

Synthesis of Functional Molecular Rod Oligomers

Casper S. Andersen and Kurt V. Gothelf*

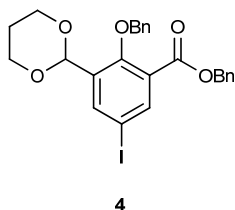
*Danish National Research Foundation: Centre for DNA Nanotechnology, Department of Chemistry
and iNANO, University of Aarhus, Langelandsgade 140, 8000 Aarhus C, Denmark*

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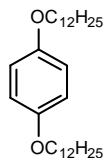
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General Methods

Standard Schlenk and vacuum line techniques were employed using argon as the inert atmosphere. Yields refer to isolated chromatographically and spectroscopic homogeneous materials, unless otherwise stated. Commercially available starting materials were used without further purification. All organic solvents used in experiments were HPLC grade. Tetrahydrofuran (THF) was distilled over sodium prior to use. Dichloromethane (DCM) and triethylamine (NEt₃) were distilled over CaH₂. Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation. Nuclear Magnetic Resonance (NMR) spectra were acquired on a Varian AS 400 spectrometer, running at respectively 400, 100 and 376 MHz for ¹H, ¹³C and ¹⁹F. Chemical shifts (δ) are reported in ppm relative to solvent signals (CHCl₃ at 7.26 ppm for ¹H NMR, CDCl₃ at 77.0 ppm for ¹³C NMR and trifluoroacetic acid at -76.55 ppm). ¹³C NMR spectra were acquired on a broad band decoupled mode. High resolution mass spectra (HRMS) were recorded on a Micromass LCT spectrometer using electrospray (ES+) ionization techniques. Matrix assisted laser desorption/absorption ionisation – time of flight (MALDI-TOF) mass spectrometry was performed using a Bruker Daltonics Autoflex spectrometer, a stainless steel target plate and the matrices dihydroxybenzoic acid (DHB) in methanol and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in dichloromethane (20 mg per ml). Compounds with dodecyloxy chains appeared to be difficult to analyze with our Micromass LCT and instead MALDI-TOF MS was used. All graphical material in the manuscript are generated using ChemBioDraw Ultra 11.0, ChemBio3D Ultra 11.0, NanoEngineer-1 and QutemolX.

Compound 4

A round-bottomed flask with **3** (1.00 g, 2.85 mmol), K_2CO_3 (1.50 g, 11.0 mmol) and acetone (15 ml) were stirred for 30 minutes. Benzylbromide (2.0 ml, 17.0 mmol) was added and the mixture was refluxed in a nitrogen atmosphere over night. The solvent was evaporated and the remaining crude material was dissolved in DCM and washed with water. Purification by flash chromatography on silica gel (EtOAc/pentane 1:20) gave **4** as a white crystalline solid (0.93 g, 1.75 mmol, 62%). Mp 81-82°C. 1H NMR ($CDCl_3$, 400 MHz): δ 8.19 (s, 1H), 8.16 (s, 1H), 7.40 (m, 10H), 5.71 (s, 1H), 5.34 (s, 2H), 4.99 (s, 2H), 4.19 (dd, $J = 11.8$ Hz, $J = 3.9$ Hz, 2H), 3.82 (t, $J = 11.9$ Hz, 2H), 2.19 (m, 1H), 1.38 (d, $J = 12.9$ Hz, 1H). ^{13}C -NMR ($CDCl_3$, 400 MHz): δ 164.0, 156.2, 140.7 (2C), 136.8, 136.0, 135.5, 128.6 (2C), 128.4 (4C), 128.1 (4C), 126.7, 96.1, 87.4, 78.0, 67.4 (2C), 67.2, 25.8. HRMS calcd 553.0488 ($[M+Na]^+$), found 553.0846.

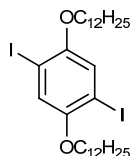
1,4-bis(dodecyloxy)benzene¹

A round-bottomed flask with hydroquinone (4.6 g, 41.6 mmol), bromododecane (39.3 ml, 187.5 mmol), K_2CO_3 (25g, 181 mmol) and CH_3CN (125 ml) was heated to reflux for 48 hours. The solution was decanted into 150 ml water and the solid material was isolated by filtration. The product was obtained by two repeated recrystallizations in hexane/methanol to yield 1,4-bis(dodecyloxy)benzene (12.3 g, 27.6 mmol, 66%). Mp 72-73°C. 1H -NMR ($CDCl_3$, 400MHz): δ 6.82 (s, 4H), 3.89 (t, $J = 6.5$ Hz, 4H), 1.75 (qui, $J = 7.1$ Hz, 4H), 1.43 (m, 4H), 1.26 (m, 36H), 0.86 (t, $J = 6.4$ Hz, 6H). ^{13}C -NMR ($CDCl_3$, 400MHz): δ 153.1 (4C), 115.3 (2C), 68.6 (2C), 31.9 (2C),

¹ Modified literature procedure, see also: Guorong Li, Xianhong Wang* and Fosong Wang, *Tetrahedron Lett.*, 2005, **46**, 8971

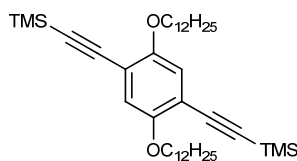
29.6 (8C) 29.4 (6C), 26.1 (2C), 22.7 (2C), 14.1 (2C). Maldi-TOF MS calcd 446.41 ($[M]^+$), found 446.26.

1,4-bis(dodecyloxy)-2,5-diiodobenzene²



A round-bottomed flask with 1,4-bis(dodecyloxy)benzene (12.3 g, 27.89 mmol), acetic acid (285 ml), concentrated sulphuric acid (2.9 ml), water (29 ml), iodine (7.72 g, 30.4 mmol) and KIO₃ (2.35 g, 11.0 mol) was heated to reflux for 6 hours. Saturated Na₂S₂O₃ was added slowly until the solution becomes yellow. During the addition the temperature is held above 80°C. Then addition is finished the solution is cooled slowly to room temperature under vigorous stirring. The suspension is filtered and the solid phase is dissolved in CHCl₃, washed with water and recrystallized in chloroform/ethanol to yield 1,4-bis(dodecyloxy)-2,5-diiodobenzene as white crystals (15.2 g, 21.8 mmol, 79%). Mp 75-76 °C. ¹H-NMR (CDCl₃, 400MHz): δ 7.17 (s, 2H), 3.92 (t, J = 6.7 Hz, 4H), 1.79 (qui, J = 7.7Hz, 4H), 1.49 (br. qui, J = 7.7 Hz, 4H), 1.26 (m, 36H), 0.88 (t, J = 7.7 Hz, 6H). ¹³C-NMR (CDCl₃, 400MHz): δ 152.8 (2C), 122.7 (2C), 86.3 (2C), 70.3 (2C), 31.9 (2C), 29.5 (14C), 26.0 (2C), 22.7 (2C), 14.1 (2C). Maldi-TOF MS calcd 698.21 ($[M]^+$), found 697.97.

2,5-bis(dodecyloxy)-1,4-bis(trimethylsilylethynyl)benzene

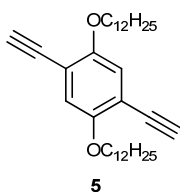


A mixture of (PPh₃)₂PdCl₂ (87 mg, 0.12 mmol), CuI (24 mg, 0.12 mmol) and 1,4-bis(dodecyloxy)-2,5-diiodobenzene (1.74 g, 2.49 mmol) was stirred under argon for 30 min. in a Schlenk flask. THF (5 ml), trimethylsilylacetylene (0.75 ml, 5.22 mmol), and NEt₃ (5 ml) were added and the mixture was stirred at room temperature under argon atmosphere for 16 hours. The solvent was removed by vacuum distillation and the crude product was dissolved in a minimum of DCM and filtered through 10 cm silica with 100 ml of DCM. The DCM was evaporated to a final volume of 50 ml and 100 ml EtOH was added. The mixture was placed at 0°C for crystallization. The product was obtained after

² Modified literature procedure, see also: González-Rojano, Norma; Arias-Marín, Eduardo; Navarro-Rodríguez, Dámaso; Weidner, Steffen, *Synlett*, 2005, **8**, 1259

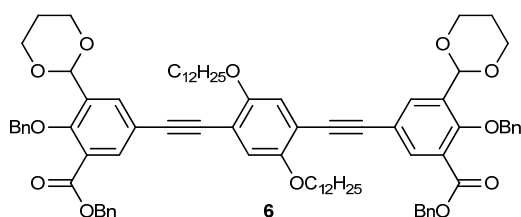
a second crystallization to yield 2,5-didodecyloxy-1,4-bis(trimethylsilylethynyl)benzene as white crystals (1.06 g, 1.73 mmol, 70%). mp 75-76°C. ¹H-NMR (CDCl₃, 400 MHz): δ 6.89 (s, 2H), 3.94 (t, J = 6.64 Hz, 4H), 1.76 (qui, J = 6.7 Hz, 4H), 1.49 (br. qui, J = 6.8 Hz, 6H), 1.26 (br. m, 32H), 0.88 (t, J = 6.7 Hz, 6H), 0.24 (s, 18H). ¹³C-NMR (CDCl₃, 400 MHz): δ 153.9 (2C), 117.0 (2C), 113.8 (2C), 101.0 (2C), 100.1 (2C), 69.3 (2C), 31.9 (2C), 29.5 (14C), 26.0 (2C), 22.7 (2C), 14.1 (2C), -0.1 (6C). Maldi-TOF MS calcd 638.49 ([M]⁺), found 638.14.

Compound 5



A round-bottomed flask with 2,5-didodecyloxy-1,4-bis(trimethylsilylethynyl)benzene (1.06 g, 1.73 mmol) and DCM (20 ml) was cooled to 0°C and TBAF (1 M in THF, 3.64 ml, 3.64 mmol) was added slowly. The reaction mixture was stirred for 20 minutes at 0°C and DCM (50 ml) was added and the solution was extracted with water. The crude product was purified by flash chromatography on silica gel (DCM/pentane, 1:5) to yield **5** (0.72 g, 94%). mp 78-79°C. ¹H-NMR (CDCl₃, 400 MHz): δ 6.95 (s, 2H), 3.96 (t, J = 7.0 Hz, 4H), 3.33 (s, 2H), 1.79 (q, J = 6.9 Hz, 4H), 1.45 (br. qui, 4H), 1.26 (m, 32H), 0.88 (t, J = 6.8, 6H). ¹³C-NMR (CDCl₃, 400MHz): δ 153.9 (2C), 117.6 (2C), 113.1 (2C), 82.4 (2C), 79.7 (2C), 69.6 (2C), 31.9 (2C), 29.7 (2C), 29.6 (6C), 29.3 (4C), 29.1 (2C), 25.9 (2C), 22.7 (2C), 14.1 (2C). Maldi-TOF MS calcd 494.41 ([M]⁺), found 494.21

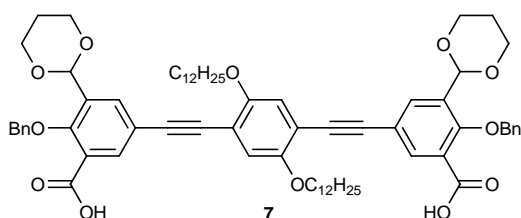
Compound 6



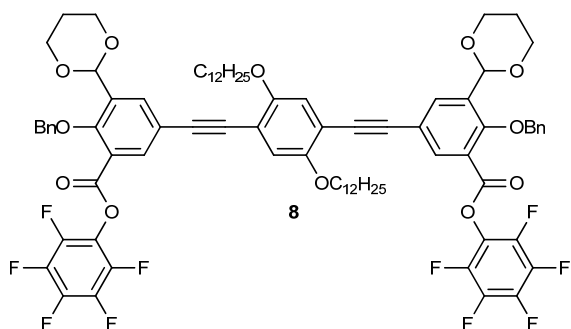
A Schlenk flask with (PPh₃)₂PdCl₂ (24 mg, 0.034 mmol, 2%), CuI (7 mg, 0.034 mmol, 2%), **4** (930 mg, 1.75 mmol) and **5** (401.5 mg, 0.85 mmol) were stirred for 30 minutes under vacuum. THF (10 ml) and NEt₃ (10 ml) were added and the mixture was stirred at room temperature under argon atmosphere for 18 hours. The solvents were removed by vacuum distillation and the crude product was purified by flash chromatography on silica gel (DCM/pentane, 1:10) to yield **6** as yellow

crystals (760 mg, 68%). mp 97-98°C. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 8.07 (s, 2H), δ 8.03 (s, 2H), 7.42 (m, 20H), 7.00 (s, 2H), 5.76 (s, 2H), 5.36 (s, 4H), 5.03 (s, 4H), 4.19 (dd, $J = 9.0$ Hz, $J = 3.8$ Hz, 4H), 4.02 (t, $J = 6$ Hz, 4H), 3.84 (t, $J = 9.0$ Hz, 4H), 2.20 (m, 2H), 1.85 (q, $J = 7.5$ Hz, 4H), 1.52 (m, 6H), 1.38-1.25 (m, 32H), 0.88 (t, $J = 7.0$ Hz, 6H). $^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz): δ 164.9 (2C), 156.2 (2C), 153.5 (2C), 137.0 (2C), 135.6 (2C), 135.3 (2C), 135.0 (2C), 134.3 (2C), 128.6 (4C), 128.4 (8C), 128.3 (4C), 128.1 (4C), 124.9 (2C), 119.7 (2C), 117.1 (2C), 113.8 (2C), 96.6 (2C), 93.3 (2C), 86.4 (2C), 78.0 (2C), 69.6 (2C), 67.5 (4C), 67.0 (2C), 31.9 (2C), 29.7 (2C), 29.6 (6C), 29.3 (4C), 29.2 (2C), 25.9 (2C), 25.7 (2C), 22.6 (2C), 14.1 (2C). Maldi-TOF MS calcd 1298.71 ($[\text{M}]^+$), found 1298.54.

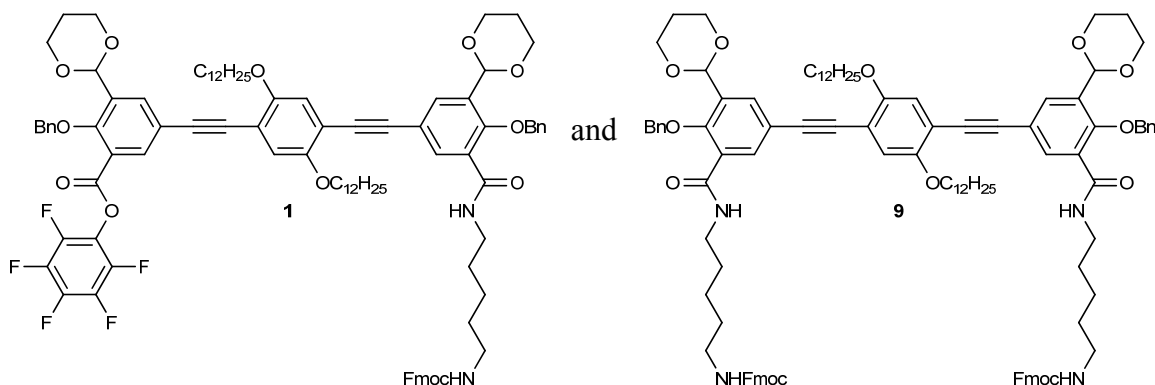
Compound 7



A round-bottomed flask with **6** (764 mg, 0.588 mmol), THF (15 ml), saturated aqueous LiOH (1 ml) and solid LiOH (10mg) were refluxed vigorously for 12 hours in an 100°C oil bath. The THF was removed under vacuum and the remaining solid material was washed with Et_2O and dissolved in toluene with 5 % volume of formic acid. The solution was washed with water. The organic phase was dried over MgSO_4 and evaporated to dryness to yield **7** as yellow crystals (650 mg, 0.58 mmol, 99 %). mp 169-170°C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (s, 2H), 8.12 (s, 2H), 7.50 (d, $J = 7.2$, 4H), 7.41 (m, 4H), 7.34 (d, $J = 4.8$, 2H), 7.03 (s, 2H), 5.81 (s, 2H), 5.13 (s, 4H), 4.24 (d, $J = 11.4$, 4H), 4.05 (t, $J = 7.1$, 4H), 3.90 (t, $J = 11.4$, 4H), 2.38 – 2.11 (m, 2H), 1.99 – 1.78 (m, 4H), 1.66 – 1.49 (m, 6H), 1.50 – 1.03 (m, 32H), 0.87 (t, $J = 6.7$, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 167.3 (2C), 155.8 (2C), 153.5 (2C), 136.4 (2C), 136.3 (2C), 135.6 (2C), 134.0 (2C), 128.8 (6C), 128.6 (4C), 123.2 (2C), 120.8 (2C), 117.0 (2C), 113.8 (2C), 96.5 (2C), 93.0 (2C), 87.0 (2C), 79.4 (2C), 69.7 (2C), 67.6 (4C), 31.9 (2C), 29.7 (2C), 29.6 (6C), 29.3 (4C), 29.2 (2C), 26.0 (2C), 25.6 (2C), 22.7 (2C), 14.1 (2C). Maldi-TOF MS calcd 1118.61 ($[\text{M}]^+$), found 1118.53.

