Supporting Information

Charge Transfer Structure-Reactivity Dependence of Fullerene/Single-Walled Carbon Nanotube Heterojunctions

Andrew J. Hilmer, Kevin Tvrdy, Jingqing Zhang, and Michael S. Strano

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

CORRESPONDING AUTHOR EMAIL ADDRESS: strano@mit.edu

TABLE OF CONTENTS

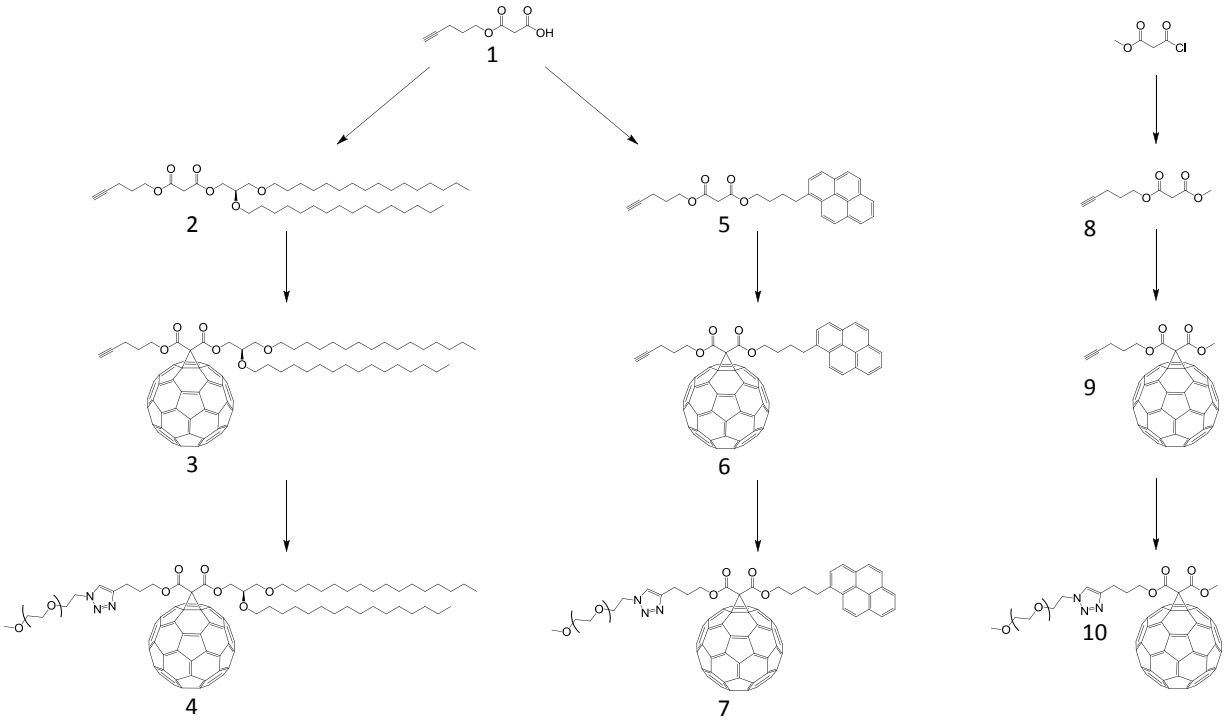


Figure S1. Synthetic scheme for PEGylated methanofullerenes **4, 7,** and **10**.

1. Synthesis

*Synthesis of **3-oxo-3-(pent-4-yn-1-yloxy)propanoic acid (1)***

To a thoroughly dried reaction vessel, equipped with a reflux condenser, was added 4.65g (0.032 moles) of Meldrum's acid. The ambient atmosphere was replaced with nitrogen before adding 3 mL of 4-pentyn-1-ol (0.032 moles), followed by 120 mL of anhydrous toluene. The solution was refluxed for 2 hours, or until TLC indicated completion of the reaction. Toluene was then removed under reduced pressure, and the resulting residue was purified by column chromatography (DCM:MeOH), eluting on a gradient from 40:1 to 20:1. Removal of solvent yielded a clear liquid which solidified upon standing. Yield: 4.25g (77%).

*Synthesis of **(R)-2,3-bis(hexadecyloxy)propyl pent-4-yn-1-yl malonate (2)***

0.315 g (1.849mmol) of compound (1), 1.0 g (2.218mmol) of 1,2-O-dihexadecyl-sn-glycerol, and 47 mg (0.388mmol) of DMAP were dissolved in anhydrous dichloromethane (8mL) and cooled in an ice bath. The ambient atmosphere was replaced with N_2, and a solution of *N,N*'-dicyclohexylcarbodiimide (0.381g, 1.849mmol) in 4mL anhydrous DCM was added dropwise. The solution was reacted at 0°C for 2 hours, allowed to warm to room temperature, and reacted overnight. The insoluble urea was filtered off, solvent removed, and the crude product purified by column chromatography, eluting with dichloromethane, to give the product as a white solid. Yield: 1.02g (80%).

*Synthesis of **(3)***

Anhydrous toluene (75mL) was added to 0.39g (541 µmol) of C60-fullerene and 0.25g (361 µmol) of compound **(2)**, and the resulting suspension was bubbled with nitrogen. The reaction vessel was surrounded with foil, and iodine (0.101g, 398µmol) was added. Under a nitrogen atmosphere, a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) – 70uL DBU (466µmol) in 50mL anhydrous toluene – was added dropwise over 1-2 hours. After complete addition, the solution was allowed to stir 24 hours. Solvent was removed in the presence of silica gel and the product purified by column chromatography, eluting on a gradient from 3:1 to 1:1 Hexanes:Toluene. Removal of solvent gave the product as a brown solid (211mg, 41%). The C71 and C85 analogues were synthesized in a similar manner.

*Synthesis of methanofullerene **(4)** - Lipid-C61-PEG*

Compound **(3)** (25mg, 17.7µmol) and mPEG-N_3-5kDa (177mg, 35.4 µmol) were dissolved in 1mL of dichloromethane, and 1mL of water was subsequently added. Then Cu(0) – 1-2 pieces – was added, followed by $CuSO_4$ (1.1mg, 4.4µmol) and sodium ascorbate (1.75mg, 8.83µmol). The resulting mixture was allowed to react at room temperature overnight under vigorous stirring. The reaction mixture was diluted with dichloromethane and washed with water. The organic layer was then dried and filtered through a short plug of regular-phase silica gel (DCM). Eluting with DCM, the PEGylated product remains immobilized, while unreacted **(3)** is eluted. The crude PEGylated product can then be eluted using 4:1 DCM:MeOH. After removal of unreacted **(3)**, the PEGylated product was purified by reversed-phase chromatography, eluting on a gradient from 4:1 to 3:2 MeOH:DCM. Removal of solvent gave the product as a brown solid (73mg, 64%). The C71 and C85 analogues were synthesized in a similar manner.

*Synthesis of **pent-4-yn-1-yl (4-(pyren-1-yl)butyl) malonate (5)***

0.372 g (2.187mmol) of compound (1), 0.6 g (2.624mmol) of 1-Pyrenebutanol, and 56 mg (0.459mmol) of DMAP were dissolved in anhydrous dichloromethane (10mL) and cooled in an ice bath. The ambient atmosphere was replaced with N_2, and a solution of *N,N*'-dicyclohexylcarbodiimide (0.451g, 2.187mmol) in 5mL anhydrous DCM was added dropwise. The solution was reacted at 0°C for 2 hours, allowed to warm to room temperature, and reacted overnight. The insoluble urea was filtered off, and the solvent removed in the presence of silica gel. The product-containing silica gel was carefully added to the top of a pre-packed column, and purified by eluting with 6:1 Hexanes:Ethyl Acetate to give the product as a white to off-white solid (0.81g, 87%).

*Synthesis of **(6)***

Anhydrous toluene (75mL) was added to 0.38g (0.527 mmol) of C60-fullerene and 0.15g (0.352 mmol) of compound **(5)**, and the resulting suspension was bubbled with nitrogen. The reaction vessel was surrounded with foil, and iodine (0.098g, 0.386mmol) was added. Under a nitrogen

atmosphere, a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) – 68uL DBU (0.460mmol) in 50mL anhydrous toluene – was added dropwise over 1-2 hours. After complete addition, the solution was allowed to stir 24 hours. Solvent was removed in the presence of silica gel and the product purified by column chromatography, eluting on a gradient from 3:1 to 1:1 Hexanes:Toluene. Removal of solvent gave the product as a brown solid (181mg, 45%).

*Synthesis of **(7)** - Pyrene-C61-PEG*

Compound **(6)** (20mg, 17.5µmol) and mPEG-N_3-5kDa (175mg, 35µmol) were dissolved in 1mL of dichloromethane, and 1mL of water was subsequently added. Then Cu(0) – 1-2 pieces – was added, followed by $CuSO_4$ (1.1mg, 4.4µmol) and sodium ascorbate (1.73mg, 8.73µmol). The resulting mixture was allowed to react at room temperature overnight under vigorous stirring. The reaction mixture was diluted with dichloromethane and washed with water. The organic layer was then dried and filtered through a short plug of regular-phase silica gel (DCM). Eluting with DCM, the PEGylated product remains immobilized, while unreacted **(6)** is eluted. The crude PEGylated product can then be eluted using 4:1 DCM:MeOH. After removal of unreacted **(6)**, the PEGylated product was purified by reversed-phase chromatography, eluting on a gradient from 8:1 to 4:1 MeOH:DCM. Removal of solvent gave the product as a brown solid (63mg, 59%).

*Synthesis of **methyl pent-4-yn-1-yl malonate (8)***

4-pentyn-1-ol (0.607mL, 6.5mmol) and triethylamine (1.09mL, 7.83mmol) were added to 15mL of anhydrous dichloromethane. The ambient atmosphere was replaced with N_2 and the solution was cooled in an ice bath. Methyl-3-chloro-3-oxopropionate (0.70mL, 6.52mmol) was added dropwise, and the reaction solution was stirred at 0°C for 30 minutes, then warmed to room temperature and stirred an additional 24 hours. Water was added, the organic layer collected, and the aqueous layer extracted with 3 volumes of ethyl acetate. The combined organic fractions were washed with sodium bicarbonate and brine, dried over $MgSO_4$, and the solvent removed under vacuum. The crude product was purified by column chromatography (DCM) to give the product as a colorless to light yellow oil (0.972g, 81%).

*Synthesis of **(9)***

Anhydrous toluene (120mL) was added to 0.646g (0.896 mmol) of C60-fullerene and 0.11g (0.597 mmol) of compound **(8)**, and the resulting suspension was bubbled with nitrogen. The reaction vessel was surrounded with foil, and iodine (0.167g, 0.776mmol) was added. Under a nitrogen atmosphere, a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) – 116uL DBU (0.775mmol) in 90mL anhydrous toluene – was added dropwise over 1-2 hours. After complete addition, the solution was allowed to stir 24 hours. Solvent was removed in the presence of silica gel and the product purified by column chromatography, eluting on a gradient from 3:1 to 1:1 Hexanes:Toluene. Removal of solvent gave the product as a brown solid (189mg, 35%).

*Synthesis of methanofullerene **(10)** - Methyl-C61-PEG*

Compound **(9)** (15mg, 16.6µmol) and mPEG-N_3-5kDa (166mg, 33.2µmol) were dissolved in 1mL of dichloromethane, and 1mL of water was subsequently added. Then Cu(0) – 1-2 pieces – was added, followed by $CuSO_4$ (1.04mg, 4.2µmol) and sodium ascorbate (1.65mg, 8.33µmol). The resulting mixture was allowed to react at room temperature overnight under vigorous stirring. The reaction mixture was diluted with dichloromethane and washed with water. The organic layer was then dried and filtered through a short plug of regular-phase silica gel (DCM). Eluting with DCM, the PEGylated product remains immobilized, while unreacted **(9)** is eluted. The crude PEGylated product can then be eluted using 4:1 DCM:MeOH. After removal of unreacted **(9)**, the PEGylated product was purified by reversed-phase chromatography, eluting on a gradient from 8:1 to 5:1 MeOH:DCM. Removal of solvent gave the product as a brown solid (50mg, 51%).

*Synthesis of **(R)-1-((1-(hexadecyloxy)-3-(pent-4-yn-1-yloxy)propan-2-yl)oxy)hexadecane (11)***

Sodium hydride (44.4mg, 1.85mmol) was placed in a reaction flask, and the ambient atmosphere replaced with nitrogen. A solution of 1,2-O-dihexadecyl-sn-glycerol (0.50g, 0.924mmol) in anhydrous THF (5mL) was then added. After 30 minutes, a solution of 1-Iodo-4-pentyne (0.210mL, 1.85mmol) in anhydrous THF (5mL) was added. The solution was heated to reflux, and allowed to react for 2 hours. The reaction was quenched with water (10mL), and the crude product extracted with DCM (3x). The combined organic layers were dried, and the solvent removed under reduced pressure. The residue was purified by column chromatography (20:1

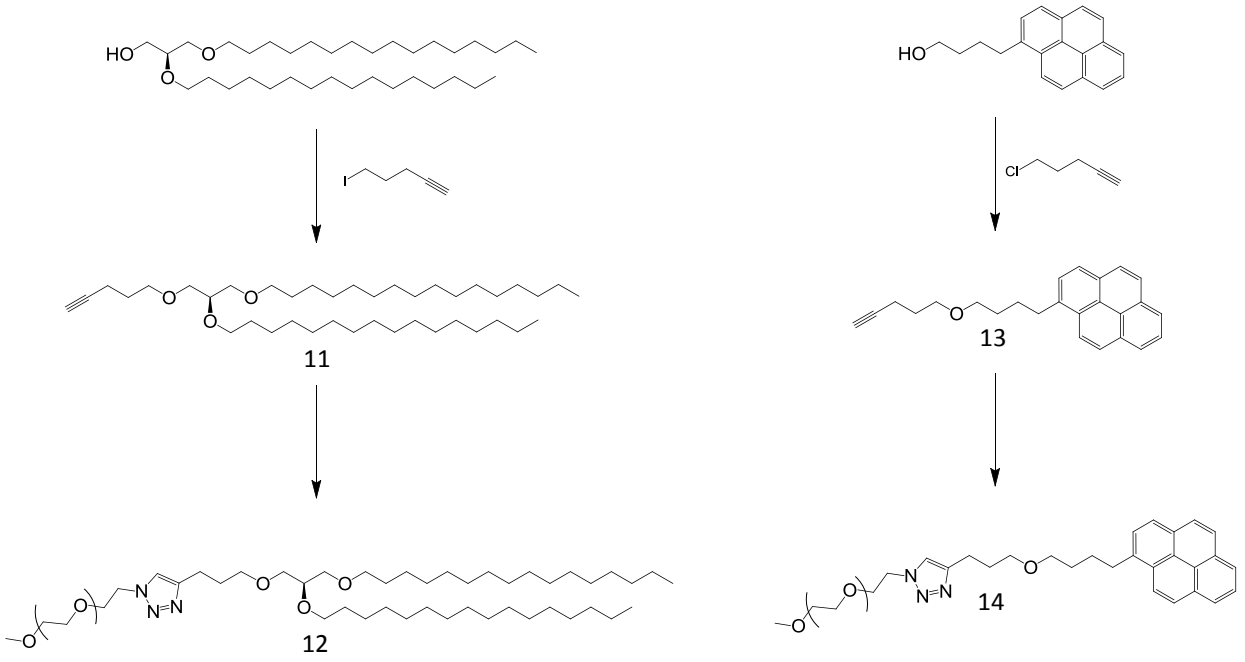


Figure S2. Synthetic scheme for control molecules **12** and **14**.

