# Synthesis of Diaryl Selenides using Electrophilic Selenium Species and Nucleophilic Boron Reagents in Ionic Liquids

Camilo S. Freitas,[a] Angelita M. Barcellos,[a] Vanessa G. Ricordi,[a] Jesus M. Pena,[b] Gelson Perin,[a] Raquel G. Jacob,[a] Eder J. Lenardão[a,*] and Diego Alves [a,*]

[a] Laboratório de Síntese Orgânica Limpa - LASOL - Universidade Federal de Pelotas - UFPel - P.O. Box 354, 96010-900, Pelotas - RS – Brazil; Tel: +55 (53) 3275-7533.

[b] Universidade de São Paulo - USP, São Paulo-SP – Brazil.

e-mail: diego.alves@ufpel.edu.br and lenardao@ufpel.edu.br

## Contents

**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. Baker silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. 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 $\delta$ ppm relative to $(CH_3)_4Si$ for $^1H$ and $CDCl_3$ for $^{13}C$ NMR. Hidrogen coupling patterns are described as singlet (s), doublet (d), double doublet (dd), triplet (t), quartet (q), quintet (qui), sextet (sex), multiplet (m), and broad (br). Coupling constants (*J*) are reported in Hertz. Mass spectra (MS) were measured on a Shimadzu GCMS-QP2010 mass spectrometer. Microwave reactions were conducted using a CEM Discover, mode operating systems working at 2.45 GHz, with a power programmable from 1 to 300 W.

**General procedure for the reaction of electrophilic selenium species with nucleophilic boron reagents:**

In a Schlenk tube under nitrogen atmosphere containing ionic liquid ([bmim][$PF_6$] or [bmim][$BF_4$]) (0.6 mL) and nucleophilic boron reagent [$ArB(OH)_2$ or $ArBF_3K$] (0.3 mmol), the corresponding arylselenium halide (ArSeCl or ArSeBr) (0.3 mmol) was added in one portion. The reaction mixture was allowed to stir at room temperature for the time indicated in Table 2 and 4. After the reaction was complete, the products were extracted into diethyl ether (3× 5 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatography on silica gel using ethyl acetate/hexanes as the eluent.

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

$^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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]

$^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 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, $CDCl_3$); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.46-7.44 (m, 4H); 7.24-7.21 (m, 6H). RMN $^{13}$C ($CDCl_3$ 100 MHz); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 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); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 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); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.67 (s, 1H); 7.53-7.44 (m, 4H); 7.31-7.26 (m, 4H). RMN $^{13}$C ($CDCl_3$ 100 MHz); $\delta$ (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]

$^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 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, $CDCl_3$); $\delta$ (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).

**4-Tolyl-4-methoxylphenyl-selenide (3l)**[1]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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 (3m)**[1]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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).

**Bis-4-methoxylphenyl-selenide (3n)**[5]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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-Chlorophenyl-4-methoxylphenyl-selenide (3o)**[1]

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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).

**1,2,3-(trimethyl)phenyl-4-methoxylphenyl-selenide (3p)**

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $\delta$ (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). HRMS calcd for $C_{16}H_{18}OSe$: 306.0523. Found: 306.0528.

**2-Pyridyl-4-methoxylphenyl-selenide (3q)**

$^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 8.41 (ddd, $J$ = 4.9, 1.9, 0.8 Hz, 1H); 7.63 (d, $J$ = 8.9 Hz, 2H); 7.36 (ddd, $J$ = 7.5, 4.9, 1.9 Hz, 1H); 7.01-6.88 (m, 4H), 3.83 (s, 3H). $^{13}$C NMR ($CDCl_3$ 50 MHz); $\delta$ (ppm): 160.3, 159.8, 149.6, 138.2, 136.5, 123.3, 120.0, 117.6, 115.3, 55.2. MS (relative intensity) *m*/*z*: 265 (68), 264 (100), 262 (63), 249 (21), 185 (25), 142 (15), 78 (59), 51 (32). HRMS calcd for $C_{12}H_{11}NOSe$: 265.0006. Found: 265.0011.

**General procedure to microwave reactions of phenylselenium chloride 1a with arylboronic acids in [bmim][$PF_6$]:**

In a 10 mL glass vial, under nitrogen atmosphere, equipped with a small magnetic stirring bar, containing the appropriate arylboronic acid (0.3 mmol) and [bmim][$PF_6$] (0.6 mL) was added PhSeCl **1a** (0.3 mmol). The mixture was then irradiated in a focused microwaves reactor (CEM Explorer) at 50 °C, using an irradiation power of 50 W. After stirring for 10 minutes, the products were extracted into diethyl ether (3× 5 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatography on silica gel

using ethyl acetate/hexanes as the eluent.

**Recycle of [bmim][$PF_6$] in the reaction of phenylselenium chloride 1a with arylboronic acid 2a:**

In a Schlenk tube under nitrogen atmosphere containing ionic liquid [bmim][$PF_6$] (0.6 mL) and 4-methoxyphenylboronic acid **2a** (0.3 mmol), phenylselenium chloride **1a** (0.3 mmol) was added in one portion. The reaction mixture was allowed to stir at room temperature for 2 hours. After the reaction was complete, the products were extracted into diethyl ether (3× 5 mL), dried over $MgSO_4$, and concentrated under vacuum. The inferior, ionic liquid phase, was separated and dried under vacuum. The recovered [bmim][$PF_6$] was used directly in the next cycle.

**References**

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[3] A. Saha, D. Saha and B. C. Ranu, *Org. Biomol. Chem.*, 2009, **7**, 1652.

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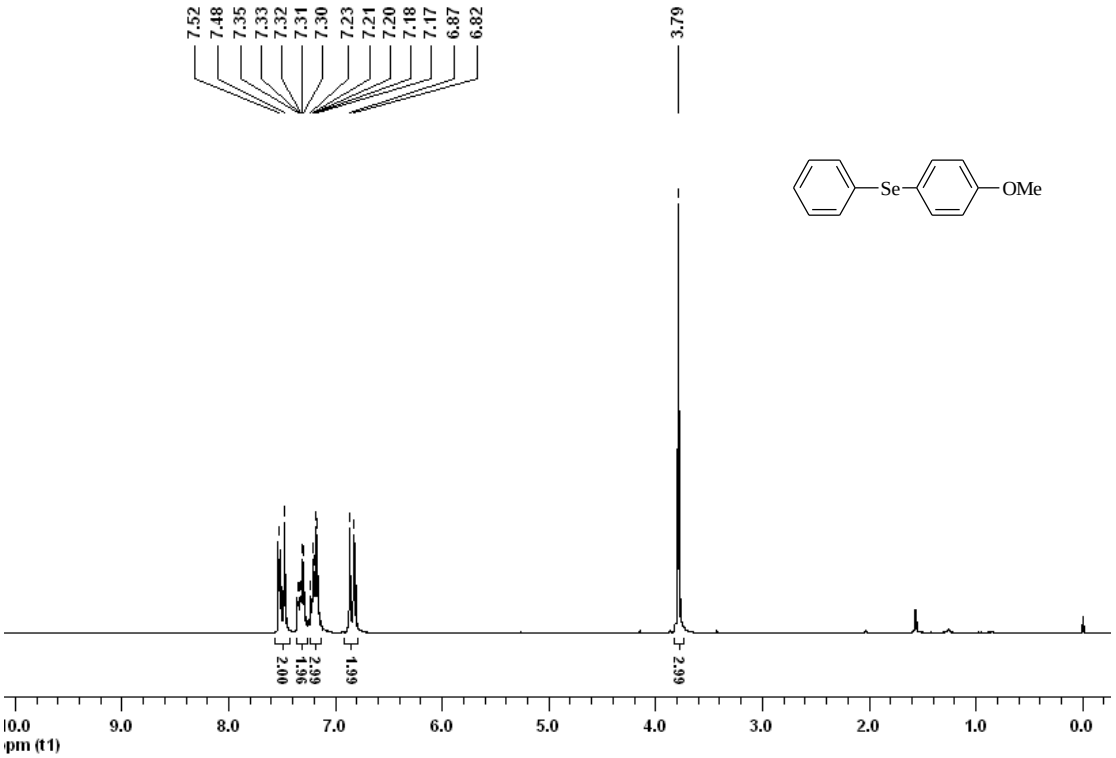
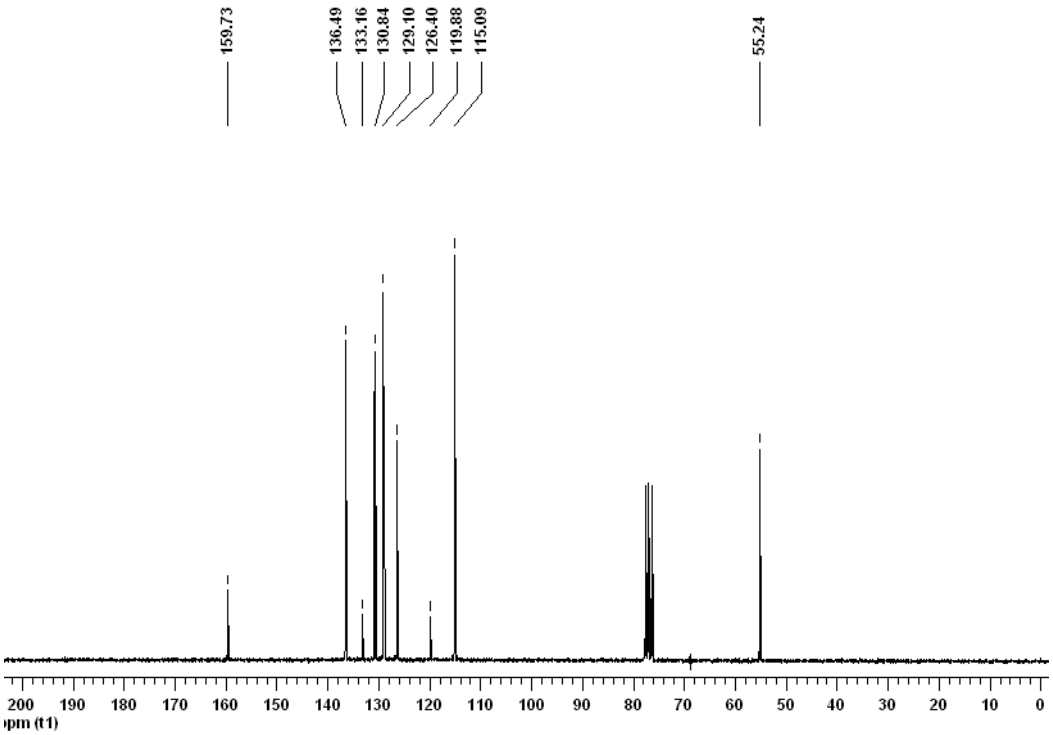
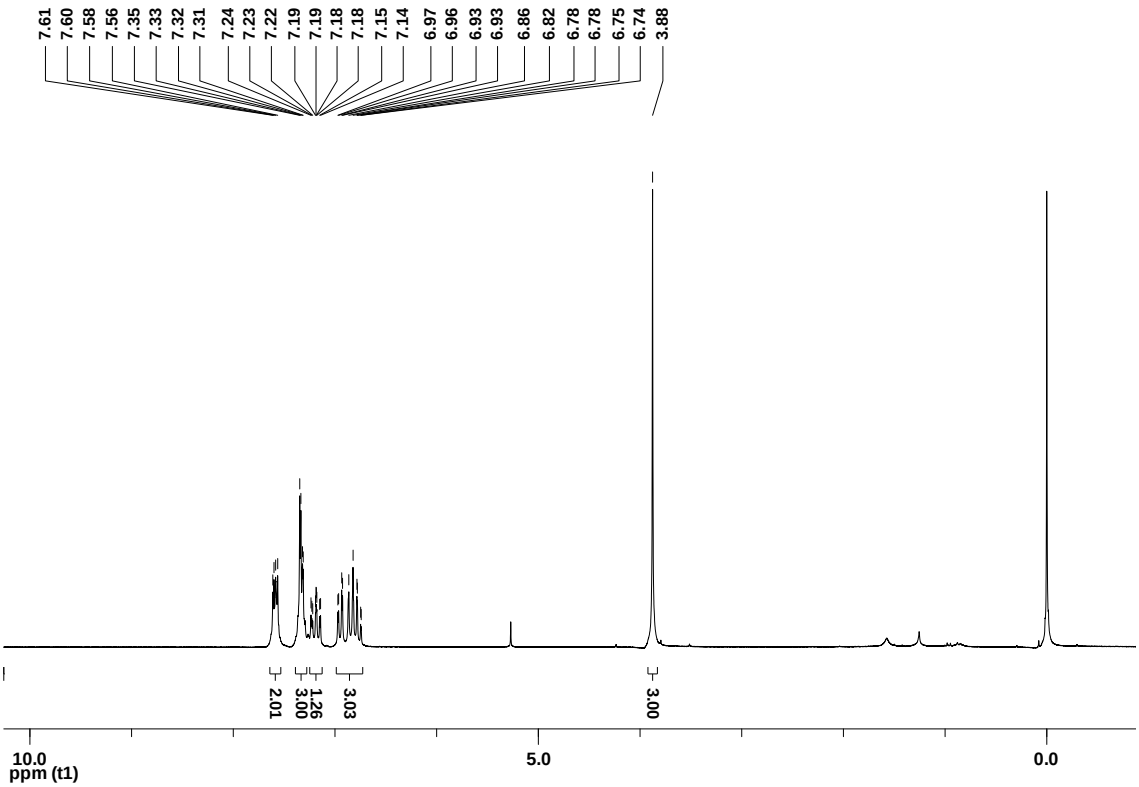
## SELECTED SPECTRA