Compound 8

A round-bottomed flask with **7** (200 mg, 0.18 mmol), *N,N*-dicyclohexylcarbodiimide (73 mg, 0.36 mmol), and THF (5 ml) was placed in a nitrogen atmosphere at 0°C. After 15 minutes pentafluorophenol (72 mg, 0.40 mmol) was added and the reaction was stirred for 16 hours at room temperature. The reaction mixture was filtered through 10 cm silica with 150 ml EtOAc. After evaporation the crude was dissolved in a minimum of DCM and crystallized by addition to cold MeOH to yield **8** as yellow crystals (200 mg, 77%). mp 75-77°C. ¹H-NMR (400 MHz, CDCl₃). δ 8.31 (d, *J*=2.3 Hz, 2H), 8.16 (d, *J*=2.3 Hz, 2H), 7.51 – 7.46 (m, 4H), 7.43 – 7.37 (m, 6H), 7.02 (s, 2H), 5.77 (s, 2H), 5.10 (s, 4H), 4.22 (d, *J* = 11.2, 4H), 4.04 (t, *J* = 6.7, 4H), 3.86 (t, *J* = 11.2, 4H), 2.33 – 2.12 (m, 2H), 1.86 (m, 4H), 1.54 (m, 6H), 1.42 – 1.17 (m, 32H), 0.86 (t, *J* = 6.9, 6H). ¹⁹F-NMR (CDCl₃, 400MHz): δ -152.7 (d, *J*=18.4 Hz, 2F), -158.1 (t, 23.2 Hz, 1F), 162.4 (t, *J*=24 Hz, 2F). ¹³C-NMR (100 MHz, CDCl₃). δ 160.1 (2C), 157.5 (2C), 153.6 (2C), 136.9 (2C), 136.5 (2C), 136.0 (2C), 135.0 (2C), 128.5 (6C), 128.2 (4C), 121.2 (2C), 120.2 (2C), 116.9 (2C), 113.7 (2C), 96.3 (2C), 92.8 (2C), 87.0 (2C), 78.4 (2C), 69.6 (2C), 67.5 (4C), 31.9 (2C), 29.6 (6C), 29.5 (2C), 29.3 (4C), 29.2 (2C), 26.0 (2C), 25.6 (2C), 22.7 (2C), 14.1 (2C) (The -OC₆F₅ group is not detectable by ¹³C-NMR due to large C-F coupling). Maldi-TOF MS calcd 1450.58 ([M]⁺), found 1450.35

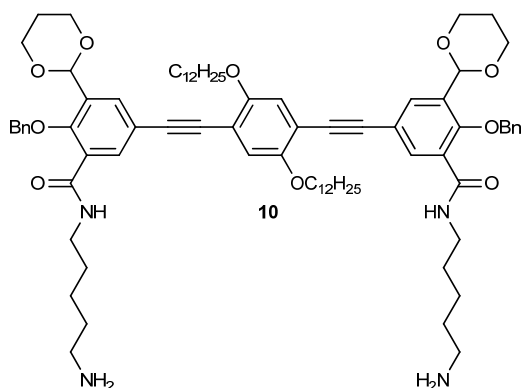
Compound 1 and compound 9

To a round-bottomed flask with **8** (1.60 g, 1.10 mmol), THF (20 ml), pyridine (1.0 ml) and DMAP (130 mg, 1.10 mmol) was a solution of N-Fmoc-cadaverine hydrochloride (318 mg, 0.88 mmol) in DMF (5 ml) added dropwise. The solution was stirred at room temperature in argon atmosphere for 2 hours. The crude product was filtered on 15 cm silica gel with 150 ml DCM. The DCM fraction contains starting material **8** and it can be recovered by crystallization with the above described method to recover 20% of starting material **8** (320 mg, 0.22 mmol, 20%). The silica gel was afterwards washed through with EtOAc. The EtOAc eluent was concentrated by vacuum distillation and the remaining crude was purified by flash chromatography on silica gel (Et₂O/hexane 1:8) to yield **1** (700 mg, 0.44 mmol, 40 %). The silica was once again washed with EtOAc. The EtOAc solution was concentrated by vacuum distillation and recrystallization in DCM/hexane to yield compound **9** as yellow crystals (360 mg, 0.21 mmol, 19%). Spectroscopic data for compound **1**. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, *J* = 2.2, 1H), 8.23 (d, *J* = 2.2, 1H), 8.16 (d, *J* = 2.2, 1H), 7.97 (d, *J* = 2.1, 1H), 7.75 (d, *J* = 7.5, 2H), 7.59 (d, *J* = 7.4, 2H), 7.49 (d, *J* = 6.7, 2H), 7.46 – 7.36 (m, 10H), 7.31 (t, *J* = 7.4, 2H), 6.99 (s, 2H), 5.79 (s, 1H), 5.77 (s, 1H), 5.10 (s, 2H), 5.00 (s, 2H), 4.79 (bt, 1H), 4.40 (d, *J* = 6.8, 2H), 4.29 – 4.17 (m, 4H), 4.02 (m, 4H), 3.96 – 3.84 (m, 4H), 3.35 (k, *J* = 6.5, 2H), 3.11 (k, *J* = 6.6, 2H), 2.34 – 2.17 (m, 2H), 1.92 – 1.81 (m, 4H), 1.58 – 1.48 (m, 6H), 1.48 – 1.18 (m, 38H), 0.86 (t, *J* = 6.0, 6H). ¹³C NMR (101 MHz, CDCl₃). δ 164.6, 160.0, 157.3, 156.3 (2C), 153.5, 153.3, 143.8 (2C), 141.1 (2C), 136.8, 136.5, 136.0 (2C), 135.0 (2C), 133.8, 133.2, 128.6 (2C), 128.5, 128.4 (2C), 128.1 (2C), 127.8, 127.5 (4C), 126.8 (2C), 124.9 (2C), 121.1, 120.5, 120.2, 119.7 (3C), 116.9 (2C), 114.1, 113.2, 96.7, 96.2, 93.6, 92.6, 87.1, 86.4, 78.4, 78.3, 69.4 (2C), 67.5 (2C), 67.4 (2C), 66.3, 47.1, 40.6, 39.5, 31.8 (2C), 29.4 (7C), 29.2 (6C), 29.1 (2C), 28.8, 25.8 (2C), 25.5 (2C), 23.8, 22.5

(2C), 14.0 (2C) (the pentafluorophenyl group is not observed due to large C-F coupling constants). Maldi-TOF MS calcd 1590.77 ($[M]^+$) found 1590.75.

Spectroscopic data for compound **9**. mp 143-145°C. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 2.3$, 2H), 7.97 (s, 2H), 7.75 (d, $J = 7.0$, 4H), 7.59 (d, $J = 7.4$, 4H), 7.50 (m, 2H), 7.45 – 7.35 (m, 12H), 7.30 (t, $J = 7.4$, 4H), 6.96 (s, 2H), 5.79 (s, 2H), 5.00 (s, 4H), 4.85 – 4.74 (m, 2H), 4.40 (d, $J = 6.8$, 4H), 4.24 (dd, $J = 5.1, 11.7$, 4H), 4.00 (t, $J = 6.5$, 4H), 3.91 (t, $J = 11.4$, 4H), 3.35 (k, $J = 9.7$, 4H), 3.11 (k, $J = 6.6$, 4H), 2.33 – 2.16 (m, 2H), 1.93 – 1.77 (m, 4H), 1.59 – 1.10 (m, 50H), 0.86 (t, $J = 6.8$, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.6 (2C), 156.3 (2C), 153.7 (2C), 153.4 (2C), 143.9 (4C), 141.2 (4C), 136.1 (2C), 135.2 (2C), 133.9 (2C), 133.1 (2C), 128.7 (6C), 128.5 (2C), 128.2 (2C), 127.7 (2C), 127.6 (4C), 127.5 (2C), 126.9 (4C), 124.9 (4C), 120.8 (2C), 119.9 (2C), 117.1 (2C), 113.8 (2C), 96.8 (2C), 93.4 (2C), 86.7 (2C), 78.5 (2C), 69.6 (2C), 67.6 (2C), 66.4 (2C), 53.4 (2C), 47.2 (2C), 40.7 (2C), 39.5 (2C), 31.9 (2C), 29.6 (8C), 29.5 (2C), 29.3 (4C), 29.1 (2C), 28.9 (2C), 25.9 (2C), 25.6 (2C), 23.9 (2C), 22.6 (2C), 14.1 (2C). Maldi-TOF MS calcd 1752.96 ($[M + \text{Na}]^+$) found 1752.91.

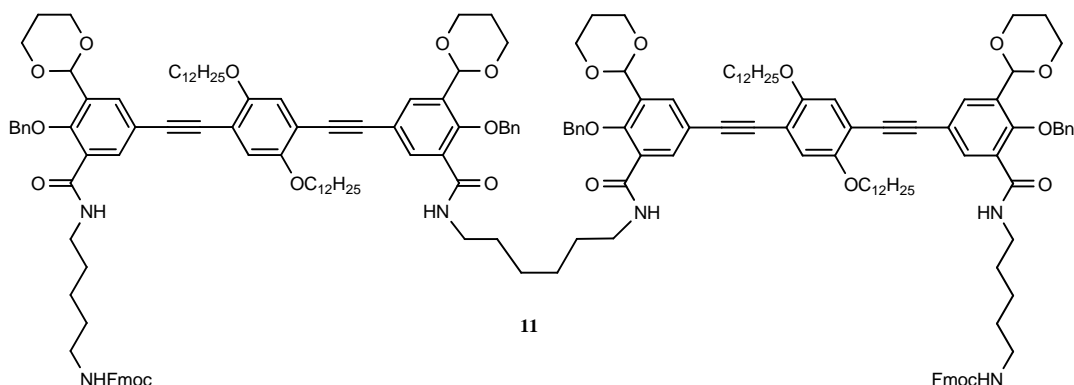
Compound 10



A round-bottomed flask with **9** (350 mg, 0.20 mmol), DCM (5ml) and diethylamine (1 ml) was placed under nitrogen atmosphere and the solution was stirred at room temperature for 12 hours. The crude product was purified by column chromatography on 10 cm silica gel (first elution with EtOAc, then elution with DCM/MeOH, 95:5). Vacuum distillation of the DCM/MeOH gave compound **10** as a yellow oil (220 mg, 0.17 mmol, 85%). ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 2H), 7.93 (s, 2H), 7.39 (m, 10H), 6.97 (s, 2H), 5.75 (s, 2H), 4.96 (s, 4H), 4.29 – 4.13 (m, 4H), 4.06 – 3.95 (m, 4H), 3.96 – 3.81 (m, 4H), 3.41 – 3.21 (m, 4H), 2.76 – 2.52 (m, 4H), 2.29 – 2.14 (m, 2H), 1.84 (s, 4H), 1.62 – 0.96 (m, 50H), 0.95 – 0.75 (t, $J = 7.1$, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.6 (2C), 153.7 (2C), 153.4 (2C), 136.1 (2C), 135.1 (2C), 133.8 (2C), 133.1 (2C), 128.7 (4C),

128.5 (2C), 127.9 (2C), 127.6 (4C), 120.6 (2C), 117.0 (2C), 113.8 (2C), 96.8 (2C), 93.4 (2C), 86.5 (2C), 78.4 (2C), 69.6 (2C), 67.5 (4C), 40.9 (2C), 39.6 (2C), 31.8 (2C), 31.5 (2C), 29.6 (8C), 29.5 (2C), 29.3 (4C), 28.9 (2C), 25.9 (2C), 25.6 (2C), 24.0 (2C), 22.6 (2C), 14.0 (2C). Maldi-TOF MS calcd 1286.82 ($[M]^+$) found 1287.14

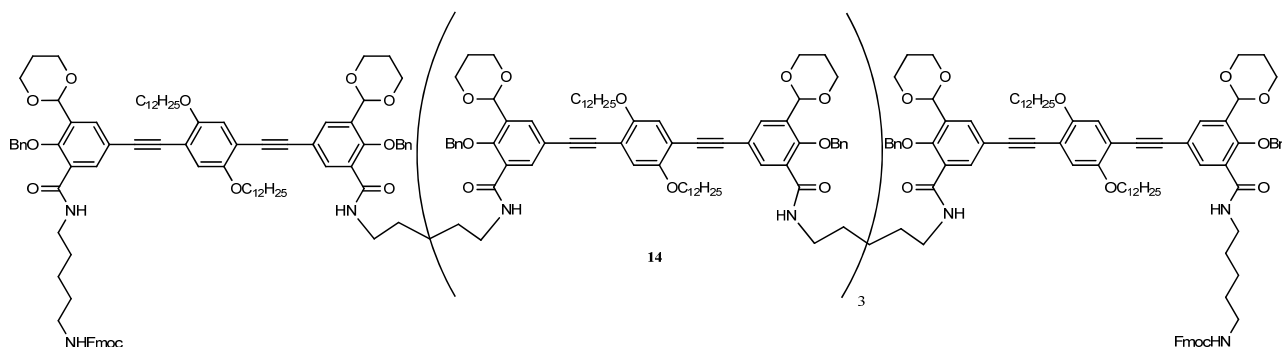
Dimer 11



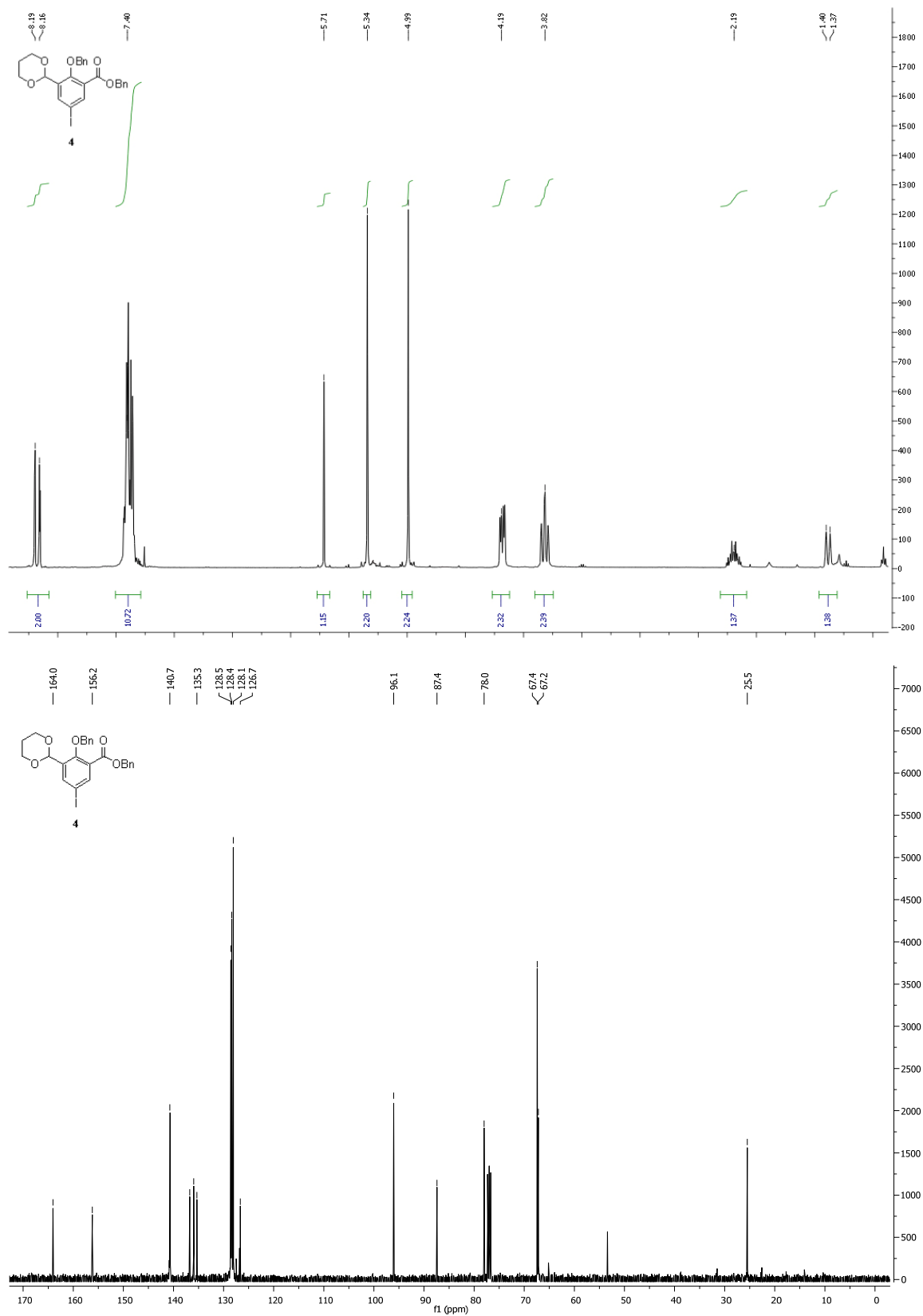
To a round-bottomed flask with **1** (64 mg, 0.04 mmol), THF (5 ml), pyridine (0.5 ml) and DMAP was slowly added a solution of 1,6-hexanediamine in THF (2.4 mg in 3 ml THF, 0.02 mmol). The reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 hours. The solvent was removed by vacuum distillation and the crude was dissolved in a minimum DCM and MeOH was added until precipitation. The solid precipitate was purified by flash chromatography on silica gel hexane/diethylether 1:1 to yield compound **11** as a yellow solid material (55 mg, 19 μ mol, 94%). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 8.22 (s, 4H), 7.96 (s, 4H), 7.74 (d, $J=7.4$ Hz, 4H), 7.59 (d, $J=7.4$ Hz, 4H), 7.41 (m, 24H), 7.39 (t, $J=7.0$ Hz, 4H), 6.99 (s, 4H), 5.78 (s, 4H), 4.99 (s, 8H), 4.76 (t, 2H), 4.39 (d, $J=6.4$ Hz, 4H), 4.22 (m, 8H), 3.99 (m, 8H), 3.91 (t, $J=12$ Hz, 8H), 3.32 (m, 8H), 3.10 (k, $J=6.4$ Hz, 4H), 2.22 (m, 4H), 1.84 (m, $J=6.4$, 8H), 1.50 (m, 12H), 1.39-1.20 (m, 84H), 0.86 (t, $J=7.2$ Hz, 12H). Maldi-TOF MS calcd 2952.670 ($[M + \text{Na}]^+$) found 2953.548.

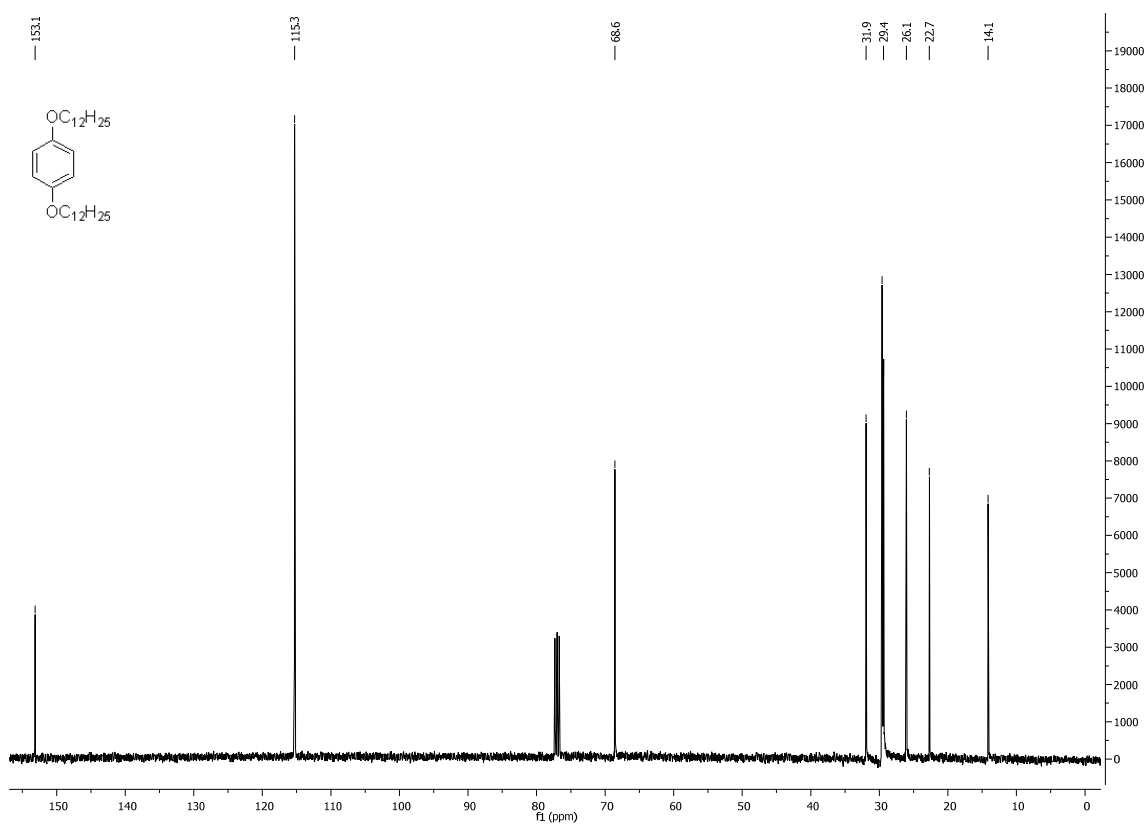
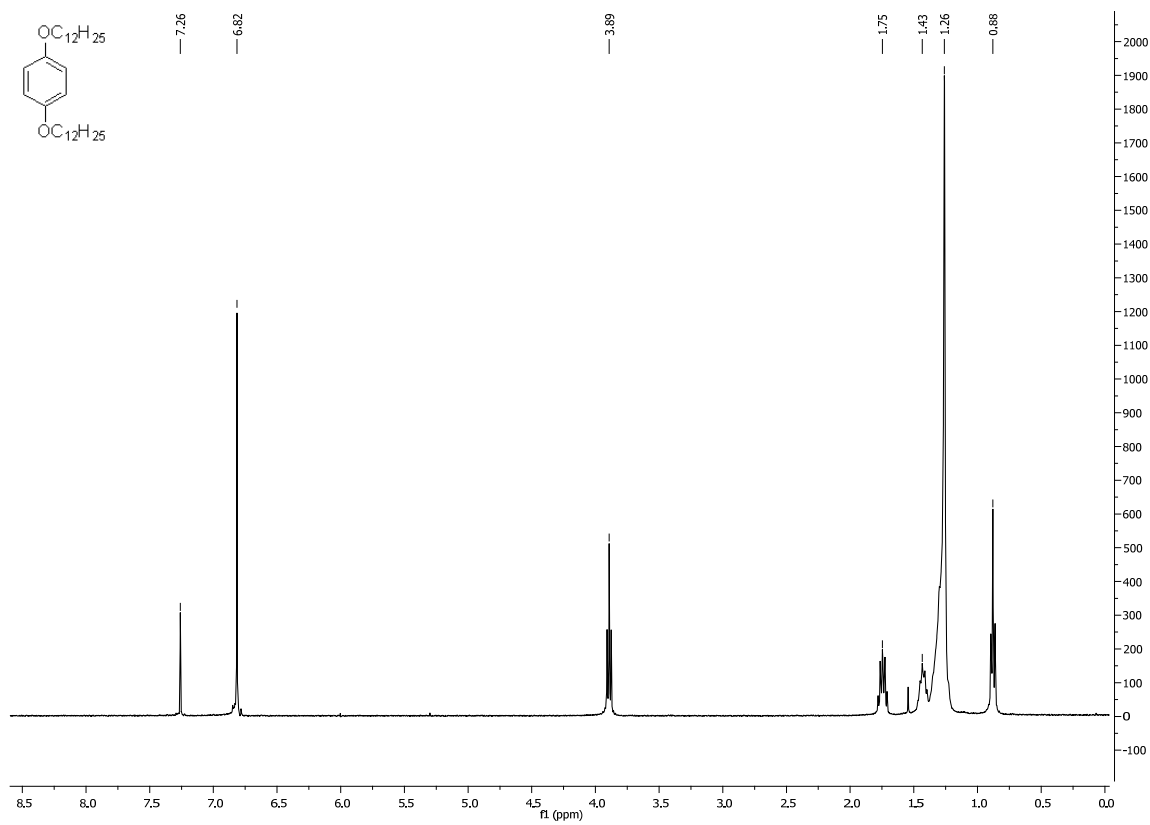
(m, 12H) 3.35 (m, 4H), 3.24 (m, 8H), 2.60 (m, 4H), 2.20 (m, 6H), 1.85 (m, 12H), 1.51 (m, 18H), 1.38-1.20 (m, 120H), 0.86 (t, $J=7.2$ Hz, 18H). It was not possible to detect **13** with Maldi-TOF MS.