Hexanes:Ethyl Acetate) to give the product as a colorless, viscous oil (65mg, 12%).

*Synthesis of **(12)** – Lipid-PEG*

Compound **(11)** (21.2mg, 0.035mmol) and mPEG-N_3-5kDa (262mg, 0.052mmol) were dissolved in 1mL of dichloromethane, and 1mL of water was subsequently added. Then Cu(0) – 1-2 pieces – was added, followed by $CuSO_4$ (2.18mg, 8.7µmol) and sodium ascorbate (3.46mg, 17.4µmol). The resulting mixture was allowed to react at room temperature overnight under vigorous stirring. The reaction mixture was diluted with dichloromethane and washed with water. The organic layer was then dried, and the solvent removed under reduced pressure. The crude product was purified by reversed phase chromatography, eluting with 9:1 MeOH:DCM. Iodine vapor was used as a TLC developing agent. Removal of the solvent gave the product as a white solid (96mg, 49%).

*Synthesis of **1-(4-(pent-4-yn-1-yloxy)butyl)pyrene (13)***

Sodium hydride (70mg, 2.92mmol) was placed in a reaction flask, and the ambient atmosphere replaced with nitrogen. A solution of 1-pyrenebutanol (0.40g, 1.46mmol) in anhydrous DMF (4mL) was then added. After 30 minutes, a solution of 1-Chloro-4-pentyne (0.463mL, 4.4mmol) in anhydrous DMF (4mL) was added. The solution was heated to 80°C, and allowed to react for 2 hours. The reaction was quenched with water (10mL), and the crude product extracted with DCM (3x). The combined organic layers were dried, and the solvent removed under reduced pressure. The residue was purified by column chromatography (20:1 Hexanes:Ethyl Acetate) to give the product as a white solid (176mg, 35%).

*Synthesis of **(14)** – Pyrene-PEG*

Compound **(13)** (12mg, 0.035mmol) and mPEG-N_3-5kDa (264mg, 0.053mmol) were dissolved in 1mL of dichloromethane, and 1mL of water was subsequently added. Then Cu(0) – 1-2 pieces – was added, followed by $CuSO_4$ (2.2mg, 8.8µmol) and sodium ascorbate (3.49mg, 17.6µmol). The resulting mixture was allowed to react at room temperature overnight under vigorous stirring. The reaction mixture was diluted with dichloromethane and washed with water. The organic layer was then dried, and the solvent removed under reduced pressure. The crude product was purified by reversed phase chromatography, eluting with MeOH:DCM. Removal of the solvent gave the product as a white solid (150mg, 80%).

2. Solvatochromism Model

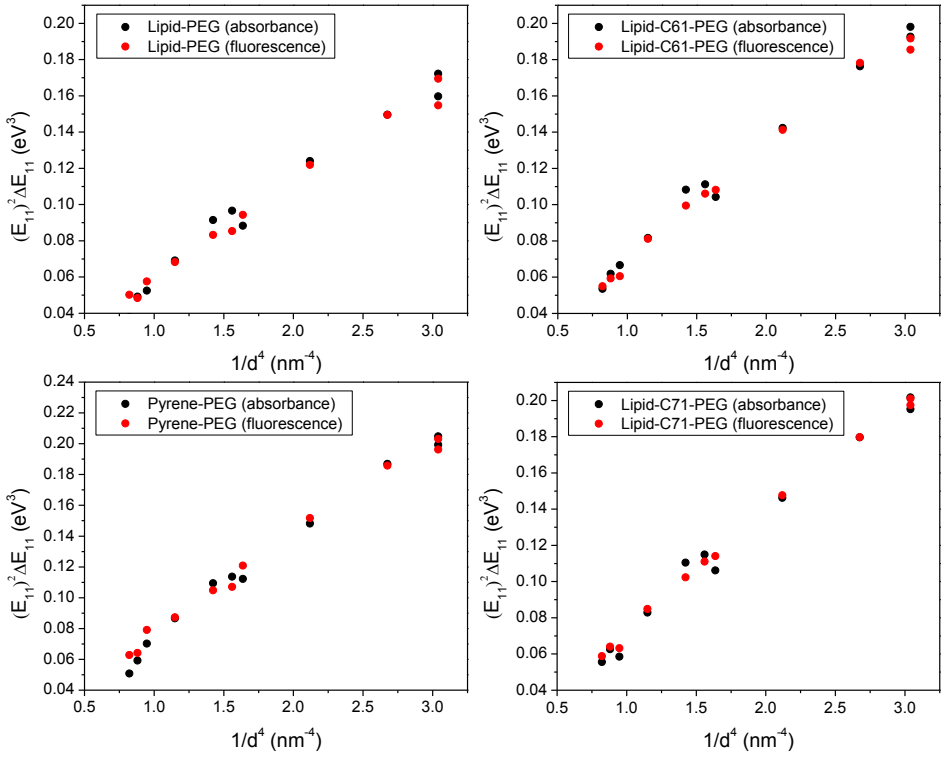


Figure S3. Comparison of solvatochromic analysis plots obtained from excitation-emission plots (red) or deconvoluted absorbance spectra (black) for the 4 amphiphilic systems in which excitation-emission plots were possible. Good agreement was observed between the two methods.

Table S1 – Comparison between predicted water coverages based on fluorescence and absorbance measturements.

	Water Coverage	
Amphiphile	Fluorescence	Absorbance
Lipid-PEG	5.7%	--
Pyrene-PEG	10.9%	11.1%
Lipid-C61-PEG	9.5-11.3%	7.4-9.3%
Lipid-C71-PEG	12-14.0%	8.8-10.8%
Lipid-C85-PEG	--	9.8-13.7%
Pyrene-C61-PEG	--	40.4-40.7%

3. Absorbance

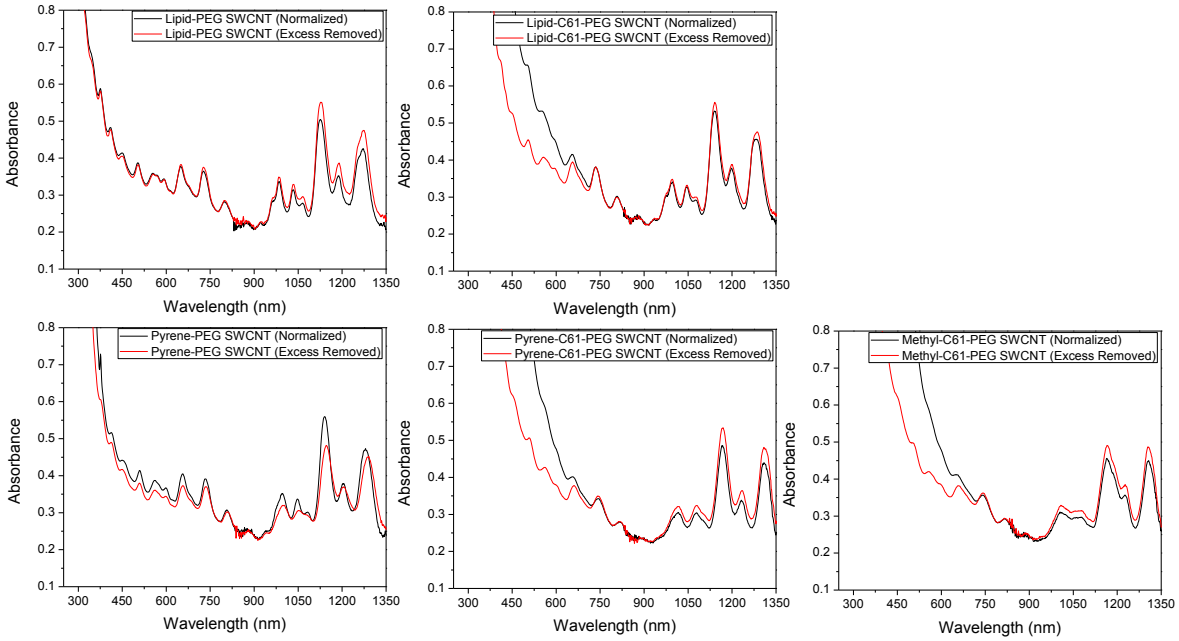


Figure S4. Absorbance spectra of SWCNT suspensions in amphiphiles *(4)*, *(7)*, *(10)*, *(12)*, and *(14)* before (black) and after (red) removal of free amphiphile using 1000 kDa MWCO centrifugal filters (Sartorius Vivaspin). In order to account for slight concentration differences, absorbance spectra have been adjusted by a constant such that their absorbance values near 900nm are similar. Despite small redistributions in chirality, most spectra taken before and after removal are fairly consistent. However, the pyrene-PEG sample shows evident decrease in peak-to-valley ratio, as well as slight peak shifting, indicating that aggregation is occurring. Visible aggregates were also observable the pyrene-PEG system after the removal of excess surfactant. The onset of C_{61} fullerene absorbance occurs below ~715nm. Therefore, among the fullerene derivatives, a decrease in the absorbance at shorter wavelengths indicates that excess surfactant is being removed from the system. Evidence of excess surfactant removal was also indicated by the presence of fullerene absorbance in the filtrate. 100 kDa MWCO membranes (Millipore, Amicon Ultra) showed no evidence of fullerene in the filtrate (data not shown).

4. AFM

Pyrene-PEG

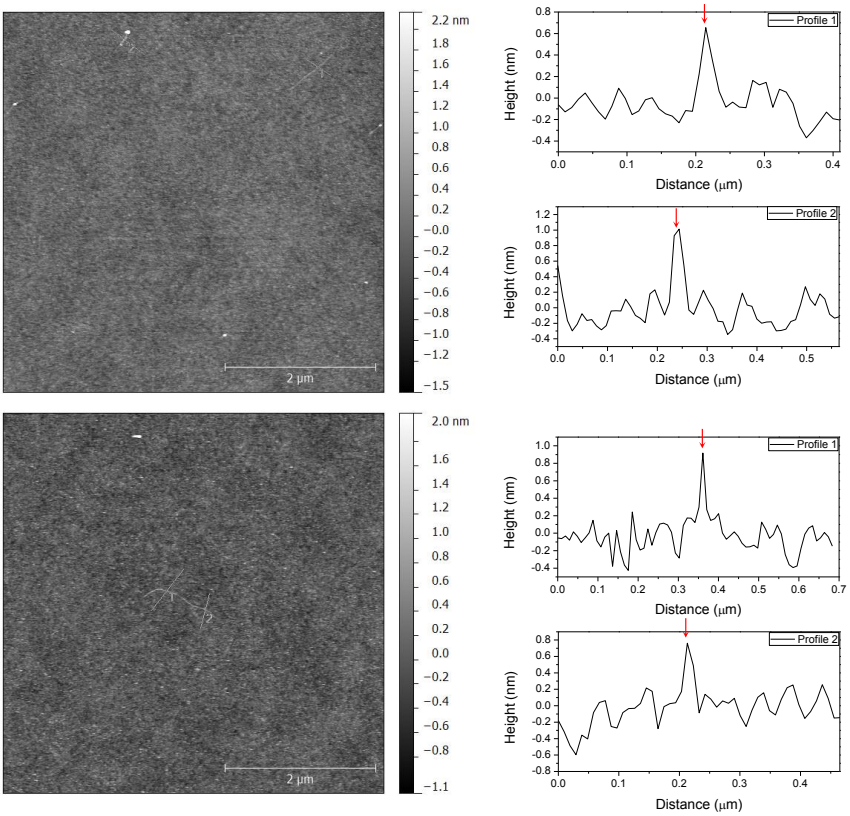


Figure S5. AFM images of the pyrene-PEG suspension, pre-centrifugal filtration, showed individually dispersed SWCNTs.

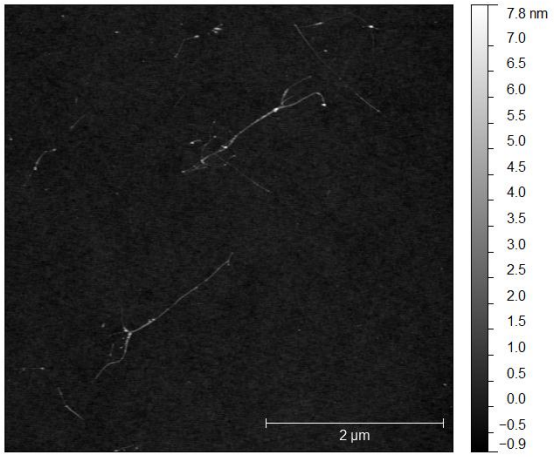


Figure S6. AFM images of the pyrene-PEG suspension, post-centrifugal filtration, showed a mixture of individually dispersed SWCNTs and small bundles.

