Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Spectral dependence of nonlinear optical properties of symmetrical octatetraynes with *p*-substituted phenyl end-groups

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I. General Information

Solvents were treated as follows: THF (POCH, analytical grade) was distilled from Na/benzophenone under N_2; acetone (ChemPur, analytical grade) was distilled from P_2O_5 under N_2. Acetonitrile (ChemPur, analytical grade) and pyridine (EuroChem, analytical grade were used as received. Solvents for workup and chromatography were used as received: hexane (Chromasolv® for HPLC, 97.0%, Aldrich), DCM (Chromasolv® for HPLC, 99.8%, Aldrich), diethyl ether (Chromasolv® for HPLC, 99.9%, Aldrich). Flash column chromatography was performed on silica gel (Macherey-Nagel Silica gel 60, 230-400 mesh). Short plug filtration was performed on silica gel (Fluka, 70-230 mesh). For thin layer chromatography Macherey-Nagel ALUGRAM® SIL G/UV254 0.20 mm plates were used with UV light as a visualizing agent.

Tetrabutyloammonium fluoride (TBAF, 1 M in THF, Aldrich), TMSC≡CH (Aldrich, 98%), chlorotriethylsilane (TMSCl, Aldrich, 99%), diisopropylamine (Aldrich, 99.95%), CuCl (Alfa Aesar, 97%), $Cu(OAc)_2$ (monohydrate, Aldrich), $Pd(PPh_3)_2Cl_2$ (Alfa Aesar), $AgNO_3$ (POCH, analytical grade), CuI (99.999%, Aldrich), KF (POCH, analytical grade), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA, 99%, distilled from KOH), *N*-bromosuccinimide (NBS, Aldrich, 99%) were used as purchased if not stated otherwise.

The ^1H, ^{13}C NMR spectra were obtained using a Bruker Avance 500 MHz spectrometer. The chemical shifts are given in ppm relative to the residuals signals of the solvents ($CDCl_3$, ^1H: 7.26 ppm, ^{13}C: 77.2 ppm; C_6D_6 ^1H: 7.16 ppm, ^{13}C: 128.1 ppm). HRMS spectra were recorded using a spectrometer with TOF mass analyzer and ESI ion source. UV-Vis spectra were recorded on a Cary 300 Bio spectrophotometer.

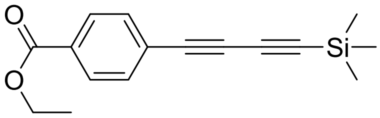
II. Preparation of materials

Known compounds

Ethyl 4-bromobenzoate (**E1-Br**),[1] 4-iodophenyl acetate (**E2-I**),[2] 4-iodophenyl benzoate (**E3-I**),[3] ethyl 4-((trimethylsilyl)ethynyl)benzoate (**E1-C_2TMS**),[4] 4-((trimethylsilyl)ethynyl)phenyl acetate (**E2-C_2TMS**),[5] 4-((trimethylsilyl)ethynyl)phenyl benzoate (**E3-C_2TMS**)[6] **and** ethyl 4-(bromoethynyl)benzoate (**E1-C_2Br**),[7] were synthesized according to the literature.

Syntheses of new materials

E1-C_4TMS ethyl 4-((trimethylsilyl)buta-1,3-diyn-1-yl)benzoate



To the solution of ethyl 4-(bromoethynyl)benzoate (1.71 g, 6.75 mmol) in 25 mL of THF CuI (64.3 mg, 0.34 mmol), $Pd(PPh_3)_2Cl_2$ (0.237 g, 0.337 mmol) and ethynyltrimethylsilane (1.43 mL, 10.12 mmol) were added under dinitrogen. Next diisopropylamine (2.36 mL, 16.9 mmol) was added dropwise and the reaction was stirred for 4 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography (DCM/hexane, v/v, 1/1) yielding 1.03 g (3.80 mmol) of orange oil. Yield 57%.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.85–7.81 (m, 2H, H_{Ar}), 7.22–7.18 (m, 2H, H_{Ar}), 4.05 (q, J = 7.1 Hz, 2H, OCH_2), 0.99 (t, J = 7.1 Hz, 3H, CH_3), 0.10 (s, 9H, $SiMe_3$).^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 165.3 (1C, *C*=O), 132.8 (1C, *C*H_{Ar}), 131.4 (1C, *C*$_{Ar}$C=O), 129.8 (1C, *C*H_{Ar}), 126.0 (1C, *C*$_{Ar}$ C≡C), 92.5 (1C, C_{Ar}C≡CC≡*C*Si), 88.7 (1C, C_{Ar}C≡C*C*≡CSi), 77.7 (1C, C_{Ar}*C*≡CC≡CSi), 76.5 (1C, C_{Ar}C≡*C*C≡CSi), 61.0 (1C, O*C*H_2), 14.2 (1C, *C*H_3), -0.5 (3C, $SiMe_3$).

HRMS(ESI): m/z calcd for $C_{16}H_{18}O_2Si$: 293.0968 [M+Na$^+$]; found: 293.0975.

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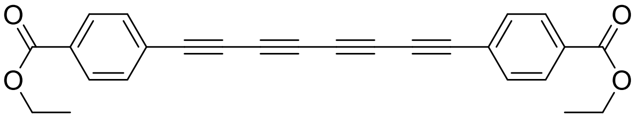
E1-C$_8$-E1: diethyl-4,4'-(octa-1,3,5,7-tetrayne-1,8-diyl)dibenzoate

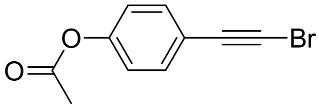


To the solution of ethyl 4-((trimethylsilyl)buta-1,3-diyn-1-yl)benzoate (0.539 g, 1.99 mmol) in 15 mL of dry acetone 1M solution of TBAF in THF (400 µL, 0.40 mmol) was added under N_2. Next chlorotrimethylsilane (253 µL, 1.99 mmol) was added dropwise and O_2 was bubbled through the solution. After 90 minutes the solution of CuCl (0.198 g, 1.99 mmol) and TMEDA (120 µL, 0.80 mmol) in 10 mL of acetone were added. The reaction was stirred for 22 h at room temperature and O_2 was bubbled. The solvent was removed under reduced pressure and the products were isolated by flash column chromatography (DCM) yielding 126 mg (0.32 mmol) of yellow solid. Yield 16%.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.84–7.81 (m, 4H, H_{Ar}), 7.10–7.07 (m, 4H, H_{Ar}), 4.05 (q, J_{HH} = 7.1 Hz, 4H, OCH_2), 0.97 (t, J_{HH} = 7.1 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 165.2 (1C, *C*=O), 133.3 (2C, *C*H_{Ar}), 132.0 (1C, C_{Ar}*C*=O), 129.8 (2C, *C*H_{Ar}), 124.7 (1C, *C*$_{Ar}$C≡C), 77.8 (1C, C≡CC≡*C*C_{Ar}), 77.1 (1C, C≡C*C*≡CC_{Ar}), 68.8 (1C, C≡*C*C≡CC_{Ar}), 64.8 (1C, ***C***≡CC≡CC_{Ar}), 61.2 (1C, O*C*H_2), 14.2 (1C, *C*H_3).

HRMS(ESI): *m/z* calcd for $C_{26}H_{18}O_4$: 395.1278 [M+H$^+$]; found: 395.1271.

E2-C$_2$Br: 4-(bromoethynyl)phenyl acetate

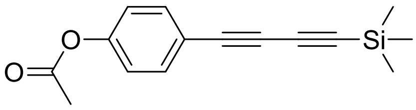


To the solution of 4-((trimethylsilyl)ethynyl)phenyl acetate (2.02 g, 8.68 mmol) in 40 mL of acetonitrile water (313 µL, 17.37 mmol) was added under N_2. Next $AgNO_3$ (1.47 g, 8.68 mmol) and KF (0.504 g, 8.68 mmol) and NBS (2.43 g, 10.4 mmol) were added. The reaction was stirred for 6 h at room temperature without an access of light. The solvent was removed under reduced pressure and the residue was purified by elution through silica gel (DCM) yielding 1.29 g (5.39 mmol) of light yellow solid. Yield 62%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47–7.43 (m, 2H, H_{Ar}), 7.07–7.03 (m, 2H, H_{Ar}), 2.29 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 169.1 (1C, *C*=O), 150.9 (1C, *C*$_{Ar}$-O), 133.3 (2C, *C*H_{Ar}), 121.8 (2C, *C*H_{Ar}), 120.4 (1C, *C*$_{Ar}$C≡C), 79.4 (1C, C_{Ar}*C*≡C), 50.1 (1C, Br*C*≡C), 21.2 (1C, CH_3).

HRMS(ESI): *m/z* calcd for $C_{10}H_7BrO_2$: 260.9521 [M+Na$^+$]; found: 260.9518.

