Supporting Information

Selective mono-esterification of symmetrical diols using resin-bound triphenylphosphine

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General Information

All reactions were carried out under nitrogen atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise stated. Solvents were extra pure grade purchase from Merck India and were dried by using reported procedure. Yields refer to chromatographically and spectroscopically homogeneous materials, unless otherwise stated. Resin-bound triphenylphosphine (3 mmol triphenylphosphine moiety/g) was purchased from

Sigma-Aldrich. Other reagents were purchased at highest available commercial quality and used without further purification. Reaction progress was monitored by thin layer chromatography (TLC) carried out on glass plates coated with silica gel G, using the solvent system EtOAc/hexane. The infrared spectra were recorded with FT-IR-3000 Hyperion Microscope (Bruker, Germany) with Vertex 80 FTIR system. ^{1}H NMR and 13C NMR spectra were recorded on Bruker av III, 500 MHz FT NMR Spectrometer using $CDCl_3$ as solvent and TMS as an internal reference. Coupling constants (*J*) are reported in Hz: singlet (s), doublet (d), triplet (t), doublet of doublet (dd), multiplet (m), or broad (b).

Experimental Procedures

Preparation of polymer-bound triphenylphosphine-iodine complex, 1.[1]

To a stirred suspension of resin-bound triphenylphosphine beads (1.0 g; 3 mmol triphenylphosphine moiety/g) in anhydrous dichloromethane (15 ml) in a 50 ml round bottom flask is added 1 molar solution of iodine in the same solvent via syringe at ambient temperature. Iodine is consumed almost immediately and at the end of addition complex **1** is already formed. It is used either as such in the subsequent reaction (see experiment below) or rapidly filtered, washed with dichloromethane and dried under vacuum at room temperature. Experimental analysis indicated that more than 90% of the phosphine moieties were halogenated.

[1]Caputo, R.; Ferreri, C.; Noviello, S.; Palumbo, G. Use of Polymeric Phosphine-Halogen Complexes in the Conversion of Epoxides to Halohydrins. *Synthesis.* **1986**, 499-501

General procedure for the synthesis of Ester and Amide in solid-phase

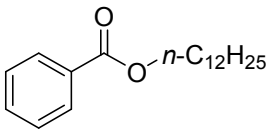
To a stirred solution of pre-formed complex **1** (1.5 mmol) in 20 ml of anhydrous THF-DCM (1:3 v/v) was added 4-DMAP (3 mmol) and carboxylic acid (1 mmol) at ambient temperature. After being stirred for 10 minutes, alcohol or amine (1 mmol) was then added to the reaction mixture and reaction mixture was allowed to stir for the time specified in the table. After completion of the reaction (as indicated by TLC), the resultant mixture was filtered and washes with dichloromethane (50 ml). The filtrate was then extracted and the combined organic layer was dried with anhydrous sodium sulphate and concentrated to give desired product in high purity.

Typical procedure for the synthesis of mono-ester (17) in solution-phase

To a stirred solution of soluble triphenylphosphine (1.5 mmol) in 20 ml of anhydrous THF-DCM (1:3 v/v) was added I_2 (1.5 mmol). To this *in situ* formed triphenylphosphonium-iodide complex, 4-DMAP (3 mmol) and benzoic acid (1 mmol) were added. The reaction mixture stirred for another 10 minutes, after which 1,6-diol was added and reaction mixture was allowed to stir for 20 minutes. Then, CH_2Cl_2 was added, and the solution was washed with brine. The organic layer was dried with anhydrous sodium sulphate and concentrated under vacuum. The residue was subjected to column chromatography (EtOAc/hexane) to give mono-ester product in 45% yield.

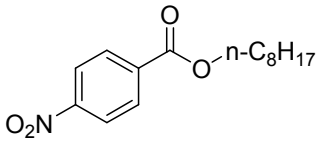
Analytical Data for some Esters and Amide Products

Dodecyl benzoate (7)



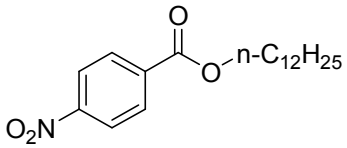
^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.90 (3H, t, *J*=7 Hz), 1.33 (2H, m), 1.28 (16H, m), 1.79 (2H, m), 4.34 (2H, t, *J*=13 Hz), 8.06 (2H, d, *J*=7.5 Hz), 7.45 (2H, t, *J*=8 Hz), 7.57 (H, t, *J*=7.5 Hz); ^{13}CNMR ($CDCl_3$, 125 MHz) δ: 166.69, 132.76, 130.56, 129.56, 128.30, 65.15, 31.92, 29.64, 29.63, 29.58, 29.54, 29.35, 29.29, 28.73, 26.05, 22.68, 14.11 ; IR (KBr pellet, ν_{max}/cm^{-1}): 3066, 2925, 2850, 1722, 1383, 1272.

Octyl 4-nitrobenzoate (10)



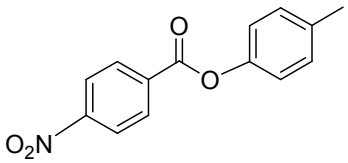
^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89 (3H, t, *J*=7 Hz), 1.45 (2H, m), 1.3 (8H, m), 1.80 (2H, m), 4.38 (2H, t, *J*=6.5 Hz), 8.23 (2H, dd, *J*=2 Hz), 8.29 (2H, dd, *J*=2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.74, 150.48, 135.89, 130.64, 123.50, 66.11, 31.76, 29.19, 29.15, 28.60, 25.97, 22.61, 14.05; IR (KBr pellet, ν_{max}/cm^{-1}): 3114, 2927, 1726, 1531, 1460, 1348, 1276.

Dodecyl 4-nitrobenzoate (11)



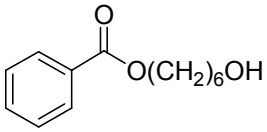
^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89(3H, t, *J*=7 Hz), 1.46 (2H, m, *J*=6 Hz), 1.32 (16H, m), 1.89 (2H, m), 4.38 (2H, t, *J*=7 Hz) 8.23 (2H, d, *J*=9 Hz), 8.29 (2H, d, *J*=7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.74, 150.49, 135.90, 130.65, 123.50, 66.12, 31.90, 29.62, 29.56, 29.50, 29.23, 29.33, 29.23, 28.60, 25.97, 22.67, 14.09 ; IR (KBr pellet, ν_{max}/cm^{-1}): 3116, 2920, 2850, 1965, 1716, 1525, 1460, 1351, 1286.

***p*-Tolyl 4-nitrobenzoate (12)**



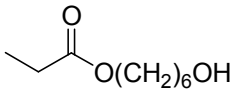
^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.44(3H, s), 7.142 (2H, d, *J*=8.5 Hz), 7.28 (2H, d, *J*=1.5 Hz), 8.399 (2H, d, *J*=7 Hz), 8.381 (2H, d, *J*=2.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.52, 150.88, 148.30, 136.15, 135.11, 135.11, 131.27, 130.17, 123.70, 121.06, 20.92; IR (KBr pellet, ν_{max}/cm^{-1}): 3107, 2920, 2854, 1728, 1523, 1398, 1349, 1282.

6-Hydroxyhexyl benzoate (17)



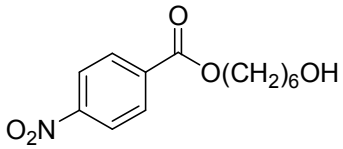
^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.46 (4H, m), 1.60 (2H, m), 1.78 (2H, m), 1.92 (1H, s), 3.65 (2H, t, *J*=6.5 Hz), 4.32 (2H, t, *J*=6.5 Hz), 7.43 (2H, t, *J*=6.5 Hz), 7.55 (1H, t, *J*=1.5 Hz), 8.04 (2H, d, *J*=5.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.75, 132.85, 130.43, 129.53, 129.53, 128.34, 128.34, 64.96, 62.76, 32.58, 28.70, 25.84, 25.42, ; IR (KBr pellet, ν_{max}/cm^{-1}): 3413, 2984, 2871, 1751, 1612, 1574, 1417, 1394, 1285.

6-Hydroxyhexyl propionate (18)



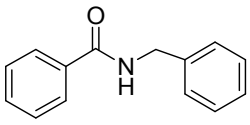
^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.13 (3H, t, *J*=7.5 Hz), 1.39 (4H, m), 1.57 (2H, m), 1.67 (2H, m), 2.33 (2H, m), 2.23 (1H, s), 3.63 (2H, t, *J*=6.5 Hz), 4.07 (2H, t, *J*=7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.73, 64.32, 62.63, 32.51, 28.57, 27.59, 25.68, 25.36, 9.11 ; IR (KBr pellet, ν_{max}/cm^{-1}): 3329, 2983, 2819, 1754, 1612, 1563, 1488, 1401, 1382, 1201.

6-Hydroxyhexyl 4-nitrobenzoate (21)



^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.48 (4H, m), 1.61 (2H, m), 1.82 (2H, m), 3.66 (2H, t, *J*=6.5 Hz), 4.38 (2H, t, *J*=7 Hz), 8.20 (2H, d, *J*=5 Hz), 8.28 (2H, d, *J*=5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.77, 150.48, 135.79, 130.65, 130.65, 123.52, 123.52, 65.94, 62.68, 32.52, 28.57, 25.78, 25.40; IR (KBr pellet, ν_{max}/cm^{-1}): 3404, 3217, 2963, 1746, 1534, 1512, 1463, 1392, 1348, 1286.

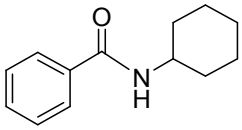
***N*-Benzylbenzamide (28)**



^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.56(2H, d, *J*=5.5 Hz), 6.91 (1H, s), 7.24 (1H, m), 7.25 (2H, d, *J*=2.5 Hz), 7.30 (2H, t, *J*=1.5 Hz), 7.34 (2H, t, *J*=7.5 Hz), 7.44 (1H, t, *J*=7.5 Hz) 7.75 (2H, d, *J*=7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.58, 138.35, 134.39, 131.51, 128.72, 128.57,

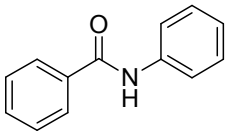
128.51, 127.82, 127.50, 127.35, 126.90, 126.12, 44.03; IR (KBr pellet, ν_{max}/cm^{-1}): 3321, 3297, 3073, 3069, 1649, 1619, 1573, 1530, 1477, 1420, 1348.

_N_-Cyclohexylbenzamide (29)



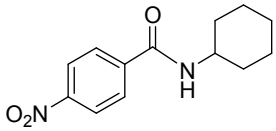
^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.22 (2H, m), 1.41 (2H, m), 1.65 (2H, t, *J*=7.5 Hz), 1.76 (2H, m), 2.03 (2H, t, *J*=4.5 Hz), 3.98 (1H, m), 5.97 (1H, s), 7.41(2H, t, *J*=7 Hz), 7.48 (1H, t, *J*=7.5 Hz), 7.74 (2H, d, *J*=7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.91, 24.910, 25.59, 33.25, 33.25, 48.66, 126.81, 126.81, 128.51, 128.51, 131.22, 135.14, 166.62; IR (KBr pellet, ν_{max}/cm^{-1}): 3418, 3384, 3094, 2983, 1656, 1579, 1516, 1462, 1336, 1301.

_N_-Phenylbenzamide (30)



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.13 (1H, t, *J*=7.5 Hz), 7.33 (2H, t, *J*=8 Hz), 7.40 (2H, t, *J*=7.5 Hz), 7.55 (1H, t, *J*=7.5 Hz), 7.73 (2H, d, *J*=8 Hz), 7.94 (2H, d, *J*=7.5 Hz), 8.66 (1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.04, 138.37, 135.14, 132.87, 132.08, 131.98, 131.59, 128.91, 128.57, 128.57, 127.32, 124.31, 120.48; IR (KBr pellet, ν_{max}/cm^{-1}): 3345, 3289, 3071, 1653, 1634, 1581, 1477, 1457, 1362, 1217.

