Supplementary Material

A convenient method for the synthesis of 3,6-dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetraalkyl esters and a study of their fluorescence properties

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CONTENTS

1. Experimental Section

General

NMR spectra were recorded on a Bruker Avance DPX-500 MHz spectrometer. Chemical shifts are reported relative to TMS as the internal standard. IR spectra were recorded on a Agilient Cary 630 FTIR spectrometer. Mass spectra were recorded under ESI/HRMS using JEOL JMS 600H mass spectrometer. Absorption spectra were recorded on a PerkinElmer UV/Vis Lambda 365 spectrometer. Fluorescence spectra were recorded on a JASCO FP-8300 spectrofluorometer. Time resolved fluorescence experiment was performed by using a IBH picosecond single photon counting system employing a 375 nm nano-LED excitation source. Cerium (IV) Ammonium Nitrate (CAN) was purchased from Merck Specialties Pvt. Ltd and was used as such without further purification. Commercial grade solvents were used. Analytical thin layer chromatography was performed on silica gel coated on aluminium sheets and was monitored using UV light of wavelength 366 nm. Gravity column chromatography was performed using 100-200 mesh silica gel and mixtures of hexane and ethyl acetate were used for elution. Dimethyl 1,3-acetone dicarboxylate, diethyl 1,3-acetone dicarboxylate and 1,5-diphenyl pentane-1,3,5-trione were commercially available and were used as such without further purification..

General experimental procedure for the synthesis of 3-oxo-1,5-diesters

Steglich esterification procedure was used for the preparation of 3-oxo-1,5-diesters **1c-1i**. To an ice-cold solution of 1,3-acetone dicarboxylic acid in dry dichloromethane (10 ml), excess of alcohol, a pinch of 4,4'-dimethyl amino pyridine (DMAP around 50 mg) and dicyclohexyl carbodiimide (DCC, 3 mmol) were added. The solution was allowed to stir; the reaction was gradually raised to room temperature after 5-10 minutes. Completion of the reaction was indicated by TLC. The reaction mixture was extracted with DCM and washed with sodium bicarbonate. The organic layer was dried over Na_2SO_4. The residue after removal of the solvent was subjected to column chromatography using silica gel 100-200 mesh and hexane-EtOAc as solvent system.

Synthesis of 3,6-dihydroxy-benzene -1,2,4,5-tetracarboxylic acid tetraalkyl esters

General Procedure

To an ice cold solution of 3-oxo-1,5-diester (100 mg) in dry CH_3CN (10ml), 30 mol% CAN was added. The solution was allowed to stir and the temperature was gradually raised to RT. After completion of the reaction as indicated by TLC, the solvent was rotary evaporated and the residue was extracted with dichloromethane and washed with brine (3×10 mL). The organic extract was dried over anhydrous Na_2SO_4 and the solvent was subsequently removed. The residue was subjected to column chromatography using silica gel 100-200 mesh and hexane-EtOAc solvent system.

Synthesis of 3,6-Dihydroxy-1,2,4,5-tetrabenzoyl benzene 4

To an ice cold solution 100 mg (0.3759 mmol) of 1,5-diphenyl pentane-1,3,5-trione in dry CH_3CN solvent (10ml), 30 mol% CAN (61.82 mg, 0.1127 mmol) was added. The solution was allowed to stir and the temperature was gradually raised to RT. After completion of the reaction as indicated by TLC, the solvent was rotary evaporated and the crude residue was

extracted with dichloromethane and washed with brine (3×10 mL). The organic extract was dried over anhydrous Na_2SO_4 and the solvent was subsequently removed. The residue was subjected to column chromatography using silica gel 100-200 mesh and hexane-EtOAc as solvent system. Elution with 2:8 ethyl acetate: hexane afforded the product **4** as a yellow powder; yield: 83 mg (42%, recovered yield: 61%, 0.1578 mmol); mp: 201-203 ^{0}C.

2. Characterisation Data

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetramethyl ester (2a)

Light yellow solid, Mp: 120.5-121.5 ºC, yield: 80 mg (41%, recovered yield: 67%, 0.2356 mmol). IR (powder): 3024, 2983, 1736, 1502, 1438, 1341, 1286, 1148 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.95 (s, 6H, C**H**$_3$), 10.54 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 149.9, 120.2, 53.2. HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd for $C_{14}H_{14}O_{10}$: 365.0587; found: 365.0567.

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetraethyl ester (2b)

Light yellow solid, Mp: 121.5-122.5 ºC, yield: 88 mg (45%, recovered yield: 54%, 0.2227 mmol). IR (powder): 3078, 2989, 1725, 1498, 1285, 1170, 961 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (t, J = 14.5 Hz, 6H, C**H**$_3$), 4.41 (q, J = 21.5 Hz, 4H, C**H**$_2$CH$_3$), 10.65 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 150.1, 120.1, 96.1, 62.2, 13.9. HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd for $C_{18}H_{22}O_{10}$: 421.3613; found: 421.3617.

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetrapropyl ester (2c)

Yellow oil; yield: 88 mg (45%, recovered yield: 60%, 0.1956 mmol). IR (Thin film): 3138, 2929, 1736, 1569, 1498, 1282, 1177, 989 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.0 (t, J = 18.5 Hz, 6H, CH_3), 1.72-1.81 (sex, 4H, C**H**$_2$CH$_3$), 4.30 (t, J = 17 Hz, 4H, OC**H**$_2$), 10.66 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 150.1, 120.2, 68.1, 21.7, 10.3. HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd for $C_{22}H_{30}O_{10}$: 477.4676; found: 477.4671.

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetrabutyl ester (2d)

Yellow oil; yield: 93 mg (47%, recovered yield: 59%, 0.1821 mmol). IR (Thin film): 3176, 2961, 2857, 1732, 1460, 1248, 1161, 1080 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10-1.18 (m, 6H, CH_3), 1.20-1.39 (m, 4H C**H**$_2$CH$_3$), 1.51-1.66 (m, 4H, C**H**$_2$CH2CH3), 4.08 (t, J = 16.5 Hz, 4H, OC**H**$_2$), 10.58 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.0, 157.0, 134.0, 66.0, 28.3, 21.6, 13.0. HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd for $C_{26}H_{38}O_{10}$: 533.5739; found: 533.5737.

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetrapentyl ester (2e)

Yellow oil; yield: 85 mg (43%, recovered yield: 51%, 0.1503 mmol). IR (Thin film): 3110, 2954, 1739, 1460, 1378, 1188, 1084, 894 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.3-1.01 (m, 6 H, C**H**$_3$), 1.82-1.60 (m, 8H, C**H**$_2$C**H**$_2$CH$_3$), 2.25-2.20 (m, 4H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 4.0-4.12 (m, 4H, OC**H**$_2$), 10.57 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6, 149.1, 127.9, 127.4, 65.4, 28.6, 28.5, 21.6, 13.0. HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd for $C_{30}H_{46}O_{10}$: 589.6802; found: : 589.6810.

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetra(iso-propyl) ester (2f)

Yellow oil; yield: 94 mg (48%, recovered yield: 61%, 0.2086 mmol). IR (Thin film): 3183, 2922, 2851, 1736, 1461, 1189, 1099, 797 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.18-1.35 (m, 12H, CHC**H**$_3$), 5.16-5.22 (m, 2H, OC**H**), 10.58 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.1, 149.1, 127.8, 69.6, 20.5. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{22}H_{30}O_{10}$: 477.4676; found: 477.4667.

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetra(t-butyl) ester (2g)

Yellow oil; yield: 92 mg (47%, recovered yield: 60%, 0.1821 mmol). IR (Thin film): 3095, 2922, 2855, 1740, 1461, 1371, 1254, 1148 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 18H, C**H**$_3$), 9.87 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 150.9, 123.0, 83.6, 28.6. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{26}H_{38}O_{10}$: 533.5739; found: 533.5743.

