

RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

Electronic Supporting information

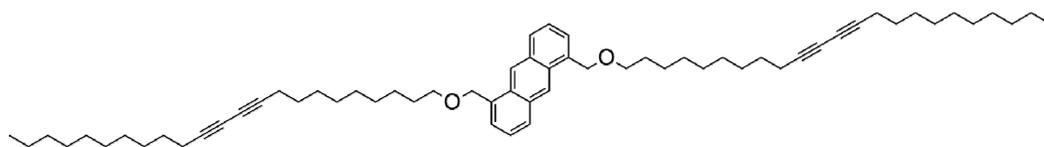
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A. Compounds: Synthesis and Spectral Characterization

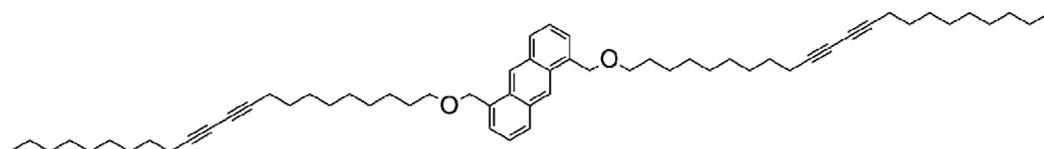
Compounds synthesized:

1. **A-[25²;C≡C-12,14]₂**



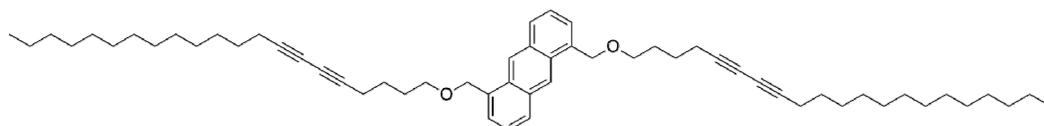
1,5-bis((tricoso-10,12-diyne-1-yloxy)methyl)anthracene

2. **A-[24²;C≡C-12,14]₂**



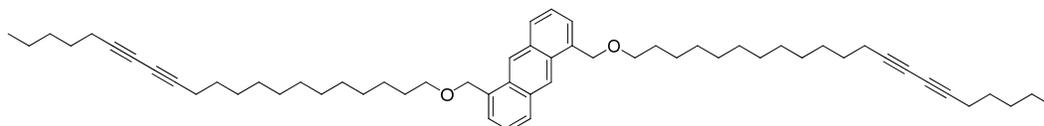
1,5-bis((docosa-10,12-diyne-1-yloxy)methyl)anthracene

3. **A-[23²;C≡C-7,9]₂**



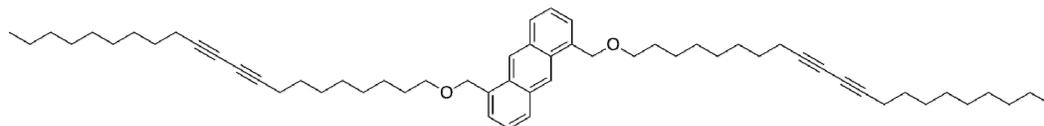
1,5-bis((hencosa-5,7-diyne-1-yloxy)methyl)anthracene

4. **A-[23²;C≡C-15,17]₂**



1,5-bis((hencosa-13,15-diyne-1-yloxy)methyl)anthracene

5. **A-[23²;C≡C-11,13]₂**



1,5-bis((hencosa-9,11-diyne-1-yloxy)methyl)anthracene

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Synthetic Procedures

Solvent Abbreviations

DCM = Dichloromethane DMF = Dimethylformamide

EA = Ethyl Acetate THF = Tetrahydrofuran

HMPA = Hexamethylphosphoramide

Dry Solvent. Reactions requiring dry and deoxygenated solvents employed THF, DCM and DMF from a Solvent Dispensing System (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.)

Purification. All crude products were purified by flash chromatography on silica gel (Whatman Purasil, 60 Å, 230-400 mesh). The eluting solvent was selected to generate an Rf of 0.1 – 0.3. Column fractions were analyzed by TLC, using UV or PMA (Phosphomolybdic Acid) as stain.

1. A-[25^{2;C≡C-12,14}]₂ (1,5-bis((tricoso-10,12-diyne-1-yloxy)methyl)anthracene)

Preparation of undec-2-yn-1-ol

Propargyl alcohol (0.9 mL, 15.5 mmol) was added to a flame-dried flask containing THF (25 mL) and HMPA (10 mL, 60 mmol). The solution was cooled to -78°C under argon atmosphere and magnetic stirring. n-butyl lithium (13.5 mL of 2.3M solution in hexane, 31 mmol) was added to the flask by syringe. The temperature was raised to -30°C and maintained for 45 mins. 1-bromooctane (2.7mL, 15.7 mmol) was added dropwise at -30°C. The solution was then stirred at room temperature for 15 hrs.

Work-up and purification: The reaction was quenched by adding saturated NH₄Cl aqueous solution (25 mL). The mixture was extracted with EA (3 X 30 mL). The organic layer was washed with water, brine then dried over MgSO₄. Solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by flash column chromatography (8% EA/hexanes then 15%EA/hexanes) and afforded undec-2-yn-1-ol 1.59g (9.5mmol, yield: 61%).

¹H NMR (300MHz, CDCl₃): δ 4.26 (s, 2H), 2.22 (t, J=7.5Hz, 2H), 1.77 (s, 1H), 1.51 (m, 2H), 1.34 (m, 10H), 0.89 (t, J=6.0Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 86.55, 78.20, 51.25, 31.77, 29.21, 29.15, 28.90, 28.54, 22.70, 18.65, 14.10.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₁₁H₂₀ONa) 191.1, found 191.1. HRMS Calcd for (M+Na)⁺ 191.1412 found 191.1408.

Preparation of undec-10-yn-1-ol (acetylene zipper reaction)

1,3-diaminopropane (25 mL) was added to a flame-dried, two-neck flask under argon by syringe. Lithium (0.35g, 50 mmol) was added to the flask and the mixture (a dark blue solution) was heated and stirred in an oil bath at 70°C. After 3 hrs, the blue color discharged and a milky white suspension was formed. The mixture was cooled to room temperature and potassium tert-butoxide (3.36 g, 30 mmol) was added all at once, affording a yellow solution. After stirring for 15 mins undec-2-yn-1-ol (1.26 g, 7.5 mmol) was added in one portion. The reaction was stirred for 10hrs at room temperature.

Work-up and purification: The mixture was poured into ice-water (100mL) extracted with EA (3 X 50mL). The organic layer was washed with 0.5M HCl solution, water, brine then dried with MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (25% EA/hexanes) afforded undec-10-yn-1-ol 1.15g (6.8 mmol, yield: 91%).

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¹H NMR (400MHz, CDCl₃): δ 3.66 (t, J=6.6Hz, 2H), 2.20 (td, J=7.2Hz and 2.5Hz, 2H), 1.96 (t, J=2.6Hz, 1H), 1.56 (m, 4H), 1.38 (m, 10H).

¹³C NMR (75 MHz, CDCl₃): δ 84.72, 68.05, 62.90, 33.00, 29.50, 29.35, 29.00, 28.62, 28.45, 26.00, 18.40.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₁₁H₂₀ONa) 191.1, found 191.2. HRMS Calcd for (M+Na)⁺ 191.1412 found 191.1415.

Preparation of 1,5-bis((undec-10-yn-1-yloxy)methyl)anthracene

Undec-10-yn-1-ol (0.25g, 1.5mmol) was added to a flame-dried two-neck flask containing DMF (5mL) under nitrogen. The solution was cooled to 0°C with magnetic stirring and sodium hydride was added all at once. After stirring for 10 mins, 1,5-bis(chloromethyl)anthracene (0.12g 0.44mmol) was added in once portion (0°C). The mixture was then stirred at room temperature for 15 hrs.

Work-up and purification: The reaction was quenched by slowly adding ice-water. The mixture was extracted with DCM (3 X 20mL). The organic layer was washed with 0.5M HCl solution, water, brine then dried with MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (40% DCM/hexanes) afforded 1,5-bis((undec-10-yn-1-yloxy)methyl)anthracene 0.12g (0.23 mmol, yield: 52%).

¹H NMR (300MHz, CDCl₃): δ 8.72 (s, 2H), 8.03 (d, J=6.0Hz, 2H), 7.52 (d, J=6.0Hz, 2H), 7.44 (dd, J=9.0Hz and 6.0Hz, 2H), 5.09 (s, 4H), 3.61 (t, J=7.5Hz, 4H), 2.16 (td, J=7.5Hz and 3.0Hz, 4H), 1.94 (t, J=3.0Hz, 2H), 1.68 (m, 4H), 1.47 (m, 24H).

¹³C NMR (75MHz, CDCl₃): δ 134.55, 131.89, 128.50, 128.16, 125.05, 123.20, 122.55, 84.70, 72.40, 70.15, 68.50, 30.80, 29.70, 29.65, 29.30, 28.70, 28.67, 28.40, 18.40.

Preparation of 1-iodododec-1-yne

1-dodecyne (1.1mL, 5 mmol) was added to a flame-dried two-neck flask containing THF (10 mL) under argon atmosphere and magnetic stirring. The mixture was cooled to -20°C and n-butyl lithium (2.2 mL of 2.3M solution in hexane, 5 mmol) was slowly added to the flask. The mixture was stirred for 1 hr at -20°C, then, the temperature was lowered to -40°C and iodine (1.40 g, 5.5 mmol) solution in 5 mL of THF was added by syringe. The reaction mixture was warmed to room temperature and stirred for 12 hrs.

Work-up and purification: The reaction was quenched by adding saturated Na₂S₂O₃ solution. The mixture was then extracted by hexanes (3 X 20 mL). The organic phase was washed with saturated Na₂S₂O₃ solution, water, and brine then dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (100% hexanes) afforded 1-iodododec-1-yne 1.34g (4.6mmol, yield: 92%).

¹H NMR (300MHz, CDCl₃): δ 2.37 (t, J=7.5Hz, 2H), 1.53 (m, 2H), 1.36 (m, 14H), 0.91 (t, J=7.5 Hz, 3H).

