Electronic supplementary information

Cu(II) anchored nitrogen-rich covalent imine network (Cu^{II}-CIN-1): An efficient and recyclable heterogeneous catalyst for the synthesis of organoselenides from aryl boronic acids in a green solvent

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IR Spectroscopy:

Fourier transform infrared (FTIR) spectra for the Cu^{II}-CIN catalyst and CIN were recorded on a Perkine Elmer, USA, FTIR 783 spectrophotometer using KBr pellets.

In the IR data for CIN material **(Figure. S1-a),** the presence imine functionality (C=N) is indicated by the absorption band at 1632 cm^{-1}and 1193 cm^{-1}due to C=N straching. For Cu^{II}-CIN catalyst **(Figure. S1-b)** C=N starching frequency is shifted to the lower frequency at 1630 cm^{-1} and 1190 cm^{-1} due to the coordination of copper through the lone pair of electron of nitrogen of Schiff-base in CIN ligand. In Cu^{II}-CIN catalyst, bands observed at 1478 and 1550 cm^{-1} indicate presence of the quadrant and semicircle stretching of the triazine ring in the spectra of the material.

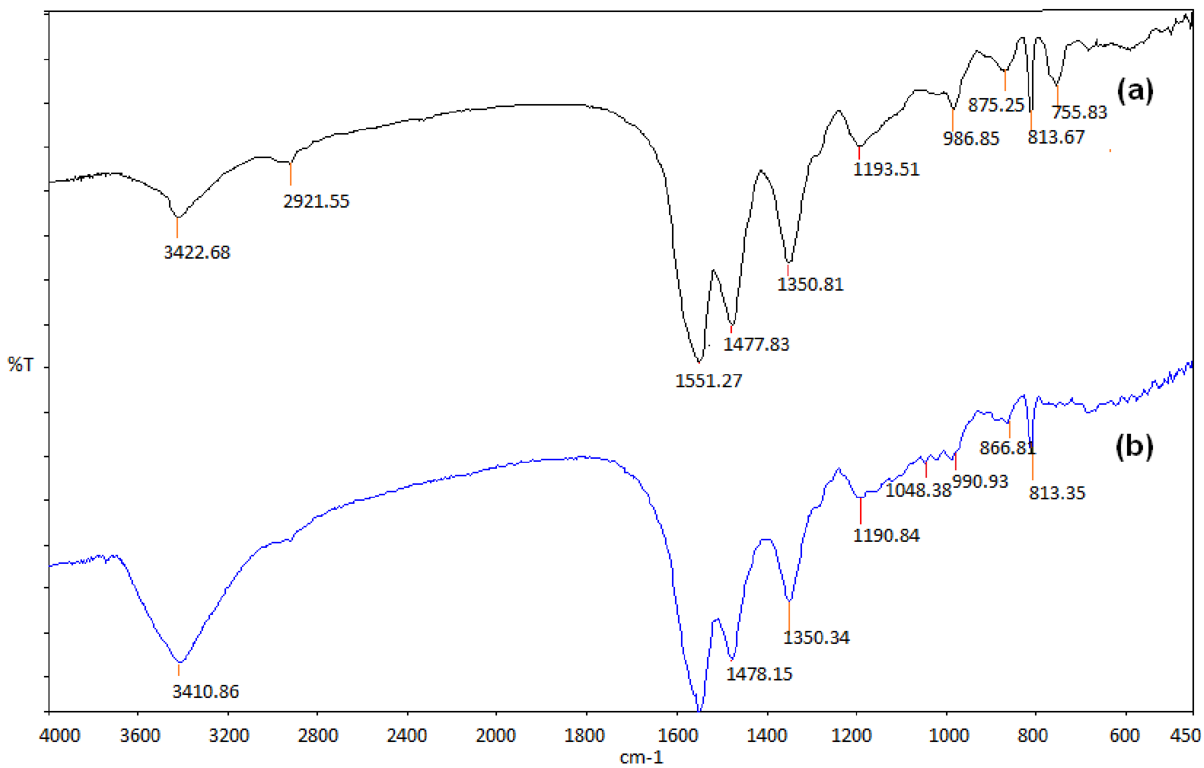
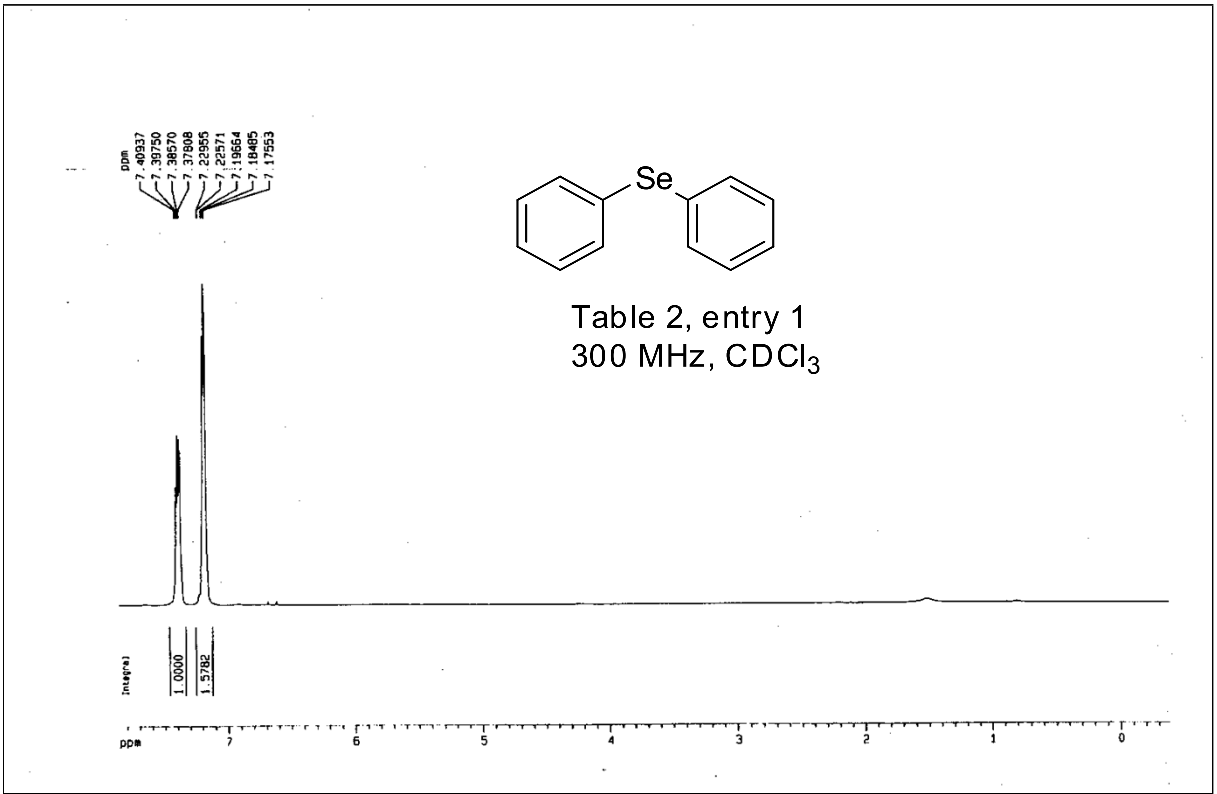


