Manuscript Details

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Title	Synthesis of new bis[1-(thiophenyl)propynones] as potential organic dyes for colorless luminescent solar concentrators (LSCs)
Article type	Research paper

Abstract

New luminophores having different aryl nuclei and propynones moieties have been obtained via Sonogashira reactions. Their optical properties were evaluated and indicated that carbonyl groups are responsible for significant bathochromic effects and high Stokes shifts. The insertion of -OMe groups on the central benzene unit gives to the fluorophore high optical efficiency (7.7%) when homogeneously dispersed in a poly(cyclohexyl methacrylate) (PCMA) film and connected to a PV cell.

Keywords	Luminescent solar concentrator; Organic dye; Solvatochromism; Sonogashira reaction.
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Suggested reviewers	Rafael Chinchilla, Anjun Qin, Youhong Tang

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Dear Professor. Yoon
I send you the revised version of the manuscript:

Synthesis of new bis[1-(thiophenyl)propynones] as potential organic dyes for colorless luminescent solar concentrators (LSCs), by Gianluigi Albano, [a] Tony Colli, [a] Luigi Nucci, [a] Rima Charaf, [a] Tarita Biver, [a] Andrea Pucci [a] and Laura Antonella Aronica [a,*]

We are grateful to reviewers for their comments and suggestions which we have substantially accepted (see respond to reviewers).
All the changes in the text have been highlighted with a yellow background.

Best regards,
Laura A. Aronica

Dear Professor. Yoon
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Synthesis of new bis[1-(thiophenyl)propynones] as potential organic dyes for colorless luminescent solar concentrators (LSCs), by Gianluigi Albano, [a] Tony Colli, [a] Luigi Nucci, [a] Rima Charaf, [a] Tarita Biver, [a] Andrea Pucci [a] and Laura Antonella Aronica [a,*]

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Best regards,
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- **Reviewer 1**

The authors have reported the synthesis of a series of bis[1-(thiophenyl)propynones having different aryl nuclei and propynones moieties via Sonogashira reactions. Their optical properties were evaluated and indicated that carbonyl groups are responsible for significant bathochromic effects and high Stokes shifts. The insertion of -OMe groups on the central benzene unit gives to the fluorophore high optical efficiency when homogeneously dispersed in a poly(cyclohexyl methacrylate) (PCMA) film and connected to a PV cell. The manuscript is well written and all the experiments have been carefully performed. The results are reasonably described and well supported by experimental data. This paper will gain wide interests, and thus is recommended for the publication in *Dyes and Pigments* with minor revisions.
1) Page 19, Figure 2(a), why the UV-Vis absorption curve of the **15** *in Acetone is lacked below 330 nm?*
In Figure 2(a) the curve of acetone solution of 15 is stopped at 330nm due to CH_3COCH_3 UV cut-off.
2) Page 10: **H2SO4, has been corrected into H_2SO_4**

- Reviewer 2

The article reported the synthesis of new bis[1-(thiophenyl)propynones] derivatives and the evaluation of their optical properties in terms of transparent solar collectors for PV. The topic is very interesting and characterization is well explained. However, there are several explanations and missing key points in the manuscript. Therefore, major revisions need to be performed before acceptance. Overall, this manuscript is well written and could be published. Bellow, some comments and remarks are listed.

1) **See answer to reviewer 1**
2) On page 11 it was written: "...a benzene ring linked to thiophenyl moieties through a C=C-C=O spacer", but should be rather "a benzene ring linked to thiophenyl moieties through a C≡C-C=O spacer solution".
C=C-C=O has been changed into C≡C-C=O

3) In Table 4, the symbol of dielectric constant is not found.

The symbol of the dielectric constant has been rewritten.

4) In Section 2.2, the new bis[1-(thiophenyl)propynones] derivatives are characterized by ^{1}H-NMR, ^{13}C-NMR, LC-MS and elemental analysis, however the LC-MS given is not very detailed. The calcd value should be provided.

Calculated LC-MS have been added.

5) On page 13, compounds ***1a,b,c,d,e,f,g,h*** *have similar structure, but compounds 1c, 1g and 1h did not show fluorescence when excited at 335 nm wavelength. Provide a related citation.*

Three more articles regarding the fluorescence behavior of nitro and chloro compounds have been added as ref 41,42,43.

[41] N. I. Rtishchev, D. V. Samoilov, V. P. Martynova, and A. V. El'tsov, *Russian Journal of General Chemistry*, **2001,** *71, 1467-1478.*

[42] V. Ya. Artyukhov, A. V. Morev, Y. P. Morozova, *Optics and Spectroscopy*, **2003**, *95, 361–367.*

[43] I. Esnal, J. Banuelos, I. Lopez Arbelo, A. Costela, I. Garcia-Moreno, M. Garzon, A. R. Agarrabeitiac , M. Jose´ Ortizc, *RSC Advances*, **2013,** 3, 1547-1556.

6) In Figure 2, the emission spectra showed a "Normalized Emission" value, whereas the emission intensity of sample reveals the maximum value of fluctuation in different solvents. Why?:

The emission spectra depicted in Figure 2 have been corrected in order to be truly "Normalized emission".

7) On page 16, the authors mentioned that **10c** showed a significant bathochromic effect together with an increasing of quantum yield due to the different geometry of **10c** and **1a**. Are there any other methods to further confirm the different geometry of **10c** and **1a?** Density Functional Theory (DFT) calculations should be used to prove the different geometry of **10c** and **1a**.

Sanda and co-workers have studied polymers having different diethynyl arylene units as core group. Depending on the geometry of the aryl nucleus, i.e. 1,4-benzene, 2,7-naphthyl and 1,4-naphthyl disubstituted moieties, very different optical properties were observed. In particular, the different geometry of the two naphthyl group involved different absorption and emission spectra (bathochromic effects) as well as quantum yields. Moreover, they found that DFT simulations were in agreement with experimental observations. For all these reasons we added the reference mentioned above as ref [44].:

[44] Hiromitsu Sogawa, Yu Miyagi, Masashi Shiotsuki, Fumio Sanda, *Macromolecules* **2013**, *46*, 8896–8904

8) Optical efficiencies (η_{opt}) were affected by the concentrations of fluorophores. So, the effect of fluorophore (**15**) concentration should be supplemented in manuscript.

We thank the reviewer for his/her comment. We have prepared new films containing different fluorophore content and a new plot has been added in the revised manuscript (Figure 5b). The optical efficiencies have been measured for all the films flanked also by a statistical analysis. This analysis resulted very beneficial since higher values of optical efficiencies have been gathered.

Reviewer 3

In this manuscript, the authors report their principal results regarding Sonogashira based synthesis of new bis[1-(thiophenyl)propynones] derivatives and the evaluation of their optical properties also in terms of transparent solar collectors for PV. They found that carbonyl groups are responsible for significant bathochromic effects and high Stokes shifts. The results are interesting. However, major revisions are needed before it can be accepted for publication in Dyes and Pigments.

1) The authors stated that the carbonyl groups are responsible for significant bathochromic effects and high Stokes shifts. However, more evidences and discussions should be provided to support the conclusion.

Considering our previous results, we added the sentence written below in order to enhance the correlation between the presence of carbonyl group and the optical properties of our fluorophores:

"A similar trend had been observed [32] when we studied the photophysical features of two triphenyl amine derivatives containing ethynyl linkers to thiophene or carbonylthiophene moieties. The presence of CO involved higher Stokes shifts and increase in both absorption and emission maximum wavelengths".

2) Melting points and colors of the new solid compounds are important. The data should be provided.

Melting points and colors of new compounds have been added.

Synthesis of new bis[1-(thiophenyl)propynones] as potential organic dyes for colorless luminescent solar concentrators (LSCs)

Gianluigi Albano, [a] Tony Colli, [a] Luigi Nucci, [a] Rima Charaf, [a] Tarita Biver, [a] Andrea Pucci [a] and Laura Antonella Aronica [a,*]

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[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy.

Highlights

•New bis[1-(thiophenyl)propynones] were easily obtained via Sonogashira reactions**.**

•Photophysical properties of all fluorophores were investigated.

•Carbonyl groups seemed to be responsible for significant bathochromic effects and high Stokes shifts

•Important solvatochromism was observed when dimethoxy functional groups were linked to the central benzene ring.

• The evaluation of a PCMA film of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) as solar collector showed promising optical efficiencies.

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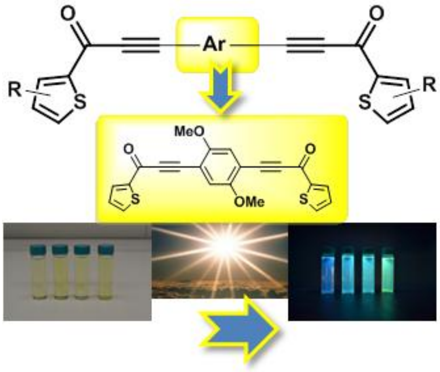
GRAPHYCAL ABSTRACT



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Keywords:

Luminescent solar concentrator

Organic dye

Solvatochromism

Sonogashira reaction

ABSTRACT

New luminophores having different aryl nuclei and propynones moieties have been obtained via Sonogashira reactions. Their optical properties were evaluated and indicated that carbonyl groups are responsible for significant bathochromic effects and high Stokes shifts. The insertion of -OMe groups on the central benzene unit gives to the fluorophore high optical efficiency (7.7%) when homogeneously dispersed in a poly(cyclohexyl methacrylate) (PCMA) film and connected to a PV cell.

1. Introduction

Climate changes due to pollution, together with the continuous increase in energy demand, have pushed research towards the use of renewable sources such as solar energy which is free and ubiquitous, and which utilization does not imply carbon dioxide emissions in the atmosphere. The exploitation of solar energy can take place by means of photo-thermal, photochemical or photovoltaic technology. The field of greatest interest concerns the photovoltaic (PV) sector, which regards with direct conversion of electromagnetic radiation into electrical energy. Solar cells produce a quantity of electrical energy, proportional to the total power of the absorbed light [1]. Hence, if the intensity of the incident light is increased a linear response in energy production will be observed: this is the principle on which geometric solar concentrators are based [2]. However, this technology has some disadvantages such as a low efficiency in diffused light conditions and the need of a good system of dispersion of excess heat due to unconverted energy [3].

To compensate for the defects of optical concentrators, luminescent solar concentrators (LSCs) were developed [4]. Since 1982, when Hermann used for the first time this term [5], the literature on LSCs has been rapidly enriched with publications[6-11] and industrial patents [12-16]. LSCs are optical devices consisting of a polymeric or glass matrix and a suitable dye dispersed within the matrix itself. The dye has the function of absorbing the incident solar radiation and re-emitting light radiation at longer wavelengths by fluorescence. The emitted light is trapped within the material and concentrated towards a solar cell on the edge of the collector, thus increasing the efficiency of the system.

Fluorophores are the driving force for light concentration in LSCs cells. An effective luminophore must meet different requirements: broad spectral absorption, good matching between the dye emitted spectrum and the external quantum efficiency of the PV-cell (generally in the red zone), large Stokes shift (no or low overlap in absorption and emission spectra), high luminescent efficiency (quantum yield, QY) and thermal- and photo-stability. Different luminophores have been investigated: quantum dots [17], lanthanide-based materials [18] and organic dyes [19], *i.e.* organic molecules featured by an extended planar π–system. Respect to the two first classes of compounds, organic dyes are usually less toxic and their optical properties can be modulated by changing portions of the carbon backbone or introducing specific functional groups. Dyes proposed for LSCs applications are coumarins, rhodamines, pyrromethane 580, naphthalimides, perylenebisimides, bipyridines, dicarbocyanins, dicyanomethylenes, oxazines, and phthalocyanines [20-33]. Among all these classes, only a very limited number of dyes have resulted in being suitable for LSCs. Therefore, a continuous investigation towards really efficient luminophores is in progress. In this context, the development of a simple synthetic methodology for obtaining π-conjugated variously functionalized systems could pave the way to new luminophores. Moreover, the application of LSC as architectural windows has also triggered interest in visible transparent fluorophores, which were found to provide acceptable optical efficiencies with a negligible degree of colored tinting [34]. Notwithstanding this exciting approach to harvesting solar energy for the building integrated photovoltaics, challenges are still open to enhance the ultimate LSC optical efficiency [10].

Here, we report our principal results regarding Sonogashira based synthesis of new bis[1-(thiophenyl)propynones] derivatives and the evaluation of their optical properties also in terms of transparent solar collectors for PV.

2. Experimental Section

2.1. Materials and apparatus

Solvents were purified by conventional methods, distilled and stored over activated molecular sieves under argon. Starting substrates thiophene-2-carbonyl chloride (**4a**), 3-methylthiophene-2-carbonyl chloride (**4b**) and 3-chlorothiophene-2-carbonyl chloride (**4c**) were purchased from Sigma Aldrich and used as received. All the other chemicals were purchased from commercial sources and used as received without purification. All the operations under inert atmosphere were carried out using standard Schlenk techniques and employing dried nitrogen. For all reactions, conversion was monitored by thin-layer chromatography (TLC) analysis on pre-coated silica gel plates

ALUGRAM® Xtra SIL G/UV$_{254}$ (0.2 mm) purchased from VWR Macherey-Nagel. Column chromatographies were performed with Fluka silica gel, pore size 60 Å, 70-230 mesh, 63-200 µm. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature in $CDCl_3$ or DMSO-d_6 solution with a Bruker Avance DRX 400 spectrometer, operating at a frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C, using the residual solvent peak as internal reference; chemical shifts (δ) values are given in parts per million (ppm) and coupling constants (J) in Hertz. Mass spectra were obtained with an Applied Biosystems-MDS Sciex API 4000 triple quadrupole mass spectrometer (Concord, Ont., Canada), equipped with a Turbo-V ion-spray (TIS) source. Elemental analyses were performed on a Elementar Vario Micro Cube CHN-analyzer.

2.2. Synthesis of bis[1-(thiophenyl)propynone] dyes

General procedure: in a typical run, diethynylarene (1.0 mmol), thiophene acid chloride (2.5 mmol), $PdCl_2(PPh_3)_2$ (2 mol%) and Et_3N (20 mL) were mixed together in a 50 mL two-necked round bottom flask. The resulting mixture was left under stirring for 28 h at 50 °C, then it was cooled to room temperature, hydrolyzed with saturated ammonium chloride solution (20 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. All the crude products were purified through column chromatography on silica gel and characterized with ^{1}H-NMR, ^{13}C-NMR, LC-MS and elemental analysis techniques.

*2.2.1. 3,3'-(1,4-Phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**)*

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), thiophene-2-carbonyl chloride (**4a**) (367 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/$CHCl_3$ 1:1), giving 288 mg (yield 83%) of 3,3'-(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**) as yellow solid. Mp: 208-210°C. ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.19 (2H, dd, *J* = 4.8, 3.8 Hz); 7.68 (4H, s); 7.75 (2H, dd, *J* = 4.8, 1.2 Hz); 8.00 (2H, dd, *J* = 3.8, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 88.53; 89.74; 122.30; 128.46; 133.05 (2C); 135.34; 135.70; 144.66; 169.35. LC-MS APCI (+): calcd for $C_{20}H_{10}O_2S_2$: 346.01; found *m/z* $[M+H]^+$: 347.1. Anal. calcd for $C_{20}H_{10}O_2S_2$: C, 69.34; H, 2.91; S, 18.51; found: C, 69.55; H, 2.86; S, 18.52.

2.2.2. 3,3'-(1,4-Phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one) ***(1b)***

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 3-methylthiophene-2-carbonyl chloride (**4b**) (402 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:5), giving 277 mg (yield 74%) of 3,3'-(1,4-phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one) (**1b**) as yellow solid. Mp: 195-198°C. ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 2.66 (6H, s); 6.98 (2H, d, *J* = 4.4 Hz); 7.56 (2H, d, *J* = 4.4 Hz); 7.66 (4H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 16.67; 89.51; 90.06; 122.35; 132.86 (2C); 132.97; 133.37; 137.62; 146.56; 169.41. LC-MS APCI (+): calcd for $C_{22}H_{14}O_2S_2$: 374.04; found *m/z* $[M+H]^+$: 375.1. Anal. calcd for $C_{22}H_{14}O_2S_2$: C, 70.56; H, 3.77; S, 17.13; found: C, 70.49; H, 3.82; S, 17.13.

2.2.3. 3,3'-(1,4-Phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) ***(1c)***

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 3-chlorothiophene-2-carbonyl chloride (**4c**) (453 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:5), giving 208 mg (yield 50%) of 3,3'-(1,4-phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (**1c**) as light yellow solid. Mp: 215-218 °C. ^{1}H-NMR (400 MHz, DMSO-d_6), δ (ppm): 7.39 (2H, d, *J* = 5.2 Hz); 7.89 (4H, s); 8.25 (2H, d, *J* = 5.2 Hz). ^{13}C-NMR (100 MHz, DMSO-d_6), δ (ppm): 89.38; 91.90; 122.05; 130.90; 131.94; 133.87 (2C); 135.99; 136.76; 167.09. LC-MS APCI (+): calcd for $C_{20}H_8Cl_2O_2S_2$: 413.93; found *m/z*

$[M+H]^+$: 415.9. Anal. calcd for $C_{20}H_8Cl_2O_2S_2$: C, 57.84; H, 1.94; S, 15.44; found: C, 58.02; H, 1.89; S, 15.43.

*2.2.4. 3,3'-(1,4-Phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**)*

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 4-phenylthiophene-2-carbonyl chloride (**4d**) (557 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:5), giving 409 mg (yield 82%) of 3,3'-(1,4-phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**) as light yellow solid. Mp: 182-185 °C.^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.33-7.36 (2H, m); 7.41-7.45 (4H, m); 7.58-7.60 (4H, m); 7.71 (4H, s); 7.83 (2H, d, *J* = 1.6 Hz); 8.21 (2H, d, *J* = 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 88.53; 90.08; 122.29; 126.40 (2C); 128.09; 129.08 (2C); 130.19; 133.08 (2C); 133.51; 134.44; 143.82; 144.97; 169.26. LC-MS APCI (+): calcd for $C_{32}H_{18}O_2S_2$: 498.07; found *m/z* $[M+H]^+$: 499.1. Anal. calcd for $C_{32}H_{18}O_2S_2$: C, 77.08; H, 3.64; S, 12.86; found: C, 77.15; H, 3.59; S, 12.86.

*2.2.5. 3,3'-(1,4-Phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**)*

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 3-ethoxythiophene-2-carbonyl chloride (**4e**) (477 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:4), giving 252 mg (yield 58%) of 3,3'-(1,4-phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**) as yellow-orange solid. Mp: 216-218 °C..^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 1.45 (6H, t, *J* = 6.8 Hz); 4.24 (4H, q, *J* = 6.8 Hz); 6.85 (2H, d, *J* = 5.2 Hz); 7.57 (2H, d, *J* = 5.2 Hz); 7.61 (4H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 15.05; 67.80; 89.73; 89.98; 116.88 (2C); 122.67; 132.64 (2C); 134.67; 161.82; 167.59. LC-

MS APCI (+): calcd for $C_{24}H_{18}O_4S_2$: 434.06; found *m/z* $[M+H]^+$: 435.4. Anal. calcd for $C_{24}H_{18}O_4S_2$: C, 66.34; H, 4.18; S, 14.76; found: C, 66.09; H, 4.21; S, 14.77.

*2.2.6. 3,3'-(1,4-Phenylene)bis(1-(benzo[b]thiophen-2-yl)prop-2-yn-1-one) (**1f**)*

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), benzo[*b*]thiophene-2-carbonyl chloride (**4f**) (492 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:3), giving 201 mg (yield 45%) of 3,3'-(1,4-phenylene)bis(1-(benzo[*b*]thiophen-2-yl)prop-2-yn-1-one) (**1f**) as orange solid. Mp: 206-208 °C..^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.42-7.46 (2H, m); 7.49-7.53 (2H, m); 7.76 (4H, s); 7.89 (2H, d, *J* = 8.0 Hz); 7.95 (2H, d, *J* = 8.0 Hz); 8.27 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 88.49; 90.41; 122.37; 123.16; 125.39; 126.46; 128.26; 132.97; 133.15 (2C); 138.73; 143.34; 144.07; 170.82. LC-MS APCI (+): calcd for $C_{28}H_{14}O_2S_2$: 446.04; found *m/z* $[M+H]^+$: 447.2. Anal. calcd for $C_{28}H_{14}O_2S_2$: C, 75.31; H, 3.16; S, 14.36; found: C, 75.55; H, 3.14; S, 14.35.

*2.2.7. 3,3'-(1,4-Phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (**1g**)*

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 5-chlorothiophene-2-carbonyl chloride (**4g**) (453 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:5), giving 324 mg (yield 78%) of 3,3'-(1,4-phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (**1g**) as light pink solid. Mp: 255-257 °C.^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.05 (1H, d, *J* = 4.1 Hz); 7.69 (2H, s); 7.80 (1H, d, *J* = 4.1 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 87.83; 90.32; 122.21; 128.01; 133.09 (2C); 134.77; 141.69; 142.88; 168.25. LC-MS APCI (+): calcd for $C_{20}H_8Cl_2O_2S_2$: 413.93; found *m/z* $[M+H]^+$: 415.9. Anal. calcd for $C_{20}H_8Cl_2O_2S_2$: C, 57.84; H, 1.94; S, 15.44; found: C, 58.08; H, 1.86; S, 15.44.

*2.2.8. 3,3'-(1,4-Phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**)*

According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 5-nitrothiophene-2-carbonyl chloride (**4h**) (479 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/AcOEt 9:1 → 7:3), giving 231 mg (yield 53%) of 3,3'-(1,4-phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**) as yellow-orange solid. Mp: 219-221 °C..^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.77 (4H, s); 7.90 (2H, d, *J* = 4.2 Hz); 7.97 (2H, d, *J* = 4.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 87.62; 92.41; 122.03; 128.20; 132.25; 133.38 (2C); 147.41; 157.18; 168.70. LC-MS APCI (+): calcd for $C_{20}H_8N_2O_6S_2$: 435.98; found *m/z* $[M+H]^+$: 437.0. Anal. calcd for $C_{20}H_8N_2O_6S_2$: C, 55.04; H, 1.85; N, 6.42; S, 14.69; found: C, 54.91; H, 1.92; N, 6.43; S, 14.70.

*2.2.9. 3,3'-([1,1'-Biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10a**)*

According to the general procedure, 4,4'-diethynyl-1,1'-biphenyl (**9a**) (202 mg, 1.0 mmol), thiophene-2-carbonyl chloride (**4a**) (367 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:4), giving 321 mg (yield 76%) of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10a**) as light yellow solid. Mp: 206-208 °C.^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.19-7.21 (2H, m); 7.66 (4H, d, *J* = 8.4 Hz); 7.73-7.76 (6H, m); 8.02 (2H, d, *J* = 4.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 87.50; 91.15; 119.73; 127.37 (2C); 128.36; 133.67 (2C); 135.05; 135.32; 142.07; 144.93; 169,62. LC-MS APCI (+): calcd for $C_{26}H_{14}O_2S_2$: 422.04; found *m/z* $[M+H]^+$: 423.2. Anal. calcd for $C_{26}H_{14}O_2S_2$: C, 73.91; H, 3.34; S, 15.18; found: C, 73.68; H, 3.35; S, 15.18.

*2.2.10. 3,3'-(Naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**)*

According to the general procedure, 2,6-diethynylnaphthalene (**9b**) (176 mg, 1.0 mmol), thiophene-2-carbonyl chloride (**4a**) (367 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:4 → CH_2Cl_2), giving 202 mg (yield 51%) of 3,3'-(naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**) as light yellow solid. Mp: 210-213 °C..^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.19-7.22 (2H, m); 7.71 (2H, d, $J = 8.4$ Hz); 7.75 (2H, d, $J = 4.4$ Hz); 7.89 (2H, d, $J = 8.4$ Hz); 8.05 (2H, d, $J = 4.4$ Hz); 8.22 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 87.60; 91.01; 119.43; 128.41; 128.74; 129.57; 133.14; 133.89; 135.15; 135.46, 144.89; 169.51. LC-MS APCI (+): calcd for $C_{24}H_{12}O_2S_2$: 396.03; found *m/z* $[M+H]^+$: 397.2. Anal. calcd for $C_{24}H_{12}O_2S_2$: C, 72.70; H, 3.05; S, 16.17; found: C, 72.77; H, 3.09; S, 16.16.

*2.2.11. 3,3'-(Naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**)*

According to the general procedure, 1,4-diethynylnaphthalene (**9c**) (176 mg, 1.0 mmol), thiophene-2-carbonyl chloride (**4a**) (367 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:4 → CH_2Cl_2), giving 266 mg (yield 67%) of 3,3'-(naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**) as yellow solid. Mp: 212-214 °C..^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.22-7.23 (2H, m); 7.73-7.76 (2H, m); 7.78 (2H, dd, $J = 4.4$, 1.2 Hz); 7.92 (2H, s); 8.09 (2H, dd, $J = 4.4$, 1.2 Hz); 8.44-8.48 (2H, m). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 88.39; 92.99; 120.78; 126.50; 128.56; 128.70; 131.87; 133.27; 135.13; 135.65; 144.82; 169.30. LC-MS APCI (+): calcd for $C_{24}H_{12}O_2S_2$: 396.03; found *m/z* $[M+H]^+$: 397.2. Anal. calcd for $C_{24}H_{12}O_2S_2$: C, 72.70; H, 3.05; S, 16.17; found: C, 72.83; H, 3.03; S, 16.17.

*2.2.12. 3,3'-(2,5-Dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**)*

According to the general procedure, 1,4-diethynyl-2,5-dimethoxybenzene (**13**) (186 mg, 1.0 mmol), thiophene-2-carbonyl chloride (**4a**) (367 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:5), giving 346 mg (yield 85%) of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-

(thiophen-2-yl)prop-2-yn-1-one) (**15**) as yellow-green solid. Mp: 264-267 (dec.) °C.^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 3.98 (6H, s); 7.19 (2H, s); 7.23-7.25 (2H, m); 7.78 (2H, dd, *J* = 4.9, 1.2 Hz); 8.15 (2H, dd, *J* = 3.8, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 56.89; 87.60; 92.59; 113.19; 116.88; 128.66; 135.78; 136.20; 145.33; 155.85; 169.08. LC-MS APCI (+): calcd for $C_{22}H_{14}O_4S_2$: 406.03; found *m/z* $[M+H]^+$: 407.2. Anal. calcd for $C_{22}H_{14}O_4S_2$: C, 65.01; H, 3.47; S, 15.78; found: C, 64.83; H, 3.41; S, 15.78.

2.3. Characterization

UV-Vis absorption measurements in solution were done using a Perkin-Elmer Lambda 650 spectrophotometer, with temperature control to within ±0.1 °C. Fluorescence measurements in solution were performed using a Horiba Jobin Yvon FluoroLog®-3 spectrofluorometer, with temperature control to within ±0.1 °C.

Quantum yields (Φ) in solution are calculated according to a comparative method, involving the use of a standard with known quantum yield, Φ_{ST} (perylene in cyclohexane, $\Phi_{ST} = 0.94$; fluorescein in 0.1 M aqueous NaOH solution, $\Phi_{ST} = 0.95$; quinine sulfate in 0.1 M aqueous H_2SO_4 solution, $\Phi_{ST} = 0.54$) [35]; the equation used is

$$\Phi_x = \Phi_{ST} \cdot \frac{\nabla_x}{\nabla_{ST}} \cdot \frac{(\eta_x)^2}{(\eta_{ST})^2}$$

where ∇_x and ∇_{ST} are the slopes of a fluorescence area *vs.* absorbance plot for the dye and standard, respectively, while η_x and η_{ST} are the refractive index of the solvents used for dye and standard solutions, respectively ($\eta_{chloroform} = 1.445$; $\eta_{cyclohexane} = 1.426$; $\eta_{water} = 1.330$).

15/PCMA thin films were prepared by drop casting, *i.e.* pouring 0.8 mL chloroform solution containing 120.0 mg of the polymer and the proper amount of fluorophore to obtain concentrations in the range 0.7-1 wt.% on 50×50×3 mm optically pure glass substrate (Edmund Optics Ltd BOROFLOAT window 50×50 TS). The glass slides were cleaned with chloroform and immerged in 6 M HCl for at least 12 h; then, they were rinsed with water, acetone and isopropanol and dried for 8 h at 120 °C. Solvent evaporation was performed on a warm hot plate (about 30 °C) and in a closed environment. The film thickness was measured by a Starrett micrometer to be 200 ± 10 μm.

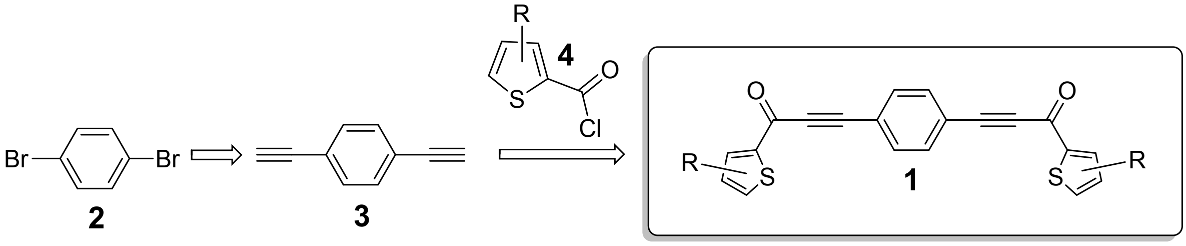
The optical efficiency of the LSC was measured by using a solar simulating lamp (ORIEL® LCS-100 solar simulator 94011A S/N: 322, AM1.5G std filter: 69 mW/cm^{-2} at 254 mm). The PV module (IXYS SLMD121H08L mono solar cell 86×14 mm) was connected to Keysight Technologies B2900 Series Precision Source/Measure Unit. The optical efficiency η_{opt} was evaluated from the concentration factor C, which is the ratio between the short circuit current measured in the case of the cell over the LSC edge (I_{LSC}) and short circuit current of the bare cell when perpendicular to the light source (I_{SC})

$$\eta_{opt} = \frac{I_{LSC}}{I_{SC} \cdot G}$$

where G is the geometrical factor (in our case, G = 13.3), which is the ratio between the area exposed to the light source and the collecting area.

3. Results and discussion

We started our study with the synthesis of (1,4-phenylene)bis(thiophenylpropynones) **1** (Scheme 1) characterized by the presence of a benzene ring linked to thiophenyl moieties through a C≡C-C=O spacer. The synthetic strategy chosen for the preparation of these compounds consists of two main steps: the synthesis of the central diethynyl functionalized nucleus and the subsequent coupling with thiophene carbonyl chlorides (Scheme 1). Both steps are based on Sonogashira cross-coupling reactions: the first is the “classic” version of the reaction [36], the second consists of the acyl copper-free Sonogashira coupling [37-38].



Scheme 1. Synthetic approach to (1,4-phenylene)bis(thiophenylpropynones) dyes **1**.

In details, 1,4-diethynylbenzene (**3**) was obtained from the reaction between commercial available 1,4-dibromobenzene (**2**) and an excess of ethynyltrimethylsilane, followed by quantitative desilylation of product **5** performed with aqueous solution of NaOH (see Scheme S1 in Supporting Information). As coupling partner of 1,4-diethynylbenzene (**3**), eight different acid chlorides were chosen (Figure 1). While compounds **4a-c** were commercially available, acid chlorides **4d-4f** were easily prepared starting from the methyl esters by hydrolysis with aqueous NaOH. The obtained carboxylic acids were converted into the acid chlorides by treatment with oxalyl chloride. Analogously, chlorides **4g-h** were obtained treating the commercial corresponding acids with $(COCl)_2$ (Scheme S2).

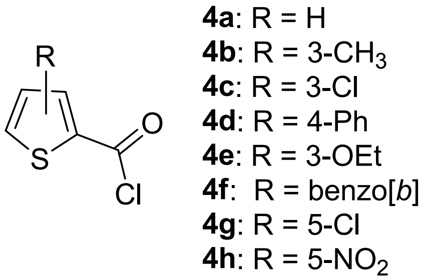
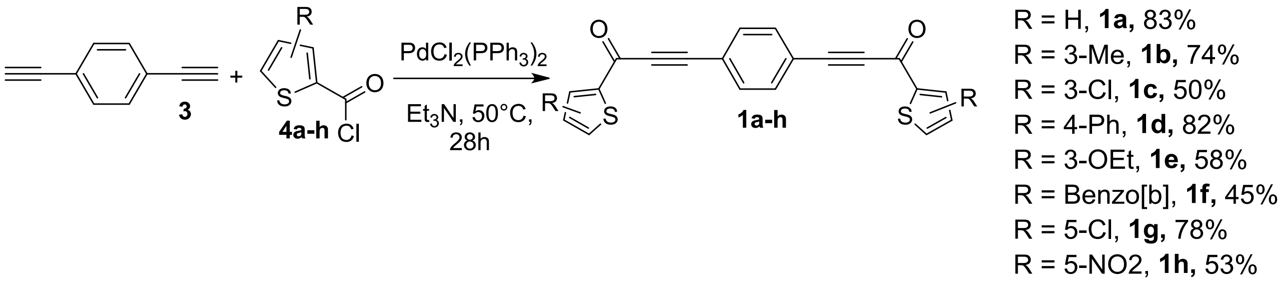


Figure 1. Chemical structure of acid chlorides chosen as coupling partner of **3** for the synthesis of (1,4-phenylene)bis(thiophenylpropynones) dyes.

Since it is known that decarbonyation and C≡C-C≡C side reactions [39-40] may occur if acid Sonogashira reactions are performed at high temperature, a preliminary cross coupling between 1,4-diethynylbenzene (**3**) and thiophene-2-carbonyl chloride (**4a**) was performed at room temperature for 28 h. The analysis of crude product indicated an almost complete conversion of the reagents but the formation of a mixture of both mono- and di-thiophene carbonyl derivatives (Scheme S3 in Supporting Information).

In order to increase the chemoselectivity of the reaction, a second run was carried out at 50 °C. In this case the total consumption of the reagents occurred and the exclusive formation of expected product **1a** was observed (yield 83%). As a consequence, the improved experimental reaction conditions (50 °C, 28 h, 1 mmol of 1,4-diethynylbenzene (**3**), 2.5 mmol of thiophene carbonyl chloride, 20 mL of Et_3N, and 2 mol% of $PdCl_2(PPh_3)_2$) were applied to the acyl Sonogashira reaction between **3** and thiophene carbonyl chlorides **4** (Scheme 2). The reactions afforded exclusively di-carbonyl compounds **1a-h** and proved amenable to acid chlorides containing both electron-donating and electron-withdrawing functionality, delivering products in good yields, regardless of the position of the functional group on the thiophene ring.



R = H, **1a,** 83%
R = 3-Me, **1b,** 74%
R = 3-Cl, **1c,** 50%
R = 4-Ph, **1d,** 82%
R = 3-OEt, **1e,** 58%
R = Benzo[b], **1f,** 45%
R = 5-Cl, **1g,** 78%
R = 5-NO2, **1h,** 53%

Scheme 2. Acyl Sonogashira reactions between 1,4-diethynylbenzene (**3**) and thiophene carbonyl chlorides **4a-h**.

Study of the optical properties of compounds **1a-h** was undertaken in $CHCl_3$ solutions. The main results obtained are collected in **Table 1**, while full absorbance and fluorescence emission spectra are depicted in Figures S1-S8 in Supporting Information.

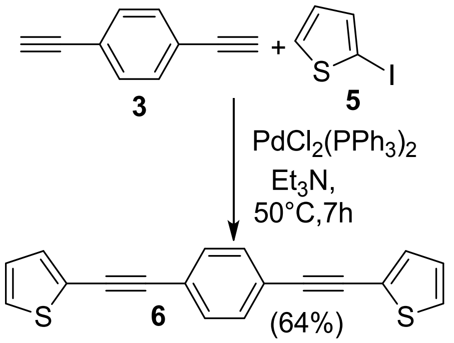
Products **1c**, **1g** and **1h**, featured by electron-withdrawing moieties did not show fluorescence when excited at 335 nm wavelength [41-43]. On the contrary, compounds **1a,b,d,e,f** showed emission spectra with high Stokes shifts (108-168 nm), indicating low auto-absorption in solution and good potentiality as fluorophores in LSC devices. Unfortunately their quantum yields were almost negligible (less than 1%).

Table 1. Photophysical properties of (1,4-phenylene)bis(thiophenylpropynones) dyes **1a-h**.

Compound	ε[a]	λ_{max}^{Abs}[b]	λ_{max}^{Fluo}[c]	SS[d]	Φ[e]
1a	3.8	335	443	108	0.2
1b	3.8	338	450	112	/[f]
1c	3.8	339	/	/	/[g]
1d	3.4	328	467	139	0.6
1e	2.5	323	507	184	0.2
1f	4.5	343	451	108	0.2
1g	5.8	340	/	/	/[g]
1h	4.6	352	/	/	/[g]

[a]Extinction coefficient (10^4 M^{-1} cm^{-1}). [b]Maximum of light absorbance (nm). [c]Maximum of light emission (nm). [d]SS = Stokes shift (nm) = λ_{max}^{Fluo} - λ_{max}^{Abs} . [e] Quantum yield (%). [f]Less than 0.1%. [g]Not determined.

In order to evaluate the effect of carbonyl group on the optical properties of (1,4-phenylene)bis(thiophenylpropynones) **1,** 1,4-diethynylbenzene **3** was reacted with 2-iodothiophene **5** affording 1,4-bis(thiophen-2-ylethynyl)benzene **6** in good yield (Scheme 3).



$\varepsilon = 5.4\ 10^4\ M^{-1}\ cm^{-1}$

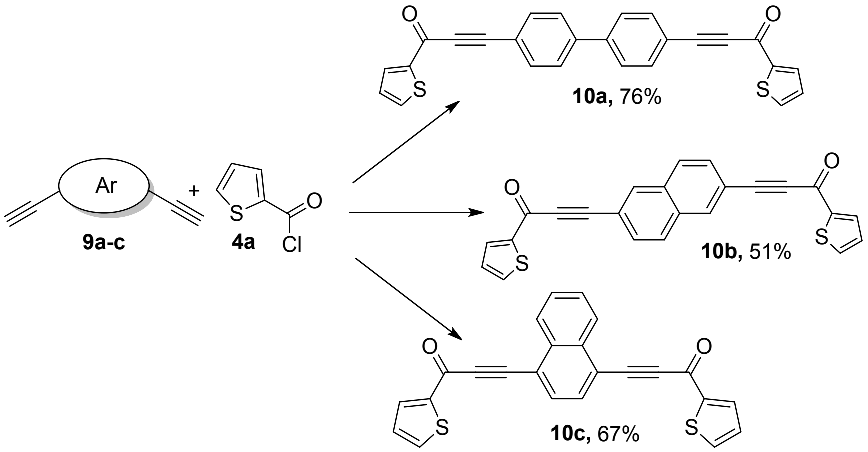
$\lambda_{max}^{Abs} = 341\ nm$; $\lambda_{max}^{Fluo} = 371\ nm$

SS = 30 nm; $\Phi = 9.9\%$

Scheme 3. Synthesis and optical properties of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**).

A comparison between optical properties of **6** (Scheme 3 and Figure S9) and **1a** (Table 1 and Figure S1) clearly indicated that the presence of CO determines an increase of the Stokes shift, a significant bathochromic effect in emission spectra, but also a dramatic reduction of quantum yield (0.2 *vs.* 9.9%). A similar trend had been observed [32] when we studied the photophysical features of two triphenyl amine derivatives containing ethynyl linkers to thiophene or carbonylthiophene moieties. The presence of CO involved higher Stokes shifts and increase in both absorption and emission maximum wavelengths.

Thus, with the aim to improve the optical properties, bis(thiophenylpropynones) containing nucleus with extended conjugation were synthesized (Scheme 4). Analogously to the synthetic sequence employed for the synthesis of derivatives **1a-h**, central units were prepared starting from the corresponding dibromo derivatives **7a-c,** which were coupled with trimethylsilylacetylene generating **8a-c**; subsequent desilylation step (KOH) afforded diynes **9a-c** in good yields (Scheme S4).



Scheme 4. Synthetic approach to arylbis(thiophenylpropinones) **10a-c**.

The optical properties of dyes **10a-c** in $CHCl_3$ solution are collected in Table 2 and Figures S10-S12. While biphenyl (**10a**) and 2,6-naphtyl (**10b**) derivatives showed optical features very similar to 3,3'-(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**) in terms of maximum absorbance and emission wavelength, 3,3'-(naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**) showed a significant bathochromic effect (λ_{max}^{Abs} = 397 nm for **10c**, 335 nm for **1a**) together with an increase of quantum yield (5.8% for **10c** *vs.* 0.2% for **1a**). Such results could be related to both the increase of π-conjugation and to the different geometry of **10c** respect to **1a** [44].

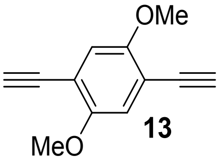
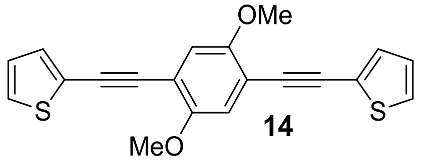
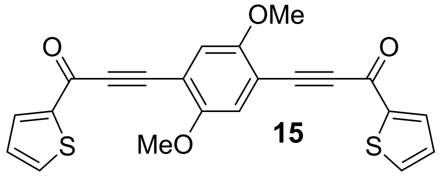
Table 2. Photophysical properties of arylbis(thiophenylpropinones) **10a-c**.

Compound	ε^{a}	$\lambda_{max}^{Abs\ b}$	$\lambda_{max}^{Fluo\ c}$	SS [d]	Φ [e]
10a	3.8	346	420	74	/ [f]
10b	5.3	346	428	82	/ [f]
10c	3,4	397	456	59	5.8

[a]Extinction coefficient (10^4 M^{-1} cm^{-1}). [b]Maximum of light absorbance (nm). [c]Maximum of light emission (nm). [d]SS = Stokes shift (nm) = λ_{max}^{Fluo} - λ_{max}^{Abs} . [e] Quantum yield (%). [f]Less than 0.1%.

Considering that the presence of an electron-donating group such as -OEt had determined a remarkable bathochromic effect and a very high SS value (Table 1, **1e**) the syntheses of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (**14**) and 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) were carried out (Scheme S5). Central nucleus 1,4-diethynyl-2,5-dimethoxybenzene (**13**) was easily prepared starting from commercially available 1,4-dibromo-2,5-dimethoxybenzene (**11**) which was coupled with ethynyltrimethylsilane affording **12** (Scheme S5, step a). After desilylation with KOH/MeOH (Scheme S5, step b), product **13** was generated in high yield. and was then successfully employed in the synthesis of **14** and **15** via Sonogashira reactions (Scheme S5, steps c-d). The optical properties in $CHCl_3$ solution of both compounds are described in Table 3 and compared with those of precursor **13** (full absorbance and fluorescence emission spectra of **13-15** are reported in Figures S13-S15 in Supporting Information). As is evident from data collected in Table 3, wavelengths of absorption and emission maxima of the three compounds vary significantly with their structure. Indeed, going from diyne **13** to compounds **14** and then to **15** the extension of conjugation determines a red-shift of the spectrum, but with an absorption maximum still peaked close to the near-UV region.

Table 3. Optical properties of dimethoxy-substituted dyes **13-15**.

Compounds	Yield (%)^{a}	ε^{b}	$\lambda_{max}^{Abs\ c}$	$\lambda_{max}^{Fluo\ d}$	SS^{e}	Φ^{f}
 **13**	85	1.0	345	373	28	12.3
 **14**	60	3.8	377	409	32	23.3
 **15**	85	1.9	403	471	68	19.2

[a]Yield of pure product. [b]Extinction coefficient (10^4 M^{-1} cm^{-1}). [c]Maximum of light absorbance (nm). [d]Maximum of light emission (nm). [e]SS = Stokes shift (nm) = λ_{max}^{Fluo} - λ_{max}^{Abs} . [f]Quantum yield (%).

Moreover, the presence of CO causes an increasing of the Stokes shift from 28 to 68 nm. If we compare the optical properties of **15** with compound **1a** it is evident that the presence of -OMe group involves a clear improvement of the quantum yield, from 0.2 for **1a** to about 20% for **14** and **15**, possibly due to a restricted molecular mobility. Furthermore, since **15** appeared as a promising fluorophore for colorless solar collectors, further investigations were carried out. Notably solvatochromism analyses were performed in solvents with different polarities but refractive index (η) close to that of acrylate polymers, *i.e.* the most common matrix for LSC devices (Table 4 and Figures 2 and 3).

Table 4. Optical properties of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) recorded in different solvents.

Solvent	η^{a}	$\square^{b}$	$\lambda_{max}^{Abs\ c}$	$\lambda_{max}^{Fluo\ d}$	SS^{e}	Φ^{f}
Toluene	1.496	2.4	401	453	52	16.1
$CHCl_3$	1.445	4.8	403	471	68	19.2
Acetone	1.359	21.0	402	471	69	38.4
Acetonitrile	1.344	38.8	403	484	81	40.8

[a] Refractive index. [b] Dielectric constant. [c] Maximum of light absorbance (nm). [d] Maximum of light emission. [e] SS = Stokes shift (nm) = λ_{max}^{Fluo} - λ_{max}^{Abs} . [f] Quantum yield (%).

