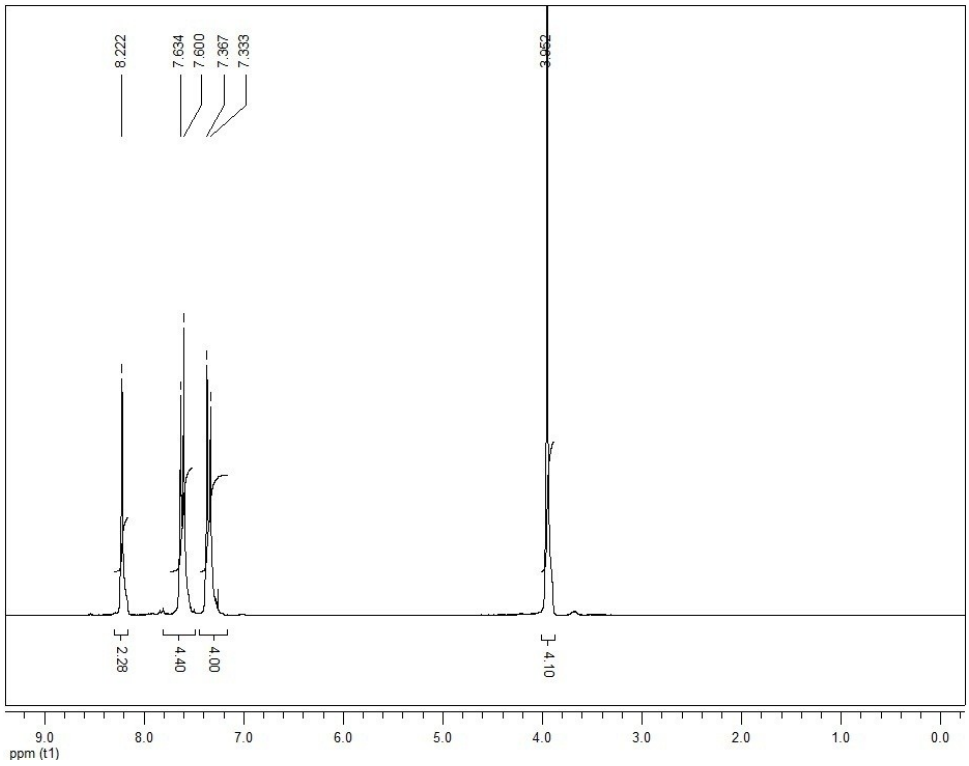
Spectral data:

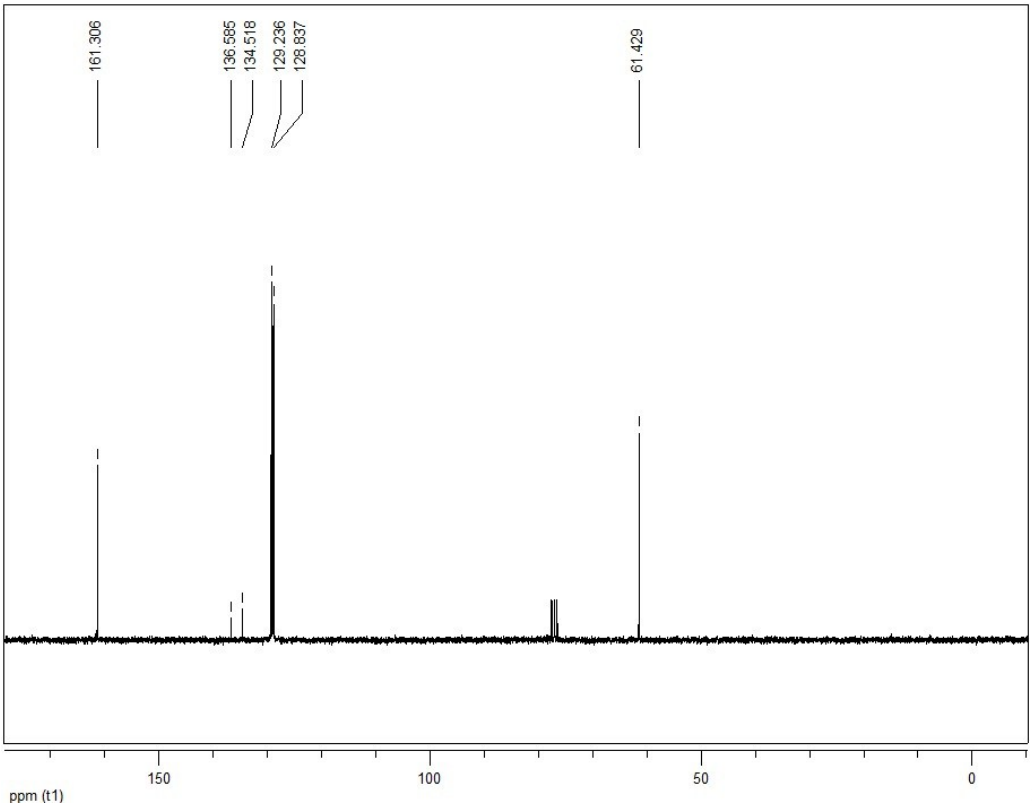
***N*,*N*-bisimine ligand (3)**



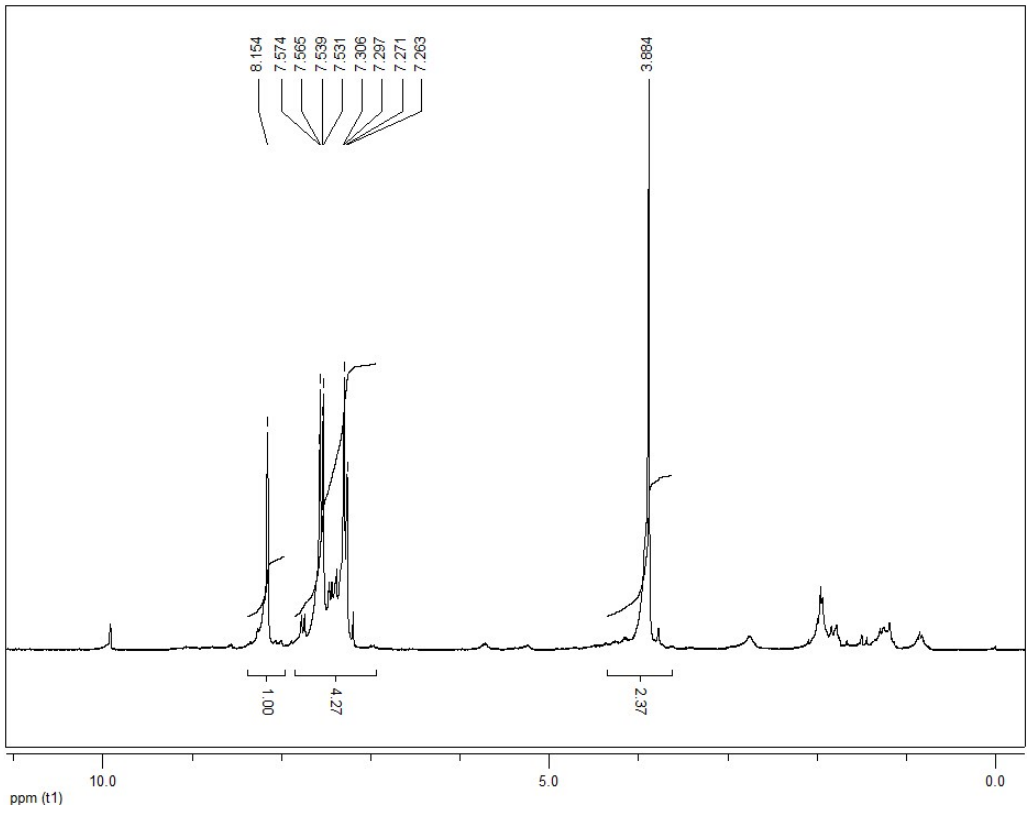
^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 3.95 (s, 4H, CH_2); 7.34 (d, 4H, CH aromatic, J =7.5 Hz); 7.60 (d, 4H, CH aromatic, J = 7.5 Hz); 8.22 (s, 2H, CH). ^{13}C-NMR (63 MHz, $CDCl_3$): δ (ppm) 61.4, 128.8, 129.2, 134.5, 136.6.



^{1}H-NMR of ***N*,*N*-bisimine ligand (3)**

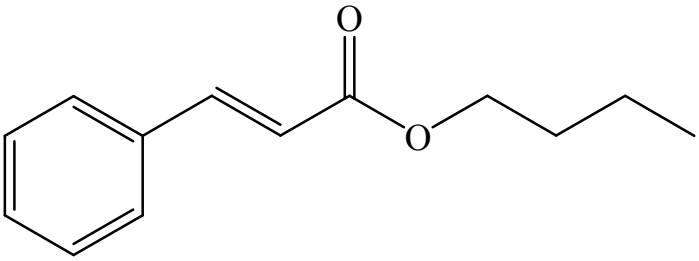


^{13}C-NMR of ***N,N*-bisimine ligand (3)**

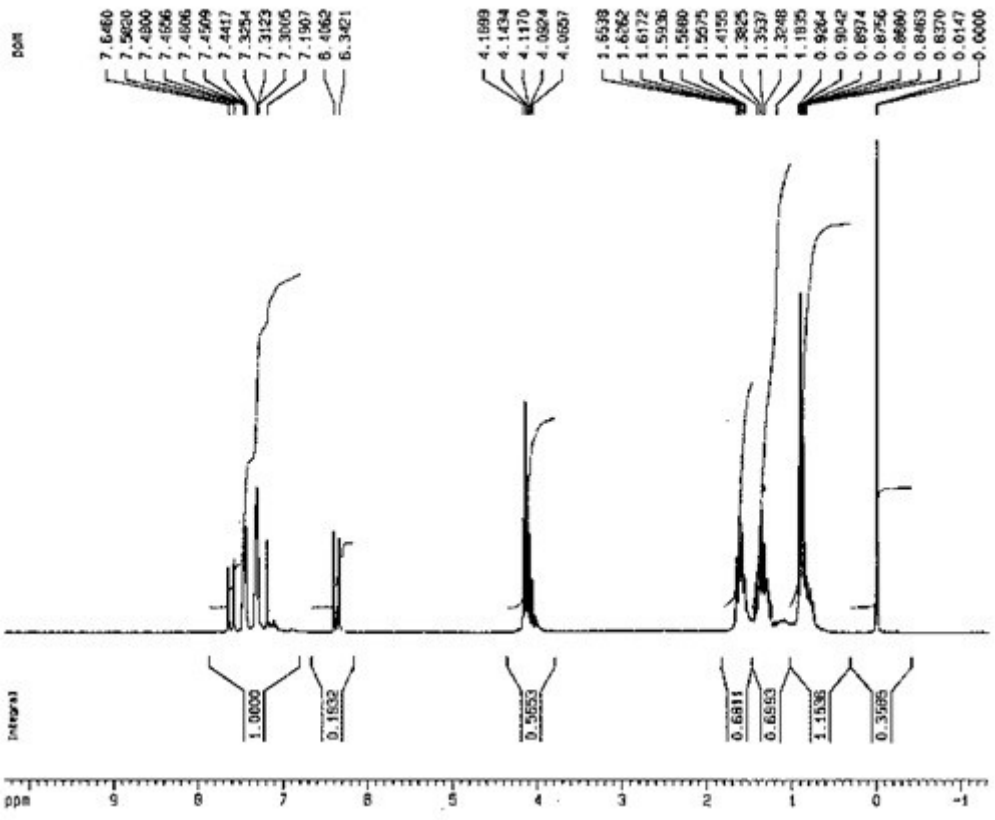


^{1}H-NMR of *N,N*-bisimine ligand (3) and palladium acetate after 30 min

3a



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 0.90 (t, 3 H, J = 7.5 Hz), 1.37 (six, 2 H, J = 7.7), 1.65 (q, 2 H, J = 7.5), 4.17 (t, 2 H, J = 6.7 Hz), 6.53 (d, 1 H, J = 16.0 Hz), 7.60 (d, 2 H, J = 8.7), 7.63 (d, 1 H, J = 16.0), 8.18 (d, 2 H, J = 8.7); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.69, 19.14, 30.66, 64.88, 122.59, 124.14, 128.59, 140.58, 141.55, 166.09.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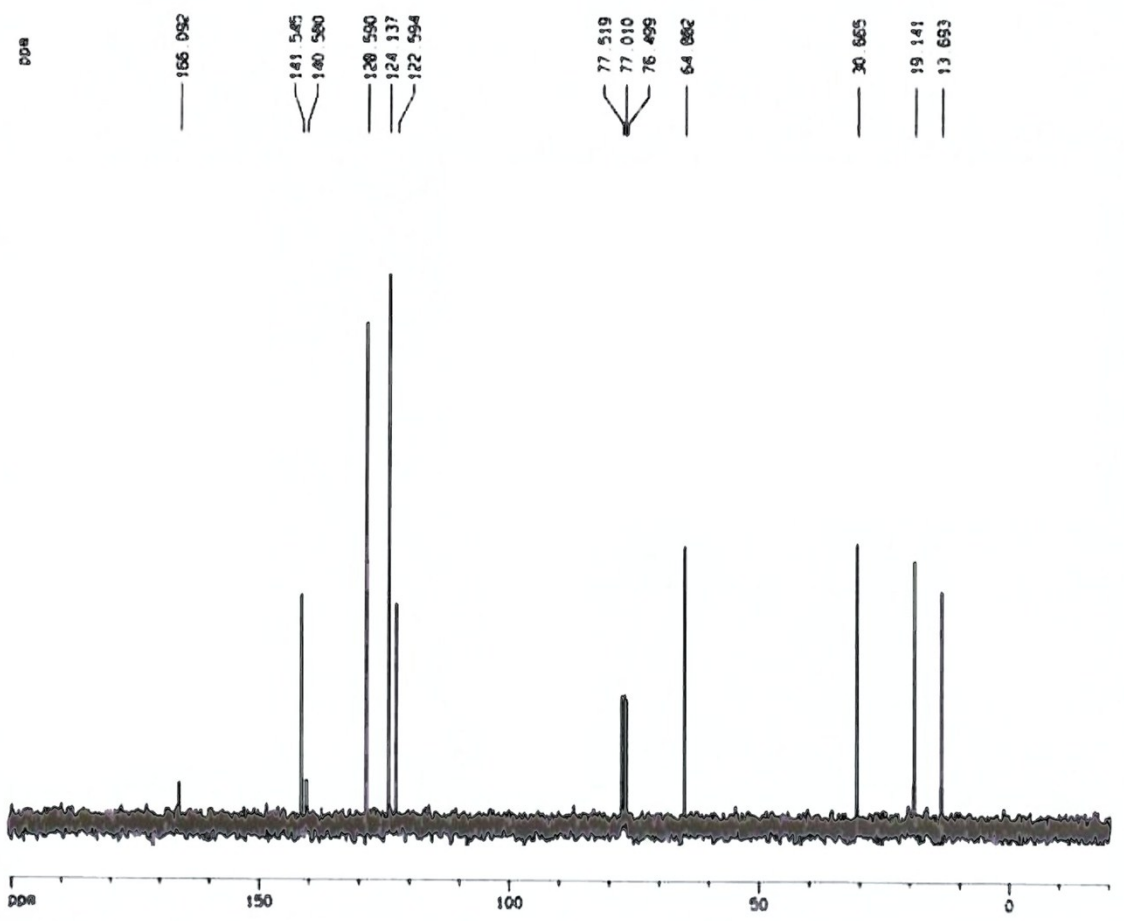
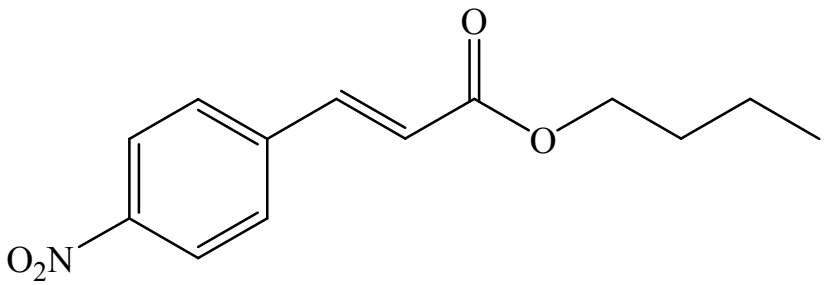
7.3005
7.1907
6.4062
6.3421
4.1699
4.1434
4.1170
4.0924
4.0557
1.6538
1.6262
1.6172
1.5936
1.5680
1.5575
1.4155
1.3825
1.3537
1.3248
1.1835
0.9264
0.9042
0.8974
0.8756
0.8680
0.8463
0.8370
0.0147
0.0000
Integral
1.0000
0.1632
0.5653
0.6811
0.6653
1.1536
0.3585
ppm
9
8
7
6
5
4
3
2
1
0
-1

