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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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Figure 1.cdx [Figure]

Figure 2 NEW.png [Figure]

Figure 3.png [Figure]

Figure 4.png [Figure]

Scheme 1.cdx [Figure]

Scheme 2.cdx [Figure]

Scheme 3.cdx [Figure]

Scheme 4.cdx [Figure]

Figure 5 NEW.png [Figure]

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No data was used for the research described in the article

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

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Best regards,
Laura A. Aronica

- 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 CH₃COCH₃ UV cut-off.

2) Page 10: **H2SO4, has been corrected into H₂SO₄**

- 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 ¹H-NMR, ¹³C-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. Agarrabeitia, 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.

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4 **Synthesis of new bis[1-(thiophenyl)propynones] as potential organic**
5 **dyes for colorless luminescent solar concentrators (LSCs)**
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9 Gianluigi Albano,^a Tony Colli,^a Luigi Nucci,^a Rima Charaf,^a Tarita Biver,^a Andrea Pucci^a and
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18 Italy.
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24 **Highlights**

- 25 •New bis[1-(thiophenyl)propynones] were easily obtained via Sonogashira reactions.
- 26 •Photophysical properties of all fluorophores were investigated.
- 27 •Carbonyl groups seemed to be responsible for significant bathochromic effects and high
28 Stokes shifts
- 29 •Important solvatochromism was observed when dimethoxy functional groups were linked to the
30 central benzene ring.
- 31 • The evaluation of a PCMA film of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-
32 2-yn-1-one) as solar collector showed promising optical efficiencies.
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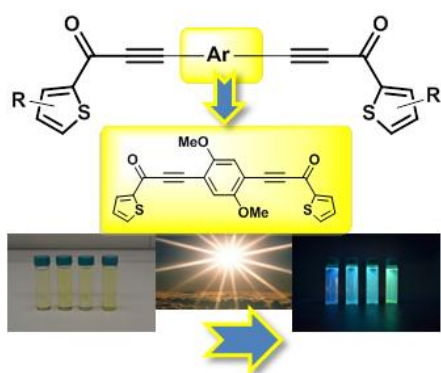
Synthesis of new bis[1-(thiophenyl)propynones] as potential organic dyes for colorless luminescent solar concentrators (LSCs)

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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GRAPHICAL ABSTRACT



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4 **Synthesis of new bis[1-(thiophenyl)propynones] as potential organic**
5 **dyes for colorless luminescent solar concentrators (LSCs)**
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24 **Keywords:**

25 Luminescent solar concentrator

26 Organic dye

27 Solvatochromism

28 Sonogashira reaction
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37 **ABSTRACT**

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39 New luminophores having different aryl nuclei and propynones moieties have been obtained via
40 Sonogashira reactions. Their optical properties were evaluated and indicated that carbonyl groups
41 are responsible for significant bathochromic effects and high Stokes shifts. The insertion of -OMe
42 groups on the central benzene unit gives to the fluorophore high optical efficiency (7.7%) when
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62 **1. Introduction**
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64 Climate changes due to pollution, together with the continuous increase in energy demand, have
65 pushed research towards the use of renewable sources such as solar energy which is free and
66 ubiquitous, and which utilization does not imply carbon dioxide emissions in the atmosphere. The
67 exploitation of solar energy can take place by means of photo-thermal, photochemical or
68 photovoltaic technology. The field of greatest interest concerns the photovoltaic (PV) sector, which
69 regards with direct conversion of electromagnetic radiation into electrical energy. Solar cells
70 produce a quantity of electrical energy, proportional to the total power of the absorbed light [1].
71 Hence, if the intensity of the incident light is increased a linear response in energy production will
72 be observed: this is the principle on which geometric solar concentrators are based [2]. However,
73 this technology has some disadvantages such as a low efficiency in diffused light conditions and the
74 need of a good system of dispersion of excess heat due to unconverted energy [3].
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88 To compensate for the defects of optical concentrators, luminescent solar concentrators (LSCs)
89 were developed [4]. Since 1982, when Hermann used for the first time this term [5], the literature
90 on LSCs has been rapidly enriched with publications[6-11] and industrial patents [12-16]. LSCs are
91 optical devices consisting of a polymeric or glass matrix and a suitable dye dispersed within the
92 matrix itself. The dye has the function of absorbing the incident solar radiation and re-emitting light
93 radiation at longer wavelengths by fluorescence. The emitted light is trapped within the material
94 and concentrated towards a solar cell on the edge of the collector, thus increasing the efficiency of
95 the system.
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104 Fluorophores are the driving force for light concentration in LSCs cells. An effective luminophore
105 must meet different requirements: broad spectral absorption, good matching between the dye
106 emitted spectrum and the external quantum efficiency of the PV-cell (generally in the red zone),
107 large Stokes shift (no or low overlap in absorption and emission spectra), high luminescent
108 efficiency (quantum yield, QY) and thermal- and photo-stability. Different luminophores have been
109 investigated: quantum dots [17], lanthanide-based materials [18] and organic dyes [19], *i.e.* organic
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121 molecules featured by an extended planar π -system. Respect to the two first classes of compounds,
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123 organic dyes are usually less toxic and their optical properties can be modulated by changing
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125 portions of the carbon backbone or introducing specific functional groups. Dyes proposed for LSCs
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127 applications are coumarins, rhodamines, pyrromethane 580, naphthalimides, perylenebisimides,
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129 bipyridines, dicarbocyanins, dicyanomethylenes, oxazines, and phthalocyanines [20-33]. Among all
130
131 these classes, only a very limited number of dyes have resulted in being suitable for LSCs.
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133 Therefore, a continuous investigation towards really efficient luminophores is in progress. In this
134
135 context, the development of a simple synthetic methodology for obtaining π -conjugated variously
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137 functionalized systems could pave the way to new luminophores. Moreover, the application of LSC
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139 as architectural windows has also triggered interest in visible transparent fluorophores, which were
140
141 found to provide acceptable optical efficiencies with a negligible degree of colored tinting [34].
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143 Notwithstanding this exciting approach to harvesting solar energy for the building integrated
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145 photovoltaics, challenges are still open to enhance the ultimate LSC optical efficiency [10].
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147 Here, we report our principal results regarding Sonogashira based synthesis of new bis[1-
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149 (thiophenyl)propynones] derivatives and the evaluation of their optical properties also in terms of
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151 transparent solar collectors for PV.
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158 **2. Experimental Section**

159 *2.1. Materials and apparatus*

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161 Solvents were purified by conventional methods, distilled and stored over activated molecular sieves
162
163 under argon. Starting substrates thiophene-2-carbonyl chloride (**4a**), 3-methylthiophene-2-carbonyl
164
165 chloride (**4b**) and 3-chlorothiophene-2-carbonyl chloride (**4c**) were purchased from Sigma Aldrich and
166
167 used as received. All the other chemicals were purchased from commercial sources and used as
168
169 received without purification. All the operations under inert atmosphere were carried out using
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171 standard Schlenk techniques and employing dried nitrogen. For all reactions, conversion was
172
173 monitored by thin-layer chromatography (TLC) analysis on pre-coated silica gel plates
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180 ALUGRAM® Xtra SIL G/UV₂₅₄ (0.2 mm) purchased from VWR Macherey-Nagel. Column
181
182 chromatographies were performed with Fluka silica gel, pore size 60 Å, 70-230 mesh, 63-200 µm.
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184 ¹H-NMR and ¹³C-NMR spectra were recorded at room temperature in CDCl₃ or DMSO-*d*₆ solution
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186 with a Bruker Avance DRX 400 spectrometer, operating at a frequency of 400 MHz for ¹H and 100
187
188 MHz for ¹³C, using the residual solvent peak as internal reference; chemical shifts (δ) values are
189
190 given in parts per million (ppm) and coupling constants (*J*) in Hertz. Mass spectra were obtained
191
192 with an Applied Biosystems-MDS Sciex API 4000 triple quadrupole mass spectrometer (Concord,
193
194 Ont., Canada), equipped with a Turbo-V ion-spray (TIS) source. Elemental analyses were
195
196 performed on a Elementar Vario Micro Cube CHN-analyzer.
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2.2. Synthesis of bis[1-(thiophenyl)propynone] dyes

201
202 General procedure: in a typical run, diethynylarene (1.0 mmol), thiophene acid chloride (2.5 mmol),
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204 PdCl₂(PPh₃)₂ (2 mol%) and Et₃N (20 mL) were mixed together in a 50 mL two-necked round bottom
205
206 flask. The resulting mixture was left under stirring for 28 h at 50 °C, then it was cooled to room
207
208 temperature, hydrolyzed with saturated ammonium chloride solution (20 mL) and extracted with
209
210 CH₂Cl₂ (3×30 mL). The combined organic phases were washed with brine, dried over anhydrous
211
212 Na₂SO₄ and the solvent was removed under vacuum. All the crude products were purified through
213
214 column chromatography on silica gel and characterized with ¹H-NMR, ¹³C-NMR, LC-MS and
215
216 elemental analysis techniques.
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2.2.1. 3,3'-(1,4-Phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**)

223
224 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), thiophene-2-
225
226 carbonyl chloride (**4a**) (367 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol) and Et₃N (20 mL) were
227
228 mixed together. The crude product was purified through column chromatography (SiO₂, *n*-
229
230 hexane/CHCl₃ 1:1), giving 288 mg (yield 83%) of 3,3'-(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-
231
232 yn-1-one) (**1a**) as yellow solid. Mp: 208-210°C. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.19 (2H, dd,
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239 $J = 4.8, 3.8$ 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
240
241 (100 MHz, CDCl_3), δ (ppm): 88.53; 89.74; 122.30; 128.46; 133.05 (2C); 135.34; 135.70; 144.66;
242
243 169.35. LC-MS APCI (+): calcd for $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}_2$: 346.01; found m/z $[\text{M}+\text{H}]^+$: 347.1. Anal. calcd for
244
245 $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}_2$: C, 69.34; H, 2.91; S, 18.51; found: C, 69.55; H, 2.86; S, 18.52.
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2.2.2. 3,3'-(1,4-Phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one) (**1b**)

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250 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 3-methylthiophene-
251
252 2-carbonyl chloride (**4b**) (402 mg, 2.5 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (14 mg, 0.02 mmol) and Et_3N (20 mL)
253
254 were mixed together. The crude product was purified through column chromatography (SiO_2 , n -
255
256 hexane/ CH_2Cl_2 1:5), giving 277 mg (yield 74%) of 3,3'-(1,4-phenylene)bis(1-(3-methylthiophen-2-
257
258 yl)prop-2-yn-1-one) (**1b**) as yellow solid. Mp: 195-198°C. ^1H -NMR (400 MHz, CDCl_3), δ (ppm):
259
260 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,
261
262 CDCl_3), δ (ppm): 16.67; 89.51; 90.06; 122.35; 132.86 (2C); 132.97; 133.37; 137.62; 146.56;
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264 169.41. LC-MS APCI (+): calcd for $\text{C}_{22}\text{H}_{14}\text{O}_2\text{S}_2$: 374.04; found m/z $[\text{M}+\text{H}]^+$: 375.1. Anal. calcd for
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266 $\text{C}_{22}\text{H}_{14}\text{O}_2\text{S}_2$: C, 70.56; H, 3.77; S, 17.13; found: C, 70.49; H, 3.82; S, 17.13.
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2.2.3. 3,3'-(1,4-Phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (**1c**)

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274 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 3-
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276 chlorothiophene-2-carbonyl chloride (**4c**) (453 mg, 2.5 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (14 mg, 0.02 mmol)
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278 and Et_3N (20 mL) were mixed together. The crude product was purified through column
279
280 chromatography (SiO_2 , n -hexane/ CH_2Cl_2 1:5), giving 208 mg (yield 50%) of 3,3'-(1,4-
281
282 phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (**1c**) as light yellow solid. Mp: 215-218
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284 °C. ^1H -NMR (400 MHz, $\text{DMSO}-d_6$), δ (ppm): 7.39 (2H, d, $J = 5.2$ Hz); 7.89 (4H, s); 8.25 (2H, d, J
285
286 = 5.2 Hz). ^{13}C -NMR (100 MHz, $\text{DMSO}-d_6$), δ (ppm): 89.38; 91.90; 122.05; 130.90; 131.94; 133.87
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288 (2C); 135.99; 136.76; 167.09. LC-MS APCI (+): calcd for $\text{C}_{20}\text{H}_8\text{Cl}_2\text{O}_2\text{S}_2$: 413.93; found m/z
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298 **[M+H]⁺: 415.9.** Anal. calcd for C₂₀H₈Cl₂O₂S₂: C, 57.84; H, 1.94; S, 15.44; found: C, 58.02; H,
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300 1.89; S, 15.43.
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304 2.2.4. 3,3'-(1,4-Phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**)
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307 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 4-
308 phenylthiophene-2-carbonyl chloride (**4d**) (557 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol)
309 and Et₃N (20 mL) were mixed together. The crude product was purified through column
310 chromatography (SiO₂, *n*-hexane/CH₂Cl₂ 1:5), giving 409 mg (yield 82%) of 3,3'-(1,4-
311 phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**) as light yellow solid. Mp: 182-185
312 °C. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.33-7.36 (2H, m); 7.41-7.45 (4H, m); 7.58-7.60 (4H, m);
313 7.71 (4H, s); 7.83 (2H, d, *J* = 1.6 Hz); 8.21 (2H, d, *J* = 1.6 Hz). ¹³C-NMR (100 MHz, CDCl₃), δ
314 (ppm): 88.53; 90.08; 122.29; 126.40 (2C); 128.09; 129.08 (2C); 130.19; 133.08 (2C); 133.51;
315 134.44; 143.82; 144.97; 169.26. LC-MS APCI (+): calcd for C₃₂H₁₈O₂S₂: 498.07; found *m/z*
316
317

318 **[M+H]⁺: 499.1.** Anal. calcd for C₃₂H₁₈O₂S₂: C, 77.08; H, 3.64; S, 12.86; found: C, 77.15; H, 3.59;
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320 S, 12.86.
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326 2.2.5. 3,3'-(1,4-Phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**)
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332 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 3-
333 ethoxythiophene-2-carbonyl chloride (**4e**) (477 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol)
334 and Et₃N (20 mL) were mixed together. The crude product was purified through column
335 chromatography (SiO₂, *n*-hexane/CH₂Cl₂ 1:4), giving 252 mg (yield 58%) of 3,3'-(1,4-
336 phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**) as yellow-orange solid. Mp: 216-
337 218 °C. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 1.45 (6H, t, *J* = 6.8 Hz); 4.24 (4H, q, *J* = 6.8 Hz);
338 6.85 (2H, d, *J* = 5.2 Hz); 7.57 (2H, d, *J* = 5.2 Hz); 7.61 (4H, s). ¹³C-NMR (100 MHz, CDCl₃), δ
339 (ppm): 15.05; 67.80; 89.73; 89.98; 116.88 (2C); 122.67; 132.64 (2C); 134.67; 161.82; 167.59. LC-
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357 MS APCI (+): calcd for C₂₄H₁₈O₄S₂: 434.06; found *m/z* [M+H]⁺: 435.4. Anal. calcd for C₂₄H₁₈O₄S₂: C,
358 66.34; H, 4.18; S, 14.76; found: C, 66.09; H, 4.21; S, 14.77.
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364 2.2.6. 3,3'-(1,4-Phenylene)bis(1-(benzo[*b*]thiophen-2-yl)prop-2-yn-1-one) (**1f**)
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366 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol),
367 benzo[*b*]thiophene-2-carbonyl chloride (**4f**) (492 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol)
368 and Et₃N (20 mL) were mixed together. The crude product was purified through column
369 chromatography (SiO₂, *n*-hexane/CH₂Cl₂ 1:3), giving 201 mg (yield 45%) of 3,3'-(1,4-
370 phenylene)bis(1-(benzo[*b*]thiophen-2-yl)prop-2-yn-1-one) (**1f**) as orange solid. Mp: 206-208
371 °C. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.42-7.46 (2H, m); 7.49-7.53 (2H, m); 7.76 (4H, s); 7.89
372 (2H, d, *J* = 8.0 Hz); 7.95 (2H, d, *J* = 8.0 Hz); 8.27 (2H, s). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm):
373 88.49; 90.41; 122.37; 123.16; 125.39; 126.46; 128.26; 132.97; 133.15 (2C); 138.73; 143.34;
374 144.07; 170.82. LC-MS APCI (+): calcd for C₂₈H₁₄O₂S₂: 446.04; found *m/z* [M+H]⁺: 447.2. Anal.
375 calcd for C₂₈H₁₄O₂S₂: C, 75.31; H, 3.16; S, 14.36; found: C, 75.55; H, 3.14; S, 14.35.
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389 2.2.7. 3,3'-(1,4-Phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (**1g**)
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391 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 5-
392 chlorothiophene-2-carbonyl chloride (**4g**) (453 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol)
393 and Et₃N (20 mL) were mixed together. The crude product was purified through column
394 chromatography (SiO₂, *n*-hexane/CH₂Cl₂ 1:5), giving 324 mg (yield 78%) of 3,3'-(1,4-
395 phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (**1g**) as light pink solid. Mp: 255-257
396 °C. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.05 (1H, d, *J* = 4.1 Hz); 7.69 (2H, s); 7.80 (1H, d, *J* =
397 4.1 Hz). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 87.83; 90.32; 122.21; 128.01; 133.09 (2C); 134.77;
398 141.69; 142.88; 168.25. LC-MS APCI (+): calcd for C₂₀H₈Cl₂O₂S₂: 413.93; found *m/z* [M+H]⁺: 415.9.
399 Anal. calcd for C₂₀H₈Cl₂O₂S₂: C, 57.84; H, 1.94; S, 15.44; found: C, 58.08; H, 1.86; S, 15.44.
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416 2.2.8. 3,3'-(1,4-Phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**)
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418 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 5-nitrothiophene-2-
419 carbonyl chloride (**4h**) (479 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol) and Et₃N (20 mL)
420 were mixed together. The crude product was purified through column chromatography (SiO₂, *n*-
421 hexane/AcOEt 9:1 → 7:3), giving 231 mg (yield 53%) of 3,3'-(1,4-phenylene)bis(1-(5-
422 nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**) as yellow-orange solid. Mp: 219-221 °C. ¹H-NMR (400
423 MHz, CDCl₃), δ (ppm): 7.77 (4H, s); 7.90 (2H, d, *J* = 4.2 Hz); 7.97 (2H, d, *J* = 4.2 Hz). ¹³C-NMR
424 (100 MHz, CDCl₃), δ (ppm): 87.62; 92.41; 122.03; 128.20; 132.25; 133.38 (2C); 147.41; 157.18;
425 168.70. LC-MS APCI (+): calcd for C₂₀H₈N₂O₆S₂: 435.98; found *m/z* [M+H]⁺: 437.0. Anal. calcd
426 for C₂₀H₈N₂O₆S₂: 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.
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439 2.2.9. 3,3'-([1,1'-Biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10a**)
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441 According to the general procedure, 4,4'-diethynyl-1,1'-biphenyl (**9a**) (202 mg, 1.0 mmol), thiophene-2-
442 carbonyl chloride (**4a**) (367 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol) and Et₃N (20 mL) were
443 mixed together. The crude product was purified through column chromatography (SiO₂, *n*-
444 hexane/CH₂Cl₂ 1:4), giving 321 mg (yield 76%) of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(1-(thiophen-2-
445 yl)prop-2-yn-1-one) (**10a**) as light yellow solid. Mp: 206-208 °C. ¹H-NMR (400 MHz, CDCl₃), δ
446 (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).
447 ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 87.50; 91.15; 119.73; 127.37 (2C); 128.36; 133.67 (2C);
448 135.05; 135.32; 142.07; 144.93; 169.62. LC-MS APCI (+): calcd for C₂₆H₁₄O₂S₂: 422.04; found *m/z*
449 [M+H]⁺: 423.2. Anal. calcd for C₂₆H₁₄O₂S₂: C, 73.91; H, 3.34; S, 15.18; found: C, 73.68; H, 3.35; S,
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465 2.2.10. 3,3'-(Naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**)
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467 According to the general procedure, 2,6-diethynylnaphthalene (**9b**) (176 mg, 1.0 mmol), thiophene-2-
468 carbonyl chloride (**4a**) (367 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol) and Et₃N (20 mL) were
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475 mixed together. The crude product was purified through column chromatography (SiO₂, *n*-
476 hexane/CH₂Cl₂ 1:4 → CH₂Cl₂), giving 202 mg (yield 51%) of 3,3'-(naphthalene-2,6-diyl)bis(1-
477 (thiophen-2-yl)prop-2-yn-1-one) (**10b**) as light yellow solid. Mp: 210-213 °C. ¹H-NMR (400 MHz,
478 CDCl₃), 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*
483 = 8.4 Hz); 8.05 (2H, d, *J* = 4.4 Hz); 8.22 (2H, s). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 87.60;
484 91.01; 119.43; 128.41; 128.74; 129.57; 133.14; 133.89; 135.15; 135.46, 144.89; 169.51. LC-MS
486 APCI (+): calcd for C₂₄H₁₂O₂S₂: 396.03; found *m/z* [M+H]⁺: 397.2. Anal. calcd for C₂₄H₁₂O₂S₂: C,
489 72.70; H, 3.05; S, 16.17; found: C, 72.77; H, 3.09; S, 16.16.
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495 2.2.11. 3,3'-(Naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**)

496 According to the general procedure, 1,4-diethynylnaphthalene (**9c**) (176 mg, 1.0 mmol), thiophene-2-
497 carbonyl chloride (**4a**) (367 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol) and Et₃N (20 mL) were
498 mixed together. The crude product was purified through column chromatography (SiO₂, *n*-
499 hexane/CH₂Cl₂ 1:4 → CH₂Cl₂), giving 266 mg (yield 67%) of 3,3'-(naphthalene-1,4-diyl)bis(1-
500 (thiophen-2-yl)prop-2-yn-1-one) (**10c**) as yellow solid. Mp: 212-214 °C. ¹H-NMR (400 MHz,
501 CDCl₃), 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);
502 8.09 (2H, dd, *J* = 4.4, 1.2 Hz); 8.44-8.48 (2H, m). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 88.39;
503 92.99; 120.78; 126.50; 128.56; 128.70; 131.87; 133.27; 135.13; 135.65; 144.82; 169.30. LC-MS
504 APCI (+): calcd for C₂₄H₁₂O₂S₂: 396.03; found *m/z* [M+H]⁺: 397.2. Anal. calcd for C₂₄H₁₂O₂S₂: C,
505 72.70; H, 3.05; S, 16.17; found: C, 72.83; H, 3.03; S, 16.17.
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520 2.2.12. 3,3'-(2,5-Dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**)

521 According to the general procedure, 1,4-diethynyl-2,5-dimethoxybenzene (**13**) (186 mg, 1.0 mmol),
522 thiophene-2-carbonyl chloride (**4a**) (367 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol) and Et₃N
523 (20 mL) were mixed together. The crude product was purified through column chromatography (SiO₂,
524 *n*-hexane/CH₂Cl₂ 1:5), giving 346 mg (yield 85%) of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-
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534 (thiophen-2-yl)prop-2-yn-1-one) (**15**) as yellow-green solid. Mp: 264-267 (dec.) °C. ¹H-NMR (400
535 MHz, CDCl₃), 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
536 MHz); 8.15 (2H, dd, *J* = 3.8, 1.2 Hz). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 56.89; 87.60; 92.59;
537 113.19; 116.88; 128.66; 135.78; 136.20; 145.33; 155.85; 169.08. LC-MS APCI (+): calcd for
538 C₂₂H₁₄O₄S₂: 406.03; found *m/z* [M+H]⁺: 407.2. Anal. calcd for C₂₂H₁₄O₄S₂: C, 65.01; H, 3.47; S,
539 15.78; found: C, 64.83; H, 3.41; S, 15.78.
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549 2.3. Characterization

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551 UV-Vis absorption measurements in solution were done using a Perkin-Elmer Lambda 650
552 spectrophotometer, with temperature control to within ±0.1 °C. Fluorescence measurements in
553 solution were performed using a Horiba Jobin Yvon FluoroLog®-3 spectrofluorometer, with
554 temperature control to within ±0.1 °C.
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558 Quantum yields (Φ) in solution are calculated according to a comparative method, involving the use of a
559 standard with known quantum yield, Φ_{ST} (perylene in cyclohexane, Φ_{ST} = 0.94; fluorescein in 0.1 M
560 aqueous NaOH solution, Φ_{ST} = 0.95; quinine sulfate in 0.1 M aqueous H₂SO₄ solution, Φ_{ST} = 0.54)
561 [35]; the equation used is
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$$568 \Phi_x = \Phi_{ST} \cdot \frac{\nabla_x}{\nabla_{ST}} \cdot \frac{(\eta_x)^2}{(\eta_{ST})^2}$$

569 where ∇_x and ∇_{ST} are the slopes of a fluorescence area vs. absorbance plot for the dye and standard,
570 respectively, while η_x and η_{ST} are the refractive index of the solvents used for dye and standard
571 solutions, respectively (η_{chloroform} = 1.445; η_{cyclohexane} = 1.426; η_{water} = 1.330).
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578 **15**/PCMA thin films were prepared by drop casting, *i.e.* pouring 0.8 mL chloroform solution
579 containing 120.0 mg of the polymer and the proper amount of fluorophore to obtain concentrations
580 in the range 0.7-1 wt.% on 50×50×3 mm optically pure glass substrate (Edmund Optics Ltd
581 BOROFLOAT window 50×50 TS). The glass slides were cleaned with chloroform and immersed
582 in 6 M HCl for at least 12 h; then, they were rinsed with water, acetone and isopropanol and dried
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593 for 8 h at 120 °C. Solvent evaporation was performed on a warm hot plate (about 30 °C) and in a
594 closed environment. The film thickness was measured by a Starrett micrometer to be 200 ± 10 μm.
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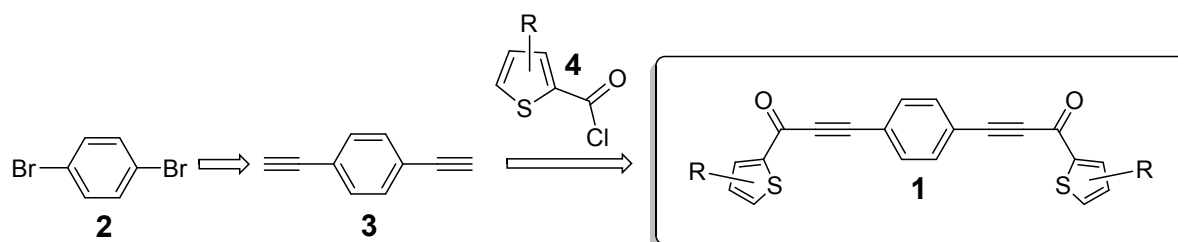
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597 The optical efficiency of the LSC was measured by using a solar simulating lamp (ORIEL® LCS-
598 100 solar simulator 94011A S/N: 322, AM1.5G std filter: 69 mW/cm² at 254 mm). The PV module
599 (IXYS SLMD121H08L mono solar cell 86×14 mm) was connected to Keysight Technologies
600 B2900 Series Precision Source/Measure Unit. The optical efficiency η_{opt} was evaluated from the
601 concentration factor C, which is the ratio between the short circuit current measured in the case of
602 the cell over the LSC edge (I_{LSC}) and short circuit current of the bare cell when perpendicular to the
603 light source (I_{SC})
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$$612 \quad \eta_{\text{opt}} = \frac{I_{\text{LSC}}}{I_{\text{SC}} \cdot G}$$

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615 where G is the geometrical factor (in our case, G = 13.3), which is the ratio between the area
616 exposed to the light source and the collecting area.
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622 **3. Results and discussion**

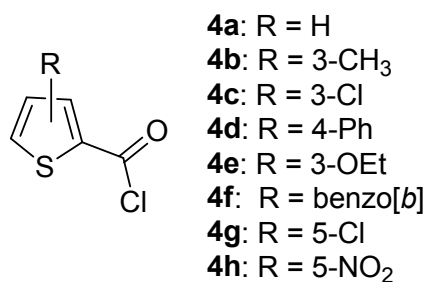
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624 We started our study with the synthesis of (1,4-phenylene)bis(thiophenylpropynones) **1** (Scheme 1)
625 characterized by the presence of a benzene ring linked to thiophenyl moieties through a **C≡C-C=O**
626 spacer. The synthetic strategy chosen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

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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).



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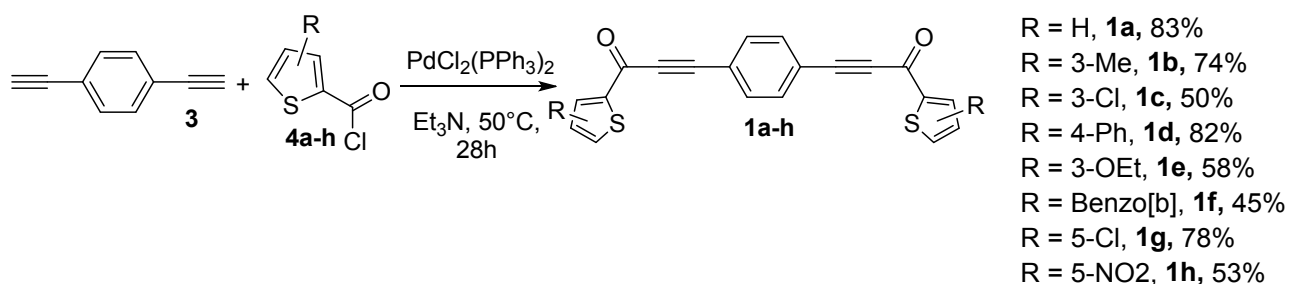
Figure 1. Chemical structure of acid chlorides chosen as coupling partner of **3** for the synthesis of (1,4-phenylene)bis(thiophenylpropynones) dyes.

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Since it is known that decarbonylation 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

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711 the formation of a mixture of both mono- and di-thiophene carbonyl derivatives (Scheme S3 in
712 Supporting Information).

715 In order to increase the chemoselectivity of the reaction, a second run was carried out at 50 °C. In
716 this case the total consumption of the reagents occurred and the exclusive formation of expected
717 product **1a** was observed (yield 83%). As a consequence, the improved experimental reaction
718 conditions (50 °C, 28 h, 1 mmol of 1,4-diethynylbenzene (**3**), 2.5 mmol of thiophene carbonyl
719 chloride, 20 mL of Et₃N, and 2 mol% of PdCl₂(PPh₃)₂) were applied to the acyl Sonogashira
720 reaction between **3** and thiophene carbonyl chlorides **4** (Scheme 2). The reactions afforded
721 exclusively di-carbonyl compounds **1a-h** and proved amenable to acid chlorides containing both
722 electron-donating and electron-withdrawing functionality, delivering products in good yields,
723 regardless of the position of the functional group on the thiophene ring.
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746 **Scheme 2.** Acyl Sonogashira reactions between 1,4-diethynylbenzene (**3**) and thiophene carbonyl chlorides **4a-h**.
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751 Study of the optical properties of compounds **1a-h** was undertaken in CHCl₃ solutions. The main
752 results obtained are collected in **Table 1**, while full absorbance and fluorescence emission spectra
753 are depicted in Figures S1-S8 in Supporting Information.
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757 Products **1c**, **1g** and **1h**, featured by electron-withdrawing moieties did not show fluorescence when
758 excited at 335 nm wavelength [41-43]. On the contrary, compounds **1a,b,d,e,f** showed emission
759 spectra with high Stokes shifts (108-168 nm), indicating low auto-absorption in solution and good
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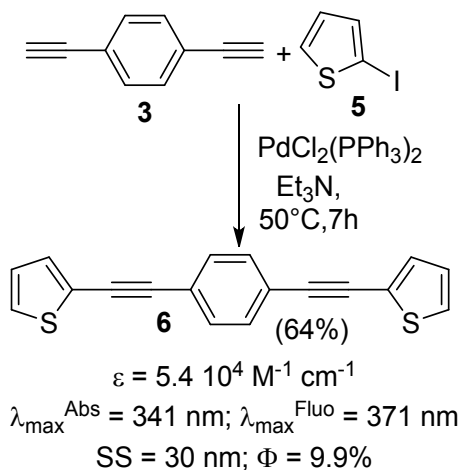
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770 potentiality as fluorophores in LSC devices. Unfortunately their quantum yields were almost
771 negligible (less than 1%).
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777 **Table 1.** Photophysical properties of (1,4-phenylene)bis(thiophenylpropynones) dyes **1a-h**.
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779 Compound	780 ϵ^a	781 $\lambda_{\max}^{\text{Abs } b}$	782 $\lambda_{\max}^{\text{Fluo } c}$	783 SS ^d	784 Φ^e
785 1a	786 3.8	787 335	788 443	789 108	790 0.2
791 1b	792 3.8	793 338	794 450	795 112	796 / ^f
797 1c	798 3.8	799 339	800 /	801 /	802 / ^g
803 1d	804 3.4	805 328	806 467	807 139	808 0.6
809 1e	810 2.5	811 323	812 507	813 184	814 0.2
815 1f	816 4.5	817 343	818 451	819 108	820 0.2
821 1g	822 5.8	823 340	824 /	825 /	826 / ^g
1h	4.6	352	/	/	/ ^g

815 ^aExtinction coefficient ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$). ^bMaximum of light absorbance (nm). ^cMaximum of light emission (nm). ^dSS =
816 Stokes shift (nm) = $\lambda_{\max}^{\text{Fluo}} - \lambda_{\max}^{\text{Abs}}$. ^eQuantum yield (%). ^fLess than 0.1%. ^gNot determined.
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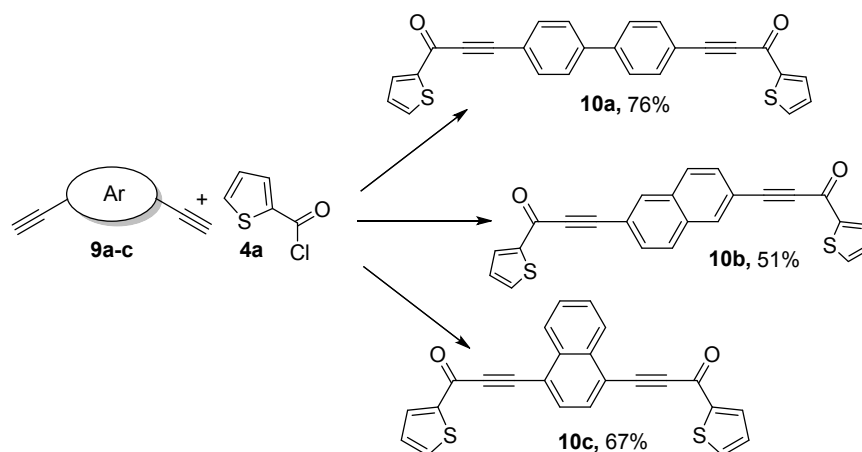
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829 In order to evaluate the effect of carbonyl group on the optical properties of (1,4-
830 phenylene)bis(thiophenylpropynones) **1**, 1,4-diethynylbenzene **3** was reacted with 2-iodothiophene
831 **5** affording 1,4-bis(thiophen-2-ylethynyl)benzene **6** in good yield (Scheme 3).
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852 **Scheme 3.** Synthesis and optical properties of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**).
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856 A comparison between optical properties of **6** (Scheme 3 and Figure S9) and **1a** (Table 1 and Figure
857 S1) clearly indicated that the presence of CO determines an increase of the Stokes shift, a significant
858 bathochromic effect in emission spectra, but also a dramatic reduction of quantum yield (0.2 vs.
859 9.9%). A similar trend had been observed [32] when we studied the photophysical features of two
860 triphenyl amine derivatives containing ethynyl linkers to thiophene or carbonylthiophene moieties.
861 The presence of CO involved higher Stokes shifts and increase in both absorption and emission
862 maximum wavelengths.
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870 Thus, with the aim to improve the optical properties, bis(thiophenylpropynones) containing nucleus
871 with extended conjugation were synthesized (Scheme 4). Analogously to the synthetic sequence
872 employed for the synthesis of derivatives **1a-h**, central units were prepared starting from the
873 corresponding dibromo derivatives **7a-c**, which were coupled with trimethylsilylacetylene generating
874 **8a-c**; subsequent desilylation step (KOH) afforded diynes **9a-c** in good yields (Scheme S4).
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Scheme 4. Synthetic approach to arylbis(thiophenylpropinones) **10a-c**.

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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-naphthyl (**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 ($\lambda_{\text{max}}^{\text{Abs}} = 397 \text{ nm}$ 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**.

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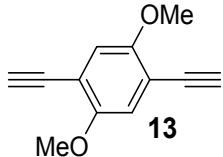
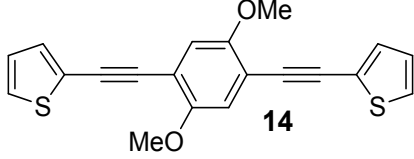
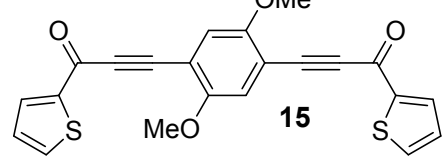
Compound	ϵ^{a}	$\lambda_{\text{max}}^{\text{Abs b}}$	$\lambda_{\text{max}}^{\text{Fluo c}}$	SS ^d	Φ^{e}
10a	3.8	346	420	74	/ ^f
10b	5.3	346	428	82	/ ^f
10c	3,4	397	456	59	5.8

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^aExtinction coefficient ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$). ^bMaximum of light absorbance (nm). ^cMaximum of light emission (nm). ^dSS = Stokes shift (nm) = $\lambda_{\text{max}}^{\text{Fluo}} - \lambda_{\text{max}}^{\text{Abs}}$. ^eQuantum yield (%). ^fLess than 0.1%.

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949 Considering that the presence of an electron-donating group such as -OEt had determined a
950 remarkable bathochromic effect and a very high SS value (Table 1, **1e**) the syntheses of 2,2'-((2,5-
951 dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (**14**) and 3,3'-((2,5-dimethoxy-1,4-
952 phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one)) (**15**) were carried out (Scheme S5). Central
953 nucleus 1,4-diethynyl-2,5-dimethoxybenzene (**13**) was easily prepared starting from commercially
954 available 1,4-dibromo-2,5-dimethoxybenzene (**11**) which was coupled with ethynyltrimethylsilane
955 affording **12** (Scheme S5, step a). After desilylation with KOH/MeOH (Scheme S5, step b), product **13**
956 was generated in high yield. and was then successfully employed in the synthesis of **14** and **15** via
957 Sonogashira reactions (Scheme S5, steps c-d). The optical properties in CHCl₃ solution of both
958 compounds are described in Table 3 and compared with those of precursor **13** (full absorbance and
959 fluorescence emission spectra of **13-15** are reported in Figures S13-S15 in Supporting Information).
960 As is evident from data collected in Table 3, wavelengths of absorption and emission maxima of the
961 three compounds vary significantly with their structure. Indeed, going from diyne **13** to compounds
962 **14** and then to **15** the extension of conjugation determines a red-shift of the spectrum, but with an
963 absorption maximum still peaked close to the near-UV region.
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Table 3. Optical properties of dimethoxy-substituted dyes **13-15**.

Compounds	Yield (%) ^a	ϵ^b	$\lambda_{\max}^{\text{Abs } c}$	$\lambda_{\max}^{\text{Fluo } d}$	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

^aYield of pure product. ^bExtinction coefficient ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$). ^cMaximum of light absorbance (nm). ^dMaximum of light emission (nm). ^eSS = Stokes shift (nm) = $\lambda_{\max}^{\text{Fluo}} - \lambda_{\max}^{\text{Abs}}$. ^fQuantum 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	ϵ^b	$\lambda_{\max}^{\text{Abs } c}$	$\lambda_{\max}^{\text{Fluo } d}$	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

^aRefractive index. ^bDielectric constant. ^cMaximum of light absorbance (nm). ^dMaximum of light emission. ^eSS = Stokes shift (nm) = $\lambda_{\max}^{\text{Fluo}} - \lambda_{\max}^{\text{Abs}}$. ^fQuantum 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, $\lambda_{\max}^{\text{Abs}}$ is constant and $\lambda_{\max}^{\text{Fluo}}$ 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].

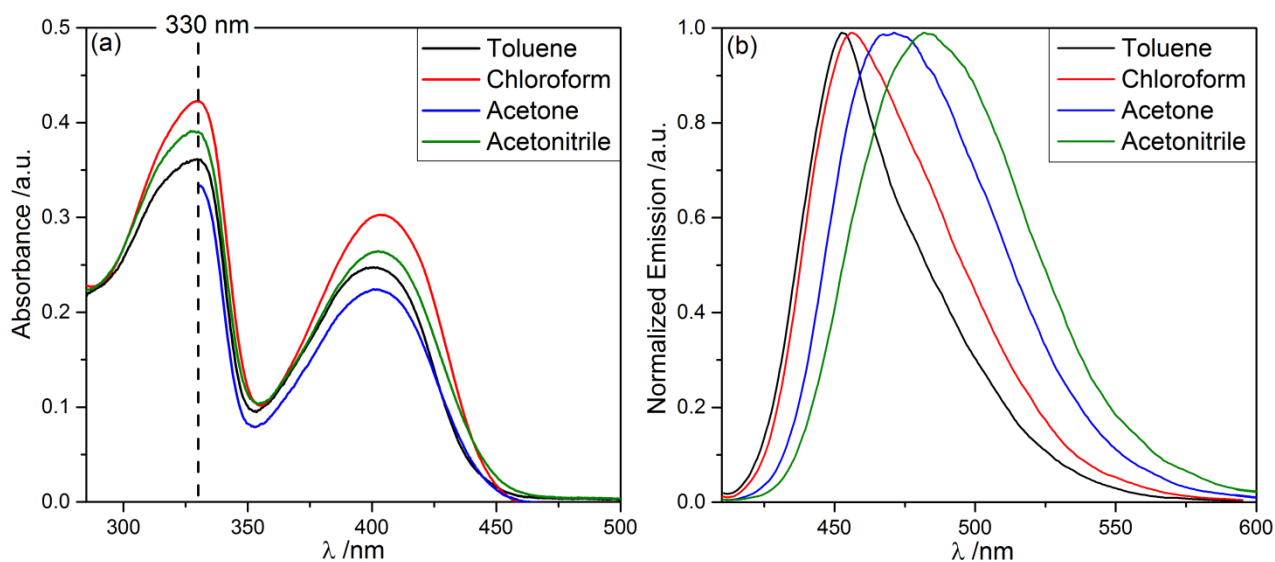


Figure 2. UV-Vis absorption (a) and emission (b) **normalized** spectra of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) in different solvents. Sample concentration: 1.7×10^{-5} M for absorption spectra, 1.0×10^{-6} M for emission spectra; cell length: 1 cm; excitation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

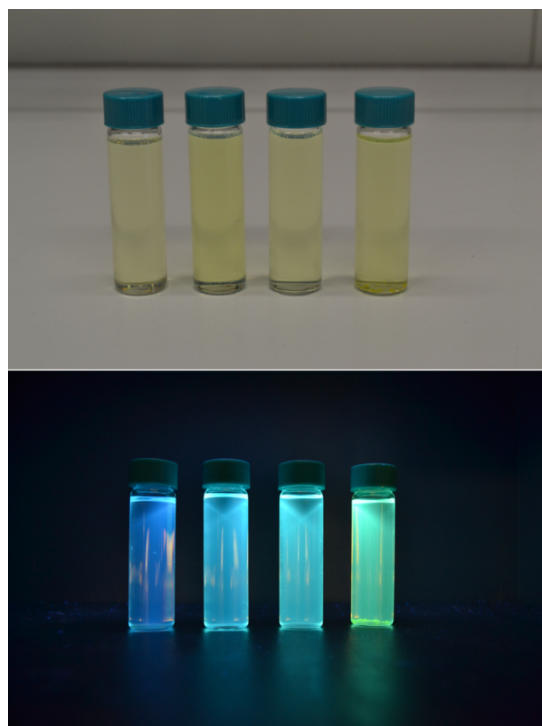


Figure 3. 1.0×10^{-6} M solutions of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) dye in different solvents (from left to right: toluene, chloroform, acetone, acetonitrile), illuminated with daylight (up photo) and irradiated with UV light at 335 nm (down photo).

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).

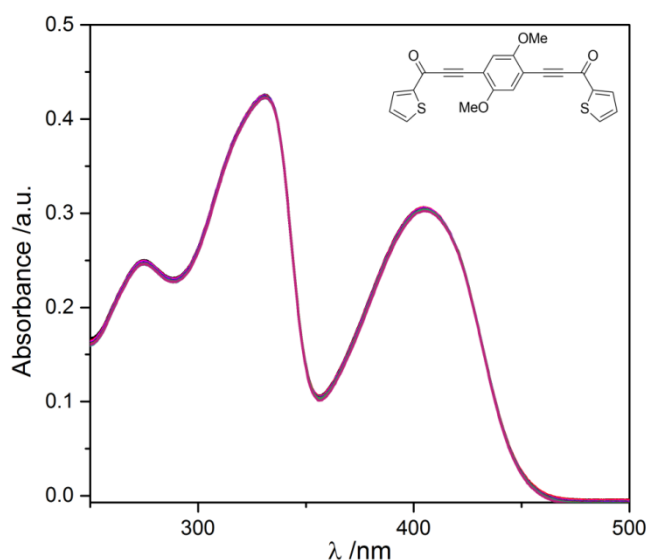
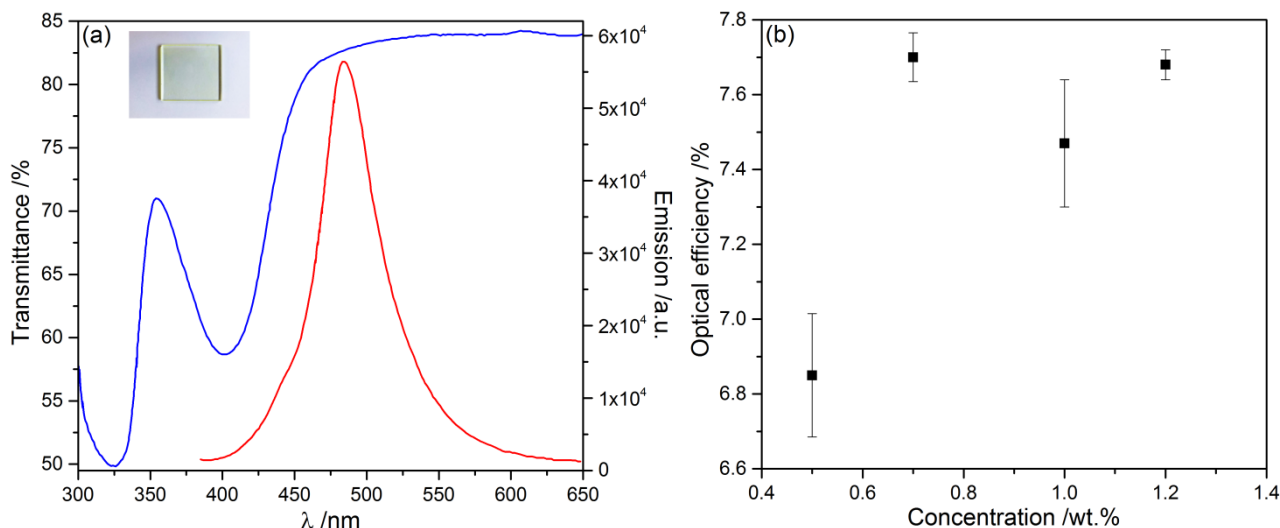


Figure 4. UV-Vis absorption spectra of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) in CHCl_3 recorded each 15 minutes for 6 h. Sample concentration: 1.7×10^{-5} M; cell length: 1 cm.

A preliminary 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

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1242 efficiencies of 7.7% was obtained and resulted higher than those of previously investigated bis-
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1244 azido fluorophores for colorless LSC and determined with the same laboratory setup [34].
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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

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1301 to a PV cell showed maximum optical efficiency of 7.7%, thus supporting the use of this compound
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1303 as fluorophore for colorless LSC devices.
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1306 1307 **Appendix A.: Supplementary data**

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1309 Supplementary data to this article can be found online at
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1312 1313 **References**

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Supporting Information

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

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and Laura Antonella Aronica*

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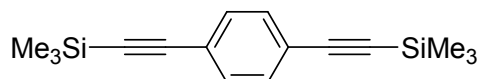
Experimental Section

Synthesis

Synthesis of diethynylarenes

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

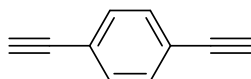
1,4-Dibromobenzene (**2**) (3.52 g, 14.9 mmol), Pd(PPh₃)₄ (215 mg, 0.19 mmol) and CuI (70 mg, 0.37 mmol) were mixed in Et₃N (50 mL), then trimethylsilylacetylene (5.2 mL, 36.6 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 7 h, then it was cooled to room temperature, hydrolyzed with saturated ammonium chloride solution (50 mL) and extracted with CH₂Cl₂ (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO₂, *n*-hexane) to give 1,4-bis((trimethylsilyl)ethynyl)benzene (**5**) (3.94 g, yield 98%).



¹H-NMR (400 MHz, CDCl₃), δ (ppm): 0.23 (18H, s); 7.37 (4H, s). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): -0.11 (3C); 96.29; 104.58; 123.17; 131.74 (2C).

Synthesis of 1,4-diethynylbenzene (3)

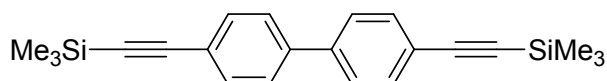
1,4-Bis((trimethylsilyl)ethynyl)benzene (**5**) (2.48 g, 9.16 mmol) and a 20 wt% NaOH aqueous solution (25 mL) were mixed in acetonitrile (50 mL) and *n*-hexane (25 mL). The resulting solution was left under stirring for 5 h at room temperature, then it was hydrolyzed with water (100 mL) and extracted with *n*-hexane (3x50 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO₂, *n*-pentane) to give 1,4-diethynylbenzene (**3**) (1.10 g, yield 95%).



¹H-NMR (400 MHz, CDCl₃), δ (ppm): 3.15 (2H, s); 7.42 (4H, s). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 79.05; 83.01; 122.55; 132.00 (2C). LC-MS APCI (+): calcd for C₁₀H₆: 126.05; found *m/z* [M+H]⁺: 127.0. Anal. calcd for C₁₀H₆: C, 95.21; H, 4.79; found: C, 95.25; H, 4.75.

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

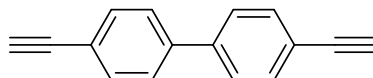
4,4'-Dibromo-1,1'-biphenyl (**7a**) (1.57 g, 5.03 mmol), Pd(PPh₃)₄ (71 mg, 0.061 mmol) and CuI (23 mg, 0.12 mmol) were mixed in Et₃N (20 mL), then trimethylsilylacetylene (1.7 mL, 12.3 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 6 h, then it was cooled 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 CH₂Cl₂ (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO₂, petroleum ether → CH₂Cl₂) to give 4,4'-bis((trimethylsilyl)ethynyl)-1,1'-biphenyl (**8a**) (1.72 g, yield 99%).



¹H-NMR (400 MHz, CDCl₃), δ (ppm): 0.24 (18H, s); 7.51 (8H, s). ¹³C-NMR (100 MHz, CDCl₃), 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)

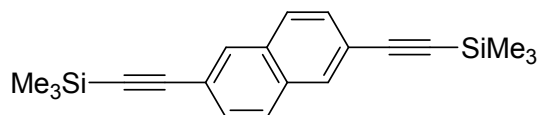
4,4'-Bis(trimethylsilyl)ethynyl-1,1'-biphenyl (**8a**) (867 mg, 2.50 mmol) and a 3.5 M aqueous KOH solution (1.6 mL, 5.6 mmol) were mixed in THF (40 mL) and methanol (10 mL). The resulting solution was left under stirring for 4 h at room temperature, then it was hydrolyzed with water (50 mL) and extracted with *n*-hexane (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO₂, *n*-hexane/CH₂Cl₂ 1:1) to give 4,4'-diethynyl-1,1'-biphenyl (**9a**) (444 mg, yield 88%).



¹H-NMR (400 MHz, CDCl₃), δ (ppm): 3.12 (2H, s); 7.51-7.56 (8H, m). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 78.05; 83.38; 121.51; 126.90 (2C); 132.64 (2C); 140.56. LC-MS APCI (+): calcd for C₁₆H₁₀: 202.08; found *m/z* [M+H]⁺: 203.1. Anal. calcd for C₁₆H₁₀: C, 95.02; H, 4.98; found: C, 95.08; H, 4.92.

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

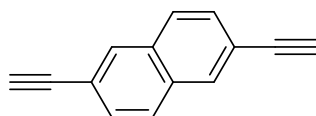
2,6-Dibromonaphthalene (**7b**) (570 mg, 2.00 mmol), Pd(PPh₃)₄ (28 mg, 0.024 mmol) and CuI (11 mg, 0.058 mmol) were mixed in Et₃N (20 mL), then trimethylsilylacetylene (0.7 mL, 5.06 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 5 h, then it was cooled 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 CH₂Cl₂ (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO₂, petroleum ether) to give 2,6-bis(trimethylsilyl)ethynynaphthalene (**8b**) (527 mg, yield 82%).



¹H-NMR (400 MHz, CDCl₃), 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). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): -0.04 (3C); 95.44; 105.15; 121.33; 127.68; 129.27; 131.71; 132.31.

Synthesis of 2,6-diethynynaphthalene (9b)

2,6-Bis(trimethylsilyl)ethynynaphthalene (**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 Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO₂, *n*-hexane/CH₂Cl₂ 1:1) to give 2,6-diethynynaphthalene (**9b**) (277 mg, yield 96%).



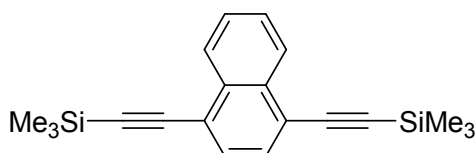
¹H-NMR (400 MHz, CDCl₃), δ (ppm): 3.16 (2H, s); 7.52 (2H, d, *J* = 8.4 Hz); 7.72 (2H, d, *J* = 8.4 Hz); 7.97 (2H, s). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 78.18; 83.66; 120.48; 127.86; 129.34; 132.04; 132.40. LC-MS APCI (+):

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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)

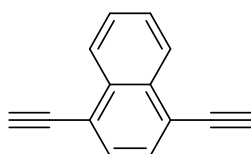
1,4-Dibromonaphthalene (**7c**) (1.43 g, 5.00 mmol), Pd(PPh₃)₄ (69 mg, 0.06 mmol) and CuI (27 mg, 0.14 mmol) were mixed in Et₃N (20 mL), then trimethylsilylacetylene (1.7 mL, 12.3 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 11 h, then it was cooled 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 CH₂Cl₂ (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ 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.



¹H-NMR (400 MHz, CDCl₃), 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). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 0.03 (3C); 101.36; 102.79; 121.54; 126.55; 127.24; 129.97; 133.08.

Synthesis of 1,4-diethynynaphthalene (9c)

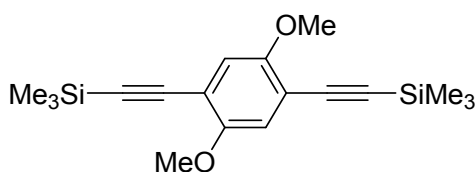
1,4-Bis((trimethylsilyl)ethynyl)naphthalene (**8c**) (1.59 g, 4.95 mmol) and a 3.5 M aqueous KOH solution (3.0 mL, 10.5 mmol) were mixed in THF (64 mL) and methanol (16 mL). The resulting solution was left under stirring for 4 h at room temperature, then it was hydrolyzed with water (80 mL) and extracted with *n*-hexane (3x50 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO₂, *n*-hexane → CH₂Cl₂) to give 1,4-diethynynaphthalene (**9c**) (698 mg, yield 80%).



¹H-NMR (400 MHz, CDCl₃), 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). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 81.39; 83.63; 120.92; 126.41; 127.44; 130.28; 133.15. LC-MS APCI (+): calcd for C₁₄H₈: 176.06; found *m/z* [M+H]⁺: 177.0. Anal. calcd for C₁₄H₈: 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)

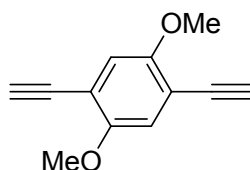
1,4-Dibromo-2,5-dimethoxybenzene (**11**) (3.02 g, 10.2 mmol), Pd(PPh₃)₄ (139 mg, 0.12 mmol) and CuI (55 mg, 0.29 mmol) were mixed in THF (30 mL) and Et₃N (10 mL), then trimethylsilylacetylene (3.5 mL, 25.3 mmol) was added dropwise to the solution. The resulting mixture was refluxed under stirring for 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 CH₂Cl₂ (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ 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%).



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2068 ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 0.29 (18H, s); 3.86 (6H, s); 6.93 (2H, s). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm):
2069 -0.02 (3C); 56.42; 100.40; 100.82; 113.44; 116.22; 154.18.
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2071 **Synthesis of 1,4-diethynyl-2,5-dimethoxybenzene (13)**

2072 2,5-Dimethoxy-1,4-bis((trimethylsilyl)ethynyl)benzene (**12**) (1.01 g, 3.05 mmol) and a 3.5 M aqueous KOH
2073 solution (1.9 mL, 6.65 mmol) were mixed in THF (45 mL) and methanol (45 mL). The resulting solution was left
2074 under stirring for 4 h at room temperature, then it was hydrolyzed with water (90 mL) and extracted with *n*-
2075 hexane (3x60 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ and
2076 the solvent was removed under vacuum. The crude product was purified through column chromatography
2077 (SiO₂, petroleum ether/CH₂Cl₂ 3:2) to give 1,4-diethynyl-2,5-dimethoxybenzene (**13**) (483 mg, yield 85%).
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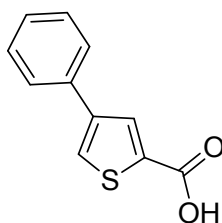


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2085 ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 3.42 (2H, s); 3.88 (6H, s); 7.00 (2H, s). ¹³C-NMR (100 MHz, CDCl₃), δ
2086 (ppm): 56.43; 79.66; 82.77; 112.66; 116.19; 154.42. LC-MS APCI (+): calcd for C₁₂H₁₀O₂: 186.07; found *m/z*
2087 [M+H]⁺: 187.1. Anal. calcd for C₁₂H₁₀O₂: C, 77.40; H, 5.41; found: C, 77.27; H, 5.38.
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2090 **Synthesis of thiophene acid chlorides**

2091 **Synthesis of 4-phenylthiophene-2-carboxylic acid**

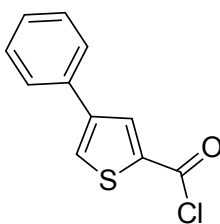
2092 Methyl 4-phenylthiophene-2-carboxylate (1.06 g, 4.86 mmol) and a 5 wt% NaOH aqueous solution (15 mL)
2093 were mixed together. The resulting solution was left under stirring for 24 h at room temperature, then it was
2094 hydrolyzed with a 2 M aqueous HCl solution (20 mL) and extracted with ethyl acetate (3x30 mL). The combined
2095 organic phases were washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under
2096 vacuum to give 4-phenylthiophene-2-carboxylic acid (963 mg, yield 97%) which was used without any
2097 further purification.
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2107 ¹H-NMR (400 MHz, CDCl₃), 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* =
2108 1.5 Hz); 8.15 (1H, d, *J* = 1.5 Hz). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 126.37 (2C); 127.89; 128.50; 129.02 (2C);
2109 133.33; 133.69; 134.63; 143.37; 167.16.
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2111 **Synthesis of 4-phenylthiophene-2-carbonyl chloride (4d)**

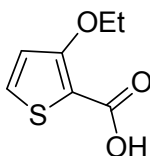
2112 4-Phenylthiophene-2-carboxylic acid (408 mg, 2.00 mmol), CH₂Cl₂ (20 mL) and 1,4-dioxane (0.5 mL) were
2113 mixed together, then oxalyl chloride (0.5 mL, 5.73 mmol) was added dropwise to the solution at 0 °C. The
2114 resulting mixture was left under stirring for 48 h at room temperature, then the solvent was removed
2115 under vacuum. The crude product was purified through column chromatography (SiO₂, CH₂Cl₂) to give 4-
2116 phenylthiophene-2-carbonyl chloride (**4d**) (263 mg, yield 59%).
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¹H-NMR (400 MHz, CDCl₃), 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). ¹³C-NMR (100 MHz, CDCl₃), 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

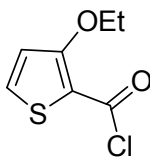
Methyl 3-ethoxythiophene-2-carboxylate (933 mg, 5.01 mmol) and a 5 wt% NaOH aqueous solution (15 mL) were mixed together. The resulting solution was left under stirring for 24 h at 50 °C, then it was hydrolyzed with a 2 M aqueous HCl solution (20 mL) and extracted with ethyl acetate (3x30 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ 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.



¹H-NMR (400 MHz, CDCl₃), 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). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 14.87; 68.42; 110.88; 116.19; 132.46; 160.38; 164.06.

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

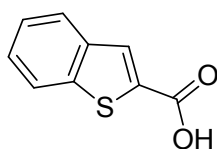
3-Ethoxythiophene-2-carboxylic acid (822 mg, 4.78 mmol) and CH₂Cl₂ (20 mL) were mixed together, then oxalyl chloride (1.3 mL, 14.9 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was left under stirring for 24 h at room temperature, then the solvent was removed under vacuum to give 3-ethoxythiophene-2-carbonyl chloride (4e) (922 mg, yield 97%) which was used without any further purification.



¹H-NMR (400 MHz, CDCl₃), δ (ppm): 1.46 (3H, t, *J* = 7.2 Hz); 4.23 (2H, q, *J* = 7.2 Hz); 6.84 (1H, d, *J* = 5.6 Hz); 7.62 (1H, d, *J* = 5.6 Hz).

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

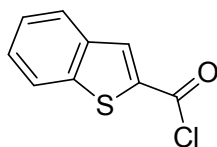
Methyl benzo[*b*]thiophene-2-carboxylate (505 mg, 2.63 mmol) and a 5 wt% NaOH aqueous solution (10 mL) were mixed together. The resulting solution was left under stirring for 24 h at room temperature, then it was hydrolyzed with a 2 M aqueous HCl solution (10 mL) and extracted with ethyl acetate (3x20 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄ 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.



¹H-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). ¹³C-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)

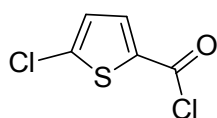
Benzo[*b*]thiophene-2-carboxylic acid (458 mg, 2.57 mmol), CH₂Cl₂ (25 mL), 1,4-dioxane (2 mL) and DMF (3 drops) were mixed together, then oxalyl chloride (1.0 mL, 11.5 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was refluxed under stirring for 48 h, then it was cooled to room 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.



¹H-NMR (400 MHz, CDCl₃), 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). ¹³C-NMR (100 MHz, CDCl₃), 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)

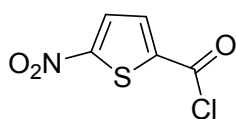
5-chlorothiophene-2-carboxylic acid (3.01 g, 18.5 mmol), CH₂Cl₂ (45 mL) and DMF (0.5 mL) were mixed together, then oxalyl chloride (4.5 mL, 52.4 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was left under stirring for 24 h at room temperature, then the solvent was removed under vacuum. The crude product was purified through column chromatography (SiO₂, CH₂Cl₂) to give 5-chlorothiophene-2-carbonyl chloride (4g) (3.13 g, yield 93%).



¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.04 (1H, d, *J* = 4.2 Hz); 7.79 (1H, d, *J* = 4.2 Hz). ¹³C-NMR (100 MHz, CDCl₃), 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 CH₂Cl₂ (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.



