Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


**SUPPORT INFORMATION**

# Synthesis of benzo[*b*]chalcogenophenes fused to selenophenes via intramolecular electrophilic cyclization of 1,3-diynes

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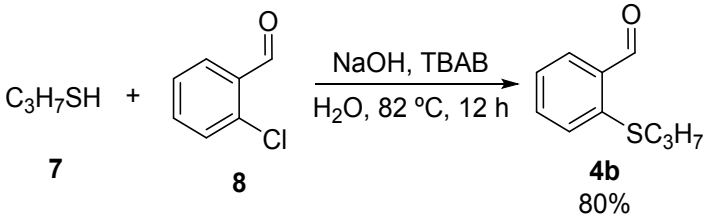
## Contents

**General Information**

The reactions were monitored by thin TLC sheets ALUGRAM® Xtra SIL G/$UV_{254}$. For visualization, TLC plates were either placed under UV light, stained with iodine vapor and 5% vanillin in 10% $H_2SO_4$ and heat. Column chromatography was performed using Merck Silica Gel (pore size 60 Å, 230-400 mesh). Carbon-13 nuclear magnetic resonance ($^{13}C$ NMR) and hydrogen nuclear magnetic resonance spectra ($^{1}H$ NMR) were obtained on Bruker Avance III HD spectrometers at 100 MHz and 400 MHz, respectively. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the internal reference for $^{1}H$ NMR and the solvent peak of $CDCl_3$ for $^{13}C$ NMR. Coupling constants (*J*) are reported in Hertz and chemical shift ($\delta$) in ppm. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), t (triplet), td (triplet of dublet), quint (quintet), sext (sextet) and m (multiplet). Low-resolution mass spectra (MS) were measured on a Shimadzu GC-MS-QP2010 mass spectrometer. The HRMS analyses were performed in a Bruker micrOTOF-QII spectrometer equipped with an APCI source operating in positive mode. The samples were solubilized in acetonitrile and analyzed by direct infusion at a constant flow rate of 180 µL/min. The acquisition parameters were: capillary: 4000 V, end plate offset: -500 V, nebulizer: 1.5 bar, dry gas: 1.5 L $min^{-1}$, and dry heater: 180 °C. The collision cell energy was set to 5.0 eV. The mass-to-charge ratio (*m*/*z*) data were processed and analyzed using Bruker Daltonics softwares: Compass Data Analysis and Isotope Pattern. Melting point (m.p.) values were measured in a Marte PFD III instrument with a 0.1 °C precision. The Oxone® and 2-methoxybenzaldehyde **4a** was purchased from Sigma-Aldrich.

**Procedure for the synthesis of 2-propylthiobenzaldehyde 4b**

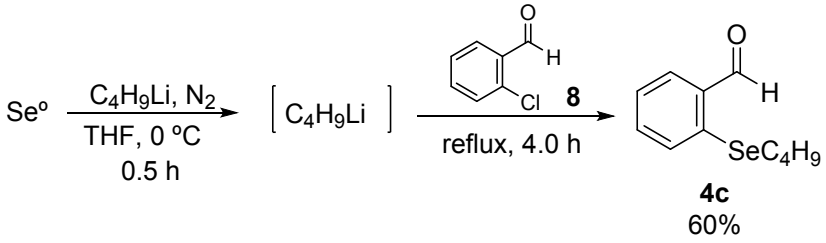



**7** **8** **4b** 80%

The compound were prepared according to a published procedure.[1] After a mixture of NaOH (0.56 g, 14 mmol), $H_2O$ (10 mL) and propanethiol **7** (1.27 mL, 14 mmol) was stirred at room temperature for 0.5 h, the corresponding 2-

chlorobenzaldehyde **8** (1.40 g, 1.12 mL, 10 mmol) and tetrabutylammonium bromide (0.10 g) were added, and the reaction mixture was stirred at 82 °C for an additional 12 h. After being cooled to room temperature, the reaction mixture was poured into 30 mL of water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography using the mixture hexane/ethyl acetate (95:5) as the eluting solution to afford 2-propylthiobenzaldehyde in 80% yield.

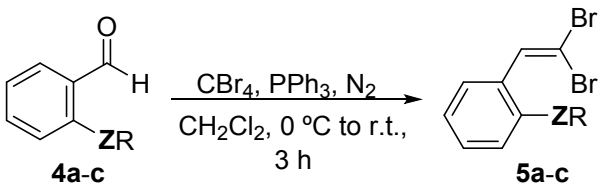
**Procedure for preparation of 2-butylselenanylbenzaldehyde 4c**




**4c**
60%

The compound were prepared according to a published procedure.[2] To a 100 mL round-bottomed flask containing a suspension of elemental selenium (0.799 g, 10 mmol) in dry THF (20.0 mL) under nitrogen atmosphere and magnetic stirring was added dropwise butyllithium (4.35 mL of a 2.3 M solution in hexane, 10 mmol) at 0 ºC. The resulting mixture was stirred for 30 min at room temperature. Then, the solution of 2-chlorobenzaldehyde **8** (1.40 g, 1.12 mL, 10 mmol) in dry THF (10.0 mL) was added and the mixture refluxed for 4 h. After this time, the mixture was cooled to 0 ºC and a saturated solution of $NH_4Cl$ (30.0 mL) was added dropwise. Ethyl acetate (20.0 mL) was added to the mixture and the organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The product was purified by flash chromatography eluted with hexane/ethyl acetate (95:5), affording the 2-butylselenanylbenzaldehyde **4c** in 60% yield.

**General procedure for the synthesis of (2,2-dibromovinyl)benzene 5a-c**

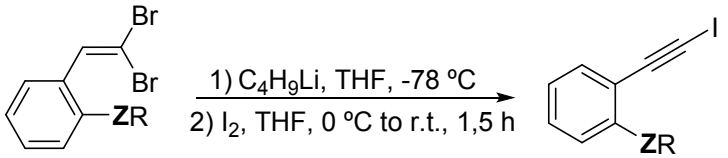



**4a-c** **5a-c**

**5a** (ZR = $OCH_3$, 90%)
**5b** (ZR = $SC_3H_7$, 95%)
**5c** (ZR = $SeC_4H_9$, 80%)

The compounds were prepared according to a published procedure.[3] To a round-bottomed flask containing the appropriate aldehyde **4** (10.0 mmol) in dry dichloromethane (30.0 mL) under nitrogen atmosphere and magnetic stirring at room temperature, a solution of $CBr_4$ (3.93 g, 12.0 mmol) in dichloromethane (20.0 mL) was added. The reaction system was cooled at 0 ºC and $Ph_3P$ (6.55 g; 25.0 mmol) was added dropwise during 30 min. Then, the resulting mixture was stirred for additional 3 h at room temperature. After that, hexane (50.0 mL) was added and the crude mixture was filtered using silica gel. The eluted part was concentrated for further purification by column chromatography (100-200 mesh silica gel) using hexane as the eluent. Yield: 80-95%.

**General procedure for the synthesis of iodoacetylenes 6a-c**

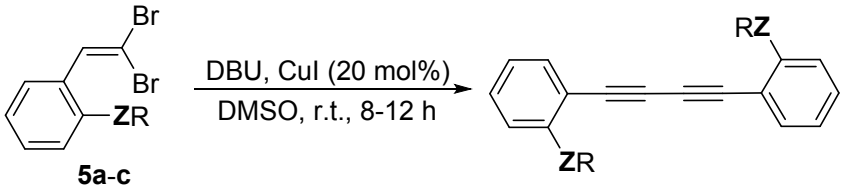



**5a-c** **6a-c**

**6a** (ZR = $OCH_3$, 89%)
**6b** (ZR = $SC_3H_7$, 80%)
**6c** (ZR = $SeC_4H_9$, 65%)

The compounds were prepared according to a published procedure, with minor changes.[4] To a two neck round-bottomed flask under nitrogen atmosphere containing the appropriate (2,2 dibromovinyl)benzene (5.0 mmol) and THF (15.0 mL), was added at -78 °C, was added dropwise butyllithium (2 equiv, 4.35 mL of a 2.3 M solution in hexane, 10.0 mmol). The mixture was stirring at -78 °C for 0.5 h, after this time a solution of $I_2$ (1.27 g, 5.0 mmol) in 5.0 mL of THF was slowly added at 0 °C and the solution was warmed to room temperature. After 1.5 h, the reaction mixture was received in a saturated aqueous $Na_2S_2O_3$ solution (15.0 mL) and the product was extracted with ethyl acetate (3x 15.0 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using silica gel and hexane as eluent. Yield: 65-89%.

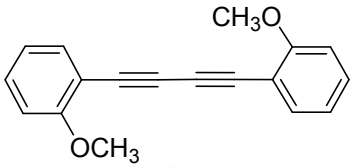
**General procedure for the synthesis of symmetric 1,3-diynes 1a, 1i and 1p**




**5a-c**

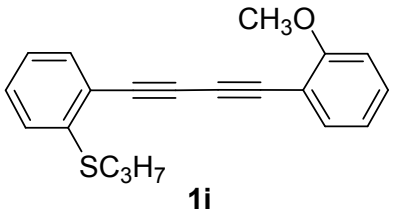
**1a** (ZR = $OCH_3$, 75%)
**1i** (ZR = $SC_3H_7$, 60%)
**1p** (ZR = $SeC_4H_9$, 54%)

The compounds were prepared according to a published procedure.[5] To a sealed tube were added DMSO (2.0 mL), the appropriate (2,2 dibromovinyl)benzene (1.0 mmol), CuI (20 mol%, 0.038 g), DBU (2.0 mmol, 0.304 g). The mixture was stirred at room temperature (25 ºC) for 8-12 h. Then a saturated sodium chloride solution (10.0 mL) was added and the product was extracted with ethyl acetate (3x 15.0 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using silica gel and eluted with hexane/ethyl acetate in different proportions. Yields: 54-75%.



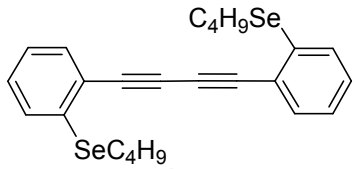

**1a**

1,4-Bis(2-methoxyphenyl)buta-1,3-diyne **1a**:[6] Yield: 0.197 g (75%); white solid, m.p: 132-134 ºC. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.47 (dd, *J* = 7.6, 1.5 Hz, 2H); 7.33-7.28 (m, 2H); 6.92-6.86 (m, 4H); 3.88 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 161.3, 134.3, 130.5, 120.4, 111.2, 110.6, 78.6, 77.9, 55.7. MS (rel. int., %) *m*/*z*: 262 ($M^+$; 100.0), 247 (18.9), 231 (10.6), 218 (25.6), 189 (29.8), 131 (10.3).




**1i**

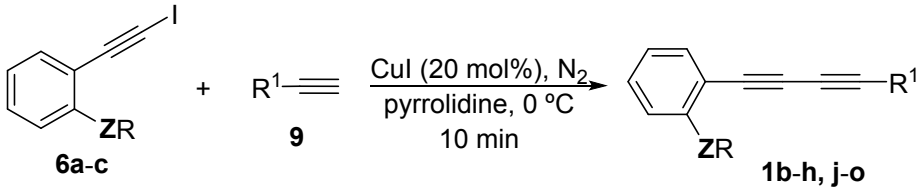
1,4-Bis[2-(propylthio)phenyl]buta-1,3-diyne **1i**: Yield: 0.210 g (60%); yellow solid, m.p: 74-76 ºC. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.50 (d, *J* = 7.6 Hz, 2H); 7.30-7.24 (m, 4H); 7.11-7.08 (m, 2H); 2.95 (t, *J* = 7.3 Hz, 4H); 1.73 (sext, *J* = 7.3 Hz, 4H); 1.06 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 141.7, 133.8, 129.3, 126.7, 124.8, 121.4, 80.8, 79.6, 34.5, 22.2, 13.6. MS (rel. int., %) *m*/*z*: 350 ($M^+$; 15.2), 321 (32.5), 277 (23.3), 147 (40.0), 41 (100.0). HRMS (APCI-QTOF) calculated mass for $C_{22}H_{23}S_2$ $[M+H]^+$: 351.1241, found: 351.1233.



**1p**

1,4-Bis[2-(butylselanyl)phenyl]buta-1,3-diyne **1p**: Yield: 0.256 g (54%); yellow solid, m.p: 43-45 ºC. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.51 (dd, *J* = 7.6, 1.5 Hz, 2H); 7.42-7.39 (m, 2H); 7.25 (td, *J* = 7.6, 1.5 Hz, 2H); 7.16 (td, *J* = 7.6, 1.5 Hz, 2H); 3.0 (t, *J* = 7.4 Hz, 4H); 1.75 (quint, *J* = 7.4 Hz, 4H); 1.48 (sext, *J* = 7.4 Hz, 4H); 0.94 (t, *J* = 7.4 Hz, 6 H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 136.4, 133.9, 130.0, 129.4, 125.8, 123.8, 81.7, 78.8, 31.7, 26.6, 23.1, 13.6. MS (rel. int., %) *m*/*z*: 474 ($M^+$; 29.4), 207 (43.5), 200 (39.9), 195 (28.3), 41 (100.0). HRMS (APCI-QTOF) calculated mass for $C_{24}H_{27}Se_2$ $[M+H]^+$: 475.0443, found: 475.0440.

**General procedure for the synthesis of unsymmetrical 1,3-diynes 1b-h, j-o**



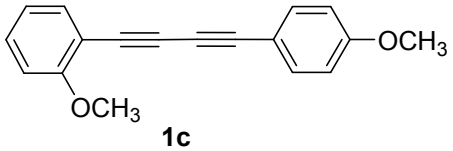
**6a-c** **9** **1b-h, j-o**

**1b** (ZR = $OCH_3$; $R^1$ = $C_6H_5$, 95%)
**1c** (ZR = $OCH_3$; $R^1$ = 4-$CH_3OC_6H_4$, 80%)
**1d** (ZR = $OCH_3$; $R^1$ = 4-$ClC_6H_4$, 70%)
**1e** (ZR = $OCH_3$; $R^1$ = 2-$ClC_6H_4$, 70%)
**1f** (ZR = $OCH_3$; $R^1$ = 2-naphthyl, 72%)
**1g** (ZR = $OCH_3$; $R^1$ = hexyl, 50%)
**1h** (ZR = $OCH_3$; $R^1$ = $C(CH_3)_2OH$, 60%)
**1j** (ZR = $SC_3H_7$; $R^1$ = $C_6H_5$, 75%)
**1k** (ZR = $SC_3H_7$; $R^1$ = 4-$CH_3C_6H_5$, 80%
**1l** (ZR = $SC_3H_7$; $R^1$ = 4-$ClC_6H_5$, 78%)
**1m** (ZR = $SC_3H_7$; $R^1$ = 2-naphthyl, 50%)
**1n** (ZR = $SC_3H_7$; $R^1$ = hexyl, 55%)
**1o** (ZR = $SC_3H_7$; $R^1$ = 2-$CH_3OC_6H_4$, 50%)

The compounds were prepared according to a published procedure, with minor changes.[7] To a 25.0 mL two-neck round-bottom flask under nitrogen atmosphere containing a solution of the appropriate iodoalkyne (1.0 mmol) and the appropriate terminal alkyne (1.3 mmol) in pyrrolidine (1.5 mL), CuI (20 mol%, 0.038 g) was added at 0 ºC. Then, the reaction mixture was stirred at room temperature (25 °C), under argon atmosphere for 10 minutes and after this time the crude reaction mixture was received in a saturated aqueous $NH_4Cl$ solution (10.0 mL) and the product was extracted with ethyl acetate (3x 15.0 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using silica gel and eluted with hexane/ethyl acetate in different proportions. Yields: 50-95%.

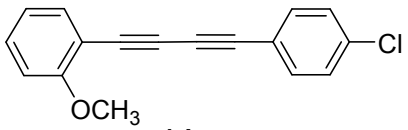

**1b**

1-Methoxy-2-(phenylbuta-1,3-diyn-1-yl)benzene **1b**: Yield: 0.220 g (95%); white solid, m.p: 48-51 ºC. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.52 (dd, *J* = 7.6, 1.5 Hz, 2H); 7.48 (dd, *J* = 7.6, 1.5 Hz, 1H); 7.36-731 (m, 4H); 6.93-6.87 (m, 2H); 3.90 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 161.4, 134.4, 132.4, 130.7, 129.0, 128.4, 122.0, 120.5, 111.0, 110.6, 82.1, 78.1, 77.6, 74.2, 55.8. MS (rel. int., %) *m*/*z*: 232 ($M^+$; 100.0), 202 (39.8), 116 (12.6), 101 (13.4), 77 (2.4). HRMS (APCI-QTOF) calculated mass for $C_{17}H_{13}O$ $[M+H]^+$: 233.0966, found: 233.0961.



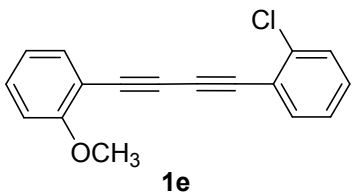

**1c**

1-Methoxy-2-[(4-methoxyphenyl)buta-1,3-diyn-1-yl]benzene **1c**: Yield: 0.210 g (80%); white solid, m.p: 106-108 ºC. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.48-7.45 (m, 3H); 7.34-7.29 (m, 1H); 6.93-6.84 (m, 4H); 3.90 (s, 3H); 3.81 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 161.3, 160.2, 134.3, 134.0, 130.5, 120.5, 114.1, 113.9, 111.2, 110.6, 82.3, 77.9, 77.5, 73.0, 55.8, 55.3. MS (rel. int., %) *m*/*z*: 262 ($M^+$; 100.0), 247 (46.7), 231 (12.6), 219 (27.5), 189 (16.4), 131 (10.8). HRMS (APCI-QTOF) calculated mass for $C_{18}H_{15}O_2$ $[M+H]^+$: 263.1072, found: 263.1069.




**1d**

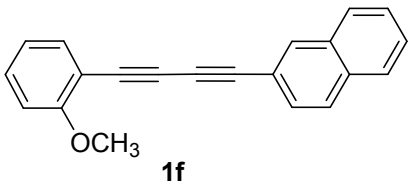
1-[(4-Chlorophenyl)buta-1,3-diyn-1-yl]-2-methoxybenzene **1d**: Yield: 0.186 g (70%); white solid, m.p: 150-152 ºC. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.48 (dd, *J* = 7.6, 1.5 Hz, 1H); 7.44 (d, *J* = 8.5 Hz, 2H); 7.35-7.33 (m, 1H); 7.30 (d, *J* = 8.5 Hz, 2H); 6.93-6.87 (m, 2H); 3.90 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 161.4, 135.2, 134.4, 133.6, 130.8, 128.8, 120.5, 120.4, 110.8, 110.6, 80.8, 78.7, 77.4, 75.2, 55.8. MS (rel. int., %) *m*/*z*: 266 ($M^+$; 100.0), 231 (45.9), 202 (64.4), 187 (23.4), 133 (17.2), 100 (25.7). HRMS (APCI-QTOF) calculated mass for $C_{17}H_{12}ClO$ $[M+H]^+$: 267.0577, found: 267.0573.




**1e**

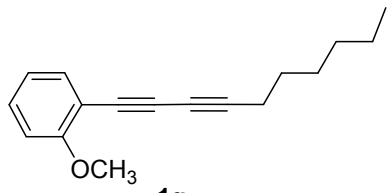
1-[(2-Chlorophenyl)buta-1,3-diyn-1-yl]-2-methoxybenzene **1e**: Yield: 0.186 g (70%); white solid, m.p: 77-79 ºC. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.54 (dd, *J* = 7.5, 1.8 Hz, 1H); 7.50 (dd, *J* = 7.5, 1.8 Hz, 1H); 7.40 (dd, *J* = 8.0,

1.2 Hz, 1H); 7.34 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 1H); 7.30-7.25 (m, 1H); 7.22 (td, *J* = 7.5, 1.2 Hz, 1H); 6.93 (dd, *J* = 7.5, 1.2 Hz, 1H); 6.90-6.87 (m, 1H); 3.90 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 161.4, 136.8, 134.5, 134.2, 130.9, 129.9, 129.4, 126.5, 122.2, 120.5, 110.8, 110.7, 79.7, 79.0, 78.5, 77.4, 55.8. MS (rel. int., %) *m*/*z*: 266 ($M^+$; 100.0), 231 (54.1), 202 (65.2), 187 (24.6), 133 (6.6), 100 (17.6). HRMS (APCI-QTOF) calculated mass for $C_{17}H_{12}ClO$ $[M+H]^+$: 267.0571, found: 267.0564.



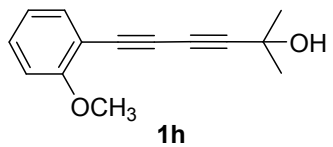
**1f**

2-[(2-Methoxyphenyl)buta-1,3-diyn-1-yl]naphthalene **1f**: Yield: 0.203 g (72%); yellow solid, m.p: 63-65 ºC. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 8.04 (s, 1H); 7.81-7.76 (m, 3H); 7.54-7.48 (m, 4H); 7.34-7.30 (m, 1H); 6.94-6.87 (m, 2H); 3.90 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 161.4, 134.4, 133.1, 132.8, 132.77, 130.7, 128.4, 128.1, 127.8, 127.7, 127.1, 126.7, 120.5, 119.2, 111.0, 110.6, 82.6, 78.3, 77.8, 74.5, 55.8. MS (rel. int., %) *m*/*z*: 282 ($M^+$; 100.0), 252 (36.5), 207 (60.2), 141 (22.0), 73 (32.1). HRMS (APCI-QTOF) calculated mass for $C_{21}H_{15}O$ $[M+H]^+$: 283.1123, found: 283.1121.



**1g**

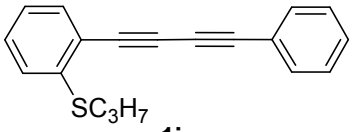
1-(Deca-1,3-diyn-1-yl)-2-methoxybenzene **1g**: Yield: 0.120 g (50%); yellowish oil. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.41 (dd, *J* = 7.6, 1.7 Hz, 1H); 7.28-7.24 (m, 1H); 6.87 (dd, *J* = 7.6, 0.8 Hz, 1H); 6.83 (d, *J* = 8.8 Hz, 1H); 3.84 (s, 3H); 2.34 (t, *J* = 7.0 Hz, 2H); 1.55 (quint, *J* = 7.0 Hz, 2H); 1.44-1.37 (m, 2H); 1.34-1.24 (m, 4H); 0.89 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 161.3, 134.3, 130.1, 120.3, 111.2, 110.5, 85.3, 78.1, 71.0, 65.2, 55.6, 31.2, 28.5, 28.2, 22.4, 19.5, 14.0. MS (rel. int., %) *m*/*z*: 240 ($M^+$; 100.0), 211 (21.4), 155 (20.5), 141 (30.6), 131 (40.6), 77 (19.0). HRMS (APCI-QTOF) calculated mass for $C_{17}H_{21}O$ $[M+H]^+$: 241.1592, found: 241.1573.



**1h**

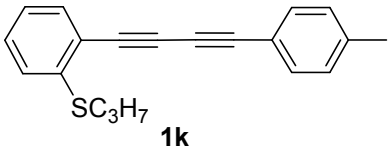
6-(2-methoxyphenyl)-2-methylhexa-3,5-diyn-2-ol **1h**: Yield: 0.128 g (60%); yellowish oil. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.43 (dd, *J* = 7.6, 1.4 Hz, 1H); 7.33-7.29 (m, 1H); 6.91-6.85 (m,2H); 3.87 (s, 3H); 1.57 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 161.3; 134.3; 130.6; 120.4; 110.7; 110.6; 87.2; 76.9; 75.2; 67.2; 65.6; 55.7; 31.0. MS

(rel. int., %) *m*/*z*: 214 ($M^+$; 55.5), 197 (8.7); 155 (13.0); 131 (9.9); 77 (11.3); 43 (100.0). HRMS (APCI-QTOF) calculated mass for $C_{14}H_{14}O_2$ $[M]^+$: 214.0988, found: 241.0991.



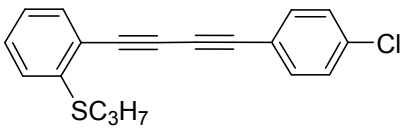
**1j**

[2-(Phenylbuta-1,3-diyn-1-yl)phenyl](propyl)sulfane **1j**: Yield: 0.207 g (75%); yellowish solid, m.p: 58-60 ºC. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.51 (dd, *J* = 7.8, 1.7 Hz, 2H); 7.48-7.46 (m, 1H); 7.34-7.22 (m, 5H); 7.10-7.06 (m, 1H); 2.93 (t, *J* = 7.3 Hz, 2H); 1.71 (sext, *J* = 7.3 Hz, 2H); 1.05 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 141.8, 133.7, 132.4, 129.3, 129.1, 128.3, 126.5, 124.7, 121.7, 121.1, 83.2, 79.5, 79.1, 73.9, 34.4, 22.1, 13.5. MS (rel. int., %) *m*/*z*: 276 ($M^+$; 20.8), 247 (100.0), 215 (10.8), 202 (8.6), 101 (1.2). HRMS (APCI-QTOF) calculated mass for $C_{19}H_{17}S$ $[M+H]^+$: 277.1051, found: 277.1048.



**1k**

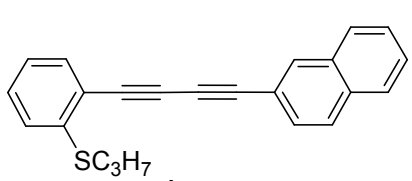
[2-(4-Tolylbuta-1,3-diyn-1-yl)phenyl](propyl)sulfane **1k**: Yield: 0.232 g (80%); yellowish solid, m.p: 45-47 ºC. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.49-7.47 (m, 1H); 7.43 (d, *J* = 8.0 Hz, 2H); 7.30-7.23(m, 2H); 7.14 (d, *J* = 8.0 Hz, 2H); 7.12-7.08 (m, 1H); 2.95 (t, *J* = 7.3, 2H); 2.36 (s, 3H); 1.73 (sext, *J* = 7.3 Hz, 2H); 1.07 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 141.7, 139.6, 133.8, 132.4, 129.24, 129.18, 126.7, 124.8, 121.5, 118.7, 83.5, 79.8, 78.8, 73.3, 34.5, 22.2, 21.6, 13.6. MS (rel. int., %) *m*/*z*: 290 ($M^+$; 25.0), 261 (100.0), 215 (8.9), 202 (11.9), 101 (2.1). HRMS (APCI-QTOF) calculated mass for $C_{20}H_{19}S$ $[M+H]^+$: 291.1202, found: 291.1200.



**1l**

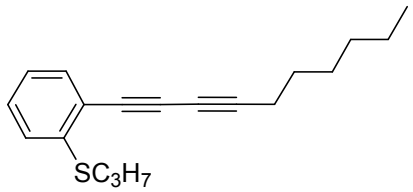
{2-[(4-Chlorophenyl)buta-1,3-diyn-1-yl]phenyl}(propyl)sulfane **1l**: Yield: 0.2418 g (78%); yellowish solid, m.p: 52-54 ºC. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.48 (dd, *J* = 7.7, 1.4 Hz, 1H); 7.45 (d, *J* = 8.5 Hz, 2H); 7.30 (d, *J* = 8.5 Hz, 2H); 7.27-7.23 (m, 2H); 7.12-7.08 (m 1H); 2.95 (t, *J* = 7.3 Hz, 2H); 1.73 (sext, *J* = 7.3 Hz, 2H); 1.06 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 141.9, 135.3, 133.8, 133.6, 129.5, 128.8, 126.6, 124.8, 121.0, 120.3, 81.9, 79.7, 79.3, 74.9, 34.5, 22.2, 13.6. MS (rel. int., %) *m*/*z*: 310 ($M^+$; 19.9), 281 (100.0), 202 (8.2), 187

(12.2), 101 (1.5). HRMS (APCI-QTOF) calculated mass for $C_{19}H_{16}ClS$ $[M+H]^+$: 311.0656, found: 311.0656.



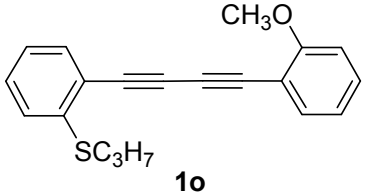
**1m**

{2-[(Naphthalen-2-yl)buta-1,3-diyn-1-yl]phenyl}(propyl)sulfane **1m**: Yield: 0.1635 g (50%); yellowish oil. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 8.38 (d, *J* = 8.3 Hz, 1H); 7.88-7.85 (m, 2H); 7.79 (dd, *J* = 7.2, 1.3 Hz, 1H); 7.62-7.58 (m, 1H); 7.55-7.52 (m, 2H); 7.46-7.42 (m, 1H); 7.33-7.27 (m, 2H); 7.15-7.11 (m, 1H); 2.99 (t, *J* = 7.3 Hz, 2H); 1.76 (sext, *J* = 7.3 Hz, 2H); 1.09 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 141.8, 133.9, 133.85, 133.1, 132.0, 129.7, 129.4, 128.4, 127.2, 126.8, 126.7, 126.2, 125.2, 124.9, 121.4, 119.5, 81.6, 80.2, 79.8, 78.5, 34.6, 22.2, 13.6. MS (rel. int., %) *m*/*z*: 326 ($M^+$; 24.1), 297 (100.0), 282 (14.6), 252 (8.7), 187 (1.9), 44 (46.9). HRMS (APCI-QTOF) calculated mass for $C_{23}H_{19}S$ $[M+H]^+$: 327.1202, found: 327.1214.



**1n**

[2-(deca-1,3-diyn-1-yl)phenyl](propyl)sulfane **1n**: Yield: 0.1562 g (55%); colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.44-7.42 (m, 1H); 7.27-7.21 (m, 2H); 7.06 (ddd, *J* = 7.7, 6.6, 2.0 Hz, 1H); 2.93 (t, *J* = 7.3 Hz, 2H); 2.37 (t, *J* = 7.1 Hz, 2H); 1.71 (sext, *J* = 7.3 Hz, 2H); 1.57 (quint, *J* = 7.1 Hz, 2H); 1.45-1.40 (m, 2H); 1.33-1.26 (m, 4H); 1.05 (t, *J* = 7.3 Hz, 3H); 0.90 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) = 141.5, 133.7, 128.9, 126.6, 124.7, 121.7, 86.6, 80.2, 72.3, 65.0, 34.5, 31.3, 28.5, 28.2, 22.5, 22.2, 19.7, 14.0, 13.6. MS (rel. int., %) *m*/*z*: 284 ($M^+$; 24.1), 255 (100.0), 241 (2.8), 184 (21.9), 41 (15.4). HRMS (APCI-QTOF) calculated mass for $C_{19}H_{24}S$ $[M]^+$: 284.1593, found: 284.1599.



**1o**

{2-[(2-Methoxyphenyl)buta-1,3-diyn-1-yl]phenyl}(propyl)sulfane **1o**: Yield: 0.153 g (50%); yellowish solid, m.p: 67-69 ºC. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) = 7.49-7.47 (m, 2H); 7.34-7.23 (m, 3H); 7.11-7.07 (m, 1H); 6.93-6.87 (m, 2H); 3.89 (s, 3H); 2.95 (t, *J* = 7.4 Hz, 2H); 1.72 (sext, *J* = 7.4 Hz, 2H); 1.06 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm) =

161.3, 141.6, 134.4, 133.8, 130.7, 129.2, 126.6, 124.8, 121.5, 120.5, 111.0, 110.6, 79.9, 79.8, 79.7, 77.6, 55.8, 34.5, 22.2, 13.5. MS (rel. int., %) *m*/*z*: 306 ($M^+$; 27.0), 277 (100.0), 200 (1.5), 131 (1.8), 175 (1.5), 77 (1.4). HRMS (APCI-QTOF) calculated mass for $C_{20}H_{19}OS$ $[M+H]^+$: 307.1157, found: 307.1145.