Pyrene-C61-PEG

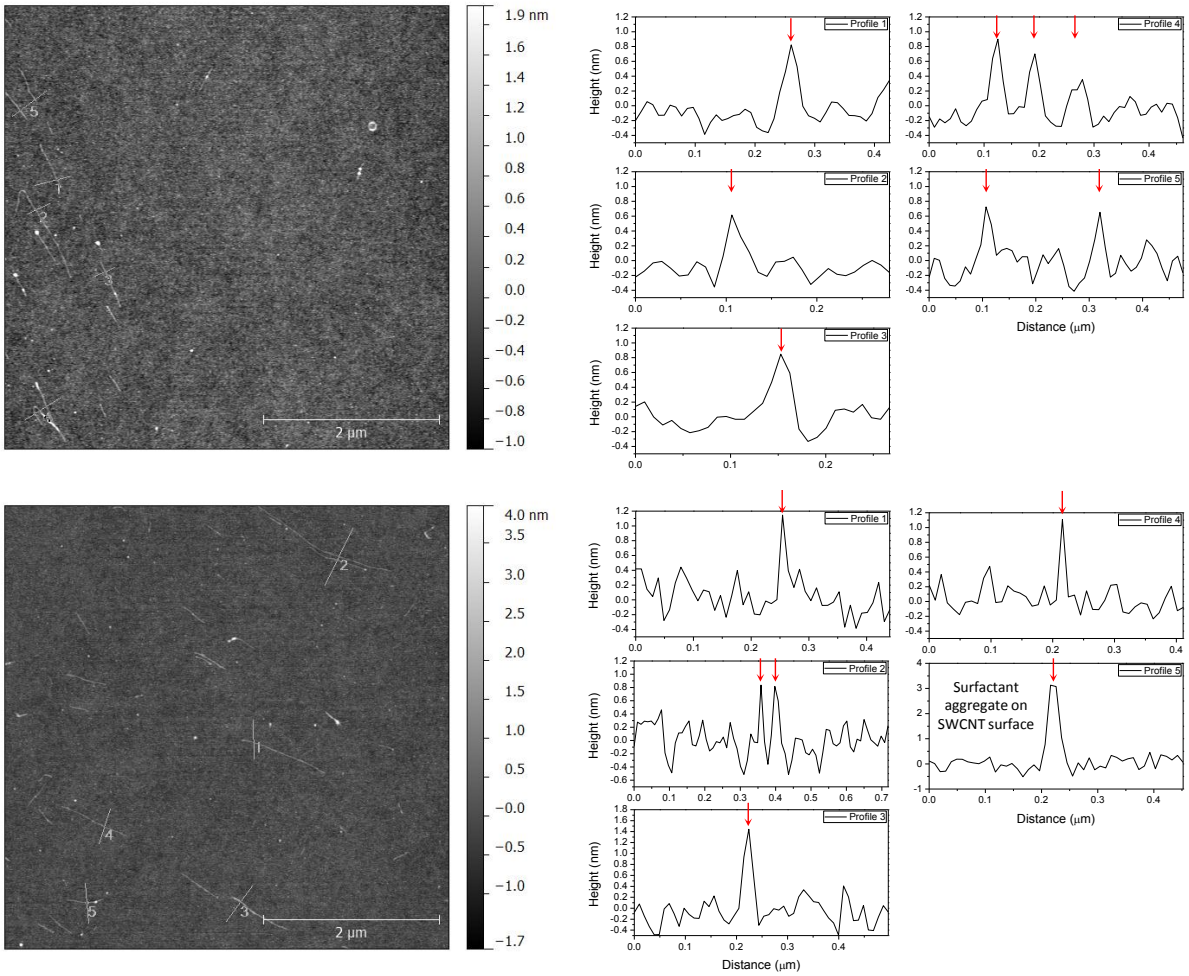


Figure S7. AFM images of the pyrene-C61-PEG suspension showed individually dispersed SWCNTs.

Lipid-PEG

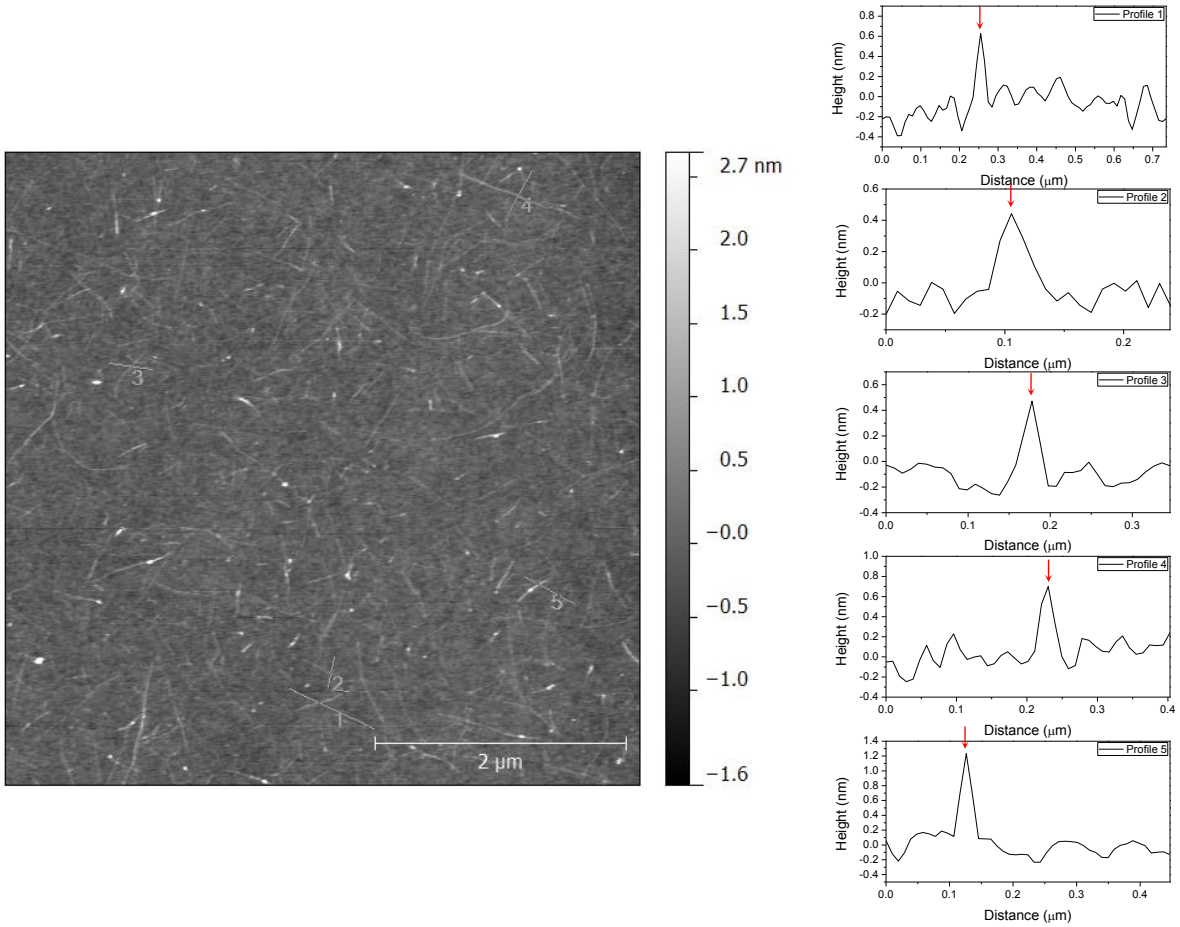


Figure S8. AFM images of the lipid-PEG suspension showed individually dispersed SWCNTs.

Lipid-C61-PEG

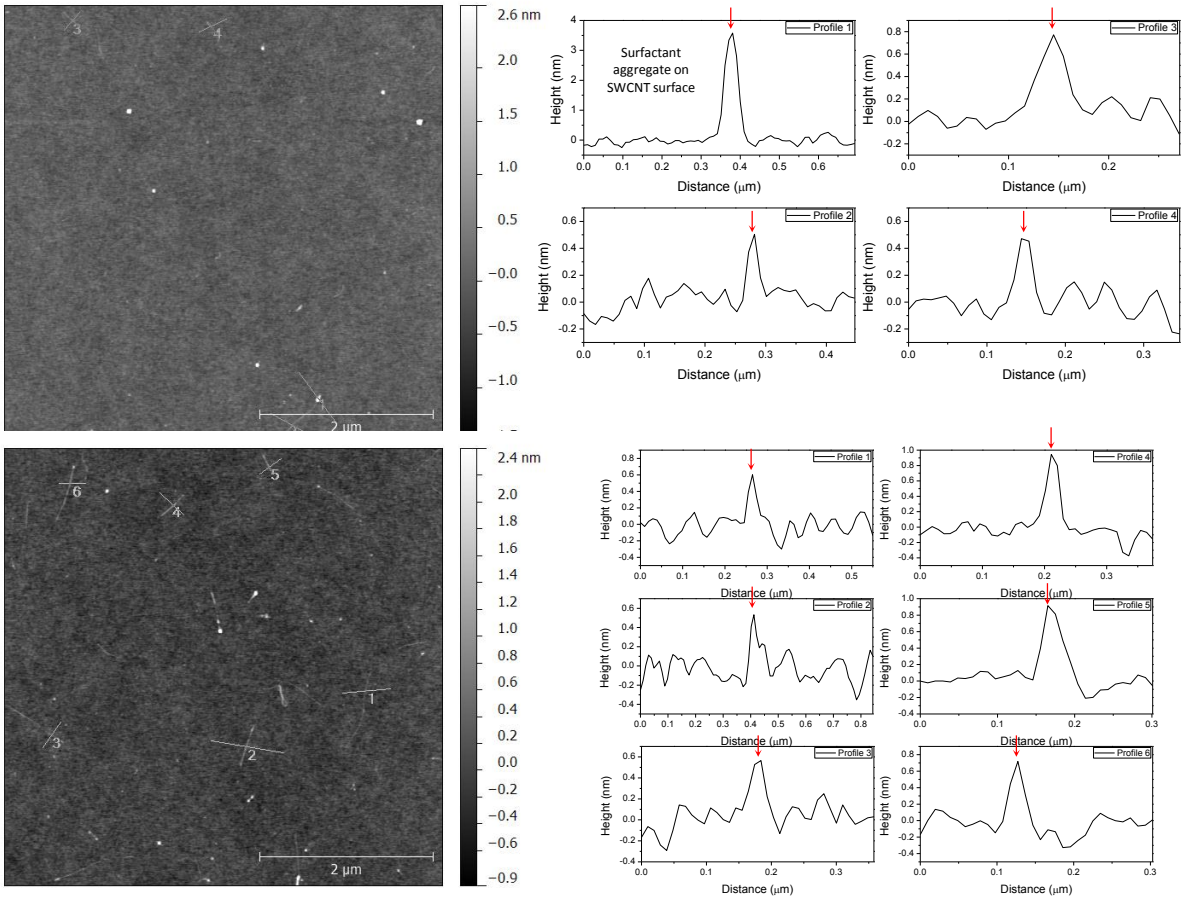


Figure S9. AFM images of the lipid-C61-PEG suspension showed individually dispersed SWCNTs.

Methyl-C61-PEG

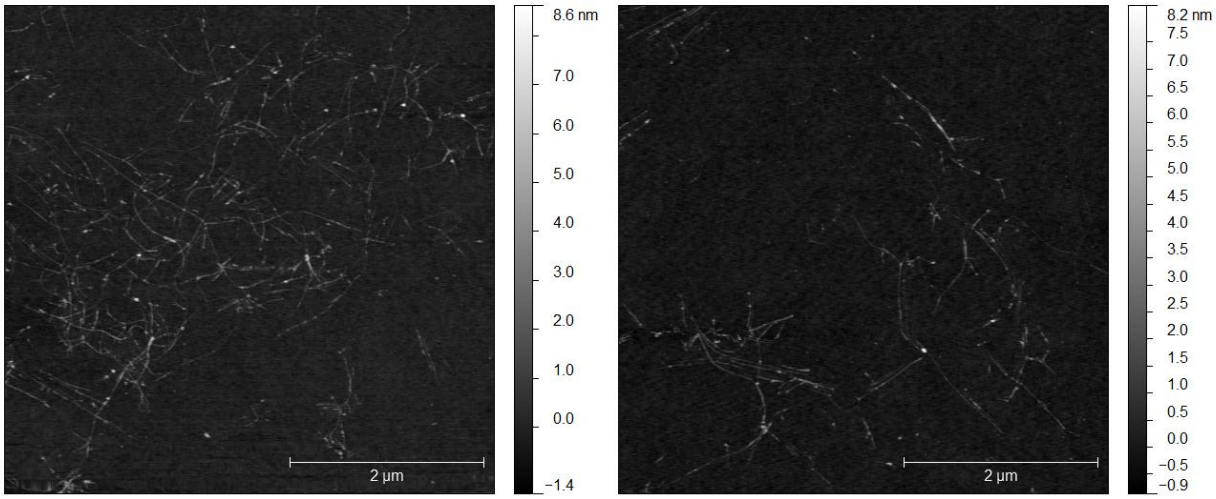


Figure S10. AFM images of the methyl-C61-PEG suspension showed bundles of SWCNTs.