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2245 ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.89 (1H, d, J = 4.4 Hz); 7.93 (1H, d, J = 4.4 Hz). ¹³C-NMR (100 MHz,
2246 CDCl₃), δ (ppm): 127.89; 136.25; 141.10; 158.21; 159.76.
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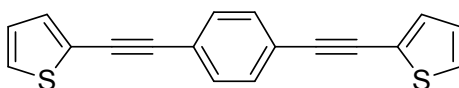
2248 **Synthesis of bis(thiophenylethynyl)arene dyes**

2249 **General procedure**

2250 In a typical run, diethynylarene (1.0 mmol), 2-iodothiophene (2.5 mmol), PdCl₂(PPh₃)₂ (2 mol%), CuI (4 mol%)
2251 and Et₃N (20 mL) were mixed together in a 50 mL two-necked round bottom flask. The resulting mixture
2252 was left under stirring for 7 h at 50 °C, then it was cooled to room temperature and left under stirring for
2253 further 17 h. The reaction mixture was then hydrolysed with saturated ammonium chloride solution (20
2254 mL) and extracted with CH₂Cl₂ (3x30 mL). The combined organic phases were washed with brine, dried over
2255 anhydrous Na₂SO₄ and the solvent was removed under vacuum. All the crude products were purified by
2256 recrystallization or column chromatography on silica gel and characterized with ¹H-NMR, ¹³C-NMR, LC-MS
2257 and elemental analysis techniques.
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2304 **1,4-Bis(thiophen-2-ylethynyl)benzene (6)**
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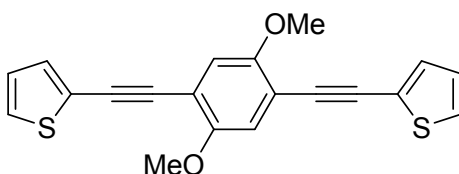
2306 According to the general procedure, 1,4-diethynylbenzene (**3**) (126 mg, 1.0 mmol), 2-iodothiophene (525
2307 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol), CuI (8 mg, 0.04 mmol) and Et₃N (20 mL) were mixed together.
2308 The crude product was purified by recrystallization from CHCl₃, giving 200 mg (yield 69%) of 1,4-bis(thiophen-
2309 2-ylethynyl)benzene (**6**).
2310



2314 ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.00-7.02 (2H, m); 7.28-7.30 (4H, m); 7.47 (4H, s). ¹³C-NMR (100 MHz,
2315 CDCl₃), δ (ppm): 84.61; 92.74; 122.86; 123.04; 127.17; 127.61; 131.30 (2C); 132.16. LC-MS APCI (+): calcd for
2316 C₁₈H₁₀S₂: 290.02; found *m/z* [M+H]⁺: 291.1. Anal. calcd for C₁₈H₁₀S₂: C, 74.45; H, 3.47; S, 22.08; found: C,
2317 74.57; H, 3.34; S, 22.09.
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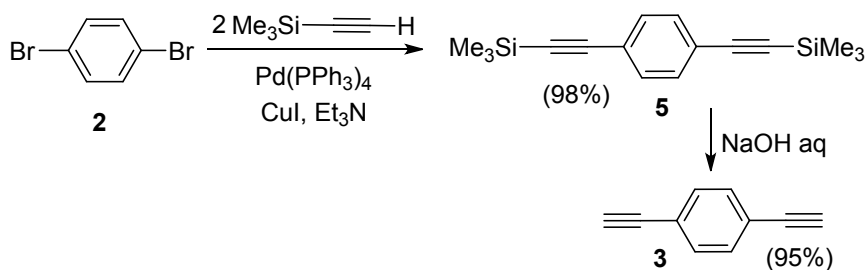
2319 **2,2'-((2,5-Dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (14)**
2320

2321 According to the general procedure, 1,4-diethynyl-2,5-dimethoxybenzene (**13**) (186 mg, 1.0 mmol), 2-
2322 iodothiophene (525 mg, 2.5 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.02 mmol), CuI (8 mg, 0.04 mmol) and Et₃N (20
2323 mL) were mixed together. The crude product was purified through column chromatography (SiO₂, *n*-
2324 hexane/CH₂Cl₂ 3:5), giving 211 mg (yield 60%) of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-
2325 diyl))dithiophene (**14**).
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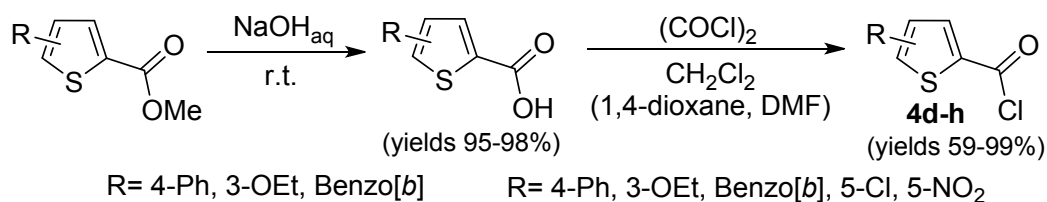


2328 ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 3.92 (6H, s); 7.03 (2H, s); 7.04-7.06 (2H, m); 7.33-7.35 (4H, m). ¹³C-NMR
2329 (100 MHz, CDCl₃), δ (ppm): 56.46; 88.26; 89.36; 113.21; 115.37; 123.19; 127.13; 127.59; 132.21; 153.78. LC-
2330 MS APCI (+): calcd for C₂₀H₁₄O₂S₂: 350.04; found *m/z* [M+H]⁺: 351.2. Anal. calcd for C₂₀H₁₄O₂S₂: C, 68.54; H,
2331 4.03; S, 18.30; found: C, 68.59; H, 4.11; S, 18.32.
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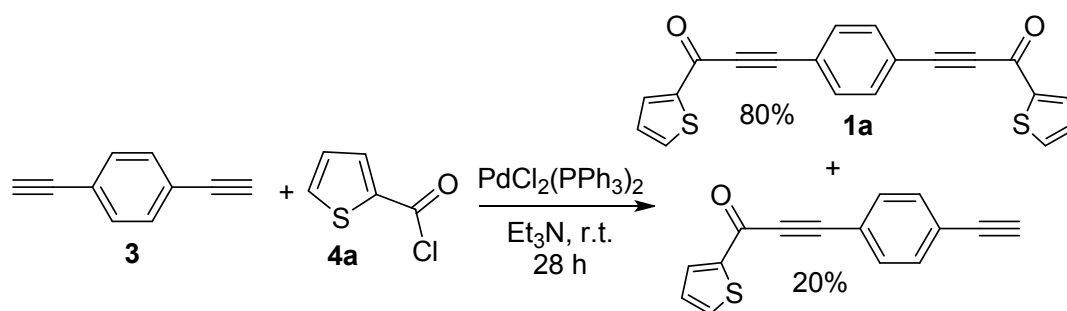
Supplementary Schemes



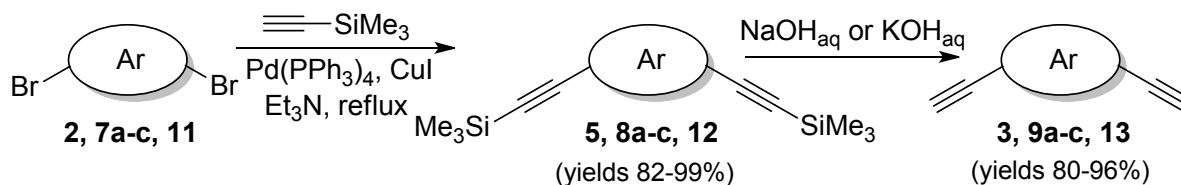
Scheme S1. Synthesis of 1,4-diethynylbenzene (**3**).



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

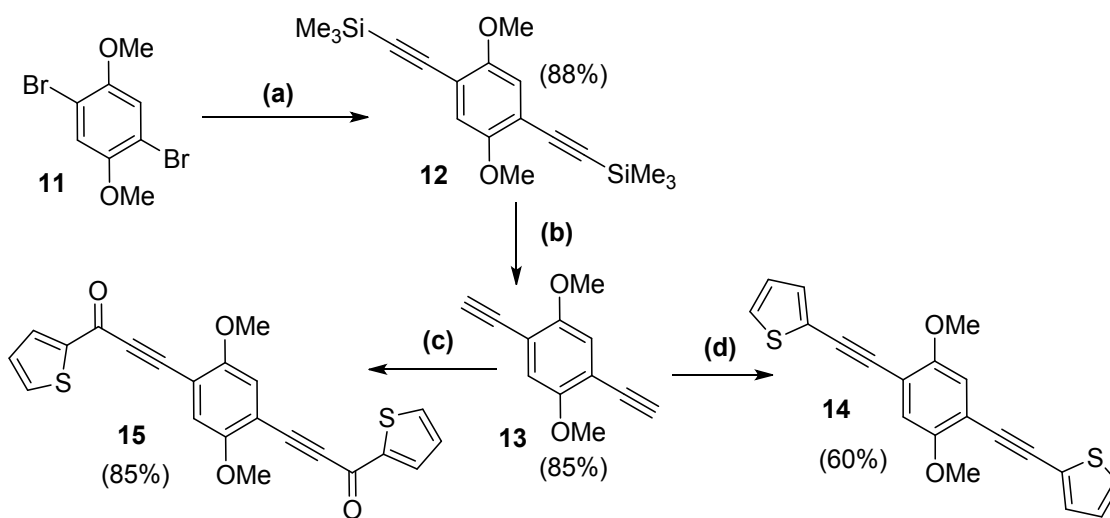


Scheme S3. Preliminary acyl Sonogashira reaction between 1,4-diethynylbenzene (**3**) and thiophene-2-carbonyl chloride (**4a**) performed at room temperature.



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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**.

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Supplementary Figures

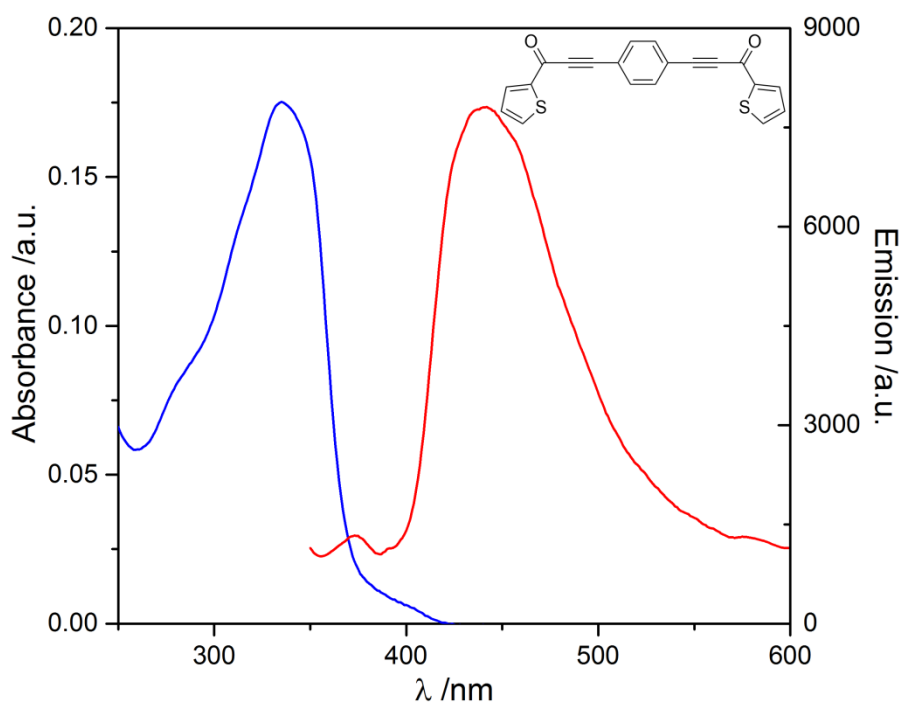


Figure S1. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

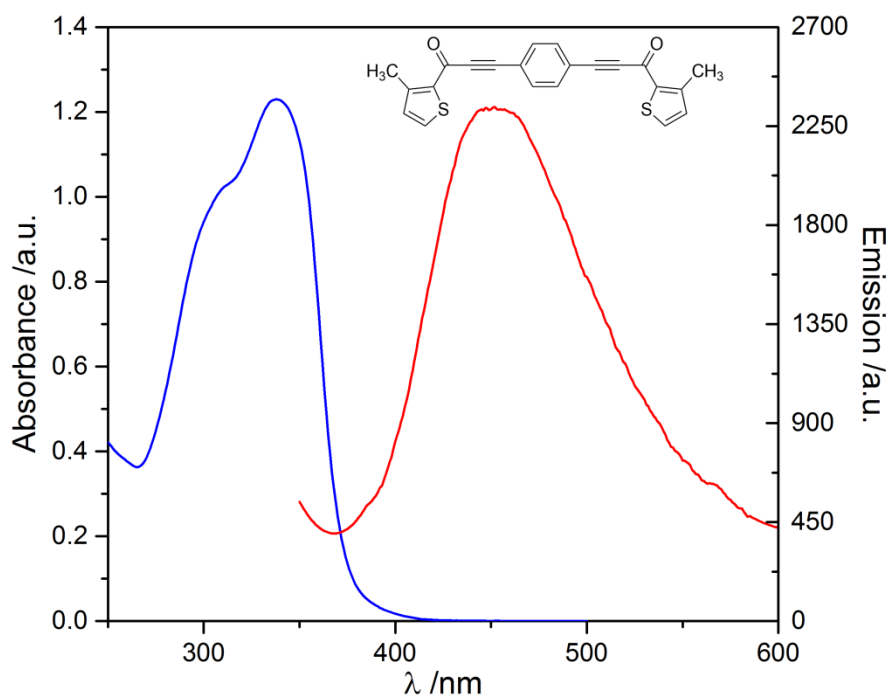


Figure S2. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one) (**1b**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

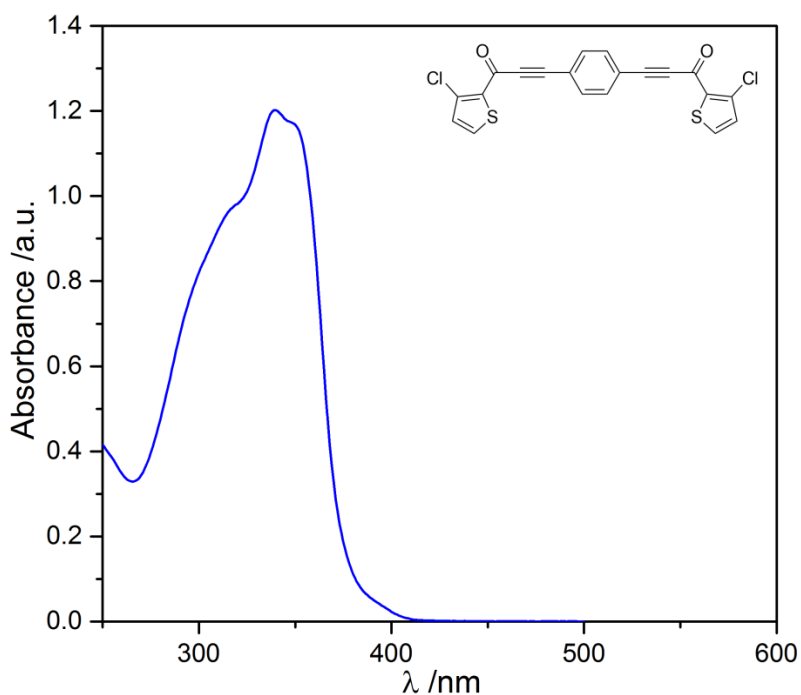


Figure S3. UV-Vis absorption spectrum (blue line) of 3,3'-(1,4-phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one) (**1c**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm.

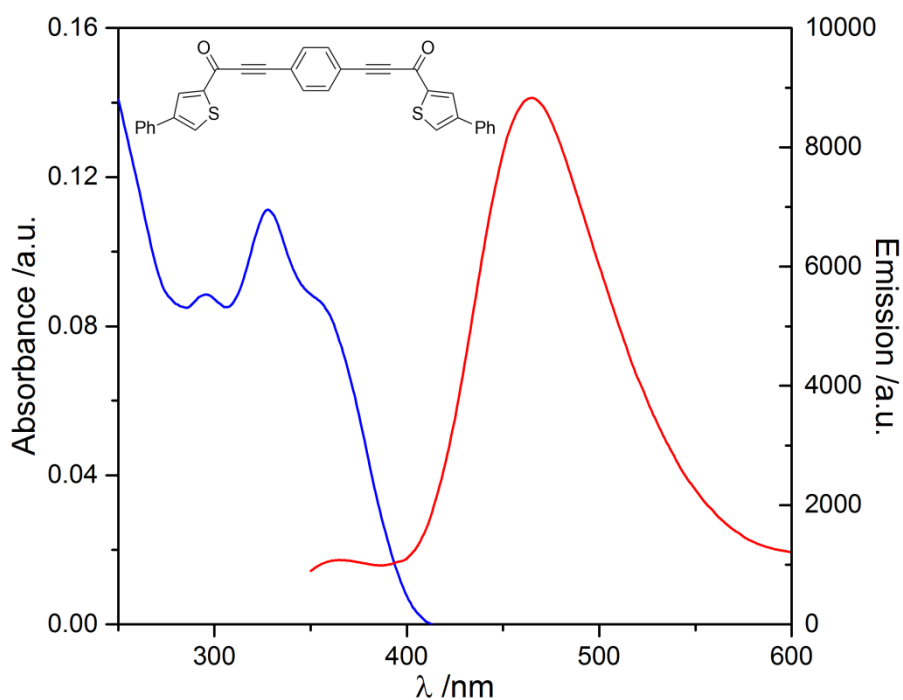


Figure S4. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

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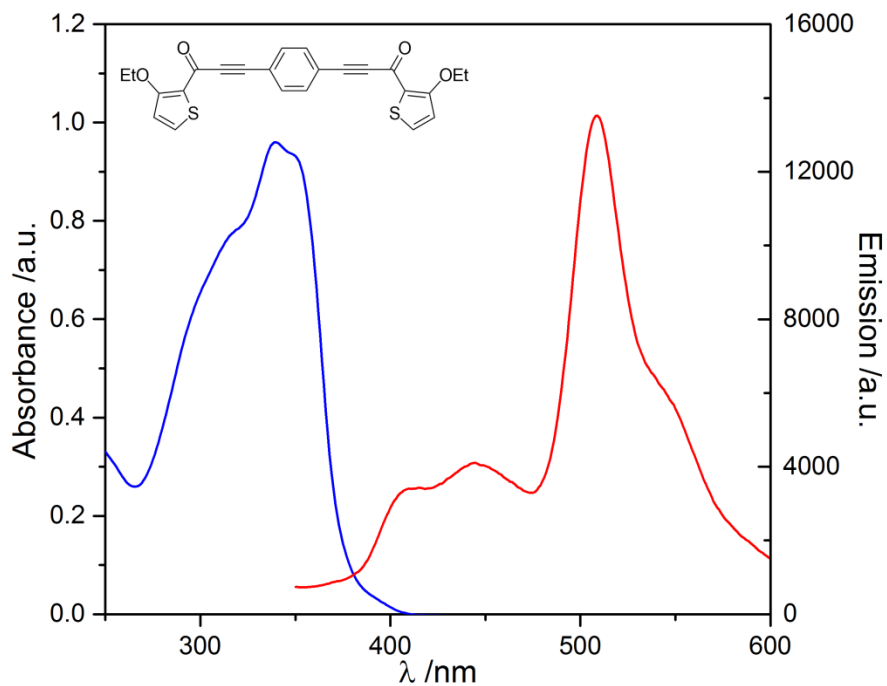


Figure S5. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

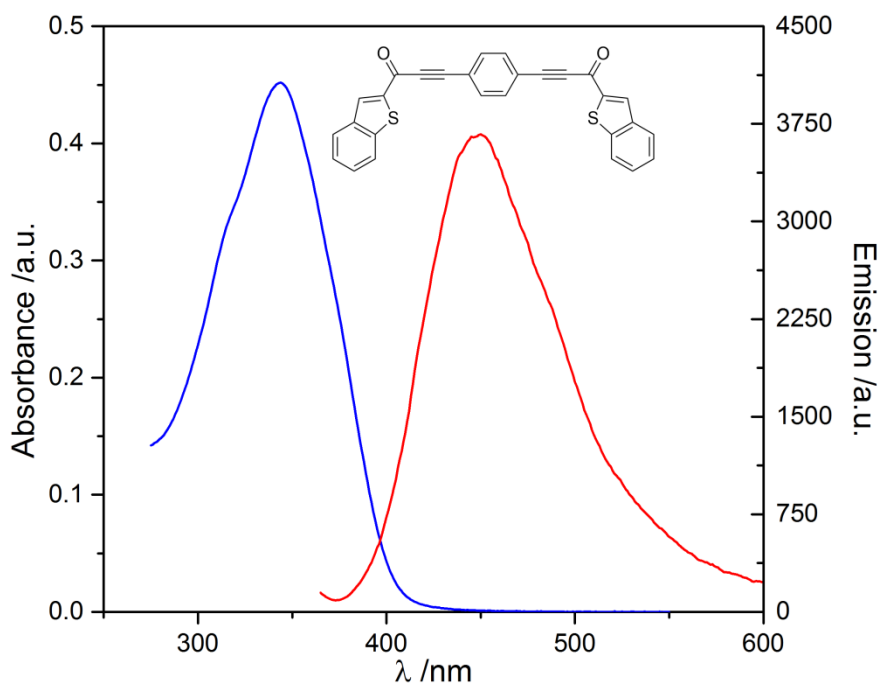
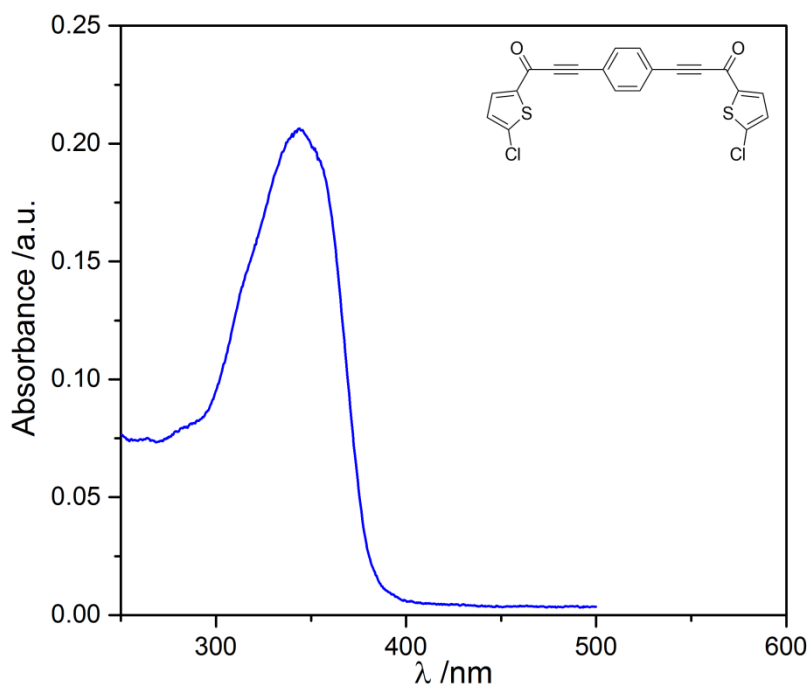
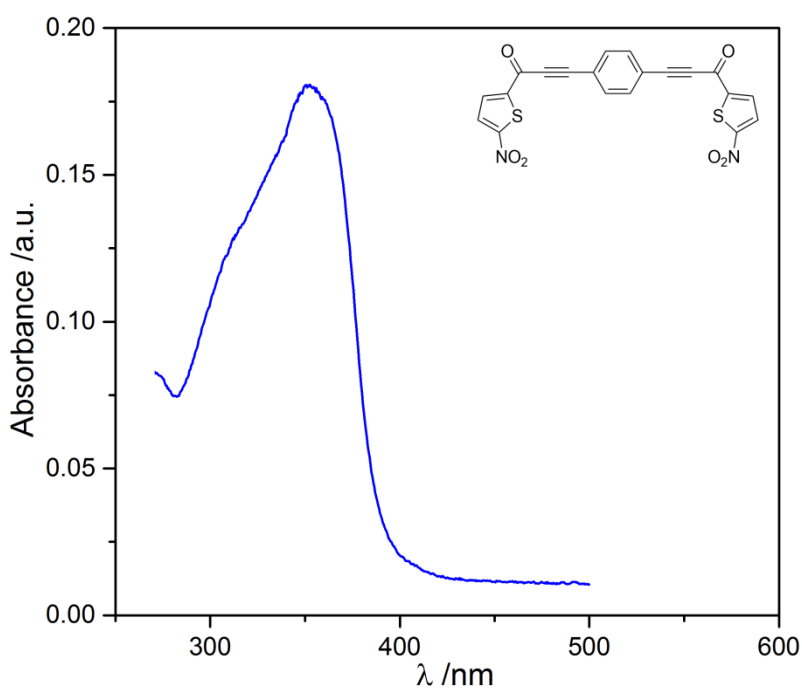


Figure S6. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(1,4-phenylene)bis(1-(benzo[b]thiophen-2-yl)prop-2-yn-1-one) (**1f**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.



2679 **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**)
2680 in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm.



2705 **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**)
2706 in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm.

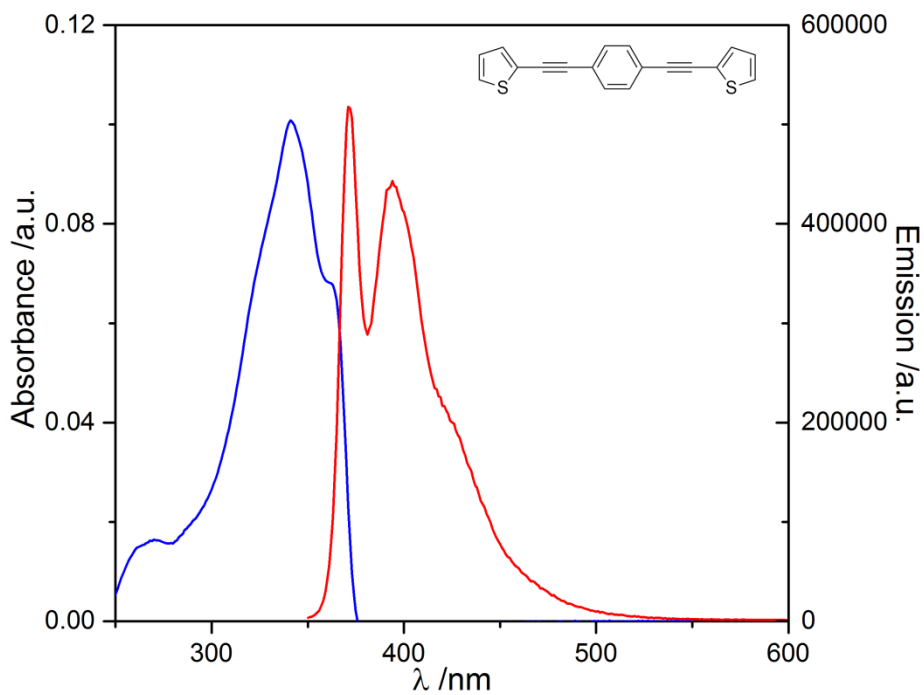


Figure S9. UV-Vis absorption (blue line) and emission (red line) spectra of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**) in CHCl₃. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

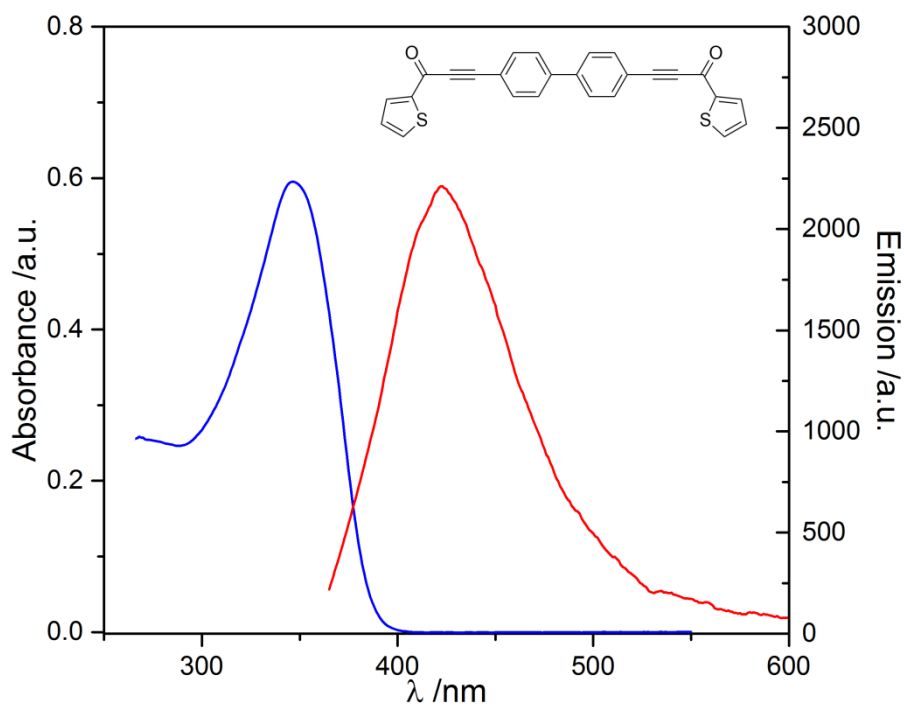


Figure S10. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10a**) in CHCl₃. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

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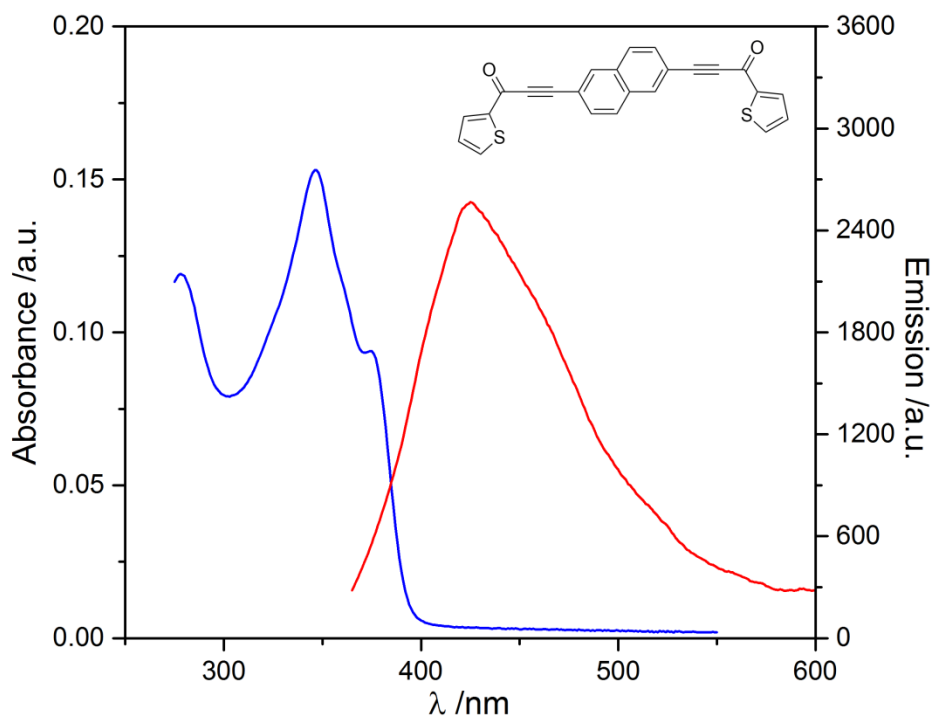


Figure S11. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**) in CHCl₃. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

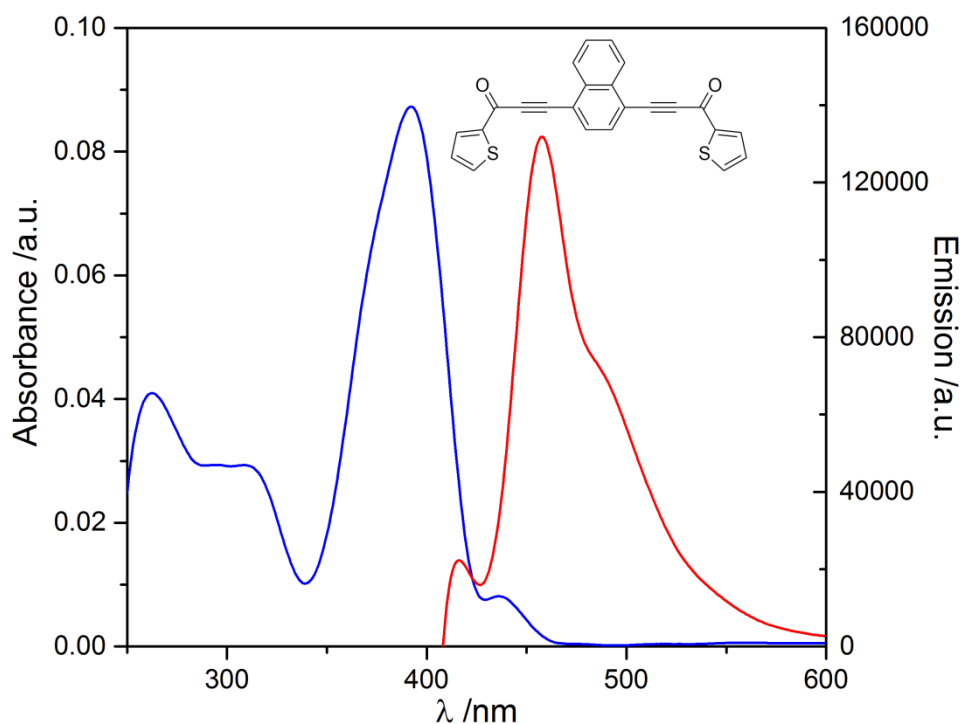


Figure S12. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**) in CHCl₃. Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

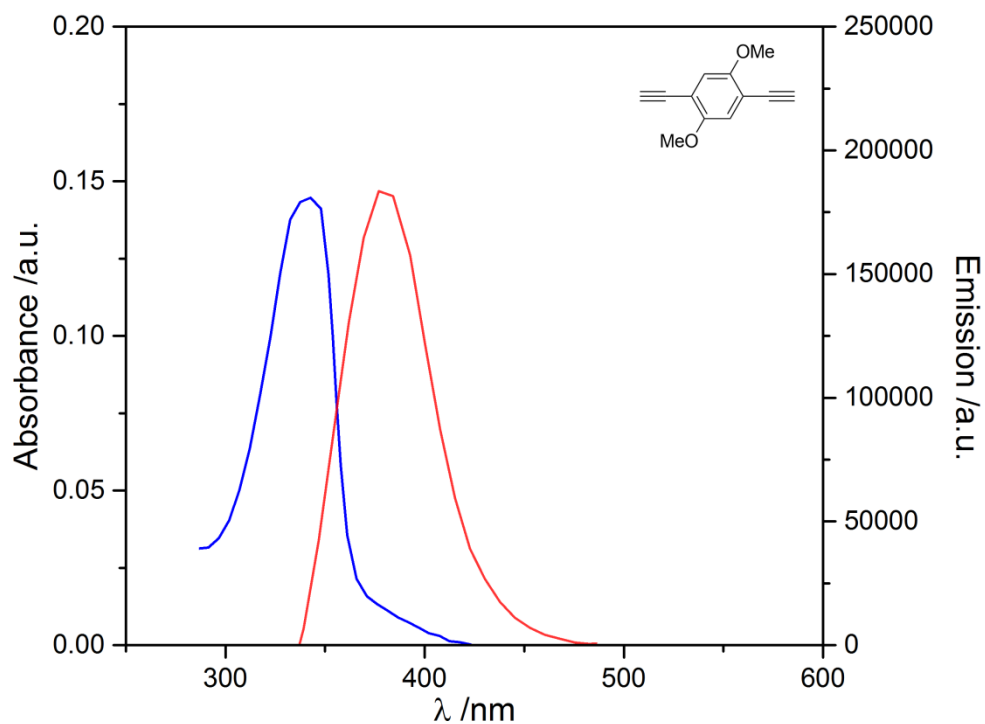


Figure S13. UV-Vis absorption (blue line) and emission (red line) spectra of 1,4-diethynyl-2,5-dimethoxybenzene (**13**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

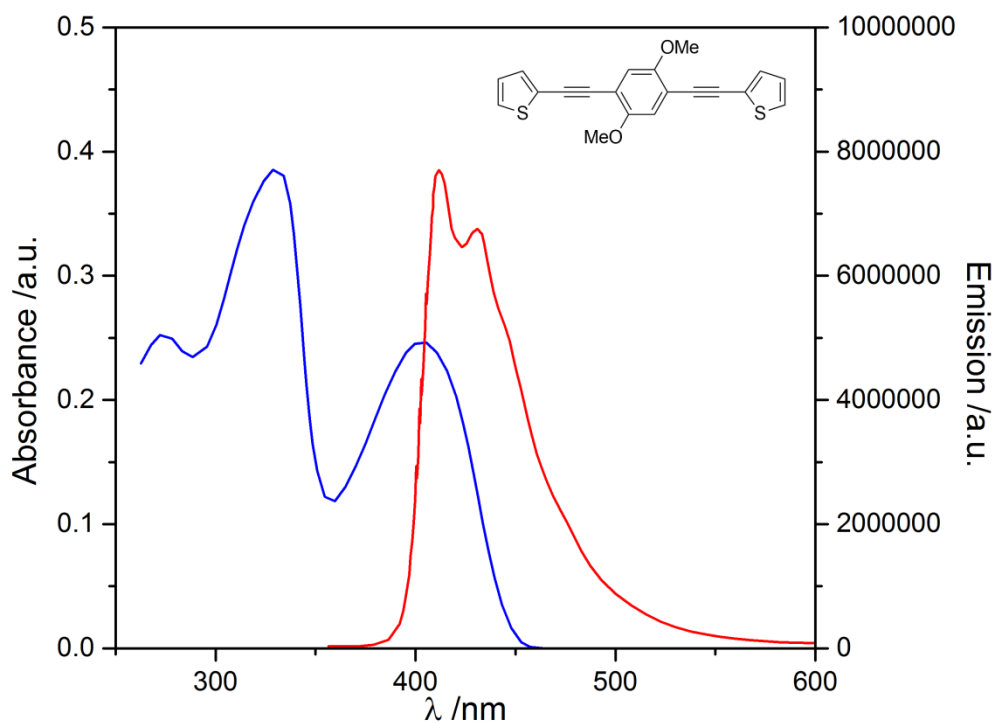


Figure S14. UV-Vis absorption (blue line) and emission (red line) spectra of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene (**14**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

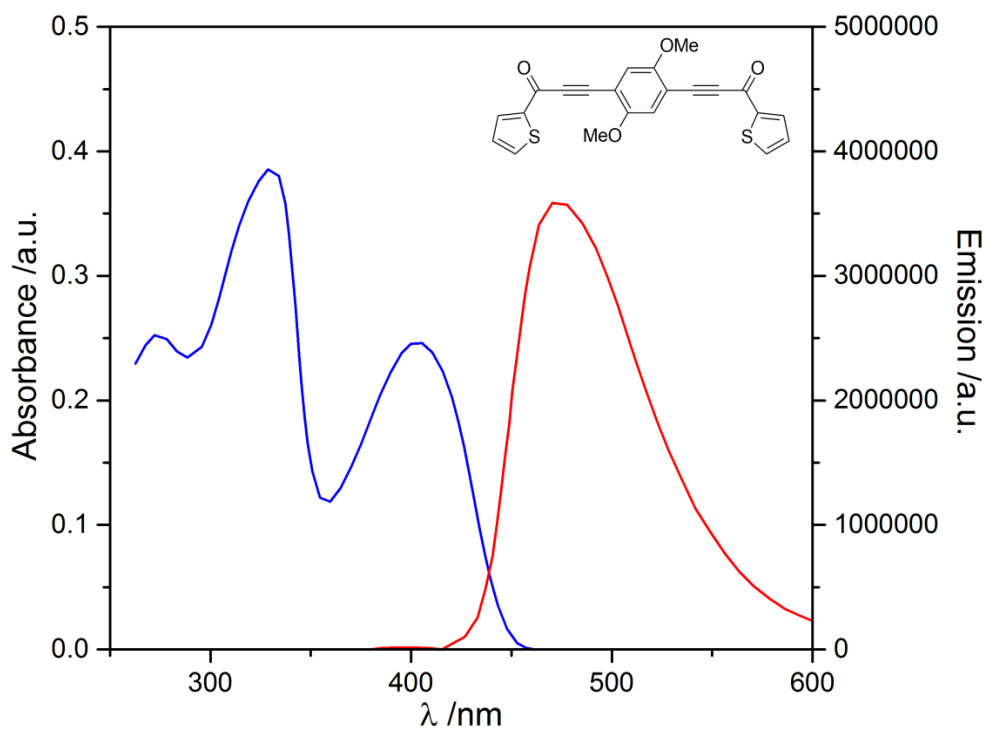


Figure S15. UV-Vis absorption (blue line) and emission (red line) spectra of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**15**) in CHCl_3 . Sample concentration: 3×10^{-6} M; cell length: 1 cm; excitation wavelength: 335 nm.

NMR Spectra

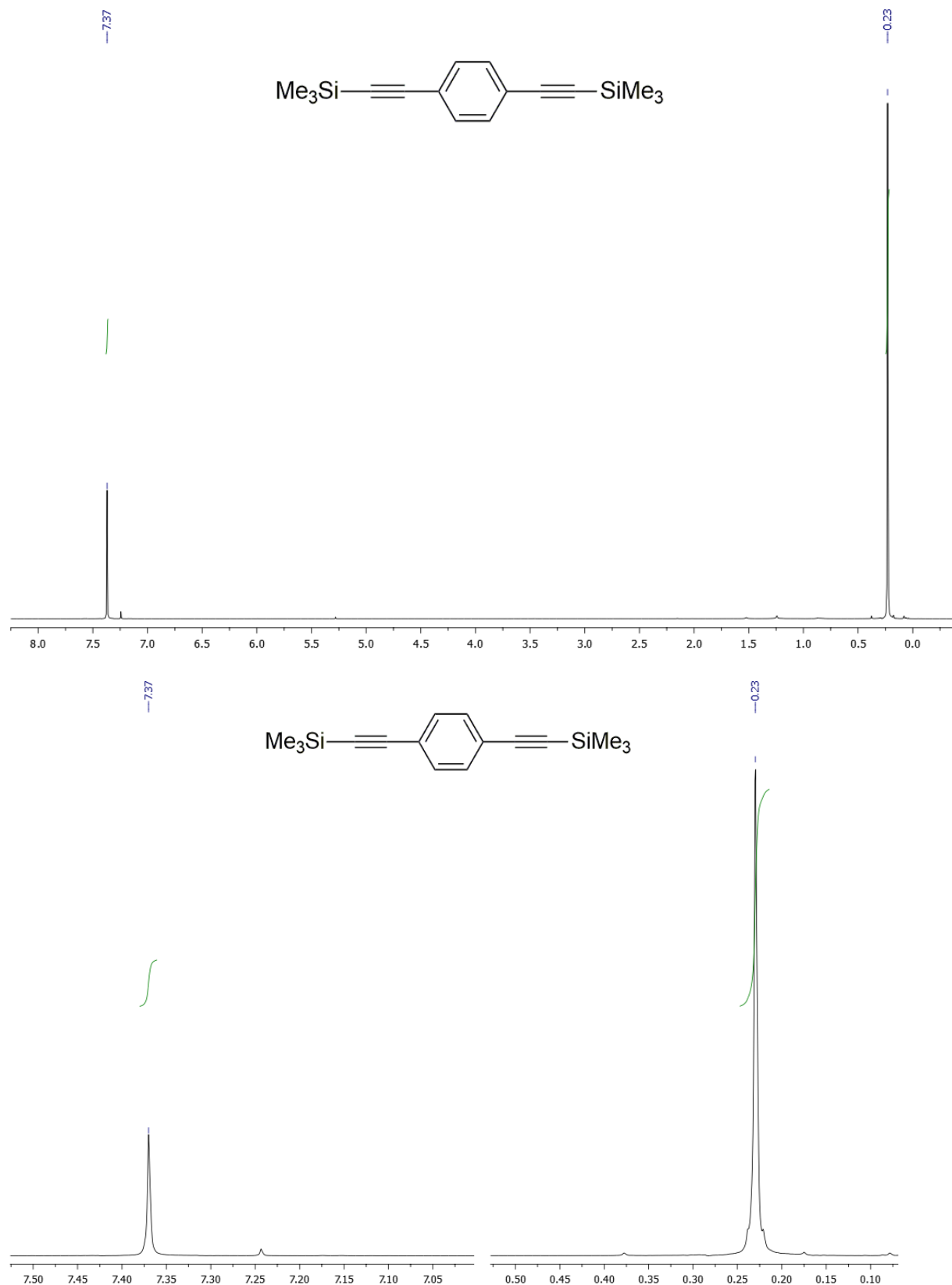


Figure S16. ¹H-NMR spectrum (400 MHz, CDCl₃) of 1,4-bis(trimethylsilyl)ethynylbenzene (5): full scale spectrum (top) and spectrum expansions (bottom).

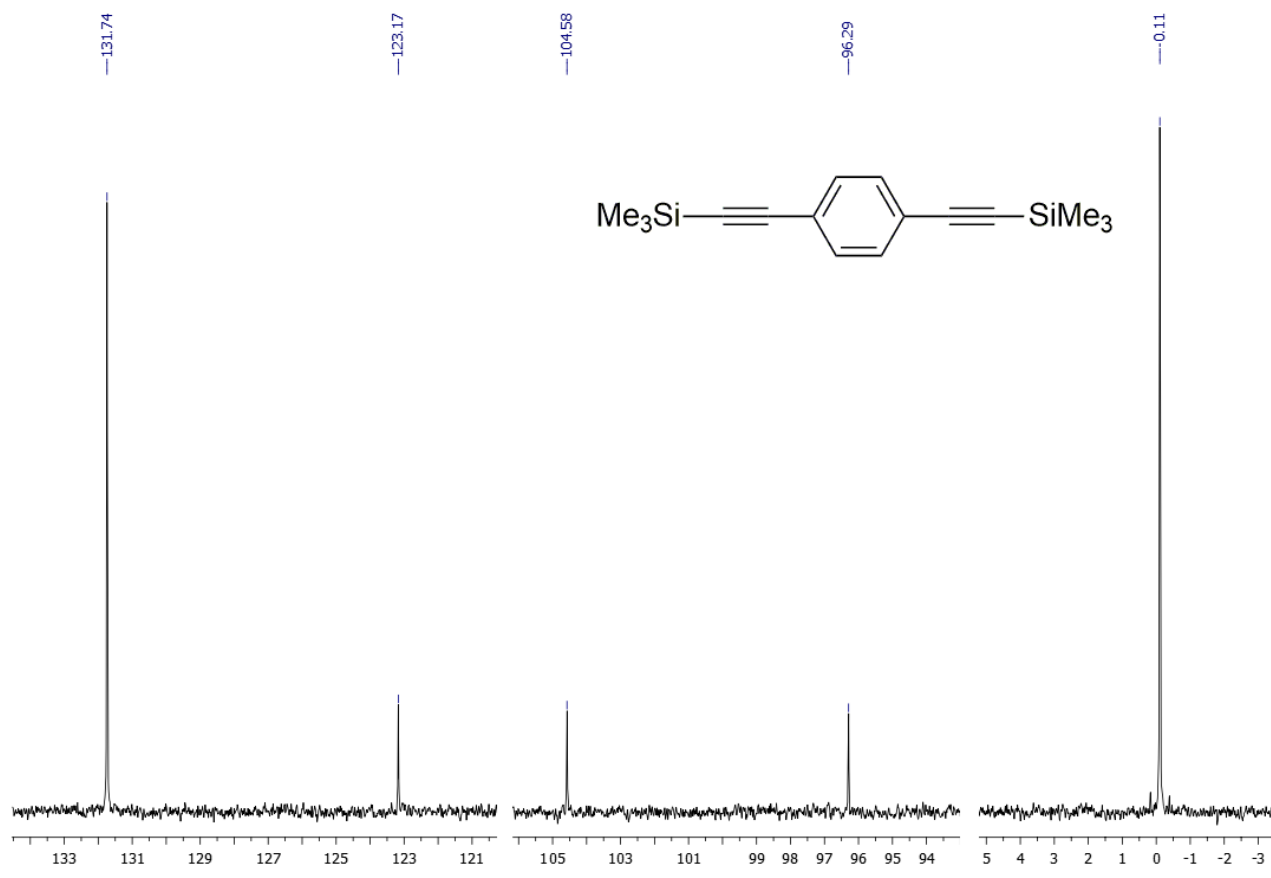
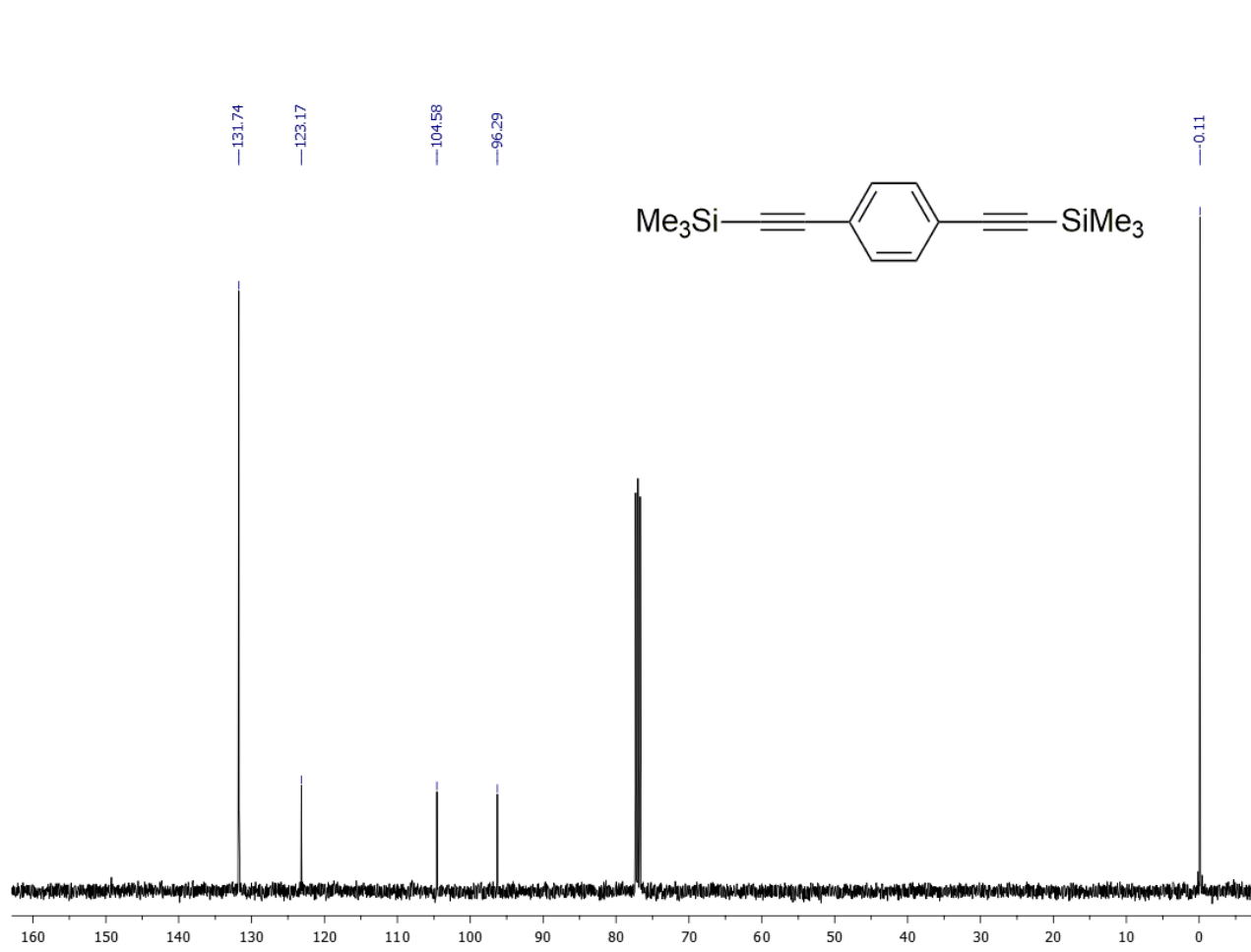


Figure S17. ¹³C-NMR spectrum (100 MHz, CDCl₃) of 1,4-bis((trimethylsilyl)ethynyl)benzene (**5**): full scale spectrum (top) and spectrum expansions (bottom).

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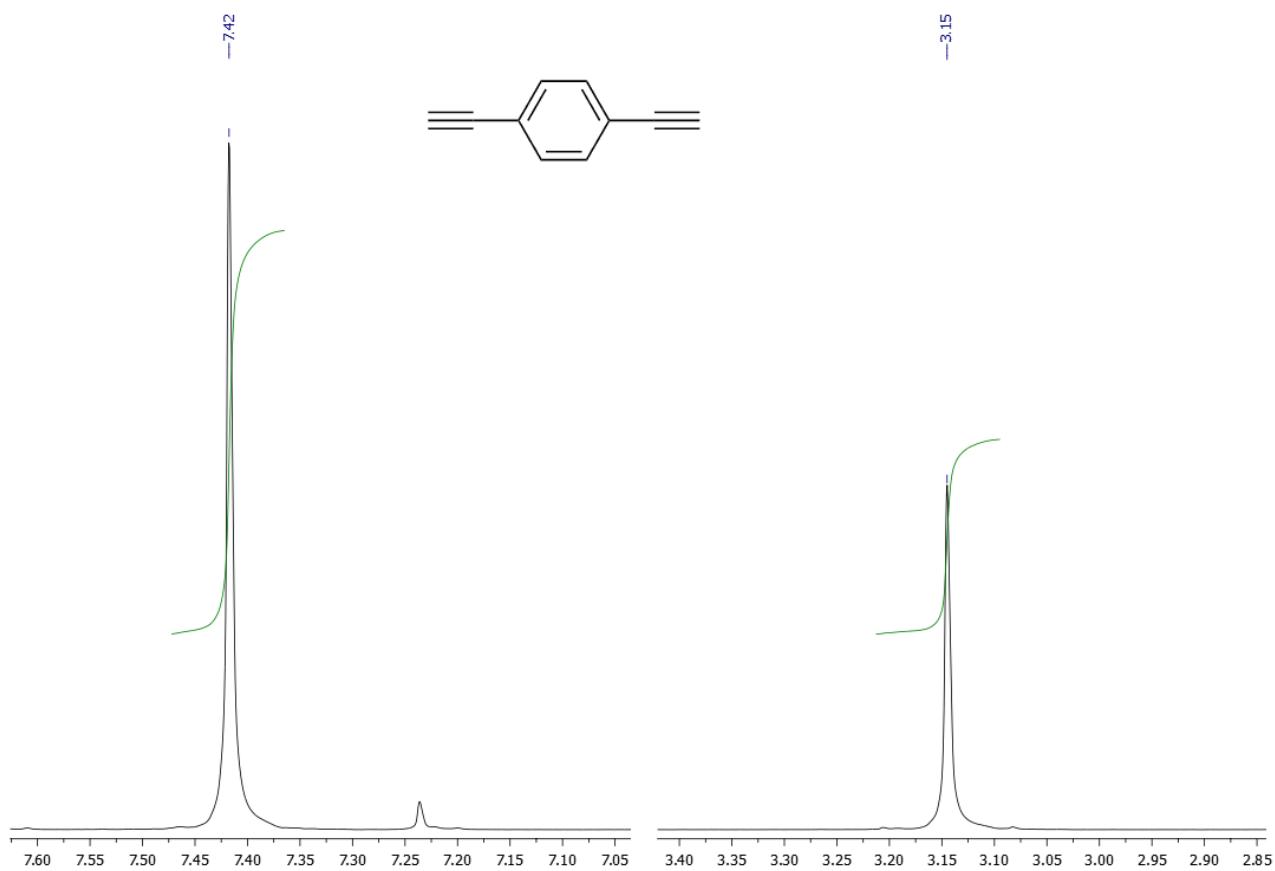
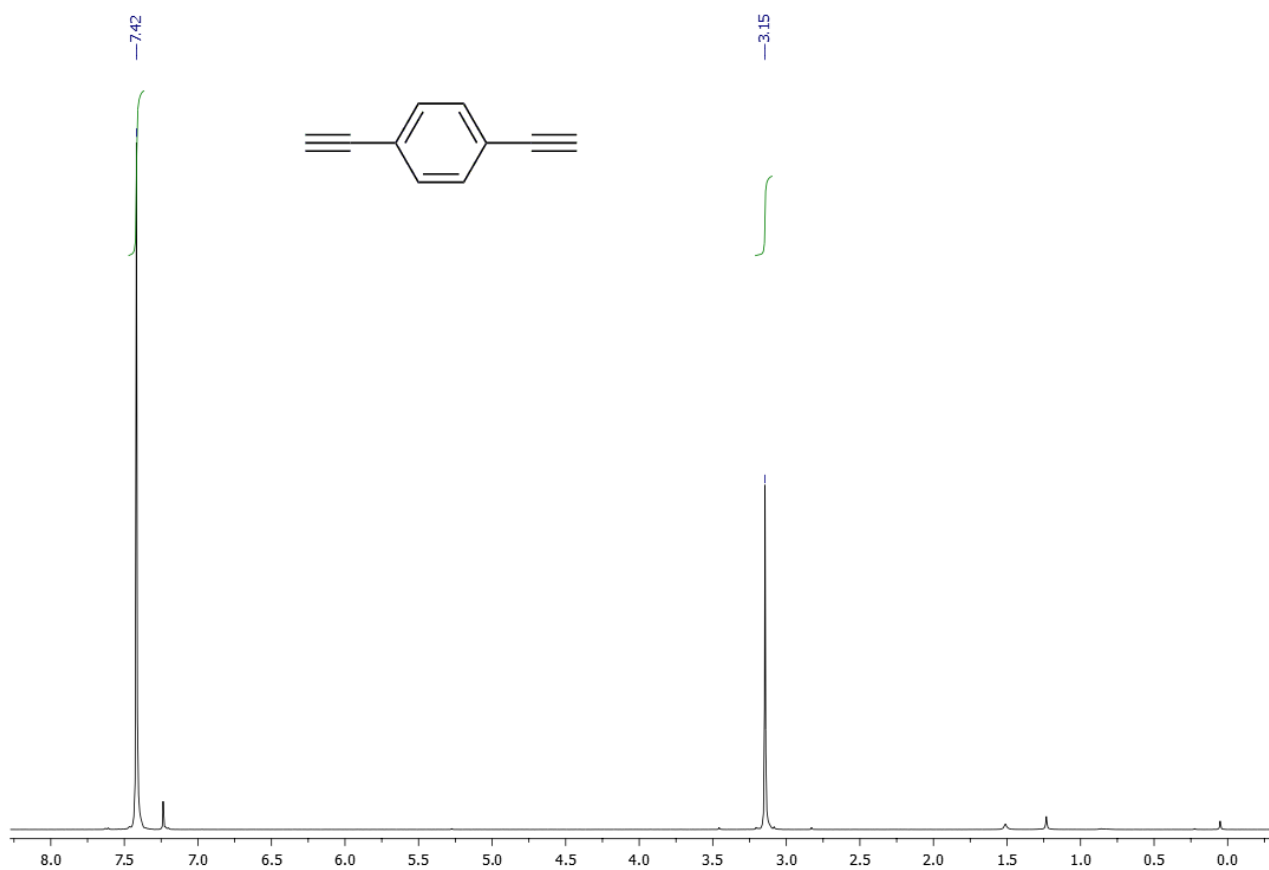


Figure S18. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 1,4-diethynylbenzene (**3**): full scale spectrum (top) and spectrum expansions (bottom).

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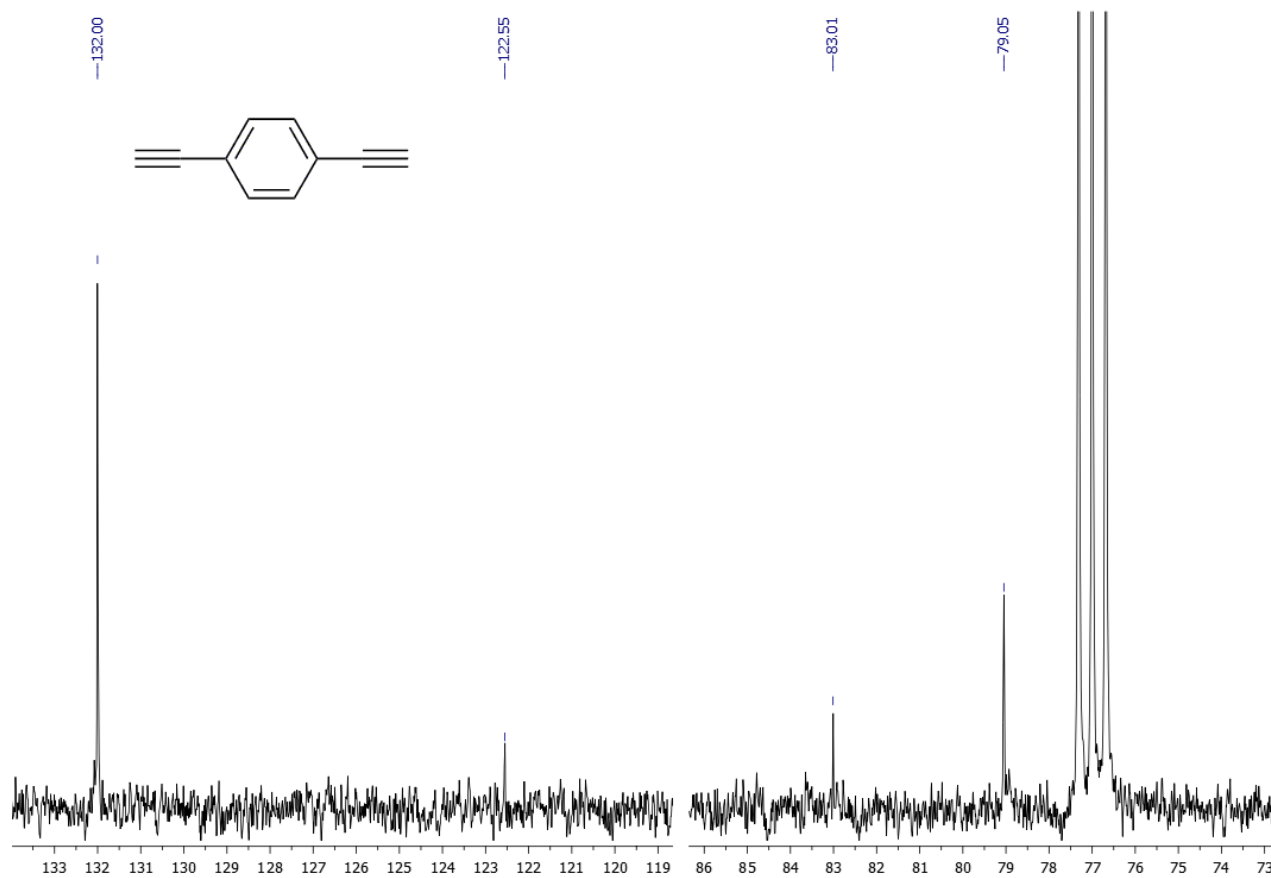
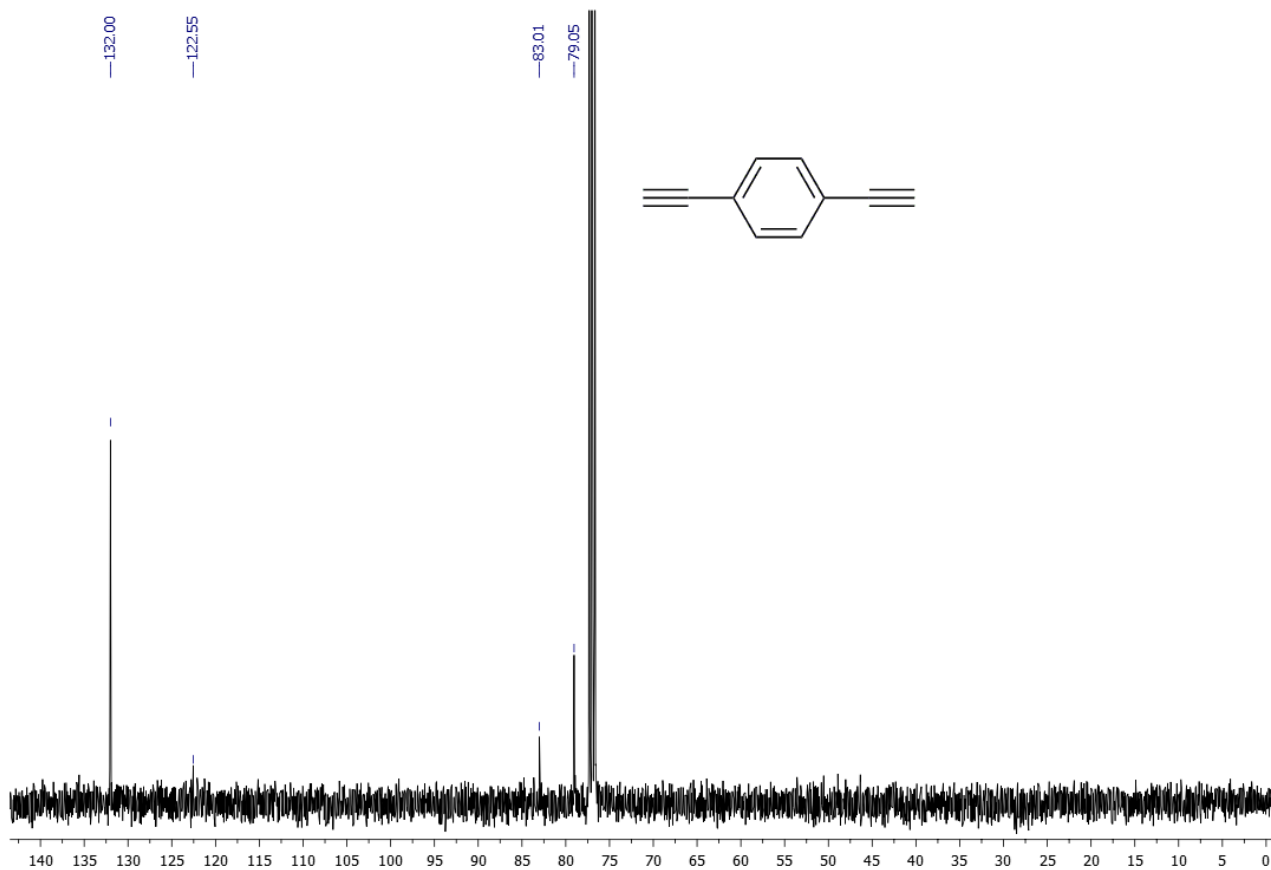


Figure S19. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 1,4-diethynylbenzene (**3**): full scale spectrum (top) and spectrum expansions (bottom).

