SUPPORTING INFORMATION

Selenium-Promoted Electrophilic Cyclization of Arylpropiolamides: Synthesis of 3-Organoselenyl Spiro[4,5]trienones

Ana Maria S. Recchi,[1] Pedro H. P. Rosa[1], Davi F. Back,[2] and Gilson Zeni*[,1]

[a] Laboratório de Síntese, Reatividade, Avaliação Farmacológica e Toxicológica de Organocalcogênios CCNE, UFSM, Santa Maria, Rio Grande do Sul, Brazil 97105-900.

E-mail: gzeni@ufsm.br; Fax: (+55)55-3220-8978; Tel: (+55)55-3220-9611.

[b] Laboratório de Materiais Inorgânicos, Departamento de Química, UFSM, Santa Maria, Rio Grande do Sul, Brazil 97105-900.

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Materials and Methods

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a NMR spectrometer at 400 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant *(J)* in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained on a 400 NMR spectrometer at 100 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), quart (quartet), quint (quintet), sex (sextet), dd (double doublet) and m (multiplet). High resolution mass spectra were recorded on a mass spectrometer using electrospray ionization (ESI).

Column chromatography was performed using Silica Gel (230-400 mesh) following the methods described by Still. Thin layer chromatography (TLC) was performed using Gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. All reagents and solvents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Acros Organics or TCI). The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques.

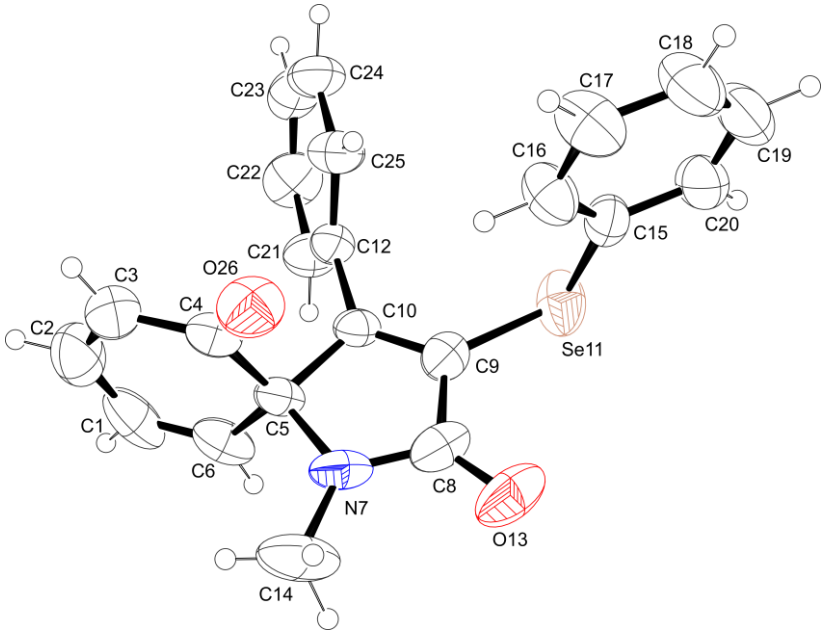


Figure S1. ORTEP drawings (ellipsoids set at 50 % probability) of the compound **2a** (CCDC 1991531).

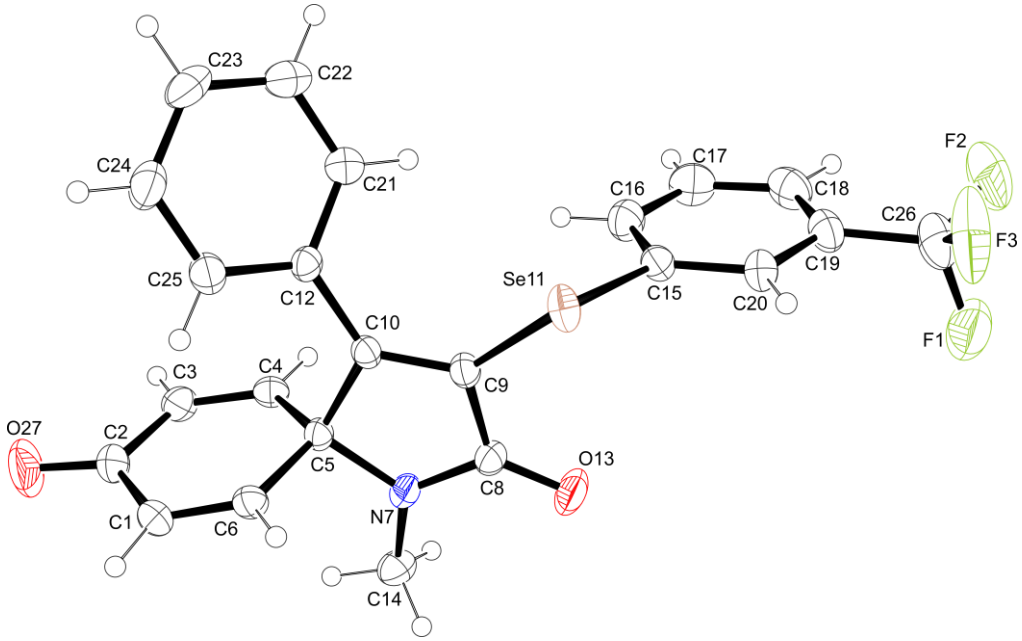


Figure S2. ORTEP drawings (ellipsoids set at 50 % probability) of the compound **2r** (CCDC 1991530).

General procedure for the preparation of 3-organoselenyl[4,5]trienones 2a-v: In a Schlenk tube, under N_2 atmosphere, containing phenyl selenium bromine (0.325 mmol), $MeNO_2$ (3 mL) was added the *N*-methyl-3-phenylpropiolamide (0.25 mmol). The resulting solution was allowed to stir at 90 °C for the time indicated in Tables 2 and 3. The mixture was diluted with ethyl acetate and washed with concentrated NH_4Cl solution. The organic phase was dried with MgSO4, the solvent was removed under reduced pressure. The residue was purified by column chromatography. **1-Methyl-4-phenyl-3-(phenylselanyl)-1-azaspiro[4,5]deca-3,7,9-triene-2,6-dione 2a.** The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a brown solid. Yield: 0.087 g (85%); mp. 121.3-122.8 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38-7.33 (m, 2H), 7.27-7.19 (m, 1H), 7.19-7.13 (m, 2H), 7.15-7.06 (m, 3H), 7.03 (dd, *J* = 8.3, 1.3 Hz, 2H), 6.93 (ddd, *J* = 9.9, 6.0, 1.8 Hz, 1H), 6.46 (ddd, *J* = 9.4, 6.0, 0.9 Hz, 1H), 6.17-6.06 (m, 2H), 2.78 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 195.0, 170.1, 155.7, 141.9, 137.8, 132.6, 131.3, 129.2, 129.0, 128.9, 128.3, 127.9, 127.9, 127.4, 127.2, 126.8, 76.6, 26.9. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as external reference) δ(ppm) 297.6. MS (EI, 70 eV; *m/z* (relative intensity)): 407 (10), 327 (28), 298 (31), 250 (51), 207 (100), 178 (25), 165 (58), 152 (63), 129 (49), 77 (19). HRMS calcd for $C_{22}H_{18}NO_2Se$ (ESI-TOF, [M + H^+]), 408.0503, found 408.0509.

1-Methyl-3-(phenylselanyl)-4-(p-tolyl)-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2b. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a black solid. Yield: 0.063 g (60%); mp. 136.9-140.1 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.40-7.36 (m, 2H), 7.15-7.10 (m, 3H), 6.99-6.96 (m, 4H), 6.97-6.92 (m, 1H), 6.46 (ddd, *J* = 9.4, 6.0, 0.9 Hz, 1H), 6.16 (dt, *J* = 9.9, 0.9 Hz, 1H), 6.11 (ddd, *J* = 9.4, 1.8, 0.9 Hz, 1H), 2.77 (s, 3H), 2.28 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) 195.2, 170.3, 156.2, 141.8, 139.4, 138.2, 132.5, 131.6, 128.9, 128.7, 128.6, 128.4, 127.9, 127.5, 127.1, 126.6, 76.44, 26.8, 21.3. MS (EI, 70 eV; *m/z* (relative intensity)): 421 (27), 343 (65), 341 (53), 312 (59), 282 (59), 264 (100), 193 (66), 165 (93), 143 (62), 115 (33), 77 (83). HRMS calcd for $C_{23}H_{20}NO_2Se$ (ESI-TOF, [M + H^+]), 422.0659, found 422.0652.

4-(2-Methoxyphenyl)-1-methyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2c. The product was isolated by column chromatography (hexane:ethyl acetate 65:35) as a black solid. Yield: 0.041 g (38%); mp. 131.9-133.8 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ

(ppm) 7.36-7.32 (m, 2H), 7.19 (ddd, *J* = 8.3, 6.4, 0.8 Hz, 1H), 7.11-7.04 (m, 3H), 6.79-6.72 (m, 3H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.26 (ddd, *J* = 9.4, 5.9, 0.8 Hz, 1H), 6.09-6.07 (m, 1H), 6.06-6.04 (m, 1H), 3.59 (s, 3H), 2.80 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 194.8, 170.1, 156.2, 153.1, 141.0, 137.8, 133.0, 130.5, 130.4, 129.6, 128.5, 128.0, 127.2, 127.0, 125.8, 120.3, 119.7, 110.4, 78.3, 54.8, 27.2. MS (EI, 70 eV; *m/z* (relative intensity)): 438 ([M + 1], 05), 437 (24); 406 (66), 326 (66), 298 (16), 280 (25); 252 (21), 207 (21); 180 (19), 165 (46), 152 (27), 135 (31), 115 (26), 77 (100). HRMS calcd for $C_{23}H_{20}NO_3Se$ (ESI-TOF, [M + H^+]), 438.0608, found 438.0612.

4-(4-Chlorophenyl)-1-methyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2e. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a black solid. Yield: 0.049 g (40%); mp. 140.0-143.0 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.35-7.30 (m, 2H), 7.17-7.06 (m, 5H), 7.00-6.89 (m, 3H), 6.47 (ddd, *J* = 9.4, 6.0, 0.9 Hz, 1H), 6.16-6.08 (m, 2H), 2.78 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) 194.9, 170.0, 153.4, 142.0, 137.6, 135.2, 133.1, 130.0, 129.6, 129.2, 129.0, 127.7, 127.5, 127.4, 127.0, 75.6, 26.9. MS (EI, 70 eV; *m/z* (relative intensity)): 443 ([M + 2], 13), 441 (38), 332 (35), 284 (30), 249 (52), 221 (19), 193 (42), 165 (59), 163 (100), 135 (13), 78 (73). HRMS calcd for $C_{22}H_{17}ClNO_2Se$ (ESI-TOF, [M + H^+]), 442.0113, found 442.0116.

1-Methyl-4-phenyl-3-(p-tolylselanyl)-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2f. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a red solid. Yield: 0.06 g (57%); mp. 113.9-116.6 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.30-7.21 (m, 3H), 7.20-7.11 (m, 2H), 7.06-6.98 (m, 2H), 6.97-6.87 (m, 3H), 6.45 (ddd, *J* = 9.4, 6.0, 0.9 Hz, 1H), 6.17-6.06 (m, 2H), 2.77 (s, 3H), 2.23 (s, 3H).^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 191.5, 170.2, 154.9, 141.9, 137.7, 137.2, 133.1, 131.3, 129.7, 129.2, 129.0, 127.9, 127.8, 127.3, 126.7, 124.1, 76.5, 26.8, 21.0. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as external reference) δ(ppm) 293.9. MS (EI, 70 eV; *m/z* (relative intensity)): 421 (19), 340 (05), 329 (27), 312 (40), 281 (18), 253 (62), 222 (19), 208 (48), 206 (51), 193 (79), 165 (66), 152 (43), 129 (47), 115 (15), 91 (100). HRMS calcd for $C_{23}H_{20}NO_2Se$ (ESI-TOF, [M + H^+]), 422.0659 found 422.0652.

4-(4-Chlorophenyl)-1-methyl-3-(p-tolylselanyl)-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2g. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a purple solid. Yield: 0.050 g (44%); mp. 125.1-128.4 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.24-7.19 (m, 2H), 7.10-7.06 (m, 2H), 6.96-6.92 (m, 1H), 6.92-6.86 (m, 4H), 6.46 (ddd,

J = 9.4, 6.0, 0.9 Hz, 1H), 6.16-6.05 (m, 2H), 2.78 (s, 3H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 195.0, 170.0, 152.0, 142.0, 137.8, 137.6, 135.0, 133.8, 130.4, 129.7, 129.6, 129.3, 128.0, 127.4, 126.9, 123.2, 76.6, 26.9, 21.0. MS (EI, 70 eV; *m/z* (relative intensity)): 455 (18), 346 (22), 281 (16), 249 (31), 221 (13), 207 (47), 193 (45), 165 (46), 162 (63), 96 (18), 91 (100), 65 (11). HRMS calcd for $C_{23}H_{19}ClNO_2Se$ (ESI-TOF, [M + H^+]), 456.0270 found 456.0270.

4-(2-Methoxyphenyl)-1-methyl-3-(p-tolylselanyl)-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2h. The product was isolated by column chromatography (hexane:ethyl acetate 75:15) as a brown oil. Yield: 0.042 g (37%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.29-7.21 (m, 2H), 7.19 (ddd, *J* = 8.3, 5.2, 4.0 Hz, 1H), 6.90-6.83 (m, 2H), 6.77-6.68 (m 3H), 6.65 (d, *J* = 8.2 Hz, 1H), 6.24 (ddd, *J* = 9.4, 6.0. 0.8 Hz, 1H), 6.10-6.00 (m, 2H), 3.60 (s, 3H), 2.79 (s, 3H), 2.22 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 194.9, 170.2, 156.3, 151.9, 141.0, 138.0, 137.2, 133.7, 131.0, 130.2, 129.8, 129.4, 127.3, 125.7, 123.8, 120.4, 119.7, 110.3, 78.4, 54.8, 27.2, 21.0. MS (EI, 70 eV; *m/z* (relative intensity)): 451 (27), 420 (64), 417 (30), 340 (100), 327 (19), 312 (16), 252 (25), 249 (49), 221 (15), 194 (13), 180 (26), 165 (61), 134 (10), 119 (28), 91 (93), 77 (33). HRMS calcd for $C_{24}H_{22}NO_3Se$ (ESI-TOF, [M + H^+]), 452.0765, found 452.0763.

3-((4-Chlorophenyl)selanyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2i. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a black oil. Yield: 0.072 g (65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.30 (d, *J* = 8.6 Hz, 3H), 7.22-7.16 (m, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.03-6.99 (m, 2H), 6.96 (ddd, *J* = 9.9, 6.0, 1.7 Hz, 1H), 6.47 (ddd, *J* = 9.4, 6.0, 0.8 Hz, 1H), 6.16 (dt, *J* = 9.9, 0.8 Hz, 1H), 6.11 (ddd, *J* = 9.4, 1.7, 0.9 Hz, 1H), 2.78 (s, 3H) .^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 194.9, 170.0, 155.7, 142.1, 137.5, 134.1, 133.6, 131.1, 129.3, 129.0, 128.7, 128.0, 127.8, 127.4, 126.9, 126.3, 76.5, 26.9. MS (EI, 70 eV; *m/z* (relative intensity)): 441 (25), 360 (11), 329 (46), 297 (12), 282 (27), 250 (61), 207 (36), 194 (43), 165 (100), 152 (61), 129 (67),112 (30), 89 (12), 75 (32). HRMS calcd for $C_{22}H_{17}ClNO_2Se$ (ESI-TOF, [M + H^+]), 442.0113 found 442.0110.

3-((4-Fluorophenyl)selanyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2j. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a brown oil. Yield: 0.035 g (33%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.37-7.32 (m, 2H), 7.28-7.22 (m, 1H), 7.20-7.15 (m, 2H), 7.01-6.97 (m, 2H), 6.92 (ddd, *J* = 9.9, 6.0, 1.7 Hz, 1H), 6.81-6.75 (m, 2H), 6.44 (ddd, *J* = 9.4, 6.0, 0.8 Hz, 1H), 6.17-6.05 (m, 2H), 2.77 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 194.9, 170.1, 162.4 (d, *J* = 248.0 Hz), 154.8, 141.8,

137.6, 135.5 (d, *J* = 8.1 Hz), 131.2, 129.3, 129.1, 127.9, (d, *J* = 4.4 Hz), 127.6, 127.4, 126.8, 122.3, 116.0 (d, *J* = 22 Hz), 76.6, 26.8. MS (EI, 70 eV; *m/z* (relative intensity)): 425 (40), 344 (15), 327 (57), 316 (65), 301 (08), 288 (14), 250 (71), 222 (39), 194 (49), 165 (100), 152 (65), 129 (74), 115 (26), 96 (37), 75 (33). HRMS calcd for $C_{22}H_{17}FNO_2Se$ (ESI-TOF, [M + H^+]), 426.0409 found 426.0415.

1-Methyl-4-phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2k. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a brown solid. Yield: 0.087 g (73%); mp. 141.7-142.8 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.58-7.52 (m, 2H), 7.37-7.32 (m, 1H), 7.25-7.19 (m, 2H), 7.18-7.12 (m, 2H), 7.03-6.99 (m, 2H), 6.96 (ddd, *J* = 9.9, 6.0, 1.7 Hz, 1H), 6.48 (ddd, *J* = 9.4, 6.0, 0.9 Hz, 1H), 6.17 (dt, *J* = 9.9, 0.9 Hz, 1H), 6.12 (ddd, *J* = 9.4, 1.7, 0.9 Hz, 1H), 2.79 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 194.7, 169.9, 156.1, 142.0, 137.3, 135.8, 130.9 (q, *J* = 32.4 Hz), 129.4, 129.2, 129.1 (q, *J* = 3.7 Hz), 128.4, 128.0, 127.6, 127.3, 127.0, 124.0 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 273.6 Hz), 76.6, 26.8. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as external reference) δ(ppm) 306.6. MS (EI, 70 eV; *m/z* (relative intensity)): 476 ([M + 1], 10), 475 (50), 394 (16), 366 (36), 346 (17), 329 (33), 300 (05), 282 (23), 250 (73), 222 (49), 194 (50), 165 (100), 152 (64), 129 (69), 115 (22), 89 (13), 75 (21). HRMS calcd for $C_{23}H_{17}F_3NO_2Se$ (ESI-TOF, [M + H^+]), 476.0377 found 476.0370.

3-(Butylselanyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 2l. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a brown oil. 0.07 g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.24 (m, 3H), 7.21-7.13 (m, 2H), 6.95 (ddd, *J* = 9.9, 6.0, 1.7 Hz, 1H), 6.51-6.42 (m, 1H), 6.14 (d, *J* = 10 Hz, 1H), 6.09 (d, *J* = 10 Hz, 1H), 3.07-2.95 (m, 1H), 2.95-2.84 (m, 1H), 2.78 (s, 3H), 1.63-1.50 (m, 2H), 1.35-1.23 (m,2H), 0.83 (s, 3H) .^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ195.2, 170.7, 152.4, 141.8, 138.1, 132.0, 129.2, 128.1, 128.0, 127.9, 127.4, 126.5, 76.3, 32.2, 26.7, 25.3, 22.5, 13.4. MS (EI, 70 eV; *m/z* (relative intensity)): 387 (40), 330 (26), 302 (18), 251 (46), 250 (100), 222 (47), 194 (34), 165 (67), 152 (35), 129 (15), 102 (05), 89 (09), 66 (04). HRMS calcd for $C_{20}H_{22}NO_2Se$ (ESI-TOF, [M + H^+]), 388.0816, found 308.0822.

