Supporting Information

The Solid Phase Synthesis of *m*-Phenylene Ethynylene Heterosequence Oligomers

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General. Unless otherwise noted, all starting materials were obtained from commercial suppliers and were used without further purification. Merrifield® resin (0.73 mmol/g) was utilized for all solid phase syntheses. The Pd(I) dimer pre-catalyst (*t*-Bu_3P(Pd(μ-Cl)(μ-2-methyl allyl)Pd)P*t*-Bu_3) was prepared according to literature procedures[21] and $Pd(tfp)_4$ (palladium tetrakis(tri 2-furyl)phosphine) catalyst was prepared according to the procedure outlined in the supplemental information section and the palladium sources $Pd_2(dba)_3$ and bis(dimethylallyl) palladium chloride dimer and phosphine source Pd(*t*-$Bu)_3$were obtained from Strem and phosphine source tri-2-furylphosphine was obtained from Lancaster. All solid phase reactions were performed in 10 mL teflon reaction vessels containing an agitator in an Argonaut Quest-210 parallel synthesizer that is run on house nitrogen. Air sensitive reagents and solutions were prepared in a glovebox under an inert atmosphere of argon. All solvents used in the glove box are reagent grade and were degassed with argon and dried over activated (heated under vacuum for 12 h) molecular sieves. All wet solvents were used unpurified from the commercial suppliers. Dry THF was obtained by drying over sodium and benzophenone. Analytical thin layer chromatography (TLC) was performed on KIESELGEL F-254 precoated sheets of silica gel 60, and flash chromatography was carried out with silica gel 60 (230-400 mesh). The ^{1}H NMR spectra were recorded at 500 or 400 MHz and ^{13}C NMR spectra were recorded at 125 or 100 MHz. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal reference. Chloroform (δ 7.26 for ^{1}H, δ 77.0 for ^{13}C) was used as an internal reference for chloroform-d. Coupling constants, *J*, are reported in Hertz (Hz). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet. Field desorption (FD) mass spectra were obtained with 70-VSE spectrometer operating a 70 eV. Low resolution matrix assisted laser desorption ionization (MALDI) mass spectra were obtained using a Voyager-DE STR spectrometer using a 2-(4-hydroxyphenylazo) benzoic acid (HABA) matrix. Analytical gel permeation chromatography (GPC) was performed using an HPLC pump, a triple detector array, and a series of three columns (7.8 x 300 mm) in a solution of 90% THF and 10% MeOH, with 1% triethylamine at 30°C. The GPC was calibrated with monodisperse polystyrene beads. Preparatory Gel Permeation Chromatography analyses were performed with an HPLC pump, a 410 Differential Diffractometer, and a series of three columns (19 x 300 mm, Ultrastyragel 10^4 Å THF, 10^2 Å THF, and 500 Å THF) in a solution of THF (99.9% +, HPLC grade), inhibitor free. High Pressure Liquid Chromatography (HPLC) analysis was performed with a solvent delivery system, using a 250 x 4.6 mm 100-5 Si silica column and a UV detector operating at 290 nm.

Section 1: Detailed Procedure of Solid Phase Method

The preparation of a H-series hexamer is used as an example:

(1) A 10 mL Teflon reaction vessel[1] was charged with 300 mg[2] of triazene loaded resin and an agitator and loaded into a Quest 210 Parallel Synthesizer and flushed with nitrogen[3] while catalyst solutions were prepared in the glove box.

(2) 2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-ethynyl-5-[(triisopropylsilanyl)-ethynyl] –benzoate[4] (2 equiv, 73.74 mg) was weighed into a 25 mL scintillation

vial. This monomer along with three gas tight syringes, a disposable syringe for DMF and HN-*i*Pr_2 and three silicone stoppers were then taken into the glove box.

(3) Three solutions were then prepared, these solutions were made slightly more concentrated than the catalyst solutions used for subsequent steps due to the sluggishness of the first reaction. First Pd(I) dimer (20 mol%, 5.52 mg) was dissolved in DMF (1 mL). A Scientific Industries Vortex-Genie 2 (inside glove box) was utilized to adequately dissolve Pd(I) in DMF. This solution was then placed into a 2.5 mL gas tight syringe. The needle was then plunged into a silicone stopper in order to protect it from air when removed from the box.

(4) $ZnBr_2$ (4 quiv, 70.25 mg) was weighed into a scintillation vial. To this was added HN-*i*Pr_2 (45 equiv, 0.49 mL) and DMF (1 mL). This solution was then mixed using the agitator and placed in a gas tight syringe and finally protected by a silicone stopper.

(5) Lastly, DMF (1 mL) was added to 2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-ethynyl-5-[(triisopropylsilanyl)-ethynyl] –benzoate[4], agitated, placed in a syringe and protected by a silicone stopper.

(6) These solutions were then removed from the glove box. The reaction vessel containing the resin was closed off and placed under nitrogen.[5] The solutions were added to the resin in the following order: Pd(I), $ZnBr_2$/HN-*i*Pr_2 and finally 2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-ethynyl-5-[(triisopropylsilanyl)-ethynyl] –benzoate[4]. The agitation rate of the synthesizer was set to mix every: 0.9 sec, up stroke: 0.3 sec, % upwards: 30% and allowed to react for 8-12 h.

(7) The next day the reaction vessel was drained by opening the valve at the bottom of the reaction vessel and setting the synthesizer to drain gas and vent. Upon drainage of the contents the reaction vessel was again sealed off and 9 mL of DMF was added to the reaction vessel. The mixture was then agitated for 30 s and drained. This procedure was repeated twice more with DMF and three more times with DMSO and CH_2Cl_2. The resin was then dried for five min under a stream of nitrogen by setting the synthesizer to drain gas and vent once again.

(8) After this overnight step dimer is present on resin therefore there are four cross-coupling steps remaining in order to construct a hexamer. In order to reduce the amount of preparation time, the catalyst solutions required for the last four steps are all prepared at the same time in the glove box. As a result, calculations are performed for each type of cross-coupling reaction and then simply doubled and prepared together. Consequently, half of each type of catalyst solution is added per required step. The catalyst solutions were again made up in the glove box. The total concentration of the mixture for each cross-coupling step must be 0.024 M. Catalyst solutions for all steps are made up at the same time. Again 2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-ethynyl-5-[(triisopropylsilanyl)-ethynyl] –benzoate[4] (147.48 mg) and 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl 3-bromo-5-iodo-benzoate[6] (147.60 mg) were weighed outside the glove box. 2 equiv of monomer were used for each step, there are 2 more of each the Pd(I) and $Pd(tfp)_4$ cross-coupling steps. Six gas tight syringes, four disposable syringes, the two pre-weighed monomers along with six silicone stoppers were taken into the glove box.

(9) Pd(I) dimer (20 mol %,11.04 mg) was added to DMF (3 mL) in a scintillation vial, agitated and placed in a gas tight syringe and sealed off in a silicone stopper. $ZnBr_2$ (4 equiv, 140.5 mg), HN-*i*Pr_2 (45 equiv, 0.98 mL) and DMF (1.5 mL) were combined in a scintillation vial, agitated and placed in a gas tight syringe and protected by a silicone stopper. Lastly, monomer 2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-ethynyl-5-[(triisopropylsilanyl)-ethynyl] –benzoate[4] was combined with DMF (2 mL), agitated, placed in a gas tight syringe and protected by a silicone stopper.

(10) $Pd(tfp)_4$ (20 mol%, 33.80 mg) was weighed into the vial containing 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl 3-bromo-5-iodo-benzoate[6]**,** DMF (2 mL) was added. The solution was agitated, added to a gas tight syringe and protected by a silicone stopper. CuI (10 mol%, 2.97 mg) was weighed into a scintillation vial, to this was added piperidine (10 equiv, 0.154 mL) and DMF (3 mL). This solution was agitated, placed in a gas tight syringe and protected by a silicone stopper. Lastly, TBAF (2 equiv, 0.312 mL) and DMF (1.5 mL) were added to a scintillation vial, agitated, placed in a gas tight syringe and protected by a silicone stopper.

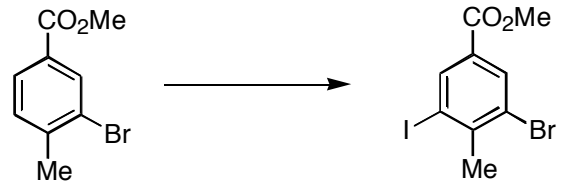
(11) All solutions were then removed from the glove box. The reaction vessel containing the resin was sealed off and the synthesizer set to metered gas and system 1. Half of each solution was added to the resin in the following order: TBAF, CuI/piperidine and finally 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl 3-bromo-5-iodo-benzoate[6]/$Pd(tfp)_4$. The agitation rate of the synthesizer was set to mix every: 0.9 sec, up stroke: 0.3 sec, % upwards: 33% and allowed to react for 2 h. After which time the washing and drying procedure described above was repeated. There are now three steps remaining in the solid phase synthesis. The previously described procedure was repeated for the Pd(I) dimer set of reaction conditions, then $Pd(tfp)_4$ and finally again Pd(I) dimer. The reaction time of each step is 2h.

(12) After the last coupling, the resin was washed as previously described but in this case the resin was dried under a stream of N_2 for 15 min. The reaction vessel containing the resin was removed from the parallel synthesizer. The resin was removed from the reaction vessel by pouring it into a sealed tube. To this sealed tube was added I_2 (1 equiv,19.79 mg) and CH_2I_2 (3 mL). The sealed tube was then degassed and refilled with N_2 three times and finally submerged into a 110˚C oil bath for 8-12 h. Upon completion of the cleavage the reaction vessel was cooled to rt. The contents were transferred to a separatory funnel using CH_2Cl_2 (~10 mL). The contents were poured into a sat. solution of $Na_2S_2O_3$ (10 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed to give a dark oil which was placed in a Kugelröhr apparatus and distilled at 90˚C under vacuum (10 mtorr) to remove any excess CH_2I_2 to give a dark viscous oil which can be purified by preparative scale GPC.