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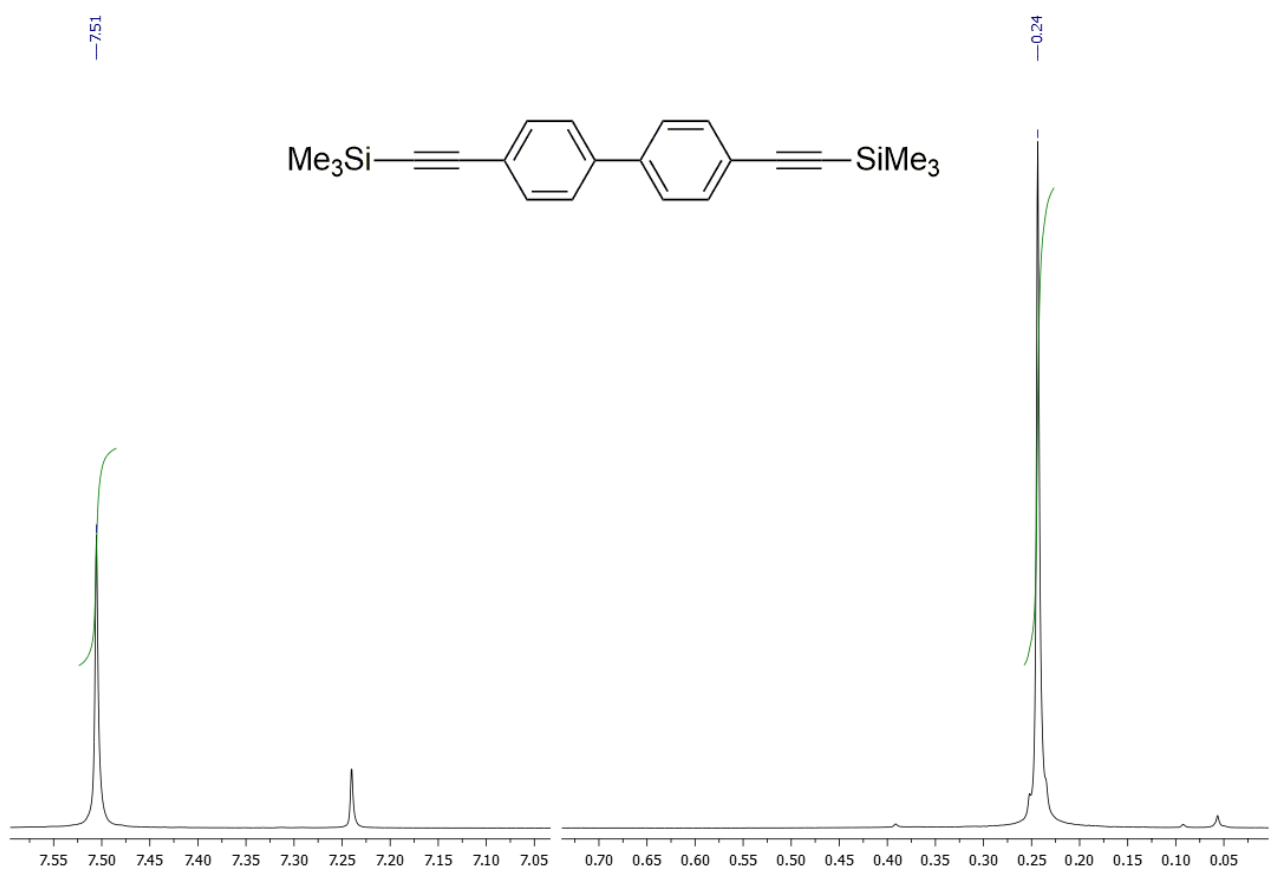
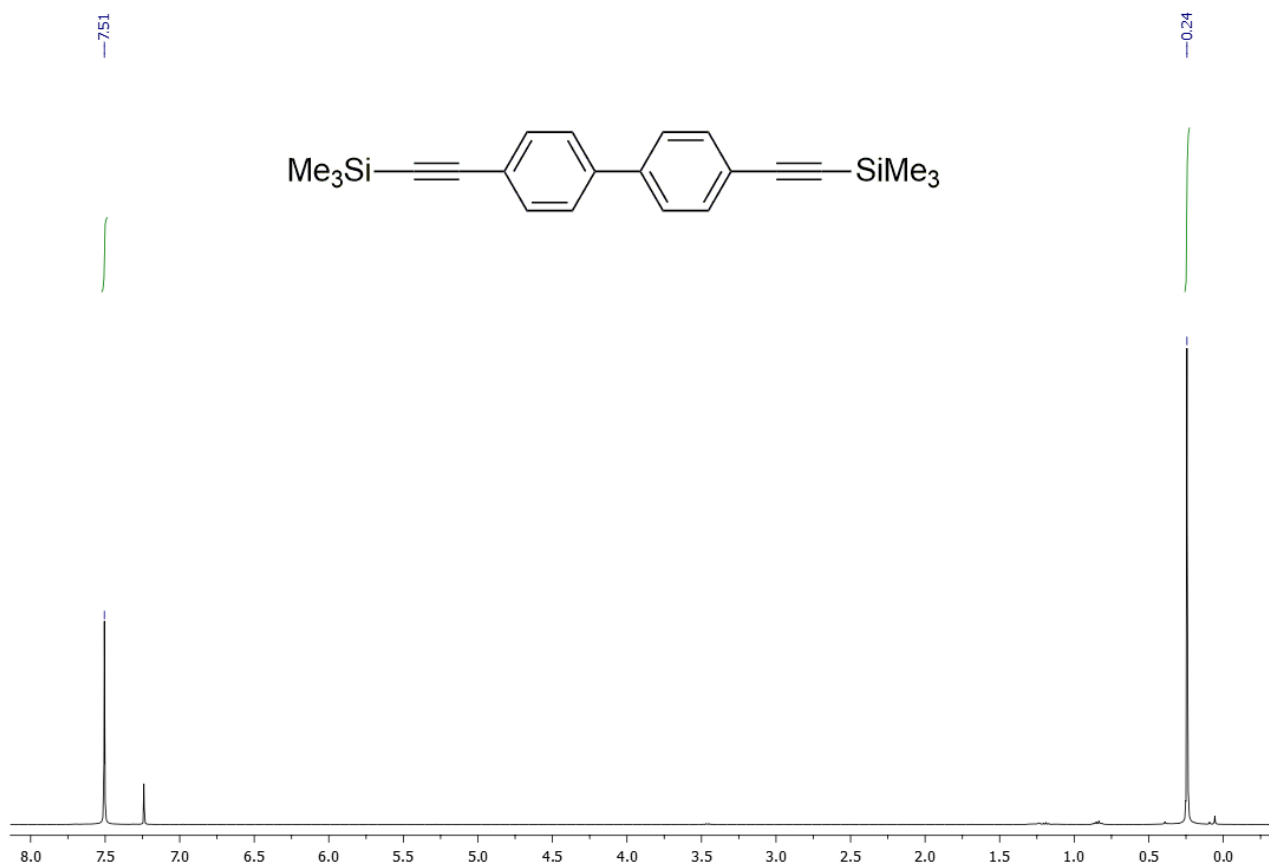


Figure S20. ^1H -NMR spectrum (400 MHz, CDCl_3) of 4,4'-bis(trimethylsilyl)ethynyl-1,1'-biphenyl (**8a**):full scale spectrum (top) and spectrum expansions (bottom).

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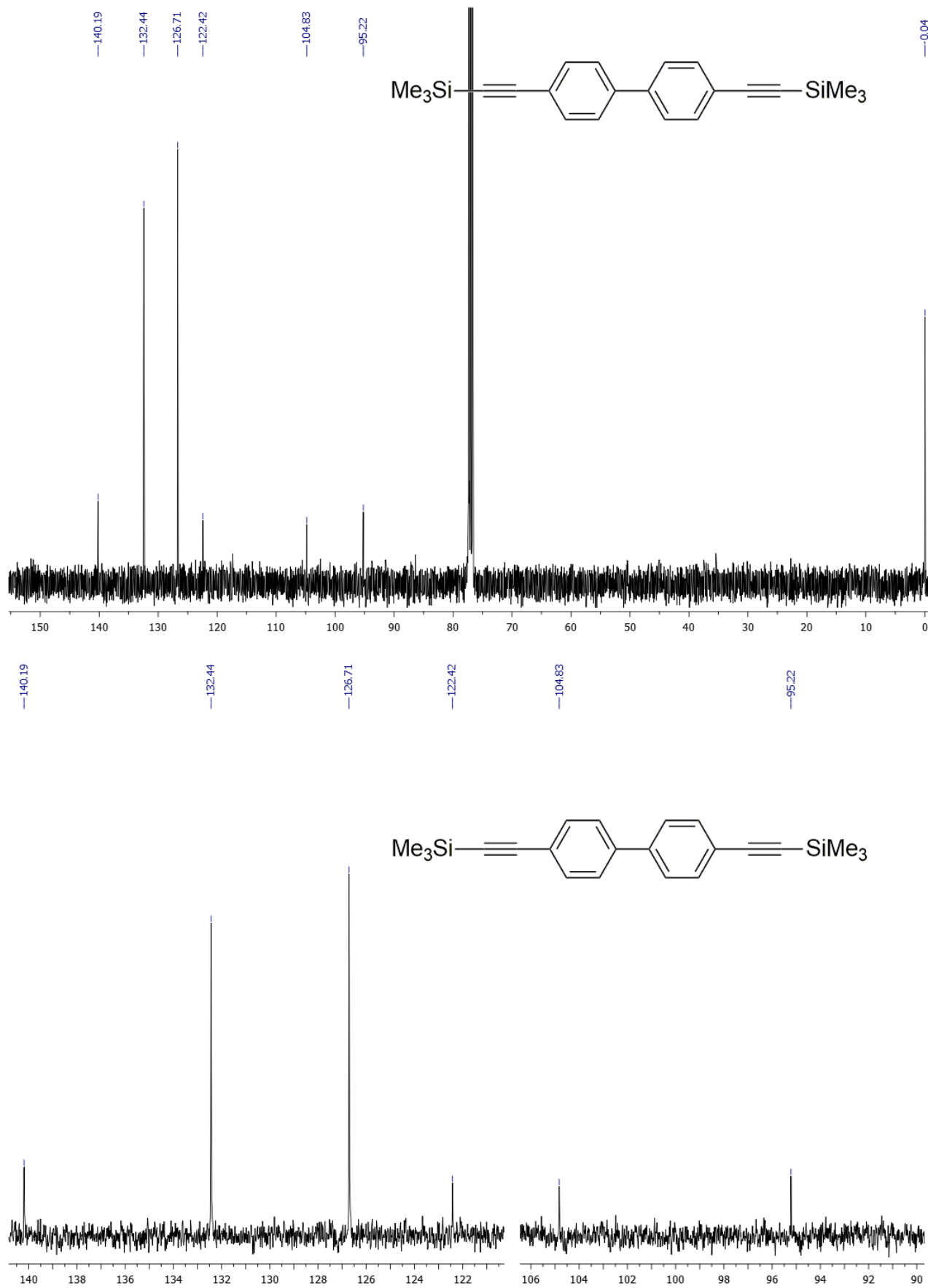


Figure S21. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 4,4'-bis(trimethylsilyl)ethynyl-1,1'-biphenyl (**8a**): full scale spectrum (top) and spectrum expansions (bottom).

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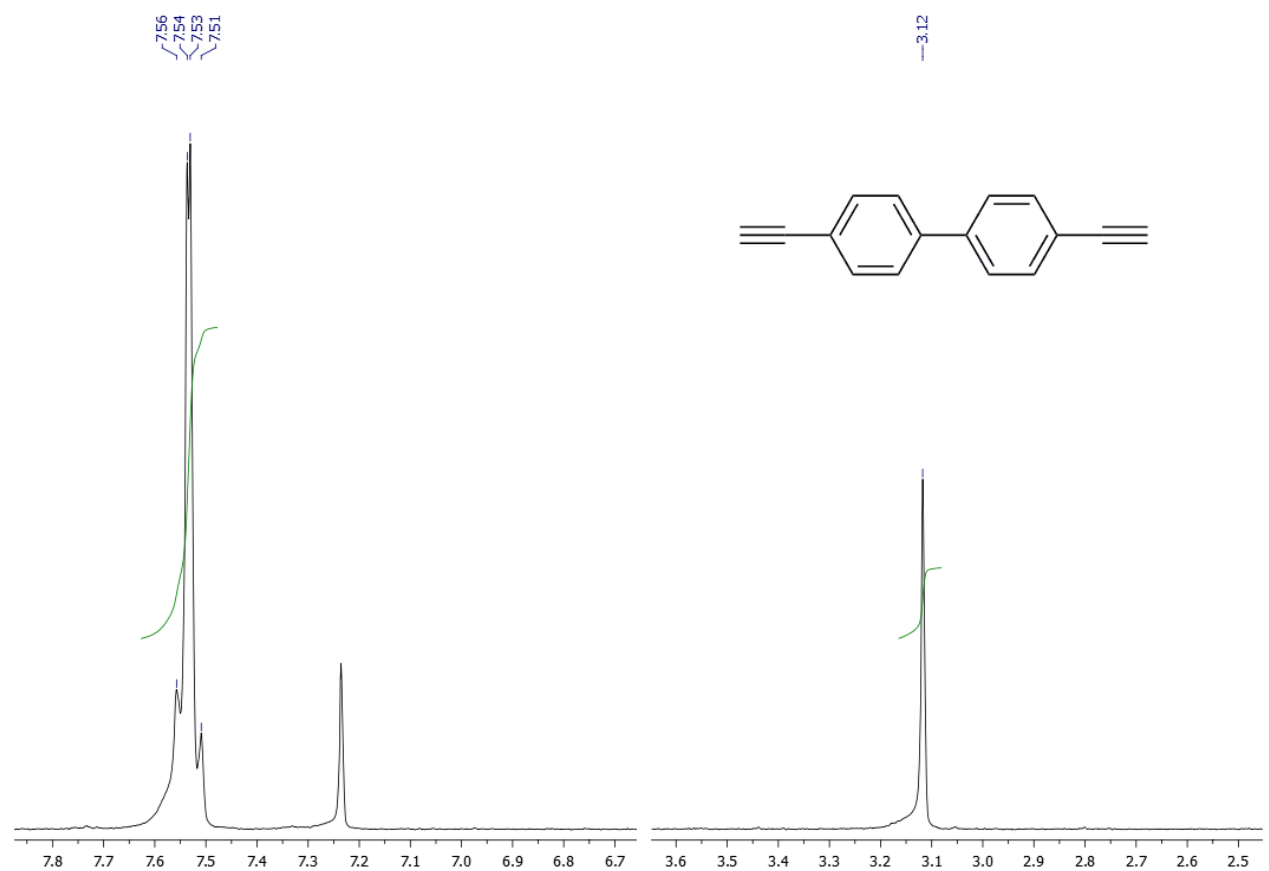
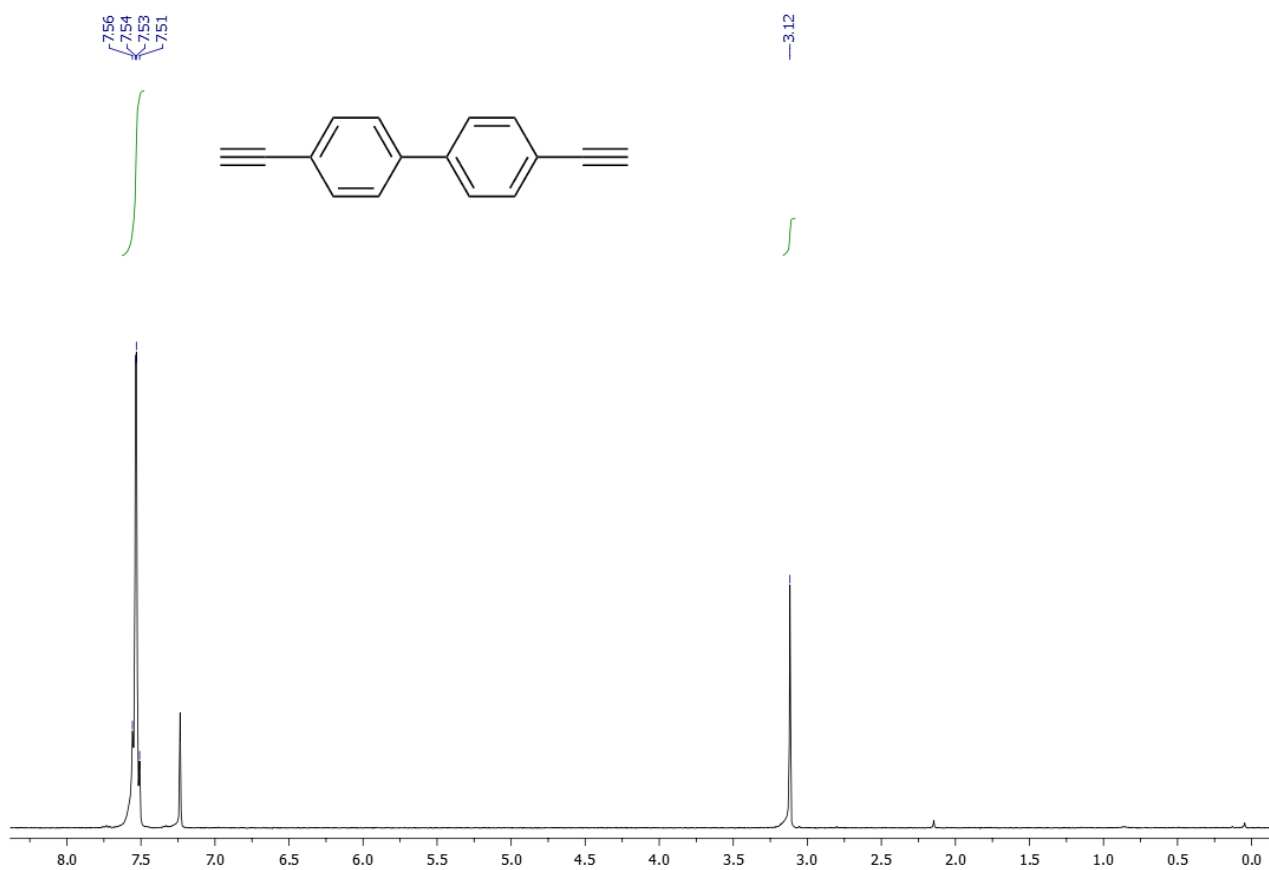


Figure S22. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 4,4'-diethynyl-1,1'-biphenyl (**9a**):full scale spectrum (top) and spectrum expansions (bottom).

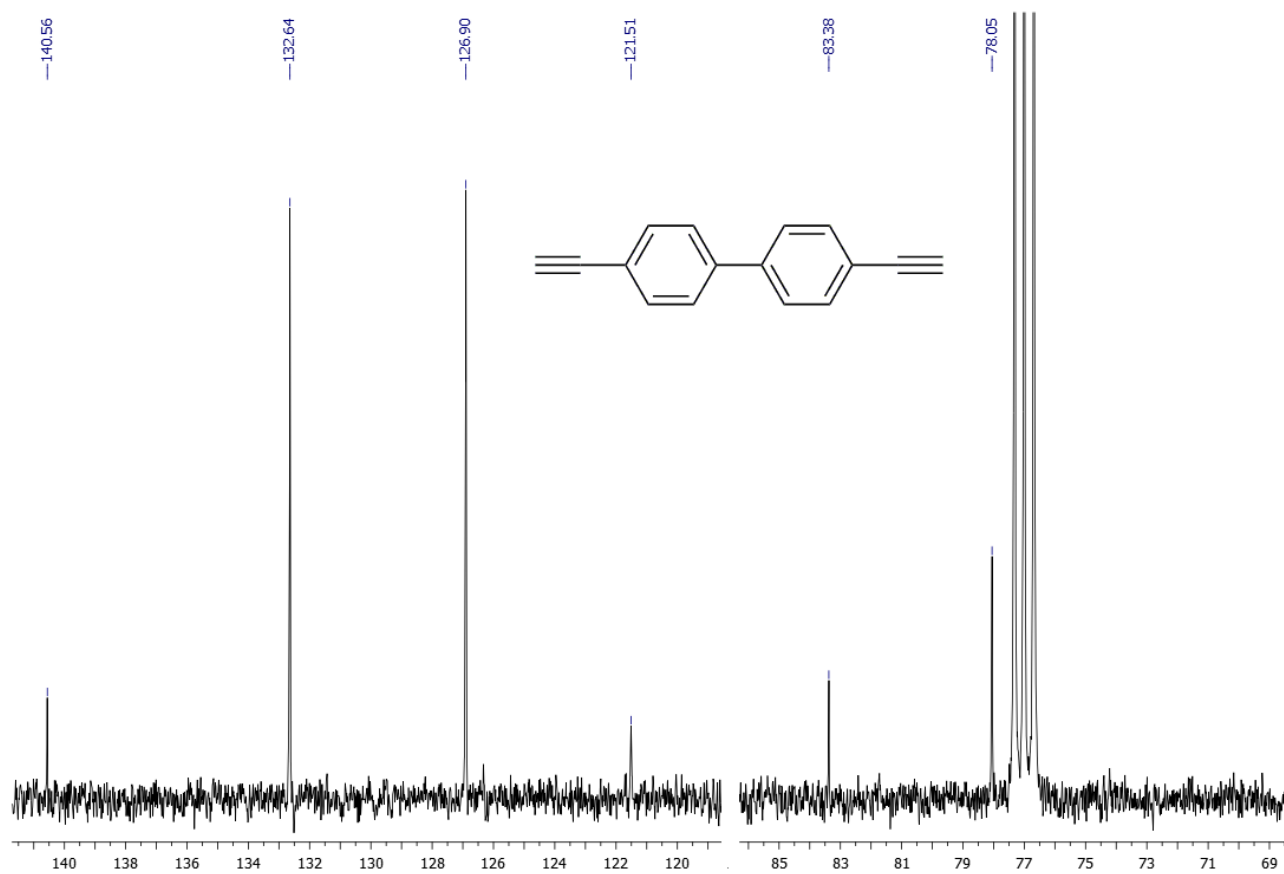
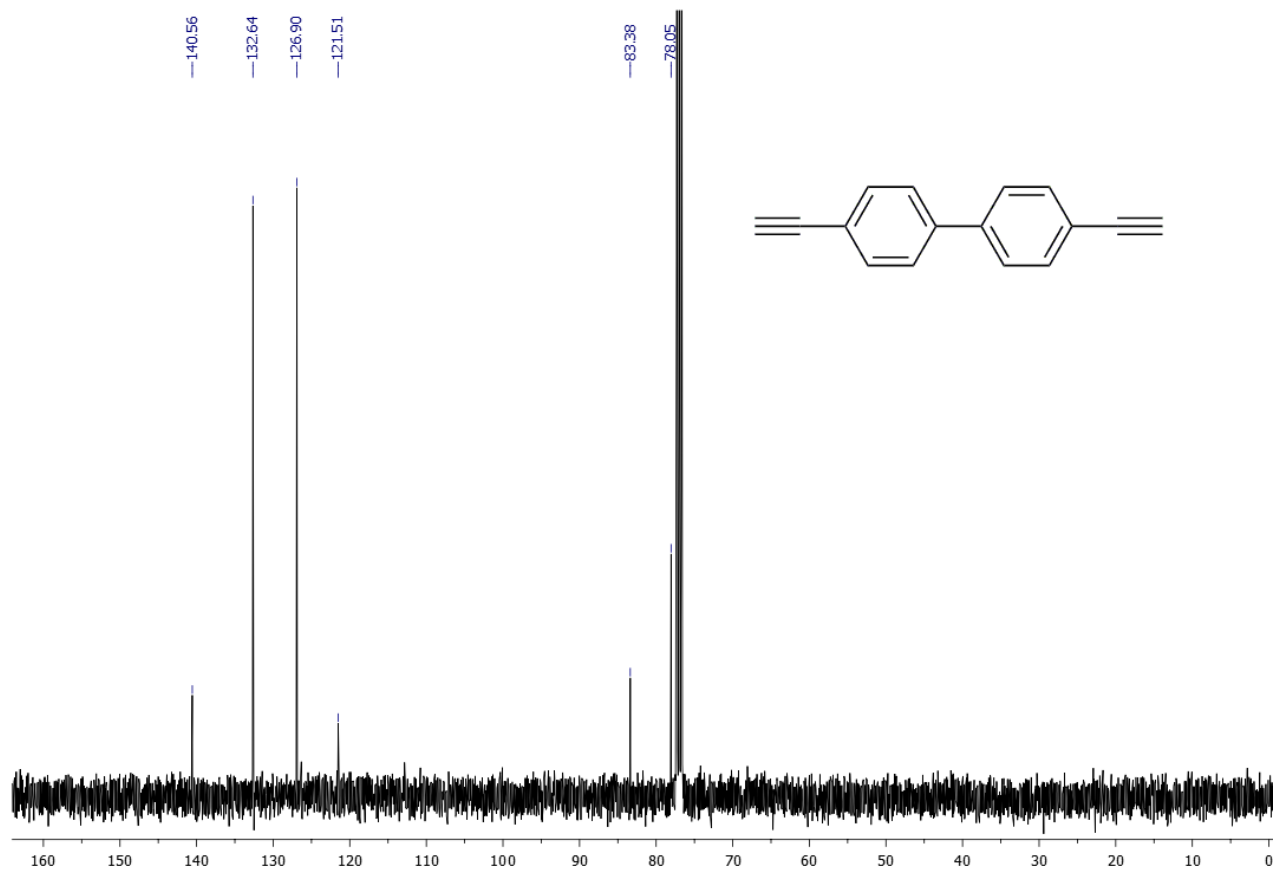
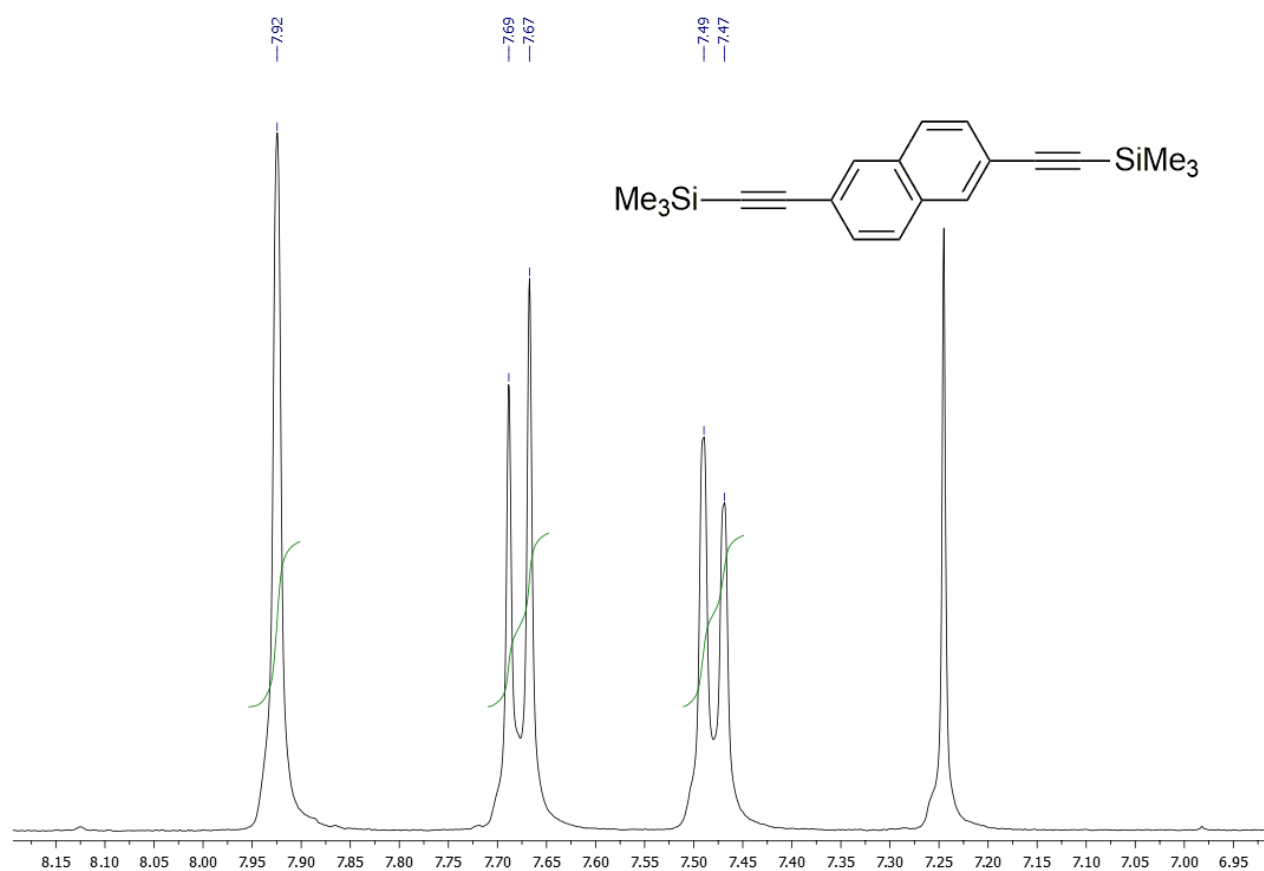


Figure S23. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 4,4'-diethynyl-1,1'-biphenyl (**9a**):full scale spectrum (top) and spectrum expansions (bottom).



3478 **Figure S24.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 2,6-bis(trimethylsilyl)ethynyl)naphthalene (**8b**):full scale spectrum (top)
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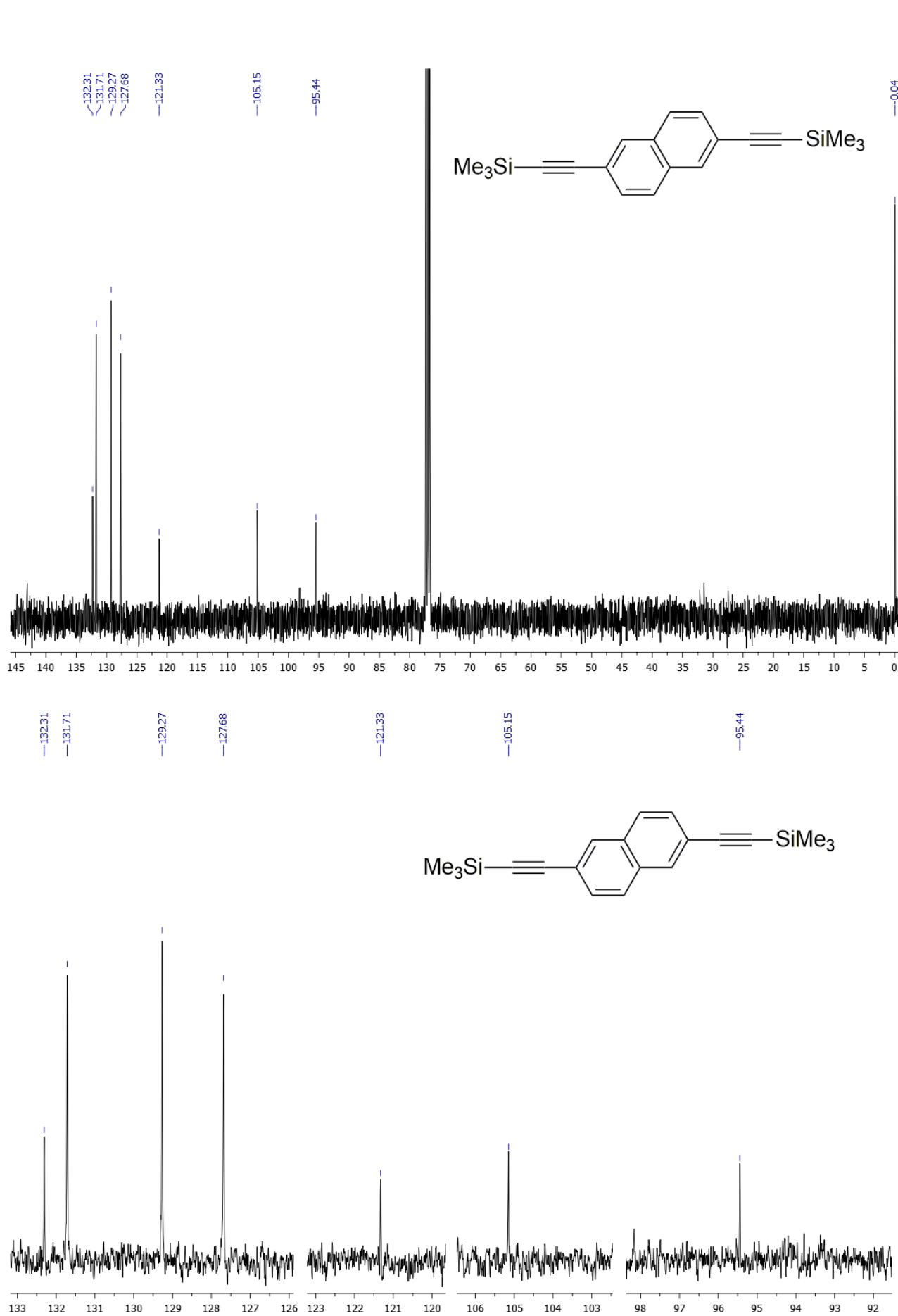
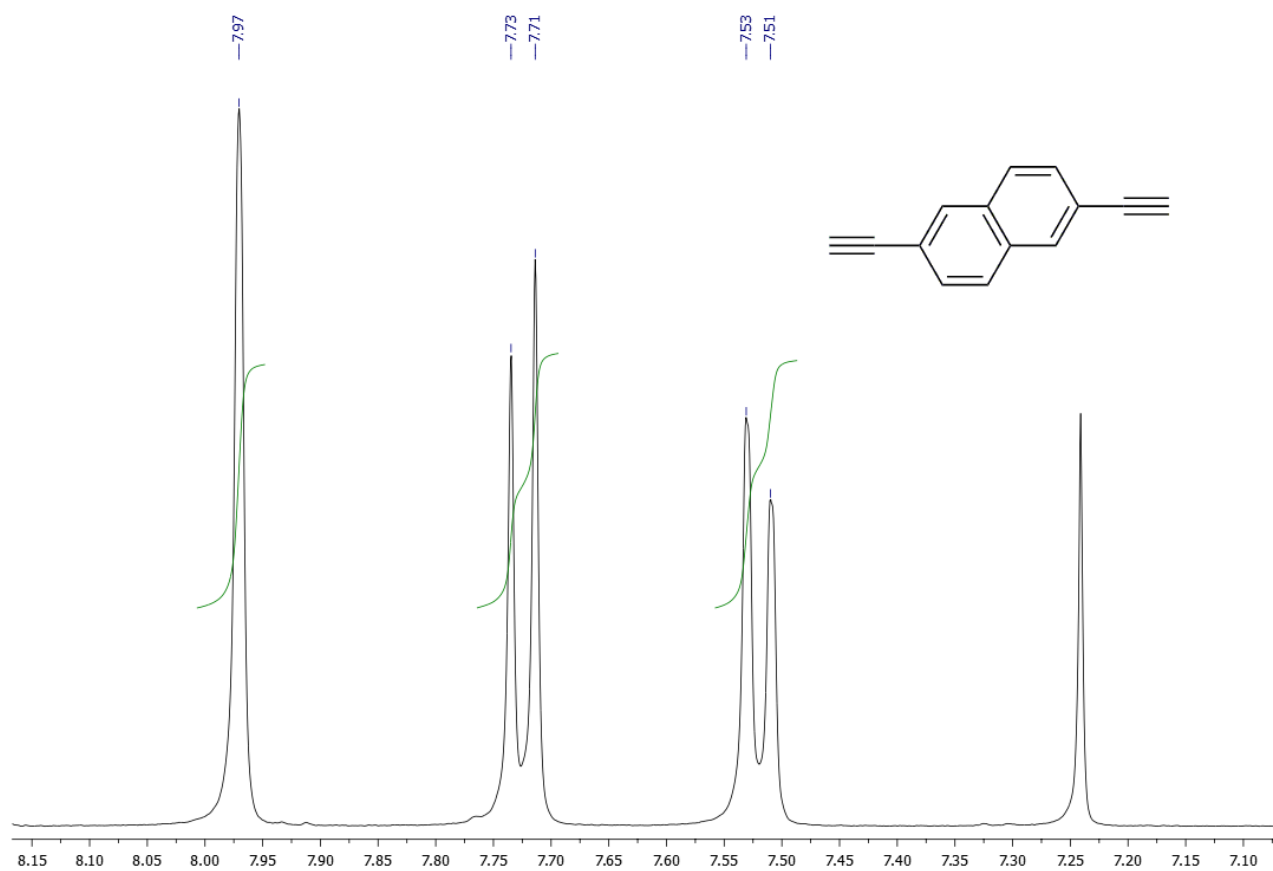
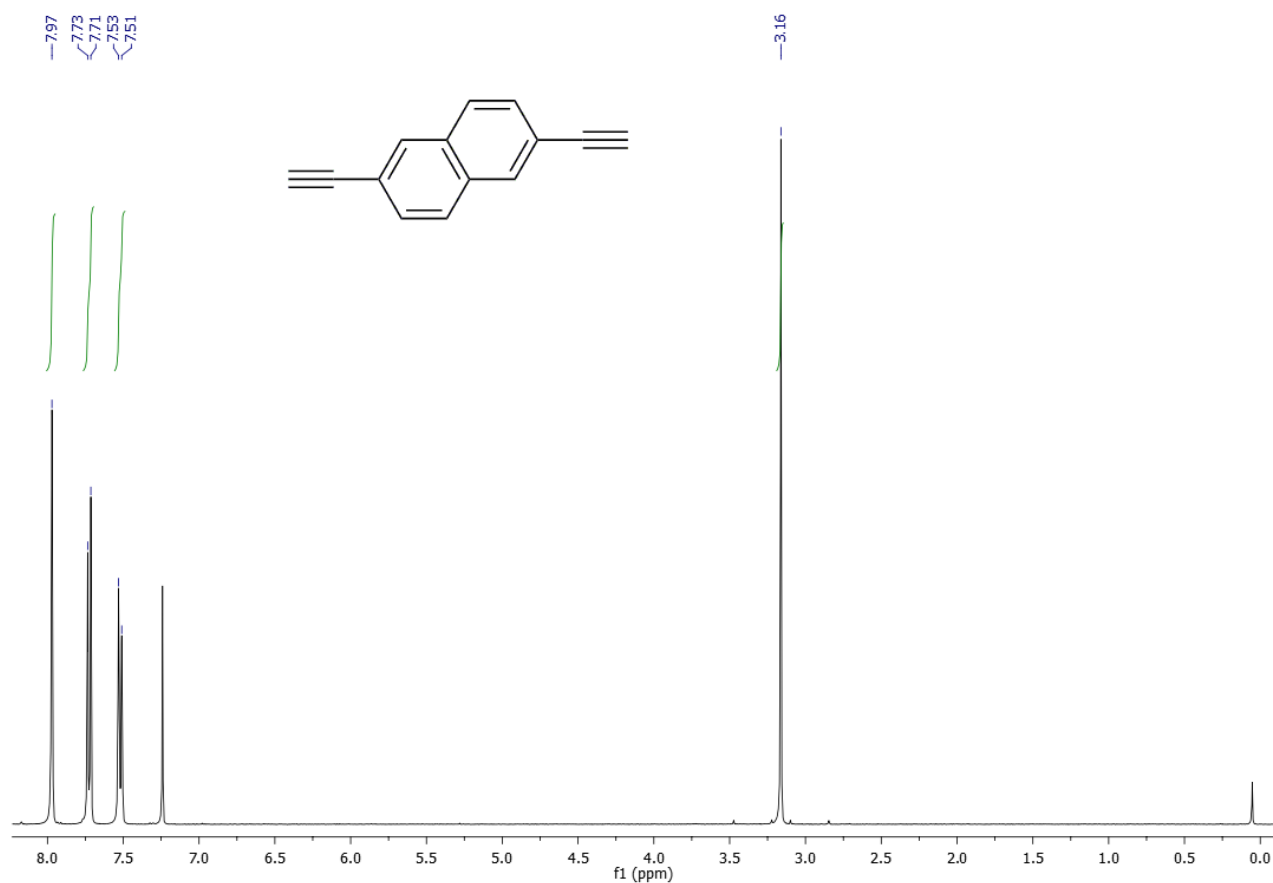


Figure S25. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 2,6-bis(trimethylsilyl)ethynyl)naphthalene (**8b**): full scale spectrum (top) and spectrum expansions (bottom).



3596 **Figure S26.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 2,6-diethynynaphthalene (**9b**):full scale spectrum (top) and spectrum
3597 expansion (bottom).
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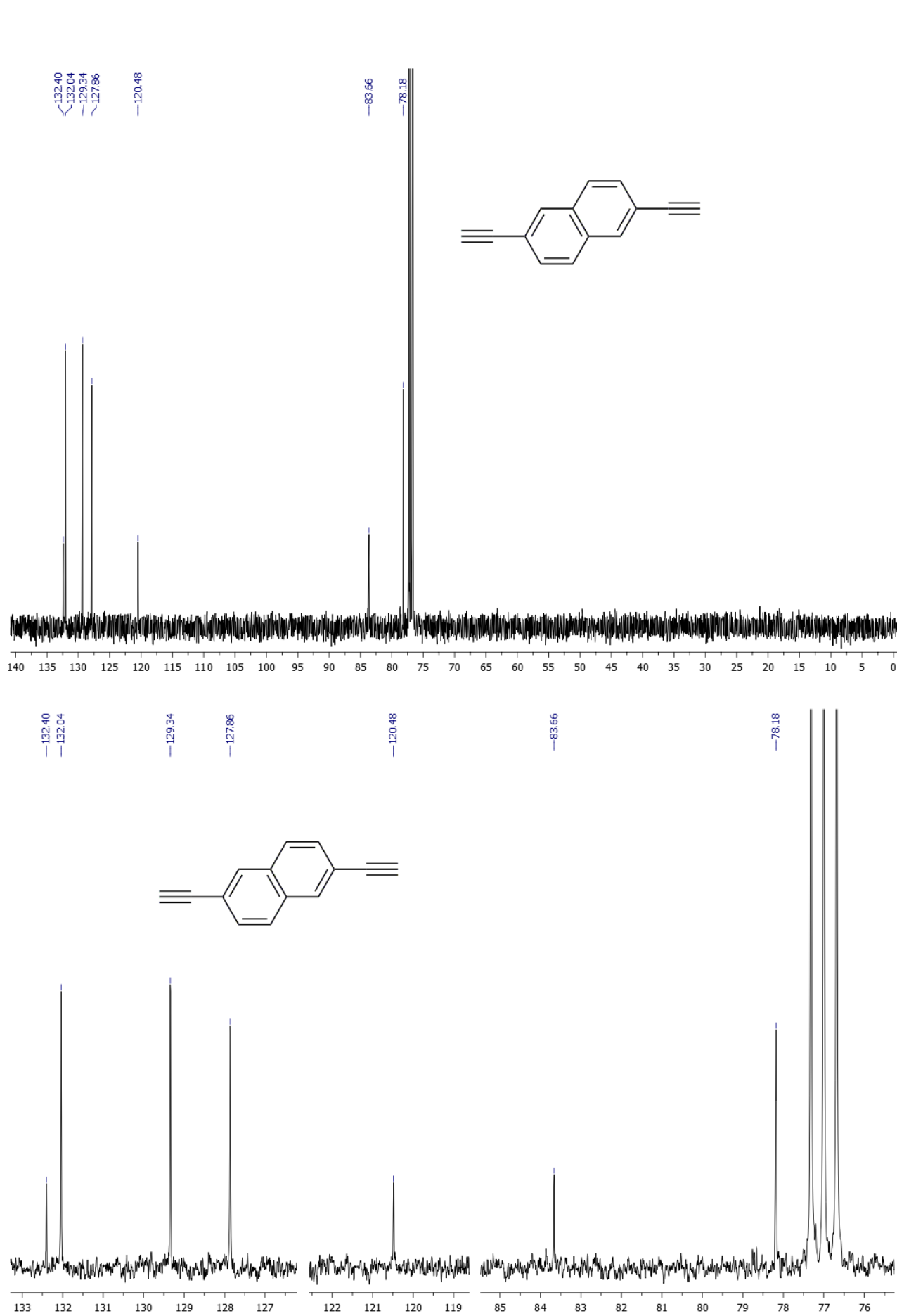


Figure S27. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 2,6-diethynyl-naphthalene (**9b**):full scale spectrum (top) and spectrum expansions (bottom).

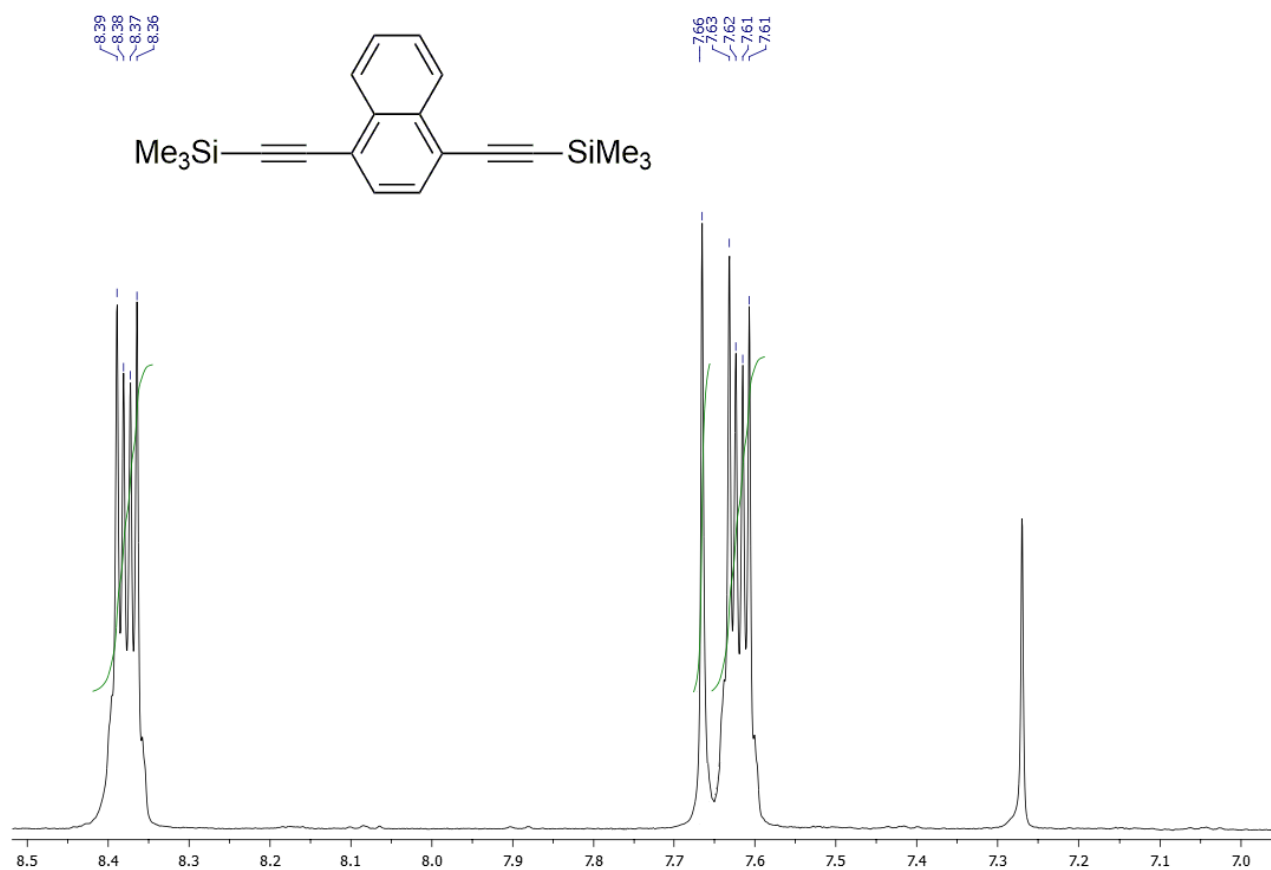
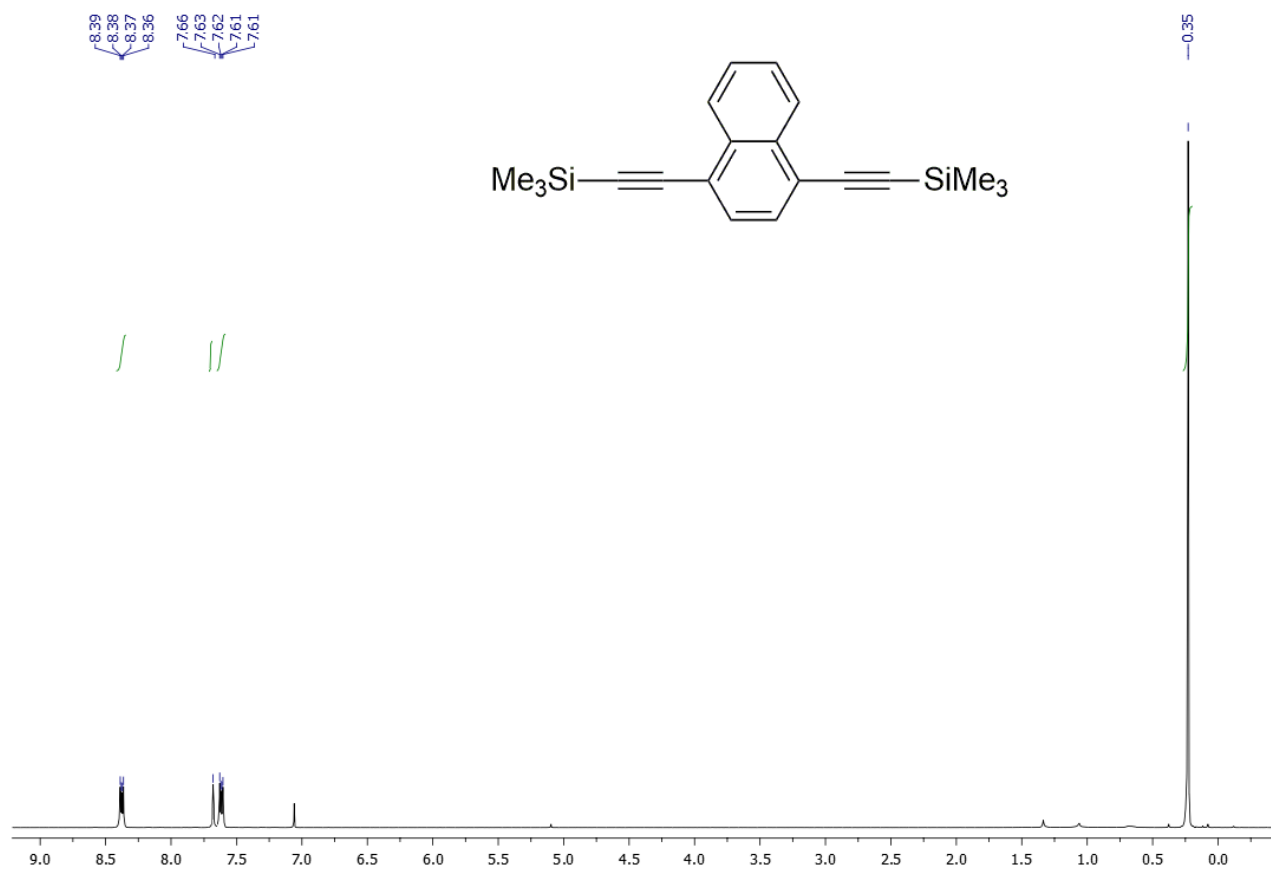


Figure S28. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 1,4-bis(trimethylsilyl)ethynynaphthalene (**8c**):full scale spectrum (top) and spectrum expansion (bottom).

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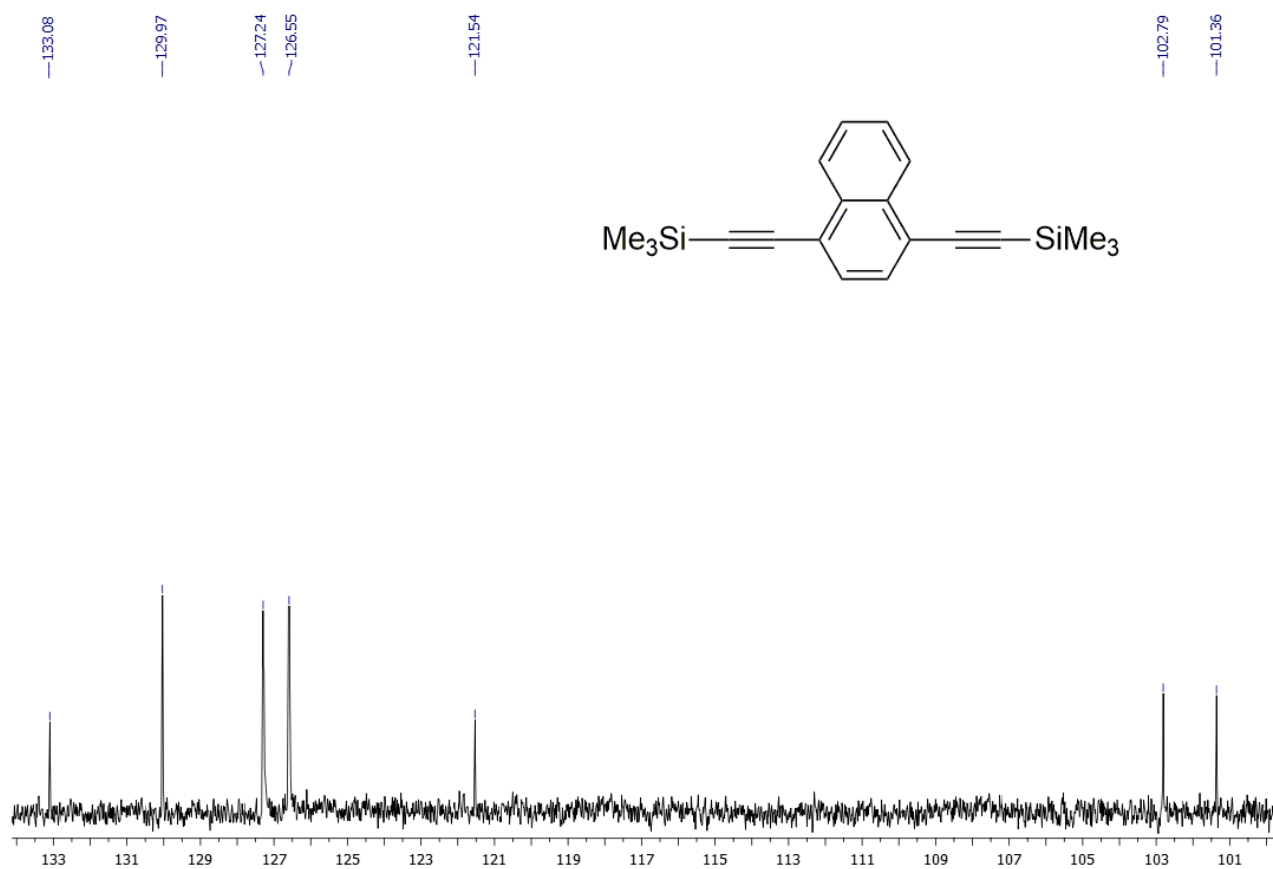
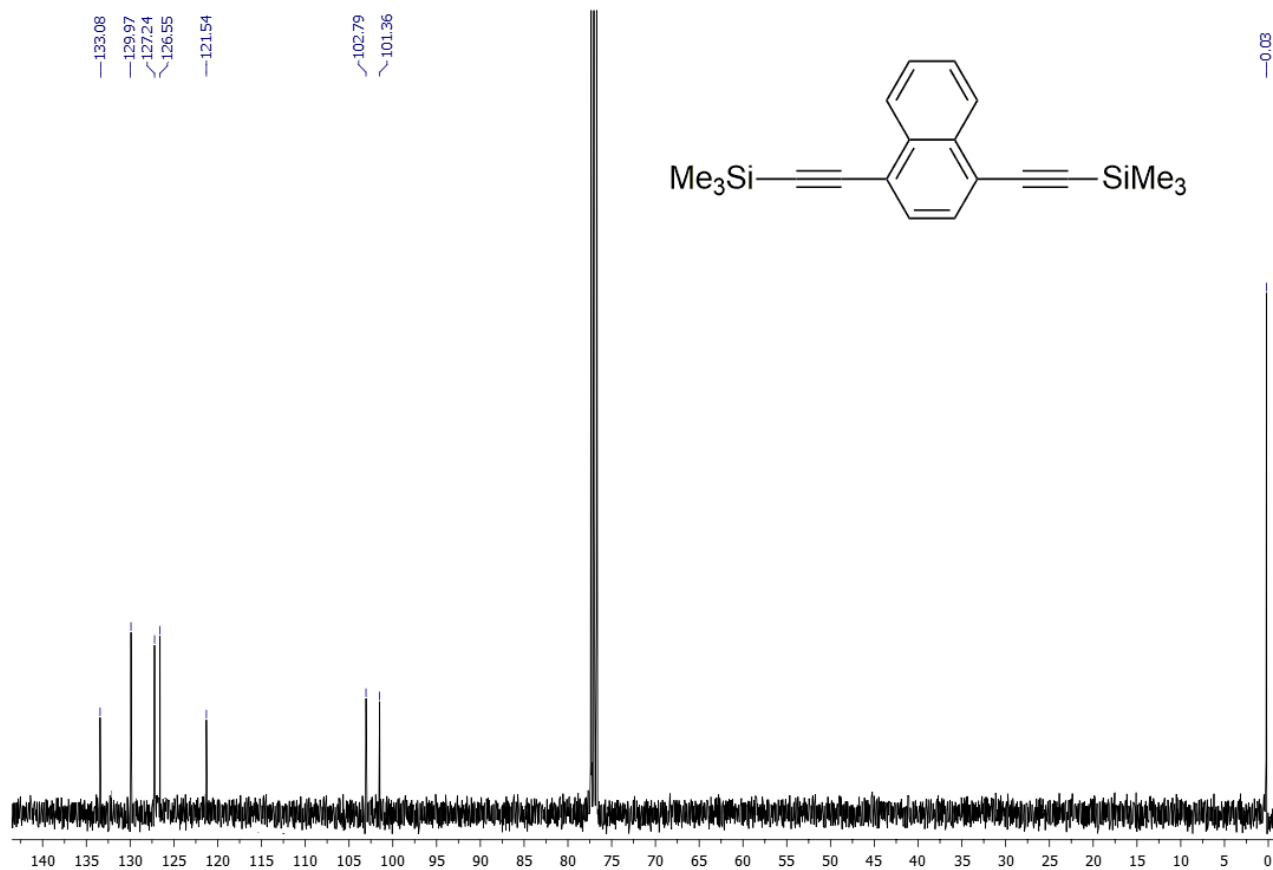


Figure S29. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 1,4-bis(trimethylsilyl)ethynynaphthalene (**8c**): full scale spectrum (top) and spectrum expansion (bottom).

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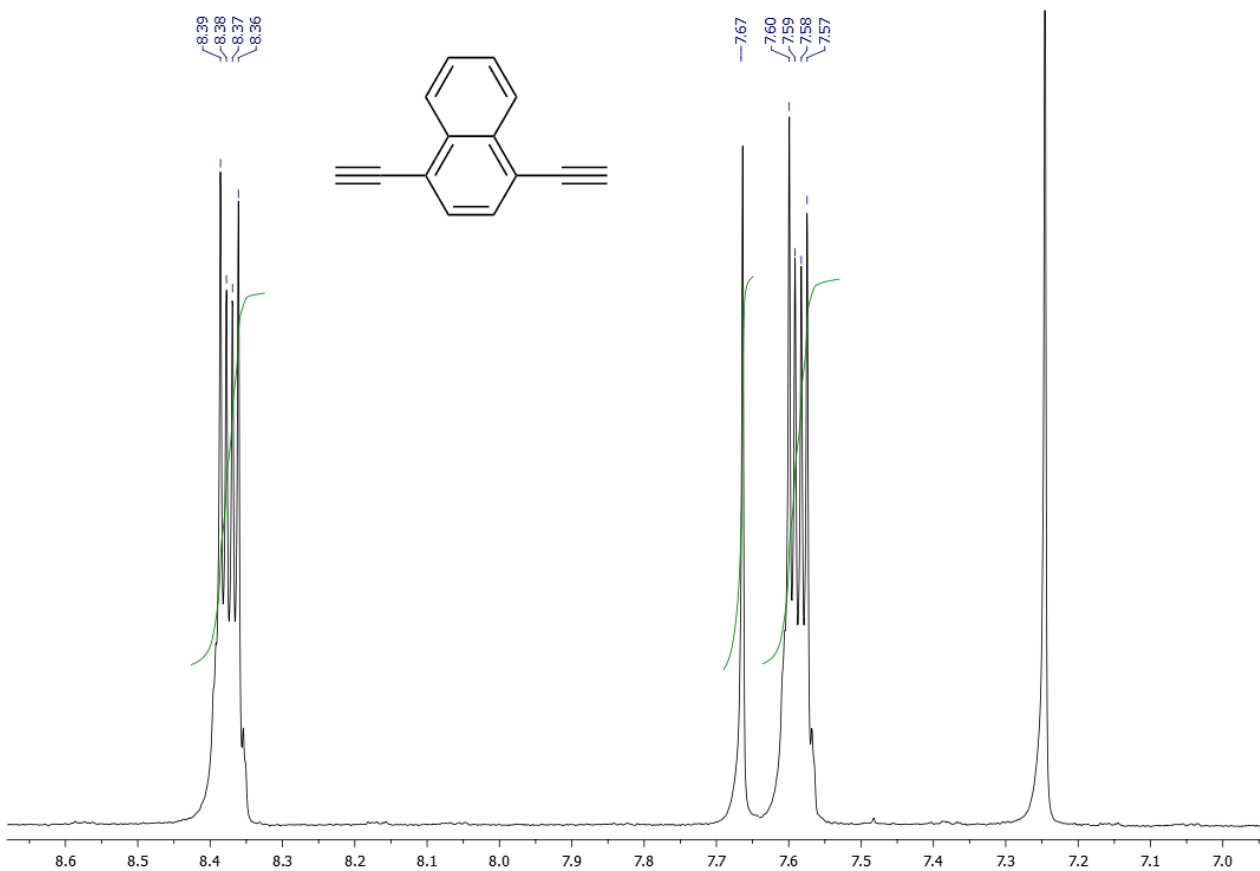
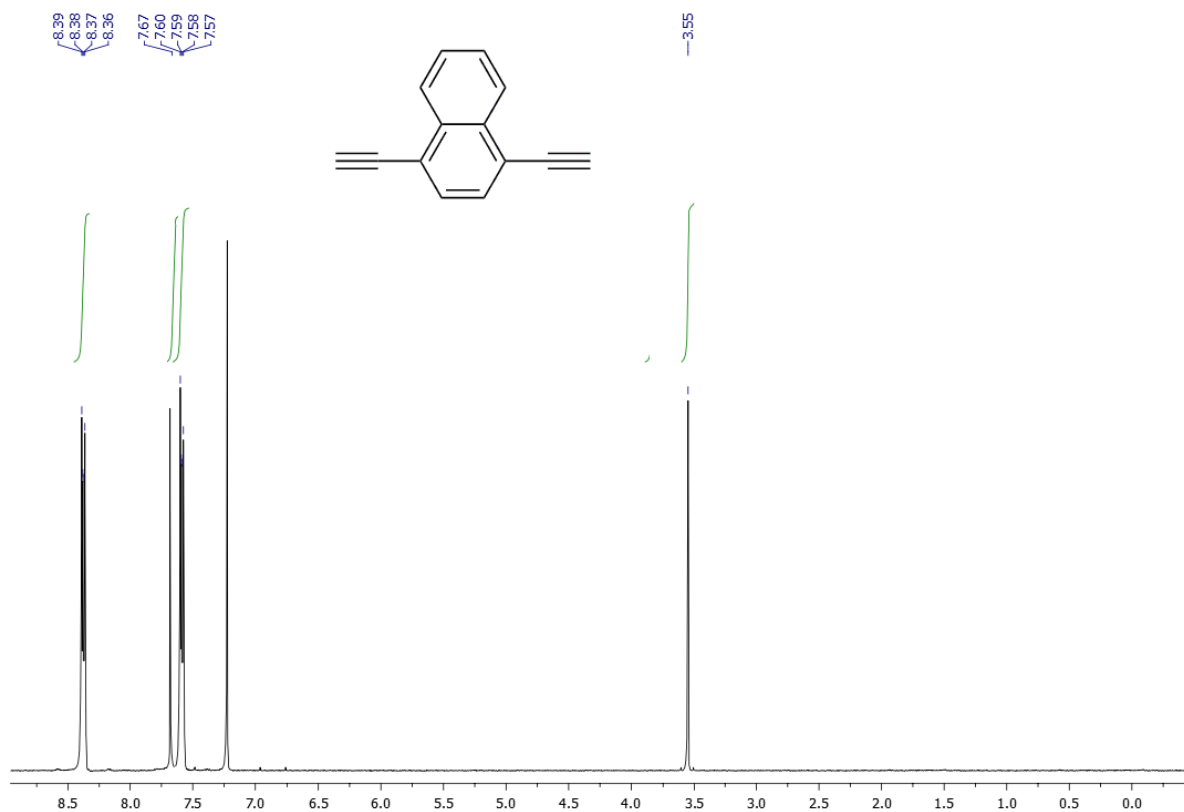


Figure S30. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 1,4-diethynynaphthalene (**9c**):full scale spectrum (top) and spectrum expansion (bottom).