^{1}H-NMR of **3a**

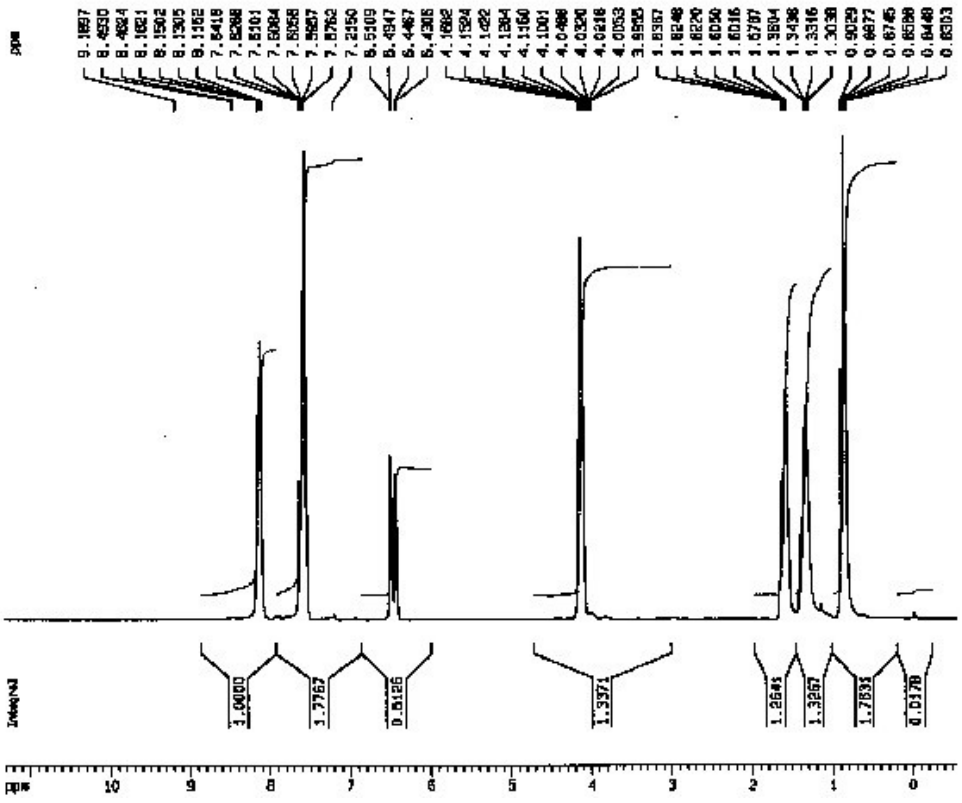


^{13}C-NMR of **3a**

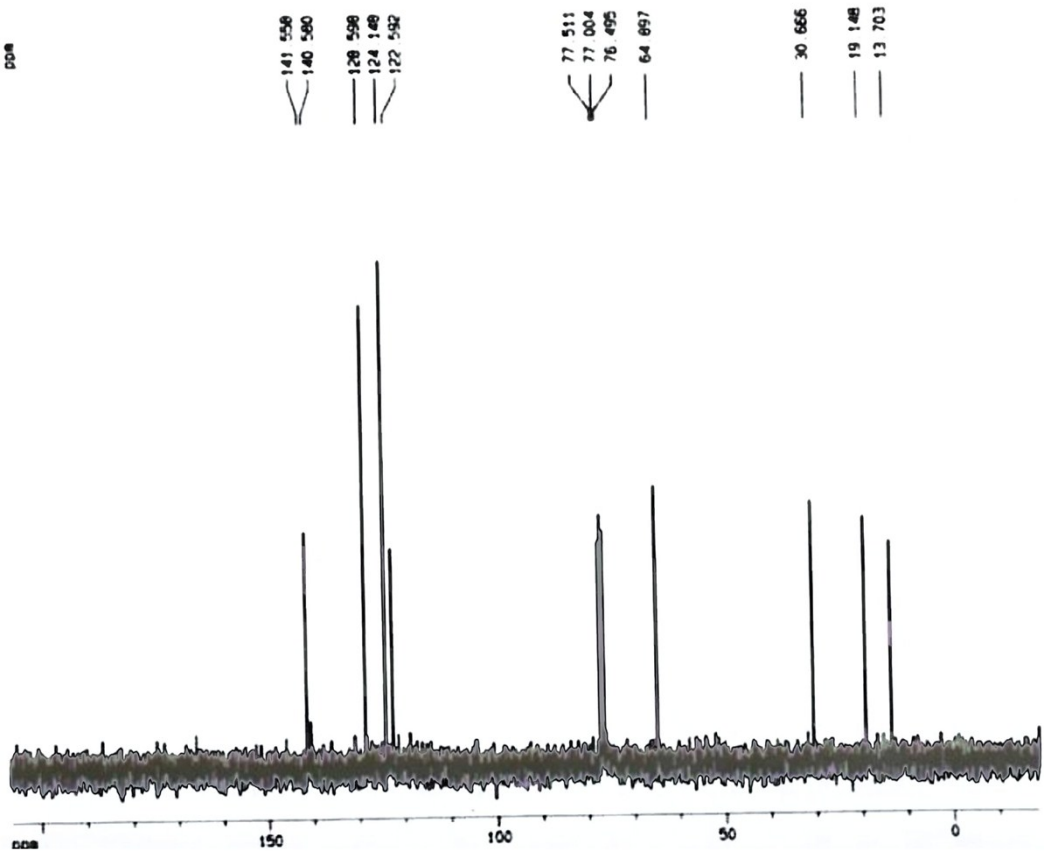
3b



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 8.31 (d, 2H, *J* =7.7), 7.57-7.64 (m, 5H), 6.47 (d, 1H, *J*= 16.0), 4.13 (t, 2H, *J* = 6.5), 1.57-1.63 (m, 2H), 1.30- 1.36 (m, 2H), 0.87 (t, 3H, *J* = 7.5); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.70, 19.15, 30.67, 64.90, 122.59, 124.15, 128.60, 140.58, 141.56.

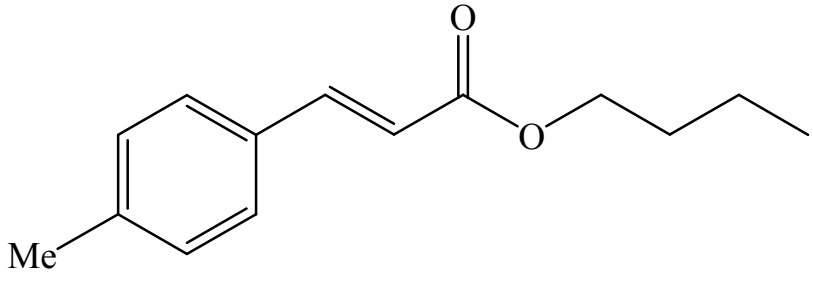


^{1}H-NMR of **3b**



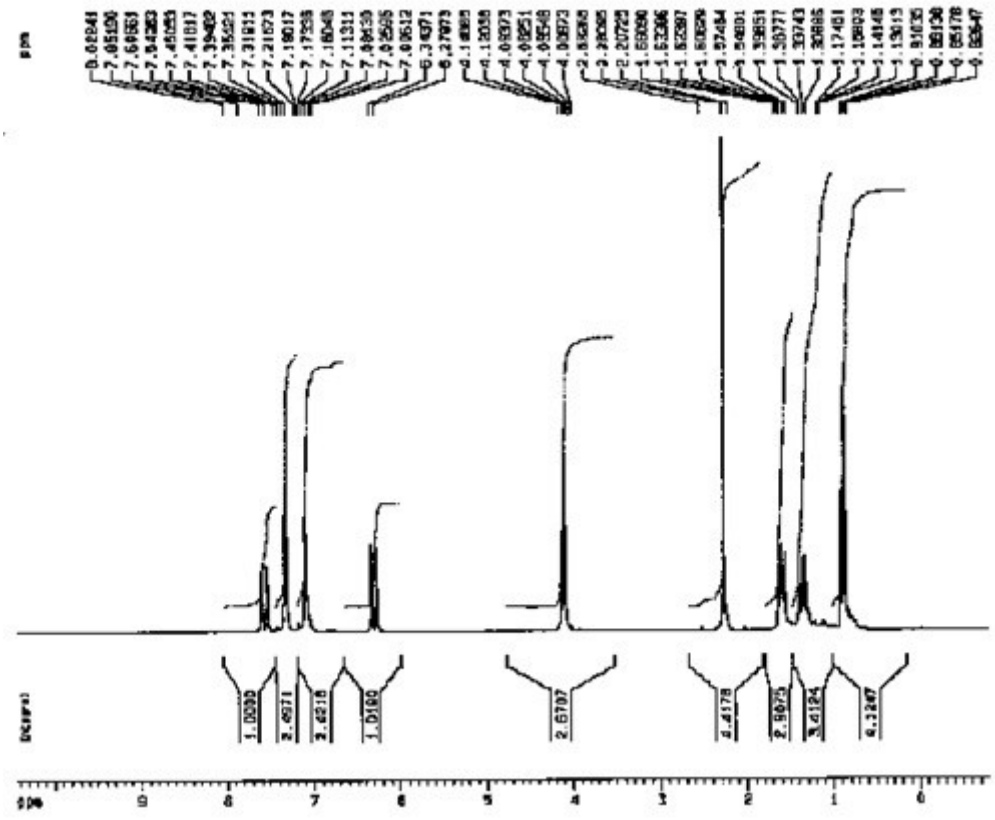
^{13}C-NMR of 3**b**

3c

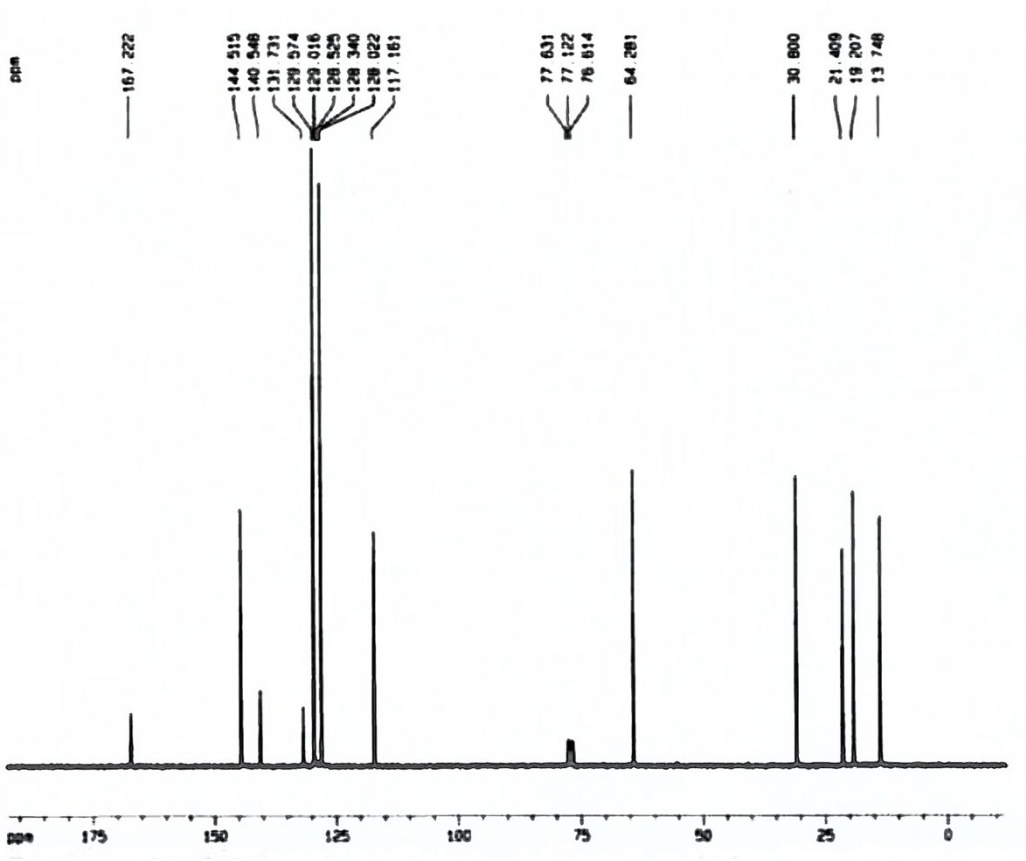


^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 0.88 (t, 3H, *J* = 7.2), 1.35 (m, 2H), 1.60 (m, 2H), 2.28 (s, 3H), 4.12 (t, 2H, *J* = 6.7), 6.31 (d, 1H, *J* = 16.0), 7.09 (d, 2H, *J* = 8.0), 7.33 (d, 2H, *J*=

8.0), 7.57 (d, 1H, *J*= 16.0); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.75, 19.21, 21.41, 30.80, 64.28, 117.16, 128.34, 129.57, 131.73, 140.55, 144.52, 167.22.

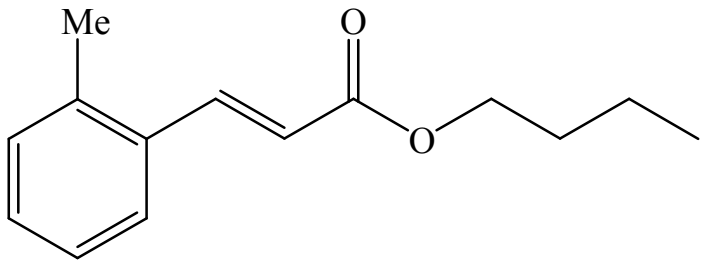


^{1}H-NMR of **3c**

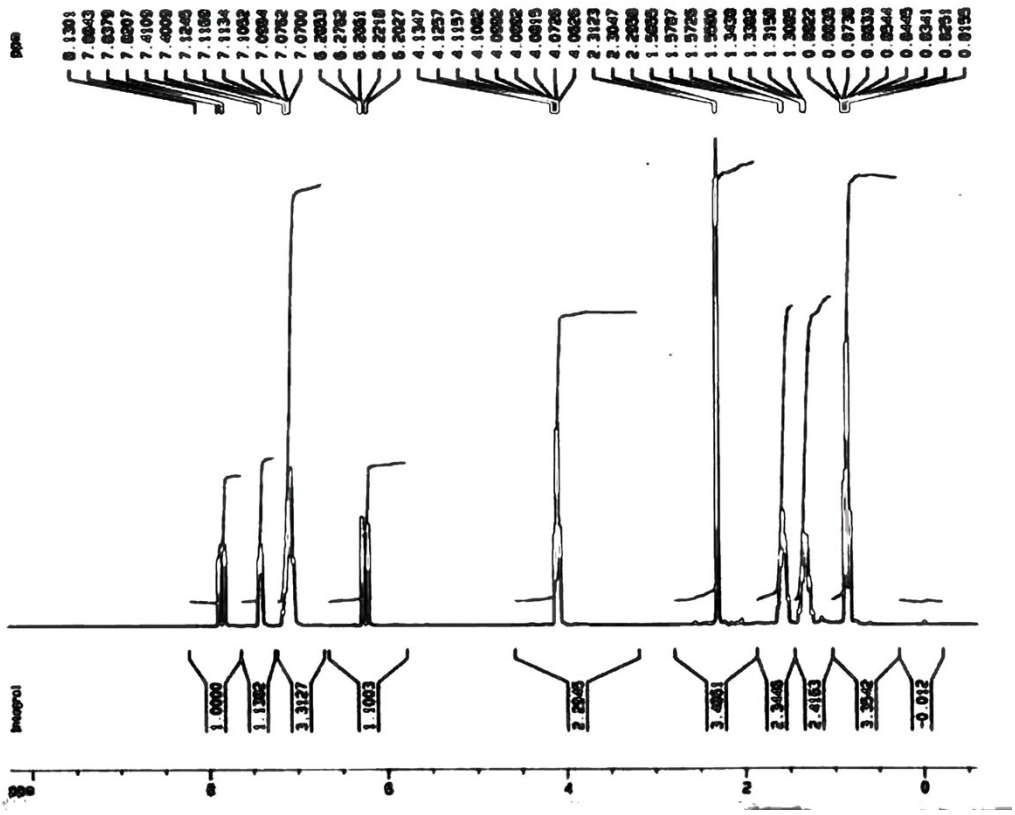


^{13}C-NMR of **3c**

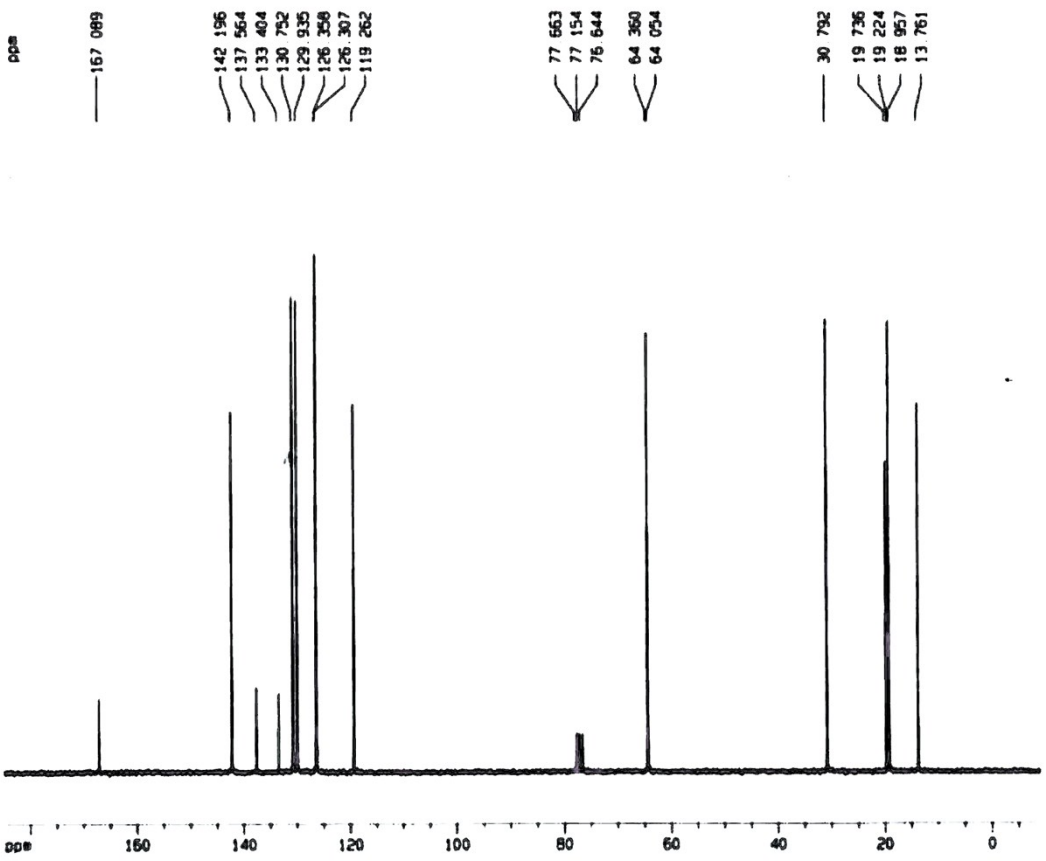
3d



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 0.85 (t, 3 H, J = 2.5 Hz), 1.32 (sex, 2 H), 1.57 (q, 2 H), 2.30 (s, 3 H), 4.11 (t, 2 H), 6.27 (dd, 1 H, J = 15.9 Hz, J = 4.8 Hz), 7.11 (m, 3 H), 7.41 (m, 1 H), 7.84 (dd, 1 H, J = 13.7 Hz, J = 4.3 Hz); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.76, 18.96, 19.74, 30.79, 64.36, 119.26, 126.31, 129.94, 130.75, 133.40, 137.56, 142.20, 167.09.

