# Supporting Information

## Direct Heteroarylation Polymerization: Guidelines for Defect-Free Conjugated Polymers

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## 1. Characterization

$^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on a Varian AS400 or Agilent DD2 500MHz apparatus in deuterated solvents. Chemical shifts were reported as δ values (ppm) relative to the residual protic solvent. Number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights were determined by size exclusion chromatography (SEC) using a high temperature Varian Polymer Laboratories GPC220 equipped with an RI detector and a PL BV400 HT Bridge Viscometer. The column set consists of 2 PL gel Mixed C (300 x 7.5 mm) columns and a PL gel Mixed C guard column. The flow rate was fixed at 1.0mL/min using 1,2,4-trichlorobenzene (TCB) (with 0.0125% BHT w/v) as eluent. The temperature of the system was set to 110 °C. All the samples were prepared at concentrations of nominally 1.0 mg/mL in TCB. Dissolution was performed using a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The sample vials were held at 110 °C with shaking for 1 h for complete dissolution. The solutions were filtered through a 2 mm porous stainless steel filter used with the 0.40 μm glass filter into a 2 mL chromatography vial. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards Easi-Vials PS-M from Varian Polymer Laboratories which were dissolved in TCB. UV-vis-NIR absorption spectra were recorded using a Varian Cary 500 in chloroform solution.

Crystals were mounted on CryoLoops with Paratone-N and optically aligned on a Bruker SMART APEX-II X-ray diffractometer with 1K CCD detector using a digital camera. Initial intensity measurements were performed using a fine-focused sealed tube, graphite-monochromated, X-ray source (Mo $K\alpha$, $\lambda$ = 0.71073 Å) at 50 kV and 30 mA. Standard APEX-II[1] software package was

used for determining the unit cells, generating the data collection strategy, and controlling data collection. SAINT was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using SCALE (SADABS).[2] The structure was solved by intrinsic phasing using XT[3] and the refinement was carried out by least squares method using XL.[4] All the calculations have been performed within the APEX-II software package or the OLEX2 GUI software.[5] All of the H atoms were generated geometrically and refined in riding model. In some cases, disorder has been added and refined using SIMU and RIGU restraints. Crystallographic data have been deposited with CCDC (**1507660** for **L5** and **1507661** for **L4**) These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.

## 2. Fabrication and testing of OFETs

Bottom-contact bottom-gate configuration was used for all OFETs devices and prepared as follows. A heavily $n^{++}$-doped $SiO_2$/Si wafer with ~300 nm thick $SiO_2$ was patterned with gold source and drain pairs by conventional photolithography and thermal deposition techniques. The substrate was then treated with plasma followed by sonication with acetone and isopropanol. The substrate was placed in a solution of dodecyltrichlorosilane (DDTS) (3 % in toluene) at room temperature for 20 min, and subsequently washed with toluene, and dried under a nitrogen flow. A polymer solution in chloroform (5 mg $mL^{-1}$) was spin-coated onto the substrate at 3000 rpm for 80 s to give the polymer film, which was further subjected to thermal annealing at

an intended temperature for 20 min under nitrogen atmosphere in a glovebox. All the OFETs were characterized in the same glove box using an Agilent B2912A Precision Source / Measure Unit. The hole and electron mobilities are calculated in the saturation regime of at least five devices according to the following equation:

$$I_{DS} = \left(\frac{WC_i}{2L}\right)\mu(V_{GS} - V_{th})^2$$

where $I_{DS}$ is the drain–source current, μ is the charge carrier mobility, $C_i$ is the capacitance per unit area of the dielectric (11.6 nF $cm^{-2}$), W (1000 μm) and L (30 μm) are OFET channel width and length, $V_{GS}$ is the gate voltage and $V_{th}$ is the threshold voltage.