As it is evident, the choice of the solvent has a great influence on the photophysical properties of **15**. In particular, as polarity increases from toluene to acetonitrile, a significant enhancement of quantum yield (*i.e.* 16.1% in toluene with respect to 40.8% in acetonitrile) and Stokes shift (from 52 to 81 nm) were detected. In the different solvents, λ_{max}^{Abs} is constant and λ_{max}^{Fluo} increases as polarity increases. This shift of the emission to lower energy is due to the stabilization of the (polar) excited state by the polar solvent molecules. The increase in the quantum yield with solvent polarity is related to a decrease of non-radiative decays, in agreement with the increased values of Stokes shift [45].

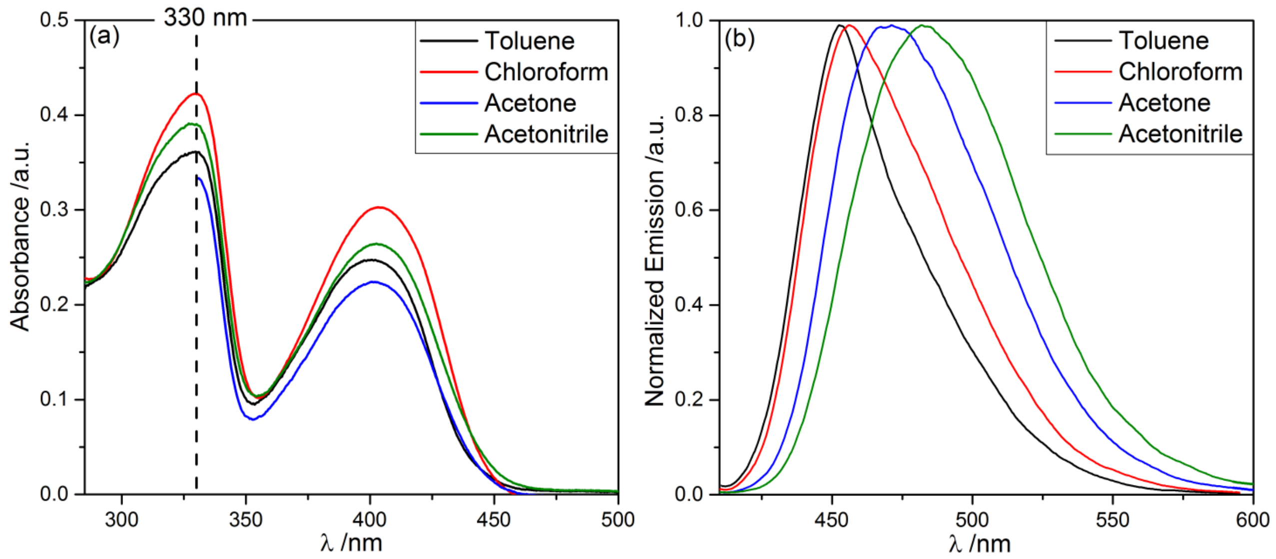


Figure 2. UV-Vis absorption (a) and emission (b) normalized spectra of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) in different solvents. Sample concentration: 1.7×10^{-5} M for absorption spectra, 1.0×10^{-6} M for emission spectra; cell length: 1 cm; excitation wavelength: 335 nm.

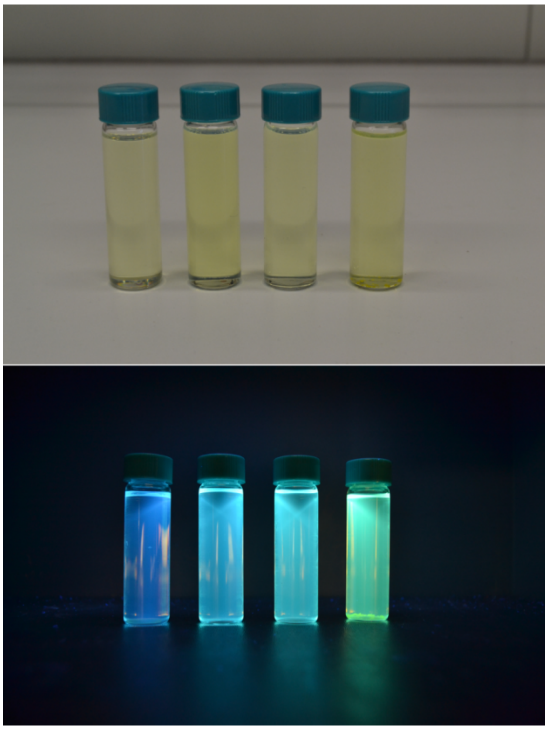


Figure 3. 1.0×10^{-6} M solutions of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) dye in different solvents (from left to right: toluene, chloroform, acetone, acetonitrile), illuminated with daylight (up photo) and irradiated with UV light at 335 nm (down photo).

All solutions were also checked for stability in time: absorption spectra collected over all the range were totally super imposable over 6 hours of continuous irradiation at the excitation wavelength (Figure 4).

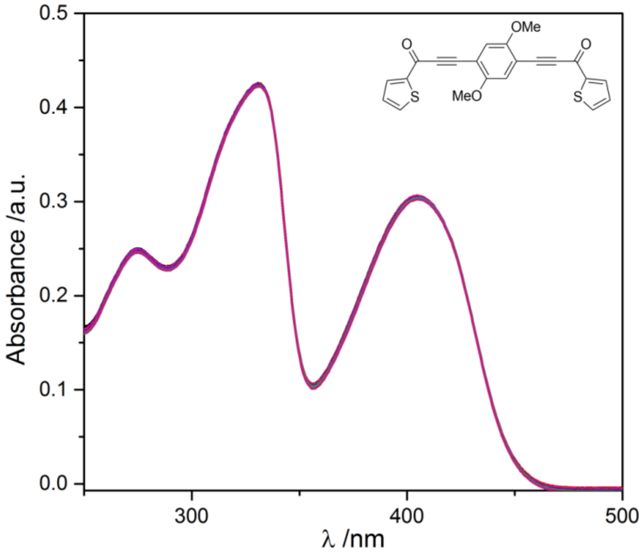


Figure 4. UV-Vis absorption spectra of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) in $CHCl_3$ recorded each 15 minutes for 6 h. Sample concentration: 1.7×10^{-5} M; cell length: 1 cm.

A preliminarily investigation of **15** as a potential fluorophore for colorless LSC was carried out by dispersing 0.7 wt.% of the dye in a polymer matrix of poly(cyclohexylmethacrylate) (PCMA). PCMA is 100% amorphous, transparent and commercially available, features that make this matrix suitable for LSC applications (Figure 5). In the PCMA film (thickness of about 200 μm), **15** showed absorption in the near-UV region with a negligible contribution in the visible range of the light spectrum (at 450 nm, about 80 % of transmitted light, Figure 5). **15** displayed an emission maximum at about 470-480 nm, in agreement with data collected in solution (Table 4). The performances of the PCMA/**15** film as solar collector were determined on optically pure 50×50×3 mm glass by using a Si-based PV cell attached to one edge of the LSC. The data acquired followed a peculiar trend, *i.e.* optical efficiency increasing with **15** content and levelling off for concentration higher than 0.7 wt% possibly due to adverse dissipative phenomena. Notably, maximum optical efficiencies of 7.7% was obtained and resulted higher than those of previously investigated bis-azido fluorophores for colorless LSC and determined with the same laboratory setup [34].

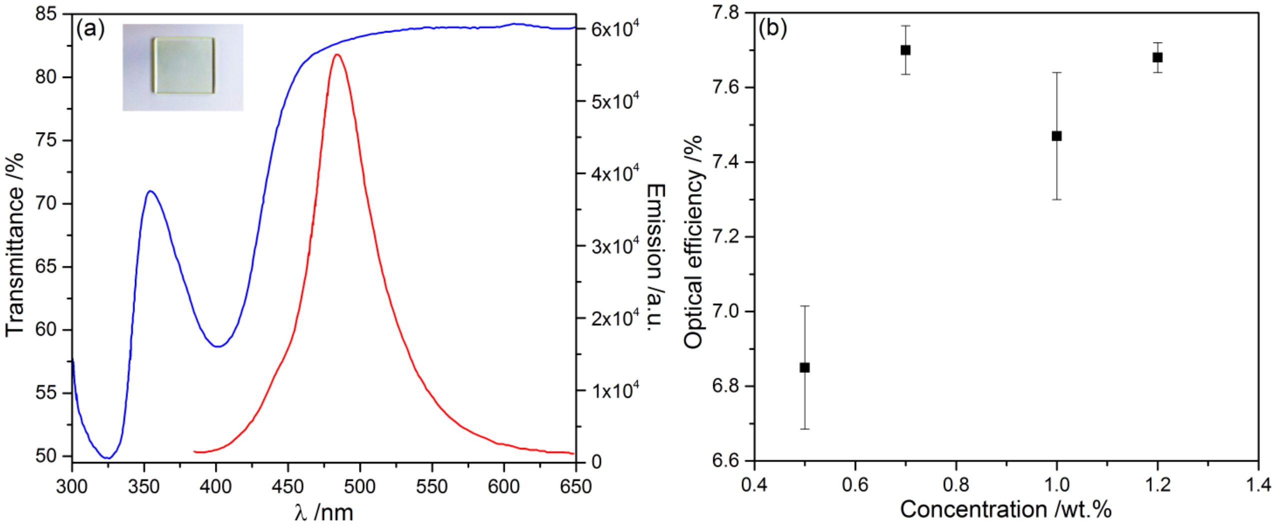


Figure 5. (a) Absorption and emission of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) in PCMA film at a concentration of 0.7 wt.%; (b) Optical efficiencies of PCMA/**15** film as a function of fluorophore concentration (wt%)

4. Conclusion

In summary, an easy methodology for the preparation of new bis(thiophenylpropynones) based on Sonogashira cross-coupling reactions has been developed. All compounds were generated in good to high yields and were tested as organic dyes for LSCs. The presence of carbonyl functional groups determined a significant bathochromic effect in emission spectra. Moreover, increasing π-conjugation of thiophenyl lateral unit determined an increase in Stokes shifts up to 180 nm, thus indicating low auto-absorption in solution. Replacement of benzene ring with naphthalene nucleus involved an increment of quantum yield but best results were obtained when -OMe groups were bonded to the central benzene ring (**15**), with quantum yield of 19.2% and SS of 68 nm. Important solvatochromism was observed when **15** was characterized in solvents with different polarity and refractive index (η), with an increase of quantum yield up to ~ 41% in acetonitrile. Finally a PCMA film of **15** connected to a PV cell showed maximum optical efficiency of 7.7%, thus supporting the use of this compound as fluorophore for colorless LSC devices.

Appendix A.: Supplementary data

Supplementary data to this article can be found online at

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Supporting Information

Synthesis of new bis[1-(thiophenyl)propynones] as potential organic dyes for colourless luminescent solar concentrators (LSCs)

Gianluigi Albano, Tony Colli, Luigi Nucci, Rima Charaf, Tarita Biver, Andrea Pucci

and Laura Antonella Aronica*

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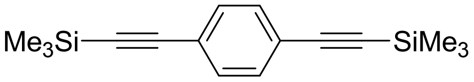
Experimental Section

Synthesis

Synthesis of diethynylarenes

Synthesis of 1,4-bis((trimethylsilyl)ethynyl)benzene (5)

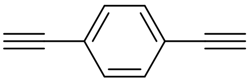
1,4-Dibromobenzene (**2**) (3.52 g, 14.9 mmol), Pd(PPh_3)$_4$ (215 mg, 0.19 mmol) and CuI (70 mg, 0.37 mmol) were mixed in Et_3N (50 mL), then trimethylsilylacetylene (5.2 mL, 36.6 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 7 h, then it was cooled to room temperature, hydrolyzed with saturated ammonium chloride solution (50 mL) and extracted with CH_2Cl_2 (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, *n*-hexane) to give 1,4-bis((trimethylsilyl)ethynyl)benzene (**5**) (3.94 g, yield 98%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 0.23 (18H, s); 7.37 (4H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): -0.11 (3C); 96.29; 104.58; 123.17; 131.74 (2C).

Synthesis of 1,4-diethynylbenzene (3)

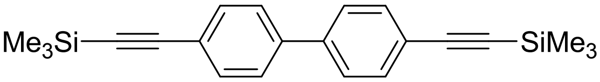
1,4-Bis((trimethylsilyl)ethynyl)benzene (**5**) (2.48 g, 9.16 mmol) and a 20 wt% NaOH aqueous solution (25 mL) were mixed in acetonitrile (50 mL) and *n*-hexane (25 mL). The resulting solution was left under stirring for 5 h at room temperature, then it was hydrolyzed with water (100 mL) and extracted with *n*-hexane (3x50 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, *n*-pentane) to give 1,4-diethynylbenzene (**3**) (1.10 g, yield 95%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 3.15 (2H, s); 7.42 (4H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 79.05; 83.01; 122.55; 132.00 (2C). LC-MS APCI (+): calcd for $C_{10}H_6$: 126.05; found *m/z* [M+H]$^+$: 127.0. Anal. calcd for $C_{10}H_6$: C, 95.21; H, 4.79; found: C, 95.25; H, 4.75.

Synthesis of 4,4'-bis((trimethylsilyl)ethynyl)-1,1'-biphenyl (8a)

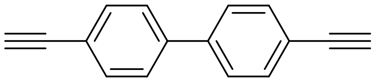
4,4'-Dibromo-1,1'-biphenyl (**7a**) (1.57 g, 5.03 mmol), Pd(PPh_3)$_4$ (71 mg, 0.061 mmol) and CuI (23 mg, 0.12 mmol) were mixed in Et_3N (20 mL), then trimethylsilylacetylene (1.7 mL, 12.3 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 6 h, then it was cooled to room temperature and left under stirring for further 18 h. The reaction mixture was then hydrolyzed with saturated ammonium chloride solution (20 mL) and extracted with CH_2Cl_2 (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, petroleum ether → CH_2Cl_2) to give 4,4'-bis((trimethylsilyl)ethynyl)-1,1'-biphenyl (**8a**) (1.72 g, yield 99%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 0.24 (18H, s); 7.51 (8H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): -0.04 (3C); 95.22; 104.83; 122.42; 126.71 (2C); 132.44 (2C); 140.19.

Synthesis of 4,4'-diethynyl-1,1'-biphenyl (9a)

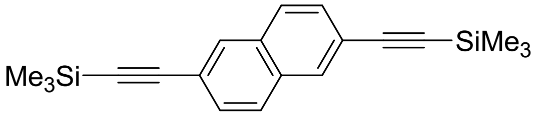
4,4'-Bis((trimethylsilyl)ethynyl)-1,1'-biphenyl (**8a**) (867 mg, 2.50 mmol) and a 3.5 M aqueous KOH solution (1.6 mL, 5.6 mmol) were mixed in THF (40 mL) and methanol (10 mL). The resulting solution was left under stirring for 4 h at room temperature, then it was hydrolyzed with water (50 mL) and extracted with *n*-hexane (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:1) to give 4,4'-diethynyl-1,1'-biphenyl (**9a**) (444 mg, yield 88%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 3.12 (2H, s); 7.51-7.56 (8H, m). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 78.05; 83.38; 121.51; 126.90 (2C); 132.64 (2C); 140.56. LC-MS APCI (+): calcd for $C_{16}H_{10}$: 202.08; found *m/z* $[M+H]^+$: 203.1. Anal. calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98; found: C, 95.08; H, 4.92.

Synthesis of 2,6-bis((trimethylsilyl)ethynyl)naphthalene (8b)

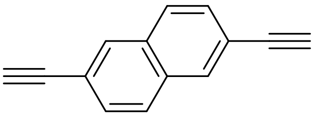
2,6-Dibromonaphthalene (**7b**) (570 mg, 2.00 mmol), $Pd(PPh_3)_4$ (28 mg, 0.024 mmol) and CuI (11 mg, 0.058 mmol) were mixed in Et_3N (20 mL), then trimethylsilylacetylene (0.7 mL, 5.06 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 5 h, then it was cooled to room temperature and left under stirring for further 19 h. The reaction mixture was then hydrolyzed with saturated ammonium chloride solution (20 mL) and extracted with CH_2Cl_2 (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, petroleum ether) to give 2,6-bis((trimethylsilyl)ethynyl)naphthalene (**8b**) (527 mg, yield 82%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 0.26 (18H, s); 7.47 (2H, d, *J* = 8.4 Hz); 7.67 (2H, d, *J* = 8.4 Hz); 7.92 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): -0.04 (3C); 95.44; 105.15; 121.33; 127.68; 129.27; 131.71; 132.31.

Synthesis of 2,6-diethynylnaphthalene (9b)

2,6-Bis((trimethylsilyl)ethynyl)naphthalene (**8b**) (527 mg, 1.64 mmol) and a 3.5 M aqueous KOH solution (1.0 mL, 3.5 mmol) were mixed in THF (20 mL) and methanol (5 mL). The resulting solution was left under stirring for 4 h at room temperature, then it was hydrolyzed with water (25 mL) and extracted with *n*-hexane (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 1:1) to give 2,6-diethynylnaphthalene (**9b**) (277 mg, yield 96%).

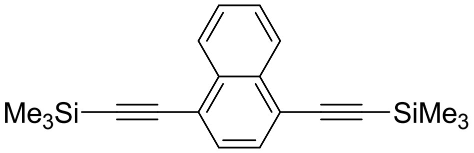


^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 3.16 (2H, s); 7.52 (2H, d, *J* = 8.4 Hz); 7,72 (2H, d, *J* = 8.4 Hz); 7.97 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 78.18; 83.66; 120.48; 127.86; 129.34; 132.04; 132.40. LC-MS APCI (+):

calcd for $C_{14}H_8$: 176.06; found *m/z* $[M+H]^+$: 177.0. Anal. calcd for $C_{14}H_8$: C, 95.42; H, 4.58; found: C, 95.50; H, 4.50.

Synthesis of 1,4-bis((trimethylsilyl)ethynyl)naphthalene (8c)

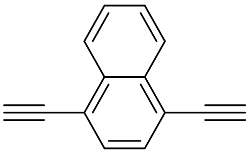
1,4-Dibromonaphthalene (**7c**) (1.43 g, 5.00 mmol), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol) and CuI (27 mg, 0.14 mmol) were mixed in Et_3N (20 mL), then trimethylsilylacetylene (1.7 mL, 12.3 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 11 h, then it was cooled to room temperature and left under stirring for further 37 h. The reaction mixture was then hydrolyzed with saturated ammonium chloride solution (20 mL) and extracted with CH_2Cl_2 (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to give 1,4-bis((trimethylsilyl)ethynyl)naphthalene (**8c**) (1.59 g, yield 99%) which was used without any further purification.



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 0.35 (18H, s); 7.62 (2H, dd, *J* = 6.6, 3.3 Hz); 7.66 (2H, s); 8.37 (2H, dd, *J* = 6.6, 3.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 0.03 (3C); 101.36; 102.79; 121.54; 126.55; 127.24; 129.97; 133.08.

Synthesis of 1,4-diethynylnaphthalene (9c)

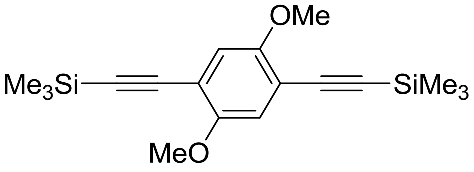
1,4-Bis((trimethylsilyl)ethynyl)naphthalene (**8c**) (1.59 g, 4.95 mmol) and a 3.5 M aqueous KOH solution (3.0 mL, 10.5 mmol) were mixed in THF (64 mL) and methanol (16 mL). The resulting solution was left under stirring for 4 h at room temperature, then it was hydrolyzed with water (80 mL) and extracted with *n*-hexane (3x50 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, *n*-hexane → CH_2Cl_2) to give 1,4-diethynylnaphthalene (**9c**) (698 mg, yield 80%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 3.55 (2H, s); 7.59 (2H, dd, *J* = 6.6, 3.3 Hz); 7.67 (2H, s); 8.38 (2H, dd, *J* = 6.6, 3.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 81.39; 83.63; 120.92; 126.41; 127.44; 130.28; 133.15. LC-MS APCI (+): calcd for $C_{14}H_8$: 176.06; found *m/z* $[M+H]^+$: 177.0. Anal. calcd for $C_{14}H_8$: C, 95.42; H, 4.58; found: C, 95.52; H, 4.48.

Synthesis of 2,5-dimethoxy-1,4-bis((trimethylsilyl)ethynyl)benzene (12)

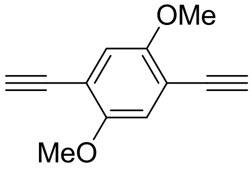
1,4-Dibromo-2,5-dimethoxybenzene (**11**) (3.02 g, 10.2 mmol), $Pd(PPh_3)_4$ (139 mg, 0.12 mmol) and CuI (55 mg, 0.29 mmol) were mixed in THF (30 mL) and Et_3N (10 mL), then trimethylsilylacetylene (3.5 mL, 25.3 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 7 h, then it was cooled to room temperature and left under stirring for further 17 h. The reaction mixture was then hydrolyzed with saturated ammonium chloride solution (40 mL) and extracted with CH_2Cl_2 (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified by recrystallization from methanol to give 2,5-dimethoxy-1,4-bis((trimethylsilyl)ethynyl)benzene (**12**) (2.97 g, yield 88%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 0.29 (18H, s); 3.86 (6H, s); 6.93 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): -0.02 (3C); 56.42; 100.40; 100.82; 113.44; 116.22; 154.18.

Synthesis of 1,4-diethynyl-2,5-dimethoxybenzene (13)

2,5-Dimethoxy-1,4-bis((trimethylsilyl)ethynyl)benzene (**12**) (1.01 g, 3.05 mmol) and a 3.5 M aqueous KOH solution (1.9 mL, 6.65 mmol) were mixed in THF (45 mL) and methanol (45 mL). The resulting solution was left under stirring for 4 h at room temperature, then it was hydrolyzed with water (90 mL) and extracted with *n*-hexane (3x60 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, petroleum ether/CH_2Cl_2 3:2) to give 1,4-diethynyl-2,5-dimethoxybenzene (**13**) (483 mg, yield 85%).

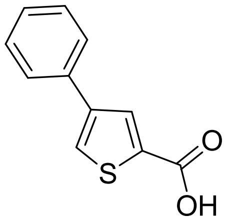


^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 3.42 (2H, s); 3.88 (6H, s); 7.00 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 56.43; 79.66; 82.77; 112.66; 116.19; 154.42. LC-MS APCI (+): calcd for $C_{12}H_{10}O_2$: 186.07; found *m/z* $[M+H]^+$: 187.1. Anal. calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41; found: C, 77.27; H, 5.38.

Synthesis of thiophene acid chlorides

Synthesis of 4-phenylthiophene-2-carboxylic acid

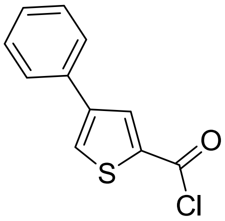
Methyl 4-phenylthiophene-2-carboxylate (1.06 g, 4.86 mmol) and a 5 wt% NaOH aqueous solution (15 mL) were mixed together. The resulting solution was left under stirring for 24 h at room temperature, then it was hydrolyzed with a 2 M aqueous HCl solution (20 mL) and extracted with ethyl acetate (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to give 4-phenylthiophene-2-carboxylic acid (963 mg, yield 97%) which was used without any further purification.



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.31-7.34 (1H, m); 7.40-7.43 (2H, m); 7.59 (2H, d, *J* = 7.3 Hz); 7.73 (1H, d, *J* = 1.5 Hz); 8.15 (1H, d, *J* = 1.5 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 126.37 (2C); 127.89; 128.50; 129.02 (2C); 133.33; 133.69; 134.63; 143.37; 167.16.

Synthesis of 4-phenylthiophene-2-carbonyl chloride (4d)

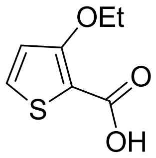
4-Phenylthiophene-2-carboxylic acid (408 mg, 2.00 mmol), CH_2Cl_2 (20 mL) and 1,4-dioxane (0.5 mL) were mixed together, then oxalyl chloride (0.5 mL, 5.73 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was left under stirring for 48 h at room temperature, then the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2) to give 4-phenylthiophene-2-carbonyl chloride (**4d**) (263 mg, yield 59%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.34-7.38 (1H, m); 7.41-7.45 (2H, m); 7.56 (2H, d, *J* = 7.2 Hz); 7.88 (1H, d, *J* = 1.4 Hz); 8.20 (1H, d, *J* = 1.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 126.34 (2C); 128.32; 129.13 (2C); 131.93; 133.93; 136.24; 137.82; 143.94; 159.81.

Synthesis of 3-ethoxythiophene-2-carboxylic acid

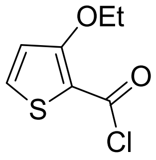
Methyl 3-ethoxythiophene-2-carboxylate (933 mg, 5.01 mmol) and a 5 wt% NaOH aqueous solution (15 mL) were mixed together. The resulting solution was left under stirring for 24 h at 50 °C, then it was hydrolyzed with a 2 M aqueous HCl solution (20 mL) and extracted with ethyl acetate (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to give 3-ethoxythiophene-2-carboxylic acid (822 mg, yield 95%) which was used without any further purification.



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 1.45 (3H, t, *J* = 7.2 Hz); 4.26 (2H, q, *J* = 7.2 Hz); 6.83 (1H, d, *J* = 5.6 Hz); 7,49 (1H, d, *J* = 5.6 Hz); 10.53 (1H, bs). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 14.87; 68.42; 110.88; 116.19; 132.46; 160.38; 164.06.

Synthesis of 3-ethoxythiophene-2-carbonyl chloride (4e)

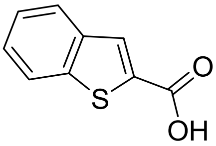
3-Ethoxythiophene-2-carboxylic acid (822 mg, 4.78 mmol) and CH_2Cl_2 (20 mL) were mixed together, then oxalyl chloride (1.3 mL, 14.9 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was left under stirring for 24 h at room temperature, then the solvent was removed under vacuum to give 3-ethoxythiophene-2-carbonyl chloride (**4e**) (922 mg, yield 97%) which was used without any further purification.



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 1.46 (3H, t, *J* = 7.2 Hz); 4.23 (2H, q, *J* = 7.2Hz); 6.84 (1H, d, *J* = 5.6 Hz); 7.62 (1H, d, *J* = 5.6 Hz).

Synthesis of benzo[*b*]thiophene-2-carboxylic acid

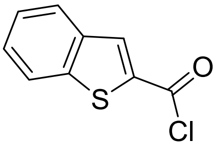
Methyl benzo[*b*]thiophene-2-carboxylate (505 mg, 2.63 mmol) and a 5 wt% NaOH aqueous solution (10 mL) were mixed together. The resulting solution was left under stirring for 24 h at room temperature, then it was hydrolyzed with a 2 M aqueous HCl solution (10 mL) and extracted with ethyl acetate (3x20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to give benzo[*b*]thiophene-2-carboxylic acid (458 mg, yield 98%) which was used without any further purification.



^{1}H-NMR (400 MHz, DMSO-d_6), δ (ppm): 7.45-7.54 (2H, m); 8.00-8.06 (2H, m); 8.12 (1H, s); 13.48 (1H, bs). ^{13}C-NMR (100 MHz, DMSO-d_6), δ (ppm): 123.89; 125.97; 126.65; 127.92; 131.13; 135.72; 139.66; 142.24; 164.45.

Synthesis of benzo[*b*]thiophene-2-carbonyl chloride (4f)

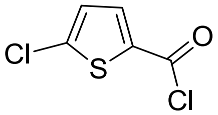
Benzo[*b*]thiophene-2-carboxylic acid (458 mg, 2.57 mmol), CH_2Cl_2 (25 mL), 1,4-dioxane (2 mL) and DMF (3 drops) were mixed together, then oxalyl chloride (1.0 mL, 11.5 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was refluxed under stirring for 48 h, then it was cooled to room temperature and the solvent was removed under vacuum to give benzo[*b*]thiophene-2-carbonyl chloride (**4f**) (453 mg, yield 90%) which was used without any further purification.



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.45 (1H, t, *J* = 8.0 Hz); 7.53 (1H, t, *J* = 8.0 Hz); 7.86 (1H, d, *J* = 8.0 Hz); 7.93 (1H, d, *J* = 8.0 Hz); 8.27 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 122.91; 125.66; 126.68; 128.75; 135.89; 136.59; 138.05; 144.07; 161.14.

Synthesis of 5-chlorothiophene-2-carbonyl chloride (4g)

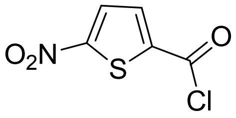
5-chlorothiophene-2-carboxylic acid (3.01 g, 18.5 mmol), CH_2Cl_2 (45 mL) and DMF (0.5 mL) were mixed together, then oxalyl chloride (4.5 mL, 52.4 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was left under stirring for 24 h at room temperature, then the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2) to give 5-chlorothiophene-2-carbonyl chloride (**4g**) (3.13 g, yield 93%).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.04 (1H, d, *J* = 4.2 Hz); 7.79 (1H, d, *J* = 4.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 128.32; 135.05; 137.57; 143.26; 158.67.

Synthesis of 5-nitrothiophene-2-carbonyl chloride (4h)

5-nitrothiophene-2-carboxylic acid (2.00 g, 11.5 mmol) and CH_2Cl_2 (30 mL) were mixed together, then oxalyl chloride (6.0 mL, 69.8 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was left under stirring for 24 h at room temperature, then it was cooled to room temperature and the solvent was removed under vacuum to give 5-nitrothiophene-2-carbonyl chloride (**4h**) (2.23 g, yield 99%) which was used without any further purification.



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.89 (1H, d, *J* = 4.4 Hz); 7.93 (1H, d, *J* = 4.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 127.89; 136.25; 141.10; 158.21; 159.76.

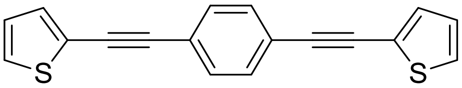
Synthesis of bis(thiophenylethynyl)arene dyes

General procedure

In a typical run, diethynylarene (1.0 mmol), 2-iodothiophene (2.5 mmol), $PdCl_2(PPh_3)_2$ (2 mol%), CuI (4 mol%) and Et_3N (20 mL) were mixed together in a 50 mL two-necked round bottom flask. The resulting mixture was left under stirring for 7 h at 50 °C, then it was cooled to room temperature and left under stirring for further 17 h. The reaction mixture was then hydrolysed with saturated ammonium chloride solution (20 mL) and extracted with CH_2Cl_2 (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. All the crude products were purified by recrystallization or column chromatography on silica gel and characterized with ^{1}H-NMR, ^{13}C-NMR, LC-MS and elemental analysis techniques.

1,4-Bis(thiophen-2-ylethynyl)benzene (6)

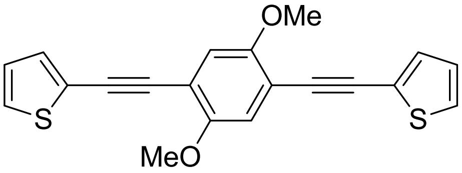
According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 2-iodothiophene (525 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (8 mg, 0.04 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified by recrystallization from $CHCl_3$, giving 200 mg (yield 69%) of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**).



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.00-7.02 (2H, m); 7.28-7.30 (4H, m); 7.47 (4H, s). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 84.61; 92.74; 122.86; 123.04; 127.17; 127.61; 131.30 (2C); 132.16. LC-MS APCI (+): calcd for $C_{18}H_{10}S_2$: 290.02; found *m/z* $[M+H]^+$: 291.1. Anal. calcd for $C_{18}H_{10}S_2$: C, 74.45; H, 3.47; S, 22.08; found: C, 74.57; H, 3.34; S, 22.09.

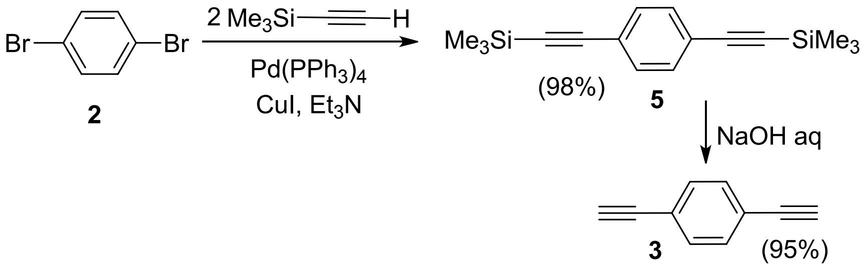
2,2'-((2,5-Dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (14)

According to the general procedure, 1,4-diethynyl-2,5-dimethoxybenzene (**13**) (186 mg, 1.0 mmol), 2-iodothiophene (525 mg, 2.5 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (8 mg, 0.04 mmol) and Et_3N (20 mL) were mixed together. The crude product was purified through column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 3:5), giving 211 mg (yield 60%) of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (**14**).

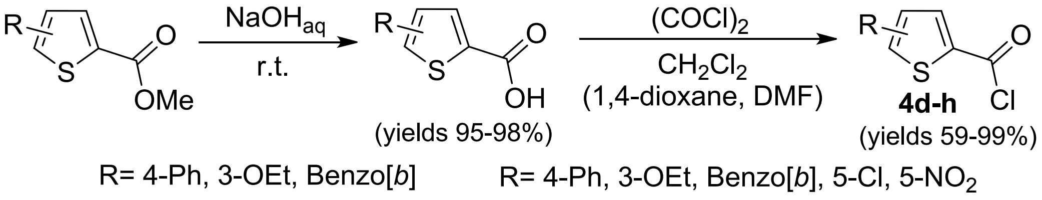


^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 3.92 (6H, s); 7.03 (2H, s); 7.04-7.06 (2H, m); 7.33-7.35 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 56.46; 88.26; 89.36; 113.21; 115.37; 123.19; 127.13; 127.59; 132.21; 153.78. LC-MS APCI (+): calcd for $C_{20}H_{14}O_2S_2$: 350.04; found *m/z* $[M+H]^+$: 351.2. Anal. calcd for $C_{20}H_{14}O_2S_2$: C, 68.54; H, 4.03; S, 18.30; found: C, 68.59; H, 4.11; S, 18.32.

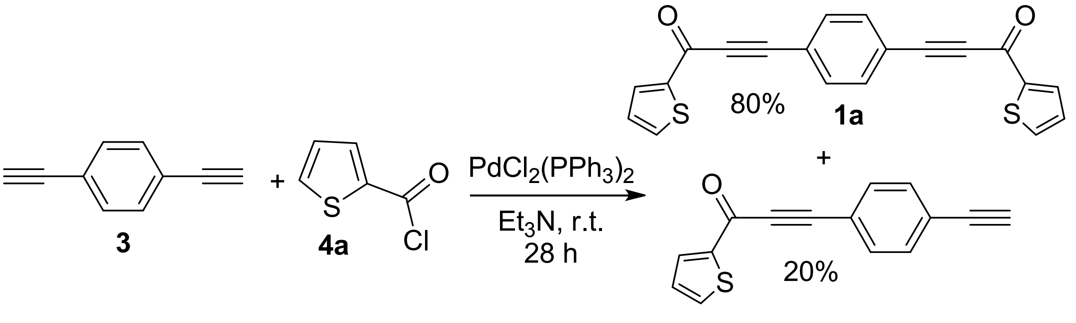
Supplementary Schemes



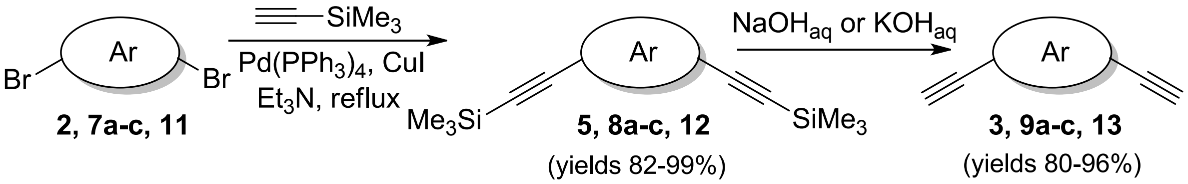
Scheme S1. Synthesis of 1,4-diethynylbenzene (**3**).



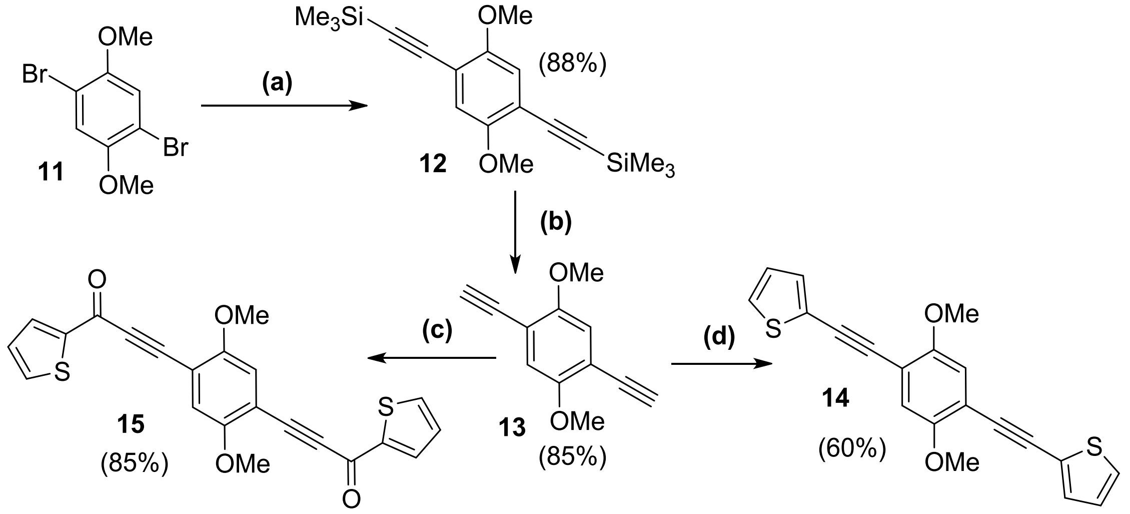
Scheme S2. General scheme for the synthesis of thiophene acid chlorides **4d-h**.



Scheme S3. Preliminary acyl Sonogashira reaction between 1,4-diethynylbenzene (**3**) and thiophene-2-carbonyl chloride (**4a**) performed at room temperature.



Scheme S4. General scheme for the synthesis of diethynylarenes **3**, **9a-c** and **13**.



Scheme S5. Synthesis of the dimethoxy-substituted dyes **14** and **15**.

Supplementary Figures

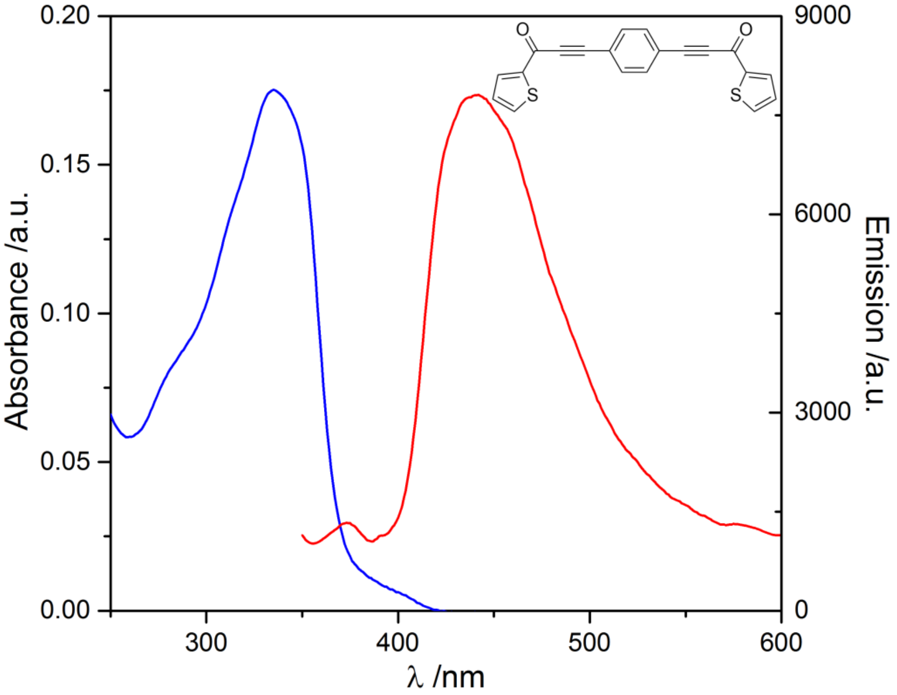


Figure S1. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

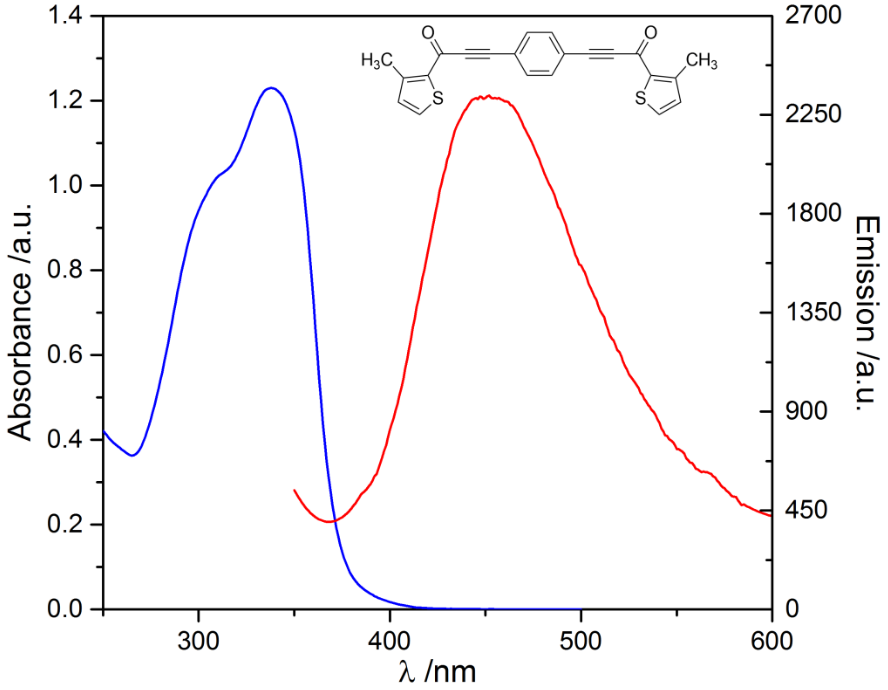


Figure S2. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one) (**1b**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

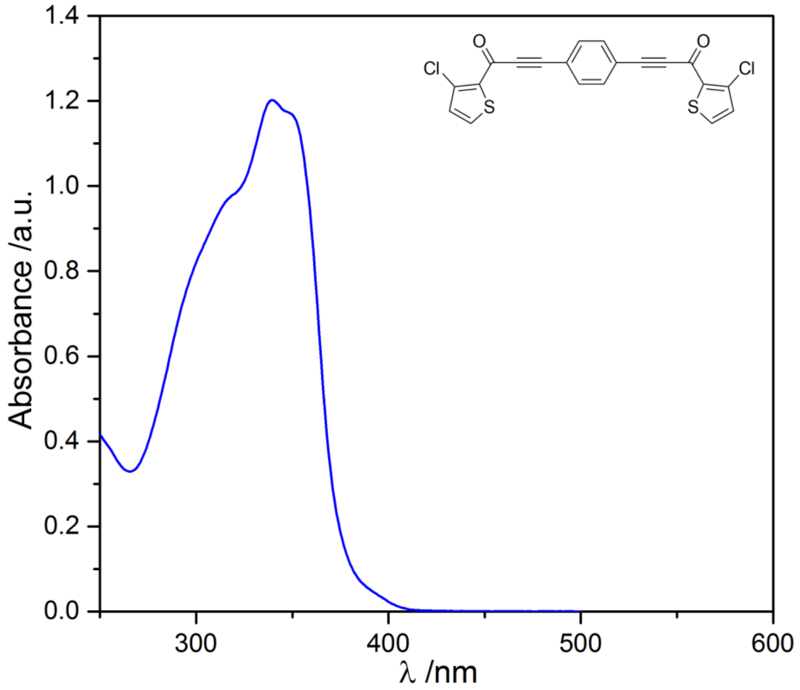


Figure S3. UV-Vis absorption spectrum (blue line) of 3,3'-(1,4-phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (**1c**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm.