E2-C$_4$TMS 4-((trimethylsilyl)buta-1,3-diyn-1-yl)phenyl acetate

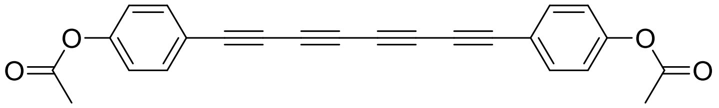


To the solution of 4-(bromoethynyl)phenyl acetate (0.292 g, 1.22 mmol) in 10 mL of THF CuI (11.6 mg, 0.06 mmol), $Pd(PPh_3)_2Cl_2$ (42.9 mg, 0.06 mmol) and ethynyltrimethylsilane (260 µL, 1.83 mmol) were added under N_2. Next, diisopropylamine (428 µL, 3.05 mmol) was added dropwise and the reaction was stirred for 2.5 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2:hexane, v/v, 1/1) yielding 0.158 g (0.62 mmol) of beige solid. Yield 50%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 2H, H_{Ar}), 7.07–7.04 (m, 2H, H_{Ar}), 2.30 (s, 3H, CH_3), 0.23 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 169.1 (1C, *C*=O), 151.4 (1C, C_{Ar}-O), 134.1 (2C, $\mathit{C}H_{Ar}$), 122.0 (2C, $\mathit{C}H_{Ar}$), 119.2 (1C, $\mathit{C}_{Ar}C\equiv C$), 91.0 (1C, $C_{Ar}C\equiv CC\equiv \mathit{C}Si$), 87.8 (1C, $C_{Ar}C\equiv C\mathit{C}\equiv CSi$), 76.0 (1C, $C_{Ar}\mathit{C}\equiv CC\equiv CSi$), 74.4 (1C, $C_{Ar}C\equiv \mathit{C}C\equiv CSi$), 21.2 (1C, CH_3), -0.3 (3C, $SiMe_3$).

HRMS(ESI): *m/z* calcd for $C_{15}H_{16}O_2Si$: 273.0812 [M+Na$^+$]; found: 273.0788.

E2-C$_8$-E2: octa-1,3,5,7-tetrayne-1,8-diylbis(4,1-phenylene) diacetate

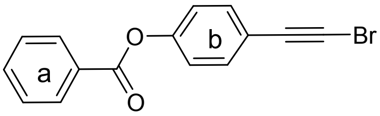


To the solution of 4-((trimethylsilyl)buta-1,3-diyn-1-yl)phenyl acetate (0.307 g, 1.20 mmol) in 15 mL of dry acetone 1M solution of TBAF in THF (240 µL, 0.24 mmol) was added under N_2. After 20 minutes chlorotrimethylsilane (152 µL, 1.20 mmol) was added dropwise and O_2 was bubbled. Next, the solution of CuCl (0.1186 g, 1.20 mmol) and TMEDA (72 µL, 0.48 mmol) in 5 mL of acetone was added. The reaction was stirred for 20 h at room temperature and O_2 was bubbled. The solvent was removed under reduced pressure and the products were isolated by flash column chromatography (DCM) yielding 0.118 g (0.32 mmol) of yellow solid. Yield 27%.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.10–7.06 (m, 4H, H_{Ar}), 6.73–6.69 (m, 4H, H_{Ar}), 1.64 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 167.7 (1C, *C*=O), 152.4 (1C, C_{Ar}-O), 134.7 (2C, $\mathit{C}H_{Ar}$), 122.2 (2C, $\mathit{C}H_{Ar}$), 117.9 (1C, $\mathit{C}_{Ar}C\equiv C$), 77.8 (1C, $C\equiv CC\equiv \mathit{C}C_{Ar}$), 75.1 (1C, $C\equiv \mathit{C}C\equiv CC_{Ar}$), 68.0 (1C, $C\equiv \mathit{C}C\equiv CC_{Ar}$), 64.6 (1C, $\mathit{C}\equiv CC\equiv CC_{Ar}$), 20.4 (1C, CH_3).

HRMS(ESI): *m/z* calcd for $C_{24}H_{14}O_4$: 389.0784 [M+Na$^+$]; found: 389.0792.

E3-C_2Br: 4-(bromoethynyl)phenyl benzoate

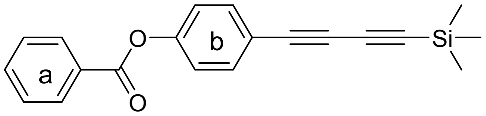


To the solution of 4-((trimethylsilyl)ethynyl)phenyl benzoate (1.60 g, 5.44 mmol) in 20 mL of acetonitrile water (196 µL, 10.88 mmol) was added under N_2. Next $AgNO_3$ (0.924 g, 5.44 mmol), KF (0.316 g, 5.44 mmol), and NBS (1.16 g, 6.53 mmol) were added. The reaction was stirred for 3.5 h at room temperature without access of light. The solvent was removed under reduced pressure and the residue was purified by elution through silica gel (DCM) yielding 1.57 g (5.22 mmol) of yellow solid. Yield 96%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (dt, J_{HH} = 8.4, 1.5 Hz, 2H, CH_{Ar} (a)), 7.68–7.63 (m, 1H, CH_{Ar} (a)), 7.55–7.50 (m, 4H, CH_{Ar} (a, b)), 7.21–7.17 (m, 2H, CH_{Ar} (b)). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 164.9 (1C, *C*=O), 151.2 (1C, C_{Ar}(b)-O), 133.9 (1C, CH_{Ar}(a)), 133.4 (2C, CH_{Ar}(b)), 130.3 (2C, CH_{Ar}(a)), 129.3 (1C, C_{Ar}(a)C=O), 128.7 (2C, CH_{Ar}(a)), 122.0 (1C, CH_{Ar}(b)), 120.5 (1C, C_{Ar}(b)C≡C), 79.4 (1C, *C*≡C), 50.2 (1C, Br*C*≡C).

HRMS(ESI): *m/z* calcd for $C_{15}H_9BrO_2$: 322.9678 [M+Na$^+$]; found: 322.9676.

E3-C_4TMS: 4-((trimethylsilyl)buta-1,3-diyn-1-yl)phenyl benzoate

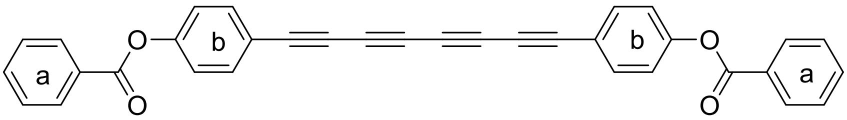


To the solution of 4-(bromoethynyl)phenyl benzoate (1.37 g, 4.55 mmol) in 30 mL of THF CuI (43.3 mg, 0.23 mmol), $Pd(PPh_3)_2Cl_2$ (0.160 g, 0.23 mmol), and ethynyltrimethylsilane (964 µL, 6.82 mmol) were added under N_2. Next diisopropylamine (1.59 mL, 11.37 mmol) was added dropwise and the reaction was stirred for 3.5 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography (DCM:hexane, v/v, 1/1) yielding 0.717 g (2.25 mmol) of brown oil. Yield 50%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20–8.17 (m, 2H, CH_{Ar} (a)), 7.67–7.63 (m, 1H, CH_{Ar} (a)), 7.57–7.54 (m, 2H, CH_{Ar} (b)), 7.54–7.50 (m, 2H, CH_{Ar} (a)), 7.22–7.18 (m, 2H, CH_{Ar} (b)), 0.24 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 164.9 (1C, *C*=O), 151.8 (1C, C_{Ar}(b)-O), 134.1 (2C, CH_{Ar}(b)), 134.0 (1C, CH_{Ar}(a)), 130.4 (2C, CH_{Ar}(a)), 129.3 (1C, C_{Ar}(a)C=O), 128.8 (2C, CH_{Ar}(a)), 122.2 (2C, CH_{Ar}(b)), 119.2 (1C, C_{Ar}(b)C≡C), 91.0 (1C, C_{Ar}(b)C≡CC≡*C*Si), 87.9 (1C, C_{Ar}(b)C≡C*C*≡CSi), 76.1 (1C, C_{Ar}(b)*C*≡CC≡CSi), 74.5 (1C,

C_{Ar}(b)C≡*C*C≡CSi), -0.3 (3C, $SiMe_3$). HRMS(ESI): *m/z* calcd for $C_{20}H_{18}O_2Si$: 341.0968 [M+Na^+]; found: 341.0973.