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetracyclohexylester (2h)

Yellow oil; yield: 89 mg (45%, recovered yield: 51%, 0.1451 mmol). IR (Thin film): 3040, 2937, 2858, 1733, 1453, 1259, 1120 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.20 (uneven triplet, 12H, $OCH^1CH_2{}^2C\mathbf{H}_2{}^3$), 2.21-2.28 (m, 8H, $OCH^1C\mathbf{H}_2{}^2CH_2{}^3$), 4.08 (q, J = 22.5 Hz, 2H, $OC\mathbf{H}^1CH_2{}^2CH_2{}^3$), 10.58 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.3, 162.6, 126.1, 70.5, 31.1, 29.7, 28.6, 22.4. HRMS (ESI): *m*/*z* $[M-Na]^+$ calcd for $C_{34}H_{46}O_{10}$: 591.7230; found: 591.7245.

3,6-Dihydroxy-benzene-1,2,4,5-tetracarboxylic acid tetrabenzyl ester (2i)

Yellow oil; yield: 85 mg (43%, recovered yield: 53%, 0.1319 mmol). IR (Thin film): 3136, 2948, 1736, 1628, 1498, 1390, 1267, 1174 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.12-5.19 (m, 4H, OC**H**$_2$), 7.17-7.29 (m, 10 **H**$_{arom}$), 10.51 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.1, 153.4, 142.4, 133.8, 130.2, 129.3, 128.4, 65.5. HRMS (ESI): *m*/*z* $[M-C_7H_7]$ calcd for $C_{38}H_{30}O_{10}$: 555.6388; found: 555.6380.

3,6-Dihydroxy-1,2,4,5-tetrabenzoyl benzene 4.

Yellow powder; yield: 83 mg (42%, recovered yield: 61%, 0.1578 mmol); mp: 201-203 ^0C. IR (Thin film): 3071, 2840, 1684, 1584, 1423, 1289, 1181, 931 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.18 - 8.06 (m, 10**H**$_{arom}$), 10.08 (s, 1H, O**H**). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.7, 148.9, 136.8, 132.7, 129.1, 128.2, 127.6, 127.4, 126.8. HRMS (ESI): *m*/*z* $[M-C_7H_7]$ calcd for $C_{34}H_{22}O_6$: 549.5349; found: 549.5345.

