Electronic Supplementary Material (ESI) for Green Chemistry

Glycerol as a Recyclable Solvent for Copper-Catalyzed Cross-Coupling Reactions of Diaryl Diselenides with Aryl Boronic Acids

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General Information: The reactions were monitored by TLC carried out on Merck silica gel (60 F_{254}) by using UV light as visualizant agent and 5% vanillin in 10% H_2SO_4 and heat as developing agents. NMR spectra were recorded with Bruker DPX 200 and DPX 400 (200 and 400 MHz) instrument using $CDCl_3$ as solvent and calibrated using tetramethylsilane as internal standard. Chemical shifts are reported in δ ppm relative to $(CH_3)_4Si$ for ^1H and $CDCl_3$ for ^{13}C NMR. Coupling constants (*J*) are reported in Hertz. Mass spectra (MS) were measured on a Shimadzu GCMS-QP2010 mass spectrometer.

General procedure for the cross-coupling using glycerol:

To a round-bottomed flask containing organic diselenide (0.25 mmol), aryl boronic acid (0.5 mmol), CuI (0.025 mmol; 0.0048g), was added glycerol (0.5 mL) and DMSO (0.5 mmol). The reaction mixture was allowed to stir at 110 °C for 30 hours. After this time, the solution was cooled to room temperature, diluted with ethyl acetate (20 mL), and washed with water (3x 20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The obtained products were purified by flash chromatography on silica gel using hexane or a mixture of ethyl acetate/hexane as the eluent.

4-Methoxyphenyl-phenyl-selenide (3a)[1]

Yield: 0.119 g (90%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, J = 8.8 Hz, 2H); 7.33-7.31 (m, 2H); 7.21-7.16 (m, 3H); 6.84 (d, J = 8.4 Hz, 2H); 3.79 (s, 3H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 159.7, 136.5, 133.2, 130.9, 129.1, 126.4, 119.9, 115.1, 55.2. MS (relative intensity) m/z: 264 (65), 262 (34), 184 (100), 153 (32), 65 (14).

2-Methoxyphenyl-phenyl-selenide (3b)[1]

Yield: 0.112 g (85%). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.61–7.56 (m, 2 H), 7.35–7.31 (m, 3 H), 7.24–7.14 (m, 1 H), 6.97-7.74 (m, 3 H), 3.88 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm): 156.9, 135.2, 131.2, 129.4, 128.6, 127.9, 127.8, 122.0, 121.6, 110.6, 55.9. MS (relative intensity) *m*/*z*: 264 (65), 262 (33), 184 (100), 169 (40), 141 (33), 77 (32).

4-Tolyl-phenyl-selenide (3c)[1]

Yield: 0.112 g (90%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.32 (m, 4H); 7.23-7.16 (m, 3H); 7.04 (d, J = 8.5 Hz, 2H); 2.33 (s, 3H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 137.6, 133.8, 132.0, 130.1, 129.1, 126.8, 21.1. MS (relative intensity) *m*/*z*: 248 (70), 246 (39), 168 (100), 153 (25), 91 (63), 65 (30).

2-Tolyl-phenyl-selenide (3d)[1]

Yield: 0.103 g (83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.38 (m, 2H); 7.35-7.32 (m, 1H); 7.27-7.17 (m, 5H); 7.08-7.04 (m, 1H); 2.40 (s, 3H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 139.8, 133.6, 132.7, 131.7, 130.7, 130.2, 129.3, 127.7, 127.1, 126.7, 22.3. MS (relative intensity) *m*/*z*: 248 (72), 246 (37), 168 (100), 153 (20), 91 (57), 65 (32).

Diphenyl-selenide (3e)[1]

Yield: 0.105 g (90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.44 (m, 4H); 7.24-7.21 (m, 6H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 132.9, 131.1, 129.3, 127.2. MS (relative intensity) *m*/*z*: 234 (30), 154 (100), 77 (20), 51 (17).

4-Chlorophenyl-phenyl-selenide (3f)[1]

Yield: 0.117 g (87%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.44 (m, 2H); 7.36 (d, J = 8.0 Hz, 2H); 7.28-7.26 (m, 3H); 7.21 (d, J = 8.0 Hz, 2H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 134.1, 133.5, 133.1, 130.6, 129.5, 129.4, 127.6. MS (relative intensity) *m*/*z*: 270 (15), 268 (36), 188 (100), 152 (27), 77 (22), 51 (18).

2-Chlorophenyl-phenyl-selenide (3g)[1]

Yield: 0.116 g (86%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.65-7.58 (m, 2H); 7.41-7.23 (m, 4H); 7.15-6.98 (m, 2H), 6.91 (dd, J = 7.6, 1.9 Hz, 1H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 135.9, 133.9, 131.6, 131.0, 129.7, 129.4, 128.7, 128.2, 127.4, 127.3. MS (relative intensity) *m*/*z*: 270 (19), 268 (41), 188 (100), 152 (32), 77 (19), 51 (19).

4-Bromophenyl-phenyl-selenide (3h)[1]

Yield: 0.134 g (86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.44 (m, 2H); 7.34 (d, J = 8.4 Hz, 2H); 7.28-7.25 (m, 5H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 134.1, 133.2, 133.0, 130.4, 130.3, 129.4, 127.6, 121.41. MS (relative intensity) *m*/*z*: 314 (68), 312 (86), 234 (84), 232 (99), 152 (100), 116 (27), 77 (58), 51 (41).

2-Bromophenyl-phenyl-selenide (3i)[2]

Yield: 0.128 g (82%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.66–7.62 (m, 2 H), 7.52–7.38 (m, 4 H), 7.07–7.00 (m, 2 H), 6.88–6.83 (m, 1 H). RMN ^{13}C ($CDCl_3$ 50 MHz); δ (ppm): 136.4, 136.2, 132.7, 130.4, 129.8, 128.9, 128.4, 127.8, 127.3, 123.4. MS (relative intensity) *m*/*z*: 312 (61), 232 (58), 207 (27), 156 (22), 152 (100), 77 (50).

3-(trifluoromethyl)phenyl-phenyl-selenide (3j)[3]

Yield: 0.116 g (77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (s, 1H); 7.53-7.44 (m, 4H); 7.31-7.26 (m, 4H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 135.1, 134.0, 133.2, 131.5 (q, J = 32.2 Hz), 129.6, 129.5, 129.4, 128.4 (q, J = 3.8 Hz), 128.2, 123.7 (q, J = 272.8 Hz), 123.6 (q, J = 3.8 Hz). MS (relative intensity) *m*/*z*: 302 (55), 222 (100), 153 (16), 77 (35), 51 (24).

2-Naphthyl-phenyl-selenide (3k)[4]

Yield: 0.104 g (73%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.98–7.97 (m, 1 H), 7.80–7.69 (m, 3 H), 7.53–7.43 (m, 5 H), 7.27–7.24 (m, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$); δ (ppm): 133.9, 132.8, 132.3, 132.0, 131.2, 130.4, 129.3, 128.7, 128.4, 127.7, 127.4, 127.3, 126.5, 126.2. MS (relative intensity) *m*/*z*: 284 (24), 204 (100), 126 (11), 115 (19), 77 (11).

Bis-4-methoxylphenyl-selenide (3l)[5]

Yield: 0.120 g (82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, J = 8.9 Hz, 4H), 6.65 (d, J = 8.9 Hz, 2H), 3.59 (s, 6H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.1, 134.4, 121.9, 114.8, 55.1. MS (relative intensity) *m*/*z*: 294 (71), 214 (100), 186 (42), 65 (17).

4-Tolyl-4-methoxylphenyl-selenide (3m)[1]

Yield: 0.111 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, J = 8.8 Hz, 2H); 7.26 (d, J = 8.0 Hz, 2H); 7.00 (d, J = 8.0 Hz, 2H); 6.79 (d, J = 8.8 Hz, 2H); 3.72 (s, 3H); 2.25 (s, 3H). RMN ^{13}C ($CDCl_3$ 100 MHz); δ (ppm): 159.4, 136.5, 135.6, 131.7, 129.9, 128.8, 120.8, 114.9, 55.1, 20.9. MS (relative intensity) *m*/*z*: 278 (65), 198 (100), 183 (43), 170 (33), 91 (32), 65 (22).

2-Tolyl-4-methoxylphenyl-selenide (3n)[1]

Yield: 0.111 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 8.8 Hz, 2H), 7.14-7.06 (m, 3H), 6.99-6.95 (m, 1H), 6.83 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.7, 137.8, 136.5, 133.8, 130.7, 129.9, 126.5, 119.2, 115.2, 55.2, 21.8. MS (relative intensity) *m*/*z*: 278 (71), 198 (100), 183 (37), 170 (30), 91 (26), 65 (24).

4-Chlorophenyl-4-methoxylphenyl-selenide (3o)[1]

Yield: 0.133 g (89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 8.8 Hz, 2H); 7.21 (d, J = 8.8

Hz, 2H); 7.14 (d, *J* = 8.8 Hz, 2H); 6.83 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); *δ* (ppm): 159.9, 136.6, 132.4, 132.0, 131.5, 129.1, 119.4, 115.2, 55.2. MS (relative intensity) *m*/*z*: 298 (35), 296 (17), 218 (100), 203 (40), 175 (27), 63 (12).

3-(Trifluoromethyl)phenyl-4-methoxylphenyl-selenide (3p)[6]

Yield: 0.131 g (79%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.55-7.50 (m, 3H), 7.42-7.23 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); *δ* (ppm): 160.3, 137.3, 135.1, 133.4, 131.4 (q, *J* = 32.2 Hz), 129.4, 126.7 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.8 Hz), 123.0 (q, *J* = 3.8 Hz), 118.5, 115.5, 55.3. MS (relative intensity) *m*/*z*: 332 (39), 252 (100), 237 (30), 209 (23), 63 (10).

1,2,3-(trimethyl)phenyl-4-methoxylphenyl-selenide (3q)[7]

Yield: 0.116 g (76%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 6.95 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.58 (s, 3H), 2.33 (s, 6H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); *δ* (ppm): 158.0, 143.2, 138.6, 130.6, 128.7, 127.8, 123.1, 114.8, 55.1, 24.2, 20.9. MS (relative intensity) *m*/*z*: 306 (100), 226 (54), 211 (22), 197 (78), 183 (18), 119 (25), 105 (12), 91 (40), 77 (25), 63 (8).

4-Methoxyphenyl-phenyl-telluride (4)[1]

Yield: 0.146 g (93%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.74 (d, *J* = 8.5 Hz, 2H), 7.57-7.53 (m, 2H), 7.18-7.15 (m, 3H), 6.78 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); *δ* (ppm): 160.0, 141.1, 136.4, 129.3, 127.2, 115.9, 115.5, 103.2, 55.1. MS (relative intensity) *m*/*z*: 314 (25), 184 (100), 169 (65), 77 (26), 63 (9), 51 (12).

4-Methoxyphenyl-phenyl-sulfide (5)[1]

Yield: 0.027 g (25%). ^{1}H NMR ($CDCl_3$, 200 MHz): *δ* 7.41 (d, *J* = 8.9 Hz, 2H); 7.26-7.09 (m, 5H); 6.89 (d, *J* = 8.9 Hz, 2H); 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); *δ* (ppm): 159.8, 138.5, 135.3, 128.9, 128.1, 125.7, 124.2, 114.9, 55.3. MS (relative intensity) m/z: 216 (100), 201 (60), 185 (8), 173 (9), 129 (19), 77 (13).

Recycle of Glycerol::

The aforementioned procedure was used with diphenyl diselenide **1a** (0.25 mmol), 4-methoxyphenylboronic acid **2a** (0.5 mmol), CuI (0.025 mmol; 0.0048g), DMSO (0.5 mmol) and glycerol (0.5 mL). After the reaction was complete, the reaction mixture was washed with a mixture of hexane/ethyl acetate (95:5) (3x 3 mL) and the upper organic phases were separated from glycerol. The product was isolated according procedure above. The resulting glycerol phase was dried under vacuum and reused for further reactions without previous purification.

