KI mediated one-pot cascade reaction for synthesis of 1,3,4-selenadiazoles

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Experimental section

I.General information

All the compounds were purchased from commercial suppliers and used without further purification. All the products were purified by column chromatography on silica gels (60−120 mesh, SRL, India). For TLC, Merck plates coated with silica gel 60, F_{254} were used. ^{1}H NMR,^{13}C NMR,^{19}F NMR were recorded using 400 MHz, 100 MHz, respectively on Bruker AV 400 NMR spectrometer using TMS as internal standard. Splitting patterns of protons were described as s (singlet), d (doublet), t (triplet) and m (multiplate).

General procedure for the synthesis of functionalized 2,5- diphenyl-1,3,4-selenadiazole

A mixture of benzaldehyde (2 mmol), hydrazine (1 mmol) and selenium powder (1 mmol), potassium persulphate (1mmol) were stirred at 140 ^{o}C for 5 h under DMSO solvent in open air in a round-bottom flask (50 mL) using a magnetic stirring bar. The reaction progress was monitored using TLC with a mixture of ethyl acetate and *n*-hexane as the eluent system. After completion of the reaction, the mixture was quenched to room temperature and ethyl acetate (5 ml) was added to the reaction mixture and the catalyst was separated by simple filtration and was extracted with ethyl acetate twice (2×20 ml). Combined extracts were washed with distilled water, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by passing through a column packed with silica gel (eluent: ethyl acetate–petroleum ether). The products obtained were known compounds and were identified by NMR spectroscopy.

III. **Spectroscopy data of functionalized 2,5- diphenyl-1,3,4-selenadiazole:**

Pale yellow solid; mp 212-214 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 8.15 (d, *J* = 8.52Hz, 1H), 8.31 (d, *J*= 8.72 Hz, 1H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 124.17, 131.15, 136.86, 150.46, 166.31

2,5-di(naphthalen-2-yl)-1,3,4-selenadiazole

White solid; mp 135-138 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.39-7.45 (m, 2H), 7.57-7.65 (m, 3H), 7.77-8.21 (m, 1H), 8.62 (s, 1H),

^{13}C NMR (100 MHz, DMSO) δ (ppm): 125.63, 127.25, 128.10, 128.61, `128.76, 129.73, 130.99, 132.60, 135.38, 167.93

2,5- diphenyl-1,3,4-selenadiazol

White solid; mp 116-118 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.30 (t, *J* = 7.16Hz, 2H), 7.50 (t, *J* = 7.56Hz, 1H), 8.13 (d, *J* = 7.92Hz, 2H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 129.03, 129.72, 131.23, 133.32, 167.79

2,5-bis(4-(trifluoromethyl)phenyl)-1,3,4-selenadiazole

White solid; mp 154-156 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.88 (d, *J* = 8.32Hz, 2H), 8.12 (t, *J* = 8.16Hz, 2H)

2,5-bis(3-fluorophenyl)-1,3,4-selenadiazole

White solid; mp 142-145 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.46-7.50 (m, 2H), 7.65 (t, *J* = 7.84Hz, 1H), 7.79 (d, *J* = 7.6Hz, 1H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 116.08, 116.30, 120.22, 120.43, 125.89, 131.22, 131.30, 133.65, 133.72, 161.20, 163.63, 166.65

2,5-bis(3-nitrophenyl)-1,3,4-selenadiazole

Yellow solid; mp 201-203 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.80 (t, *J* = 7.96Hz, 1H), 8.34 (d, *J* = 7.72Hz, 1H), 8.44-8.47 (m, 1H), 8.60 (t, *J* = 1.64Hz, 1H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 124.13, 127.79, 130.99, 132.90, 135.82, 148.32, 165.97

2,5-bis(4-fluorophenyl)-1,3,4-selenadiazole

White solid; mp 151-154 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.33 (q, *J* = 8.76Hz, 2H), 7.98-8.21 (m, 2H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 115.98, 116.20, 127.84, 132.52, 132.61, 164.12, 166.61, 166.83

2,5-di([1,1'-biphenyl]-4-yl)-1,3,4-selenadiazole

Brown solid; mp 145-147 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.36 (t, *J* = 7.28Hz, 1H), 7.42-7.73 (m, 2H), 8.02 (d, *J* = 8.28Hz, 1H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 127.20, 127.34, 128.72, 129.51, 129.95, 130.47, 139.38, 144.78, 167.77

2,5-di(thiophen-3-yl)-1,3,4-selenadiazole

Off white solid; mp 232-237 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.17 (t, *J* = 3.8Hz, 1H), 7.71 (t, *J* = 2.48Hz, 1H), 8.84 (d, *J* = 4.72Hz, 1H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 128.78, 133.68, 133.73, 163.52

2,5-bis(2-chlorophenyl)-1,3,4-selenadiazole

White solid; mp 128-131 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.40-7.44 (m, 1H), 7.51-7.53 (m, 1H), 7.75 (d, *J* = 6.84Hz, 1H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 127.72, 131.03, 131.15, 131.89, 133.06, 167.34

2,5-bis(2-bromophenyl)-1,3,4-selenadiazole

Light brown solid; mp 125-127 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.41-7.49 (m, 1H), 7.70-7.55 (m, 1H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 120.38, 128.18, 131.03, 132.99, 134.21, 167.85

2,5-di-p-tolyl-1,3,4-selenadiazole

Off white solid; mp 143-146 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 7.27 (d, *J* = 7.92Hz, 2H), 7.83 (t, *J* = 8.08Hz, 2H)

^{13}C NMR (100 MHz, DMSO) δ (ppm): 128.45, 129.54, 129.78, 143.47, 167.81

2,2'-(1,3,4-selenadiazole-2,5-diyl)diphenol

White solid; mp 162-165 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 6.97 (t, *J* = 7.6Hz, 1H), 7.05 (d, *J* = 8.4Hz, 1H), 7.37 (t, *J* = 7.6Hz, 1H), 7.97 (t, *J* = 7.4Hz, 1H)

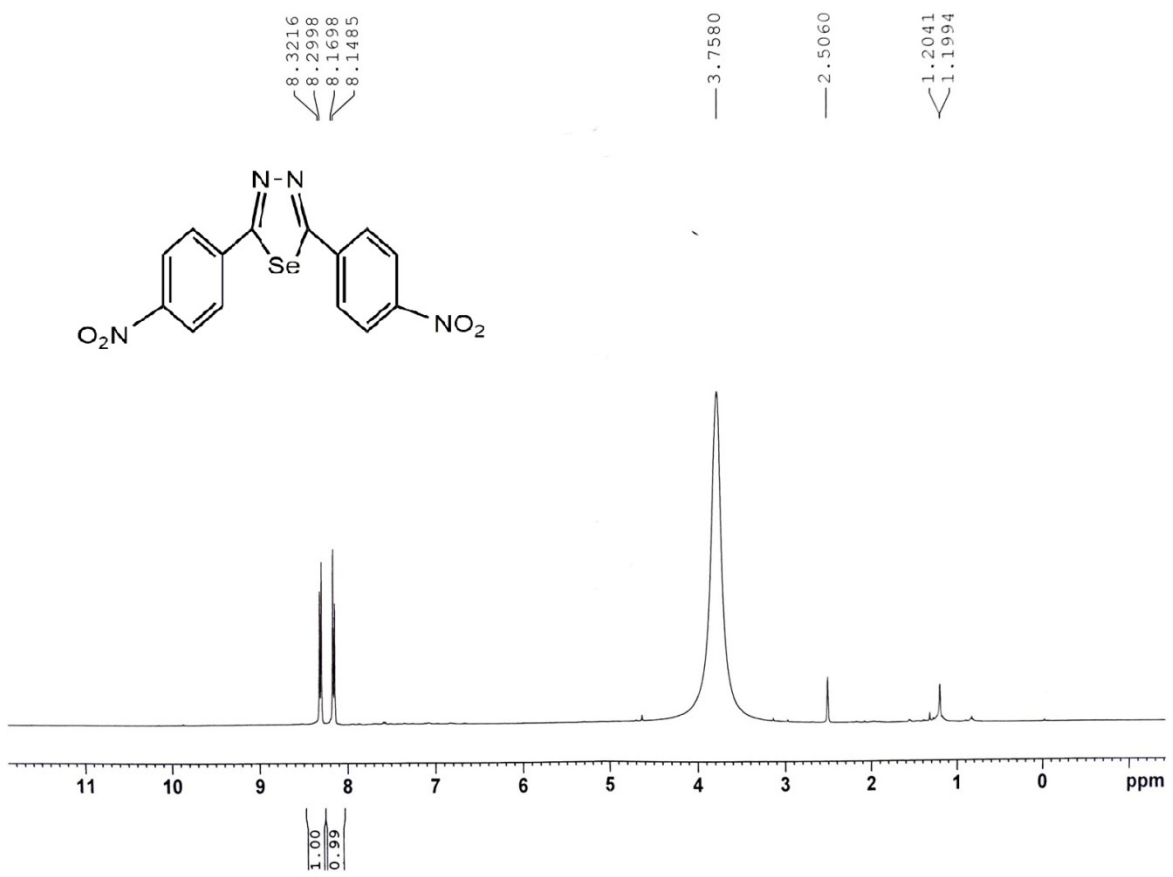
^{13}C NMR (100 MHz, DMSO) δ (ppm): 111.07, 116.90, 119.95, 120.25, 129.57, 133.15, 155.85

