Supporting Information for

Folding a Conjugated Chain: Oligo(*o*-phenyleneethynylene-*alt*-*p*-phenyleneethynylene)

Ningbo Zhu, Wei Hu, Shuliang Han, Qi Wang, and Dahui Zhao*

Beijing National Laboratory for Molecular Sciences (BNLMS), Department of Applied Chemistry and the Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Email: dhzhao@pku.edu.cn

Table of Contents

I. General Methods. Chemicals and solvents were purchased and used as received unless otherwise indicated. All air and water sensitive reactions were performed under nitrogen atmosphere using standard Schlenk procedures. Toluene was distilled from sodium and benzophenone ketyl. Diisopropylamine was dried over solid KOH and distilled. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury plus 300 MHz using $CDCl_3$ as solvent unless otherwise noted. All chemical shifts were reported in parts per million (ppm). ^{1}H NMR chemical shifts were referenced to TMS (0.0 ppm) or $CHCl_3$ (7.26 ppm), and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.0 ppm). Absorption spectra were recorded on a PerkinElmer Lambda 35 UV-vis Spectrometer. Photoluminescence spectra were recorded on a PerkinElmer LS55 Luminescence Spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III or AUTOFLEX III time-of-flight (TOF) mass spectrometer using a 337 nm nitrogen laser with dithranol as matrix. Elemental analyses were performed using a German Vario EL III elemental analyzer.

II. Absorption and Emission Spectra.

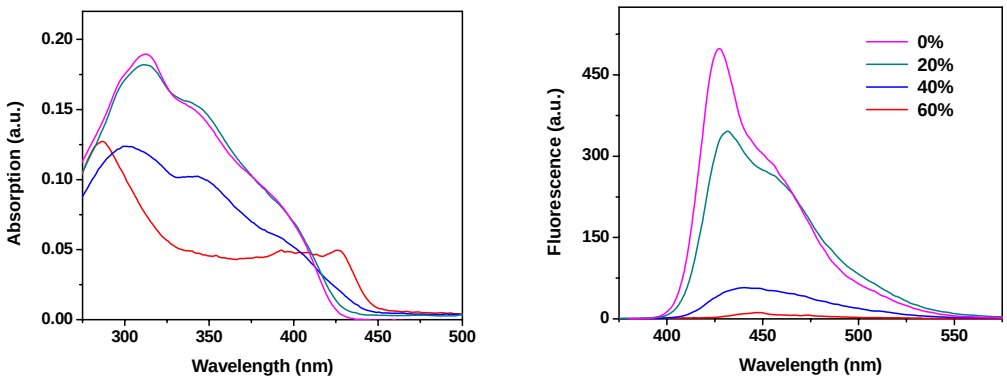


Figure S1. UV-vis absorption and fluorescence emission spectra of oligomer **1** in a series of chloroform-acetonitrile co-solvents; the legend shows the volume percentage of acetonitrile.

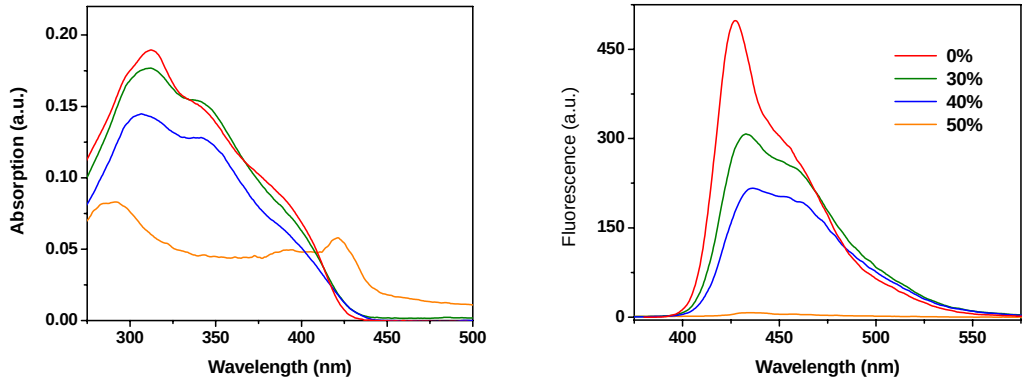


Figure S2. UV-vis absorption and fluorescence emission spectra of oligomer **1** in a series of chloroform-methanol co-solvents; the legend shows the volume percentage of methanol.

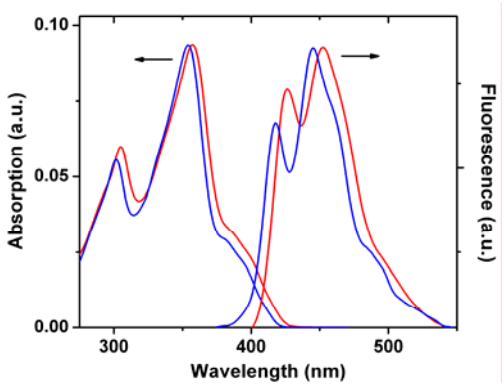
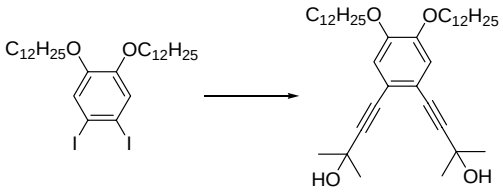


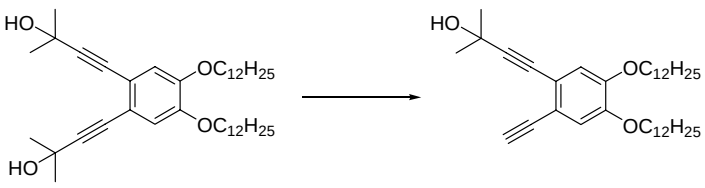
Figure S3. UV-vis absorption and fluorescence emission spectra of **MC** in chloroform (red) and cyclohexane (blue).

III. Synthetic Procedures and Characterization Data.



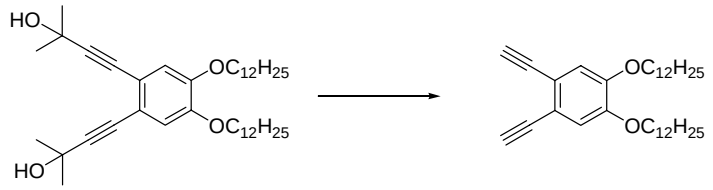
5

4,4'-(4,5-bis(dodecyloxy)-1,2-phenylene)-bis(2-methylbut-3-yn-2-ol) 5. A tube containing 1,2-bis(dodecyloxy)-4,5-diiodobenzene (3.4 g, 4.9 mmol), $Pd(PPh_3)_2Cl_2$ (0.063 g, 0.09 mmol), and CuI (0.07 g, 0.3 mmol) was evacuated and back-filled with nitrogen three times. Then degassed 2-methylbut-3-yn-2-ol (1.5 mL, 15.3 mmol) and *i*-Pr_2NH (30 mL) were added to the tube under nitrogen atmosphere. The tube was sealed and the reaction mixture was stirred at rt for 3 h. Then the salt formed was filtered out and the solvent was removed in vacuo. The solid residue was dissolved in 20 mL ethyl acetate, washed with saturated aq. NH_4Cl and brine sequentially, and then dried over anhydrous Na_2SO_4. The solvent was then evaporated and the residue was purified by flash column chromatography over silica gel with petroleum ether (PE)/ethyl acetate (EtOAc) (3:1, v/v) as eluent to give the product as white powder: 2.9 g (93%); mp: 54-56 ^oC. TLC (PE/EtOAc, 2:1, v/v) R_f = 0.5. ^1H NMR (300 MHz, $CDCl_3$): δ 6.86 (2H, s), 3.96 (4H, t, J = 6.6 Hz), 2.42 (2H, br), 1.80 (4H, m), 1.62 (12H, s), 1.2-1.5 (36H, m), 0.87 (6H, t, J = 6.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7, 118.2, 115.4, 96.3, 80.9, 69.0, 65.5, 31.9, 31.5, 29.61, 29.56, 29.3, 25.9, 22.6, 14.1.



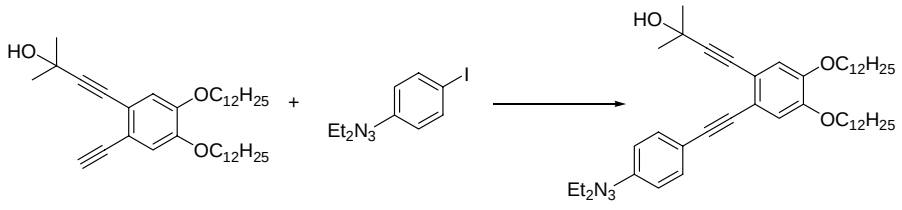
5 **6**

4-(4,5-bis(dodecyloxy)-2-ethynylphenyl)-2-methylbut-3-yn-2-ol 6. Compound **5** (2.4 g, 3.9 mmol)**,** KOH (0.19 g, 3.4 mmol) and K_2CO_3 (2.20 g, 17.1 mmol) were added to toluene (15 mL) in a flask. The reaction mixture was heated and stirred at 70 ^oC. After 20 min (checked the reaction with TLC every 5 min upon adding KOH until diethynyl product started to appear) the reaction mixture was cooled to rt and 15 mL EtOAc was added to it. The organic solution was decanted, washed with 2 M HCl and brine sequentially, and then dried over anhydrous Na_2SO_4. The solvent was then evaporated and the residue was purified by flash column chromatography over silica gel, eluted with EtOAc/PE (1:6, v/v), to give **6** as a yellow solid (1.5 g, 69%); mp: 38-39 ^oC. TLC (PE/EtOAc, 5:1) R_f = 0.51. ^1H NMR (300 MHz, $CDCl_3$): δ 6.94 (1H, s), 6.87 (1H, s), 3.97 (4H, m), 3.21 (s, 1H), 2.04 (1H, br), 1.80 (4H, m), 1.63 (6H, s), 1.2-1.5 (36H, m), 0.88 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.2, 148.7, 118.5, 117.2, 116.3, 115.6, 96.2, 82.4, 80.6, 79.2, 68.9, 68.8, 65.4, 31.8, 31.3, 29.61, 29.57, 29.53, 29.2, 29.1, 28.9, 25.8, 22.6, 13.9.



5 **15**

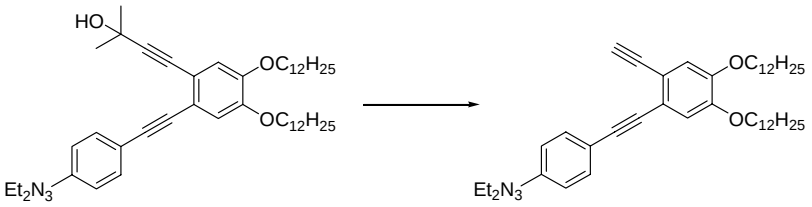
1,2-bis(dodecyloxy)-4,5-diethynylbenzene 15. Compound **5** (0.61 g 1.0 mmol) and KOH (0.15 g, 2.6 mmol) were added to toluene (10 mL) in a flask. The mixture was heated at 100 ^oC and stirred for 2 h. Then the reaction mixture was diluted with 15 mL PE. The organic solution was decanted, washed with 2 M HCl and brine sequentially, and then dried over anhydrous Na_2SO_4. The solvent was then evaporated and the residue was purified with flash column chromatography over silica gel, eluted with dichloromethane (DCM)/PE (1:5, v/v), to give **15** as a white crystalline solid (0.47 g, 95%); mp: 60-61 ^oC. TLC (DCM/PE, 1:4) R_f = 0.5. ^1H NMR: (300 MHz, $CDCl_3$) δ 6.95 (s, 2H), 3.98 (t, 4H, J = 6.6 Hz), 3.25 (s, 2H), 1.81 (m, 4H), 1.2-1.5 (m, 36H), 0.88 (t, 6H, J = 6.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.2, 117.7, 116.3, 82.1, 79.4, 69.0, 31.9, 29.60, 29.56, 29.3, 28.9, 25.9, 22.6, 14.0.



6 **7**

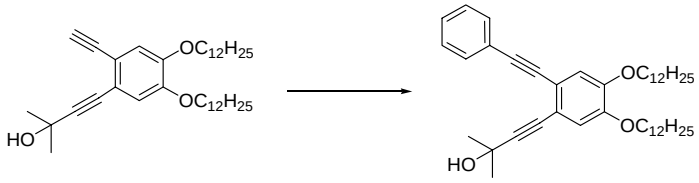
7. Compound **6** (520 mg, 0.94 mmol), CuI (3 mg, 0.016 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg, 0.021 mmol), and (4-iodophenyl)-diethyltriazene[1] (287 mg, 0.95 mmol) were added into a sealed tube. The tube was evacuated and back-filled with nitrogen three times. Then degassed *i*-Pr_2NH (15 mL) was added into the tube under N_2 atmosphere. The tube was then sealed and the reaction mixture was stirred at rt for 14 h. The solvent was then removed in vacuo. The solid residue was dissolved in 20 mL EtOAc. After washed with 1 M HCl, saturated NH_4Cl solution and brine sequentially, the solution was dried over anhydrous Na_2SO_4. Purification was performed by flash column chromatography over silica gel with EtOAc/PE (1:7, v/v) as eluent to afford **7** (640

mg, 93%); mp: 35-36 °C. TLC (PE/EtOAc, 5:1) R_f = 0.45. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (2H, m), 7.41 (2H, m), 6.99 (1H, s), 6.92 (1H, s), 4.00 (4H, m), 3.78 (4H, q, J = 7.1 Hz), 2.11 (1H, br), 1.82 (4H, m), 1.65 (6H, s), 1.4-1.5 (4H, m), 1.2-1.4 (38H, m), 0.88 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 148.9, 148.7, 132.0, 120.3, 119.6, 118.9, 117.8, 115.9, 115.7, 96.1, 92.2, 88.2, 81.1, 69.0, 65.5, 31.8, 31.5, 29.60, 29.56, 29.52, 29.3, 29.0, 25.9, 22.6, 14.0.



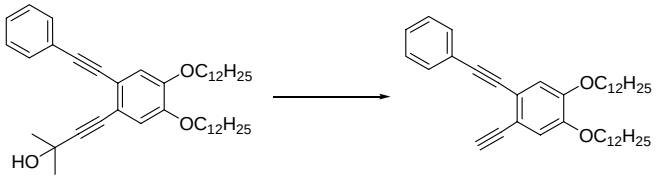
7 **8**

8. Compound **7** (480 mg, 0.66 mmol) and KOH (396 mg, 7.0 mmol) were added into toluene (15 mL) in a flask. Then the mixture was stirred at 60 °C overnight. Then 15 mL PE was added to the reaction mixture. The organic solution was decanted, washed with 2 M HCl and brine sequentially, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the solid residue was purified by flash chromatography over silica gel, eluted with DCM/PE (1:3, v/v) to give **8** as a tacky yellow material (405 mg, 91%). TLC (PE/DCM, 3:1) R_f = 0.31. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (2H, m), 7.39 (2H, m), 6.99 (1H, s), 6.98 (1H, s), 4.01 (4H, m), 3.78 (4H, q, J = 7.1 Hz), 3.29 (1H, s), 1.82 (4H, m), 1.47 (4H, m), 1.20-1.40 (36H, m), 0.88 (6H, t, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.7, 149.2, 148.5, 131.9, 120.2, 119.5, 119.4, 117.0, 116.3, 115.3, 92.5, 87.9, 82.4, 79.3, 68.8, 68.7, 31.8, 29.56, 29.53, 29.49, 29.2, 28.9, 25.8, 28.5, 22.5, 13.9.



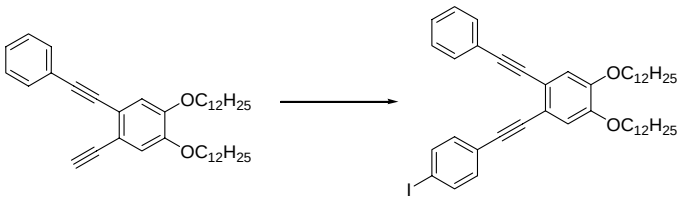
6 **9**

4-(4,5-bis(dodecyloxy)-2-(phenylethynyl)phenyl)-2-methylbut-3-yn-2-ol 9. Compound **6** (610 mg, 1.1 mmol), CuI (4 mg, 0.021 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and iodobenzene (1.0 mL, 8.0 mmol) in a sealed tube were evacuated and backfilled with nitrogen three times. Then degassed *i*-Pr_2NH (10 mL) was added into it via a syringe. The reaction mixture was stirred under nitrogen atmosphere at rt for 12 h. The solvent was then removed in vacuo. The solid mixture was dissolved in 15 mL chloroform and washed with 1 M HCl, saturated aq. NH_4Cl and dried over anhydrous Na_2SO_4. Purification was performed by flash column chromatography over silica gel with EtOAc/PE (1:7, v/v) as eluent and afforded **9** as a solid (604 mg, 87%); mp: 60-61 °C. TLC (PE/EtOAc, 6:1) R_f = 0.42. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (2H, m), 7.34 (3H, m), 6.96 (1H, s), 6.91 (1H, s), 3.99 (4H, m), 2.03 (1H, br), 1.82 (4H, m), 1.64 (6H, s), 1.2-1.5 (36H, m), 0.88 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.9, 131.4, 128.3, 128.1, 123.4, 118.5, 117.9, 115.8, 115.7, 96.2, 91.5, 88.4, 81.1, 69.1, 65.7, 31.9, 31.6, 29.67, 29.63, 29.59, 29.3, 29.0, 25.9, 22.7, 14.1.



