

Electronic Supporting Information

Cycloaddition of Benzyne to SWCNT: Towards Carbon Nanotube-Based Paddle Wheels

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Experimental section

General. All reactions were carried out under Argon using oven-dried glassware. 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**3a**)¹ and 4-bromo-1,2-bis(hexyloxy)benzene (**4**)² were prepared following published procedures. Single-walled carbon nanotubes (SWCNTs), prepared by CCVD process, were purchased from Nanocyl (www.nanocyl.com). Commercial reagents and anhydrous solvents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification. TLC was performed on Merck silica gel 60 F₂₅₄, chromatograms were visualized with UV light (254 and 360 nm). Column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a Varian-Mercury 300 MHz and a Bruker WM-500 MHz. Mass spectra (EI) were performed using HP-5988A working at 70 eV. High-resolution mass spectra (HRMS) were recorded on Micromass Autospec spectrometer. Melting points were determined on a Gallenkamp instrument. UV-vis-NIR absorption spectra were obtained in dimethylformamide (DMF) using quartz cuvettes on a UV-3600 Shimadzu spectrophotometer. FT-IR spectra were recorded on an AVATAR 370 Thermo Nicolet spectrometer. Raman spectra were recorded at room temperature in the ambient atmosphere using a Renishaw in Via Microscope (532nm and 785nm) and averaging 3 scans of different areas of the samples. The thermogravimetric analyses were performed with a TGA Q500 (TA Instruments) at 10°C/min under N₂.

X-ray Photoelectron Spectroscopy (XPS). Surface analysis was carried out on a VG Escalab 200R electron spectrometer provided with MgK α_1 X-ray ($h\nu = 1254.6$ eV, $1 \text{ eV} = 1.6302 \times 10^{-19}$ J) 120 watts source and a hemispherical electron analyser. The samples were deposited as a thin film on double side adhesive tape and then mounted on a sample rod, placed in a pretreatment chamber and degassed at 573 K and 10^{-5} mbar for 2 h prior to being transferred to the analysis chamber. Before the spectra were recorded, the samples were maintained in the analysis chamber under a residual pressure ca. 2×10^{-9} mbar

¹ D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis*, 2002,1454.

² C. Romero, D. Peña, D. Pérez and E. Guitián, *Chem. Eur. J.* 2006, **12**, 5677.

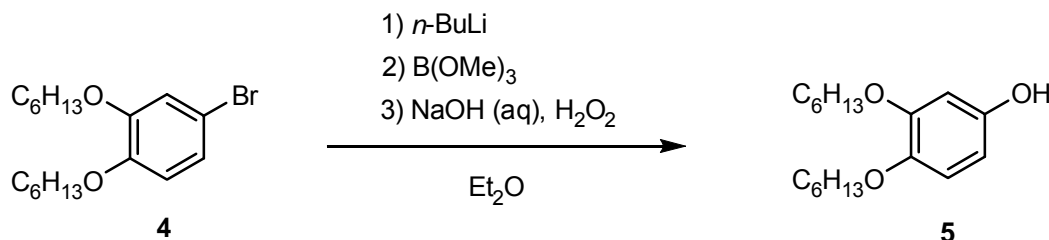
for 2 h. The area under analysis was around 2.4 mm² and the pass energy of the analyser was set at 20 eV, for which the resolution measured by the full width at half maximum (FWHM) of the Au4f_{7/2} core level was 0.86 eV. Charging effects were corrected by calibrating spectra to the binding energy of C1s peak at 284.9 eV due to adventitious carbon. This reference gave BE values with an accuracy of ±0.1 eV. Data processing was performed with the *XPS peak* software, the spectra were decomposed with the least squares fitting routine provided with this software using Gauss/Lorentz (90/10) product function and after subtracting a Shirley background. Atomic fractions were calculated using peak areas normalized on the basis of sensitivity factors. Atomic ratios were computed from the intensity ratios normalized by atomic sensitivity factors³.

Transmission Electron Microscopy (TEM) were recorded using a TEM JEOL-JEM 2100 (200kV), with magnification of 250,000 times. The samples were prepared in a solution of methanol (10mg/ml), and then ultrasonicated for 5min and drop casted on a “Lacey” formvar micromembrane stabilized with carbon. The operation beam current was fixed to 105µA.

³ C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.H. Raymond and L.H. Gale, *Surf. Interface Anal.* 1981, **3**, 211.

Synthesis and characterization of compounds 3b-7

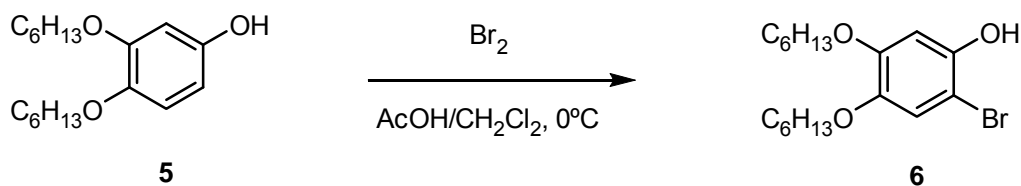
3,4-bis(hexyloxy)phenol (**5**)



To a solution of **4** (3.82 g, 10.7 mmol) in Et₂O (100 mL) *n*-BuLi (7.00 mL of 2.30 solution in hexane, 16.1 mmol) was added dropwise at room temperature, and the resulting suspension was stirred for 3 h. Then B(OMe)₃ (2.64 mL, 23.6 mmol) was added and the mixture was stirred overnight at room temperature. A solution of NaOH (7.88 g in 40 mL of H₂O, 197 mmol) and 30% H₂O₂ (25.2 mL, 247 mmol) were added and the mixture was stirred for 1 h. The organic phase was separated and the aqueous phase was extracted with Et₂O (3 x 100 mL). The combined organic phases were dried over Na₂SO₄. The solvent was evaporated under reduced pressure, and the residue was separated by column chromatography on silica gel with 10% AcOEt in hexane to afford **5** (2.24 g, 71 %) as a white solid.

