Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Fast Construction of Dianthraceno[*a,e*]pentalenes for OPV Applications

Zhongbo Zhang,[a,b] Haijun Fan[a] and Xiaozhang Zhu[a,b,*]

[a]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

[b]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Contents

Synthesis

General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen or argon. Air- and moisture-sensitive liquids and solutions were transferred via syringe or Teflon cannula. Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with 0.25 mm, 300–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin-layer chromatography plates were visualized by exposure to ultraviolet light (UV). Organic solutions were concentrated by rotary evaporation at ca. 15 Torr (evacuated with a diaphragm pump).

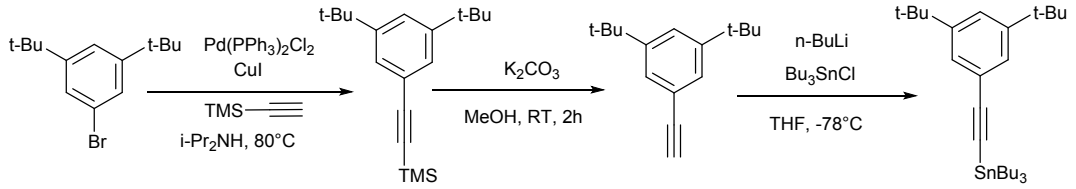
Materials. All reagents were purchased from commercial suppliers and used without further purification unless otherwise specified.

Instruments. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were measured on BRUKER AVANCE 300 and BRUKER DMX 400 spectrometers. Chemical shifts for hydrogens are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent ($CDCl_3$: δ 7.26). ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.16, $CDCl_2CDCl_2$: δ 73.37). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), coupling constant in Hertz (Hz), and integration. Melting points of solid materials were determined on a X-4 melting-point apparatus and are uncorrected. High resolution mass spectra (HRMS) were determined on a Bruker Apex IV Fourier Transform Mass Spectrometer (EI) and Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (ESI). All the ultraviolet-visible (UV-vis) absorption spectra were recorded on a TU-1810DSPC spectrometer of Beijing Purkinje General Instrument Co. Ltd. at room temperature in CH_2Cl_2 with a conventional 1.0 cm quartz cell. Cyclic voltammetry (CV) was performed on a CHI620D potentiostat. Fluorescent quantum yields (FLQY) were measured on Absolute PL Quantum Yield Spectrometer C11347 from Hamamatsu. All measurements were carried out in a one-compartment cell under N_2 atmosphere, equipped with a glassy-carbon electrode, a carbon counter electrode, and an Ag/AgCl reference electrode. The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium perchlorate (TBAP). All potentials were corrected against Fc/Fc^{+}. CV was measured

with a scan rate of 100 mV/s.

Preparation of Substrates

Scheme S1. Synthesis of compound 3a.



((3,5-Di-*tert*-butylphenyl)ethynyl)trimethylsilane (1a).

Yellow solid (95%). Spectroscopic data match those previously reported.

^{1}H NMR (300MHz, $CDCl_3$): δ 7.37 (t, *J* = 1.8 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 2H), 1.31 (s, 18H), 0.26 (s, 9 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 150.7, 126.2, 123.0, 122.0, 106.4, 92.5, 34.8, 31.3, 0.1.

1,3-Di-*tert*-butyl-5-ethynylbenzene (2a).

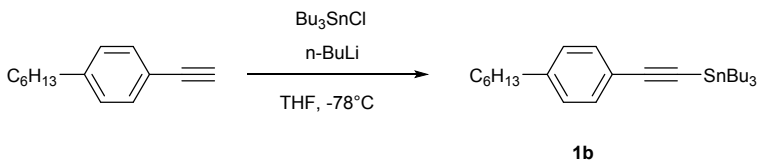
Colorless solid (99%). Spectroscopic data match those previously reported.

^{1}H NMR (300MHz, $CDCl_3$): δ 7.42 (t, *J* = 1.8 Hz, 1 H), 7.35 (d, *J* = 1.8 Hz, 2H), 3.02 (s, 1H), 1.31 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$): δ 150.9, 126.4, 123.3, 121.0, 84.8, 34.8, 31.3.

Tributyl((3,5-di-*tert*-butylphenyl)ethynyl)stannane (3a)

To a solution of 1,3-di-*tert*-butyl-5-ethynylbenzene (**2a**) (214 mg, 1 mmol) in THF (5 ml) at –78 °C was added *n*-BuLi (0.66 ml, 1.6 M in hexane). After stirring for 1 h, tributylchlorostannane (0.3 ml, 1.1 mmol) was added and the mixture was stirred for 1 h at the same temperature. The reaction mixture was stirred for an additional hour at room temperature, quenched with water and extracted with DCM (5 ml × 3). The organic layer was dried over anhydrous $MgSO_4$. Then evaporated to yield a light yellow oil. Yield: 500 mg (99%). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.34 (t, *J* = 1.9 Hz, 1H), 7.30 (d, *J* = 1.9 Hz, 2H), 1.67–1.58 (m, 6H), 1.38 (q, *J* = 7.3 Hz, 6H), 1.31 (s, 18H), 1.06 (dd, *J* = 9.2, 7.3 Hz, 6H), 0.94 (q, *J* = 7.3 Hz, 9H).

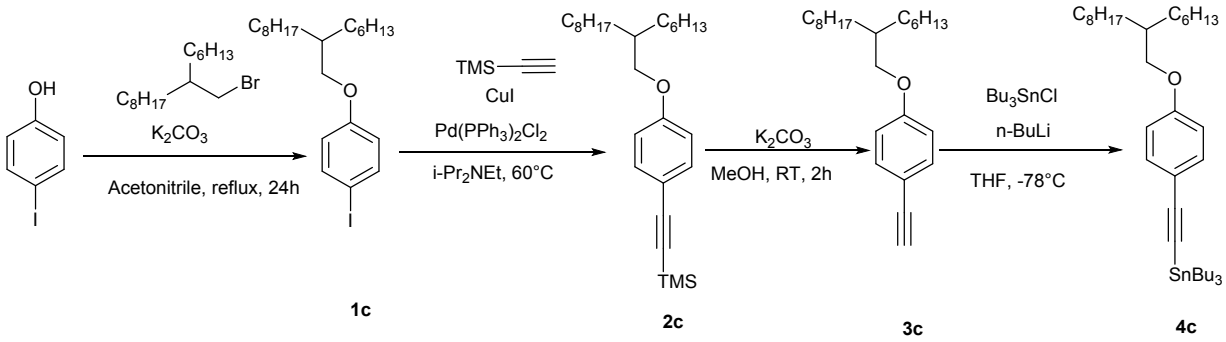
Scheme S2. Synthesis of compound 1b.



Tributyl((4-hexylphenyl)ethynyl)stannane (1b)

To a solution of 1-ethynyl-4-hexylbenzene (186 mg, 1 mmol) in THF (5 ml) at –78 °C was added *n*-BuLi (0.66 ml, 1.6 M in hexane). After stirring for 1 h, tributylchlorostannane (0.3 ml, 1.1 mmol) was added and the mixture was stirred for 1 h at the same temperature. The reaction mixture was stirred for an additional hour at room temperature, quenched with water and extracted with DCM (5 ml × 3). The organic layer was dried over anhydrous $MgSO_4$. Then evaporated to yield a light yellow oil. Yield: 470 mg (99%). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.36 (d, 2H), 7.08 (d, 2H), 2.58 (t, 2H), 1.60 (m, 6H), 1.43–1.28 (m, 14H), 1.06 (t, 4H), 0.94 (m, 14H).

Scheme S3. Synthesis of compound 4c.



1-((2-Hexyldecyl)oxy)-4-iodobenzene (1c)

In a 250 mL flask, 4-iodophenol (4.4 g, 20 mmol), 7-(bromomethyl)pentadecane (18.3 g, 60 mmol), K_2CO_3 (8.3 g, 60 mmol) were dissolved in acetonitrile (10 ml). The mixture was refluxed for 48 h. After cooling down to room temperature, the solid was removed by filtration, and the solvent was removed by rotary evaporation. The pale yellow oil was extracted with ether and washed with water. The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation. The crude product was purified by column chromatography. A pale yellow oil was obtained (**1c**). Yield 8 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.7 Hz, 2H), 6.67 (d, J = 8.7 Hz, 2H), 3.78 (d, J = 5.7 Hz, 2H), 1.79–1.72 (m, 1H), 1.37–1.21 (m, 24H), 0.88 (t, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.41, 138.24, 117.12, 82.42, 71.18, 38.03, 32.06, 32.00, 31.50, 31.48, 30.16, 29.83, 29.73, 29.48, 26.98, 26.96, 22.83, 14.27; HRMS (EI) calcd for $C_{22}H_{37}IO$ $[M]^+$: 444.1889, found 444.1882.

((4-((2-Hexyldecyl)oxy)phenyl)ethynyl)trimethylsilane (2c)

A mixture of 1-((2-hexyldecyl)oxy)-4-iodobenzene (**1c**) (2.22 g, 5 mmol), $(PPh_3)_2PdCl_2$ (70 mg, 0.1 mmol), and CuI (48 mg, 0,25 mmol), (trimethylsilyl)acetylene (1.41 ml, 10 mmol) in 30 mL of Ethyldiisopropylamine was stirred for 6 h at 60˚C under nitrogen. After filtration, the filtrate was

evaporated under reduced pressure and the residue was column chromatographed on silica gel with Petroleum ether as an eluent to give **2c** in 99% yield (2.05 g) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.81 (d, *J* = 5.7 Hz, 2H), 1.81–1.70 (m, 1H), 1.29 (dd, *J* = 14.6, 6.7 Hz, 24H), 0.88 (t, *J* = 6.6 Hz, 6H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.74, 133.53, 115.07, 114.50, 105.54, 92.29, 71.08, 38.06, 32.08, 32.02, 31.50, 30.17, 29.84, 29.75, 29.50, 26.99, 26.97, 22.84, 14.28, 0.24; HRMS (EI) calcd for $C_{27}H_{46}OSi$ $[M]^+$: 414.3318, found 414.3313.

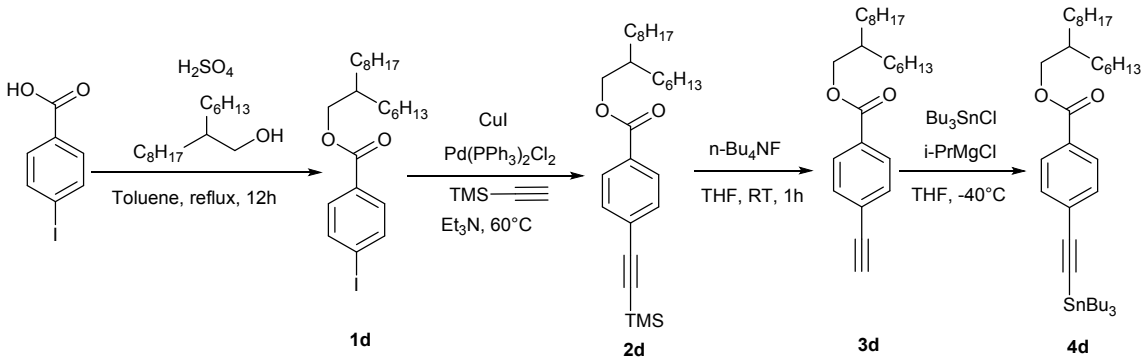
1-Ethynyl-4-((2-hexyldecyl)oxy)benzene (3c)

Compound **2c** (1.66 g, 4 mmol) was dissolved in 40 mL of methanol. After K_2CO_3 (1.11 g, 8 mmol) was added, the mixture was stirred for 4 h at room temperature. After water (50 mL) was added, the product was extracted with DCM and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography with silica gel and petroleum ether. A colorless oil was obtained (**3c**). Yield 1.37g, 100%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 3.82 (d, *J* = 5.7 Hz, 2H), 2.99 (d, *J* = 1.1 Hz, 1H), 1.76 (d, *J* = 6.4 Hz, 1H), 1.29 (t, *J* = 11.0 Hz, 24H), 0.87 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.95, 133.66, 114.64, 113.94, 83.97, 75.73, 71.13, 38.05, 32.06, 32.00, 31.50, 31.48, 30.15, 29.82, 29.73, 29.48, 26.98, 26.96, 22.83, 14.26; HRMS (EI) calcd for $C_{24}H_{38}O$ [M]+: 342.2923, found 342.2918.

Tributyl((4-((2-hexyldecyl)oxy)phenyl)ethynyl)stannane (4c)

To a solution of 1-ethynyl-4-((2-hexyldecyl)oxy)benzene (342 mg, 1 mmol) in THF(10 ml) at –78 °C was added *n*-BuLi (0.66 ml, 1.6 M in hexane). After stirring for 1 h, tri-*n*-butyltin chloride (0.3 ml, 1.1mmol) was added and the mixture was stirred for 1 h at the same temperature. The reaction mixture was stirred for an additional hour at room temperature, quenched with aqueous ammonium chloride (saturated, 10ml) and extracted with DCM (5 ml × 3). Then evaporated to yield a light yellow liquid. Yield: 625 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.81 (d, *J* = 5.7 Hz, 2H), 1.75 (d, *J* = 5.8 Hz, 1H), 1.71–1.56 (m, 6H), 1.39–1.26 (m, 28H), 1.04 (dd, *J* = 9.3, 6.8 Hz, 4H), 0.90 (dt, *J* = 11.3, 7.2 Hz, 19H).

Scheme S4. Synthesis of compound 4d.



2-Hexyldecyl 4-iodobenzoate (1d)

Yellow solid (95%). Spectroscopic data match those previously reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 4.21 (d, J = 5.6 Hz, 2H), 1.84–1.69 (m, 1H), 1.39–1.25 (m, 24H), 0.87 (t, J = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.35, 137.84, 131.12, 130.20, 100.65, 68.18, 37.56, 32.04, 31.95, 31.57, 30.08, 29.75, 29.68, 29.44, 26.90, 26.88, 22.82, 22.79, 14.26, 14.24.

2-Hexyldecyl 4-((trimethylsilyl)ethynyl)benzoate (2d)

A mixture of **1d** (2.36 g, 5 mmol), $(PPh_3)_2PdCl_2$ (70 mg, 0.1 mmol), and CuI (48 mg, 0,25 mmol), (trimethylsily1)acetylene (1.41 ml, 10 mmol) in 30 mL of triethylamine was stirred for 6 h at 60˚C under nitrogen. After filtration, the filtrate was evaporated under reduced pressure and the residue was column chromatographed on silica gel with Petroleum ether as an eluent to give **2c** in 76% yield (1.68 g) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 4.22 (d, J = 5.7 Hz, 2H), 1.76 (d, J = 6.2 Hz, 1H), 1.36–1.23 (m, 24H), 0.91–0.86 (m, 6H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.25, 131.98, 130.27, 129.43, 127.79, 104.28, 97.67, 68.12, 37.57, 32.04, 31.95, 31.59, 30.08, 29.75, 29.69, 29.45, 26.90, 26.88, 22.82, 22.79, 14.24; HRMS (EI) calcd for $C_{28}H_{46}O_2Si$ $[M]^+$: 442.3267, found 442.3261.

2-Hexyldecyl 4-ethynylbenzoate (3d)

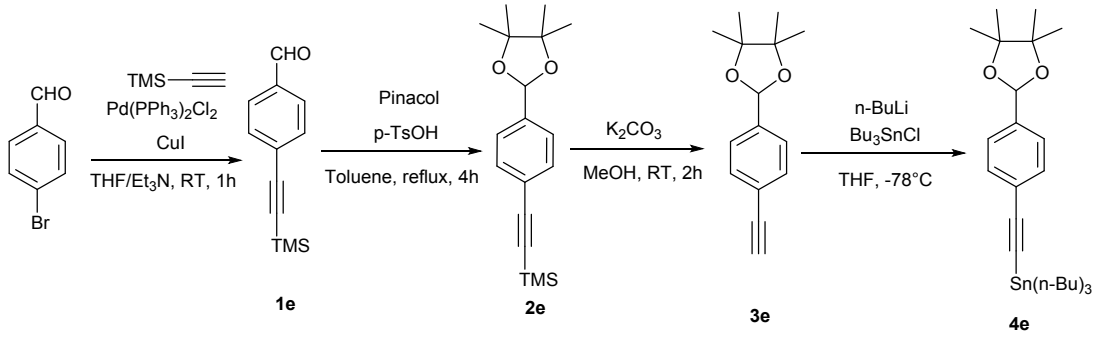
Compound **2d** (1.77 g, 4 mmol) was dissolved in 40 mL of methanol. After Tetrabutylammonium fluoride (1.15 g, 4.4 mmol) was added, the mixture was stirred for 1 h at room temperature. After water (50 mL) was added, the product was extracted with DCM and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography with silica gel and petroleum ether. A colorless oil was obtained (**3c**). Yield 1.48g, 100%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 4.23 (d, J = 5.7 Hz, 2H), 3.22 (s, 1H), 1.77 (t, J = 5.9 Hz, 1H), 1.40–1.25 (m, 24H), 0.88 (d,

J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.19, 132.20, 130.74, 129.54, 126.76, 83.00, 80.07, 68.17, 37.58, 32.05, 31.96, 31.59, 30.09, 29.76, 29.69, 29.45, 26.91, 26.89, 22.82, 22.80, 14.25, 14.24; HRMS (EI) calcd for $C_{25}H_{38}O_2$ $[M]^+$: 370.2872, found 370.2867.