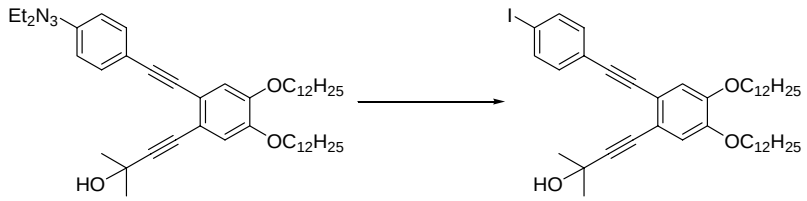
9 **10**

10. Compound **9** (346 mg, 0.55 mmol**)** and KOH (185 mg, 3.3 mmol) were added into toluene (10 mL) in a flask. The mixture was stirred at 60 ^{o}C overnight. Then 15 mL PE was added to the mixture. The organic solution was washed with 2 M HCl and brine sequentially and then dried over anhydrous Na_2SO_4. The solvent was then evaporated and the compound was purified by flash chromatography over silica gel, eluted with DCM/PE (1:3, v/v) to give **10** as white powder (260 mg, 83%); mp: 58 ^{o}C. TLC (PE/DCM, 3:1) R_f = 0.41. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (2H, m), 7.34 (3H, m), 6.99 (1H, s), 6.98 (1H, s), 4.00 (4H, m), 3.27 (1H, s), 1.82 (4H, m), 1.45 (4H, m), 1.2-1.4 (32H, m), 0.88 (6H, m). ^{13}C NMR (50 MHz, $CDCl_3$) : δ 149.5, 149.1, 131.6, 128.3, 128.1, 123.5, 119.2, 117.4, 116.8, 115.9, 91.9, 88.2, 82.5, 79.4, 69.22, 69.19, 31.9, 29.67, 29.64, 29.59, 29.3, 29.1, 25.9, 22.7, 14.1. FT-IR (KBr): 3294, 3053, 2847, 2211, 2104, 1689, 1591, 1507, 1460, 1393, 1340, 1249, 1208, 1083, 852, 757, 601 cm^{-1}.



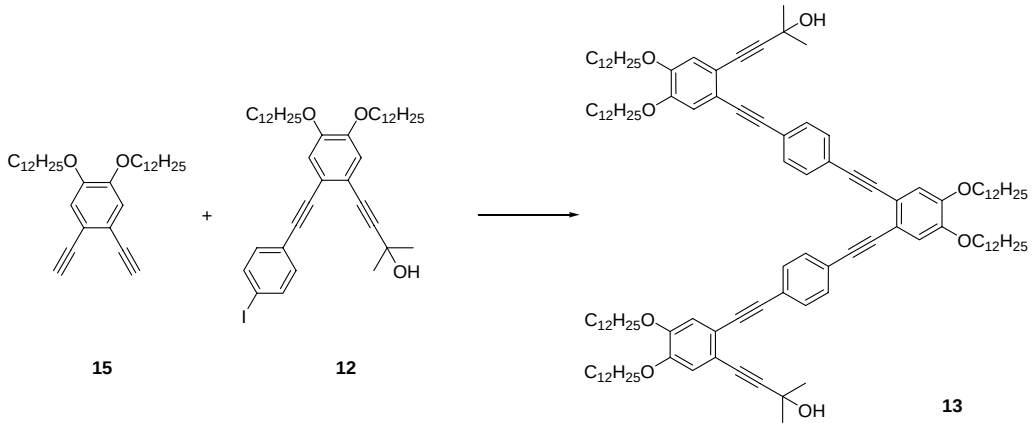
10 **11**

11. A Schlenk tube containing compound **10** (97 mg, 0.17 mmol), CuI (3 mg, 0.016 mmol), $Pd(PPh_3)_4$ (10 mg, 0.0087 mmol), and 1,4-diiodobenzene (146 mg, 0.44 mmol) was evacuated and backfilled with nitrogen three times. A degassed mixture of *i*-Pr_2NH (5.0 mL) and toluene (10.0 mL) was then added under nitrogen atmosphere. The reaction mixture was stirred at rt for 14 h. Then the solvent was removed in vacuo. The solid mixture was dissolved in 20 mL of chloroform, washed with 1 M HCl, saturated aq. NH_4Cl and brine sequentially, and then dried over anhydrous Na_2SO_4. Solvent was then removed in vacuo. Purification of the residue was performed by flash column chromatography over silica gel with DCM/PE (1:7, v/v) as eluent to afford **11** as a solid (92 mg, 70%); mp: 88-89 ^{o}C. TLC (PE/DCM, 3:1) R_f = 0.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (2H, m), 7.53 (2H, m), 7.34 (3H, m), 7.27 (2H, m), 7.02 (1H, s), 7.00 (1H, s), 4.03 (4H, m), 1.83 (4H, m), 1.2-1.5 (36H, m), 0.88 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 149.3, 149.1, 137.4, 132.9, 131.4, 128.3, 128.1, 123.4, 123.1, 118.8, 118.2, 115.8, 115.7, 93.8, 92.1, 91.0, 90.1, 88.5, 69.13, 69.10, 31.9, 29.66, 29.63, 29.58, 29.35, 29.33, 29.1, 25.9, 22.7, 14.1. FT-IR (KBr): 2918, 2848, 2209, 1590, 1507, 1465, 1359, 1243, 1200, 1079, 997, 855, 815, 755, 691 cm^{-1}.



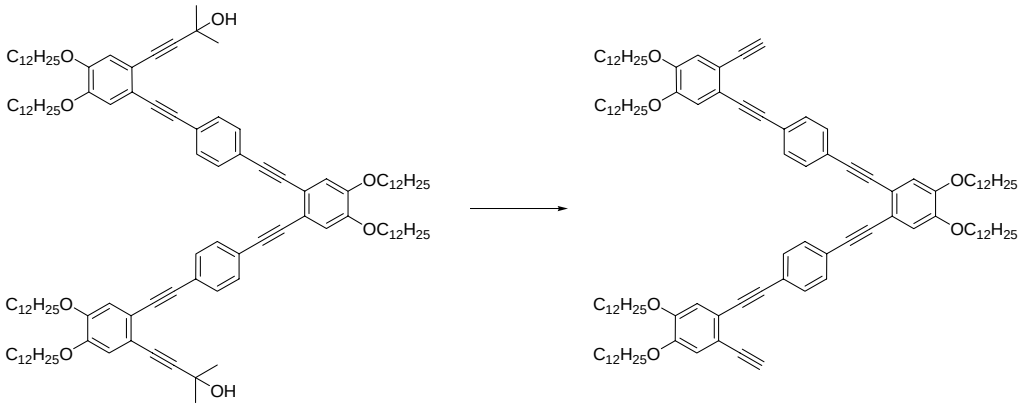
7 **12**

12. Compound **7** (233 mg, 0.32 mmol) was dissolved in 2 mL MeI. The reaction mixture was sealed in a Schlenk tube and stirred at 120 ^{o}C for 40 h. Then the solvent was removed via distillation. The solid residue was dissolved in 15 mL chloroform and washed with saturated aq. NH_4Cl and then dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography over silica gel with EtOAc/PE (1:7, v/v) as eluent and afforded **12** (235 mg, 96%); mp: 74-75 ^{o}C. TLC (PE/EtOAc, 7:1) R_f = 0.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (2H, d, J = 8.1 Hz), 7.27 (2H, d, J = 8.4 Hz), 6.97 (1H, s), 6.92 (1H, s), 4.00 (4H, m), 2.03(1H, br), 1.83 (4H, m), 1.64 (6H, s), 1.45 (4H, m), 1.25-1.43 (32H, m), 0.88 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.2, 149.0, 137.5, 132.9, 123.0, 118.2, 118.1, 115.9, 115.8, 96.4, 93.9, 90.6, 89.9, 81.0, 69.15, 69.11, 65.7, 31.9, 31.6, 29.7, 29.6, 29.35, 29.33, 29.1, 25.9, 22.7, 14.1. FT-IR (KBr): 3538, 3397, 2919, 2860, 2219, 1595, 1515, 1467, 1372, 1251, 1156, 1097, 1000, 958, 855, 816, 720 cm^{-1}.



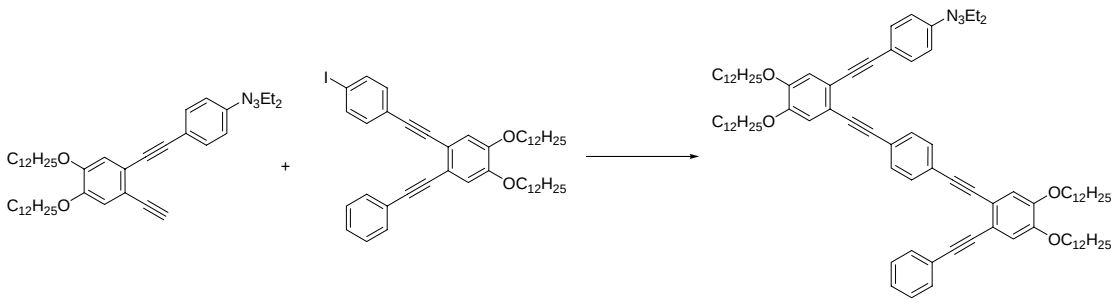
15 **12** **13**

13. A Schlenk tube containing compound **15** (49 mg, 0.10 mmol), **12** (152 mg, 0.20 mmol), CuI (1 mg, 0.005 mmol), and $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) was evacuated and back-filled with nitrogen three times. To this tube was added degassed *i*-Pr_2NH (10 mL). The reaction mixture was sealed under nitrogen atmosphere and stirred at 50^{o}C for 16 h. Then the solution was cooled to rt and the solvent was removed in vacuo. The solid residue was dissolved in 15 mL chloroform, washed with 1 M HCl, saturated aq. NH_4Cl, and dried over anhydrous Na_2SO_4. The solvent was then removed and purification of the residue was performed by flash column chromatography over silica gel with EtOAc/PE (1:10, v/v) as eluent to afford **13** as yellow powder (157 mg, 90%); mp: 89-90 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (8H, s), 7.02 (2H, s), 6.98 (2H, s), 6.91 (2H, s), 4.01 (12H, m), 2.24 (2H, br), 1.83 (12H, m), 1.64 (12H, s), 1.2-1.5 (108H, m), 0.88 (18H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.3, 149.2, 149.0, 131.3, 123.2, 123.1, 118.6, 118.3, 118.1, 115.9, 115.7, 96.4, 92.0, 91.4, 90.6, 90.5, 81.0, 69.1, 65.6, 31.9, 31.6, 29.7, 29.62, 29.58, 29.3, 29.1, 25.9, 22.6, 14.1. FT-IR (KBr): 3531, 3431, 2921, 2849, 2212, 1596, 1514, 1464, 1364, 1245, 1204, 1094, 845, 721 cm^{-1}.



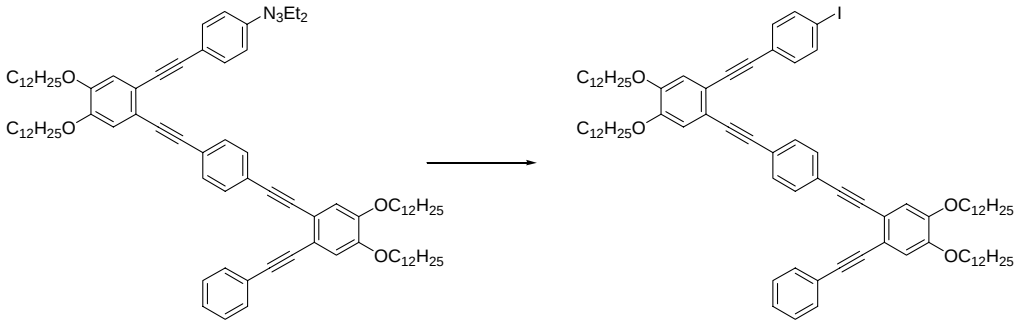
13 **3**

3. Compound **13** (56 mg, 0.032 mmol) and KOH (60 mg, 1.07 mmol) were added to toluene (10 mL) in a flask. The mixture was heated at 60^{o}C overnight with stirring. Then 15 mL PE was added to the reaction mixture. The organic solution was decanted, washed with 2 M HCl and brine sequentially, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the solid residue was purified by flash column chromatography over silica gel, eluted with DCM/PE (1/3, v/v) to give **3** as a yellow solid. (48 mg, 92%); mp: 84-85 ^{o}C. TLC (PE/DCM, 3:1) R_f = 0.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (8H, s), 7.03 (2H, s), 6.99 (4H, s), 4.01 (12H, m), 3.30 (2H, s), 1.84 (12H, m), 1.45 (12H, m), 1.20-1.42 (96H, m), 0.88 (18H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.5, 149.3, 149.2, 131.5, 131.3, 123.23, 123.17, 118.9, 118.6, 117.5, 116.7, 115.8, 92.0, 91.7, 90.5, 90.2, 82.4, 79.6, 69.2, 31.9, 29.68, 29.65, 29.60, 29.4, 29.1, 26.0, 22.7, 14.1. FT-IR (KBr): 3280, 2921, 2850, 1595, 1512, 1463, 1355, 1249, 1206, 1086, 846, 721 cm^{-1}. ESI MS: Calcd. for $C_{114}H_{167}O_6$: 1632.3. Found: 1632.3 (M^+).



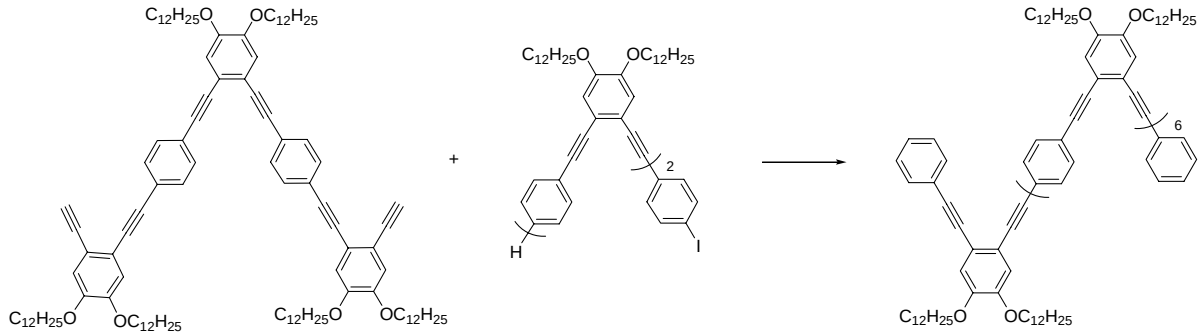
8 **11** **14**

14. A Schlenk tube containing compound **11** (42 mg, 0.054 mmol), CuI (1 mg, 0.005 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol), and **8** (36 mg, 0.054 mmol) was evacuated and backfilled with nitrogen three times. Degassed *i*-Pr_2NH (10 mL) was added under nitrogen atmosphere. The reaction mixture was stirred at rt for 16 h. Then the solvent was removed. The solid mixture was dissolved in 20 mL PE, washed with 1 M HCl and saturated NH_4Cl solution, and then dried over anhydrous Na_2SO_4. Solvent was then removed in vacuo and the residue was purified by flash column chromatography over silica gel with DCM/PE (2:5, v/v) as eluent to afford **14** as a yellow solid**.** (64 mg, 89%); mp: 69-71 ^{o}C. TLC (PE/DCM, 2:1) R_f = 0.50. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.58 (8H, m), 7.40 (2H, m), 7.32 (3H, m), 7.02 (3H, m), 7.01 (1H, s), 4.04 (8H, m), 3.77 (4H, q, J = 7.2 Hz), 1.85 (8H, m), 1.2-1.55 (78H, m), 0.88 (12H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.9, 149.3, 149.2, 148.9, 132.1, 131.4, 131.3, 128.3, 128.1, 123.5, 123.3, 123.1, 120.4, 119.6, 119.2, 118.8, 118.5, 118.1, 115.8, 115.7, 92.0, 92.2, 92.0, 91.8, 90.5, 90.8, 90.6, 88.6, 83.3, 69.1, 31.9, 29.67, 29.64, 29.59, 29.4, 29.1, 26.0, 22.7, 14.1. FT-IR (KBr): 2919, 2848, 2206, 1594, 1512, 1461, 1358, 1242, 1202, 1282, 1082, 843 cm^{-1}.