References

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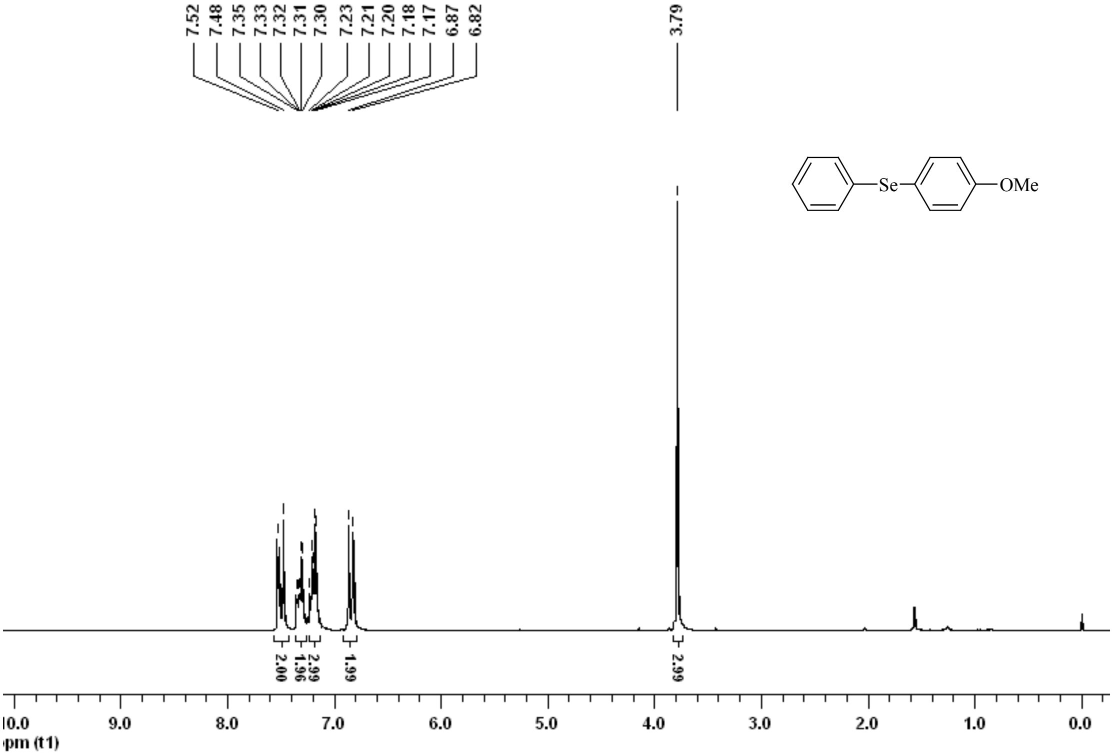
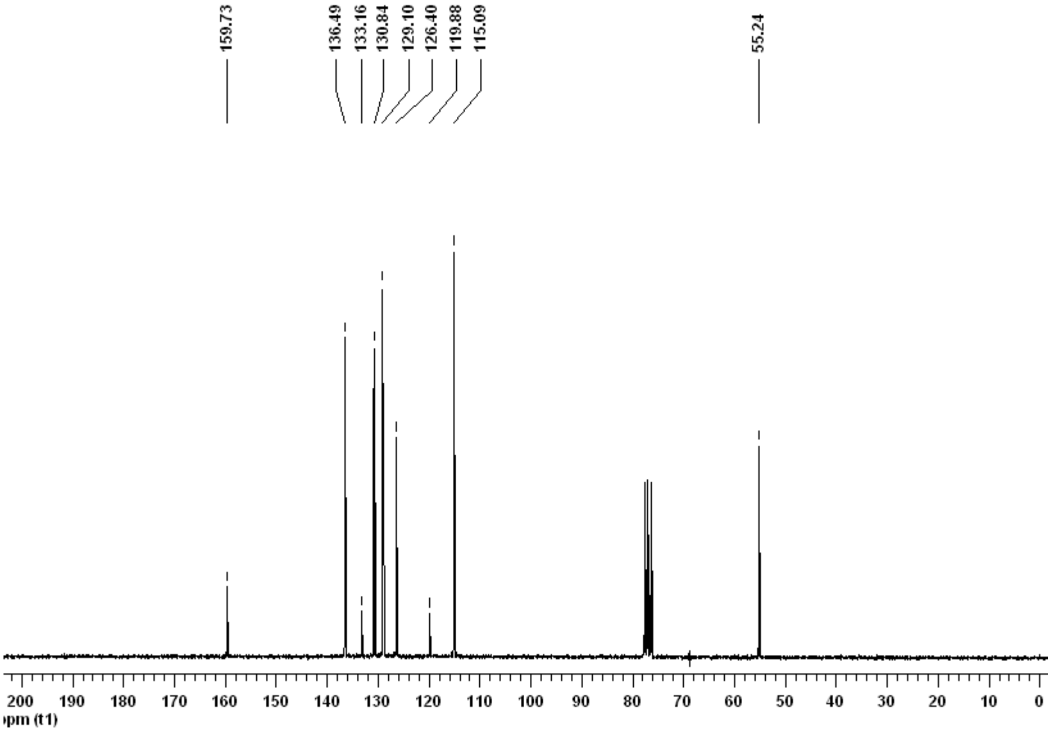
SELECTED SPECTRA



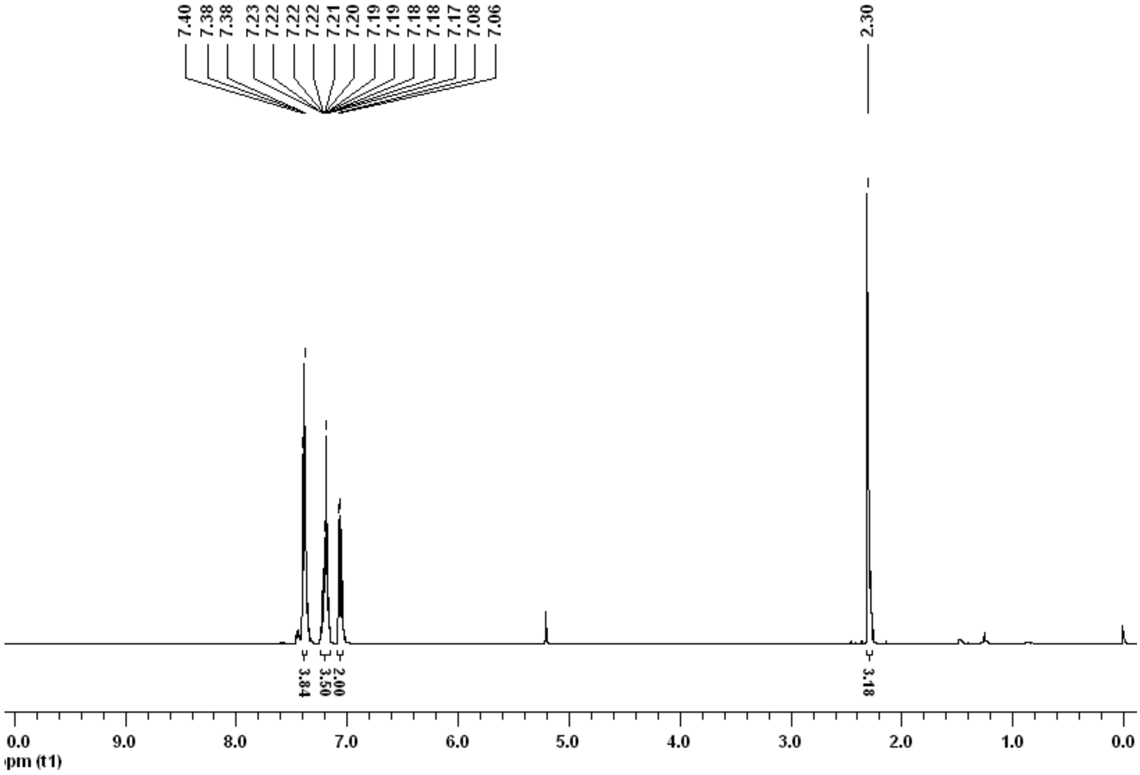
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of *4-Methoxyphenyl-phenyl-selenide* ***(3a)***



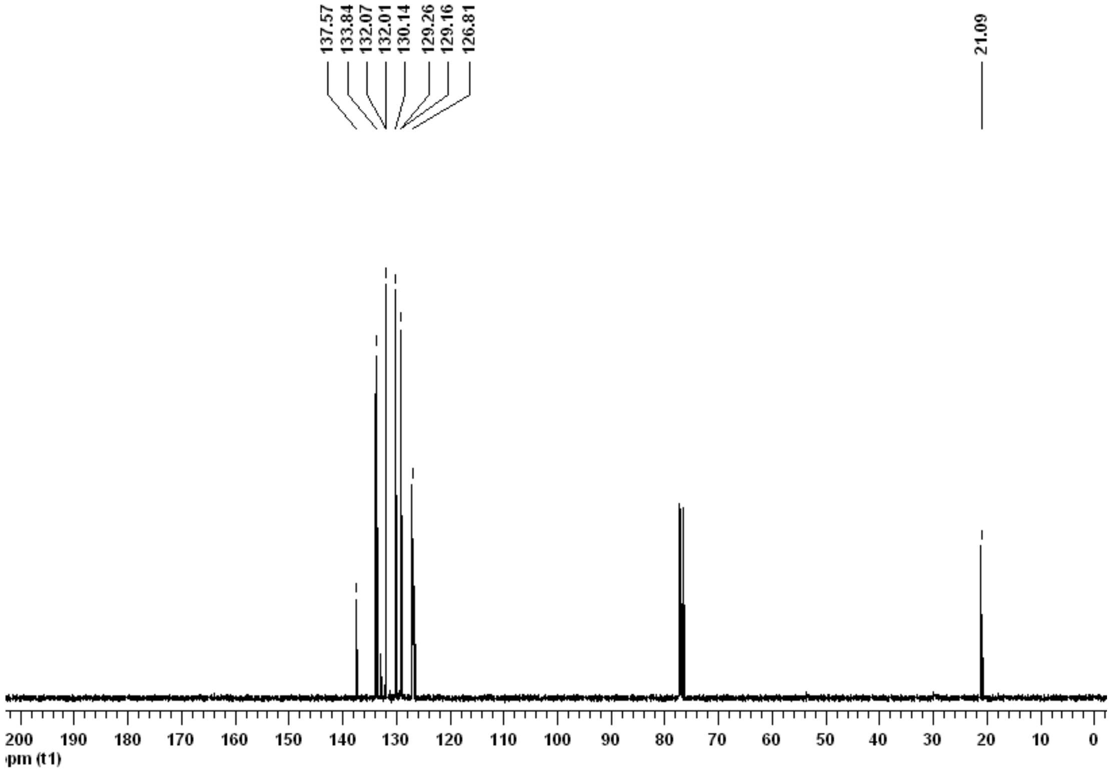
^{13}C NMR (100 MHz, CDCl$_3$) spectrum of *4-Methoxyphenyl-phenyl-selenide* ***(3a)***

^{1}H NMR (200 MHz, $CDCl_3$) spectrum of *2-Methoxyphenyl-phenyl-selenide* ***(3b)***