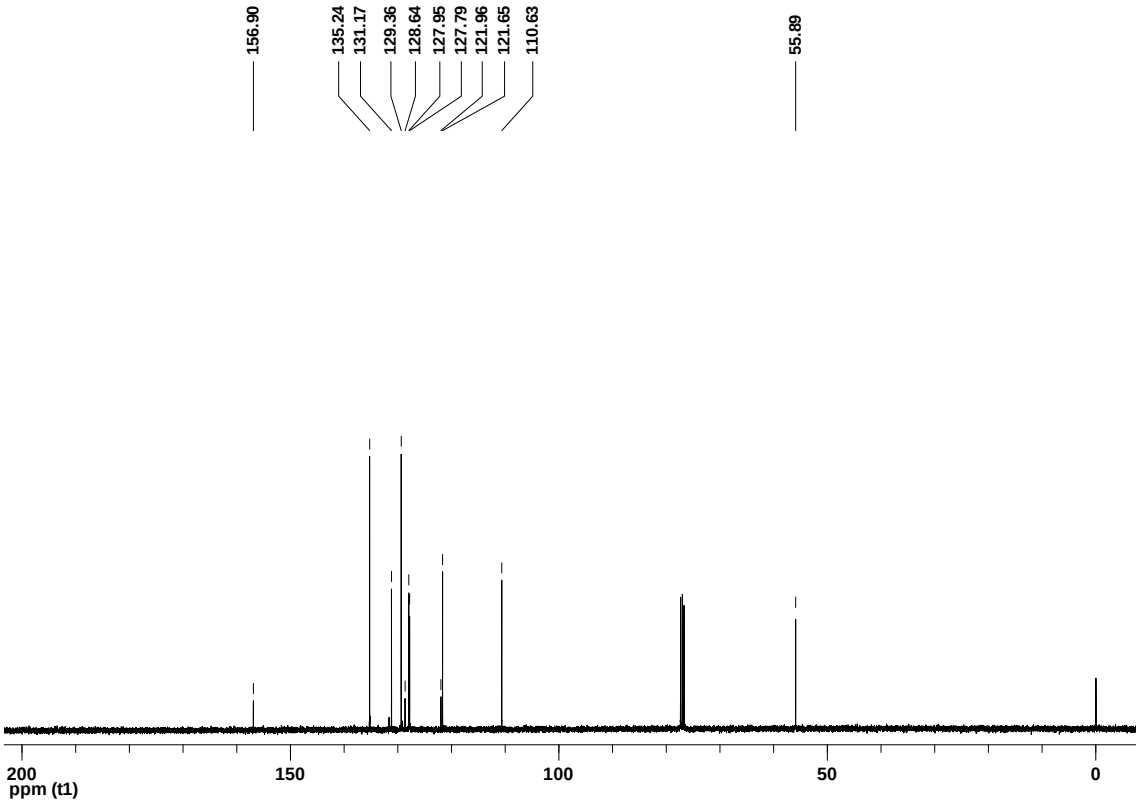

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *4-Methoxyphenyl-phenyl-selenide* ***(3a)***



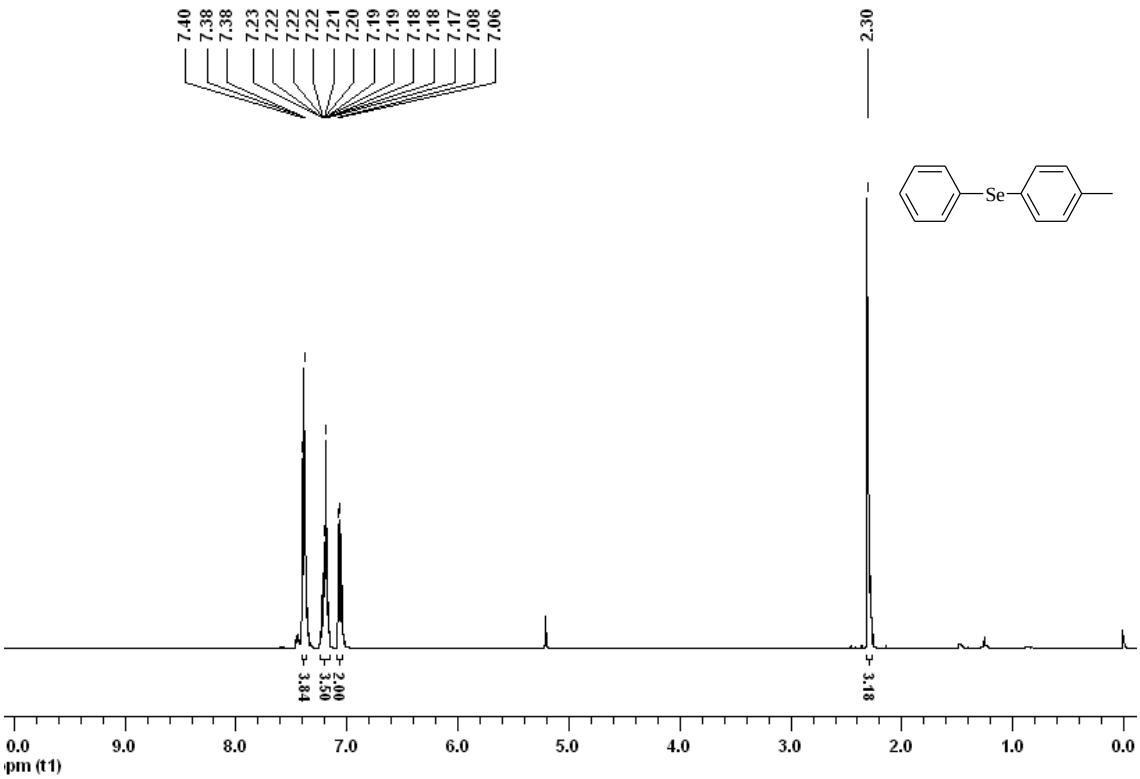

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *4-Methoxyphenyl-phenyl-selenide* ***(3a)***



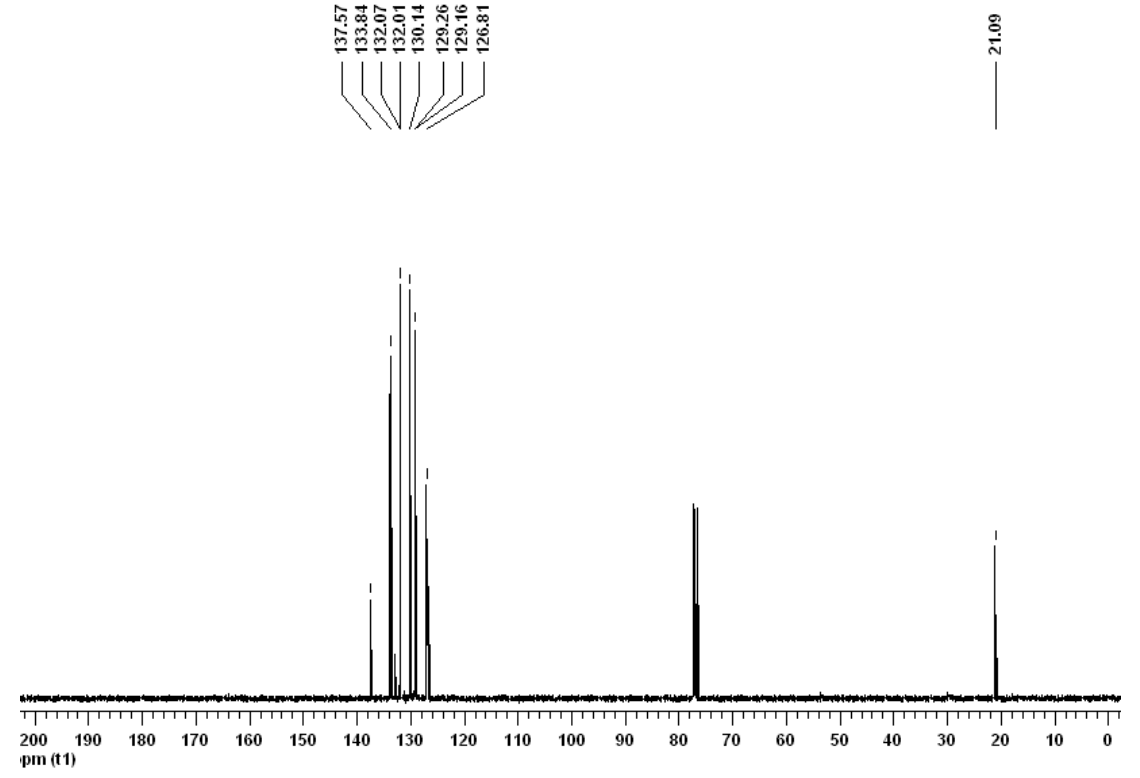

$^{1}$H NMR (200 MHz, $CDCl_3$) spectrum of *2-Methoxyphenyl-phenyl-selenide* ***(3b)***



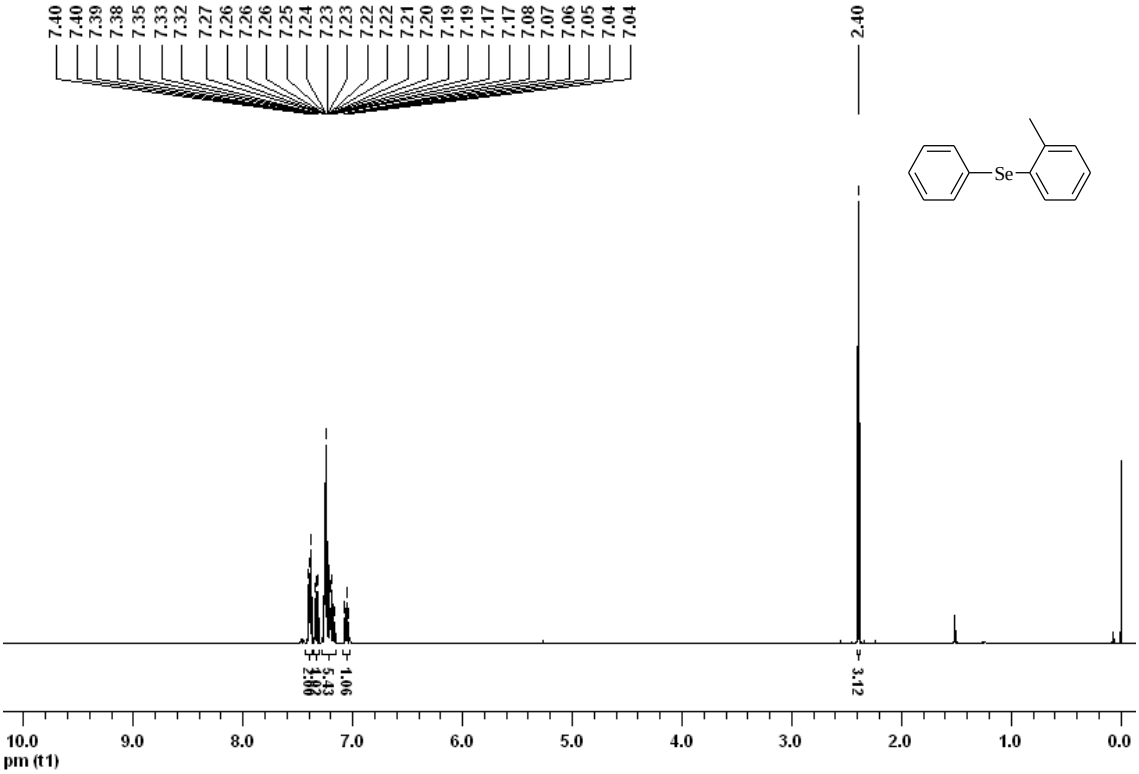

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *2-Methoxyphenyl-phenyl-selenide* ***(3b)***



