Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis, characterization and optoelectronic investigations of bithiophene substituted 1,3,4-oxadiazole derivatives as green fluorescent materials

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General procedure for the synthesis of intermediate 1(a-e).

4-bromobenzohydrazide (5.0 g, 2.50 mmol) and different aryl/heteroaryl carboxylic acids (5.0 g, 2.5 mmol) were dissolved in $POCl_3$ (50 ml). The mixture was refluxed for 12 h at 100 ^oC. Completion of the reaction was monitored by TLC. After completion of the reaction, allowed the reaction mixture to reach room temperature, the quenching of reaction mixture in ice water bath was carefully carried out under efficient fume hood. The solid that separated was collected by filtration and then washed with saturated $NaHCO_3$ solution to remove excess of un-reacted carboxylic acid, the crude product was subjected to re-crystallization from ethanol, followed by column chromatography on silica gel using plane chloroform as an eluting solvent to obtain desired compound in 80-85% yield.

Synthesis of 2-(4-bromophenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (1a) [31]

White solid, yield: 88 %. MP = 146-147 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J*=8.4 Hz, 2H), 7.72 (d, *J*= 8.4 Hz, 2H), 7.59 (d, *J*=8.0 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.12, 150.17, 132.35, 130.01, 126.95, 125.70, 125.18, 123.22, 39.89, 31.25; LC-MS (ESI): *m/z* calculated for $C_{18}H_{17}BrN_2O$ [M+H] 358.24. Found 358.47; Anal. Calcd (%) for $C_{18}H_{17}BrN_2O$: C 60.52, H 4.84, N 7.84. Found: C 60.58, H 4.83, N 7.75.

Synthesis of 2-(4-bromophenyl)-5-(thiophen-2-yl)-1,3,4-oxadiazole (1b) [32]

^1H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J=8.8 Hz*, 2H), 7.88 (d, *J*=4 Hz, 1H), 7.72 (d, *J*=8.4 Hz, 2H), 7.62 (d, *J*=4.8, 1H), 7.24 (t, *J*=4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.31, 161.10, 132.22, 129.71, 127.95, 127.42, 125.44, 125.10, 123.15; LC-MS (ESI): *m/z* calculated for $C_{12}H_7BrN_2OS$ [M+H] 308.17. Found 308.31; Anal. Calcd (%) for $C_{12}H_7BrN_2OS$: C 46.92, H 2.30, N 9.12. Found: C 46.84, H 2.35, N 9.27.

Synthesis of 2-(4-bromophenyl)-5-(biphenyl)-1,3,4-oxadiazole (1c) [33]

White solid, yield: 82 %. Mp = 204-206 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.24(d, *J*=8.4 Hz, 2H), 8.07 (d, *J*=8.4 Hz, 2H), 7.791 (d, *J*=11.6 Hz, 2H), 7.716 (d, *J*=8.8, 2H), 7.683 (d, *J*=7.6, 2H), 7.450 (d, *J*=4, 2H), 7.508 (t, *J*=14.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.32, 136.44, 132.35, 130.01, 129.82, 128.61, 128.04, 127.91, 127.75, 125.28, 125.14,

123.21; LC-MS (ESI): *m/z* calculated for $C_{20}H_{13}BrN_2O$ [M+H] 378.23. Found 378.37; Anal. Calcd (%) for $C_{20}H_{13}BrN_2O$: C 63.68, H 3.47, N 7.43. Found: C 63.72, H 3.51, N 7.46.

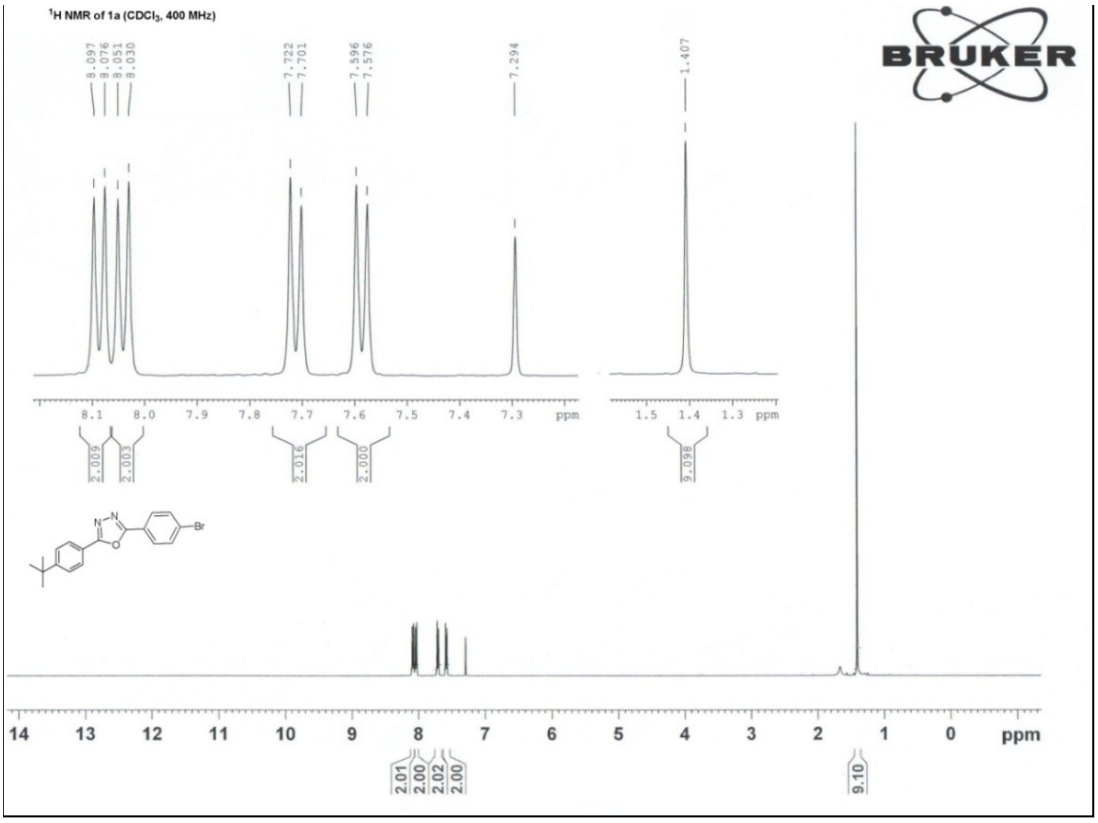
Synthesis of 2-(4-bromophenyl)-5-(perfluorophenyl)-1,3,4-oxadiazole (1d)