Mp 82.5-84.3°C; **¹H NMR** (500 MHz, CDCl₃) δ ppm 6.74 (d, *J* = 8.6 Hz, 1H), 6.42 (d, *J* = 2.8 Hz, 1H), 6.30 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.92 (t, *J* = 6.8 Hz, 2H), 3.85 (t, *J* = 6.7 Hz, 2H), 1.79-1.71 (m, 4H), 1.47-1.38 (m, 4H), 1.35-1.27 (m, 8H), 0.89 (t, *J* = 6.6 Hz, 6H), 6.00 (s, 1H), 7.30-7.29 (m, 1H), **¹³C NMR** (125 MHz, CDCl₃) δ ppm 150.85 (C), 150.30 (C), 142.30 (C), 116.53 (CH), 106.30 (CH), 102.23 (CH), 70.98 (CH₂), 68.86 (CH₂), 31.53 (CH₂), 29.33 (CH₂), 29.02 (CH₂), 25.62 (2CH₂), 22.53 (2CH₂), 13.94 (2CH₃), **MS (EI)** *m/z* (rel. intensity %) 294 (M⁺, 28), 210 (14), 126 (100); **HRMS (EI)** calcd. C₁₈H₃₀O₃ 294.2195, found 294.2197.

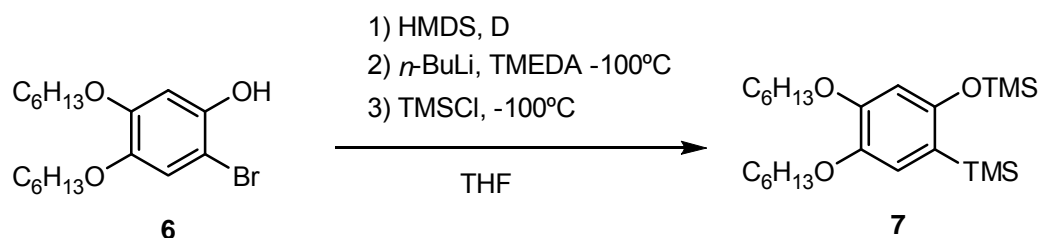
2-bromo-4,5-bis(hexyloxy)phenol (**6**)



3,4-Bis(hexyloxy)phenol (**5**, 3.06 g, 10.4 mmol) was dissolved in glacial acetic acid (200 mL) and CH_2Cl_2 (20 mL), and cooled to 0°C . Then a solution of bromine (0.43 mL, 8.30 mmol) in glacial acetic acid (25 mL) was added to it dropwise. After X h the reaction was quenched with a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_5$ (50 mL) and Et_2O (50 mL). The aqueous phase was extracted with Et_2O (2 x 25 mL). The combined organic phases were dried with Na_2SO_4 . The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2 , 10% CH_2Cl_2 in hexane) to afford **6** (2.44 g, 63 %) as a brown oil.

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ ppm 6.95 (s, 1H), 6.60 (s, 1H), 5.25 (s, 1H), 3.92 (t, $J = 6.6$ Hz, 2H), 3.90 (t, $J = 6.6$ Hz, 2H), 1.84-1.71 (m, 4H), 1.51-1.39 (m, 4H), 1.38-1.28 (m, 8H), 0.90 (t, $J = 6.5$ Hz, 6H) $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ ppm 150.35 (C), 146.98 (C), 143.46 (C), 117.91 (CH), 101.97 (CH), 98.56 (C), 70.75 (CH_2), 69.21 (CH_2), 31.59 (CH_2), 31.55 (CH_2), 29.32 (CH_2), 29.04 (CH_2), 25.66 (2CH_2), 22.60 (2CH_2), 14.02 (2CH_3); **MS (EI)** m/z (rel. intensity %) 374 (36.1), 372 (35.7) 204 (100.0), 206 (98.8); **HRMS (EI)** calcd. $\text{C}_{18}\text{H}_{29}\text{BrO}_3$ 372.1300, found 372.1303; $\text{C}_{18}\text{H}_{29}\text{BrO}_3$ 374.1280, found 374.1270.

(4,5-bis(hexyloxy)-2-(trimethylsilyl)phenoxy)trimethylsilane (7)



In a round bottom flask of 250 mL a solution of 2-bromo-4,5-bis(hexyloxy)phenol (**6**, 2.44 g, 6.56 mmol) and HMDS (1.71 mL, 7.87 mmol) in THF (20 mL) was warmed to 80°C for 45 min.

The mixture was placed under reduced pressure to remove the solvent and under vacuum to remove the NH₃ and excess of HMDS for 45 min.

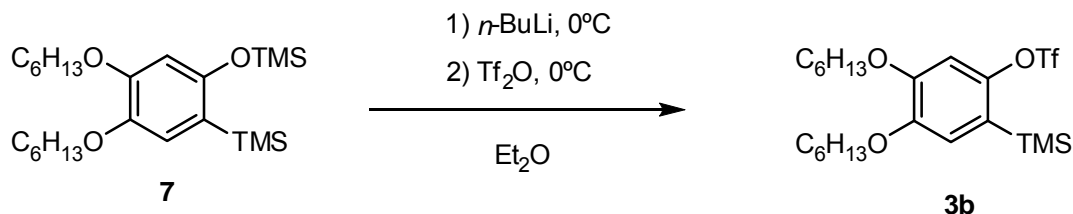
After checking by ¹H NMR the quantitative formation of the corresponding silyl ether, the crude was dissolved in dry THF (40 mL). Then TMEDA (0.50 mL, 3.28 mmol) was added, the solution was cooled to -100°C, and *n*-BuLi (5.42 mL, 2.42 M in hexan, 13.1 mmol) was added dropwise. The mixture was stirred for 1 h until the temperature reached -30°C. Then, it was cooled to again to -100°C, TMSCl (2.68 mL, 21.0 mmol) was added, and it was stirred for 1 h until the temperature reached -30°C. The reaction was worked up with a saturated solution of NaHCO₃ (50 mL) and the aqueous layer was extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and were concentrated under reduced pressure.

The residue was purified by column chromatography (Al₂O₃; 10% CH₂Cl₂ in hexane), obtaining **7**, (1.60 g, 56%) as a colourless oil.

¹H NMR (300 MHz, CDCl₃) δ ppm 6.87 (s, 1H), 6.36 (s, 1H), 3.95 (t, *J* = 6.6, 4H), 3.94 (t, *J* = 6.2, 4H), 1.87-1.70 (m, 4H), 1.54-1.41 (m, 4H), 1.01-0.85 (m, 8H), 1.41-1.29 (m, 6H), 0.31 (s, 9H), 0.23 (s, 9H); **¹³C NMR** (75 MHz, CDCl₃) δ ppm 155.22 (C), 151.22 (C), 143.01 (C), 122.29 (CH), 119.95 (C), 104.01 (CH), 70.85 (CH₂), 68.97 (CH₂), 31.67 (CH₂), 31.61 (CH₂), 29.65 (CH₂), 29.22 (CH₂), 25.74 (CH₂), 22.64 (CH₂), 14.04 (2CH₃), 0.69 (3CH₃), -0.75 (3CH₃); **MS**

(EI) m/z (rel. intensity %) 438 (M^+ , 100), 269 (24); **HRMS (EI)** calcd.
 $C_{24}H_{46}O_3Si_2$ 438.2986, found 438.2990.