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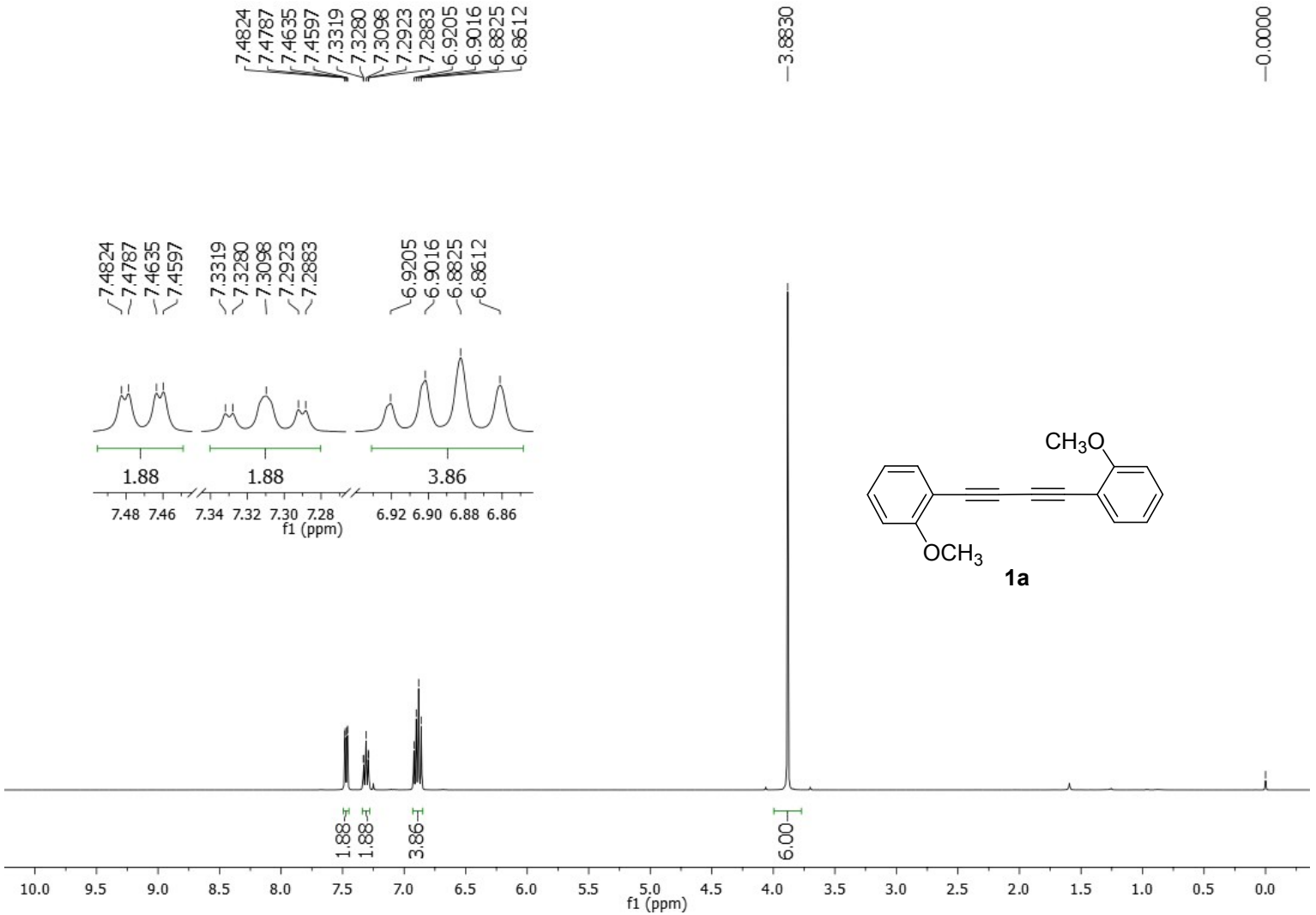