Fig. S1: FT IR spectra of (a) CIN-1 and (b) CIN-1 supported Cu (II) catalyst (Cu^{II}-CIN-1).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7.37808
7.22955
7.22571
7.19664
7.18485
7.17553
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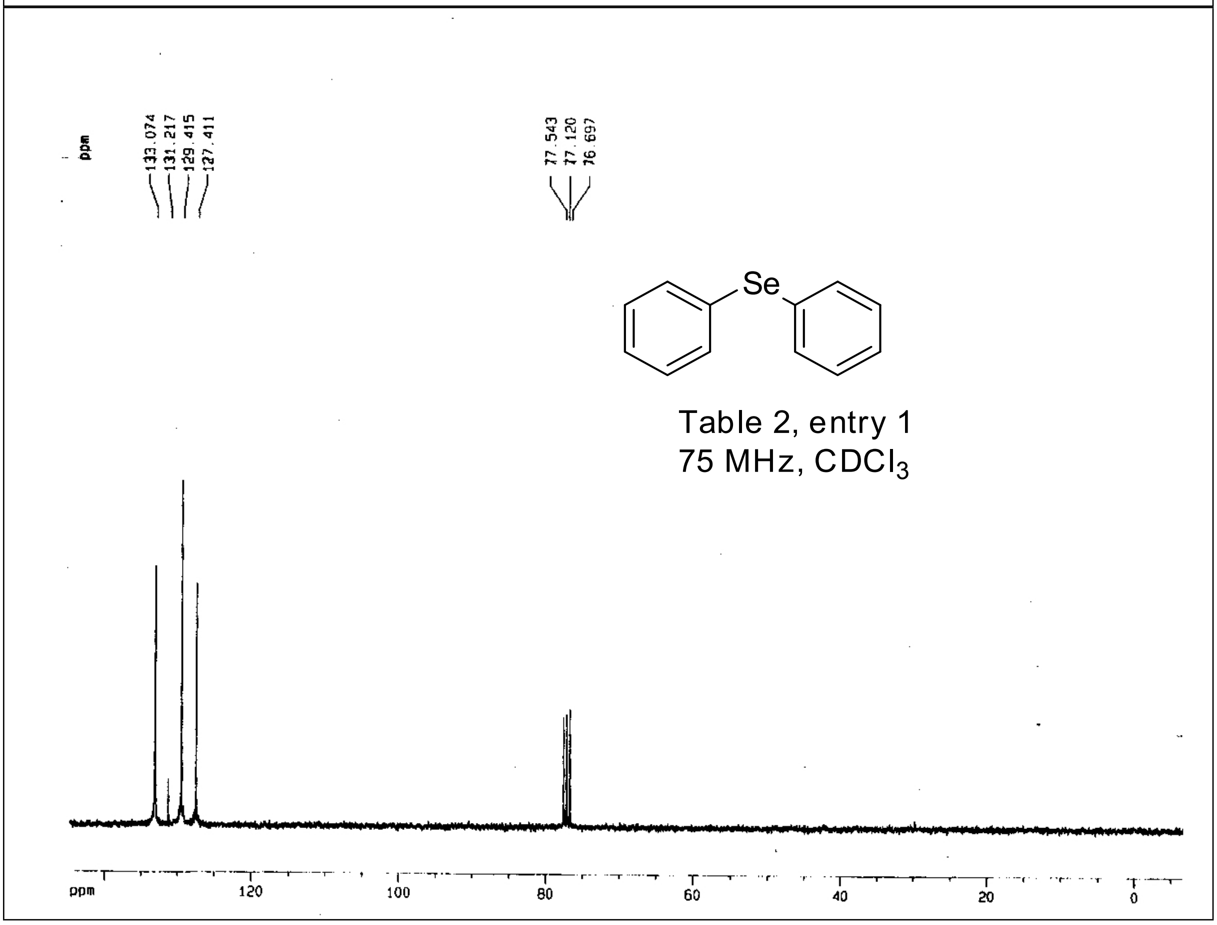
ppm
7
6
5
4
3
2
1
0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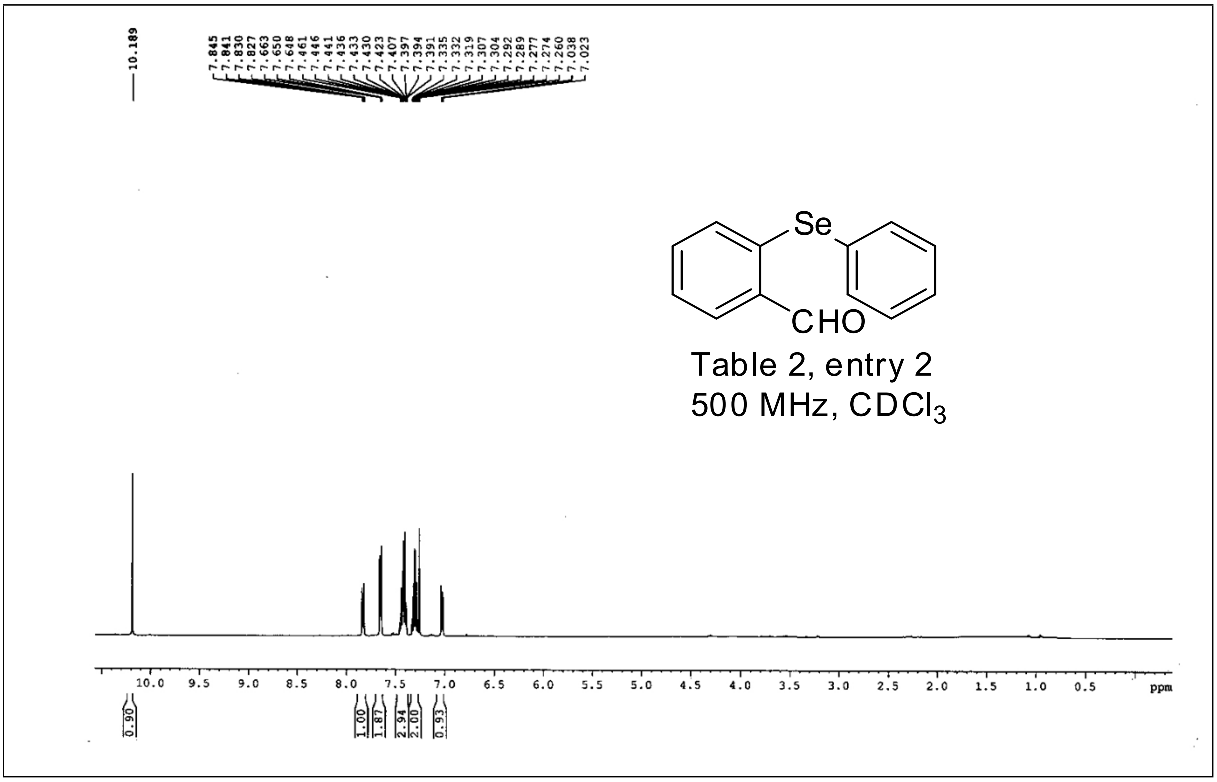
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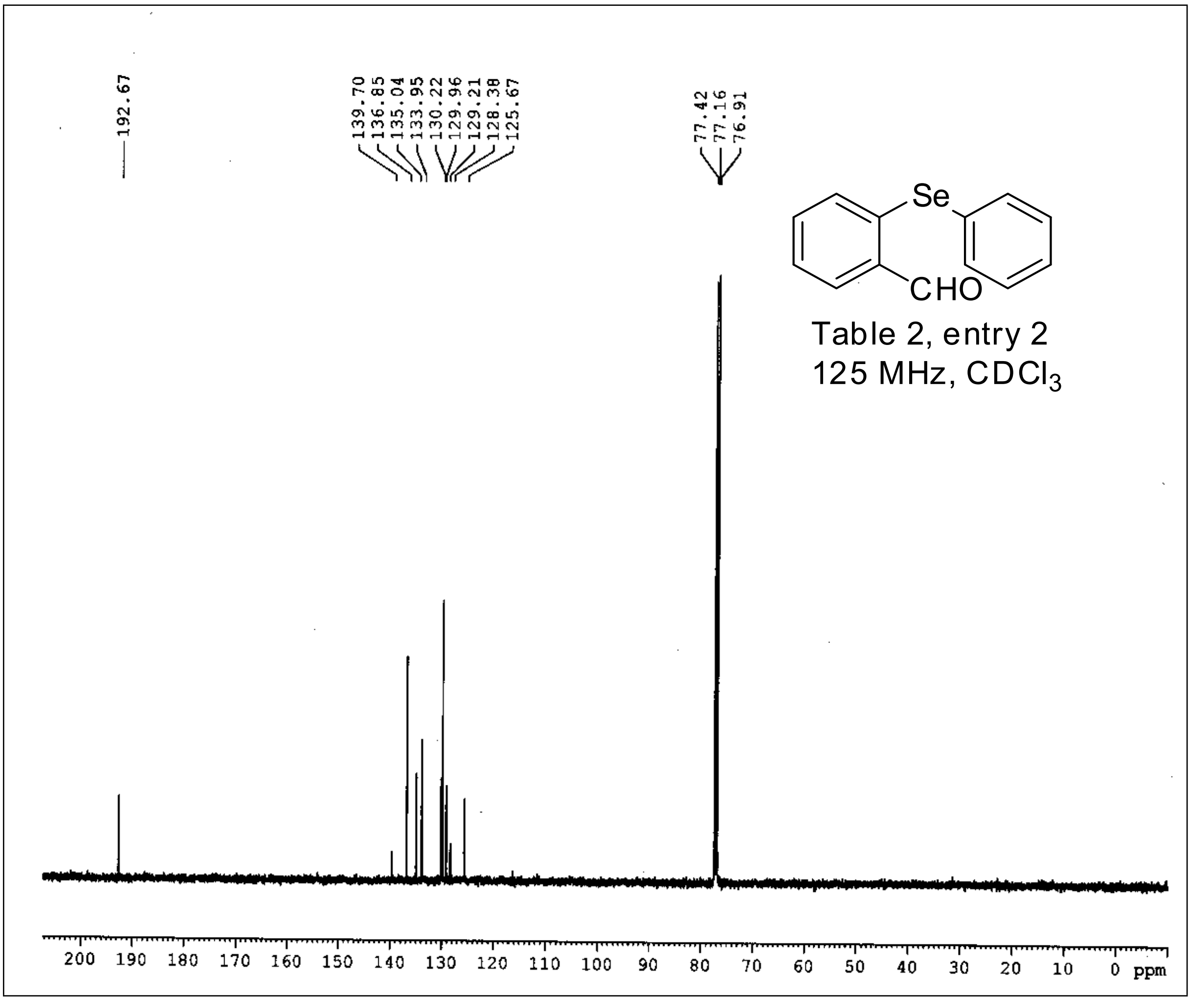
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139.70
136.85
135.04
133.95
130.22
129.96
129.21
128.38
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77.42
77.16
76.91
Se
CHO
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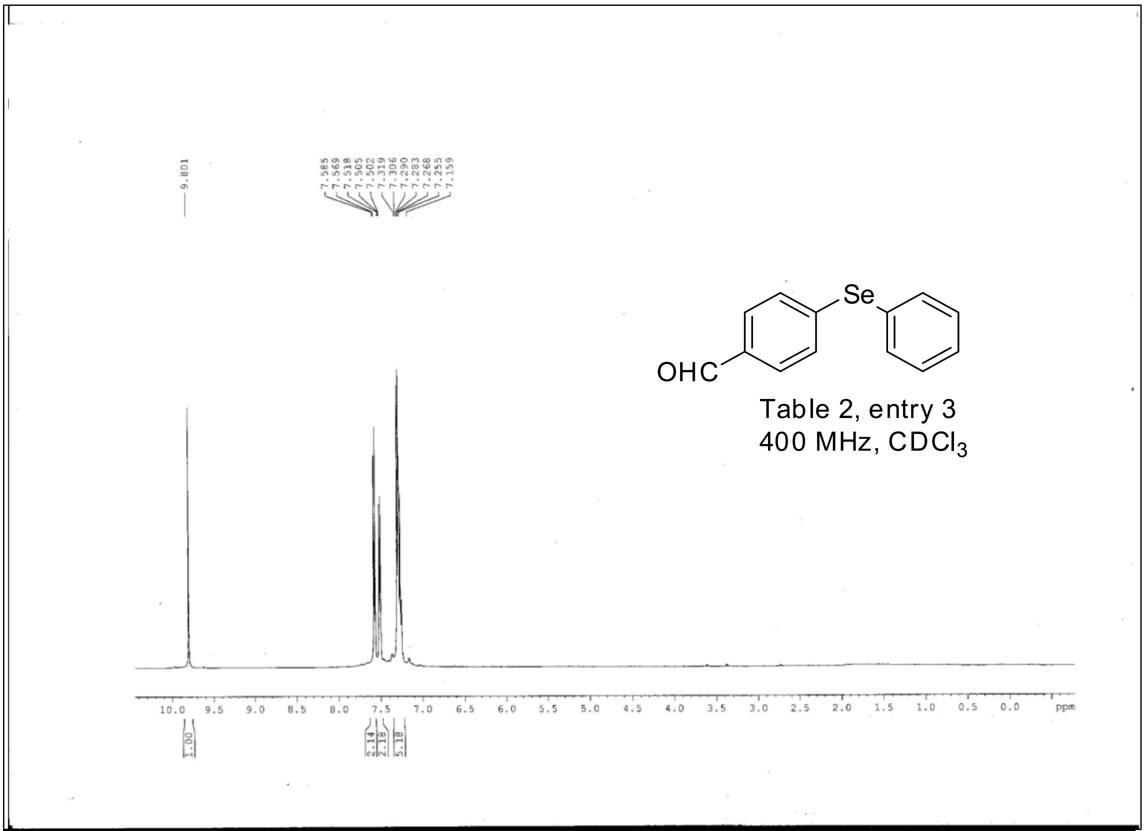
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7.585
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7.518
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7.502
7.319
7.306
7.290
7.283
7.268
7.255
7.159
Se
OHC
Table 2, entry 3
400 MHz, CDCl3