E3-C_8-E3: **octa-1,3,5,7-tetrayne-1,8-diylbis(4,1-phenylene) dibenzoate**

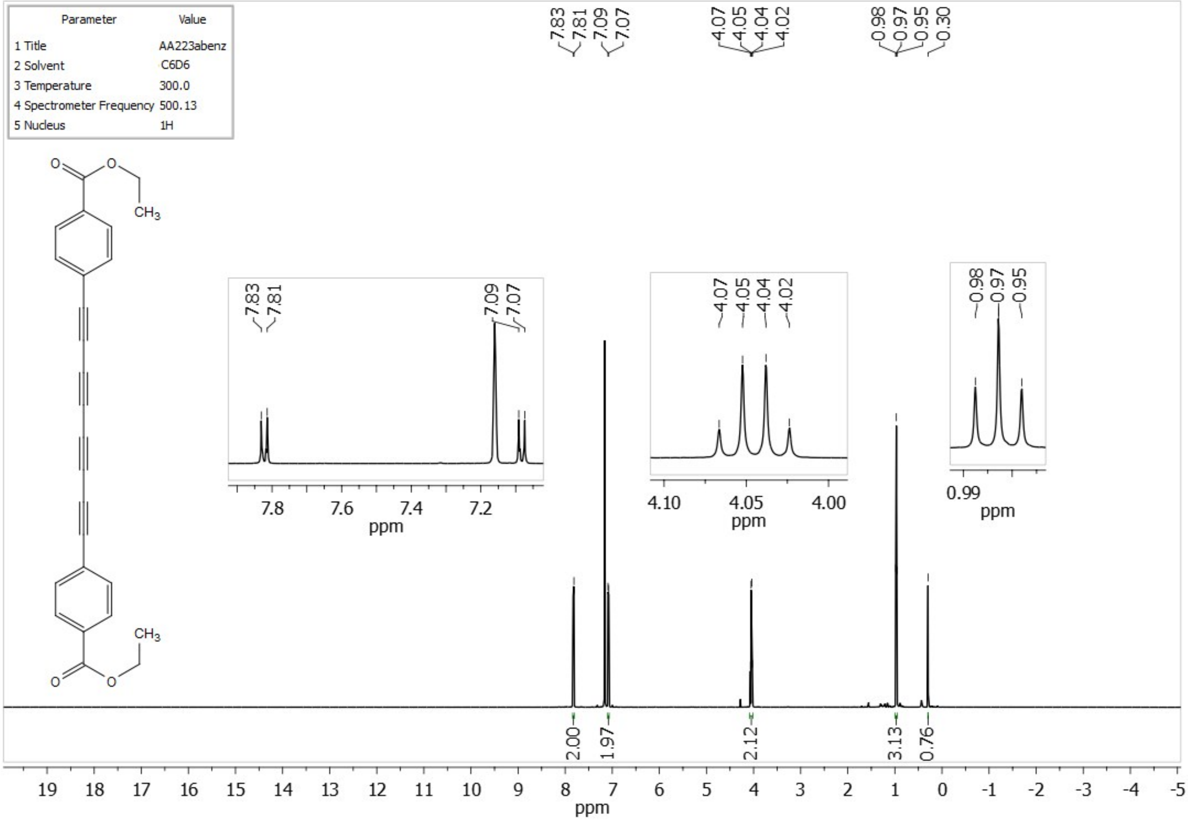


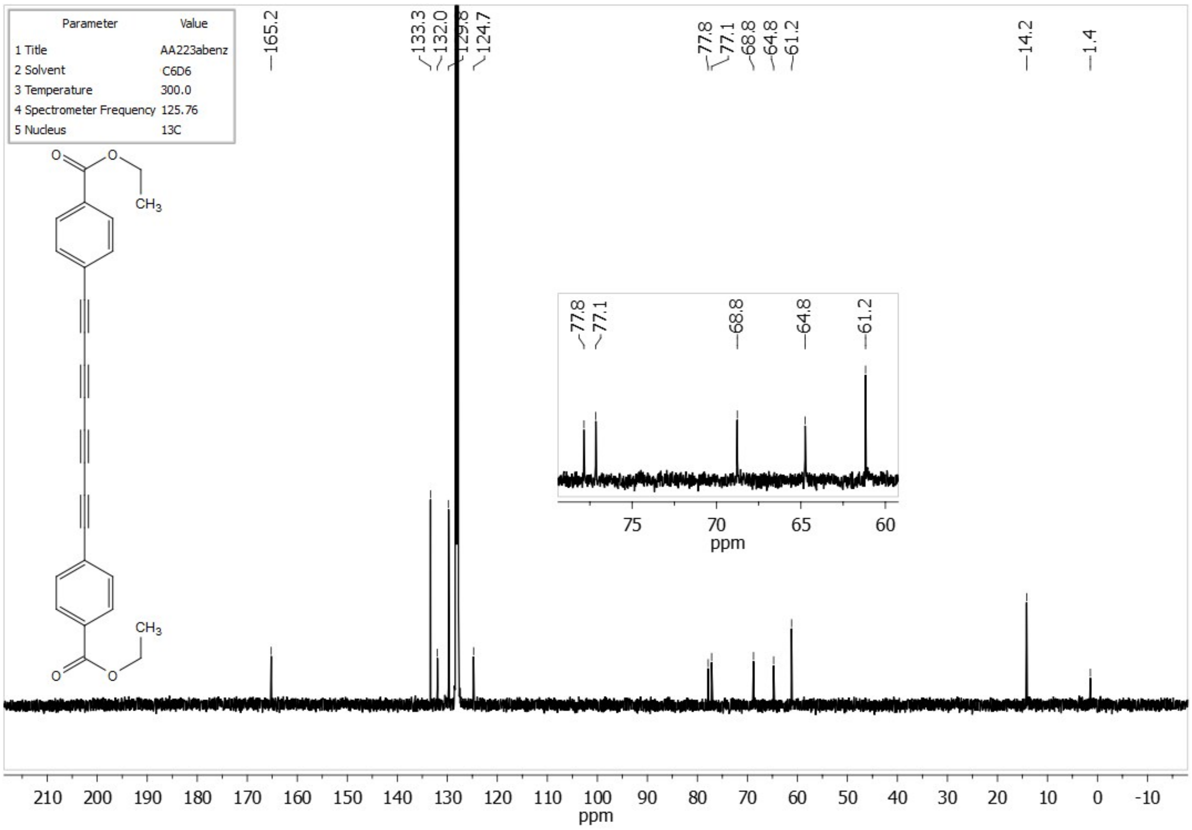
4-(buta-1,3-diyn-1-yl)phenyl benzoate (13.1 mg, 0.05 mmol) was dissolved in pyridine (7 mL) and copper(II) acetate monohydrate (53.1 mg, 0.27 mmol) was added. The mixture was stirred for 25 h at 50 °C. Next, the solvent was removed under reduced pressure and the product was purified by passing trough short silica gel plug (diethyl ether) yielding 10.3 mg (0.020 mmol) of yellow solid. Yield: 40%.

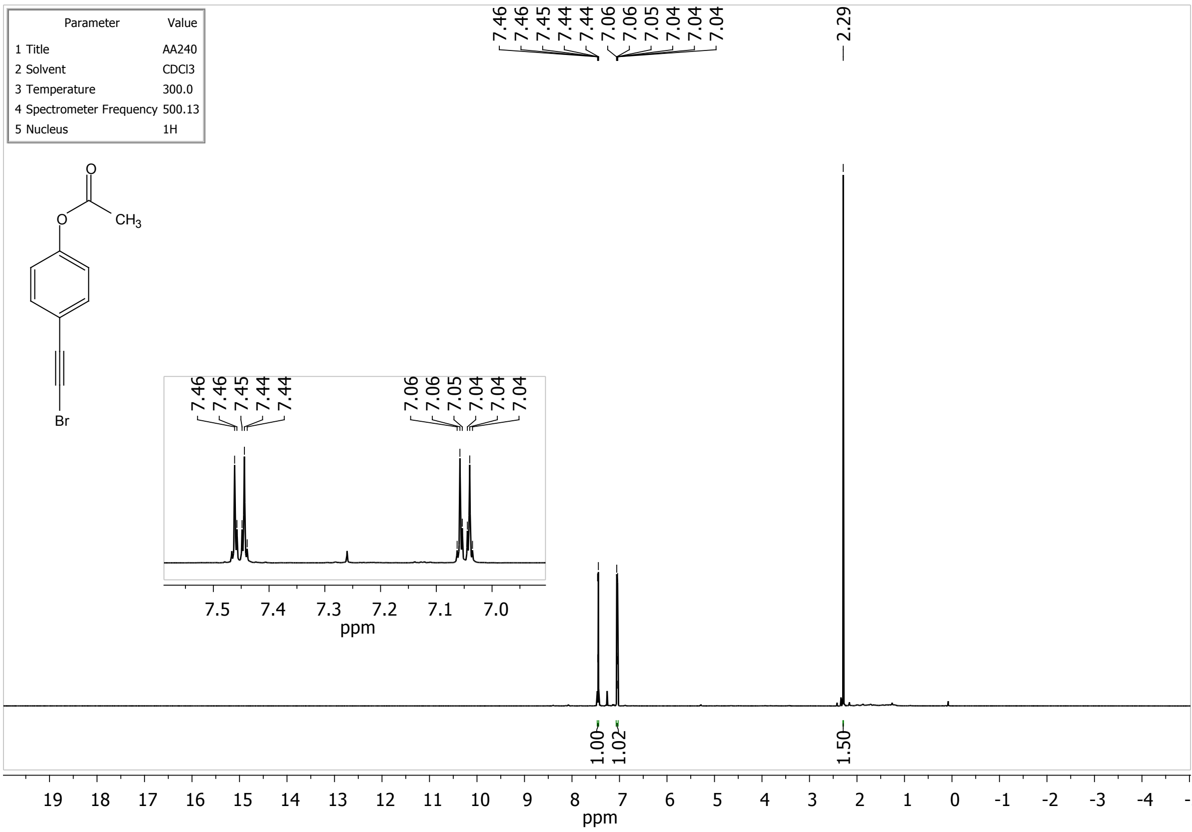
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (dd, J_{HH} = 8.3, 1.2 Hz, 4H, CH_{Ar} (a)), 7.66 (t, *J* = 7.5 Hz, 2H, CH_{Ar} (a)), 7.63–7.60 (m, 4H, CH_{Ar} (b)), 7.53 (t, *J* = 7.8 Hz, 4H, CH_{Ar} (a)), 7.25–7.22 (m, 4H, CH_{Ar} (b)). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 164.8 (1C, *C*=O), 152.3 (1C, C_{Ar}(b)-O), 134.7 (2C, *C*H_{Ar}(b)), 134.1(1C, *C*H_{Ar}(a)), 130.4 (2C, *C*H_{Ar}(a)), 129.2 (1C, C_{Ar}(a)C=O), 128.8 (2C, *C*H_{Ar}(a)), 122.4 (2C, *C*H_{Ar}(b)), 118.3 (1C, C_{Ar}(b)C≡C), 74.8 (1C, C≡C*C*≡CC_{Ar}(b)), 67.5 (1C, C≡*C*C≡CC_{Ar}(b)), 63.8 (1C, *C*≡CC≡CC_{Ar}(b)). One signal of atom from carbon chain is overlapped by the solvent signal.