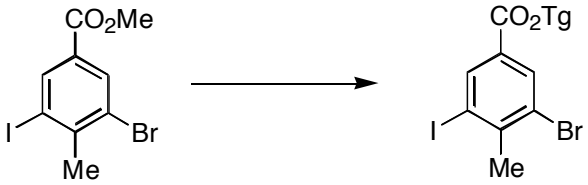
(13) In order to purify by prep-GPC the wax was dissolved in THF (4 mL). The solution was filtered through Acrodisc 13 mm Syringe Filters with a 0.45μm Nylon membrane into another scintillation vial. The 4 mL of solution was split into 8 runs (0.5 mL each). The pump was set to 6mL/min. At this flow rate the

retention time of a hexamer is approximately 24 min. In general (see crude GPC's of oligomers) a high MW shoulder appeared first. The shoulder was collected into a waste vial. Once an inflection point was reached the desired oligomer started to elute and was collected in a separate vial. This procedure was repeated 7 more times. When all fractions were collected they were concentrated to reveal a light yellow viscous oil. In general this procedure was repeated a second time in order to remove all high molecular weight impurities. Alternatively oligomers can be purified by silica gel column chromatography however it has been found that oligomer loss is less with preparatory-GPC. Also note that the solid phase synthesis could also be performed in a Schlaker flask as opposed to a parallel synthesizer.

Section 2: Synthesis of 3-bromo-5-iodo arene monomer



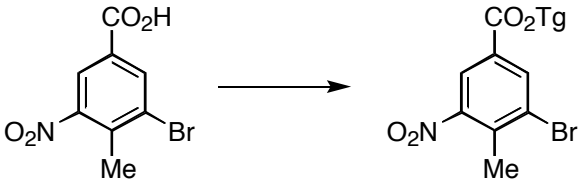
Methyl 3-bromo-5-iodo-4-methyl-benzoate. A 200 mL round bottom flask was fitted with a magnetic stirrer and charged with methyl 3-bromo-4-methylbenzoate (11.69 g, 51.0 mmol) and H_2SO_4 (30 mL). To this was added N-iodosuccinamide (13.4 g, 59.6 mmol) over the course of 30 min. The reaction mixture was allowed to stir for 2 h and was then poured over ice and extracted with CH_2Cl_2 (4 x 150 mL). The combined organic layers were then washed with sat. $Na_2S_2O_3$ (3 x 50 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo to give a white solid which was recrystallized from hexanes to give the desired product (13.03 g, 36.21 mmol, 72%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 1.7 Hz, 1H), 8.16 (d, J = 1.7 Hz, 1H), 3.91 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ164.3, 145.4, 139.3, 133.6, 130.3, 123.3, 100.5, 52.5, 29.6; MS (FD-LR) 353.9; Anal. Calcd for $C_9H_8BrIO_2$: C, 30.45; H, 2.27; N, 0; found C, 30.29; H, 2.15; N, 0.12.



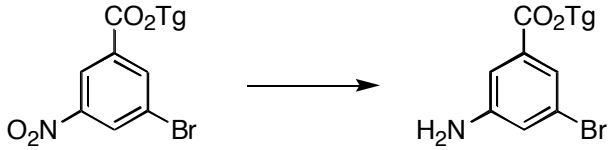
2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl 3-bromo-5-iodo-4-methyl-benzoate . A 500 mL round bottom flask was charged with methyl 3-bromo-5-iodo-4-methyl-benzoate (20.09 g, 56.6 mmol), K_2CO_3 (800 mg, 5.79 mmol), and tri(ethylene glycol) monomethyl ether (100 mL, 625 mmol) and attached to a Kugelröhr apparatus. The reaction mixture

was then heated to 35 ˚C overnight under vacuum (10 mtorr) after which time the temperature was raised to 80˚C to drive off excess tri(ethylene glycol) monomethyl ether leaving a dark brown oil which was purified by silica gel column chromatography (2:1 hex:EtOAc) to give the desired product (16.87g, 34.6 mmol, 61.1%) as a clear oil that crystallized to a white solid upon standing at below 0˚C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 1.7 Hz, 1H), 8.18 (d, *J* = 1.7 Hz, 1H), 4.47-4.45 (m, 2H), 3.83-3.81 (m, 2H), 3.71-3.64 (m, 6H), 3.55-3.53 (m, 2H), 3.37 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 145.5, 139.4, 133.7, 130.4, 123.3, 100.5, 71.9, 70.64, 70.59, 69.0, 64.6, 59.0, 29.6; MS (LR-FD) 487.9; Anal. Calcd for $C_{15}H_{20}BrIO_5$: C, 36.98; H, 4.14; N, 0; found C, 36.90; H, 4.15; N, 0.

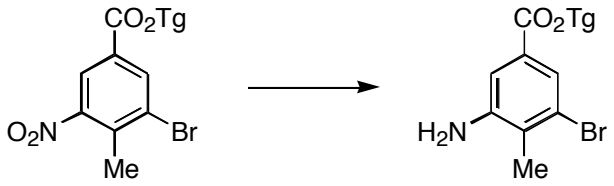
Section 3: Synthesis of tetrafluoroborate salts



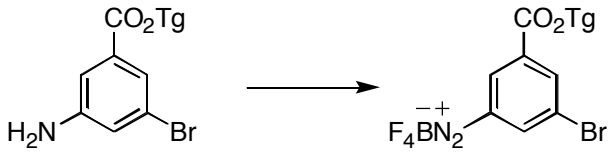
2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-bromo-4-methyl-5-nitro-benzoate (5). A 500 mL round bottom flask was fitted with a stir bar and charged with 3-bromo-4-methyl-5-nitro-benzoic acid (14.82 g, 57.0 mmol), tri(ethylene glycol)monomethyl ether (20 mL, 125 mmol), diphenylammonium triflate (1.84 g, 5.77 mmol), and toluene (150 mL) and was fitted with a reflux condenser. The reaction mixture was then heated in a 120˚C oil bath and allowed reflux overnight (16 h) after which the solvent was removed in vacuo. The excess tri(ethylene glycol)monomethyl ether was removed by distillation under vacuum in a Kugelröhr apparatus (90˚C, 10 mtorr) to give a black oil that was purified by silica gel column chromatography (4:1 hex:EtOAc) to give the desired product (10.32g, 25.4 mmol, 45%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 1.6 Hz, 1H), 8.34 (d, *J* = 1.7 Hz, 1H), 4.51-4.49 (m, 2H), 3.84-3.82 (m, 2H), 3.71-3.63 (m, 6H), 3.54-3.52 (m, 2H), 3.36 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ171.4, 163.6, 137.3, 137.1, 130.1, 127.5, 124.3, 72.1, 70.94, 70.90, 70.8, 69.1, 65.3, 59.3, 14.4.



2-[2-(2-Methoxyethoxy) ethoxy] ethyl 5-bromo-3-aminobenzoate. A 250 mL 3-neck round bottom flask was equipped with a magnetic stir bar, nitrogen inlet, and reflux condenser and was charged with 2-[2-(2-Methoxyethoxy) ethoxy] ethyl 5-bromo-3-nitrobenzoate (6.1 g, 15.55 mmol) and NEt_3 (20 mL) and was sparged with nitrogen for 10 min at 45 ˚C after which was added Pt/C (1.21 g, 0.311 mmol) and NEt_3 (12.5 mL). Using a syringe, formic acid (2.93 mL, 77.77 mmol) was added to the reaction mixture over 15 min. The mixture was then heated to 80 ˚C for 5 h. The reaction was then cooled and filtered through Celite 545 eluting with CH_2Cl_2 which was then transferred to a separatory funnel and washed with sodium bicarbonate (2 x 150 mL), water (2 x 150 mL), and finally brine (2 x 150 mL). The organic washings were dried over $MgSO_4$, filtered and the solvent removed to give a black oil which was purified by silica gel column chromatography (10:1, EtOAc:hex) to give the desired product (4.39 g, 12.12 mmol, 78%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, *J* = 1.6Hz, 1H), 7.21 (t, *J* = 1.5 Hz, 1H), 6.93(t, *J* = 2.1Hz, 1H), 4.40 (m, 2H), 4.00 (s, 2H), 3.67-3.65 (m, 2H), 3.64-3.60 (m, 6H), 3.51-3.49 (m, 2H), 3.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 148.3, 132.6, 123.0, 122.1, 121.8, 114.8, 72.1, 70.9, 70.7, 69.2, 64.5, 59.2; MS (FD), m/z 361.1 [M^+]. Calcd. for $C_{14}H_{20}BrNO_5$: C, 46.42, H, 5.57, N, 3.87; Found: C, 46.41, H, 5.28, N, 3.77.

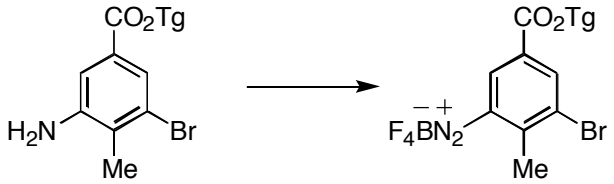


2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-amino-5-bromo-4-methyl-benzoate. A 3-neck 250 mL round bottom flask was equipped with a magnetic stirrer, condenser, rubber septum, and a ground glass stopper and was charged with 2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-bromo-4-methyl-5-nitro-benzoate (10.32g, 25.4 mmol), Pt/C (2.18g, 0.109 mmol), and Et_3N (85 mL). The mixture was heated to 45 ˚C and sparged with dry nitrogen for 15 min after which formic acid (6.0 mL, 159 mmol) was added by syringe over 15 min under positive nitrogen pressure. The reaction mixture was then heated to reflux for 5 h after which point the reaction was cooled to room temperature and filtered through Celite 545 and washed with CH_2Cl_2. The CH_2Cl_2 solution was then washed with sat. $NaHCO_3$ (2 x 150 mL), brine (2 x 150 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to give a black oil that was purified through silica gel column chromatography (1:2 hex:EtOAc) to give the desired product (5.31 g,14.1 mmol, 56%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.6 Hz, 1H), 7.29 (d, *J* = 1.6 Hz, 1H), 4.44-4.42 (m, 2H), 3.82-3.80 (m, 2H), 3.70-3.68 (m, 2H), 3.67-3.64 (m, 4H), 3.55-3.53 (m, 2H), 3.37 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ165.9, 145.9, 129.6, 127.0, 125.8, 123.9, 115.0, 72.1, 70.9, 70.9, 70.8, 69.4, 64.4, 59.3, 9.2.



3-Bromo-5-[2-(2-Methoxyethoxy) ethoxy] ethyl benzene diazonium Tetrafluroborate.