**Figure S1**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1a**.

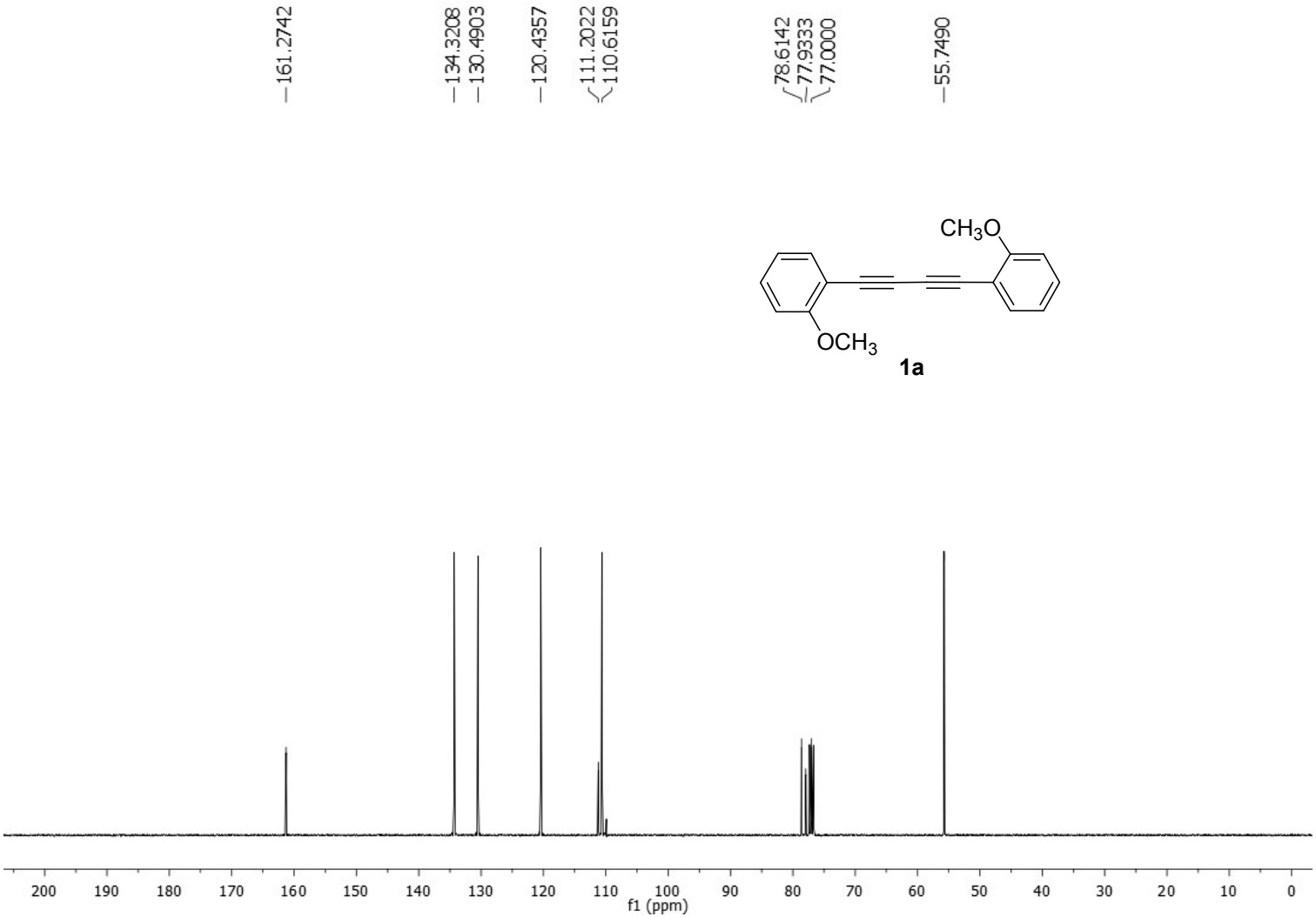



**Figure S2**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1a**.

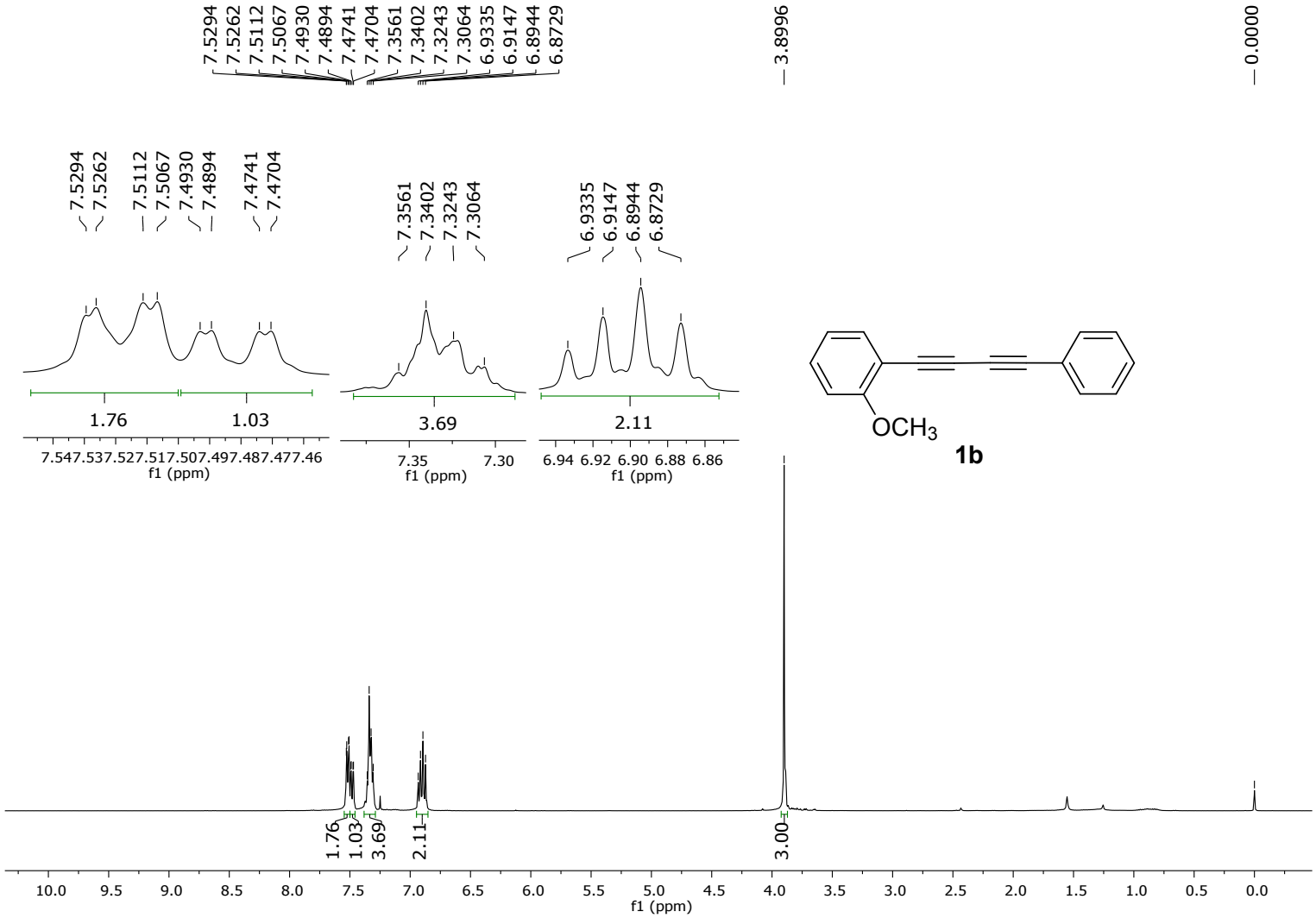



**Figure S3**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1b**.

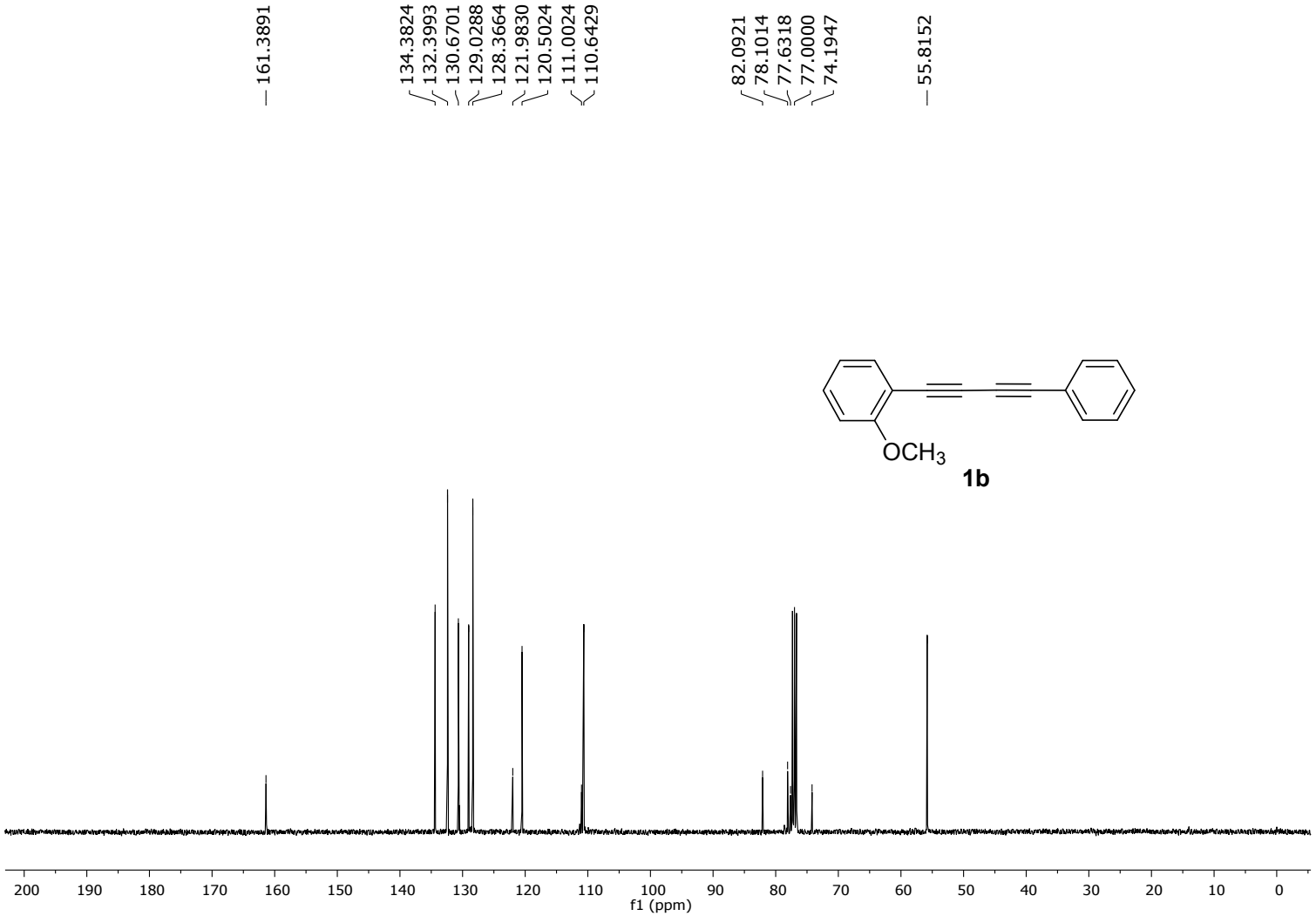



**Figure S4**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1b**.

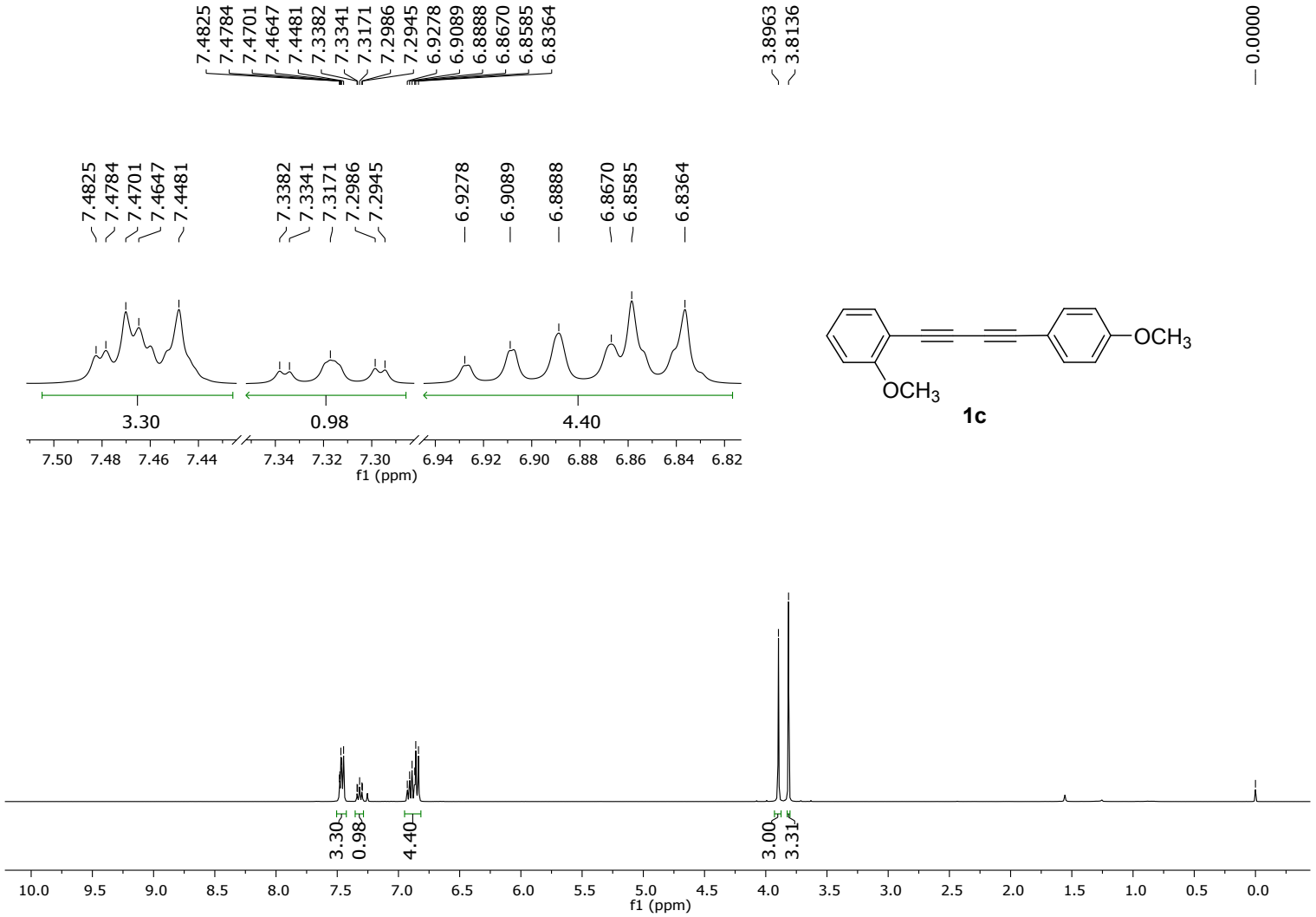



**Figure S5**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1c**.

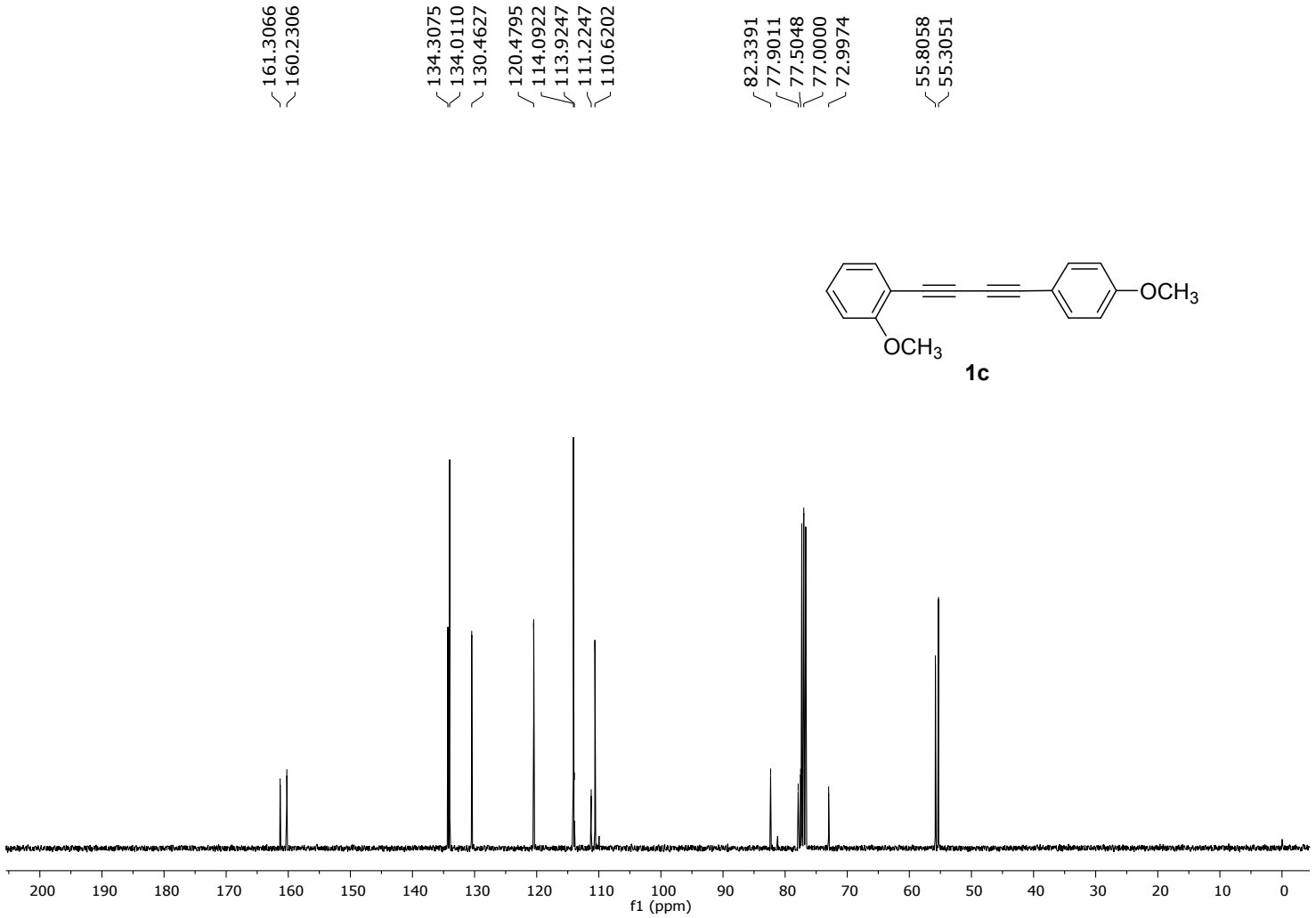



**Figure S6**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1c**.

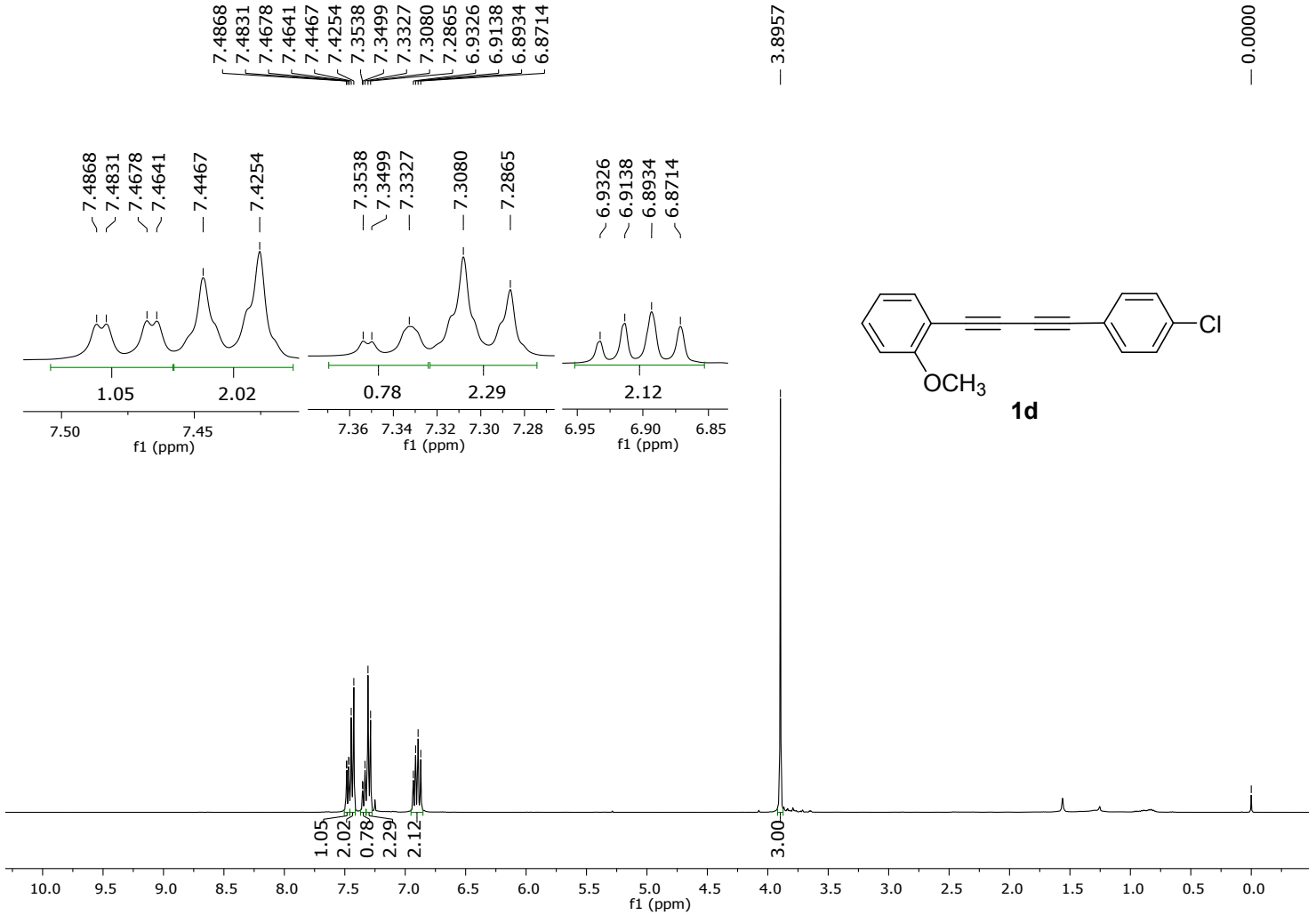



**Figure S7**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1d**.

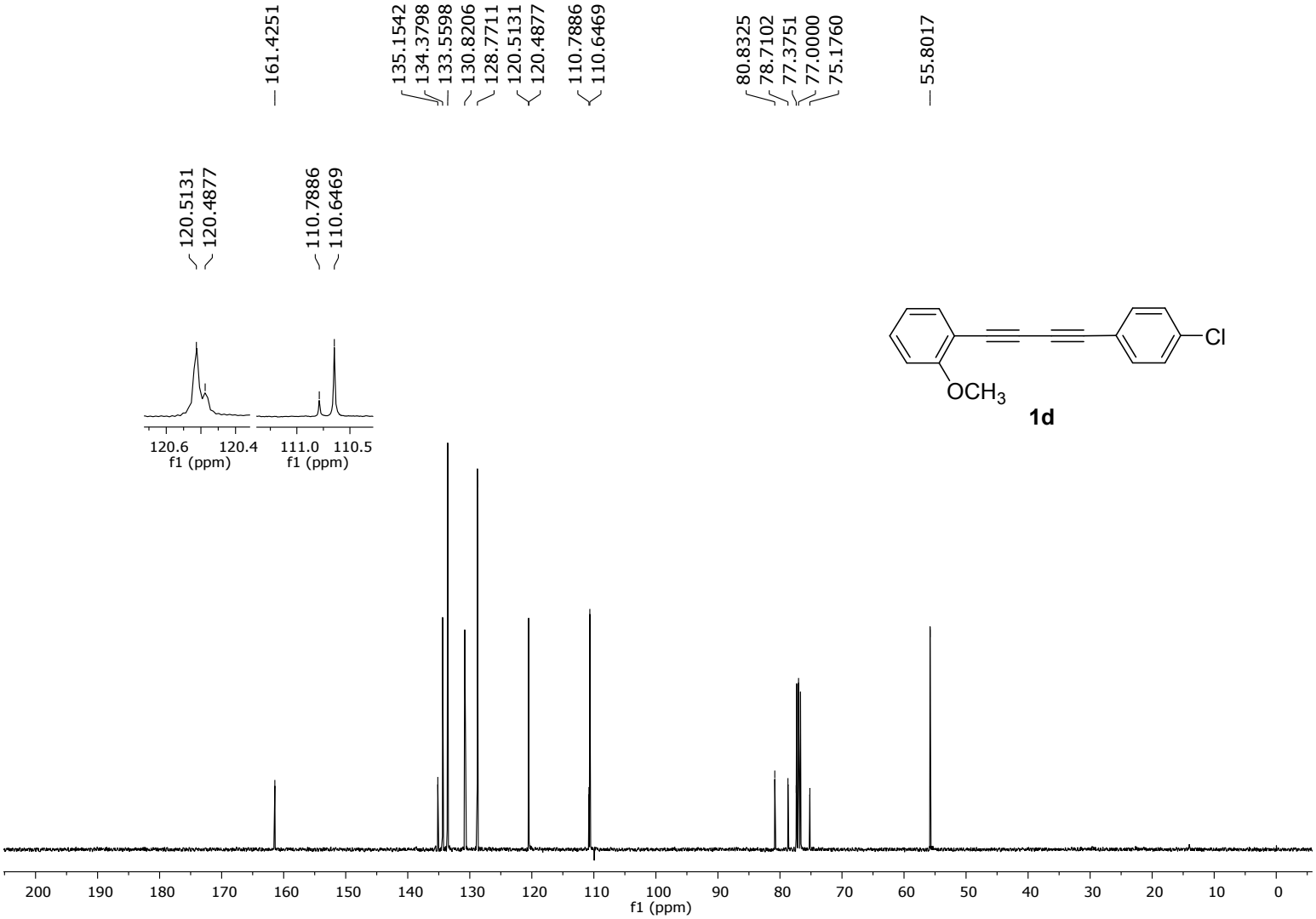



**Figure S8**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1d**.

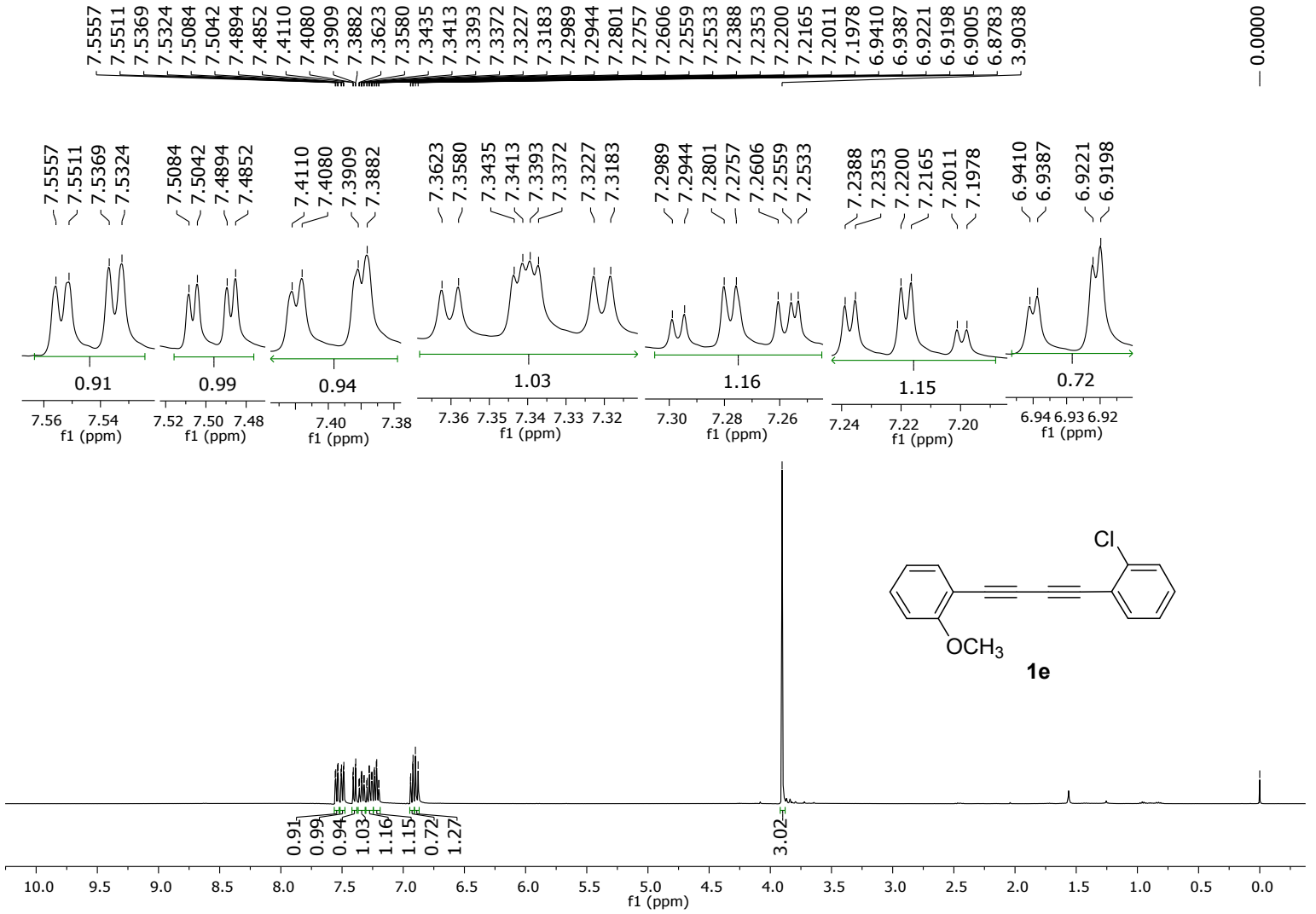



**Figure S9**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1e**.

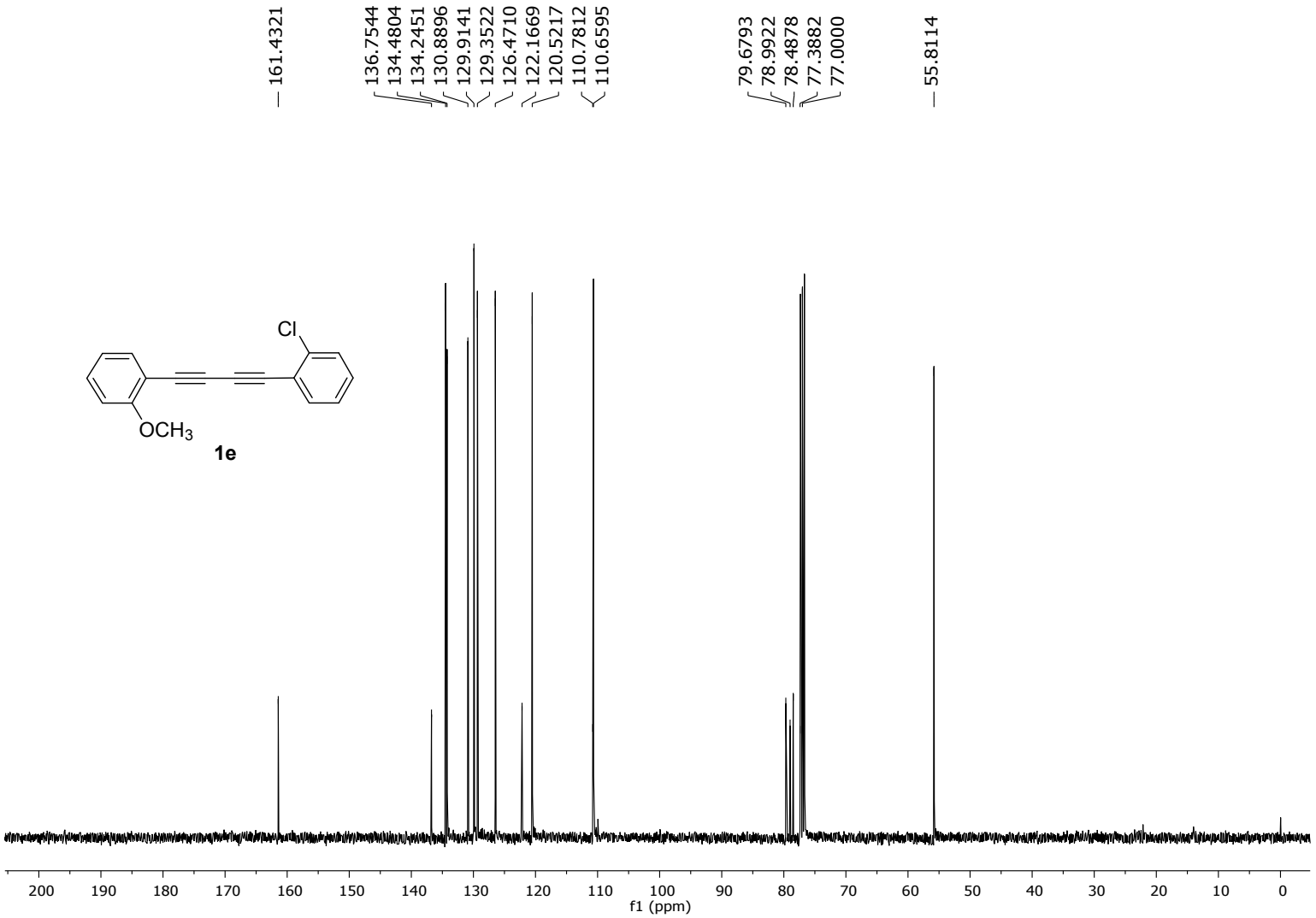



**Figure S10**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1e**.

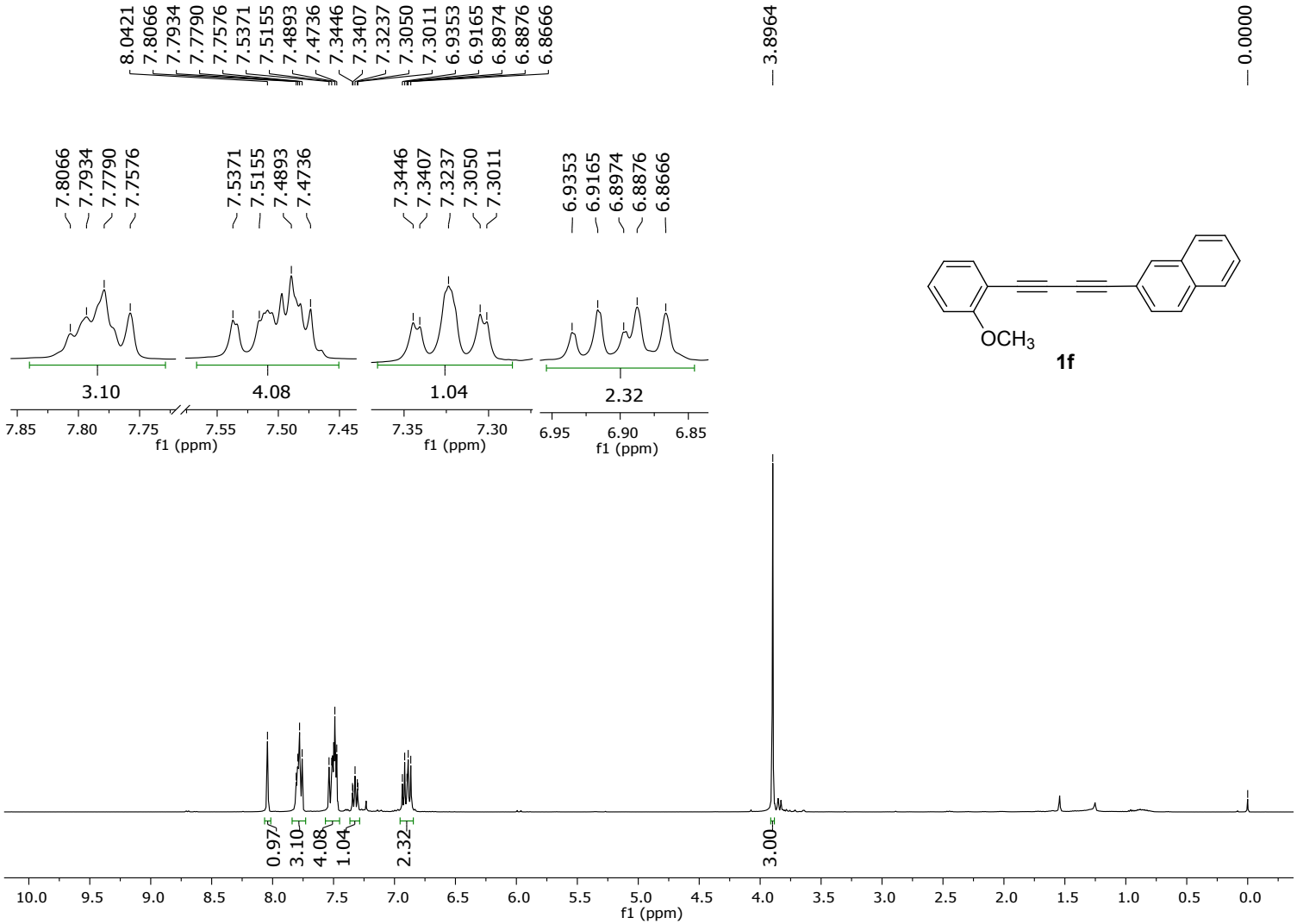



**Figure S11**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1f**.

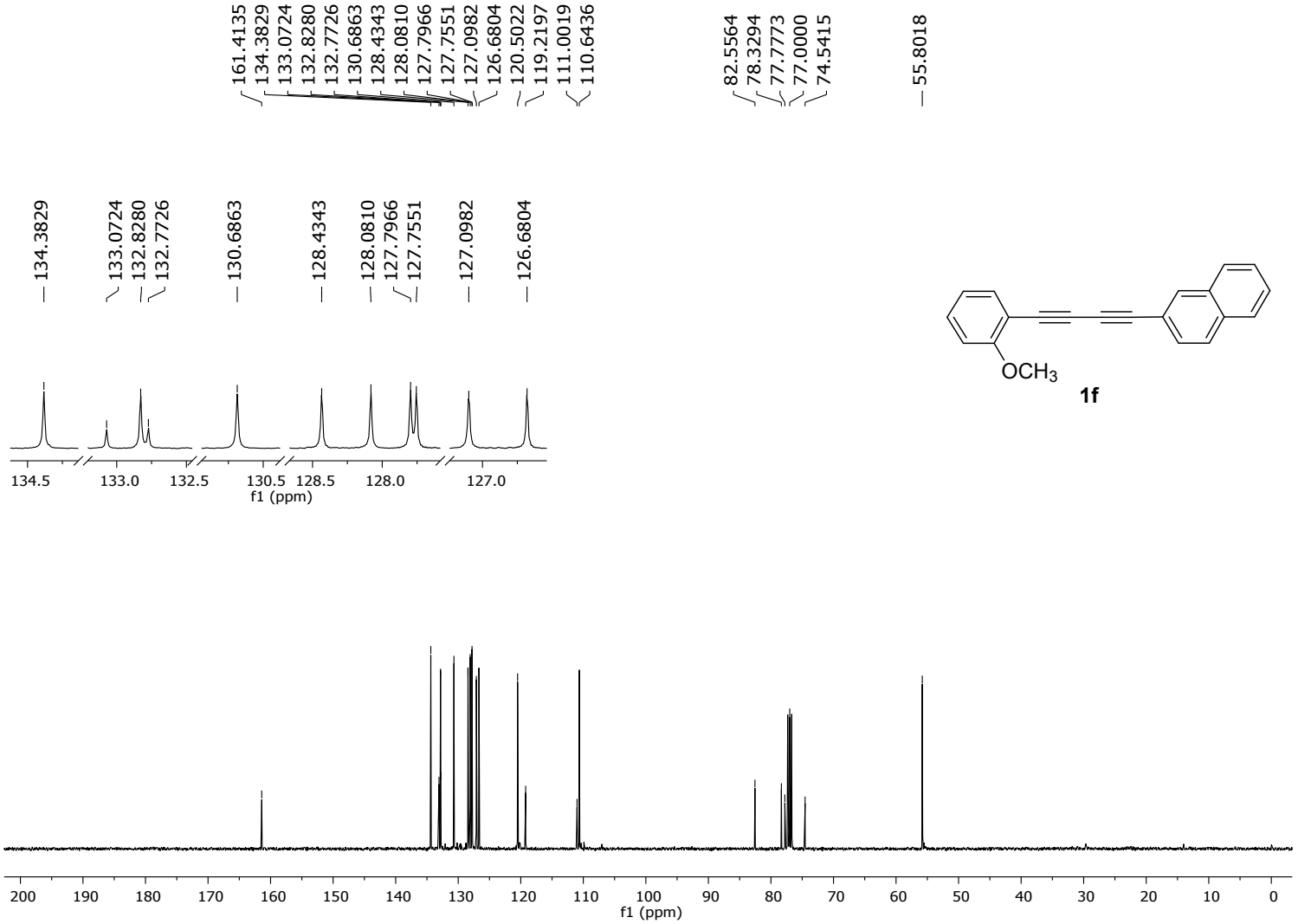



**Figure S12**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1f**.

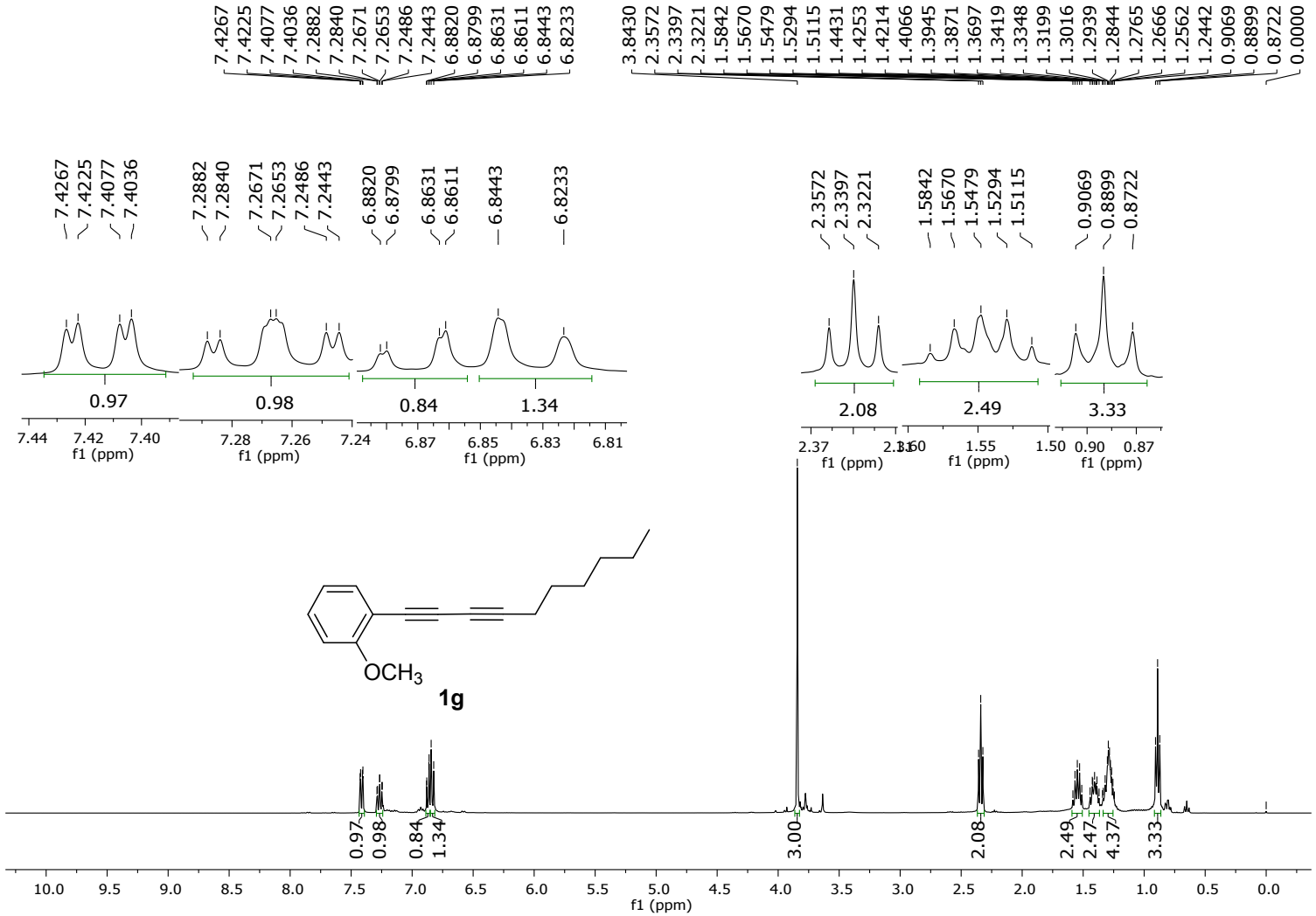