HRMS(ESI): *m/z* calcd for $C_{34}H_{18}O_4$: 513.1097 [M+Na^+]; found: 513.1098.

III. NMR spectra of materials







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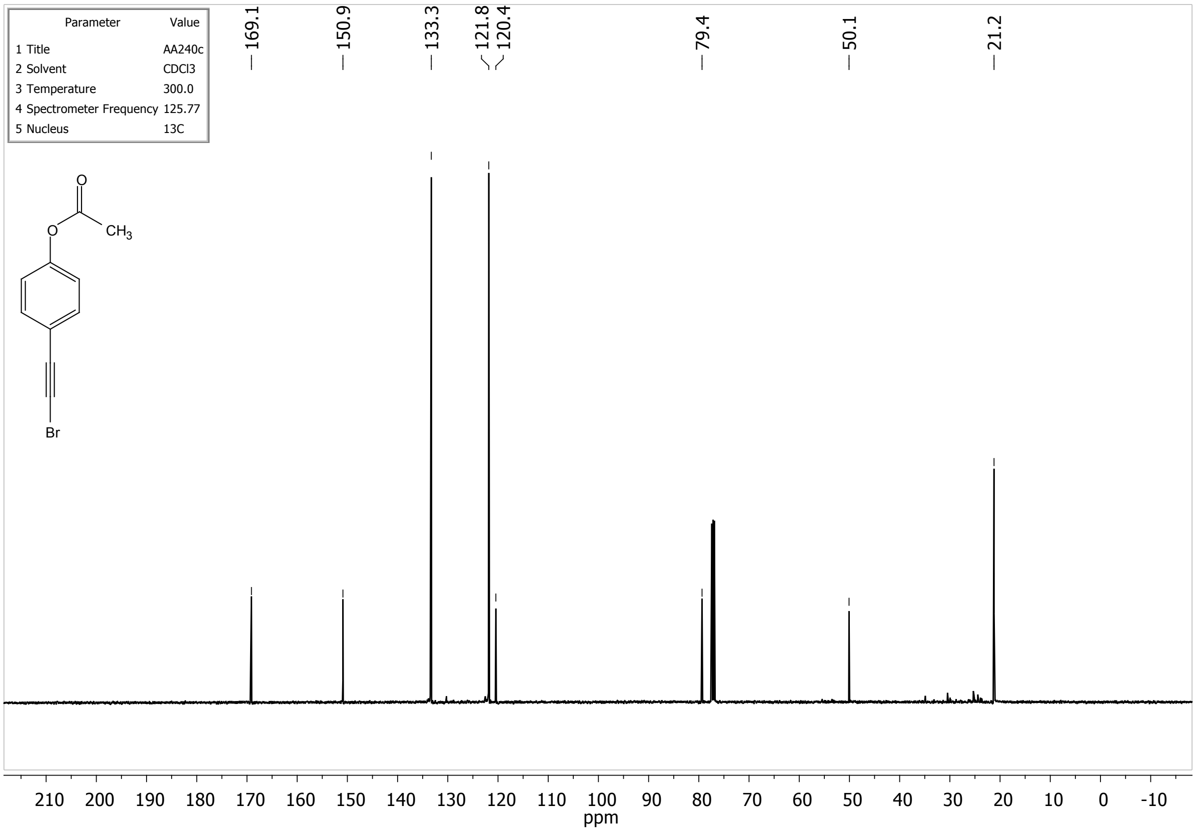

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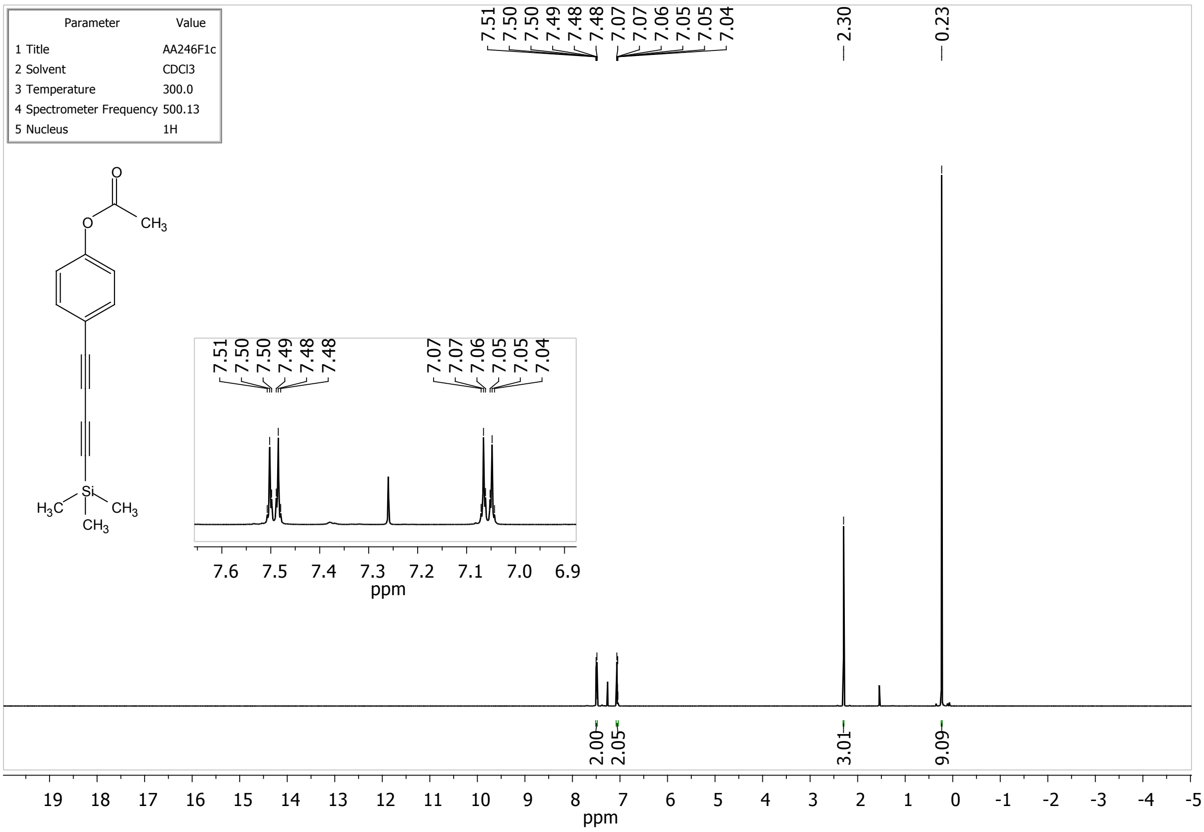

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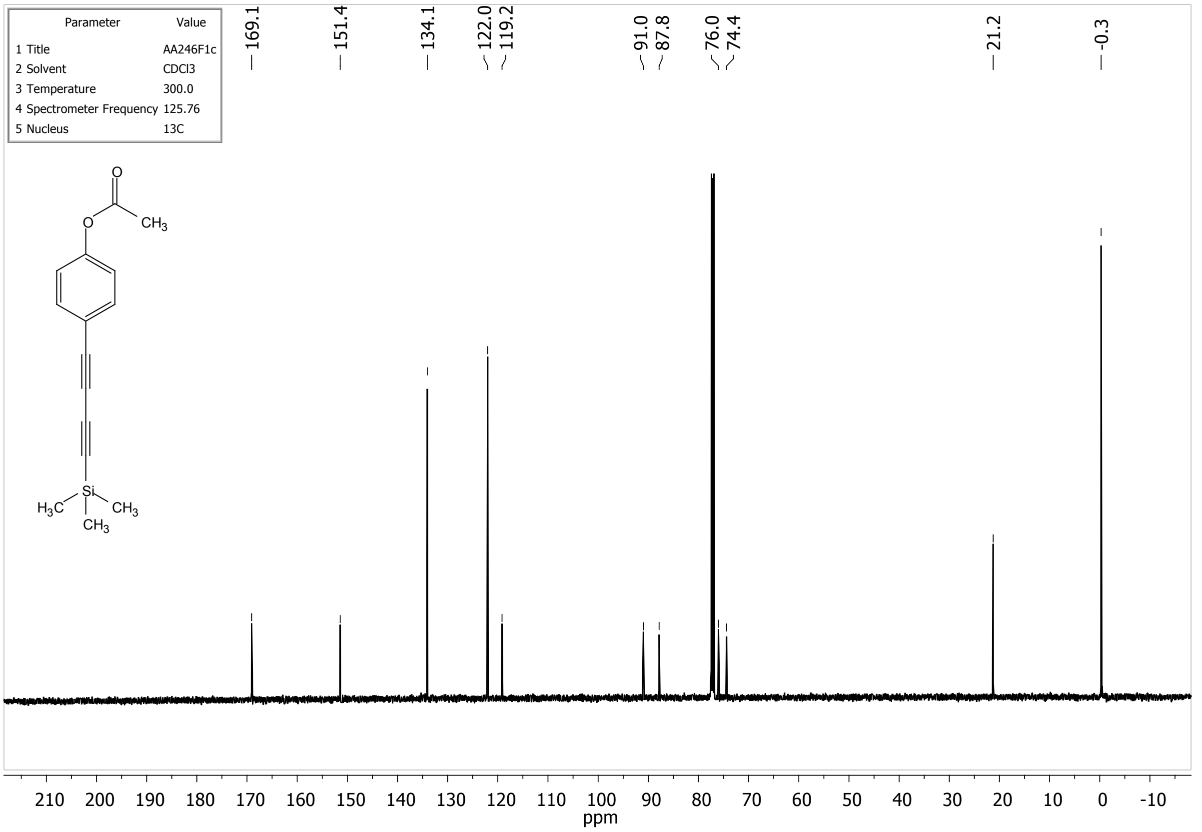

