

Supporting Information

Solvent-Free C-H Alkynylation of Azulenes

Agata Jarszak-Tyl, Bartłomiej Pigulski,* Sławomir Szafert*

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

B.P.: bartlomiej.pigulski@chem.uni.wroc.pl

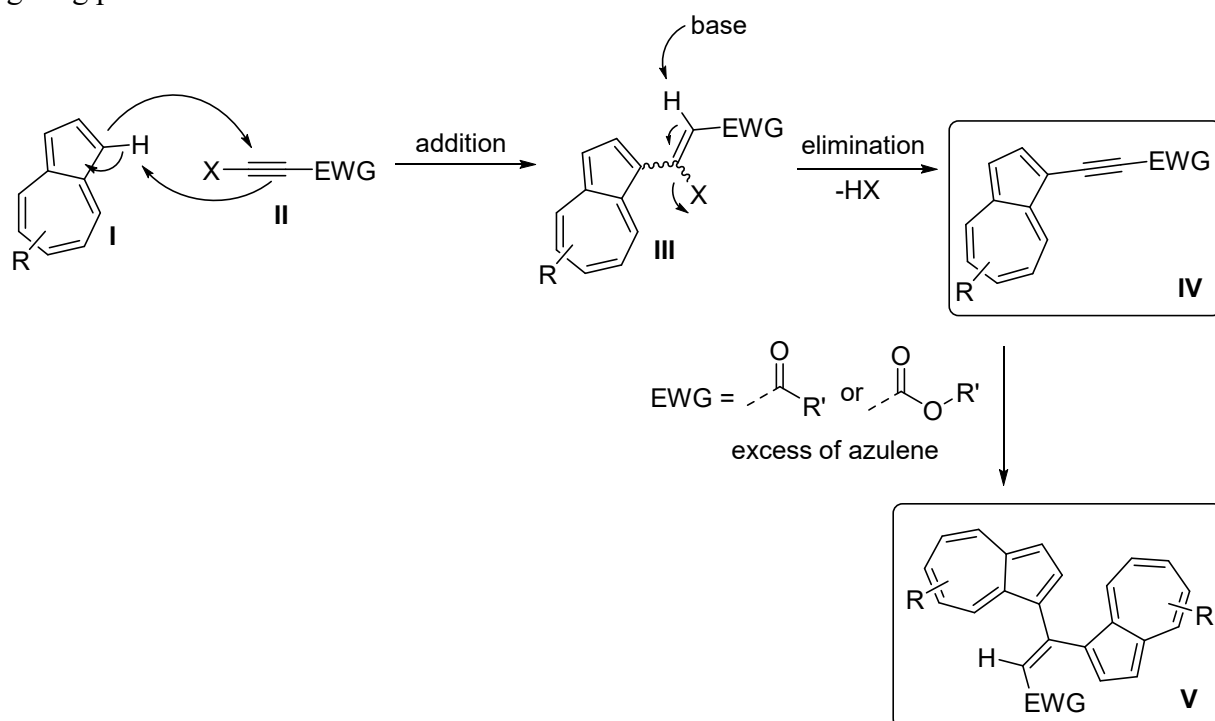
S.S.: slawomir.szafert@chem.uni.wroc.pl

Table of content

1.	Proposed mechanism.....	3
2.	Experimental.....	4
2.1.	General information.....	4
2.2.	Synthesis of starting materials	5
2.3.	Synthesis of alkynylated azulenes	6
2.4.	Synthesis of bisazulenyl ethenes.....	17
2.5.	Synthesis of azulenyl thiophenes.....	20
3.	Additional experiments.....	22
3.1.	Comparison of solvent-free reaction with reactions in solution	22
3.2.	Double alkynylation of azulene	25
4.	X-ray crystallography details.....	27
5.	Optical properties.....	31
6.	NMR spectra	35
7.	References	60

1. Proposed mechanism

We propose possible reaction mechanism (Scheme S1). In our opinion reaction might follow the addition-elimination mechanism. It is known that haloalkynes react with some nucleophiles (e.g. amines) giving alkenes which later undergo elimination under basic conditions.¹ Thus we postulate formation of compound **III** which undergo immediate elimination in the presence of basic Al_2O_3 yielding compound **IV**. If an excess of azulene is available then for alkynes with carbonyl group further Michael-type addition is possible giving product **V**.



Scheme S1. Proposed mechanism of the reaction.

2. Experimental

2.1. General information

Commercially available azulene **1a** (99%, Alfa Aesar), guaiazulene **1b** (99%, Alfa Aesar), NBS (99%, Sigma Aldrich), AgF (98%, Alfa Aesar), and Al₂O₃ (Brockmann Grade I, basic, Alfa Aesar) were used without further purification. All solvents for chromatography were used without further purification. CH₂Cl₂ for reaction was distilled over CaH₂, acetonitrile for reaction was distilled over P₂O₅. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 500 MHz and Bruker Avance III 600 MHz spectrometers with the use of broadband (BBO) or an inverse broadband (BBI) probes. For all the ¹H NMR spectra, the chemical shifts are given in ppm relative to the solvent residual peaks (CDCl₃, ¹H NMR: 7.26 ppm, ¹³C NMR: 77.16 ppm). Coupling constants are given in Hz. HRMS spectra were recorded using Bruker apex ultra FT-ICR, Bruker MicrOTOF-Q and Shimadzu q-TOF LCMS 9030 spectrometers with ESI ion source. IR spectra were recorded using a Bruker Vertex 70 FTIR and Thermo Scientific Nicolet iS10 spectrometers. UV/Vis spectra were recorded using Thermo Scientific Evolution 201 spectrophotometer. Agilent GCMSD 7820A chromatograph with 5977B detector and DB-17MS (30 m, 0.25 mm) column (He as carrier gas) was used for GC-MS (gas chromatography coupled to mass spectrometry) measurements.

X-ray diffraction data were collected with KUMA KM4 CCD and Xcalibur (Ruby) diffractometers (ω scan technique). The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix, least-squares on F² by use of the SHELXTL package.² Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined.

2.2. Synthesis of starting materials

Synthesis of starting azulenes

4,8-Dimethyl-6-phenylazulene (**1c**) was synthesized by condensation of pyrylium salt with the sodium salt of cyclopentadiene.³ Pyrylium iodide was used as the pyrylium salt and was prepared according to the known procedure.⁴

Synthesis of starting 1-haloalkynes

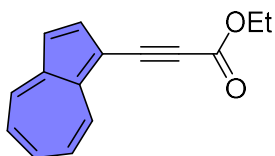
The starting 1-haloacetylenes and 1-halopolyynes (**2a-k**) were obtained according to the known procedures.⁵⁻⁷ Bromobutadiyne **2e** is new.

(2e) 5-Bromo-1-phenylpenta-2,4-diyne-1-one.

Known 1-aryl-3-(trimethylsilyl)ynone⁸ was brominated according to general procedure for the bromination of trimethylsilyl-protected polyynes.⁶ 1-Aryl-3-(trimethylsilyl)ynone (1.204 g, 0.005 mol) was dissolved in acetonitrile (50 mL). Next *N*-bromosuccinimide (1.124 g, 0.006 mol), AgF (0.668 g, 0.005 mol), and H₂O (191 μ L) were added. The flask was wrapped with aluminum foil and the mixture was stirred for 22 h. Next, the solvent was removed under reduced pressure, and the product was purified by passing through a short silica gel plug (hexane/ CH₂Cl₂; v/v; 1/1) to give **2e** as orange solid in 93% yield (1.573 g, 0.005 mol). ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.12-8.10 (m, 2H), 7.65-7.62 (m, 1H), 7.53-7.47 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*): δ = 176.7, 136.5, 134.8, 129.8, 128.9, 77.3, 70.1, 64.4, 51.3. ATR-FTIR (cm⁻¹, diamond): 2210 (C \equiv C), 1627 (C=O). HRMS(ESI): *m/z* calcd for C₁₁H₅BrONa: 254.9416 [M+Na⁺]; found: 254.9401.

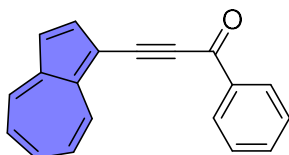
2.3. Synthesis of alkynylated azulenes

(3aa) Ethyl 3-(azulen-1-yl)propynoate. *General Procedure.*



Ethyl 3-bromo-2-propynoate (**2a**, 0.045 g, 0.254 mmol) and azulene (**1a**, 0.008 g, 0.062 mmol) were placed in a mortar and grinded for 15 min at room temperature with a 10-fold amount (by weight) of basic aluminium oxide (1.106 g). After this time, the mixture was placed in a vial and left for 5 days. Then, the reaction mixture was treated with CH₂Cl₂, filtered, the solvent was evaporated, and the residue was placed on a silica gel column and eluted with a mixture of hexanes/diethyl ether (3/1; v/v). The obtained fraction was purified by preparative TLC (neutral aluminium oxide, CH₂Cl₂/hexane; v/v; 1/1) to afford pure product as a purple oil (0.002 g, 0.009 mmol), yield, 15%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.71 (d, *J* = 9.7 Hz, 1H), 8.39 (d, *J* = 9.3 Hz, 1H), 8.08 (d, *J* = 4.1 Hz, 1H), 7.77 (t, *J* = 9.9 Hz, 1H), 7.44 (t, *J* = 9.7 Hz, 1H), 7.39 (t, *J* = 9.7 Hz, 1H), 7.32 (d, *J* = 4.1 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 155.1, 144.4, 142.9, 141.4, 139.5, 138.2, 137.0, 126.7, 126.1, 118.6, 106.4, 86.7, 84.8, 61.9, 14.4. ATR-FTIR (cm⁻¹, diamond): 2156 (C≡C), 1693 (C=O). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 240 (11500), 307 (13000), 320 (14000), 391 (7000). HRMS(ESI): *m/z* calcd for C₁₅H₁₃O₂: 225.0910 [M+H⁺]; found: 225.0914.

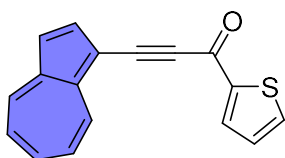
(3ab) 3-(Azulen-1-yl)-1-phenylprop-2-yn-1-one.



3-Bromo-1-phenylprop-2-yn-1-one (**2b**, 0.136 g, 0.649 mmol), azulene (**1a**, 0.064 g, 0.499 mmol) and Al₂O₃ (basic, 2.00 g) were reacted according to the procedure for **3aa**. Reaction time: 24 h, purification: silica gel column hexane/CH₂Cl₂; v/v; 1/2). Product was obtained as a dark brown powder (0.088 g, 0.343 mmol), yield: 69%. ¹H NMR (500 MHz, Chloroform-*d*): δ

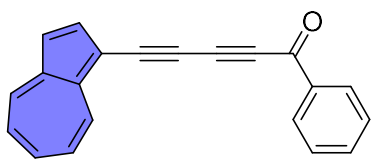
= 8.83 (d, $J = 9.6$ Hz, 1H), 8.43 (d, $J = 9.5$ Hz, 1H), 8.33 (dd, $J = 8.3, 1.3$ Hz, 2H), 8.18 (d, $J = 4.1$ Hz, 1H), 7.81 (t, $J = 9.9$ Hz, 1H), 7.66-7.61 (m, 1H), 7.56 (dd, $J = 10.7, 4.4$ Hz, 2H), 7.51 (t, $J = 9.7$ Hz, 1H), 7.44 (t, $J = 9.7$ Hz, 1H), 7.39 (d, $J = 4.1$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*): $\delta = 178.1, 144.7, 143.4, 141.6, 139.7, 138.3, 137.7, 137.2, 133.7, 129.6, 128.7, 127.1, 126.5, 119.1, 107.1, 94.6, 92.6$. ATR-IR (cm^{-1} , Ge crystalplate): 2162 (C \equiv C), 1626 (C=O). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 232 (18000), 293 (22000), 323 (10000), 345 (11000), 417 (19500). HRMS(ESI): m/z calcd for $\text{C}_{19}\text{H}_{12}\text{ONa}$: 279.0780 [$\text{M}+\text{Na}^+$]; found: 279.0781.

(3ac) 3-(Azulen-1-yl)-1-(thiophen-2-yl)prop-2-yn-1-one.



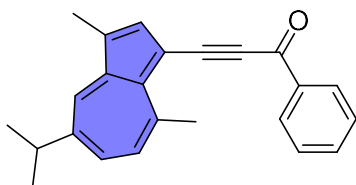
3-Bromo-1-(thiophen-2-yl)prop-2-yn-1-one (**2c**, 0.078 g, 0.362 mmol), azulene (**1a**, 0.036 g, 0.281 mmol) and Al_2O_3 (basic, 1.605 g) were reacted according to the procedure for **3aa**. Reaction time: 4 days, purification: silica gel column (hexane/diethyl ether; v/v; 3/1). Product was obtained as a dark brown powder (0.061 g, 0.233 mmol), yield: 82%. ^1H NMR (500 MHz, Chloroform-*d*): $\delta = 8.82$ (d, $J = 9.6$ Hz, 1H), 8.42 (d, $J = 9.5$ Hz, 1H), 8.15 (d, $J = 4.1$ Hz, 1H), 8.09 (dd, $J = 3.8, 1.2$ Hz, 1H), 7.81 (t, $J = 9.9$ Hz, 1H), 7.72 (dd, $J = 4.9, 1.2$ Hz, 1H), 7.51 (t, $J = 9.7$ Hz, 1H), 7.44 (t, $J = 9.7$ Hz, 1H), 7.38 (d, $J = 4.1$ Hz, 1H), 7.22 (dd, $J = 4.9, 3.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*): $\delta = 169.9, 145.6, 144.6, 143.4, 141.5, 139.7, 138.3, 137.0, 134.3, 134.0, 128.4, 127.1, 126.5, 119.1, 106.7, 94.0, 91.3$. ATR-FTIR (cm^{-1} , Ge crystalplate): 2166 (C \equiv C), 1605 (C=O). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 233 (28000), 294 (33000), 347 (13500), 421 (26000). HRMS(ESI): m/z calcd for $\text{C}_{17}\text{H}_{10}\text{OSNa}$: 285.0341 [$\text{M}+\text{Na}^+$]; found: 285.0347.

(3ae) 5-(Azulen-1-yl)-1-phenylpenta-2,4-diyn-1-one.



5-Bromo-1-phenylpenta-2,4-diyn-1-one (**2e**, 0.043 g, 0.184 mmol), azulene (**1a**, 0.026 g, 0.202 mmol) and Al₂O₃ (basic, 1.236 g) were used according to the procedure for **3aa**. Reaction time: 7 d, purification: silica gel column (hexane/CH₂Cl₂; v/v; 1/2). Product was obtained as a dark brown powder (0.032 g, 0.114 mmol), yield: 57%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.68 (d, *J* = 9.6 Hz, 1H), 8.39 (d, *J* = 9.5 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.07 (d, *J* = 4.1 Hz, 1H), 7.78 (t, *J* = 9.9 Hz, 1H), 7.67-7.60 (m, 1H), 7.55-7.50 (m, 2H), 7.46 (t, *J* = 9.7 Hz, 1H), 7.41 (t, *J* = 9.7 Hz, 1H), 7.32 (d, *J* = 4.1 Hz, 1H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 177.3, 145.1, 143.0, 141.3, 139.8, 138.3, 137.1, 137.1, 134.3, 129.7, 128.8, 127.0, 126.2, 118.8, 107.2, 85.2, 80.9, 80.0, 78.2. ATR-FTIR (cm⁻¹, Ge crystalplate): 2172 (C≡C), 1627 (C=O). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 233 (22000), 275 (23000), 306 (22400), 441 (18000). HRMS(ESI): *m/z* calcd for C₂₁H₁₂ONa: 303.0780 [M+Na⁺]; found: 303.0782.

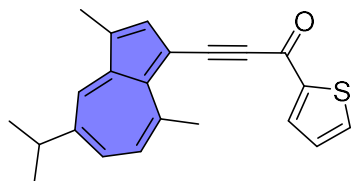
(3bb) 3-(5-Isopropyl-3,8-dimethylazulen-1-yl)-1-phenylprop-2-yn-1-one.



3-Bromo-1-phenylprop-2-yn-1-one (**2b**, 0.240 g, 1.15 mmol), guaiazulene (**1b**, 0.200g, 1.01 mmol) and Al₂O₃ (basic, 4.40 g) were reacted according to the procedure for **3aa**. Reaction time: 18 h, purification: silica gel column (CH₂Cl₂/hexane; v/v; 4/1). Product was obtained as a dark brown oil (0.246g, 0.753 mmol), yield: 75%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.23 (dd, *J* = 5.1, 3.4 Hz, 2H), 8.20 (d, *J* = 2.0 Hz, 1H), 7.90 (s, 1H), 7.63-7.57 (m, 1H), 7.55-7.48 (m, 3H), 7.21 (d, *J* = 10.8 Hz, 1H), 3.36 (s, 3H), 3.11 (hept, *J* = 6.9 Hz, 1H), 2.61 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 178.0, 148.7, 145.0,

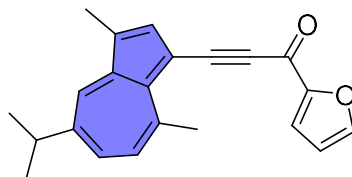
143.1, 140.8, 140.7, 138.2, 137.1, 135.1, 133.3, 130.7, 129.3, 128.6, 126.7, 103.1, 97.7, 95.1, 38.3, 26.8, 24.7, 13.0. ATR-FTIR (cm^{-1} , Ge crystalplate): 2144 ($\text{C}\equiv\text{C}$), 1614 ($\text{C}=\text{O}$). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 245 (31000), 302 (26000), 443 (28000). HRMS(ESI): m/z calcd for $\text{C}_{24}\text{H}_{23}\text{O}$: 327.1743 [$\text{M}+\text{H}^+$]; found: 327.1743.

(3bc) 3-(5-Isopropyl-3,8-dimethylazulen-1-yl)-1-(thiophen-2-yl)prop-2-yn-1-one.



3-Bromo-1-(thiophen-2-yl)prop-2-yn-1-one (**2c**, 0.071g, 0.330 mmol), guaiiazulene (**1b**, 0.064 g, 0.323 mmol) and Al_2O_3 (basic, 1.149 g) were reacted according to the procedure for **3aa**. Reaction time: 48 h, purification: silica gel column (hexane/diethyl ether; v/v; 3/1). Product was obtained as a dark brown solid (0.096 g, 0.298 mmol), yield: 90%. ^1H NMR (500 MHz, Chloroform-*d*): δ = 8.19 (d, J = 2.0 Hz, 1H), 7.97 (dd, J = 3.8, 1.2 Hz, 1H), 7.87 (s, 1H), 7.67 (dd, J = 4.9, 1.2 Hz, 1H), 7.53 (dd, J = 10.8, 2.0 Hz, 1H), 7.23-7.16 (m, 2H), 3.36 (s, 3H), 3.11 (hept, J = 6.9 Hz, 1H), 2.60 (s, 3H), 1.38 (d, J = 6.9 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*): δ = 169.9, 148.7, 146.2, 145.1, 143.2, 140.8, 140.5, 137.1, 135.2, 133.8, 133.2, 130.7, 128.2, 126.8, 102.9, 96.3, 94.4, 38.3, 26.9, 24.7, 13.0. ATR-FTIR (cm^{-1} , diamond crystalplate): 2154 ($\text{C}\equiv\text{C}$), 1721 ($\text{C}=\text{O}$). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 246 (16000), 304 (19000), 449 (18000). HRMS(ESI): m/z calcd for $\text{C}_{22}\text{H}_{21}\text{OS}$: 333.1307 [$\text{M}+\text{H}^+$]; found: 333.1308.

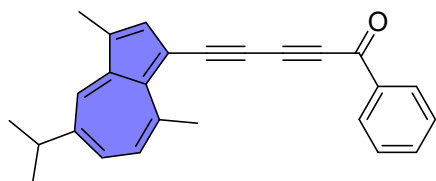
(3bd) 1-(Furan-2-yl)-3-(5-isopropyl-3,8-dimethylazulen-1-yl)prop-2-yn-1-one.



3-Bromo-1-(furan-2-yl)prop-2-yn-1-one (**2d**, 0.046 g, 0.214 mmol), guaiiazulene (**1b**, 0.046 g, 0.232 mmol) and Al_2O_3 (basic, 0.920 g) were reacted according to the procedure for **3aa**.

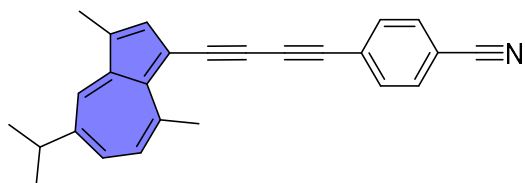
Reaction time: 26 h, purification: silica gel column (CH₂Cl₂/hexane; v/v; 1/1) then preparative TLC (silica gel, CH₂Cl₂). Product was obtained as a dark brown oil (0.056 g, 0.177 mmol), yield: 78%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.19 (d, *J* = 2.0 Hz, 1H), 7.85 (s, 1H), 7.66 (d, *J* = 0.9 Hz, 1H), 7.53 (dd, *J* = 10.8, 2.0 Hz, 1H), 7.36-7.33 (m, 1H), 7.21 (d, *J* = 10.8 Hz, 1H), 6.59 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.37 (s, 3H), 3.11 (hept, *J* = 6.9 Hz, 1H), 2.59 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 165.2, 154.1, 148.6, 146.8, 145.1, 143.1, 140.7, 140.6, 137.0, 135.1, 130.7, 126.7, 118.3, 112.4, 102.7, 96.9, 94.2, 38.2, 26.7, 24.5, 12.9. FTIR (cm⁻¹, KBr pellet): 1731 (C=O), 2120 (C≡C). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 302 (20000), 357 (9000), 447 (21000). HRMS(ESI): *m/z* calcd for C₂₂H₂₁O₂: 317.1536 [M+H⁺]; found: 317.1535.

(3be) 5-(5-Isopropyl-3,8-dimethylazulene-1-yl)-1-phenylpenta-2,4-diyn-1-one.



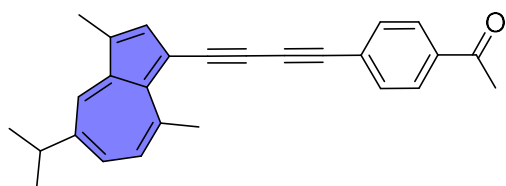
5-Bromo-1-phenylpenta-2,4-diyn-1-one (**2e**, 0.036 g, 0.154 mmol), guaiazulene (**1b**, 0.031 g, 0.156 mmol) and Al₂O₃ (basic, 0.834 g) were reacted according to the procedure for **3aa**. Reaction time: 24 h, purification: silica gel column (hexane/diethyl ether; v/v; 3/1). Product was obtained as a dark brown powder (0.023 g, 0.066 mmol), yield: 41%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.18 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.15 (d, *J* = 2.0 Hz, 1H), 7.77 (s, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 3H), 7.14 (d, 8.3 Hz, 1H), 3.23 (s, 3H), 3.11 (hept, *J* = 6.9 Hz, 1H), 2.57 (s, 3H), 1.36 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 177.4, 148.8, 144.9, 142.7, 141.2, 140.2, 137.2, 137.2, 135.2, 134.1, 130.3, 129.7, 128.7, 126.6, 103.0, 90.1, 81.7, 81.3, 78.3, 38.2, 26.7, 24.6, 13.0. ATR-FTIR (cm⁻¹, Ge crystalplate): 2161 (C≡C), 1630 (C=O). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 287 (21000), 473 (16000). HRMS(ESI): *m/z* calcd for C₂₆H₂₃O: 351.1743 [M+H⁺]; found: 351.1743.

(3bf) 4-((5-Isopropyl-3,8-dimethylazulen-1-yl)buta-1,3-diyn-1-yl)benzonitrile.



4-(Chlorobuta-1,3-diyn-1-yl)benzonitrile (**2f**, 0.051 g, 0.275 mmol), guaiiazulene (**1b**, 0.069 g, 0.347 mmol) and Al₂O₃ (basic, 1.050 g) were reacted according to the procedure for **3aa**. Reaction time: 4 d, purification: silica gel column (hexane/CH₂Cl₂; v/v; 2/1). Product was obtained as a dark green powder (0.038 g, 0.109 mmol), yield: 40%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.11 (d, *J* = 2.0 Hz, 1H), 7.73 (s, 1H), 7.64-7.54 (m, 4H), 7.43 (dd, *J* = 10.7, 2.0 Hz, 1H), 7.05 (d, *J* = 10.8 Hz, 1H), 3.23 (s, 3H), 3.11 (hept, *J* = 6.9, 1H), 2.57 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 148.3, 143.8, 142.2, 139.7, 139.4, 136.8, 134.9, 132.7, 132.1, 129.3, 128.0, 126.2, 118.7, 111.6, 104.1, 86.2, 81.2, 80.3, 78.1, 38.2, 26.6, 24.6, 13.0. ATR-FTIR (cm⁻¹, Ge crystalplate): 2227(C≡N), 2187 (C≡C), 2129 (weak, C≡C). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 241 (23000), 257 (22000), 286 (19000), 316 (20000), 334 (19000), 449 (22000). HRMS(ESI): *m/z* calcd for C₂₆H₂₂N: 348.1747 [M+H⁺]; found: 348.1723.

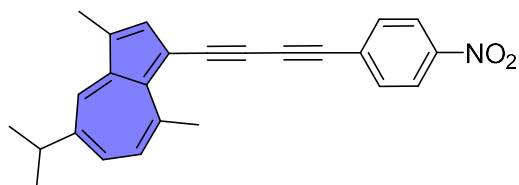
(3bg) 1-(4-((5-Isopropyl-3,8-dimethylazulen-1-yl)buta-1,3-diyn-1-yl)phenyl)ethan-1-one.



1-(4-(Chlorobuta-1,3-diyn-1-yl)phenyl)ethan-1-one (**2g**, 0.031 g, 0.125 mmol), guaiiazulene (**1b**, 0.046 g, 0.232 mmol) and Al₂O₃ (basic, 0.770 g) were reacted according to the procedure for **3aa**. Reaction time: 4 d, purification: silica gel column (CH₂Cl₂/hexane; v/v; 1/1). Product was obtained as a dark brown solid (0.028 g, 0.077 mmol), yield: 51%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.11 (d, *J* = 2.0 Hz, 1H), 7.95-7.89 (m, 2H), 7.73 (s, 1H), 7.62-7.57 (m, 2H), 7.42 (dd, *J* = 10.8, 2.1 Hz, 1H), 7.03 (d, *J* = 10.8 Hz, 1H), 3.24 (s, 3H), 3.06 (hept, *J* = 6.9 Hz, 1H), 2.61 (s, 3H), 2.57 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz,

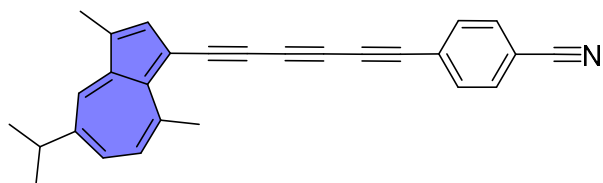
Chloroform-*d*): δ = 197.3, 148.4, 143.5, 142.2, 139.6, 139.3, 136.7, 136.4, 134.9, 132.4, 129.2, 128.4, 127.9, 126.1, 104.5, 85.3, 82.2, 79.2, 78.3, 38.2, 26.8, 26.6, 24.7, 13.0. FTIR (cm^{-1} , KBr pellet): 1737 (C=O), 2120 (C \equiv C), 2179 (C \equiv C). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 246 (13000), 317 (11000), 446 (9000). HRMS(ESI): m/z calcd for $\text{C}_{27}\text{H}_{25}\text{O}$: 365.1900 [$\text{M}+\text{H}^+$]; found: 365.1900.

(3bh) 7-Isopropyl-1,4-dimethyl-3-((4-nitrophenyl)buta-1,3-diyn-1-yl)azulene.



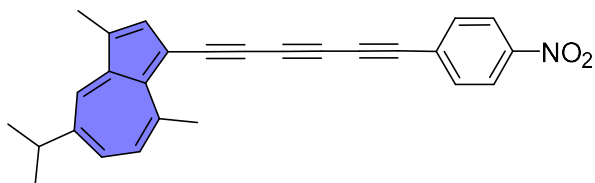
1-(Chlorobuta-1,3-diyn-1-yl)-4-nitrobenzene (**2h**, 0.066 g, 0.321 mmol), guaiazulene (**1b**, 0.095 g, 0.479 mmol) and Al_2O_3 (basic, 1.600 g) were reacted according to the procedure for **3aa**. Reaction time: 24 h, purification: silica gel column (CH_2Cl_2 /hexane; v/v; 1/3) then preparative TLC (silica gel, CH_2Cl_2 /hexane; v/v; 1/2). Product was obtained as dark brown solid (0.036 g, 0.098 mmol), yield: 31%. ^1H NMR (500 MHz, Chloroform-*d*): δ = 8.23-8.16 (m, 2H), 8.12 (d, J = 2.0 Hz, 1H), 7.73 (s, 1H), 7.67-7.61 (m, 2H), 7.44 (dd, J = 10.8, 2.0 Hz, 1H), 7.06 (d, J = 10.8 Hz, 1H), 3.24 (s, 3H), 3.07 (hept, J = 7.0 Hz, 1H), 2.58 (s, 3H), 1.36 (d, J = 6.9 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*): δ = 148.4, 147.0, 143.9, 142.2, 139.9, 139.5, 136.8, 135.0, 132.8, 130.1, 129.4, 126.2, 123.8, 104.0, 86.9, 81.4, 81.2, 78.2, 38.2, 26.6, 24.7, 13.0. FTIR (cm^{-1} , KBr pellet): 2128 (C \equiv C), 2180 (C \equiv C). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 244 (20000), 323 (22000), 410 (11000), 468 (15000). HRMS(ESI): m/z calcd for $\text{C}_{25}\text{H}_{22}\text{NO}_2$: 368.1645 [$\text{M}+\text{H}^+$]; found: 368.1647.

(3bi) 4-((5-isopropyl-3,8-dimethylazulen-1-yl)hexa-1,3,5-triyn-1-yl)benzonitrile.



4-(Bromohexa-1,3,5-triyn-1-yl)benzonitrile (**2i**, 0.036 g, 0.141 mmol), guaiiazulene (**1b**, 0.038 g, 0.192 mmol) and Al₂O₃ (basic, 1.164 g) were reacted according to the procedure for **3aa**. Reaction time: 5 d, purification: silica gel column (hexane/diethyl ether; v/v; 3/1) then preparative TLC (silica gel, CH₂Cl₂/hexane; v/v; 1/2). Product was obtained as a dark brown powder (0.045g, 0.012 mmol), yield: 85%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.11 (d, *J* = 2.0 Hz, 1H), 7.73 (s, 1H), 7.63-7.56 (m, 4H), 7.45 (dd, *J* = 10.8, 2.0 Hz, 1H), 7.06 (d, *J* = 10.9 Hz, 1H), 3.20 (s, 3H), 3.07 (hept, *J* = 6.9 Hz, 1H), 2.56 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 6H). ¹³C {¹H} NMR (126 MHz, Chloroform-*d*): δ = 148.6, 144.3, 142.6, 140.9, 139.7, 137.0, 135.1, 133.3, 132.2, 129.7, 127.0, 126.4, 118.4, 112.4, 103.2, 82.3, 79.6, 79.3, 77.6, 71.0, 67.9, 38.2, 26.6, 24.6, 13.0. ATR-FTIR (cm⁻¹, diamond crystalplate): 2227 (C≡N), 2139 (C≡C), 2085 (weak, C≡C). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 270 (37000), 306 (29000), 438 (27000), 470 (19000). HRMS(ESI): *m/z* calcd for C₂₈H₂₂N: 372.1747 [M+H⁺]; found: 372.1750.

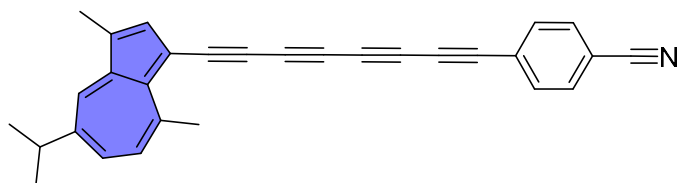
(3bj) 7-Isopropyl-1,4-dimethyl-3-((4-nitrophenyl)hexa-1,3,5-triyn-1-yl)azulene.