**Figure S13**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1g**.

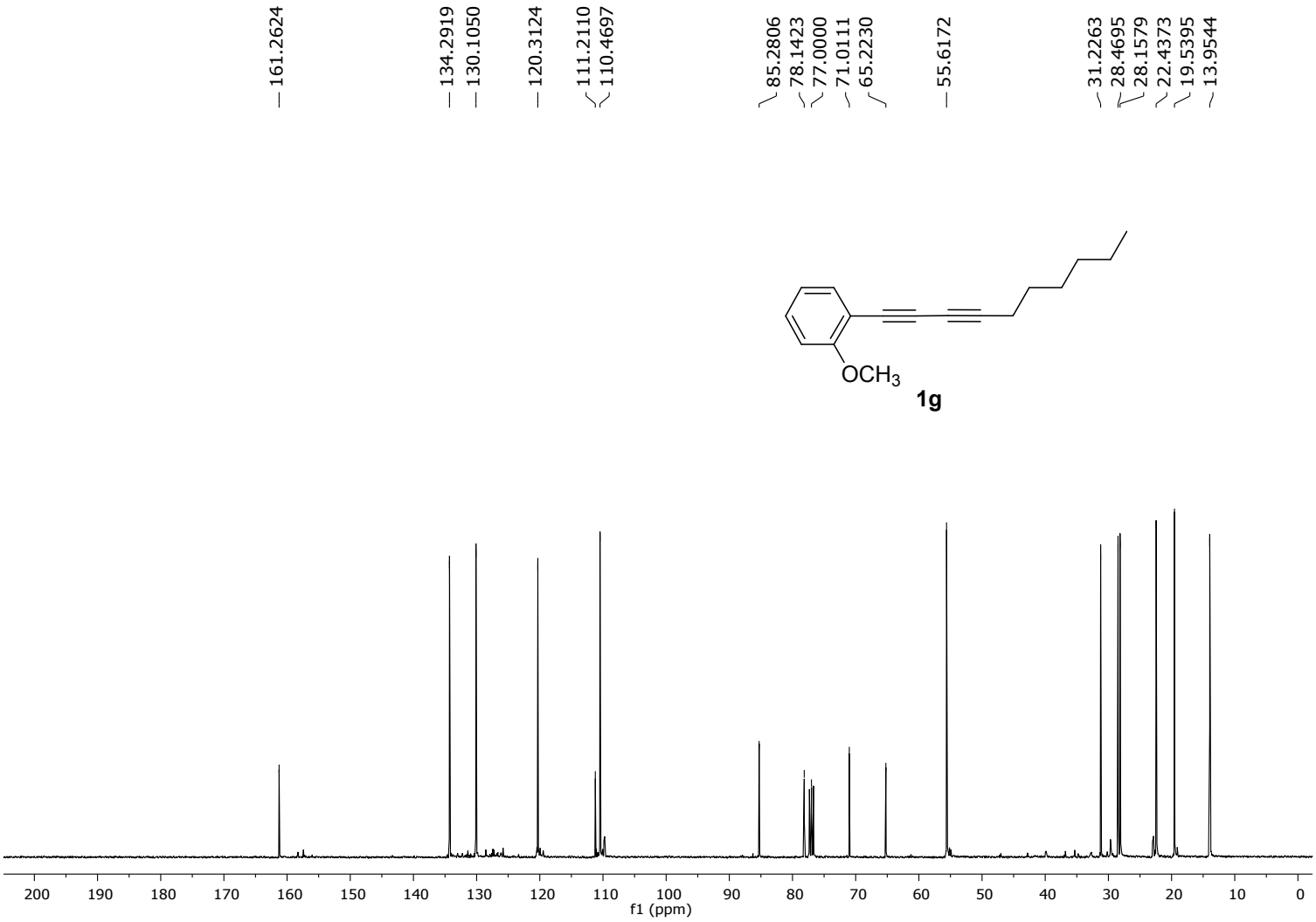



**Figure S14**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1g**.

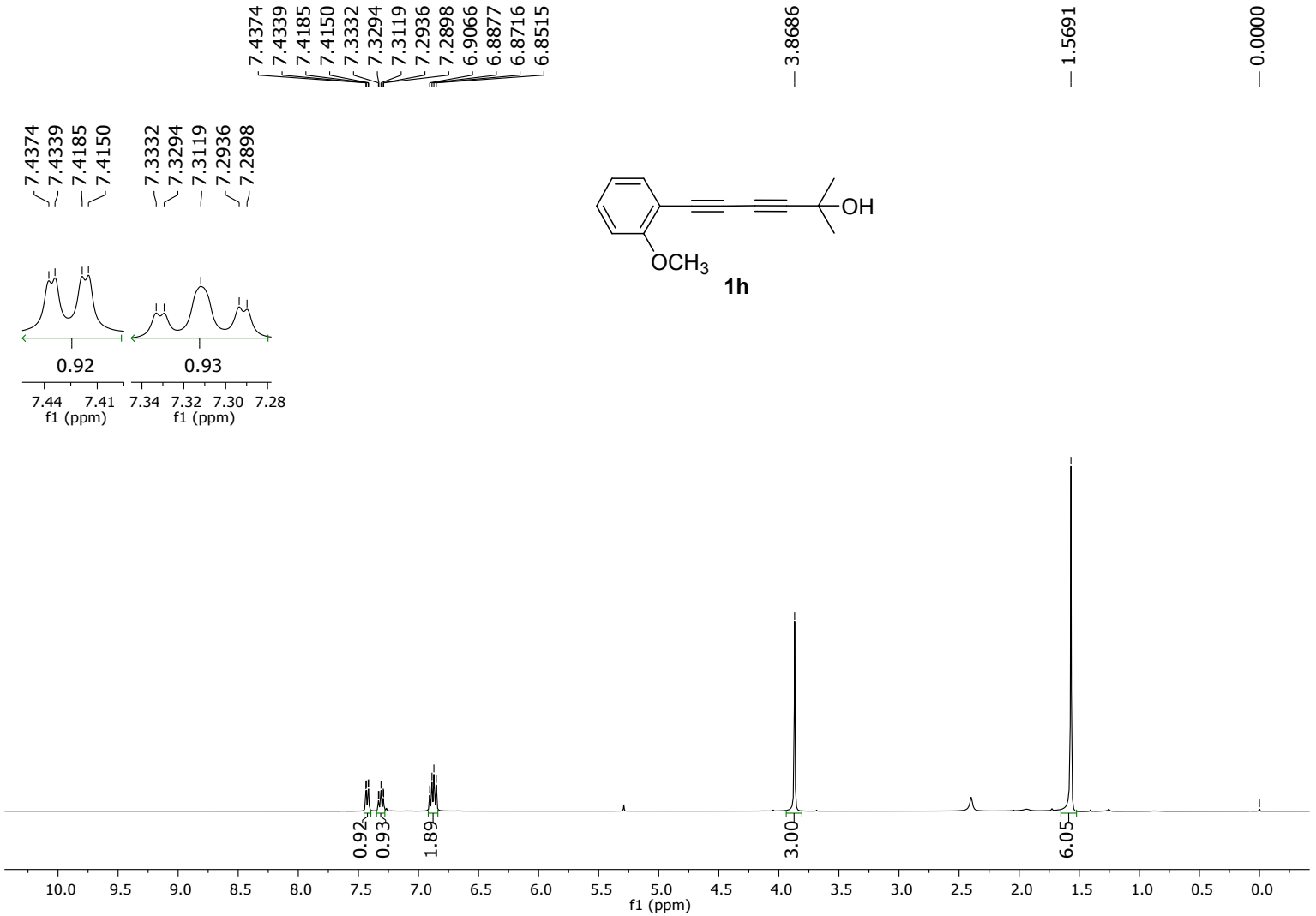



**Figure S15**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1h**.

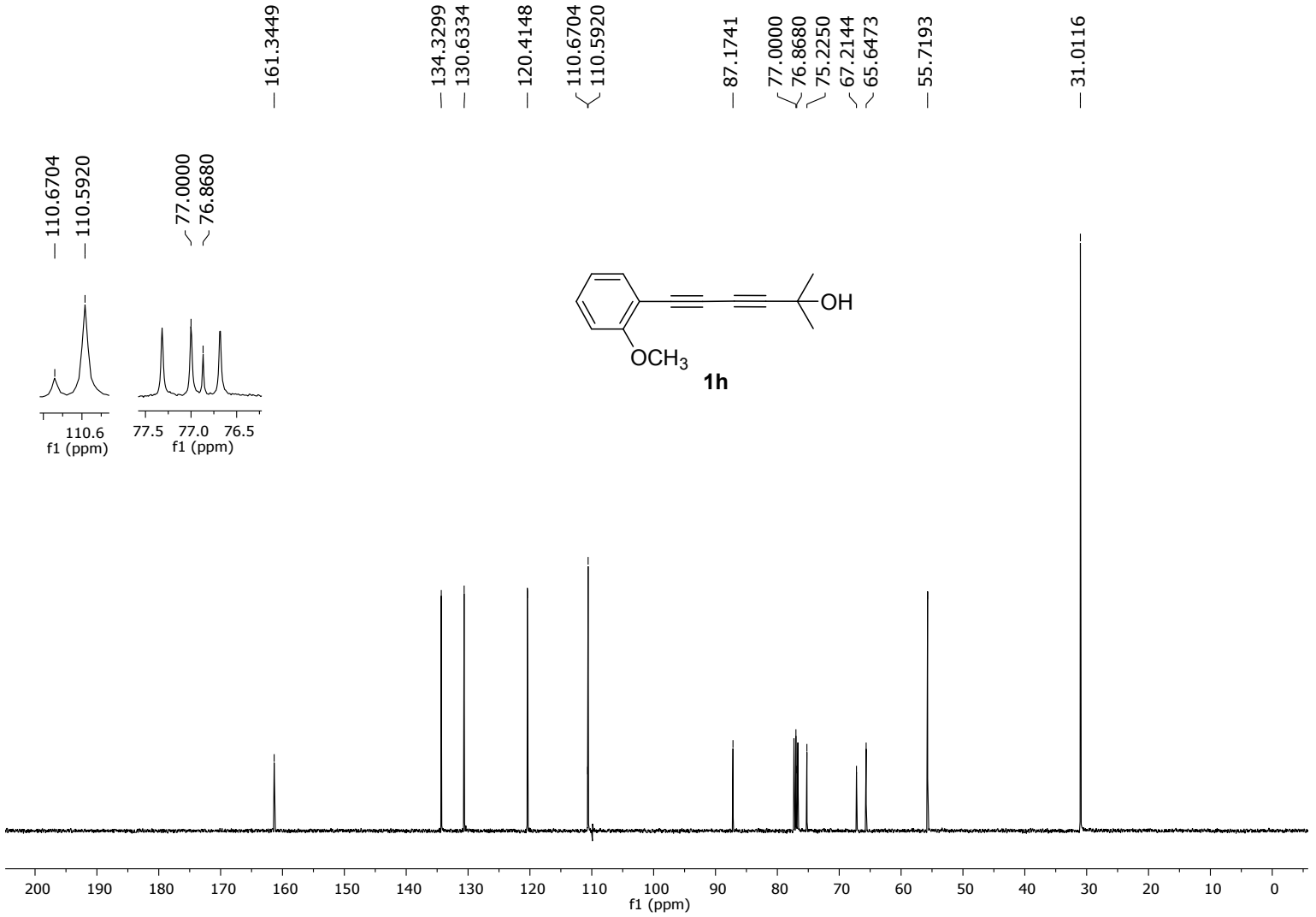



**Figure S16**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1h**.

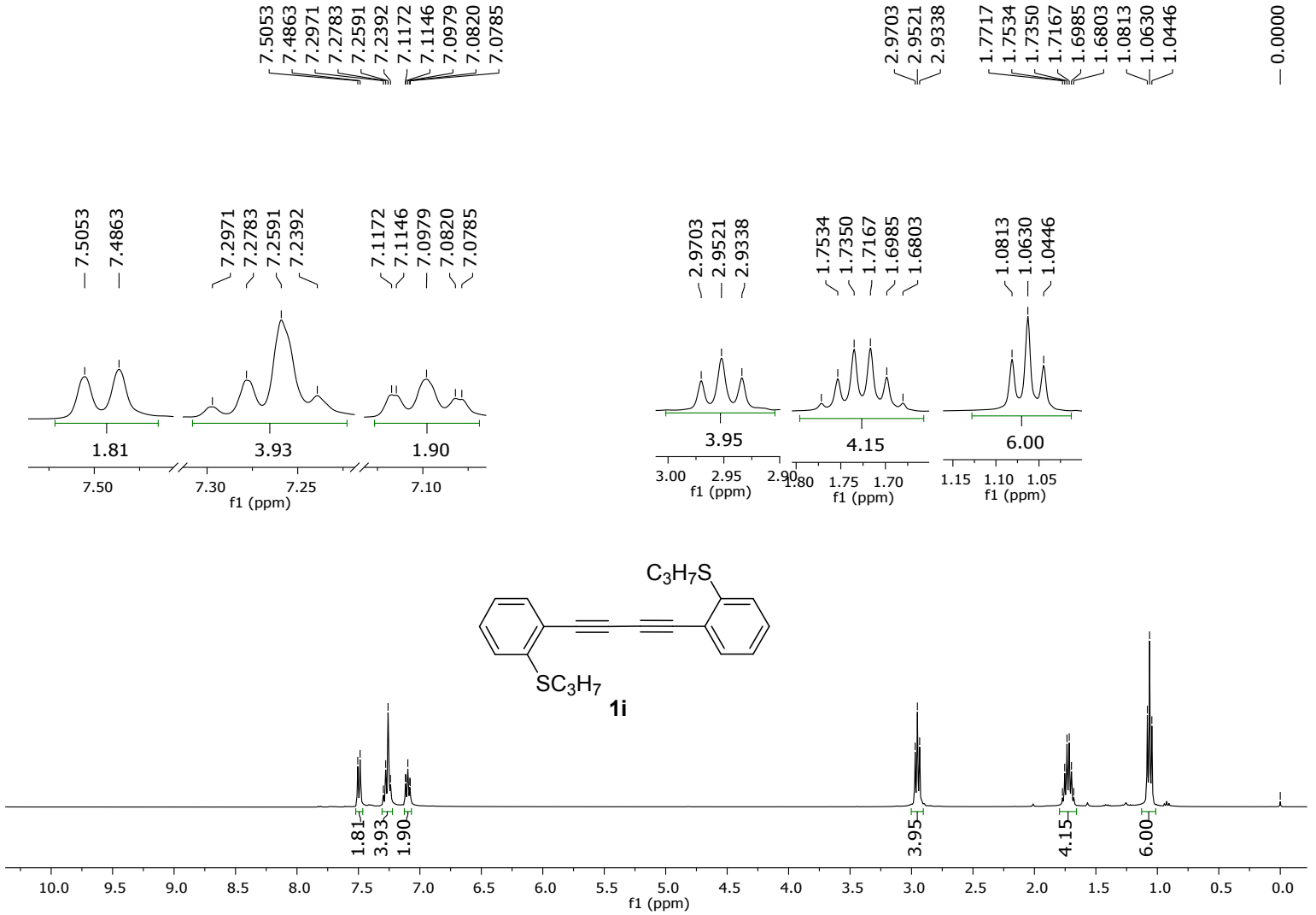



**Figure S17**: $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **1i**.

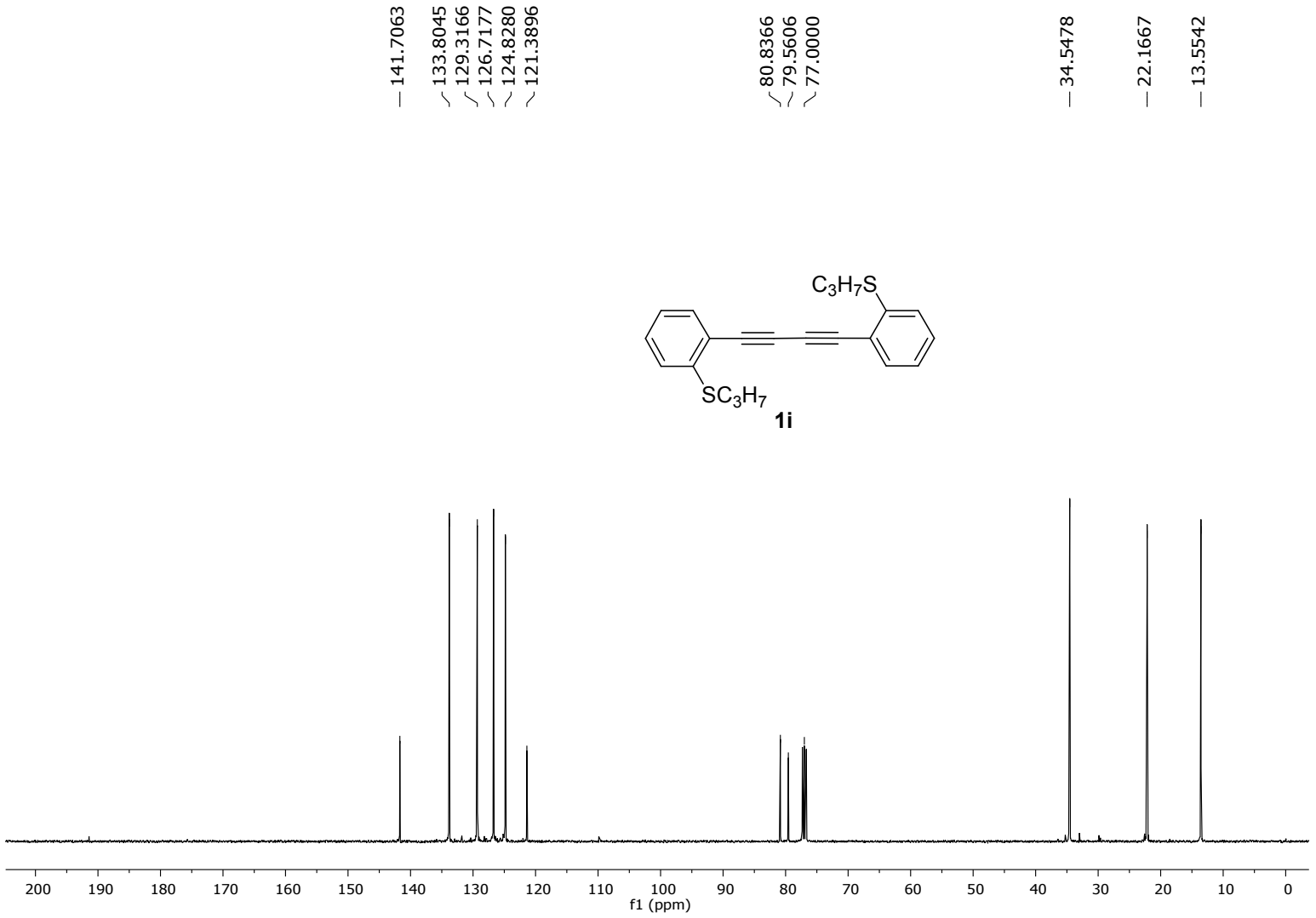



**Figure S18**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1i**.

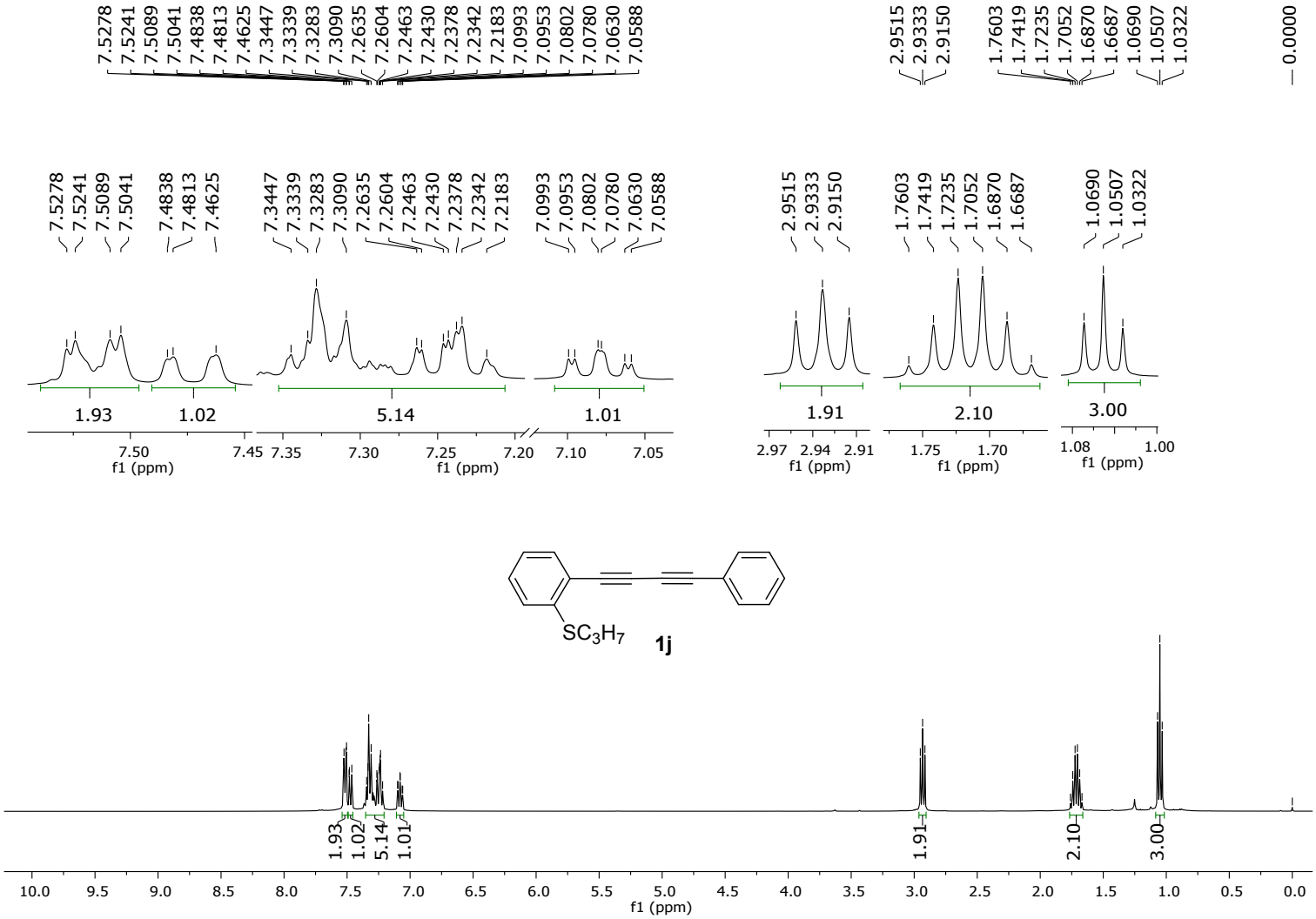



**Figure S19**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1j**.

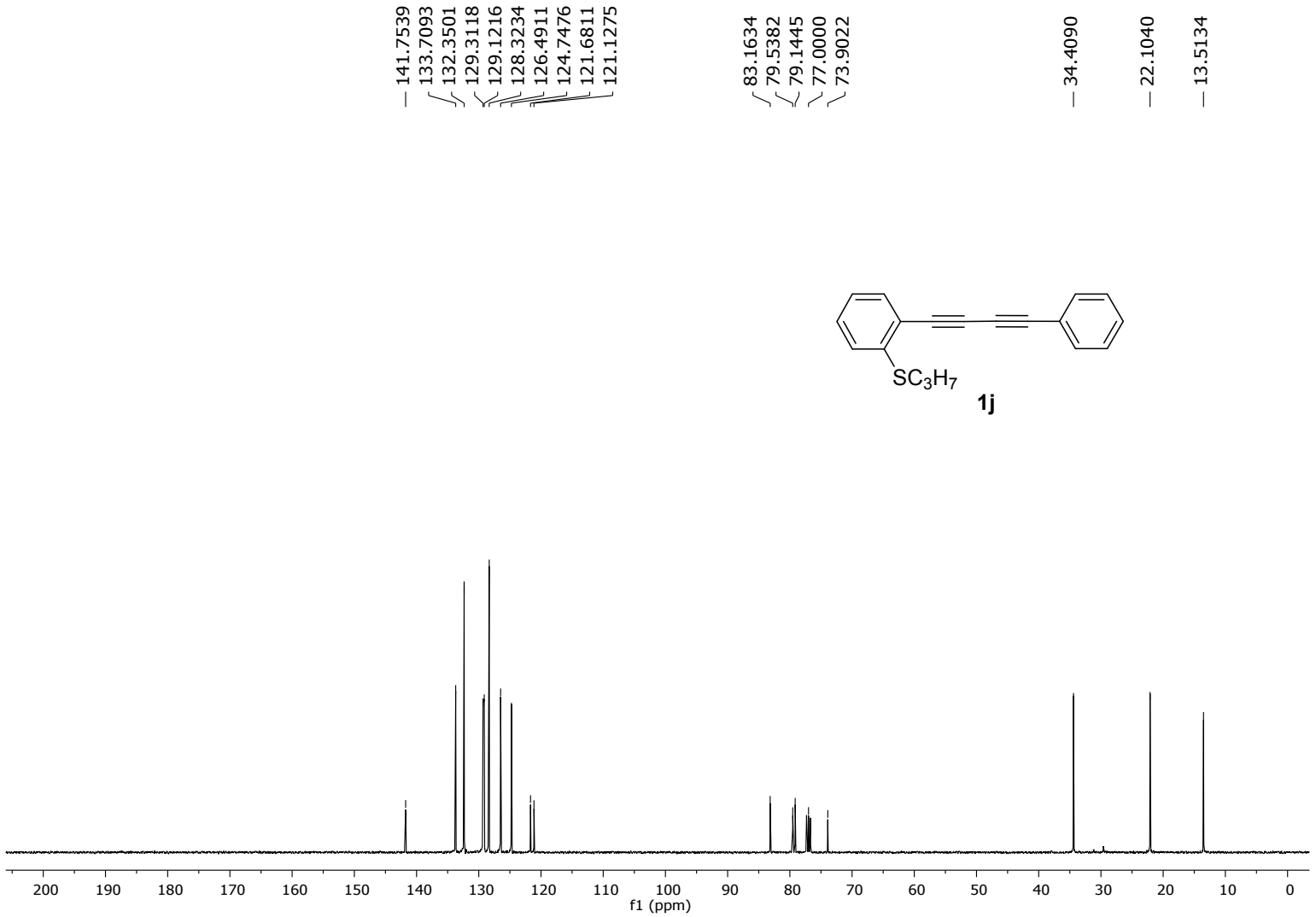



**Figure S20**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1j**.

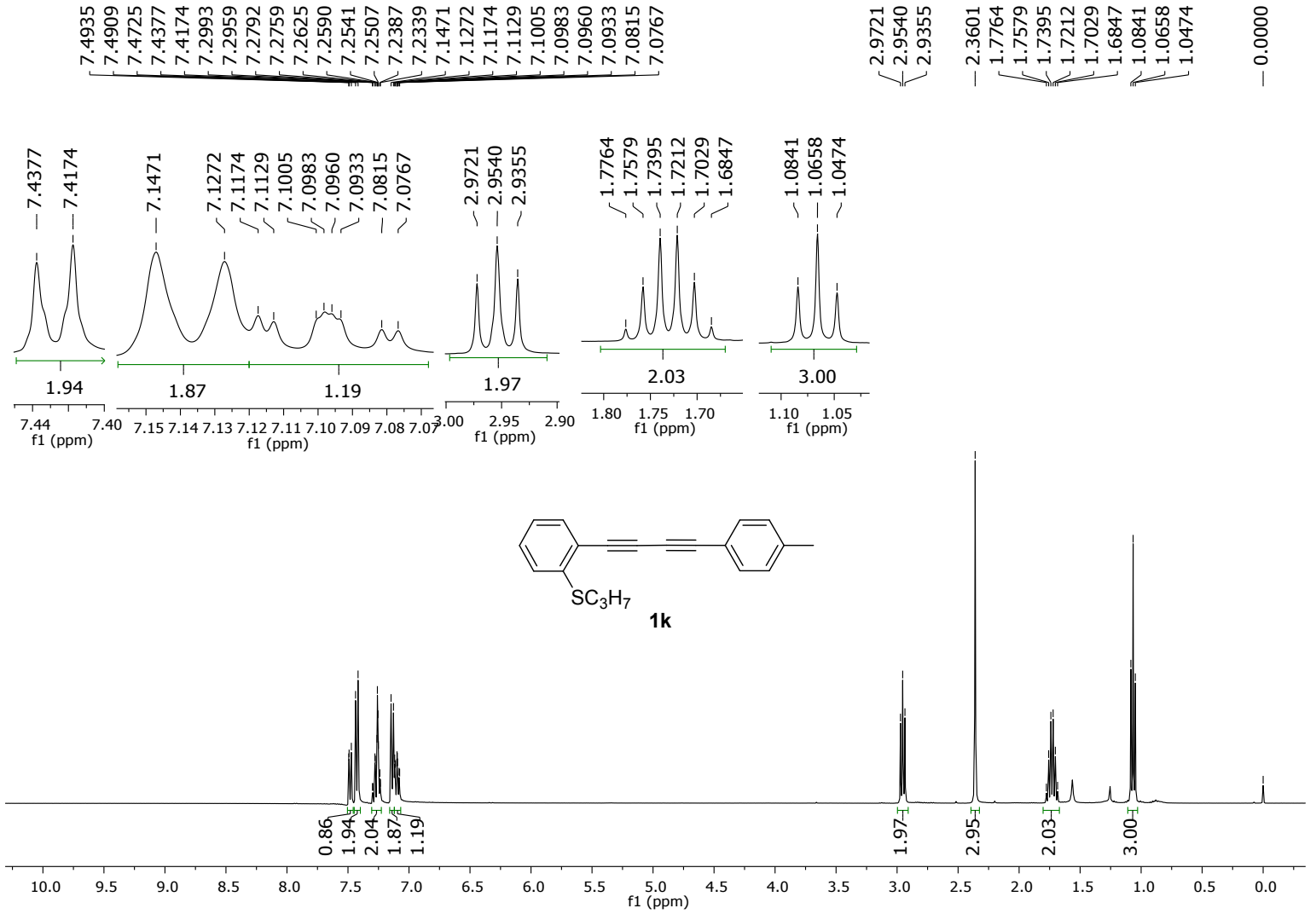



**Figure S21**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1k**.

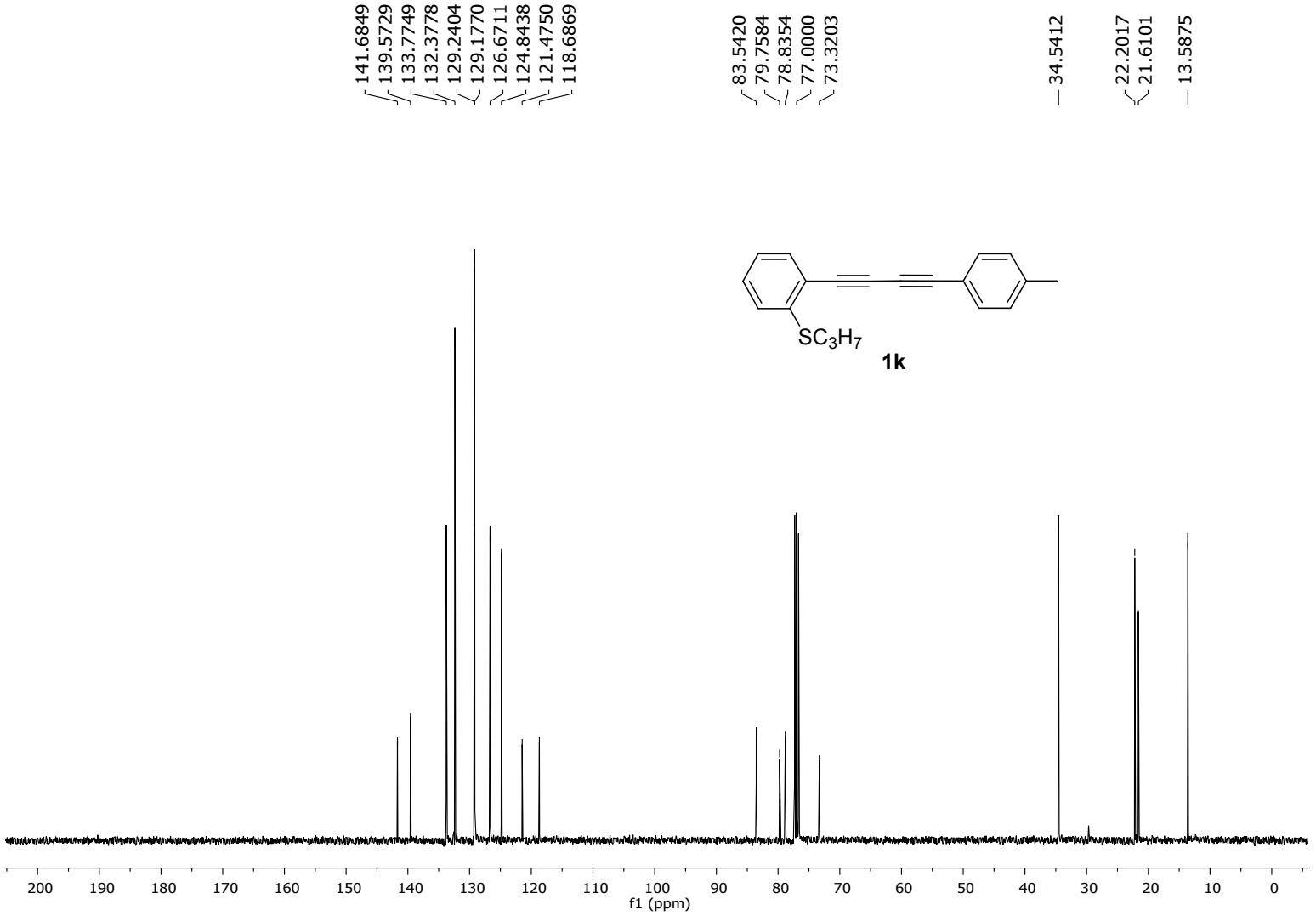



**Figure S22**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1k**.

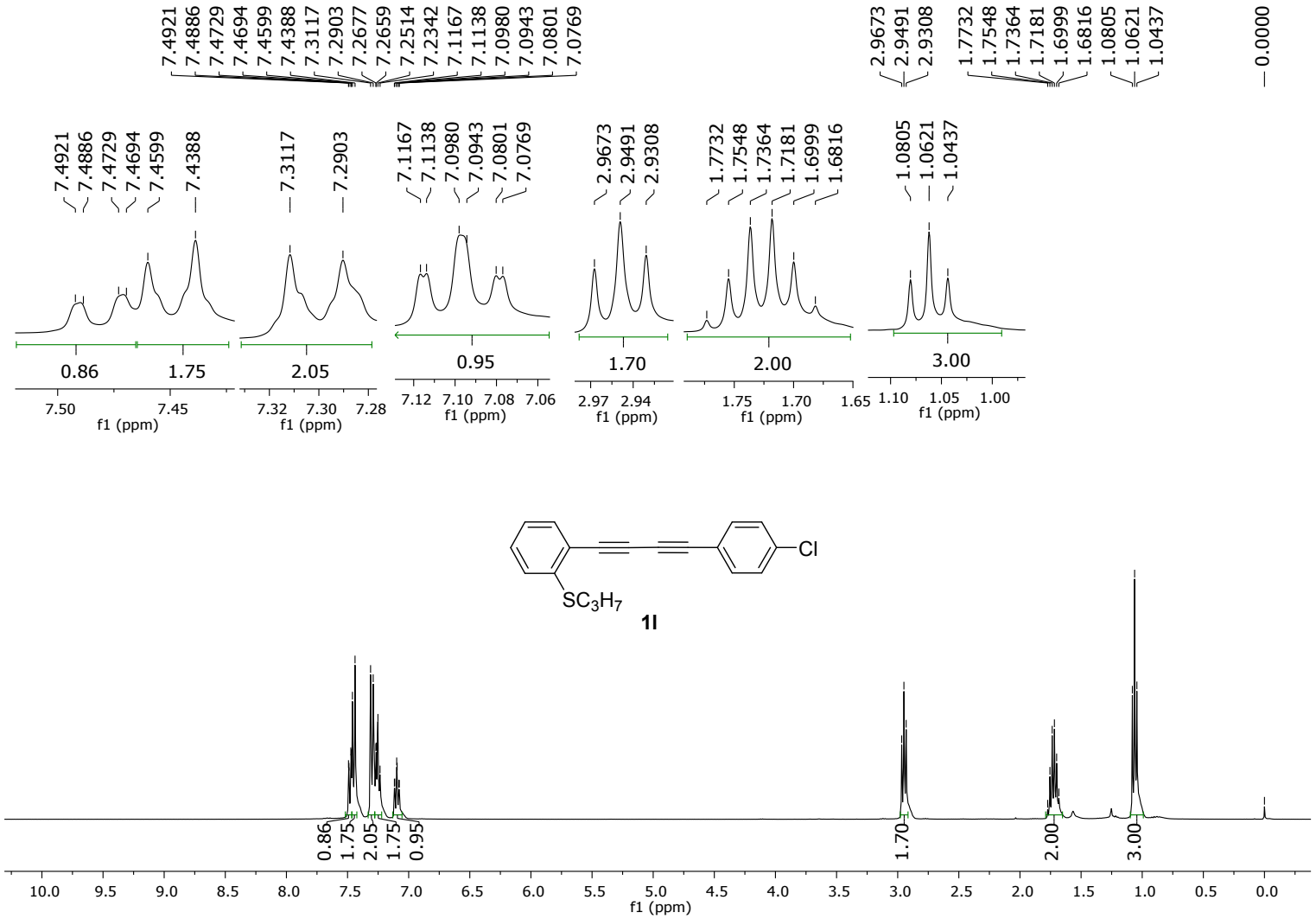



**Figure S23**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1l**.

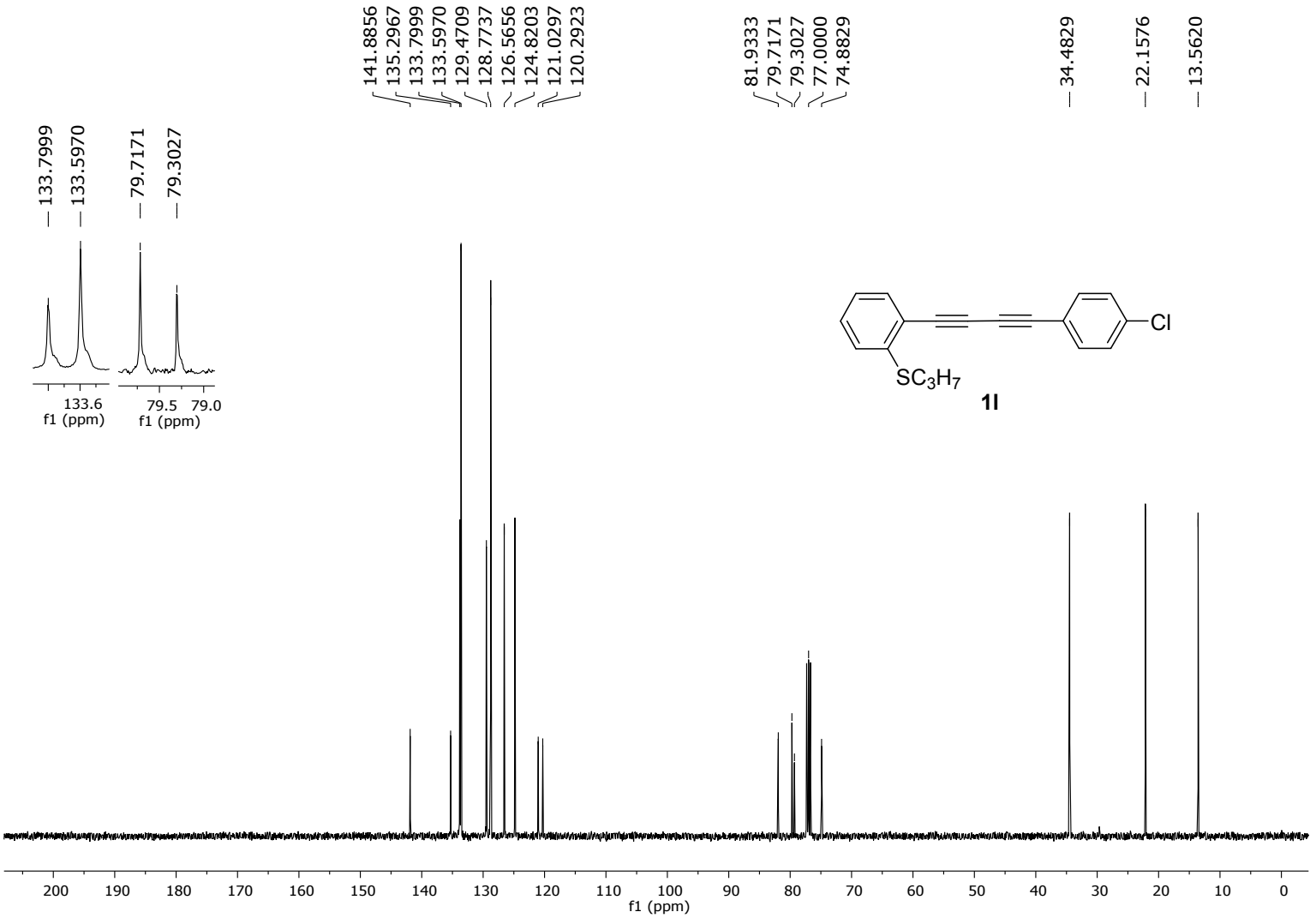



**Figure S24**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1l**.

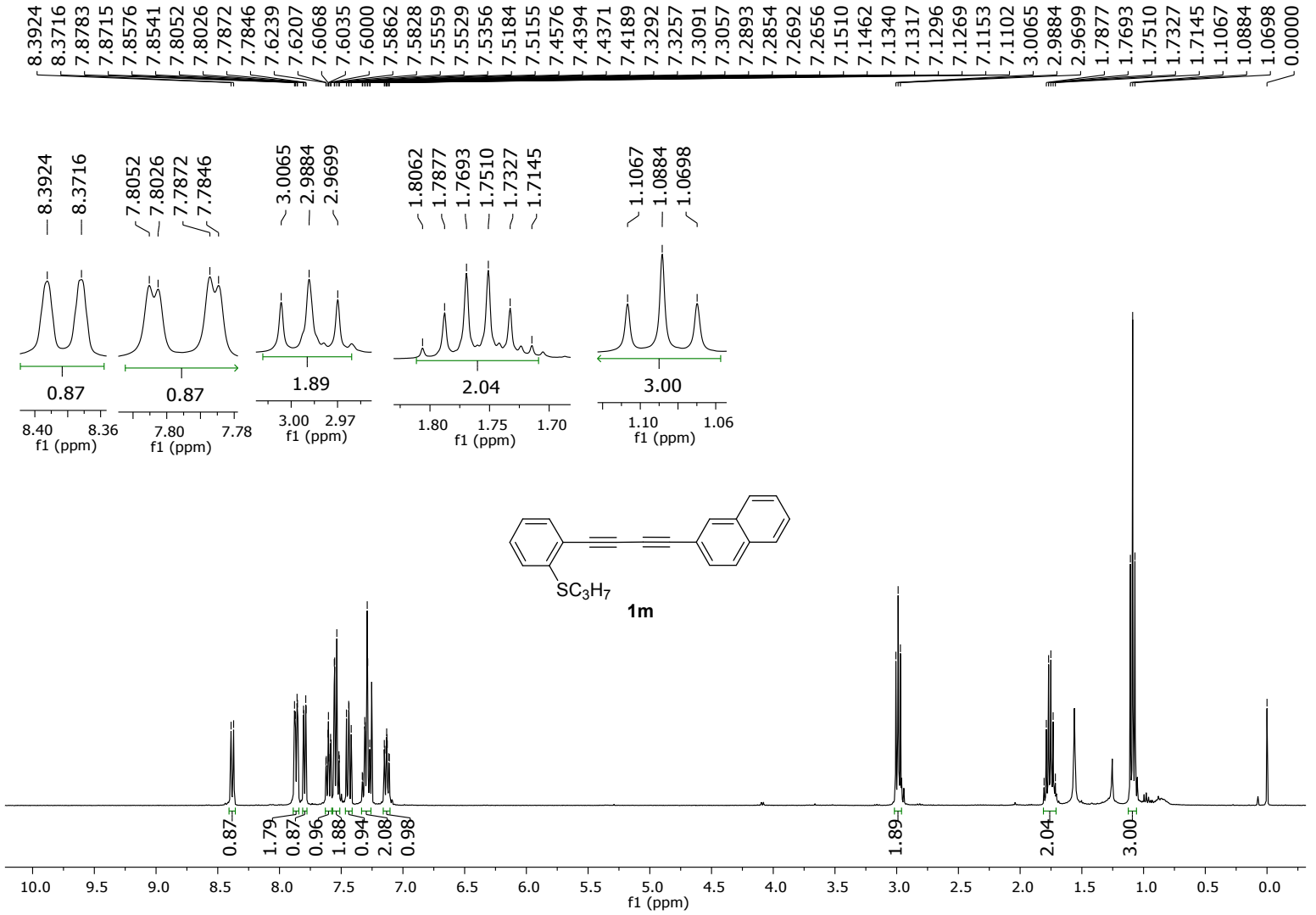