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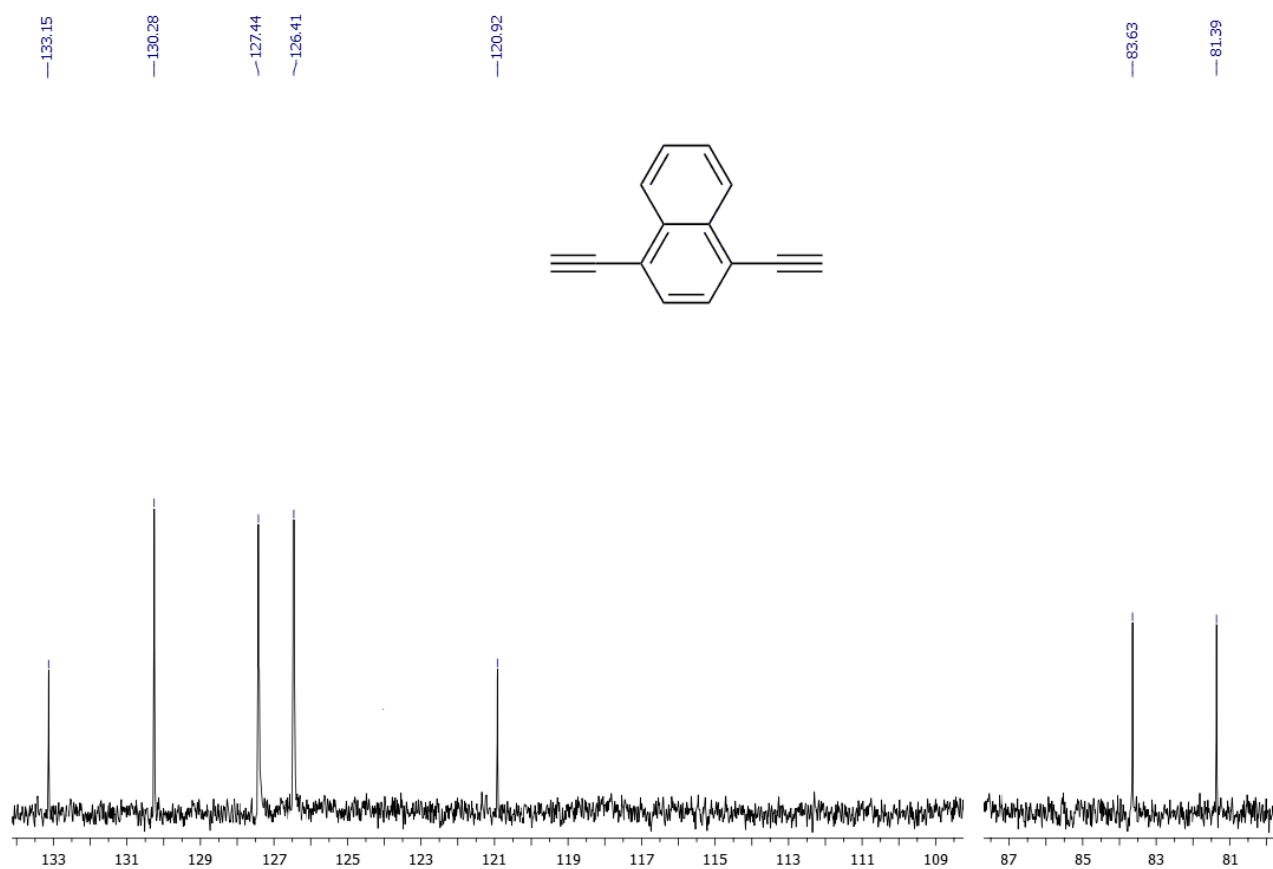
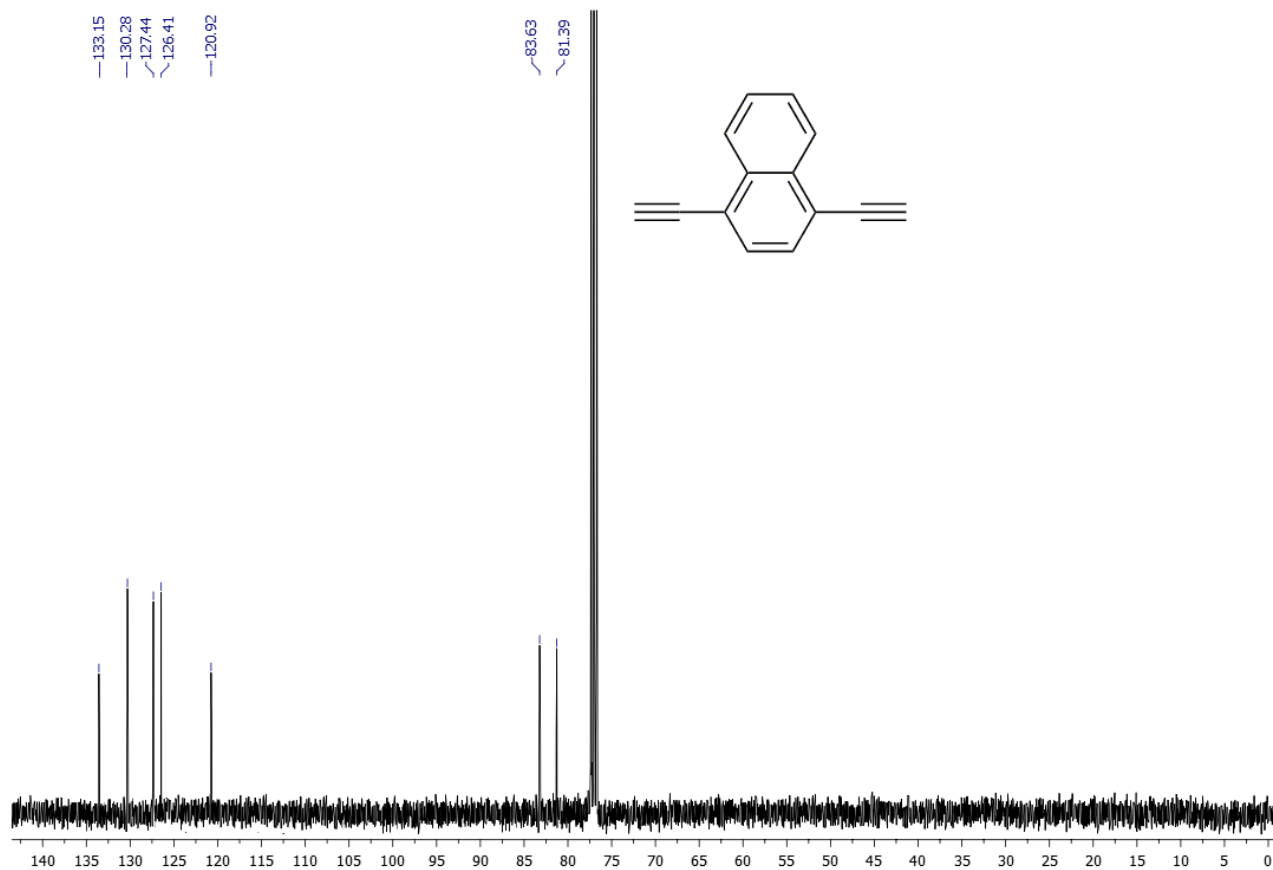


Figure S31. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 1,4-diethynynaphthalene (**9c**):full scale spectrum (top) and spectrum expansions (bottom).

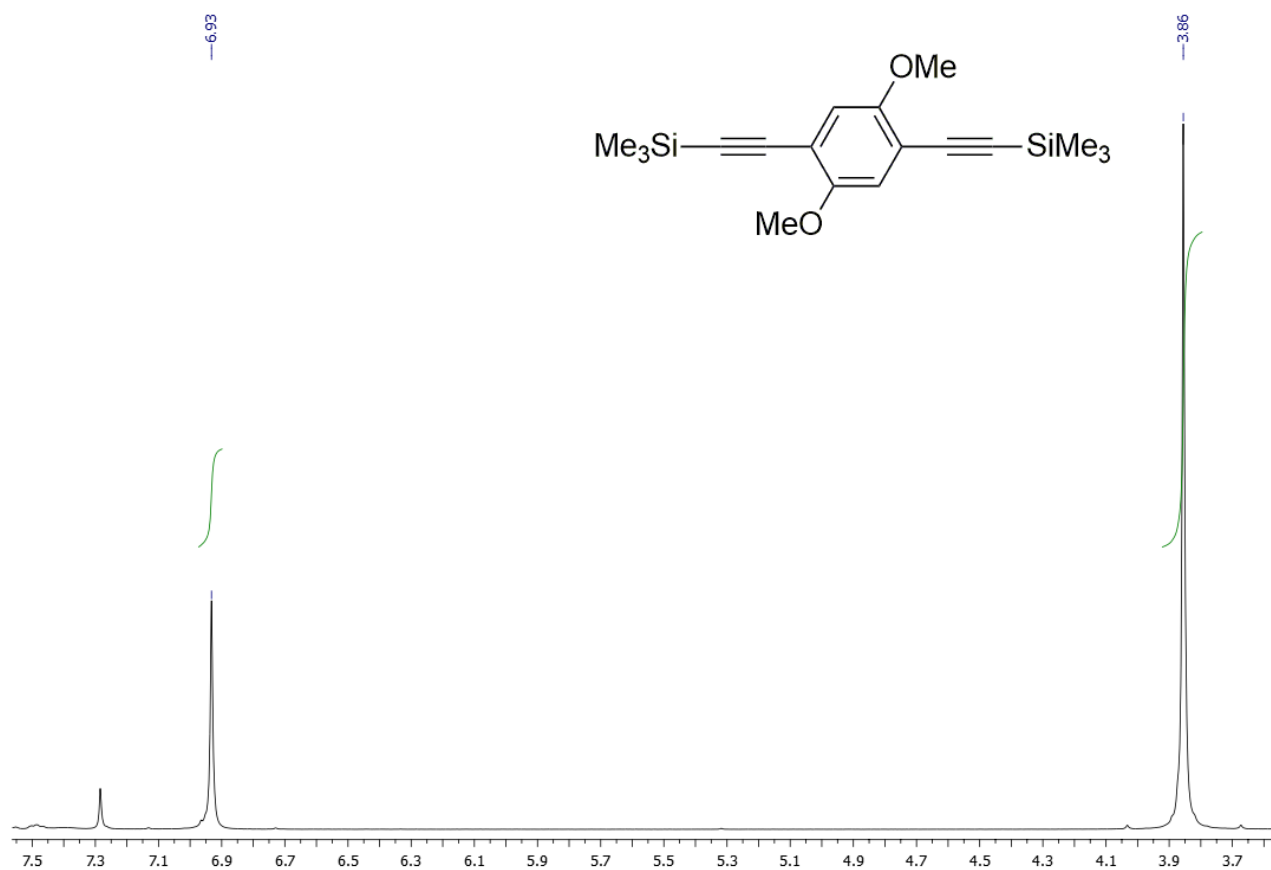
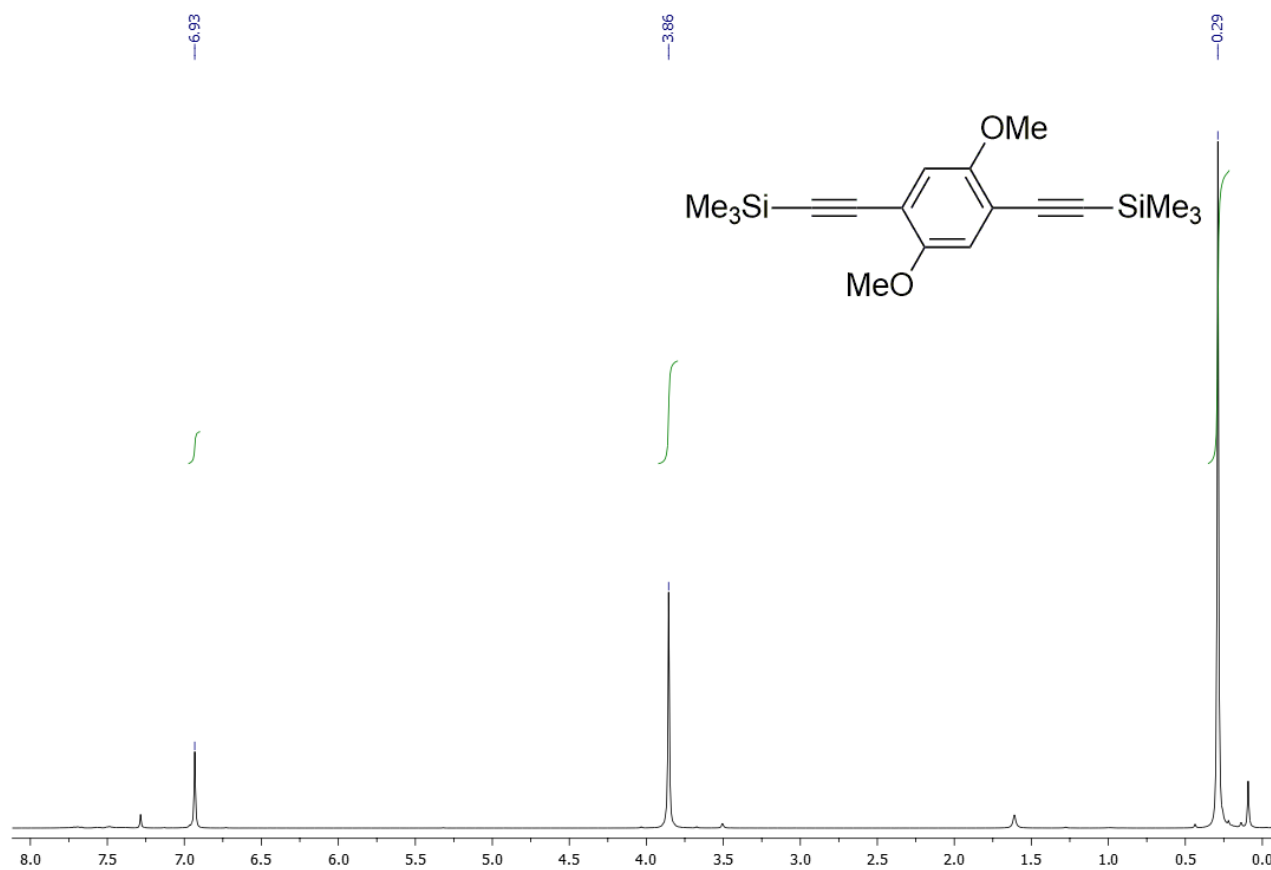


Figure S32. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 2,5-dimethoxy-1,4-bis(trimethylsilyl)ethynylbenzene (**12**): full scale spectrum (top) and spectrum expansion (bottom).

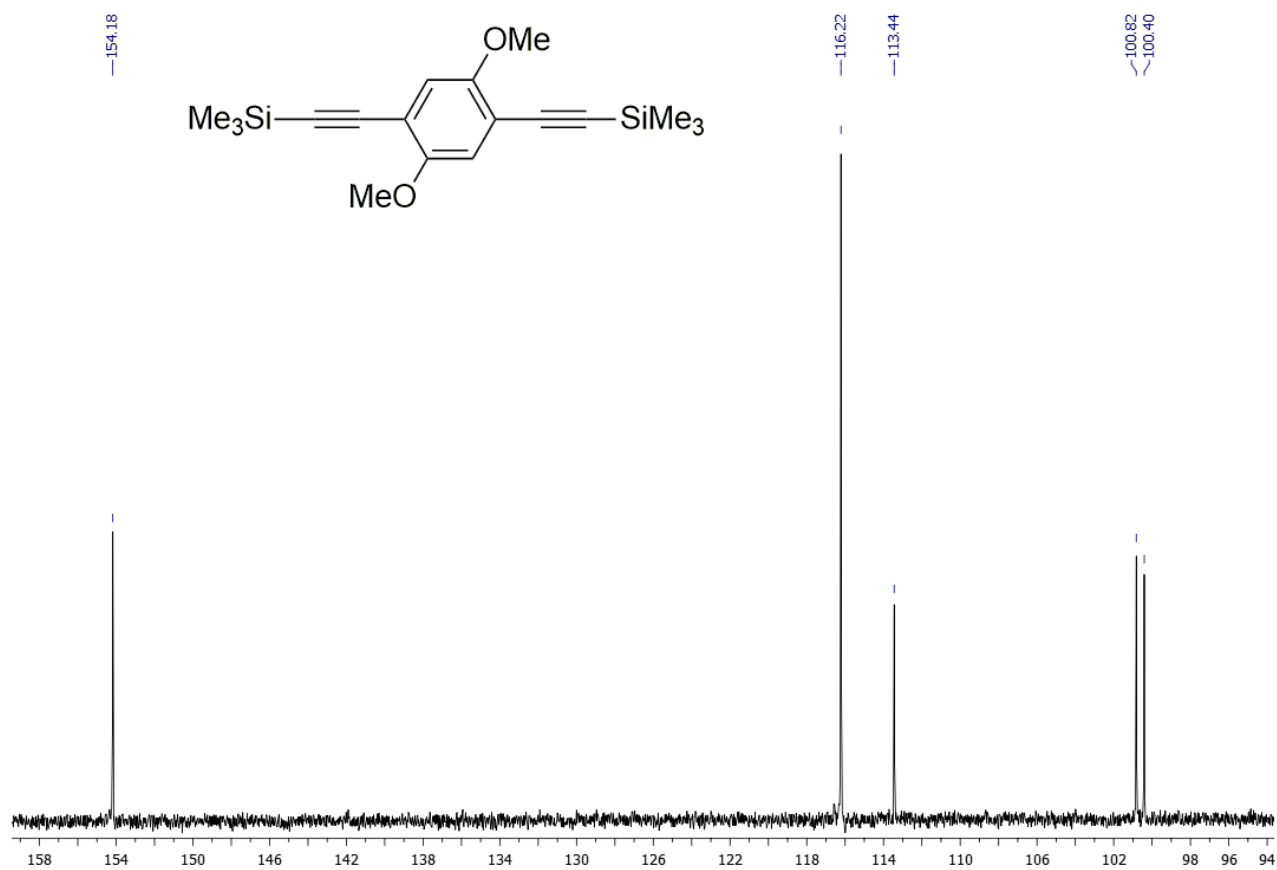
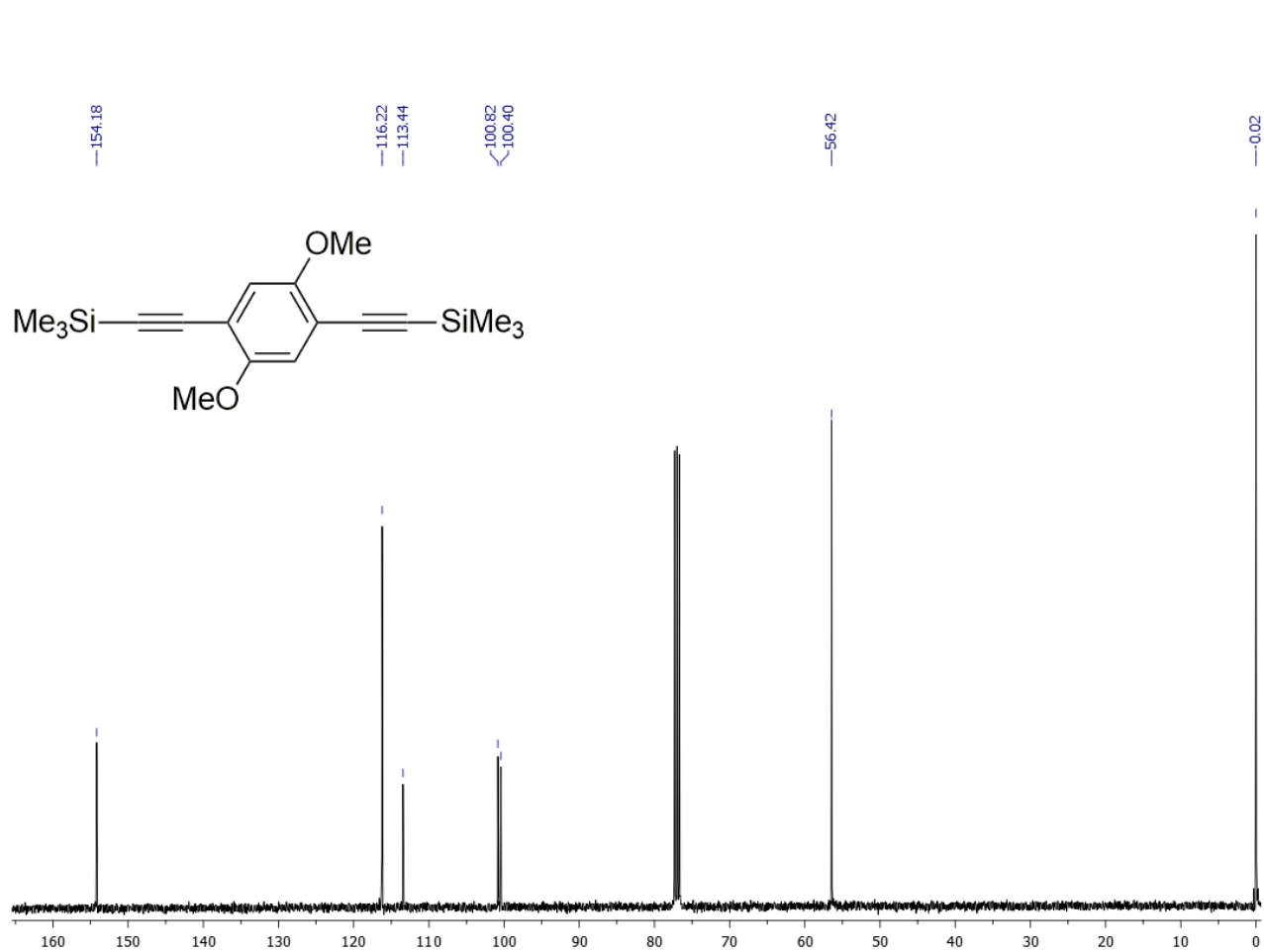


Figure S33. ¹³C-NMR spectrum (100 MHz, CDCl₃) of 2,5-dimethoxy-1,4-bis(trimethylsilyl)ethynylbenzene (**12**): full scale spectrum (top) and spectrum expansion (bottom).

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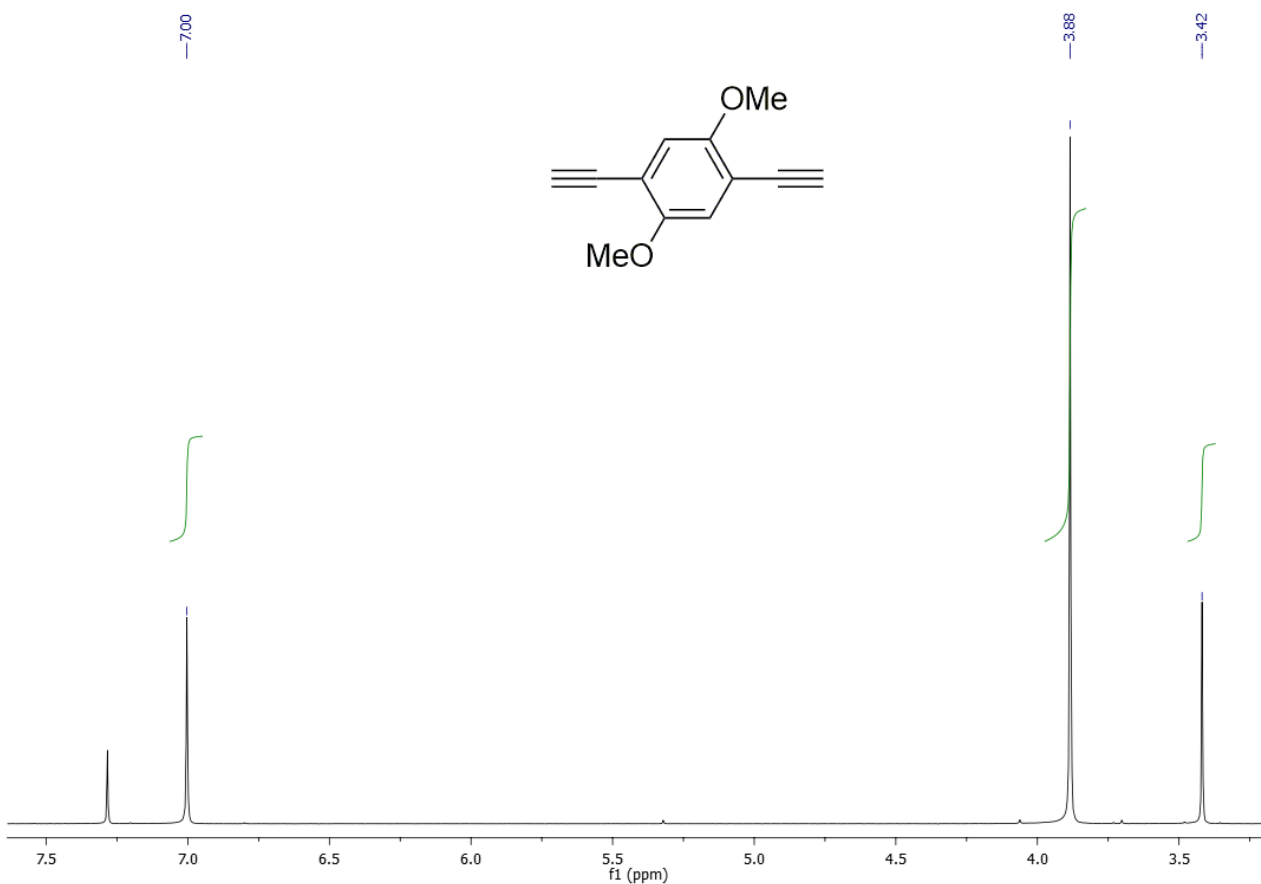
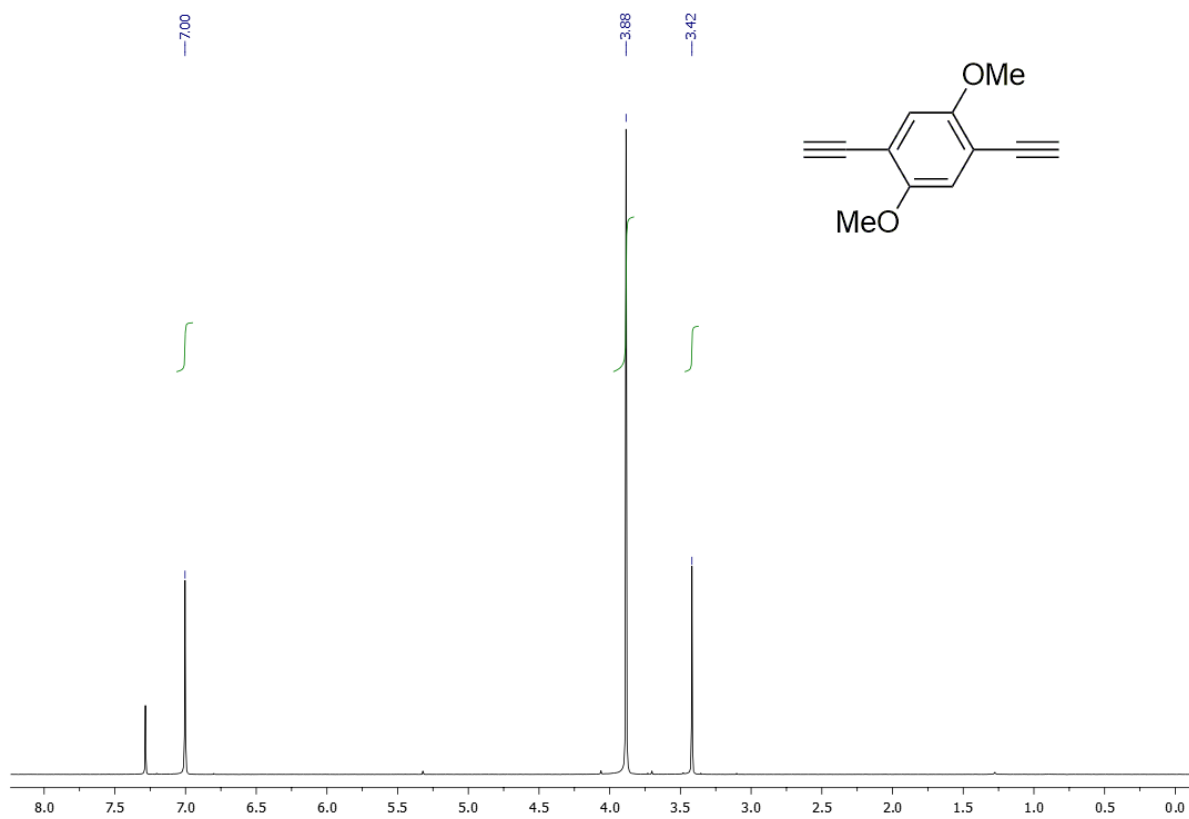


Figure S34. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 1,4-diethynyl-2,5-dimethoxybenzene (**13**): full scale spectrum (top) and spectrum expansion (bottom).

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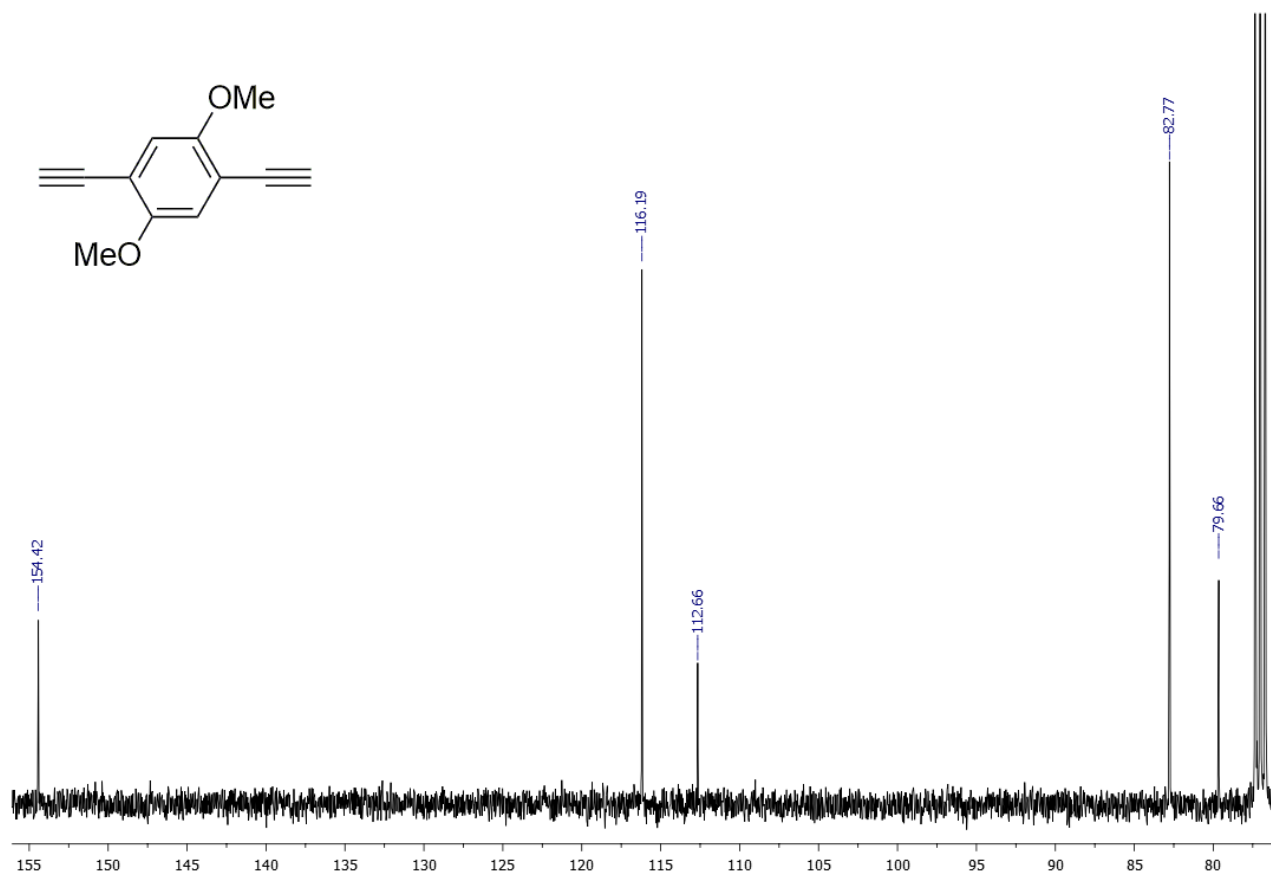
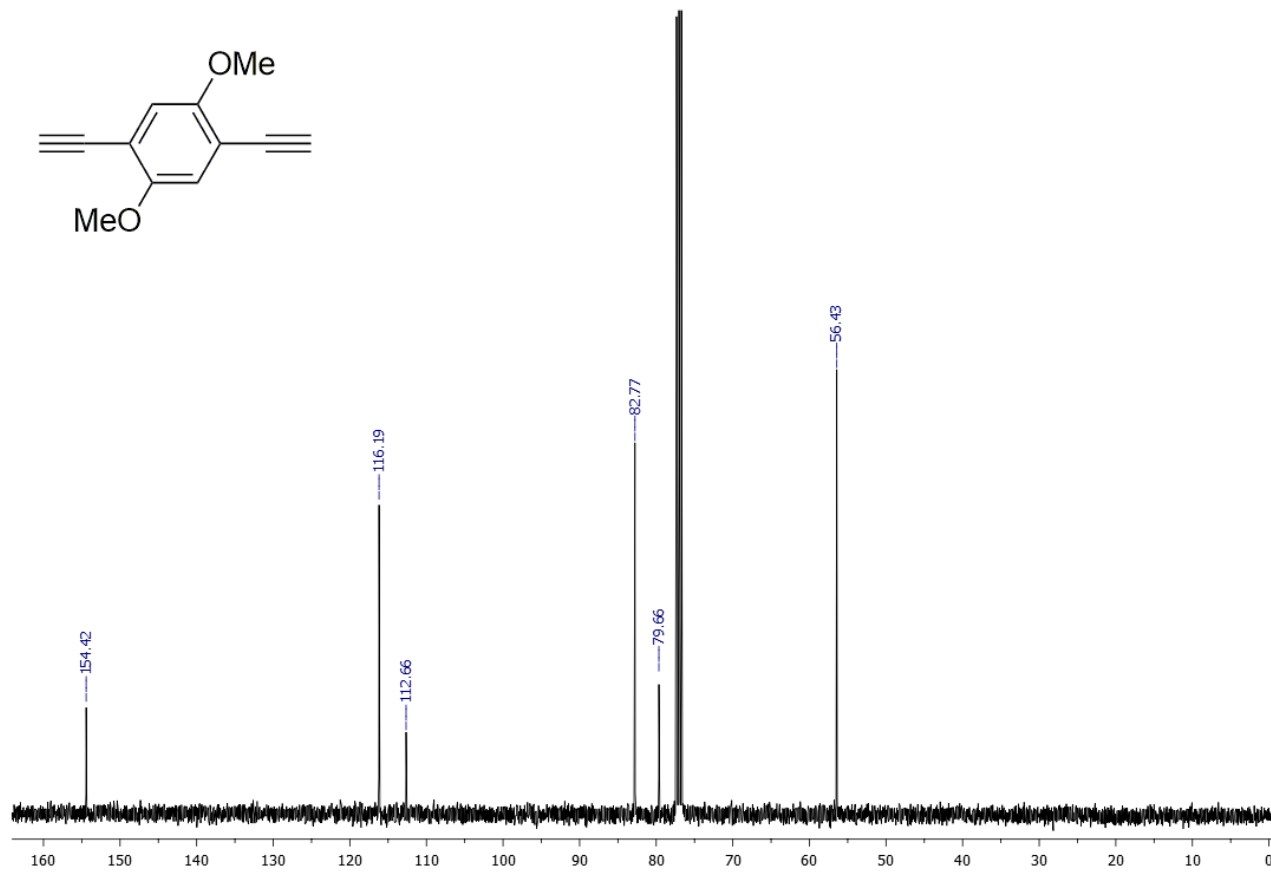


Figure S35. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 1,4-diethynyl-2,5-dimethoxybenzene (**13**):full scale spectrum (top) and spectrum expansion (bottom).

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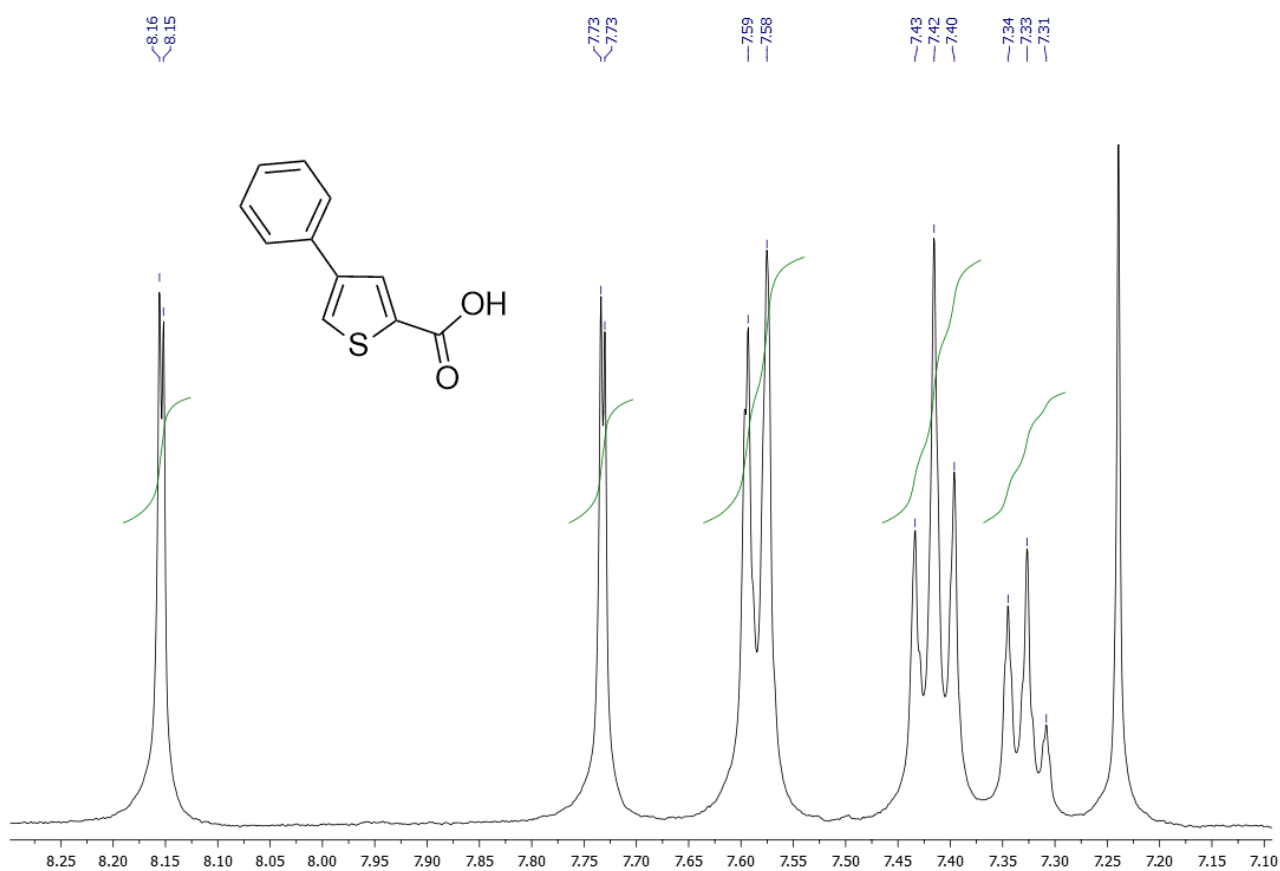
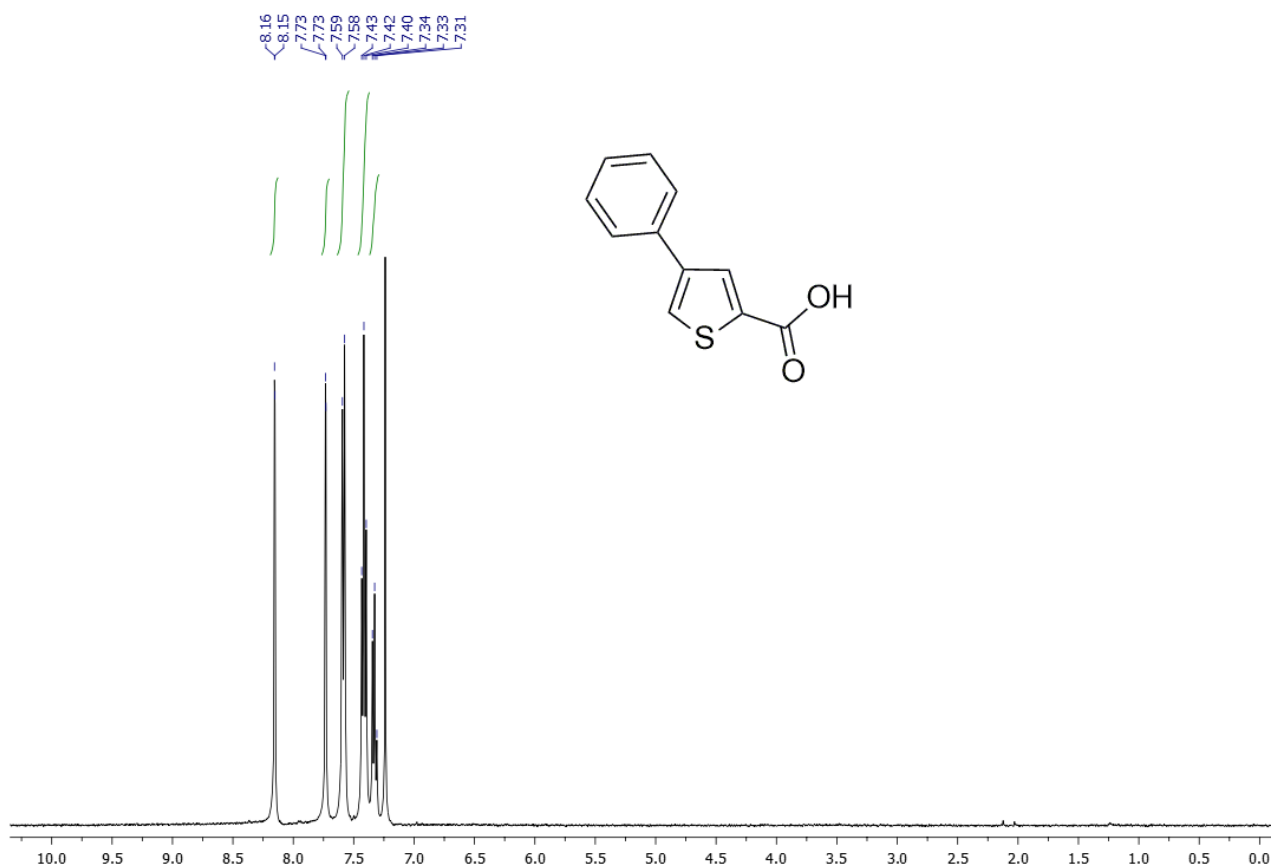


Figure S36. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 4-phenylthiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansion (bottom).

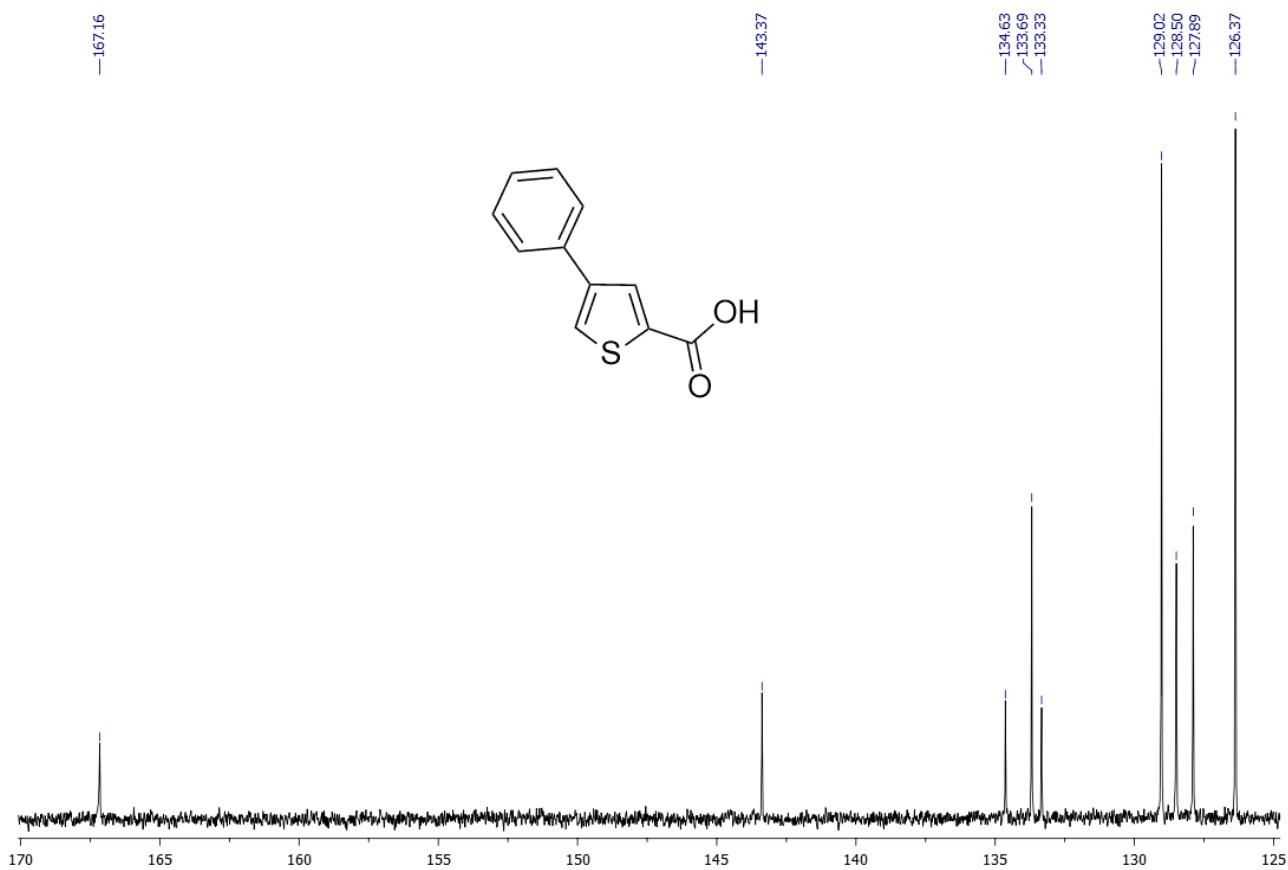
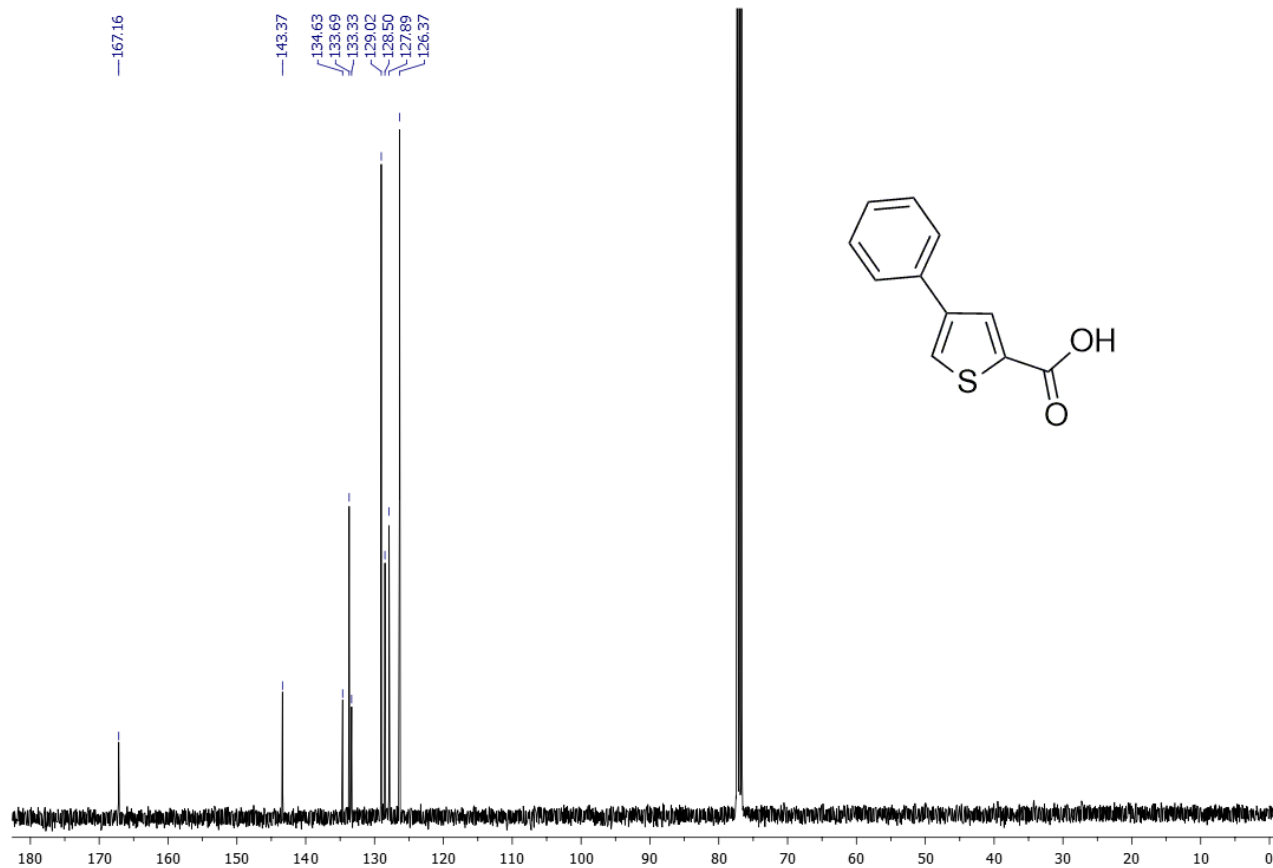
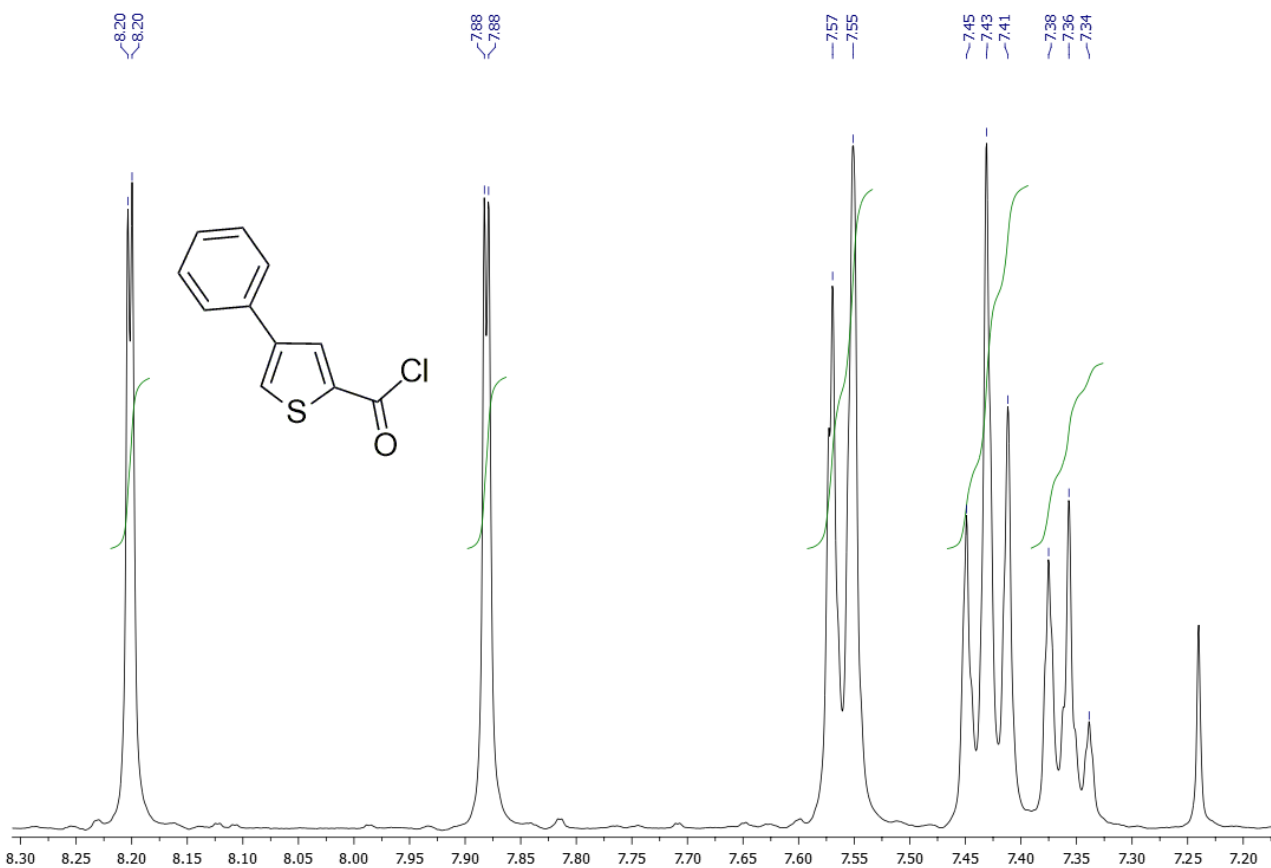
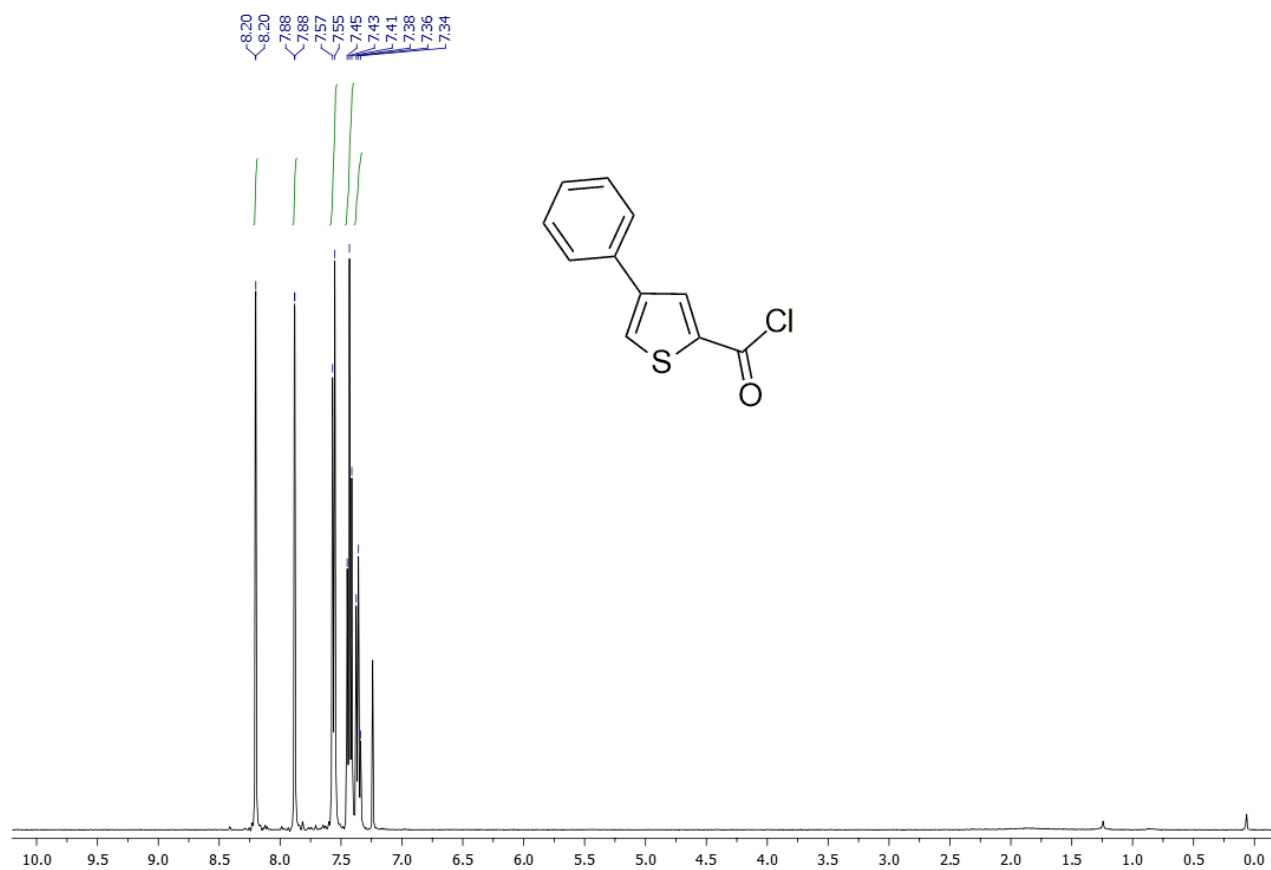


Figure S37. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 4-phenylthiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansion (bottom).



4304 **Figure S38.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 4-phenylthiophene-2-carbonyl chloride (**4d**): full scale spectrum (top)
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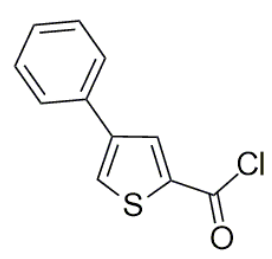
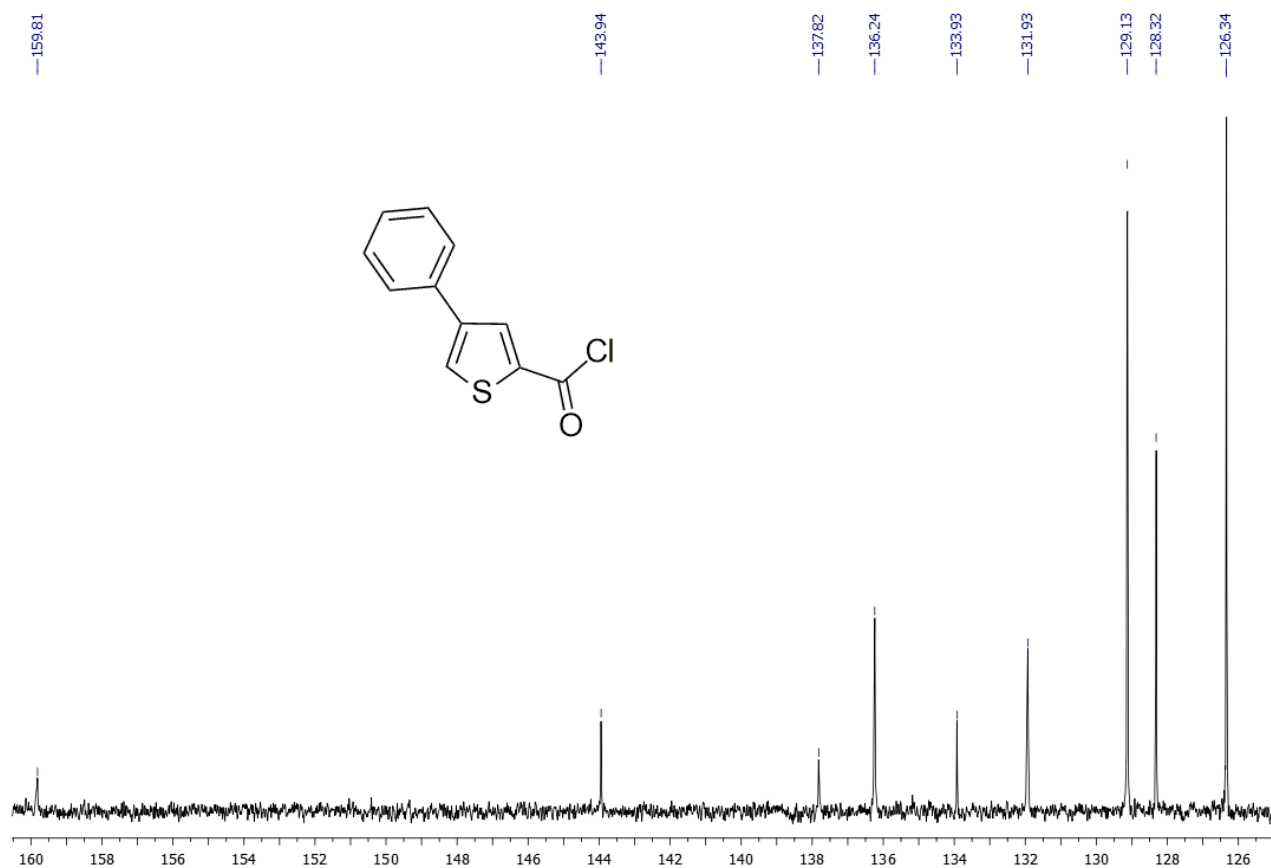
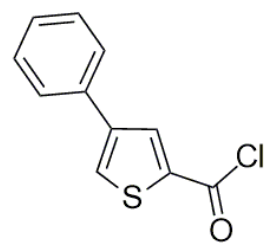
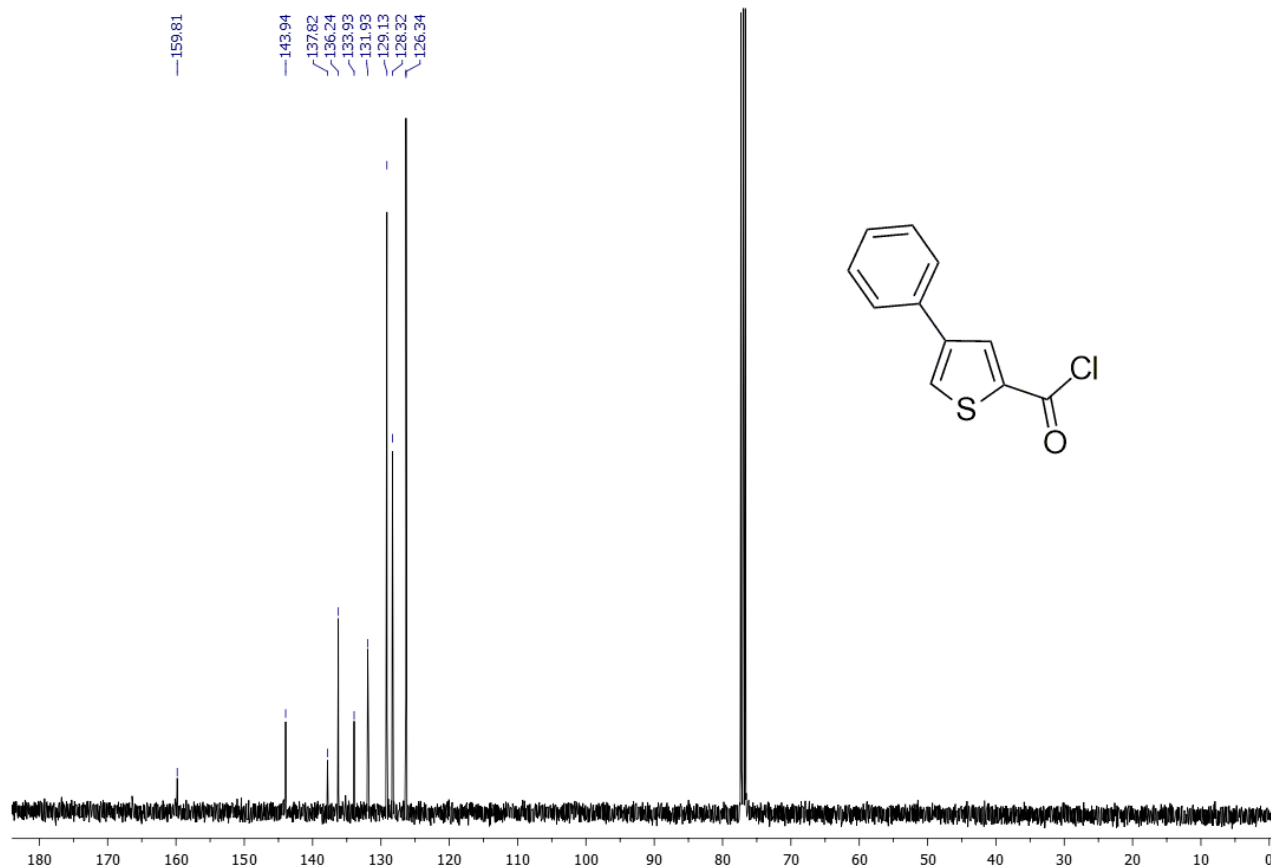


Figure S39. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 4-phenylthiophene-2-carbonyl chloride (**4d**): full scale spectrum (top) and spectrum expansion (bottom).

