Supporting information for “Benchtop” biaryl coupling using Pd/Cu co-catalysis. Application to the synthesis of conjugated polymers

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Materials and Methods

GPC

Size exclusion chromatography (SEC) was carried out on one of two systems: (1) an Agilent system with a 1260 Infinity isocratic pump, degasser, and thermostatted column chamber held at 30 °C containing Aglient 5 µm MIXED-C columns with a combined operating range of 200–2 000 000 g mol^{-1}relative to polystyrene standards, or (2) an Agilent system with a 1260 Infinity II isocratic pump, degasser, and thermostatted column chamber held at 30 °C containing Aglient PLgel 10 µm MIXED-B with a combined operating range of 500–10 000 000 g mol^{-1} relative to polystyrene standards. Chloroform with 50 ppm amylene was used as the mobile phase on system (2), while tetrahydrofuran was used as a mobile phase on system (1). System (1) was equipped with an Agilent 1260 Infinity refractometer, bi dual angle dynamic and static light scattering. System (2) was equipped with a suite of detectors from Wyatt Technologies, which provided measurement of polymer concentration, molecular weight, and viscosity. Static light scattering was measured using a DAWN HELEOS II Peltier system with differential refractive index measured with an Optilab TrEX, and differential viscosity measured using a Viscostar II.

NMR

Spectrum were taken on the 500 MHz Bruker prodigy at University of Texas at Austin. Polymer spectrum were taken on a 400 MHZ Bruker NMR at Oklahoma State University. NMR solvents were purchased from Sigma Aldrich: DMSO-d6, and Cambridge isotopes; D_2O, d-THF, $CDCl_3$, CD_3OD

MALDI-TOF

MALDI SPECTRUM were attempted on the AB **Voyager**-DE PRO **MALDI**-TOF. Laser power was set to 2200 with a gate of 0.15%. The potential was set to 25 Kv with a 1200 nS delay. For all other samples the laser power was between 1600-1900 with a gate of 0.05%. The potential was set to 20 Kv with a 230 nS delay.

GC-MS

The GC/MS system was a single quadrupole mass spectrometer interfaced with an Agilent Technologies 7820A gas chromatograph. This instrument uses electron impact (EI) ionization and has an attached autosampler tray.

Parameters: practical m/z range: 15-600.

LC-MS

The LC-MS system was a single quadrupole mass spectrometer coupled with an electrospray (ESI) source. This instrument uses an autosampler and is interfaced with an Agilent 1200 series liquid chromatography system that has a diode-array (UV-Vis) detector.

Parameters: m/z range: 50-2000.

Column: Agilent ZORBAX Eclipse Plus C18 narrow bore column; 2.1 mm internal diameter; 50 mm length; 5 micron particle size;

Purchased chemicals and known compounds

Boronic acids were used directly from commercial sources. All of the boronic acids, palladium, and copper sources were purchased from Sigma Aldrich unless otherwise noted.

Determination of hydrogen peroxide concentrations in situ

To verify the mechanism of action for the oxidative couplings, we sought out a means to test the reactions for the formation of peroxide. Using the AquaPhoenix Scientific Hydrogen

Peroxide LR Test Kit, we set up a series of experiments to confirm the presence of peroxide in our polymerization reactions.

For peroxide concentration testing all reactions were run for 16 hours. Following the procedure specified in the Test Kit; 500 uL of crude reaction solution was diluted with water (2 mL). Ferroin indicator (8 drops) was then added to the diluted solution. Afterwards, Ceric Sulfate was added dropwise until the solution turned from orange to blue. The number of drops needed to convert the solution from orange to blue (Figure S1)was used to calculate the amount of H_2O_2 in ppm (Table S1). Based on the results of, we can conclude that peroxide is formed by the Pd/Cu cocatalyst system.

Note: This method will be affected by organics and metals present in the reaction. For this reason, several control experiments were run to ensure the results we observed were from the presence of peroxide and not due to the reagents present in the reaction.

Table S1. The reaction (entry 1) and different controls (entries 2-5) were tested for peroxide formation in situ.

Entry	**1**	**2**	**3**	**4**	**5**
$Cu(OAc)_2$	2 mg	2 mg	0 mg	0 mg	0 mg
Pd(OAc)	2 mg	2 mg	0 mg	0 mg	0 mg
$PhB(OH)_2$	30 mg	0 mg	0 mg	30 mg	30 mg
DMSO	950 uL	950 uL	950 uL	0 mg	950 uL
H_2O	50 uL	50 uL	50 uL	2000 uL	50 uL

Ceric Sulfate soln. (drops)	4	2	2	2	2

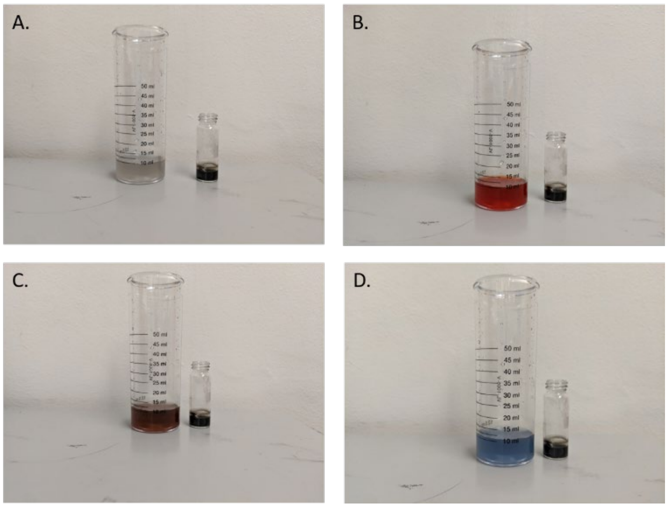
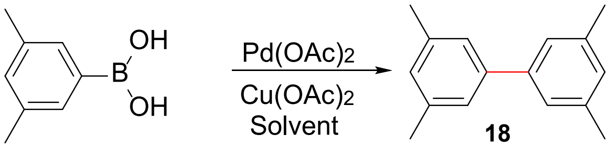


Figure S1. A) The reaction mixture is shown after being diluted to 2mL B. To the mixture, 8 drops of Ferroin indicator were added. C) After the addition of one drop of Ceric Sulfate, a color change can be observed in the indicator solution. D) After 4 drops, the solution completely changed from orange to blue.

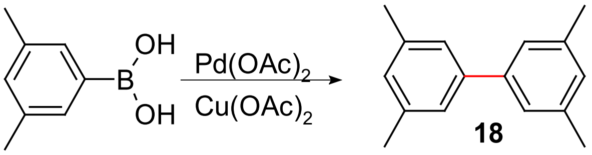
Synthesis and characterization of small molecules and polymers

General homocoupling procedure for solvent screening



Commercially available 3,5-dimethylphenylboronic acid (50 mg, 0.3 mmol) was placed in a vial with $Pd(OAc)_2$, (2 mg, 0.01 mmol) and $Cu(OAc)_2$, (2 mg, 0.01 mmol). A different solvent (1.5 mL) was added to the solids (**Table S2**), and the vessel was allowed to stir on the countertop open to air for 14h. Volatile solvents were capped with a septum. An air balloon was connected to the septum through a needle to ensure that the reaction had ample oxygen for the reaction to take place. After stirring the reaction was mixed extracted with ether thrice. The resulting ethereal solution was evaporated. The crude material was analyzed by GC-MS, NMR, and weighed to determine yield and conversion. [1]

Table S2. Conversion as calculated by ^{1}H-NMR spectroscopy. Yield was determined by GC-MS. * solvent was wet ** sometime the Chan Lam product, 3,5-dimethylanisole, was produced instead.



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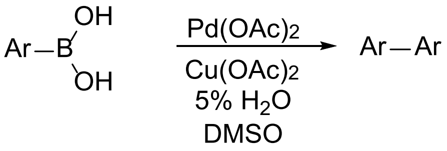
solvent	**conv.**	**solvent**	**conv.**	**solvent**	**conv.**
DMSO	50	CH_2Cl_2	8	MeCN	45
DMSO*	100	$CHCl_3$	21	$(CH_3)_2CO$*	100
DMF	100	Et_2O	10	1,4 -dioxane	66
MeOH**	100	THF	68	EtOAc	32

General benchtop homocoupling procedure



$$\text{Ar}-\text{B(OH)}_2 \xrightarrow[\text{Cu(OAc)}_2,\ 5\%\ H_2O,\ \text{DMSO}]{\text{Pd(OAc)}_2} \text{Ar}-\text{Ar}$$

.

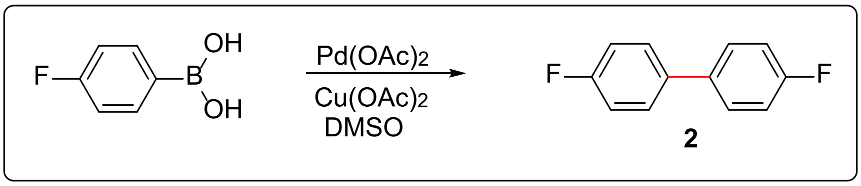
The respective substituted phenyl boronic acids (PBAs) (0.3 mmol) were placed in a vial with $Pd(OAc)_2$, (0.7 mg, 0.003 mmol) and $Cu(OAc)_2$, (0.7 mg, 0.004 mmol). A solution of 5% H_2O in DMSO (1.7 mL) was added to mixture of solids, and the vessel was allowed to stir on the countertop open to air for 14h. After which the reaction was diluted with 1M KHF_2 (40 mL).* The organic compounds were extracted with three consecutive EtOAc washes. The organic layer was washed with 1M KHF_2, dried with Na_2SO_4 and filtered through cotton. The solvent was removed under vacuum to yield product without the need for further purification.* *

* Compounds that contained basic functional groups were washed with saturated K_2CO_3 (aq), and compounds that contained carboxylic acids were washed with HCl (1M).

**Some compounds required further purification. The procedure for the purification of these compounds are explained before their respective characterization below.

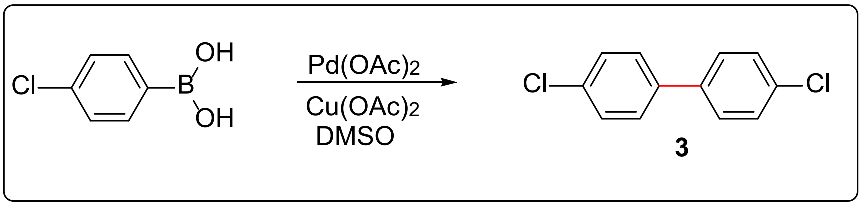
Note: Boric acid (5 equiv.) was added to reactions that contained bpin esters and/or aniline substrates.

Synthesis of 4,4-difluoro-1,1-biphenyl, 2



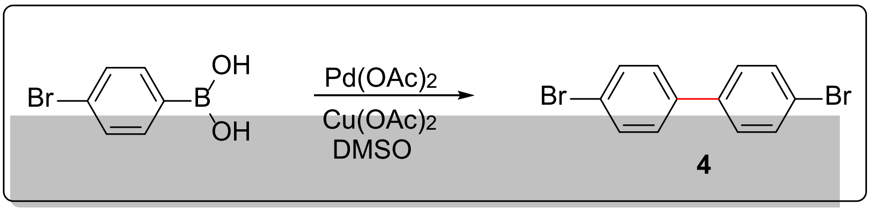
The starting material, 4-fluoro boronic acid, was subjected to general benchtop homocoupling conditions. The white solid, 4,4-difluoro-1,1-biphenyl, was produced after workup without the need for further purification, (23 mg , 80%). EI-MS (m/z): 190.10 The spectroscopic data of **2** was in agreement with previously reported data.[2]

Synthesis dicholoro-1,1'-biphenyl, 3



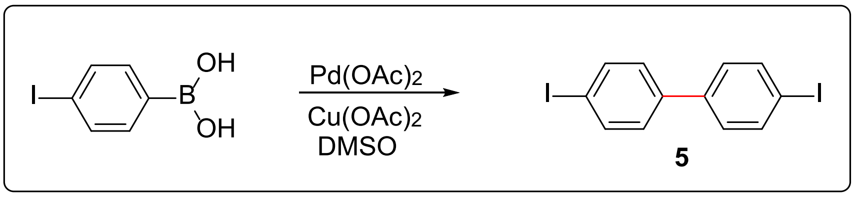
The starting material, 4-chlorophenylboronic acid, was subjected to general benchtop homocoupling conditions. Product, 4,4'-dicholoro-1,1'-biphenyl, was produced after workup without the need for further purification, (23 mg ,68 %). EI-MS (m/z): 222.10. Characterization was in agreement with previously reported literature.[2]

Synthesis of 4,4-dibromo-1,1-biphenyl, 4



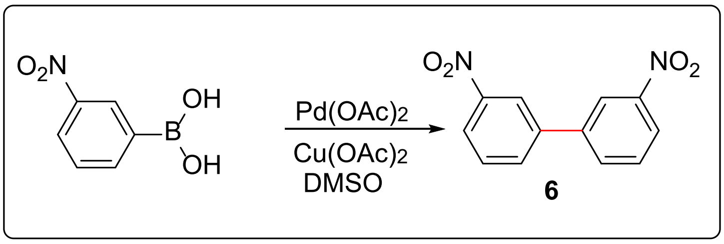
The starting material, 4-bromophenylboronic acid, was subjected to general benchtop homocoupling conditions. The white solid, 4,4-dibromo-1,1-biphenyl, was produced after workup without the need for further purification, (47 mg , quant). ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.56 (d, *J* = 8.5 Hz, 4 H), 7.41 (d, *J* = 8.5 Hz, 4 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 138.6, 131.8, 128.2, 121.7 ppm. Characterization was in agreement with previously reported literature.[2]

Synthesis of 4,4'-diiodo-1,1'-biphenyl, 5



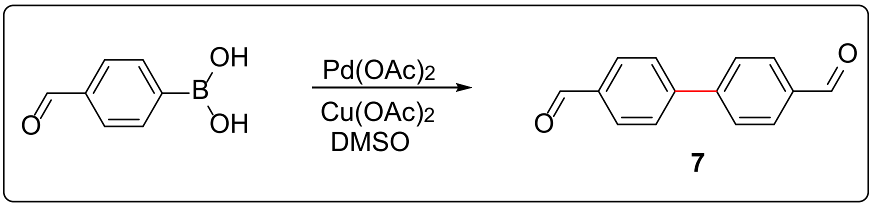
The starting material, 4-iodophenylboronic acid, was subjected to general benchtop homocoupling conditions. The white solid, 4,4'-diiodo-1,1'-biphenyl, was produced after workup without the need for further purification, (39 mg, 65%). ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.76 (d, *J* = 8.5 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 1 H) ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 139.6, 138.0, 128.7, 93.5 Characterization was in agreement with previously reported literature.[2]