**Figure S25**: $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **1m**.

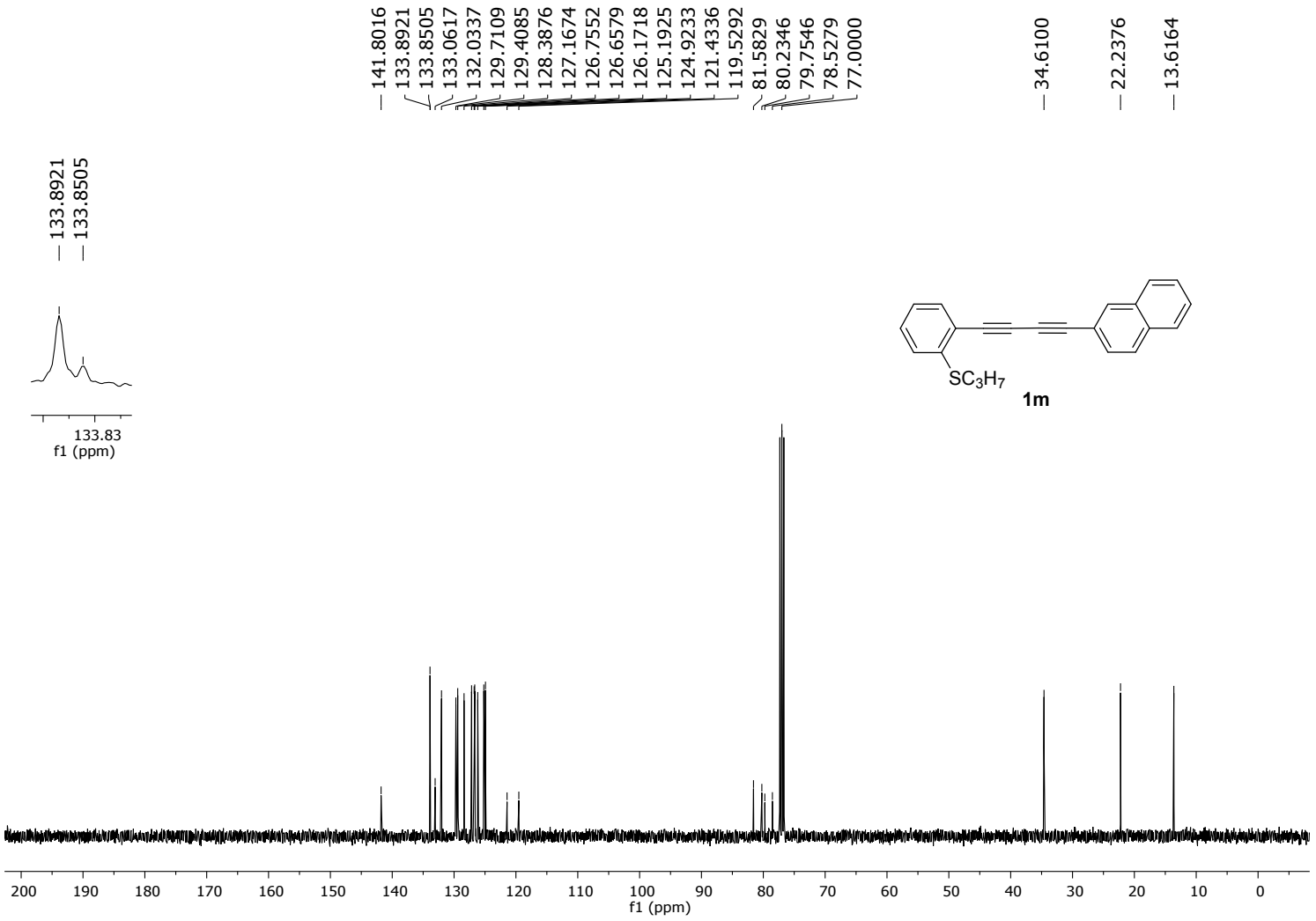



**Figure S26**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1m**.

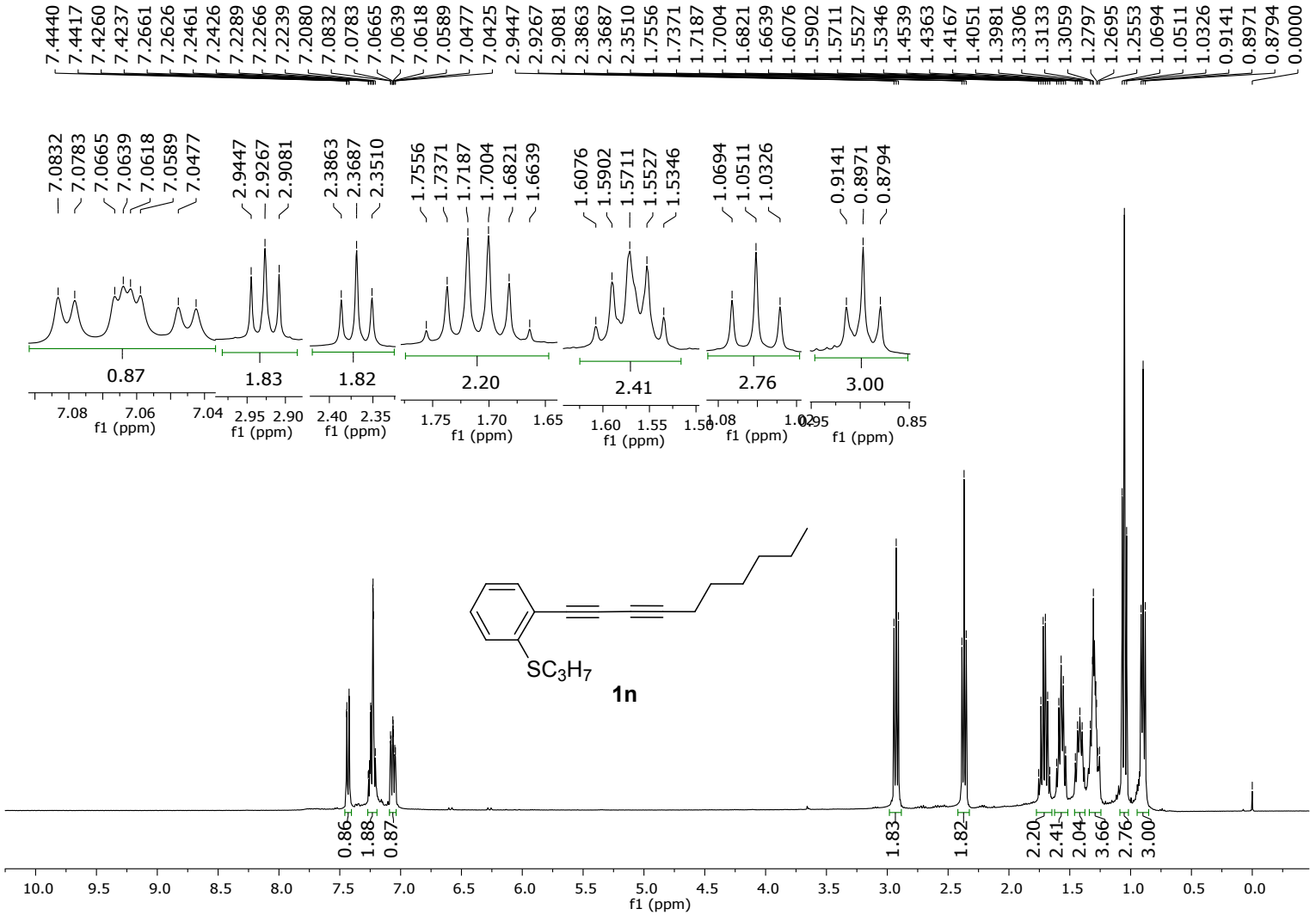



**Figure S27**: $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of compound **1n**.

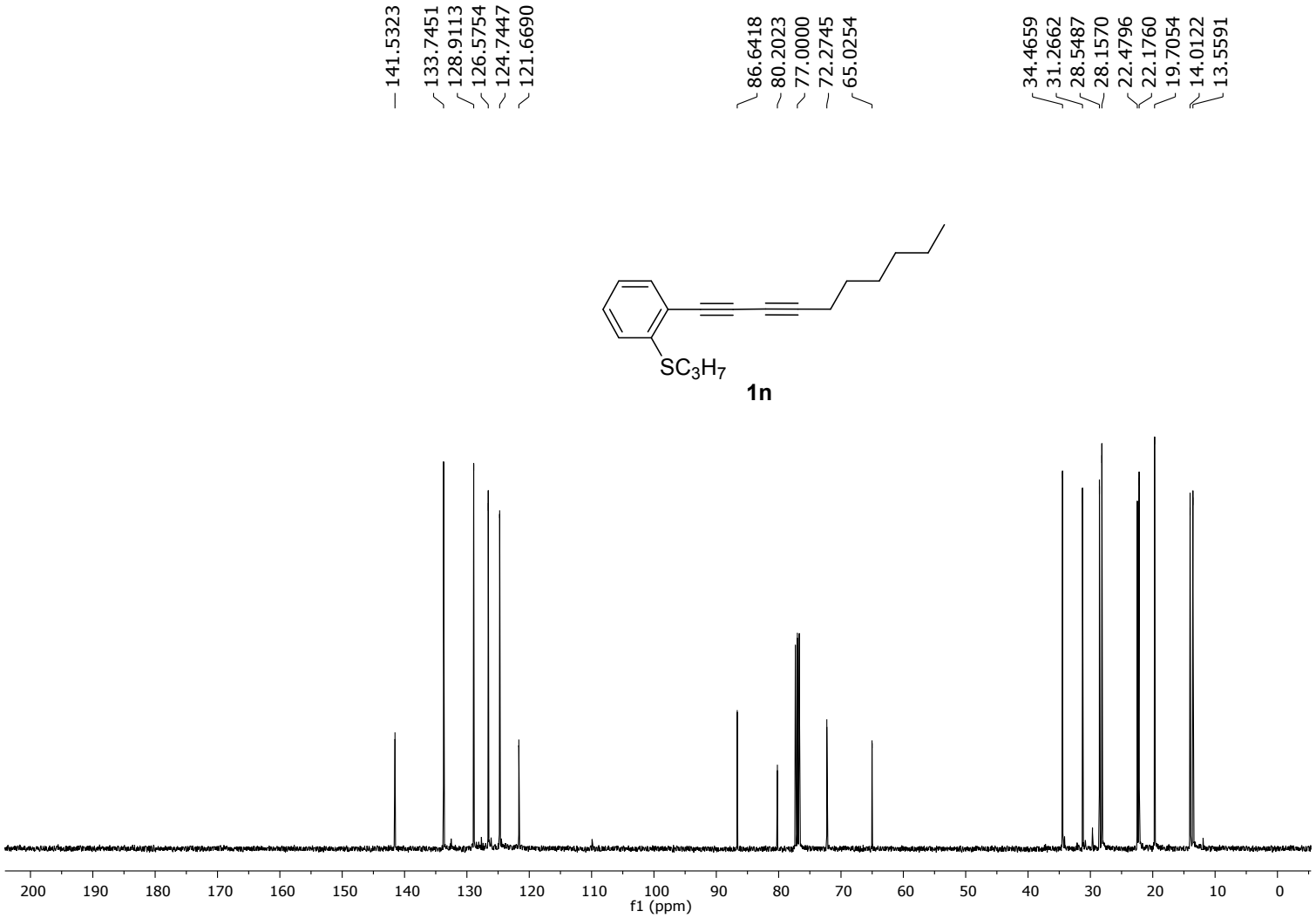



**Figure S28**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1n**.

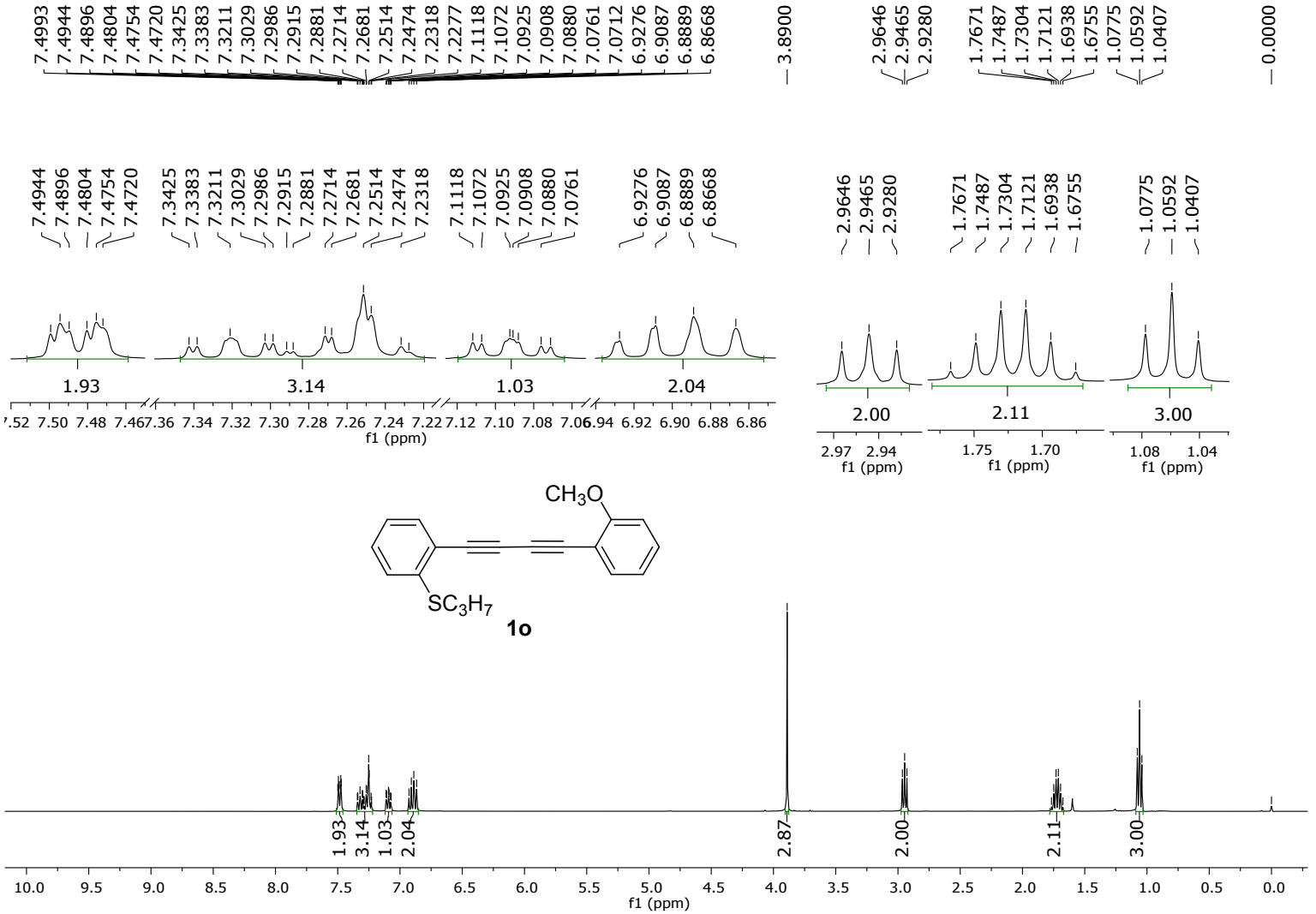



**Figure S29**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1o**.

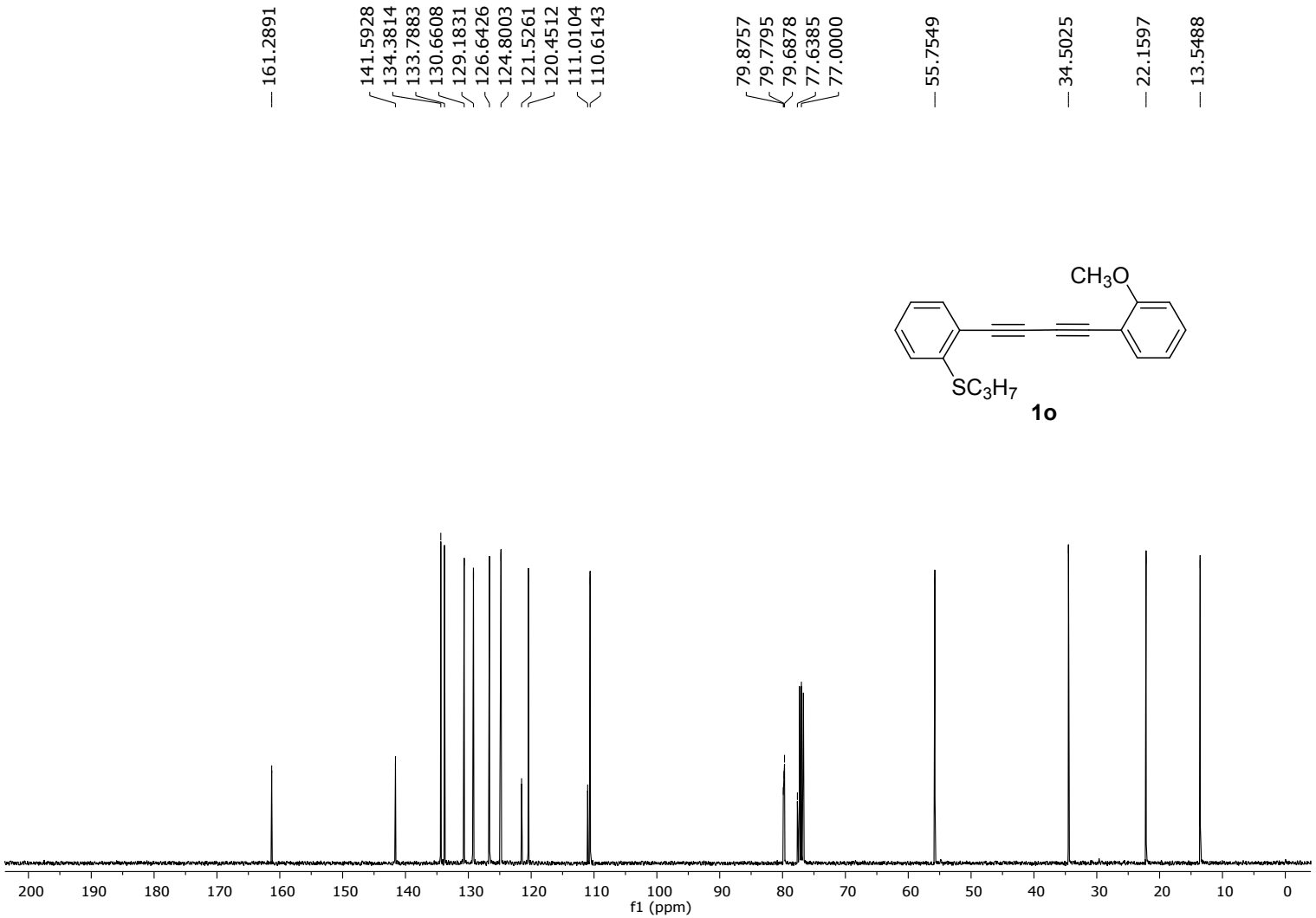



**Figure S30**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1o**.

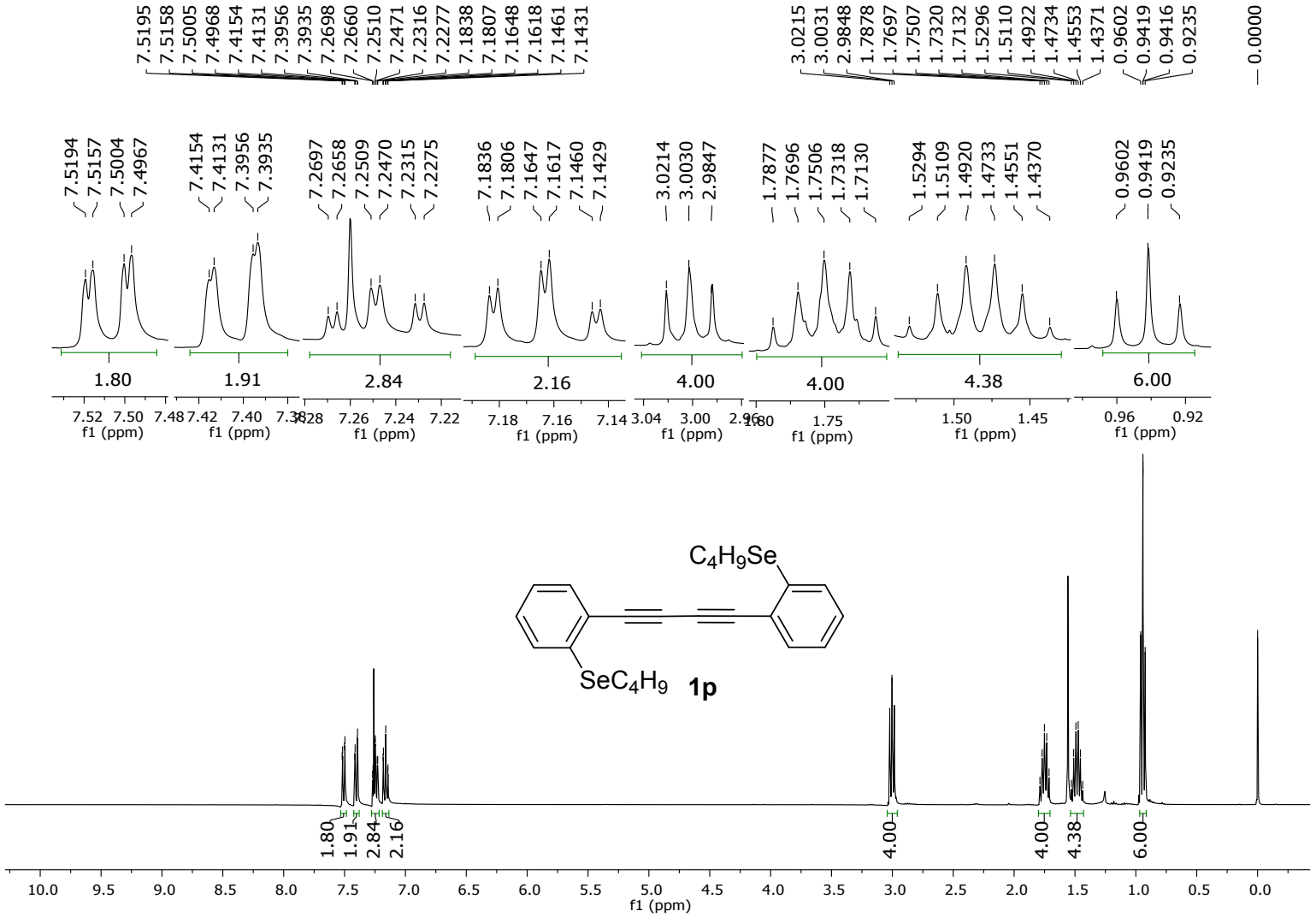



**Figure S31**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **1p**.

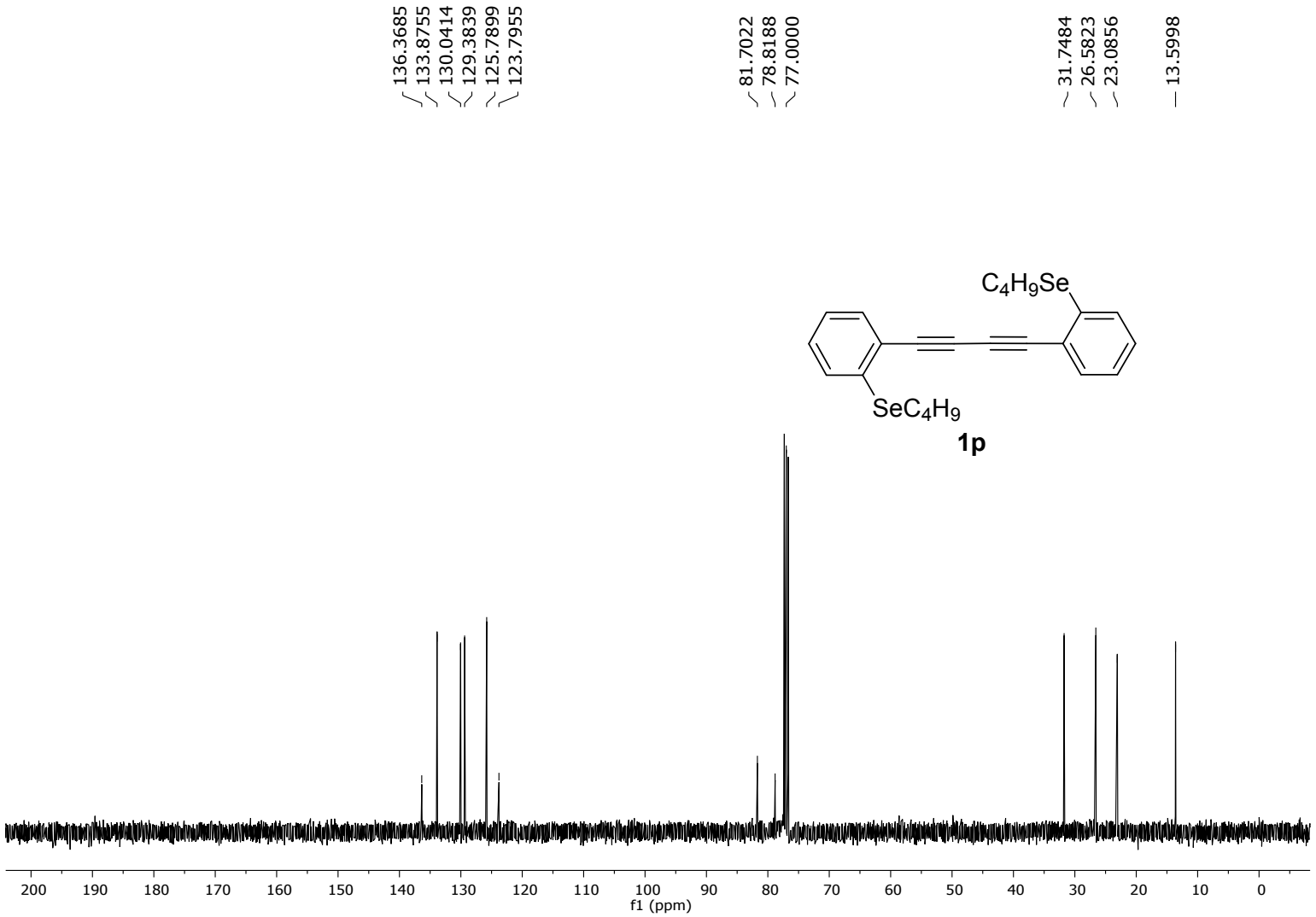



**Figure S32**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1p**.

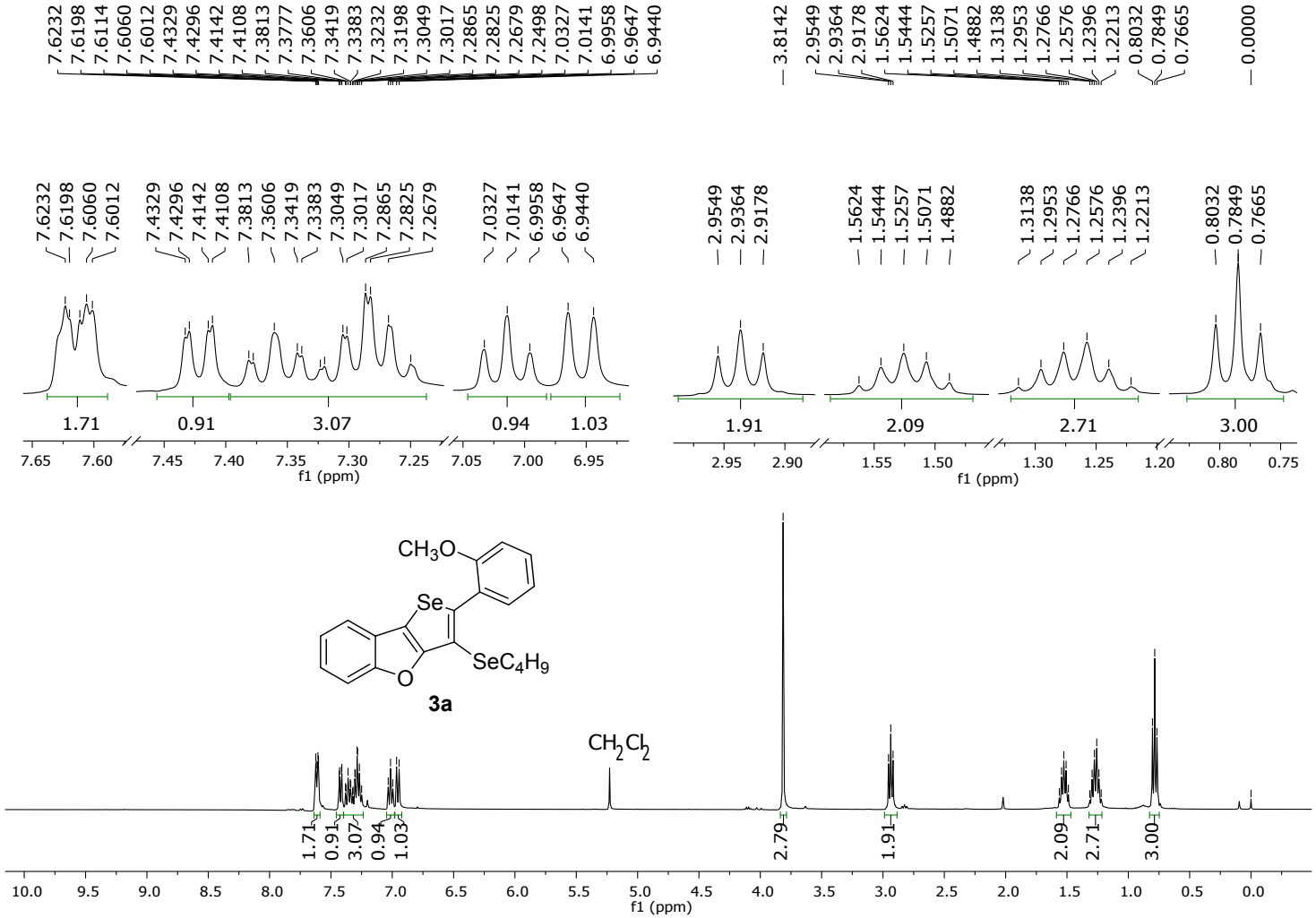



**Figure S33**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**.

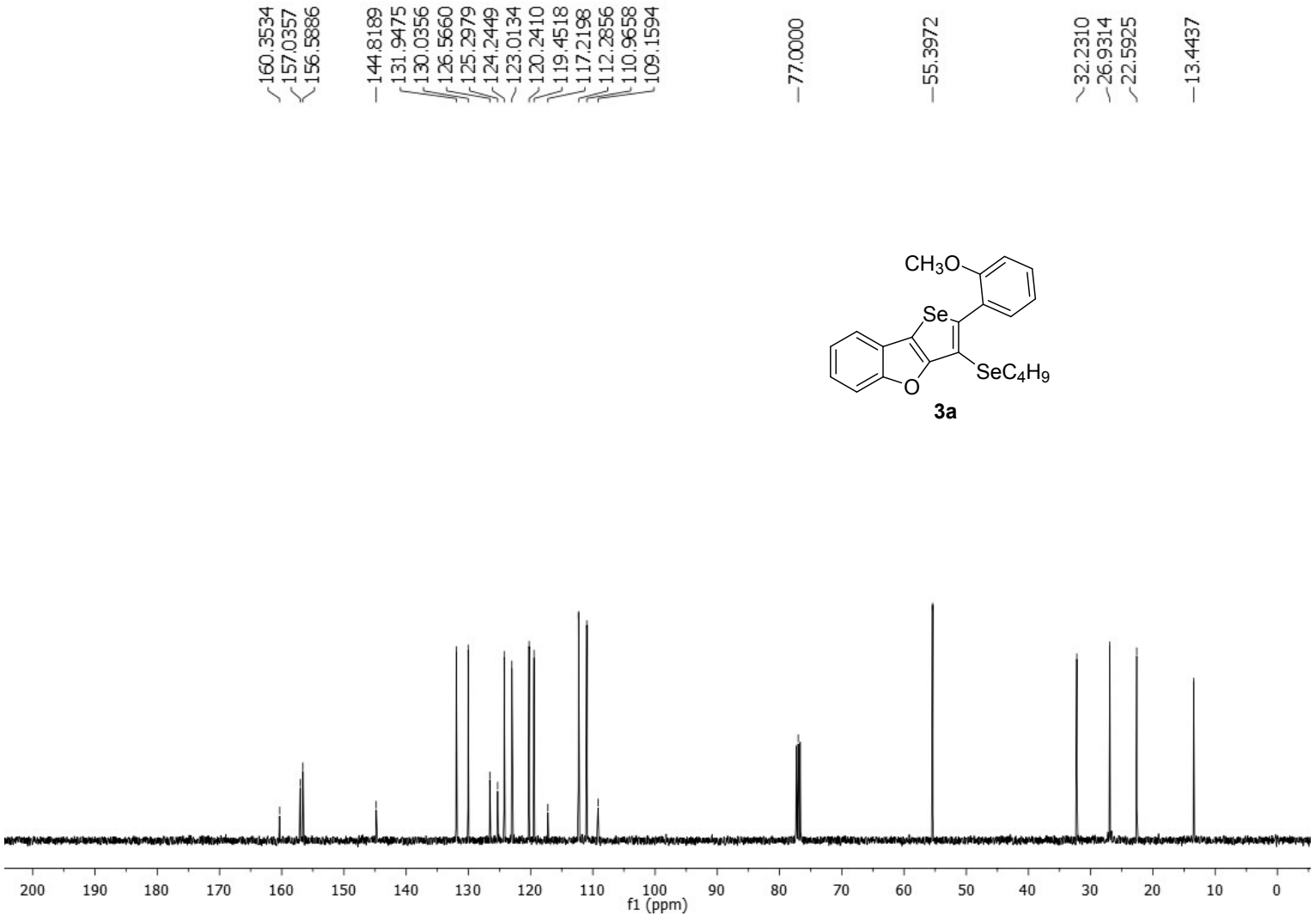



**Figure S34**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**.

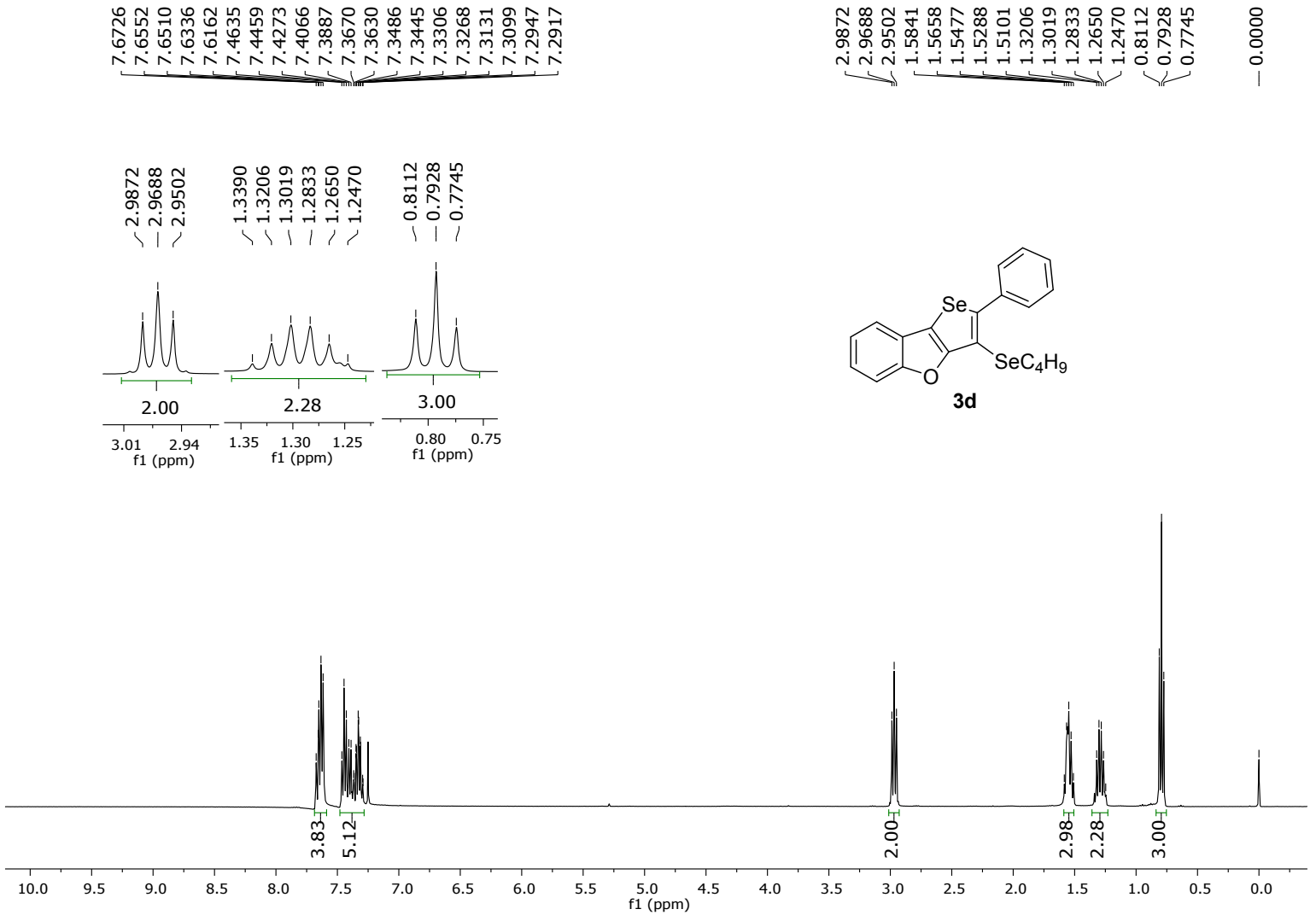



**Figure S35**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**.

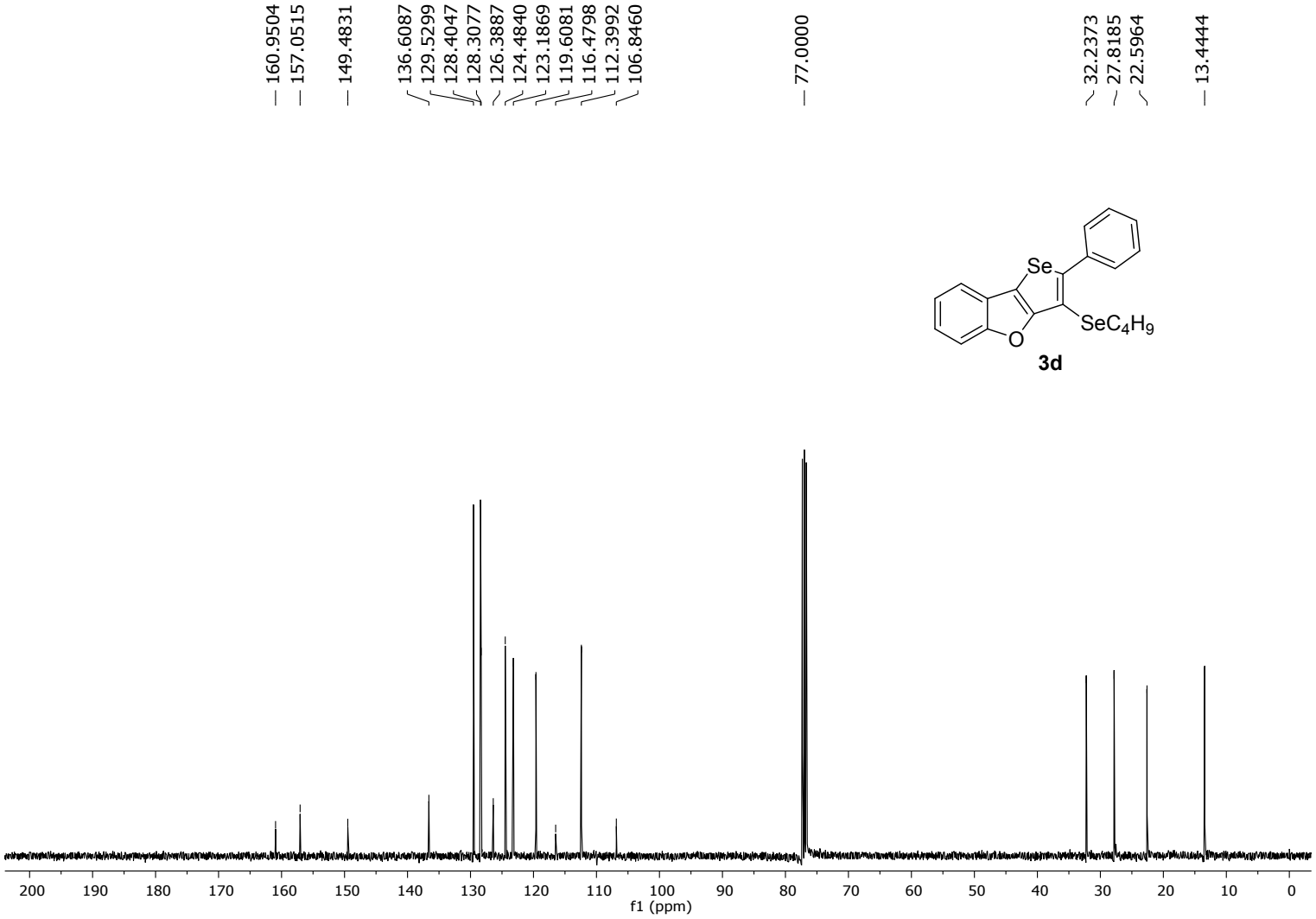



**Figure S36**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**.

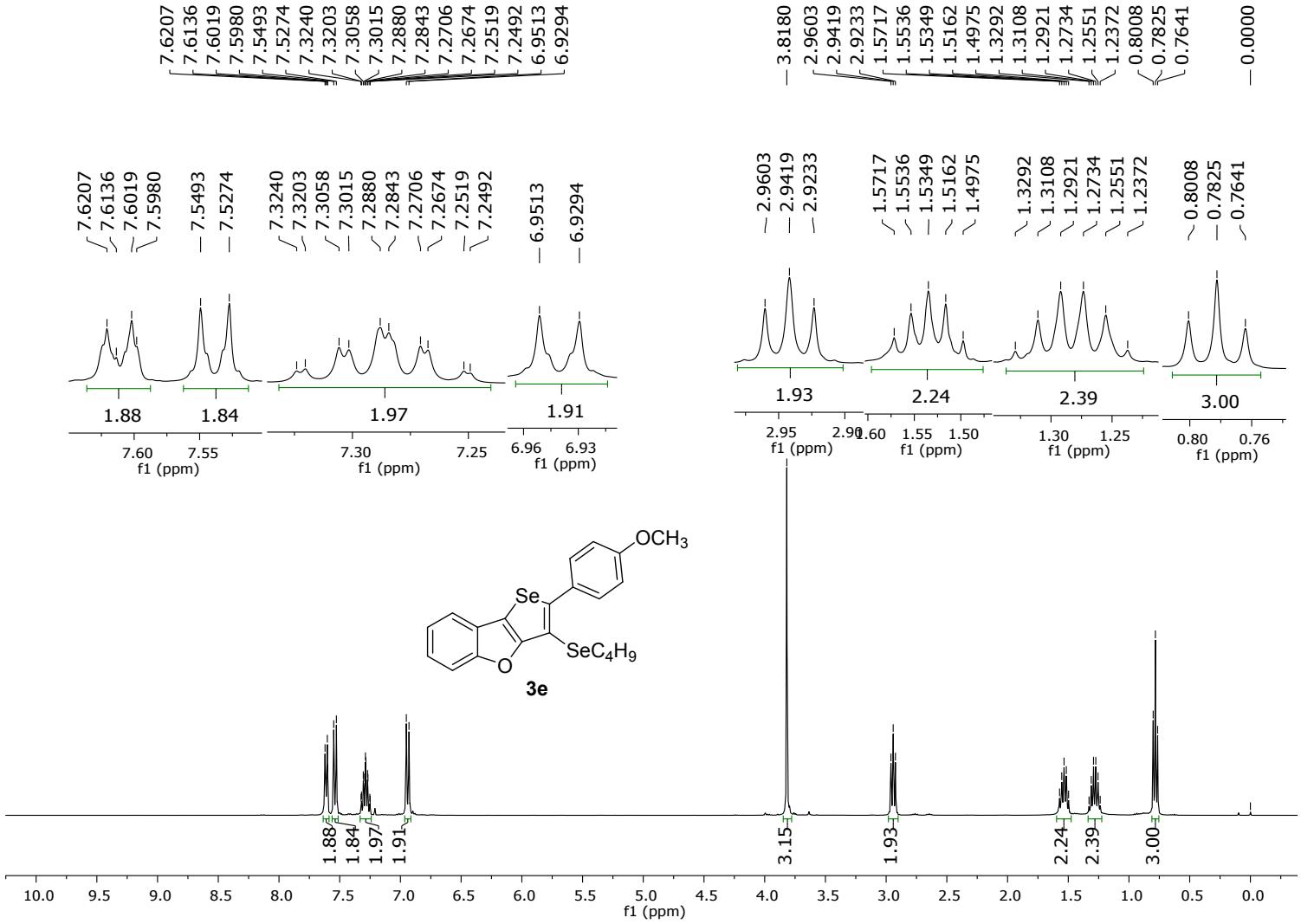