_N_-Cyclohexyl-4-nitrobenzamide (32)



^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.25 (2H, m), 1.44 (2H, m), 1.69 (2H, m), 1.77 (2H, m), 2.04 (2H, m), 3.985 (1H, m), 6.07 (1H, s), 7.90 (2H, d, *J*=7 Hz), 8.26 (2H, d, *J*=1.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.60, 149.47, 140.69, 128.05, 128.05, 123.76, 123.76, 49.25, 33.10, 33.10, 25.46, 24.86, 24.86; IR (KBr pellet, ν_{max}/cm^{-1}): 3054, 2973, 1658, 1621, 1534, 1459, 1351, 1291, 1216, 1106.

^{1}H and ^{13}C NMR Spectra for Selected Compounds

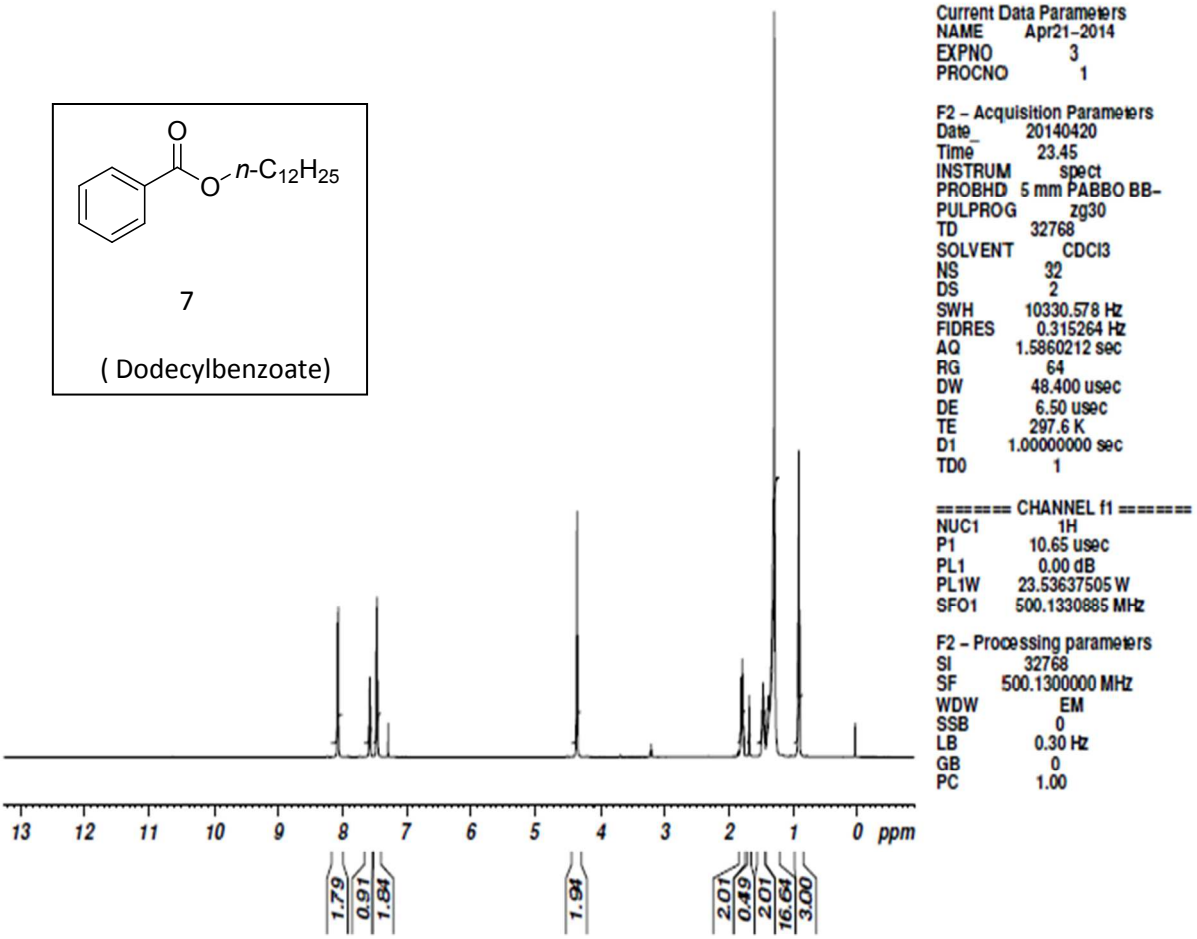


Fig :- ^{1}H NMR of Dodecylbenzoate (7)

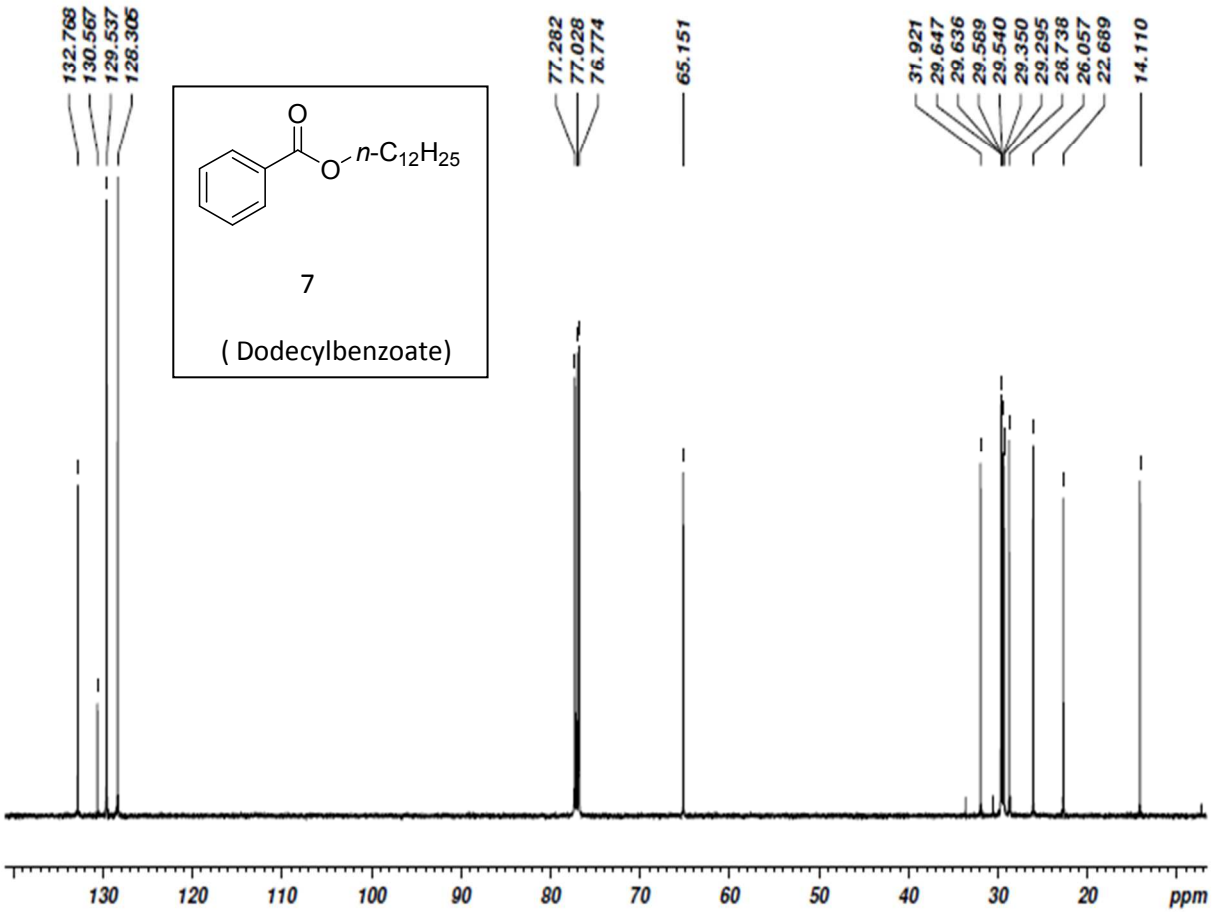


Fig :- ^{13}C NMR of Dodecylbenzoate (7)

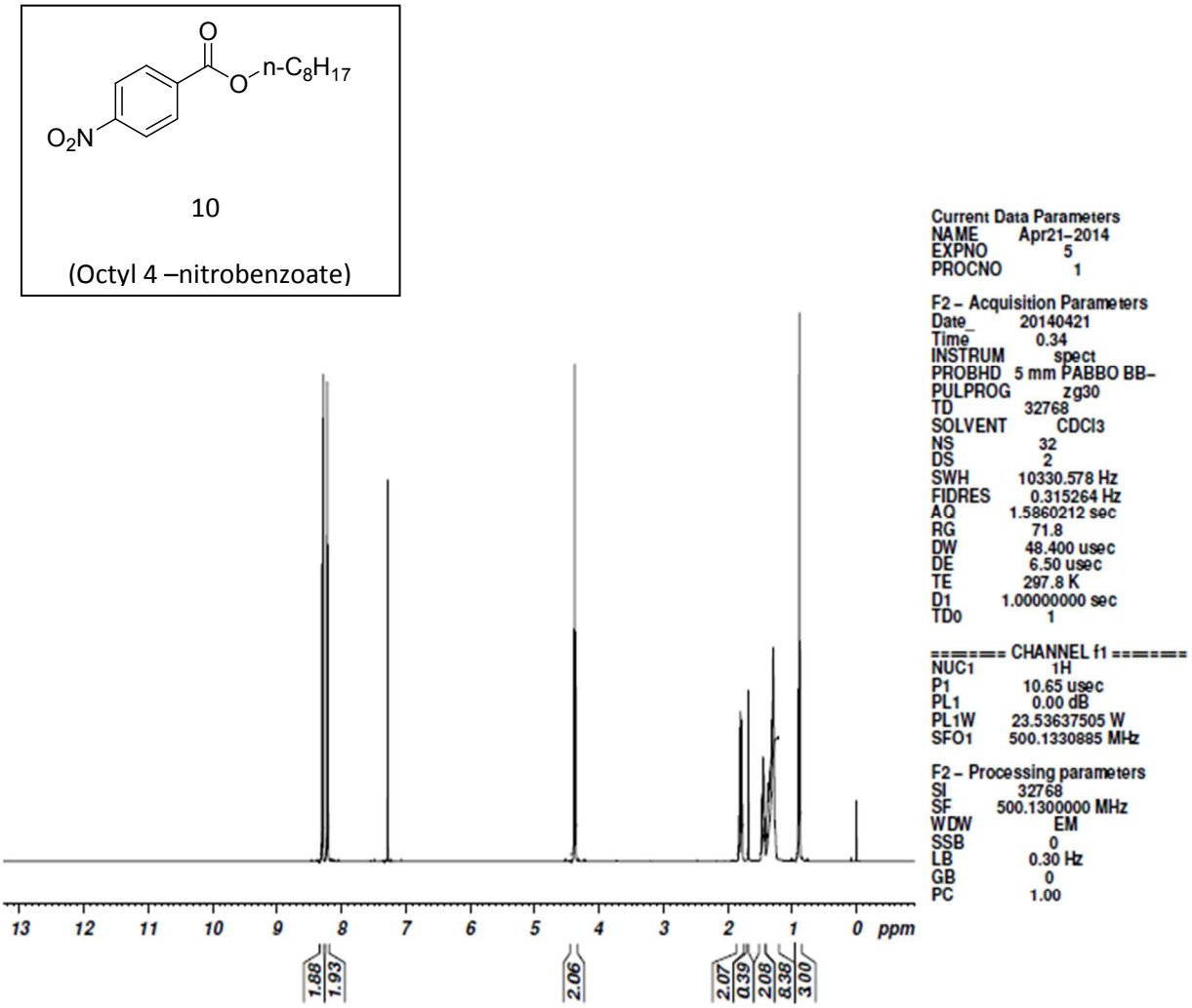


Fig :- ^{1}H NMR of Octyl 4 –nitrobenzoate (10)