14 **4**

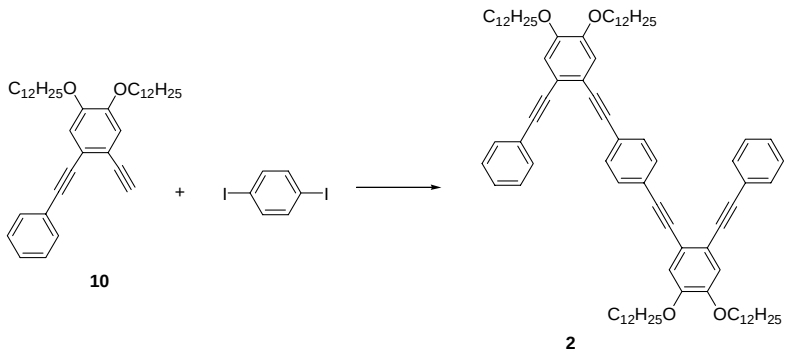
4. Compound **14** (63.7 mg, 0.048mmol) was dissolved in iodomethane (1 mL) under nitrogen atmosphere. The reaction tube was then sealed and the mixture was heated at 120 °C for 20 h. Then the solvent was removed. The reaction mixture was dissolved in dichloromethane (10 mL), washed with saturated aq. NH_4Cl solution, and dried over anhydrous Na_2SO_4. Solvent was then removed in vacuo and the purification of the residue was performed by flash column chromatography over silica gel with DCM/PE (1:3, v/v) as eluent to afford **4** as a solid. (60 mg, 93%); mp: 96-97 °C. TLC (PE / DCM, 3:1) R_f = 0.46. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (2H, m), 7.55 (2H, m), 7.50 (4H, m) 7.35 (3H, m), 7.26 (2H, m), 7.03 (1H, s), 7.02 (1H, s), 7.01 (2H, m), 4.04 (8H, m), 1.85 (8H, m), 1.2-1.5 (72H, m), 0.88 (12H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.28, 149.25, 149.2, 149.1, 137.5, 132.8, 131.40, 131.36, 131.25, 128.3, 128.2, 123.5, 123.3, 123.04, 123.02, 118.8, 118.5, 118.34, 118.28, 115.72, 115.69, 115.65, 93.9, 92.1, 91.9, 91.8, 91.1, 90.7, 90.5, 90.1, 88.6, 69.1, 31.9, 29.67, 29.64, 29.59, 29.3, 29.1, 25.9, 22.7, 14.1. FT-IR (KBr): 2919, 2848, 2208, 1591, 1513, 1465, 1359, 1242, 1200, 1080, 998, 824, 752 cm^{-1}. ESI MS: Calcd. for $C_{86}H_{117}IO_4$: 1340.8. Found: 1340.8 (M^+).



3 **4** **1**

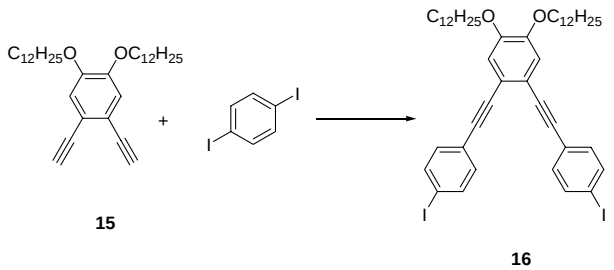
1. A sealed tube containing compound **3** (28 mg, 0.017 mmol), **4** (51 mg, 0.038 mmol), CuI (1 mg, 0.005 mmol), and $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) was evacuated and back-filled with nitrogen three times. To this tube was added degassed solvent mixture (5 mL toluene and 5 mL *i*-Pr_2NH). The reaction mixture was then sealed under nitrogen atmosphere and stirred at 50 °C for 16 h. Then the solvent was removed in vacuo. The solid residue was dissolved in 15 mL chloroform, washed with 1 M HCl and saturated aq. NH_4Cl and brine sequentially, and then dried over anhydrous Na_2SO_4. The solution was condensed and purification of the residue was performed by flash column chromatography over silica gel with PE/DCM/chloroform (4:1:2, v/v) as eluent to afford **1** as a yellow solid (48 mg, 69%); mp: 88-90 °C. TLC (PE/DCM/chloroform, 4:1:2) R_f = 0.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.56 (28H, m), 7.31 (6H, m), 6.97-7.00 (14H, m), 3.98 (28H, m),

1.81 (28H, m), 1.44 (28H, m), 1.2-1.4 (224H, m), 0.87 (42H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 149.2, 149.1, 131.4, 128.3, 128.2, 123.5, 123.4, 123.29, 123.26, 123.15, 121.0, 118.8, 118.55, 118.50, 118.4, 115.7, 114.1, 92.1, 92.04, 91.96, 91.90, 90.8, 90.7, 88.6, 69.3, 69.15, 69.12, 31.9, 31.6, 29.71, 29.68, 29.62, 29.42, 29.37, 29.31, 29.1, 26.0, 25.7, 22.7, 22.6, 14.1, 14.0. FT-IR (KBr): 2920, 2845, 2210, 1730, 1594, 1518, 1462, 1360, 1244, 1198, 1083, 916, 842, 721, 614 cm^{-1}. MALDI-TOF MS: Calcd. for $C_{286}H_{398}O_{14}$: 4060.2. Found: 4061.2 ($M + H^+$). Anal. Calcd. for $C_{286}H_{398}O_{14}$: C, 84.60; H, 9.88. Found: C, 84.48; H, 9.60.



10 2

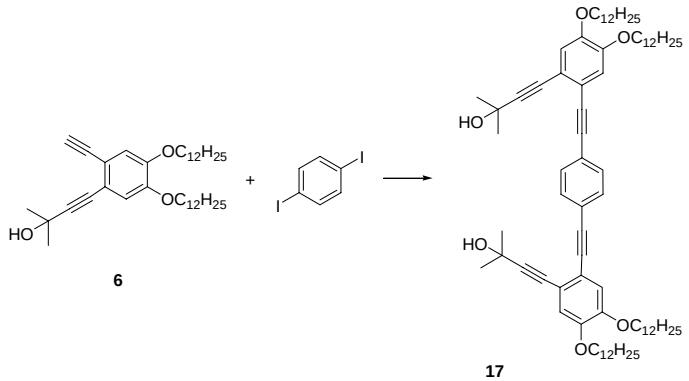
2. A sealed tube containing compound **10** (50 mg, 0.088 mmol), 1,4-diiodobenzene (14 mg, 0.044 mmol), CuI (1 mg, 0.005 mmol) and $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) was evacuated and back-filled with nitrogen three times. To this tube was added degassed *i*-Pr_2NH (20 mL) using syringe. The reaction mixture was sealed in nitrogen atmosphere, stirred at 50 ^{o}C for 2 h, and then cooled to rt. Then the solvent was removed. The solid residue was dissolved in 15 mL chloroform, washed with 1 M HCl, saturated aq. NH_4Cl, and dried over anhydrous Na_2SO_4. The solvent was then evaporated and purification of the residue was performed by flash column chromatography over silica gel with DCM/PE (1:3, v/v) as eluent to give **2** as white powder (47 mg, 88%); mp: 132-133 ^{o}C. TLC (PE/DCM, 3:1) R_f = 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (4H, m), 7.50 (4H, s), 7.33 (6H, m), 7.03 (2H, s), 7.02 (2H, s), 4.03 (8H, t, J = 6.6 Hz), 1.85 (8H, m), 1.48 (8H, m), 1.2-1.4 (64H, m), 0.88 (18H, t, J = 6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.3, 149.1, 131.44, 131.36, 128.3, 128.1, 123.5, 123.2, 118.7, 118.4, 115.7, 92.1, 91.9, 90.6, 88.6, 69.1, 31.9, 29.70, 29.66, 29.62, 29.4, 29.1, 26.0, 22.7, 14.1. FT-IR (KBr): 2918, 2817, 2209, 1678, 1591, 1512, 1460, 1357, 1242, 1200, 1081, 993, 848, 751, 689 cm^{-1}. MALDI-TOF MS: calcd. for $C_{86}H_{118}O_4$: 1214.9. Found: 1214.5 (M^+). Anal. Calcd. for $C_{86}H_{118}O_4$: C, 84.95; H, 9.78. Found: C, 84.64; H, 9.56.



15 16

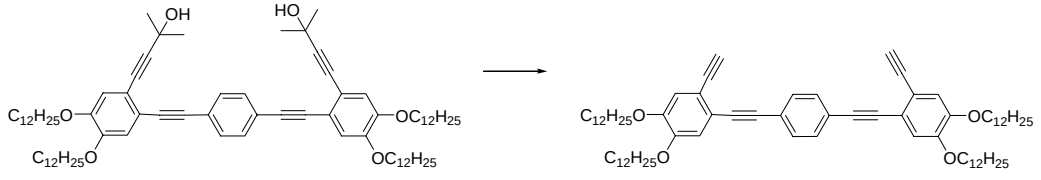
16. Compound **15** (0.33 g, 0.67 mmol), 1,4-diiodobenzene (2.0 g, 6.1 mmol), CuI (5 mg, 0.025 mmol), and $Pd(PPh_3)_4$ (32 mg, 0.027 mmol) were added into a sealed tube. The tube was evacuated and back-filled with nitrogen three times. To this tube was added degassed mixed solvent of toluene (15 mL) and *i*-Pr_2NH (15 mL). The reaction tube was sealed under nitrogen atmosphere and stirred at 50^{o}C for 12 h. Then reaction mixture

was cooled to rt and the solvent was removed in vacuo. The solid residue was re-dissolved in chloroform (25 mL), washed with 1 M HCl and saturated aq. NH_4Cl, and then dried over anhydrous Na_2SO_4. The solution was then condensed in vacuo, and purification of the residue was performed by flash column chromatography over silica gel with DCM/PE (1:5, v/v) as eluent to afford **16** as white powder (443 mg, 73%); mp: 72-73 ^oC**.** ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (4H, m), 7.24 (4H, m), 7.00 (2H, s), 4.02 (4H, t, J = 6.4 Hz), 1.85 (4H, m), 1.2-1.55 (36H, m), 0.88 (6H, t, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.3, 137.5, 132.8, 123.0, 118.3, 115.7, 94.0, 91.1, 90.0, 69.2, 69.1, 31.9, 29.68, 29.65, 29.60, 29.4, 29.1, 25.9, 22.7, 14.1. FT-IR (KBr): 2919, 2850, 2208, 1643, 1511, 1469, 1361, 1245, 1207, 1082, 998, 817, 715 cm^{-1}.



6 17

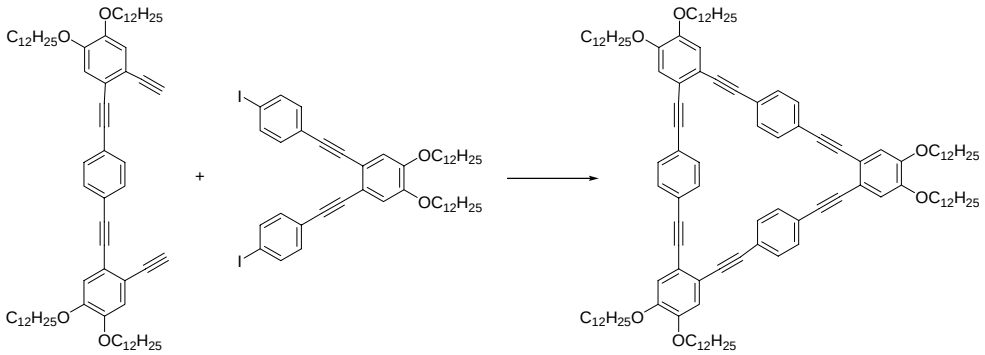
17. Compound **6** (165 mg, 0.30 mmol), 1,4-diiodobenzene (50 mg, 0.15 mmol), CuI (1.5 mg, 0.008 mmol), and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol) were added to a sealed tube containing 10 mL degassed *i*-Pr_2NH under nitrogen atmosphere. The reaction mixture was stirred at rt overnight. After the solvent was removed, the solid residue was dissolved in 15 mL CH_2Cl_2. The solution was washed with saturated aq. NH_4Cl and brine, and then dried over anhydrous Na_2SO_4. Removing the solvent followed by purification performed over silica gel column chromatography, with PE/EtOAc (5:1, v/v) as eluent, gave the product as a white solid (150 mg, 84 %); mp: 85-86 ^oC. TLC (PE/EtOAc, 3:1, v/v) R_f = 0.4. ^1H NMR (300 MHz, $CDCl_3$) : δ 7.51 (4H, s), 6.98 (2H, s), 6.92 (2H, s), 4.01 (8H, m), 2.05 (2H, br), 1.83 (8H, m), 1.65 (12H, s), 1.2-1.5 (72H, m), 0.88 (12H, m). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 149.2, 149.0, 131.4, 123.1, 118.3, 118.1, 115.9, 115.8, 96.3, 91.4, 90.4, 81.1, 69.14, 69.11, 65.7, 31.9, 31.6, 29.7, 29.6, 29.35, 29.34, 29.1, 25.9, 22.7, 14.1.



17 18

18. Compound **17** (240 mg, 0.20 mmol) and KOH (100 mg, 1.8 mmol) were added into toluene (10 mL) under N_2 atmosphere. The reaction mixture was stirred at 100 ^oC for 2.5 h. Then 15 mL PE was added to the cooled reaction mixture. The organic solution was washed with 2 M HCl, saturated aq. NH_4Cl and brine sequentially and dried over anhydrous Na_2SO_4. The solvent was evaporated and the solid residue was purified by flash column chromatography over silica gel, eluted with DCM/PE (1/3, v/v) to **18** as a yellow solid. (179 mg, 77%); mp: 77-78 ^oC. TLC (PE/DCM, 3:1) R_f = 0.4. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (4H, s), 6.99 (4H, s), 4.01

(8H, m), 3.29 (2H, s), 1.83 (8H, m), 1.47 (8H, m), 1.2-1.4 (64H, m), 0.88 (12H, t, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 149.1, 131.4, 123.1, 118.8, 117.3, 116.4, 115.6, 91.7, 90.1, 82.4, 79.6, 69.1, 31.9, 29.69, 29.65, 29.61, 29.4, 29.0, 25.9, 22.7, 14.1. FT-IR (KBr): 3258, 2920, 2850, 2202, 1736, 1594, 1511, 1466, 1346, 1251, 1208, 1090, 830, 719 cm^{-1}.

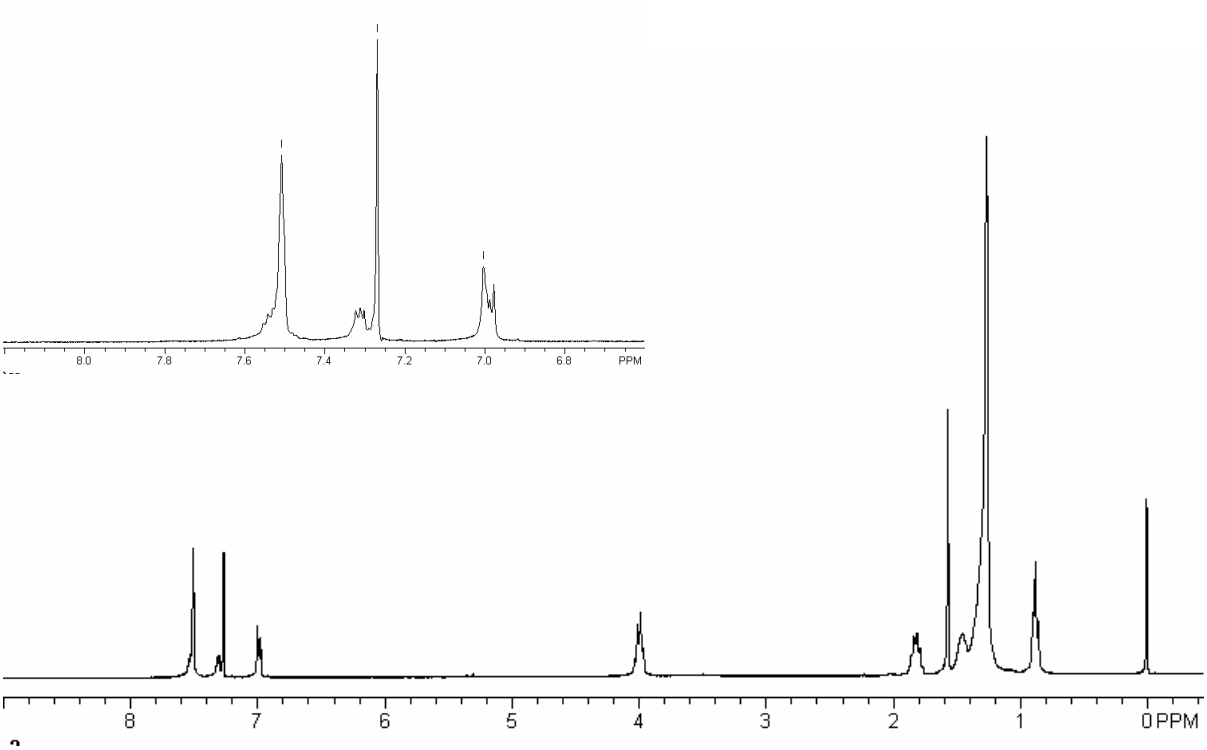


MC. A sealed tube containing compound **16** (25 mg, 0.028 mmol), **18** (30 mg, 0.028 mmol), CuI (2 mg, 0.01 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) were evacuated and back-filled with nitrogen three times. To this tube was added degassed *i*-Pr_2NH (40 mL) using a syringe. The reaction mixture was sealed under nitrogen atmosphere and stirred at 50 ^{o}C for 2 h. Then the solvent was removed in vacuo. The solid residue was dissolved in 15 mL chloroform, washed with 1 M HCl and saturated aq. NH_4Cl, and then dried over anhydrous Na_2SO_4. Purification of the residue was performed by flash column chromatography over silica gel with DCM/PE (1:10, v/v) as eluent to give **MC** as a green solid (18 mg, 37%); mp: 64-65 ^{o}C. TLC (PE/DCM, 5:2) R_f = 0.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (12H, s), 7.03 (6H, s), 4.04 (12H, t, J = 6.5 Hz), 1.85 (12H, m), 1.48 (12H, m), 1.2-1.4 (96H, m), 0.89 (18H, t, J = 6.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.2, 131.2, 123.2, 118.5, 115.6, 92.0, 90.7, 69.1, 31.9, 29.72, 29.68, 29.66, 29.43, 29.38, 29.1, 26.0, 22.7, 14.1. FT-IR (KBr): 2921, 2851, 1639, 1520, 1482, 1363, 1244, 1203, 1077, 824, 717 cm^{-1}. MALDI-TOF MS: Calcd. for $C_{120}H_{168}O_6$: 1705.3. Found: 1704.8 (M^+). Anal. Calcd. for $C_{120}H_{168}O_6$: C, 84.45; H, 9.92. Found: C, 84.55; H, 10.06.