3. ^1H NMR and ^{13}C NMR Spectra of 2a-2i and 4

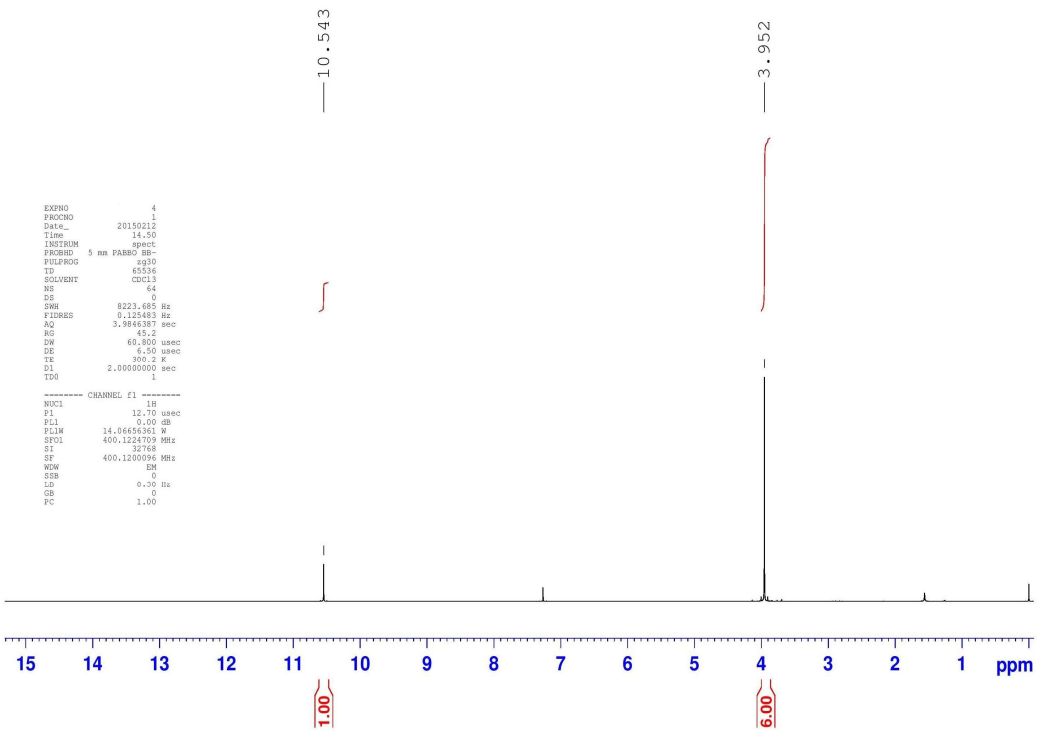

Figure 1 ^{1}H NMR Spectrum of 2a

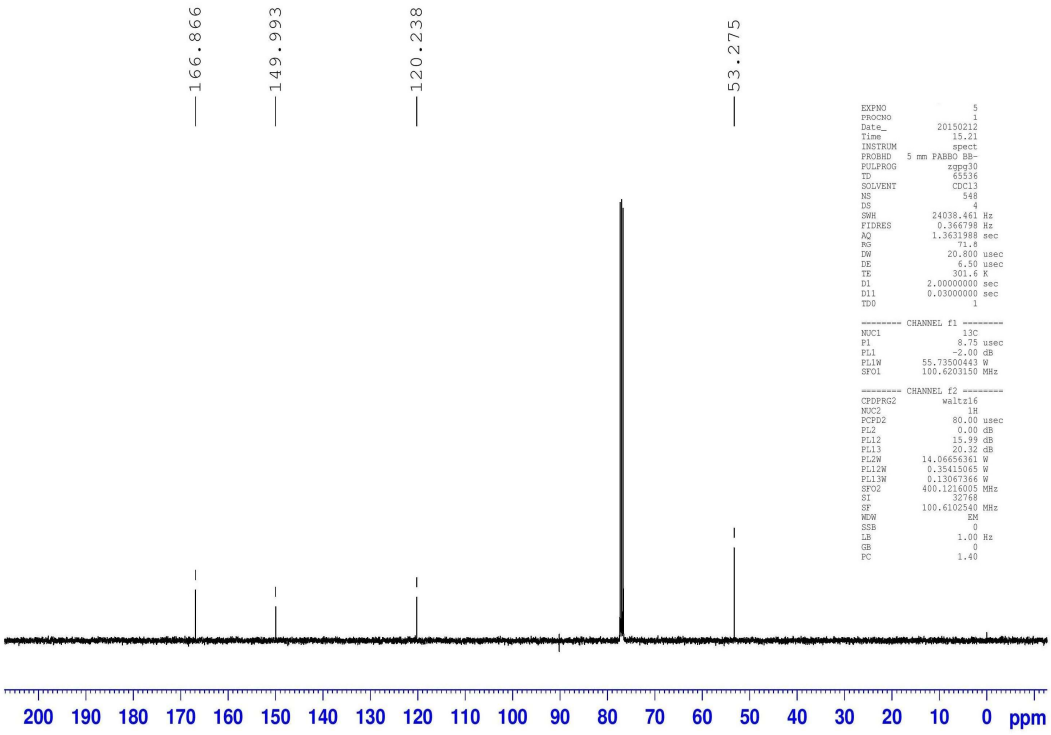

Figure 2 ^{13}C NMR Spectrum of 2a

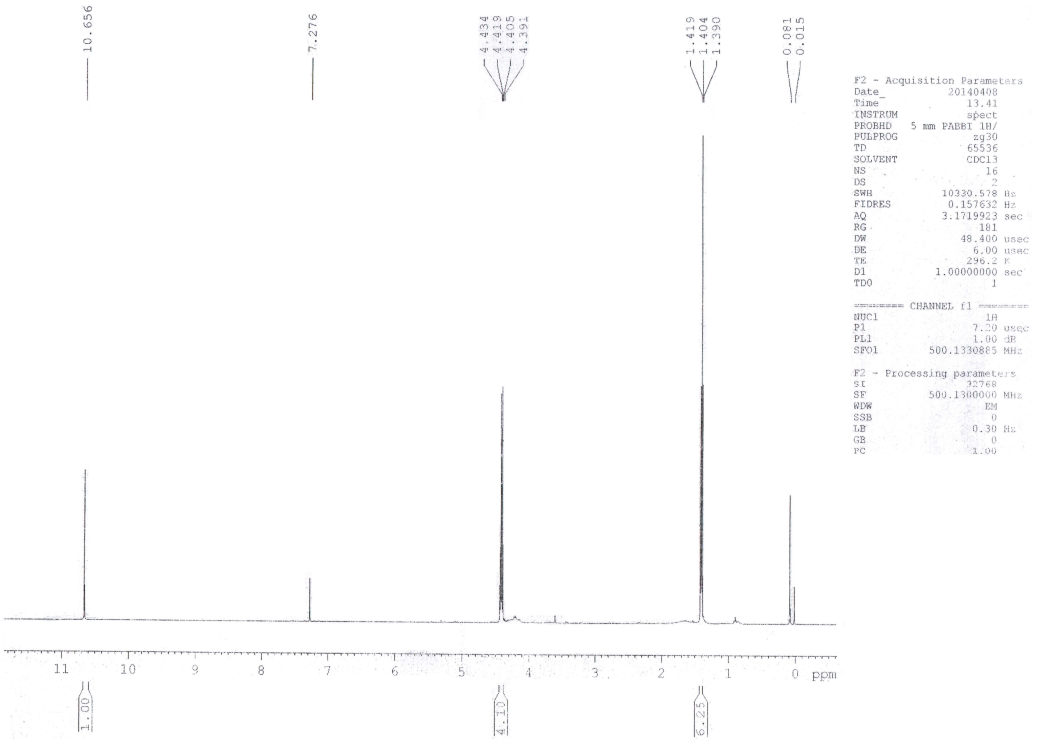

Figure 3 ^{1}H NMR spectrum of 2b

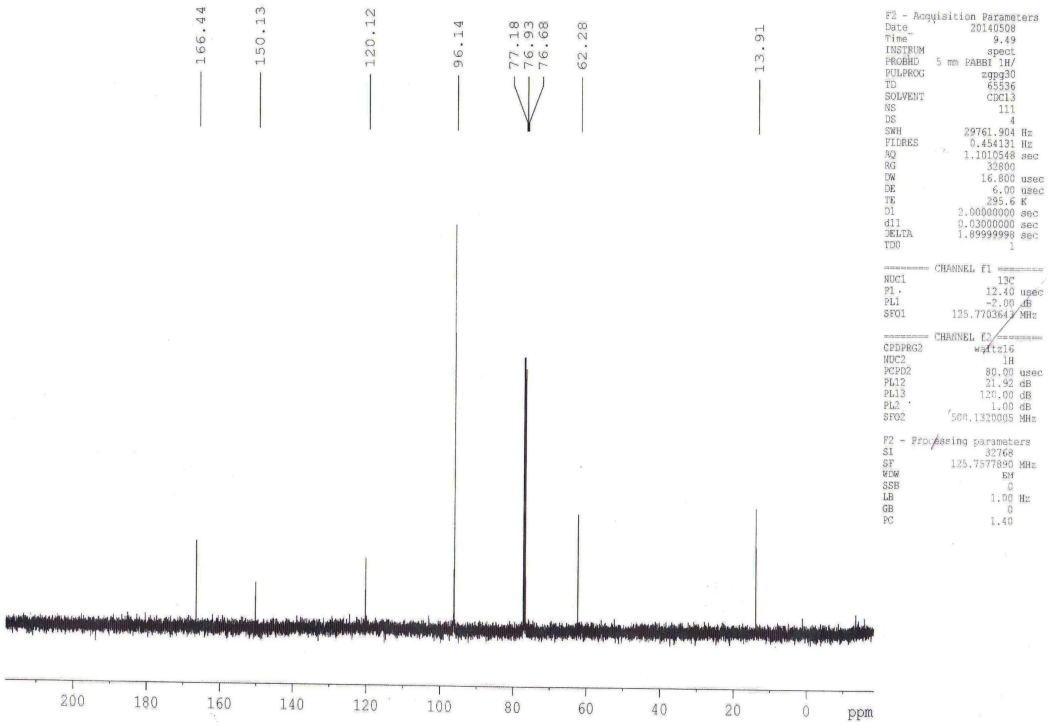