2-Hexyldecyl 4-((tributylstannyl)ethynyl)benzoate (4d)

To a solution of 2-hexyldecyl 4-ethynylbenzoate (**3d**) (370 mg, 1 mmol) in THF (10 ml) at –78 °C was added *i*-PrMgCl (0.53 ml, 2.0 M in hexane). After stirring for 1 h, tri-*n*-butyltin chloride (0.3 ml, 1.1 mmol) was added and the mixture was stirred for 1 h at the same temperature. The reaction mixture was stirred for an additional hour at room temperature, quenched with aqueous ammonium chloride (saturated, 10ml) and extracted with DCM (5 ml × 3). Then evaporated to yield a light yellow liquid. Yield: 653 mg (99%). ^{1}H NMR (300MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 4.21 (d, *J* = 5.7 Hz, 2H), 1.75 (m, 1H), 1.59, (m, 6H), 1.41 (m, 33H), 1.07 (t, 4H), 0.95 (m, 14H).

Scheme S5. Synthesis of compound 4e



4-((Trimethylsilyl)ethynyl)benzaldehyde (1e)

Light yellow solid (95%). Spectroscopic data match those previously reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 2.57 (s, 3H), 0.25 (s, 9H).

Trimethyl((4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl)ethynyl)silane (2e)

A mixture of **1e** (1.01 g, 5 mmol), pinacol (1.18 g, 10 mmol) and *p*-toluenesulfonic acid (43 mmol, 0.25 mmol) was refluxed in dry toluene (30 mL) for 4 h using a Dean-Stark apparatus. After cooling to room temperature, saturated sodium bicarbonate solution was added to the mixture and stirred for 30 min. The suspension was filtered and the residue was washed with toluene. The filtrate was washed with brine (3 × 20 mL), dried over sodium sulfate and finally concentrated in vacuo to provide the title compound. Yield: 1.38 g, 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 5.95 (s,

1H), 1.31 (s, 6H), 1.24 (s, 6H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.32, 131.99, 126.21, 123.40, 105.09, 99.53, 94.45, 82.91, 77.48, 77.16, 76.84, 24.35, 22.31, 0.11; HRMS (EI) calcd for $C_{18}H_{26}O_2Si$ $[M]^+$: 302.1702, found 302.1695.

2-(4-Ethynylphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (3e)

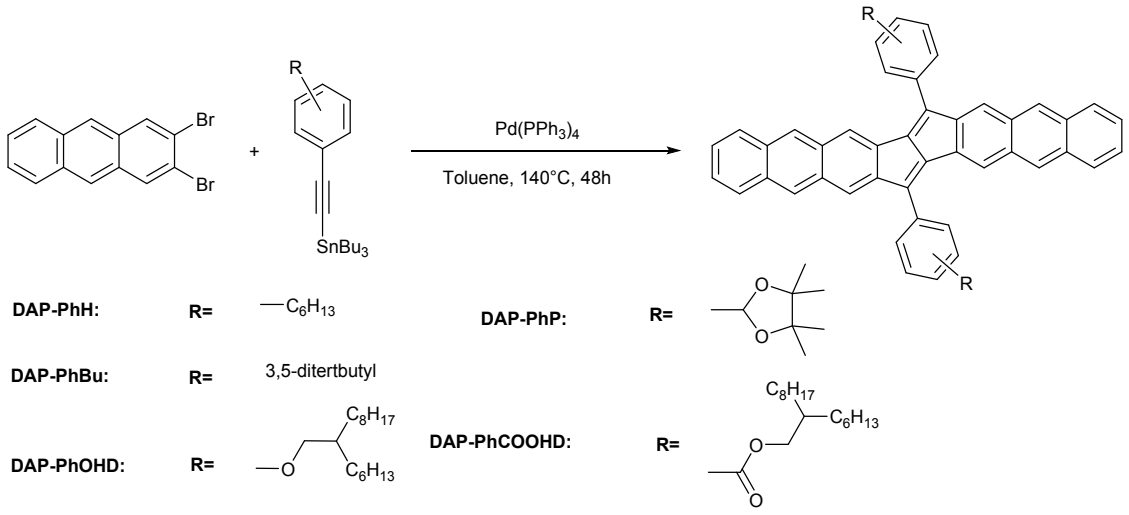
A mixture of **3e** (1.51 g, 5 mmol) and K_2CO_3 (1.38 g, 10 mmol) was stirred in 40 ml methanol room temperature 2h. After water (20 mL) was added, the product was extracted with DCM and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography with silica gel. A white solid was obtained (**3e**). Yield: 1.1 g, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 5.96 (s, 1H), 3.07 (s, 1H), 1.32 (s, 6H), 1.25 (s, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.75, 132.24, 126.38, 122.42, 99.52, 83.71, 83.02, 24.42, 22.36; HRMS (EI) calcd for $C_{15}H_{18}O_2$ $[M]^+$: 230.1307, found 230.1302.

Tributyl((4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl)ethynyl)stannane (4e)

To a solution of **3e** (230 mg, 1 mmol) in THF (10 ml) at –78 °C was added *n*-BuLi (0.66 ml, 1.6 M in hexane). After stirring for 1 h, tri-*n*-butyltin chloride (0.3 ml, 1.1 mmol) was added and the mixture was stirred for 1 h at the same temperature. The reaction mixture was stirred for an additional hour at room temperature, quenched with aqueous ammonium chloride (saturated, 10ml) and extracted with DCM (5 ml × 3) and dried over anhydrous $MgSO_4$. Then evaporated to yield a colorless liquid. Yield: 515 mg (99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 5.95 (s, 1H), 1.61 (m, 6H), 1.38 (dt, *J* = 14.7, 7.3 Hz, 6H), 1.31 (s, 6H), 1.24 (s, 6H), 1.17–0.98 (m, 6H), 0.92 (t, *J* = 7.3 Hz, 9H).

Synthesis of dianthracenopentalene derivatives

Scheme S6. General Procedure for the synthesis of dianthracenopentalene derivatives.



A degassed anhydrous toluene (4 ml, 0.05 M) solution of 2,3-dibromoanthracene (0.40 mmol), $Pd(PPh_3)_4$ (5 mol%) and tributyl((R-phenyl)ethynyl)stannane (0.48 mmol) were heated at 140 ºC for 48 h. After cooling to room temperature, aqueous KF was added and extracted with dichloromethane for three times. The combined organic extracts was dried over sodium sulfate and concentrated under vacuum. The crude product was purified by flash column chromatography.

7,16-Bis(3,5-di-tert-butylphenyl)pentaleno[1,2-*b*:4,5-*b*']dianthracene (DAP-PhBu)

Red solid (12%). Spectroscopic data match those previously reported.

^{1}H NMR (400MHz, $CDCl_3$): δ 8.29 (s, 2H), 8.20 (s, 2H), 8.11 (s, 2H), 7.85–7.92 (m, 10H), 7.64 (s, 2H), 7.41 (m, 4H), 1.54 (s, 36H).

^{13}C NMR (100MHz, $CDCl_3$): δ 151.5, 147.5, 145.0 137.5, 133.9, 132.6, 132.3, 132.1, 131.7, 128.5, 128.4, 127.5, 125.9, 125.7, 123.7, 122.8, 122.2, 120.9, 35.5, 31.9.

7,16-Bis(4-hexylphenyl) pentaleno[1,2-*b*:4,5-*b*']dianthracene (DAP-PhH)

Red solid. (12%)

^{1}H NMR (300MHz, $CDCl_3$): δ 8.18 (s, 4H), 8.13 (s, 2H), 7.87 (m, 4H), 7.85 (s, 4H), 7.77 (s, 2H), 7.49 (d, 4H), 7.40 (d, 4H), 2.82 (t, J = 7.2Hz, 4H), 1.81 (m, 4H), 1.43–0.88 (m, 18H); ^{13}C NMR (100MHz, $CDCl_3$): δ 147.47, 144.95, 143.89, 136.39, 132.52, 132.23, 131.96, 131.79, 131.54, 129.17, 129.12, 128.38, 127.81, 127.41, 125.90, 125.70, 121.98, 120.72, 36.35, 32.05, 31.69, 29.93, 29.47, 22.94, 11.42; HRMS (MALDI) calcd for $C_{56}H_{50}$ $[M]^+$: 722.3913, found 722.3905.

Bis(2-hexyldecyl) 4,4'-(pentaleno[1,2-*b*:4,5-*b*']dianthracene-7,16-diyl)dibenzoate (DAP-PhCOOHD)

Red solid (9%).

^{1}H NMR (400MHz, $CDCl_3$): δ 8.38 (d, 4H), 8.21(s, 4H), 8.11 (s, 2H), 8.04 (d, 4H), 7.90 (m, 4H), 7.75 (s, 2H), 7.43 (m, 4H), 4.37 (d, 4H), 1.88 (m, 2H), 1.34–1.25 (m, 48H), 0.92–0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.63, 146.63, 145.87, 139.22, 135.73, 132.69, 132.36, 131.95, 131.26, 130.91, 130.79, 130.38, 129.12, 128.40, 128.31, 128.15, 127.60, 126.20, 125.96, 122.55, 120.90, 68.20, 37.74, 32.09, 32.04, 31.68, 30.19, 29.85, 29.79, 29.51, 27.02, 26.98, 22.86, 14.32, 14.28; HRMS (MALDI) calcd for $C_{78}H_{90}O_4$ $[M]^+$: 1090.6839, found 1090.6824.

7,16-Bis(4-((2-hexyldecyl)oxy)phenyl)pentaleno[1,2-*b*:4,5-*b*']dianthracene (DAP-PhOHD)

Red solid (14%).

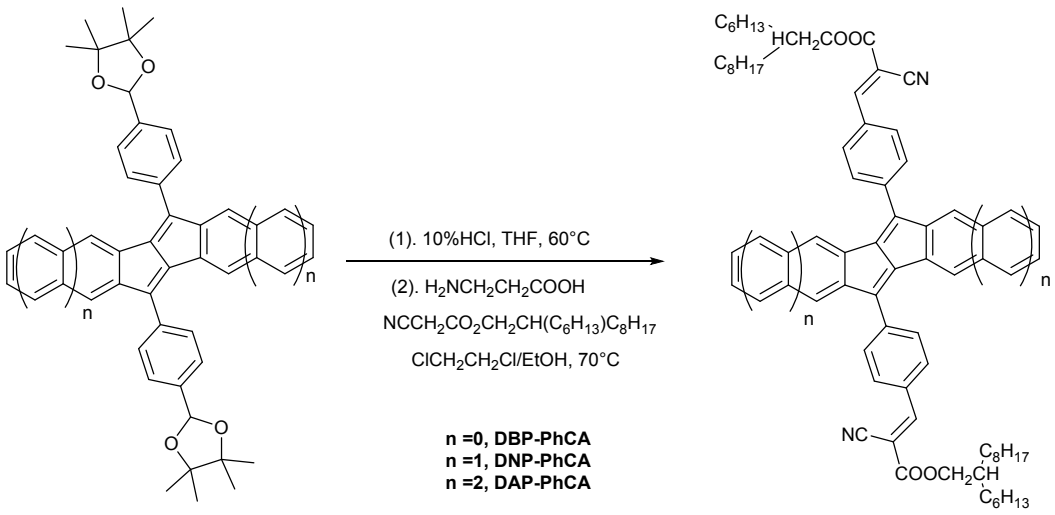
^{1}H NMR (300MHz, $CDCl_3$): δ 8.11 (d, *J* = 4H), 8.16(s, 2H), 7.89 (d, 8H), 7.79 (s, 2H), 7.41 (m, 4H), 7.22 (d, 4H), 4.03 (d, 4H), 1.91 (m, 2H), 1.35 (m, 48H), 0.92 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.78, 147.42, 144.36, 135.75, 132.35, 132.06, 131.77, 131.45, 130.42, 128.31, 128.27, 127.68, 127.19, 126.58, 125.71, 125.52, 121.58, 120.38, 114.92, 71.11, 38.23, 32.12, 31.57, 30.28, 29.94, 29.84, 29.58, 27.12, 27.09, 22.92, 22.90, 14.36, 14.33; HRMS (MALDI) calcd for $C_{76}H_{90}O_2$ $[M]^+$: 1034.6941, found 1034.6927.

7,16-Bis(4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl)pentaleno[1,2-*b*:4,5-*b*']dianthracene (DAP-PhP)

Purple solid (16%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 9.6 Hz, 4H), 8.12 (s, 2H), 7.96 (d, *J* = 7.8 Hz, 4H), 7.90 (d, *J* = 7.3 Hz, 4H), 7.83 (d, *J* = 7.8 Hz, 4H), 7.75 (s, 2H), 7.42 (s, 4H), 6.18 (s, 2H), 1.44 (s, 24H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.46, 145.42, 140.35, 136.30, 135.22, 132.70, 132.41, 132.27, 131.60, 131.56, 129.17, 128.45, 128.35, 127.97, 127.43, 127.31, 125.95, 125.71, 122.24, 120.81, 100.17, 83.17, 29.87, 24.78, 22.53; HRMS (MALDI) calcd for $C_{59}H_{50}O_4$ $[M]^+$: 810.3709, found 810.3701.

Scheme S7. Synthesis of DBP-PhCA, DNP-PhCA and DAP-PhCA.



Protected materials, were deprotected by heating their solution in a 1:2 mixtures of 10% HCl: THF to 60 ° C under an inert atmosphere for 48 h. After cooling to the room temperature, the suspension was filtered and the residue was washed with methanol. The purple solid residue was obtained and was dissolved in dichloroethane:ethanol (1:1) without purification. Then β-Alanine (5 mol%) and 2-hexyldecyl 2-cyanoacetate (2.0 equivalent) were added. The mixture was stirred at 70˚C for 24 h. After cooling to room temperature, the solid was removed by filtration and washed with chloroform. The solvent was removed by vacuum evaporation and the crude product was purified by column chromatography with silica gel.

Bis(2-hexyldecyl) 3,3'-(indeno[2,1-*a*]indene-5,10-diylbis(4,1-phenylene))(2*E*,2'*E*)-bis(2-cyanoacrylate) (DBP-PhCA)

Red solid (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 2H), 8.17 (d, *J* = 8.0 Hz, 4H), 7.81 (d, *J* = 8.0 Hz, 4H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.94 (ddd, *J* = 30.9, 16.1, 7.4 Hz, 6H), 4.26 (d, *J* = 5.6 Hz, 4H), 1.79 (q, *J* = 5.9 Hz, 2H), 1.43–1.26 (m, 48H), 0.89 (q, *J* = 6.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.83, 153.96, 149.21, 144.75, 140.02, 139.05, 134.67, 132.02, 131.72, 129.50, 128.79, 128.30, 122.77, 122.51, 115.63, 103.61, 69.82, 37.55, 32.12, 32.03, 31.40, 30.14, 29.80, 29.77, 29.54, 26.93, 26.90, 14.33; HRMS (MALDI) calcd for $C_{68}H_{84}N_2O_4$ $[M]^+$: 992.6431, found 992.6427.

Bis(2-hexyldecyl) 3,3'-(pentaleno[1,2-*b*:4,5-*b*']dinaphthalene-6,13-diylbis(4,1-phenylene))(2*E*,2'*E*)-bis(2-cyanoacrylate) (DNP-PhCA)

Blue solid (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 2H), 8.29 (d, *J* = 8.3 Hz, 4H), 8.05–7.99 (m, 4H), 7.81 (s, 2H),

7.67–7.58 (m, 4H), 7.52 (s, 2H), 7.36 (tt, *J* = 7.1, 5.2 Hz, 4H), 4.29 (d, *J* = 5.7 Hz, 4H), 1.91–1.76 (m, 2H), 1.30 (dt, *J* = 17.4, 10.0 Hz, 48H), 0.90 (q, *J* = 7.1, 6.4 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.84, 154.02, 146.85, 145.81, 139.57, 136.97, 134.16, 133.40, 131.90, 131.38, 129.79, 129.25, 129.04, 127.27, 126.88, 122.25, 121.45, 115.67, 103.53, 69.77, 37.53, 32.07, 31.99, 31.37, 30.10, 29.77, 29.73, 29.49, 26.90, 26.87, 22.85, 14.29, 0.15; HRMS (MALDI) calcd for $C_{76}H_{88}N_2O_4$ $[M]^+$: 1092.6744, found 1092.6739.