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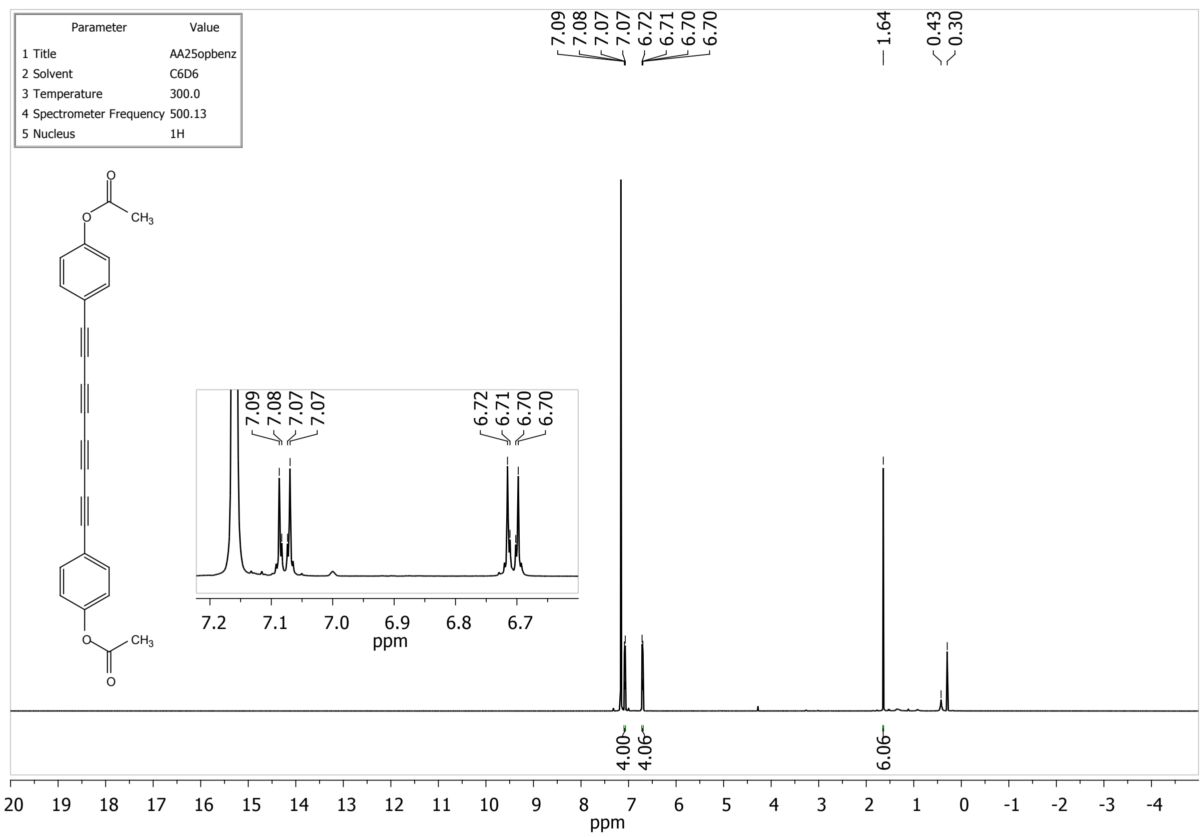
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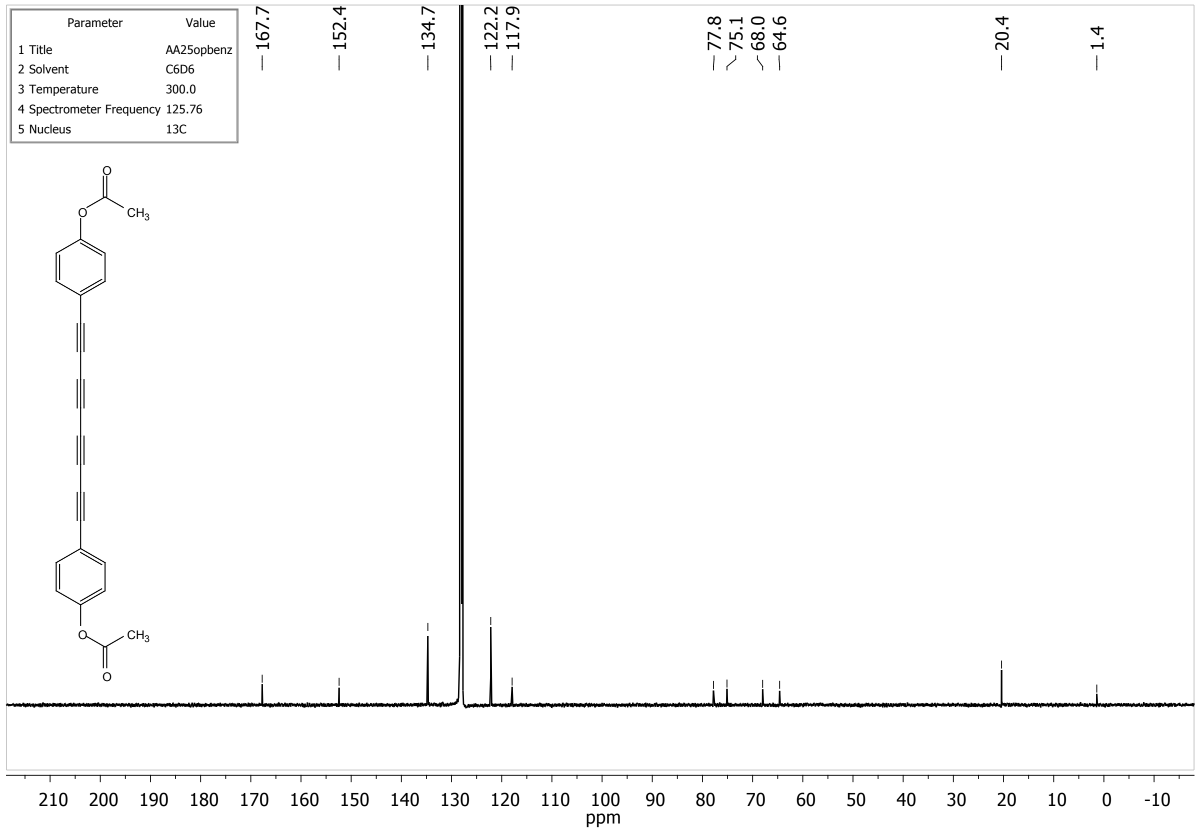
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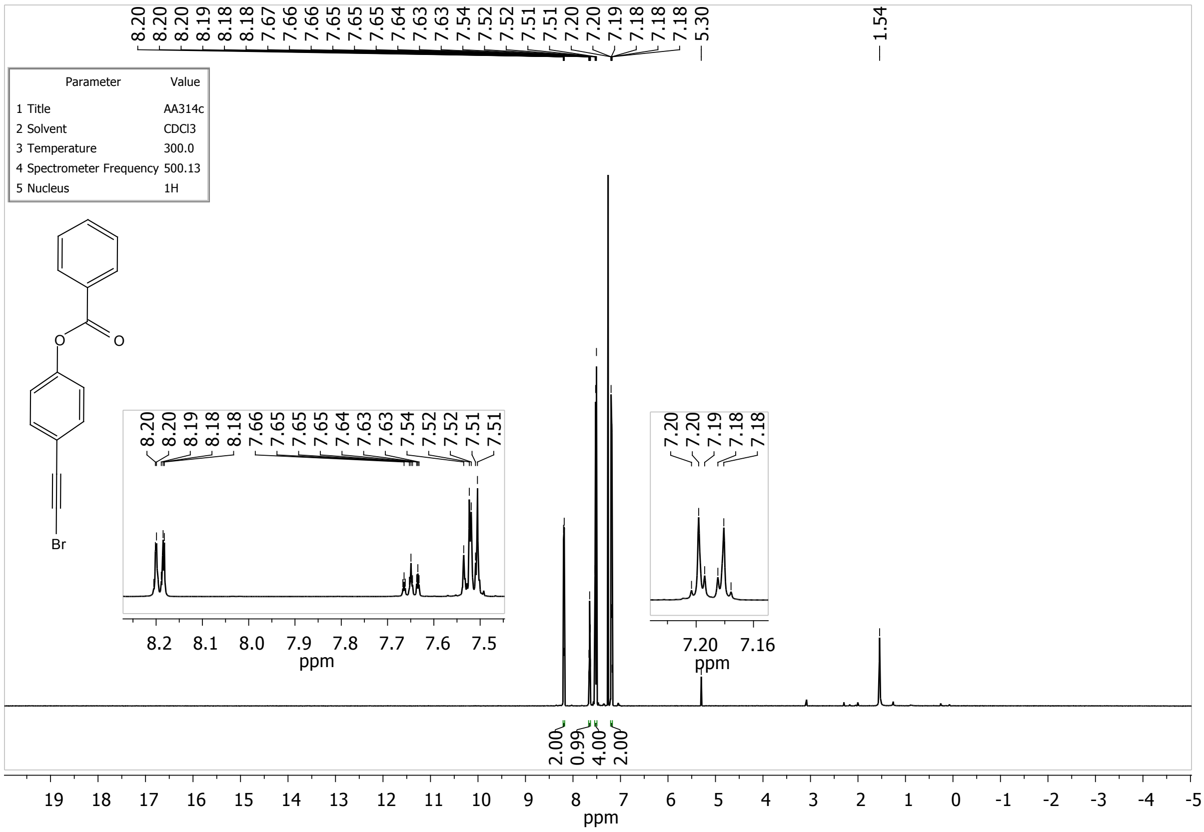
2 Solvent C6D6
3 Temperature 300.0
4 Spectrometer Frequency 125.76
5 Nucleus 13C
O
CH3
167.7
152.4
134.7
122.2
117.9
77.8
75.1
68.0
64.6
20.4
1.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