1-Methyl-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2m. The product was isolated by column chromatography (hexane:ethyl acetate 65:35) as a white solid. Yield: 0.054 g (67%); mp. 135.1-135.9 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.35 (m. 2H), 7.29-7.20 (m, 1H), 7.20-7.13 (m, 3H), 7.13-7.07 (m, 4H), 6.50 (d, *J* = 10.2 Hz, 2H), 6.42 (d, *J* = 10.2 Hz, 2H), 2.90 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 183.8, 168.7,

154.1, 144.9, 133.8, 133.0, 131.1, 130.0, 129.3, 128.9, 128.1, 127.9, 127.8, 127.0, 69.0, 26.3. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as external reference) δ(ppm) 313.8. MS (EI, 70 eV; *m/z* (relative intensity)): 407 (17), 250 (28), 222 (44), 207 (05), 178 (07), 165 (11), 152 (05), 129 (100), 101 (06), 77 (06). HRMS calcd for $C_{22}H_{18}NO_2Se$ (ESI-TOF, [M + H^+]), 408.0503, found 408.0510.

4-(3-Methoxyphenyl)-1-methyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2n. The product was isolated by column chromatography (hexane:ethyl acetate 75:25) as an orange solid. Yield: 0.077 g (72%); mp. 141.8-144.9 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.36 (m, 2H), 7.19-7.14 (m, 1H), 7.13-7.07 (m, 3H), 6.77 (ddd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 6.69 (ddd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 6.61-6.60 (m, 1H), 6.50 (d, *J* = 10.3 Hz, 2H), 6.43 (d, *J* = 10.3 Hz, 2H), 3.68 (s, 3H), 2.89 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 183.8, 168.6, 159.0, 153.6, 145.0, 133.8, 133.0, 130.1, 129.2, 128.9, 127.8, 127.0, 120.2, 114.8, 113.9, 68.9, 55.1, 26.3. MS (EI, 70 eV; *m/z* (relative intensity)): 437 (09), 356 (06), 280 (10), 252 (41), 207 (08), 159 (100), 116 (18), 77 (14). HRMS calcd for $C_{23}H_{20}NO_3Se$ (ESI-TOF, [M + H^+]), 438.0608, found 438.0615.

1-Methyl-4-(naphthalen-1-yl)-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2o. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as an orange solid. Yield: 0.099 g (88%); mp. 127.2-129.8. ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.72-7.67 (m, 1H), 7.61-7.56 (m, 2H), 7.46-7.43 (m, 2H), 7.15-7.08 (m, 1H), 6.98-6.94 (m, 2H), 6.89 (dtd, *J* = 7.4, 4.0, 1.3 Hz, 2H), 6.70-6.63 (m, 3H), 6.53-6.45 (m, 2H), 5.99 (dd, *J* = 10.1, 1.8 Hz, 1H), 2.99 (s, 3H).^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 183.6, 168.7, 149.0, 144.6, 144.5, 134.9, 133.8, 133.4, 133.1, 132.4, 130.1, 129.3, 128,6, 127.9, 127.4, 126.4, 125.8, 124.9, 124.0, 123.9, 70.7, 26.6. MS (EI, 70 eV; *m/z* (relative intensity)): 457 [(M+2), 15], 455 (08), 300 (18), 272 (14), 243 (04), 228 (05), 179 (100), 151 (29), 77 (04). HRMS calcd for $C_{26}H_{20}NO_2Se$ (ESI-TOF, [M + H^+]), 458.0659, found 458.0665.

1-Methyl-4-phenyl-3-(p-tolylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2p. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a white solid. Yield: 0.051 g (49%); mp. 155.2-157.8 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.30-7.22 (m, 3H), 7.21-7.15 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.50 (d, *J* = 10.2 Hz, 2H), 6.41 (d, J = 10.2 Hz, 2H), 2.89 (s, 3H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 183.9, 168.7, 153.4, 145.0, 138.0, 134.2, 132.9, 131.1, 130.4, 129.7, 129.1, 128.1, 128.0, 123.0, 68.9, 26.3, 21.0. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as external reference) δ(ppm) 310.0. MS (EI, 70 eV; *m/z* (relative intensity)): 421 (24), 250

(23), 222 (54), 165 (11), 129 (100), 101 (06). HRMS calcd for $C_{23}H_{20}NO_2Se$ (ESI-TOF, [M + H^+]), 422.0659 found 422.0664.

3-((4-Chlorophenyl)selanyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2q. The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a white solid. Yield: 0.052 g (48%); mp. 187.4-188.4 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.33-7.26 (m, 3H), 7.23-7.17 (m, 2H), 7.09-7.04 (m, 4H), 6.49 (d, *J* = 10.3 Hz, 2H), 6.42 (d, *J* = 10.3 Hz, 2H), 2.89 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 183.7, 168.5, 154.1, 144.7, 135.5, 134.4, 133.1, 131.0, 129.9, 129.4, 129.1, 128.2, 128.0, 124.9, 69.1, 26.3. MS (EI, 70 eV; *m/z* (relative intensity)): 441 (12), 250 (26), 222 (50), 165 (13), 129 (100), 101 (07), 75 (08). HRMS calcd for $C_{22}H_{17}ClNO_2Se$ (ESI-TOF, [M + H^+]), 442.0113 found 442.0109.

1-Methyl-4-phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2r. The product was isolated by column chromatography (hexane:ethyl acetate 75:25) as a white solid. Yield: 0.086 g (72%); mp. 148.2-149.6 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm). 7.56 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.26-7.18 (m, 2H), 7.19-7.12 (m, 2H), 7.09-7.02 (m, 2H), 6.52 (d, *J* = 10.2 Hz, 2H), 6.43 (d, *J* = 10.2 Hz, 2H), 2.92 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 183.6, 168.3, 154.2, 144.5, 137.1, 133.1, 131.0 (q, *J* = 32.5 Hz), 130.7, 130.6, 130.4 (q, *J* = 3.8 Hz), 129.6, 129.4, 129.2, 128.1, 127.8, 124.6 (q, *J* = 3.8 Hz), 120.6 (q, *J*= 272.7 Hz), 69.2, 26.3. MS (EI, 70 eV; *m/z* (relative intensity)): 475 (03), 250 (36), 222 (52), 165 (11), 129 (100), 75 (06). HRMS calcd for $C_{23}H_{17}F_3NO_2Se$ (ESI-TOF, [M + H^+]), 476.0377 found 476.0383.

3-(Butylselanyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2s. The product was isolated by column chromatography (hexane:ethyl acetate 85:15) as a grey solid. Yield: 0.085 g (88%); m.p.: 84.5-85.5°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38-7.30 (m, 3H), 7.30-7.22 (m, 2H), 6.50 (d, *J*= 10.3 Hz, 2H), 6.43 (d, *J* = 10.3 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.91 (s, 3H), 1.56 (qt, *J* = 7.4 Hz, 2H), 1.29 (sext, *J* = 7.4 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): 183.9, 169.2, 151.2, 146.3, 132.8, 131.9, 129.4, 128.9, 128.3, 128.0, 68,7, 32.4, 26.2, 25.1, 13.4. MS (EI, 70 eV; *m/z* (relative intensity)): 387 (10), 385 (05), 331 (06), 306 (22), 250 (17), 222 (100), 207 (15), 165 (45), 152 (09), 129 (54), 101 (05). HRMS calcd for $C_{20}H_{22}NO_2Se$ (ESI-TOF, [M + H^+]), 388.0816, found 308.0819.

3-(Butylselanyl)-1-methyl-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2t. The product was isolated by column chromatography (hexane:ethyl acetate 85:15) as a yellow oil. Yield: 0.03 g (29%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.17-7.12 (m, 4H), 6.48 (d, *J* =

10.3 Hz, 2H), 6.43 (d, *J* = 10.3 Hz, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.90 (s, 3H), 2.34 (s, 3H), 1.57 (qt, *J* = 7.4 Hz, 2H), 1.30 (sext, *J* = 7.4 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 184.1, 169.49, 151.6, 145.5, 139.7, 132.8, 129.1, 129.0, 128.4; 127.9, 68.7, 32.5, 26.28, 25.2, 22.6, 21.3, 13.4. MS (EI, 70 eV; *m/z* (relative intensity)): 401 (10), 345 (23), 320 (19), 236 (100), 207 (14), 179 (21), 165 (12), 143 (59), 115 (27). HRMS calcd for $C_{21}H_{24}NO_2Se$ (ESI-TOF, [M + H^+]), 402.0972, found 402.0972.

1-Butyl-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2u. The product was isolated by column chromatography (hexane:ethyl acetate 85:15) as an orange oil. Yield: 0.091 g (81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.31 (m, 2H), 7.27-7.17 (m, 1H), 7.20-7.10 (m, 3H), 7.12-7.00 (m, 4H), 6.54 (d, *J* = 10.1 Hz, 2H), 6.37 (d, *J* = 10.1 Hz, 2H), 3.31-3.25 (m, 2H), 1.57 (t, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 184.0, 168.8, 153.7, 145.4, 133.9, 132.4, 131.1, 130.5, 129.2, 128.8, 128.0, 128.0, 127.8, 127.0, 77.32, 69.5, 41.5, 31.8, 20.1, 13.6. MS (EI, 70 eV; *m/z* (relative intensity)):.449 (08), 292 (30), 264 (22), 222 (10), 193 (19), 165 (37), 129 (100), 101 (06), 77 (07). HRMS calcd for $C_{25}H_{24}NO_2Se$ (ESI-TOF, [M + H^+]), 450.0972, found 450.0975.

1-Methyl-4-phenyl-3-(phenyltellanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2v. The product was isolated by column chromatography (hexane:ethyl acetate 85:15) as a green solid. Yield: 0.051 g (45%). mp. 135.1-135.9 ºC ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.35 (m, 2H), 7.29-7.20 (m, 1H) 7.20-7.13 (m, 3H), 7.13-7.07 (m, 4H), 6.50 (d, *J* = 10.2 Hz, 2H), 6.42 (d, *J* = 10.2 Hz, 2H), 2.90 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 183.9, 170.9, 158.1, 153.3, 145.0, 139.8, 132.9, 132.0, 129.1, 129.0, 128.329, 128.1, 127.9, 118.2, 110.9, 71.1, 26.5. MS (EI, 70 eV; *m/z* (relative intensity)): 222 (07), 206 (08), 129 (100), 77 (13). HRMS calcd for $C_{22}H_{18}NO_2Te$ (ESI-TOF, [M + H^+]), 450.0400, found 450.0400.

1-Methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 2v'. The product was isolated by column chromatography (hexane:ethyl acetate 75:25) as a yellow solid. Yield: 0.026 g (42%); mp. 136.3-138.7 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.50-7.47 (m, 2H), 7.40-7.36 (m, 2H), 7.36-7.32 (m, 1H), 6.65 (s, 1H), 6.57 (d, *J* = 2.6 Hz, 4H), 2.84 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 184.1, 170.0 156.1, 145.9, 132.8, 130.8, 130.6, 129.0, 126.6, 124.1, 66.9, 25.0. MS (EI, 70 eV; *m/z* (relative intensity)): 193 (18), 165 (100), 164 (21), 129 (98). HRMS calcd for $C_{16}H_{14}NO_2$ (ESI-TOF, [M + H^+]), 252.1025, found 252,1020.

General procedure for Suzuki Cross-Coupling: In a Schlenk tube, containing $Pd(PPh_3)_4$ (0.1 eq) and boronic acid (3 eq) in DMF (3 mL) was added the 3-organoselenyl[4,5]trienones

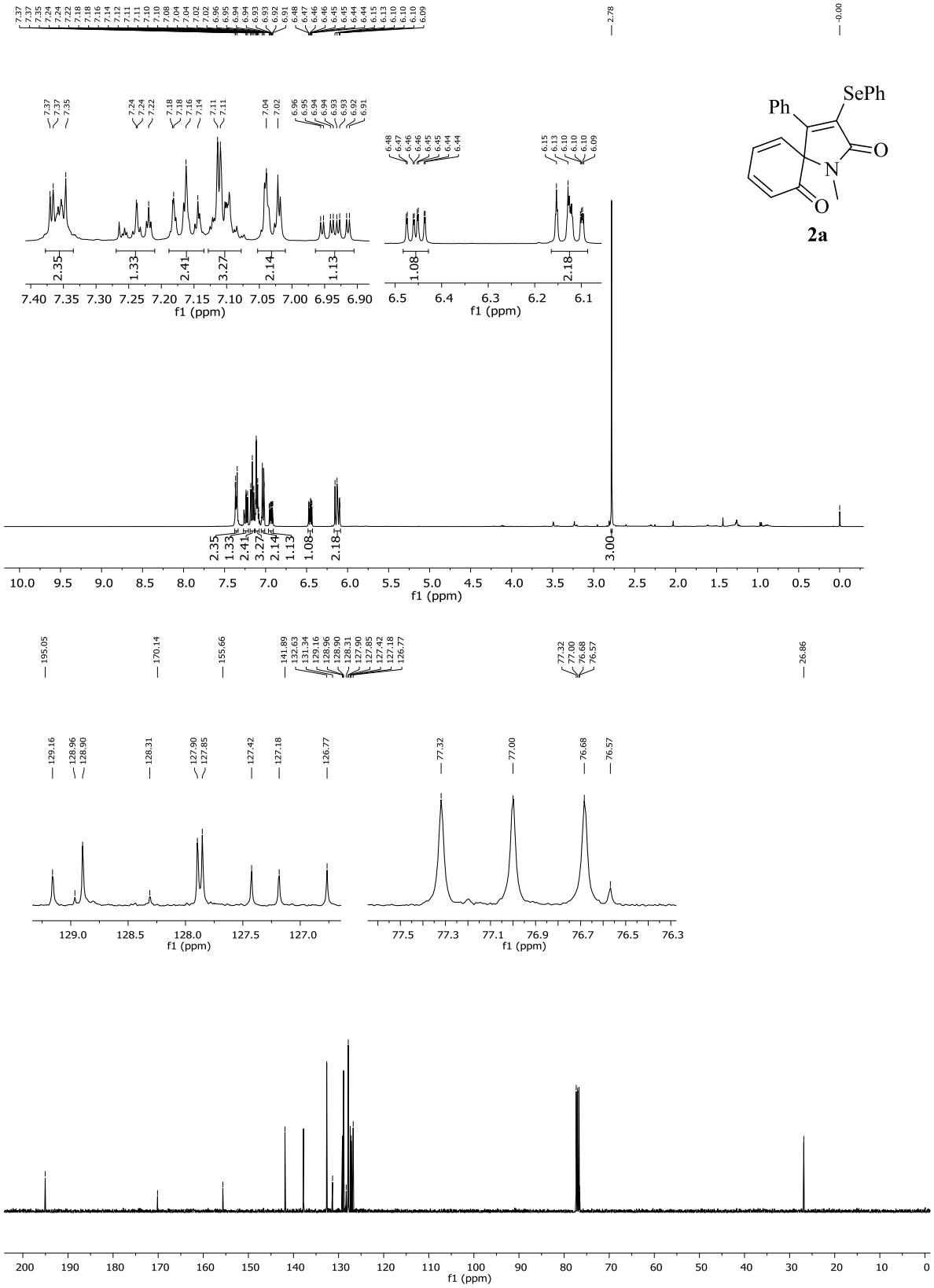
(0.25 mmol). After that, $Cu(OAc)_2 \cdot H_2O$ (1.2 eq) were added to the reaction mixture. The reaction was then heated in oil bath for 24 h at 80 °C. The mixture was diluted with ethyl acetate and washed with concentrated NH_4Cl solution. The organic phase was dried with MgSO4, the solvent was removed under reduced pressure. The residue was purified by column chromatography. **1-Methyl-3,4-diphenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 3a.** The product was isolated by column chromatography (hexane:ethyl acetate 75:25) as a yellow solid. Yield: 0.055 g (68%); mp. 179.9-181.3 ºC ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46-7.37 (m, 2H), 7.31-7.17 (m, 6H), 7.15-7.06 (m, 2H), 6.59 (d, *J* = 10.1 Hz, 2H), 6.46 (d, *J* = 10.1 Hz, 2H), 2.95 (s, 3H).^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 184.0, 169.5, 149.7, 145.6, 135.3, 133.8, 133.1, 131.8, 130.5, 129.4, 129.2, 128.5, 128.3, 128.1, 67.0, 26.1. MS (EI, 70 eV; *m/z* (relative intensity)): 327 (32), 299 (41), 270 (31), 239 (05), 222 (13), 178 (21), 152 (15), 77 (04). HRMS calcd for $C_{22}H_{18}NO_2$ (ESI-TOF, [M + H^+]), 328.1338, found 328.1345.

1-Methyl-4-phenyl-3-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 3b. The product was isolated by column chromatography (hexane:ethyl acetate 75:25) as a yellow solid. Yield: 0.060 g (70%); mp. 161.8-164.9 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.36-7.28 (m, 2H), 7.28-7.24 (m, 2H), 7.23-7.19 (m, 1H), 7.14-7.03 (m, 4H), 6.59 (d, *J* = 10.2 Hz, 2H), 6.45 (d, *J* = 10.2 Hz, 2H), 2.95 (s, 3H), 2.29 (s, 3H).^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 184.1, 169.7, 148.8, 145.8, 144.9, 138.6, 135.2, 133.0, 132.0, 129.2, 129.0, 128.8, 128.5, 128.4, 66.9, 26.1, 21.2. MS (EI, 70 eV; *m/z* (relative intensity)): 341 (93), 313 (100), 298 (11), 284 (37), 270 (15), 236 (21), 191 (28), 165 (17), 77 (03). HRMS calcd for $C_{23}H_{20}NO_2$ (ESI-TOF, [M + H^+]), 342.1494, found 342.1489.