¹³C NMR (75MHz, CDCl₃): δ 95.10, 67.80, 32.00, 29.62, 29.55, 29.20, 29.05, 28.72, 28.40, 22.60, 20.85, 14.05.

m/s (EI) m/z Calcd for M⁺ (C₁₂H₂₁I) 292.1, found 292.0. HRMS Calcd for M⁺ 292.0688 not found.

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Preparation of **1**; 1,5-bis((tricoso-10,12-diyne-1-yloxy)methyl)anthracene (Cadiot-Chodkiewicz cross-coupling reactions)

To a two-neck flask under argon were added 1,5-bis((undec-10-yn-1-yloxy)methyl)anthracene (0.12g, 0.23mmol), 1-iodododec-1-yne (0.16g, 0.55mmol) and pyrrolidine (3mL). The mixture was cooled to 0°C and copper iodide (0.017g, 0.09mmol) was added all at once. The reaction mixture was stirred at room temperature for 12 hrs.

Work-up and purification: The reaction was quenched by adding saturated NH₄Cl aqueous solution (20 mL). The mixture was extracted with DCM (3 X 20mL). The organic phase was washed with water and brine then dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (30% DCM/hexanes) afforded compound **1**, 1,5-bis((tricoso-10,12-diyne-1-yloxy)methyl)anthracene 0.12g (0.14mmol, yield: 61%).

Spectral Data for **1**; A-[25²;C≡C-12,14]₂

¹H NMR (300MHz, CDCl₃): δ 8.73 (s, 2H), 8.04 (d, J=9.0Hz, 2H), 7.53 (d, J=9.0Hz, 2H), 7.44 (dd, J=9.0Hz and 6.0Hz, 2H), 5.10 (s, 4H), 3.61 (t, J=6.0Hz, 4H), 2.24 (m, 8H), 1.67 (m, 4H), 1.53 (m, 8H), 1.40 (m, 48H), 0.90 (t, J=6.0Hz, 6H).

¹³C NMR (75MHz, CDCl₃): δ 133.94, 132.07, 129.80, 129.26, 125.74, 124.75, 123.54, 77.57, 77.22, 71.72, 70.45, 66.99, 65.26, 31.90, 29.82, 29.57, 29.48, 29.41, 29.38, 29.31, 29.10, 29.00, 28.86, 28.82, 28.36, 28.33, 28.25, 26.27, 22.68, 19.20, 14.12.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₆₂H₉₀O₂Na) 889.7, found 889.9. HRMS Calcd for (M+Na)⁺ 889.6839 found 889.6821.

A-[24²;C≡C-12,14]₂, A-[23²;C≡C-11,13]₂, A-[23²;C≡C-7,9]₂ and A-[23²;C≡C-15,17]₂ were prepared using similar procedures. Their spectral data are provided below:

Spectral data for **2**; A-[24²;C≡C-12,14]₂ (1,5-bis((docosa-10,12-diyne-1-yloxy)methyl)anthracene)

¹H NMR (300MHz, CDCl₃): δ 8.73 (s, 2H), 8.04 (d, J=9.0Hz, 2H), 7.52 (d, J=6.0Hz, 2H), 7.44 (dd, J=9.0Hz and 6.0Hz, 2H), 5.10 (s, 4H), 3.61 (t, J=6.0Hz, 4H), 2.24 (m, 8H), 1.67 (m, 4H), 1.53 (m, 8H), 1.40 (m, 44H), 0.90 (t, J=6.0Hz, 6H).

¹³C NMR (75MHz, CDCl₃): δ 133.95, 132.07, 129.80, 129.26, 125.73, 124.74, 123.54, 77.57, 77.23, 71.71, 70.45, 66.94, 65.27, 31.92, 29.80, 29.55, 29.46, 29.40, 29.40, 29.33, 29.07, 28.98, 28.84, 28.80, 28.33, 28.21, 26.20, 22.05, 19.01, 13.97.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₆₀H₈₆O₂Na) 861.7, found 861.3. HRMS Calcd for (M+Na)⁺ 861.6526 found 861.6530.

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Spectral data for 3; A-[23²;C≡C-7,9]₂ (1,5-bis((henicosa-5,7-diyne-1-yloxy)methyl)anthracene)

¹H NMR (300MHz, CDCl₃): δ 8.70(s, 2H), 8.05 (d, J=9.0Hz, 2H), 7.52 (d, J=6.0Hz, 2H), 7.44 (dd, J=9.0Hz and 6.0Hz, 2H), 5.09 (s, 4H), 3.64 (t, J=6.0Hz, 4H), 2.26 (m, 8H), 1.80 (m, 4H), 1.66 (m, 4H), 1.50 (m, 4H), 1.28 (m, 40H), 0.90 (t, J=7.5Hz, 6H).

¹³C NMR (75MHz, CDCl₃): δ 133.76, 132.05, 129.74, 129.32, 125.73, 124.79, 123.64, 77.68, 77.22, 71.70, 69.67, 65.66, 65.24, 31.93, 29.68, 29.65, 29.63, 29.49, 29.36, 29.11, 28.87, 28.36, 28.05, 27.96, 25.17, 22.70, 19.20, 18.98, 14.12.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₅₈H₈₂O₂Na) 833.6, found 833.8. HRMS Calcd for (M+Na)⁺ 833.6213 not found.

Spectral data for 4; A-[23²;C≡C-15,17]₂ (1,5-bis((henicosa-13,15-diyne-1-yloxy)methyl)anthracene)

¹H NMR (300MHz, CDCl₃): δ 8.72(s, 2H), 8.03 (d, J=6.0Hz, 2H), 7.52 (d, J=6.0Hz, 2H), 7.44 (dd, J=9.0Hz and 6.0Hz, 2H), 5.10 (s, 4H), 3.61 (t, J=6.0Hz, 4H), 2.26 (m, 8H), 1.68 (m, 4H), 1.54 (m, 8H), 1.28 (m, 40H), 0.91 (t, J=7.5Hz, 6H).

¹³C NMR (75MHz, CDCl₃): δ 133.95, 132.06, 129.80, 129.24, 125.69, 124.74, 123.52, 77.55, 77.21, 71.70, 70.53, 65.25, 64.67, 31.00, 29.85, 29.59, 29.57, 29.56, 29.46, 29.25, 29.09, 28.86, 28.61, 28.35, 28.05, 26.30, 22.17, 19.21, 13.92.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₅₈H₈₂O₂Na) 833.6, found 833.9. HRMS Calcd for (M+Na)⁺ 833.6213 found 861.6248.

Spectral data for 5; A-[23²;C≡C-11,13]₂ (1,5-bis((henicosa-9,11-diyne-1-yloxy)methyl)anthracene)

¹H NMR (300MHz, CDCl₃): δ 8.73 (s, 2H), 8.04 (d, J=9.0Hz, 2H), 7.53 (d, J=9.0Hz, 2H), 7.45 (dd, J=9.0Hz and 6.0Hz, 2H), 5.10 (s, 4H), 3.61 (t, J=6.0Hz, 4H), 2.24 (m, 8H), 1.67 (m, 4H), 1.53 (m, 8H), 1.38 (m, 40H), 0.90 (t, J=6.0Hz, 6H).

¹³C NMR (75MHz, CDCl₃): δ 133.93, 132.06, 129.80, 129.26, 125.74, 124.75, 123.54, 77.57, 77.51, 71.72, 70.40, 67.82, 65.29, 31.88, 29.80, 29.45, 29.28, 29.25, 29.12, 29.05, 28.87, 28.77, 28.37, 28.33, 26.24, 22.68, 19.22, 19.19, 14.12.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₅₈H₈₂O₂Na) 833.6, found 833.5. HRMS Calcd for (M+Na)⁺ 833.6213 found 861.6221.

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Spectral Data for other synthetic intermediates are:

Dec-2-yn-1-ol: (from propargyl alcohol and 1-bromoheptane)

¹H NMR (300MHz, CDCl₃): δ 4.26 (s, 2H), 2.23 (t, J=7.8Hz, 2H), 1.76 (s, 1H), 1.53 (m, 2H), 1.33 (m, 8H), 0.89 (t, J=6.5Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 86.57, 77.95, 51.30, 32.00, 29.20, 28.74, 28.32, 22.50, 18.60, 14.50.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₁₀H₁₈ONa) 177.1, found 177.3. HRMS Calcd for (M+Na)⁺ 177.1255 found 177.1250.

Dec-9-yn-1-ol (intermediate in the preparation of 5):

¹H NMR: ¹H NMR (400MHz, CDCl₃): δ 3.64 (t, J=6.6Hz, 2H), 2.22 (td, J=7.0Hz and 2.8Hz, 2H), 1.96 (t, J=2.6Hz, 1H), 1.56 (m, 4H), 1.37 (m, 8H).

¹³C NMR (75 MHz, CDCl₃): δ 85.00, 68.15, 63.00, 33.05, 29.70, 29.13, 29.00, 28.40, 26.50, 18.30.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₁₀H₁₈ONa) 177.1, found 177.1. HRMS Calcd for (M+Na)⁺ 177.1255 found 177.1252.

Tetradec-2-yn-1-ol: (from propargyl alcohol and 1-bromoundecane)

¹H NMR (300MHz, CDCl₃): δ 4.25 (m, 2H), 2.20 (t, J=7.5Hz, 2H), 1.60 (s, 1H), 1.50 (m, 2H), 1.31 (m, 16H), 0.88 (t, J = 7.0 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 86.60, 78.22, 51.41, 31.82, 29.65, 29.61, 29.45, 29.30, 29.15, 28.80, 28.50, 22.62, 18.75, 14.00.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₁₄H₂₆ONa) 233.2, found 233.4. HRMS Calcd for (M+Na)⁺ 233.1881 not found.

Tetradec-13-yn-1-ol (intermediate in the preparation of 4):

¹H NMR (300MHz, CDCl₃): δ 3.64 (t, J = 6.5 Hz, 2H), 2.18 (td, J = 6.9, 2.5 Hz, 2H), 1.94 (t, J = 2.6 Hz, 1H), 1.64 (s, 1H), 1.55 (m, 4H), 1.30 (m, 16H).