5. Deconvolution of SWCNT Fluorescence Spectra

A custom-designed MATLAB program was used to determine the fluorescence emission peak center, and intensity of each nanotube in an automated fashion. The fluorescence spectra were fitted using a sum of $N = 11$ Lorentzian lineshapes (10 nanotube peaks and 1 G-prime peak). The fluorescence intensity at any energy, E, is a sum over the contributions of all the species present in solution:

$$I(E) = \sum_{i=1}^{N} \frac{C_i}{2\pi} \frac{\Gamma_i}{\left(E - E_{0,i}\right)^2 + \Gamma_i^2/4}$$

The parameters to be estimated for the Lorentzian profile of the i^{th} entity have been outlined below.

C_i – area under the peak

Γ_i – full width at half maximum (FWHM, meV)

$E_{0,i}$ – peak center in terms of energy (meV)

Initial guesses for the peak areas were calculated from the spectra. The area under the i^{th} peak was expressed as a fraction of the total area under the spectrum. This fraction was determined from the intensity of the peak in question. The FWHM and peak center for the G-prime peak were kept constant (11 meV and 1261.3 meV respectively) and only its peak area was floated. For the sodium cholate, lipid-PEG, pyrene-PEG, lipid-C61-PEG, and lipid-C71-PEG, peak centers, $E_{0,i}$, were obtained from excitation-emission plots, and each Γ_i ($E_{0,i}$) was constrained within a 7 meV (0.2 meV) window to maintain the physical validity of the fit. For the pyrene-C61-PEG and lipid-C85-PEG samples, for which little PL was observable in the excitation-emission plots, each Γ_i ($E_{0,i}$) was constrained within a 7 meV (25 meV) window. In all, 31 parameters were used to fit a single fluorescence spectrum. Examples of fits to experimental data are provided, below:

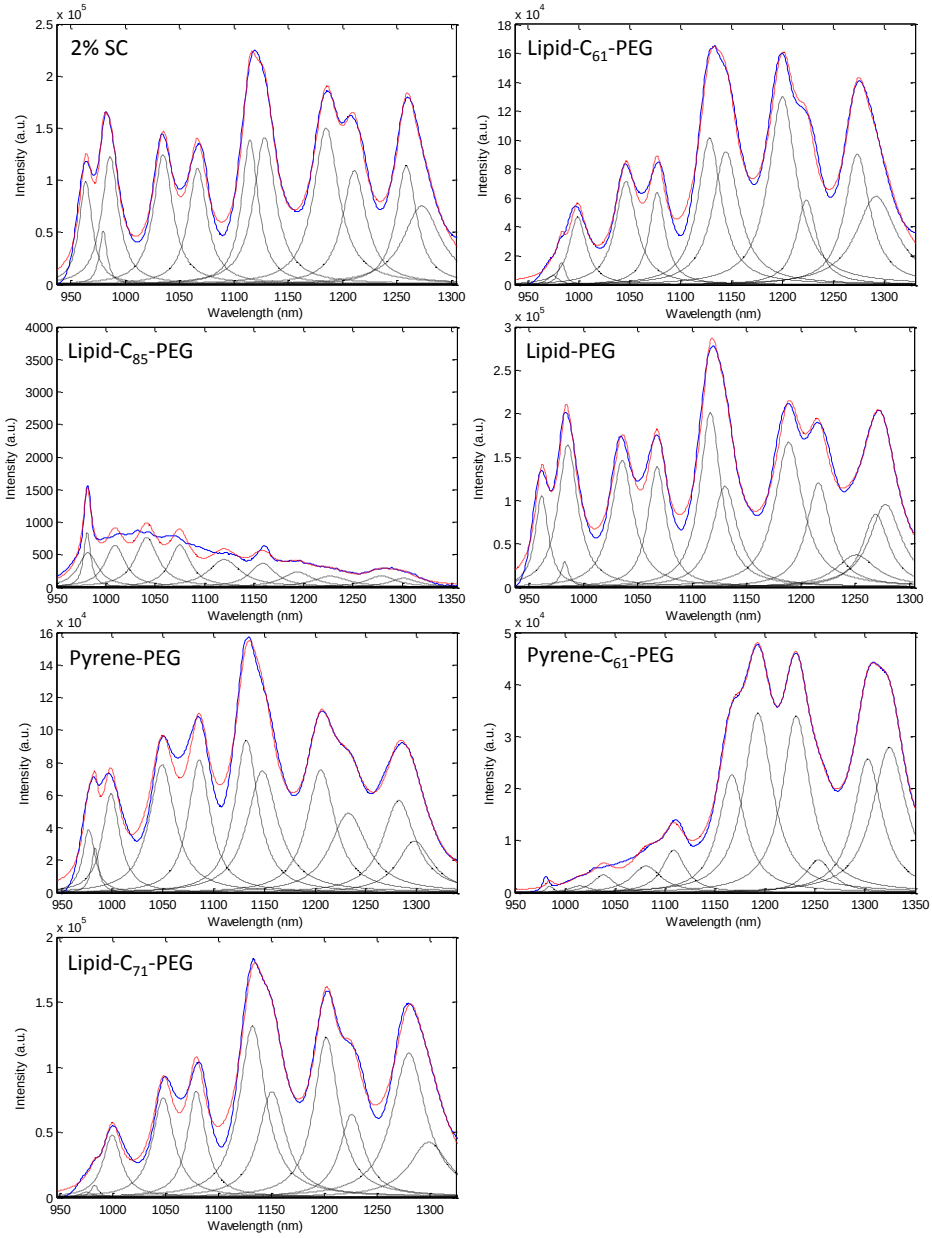


Figure S11. Examples of peak-fitting for the SWCNT suspensions utilized in this study.

6. MALDI-TOF

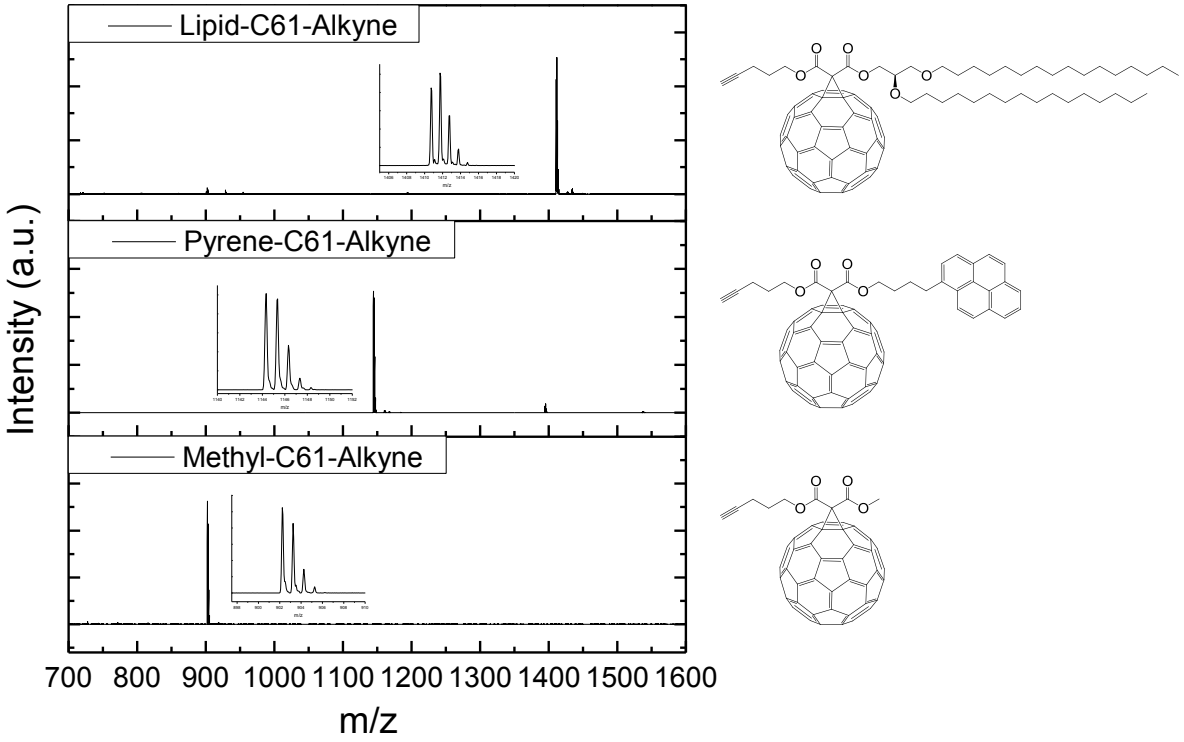


Figure S12. MALDI-TOF for the three methanofullerene intermediates, (3), (6), and (9).

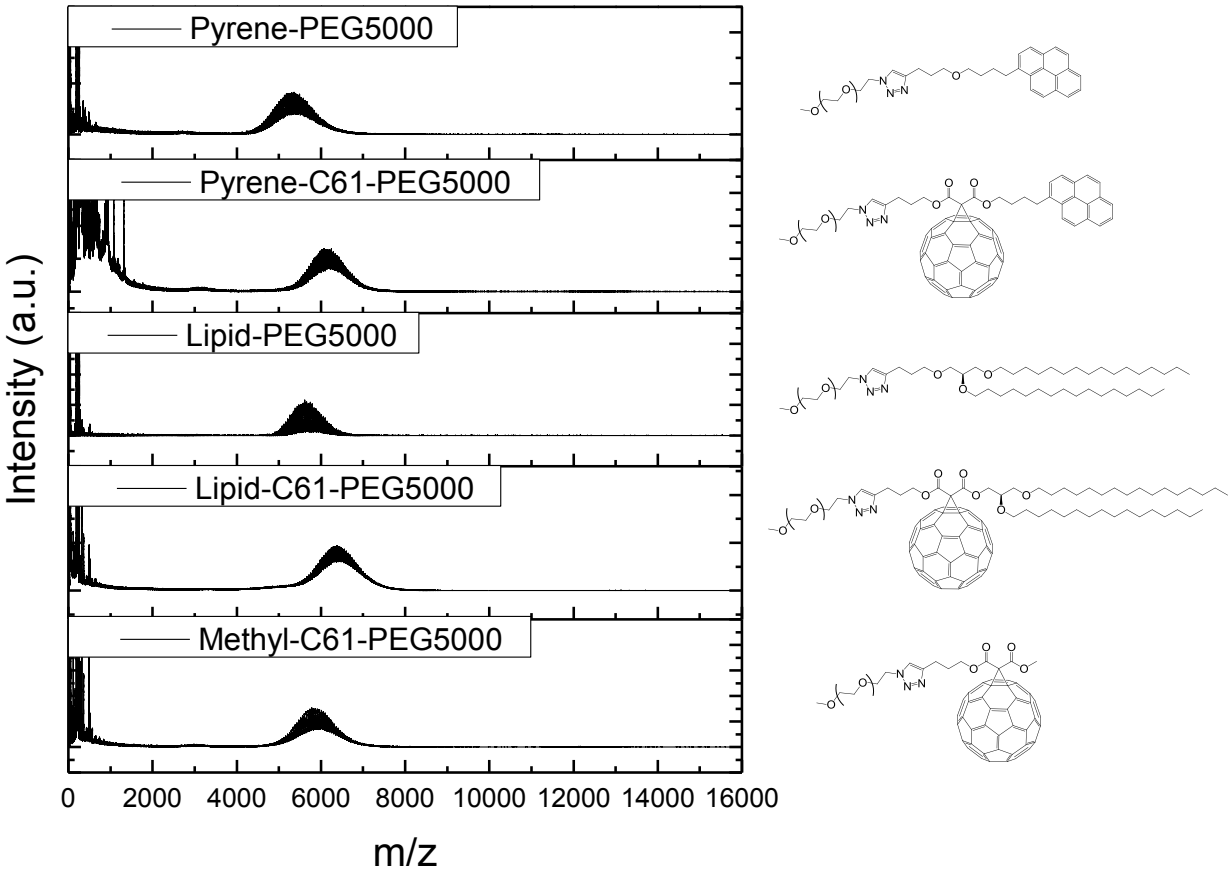


Figure S13. MALDI-TOF on the PEGylated amphiphiles (4), (7), (10), (12) and (14).

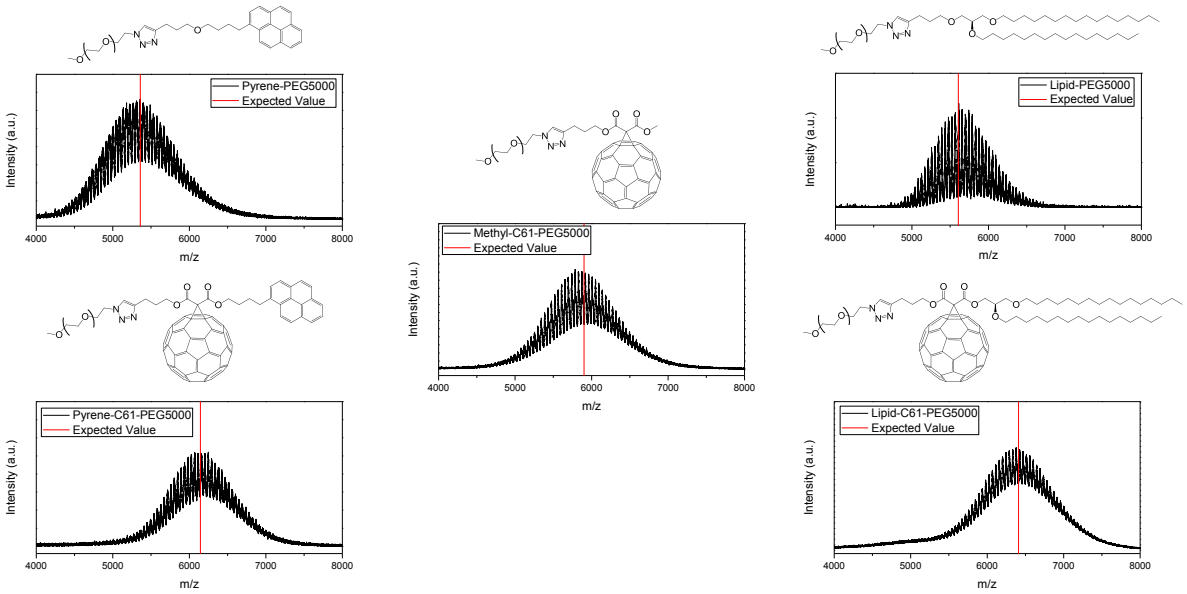


Figure S14. Zoomed-in MALDI-TOF on the PEGylated amphiphiles (4), (7), (10), (12) and (14), along with expected values.