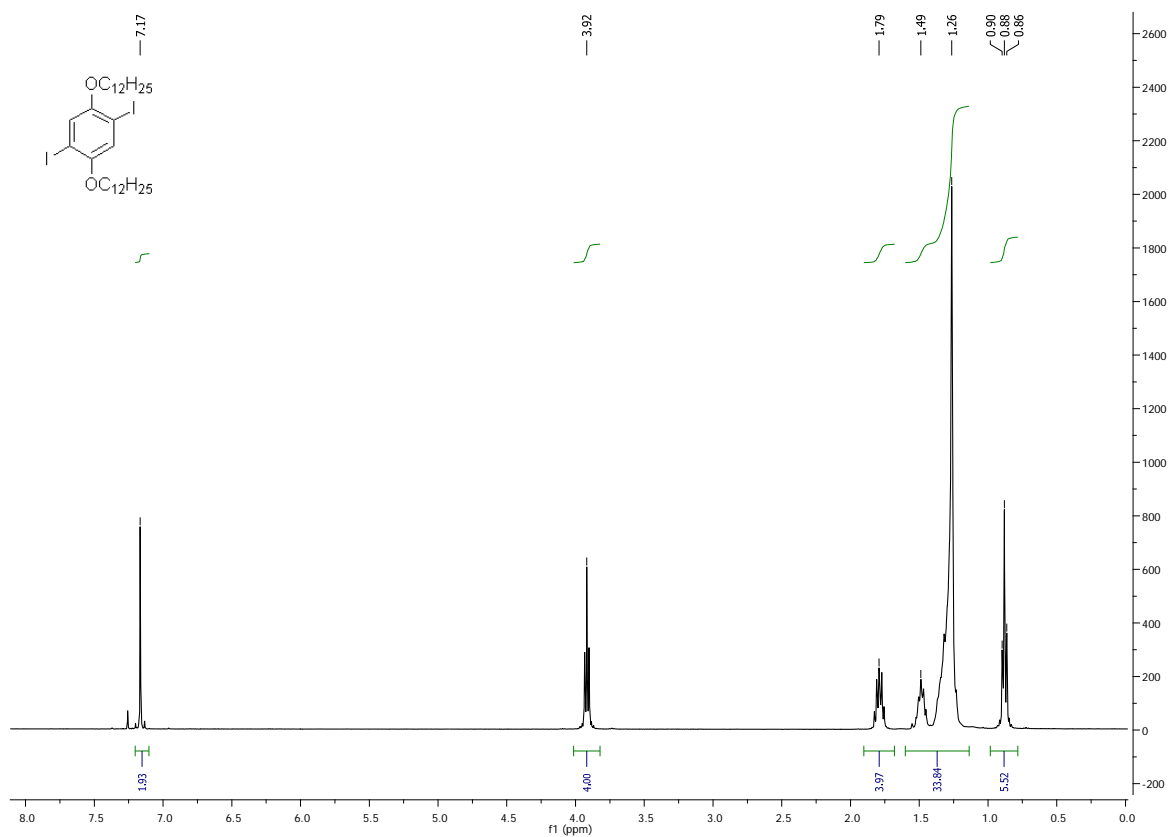
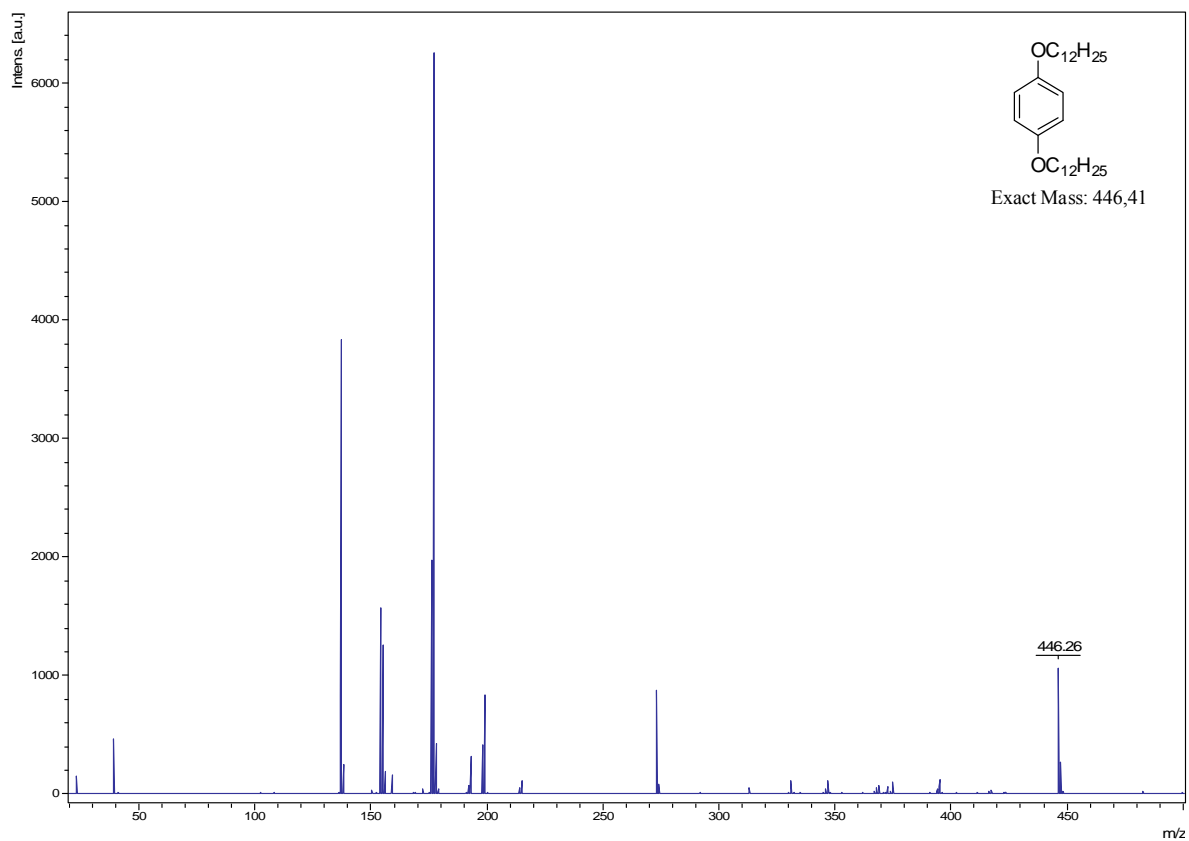
Pentamer 14

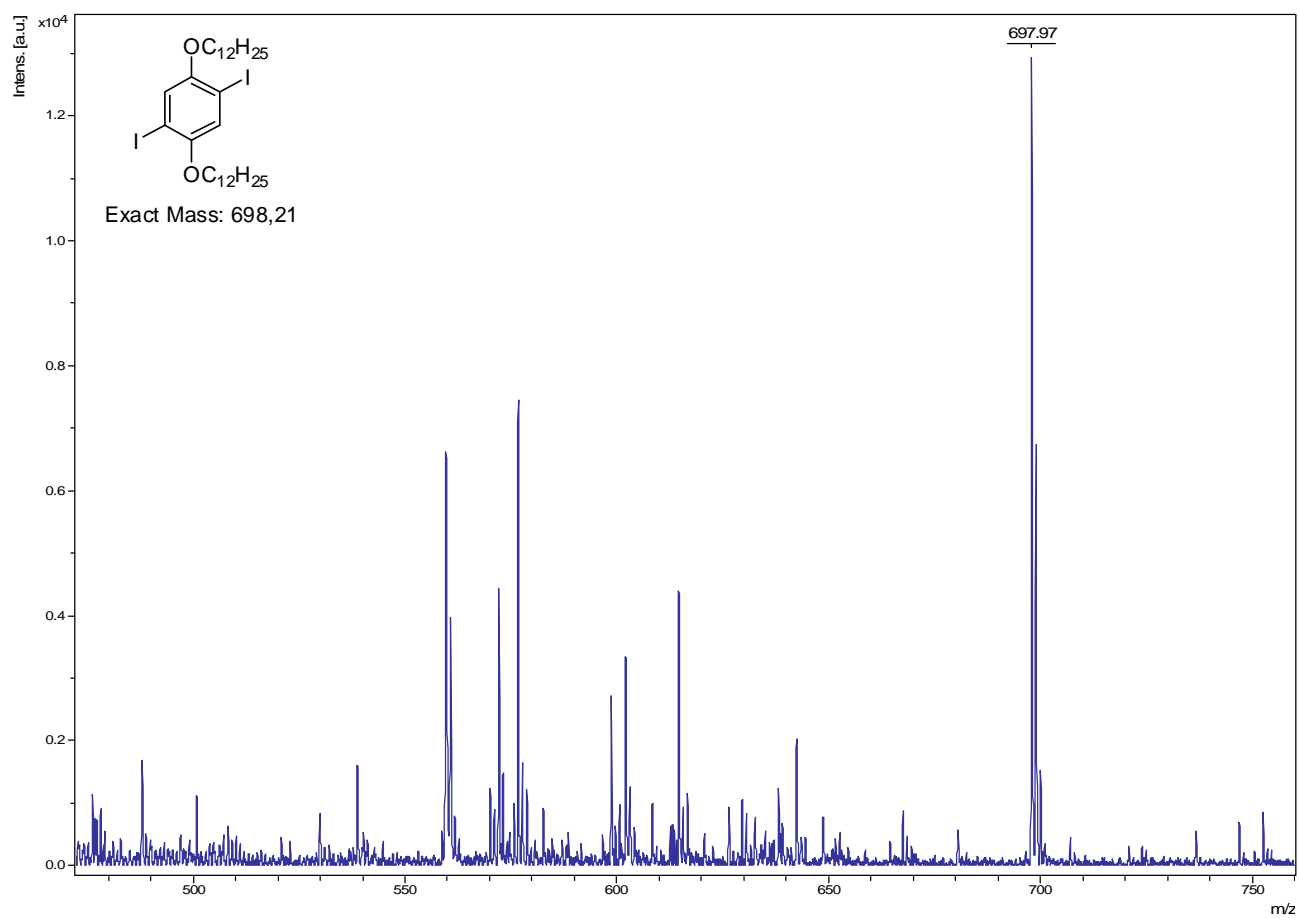
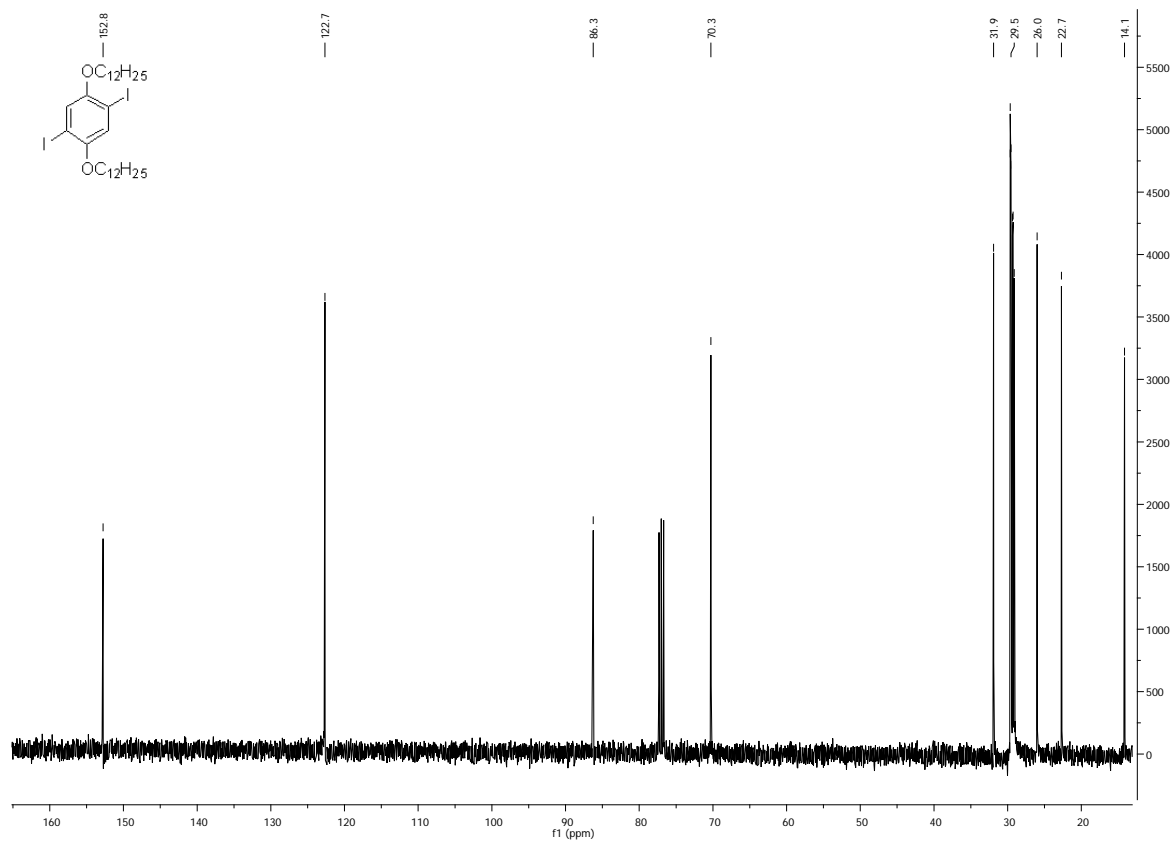


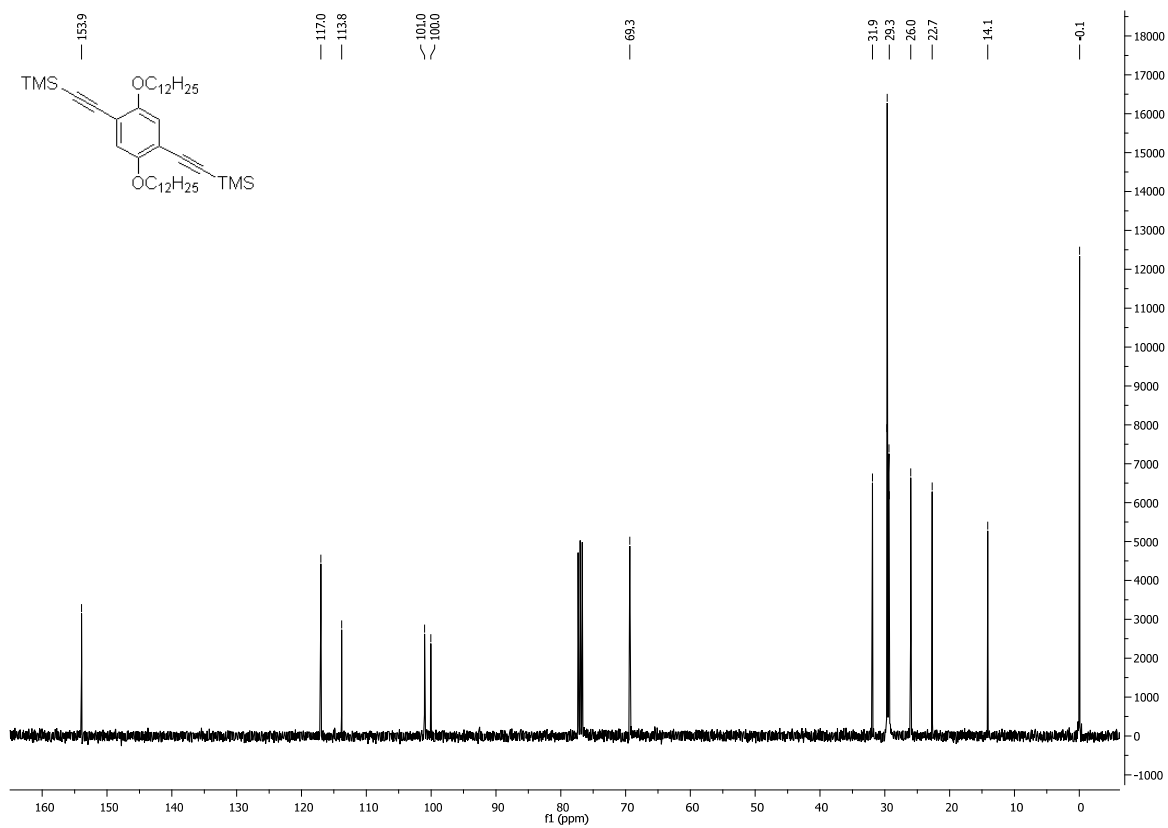
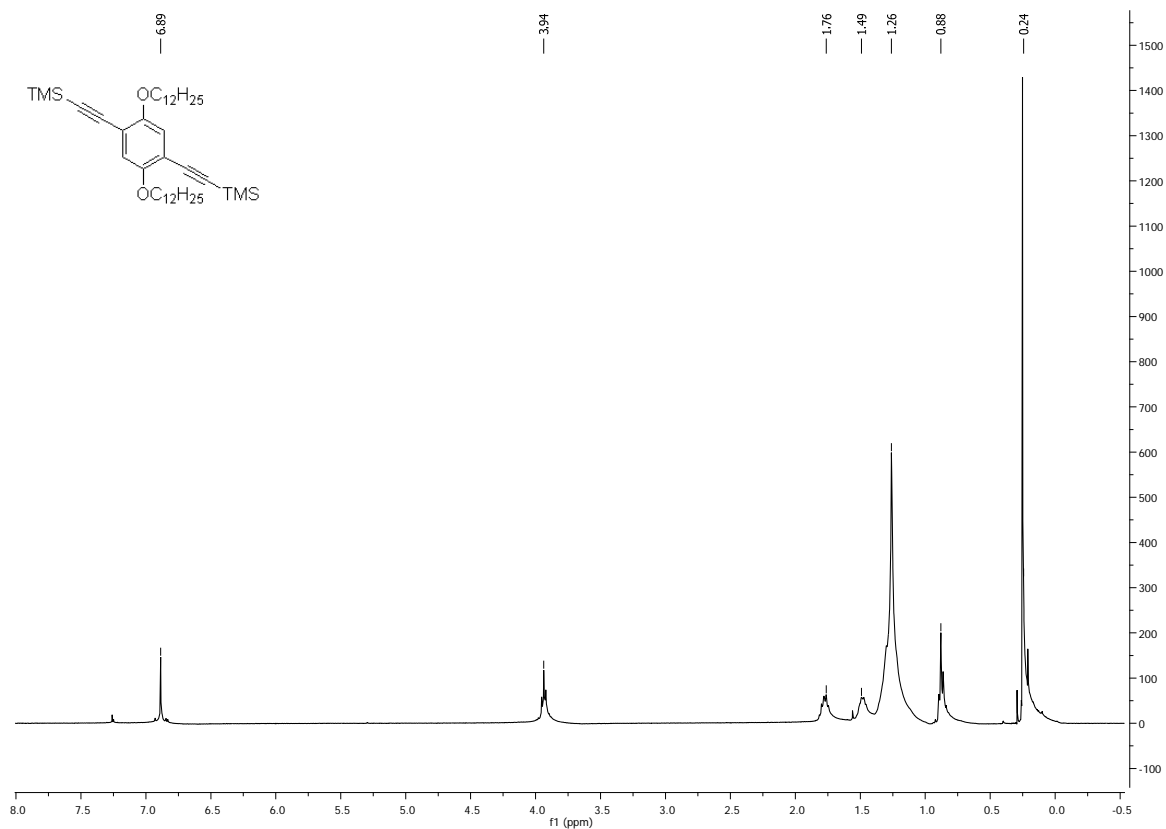
To a round-bottomed flask with **1** (44 mg, 28 μmol), THF (5 ml), pyridine (1 ml) and DMAP (3 mg, 56 μmol) was slowly added a solution of compound **13** in THF (50 mg in 2 ml THF, 14 μmol). The reaction mixture was stirred for 16 hours at room temperature under nitrogen atmosphere. The solvent was removed by vacuum distillation and the crude product was purified by flash chromatography on silica gel (hexane/diethylether 1:4). The pentamer **14** precipitated directly from the chromatography fraction and was isolated by filtration as a yellow solid (68 mg, 11 μmol , 75%) $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 8.22 (s, 10H), 7.96 (s, 10H), 7.74 (d, $J=8$ Hz, 4H), 7.58 (d, $J=8$ Hz, 4H), 7.40-7.30 (m, 58H), 7.00 (s, 10H), 5.78 (s, 10H), 4.98 (s, 20H), 4.80 (m, 2H), 4.38 (d, $J=6$ Hz, 4H), 4.23 (m, 20H), 4.03 (m, 20H), 3.91 (m, 20H) 3.35 (m, 10H), 3.24 (m, 10H), 3.09 (m, 4H), 2.23 (m, 10H), 1.84 (m, 20H), 1.50 (m, 24H), 1.39-1.20 (m, 202H), 0.85 (m, 30H). Maldi-TOF MS: calcd 6474.516 ($[\text{molecular mass}]^+$) found 6471.516 (The best results was obtained using DCTB matrix, decreasing the resolution and switching off the smoothing and the background subtraction. This produces a broader peak close to the average molecular mass).