1-(Bromohexa-1,3,5-triyn-1-yl)-4-nitrobenzene (**2j**, 0.089 g, 0.325 mmol), guaiiazulene (**1b**, 0.097 g, 0.489 mmol) and Al₂O₃ (basic, 1.850 g) were reacted according to the procedure for **3aa**. Reaction time: 3 d, purification: silica gel column (CH₂Cl₂/hexane; v/v; 1/2) then preparative TLC (silica gel, CH₂Cl₂/hexane; v/v; 1/2). Product was obtained as a dark brown solid (0.029 g, 0.074 mmol), yield: 23%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.21-8.16 (m, 2H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.73 (s, 1H), 7.66-7.62 (m, 2H), 7.45 (dd, *J* = 10.8, 1.9 Hz,

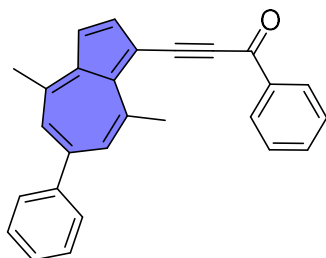
1H), 7.06 (d, $J = 10.9$ Hz, 1H), 3.20 (s, 3H), 3.07 (hept, $J = 6.9$ Hz, 1H), 2.56 (s, 3H), 1.36 (d, $J = 6.9$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*): $\delta = 148.4, 147.3, 144.3, 142.4, 140.8, 139.6, 136.9, 134.9, 133.4, 129.6, 128.8, 126.3, 123.7, 103.0, 82.5, 80.3, 79.3, 71.4, 67.8, 38.1, 26.5, 24.5, 12.9$ (one C=C signal under solvent). FTIR (cm^{-1} , KBr pellet): 2080 (C=C), 2135 (C=C). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 251 (33000), 335 (27000), 438 (23000), 485 (17000). HRMS(ESI): m/z calcd for $\text{C}_{27}\text{H}_{22}\text{NO}_2$: 392.1645 [$\text{M}+\text{H}^+$]; found: 392.1648.

(3bk) 4-((5-Isopropyl-3,8-dimethylazulen-1-yl)octa-1,3,5,7-tetrayn-1-yl)benzotrile.



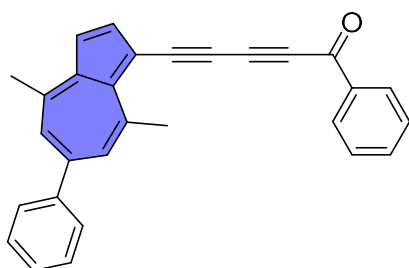
4-(Iodocta-1,3,5,7-tetrayn-1-yl)benzotrile (**2k**, 0.004 g, 0.012 mmol), guaiazulene (**1b**, 0.011 g, 0.055 mmol) and Al_2O_3 (basic, 0.675 g) were reacted according to the procedure for **3aa**. Reaction time: 11 d, purification: silica gel column (hexane/diethyl ether; v/v; 3/1) then preparative TLC (silica gel, CH_2Cl_2 /hexane; v/v; 1/2). Product was obtained as a dark brown solid (0.002 g, 0.005 mmol), yield: 47%. ^1H NMR (500 MHz, Chloroform-*d*): $\delta = 8.12$ (d, $J = 2.0$ Hz, 1H), 7.73 (s, 1H), 7.65-7.57 (m, 4H), 7.46 (dd, $J = 10.8, 2.0$ Hz, 1H), 7.07 (d, $J = 10.9$ Hz, 1H), 3.19 (s, 3H), 3.07 (hept, $J = 6.9$ Hz, 1H), 2.55 (s, 3H), 1.35 (d, $J = 6.9$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*): $\delta = 148.7, 144.7, 142.8, 141.5, 139.9, 137.1, 135.1, 133.5, 132.3, 129.91, 126.5, 126.3, 118.3, 112.9, 102.7, 80.9, 79.7, 79.1, 76.0, 70.5, 69.6, 67.2, 64.4, 38.2, 26.7, 24.6, 13.0$. ATR-FTIR (cm^{-1} , diamond crystalplate): 2221 (C=N), 2182 (weak C=C), 2158 (weak, C=C), 2089 (C=C). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 251 (31000), 281 (35000), 327 (32000), 468 (27000). HRMS(ESI): m/z calcd for $\text{C}_{30}\text{H}_{22}\text{N}$: 396.1747 [$\text{M}+\text{H}^+$]; found: 396.1730.

(3cb) 3-(4,8-Dimethyl-6-phenylazulen-1-yl)-1-phenylprop-2-yn-1-one.



3-Bromo-1-phenylprop-2-yn-1-one (**2b**, 0.030 g, 0.143 mmol), 4,8-dimethyl-6-phenylazulene (**1c**, 0.020 g, 0.087 mmol) and Al₂O₃ (basic, 1.305 g) were reacted according to the procedure for **3aa**. Reaction time: 3 d, purification: silica gel column (hexane/diethyl ether; v/v; 3/1). Product was obtained as a dark brown powder (0.017 g, 0.047 mmol), yield: 54%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.28-8.21 (m, 2H), 8.06 (d, *J* = 4.3 Hz, 1H), 7.65-7.57 (m, 3H), 7.54-7.44 (m, 7H), 7.39 (d, *J* = 4.3 Hz, 1H), 3.48 (s, 3H), 2.97 (s, 3H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 178.2, 151.0, 150.0, 147.9, 145.1, 142.2, 140.1, 139.4, 138.9, 138.1, 133.5, 131.2, 130.0, 129.4, 129.0, 128.8, 128.6, 128.5, 117.6, 106.7, 97.3, 94.7, 28.2, 26.3. ATR-FTIR (cm⁻¹, Ge crystalplate): 2144 (C≡C), 1609 (C=O). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 251 (28000), 310 (29000), 359 (21000), 424 (26000). HRMS(ESI): *m/z* calcd for C₂₇H₂₁O: 361.1587 [M+H⁺]; found: 361.1586.

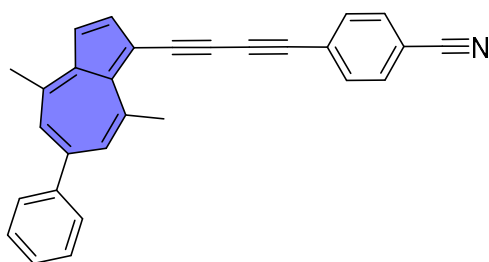
(3ce) 5-(4,8-Dimethyl-6-phenylazulen-1-yl)-1-phenylpenta-2,4-diyne-1-one.



5-Bromo-1-phenylpenta-2,4-diyne-1-one (**2e**, 0.052 g, 0.215 mmol), 4,8-dimethyl-6-phenylazulene (**1c**, 0.050 g, 0.214 mmol) and Al₂O₃ (basic, 1.755 g) were reacted according to the procedure for **3aa**. Reaction time: 7 d, purification: silica gel column (hexane/diethyl ether; v/v; 3/1). Product was obtained as a dark brown solid (0.035 g, 0.091 mmol), yield: 43%. ¹H NMR (500 MHz, Chloroform-*d*) δ = 8.20 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.96 (d, *J* = 4.3 Hz, 1H), 7.63 (dt, *J* = 7.5, 3.1 Hz, 3H), 7.55-7.41 (m, 7H), 7.33 (d, *J* = 4.4 Hz, 1H), 3.37 (s,

3H), 2.95 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*): δ = 177.4, 151.0, 150.0, 148.0, 145.1, 142.0, 139.5, 139.3, 137.2, 134.2, 130.8, 129.9, 129.7, 129.0, 128.7, 128.7, 128.6, 117.5, 106.6, 89.6, 81.3, 80.8, 78.1, 28.1, 26.2. ATR-FTIR (cm^{-1} , Ge crystalplate): 2168 ($\text{C}\equiv\text{C}$), 1623 ($\text{C}=\text{O}$). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 254 (23500), 321 (23500), 451 (15000). HRMS(ESI): m/z calcd for $\text{C}_{29}\text{H}_{21}\text{O}$: 385.1587 [$\text{M}+\text{H}^+$]; found: 385.1595.

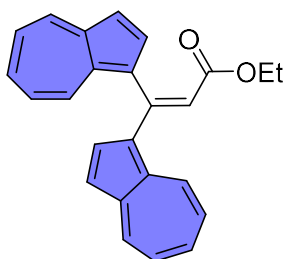
(3cf) 4-((4,8-Dimethyl-6-phenylazulen-1-yl)buta-1,3-diyn-1-yl)benzotrile.



4-(Chlorobuta-1,3-diyn-1-yl)benzotrile (**2f**, 0.039 g, 0.210 mmol), 4,8-dimethyl-6-phenylazulene (**1c**, 0.033 g, 0.142 mmol) and Al_2O_3 (basic, 1.470 g) were reacted according to the procedure for **3aa**. Reaction time: 15 d, purification: silica gel column (hexane/diethyl ether; v/v; 3/1). Product was obtained as a dark green powder (0.007 g, 0.018 mmol), yield: 11%. ^1H NMR (500 MHz, Chloroform-*d*): δ = 7.92 (d, J = 4.3 Hz, 1H), 7.64-7.58 (m, 6H), 7.52-7.47 (m, 2H), 7.45 (dt, J = 9.7, 4.3 Hz, 1H), 7.41 (s, 1H), 7.37 (s, 1H), 7.33 (d, J = 4.3 Hz, 1H), 3.37 (s, 3H), 2.94 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*): δ = 150.7, 149.7, 147.6, 145.3, 141.3, 138.7, 138.3, 132.7, 132.2, 130.1, 129.2, 128.9, 128.7, 128.4, 128.0, 118.6, 117.2, 111.7, 107.8, 86.0, 81.2, 80.1, 78.2, 28.0, 26.2. ATR-FTIR (cm^{-1} , Ge crystalplate): 2223 ($\text{C}\equiv\text{N}$), 2182 ($\text{C}\equiv\text{C}$), 2130 (weak, $\text{C}\equiv\text{C}$). UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]) = 253 (28000), 339 (29000), 407 (19000), 434 (20000). HRMS(ESI): m/z calcd for $\text{C}_{29}\text{H}_{20}\text{N}$: 382.1590 [$\text{M}+\text{H}^+$]; found: 382.1570.

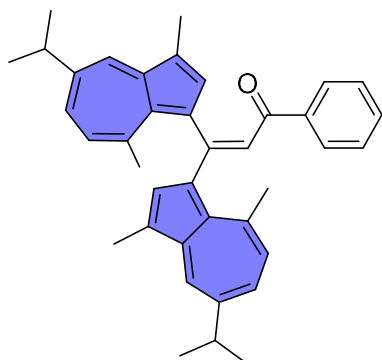
2.4. Synthesis of bisazulenyl ethenes

(4aa) Ethyl 3,3-bis(azulen-1-yl)propenoate.



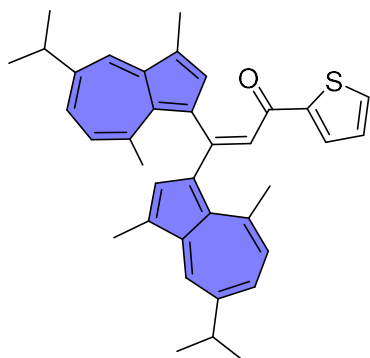
Ethyl 3-bromo-2-propynoate (**2a**, 0.042 g, 0.237 mmol), azulene (**1a**, 0.092 g, 0.719 mmol) and Al₂O₃ (basic, 1.623 g) were reacted according to the procedure for **3aa**. Reaction time: 2 d, purification: preparative TLC (neutral aluminium oxide, CH₂Cl₂). Product was obtained as a dark green oil (0.004 g, 0.011 mmol), yield: 17%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.37 (d, *J* = 9.3 Hz, 1H), 8.33 (d, *J* = 9.3 Hz, 1H), 8.25 (d, *J* = 9.9 Hz, 1H), 8.05 (d, *J* = 9.8 Hz, 1H), 7.86 (d, *J* = 3.9 Hz, 1H), 7.69 (d, *J* = 4.1 Hz, 1H), 7.59 (t, *J* = 9.7 Hz, 1H), 7.55 (t, *J* = 9.7 Hz, 1H), 7.43 (d, *J* = 3.9 Hz, 1H), 7.30 (d, *J* = 4.1 Hz, 1H), 7.22 (d, *J* = 9.5 Hz, 1H), 7.18 (d, *J* = 9.6 Hz, 1H), 7.06 (t, *J* = 9.9 Hz, 1H), 7.00 (t, *J* = 9.8 Hz, 1H), 6.49 (s, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 0.99 (t, *J* = 7.1 Hz, 3H). ¹³C {¹H} NMR (126 MHz, Chloroform-*d*): δ = 167.0, 147.8, 144.0, 142.8, 139.7, 139.3, 138.6, 137.9, 137.8, 137.3, 137.2, 137.2, 136.1, 135.6, 131.9, 129.6, 124.9, 124.6, 124.0, 123.9, 118.1, 117.5, 117.3, 59.8, 14.2. ATR-FTIR (cm⁻¹, diamond crystalplate): 1706 (C=O). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 237 (34000), 283 (32000), 386 (14000). HRMS(ESI): *m/z* calcd for C₂₅H₂₁O₂; 353.1536 [M+H⁺]; found: 353.1538.

(4bb) 3,3-Bis(5-isopropyl-3,8-dimethylazulen-1-yl)-1-phenylprop-2-en-1-one.



3-Bromo-1-phenylprop-2-yn-1-one (**2b**, 0.023 g, 0.110 mmol), guiazulene (**1b**, 0.061 g, 0.308 mmol) and Al₂O₃ (basic, 0.643 g) were reacted according to the procedure for **3aa**. Reaction time: 1 h, purification: silica gel column (hexane/diethyl ether; v/v; 3/1). Product was obtained as a dark brown solid (0.057 g, 0.109 mmol), yield: 95%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.23 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 10.8, 1.9 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.40 (d, *J* = 13.9 Hz, 2H), 7.37 (dd, *J* = 10.7, 1.9 Hz, 1H), 7.22-7.15 (m, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 10.7 Hz, 1H), 6.65 (s, 1H), 3.14 (hept, *J* = 6.9 Hz, 1H), 3.06 (hept, *J* = 6.9 Hz, 1H), 3.04 (s, 3H), 2.72 (s, 3H), 2.52 (s, 6H, two singlet overlapped), 1.41 (d, *J* = 6.9 Hz, 6H), 1.37 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 190.9, 151.7, 146.6, 146.0, 142.9, 142.6, 141.5, 141.4, 140.8, 140.1, 139.7, 135.5, 135.3, 134.9, 133.8, 133.5, 133.3, 131.7, 130.6, 129.8, 128.3, 128.2, 127.5, 127.5, 127.5, 124.8, 124.7, 38.1, 38.1, 28.1, 26.6, 24.9, 24.8, 14.3, 13.0. ATR-FTIR (cm⁻¹, diamond crystalplate): 1682 (C=O). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 248 (25000), 292 (21000), 450 (6000). HRMS(ESI): *m/z* calcd for C₃₉H₄₁O: 525.3152 [M+H⁺]; found: 525.3150.

(4bc) 3,3-Bis(5-isopropyl-3,8-dimethylazulen-1-yl)-1-(thiophen-2-yl)prop-2-en-1-one.

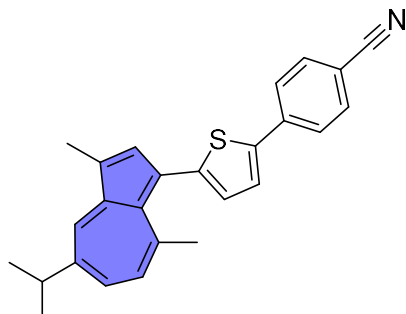


3-Bromo-1-(thiophen-2-yl)prop-2-yn-1-one (**2c**, 0.079 g, 0.367 mmol), guaiazulene (**1b**, 0.141 g, 0.711 mmol) and Al₂O₃ (basic, 1.716 g) were reacted according to the procedure for **3aa**. Reaction time: 1 h, purification: silica gel column (hexane/diethyl ether; v/v; 3/1). Product was obtained as dark brown solid (0.200 g, 0.377 mmol), yield: 92%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.21 (dd, *J* = 14.7, 2.0 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.45 – 7.39 (m, 3H), 7.30 (s, 1H), 7.20 (d, *J* = 10.8 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.76 (s, 1H), 3.11 (m, 2H), 3.01 (s, 3H), 2.74 (s, 3H), 2.59 (s, 3H), 2.50 (s, 3H), 1.40 (d, *J* = 6.9 Hz, 6H) 1.40 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ = 180.1, 152.6, 148.3, 146.7, 146.3, 142.7, 142.7, 141.4, 141.3, 140.8, 139.8, 135.3, 135.1, 134.6, 133.8, 133.4, 132.2, 131.6, 130.0, 129.9, 128.4, 127.8, 127.8, 125.2, 124.9, 124.6, 38.1, 38.1, 27.9, 26.8, 24.8, 24.8, 13.2, 13.0. ATR-FTIR (cm⁻¹, Ge crystalplate): 1623 (C=O). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 249 (45000), 297 (43000), 472 (14000). HRMS(ESI): *m/z* calcd for C₃₇H₃₉OS: 531.2716 [M+H⁺]; found: 531.2717.

2.5. Synthesis of azulenyl thiophenes

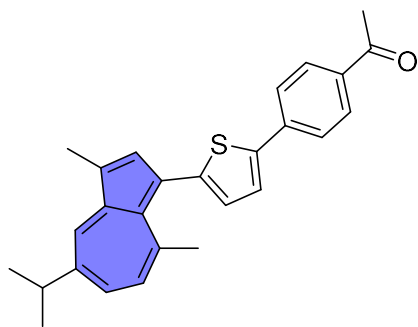
(5bf) 4-(5-(5-isopropyl-3,8-dimethylazulen-1-yl)thiophen-2-yl)benzonitrile. **General**

Procedure.



4-((5-Isopropyl-3,8-dimethylazulen-1-yl)buta-1,3-diyne-1-yl)benzonitrile (**3bf**, 0.014g, 0.040 mmol) was dissolved in MeCN (4 mL) and the solution was heated to 70 °C under N₂. Then, Na₂S·H₂O (60% of Na₂S, 0.709 mmol) was added and the mixture was stirred overnight. After this time water (20 mL) was added and the product was extracted with Et₂O (3 × 10 mL). Combined organic layers were washed twice with H₂O (2 × 20 mL), dried over Na₂SO₄, filtered, and the solvent was evaporated under reduced pressure. Compound **5bf** (0.0115 g, 0.030 mmol) was isolated as a green solid; yield: 74%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.22 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.67-7.61 (m, 3H), 7.43 (dd, *J* = 10.7, 1.9 Hz, 1H), 7.40 (d, *J* = 3.7 Hz, 1H), 7.01 (d, *J* = 10.7 Hz, 1H), 6.91 (d, *J* = 3.7 Hz, 1H), 3.10 (hept, *J* = 7.0 Hz, 1H), 2.66 (two overlapped singlets, 6H), 1.38 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 146.5, 145.3, 141.3, 141.2, 140.9, 139.1, 138.8, 135.6, 134.3, 133.4, 132.9, 129.7, 128.2, 125.7, 124.9, 124.6, 119.2, 119.2, 110.1, 38.0, 27.1, 24.8, 12.9. ATR-FTIR (cm⁻¹, diamond crystalplate): 2223 (C≡N). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 242 (24200), 292 (28500), 319 (20000), 401 (10300). HRMS(ESI): *m/z* calcd for C₂₆H₂₄NS: 382.1624 [M+H⁺]; found: 382.1627.

(5bg) 1-(4-(5-(5-Isopropyl-3,8-dimethylazulen-1-yl)thiophen-2-yl)phenyl)ethan-1-one.

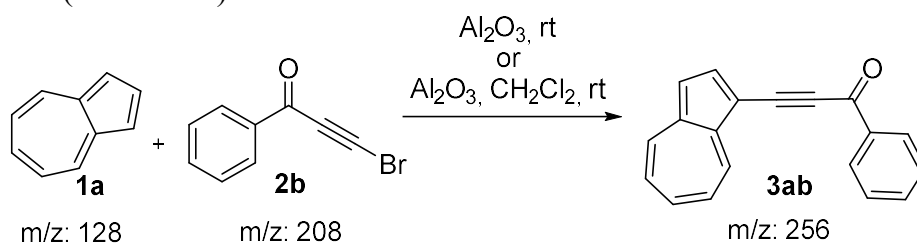


1-(4-((5-Isopropyl-3,8-dimethylazulen-1-yl)buta-1,3-diyne-1-yl)phenyl)ethan-1-one (**3bg**, 0.039 g, 0.128 mmol), MeCN (4 mL) and Na₂S·H₂O (0.178 g, 1.854 mmol) were used according to the procedure for **5bf**. Reaction time: 16 h. Product was obtained as green solid (0.024 g, 0.060 mmol), yield: 55%. ¹H NMR (500 MHz, Chloroform-*d*): δ = 8.22 (d, *J* = 2.1 Hz, 1H), 8.00-7.94 (m, 2H), 7.74-7.69 (m, 2H), 7.65 (s, 1H), 7.43 (m, 2H), 7.00 (d, *J* = 10.8 Hz, 1H), 6.91 (d, *J* = 3.7 Hz, 1H), 3.10 (hept, *J* = 6.9 Hz, 1H), 2.68 (s, 3H), 2.66 (s, 3H), 2.62 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ = 197.5, 146.6, 144.6, 142.1, 141.1, 141.0, 139.3, 138.8, 135.5, 135.5, 134.3, 133.3, 129.7, 129.3, 128.1, 125.3, 124.5, 124.4, 119.6, 38.0, 27.1, 26.7, 24.8, 12.9. ATR-FTIR (cm⁻¹, diamond crystalplate): 1667 (C=O). UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [dm³mol⁻¹cm⁻¹]) = 243 (17300), 292 (19600), 403 (6300). HRMS(ESI): *m/z* calcd for C₂₇H₂₆OSNa: 421.1602 [M+Na⁺]; found: 421.1597.

3. Additional experiments

3.1. Comparison of solvent-free reaction with reactions in solution

Gas chromatography coupled to mass spectrometry (GC-MS) was used to get additional insight in the reaction mechanism. Reaction between azulene **1a** and alkyne **2b** was used as a model reaction (Scheme S2).



Scheme S2. Model reaction between **1a** and **2b**.

Procedures of model reactions:

Solvent-free reaction: 3-Bromo-1-phenylprop-2-yn-1-one (**2b**, 0.136 g, 0.649 mmol), azulene (**1a**, 0.064 g, 0.499 mmol) and Al_2O_3 (activity I, basic, 2.00 g) were grinded in a mortar for 15 minutes. The reaction mixture after grinding was left in a vial and 50 μL of mesitylene was added as a GC standard. Samples of reaction mixture (10 mg) were taken out from the reaction mixture, diluted with 5 mL of CH_2Cl_2 , filtrated off, transferred to 1.5 mL GC vial and measured immediately.

Reaction in CH_2Cl_2 (with initial grinding): 3-Bromo-1-phenylprop-2-yn-1-one (**2b**, 0.136 g, 0.649 mmol), azulene (**1a**, 0.064 g, 0.499 mmol) and Al_2O_3 (activity I, basic, 2.00 g) were grinded in a mortar for 15 minutes. The reaction mixture after grinding was diluted with 50 mL of CH_2Cl_2 and 50 μL of mesitylene was added as a GC standard. Next reaction mixture was stirred at room temperature. Samples of reaction mixture (0.5 mL) were taken out from the reaction mixture after given time, diluted to 5 mL with CH_2Cl_2 , filtrated off, transferred to 1.5 mL GC vial and measured immediately.

Reaction in CH_2Cl_2 (without initial grinding): 3-Bromo-1-phenylprop-2-yn-1-one (**2b**, 0.136 g, 0.649 mmol), azulene (**1a**, 0.064 g, 0.499 mmol) and Al_2O_3 (activity I, basic, 2.00 g) were

placed in 100 mL round bottomed flask, diluted with 50 mL of CH_2Cl_2 and 50 μL of mesitylene was added as a GC standard. Next reaction mixture was stirred at room temperature. Samples of reaction mixture (0.5 mL) were taken out from the reaction mixture after given time, diluted to 5 mL with CH_2Cl_2 , filtrated off, transferred to 1.5 mL GC vial and measured immediately.

Solvent-free reaction

All chromatograms were normalized to mesitylene peak and are shown in Figure S1. Peaks of both substrates (**1a** and **2b**, $t = 8.31$ min. and $t = 9.15$ min.) are diminishing over time and after 24 h substrates are fully consumed. Peak of product gradually rises ($t = 22.15$ min.) but no significant change was observed between measurements after 7 h and 24 h when reaction was fully completed.

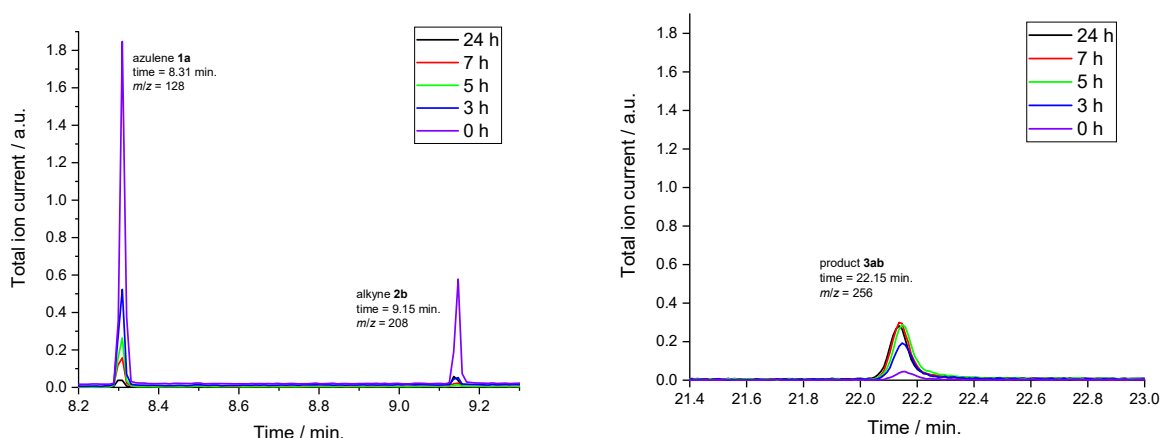


Figure S1. Fragments of chromatograms from reaction carried out without solvent.

Reaction in CH_2Cl_2 (with initial grinding)

All chromatograms were normalized to mesitylene peak and are shown in Figure S2. There is no significant change in peak derived from azulene ($t = 8.31$ min.) even after 24 h. The amount of alkyne **2b** is decreasing probably due to its decomposition in solution (additional peaks from decomposition products are observed). The amount of product ($t = 22.15$ min.) is at the same level directly after grinding and after 24 h of stirring in solution. The reaction does not occur in solution, only degradation of alkyne **2b** was observed.

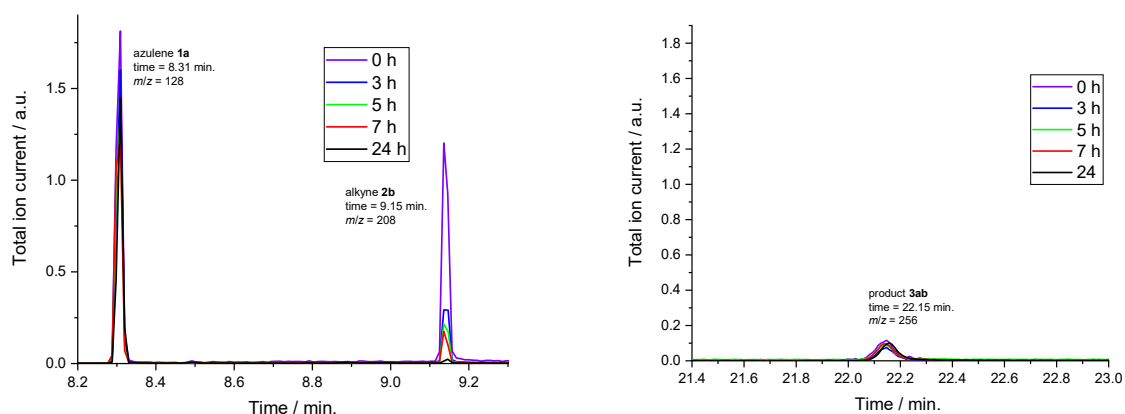


Figure S2. Fragments of chromatograms from reaction carried out in CH_2Cl_2 (after 15 min. of grinding).

Reaction in CH_2Cl_2 (without initial grinding)

All chromatograms were normalized to mesitylene peak and are shown in Figure S3. There is no significant change in peak derived from azulene ($t = 8.31$ min.), even after 24 h. The amount of alkyne **2b** is decreasing probably due to its decomposition in solution (additional peaks from decomposition products are observed). There is no detectable amount of product after 24 h of stirring in solution. The reaction does not occur in solution, only degradation of alkyne **2b** was observed.

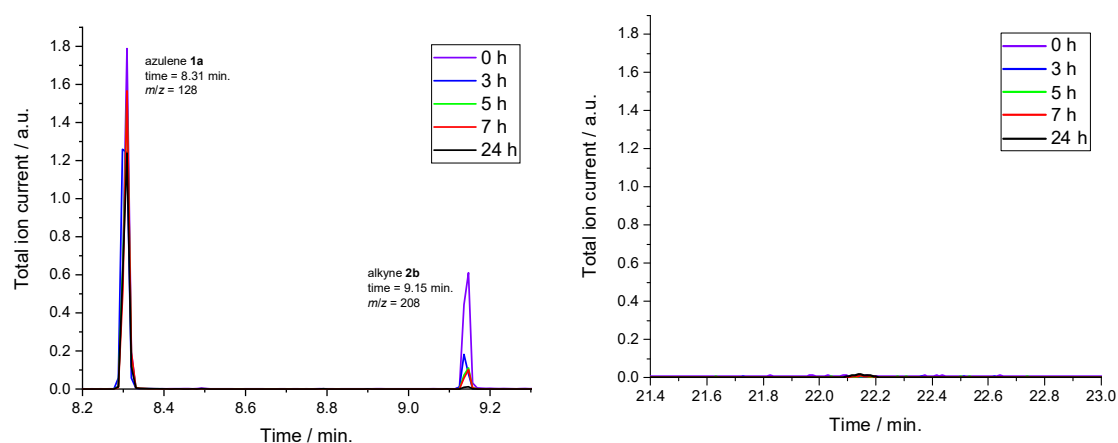


Figure S3. Fragments of chromatograms from reaction carried out in CH_2Cl_2 (without grinding).

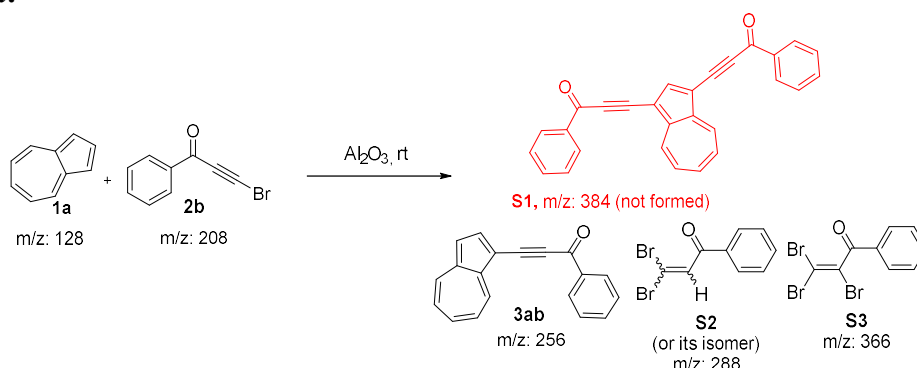
3.2. Double alkylation of azulene

Gas chromatography coupled to mass spectrometry (GC-MS) and ^1H NMR were used to check the possibility of double alkylation of azulene. Reaction between azulene **1a** and alkyne **2b** was used as a model reaction. Higher excess of alkyne (5 equiv instead 1.3 equiv) was used in order to facilitate second alkylation.

Procedure of a model reaction:

3-Bromo-1-phenylprop-2-yn-1-one (**2b**, 0.163 g, 0.780 mmol), azulene (**1a**, 0.020 g, 0.156 mmol) and Al_2O_3 (activity I, basic, 2.00 g) were grinded in a mortar for 15 minutes. Next reaction mixture was left in a vial and samples (10 mg) for ^1H NMR and GC-MS measurements were taken out after 24. *GC-MS samples:* Solid sample was diluted to 1.5 mL of CH_2Cl_2 , filtrated and transferred to 1.5 mL GC vial. *^1H NMR samples:* Solid sample was place in syringe filter and washed with CDCl_3 (0.4 mL) directly to NMR tube.