Figure 4 ^{13}C NMR spectrum of 2b

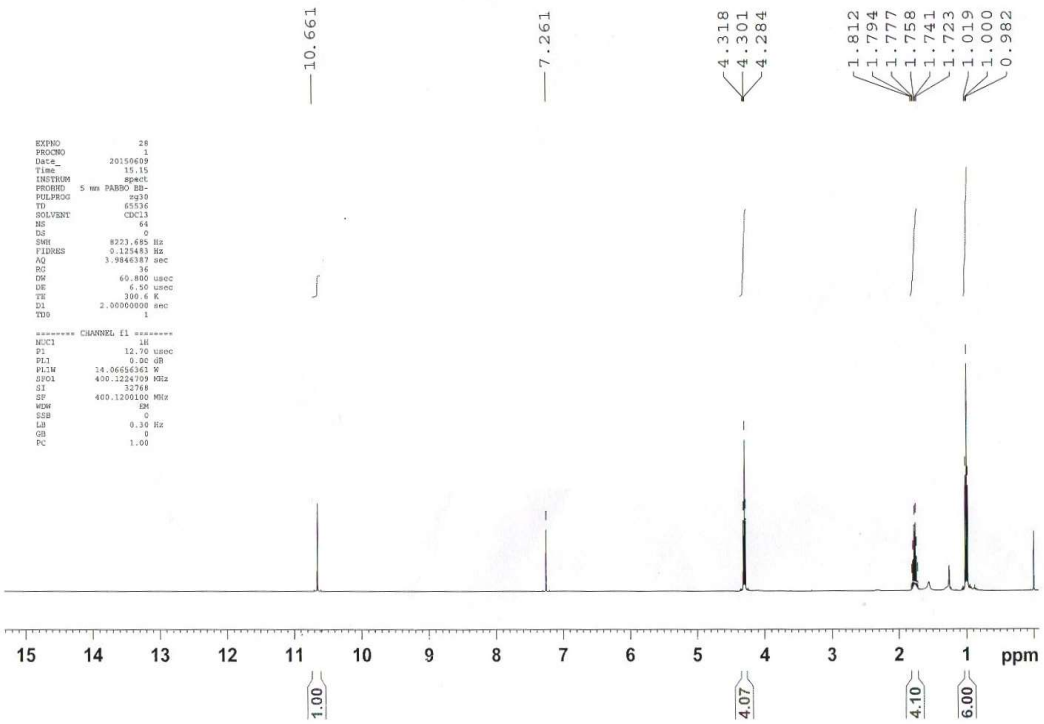

Figure 5 ^{1}H NMR spectrum of 2c

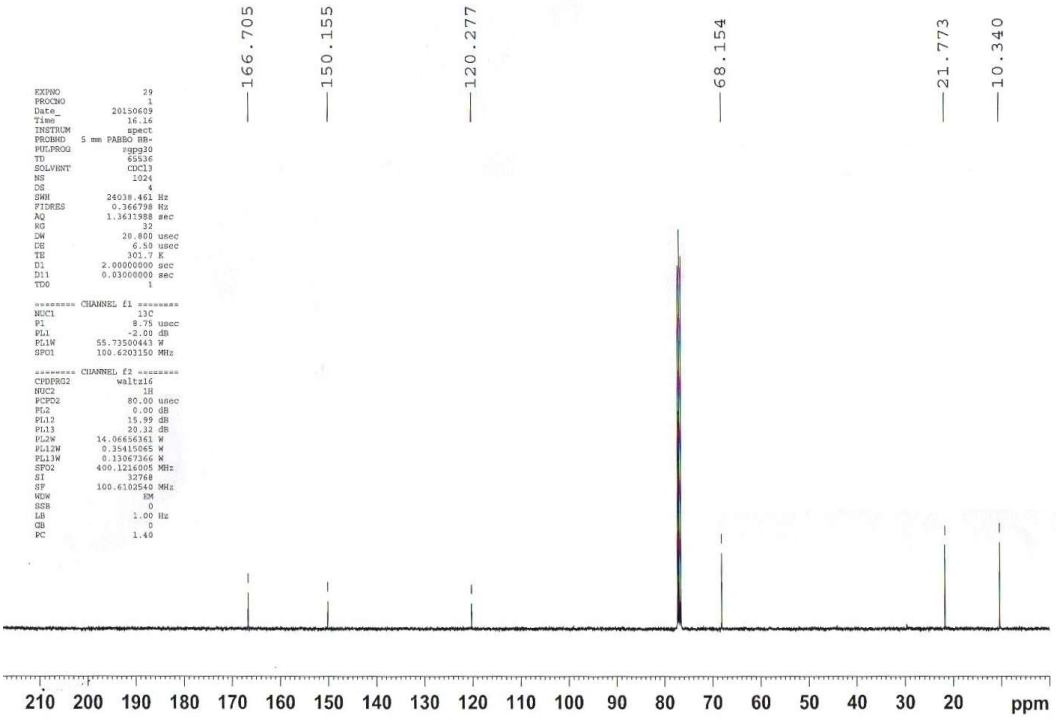

Figure 6 ^{13}C NMR spectrum of 2c

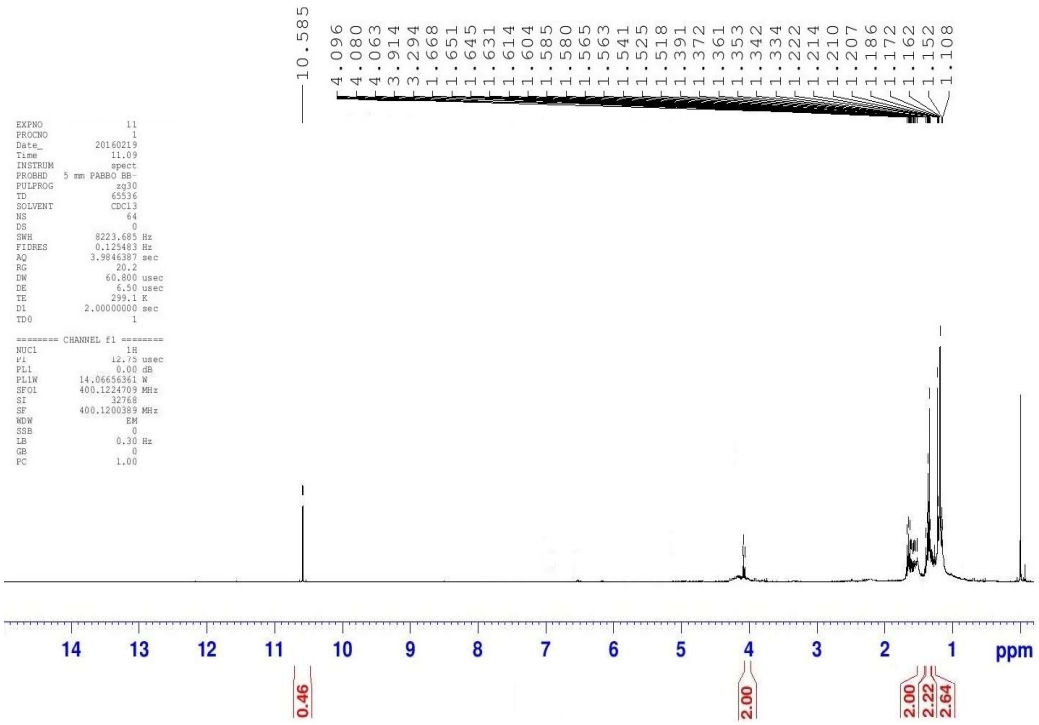

Figure 7 ^{1}H NMR spectrum of 2d