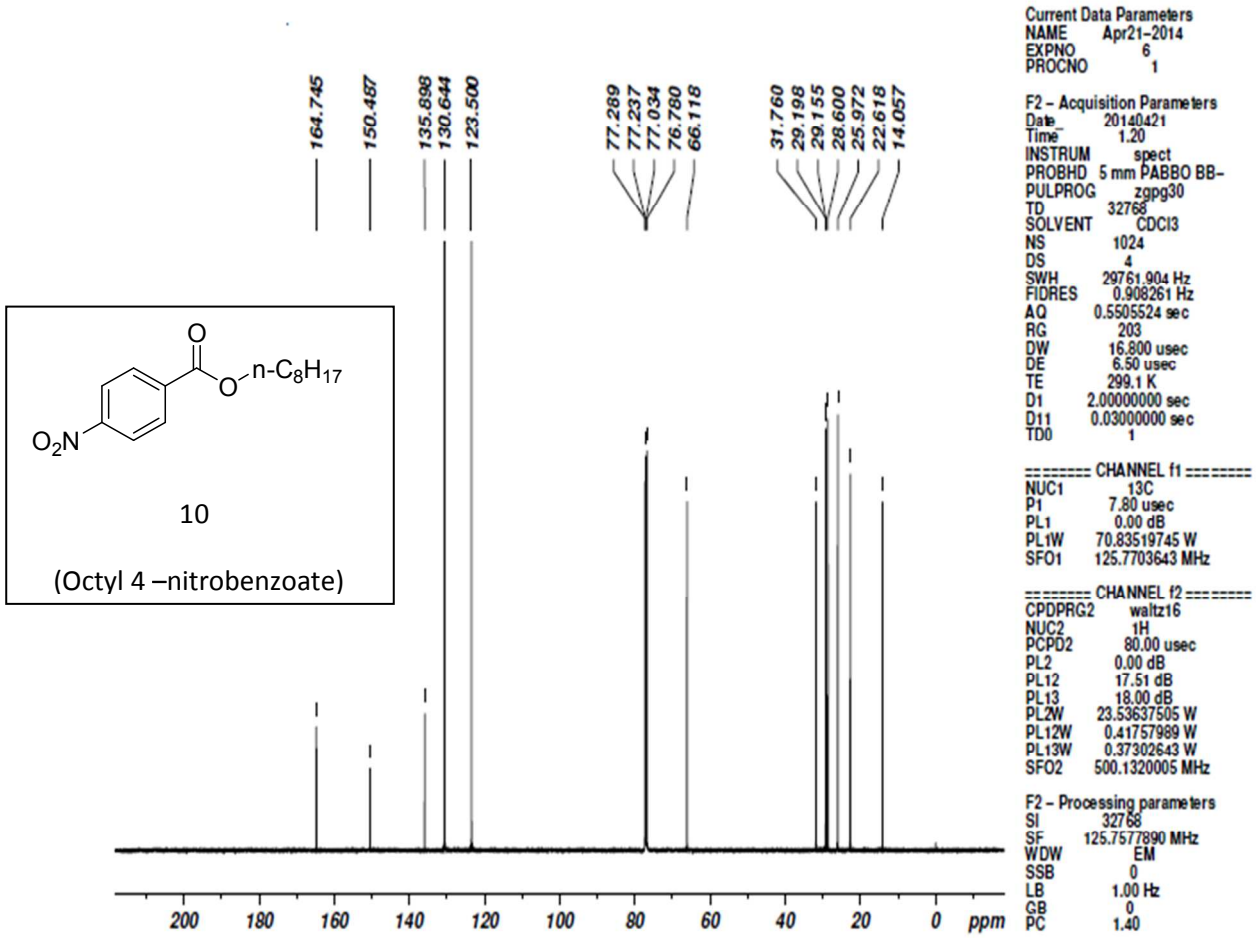


Fig :- ^{13}C NMR of octyl 4 –nitrobenzoate (10)

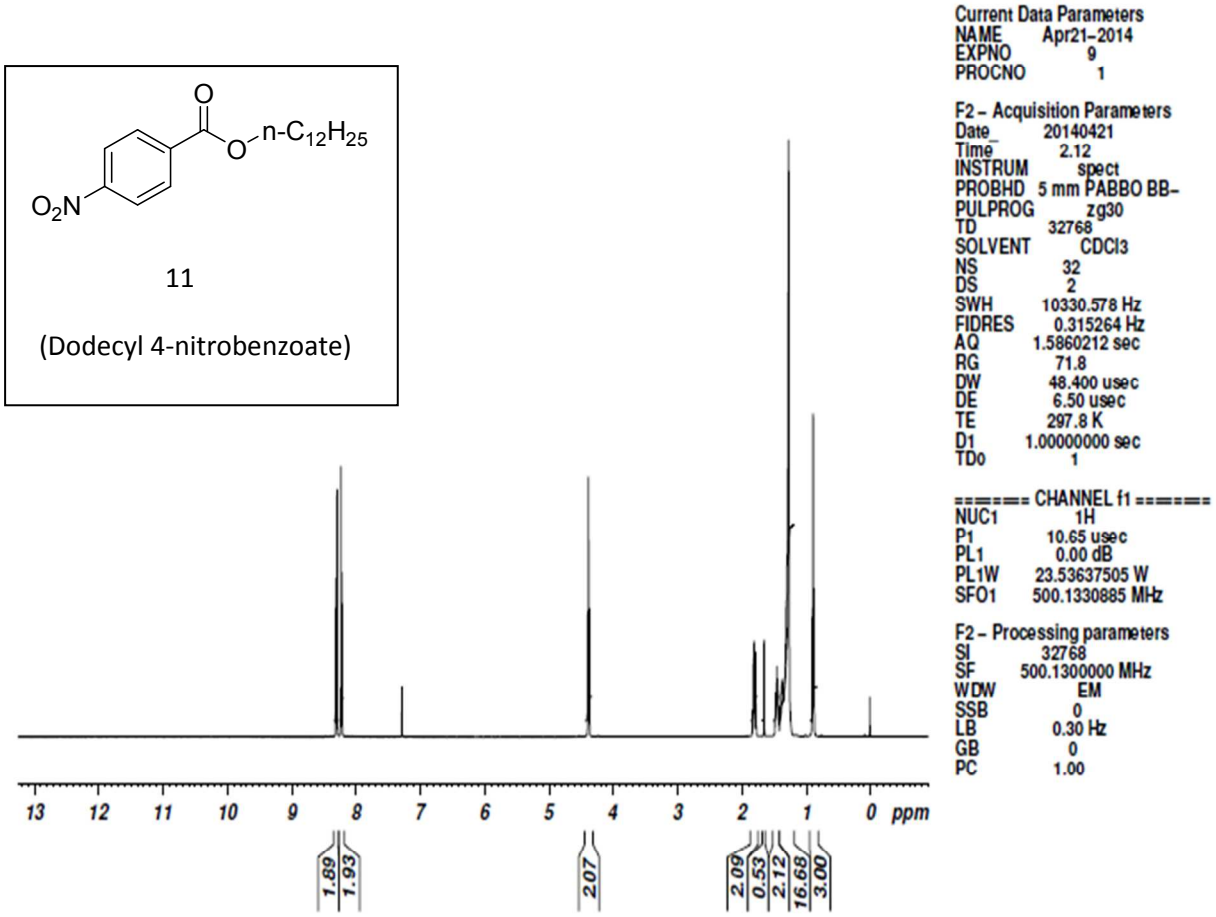


Fig :- ^{1}H NMR of Dodecyl 4-nitrobenzoate(11)

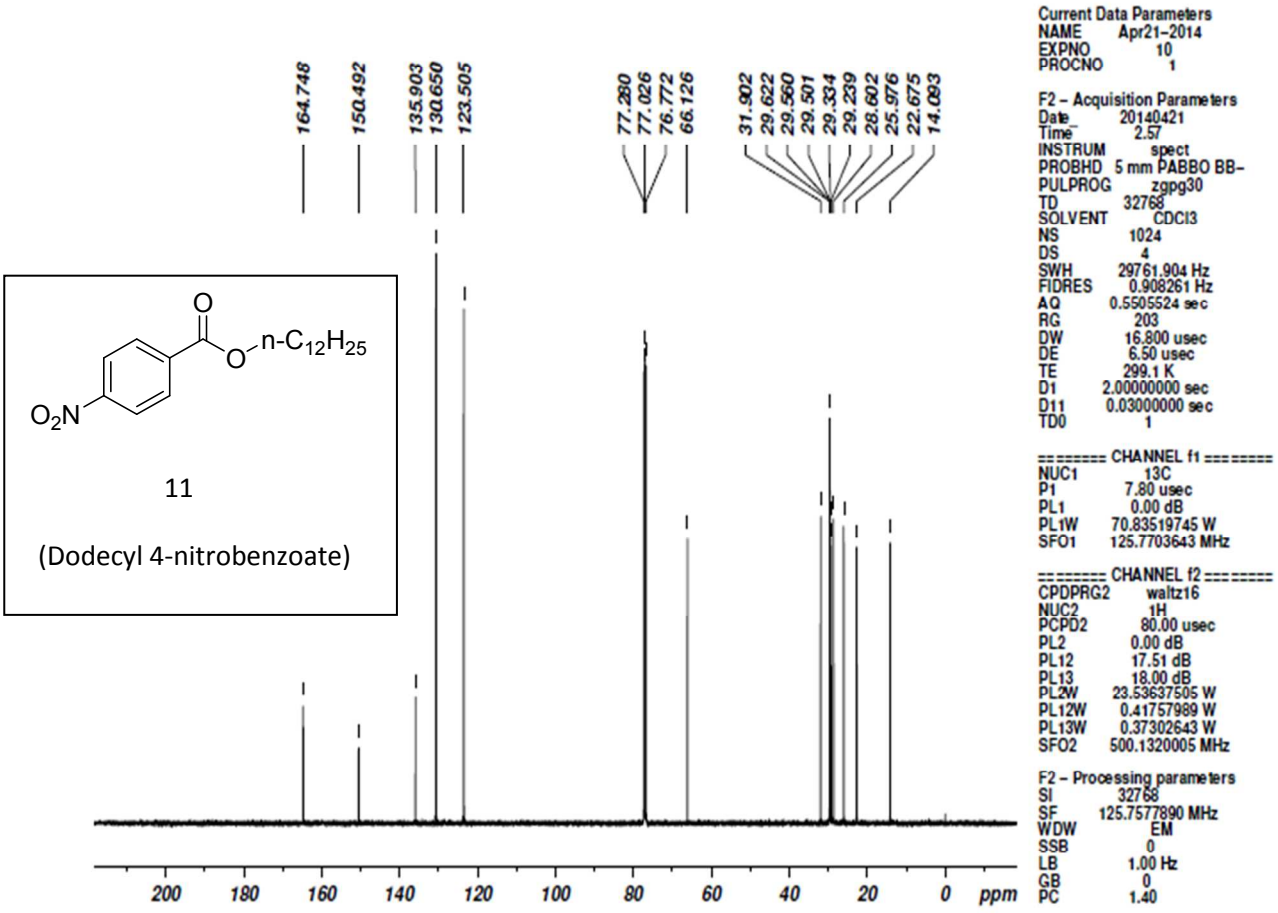


Fig :- ^{13}C NMR of Dodecyl 4-nitrobenzoate(11)