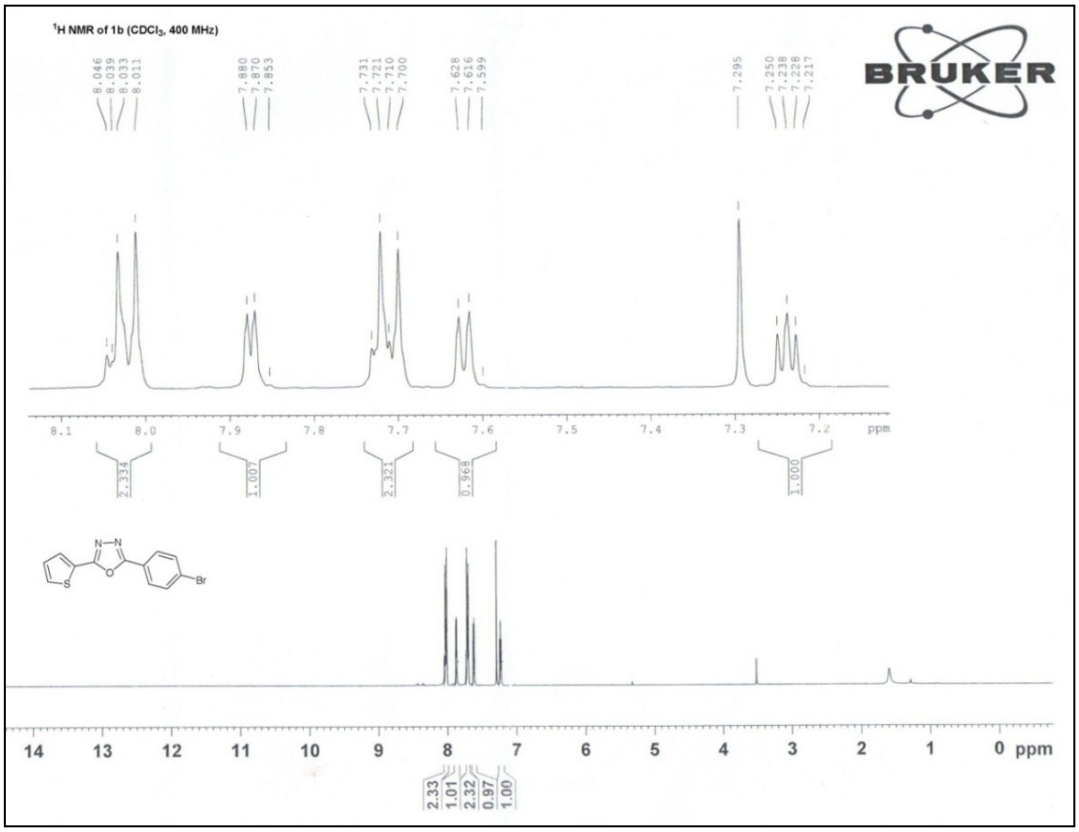
White solid, yield: 87 %. Mp = 203~204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.926 (d, *J*=8.8, 2H), 7.627 (d, *J*=8.4, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.58, 144.72, 143.44, 138.27, 132.56, 129.75, 125.22, 123.21, 120.51; ^{19}F NMR (400 MHz, $CDCl_3$) δ: -135.33, -147.23, -159.49; LC-MS (ESI): *m/z* calculated for $C_{14}H_4BrF_5N_2O$ [M+H] 392.09, found 392.18; Anal. Calcd (%) for $C_{14}H_4BrF_5N_2O$: C 43.00, H 1.03, N 7.17. Found: C 43.13, H 1.15, N 7.22.