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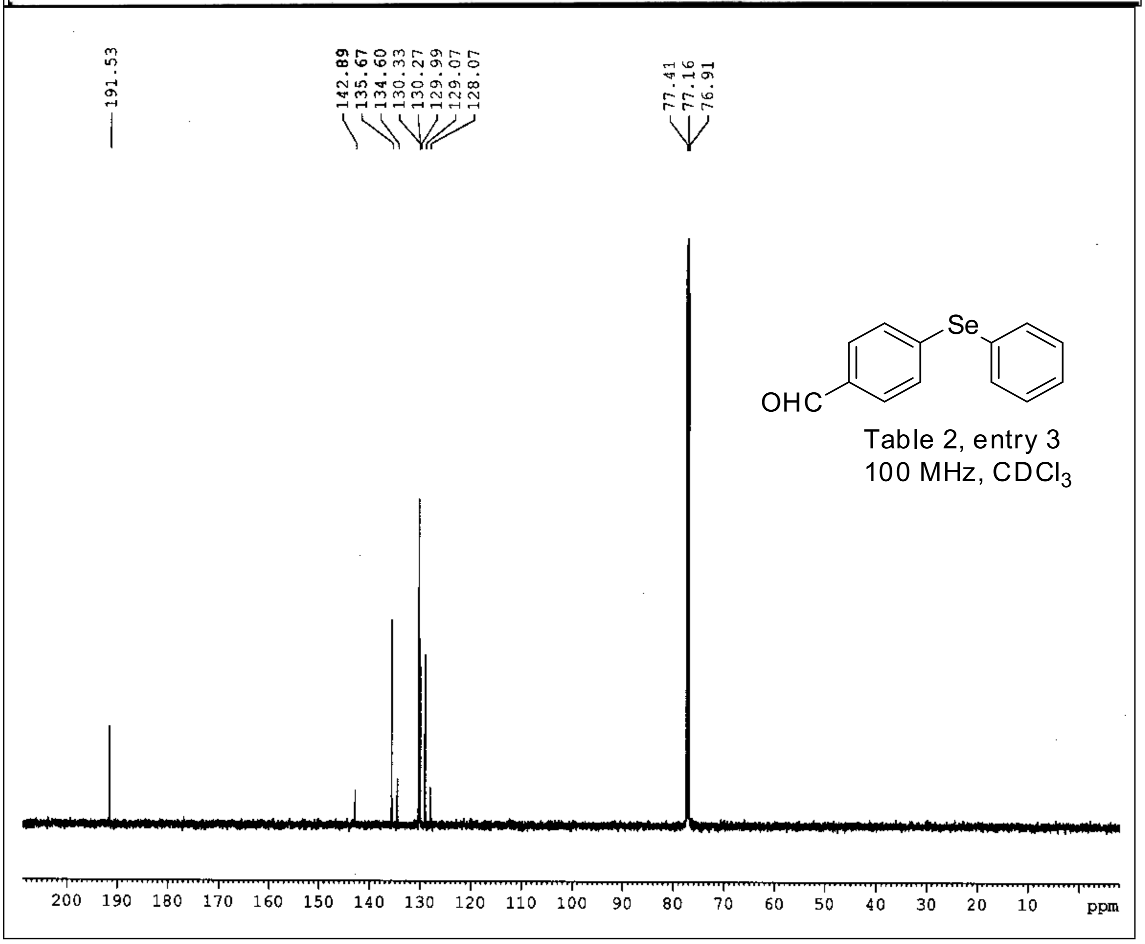
1.00
2.14
2.18
5.18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142.89
135.67
134.60
130.33
130.27
129.99
129.07
128.07
77.41
77.16
76.91
Se
OHC
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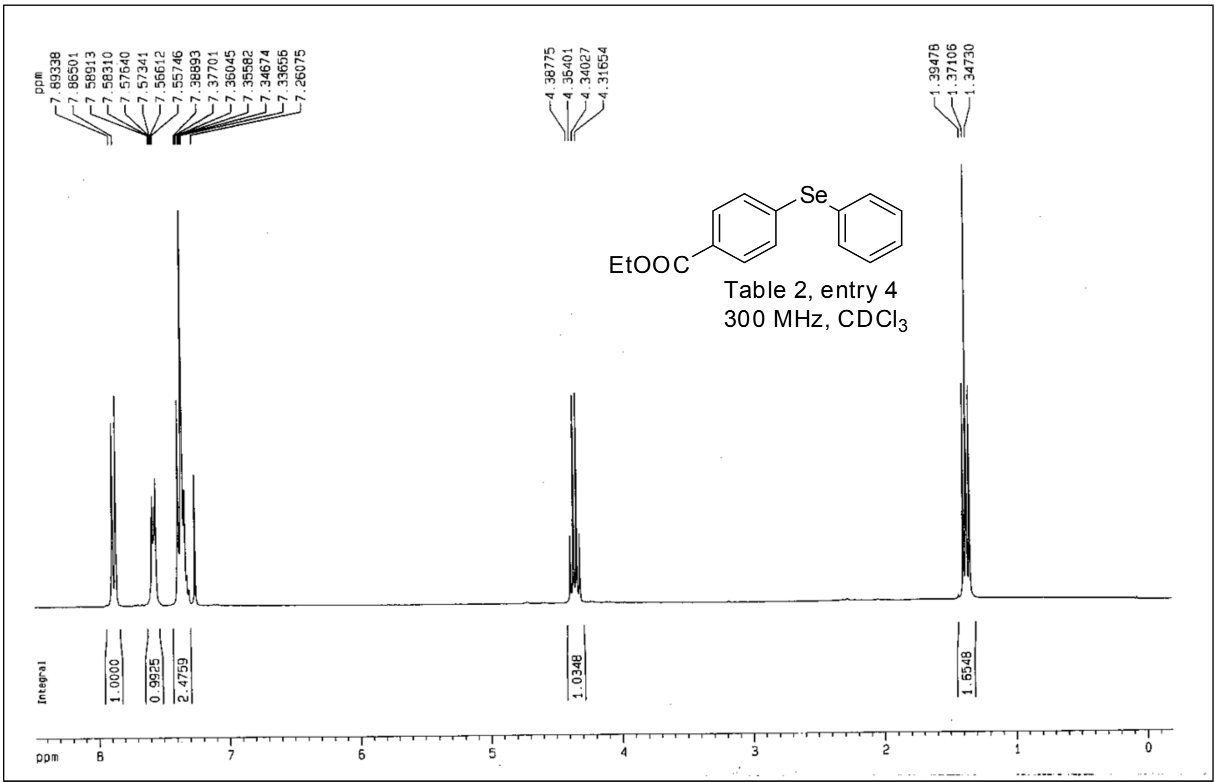
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7.56612
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7.37701
7.36045
7.35582
7.34674
7.33656
7.26075
4.38775
4.36401
4.34027
4.31654
1.39478
1.37106
1.34730
Se
EtOOC
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300 MHz, $CDCl_3$
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ppm
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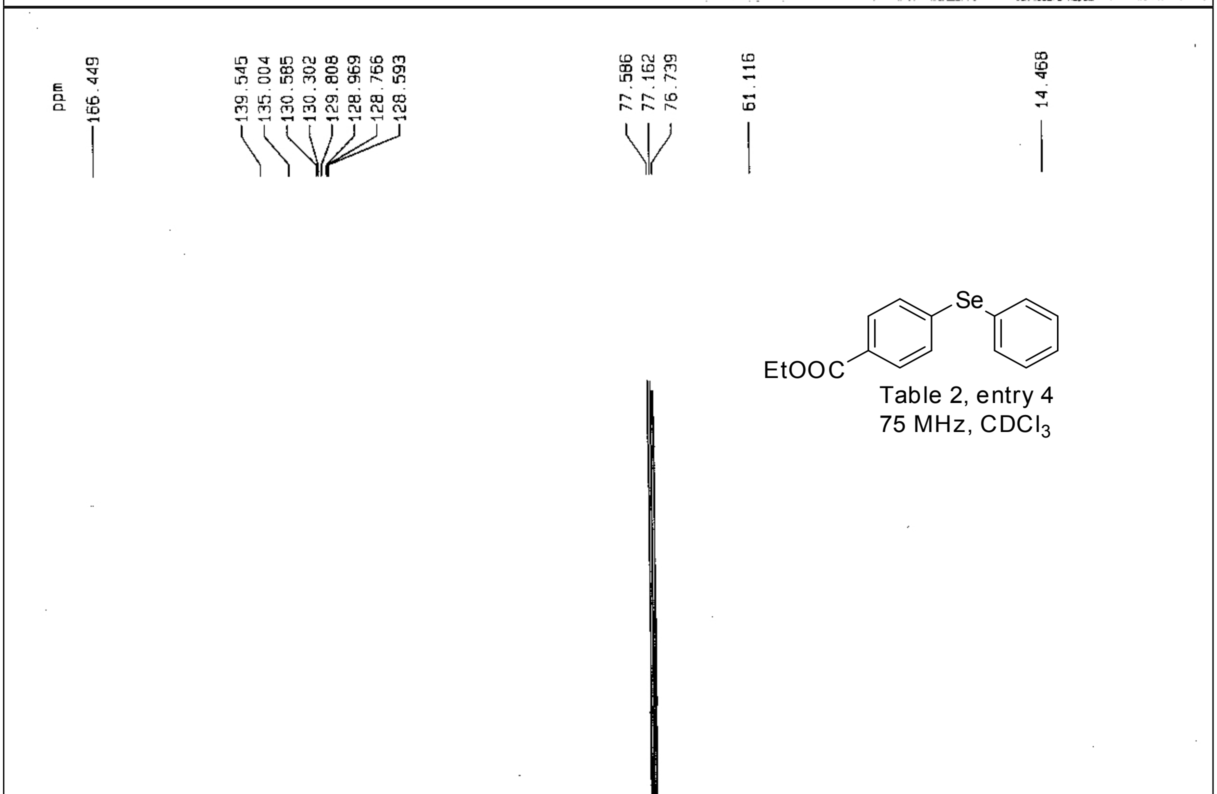
7
6
5
4
3
2
1
0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139.545
135.004
130.585
130.302
129.808
128.969
128.766
128.593
77.586
77.162
76.739
61.116
14.468
Se
EtOOC
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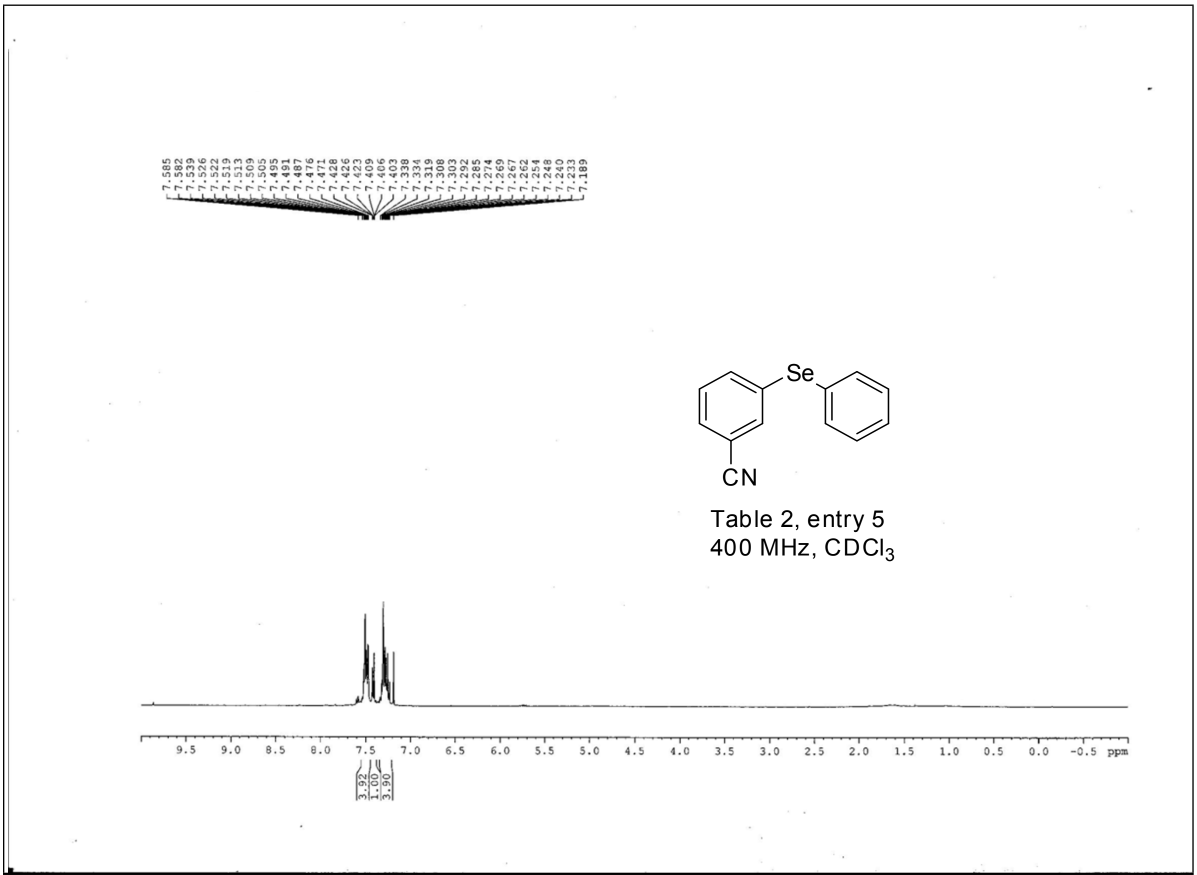
140
120
100
80
60
40
20
0