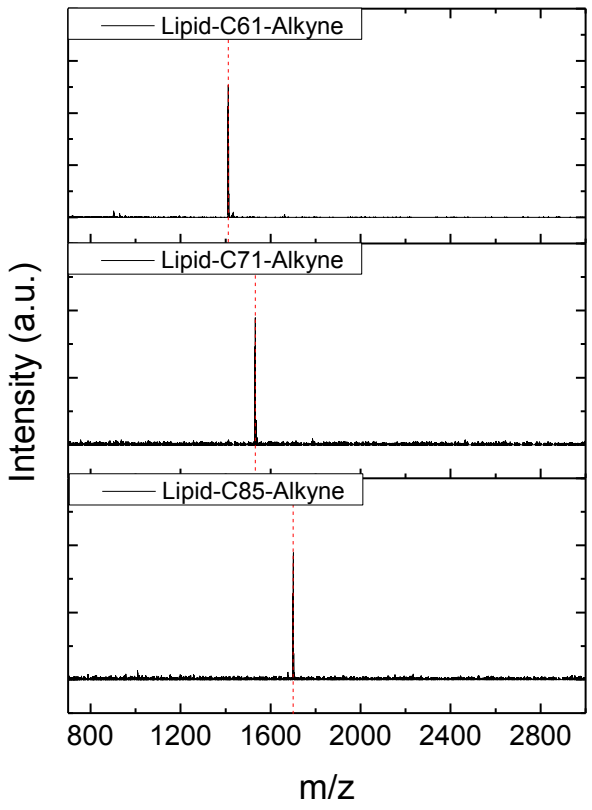


Figure S15. MALDI-TOF comparing the three methanofullerenes intermediates used for the fullerene family analysis.

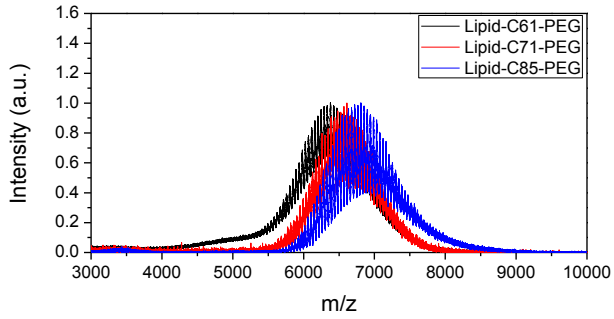
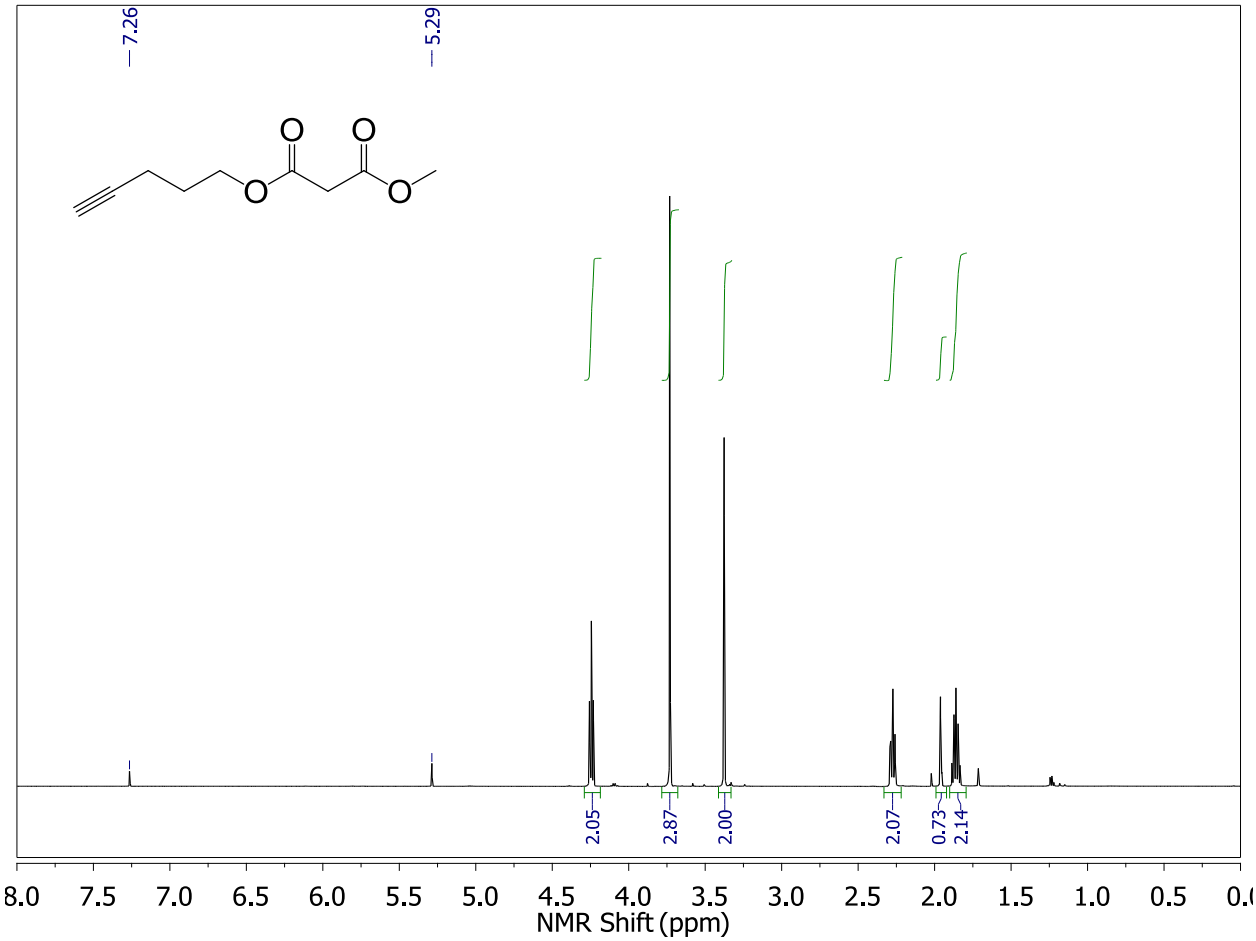
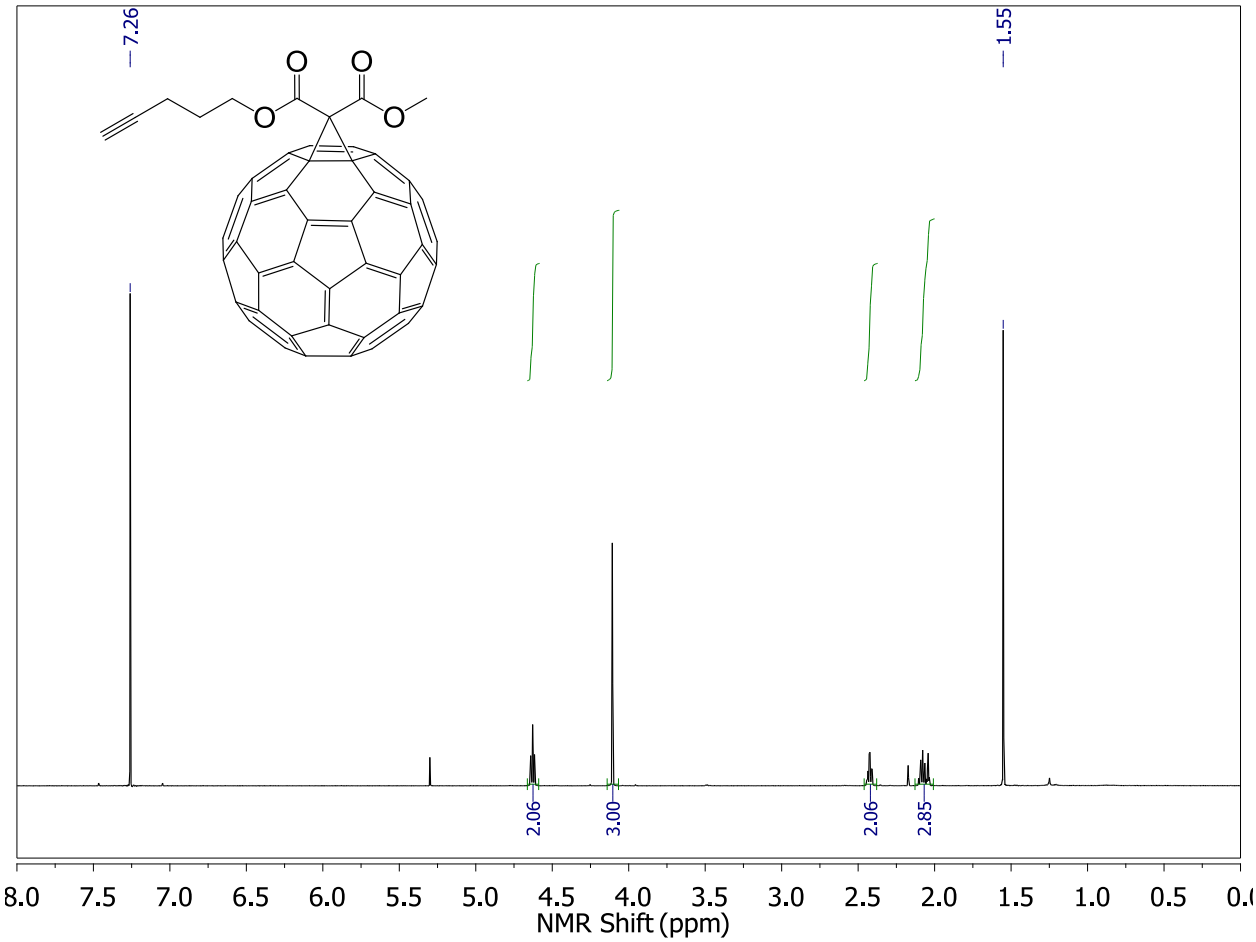


Figure S16. MALDI-TOF comparing the three PEGylated methanofullerenes used for the fullerene family analysis.