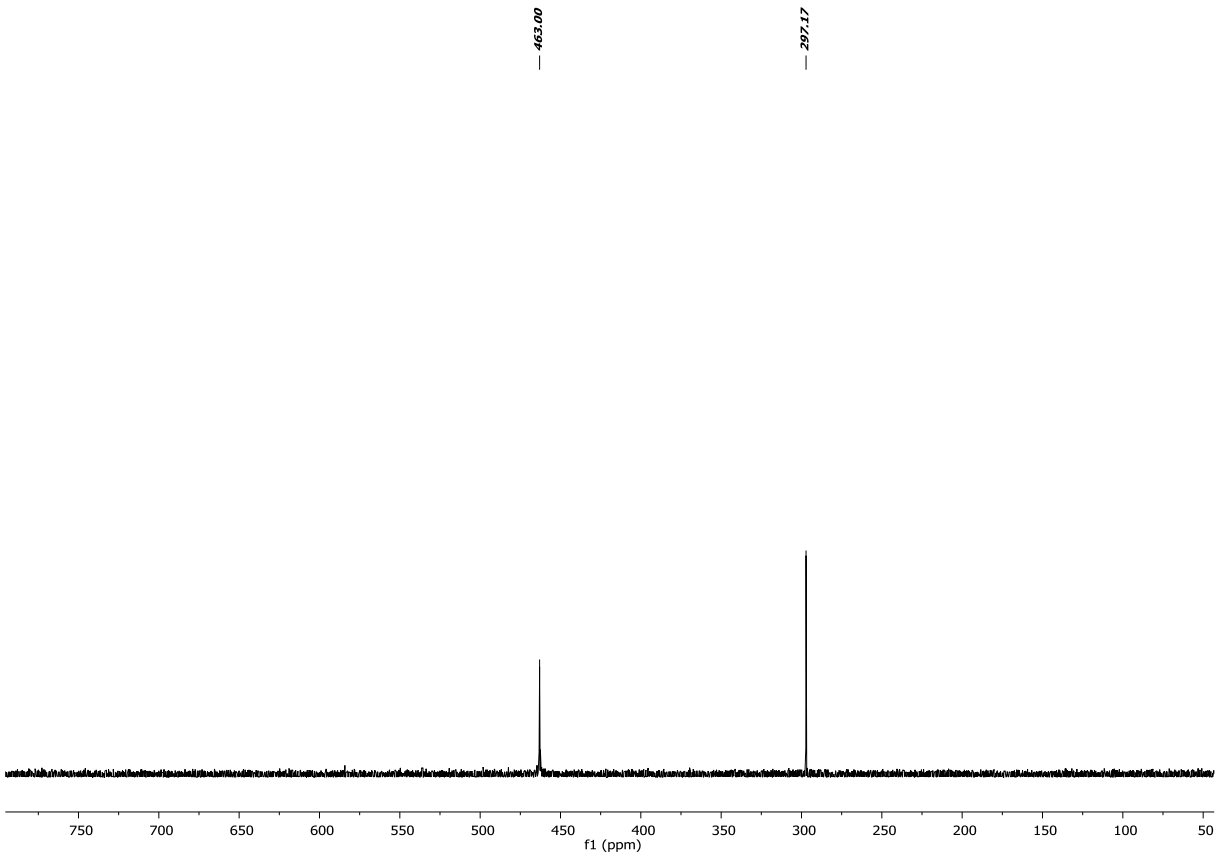
3-(4-Chlorophenyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione 3c. The product was isolated by column chromatography (hexane:ethyl acetate 75:25) as a yellow solid. Yield: 0.056 g (62%); mp. 124.8-126.5 ºC ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.41-7.34 (m, 2H), 7.33-7.18 (m, 5H), 7.12-7.07 (m, 2H), 6.58 (d, *J* = 10.2 Hz, 2H), 6.47 (d, *J* = 10.2 Hz, 2H), 2.95 (s, 3H).^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 183.9, 169.1, 150.2, 145.2, 134.6, 134.1, 133.2, 131.5, 130.7, 129.4, 128.9, 128.7, 128.4, 128.2, 67.0, 26.1. MS (EI, 70 eV; *m/z* (relative intensity)): 363 [M+2 (20)], 361 (58), 333 (100), 304 (35), 270 (08), 256 (15), 239 (17), 222 (31), 176 (40), 165 (10), 151 (14), 121 (13), 119 (11), 77 (03). HRMS calcd for $C_{22}H_{17}ClNO_2$ (ESI-TOF, [M + H^+]), 362.0948, found 362.0951.

1-Methyl-4-phenyl-3-(p-tolyl)-1-azaspiro[4.5]deca-3,7,9-triene-2,6-dione 3d. The product was isolated by column chromatography (hexane:ethyl acetate 75:25) as a brown solid. Yield: 0.048 g (37%); mp. 135.2-139.4. ºC ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.33-7.15 (m, 5H), 7.08-6.98 (m, 4H), 6.93 (ddd, *J* = 9.9, 6.0, 1.7 Hz, 1H), 6.48 (ddd, *J* = 9.4, 6.0, 0.9 Hz, 1H), 6.19 (ddd, *J* = 9.4, 1.8, 0.9 Hz, 1H), 6.12 (dt, *J* = 9.9, 0.9 Hz, 1H), 2.82 (s, 3H), 2.27 (s, 3H).^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz,): δ 196.1, 171.1, 149.1, 141.8, 138.6, 138.1, 134.8, 132.1, 129.3, 128.8, 128.7, 128.3, 128.2, 127.8, 127.5, 126.7, 74.8, 26.6, 21.2. MS (EI, 70 eV; *m/z* (relative intensity)): 341 (77), 313 (100), 298 (11), 284 (38), 270 (15), 255 (06), 236 (21), 222 (12), 191 (30), 165 (23), 120 (08). HRMS calcd for $C_{23}H_{20}NO_2$ (ESI-TOF, [M + H^+]), 342.1499, found 342.1492.

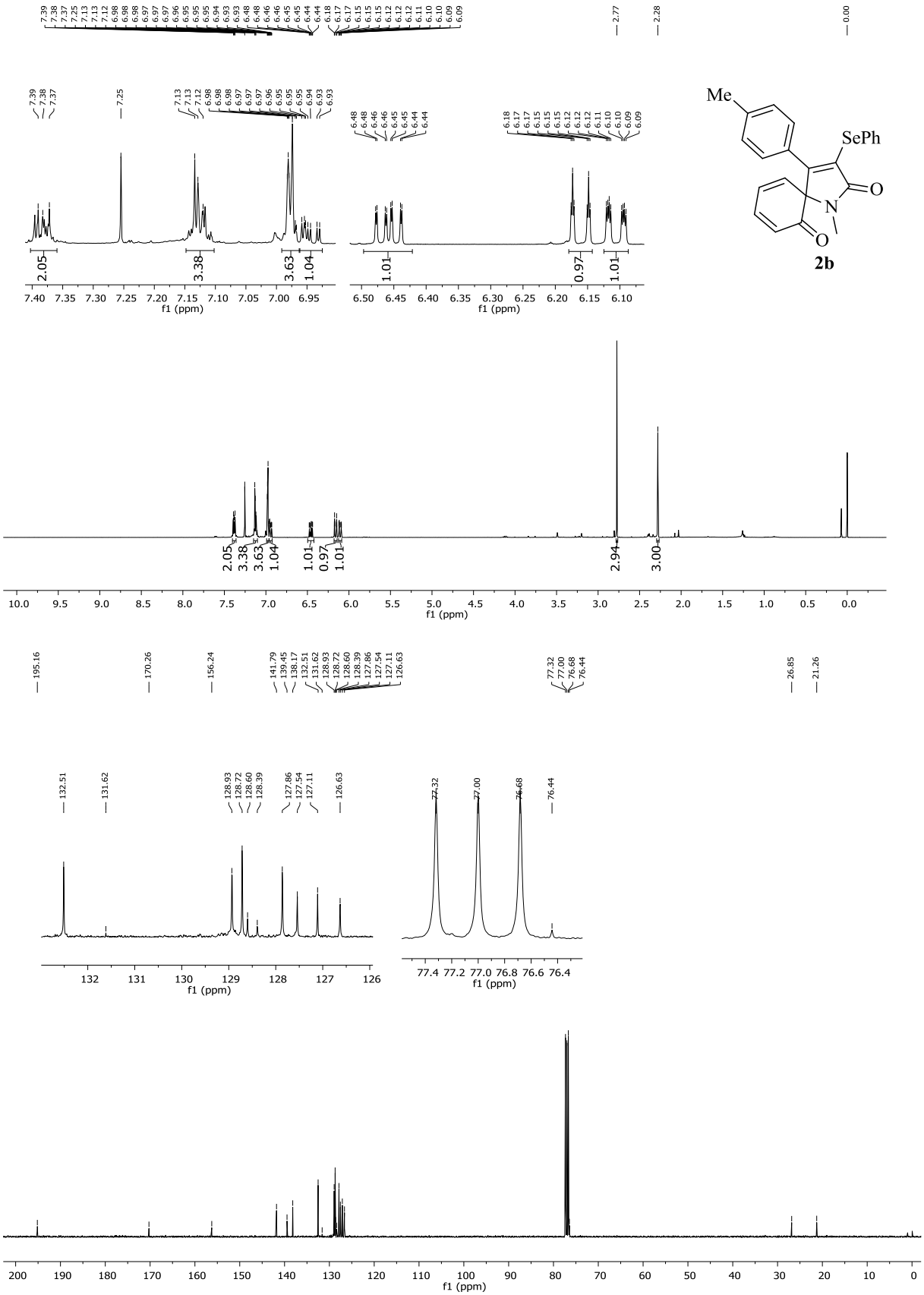
SPECTRA



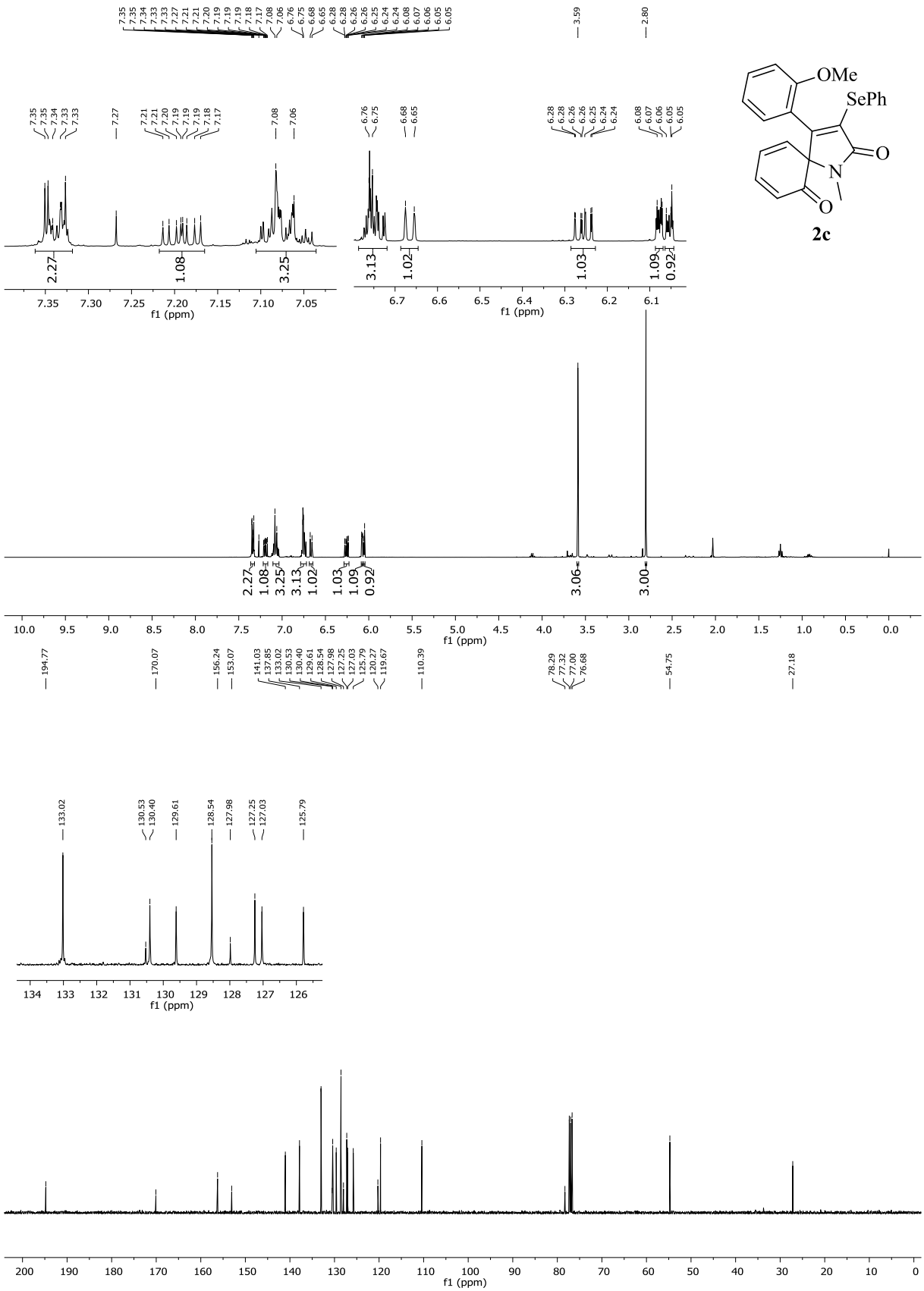
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2a** in $CDCl_3$.



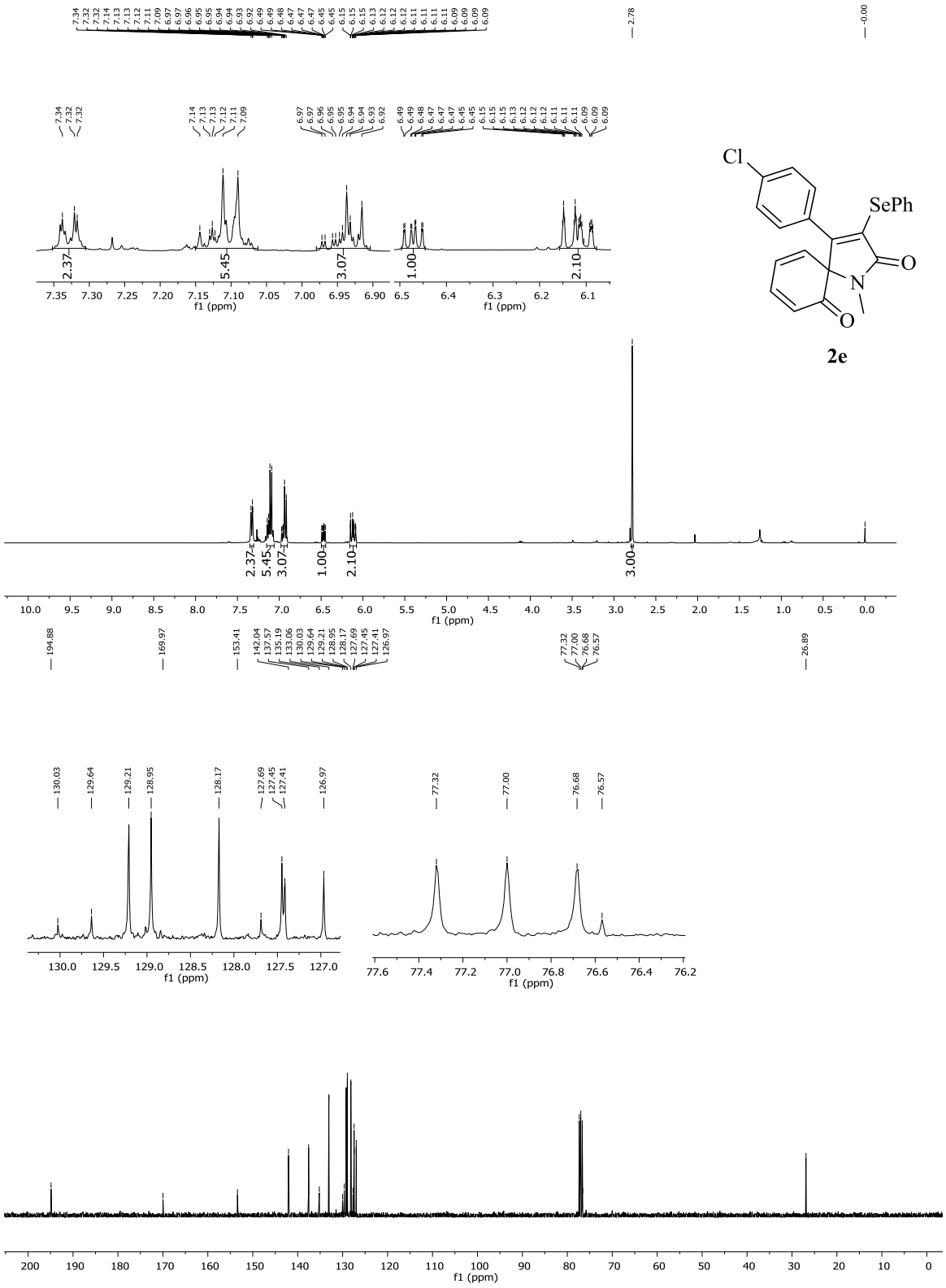
^{77}Se NMR (77MHz, in $CDCl_3$ with diphenyl diselenide as external reference) for **2a**.



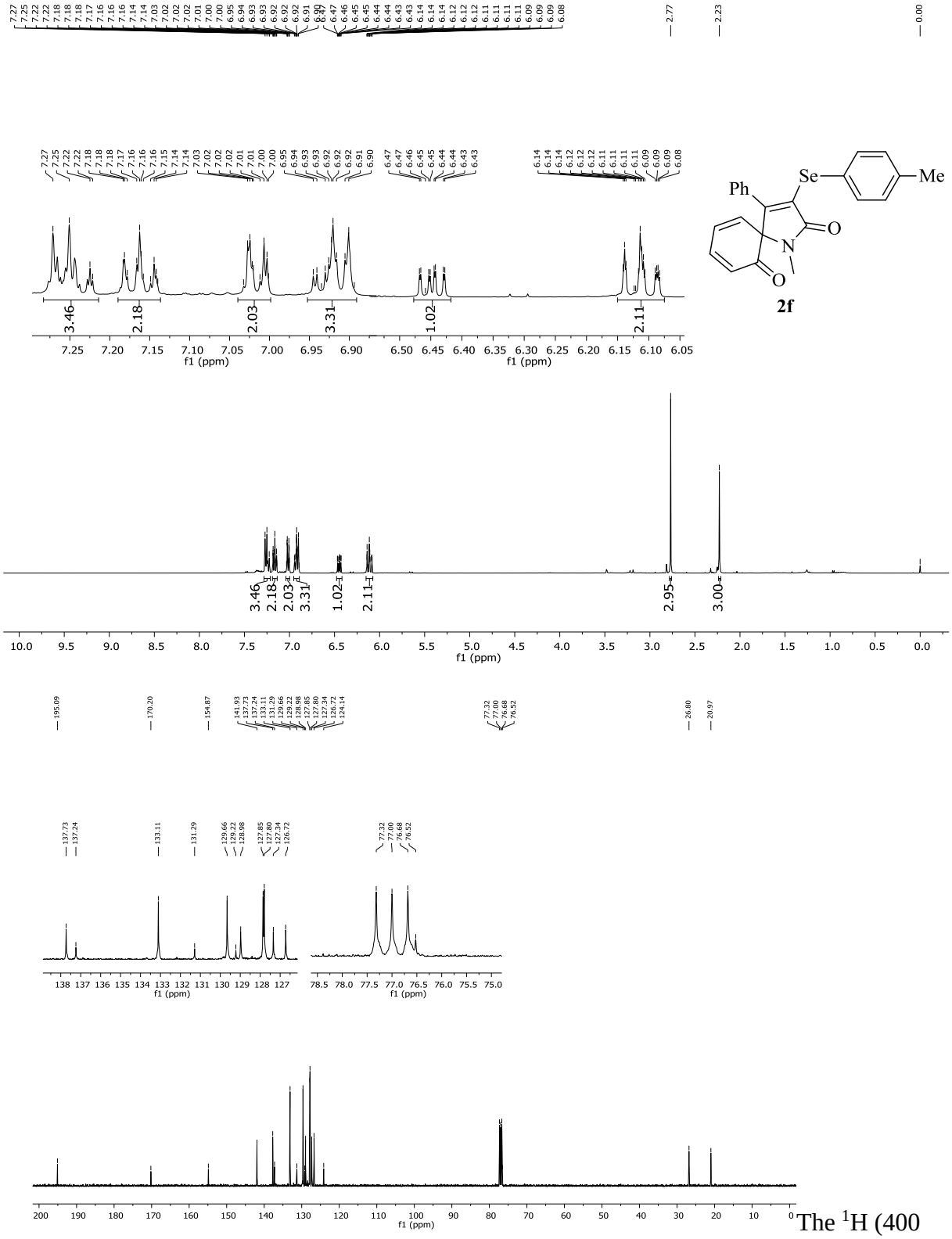
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2b** in $CDCl_3$.