Se
CN
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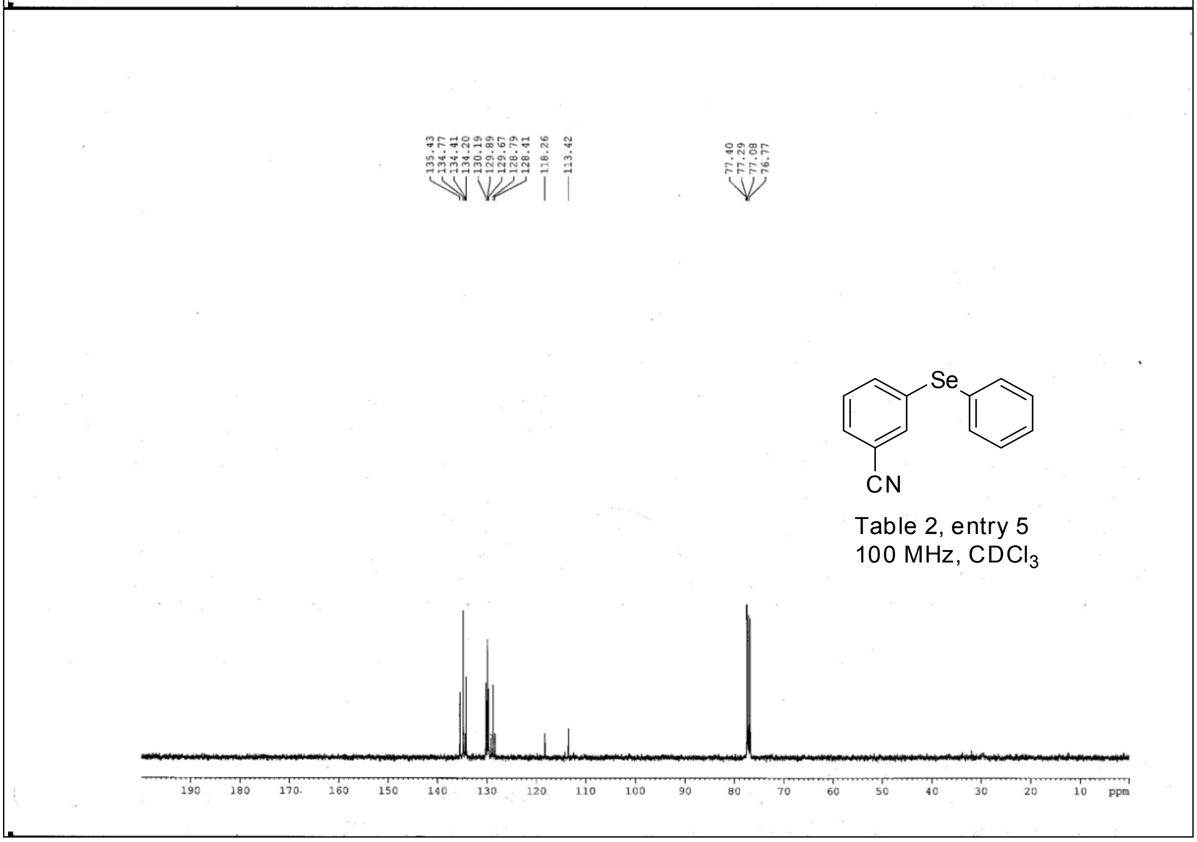
ppm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134.77
134.41
134.20
130.19
129.89
129.67
128.79
128.41
118.26
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77.40
77.29
77.08
76.77
Se
CN
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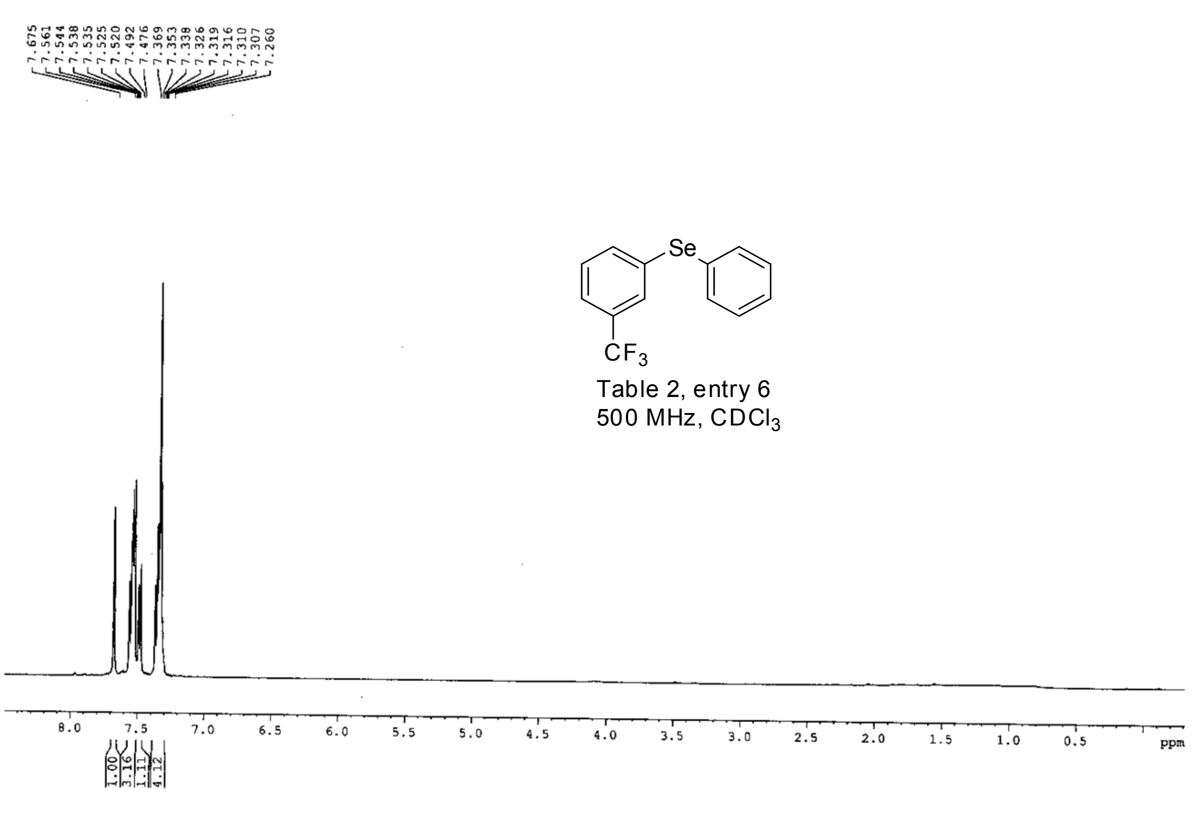
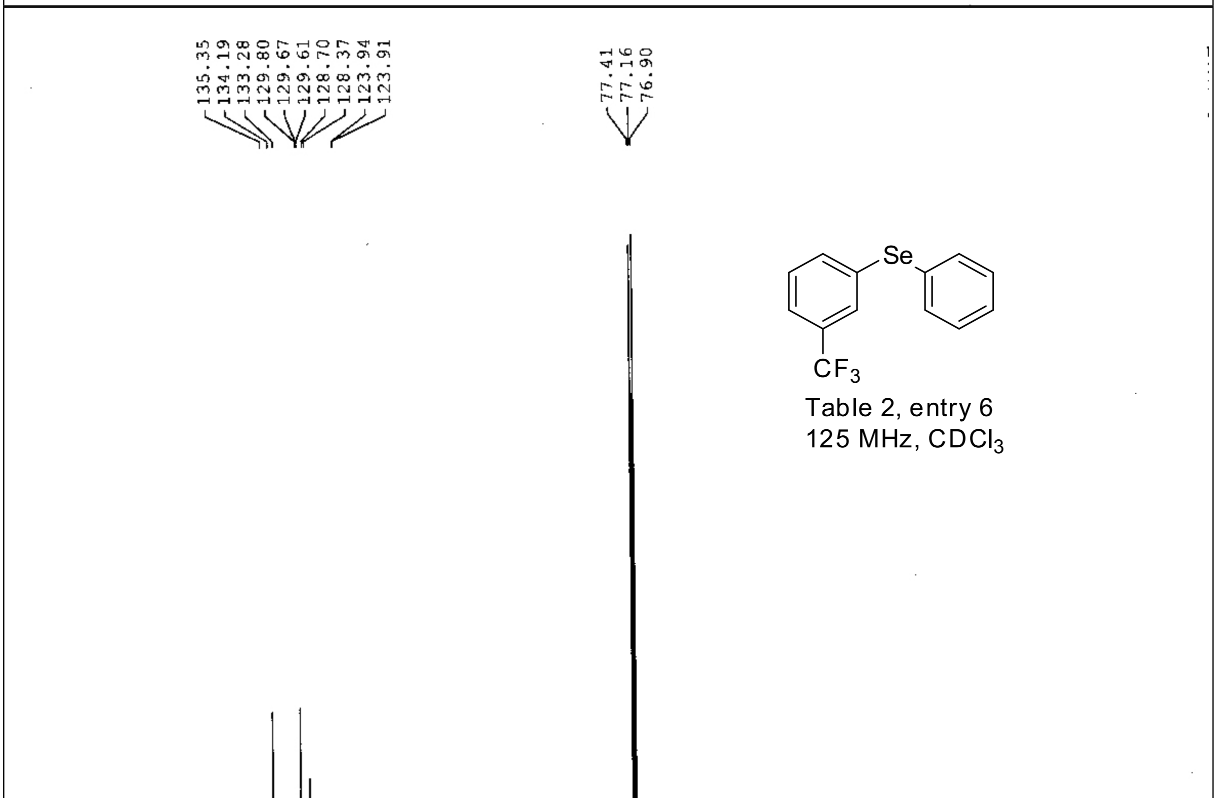
ppm