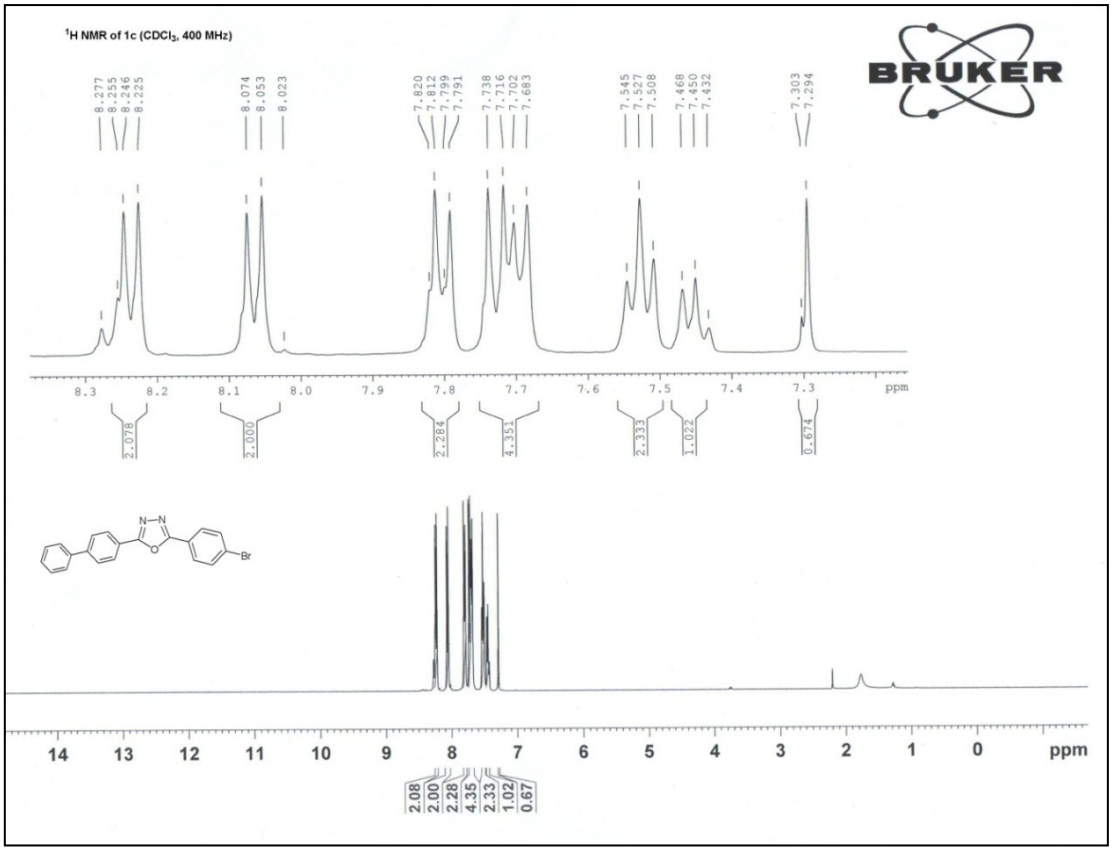
Synthesis of 2-(4-bromophenyl)-5-(naphthalen-2-yl)-1,3,4-oxadiazole (1e) [34]

White solid, yield: 85 %. Mp = 145-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.640(s, 1H), 8.212 (d, *J*=8.4 Hz, 1H), 8.073 (d, *J*=8.4 Hz, 2H), 8.002 (d, *J*=8.4, 1H), 7.923 (d, *J*=6.4, 2H), 7.719 (d, *J*=8.4, 2H), 7.615 (t, *J*=7.6, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.41, 134.33, 134.10, 133.91, 132.34, 129.72, 128.63, 128.14, 126.30, 125.82, 125.33, 124.60, 123.11; LC-MS (ESI): *m/z* calculated for $C_{18}H_{11}BrN_2O$ [M+H] 352.2 Found 352.25; Anal. Calcd (%) for $C_{18}H_{11}BrN_2O$: C 61.56, H 3.16, N 7.98. Found: C 61.61, H 3.14, N 7.87.

^{1}H NMR of compounds 1a-e.