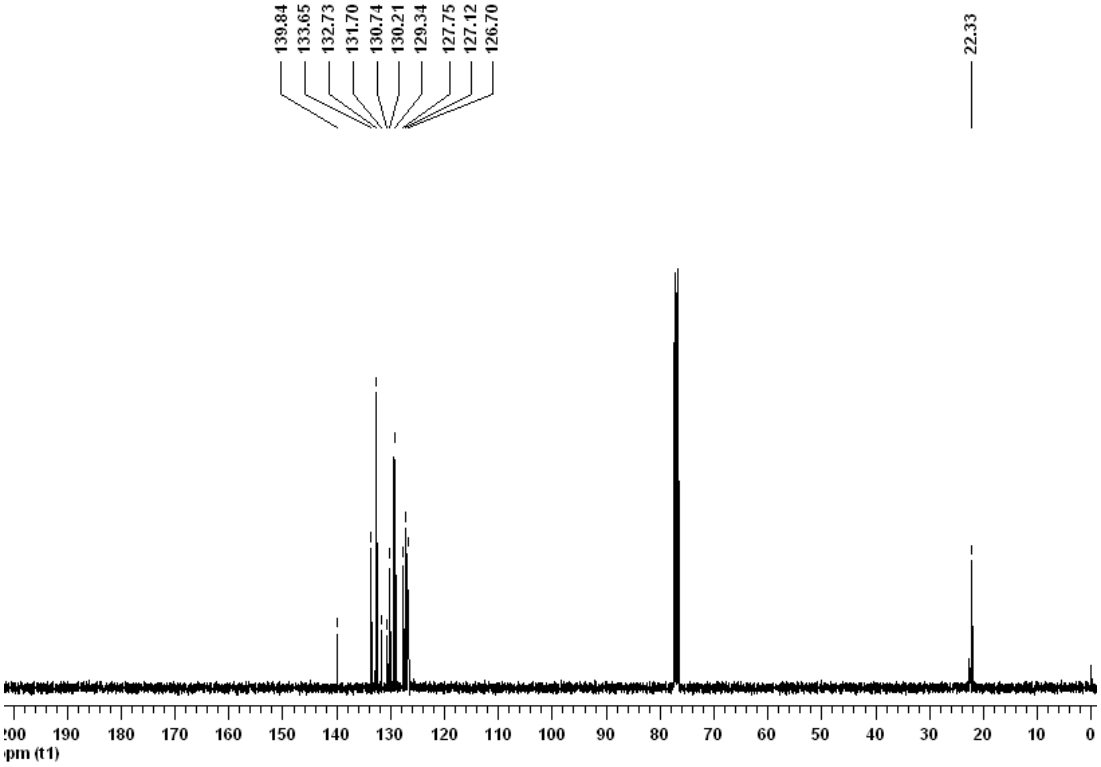

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *4-Tolyl-phenyl-selenide* ***(3c)***




$^{13}$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)***

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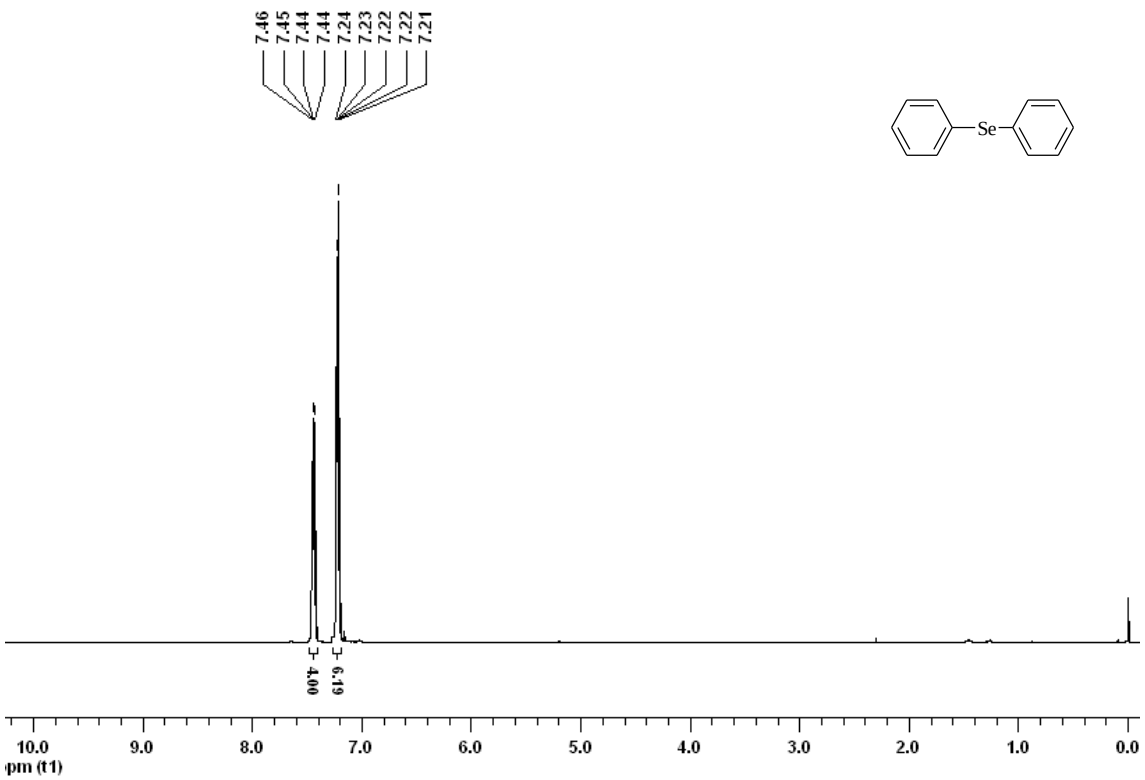
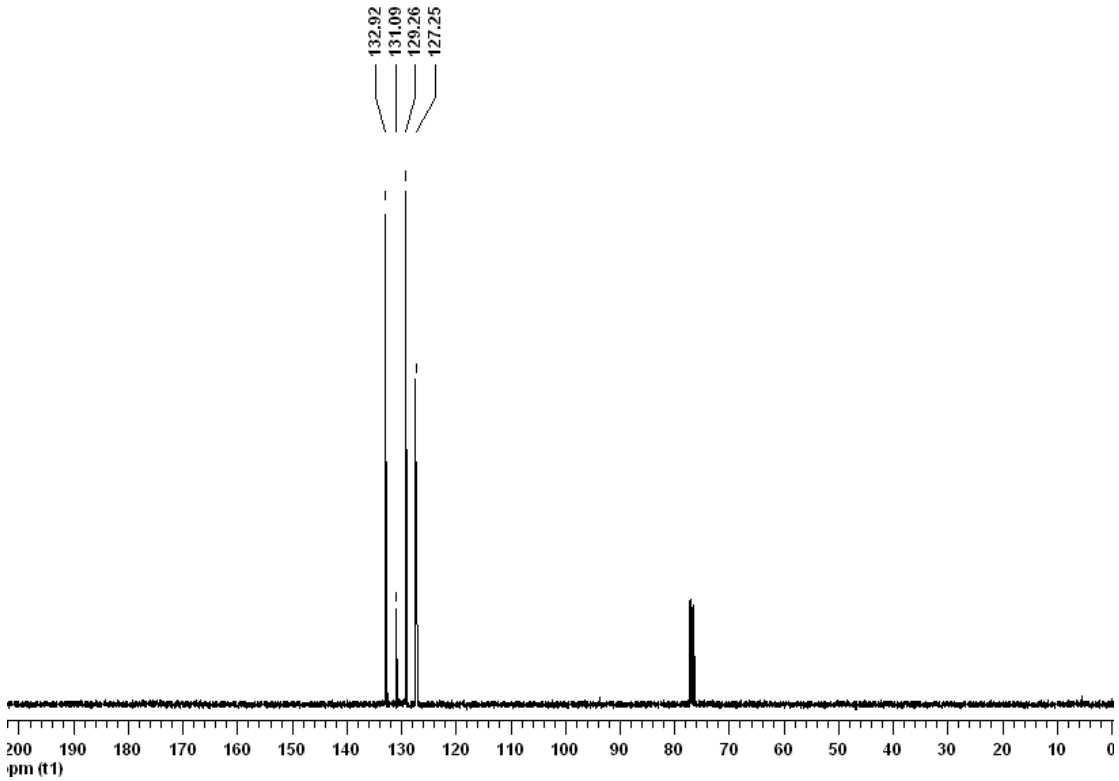
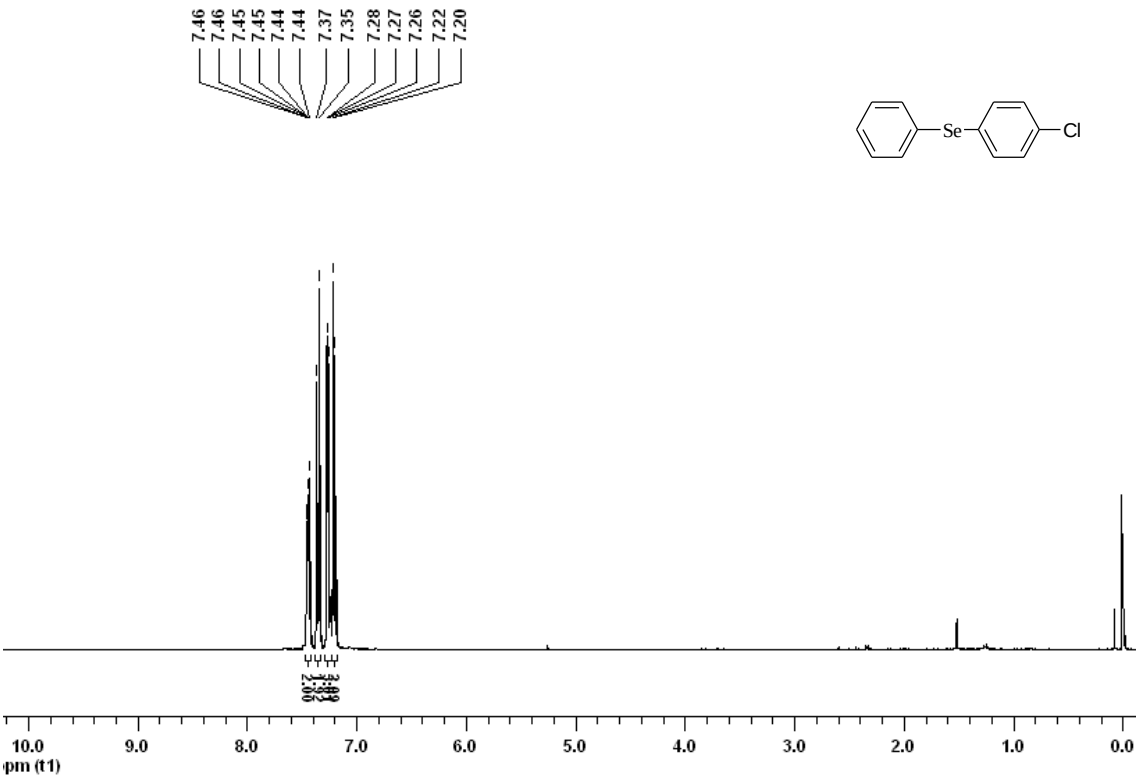


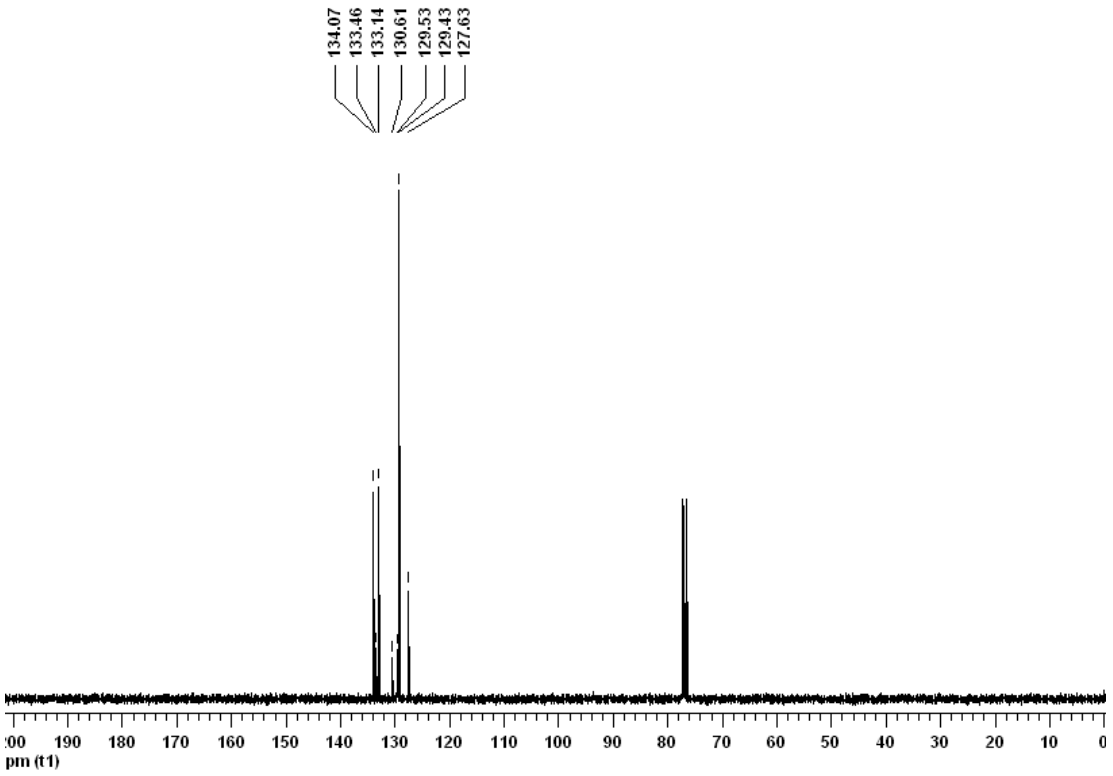

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *diphenyl-selenide* ***(3e)***