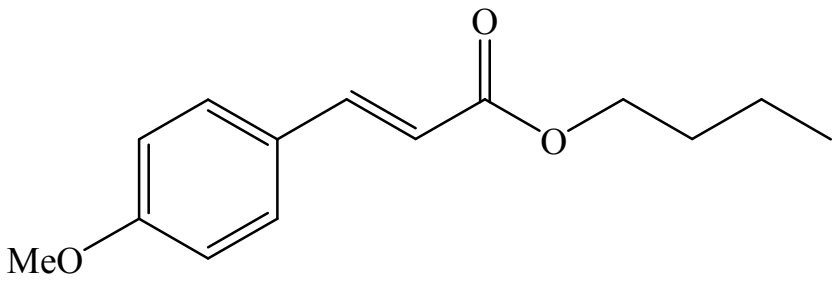


^{1}H-NMR of **3d**



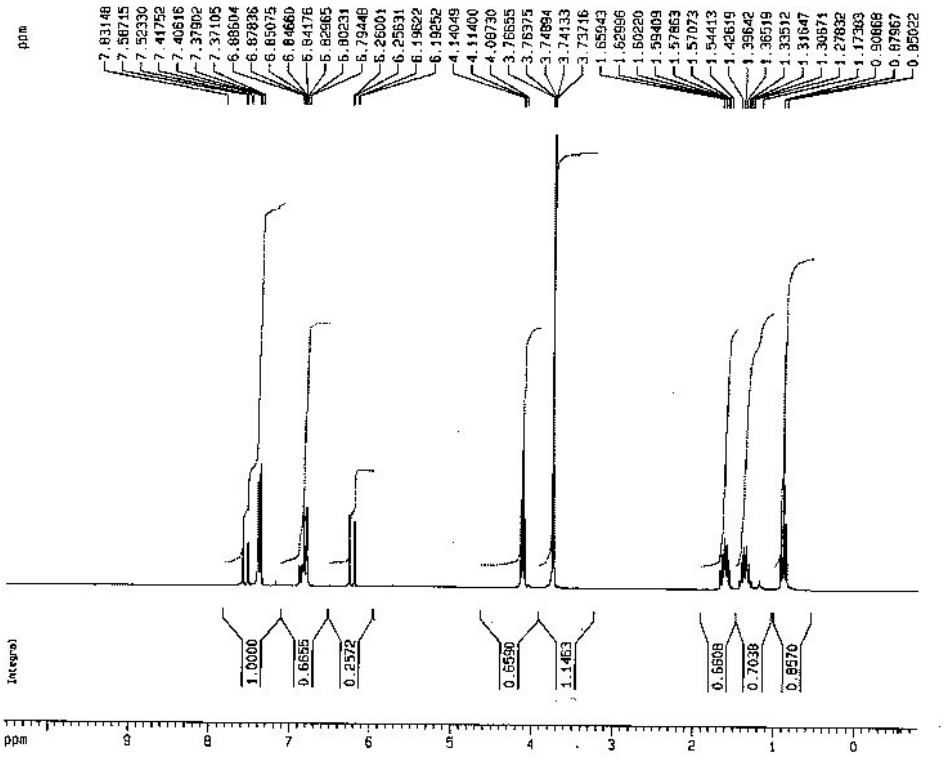
^{13}C-NMR of **3d**

3e

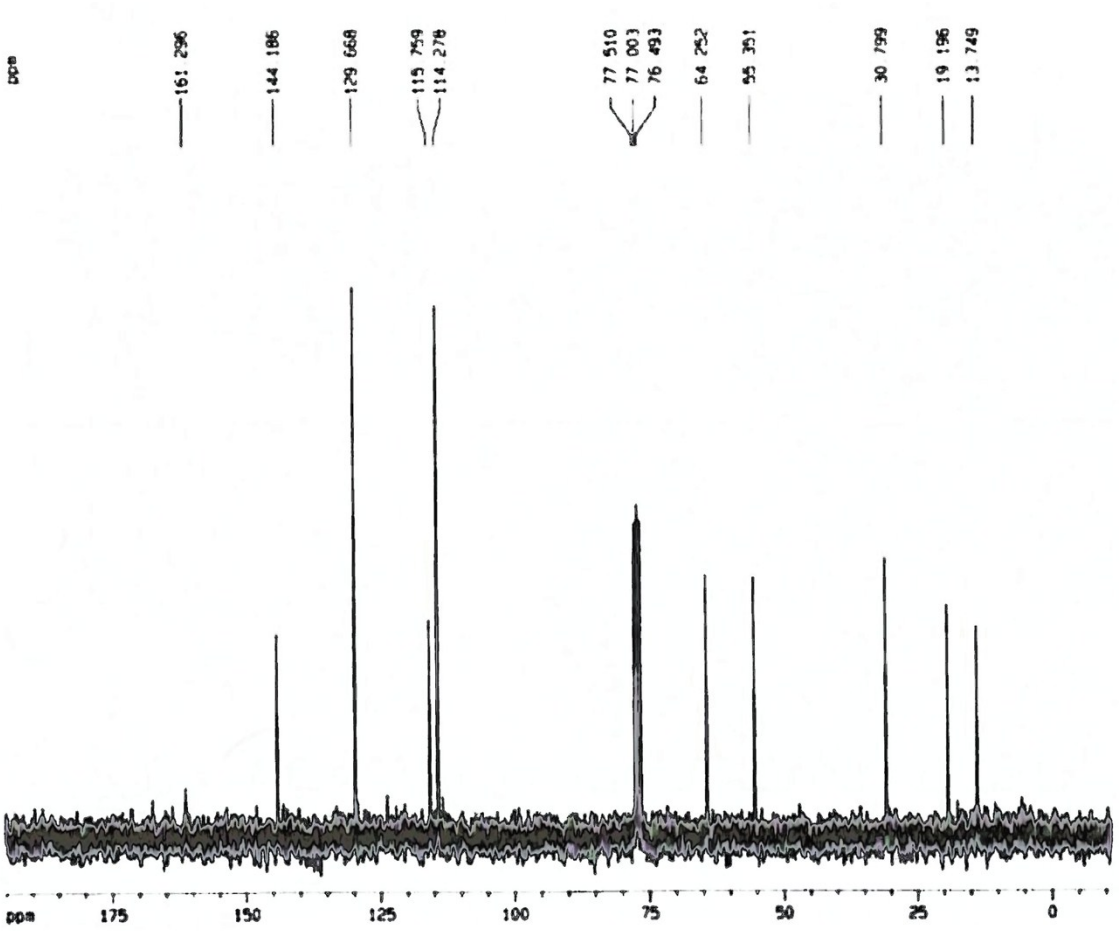


^{1}H NMR (250 MHz, $CDCl_3$) (ppm): 0.87 (t, 3H, J = 7.2), 1.27-1.42 (m, 2H), 1.54-1.65 (m, 2H), 4.11 (t, 3H, J = 6.7), 3.73 (s, 3H), 6.22 (d, 1H, J = 16.0), 6.81 (d, 2 H, J = 8.7), 7.38 (d,

2H, J = 8.7), 7.55 (d, 1H, J = 16.0). ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.75, 19.20, 30.80, 55.35, 64.25, 114.28, 115.76, 129.67, 144.19, 161.30.

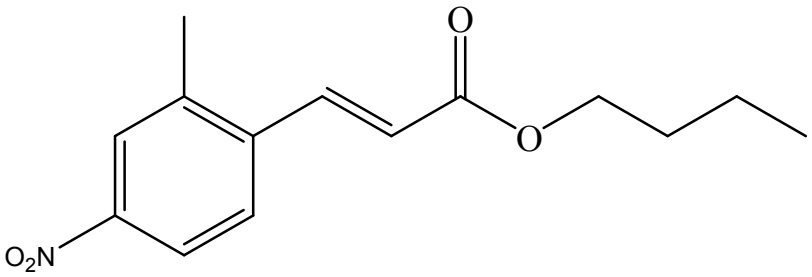


^{1}H-NMR of **3e**



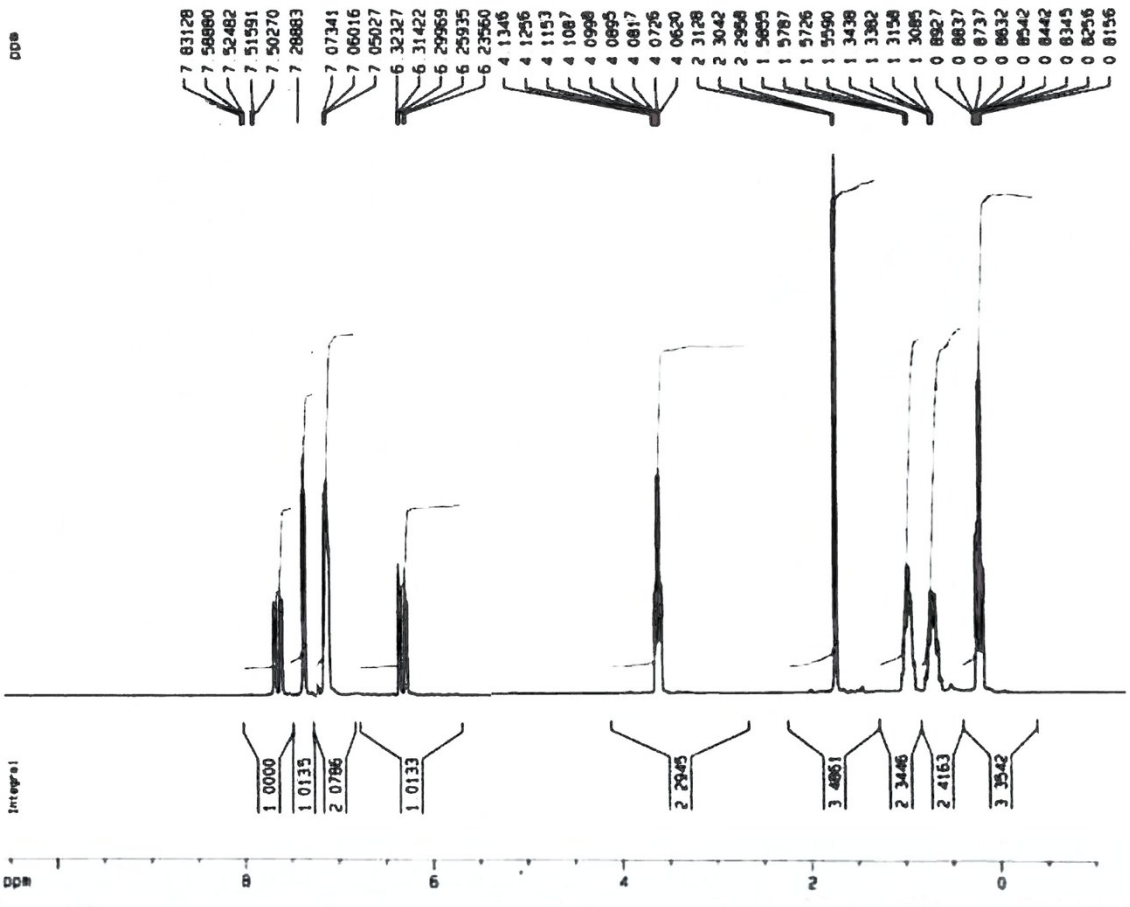
^{13}C-NMR of **3e**

3f

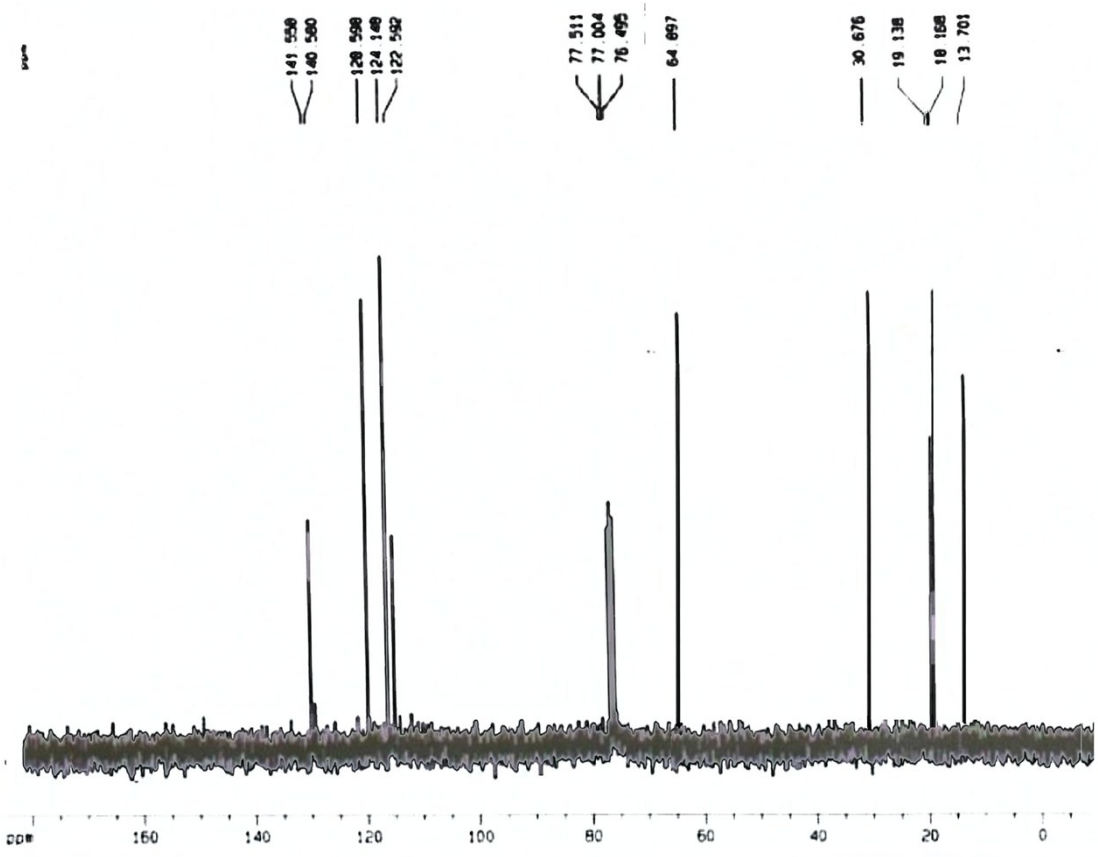


^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 0.85 (t, 3 H, J = 2.5 Hz), 1.32 (sex, 2 H), 1.57 (q, 2H), 2.30 (s, 3 H), 4.11 (t, 2 H), 6.30 (dd, 1 H, J = 16 Hz, J = 5.9 Hz), 7.06 (m, 2 H), 7.28 (s, 1 H),

7.52 (dd, 1 H, J = 18.2 Hz, J = 5.5 Hz),); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.70, 18.16, 19.14, 30.67, 64.90, 122.60, 124.15, 128.60, 140.58, 141.56.