Bis(2-hexyldecyl) 3,3'-(pentaleno[1,2-*b*:4,5-*b*'] dianthracene-7,16-diylbis(4,1-phenylene)) (2*E*,2'*E*)-bis(2-cyanoacrylate) (DAP-PhCA)

Blue solid (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 2H), 8.28–8.21 (m, 4H), 8.10 (d, *J* = 3.4 Hz, 4H), 7.98 (dd, *J* = 8.3, 2.4 Hz, 6H), 7.83 (q, *J* = 3.6 Hz, 4H), 7.63 (d, *J* = 2.4 Hz, 2H), 7.40 (dd, *J* = 6.5, 3.1 Hz, 4H), 4.30 (d, *J* = 5.7 Hz, 4H), 1.92–1.77 (m, 2H), 1.47–1.29 (m, 48H), 0.92 (dt, *J* = 10.5, 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.82, 153.97, 146.22, 145.95, 139.69, 135.20, 132.70, 132.36, 131.83, 131.71, 131.64, 131.02, 130.51, 129.82, 128.38, 128.30, 128.23, 127.72, 126.26, 126.03, 122.67, 121.03, 115.75, 103.29, 69.75, 37.51, 32.08, 32.01, 31.36, 30.13, 29.85, 29.80, 29.76, 29.51, 26.90, 26.87, 22.86, 14.31; HRMS (MALDI) calcd for $C_{84}H_{92}N_2O_4$ $[M]^+$: 1192.7057, found 1192.7052.

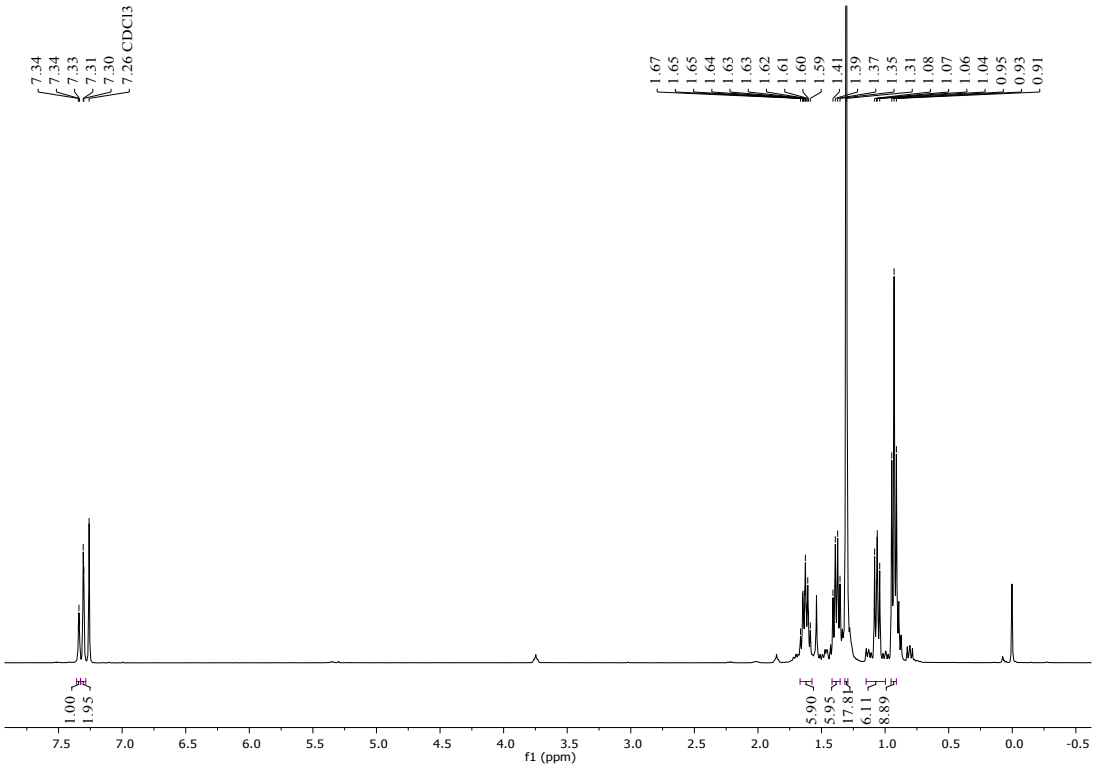
Device Fabrication and Characterization.

The solution-processed small-molecule BHJ solar cells adopted a traditional indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/ **DAP-PhCA**:$PC_{71}BM$/Ca (20 nm)/Al (60 nm) structure. Prior to device fabrication, the ITO glasses (1.5 × 1.5 cm^2) were cleaned ultrasonically with detergent, deionized water, acetone, and isopropyl alcohol. After routine solvent cleaning, the ITO substrates were treated with UV ozone for 20 min and then a PEDOT:PSS (Baytron P VP AI 4083) layer (~30 nm) was spin-coated onto the clean ITO glass and dried at 150 °C for 15 min. The photoactive blend was spin-coated onto PEDOT:PSS surface from its chloroform solution. Subsequently, the films were transferred into a vacuum evaporator and 20 nm Ca and 60 nm of Al was deposited as the cathode. The active area of each device was 3.08 mm^2, defined by a shadow mask. For

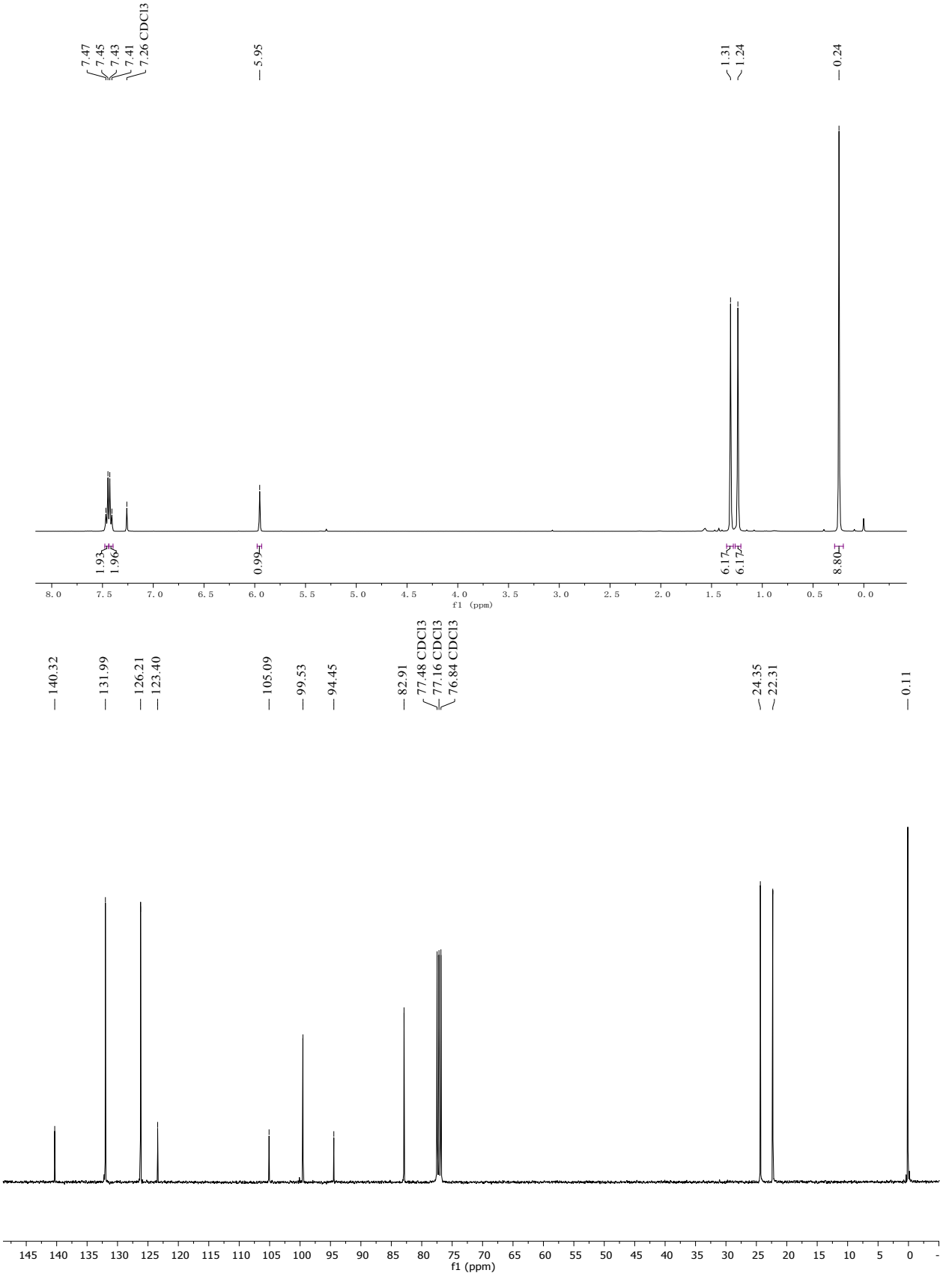
photovoltaic measurements, the *J*−*V* curve was recorded by a Precision Source/Measure Unit (B2912A; Agilent Technologies) and an AAA grade solar simulator (XES-70S1, 7 × 7 cm^2 beam size; SAN-EI Electric Co. Ltd.) coupled with AM 1.5G solar spectrum filters was taken as the light source. The light power on the surface of the sample was calibrated to be 100 mW cm^{-2} by using a standard monocrystalline silicon reference cell (SRC-1000-TC-QZ, 2 × 2 cm^2; VLSI Standards Inc.). The EQE was measured by a Solar Cell Spectral Response Measurement System (QE-R3011; Enlitech Co. Ltd.) with the light intensity at each wavelength also calibrated by a standard single crystal Si photovoltaic cell.

NMR Charts

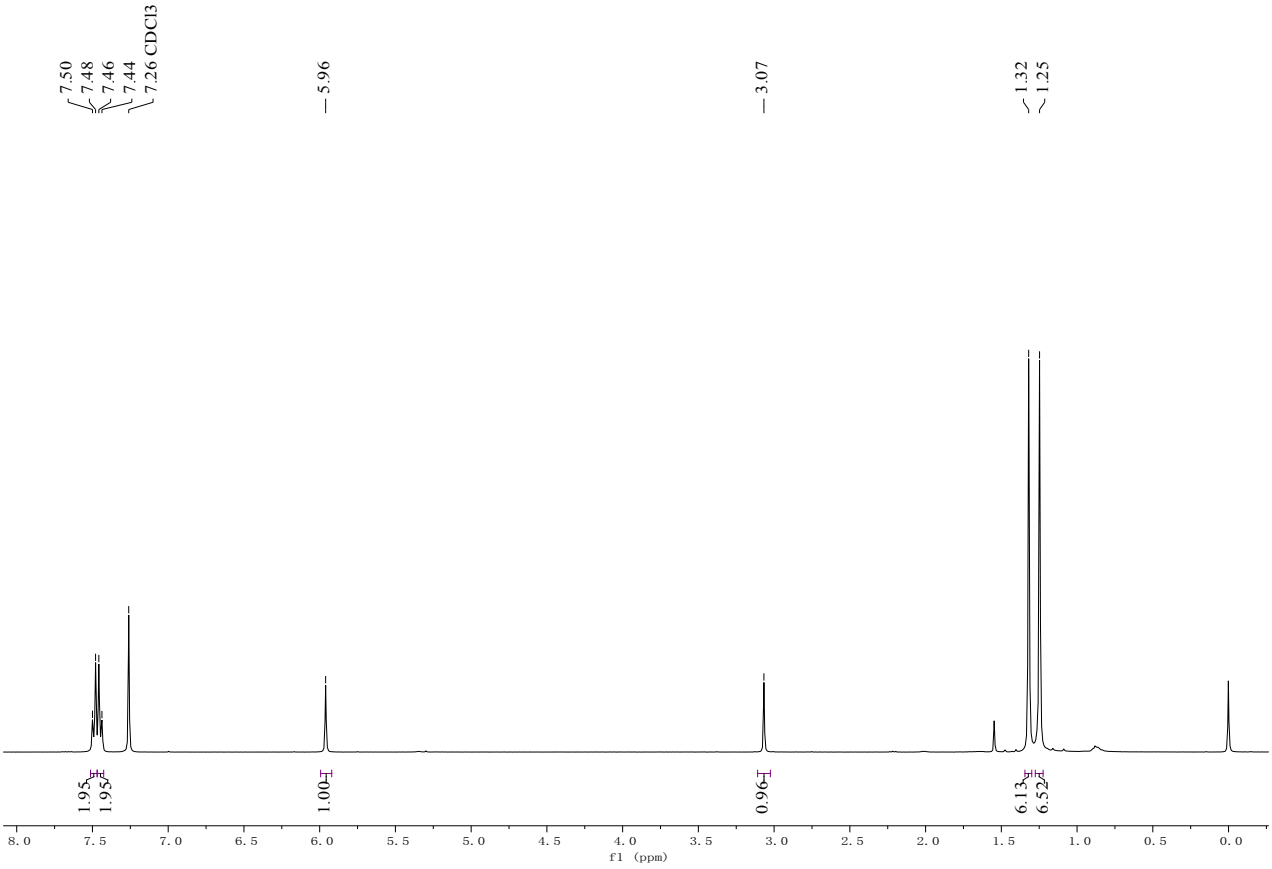
Tributyl((3,5-di-*tert*-butylphenyl)ethynyl)stannane (3a)

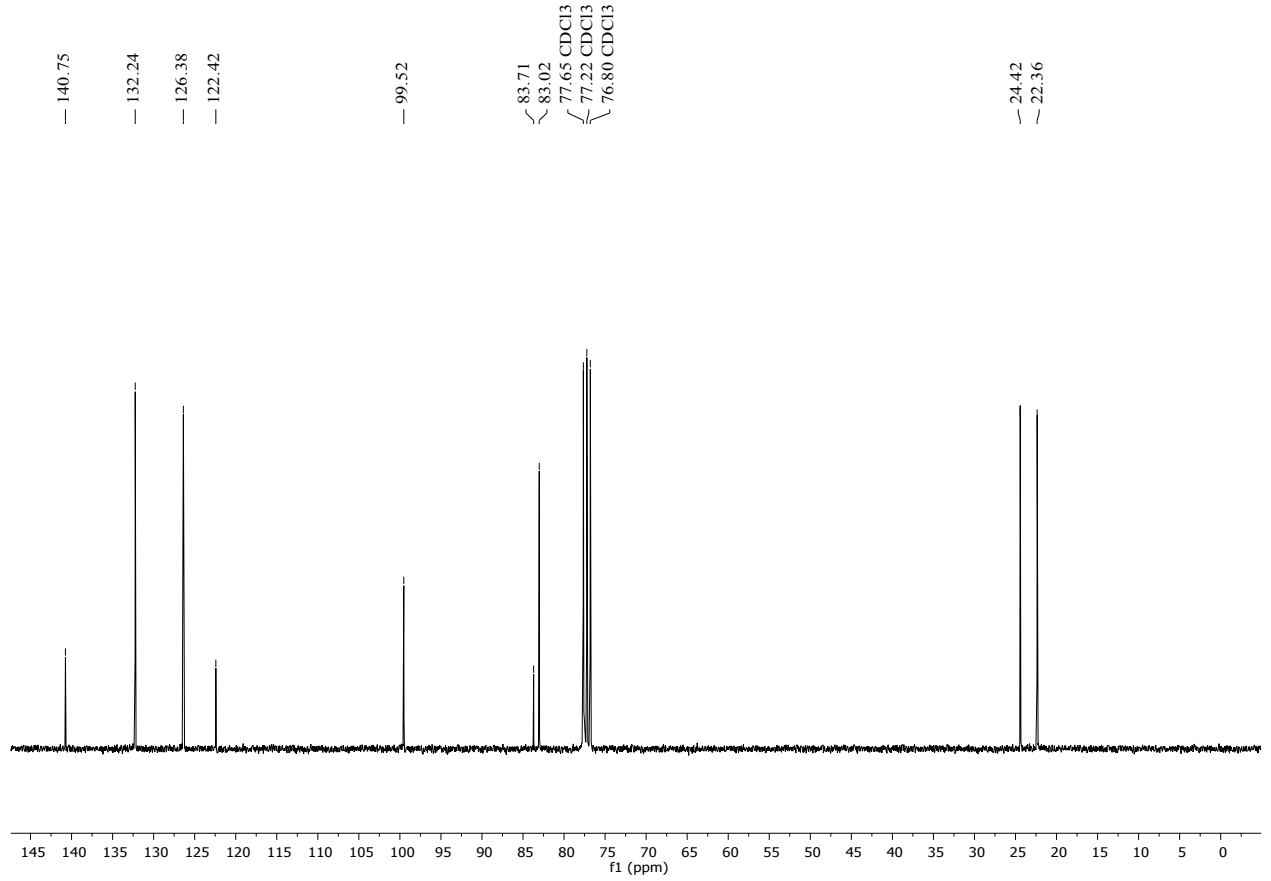


Trimethyl((4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl)ethynyl)silane (2e)