4,4'-(1,3,4-selenadiazole-2,5-diyl)bis(2-methoxyphenol)

Off white solid; mp 187-189 ^{o}C

^{1}H NMR (400 MHz, DMSO) δ(ppm): 6.89-6.95 (m, 2H), 7.08 (d, *J* = 1.6Hz, 1H)

II.Scanned copies of ^{1}H, ^{13}C, NMR spectra of the functionalized diethyl 2,5- diphenyl-1,3,4-selenadiazole: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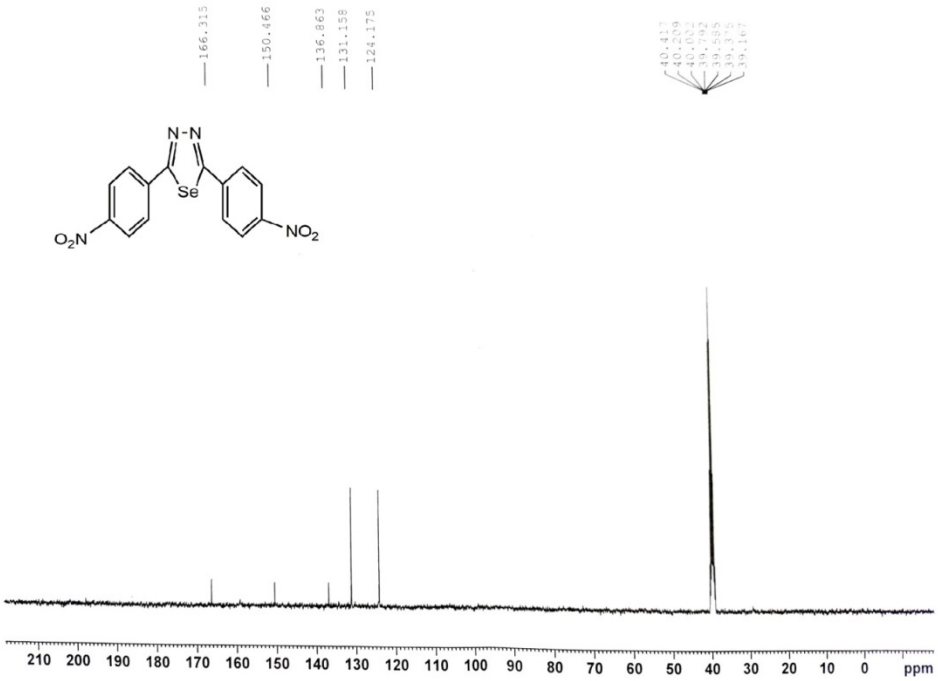
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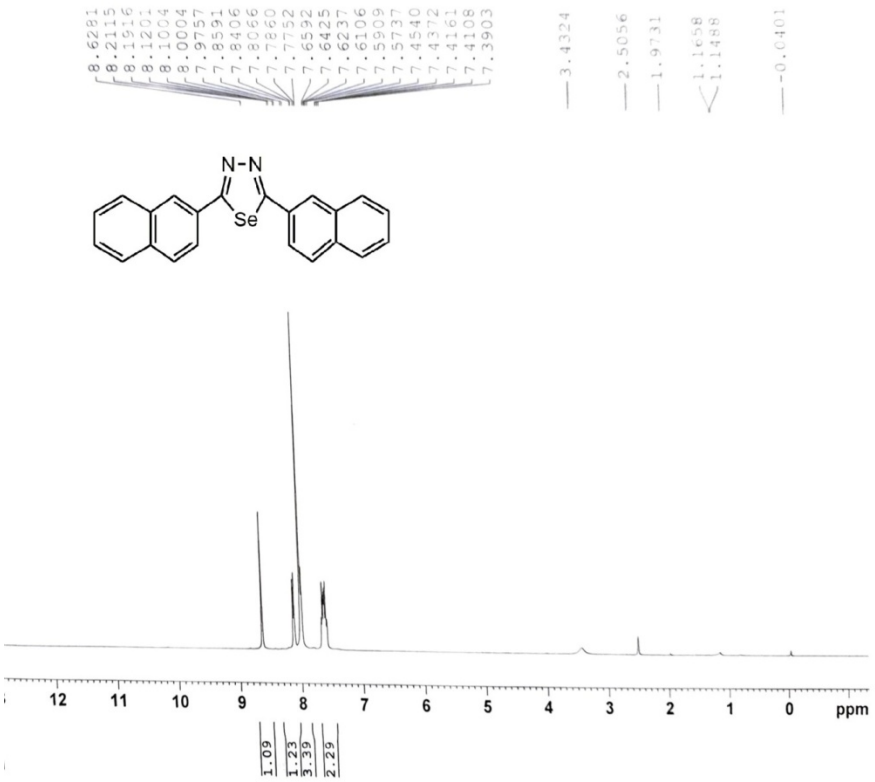
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7.4540
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7.4161
7.4108
7.3903