¹³C NMR (75 MHz, CDCl₃): δ 84.80, 68.05, 63.00, 32.72, 29.55, 29.52, 29.50, 29.45, 29.40, 29.01, 28.73, 28.45, 25.71, 18.30.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₁₄H₂₆ONa) 233.2, found 233.2. HRMS Calcd for (M+Na)⁺ 233.1881 found 233.1875.

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1,5-bis((hex-5-yn-1-yloxy)methyl)anthracene (intermediate in the preparation of 3):

¹H NMR (300MHz, CDCl₃): δ 8.73 (s, 2H), 8.03 (d, J=6.0Hz, 2H), 7.50 (d, J=6.0Hz, 2H), 7.45 (dd, J=7.5Hz and 6.0Hz, 2H), 5.10 (s, 4H), 3.61 (t, J=7.5Hz, 4H), 2.15 (td, J=6.0Hz and 3.0Hz, 4H), 1.95 (t, J=3.0Hz, 2H), 1.69 (m, 4H), 1.47 (m, 4H).

¹³C NMR (75MHz, CDCl₃): δ 135.05, 132.00, 128.70, 127.95, 125.05, 123.15, 122.70, 83.95, 73.05, 70.10, 68.60, 29.30, 26.67, 18.50.

1,5-bis((tetradec-13-yn-1-yloxy)methyl)anthracene (intermediate in the preparation of 4):

¹H NMR (300MHz, CDCl₃): δ 8.72 (s, 2H), 8.03 (d, J=6.0Hz, 2H), 7.50 (d, J=6.0Hz, 2H), 7.44 (dd, J=7.0Hz and 6.0Hz, 2H), 5.09 (s, 4H), 3.60 (t, J=7.5Hz, 4H), 2.14 (td, J=7.0Hz and 3.0Hz, 4H), 1.96 (t, J=3.0Hz, 2H), 1.65 (m, 4H), 1.42 (m, 36H).

¹³C NMR (75MHz, CDCl₃): δ 134.40, 131.80, 127.05, 128.10, 124.95, 123.15, 122.43, 84.50, 73.00, 70.50, 68.50, 30.15, 29.70, 29.68, 29.64, 29.60, 29.55, 29.47, 28.71, 28.60, 28.44, 18.40.

1,5-bis((dec-9-yn-1-yloxy)methyl)anthracene (intermediate in the preparation of 5):

¹H NMR (300MHz, CDCl₃): δ 8.73 (s, 2H), 8.04 (d, J=7.0Hz, 2H), 7.53 (d, J=6.5Hz, 2H), 7.45 (dd, J=8.5Hz and 6.0Hz, 2H), 5.10 (s, 4H), 3.62 (t, J=7.0Hz, 4H), 2.16 (td, J=7.0Hz and 3.0Hz, 4H), 1.95 (t, J=3.0Hz, 2H), 1.68 (m, 4H), 1.47 (m, 20H).

¹³C NMR (75MHz, CDCl₃): δ 134.62, 132.05, 128.30, 128.12, 124.97, 123.22, 122.80, 84.70, 72.70, 70.23, 68.50, 31.03, 30.00, 29.75, 29.55, 28.73, 28.12, 18.50.

1-iodohept-1-yne (intermediate in the preparation of 4):

¹H NMR (300MHz, CDCl₃): δ 2.41 (t, J=7.0Hz, 2H), 1.49 (m, 2H), 1.34 (m, 4H), 0.90 (t, J=7.0 Hz, 3H).

¹³C NMR (75MHz, CDCl₃): δ 94.50, 68.52, 30.60, 27.83, 20.85, 19.76, 14.10.

m/s (EI) m/z Calcd for M⁺ (C₇H₁₁I) 222.0, found 222.1. HRMS Calcd for M⁺ 221.9905 found 221.9910.

1-iodopentadec-1-yne (intermediate in the preparation of 3):

¹H NMR (300MHz, CDCl₃): δ 2.35 (t, J = 6.9 Hz, 2H), 1.35 (m, 22H), 0.88 (t, J = 6.7 Hz, 3H).

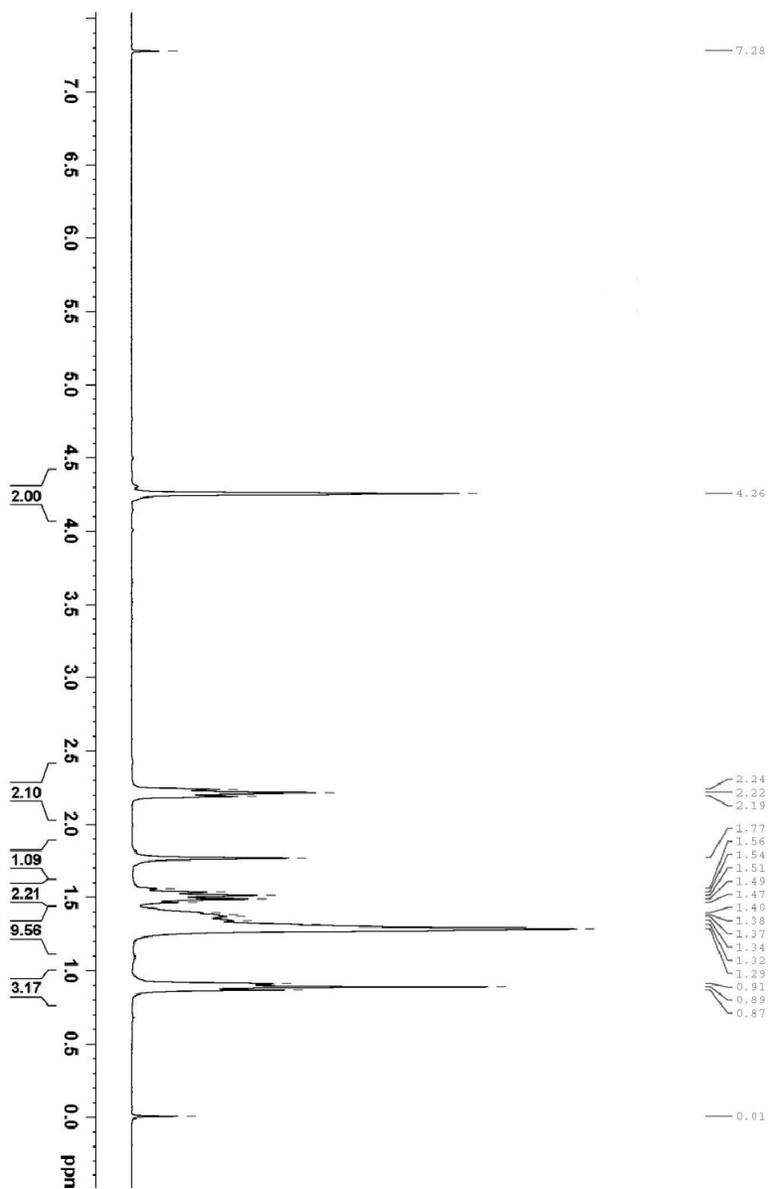
¹³C NMR (75MHz, CDCl₃): δ 94.82, 67.55, 31.91, 29.65, 29.61, 29.58, 29.55, 29.41, 29.30, 29.04, 28.70, 28.42, 22.64, 20.82, 14.05.

m/s (EI) m/z Calcd for M⁺ (C₁₅H₂₇I) 334.1, found 334.3. HRMS Calcd for M⁺ 334.1157 not found.

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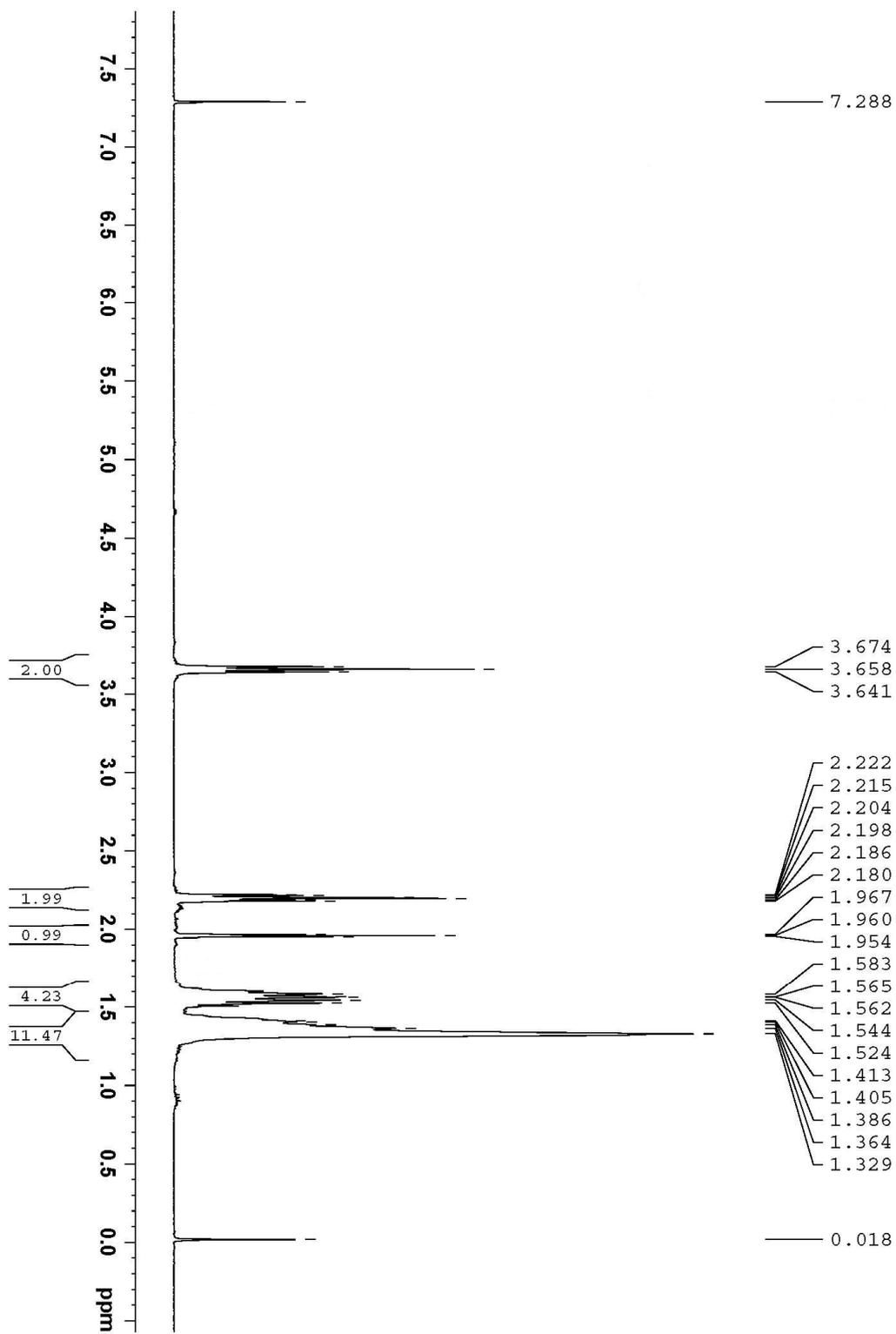
B. NMR spectra of selected compounds.