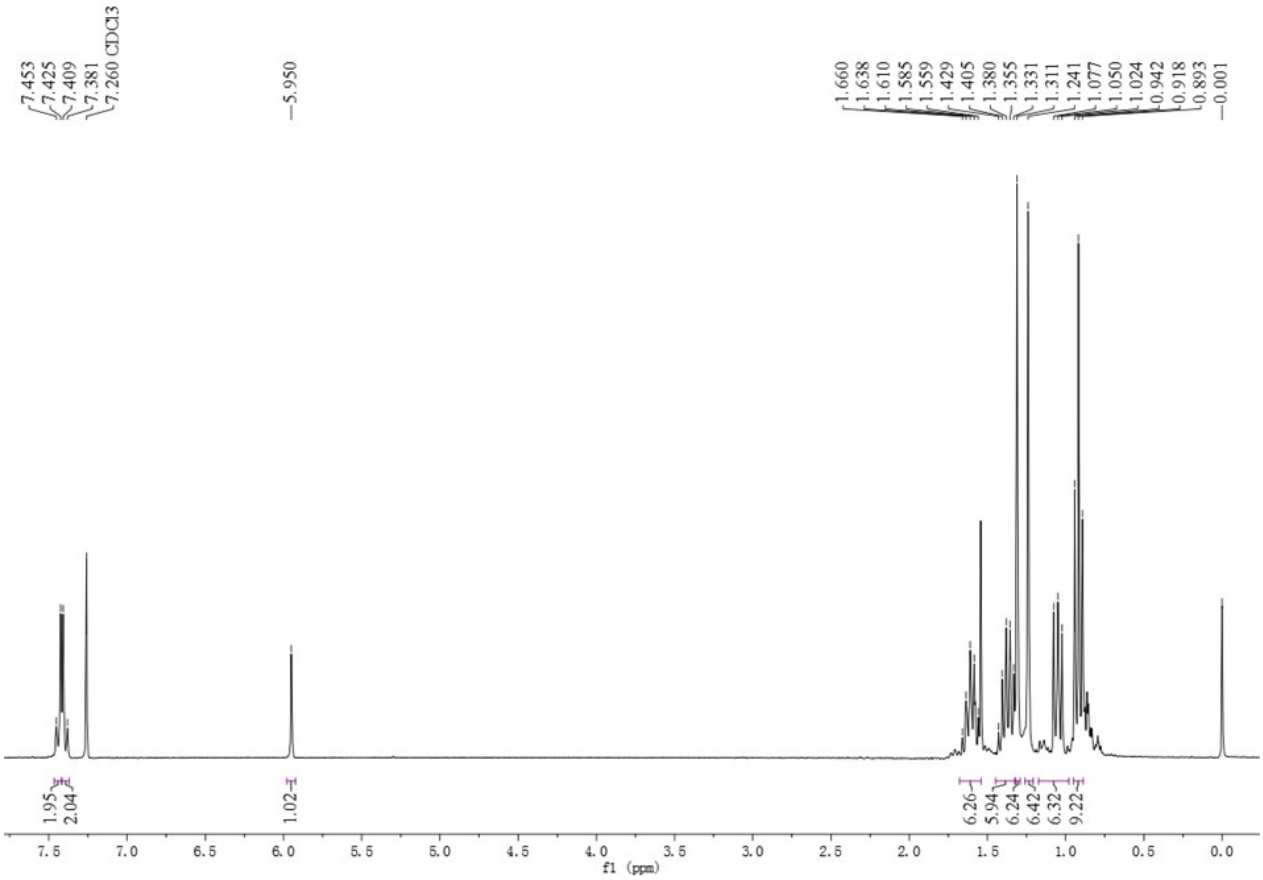


2-(4-Ethynylphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (3e)

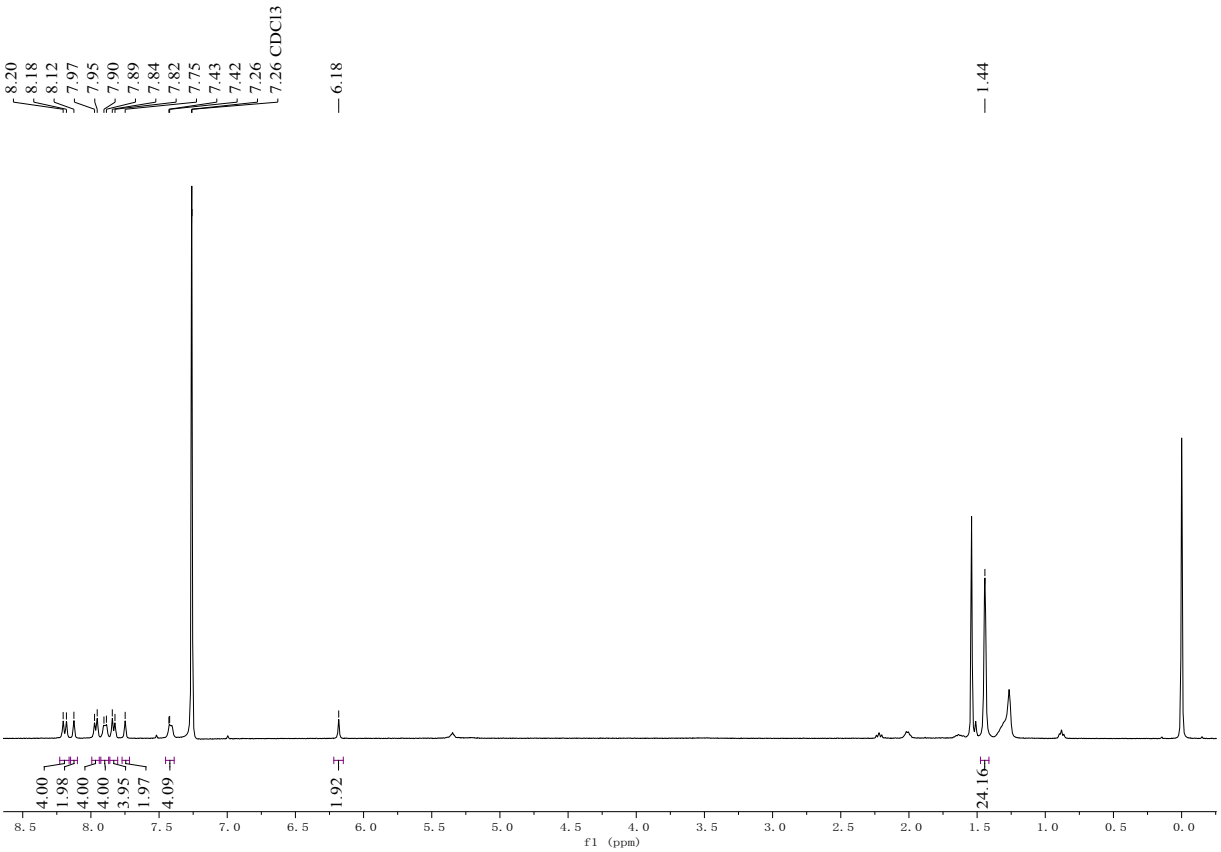


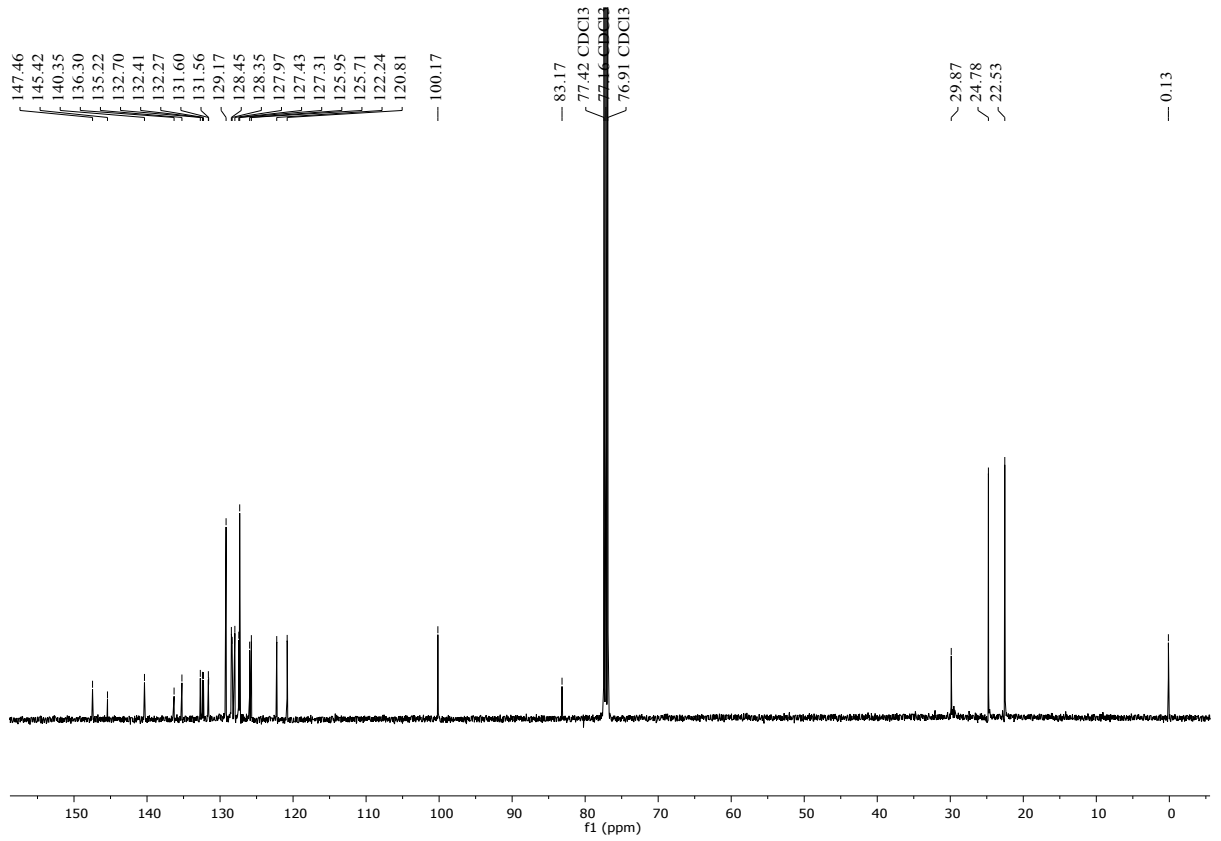


Tributyl((4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl)ethynyl)stannane (4e)

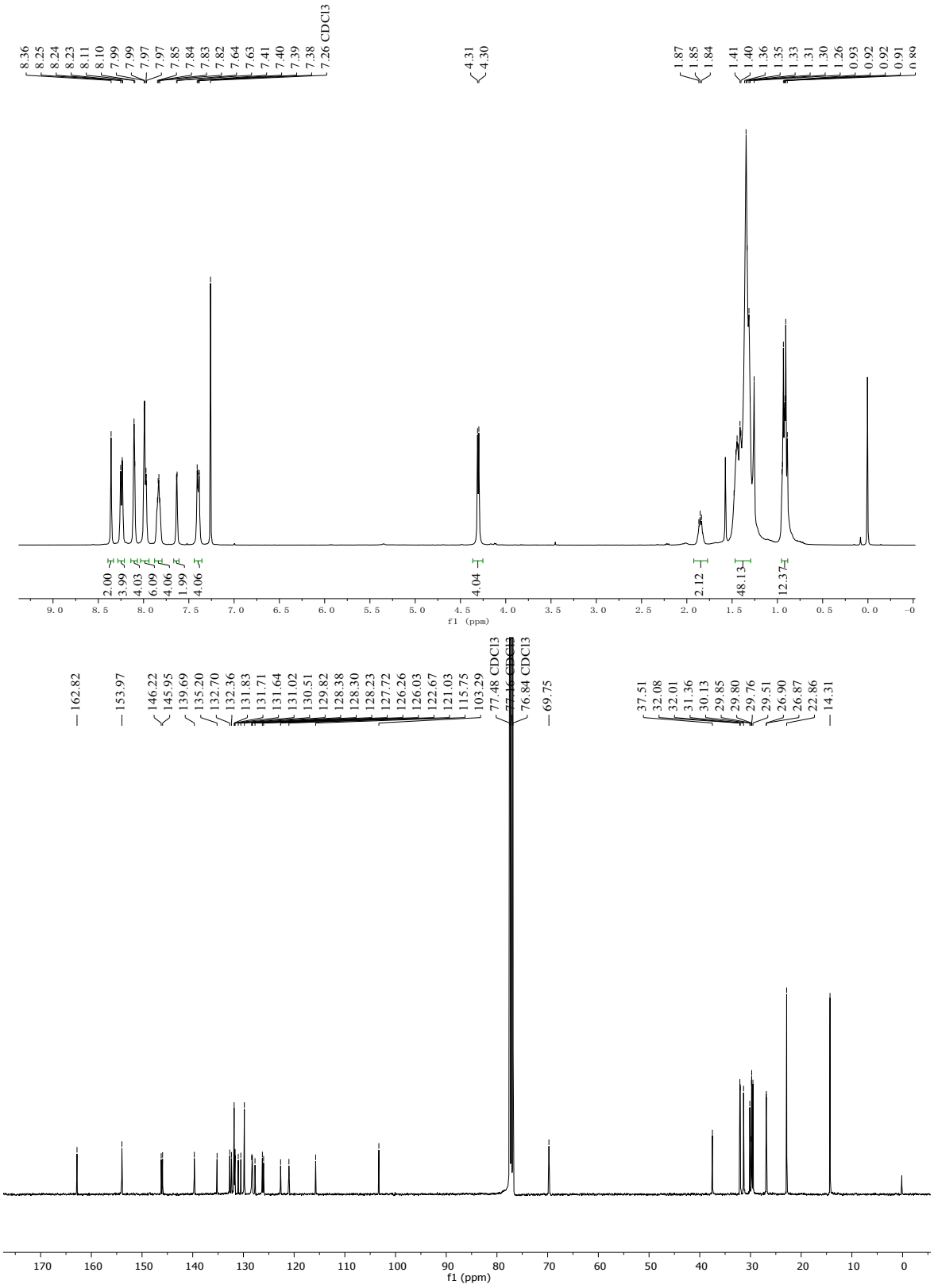


7,16-Bis(4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl)pentaleno[1,2-*b*:4,5-*b*']dianthracene (DAP-PhBu)