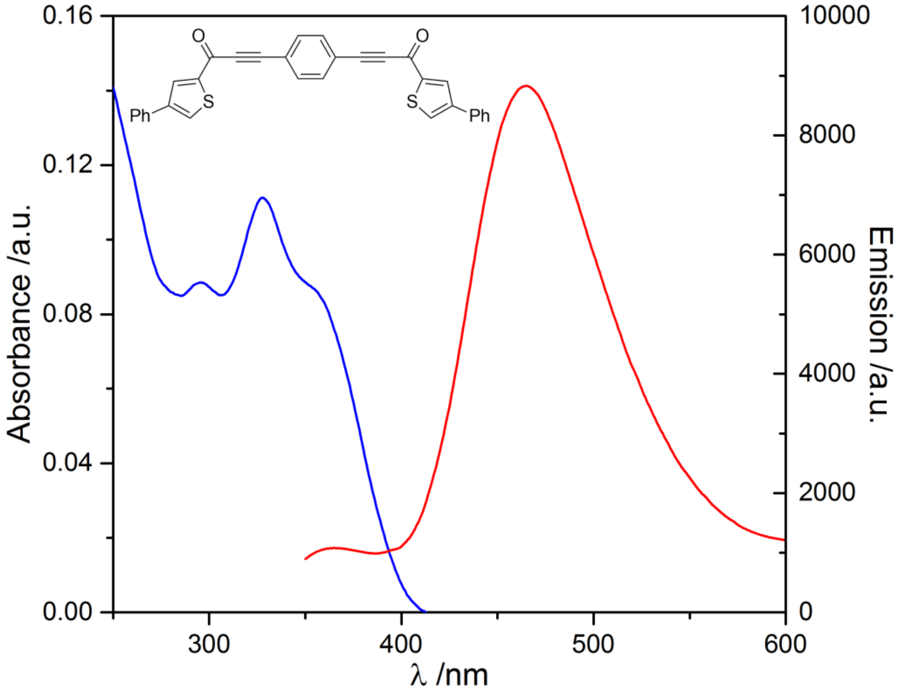


Figure S4. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

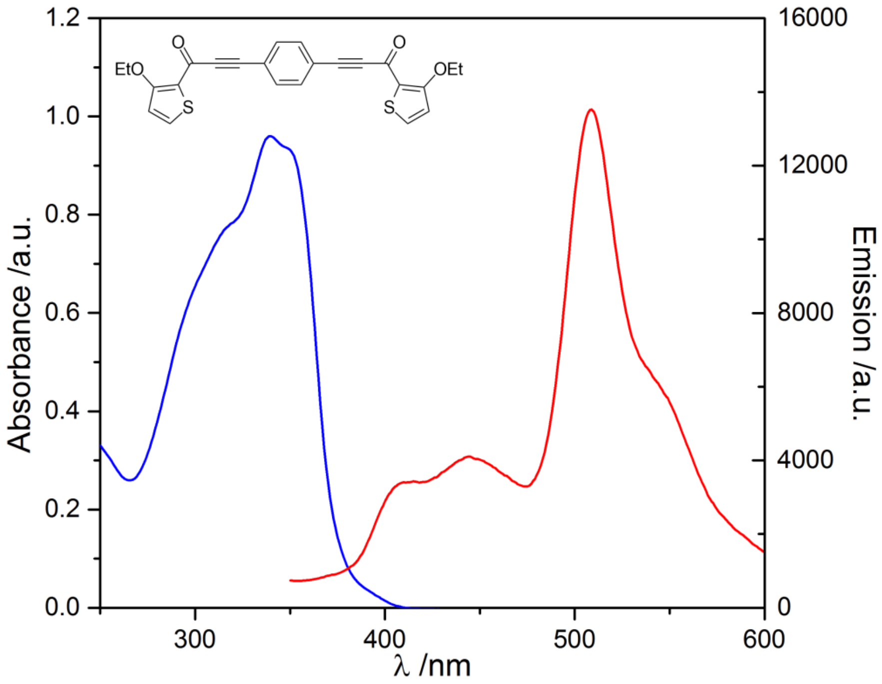


Figure S5. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

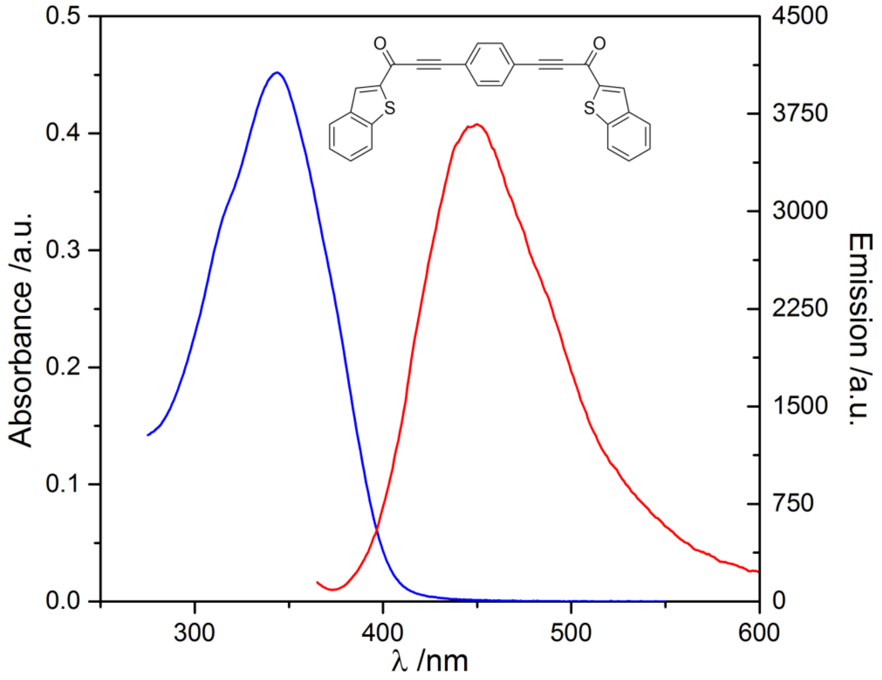


Figure S6. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(benzo[*b*]thiophen-2-yl)prop-2-yn-1-one) (**1f**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

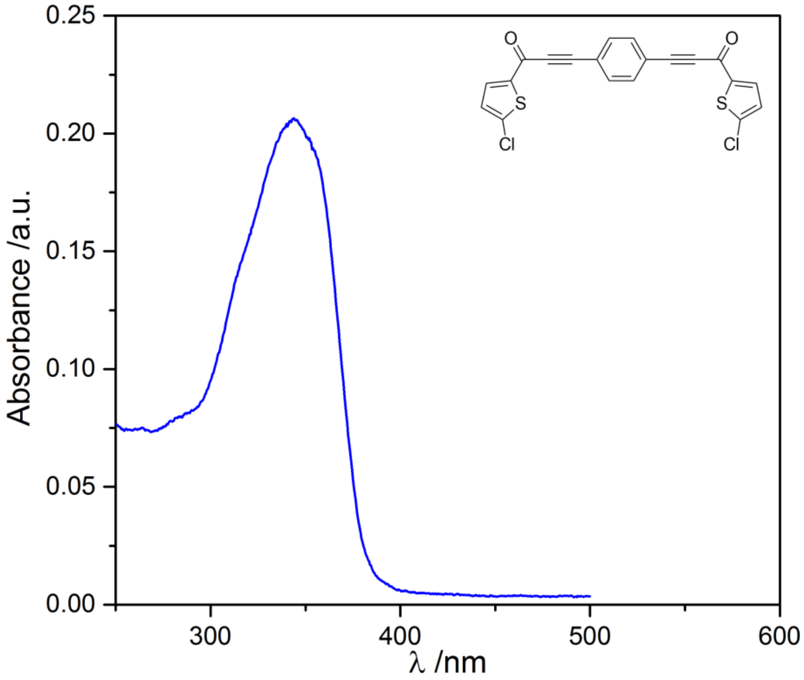


Figure S7. UV-Vis absorption spectrum (blue line) of 3,3'-(1,4-phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (**1g**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm.

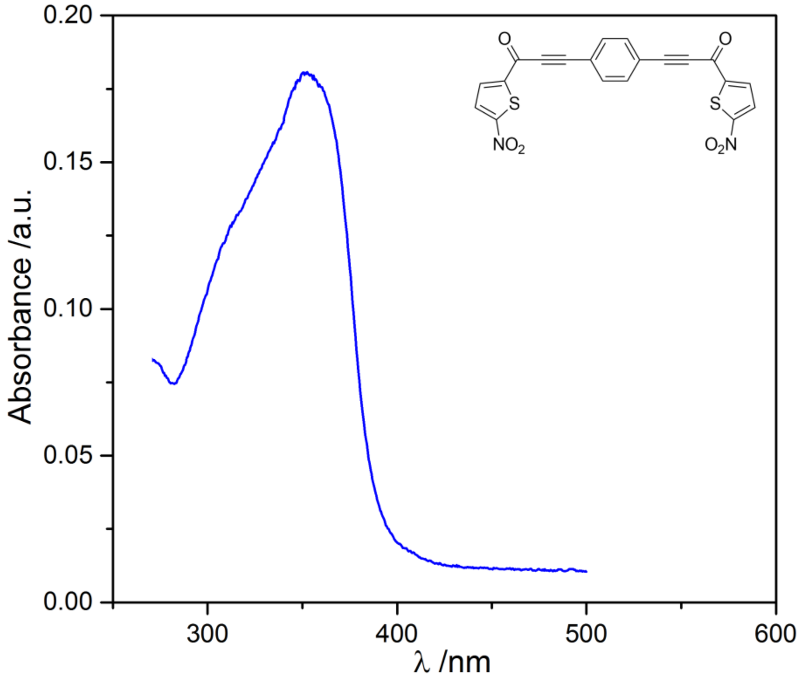


Figure S8. UV-Vis absorption spectrum (blue line) of 3,3'-(1,4-phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm.

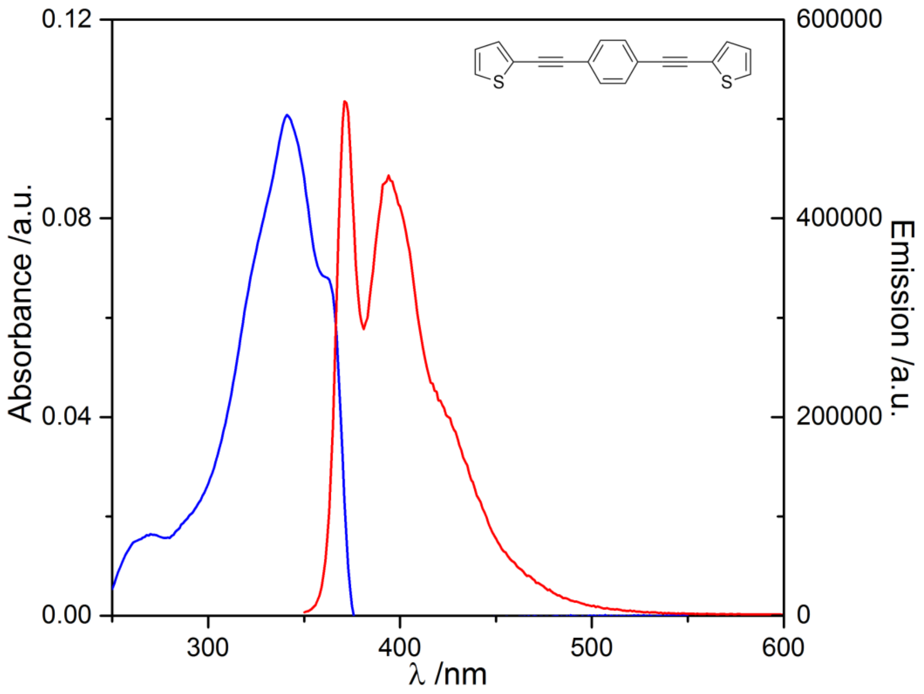


Figure S9. UV-Vis absorption (blue line) and emission (red line) spectra of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

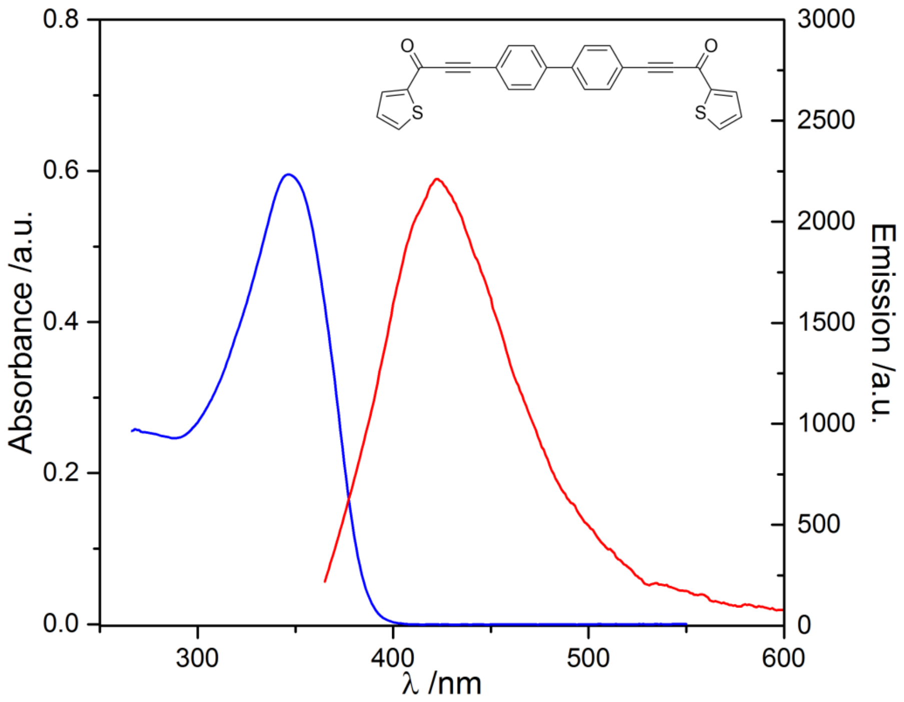


Figure S10. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10a**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

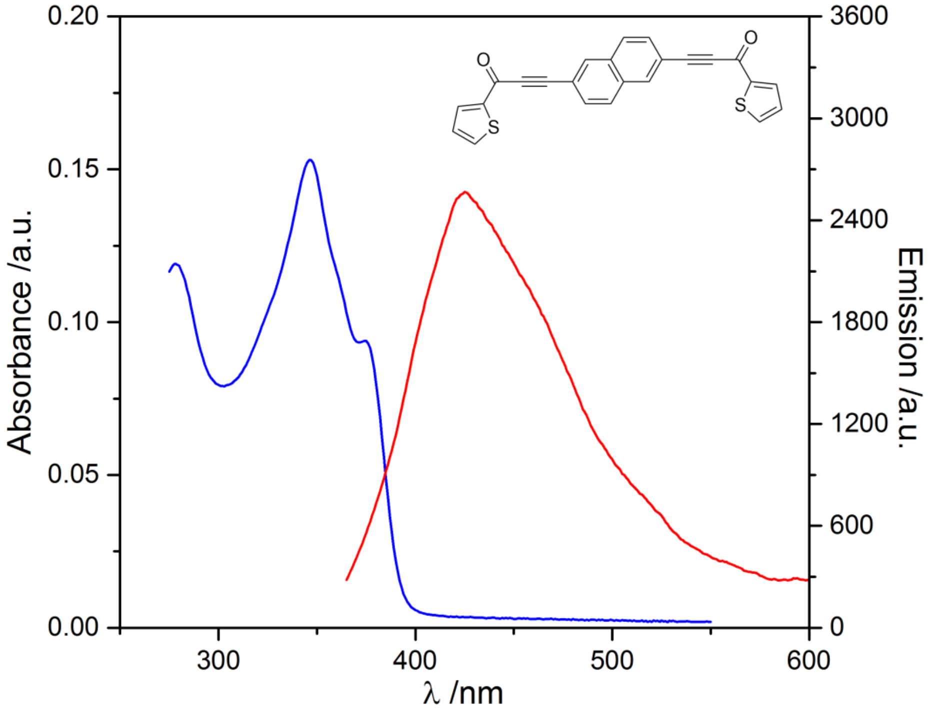


Figure S11. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

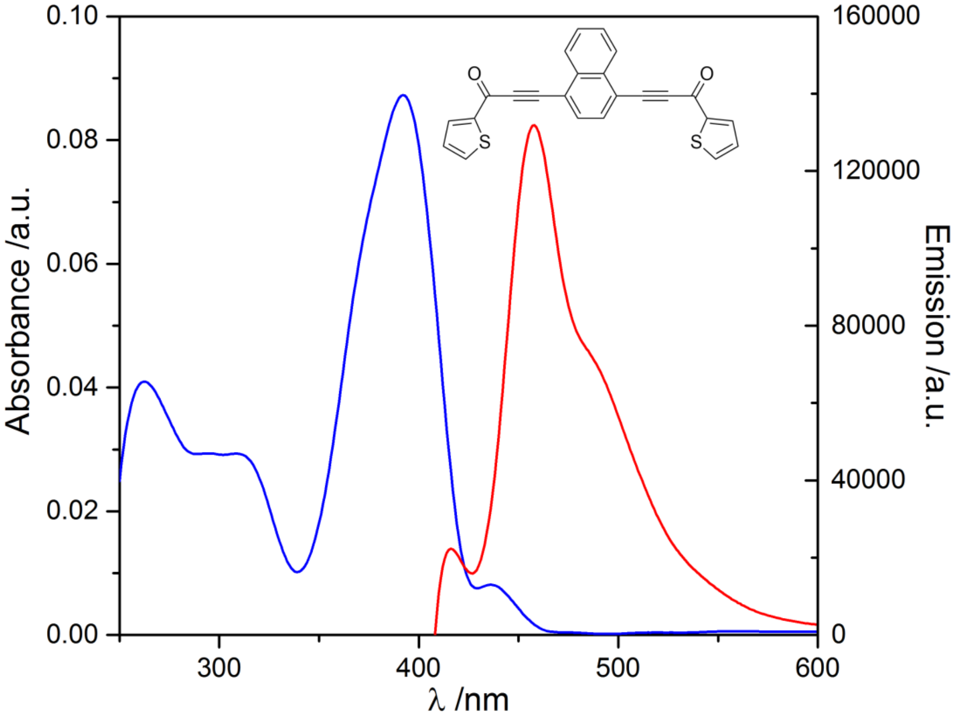


Figure S12. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

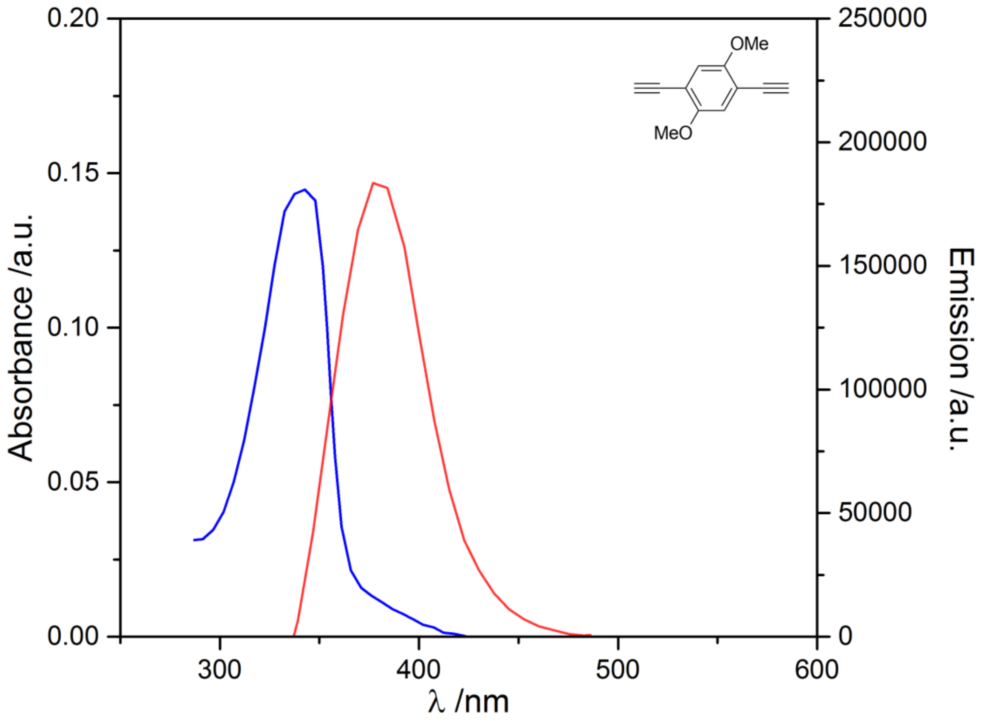


Figure S13. UV-Vis absorption (blue line) and emission (red line) spectra of 1,4-diethynyl-2,5-dimethoxybenzene (**13**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

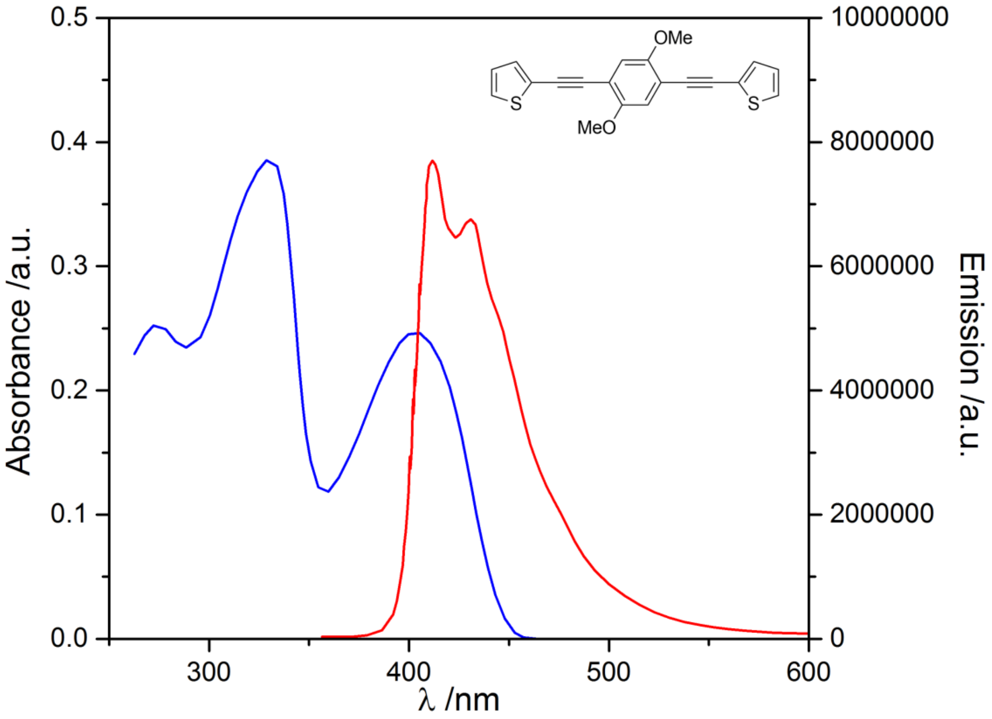


Figure S14. UV-Vis absorption (blue line) and emission (red line) spectra of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (**14**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

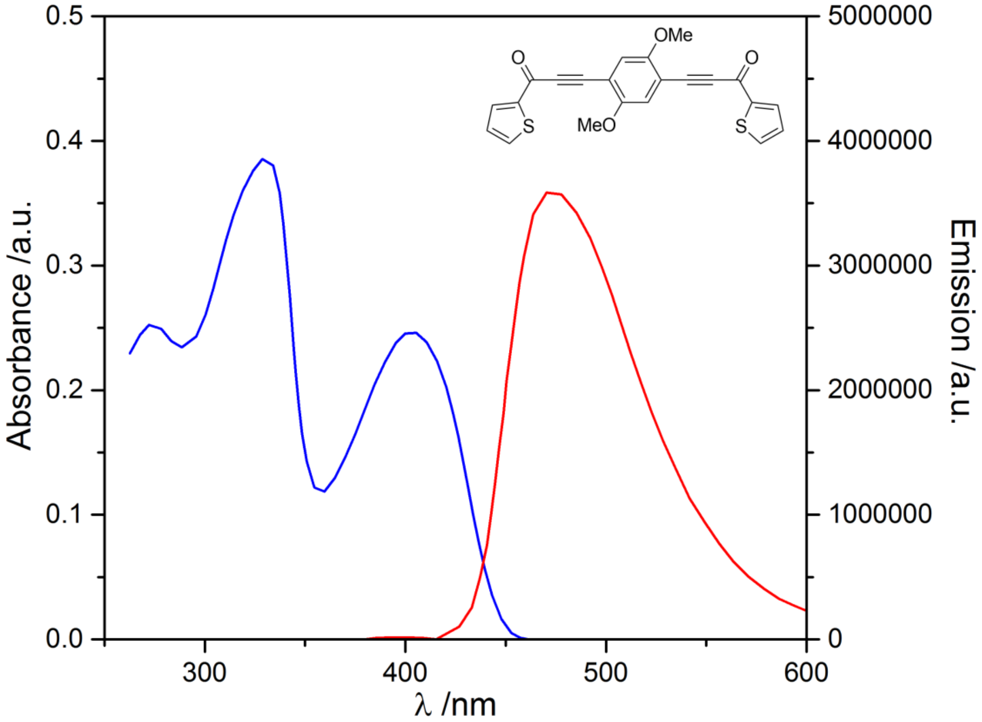


Figure S15. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) in $CHCl_3$. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

NMR Spectra

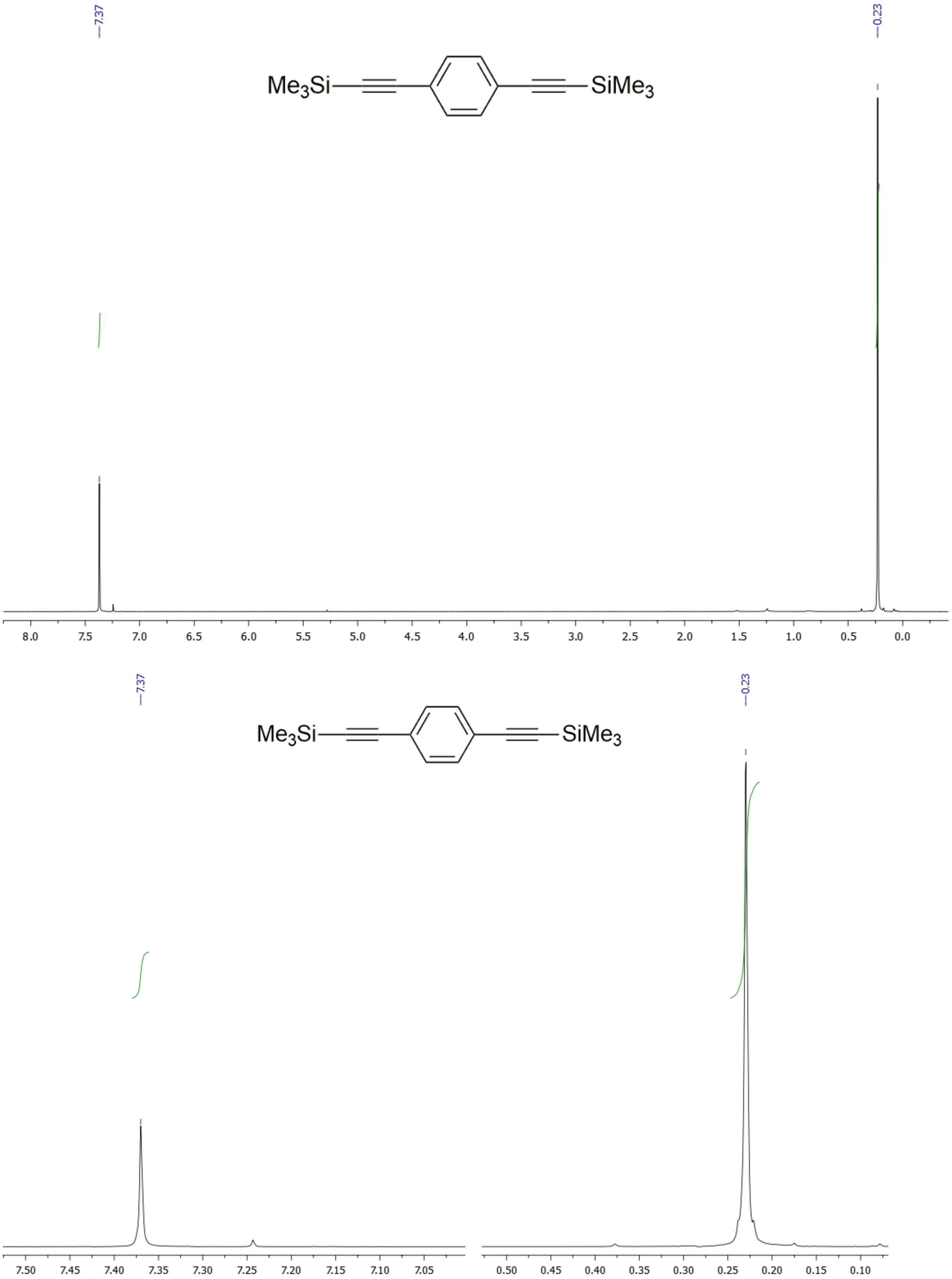


Figure S16. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 1,4-bis((trimethylsilyl)ethynyl)benzene (**5**): full scale spectrum (top) and spectrum expansions (bottom).

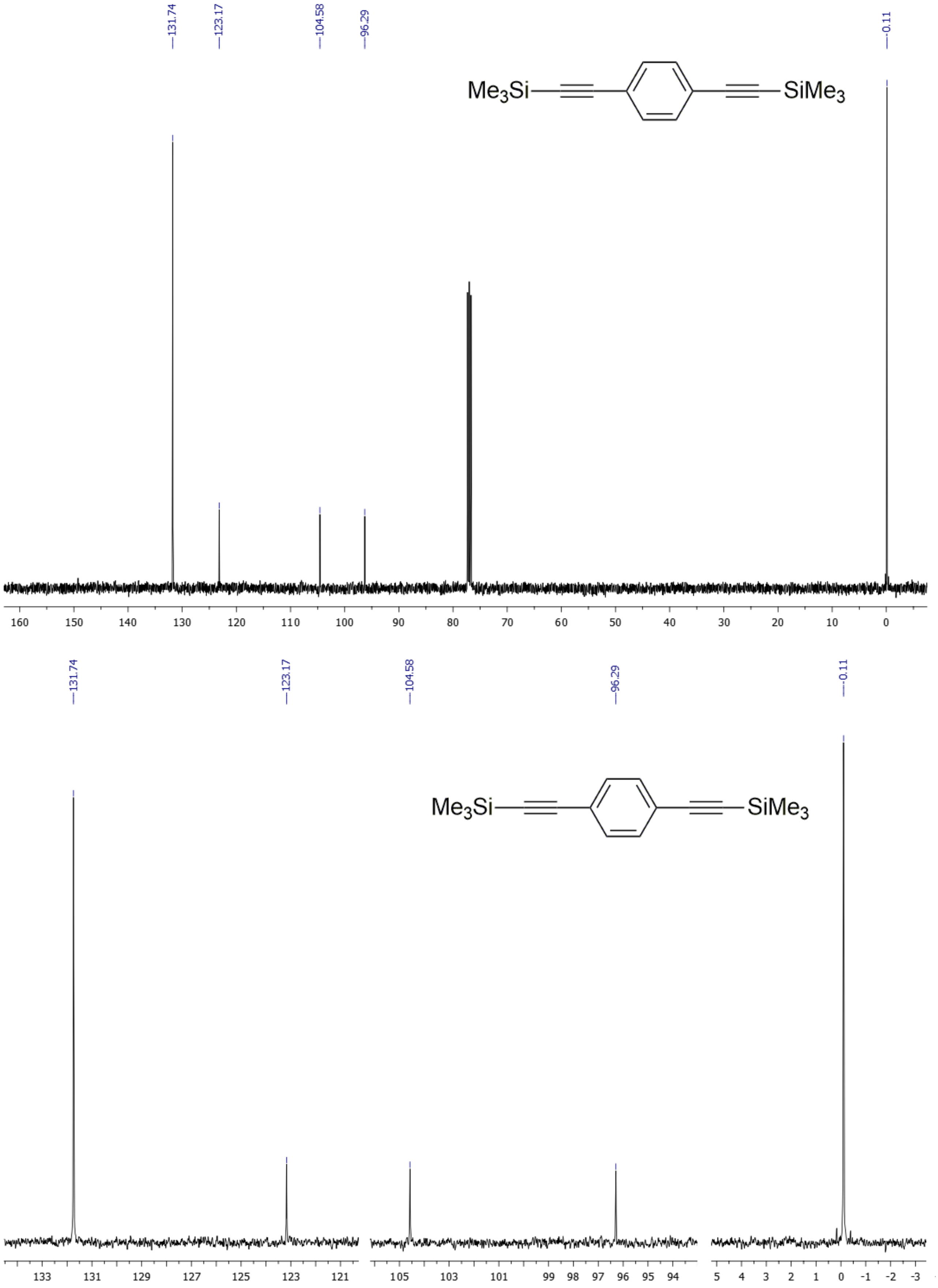


Figure S17. ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of 1,4-bis((trimethylsilyl)ethynyl)benzene (**5**): full scale spectrum (top) and spectrum expansions (bottom).

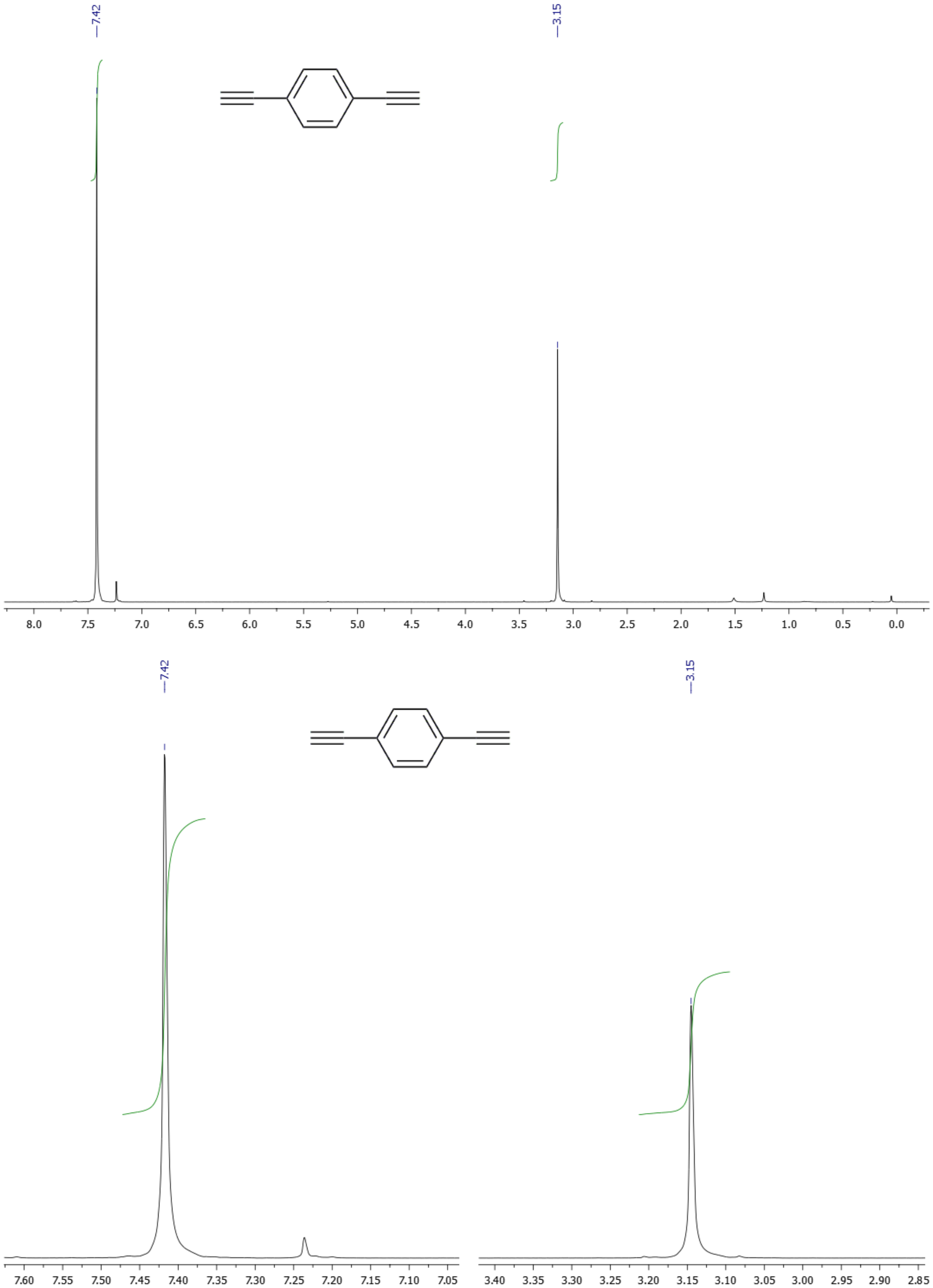


Figure S18. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 1,4-diethynylbenzene (**3**): full scale spectrum (top) and spectrum expansions (bottom).

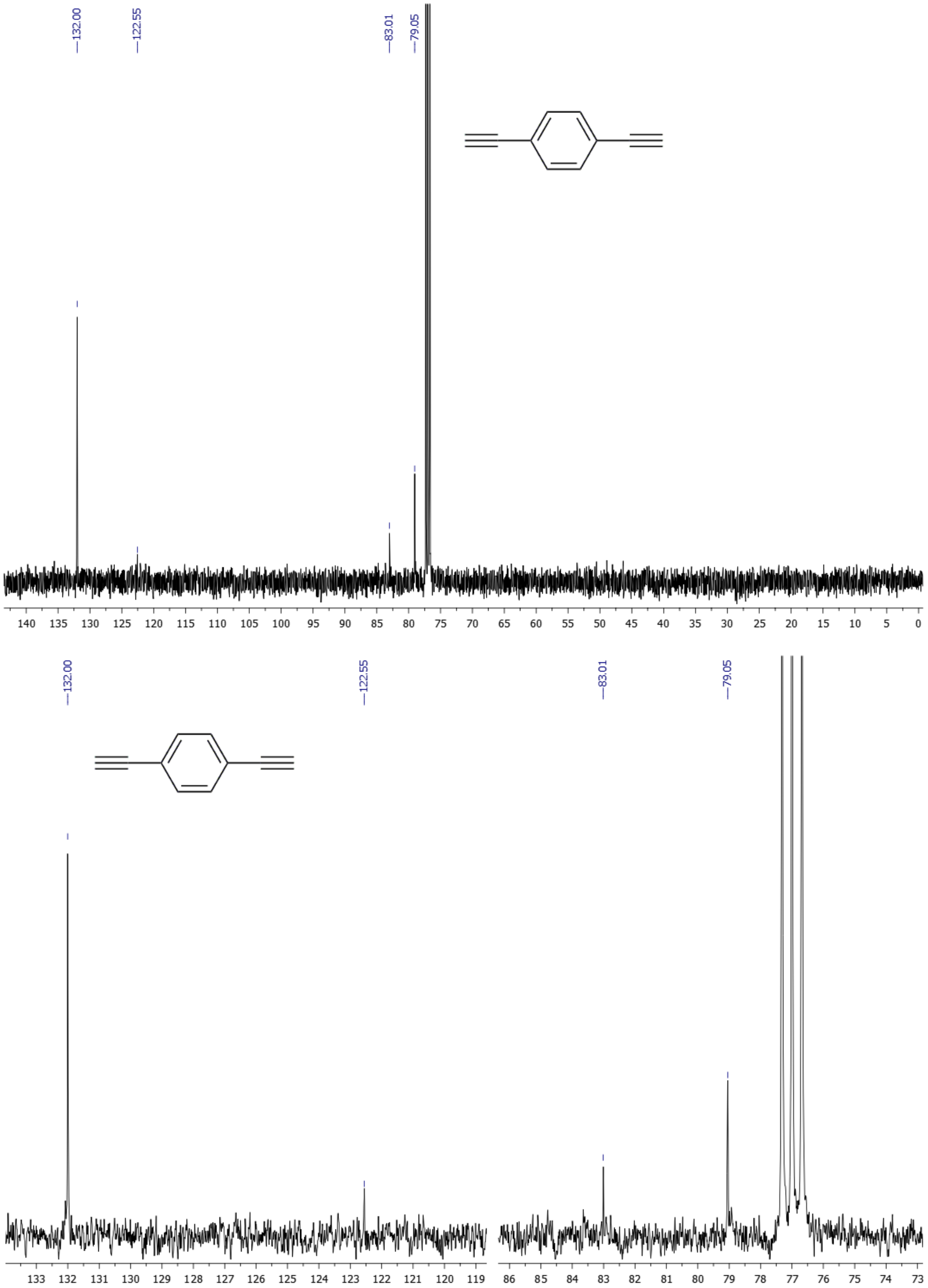


Figure S19. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 1,4-diethynylbenzene (**3**): full scale spectrum (top) and spectrum expansions (bottom).

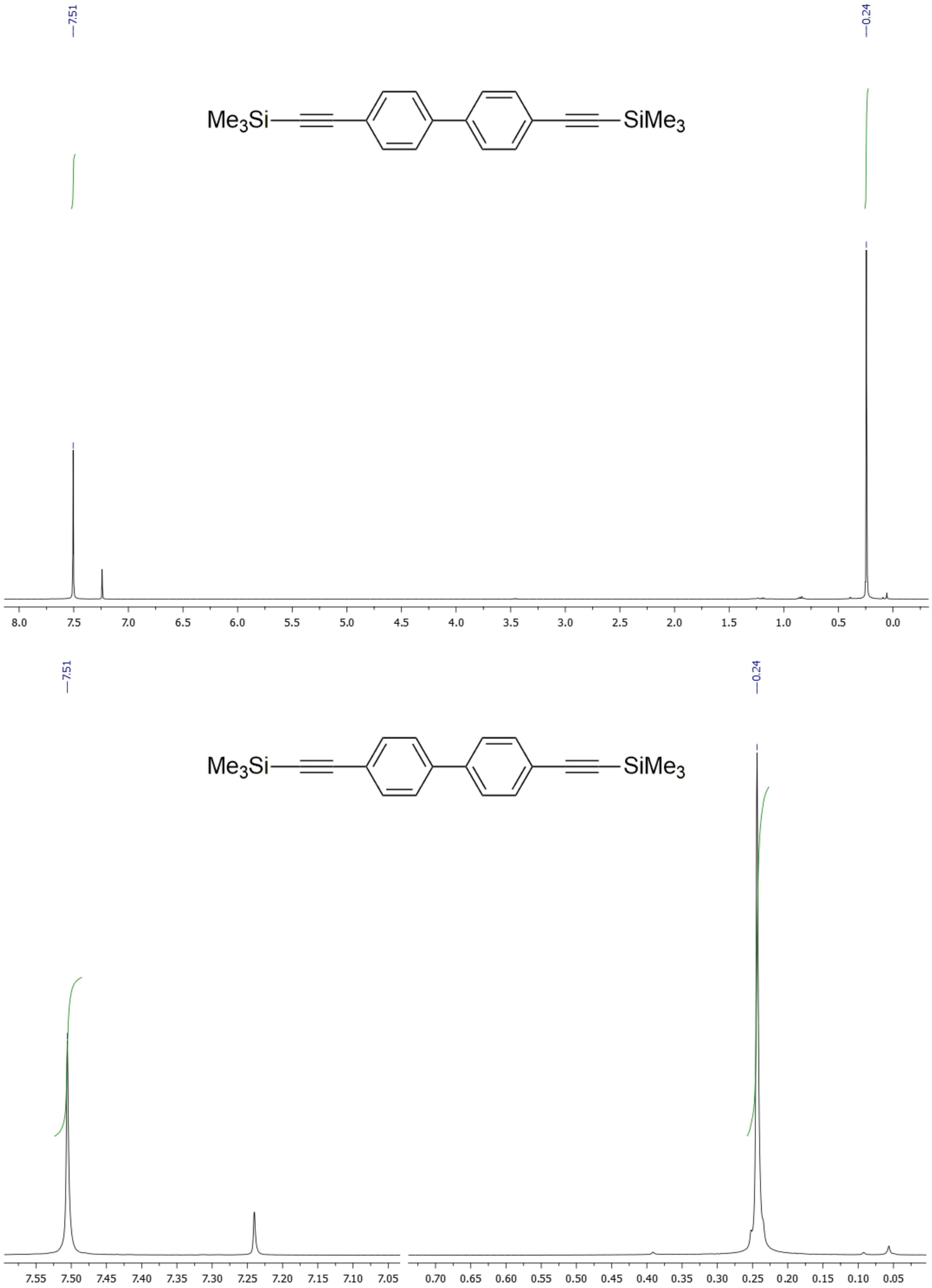


Figure S20. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 4,4'-bis((trimethylsilyl)ethynyl)-1,1'-biphenyl (**8a**):full scale spectrum (top) and spectrum expansions (bottom).