^1H NMR undec-2-yn-1-ol



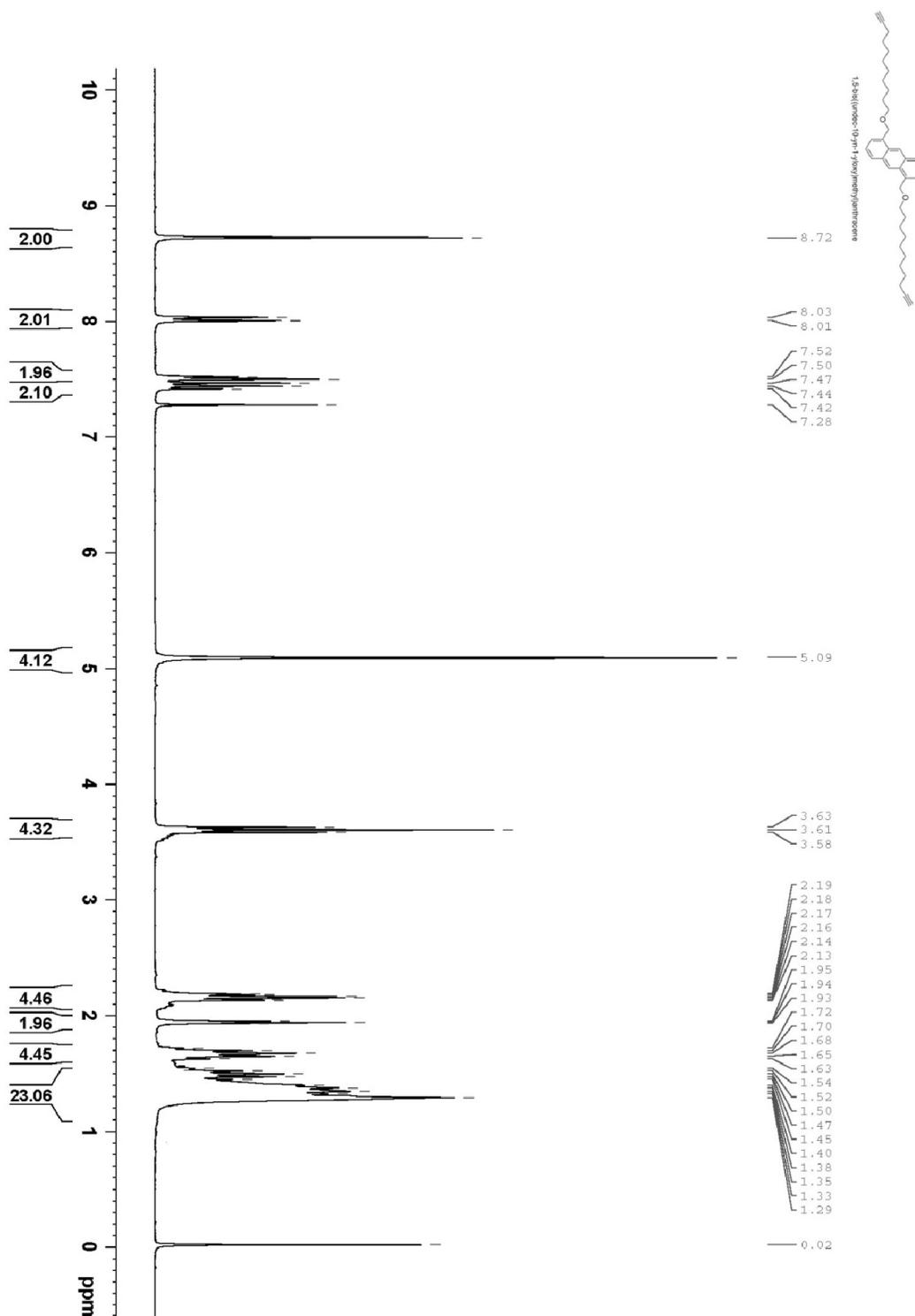
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¹H NMR undec-10-yn-1-ol



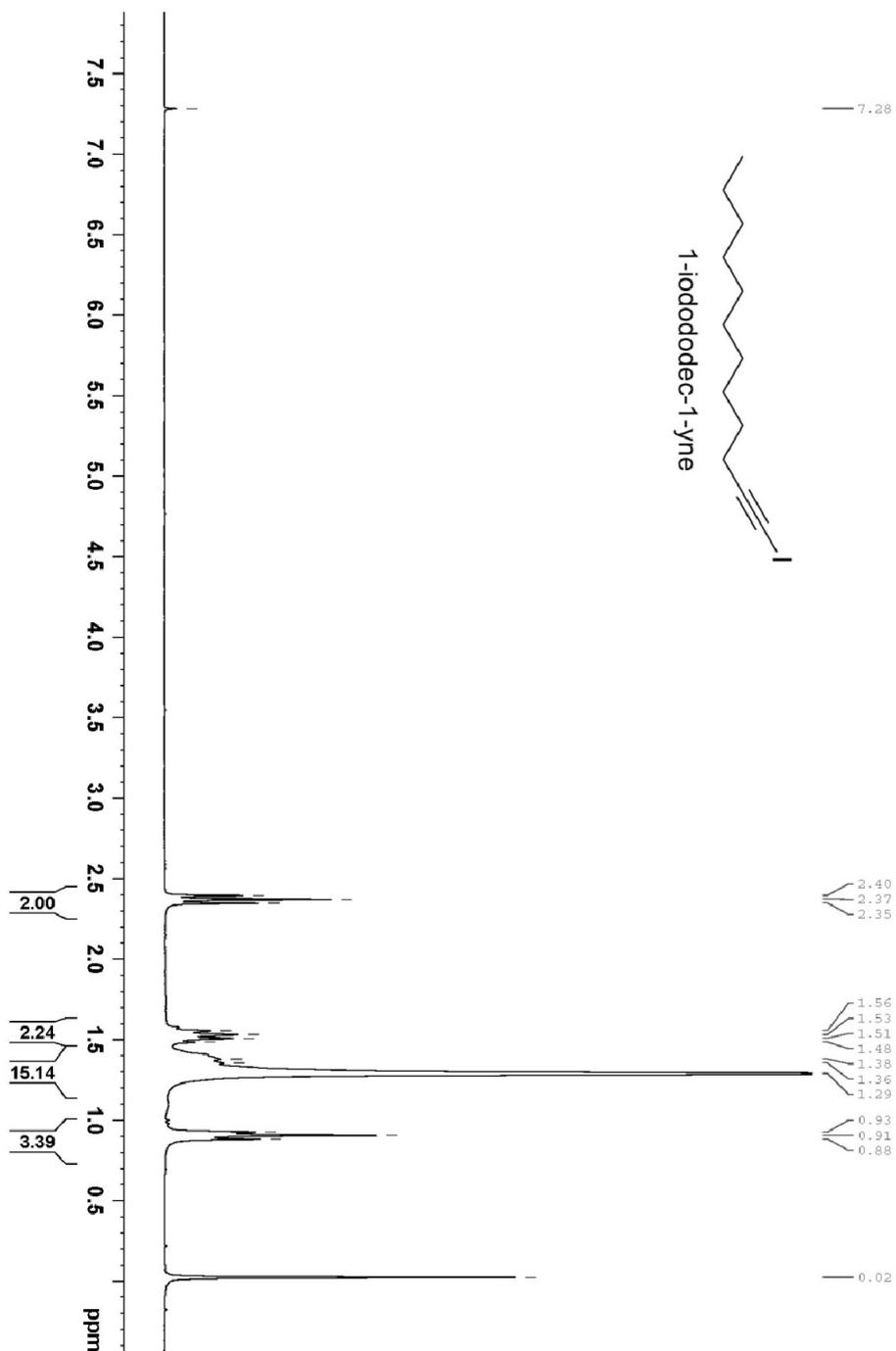
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¹H NMR 1,5-bis((undec-10-yn-1-yloxy)methyl)anthracene