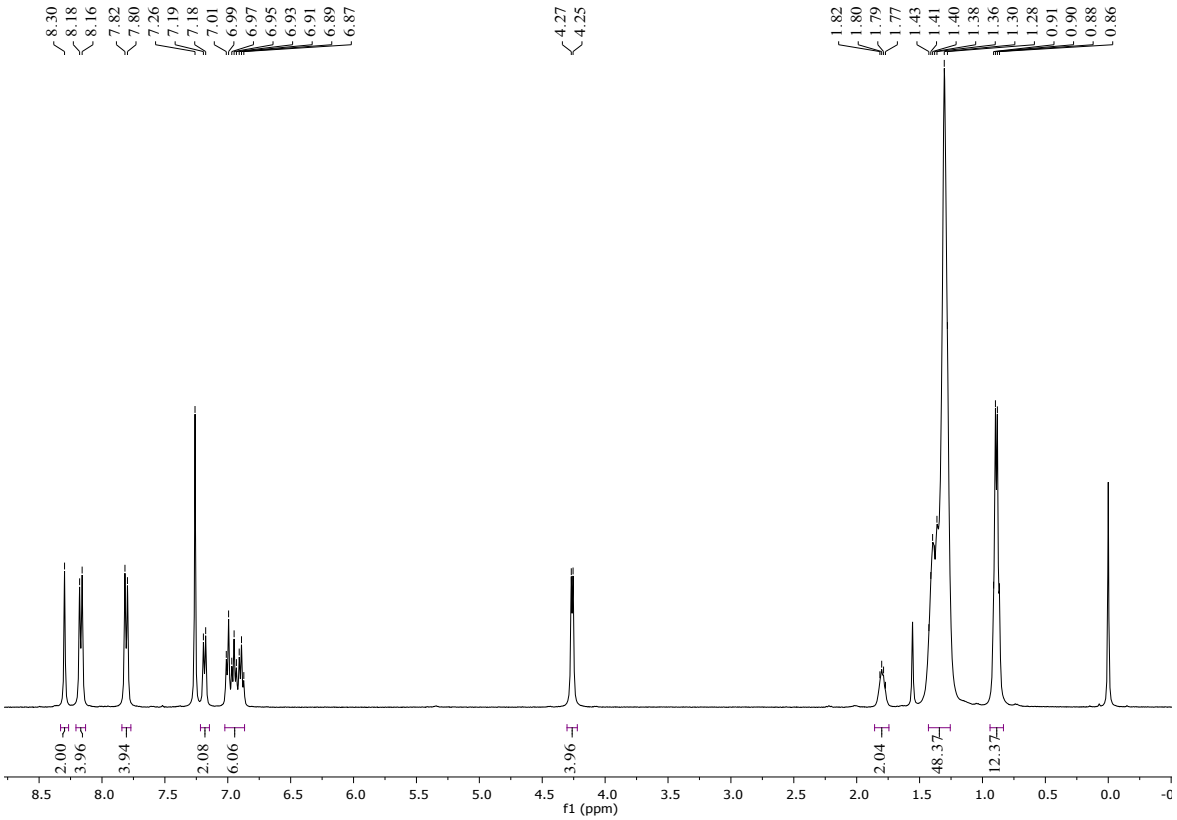


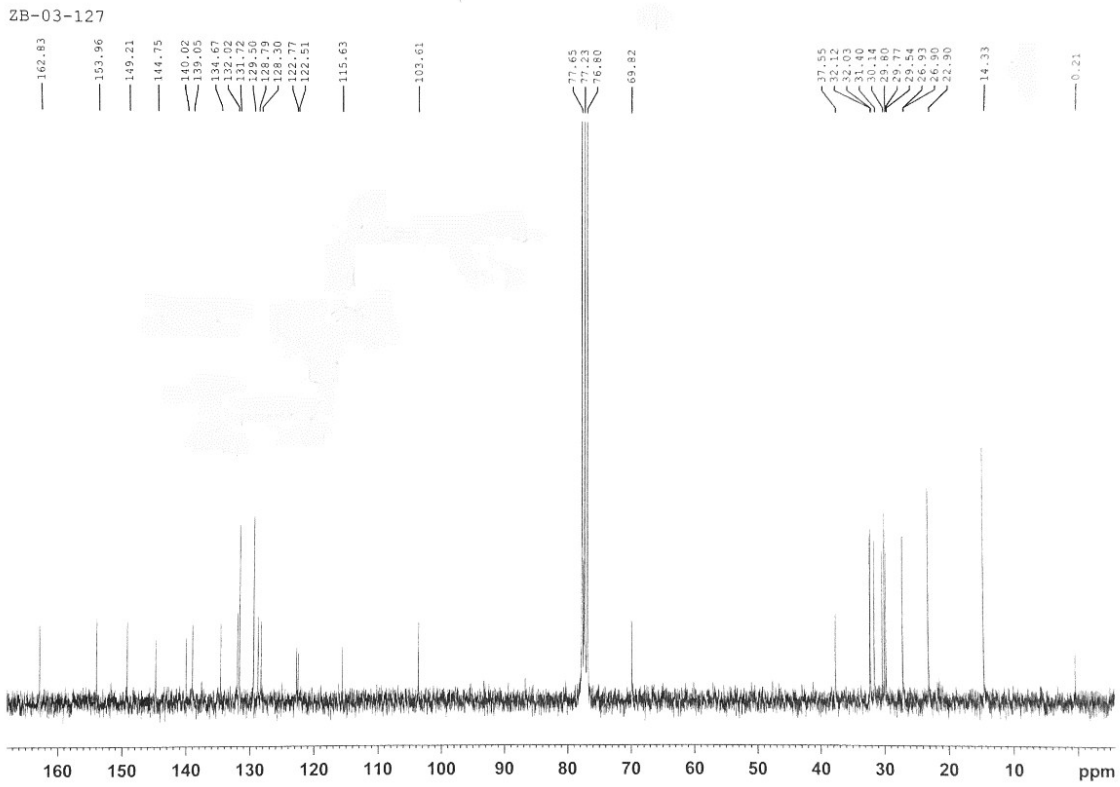
Bis(2-hexyldecyl) 3,3'-(pentaleno[1,2-*b*:4,5-*b*']dianthracene-7,16-diylbis(4,1-phenylene))(2*E*,2'*E*)-bis(2-cyanoacrylate) (DAP-PhCA)



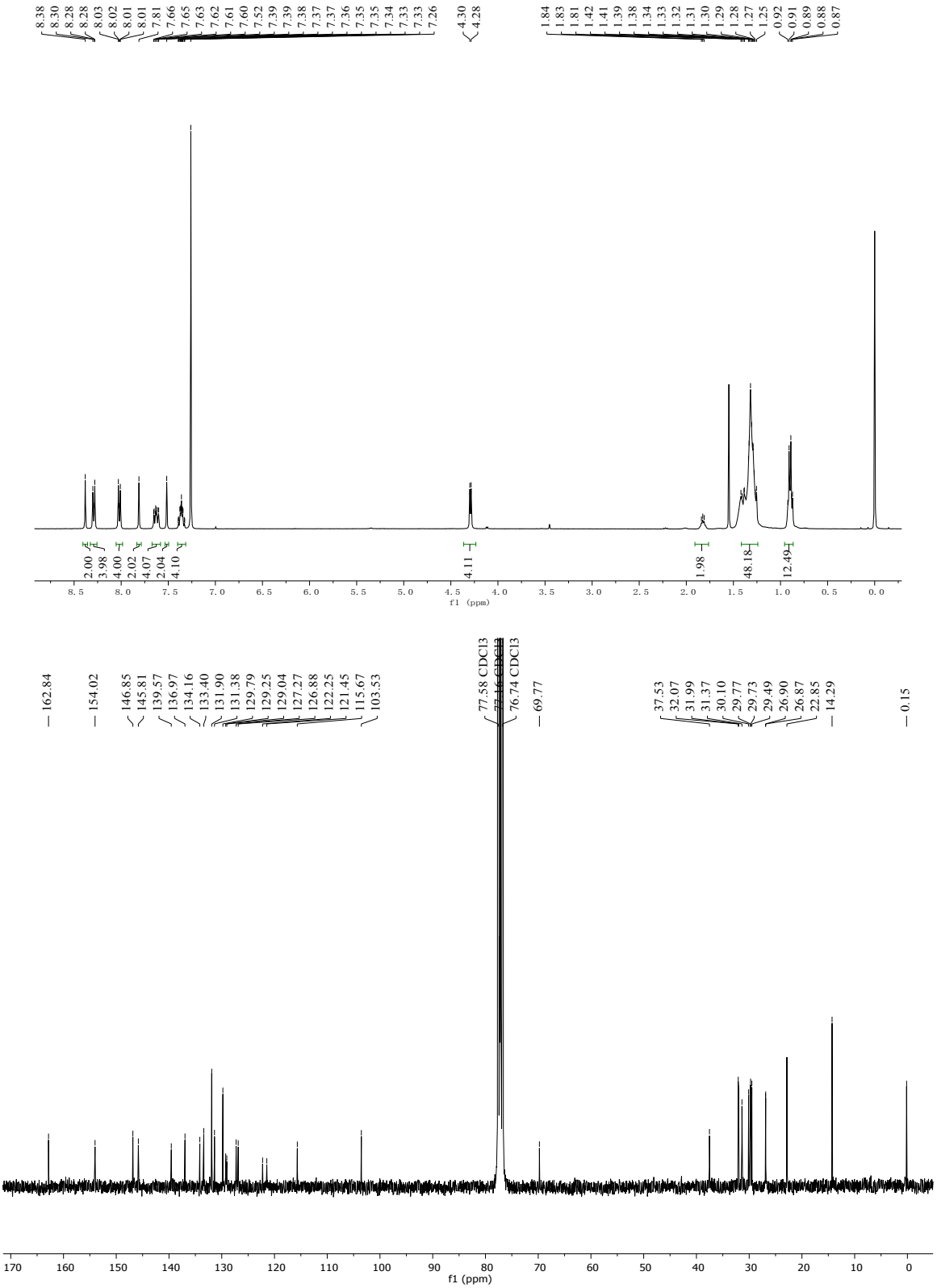
Bis(2-hexyldecyl) 3,3'-(indeno[2,1-*a*]indene-5,10-diylbis(4,1-phenylene))(2*E*,2'*E*)-bis(2-

cyanoacrylate) (DBP-PhCA)

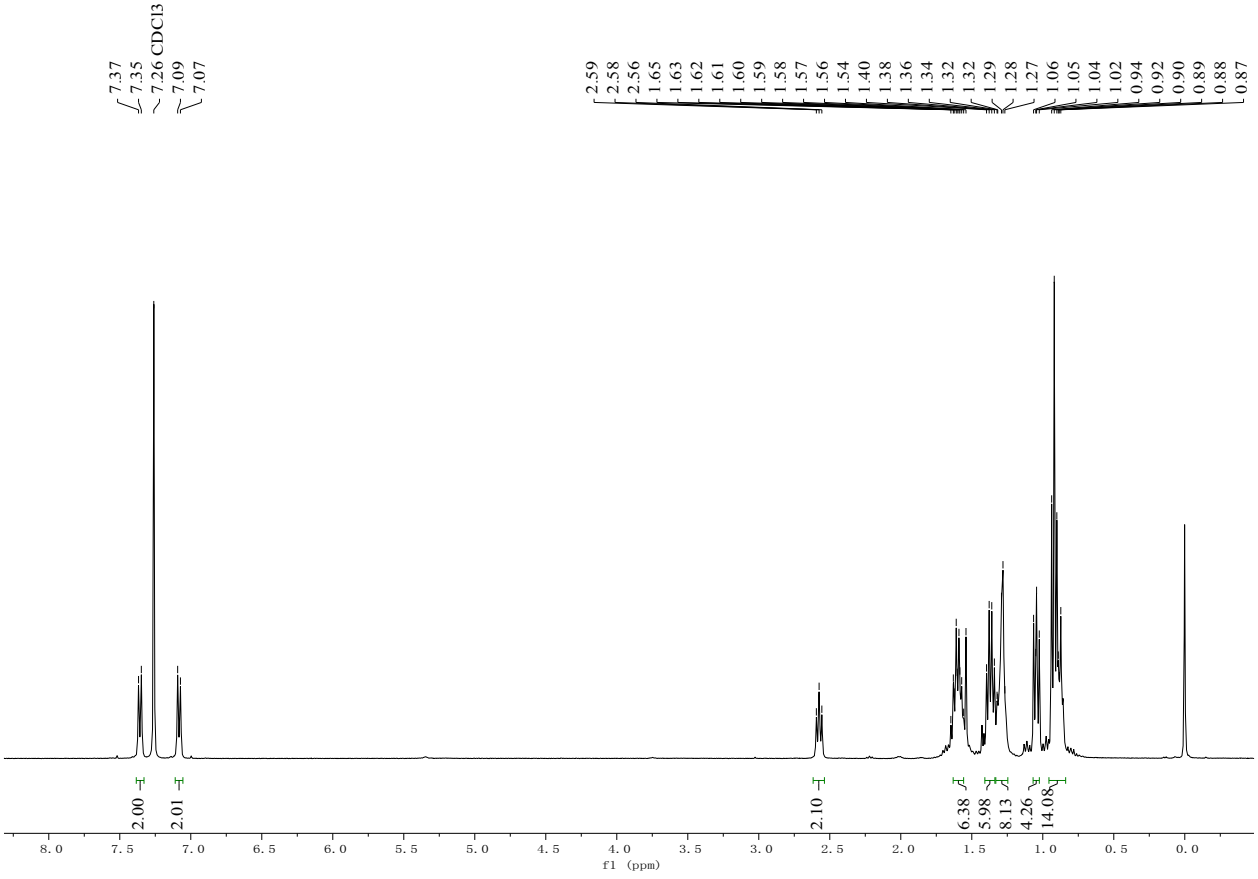




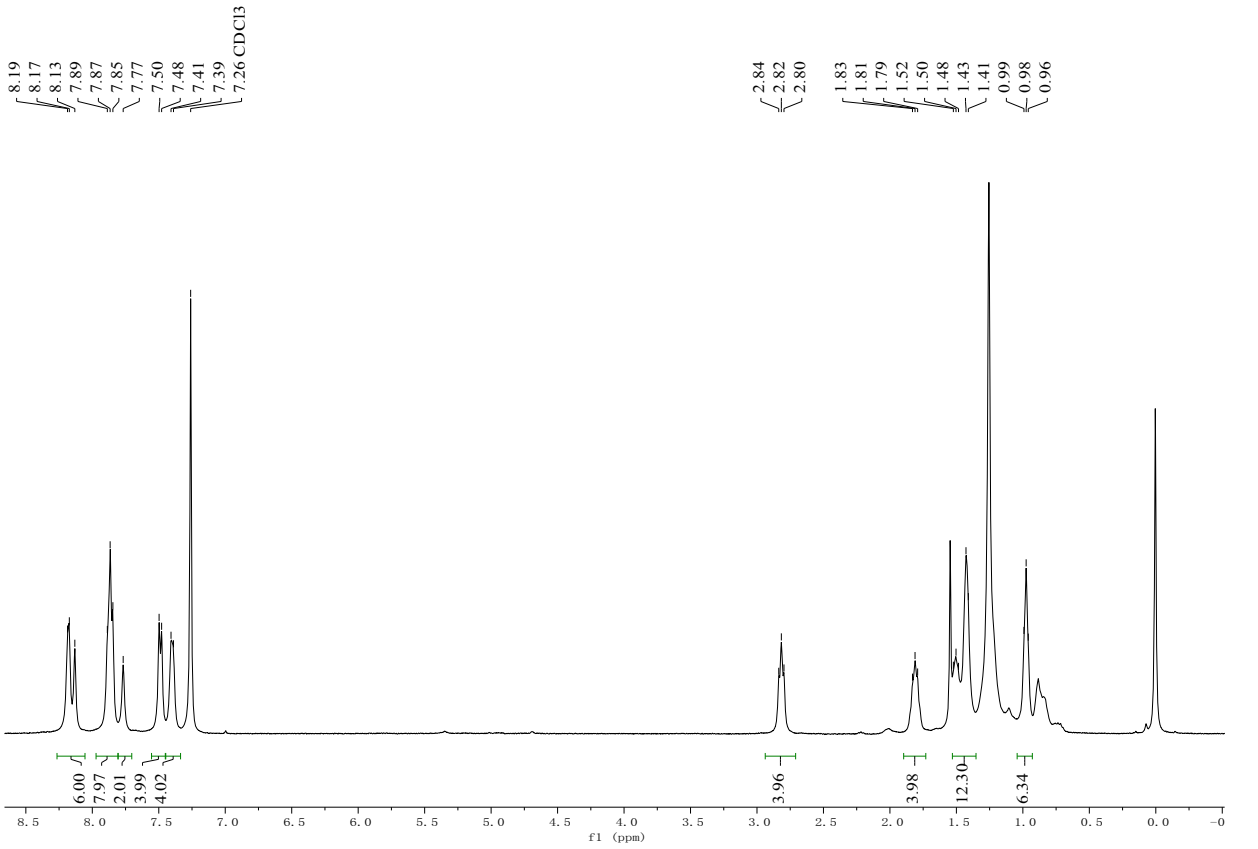
Bis(2-hexyldecyl) 3,3'-(pentaleno[1,2-*b*:4,5-*b*']dinaphthalene-6,13-diylbis(4,1-phenylene))(2*E*,2'*E*)-bis(2-cyanoacrylate) (DNP-PhCA)

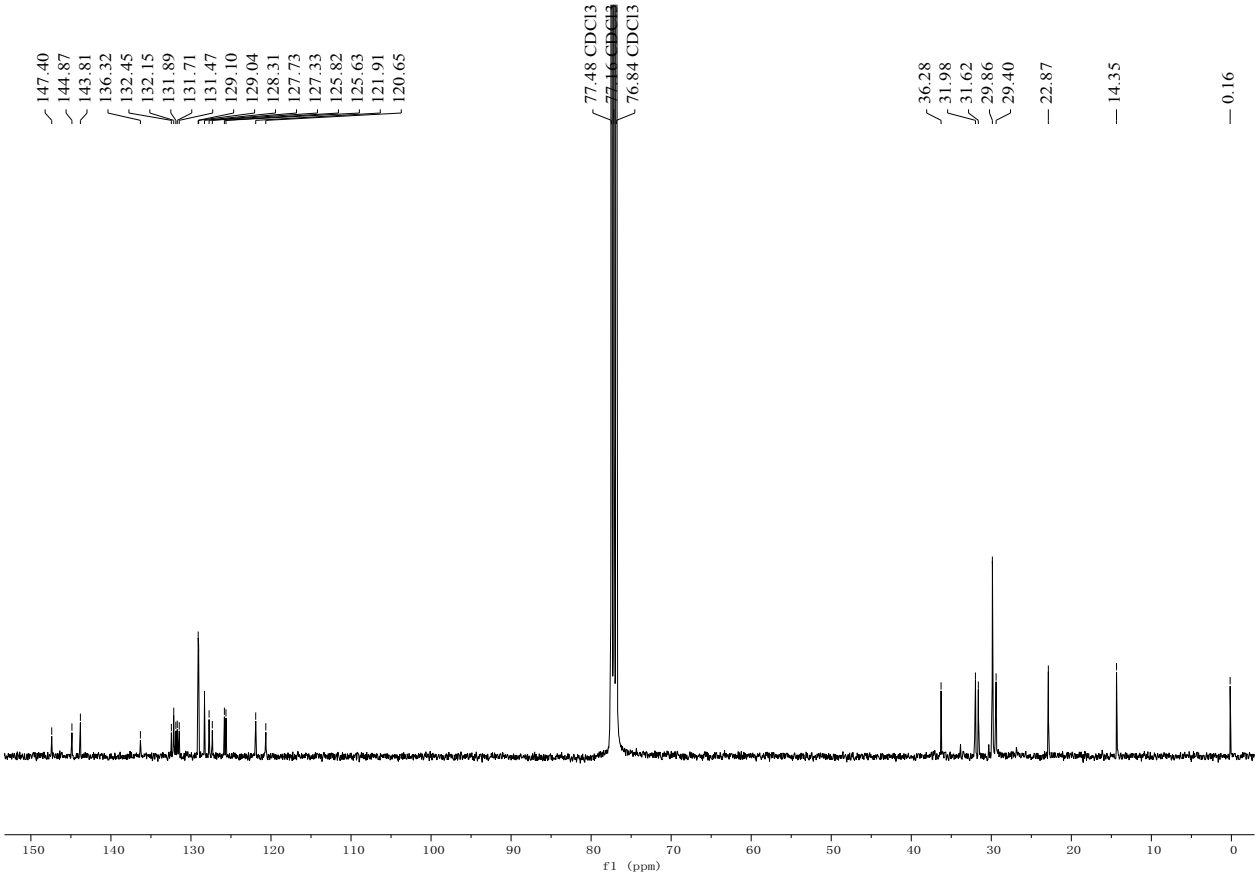


Tributyl((4-hexylphenyl)ethynyl)stannane (1b)