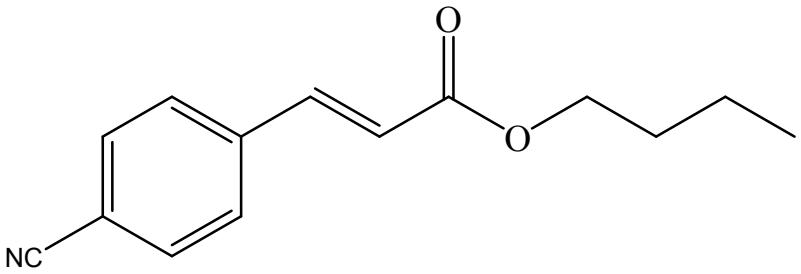


^{1}H-NMR of **3f**

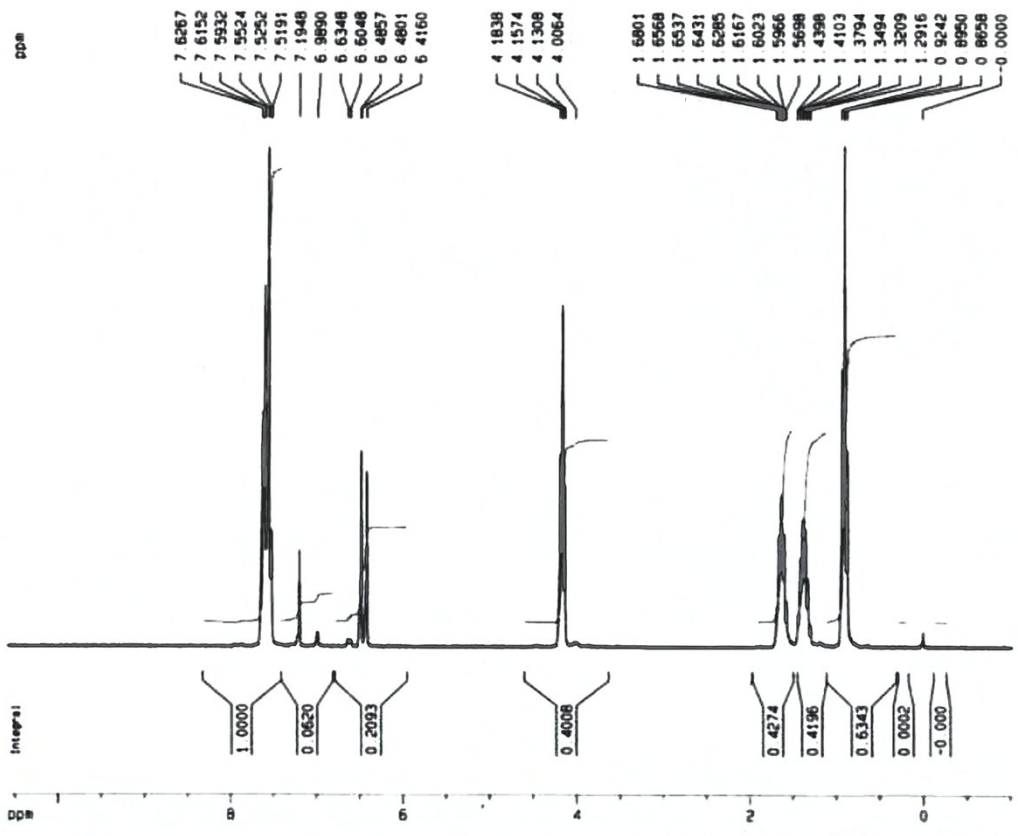


^{13}C-NMR of **3f**

3g



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 0.89 (t, 3 H, J = 7.25 Hz), 1.35 (six, 2 H, J = 7.5 Hz), 1.64 (q, 2 H, J = 6.7), 4.16 (t, 2 H, J = 6.5 Hz), 6.48 (d, 1 H, J = 16 Hz), 7.59, (m, 5 H); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.68, 19.12, 27.82, 30.64, 64.75, 113.27, 118.31, 121.84, 128.35, 132.58, 138.55, 142.03, 166.14.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6.4801
6.4160
4.1838
4.1574
4.1308
4.0064
1.6801
1.6568
1.6537
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1.6285
1.6167
1.6023
1.5966
1.5698
1.4398
1.4103
1.3794
1.3494
1.3209
1.2916
0.9242
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0.8658
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Integral
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0.2093
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ppm
8
6
4
2
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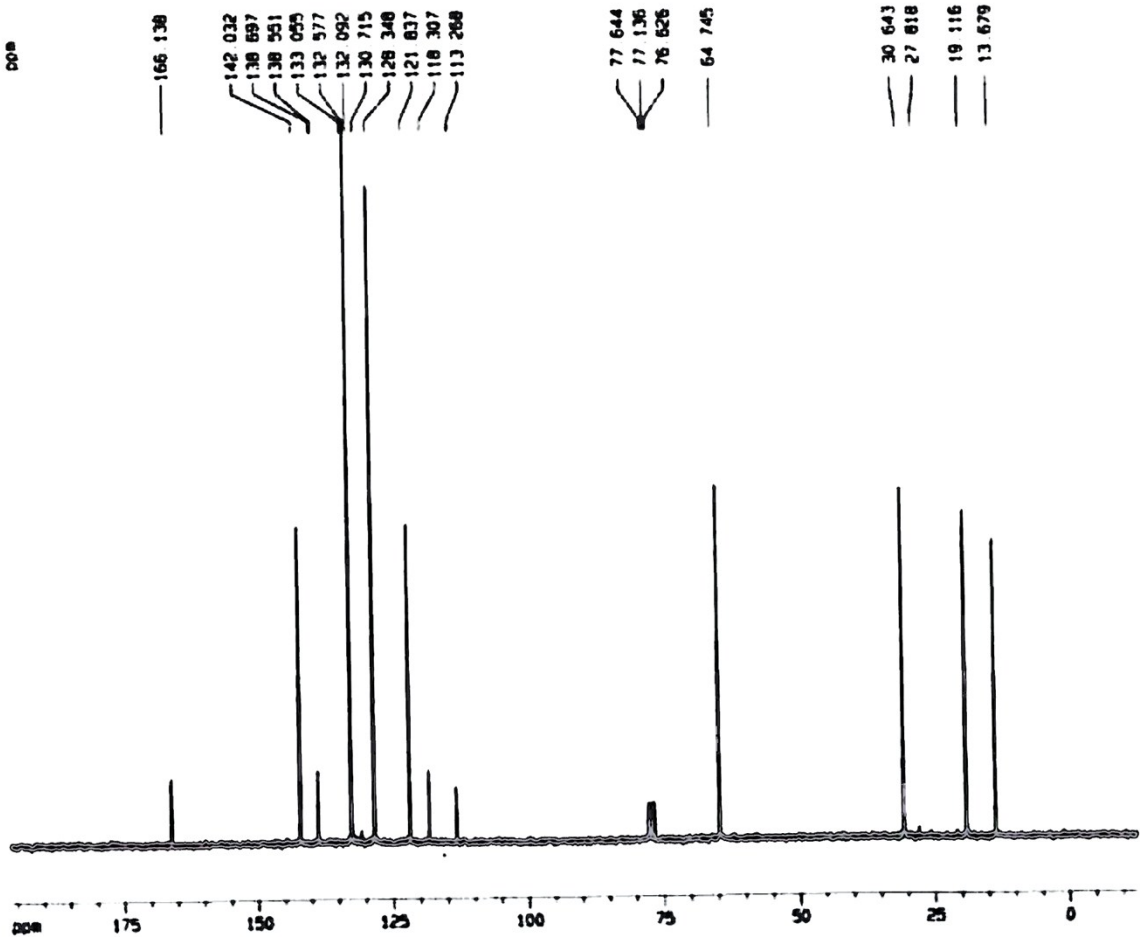
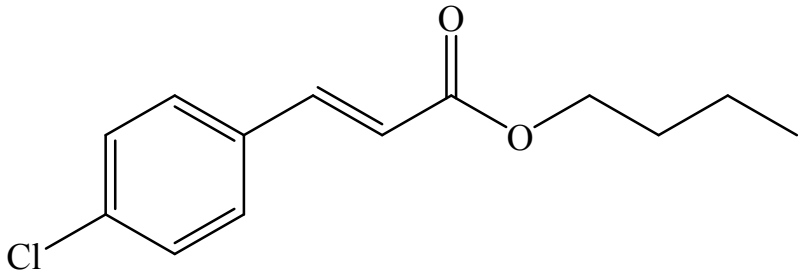
^{1}H-NMR of **3g**

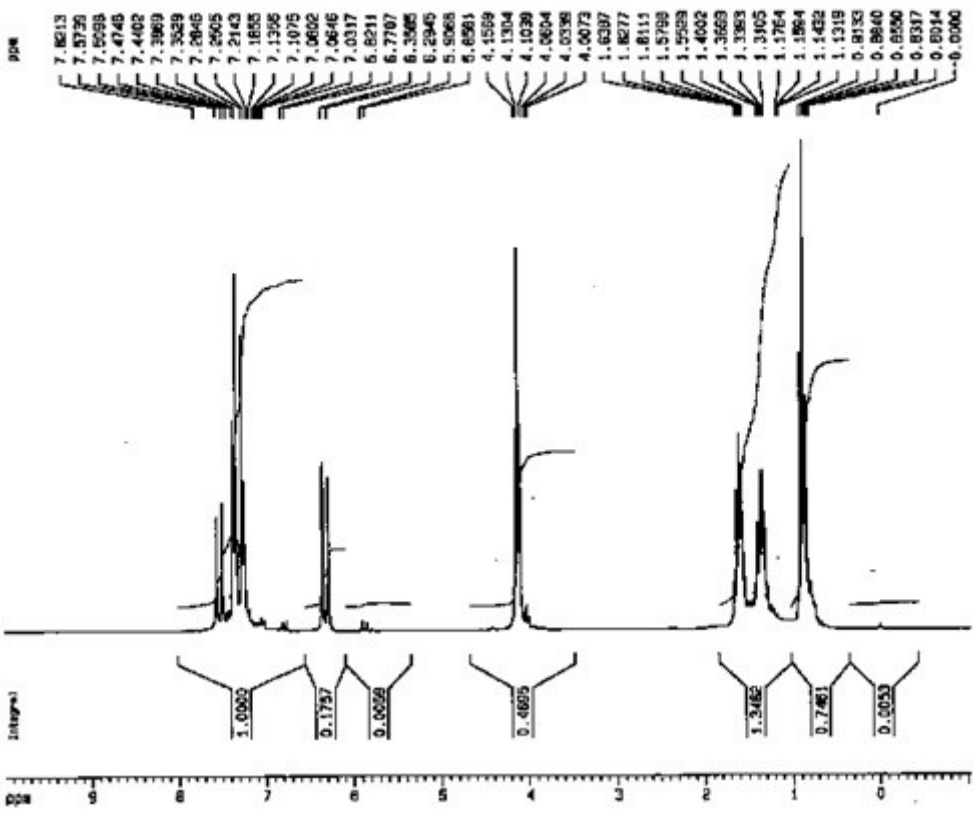


^{13}C-NMR of **3g**

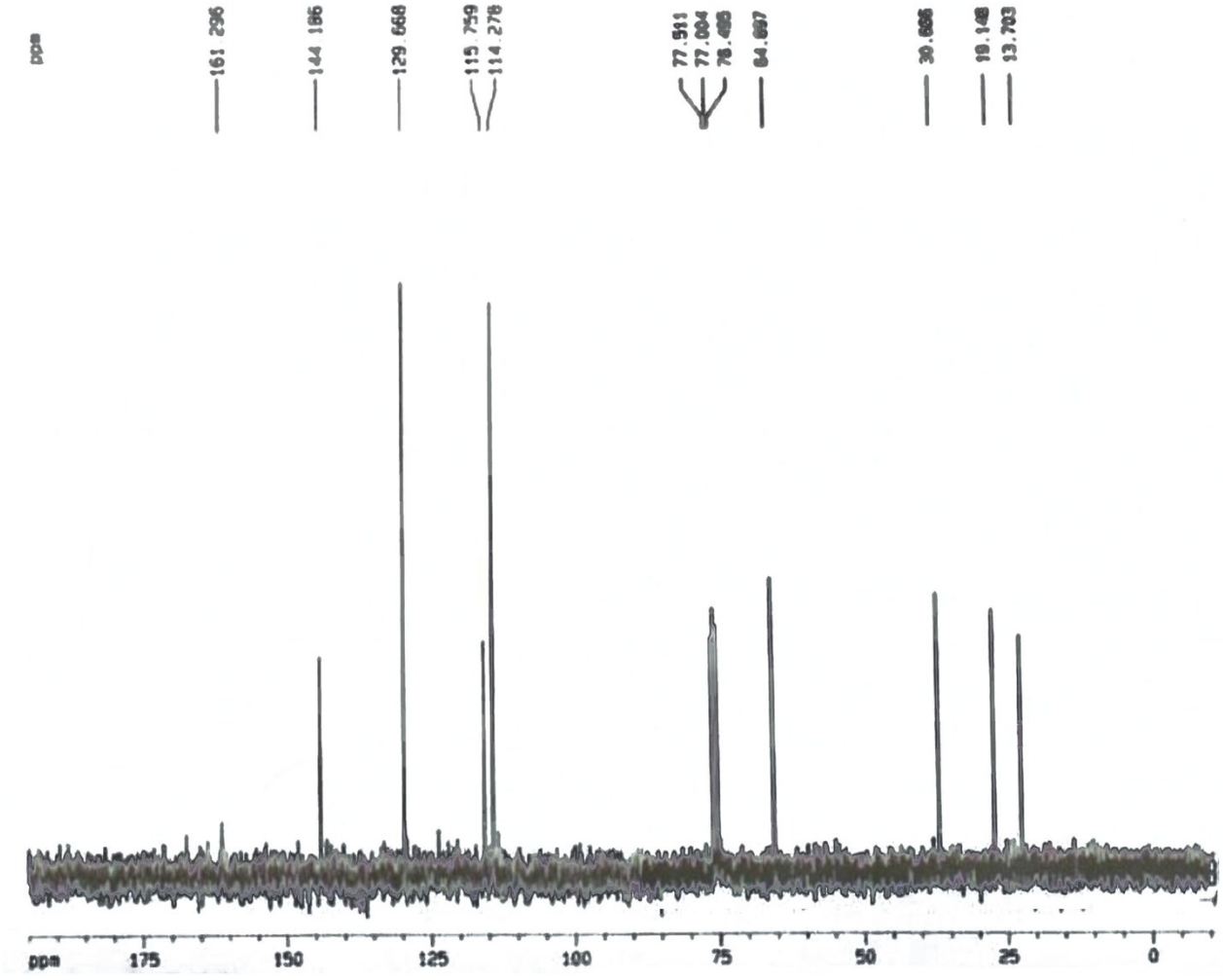
3h



: ^{1}H NMR (250 MHz, $CDCl_3$) (ppm): 7.54 (d, 1H, *J* = 16.0), 7.25-7.44 (m, 4H), 6.32 (d, 1H, *J* = 16.0), 4.13 (t, 3H, *J* = 6.5), 1.55.1.63 (m, 2H), 1.31-1.40 (m, 2H), 0.88 (t, 3H, *J* = 7.2); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.70, 19.15, 30.67, 64.90, 114.28, 115.76, 129.67, 144.19, 161.30.