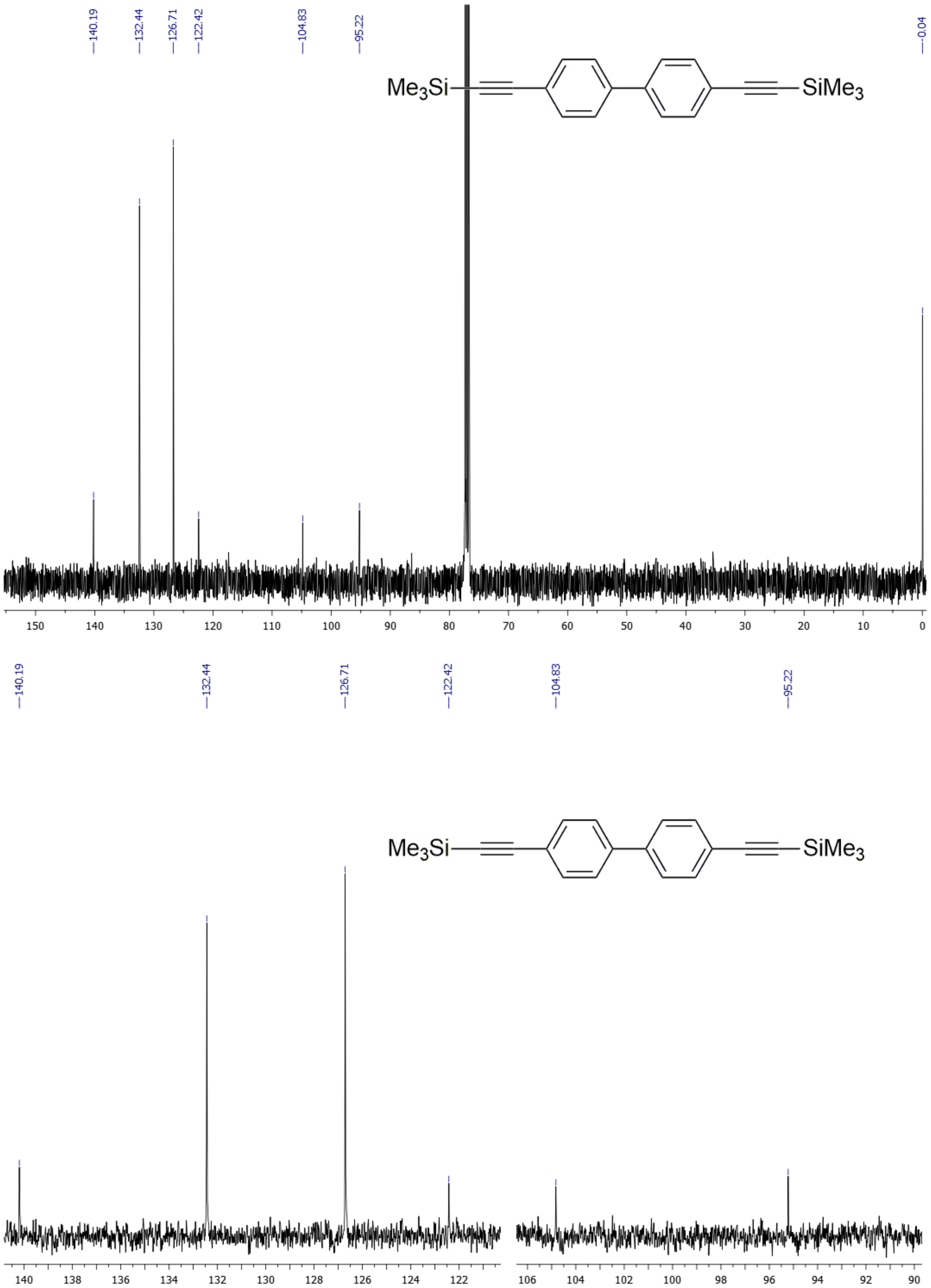


Figure S21. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 4,4'-bis((trimethylsilyl)ethynyl)-1,1'-biphenyl (**8a**):full scale spectrum (top) and spectrum expansions (bottom).

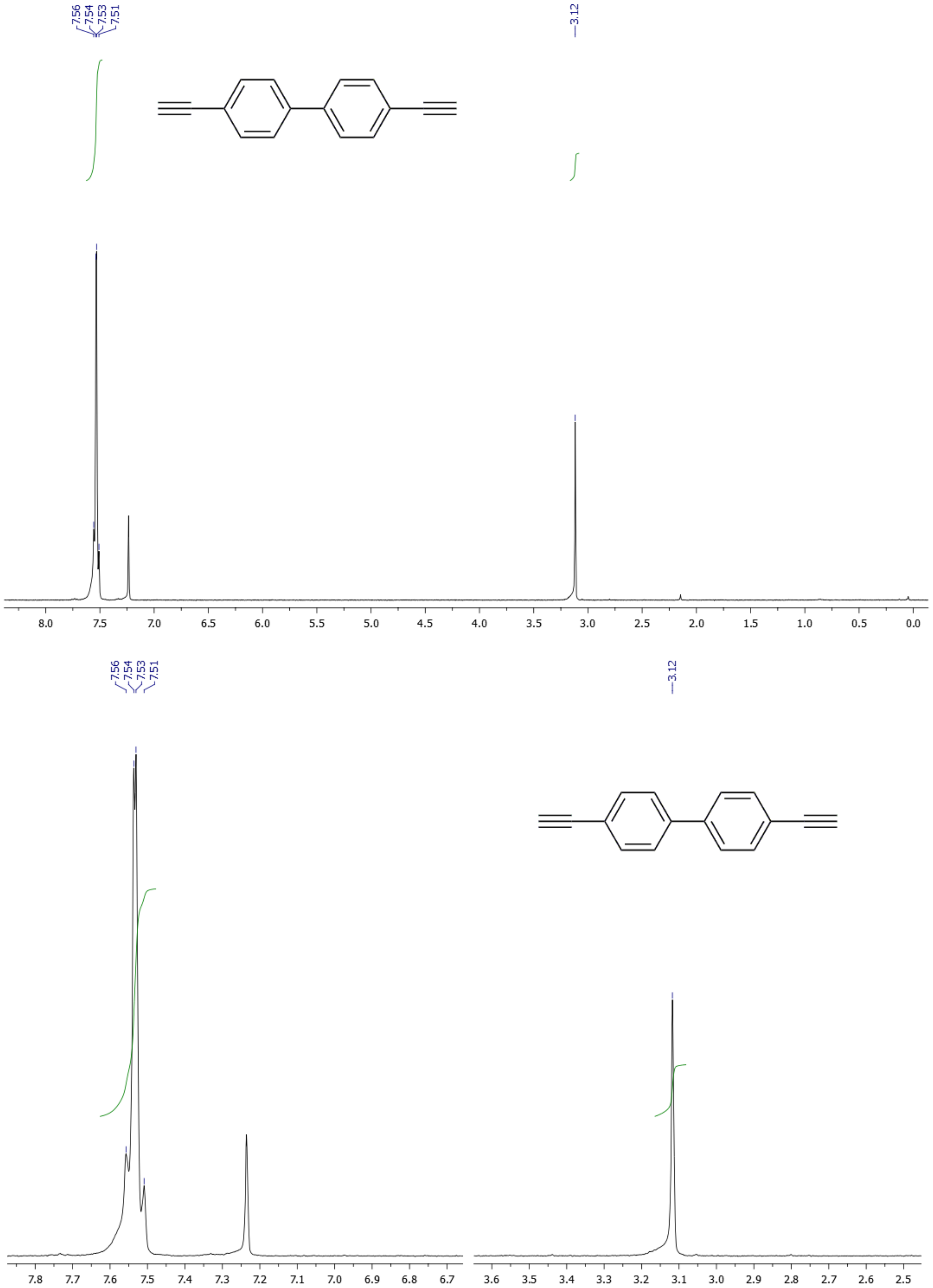


Figure S22. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 4,4'-diethynyl-1,1'-biphenyl (**9a**):full scale spectrum (top) and spectrum expansions (bottom).

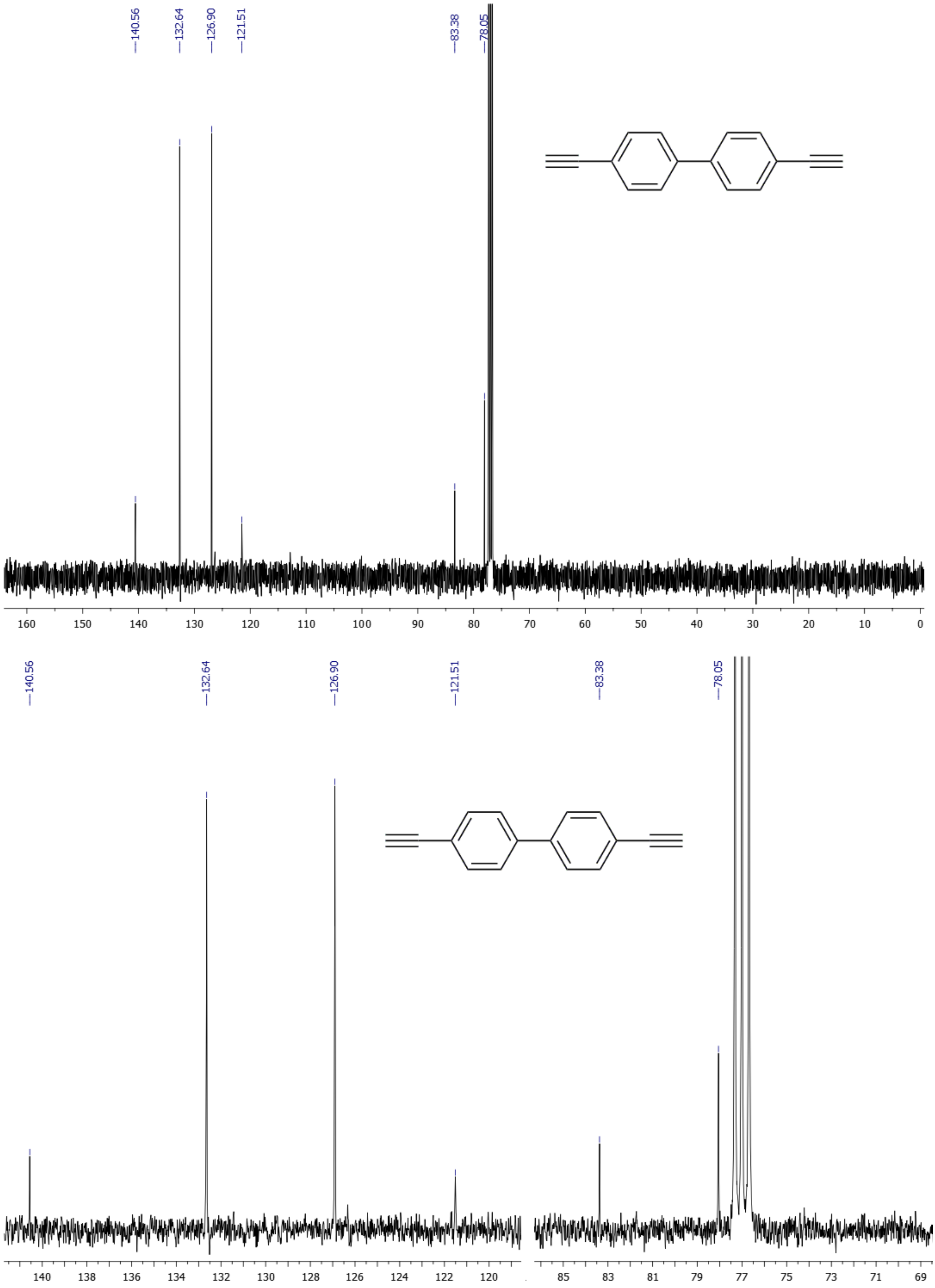


Figure S23. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 4,4'-diethynyl-1,1'-biphenyl (**9a**):full scale spectrum (top) and spectrum expansions (bottom).

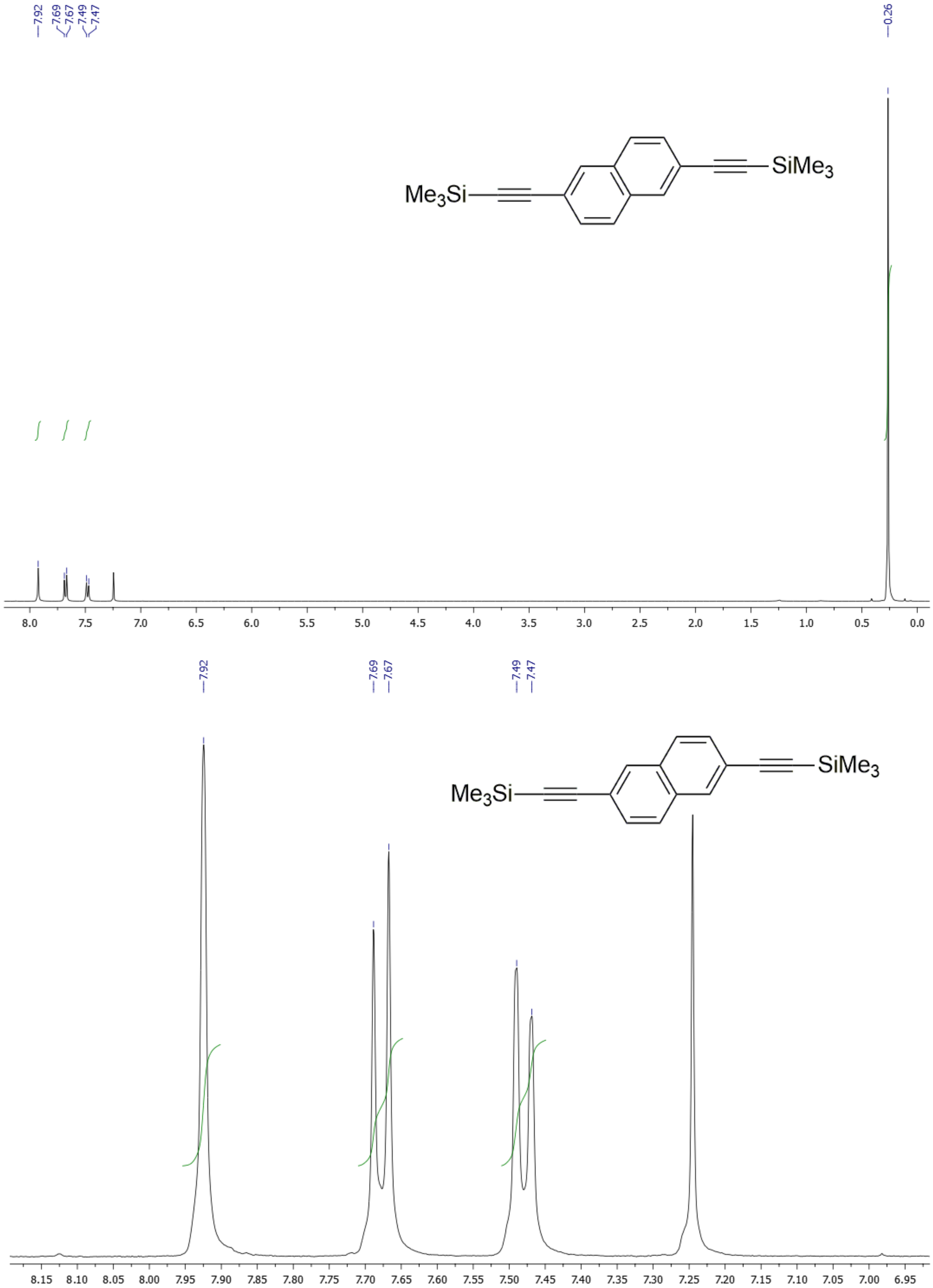


Figure S24. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 2,6-bis((trimethylsilyl)ethynyl)naphthalene (**8b**):full scale spectrum (top) and spectrum expansion (bottom).

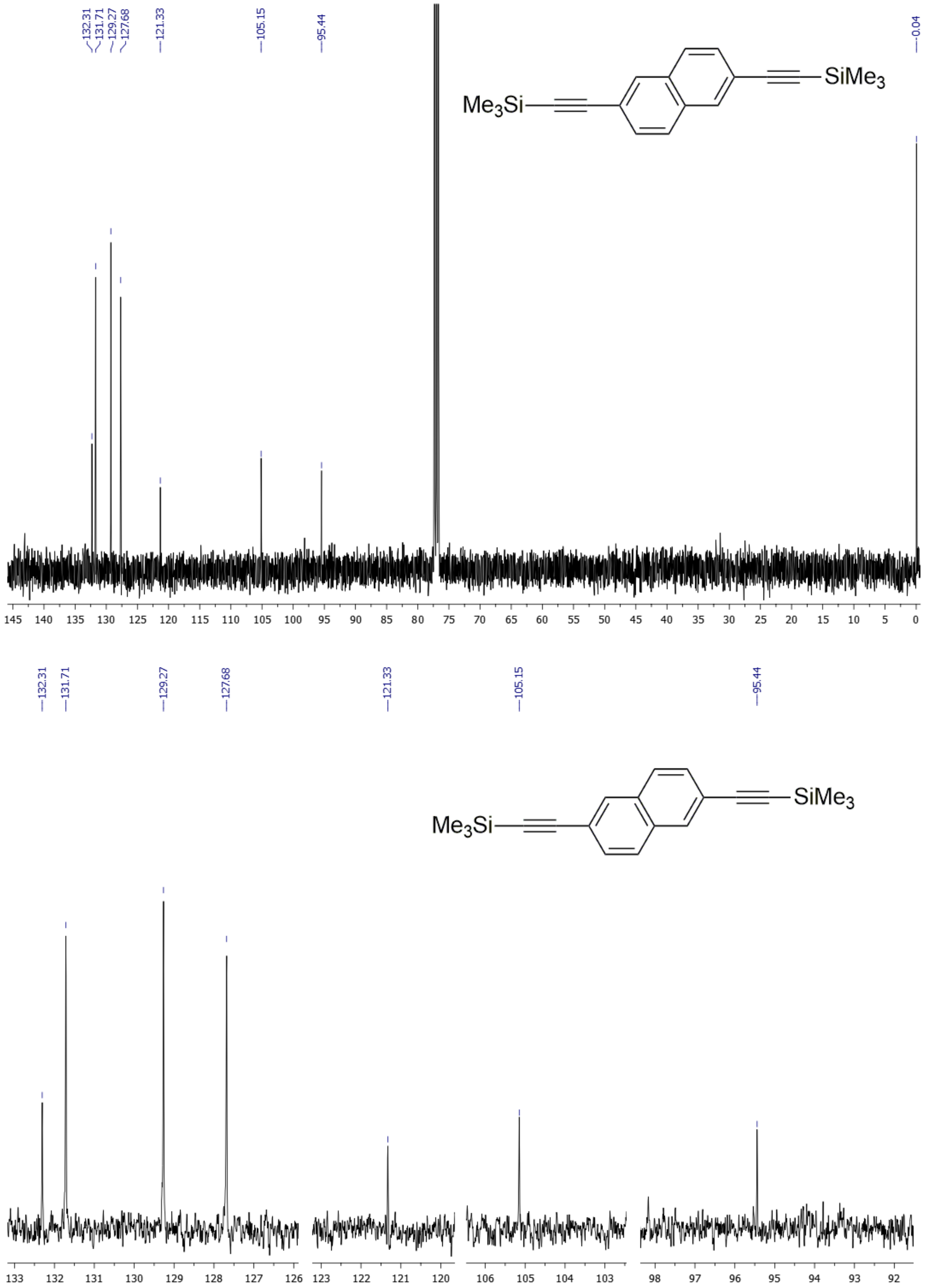


Figure S25. ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of 2,6-bis((trimethylsilyl)ethynyl)naphthalene (**8b**):full scale spectrum (top) and spectrum expansions (bottom).

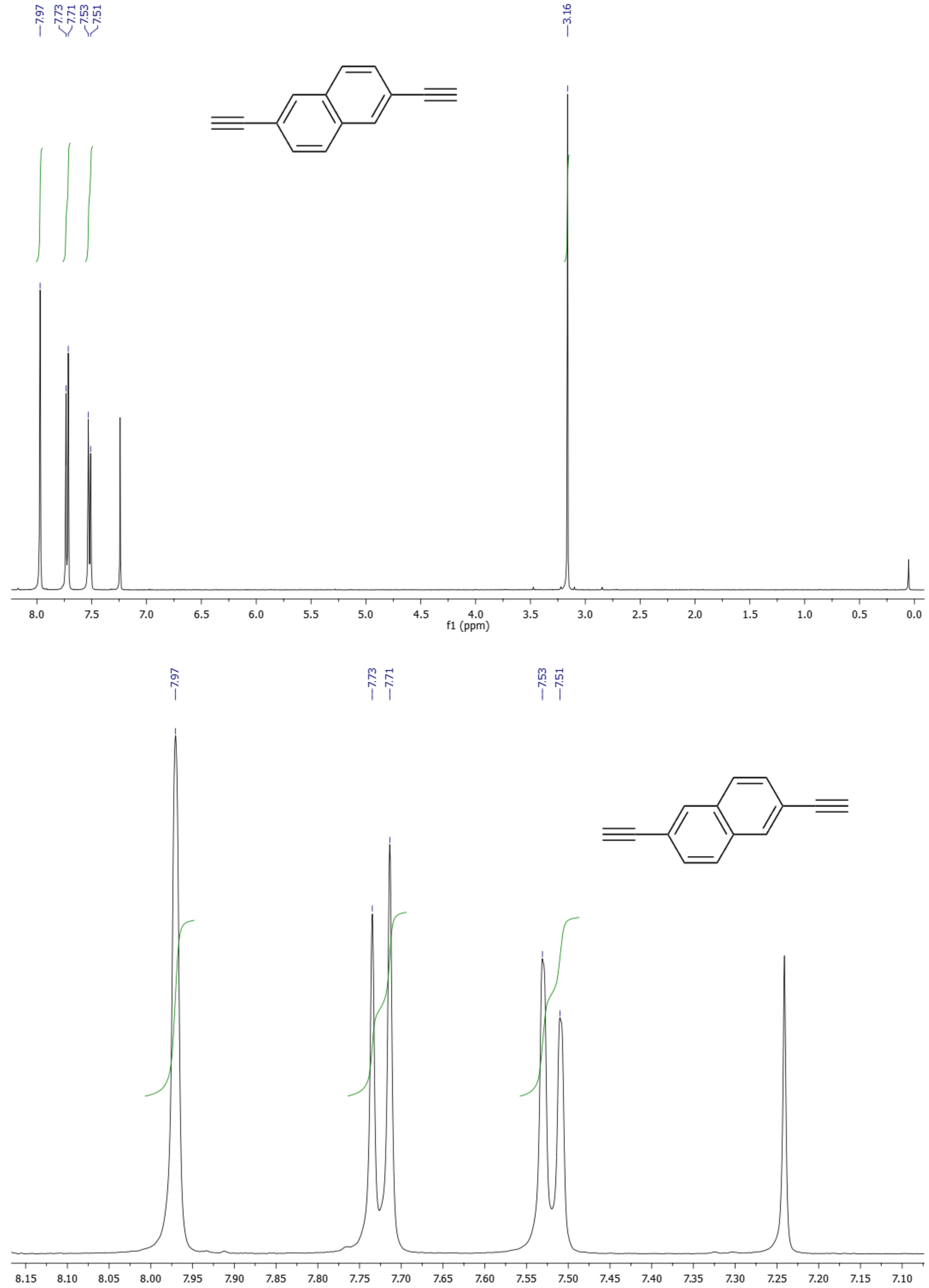


Figure S26. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 2,6-diethynylnaphthalene (**9b**):full scale spectrum (top) and spectrum expansion (bottom).

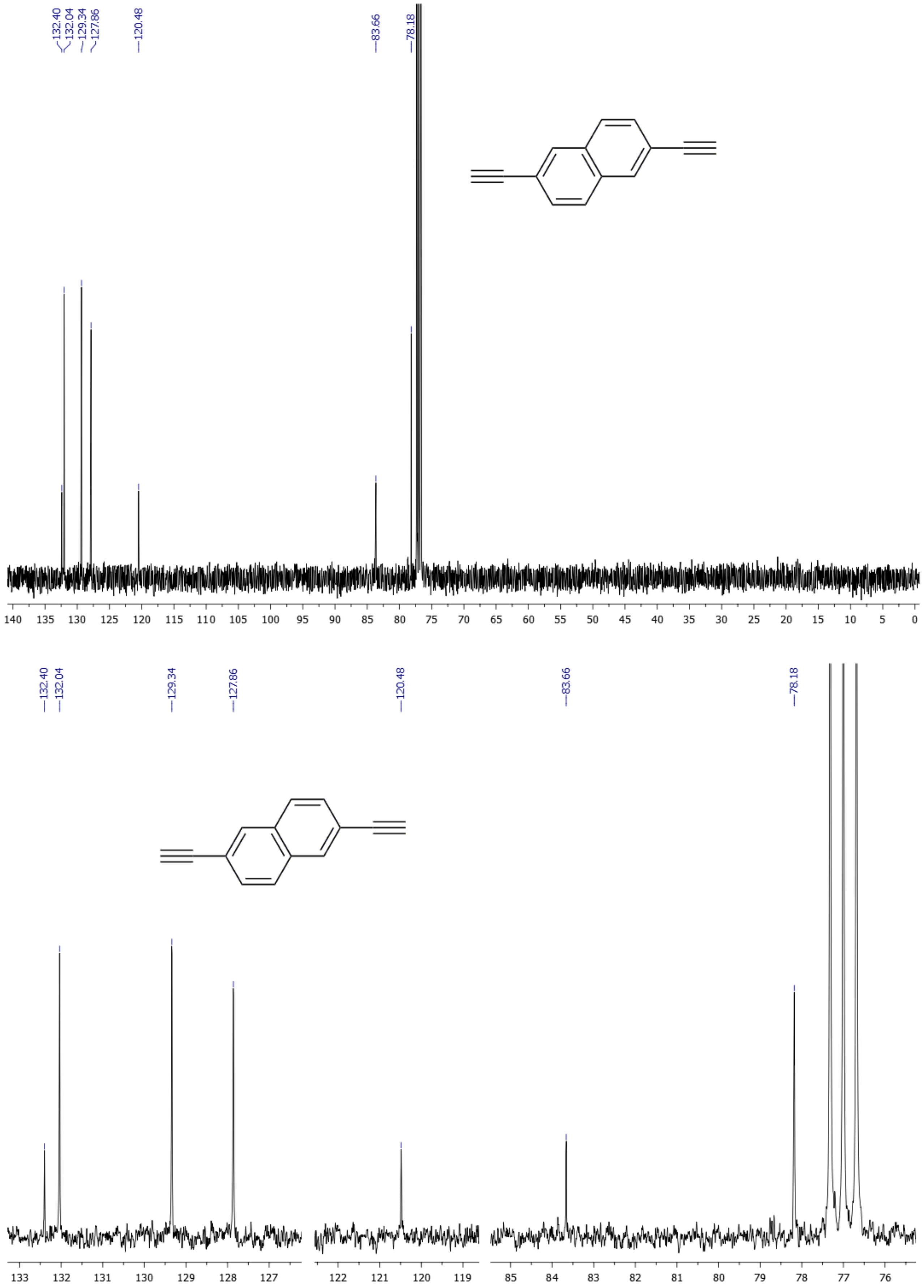


Figure S27. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 2,6-diethynylnaphthalene (**9b**):full scale spectrum (top) and spectrum expansions (bottom).

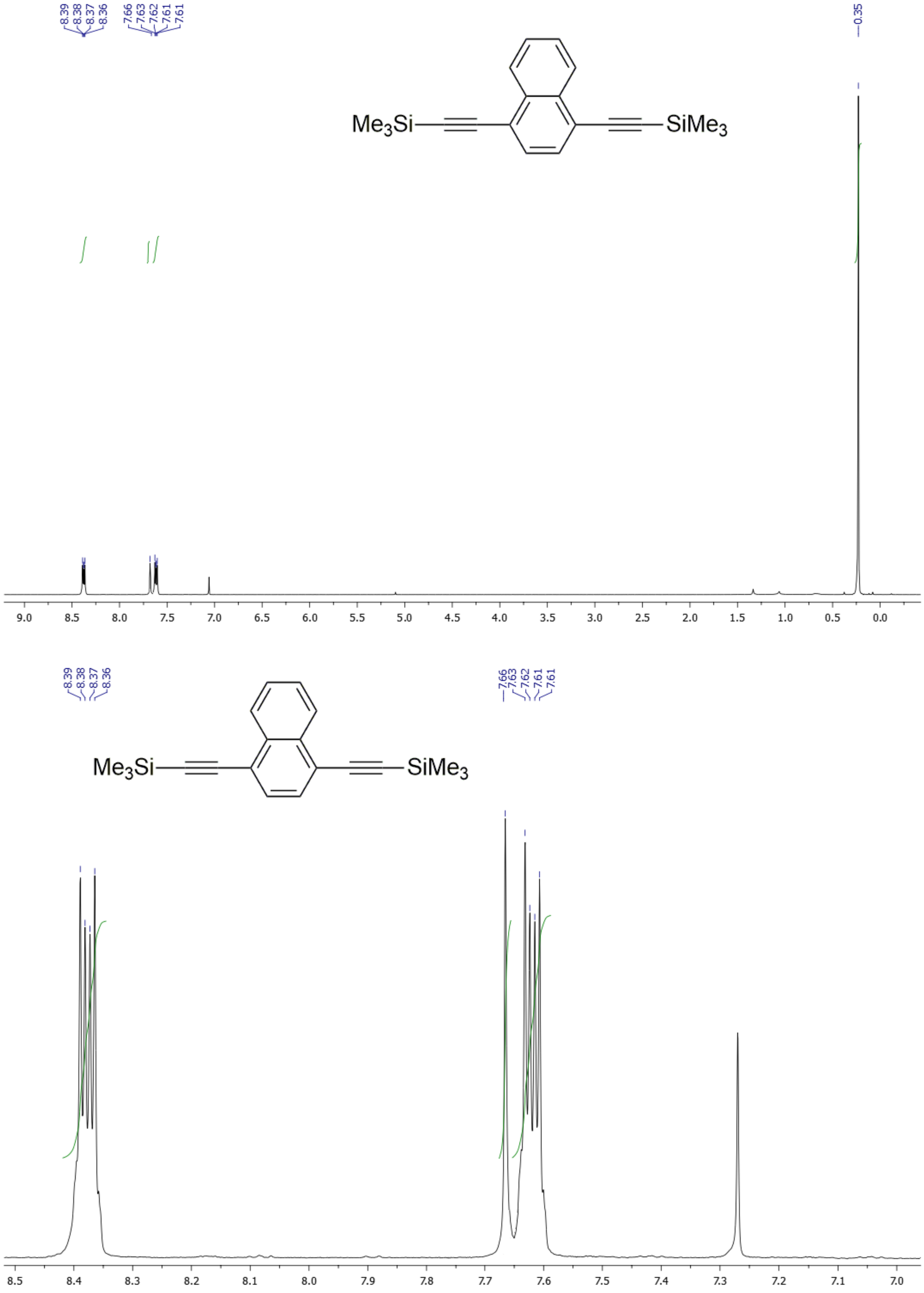


Figure S28. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 1,4-bis((trimethylsilyl)ethynyl)naphthalene (**8c**):full scale spectrum (top) and spectrum expansion (bottom).

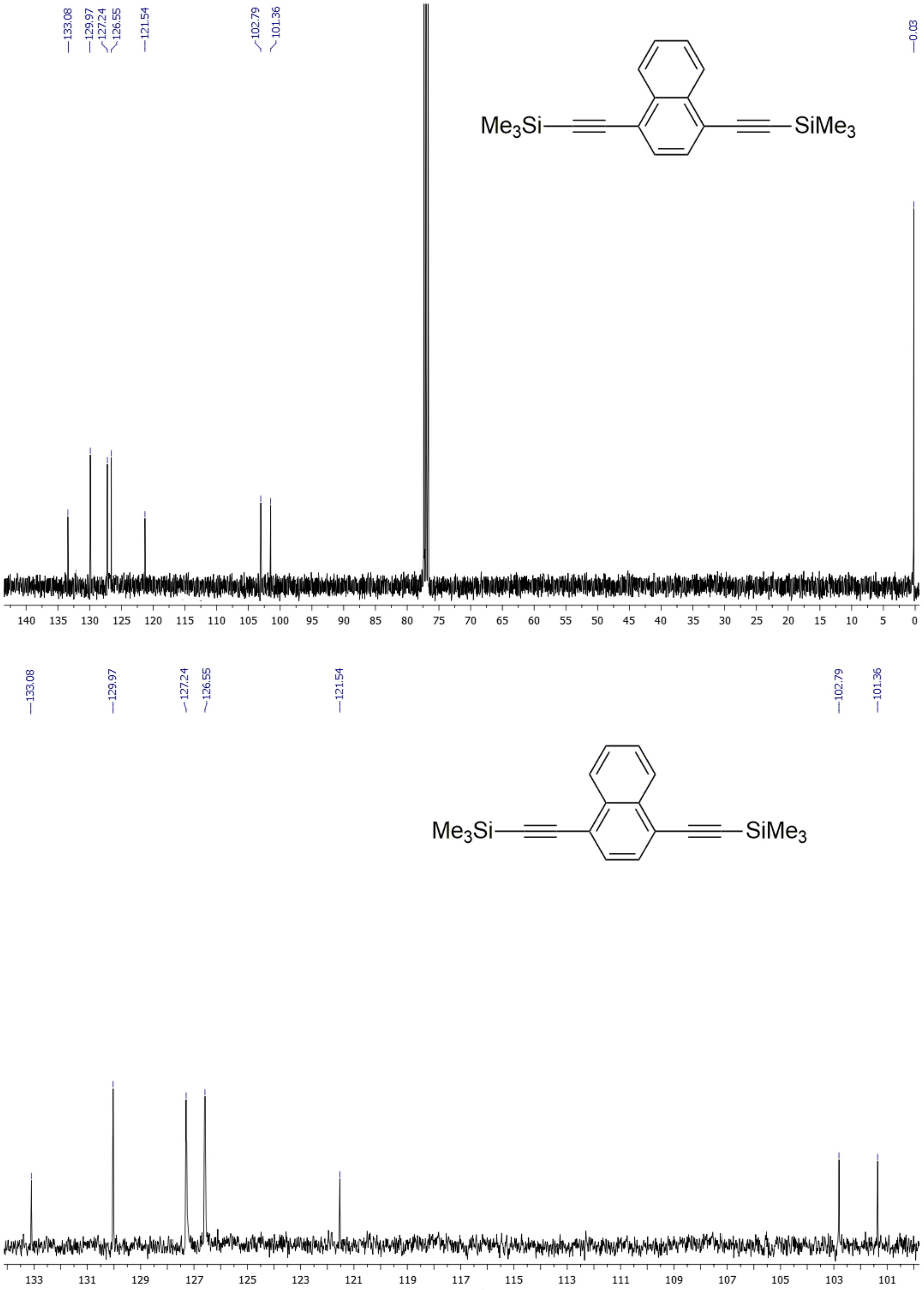


Figure S29. ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of 1,4-bis((trimethylsilyl)ethynyl)naphthalene (**8c**):full scale spectrum (top) and spectrum expansion (bottom).

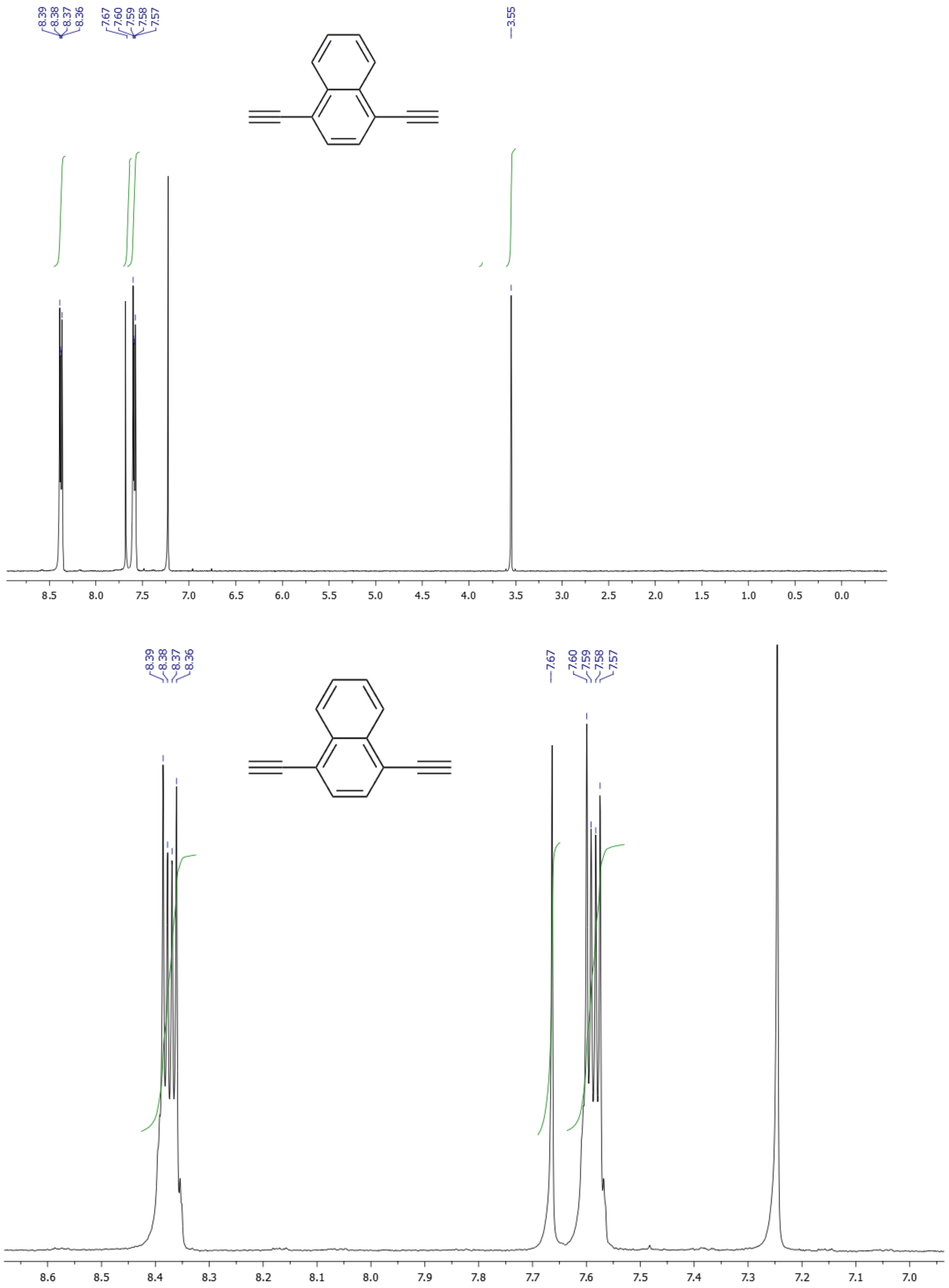


Figure S30. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of 1,4-diethynylnaphthalene (**9c**):full scale spectrum (top) and spectrum expansion (bottom).

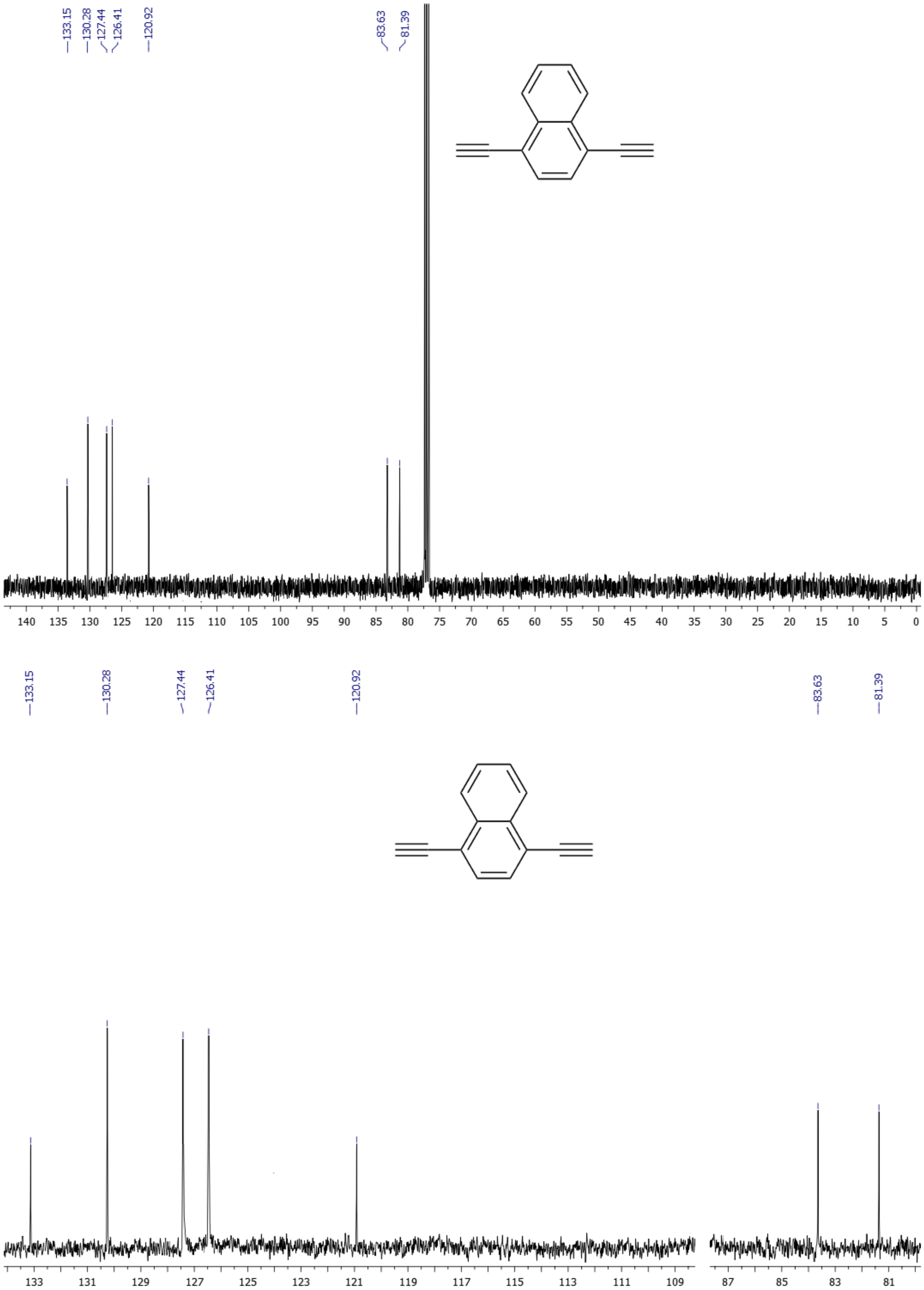


Figure S31. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 1,4-diethynylnaphthalene (**9c**):full scale spectrum (top) and spectrum expansions (bottom).

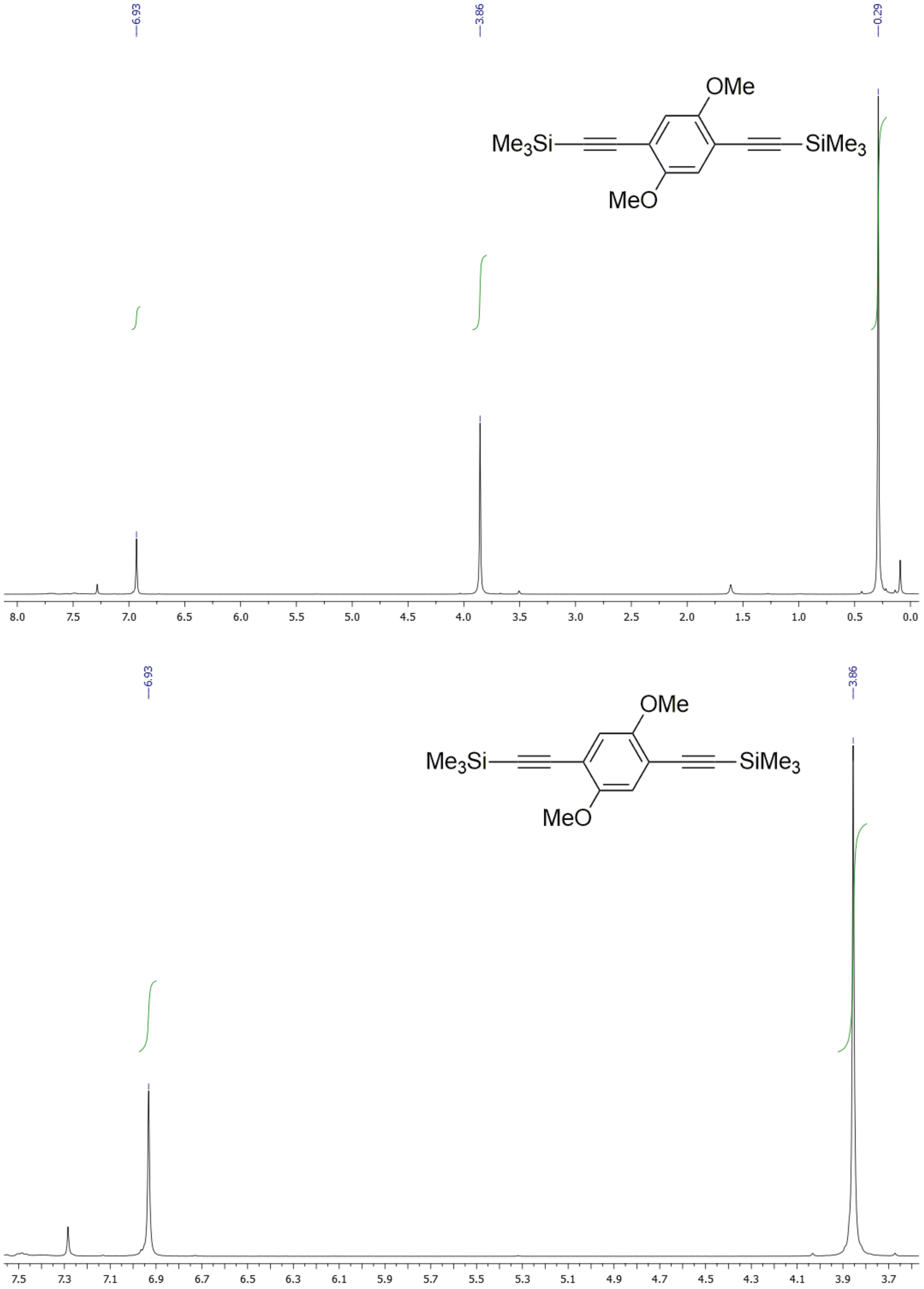


Figure S32. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 2,5-dimethoxy-1,4-bis((trimethylsilyl)ethynyl)benzene (**12**):full scale spectrum (top) and spectrum expansion (bottom).