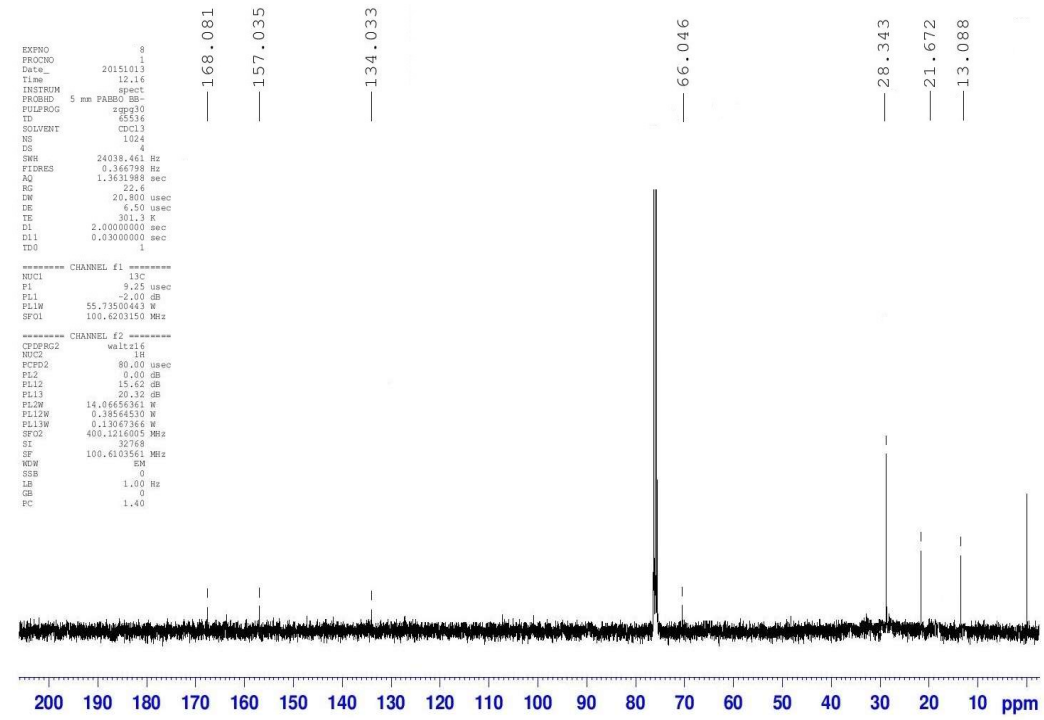

Figure 8 ^{13}C NMR spectrum of 2d

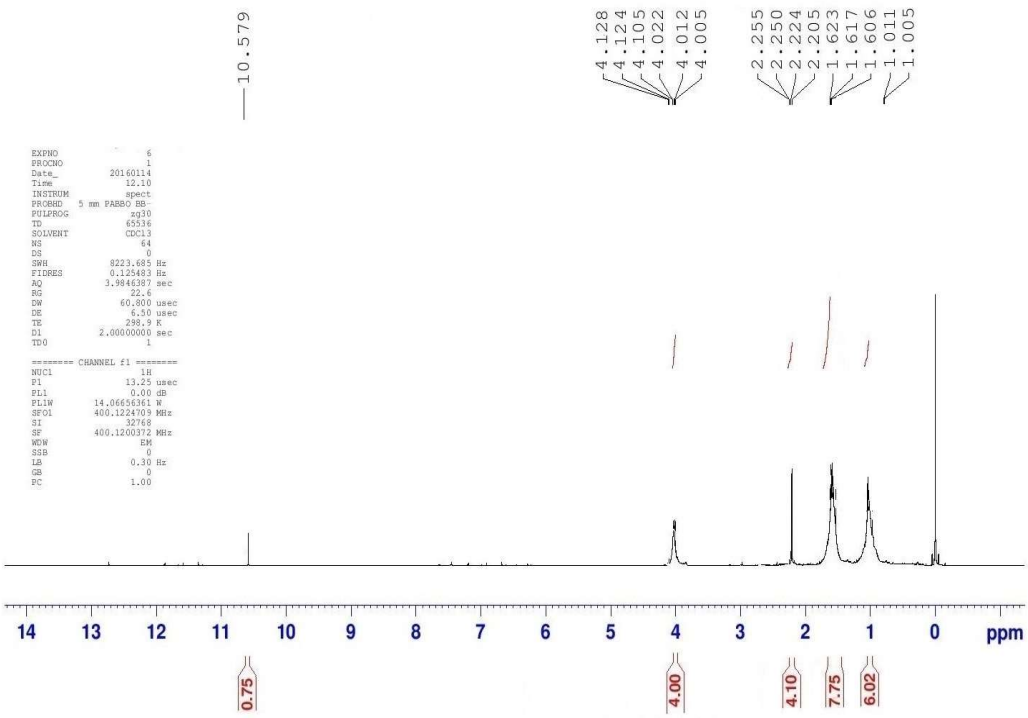

Figure 9 ^{1}H NMR spectrum of 2e

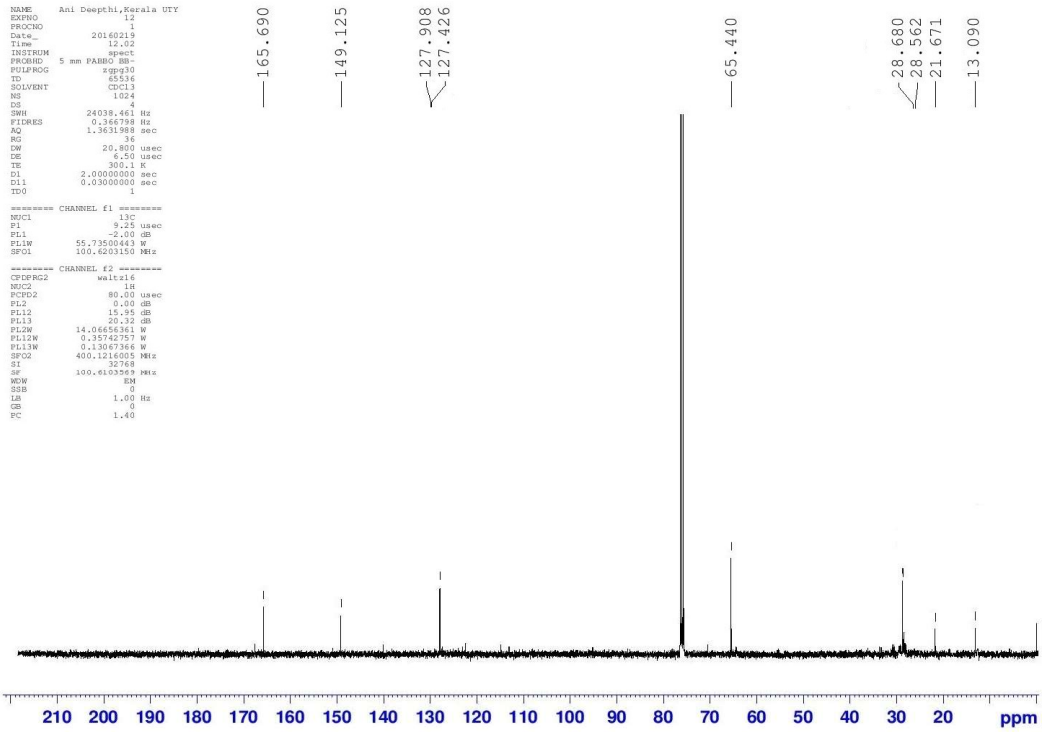

Figure 10 ^{13}C NMR spectrum of 2e

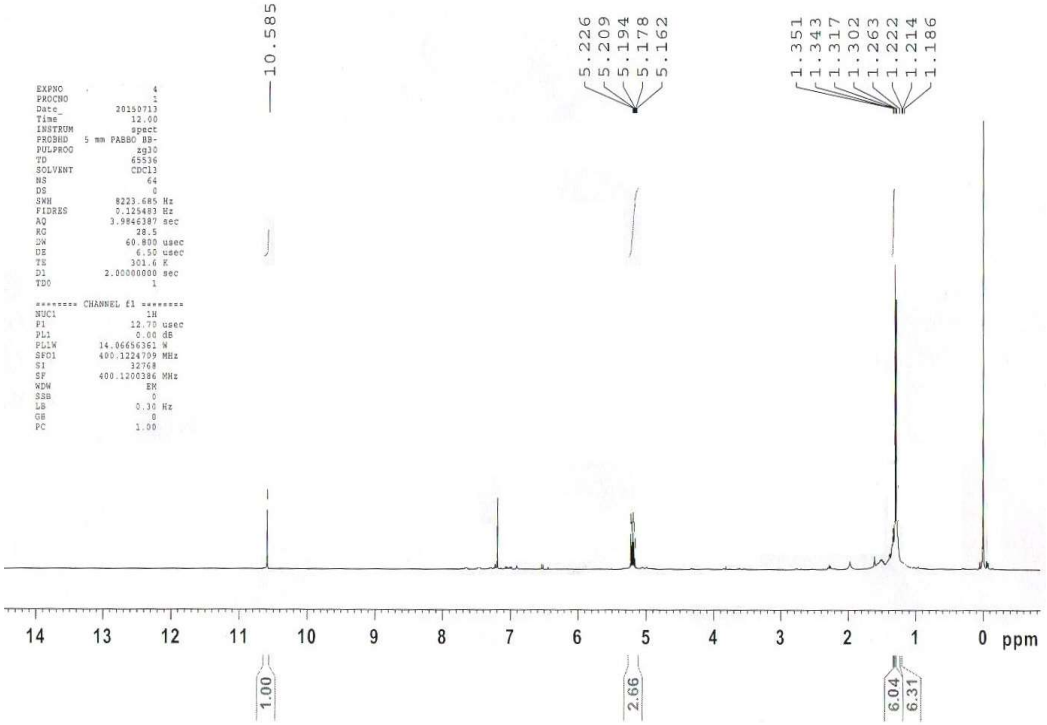

Figure 11 ^{1}H NMR spectrum of 2f