7.675
7.561
7.544
7.538
7.535
7.525
7.520
7.492
7.476
7.369
7.353
7.338
7.326
7.319
7.316
7.310
7.307
7.260
Se
CF_3
Table 2, entry 6
500 MHz, $CDCl_3$
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
3.16
1.11
4.12


135.35
134.19
133.28
129.80
129.67
129.61
128.70
128.37
123.94
123.91
77.41
77.16
76.90
Se
CF_3
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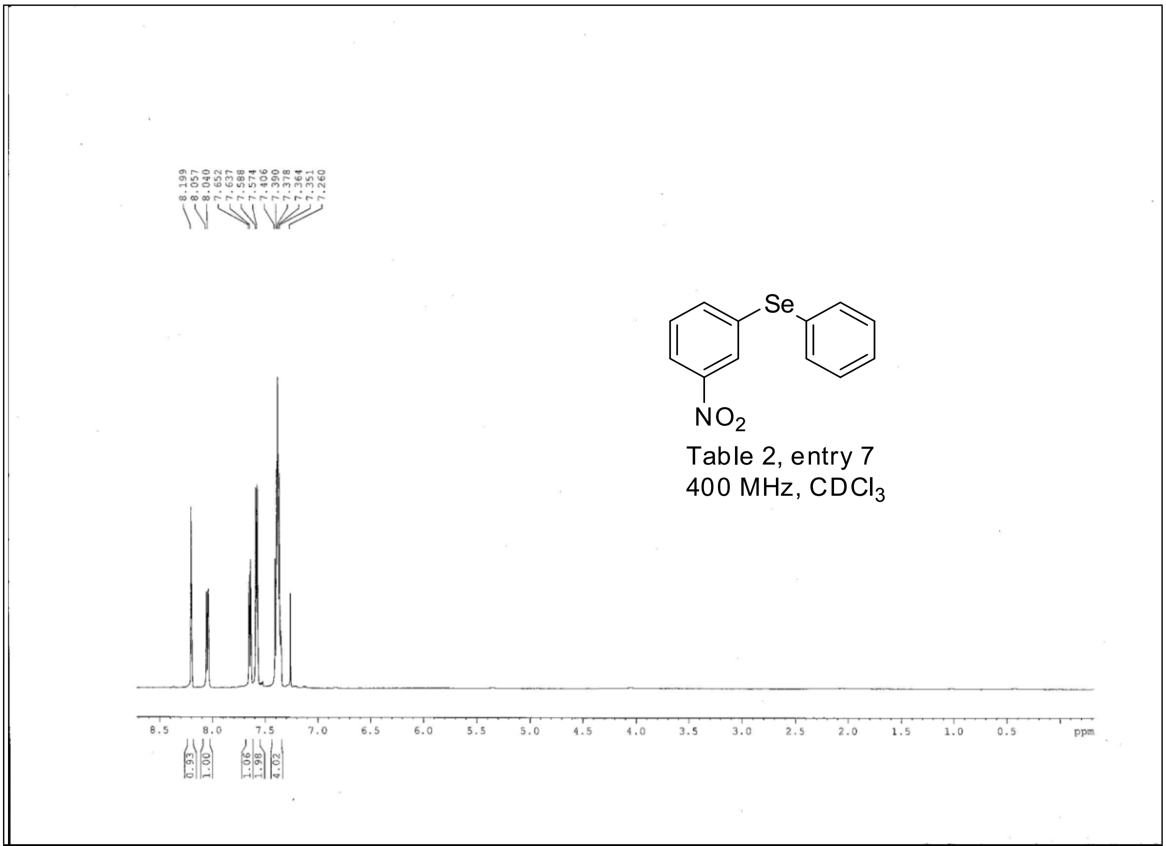
Se
NO2
Table 2, entry 7
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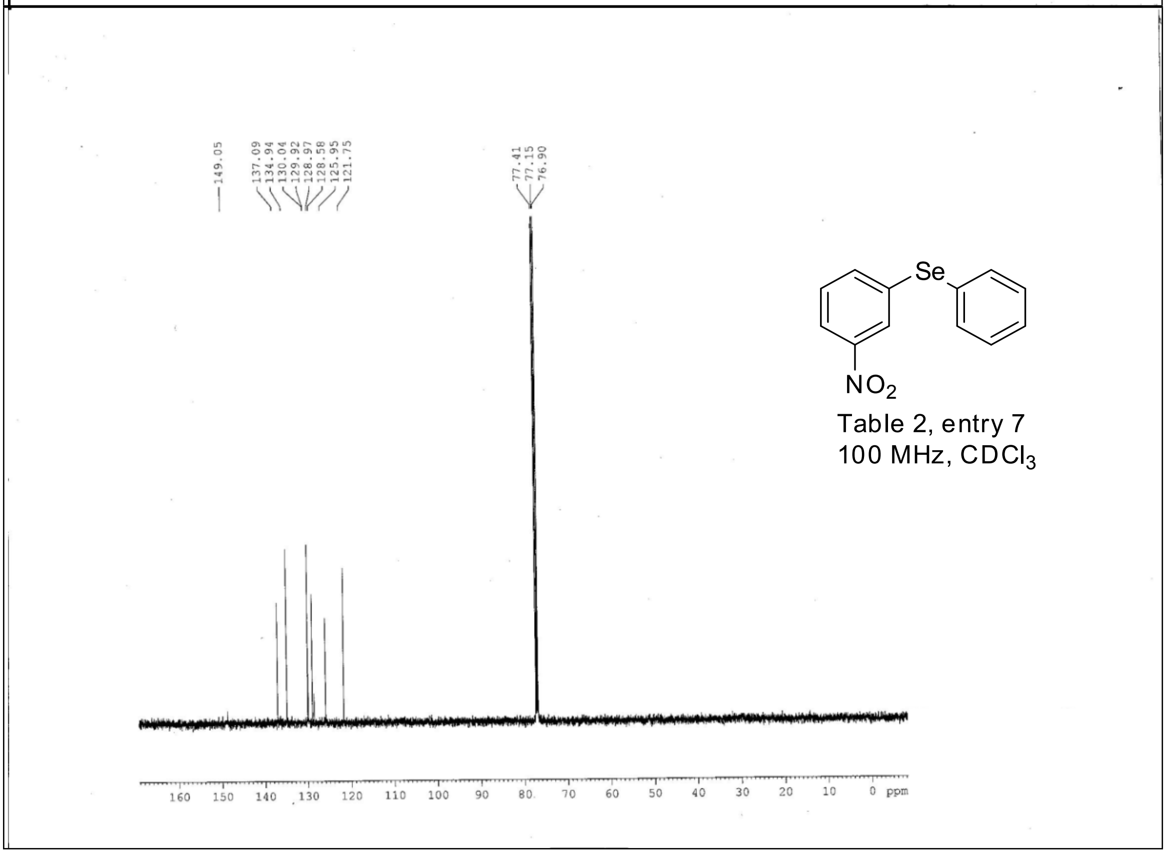
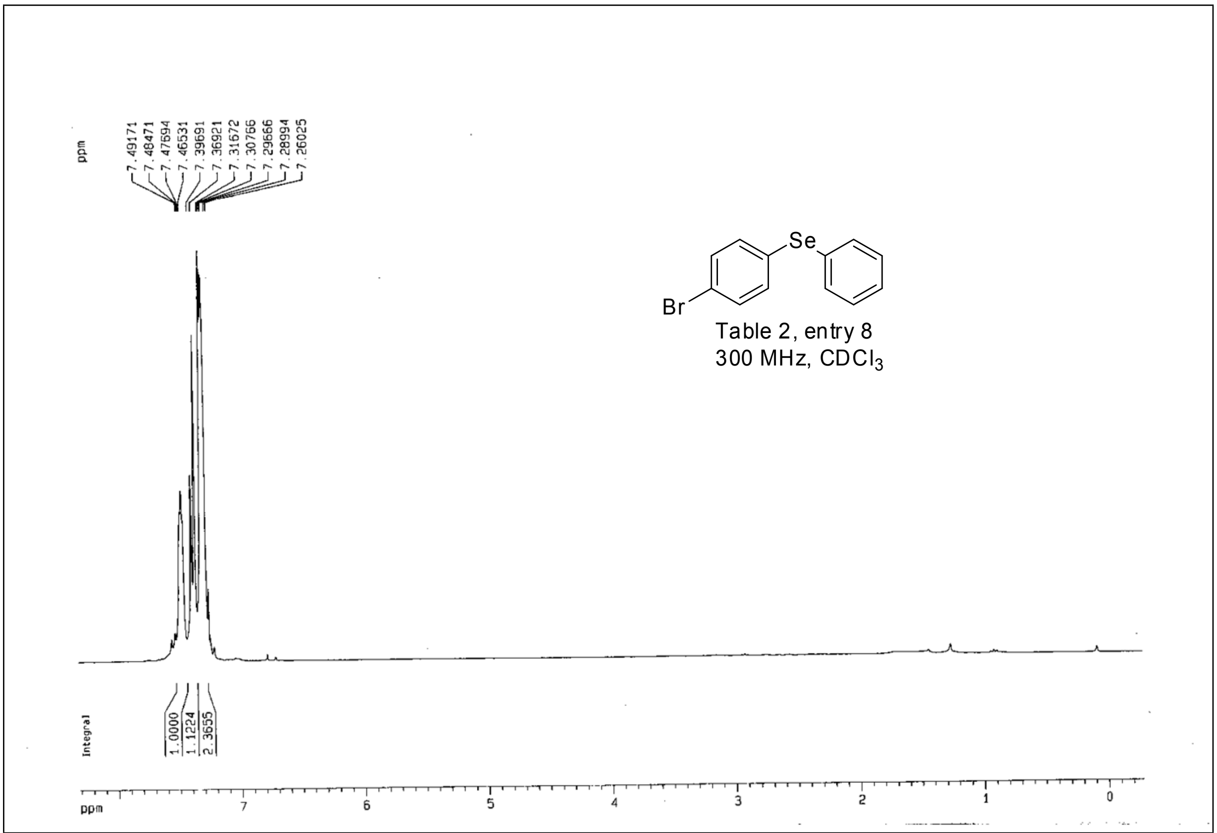