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7.812
7.799
7.791
7.738
7.716
7.702
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7.527
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7.468
7.450
7.432
7.303
7.294
ppm
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2.000
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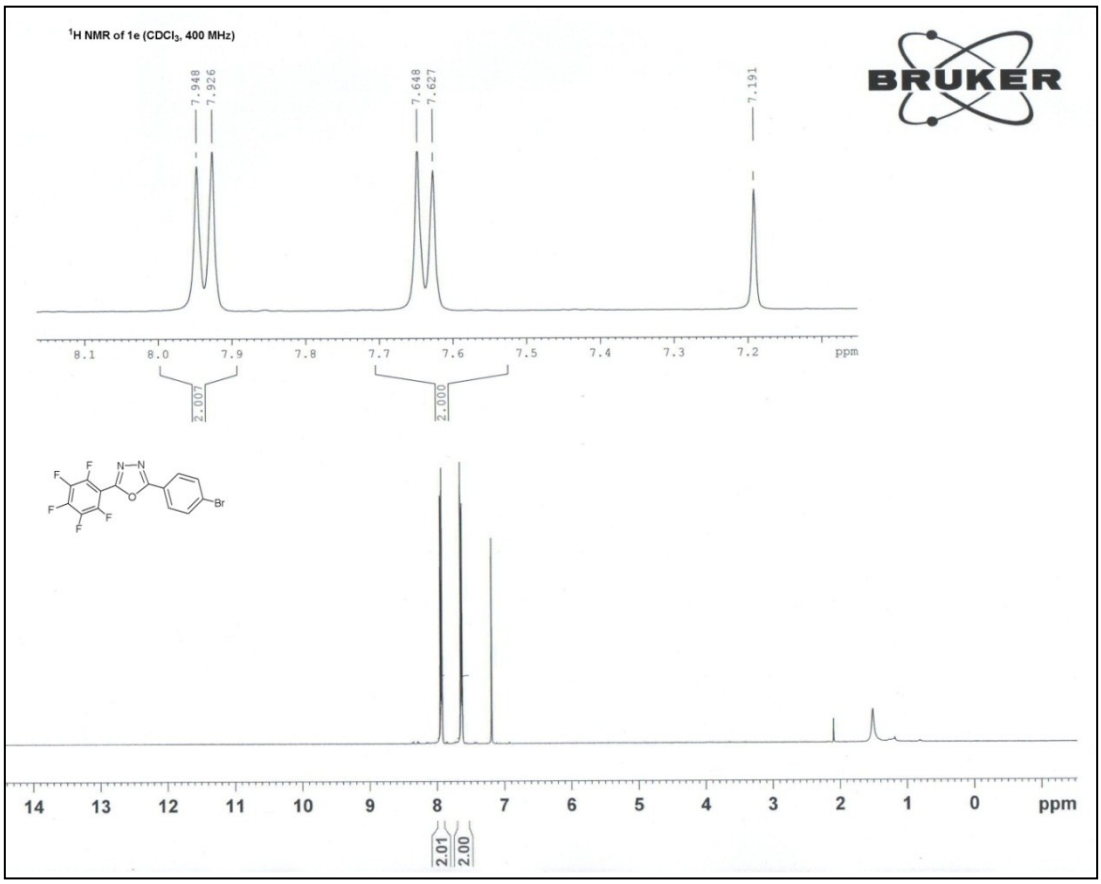
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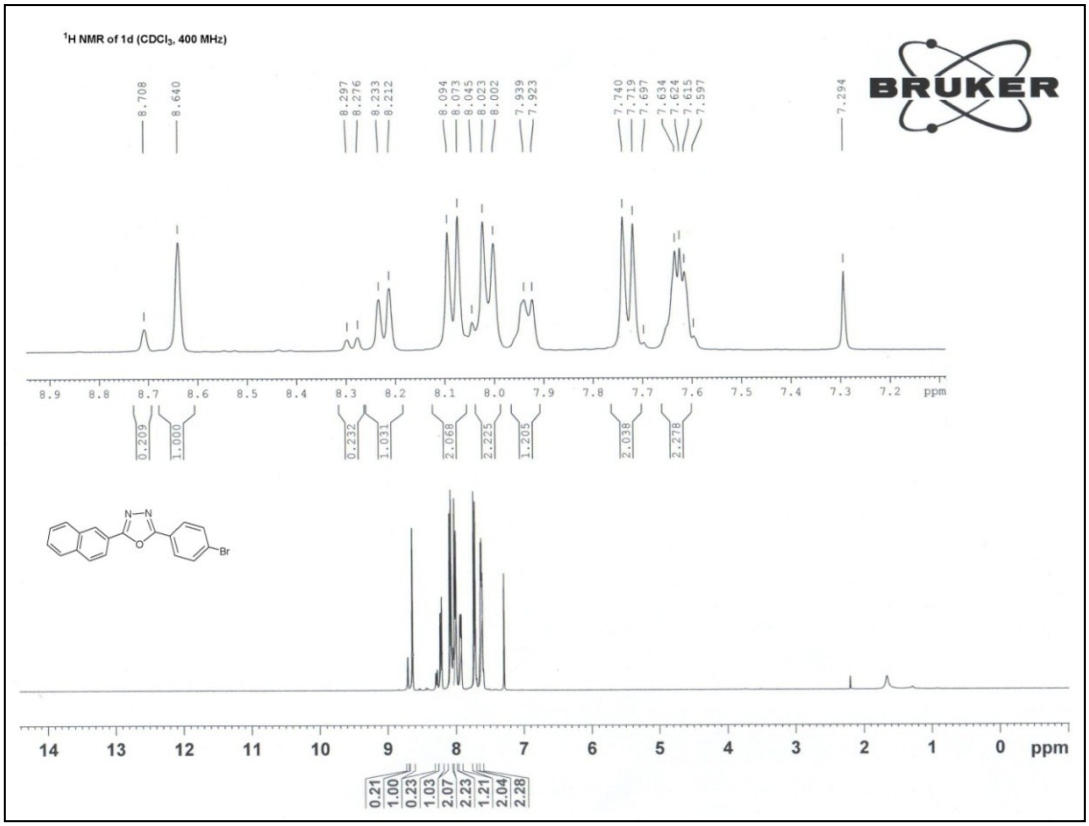
2.00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8.233