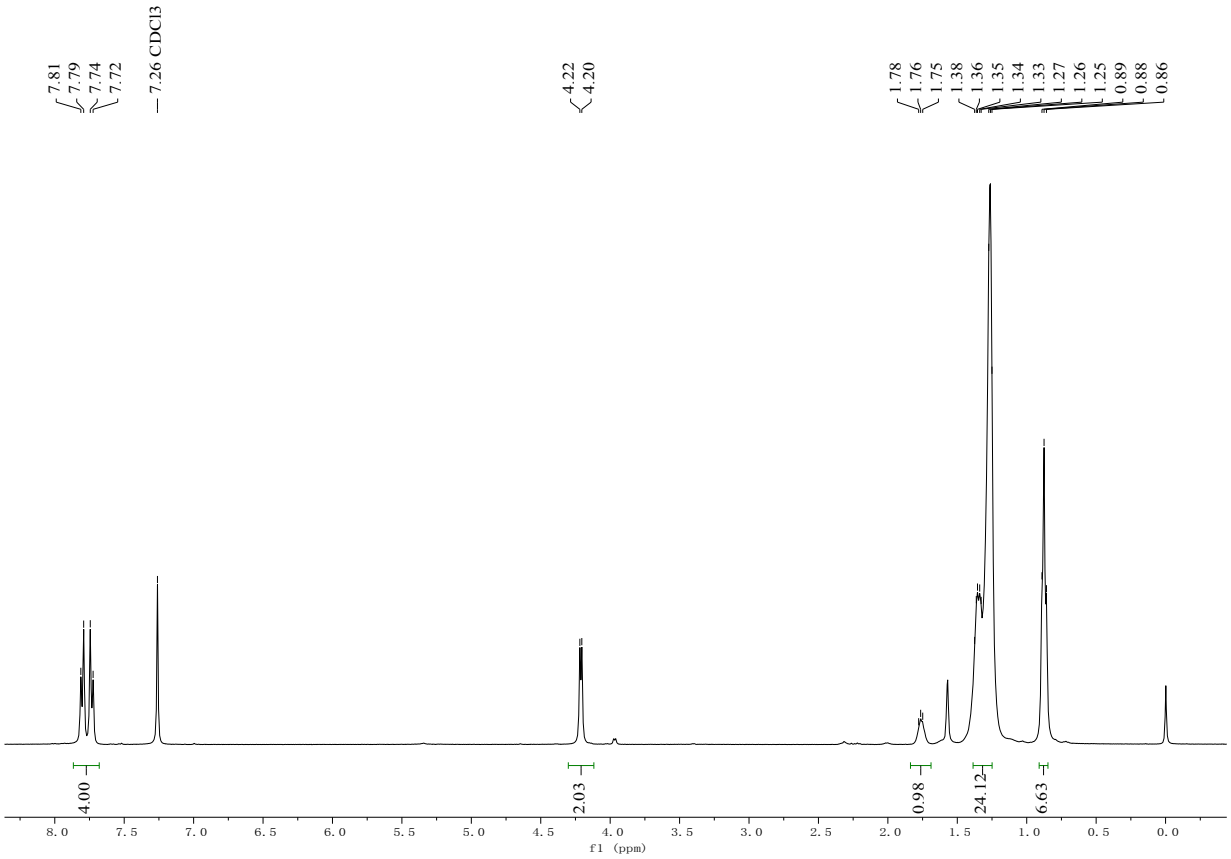

7.37
7.35
7.26 CDCl3
7.09
7.07
2.59
2.58
2.56
1.65
1.63
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.54
1.40
1.38
1.36
1.34
1.32
1.32
1.29
1.28
1.27
1.06
1.05
1.04
1.02
0.94
0.92
0.90
0.89
0.88
0.87
2.00
2.01
2.10
6.38
5.98
8.13
4.26
14.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

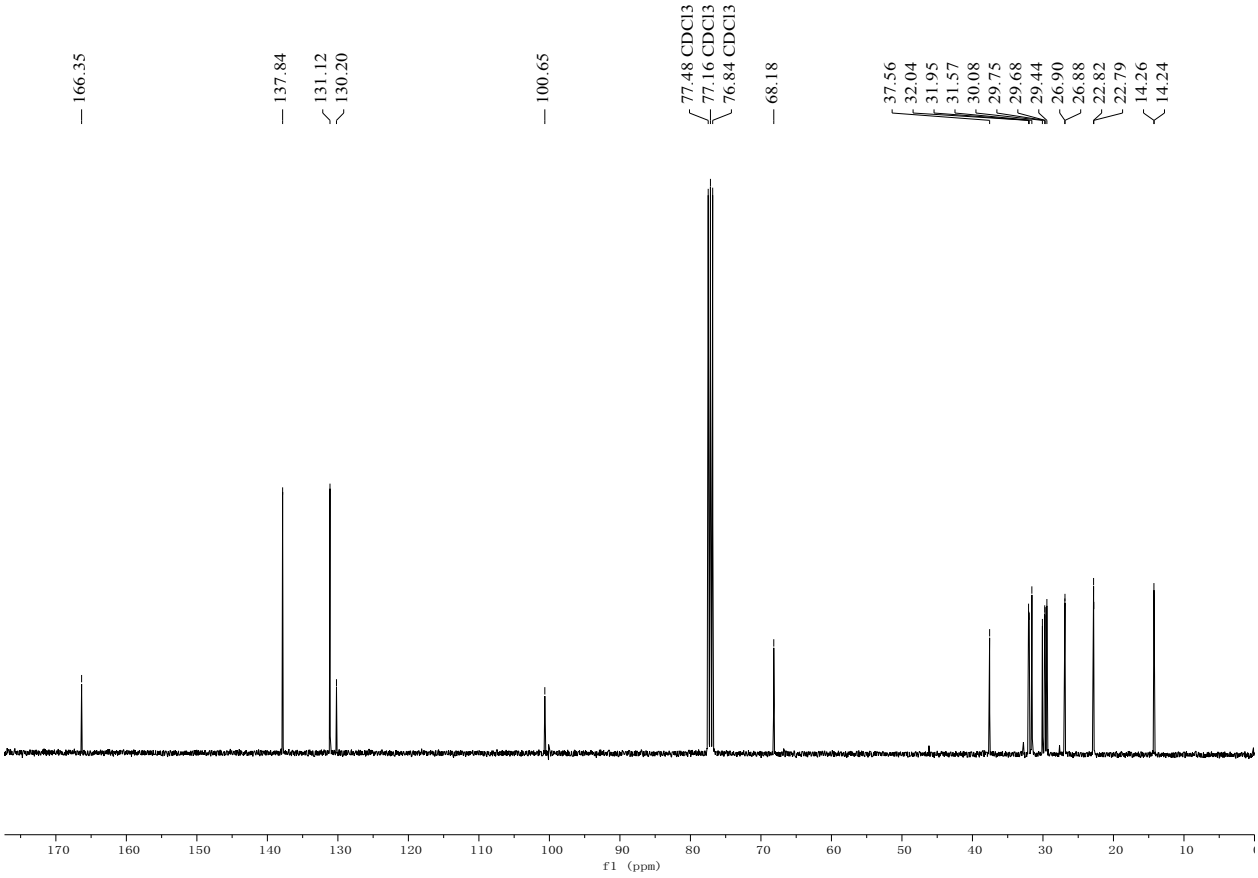
7,16-Bis(4-hexylphenyl)pentaleno[1,2-*b*:4,5-*b*']dianthracene (DAP-PhH)



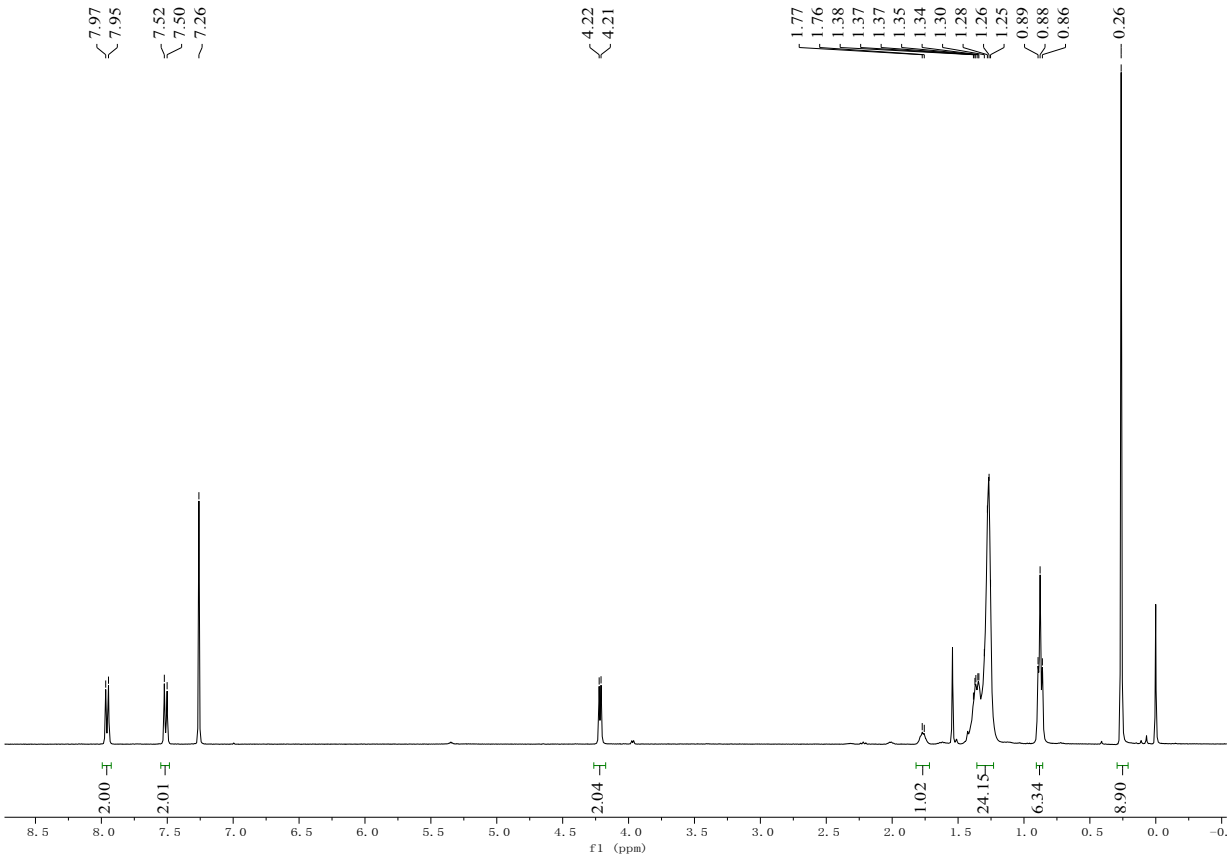


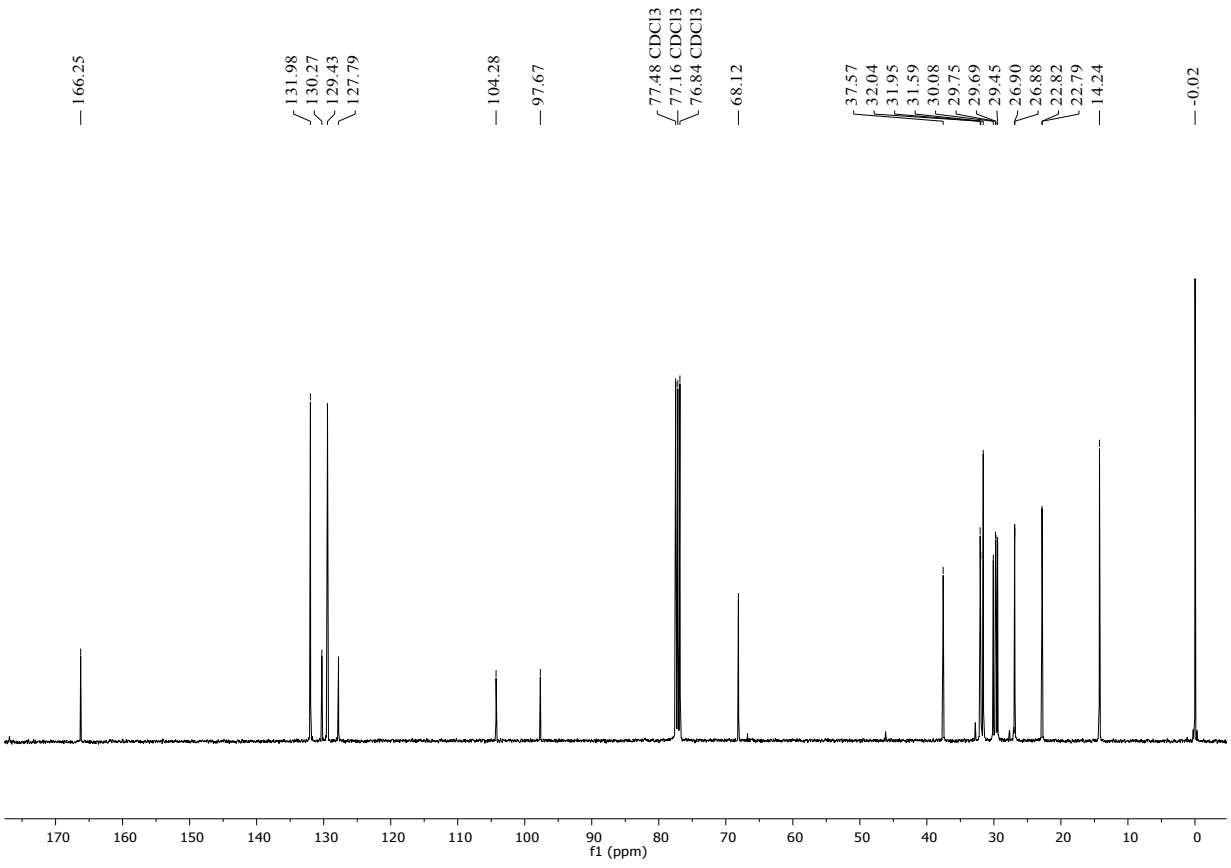
2-Hexyldecyl 4-iodobenzoate (1d)