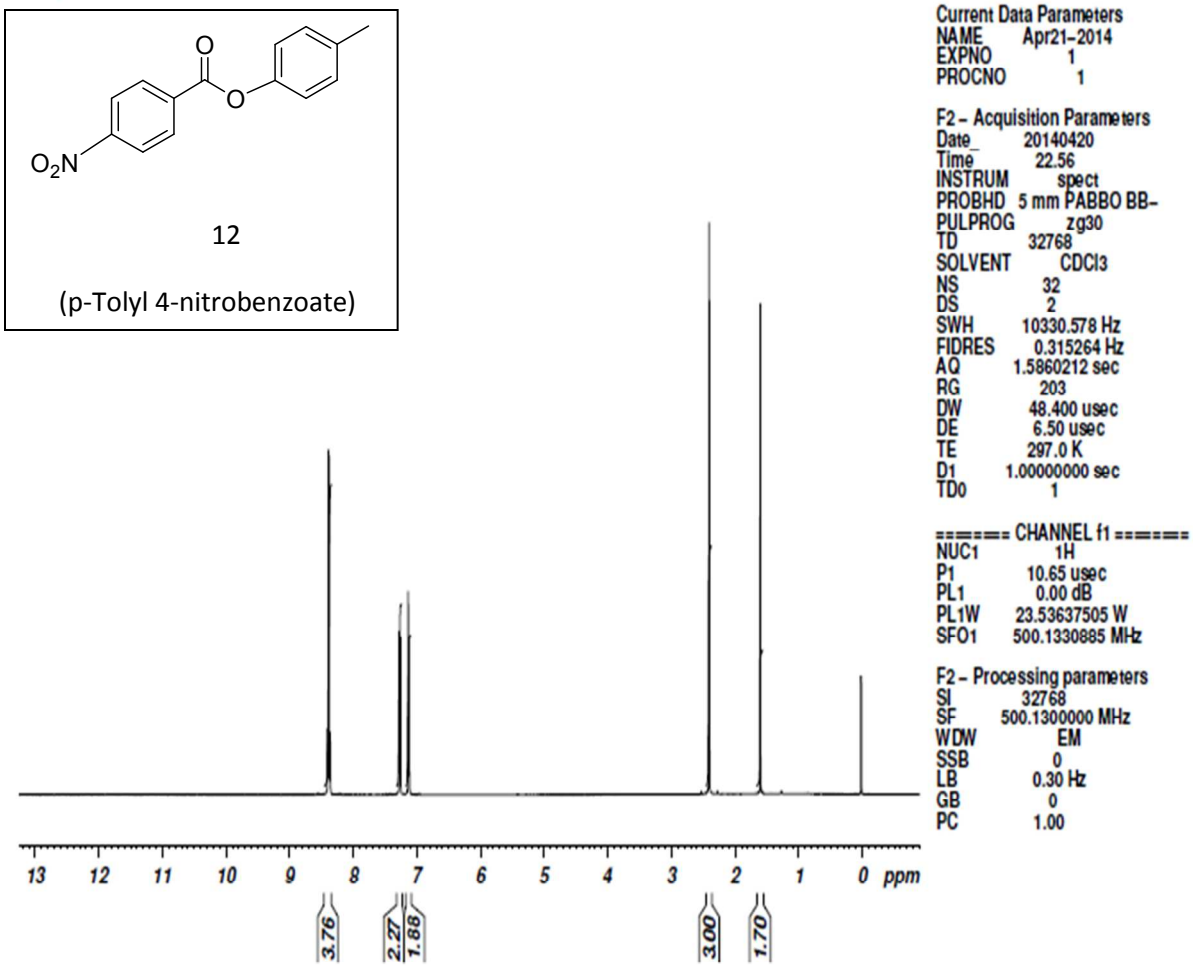


Fig :- ^{1}H NMR of *p*-tolyl 4-nitrobenzoate (12)

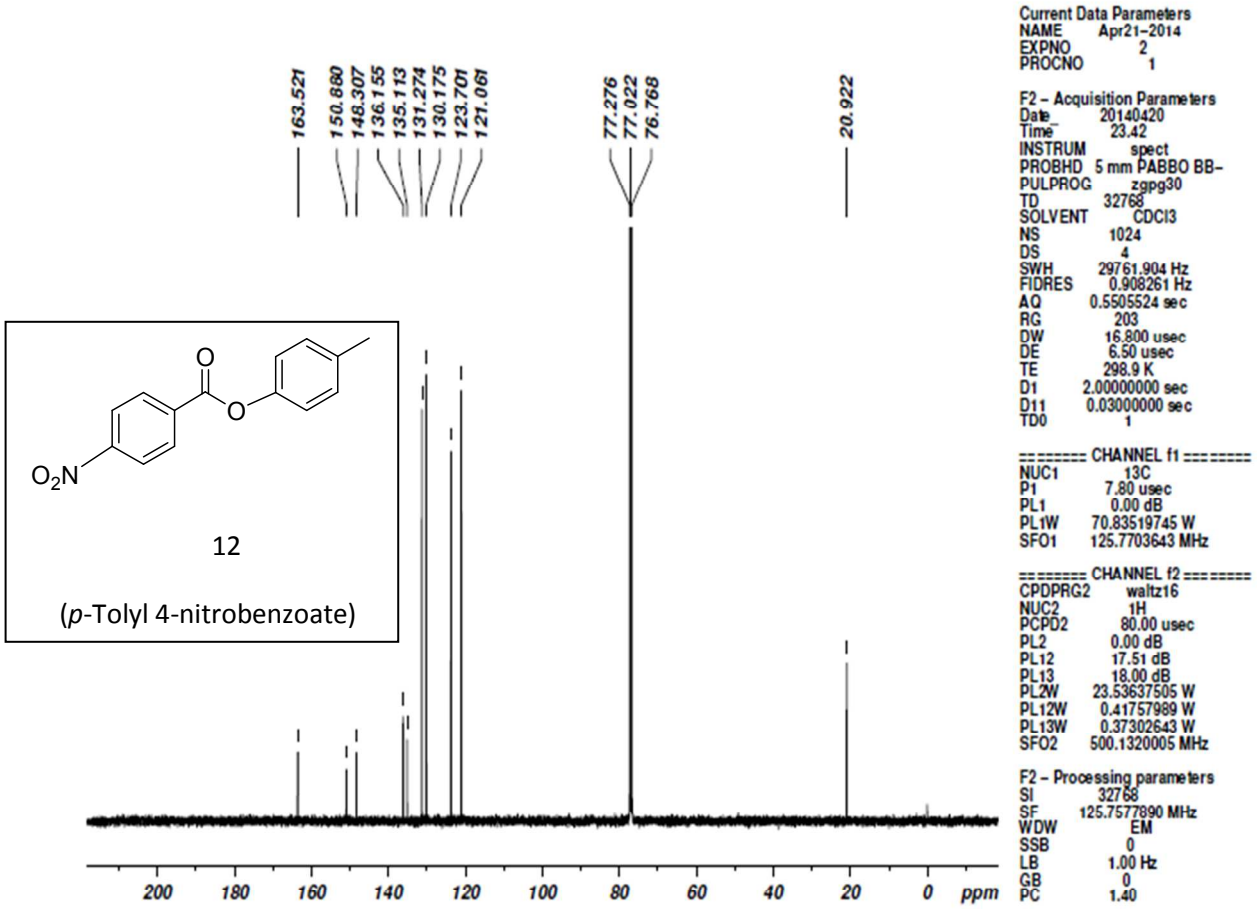


Fig :- ^{13}C NMR of p-Tolyl 4-nitrobenzoate (12)

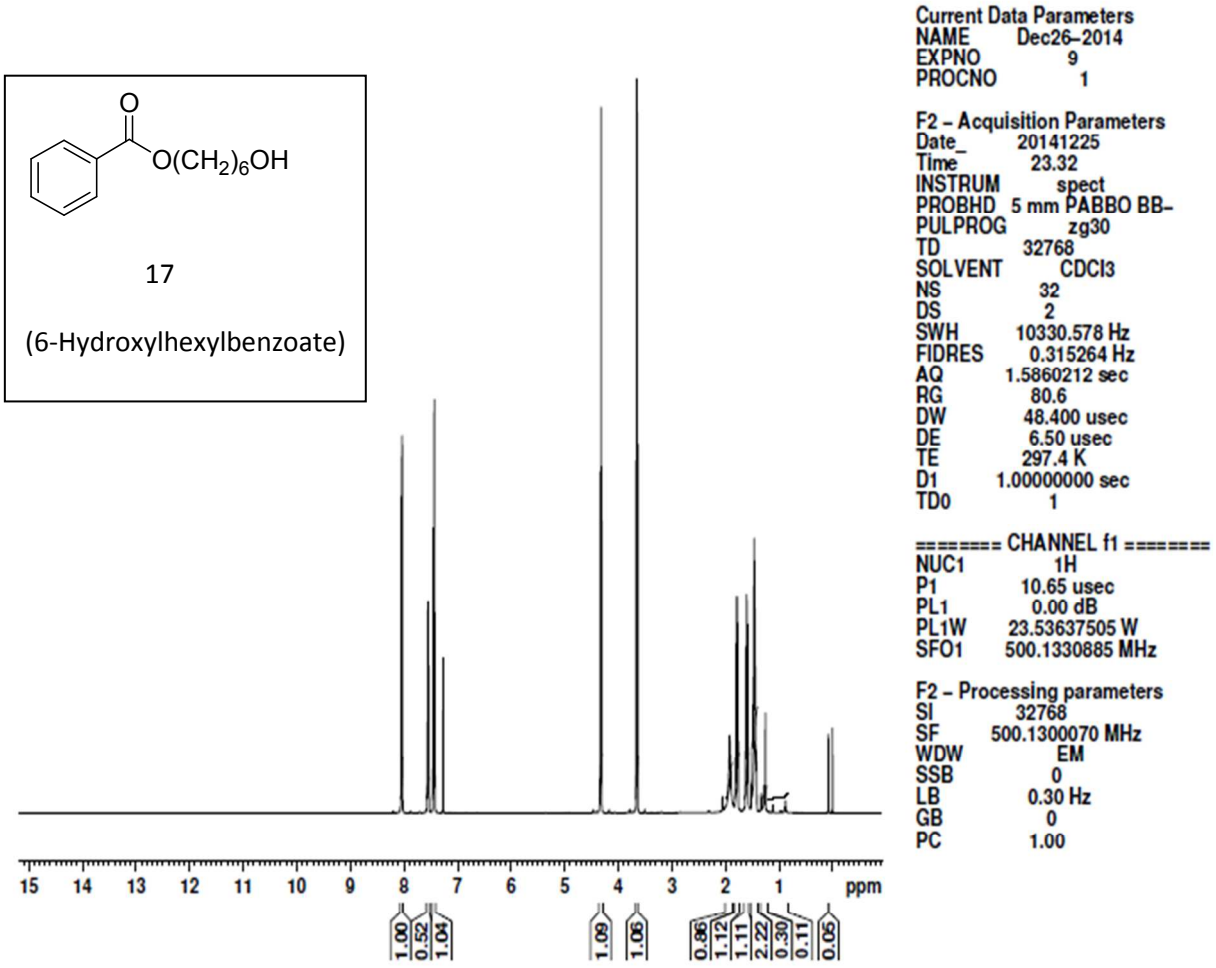


Fig :- ^{1}H NMR of 6-Hydroxylhexylbenzoate (23)