4,5-bis(hexyloxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**3b**)

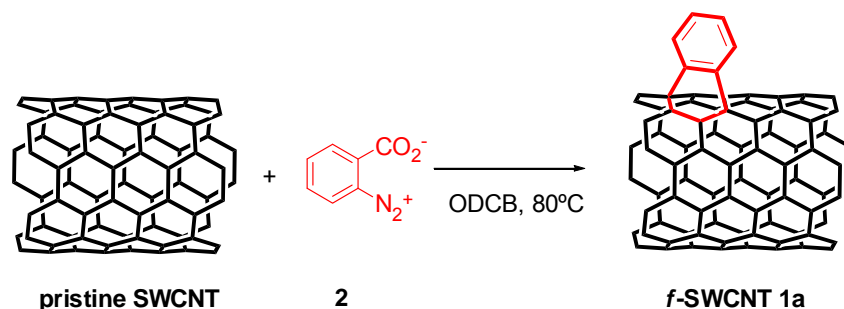


To a solution of **7** (1.52 g, 3.46 mmol) in Et₂O (40 mL) cooled to 0°C, *n*-BuLi (2.86 mL of 2.42 M solution in hexane, 6.92 mmol) was added dropwise, and the resulting suspension was stirred for 4 h. The solution was cooled again to 0°C and trifluoromethanesulfonic anhydride (1.23 mL, 6.92 mmol) was added and the resulting mixture was stirred overnight. The reaction was quenched with a saturated aqueous solution of NaHCO₃ (70 mL). The aqueous phase was extracted with Et₂O (3 x 70 mL). The combined organic phases were dried with Na₂SO₄. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography with silica gel to afford **3b** (1.47 g, 85 %) as colourless oil.

¹H NMR (300 MHz, CDCl₃) δ ppm 6.92 (s, 1H), 6.85 (s, 1H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.86-1.77 (m, 4H), 1.52-1.43 (m, 4H), 1.39-1.31 (m, 8H), 0.93-0.89 (m, 6H), 0.34 (s, 9H); **¹³C NMR** (75 MHz, CDCl₃) δ ppm 150.91 (C), 148.36 (C), 147.92 (C), 122.86 (C), 119.67 (CH), 105.89 (CH), 69.84 (CH₂), 69.30 (CH₂), 29.27 (CH₂), 28.90 (CH₂), 31.57 (CH₂), 31.50 (CH₂), 25.67 (CH₂), 25.61 (CH₂), 22.60 (CH₂), 22.56 (CH₂), 13.98 (CH₃), 13.95 (CH₃), -0.68 (3CH₃); **MS (EI)** *m/z* (rel. intensity %) 498 (M⁺, 46), 181 (100); **HRMS (EI)** calcd. C₂₂H₃₇F₃O₅SSi (M⁺) 498.2083, found 498.2087.

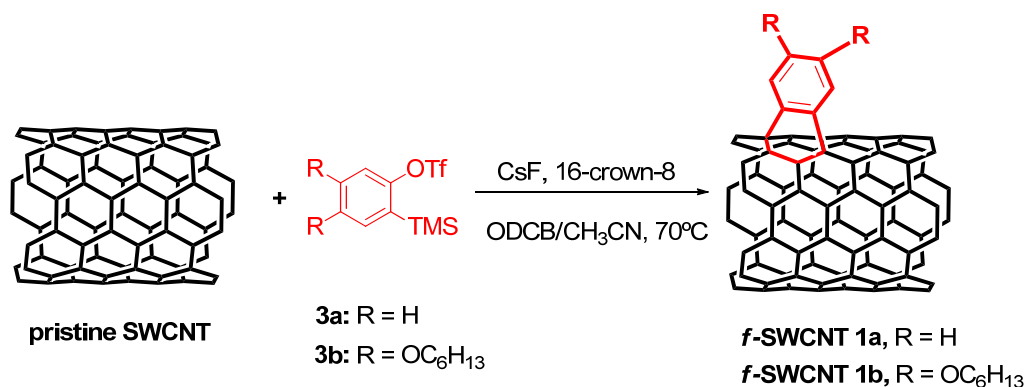
General procedure for functionalization of SWCNT with arynes.

Procedure (i):



To a suspension of SWCNT in ODCB heated to 80°C a suspension of the diazonium salt **2** in THF, prepared by a modification of Friedmann and Logullo's method, was added for 4 h through a pipette.^{4,5} The resulting mixture was filtered and washed with H₂O and hexane. The solid was purified by washing several times with Et₂O, DMF and MeOH to afford compound *f*-SWCNT **1a**.

Procedure (ii):



To a suspension under Argon of SWCNT in ODCB a solution of 2-(trimethylsilyl)aryl trifluoromethanesulfonate in CH₃CN was added. Then 18-crown-6 ether and dry CsF were added and the mixture was refluxed overnight. The resulting suspension was filtered (filter from MILLIPORE, FLGP type, $\Phi=$

⁴ L.Friedmann and F. M. Logullo, *J. Am. Chem. Soc.*, 1963, **85**, 1549.

⁵ For a detailed experimental procedure see A. Cobas, E. Guitián, L. Castedo, *J. Org. Chem.* 1993, **58**, 3113.

0.2 μm) and washed with H_2O and hexane. The solid was purified by washing several times with Et_2O , DMF and MeOH to afford *f*-SWCNT **1a** and **1b**.

Fig. S1. Raman spectra (785 nm, 1.58 eV) of pristine SWCNT (black line) and *f*-SWCNT **1a** (blue line), normalized at the G-band.

Fig. S2. TGA profile of SWCNT and *f*-SWCNT **1a** (prepared by procedure (i)). The thermogravimetric analysis showed a loss of weight of about 16% for *f*-SWCNT **1a**, corresponds to 1 benzene functional group *per* 35 carbon atoms.

Fig. S3. TGA profiles of SWCNT (black line), *f*-SWCNT **1a** (blue line) and *f*-SWCNT **1b** (red line). The TGA profiles were recorded in N₂ from 50 to 1000°C with a ramp of 10°C min⁻¹.

Fig. S4. C1s and O1s high resolution spectra for *f*-SWCNT **1a**, *f*-SWCNT **1b** and SWCNT.

Table S1. Atomic percentages derived from XPS for pristine SWCNT, *f*-SWCNT **1a** and **1b**.