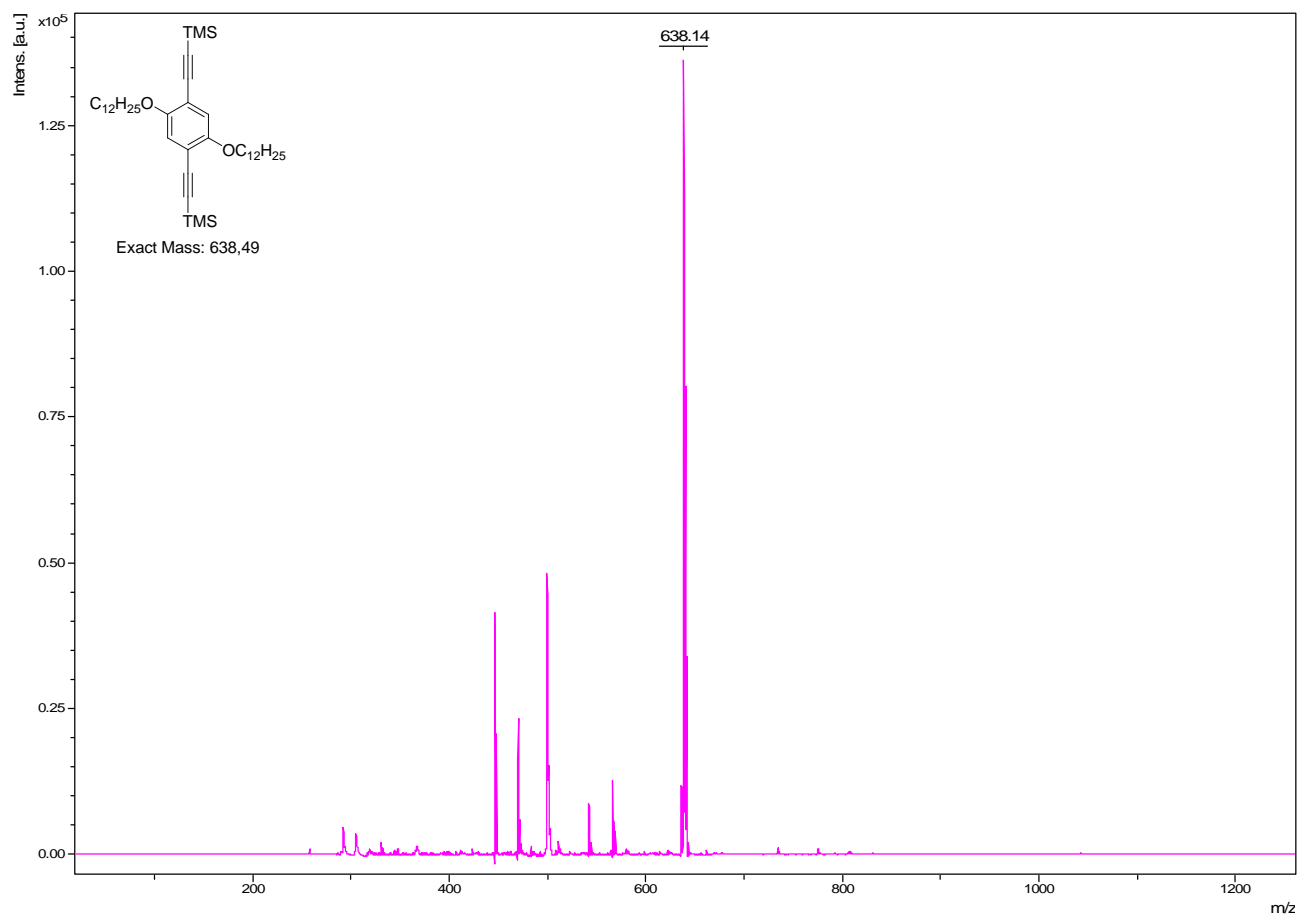


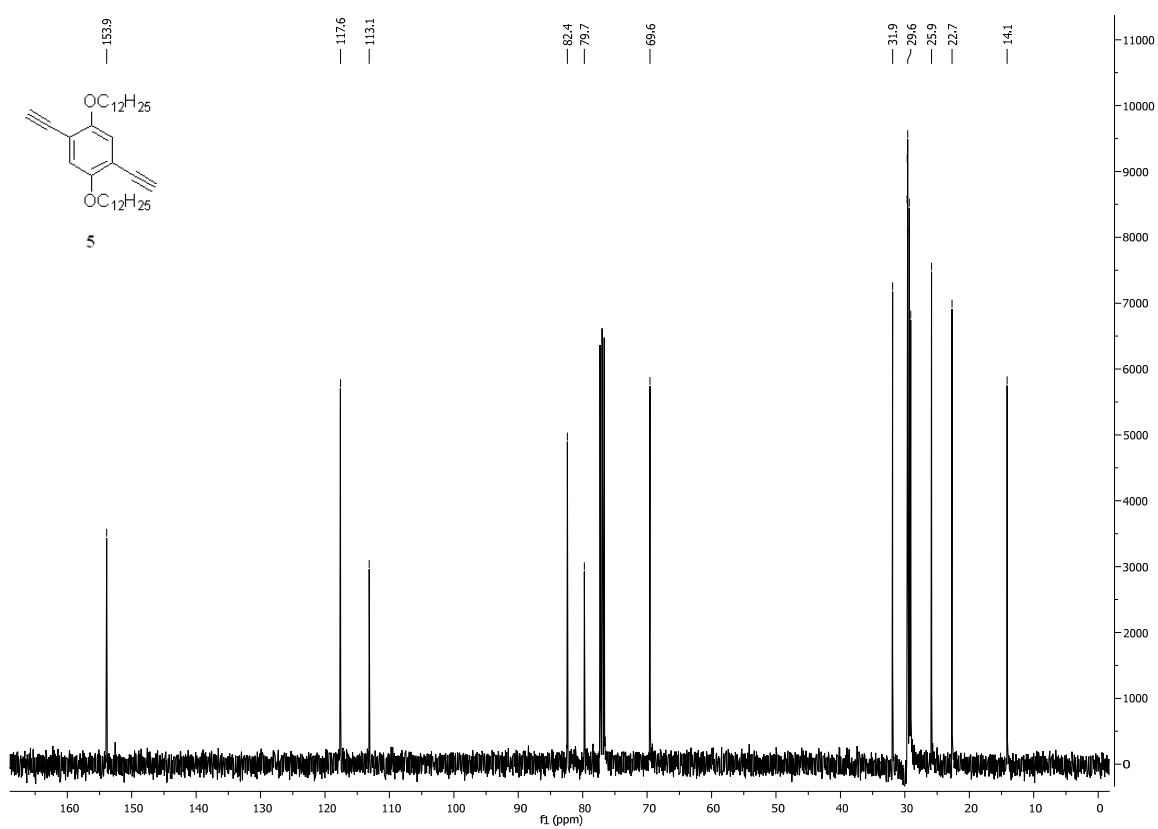
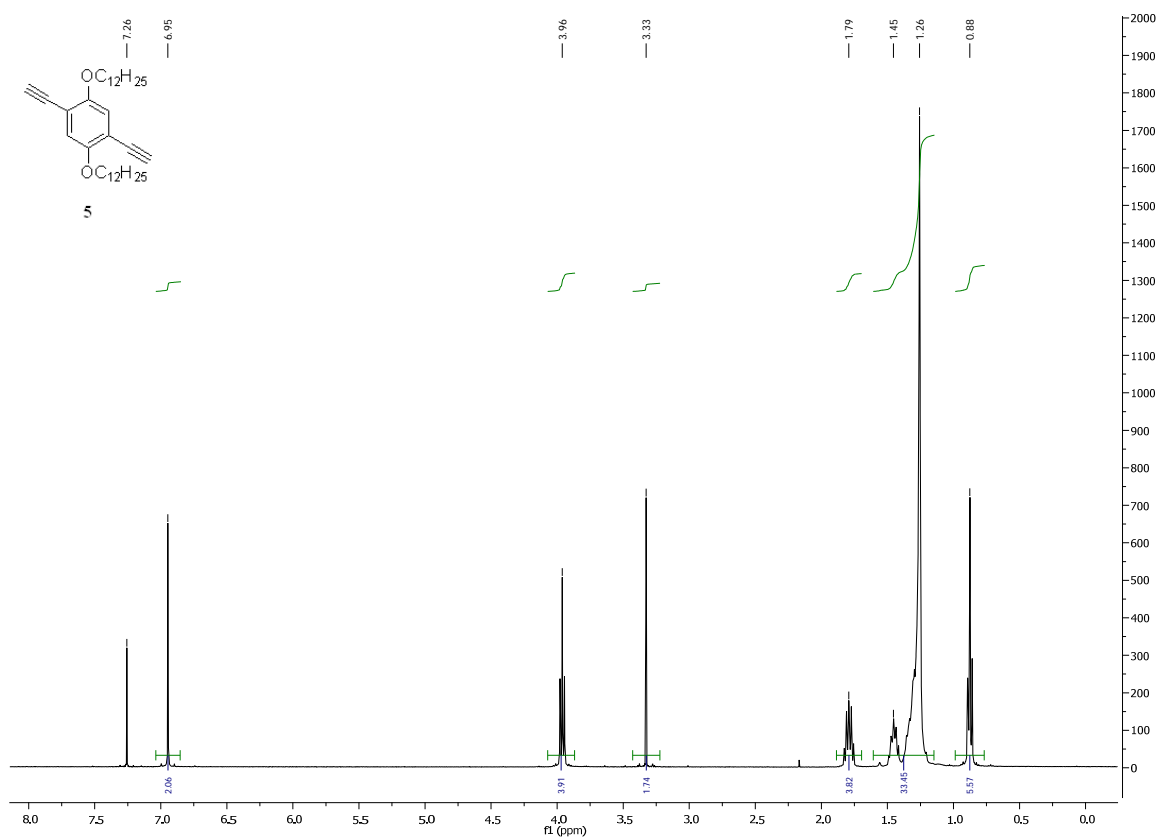


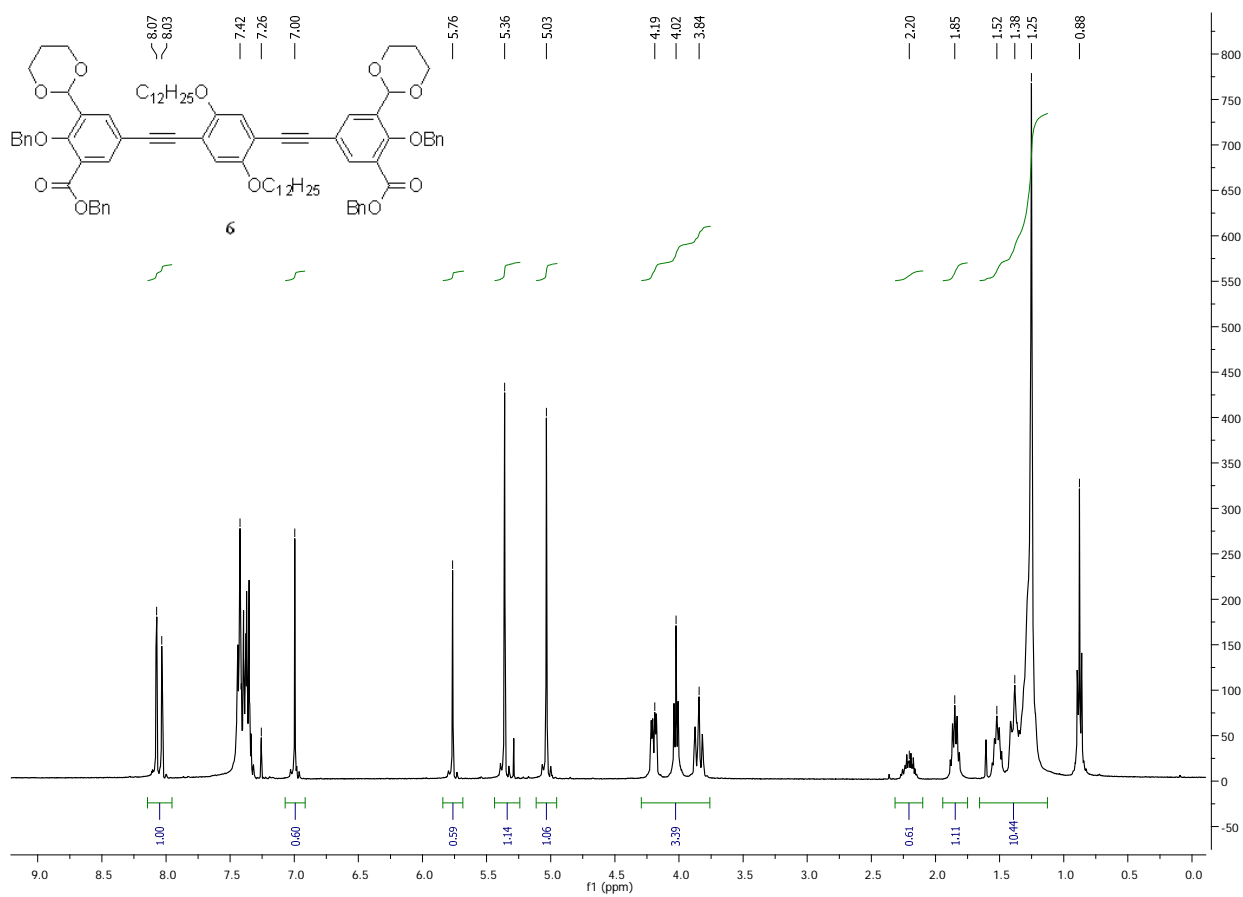
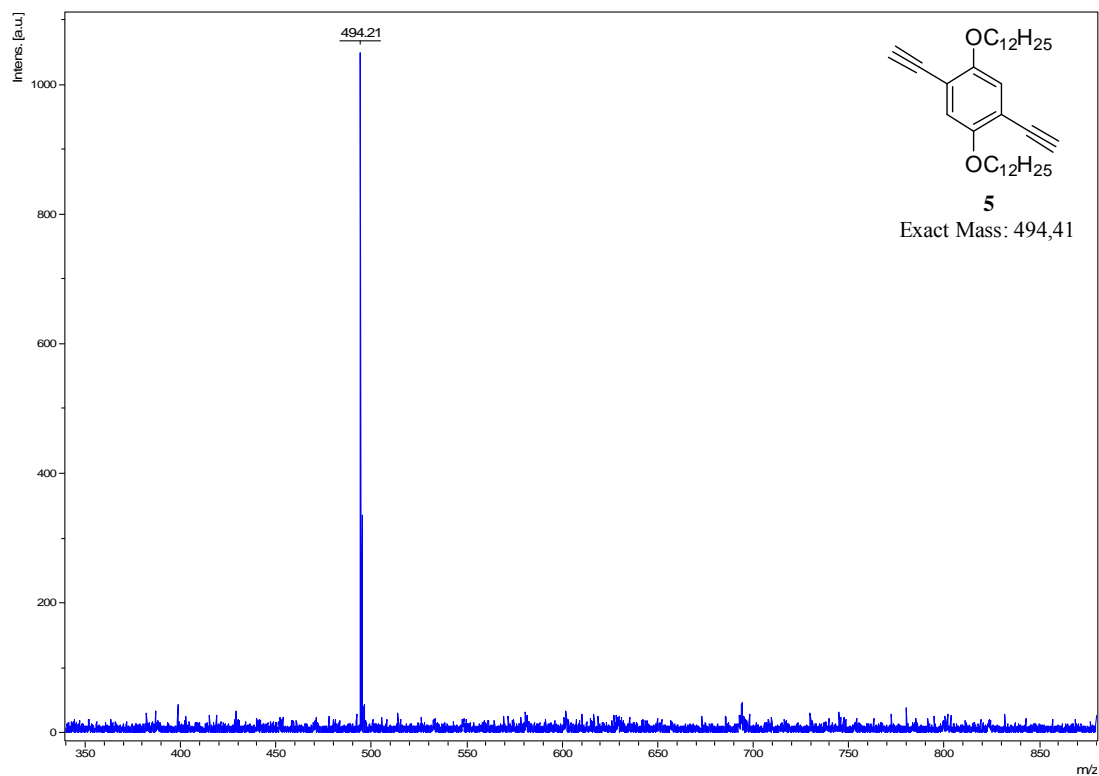