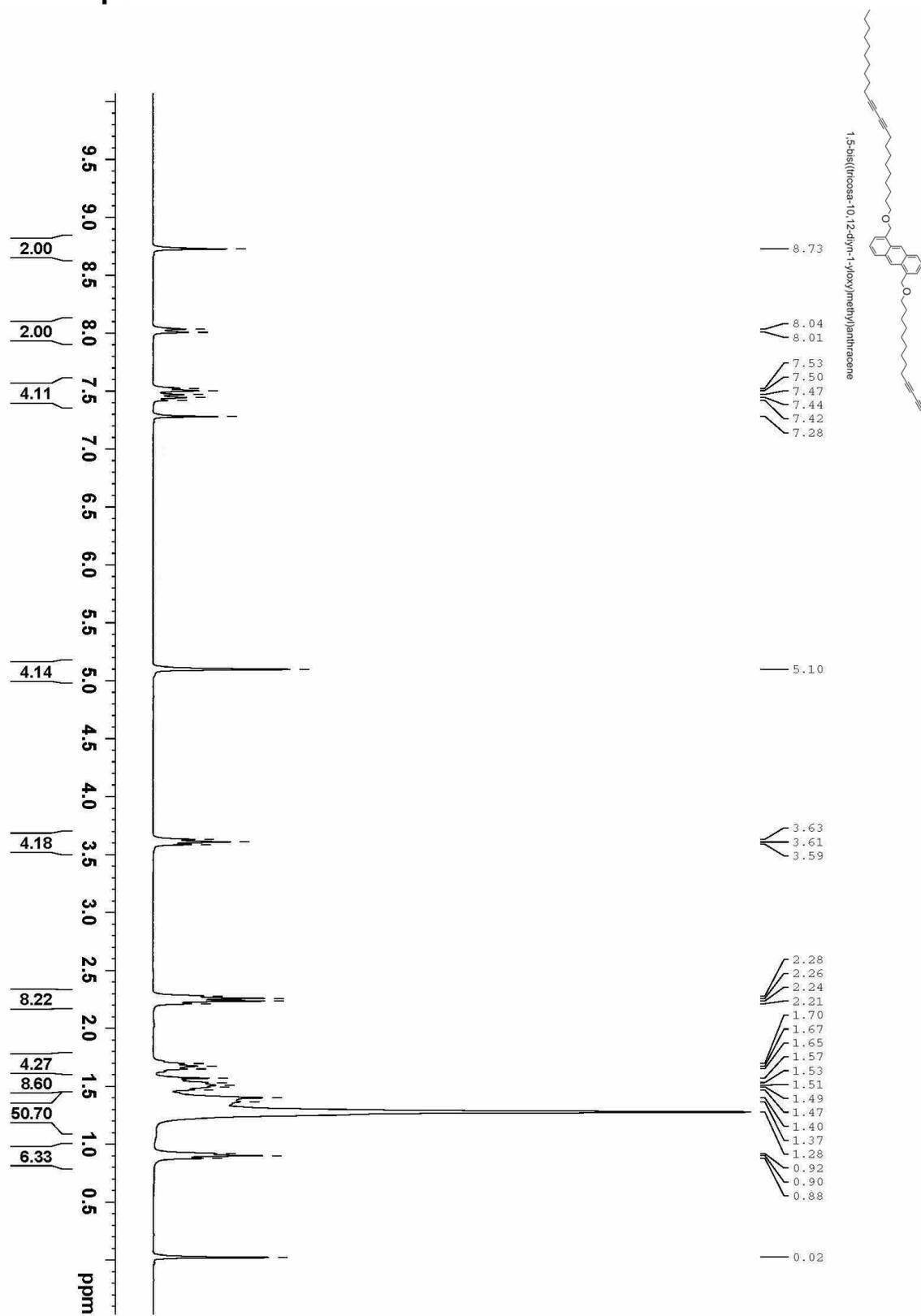
RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

¹H NMR 1-iodododec-1-yne



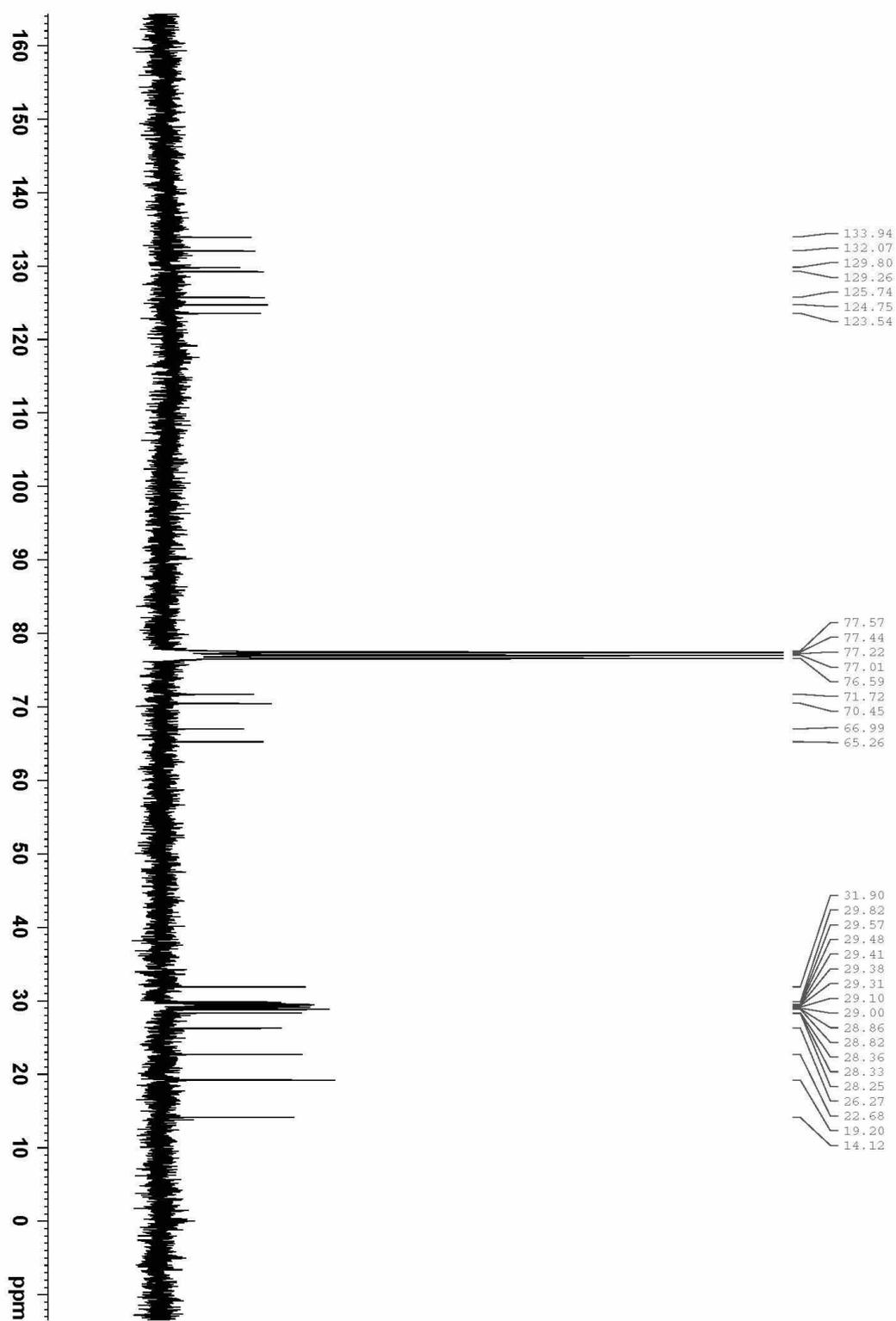
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¹H NMR Compound 1



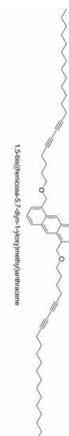
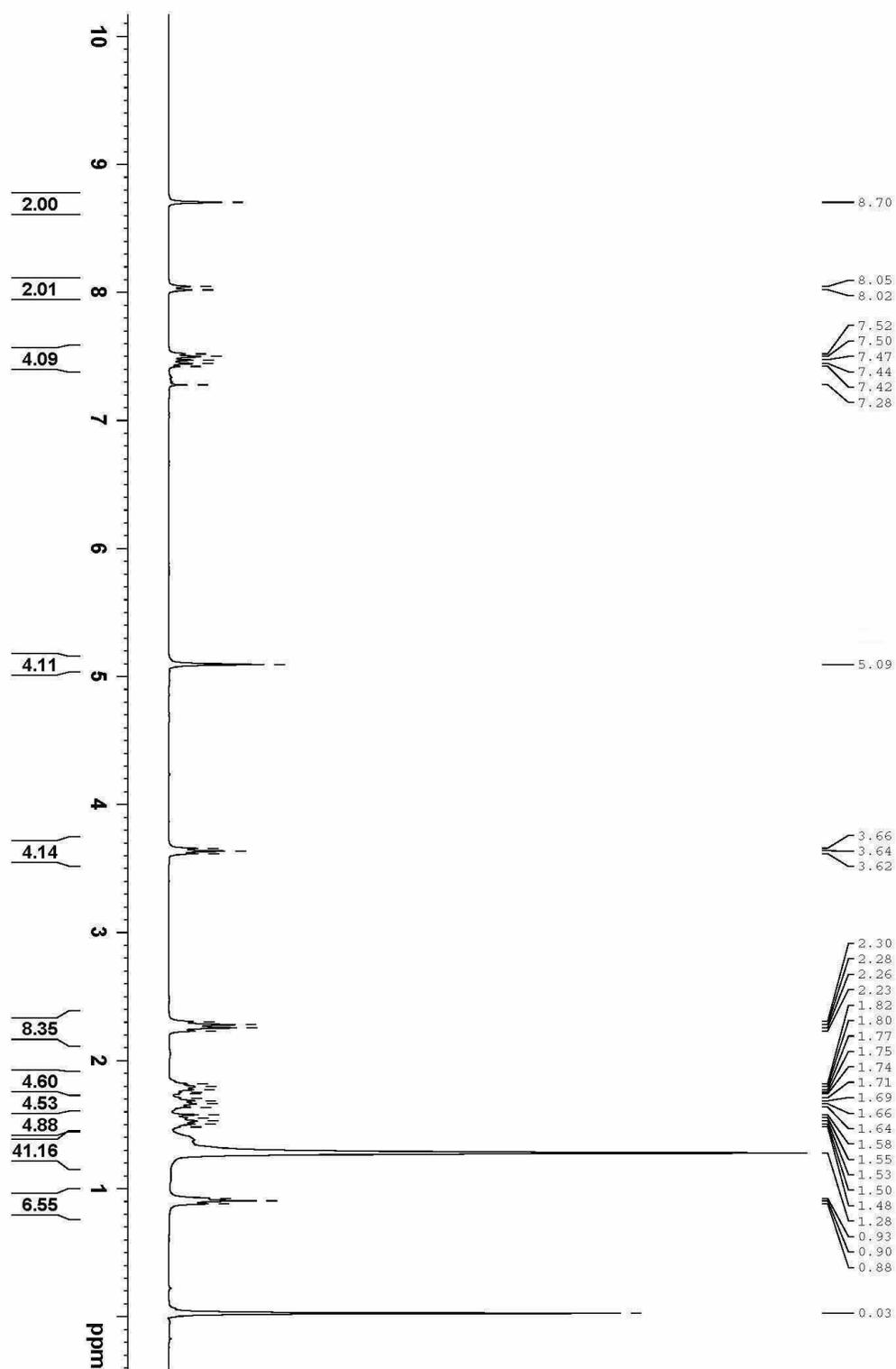
RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