Discussion:



Scheme S3. Reaction of azulene **1a** with higher excess (5 equiv) of alkyne **2b**.

Chromatogram after 24 h is shown in Figure S4. After 24 h there was no trace of both substrates and peak of monoalkynylated product **3ab** was observed ($t = 22.15$ min.; m/z : 256) but no even trace of dialkynylated product **S1** is visible. In addition to that, two new peaks appear with $m/z = 288$ and $m/z = 366$. Their m/z and isotope pattern is consistent with compounds **2b**+HBr (**S2**) and **2b**+ Br_2 (**S3**), respectively (Scheme S3). Such species are probably products of decomposition of alkyne **2b** which was used in large excess.

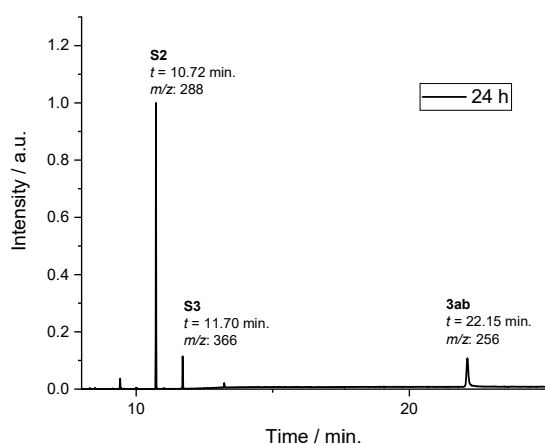


Figure S4. Chromatogram of reaction carried out with higher excess of **2b** (5 equiv) after 24 h of aging of reaction mixture in a vial.

^1H NMR spectra of reaction mixture after 24 h and spectrum of pure **3ab** are shown in Figure S5. Compound **3ab** is clearly visible in the reaction mixture after 24 h along with an additional set of signals (singlet and set of signals from phenyl group) possibly derived from decomposition product **S2**. There are no signals of other azulene-containing molecule than **3ab** and no even traces of double alkylation product **S1**.

In our opinion reactivity of azulene in this solvent-free reaction strongly depends on its nucleophilicity. After first alkylation azulene is much less nucleophilic and thus second alkylation is not observed.

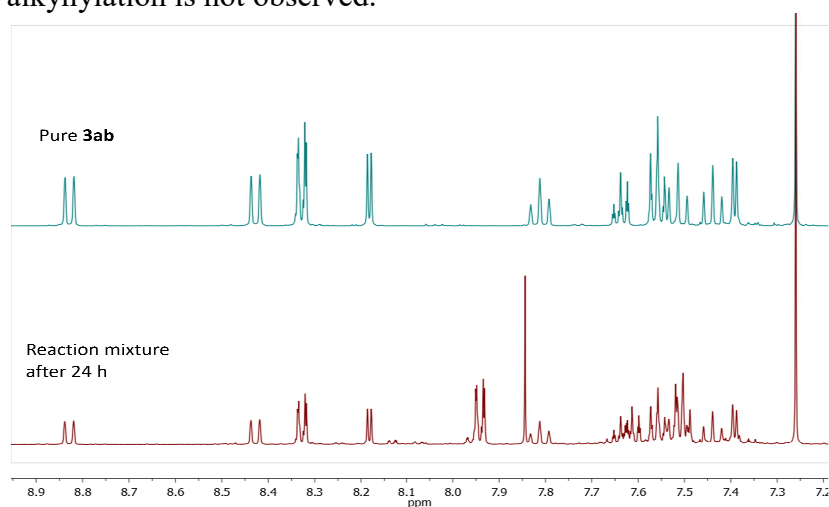


Figure S5. ^1H NMR spectra of reaction mixture after 24 h and pure **3ab** (CDCl_3 , 500 MHz, 300 K).

4. X-ray crystallography details

Molecular structures of analyzed azulene derivatives. Thermal ellipsoids are given with 50% probability. Crystals were grown by slow evaporation of hexane/ CH_2Cl_2 solutions.

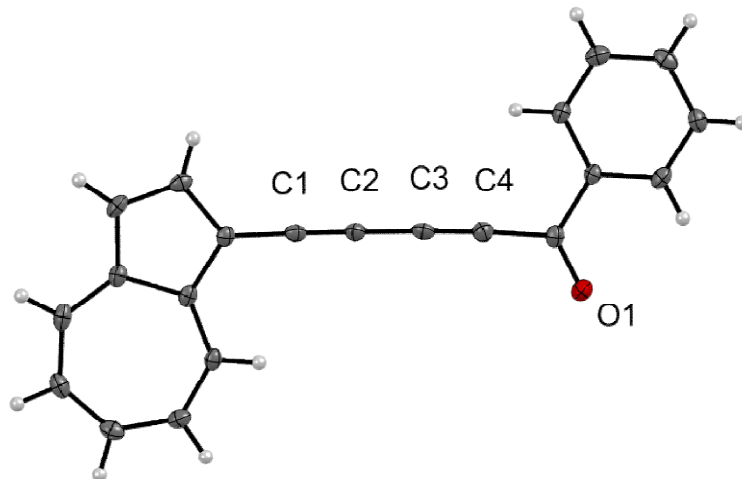


Figure S6. Molecular structure of **3ae**.

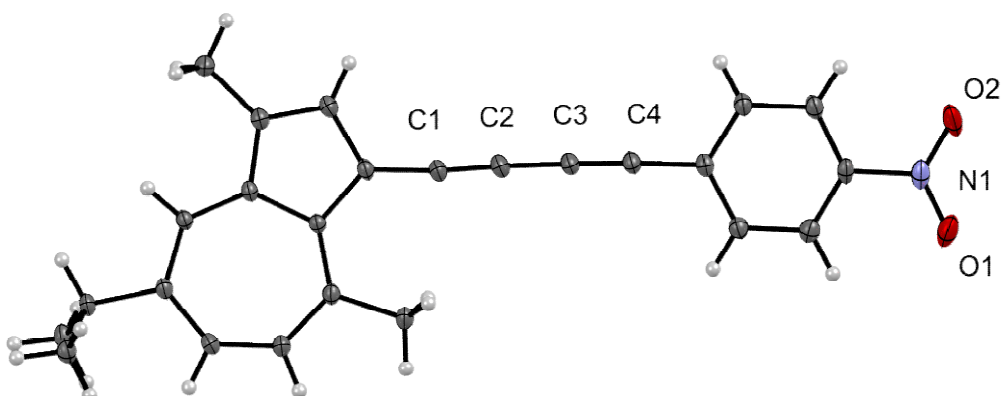


Figure S7. Molecular structure of **3bh**.

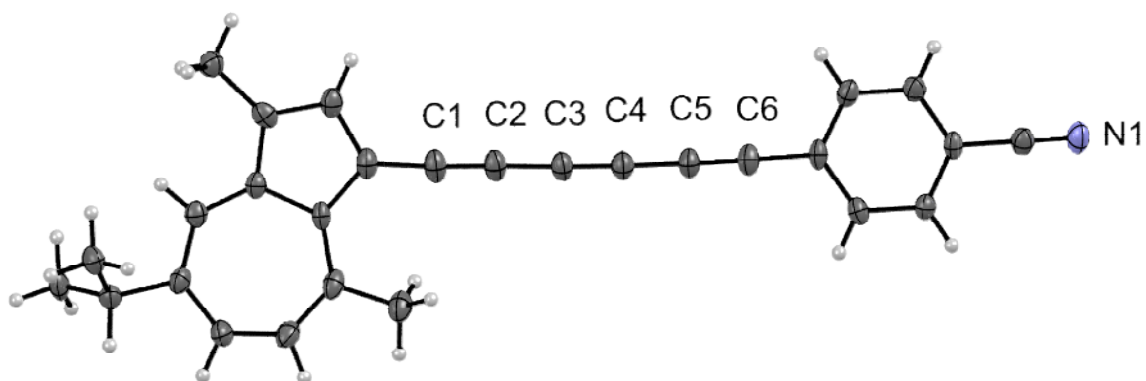


Figure S8. Molecular structure of **3bi**.

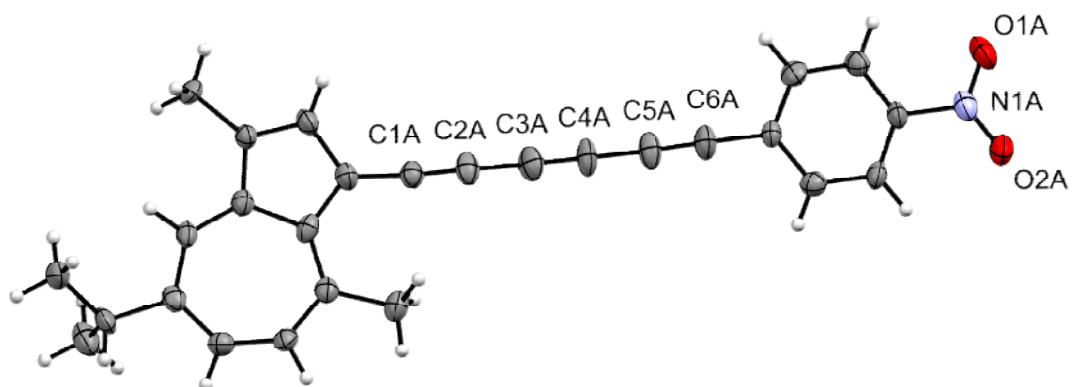


Figure S9. Molecular structure of **3bj**.

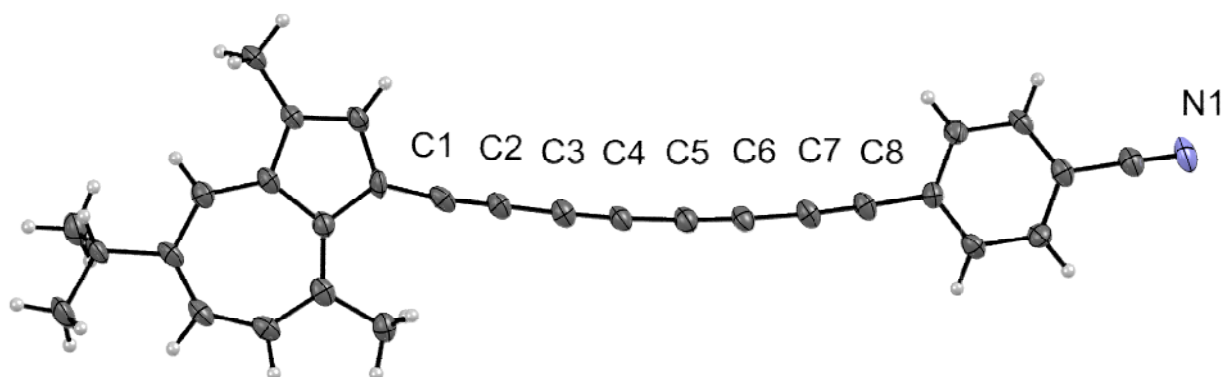


Figure S10. Molecular structure of **3bk**.

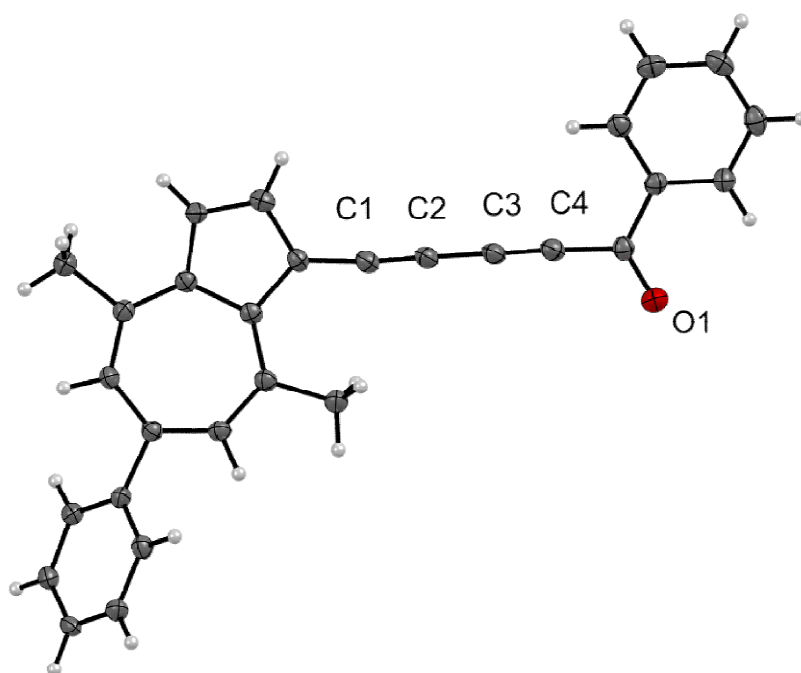


Figure S11. Molecular structure of **3ce**.

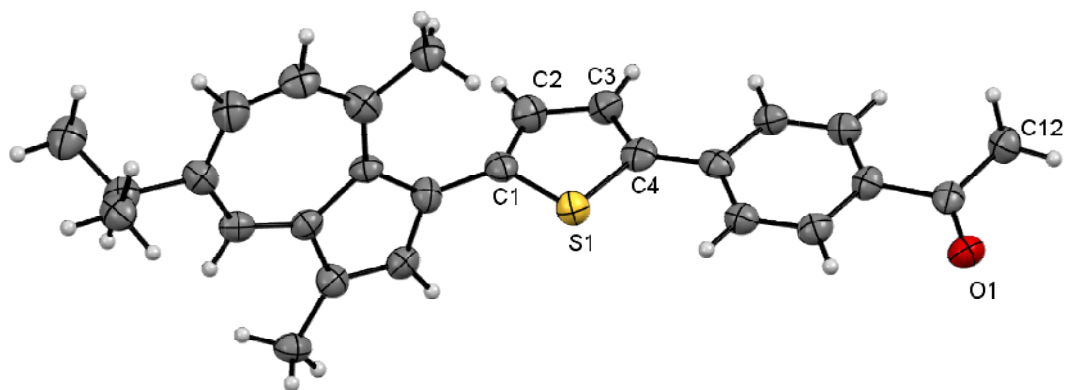


Figure S12. Molecular structure of **5bg**.

Table S1. Details of X-ray single crystal diffraction experiment for **3ae**, **3bh**, **3bi**, **3bj**, **3bk**, **3ce**, **5bg**.

Compound	3ae	3bh	3bi	3bj	3bk	3ce	5bg
CCDC number	1970441	1970437	1970436	1970438	1970435	1970439	1970440
chemical formula	C ₂₁ H ₁₂ O	C ₂₅ H ₂₁ NO ₂	C ₂₈ H ₂₁ N	C ₂₇ H ₂₁ NO ₂	C ₃₀ H ₂₁ N	C ₂₉ H ₂₀ O	<u>C₂₇H₂₆OS</u>
<i>M_r</i>	280.31	367.43	371.46	391.47	395.48	384.45	398.54
crystal size (mm)	0.3×0.01×0.01	0.82×0.47×0.17	0.4×0.3× 0.03	0.25×0.16×0.06	0.8×0.06×0.03	0.2×0.2×0.03	<u>0.54×0.16×0.03</u>
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	orthorhombic
space group	<i>P2₁/c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P2₁/n</i>	<u><i>Pca2₁</i></u>
T (K)	100	100	100	100	100	100	100
<i>a</i> (Å)	17.413 (3)	6.917(2)	8.156 (3)	7.653 (2)	7.594 (3)	6.921 (3)	<u>23.690 (5)</u>
<i>b</i> (Å)	3.830 (3)	10.694 (2)	8.911 (3)	16.102 (5)	10.028 (3)	12.804 (3)	<u>16.013 (3)</u>
<i>c</i> (Å)	21.881 (2)	14.206 (4)	15.671 (5)	17.021 (5)	15.437(3)	22.410 (2)	<u>5.510 (2)</u>
α (°)	90	73.17 (2)	101.68 (2)	76.24 (3)	99.94 (2)	90	90
β (°)	108.59 (2)	81.00 (3)	96.05 (3)	89.86 (3)	95.43 (2)	94.58 (4)	90
γ (°)	90	71.94 (3)	113.08 (3)	81.03 (3)	109.53 (2)	90	90
<i>V</i> (Å ³)	1383.2 (2)	953.7 (5)	1004.2 (6)	2011.1 (11)	1076.6 (6)	1979.53 (17)	<u>2090.4 (10)</u>
<i>Z</i>	4	2	2	4	2	4	4
radiation	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Cu <i>K</i> α
μ (mm ⁻¹)	0.08	0.08	0.07	0.08	0.07	0.08	1.48
<i>T</i> _{min}	0.891	0.830	0.735	0.98	0.793	0.674	<u>0.074</u>
<i>T</i> _{max}	1.000	1.000	1.000	0.995	1.000	1.000	1.000
no. of obsd reflns	1732	5839	2925	2815	1724	2298	<u>3521</u>
no. of par.	199	257	266	602	284	273	<u>267</u>
R1	0.057	0.065	0.069	0.097	0.074	0.067	<u>0.102</u>
<i>wR</i> (<i>F</i> ²)	0.102	0.192	0.201	0.303	0.176	0.176	<u>0.316</u>
<i>S</i>	1.01	1.03	1.03	0.98	0.99	1.03	<u>1.07</u>

5. Optical properties

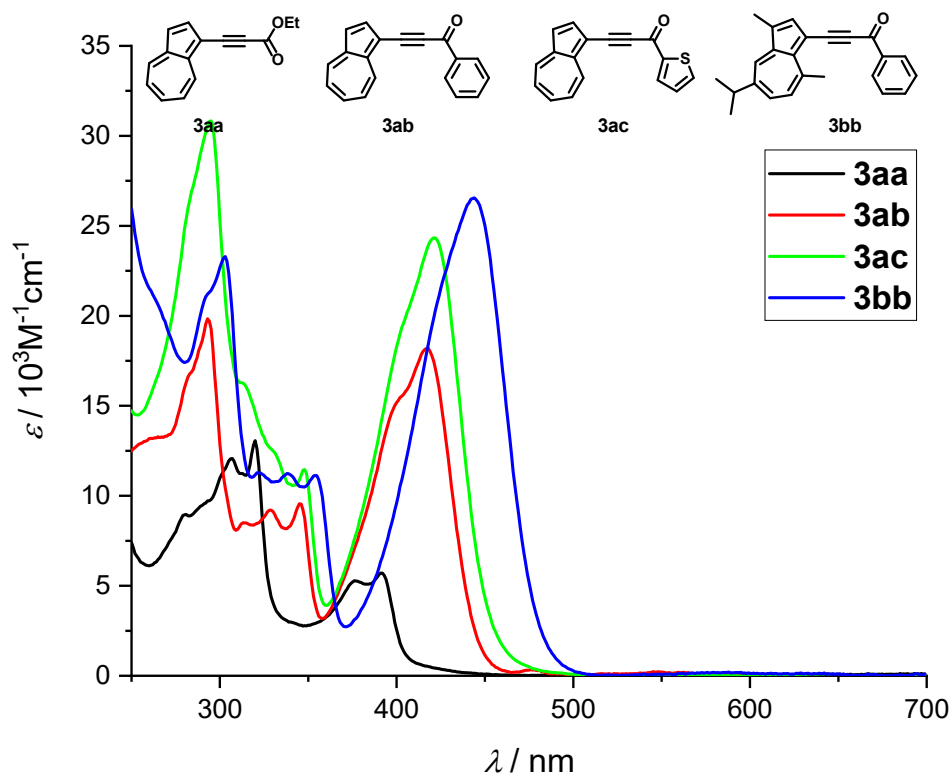


Figure S13. UV/Vis spectra of compounds **3aa**, **3ab**, **3ac** and **3bb** (CH_2Cl_2 , rt).

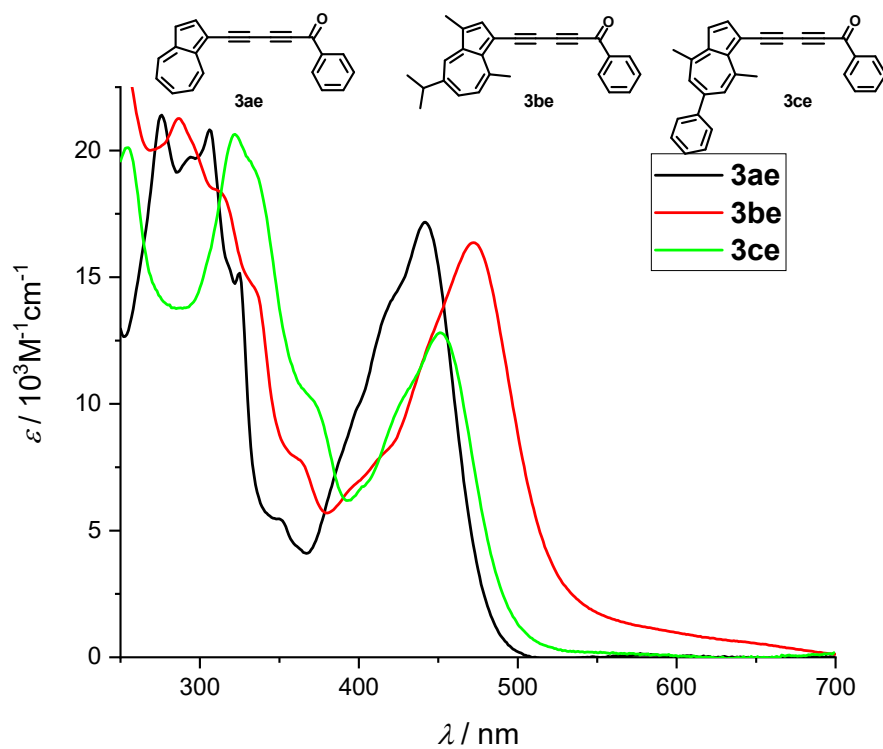


Figure S14. UV/Vis spectra of compounds **3ae**, **3be** and **3ce** (CH_2Cl_2 , rt).

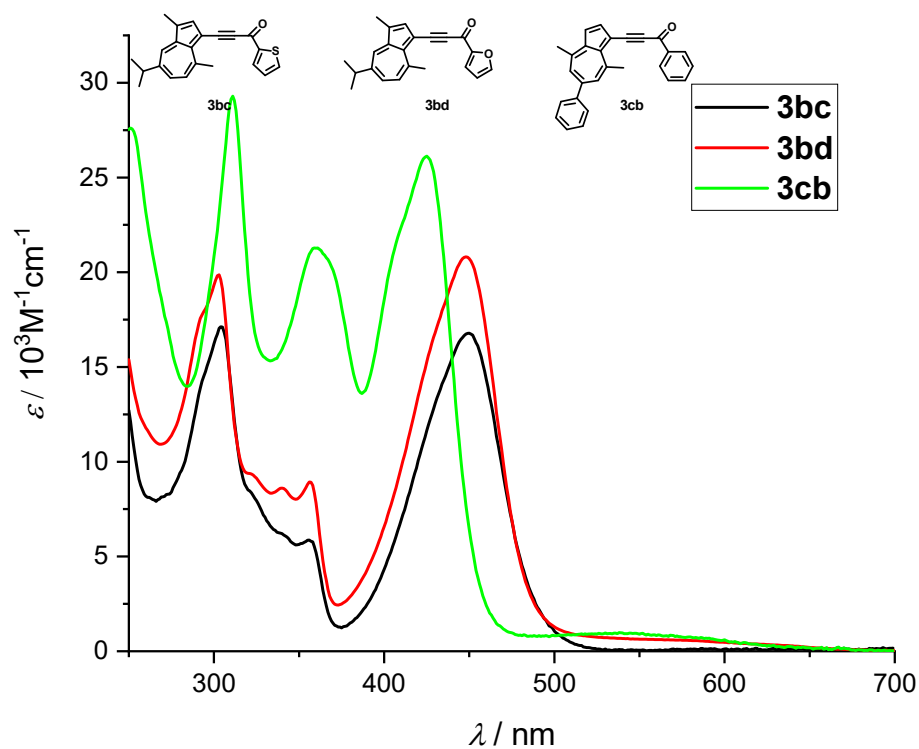


Figure S15. UV/Vis spectra of compounds **3bc**, **3bd** and **3cb** (CH_2Cl_2 , rt).

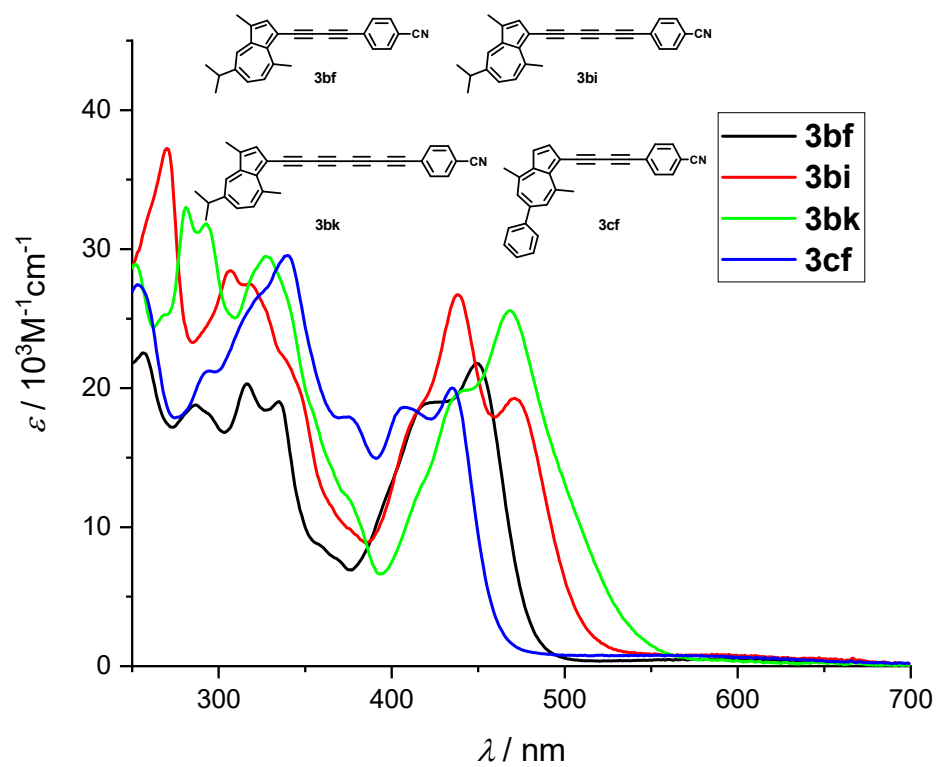


Figure S16. UV/Vis spectrum of compounds **3bf**, **3bi**, **3bk** and **3cf** (CH_2Cl_2 , rt).

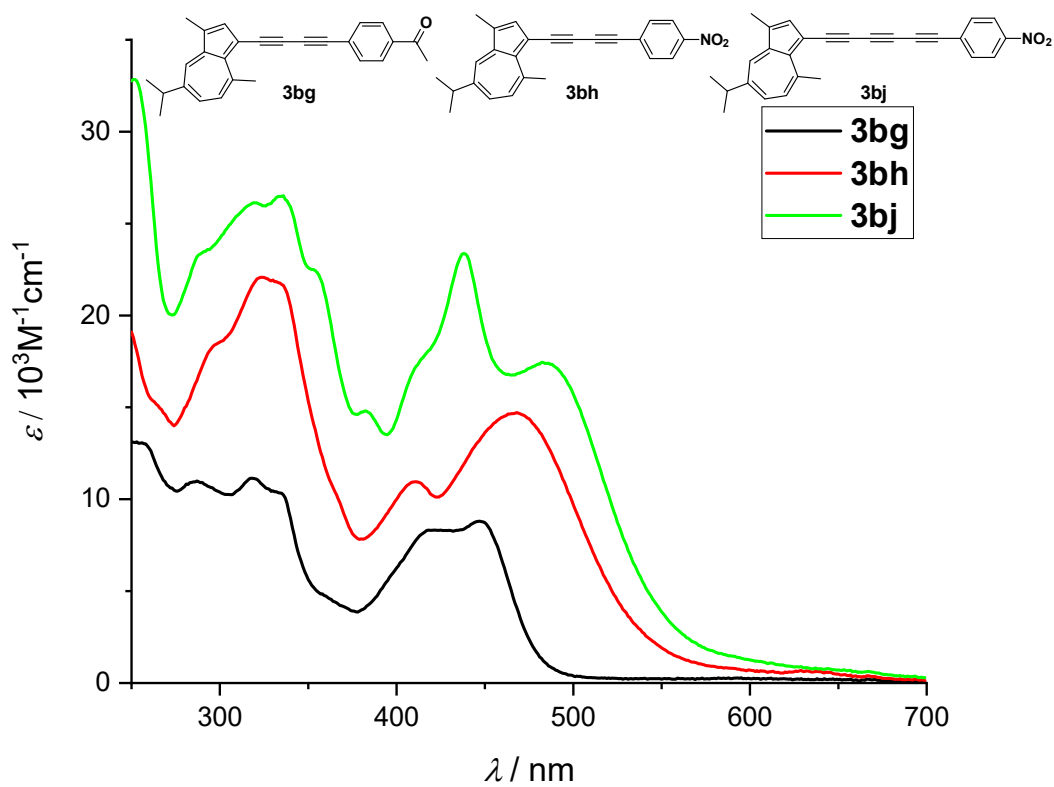


Figure S17. UV/Vis spectrum of compound **3bg**, **3bh** and **3bj** (CH_2Cl_2 , rt).

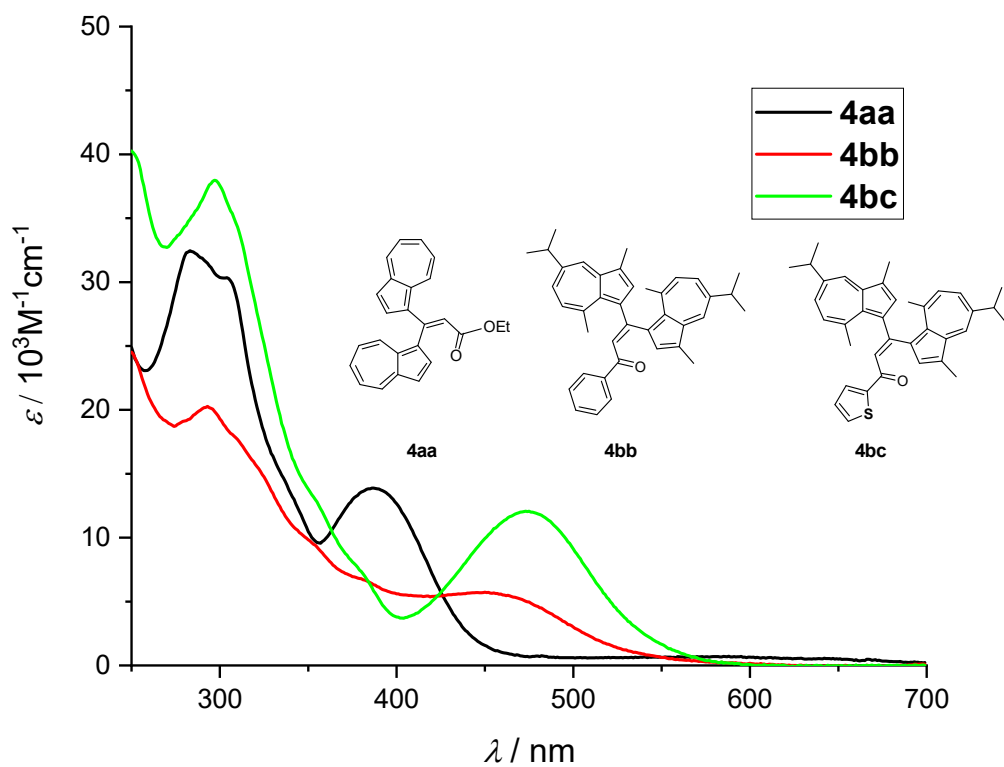


Figure S18. UV/Vis spectra of compounds **4aa**, **4bb**, **4bc** (CH_2Cl_2 , rt).