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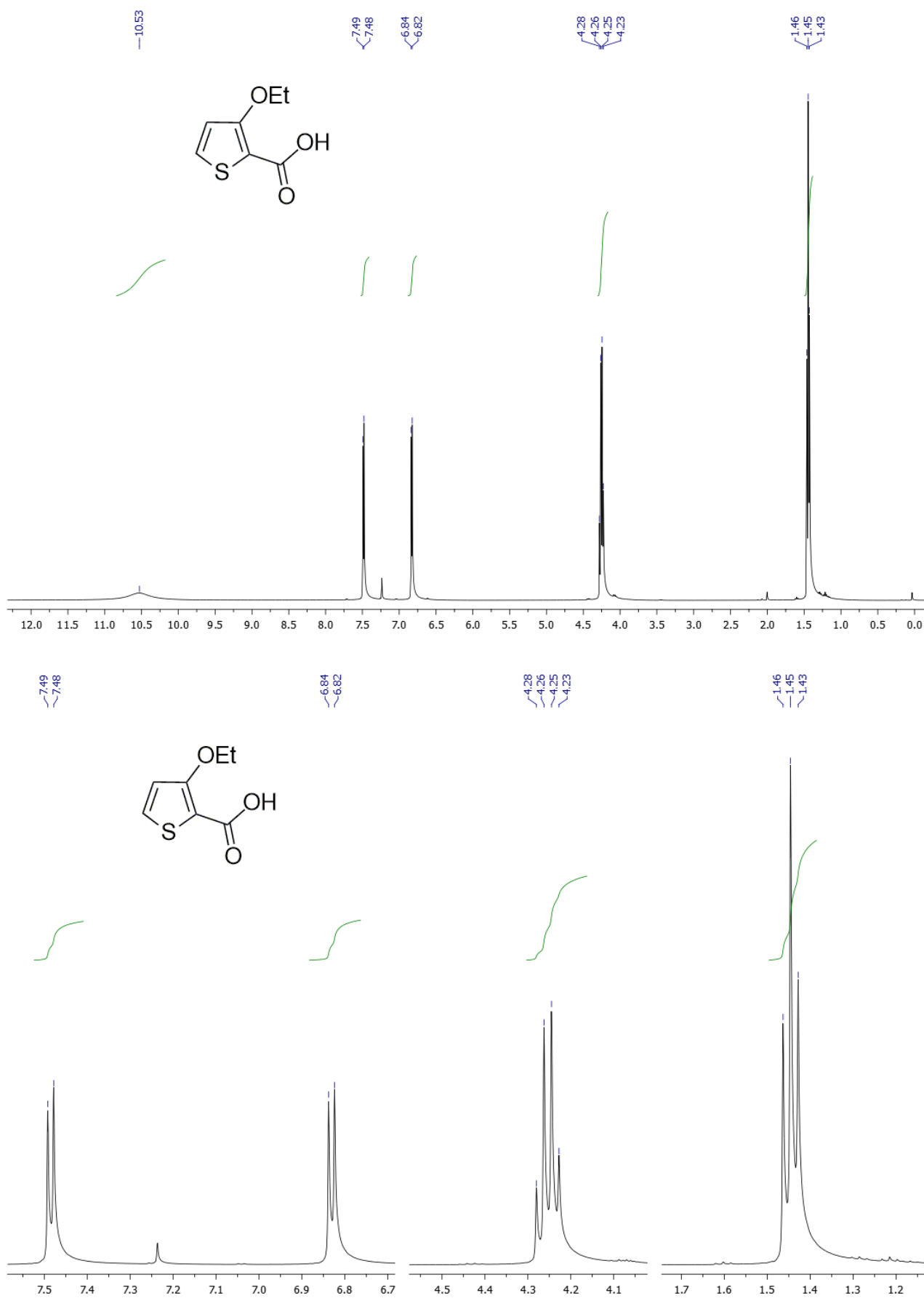


Figure S40. ¹H-NMR spectrum (400 MHz, CDCl₃) of 3-ethoxythiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansions (bottom).

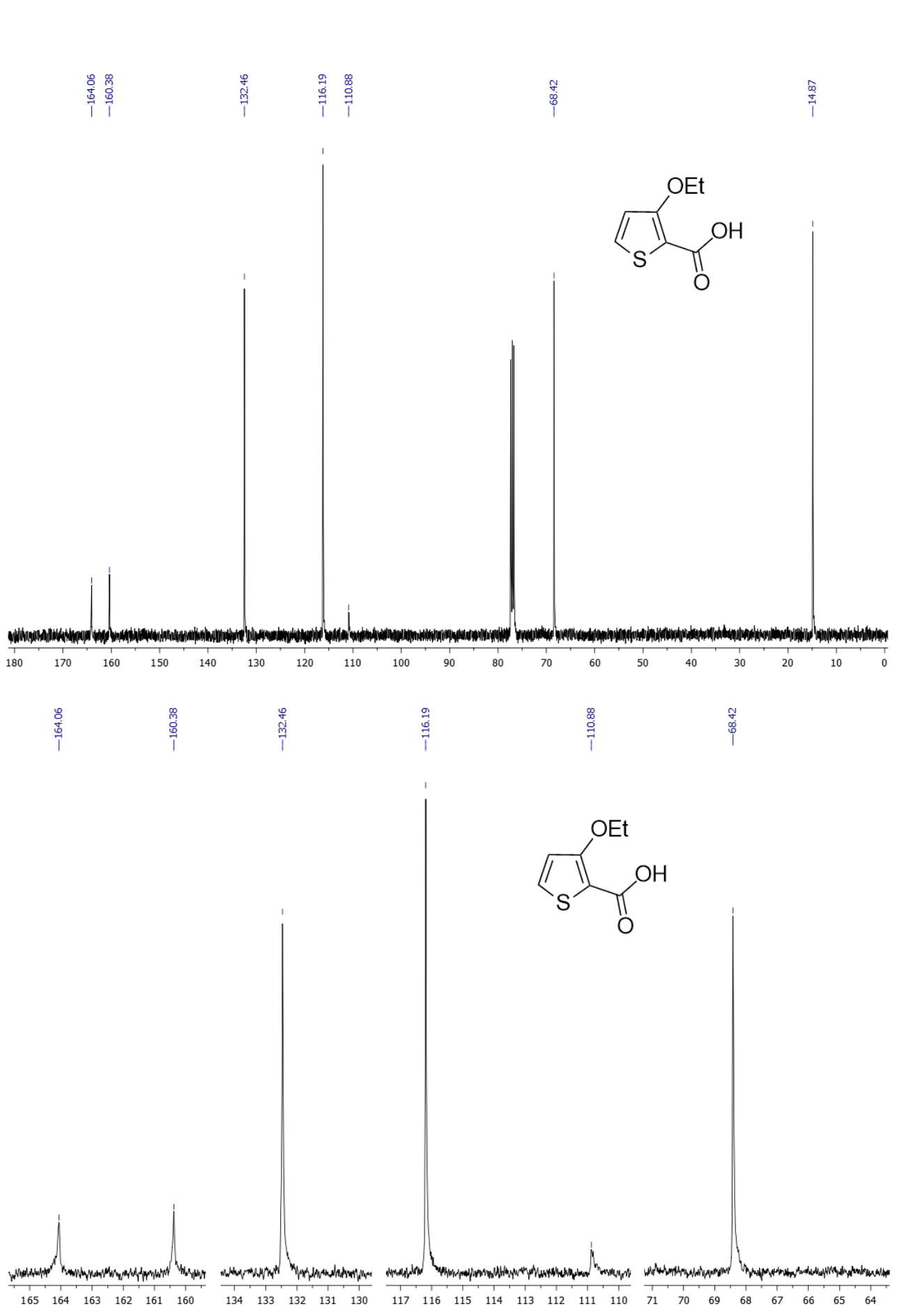
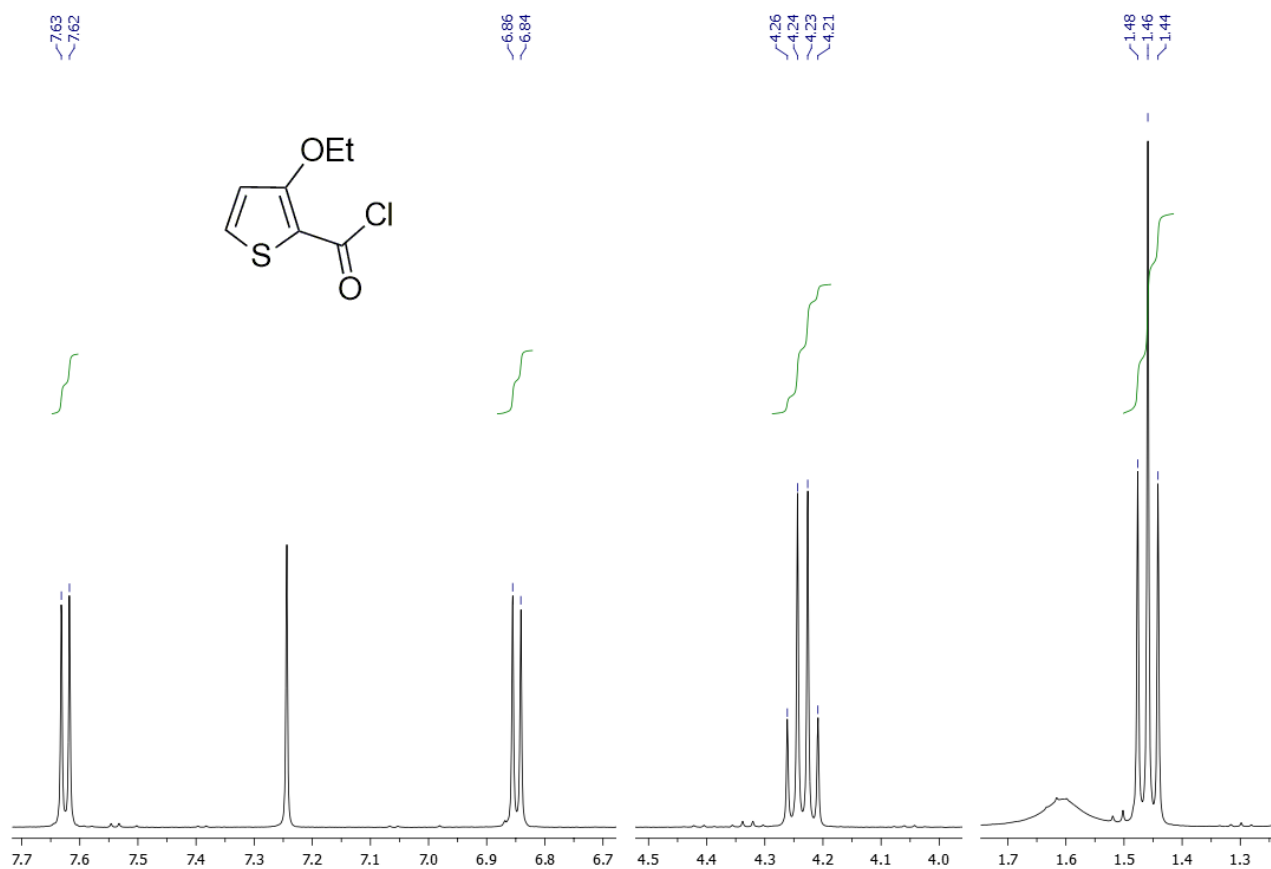
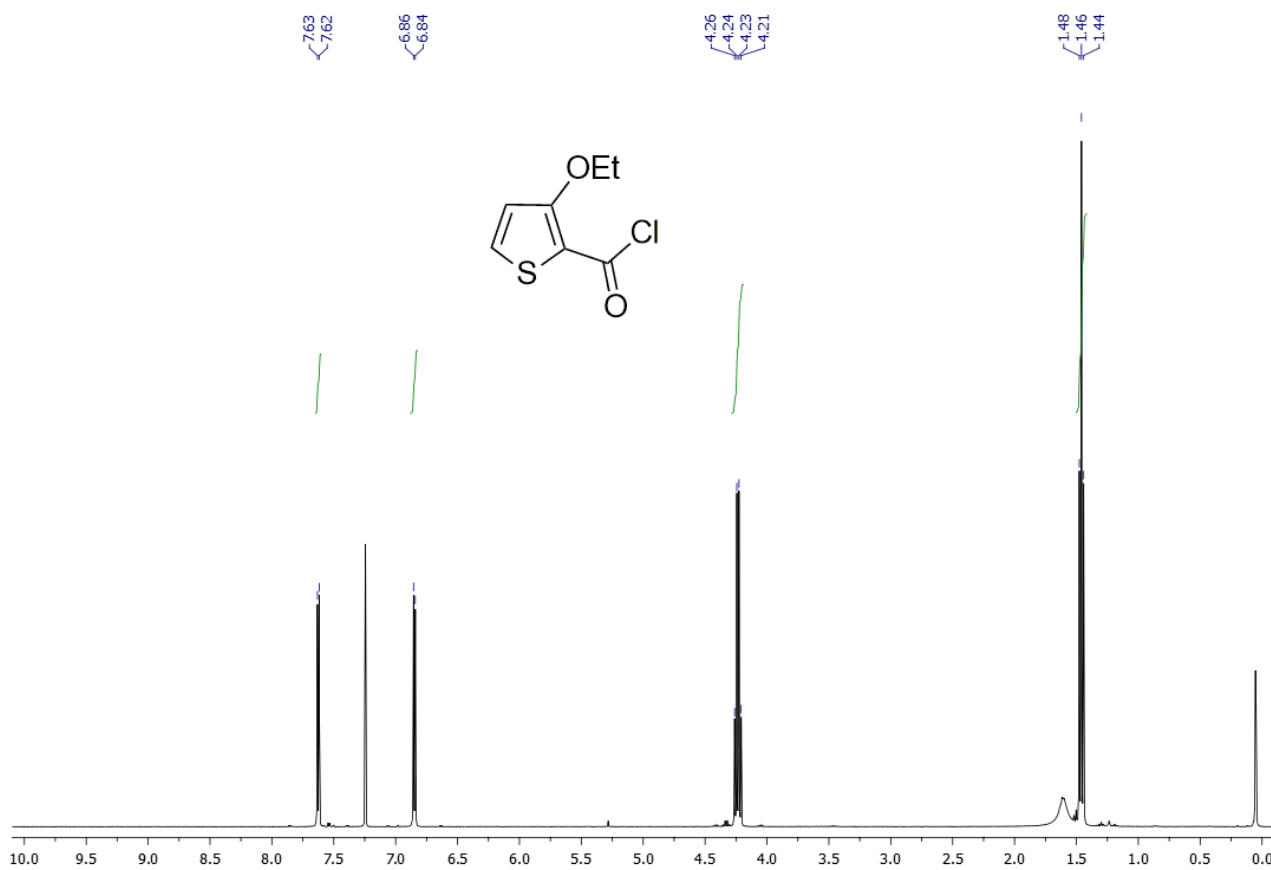


Figure S41. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 3-ethoxythiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansions (bottom).



4539 **Figure S42.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3-ethoxythiophene-2-carbonyl chloride (**4e**): full scale spectrum (top)
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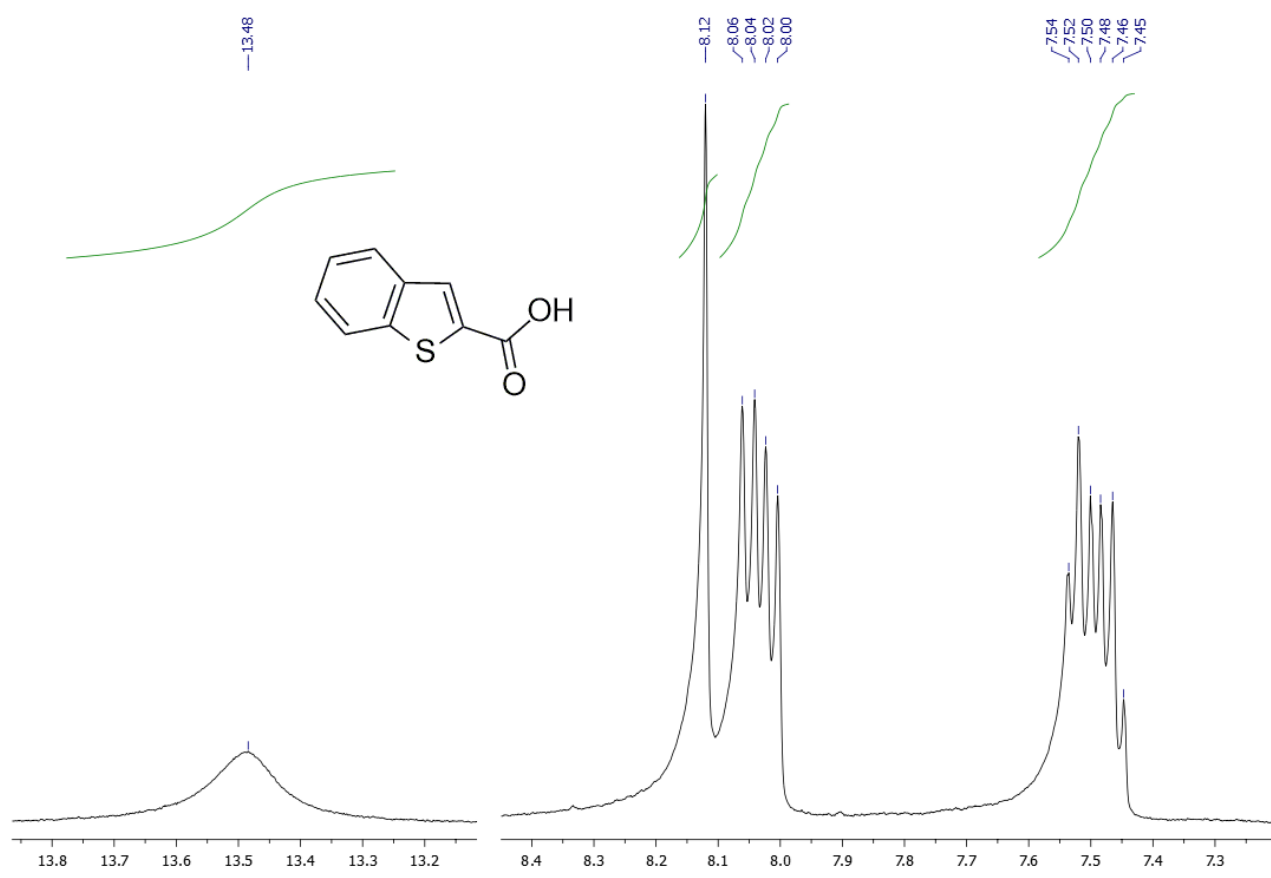
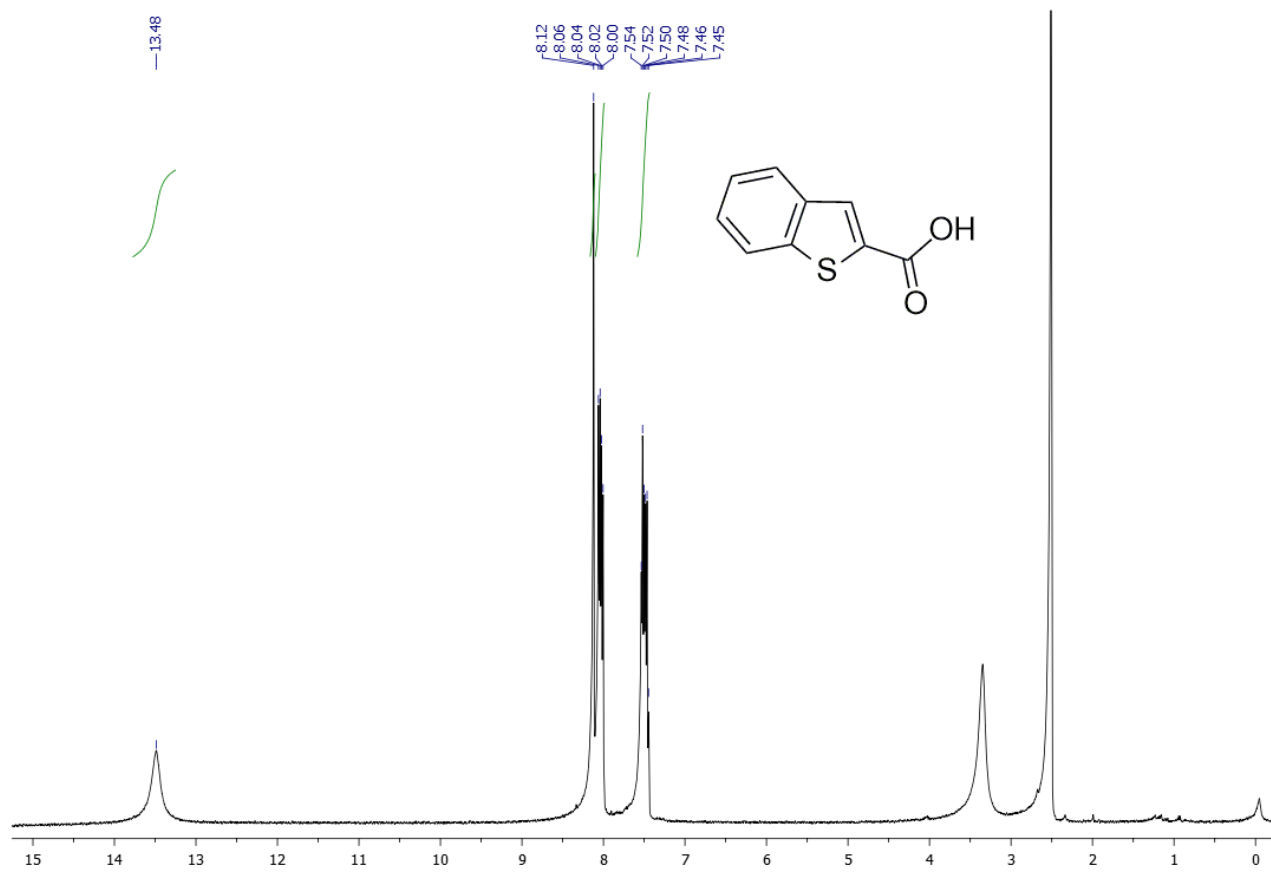
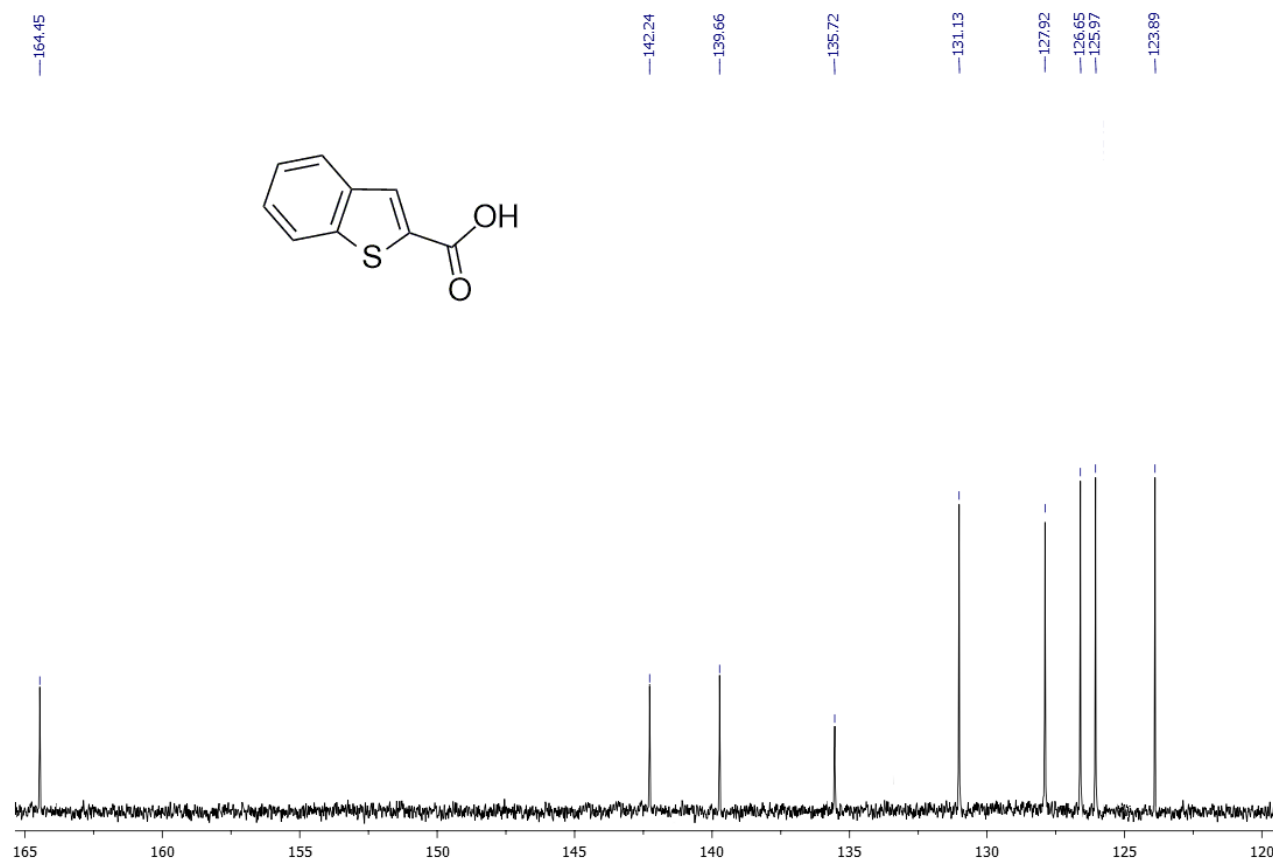
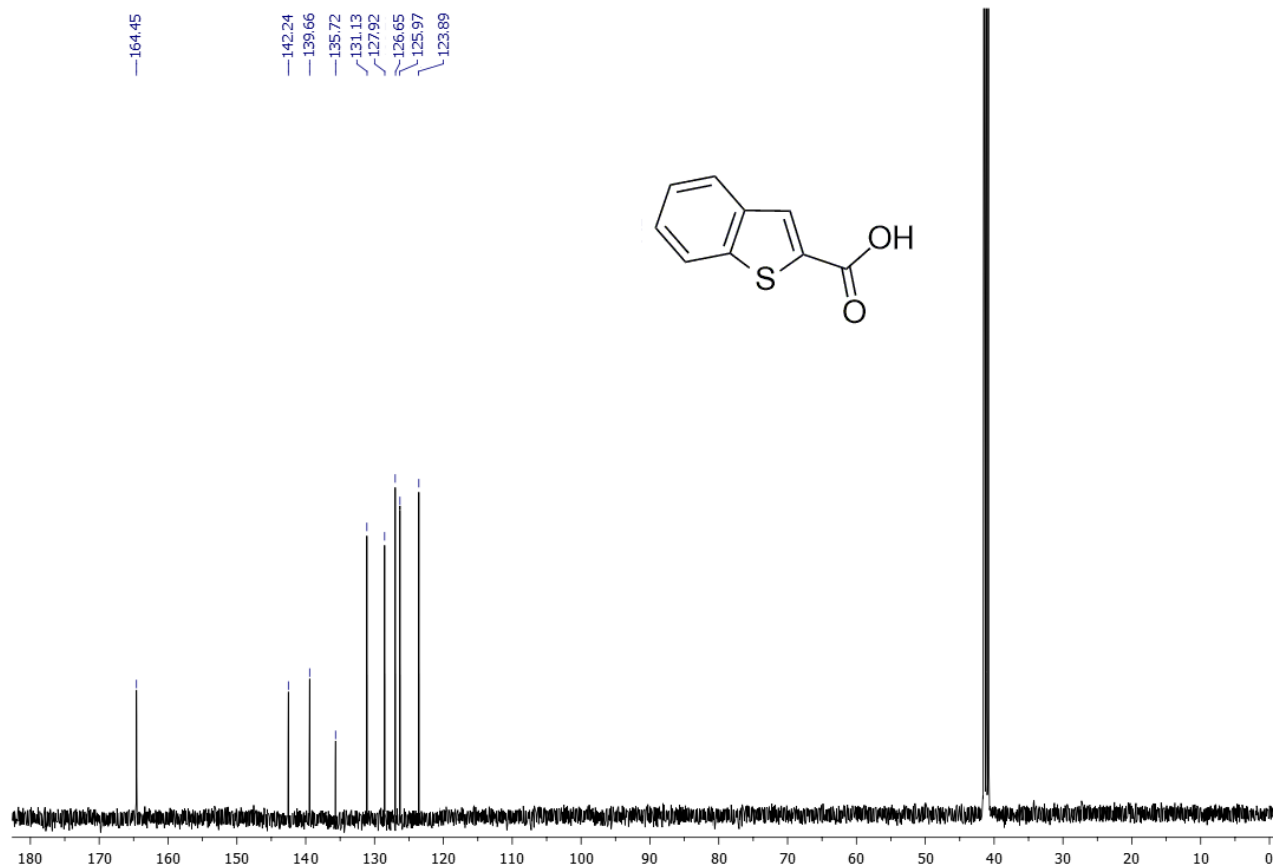


Figure S43. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of benzo[*b*]thiophene-2-carboxylic acid: full scale spectrum (top) and spectrum expansion (bottom).



4657 **Figure S44.** ^{13}C -NMR spectrum (100 MHz, CDCl_3) of benzo[*b*]thiophene-2-carboxylic acid: full scale spectrum (top) and
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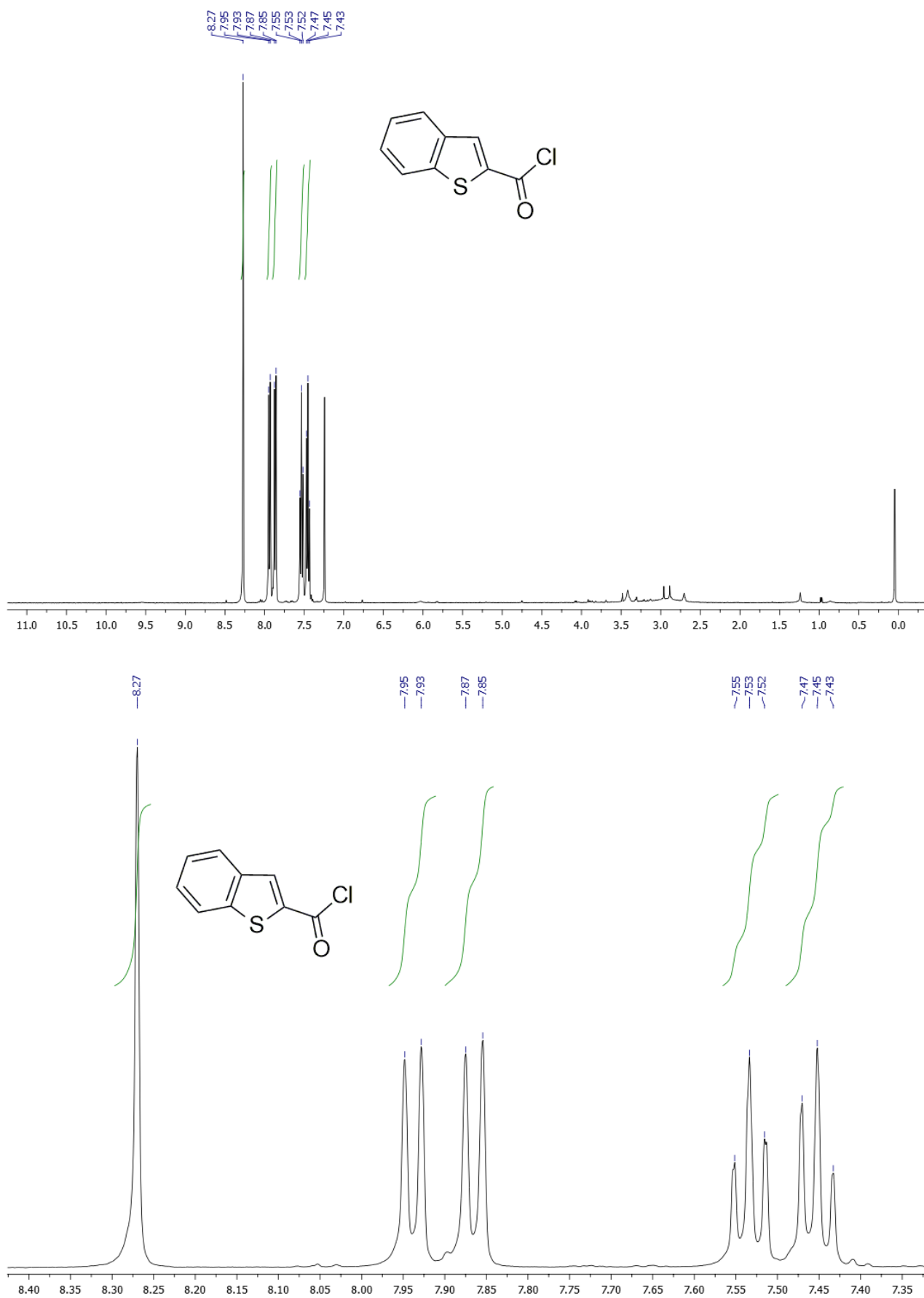


Figure S45. ¹H-NMR spectrum (400 MHz, CDCl₃) of benzo[*b*]thiophene-2-carbonyl chloride (4f): full scale spectrum (top) and spectrum expansion (bottom).

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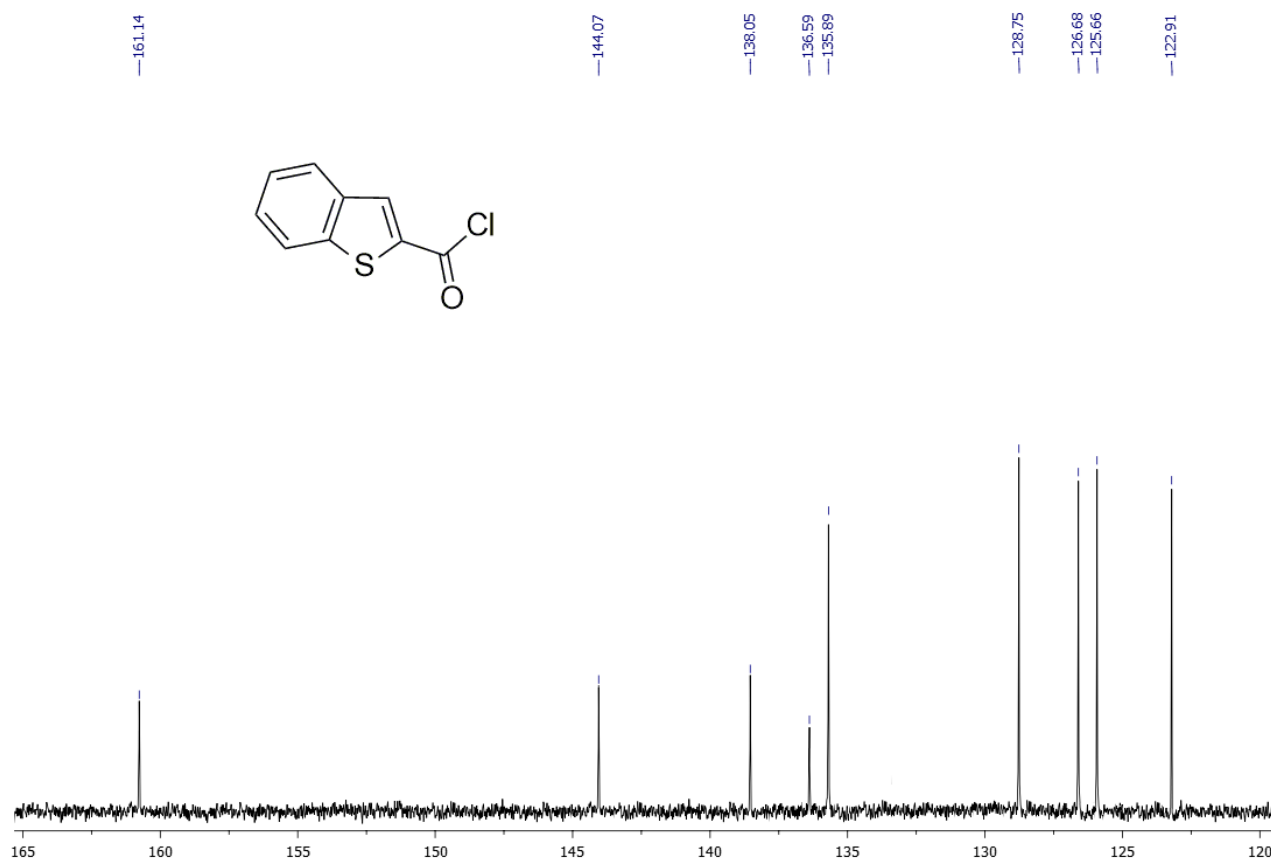
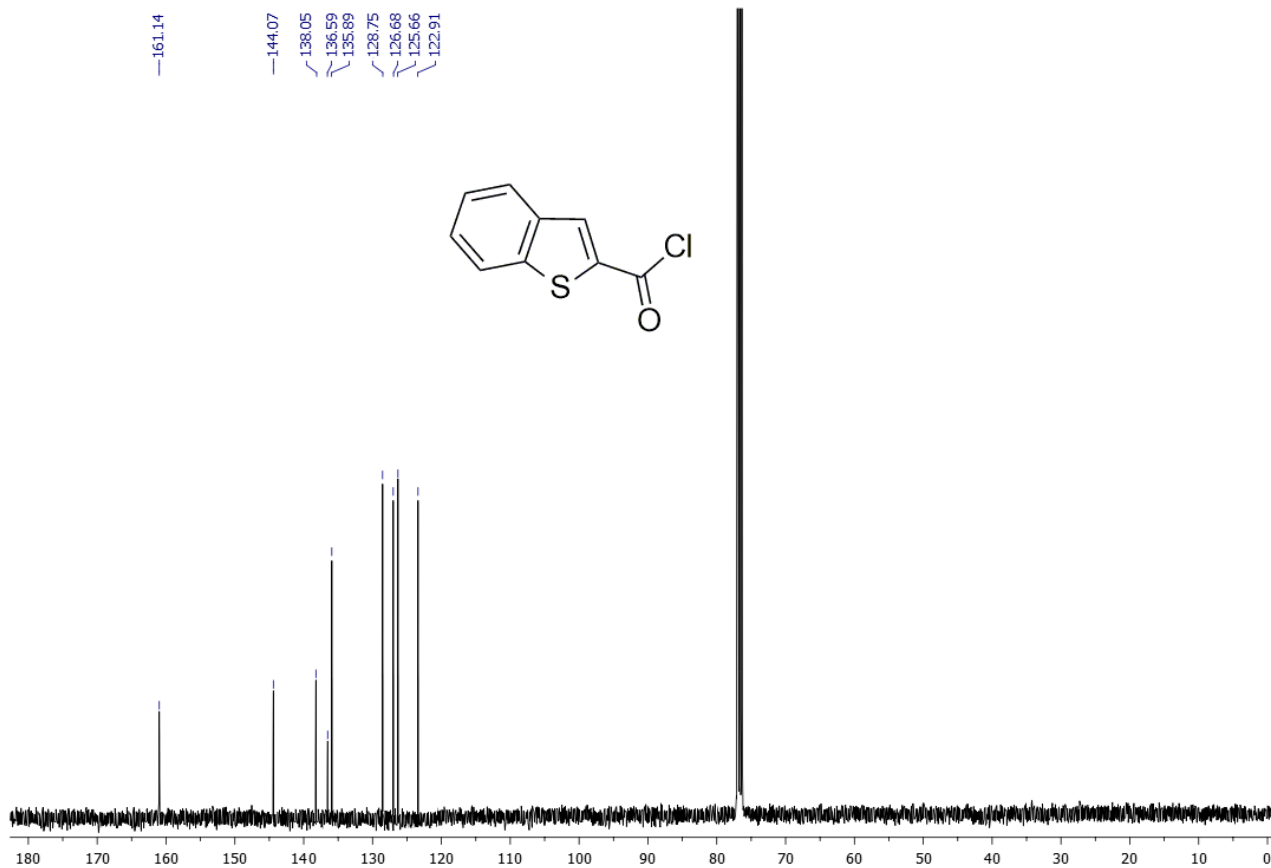


Figure S46. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of benzo[*b*]thiophene-2-carbonyl chloride (4f): full scale spectrum (top) and spectrum expansion (bottom).

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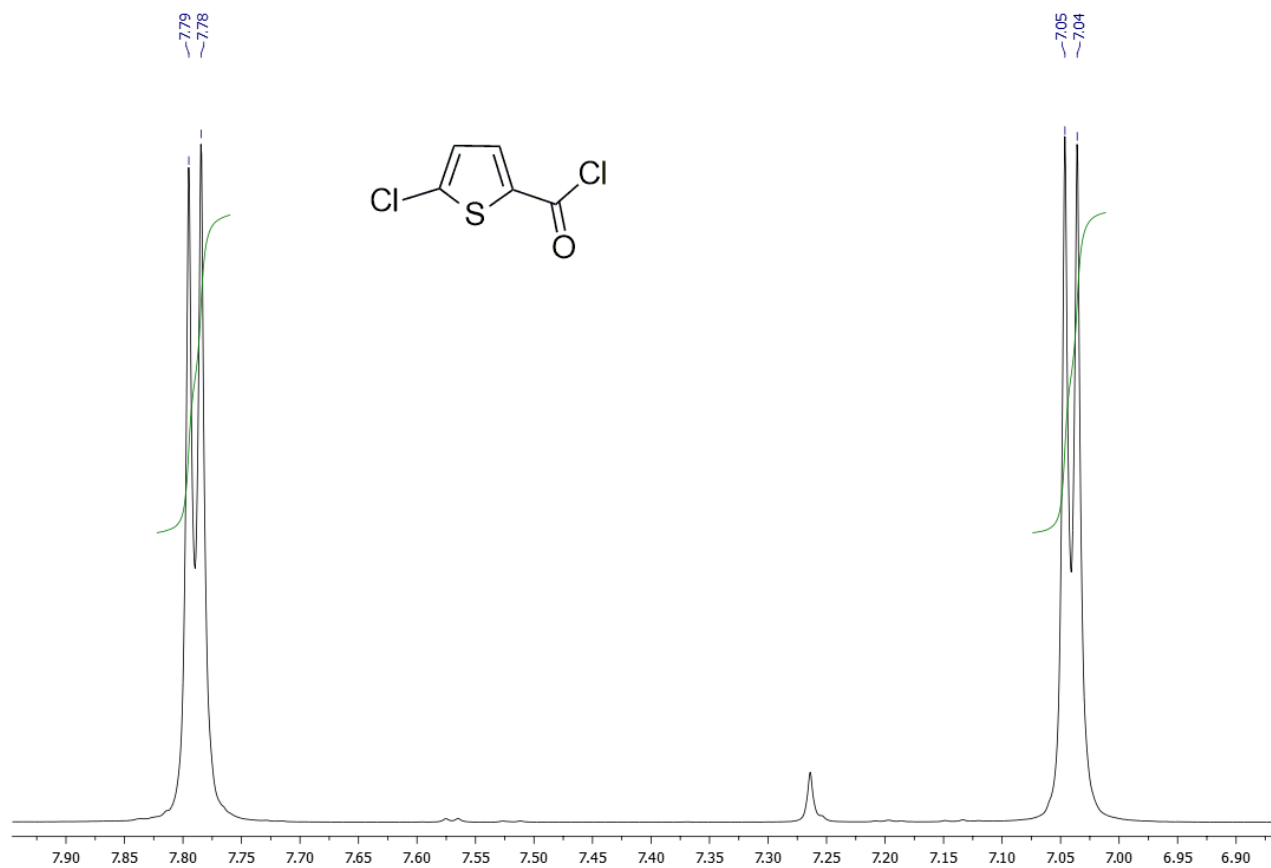
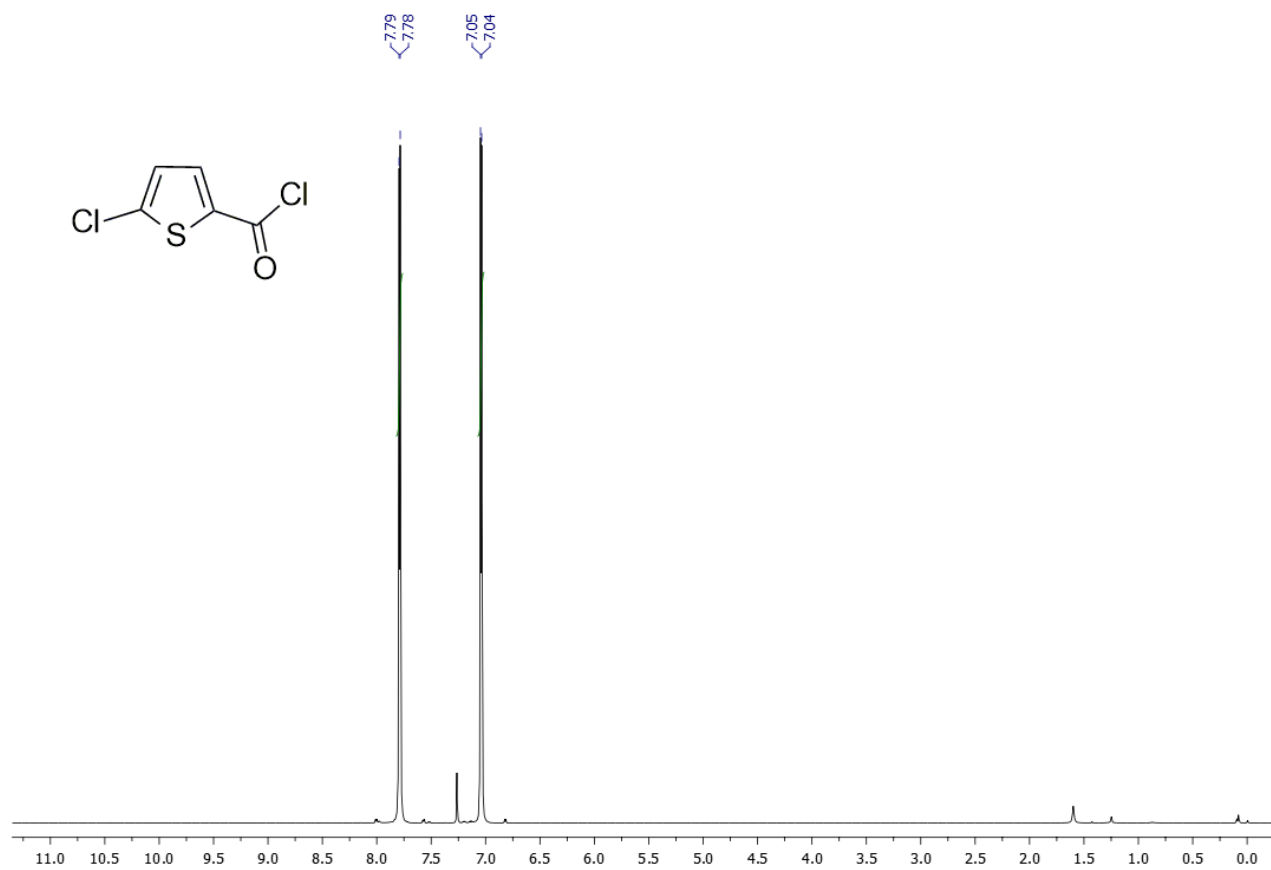


Figure S47. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 5-chlorothiophene-2-carbonyl chloride (**4g**): full scale spectrum (top) and spectrum expansion (bottom).

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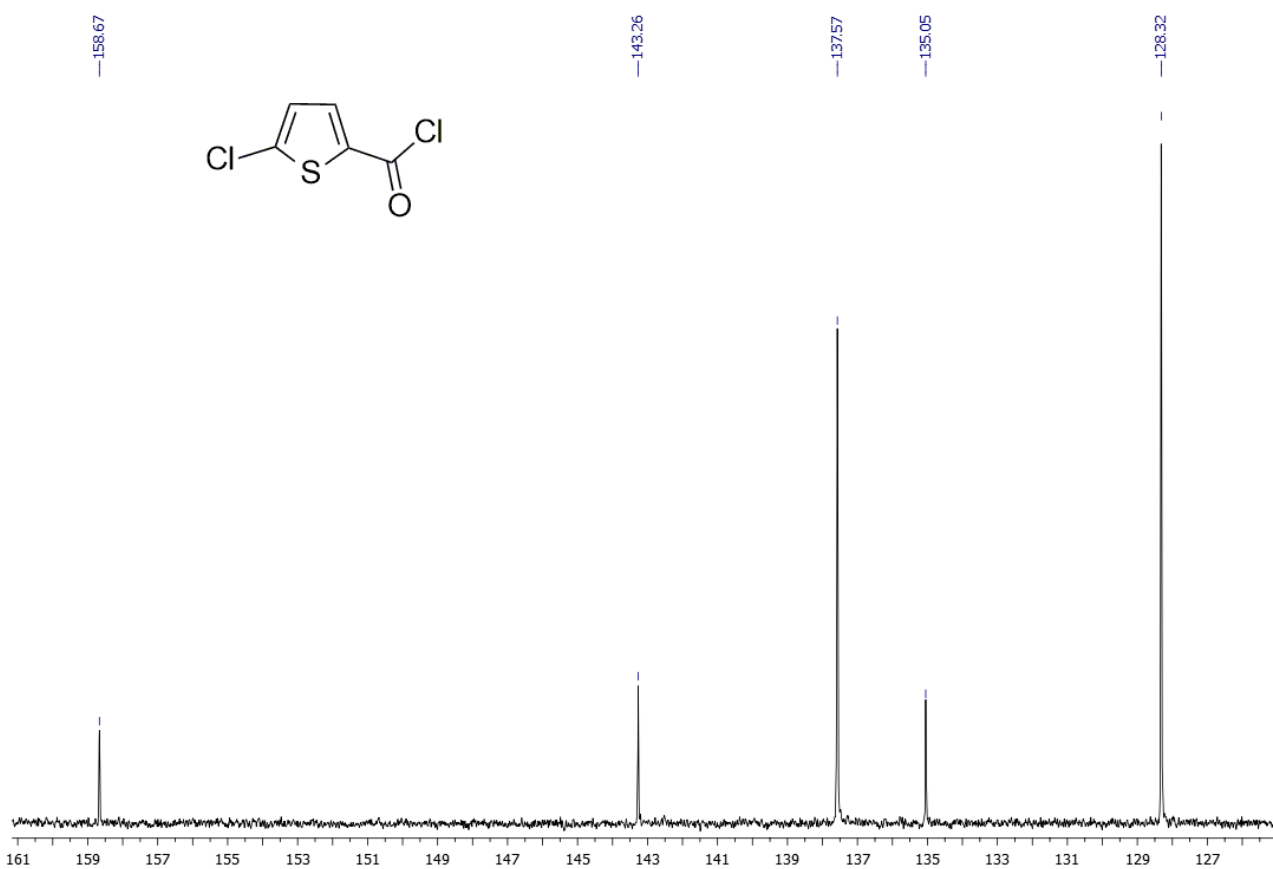
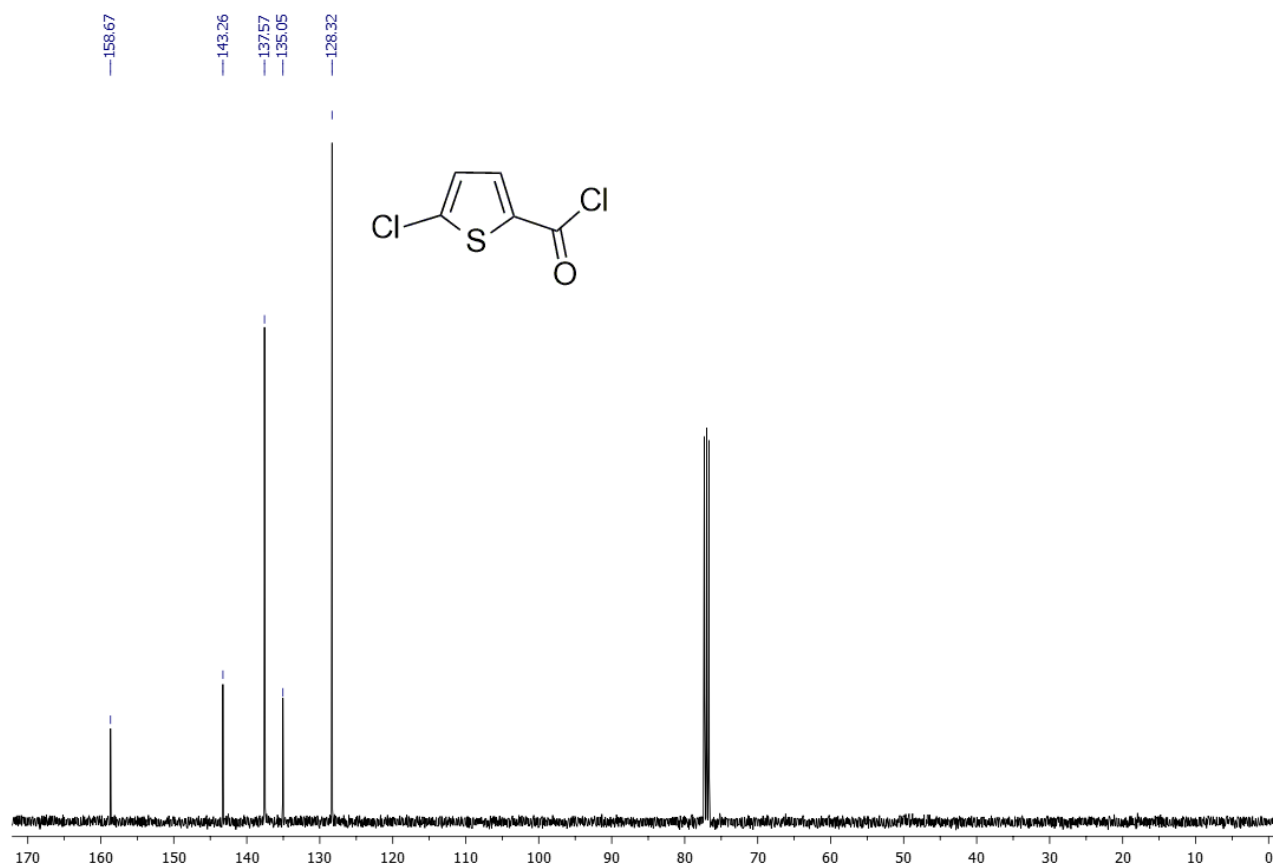


Figure S48. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 5-chlorothiophene-2-carbonyl chloride (**4g**): full scale spectrum (top) and spectrum expansion (bottom).

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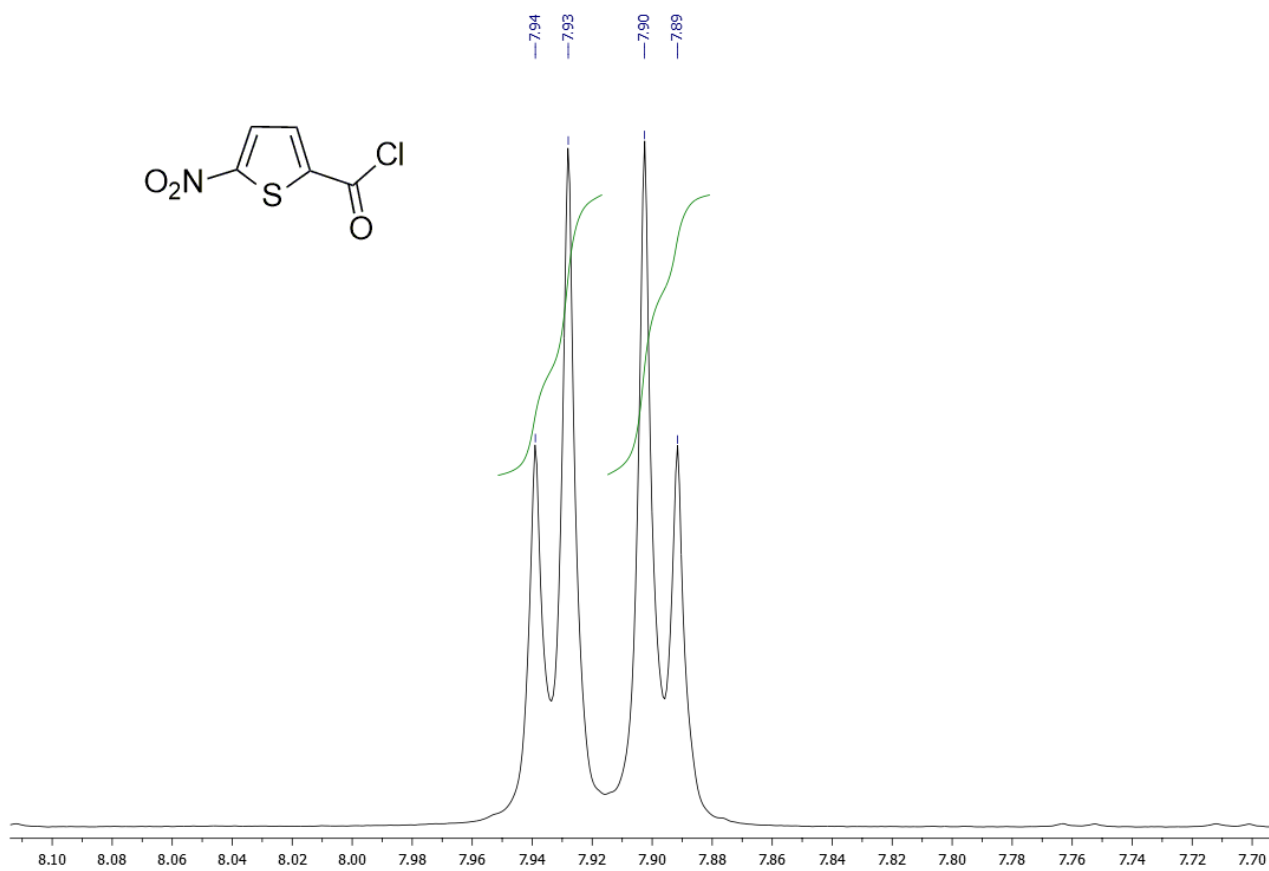
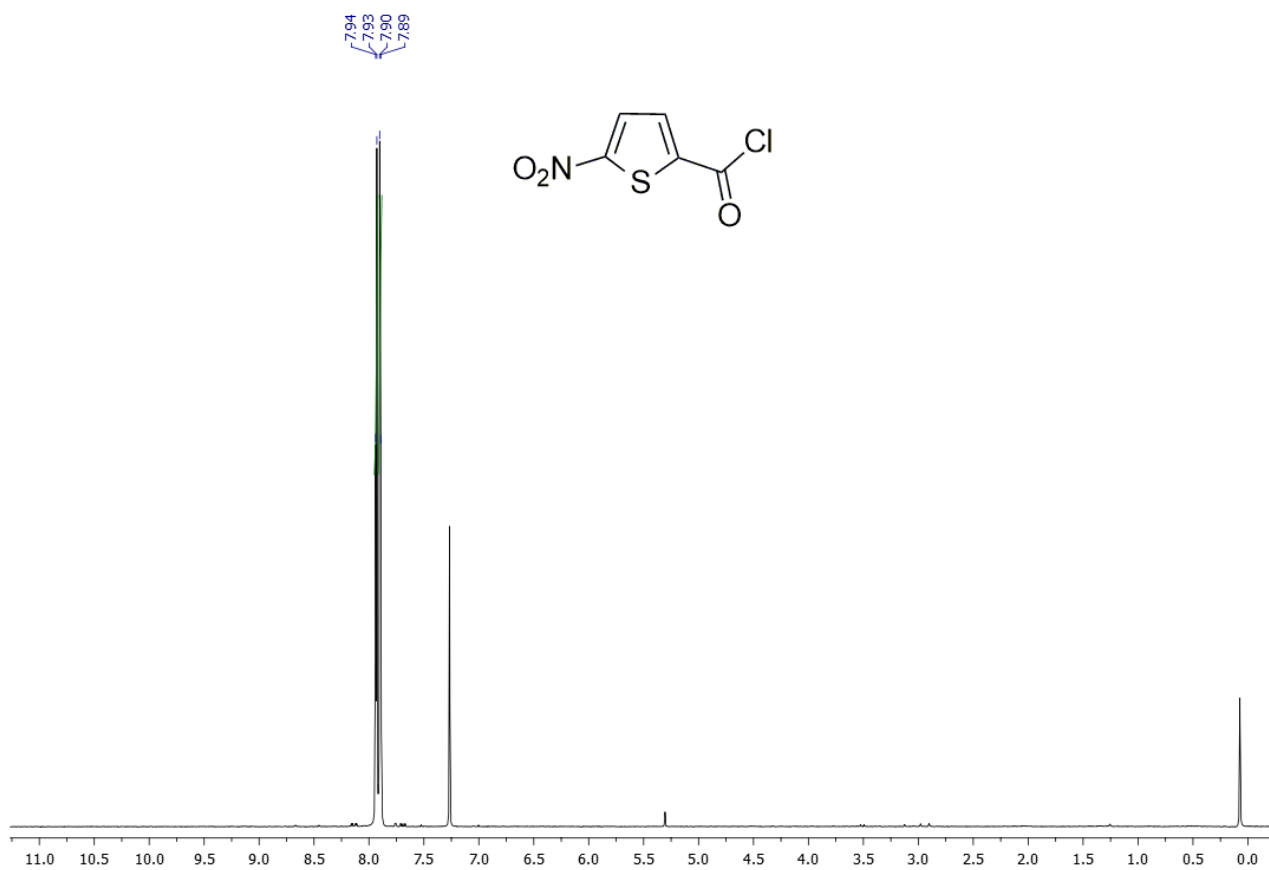


Figure S49. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 5-nitrothiophene-2-carbonyl chloride (**4h**): full scale spectrum (top) and spectrum expansion (bottom).