A flame-dried three-neck 250 mL round bottom flask equipped with a magnetic stir bar, an oven-dried addition funnel capped with a rubber septum, a nitrogen inlet, and a rubber septum was sparged with nitrogen for 15 min. BF_3•$(OEt)_2$ (6.0 mL, 47.3 mmol) was added by syringe to the reaction flask which was then cooled to –10 to –15 ˚C in an acetone/ice bath. In a separate 100 mL round bottom flask 2-[2-(2-Methoxyethoxy) ethoxy] ethyl 5-bromo-3-aminobenzoate (4.3 g, 11.9 mmol) was dissolved in dry THF (45 mL) and transferred to the addition funnel via cannula. The contents of the addition funnel was added to the BF_3• $(OEt)_2$ solution over 5 min. *T*-butyl nitrite (4.94 mL, 41.5 mmol) was added to the addition funnel and diluted with dry THF (39 mL). This solution was dispensed into the reaction mixture over 30 min. After complete addition the mixture was allowed to stir at –10 ˚C for an additional 15 min after which the mixture was allowed to warm to 0 ˚C. Et_2O (250 mL) was then added to the mixture leading to the formation of an orange suspension, which was placed in a freezer overnight to give the desired product (4.44 g, 9.6 mmol, 81%) as an orange powder after filtration. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.83 (s, 1H), 8.70 (s, 1H) 4.46-4.44 (m, 2H), 3.80-3.78 (m, 2H), 3.65-3.55 (m, 6H), 3.46-3.44 (m, 2H), 3.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 144.4, 137.9, 134.4, 132.5, 124.2, 117.7, 71.9, 70.5, 70.4, 70.3, 68.7, 66.1, 58.9; MS (FD), m/z 348.0 [M^+-N_2]. Calcd. for $C_{14}H_{18}BBrF_4N_2O_5$: C, 36.47, H, 3.94, N, 6.08; Found: C, 36.22, H, 3.87, N, 5.77.



3-Bromo-5-[2-(2-Methoxyethoxy) ethoxy] ethyl benzene diazonium Tetrafluroborate (9).

A flame dried three necked 250 mL round bottom flask equipped with a magnetic stir bar, an oven dried addition funnel that had been capped with a rubber septum, a nitrogen inlet, and another rubber septum was sparged with N_2 for 15 min. BF_3.$(OEt)_2$ (6.0 mL, 47.3 mmol) was added by syringe and cooled to –10 to -15˚C in an acetone/ice bath. In a separate flame dried vial, 2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3-amino-5-bromo-4-methyl-benzoate (4.186 g, 11.1 mmol) was dissolved in dry THF (45 mL) and transferred to the addition funnel via cannula. The contents of the addition funnel was slowly added to the BF_3.$(OEt)_2$ over 5 min. t-butyl nitrite (4.94 mL, 42.5 mmol) was then added to the addition funnel and diluted with dry THF (39 mL). This solution was then dispensed into

the reaction mixture over 30 min. After complete addition the mixture was allowed to stir at –10˚C for an additional 15 min after which time the contents of the flask were warmed to 0˚C. Et_2O (250 mL) was then added to the mixture leading to the formation of a milky white suspension that was placed in a freezer overnight to give the desired product (4.44 g, 9.6 mmol, 81%) as a white powder after filtration. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H, Ar-*H*), 8.74 (s, 1H), 4.51-4.49 (m, 2H), 3.86-3.84 (m, 2H), 3.70-3.68 (m, 2H), 3.64-3.62 (m, 2H), 3.59-3.57 (m, 2H), 3.50-3.48 (m, 2H), 3.29 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 147.8, 144.5, 133.3, 131.9, 127.4, 118.1, 72.0, 70.66, 70.60, 70.5, 68.8, 66.0, 59.1, 21.0; MS (LR-FD) 386.7 $[M^{-BF4}]^+$, HRMS (ESI) calcd. $C_{15}H_{20}BrN_2O_5$ (-BF_4) 387.0556, found 387.0574; Anal. Calcd. for $C_{15}H_{20}BBrF_4N_2O_5$: C, 37.93, H, 4.24, N, 5.90; found C 37.58, H, 4.24, N, 5.76.

Section 4: Preparation of Pd(I) dimer pre-catalyst

A solution of tri-*tert*-butyl phosphine (0.639 g, 3.02 mmol) in 20 mL of MeOH was added to a stirred suspension of $[(2\text{-methylallyl})PdCl]_2$ (0.560g, 1.51 mmol) in 40 mL of MeOH under argon, immediately followed by the addition of NaOH (60.5 mg, 1.51 mmol) in 20 mL of MeOH. The solution turned yellow and was stirred at room temperature for 1 h. The precipitate was collected by filtration, washed with a small amount of MeOH, dissolved in benzene and passed through a PTFE filter (pore size 0.45 μm). The filtrate was evaporated to give 1.06 g (91%) of pure Pd(I) dimer pre-catalyst as a yellow powder. The ^{1}H and ^{13}C NMR spectra corresponded to the values reported in the literature for this compound.[7]

Section 5: Preparation of Pd(tri-2-furylphosphine)$_4$ catalyst

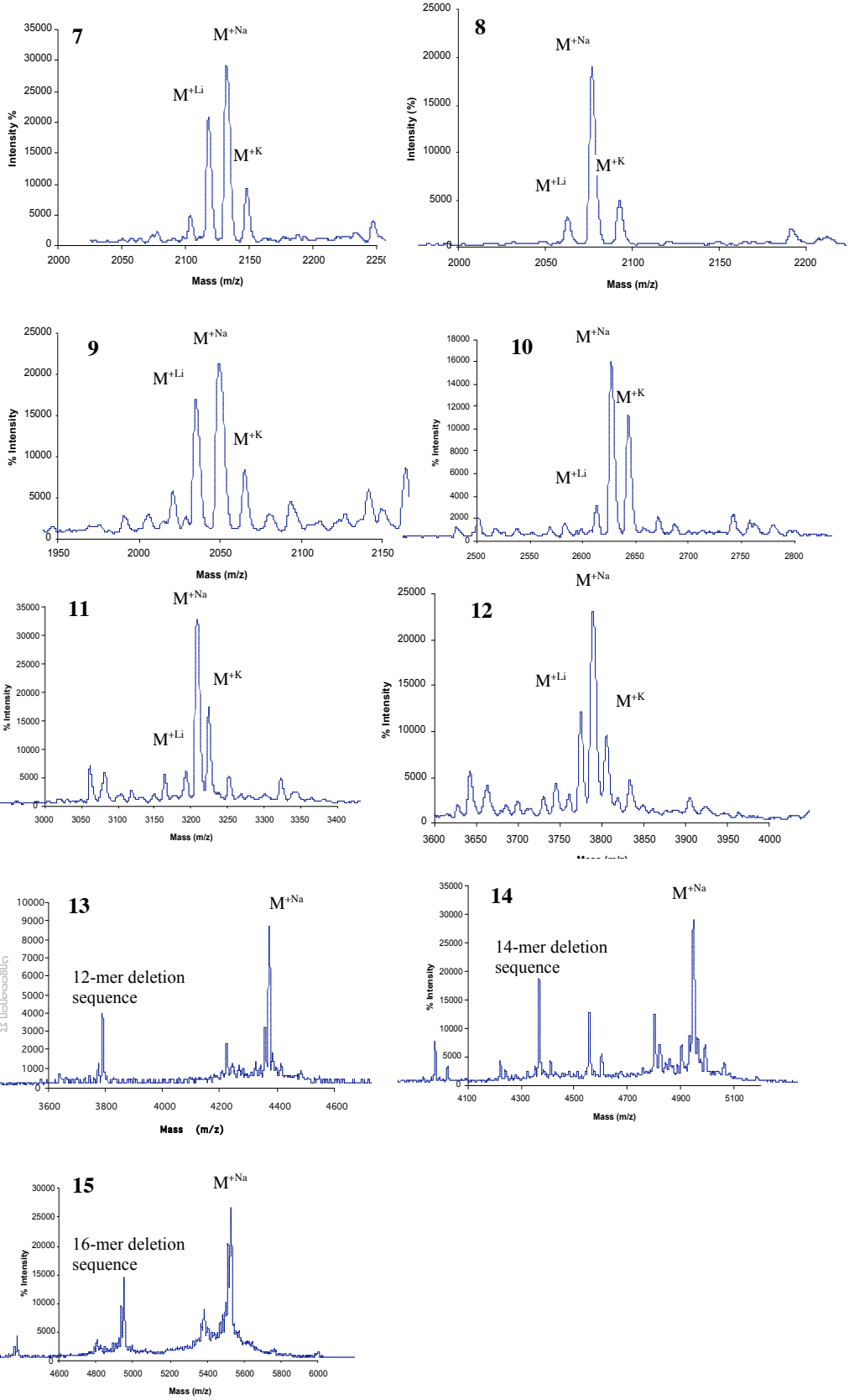
Tri-2-furylphosphine (4.729 g, 20.30 mmol) was weighed into a 200 mL round bottom flask containing a stir bar inside a glove box. THF (~30 mL) was added to this solid until it dissolved. To this solution $Pd_2(dba)_3$ (2.32 g, 2.53 mmol) was added and the solution was allowed to stir for 10 min upon which time the solution turned green. This solution was then filtered through a coarse frit charged with celite to produce a bright yellow solution. This solution was then layered with pentane and placed in a freezer overnight. The resulting white powder (2.70 g, 2.49 mmol, 73 %) was then isolated and dried by vacuum filtration. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (s, 18H), 6.19 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 120.4, 120.2, 110.5; LRMS (ESI) calcd. $C_{48}H_{36}O_{12}P_4Pd$ 1035.11, found 1075.0 (M^{+K+}); Anal. Calcd. for $C_{48}H_{36}O_{12}P_4Pd$: C, 55.70, H, 3.51; found C 55.97, H, 3.43.

References

1. Part # 900087 sold by Biotage. All components of Argonaut Quest-210 Parallel Synthesizer are now sold by Biotage.
2. If less than 300 mg of resin was used inconsistent results were obtained.
3. Quest-210 Parallel Synthesizer settings are set to drain gas and vent.
4. Monomer **3** from main text.