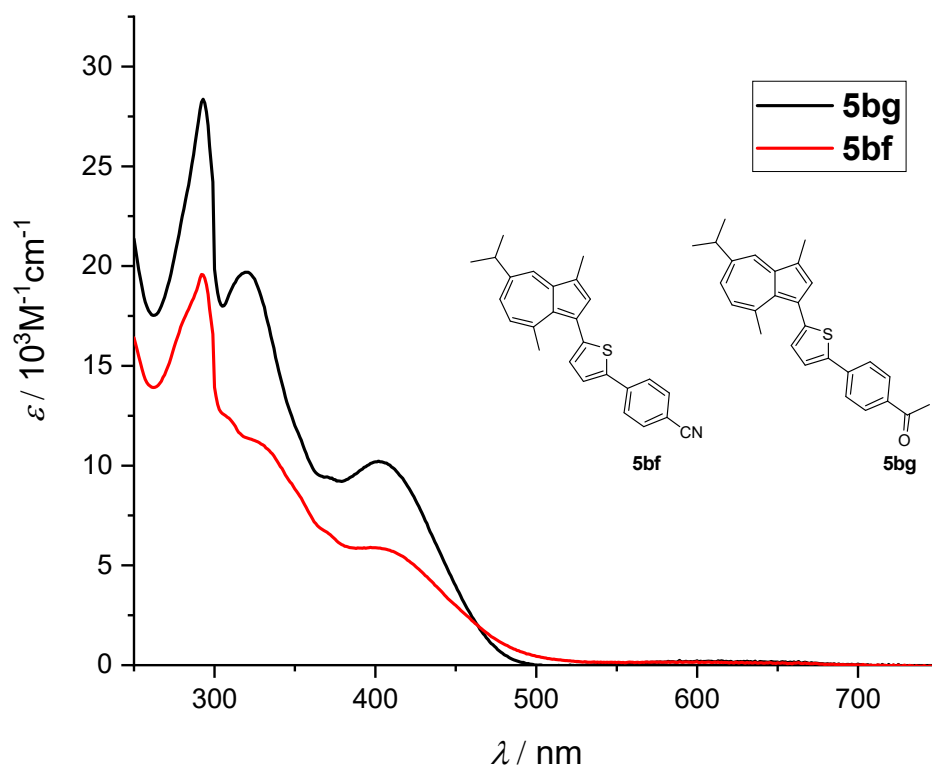


Figure S19. UV/Vis spectra of compounds **5bf** and **5bg** (CH₂Cl₂, rt).

6. NMR spectra

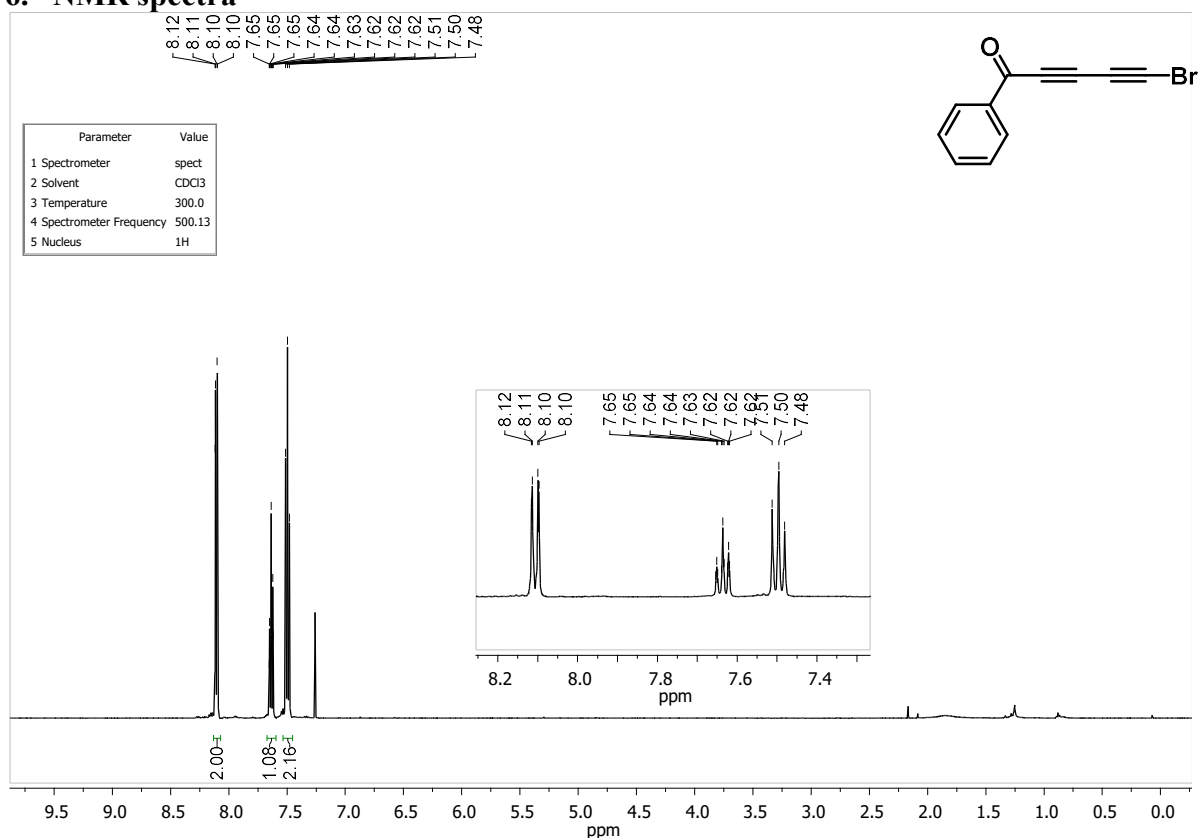


Figure S20. ¹H NMR spectrum of compound 2e.

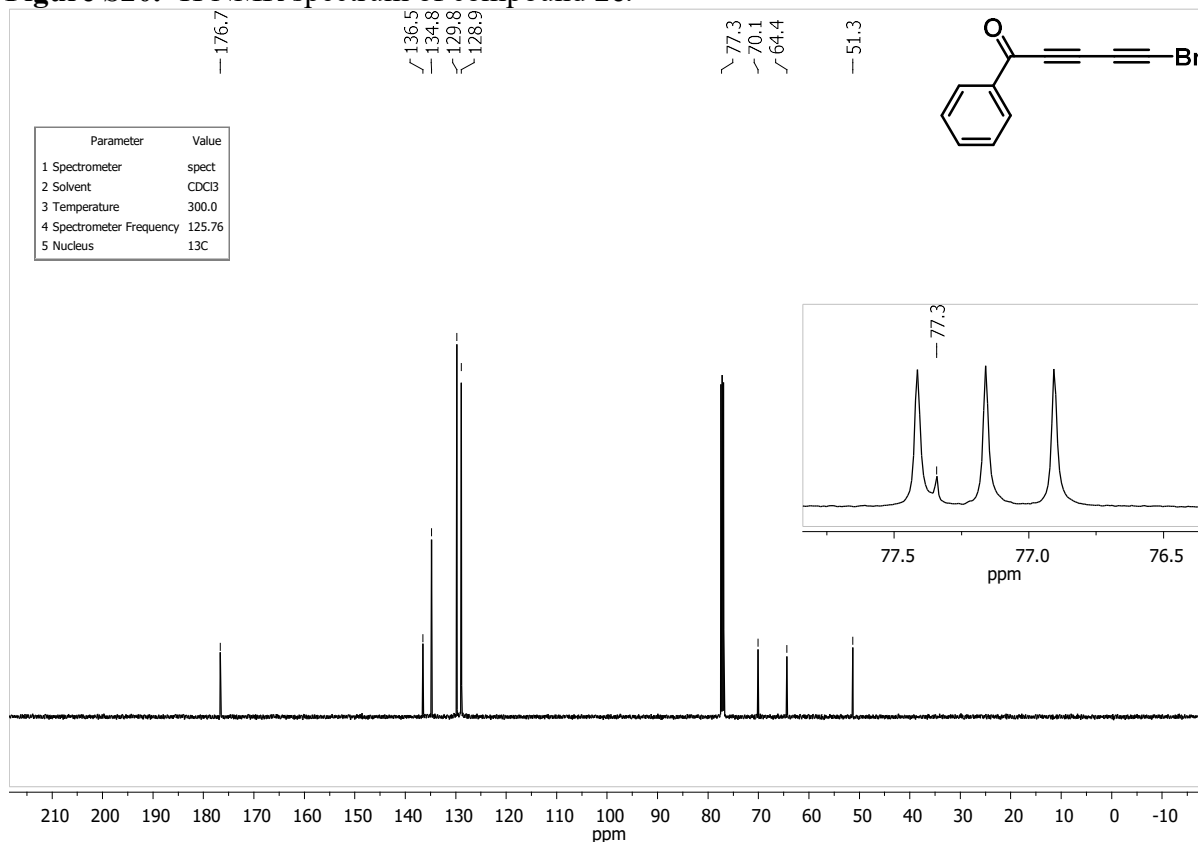


Figure S21. ¹³C NMR spectrum of compound 2e.

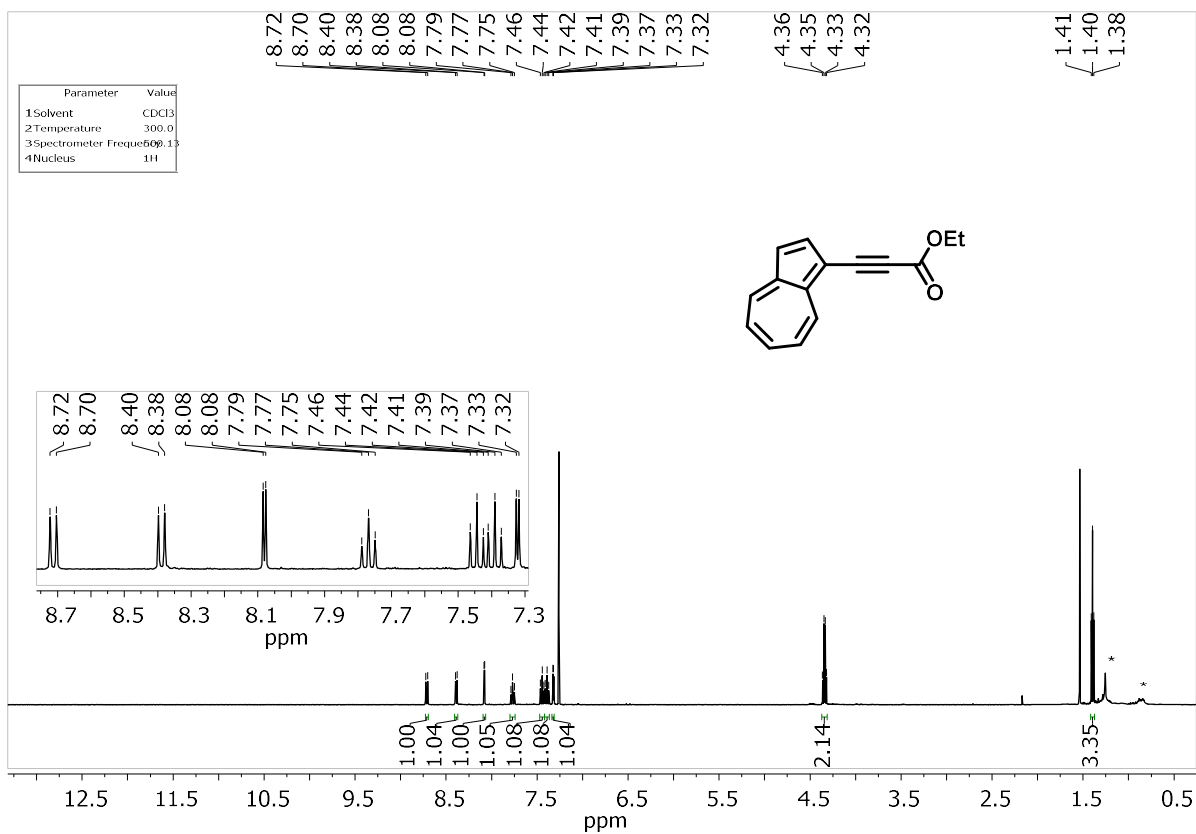


Figure S22. ^1H NMR spectrum of compound **3aa**.

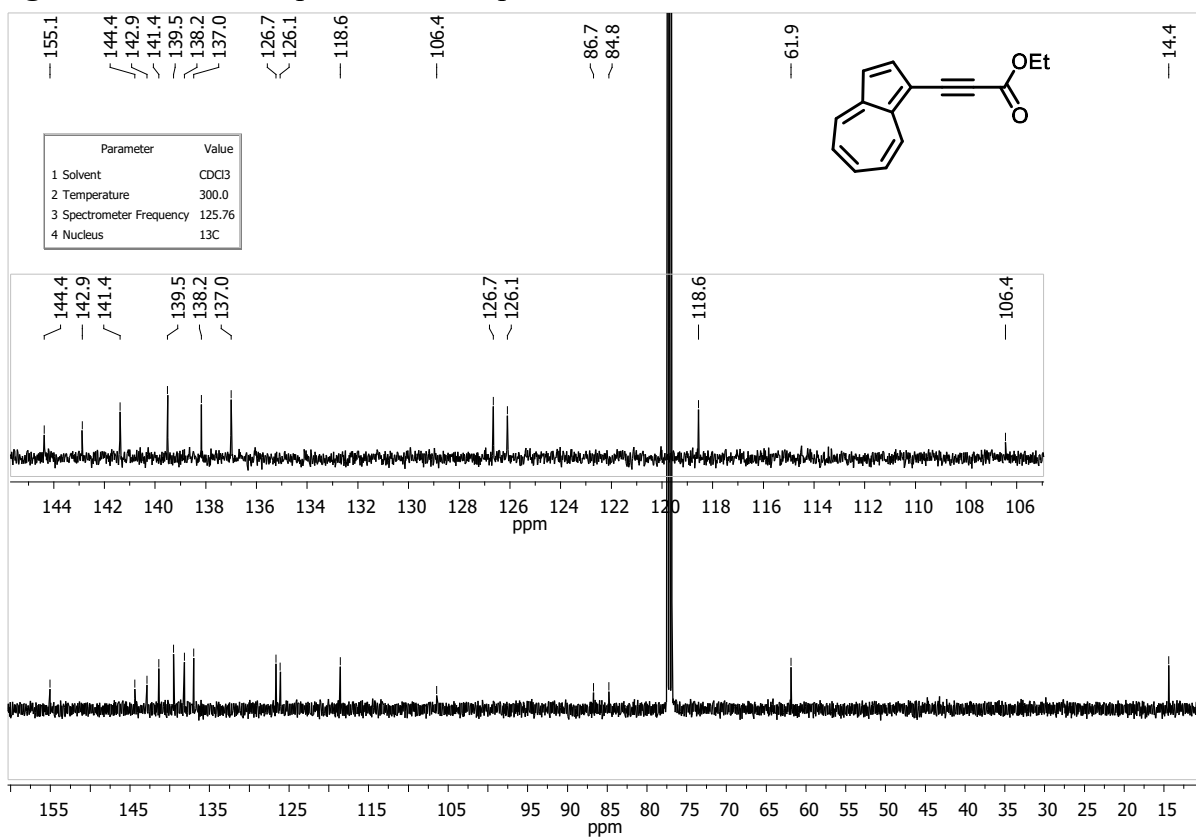


Figure S23. ^{13}C NMR spectrum of compound **3aa**.

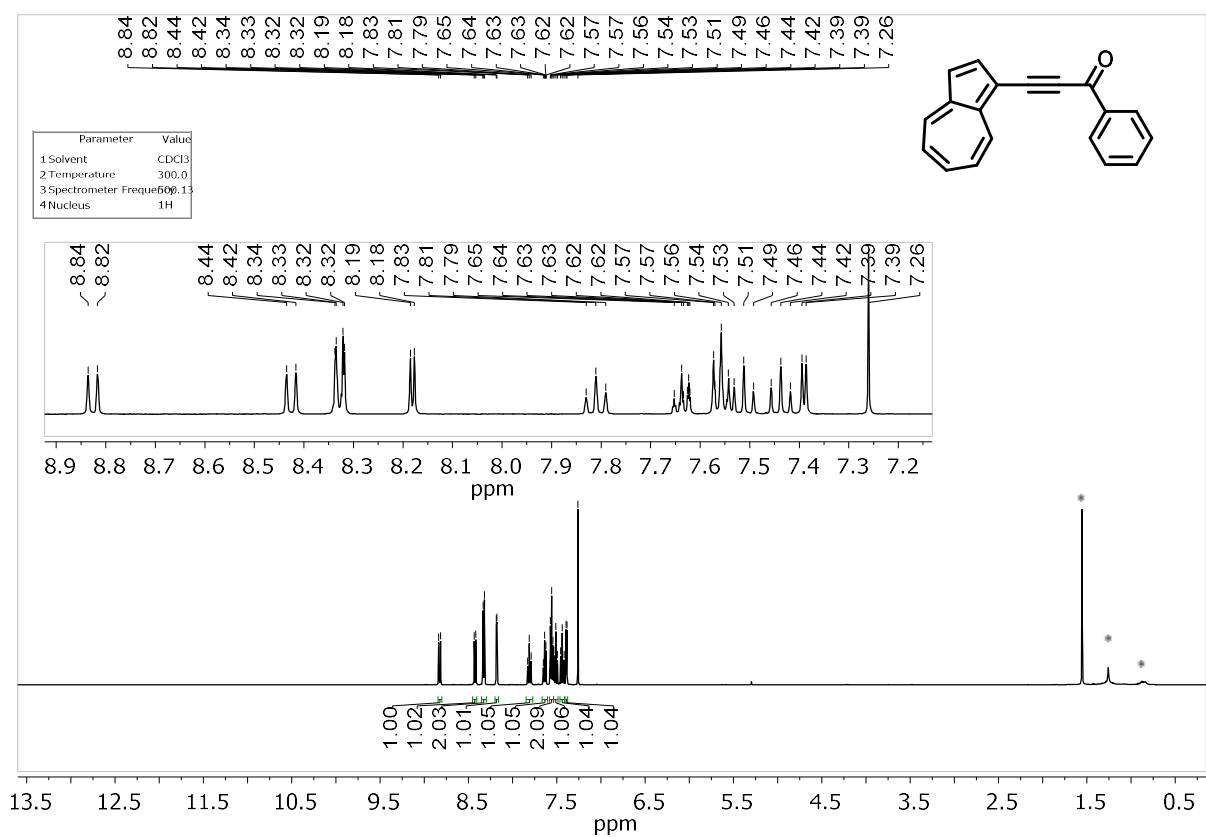


Figure S24. ¹H NMR spectrum of compound **3ab**.

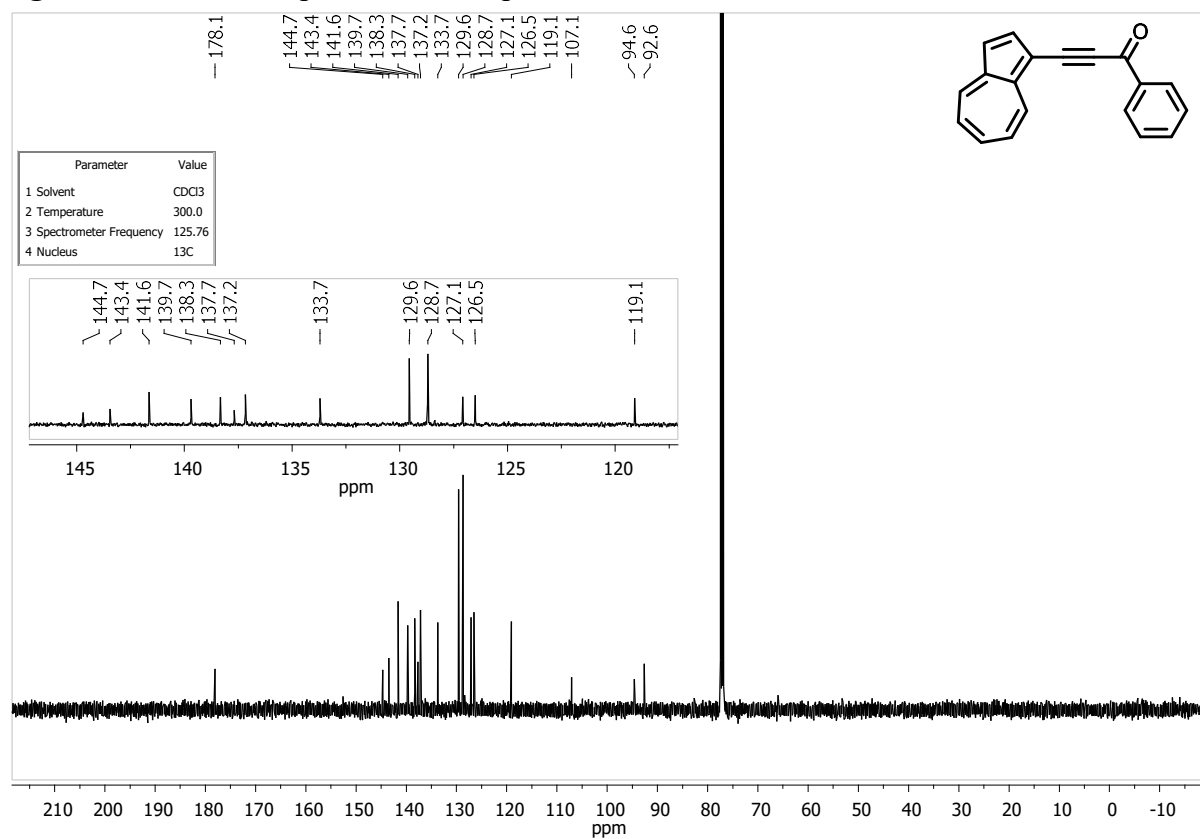


Figure S25. ¹³C NMR spectrum of compound **3ab**.

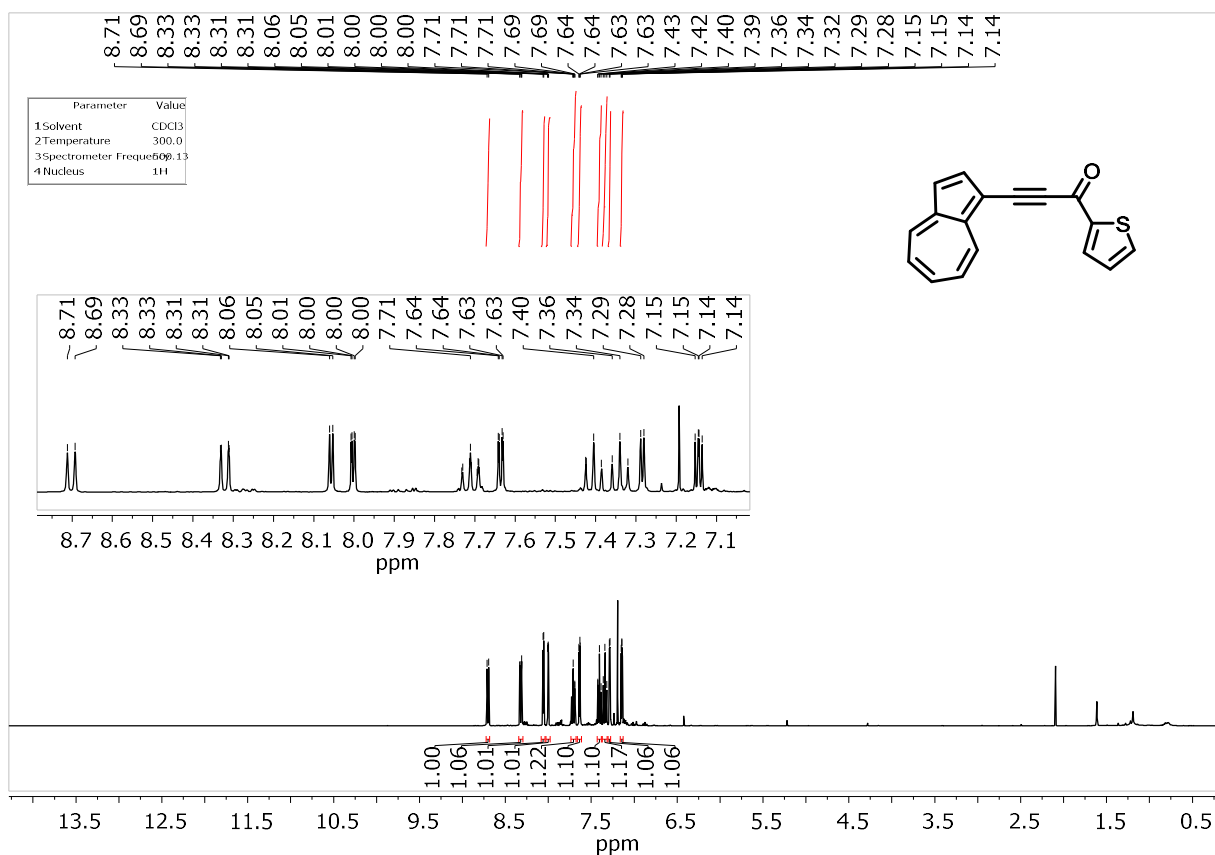


Figure S26. ^1H NMR spectrum of compound **3ac**.

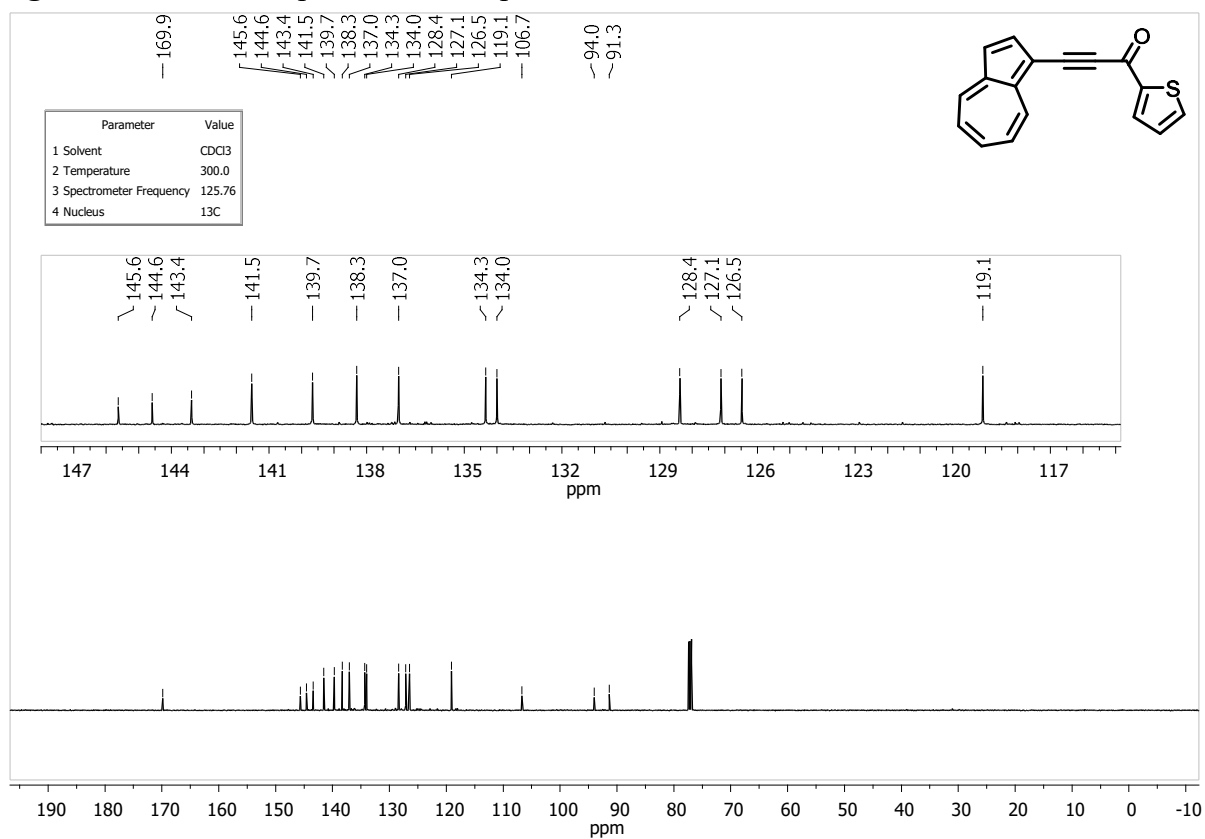


Figure S27. ^{13}C NMR spectrum of compound **3ac**.

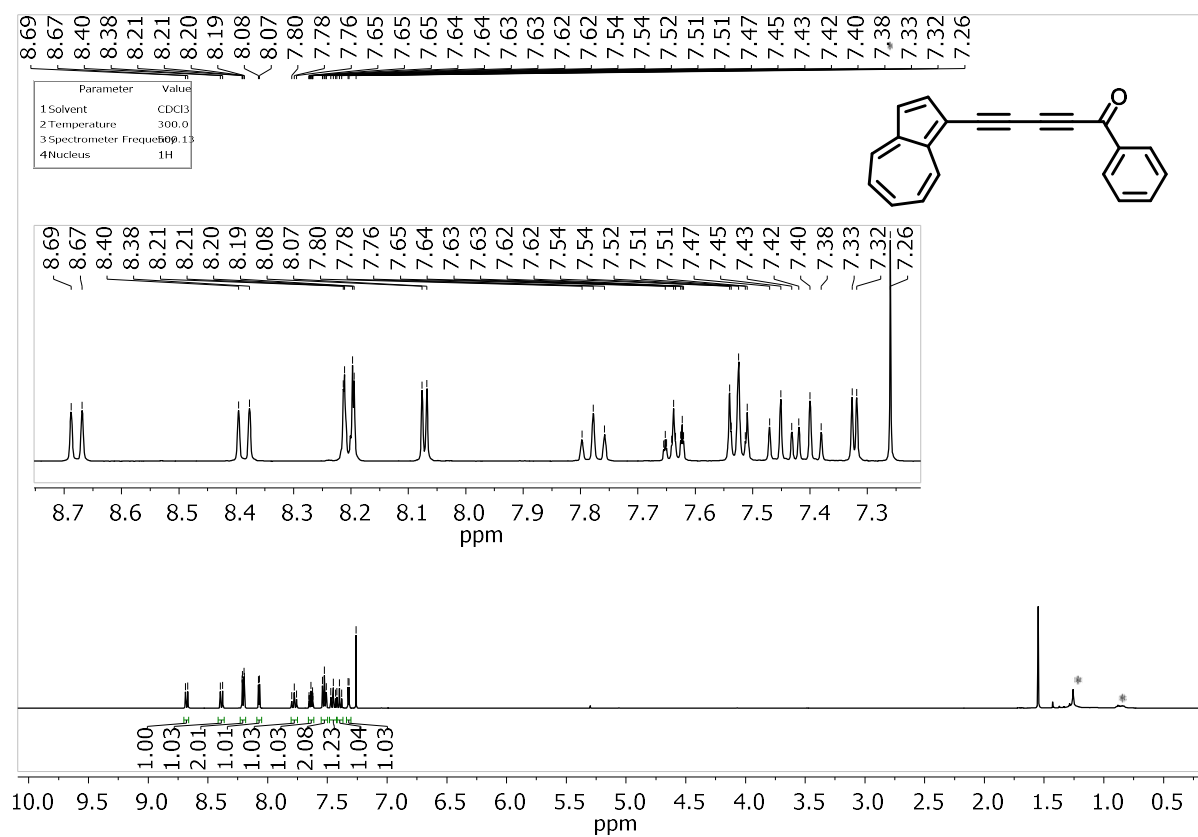


Figure S28. ^1H NMR spectrum of compound 3ae.