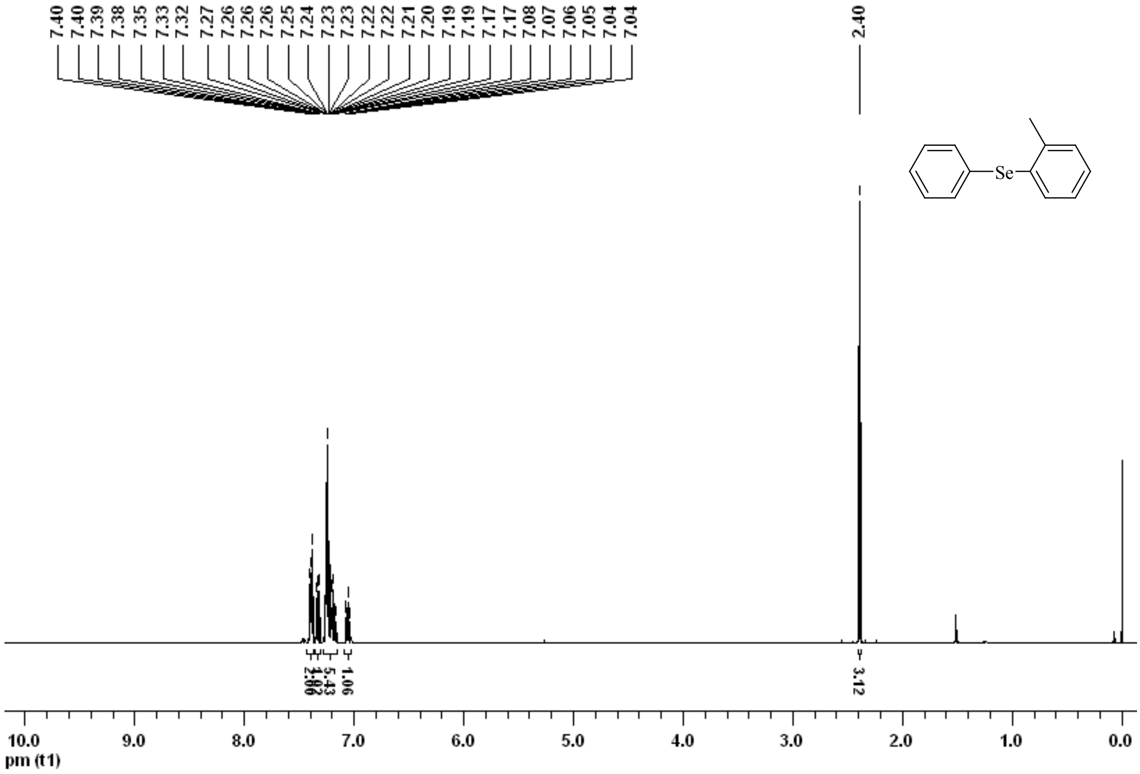
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *2-Methoxyphenyl-phenyl-selenide* ***(3b)***



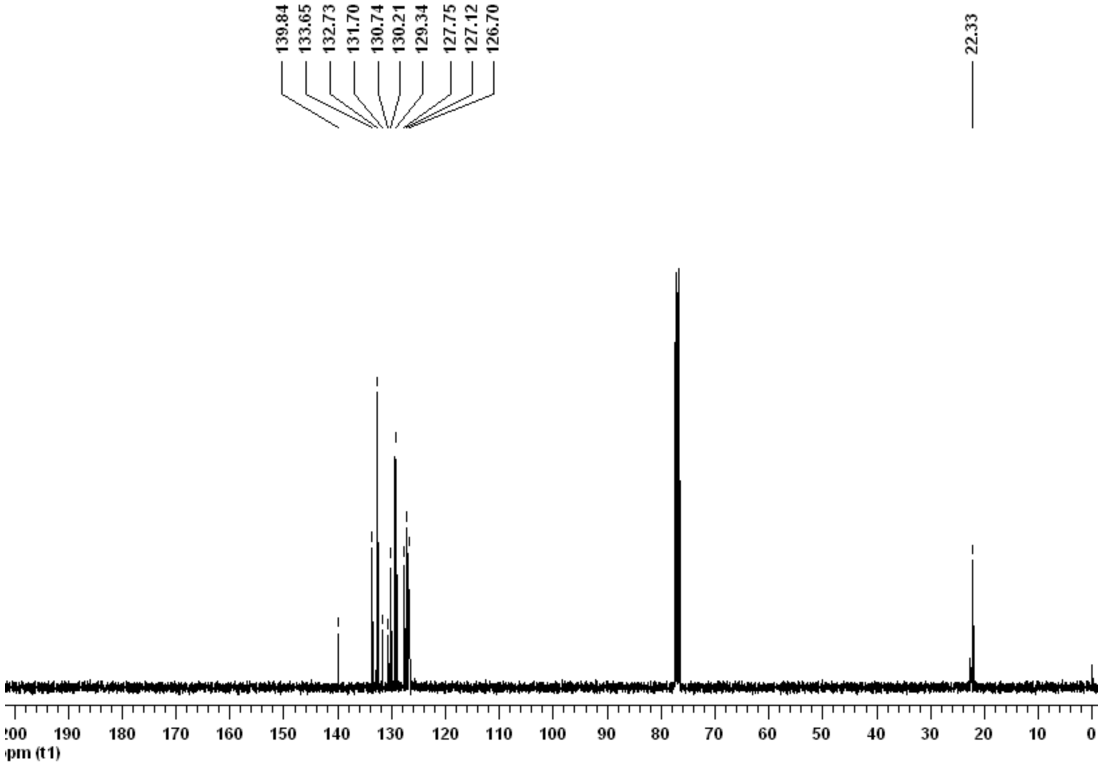
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of *4-Tolyl-phenyl-selenide* ***(3c)***



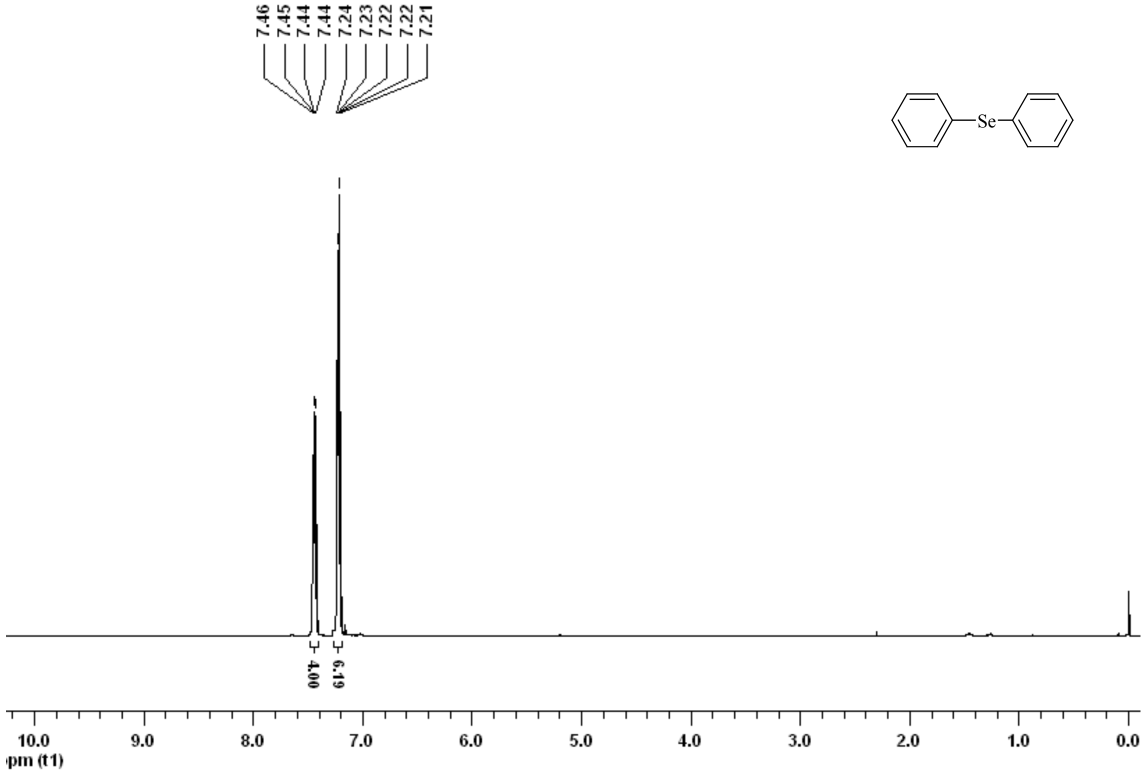
^{13}C NMR (100 MHz, CDCl$_3$) spectrum of *4-Tolyl-phenyl-selenide* ***(3c)***



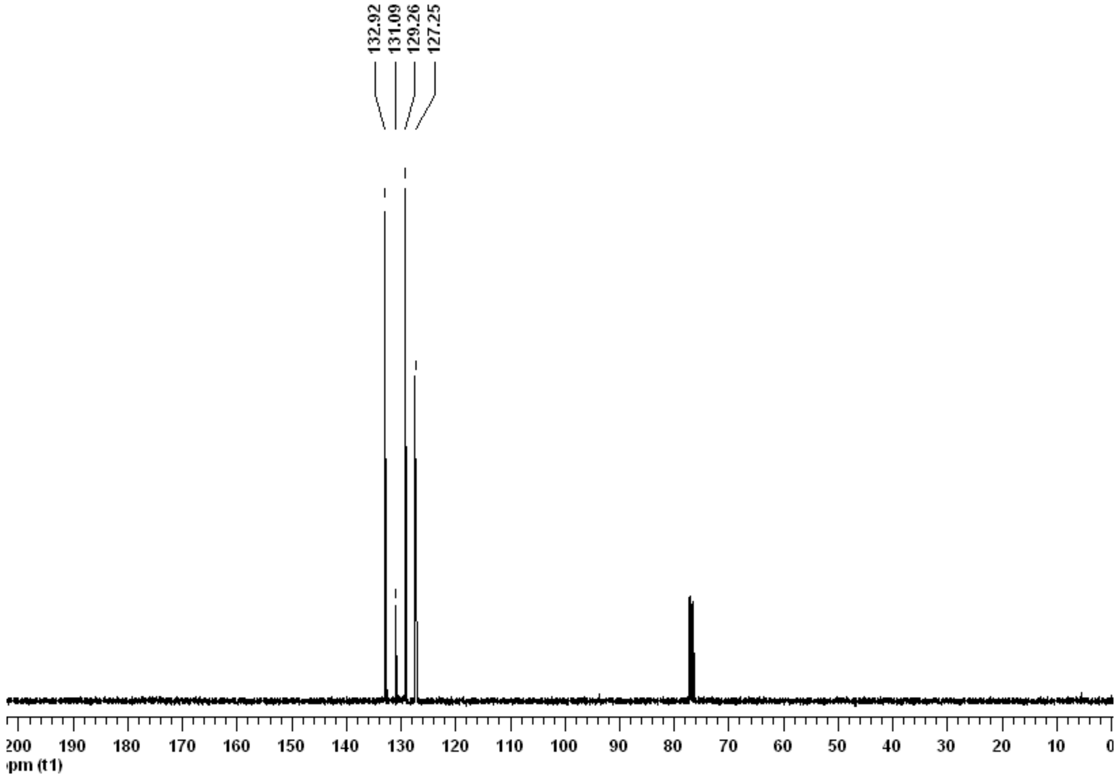
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *2-Tolyl-phenyl-selenide* ***(3d)***