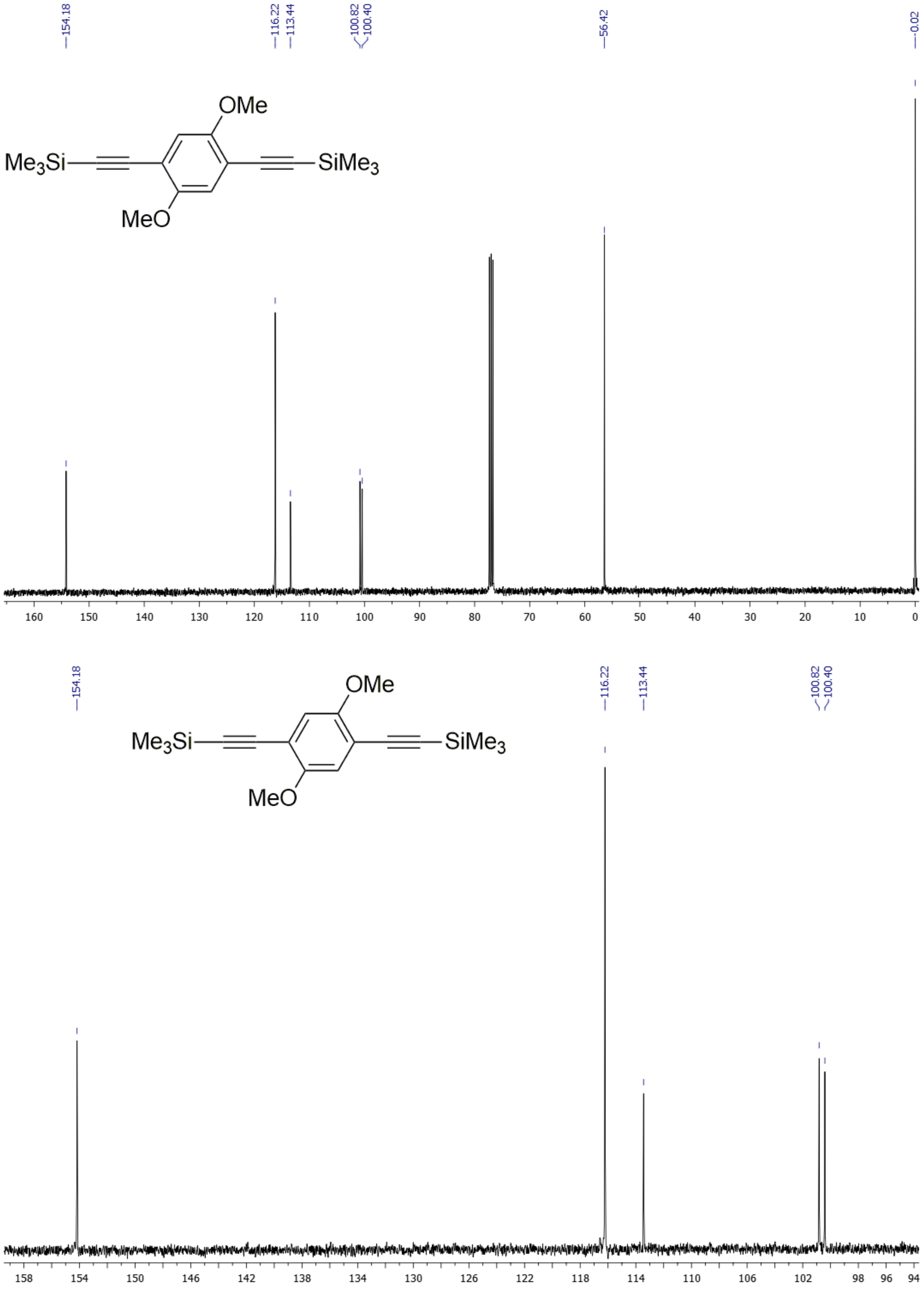


Figure S33. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 2,5-dimethoxy-1,4-bis((trimethylsilyl)ethynyl)benzene (**12**):full scale spectrum (top) and spectrum expansion (bottom).

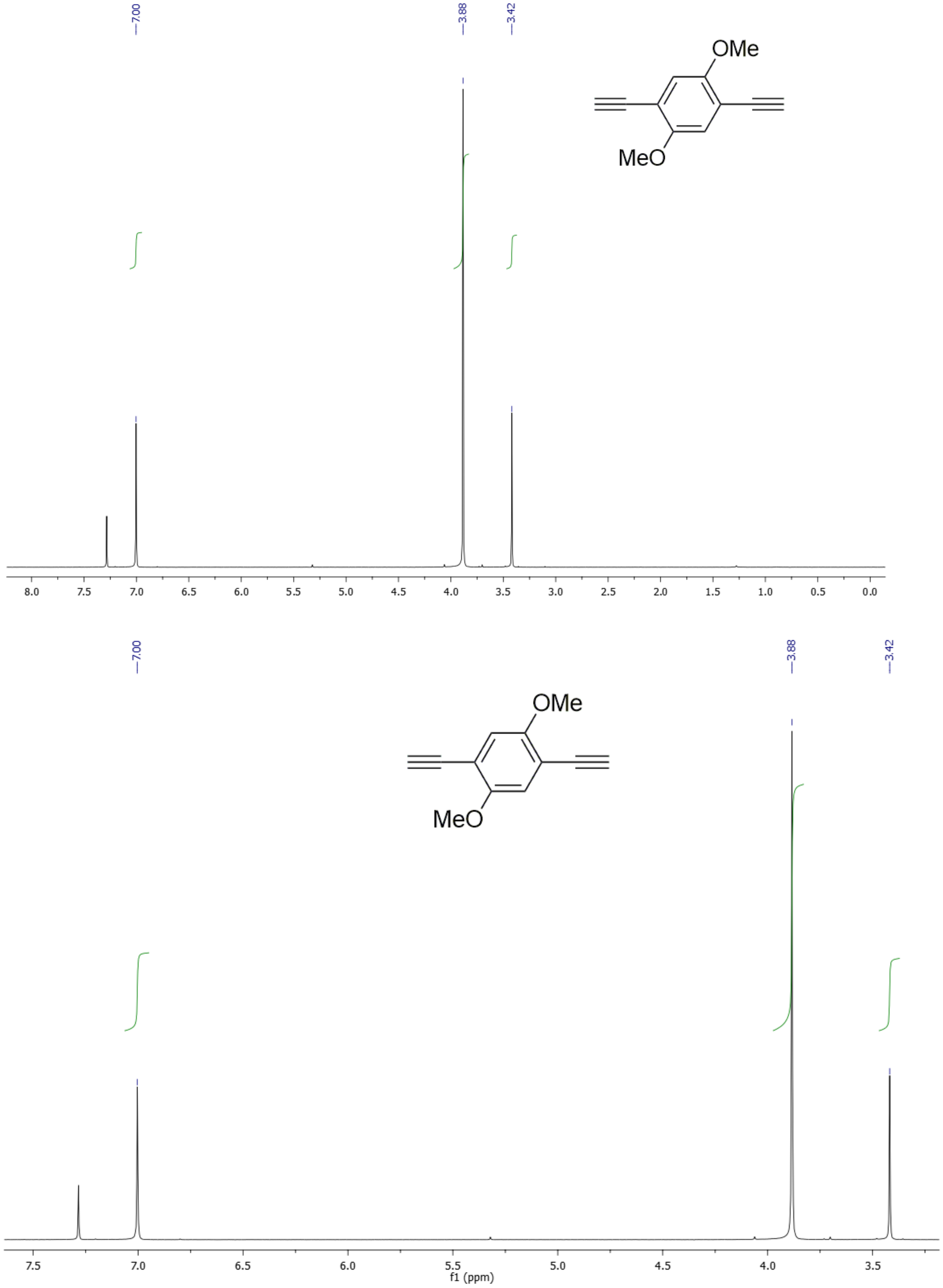


Figure S34. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 1,4-diethynyl-2,5-dimethoxybenzene (**13**):full scale spectrum (top) and spectrum expansion (bottom).

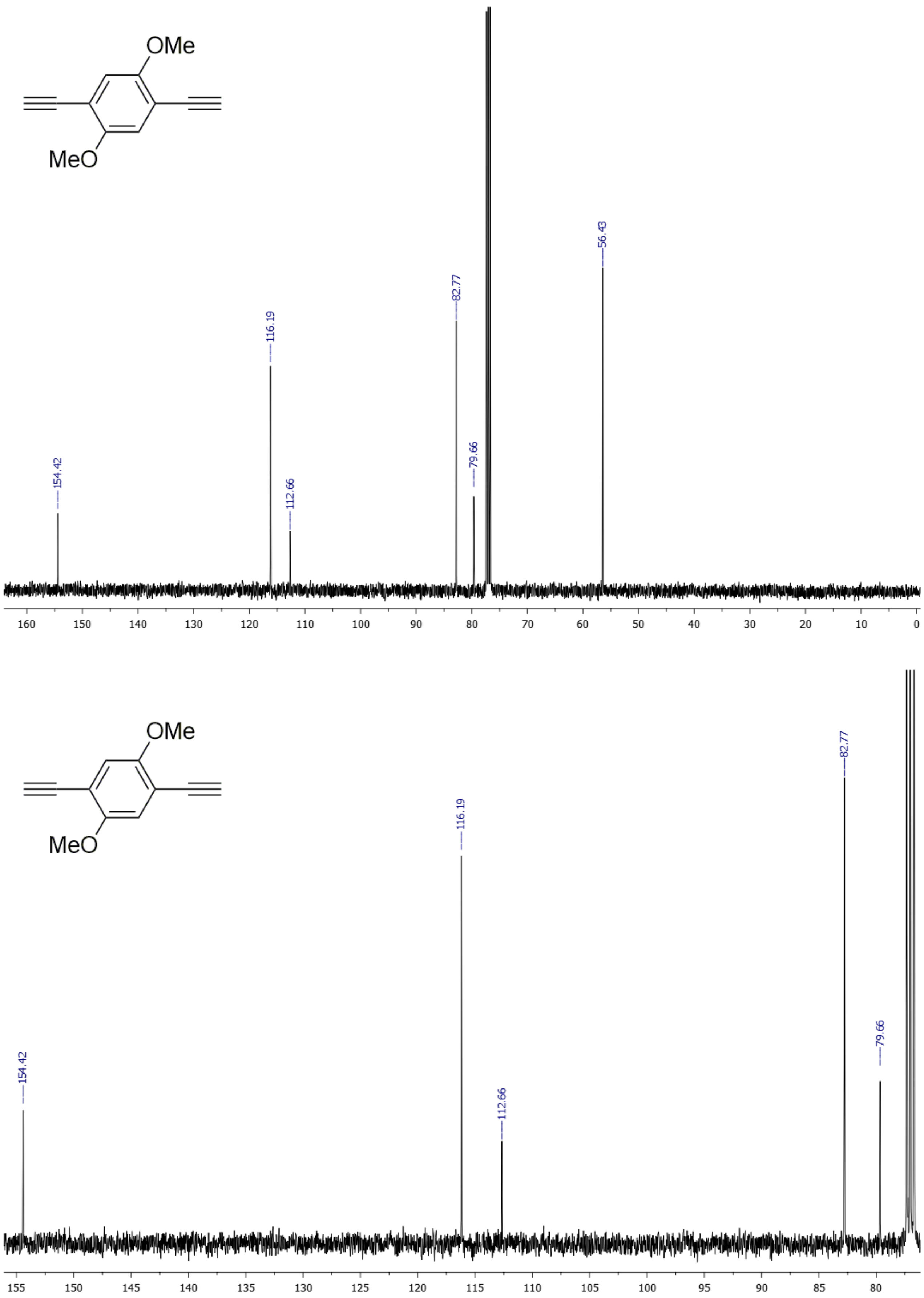


Figure S35. ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of 1,4-diethynyl-2,5-dimethoxybenzene (**13**):full scale spectrum (top) and spectrum expansion (bottom).

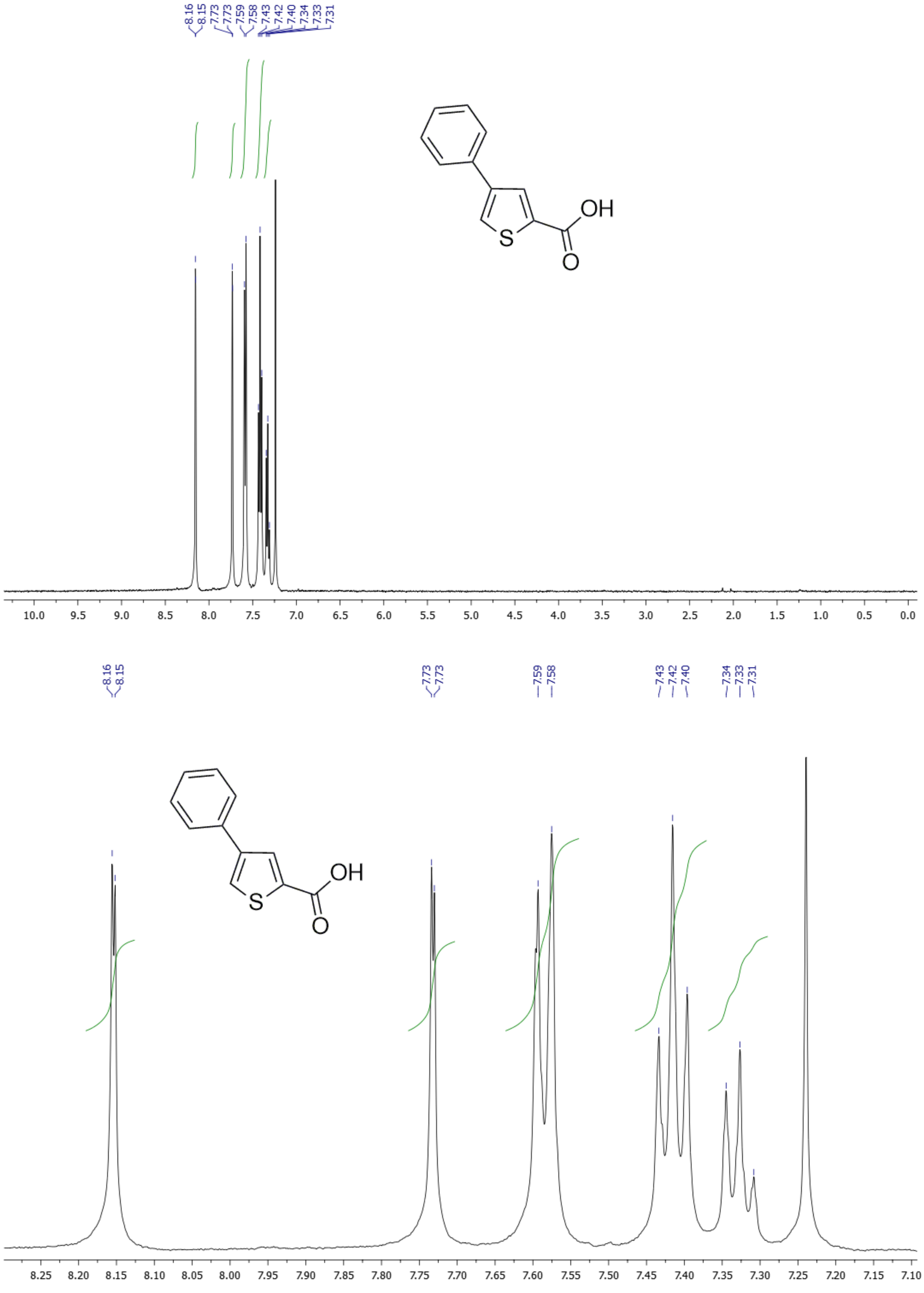


Figure S36. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 4-phenylthiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansion (bottom).

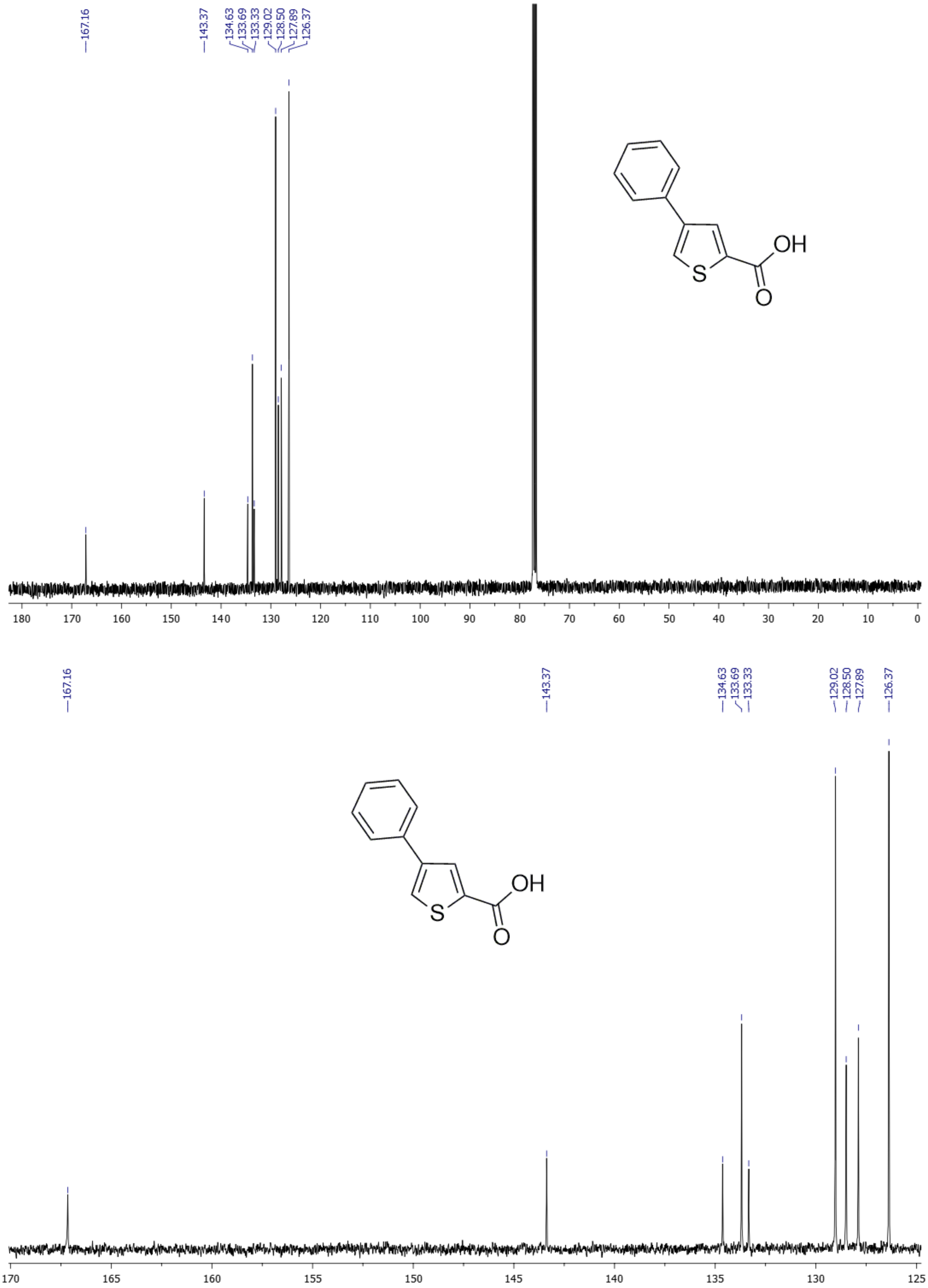


Figure S37. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 4-phenylthiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansion (bottom).

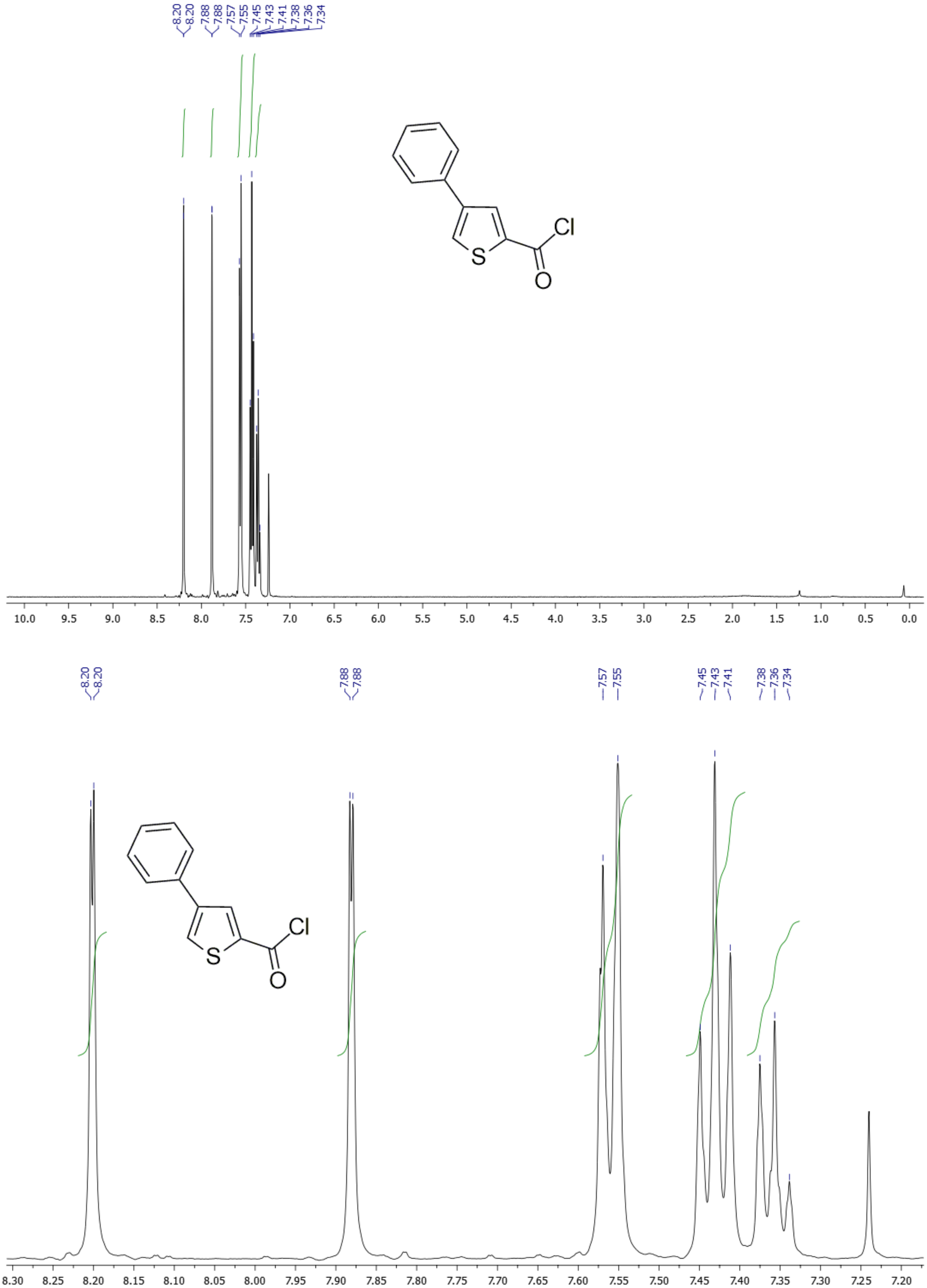


Figure S38. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 4-phenylthiophene-2-carbonyl chloride (**4d**): full scale spectrum (top) and spectrum expansion (bottom).

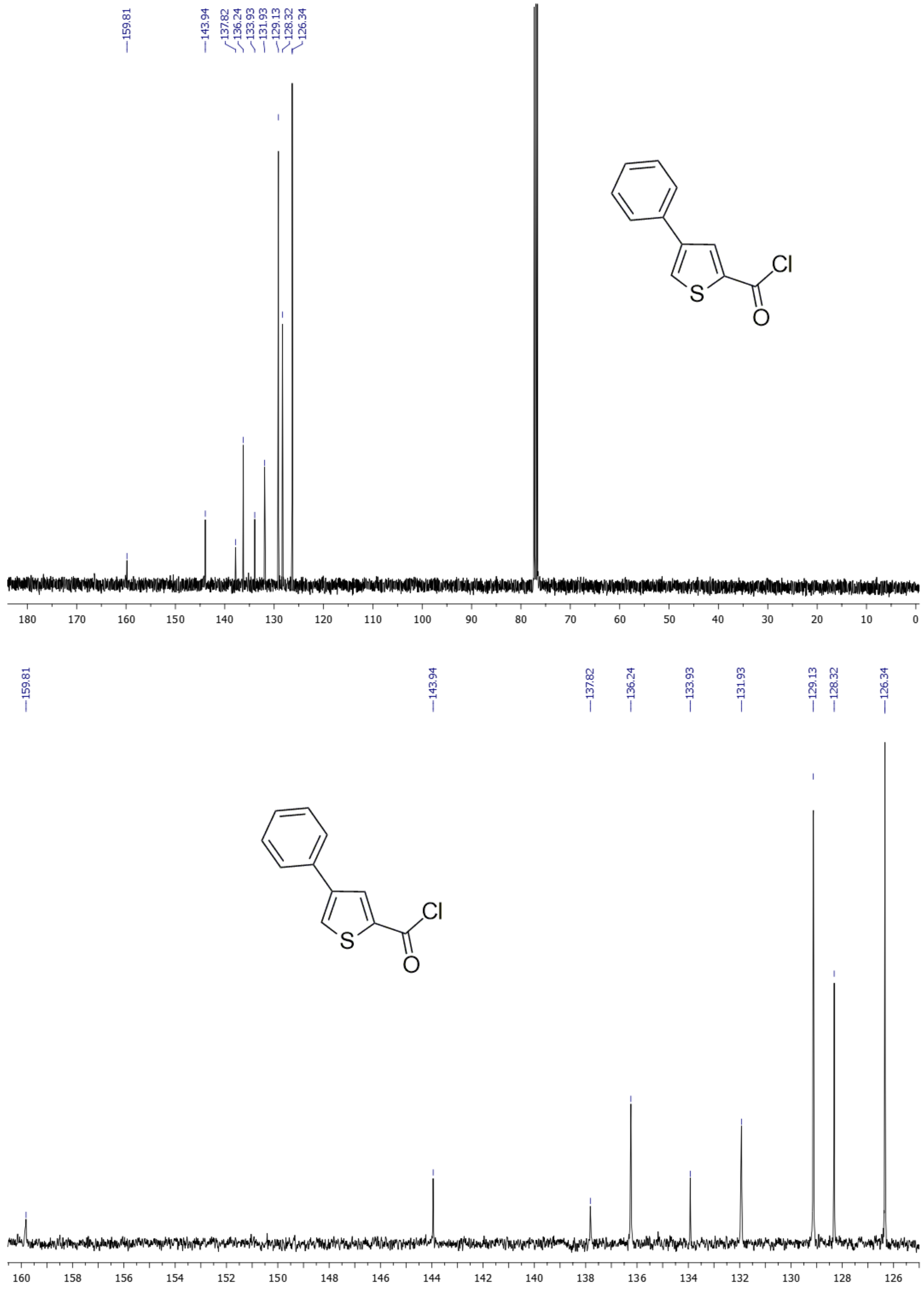


Figure S39. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 4-phenylthiophene-2-carbonyl chloride (**4d**): full scale spectrum (top) and spectrum expansion (bottom).

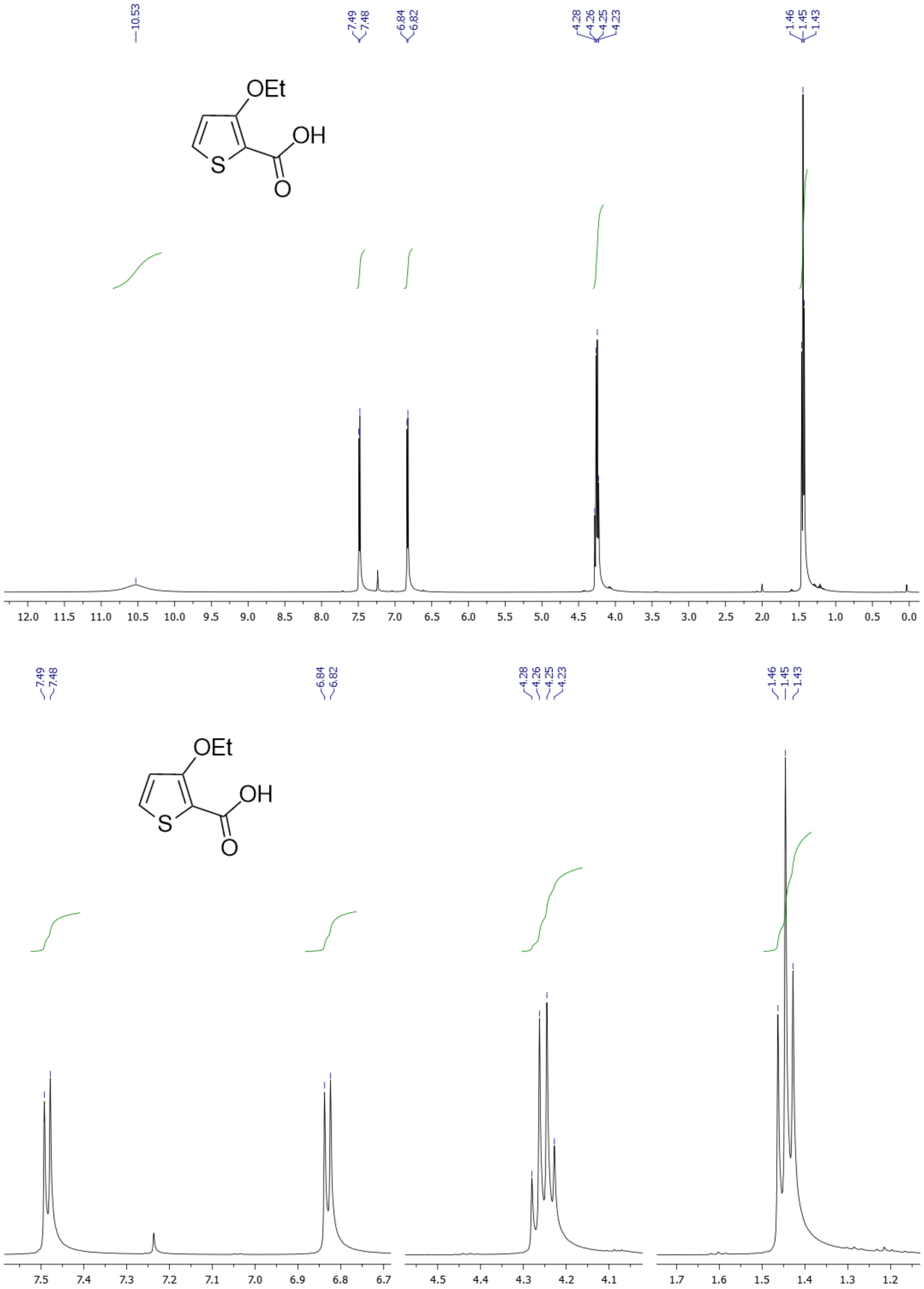


Figure S40. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3-ethoxythiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansions (bottom).

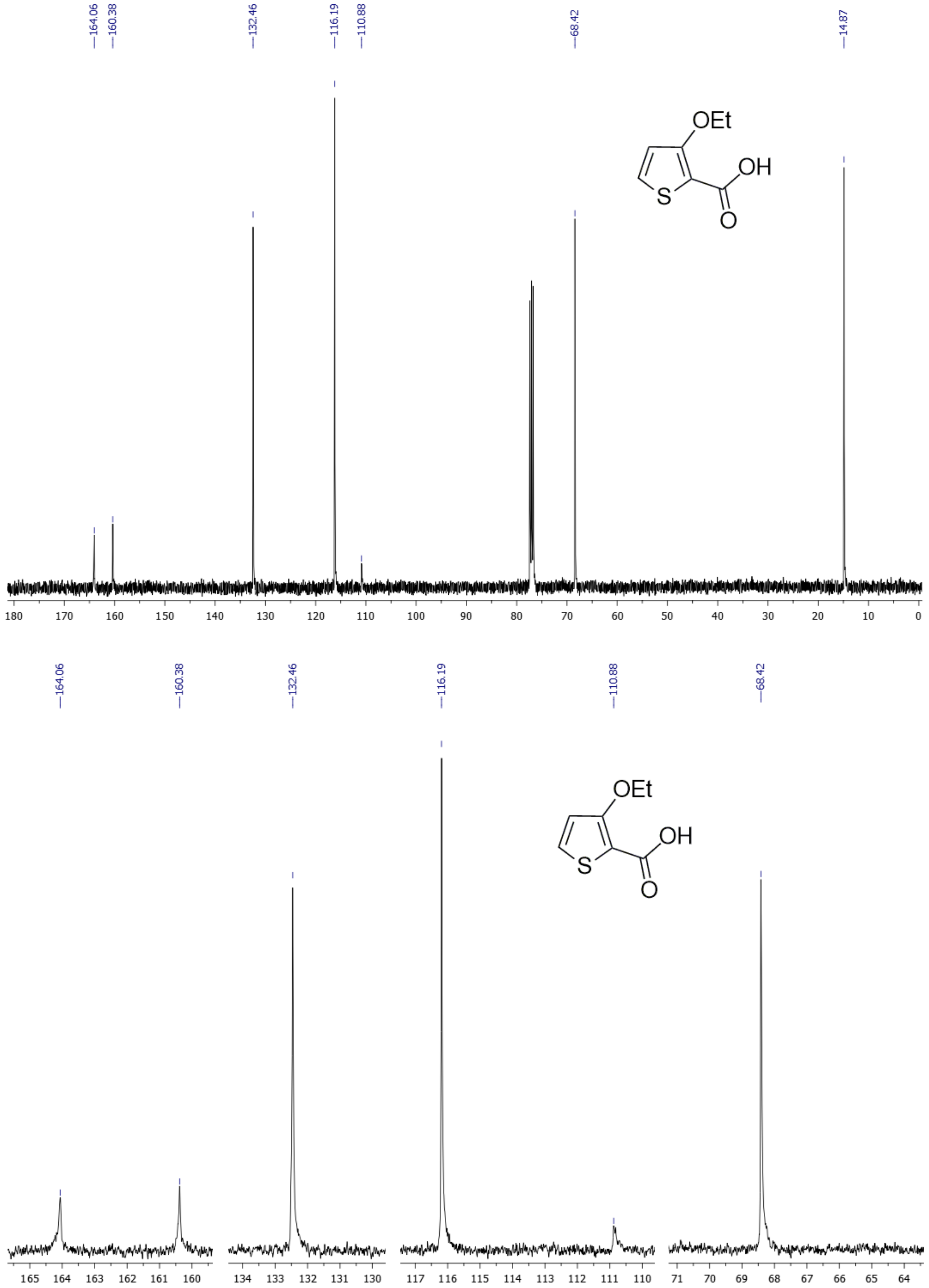


Figure S41. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3-ethoxythiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansions (bottom).

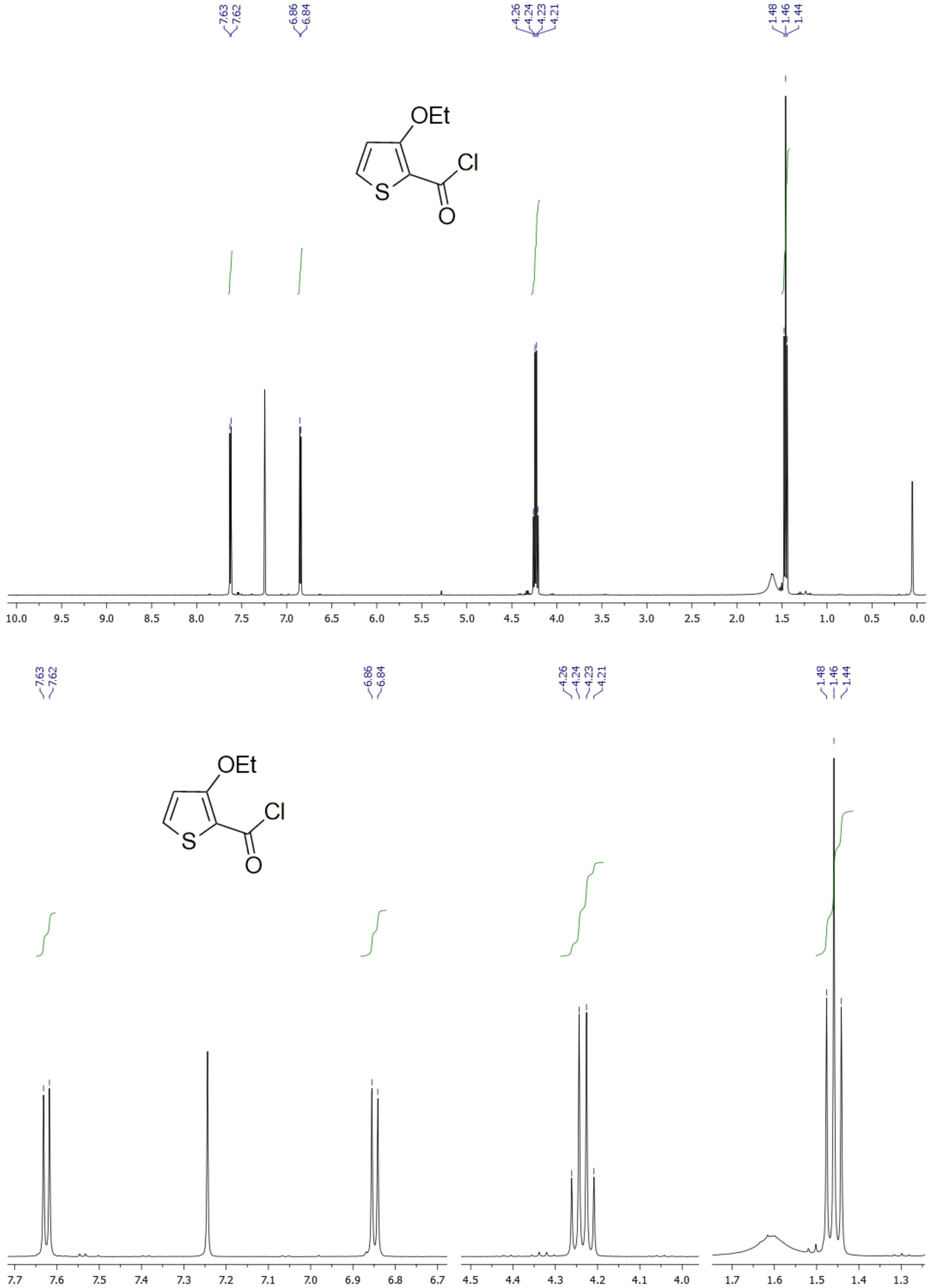


Figure S42. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3-ethoxythiophene-2-carbonyl chloride (**4e**): full scale spectrum (top) and spectrum expansions (bottom).

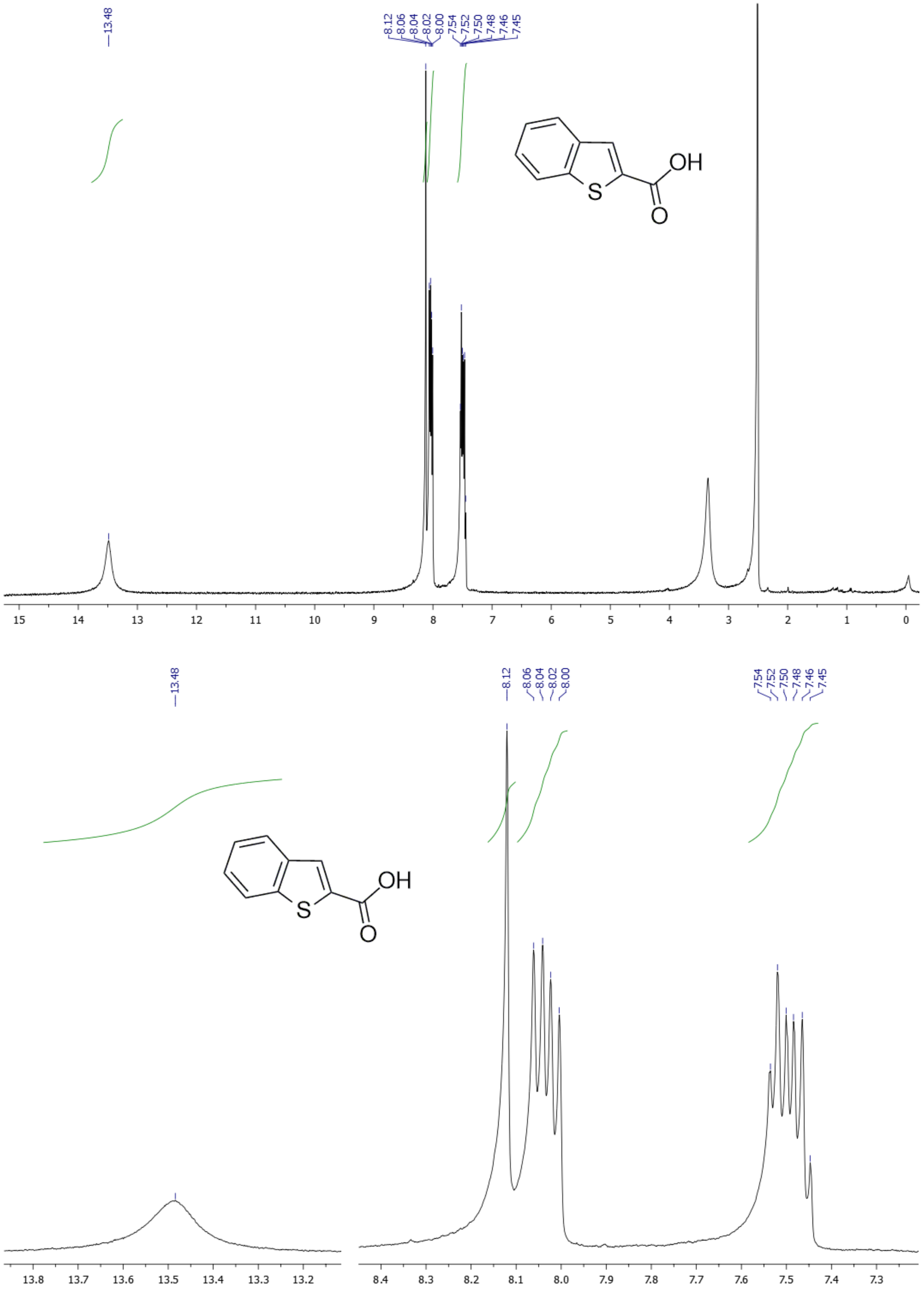


Figure S43. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of benzo[*b*]thiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansion (bottom).

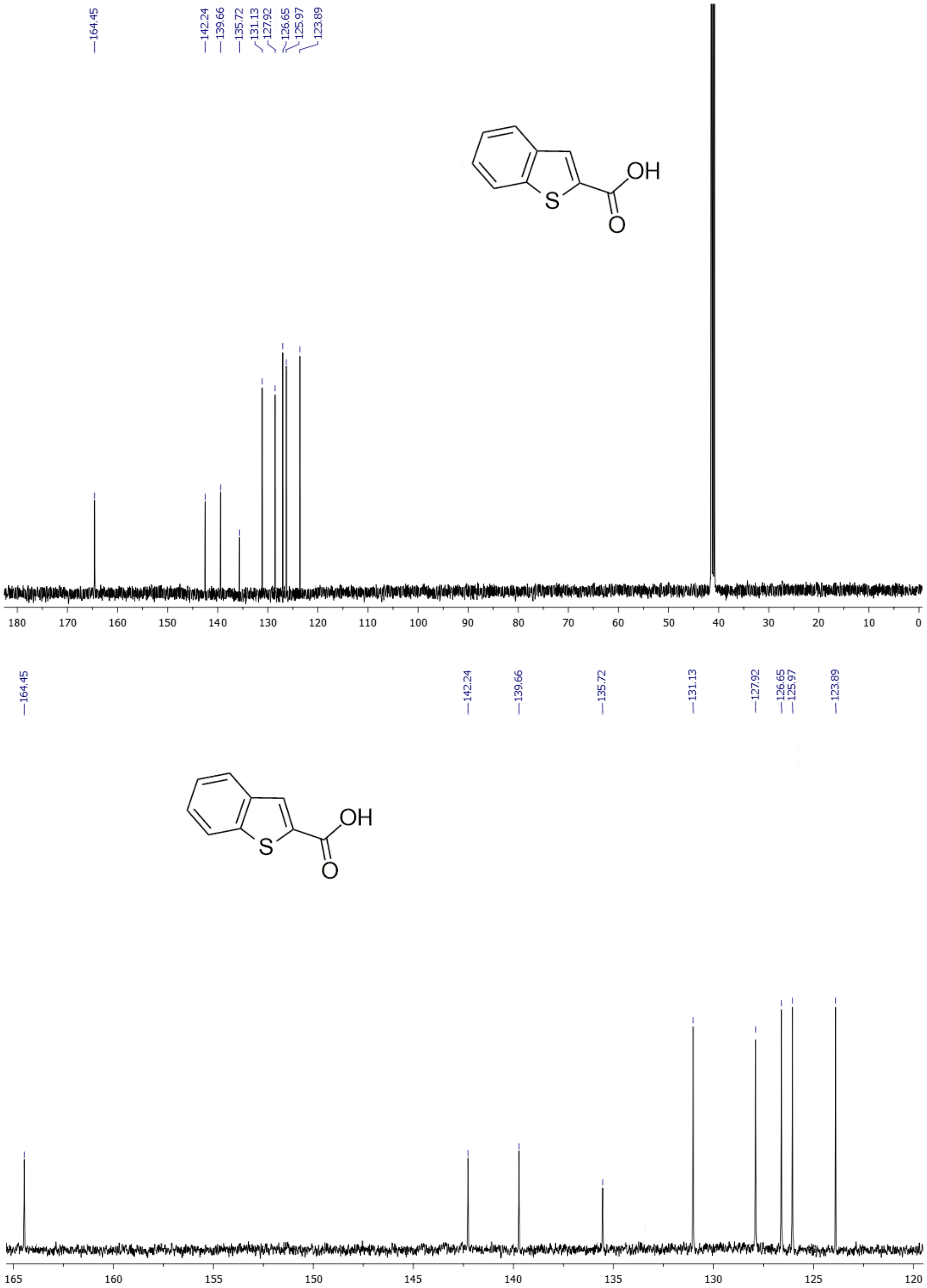


Figure S44. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of benzo[*b*]thiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansion (bottom).