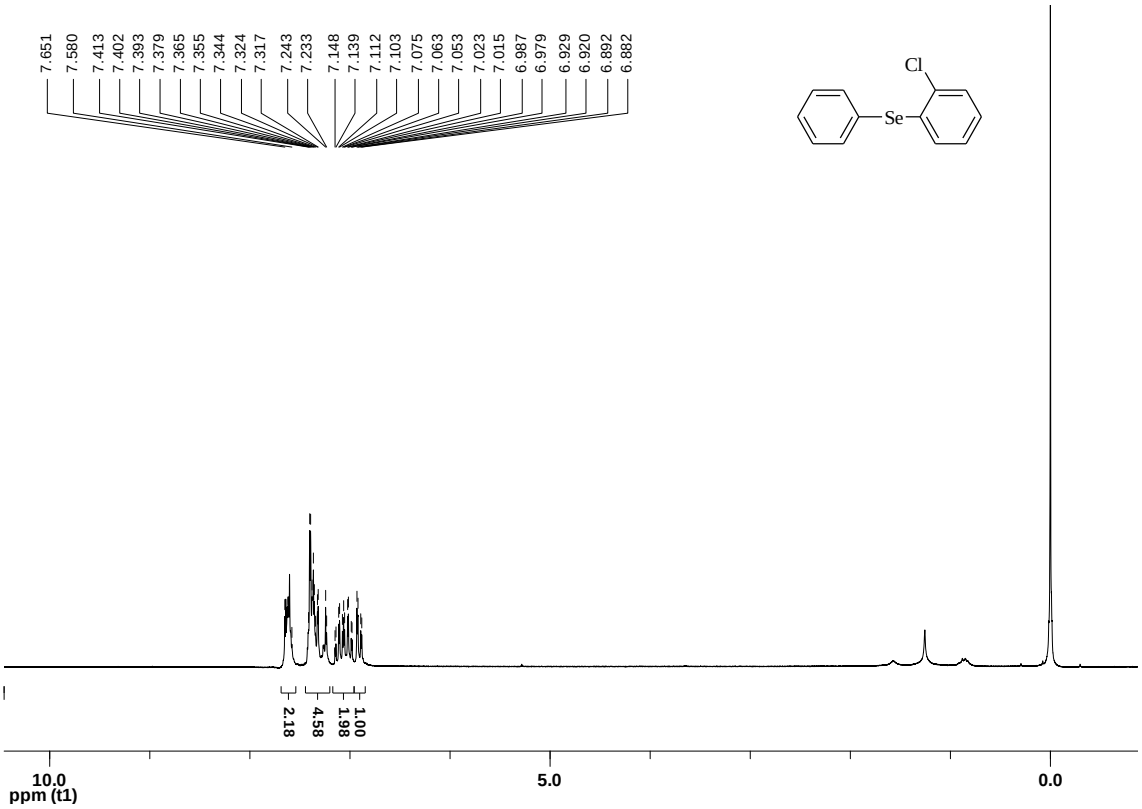

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *diphenyl-selenide* ***(3e)***



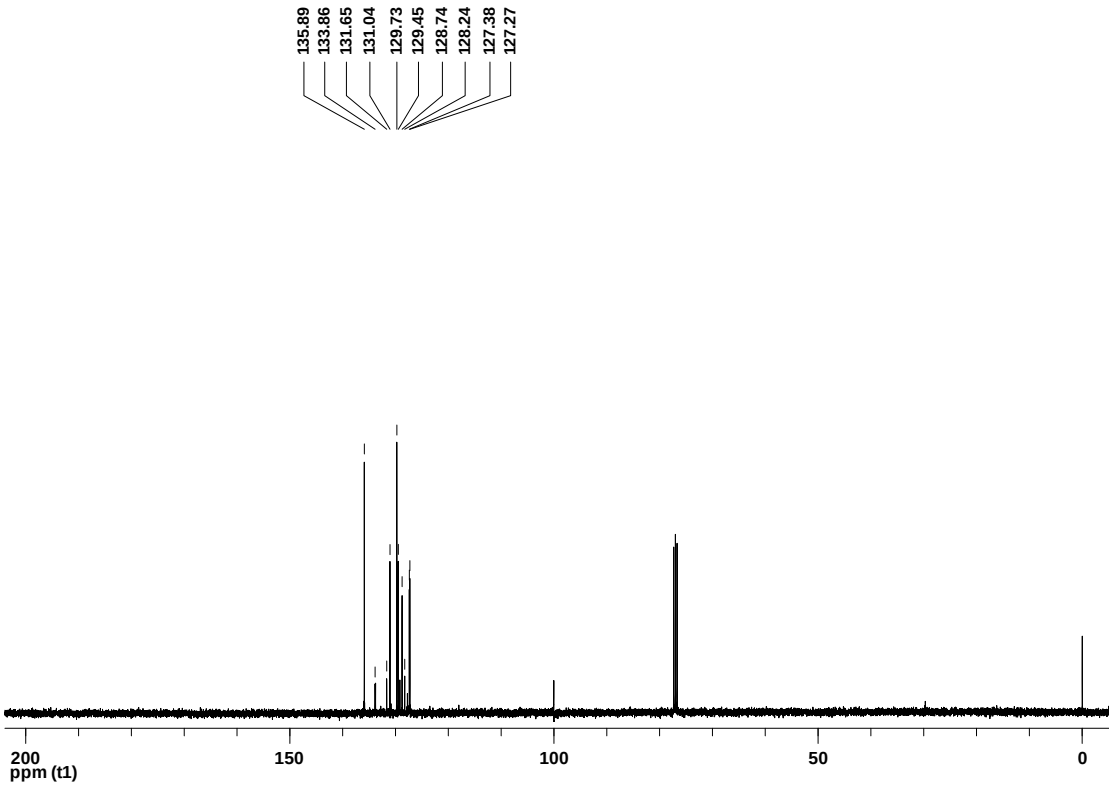

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *4-Chlorophenyl-phenyl-selenide* ***(3f)***



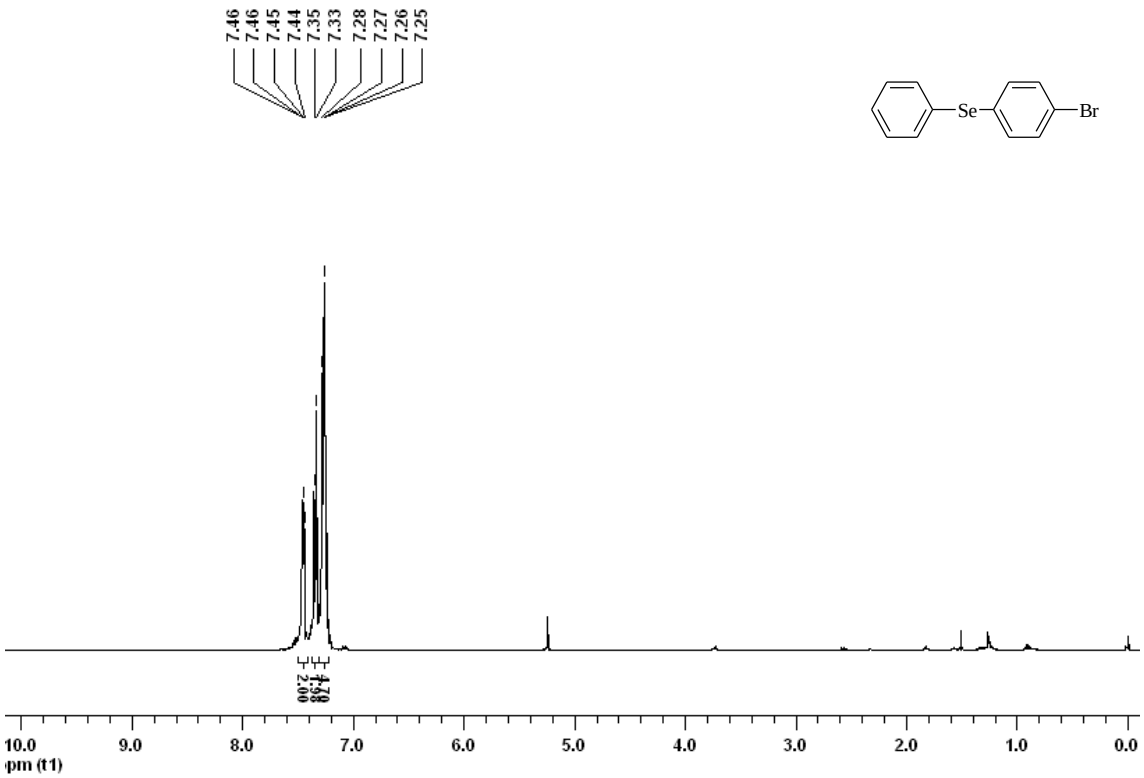

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *4-Chlorophenyl-phenyl-selenide* ***(3f)***



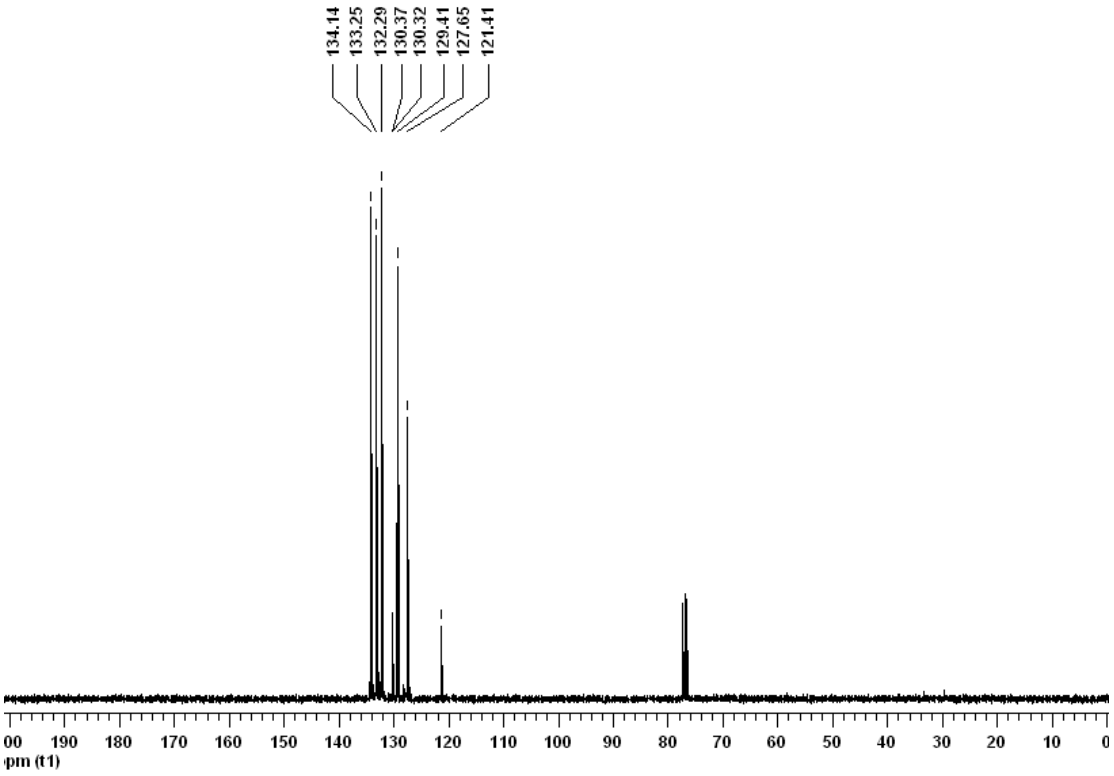

$^{1}$H NMR (200 MHz, $CDCl_3$) spectrum of *2-Chlorophenyl-phenyl-selenide* ***(3g)***