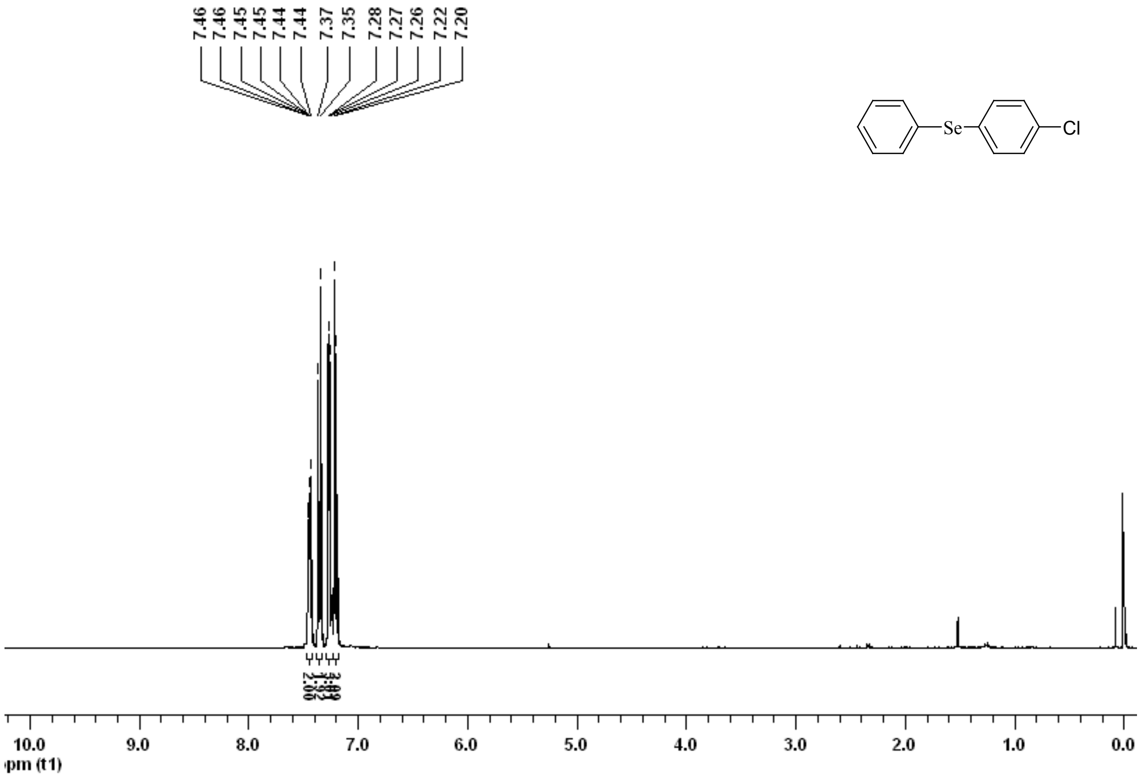
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *2-Tolyl-phenyl-selenide* ***(3d)***



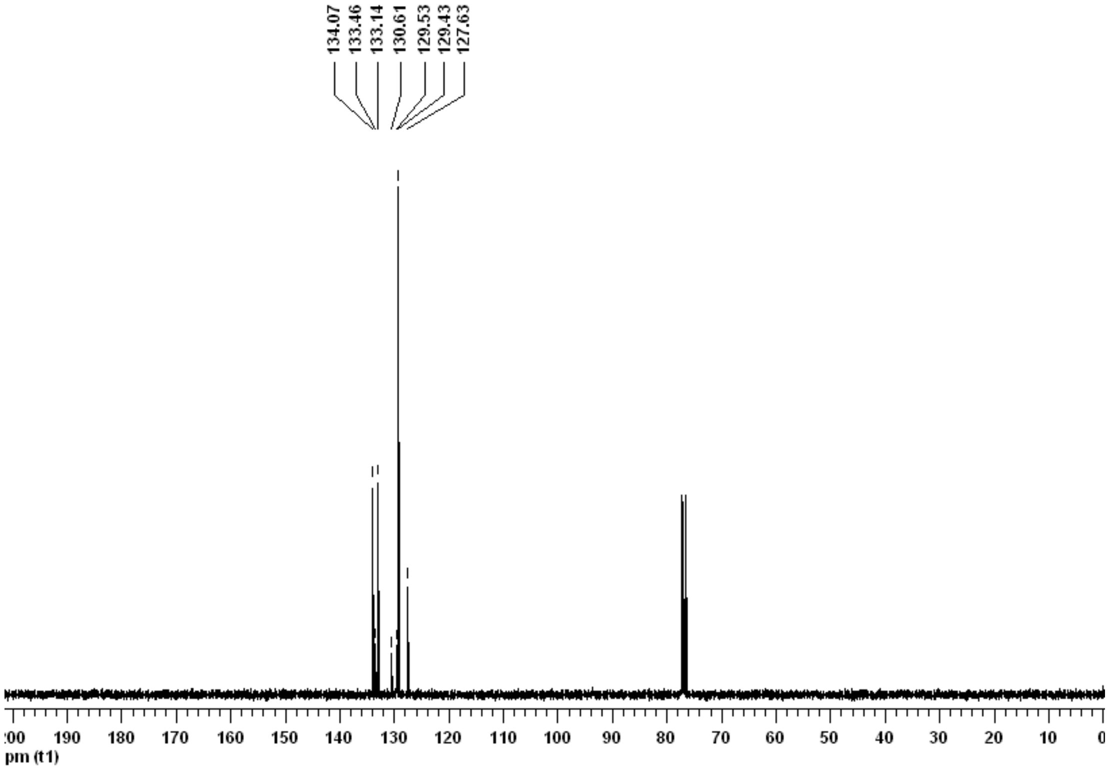
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of *diphenyl-selenide* ***(3e)***



^{13}C NMR (100 MHz, CDCl$_3$) spectrum of *diphenyl-selenide* ***(3e)***



^{1}H NMR (400 MHz, CDCl$_3$) spectrum of *4-Chlorophenyl-phenyl-selenide* ***(3f)***



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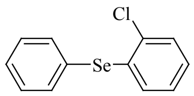
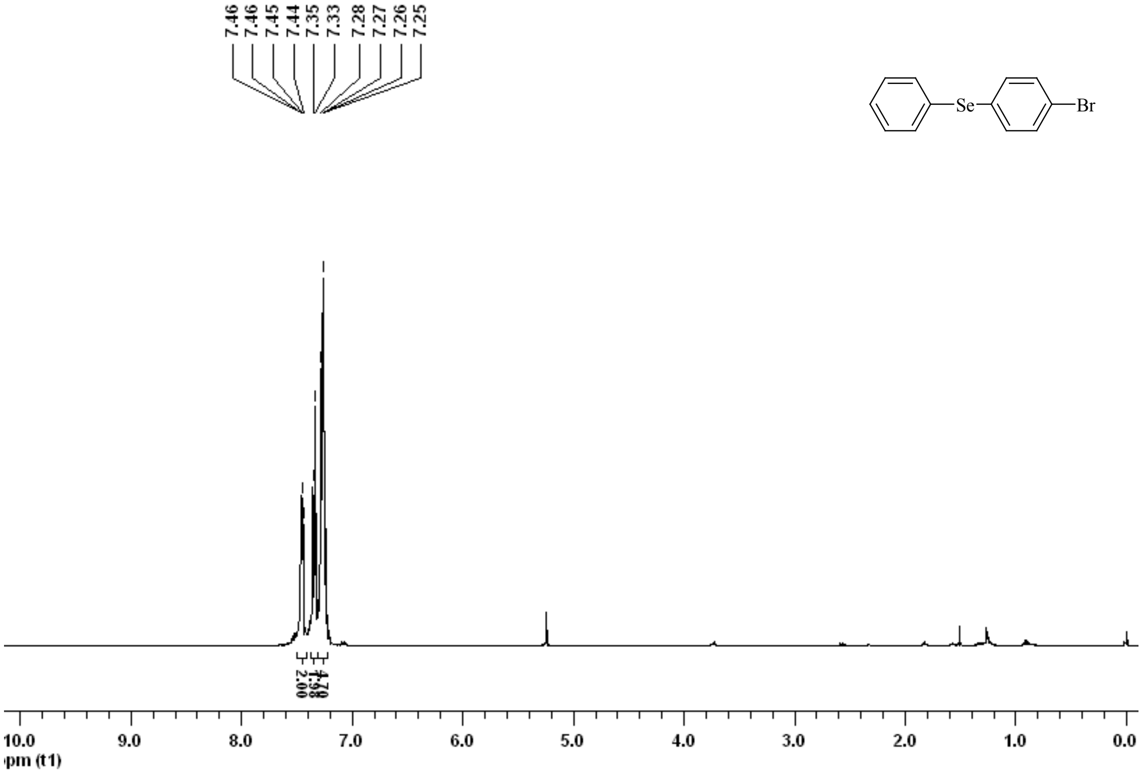
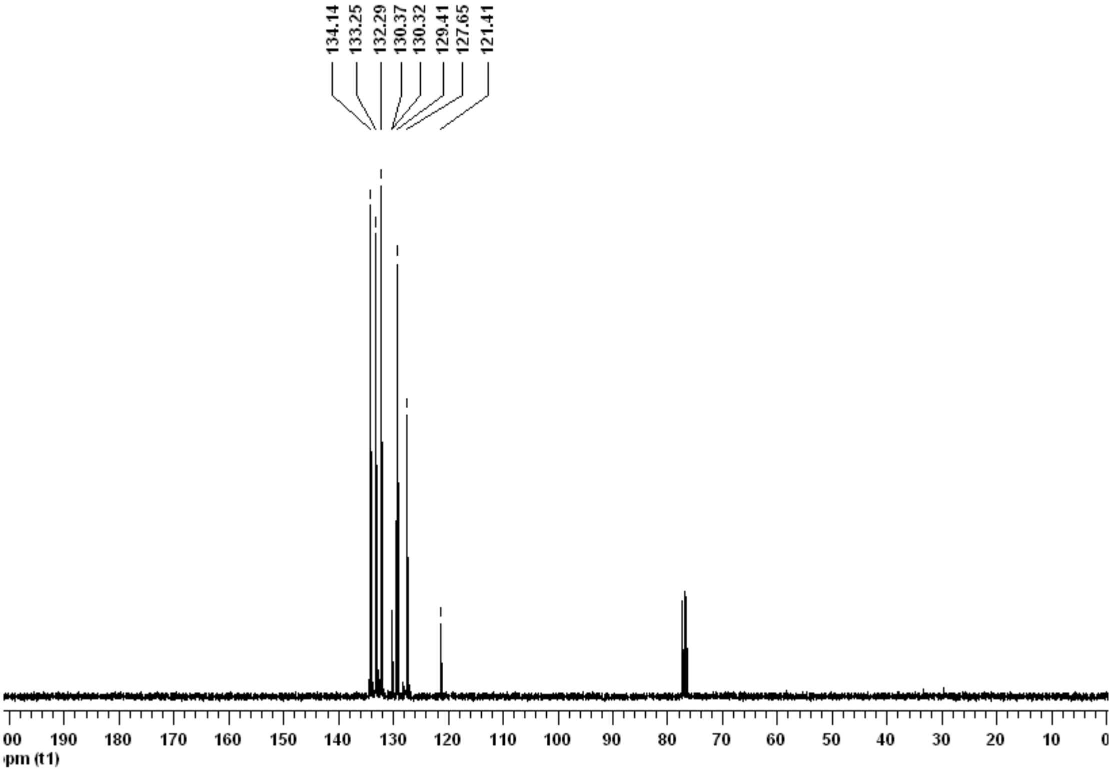


^{1}H NMR (200 MHz, $CDCl_3$) spectrum of *2-Chlorophenyl-phenyl-selenide* ***(3g)***

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *2-Chlorophenyl-phenyl-selenide* ***(3g)***