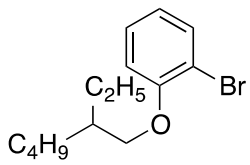
## 3. Syntheses

**3.1 Materials.** 2-Bromophenol, 2-bromopropane, 1-bromo-2-ethylhexane, bromocyclopentane, bromocycloheptane, (bromomethyl)cyclohexane, phosphorus trichloride, were commercially available and used without any further purification. 2,6-Dibromo-4,8-bis(didodecyl)benzo[1,2-*b*:4,5-*b*′]dithiophene ($Br_2$-BDT-$C_{12}$), 4,8-bis(didodecyl)benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT-$C_{12}$), 4,8-Bis(2-thienyl)-6-(2-octyldodecyl)-[1,2,5]thiadiazolo[3,4-e]isoindole-5,7-Dione (TID), 4,8-Bis(5-bromo-thiophen-2-yl)-6-(2-octyldodecyl)-[1,2,5]thiadiazolo[3,4-e]isoindole-5,7-Dione ($Br_2$-TID) and 4,8-bis(didodecyl)-2,6-bis-trimethylstannanyl-benzo[1,2-b ;4,5-b']dithiophene were supplied by **Merck Chemicals Ltd.** 1-bromo-2-(isopropoxy)benzene, tris(2-isopropoxyphenyl)phosphine (L1)[6], 2,6-Dibromo-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene ($Br_2$-BDT-OEH)[7], 4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT-OEH)[8], (3,6-bis(5-bromo-thiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]-pyrrole-1,4-dione ($Br_2$-DPP)[9],

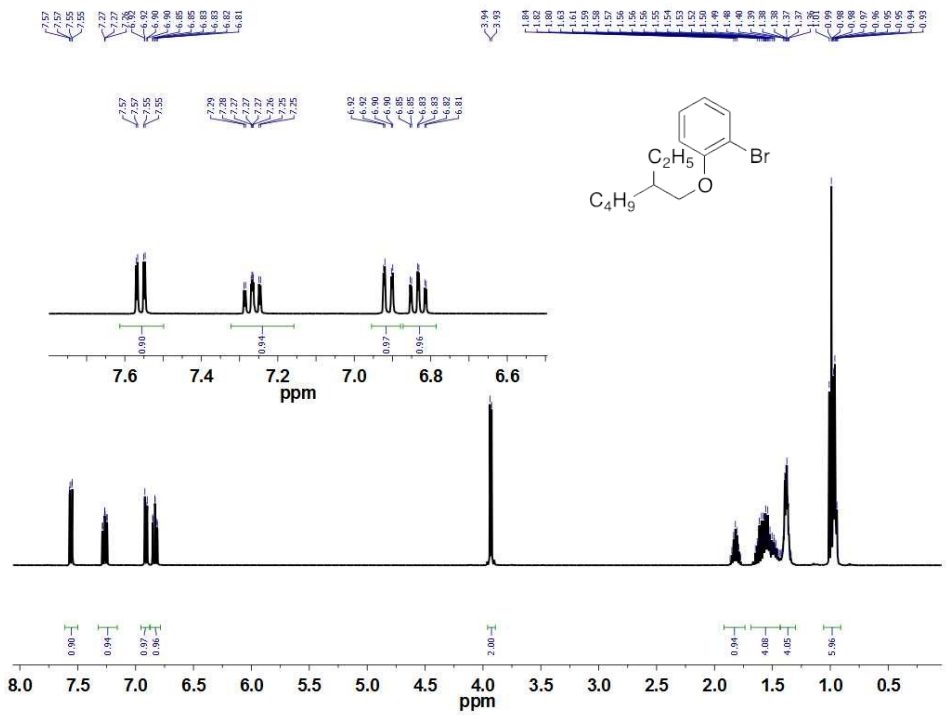
(3,6-bis(thiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]-pyrrole-1,4-dione (DPP)[9] and 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′] dithiophene[10] were synthesized according to literature.