8.212
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8.073
8.045
8.023
8.002
7.939
7.923
7.740
7.719
7.697
7.634
7.624
7.615
7.597
7.294
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
0.209
1.000
0.232
1.031
2.066
2.225
1.205
2.038
2.278
N
N
O
Br
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.21
1.00
0.23
1.03
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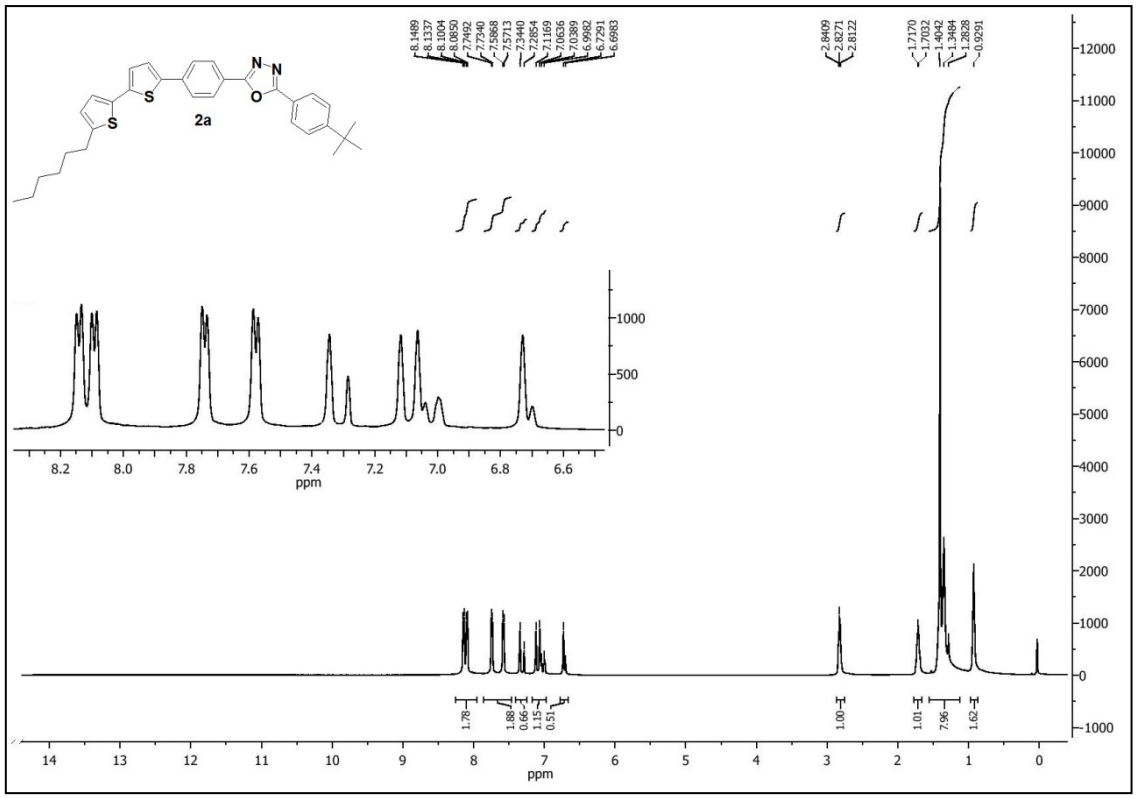
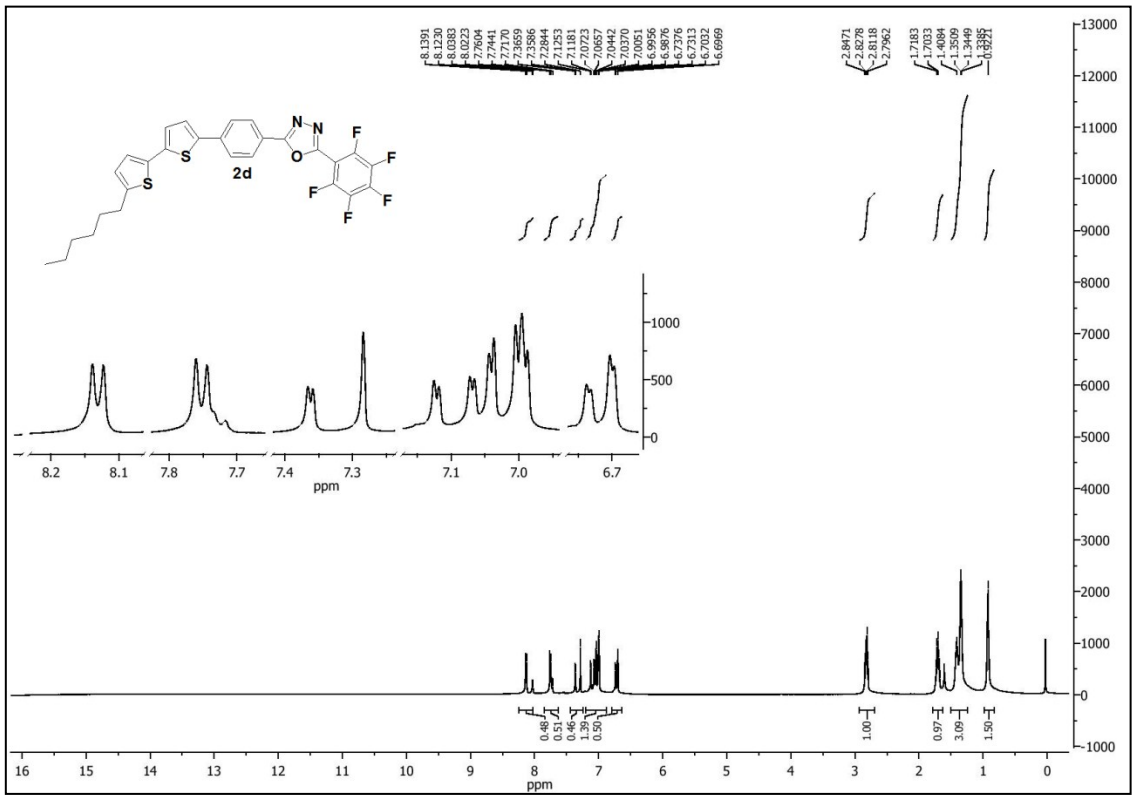
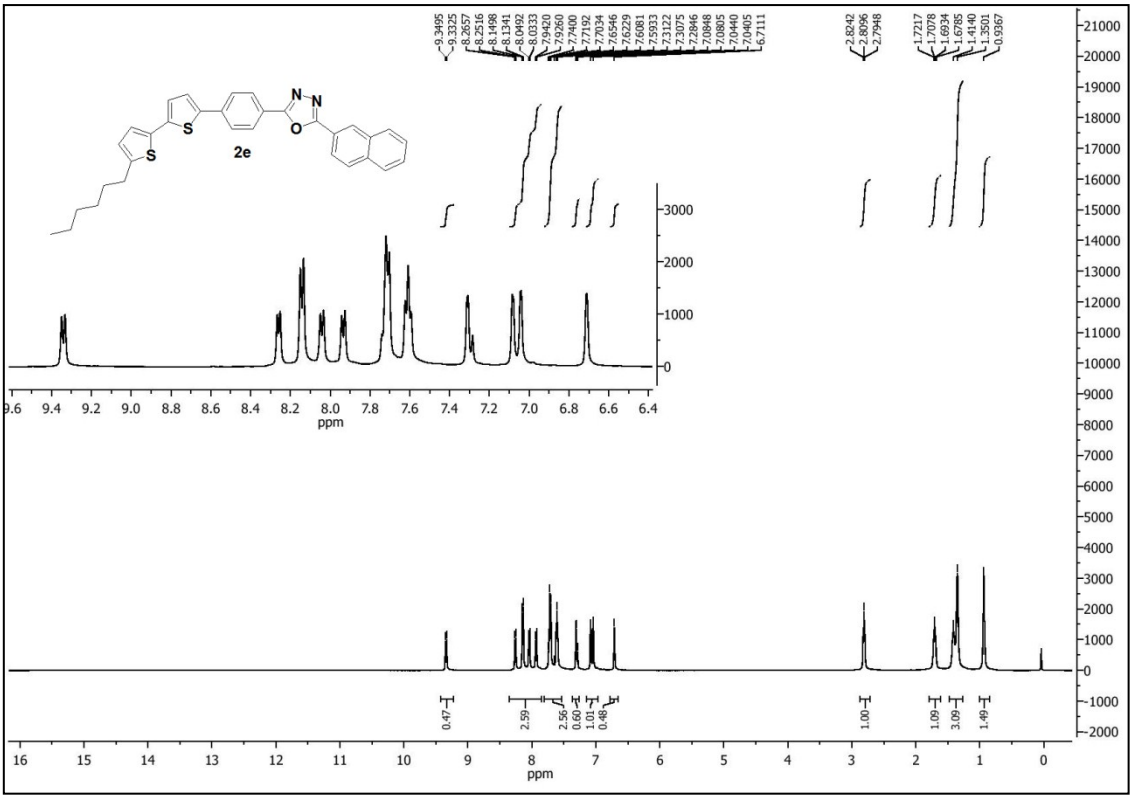
2.23
1.21
2.04
2.28