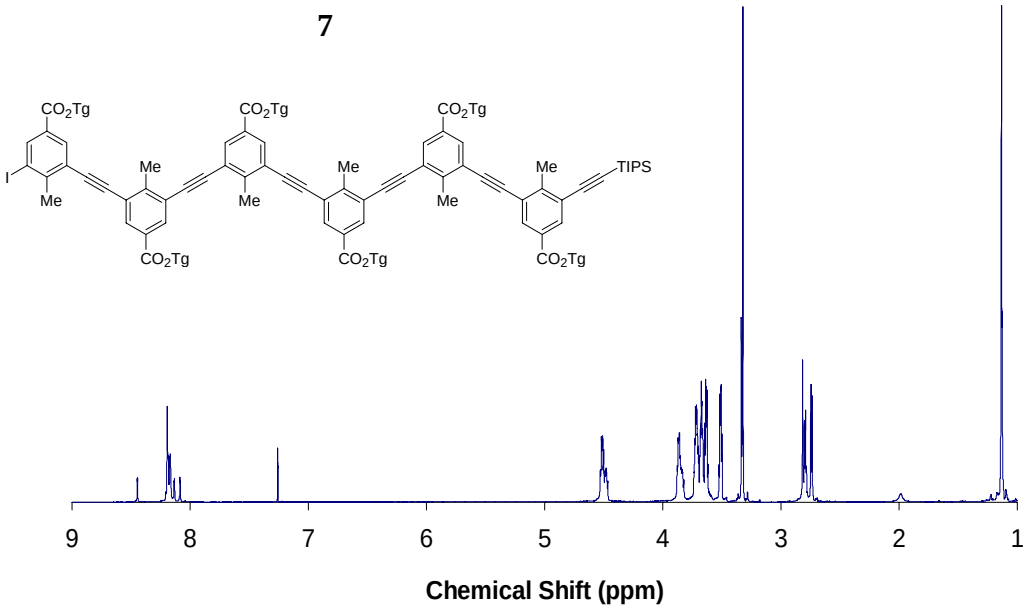
5. Quest-210 Parallel Synthesizer settings are set to metered gas and system 1.
6. Monomer **5** from main text.
7. Werner, H.; Kühn, A. *J. Organomet. Chem.* **1979**, *179*, 439-445.

Section 6a- Oligomer Characterization: MALDI data

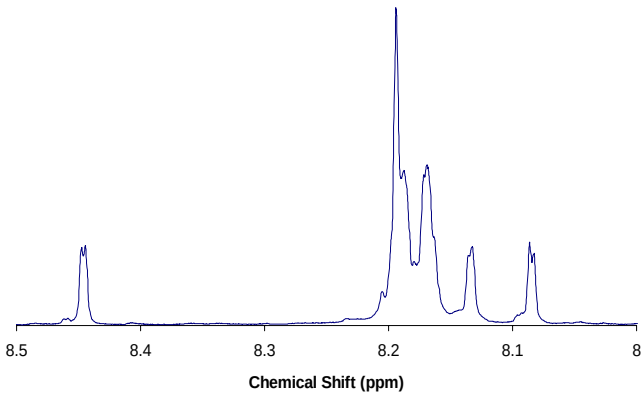


Section 6b- ^{1}H NMR data for oligomers 7-15

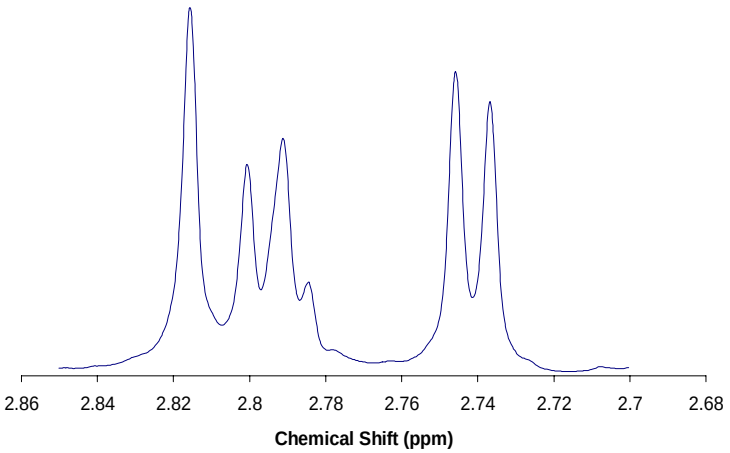
7



Aromatic Region



Methyl Region



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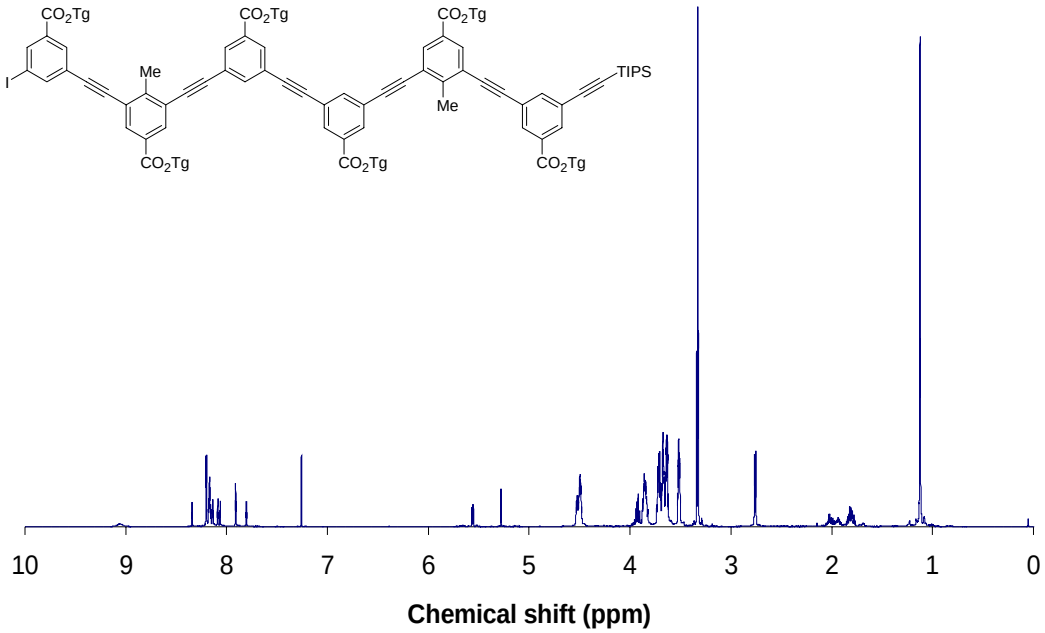

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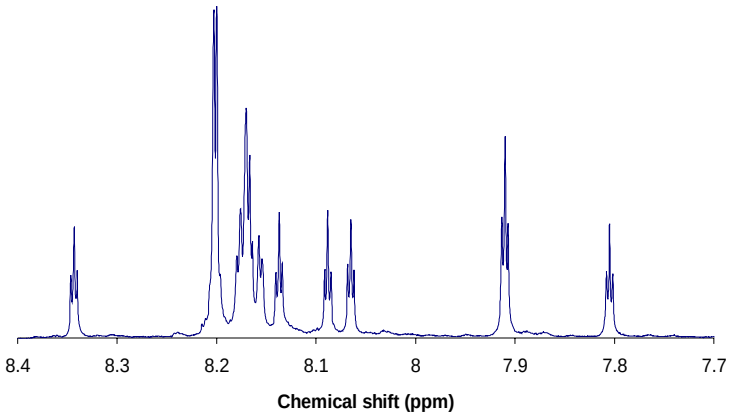

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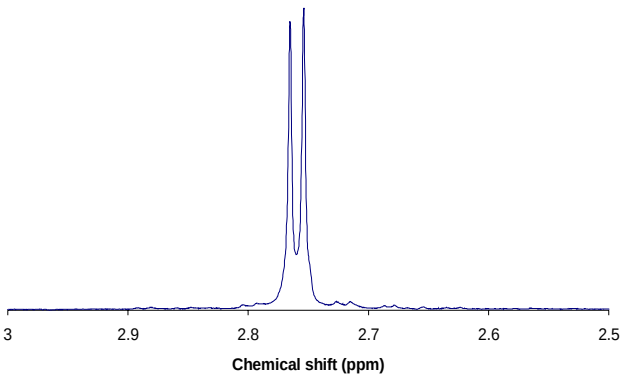

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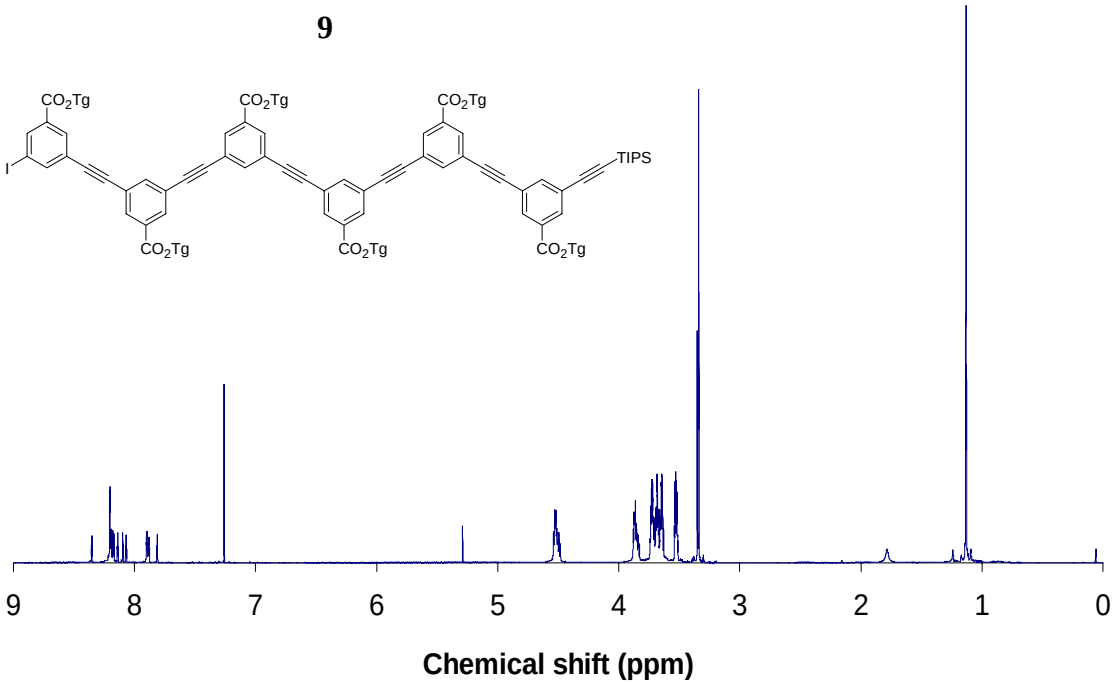