Table S2. Comparative study of the functionalization for *f*-SWCNT **1a** and **1b**.

Fig. S5. Radial breathing modes (RBM) of SWCNT Raman spectra. The figure shows the calculated diameters of our SWCNTs range from 0.88 to 1.49 nm (with laser of 1.58 eV, 785 nm) and from 0.79 to 1.77 nm (laser of 2.33 eV, 532 nm).

Fig. S6. UV-Visible-NIR spectra, recorded in DMF, of pristine SWCNT and *f*-SWCNTs **1a** and **1b**.

Fig. S7. FT-IR spectra of *f*-SWCNT **1b** in KBr pellets.

Fig. S8. ^1H NMR spectra (500 MHz, CDCl_3) of compound **5**.

Fig. S9. ^{13}C -DEPT NMR spectra (125 MHz, CDCl_3) of compound **5**.

Fig. S10. ^1H NMR spectra (300 MHz, CDCl_3) of compound **6**.

Fig. S11. ^{13}C -DEPT NMR spectra (125 MHz, CDCl_3) of compound **6**.

Fig. S12. ^1H NMR spectra (300 MHz, CDCl_3) of of compound **7**.

Fig. S13. ^{13}C -DEPT NMR spectra (75 MHz, CDCl_3) of compound **7**.

Fig. S14. ^1H NMR spectra (300 MHz, CDCl_3) of compound **3b**.

Fig. S15. ^{13}C -DEPT NMR spectra (75 MHz, CDCl_3) of compound **3b**.

Fig. S1.

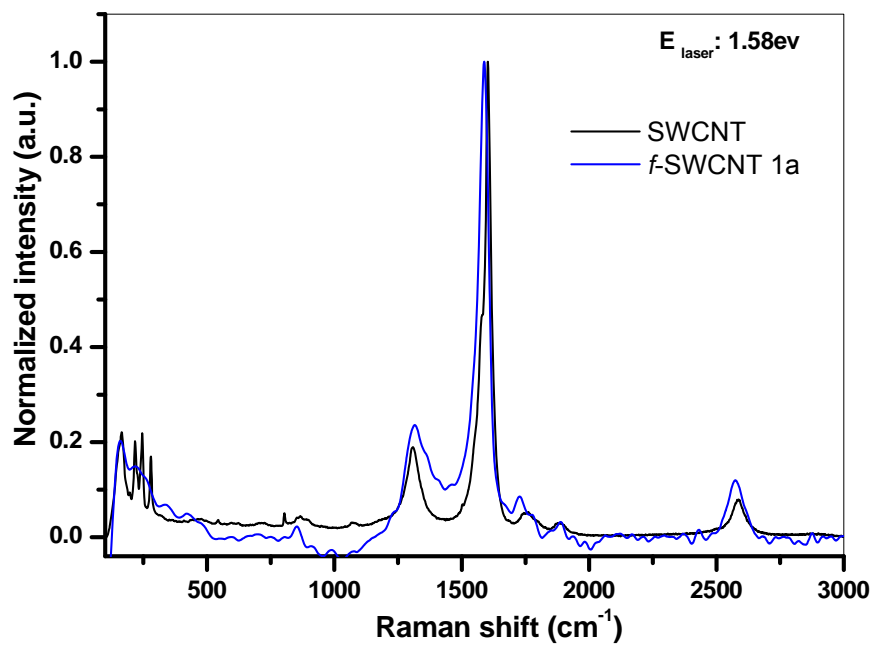


Fig. S2

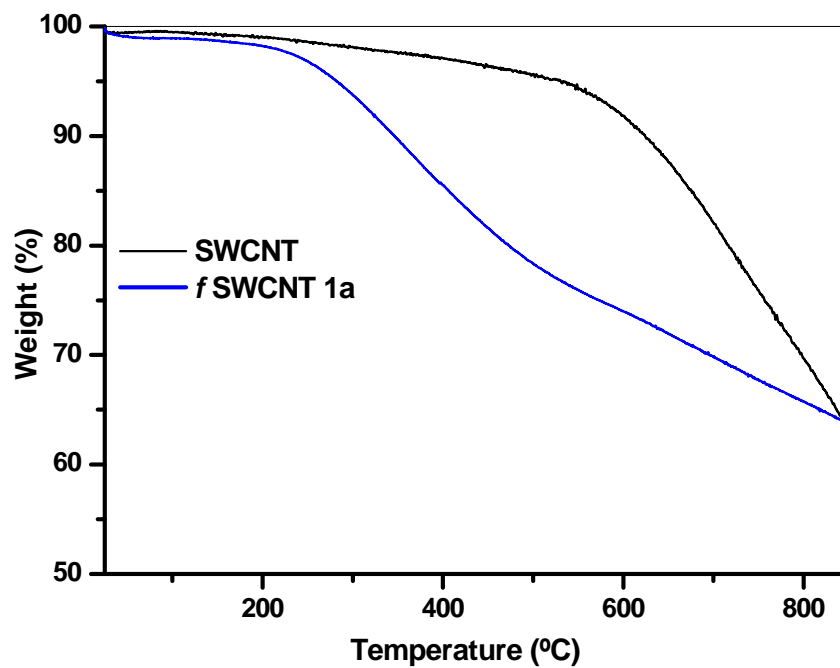


Fig. S3.

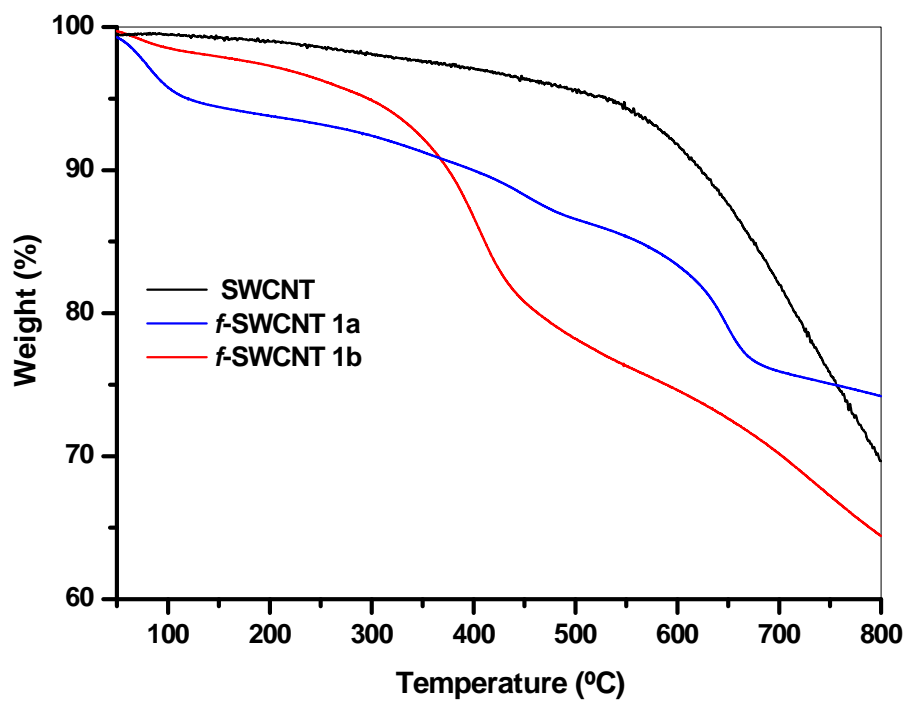


Fig. S4.