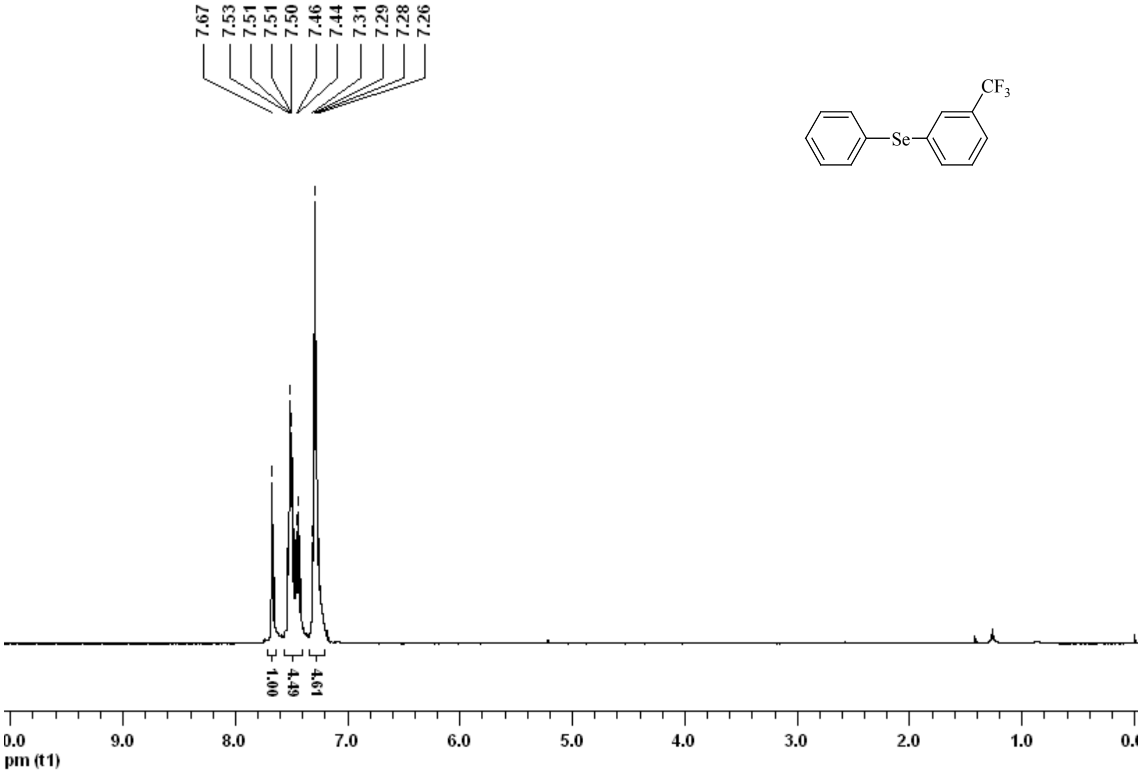
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *4-Bromophenyl-phenyl-selenide* ***(3h)***



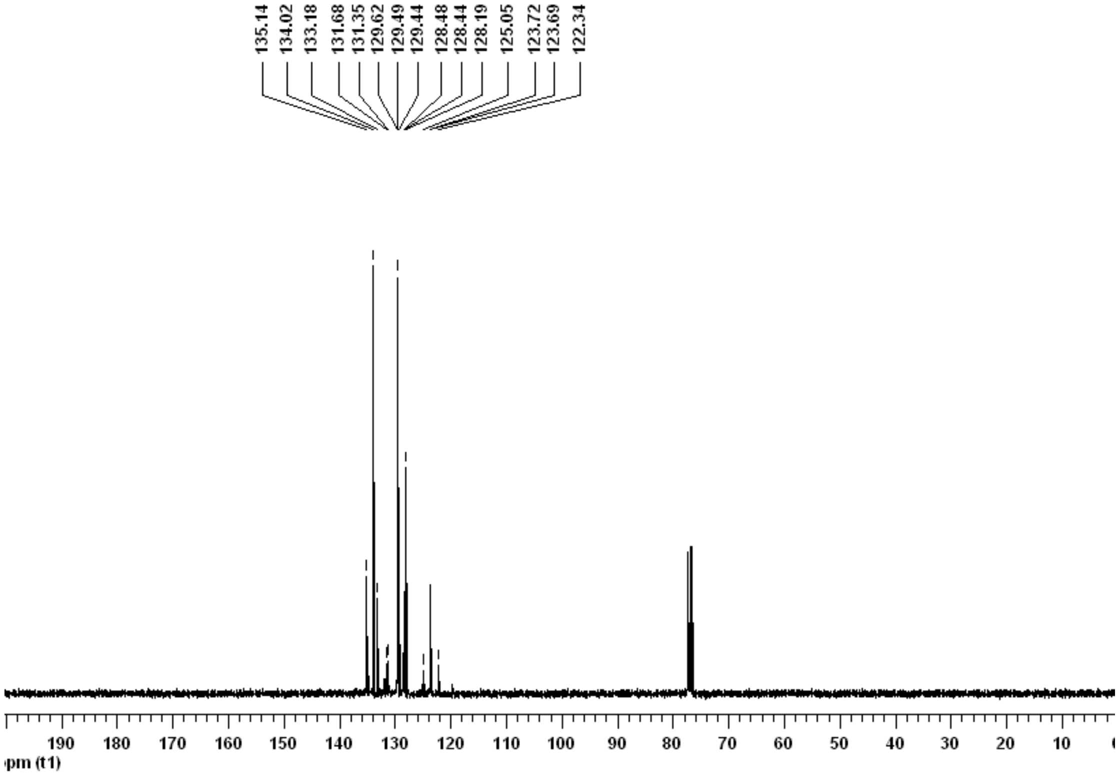
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *4-Bromophenyl-phenyl-selenide* ***(3h)***

^{1}H NMR (200 MHz, $CDCl_3$) spectrum of *2-Bromophenyl-phenyl-selenide* ***(3i)***

^{13}C NMR (50 MHz, $CDCl_3$) spectrum of *2-Bromophenyl-selenide* ***(3i)***



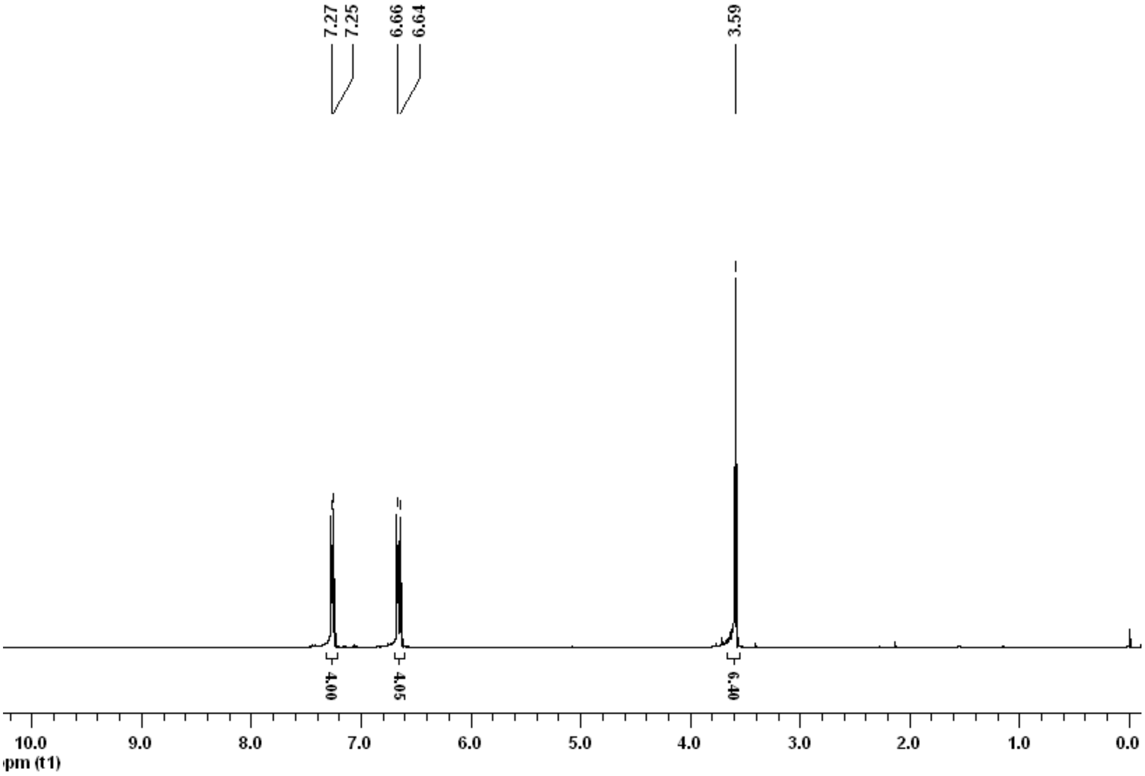
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *3-(trifluoromethyl)phenyl-phenyl-selenide* ***(3j)***



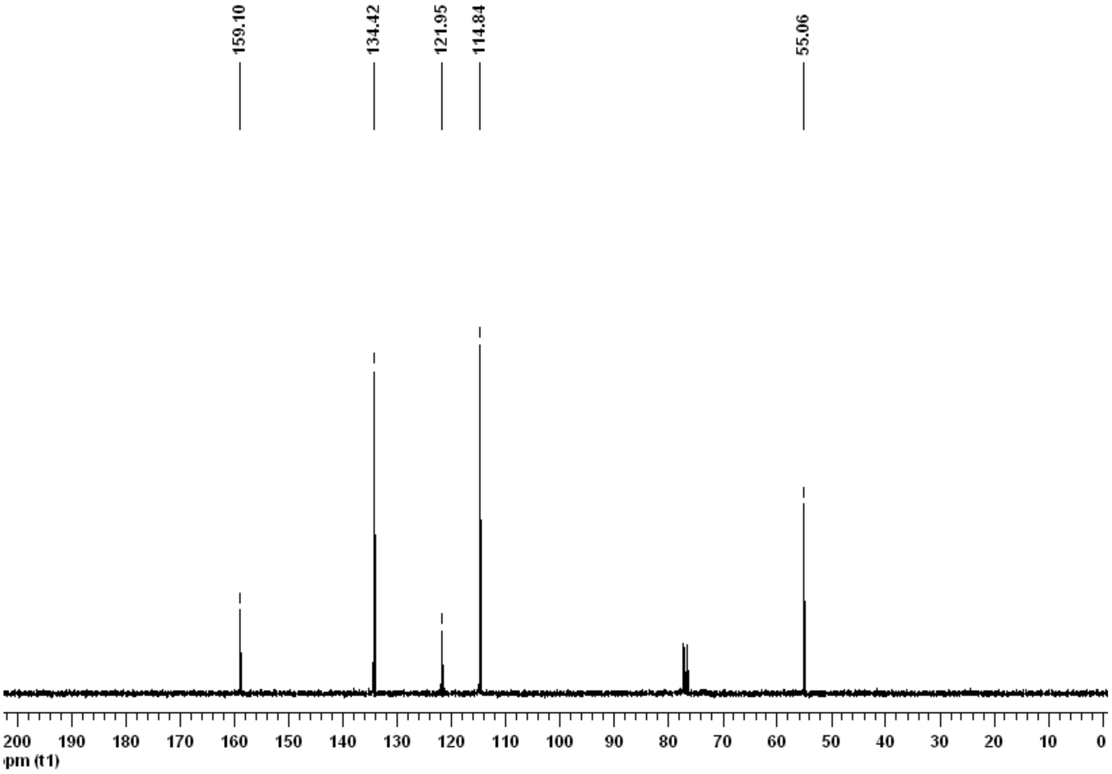
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *3-(trifluoromethyl)phenyl-phenyl-selenide* ***(3j)***

^{1}H NMR (200 MHz, $CDCl_3$) spectrum of *2-Naphthyl-phenyl-selenide* ***(3k)***