3.4324
2.5056
1.9731
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Se
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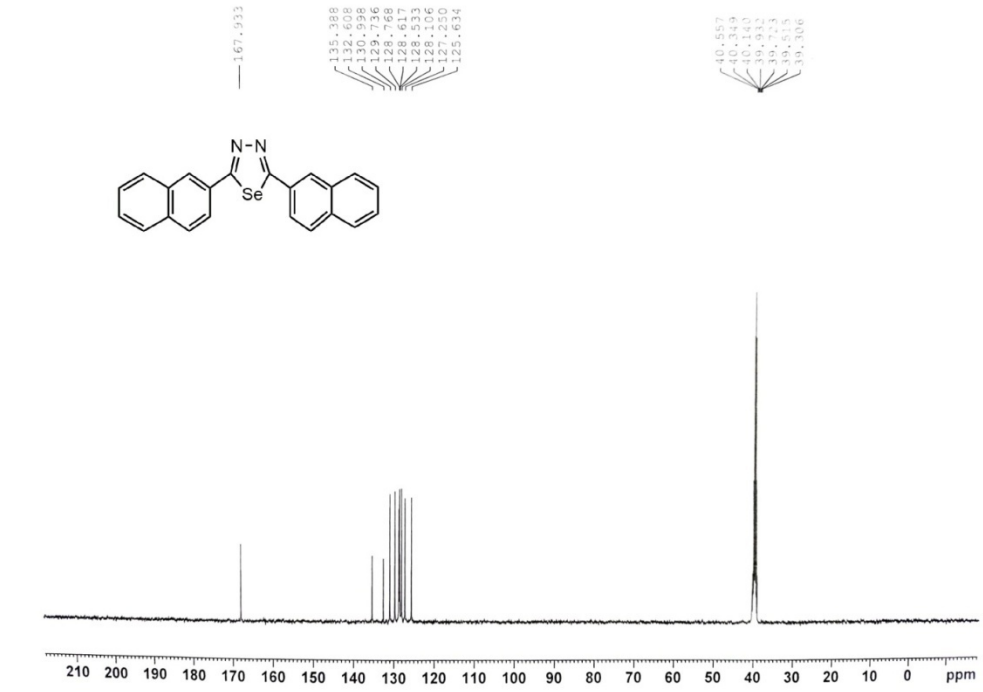
1.23
3.39
2.29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40.140
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Se
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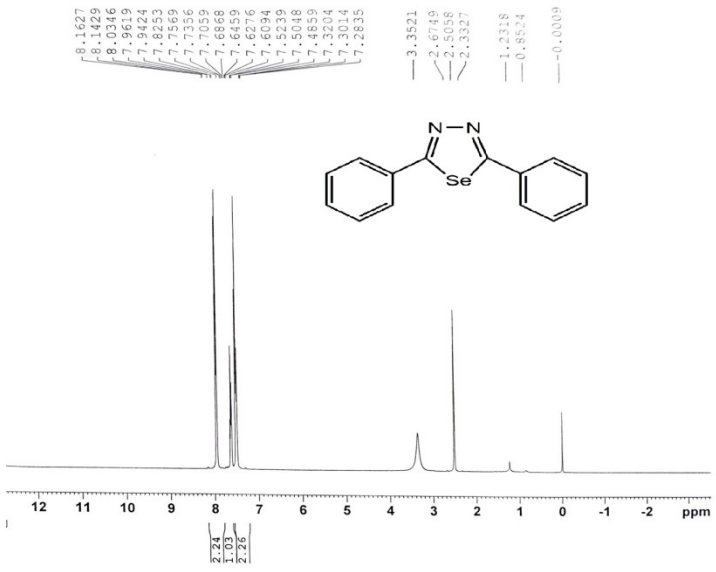
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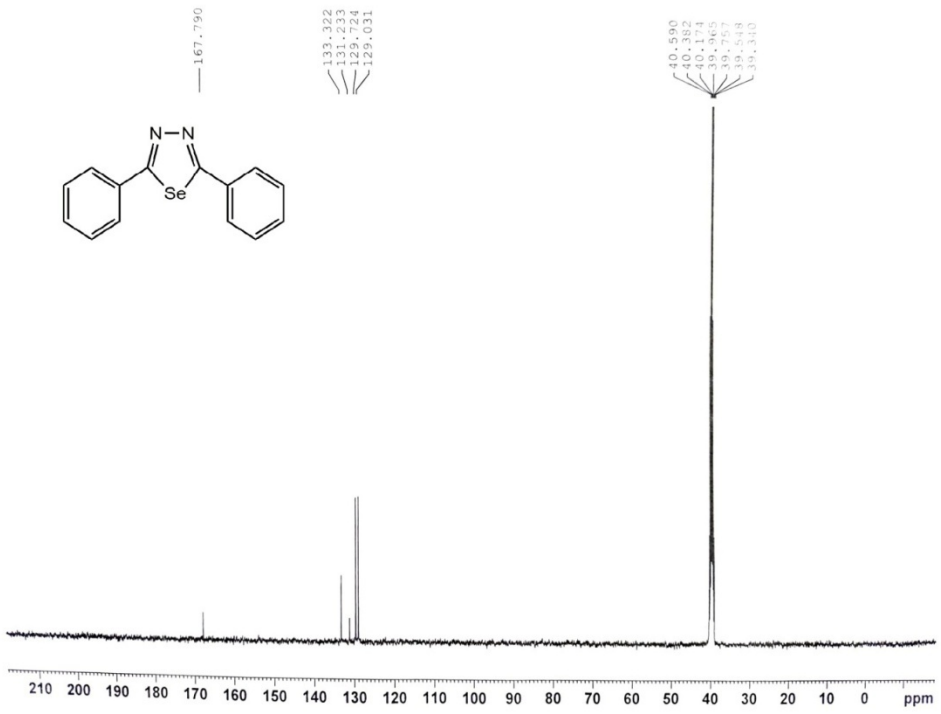
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Se
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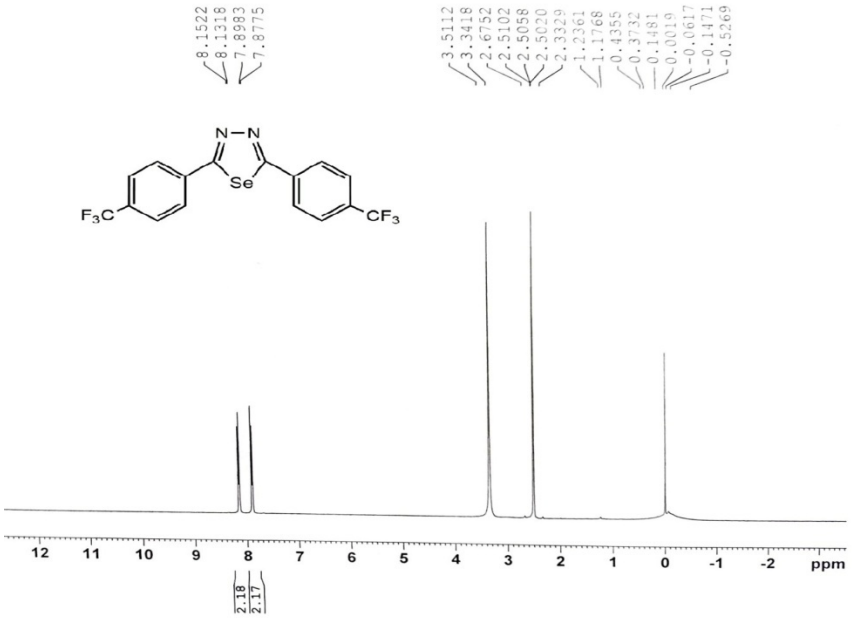