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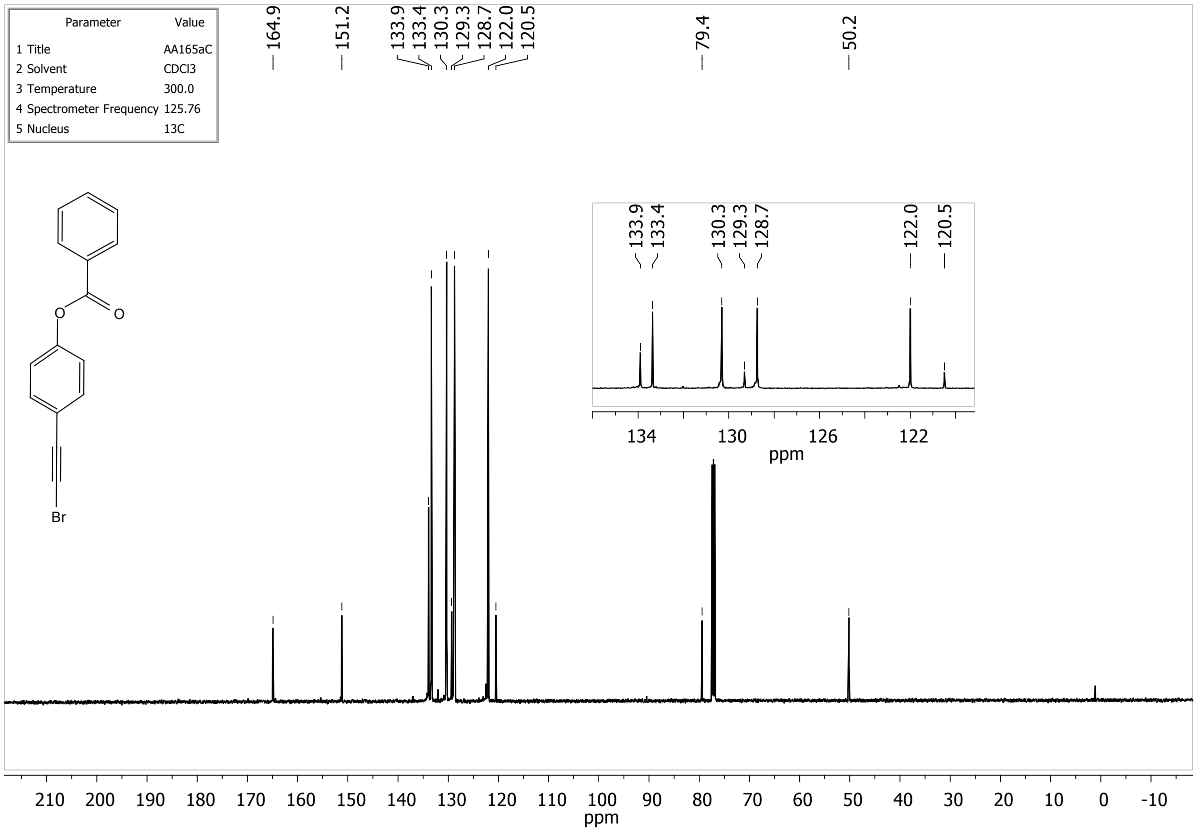
1 Title	AA314c
2 Solvent	CDCl3
3 Temperature	300.0
4 Spectrometer Frequency	500.13
5 Nucleus	1H



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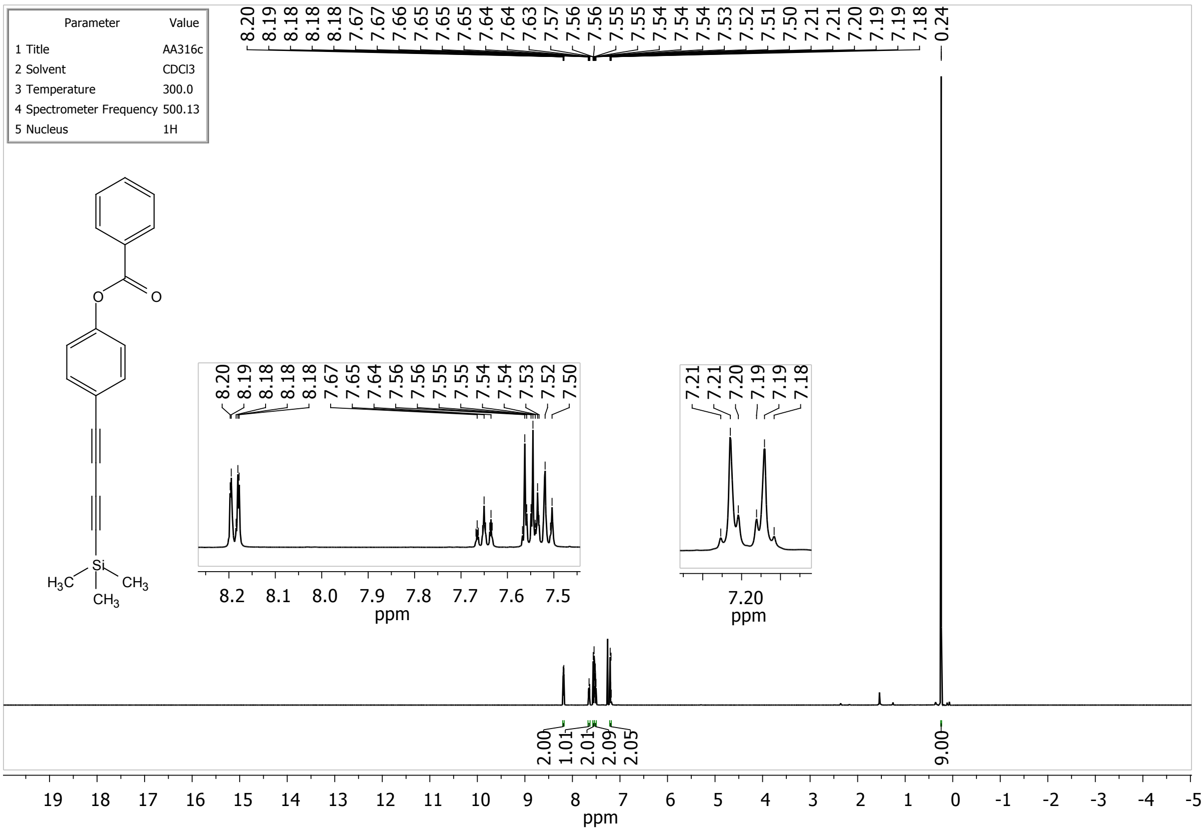
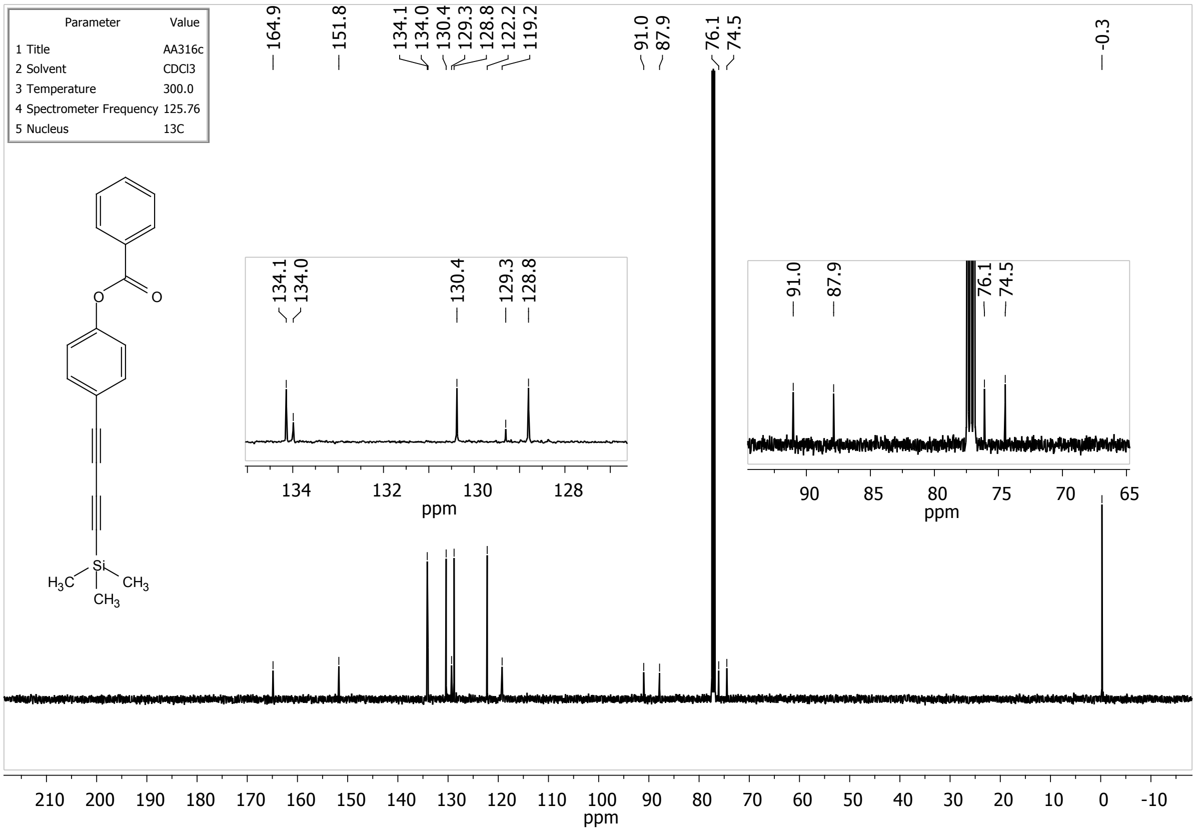
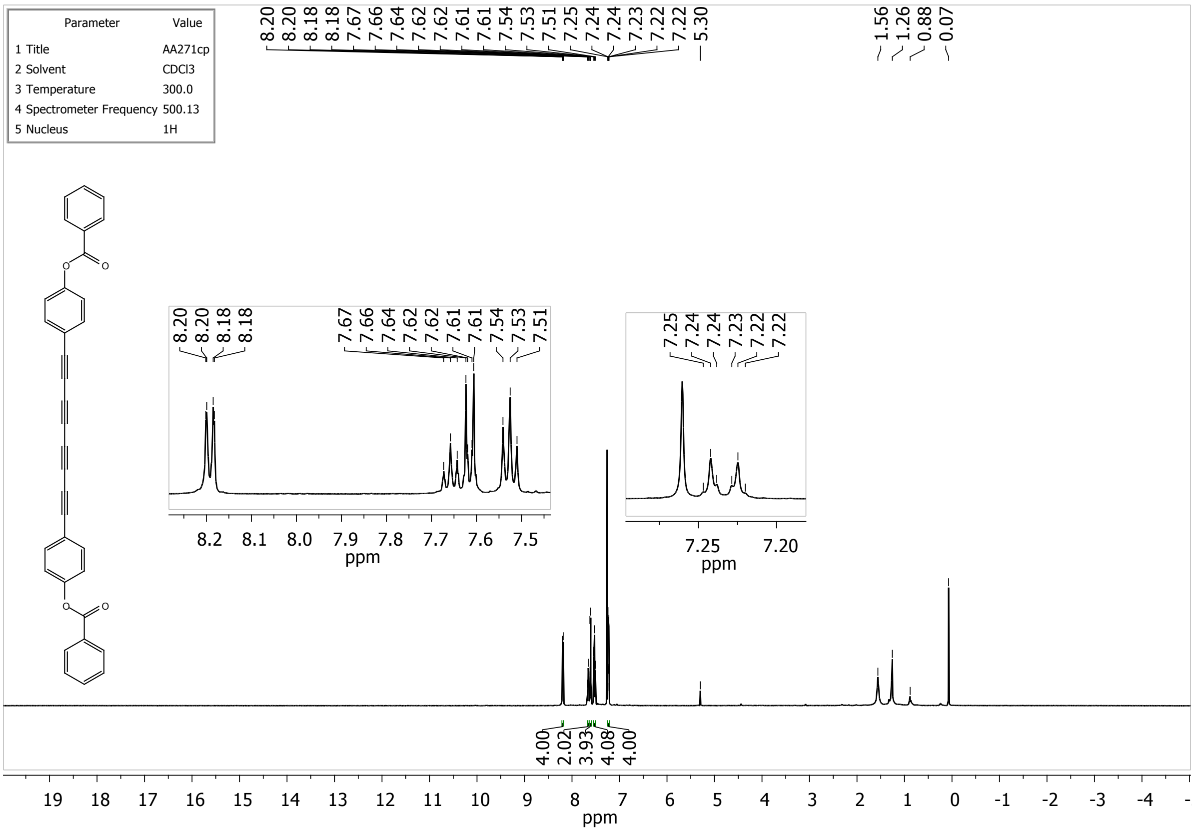
1 Title	AA165aC
2 Solvent	CDCl3
3 Temperature	300.0
4 Spectrometer Frequency	125.76
5 Nucleus	13C