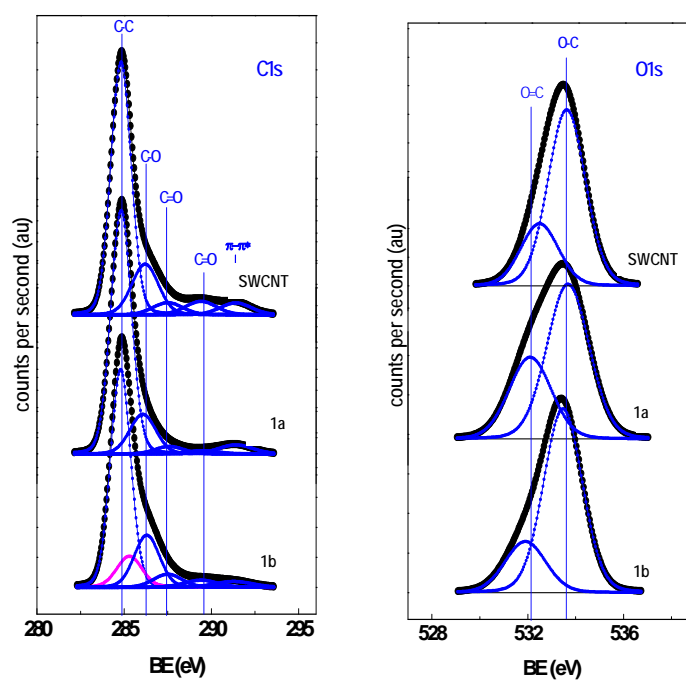


Table S1

Sample	O (%at)	C (%at)
SWCNT	7.6	92.4
<i>f</i> -SWCNT 1a	1.8	98.2
<i>f</i> -SWCNT 1b	6.5	93.5

Table S2.

Sample	^aTGA weight loss (%)	Functional group coverage	^cRaman D/G ratio
<i>f</i> -SWCNT 1a (procedure i)	16	35	0.24
<i>f</i> -SWCNT 1a (procedure ii)	9	64	0.30
<i>f</i> -SWCNT 1b (procedure ii)	15	130	0.21

^aTGA-determined weight loss. ^b Calculated D/G ratios from Raman spectra

Fig. S5.

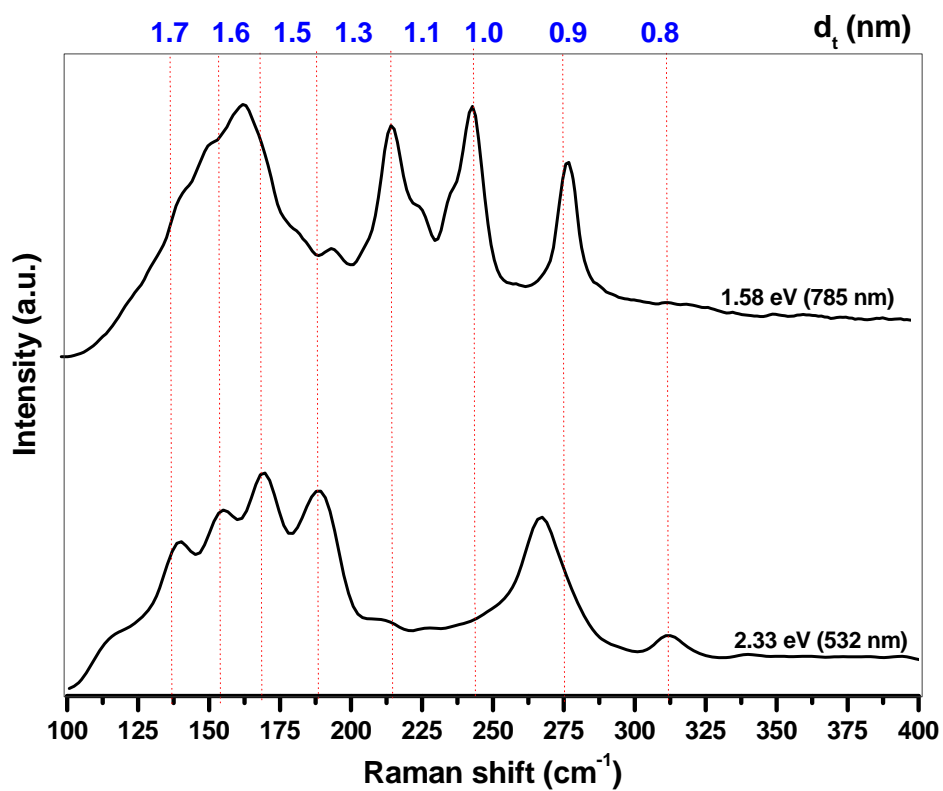


Fig. S6

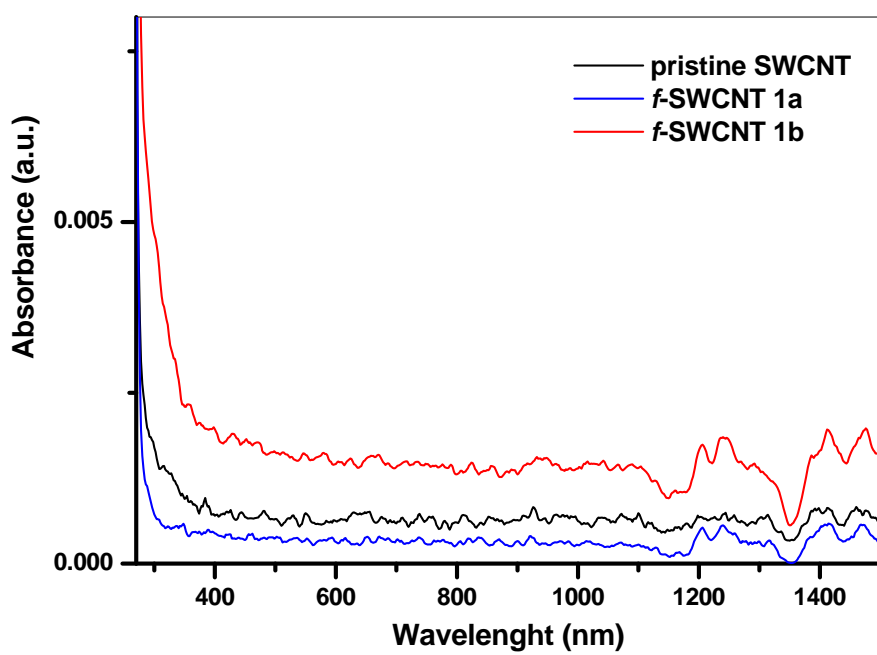


Fig. S7.