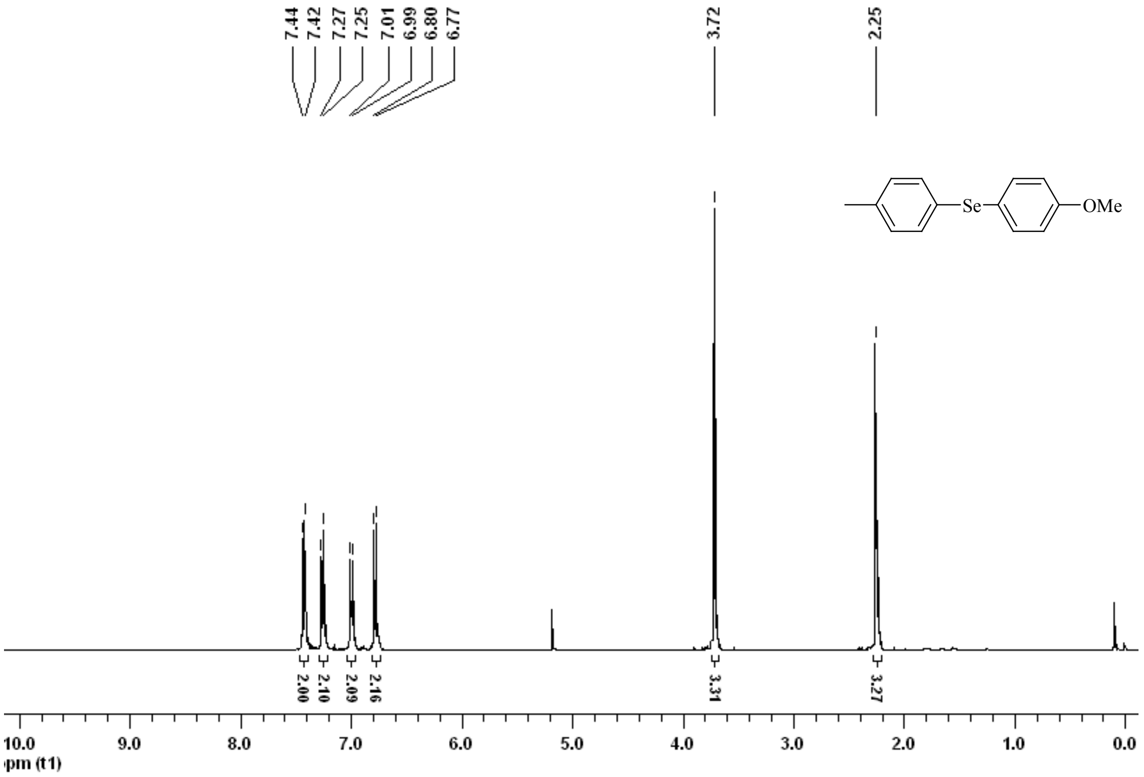
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of *2-Naphthyl-phenyl-selenide* ***(3k)***



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Bis-4-methoxylphenyl-selenide **(3l)***



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Bis-4-methoxylphenyl-selenide **(3l)***



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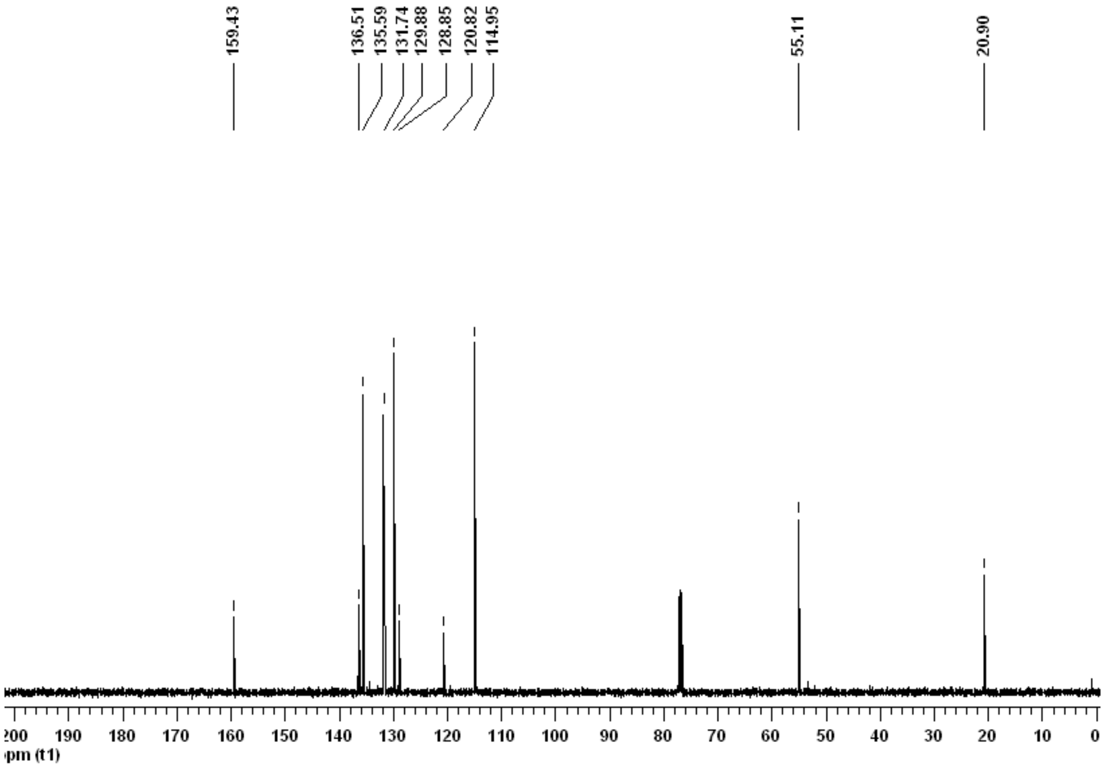
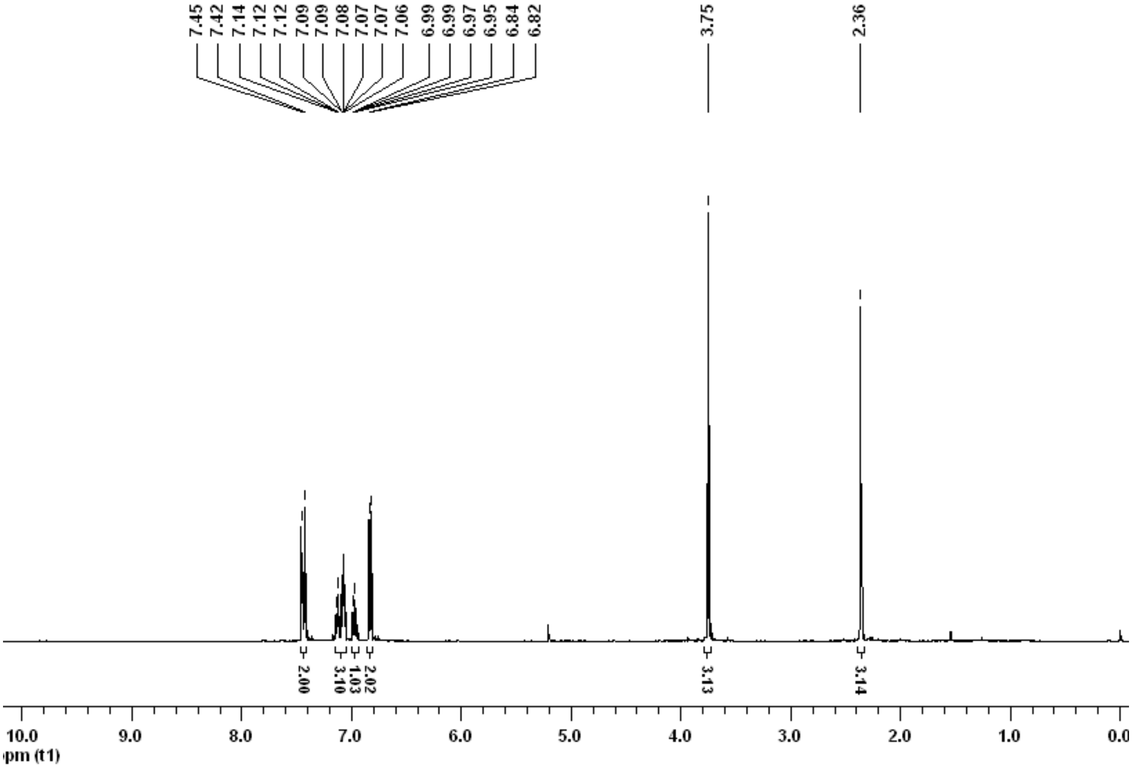
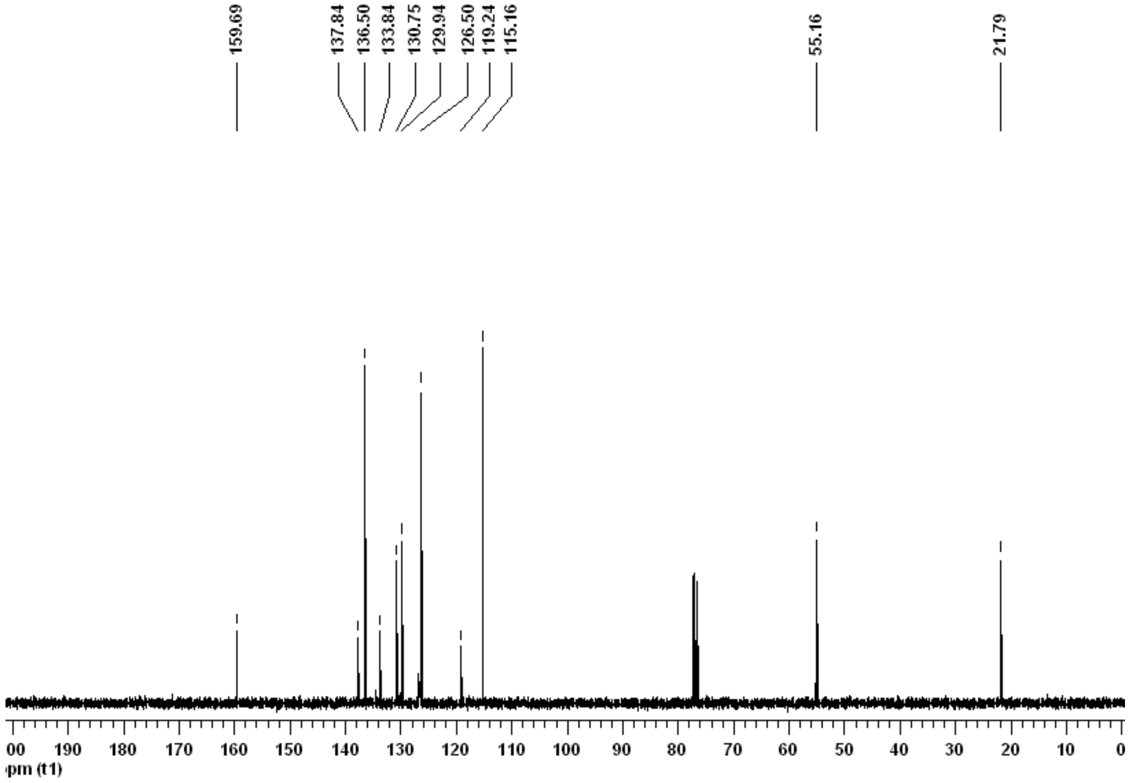