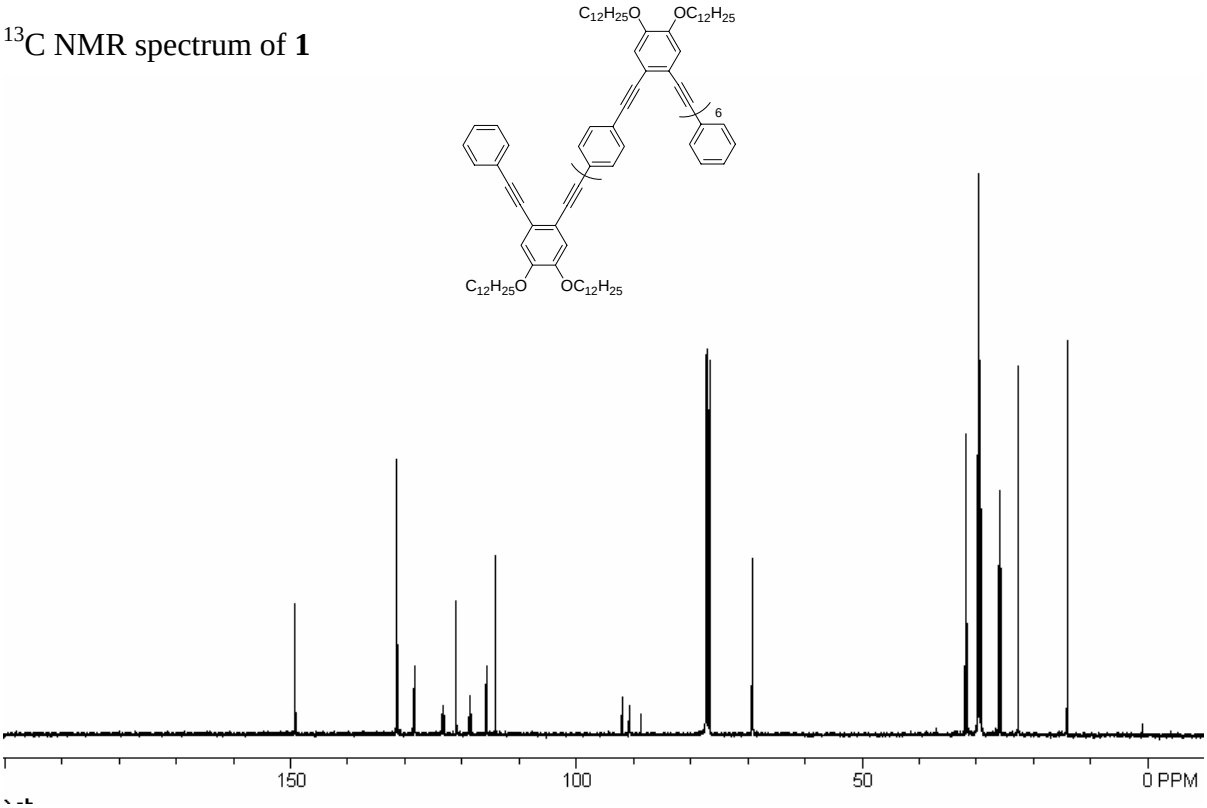
References

1. Holmes, B. T.; Pennington, W. T.; Hanks, T. W. *Synth. Commun.* **2003**, *33*, 2447.

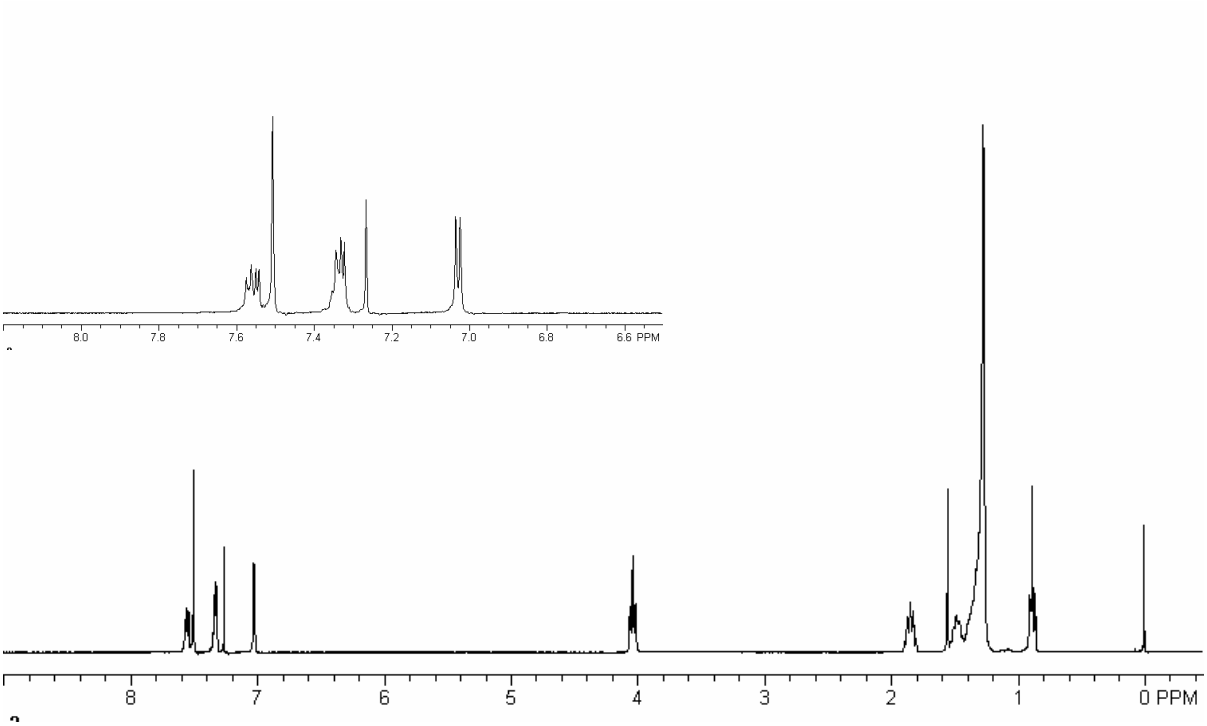
^{1}H NMR spectrum of **1** (inset shows the aromatic region)



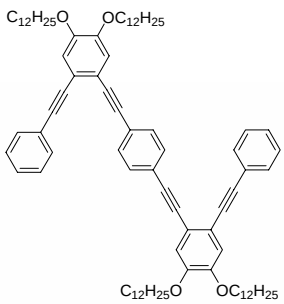
^{13}C NMR spectrum of **1**



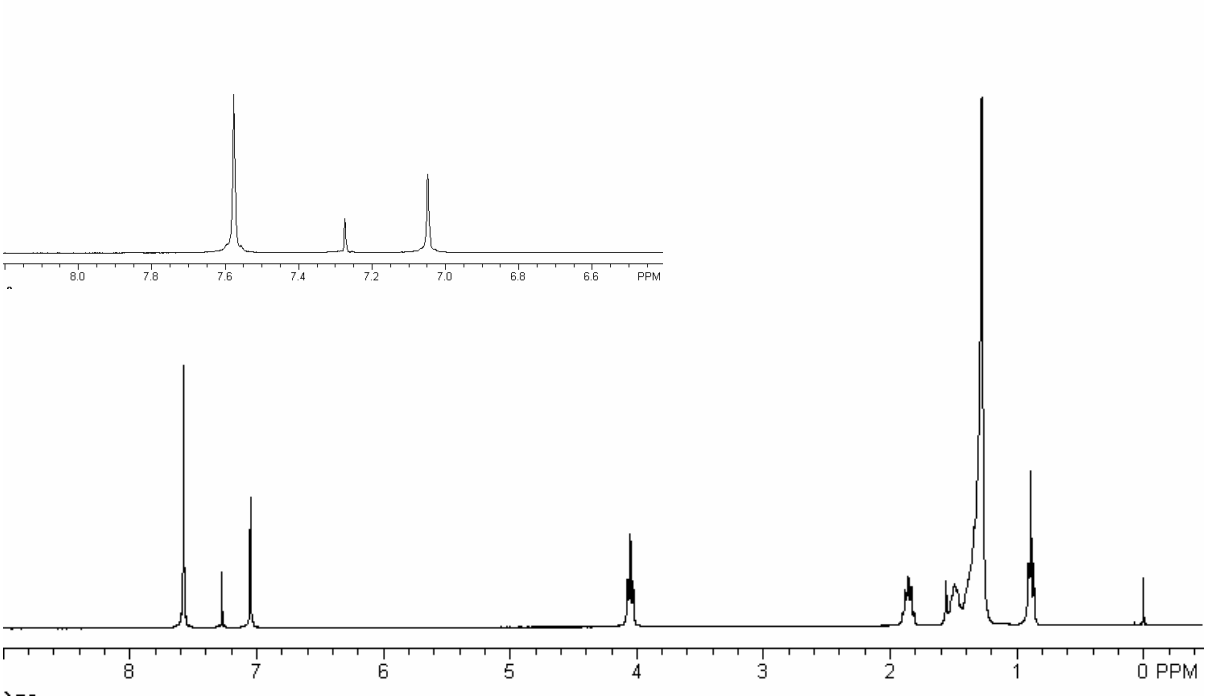
^{1}H NMR spectrum of **2** (inset shows the aromatic region)



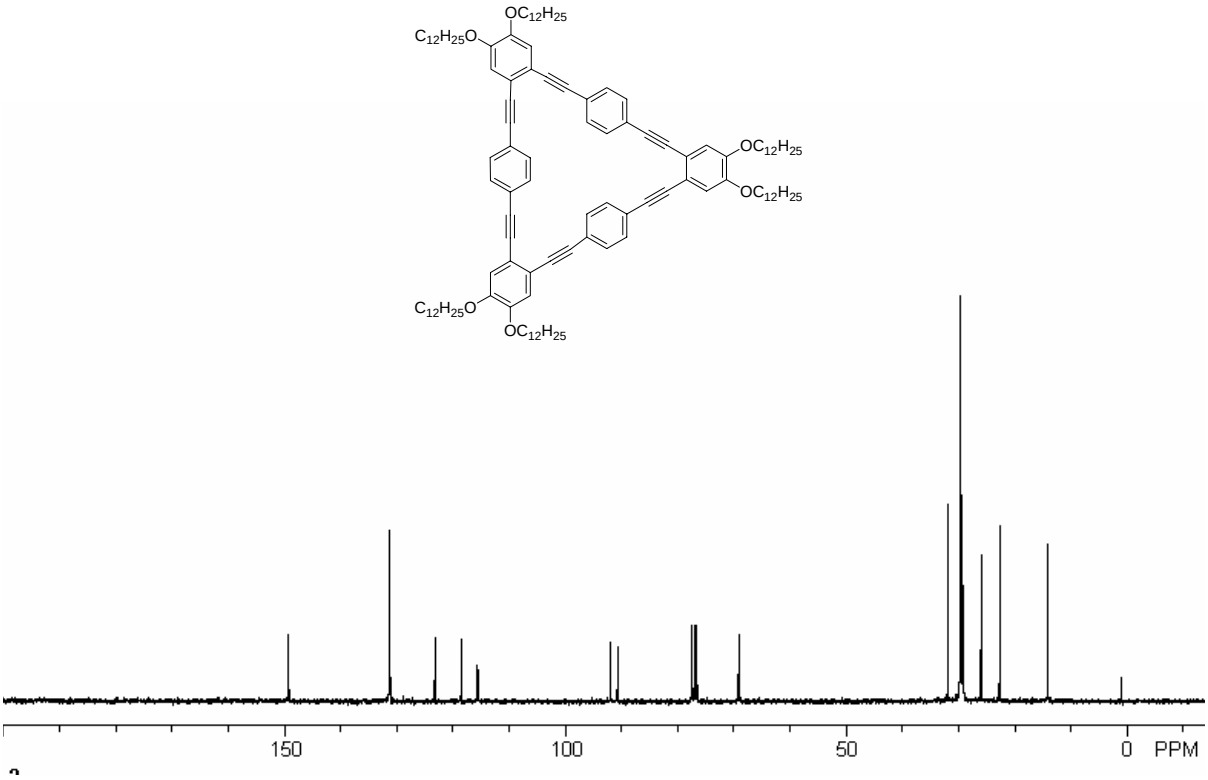
^{13}C NMR spectrum of **2**



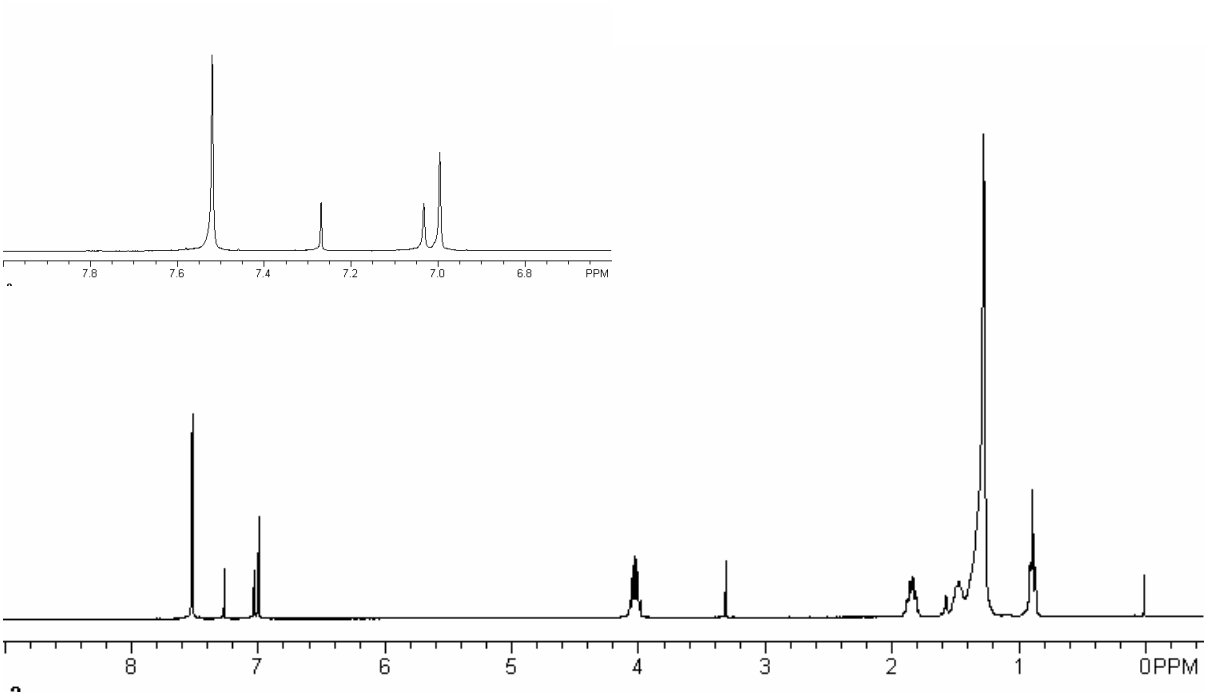
^{1}H NMR spectrum of **MC** (inset shows the aromatic region)