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1.2361
1.1768
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0.3732
0.1481
0.0019
-0.0617
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N
N
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CF3
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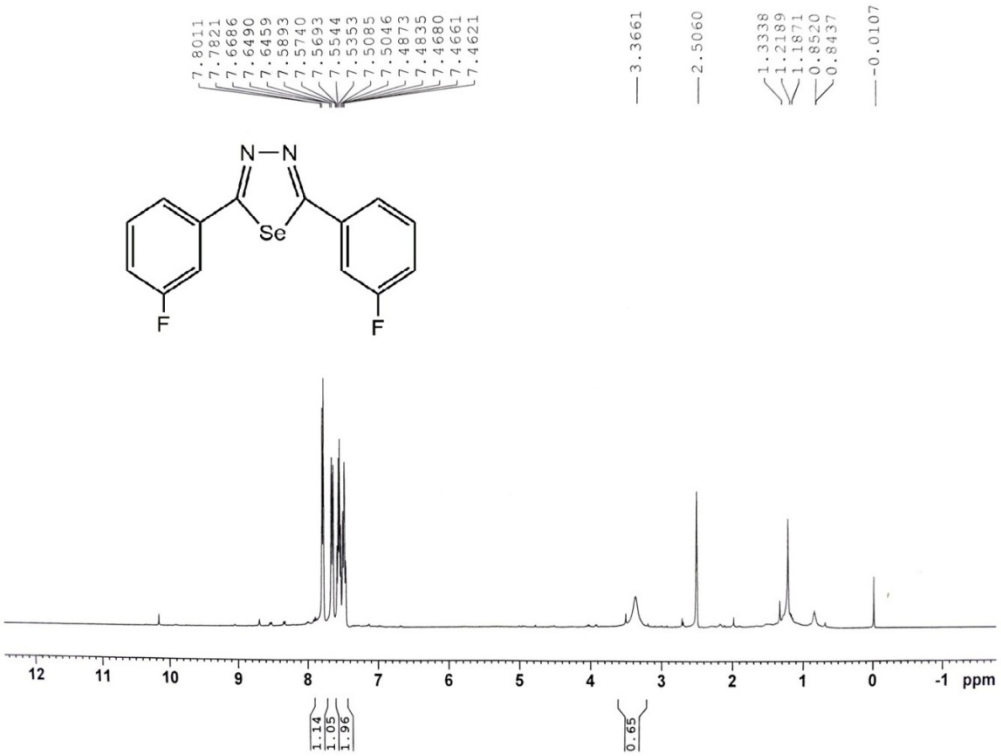
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7.4621
3.3661
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N
Se
F
F
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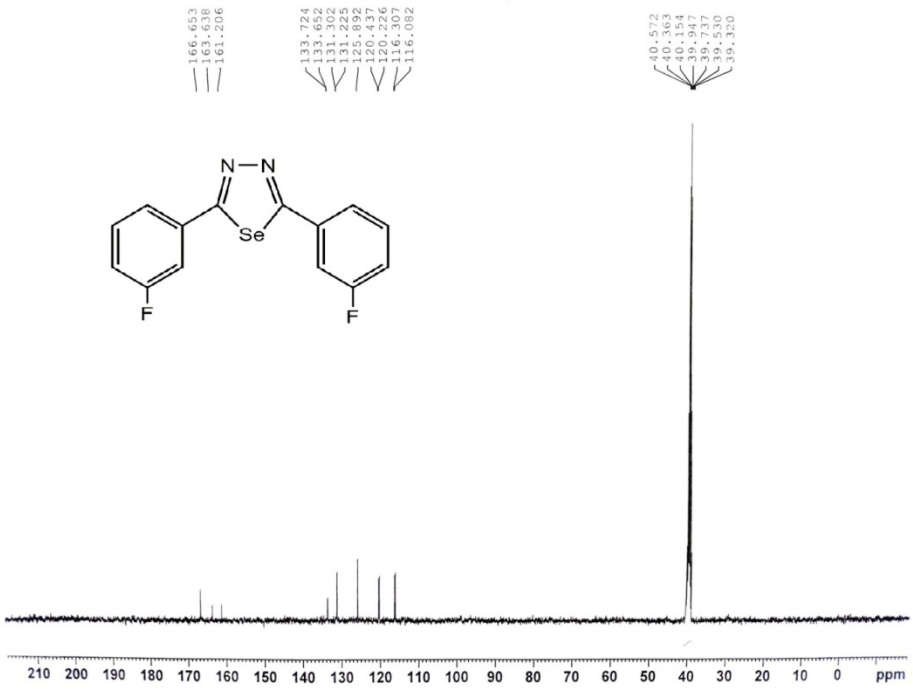