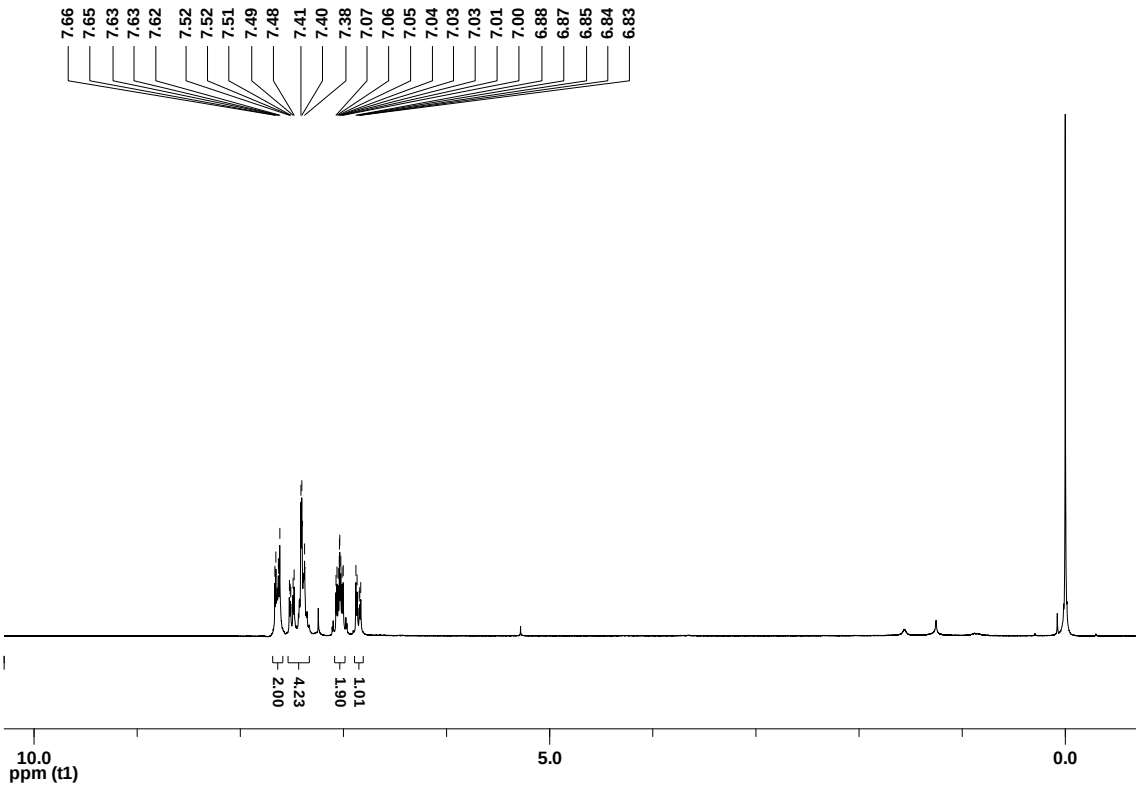

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *2-Chlorophenyl-phenyl-selenide* ***(3g)***




$^{1}$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)***

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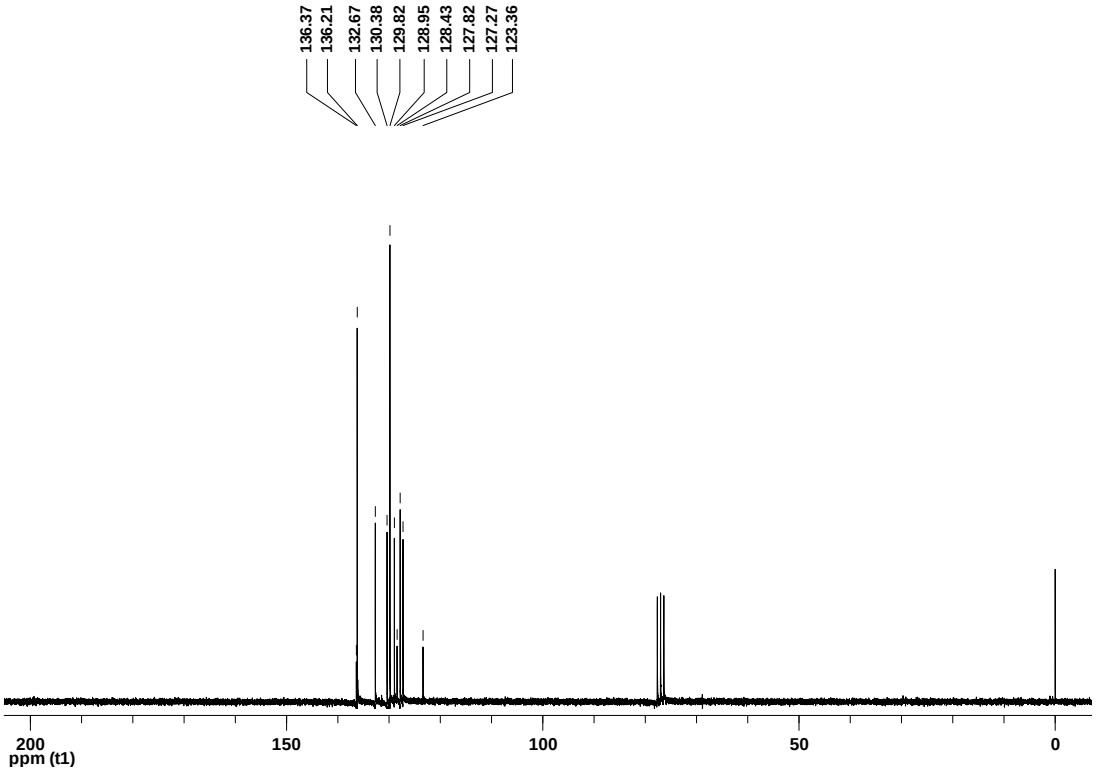


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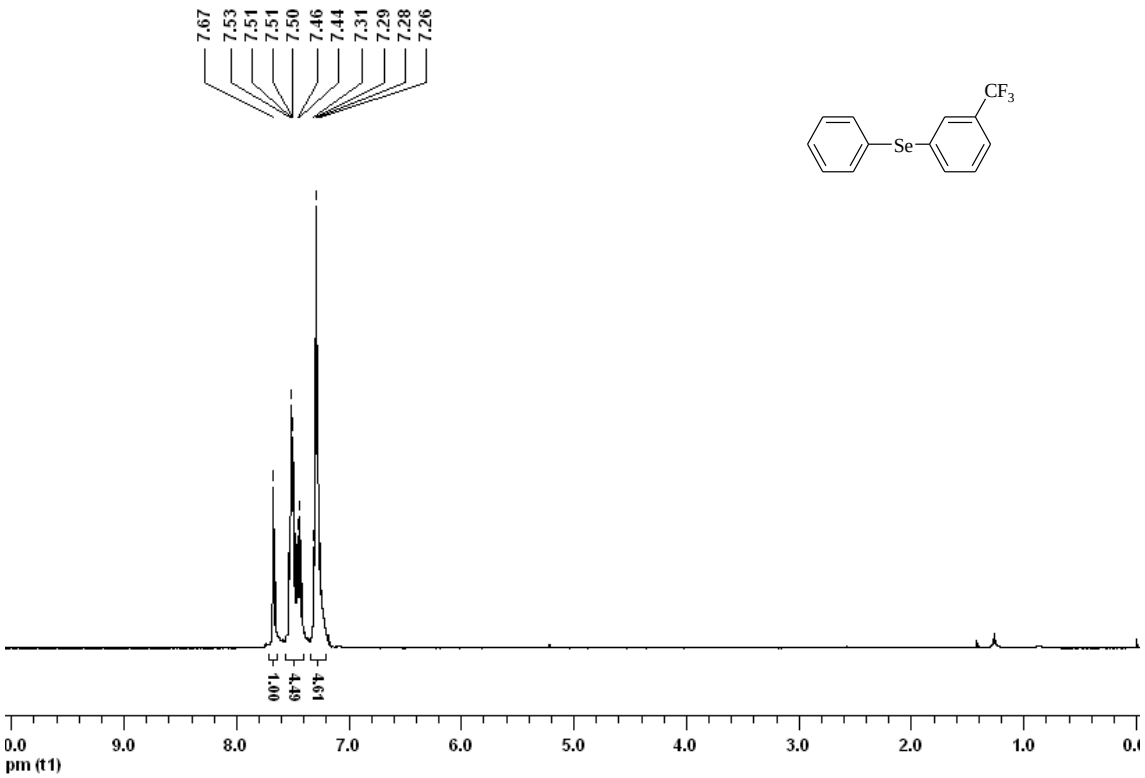
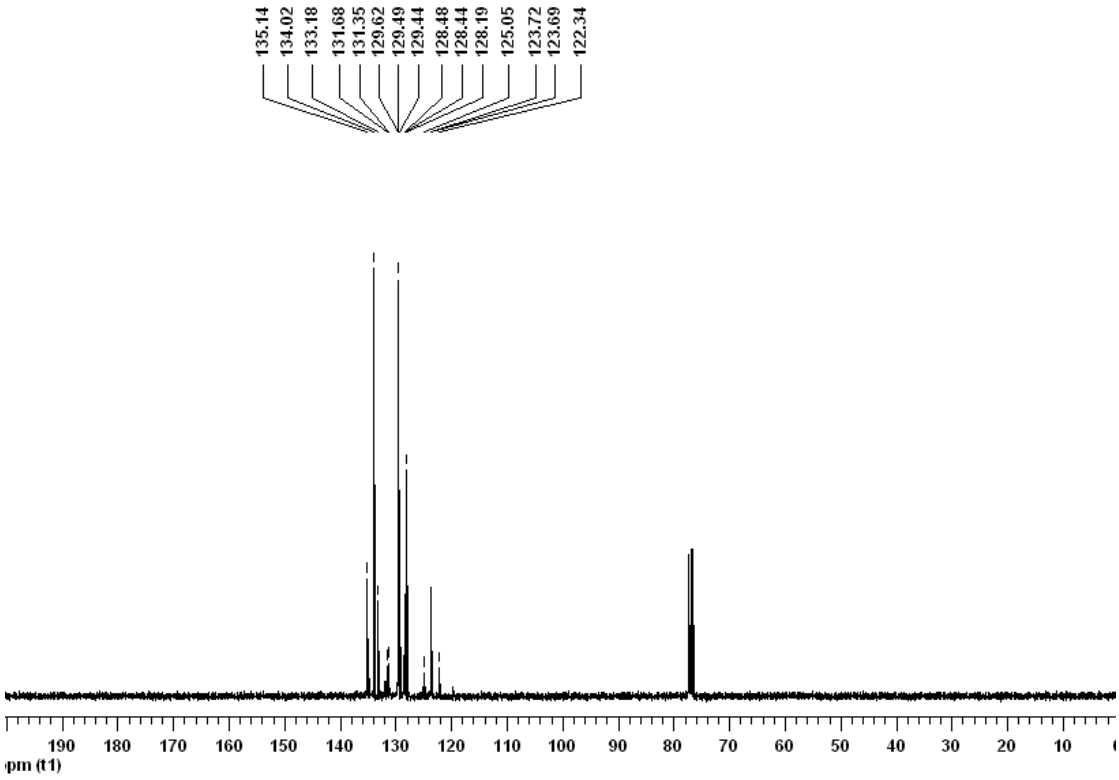
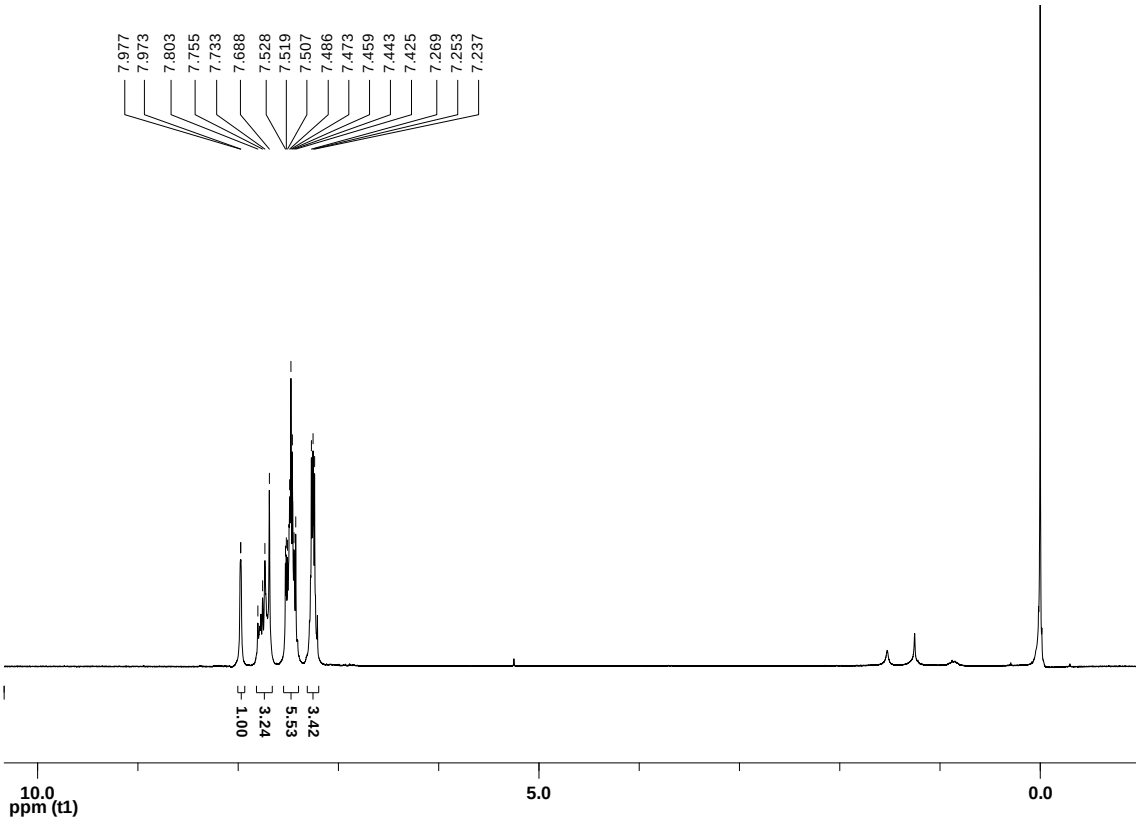