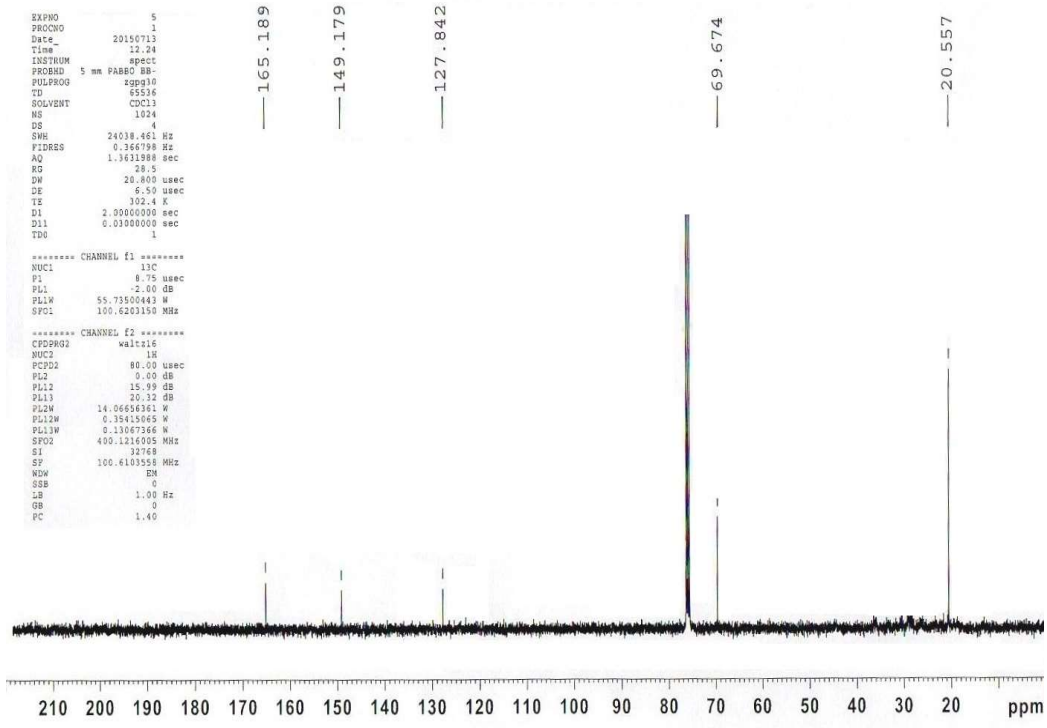

Figure 12 ^{13}C NMR spectrum of 2f

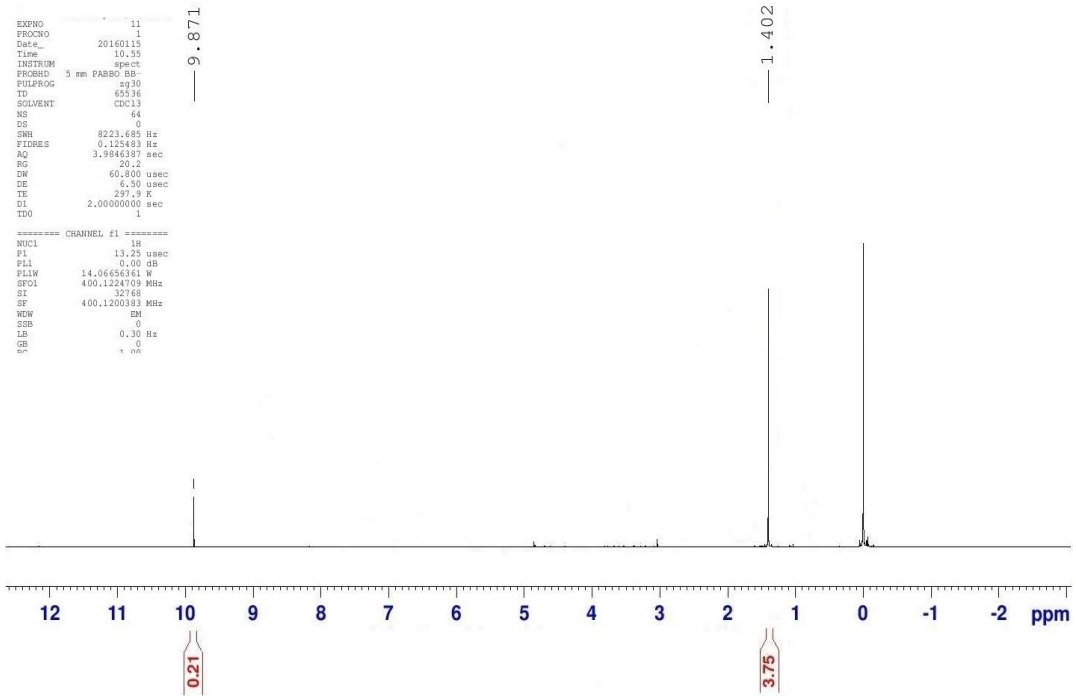

Figure 13 ^{1}H NMR spectrum of 2g

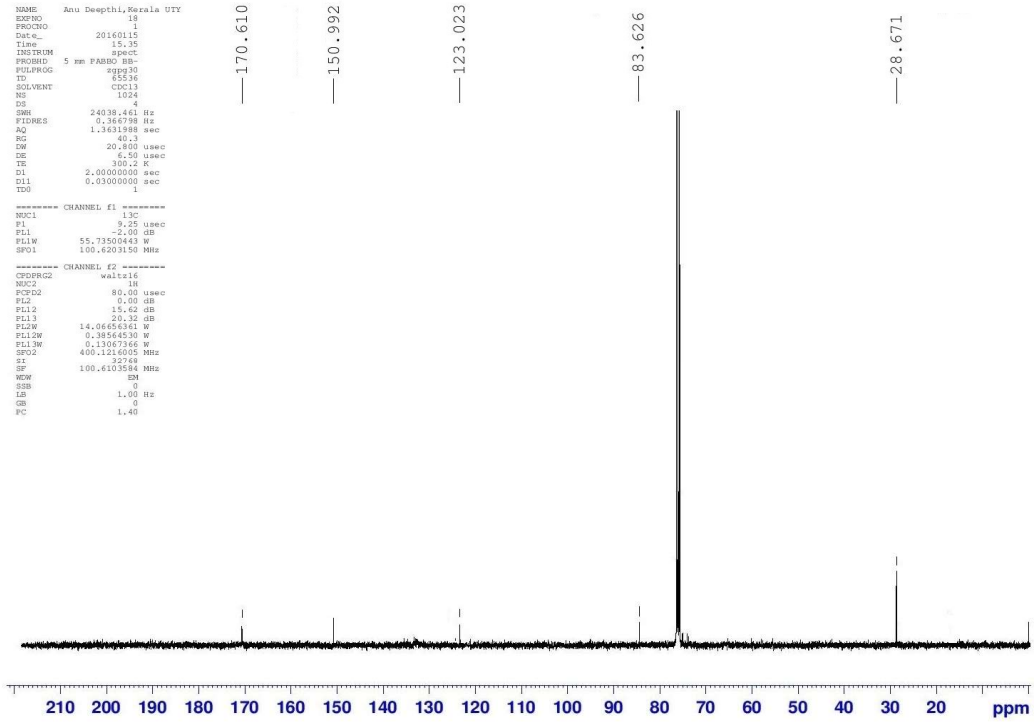

Figure 14 ^{13}C NMR spectrum of 2g

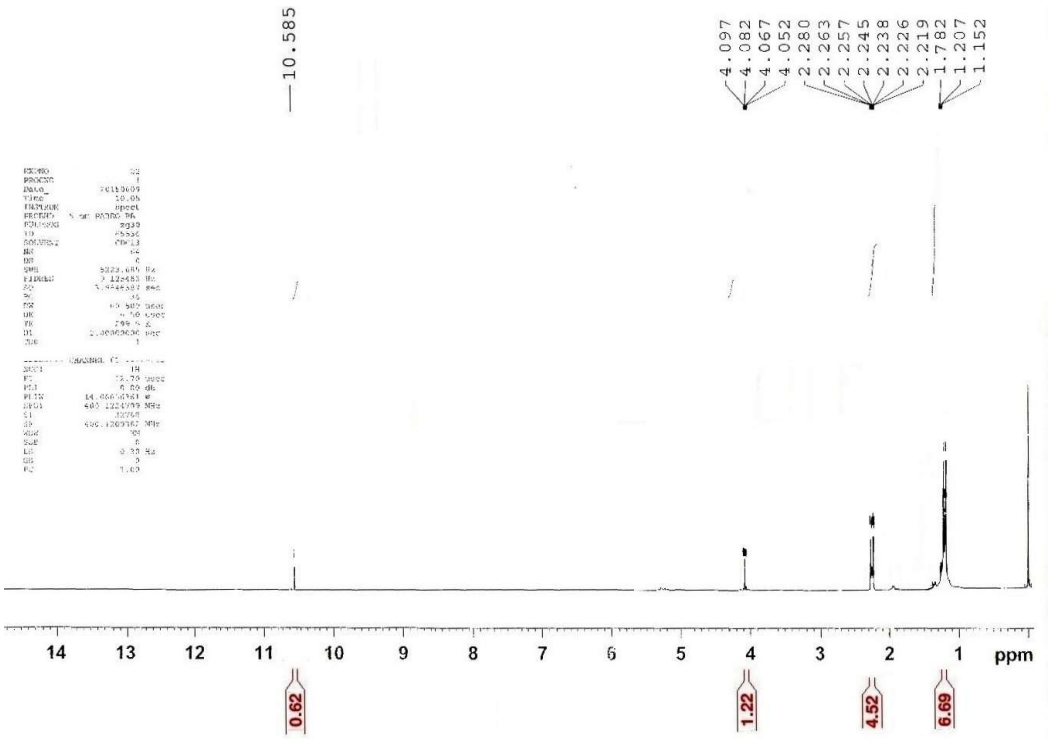

Figure 15 ^{1}H NMR spectrum of 2h