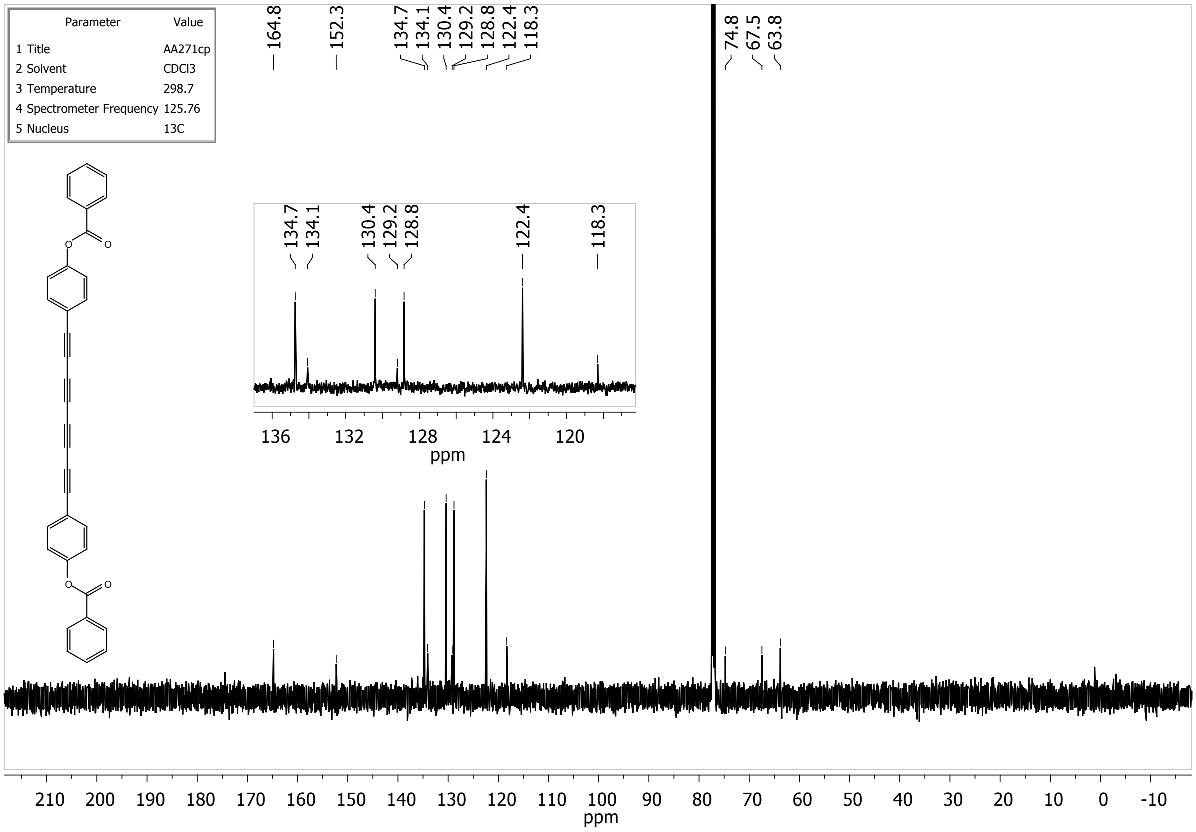
Parameter	Value
1 Title	AA316c
2 Solvent	CDCl3
3 Temperature	300.0
4 Spectrometer Frequency	500.13
5 Nucleus	1H



Parameter	Value
1 Title	AA316c
2 Solvent	CDCl3
3 Temperature	300.0
4 Spectrometer Frequency	125.76
5 Nucleus	13C



Parameter	Value
1 Title	AA271cp
2 Solvent	CDCl3
3 Temperature	300.0
4 Spectrometer Frequency	500.13
5 Nucleus	1H



Parameter	Value
1 Title	AA271cp
2 Solvent	CDCl3
3 Temperature	298.7
4 Spectrometer Frequency	125.76
5 Nucleus	13C

IV. Crystal structures of octatetraynes

X-ray diffraction data were collected with the Xcalibur diffractometer with Ruby CCD camera (ω scan technique) equipped with an Oxford Cryosystem-Cryostream cooler at 100 K. 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 using the SHELXTL Package.[8]

Table SI. Summary of crystallographic data for **E1-C$_8$-E1** and **E2-C$_8$-E2**.