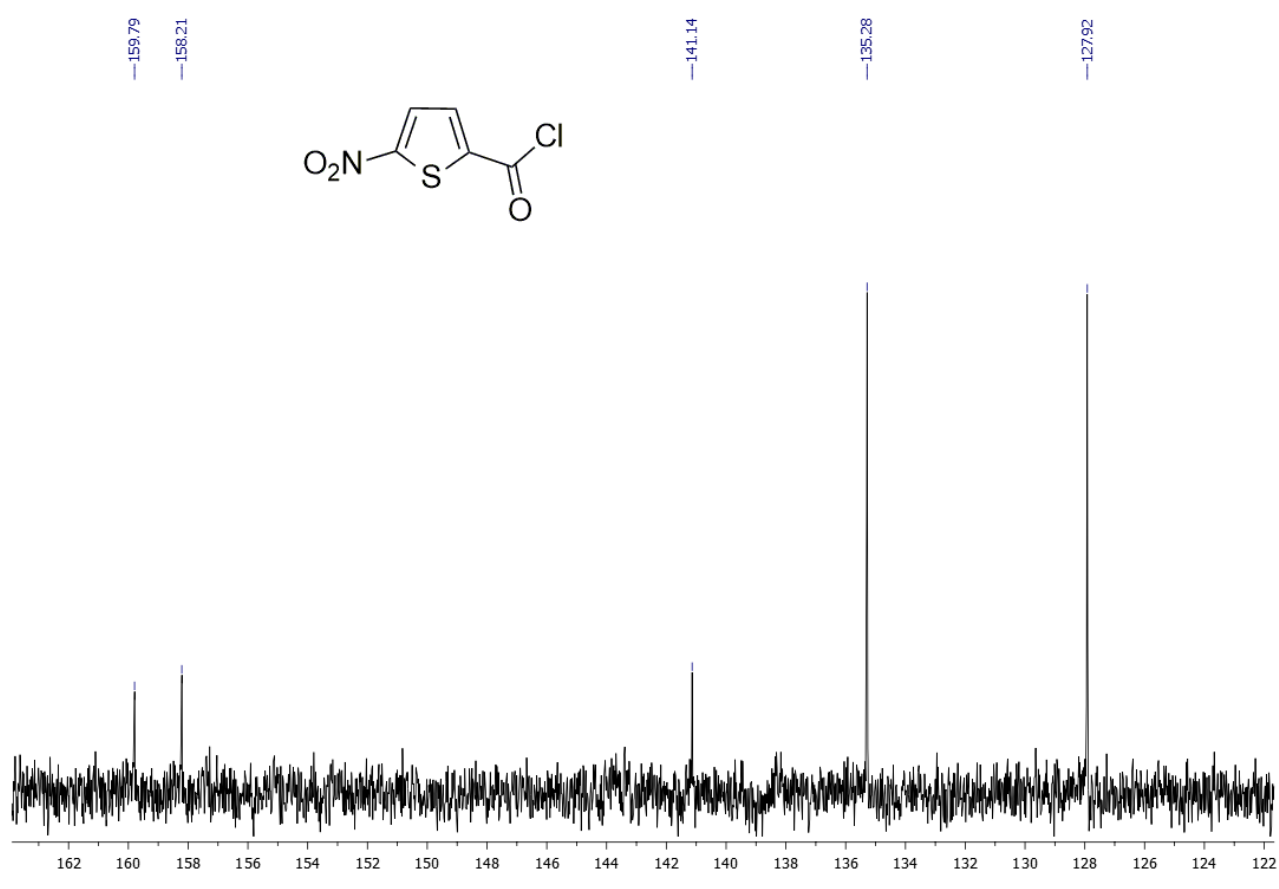
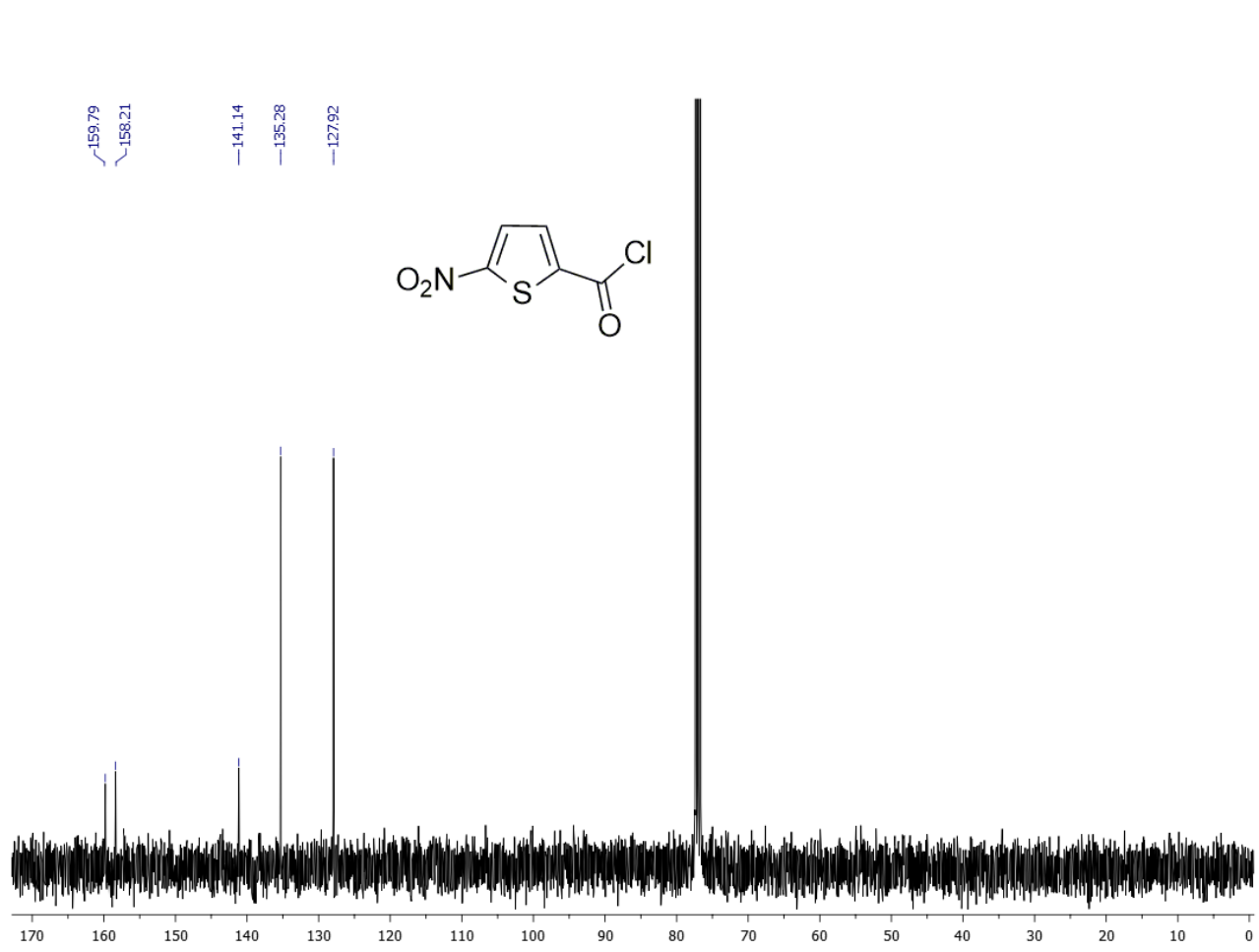
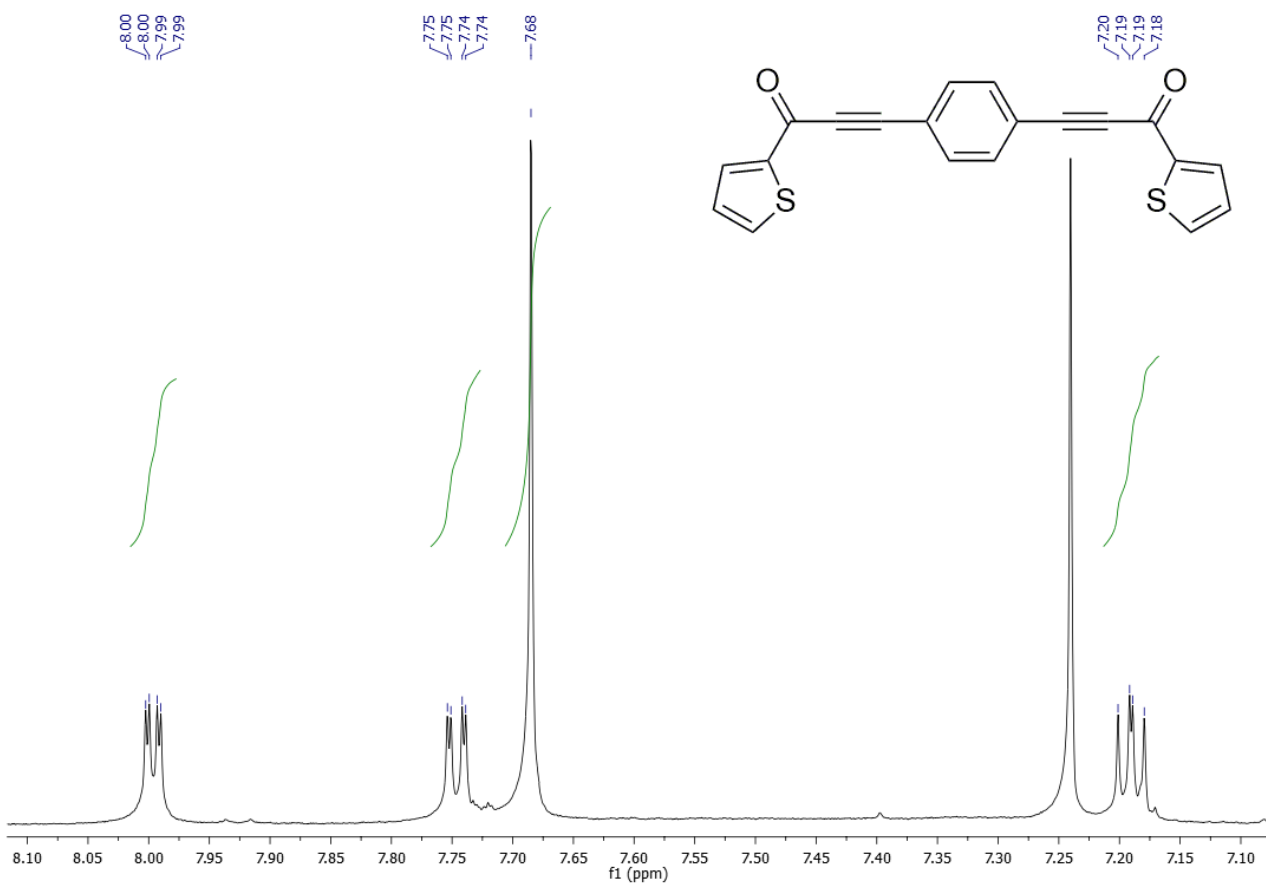
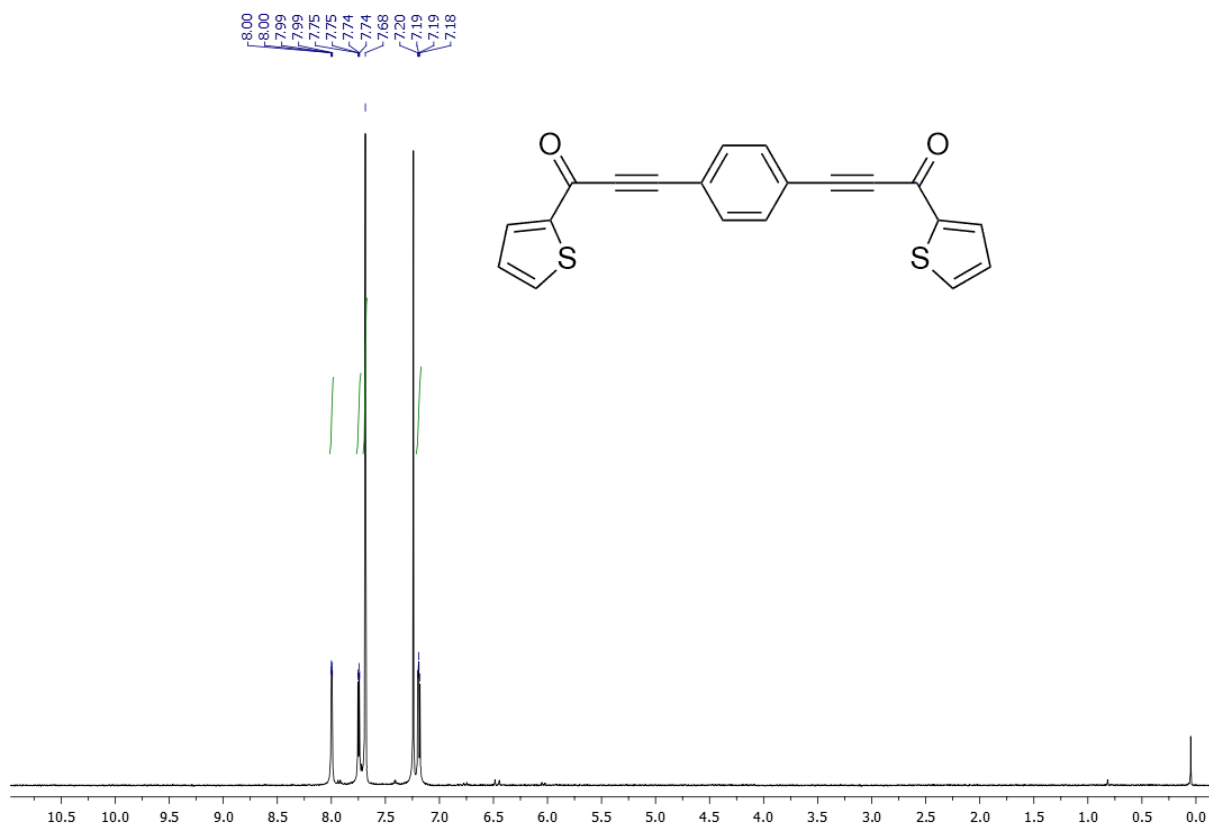
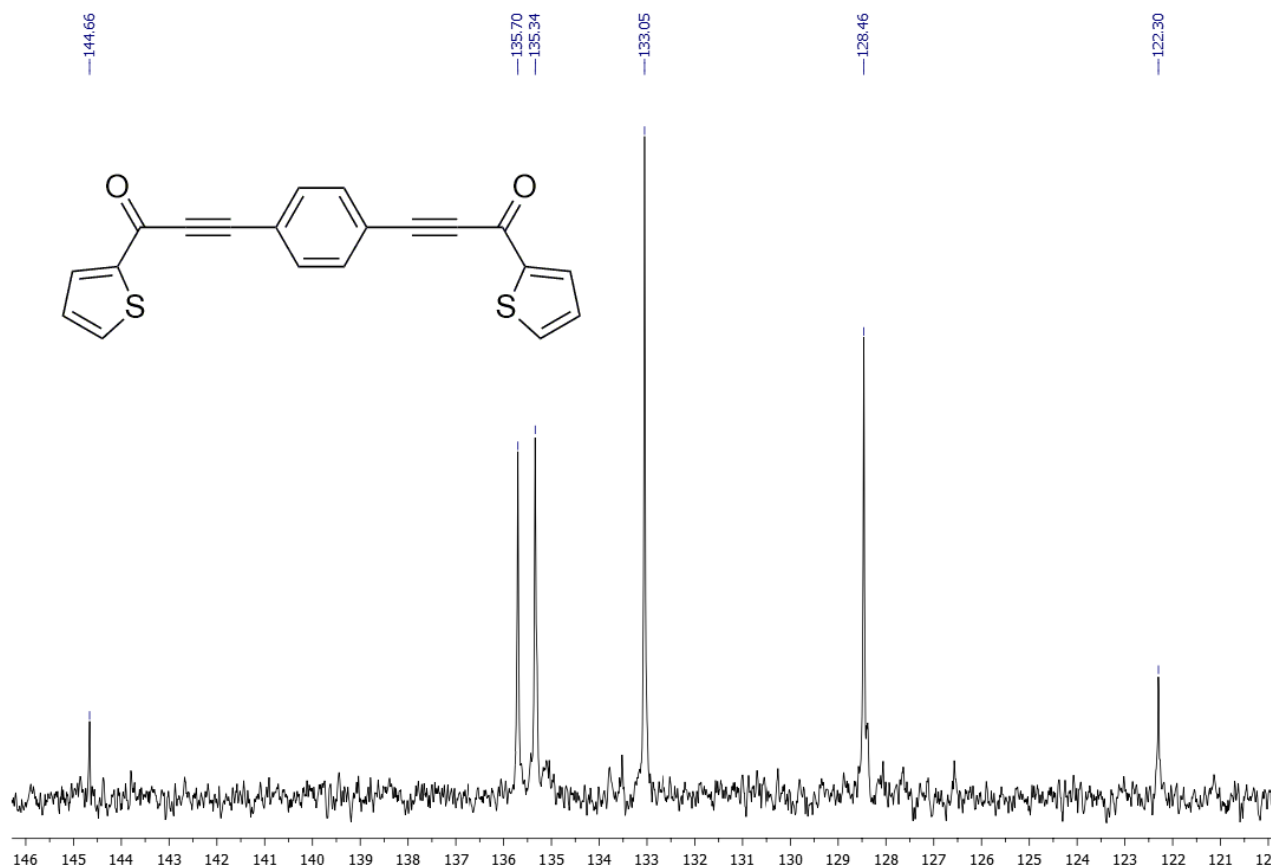
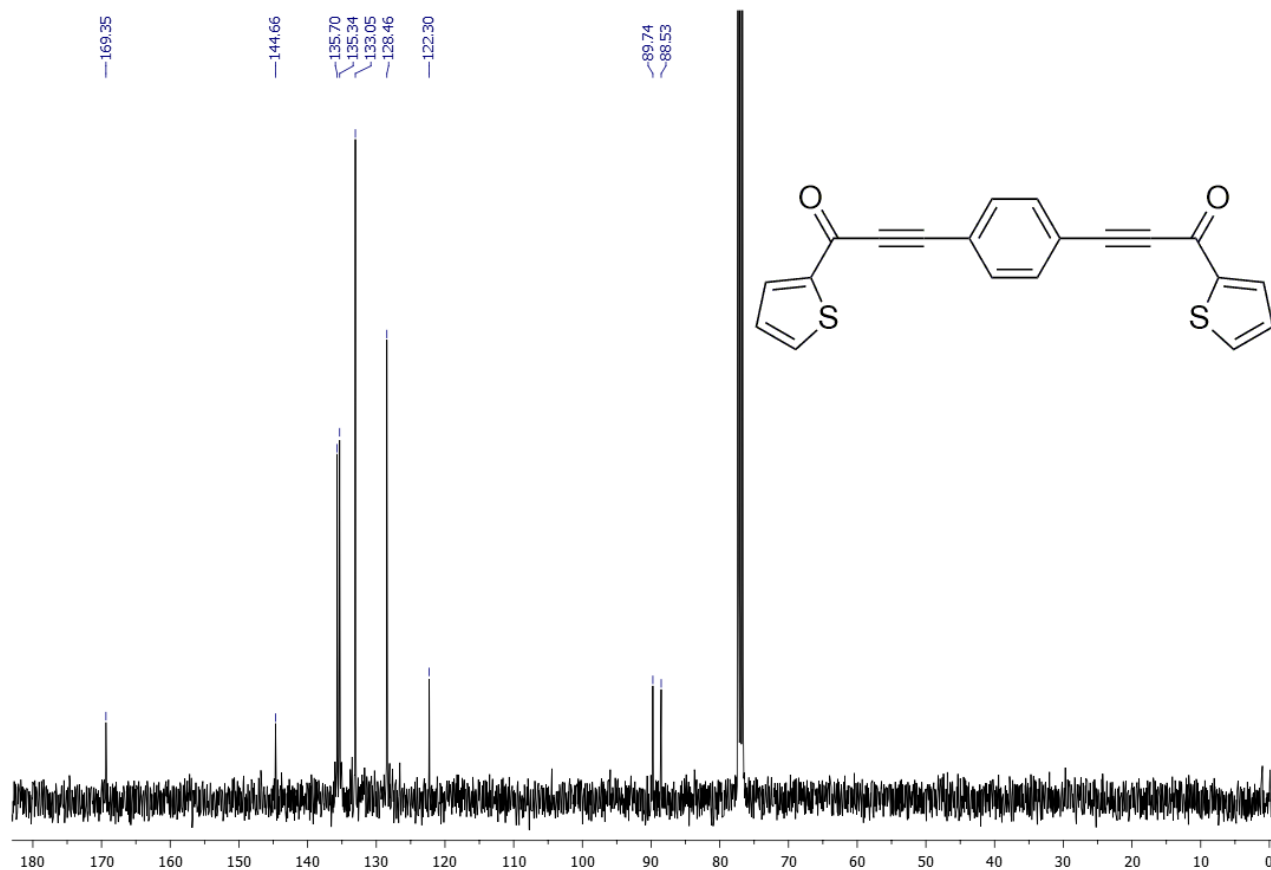


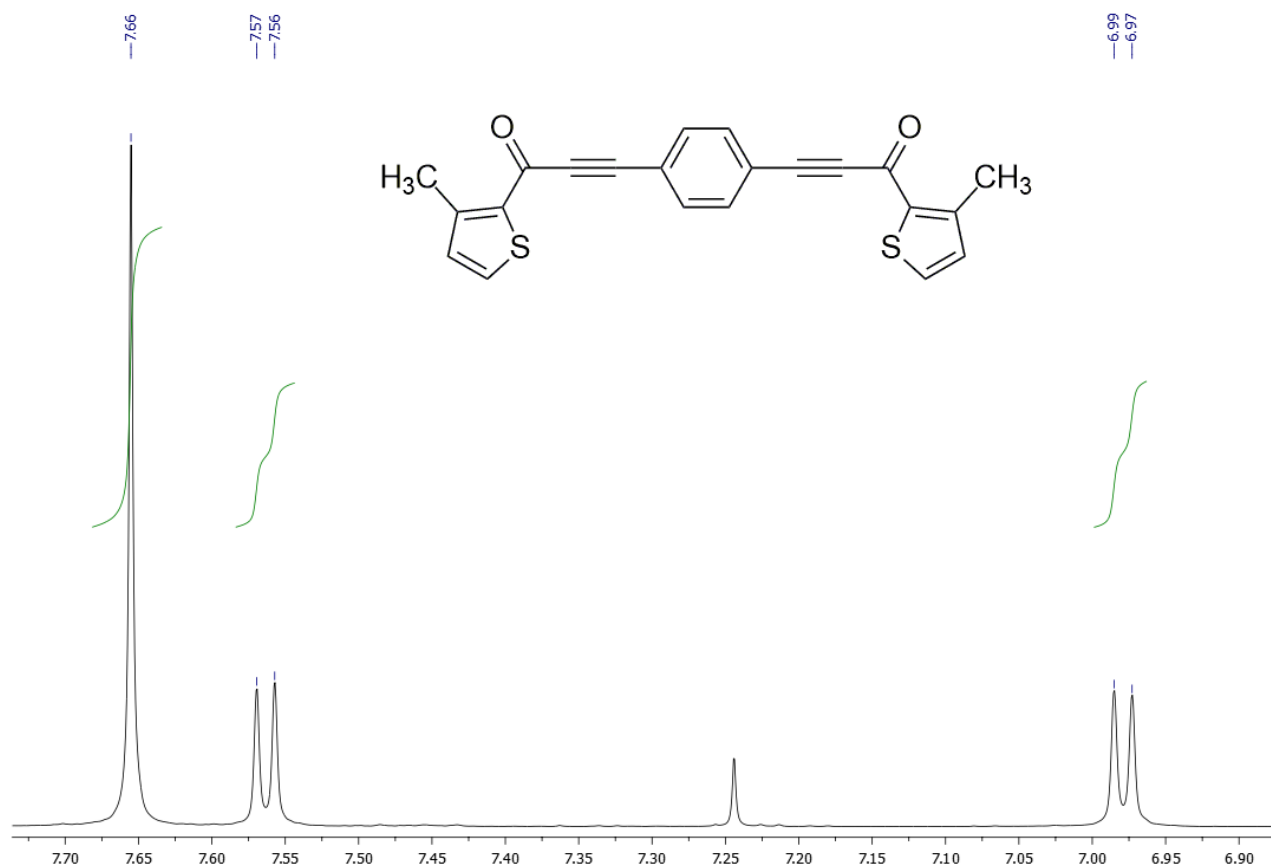
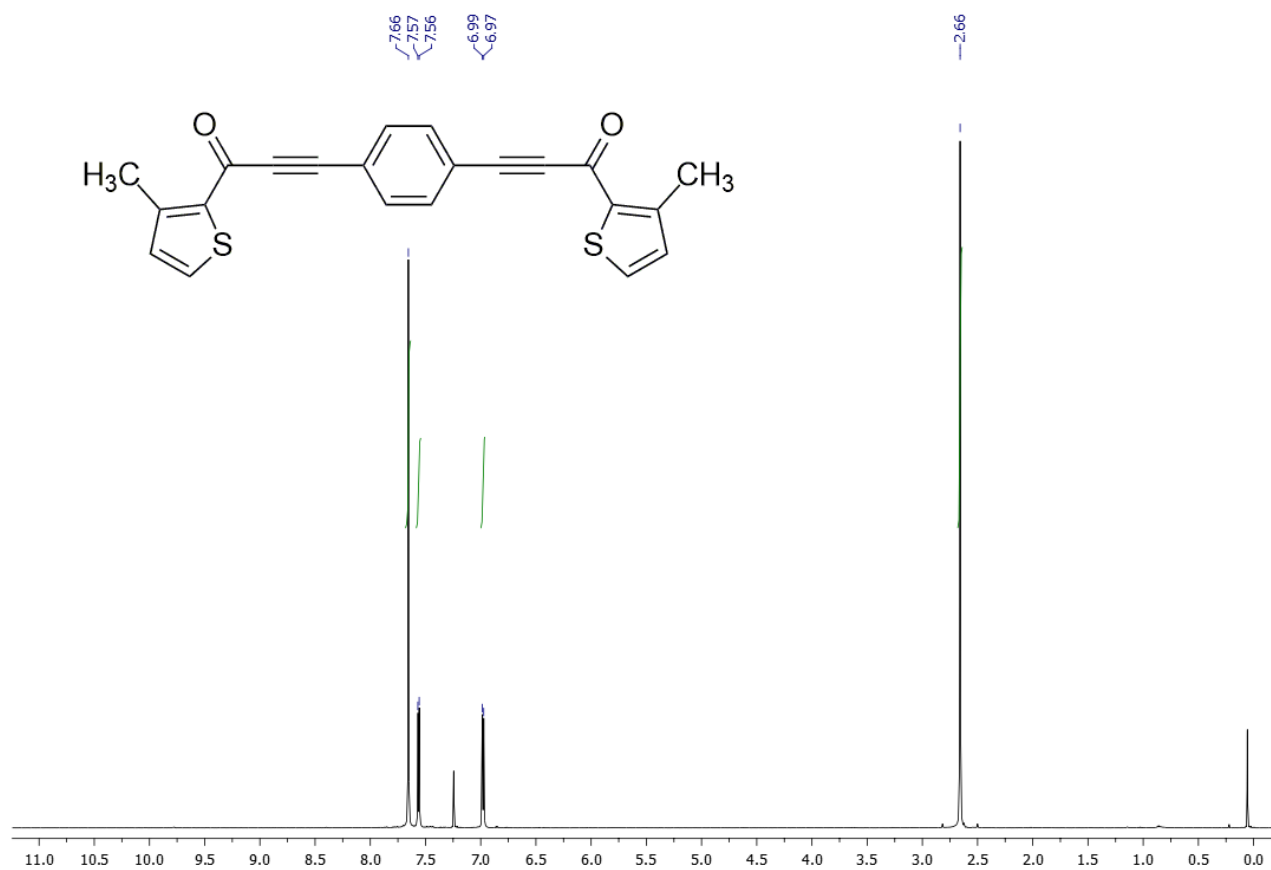
Figure S50. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 5-nitrothiophene-2-carbonyl chloride (**4h**): full scale spectrum (top) and spectrum expansion (bottom).



5070 **Figure S51.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1a**): full
5071 scale spectrum (top) and spectrum expansion (bottom).
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5130 **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
5131 scale spectrum (top) and spectrum expansion (bottom).
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5189 **Figure S53.** $^1\text{H-NMR}$ 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).

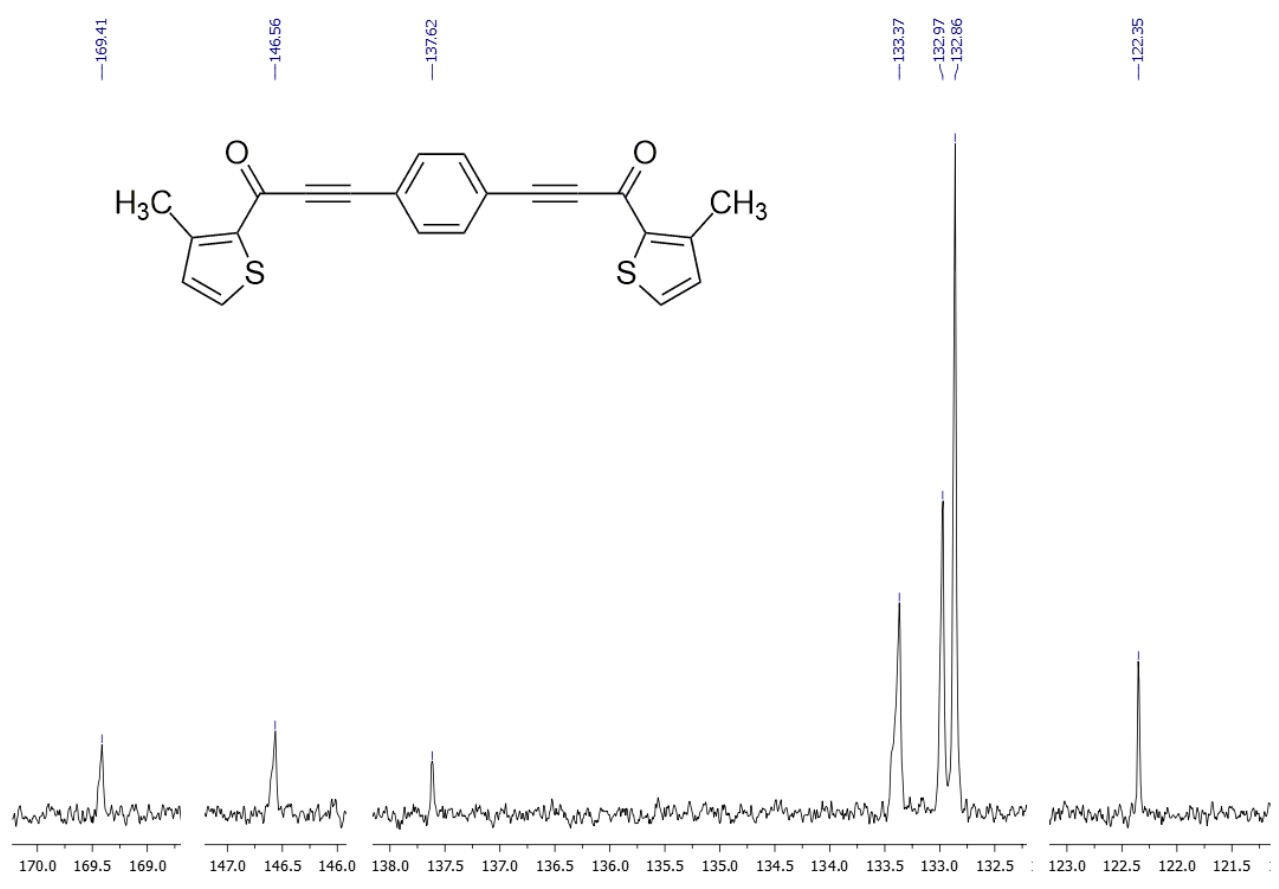
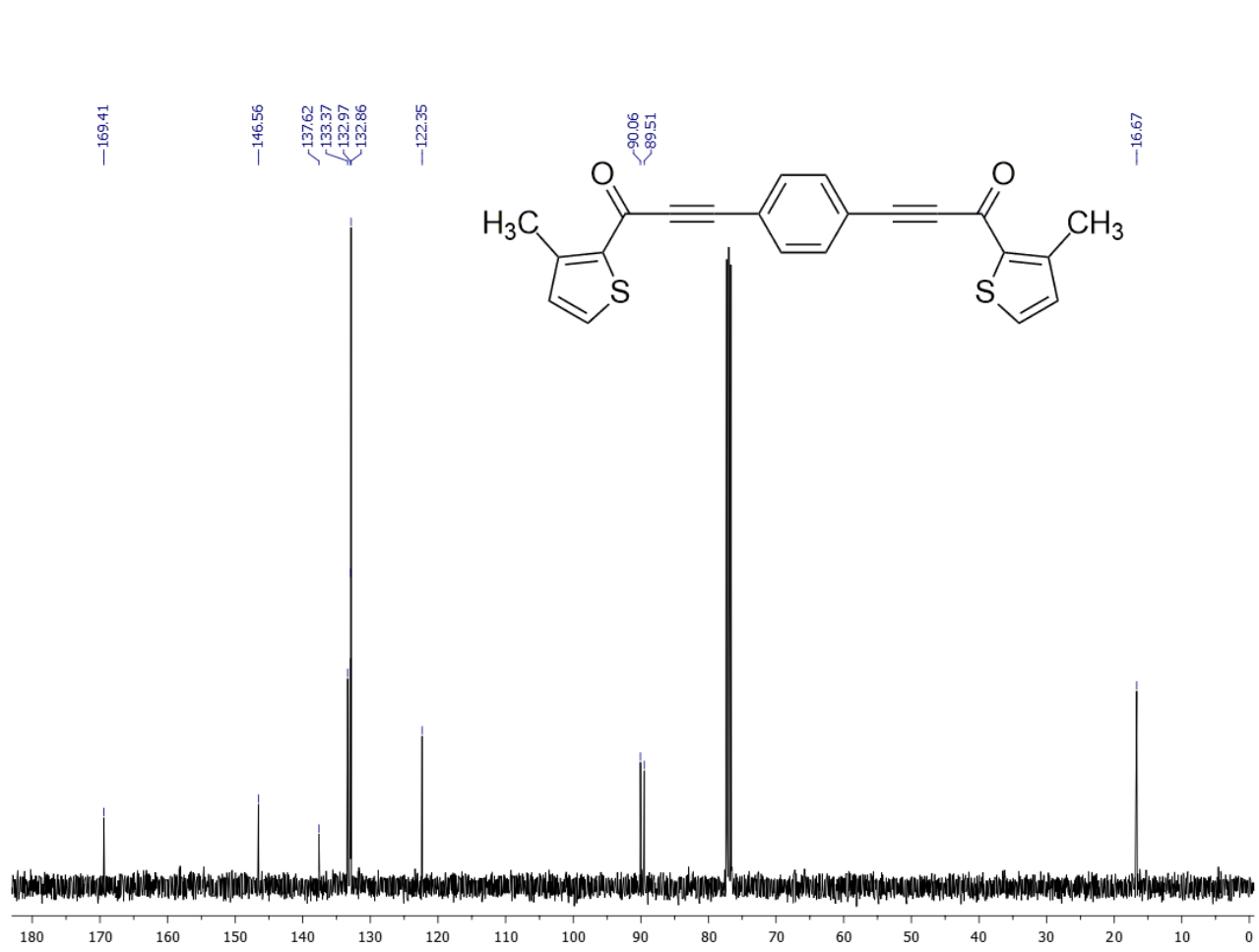
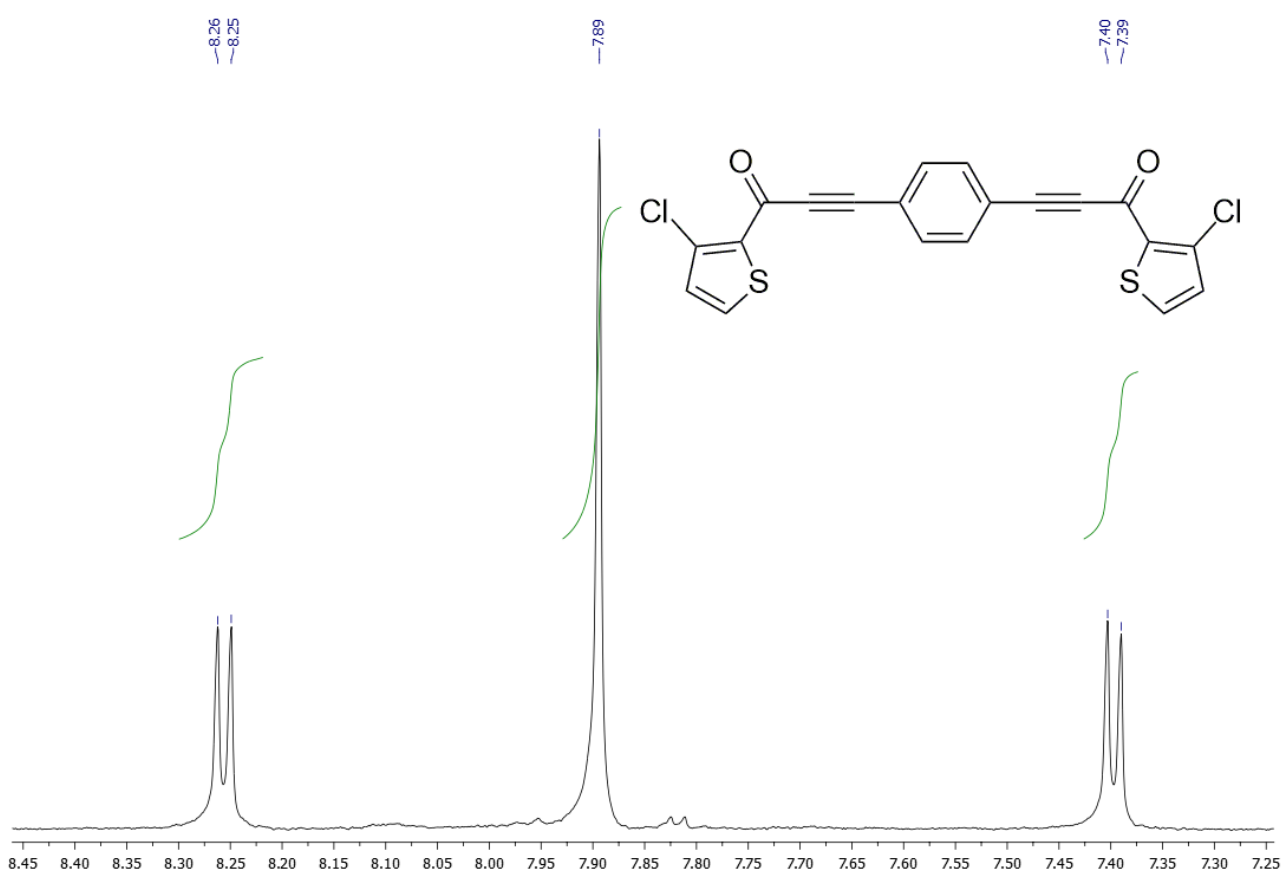
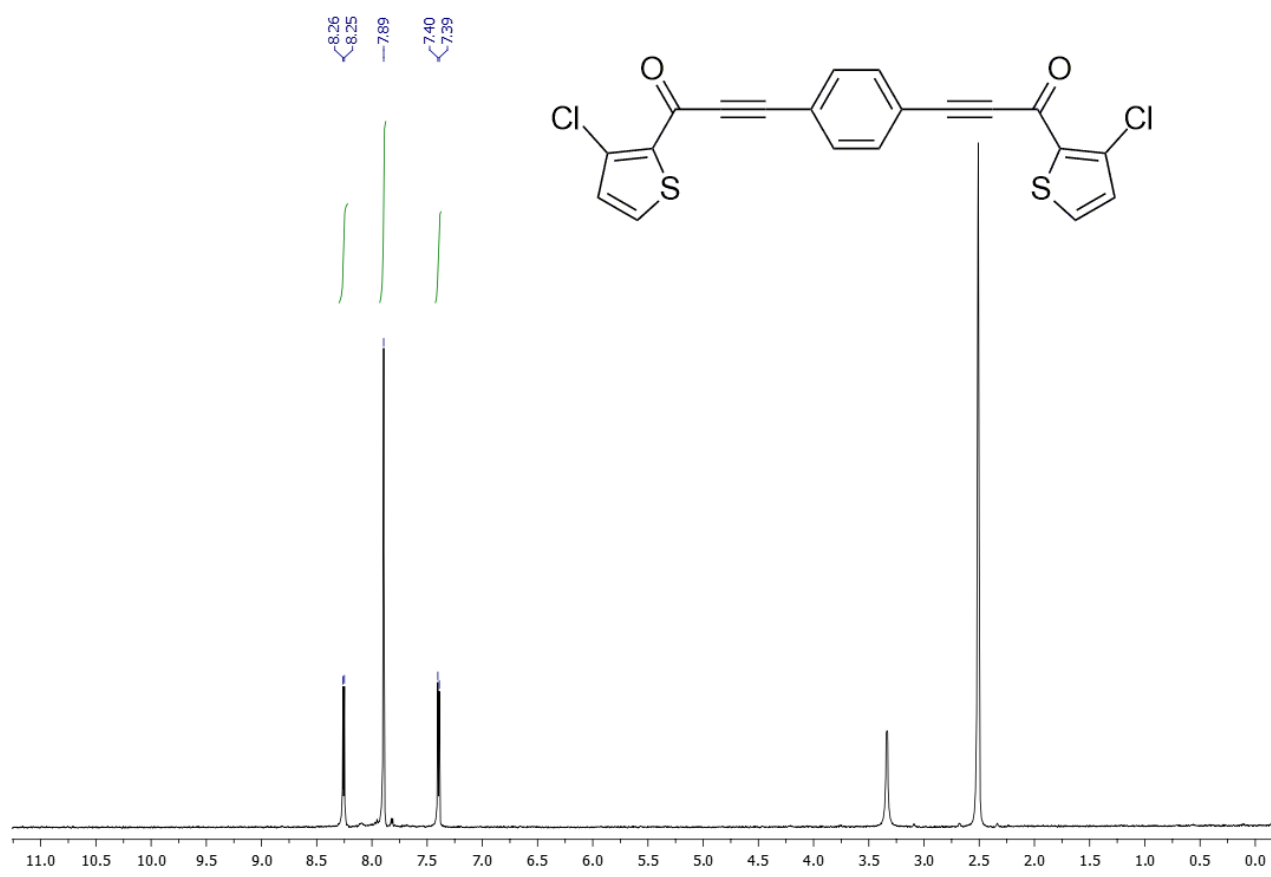
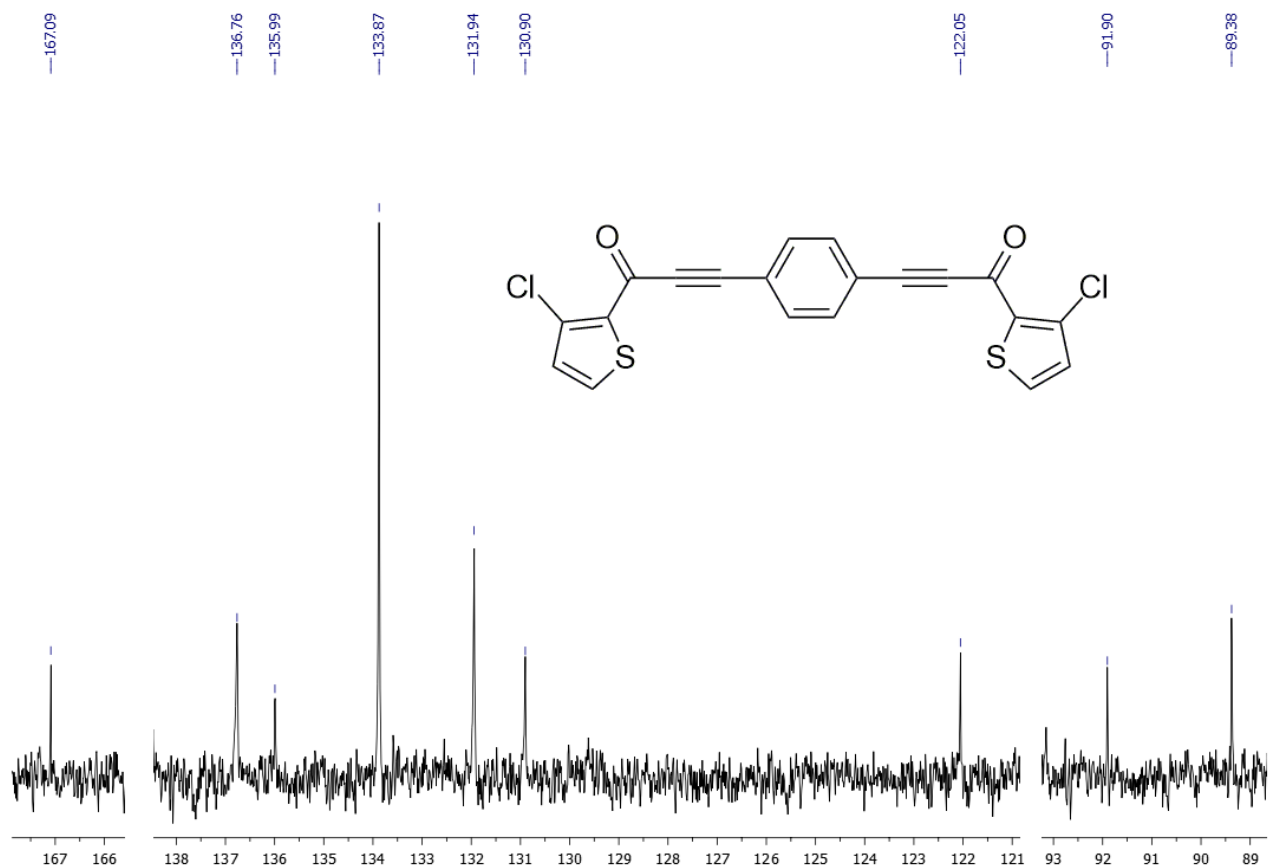
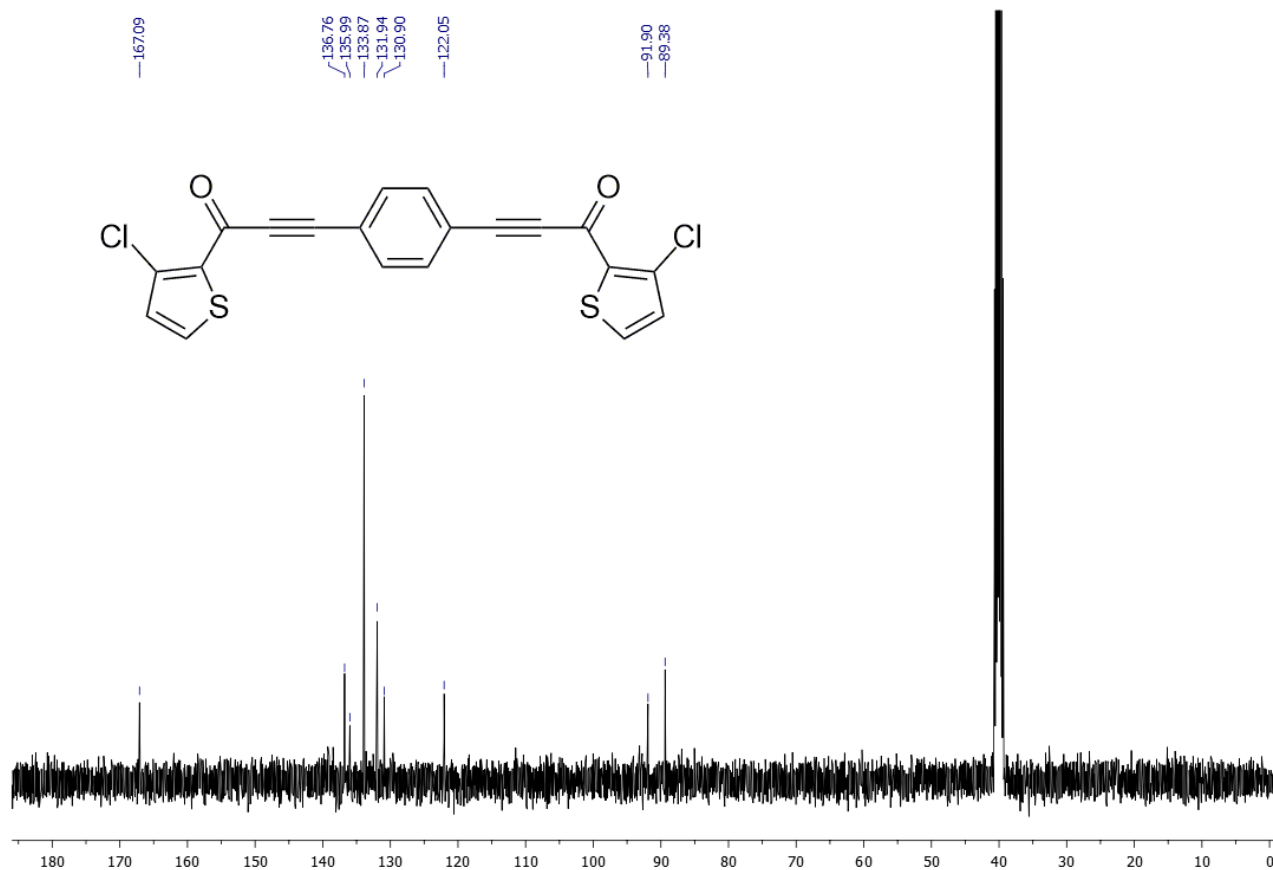


Figure S54. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(3-methylthiophen-2-yl)prop-2-yn-1-one) (**1b**): full scale spectrum (top) and spectrum expansions (bottom).



5307 **Figure S55.** ¹H-NMR spectrum (400 MHz, CDCl₃) of 3,3'-(1,4-phenylene)bis(1-(3-chlorothiophen-2-yl)prop-2-yn-1-one)
5308 (**1c**): full scale spectrum (top) and spectrum expansion (bottom).



5366 **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)
5367 (**1c**): full scale spectrum (top) and spectrum expansions (bottom).

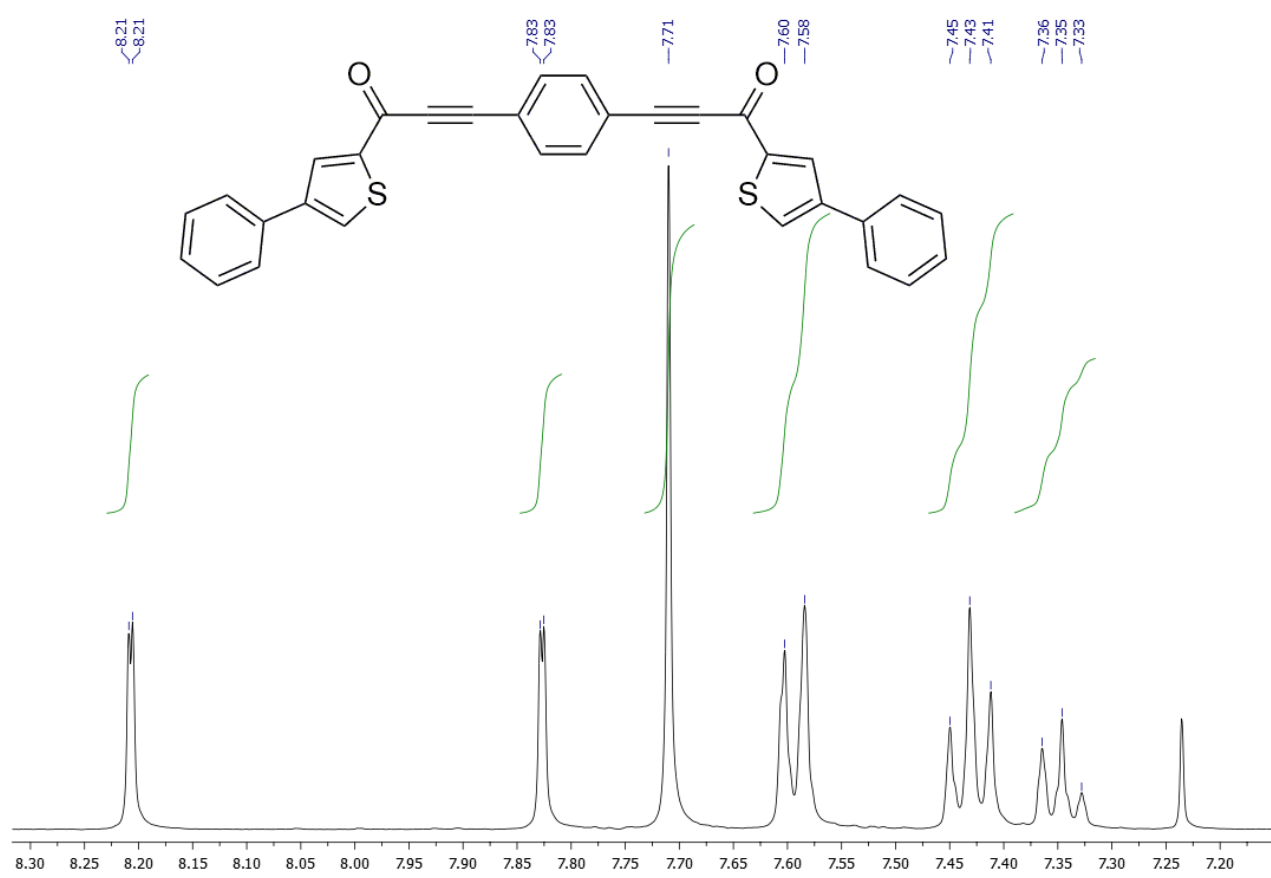
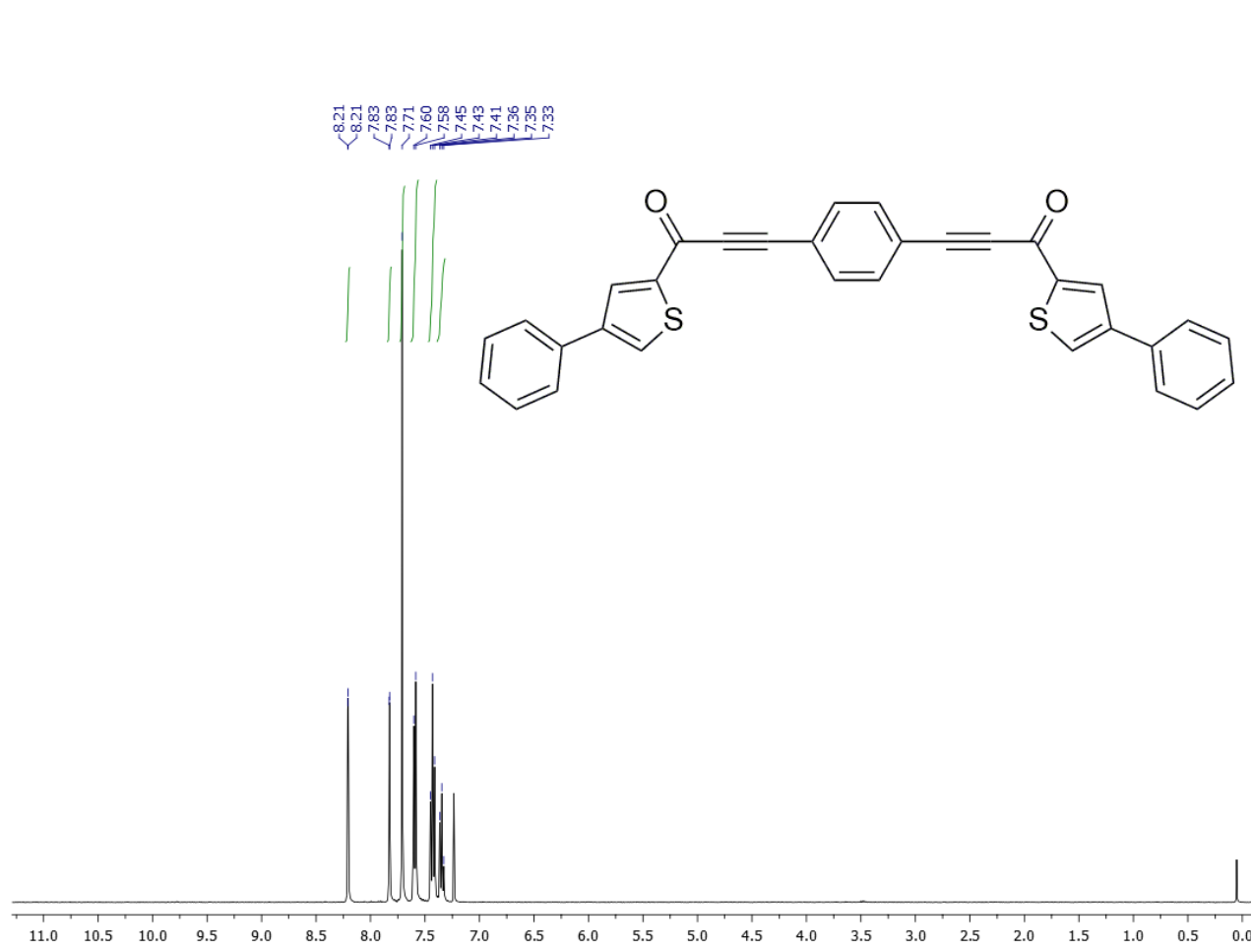
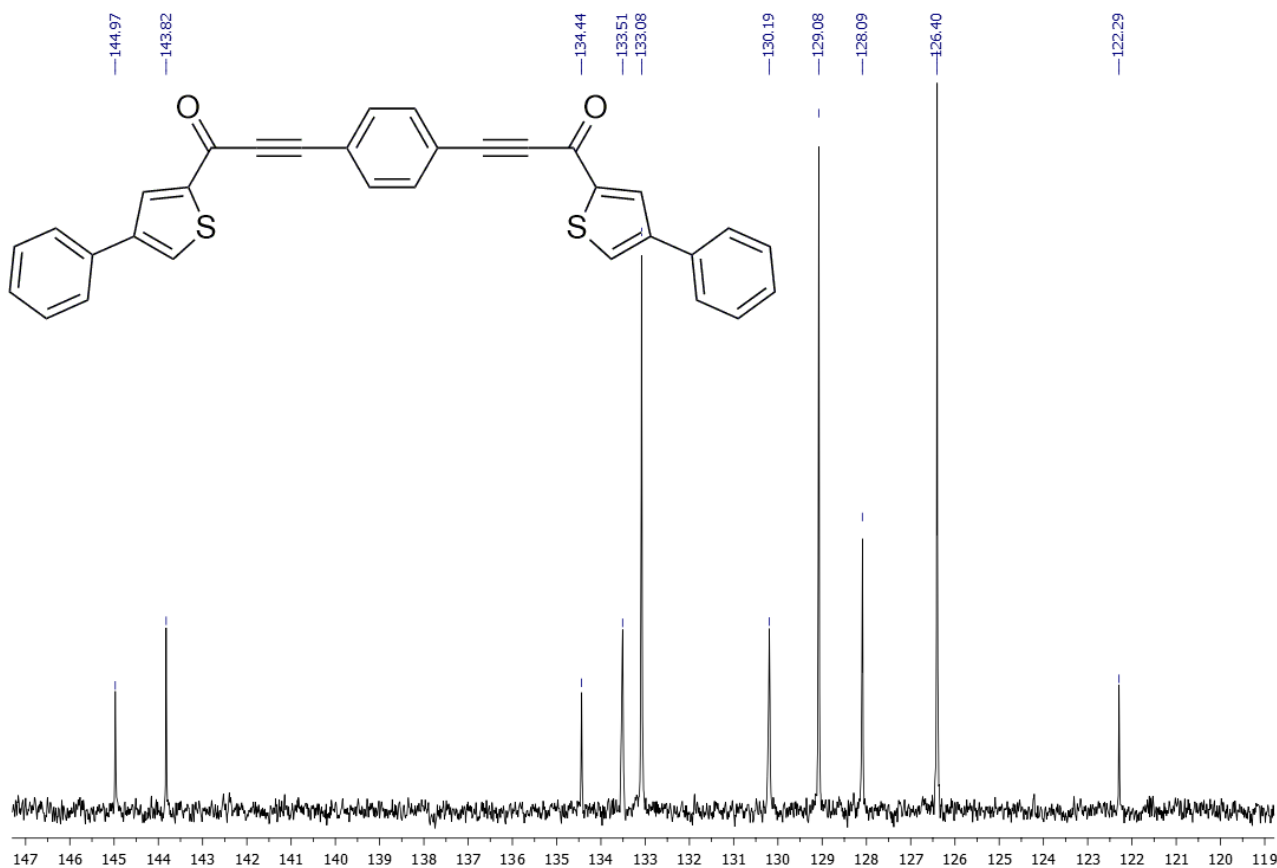
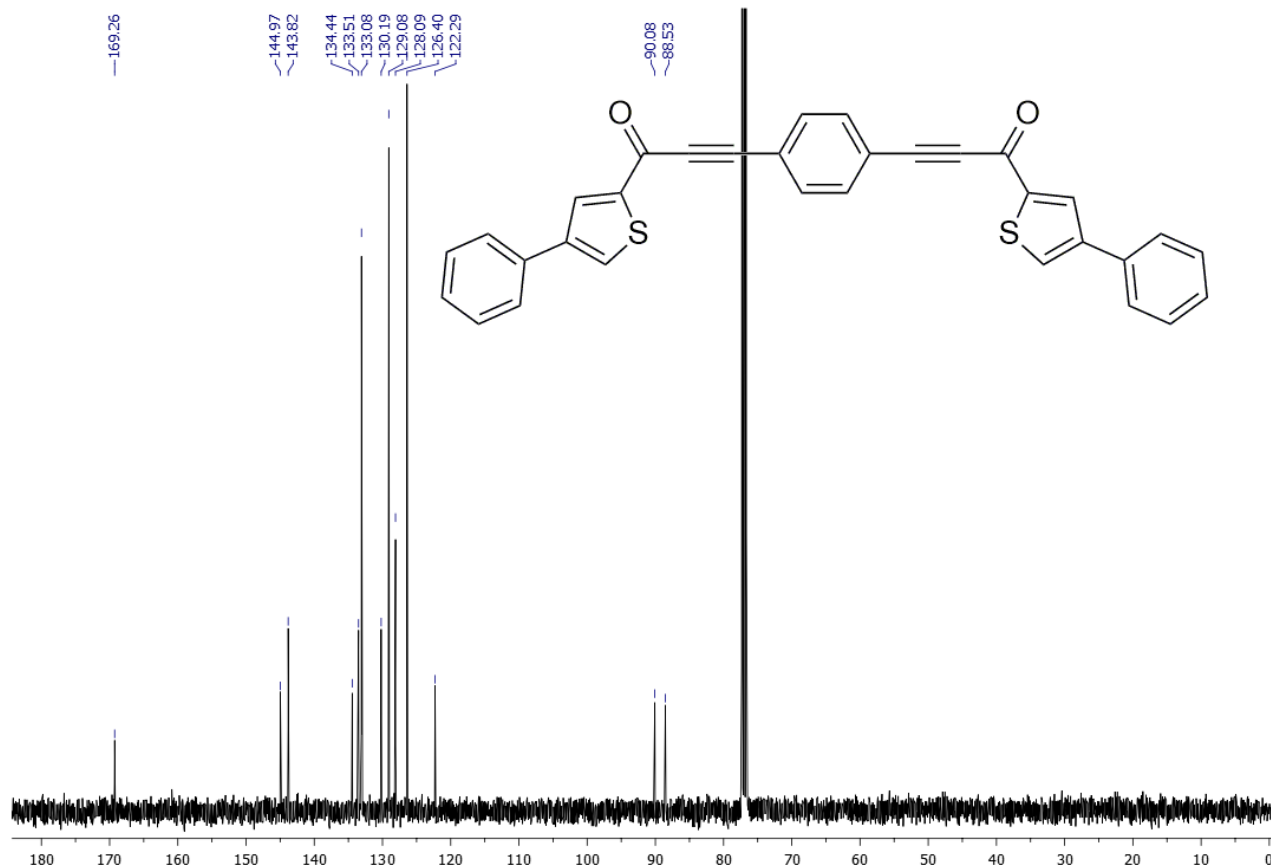
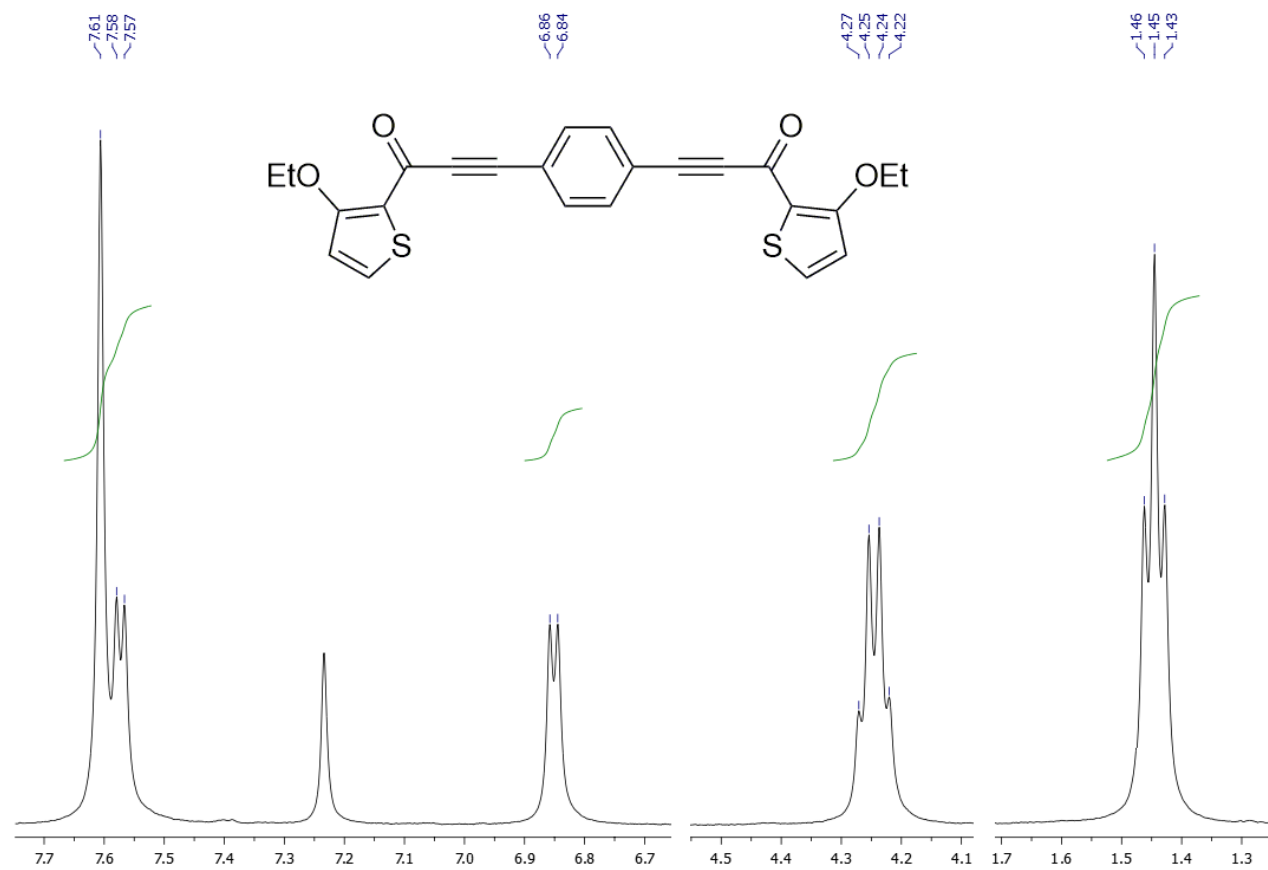
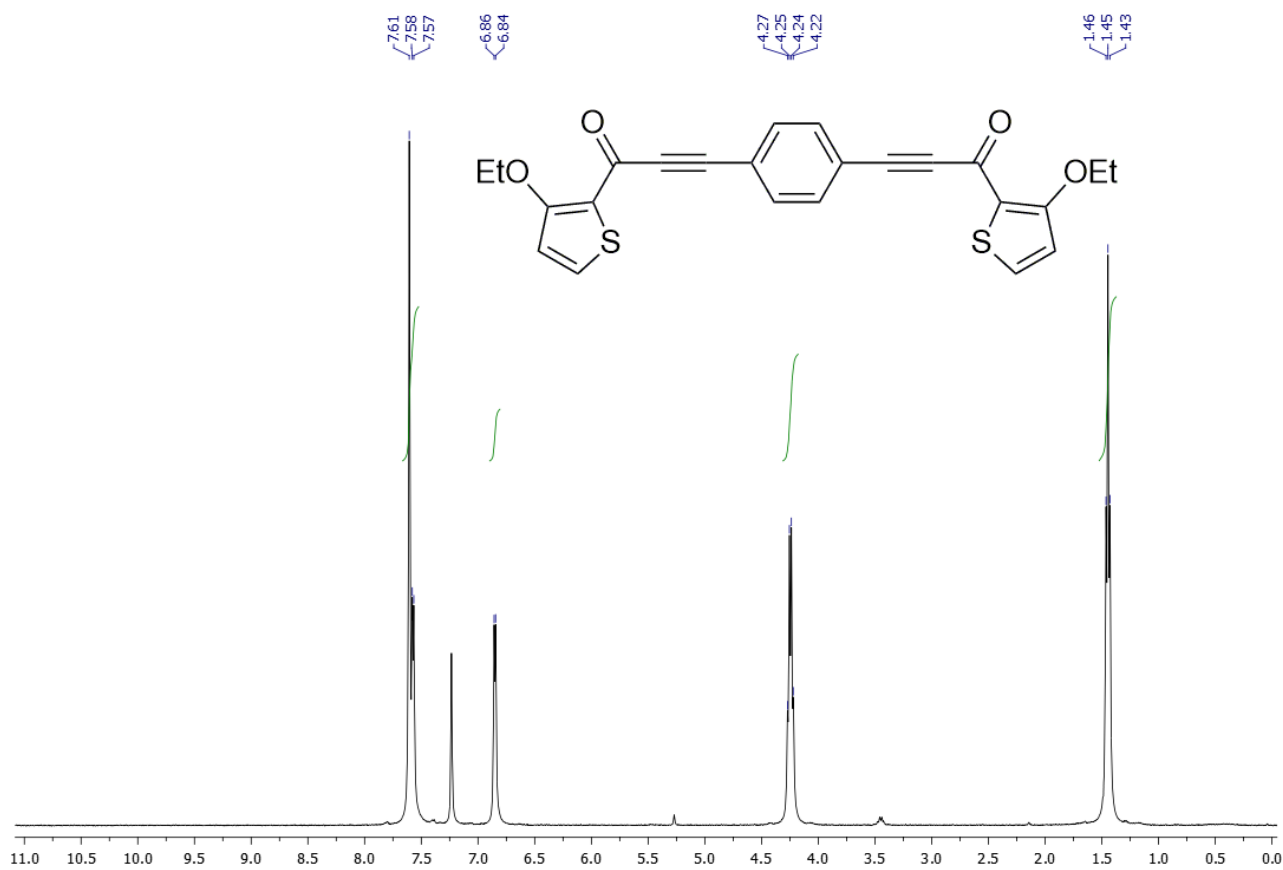


Figure S57. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(4-phenylthiophen-2-yl)prop-2-yn-1-one) (**1d**): full scale spectrum (top) and spectrum expansion (bottom).