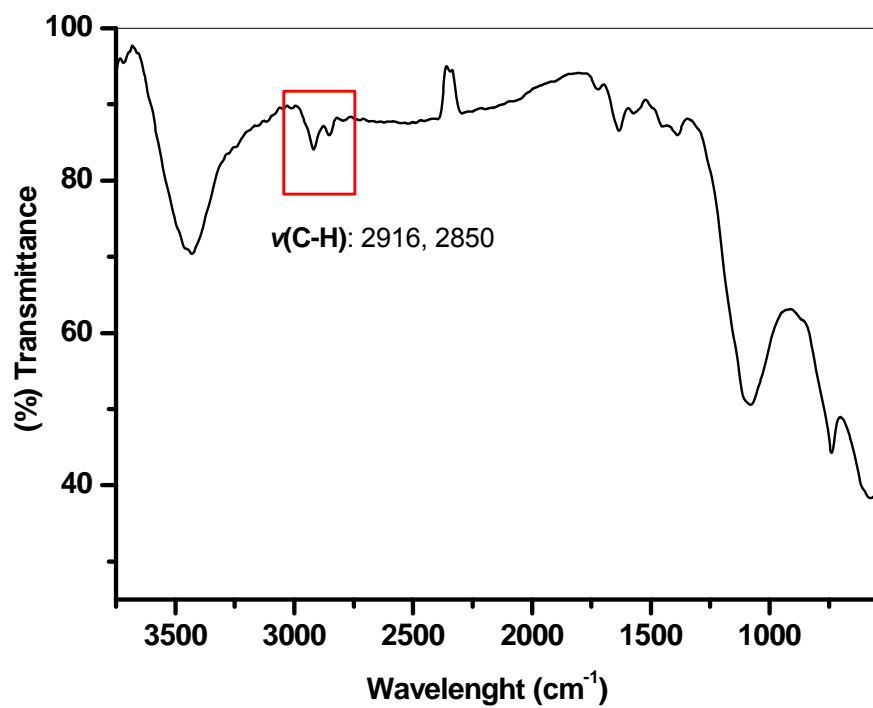


Fig. S8.

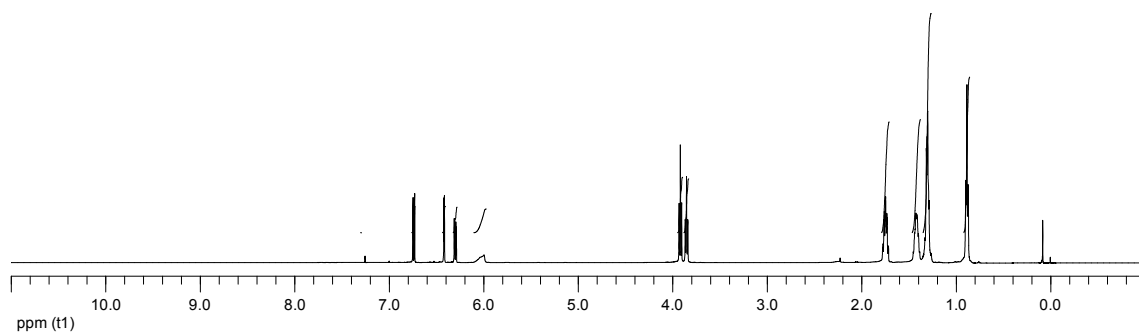
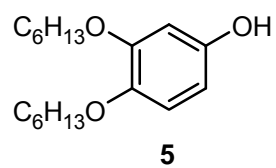


Fig. S9.

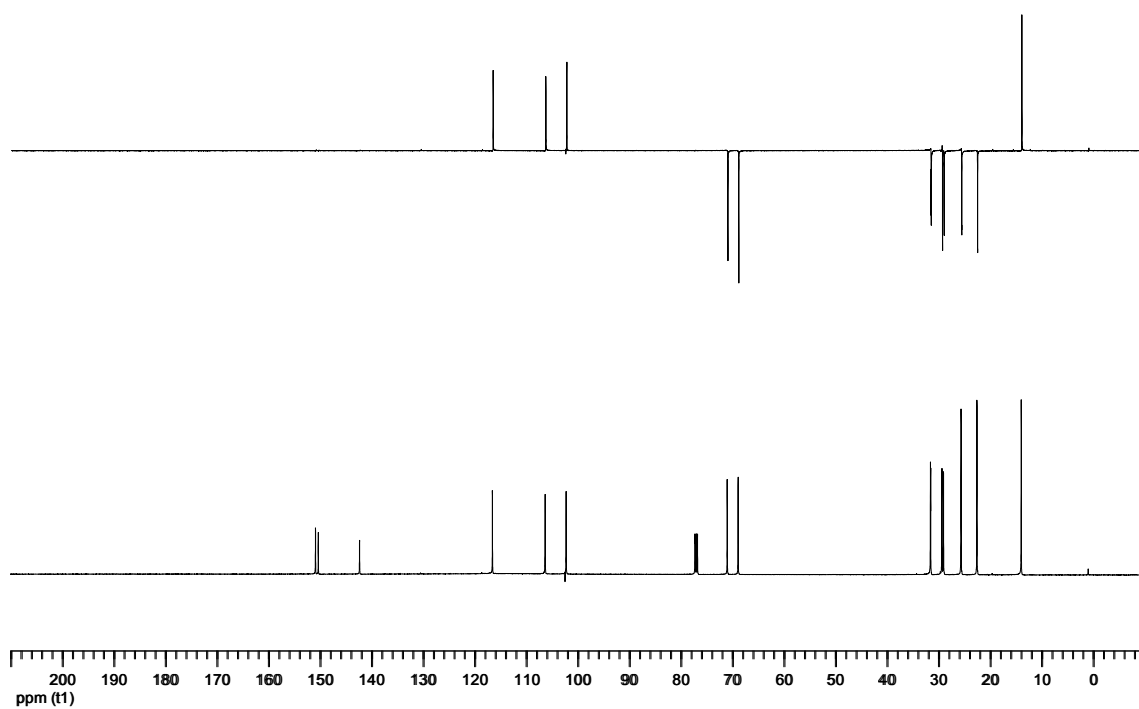
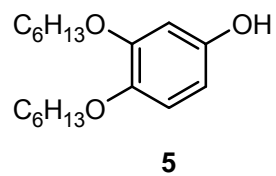


Fig. S10.