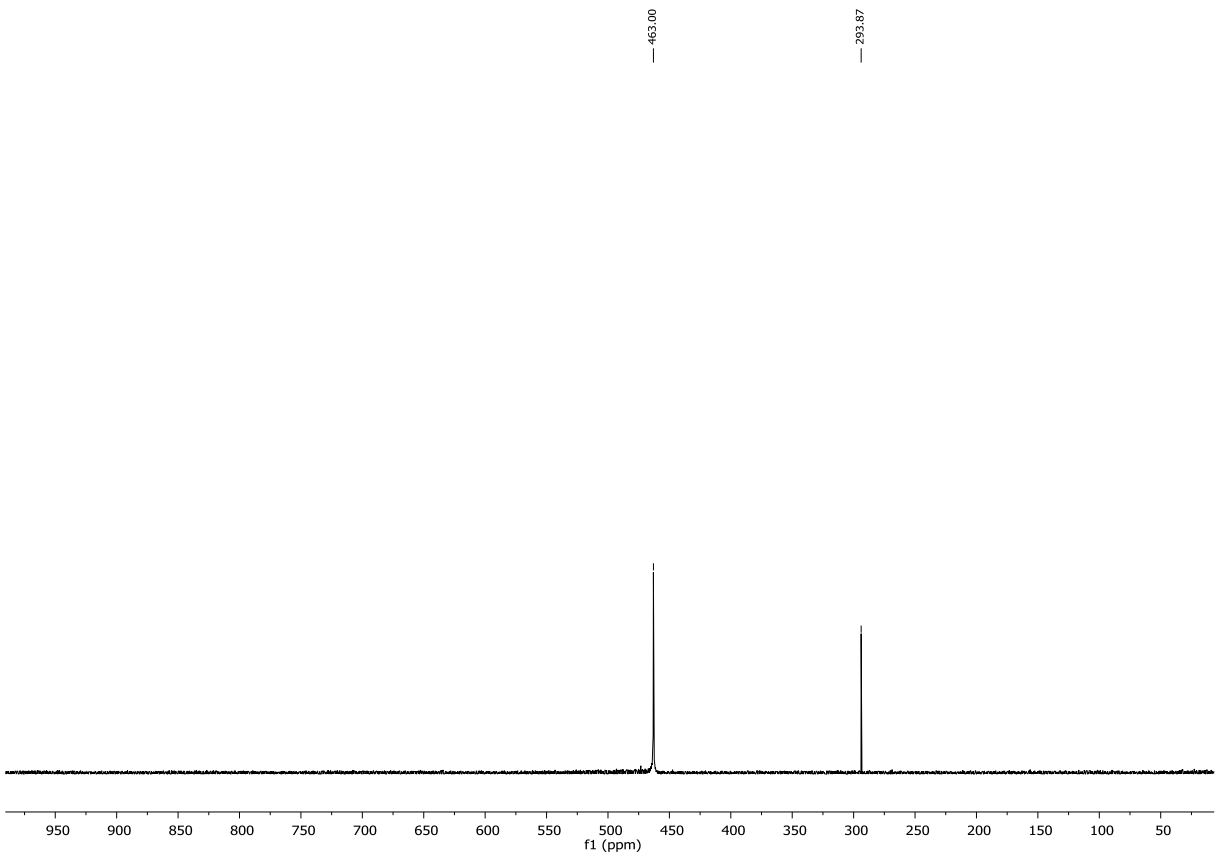
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2c** in $CDCl_3$.



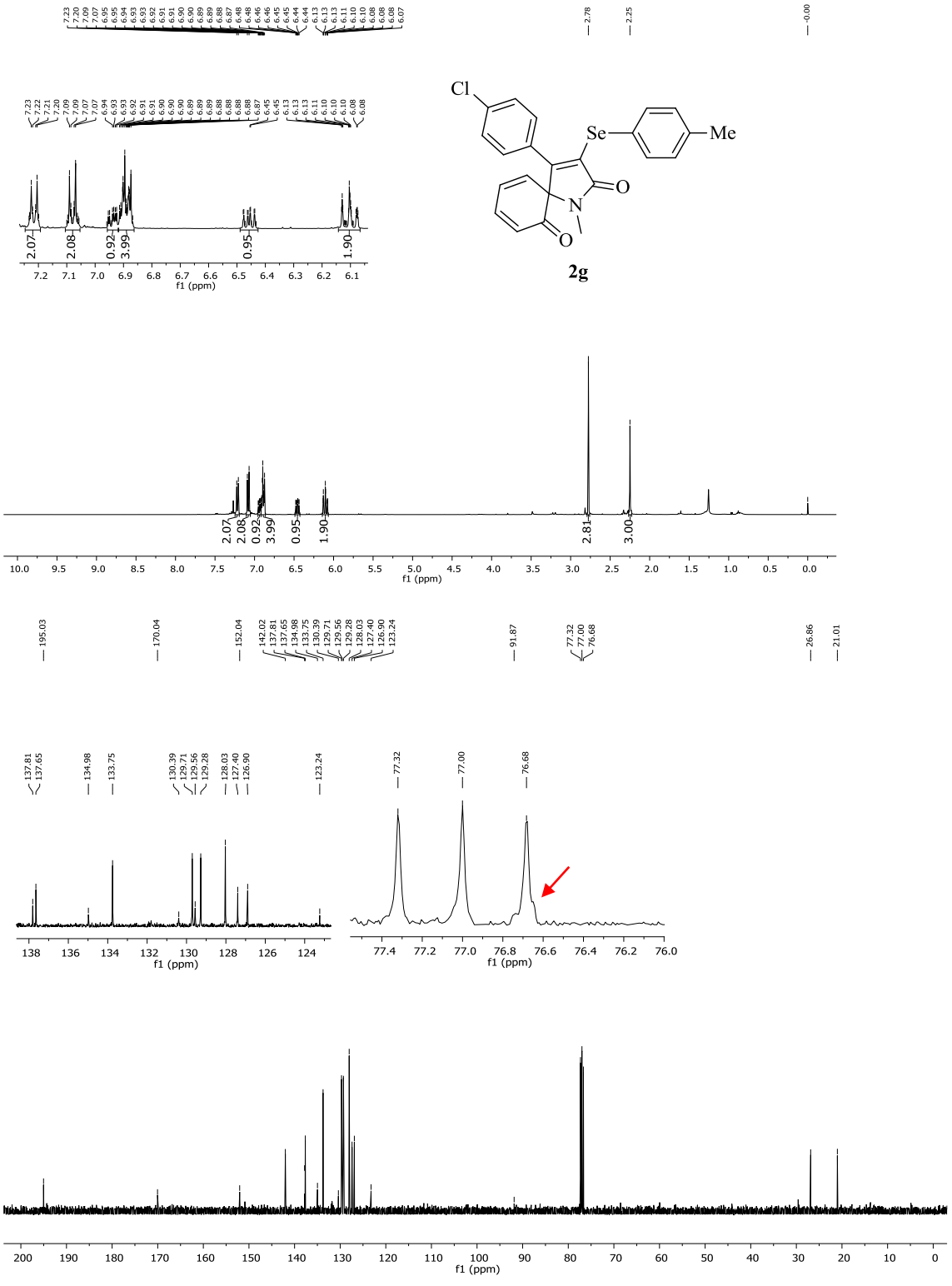
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2e** in $CDCl_3$.



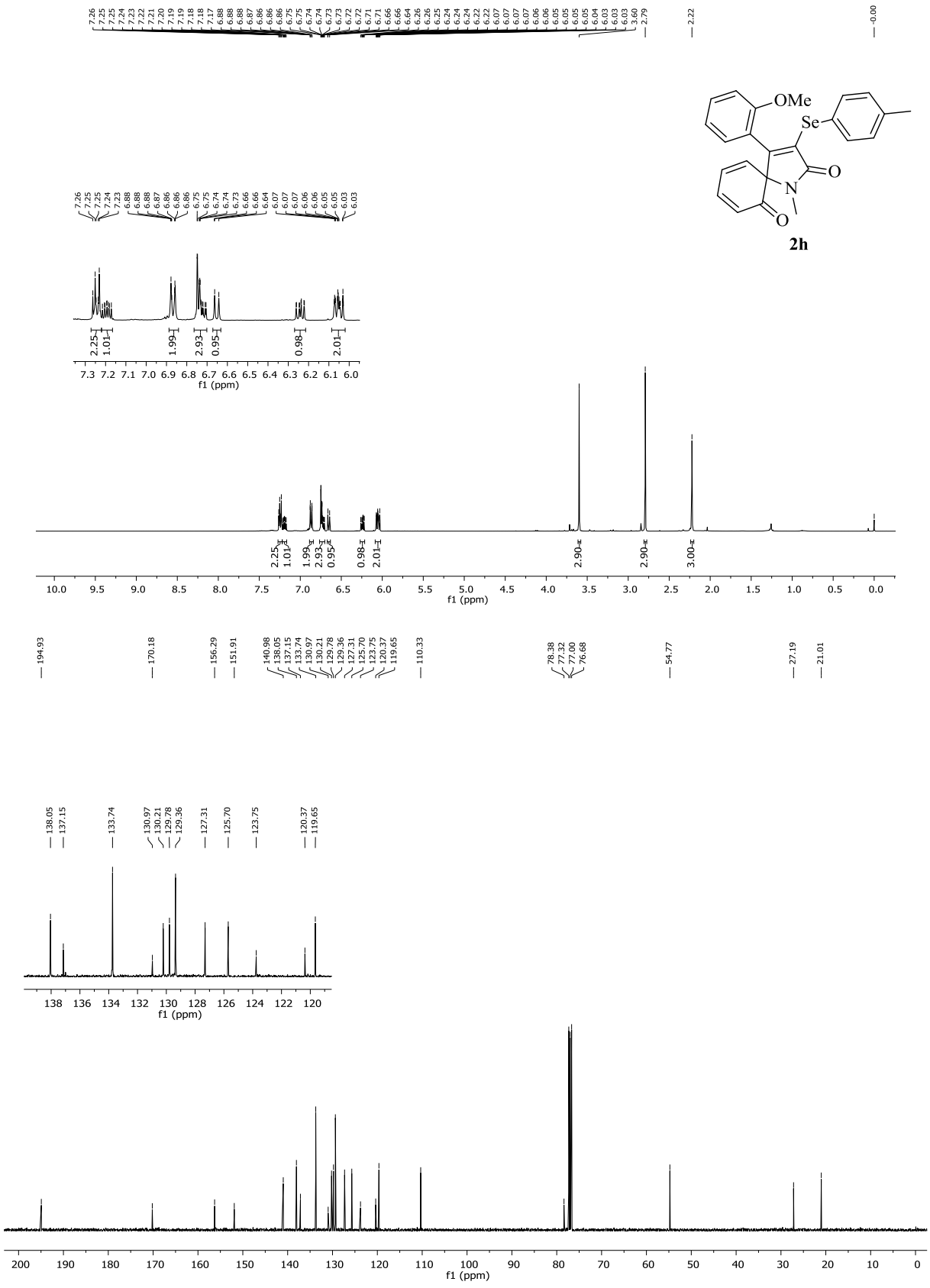
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2f** in $CDCl_3$.



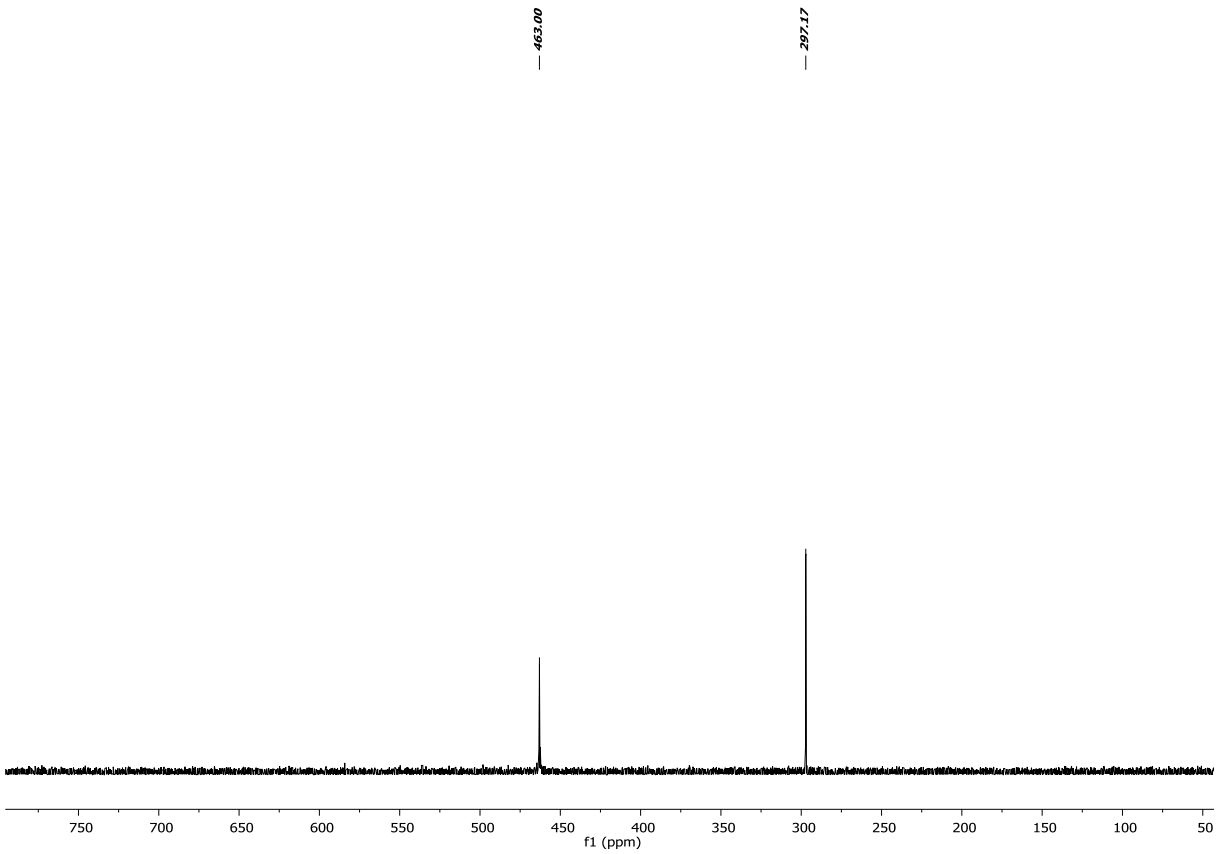
^{77}Se NMR (77MHz, in $CDCl_3$ with diphenyl diselenide as external reference) for **2f**.



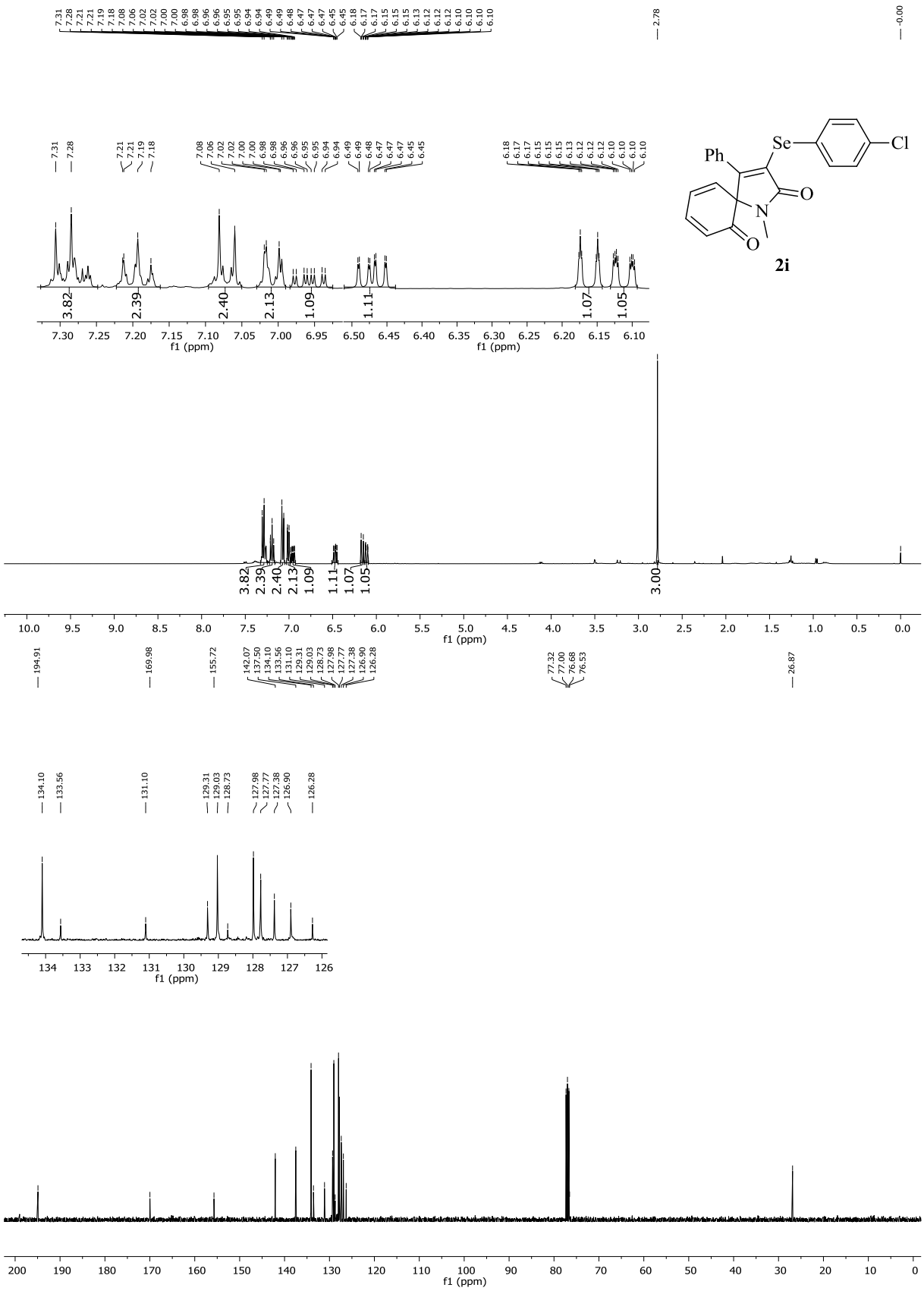
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2g** in $CDCl_3$.