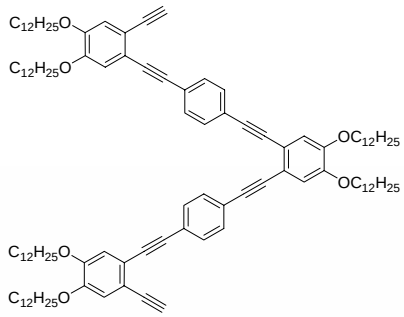
^{13}C NMR spectrum of **MC**

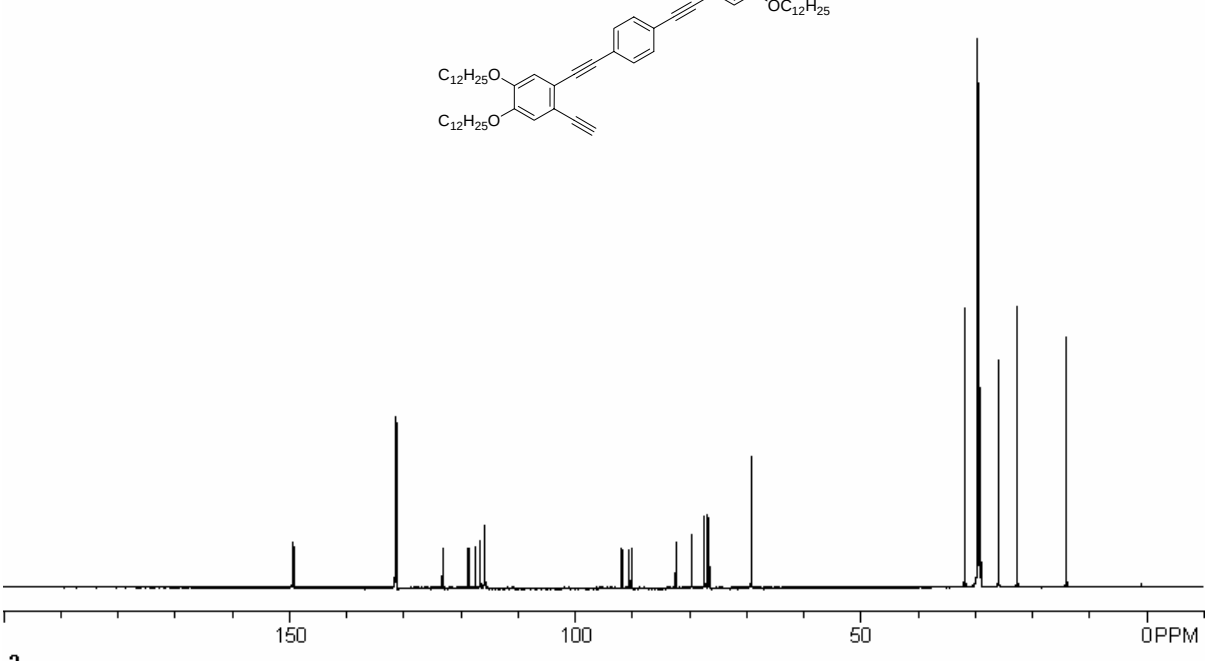


^{1}H NMR spectrum of **3** (inset shows the aromatic region)

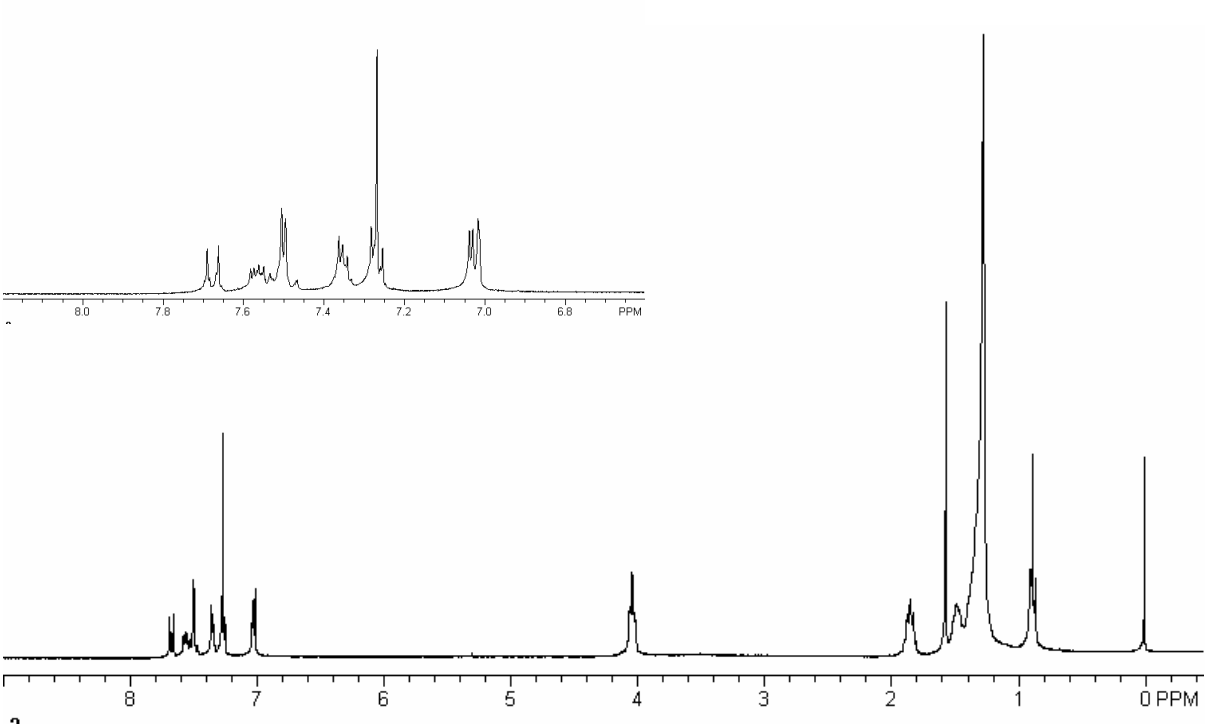


^{13}C NMR spectrum of **3**

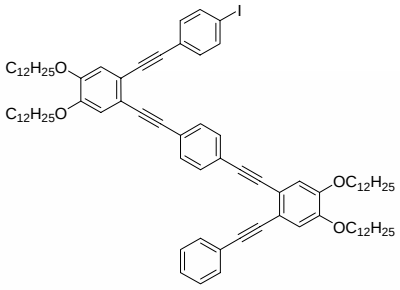




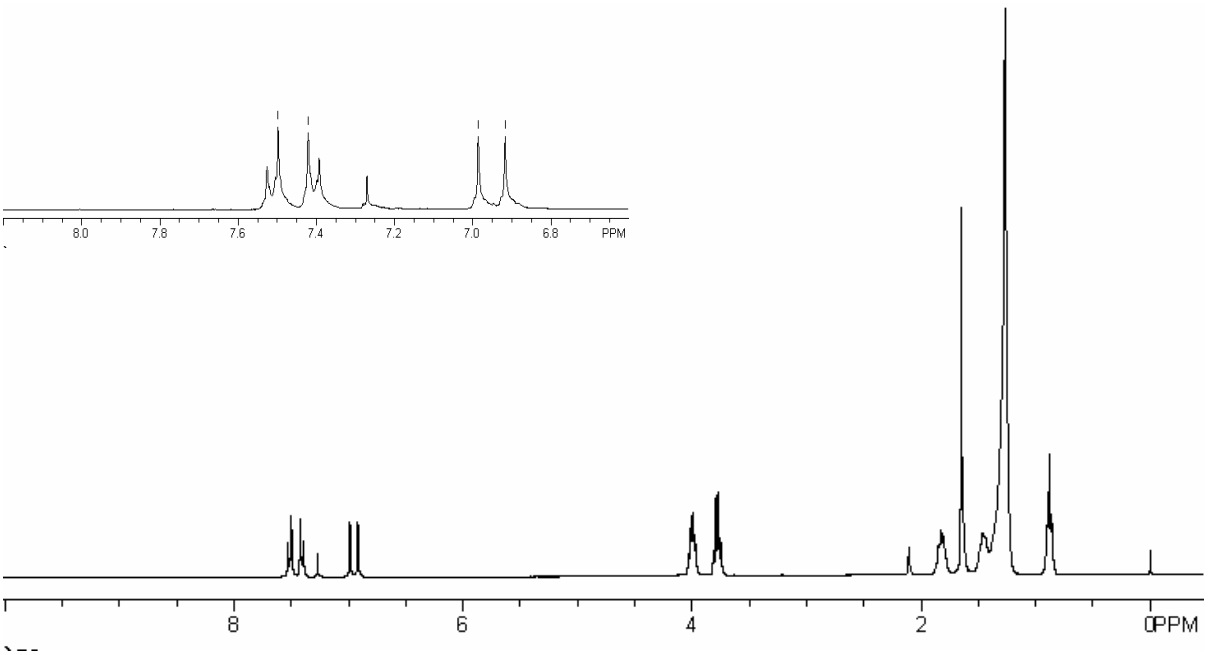
^{1}H NMR spectrum of **4** (inset shows the aromatic region)



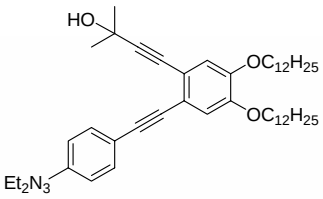
^{13}C NMR spectrum of **4**

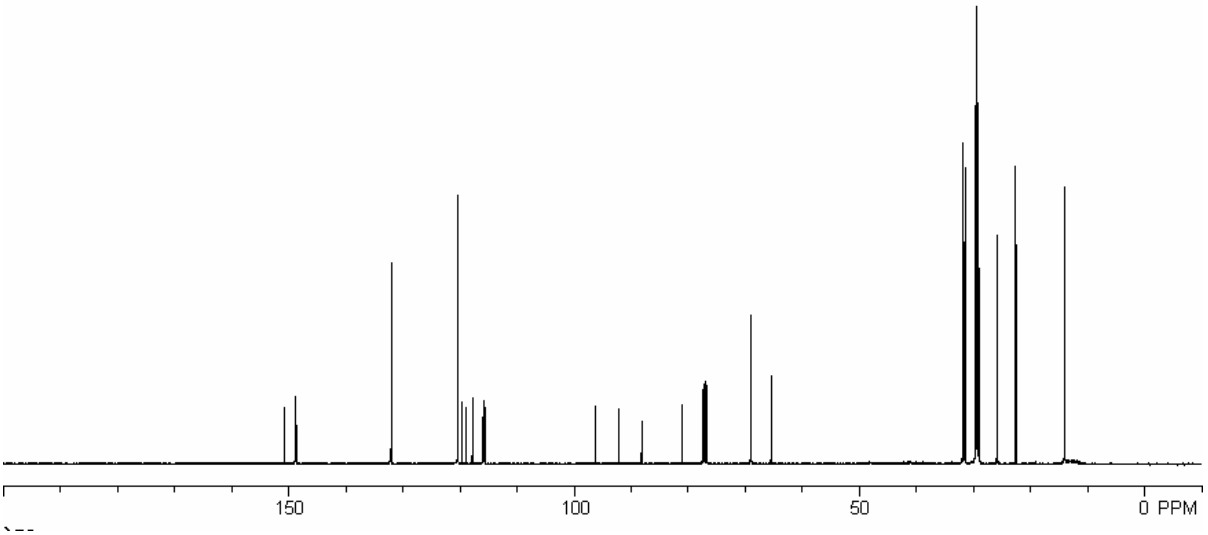


^{1}H NMR spectrum of **7** (inset shows the aromatic region)