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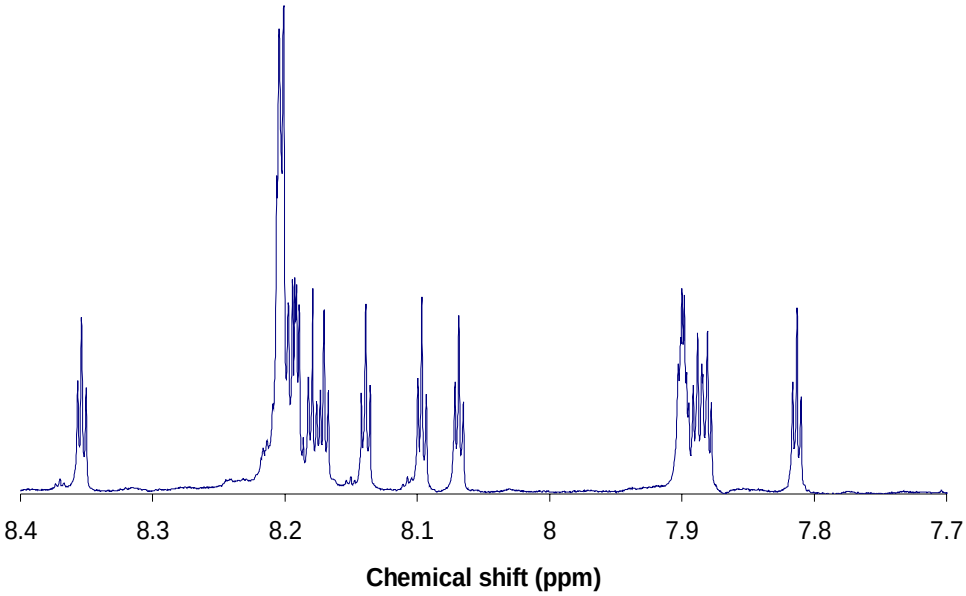

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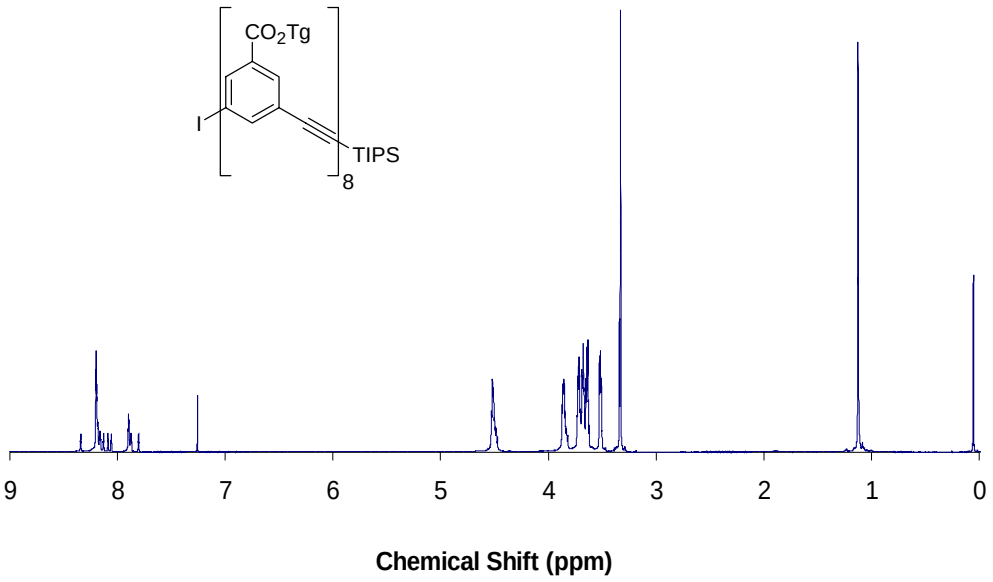

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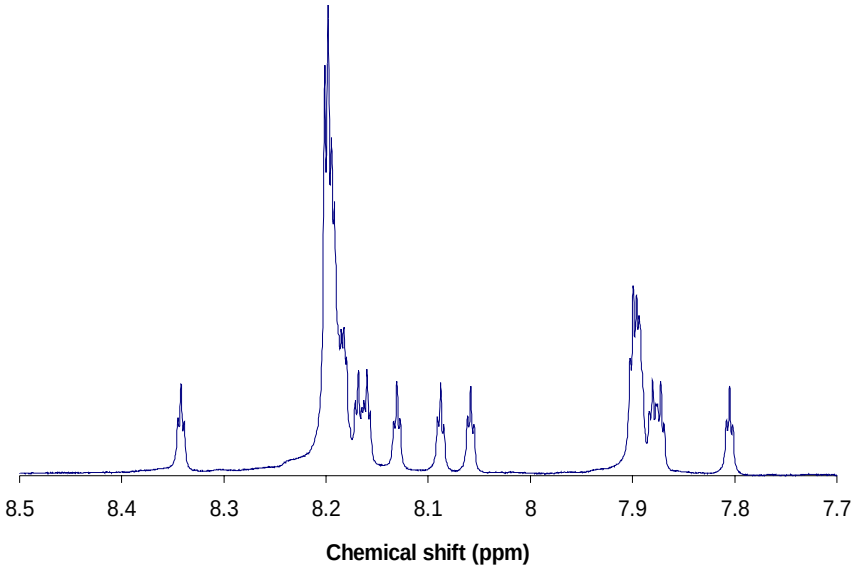

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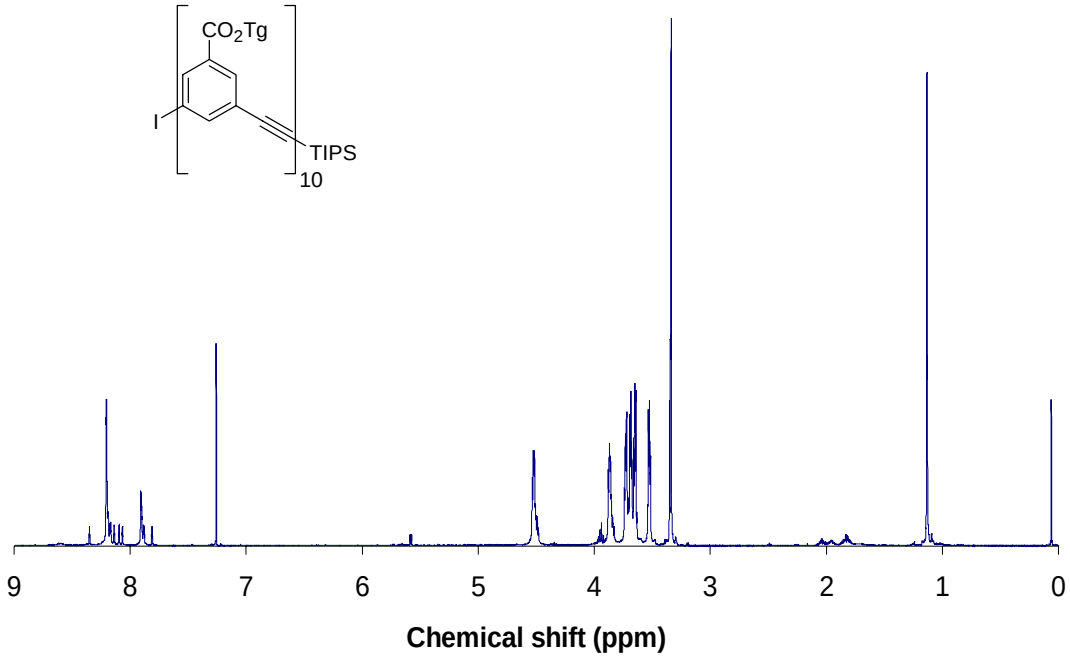

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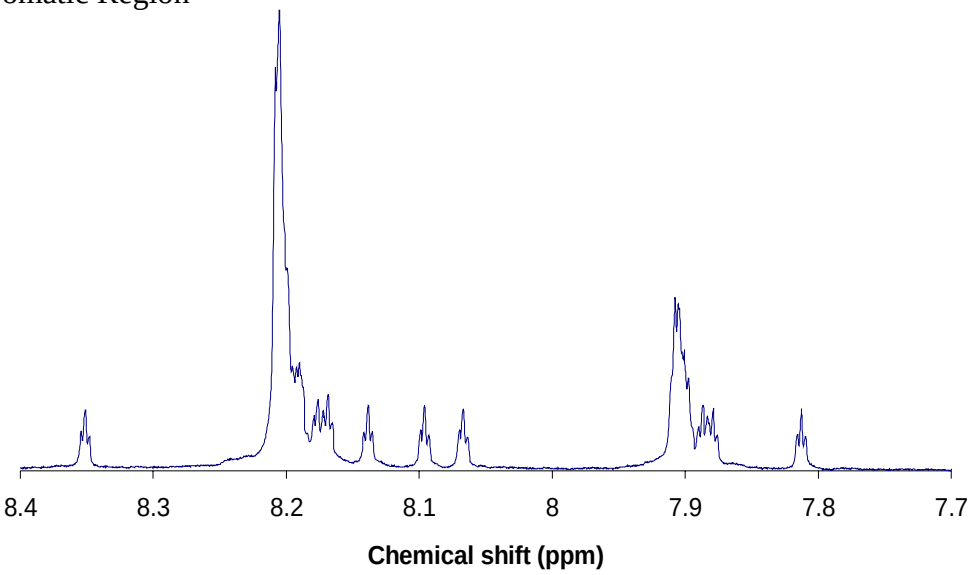

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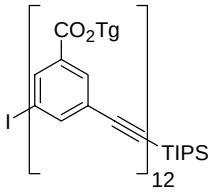