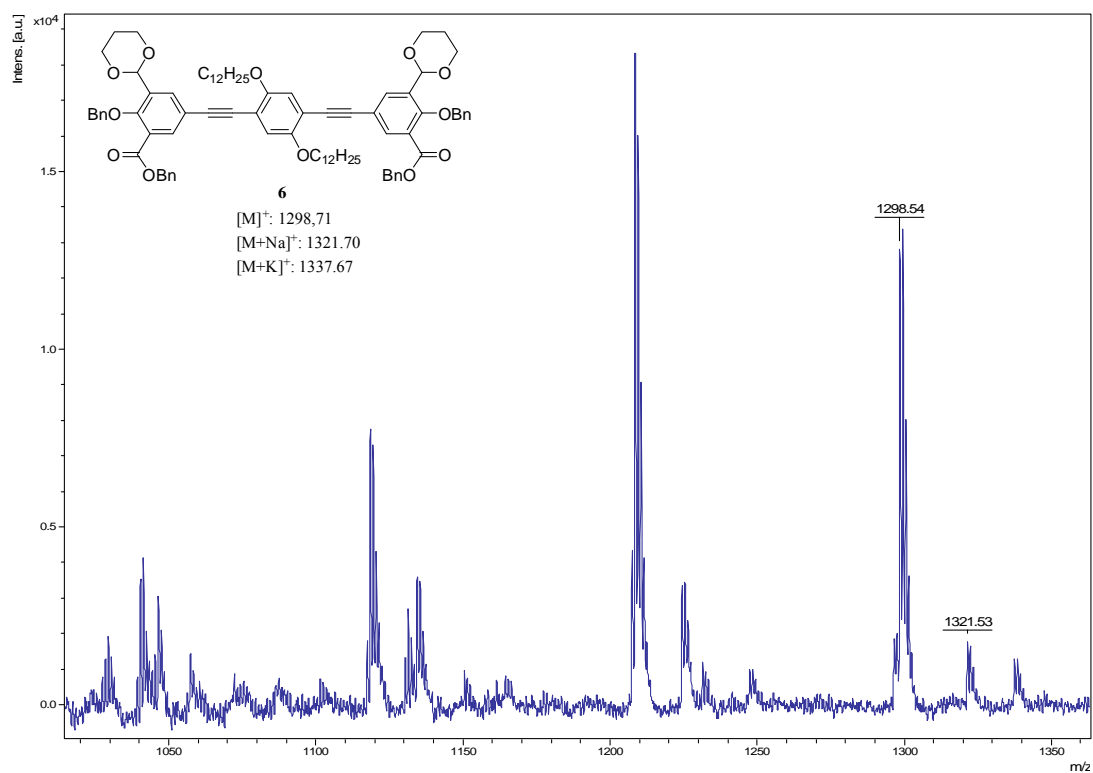
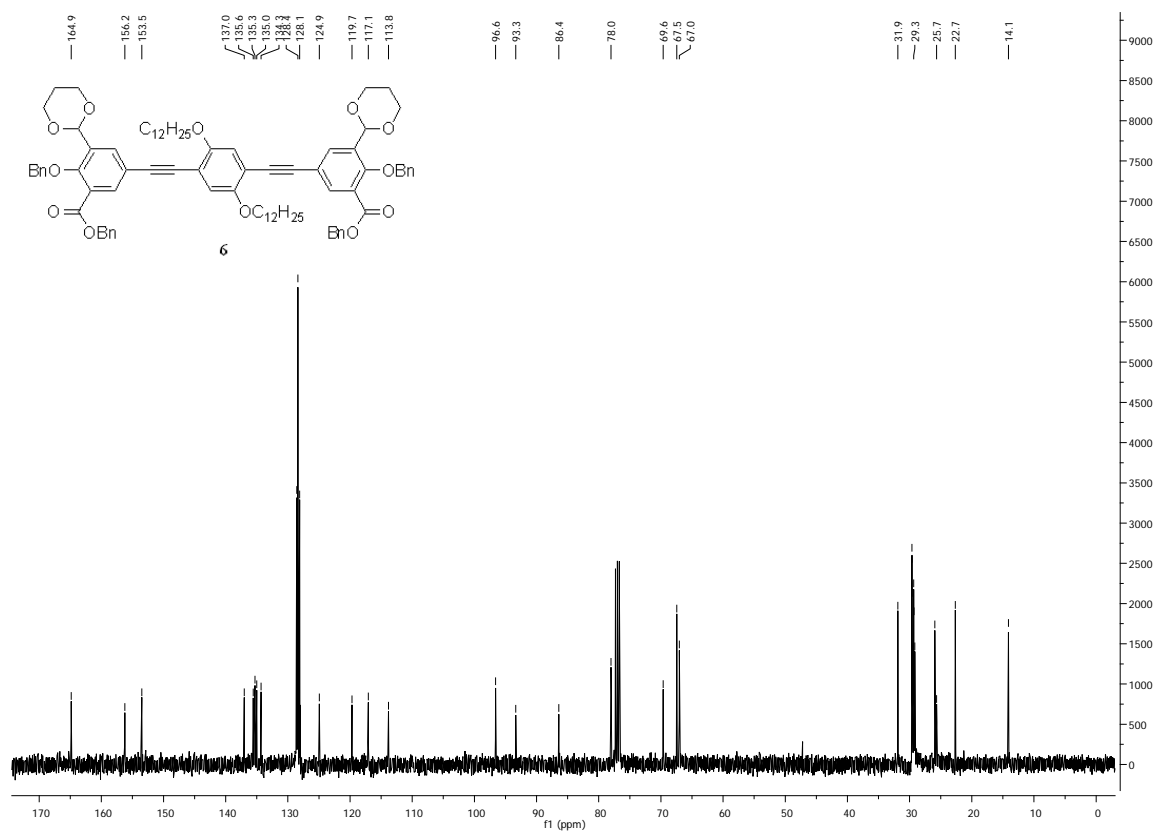


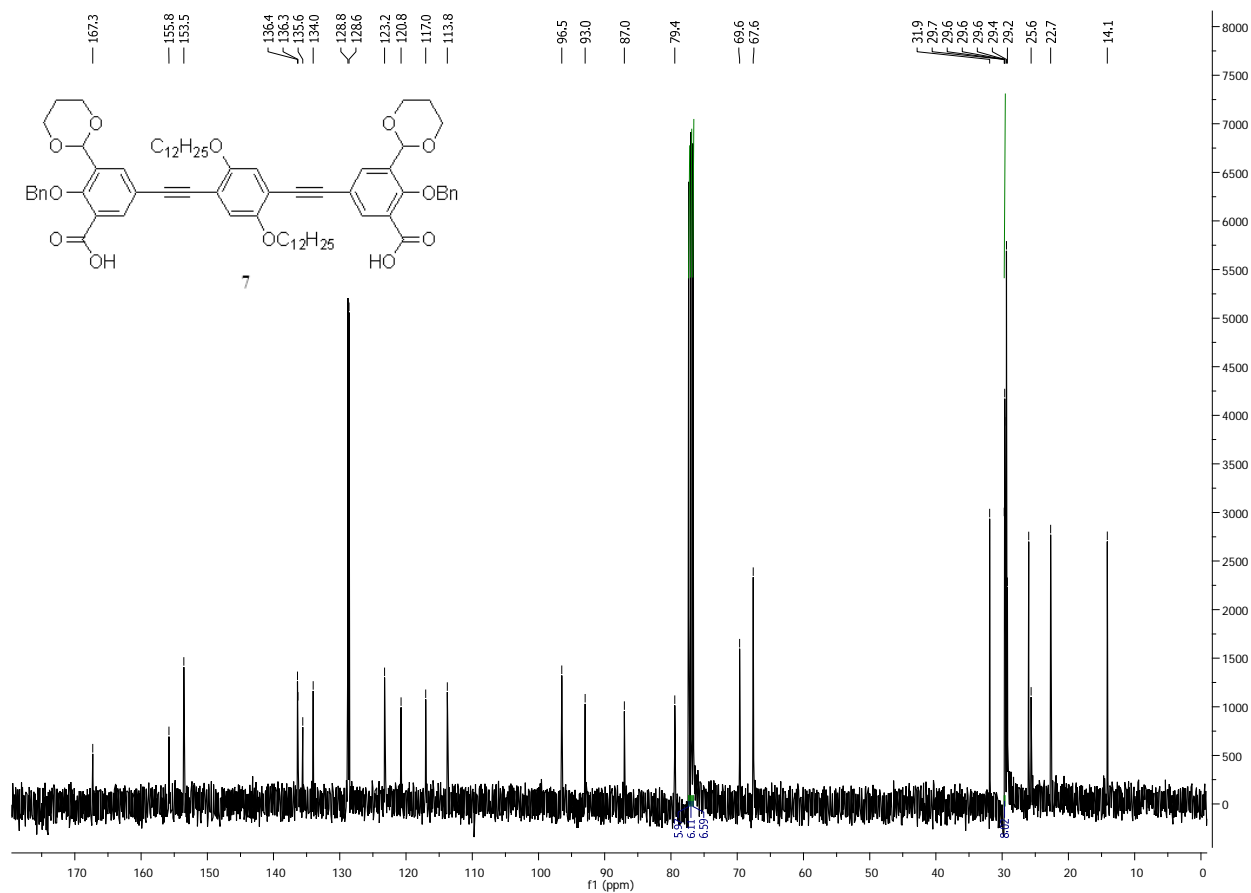
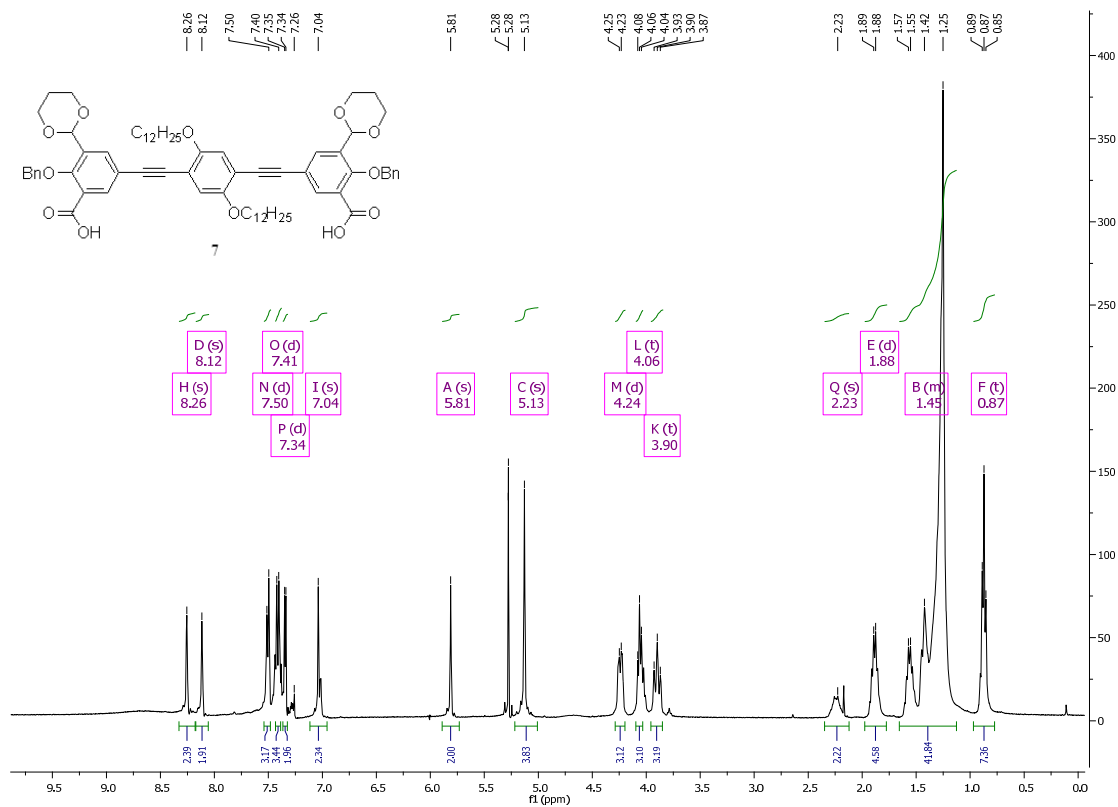


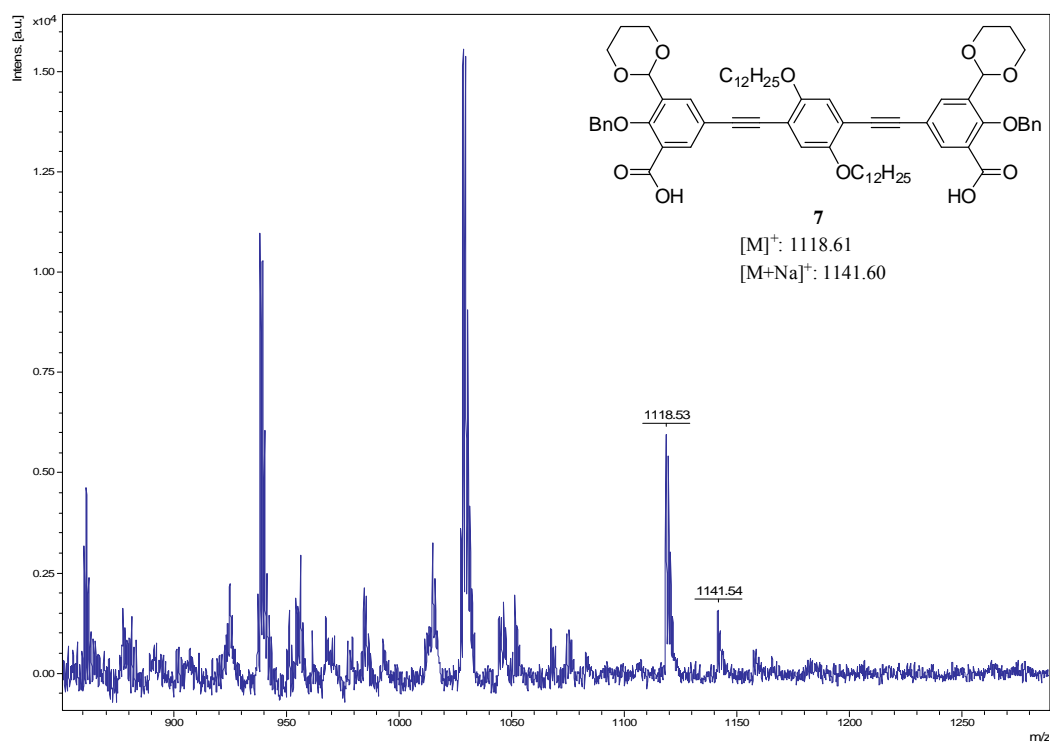
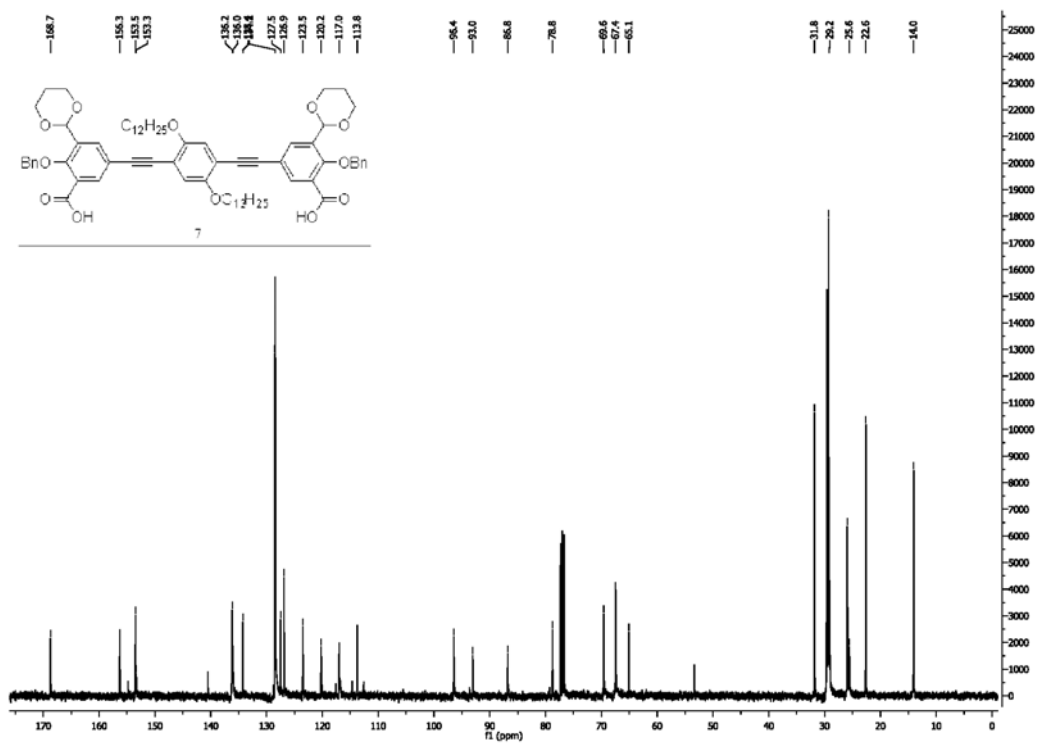