Se
NO2
Table 2, entry 7
100 MHz, CDCl3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7.47694
7.46531
7.39691
7.36921
7.31672
7.30766
7.29666
7.28994
7.26025
Se
Br
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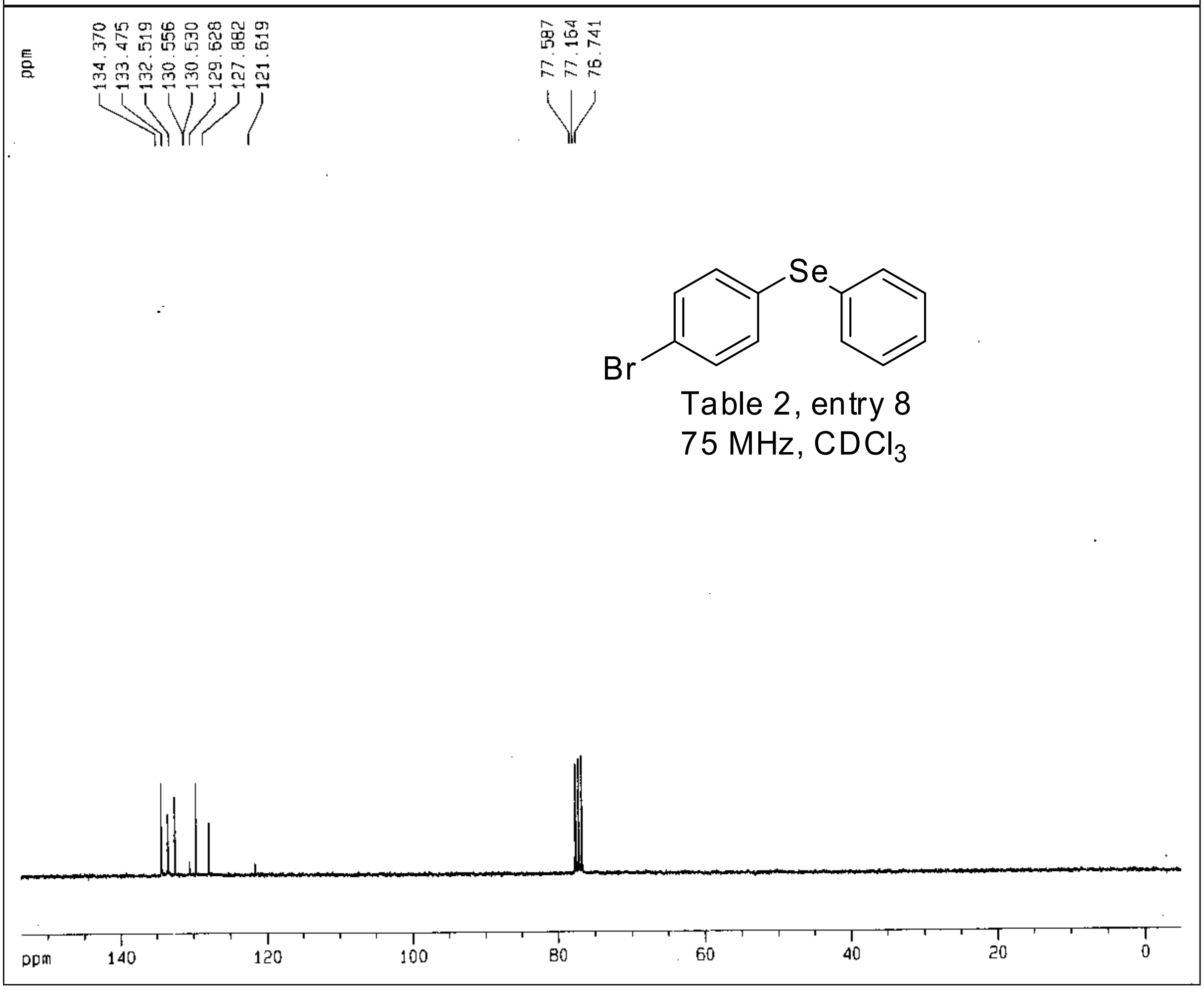
ppm
7
6
5
4
3
2
1
0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133.475
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130.556
130.530
129.628
127.882
121.619
77.587
77.164
76.741
Se
Br
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75 MHz, CDCl3
ppm
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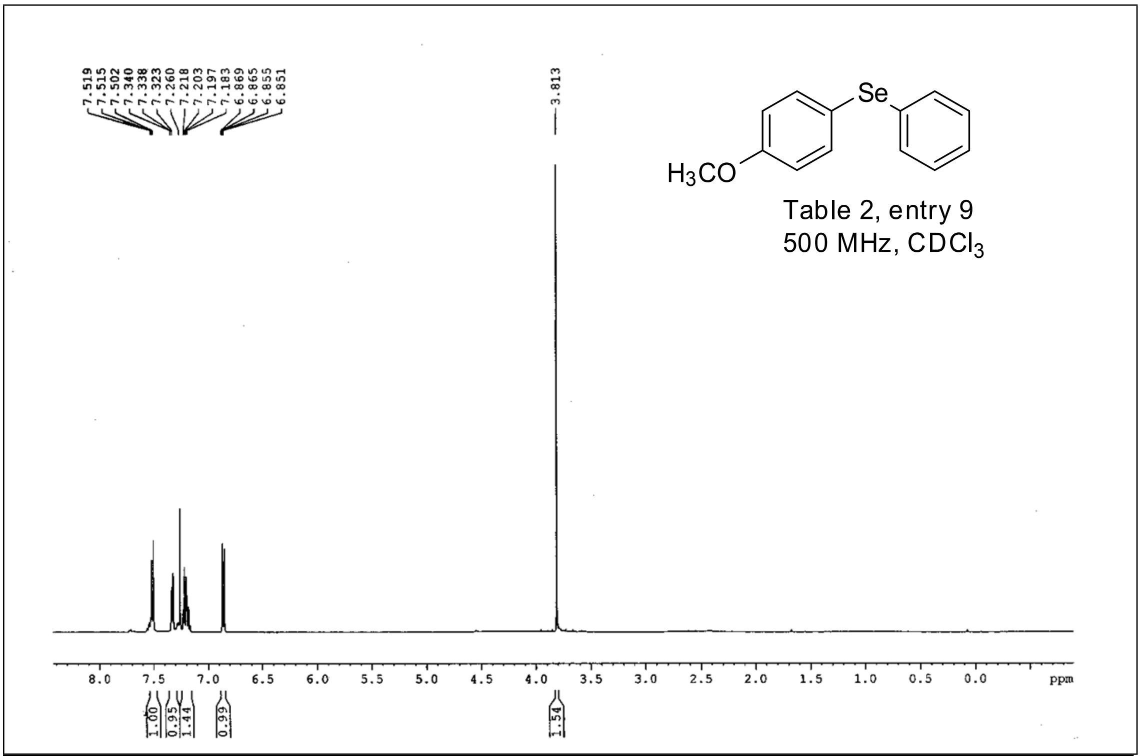
120
100
80
60
40
20
0


7.519
7.515
7.502
7.340
7.338
7.323
7.260
7.218
7.203
7.197
7.183
6.869
6.865
6.855
6.851
3.813
Se
H3CO
Table 2, entry 9
500 MHz, CDCl3
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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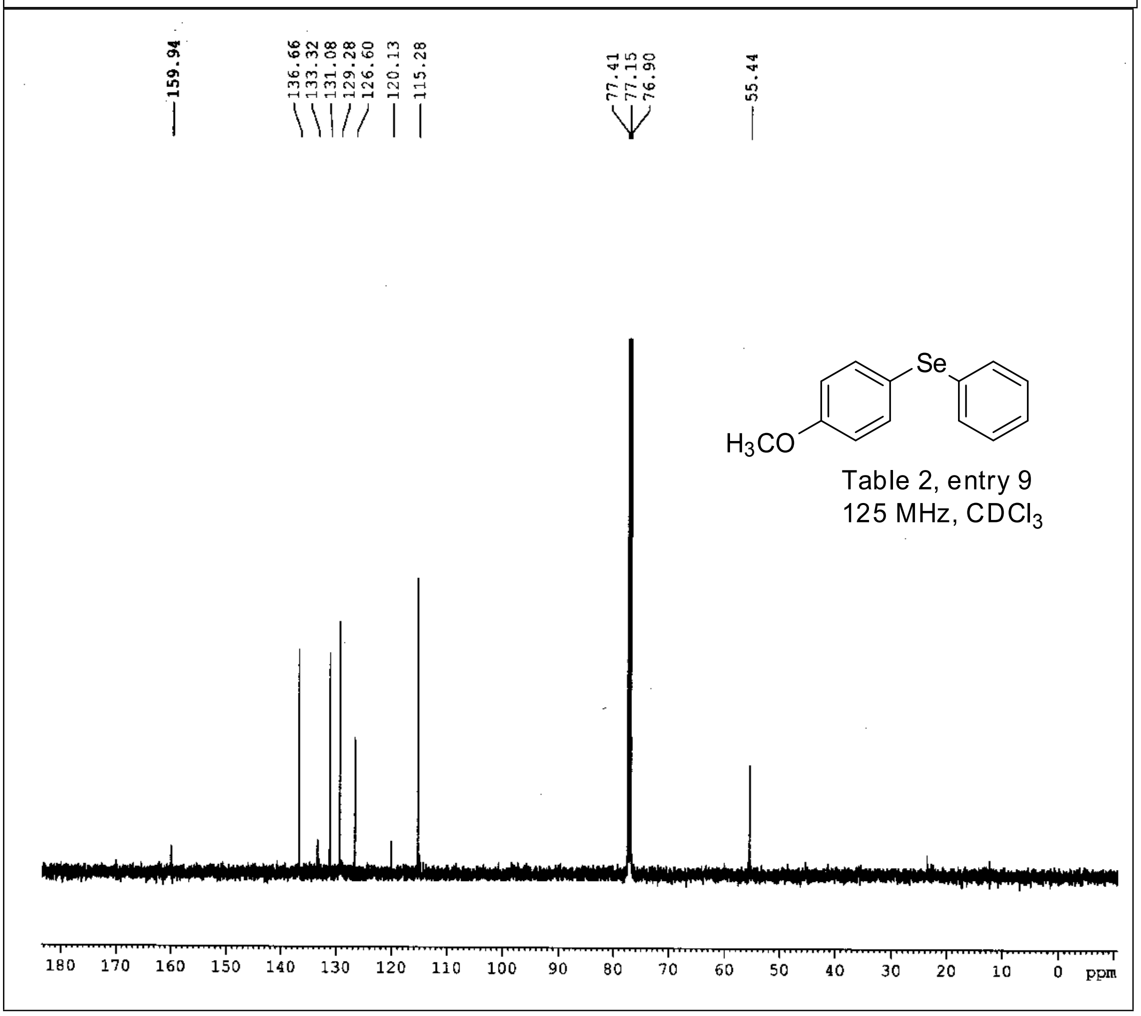
0.95
1.44
0.99
1.54