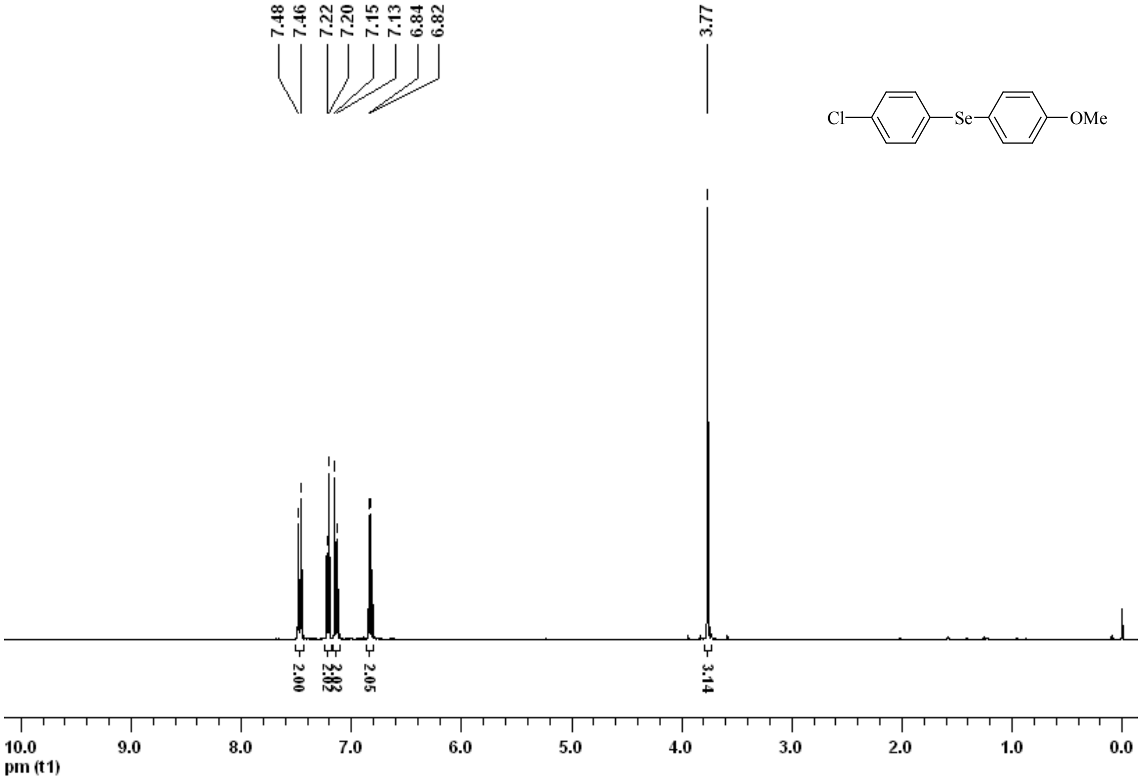
^{13}C NMR (100 MHz, CDCl$_3$) spectrum of *4-Tolyl-4-methoxylphenyl-selenide **(3m)***



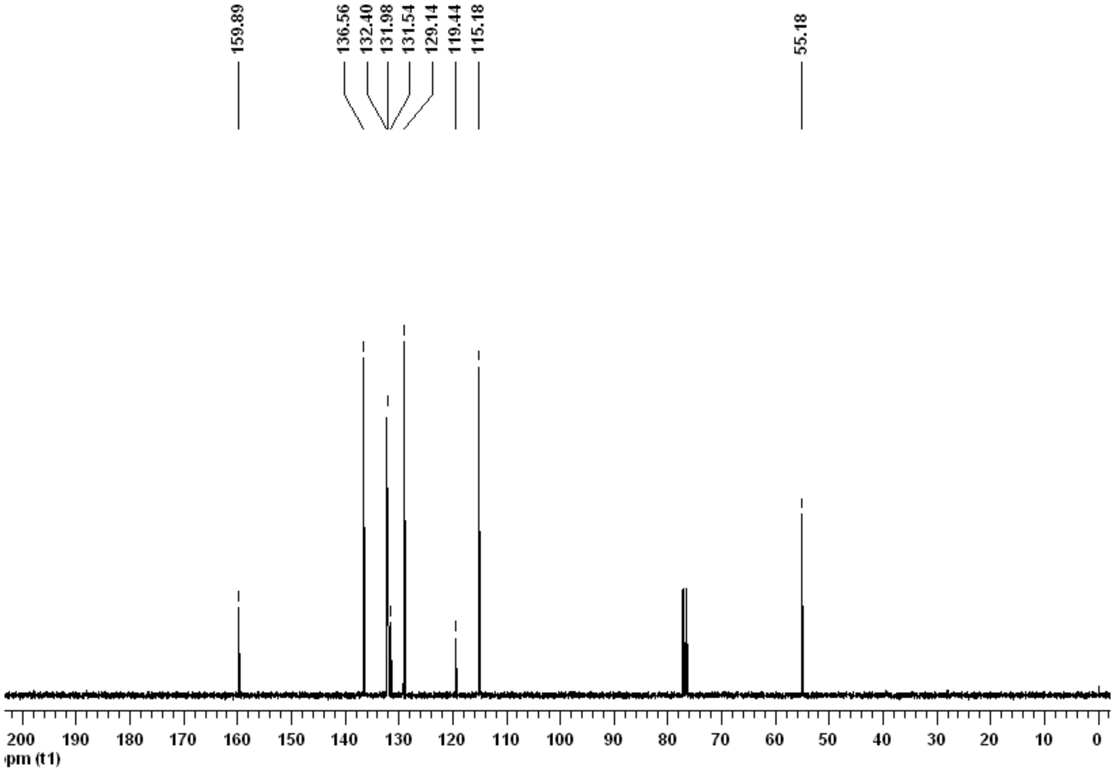
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *2-Tolyl-4-methoxylphenyl-selenide* ***(3n)***



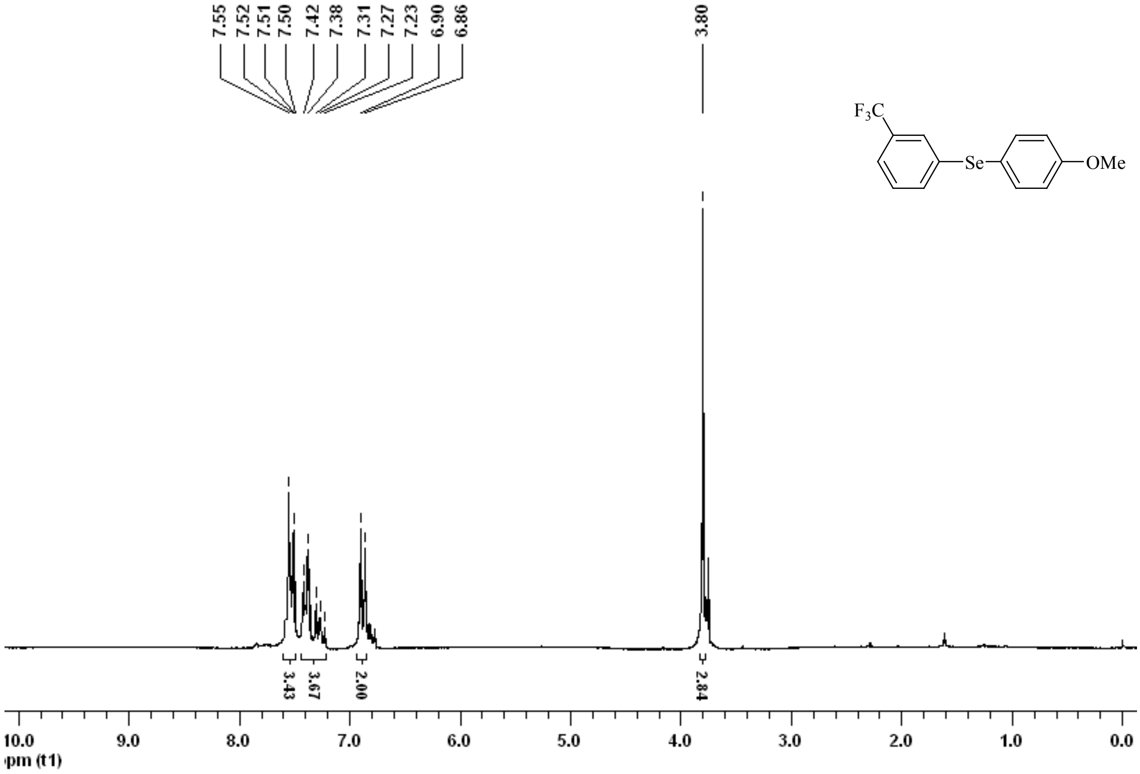
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *2-Tolyl-4-methoxylphenyl-selenide* ***(3n)***



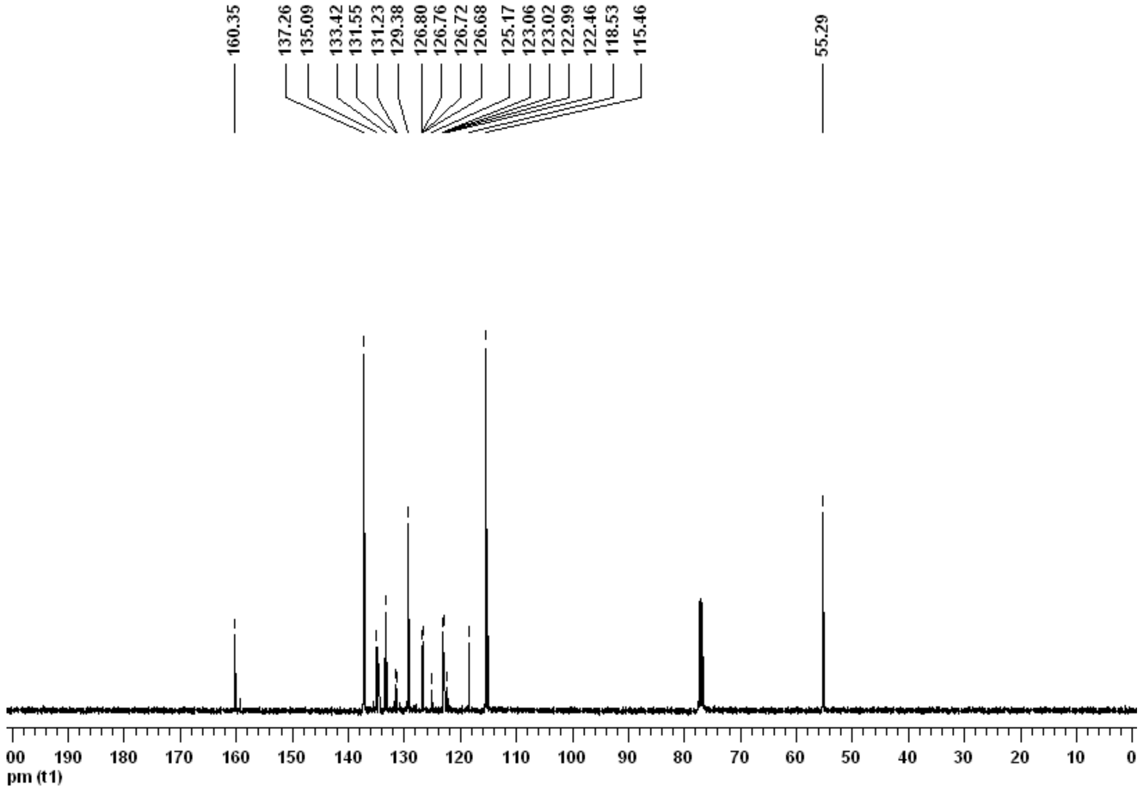
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *4-Chlorophenyl-4-methoxylphenyl-selenide* ***(3o)***