**Figure S37**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**.

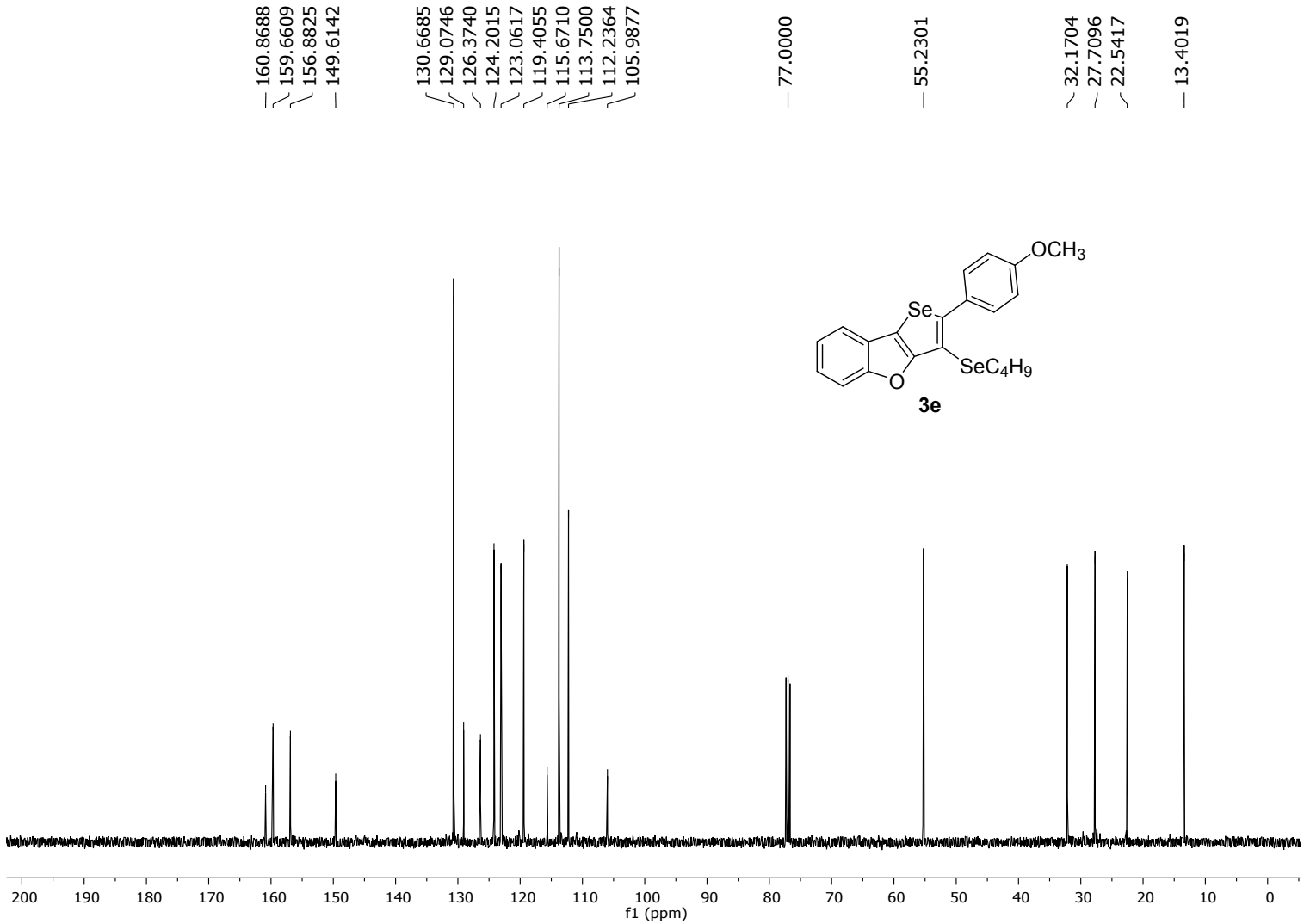



**Figure S38**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**.

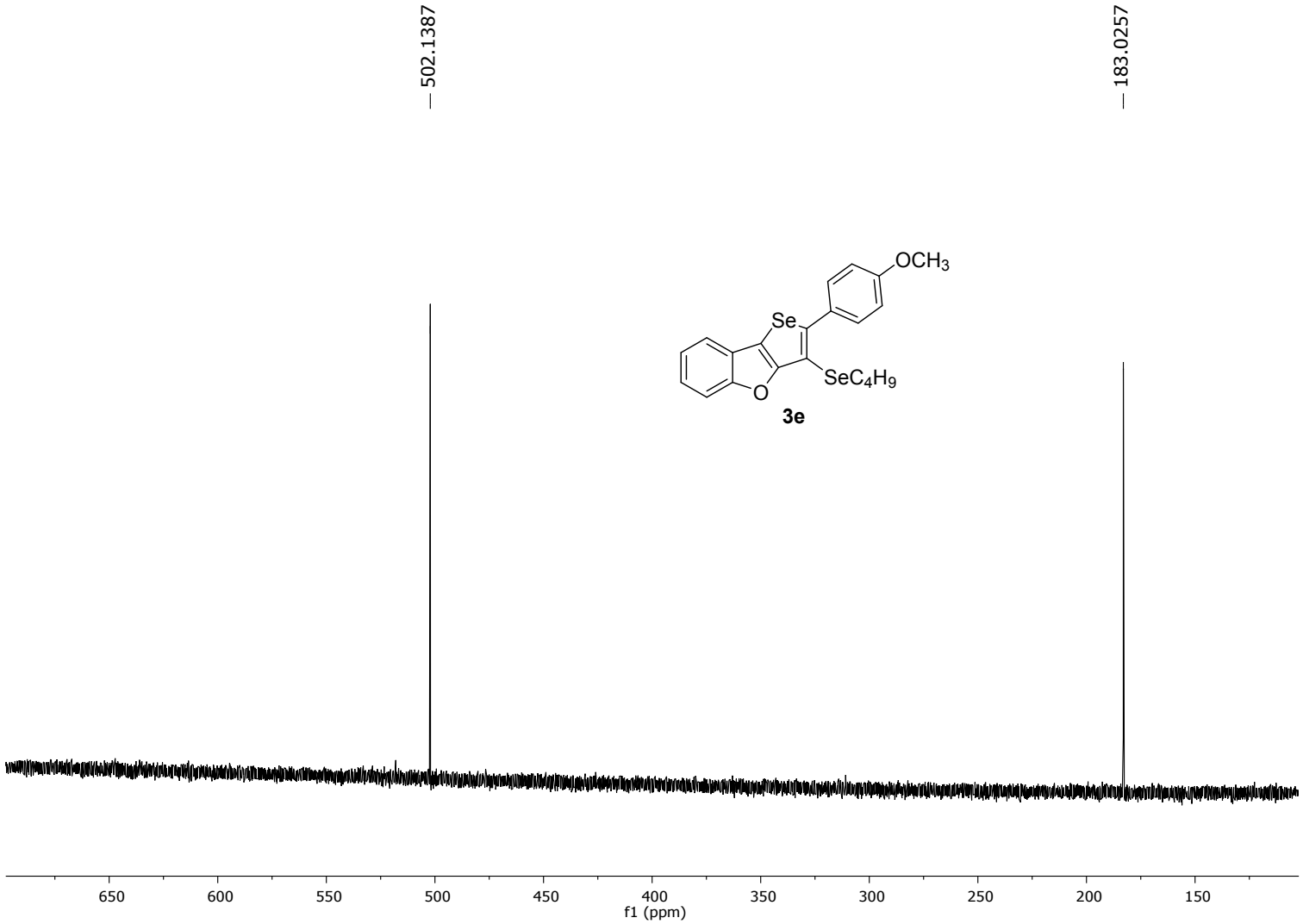



**Figure S39**: $^{77}Se$ NMR (76 MHz, $CDCl_3$) spectrum of compound **3e**.

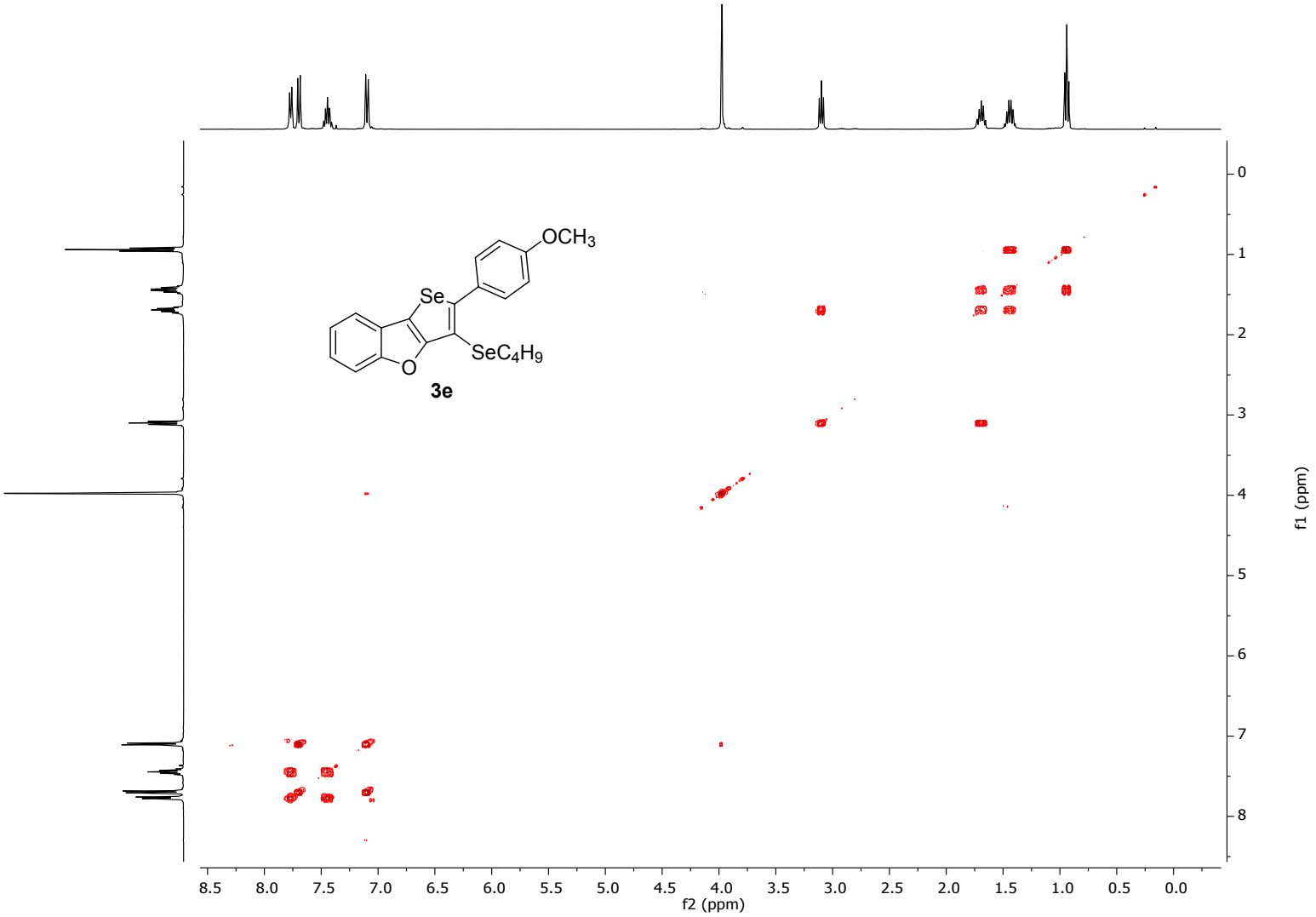



**Figure S40**: COSY NMR-2D (400 MHz, $CDCl_3$) spectrum of compound **3e**.

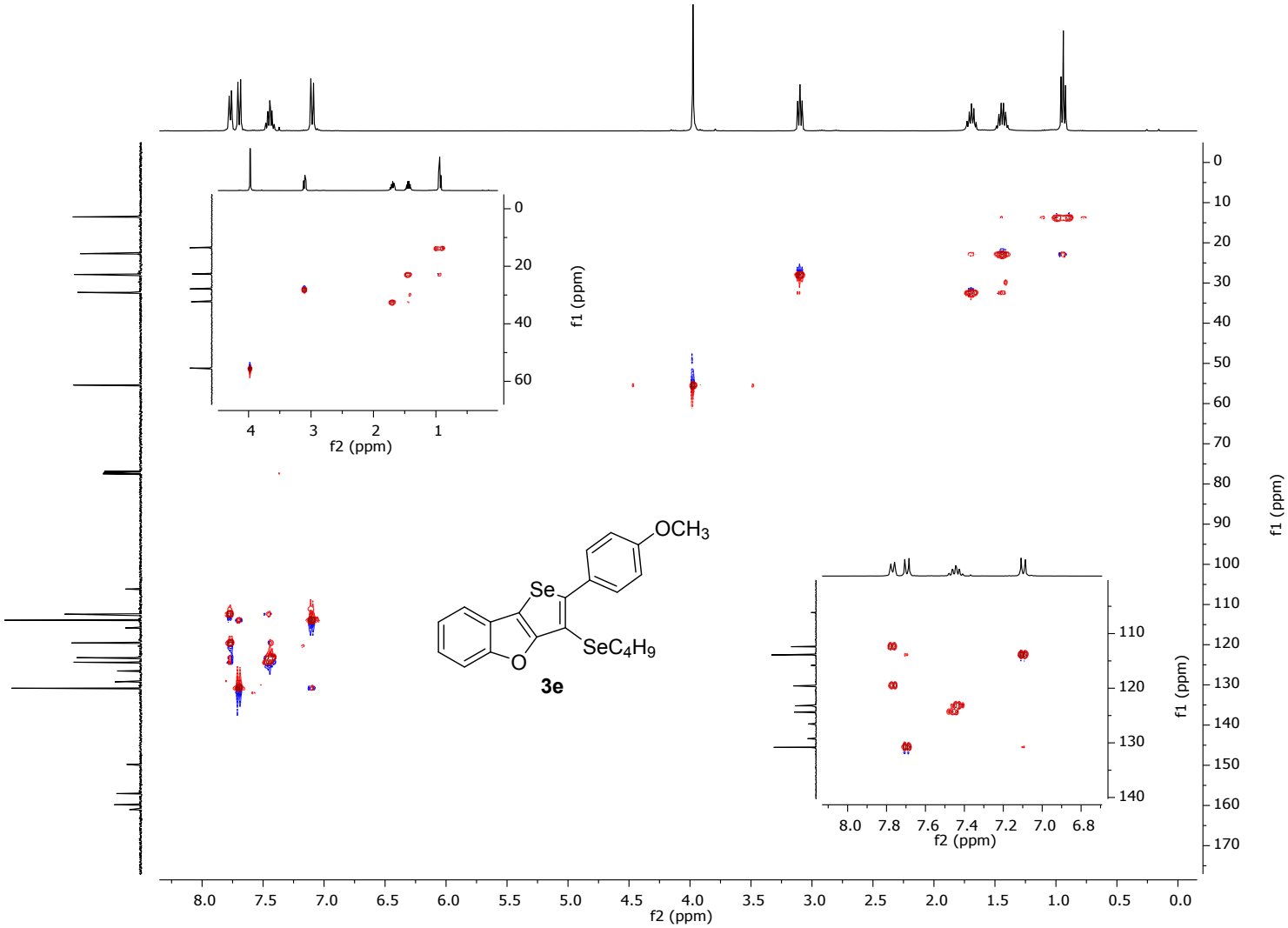



**Figure S41**: $^{1}H$-$^{13}C$ HSQC NMR-2D (400 MHz, $CDCl_3$) spectrum of compound **3e**.

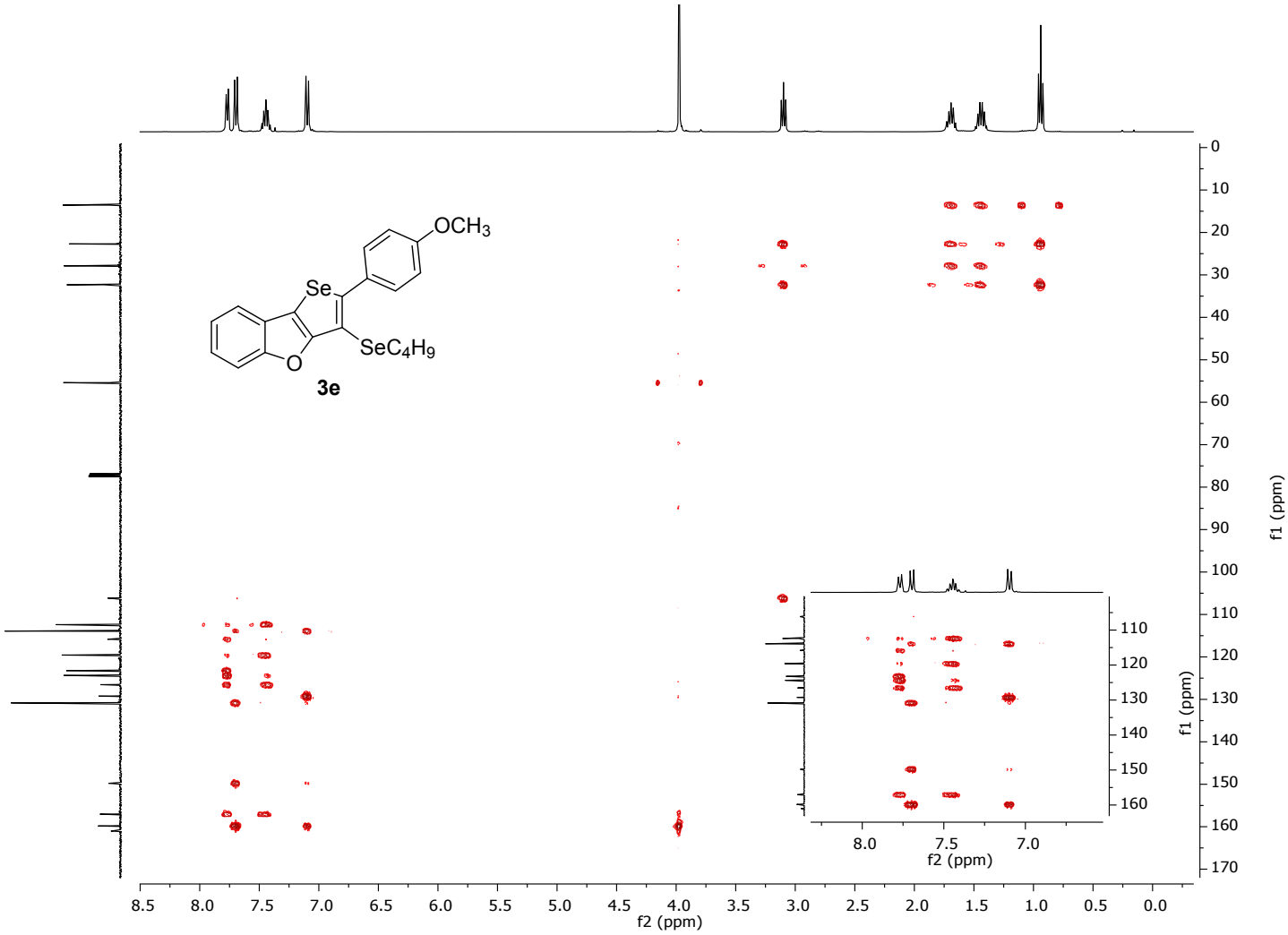



**Figure S42**: $^{1}H$-$^{13}C$ HMBC NMR-2D (400 MHz, $CDCl_3$) spectrum of compound **3e**.

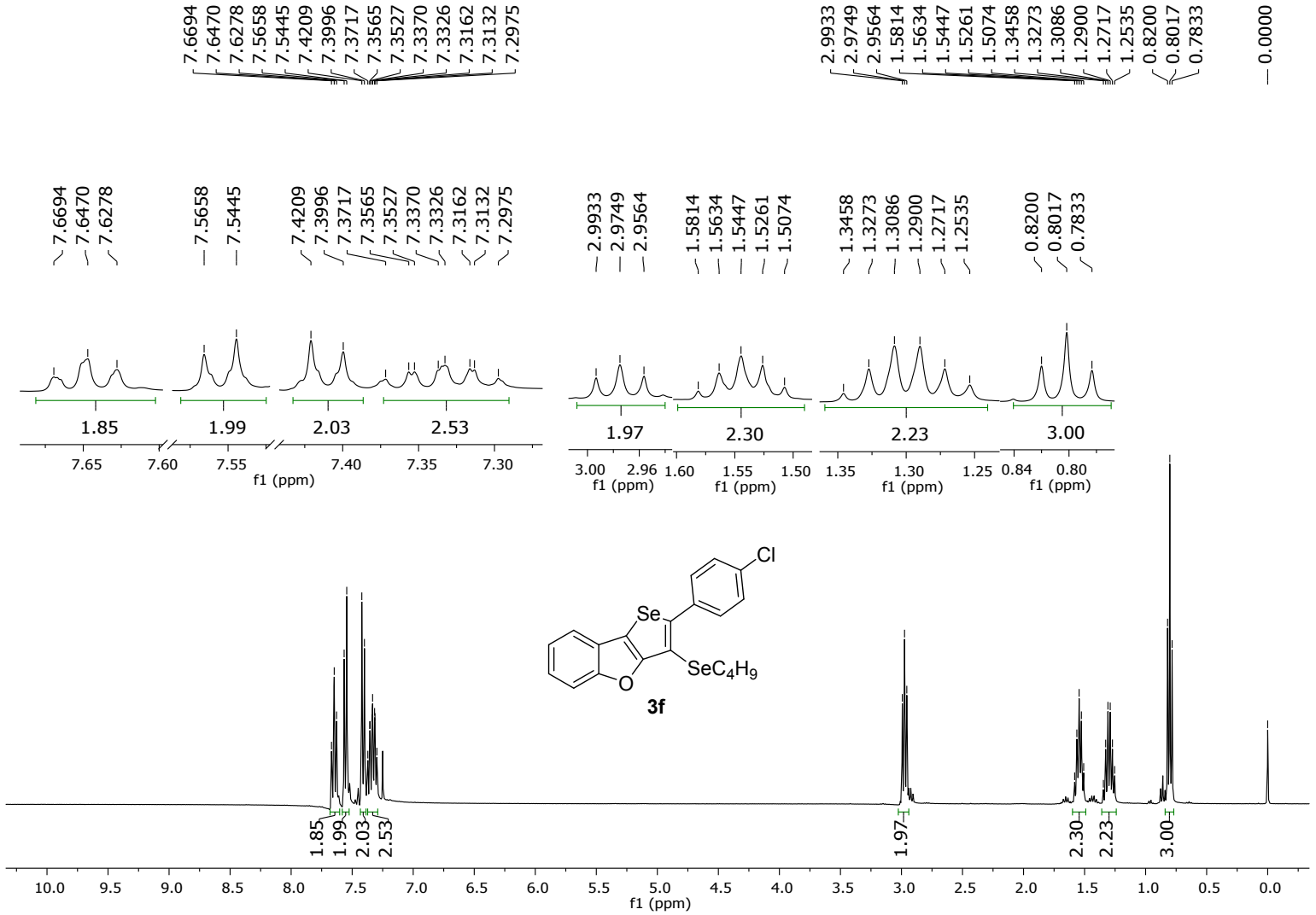



**Figure S43**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**.

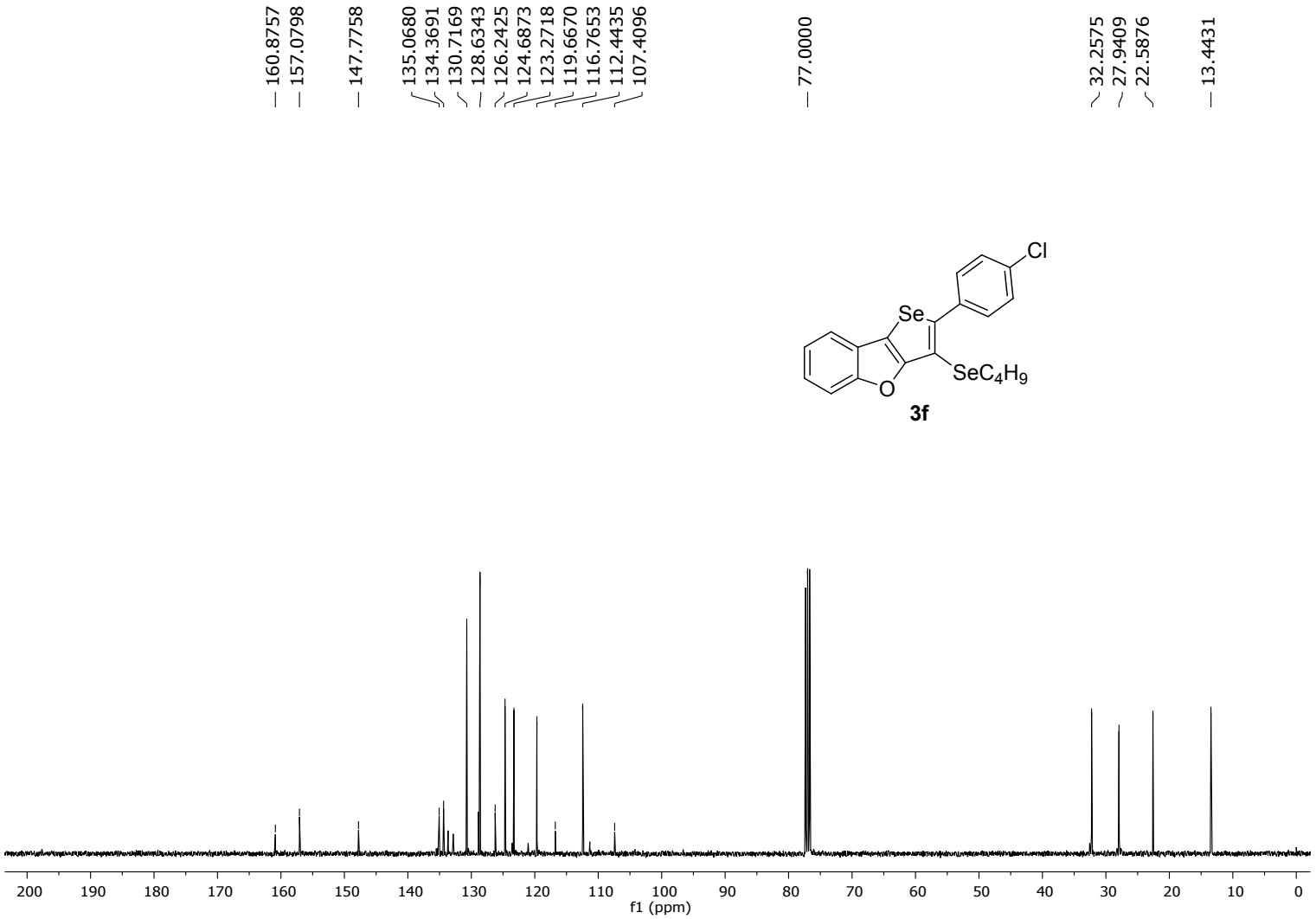



**Figure S44**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3f**.

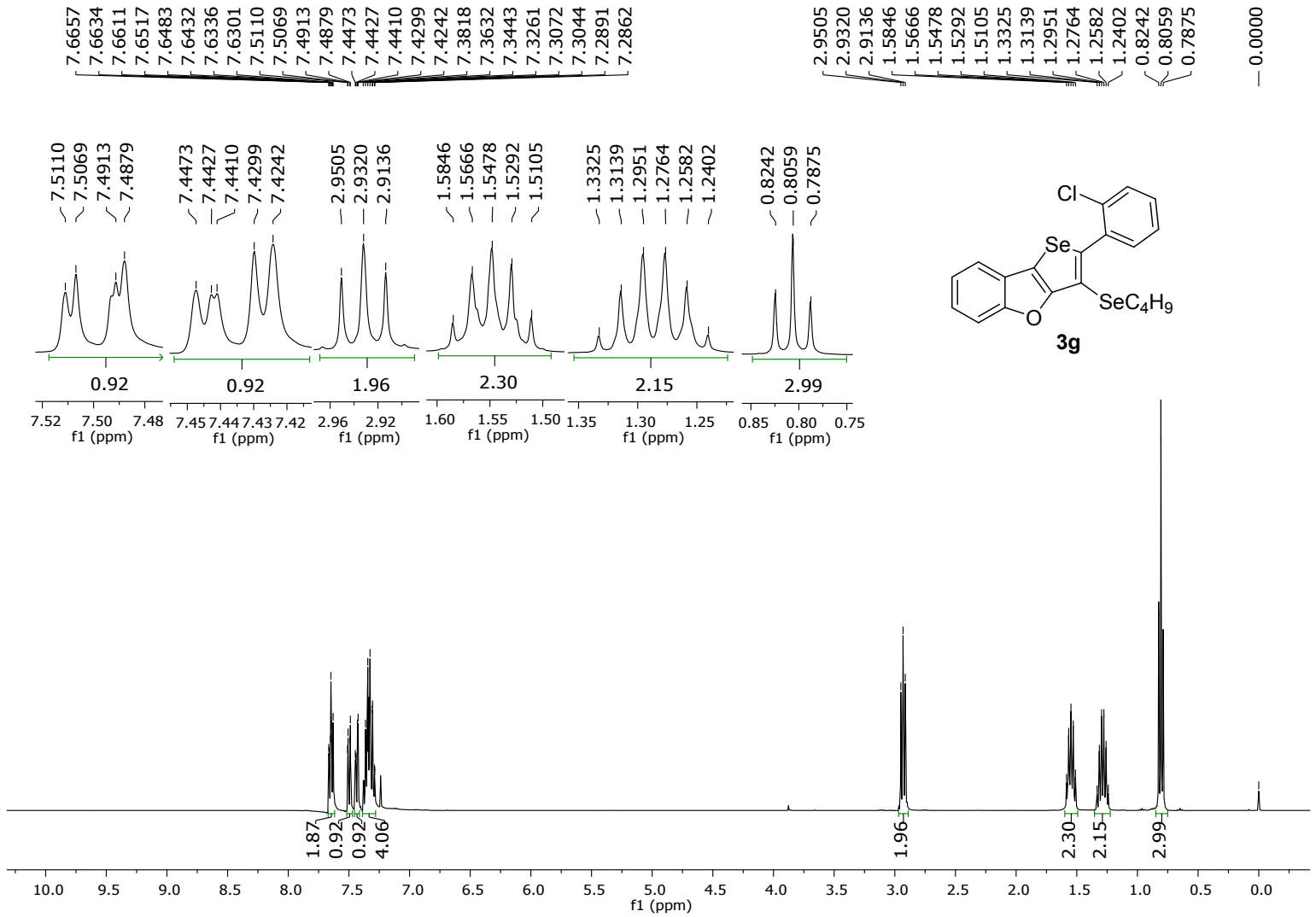



**Figure S45**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**.

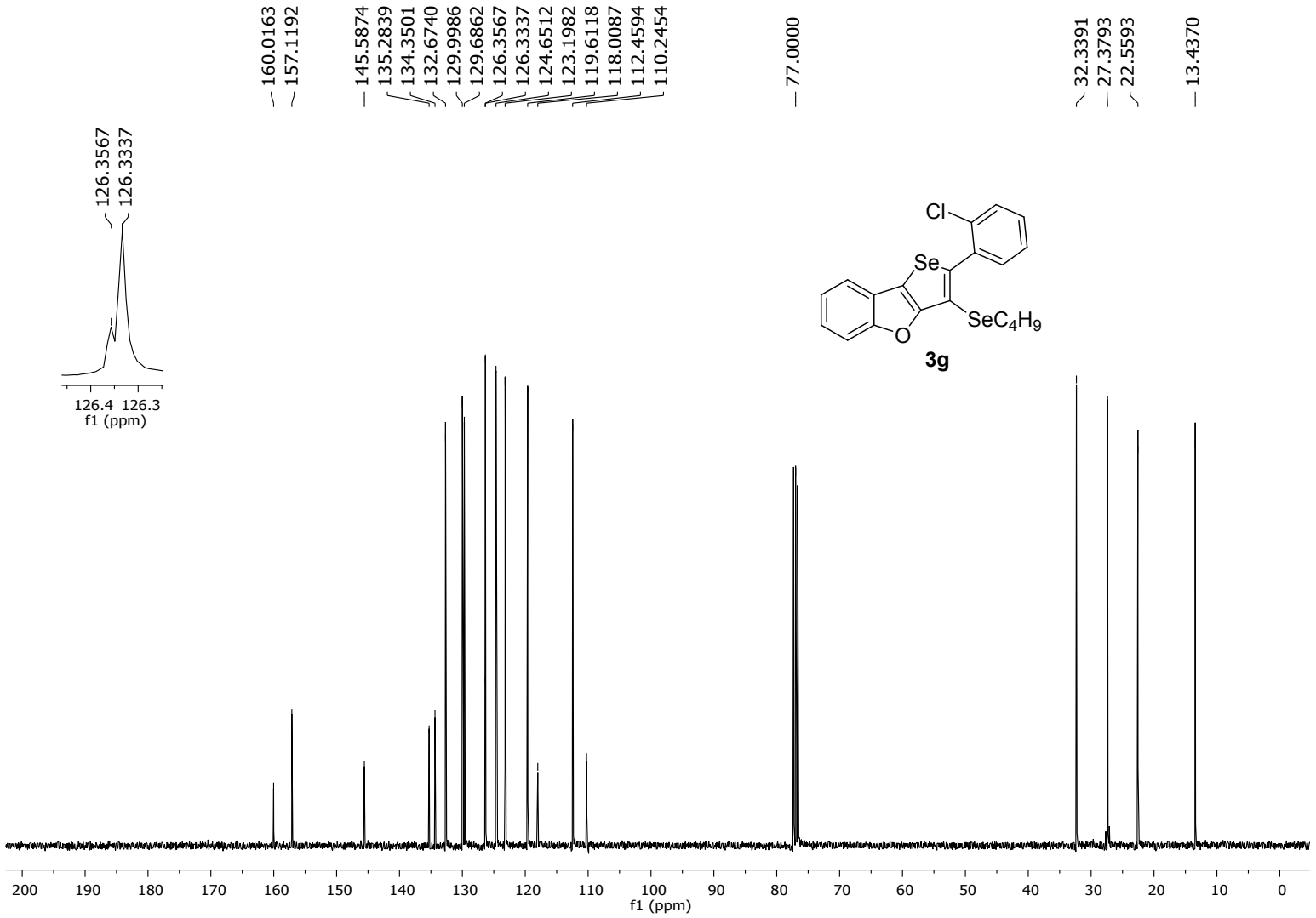



**Figure S46**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3g**.

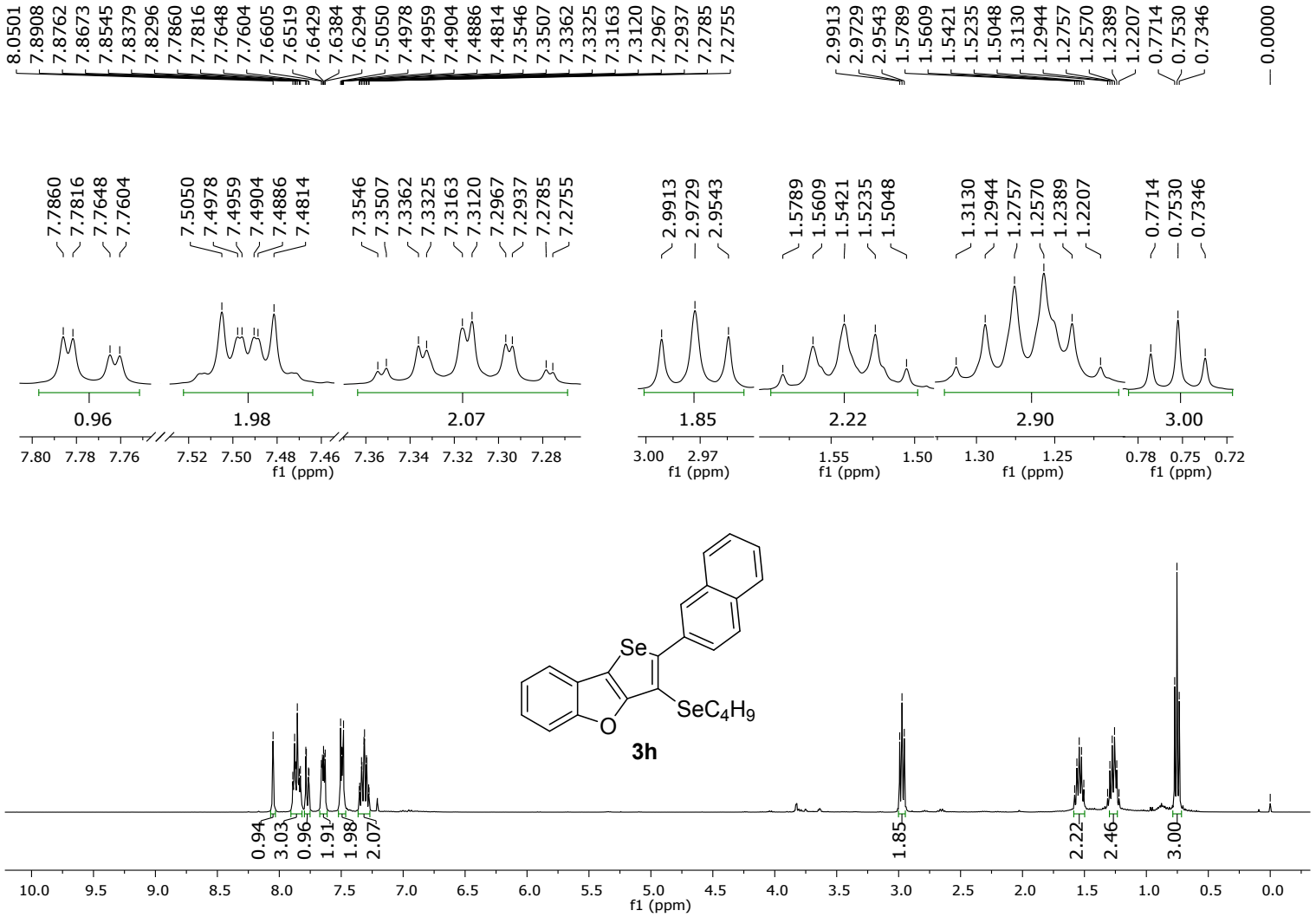



**Figure S47**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**.

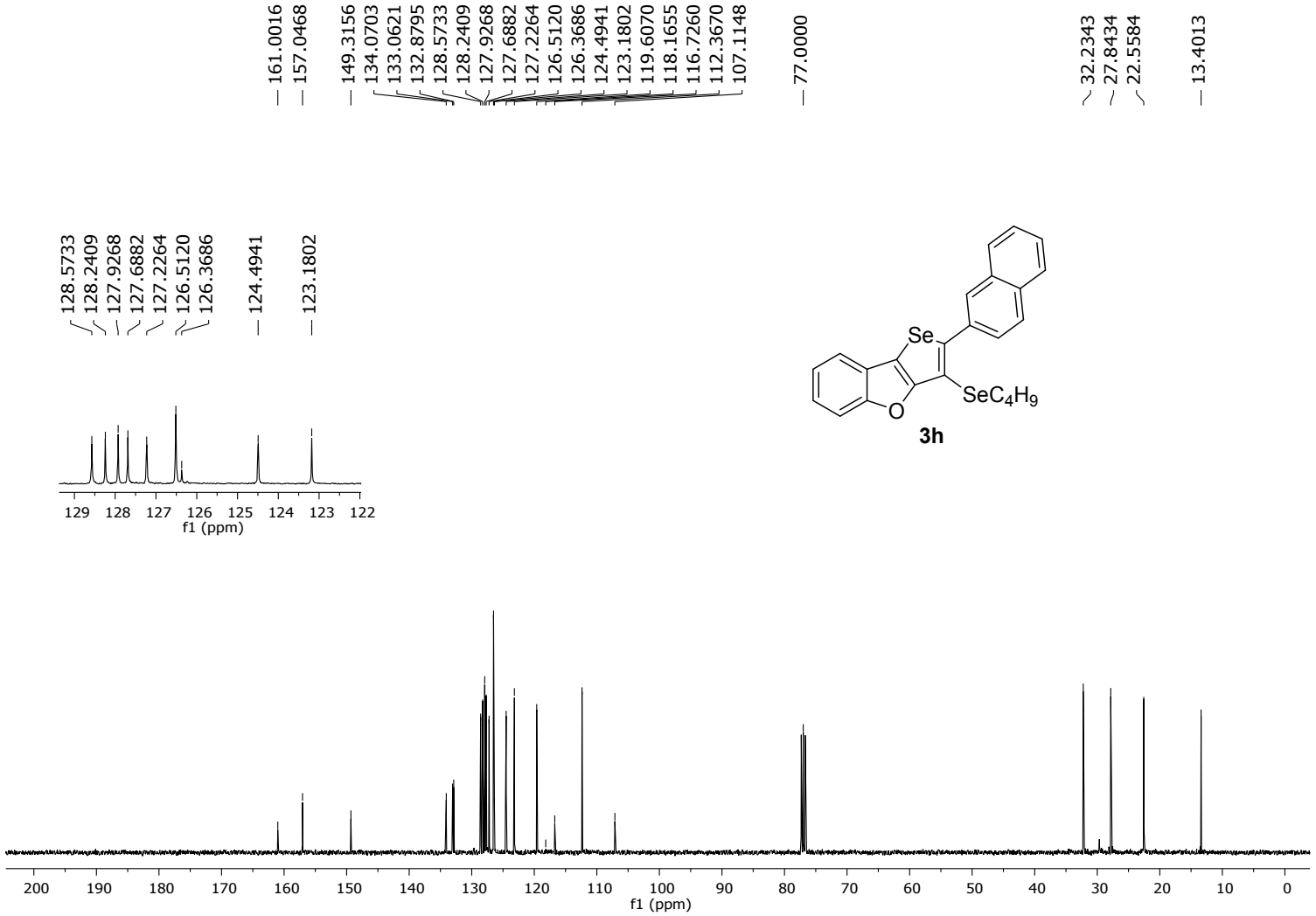