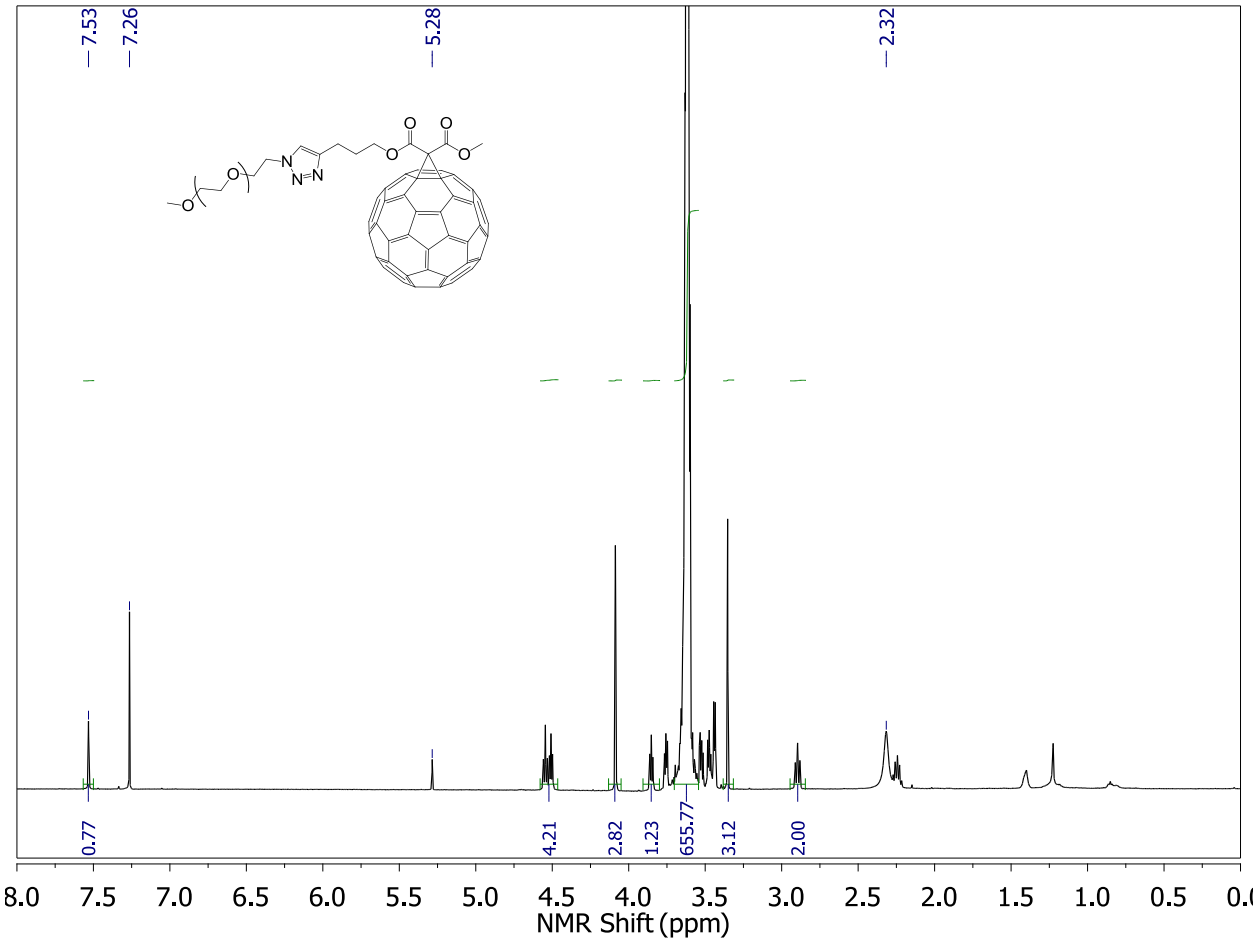
7. NMR



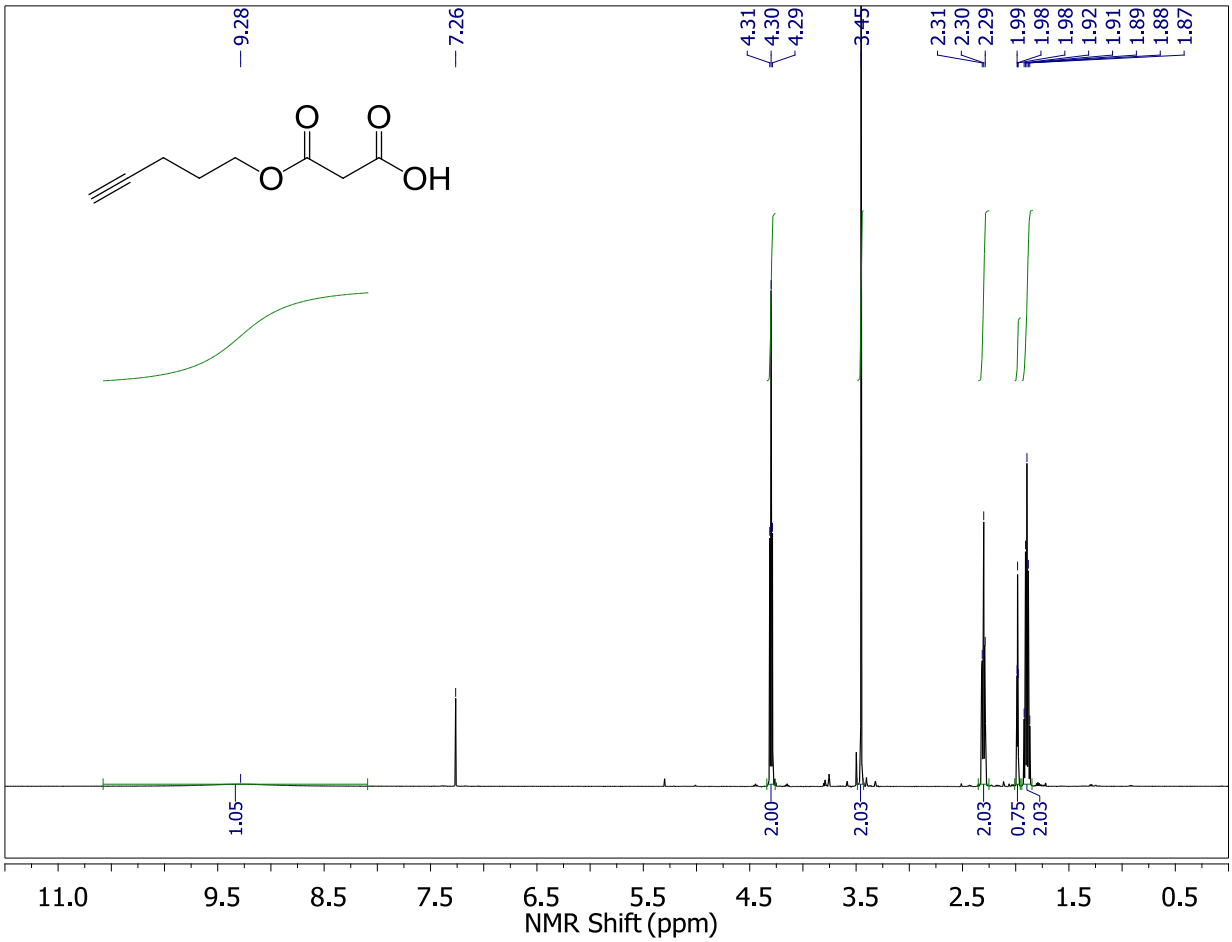
^{1}H-NMR in $CDCl_3$



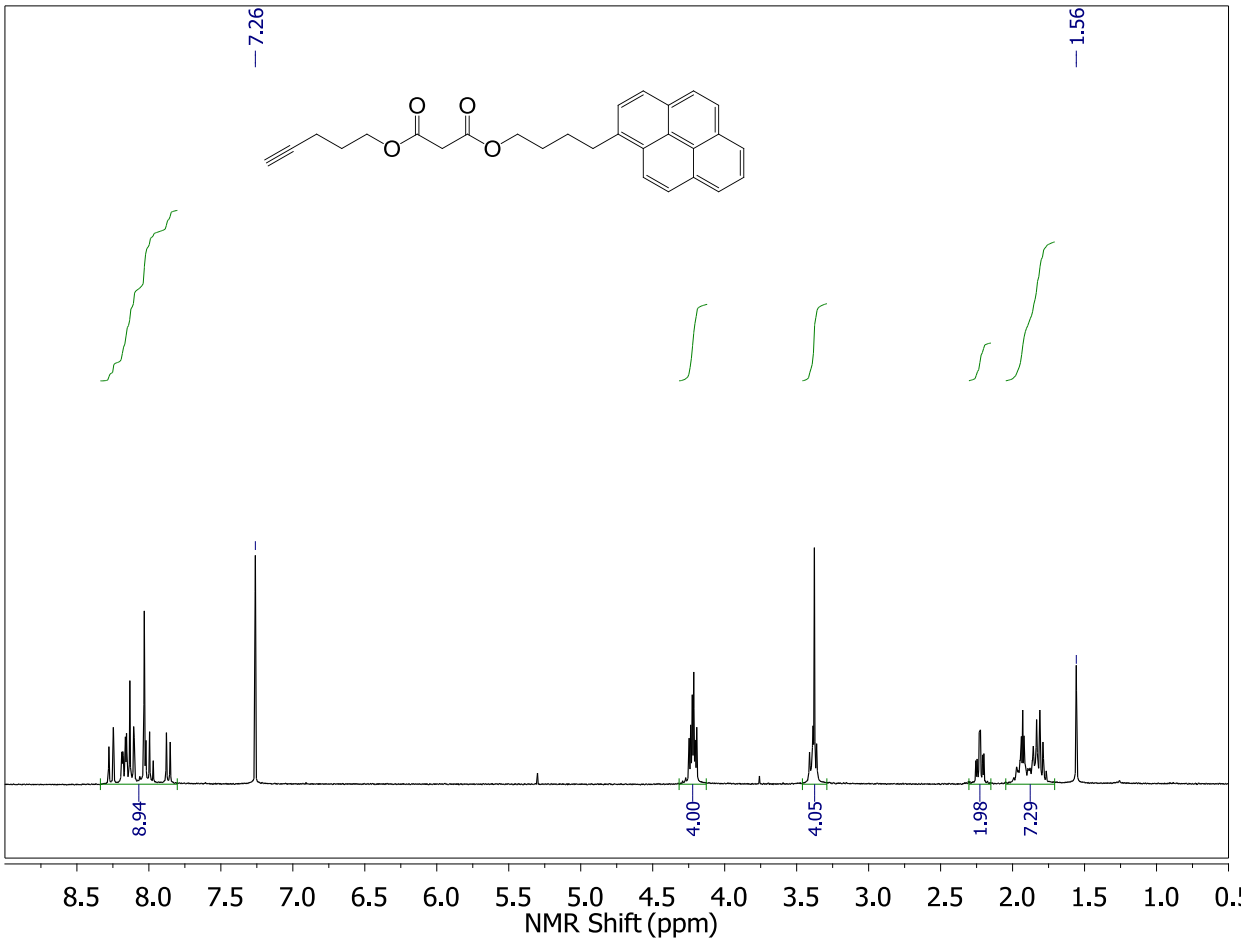
^{1}H-NMR in $CDCl_3$



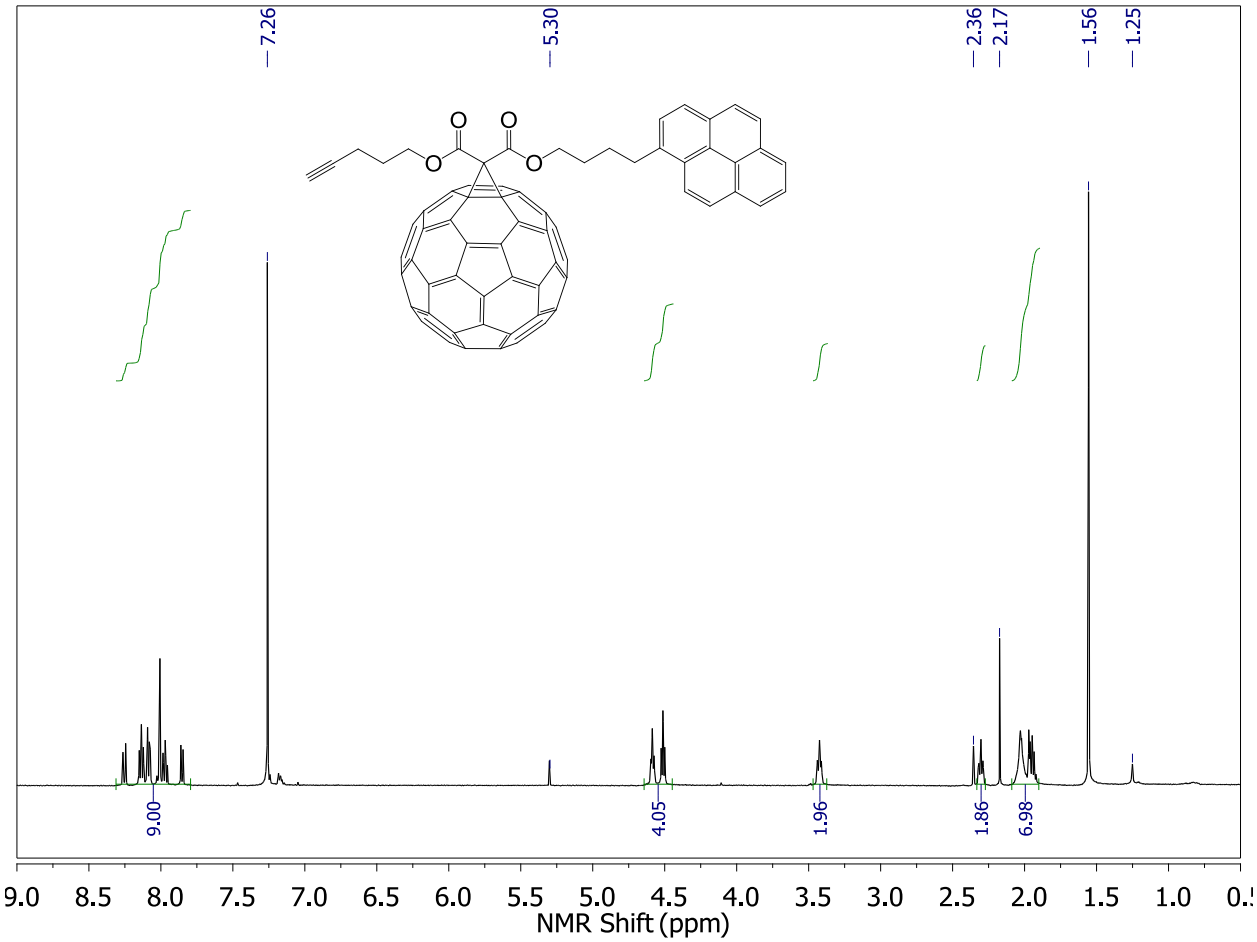
^{1}H-NMR in $CDCl_3$



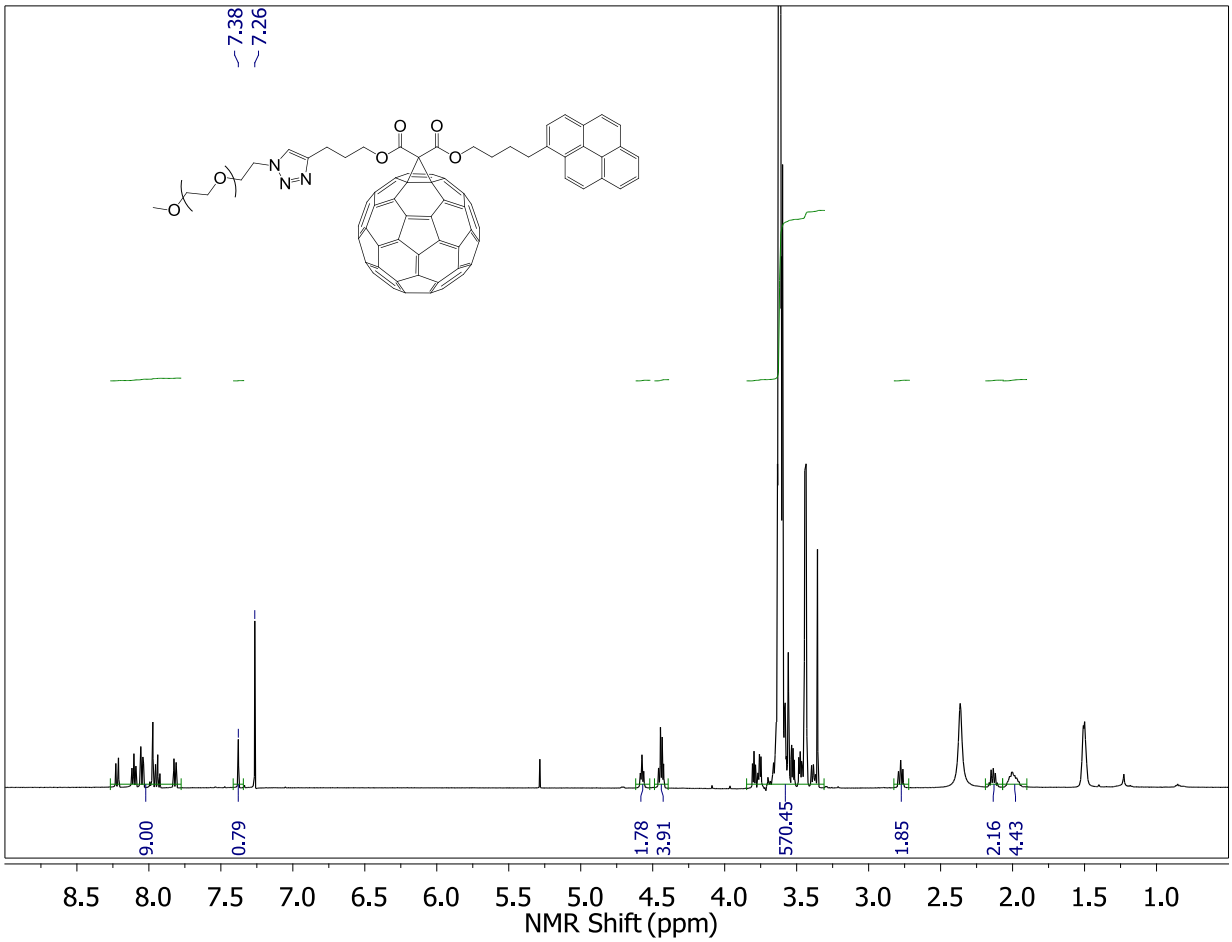