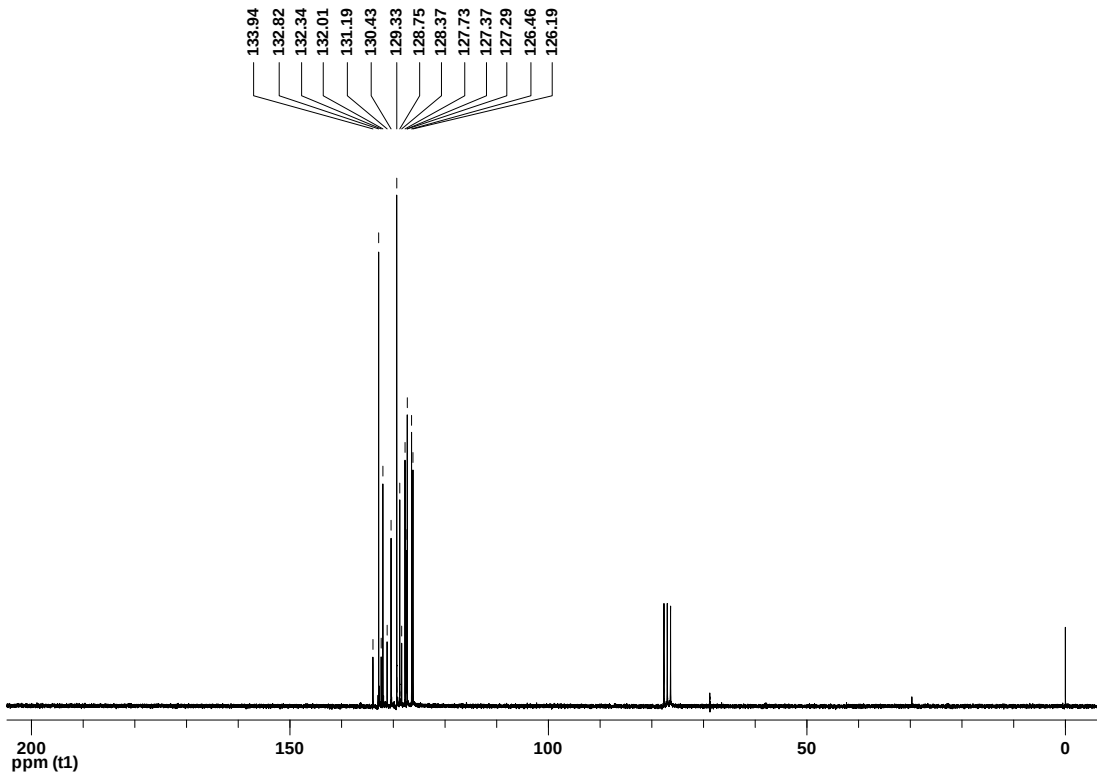

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *3-(trifluoromethyl)phenyl-phenyl-selenide* ***(3j)***



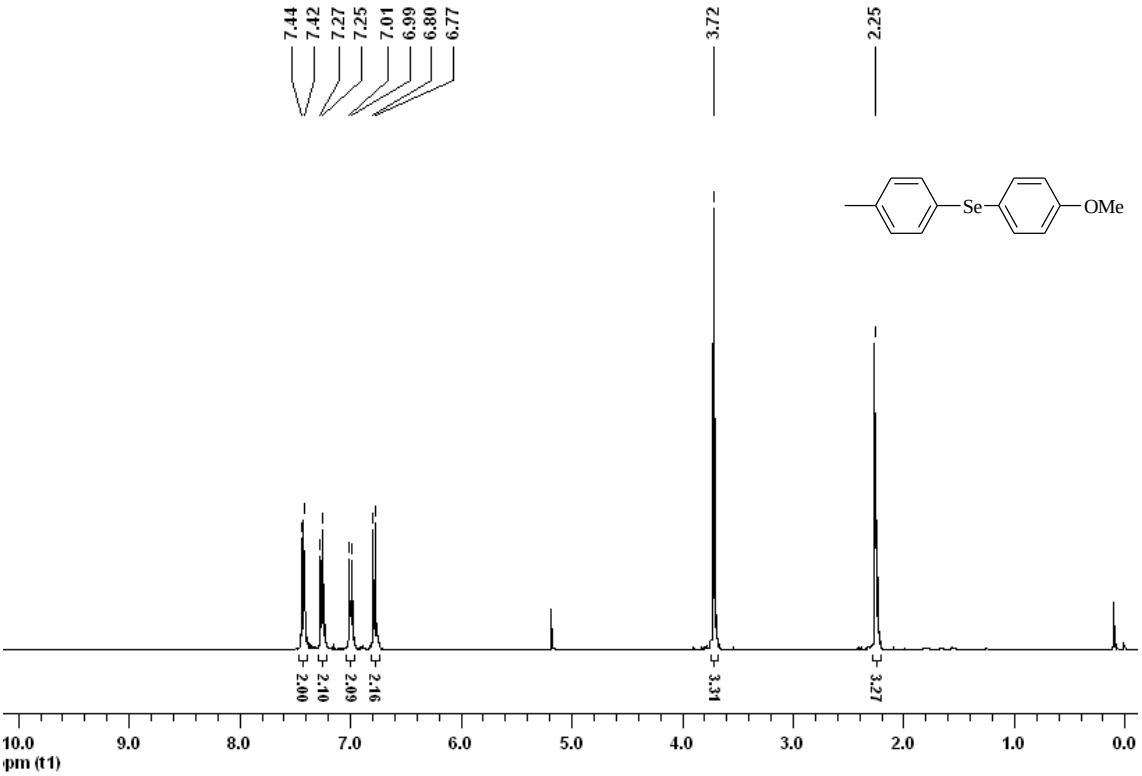

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *3-(trifluoromethyl)phenyl-phenyl-selenide* ***(3j)***



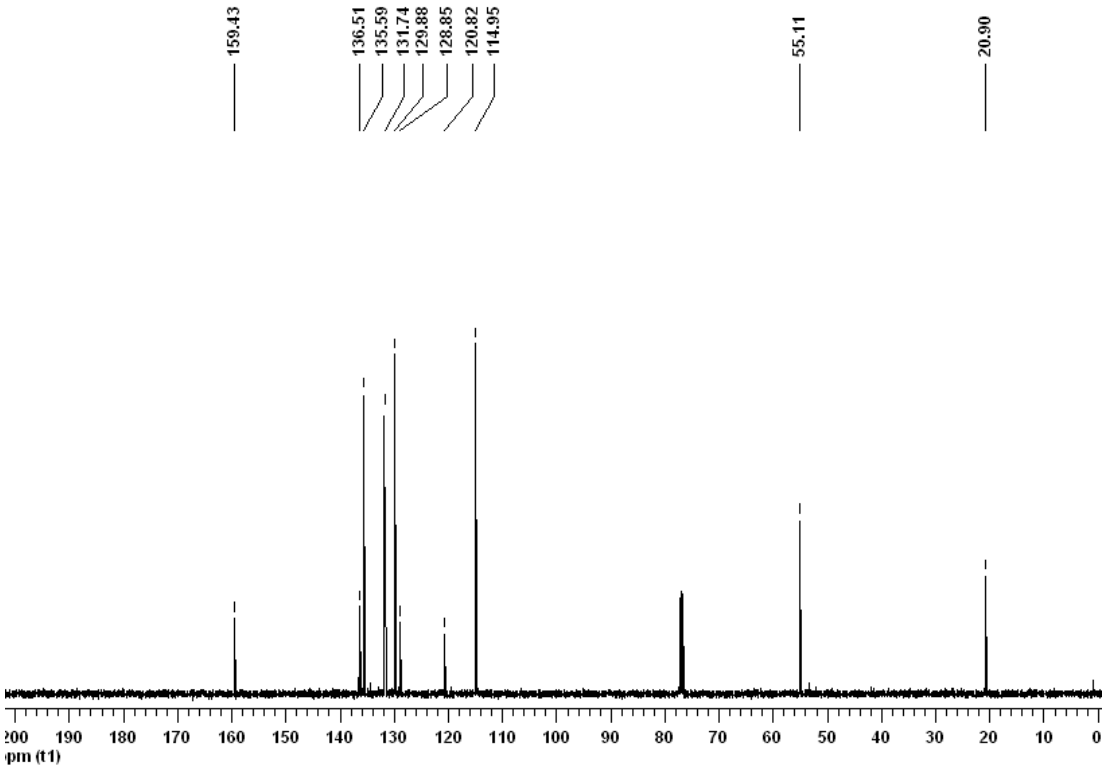

$^{1}$H NMR (200 MHz, $CDCl_3$) spectrum of *2-Naphthyl-phenyl-selenide* ***(3k)***



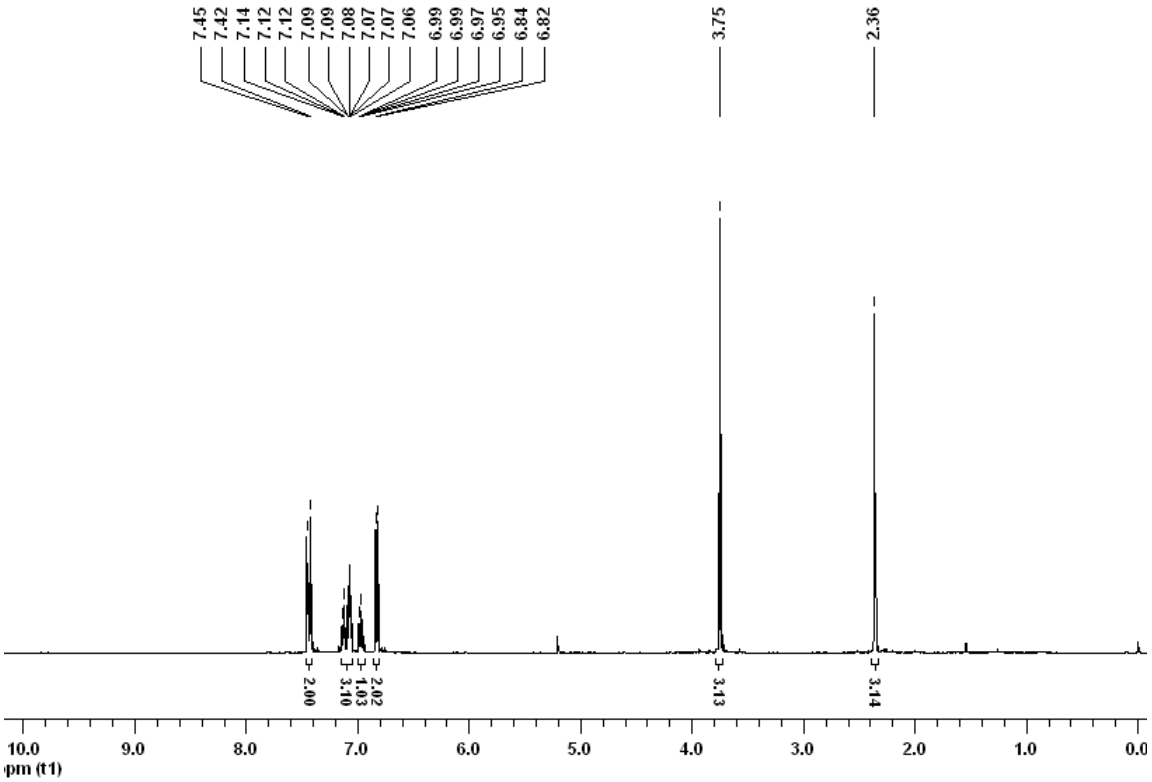

$^{13}$C NMR (50 MHz, $CDCl_3$) spectrum of *2-Naphthyl-phenyl-selenide* ***(3k)***