^{1}H NMR of compounds 2a, 2d & 2e.



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1.7078
1.6934
1.6785
1.4140
1.3501
0.9367
2e
S
S
N
N
O
ppm
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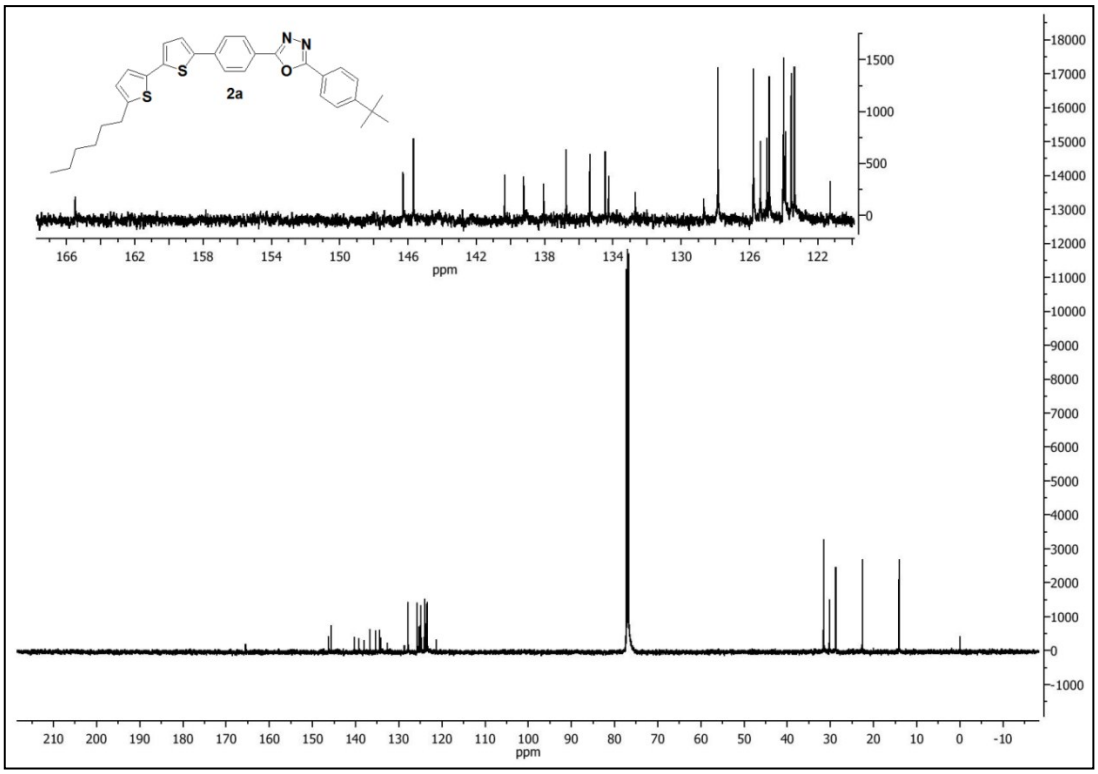
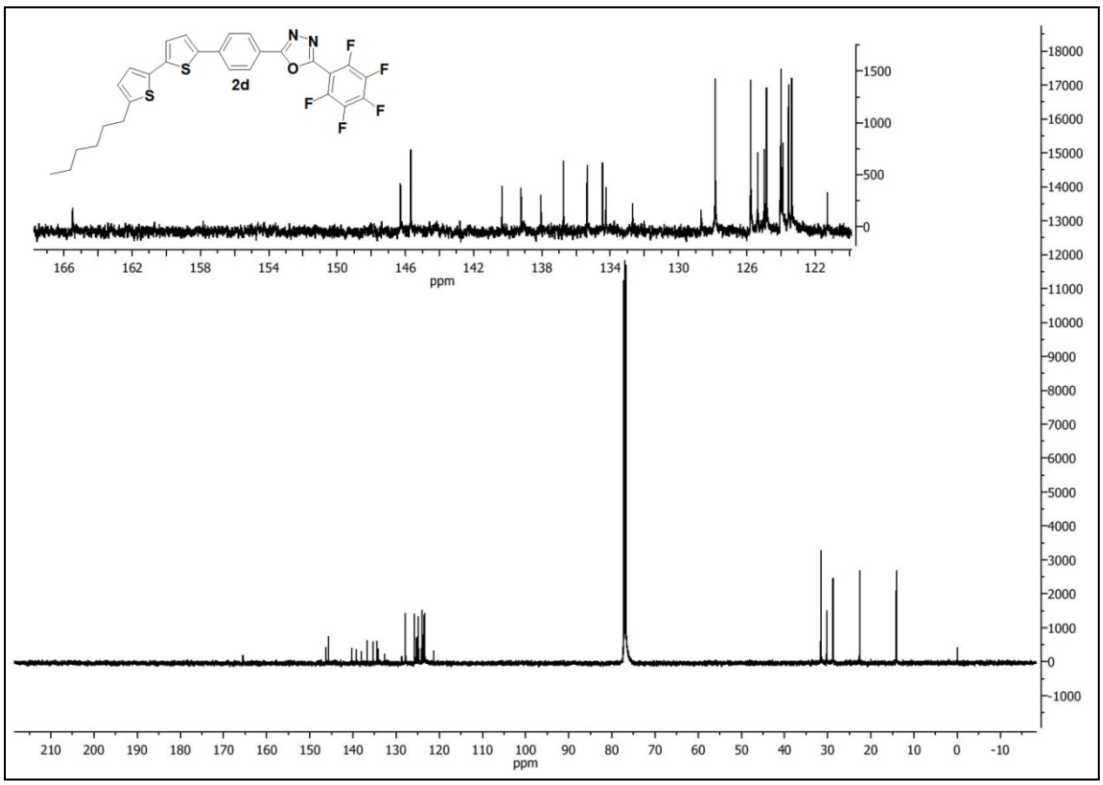
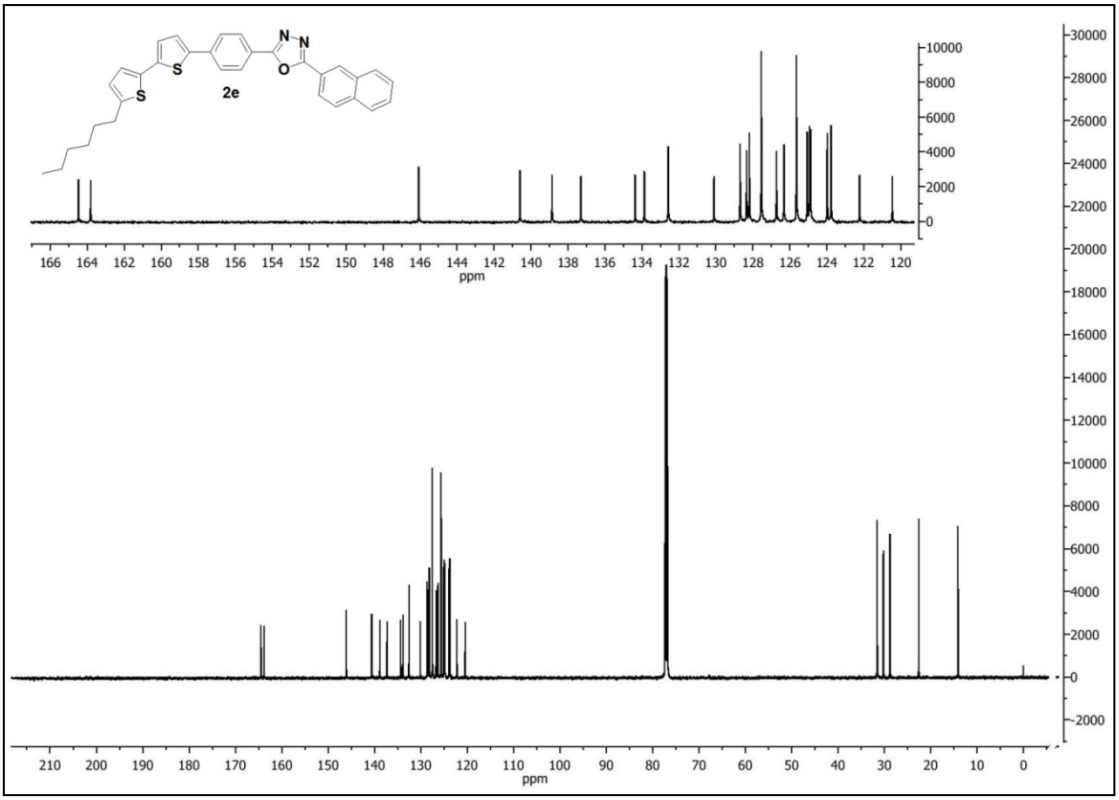
3.09
1.49
ppm