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Se
F
F
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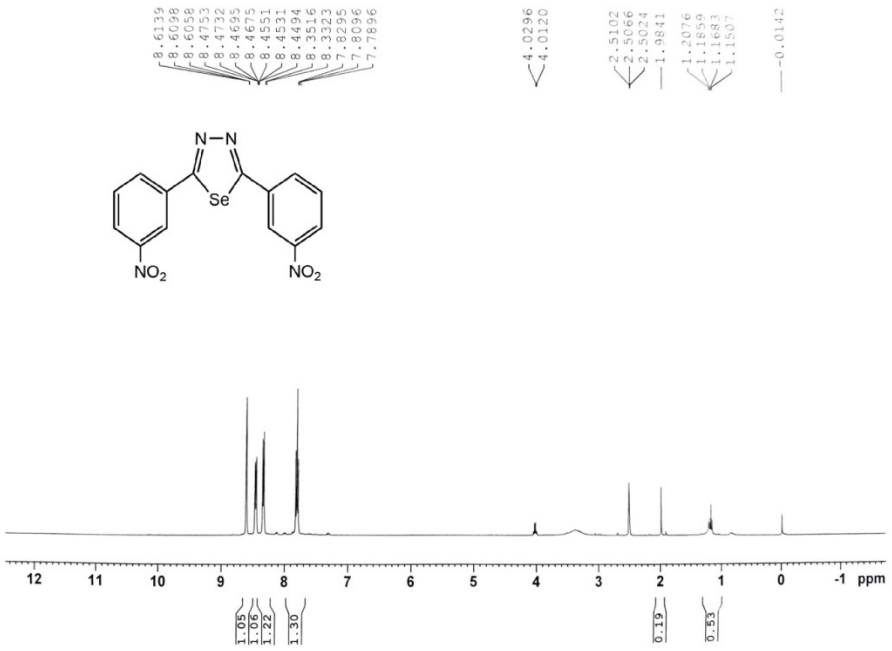
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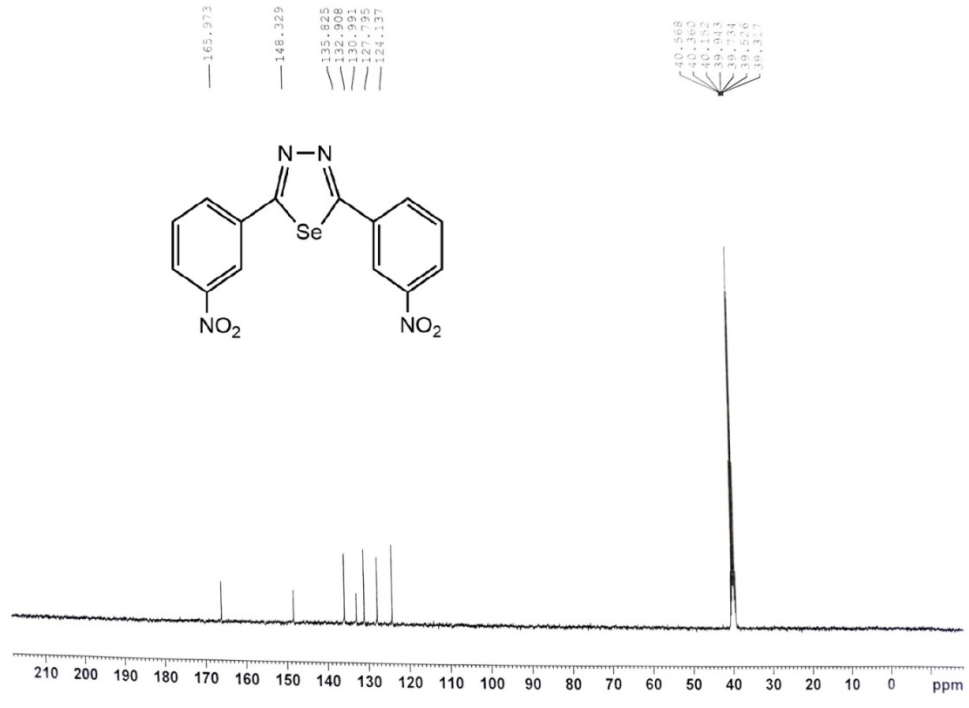
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NO2
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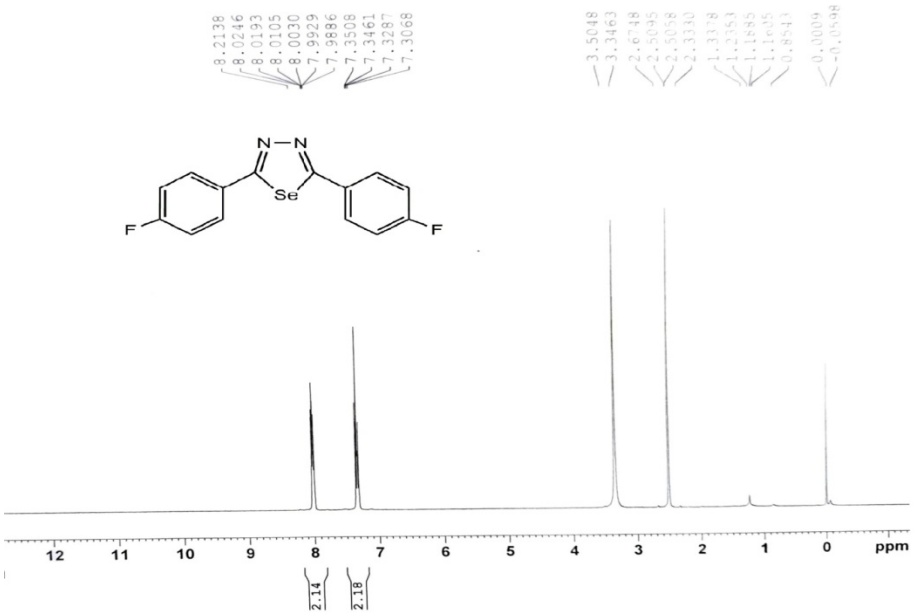
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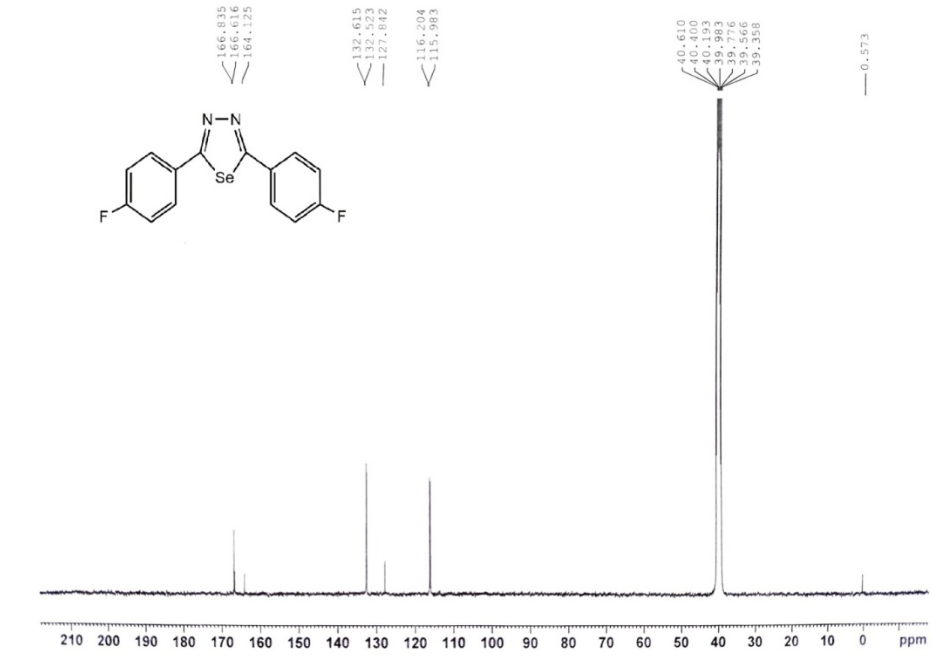
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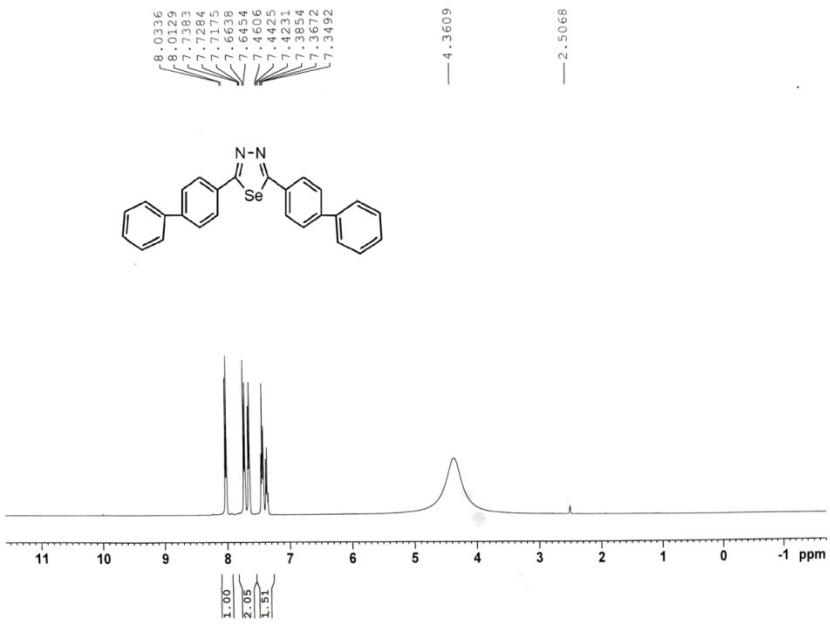