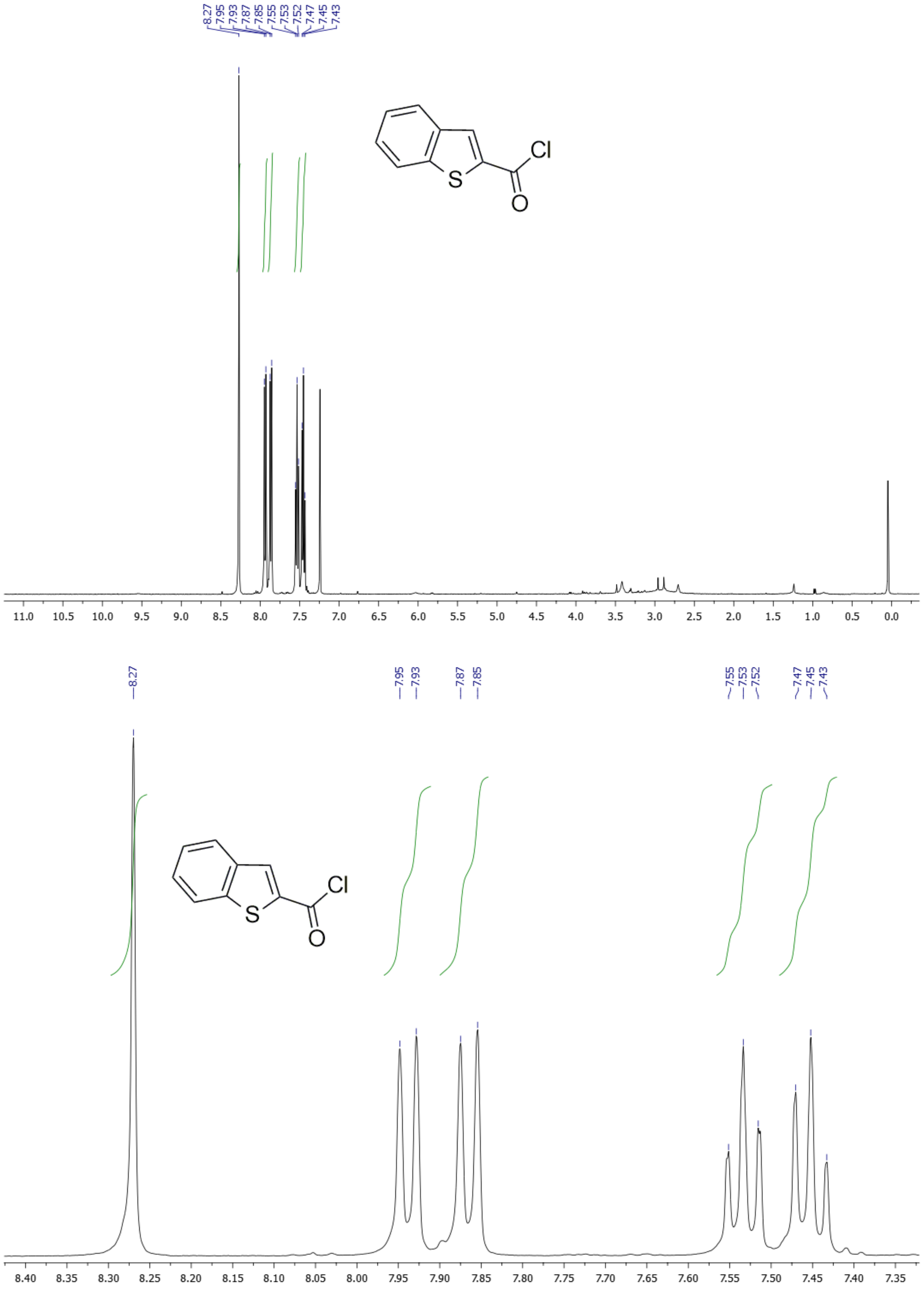


Figure S45. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of benzo[*b*]thiophene-2-carbonyl chloride (**4f**): full scale spectrum (top) and spectrum expansion (bottom).

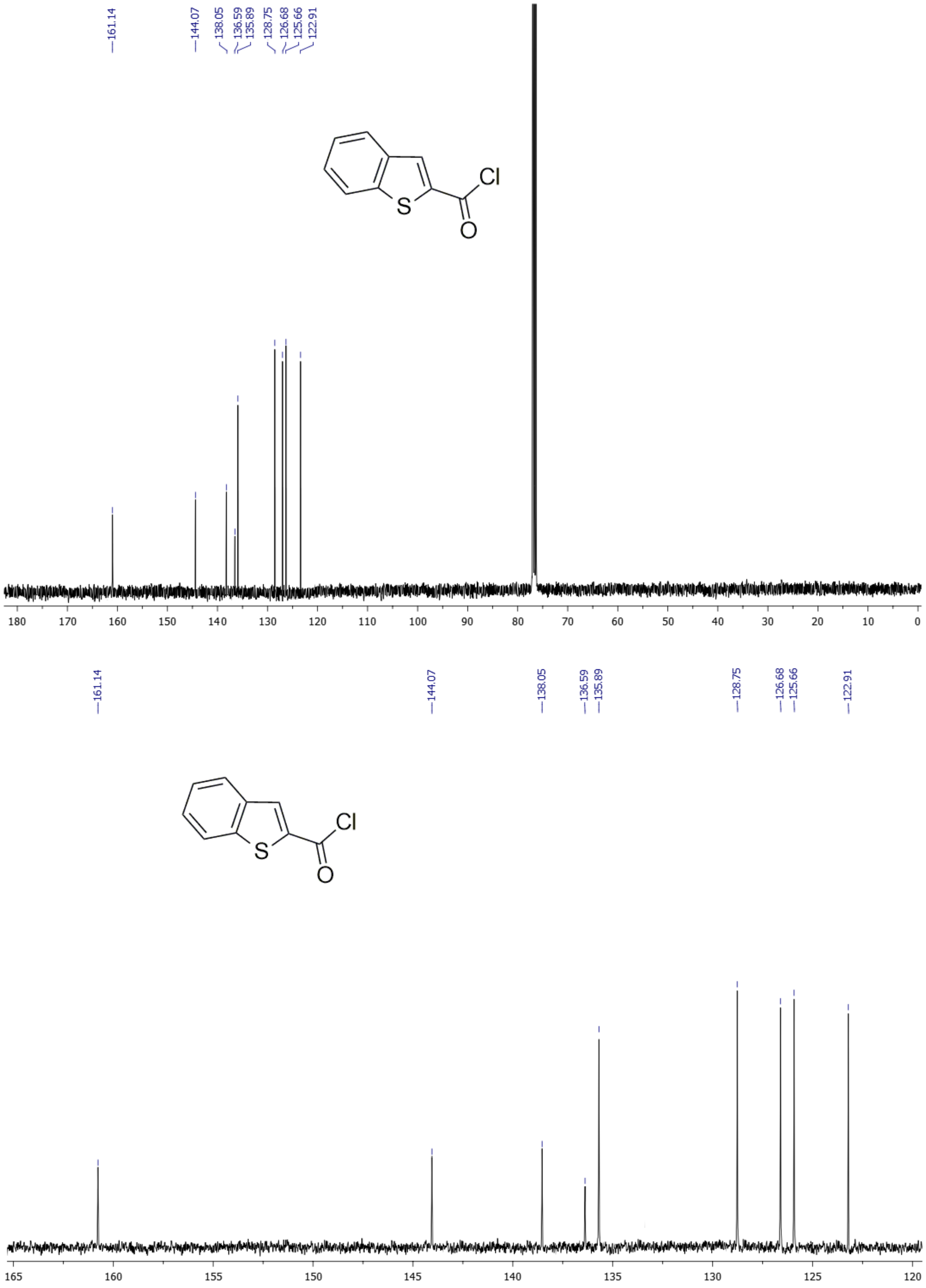


Figure S46. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of benzo[*b*]thiophene-2-carbonyl chloride (**4f**): full scale spectrum (top) and spectrum expansion (bottom).

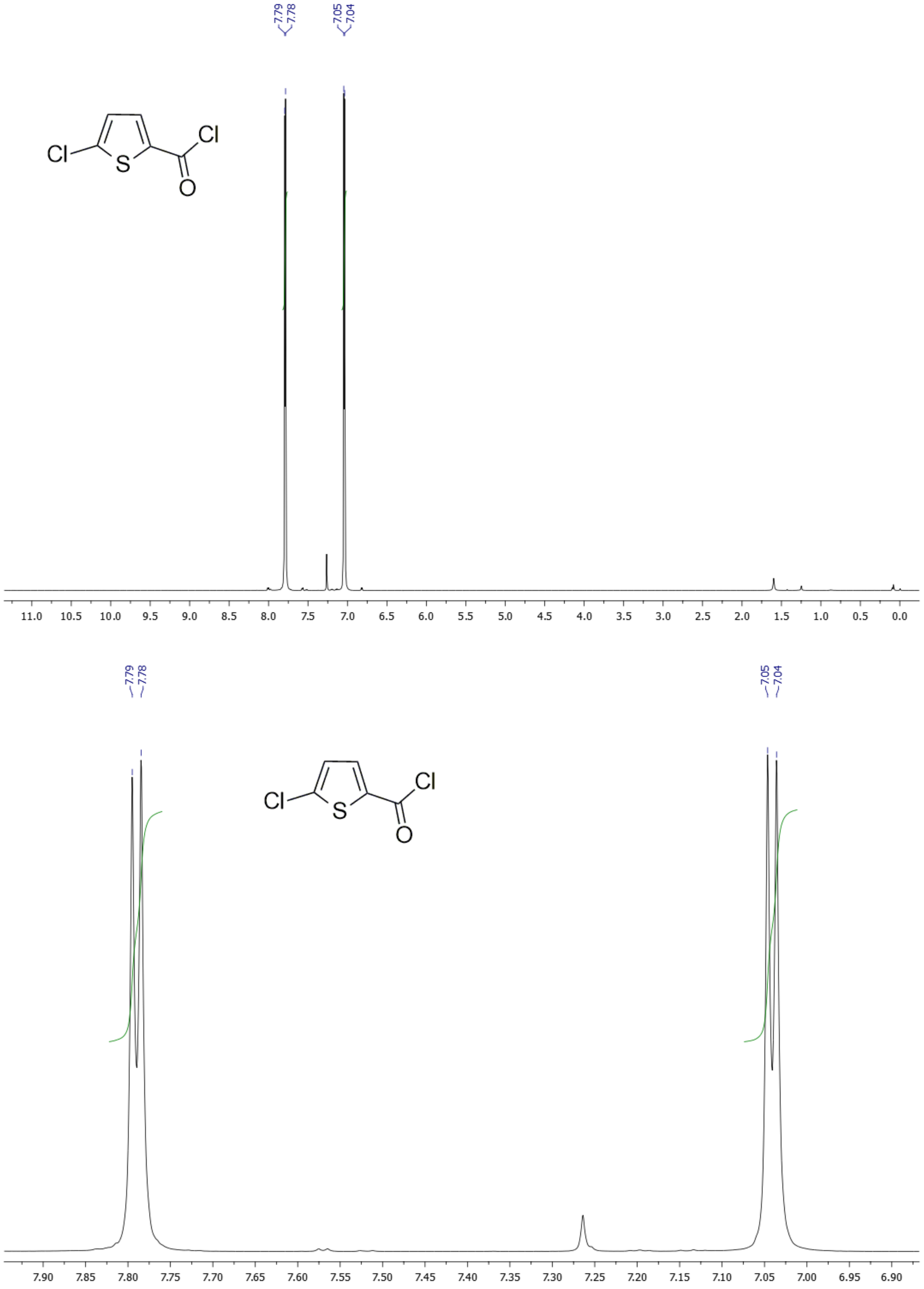


Figure S47. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 5-chlorothiophene-2-carbonyl chloride (**4g**): full scale spectrum (top) and spectrum expansion (bottom).

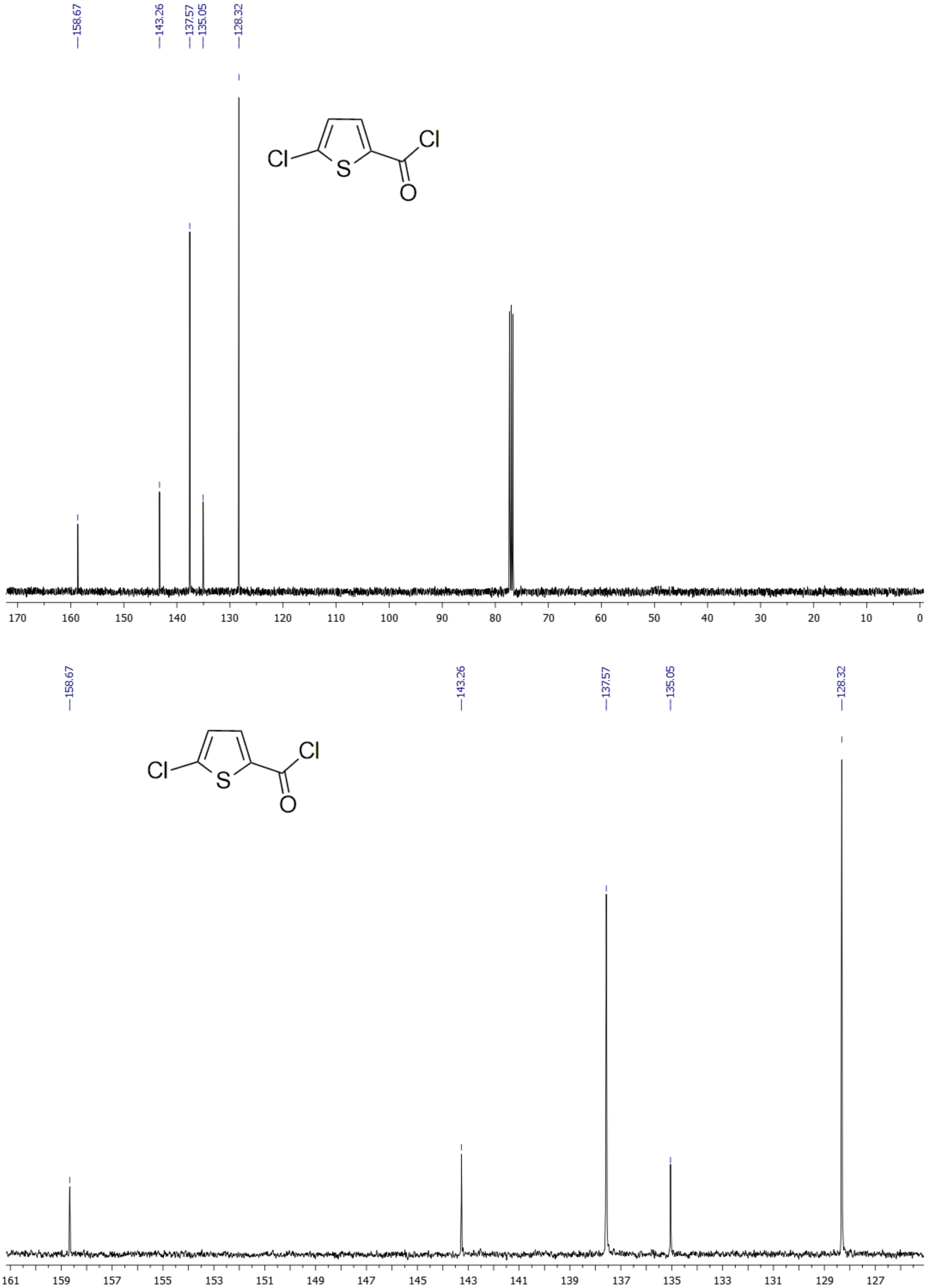


Figure S48. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 5-chlorothiophene-2-carbonyl chloride (**4g**): full scale spectrum (top) and spectrum expansion (bottom).

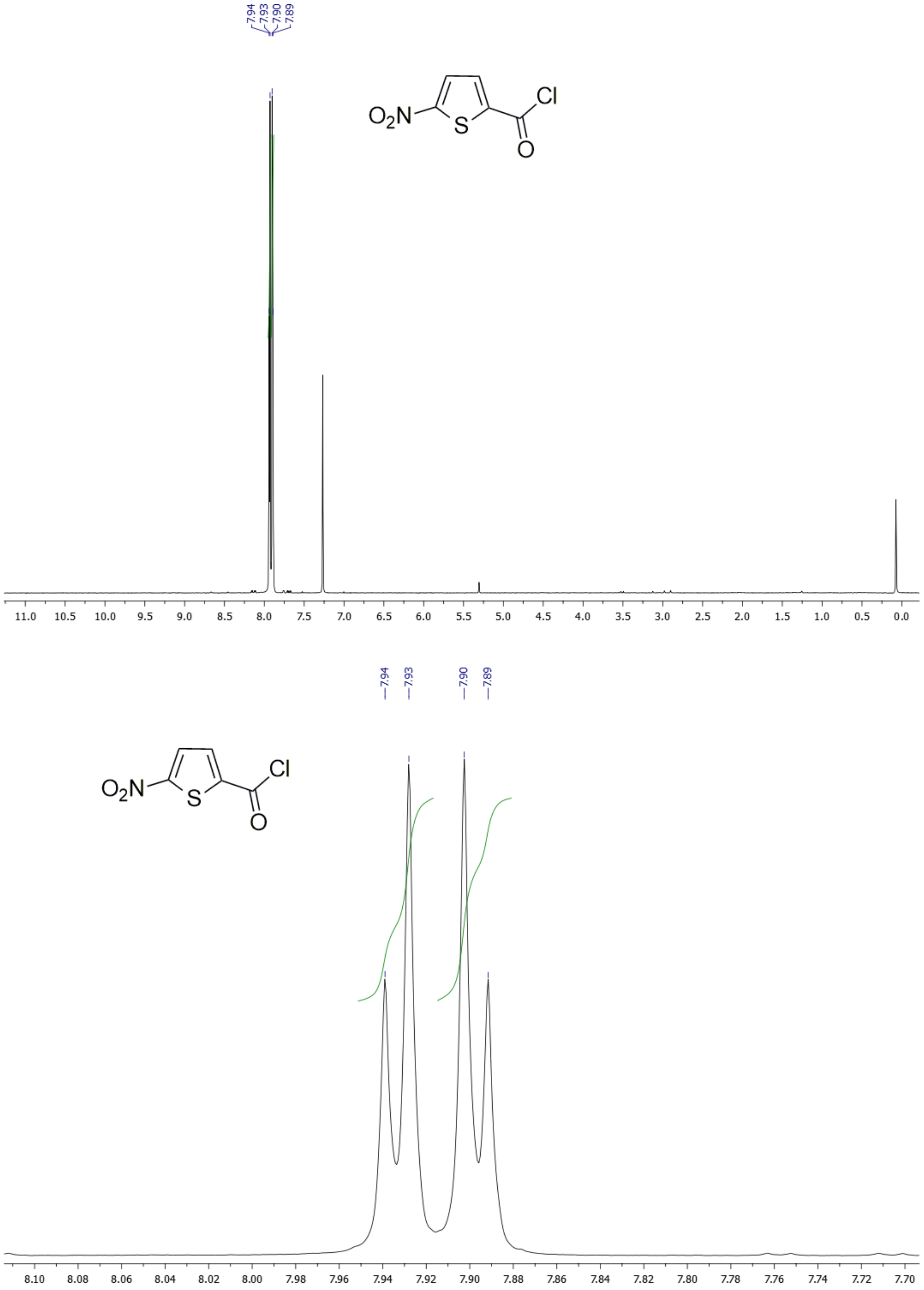


Figure S49. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 5-nitrothiophene-2-carbonyl chloride (**4h**): full scale spectrum (top) and spectrum expansion (bottom).

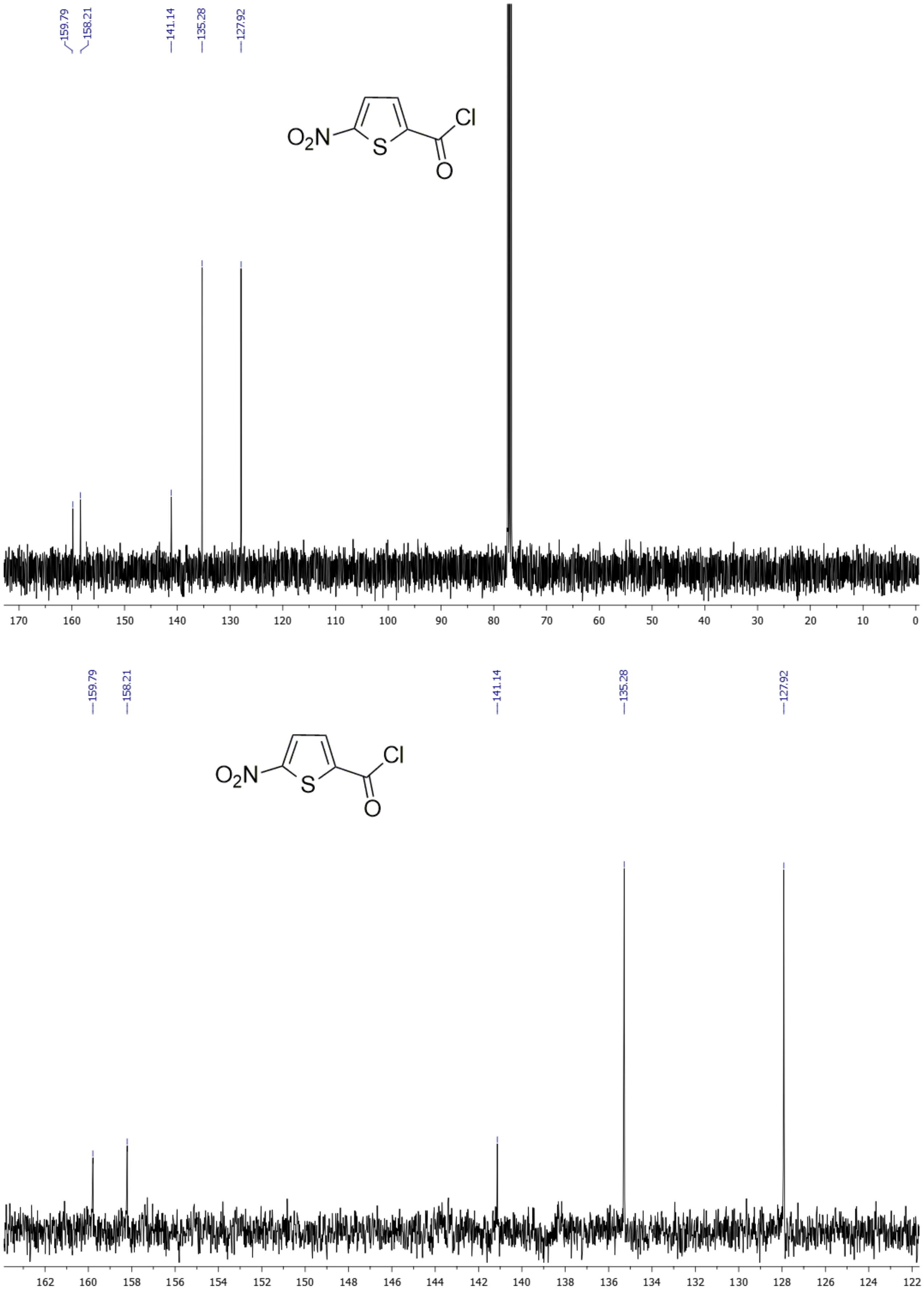


Figure S50. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 5-nitrothiophene-2-carbonyl chloride (**4h**): full scale spectrum (top) and spectrum expansion (bottom).

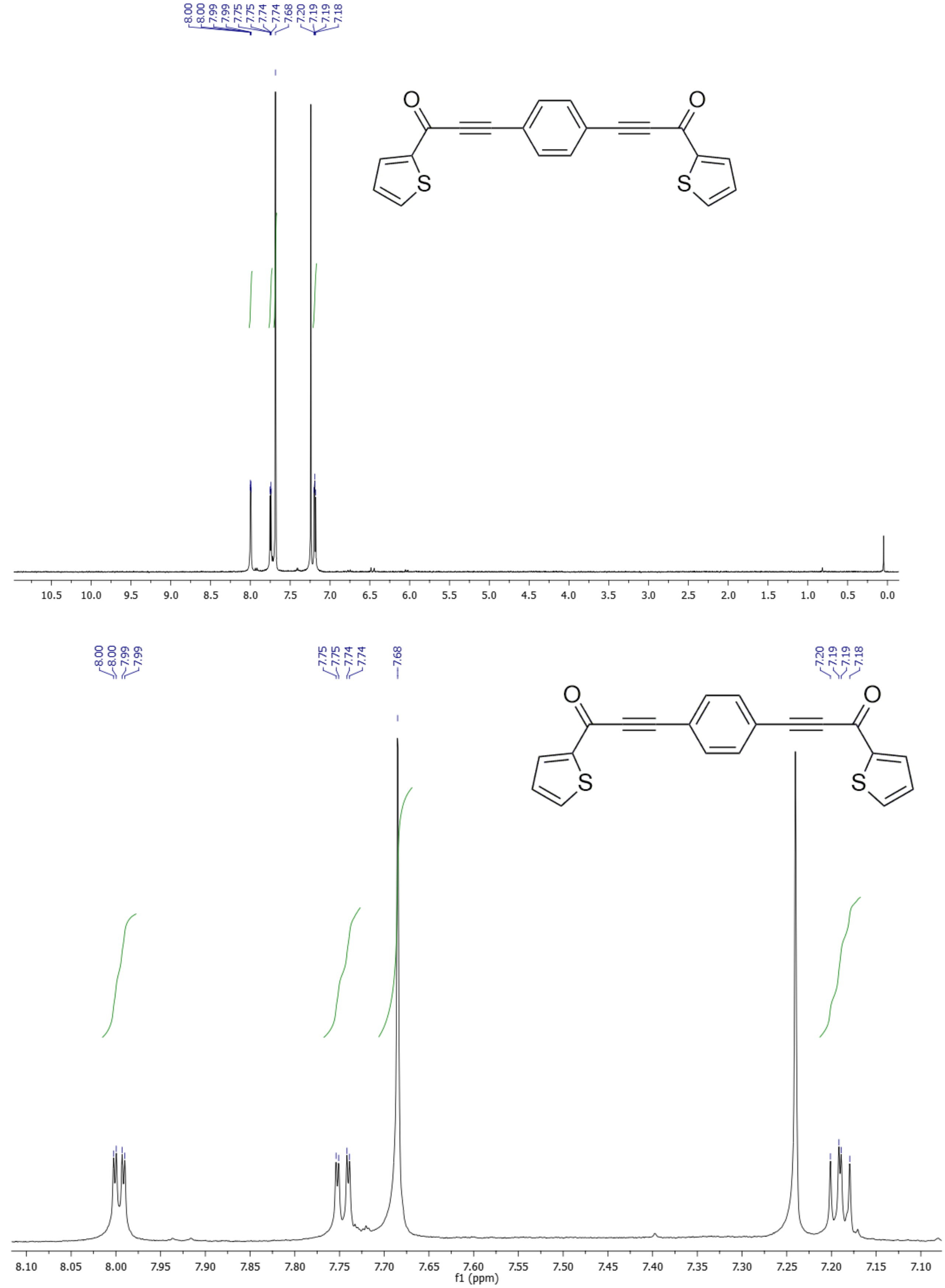


Figure S51. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**): full scale spectrum (top) and spectrum expansion (bottom).

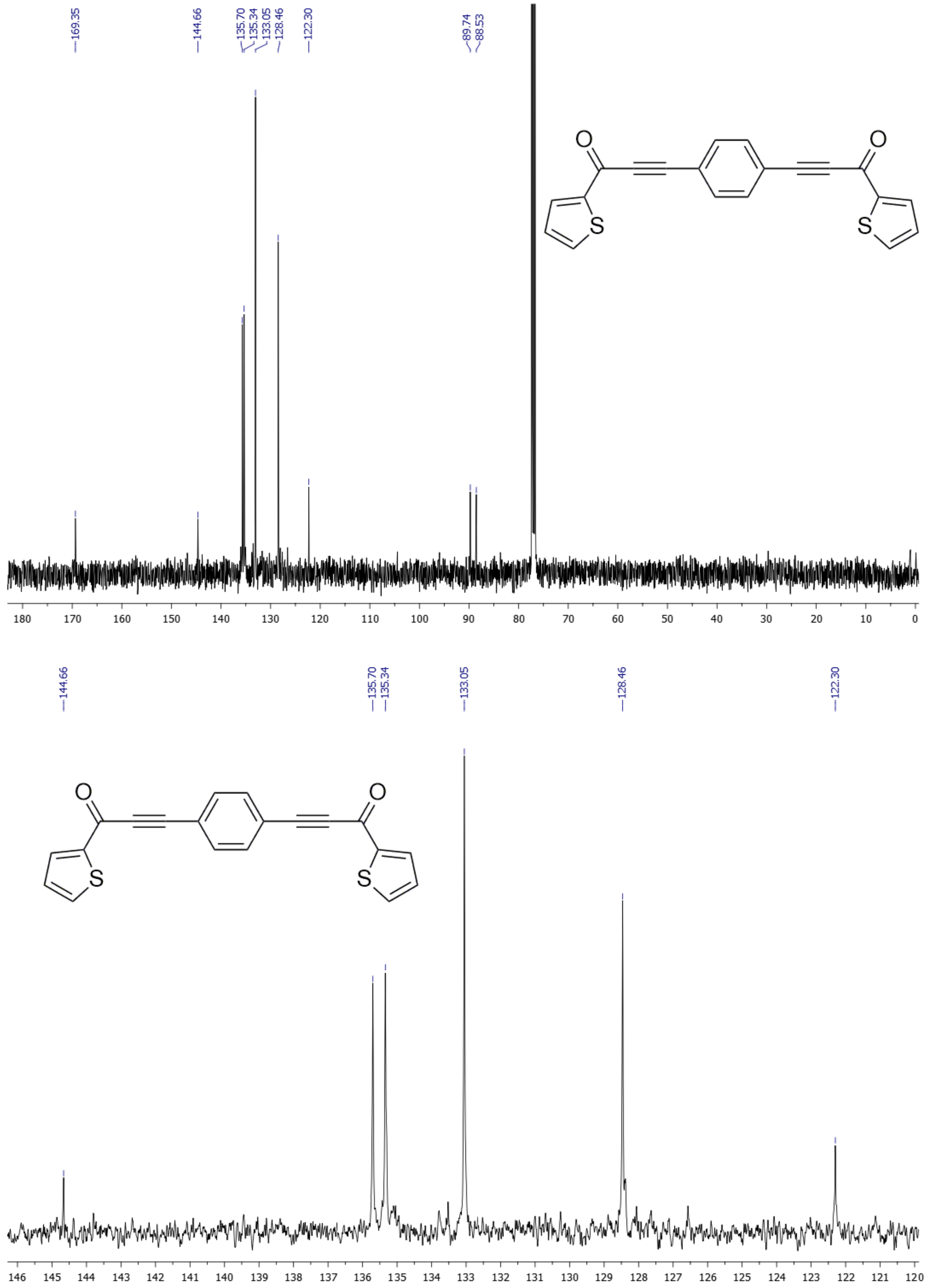


Figure S52. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**): full scale spectrum (top) and spectrum expansion (bottom).

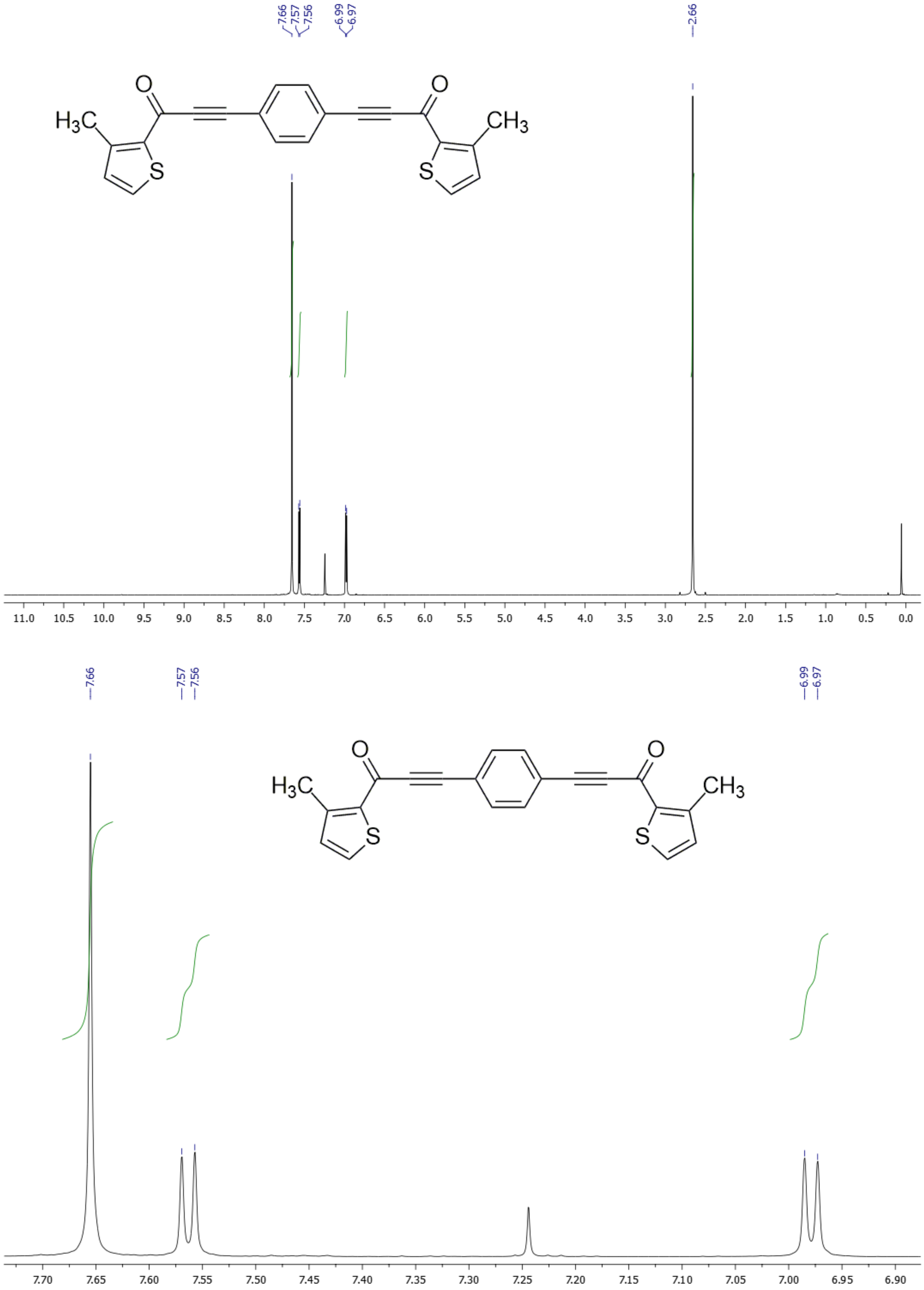


Figure S53. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one) (**1b**): full scale spectrum (top) and spectrum expansion (bottom).

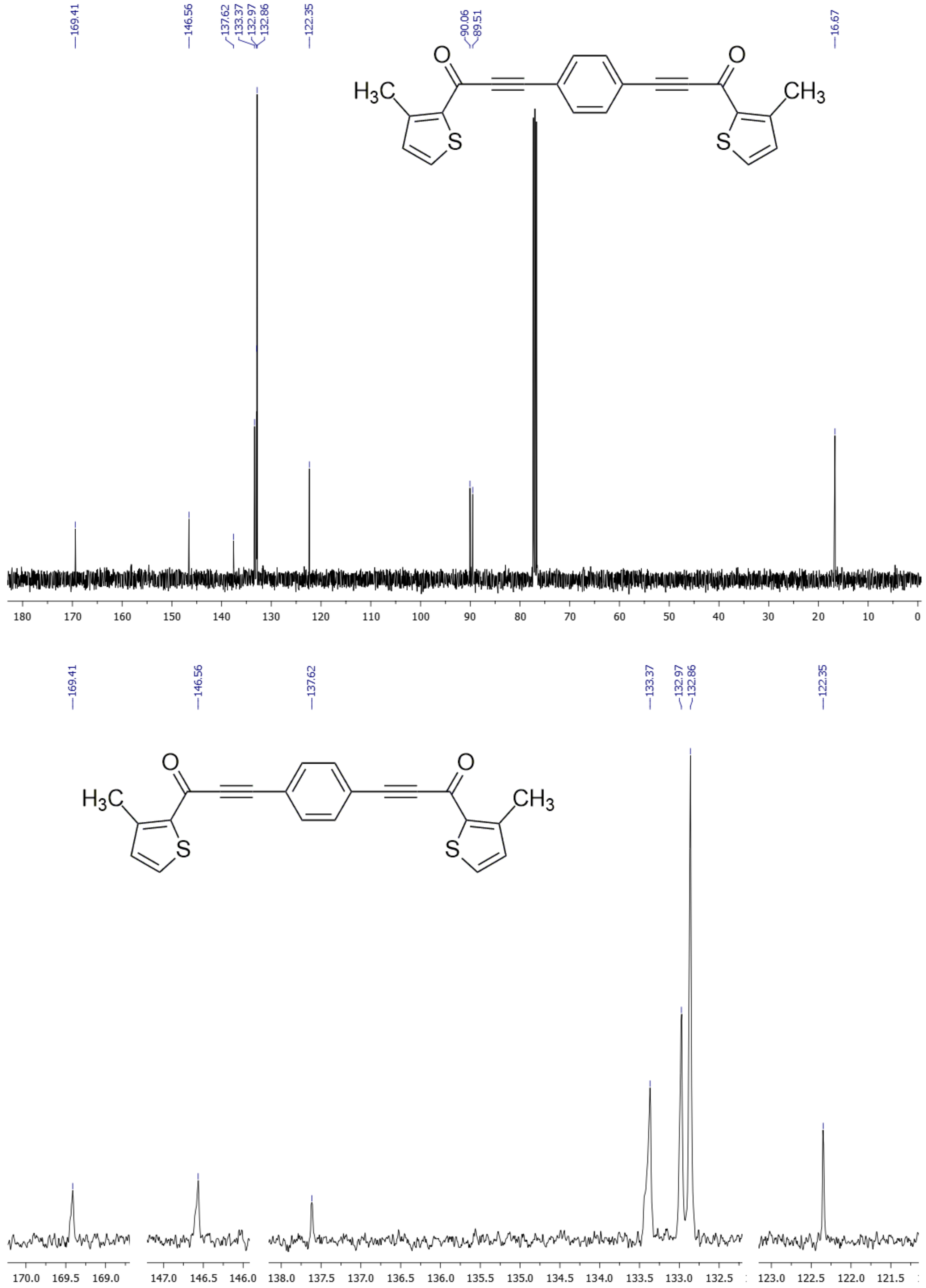


Figure S54. ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of 3,3'-(1,4-phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one) (**1b**): full scale spectrum (top) and spectrum expansions (bottom).

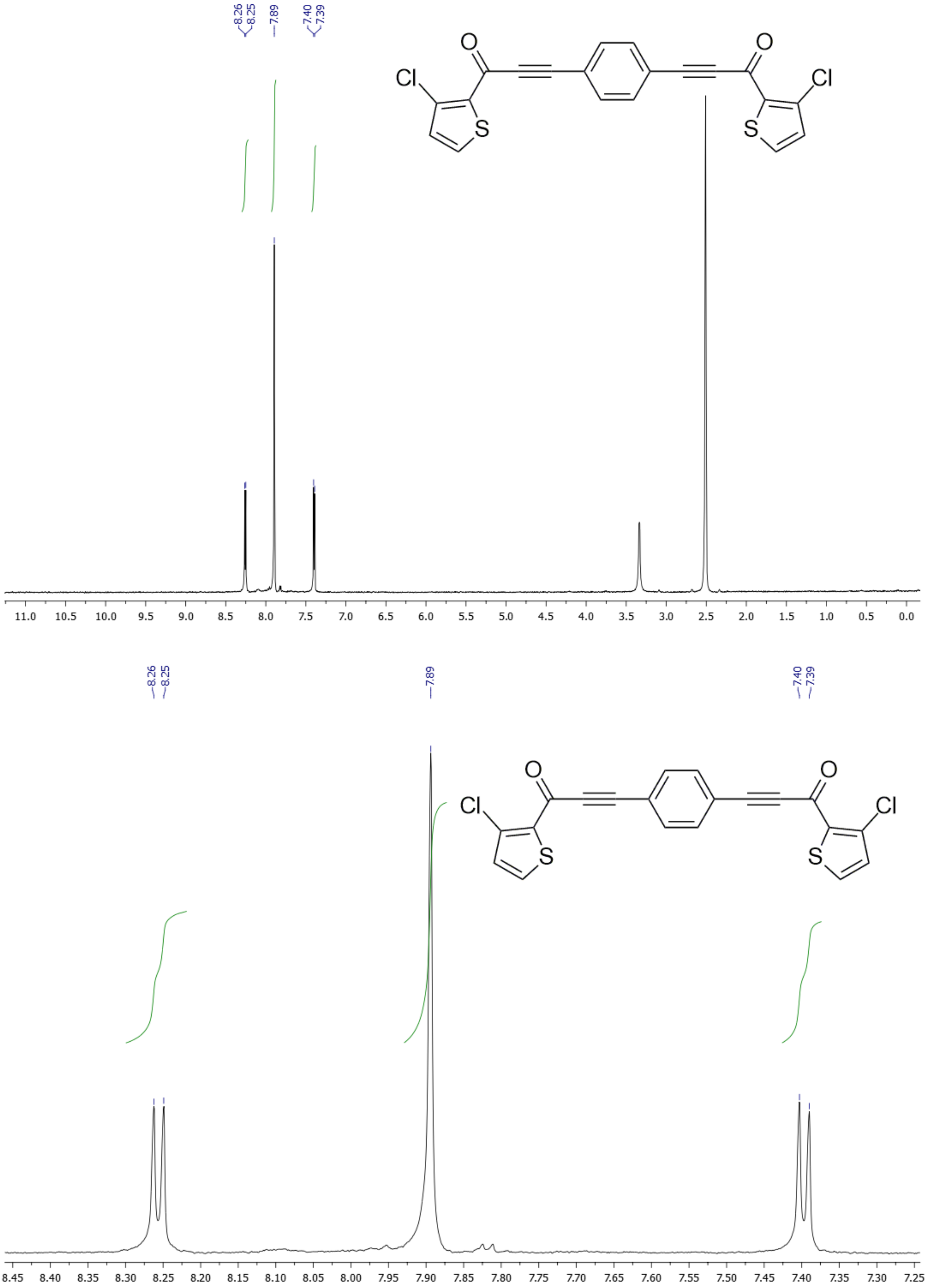


Figure S55. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (**1c**): full scale spectrum (top) and spectrum expansion (bottom).