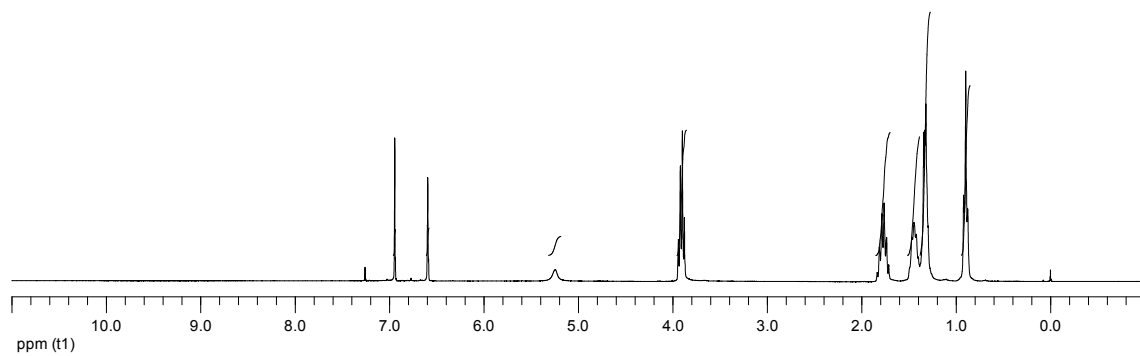
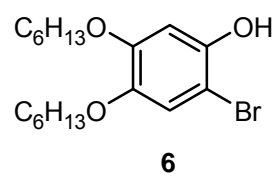


Fig. S11.

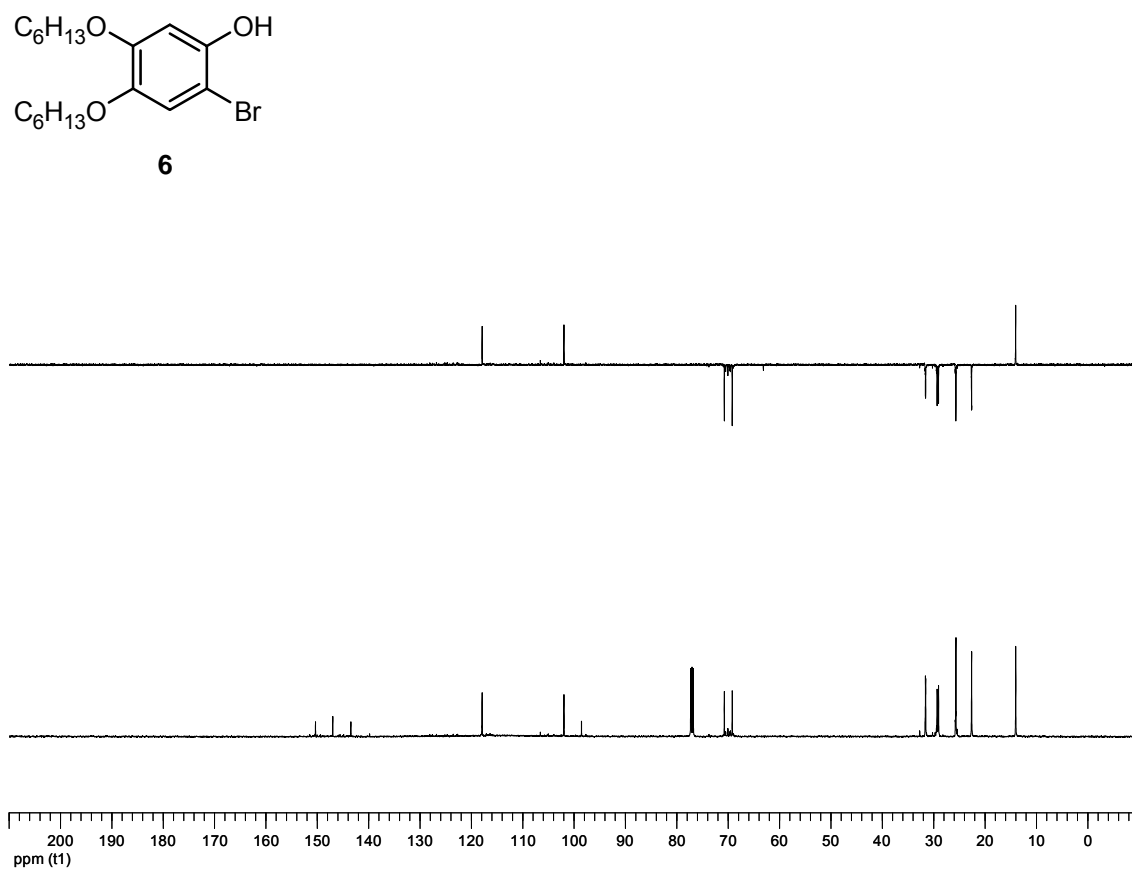


Fig. S12.