^{1}H-NMR in $CDCl_3$



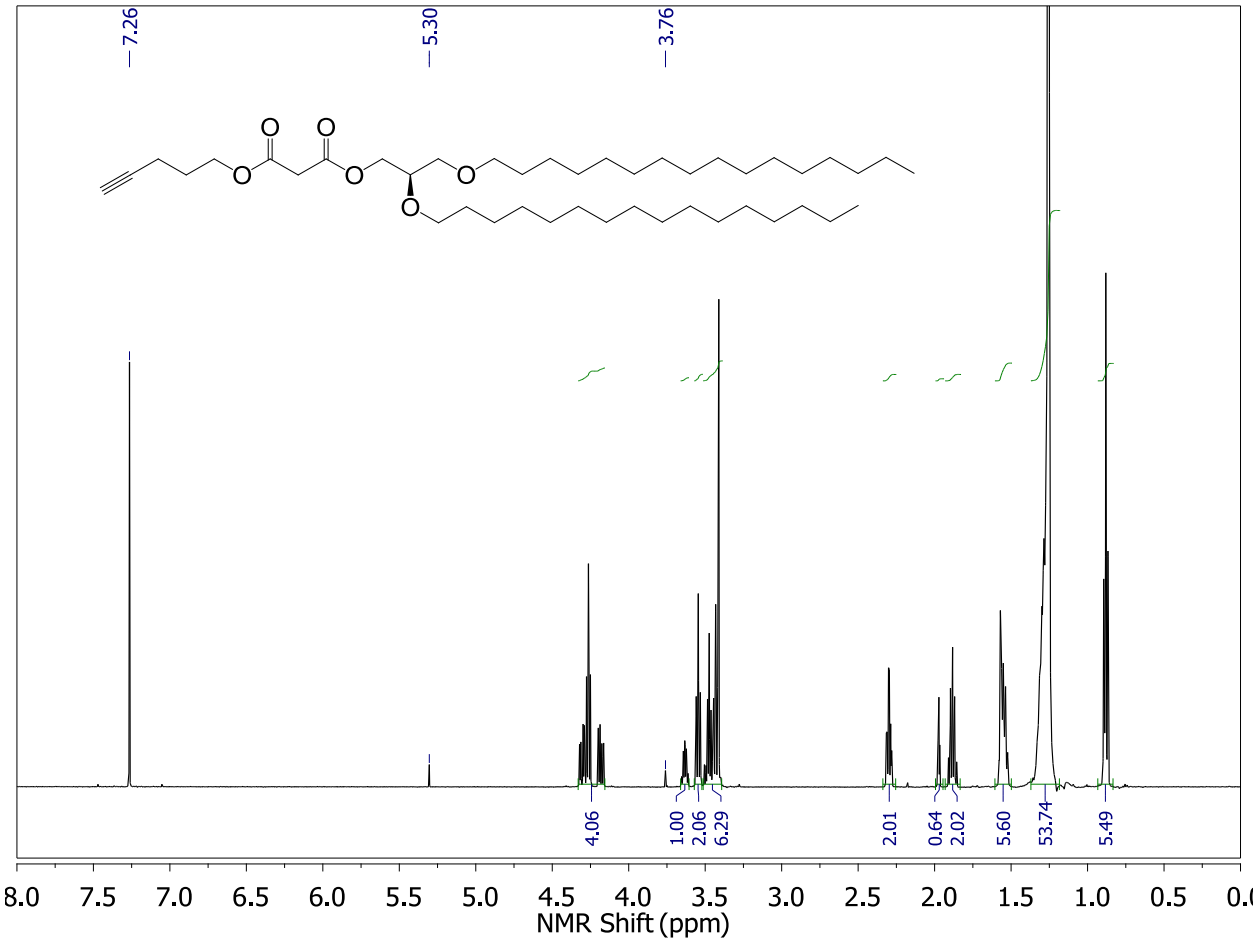
^{1}H-NMR in $CDCl_3$



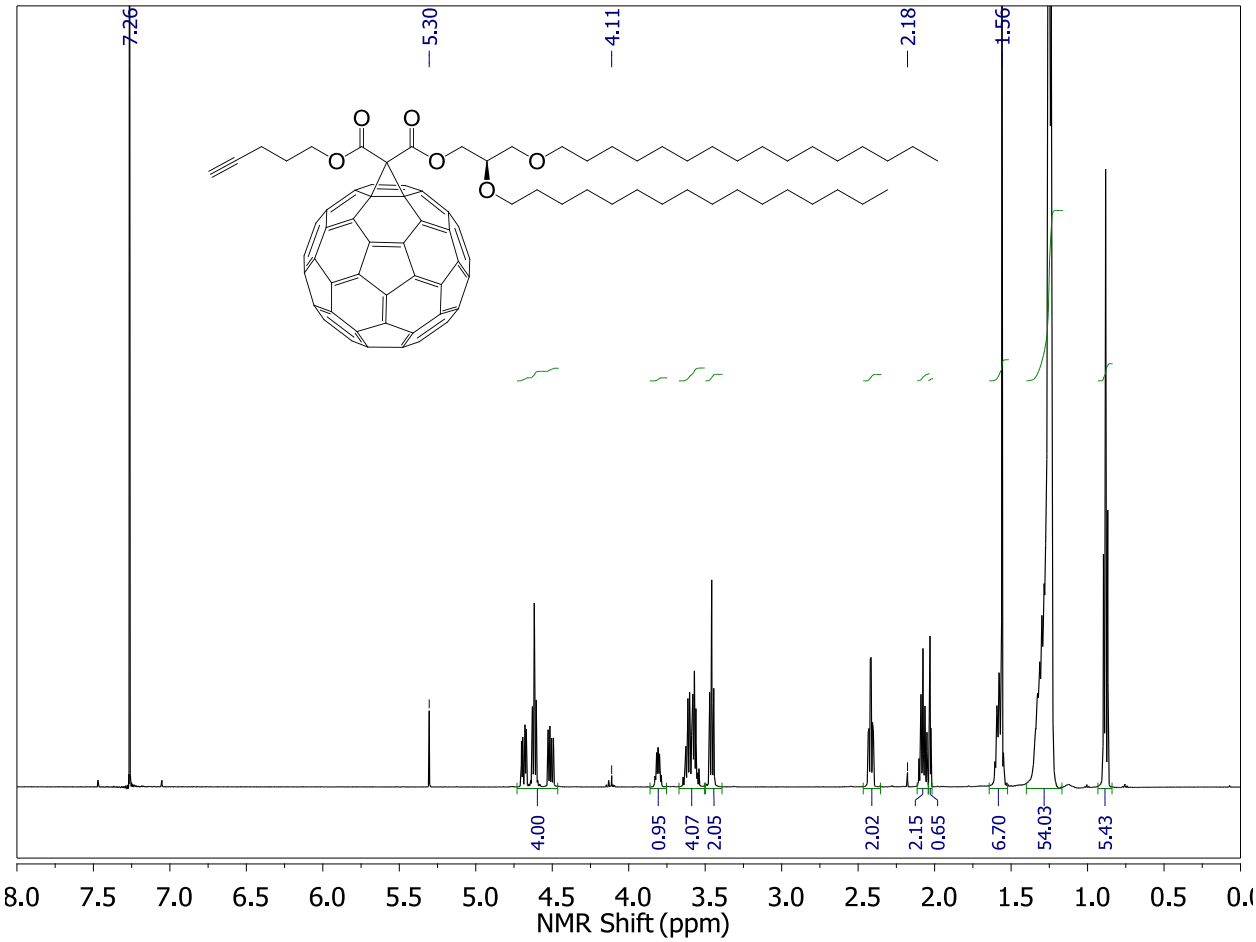
^{1}H-NMR in $CDCl_3$



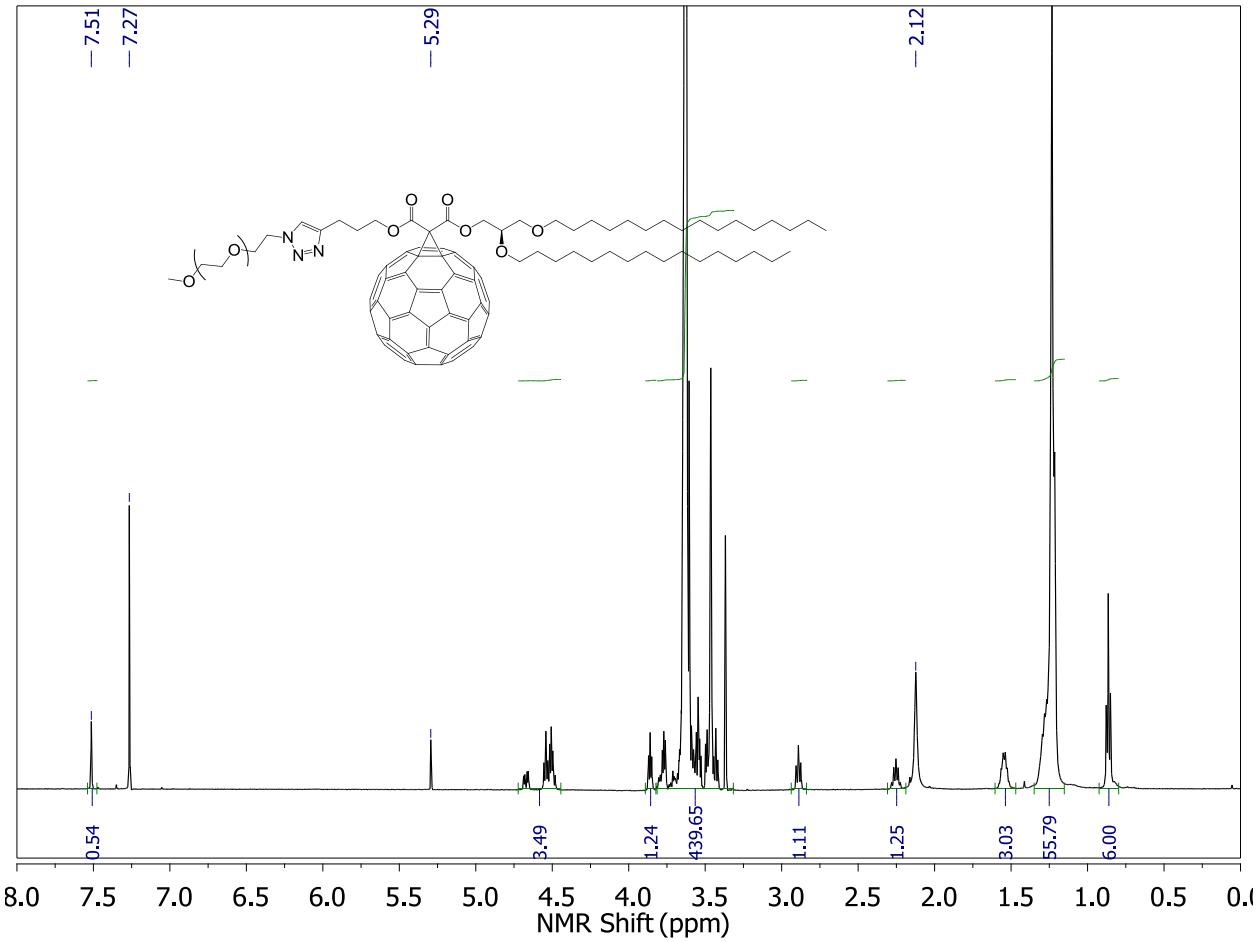
^{1}H-NMR in $CDCl_3$



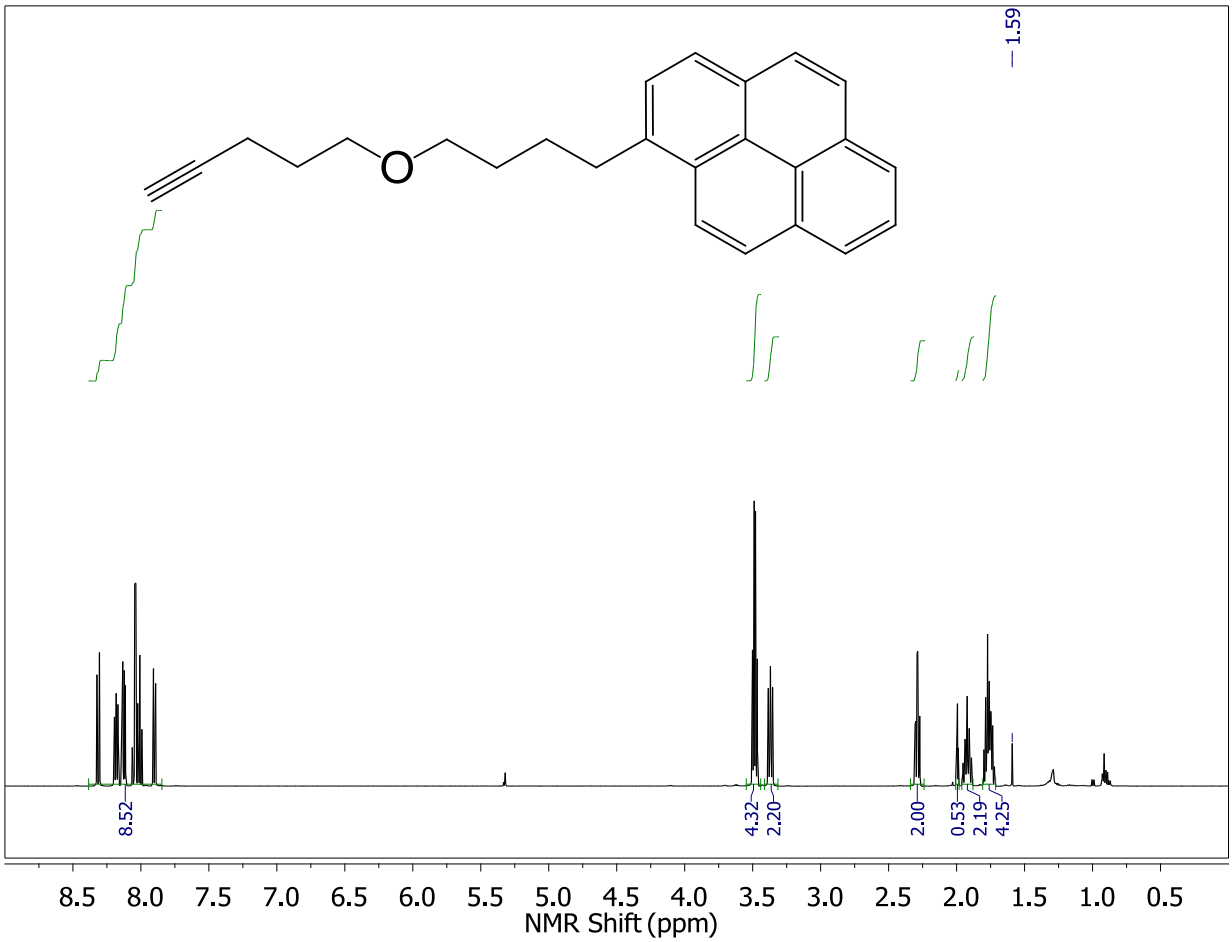