Synthesis of 3,3'-dinitro-1,1'-biphenyl, 6



The starting material, 3-nitrophenylboronic acid, was subjected to general benchtop homocoupling conditions. The slightly yellow solid, 3,3'-dinitro-1,1'-biphenyl, was produced after workup without the need for further purification, (34.5 mg, 92% pure by NMR, 85% yield). ^{1}H NMR (400 MHz, acetone) δ = 8.66 - 8.62 (m, 2 H), 8.39 (ddd, *J* = 1.0, 2.3, 8.2 Hz, 2 H), 8.22 (ddd, *J* = 1.0, 1.8, 7.8 Hz, 2 H), 7.90 - 7.84 (m, 2 H); ^{13}C NMR (101MHz, acetone) δ = 141.6, 135.0, 131.9, 124.6, 123.5 ppm. Characterization was in agreement with previously reported literature.[3]

Synthesis of [1,1'-biphenyl]-4,4'-dicarbaldehyde, 7



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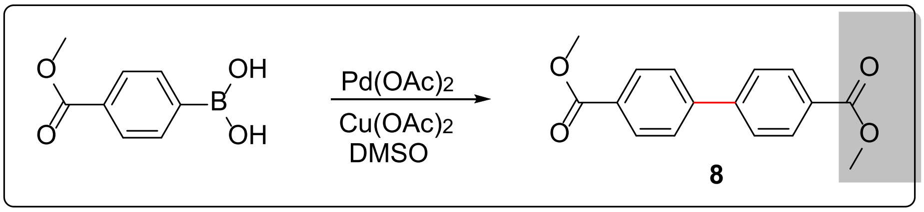
The starting material, (4-formylphenyl)boronic acid, was subjected general benchtop homocoupling conditions. The white solid, [1,1'-biphenyl]-4,4'-dicarbaldehyde, was produced after workup without the need for further purification, (28 mg , 90%). ^{1}H NMR (500MHz ,Acetone) δ = 10.18 (s, 2 H), 8.16 - 8.05 (m, 4 H), 8.02 (d, *J* = 8.2 Hz, 4 H); EI-MS (m/z): 209.1. Characterization was in agreement with previously reported literature.[4]

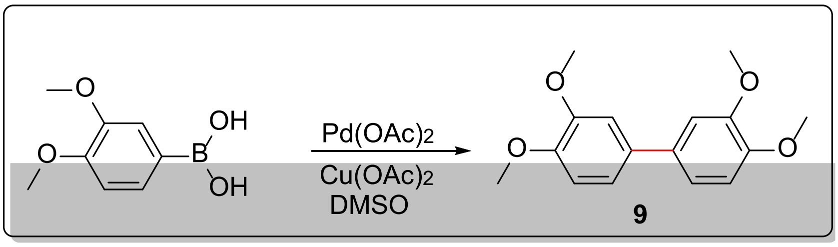
Synthesis of dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate, 8



8

The starting material, (4-(methoxycarbonyl)phenyl)boronic acid, was subjected to general benchtop homocoupling conditions. The white solid, dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate, was produced after workup without the need for further purification, (21.5 mg , 53%). EI-MS (m/z): 270.2. Characterization was in agreement with previously reported literature.[5]

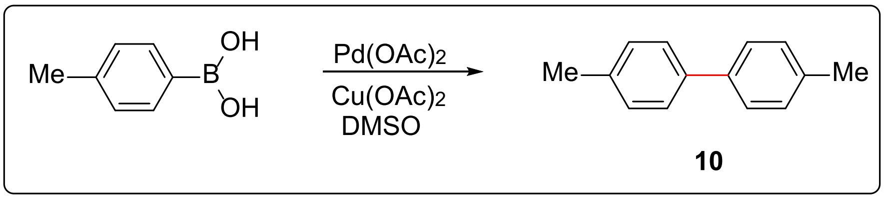
Synthesis of 3,3',4,4'-tetramethoxy-1,1'-biphenyl, 9



9

The starting material, (3,4-dimethoxyphenyl)boronic acid, was subjected to general benchtop homocoupling conditions. The resulting white solid, 3,3',4,4'-tetramethoxy-1,1'-biphenyl, was produced after workup without the need for further purification, (35 mg, 85%). EI-MS (m/z): 274.20. Characterization was in agreement with previously reported literature.[6]

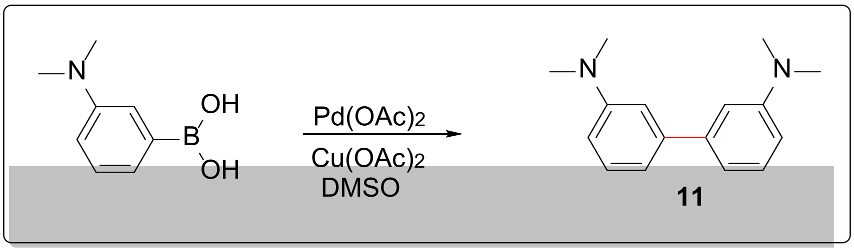
Synthesis of 4,4'-dimethyl-1,1'-biphenyl, 10



10

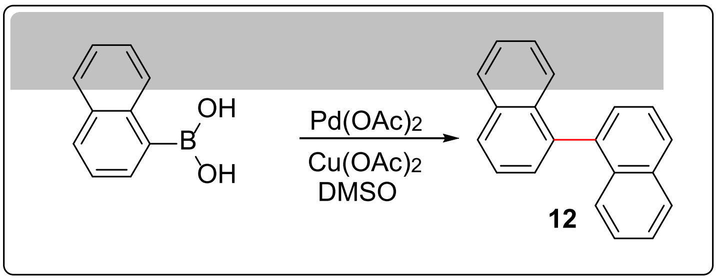
The starting material, 4-methylphenylboronic acid, was subjected to general benchtop homocoupling conditions. The resulting white solid, 4,4'-dimethyl-1,1'-biphenyl, was produced after workup without the need for further purification as a colorless solid, (27 mg, quant). ^{1}H NMR (500MHz , CHLOROFORM-d) δ = 7.49 (dd, J = 4.1, 7.8 Hz, 4 H), 7.29 - 7.10 (m, 4 H), 2.39 (br. s., 6 H); ^{13}C NMR (126MHz , CHLOROFORM-d) δ = 138.0, 136.4, 129.2, 126.5, 20.8 ppm. Characterization was in agreement with previously reported literature.[2]

Synthesis of N^3,N^3,$N^{3'}$,$N^{3'}$-tetramethyl-[1,1'-biphenyl]-4,4'-diamine, 11



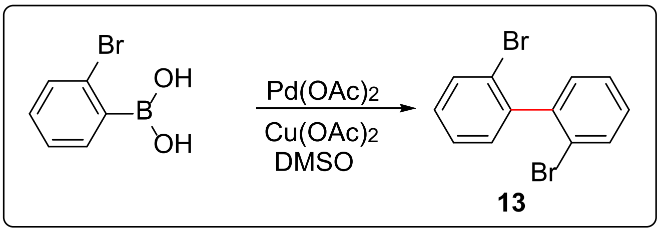
The starting material, (3-(dimethylamino)phenyl)boronic acid, was subjected to general benchtop homocoupling conditions. The resulting tan solid, N^3,N^3,$N^{3'}$,$N^{3'}$-tetramethyl-[1,1'-biphenyl]-3,3'-diamine, was produced after workup without the need for further purification, (33 mg , 90%). ^{1}H NMR (500MHz , CHLOROFORM-d) δ = 7.36 - 7.29 (m, 1 H), 6.99 - 6.90 (m, 2 H), 6.75 (dd, J = 2.0, 9.0 Hz, 1 H), 3.01 (s, 7 H) ^{13}C NMR (126MHz , CHLOROFORM-d) δ = 138.3, 136.7, 129.4, 126.8, 21.1 Characterization was in agreement with previously reported literature.[7]

Synthesis of 1,1'-binaphthalene, 12



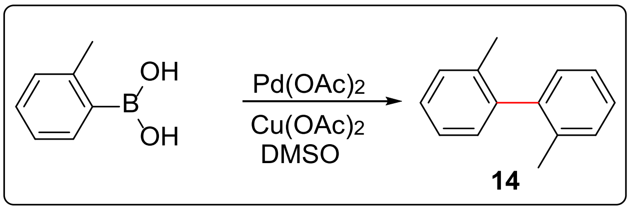
The starting material, naphthalen-1-ylboronic acid, was subjected to the reaction conditions described in the substrate screening protocol. The resulting white solid, 1,1'-binaphthalene, was produced after workup without the need for further purification, (33 mg, 85% pure by NMR, 72% yield). ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.94 (dd, J = 4.6, 8.2 Hz, 2 H), 7.58 (dd, J = 7.0, 8.2 Hz, 1 H), 7.51 - 7.45 (m, 2 H), 7.39 (d, J = 8.2 Hz, 1 H), 7.27 (ddd, J = 1.1, 6.9, 8.2 Hz, 1 H). ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 138.4, 133.5, 132.8, 128.1, 127.9, 127.8, 126.5, 126.4, 126.0, 125.8, 125.8, 125.4, 125.2, 121.5, 126.6, 108.6, 108.0, 41.3 ppm. Characterization was in agreement with previously reported literature.[7]

Synthesis of 2,2'-dibromo-1,1'-biphenyl, 13



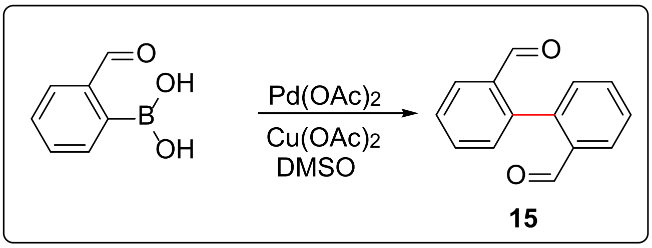
The starting material, 2-bromophenylboronic acid, was subjected to the reaction conditions described in the substrate screening protocol. The resulting white solid, 2,2'-dibromo-1,1'-biphenyl, was produced after workup without the need for further purification, (44 mg , 95%). EI-MS (m/z): 311.88. Characterization was in agreement with previously reported literature.[8]

Synthesis of 2,2'-dimethyl-1,1'-biphenyl, 14



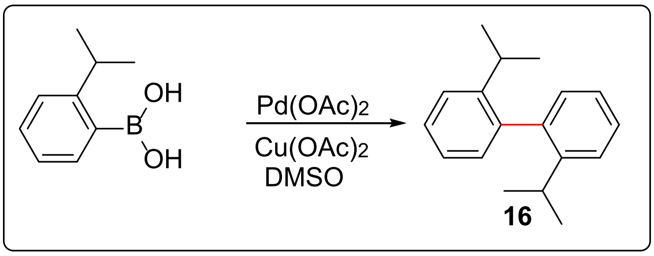
The starting material, 2-methylphenylboronic acid, was subjected to the reaction conditions described in the substrate screening protocol. The resulting white solid, 2,2'-dimethyl-1,1'-biphenyl, was produced after workup without the need for further purification, (27 mg , quant). ^{1}H NMR (500MHz ,Acetone) $\delta = 7.36 - 7.16$ (m, 6 H), 7.12 - 7.01 (m, 2 H), 2.04 (m, 7 H). ^{13}C NMR (126MHz ,Acetone) $\delta = 141.6$, 135.4, 129.8, 129.8, 129.0, 129.0, 127.2, 127.2, 125.6, 125.6, 19.0, 19.0 ppm. Characterization was in agreement with previously reported literature.[7]

Synthesis of [1,1'-biphenyl]-2,2'-dicarbaldehyde, 15



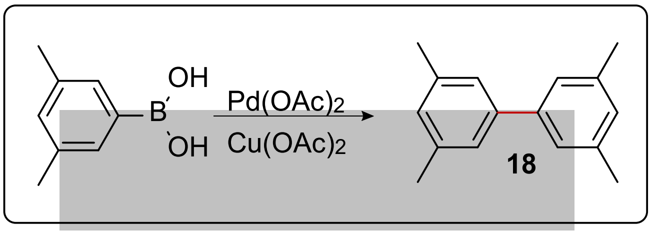
The starting material, 2-formylphenylboronic acid, was subjected to the reaction conditions described in the substrate screening protocol. The resulting white solid, [1,1'-biphenyl]-2,2'-dicarbaldehyde, was produced after workup without the need for further purification, (32 mg, 60% pure by NMR (wet), 60 % yield). ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 10.55 (s, 2 H), 8.02 - 7.93 (m, 2 H), 7.86 (d, J = 7.0 Hz, 2 H), 7.63 - 7.52 (m, 4 H) ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 194.7, 141.3, 135.5, 133.0, 130.8, 127.9, 84.4 Characterization was in agreement with previously reported literature.[9]

Synthesis of 2,2'-diisopropyl-1,1'-biphenyl, 16



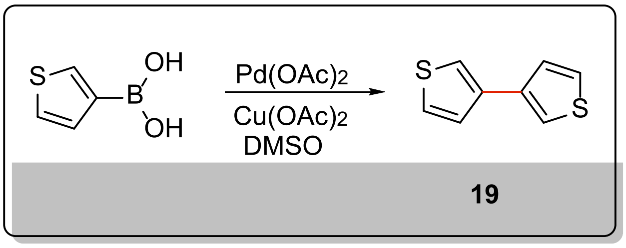
The starting material, 2-isopropylphenylboronic acid, was subjected to general benchtop homocoupling conditions. The resulting white solid, 2,2'-diisopropyl-1,1'-biphenyl, was produced after workup without the need for further purification, (21.4 mg , 60%). EI-MS (m/z): 238.3. Characterization was in agreement with previously reported literature.[10]

Synthesis of 3,3',5,5'-tetramethyl-1,1'-biphenyl, 18



The starting material, 3,5- dimethylphenylboronic acid, was subjected to general benchtop homocoupling conditions. The resulting white solid, 3,3',5,5'-tetramethyl-1,1'-biphenyl, was produced after workup without the need for further purification, (31 mg , quant.). EI-MS (m/z): 210.10. Characterization was in agreement with previously reported literature.[11]