159.94
136.66
133.32
131.08
129.28
126.60
120.13
115.28
77.41
77.15
76.90
55.44
Se
H3CO
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125 MHz, CDCl3
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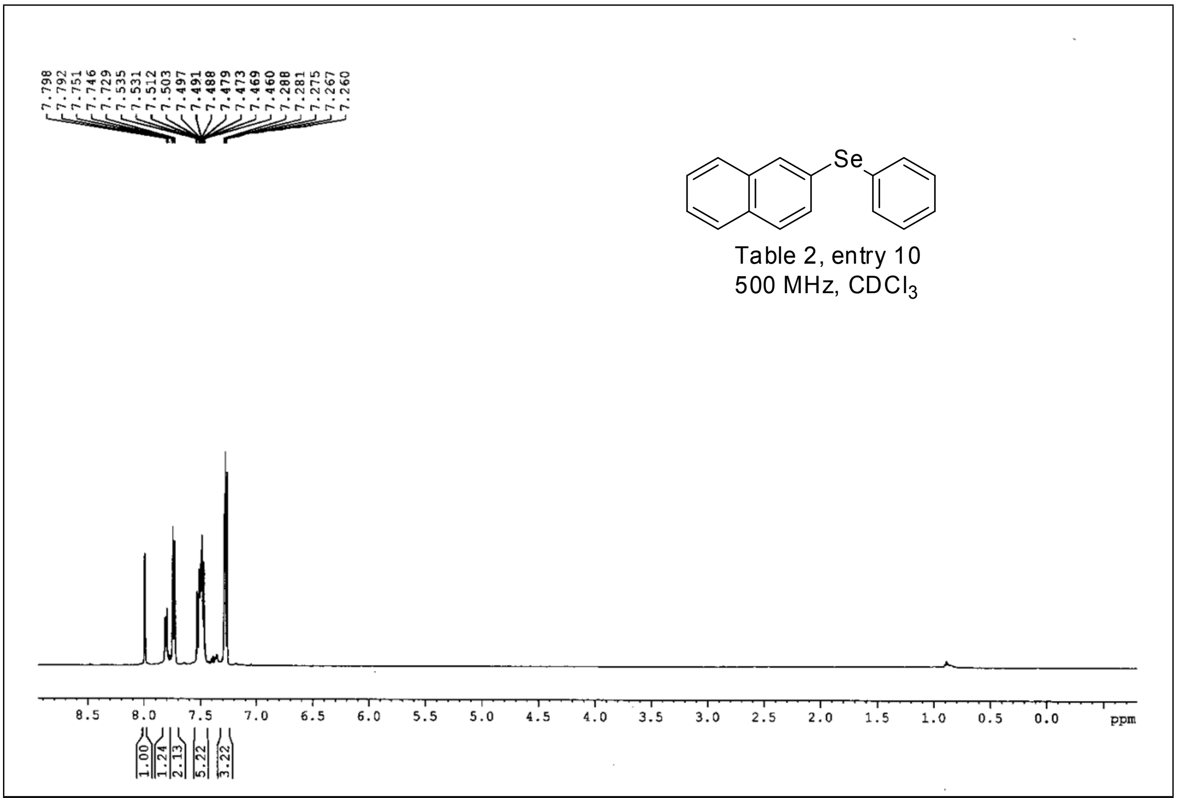
7.798
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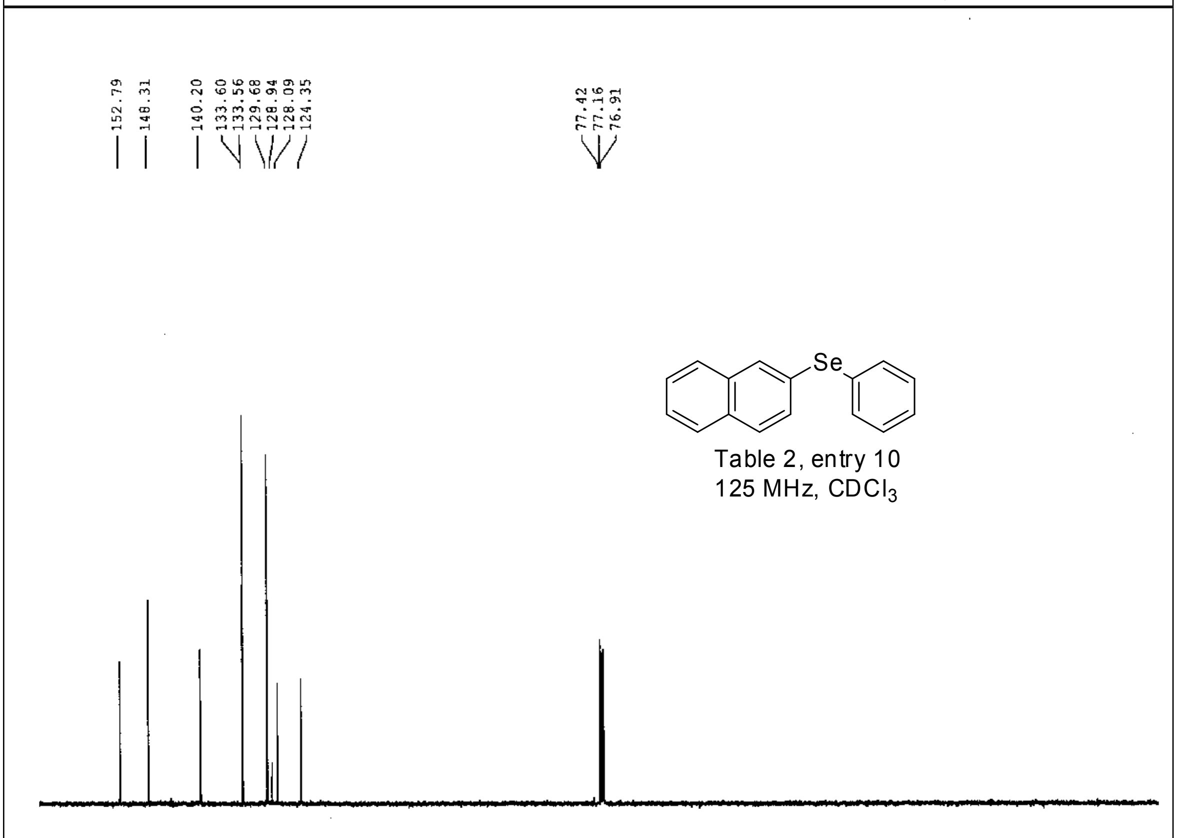
7.729
7.535
7.531
7.512
7.503
7.497
7.491
7.488
7.479
7.473
7.469
7.460
7.288
7.281
7.275
7.267
7.260
Se
Table 2, entry 10
500 MHz, CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.24
2.13
5.22
3.22


152.79
148.31
140.20
133.60
133.56
129.68
128.94
128.09
124.35
77.42
77.16
76.91
Se
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125 MHz, CDCl3
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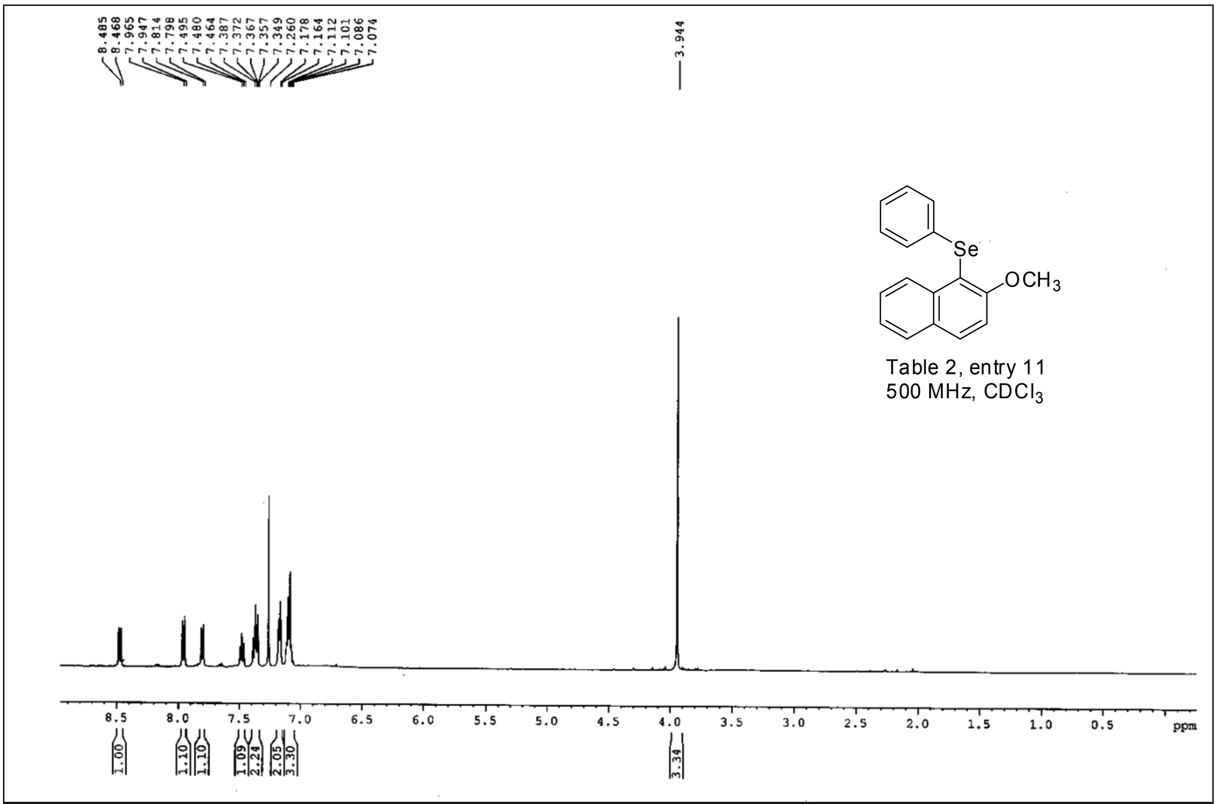
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8.468
7.965
7.947
7.814
7.798
7.495
7.480
7.464
7.387
7.372
7.367
7.357
7.349
7.260
7.178
7.164
7.112
7.101
7.086
7.074
3.944
Se
OCH3
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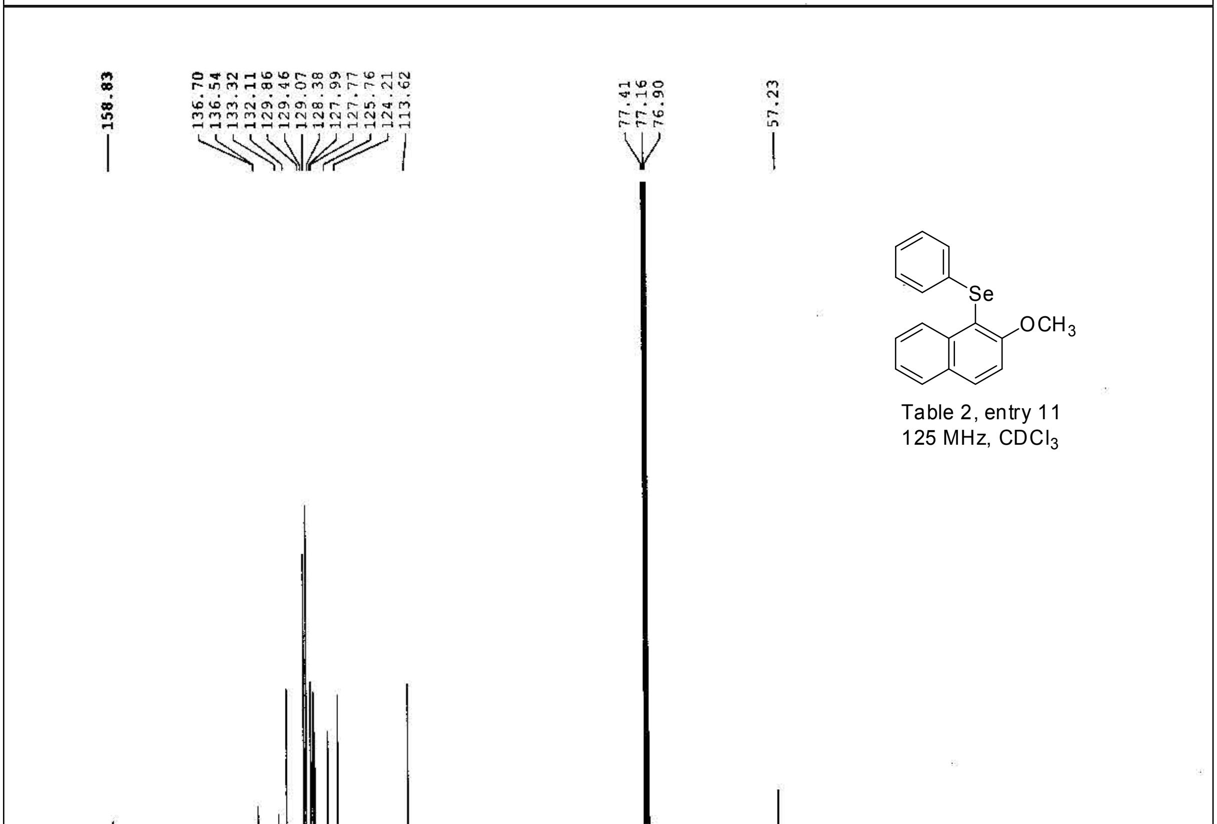
1.10
1.09
2.24
2.05
3.30
3.34
ppm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136.70
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127.99
127.77
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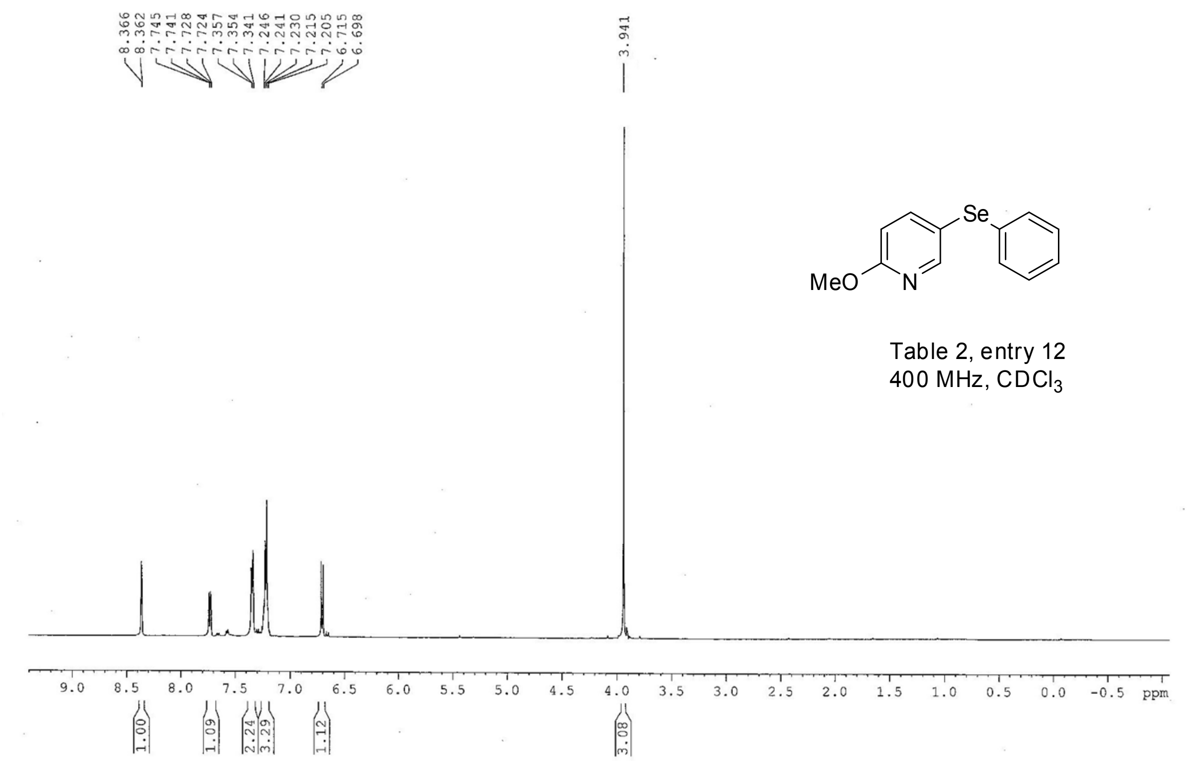
77.16
76.90
57.23
Se
OCH3
Table 2, entry 11
125 MHz, CDCl3
ppm