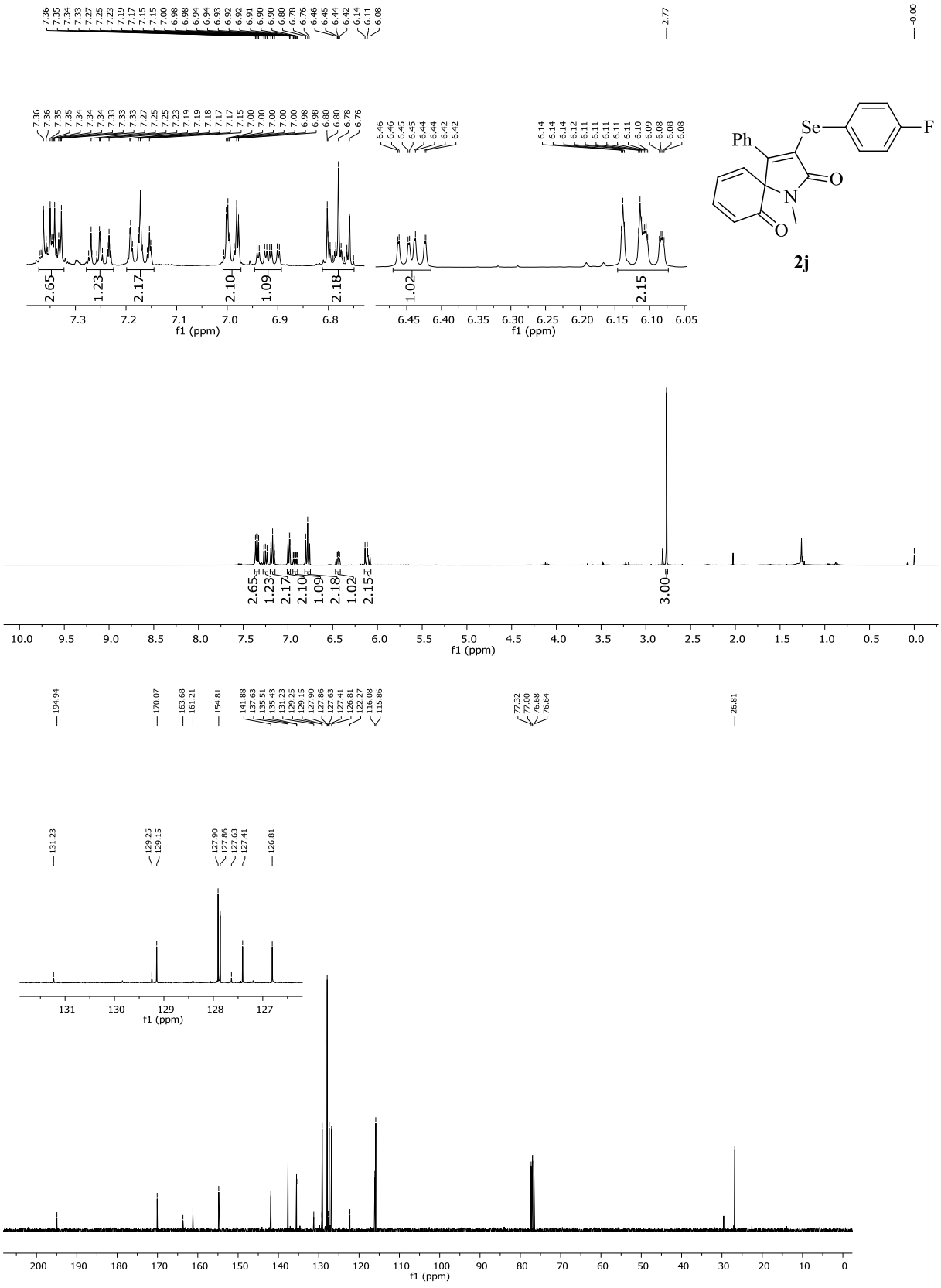
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2h** in $CDCl_3$.



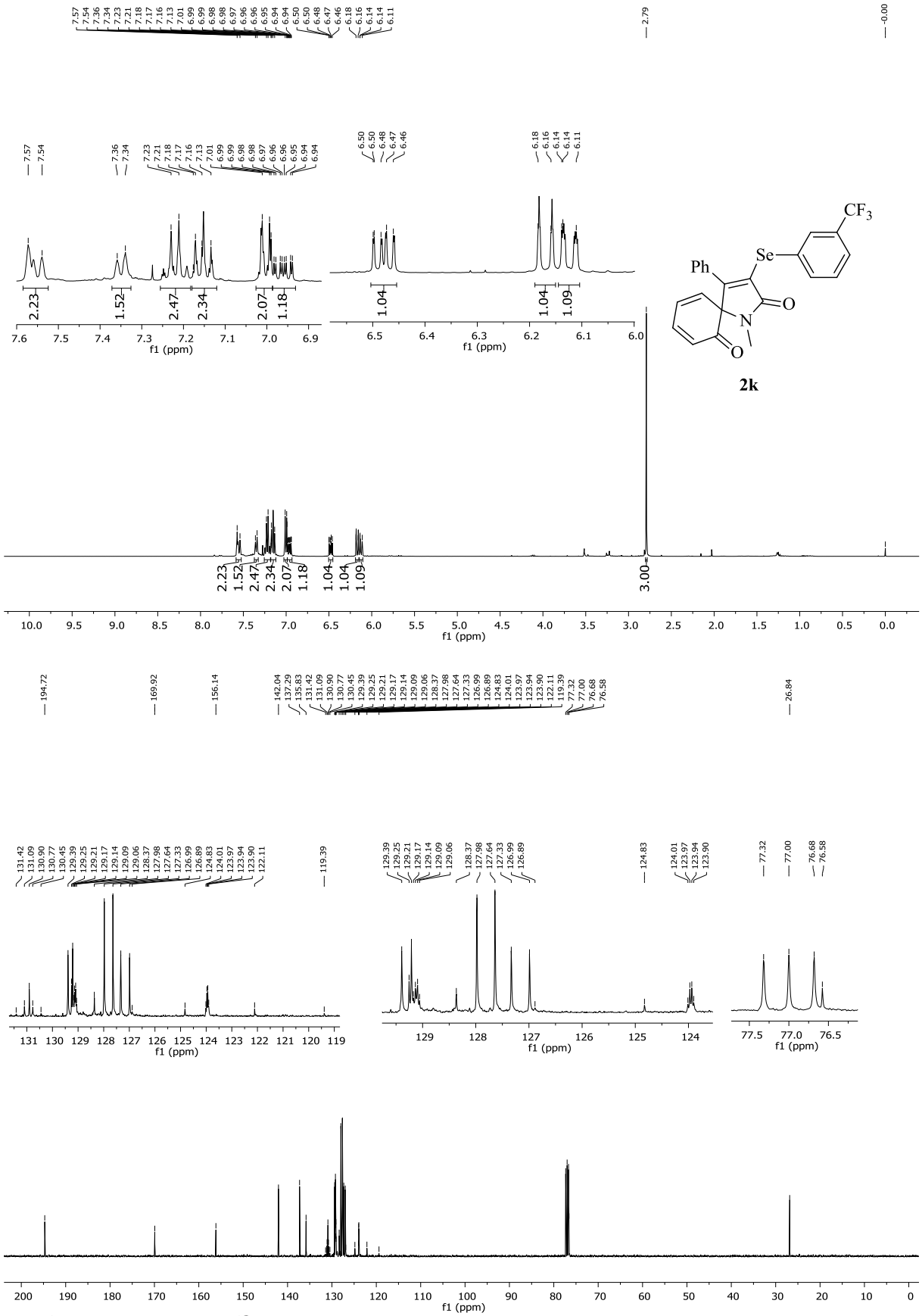
^{77}Se NMR (77MHz, in $CDCl_3$ with diphenyl diselenide as external reference) for **2h**.



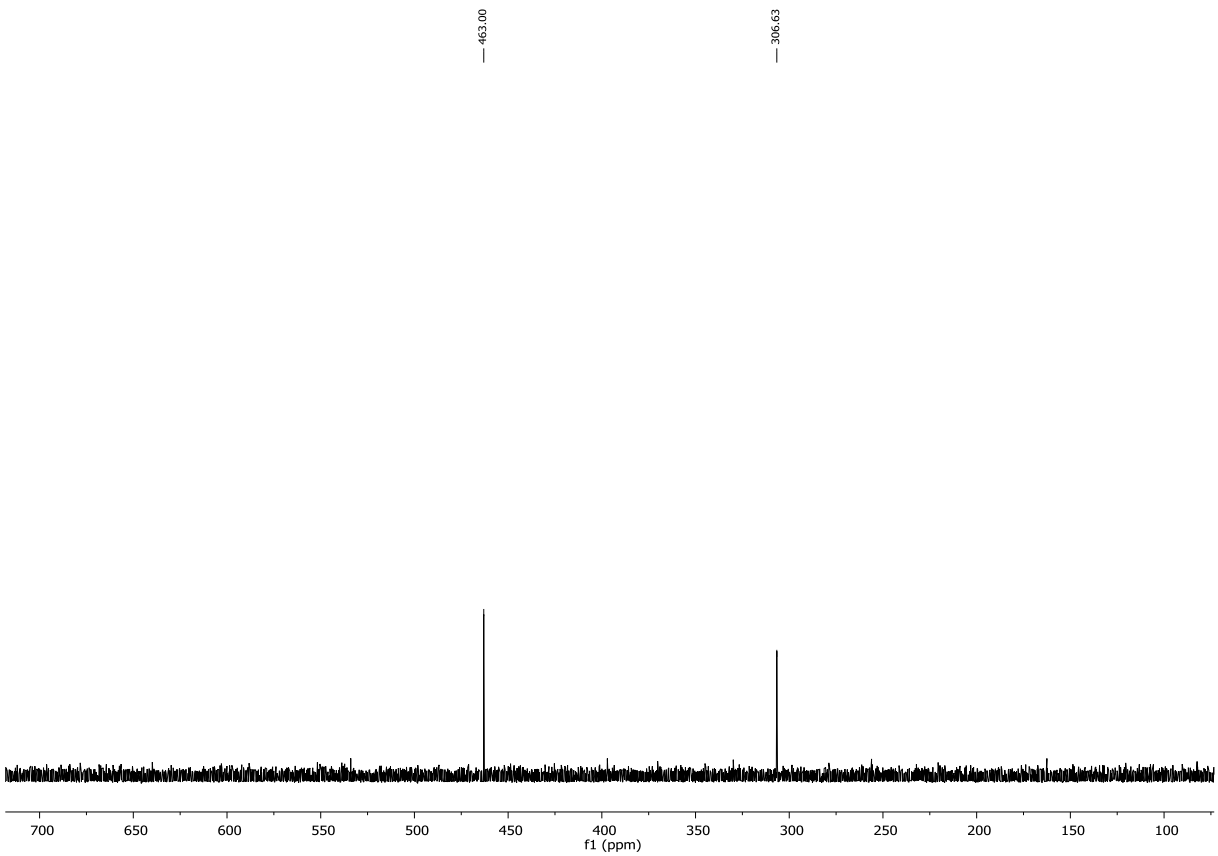
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2i** in $CDCl_3$.



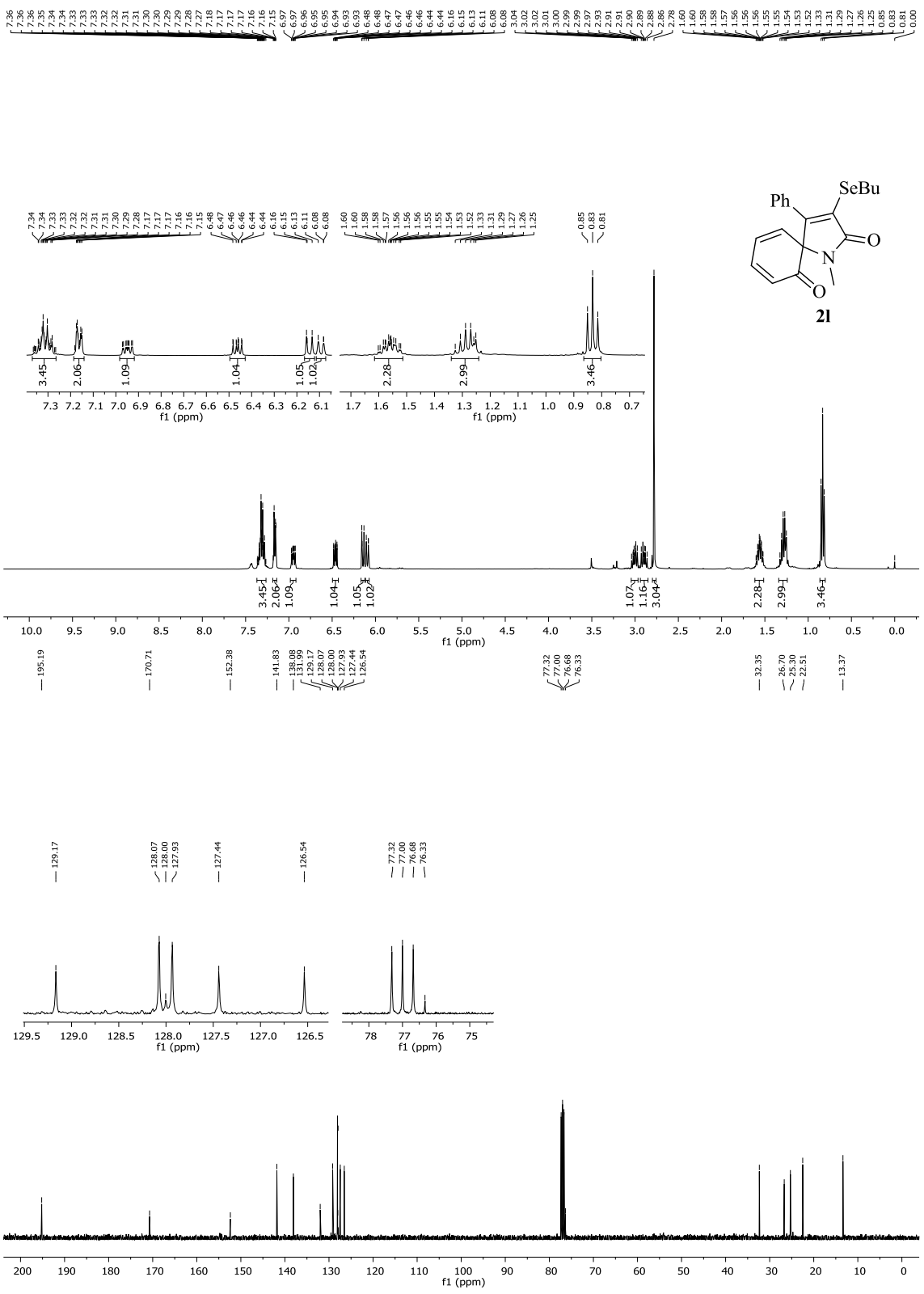
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2j** in $CDCl_3$.



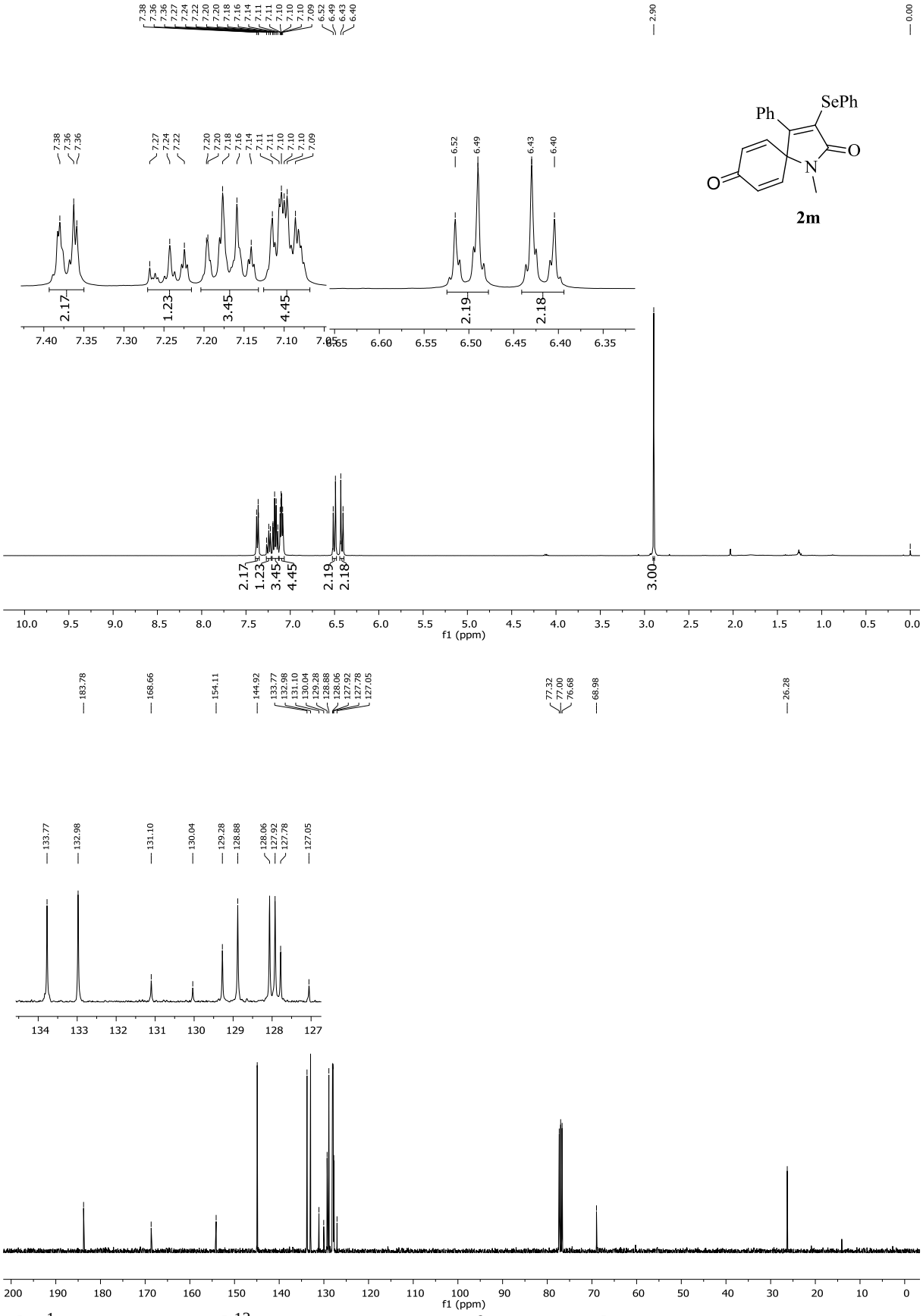
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2k** in $CDCl_3$.