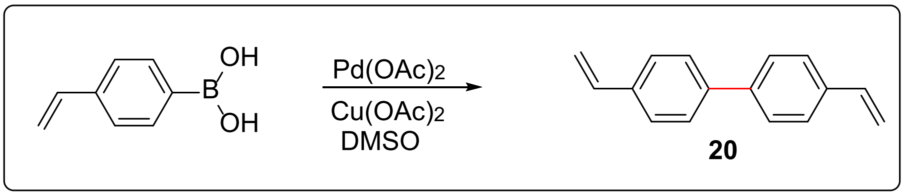
Synthesis of [2,2'-bithiophene]-3,3'-dicarbaldehyde, 19



19

The starting material, 3-thienylboronic acid, was subjected to general benchtop homocoupling conditions. The resulting crude was purified by silica gel chromatography (3:2 EtOAc/hexanes) to produce a white solid **19** (11 mg, 45%). EI-MS (m/z): 165.90 Characterization was in agreement with previously reported literature.[11]

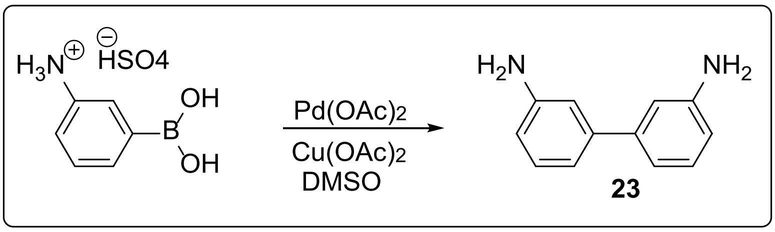
Synthesis of 4,4'-divinyl-1,1'-biphenyl, 20



20

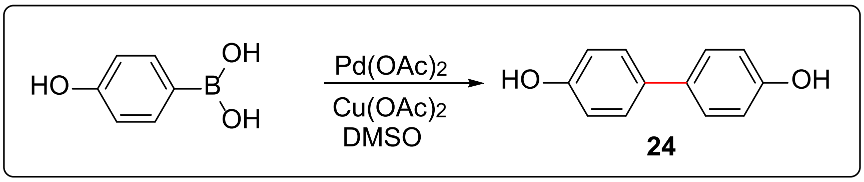
The starting material, 4-vinylphenylboronic acid, was subjected to general benchtop homocoupling conditions. The resulting white solid, 4,4'-divinyl-1,1'-biphenyl, was produced after workup without the need for further purification, (31 mg, quant). EI-MS (m/z): 206.8. Characterization was in agreement with previously published literature.[12]

Synthesis of [1,1'-biphenyl]-3,3'-diamine, 23



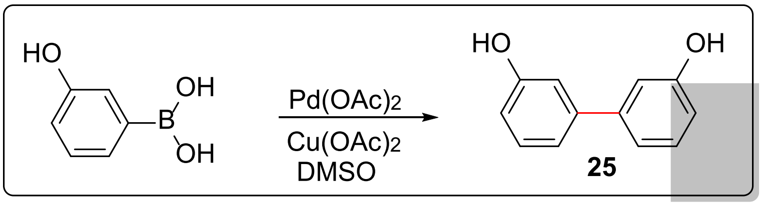
The starting material, 3-boronobenzenaminium hydrogen sulfate salt, was subjected to general benchtop homocoupling conditions. The resulting brown residue, [1,1'-biphenyl]-3,3'-diamine was analyzed for yield by NMR (75%). ^{1}H NMR (500 MHz, CD_3OD_SPE) δ 7.15 (t, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 2.0 Hz, 2H), 6.92 (dt, *J* = 7.5, 1.3 Hz, 2H), 6.73 – 6.67 (m, 2H). ESI-MS (m/z): 186.1; Characterization was in agreement with previously reported literature.[13]

Synthesis of [1,1'-biphenyl]-4,4'-diol, 24



The starting material, 4-hydroxyphenylboronic acid, was subjected to general benchtop homocoupling conditions. The resulting white solid, [1,1'-biphenyl]-4,4'-diol, was produced after workup without the need for further purification, (27 mg , 95%). ^{1}H NMR (500MHz ,Acetone) δ = 7.41 (d, *J* = 8.9 Hz, 5 H), 6.89 (d, *J* = 8.9 Hz, 4 H); ^{13}C NMR (126MHz ,Acetone) δ = 206.4, 157.3, 133.4, 128.3, 116.5 ppm. Characterization was in agreement with previously reported literature.[14]

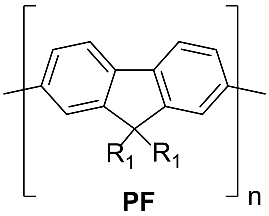
Synthesis of [1,1'-biphenyl]-3,3'-diol, 25



The starting material, (3-hydroxyphenyl) boronic acid, was subjected to general benchtop homocoupling conditions. The resulting white solid, 1,1'-biphenyl]-3,3'-diol, was produced after workup without the need for further purification, (25 mg, 90%). ESI-MS (M^{-H}): 185.1. Characterization was in agreement with previously reported literature. [15]

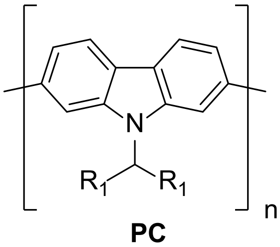
General Polymerization conditions:

All polymerization reactions were performed at room temperature and open to air unless otherwise noted. All starting monomers, $Pd(OAc)_2$ and $Cu(OAc)_2$ were purchased from Aldrich and used as received. Solvents were purchased from Fisher Scientific and used without further purification. ^{1}H NMR spectra were measured on a Bruker Avance 400 MHz instrument. Number average molecular weight (Mn) and polydispersity (Đ) were determined by gel permeation chromatography (GPC) using a Waters pump with a Waters 2410 refractive index detector. THF was used as an eluent at 35 °C with a flow rate of 1.0 mL min^{-1}. The instrument was calibrated with polystyrene standards and data were analyzed using Breeze software.



Poly (9,9-Dioctylfluorene) (PF), 26

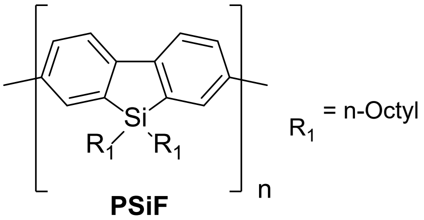
9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (100 mg, 0.179 mmol), Pd(OAc)$_2$ (2.4 mg, 0.011 mmol), Cu(OAc)$_2$ (3.2 mg, 0.0179 mmol) and boric acid (55 mg, 0.895 mmol) were added to a 10 mL reaction vessel equipped with a stir bar followed by DMSO (2 mL). Then the reaction vessel was covered with a Kimwipe and stir at room temperature for 48 h. The reaction mixture was precipitated in methanol (20 mL) to give and light yellow precipitate. The resulting precipitate was filtered through a cellulose thimble, and subjected to Soxhlet extraction with methanol, acetone, and chloroform. The solvent was removed to yield a greenish-yellow polymer (45 mg, 65%). ^{1}H NMR (400 MHz, CDCl$_3$, δ) 7.66-7.86 (m, broad, 6H), 2.11 (t, broad, 4H), 1.09-1.26 (m, broad, 28H), 0.73 (t, broad, 6H). Mn = 7.9 kDa and (Đ) = 2.2.



Poly (9-(9-Heptadecanyl)-9*H*-carbazole) (PC), 27

9-(9-Heptadecanyl)-9H-carbazole-2,7-diboronic acid bis(pinacol) ester (200 mg, 0.30 mmol), Pd(OAc)$_2$ (3.4 mg, 0.015 mmol), Cu(OAc)$_2$ (5.5 mg, 0.03 mmol) and boric acid (56.4 mg, 0.9 mmol) were added to a 10 mL reaction vessel equipped with a stir bar followed by DMSO (4 mL). Then the reaction vessel was covered with a Kimwipe and stir under room temperature for 48h. The reaction mixture was precipitated in methanol (40 mL) to give off white precipitate. The resulting precipitate was filtered through a cellulose thimble, and subjected to

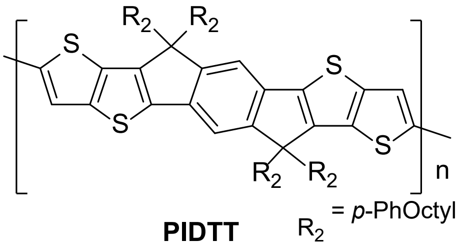
Soxhlet extraction with methanol, acetone, and chloroform. The solvent was removed to yield a greenish-brown polymer (20 mg, 16 %). ^{1}H NMR (400 MHz, CDCl3, δ) 7.62-8.28 (m, broad, 6H), 1.15-1.29 (m, broad, 28H), 0.81 (m, broad, 6H); Mn = 6.54 kDa and (Đ) = 1.4.



PSiF

Poly (9,9-Dioctyl-9*H*-9-silafluorene) (PSiF*), 28*

9,9-Dioctyl-9H-9-silafluorene-2,7-bis(boronic acid pinacol ester) (200 mg, 0.30 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), $Cu(OAc)_2$ (5.4 mg, 0.03 mmol) and boric acid (55.6 mg, 0.9 mmol) were added to a 10 mL reaction vessel equipped with a stir bar followed by DMSO (4 mL). Then the reaction vessel was covered with a Kimwipe and stir under room temperature for 48h. The reaction mixture was precipitated in methanol (40 mL) to give off white precipitate. The resulting precipitate was filtered through a cellulose thimble, and subjected to Soxhlet extraction with methanol, acetone, and chloroform. The solvent was removed to yield a greenish-brown polymer (20 mg, 16%). ^{1}H NMR (400 MHz, CDCl3, δ) 7.73-8 (m, broad, 6H), 1.18-1.29 (m, broad, 28H), 0.84 (m, broad, 6H); Mn = 4.90 kDa and (Đ) = 1.8.



PIDTT

Poly(6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydro-dithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene) (PIDTT), 29

6,12-Dihydro-6,6,12,12-tetrakis(4-octylphenyl)-2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan -2-yl)dithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene (200 mg, 0.14

mmol), $Pd(OAc)_2$ (1.6 mg, 0.007 mmol), $Cu(OAc)_2$ (2.6 mg, 0.015 mmol) and boric acid (26.8 mg, 0.43 mmol) were added to a 10 mL reaction vessel equipped with a stir bar followed by DMSO (4 mL) was added to the reaction mixture. Then the reaction vessel was covered with a Kimwipe and stir under room temperature for 48h. The reaction mixture was precipitated in methanol (40 mL) to give off white precipitate. The resulting precipitate was filtered through a cellulose thimble, and subjected to Soxhlet extraction with methanol, acetone, and chloroform. The solvent was removed to yield a dark red polymer (35 mg, 22 %). ^{1}H NMR (400 MHz, CDCl3, δ). 7.37-7.46 (s, broad, 2H), 7.22-7.29 (s, broad, 2H) 6.96-7.15 (m, broad, 16H), 1.07-1.31(m, broad, 56H) 0.78 (m, broad, 12H); ^{13}C NMR (100 MHz, CDCl3, δ) 142.3, 142.1, 140.6, 140.3, 140.2, 140.1, 129.0, 128.9, 128.9, 128.8, 128.4, 128.2, 35.9, 32.2, 31.6, 30.0, 29.8, 29.6, 23, 14.5; Mn = 4.64 kDa and (Đ) = 2.1.

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Table S3. Table of polymer characterization results

Polymer	M_n* (kDa)	M_w* (kDa)	Đ*	Isolate Yield (%)
PF	7.9	17.4	2.2	65
PC	6.5	8.8	1.4	16
PSiF	4.9	7.1	1.8	16
PIDTT	4.6	9.7	2.1	22

*The number-average molecular weight and the PDI were measured by GPC on polystyrene standards.

NMR Spectrum

Figure S2

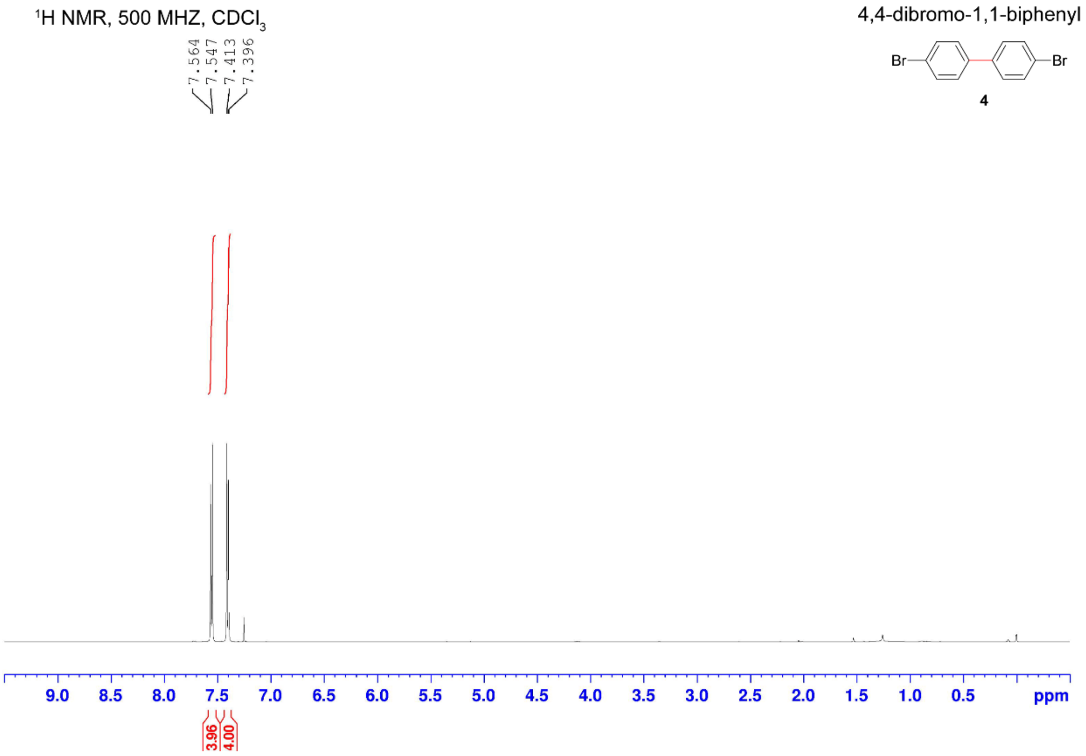
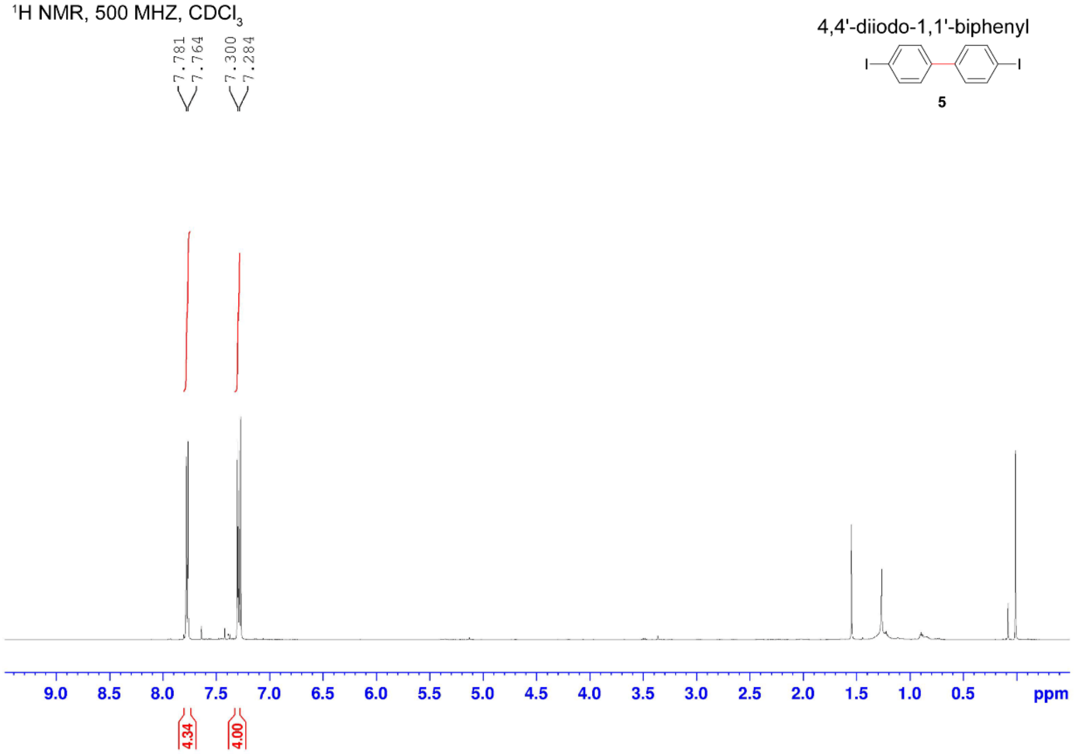