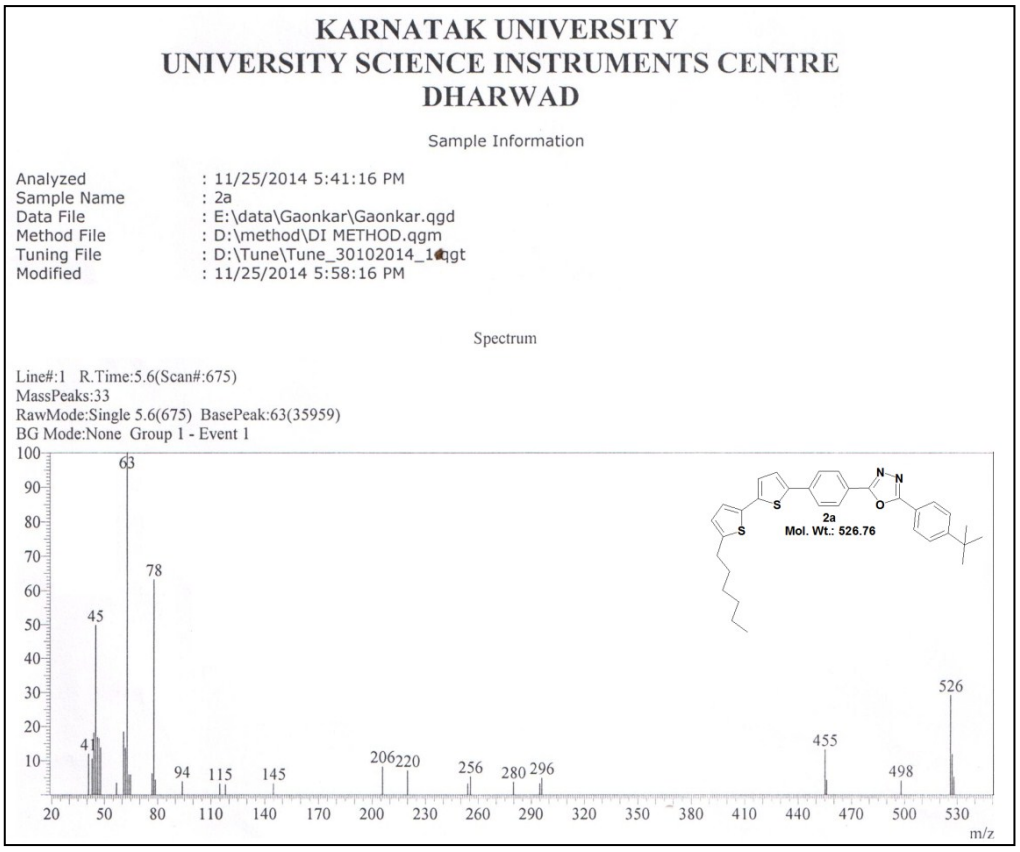
^{13}C NMR of compounds 2a, 2d & 2e.