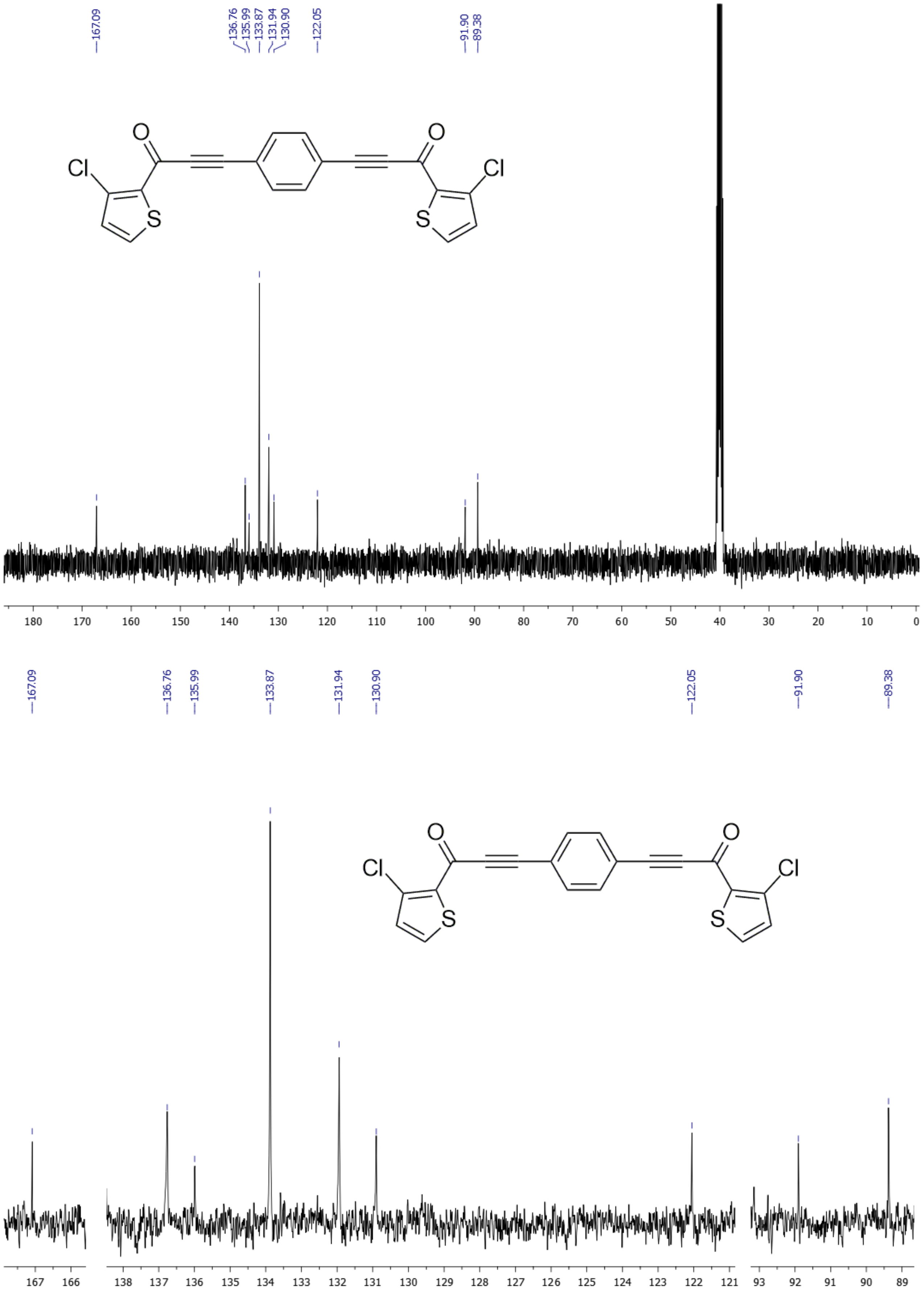


Figure S56. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (**1c**): full scale spectrum (top) and spectrum expansions (bottom).

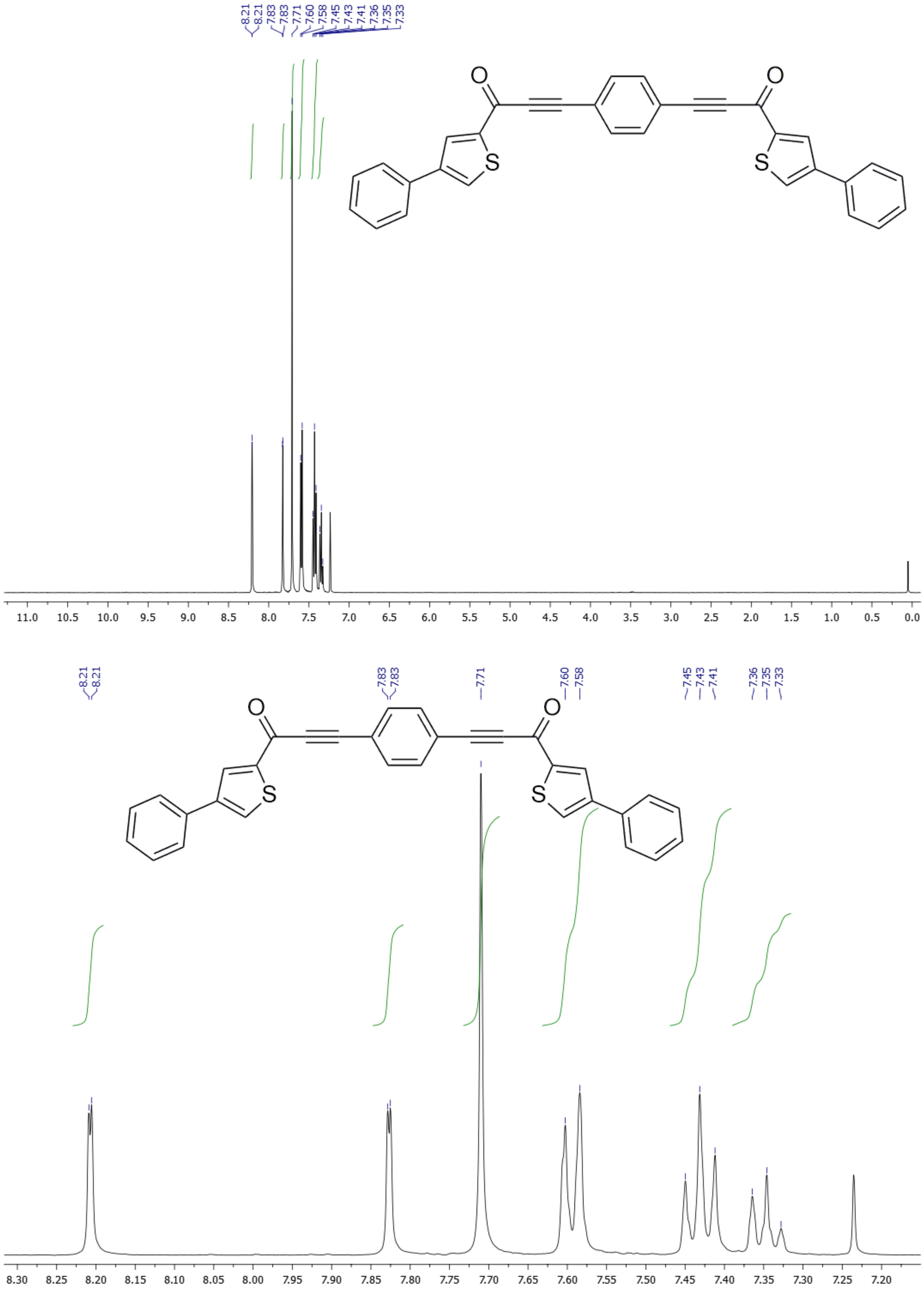
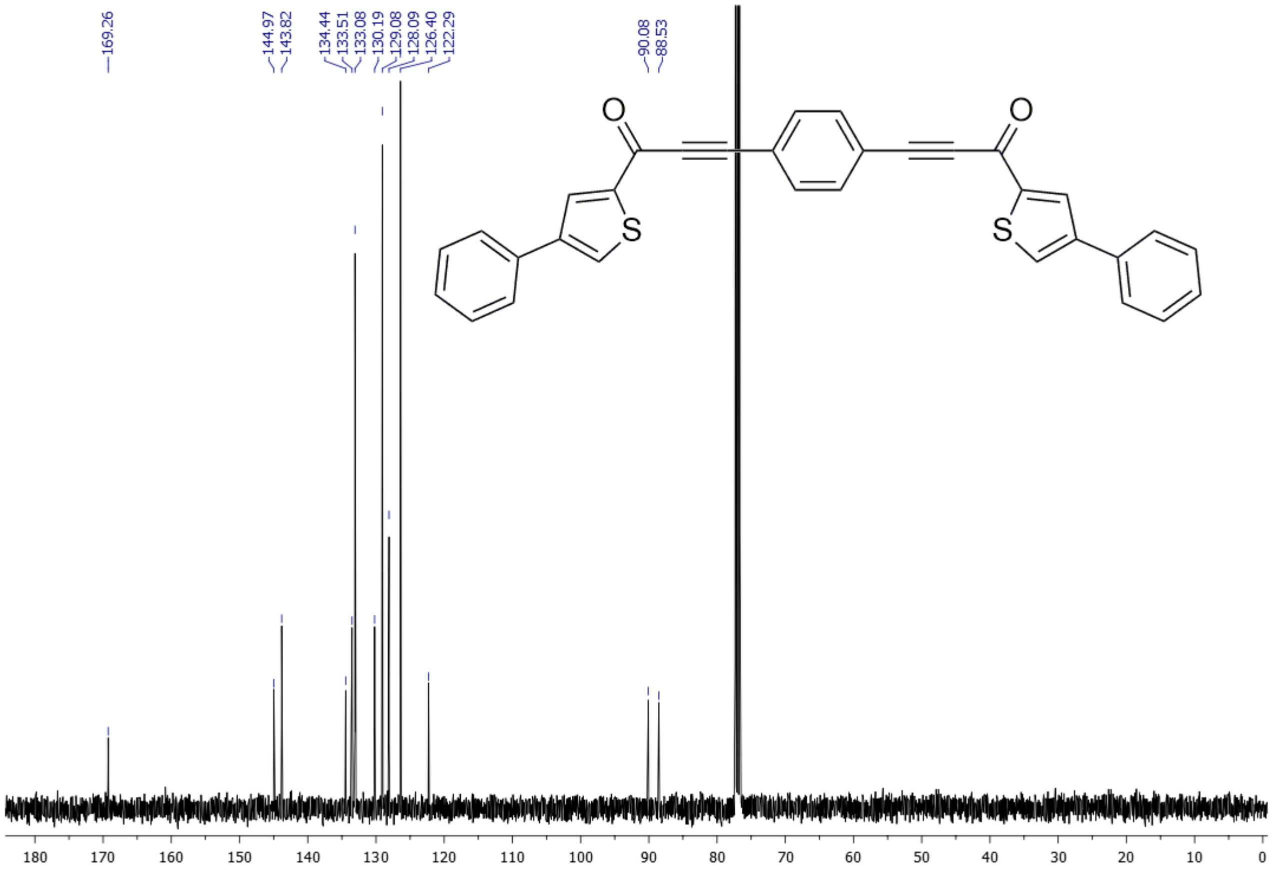


Figure S57. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**): full scale spectrum (top) and spectrum expansion (bottom).



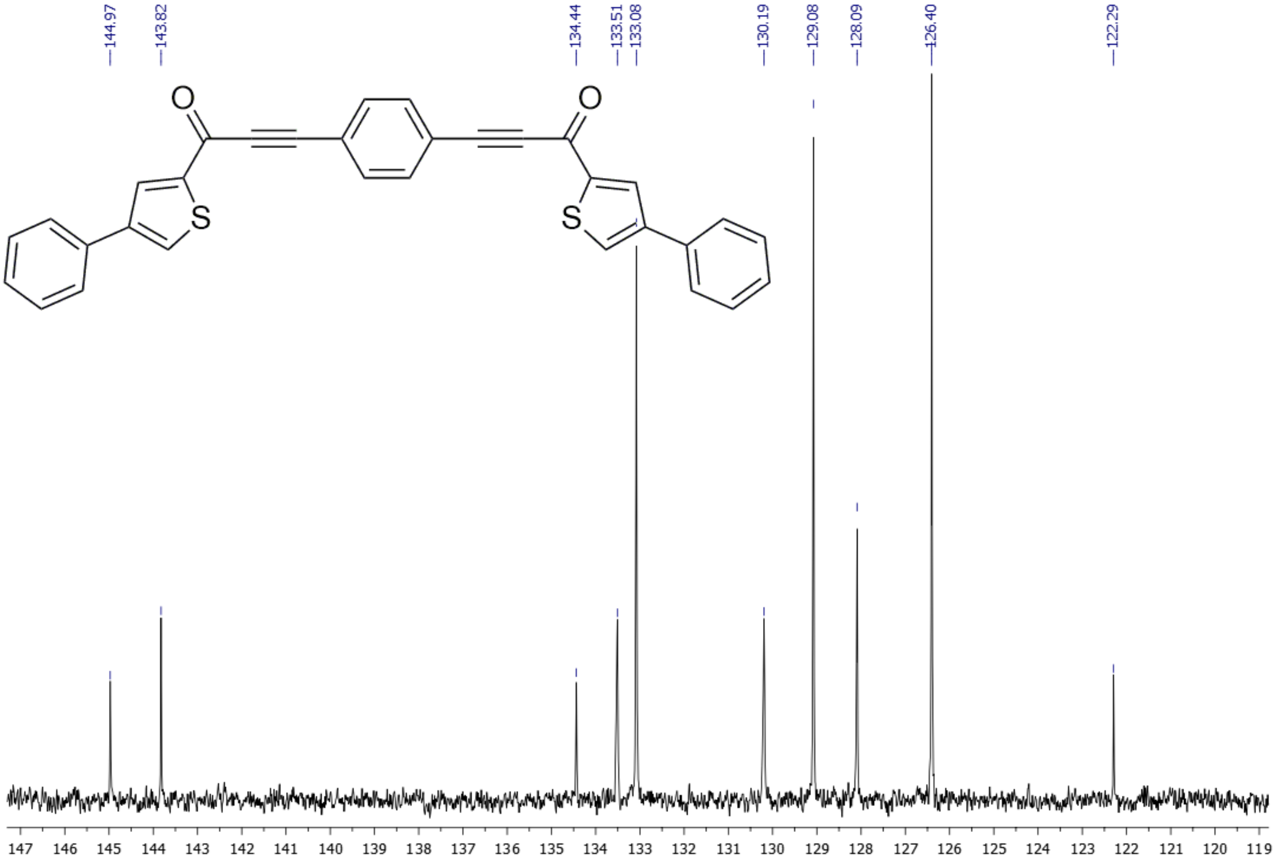


Figure S58. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**): full scale spectrum (top) and spectrum expansion (bottom).

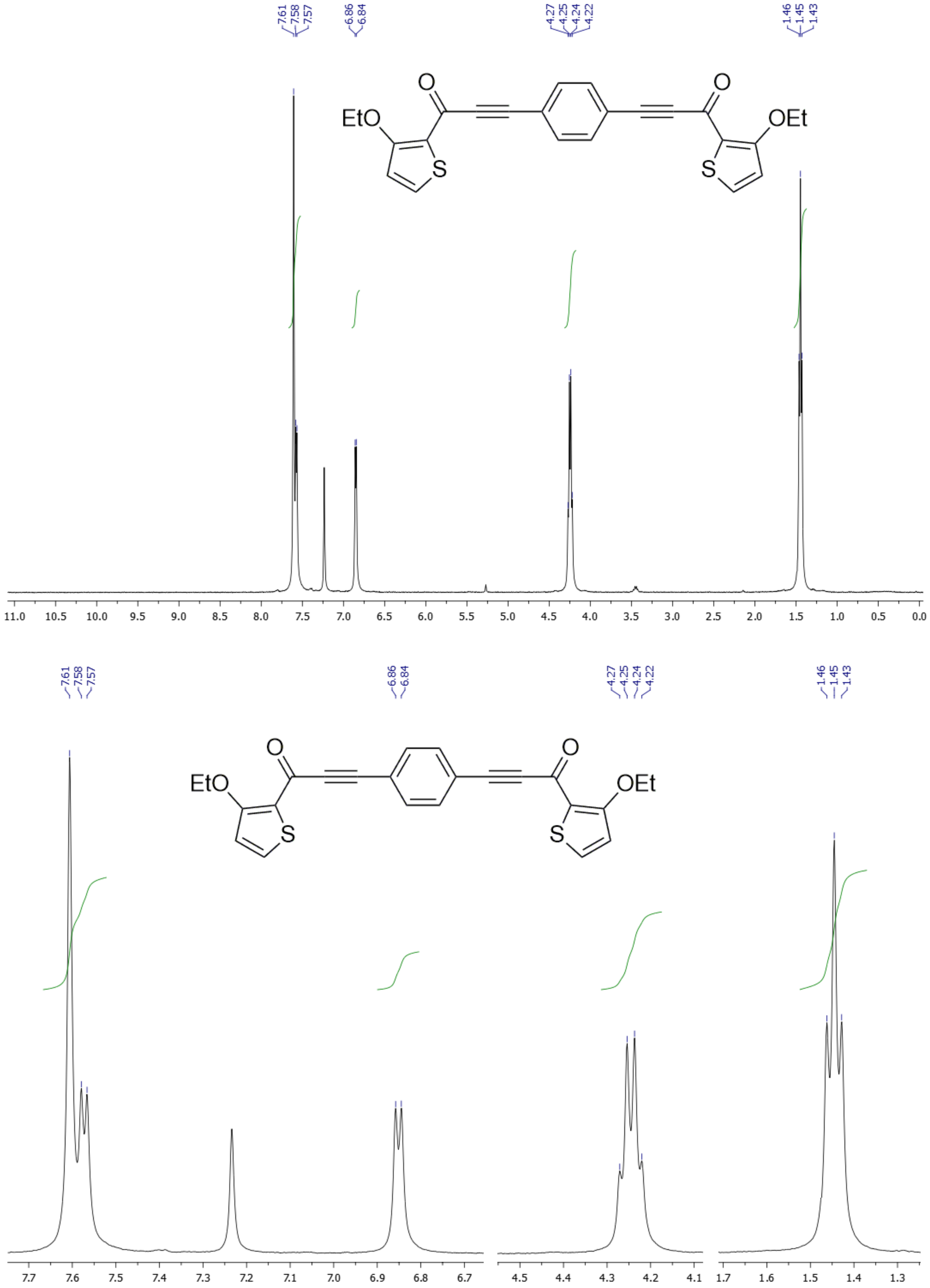


Figure S59. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of 3,3'-(1,4-phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**): full scale spectrum (top) and spectrum expansions (bottom).

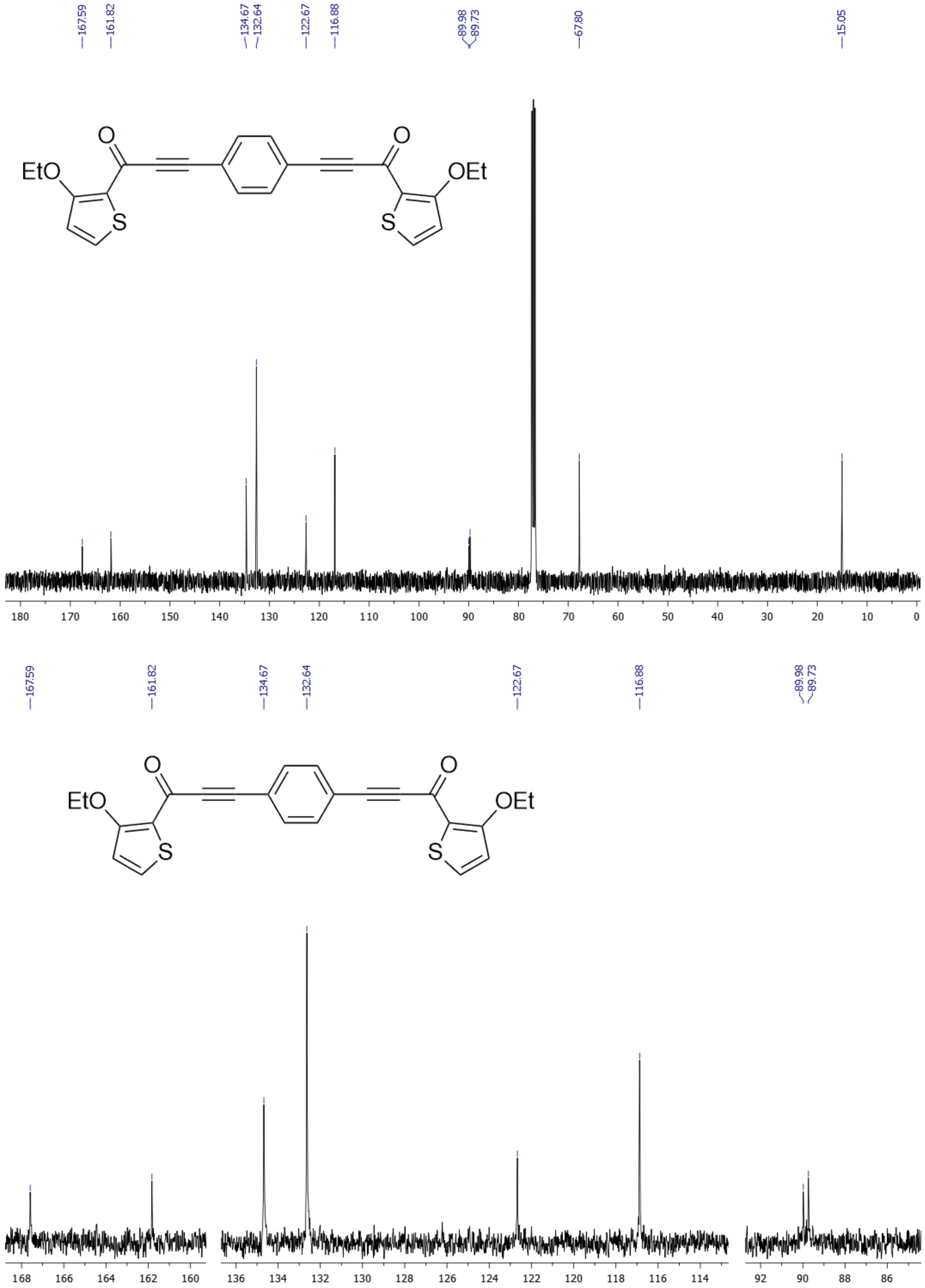


Figure S60. ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of 3,3'-(1,4-phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**): full scale spectrum (top) and spectrum expansions (bottom).

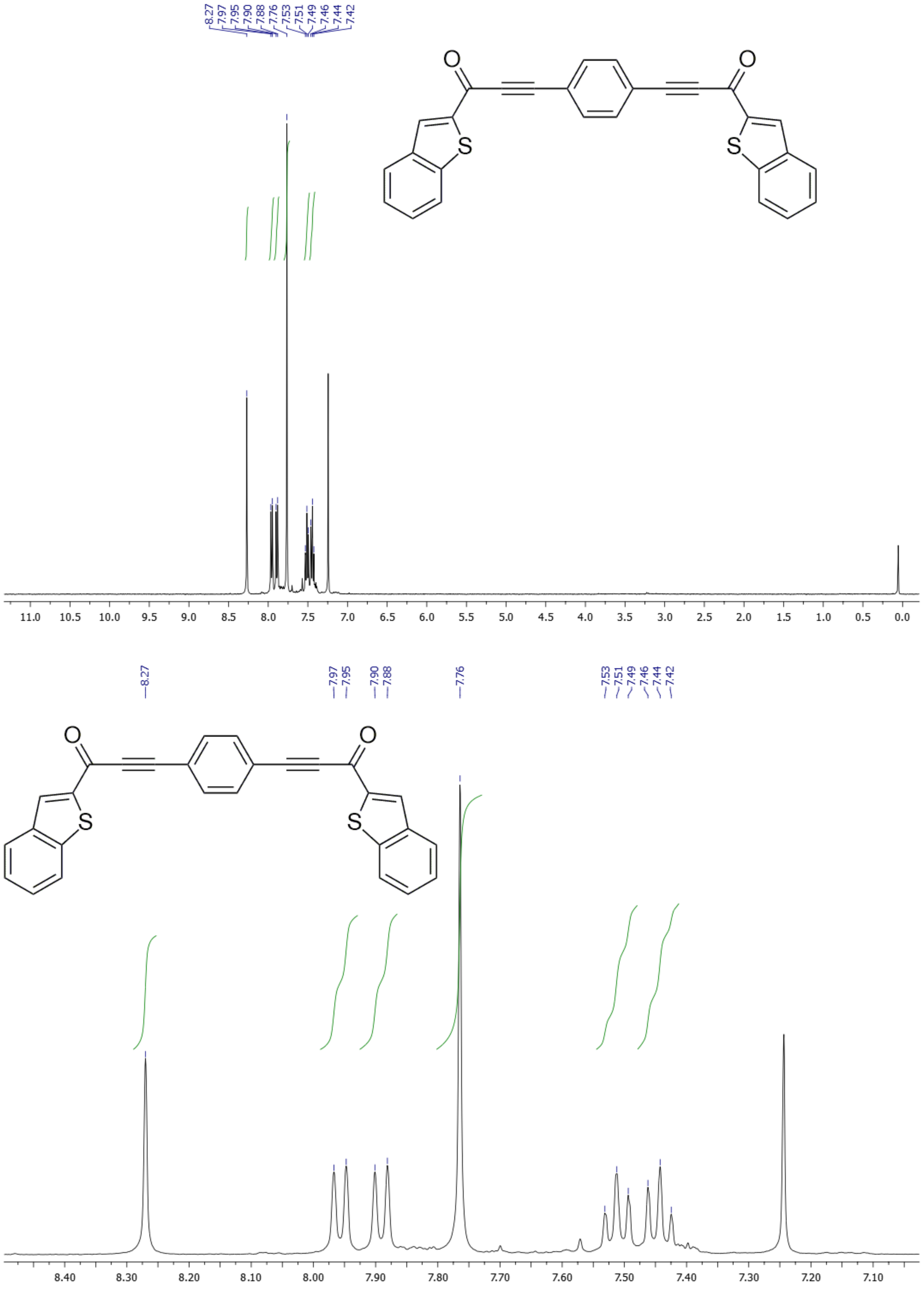


Figure S61. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(benzo[*b*]thiophen-2-yl)prop-2-yn-1-one) (**1f**): full scale spectrum (top) and spectrum expansion (bottom).

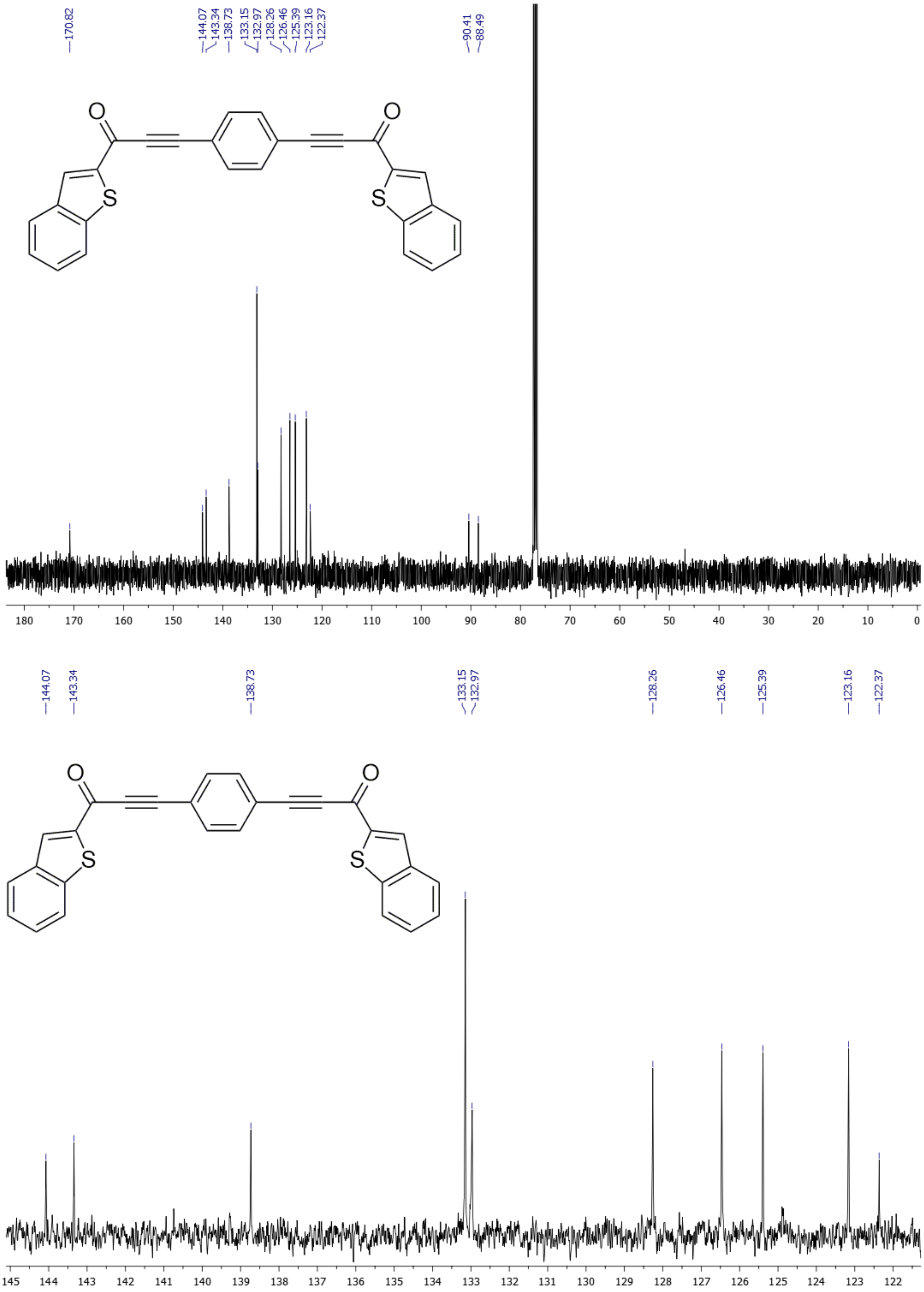


Figure S62. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(benzo[*b*]thiophen-2-yl)prop-2-yn-1-one) (**1f**): full scale spectrum (top) and spectrum expansion (bottom).

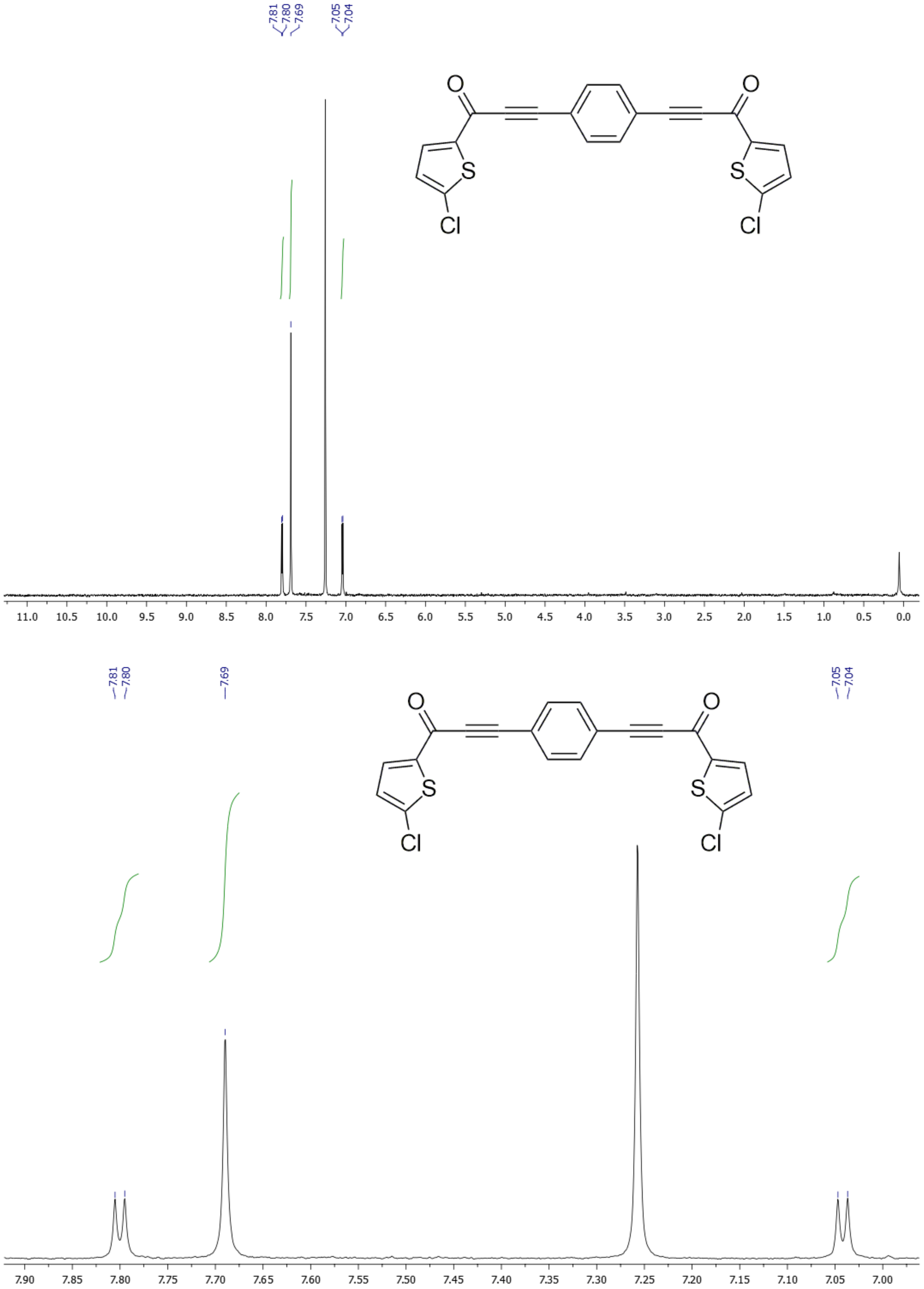


Figure S63. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (**1g**): full scale spectrum (top) and spectrum expansion (bottom).

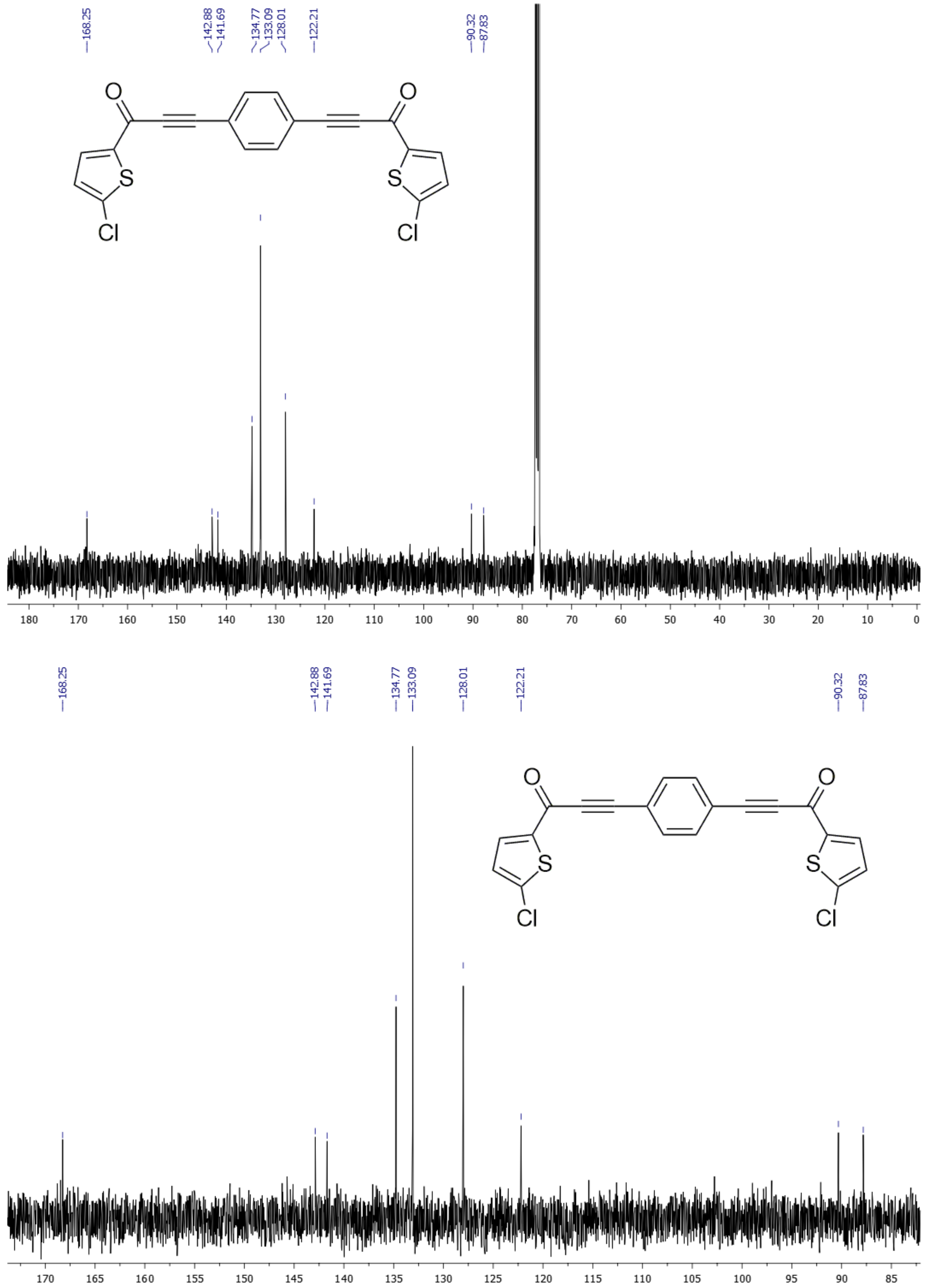


Figure S64. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (**1g**): full scale spectrum (top) and spectrum expansion (bottom).

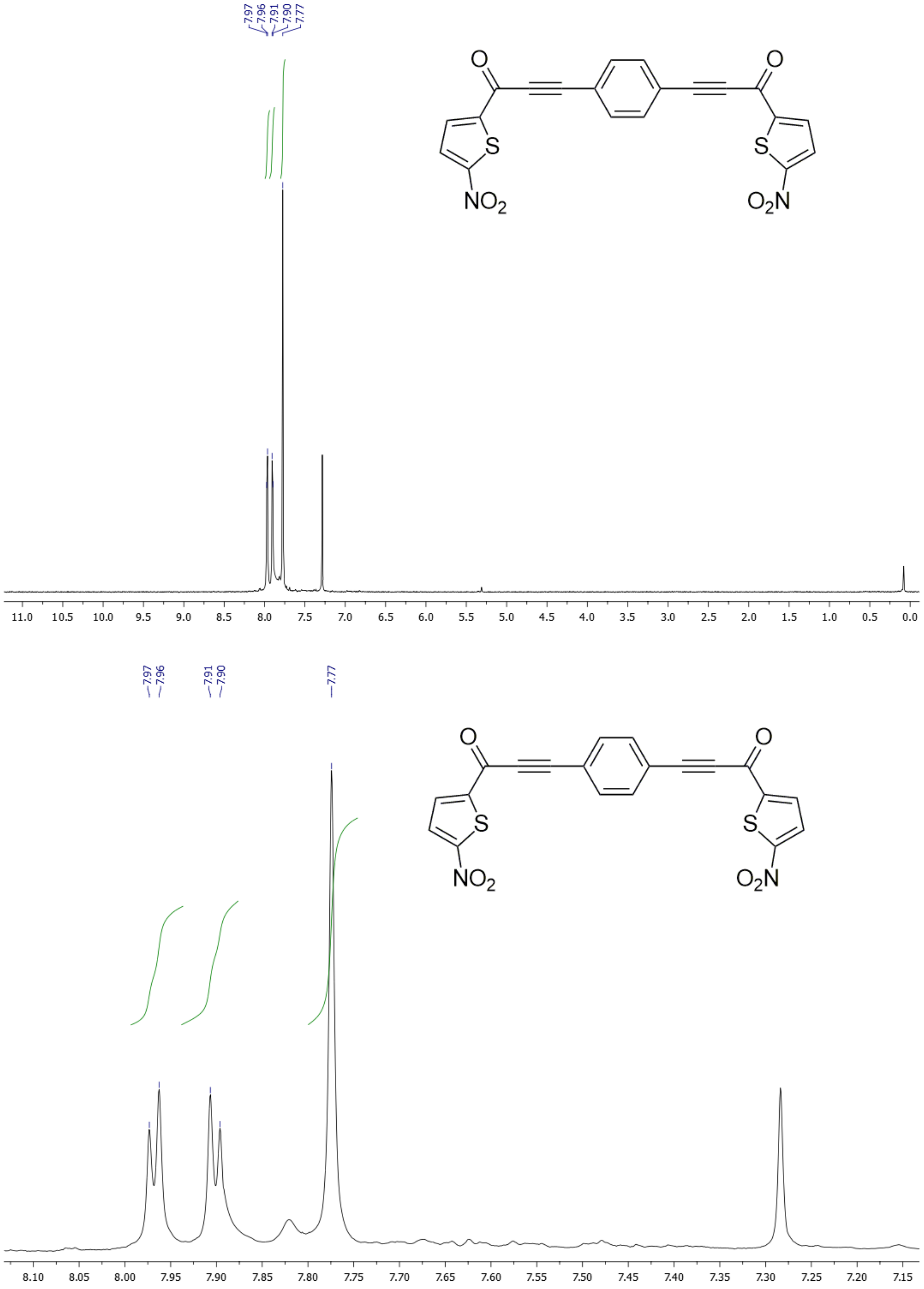


Figure S65. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**): full scale spectrum (top) and spectrum expansion (bottom).

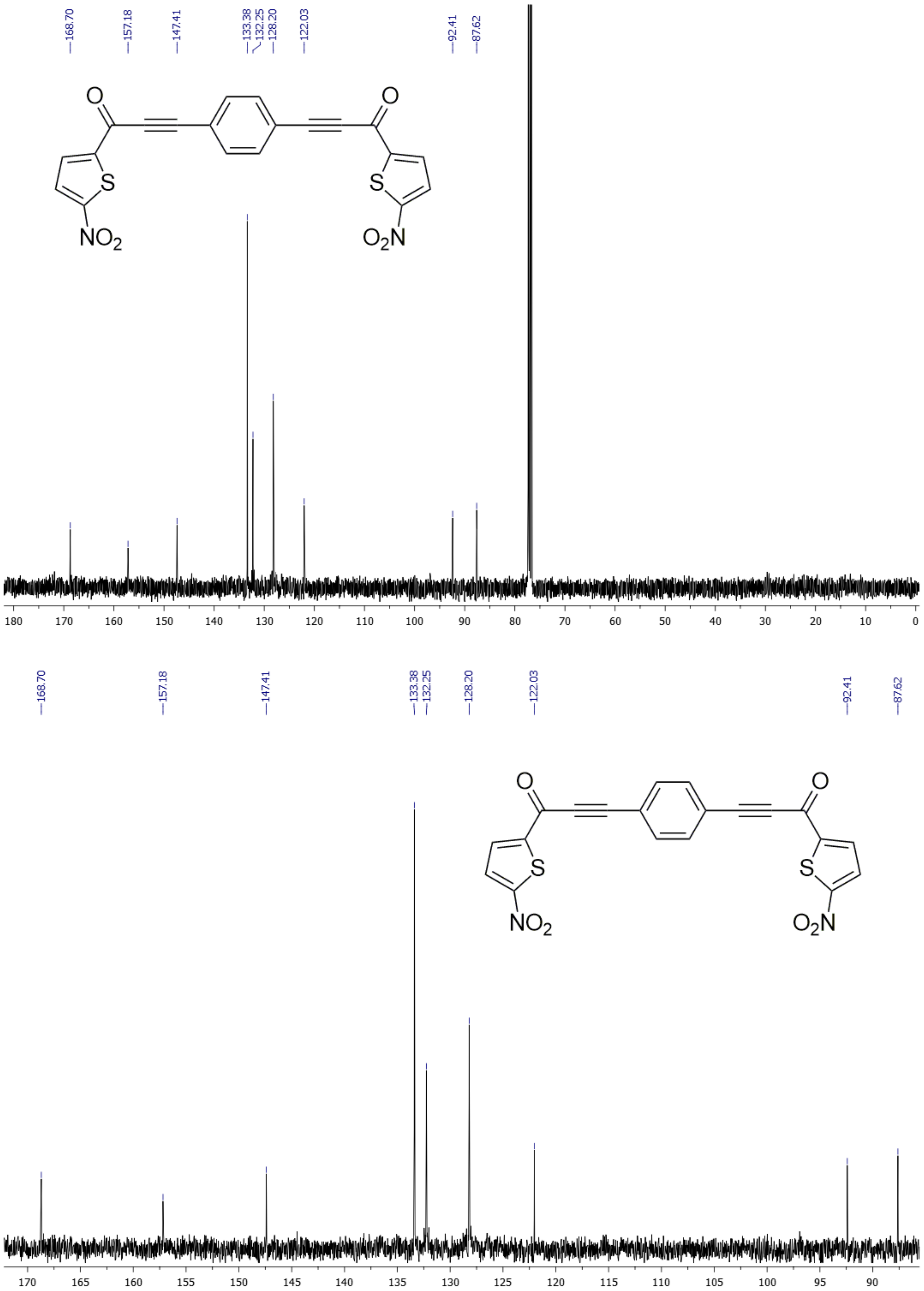


Figure S66. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(1,4-phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**): full scale spectrum (top) and spectrum expansion (bottom).