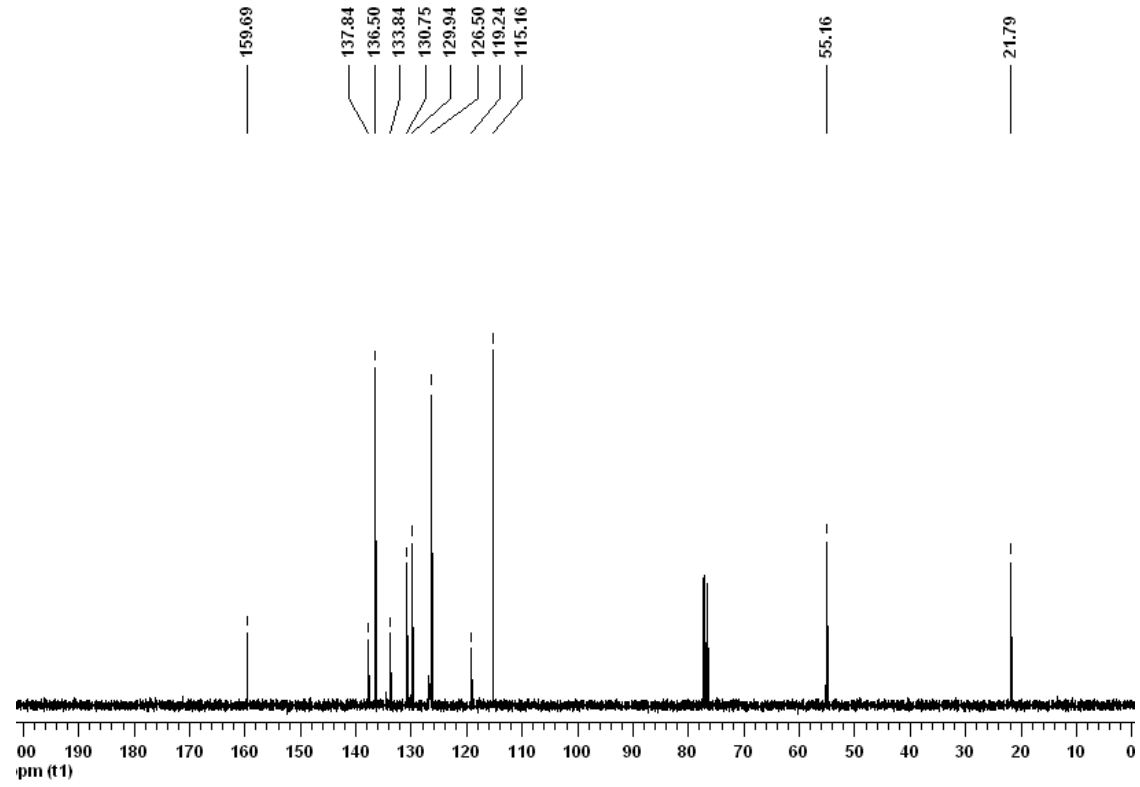

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *4-Tolyl-4-methoxylphenyl-selenide* ***(3l)***



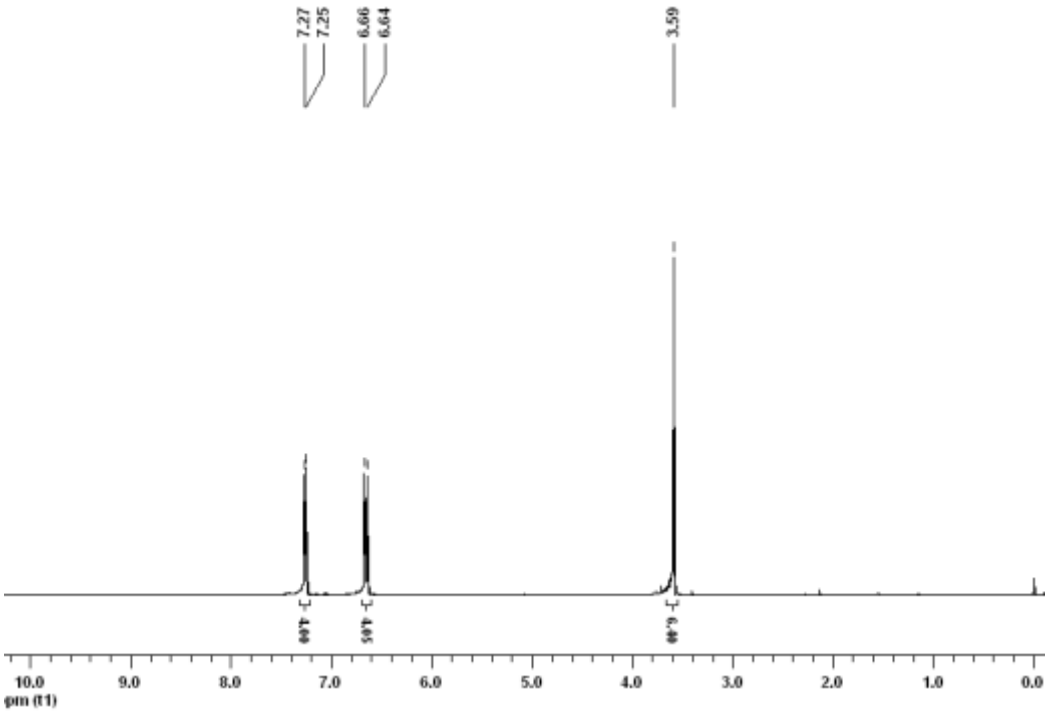

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *4-Tolyl-4-methoxylphenyl-selenide* ***(3l)***



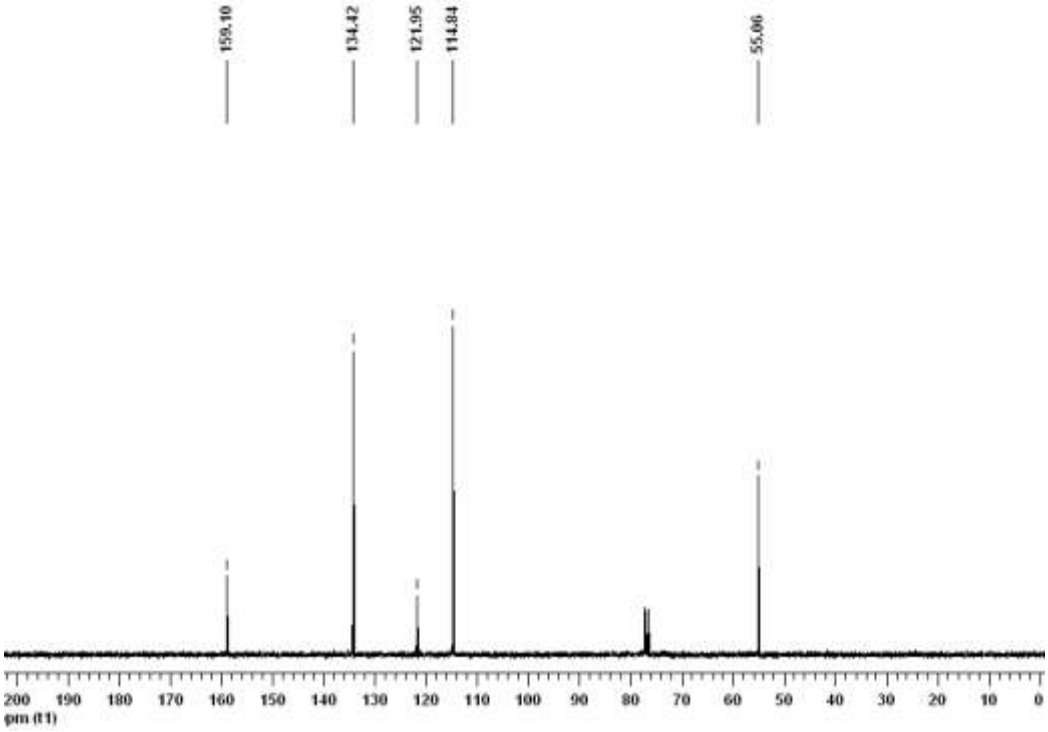

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *2-Tolyl-4-methoxylphenyl-selenide* ***(3m)***



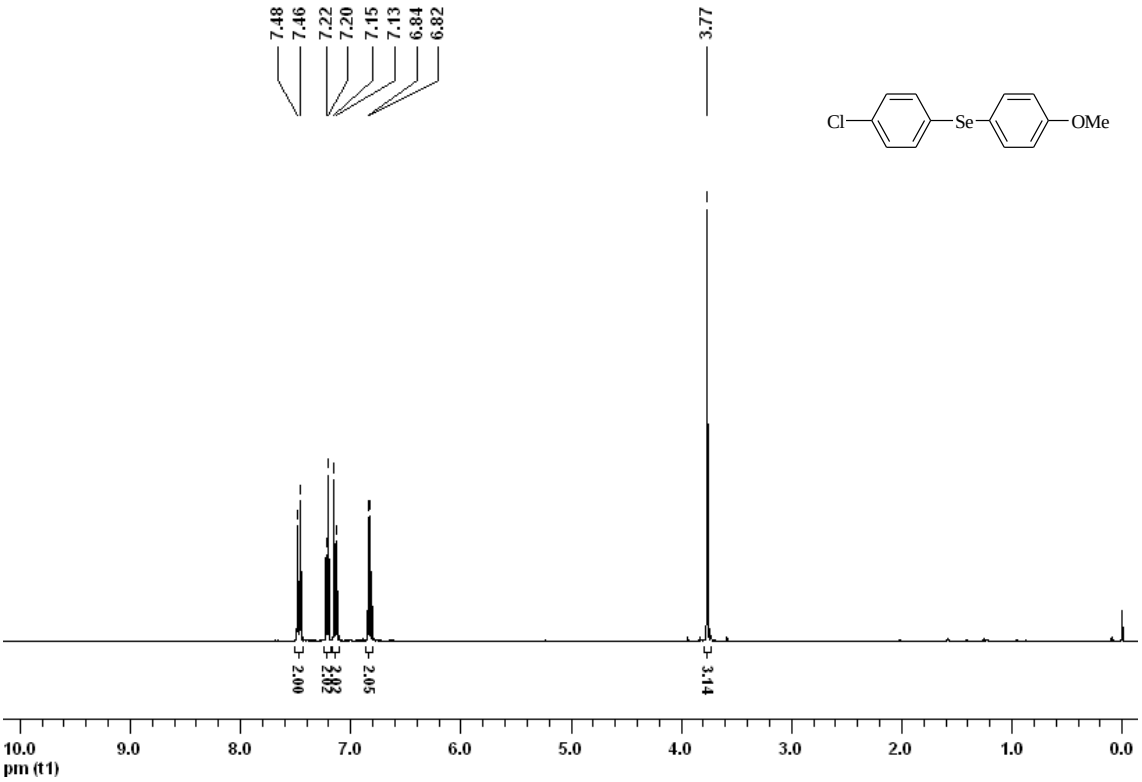

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *2-Tolyl-4-methoxylphenyl-selenide* ***(3m)***



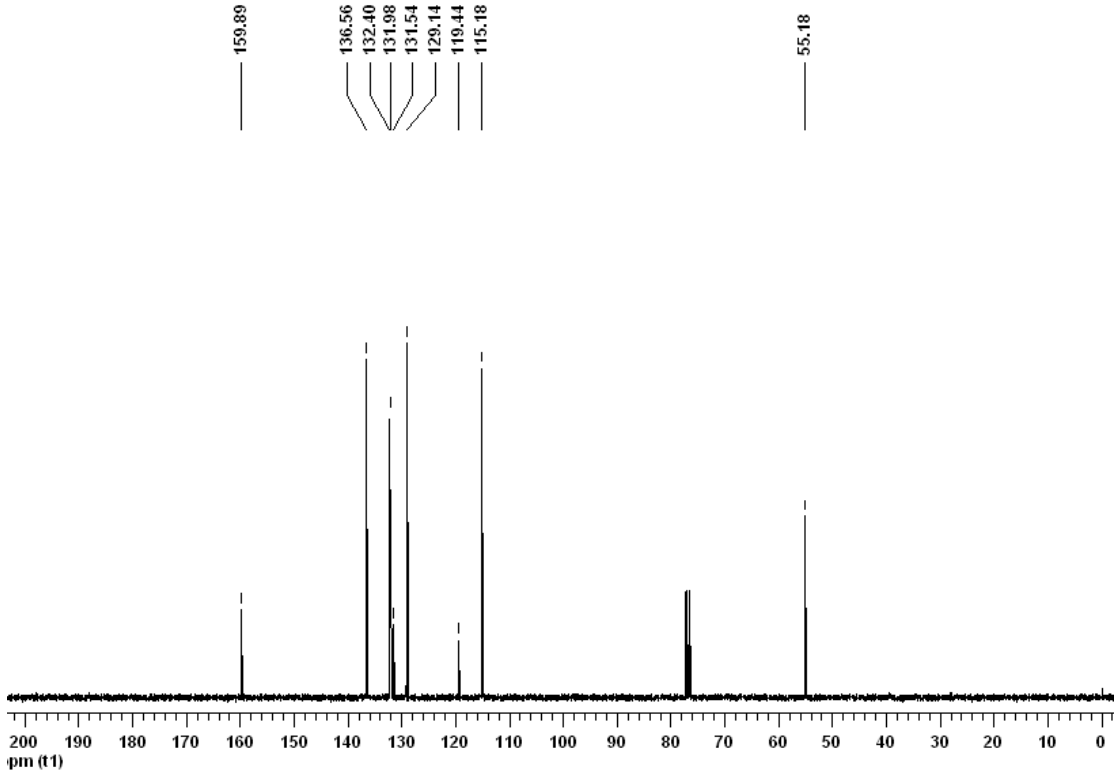

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *Bis-4-methoxylphenyl-selenide* ***(3n)***