Figure S3



^{1}H NMR, 500 MHZ, $CDCl_3$
7.781
7.764
7.300
7.284
4,4'-diiodo-1,1'-biphenyl
I
I
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.34
4.00

Figure S4

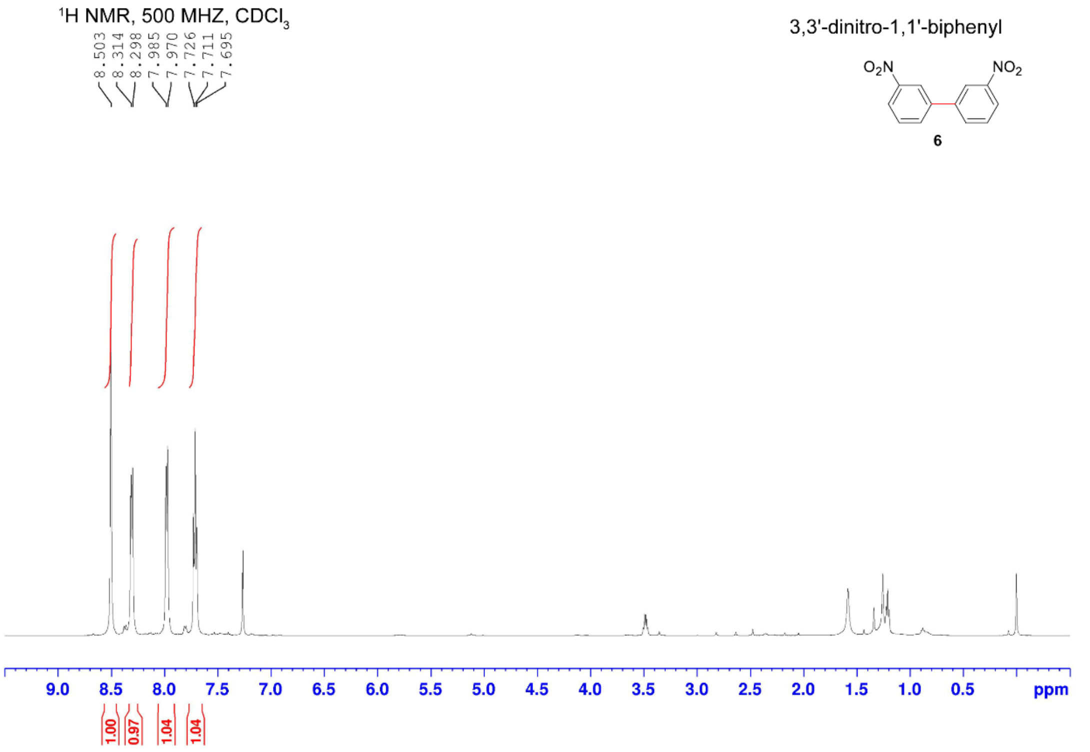


Figure S5

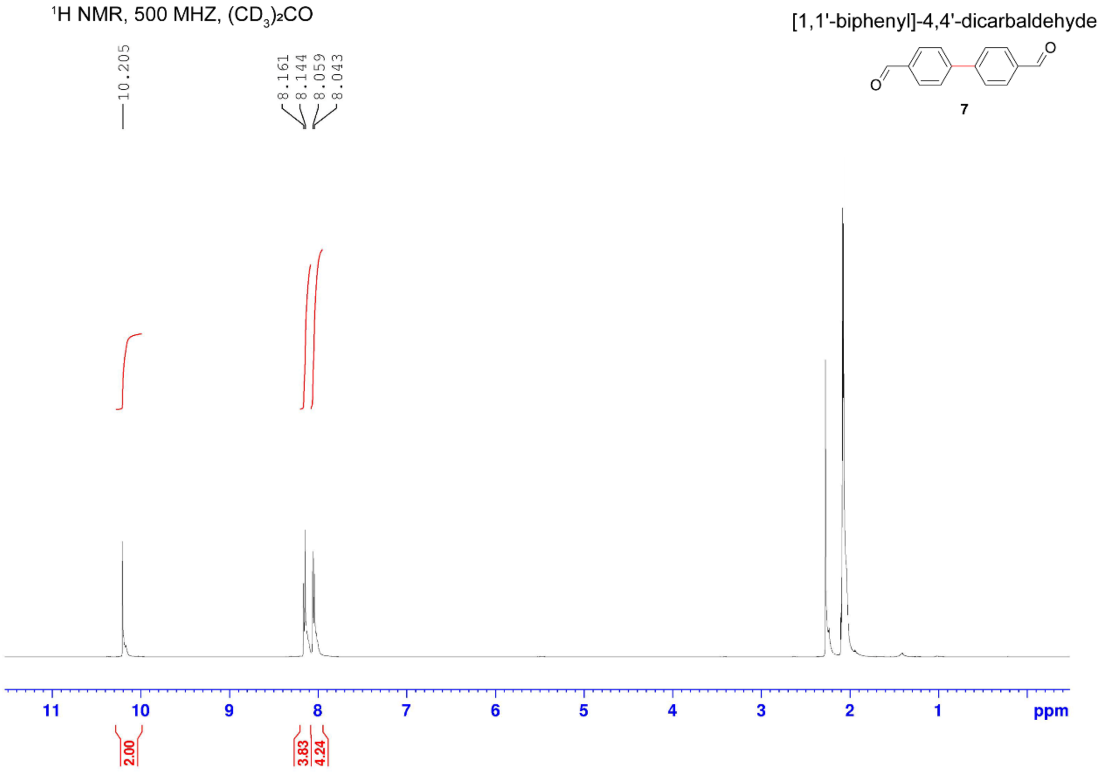


Figure S6

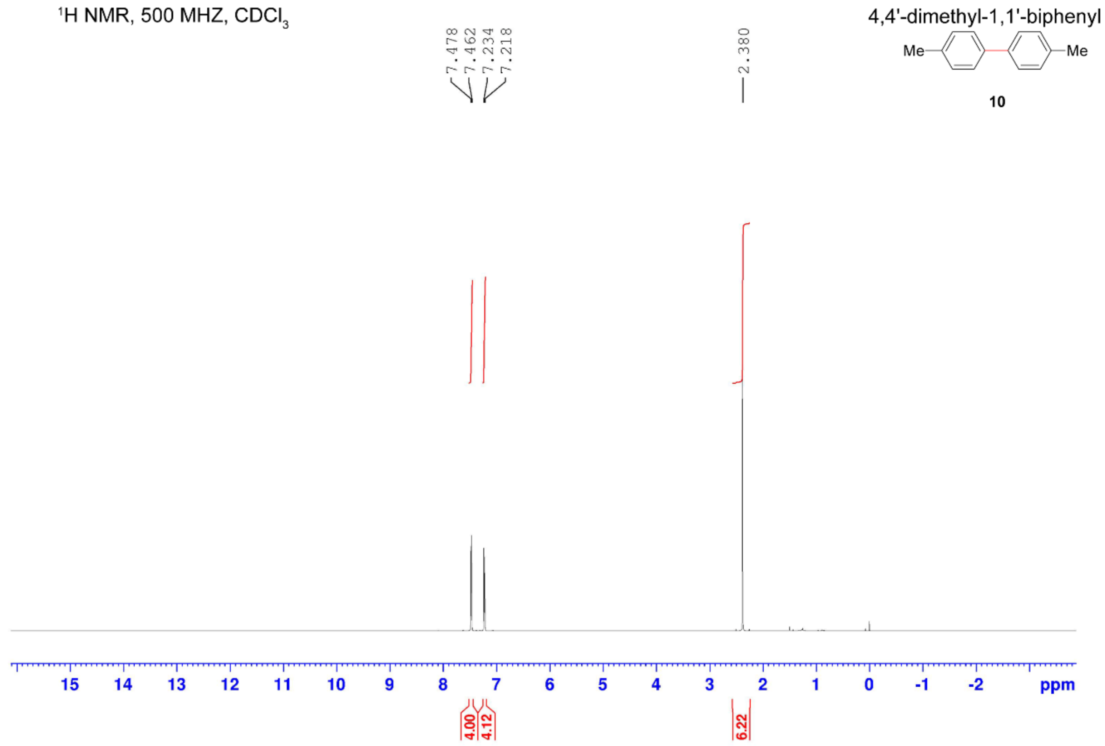


Figure S7

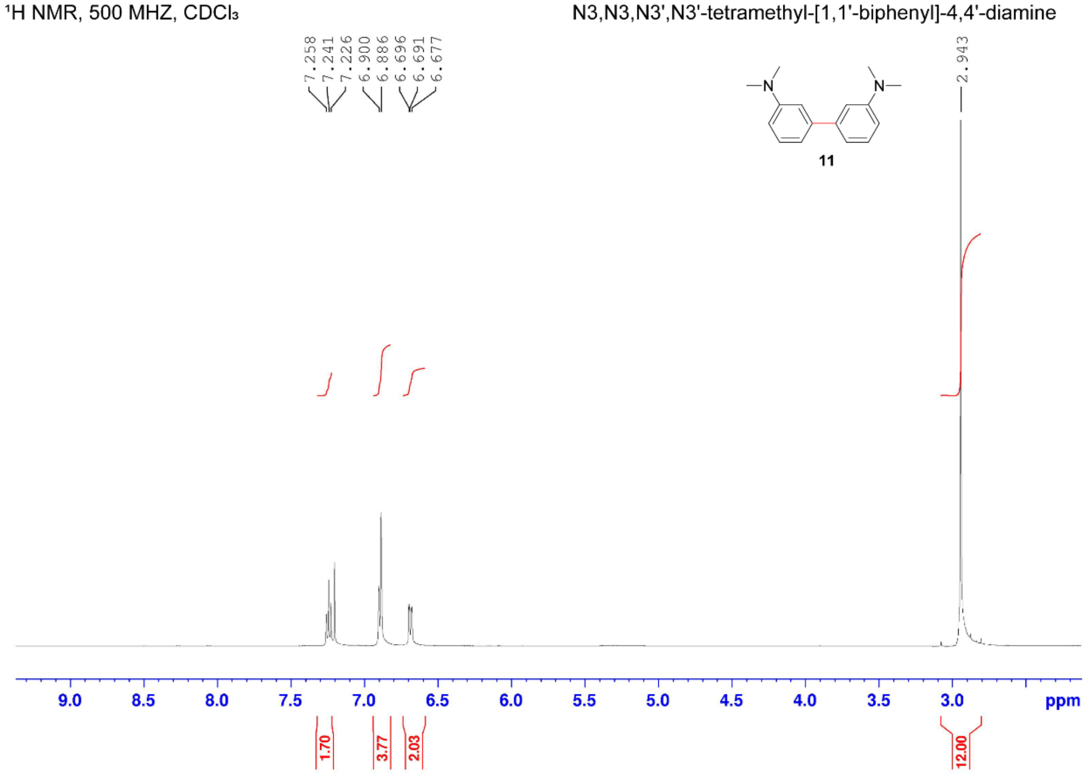
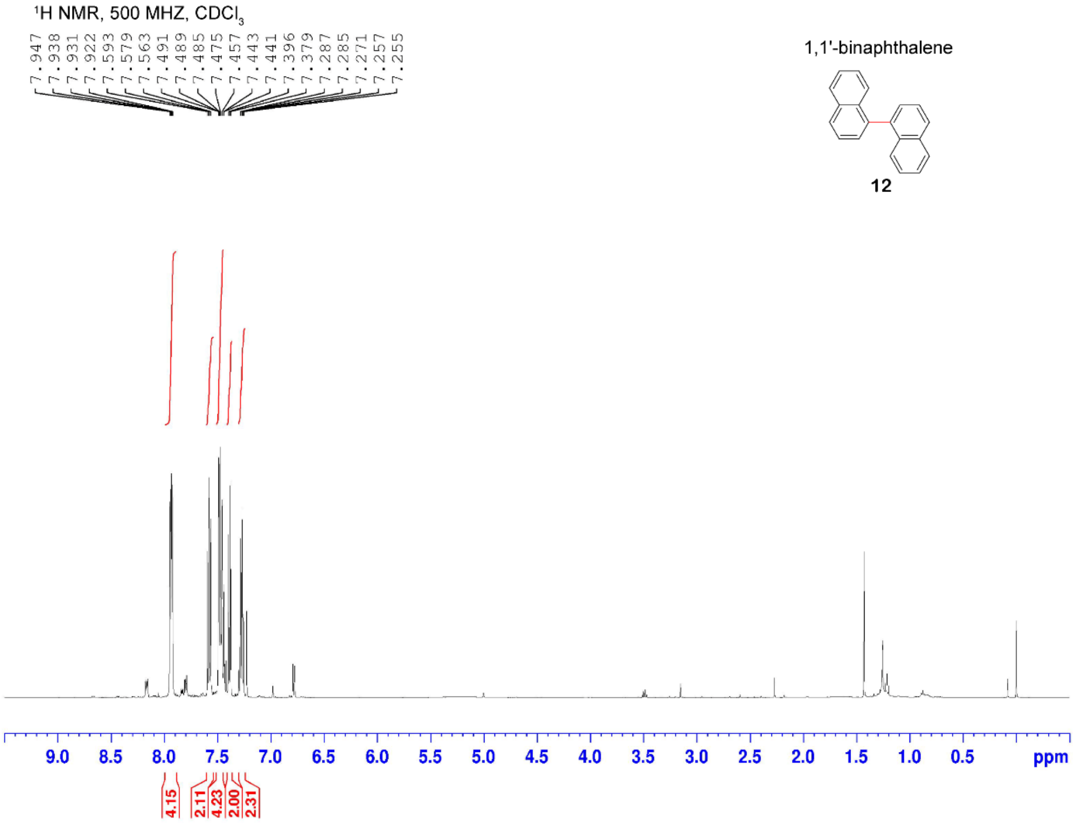