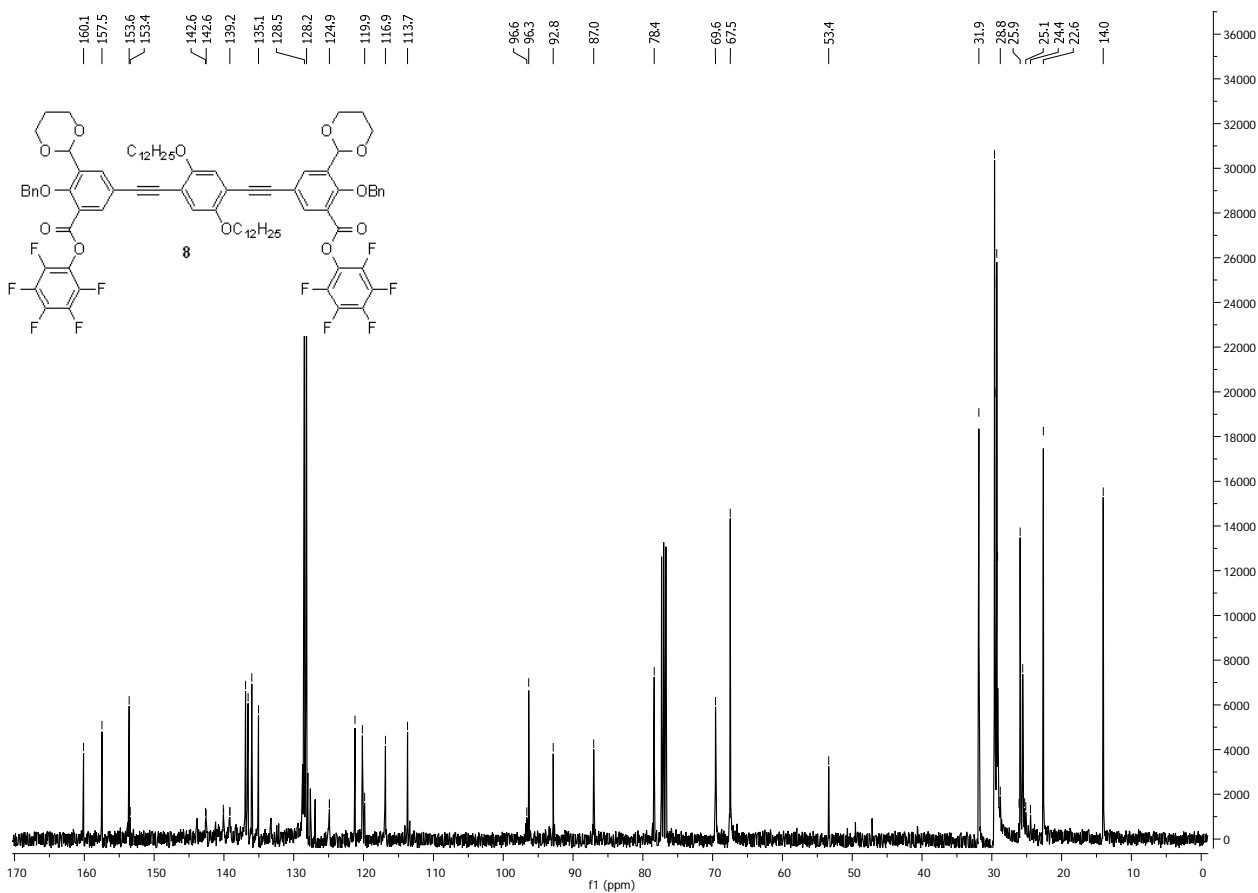
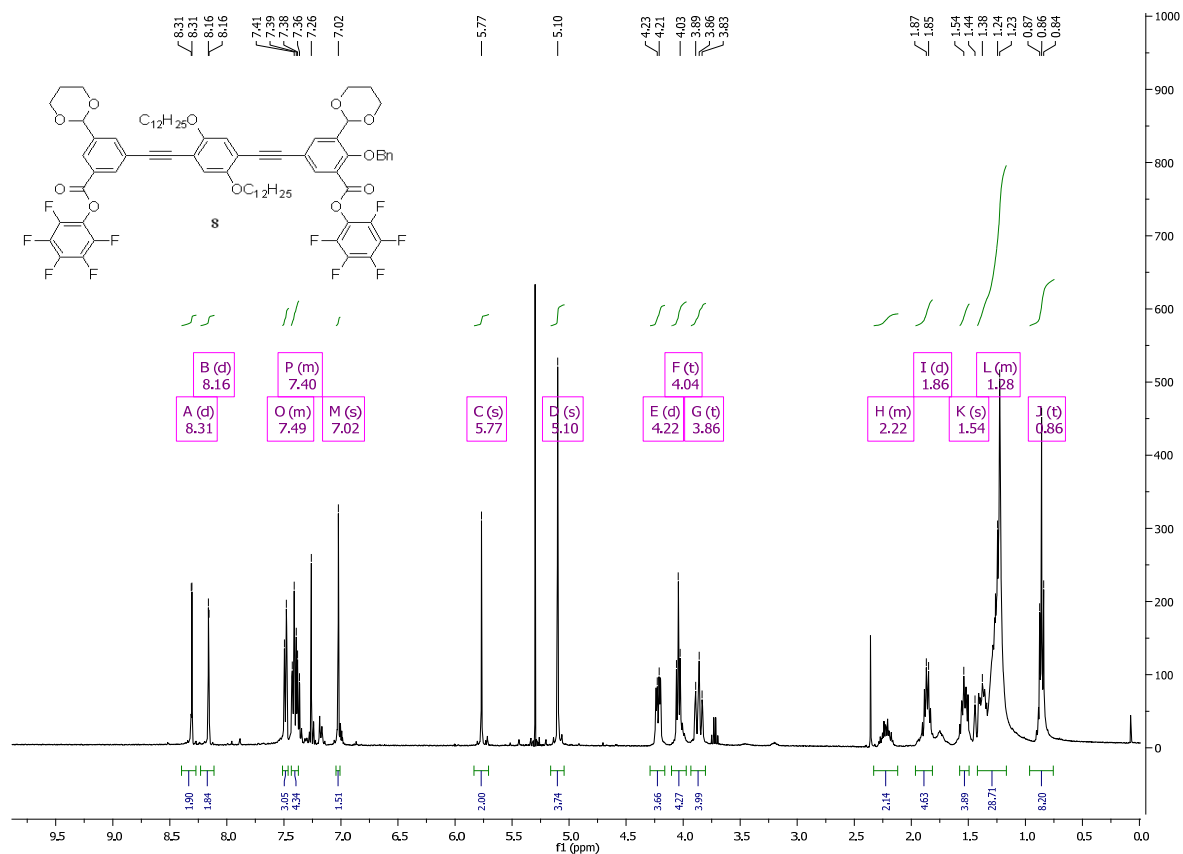


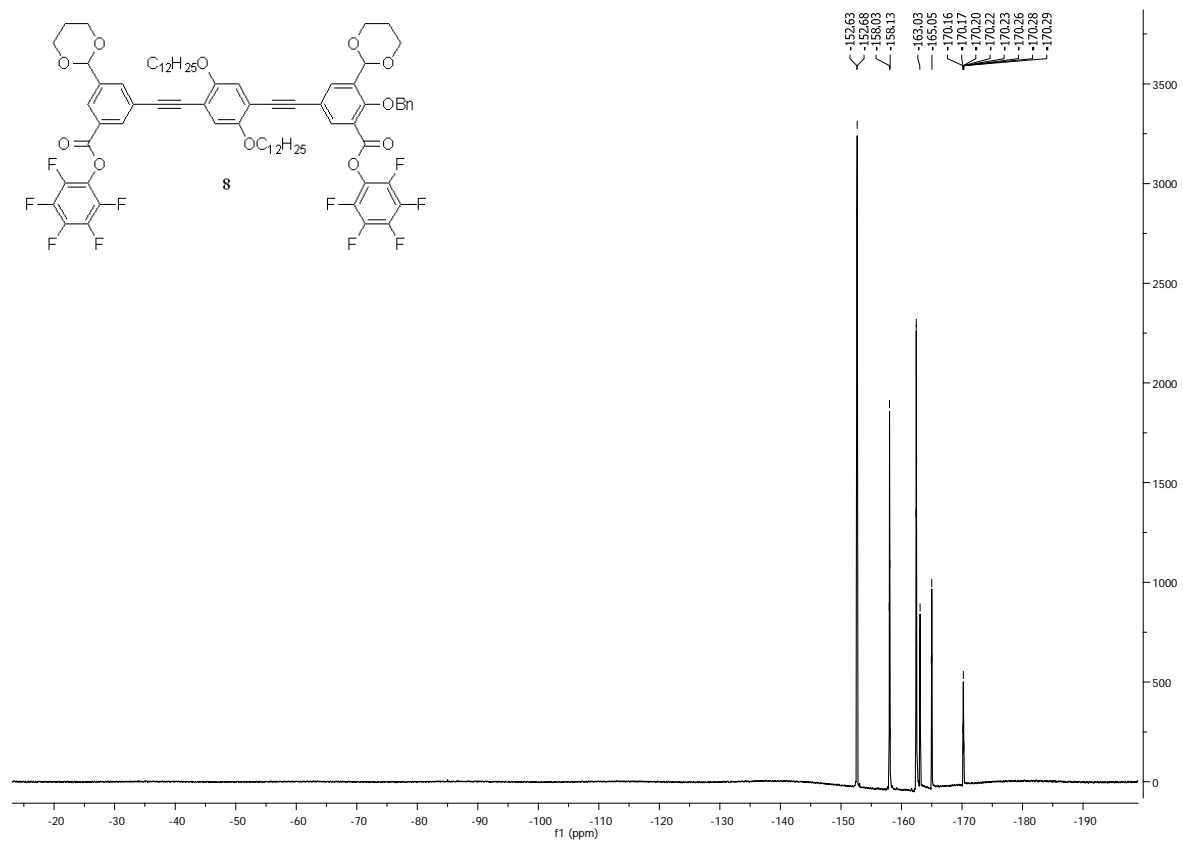


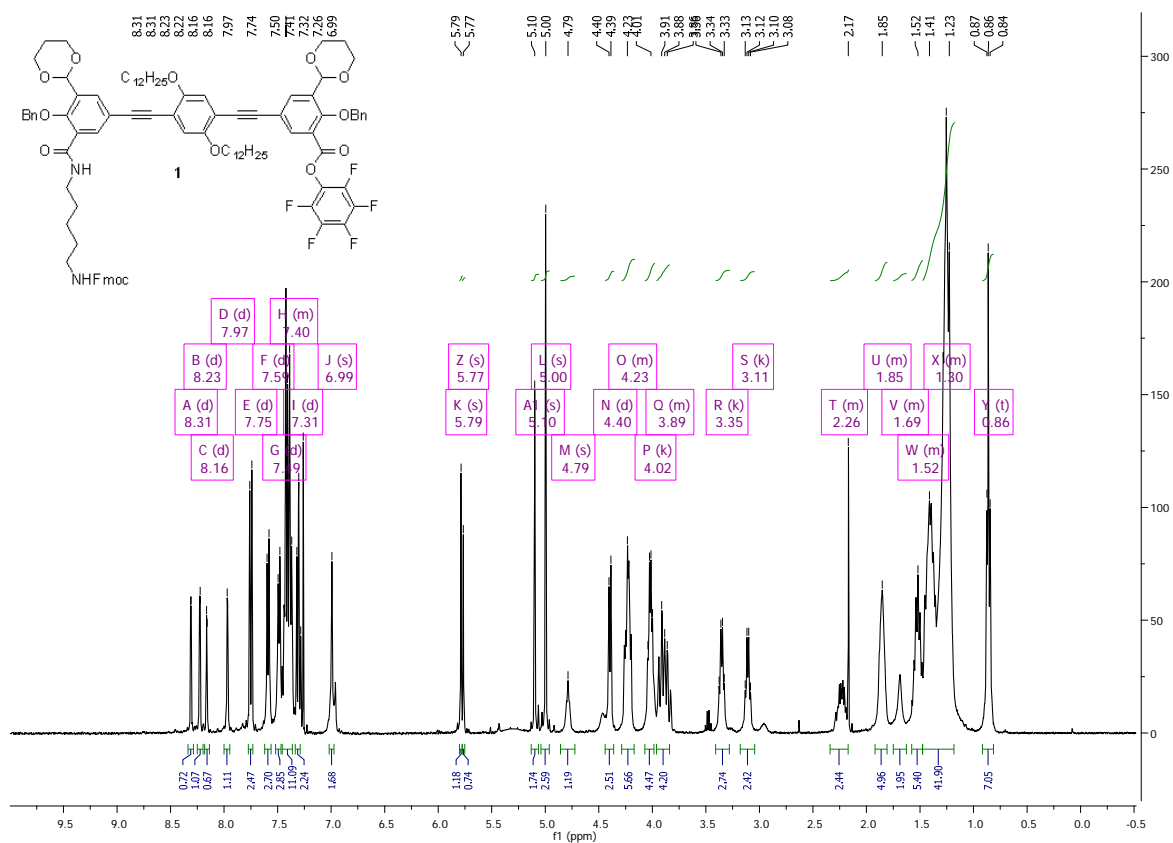
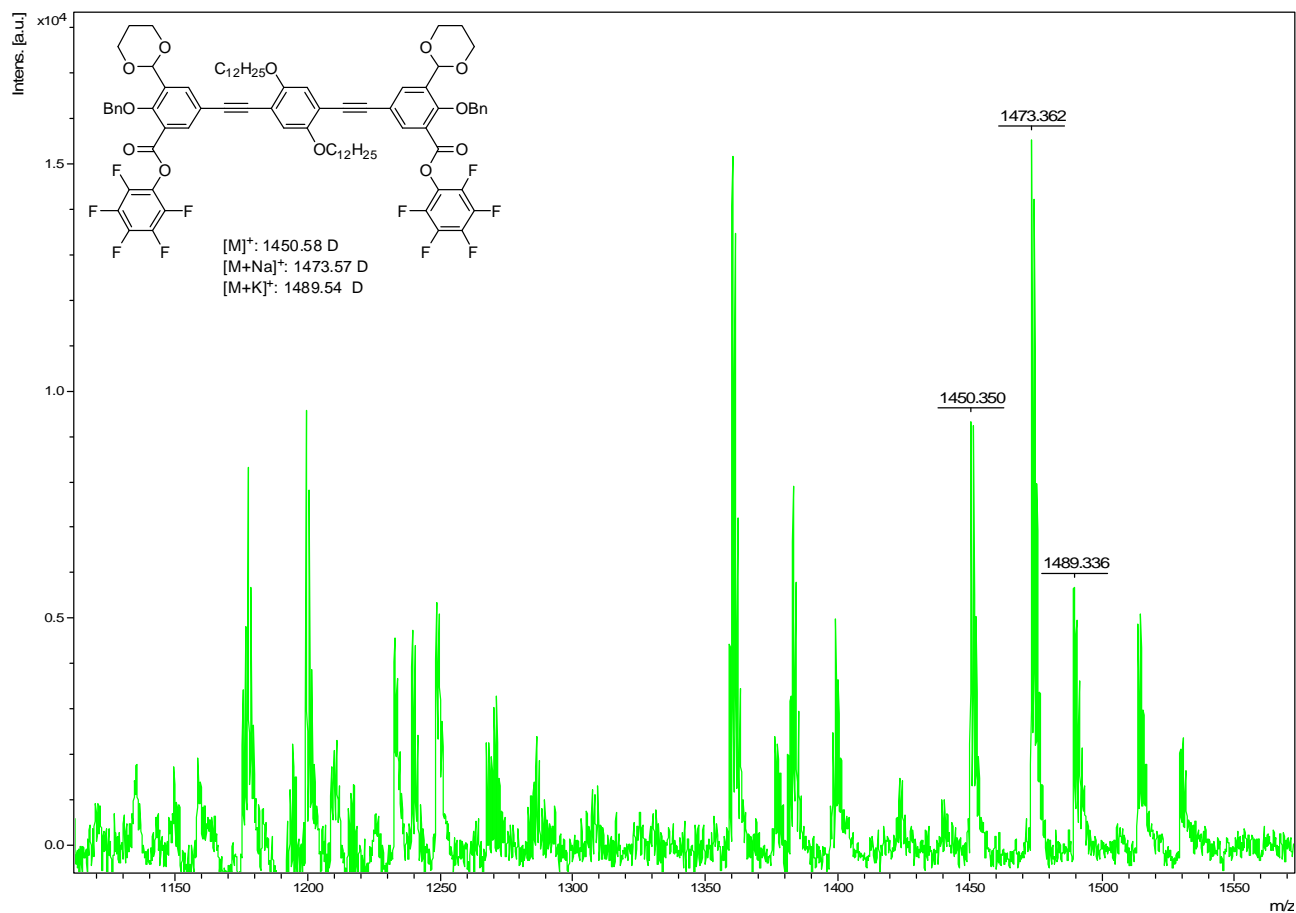


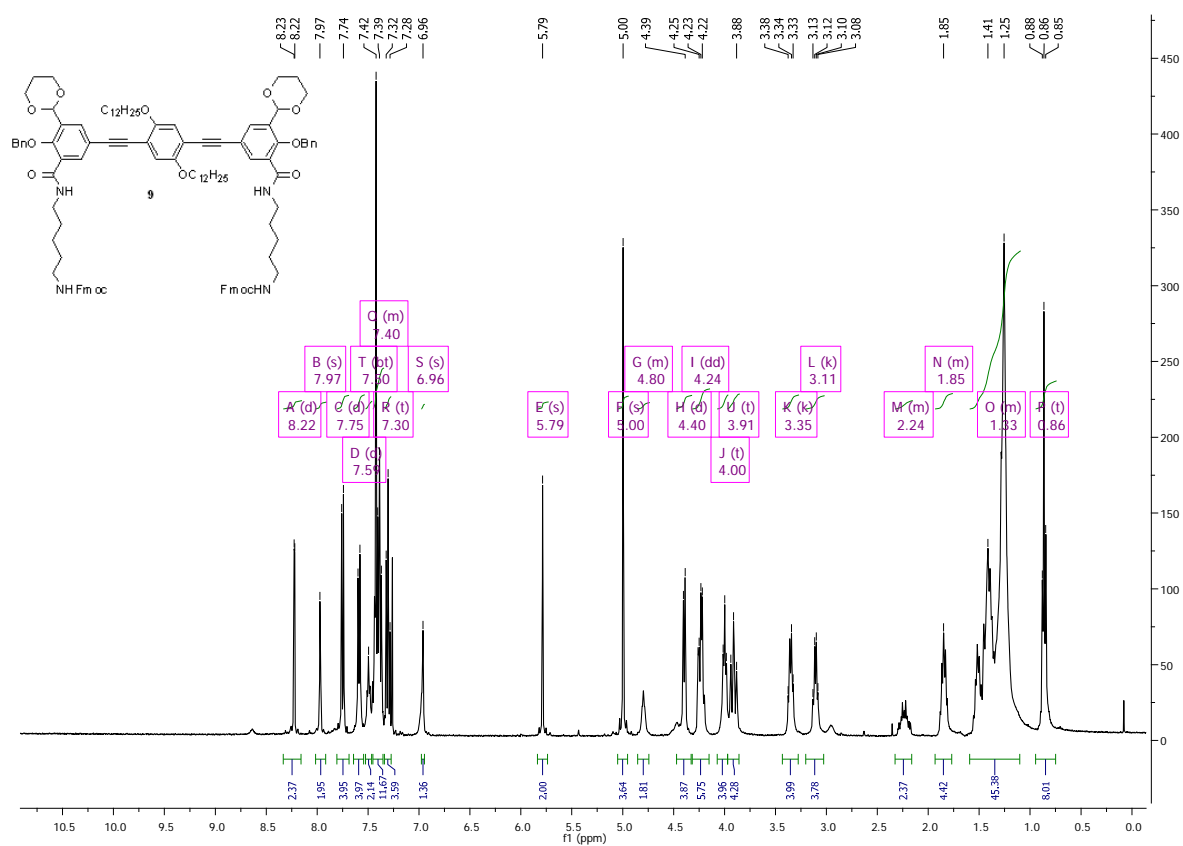
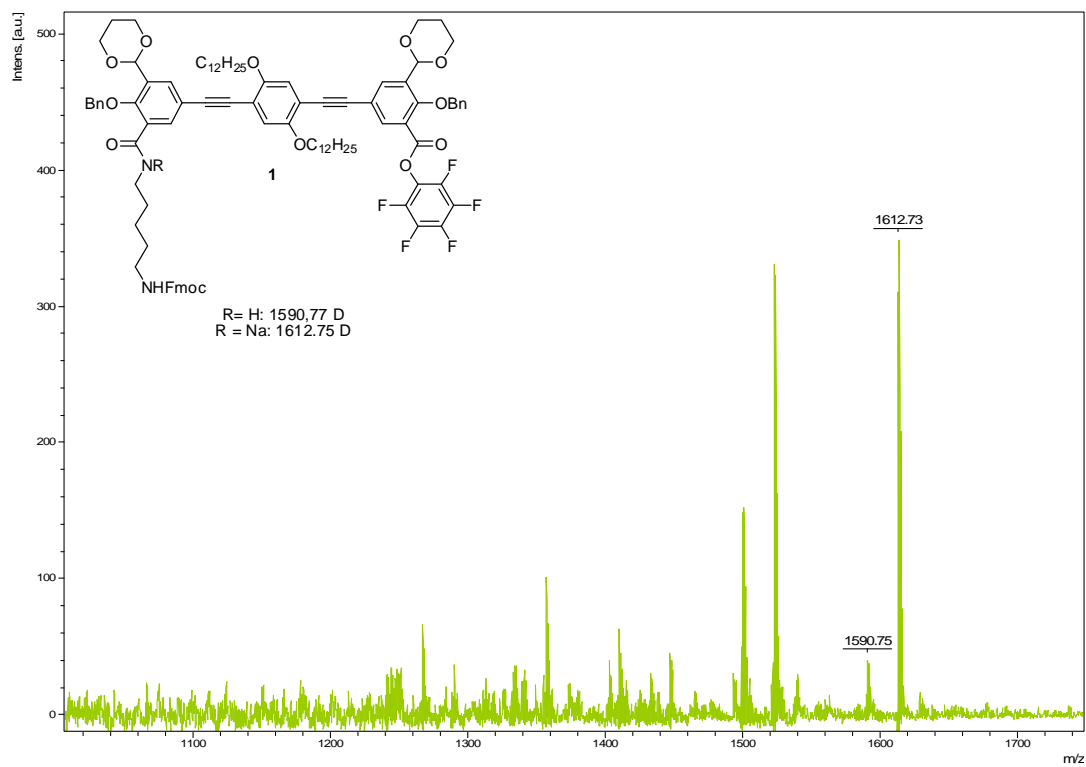