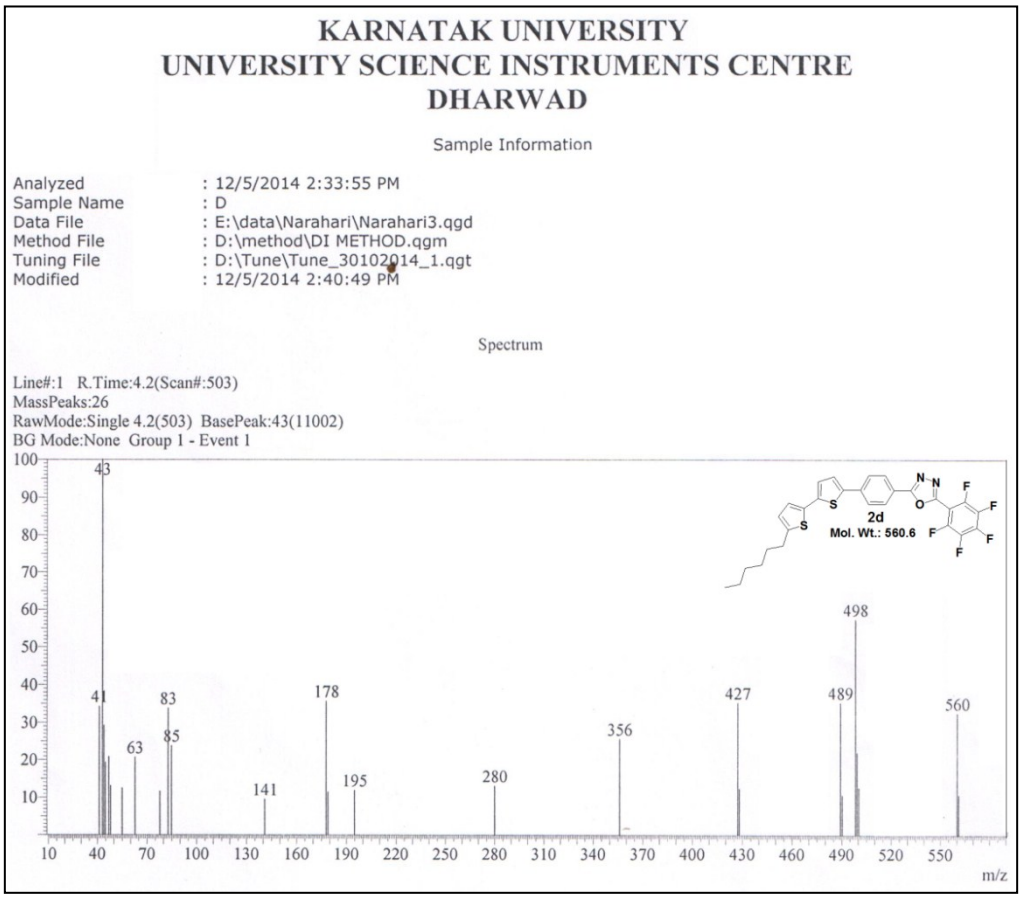





2e
S
S
N
N
O
ppm
ppm

Mass Spectrum of compounds 2a, 2d & 2e.





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