5484 **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).



5543 **Figure S59.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one)
5544 (**1e**): full scale spectrum (top) and spectrum expansions (bottom).
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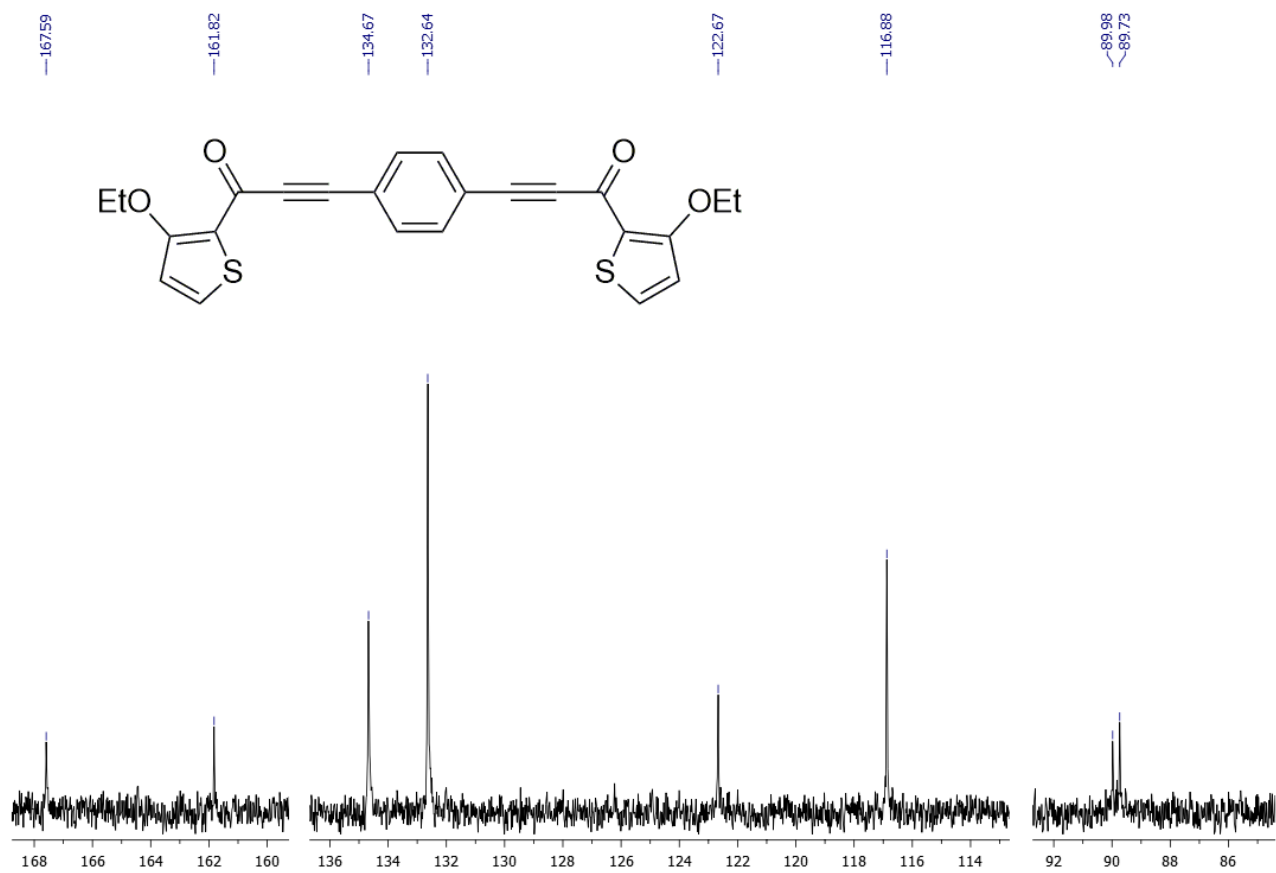
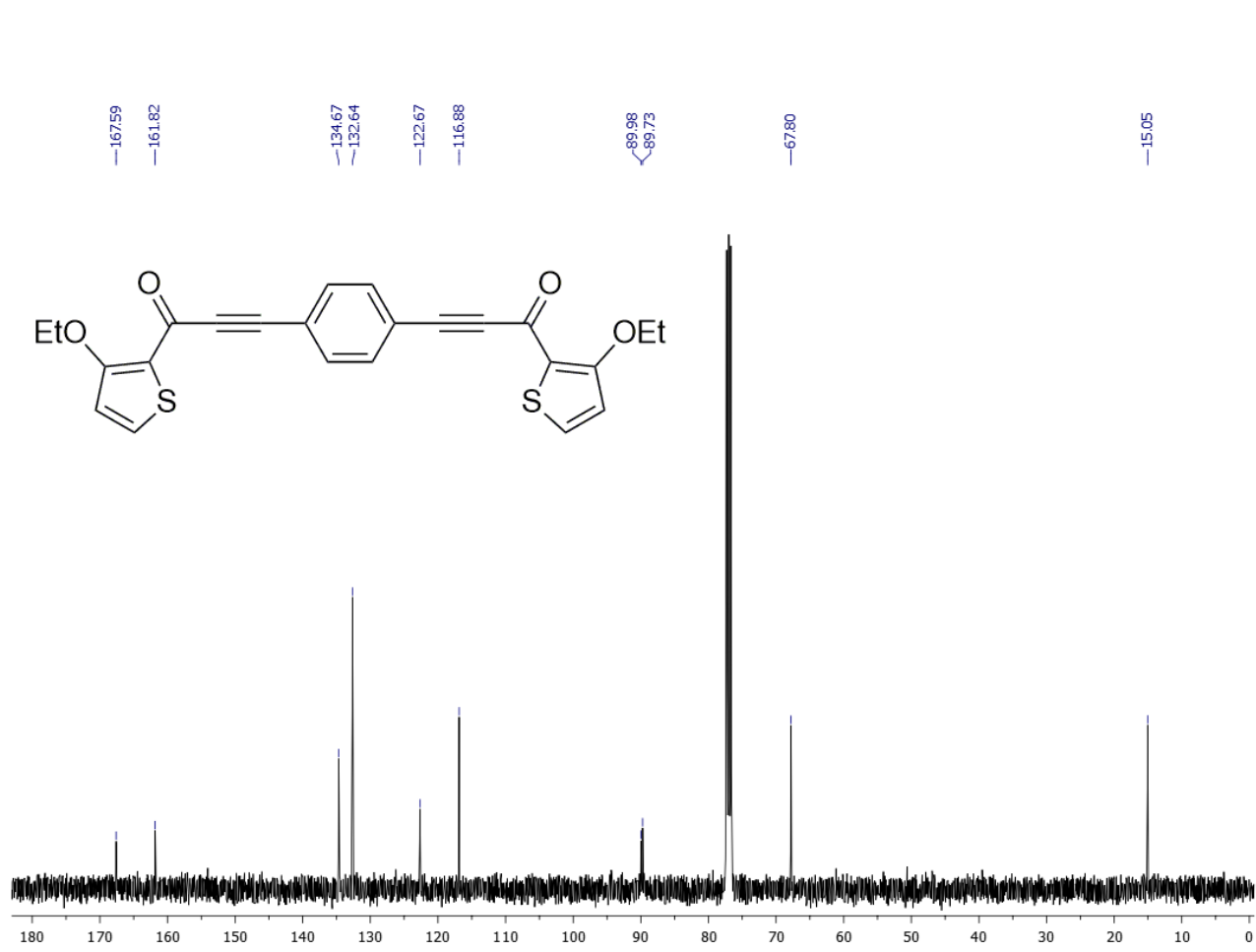


Figure S60. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(3-ethoxythiophen-2-yl)prop-2-yn-1-one) (**1e**): full scale spectrum (top) and spectrum expansions (bottom).

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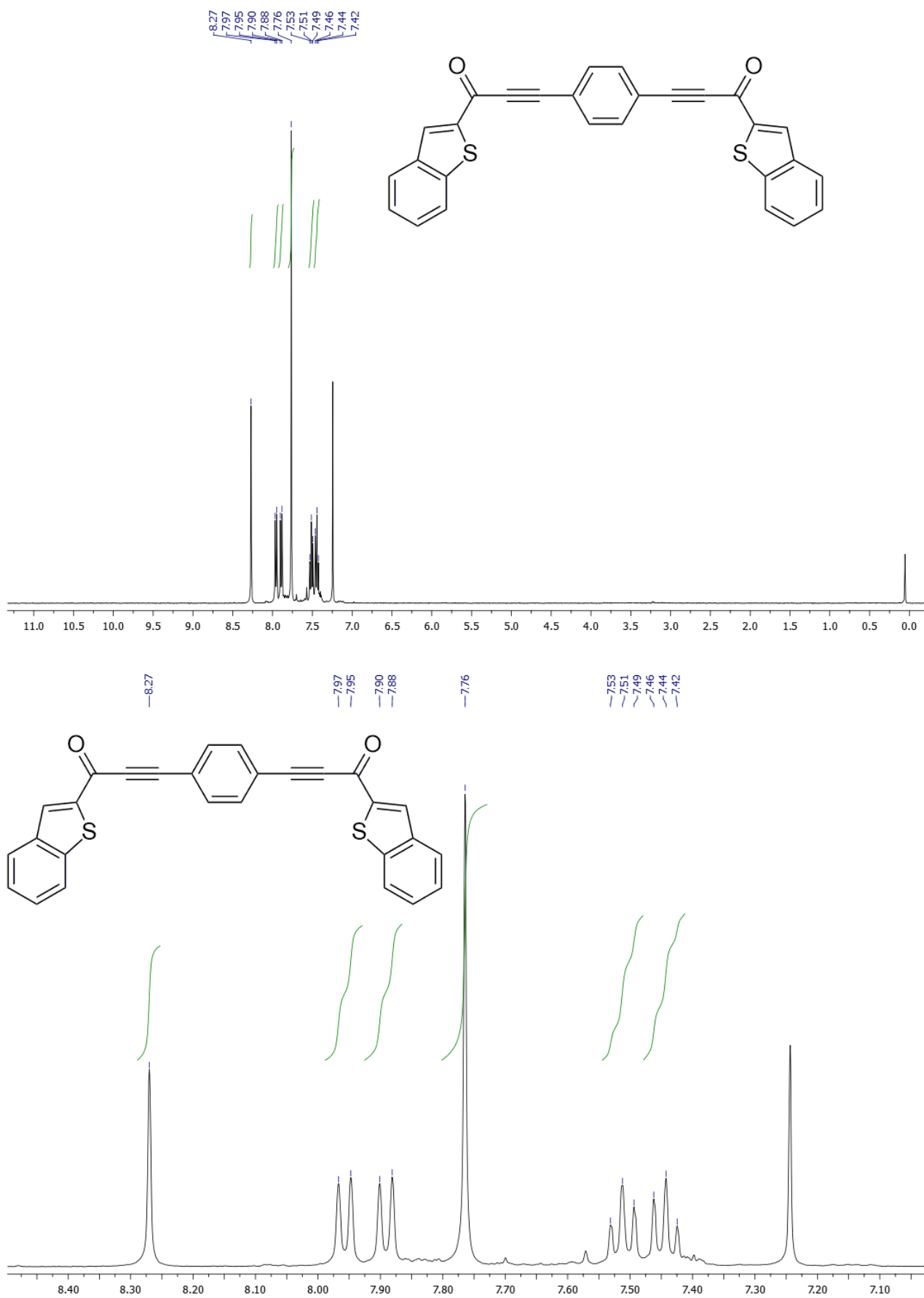
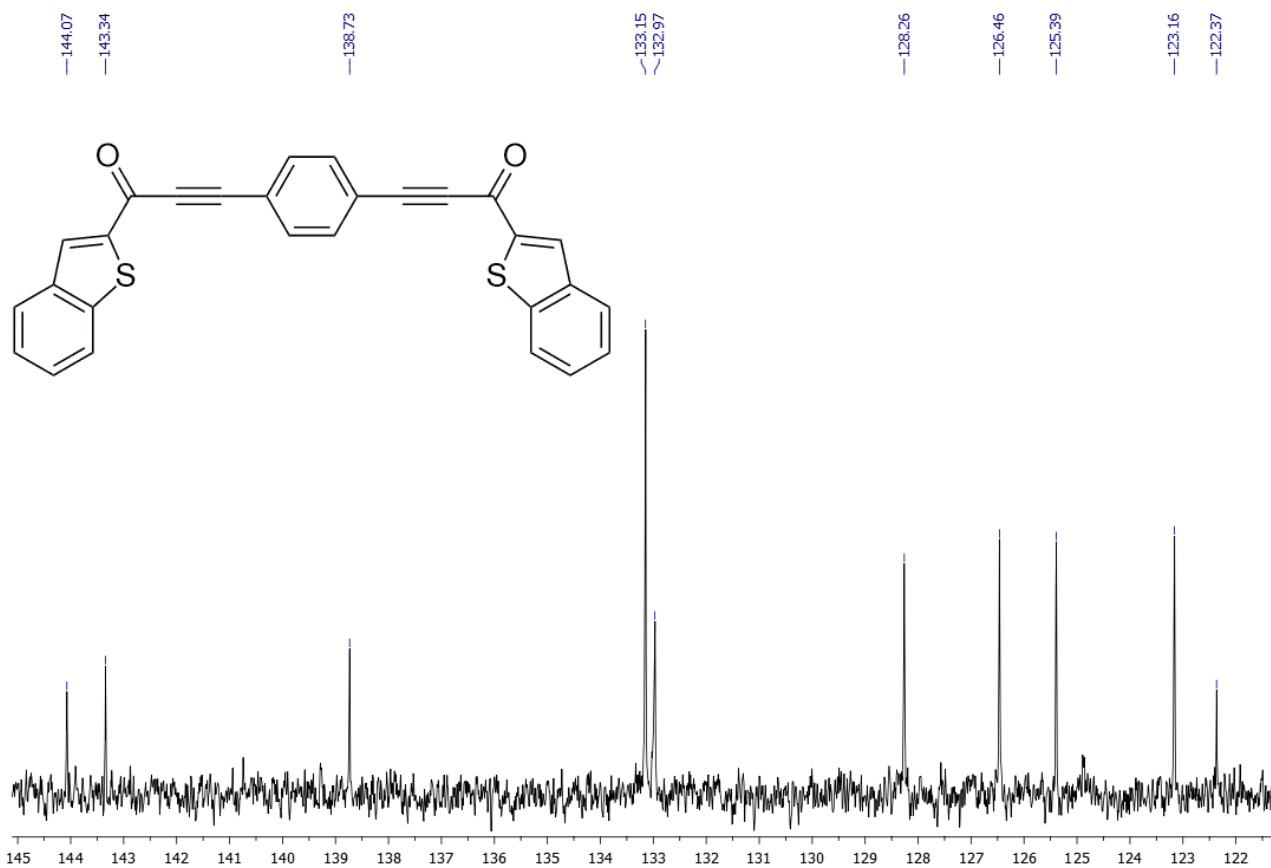
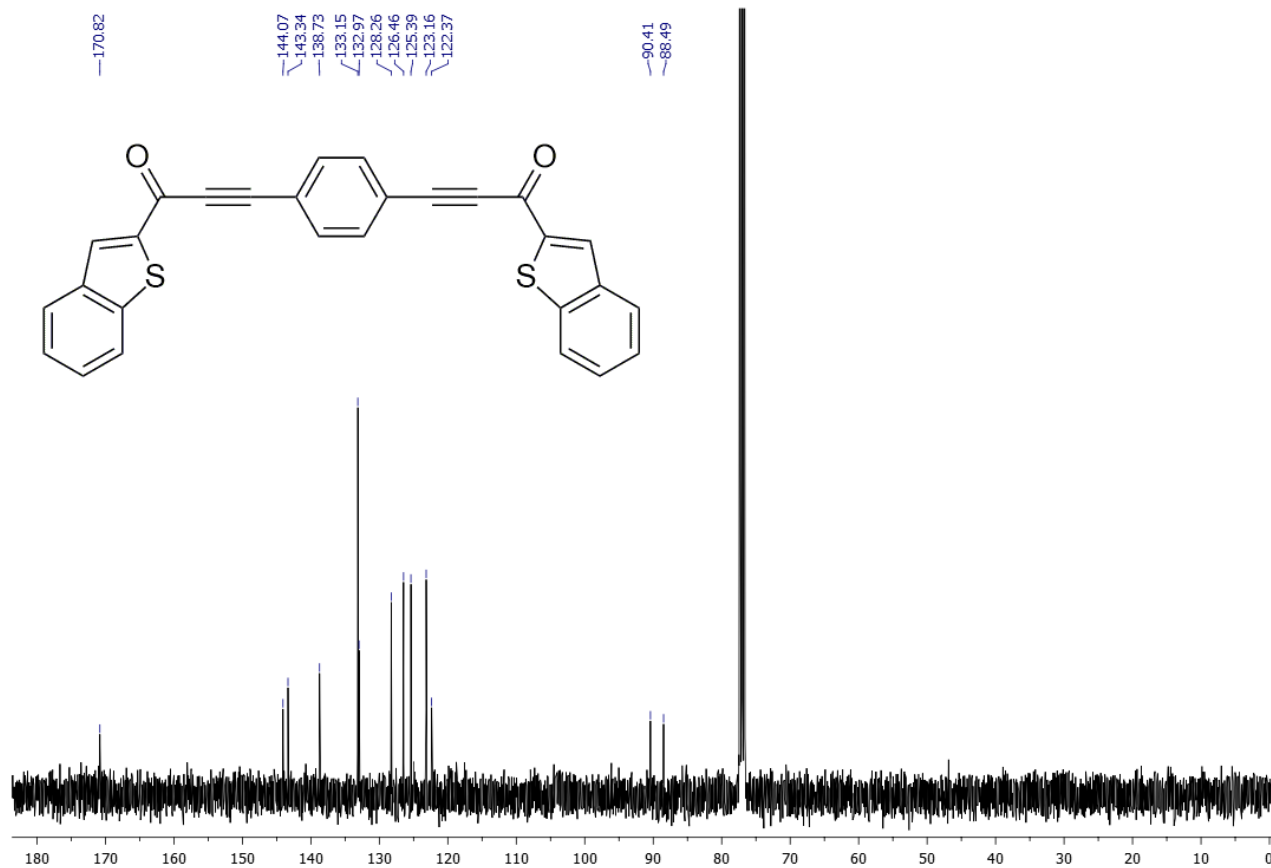


Figure S61. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(benzo[b]thiophen-2-yl)prop-2-yn-1-one) (1f): full scale spectrum (top) and spectrum expansion (bottom).



5720 **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).

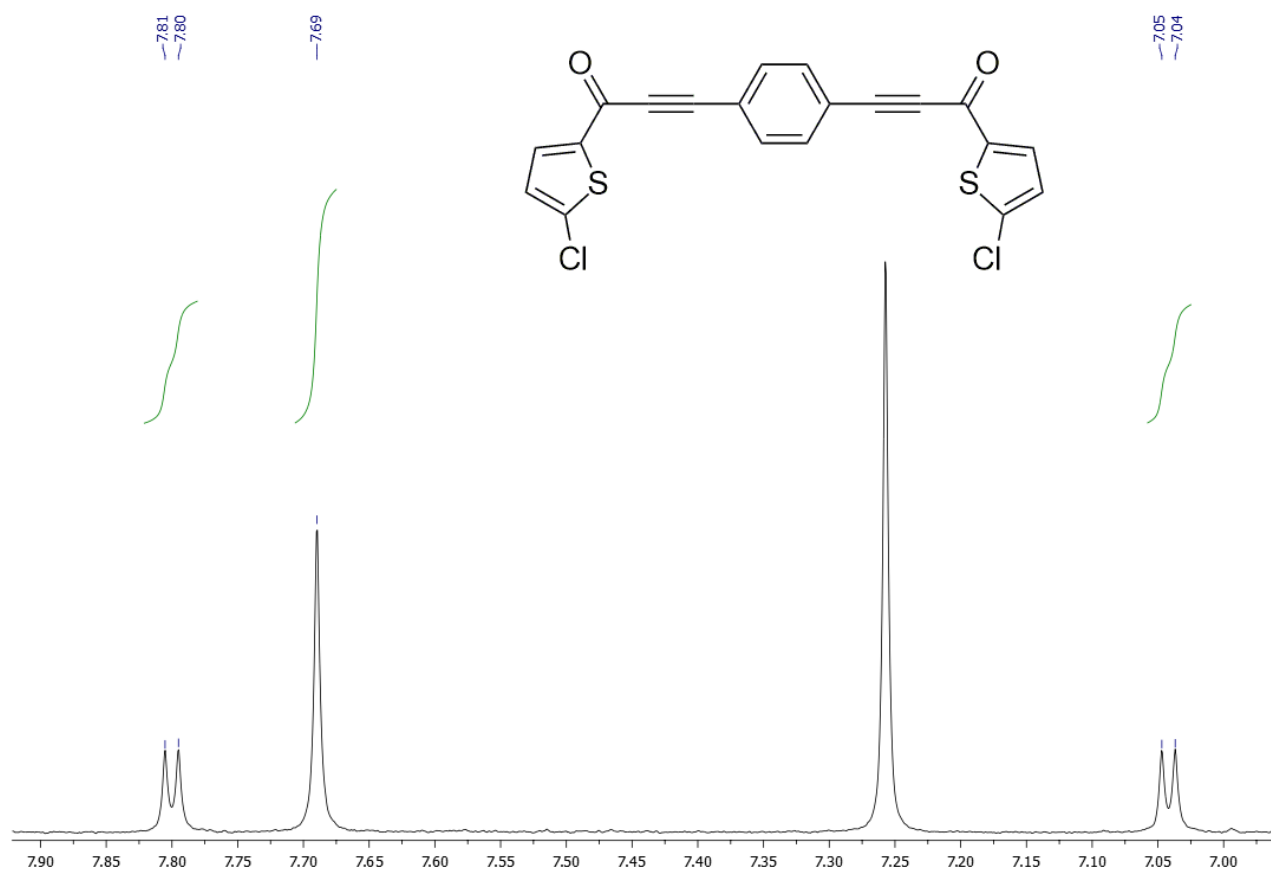
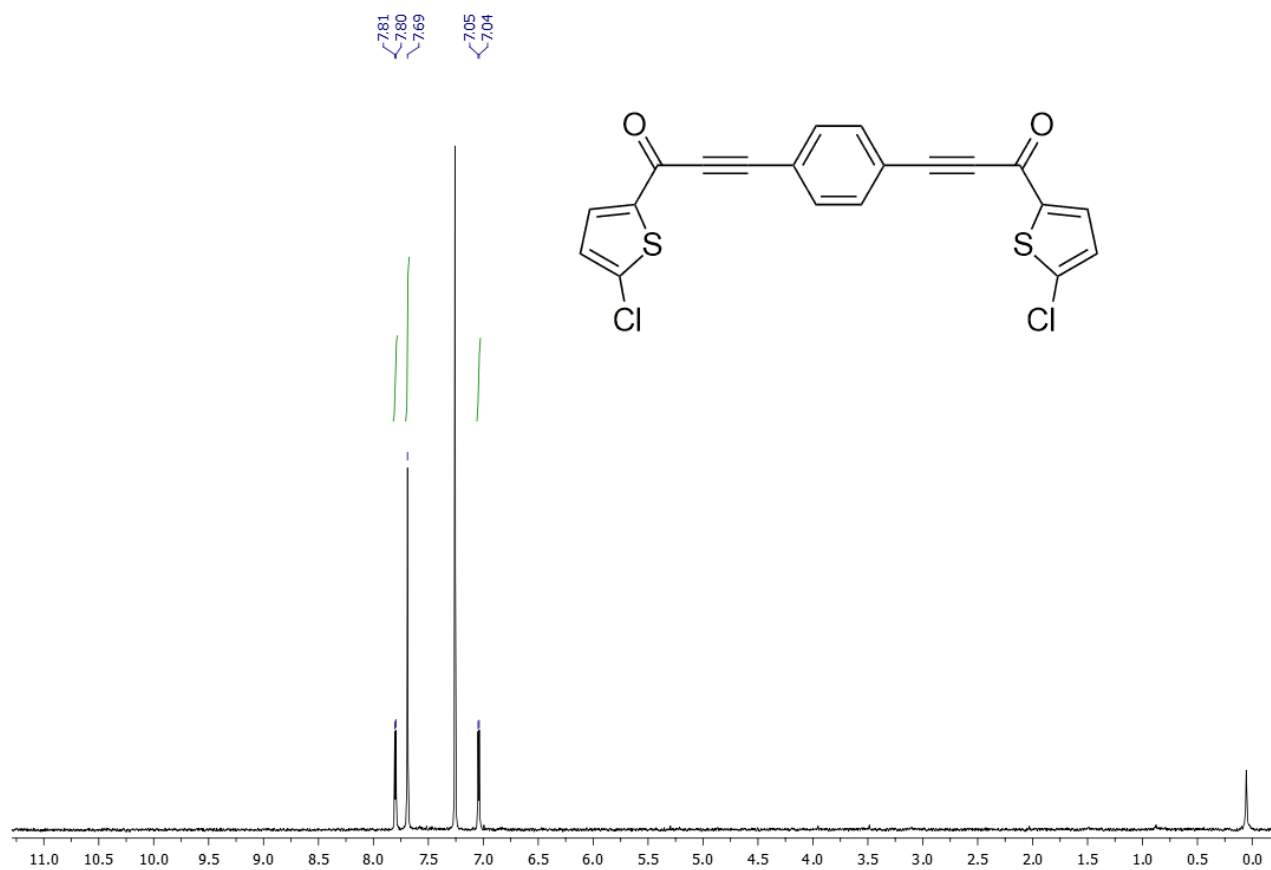
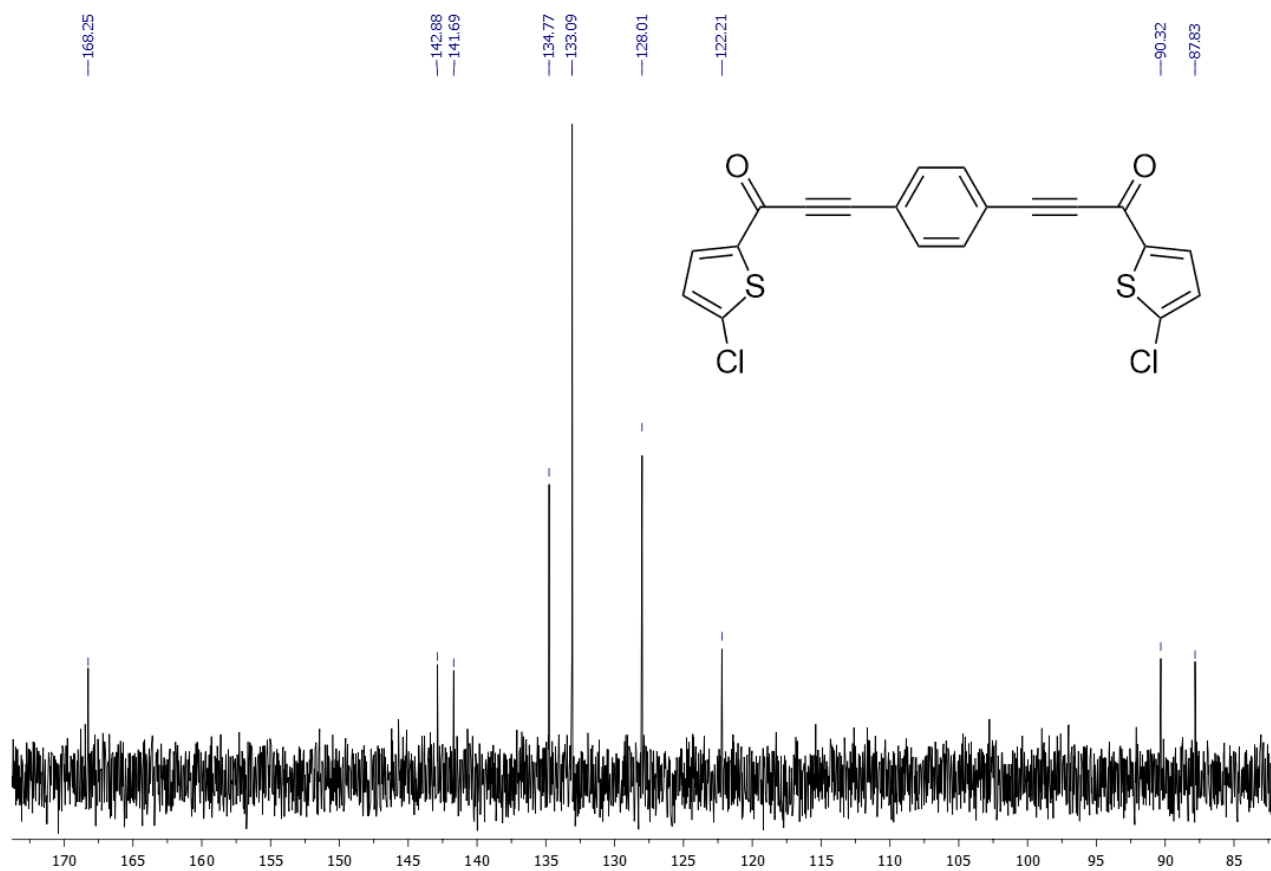
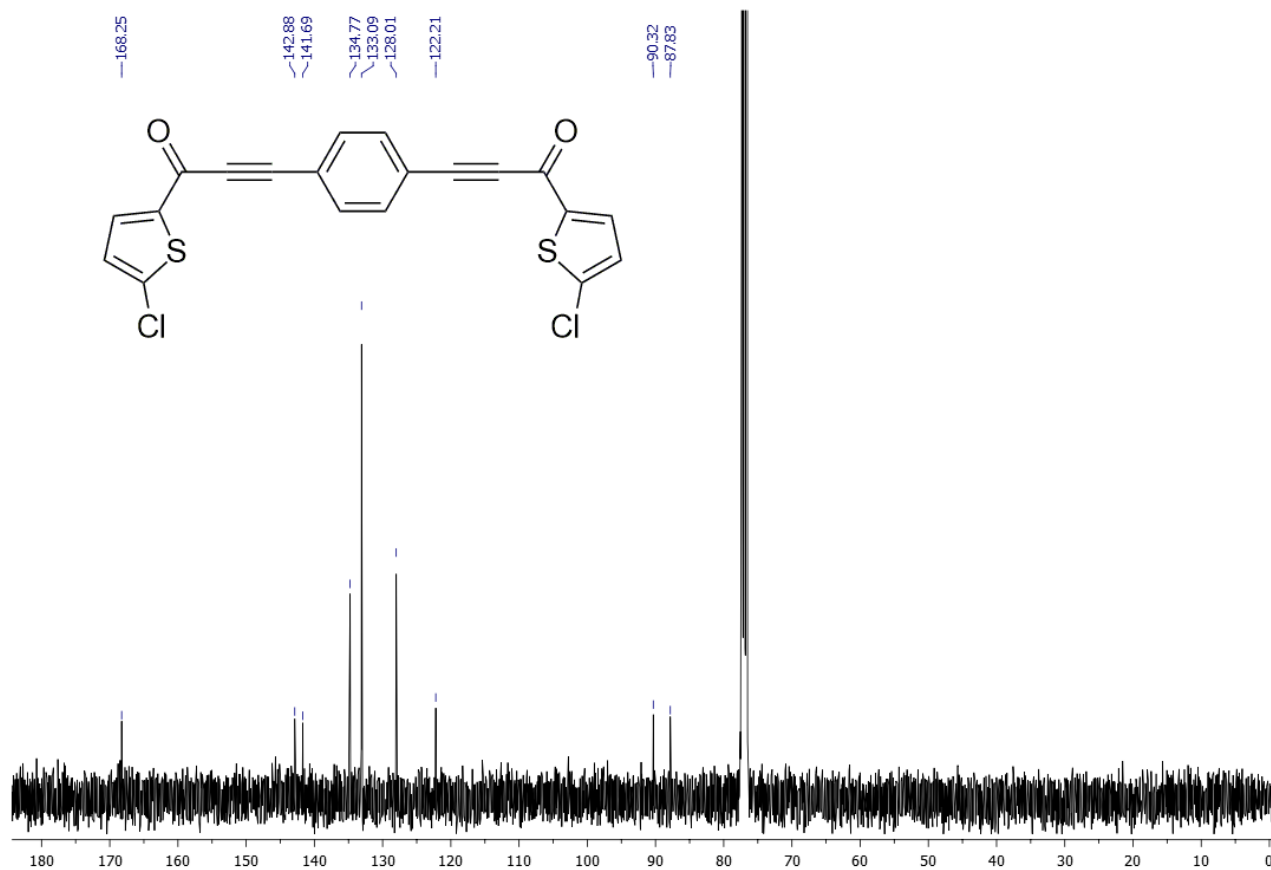
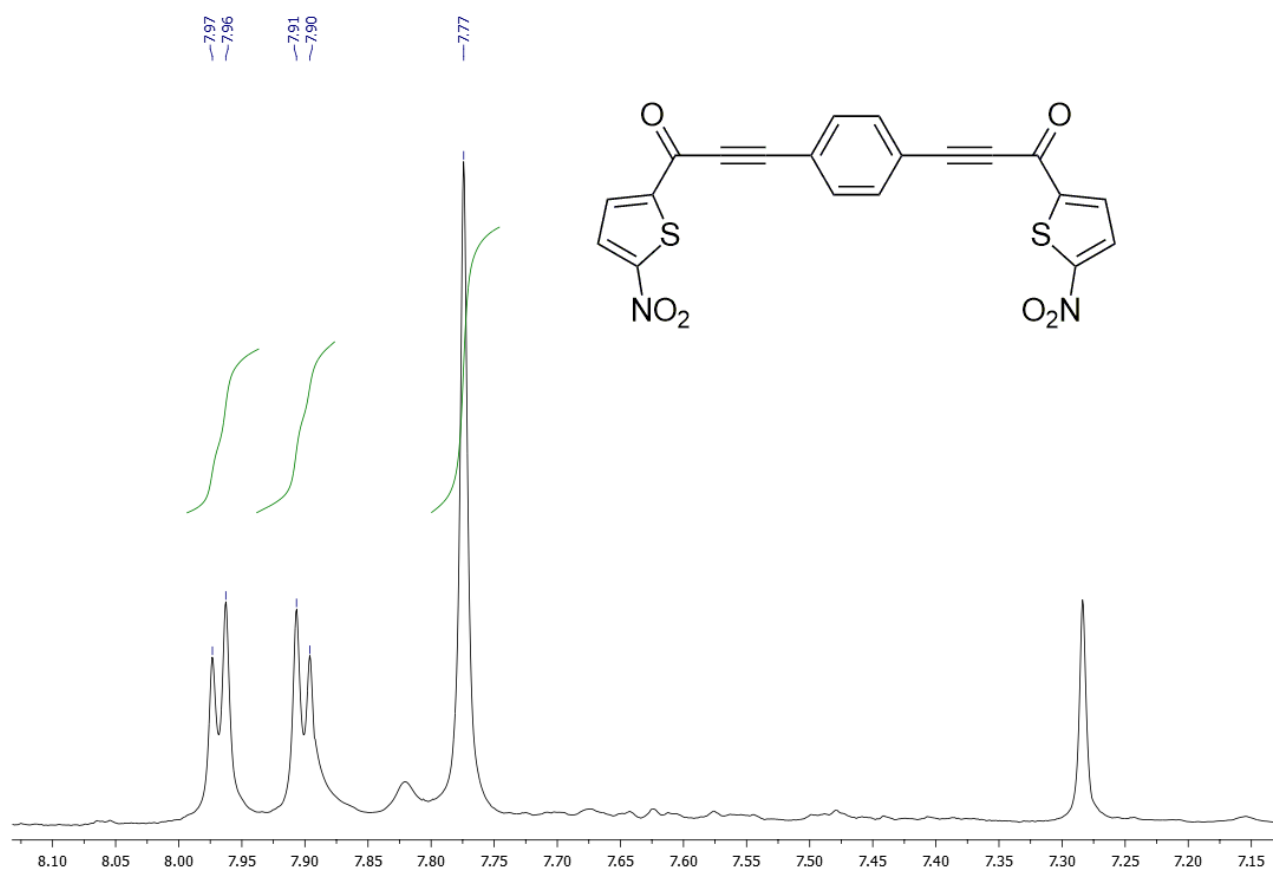
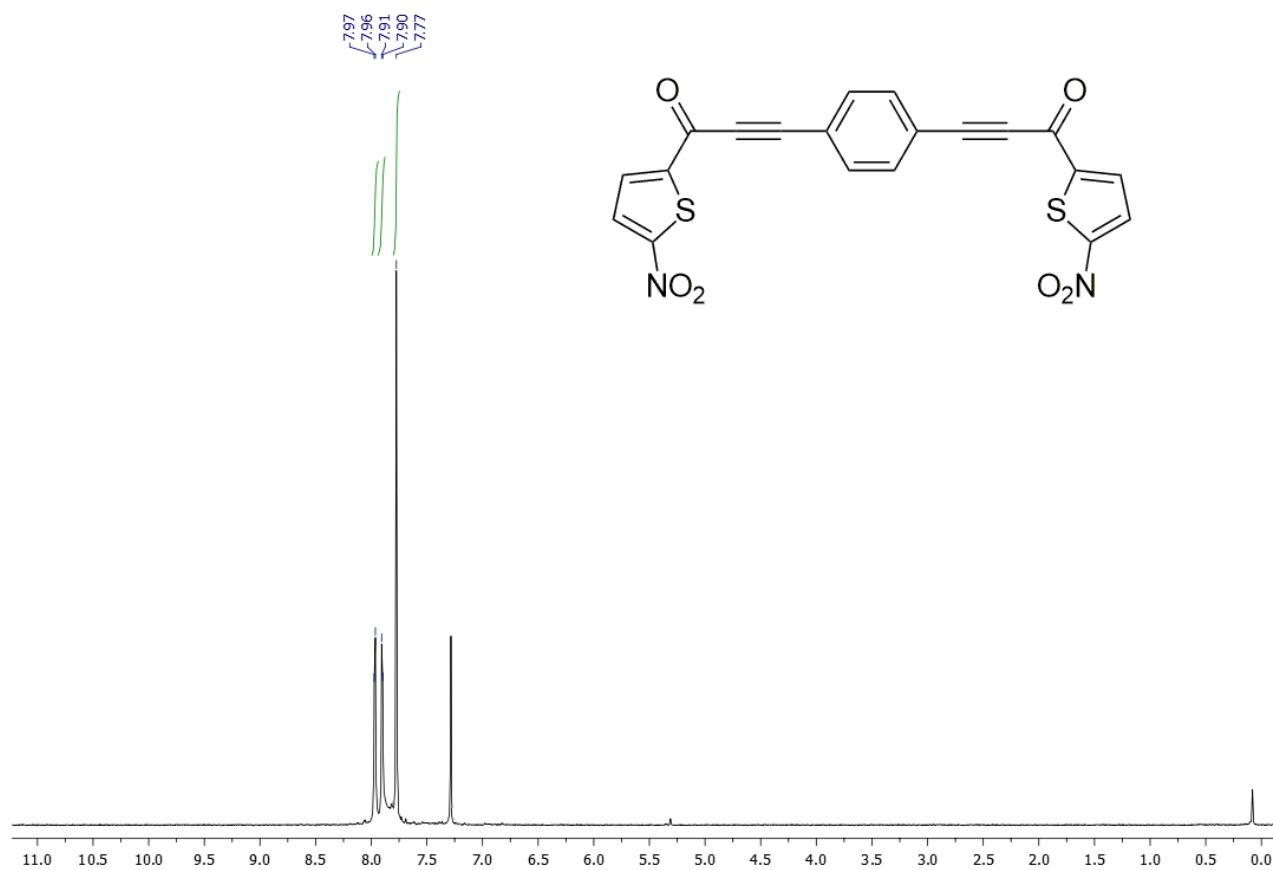


Figure S63. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(5-chlorothiophen-2-yl)prop-2-yn-1-one) (**1g**): full scale spectrum (top) and spectrum expansion (bottom).



5838 **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)
5839 (**1g**): full scale spectrum (top) and spectrum expansion (bottom).



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5897 **Figure S65.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**):
5898 full scale spectrum (top) and spectrum expansion (bottom).
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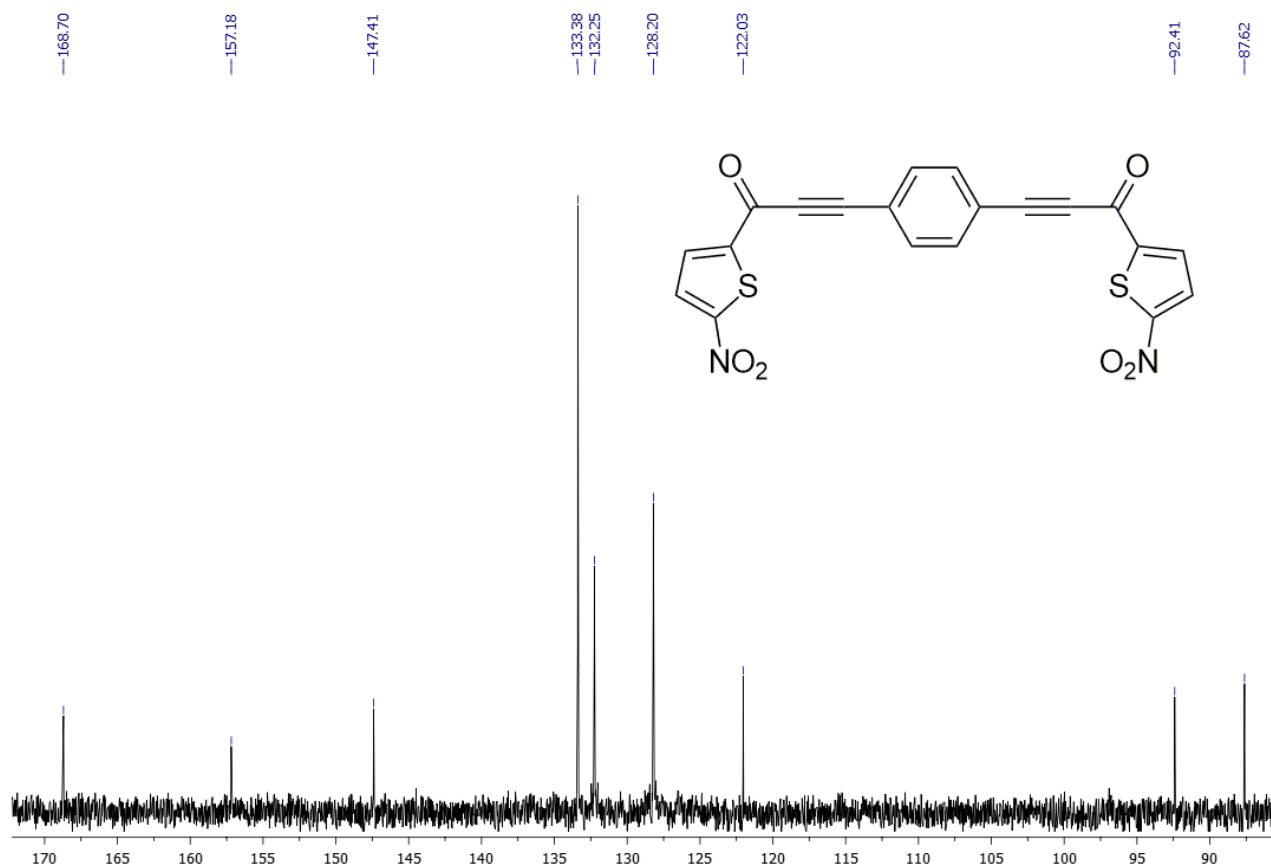
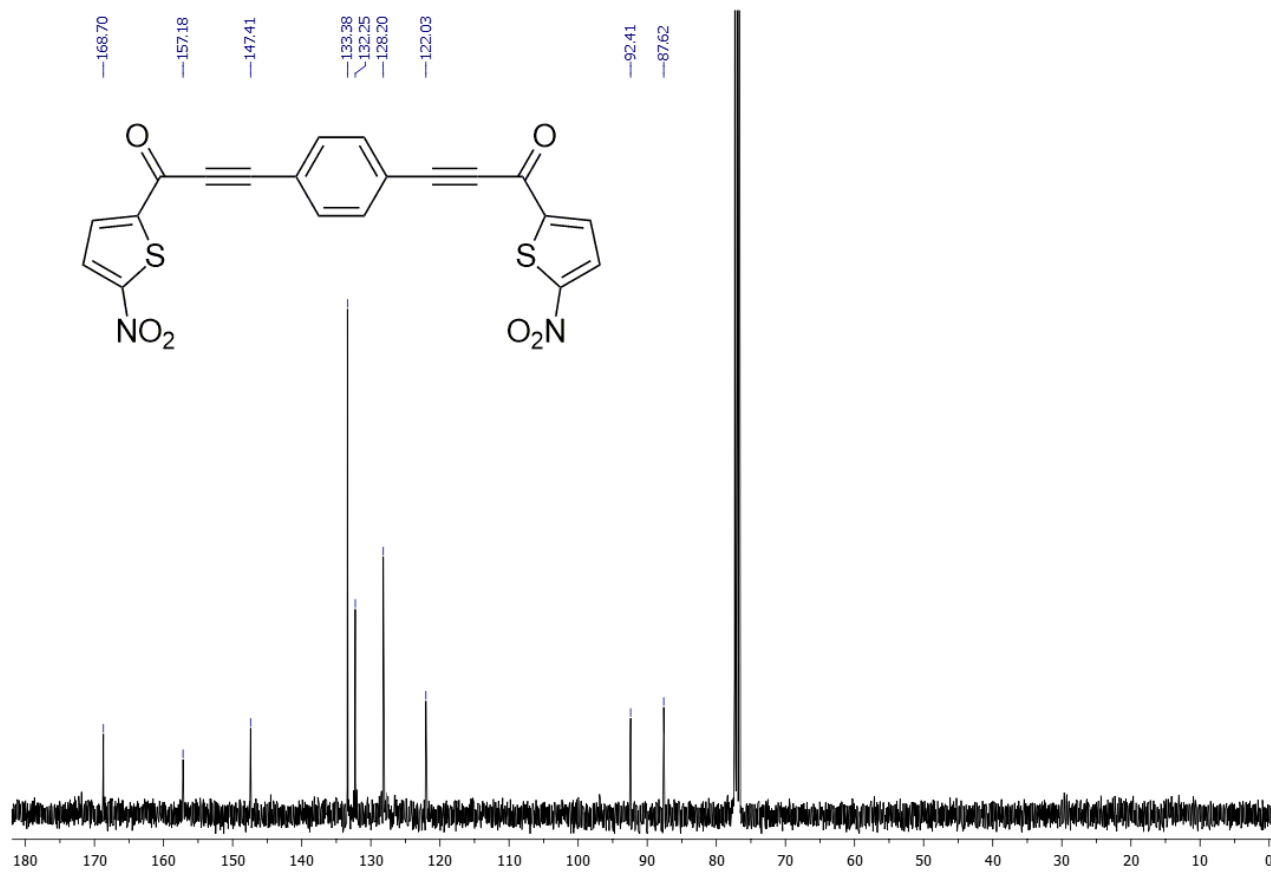
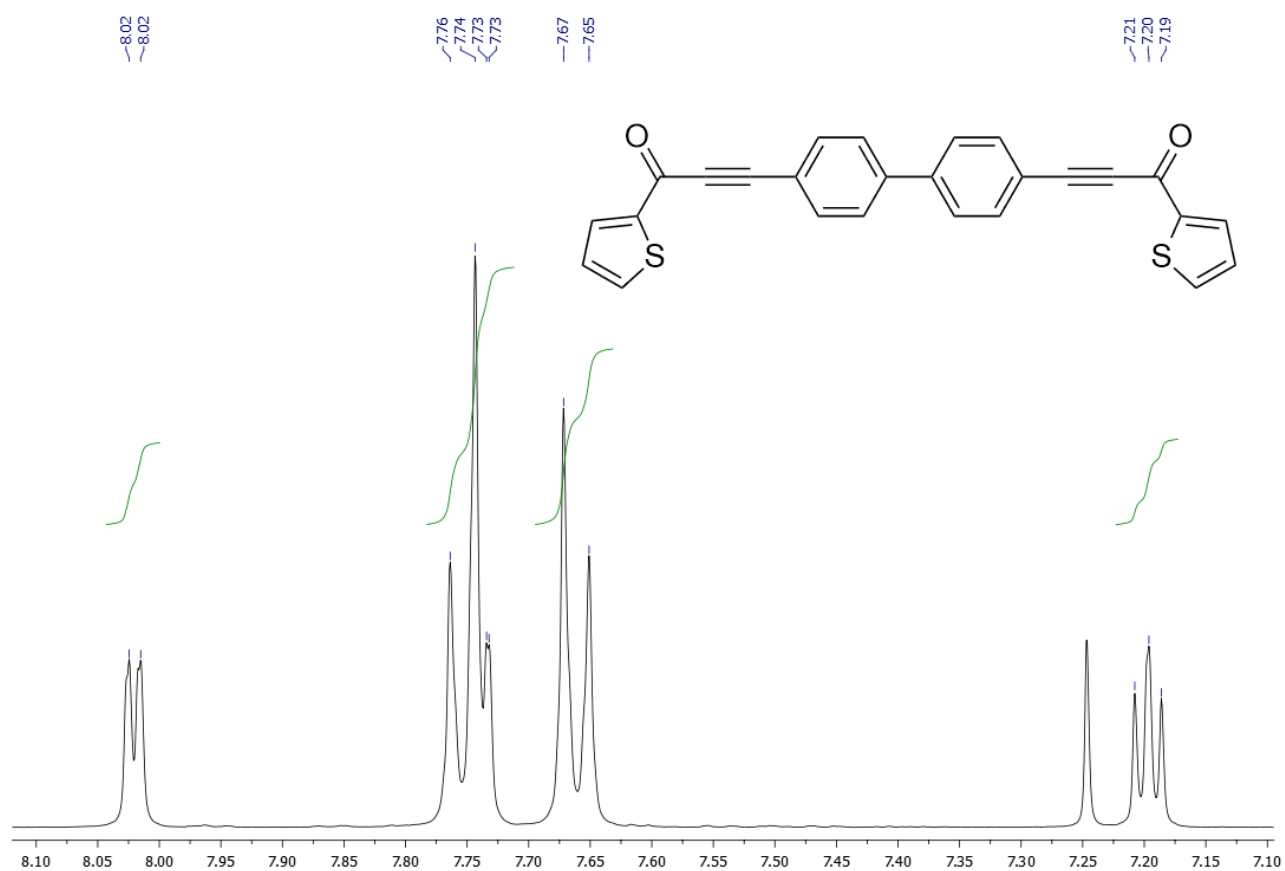
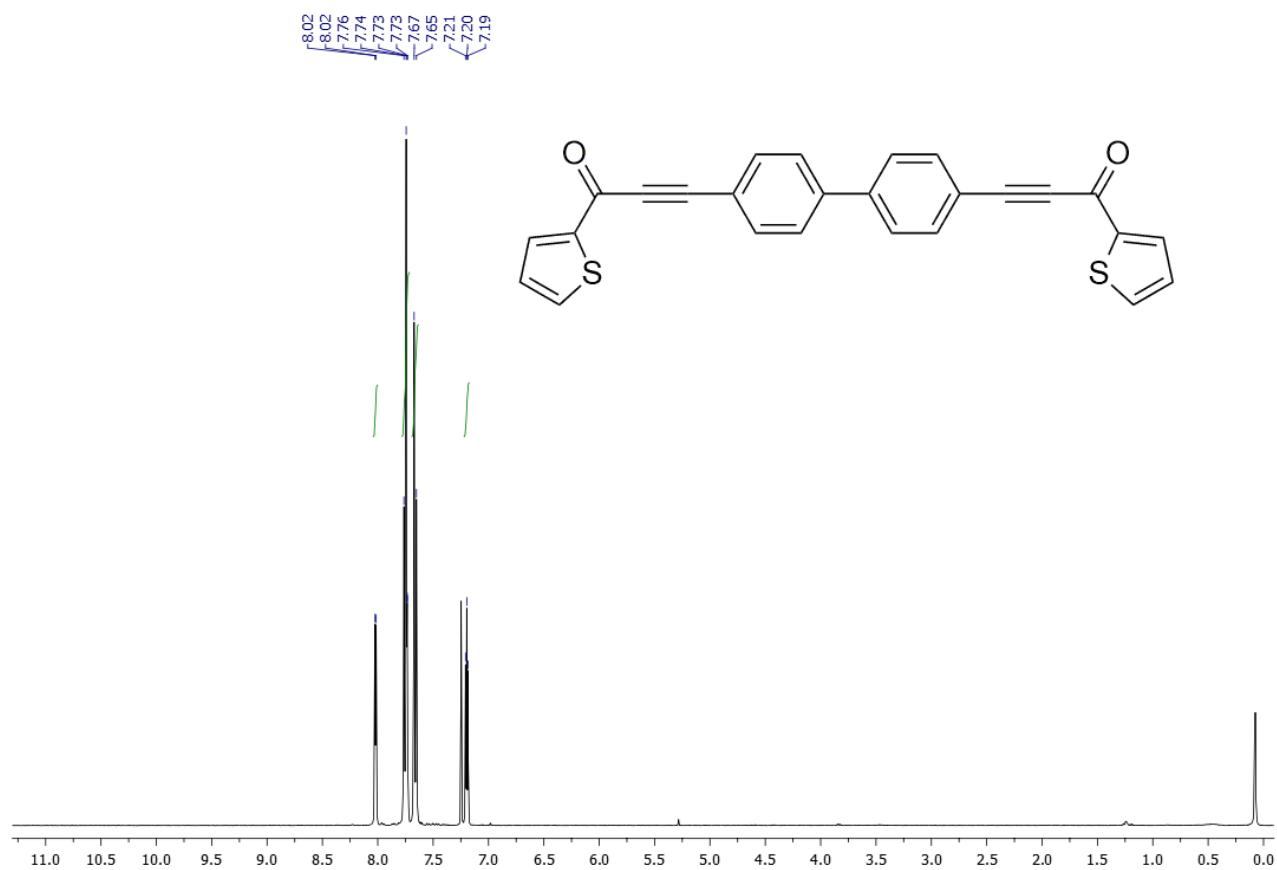
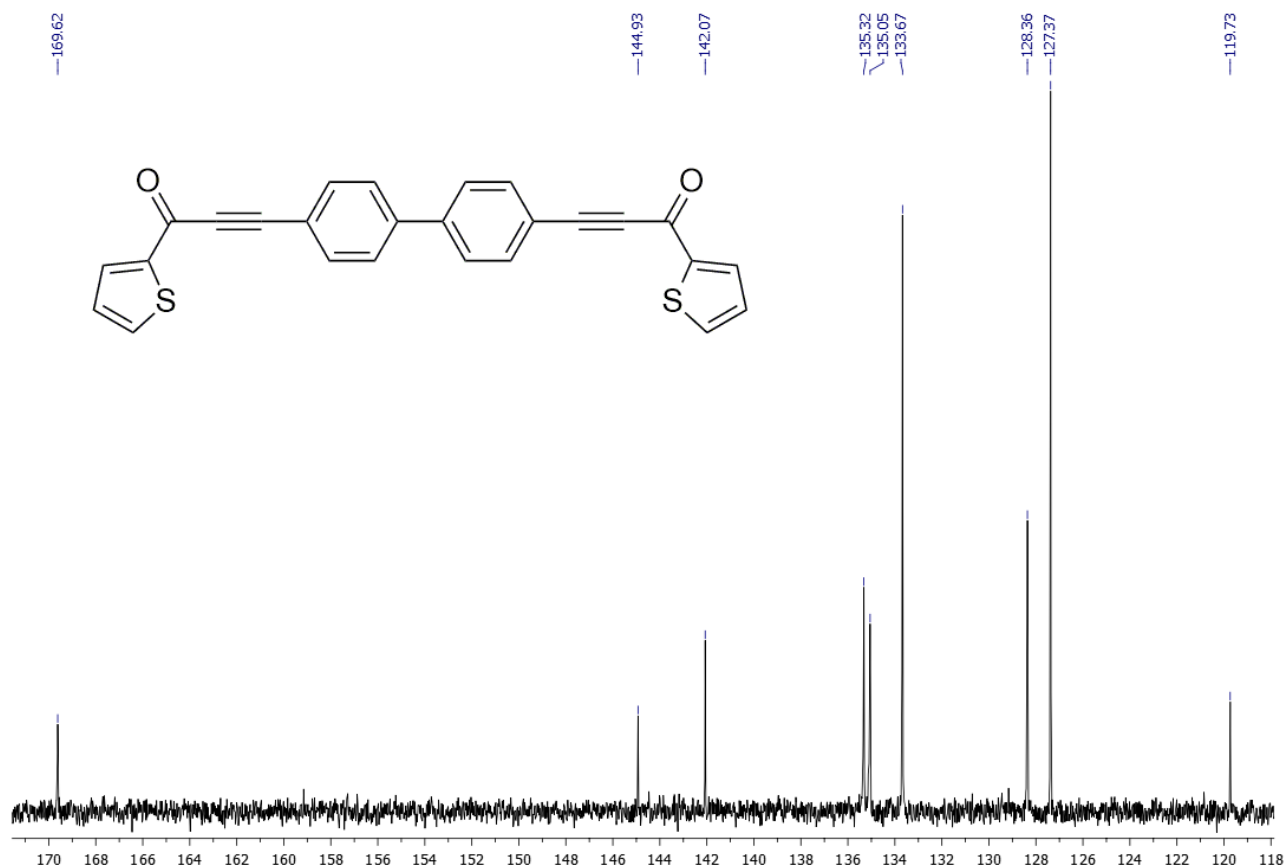
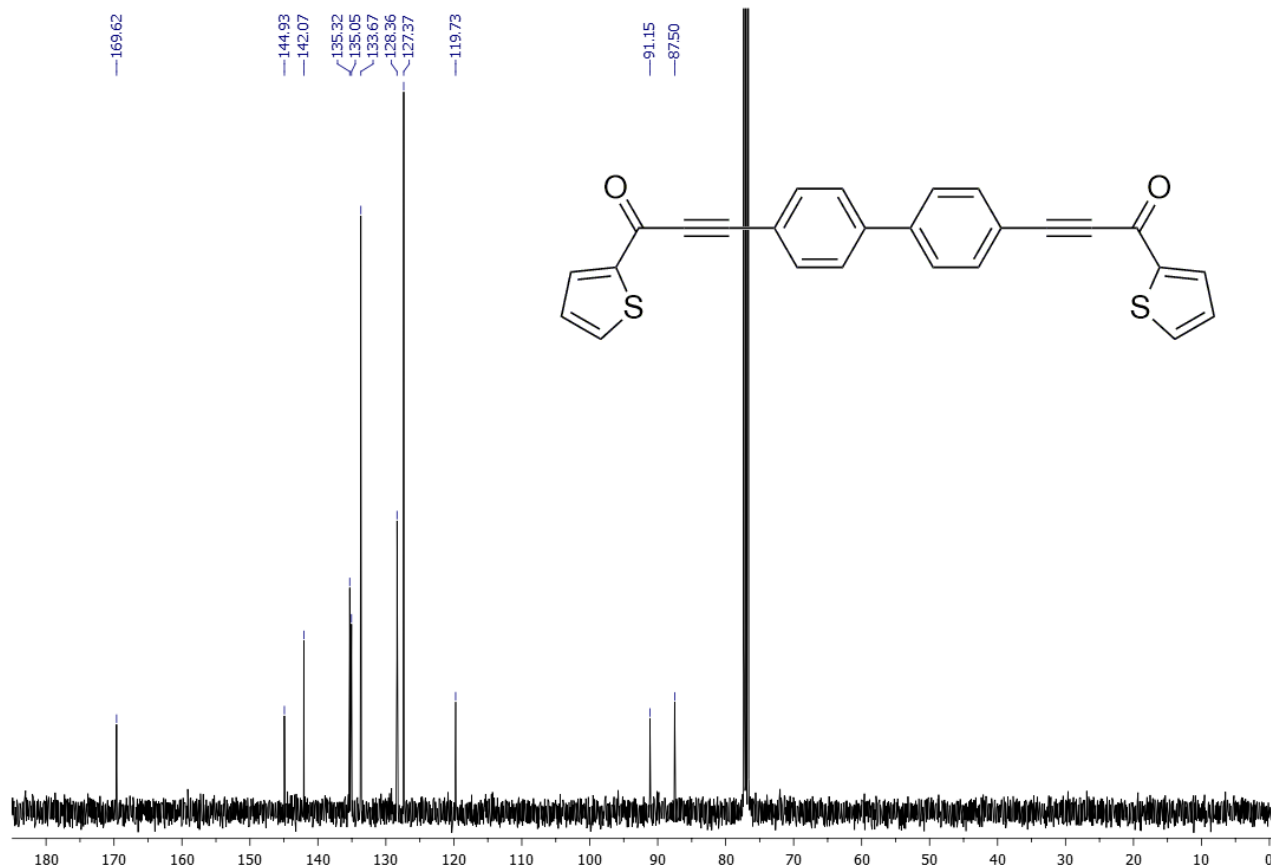


Figure S66. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 3,3'-(1,4-phenylene)bis(1-(5-nitrothiophen-2-yl)prop-2-yn-1-one) (**1h**): full scale spectrum (top) and spectrum expansion (bottom).



6015 **Figure S67.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one)
6016 (10a): full scale spectrum (top) and spectrum expansion (bottom).
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6074 **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)
6075 (**10a**): full scale spectrum (top) and spectrum expansion (bottom).