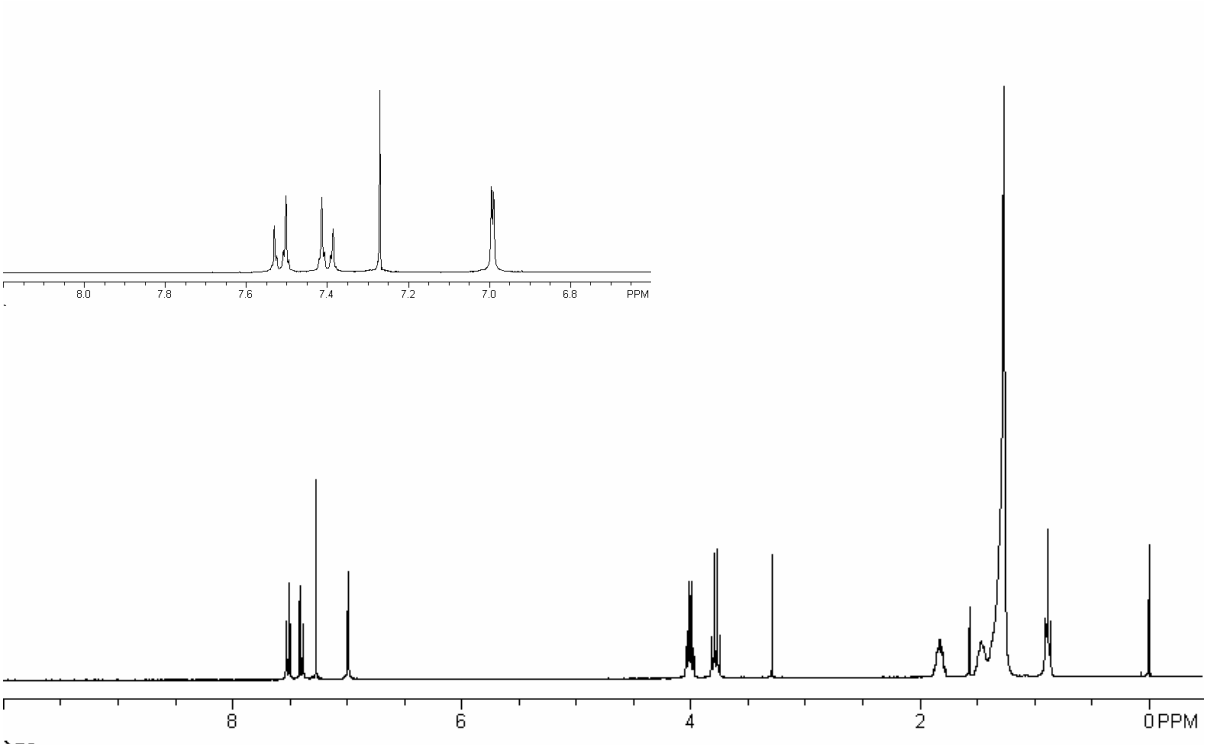


^{13}C NMR spectrum of **7**

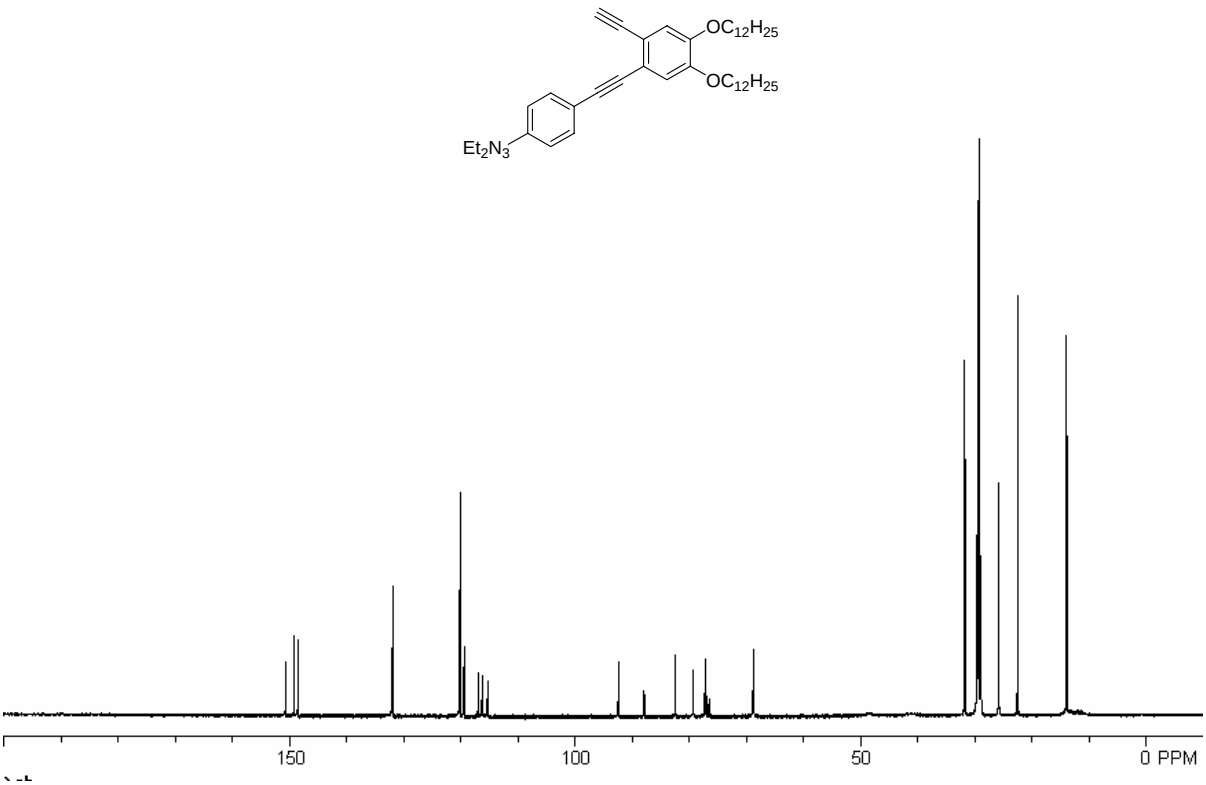




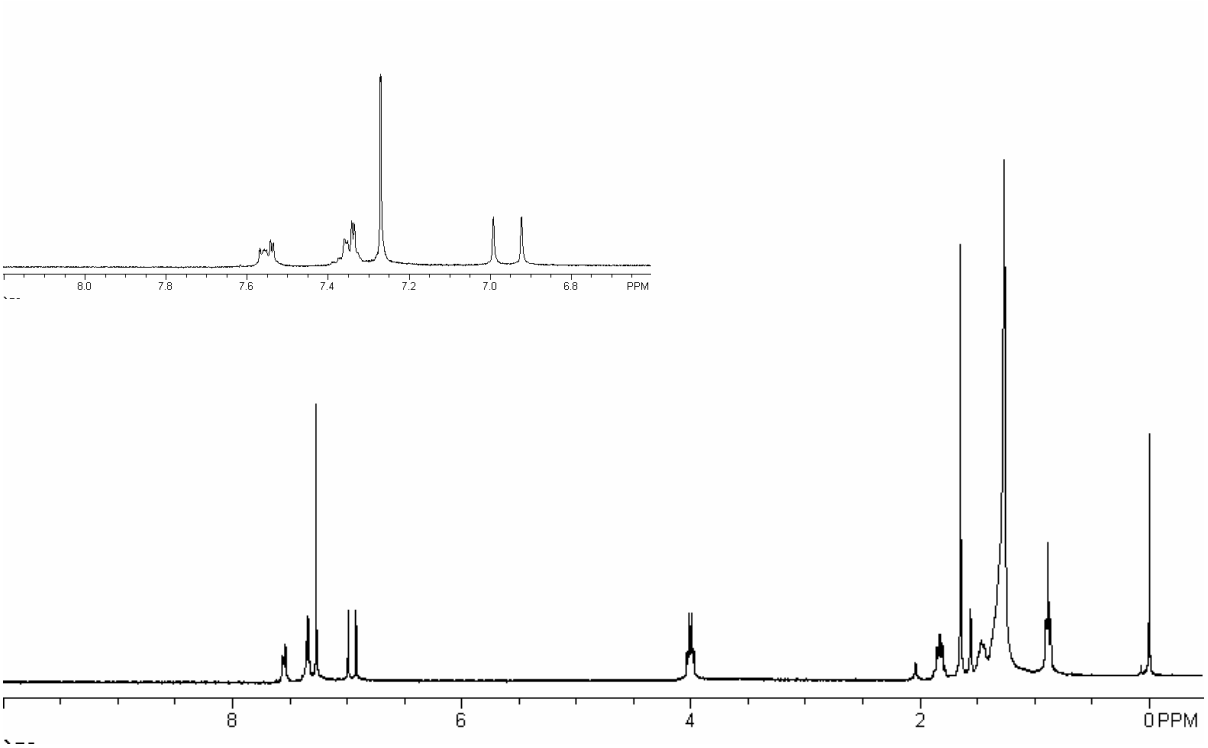
^{1}H NMR spectrum of **8** (inset shows the aromatic region)



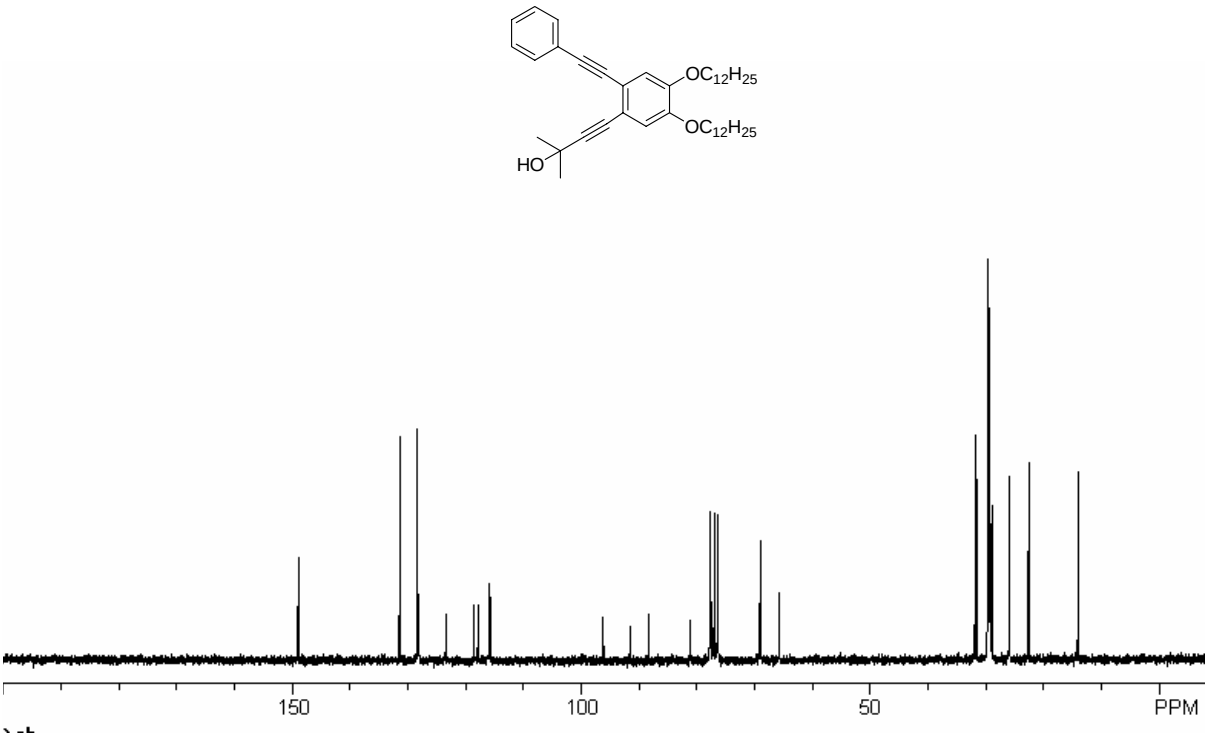
^{13}C NMR spectrum of **8**



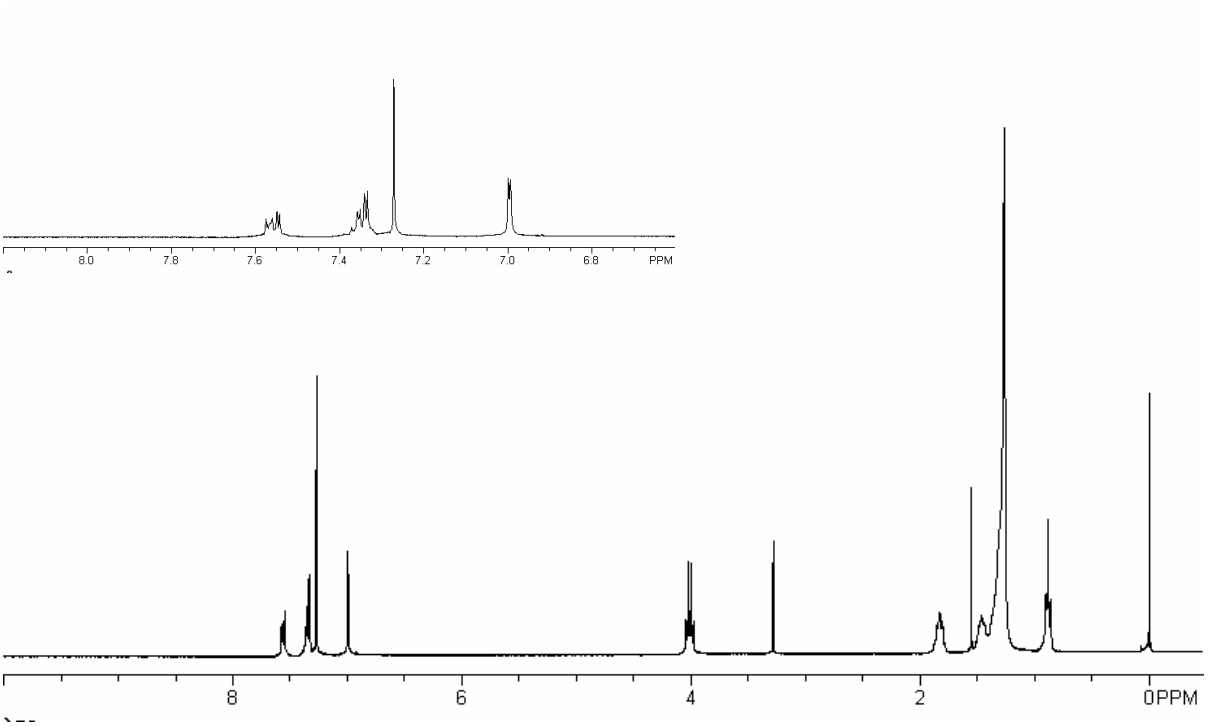
^{1}H NMR spectrum of **9** (inset shows the aromatic region)



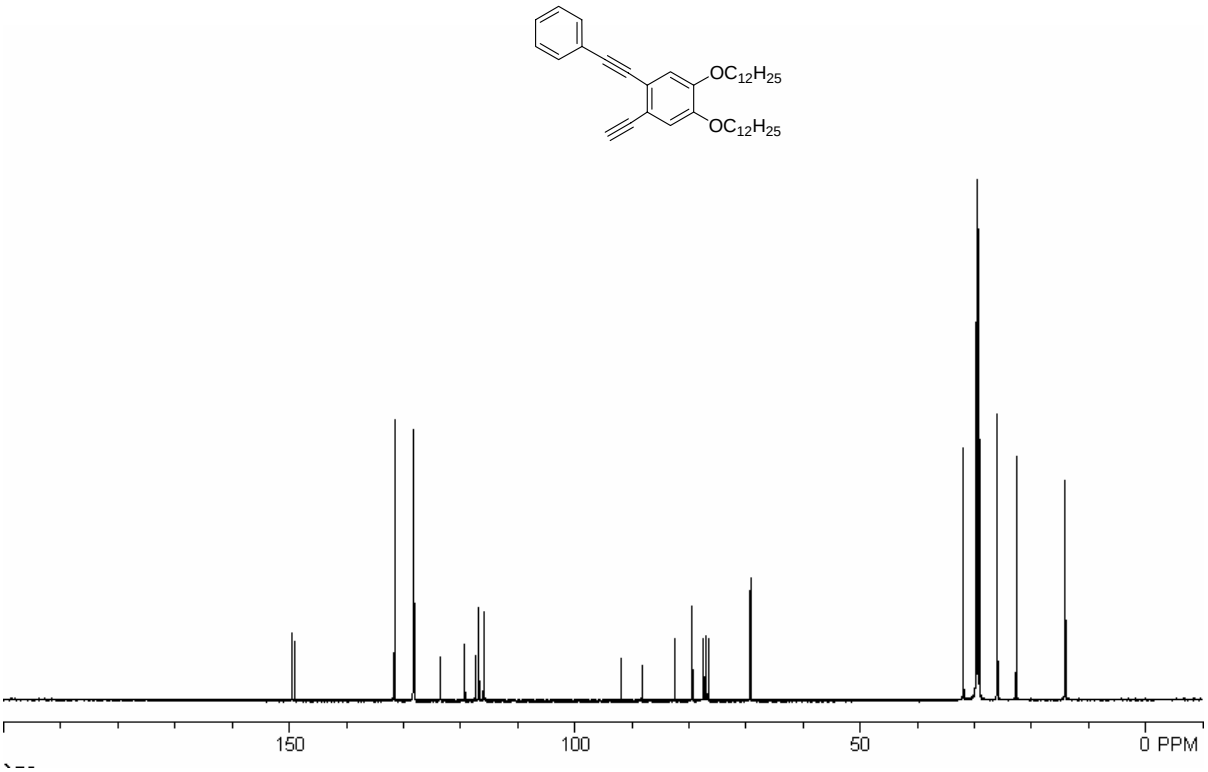
^{13}C NMR spectrum of **9**



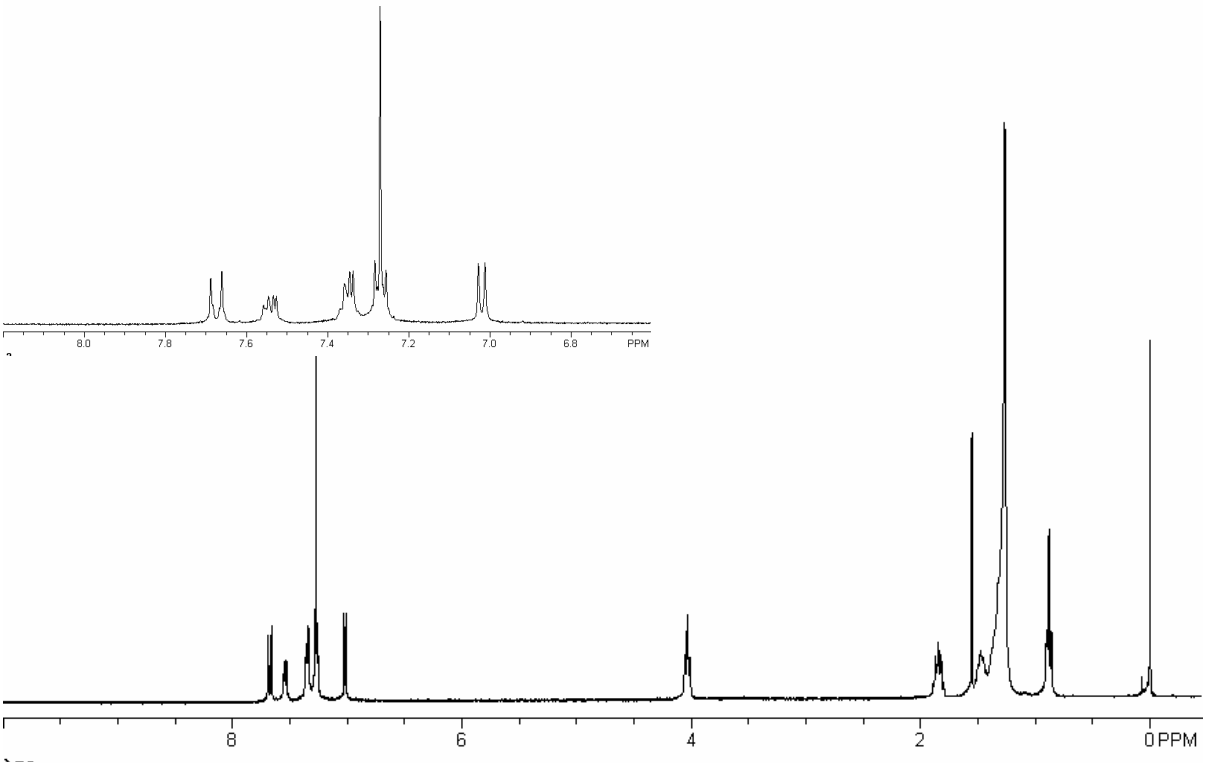
^{1}H NMR spectrum of **10** (inset shows the aromatic region)