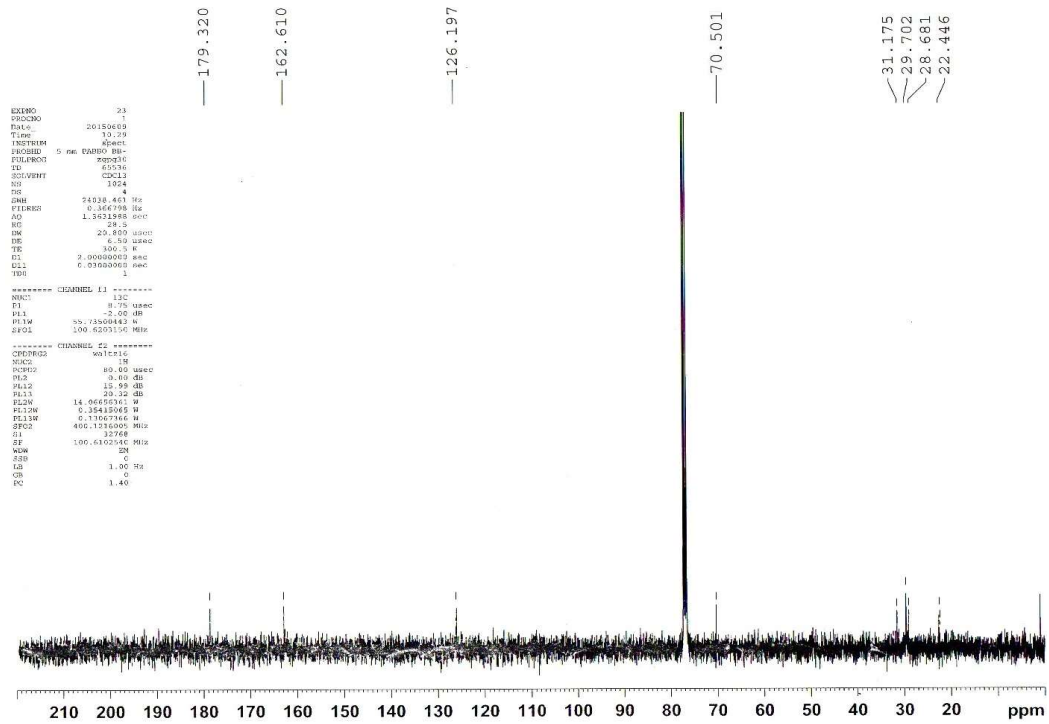

Figure 16 ^{13}C NMR spectrum of 2h

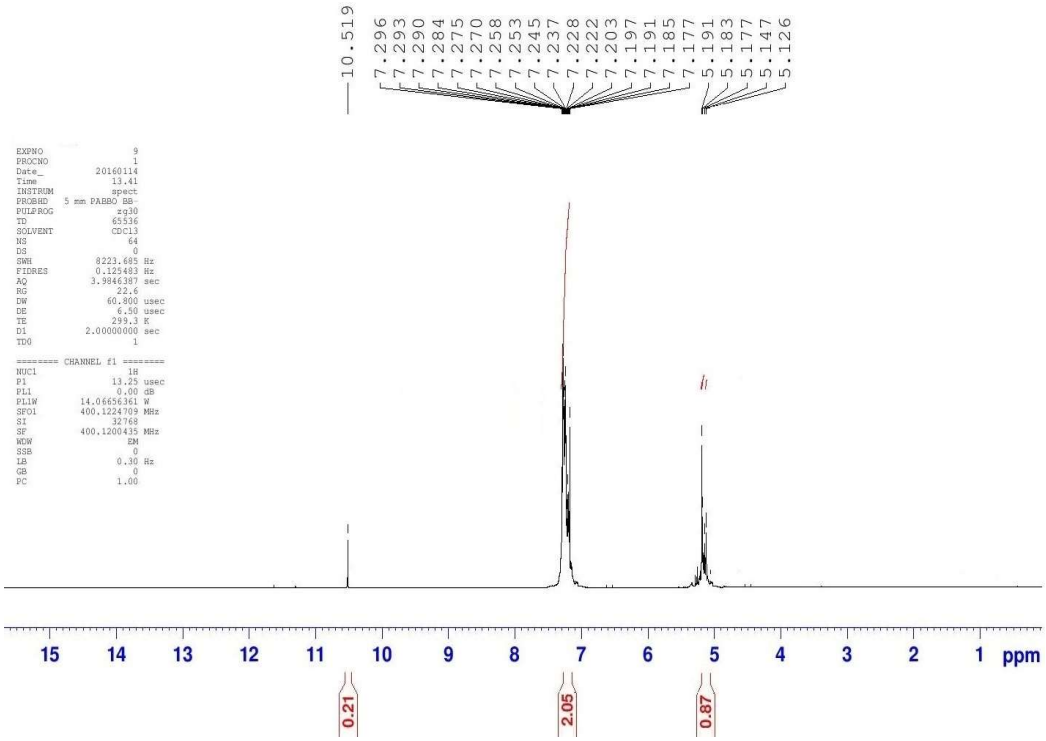

Figure 17 ^{1}H NMR spectrum of 2i

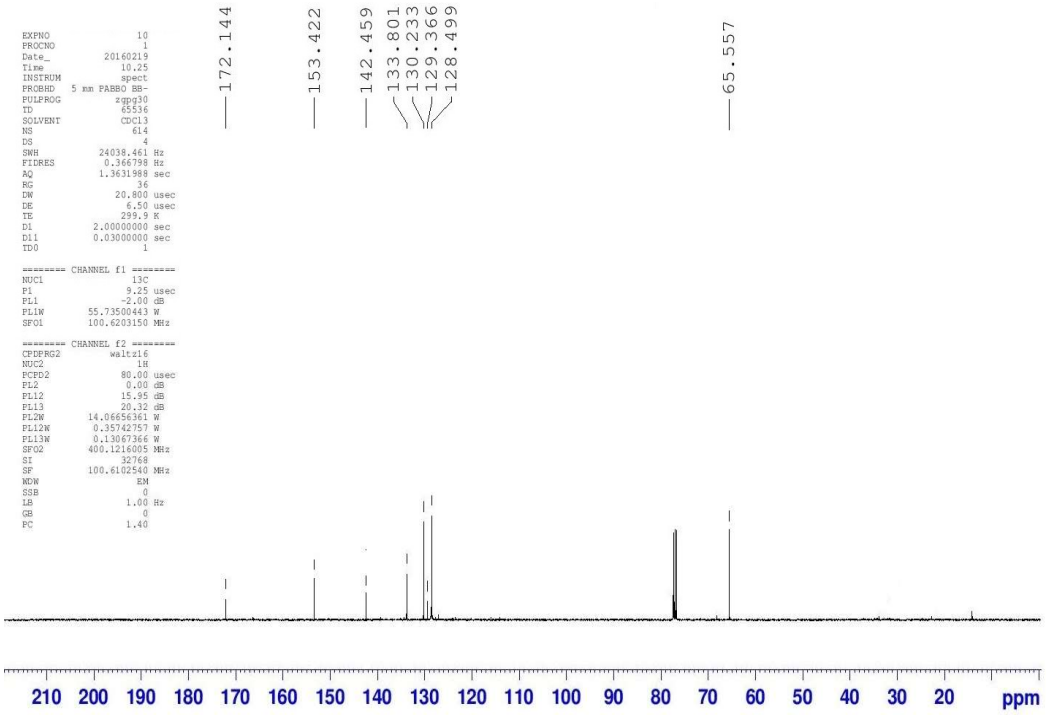

Figure 18 ^{13}C NMR spectrum of 2i

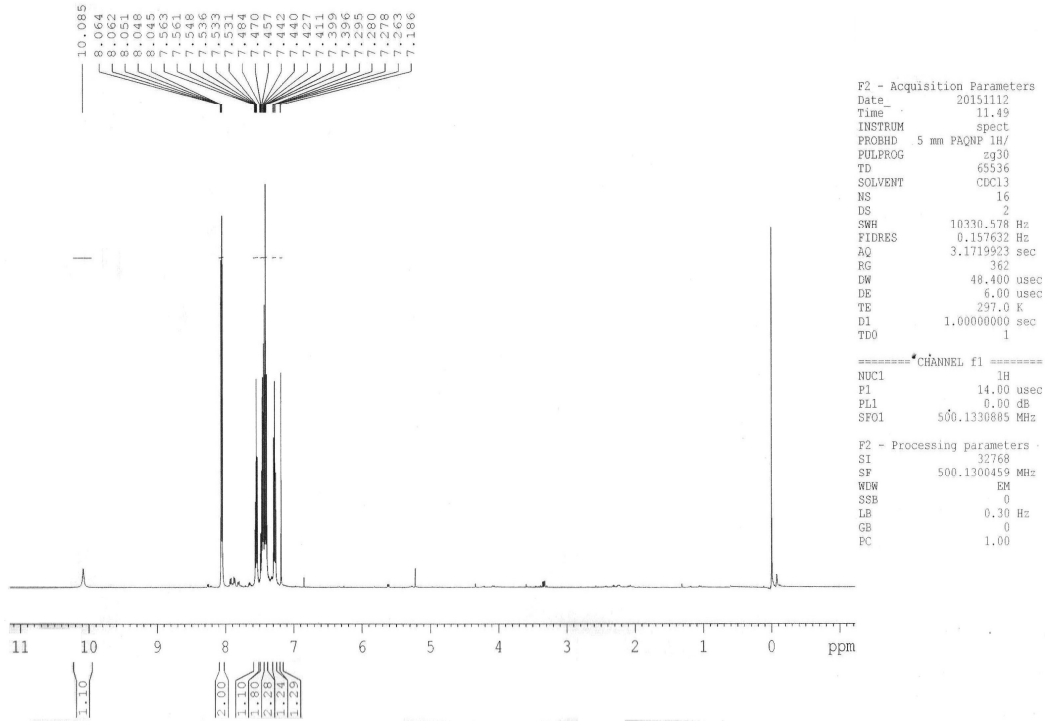

Figure 19 ^{1}H NMR spectrum of 4