^{1}H-NMR in $CDCl_3$



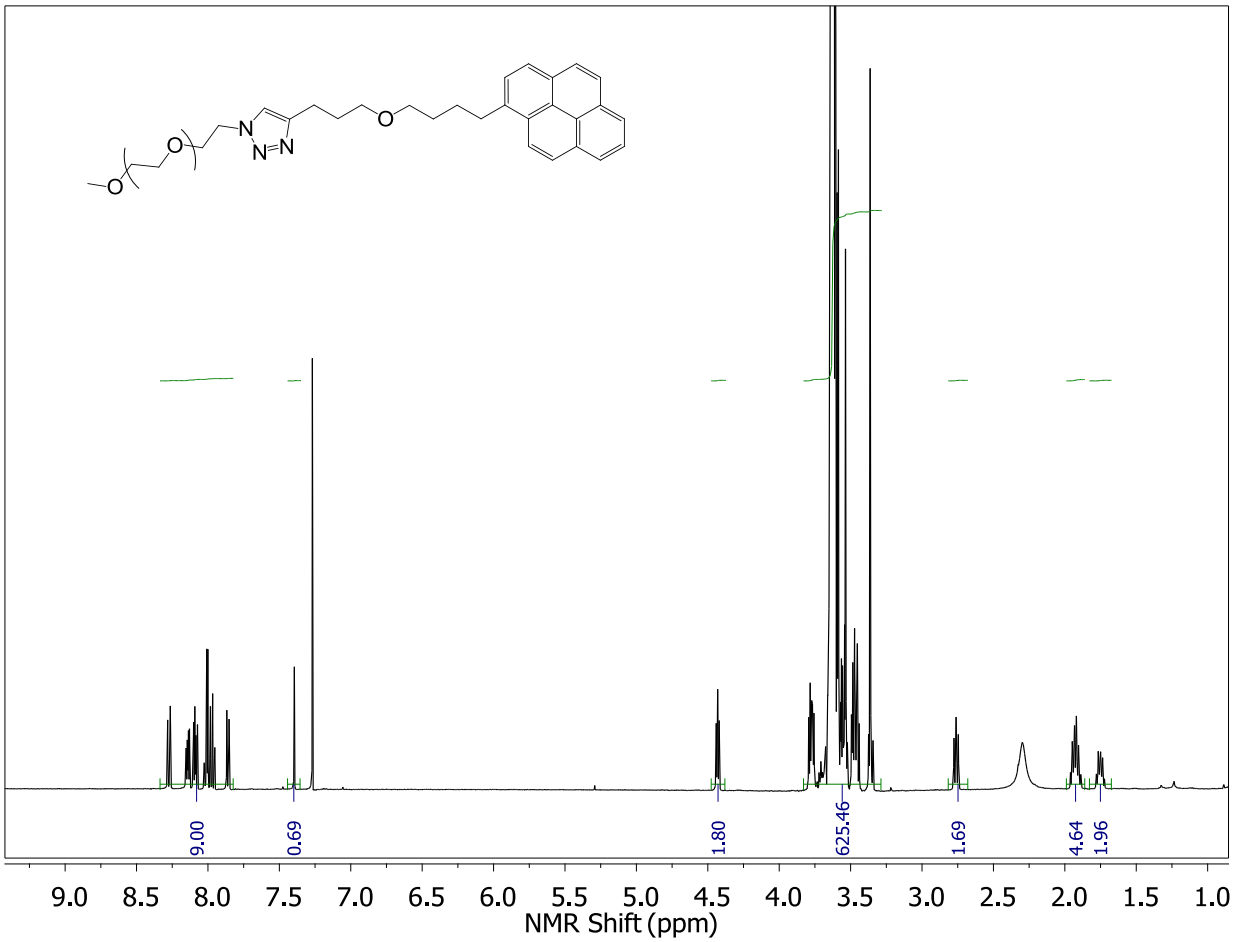
^{1}H-NMR in $CDCl_3$



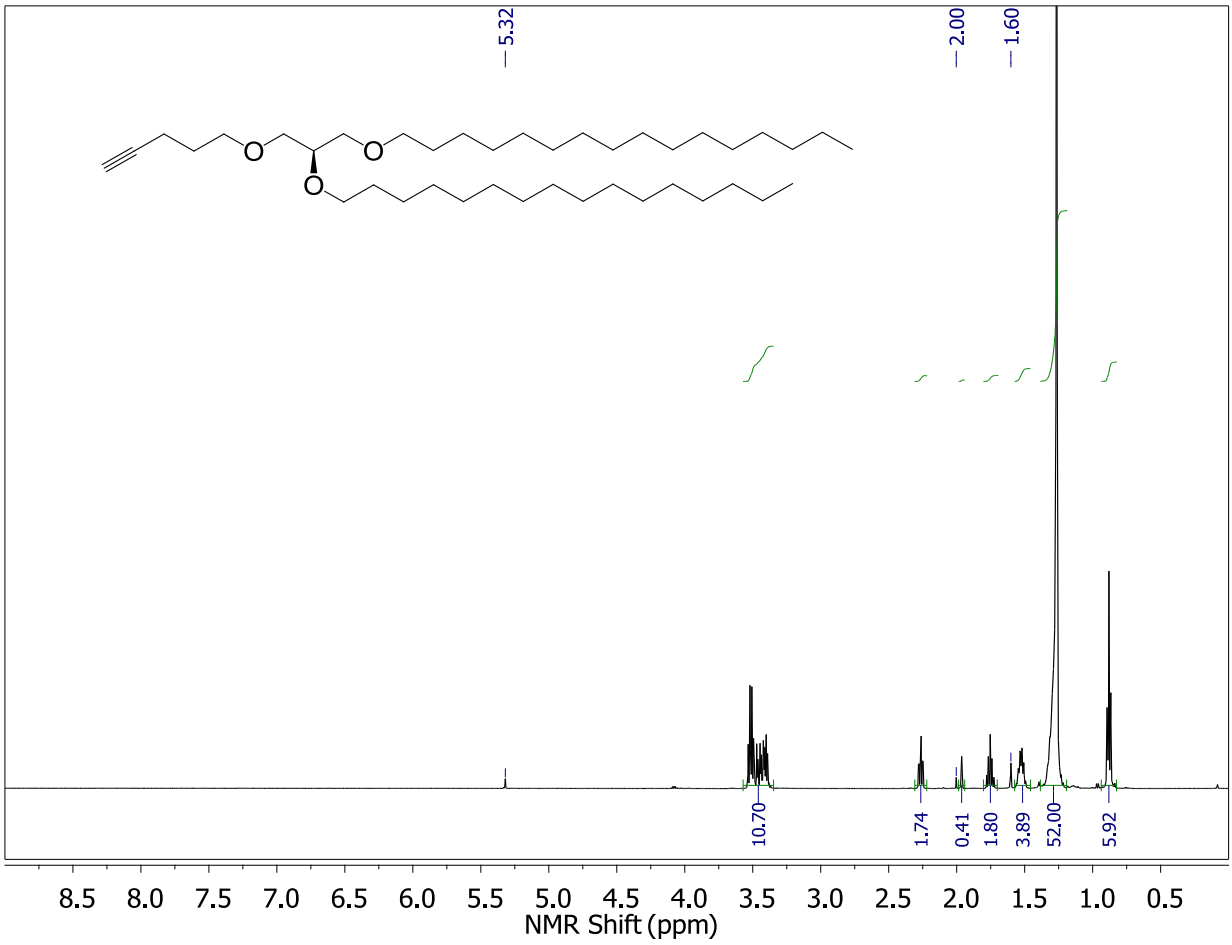
^{1}H-NMR in $CDCl_3$



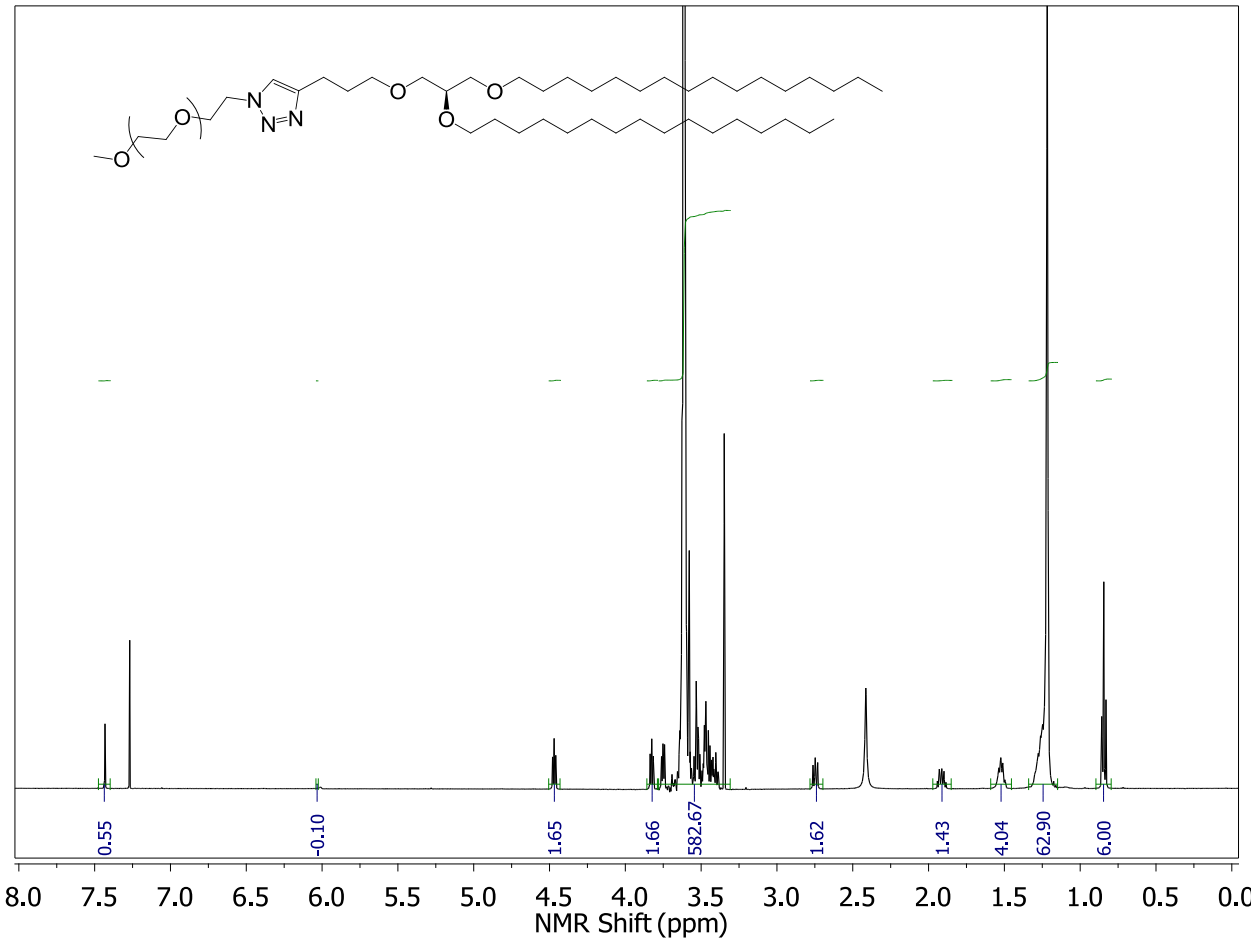
^{1}H-NMR in CD_2Cl_2



^{1}H-NMR in $CDCl_3$



^{1}H-NMR in CD_2Cl_2



^{1}H-NMR in $CDCl_3$