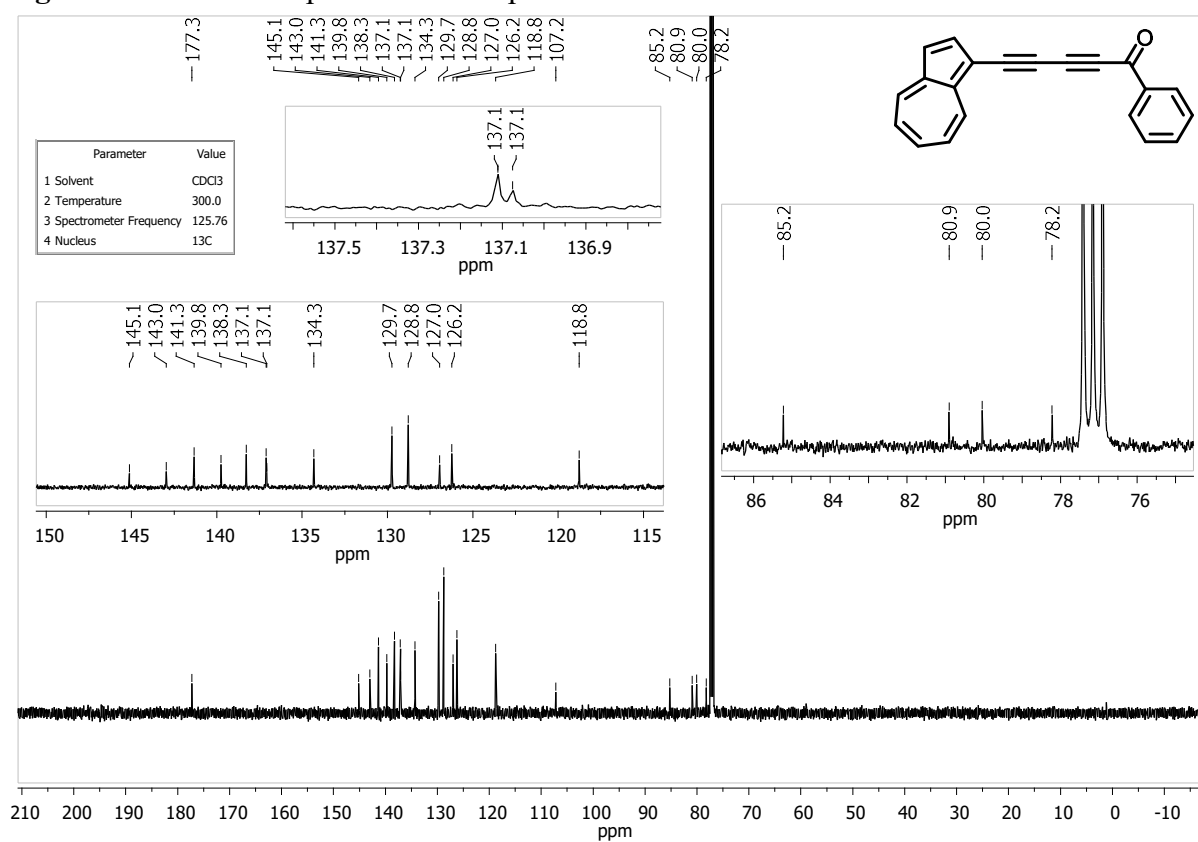


Figure S29. ^{13}C NMR spectrum of compound 3ae.

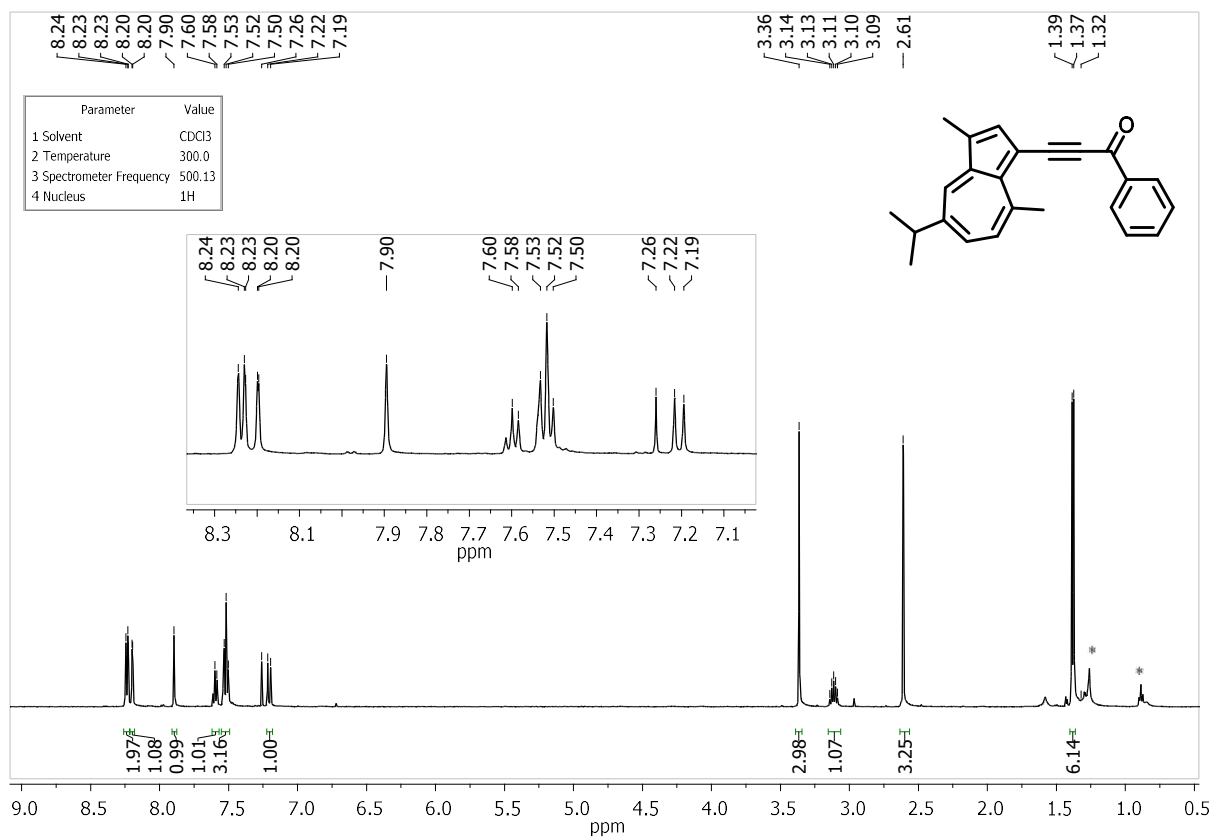


Figure S30. ¹H NMR spectrum of compound **3bb**.

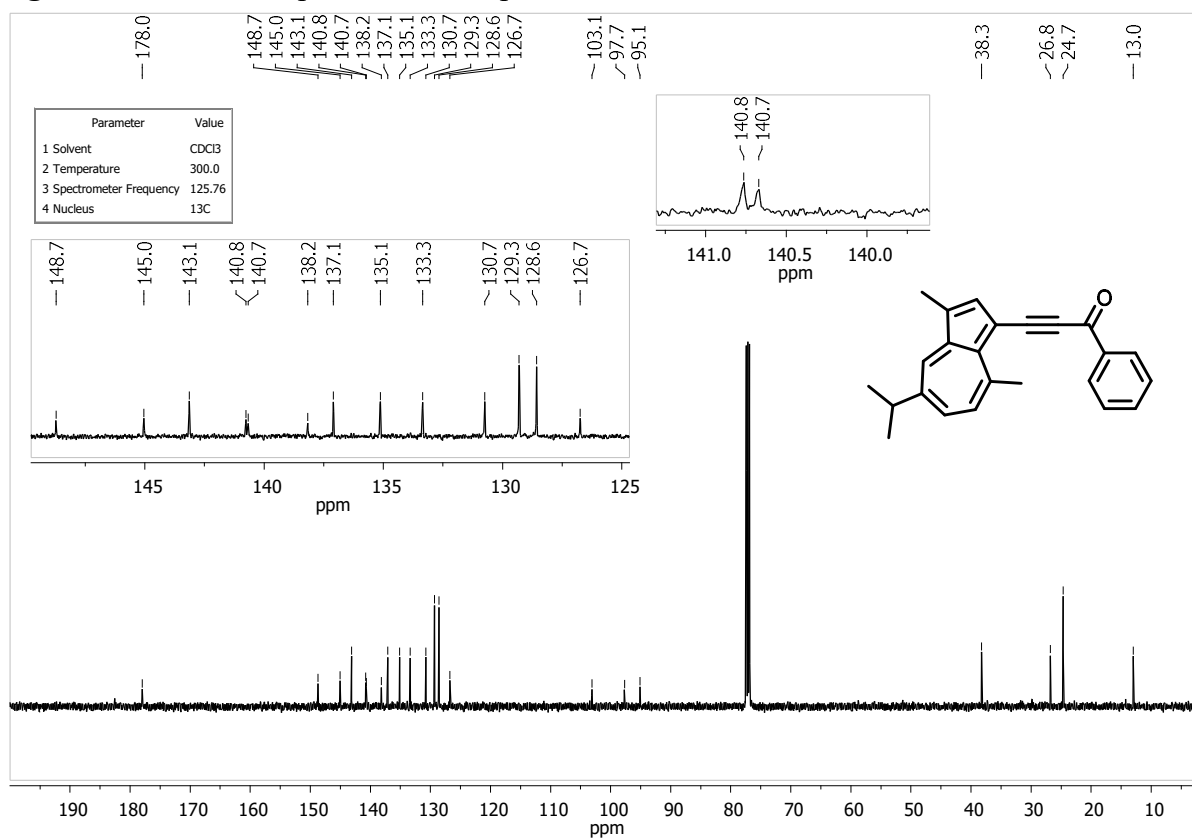


Figure S31. ¹³C NMR spectrum of compound **3bb**.

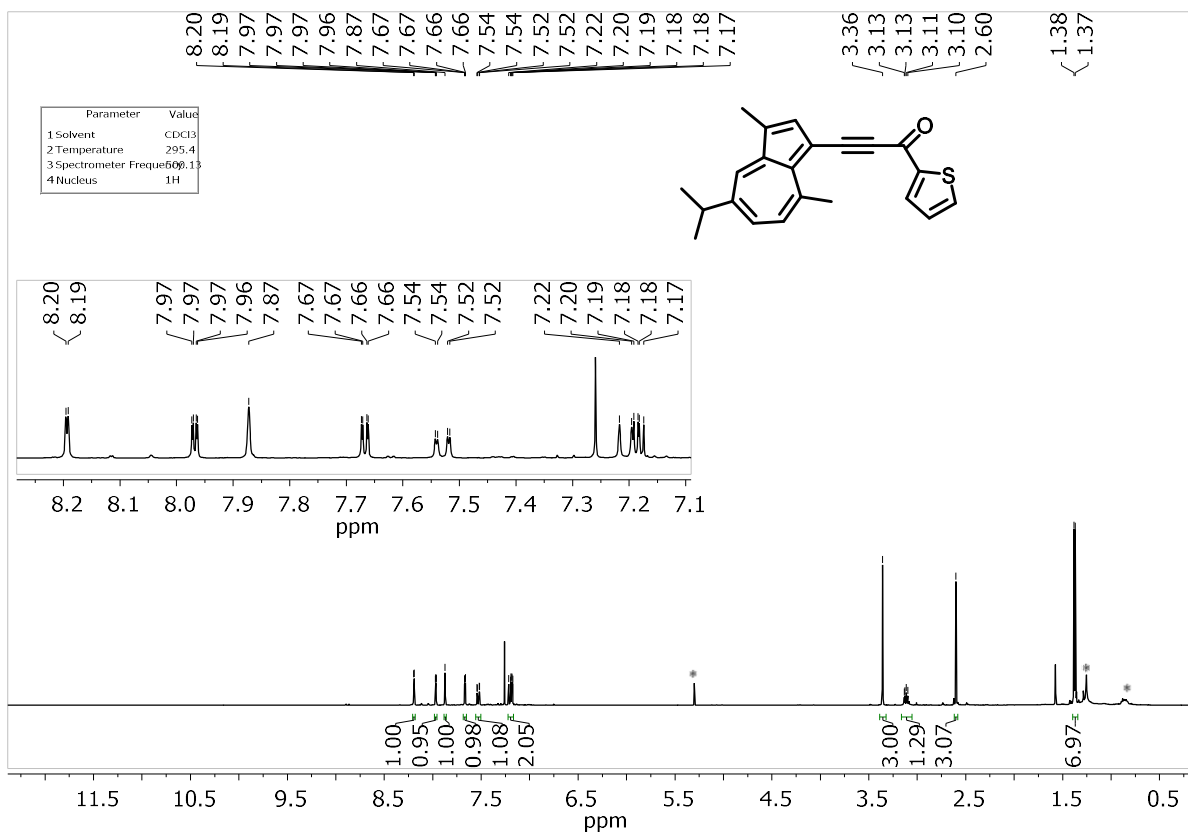


Figure S32. ¹H NMR spectrum of compound **3bc**.

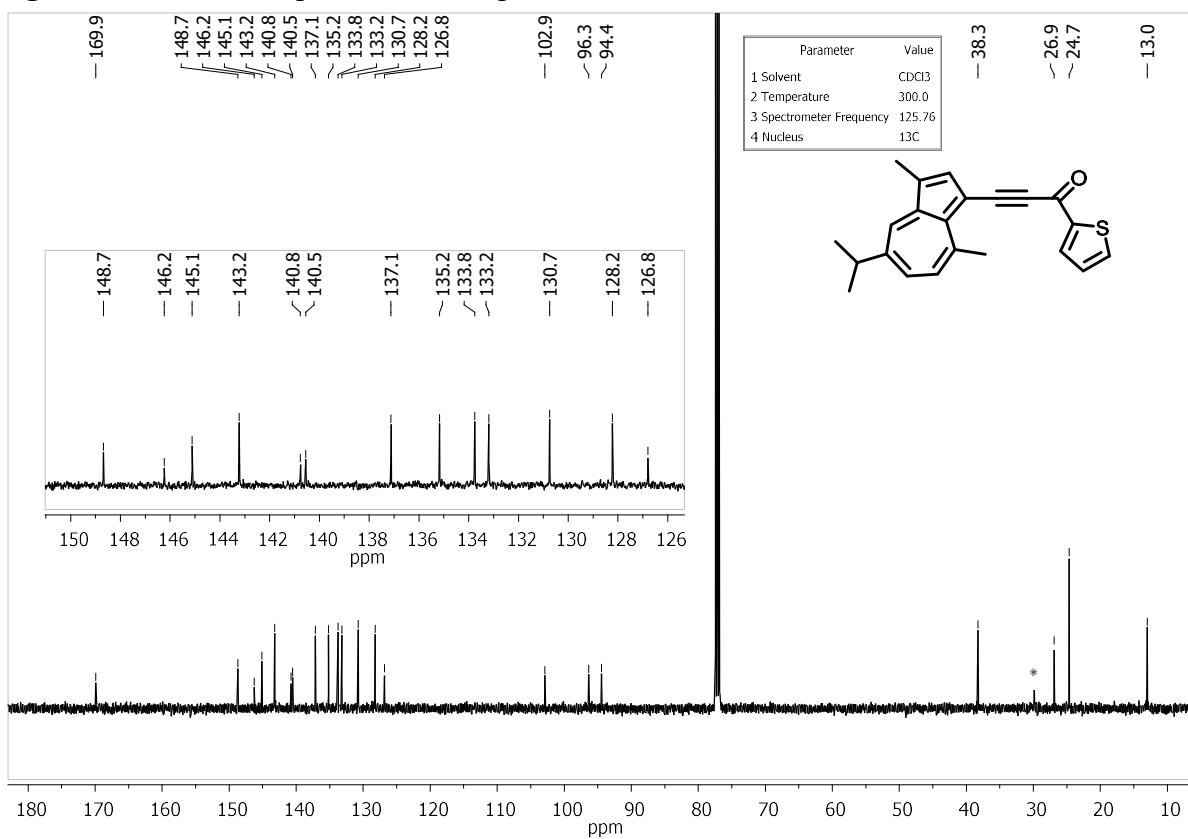


Figure S33. ¹³C NMR spectrum of compound **3bc**.

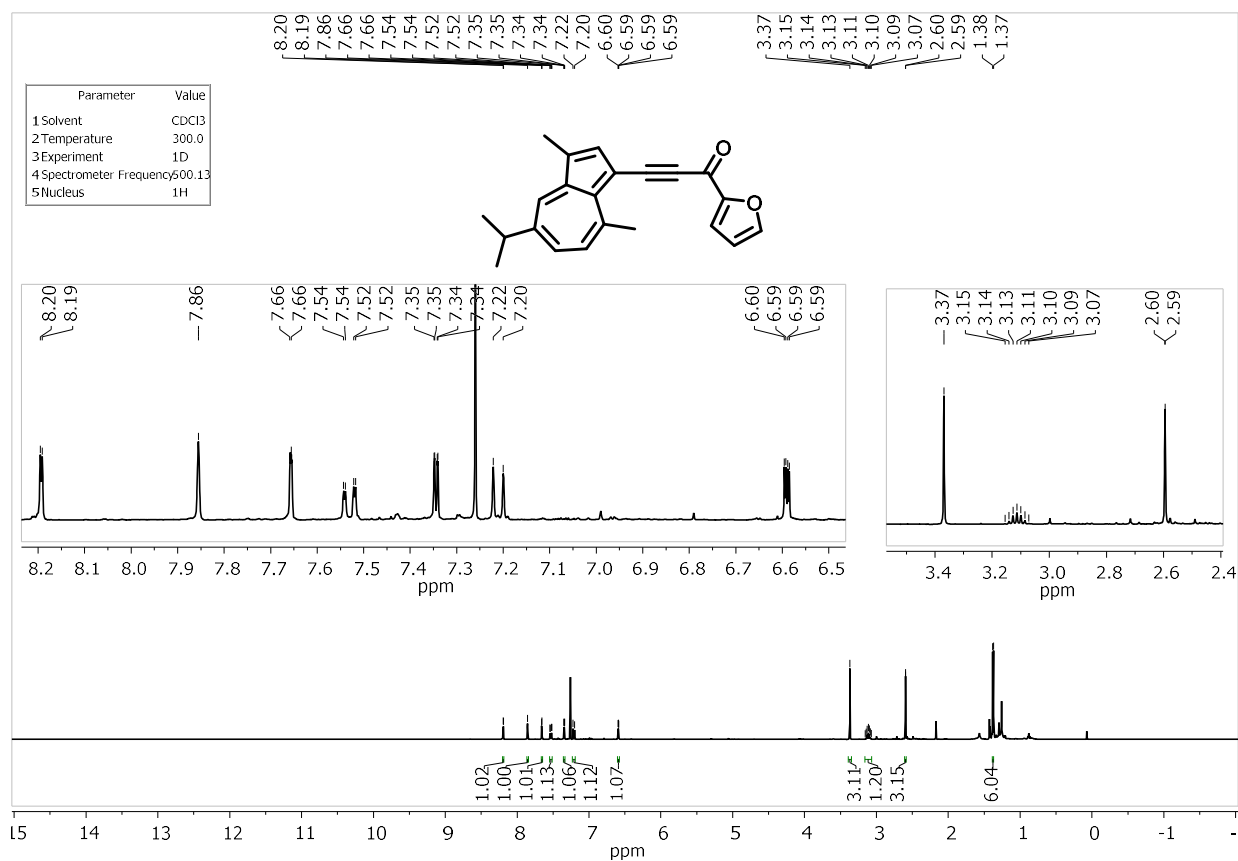


Figure S34. ¹H NMR spectrum of compound 3bd.

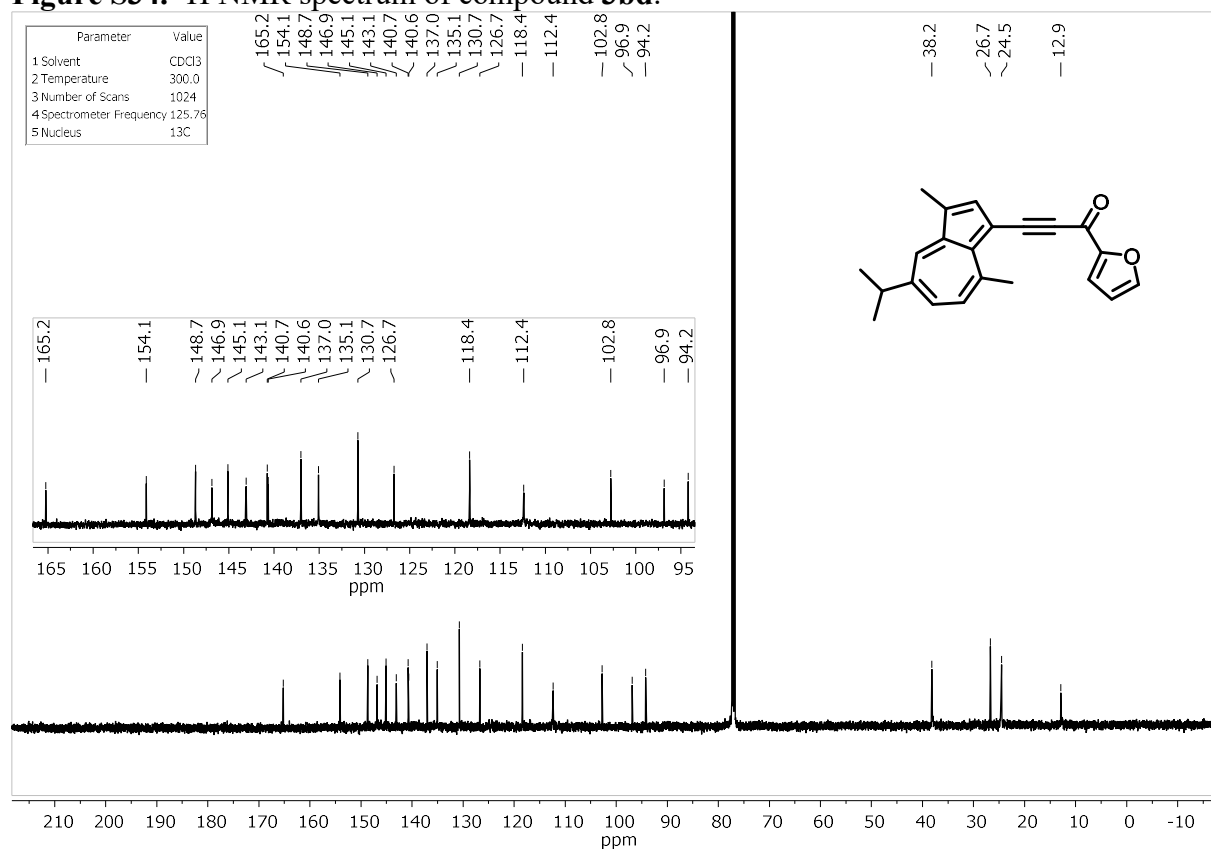


Figure S35. ¹³C NMR spectrum of compound 3bd.

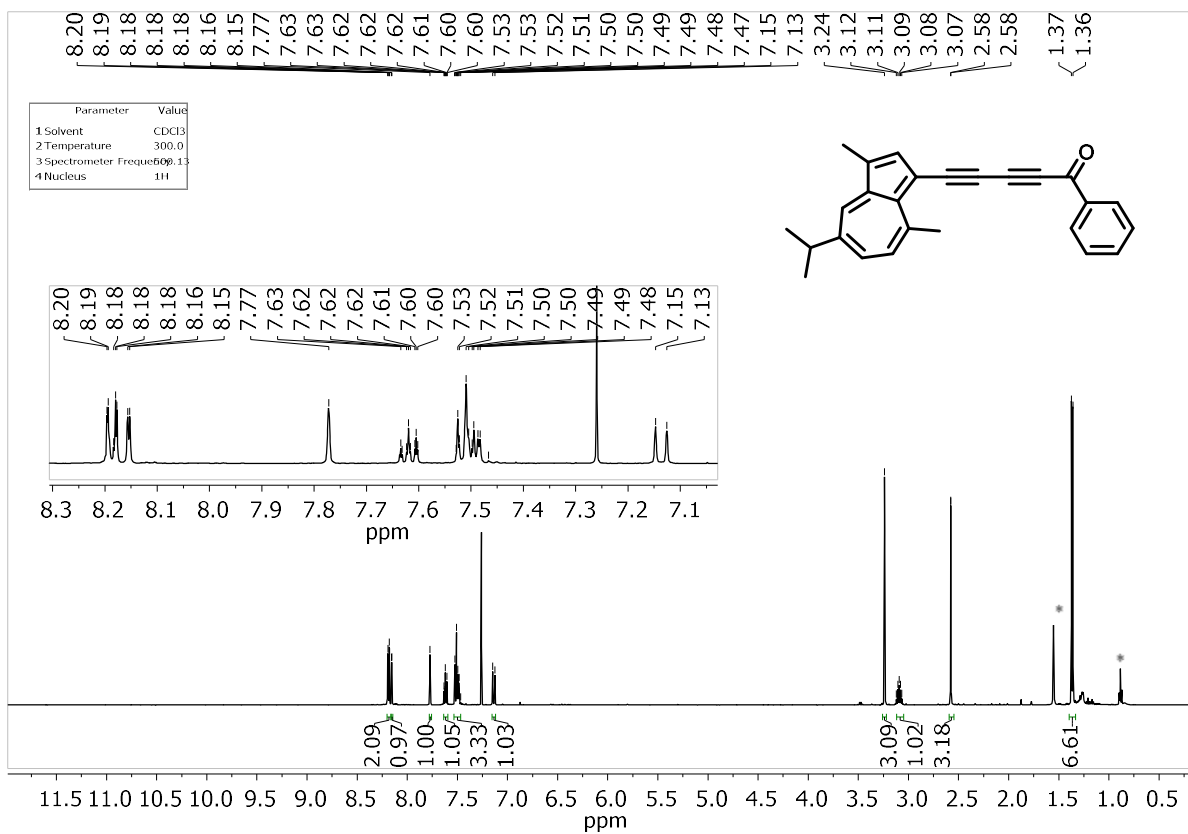


Figure S36. ¹H NMR spectrum of compound 3be.

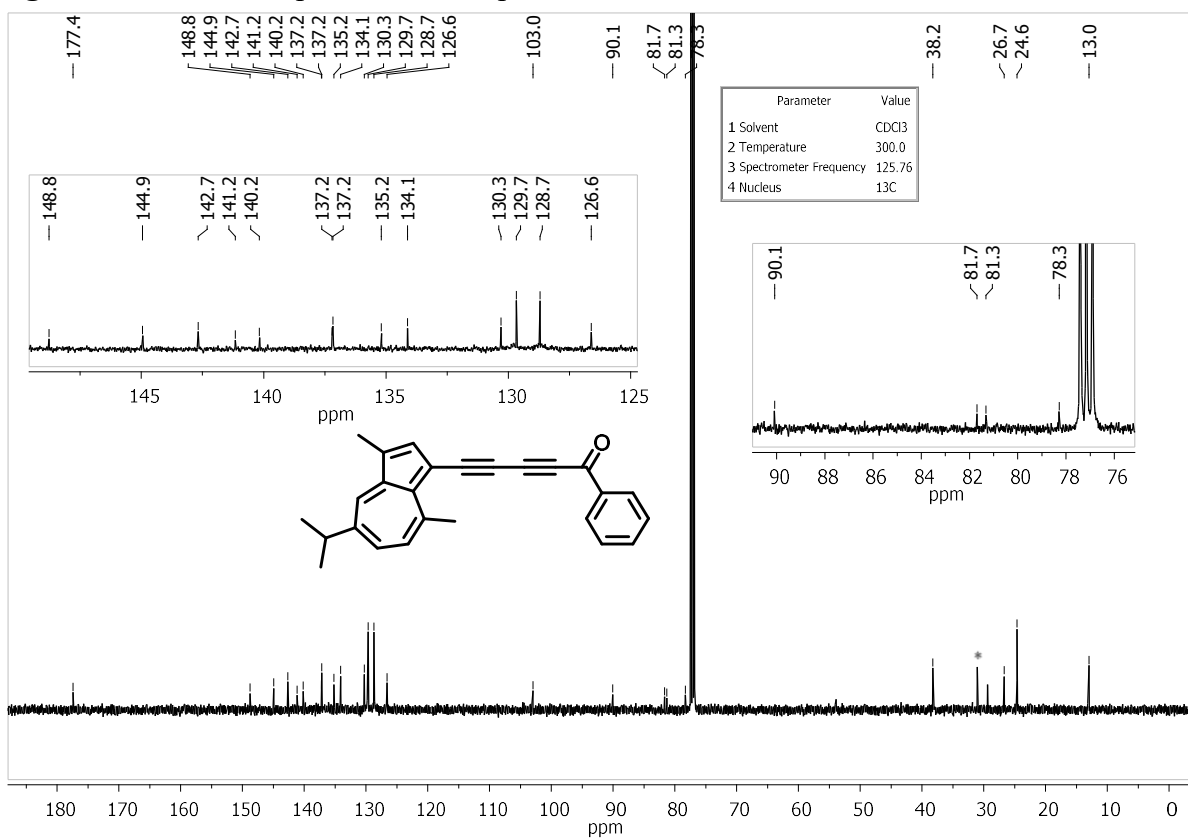


Figure S37. ¹³C NMR spectrum of compound 3be.

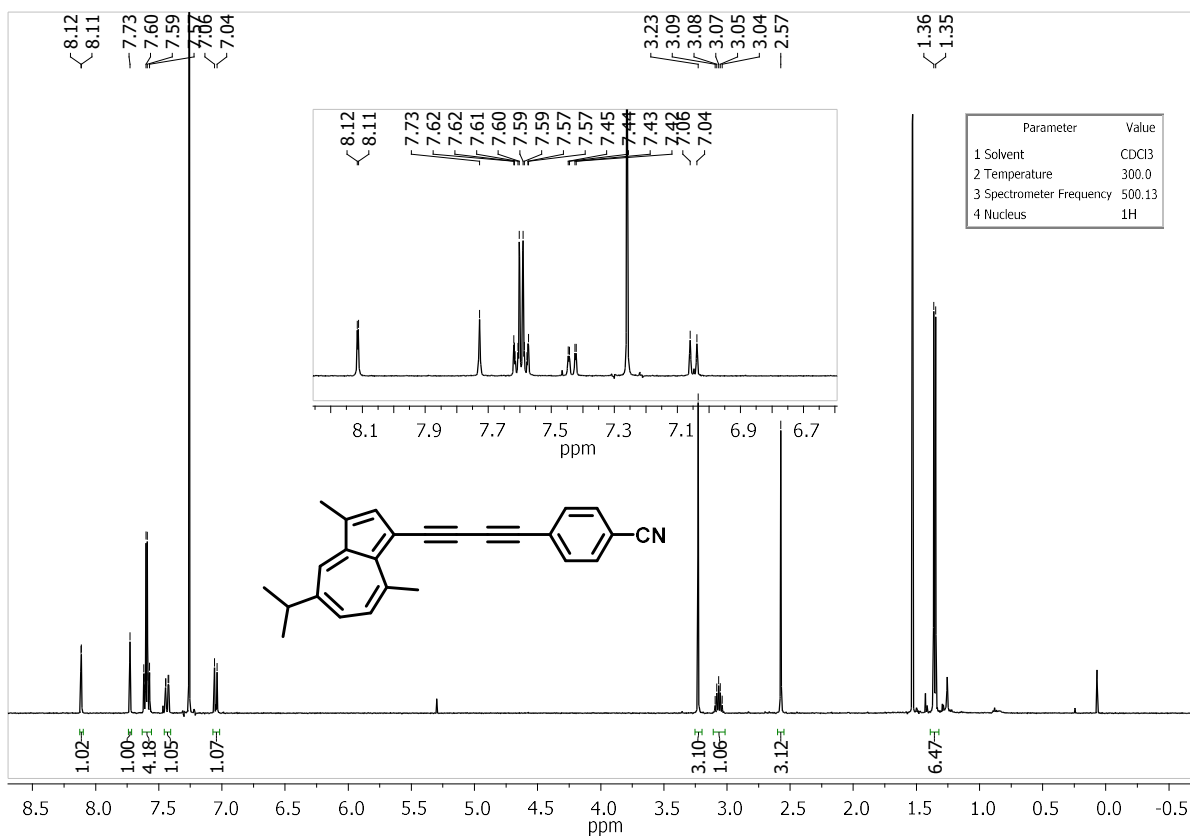


Figure S38. ¹H NMR spectrum of compound **3bf**.