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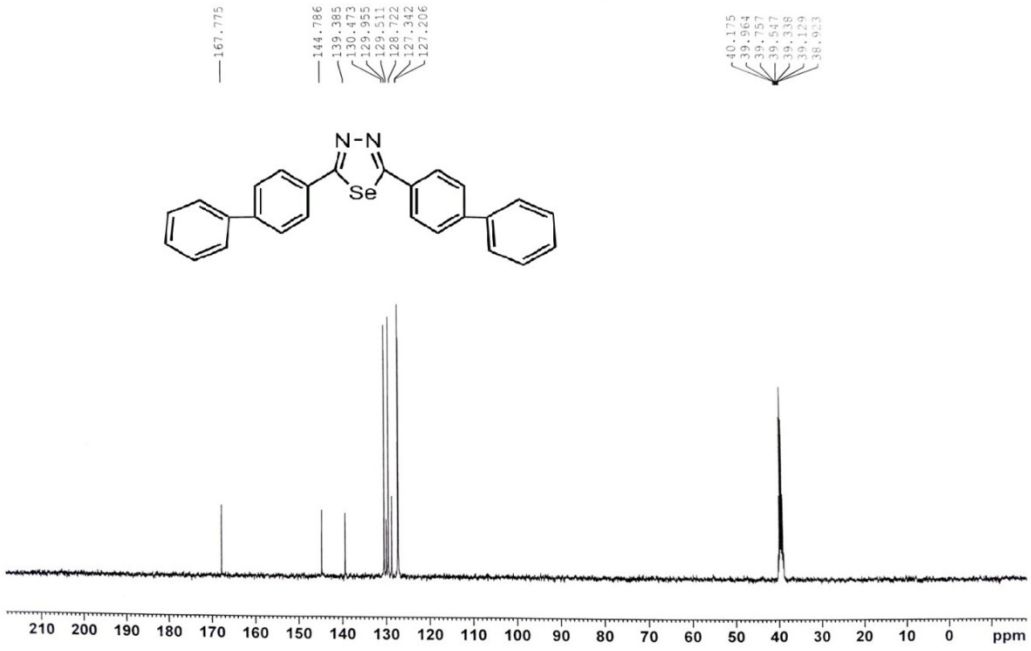
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Se
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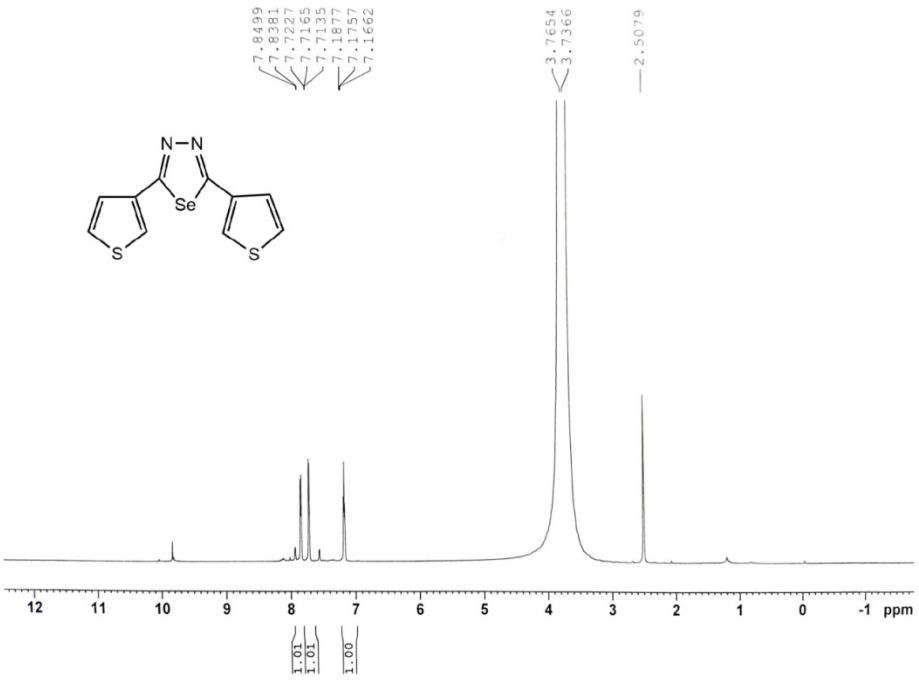
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S
S
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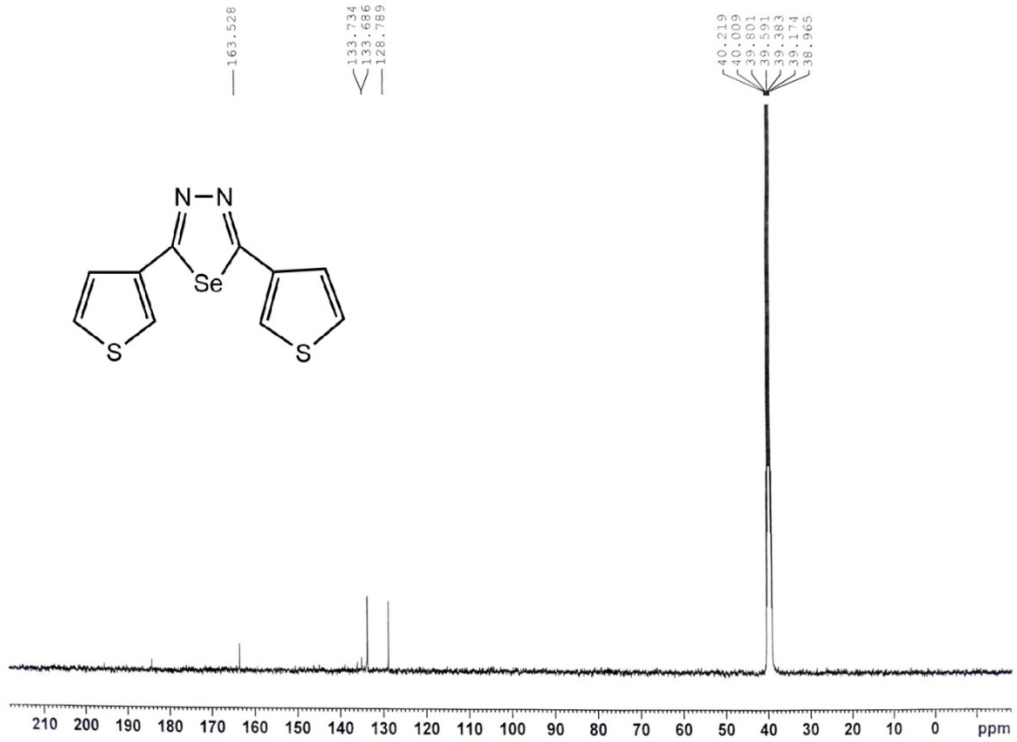
1.00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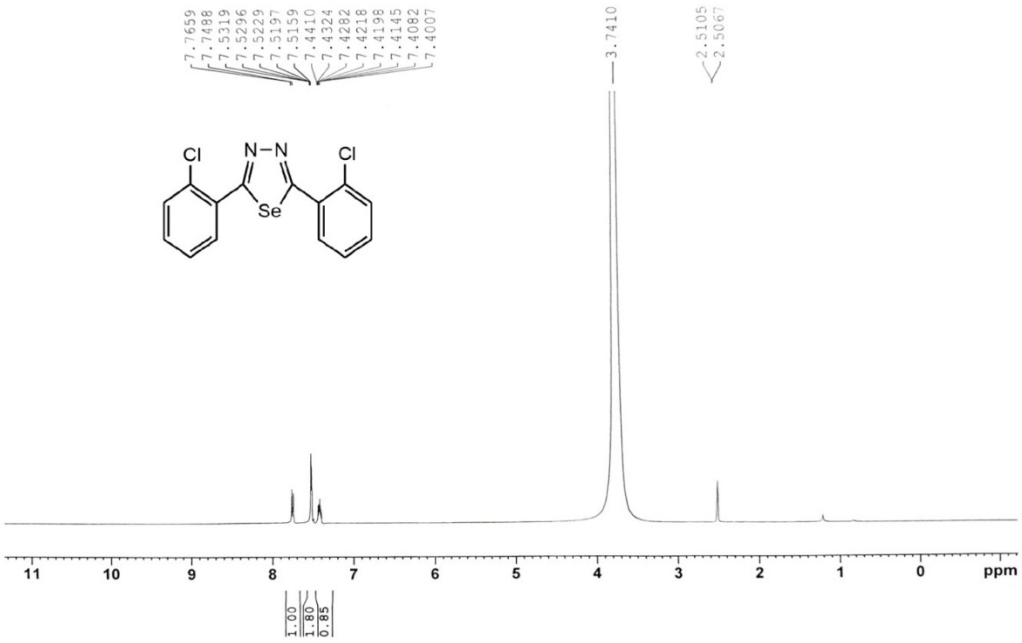
N–N
Se
S
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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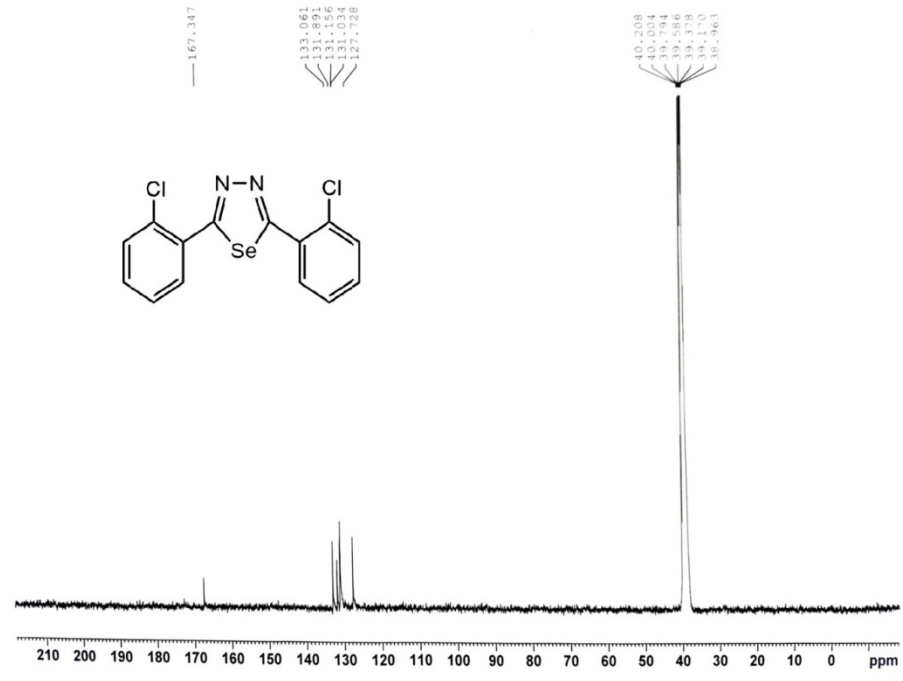