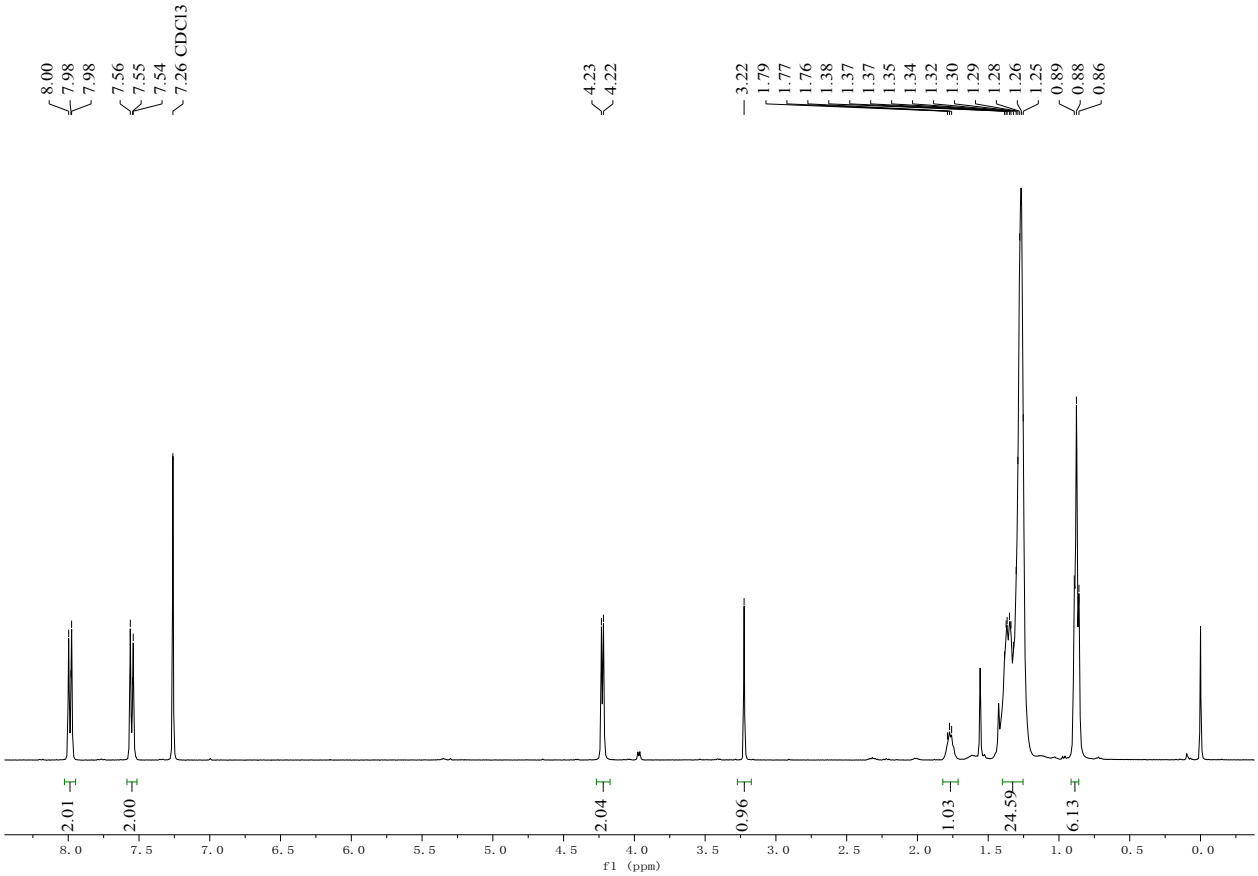


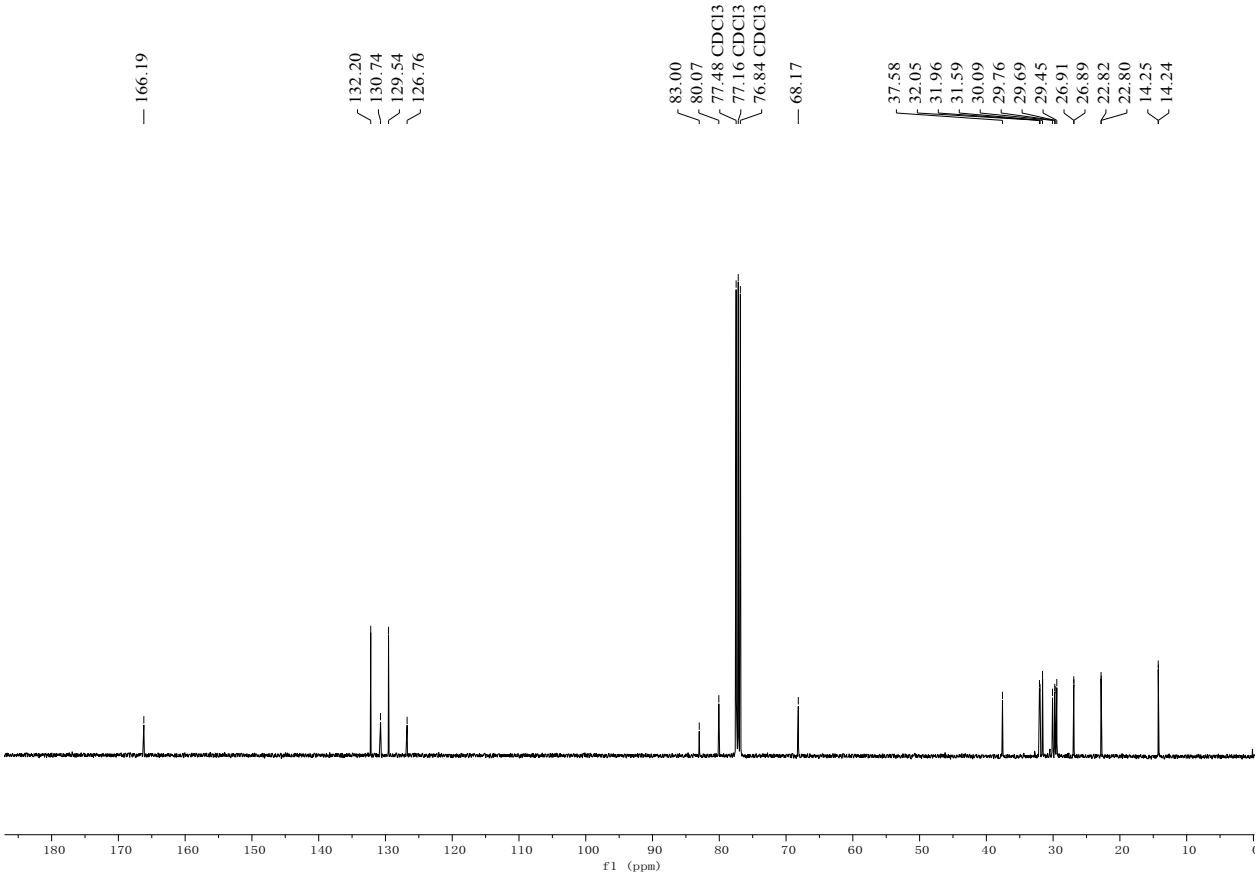
2-Hexyldecyl 4-((trimethylsilyl)ethynyl)benzoate (2d)



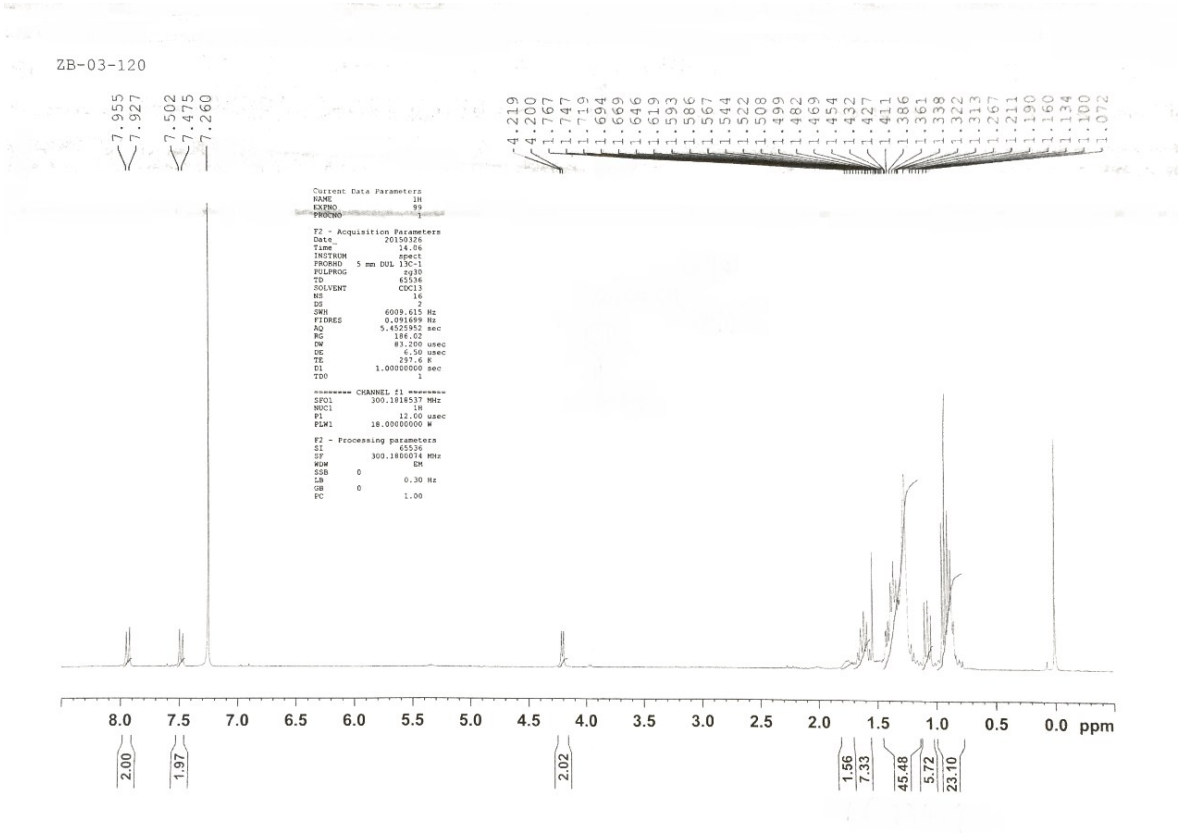


2-Hexyldecyl 4-ethynylbenzoate (3d)

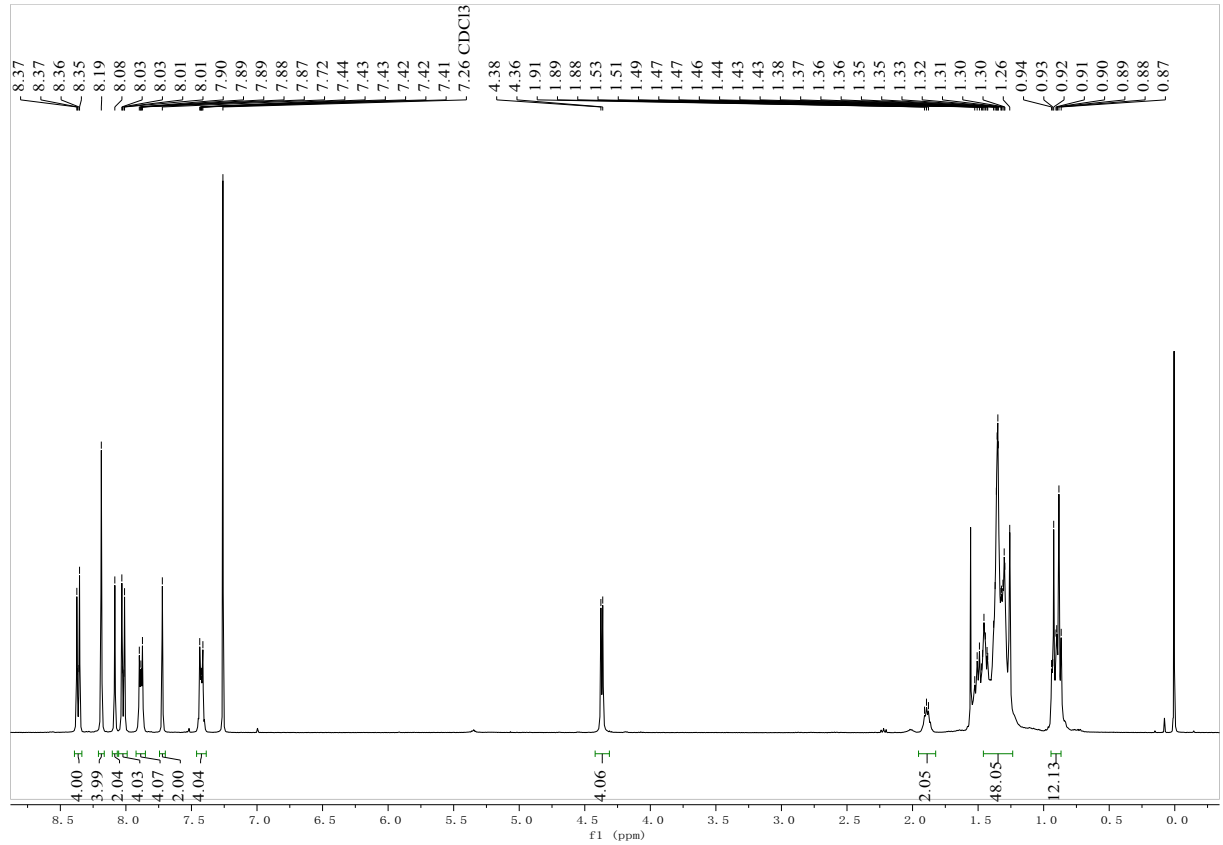


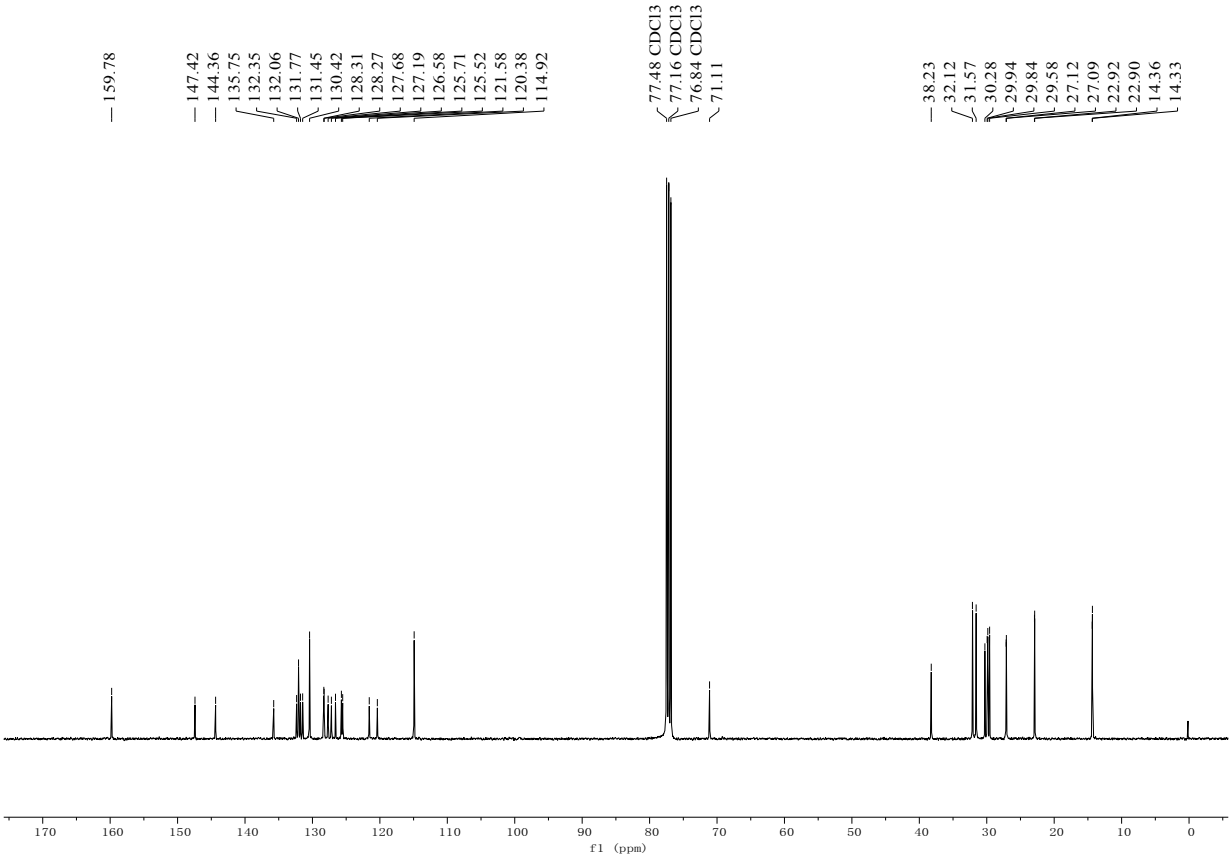


2-Hexyldecyl 4-((tributylstannyl)ethynyl)benzoate 4d)