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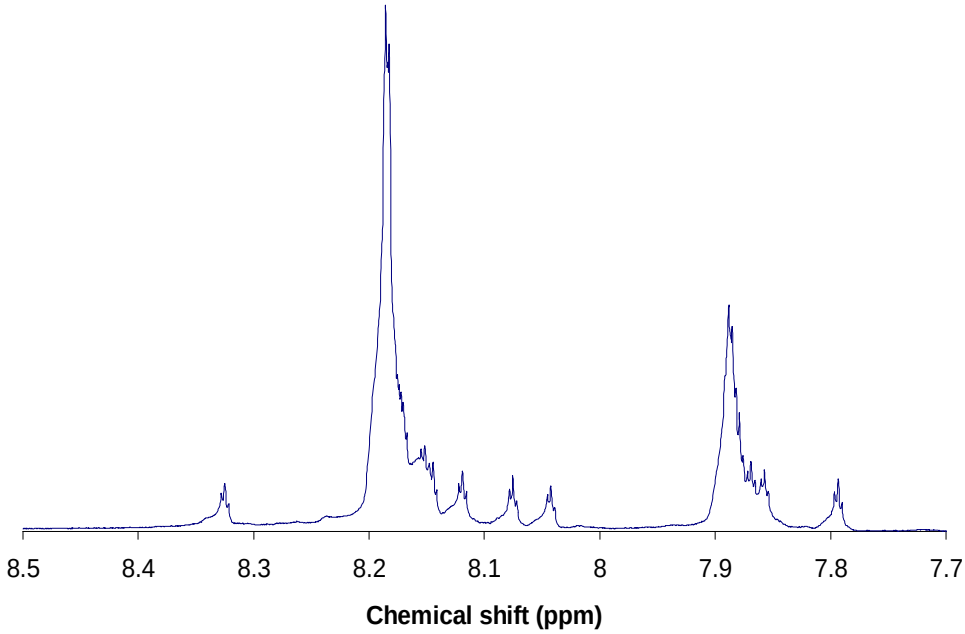

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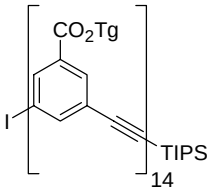

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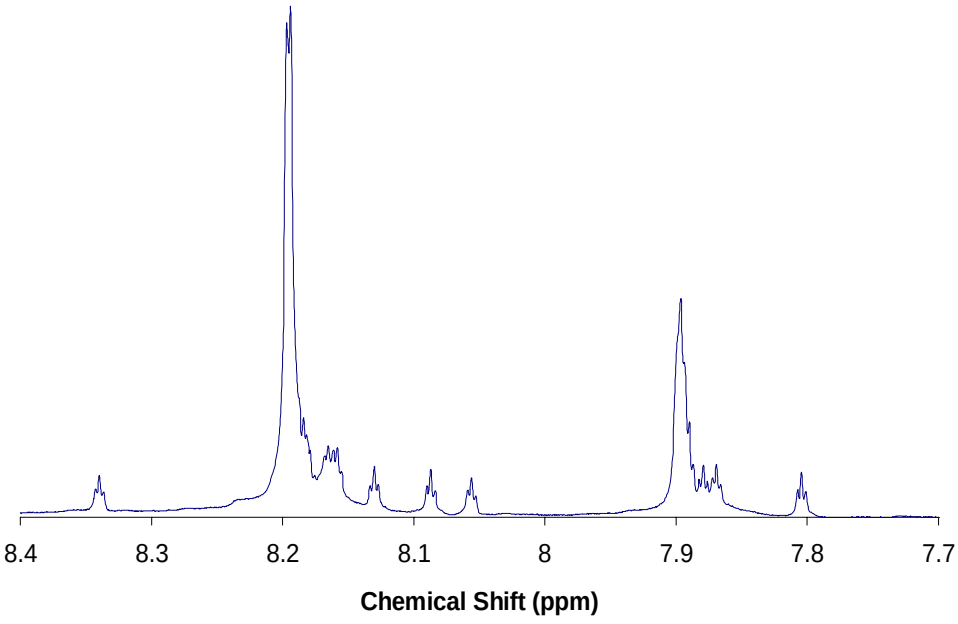

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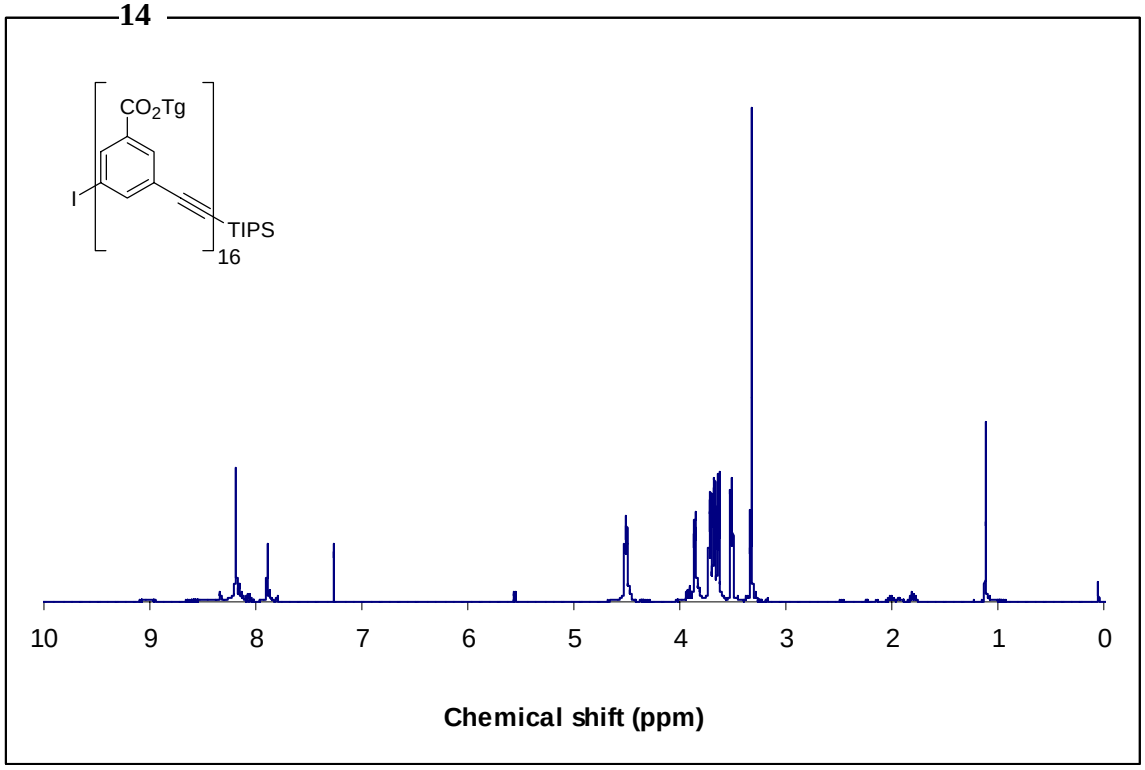

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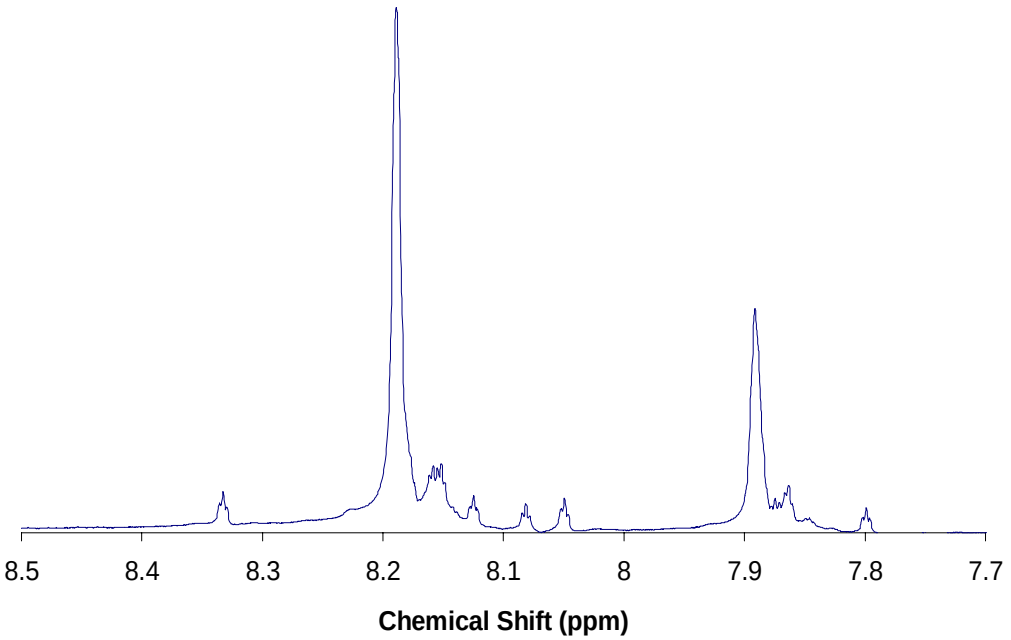

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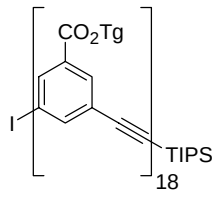