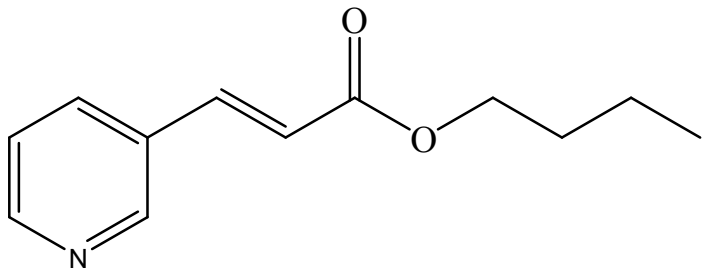


^{1}H-NMR of **3h**

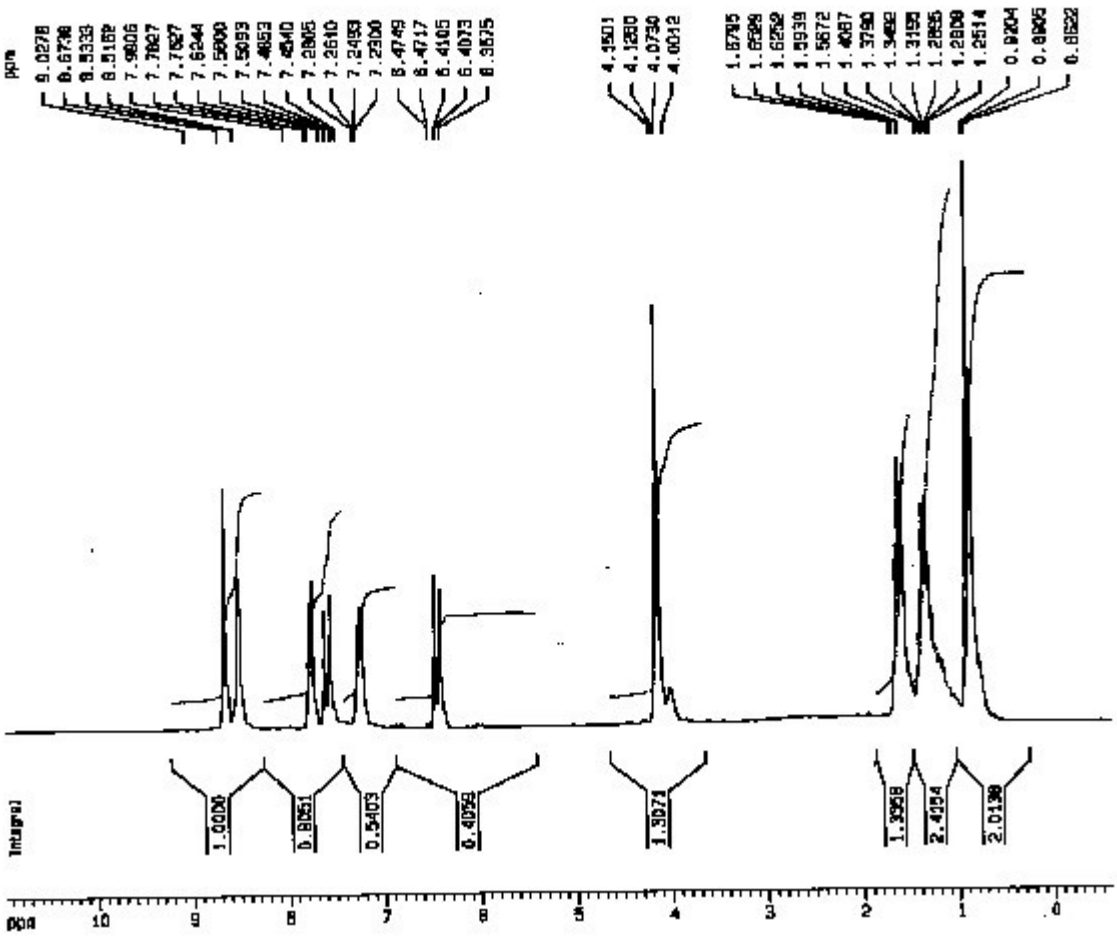


^{13}C-NMR of **h**

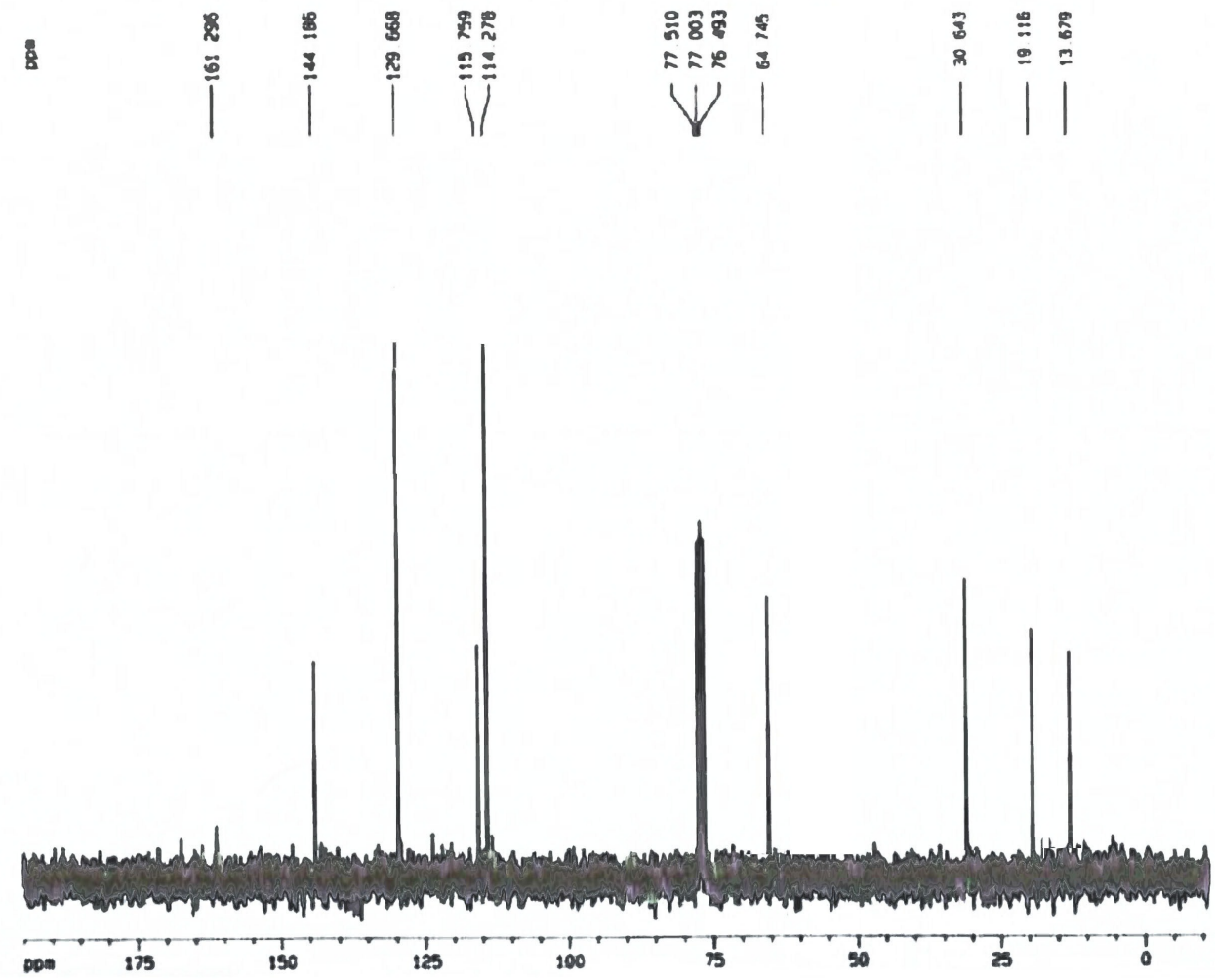
3i



^{1}H NMR (250 MHz, $CDCl_3$) (ppm): 8.67 (s, 1H), 8.52 (d, 1H, *J* = 4.2), 7.76 (d, 1H, *J* = 7.5), 7.59 (d, 1H, *J* = 16.0), 7.28-7.23 (m, 1H), 6.44 (d, 1H, *J* = 16.0), 4.15 (t, 2H, *J* = 6.5), 1.67-1.56 (m, 2H), 1.40-1.25 (m, 2H), 0.89 (t, 3H, *J* = 7.5); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.68, 19.12, 27.82, 30.64, 64.75, 114.28, 115.76, 129.67, 144.19, 161.29.

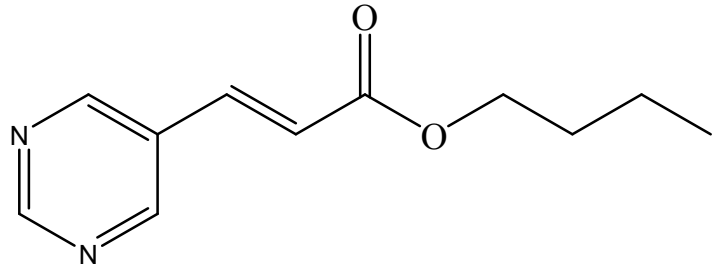


^{1}H-NMR of **3i**

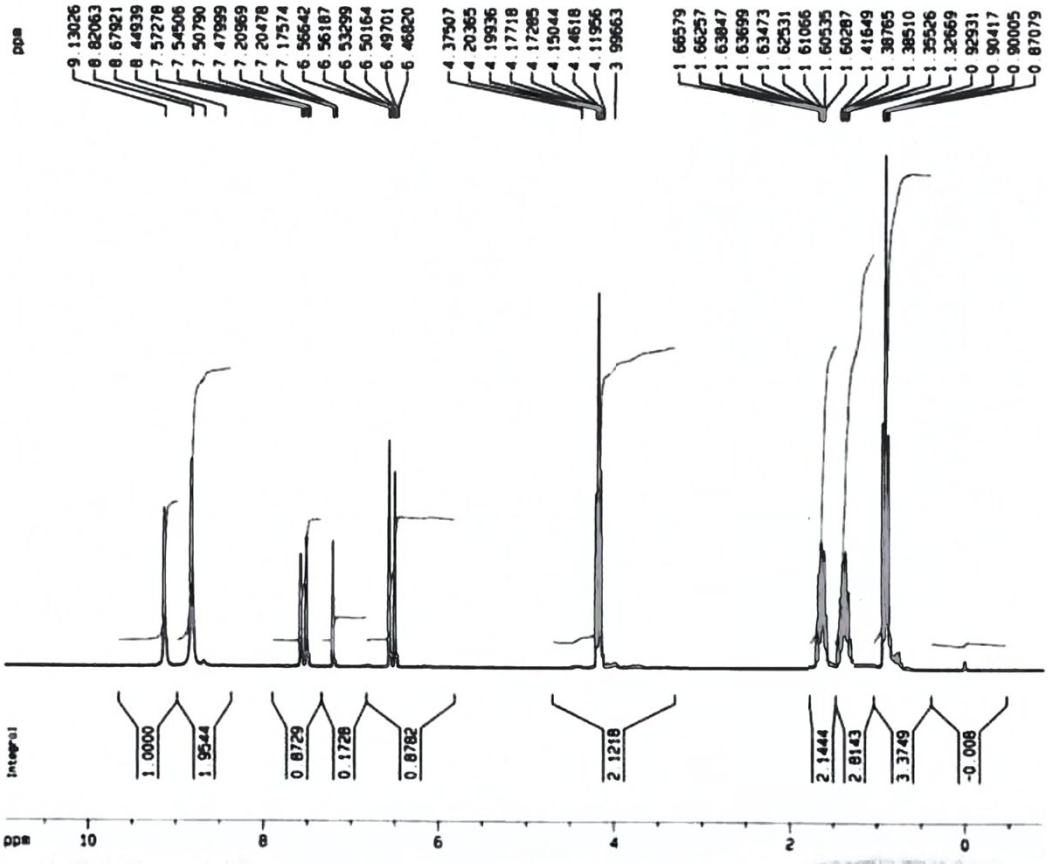


^{13}C-NMR of **3i**

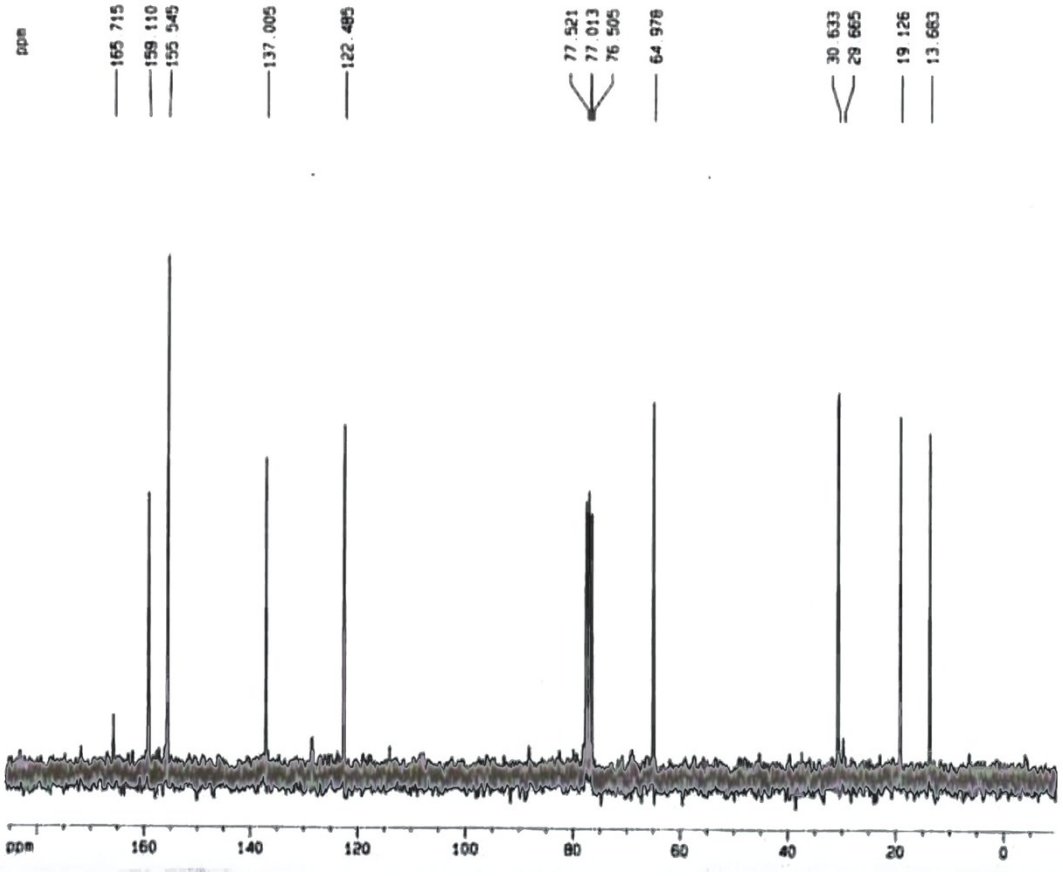
3j



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 0.90 (t, 3 H, J = 7.5 Hz), 1.39 (six, 2 H, J = 7.5 Hz), 1.61 (q, 2 H, J = 6 Hz), 4.17 (t, 2 H, J = 5.5 Hz), 6.53 (d, 1 H, J = 15 Hz), 7.52 (d, 1 H, J = 15 Hz), 8.82 (s, 2 H), 9.13 (s, 1 H); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 13.68, 19.13, 30.63, 64.98, 122.49, 137.00, 155.55, 159.11, 165.71.

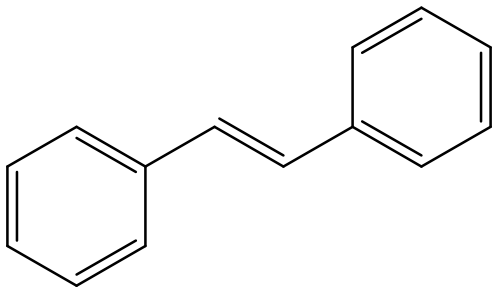


^{1}H-NMR of **3j**

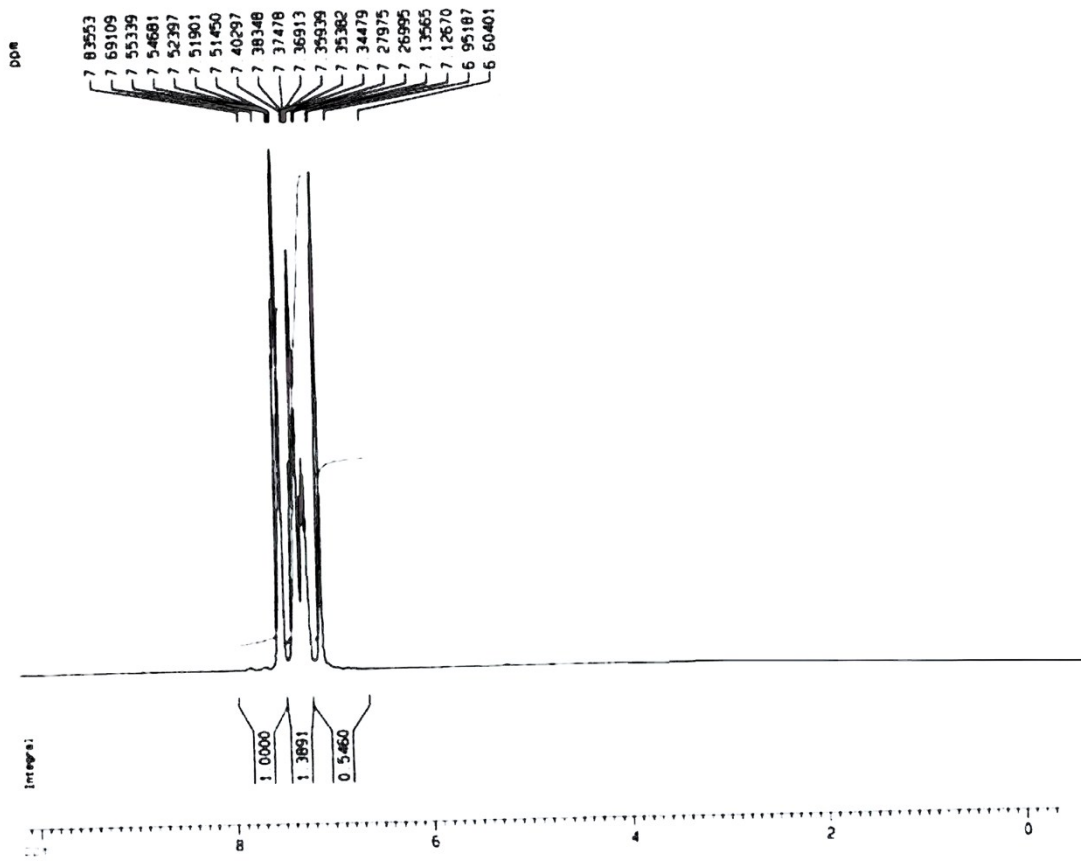


^{13}C-NMR of **3j**

3k



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 7.13 (d, 2 H, J =16.3), 7.31 (m, 6 H), 7.52 (m, 4 H); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 122.59, 124.15, 128.60, 136.58, 137.55.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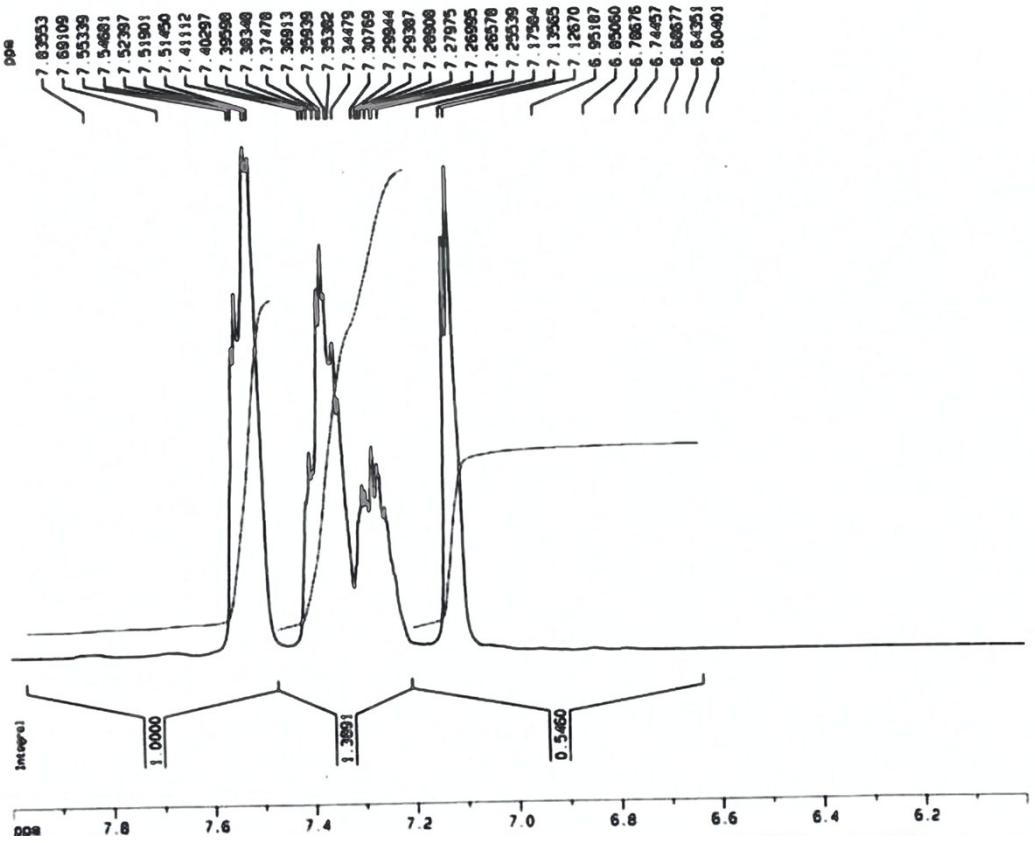
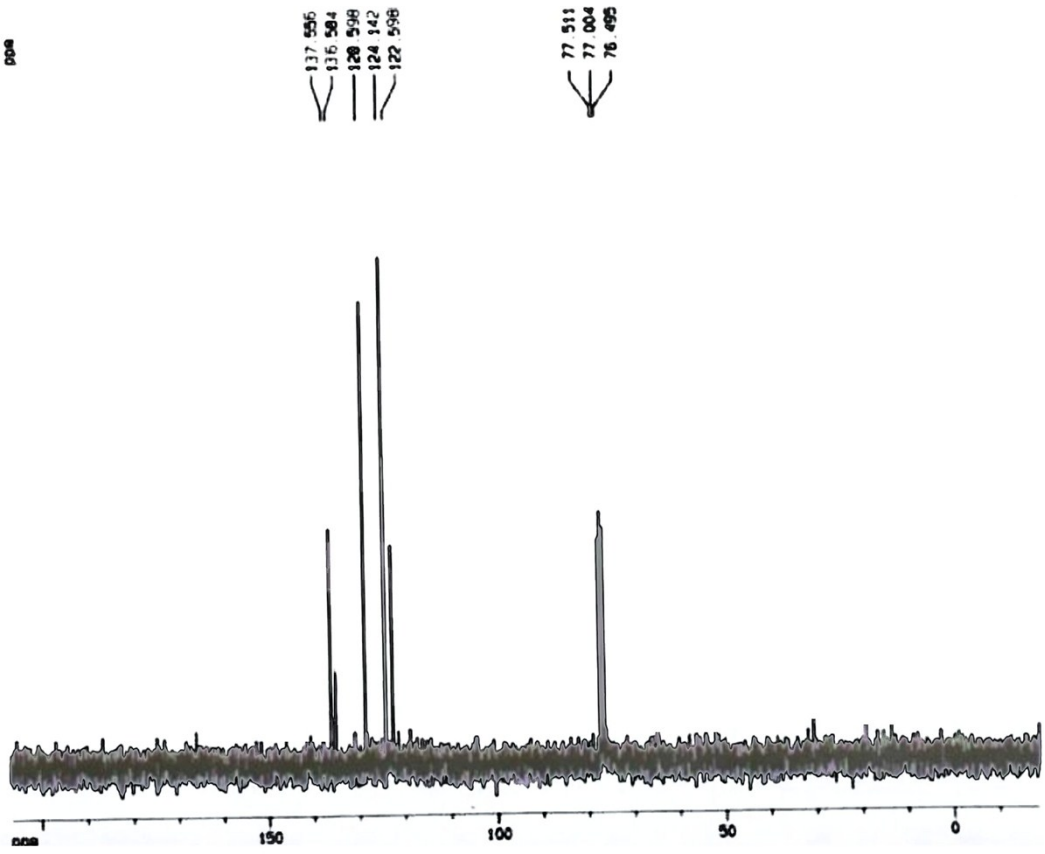
7.36913
7.35939
7.35382
7.34479
7.27975
7.26995
7.13565
7.12670
6.95187
6.60401
Integral
1.0000
1.3891
0.5460
8
6
4
2
0