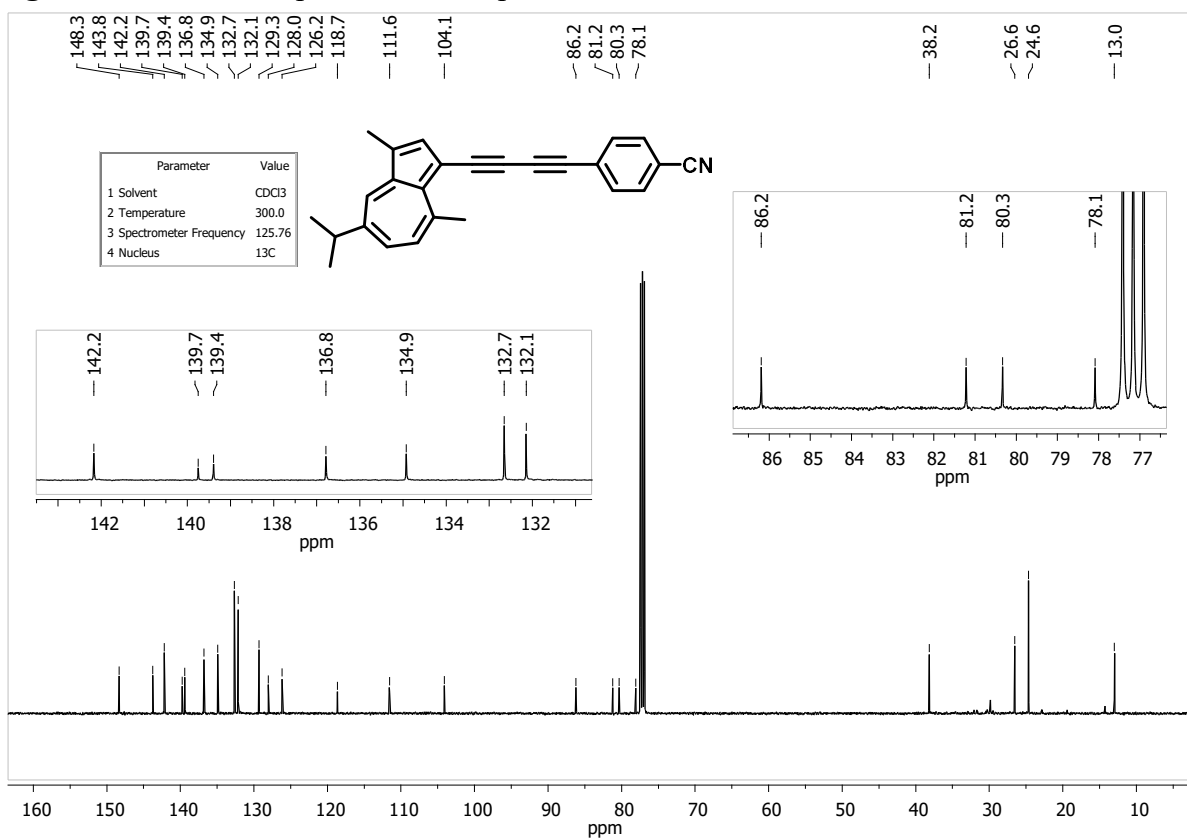


Figure S39. ¹³C NMR spectrum of compound **3bf**.

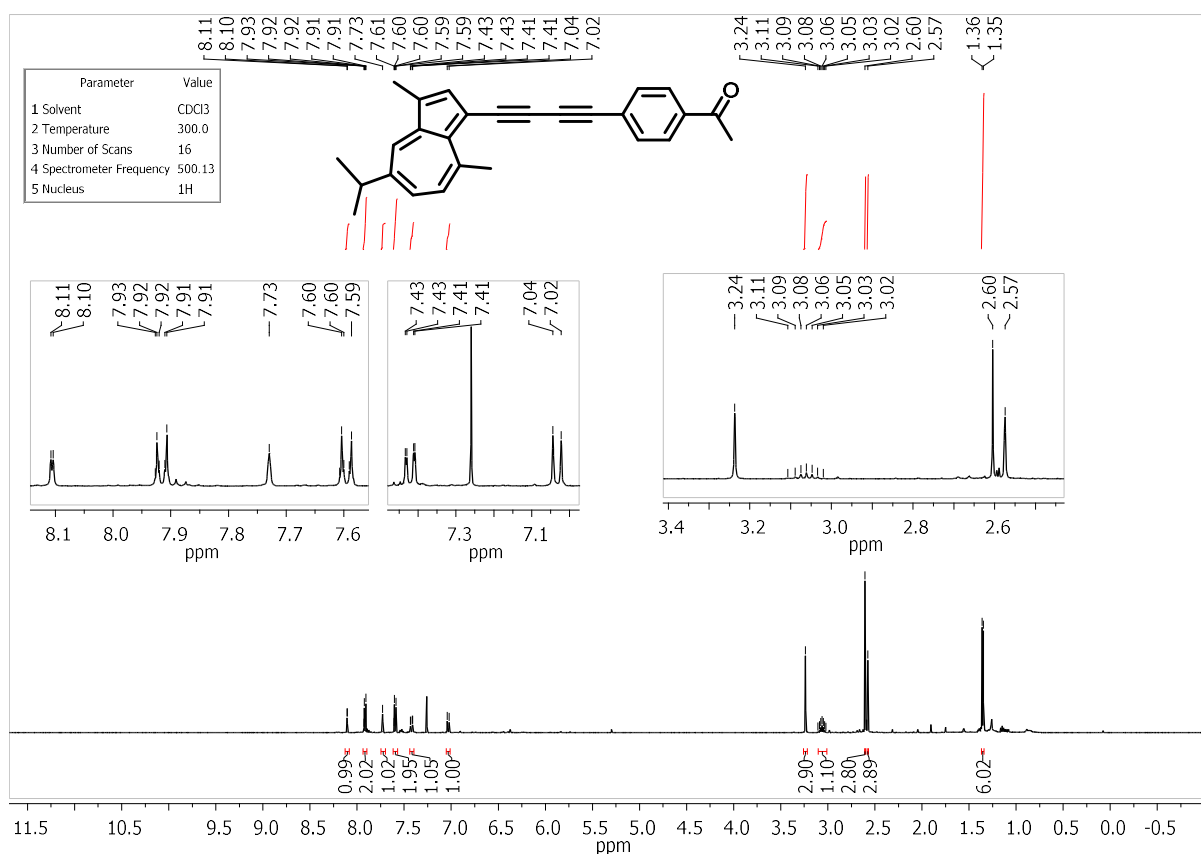


Figure S40. ¹H NMR spectrum of compound 3bg.

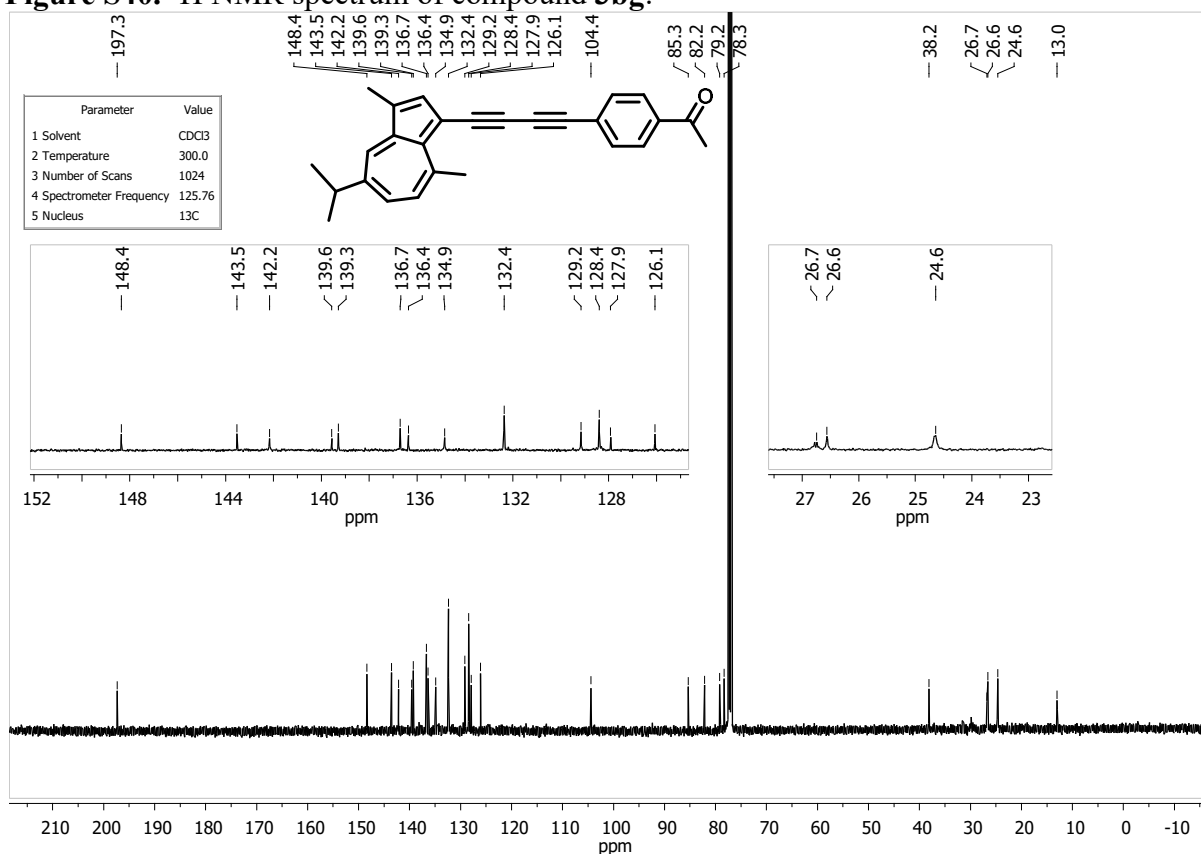


Figure S41. ^{13}C NMR spectrum of compound **3bg**.

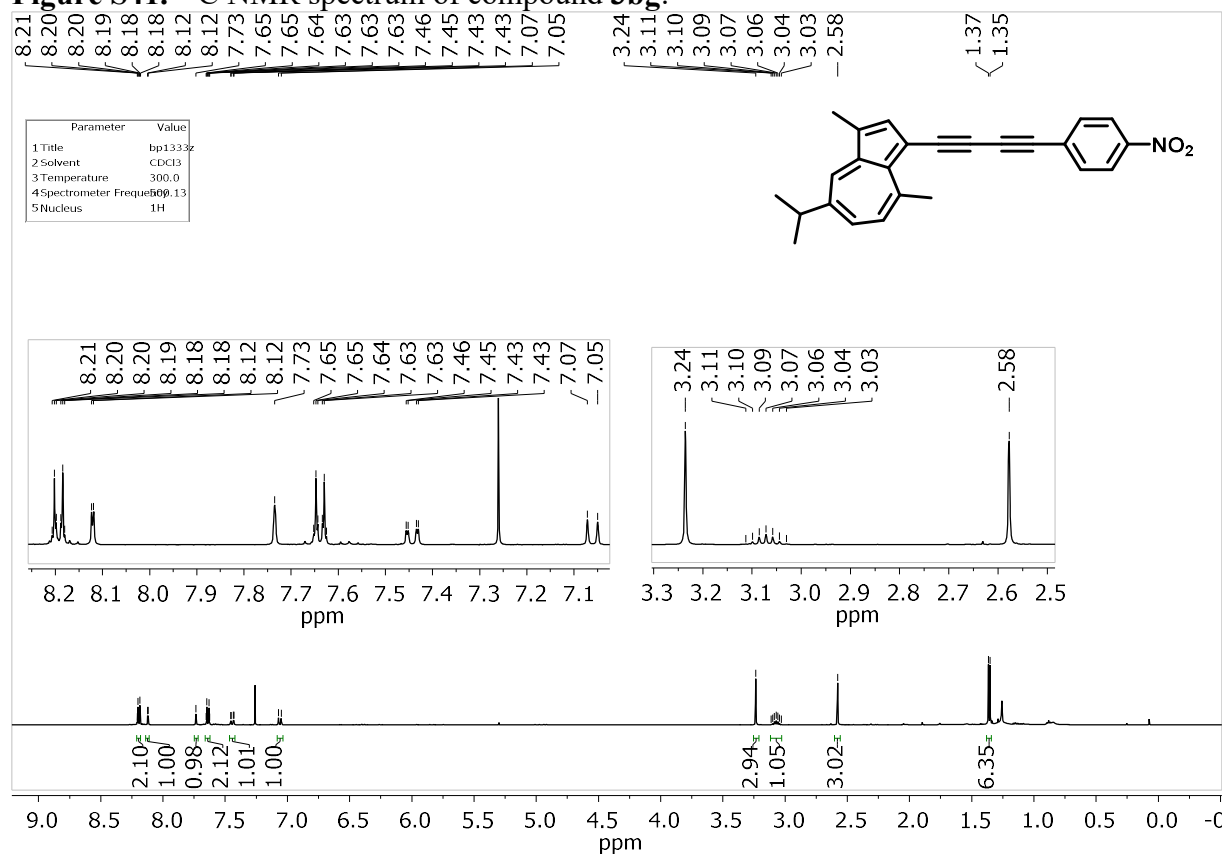


Figure S42. ^{13}C NMR spectrum of compound **3bh**.

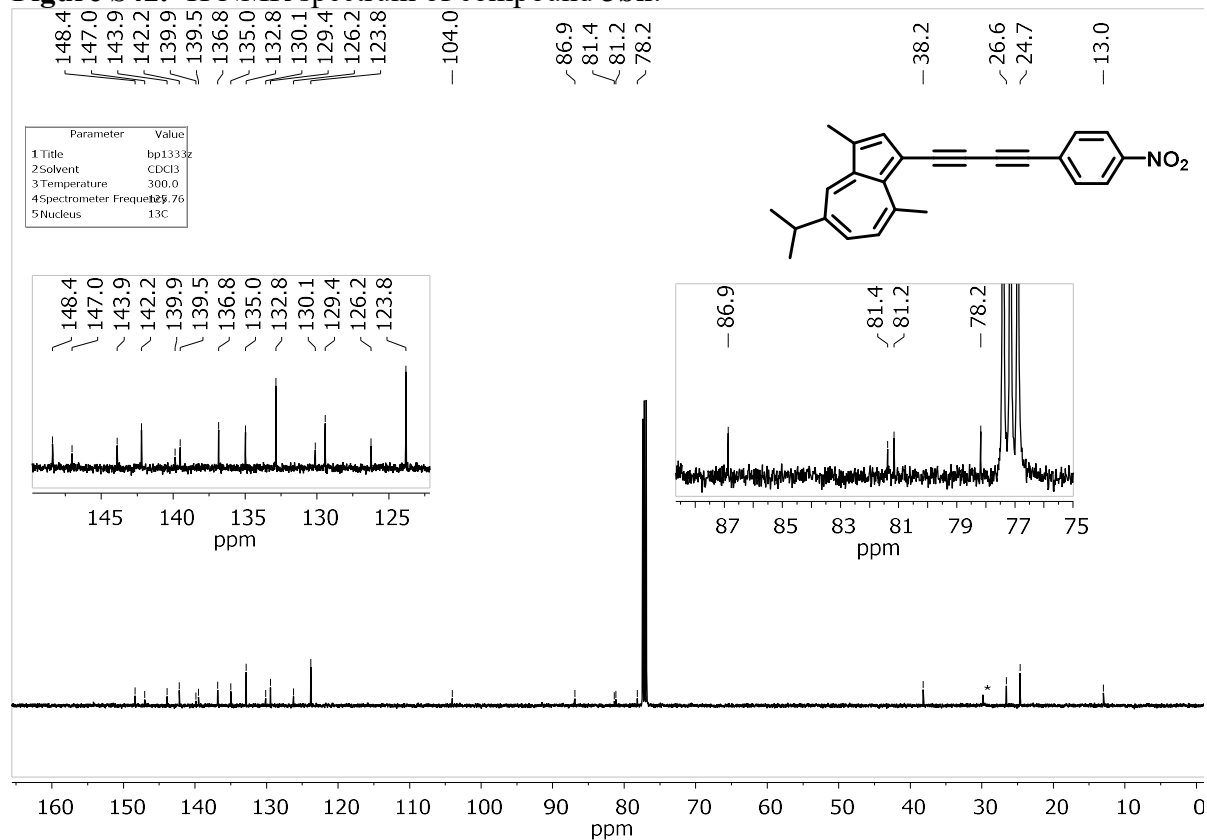


Figure S43. ^{13}C NMR spectrum of compound **3bh**.

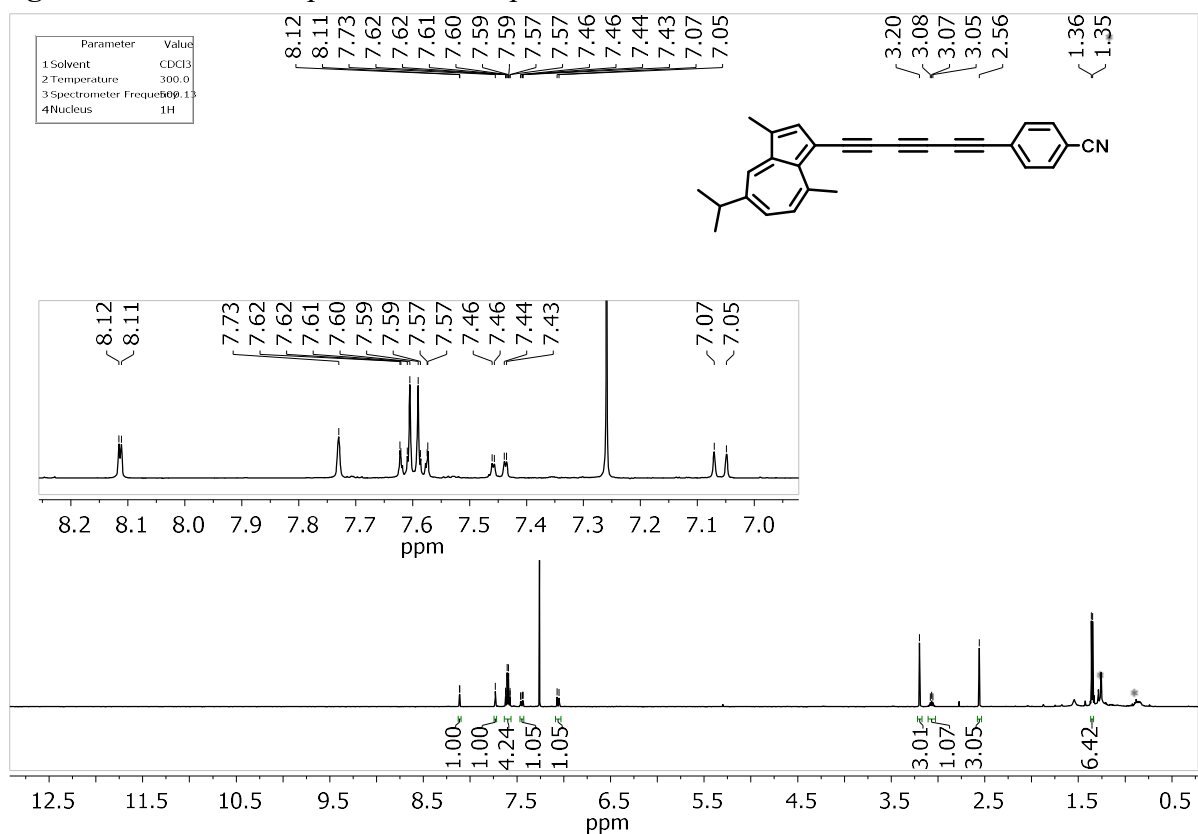


Figure S44. ^1H NMR spectrum of compound **3bi**.

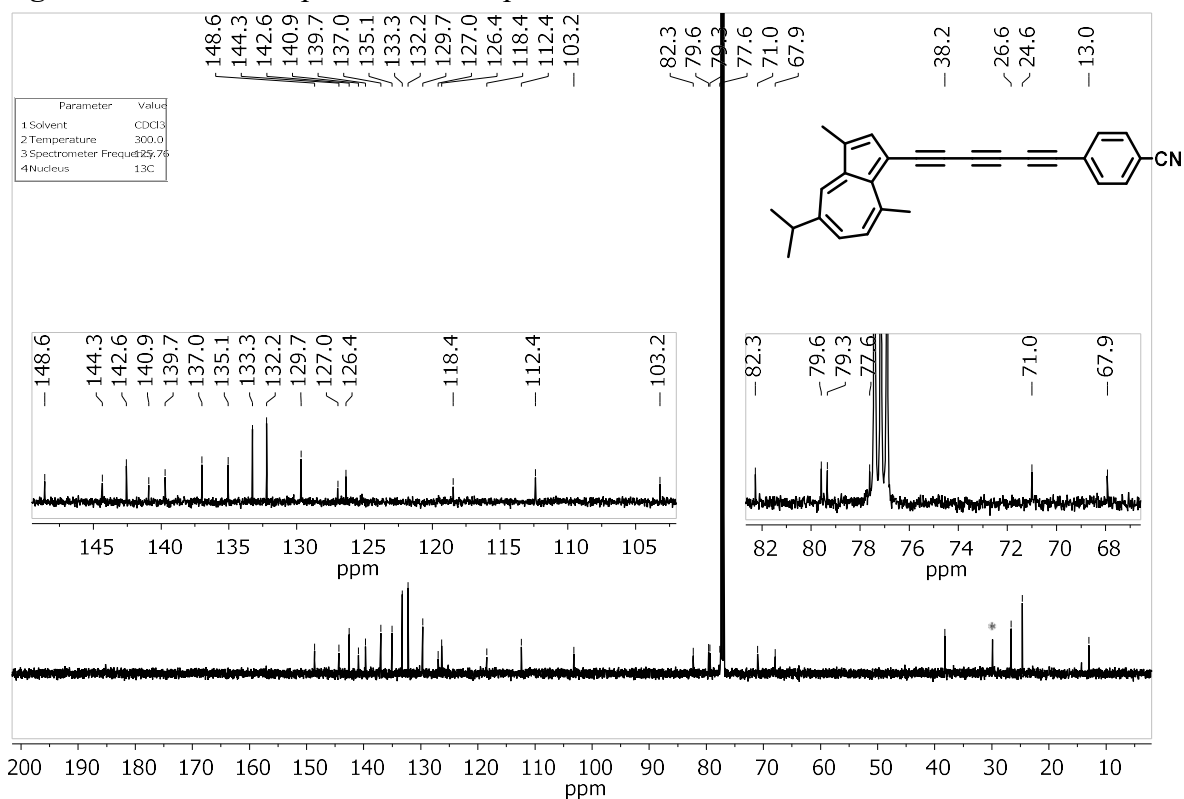


Figure S45. ^{13}C NMR spectrum of compound **3bi**.

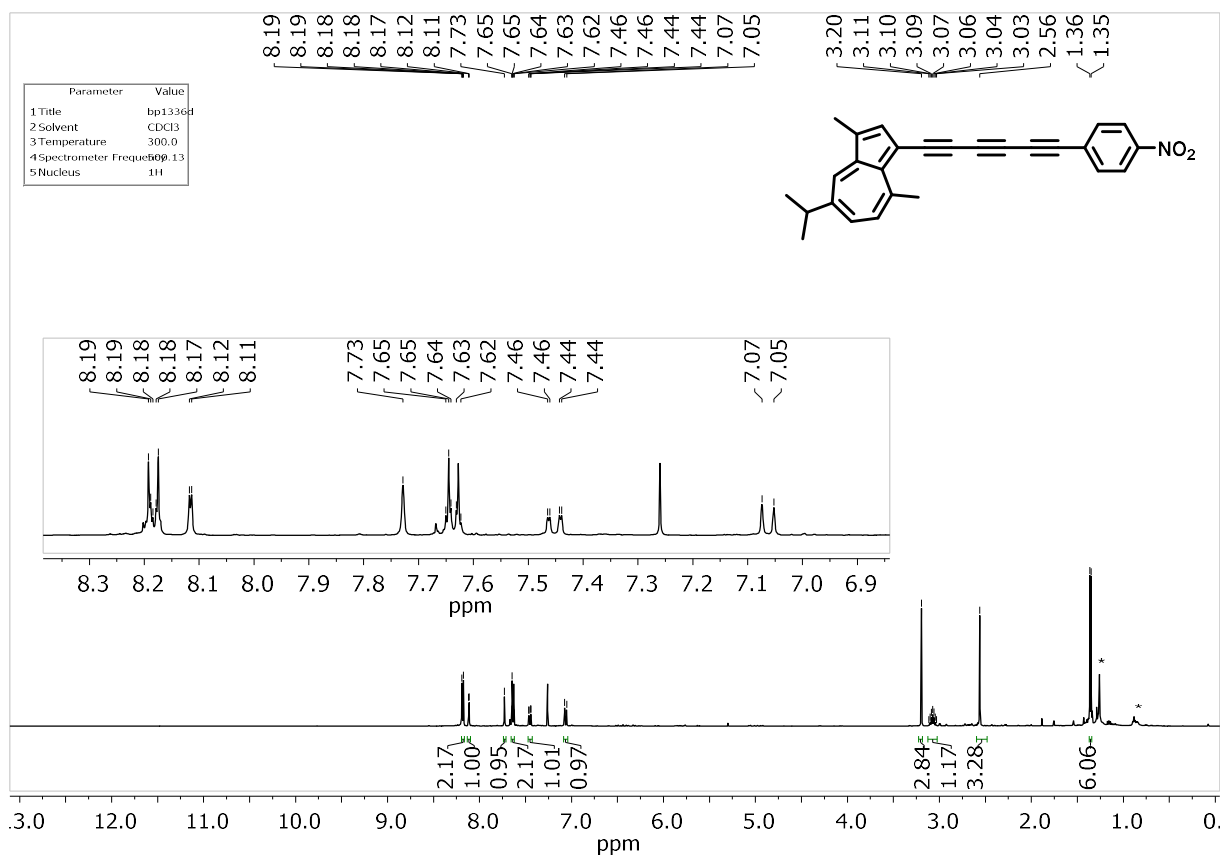


Figure S46. ^1H NMR spectrum of compound **3bj**.

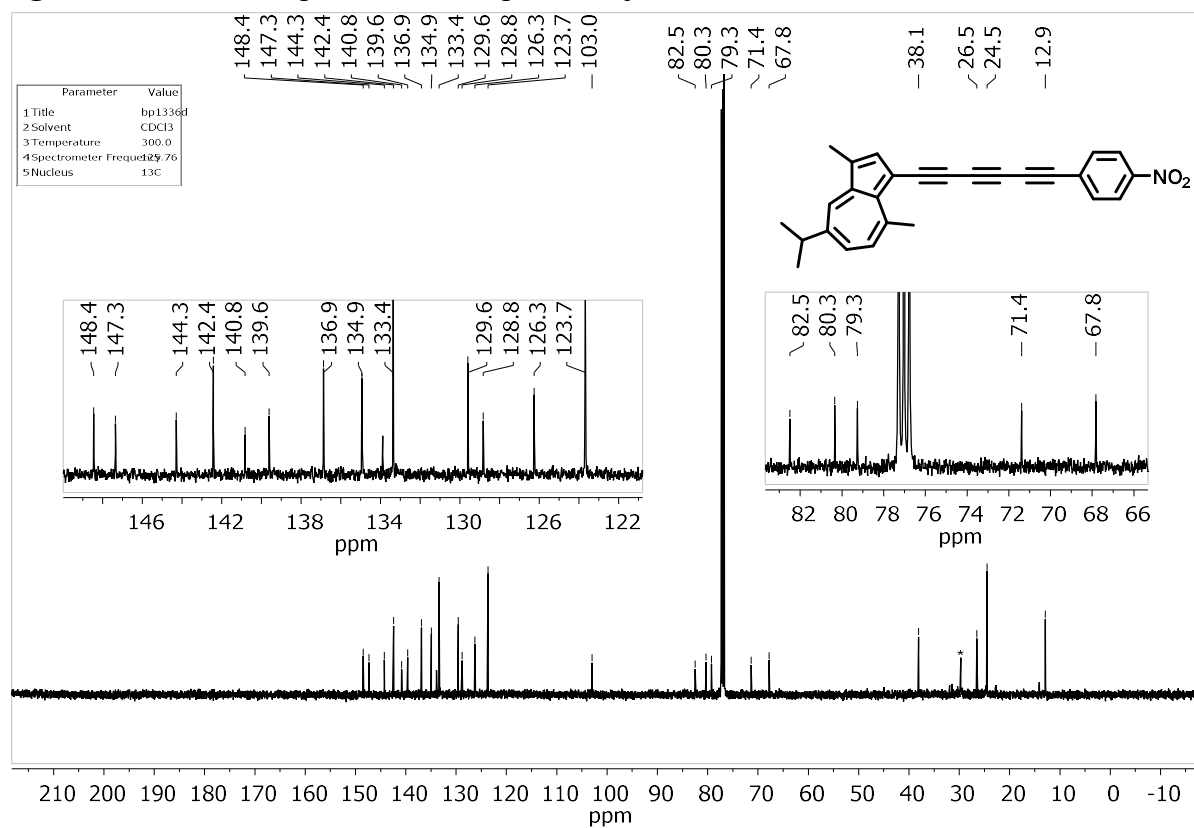


Figure S47. ^{13}C NMR spectrum of compound **3bj**.

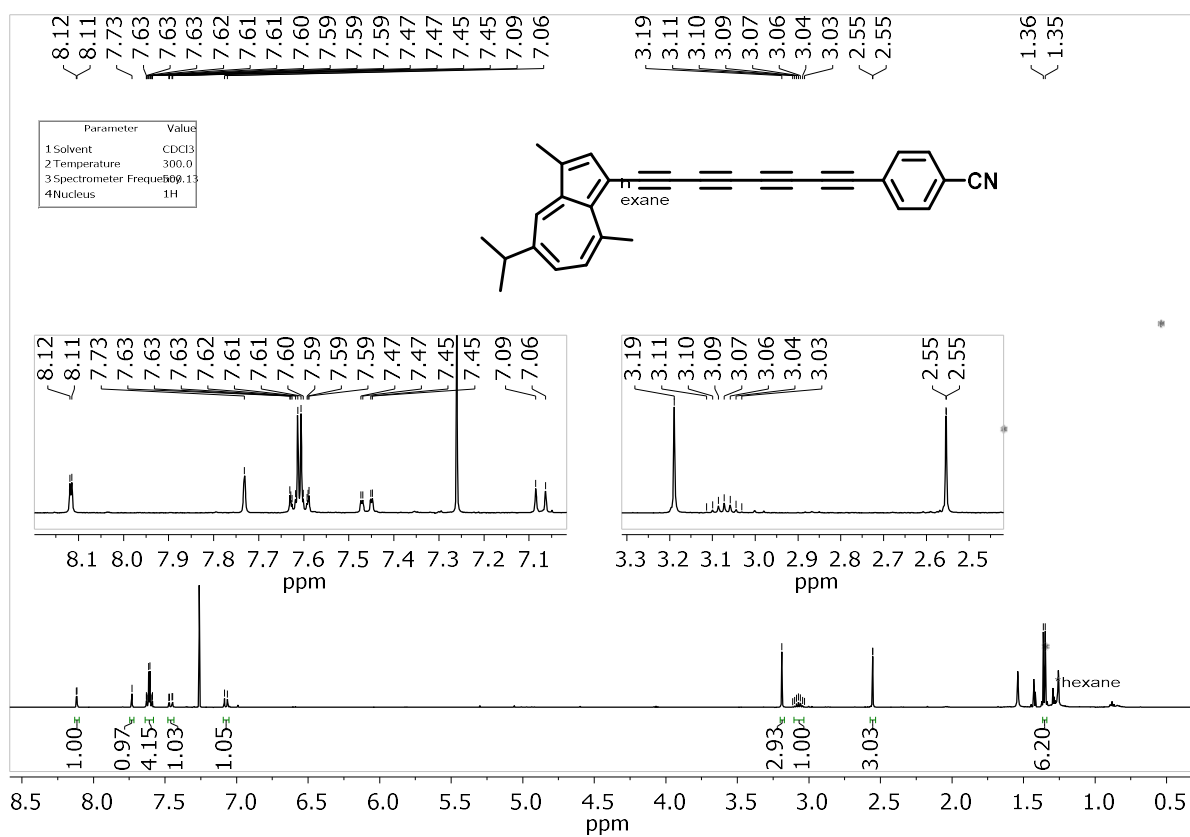


Figure S48. ^1H NMR spectrum of compound **3bk**.