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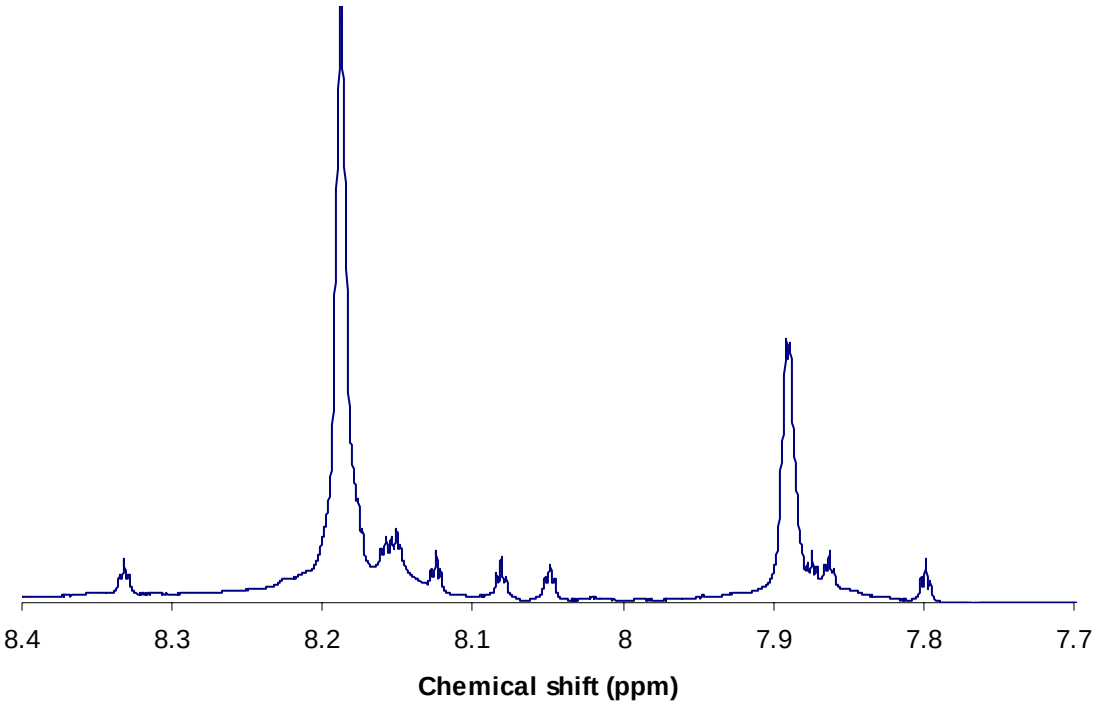
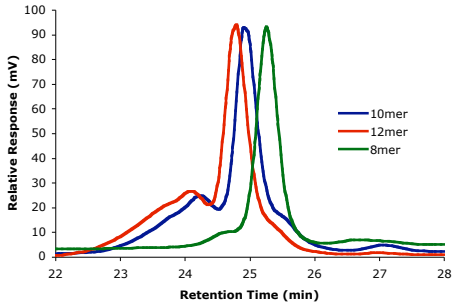
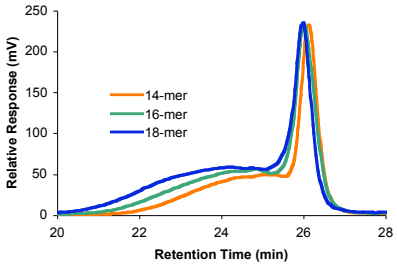


Section 6c- Oligomer Characterization: Crude and Purified GPC spectra

(i) Crude GPC spectra

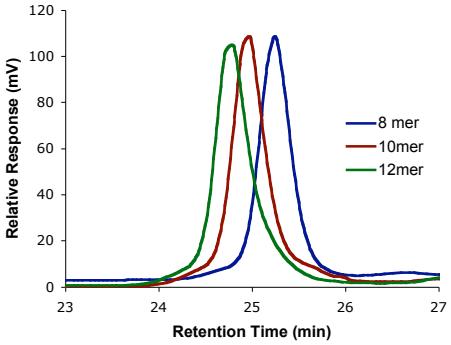


Eluting solvent: THF (**10-12**)

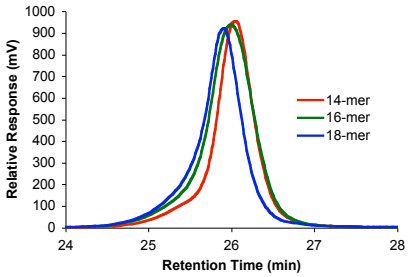


Eluting solvent: 89 THF:10 MeOH: 1 NEt_3(**13-15**)

(ii) Purified GPC spectra

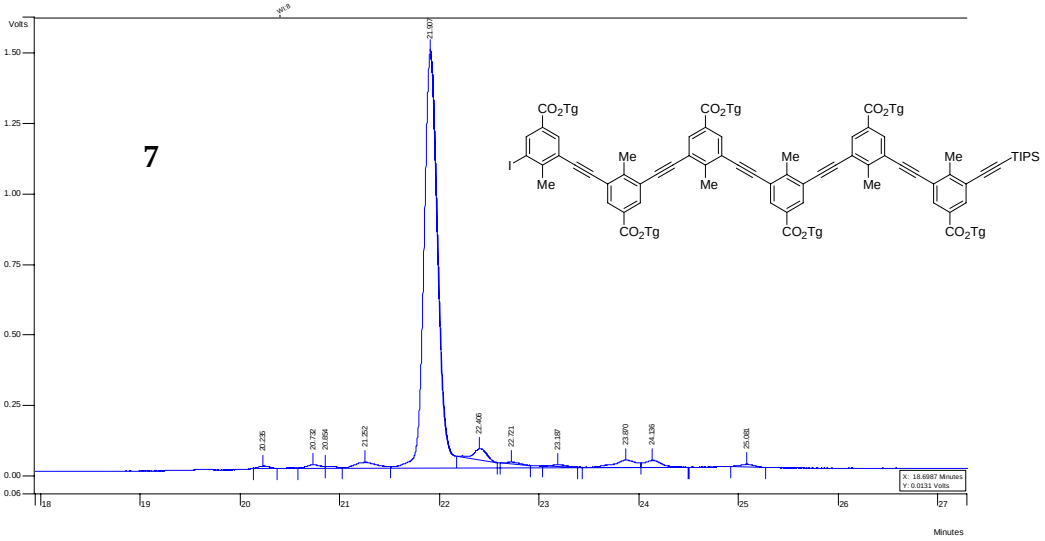


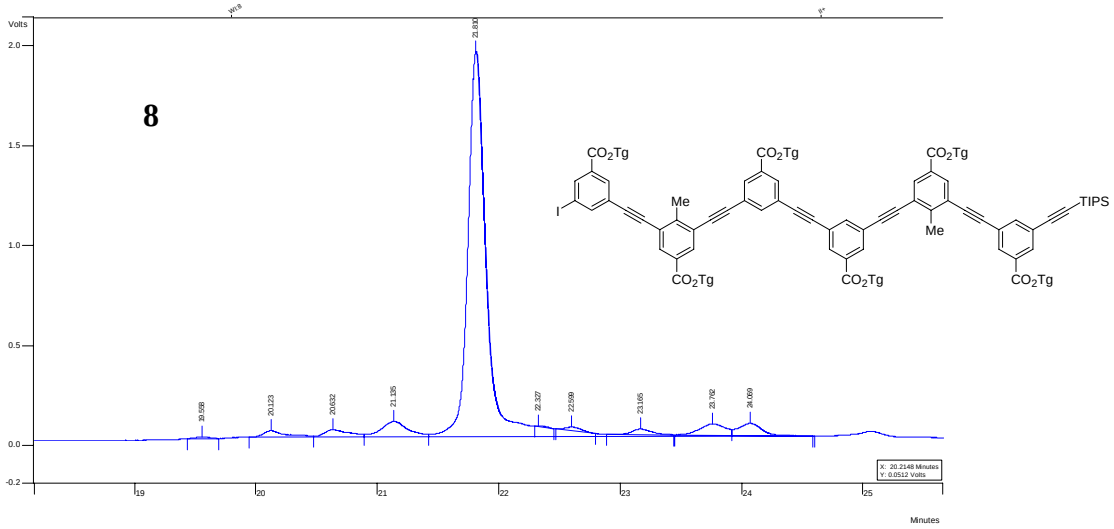
Eluting solvent: THF (**10-12**)

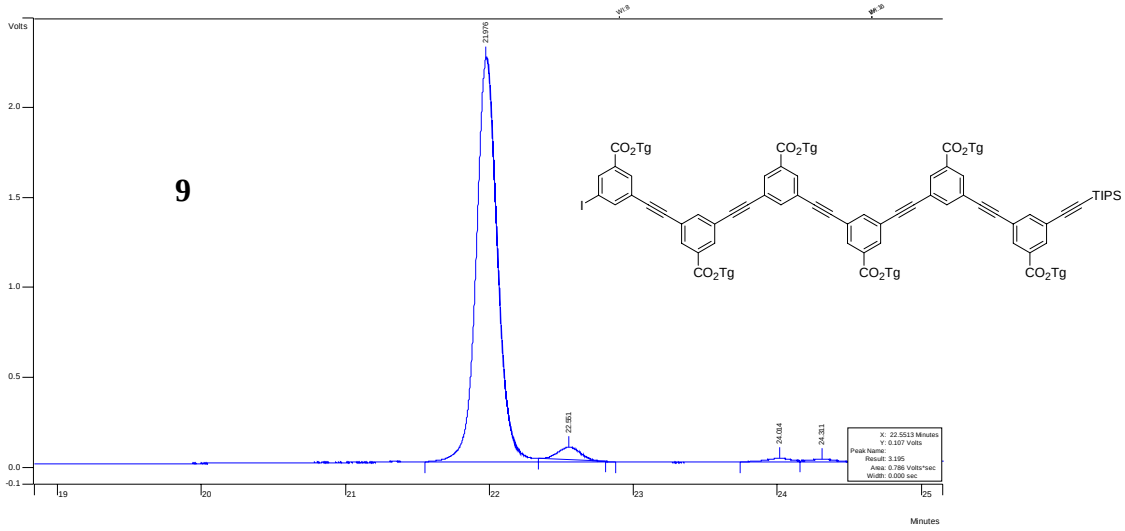


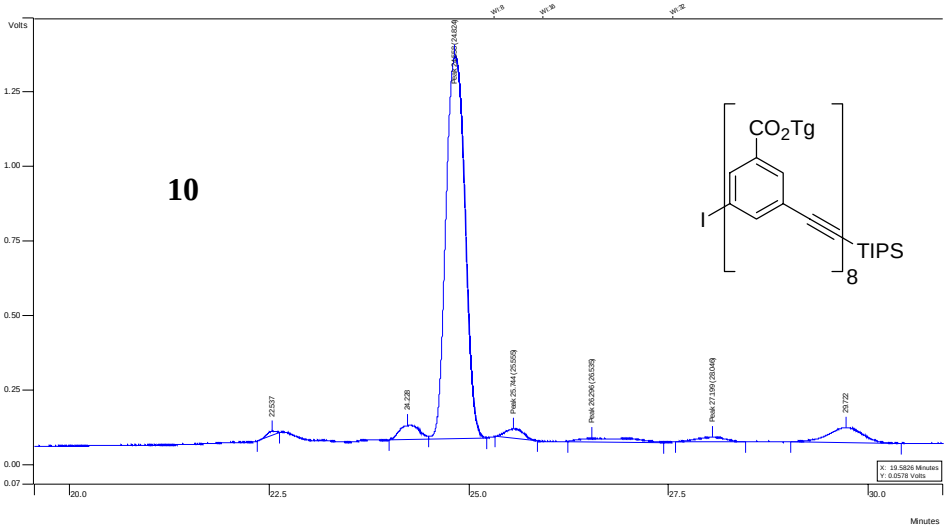
Eluting solvent: 89 THF:10 MeOH: 1 NEt_3 (**13**-**15**)