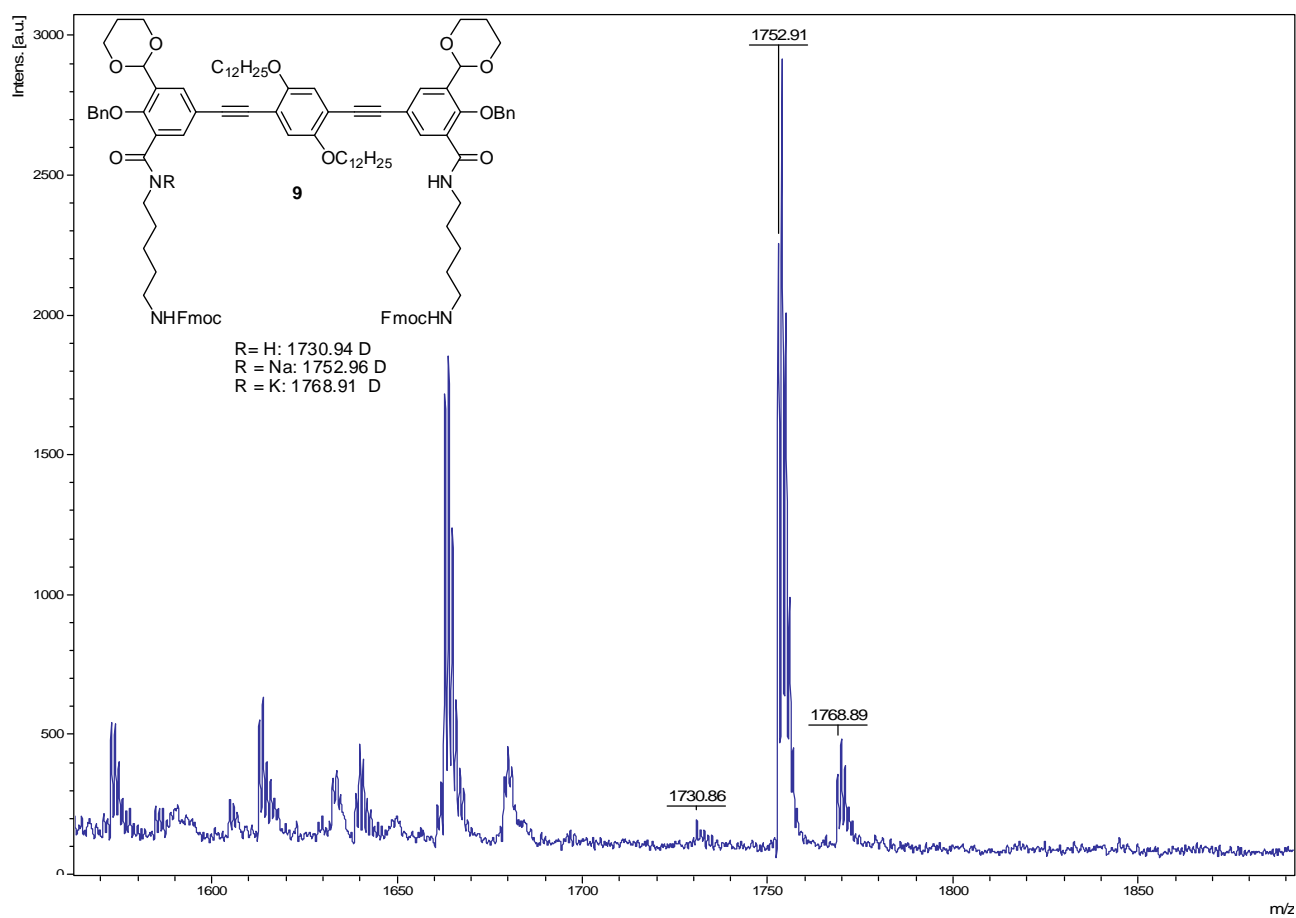
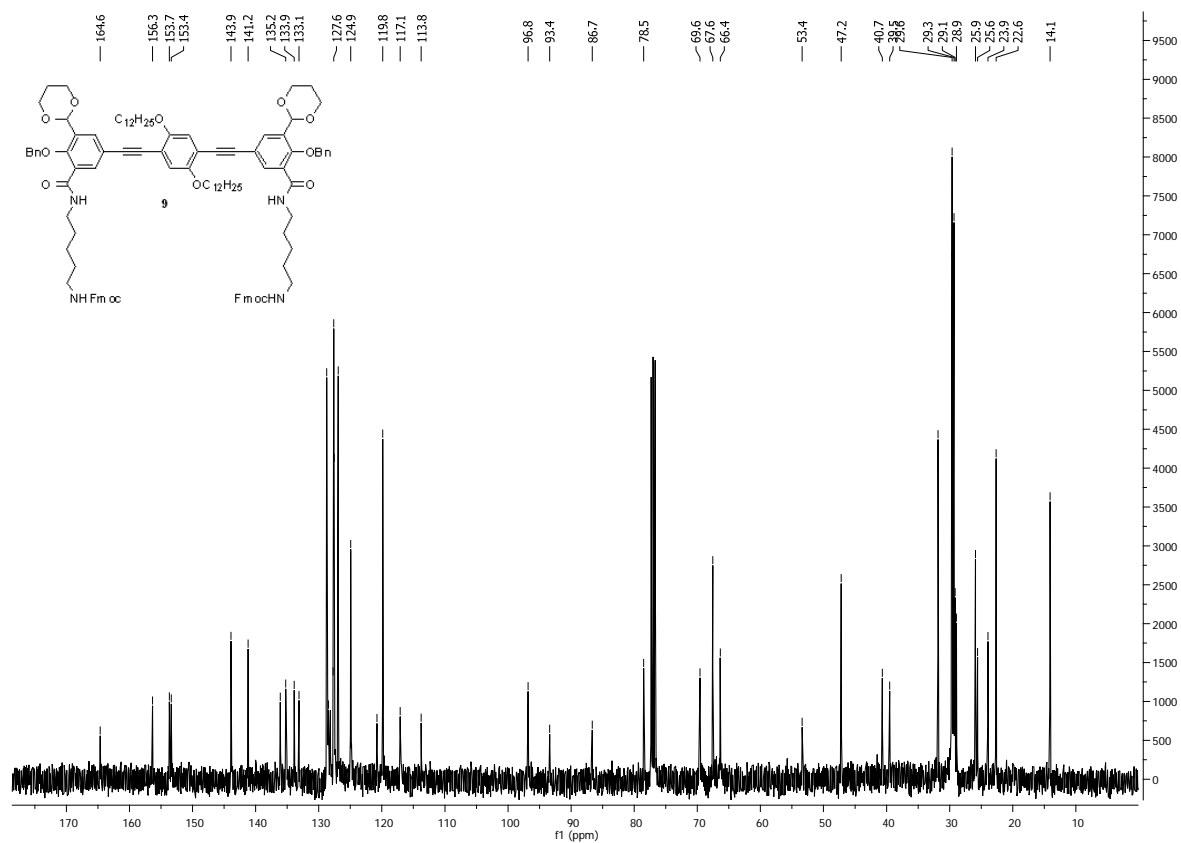


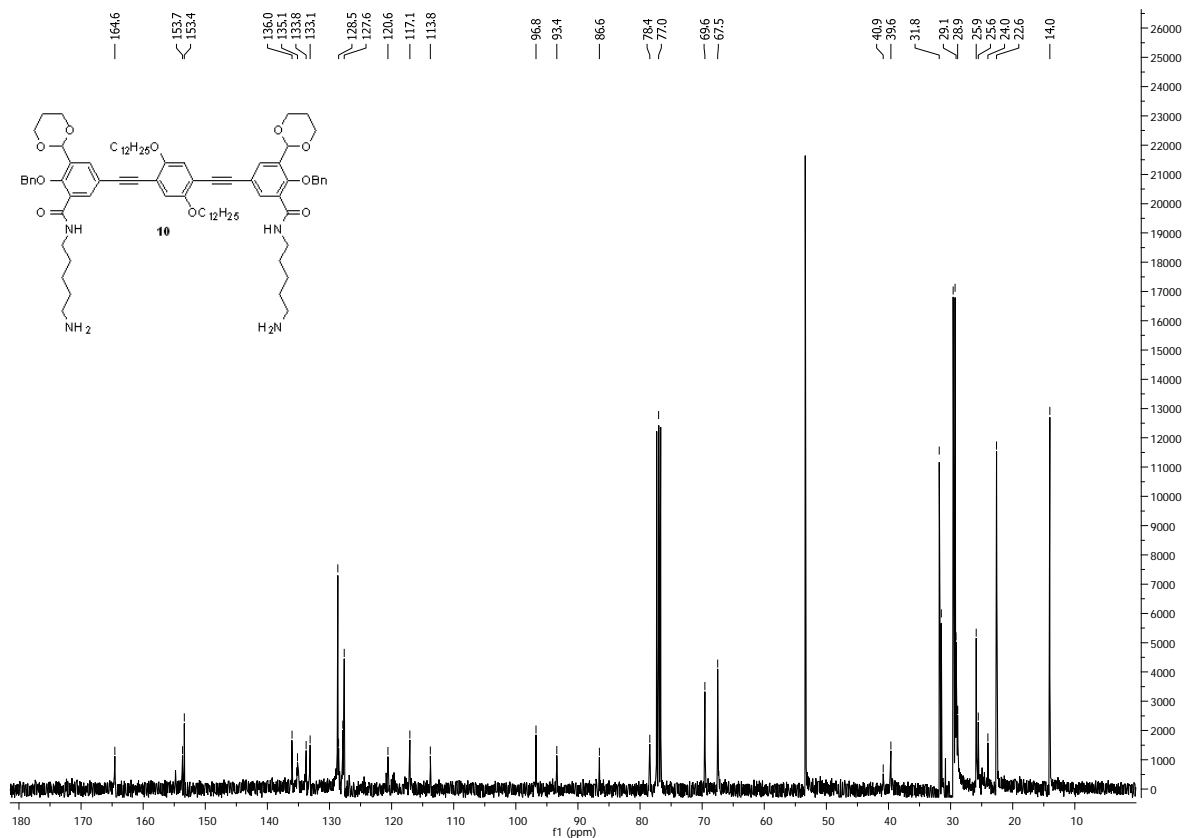
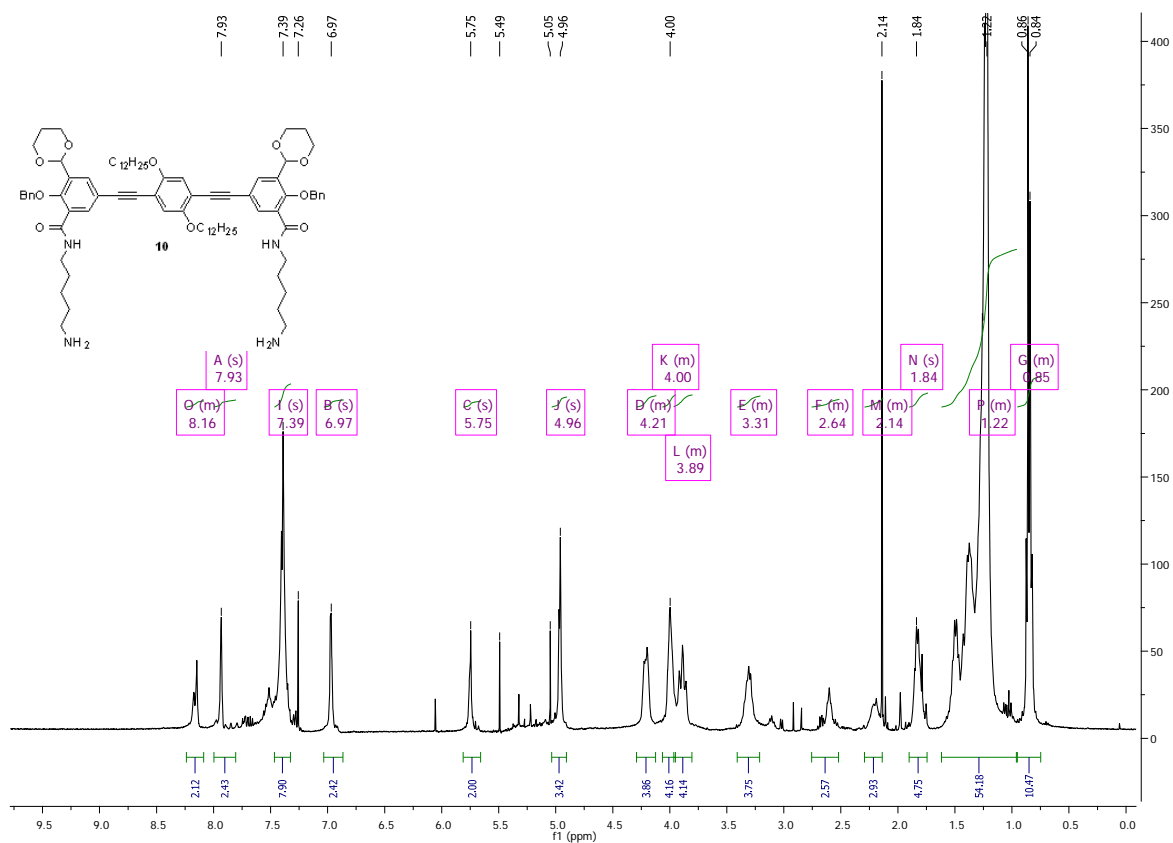