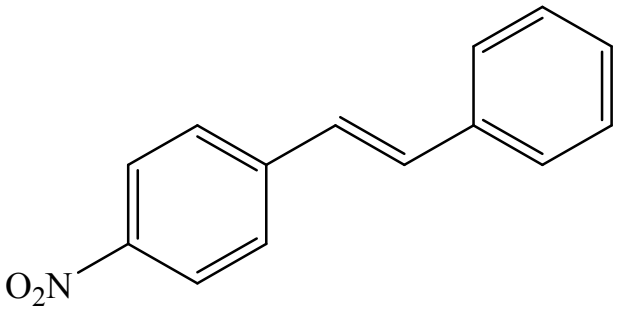
^{1}H-NMR of **3k**


ppm
7.83553
7.69109
7.55339
7.54681
7.52397
7.51901
7.51450
7.41112
7.40297
7.39598
7.38348
7.37478
7.36913
7.35939
7.35382
7.34479
7.30769
7.29944
7.29387
7.28908
7.27975
7.26995
7.26578
7.25539
7.17584
7.13565
7.12670
6.95187
6.85060
6.78676
6.74457
6.68577
6.64351
6.60401
Integral
1.0000
1.3691
0.5460
ppm
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2

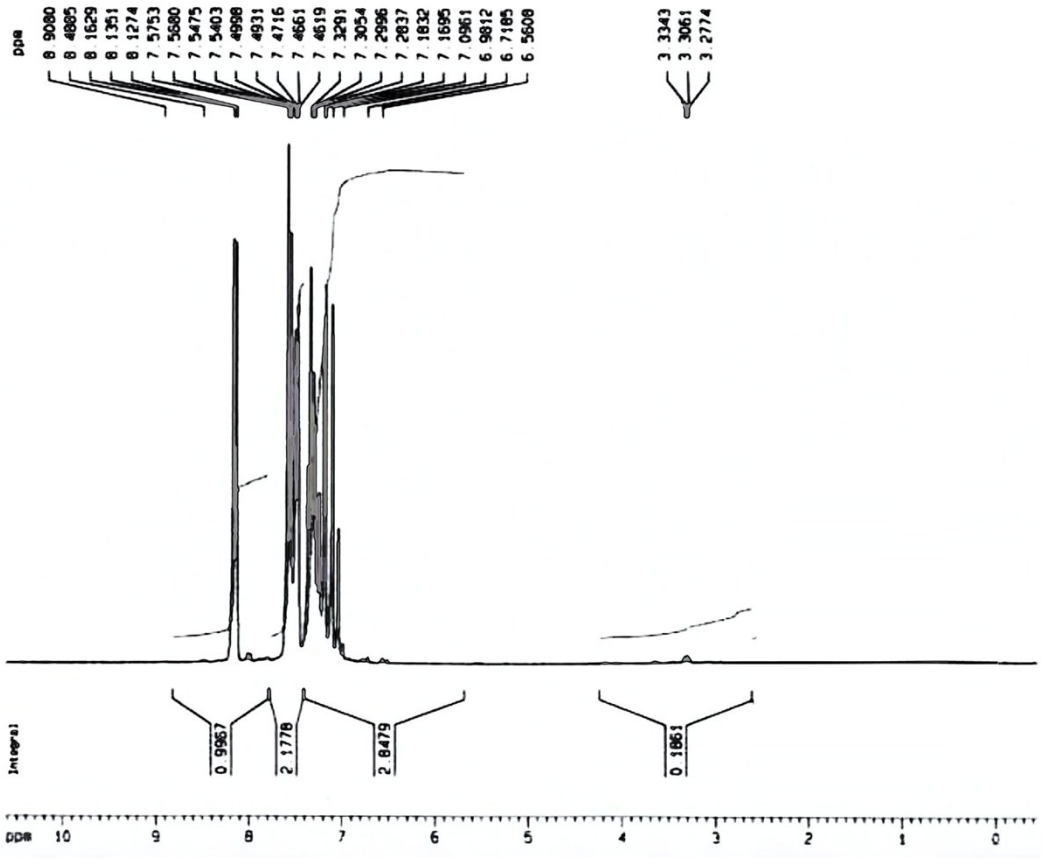

ppm
137.556
136.584
128.598
124.142
122.598
77.511
77.004
76.495
150
100
50
0

^{13}C-NMR of **3k**

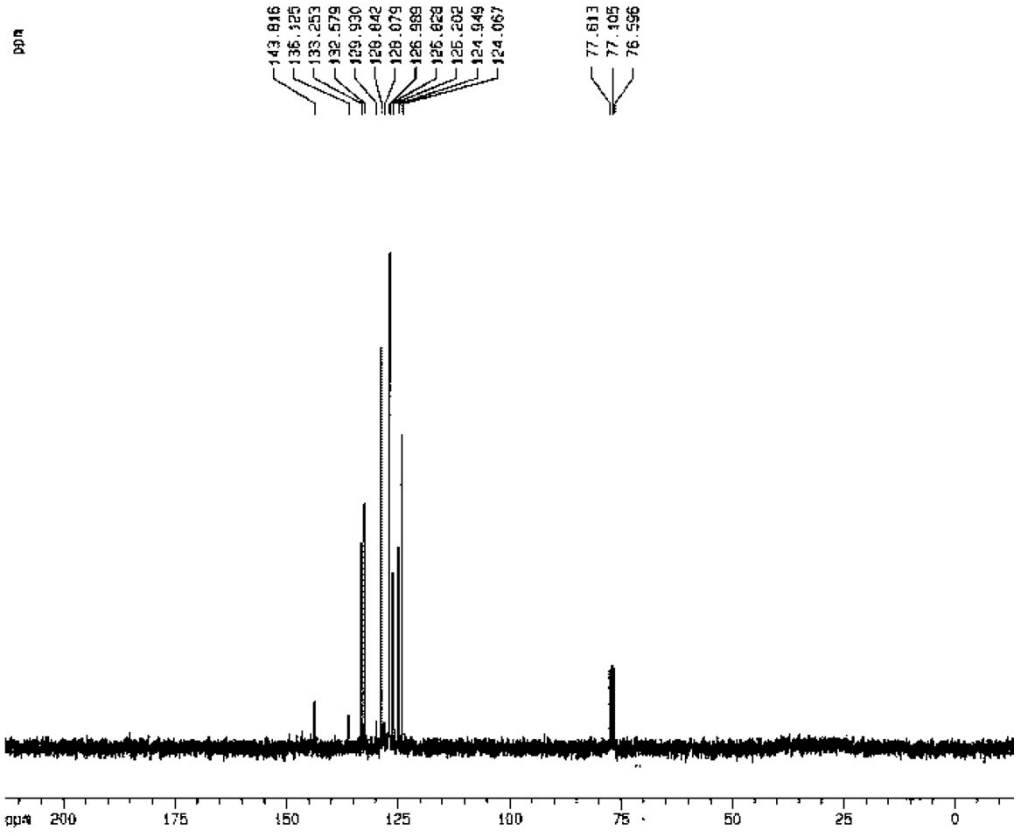
3l



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 6.98-7.57 (m, 9 H), 8.14 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) (ppm): 124.07, 124.95, 126.20, 126.93, 127.00, 128.08, 129.04, 129.93, 132.58, 133.25, 136.13, 143.82.

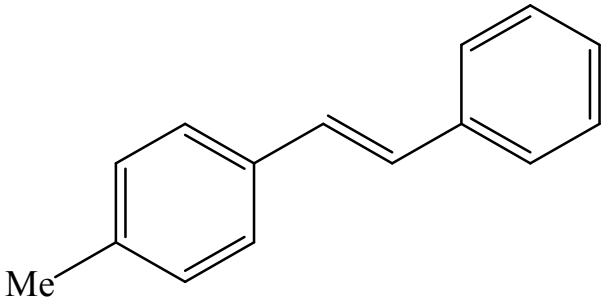


^{1}H-NMR of **3l**

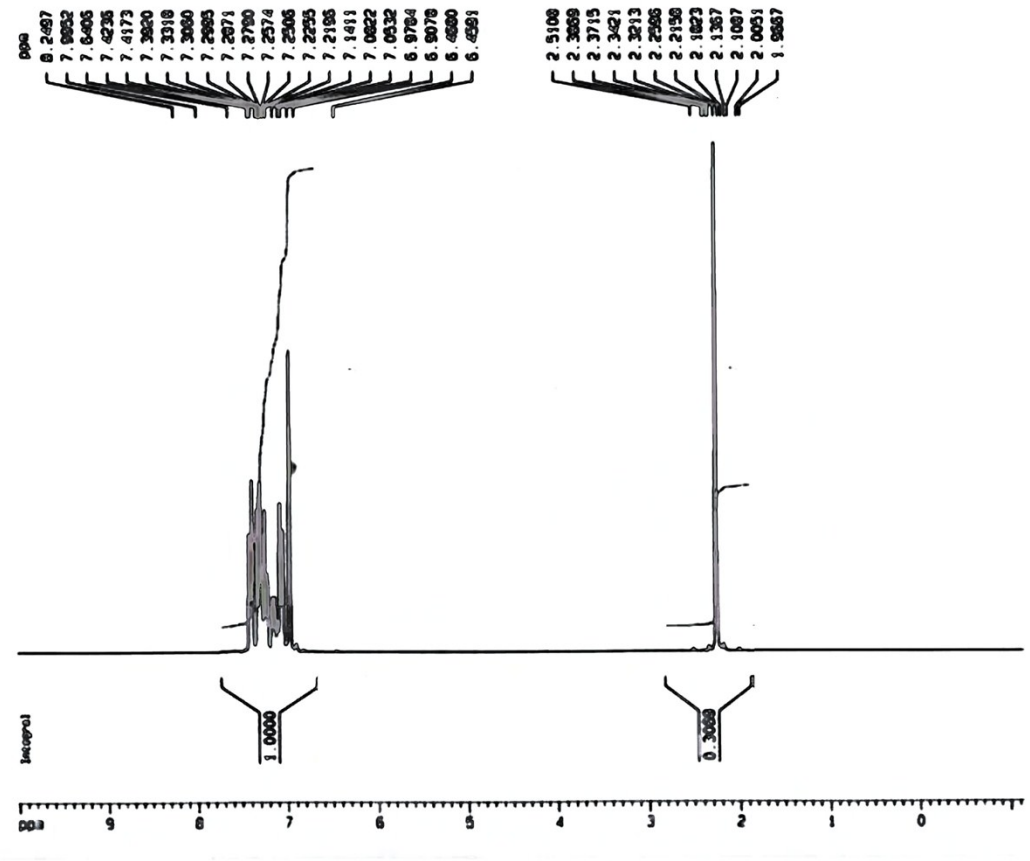


^{13}C-NMR of **3l**

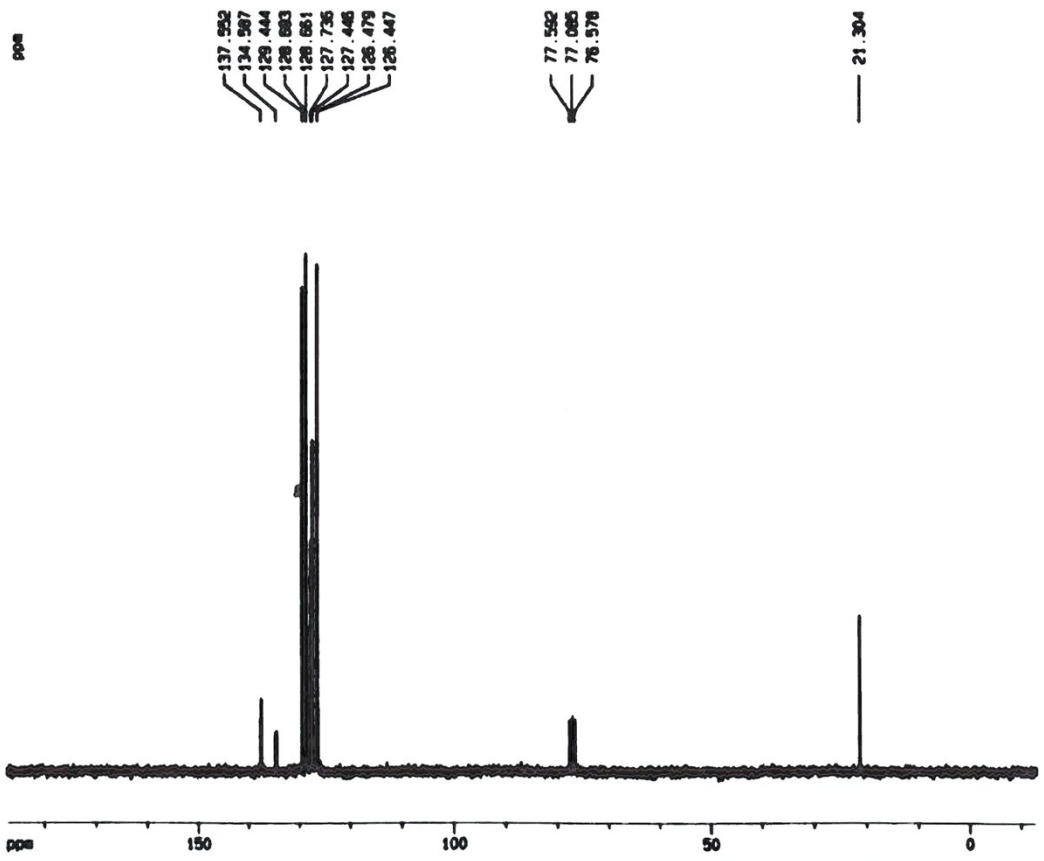
3m



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 2.26 (s, 3 H), 6.91-7.64 (m, 11 H); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 21.30, 126.45, 126.48, 127.45, 127.74, 128.69, 129.44, 134.59, 137.55.