Figure S8



1,1'-binaphthalene

12

Figure S9

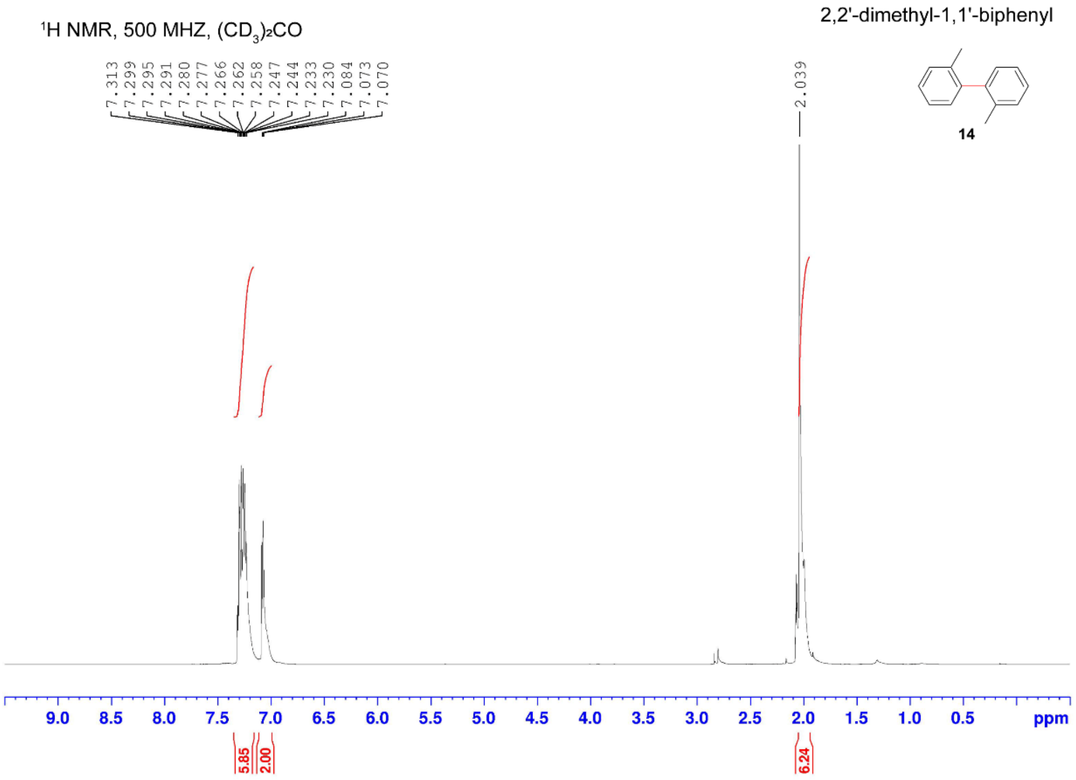


Figure S10

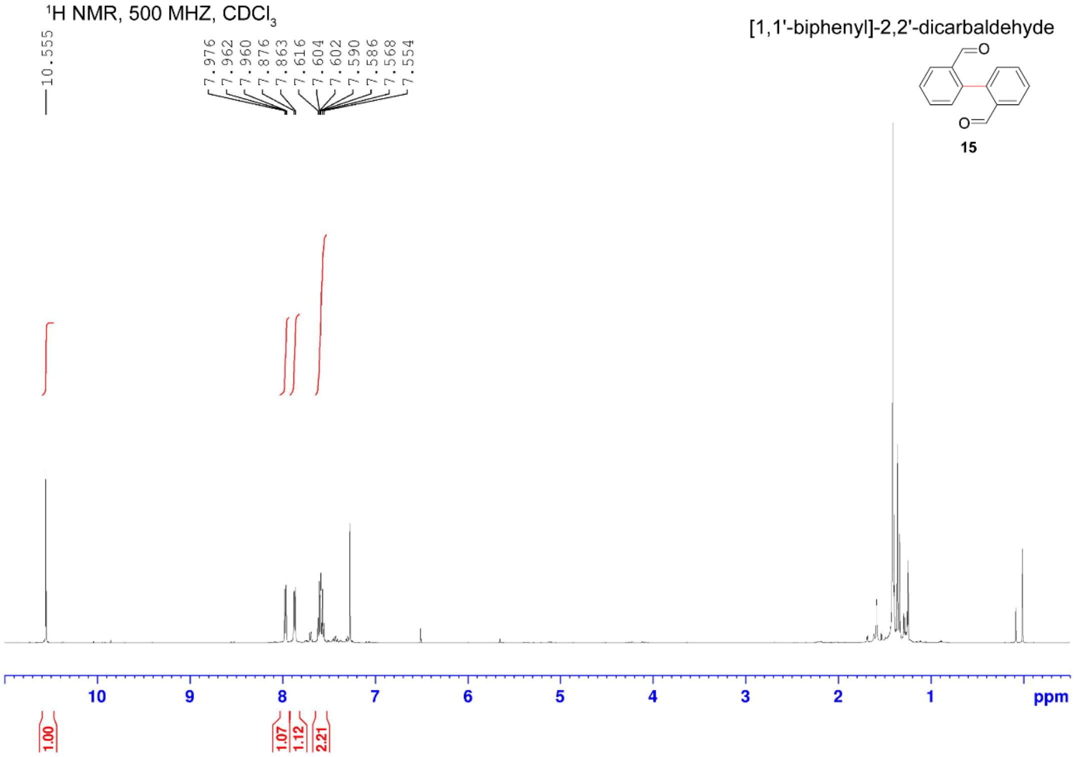


Figure S11

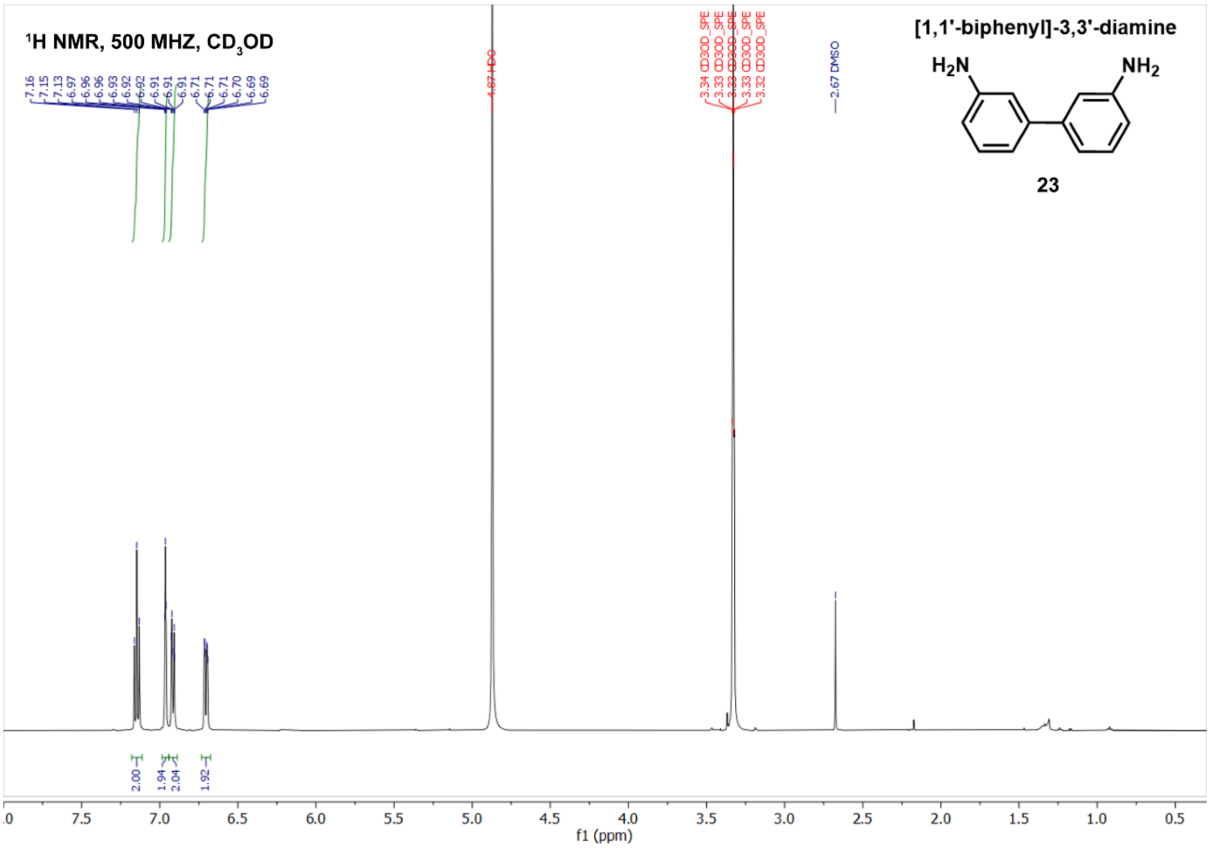


Figure S12

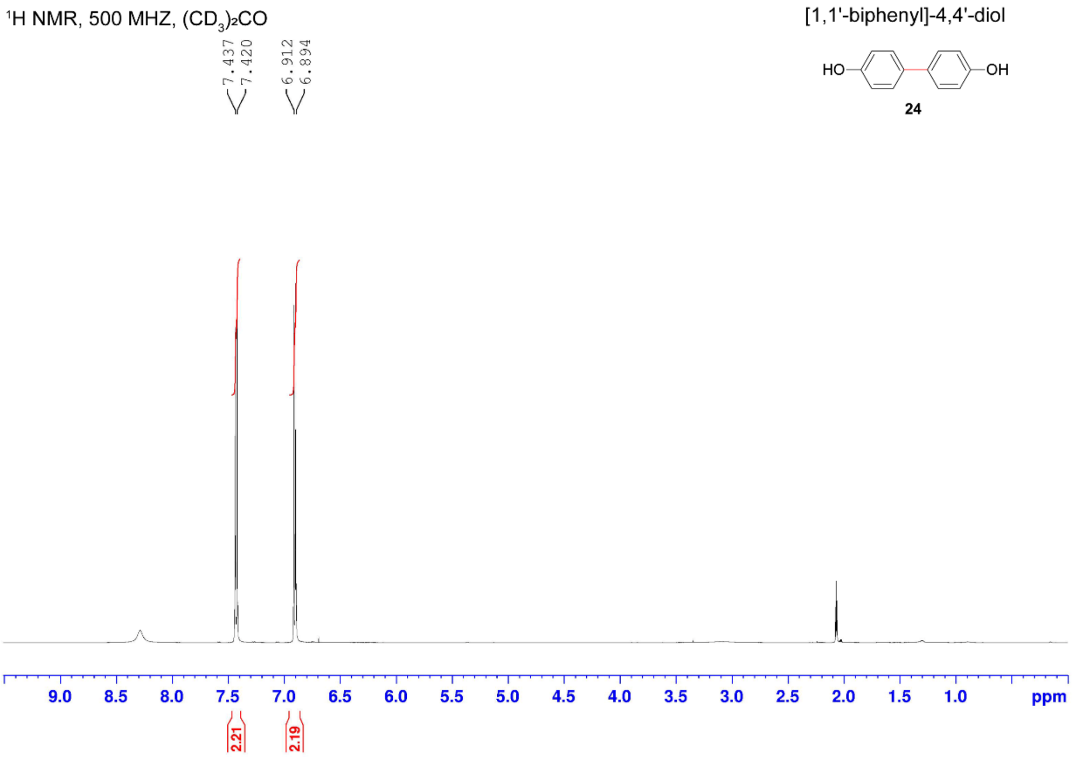


Figure S13. ^{1}H NMR of PF, 400 MHZ, $CDCl_3$

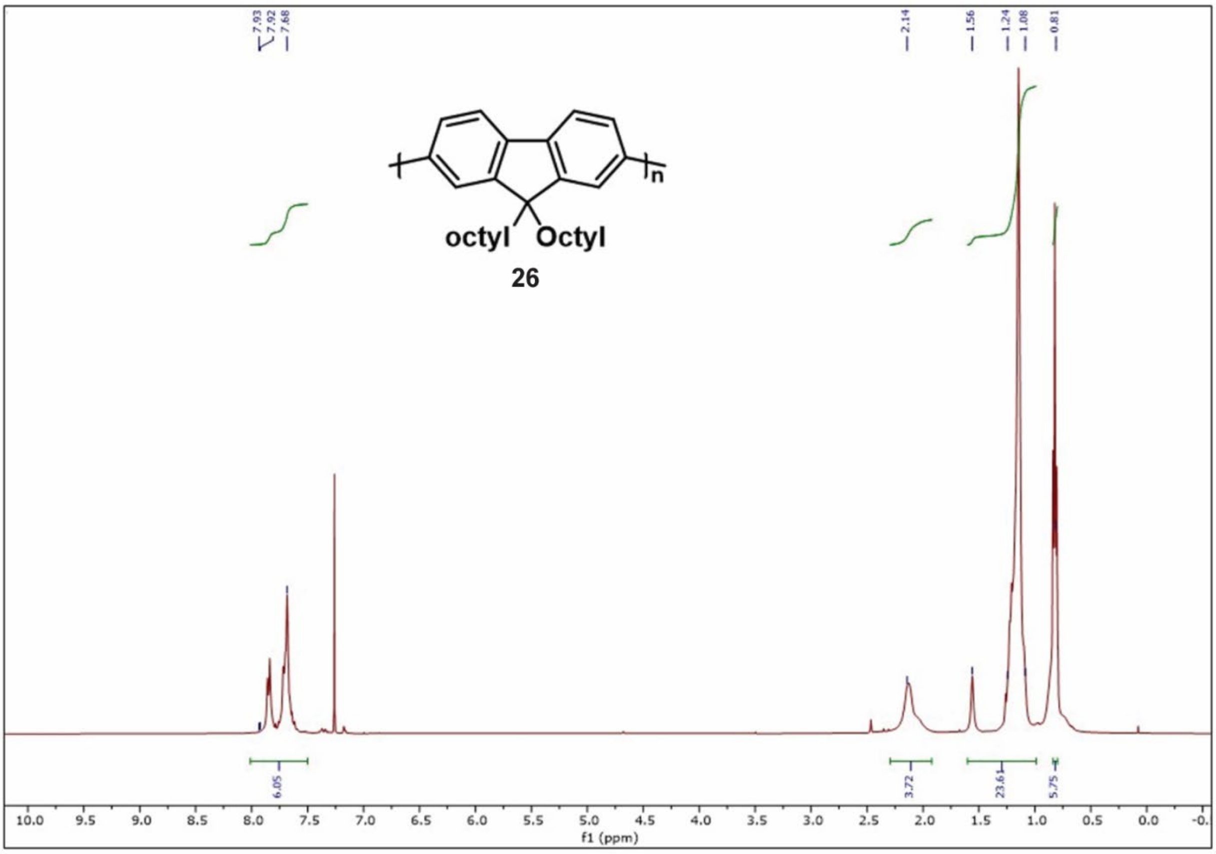