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8.362
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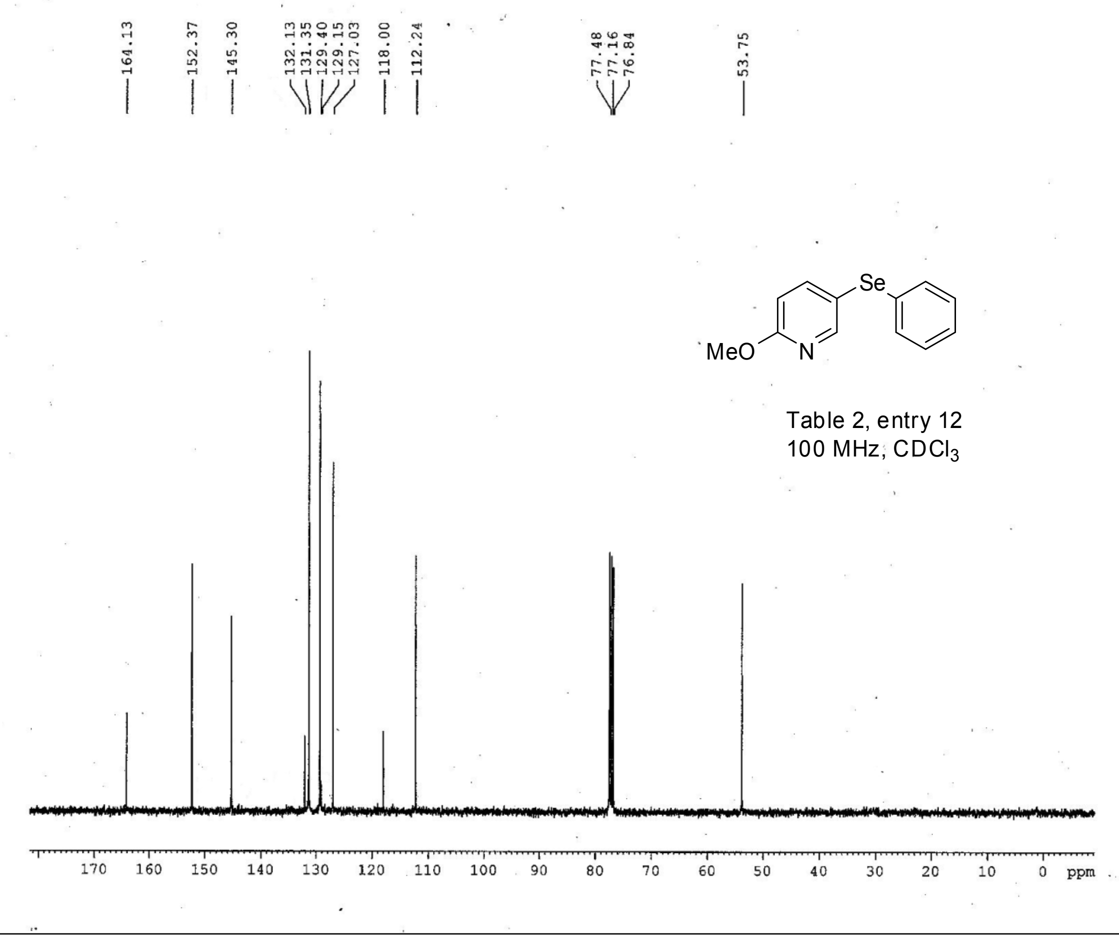
7.741
7.728
7.724
7.357
7.354
7.341
7.246
7.241
7.230
7.215
7.205
6.715
6.698
3.941
Se
MeO
N
Table 2, entry 12
400 MHz, CDCl3
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00
1.09
2.24
3.29
1.12
3.08



164.13
152.37
145.30
132.13
131.35
129.40
129.15
127.03
118.00
112.24
77.48
77.16
76.84
53.75
Se
MeO
N
Table 2, entry 12
100 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Diphenylselane (Table 2, entry 1):

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17–7.22 (m, 6H), 7.37-7.40 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 127.4(4C), 129.4 (2C), 131.2 (2C), 133.1(4C).

2-(Phenylselanyl)benzaldehyde (Table 2, entry 2):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8 Hz, 1H),7.26–7.34 (m, 2H), 7.39-7.66 (m, 3H), 7.83 (d, *J* = 2 Hz, 2H), 7.84 (d, *J* = 2 Hz, 1H), 10.19 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 125.7, 128.4 (2C), 129.2, 129.9, 130.2 (2C), 133.9, 135.0, 136.8 (2C), 139.7, 192.7.

4-(Phenylselanyl)benzaldehyde (Table 2, entry 3):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.31 (m, 5H), 7.51 (d, *J* = 5 Hz, 2H), 7.57 (d, *J* = 6 Hz, 2H), 9.8 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 127.9, 129.0, 129.9 (2C), 130.1 (2C), 130.2 (2C), 134.5, 135.6 (2C), 142.8, 191.4.

Ethyl-4-(phenylselanyl)benzoate (Table 2, entry 4):

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (t, 3H), 4.35 (q, 2H), 7.34–7.39 (m, 5H), 7.56–7.59 (m, 2H), 7.87 (d, *J* = 9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 61.1, 128.6 (2C), 128.7, 128.9 (2C), 129.8 (2C), 130.3, 130.6 (2C), 135.0, 139.5, 166.4.

3-(Phenylselanyl)benzonitrile (Table 2, entry 5):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.33 (m, 3H), 7.40 (t, 1H), 7.42 (t, 1H), 7.47-7.58 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 113.4, 118.3, 128.4, 128.7, 129.7, 129.9 (2C), 130.1, 134.2, 134.4, 134.7 (2C), 135.4.

Phenyl(3-(trifluromethyl)phenyl)selane (Table 2, entry 6):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.37 (m, 4H), 7.48 (d, J = 8 Hz, 1H), 7.52-7.54 (m, 3H), 7.67 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 123.9 (2C), 128.3 (2C), 128.7, 129.6, 129.7, 129.8 (2C), 133.2, 134.2 (2C), 135.3

(3-Nitrophenyl)(phenyl)selane (Table 2, entry 7):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.40 (m, 4H), 7.58 (d, J = 7 Hz, 2H), 7.64 (d, J = 8 Hz, 1H), 8.05 (d, J = 9 Hz, 1H), 8.19 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 121.7, 125.9, 128.6, 128.9, 129.9 (2C), 130.0, 134.9 (2C), 137.1 (2C), 149.0.

(4-Bromophenyl)(phenyl)selane(Table 2, entry 8):

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26−7.31 (m, 5H), 7.37-7.39 (m, 2H), 7.47-7.49 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 121.6, 127.9, 124.6, 130.5 (2C), 130.6, 132.5 (2C), 133.5 (2C), 134.4 (2C).

(4-Methoxyphenyl)(phenyl)selane (Table 2, entry 9):

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.86 (d, J = 7 Hz, 2H), 7.18-7.21 (m, 3H), 7.32 (d, J = 7 Hz, 2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 115.3 (2C), 120.2, 126.6, 129.4 (2C), 131.1 (2C), 133.4 (2C), 136.6 (2C), 159.8.

Naphthalen-2-yl(phenyl)selane (Table 2, entry 10):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.28 (m, 3H), 7.46−7.53 (m, 5H), 7.74 (d, *J* = 11 Hz, 2H), 7.79-7.85 (m, 1H), 7.99 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) 126.4, 126.6, 127.5, 127.6, 127.9, 128.6, 128.9, 129.5 (2C), 130.6, 131.4, 132.2, 132.6, 133.0 (2C), 134.2.

(2-Methoxynaphthalen-1-yl)(phenyl)selane(Table 2, entry 11):

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.1 (d,*J* = 7 Hz, 3H), 7.17 (d, *J* = 7 Hz, 2H), 7.35−7.38 (m, 2H), 7.48 (t, *J* = 8 Hz, 1H), 7.80 (d, *J* = 8 Hz, 1H), 7.95 (d, *J* = 9 Hz, 1H), 8.47 (d, *J* = 9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 57.2, 113.6, 124.2, 125.7, 127.7, 127.9, 128.4, 129.0 (2C), 129.4 (2C), 129.8, 132.1, 133.3, 136.5.

2-Methoxy-5-(phenylselanyl)pyridine(Table 2, entry 12):

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 6.70 (d, *J* = 7 Hz, 1 H), 7.20-7.24 (m, 3H), 7.34-7.36 (m, 2H), 7.73 (dd, J_1 = 8.4, J_2 = 5.2, 1H), 8.37 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 53.7, 112.2, 118.0, 127.0, 129.4 (2C), 131.4 (2C), 132.1, 145.3, 152.4, 164.1.