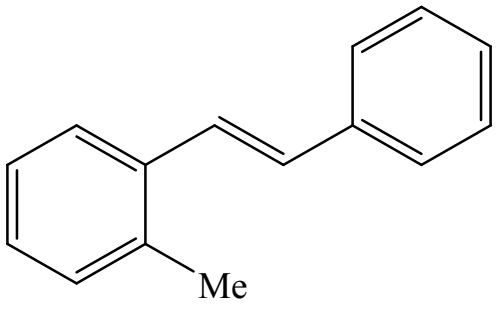


^{1}H-NMR of **3m**

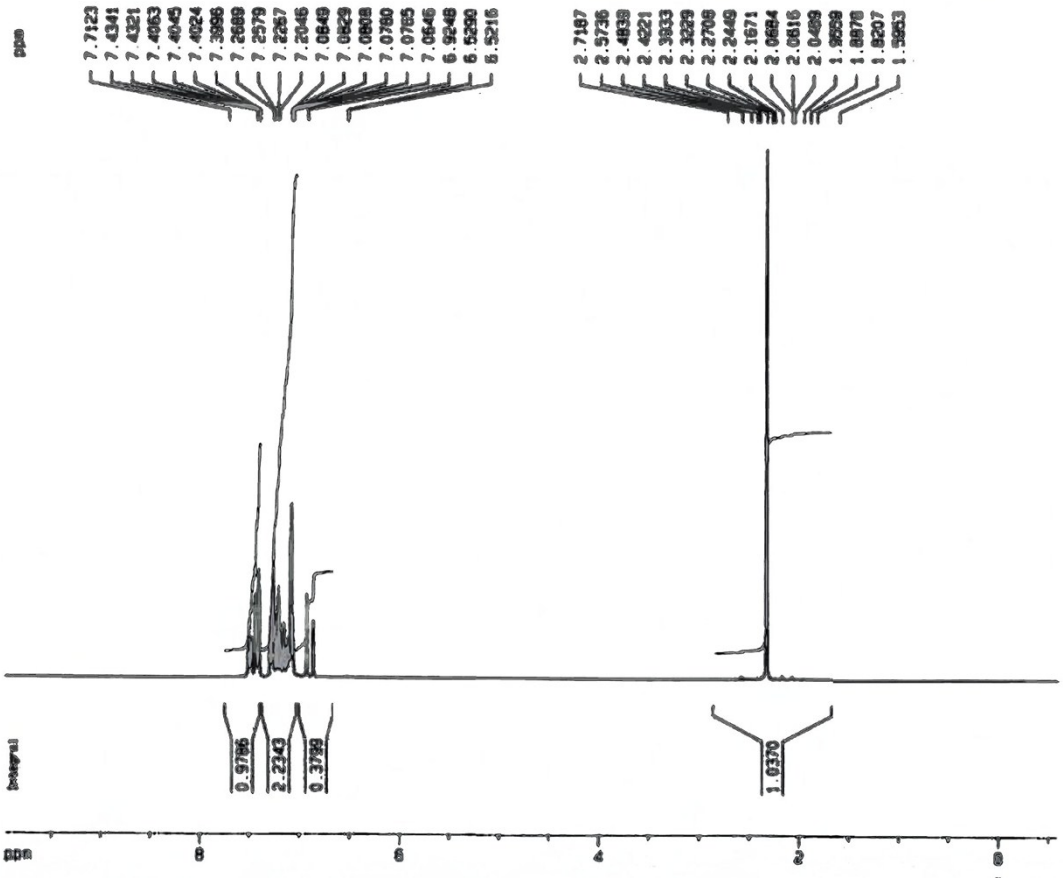


^{13}C-NMR of **3m**

3n

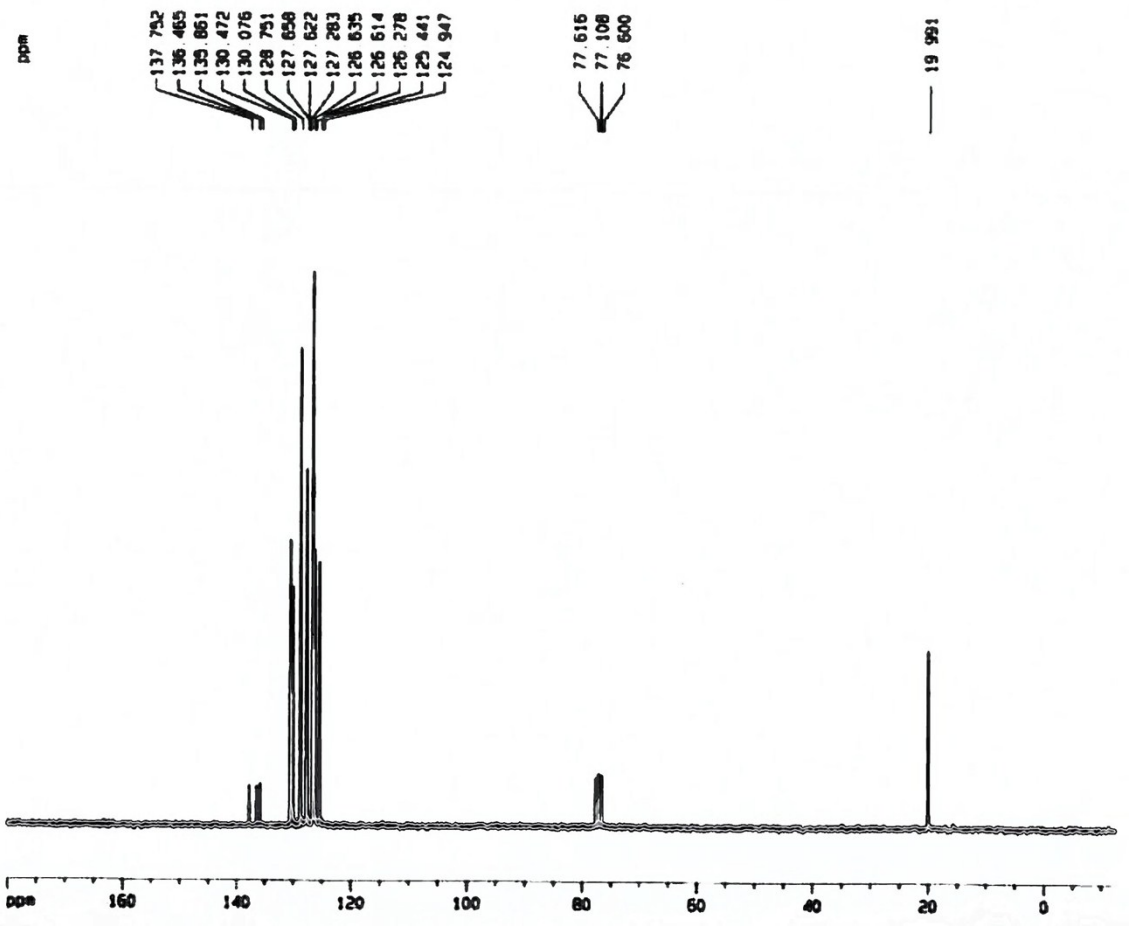


^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 2.32 (s, 3 H), 6.89 (d, 1 H, J = 16.25), 7.06-7.29 (m, 7 H), 7.40-7.52 (m, 3 H); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 19.99, 124.95,125.44, 126.28, 126.61, 126.63, 127.28, 127.62, 127.66, 128.75, 130.08, 130.47, 135.86, 136.47, 137.75.



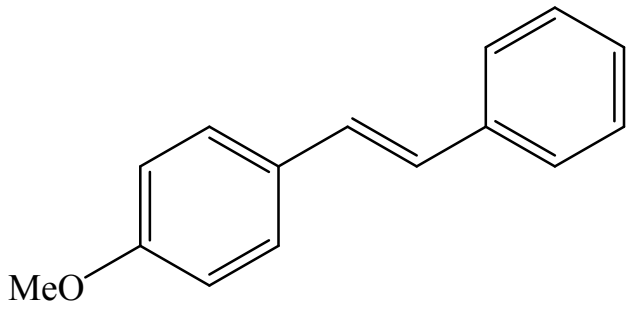
^{1}H-NMR of **3n**

ppm
7.80484
7.74741
7.71226
7.56843
7.51940
7.49838
7.47520
7.43985
7.43806
7.43406
7.43214
7.40985
7.40634
7.4054
7.40238
7.39961
7.29092
7.28591
7.26891
7.25792
7.25132
7.22815
7.22668
7.20462
7.18312
7.15399
7.11077
7.10873
7.08489
7.08292
7.08085
7.07800
7.07648
7.06460
7.02962
6.98577
6.96302
6.92475
6.86014
6.80723
6.77542
6.75240
Integral
0.9786
2.2343
0.3905
ppm
7.8
7.6
7.4
7.2
7.0
6.8
6.6

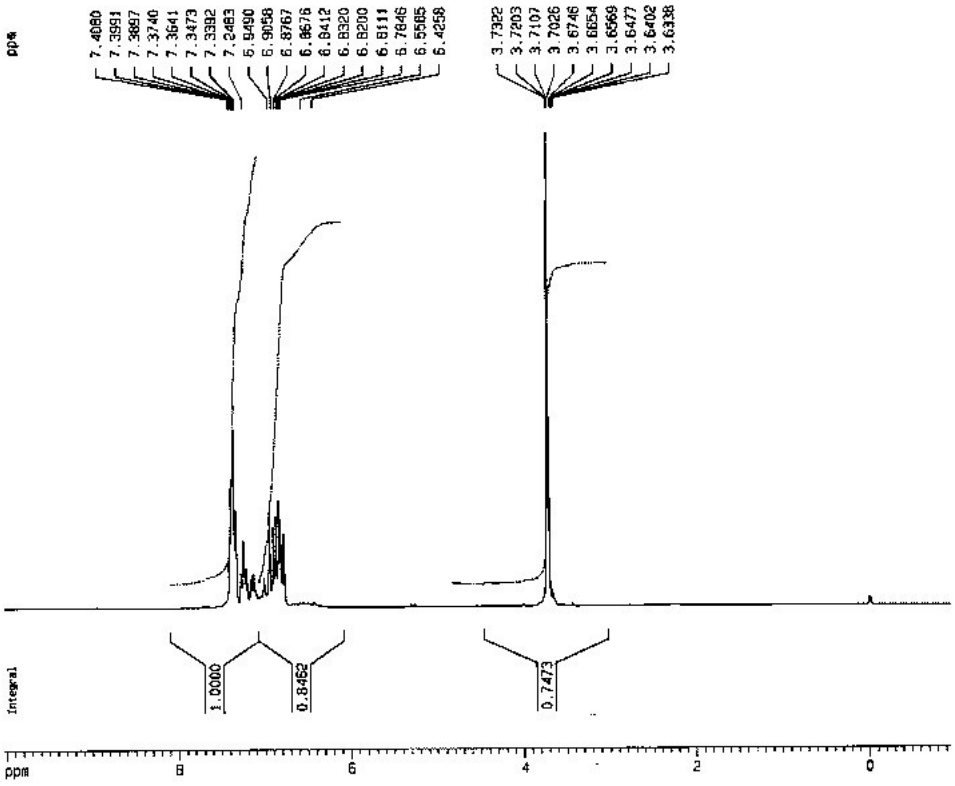


^{13}C-NMR of **3n**

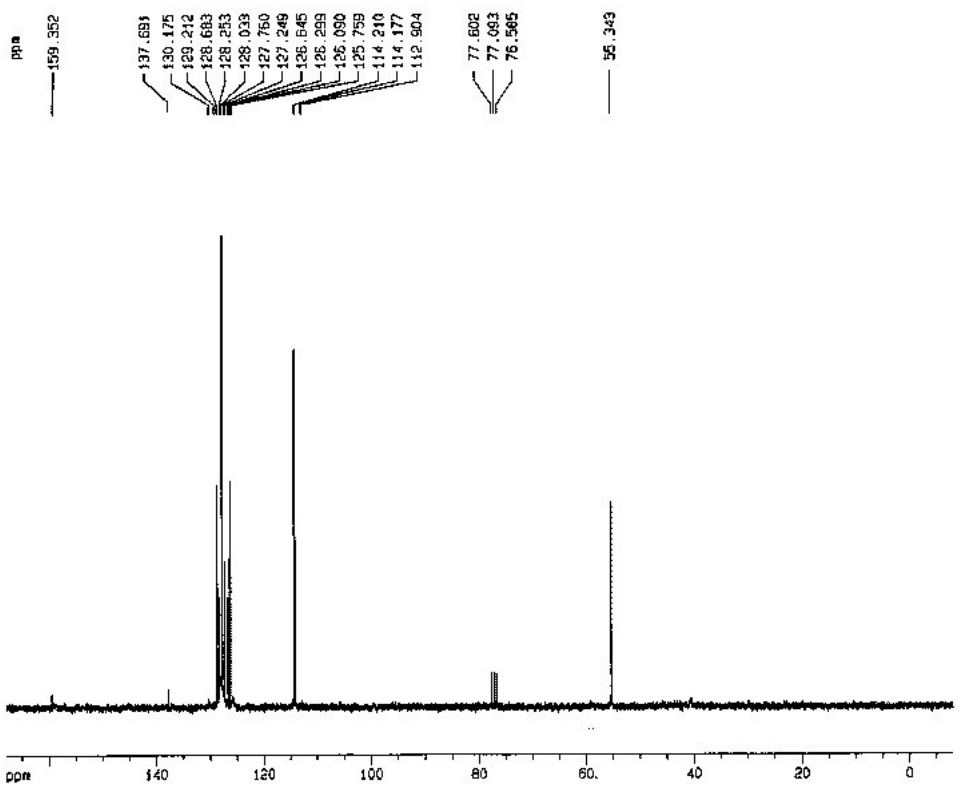
3o



^{1}H NMR (250 MHz, $CDCl_3$) (ppm): 3.72 (s, 3 H), 6.42- 7.40 (m, 11H). ^{13}C NMR (62.9 MHz, $CDCl_3$) (ppm): 159.3, 137.6, 130.1, 129.2, 128.6, 128.2, 127.2, 126.0, 125.7, 114.1, 55.3.

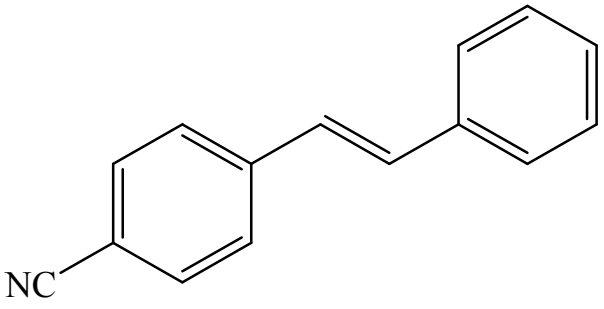

ppm
7.4080
7.3991
7.3897
7.3740
7.3641
7.3473
7.3392
7.2483
6.9490
6.9056
6.8767
6.8676
6.8412
6.8320
6.8200
6.8111
6.7846
6.5585
6.4258
3.7322
3.7203
3.7107
3.7026
3.6746
3.6654
3.6569
3.6477
3.6402
3.6338
Integral
1.0000
0.8462
0.7473
ppm
8
6
4
2
0

^{1}H-NMR of **3o**

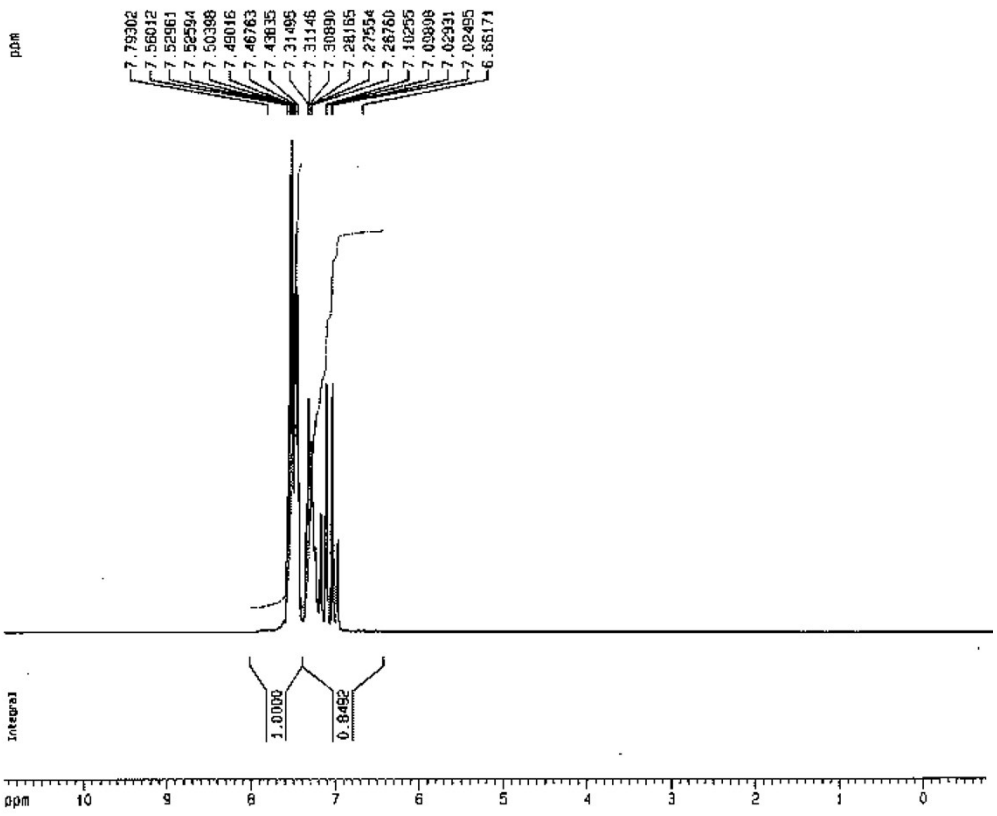


^{13}C-NMR of **3o**

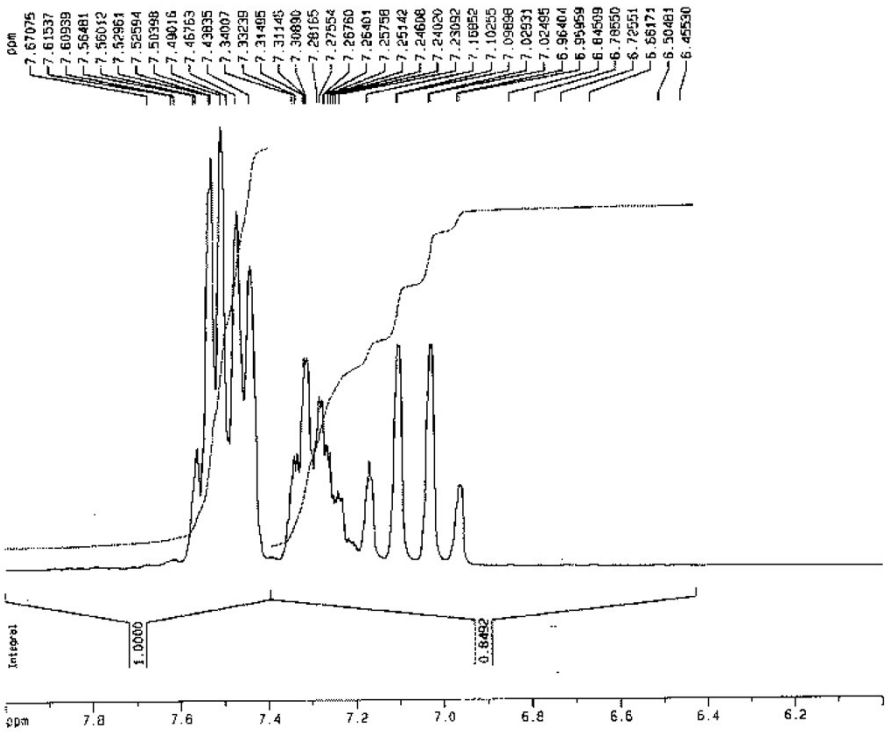
3p



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 6.99 (d, 1 H, J =16.3), 7.13 (d, 1 H, J =16.5), 7.31-7.26 (m, 3 H), 7.56-7.43 (m, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) (ppm): 110.55, 119.06, 126.71, 126.86, 126.92, 128.65, 128.86, 132.39, 132.49, 136.27, 141.82.