	E1-C$_8$-E1	**E2-C$_8$-E2**
molecular formula	$C_{26}H_{18}O_4$	$C_{24}H_{14}O_4$
molecular weight	394.40	366.35
crystal system	triclinic	monoclinic
space group	P-1	C2/c
T [K]	100(2)	100(2)
a [Å]	3.8538(9)	40.449(19)
b [Å]	10.179(3)	3.8627(10)
c [Å]	13.000(3)	11.605(3)
α [°]	97.18(5)	90
β [°]	96.03(5)	94.87(5)
γ [°]	100.60(6)	90
V [Å^3]	493.0(6)	1806.8(11)
Z	1	4
d_{calc} [g/cm^3]	1.328	1.347
μ [mm^{-1}]	0.089	0.092
crystal dimensions [mm]	0.25 x 0.17 x 0.06	0.29 x 0.23 x 0.03
R_{int}	0.014	0.022
$R[F^2 > 2\sigma(F^2)]$	0.038	0.049
$wR_2(F^2)$	0.099	0.108

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[8] G. M.Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.

V. Higher-order NLO effects

In general, the higher the order of nonlinear absorption, the more difficult the analysis of the experimental data is. First, because of the small difference between the line-shapes of the open aperture curves produced by subsequent multiphoton processes. For example, it is rather difficult to distinguish between 3PA and 4PA, because both processes produce almost the same open aperture line-shapes, contrary to 2PA which is significantly broader than 3PA. The difference is even smaller, if one compares higher order processes, such as 4PA and 5PA, which presumably occur simultaneously above 1000 nm. This situation prevents us from drawing clear conclusions about the NLO properties of the investigated compounds above 825 nm and we refrain from quantitative determination of higher-order NLO parameters (σ(4) or σ(5)).

Moreover, higher-order processes can mix together very easily due to the overlap of the spectral regions corresponding to many possible multiphoton transitions. For instance, the overlap between UV-Vis bands plotted versus the wavelength scale multiplied by 3 and 4, enabling simultaneous 3PA and 4PA, occurs over much broader spectral range than the overlap between UV-Vis bands plotted as a function of doubled and tripled wavelength, enabling both 2PA and 3PA.

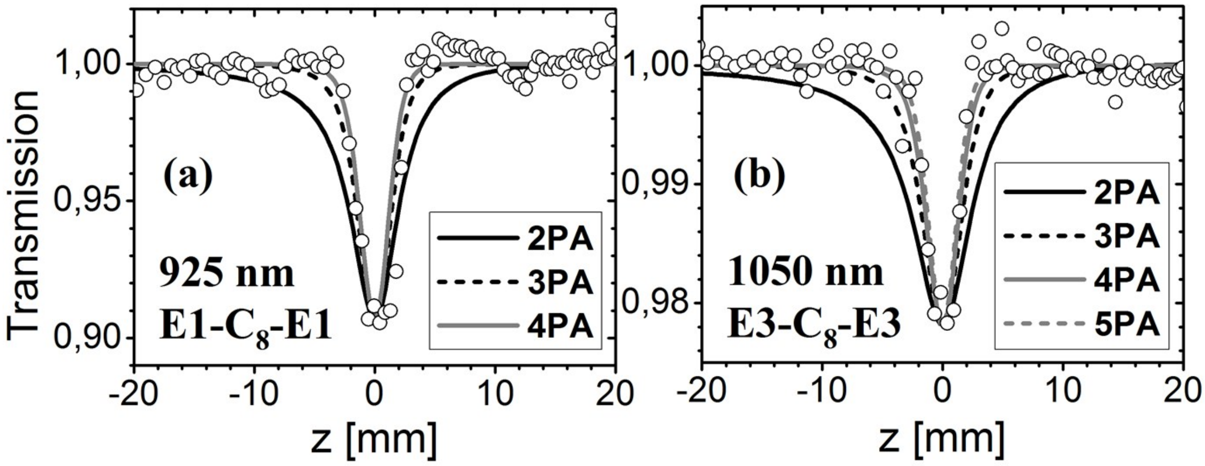

Figure S1. Examples of open-aperture f-scan curves which probably reveal higher-order absorption phenomena.

We attempted to fit some of the experimental data above 850 nm using f-scan modification of the 4PA and 5PA theoretical curves based on equations given by Corrêa et al. [D. S. Corrêa, L. De Boni, L. Misoguti, I. Cohanoschi, F. E. Hernandez, C. R. Mendonça Opt. Commun., 2007, 277, 440–445], which is shown in Figure S1(a) and S1(b) for **E1-C$_8$-E1** at 925 nm and

E3-C$_8$-E3 at 1050 nm, respectively. Based on these results one may conclude that the investigated octatetraynes are capable of exhibiting 4PA and 5PA. However, one should also be concerned that the measured open aperture curves may be contaminated by the residues of artefacts remaining after division of the sample experimental curve by the solvent experimental curve. In some cases this correction procedure may be not perfect, and the artefacts, which are present in both solvent and solution, may be observed in the corrected open aperture trace and interpreted as higher-order nonlinear absorption.

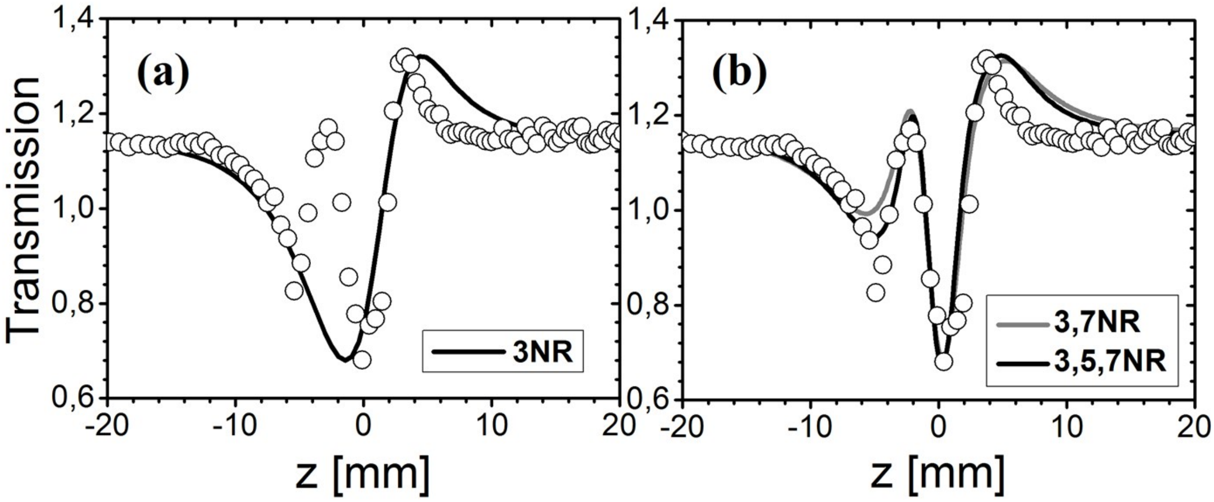

Figure S2. Closed aperture *f*-scan curve measured in **E1-C$_8$-E1** at 1300 nm, showing positive 3NR with possible contribution of negative higher-order effects. Theoretical curves (solid lines) correspond to: (a) pure 3NR, and (b) a mixture of positive 3NR and negative 7NR (grey) compared with a mixture of positive 3NR, positive 5NR and negative 7NR (black).

Finally, it should be mentioned that the multiphoton absorption can be accompanied by the nonlinear refraction of the same order, which is somehow imposed by the nonlinear Kramers-Krönig relations that link the real and imaginary parts of any n-th order hyperpolarizability.[9] Figure 6 (in the manustript) is a good illustration of this behaviour, showing the interdependences of the dispersion of 2PA and the nonlinear refraction supposedly originating from third-order optical nonlinearity (3NR). In general, if 3PA, 4PA or 5PA is observed, one may expect also the 5th-, 7th- and 9th-order nonlinear refraction (5NR, 7NR and 9NR), respectively. Nonlinear absorption and nonlinear refraction of the same order may appear in close spectral proximity, but not necessarily at the same wavelengths. However, if the higher-order nonlinear refractive index has the same sign as that of 3NR of the sample (the effective nonlinear refraction incorporating those of the solute, solvent and the cell), the contribution of

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[9] D. C. Hutchings, M. Sheik-Bahae, D. J. Hagan, E. W. van Stryland, Opt. Quant. Electron., 1992, 24, 1-30.

this phenomenon will be difficult to distinguish. On the other hand, if this parameter is of the opposite sign of that from the 3NR, it will cause opposite transmittance variations. These variations will be stronger at small |z| distances, whereas at larger distances they will decay quickly, failing to completely suppress the third-order nonlinearity that may be coming mostly from the solvent and the cuvette glass (as it was shown in Figure 7 in the manustript).

An example of the closed aperture trace, likely affected by a higher-order nonlinear refraction is shown in Figure S2(a), where the experimental data, obtained in **E1-C$_8$-E1** at 1300 nm, are fitted by a theoretical curve corresponding to 3NR. Such fitting was performed in all cases, in order to extract the effective Re(γ) values. However, the same experimental curve can be relatively well fitted by a theory assuming simultaneous positive 3NR and negative 7NR, which is shown in Figure S2(b) (grey line). In this case the nonlinear phase shift caused by the higher-order effect is around twice larger than the phase shift due to the usual third-order phenomenon. The theoretical fit can be slightly improved by including some contribution of a positive 5NR (black line). Similar closed aperture traces were occasionally observed in the investigated compounds at various wavelengths in the near-infrared regime. Such results were also not well repeatable between different series of measurements, which we attribute to large sensitivity of the higher-order phenomena to the incident laser power.