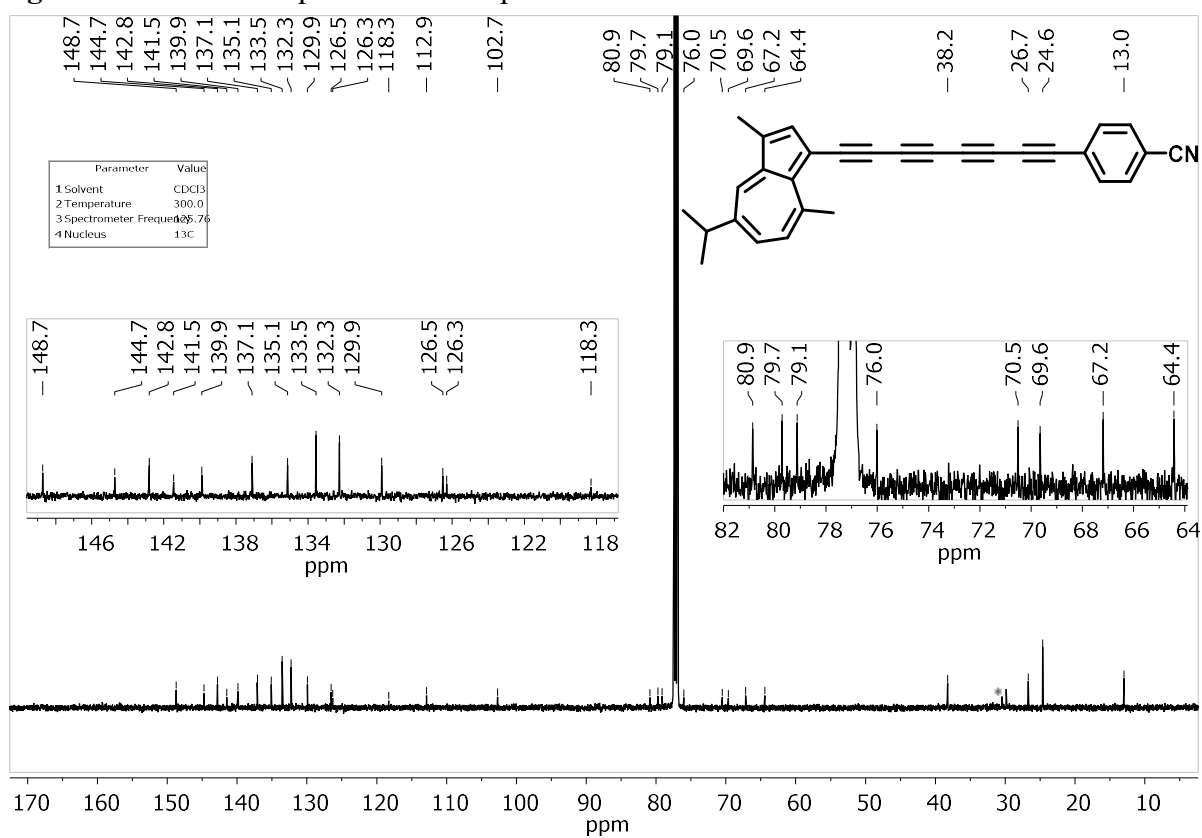


Figure S49. ^{13}C NMR spectrum of compound **3bk**.

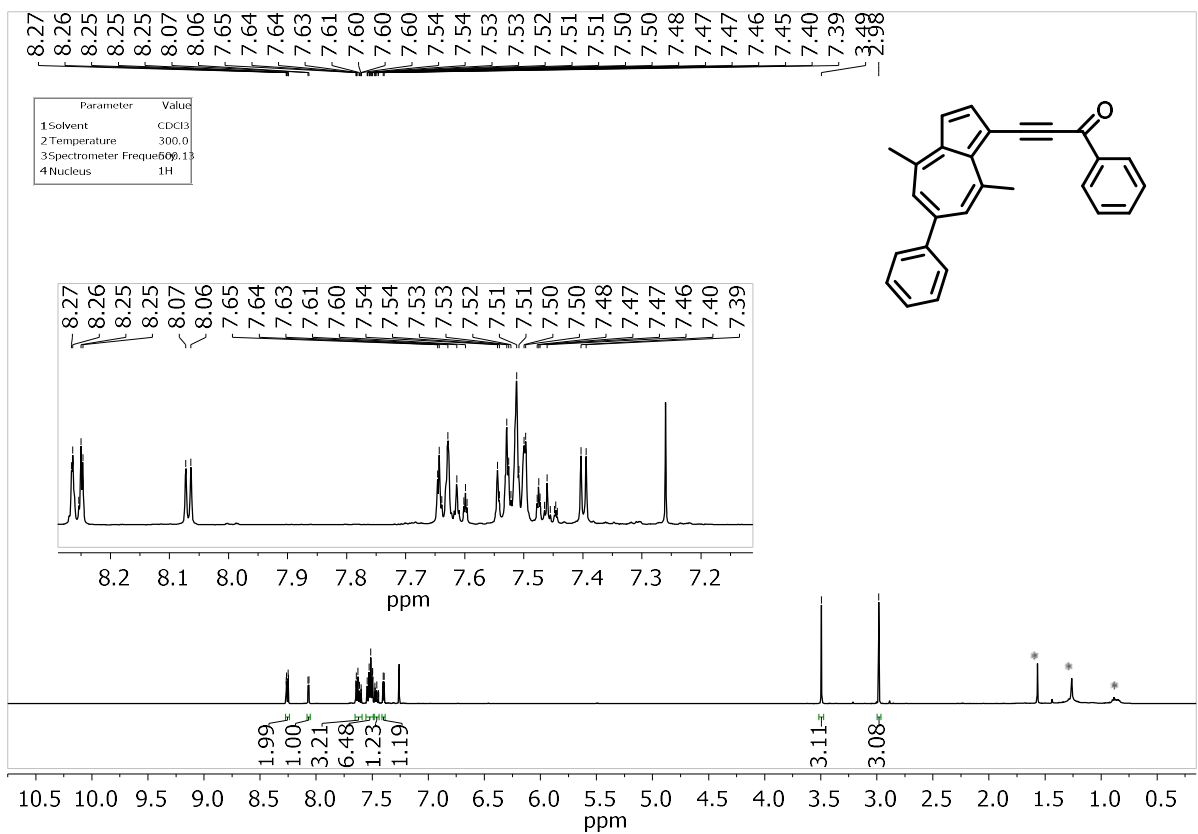


Figure S50. ¹H NMR spectrum of compound 3cb.

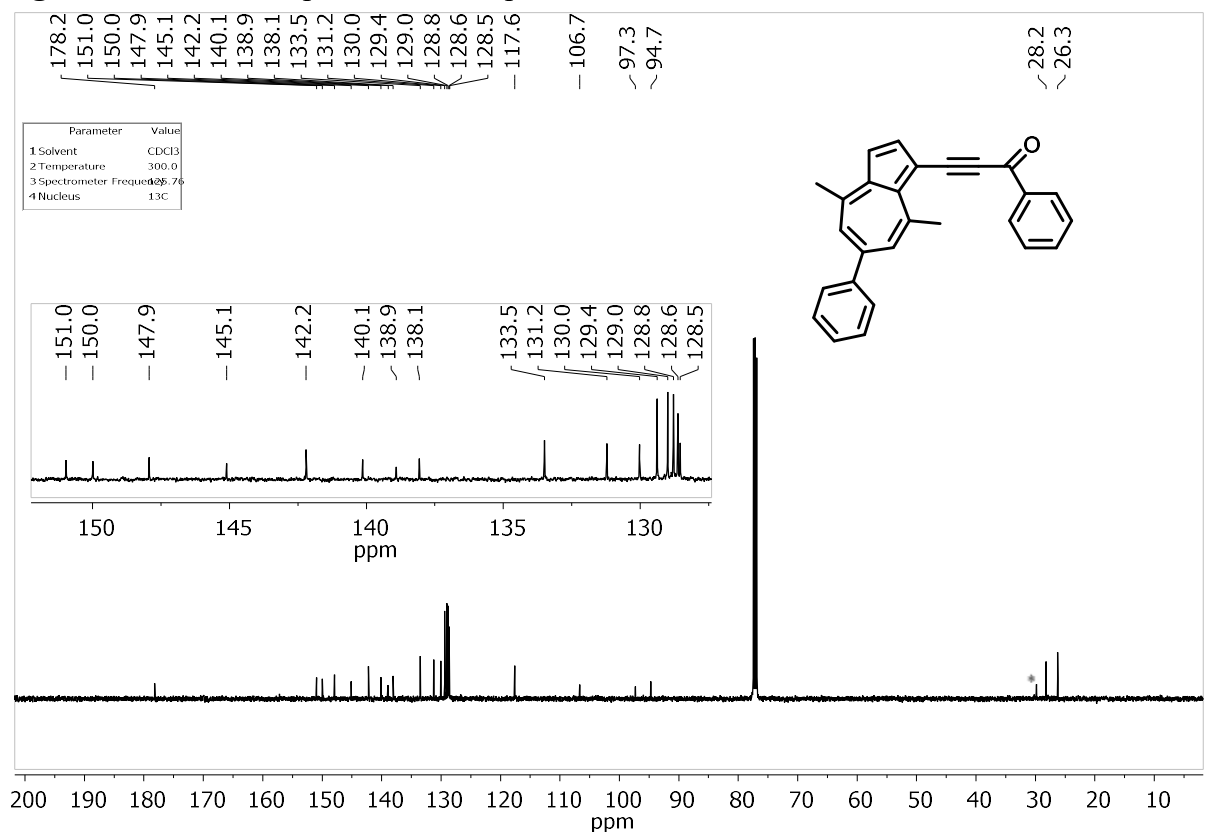


Figure S51. ¹³C NMR spectrum of compound 3cb.

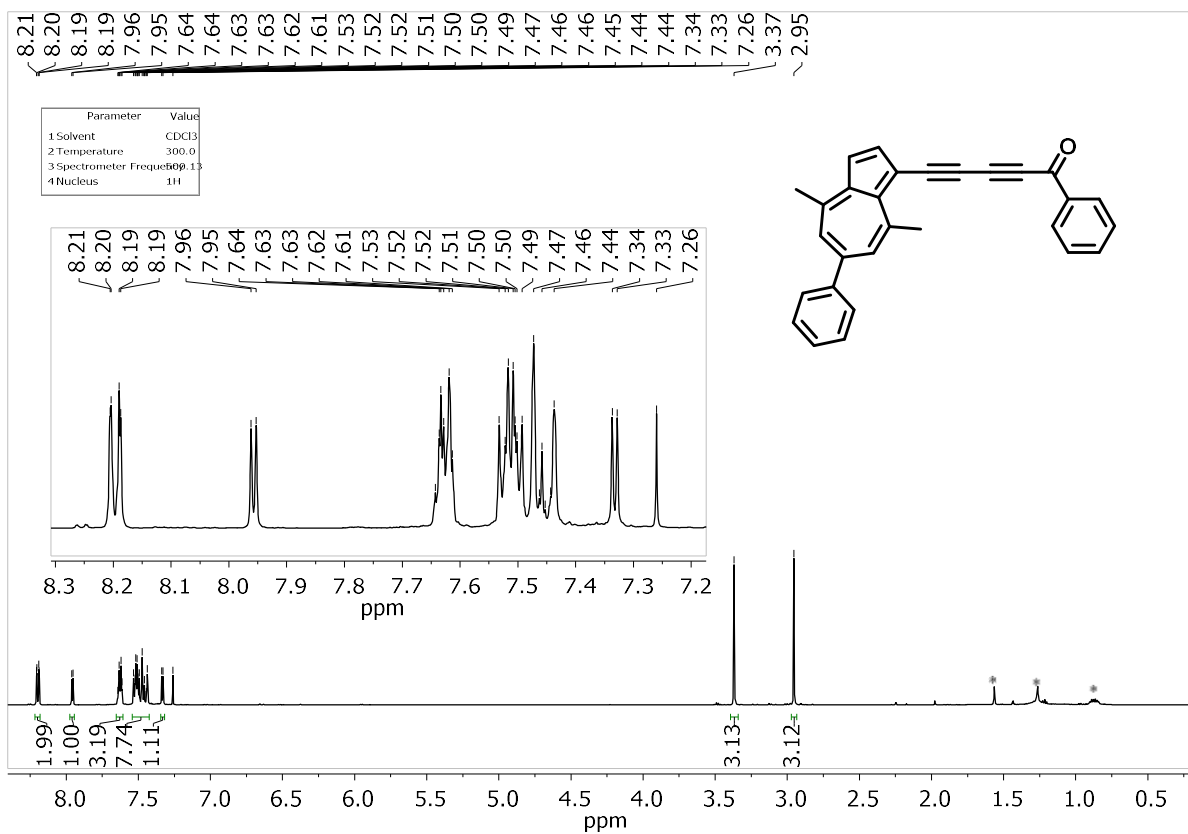


Figure S52. ¹H NMR spectrum of compound 3ce.

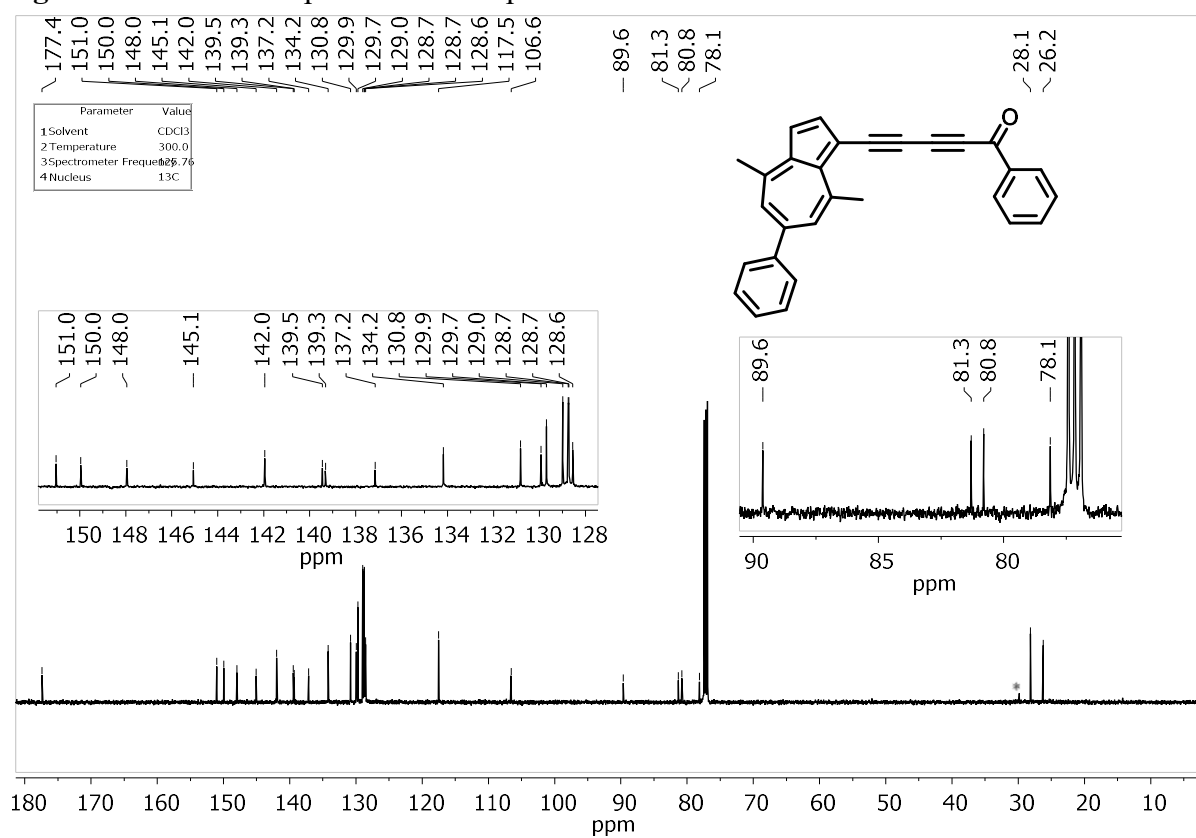


Figure S53. ¹³C NMR spectrum of compound 3ce.

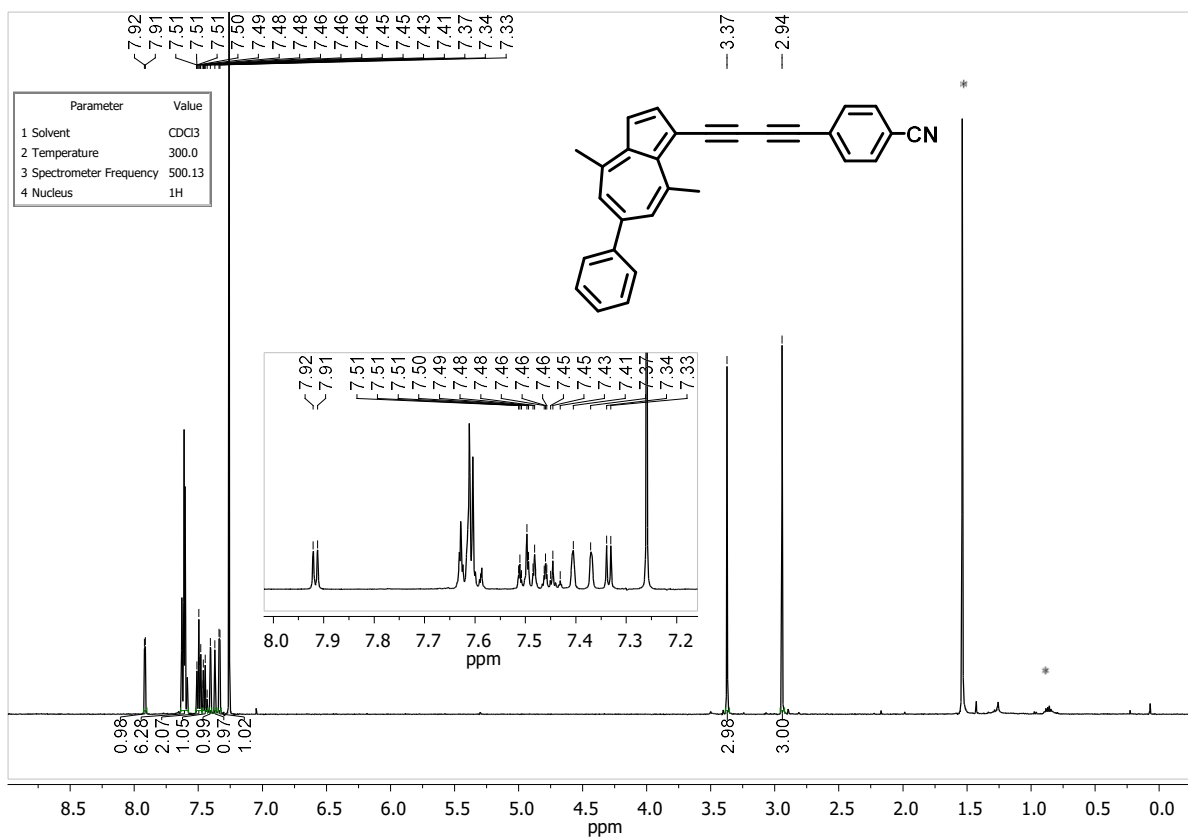


Figure S54. ^1H NMR spectrum of compound 3cf.

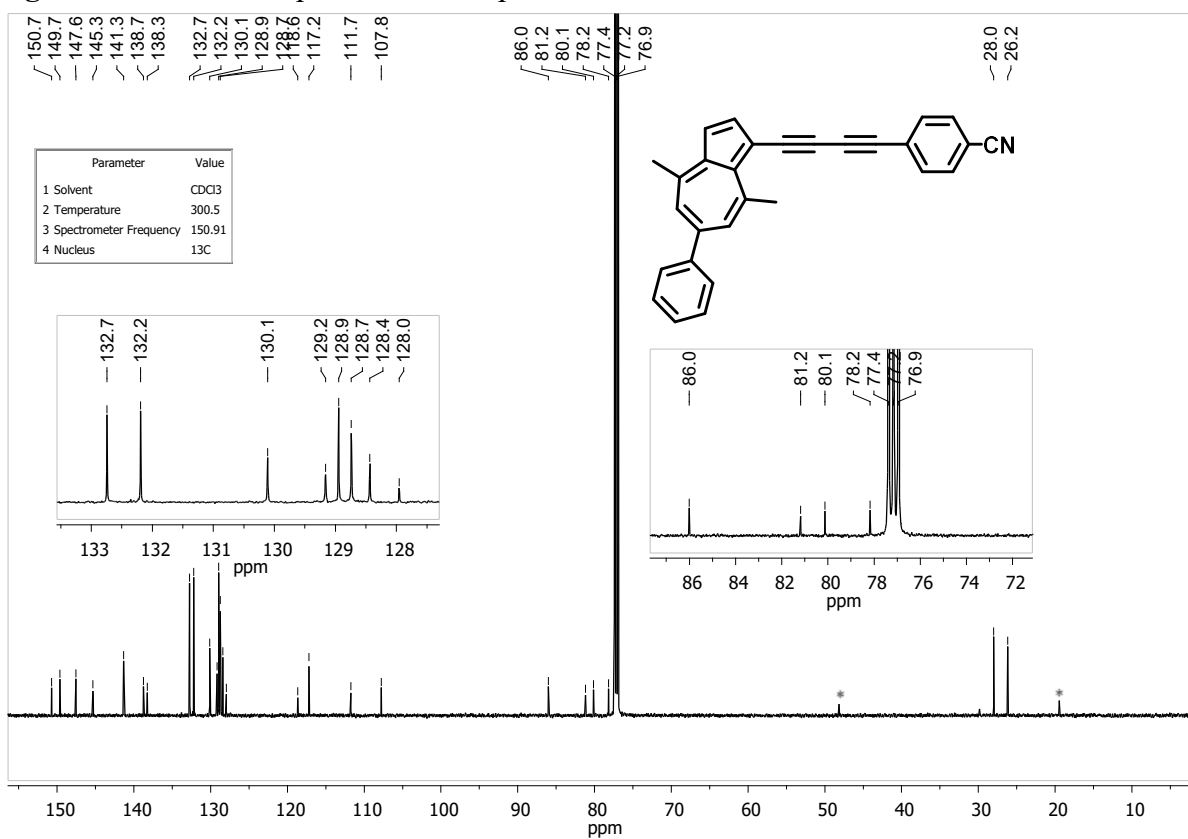


Figure S55. ^{13}C NMR spectrum of compound 3cf.

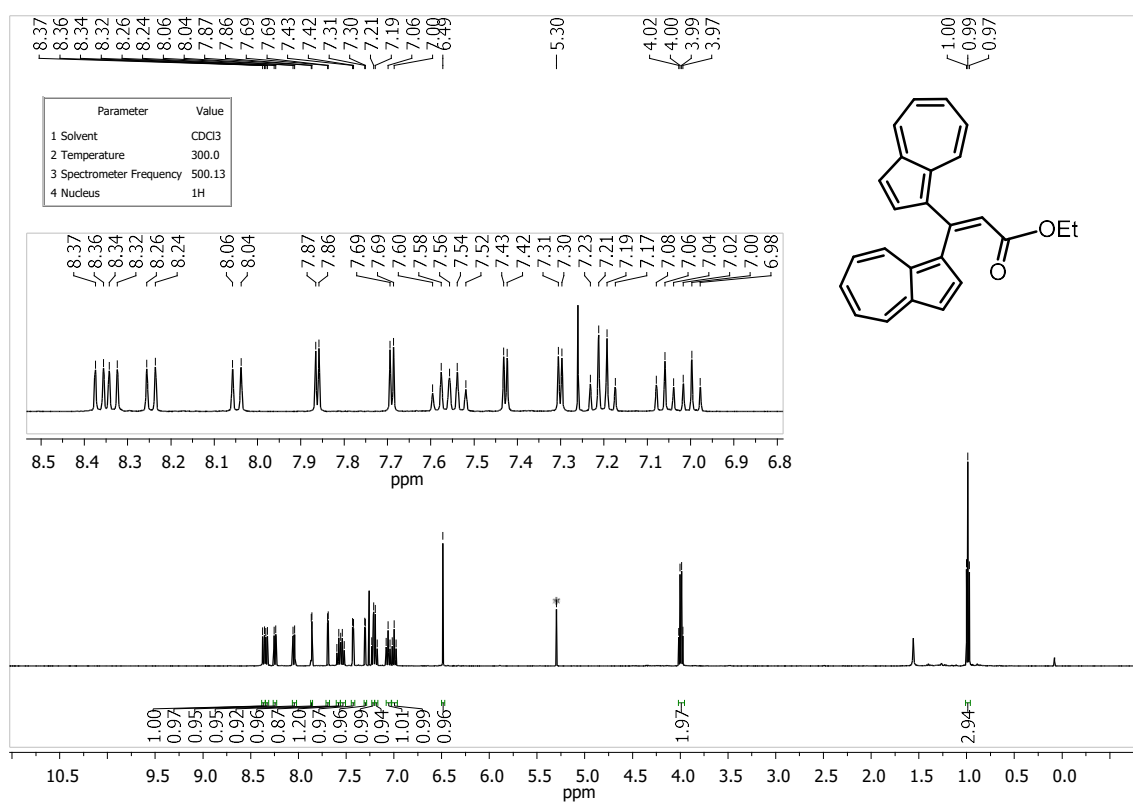


Figure S56. ^1H NMR spectrum of compound 4aa.

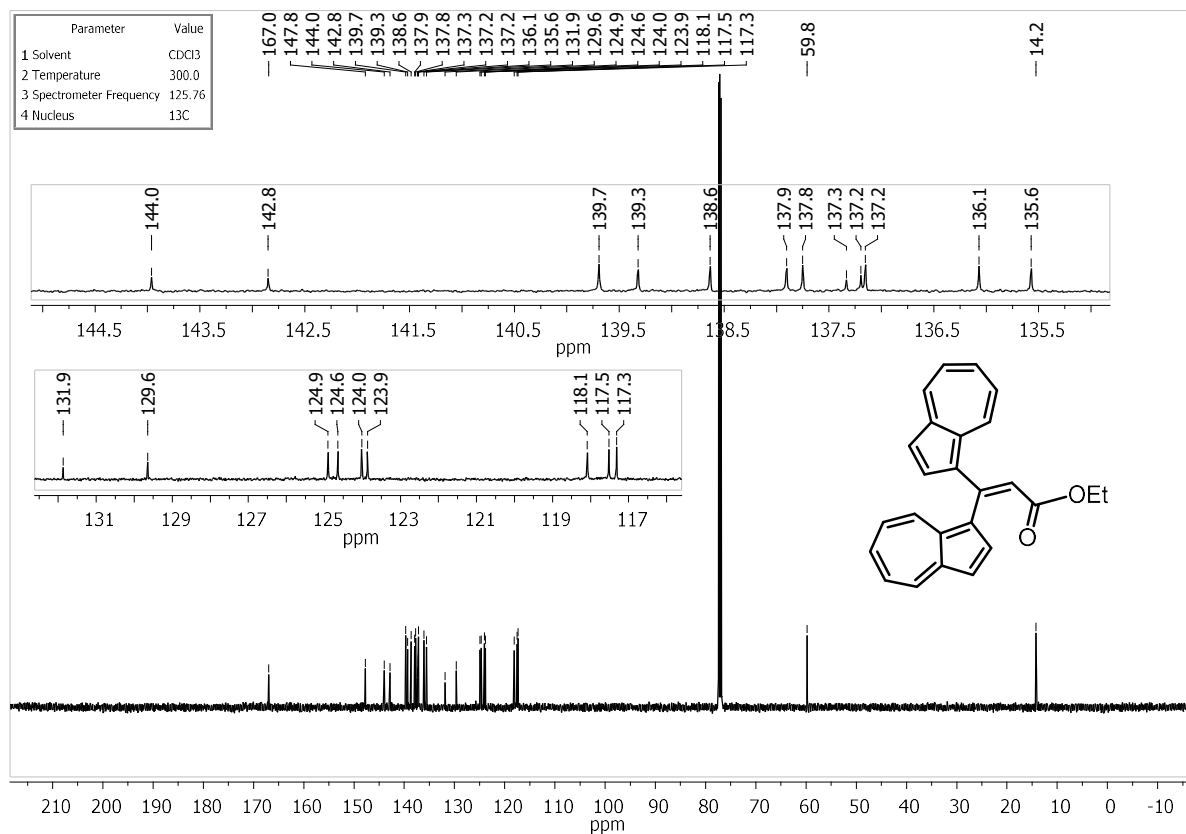


Figure S57. ^{13}C NMR spectrum of compound 4aa.

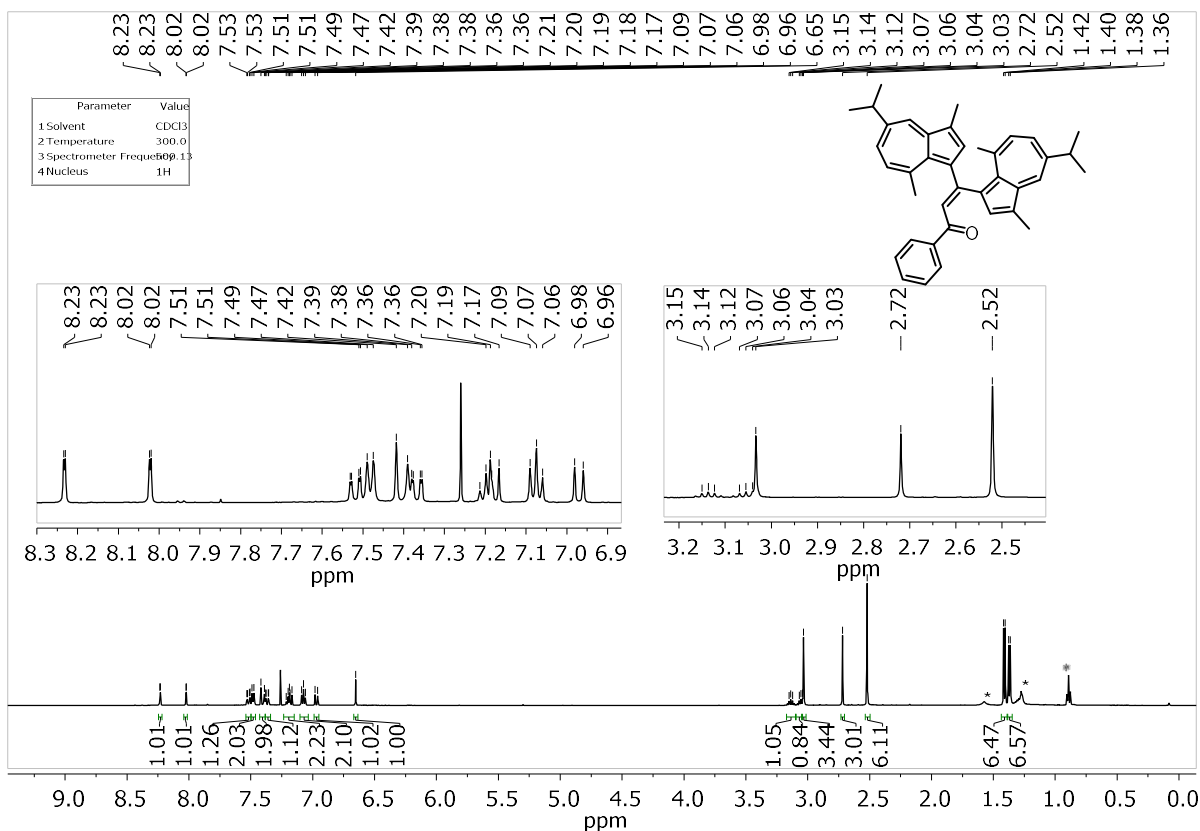


Figure S58. ^1H NMR spectrum of compound 4bb.