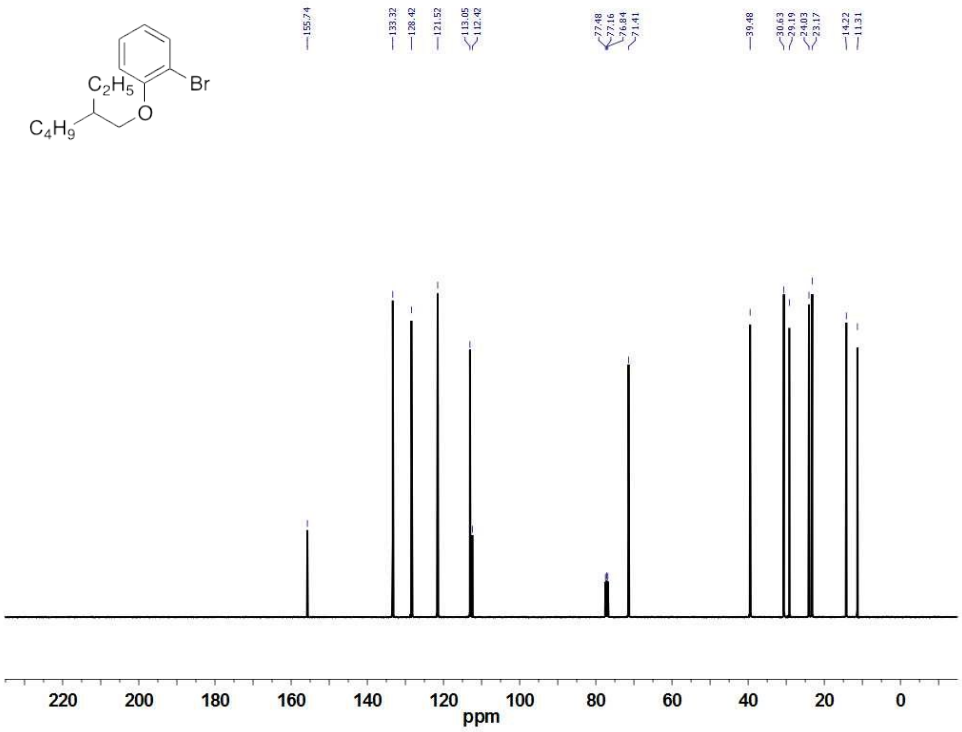
### 3.2 General procedure 1 for the synthesis of 1-bromo-2-(alkoxy)benzene :

**3.2.1 1-bromo-2-(2-ethylhexyloxy)benzene :** In a flask, a mixture of 2-bromophenol (1eq), $K_2CO_3$ (1.5eq) and acetonitrile ([0.1M]) was stirred at room temperature for 30 min. Then 1-bromo-2-ethylhexane was added and the mixture was heated under reflux until complete consumption of 2-bromophenol (reaction monitored by TLC). Then the reaction the mixture was cooled to room temperature and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography using silica gel and a mixture of hexanes/chloroform (90/10) as eluent to afford the desired compound as a colorless oil (Y = 90%).