Figure S14. ^{1}H NMR of PC, 400 MHZ, CDCl$_3$

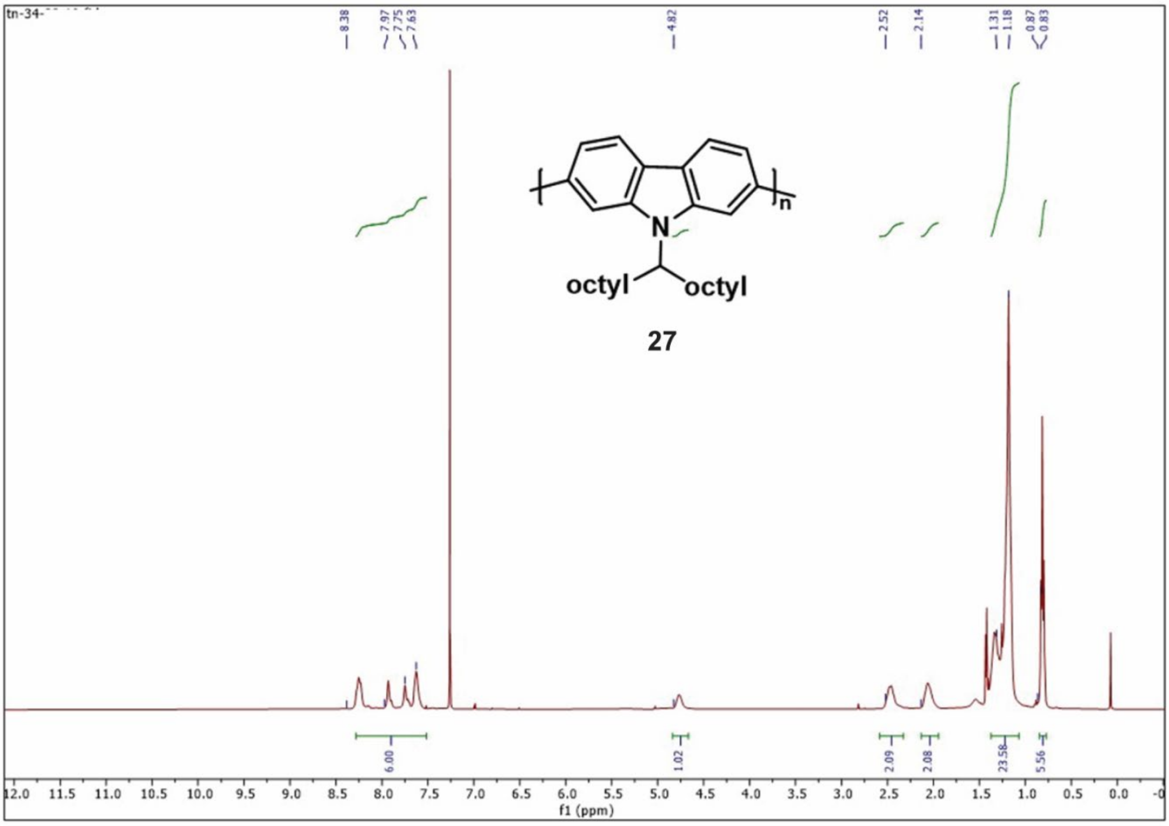


Figure S15 ^{1}H NMR of PSiF, 400 MHZ, CDCl$_3$

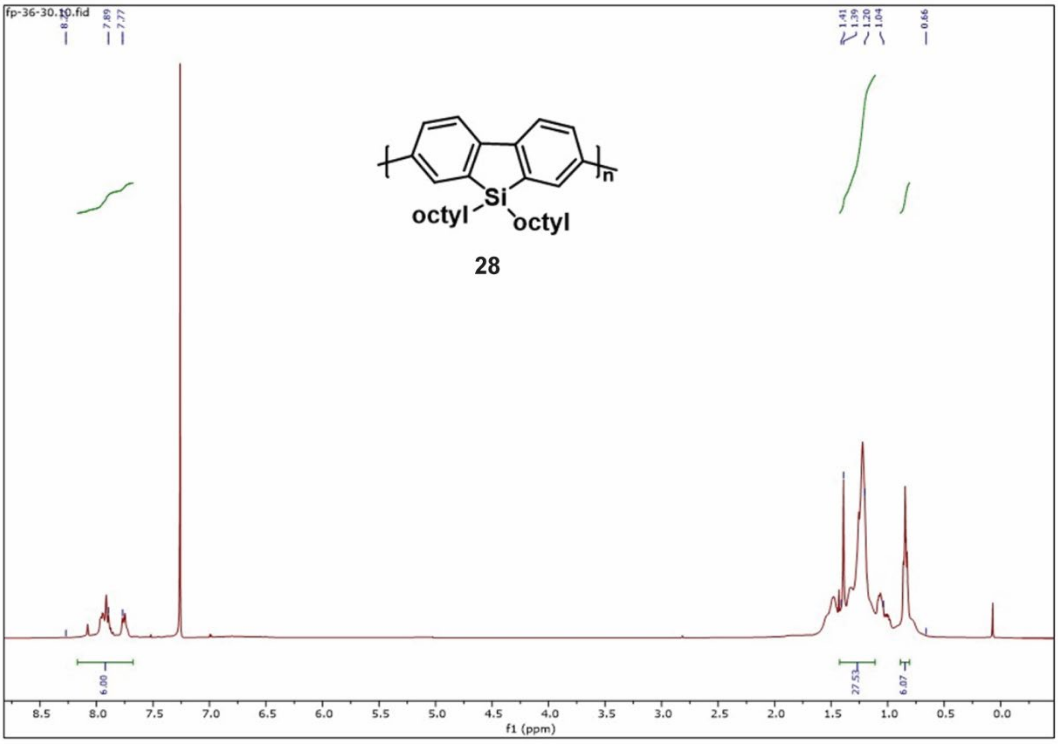


Figure S16. ^{1}H NMR of PIDTT, 400 MHZ, $CDCl_3$

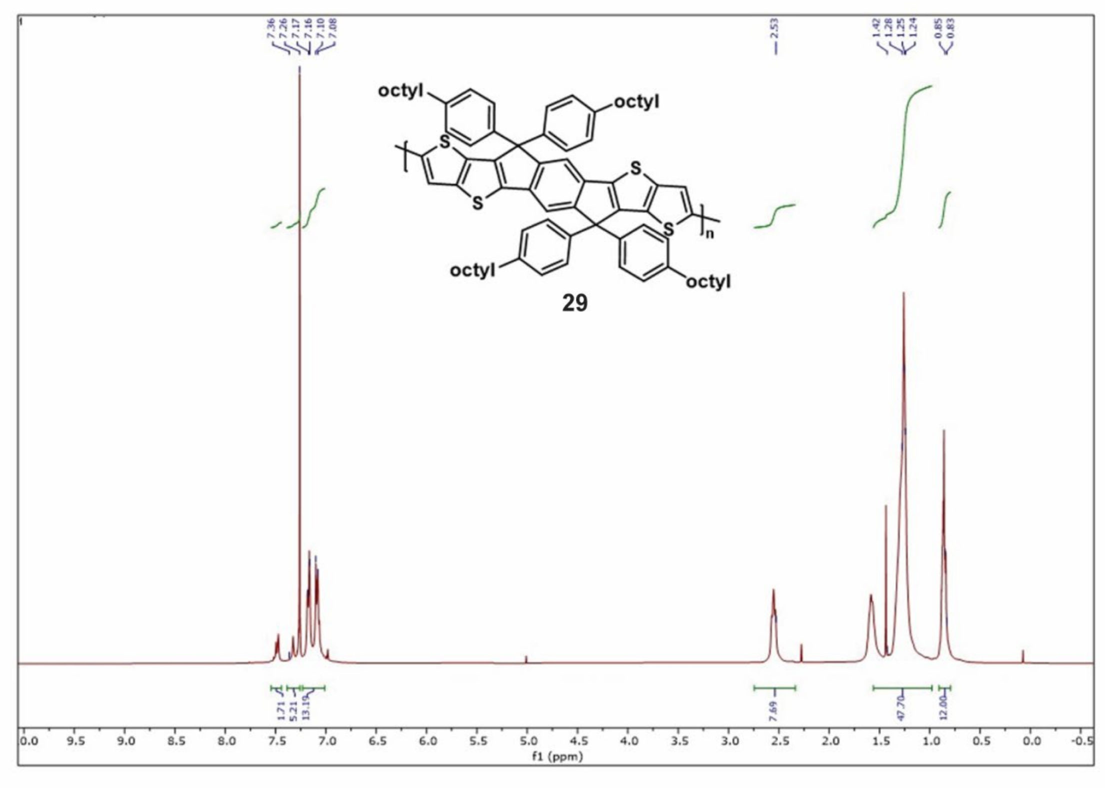
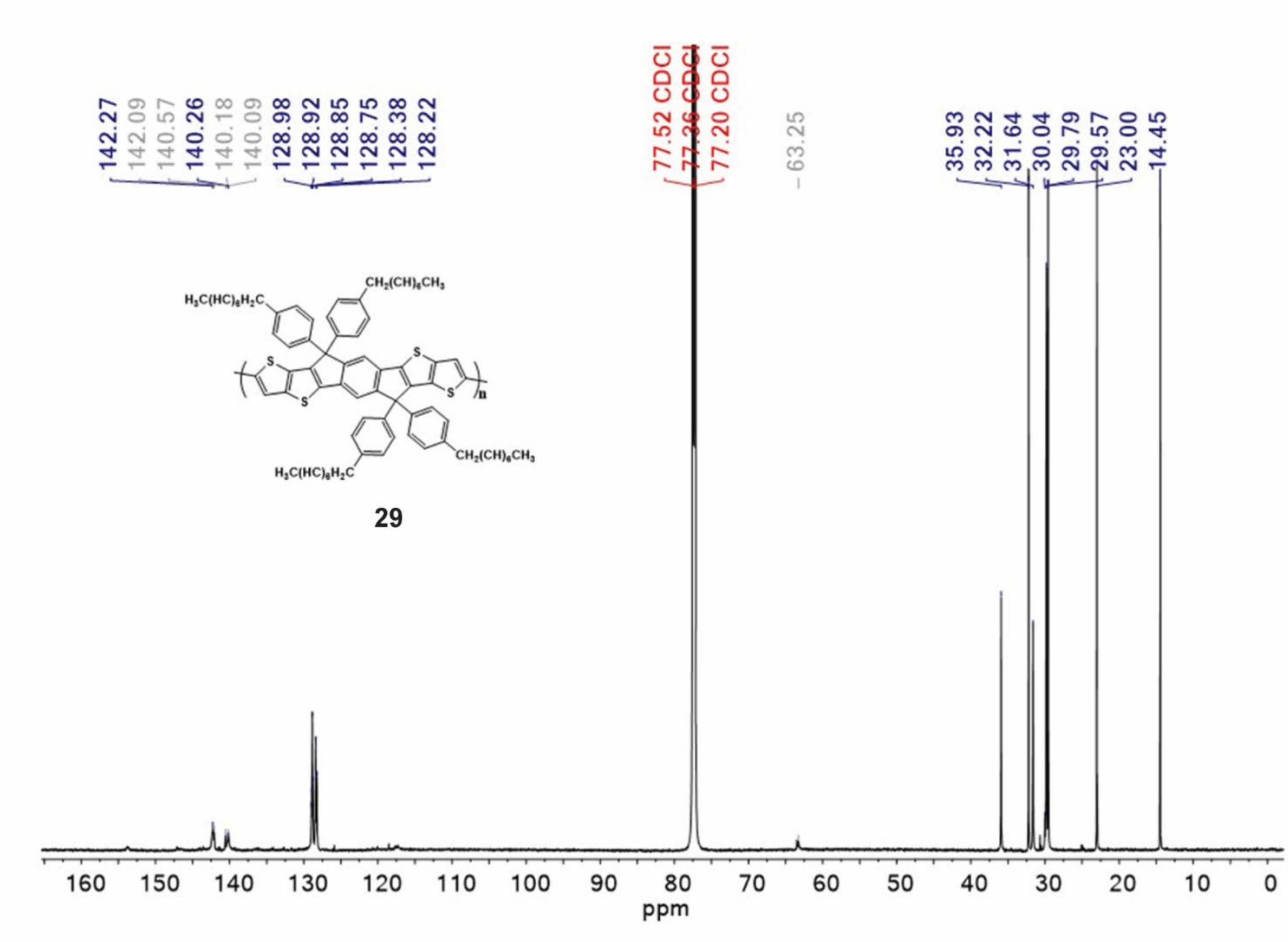