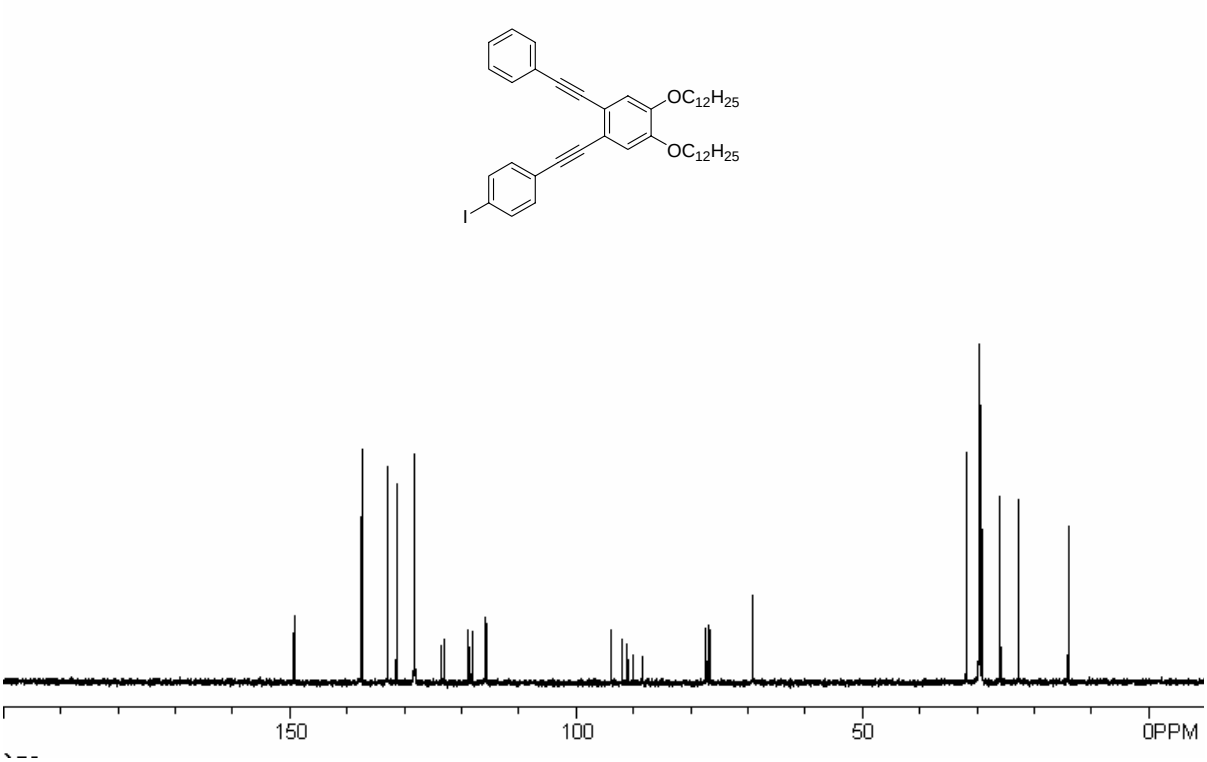
^{13}C NMR spectrum of **10**



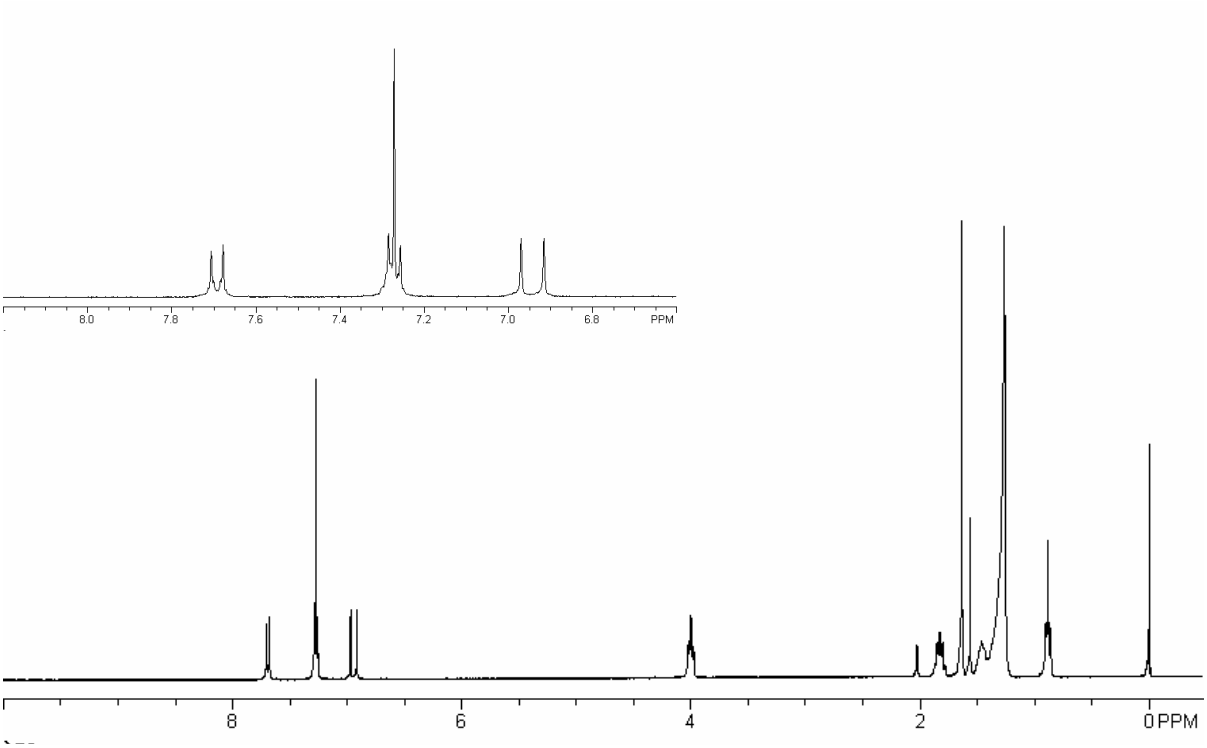
^{1}H NMR spectrum of **11** (inset shows the aromatic region)



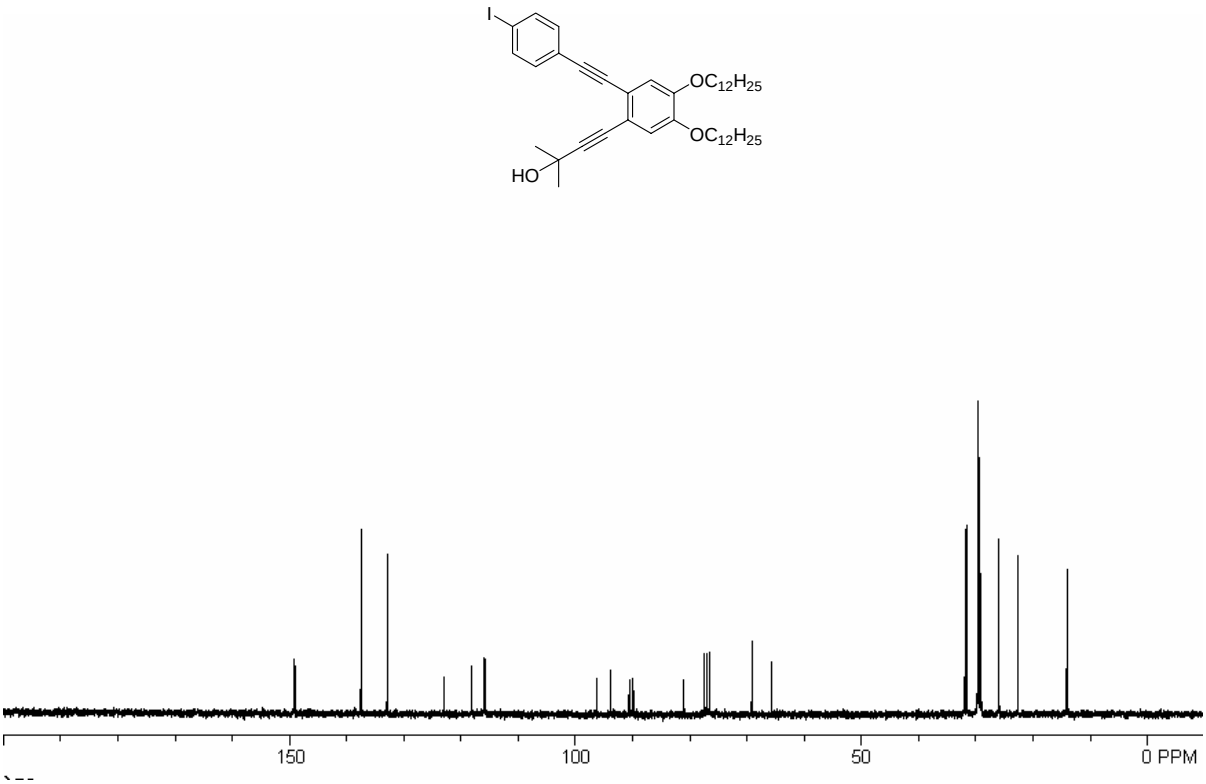
^{13}C NMR spectrum of **11**



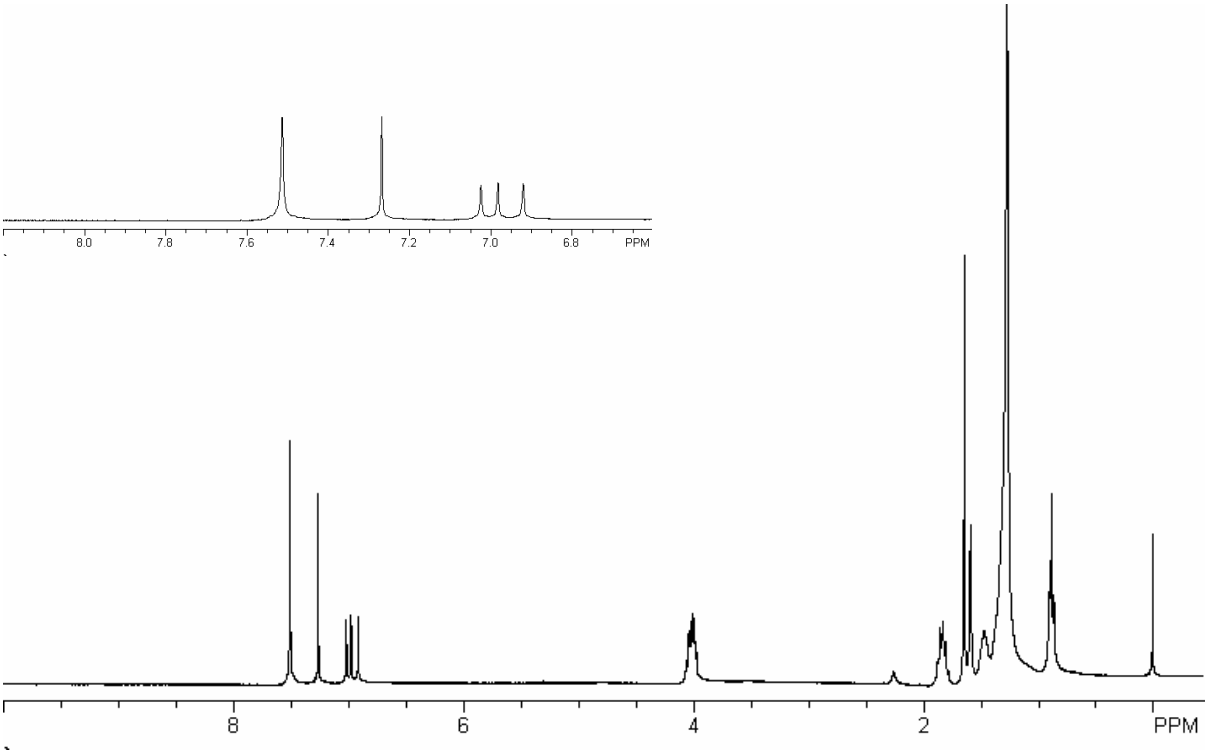
^{1}H NMR spectrum of **12** (inset shows the aromatic region)



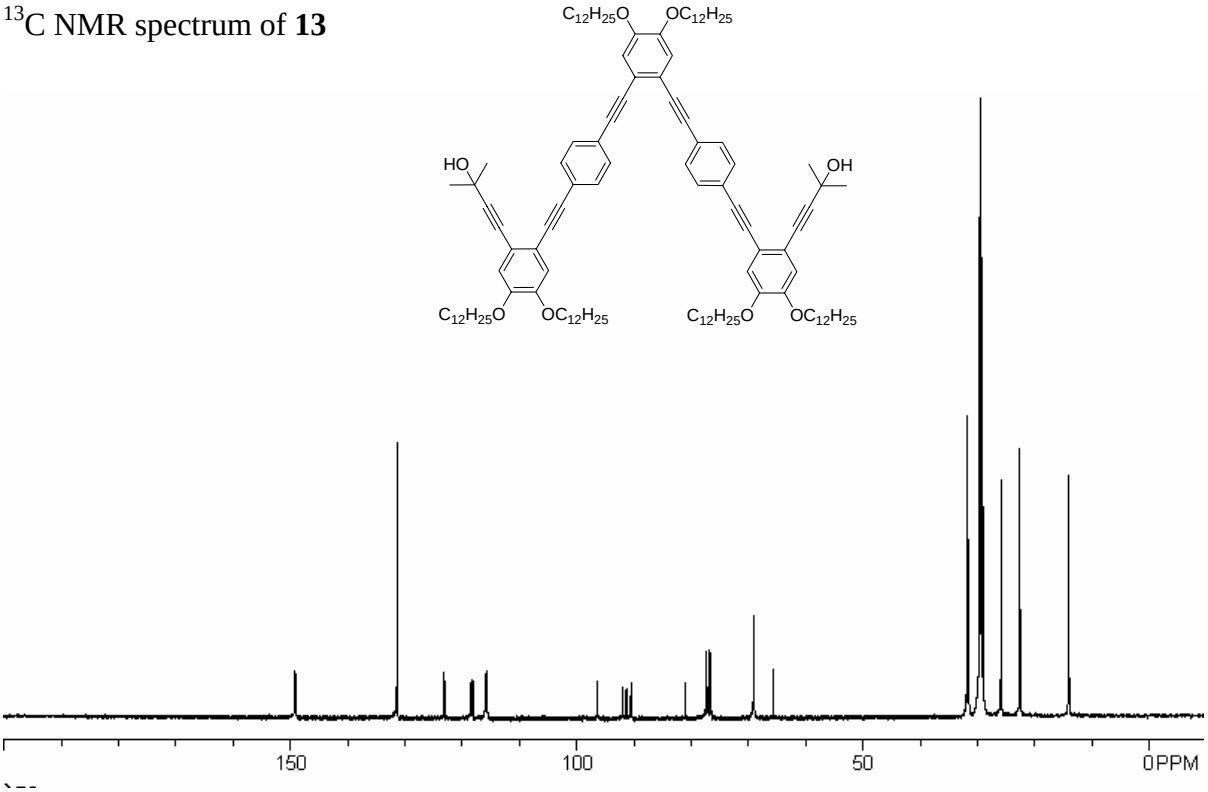
^{13}C NMR spectrum of **12**



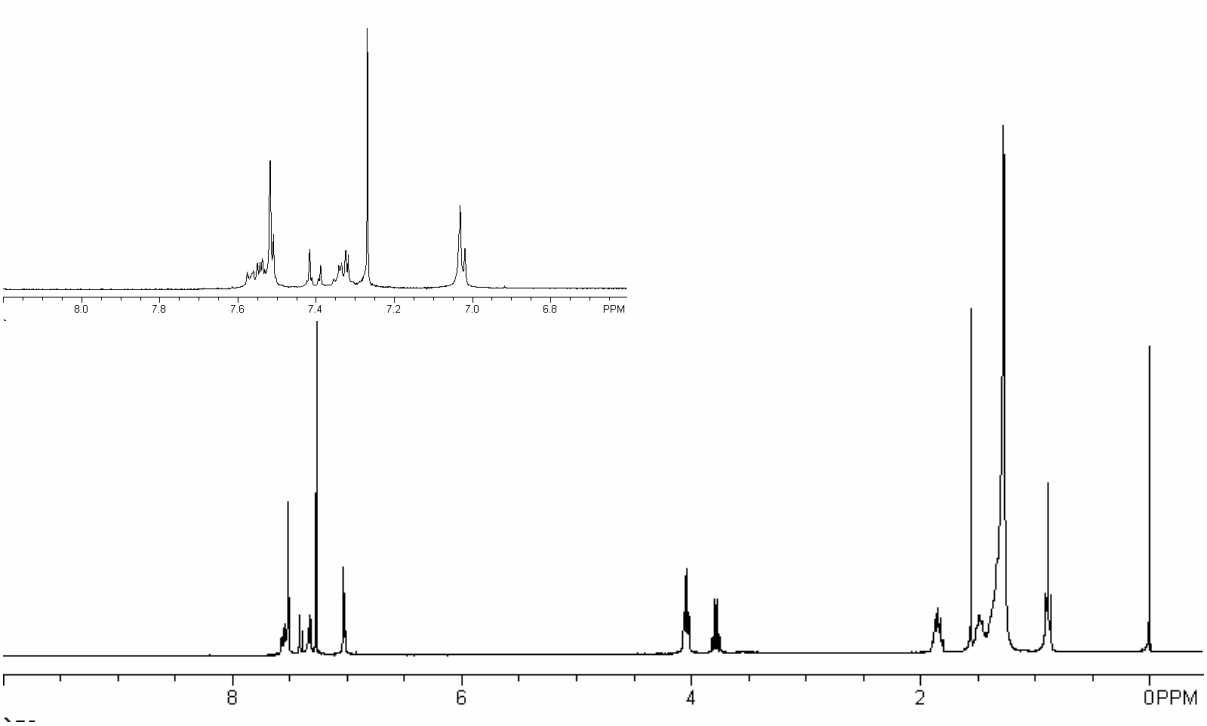
^{1}H NMR spectrum of **13** (inset shows the aromatic region)