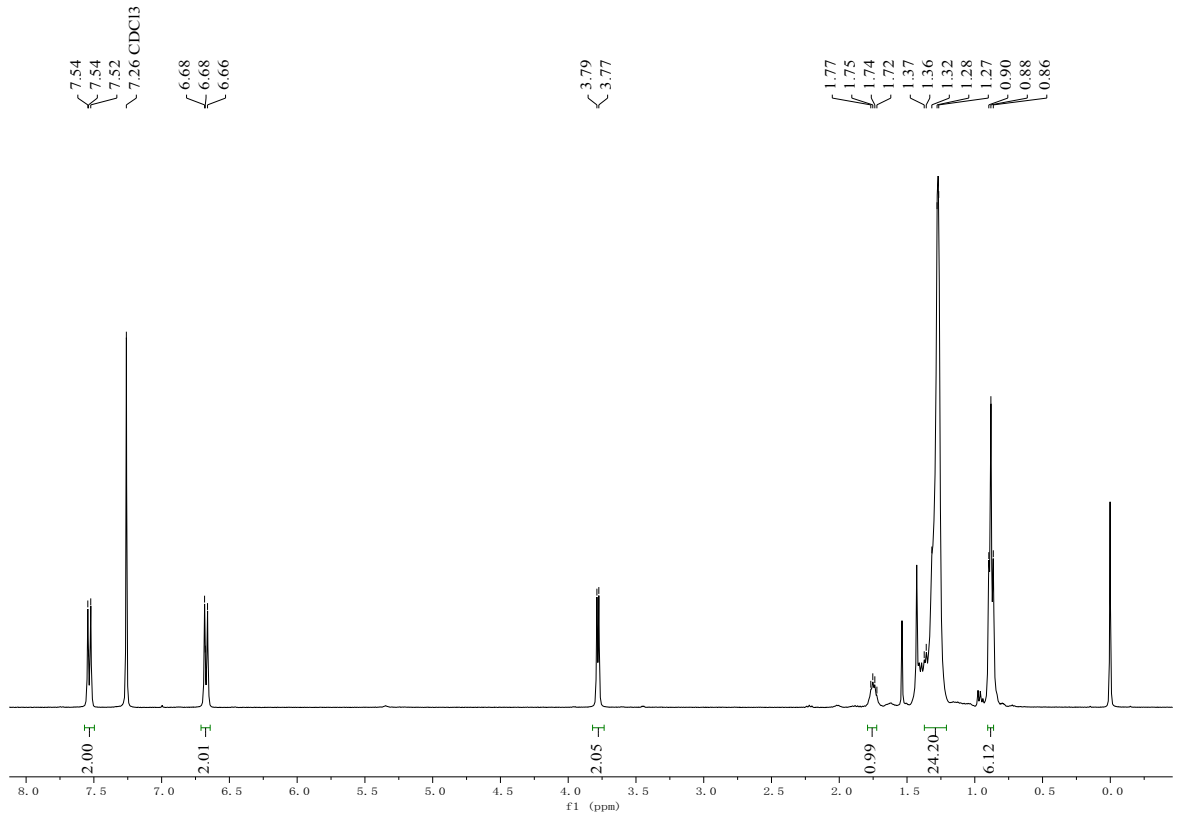


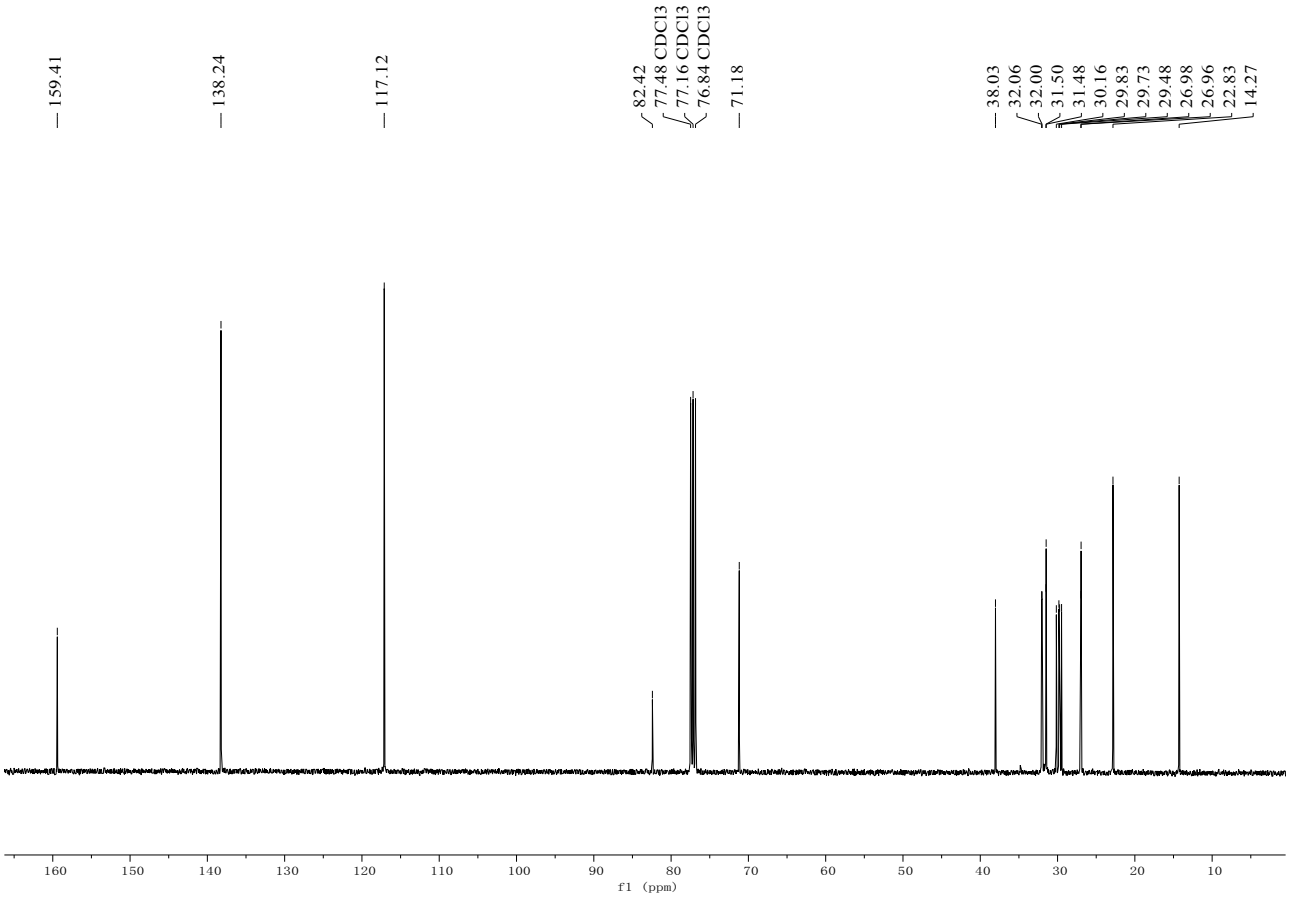
Bis(2-hexyldecyl) 4,4'-(pentaleno[1,2-*b*:4,5-*b*']dianthracene-7,16-diyl)dibenzoate (DAP-PhCOOHD)



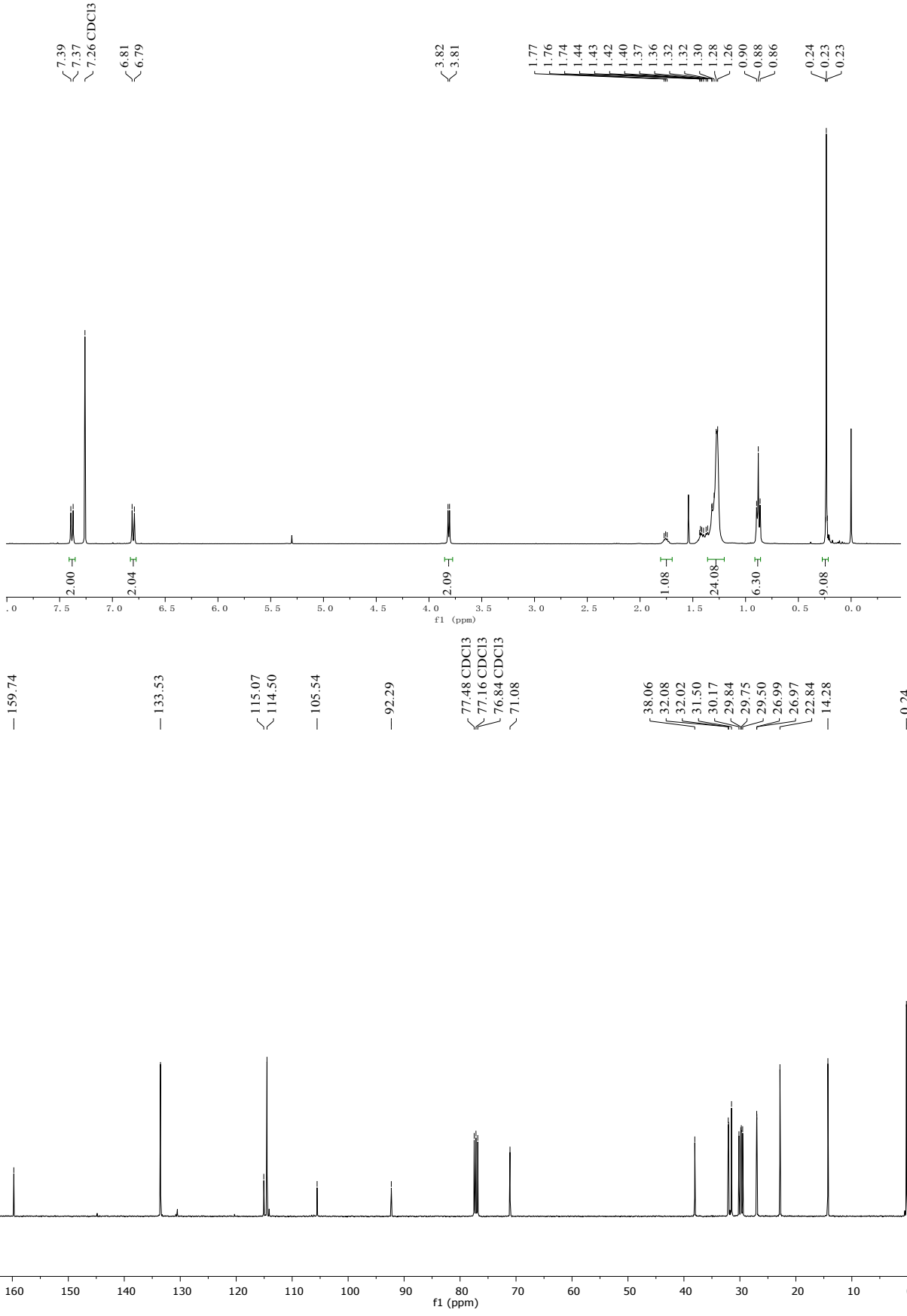


1-((2-Hexyldecyl)oxy)-4-iodobenzene (1c)

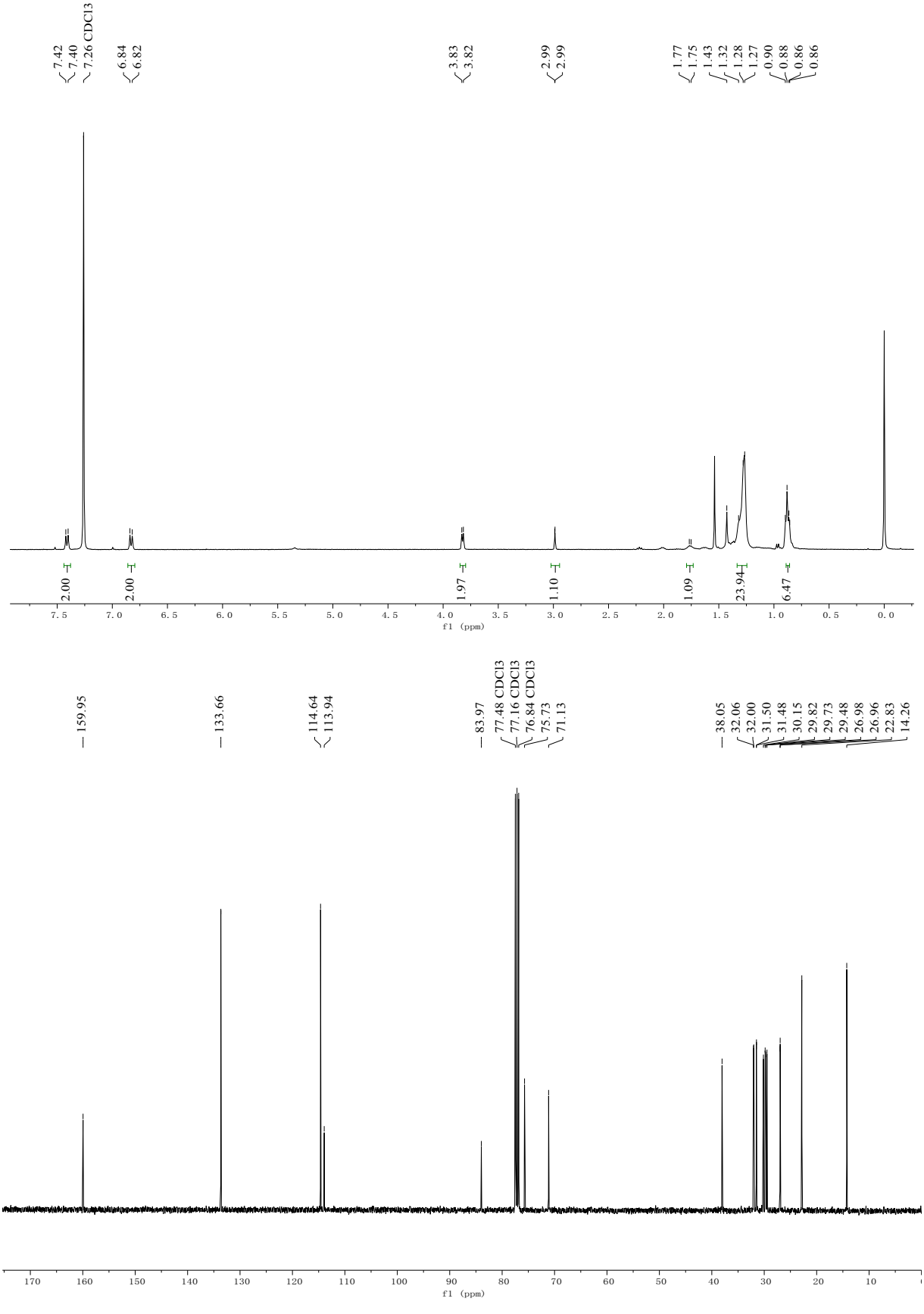




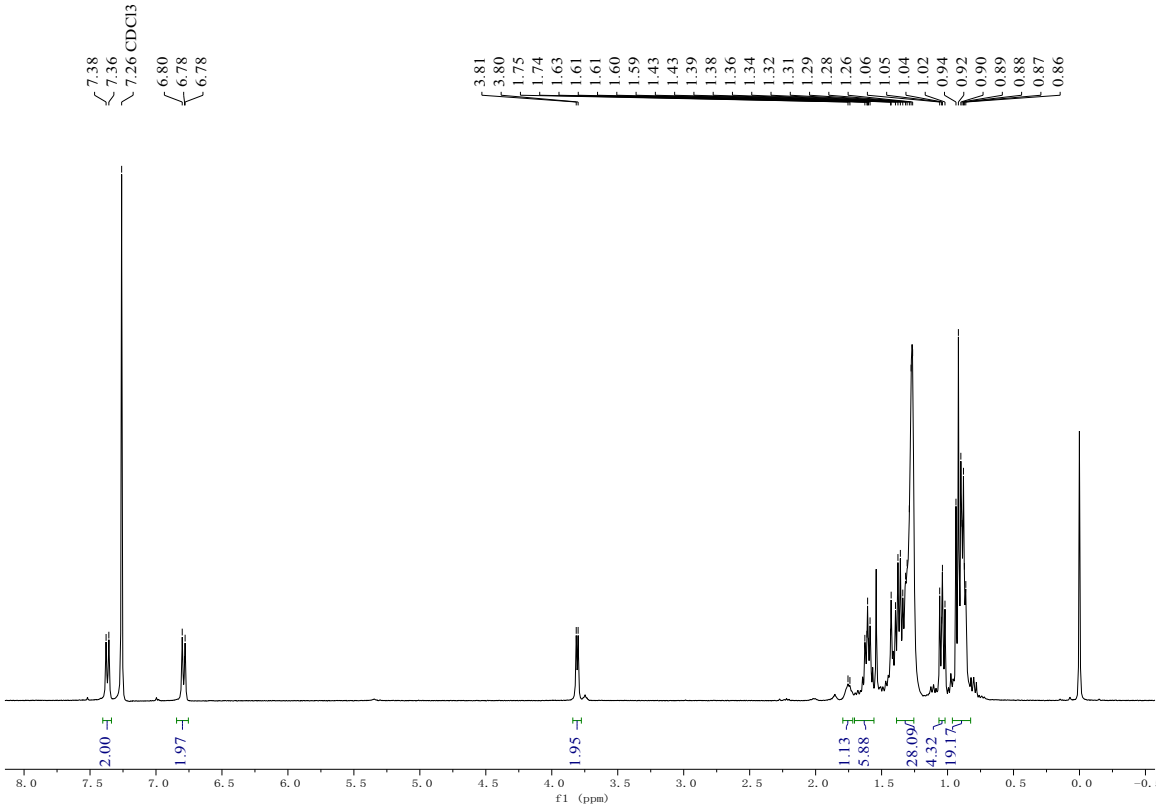
((4-((2-Hexyldecyl)oxy)phenyl)ethynyl)trimethylsilane (2c)



1-Ethynyl-4-((2-hexyldecyl)oxy)benzene (3c)



Tributyl((4-((2-hexyldecyl)oxy)phenyl)ethynyl)stannane (4c)



7,16-Bis(4-((2-hexyldecyl)oxy)phenyl)pentaleno[1,2-*b*:4,5-*b*']dianthracene (DAP-PhOHD)