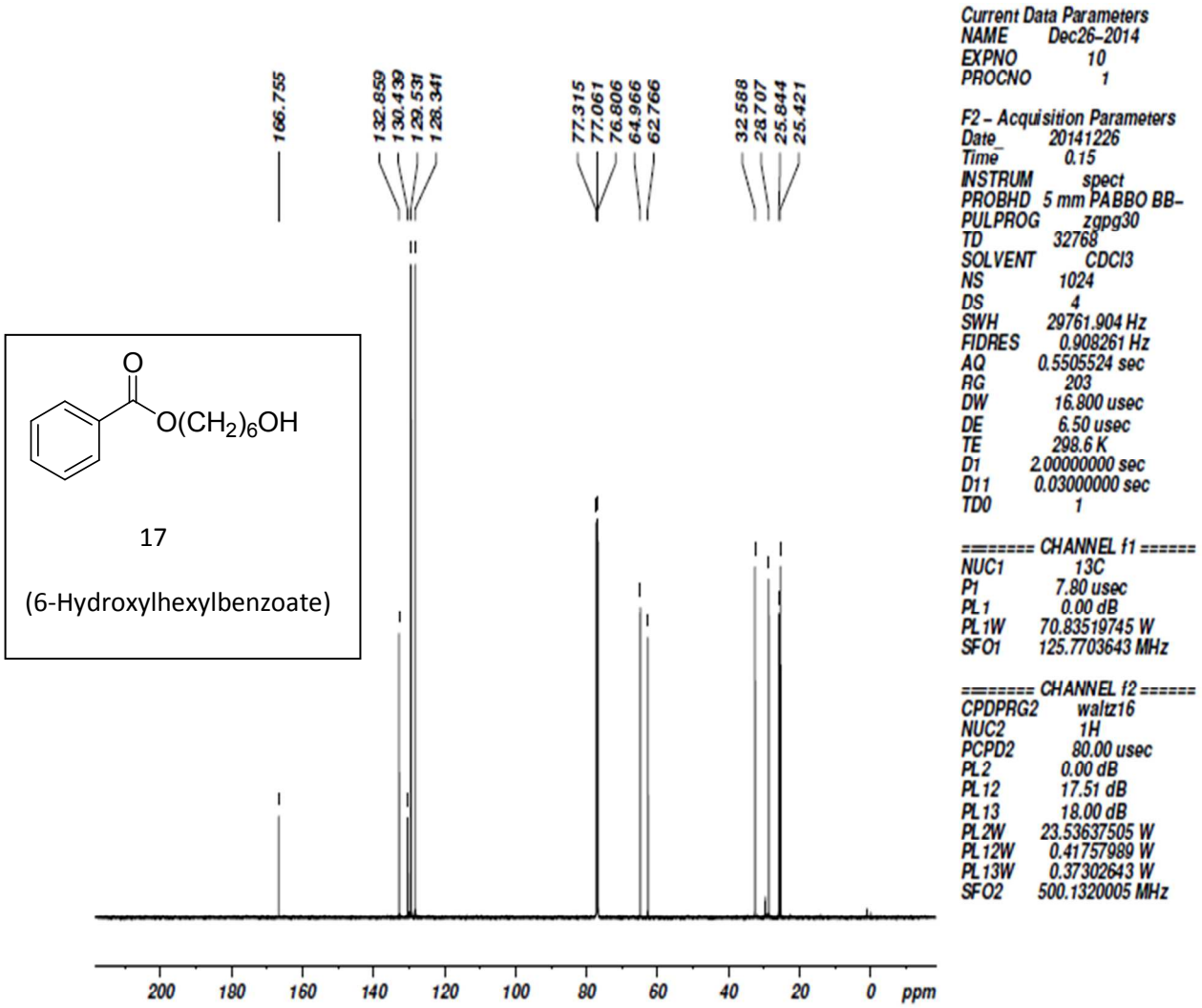
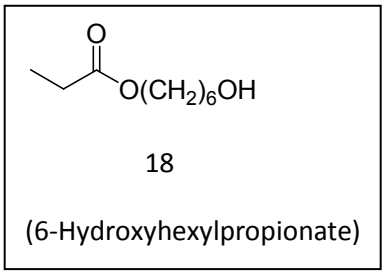


Fig :- ^{13}C NMR of 6-Hydroxylhexylbenzoate (23)



18

(6-Hydroxyhexylpropionate)

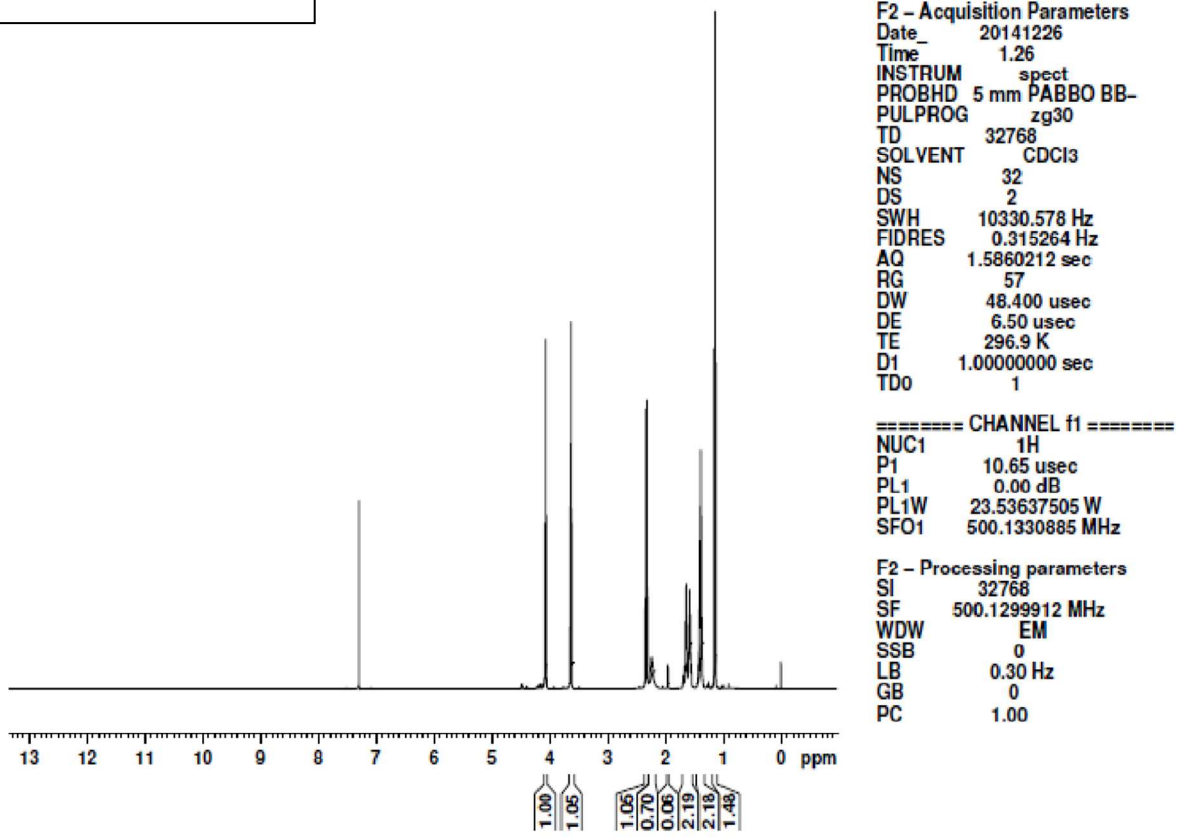
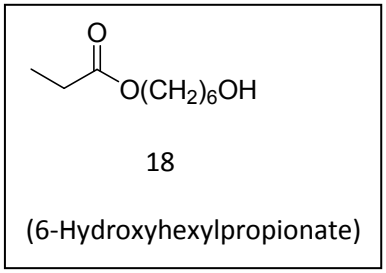
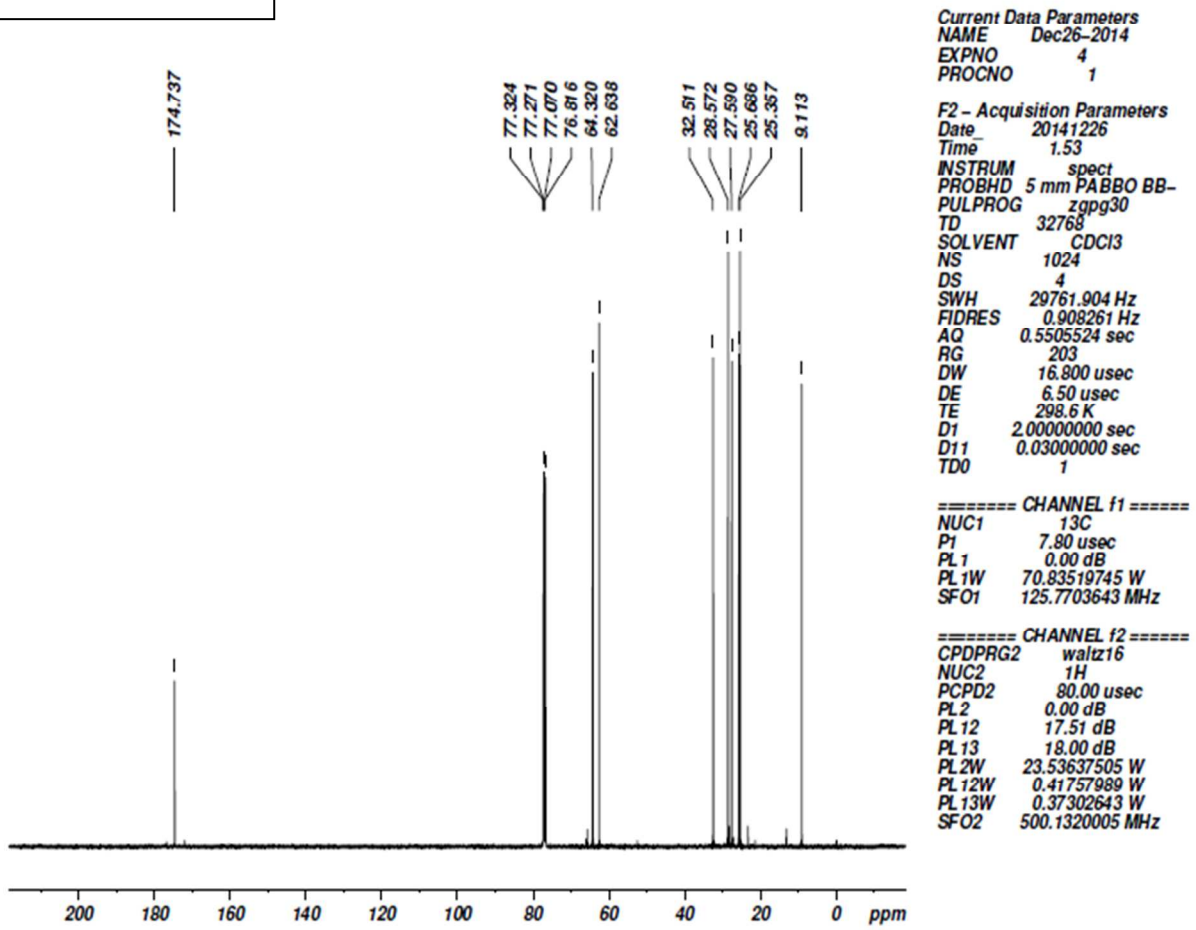


Fig :- ^{1}H NMR of 6-hydroxyhexylpropionate (18)



18

(6-Hydroxyhexylpropionate)



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PROCNO 1

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PL1W 70.83519745 W
SFO1 125.7703643 MHz

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PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.51 dB
PL13 18.00 dB
PL2W 23.53637505 W
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PL13W 0.37302643 W
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Fig :- ^{13}C NMR of 6-Hydroxyhexylpropionate (18)