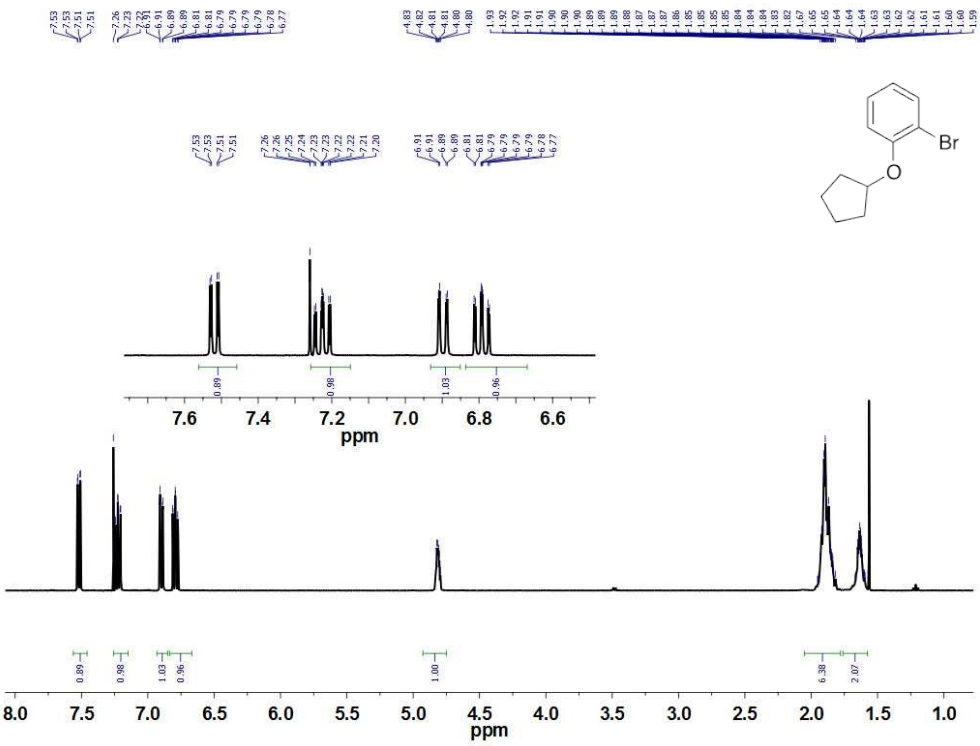


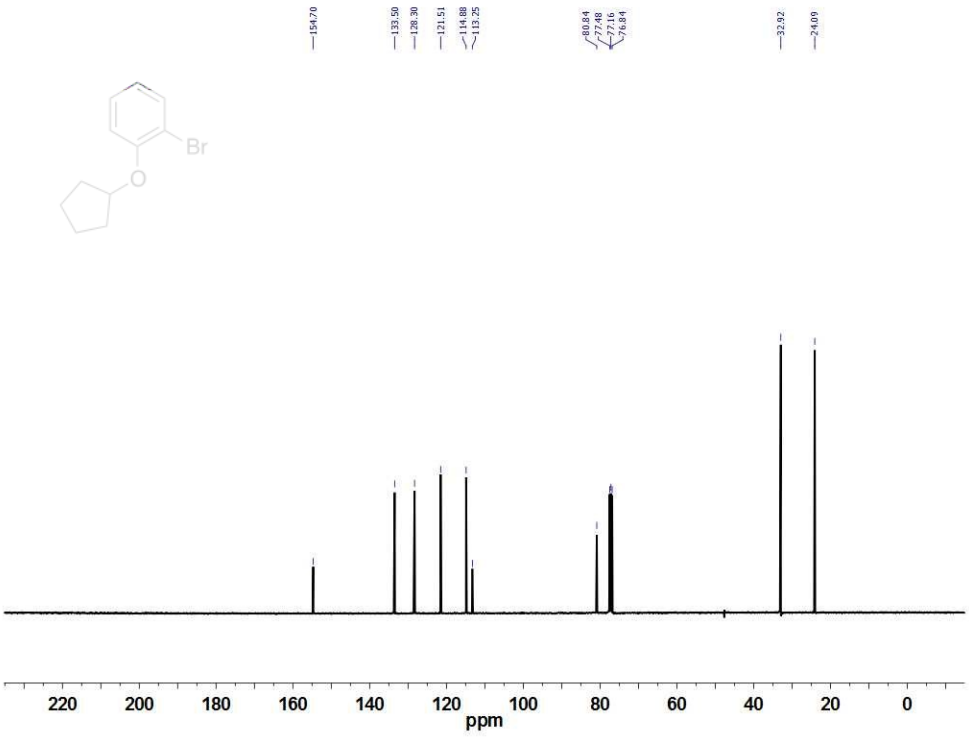

$^1$H NMR 400 MHz ($CDCl_3$) δ (ppm): 0.93-1.01 (m, 6H); 1.34-1.43 (m, 4H); 1.45-1.65 (m, 4H); 1.82 (hept, *J*= 6.1 Hz, 1H); 3.93 (d, *J*= 5.6 Hz, 2H); 6.83 (td, *J*= 7.6, 1.4 Hz, 1H); 6.91 (dd, *J*= 8.2, 1.4 Hz, 1H); 7.27 (ddd, *J*= 8.2, 7.5, 1.6 Hz, 1H). $^{13}$C NMR 100 MHz ($CDCl_3$) δ (ppm): 11.3; 14.2; 23.2; 24.1; 29.2; 30.6; 39.5; 71.4; 112.4; 113.1; 121.5; 128.4; 133.3; 155.7;


C2H5
Br