ppm
7.79302
7.56012
7.52961
7.52594
7.50398
7.49016
7.46763
7.43835
7.31495
7.31146
7.30890
7.28165
7.27554
7.26760
7.10255
7.03908
7.02931
7.02495
6.65171
Integral
1.0000
0.8492
ppm
10
9
8
7
6
5
4
3
2
1
0

^{1}H-NMR of **3p**


ppm
7.67075
7.61537
7.60939
7.56481
7.56012
7.52961
7.52594
7.50398
7.49016
7.46763
7.43835
7.34007
7.33239
7.31495
7.31146
7.30890
7.28165
7.27554
7.26760
7.26401
7.25758
7.25142
7.24608
7.24020
7.23092
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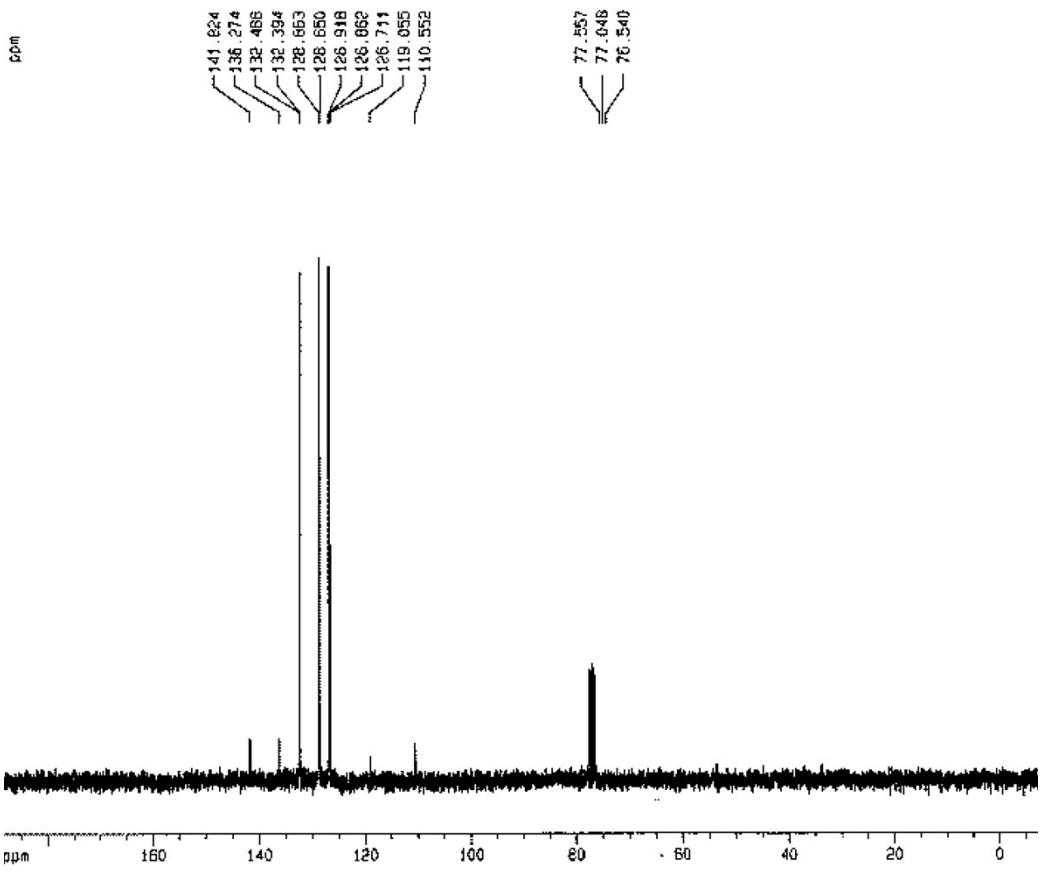
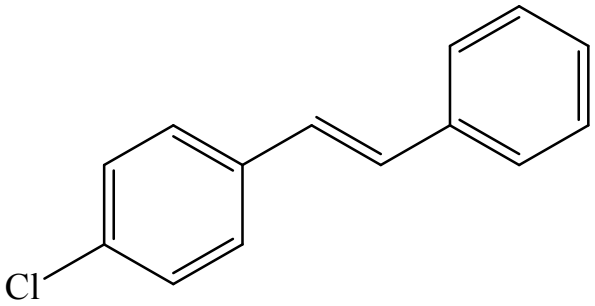
6.96404
6.95959
6.84509
6.78650
6.72951
6.65171
6.50481
6.45530
Integral
1.0000
0.8492
ppm
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2

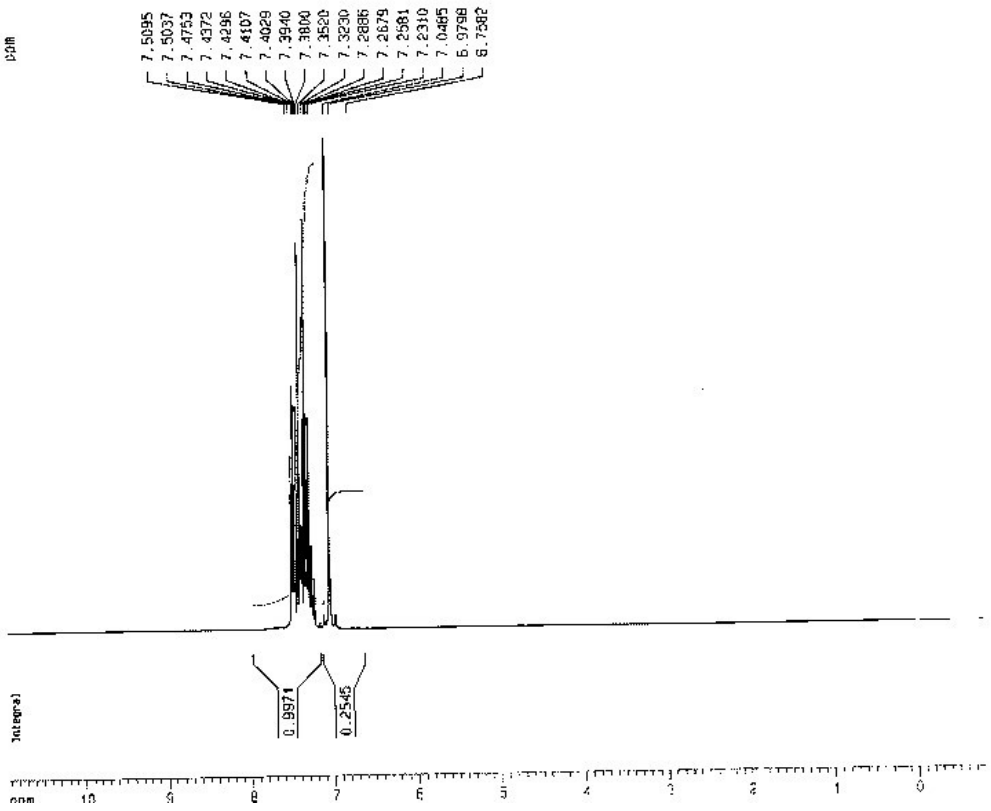


^{13}C-NMR of **3p**

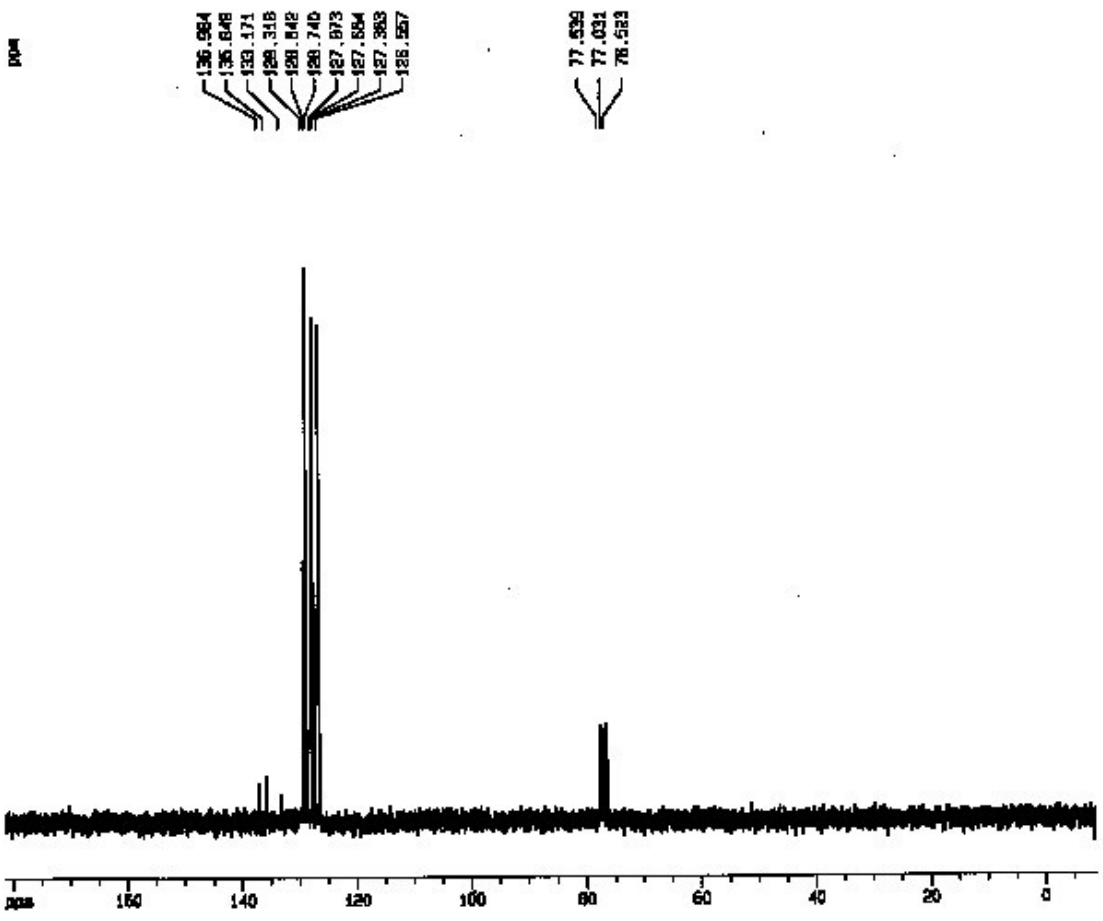
3q



^{1}H NMR (250 MHz, $CDCl_3$) (ppm): 7.5- 7.23 (m, 11H). ^{13}C NMR (62.9 MHz, $CDCl_3$) (ppm): 136.9, 135.8, 133.1, 129.3, 128.8, 128.7, 127.8, 127.6, 127.3, 126.5.

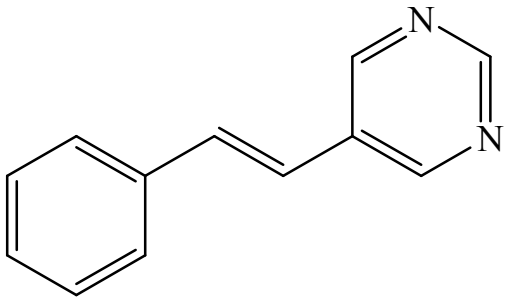

7.5095
7.5037
7.4753
7.4372
7.4296
7.4107
7.4029
7.3940
7.3800
7.3520
7.3230
7.2886
7.2679
7.2581
7.2310
7.0485
6.9798
6.7582
0.9971
0.2545

^{1}H-NMR of **3q**

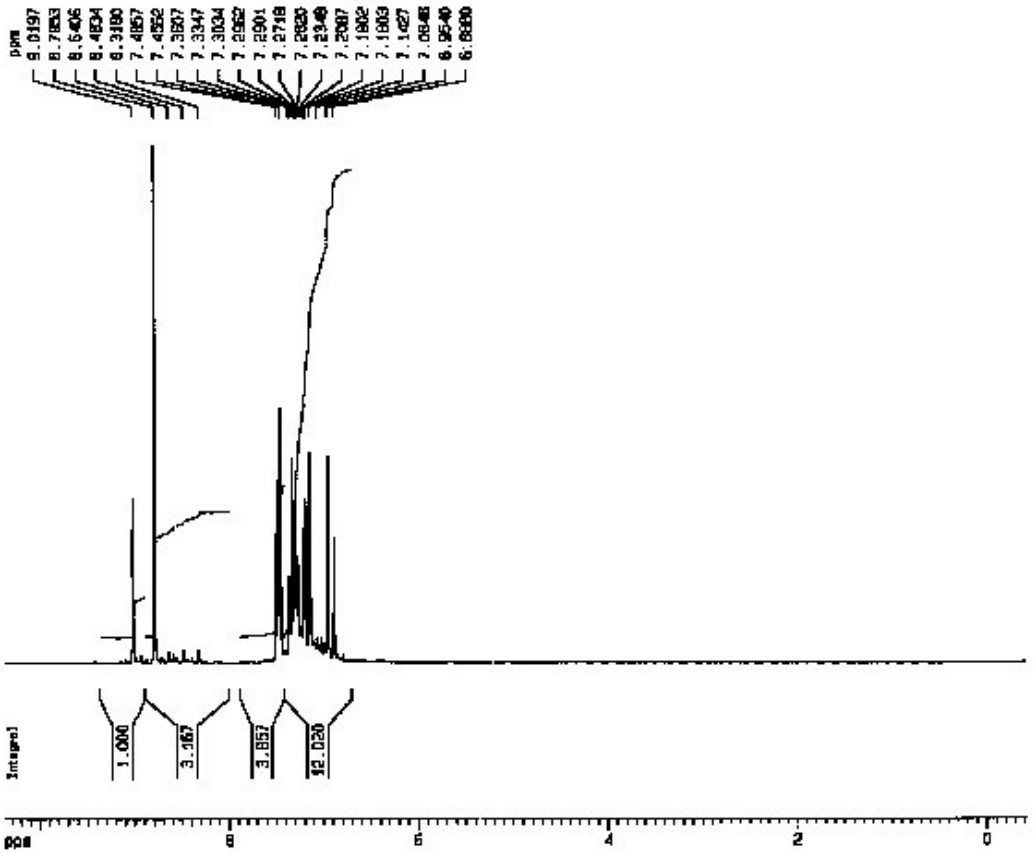


^{13}C-NMR of **3q**

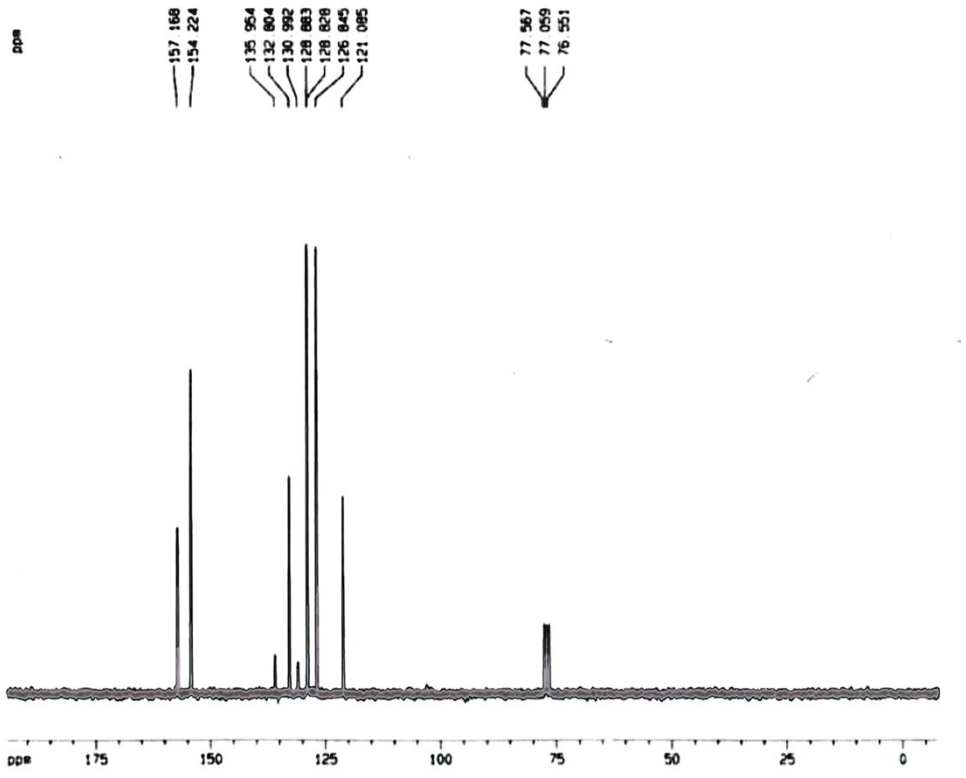
3r



^{1}H NMR (250 MHz, $CDCl_3$): (ppm) 6.92 (d, 1H, J = 16.5), 7.17 (d, 1H, J = 16.5), 7.23-7.48 (m, 3H), 7.45-7.48 (d, 2H, J = 7.2), 8.79 (s, 2H), 9.01 (s, 1H); ^{13}C NMR (62.9 MHz ,$CDCl_3$): (ppm) 121.08, 126.84, 128.83, 128.88, 130.99, 132.80, 135.95, 154.22, 157.17.



^{1}H-NMR of **3r**


ppm
157.168
154.224
135.954
132.804
130.992
128.883
128.828
126.845
121.085
77.567
77.059
76.551
ppm
175
150
125
100
75
50
25
0

^{13}C-NMR of **3r**