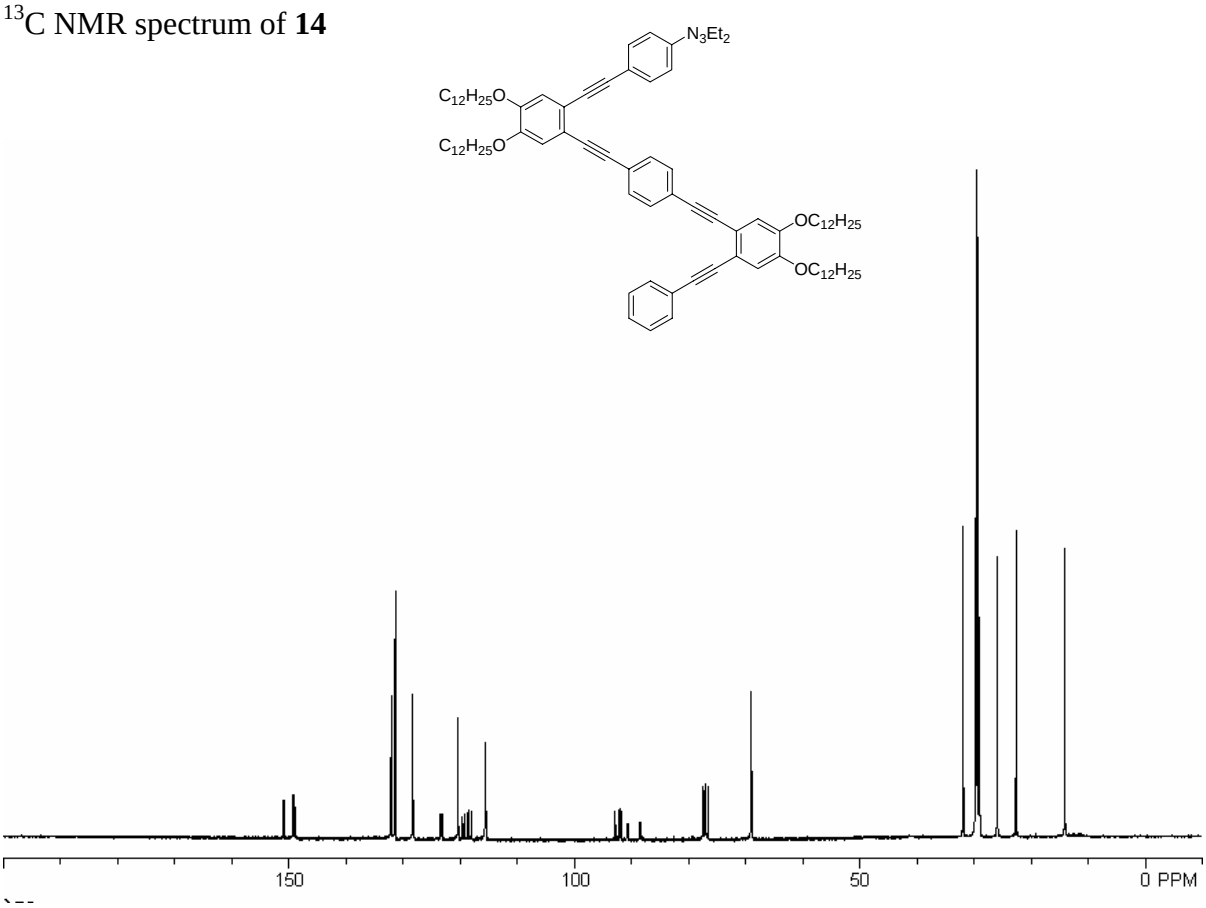
^{13}C NMR spectrum of **13**



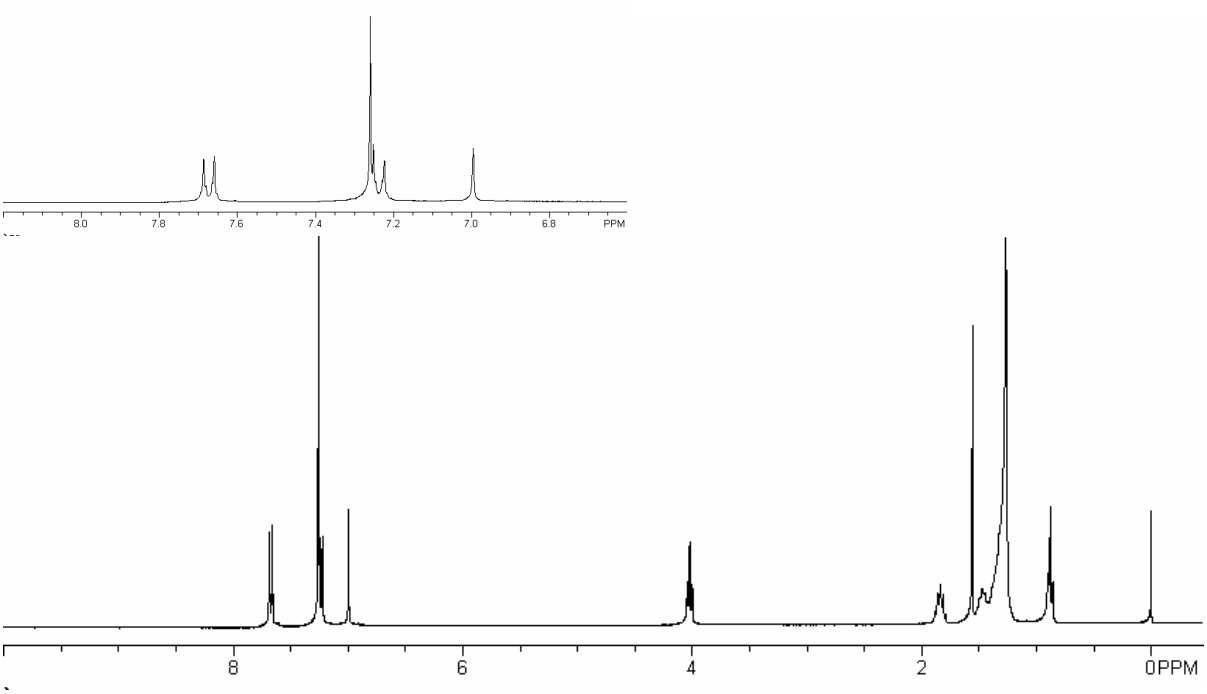
^{1}H NMR spectrum of **14** (inset shows the aromatic region)



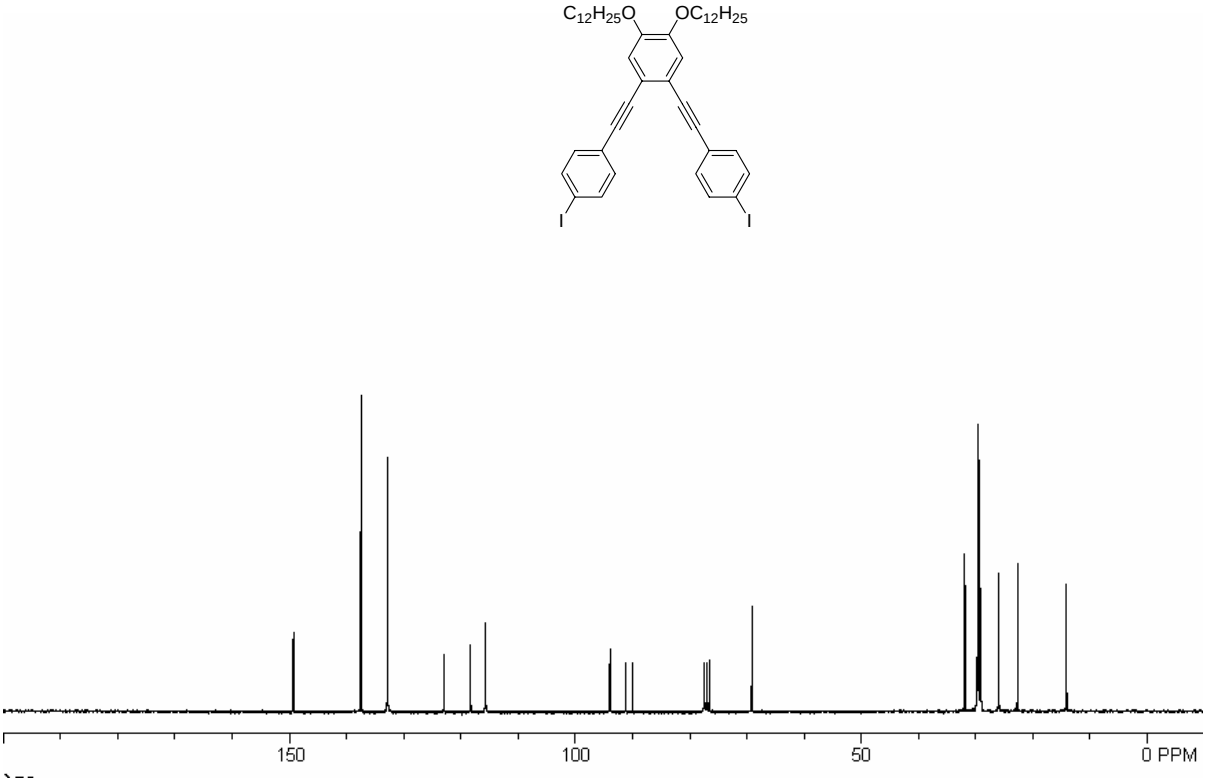
^{13}C NMR spectrum of **14**



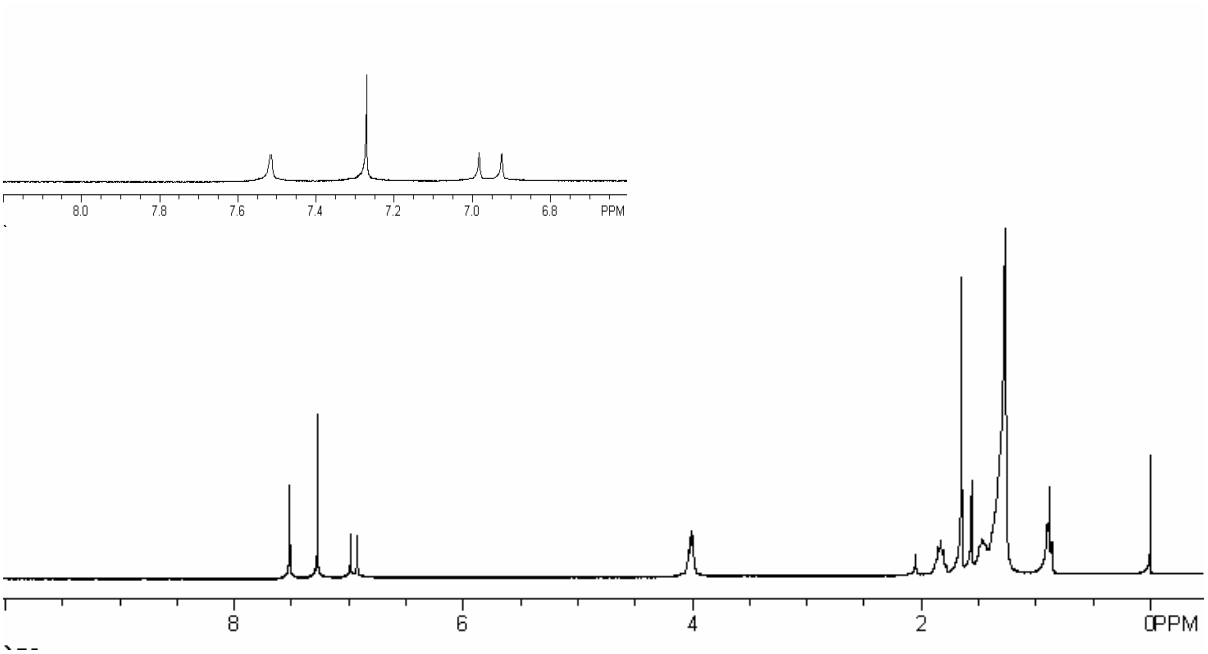
^{1}H NMR spectrum of **16** (inset shows the aromatic region)



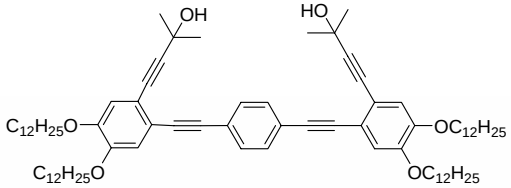
^{13}C NMR spectrum of **16**

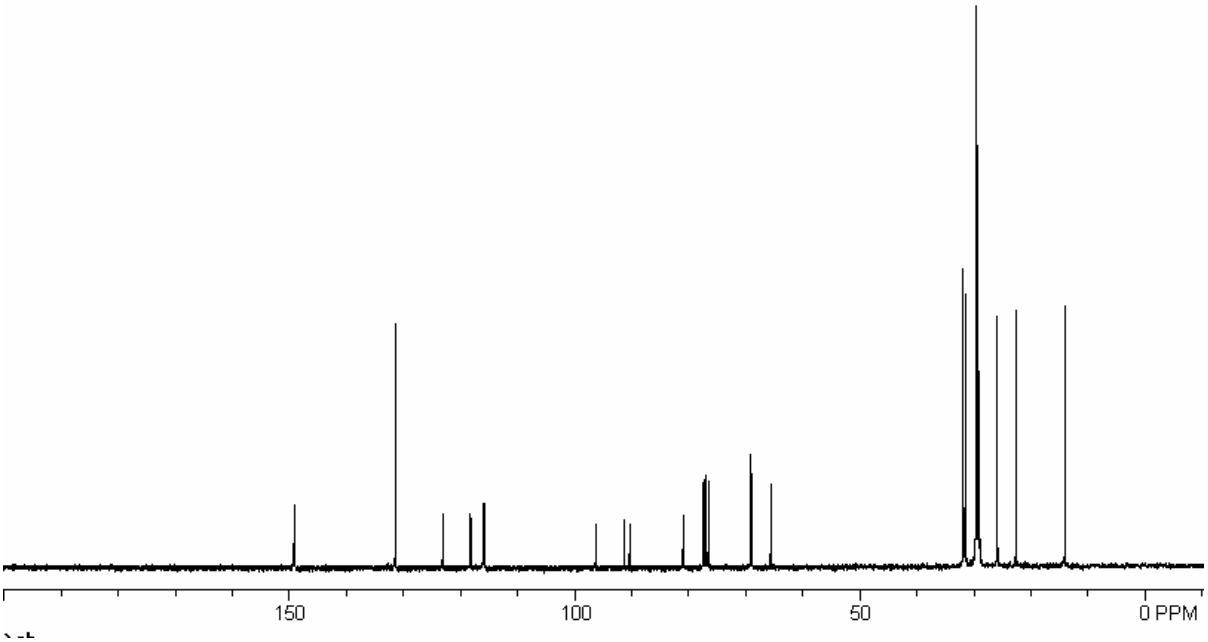


^{1}H NMR spectrum of **17** (inset shows the aromatic region)

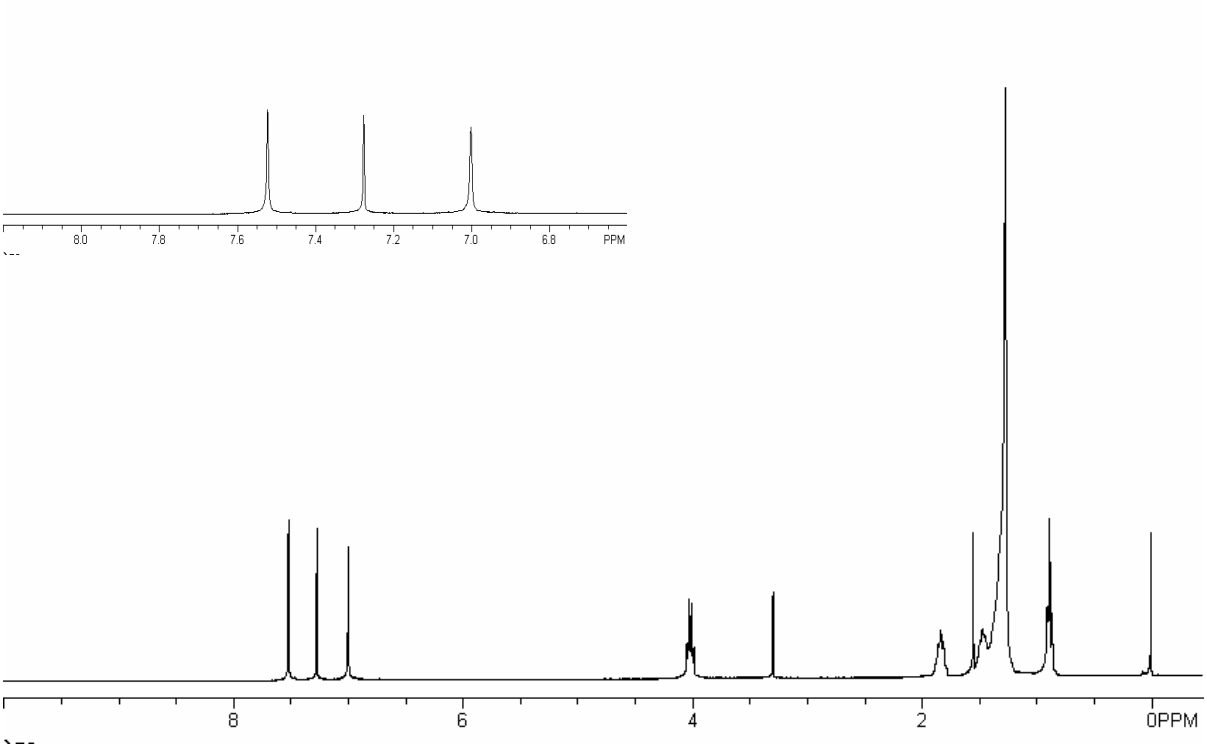


^{13}C NMR spectrum of **17**





^{1}H NMR spectrum of **18** (inset shows the aromatic region)



^{13}C NMR spectrum of **18**