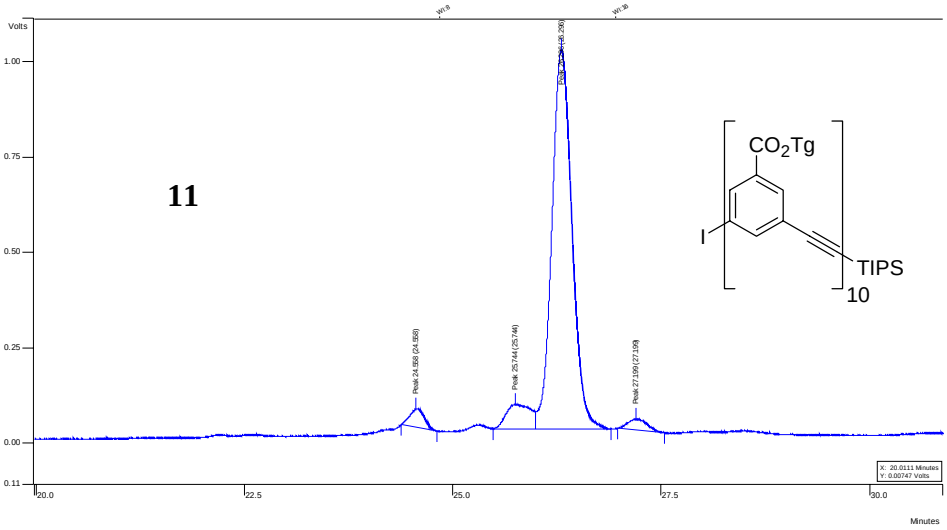
Section 6d- HPLC data for 7-15

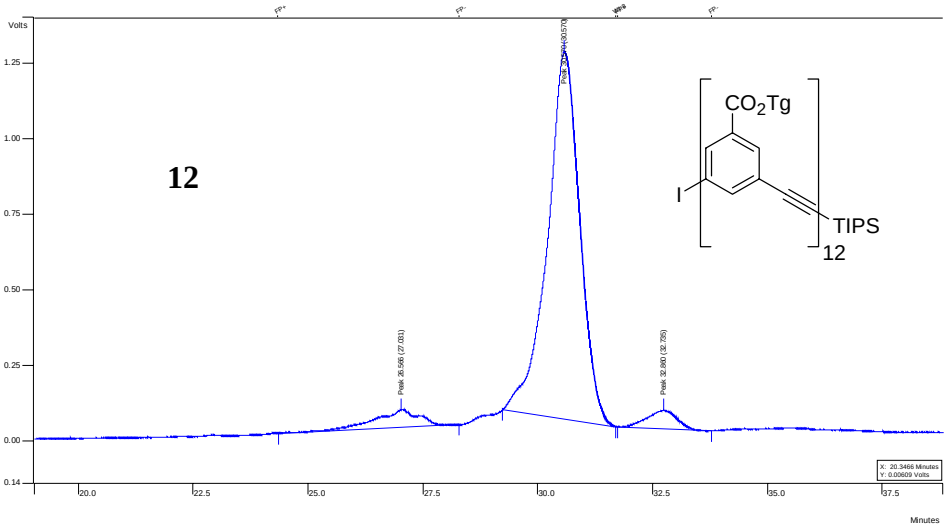


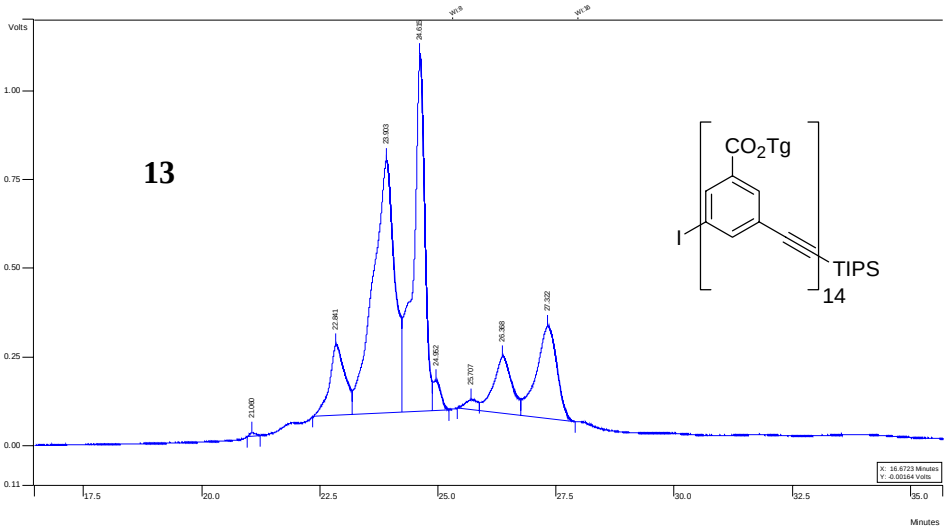


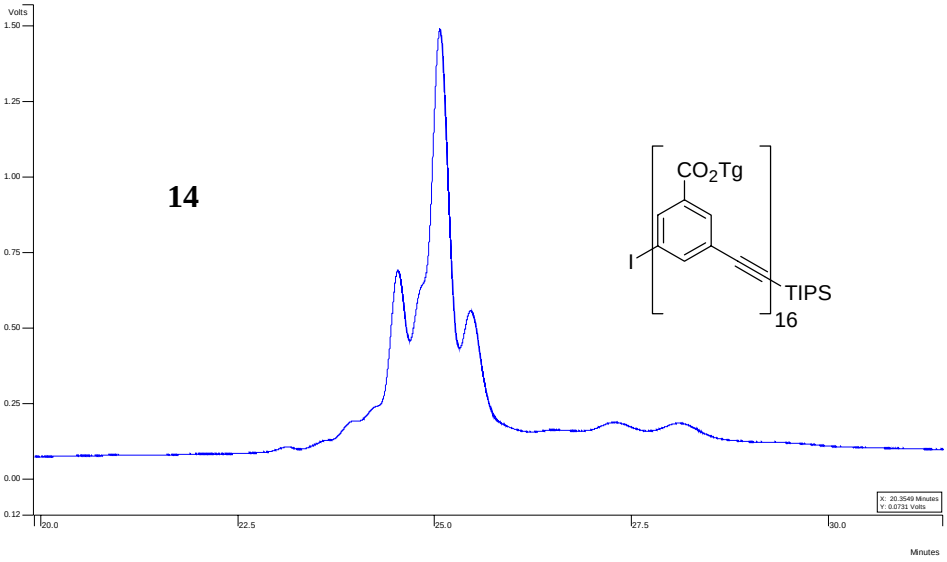

9
Volts
2.0
1.5
1.0
0.5
0.0
-0.1
21.976
22.551
24.014
24.321
19
20
21
22
23
24
25
Minutes
CO2Tg
I
TIPS

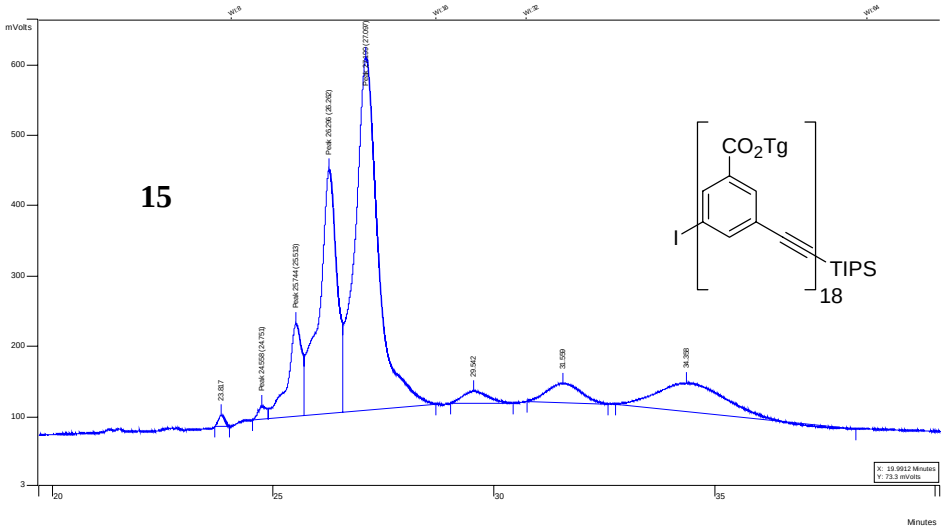

10
Volts
1.25
1.00
0.75
0.50
0.25
0.00
0.07
23.337
24.228
Peak 25.344 (265959)
Peak 26.056 (265329)
Peak 27.199 (280449)
29.722
20.0
22.5
25.0
27.5
30.0
Minutes
CO2Tg
I
TIPS
8


11
Volts
1.00
0.75
0.50
0.25
0.00
0.11
Peak 24.558 (24.359)
Peak 25.744 (25.746)
Peak 27.199 (27.199)
X: 20.0111 Minutes
Y: 0.00747 Volts
20.0
22.5
25.0
27.5
30.0
Minutes
CO2Tg
I
TIPS
10


12
Volts
1.25
1.00
0.75
0.50
0.25
0.00
0.14
Peak 26.566 (27.031)
Peak 32.800 (32.755)
X: 20.3466 Minutes
Y: 0.00609 Volts
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
Minutes
CO2Tg
I
TIPS
12


13
Volts
1.00
0.75
0.50
0.25
0.00
0.11
21.000
22.841
23.603
24.632
24.852
25.707
26.368
27.322
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
Minutes
CO2Tg
I
TIPS
14


14
Volts
1.50
1.25
1.00
0.75
0.50
0.25
0.00
0.12
20.0
22.5
25.0
27.5
30.0
Minutes
CO2Tg
I
TIPS
16


15
mVolts
600
500
400
300
200
100
3
20
25
30
35
Minutes
23.817
Peak 24.558 (24.753)
Peak 25.744 (25.515)
Peak 26.295 (26.292)
Peak 27.089 (27.097)
29.942
31.559
34.388
X: 19.9912 Minutes
Y: 73.3 mVolts
CO2Tg
I
TIPS
18