^{13}C NMR Compound 1



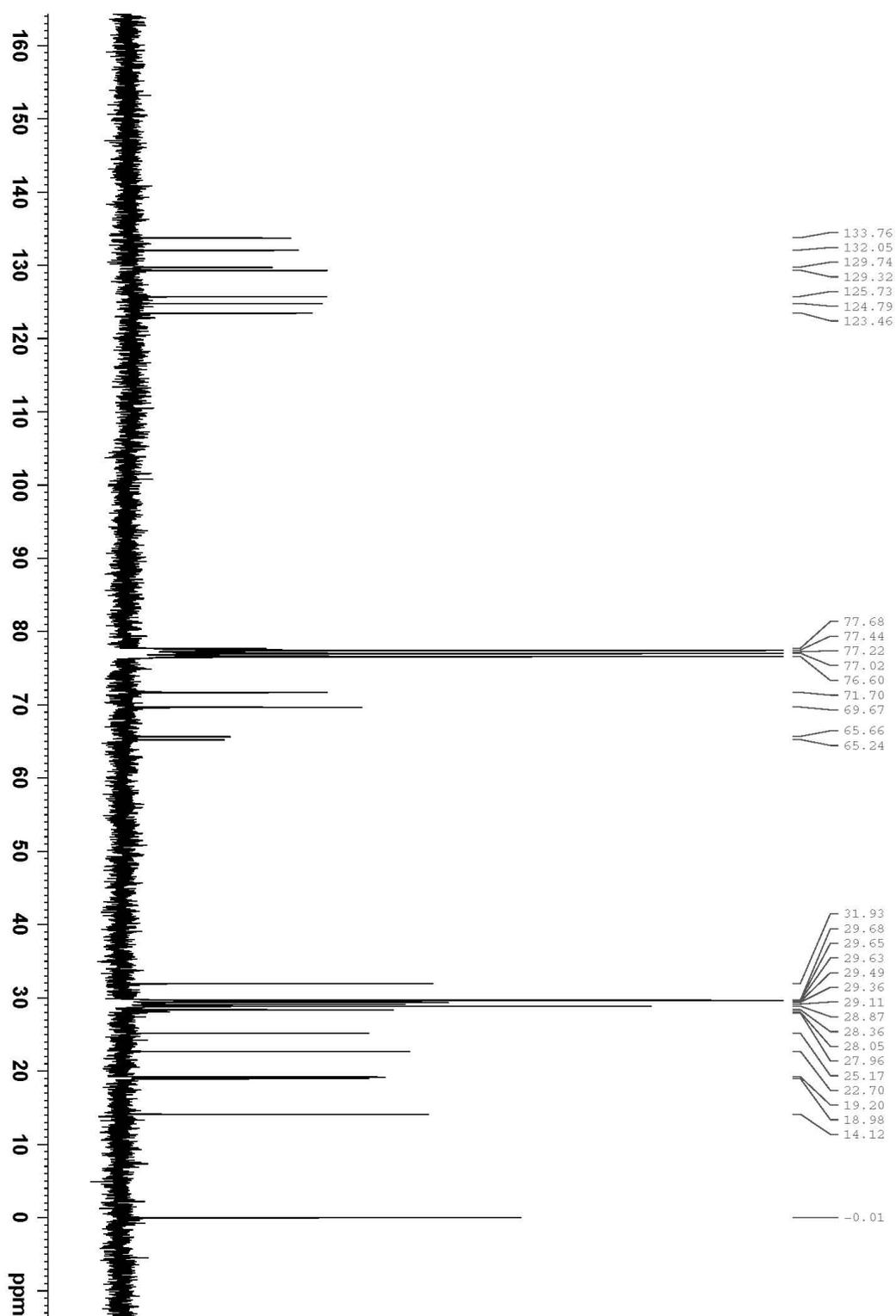
RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

¹H NMR Compound 3



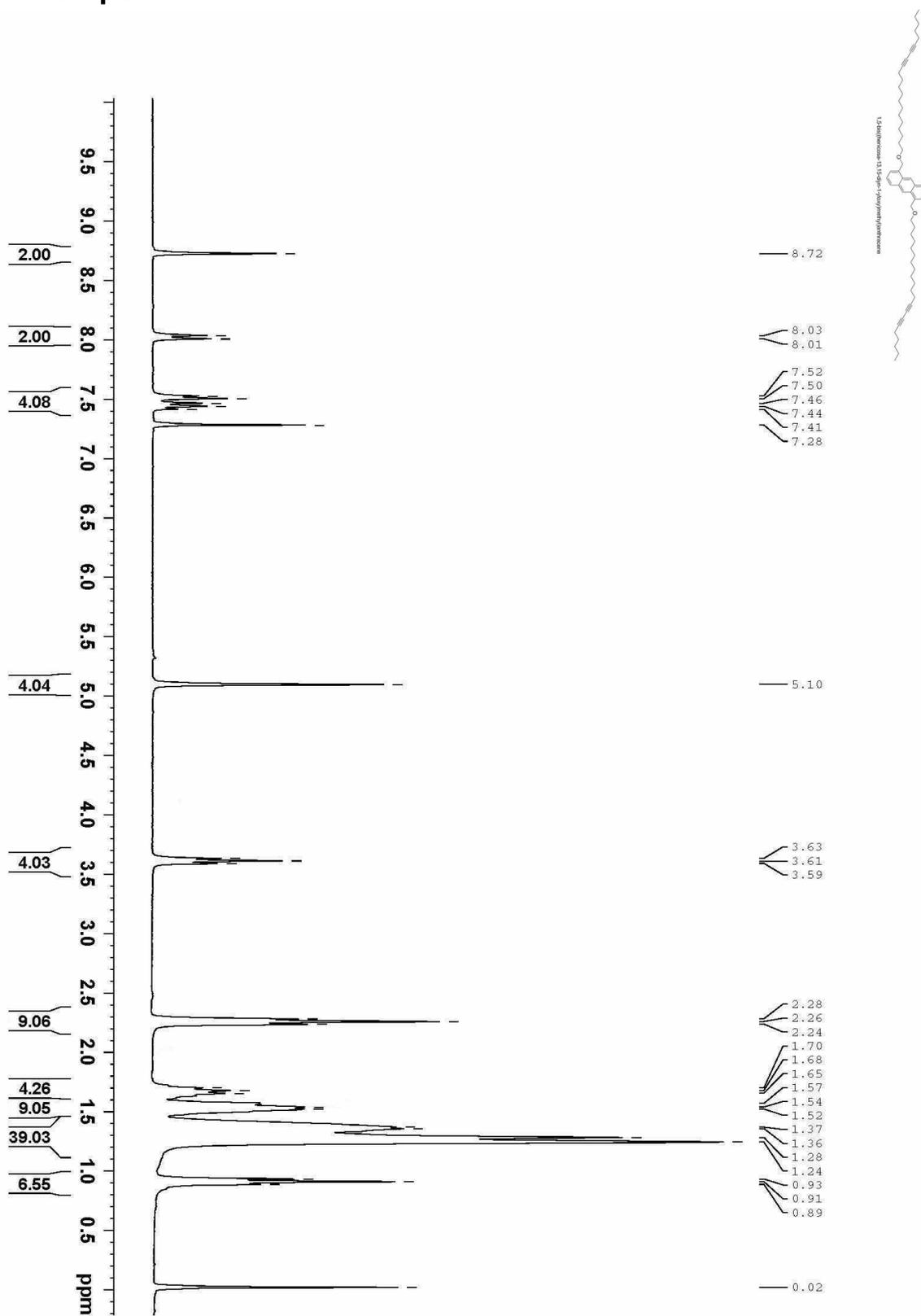
RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

^{13}C NMR Compound 3



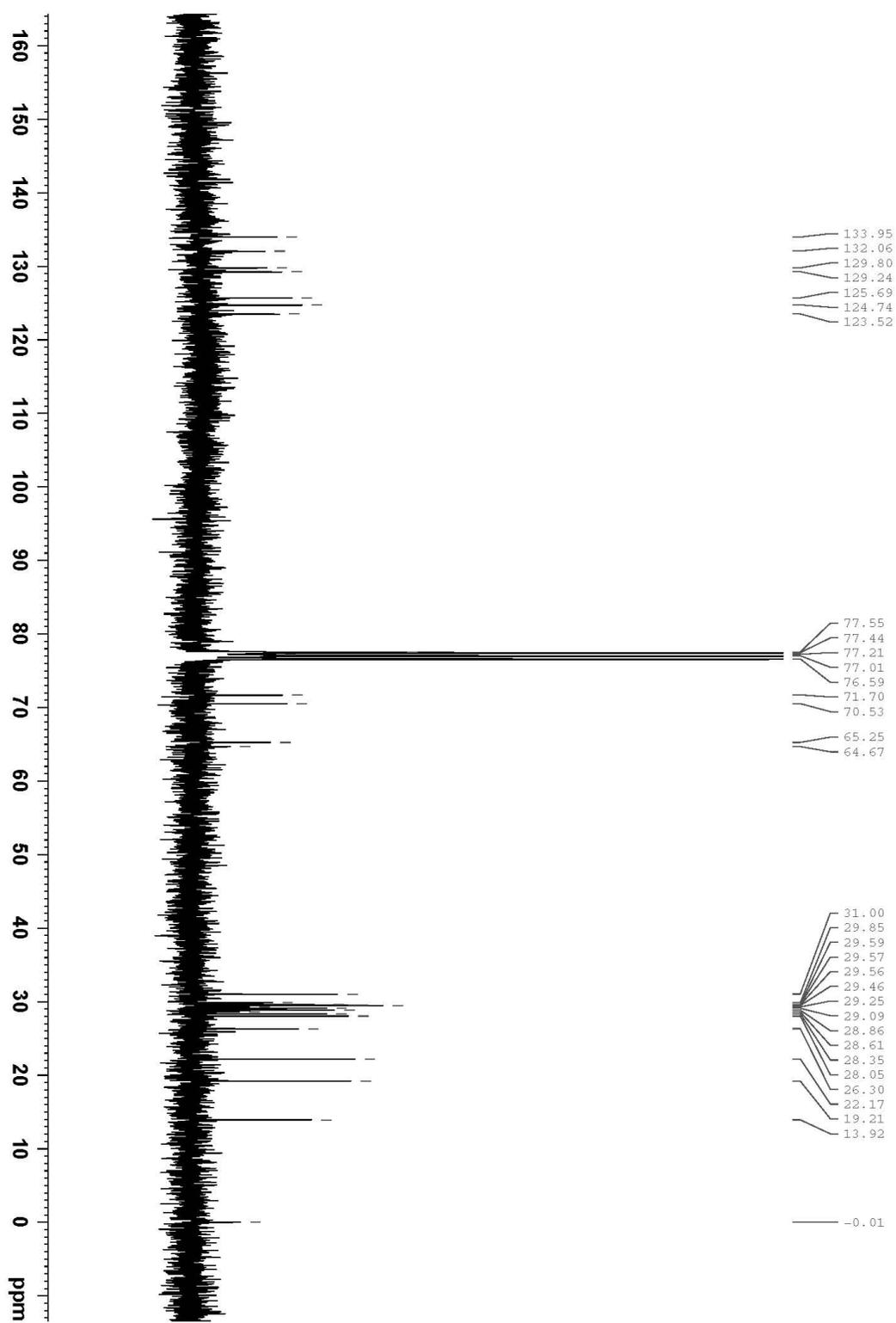
RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