**Figure S48**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3h**.

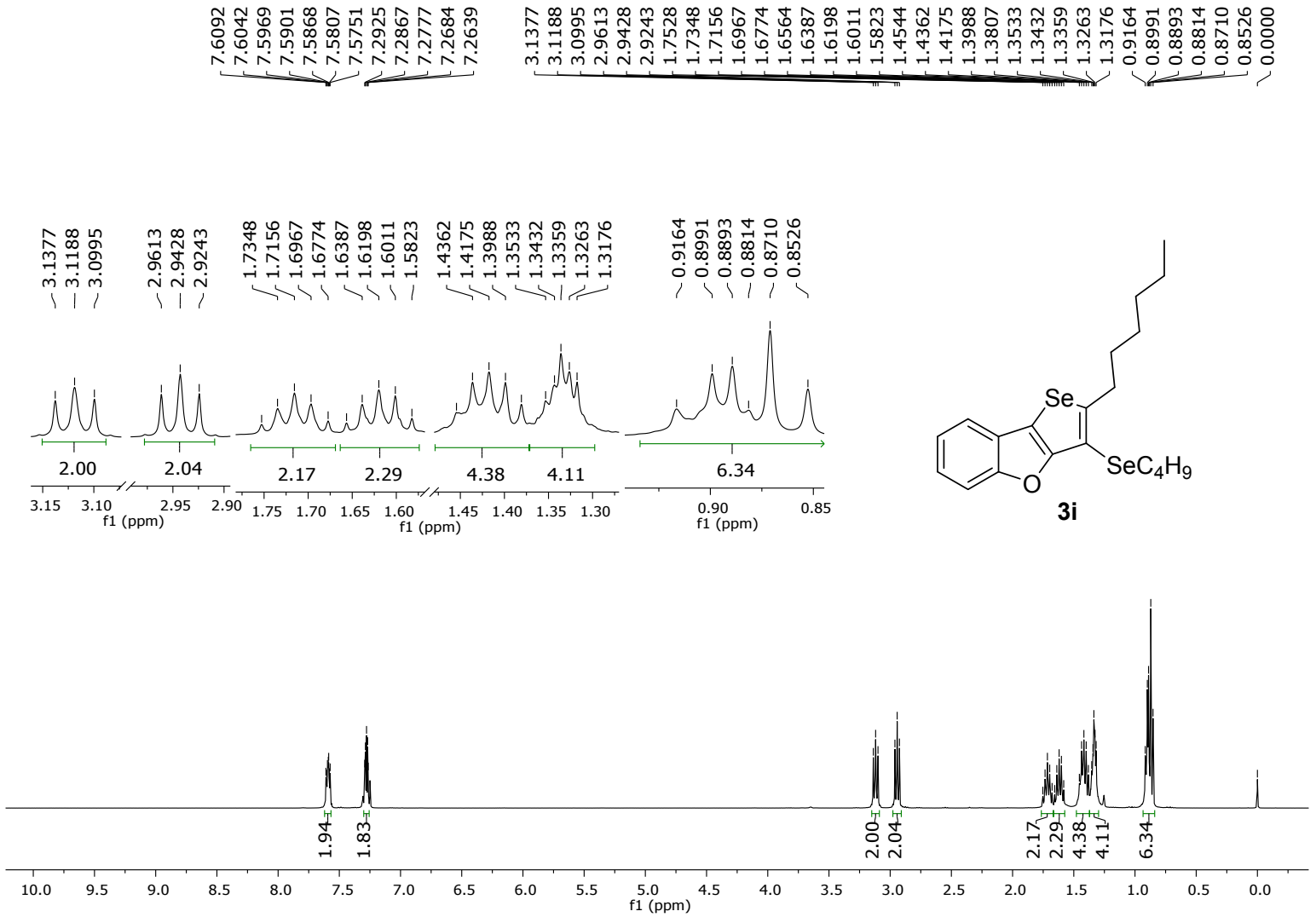



**Figure S49**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**.

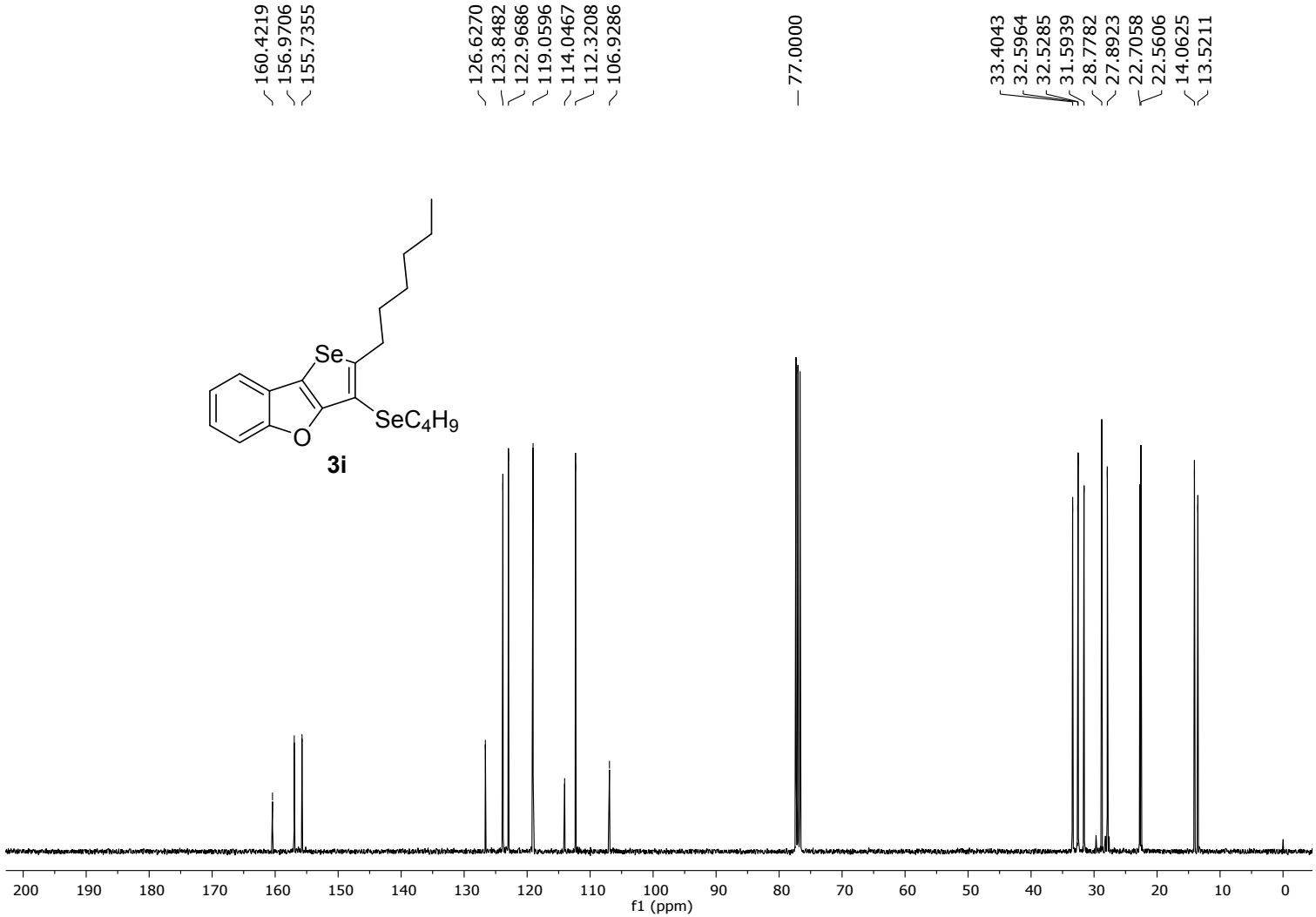



**Figure S50**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**.

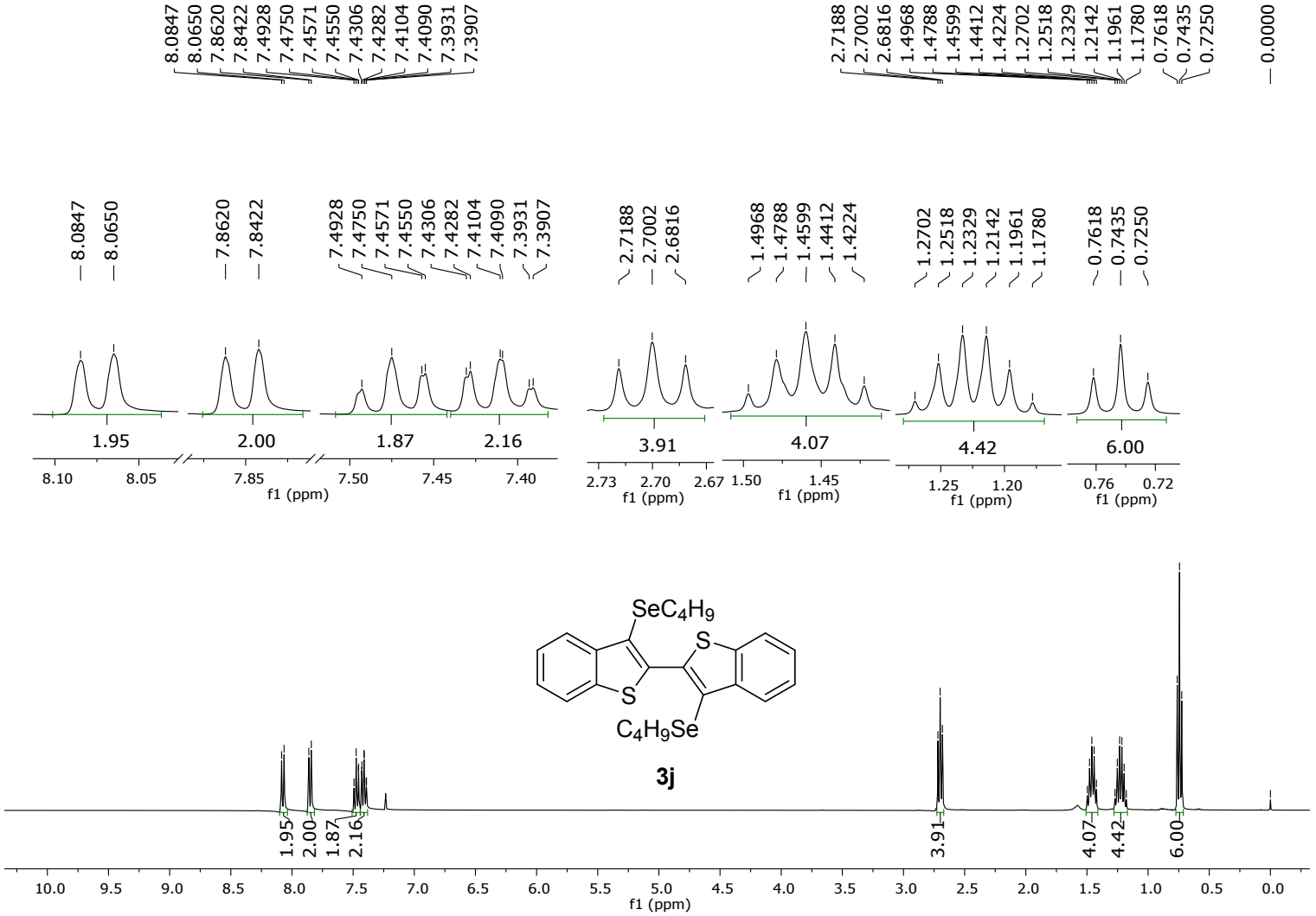



**Figure S51**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**.

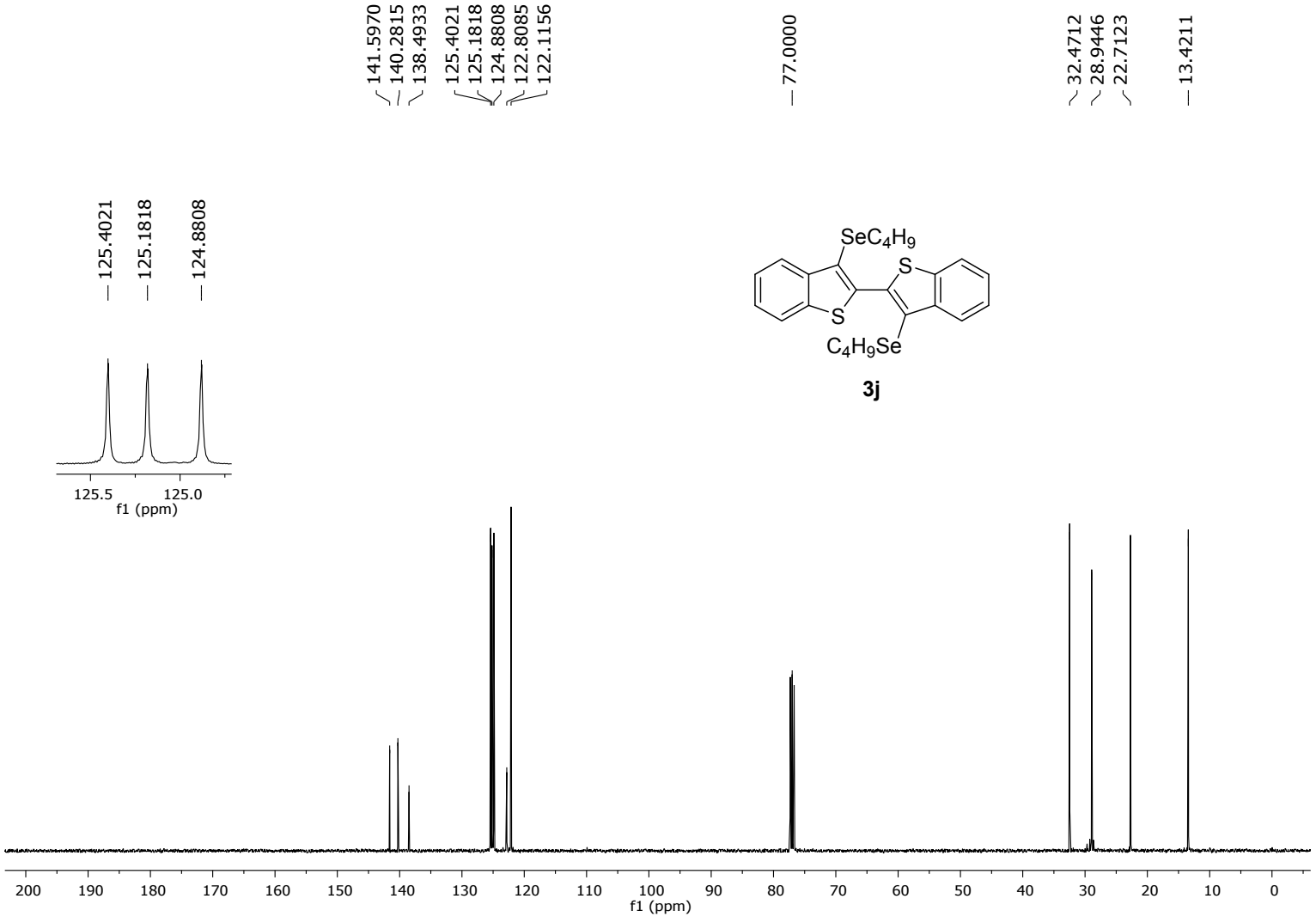



**Figure S52**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**.

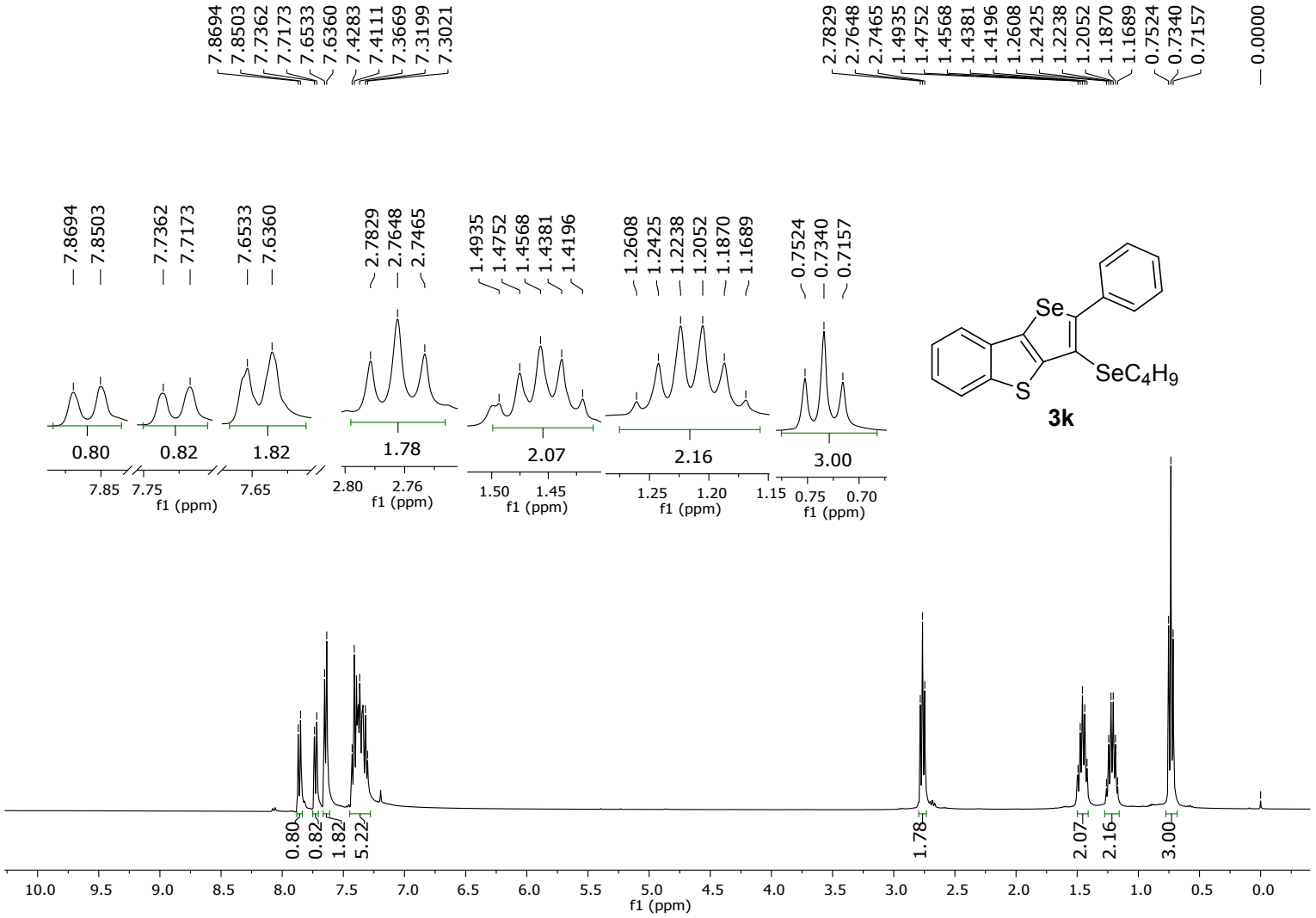



**Figure S53**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**.

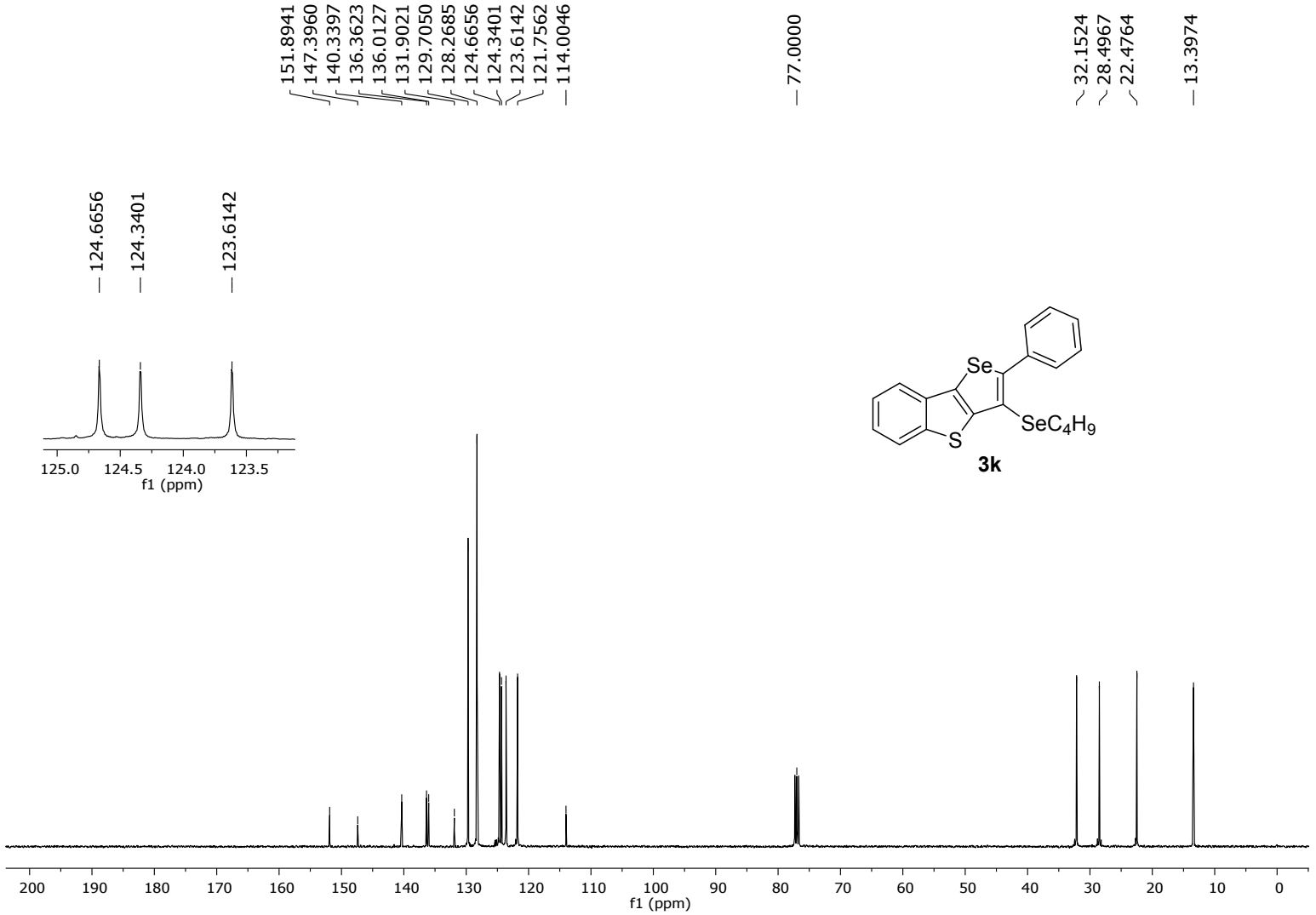



**Figure S54**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3k**.

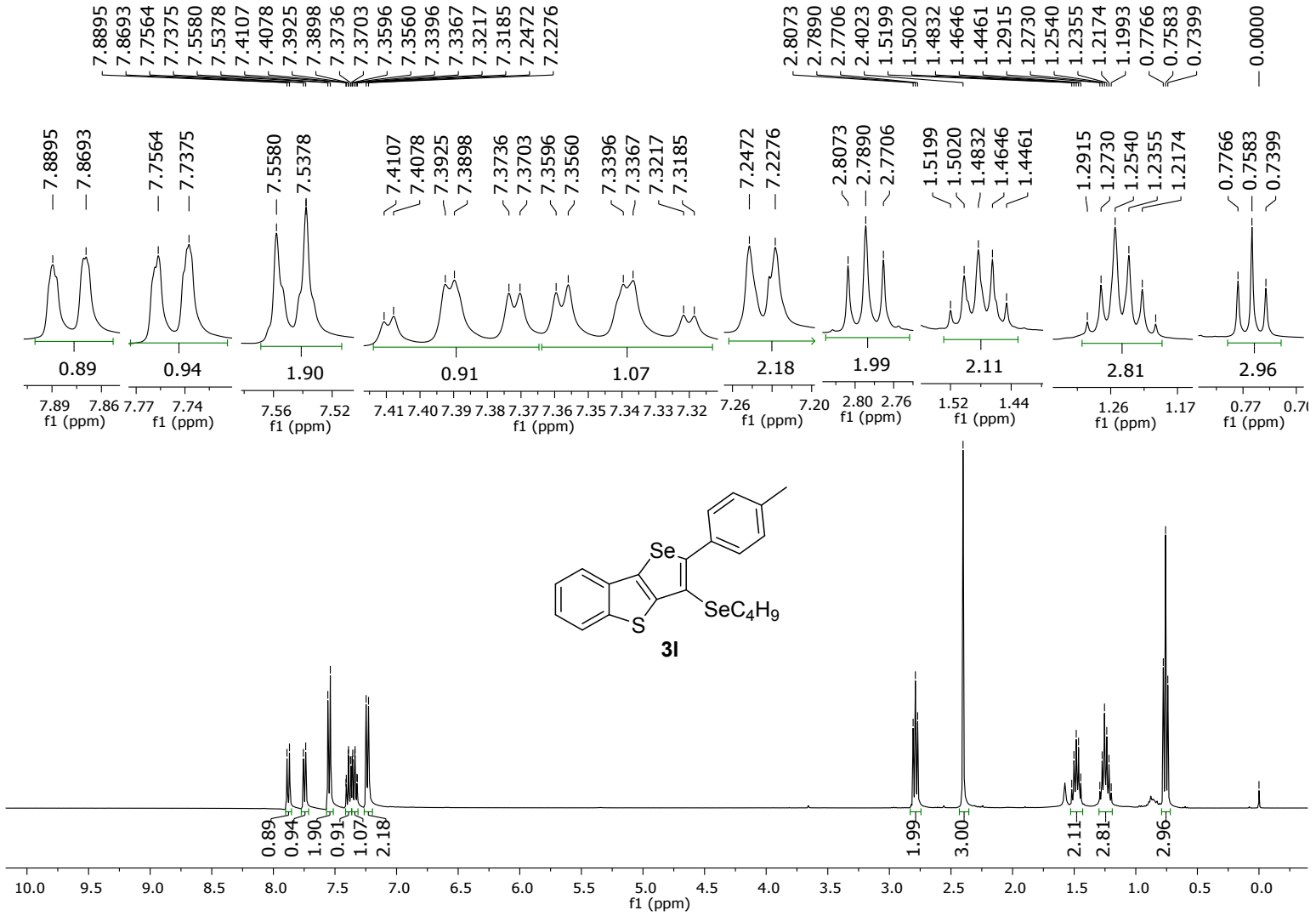



**Figure S55**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**.

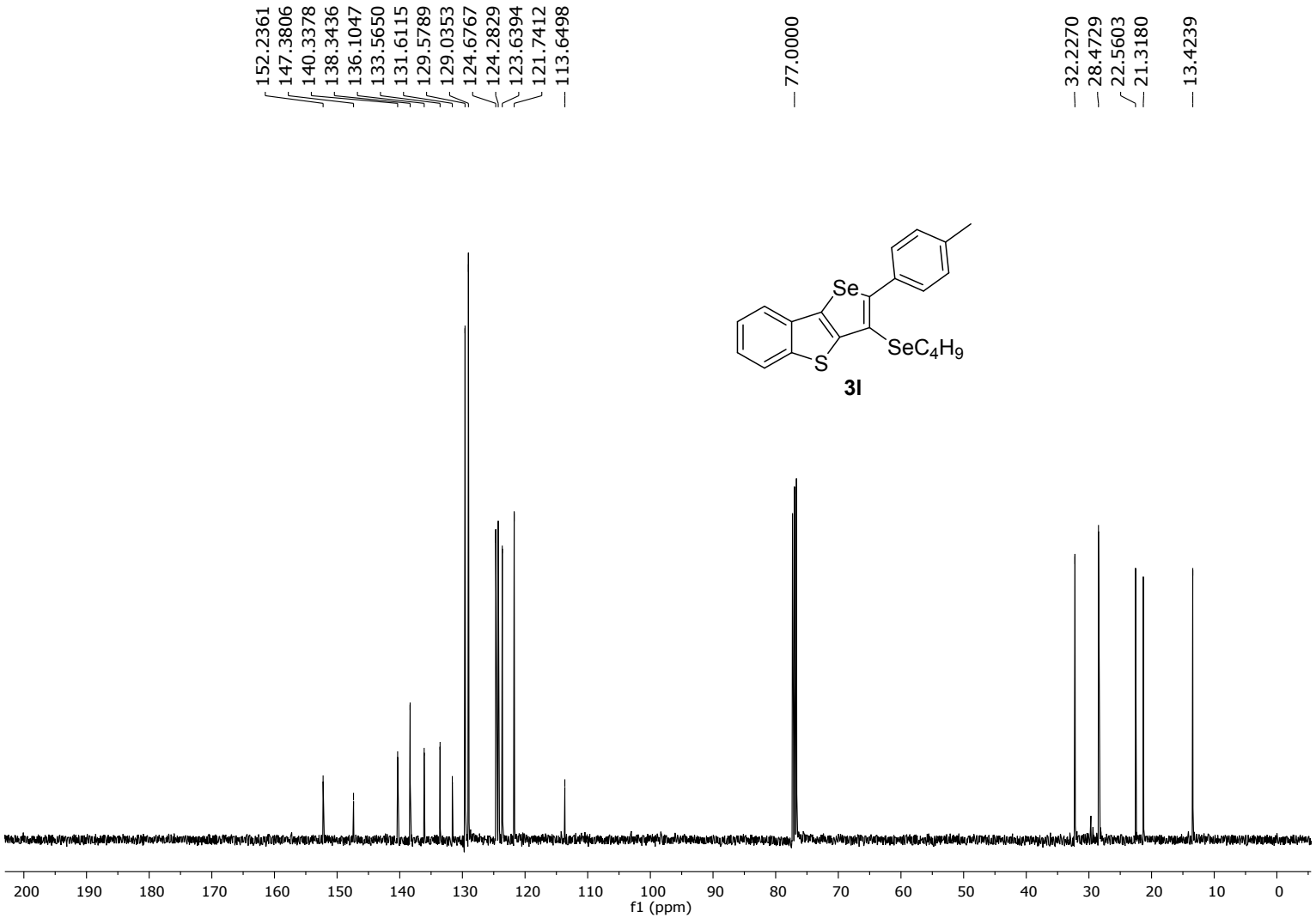



**Figure S56**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3l**.

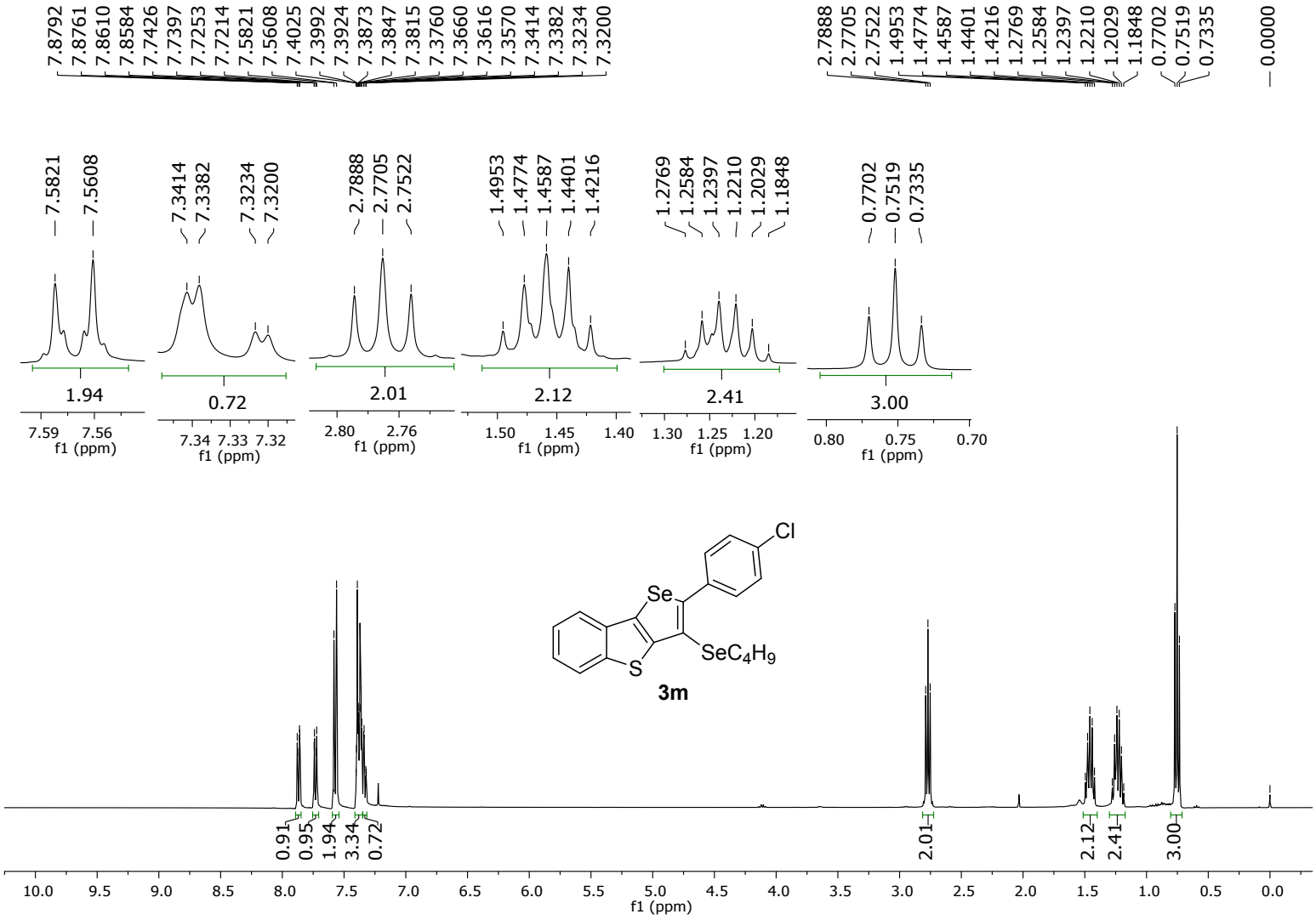



**Figure S57**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**.

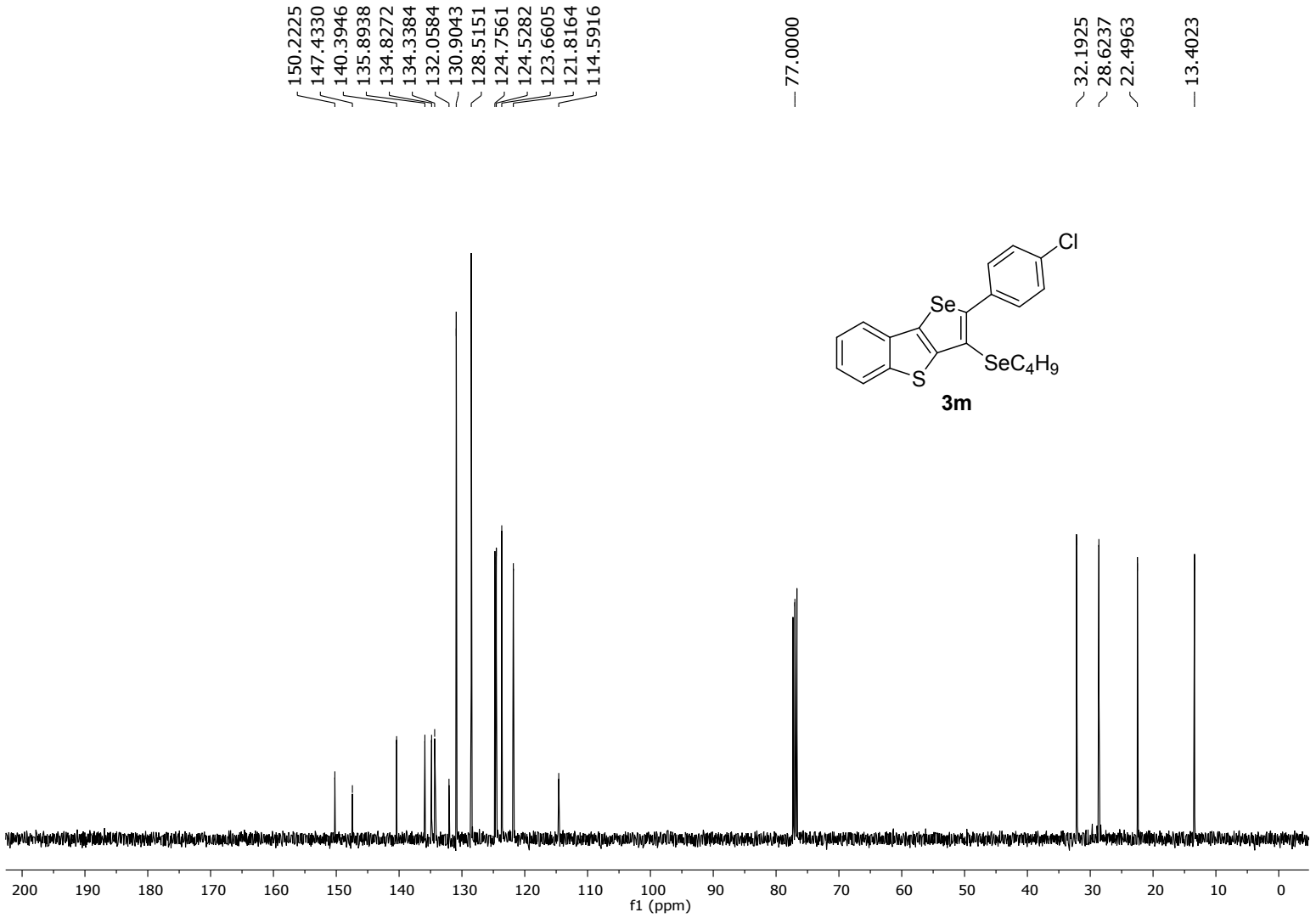



**Figure S58**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3m**.

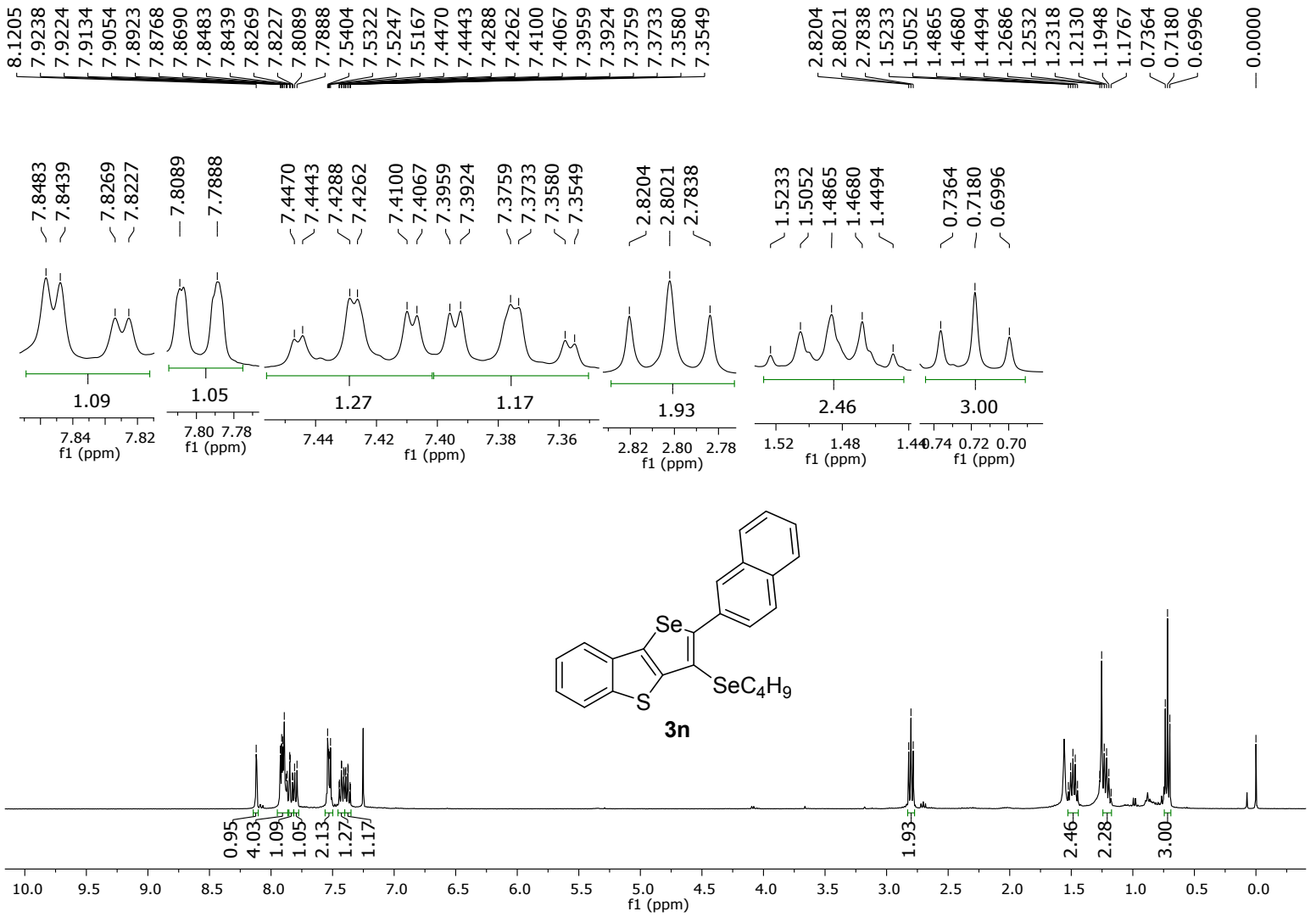



**Figure S59**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**.

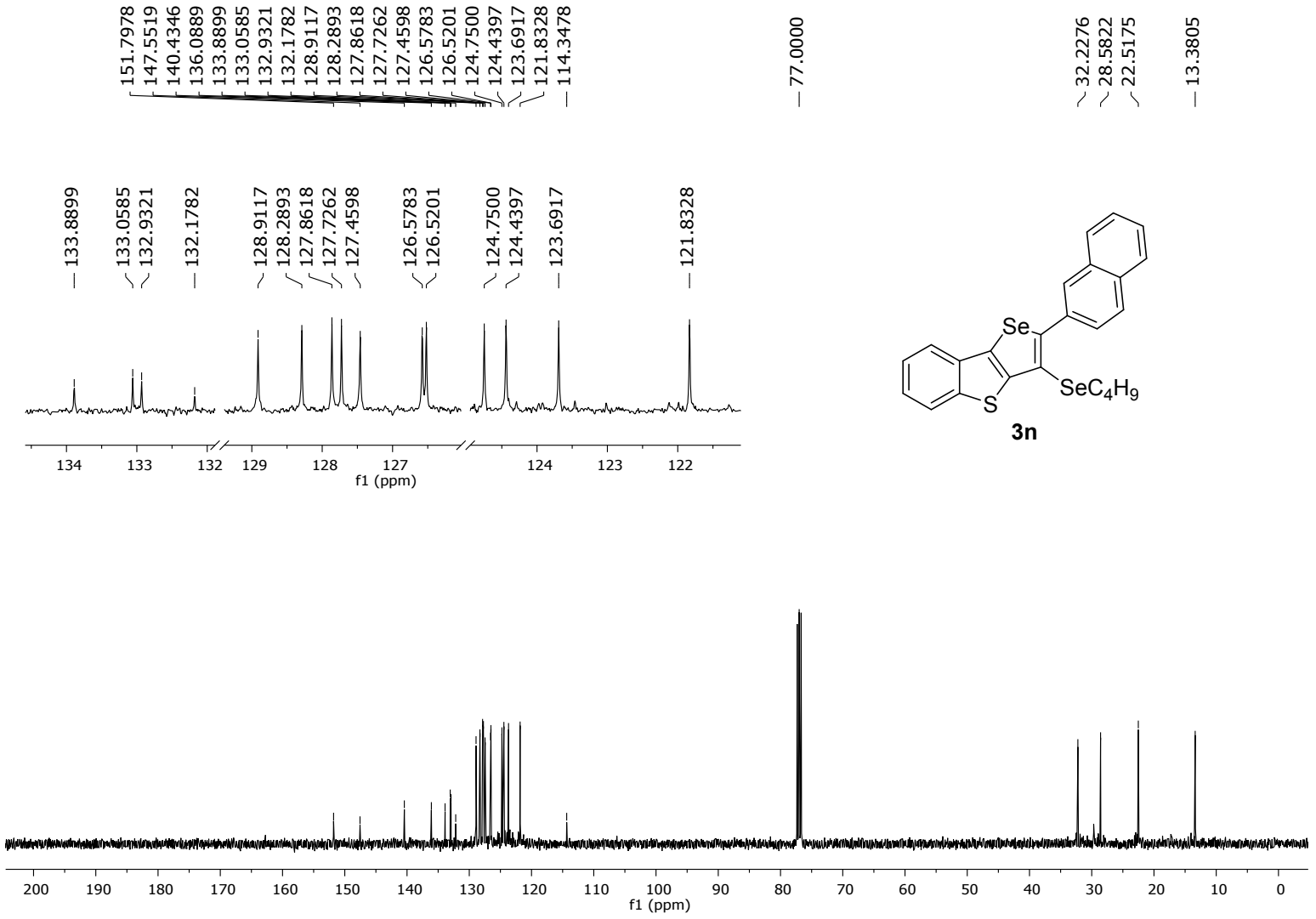