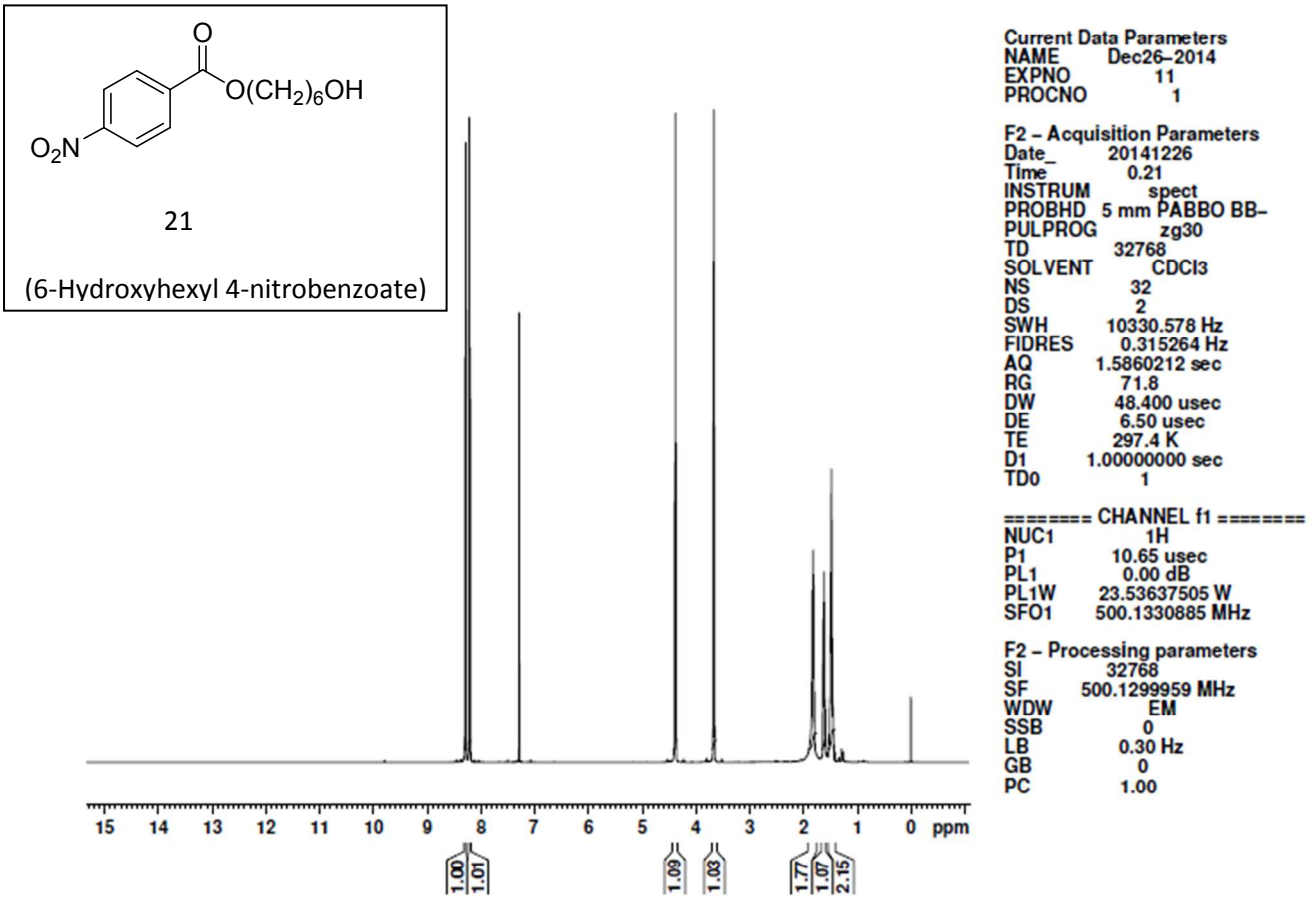

Fig :- ^{1}H NMR of 6-hydroxyhexyl 4-nitrobenzoate(21)

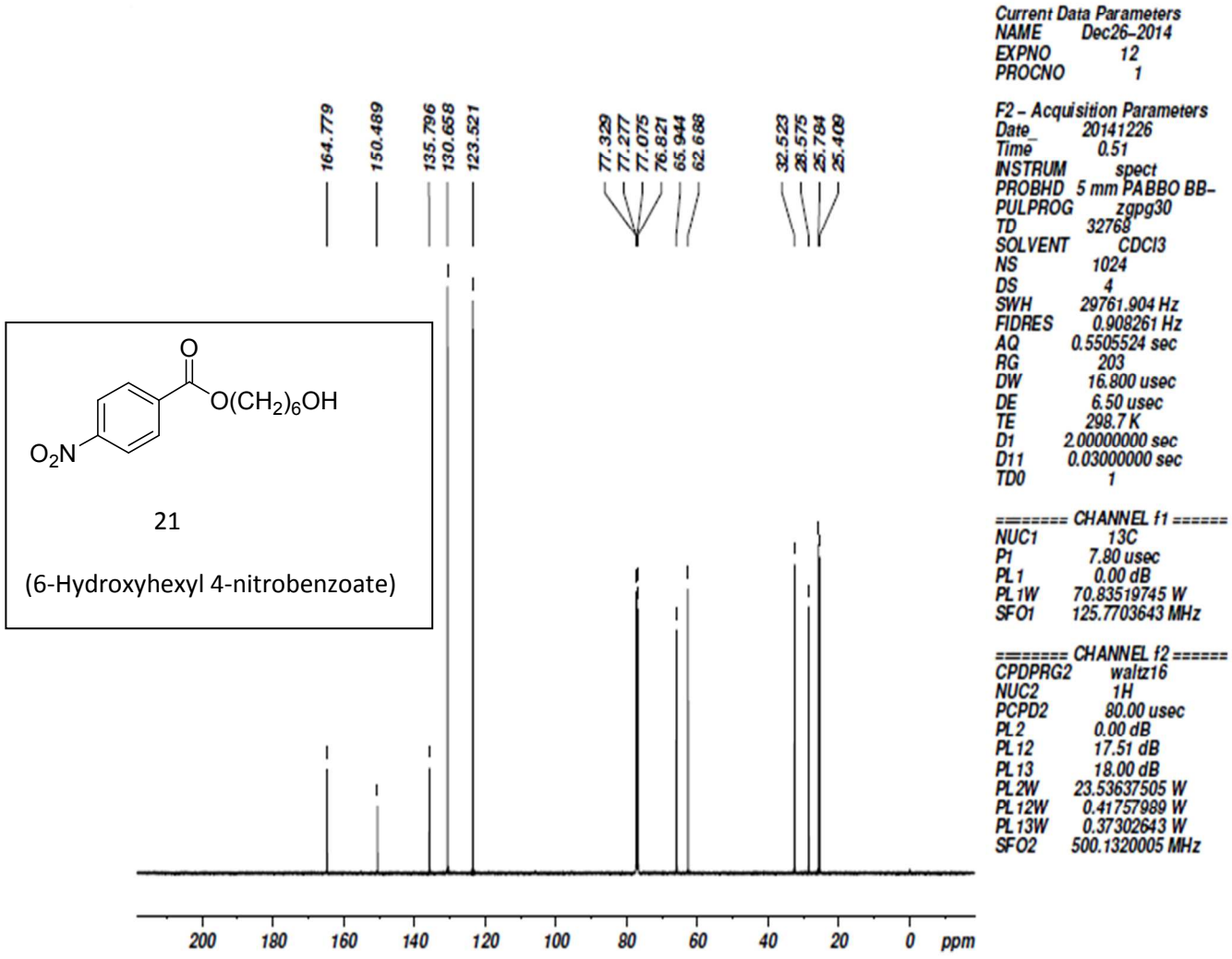

Fig :- ^{13}C NMR of 6-Hydroxyhexyl 4-nitrobenzoate(21)

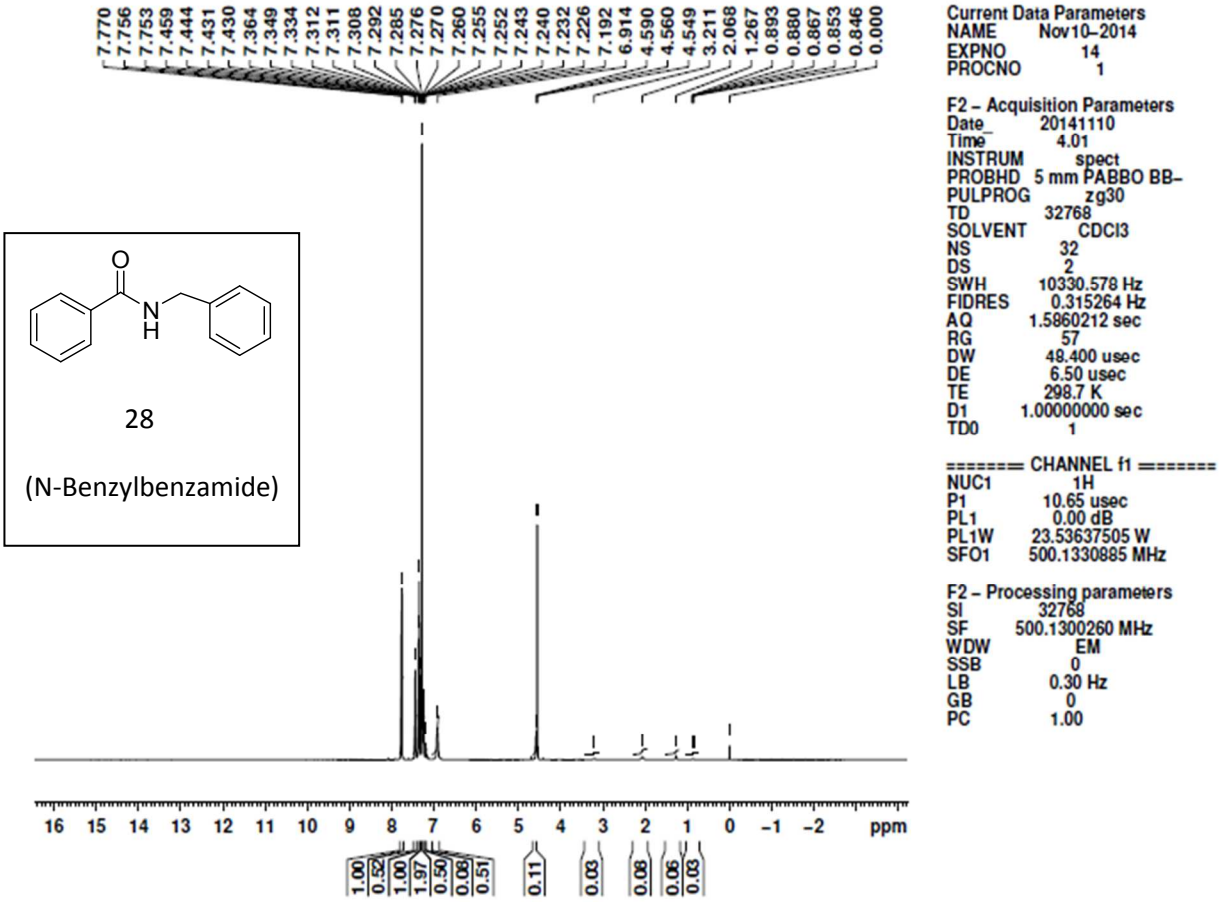

Fig :- ^{1}H NMR of N-Benzylbenzamide (28)

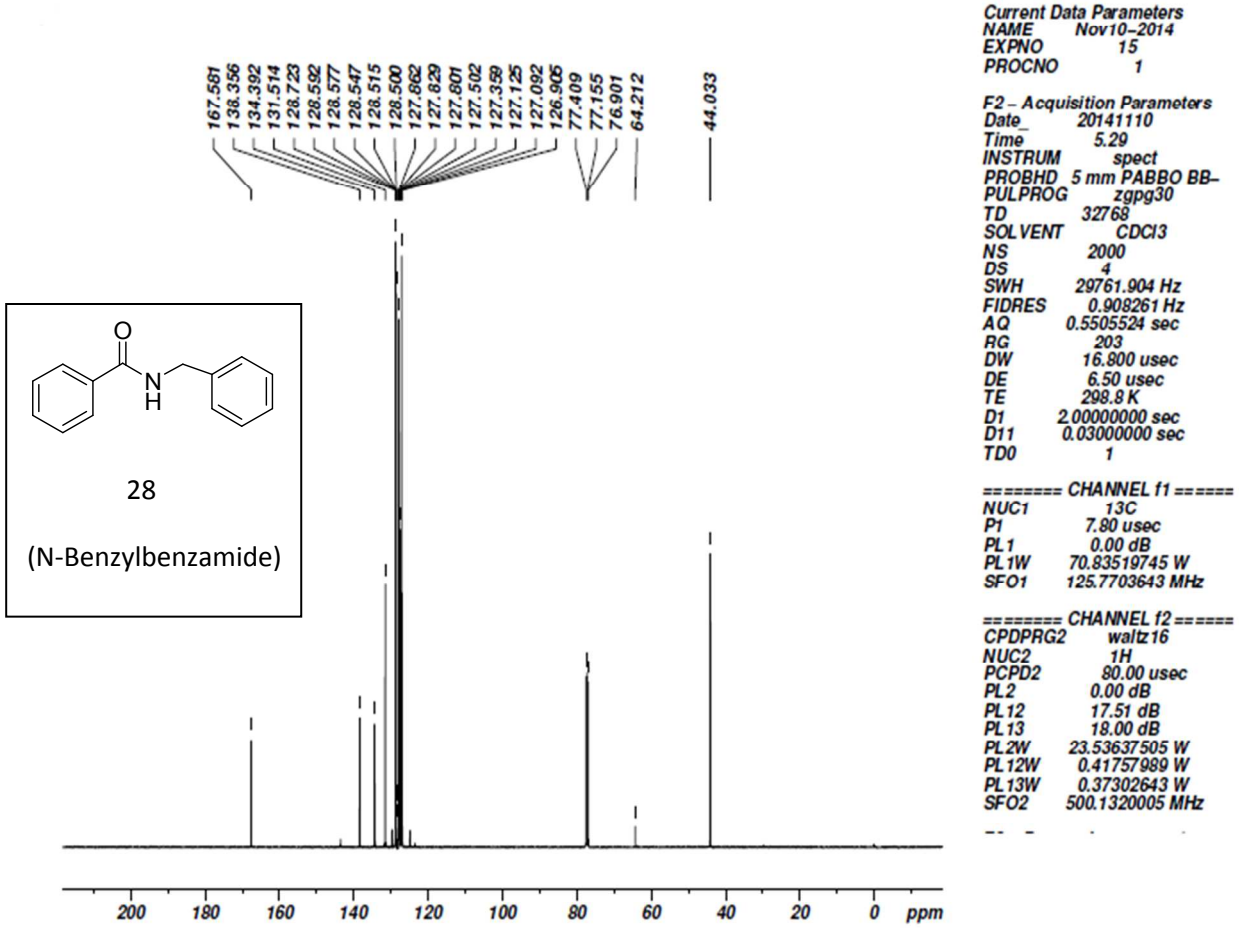

Fig :- ^{13}C NMR of N-Benzylbenzamide (28)