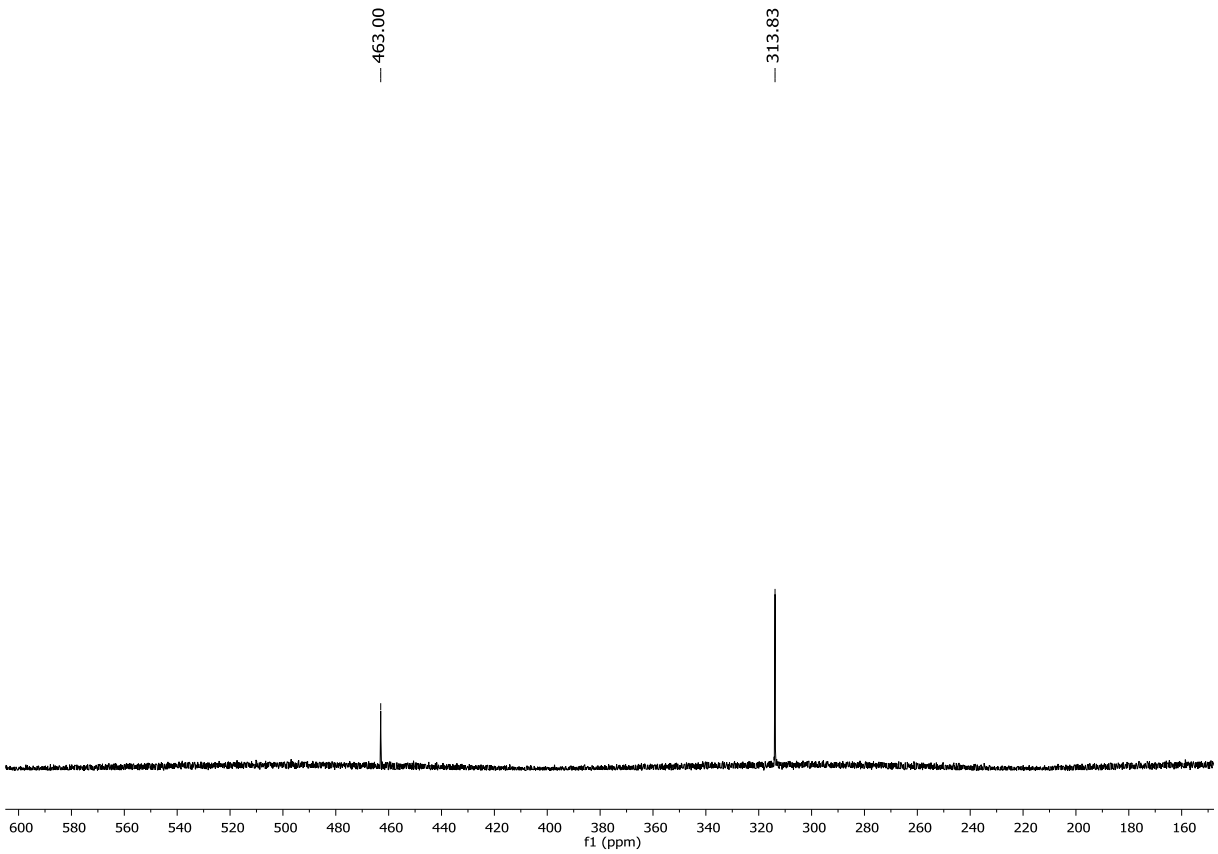
^{77}Se NMR (77MHz, in $CDCl_3$ with diphenyl diselenide as external reference) for **2k**.



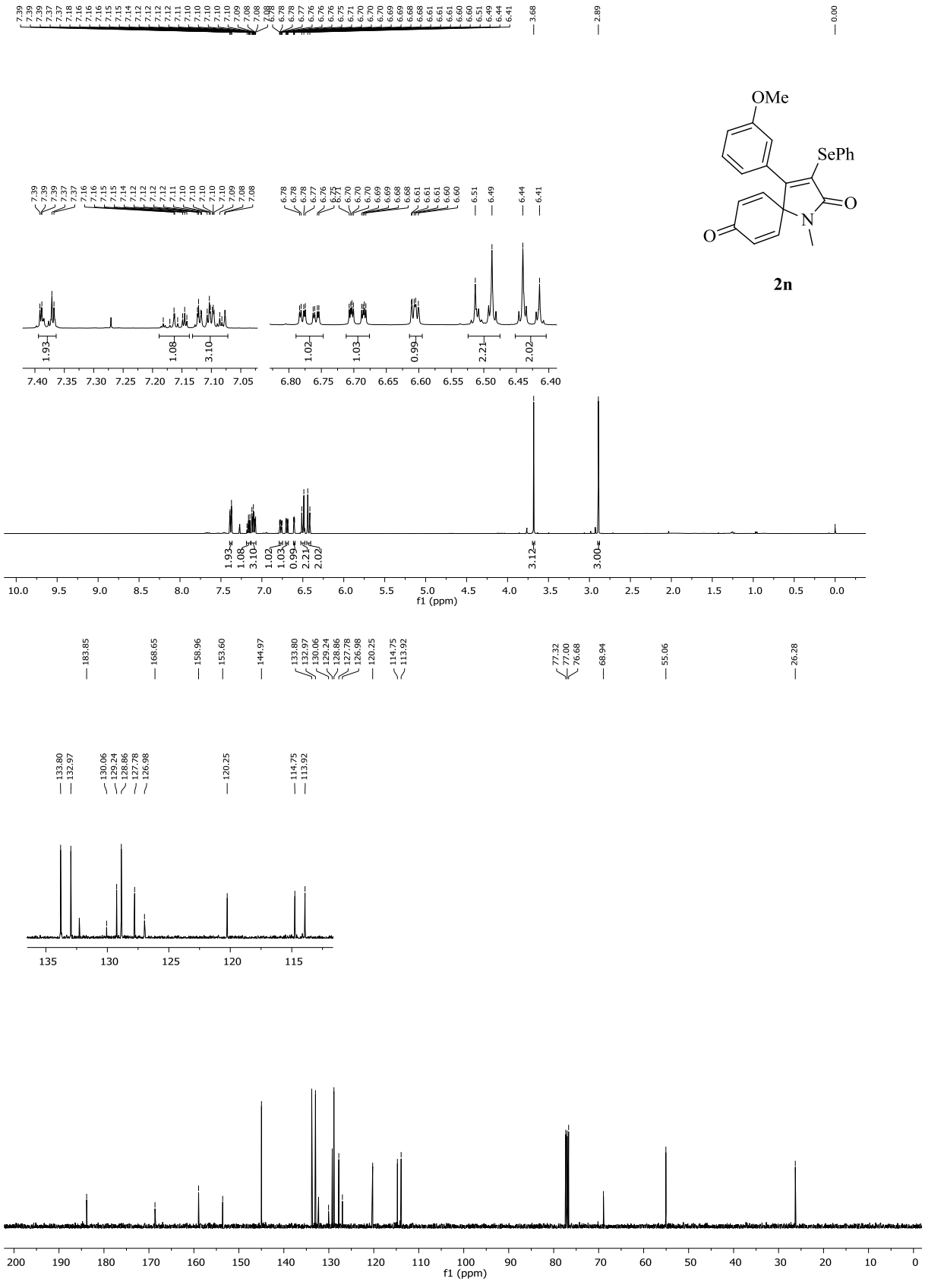
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2l** in $CDCl_3$.



The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2m** in $CDCl_3$.

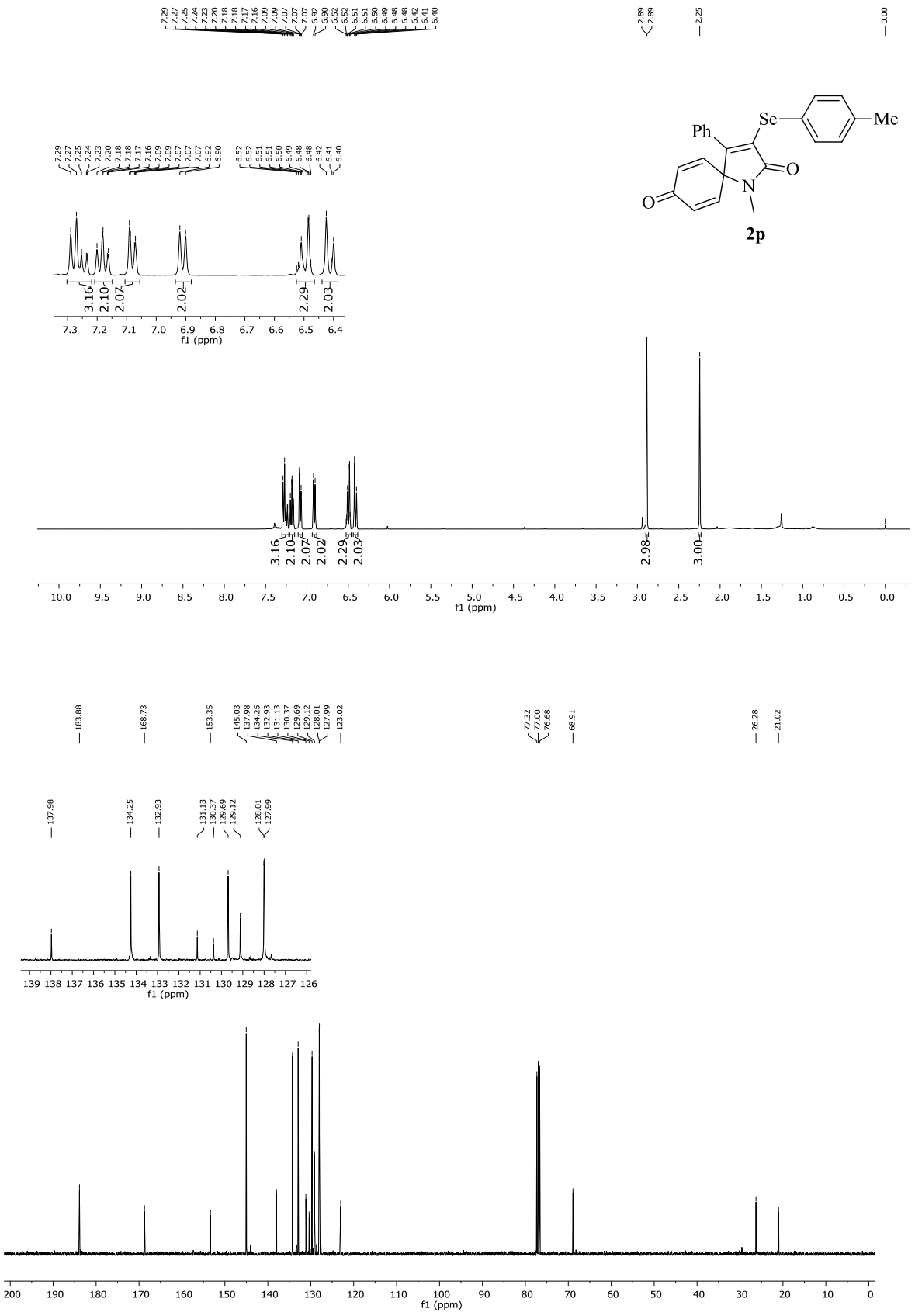


^{77}Se NMR (77MHz, in $CDCl_3$ with diphenyl diselenide as external reference) for **2m**.

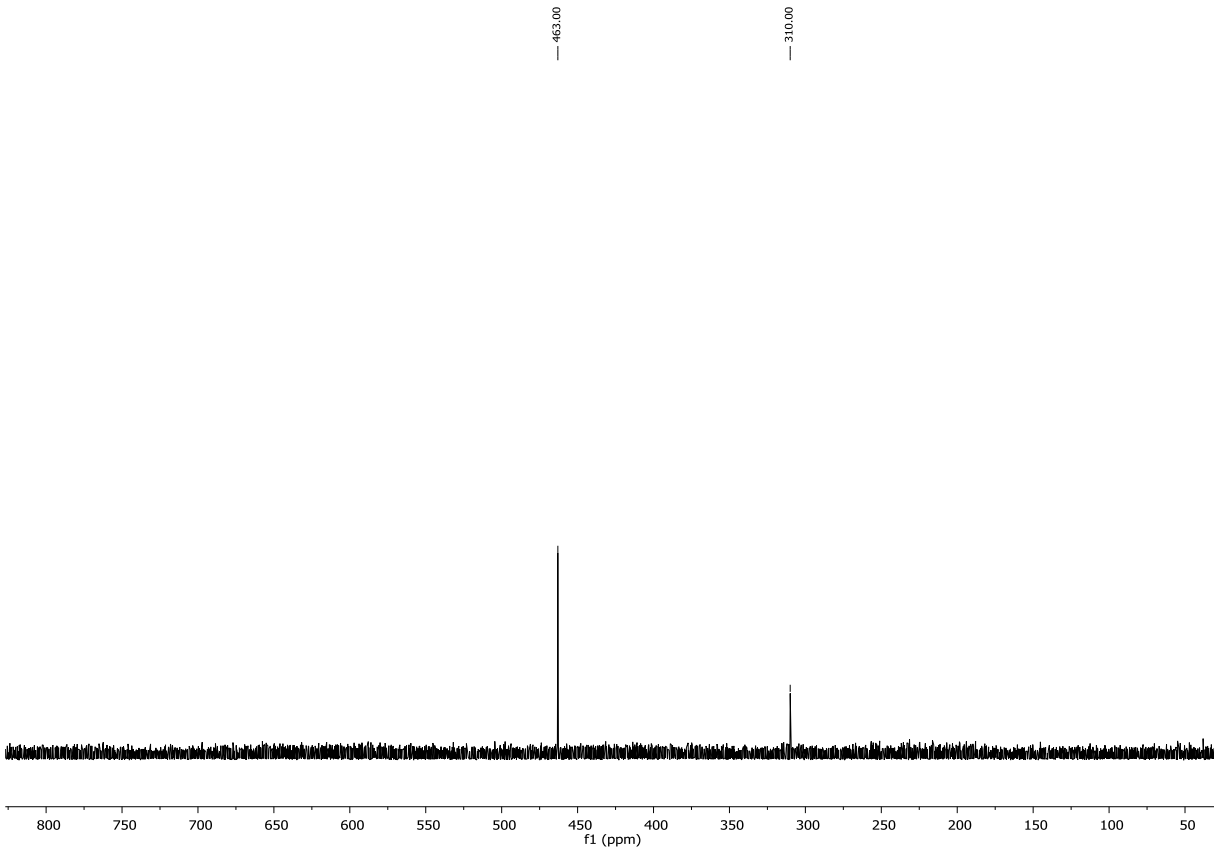


The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2n** in $CDCl_3$.

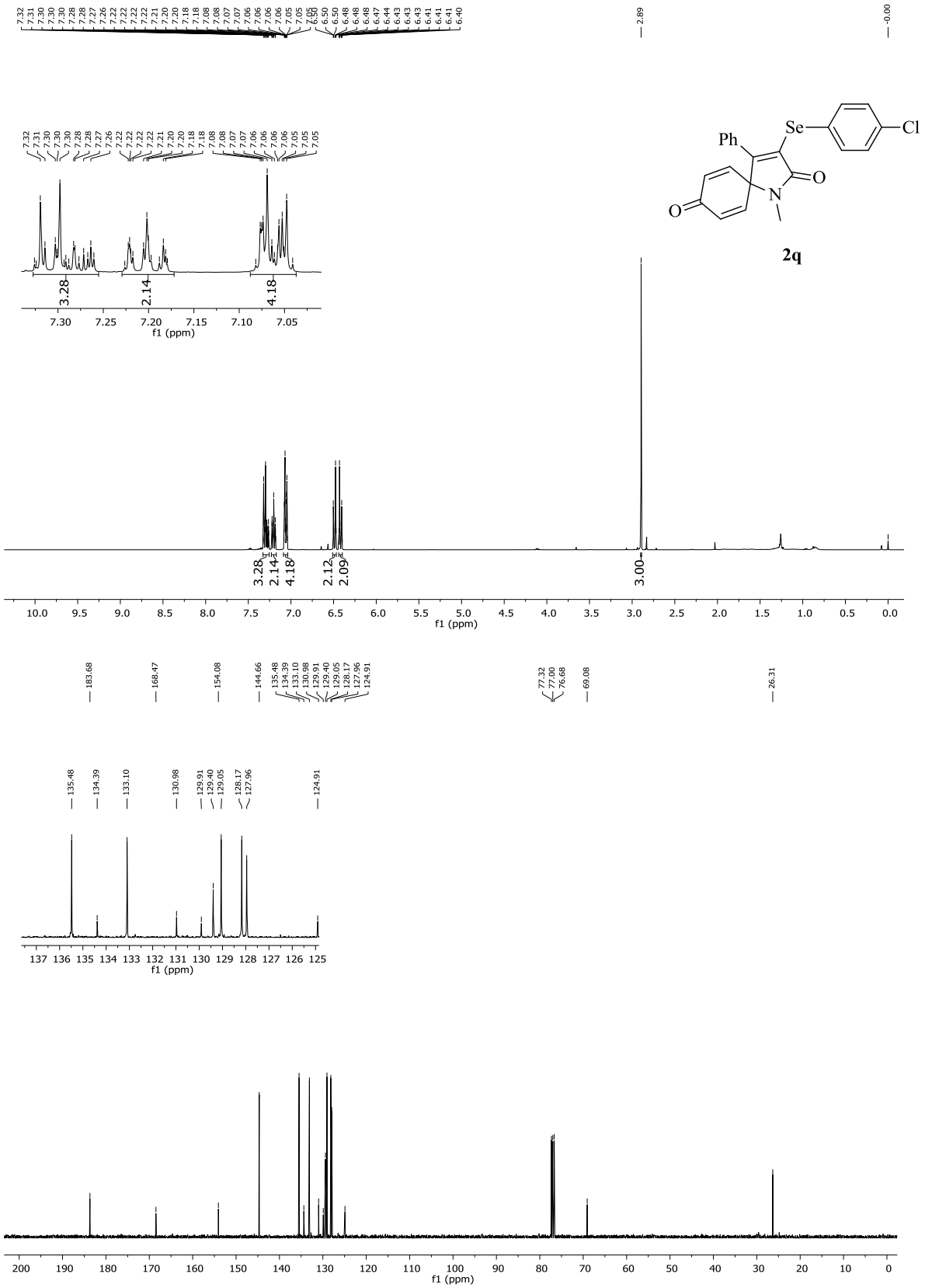
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2o** in $CDCl_3$.