**Figure S60**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3n**.

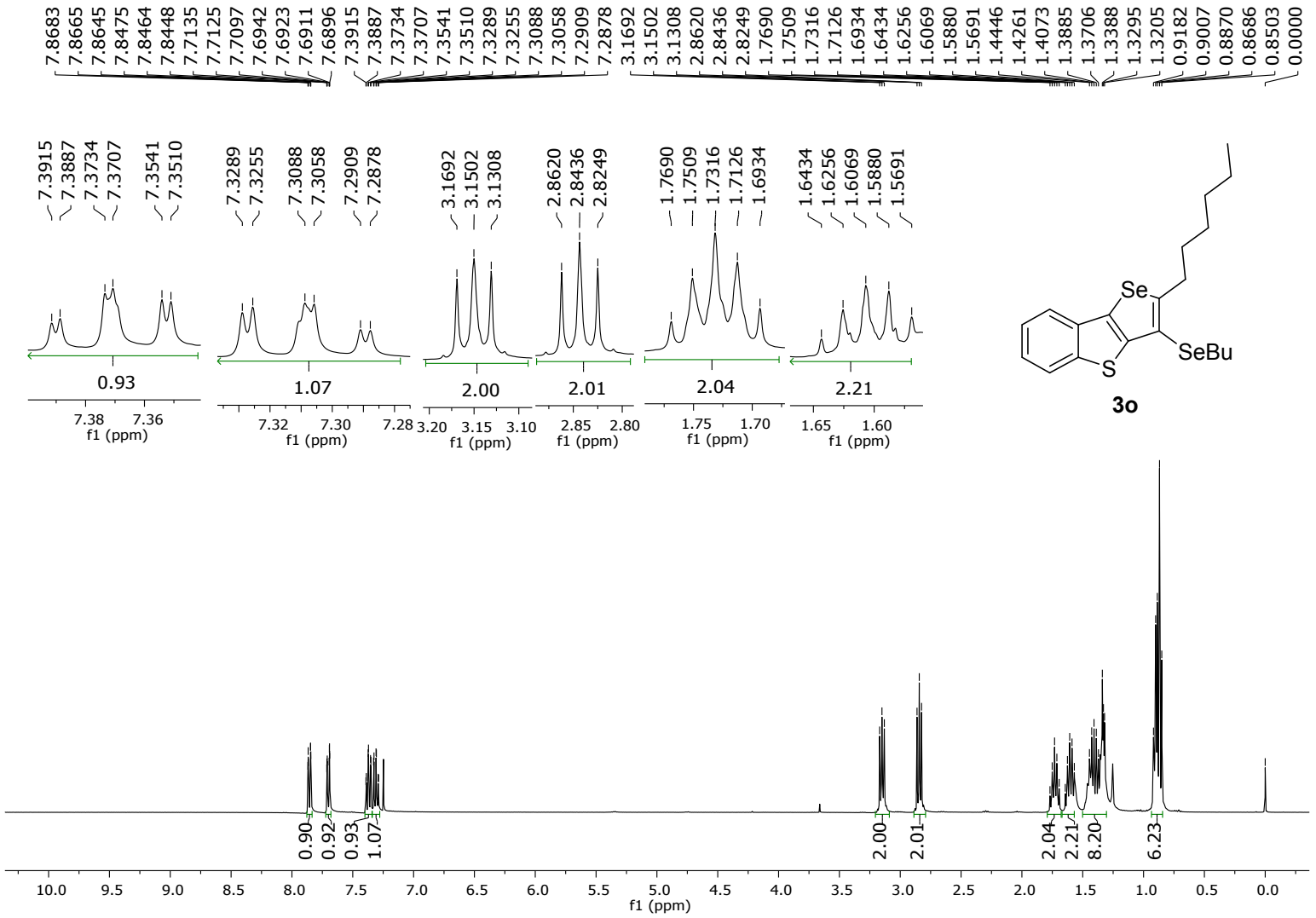



**Figure S61**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**.

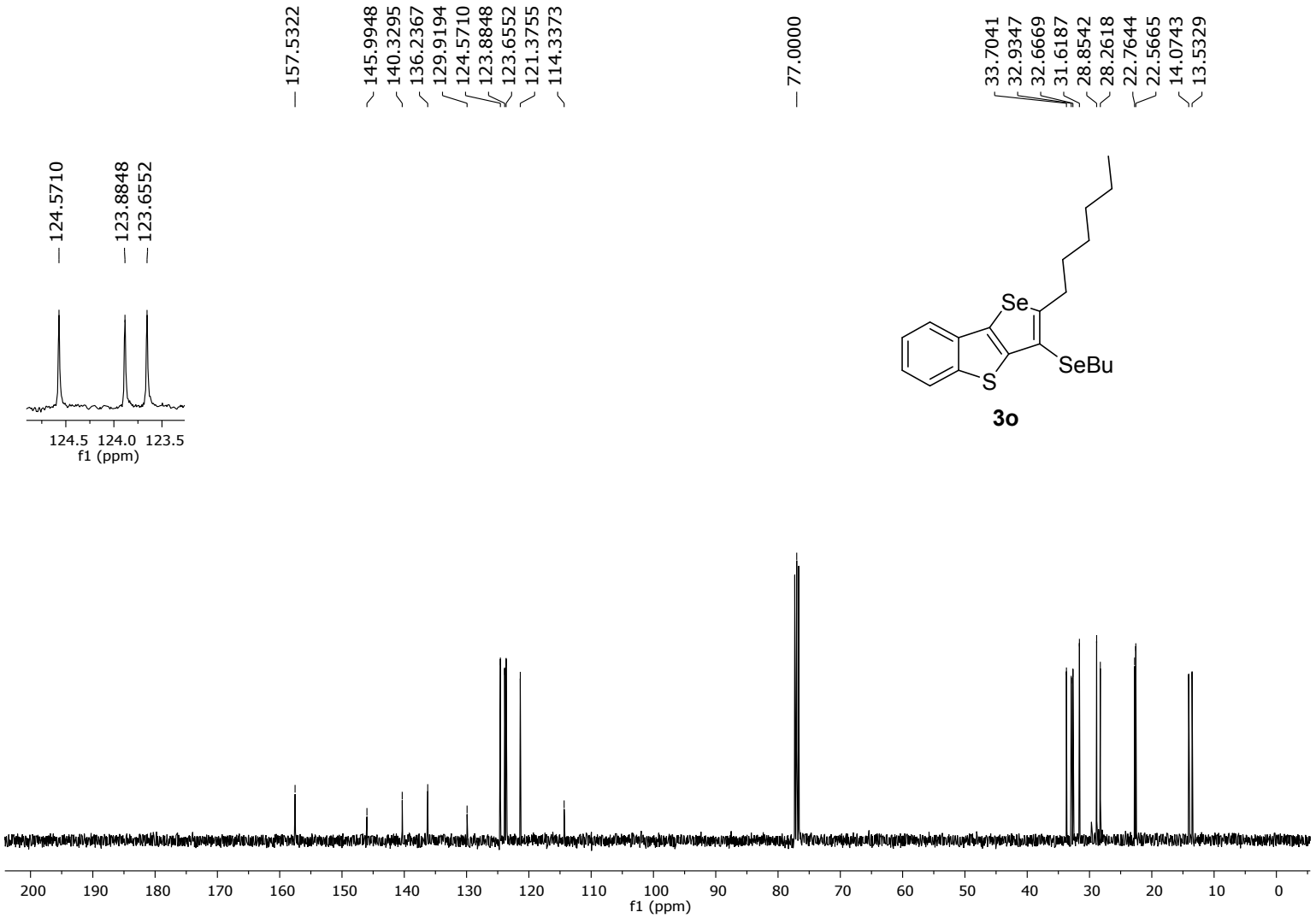



**Figure S62**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3o**.

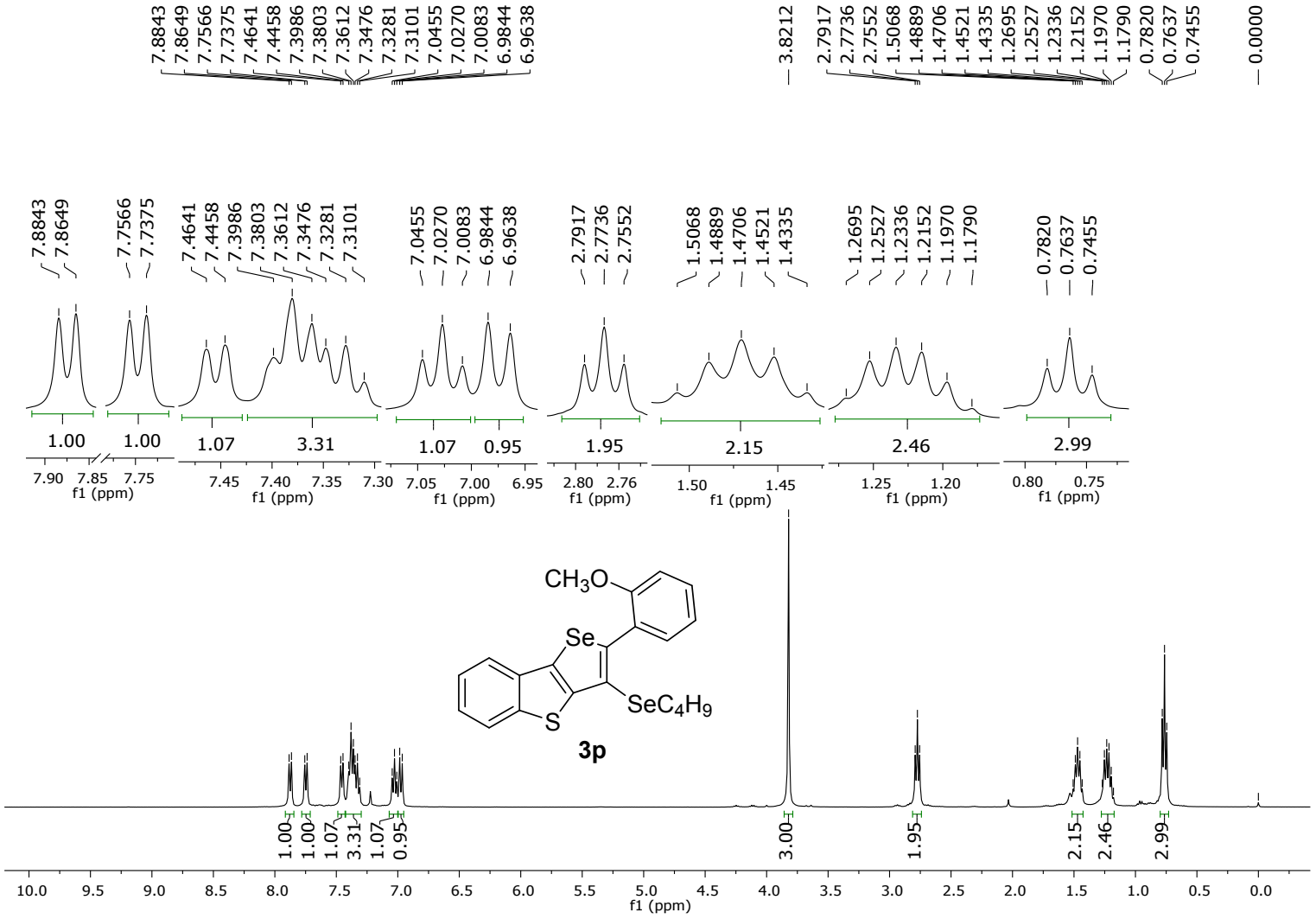



**Figure S63**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**.

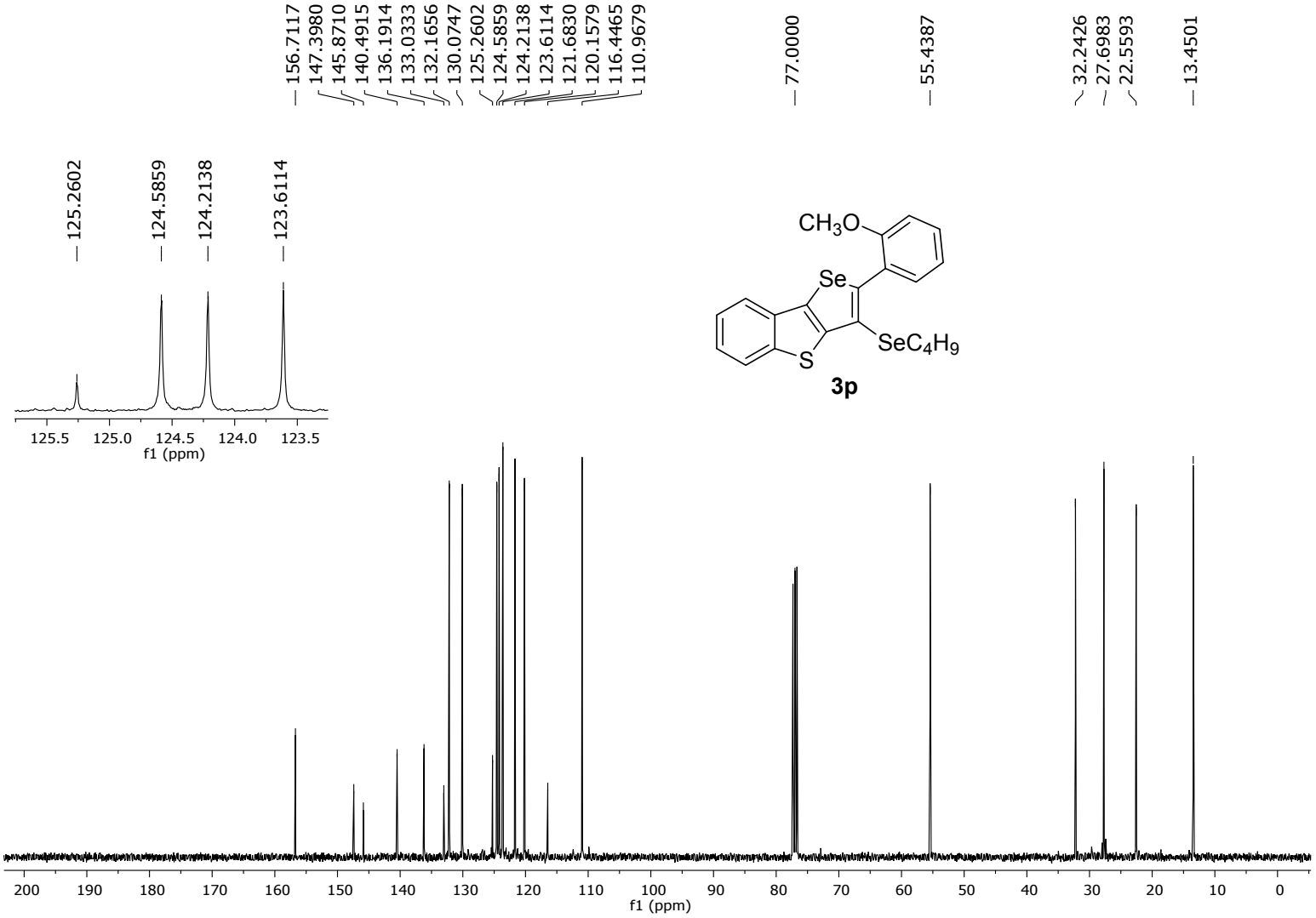



**Figure S64**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3p**.

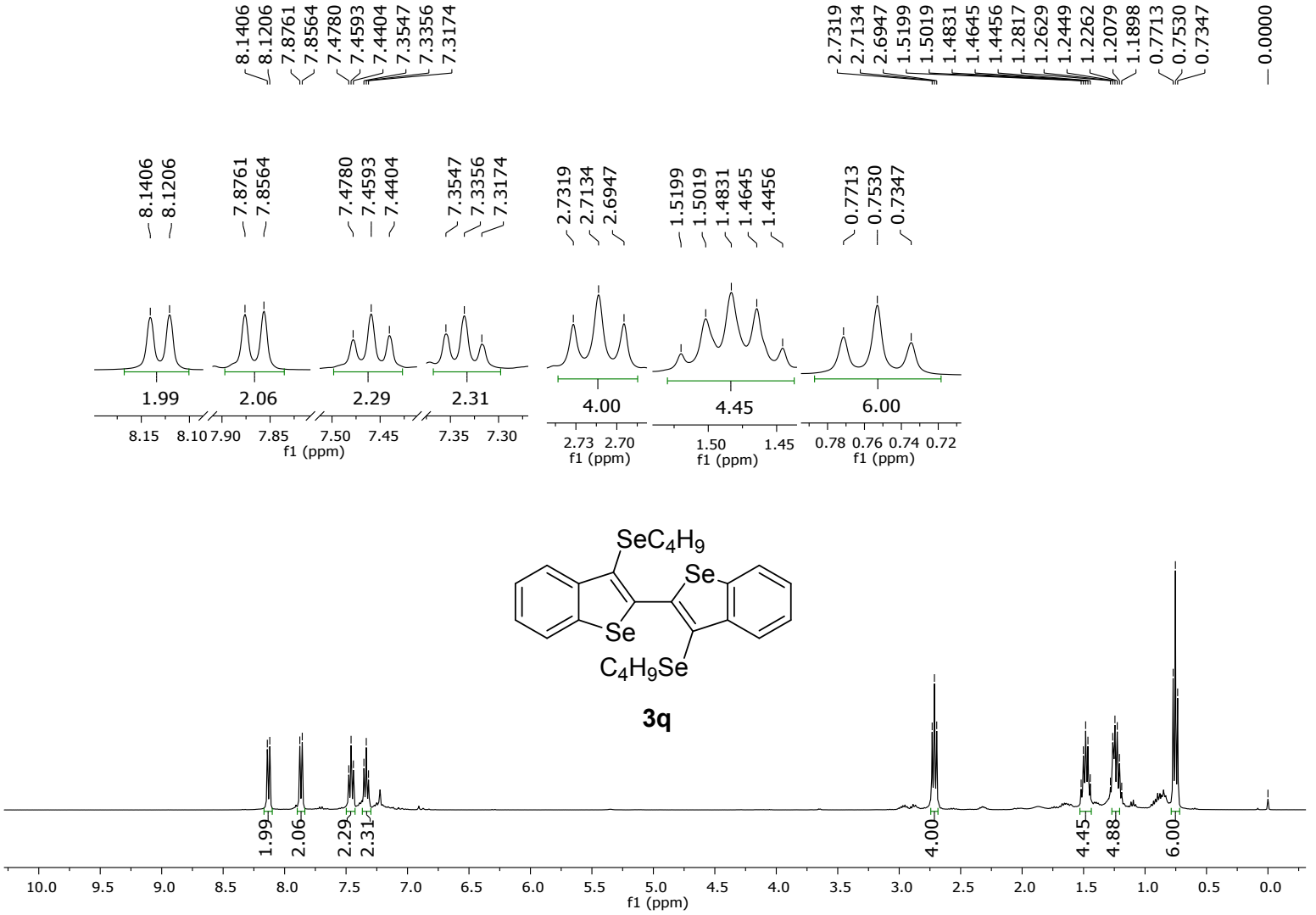



**Figure S65**: $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of compound **3q**.

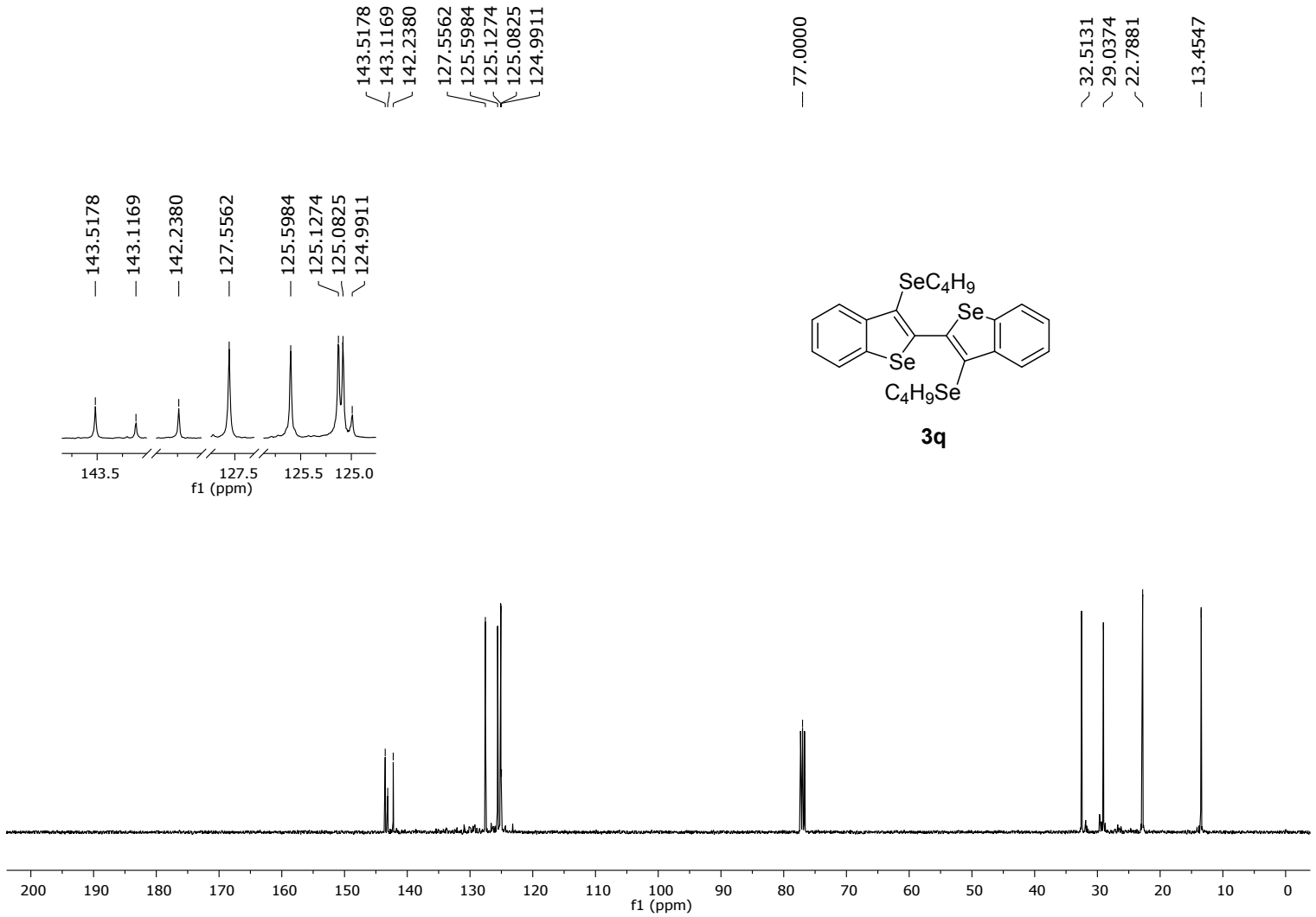
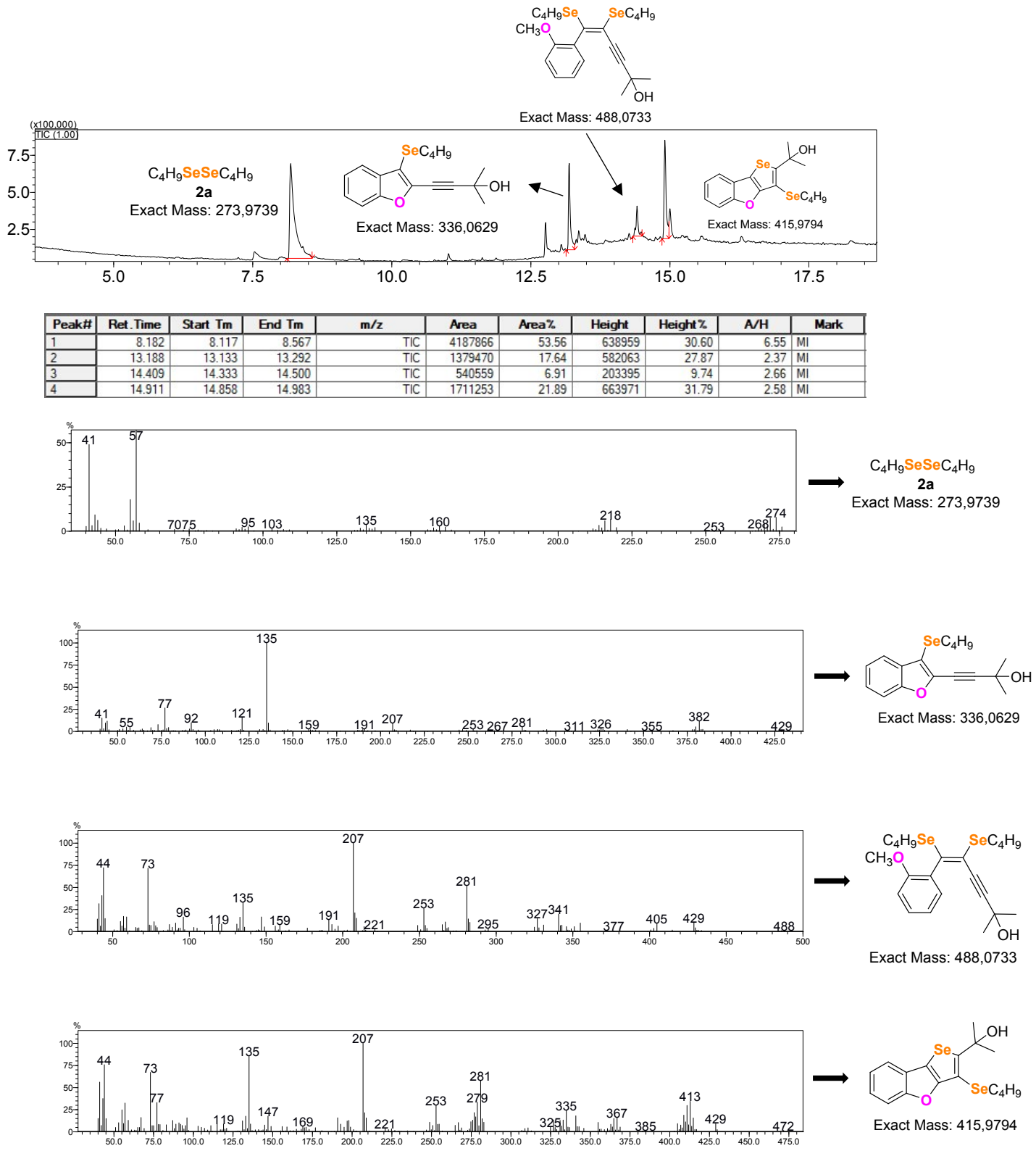



**Figure S66**: $^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3q**.




| Peak# | Ret.Time | Start Tm | End Tm | m/z | Area | Area% | Height | Height% | A/H | Mark |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 8.182 | 8.117 | 8.567 | TIC | 4187866 | 53.56 | 638959 | 30.60 | 6.55 | MI |
| 2 | 13.188 | 13.133 | 13.292 | TIC | 1379470 | 17.64 | 582063 | 27.87 | 2.37 | MI |
| 3 | 14.409 | 14.333 | 14.500 | TIC | 540559 | 6.91 | 203395 | 9.74 | 2.66 | MI |
| 4 | 14.911 | 14.858 | 14.983 | TIC | 1711253 | 21.89 | 663971 | 31.79 | 2.58 | MI |

**Figure S67**: Cyclization reaction of 1,3-diyne **1h** with dibutyl diselenide **2a** promoted by Oxone®.