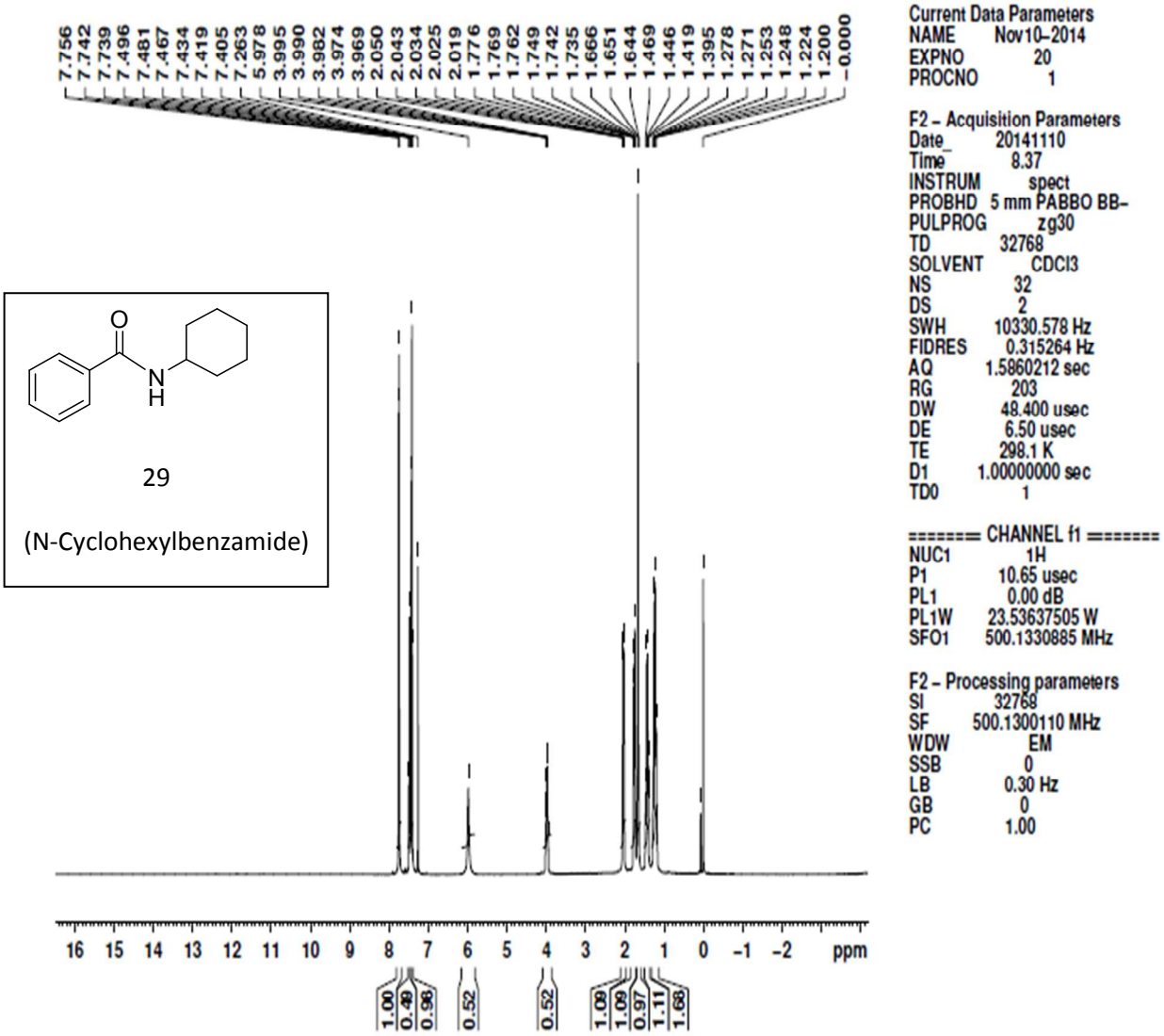

Fig :- ^{1}H NMR of N-Cyclohexylbenzamide(29)

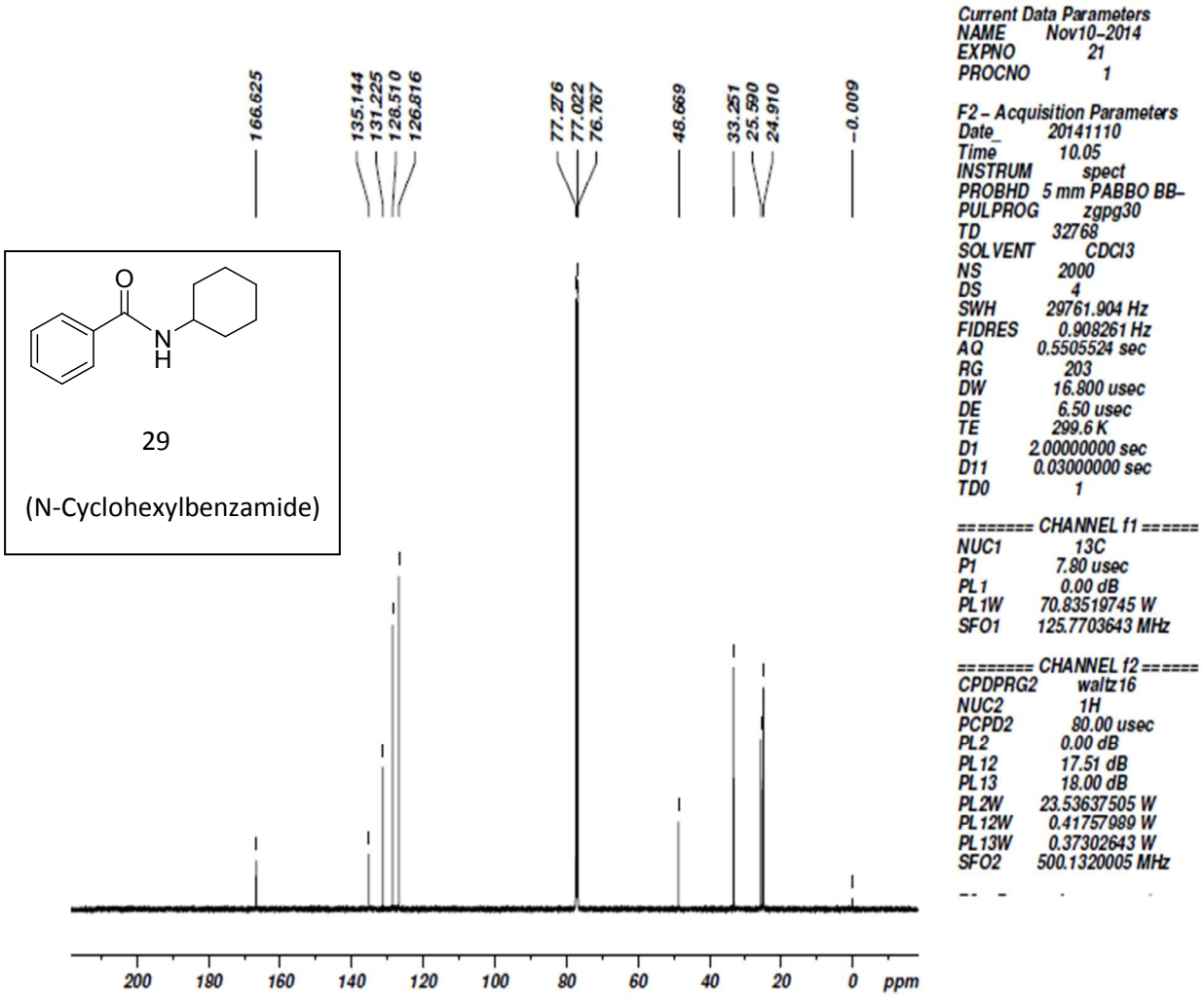

Fig :- ^{13}C NMR of N-Cyclohexylbenzamide(29)

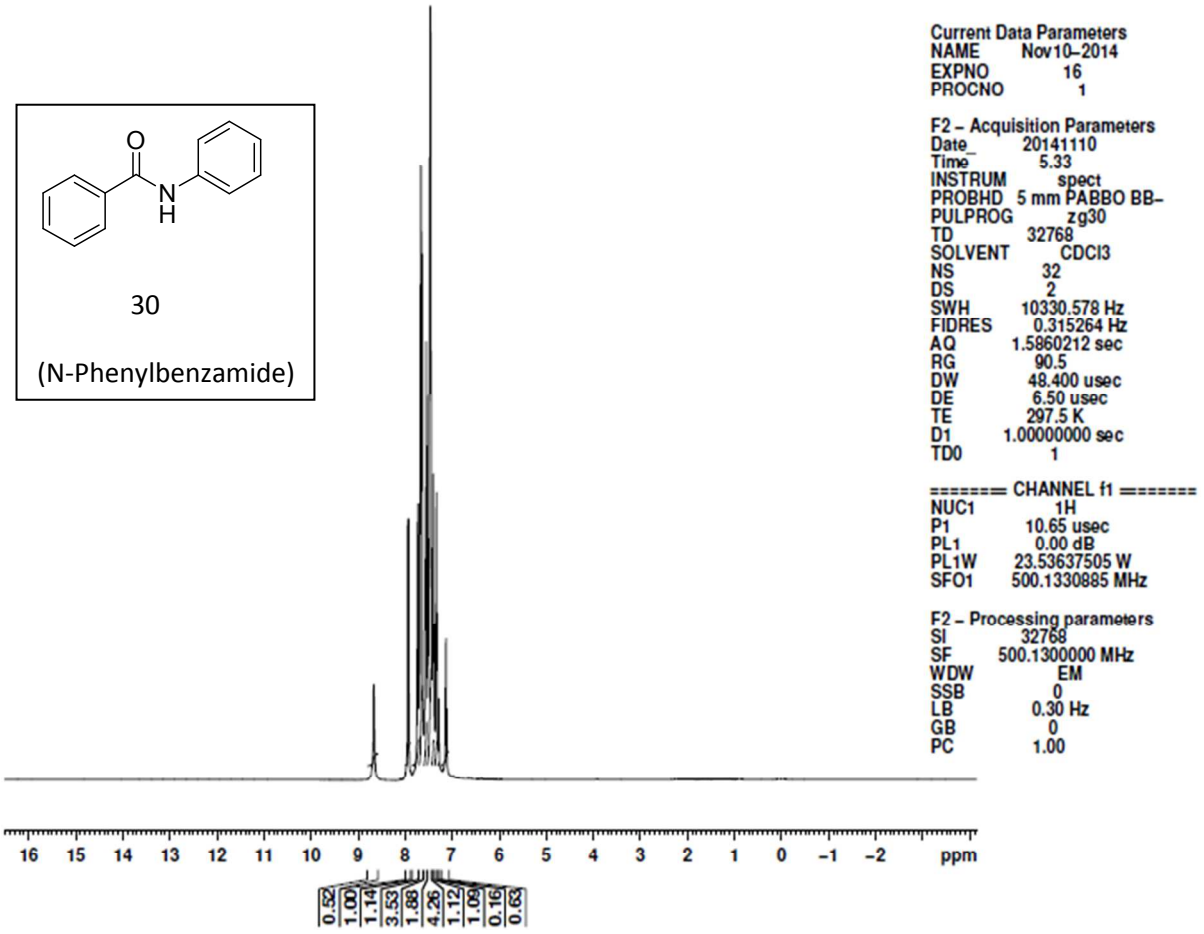

Fig :- ^{1}H NMR of N-Phenylbenzamide(30)