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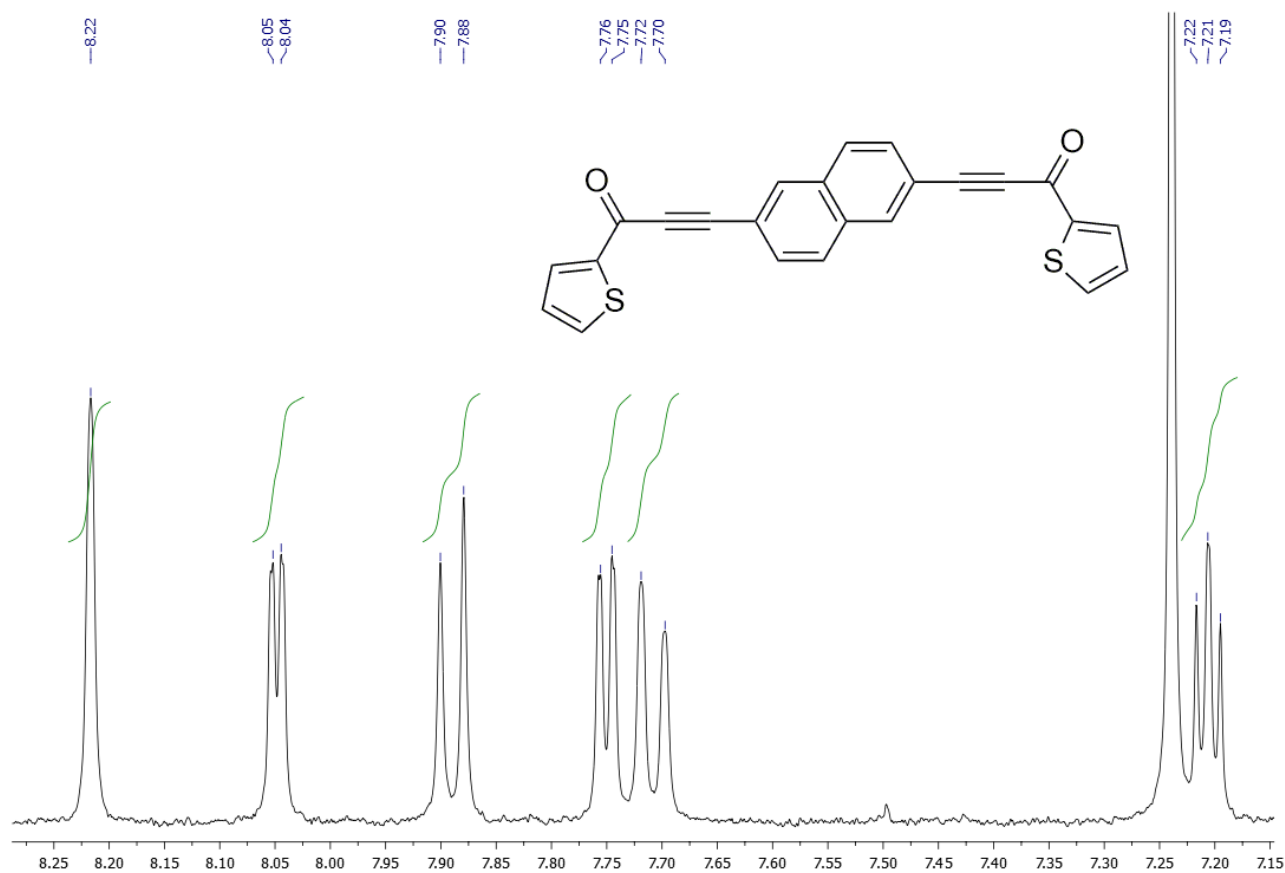
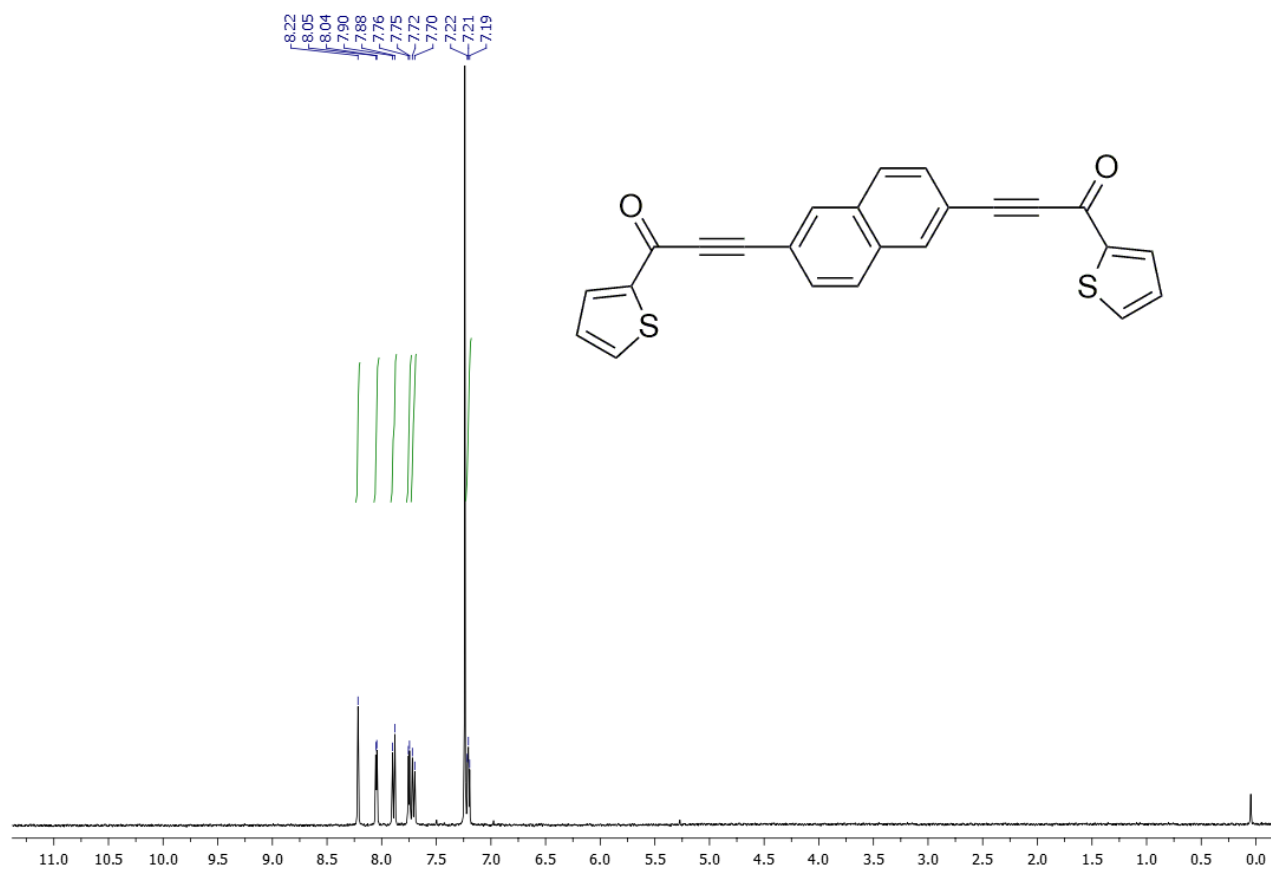


Figure S69. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**): full scale spectrum (top) and spectrum expansion (bottom).

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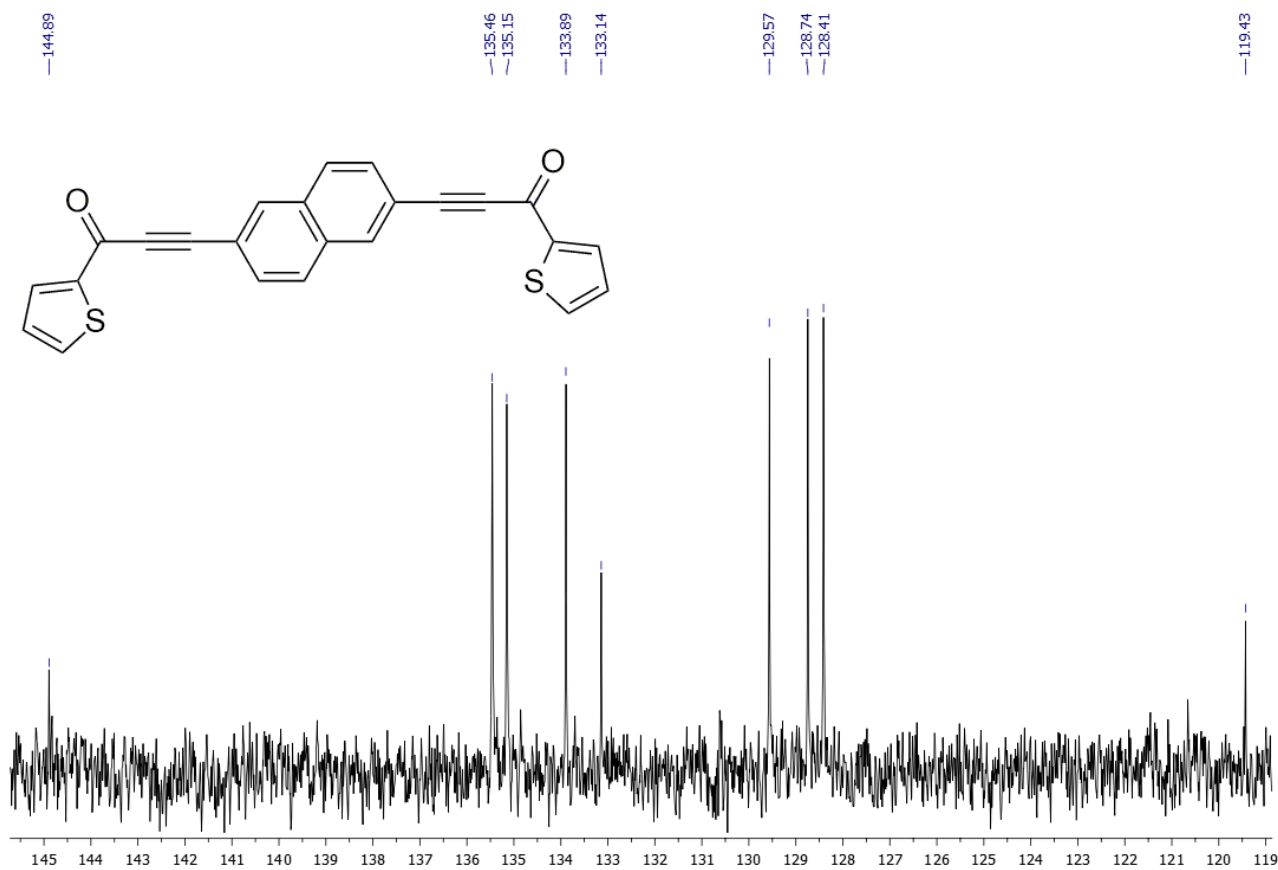
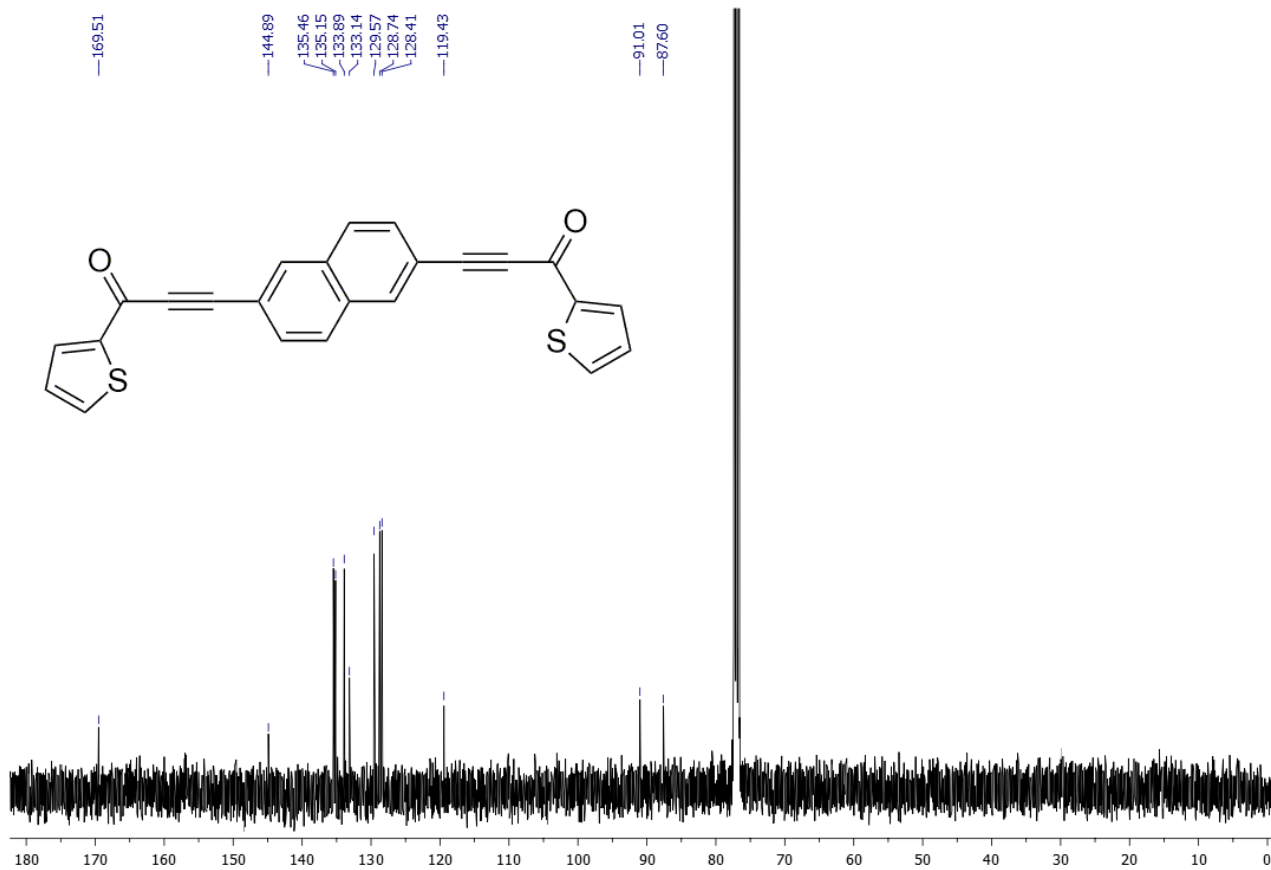


Figure S70. ¹³C-NMR spectrum (100 MHz, CDCl₃) of 3,3'-(naphthalene-2,6-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10b**): full scale spectrum (top) and spectrum expansion (bottom).

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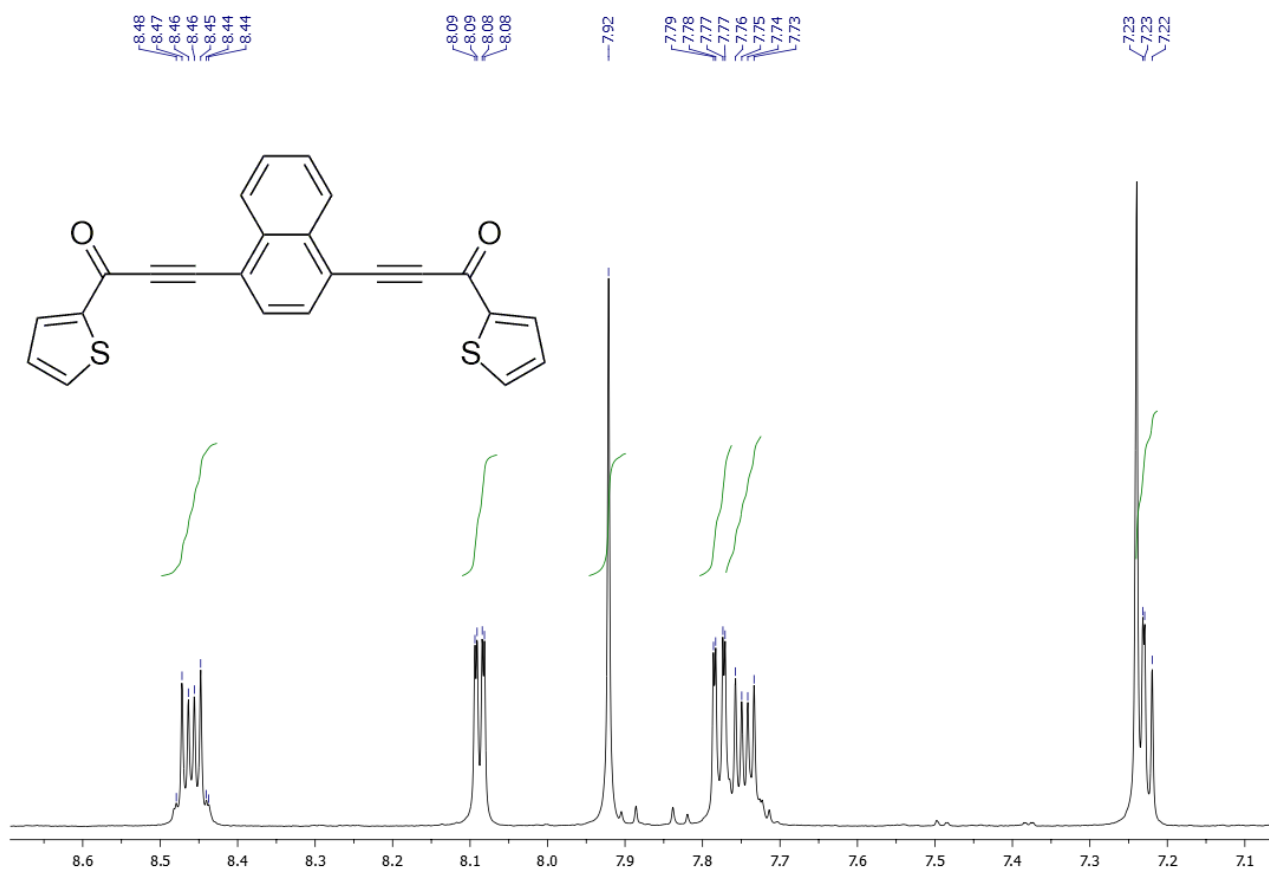
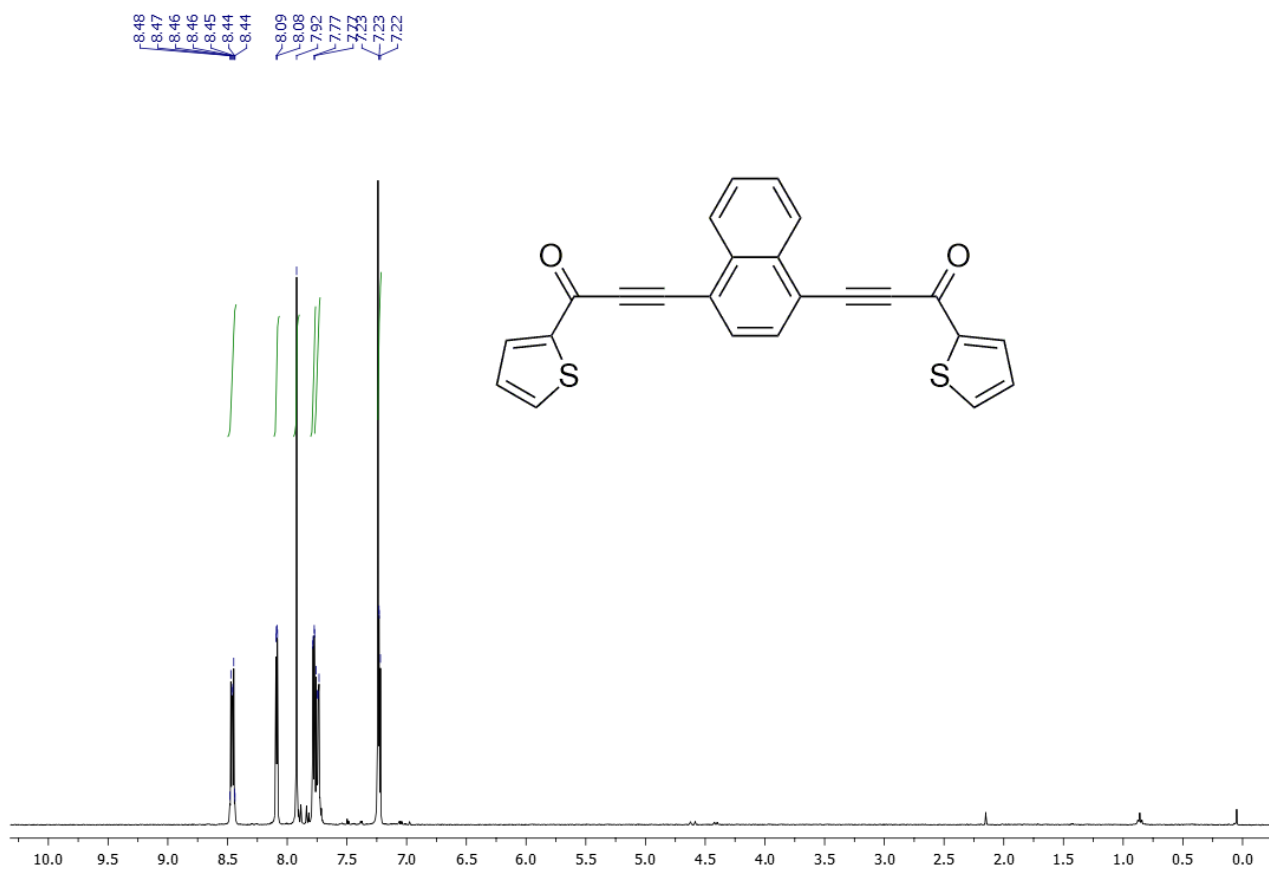
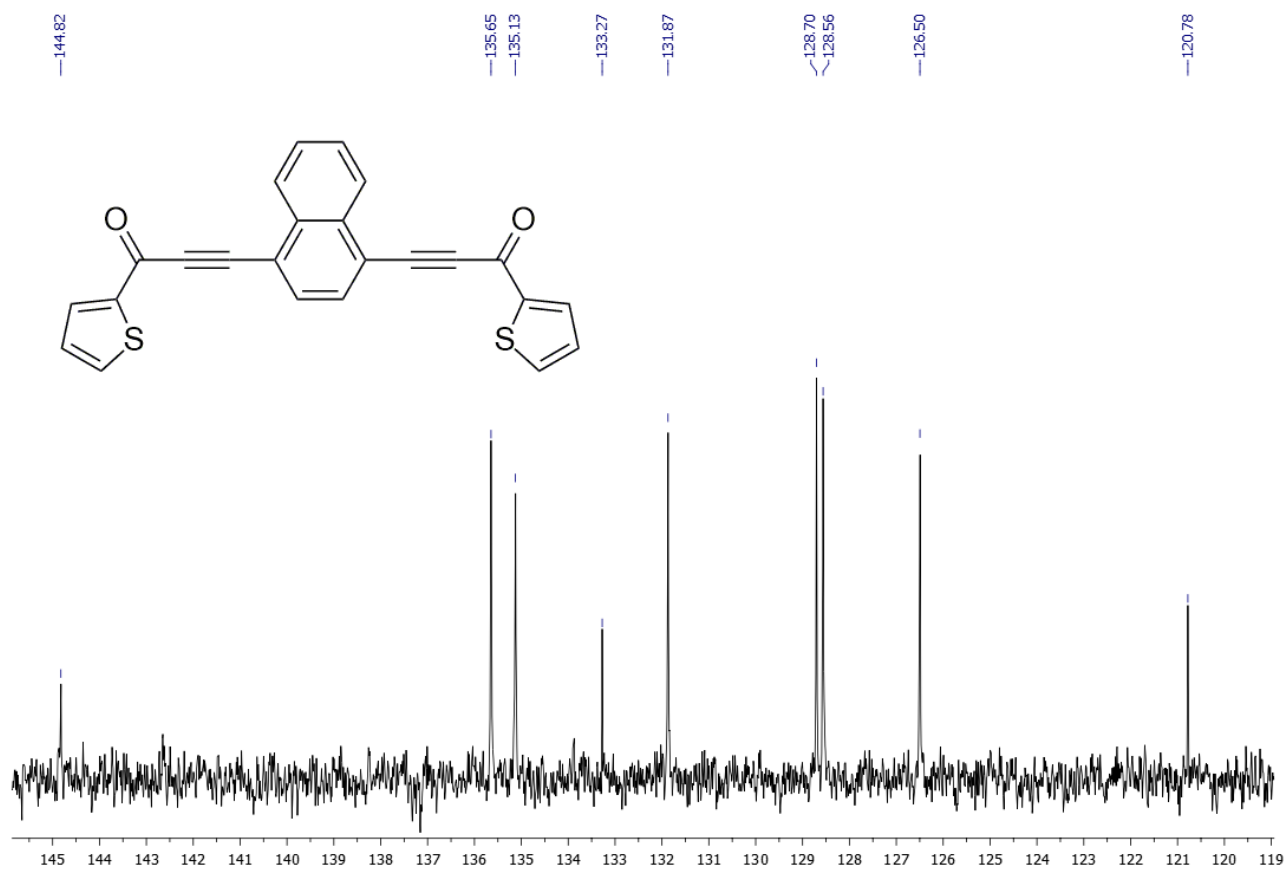
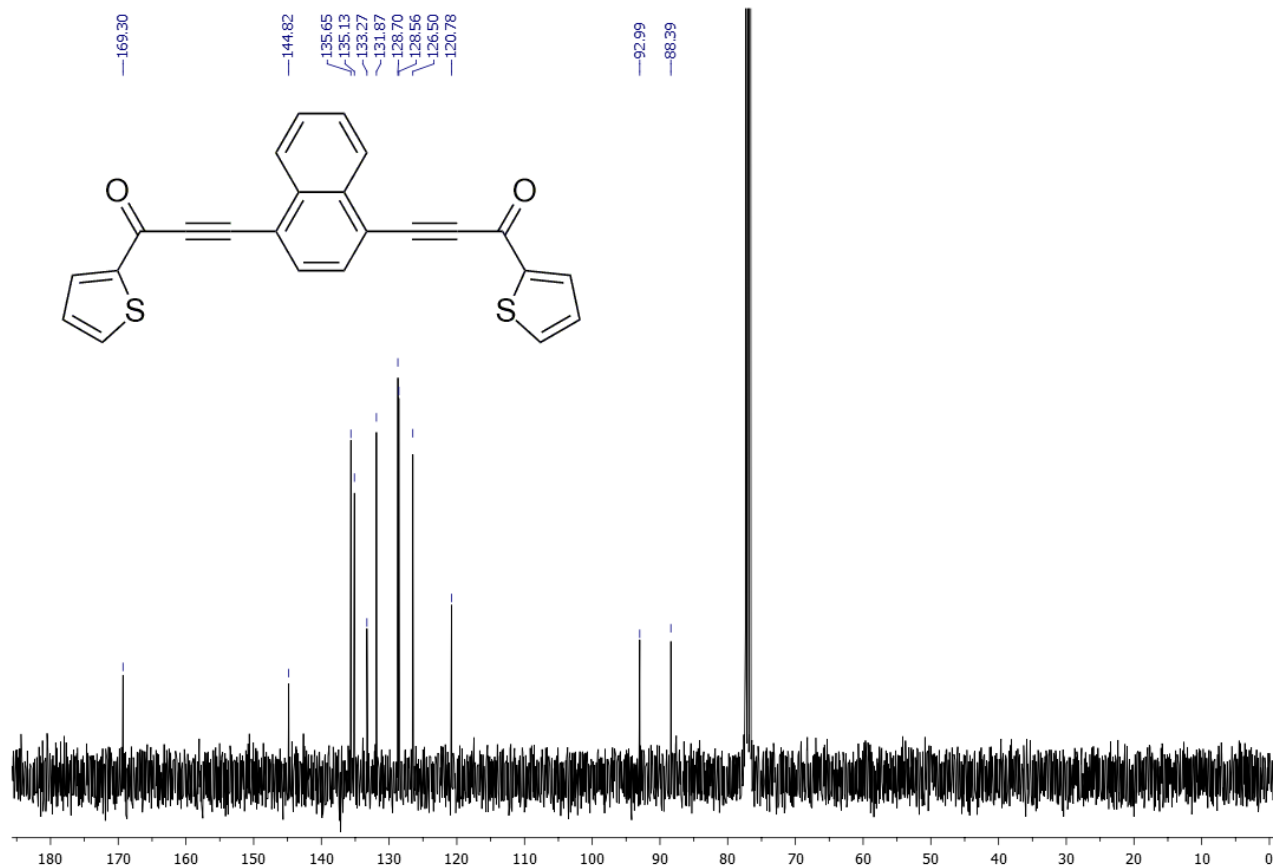


Figure S71. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(naphthalene-1,4-diyl)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**10c**): full scale spectrum (top) and spectrum expansion (bottom).



6310 **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**):
6311 full scale spectrum (top) and spectrum expansion (bottom).
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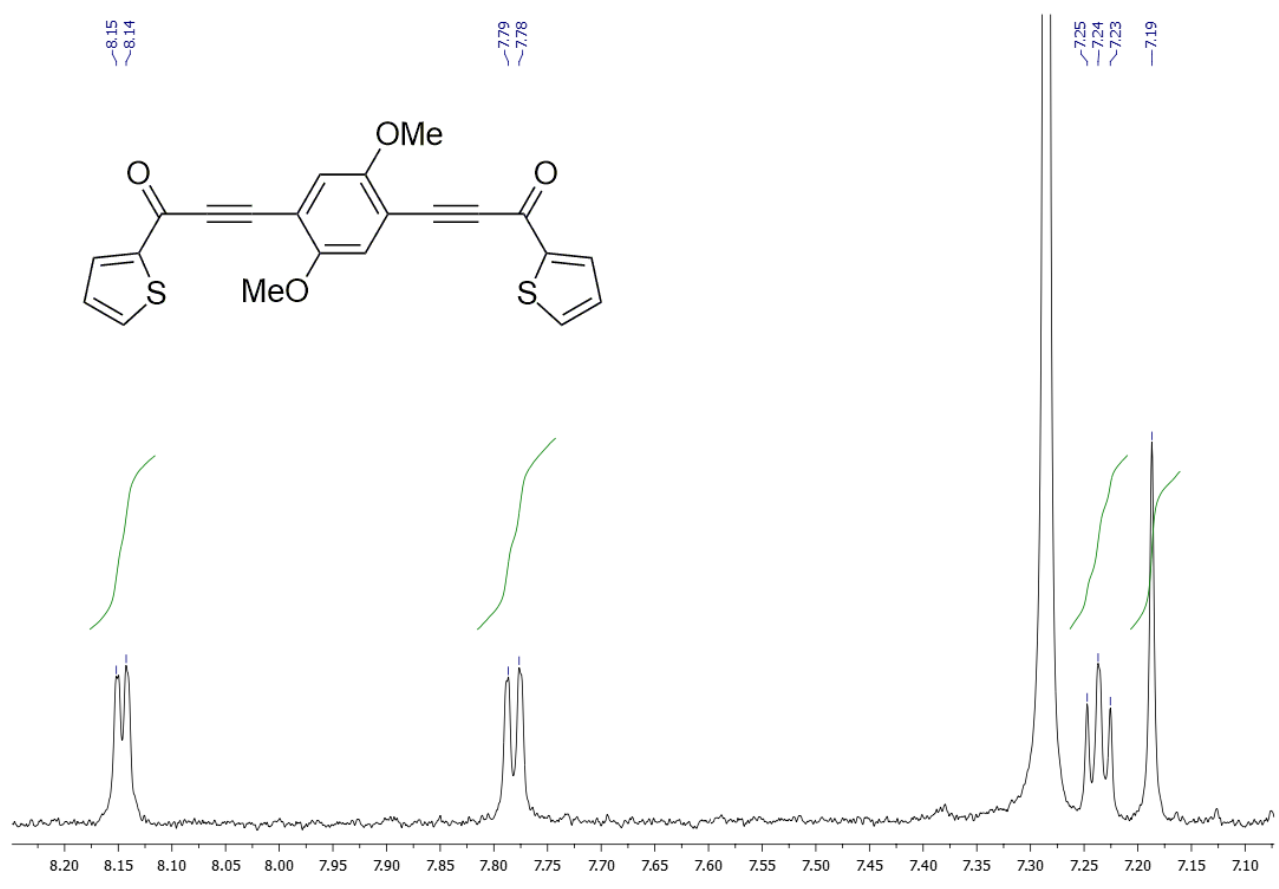
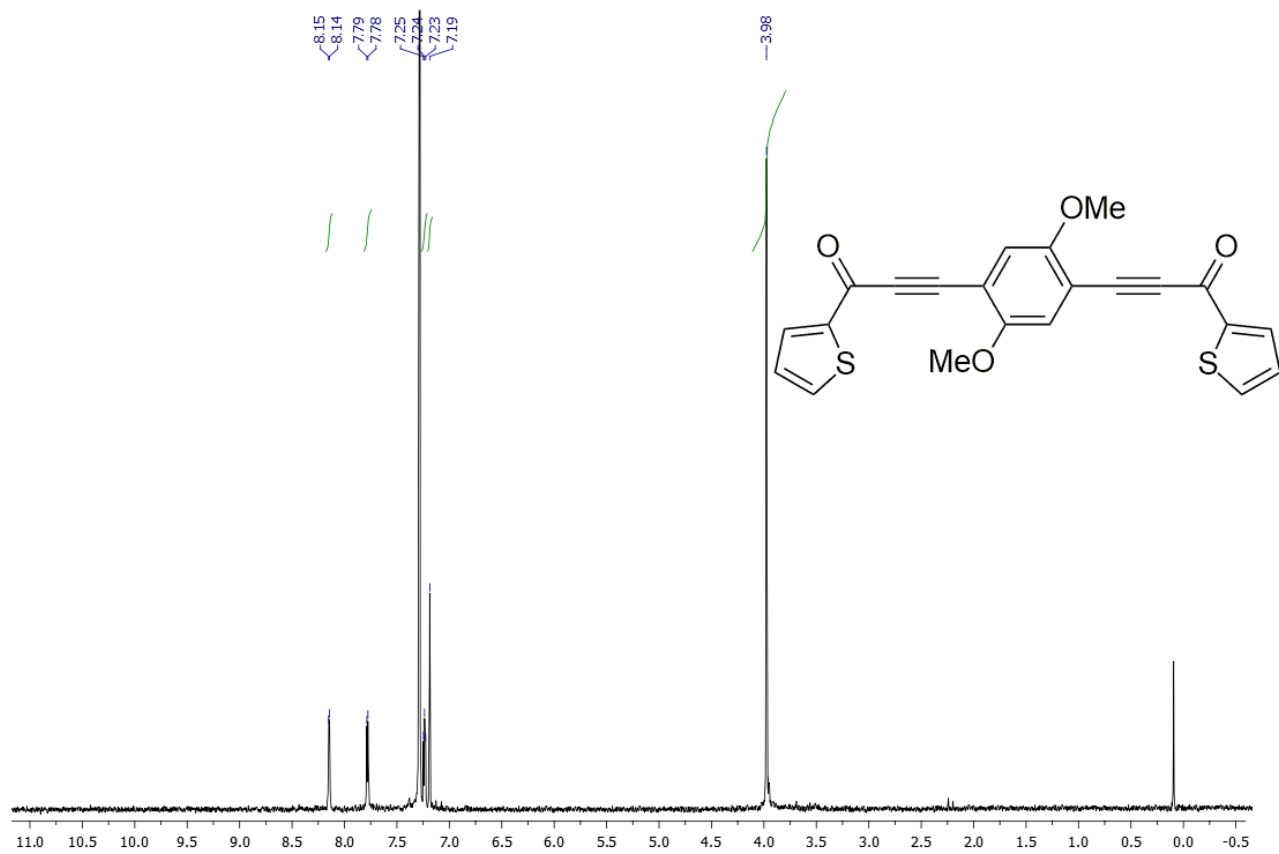
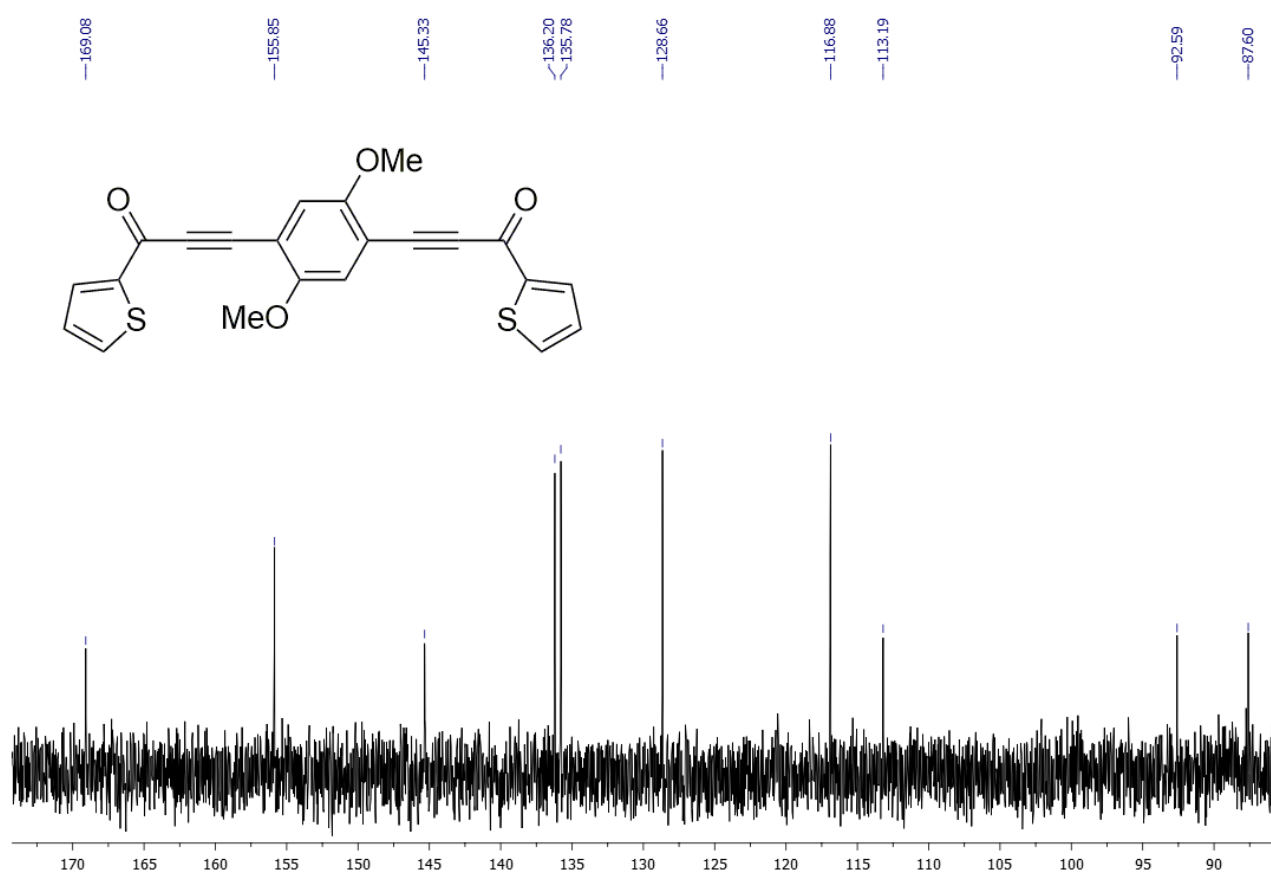
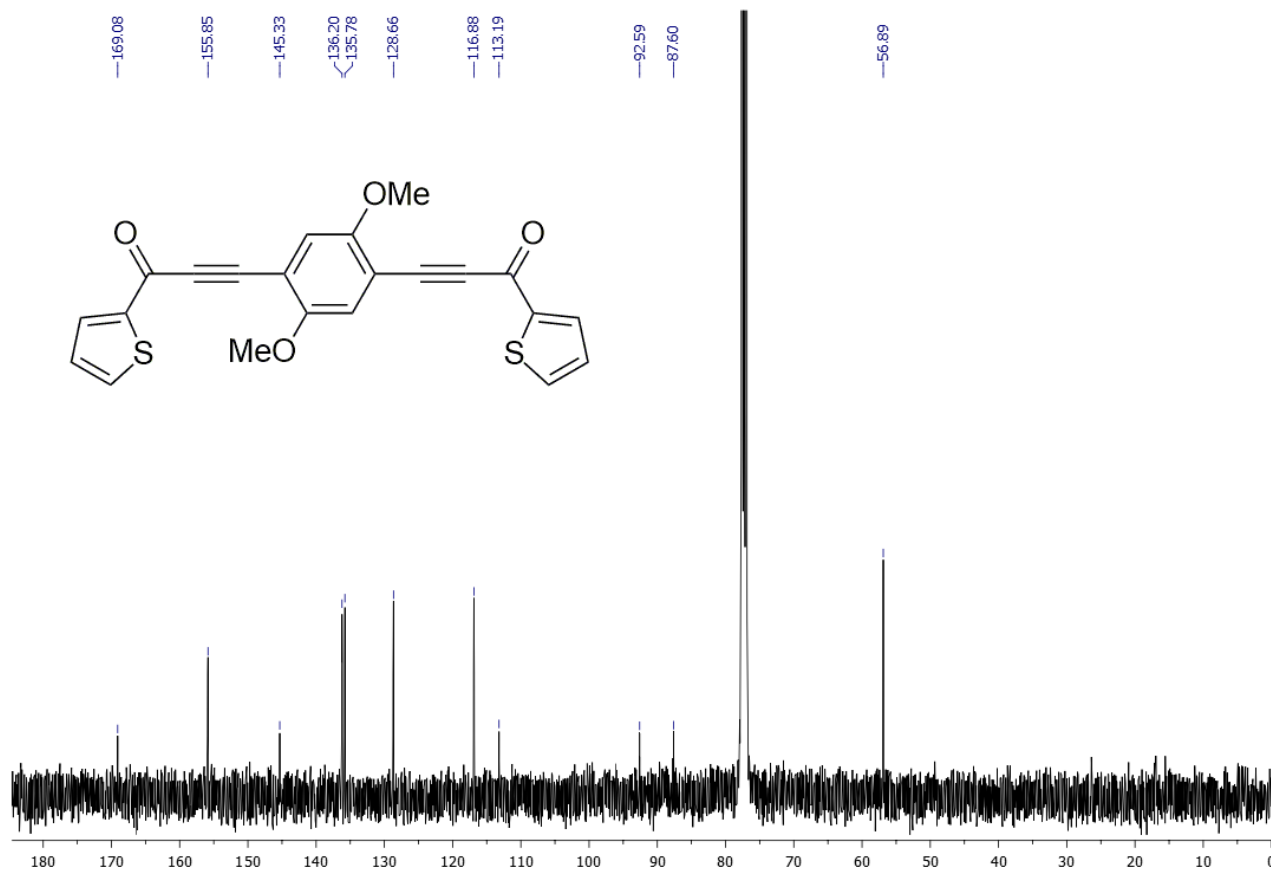


Figure S73. $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-(thiophen-2-yl)prop-2-yn-1-one) (15): full scale spectrum (top) and spectrum expansion (bottom).



6428 **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).

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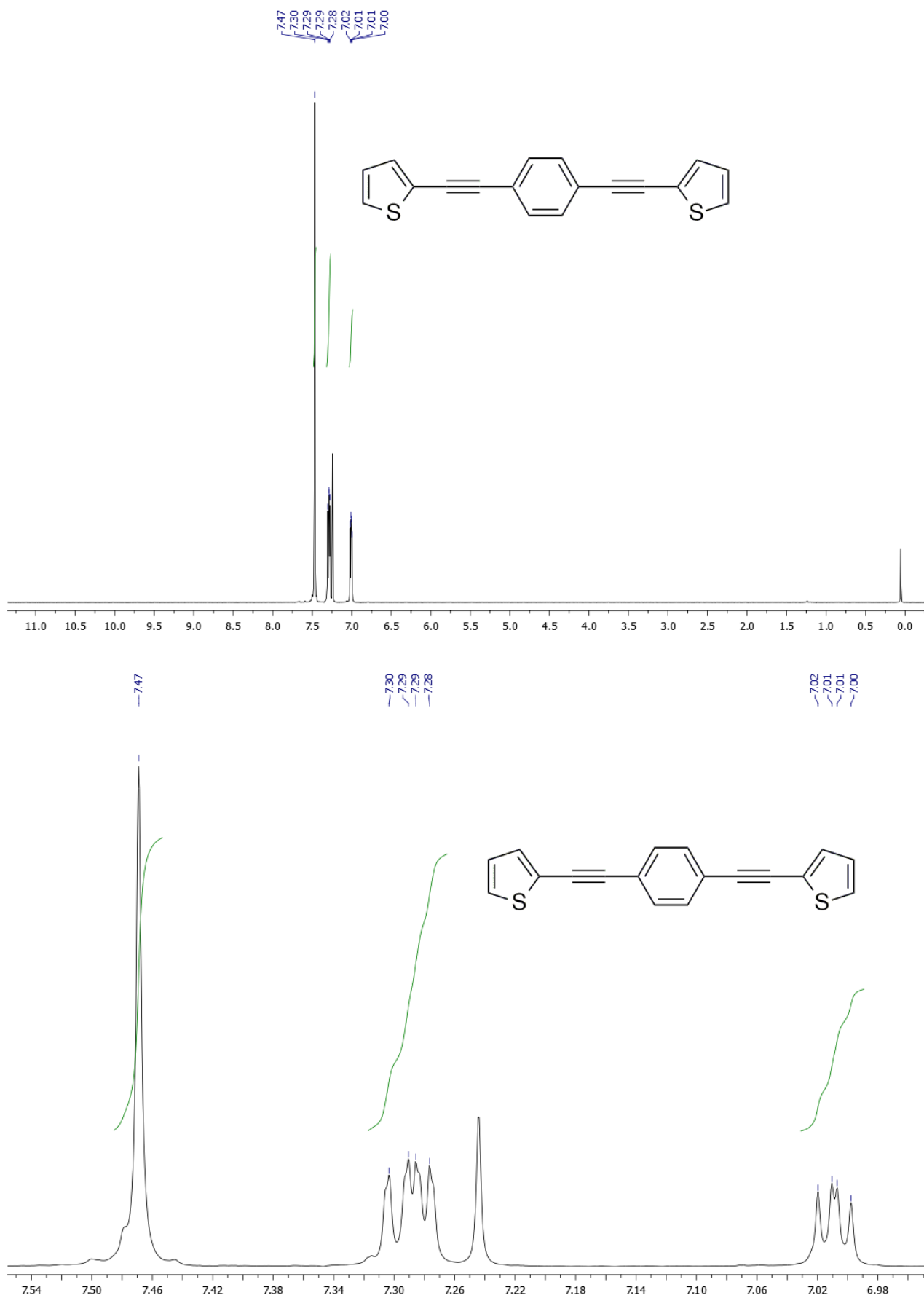


Figure S75. ¹H-NMR spectrum (400 MHz, CDCl₃) of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**): full scale spectrum (top) and spectrum expansion (bottom).

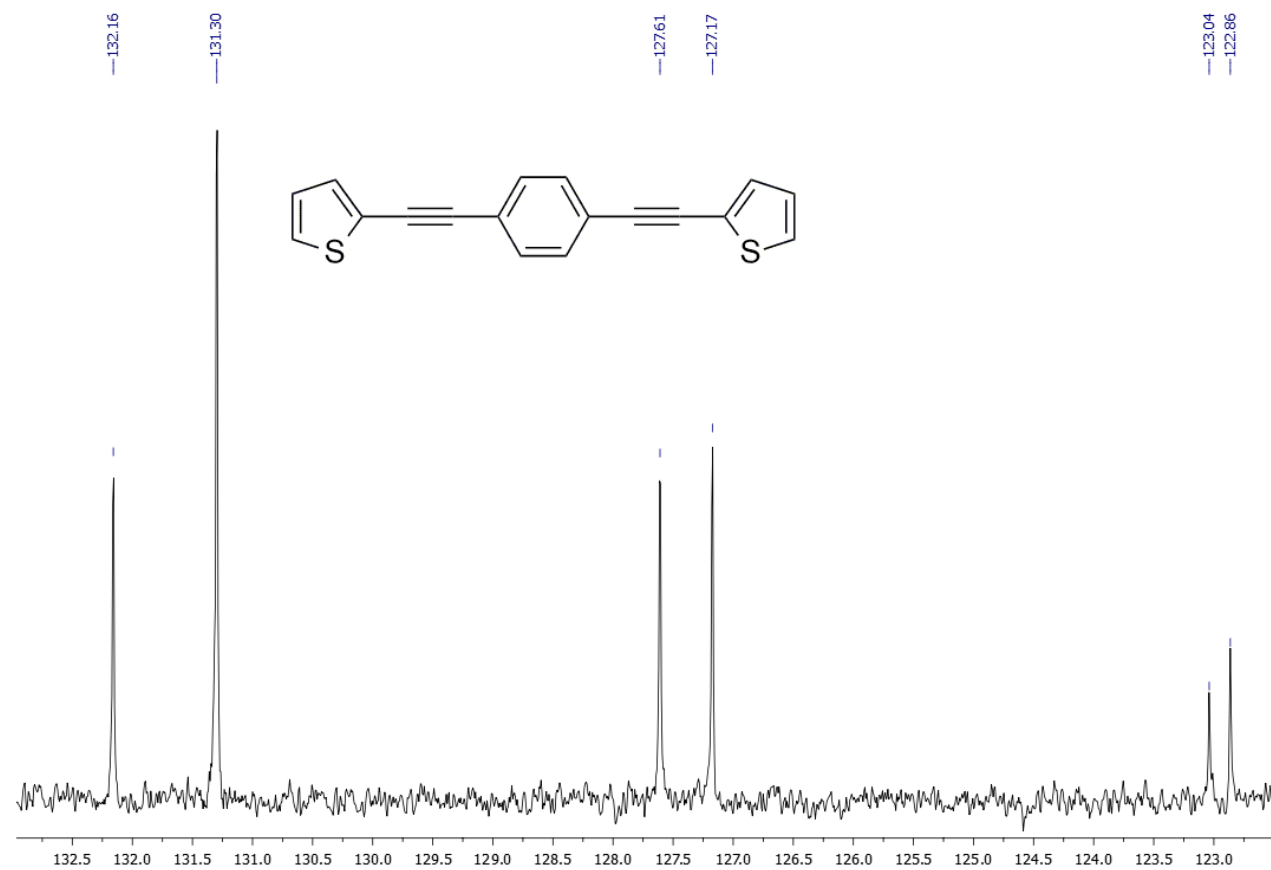
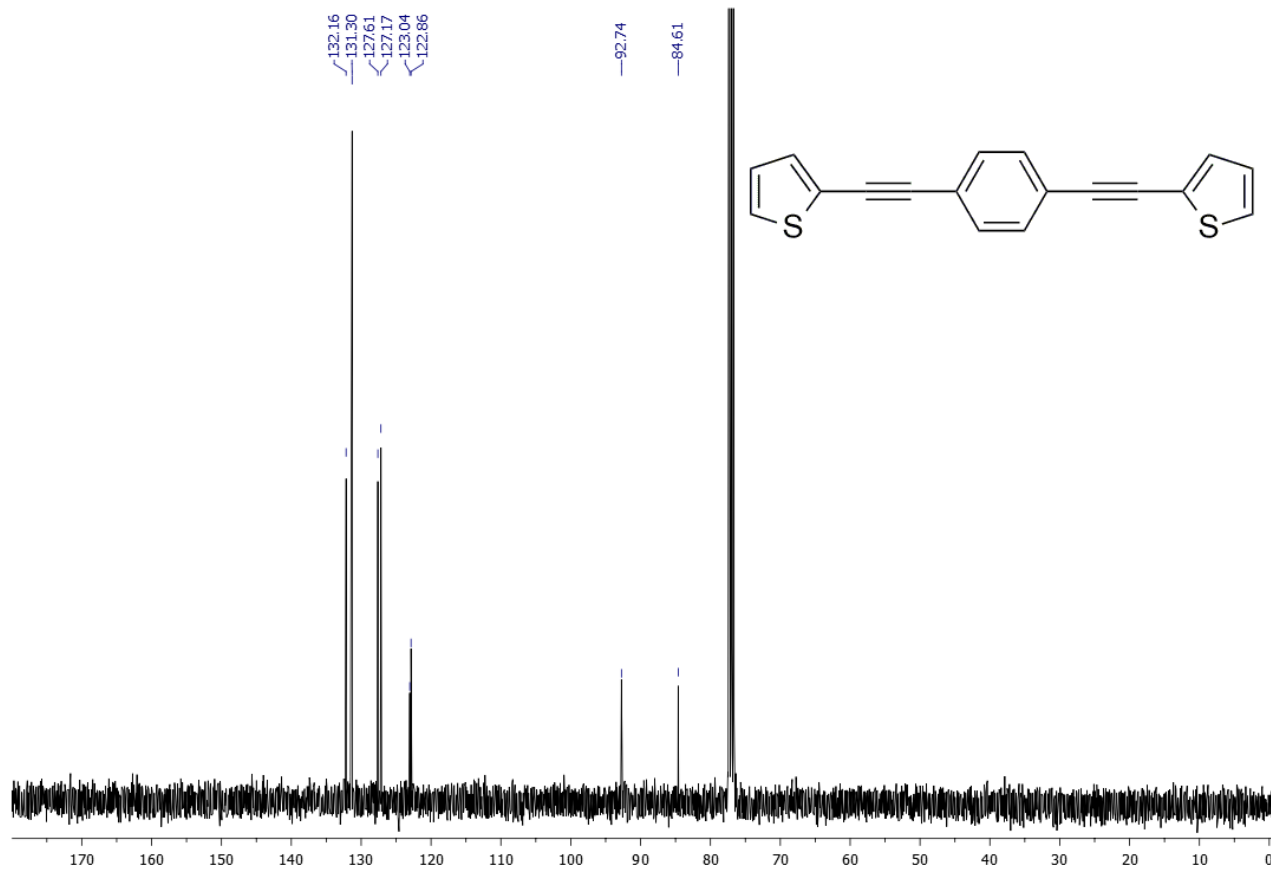
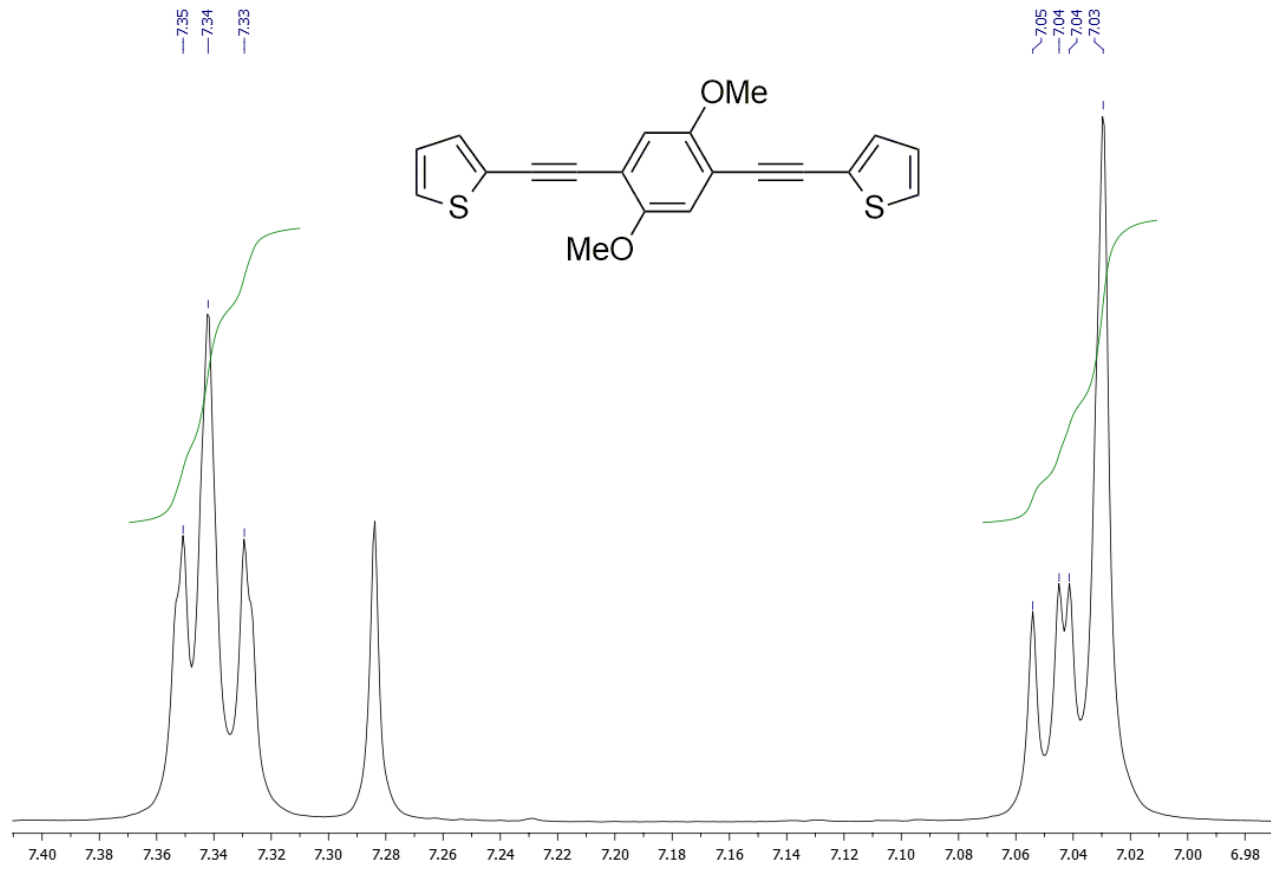
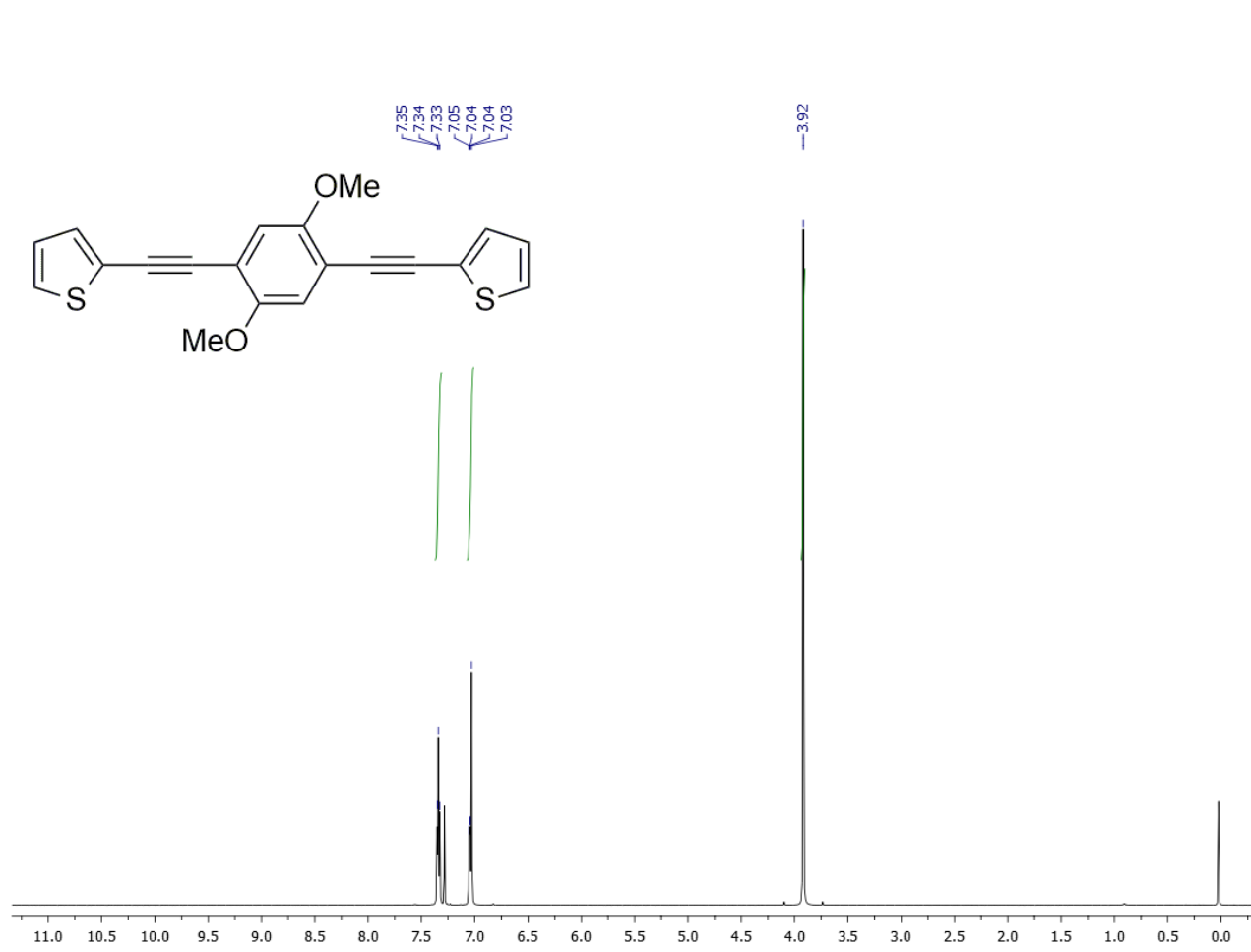
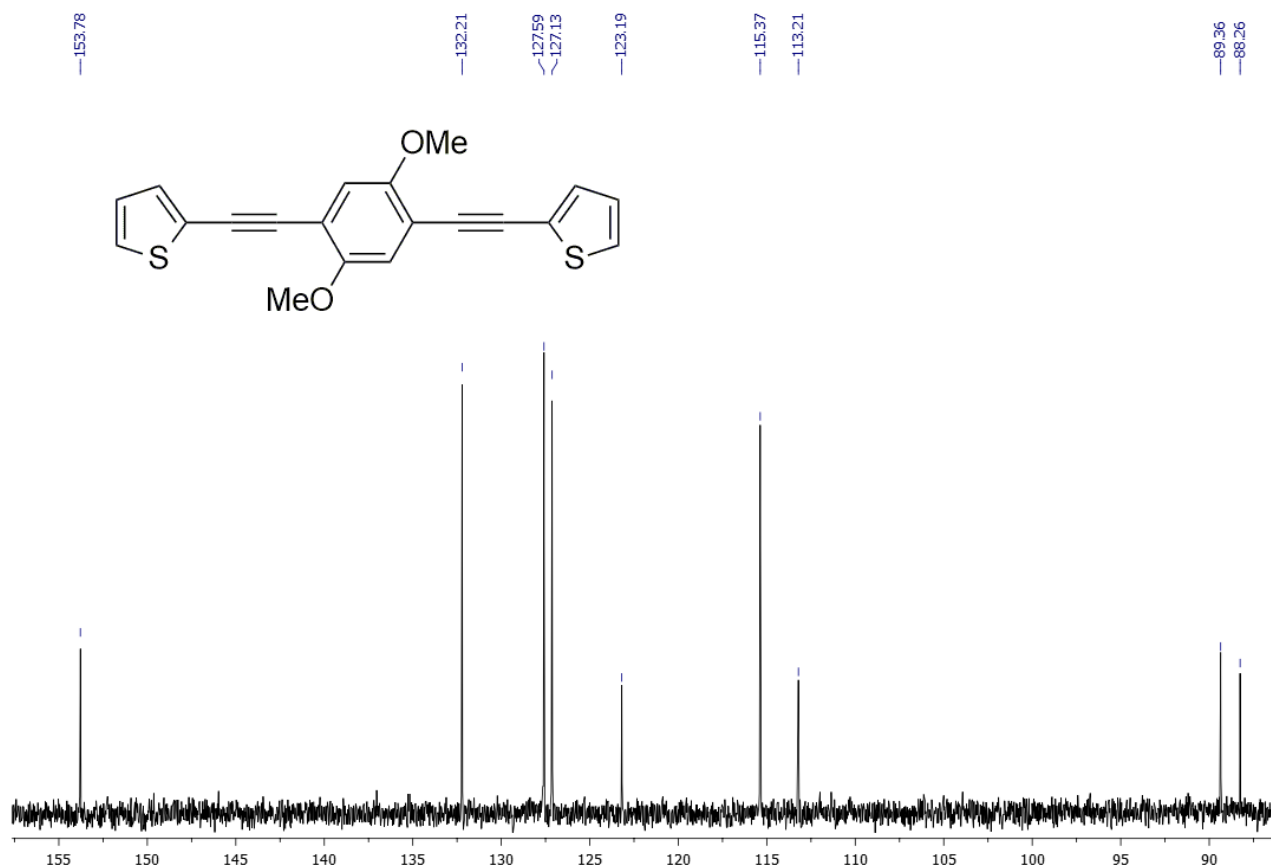
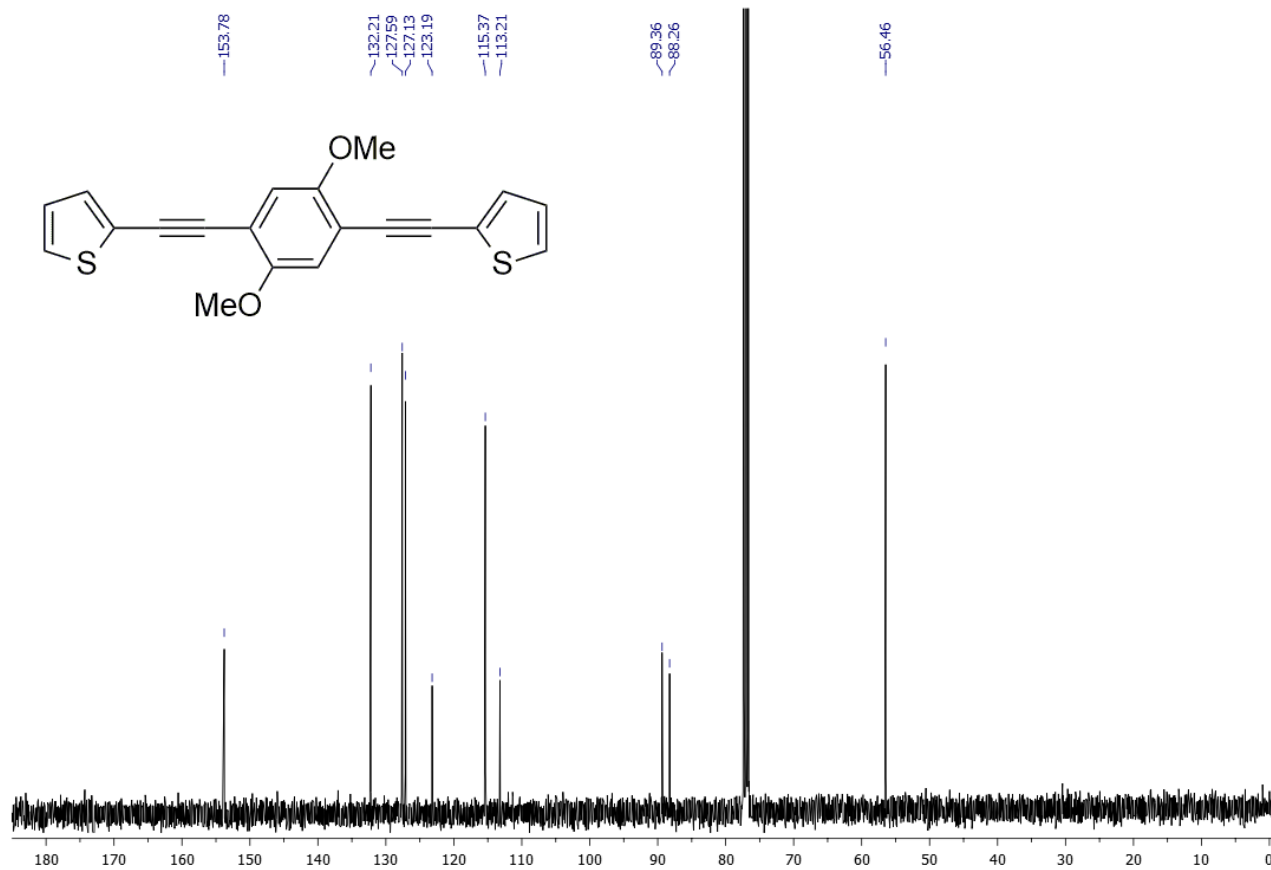


Figure S76. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of 1,4-bis(thiophen-2-ylethynyl)benzene (**6**): full scale spectrum (top) and spectrum expansion (bottom).



6605 **Figure S77.** $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3) of 2,2'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dithiophene
6606 (**14**): full scale spectrum (top) and spectrum expansion (bottom).



6664 **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
6665 (**14**): full scale spectrum (top) and spectrum expansion (bottom).
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Declaration of interests

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.