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Se
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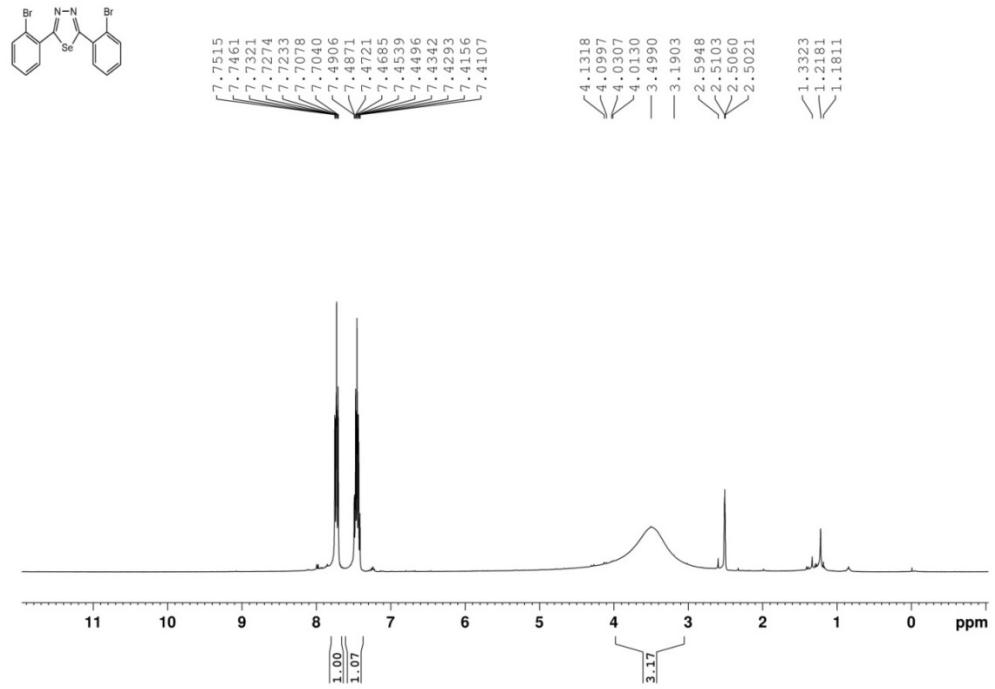
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2.5103
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2.5021
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1.2181
1.1811
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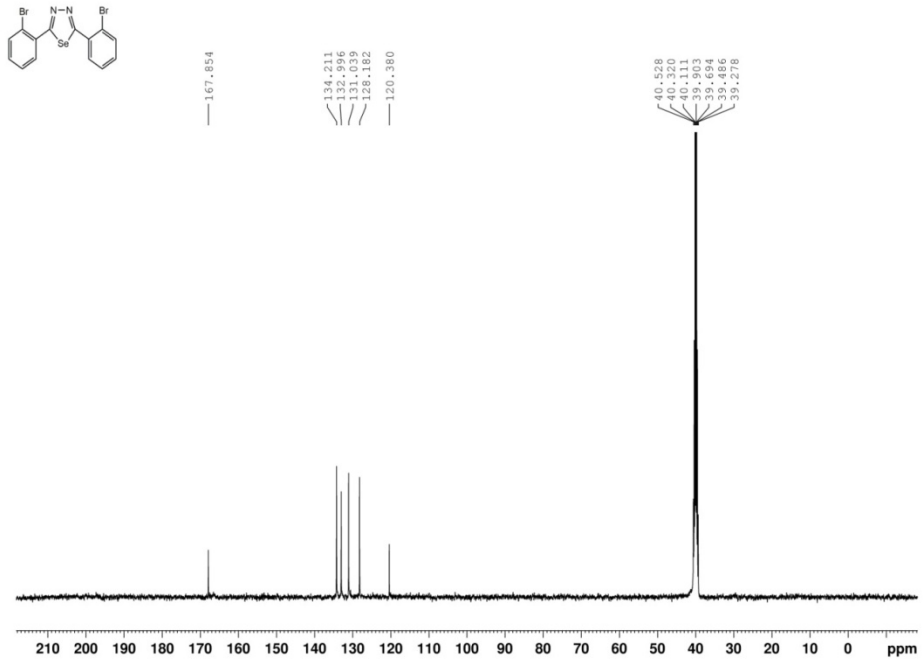
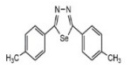
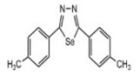
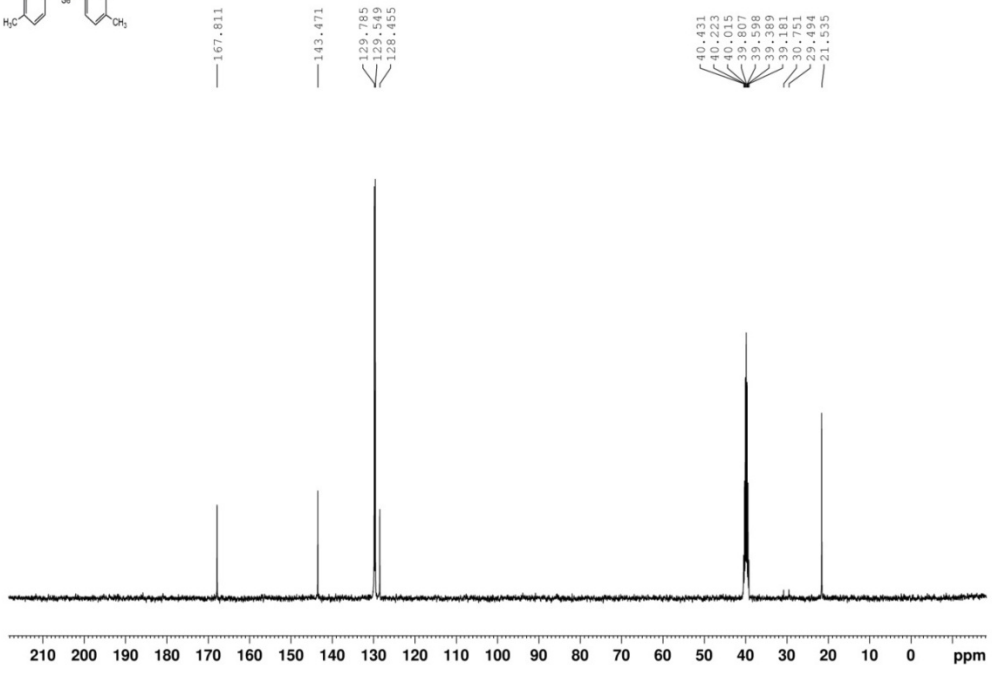
1.00
1.07
3.17