Figure S17. ^{13}C NMR of PIDTT, 100 MHZ, $CDCl_3$



GC-MS Spectrum

Figure S18. GC-MS or compounds 2 and 3 gas chromatograph (top) mass spectrum (bottom)

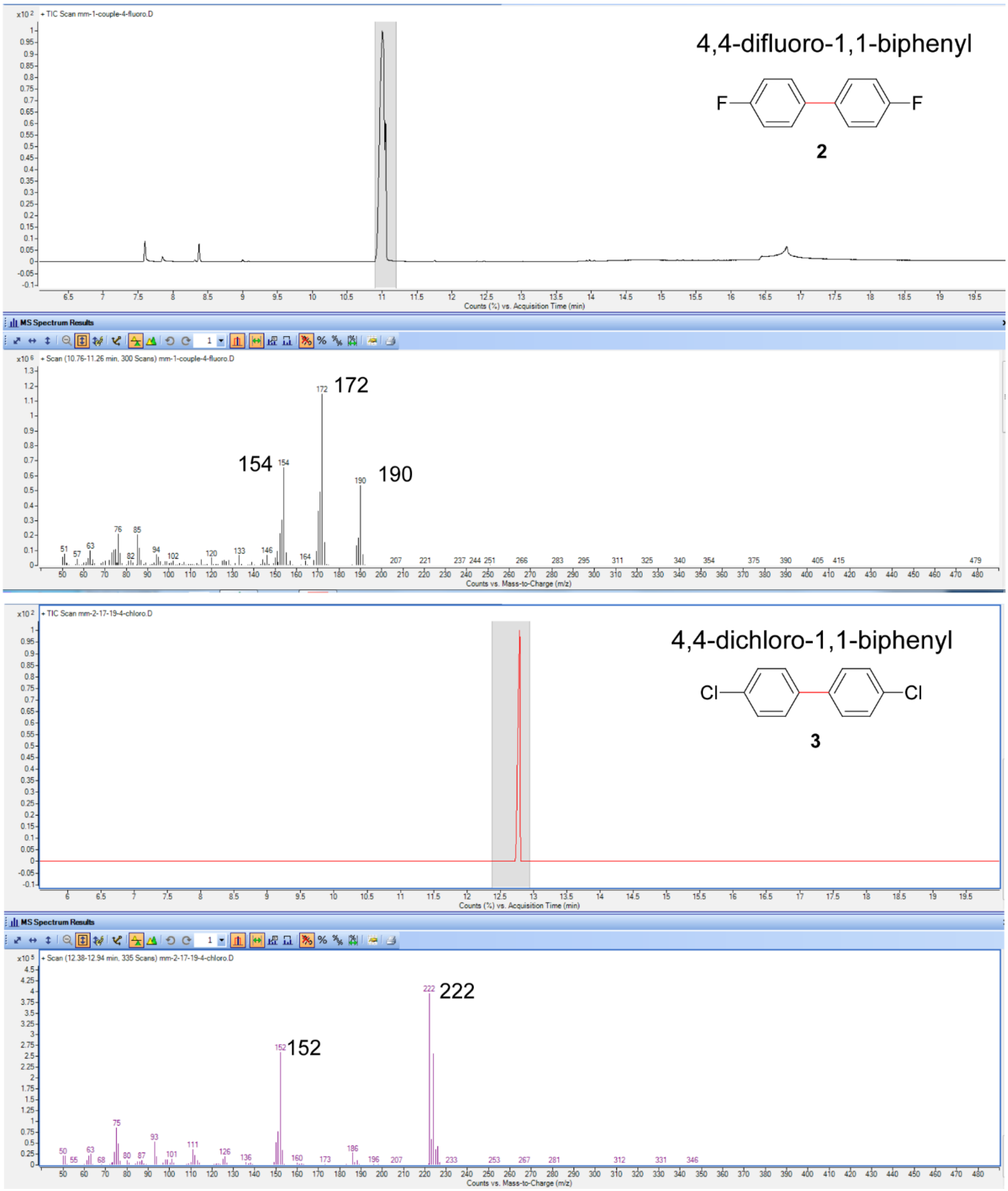
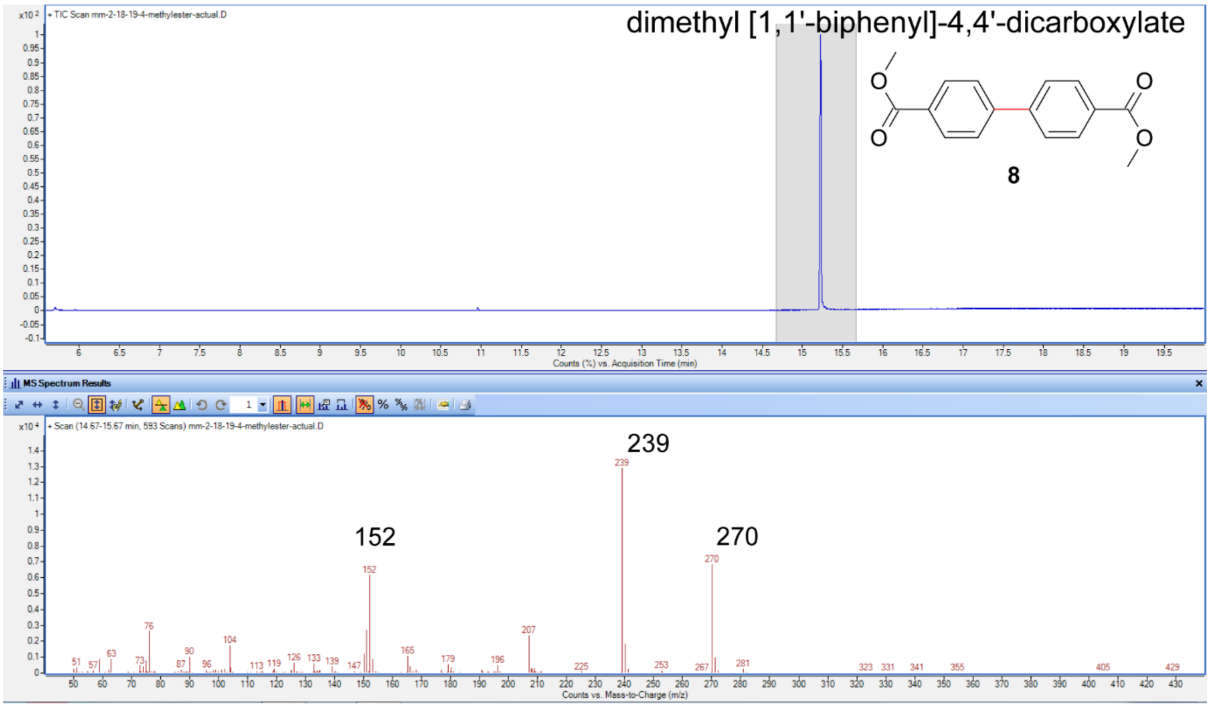


Figure S19 GC-MS or compounds 2 and 3 gas chromatograph (top) mass spectrum (bottom)



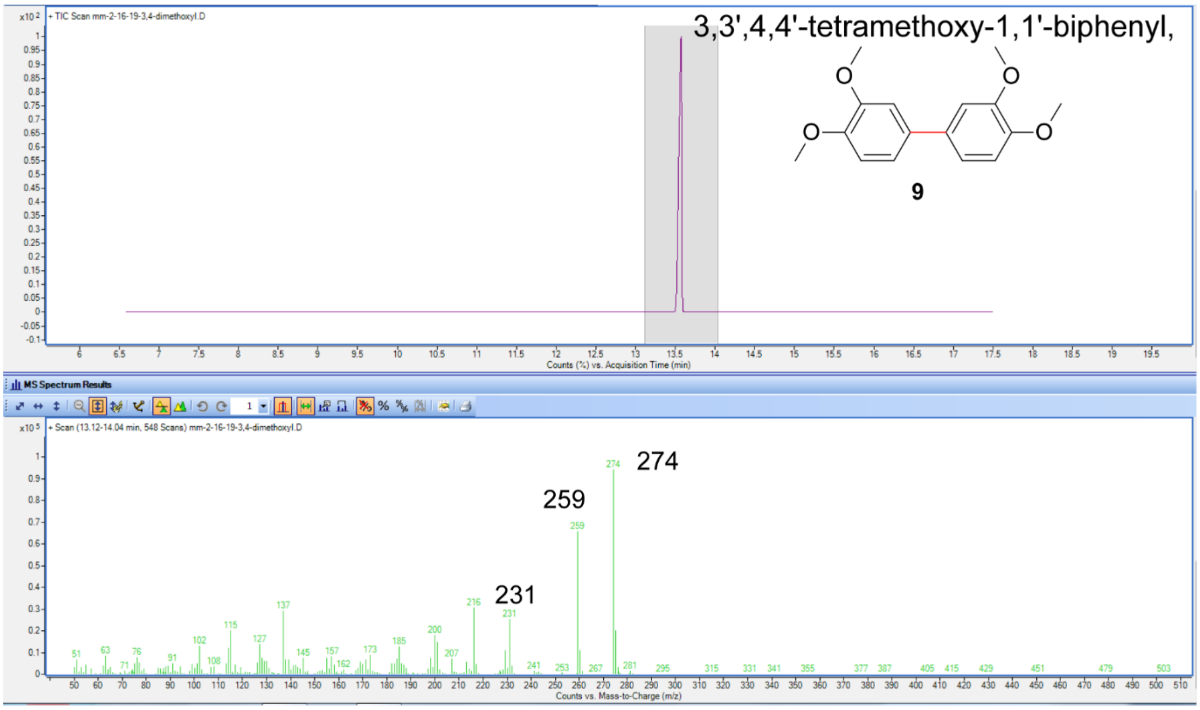


Figure 20. **GC-MS or compounds 13 and 16 gas chromatograph (top) mass spectrum (bottom)**

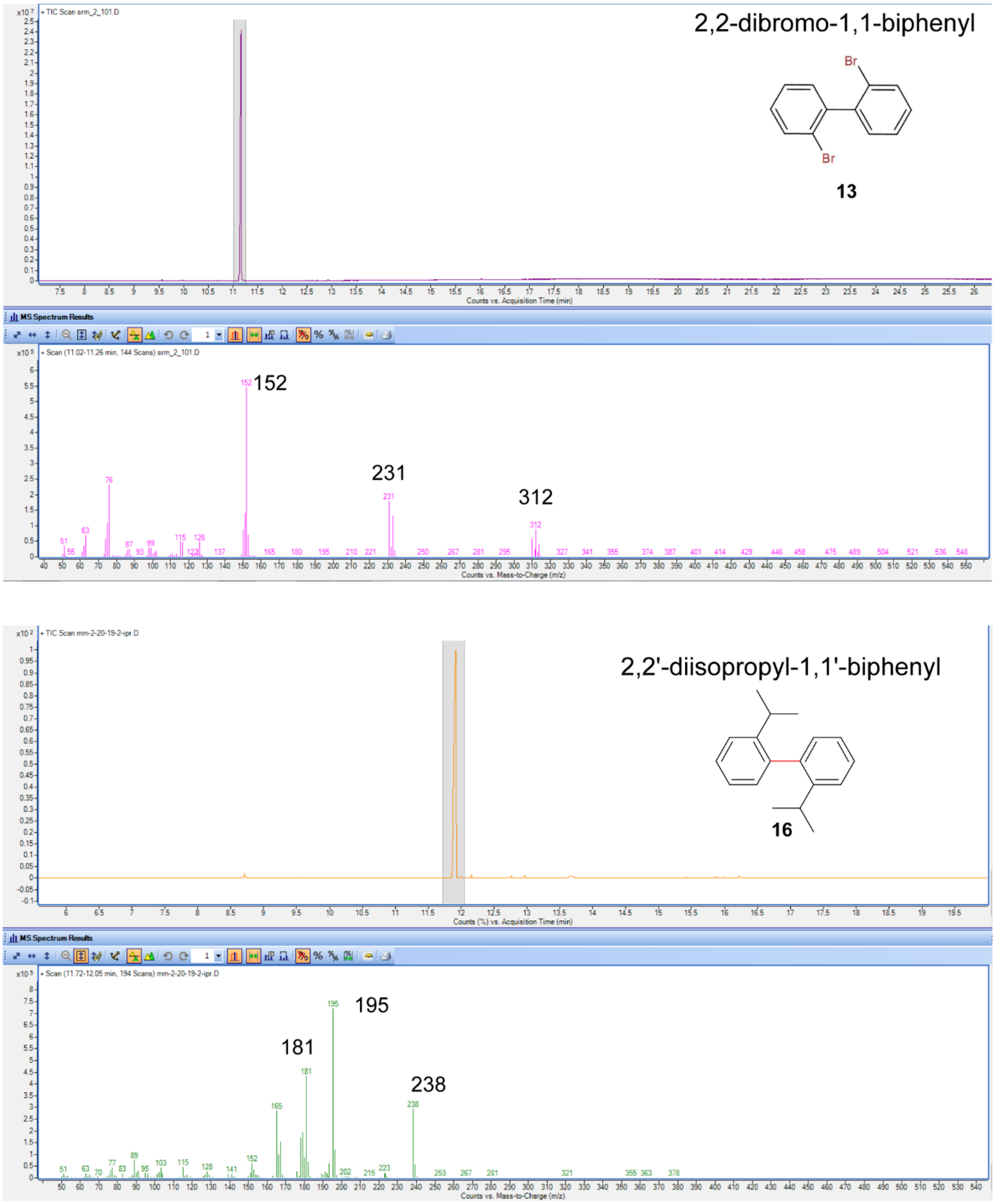


Figure S21. GC-MS or compound 18 gas chromatograph (top) mass spectrum (bottom)