¹H NMR Compound 4



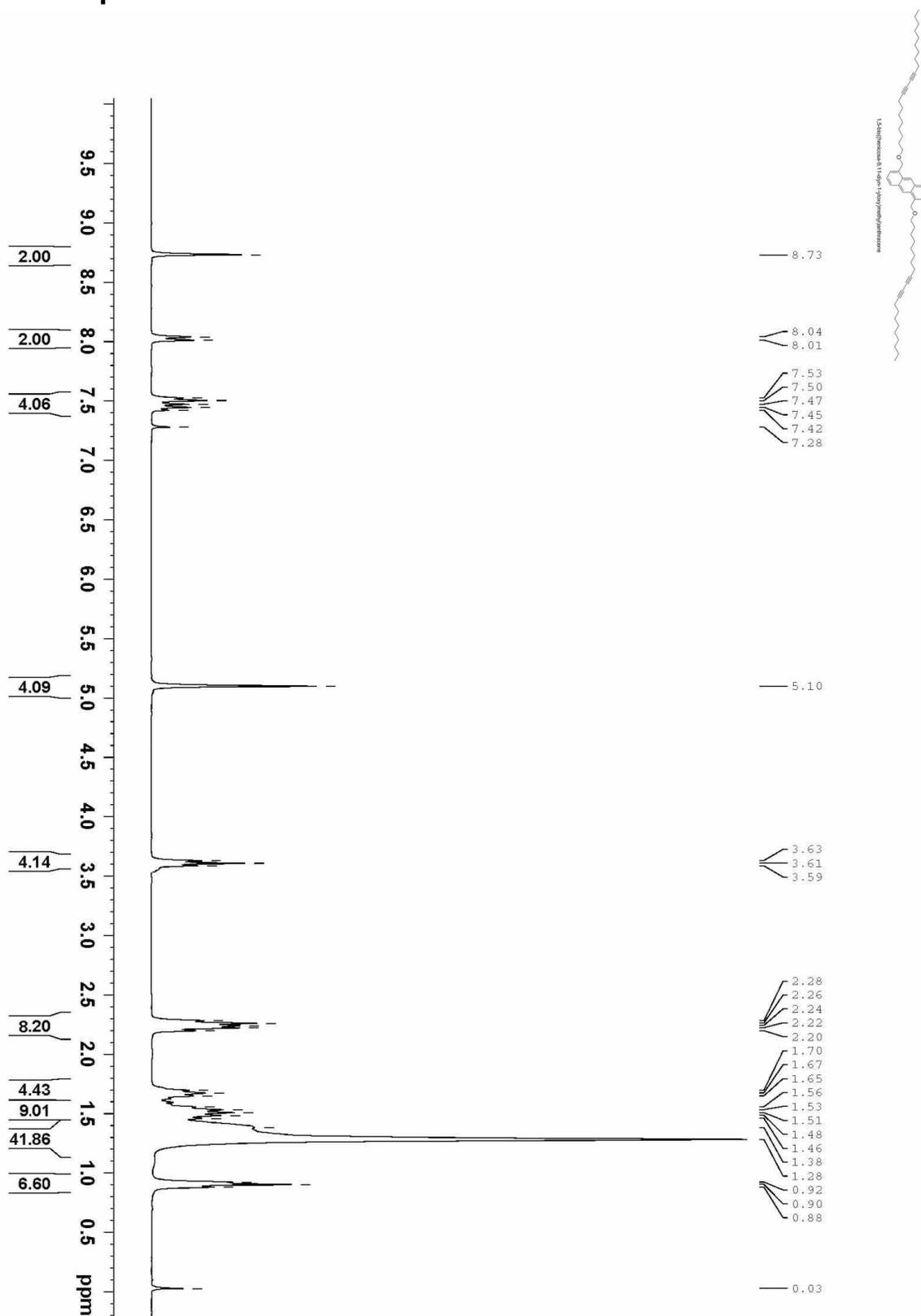
RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

^{13}C NMR Compound 4



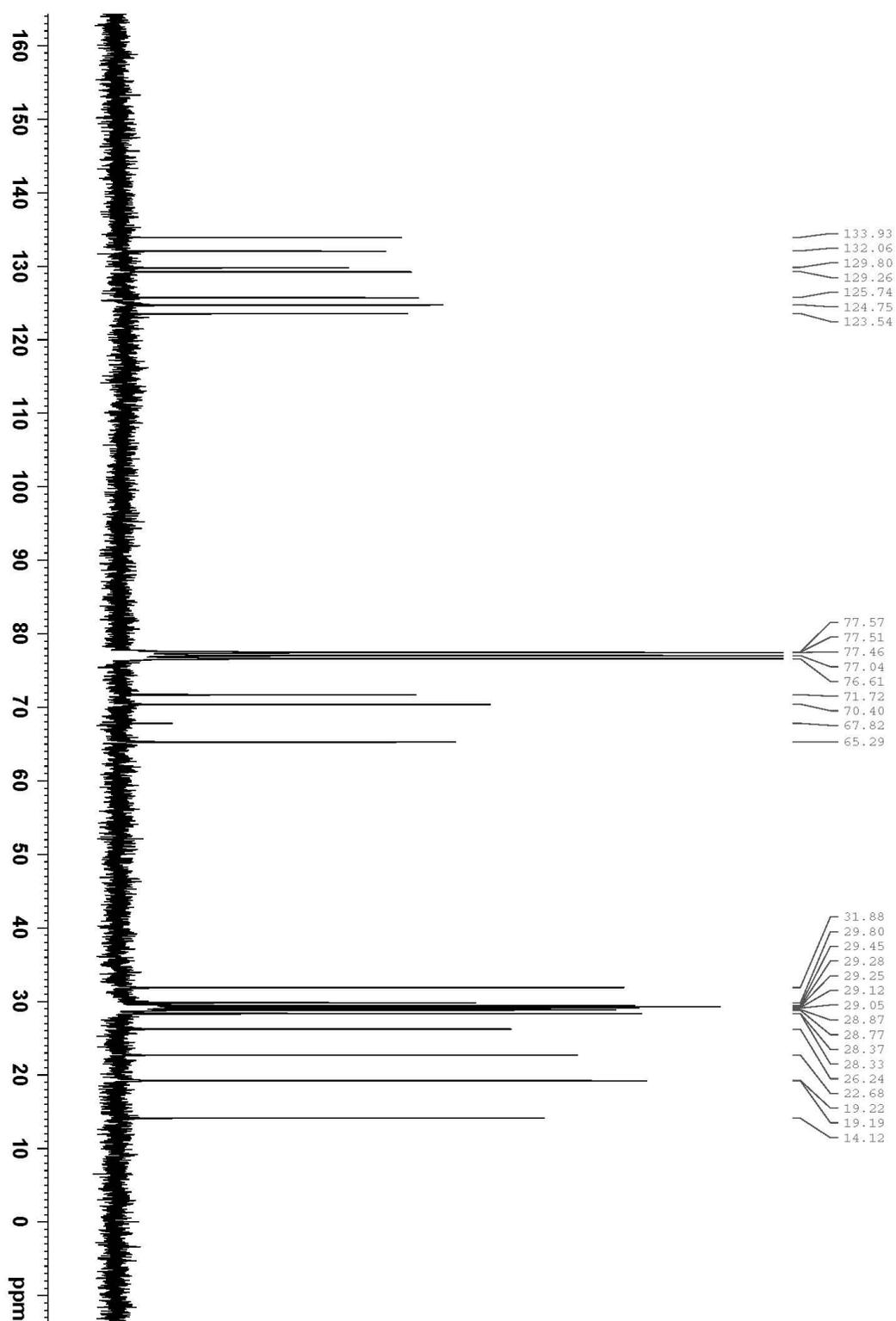
RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

¹H NMR Compound 5



RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

^{13}C NMR Compound 5



RSC 2011 Xue - Zimmt diyne shape - Electronic Supporting Information.