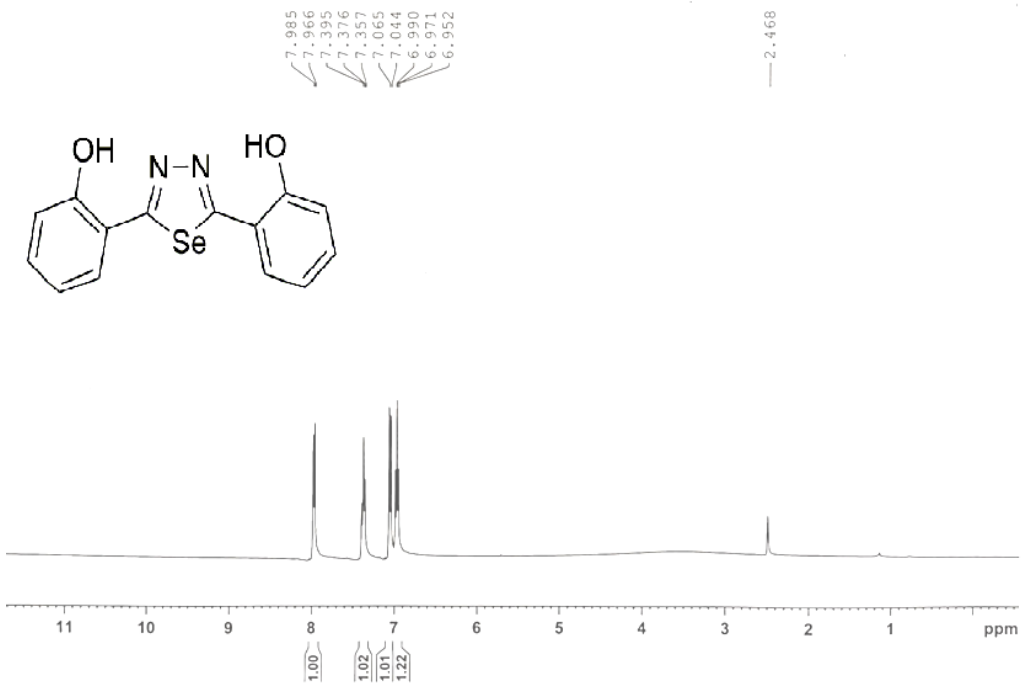

Br
N–N
Br
Se
167.854
134.211
132.996
131.039
128.182
120.380
40.528
40.320
40.111
39.903
39.694
39.486
39.278
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

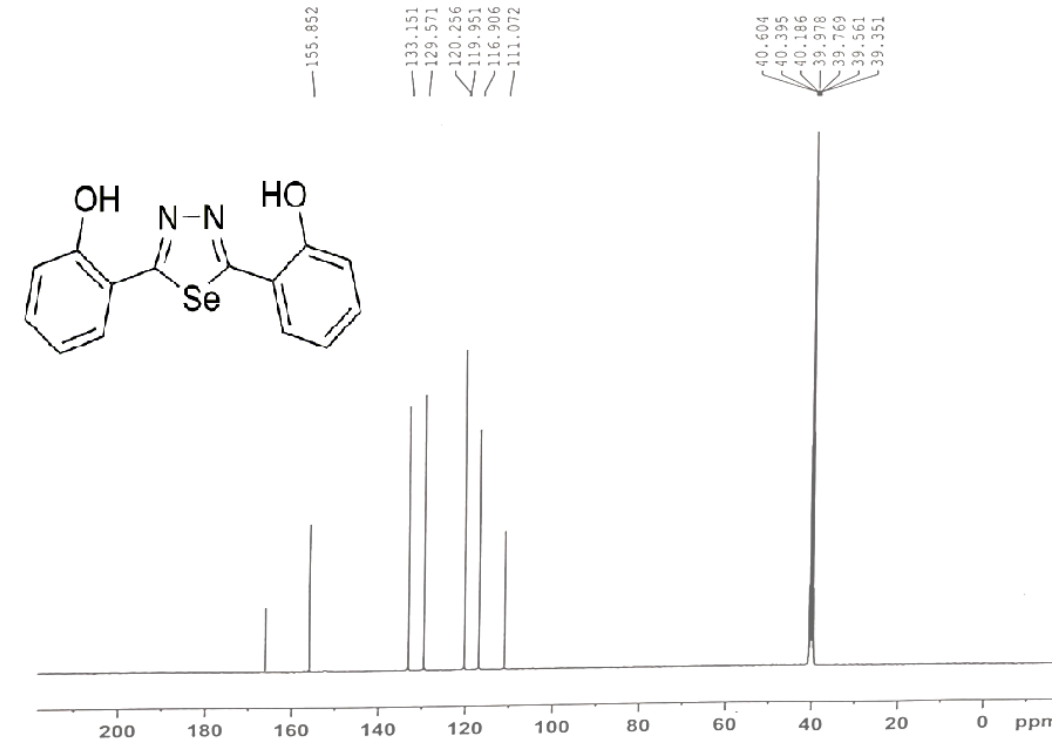


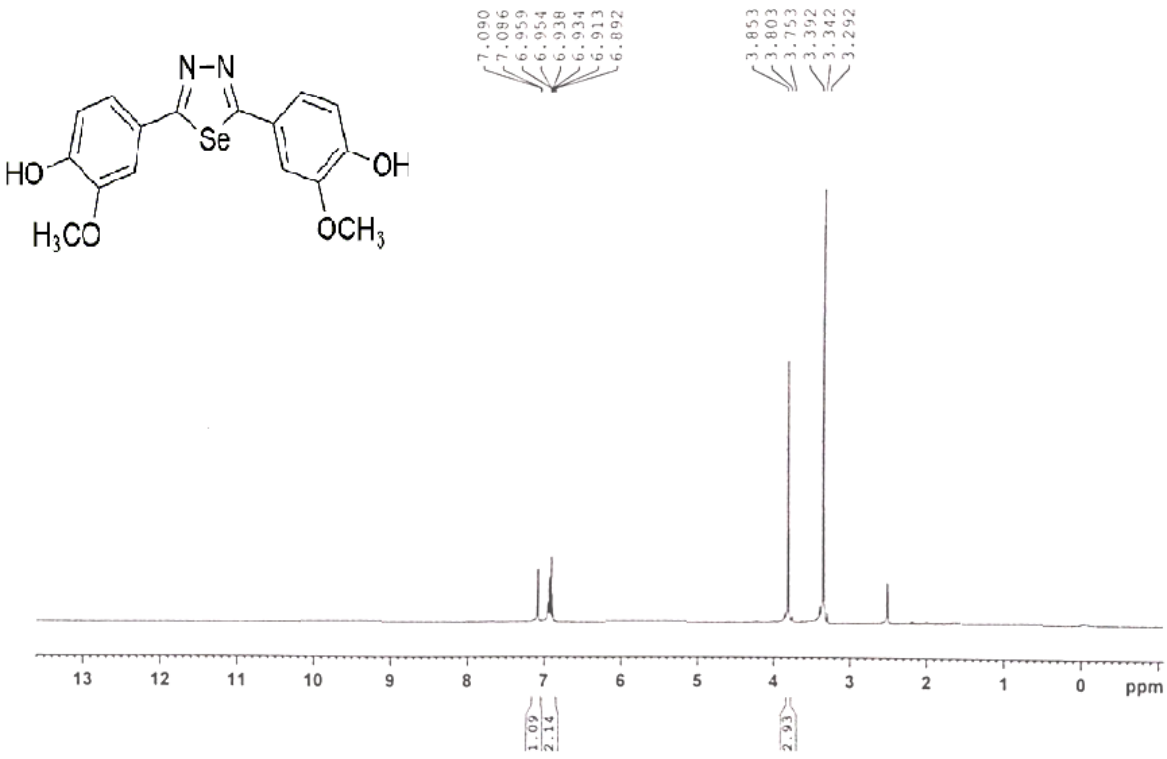
7.8506
7.8304
7.8196
7.2842
7.2644
2.3417
2.3305
1.1760
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
0.42
2.00
2.08
1.82
3.09




167.811
143.471
129.785
129.549
128.455
40.431
40.223
40.015
39.807
39.598
39.389
39.181
30.751
29.494
21.535
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.985
7.966
7.395
7.376
7.357
7.065
7.044
6.990
6.971
6.952
2.468
OH
N–N
HO
Se
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.01
1.22


155.852
133.151
129.571
120.256
119.951
116.906
111.072
40.604
40.395
40.186
39.978
39.769
39.561
39.351
OH
N–N
HO
Se
200
180
160
140
120
100
80
60
40
20
0
ppm


N–N
Se
HO
OH
H3CO
OCH3
7.090
7.086
6.959
6.954
6.938
6.934
6.913
6.892
3.853
3.803
3.753
3.352
3.342
3.292
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.09
2.14
2.93