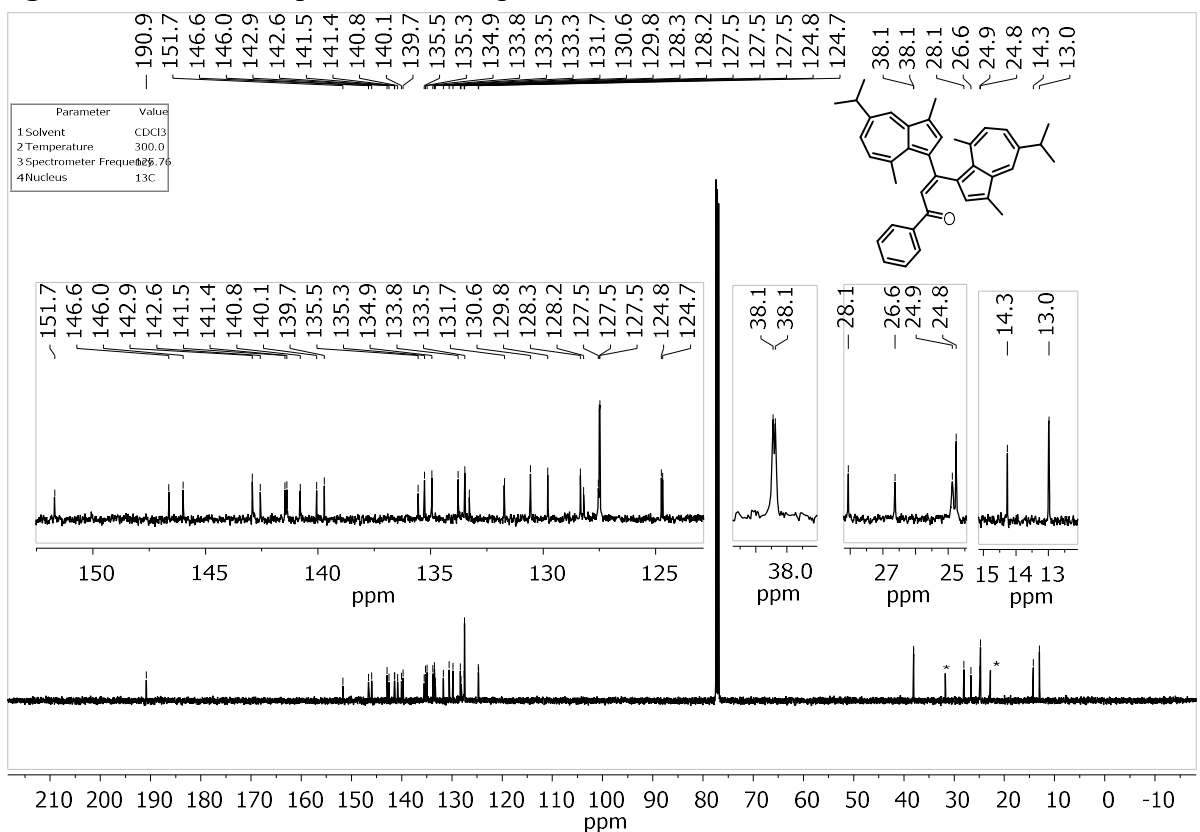


Figure S59. ^{13}C NMR spectrum of compound 4bb.

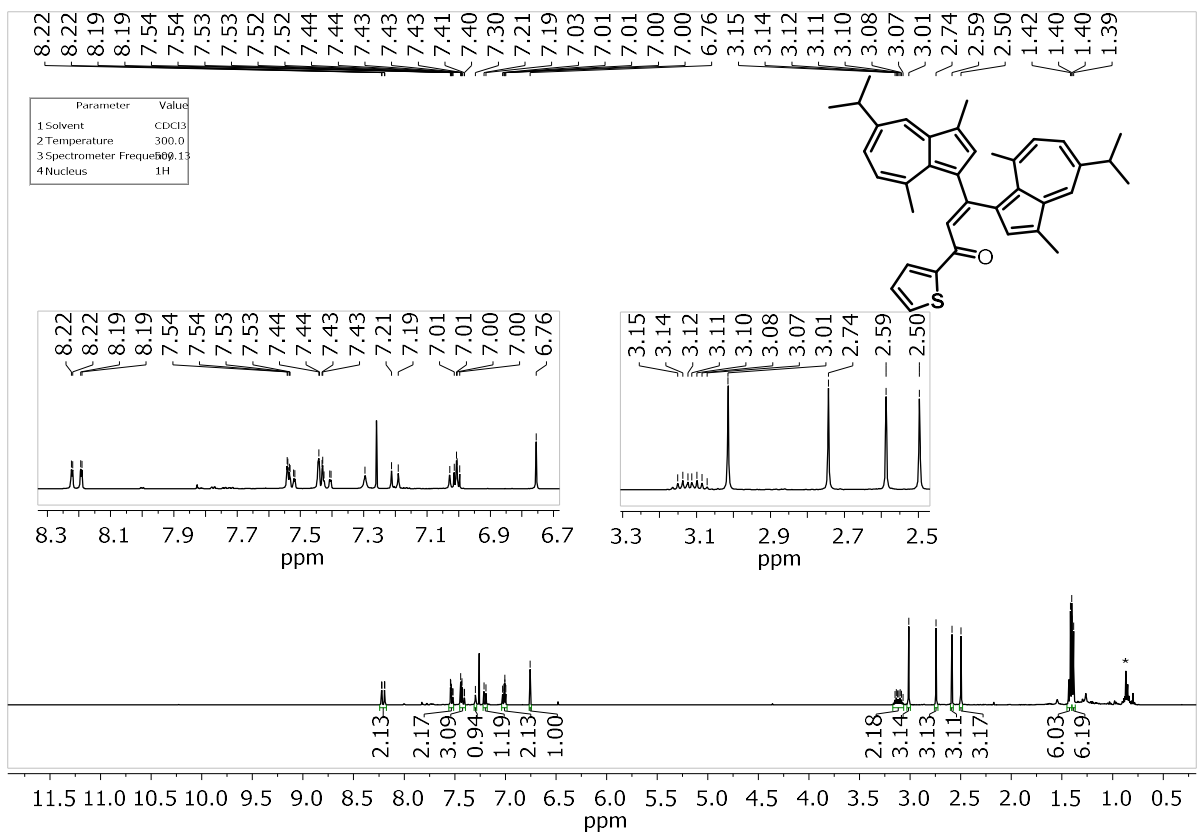


Figure S60. ¹H NMR spectrum of compound 4bc.

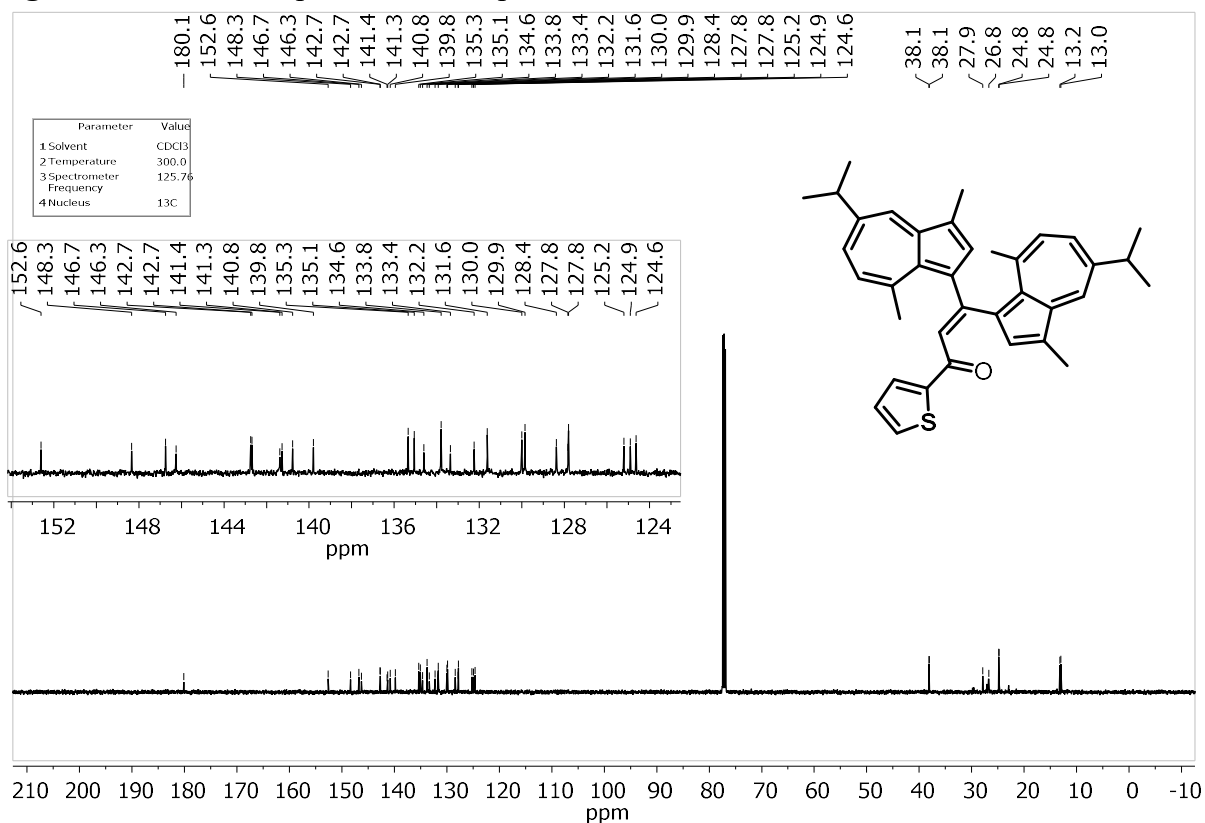


Figure S61. ¹³C NMR spectrum of compound 4bc.

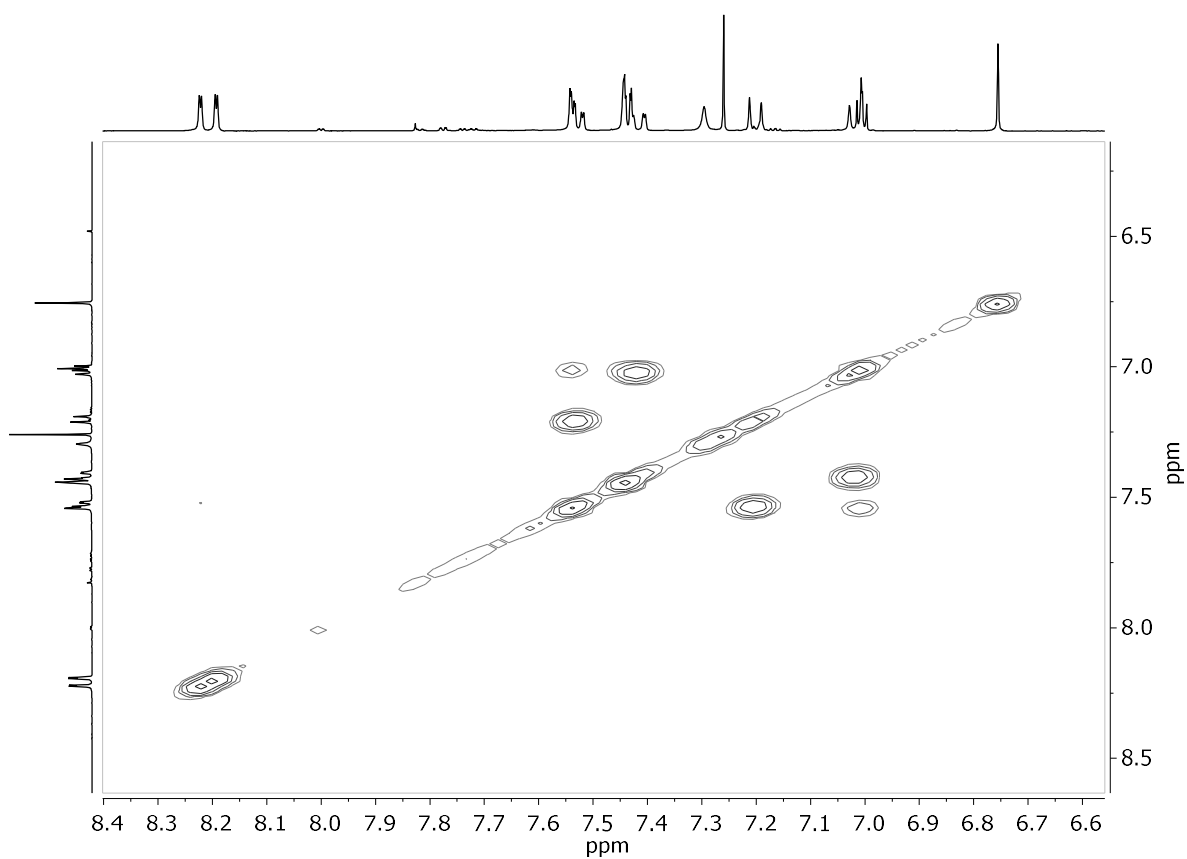


Figure S62. Part of COSY spectrum of compound **4bc**.

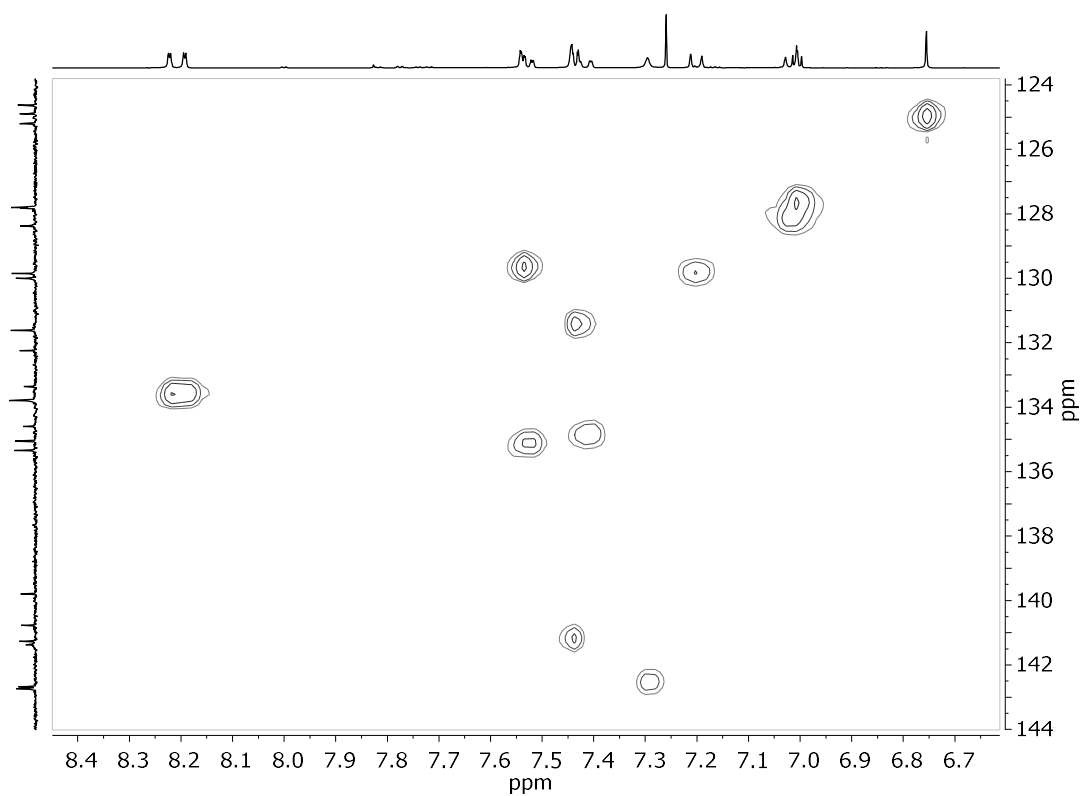


Figure S63. Part of HSQC spectrum of compound **4bc**.

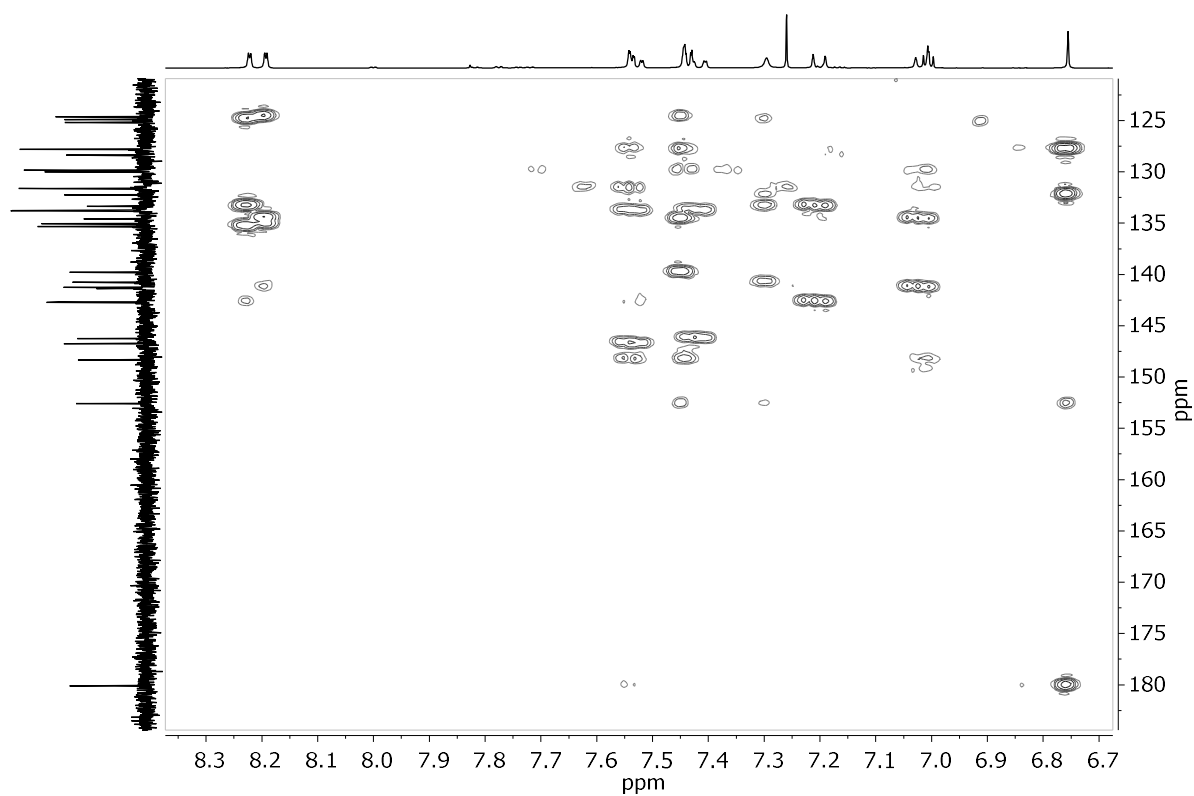


Figure S64. Part of HMBC spectrum of compound **4bc**.

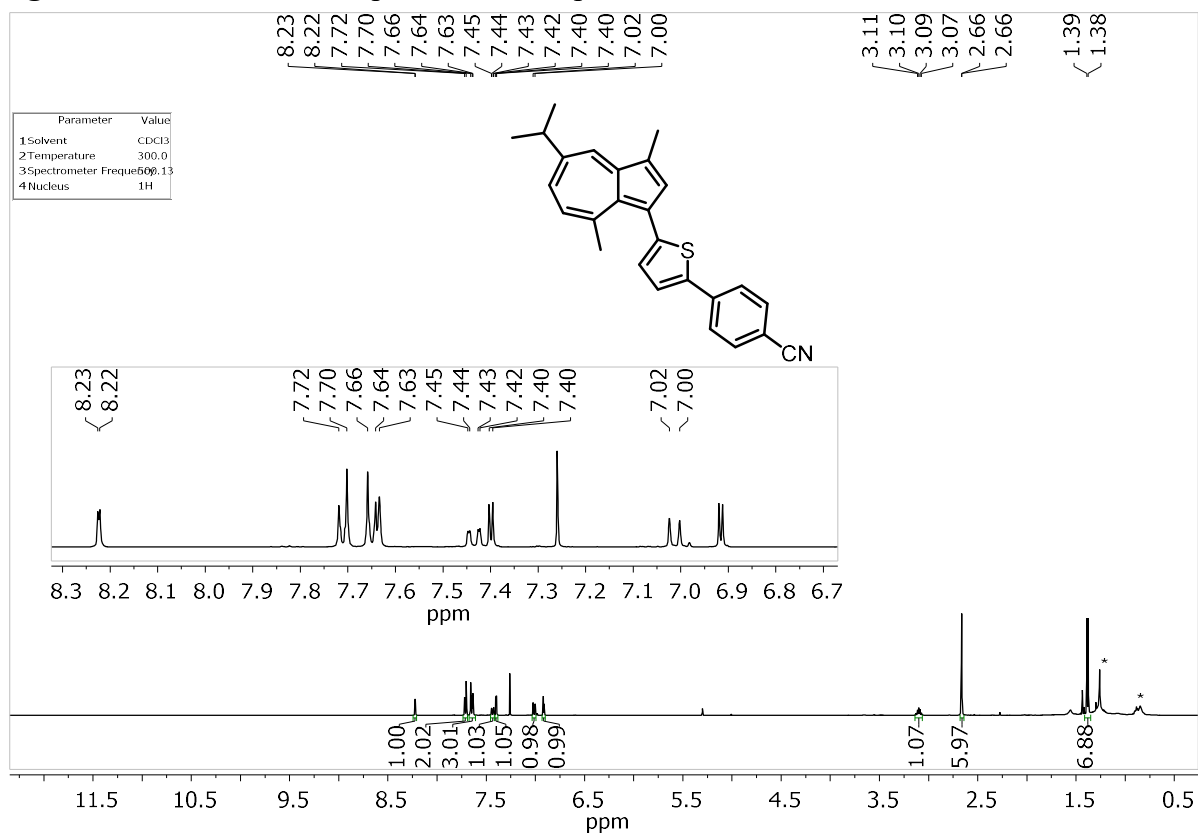


Figure S65. ¹H NMR spectrum of compound **5bf**.

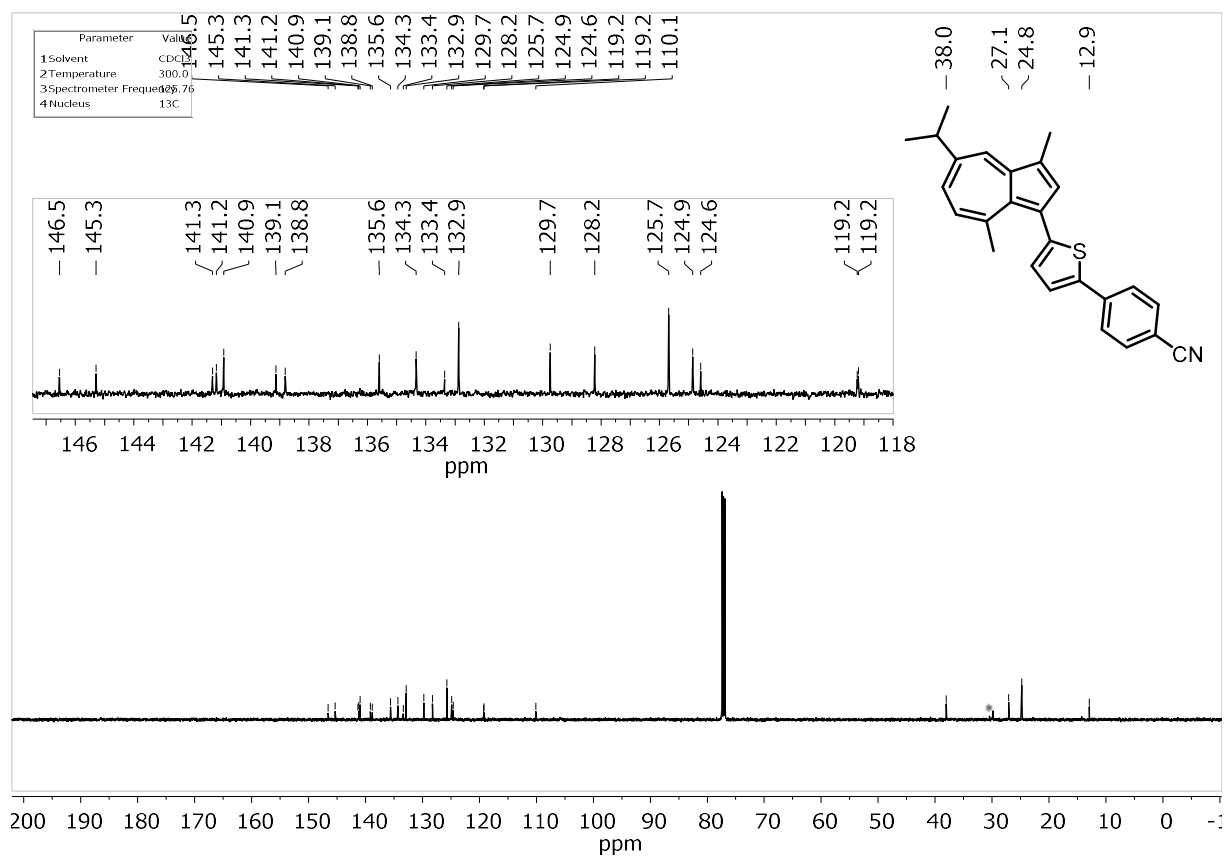


Figure S66. ¹³C NMR spectrum of compound **5bf**.

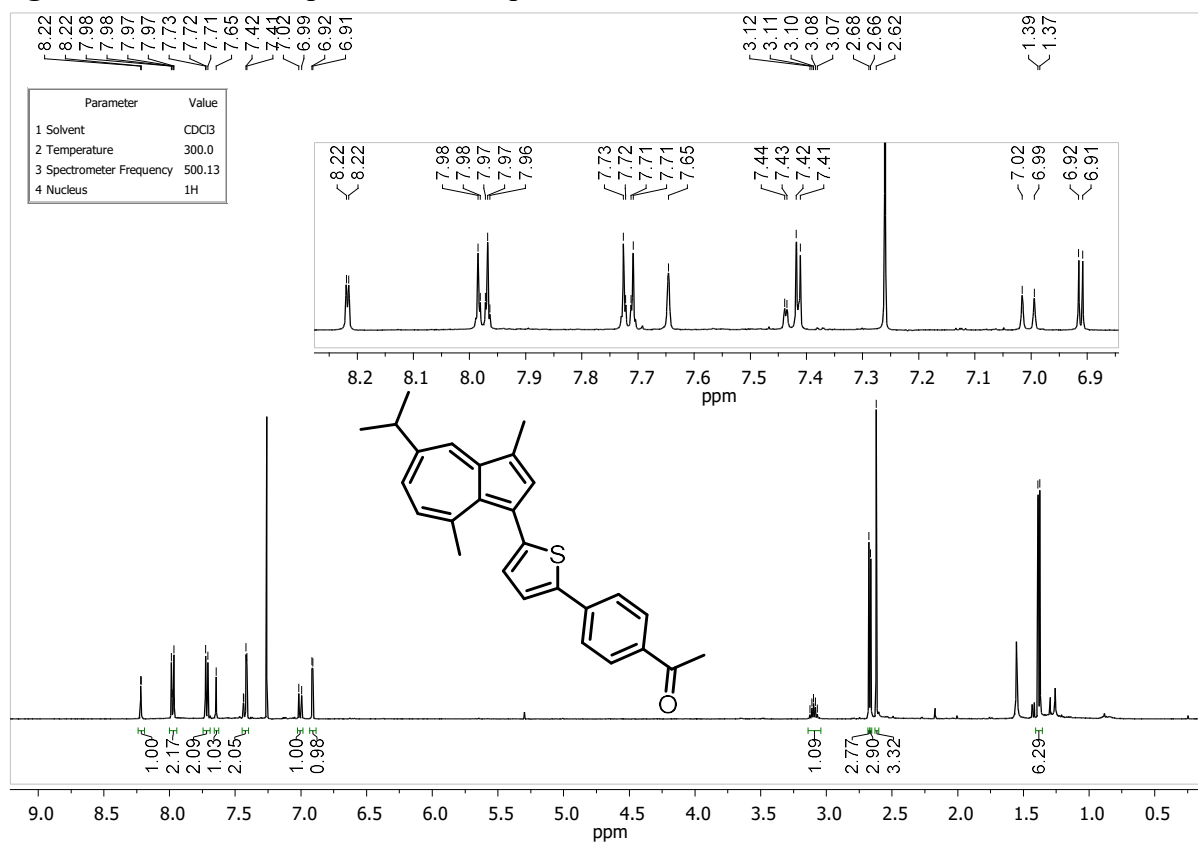


Figure S67. ¹H NMR spectrum of compound **5bg**.

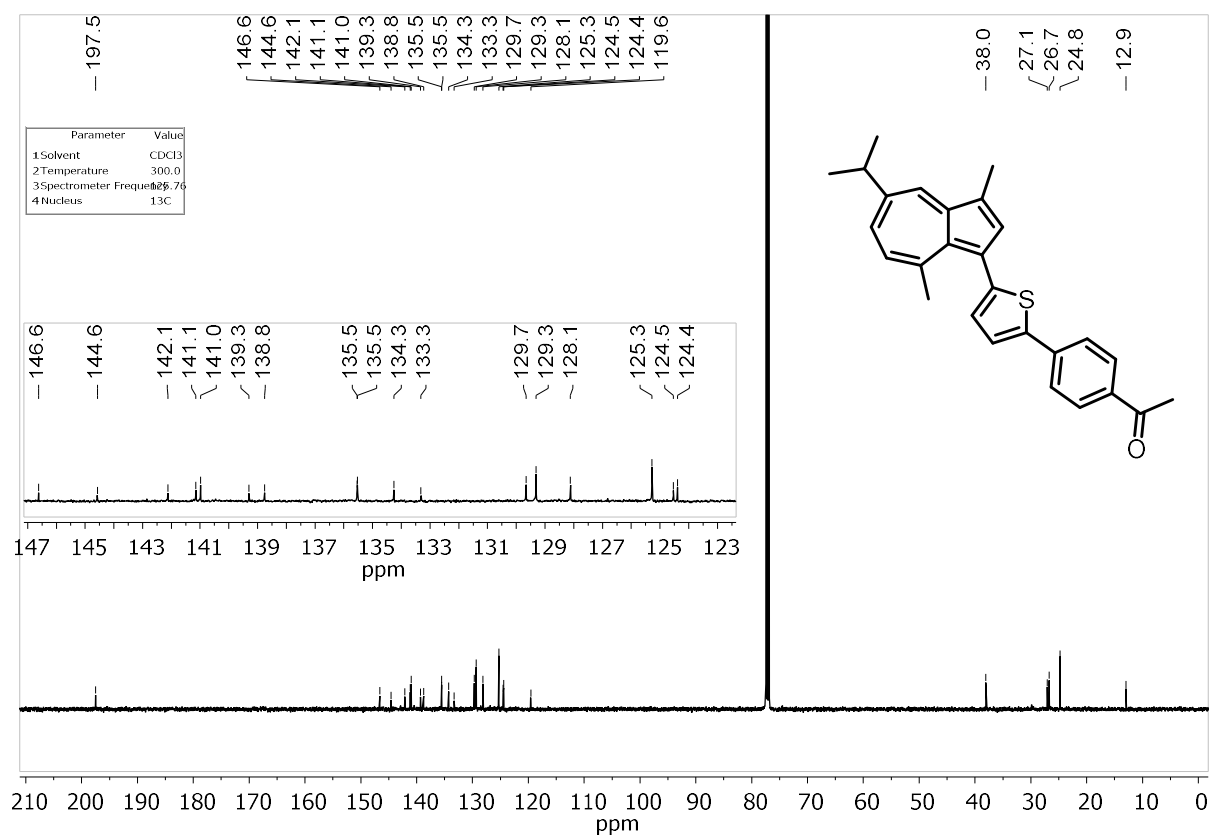


Figure S68. ¹³C NMR spectrum of compound **5bg**.

7. References

- (1) Gulia, N.; Pigulski, B.; Szafert, S.: Base-Promoted Double Amination of 1-Haloalkynes: Direct Synthesis of Ene-1,1-diamines. *Eur. J. Org. Chem.* **2020**, 2020, 5610-5615.
- (2) Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112-122.
- (3) Matěnová, M.; Lorelei Horhoiu, V.; Dang, F.-X.; Pospíšil, P.; Alster, J.; Burda, J. V.; Silviu Balaban, T.; Pšenčík, J.: Energy transfer in aggregates of bacteriochlorophyll c self-assembled with azulene derivatives. *Phys. Chem. Chem. Phys.* **2014**, 16, 16755-16764.
- (4) DiMauro, E. F.; Kozlowski, M. C.: Phosphabenzenes as electron withdrawing phosphine ligands in catalysis. *J. Chem. Soc., Perkin Trans. 1* **2002**, 439-444.
- (5) Pigulski, B.; Gulia, N.; Szafert, S.: Synthesis of Long, Palladium End-Capped Polyynes through the Use of Asymmetric 1-Iodopolyynes. *Chem. – Eur. J.* **2015**, 21, 17769-17778.
- (6) Gulia, N.; Pigulski, B.; Szafert, S.: Palladium End-Capped Polyynes via Oxidative Addition of 1-Haloalkynes to Pd(PPh₃)₄. *Organometallics* **2015**, 34, 673-682.
- (7) Pigulski, B.; Arendt, A.; Tomilin, D. N.; Sobenina, L. N.; Trofimov, B. A.; Szafert, S.: Transition-Metal Free Mechanochemical Approach to Polyne Substituted Pyrroles. *J. Org. Chem.* **2016**, 81, 9188-9198.
- (8) Walton, D. R. M.; Waugh, F.: Friedel-crafts reactions of bis(trimethylsilyl)polyynes with acyl chlorides; a useful route to terminal-alkynyl ketones. *J. Organomet. Chem.* **1972**, 37, 45-56.