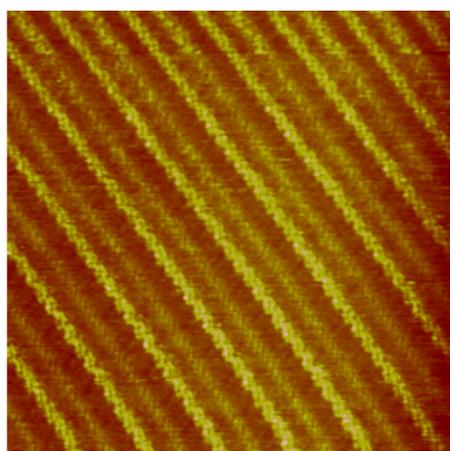
C. STM Sample Preparation and Acquisition Protocols

Scanning tunneling microscopy data was acquired using a Digital Instruments NanoScope STM interfaced to a Digital Instruments NanoScope IIIa controller. Data collected from the solution – graphite or air – graphite interfaces (HOPG, ZYB grade, Momentive Performance, Strongsville, OH) used mechanically cut 87/13 Pt/Rh tips (0.25 mm, Omega Engineering, Stamford, CT) or 80/20 Pt/Ir tips (0.25 mm, Goodfellow, Oakdale, PA). Sample solutions were prepared from 2 – 5 mg of compound in 200 μ L of phenyl octane (Aldrich, 98%) at 20 °C. Solutions were filtered (Anatop Plus 0.02 μ m filters, Whatman) and equilibrated at the temperature of the STM room (15 – 20 °C). A solution drop (5 μ L) was deposited on a recently cleaved HOPG surface. Samples were imaged immediately or after annealing at 40 °C for 1 hour. The STM tip was engaged through the solution and scanned in constant height mode. Tip scan velocities were in the range 0.20 – 1.2 μ m/s. Multiple samples of each compound were prepared and imaged to evaluate monolayer morphology and unit cells. For all compounds, high resolution data was obtained only in constant height mode. Thermal drift could not be eliminated during data acquisition. Small or moderate thermal drift distortions do not prevent morphology or unit cell evaluation. To determine the unit cell of each monolayer, thermal drift effects were removed using a program that solves for the x- and y-thermal drift velocities in consecutively captured images obtained using opposite slow scan directions. The program minimizes differences in the two scans' unit cell parameters. This correction is valid if thermal drift velocities remain relatively constant in consecutive scans. Reported unit cell parameters are averages of thermal drift corrected STM data from three or more independently prepared and scanned sets of samples. STM scanner x- and y-calibration was performed prior to monolayer formation using sequentially captured HOPG scans (10 nm scale) corrected for thermal drift.

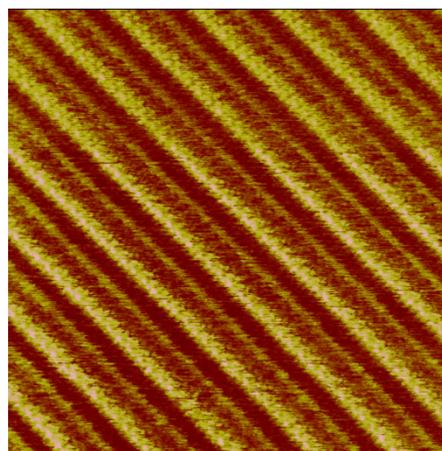
Within ten minutes of depositing a phenyl octane solution of **1**, **2**, **5** or the mixture of **3** and **4** on HOPG (concentrations 1 - 2 mg /100 μ L), monolayers were observed. Additional annealing increased domain sizes and image quality but did not alter monolayer morphology. Deposition of a phenyl octane solution containing **3** or **4** on HOPG (concentrations of 1 - 2 mg /100 μ L), did not yield detectable monolayers within 24 hours.

Phenyl octane free (“dry”) monolayers or **1** were prepared by rinsing a preformed monolayer of **1** (40°C annealed for 40 minutes) with 1-2 mL of cold ethanol or cold tetradecane. The HOPG substrate was then dried in air prior to imaging. An STM image of a “dry” monolayer prior to irradiation is reproduced here.

UV irradiation was performed using a Spectronics 11SC-1 short wave UV lamp (254nm). A “dry” monolayer of **1** on HOPG sample was placed 2-5cm below the UV lamp and irradiated for 5-40 mins under nitrogen atmosphere. In all cases, no monolayer was observed after irradiation.



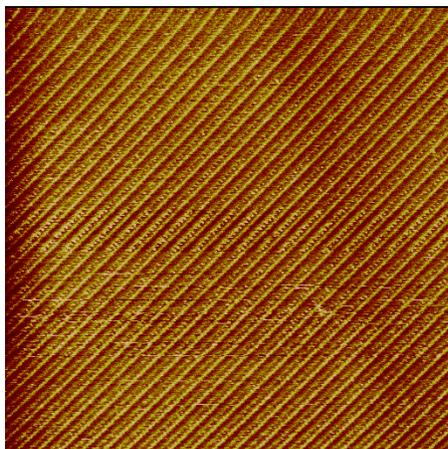
30 nm \times 30 nm STM images (0.8V, 100 pA) of **1** monolayers at (left) the phenyl octane / HOPG interface; (right) the air / HOPG interface after EtOH rinsing and air drying of the sample (left). (Neither image is corrected for thermal drift.)



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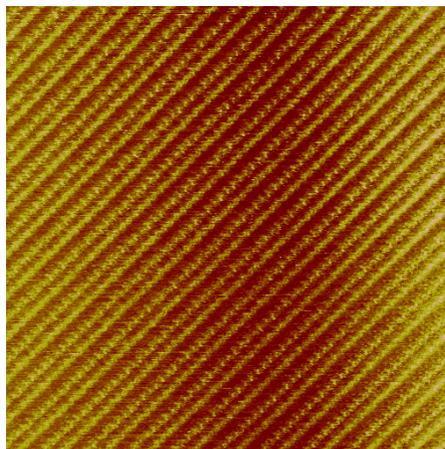
D. STM images of large domains formed by compounds 1 - 5 at the phenyloctane - HOPG interface.

Compound 1



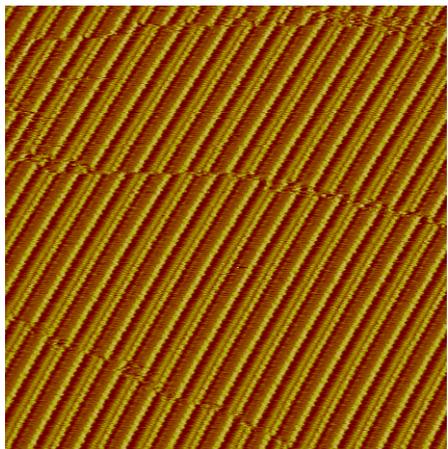
100 nm × 100 nm (0.8V, 0.1nA)
Constant height

Compound 2



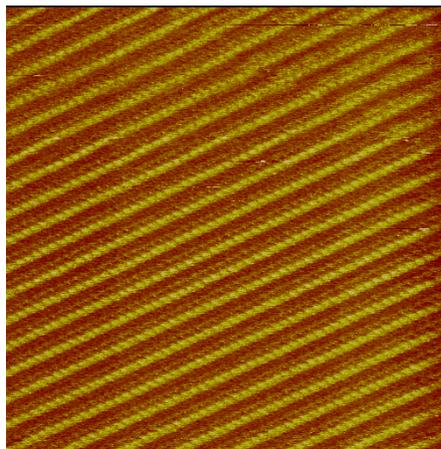
50 nm × 50 nm (0.8V, 0.1nA)
Constant height

Compound 3 + 4



75 nm × 75 nm (0.8V, 0.1nA)
Constant height

Compound 5



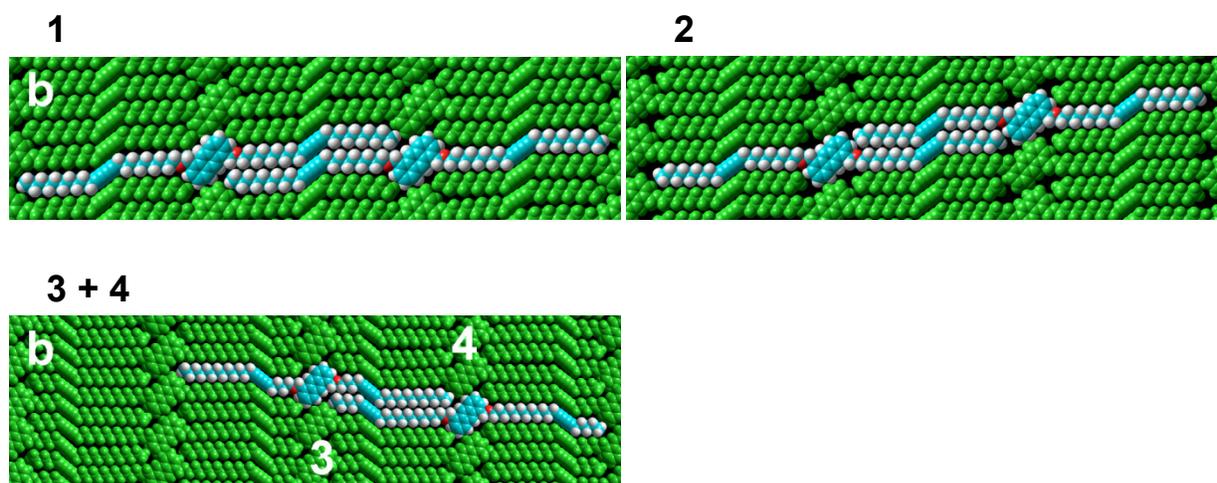
50 nm × 50 nm (0.8V, 0.1nA)
Constant height

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E. Unit cell data from STM scans and molecular mechanics simulations.

Compound	Experimental (STM) Unit Cell Parameters			Simulation Unit Cell Parameters		
	a (nm)	b (nm)	α ($^\circ$)	a (nm)	b (nm)	α ($^\circ$)
1	3.76±0.04	0.95±0.02	90.1±1.7	3.79	0.94	88.6
2	3.72±0.02	0.95±0.03	91.3±2.5	3.79	0.91	91.1
3	No ML	No ML	No ML	4.70	0.99	90.3
4	No ML	No ML	No ML	4.64	0.92	78.9
3 + 4	7.16±0.07	0.95±0.02	83.5±3.3	7.21	0.93	78.5
5	3.53±0.06	0.97±0.04	78.8±4.0	3.56	0.90	82.7

F. CPK models of molecular mechanics simulation for monolayers assembled by 1, 2 and 3 + 4.



G. Molecular mechanics simulations of monolayer sections

Molecular mechanics (MM) minimizations were performed on monolayer sections consisting of 4 - 6 anthracene columns, containing 4 - 6 molecules. The HOPG surface was modeled as a single layer, graphene sheet 10 - 20% larger than the monolayer section. Atomic charges were assigned using Mulliken population analysis in AM1. Side chains were $\omega \leftrightarrow 2$ or $\omega \leftrightarrow 3$ packed and aligned on the graphene sheet. Minimizations were run until the MM energy of the sample decreased less than 10^{-5} kcal/mole in 24 hours. MM ref: U. Burkert and N. L. Allinger, Eds. Molecular Mechanics, 1982, ACS Monograph, No. 177; AM1 ref. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.