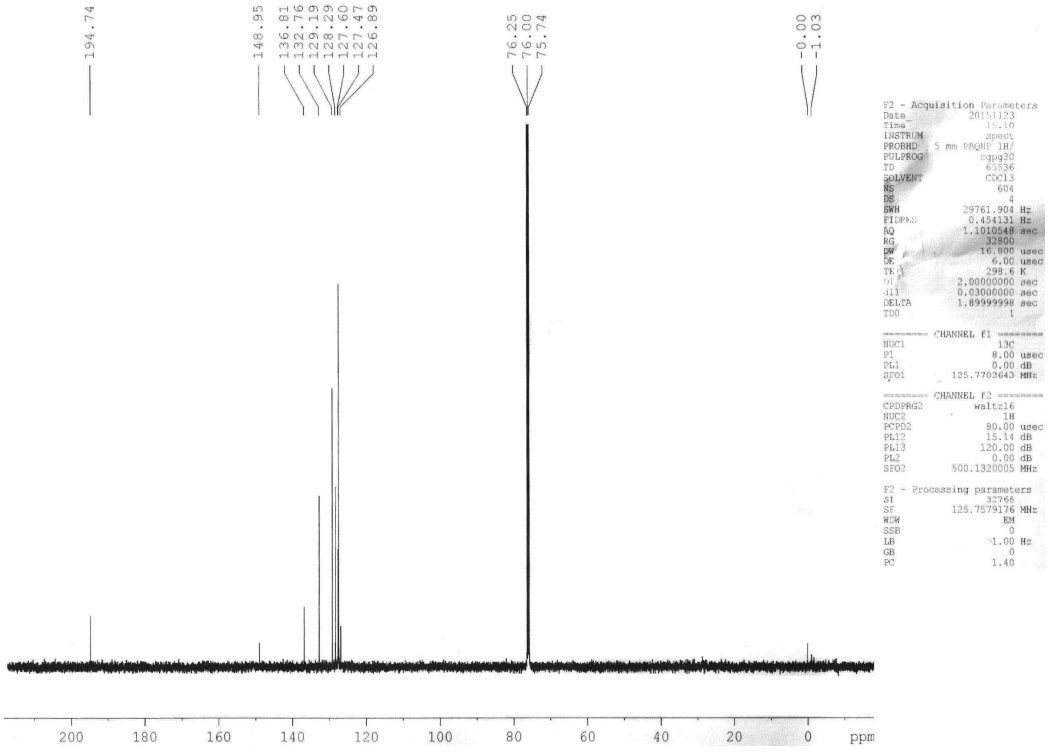

Figure 20 ^{13}C NMR spectrum of 4

4. Fluorescence decay profile of representative compound 2b

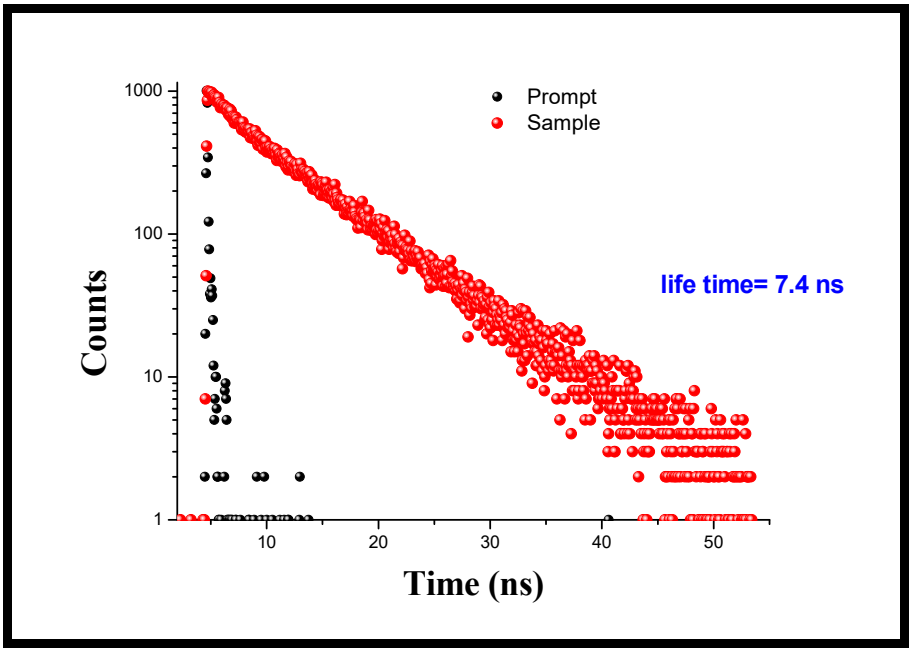

Figure 21 Fluorescence life time decay profile for the representative compound 2b with λmax 377 nm in acetonitrile solvent