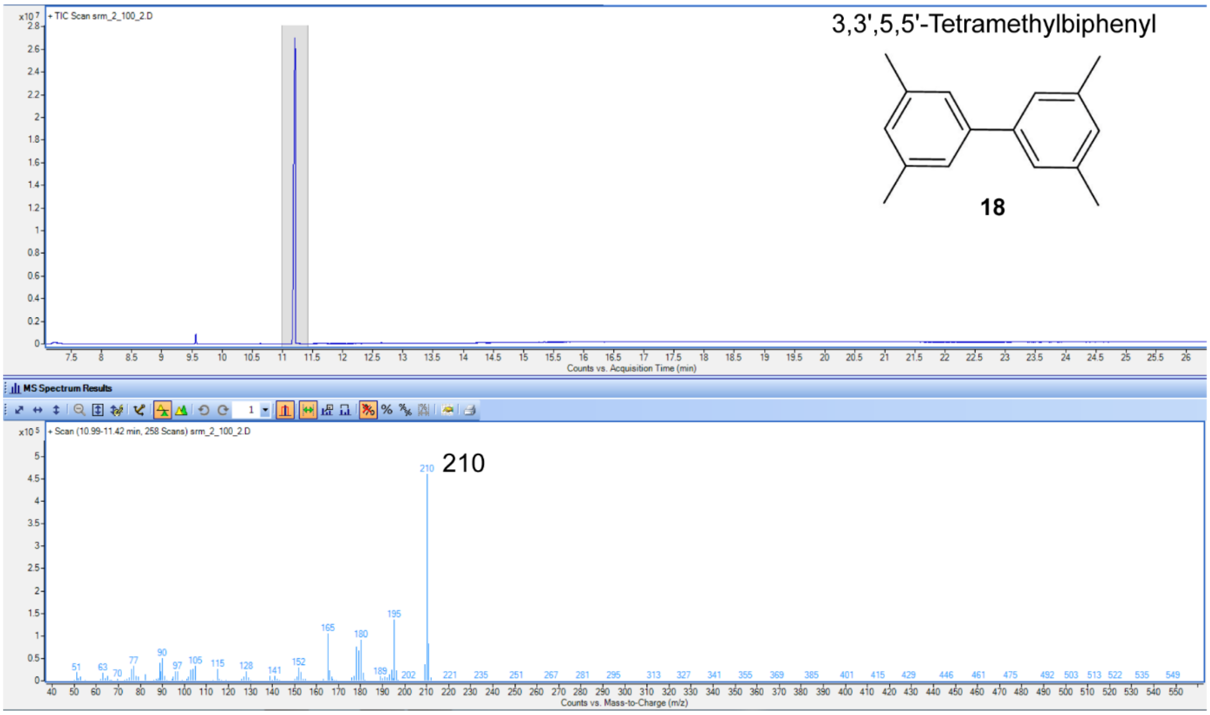
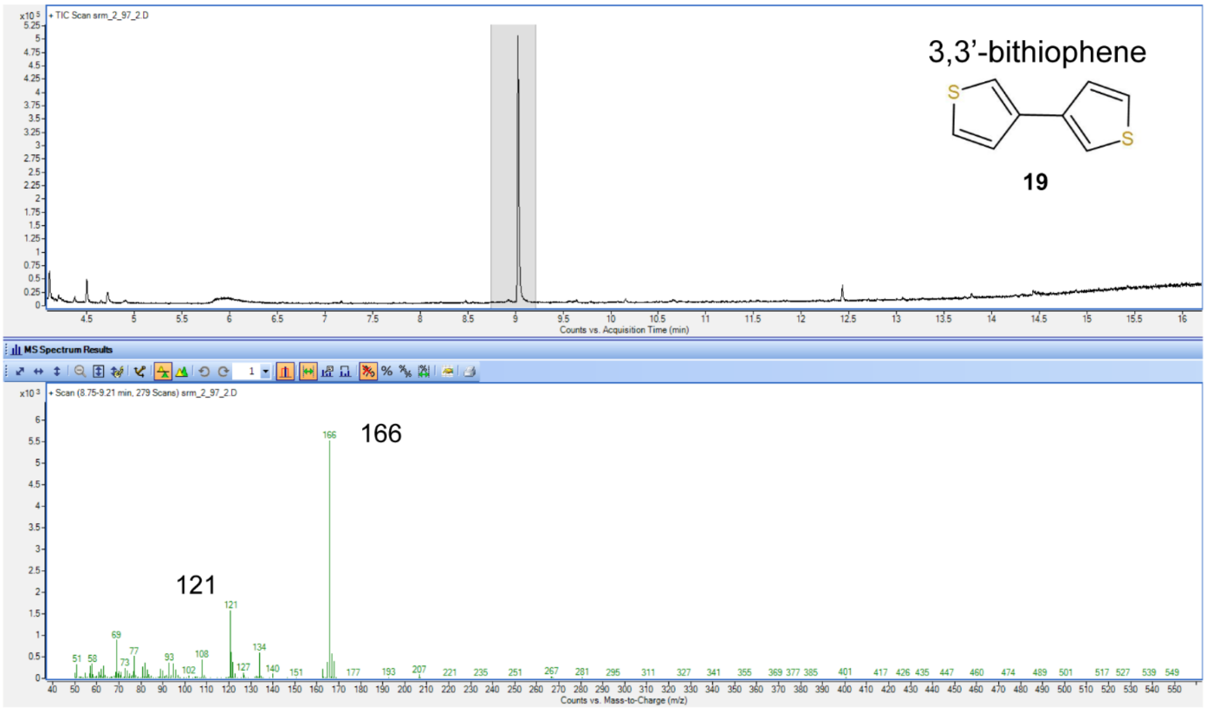
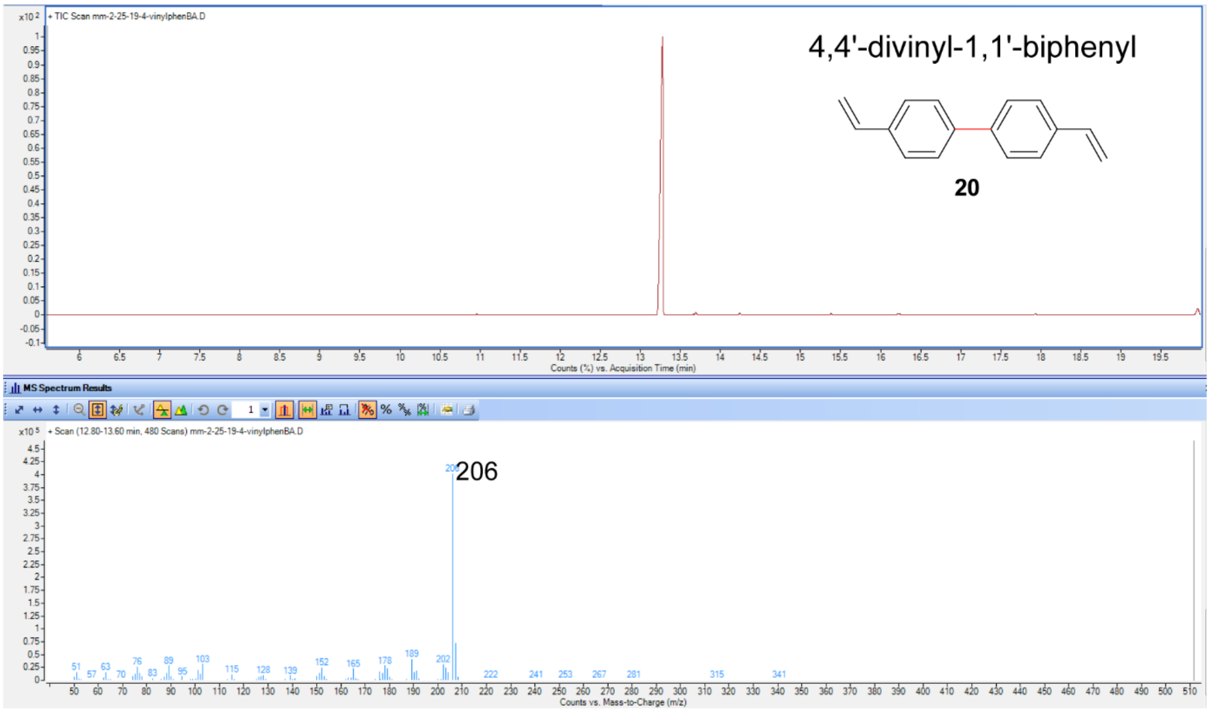


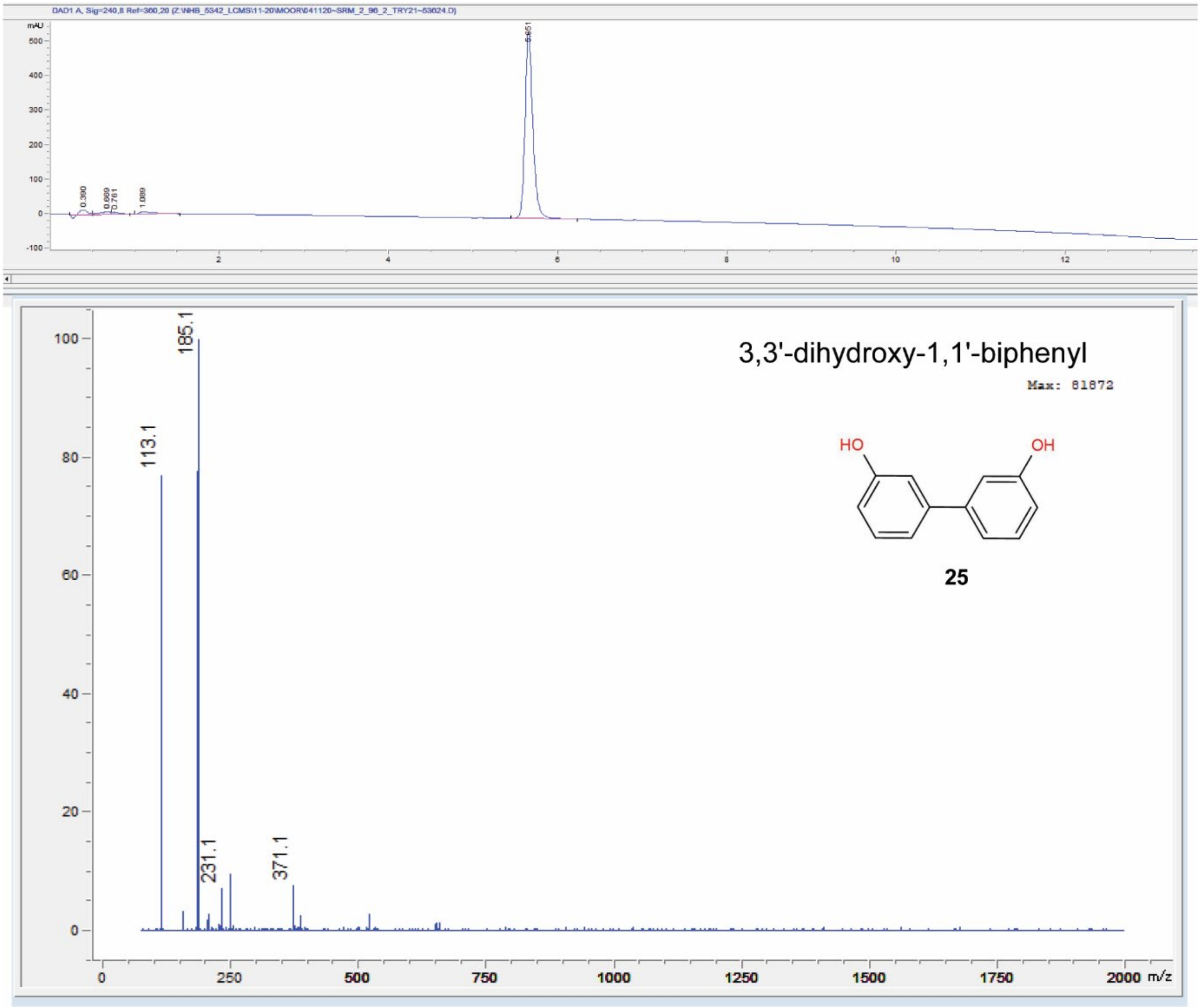
Figure S22. GC-MS or compounds 19 and 20 gas chromatograph (top) mass spectrum (bottom)





LC-MS Spectra

Figure S23. LC-MS or compound 25 liquid chromatograph (top) mass spectrum (bottom)



GPC Spectrum

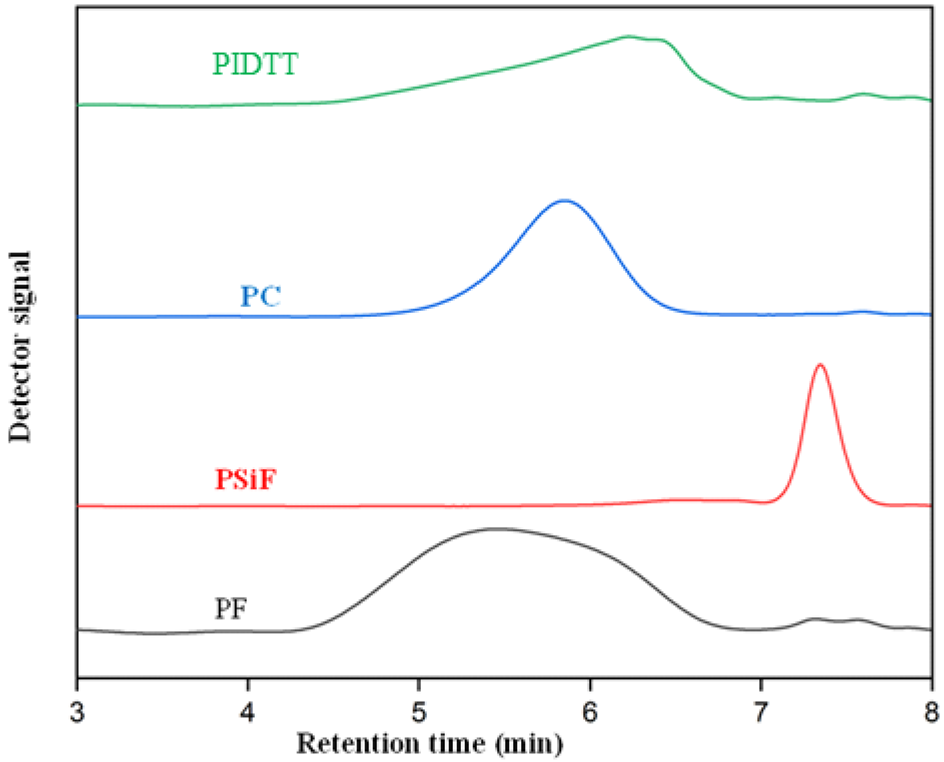


Figure S24. GPC traces of synthesized polymers

Table S4. The amount (% mass) of metal in each polymer was determined by Energy-dispersive X-ray spectroscopy (EDS).

Entry	Pd mass %	Cu mass %
PF	0.03	0.15
PSiF	0.28	0.38
PC	6.5	0.45

PIDTT	8.5	0.67

MALDI-TOF Spectra

Figure S25. MALDI – TOF. Spectrum of para polyphenylene oligomers.