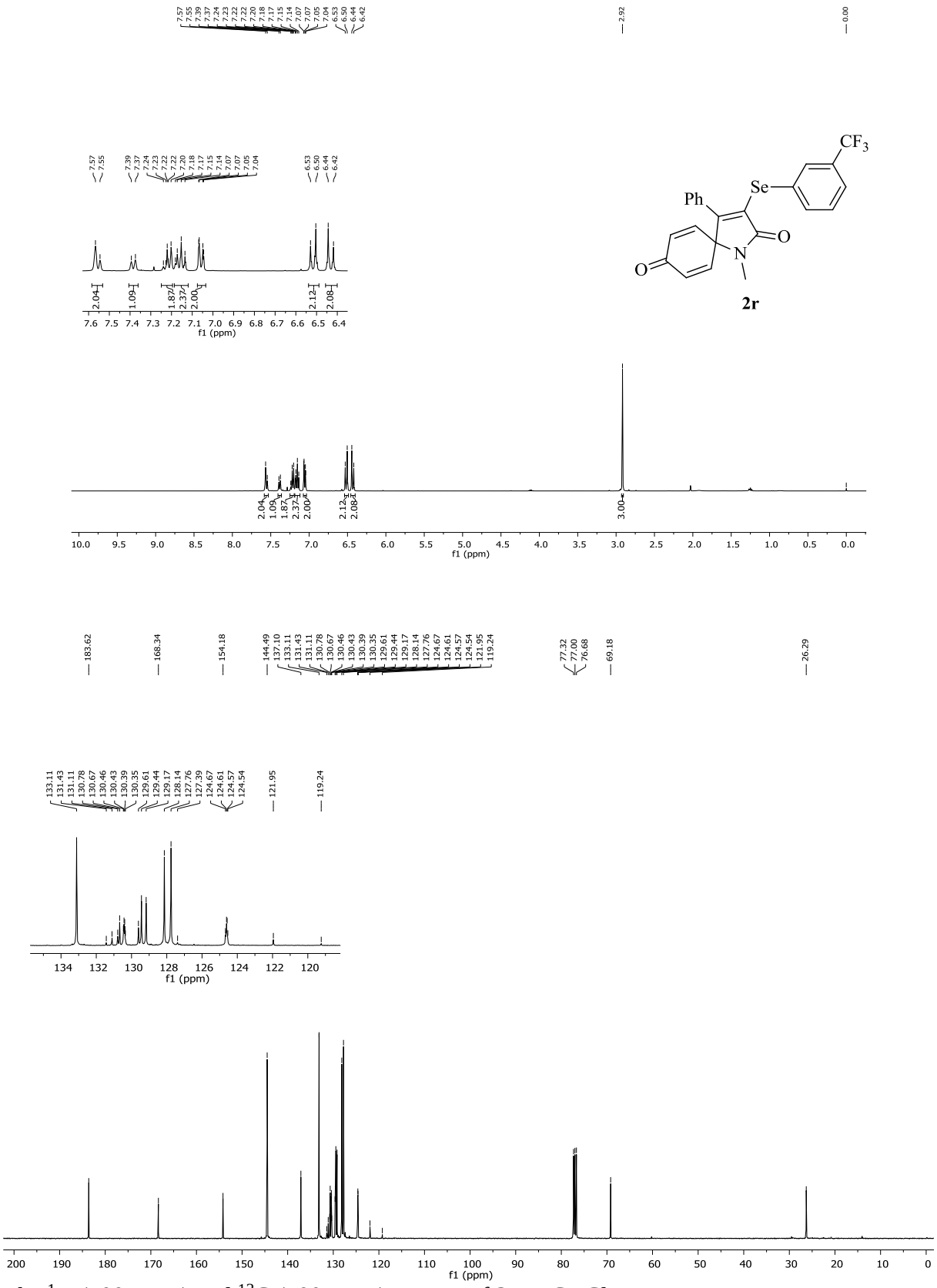
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2p** in $CDCl_3$.



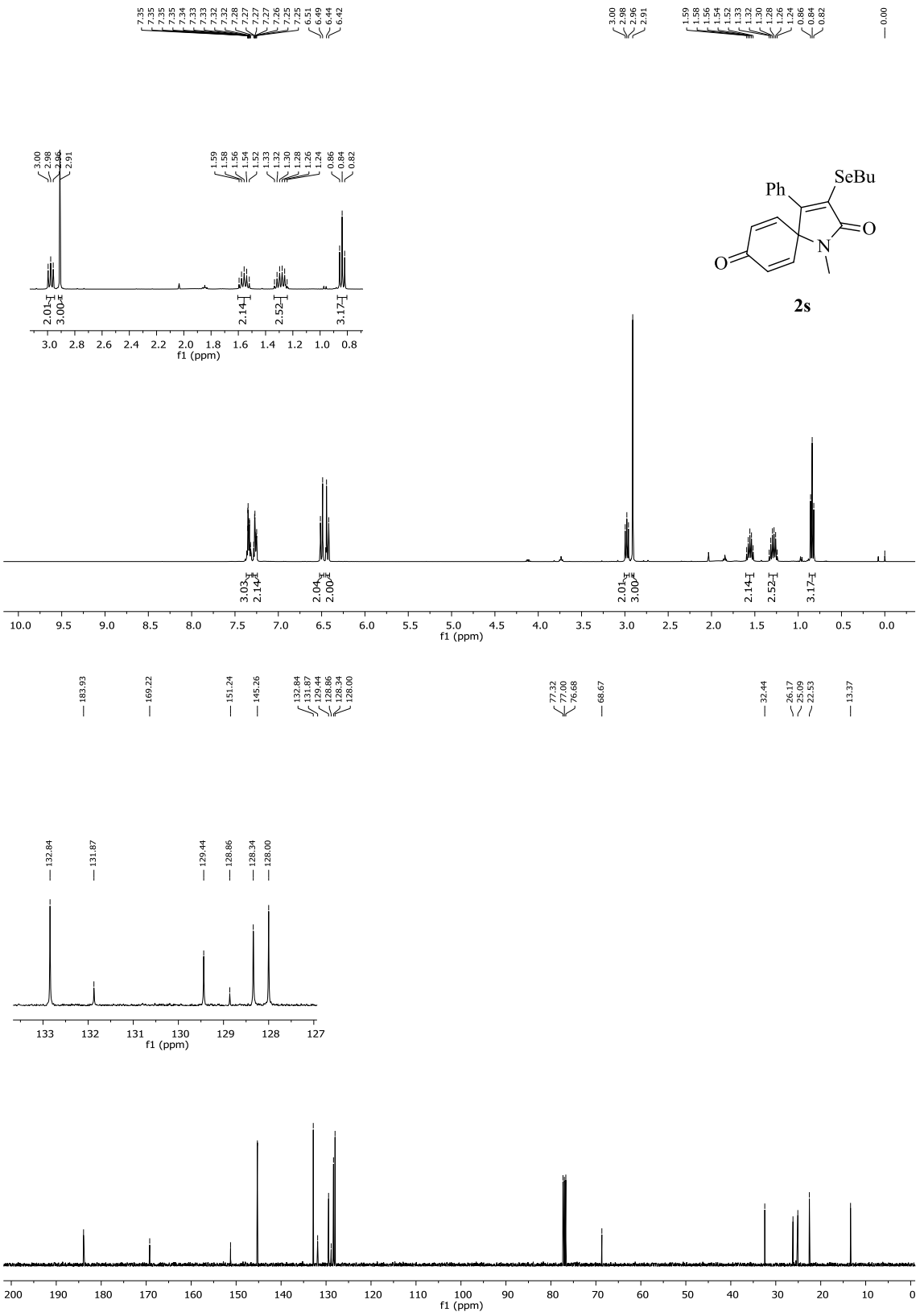
^{77}Se NMR (77MHz, in $CDCl_3$ with diphenyl diselenide as external reference) for **2p**.



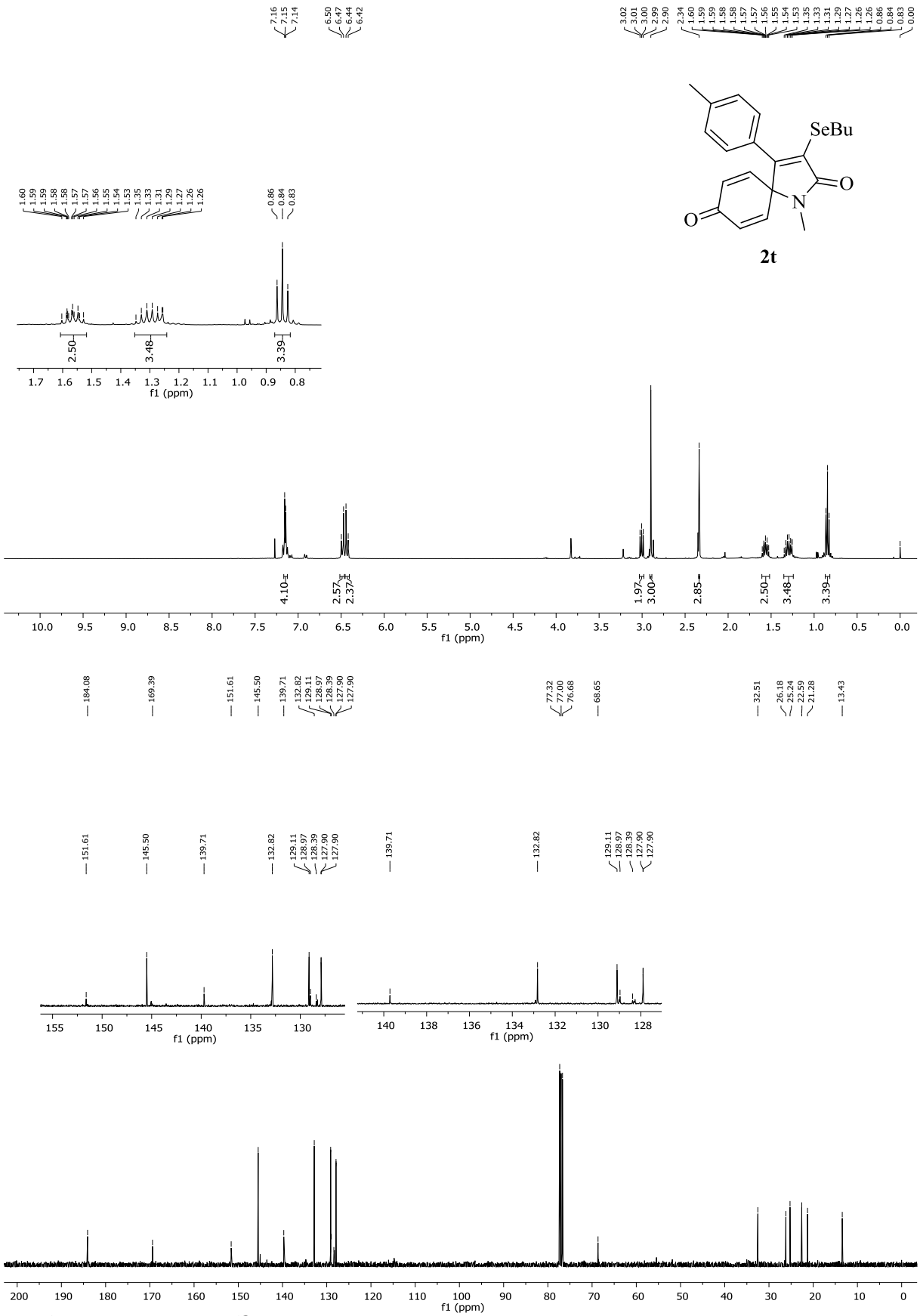
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2q** in $CDCl_3$.



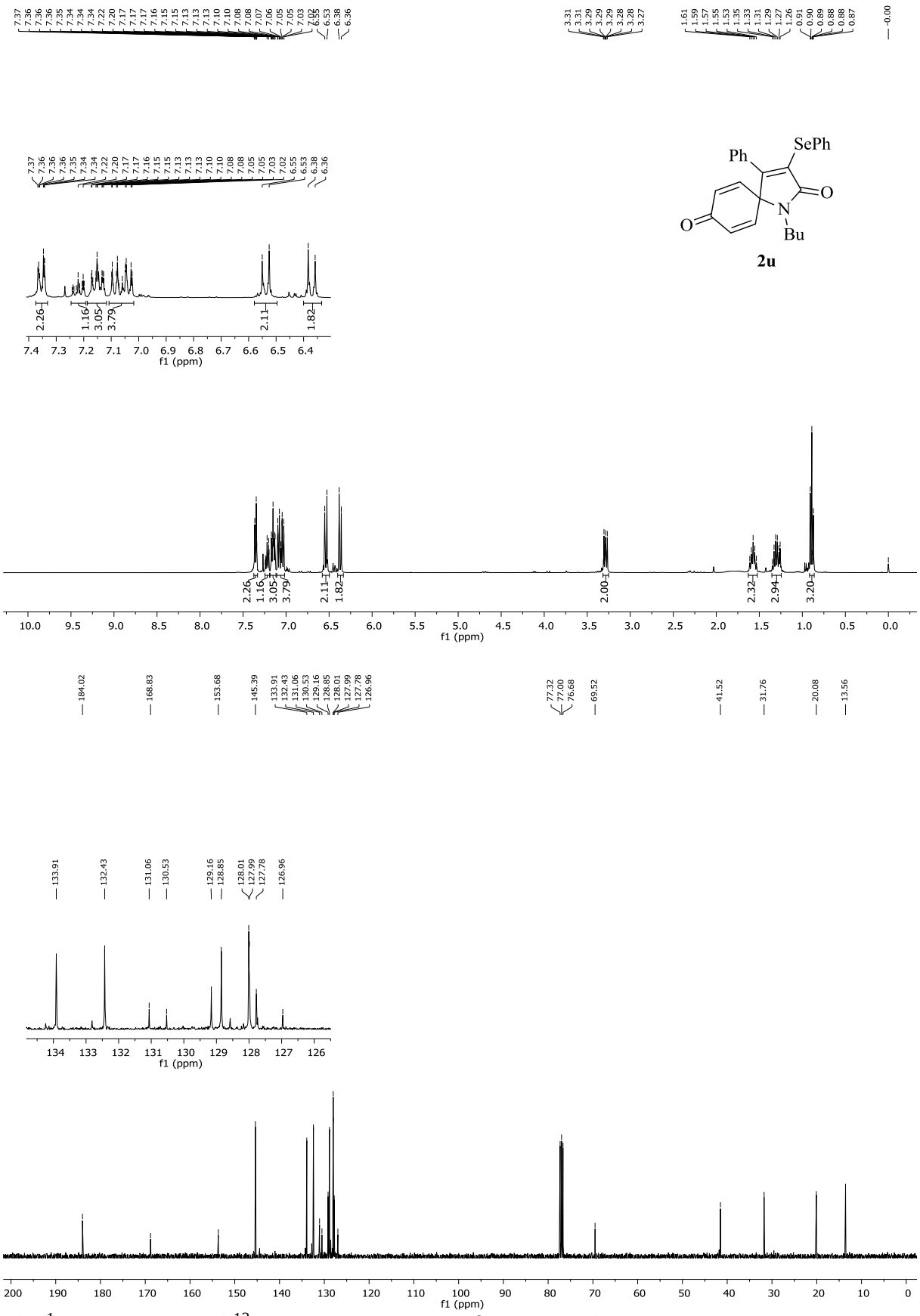
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2r** in $CDCl_3$.



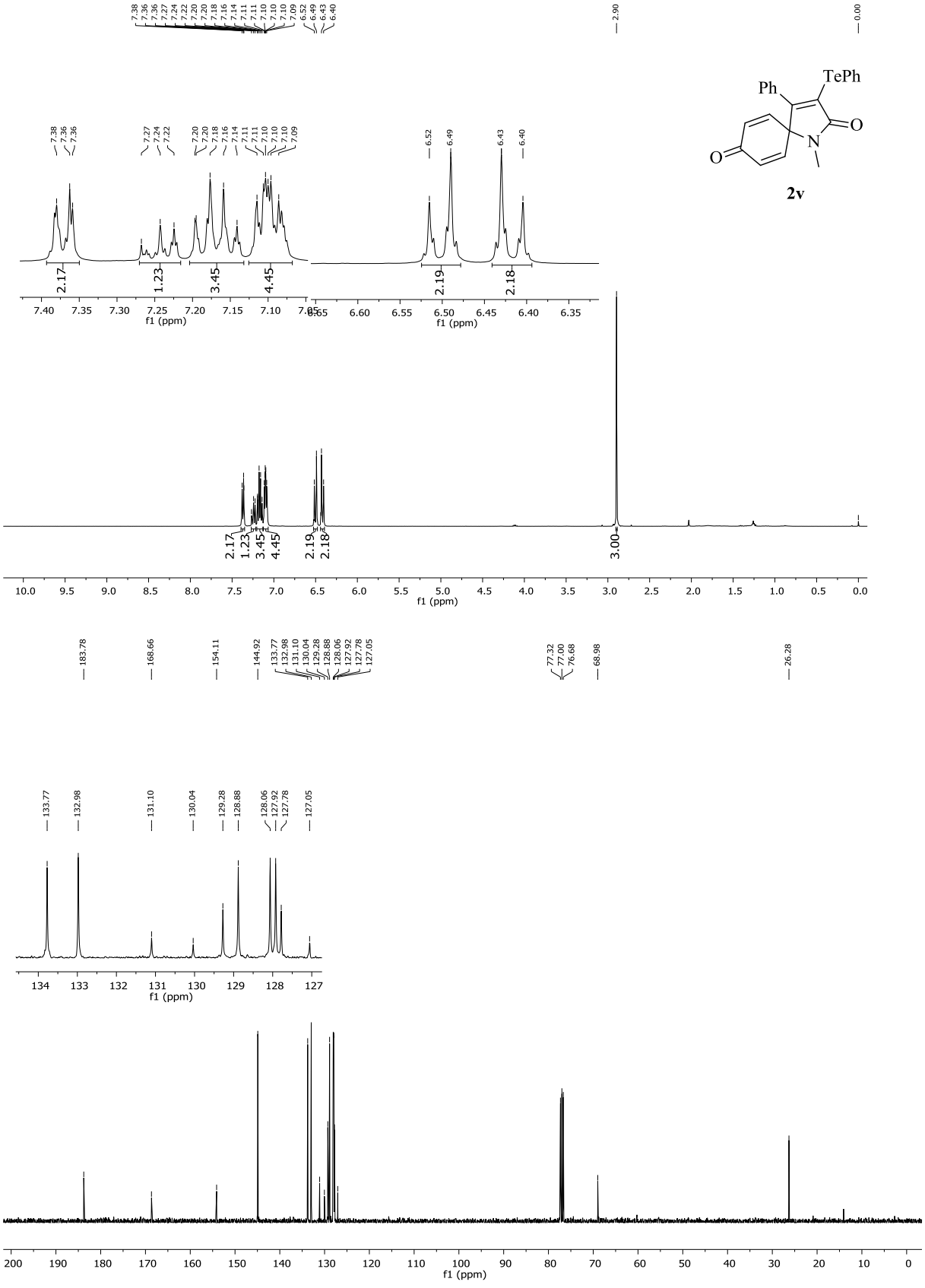
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2s** in $CDCl_3$.