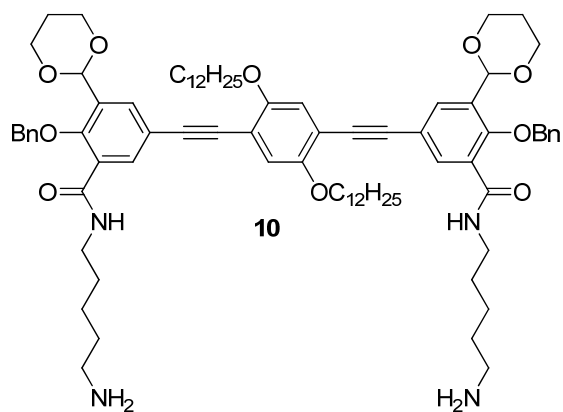




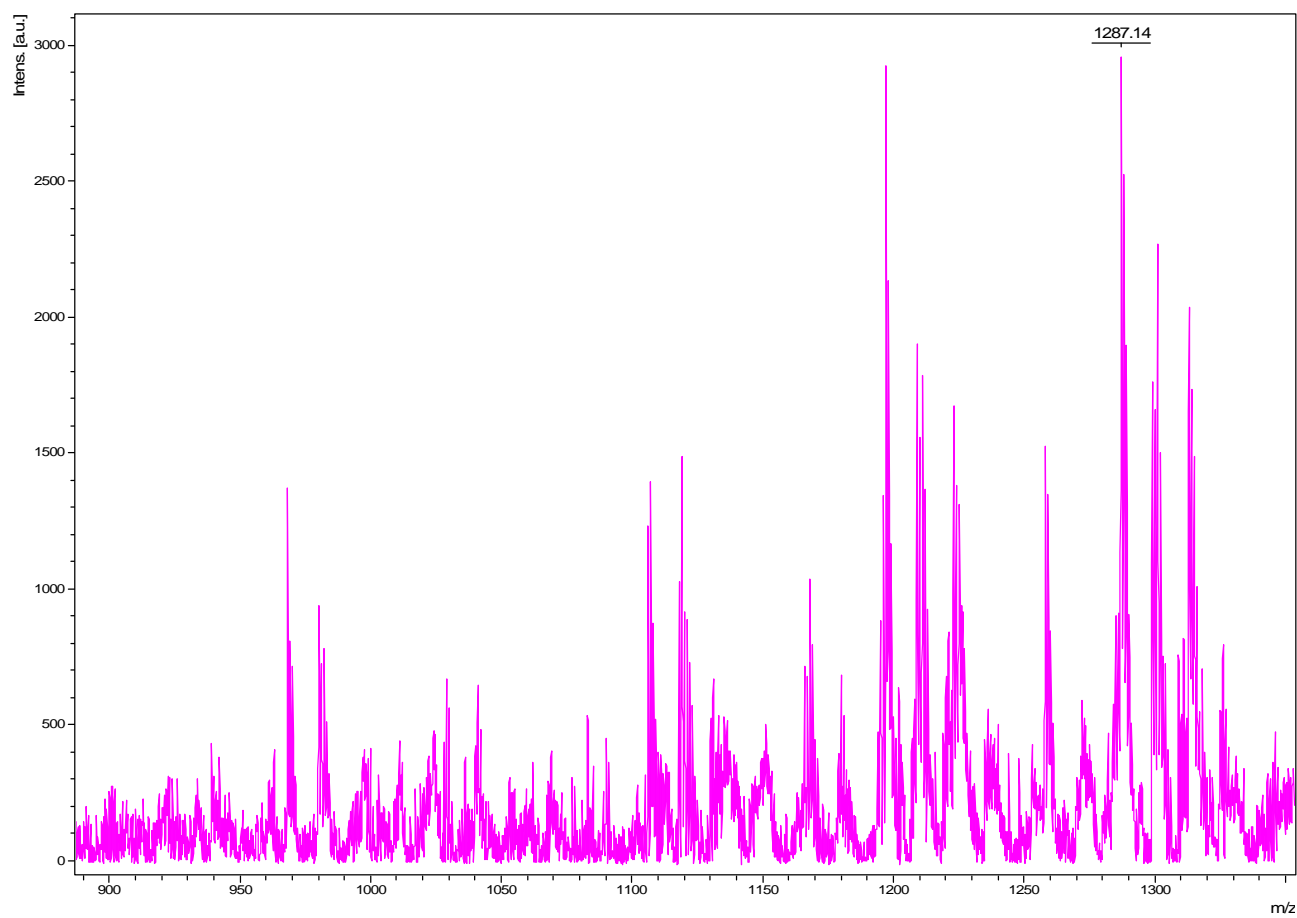


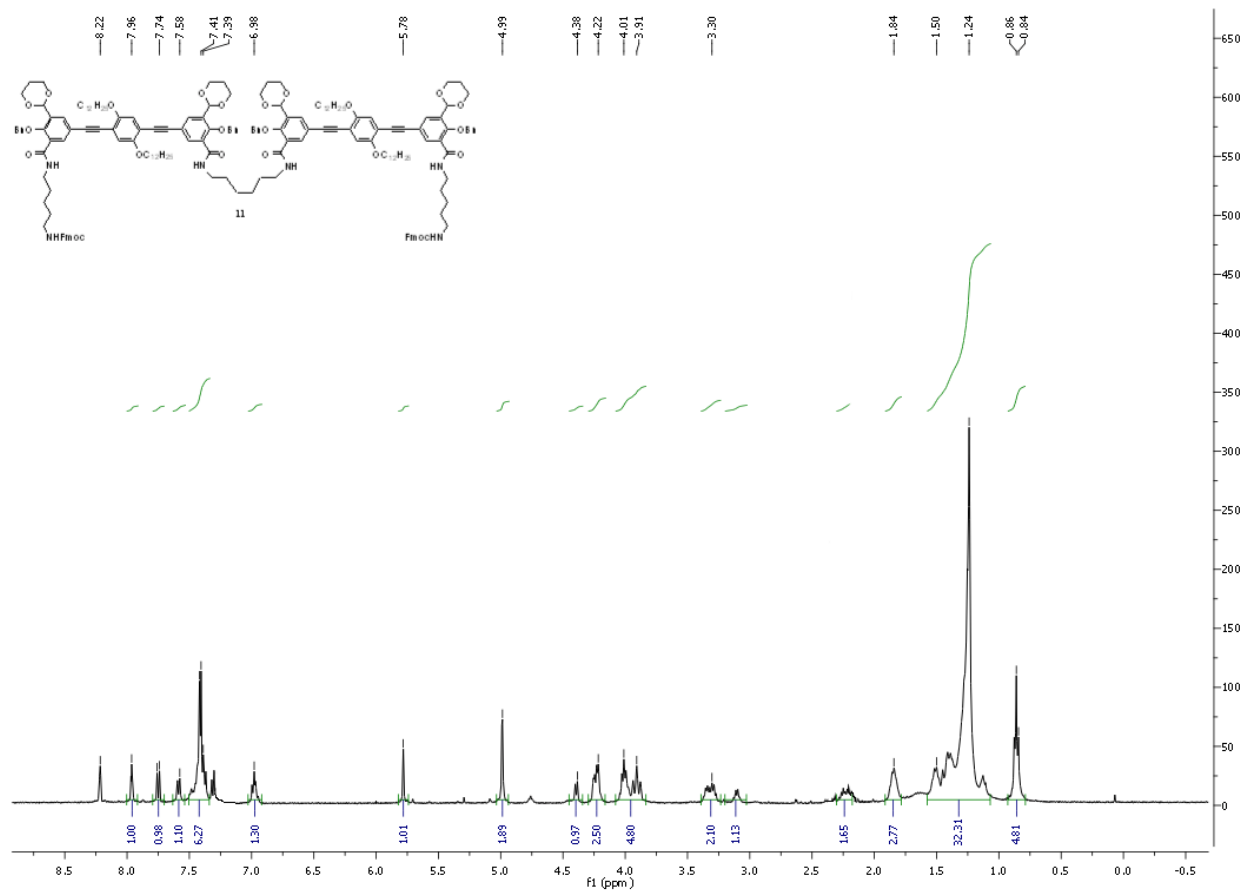


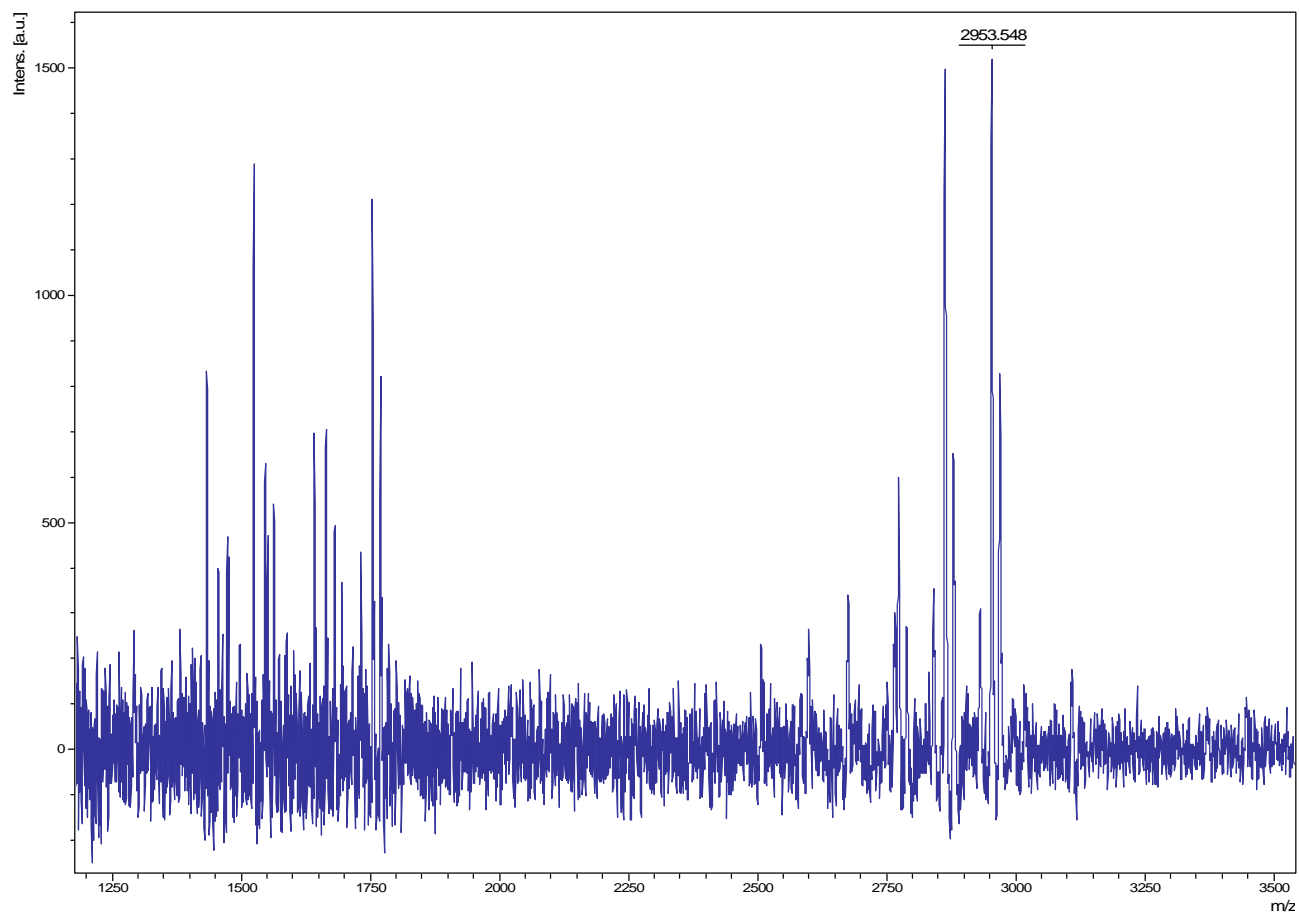


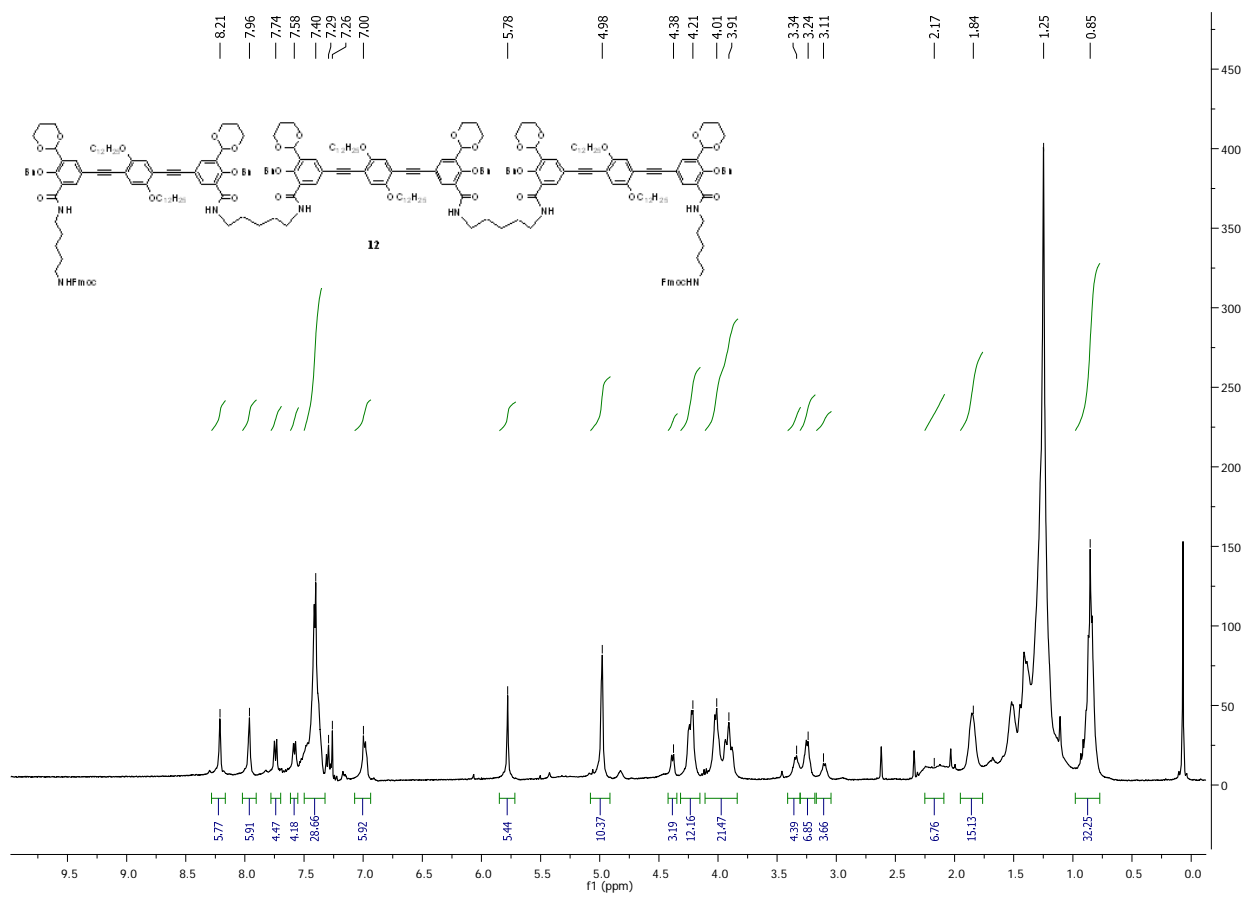


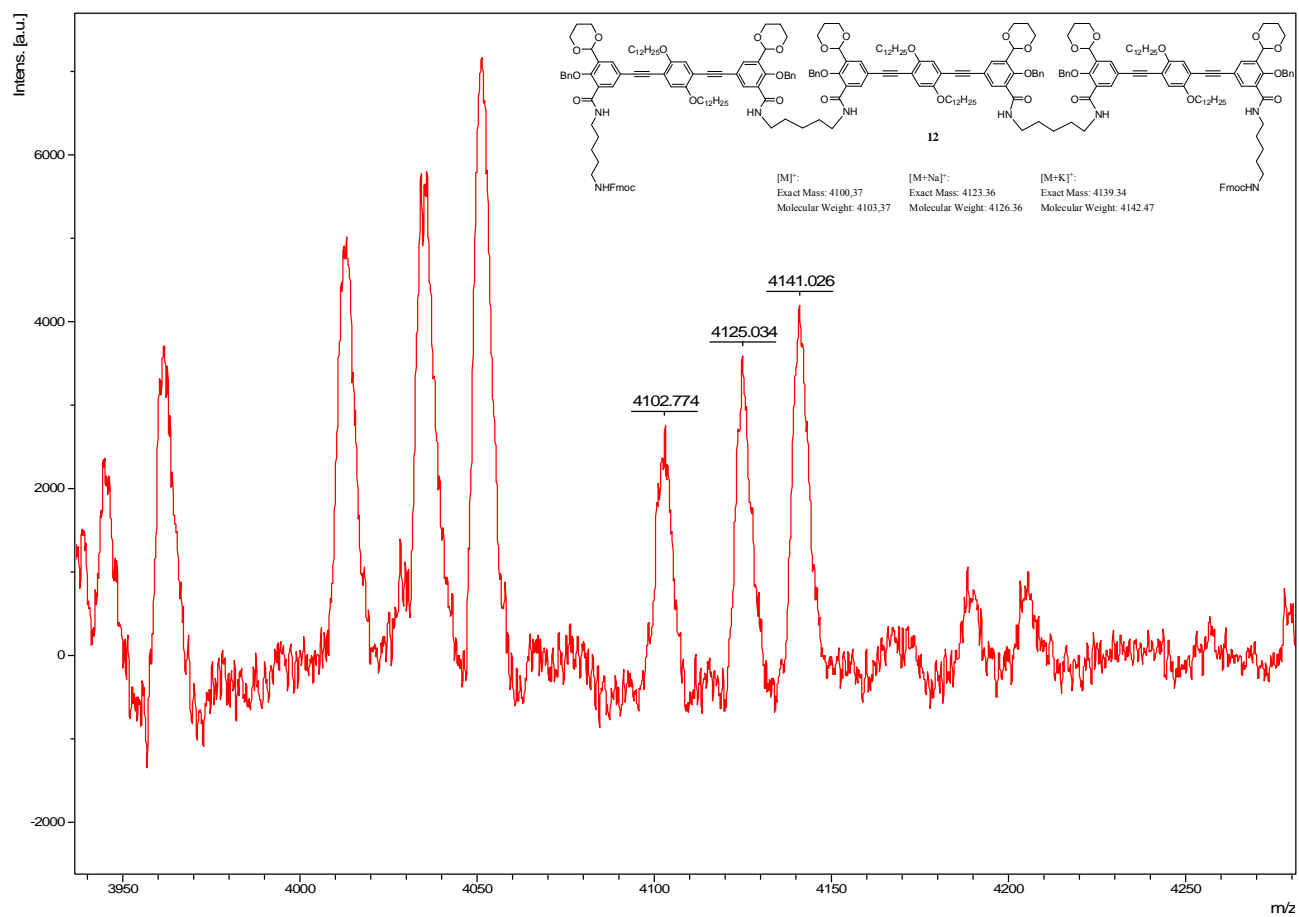
Exact Mass: 1286,82

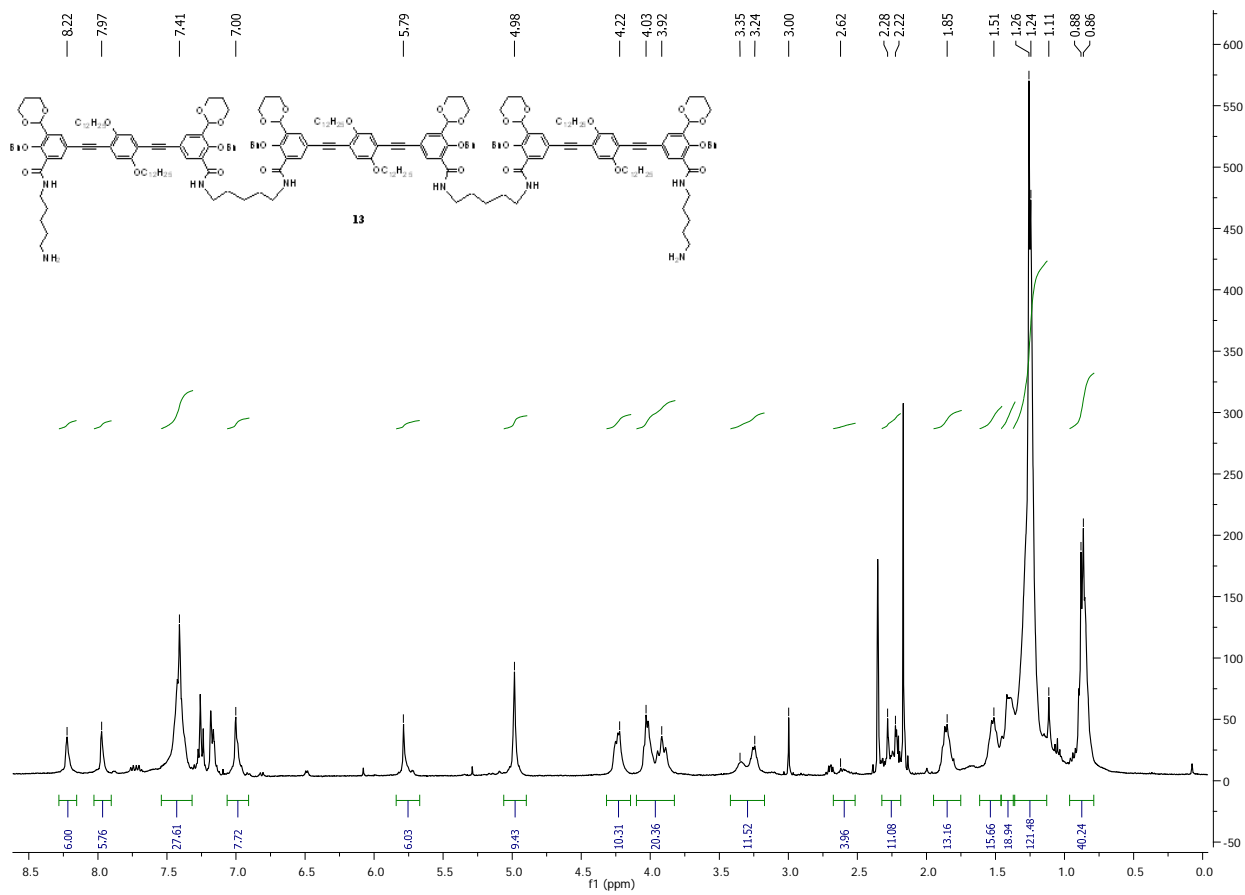


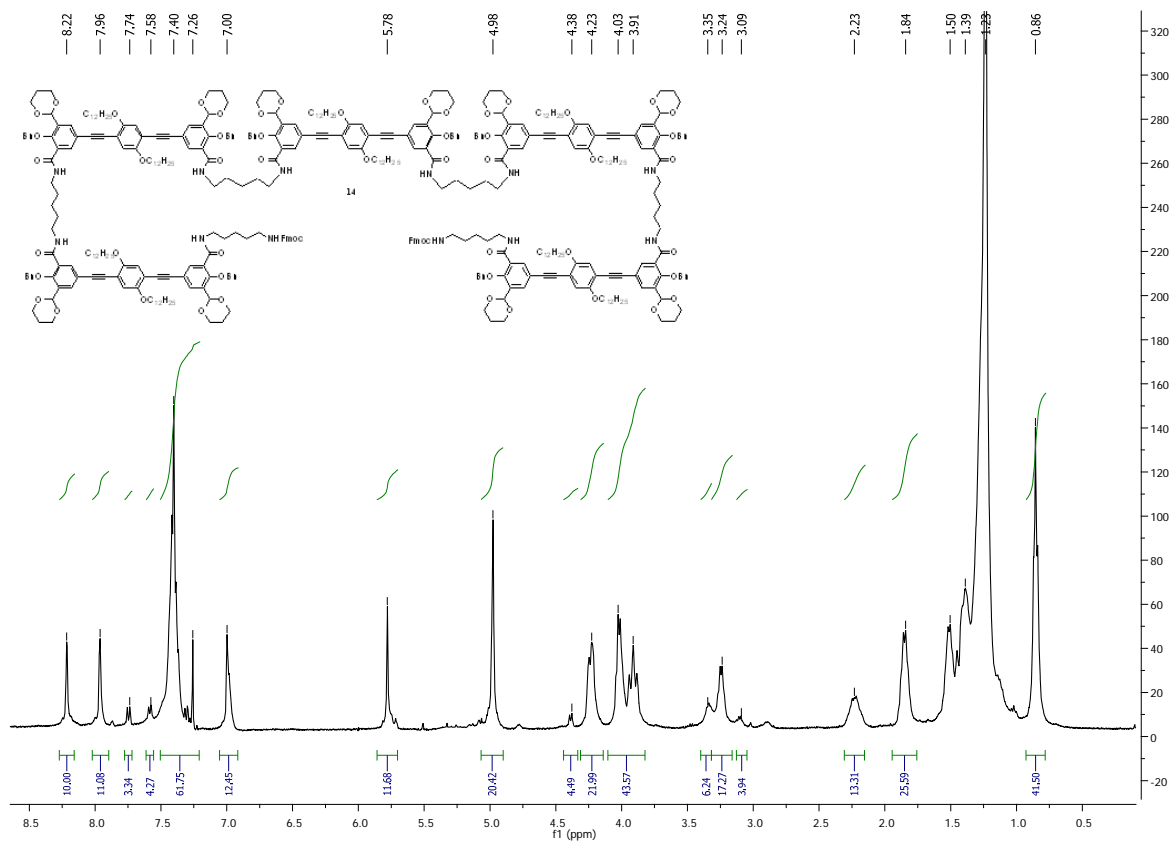












Multiple Spectra Report