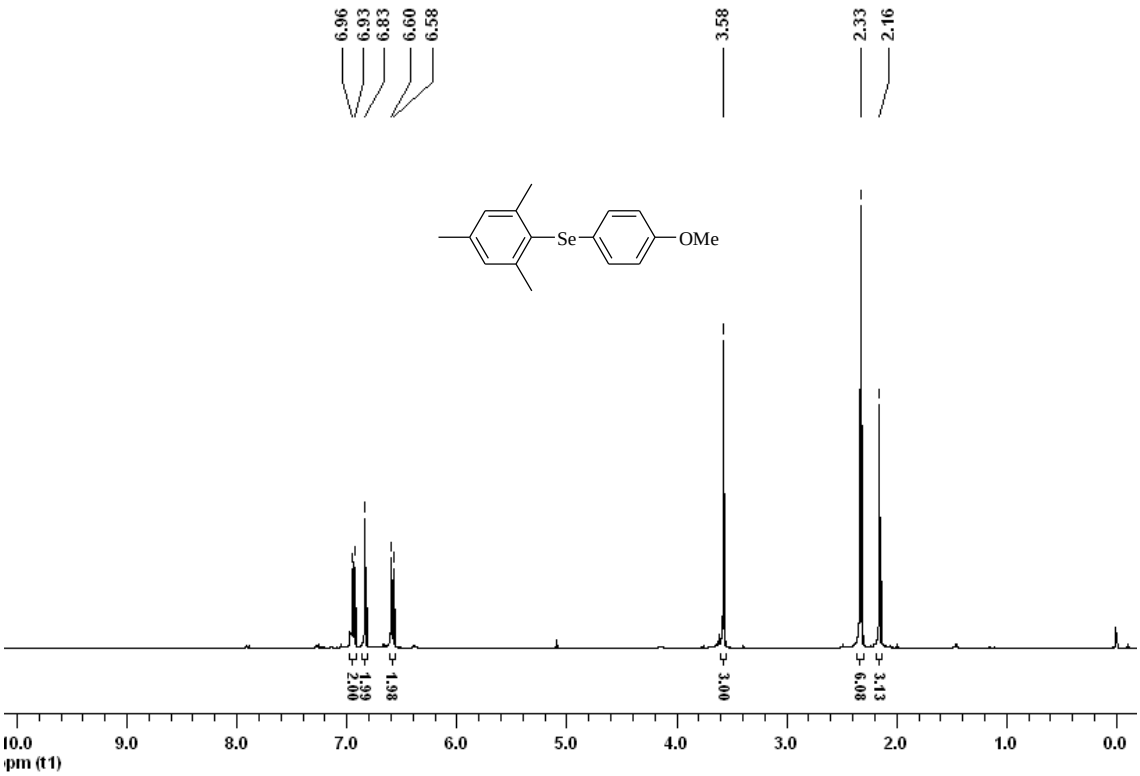

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *Bis-4-methoxylphenyl-selenide* ***(3n)***



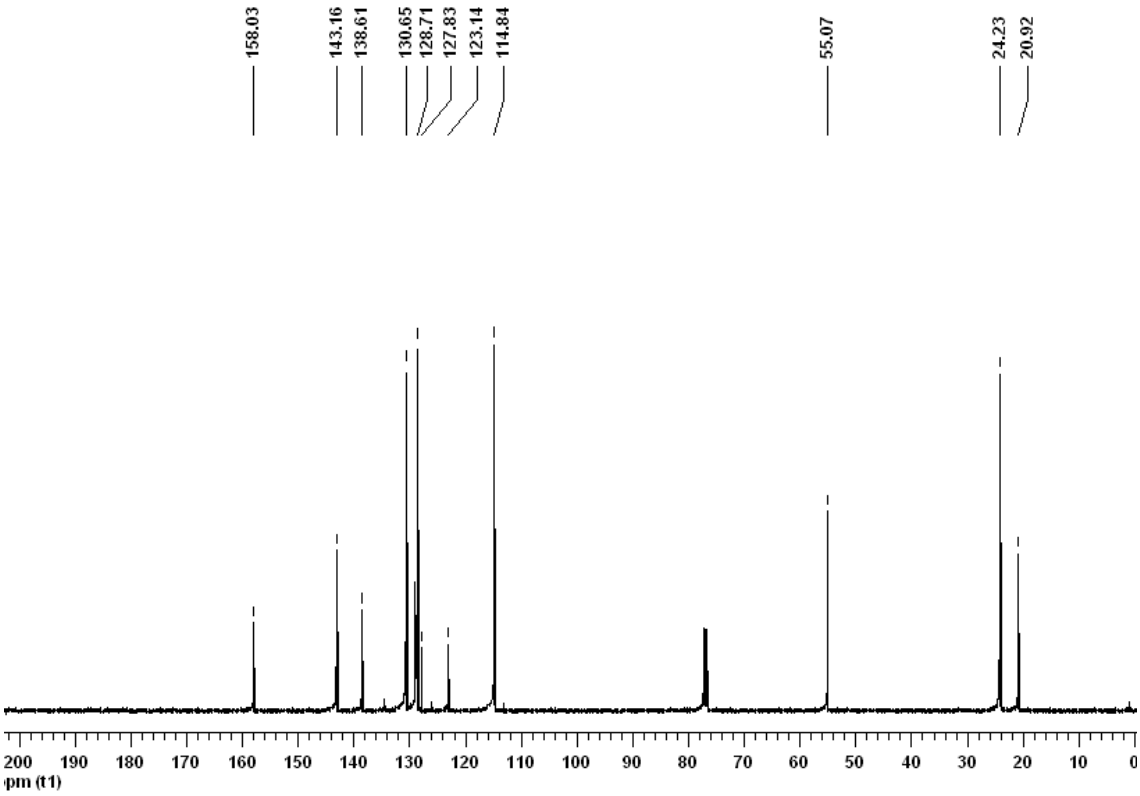

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of *4-Chlorophenyl-4-methoxylphenyl-selenide* ***(3o)***



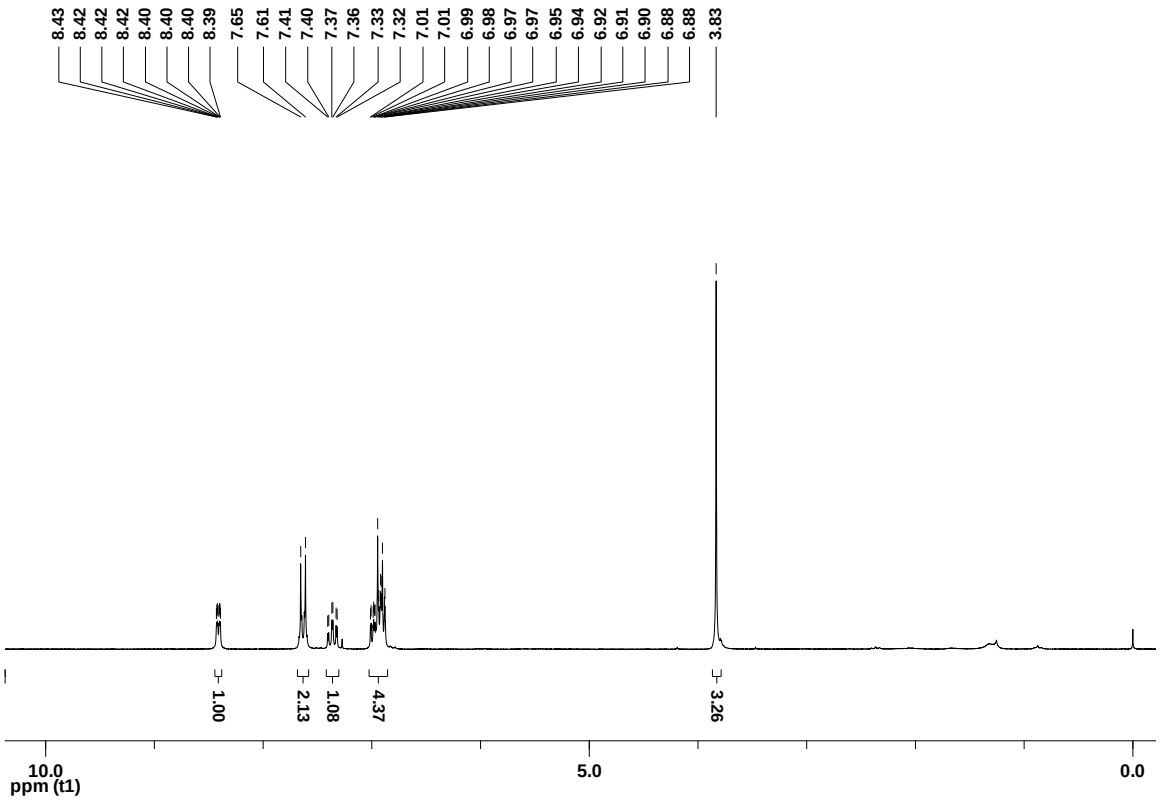

$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of *4-Chlorophenyl-4-methoxylphenyl-selenide* ***(3o)***



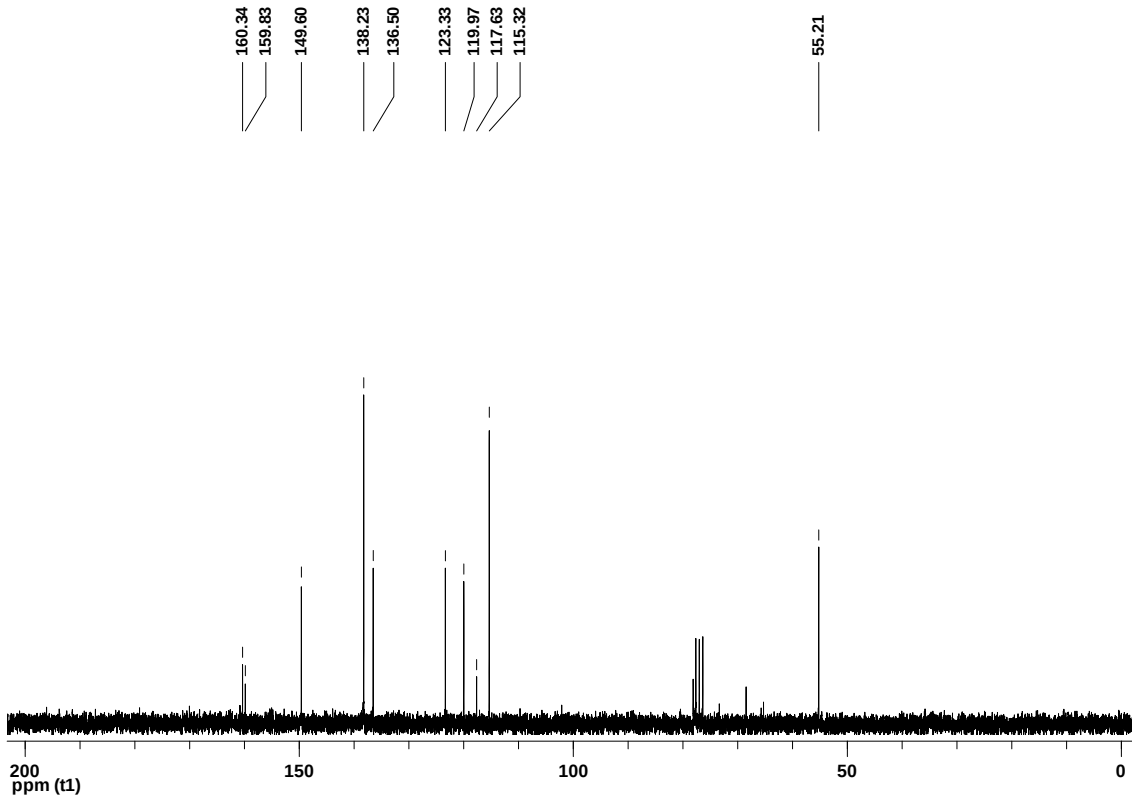

*$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of 1,2,3-(trimethyl)phenyl-4-methoxylphenyl-selenide* ***(3p)***




*$^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of 1,2,3-(trimethyl)phenyl-4-methoxylphenyl-selenide* ***(3p)***




*$^{1}$H NMR (200 MHz, $CDCl_3$) spectrum of 2-Pyridyl-4-methoxylphenyl-selenide* ***(3q)***




*$^{13}$C NMR (50 MHz, $CDCl_3$) spectrum of 2-Pyridyl-4-methoxylphenyl-selenide* ***(3q)***