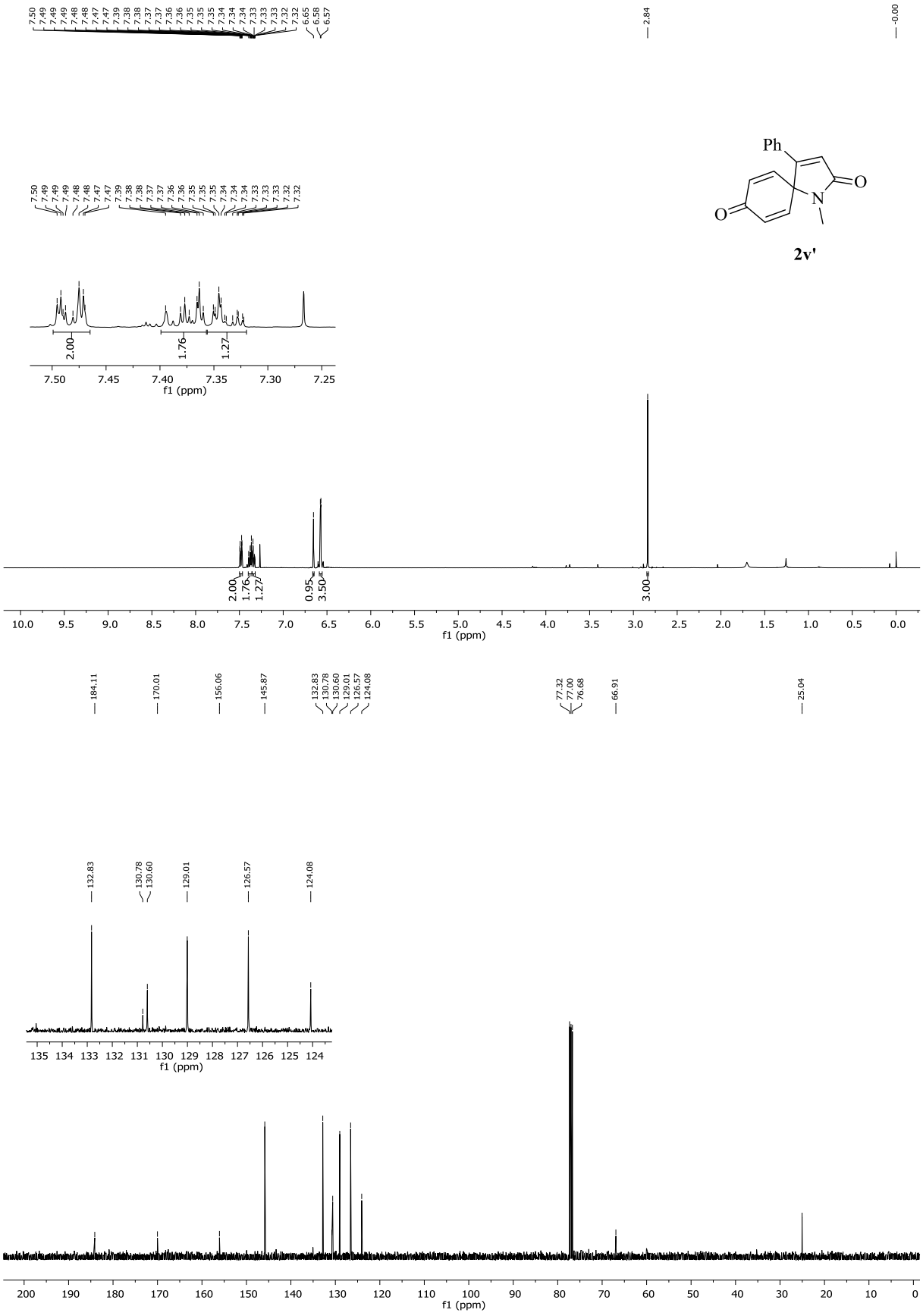
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2t** in $CDCl_3$.



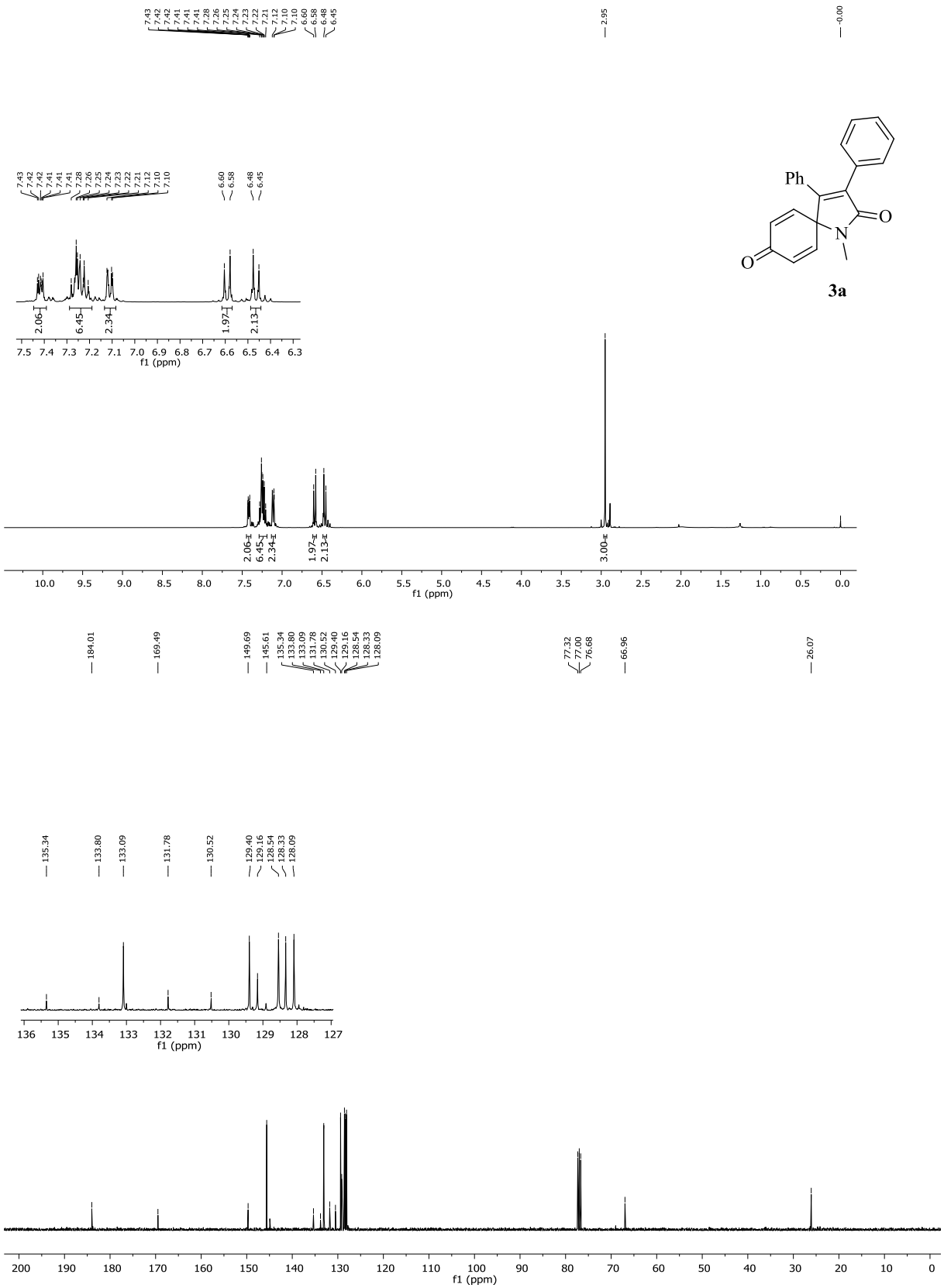
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2u** in $CDCl_3$.



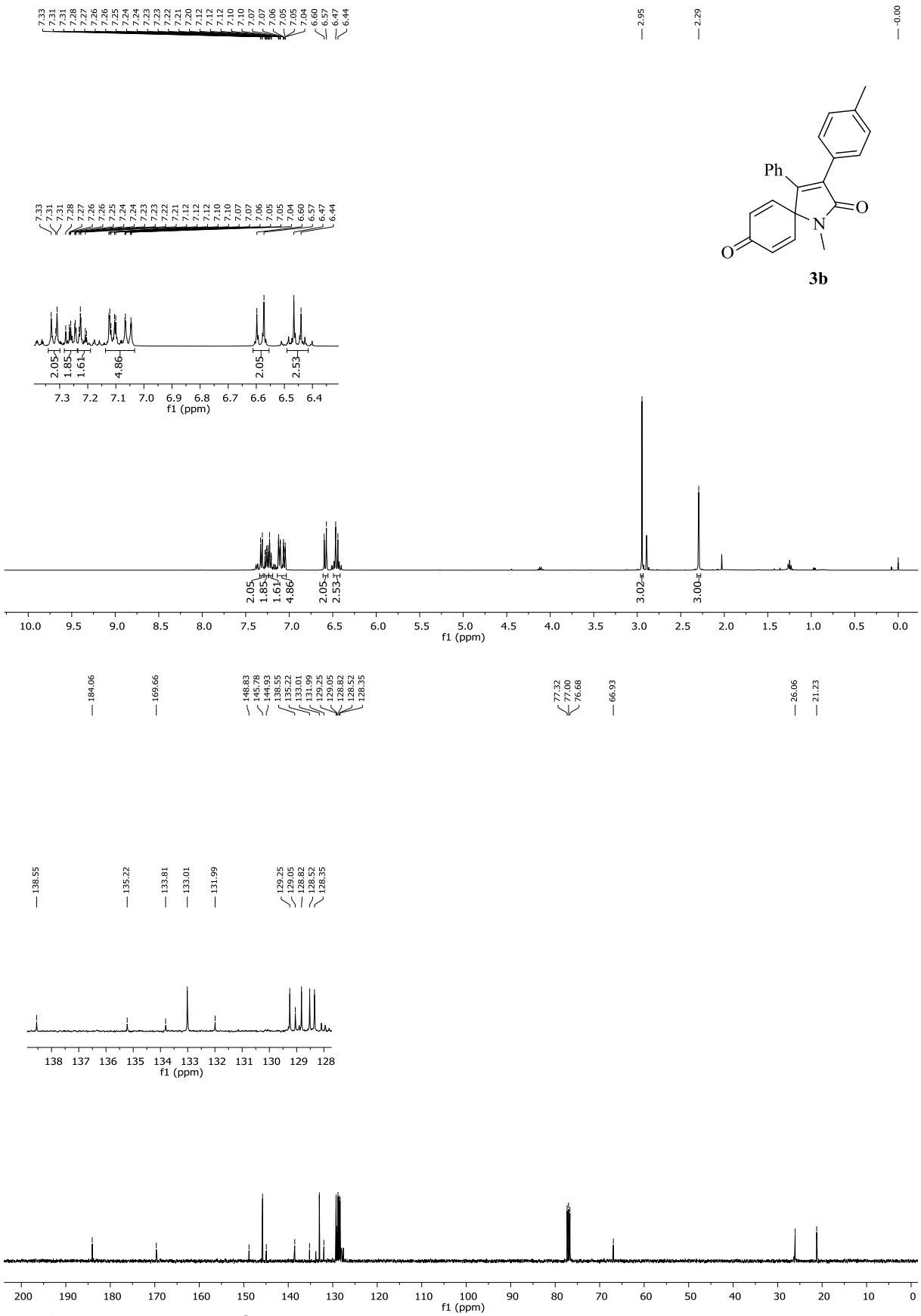
he ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2v** in $CDCl_3$.



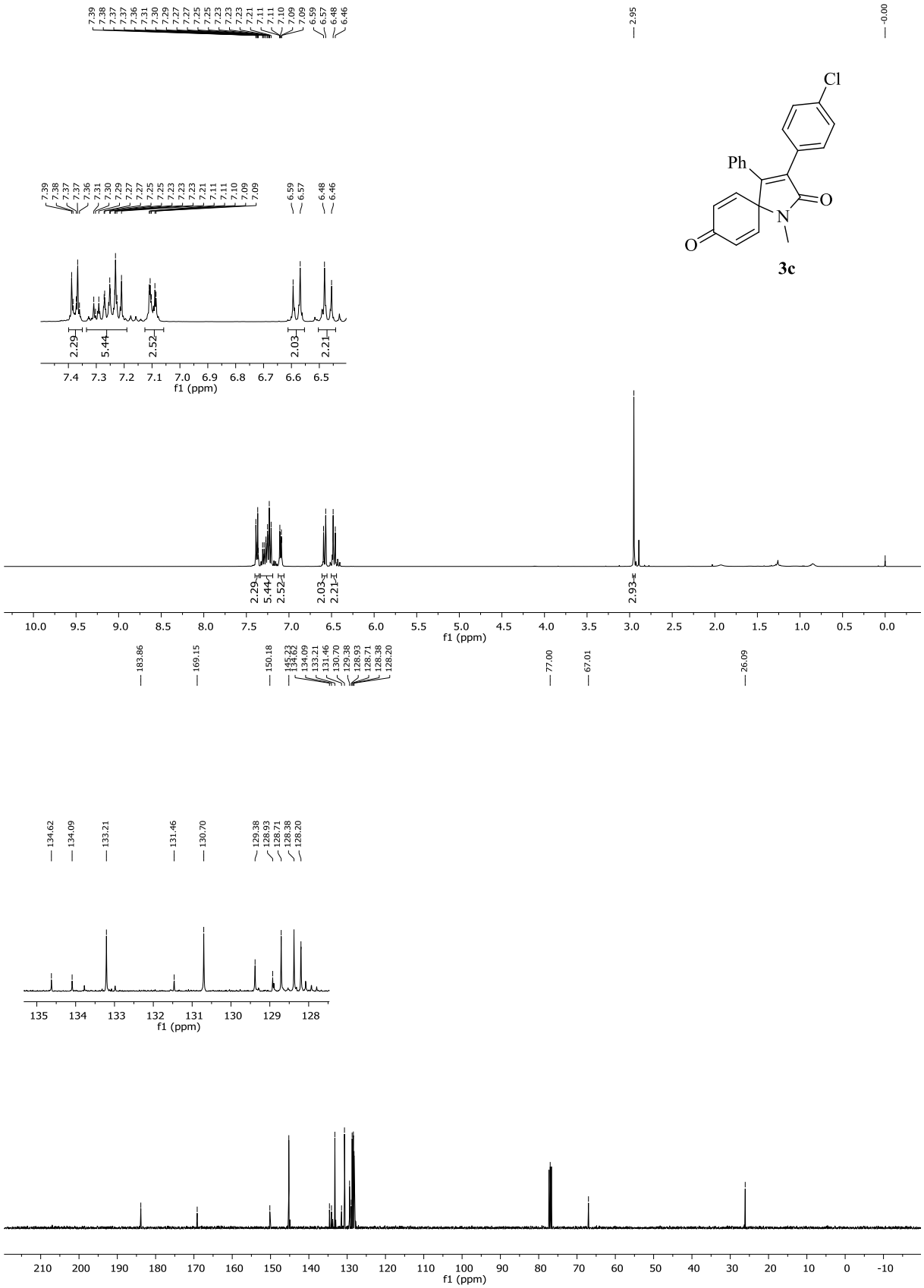
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **2v'** in $CDCl_3$.



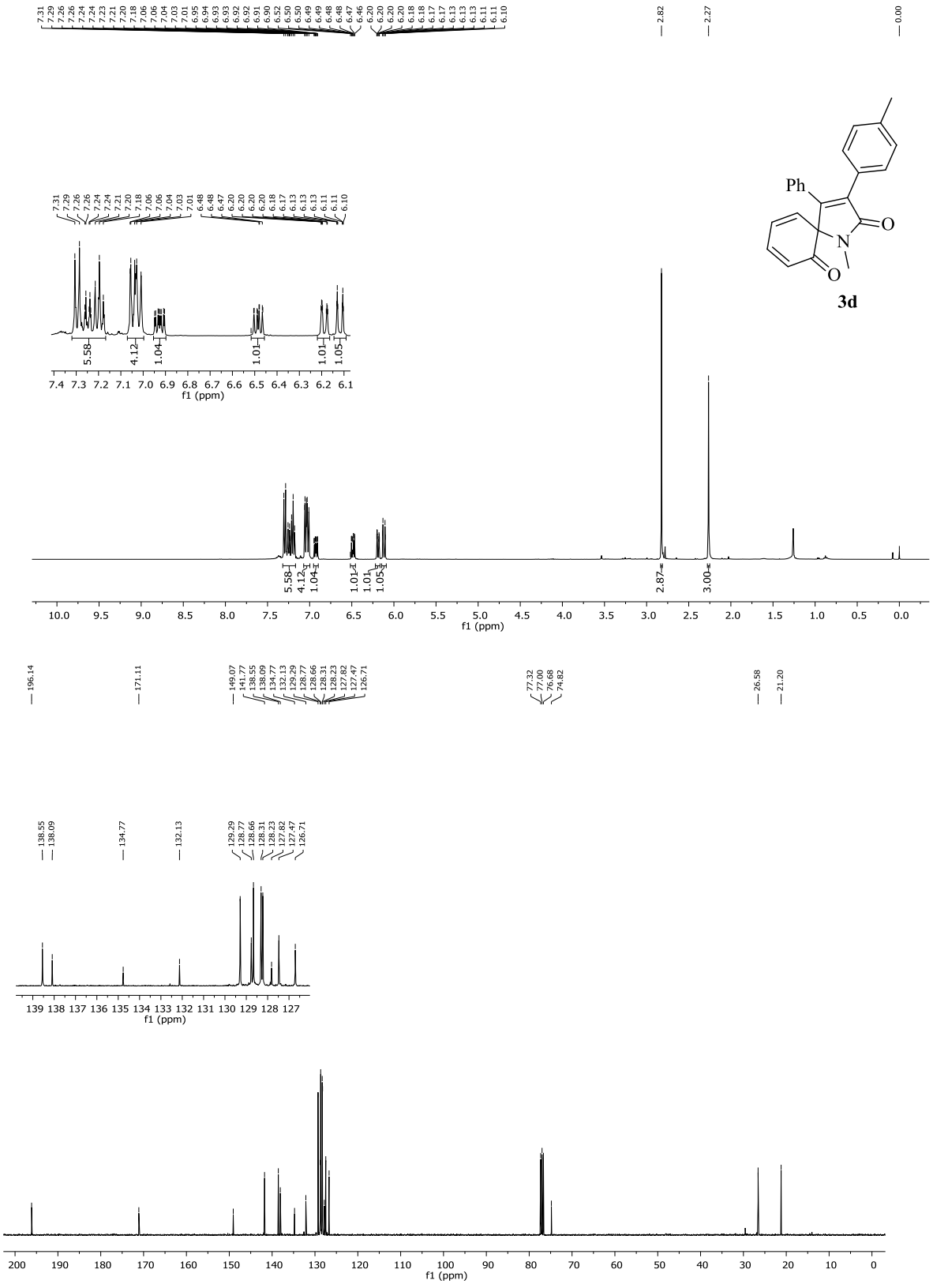
The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **3a** in $CDCl_3$.



The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **3b** in $CDCl_3$.



The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **3c** in $CDCl_3$.



The ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of **3d** in $CDCl_3$.