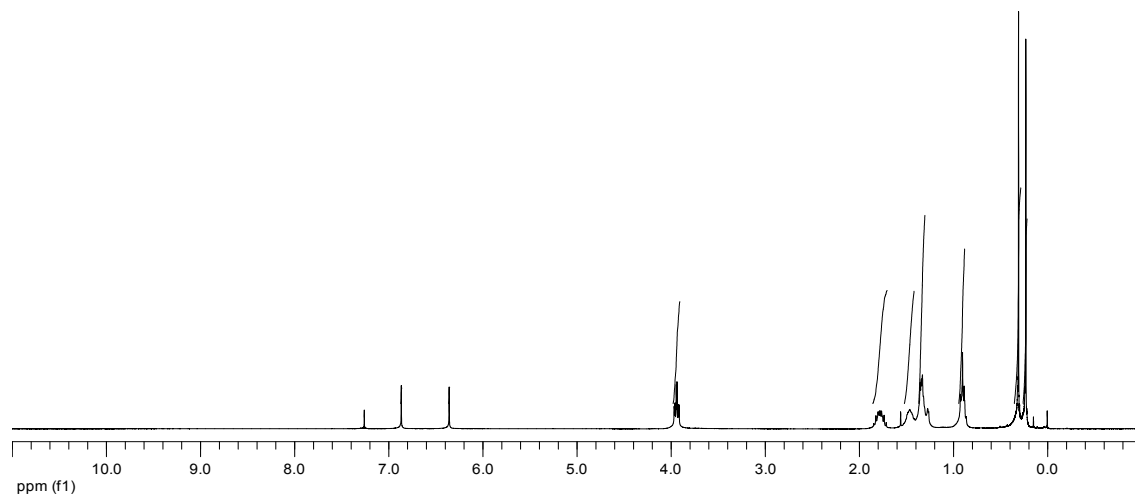
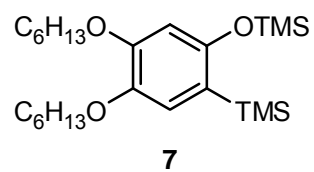


Fig. S13.

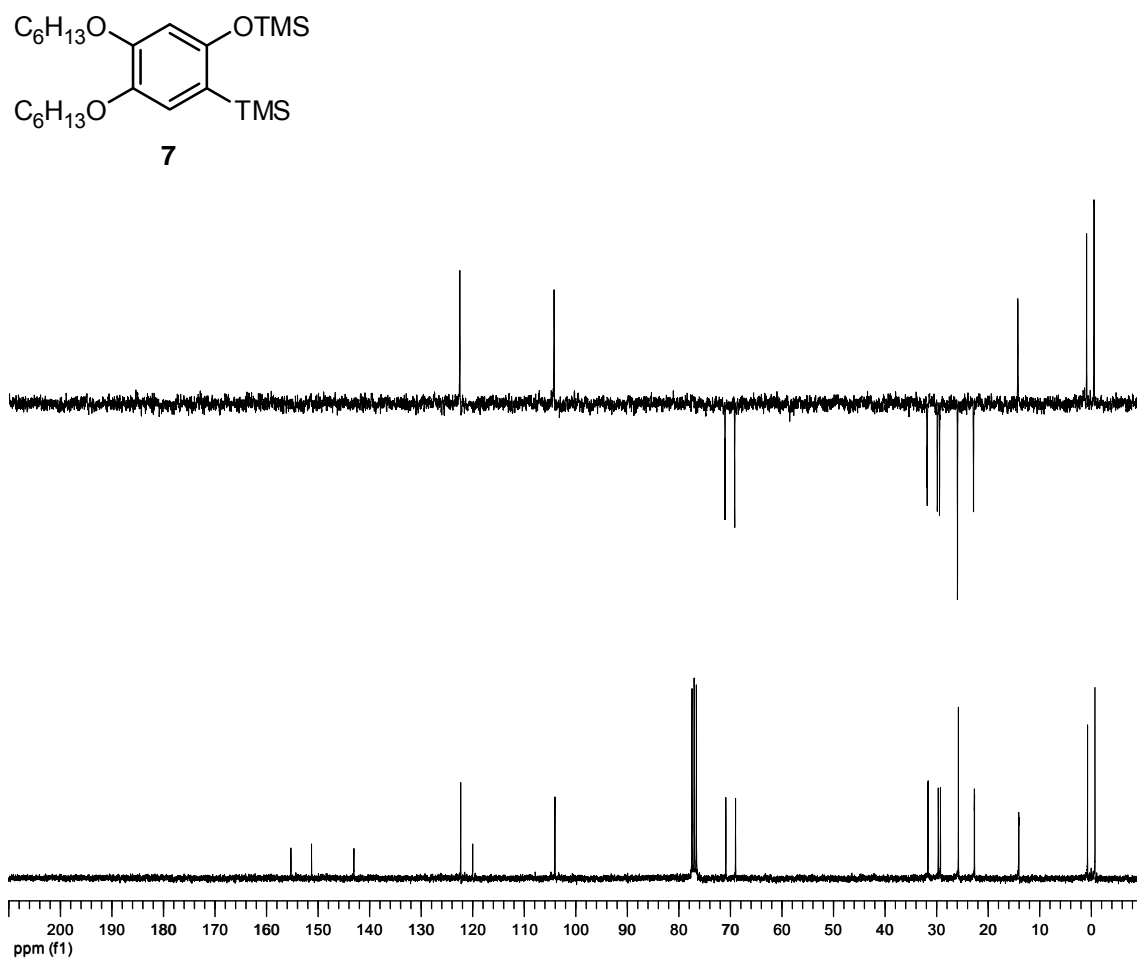


Fig. S14.

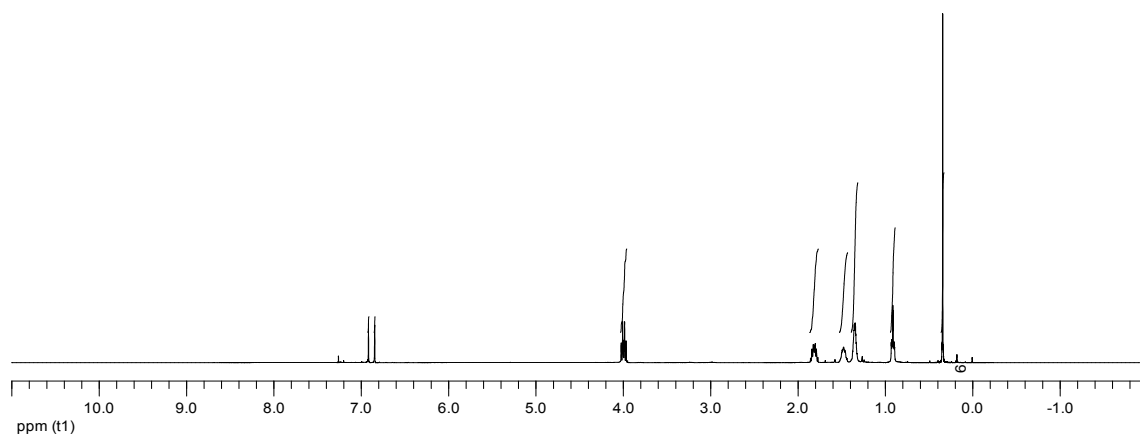
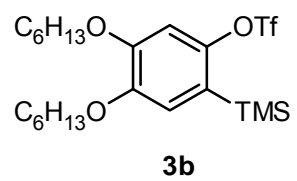


Fig. S15.