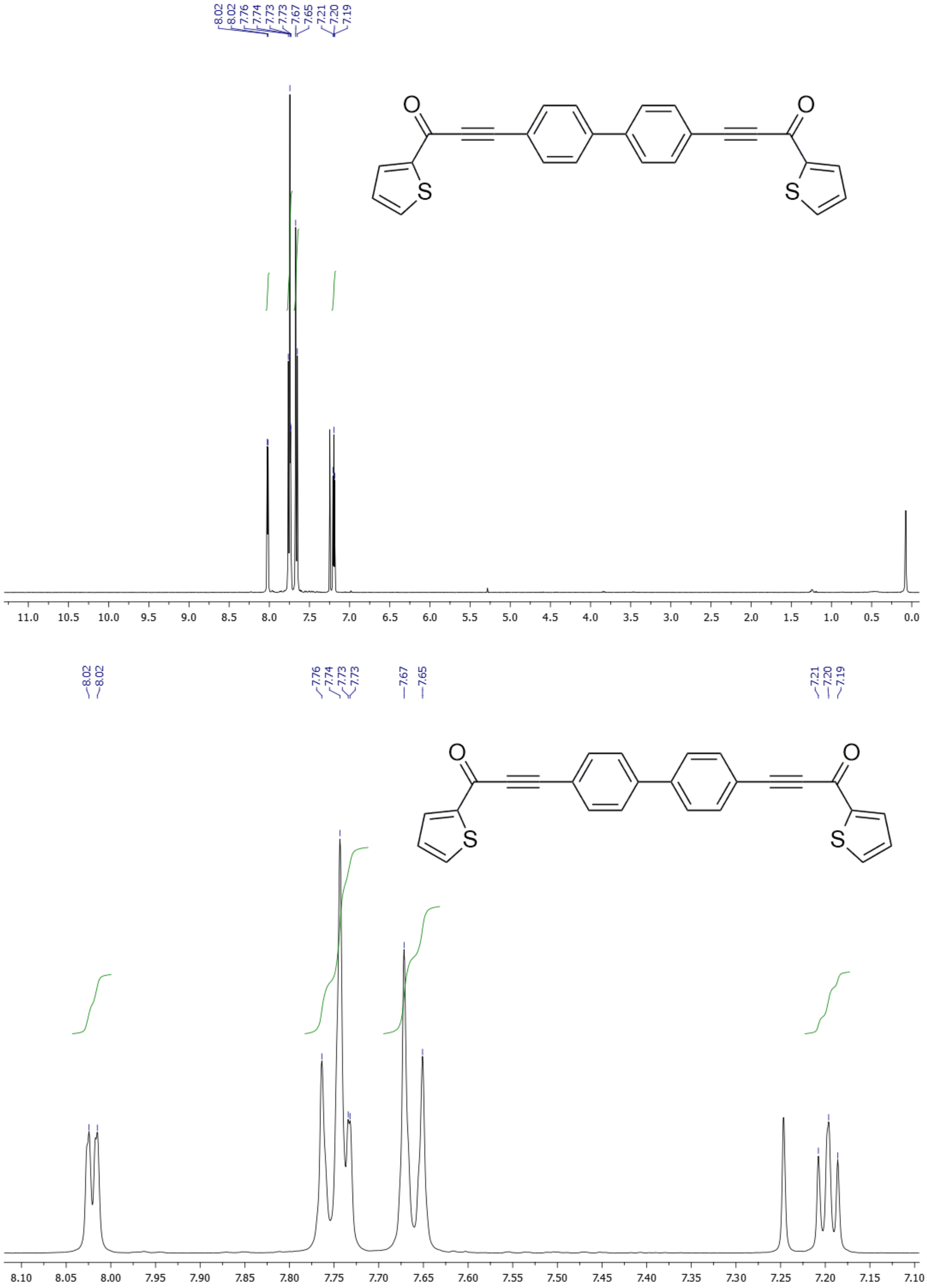


Figure S67. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10a**): full scale spectrum (top) and spectrum expansion (bottom).

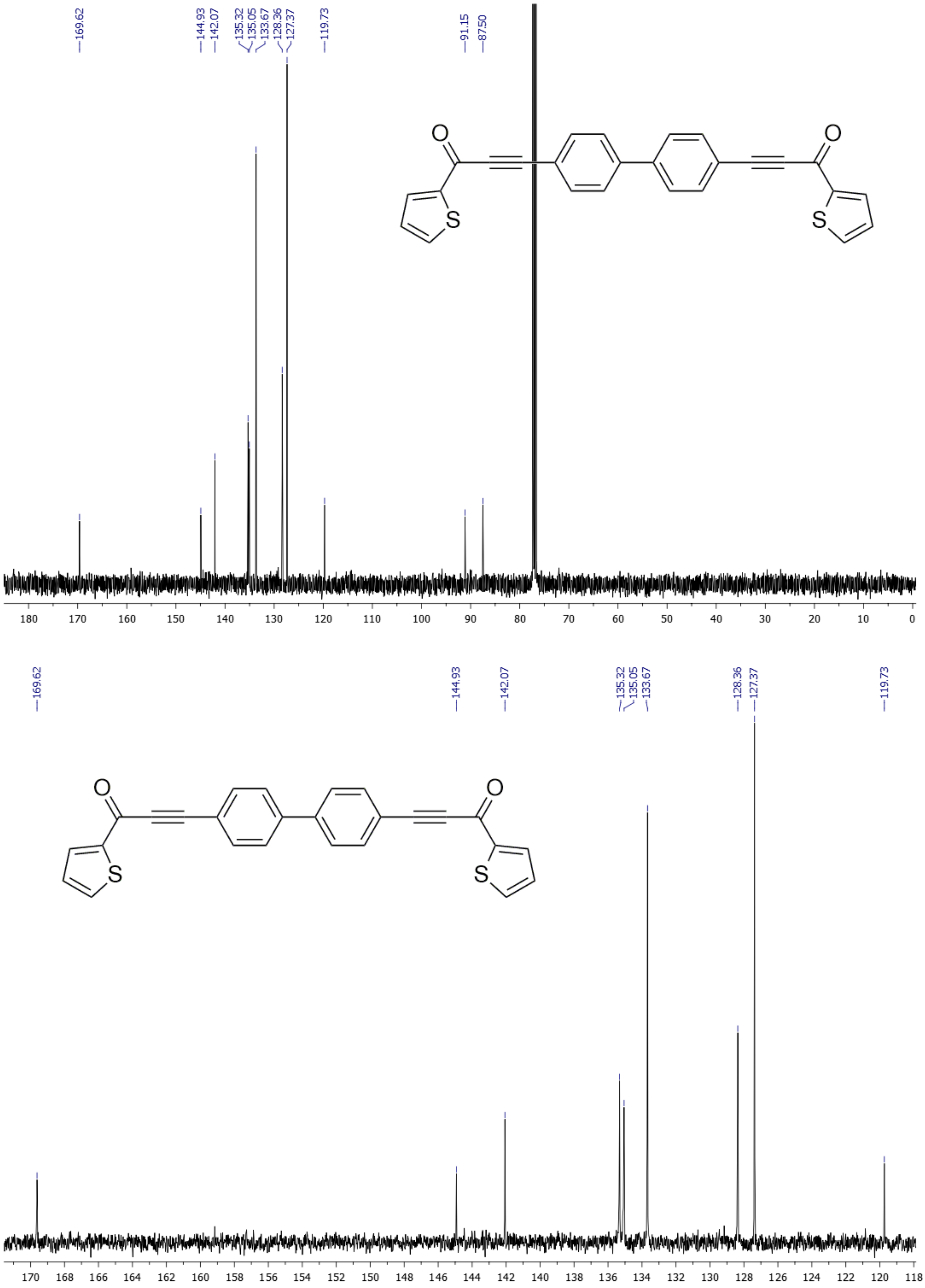


Figure S68. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10a**): full scale spectrum (top) and spectrum expansion (bottom).

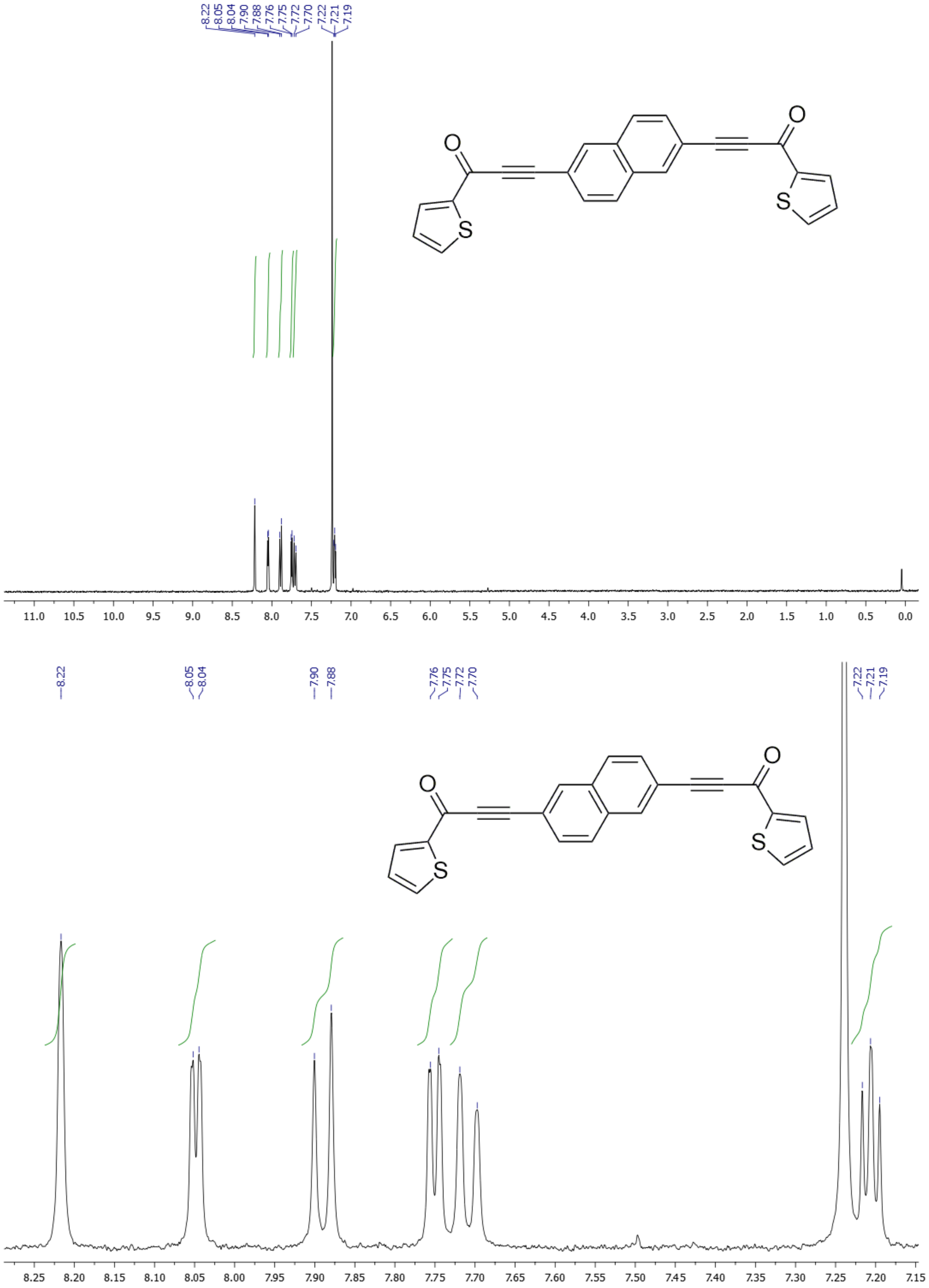


Figure S69. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**): full scale spectrum (top) and spectrum expansion (bottom).

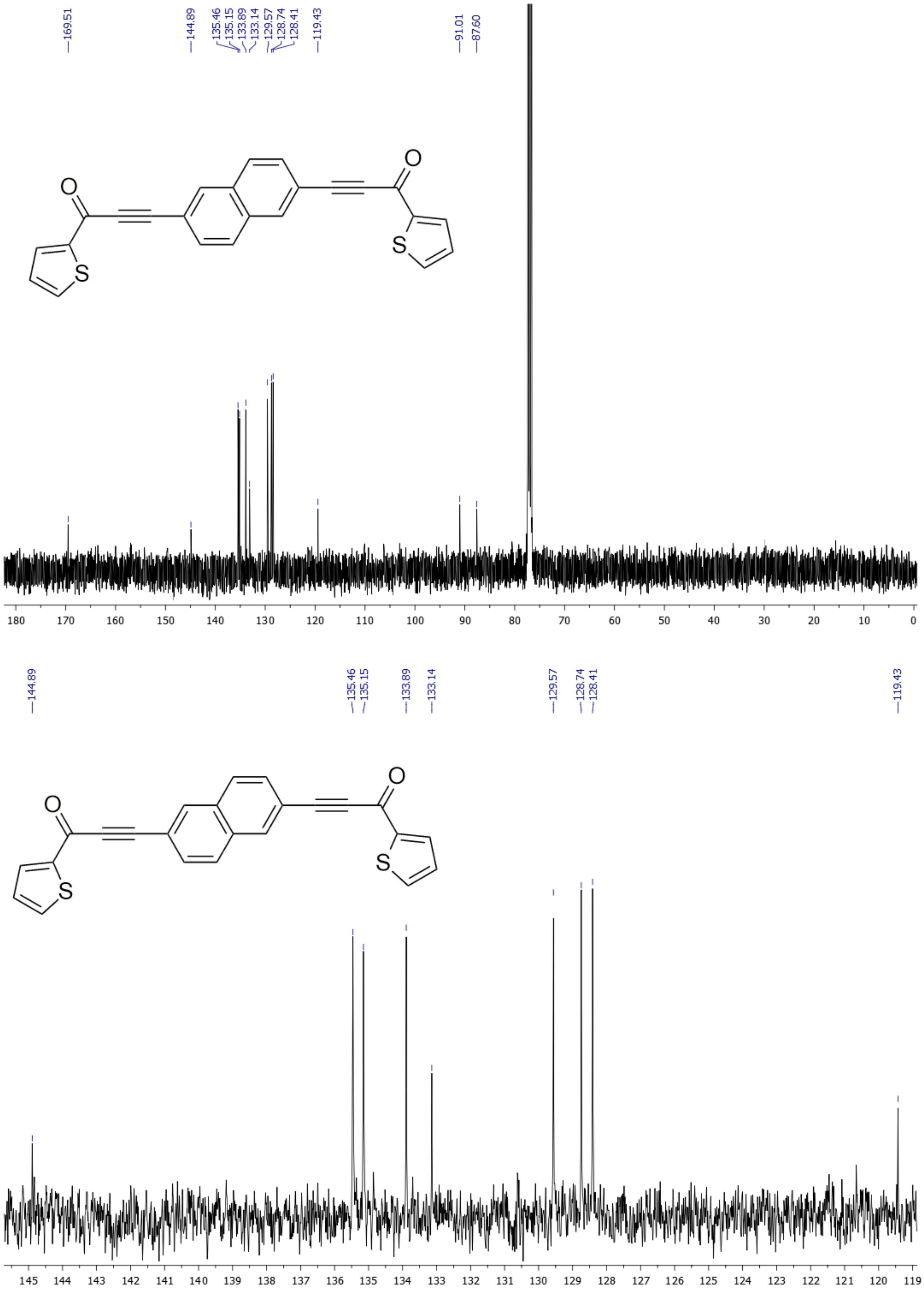


Figure S70. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**): full scale spectrum (top) and spectrum expansion (bottom).

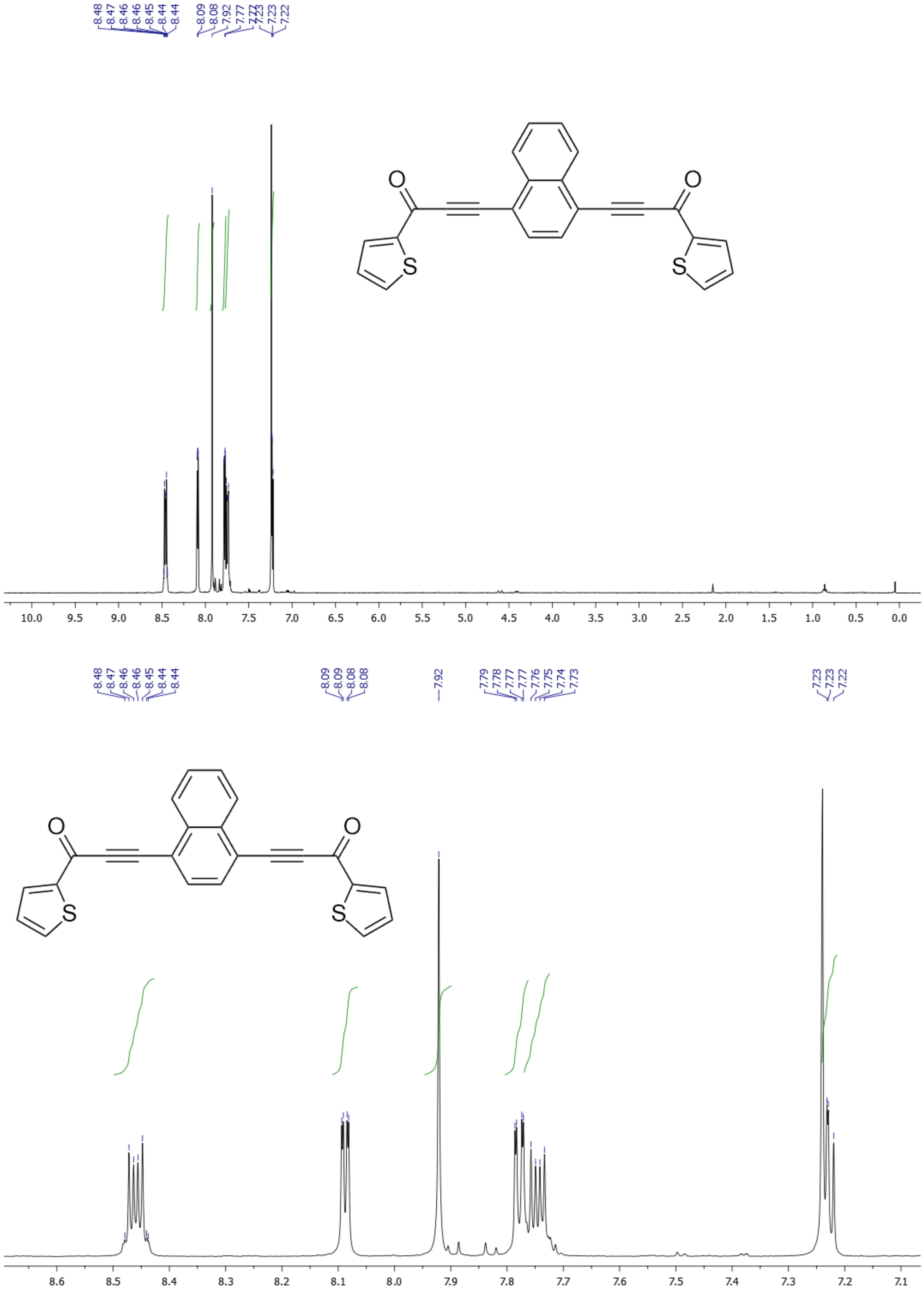


Figure S71. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**): full scale spectrum (top) and spectrum expansion (bottom).

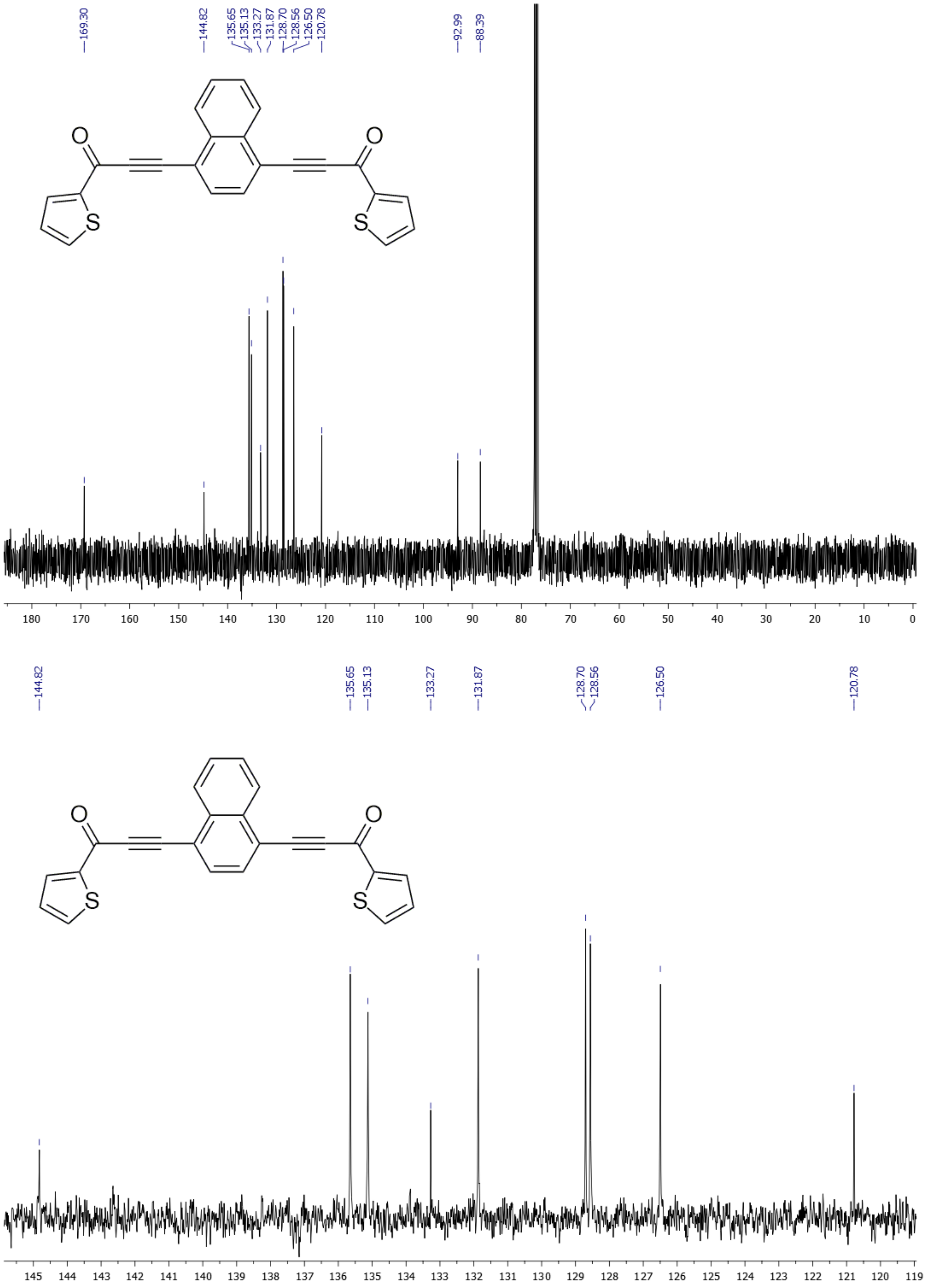


Figure S72. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**): full scale spectrum (top) and spectrum expansion (bottom).

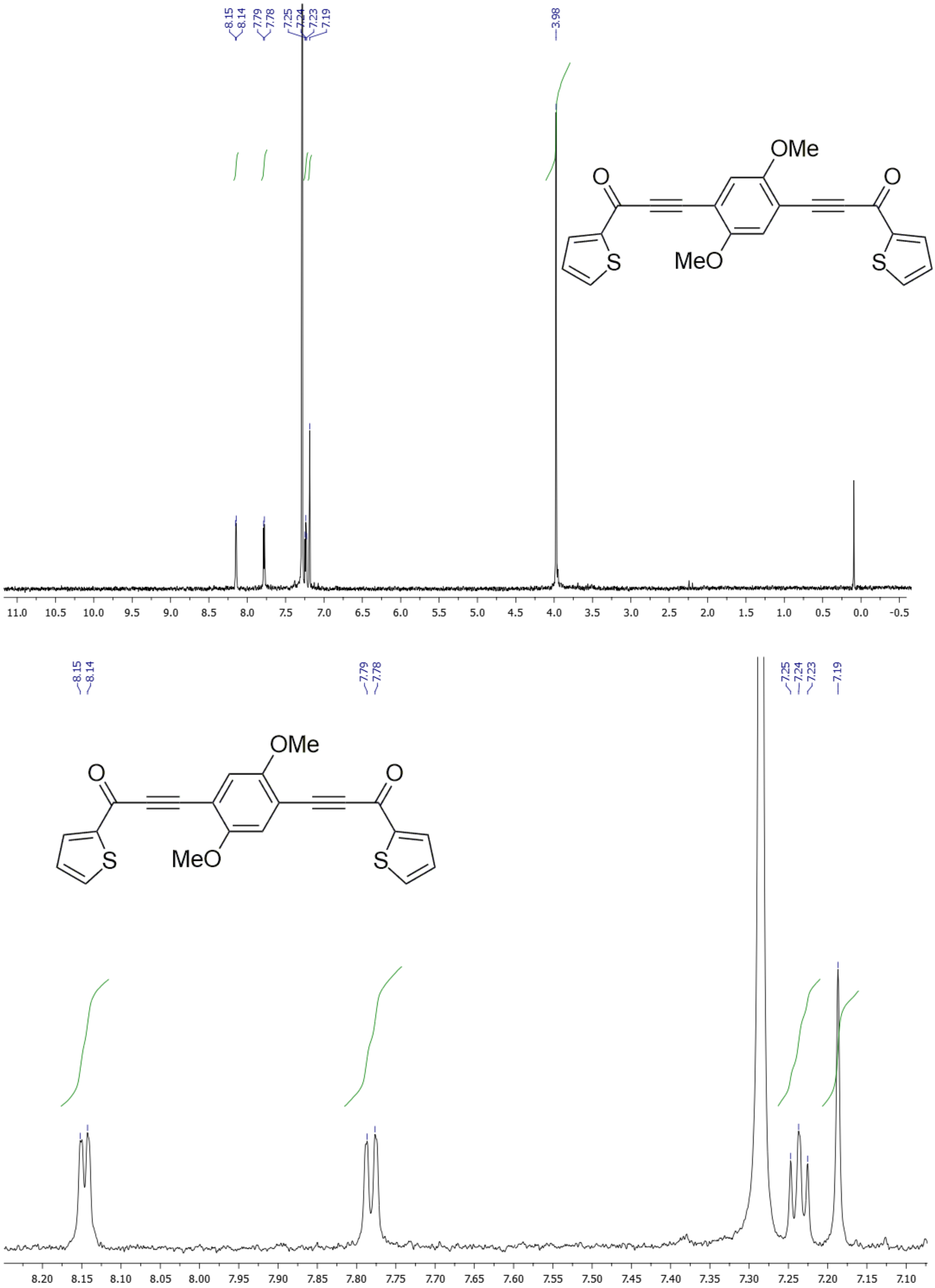


Figure S73. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**): full scale spectrum (top) and spectrum expansion (bottom).

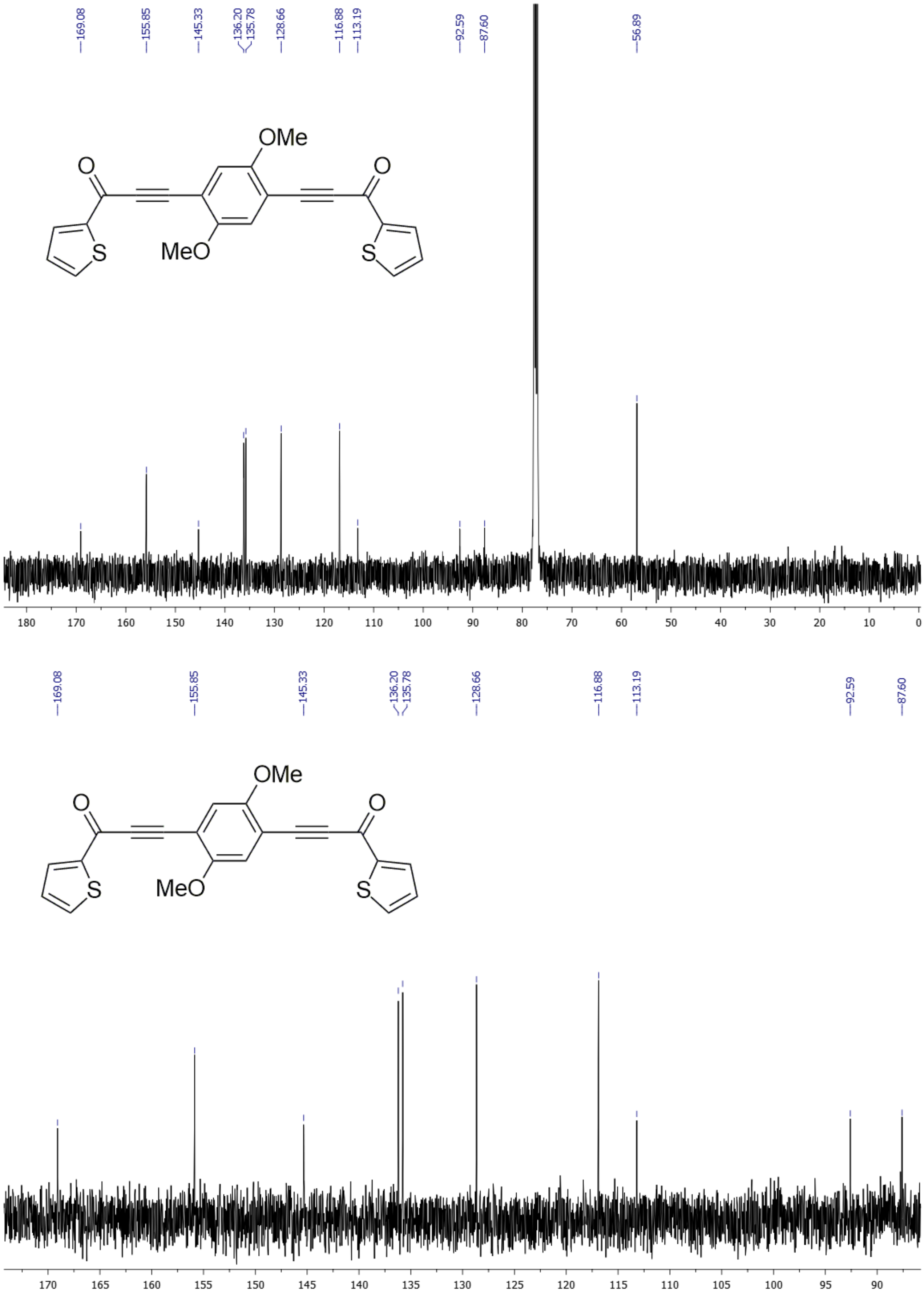


Figure S74. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**): full scale spectrum (top) and spectrum expansion (bottom).

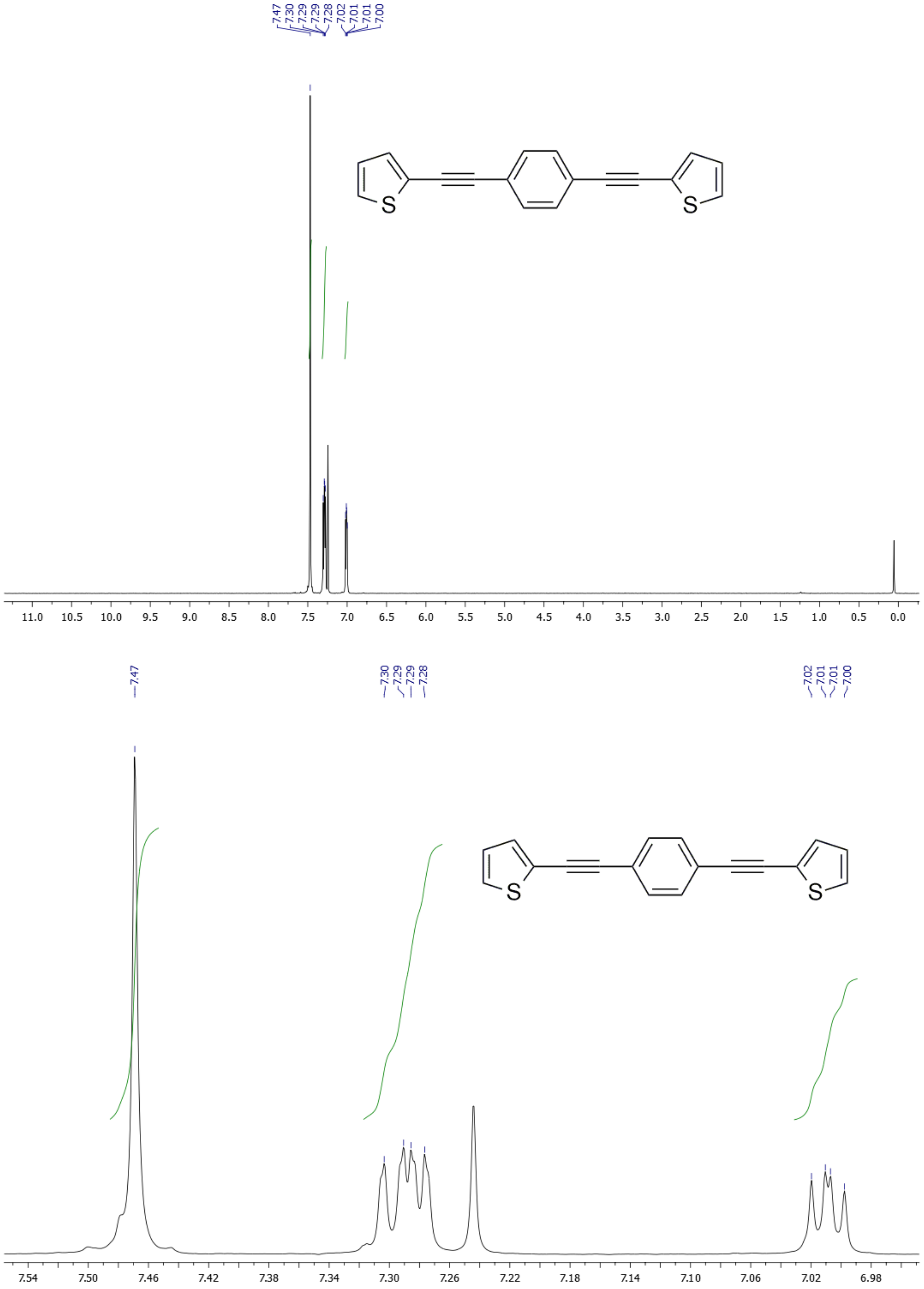


Figure S75. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**): full scale spectrum (top) and spectrum expansion (bottom).

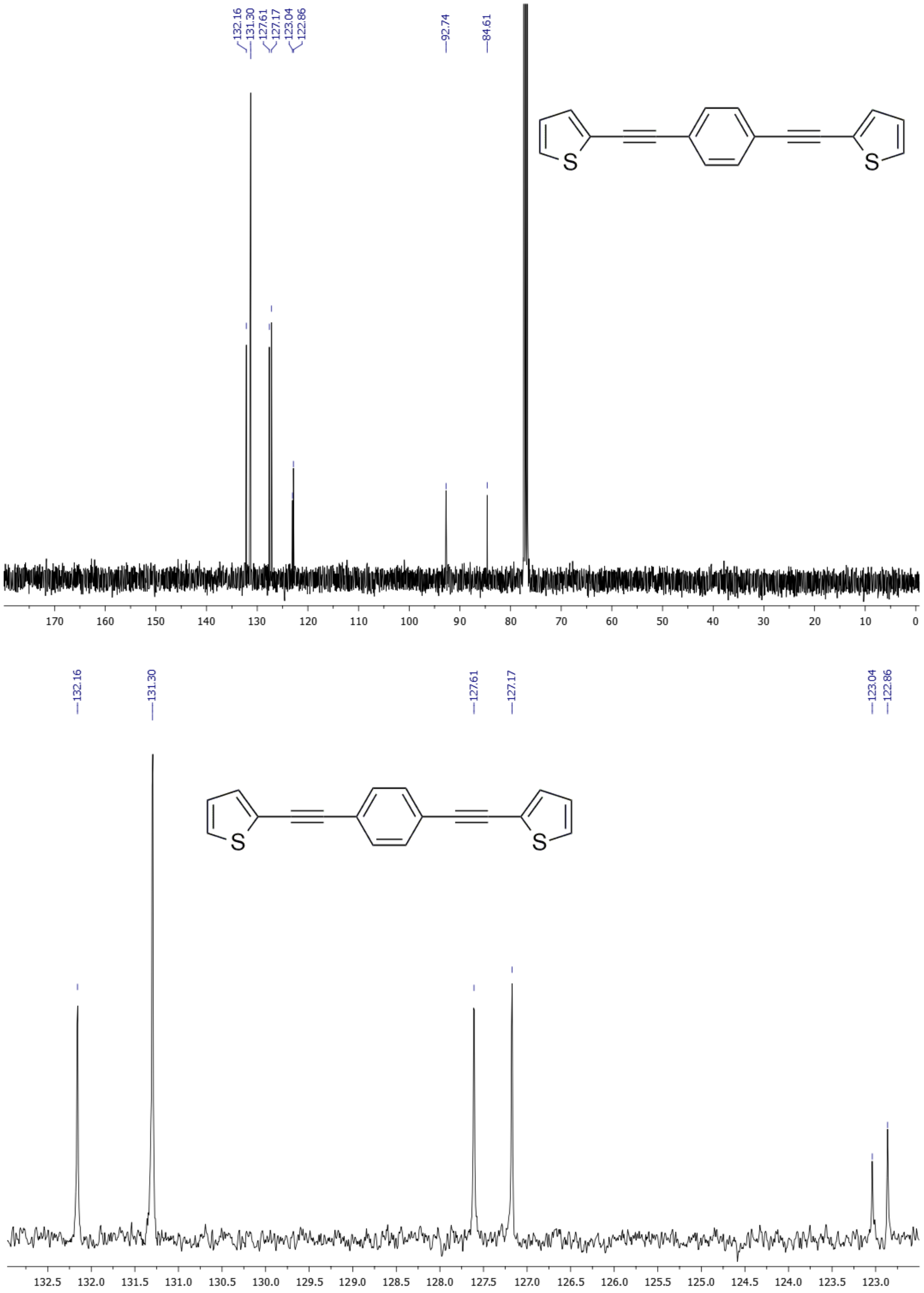


Figure S76. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**): full scale spectrum (top) and spectrum expansion (bottom).

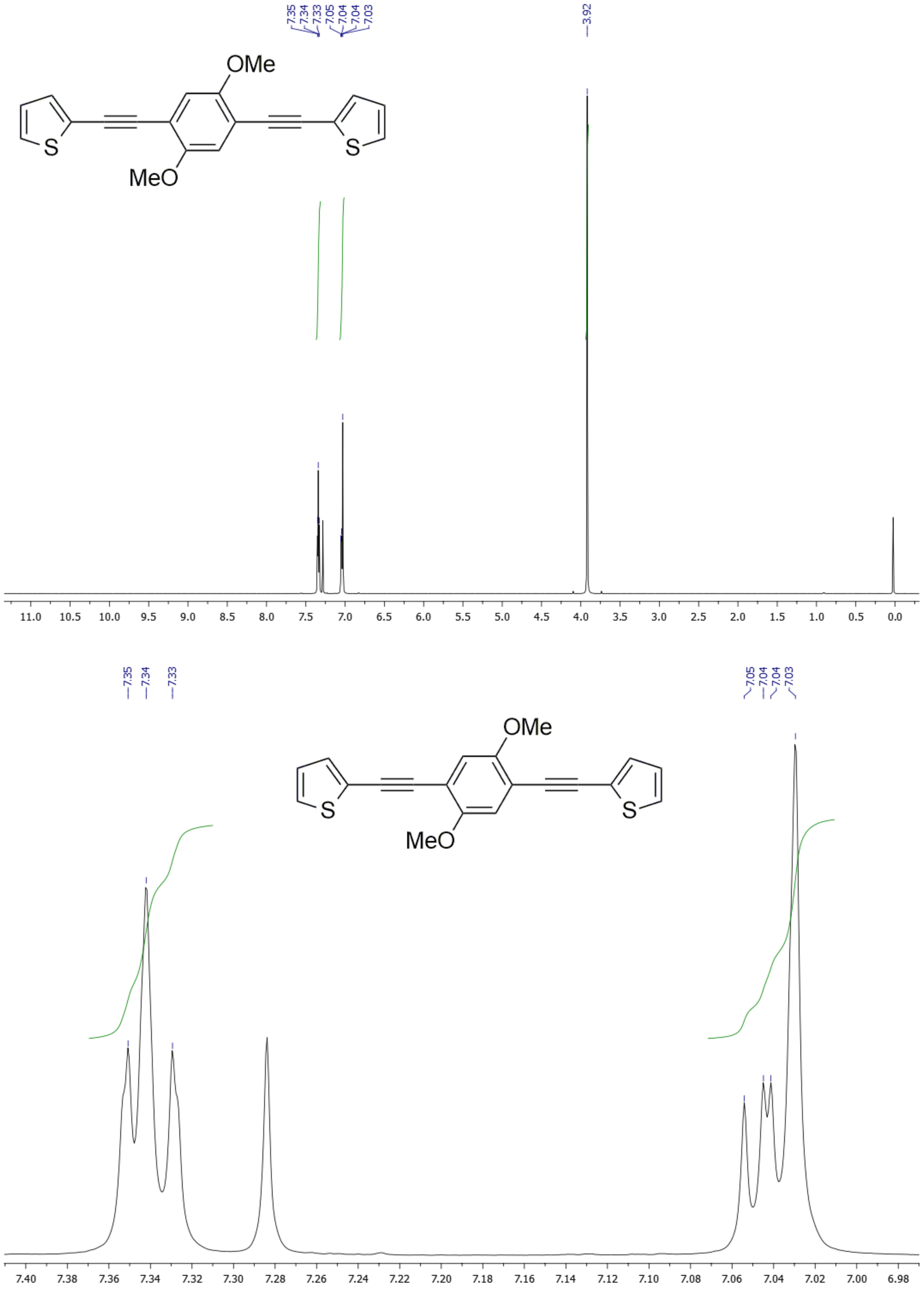


Figure S77. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (**14**): full scale spectrum (top) and spectrum expansion (bottom).

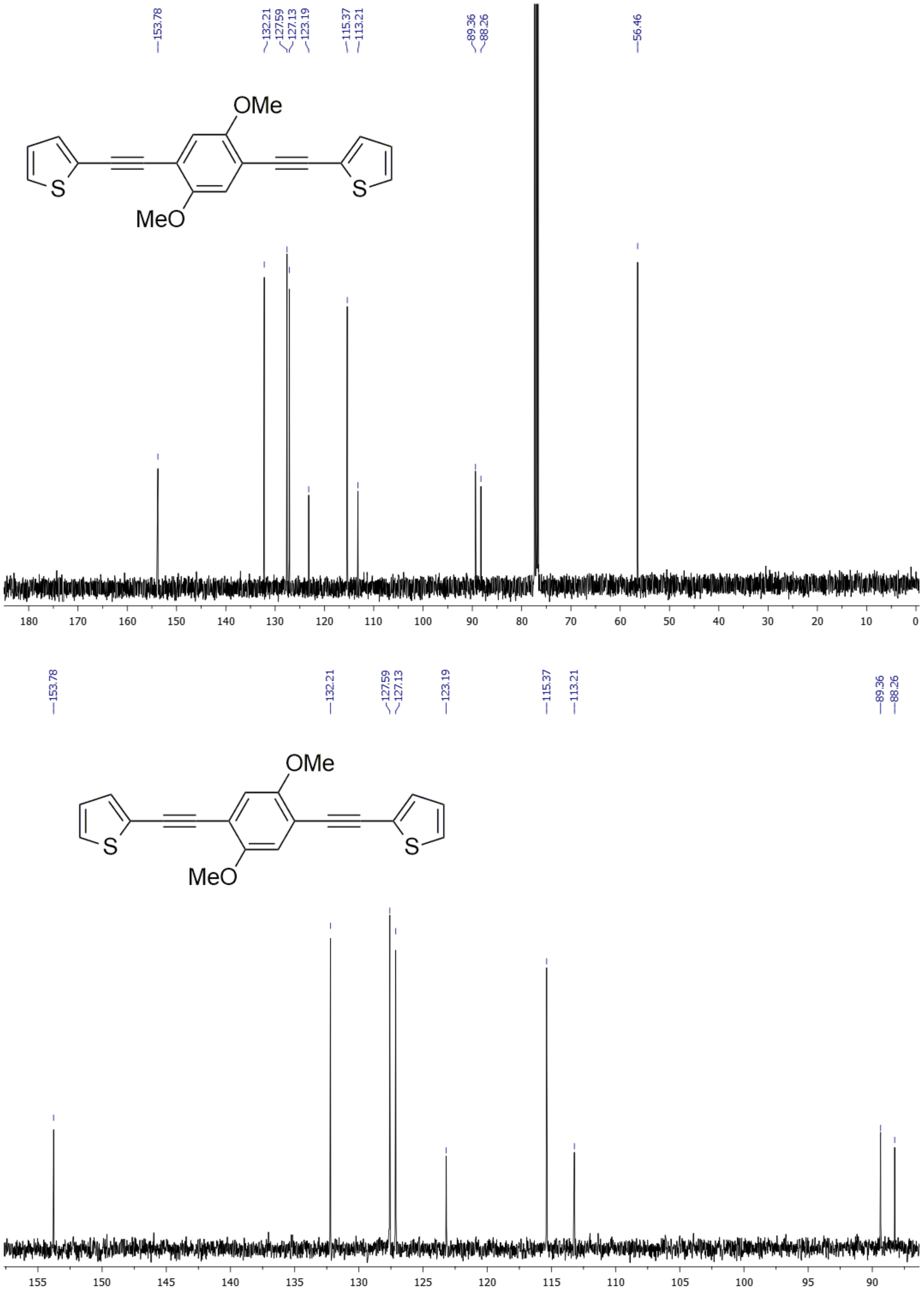


Figure S78. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (**14**): full scale spectrum (top) and spectrum expansion (bottom).

Declaration of interests

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dear Professor. Yoon
I send you the revised version of the manuscript:

Synthesis of new bis[1-(thiophenyl)propynones] as potential organic dyes for colorless luminescent solar concentrators (LSCs), by Gianluigi Albano, [a] Tony Colli, [a] Luigi Nucci, [a] Rima Charaf, [a] Tarita Biver, [a] Andrea Pucci [a] and Laura Antonella Aronica [a,*]

In our revised manuscript we describe the first example of new rod-like bis[1-(thiophenyl)propynones] based fluorophore, easily prepared via Sonogashira reactions. By modulating the properties of the lateral heterocycle and of the central nucleus it was possible to obtain a fluorophore featured by optical stability, marked solvatochromism, and high optical efficiency when dispersed in a PCMA film (7.7%) and connected to a PV cell, **,** i.e. a fluorophore potentially interesting for the use in colorless LSC devices.