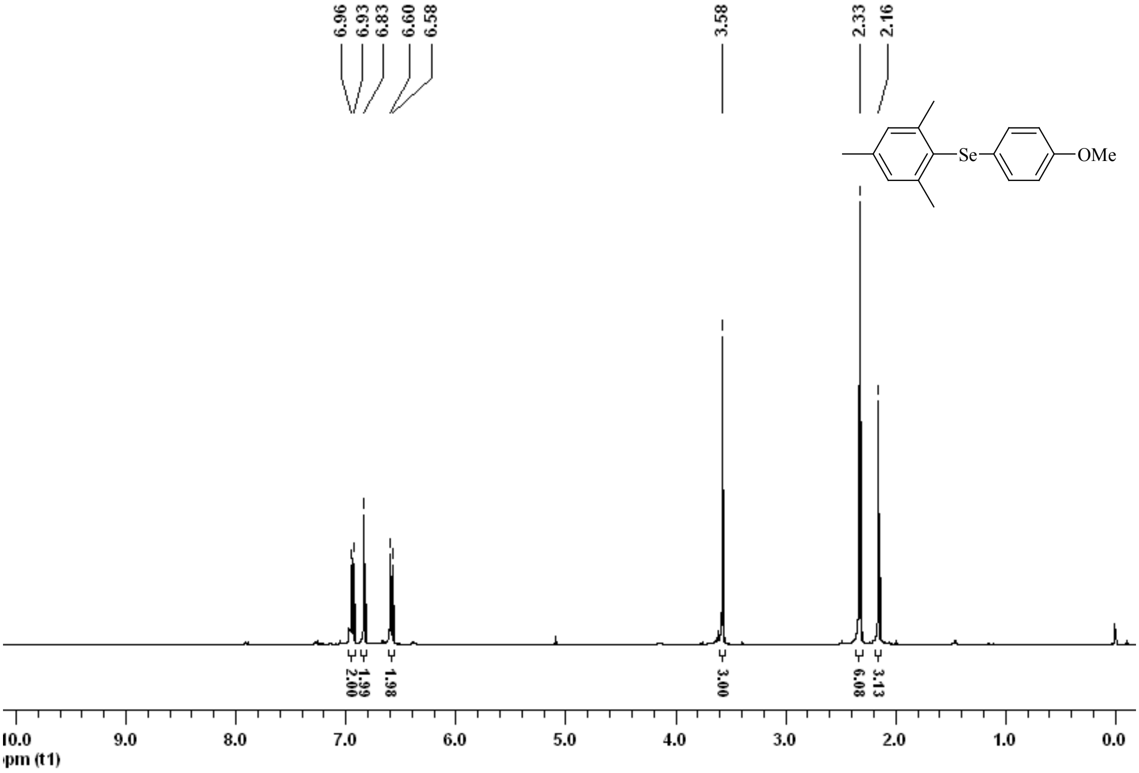
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *4-Chlorophenyl-4-methoxylphenyl-selenide* ***(3o)***



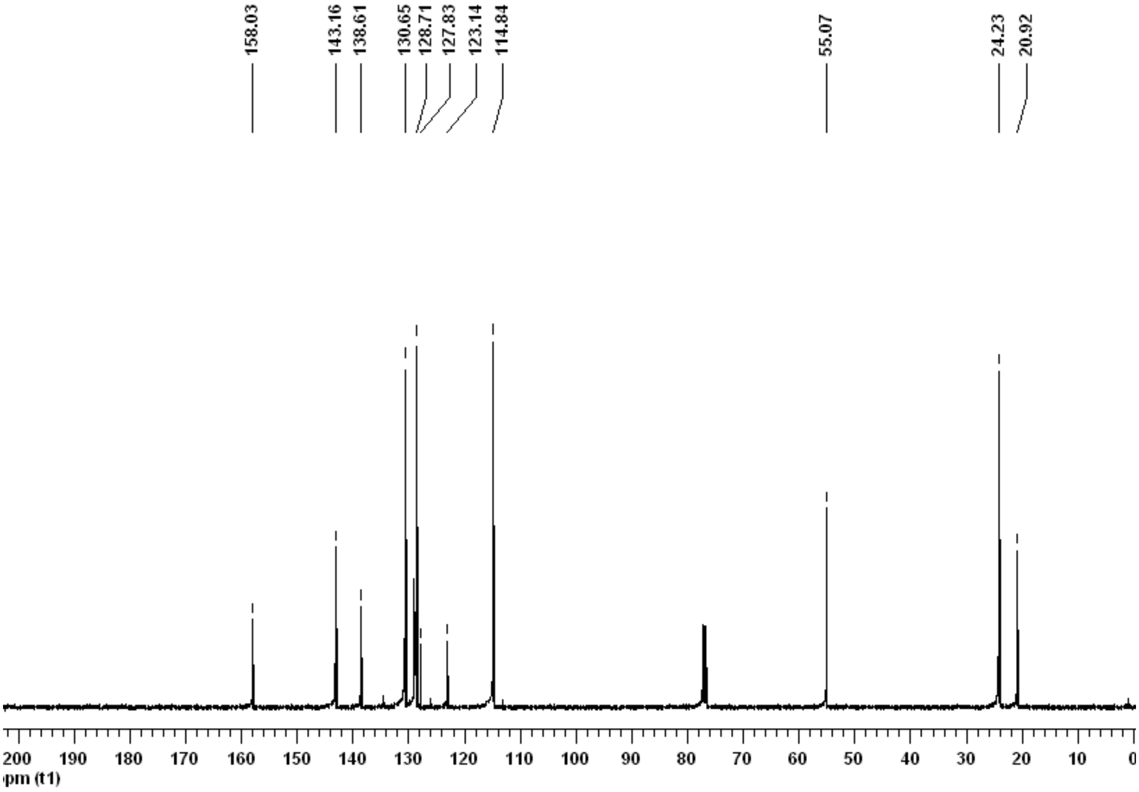
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *3-(trifluoromethyl)phenyl-4-methoxylphenyl-selenide* ***(3p)***



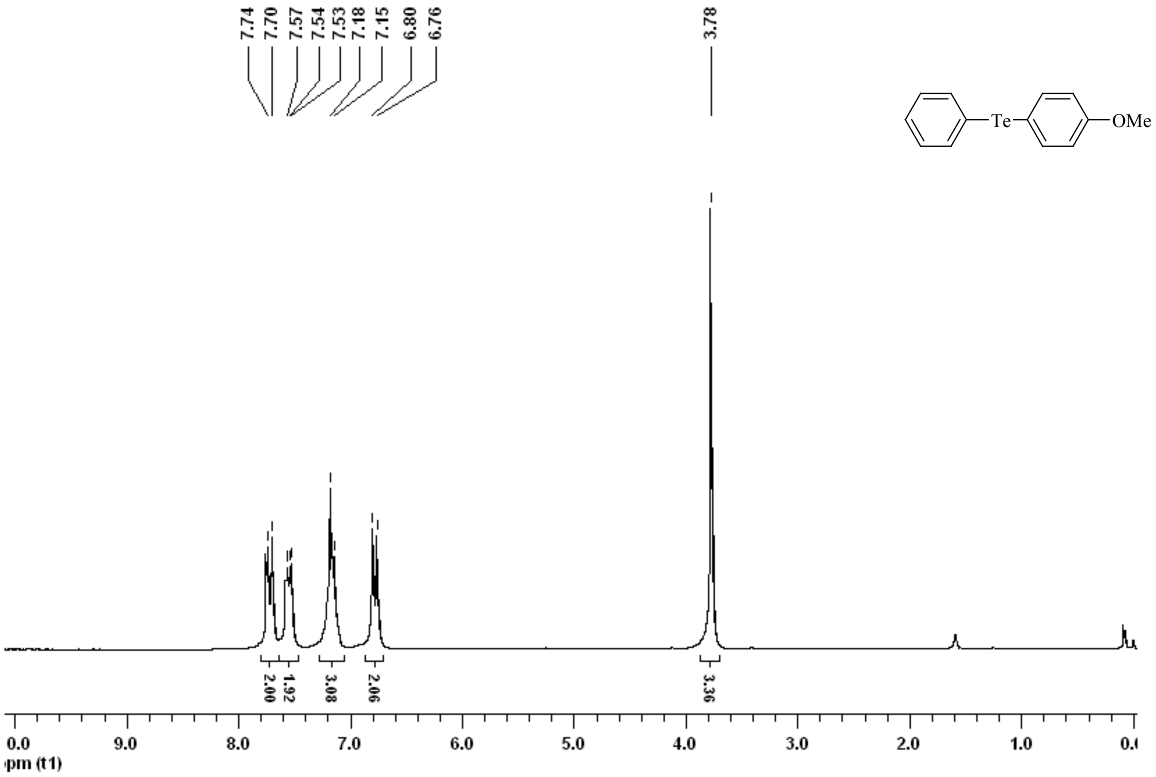
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *3-(trifluoromethyl)phenyl-4-methoxylphenyl-selenide* ***(3p)***



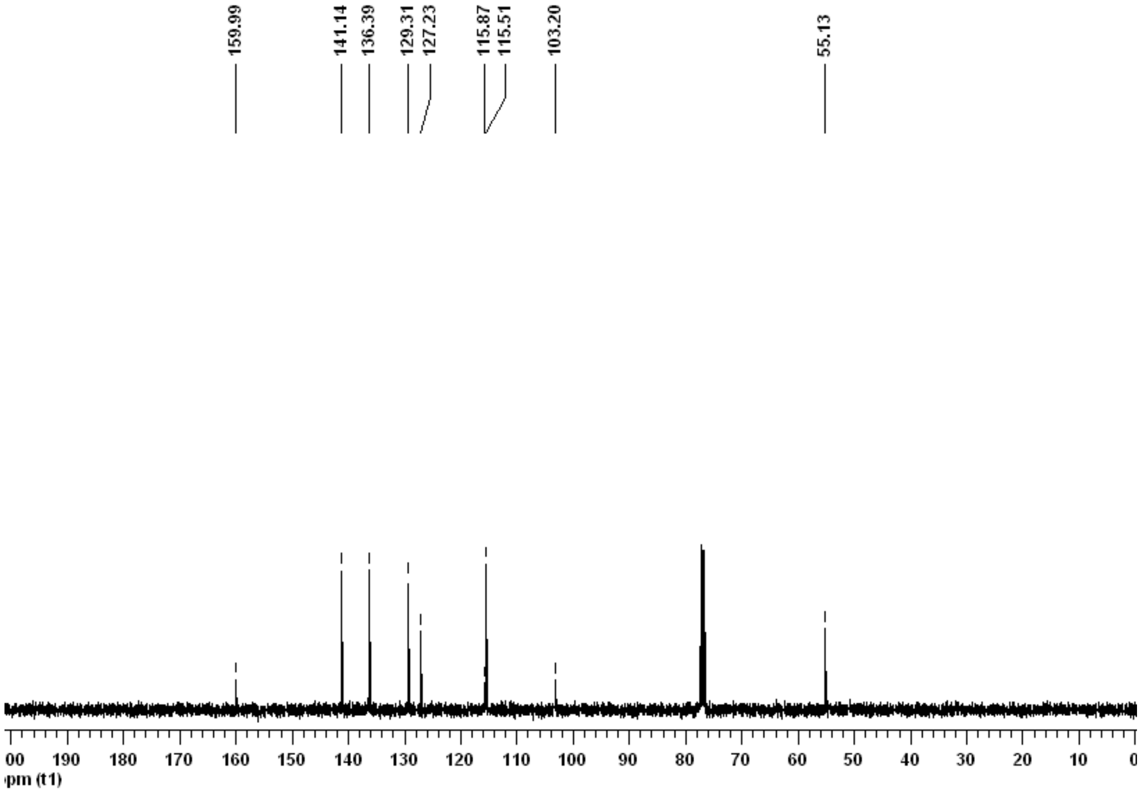
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of *1,2,3-(trimethyl)phenyl-4-methoxylphenyl-selenide* ***(3q)***



^{13}C NMR (100 MHz, CDCl$_3$) spectrum of *1,2,3-(trimethyl)phenyl-4-methoxylphenyl-selenide* ***(3q)***



^{1}H NMR (400 MHz, CDCl$_3$) spectrum of *4-methoxylphenyl-phenyl-telluride* ***(4)***



^{13}C NMR (100 MHz, CDCl$_3$) spectrum of *4-methoxylphenyl-phenyl-telluride* ***(4)***

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *4-methoxylphenyl-phenyl-sufide* ***(5)***

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^{3}C NMR (100 MHz, $CDCl_3$) spectrum of *4-methoxylphenyl-phenyl-sufide* ***(5)***