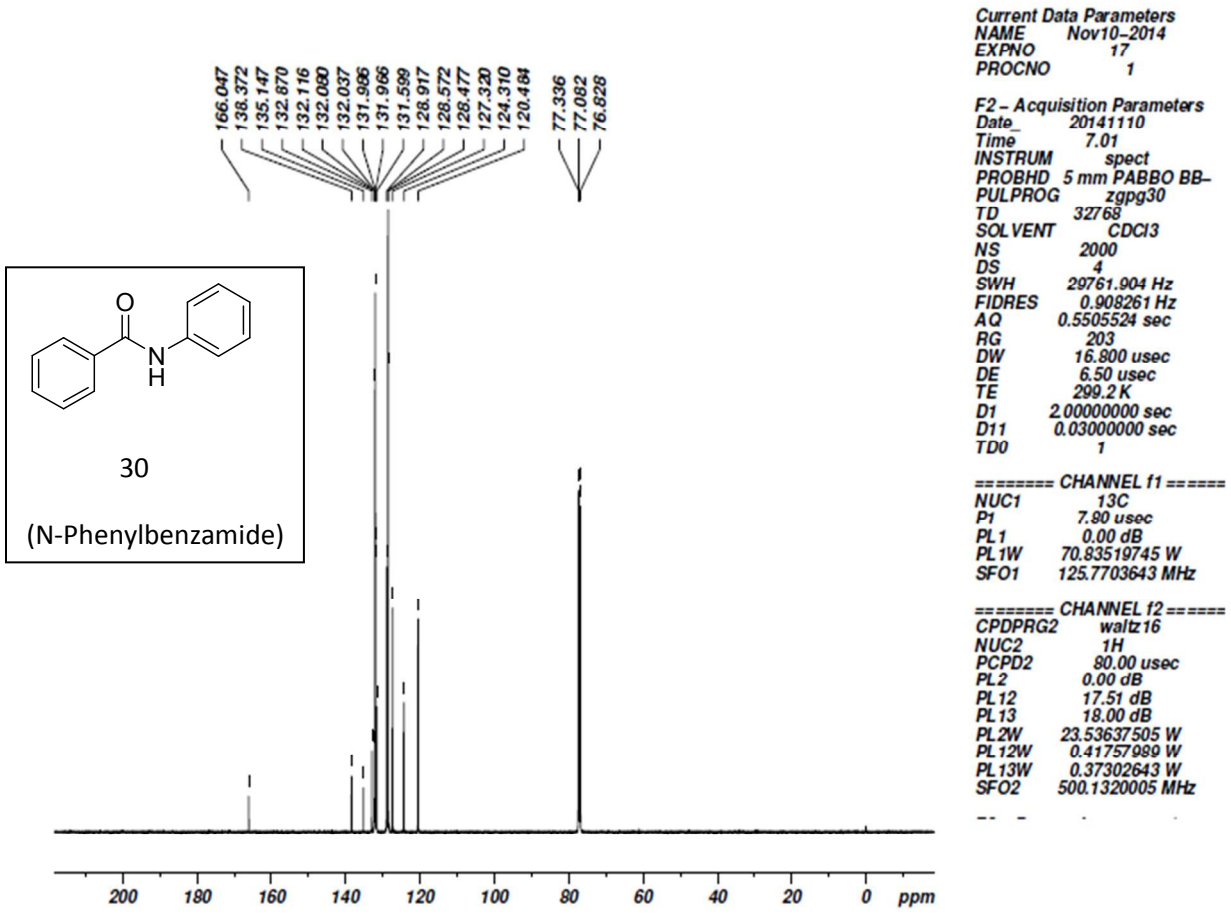

Fig :- ^{13}C NMR of N-Phenylbenzamide (30)

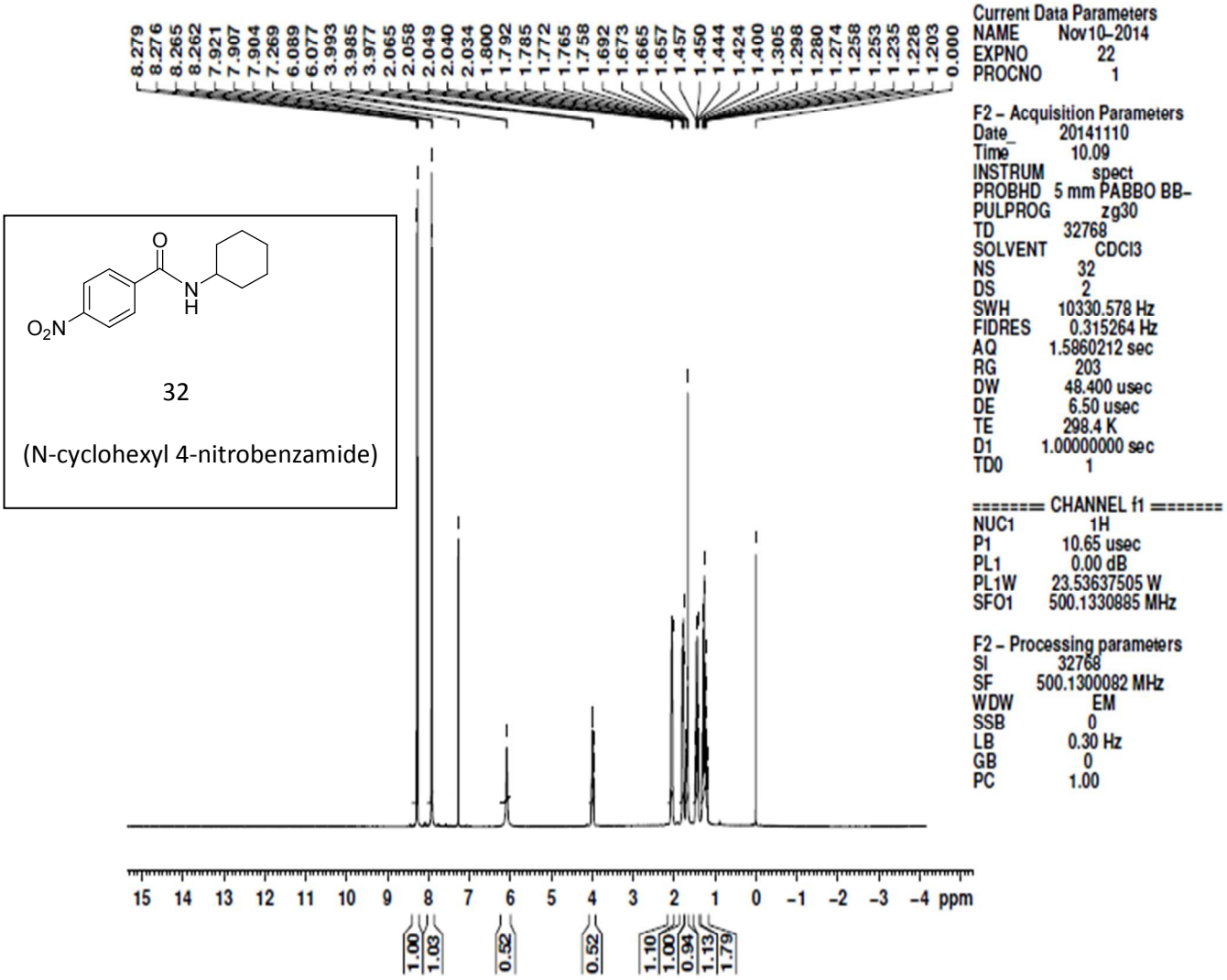

Fig :- ^{1}H NMR of N-Cyclohexyl 4-nitrobenzamide (32)

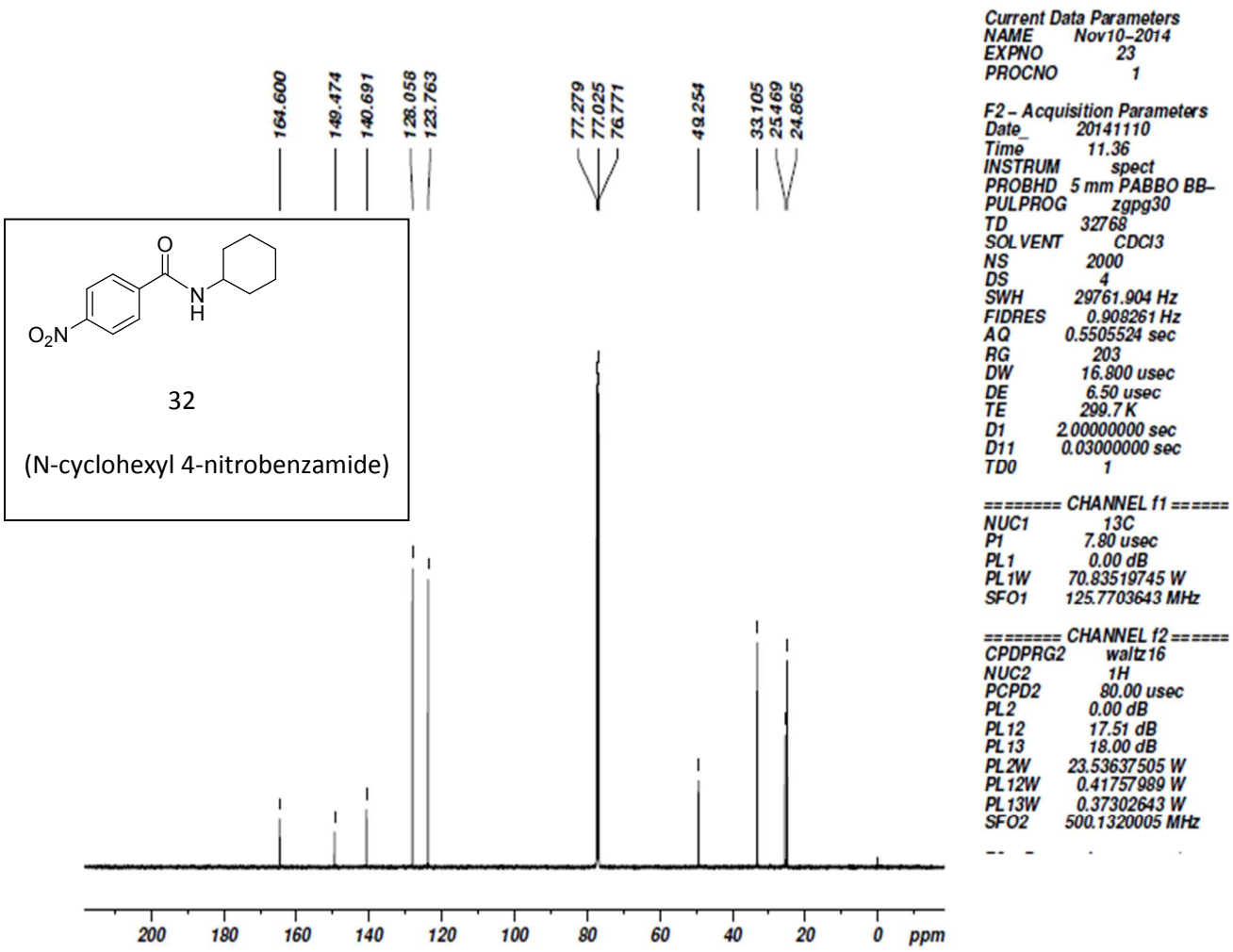

Fig :- ^{13}C NMR of N-Cyclohexyl 4-nitrobenzamide (32)