C4H9
O
ppm

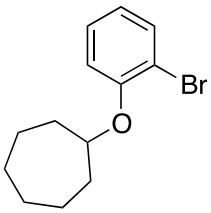

C2H5
Br
C4H9
O
ppm

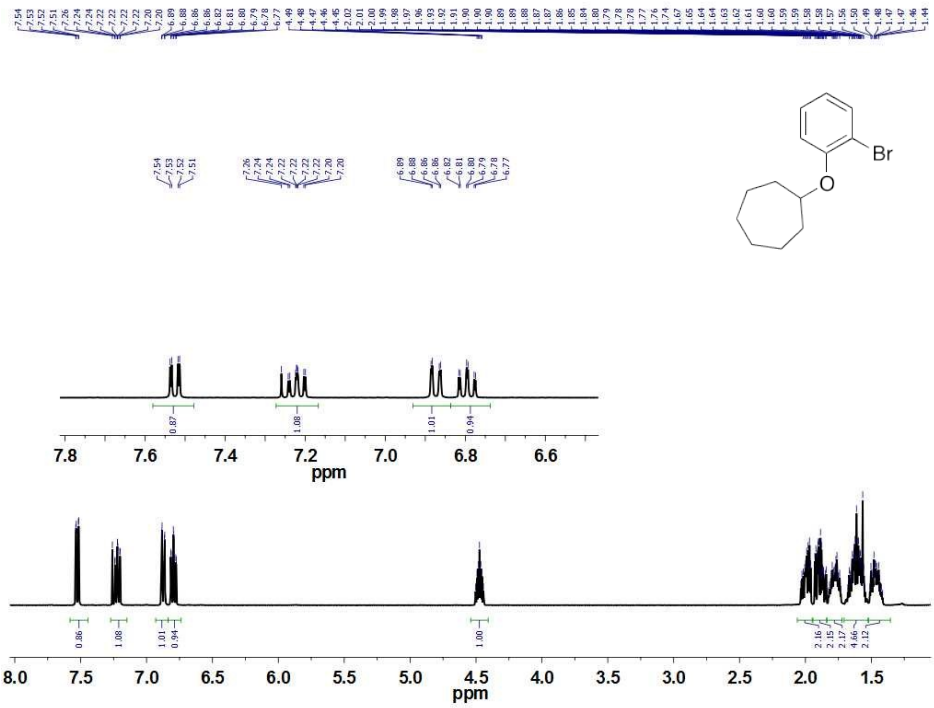
**3.2.2 1-bromo-2-(cyclopentyloxy)benzene:** This precursor was synthesized and purified according to general procedure 1 and obtained as a colorless oil (Y = 86%). $^{1}$H NMR 400 MHz ($CDCl_3$) δ (ppm): 1.59-1.67 (m, 2H); 1.82-1.95 (m, 6H); 4.80-4.83 (m, 1H); 6.79 (td, *J*= 7.9, 1.4, 1H); 6.90 (dd, *J*= 8.3, 1.3 Hz, 1H), 7.23 (ddd, *J*= 8.2, 7.4, 1.6 Hz, 1H), 7.52 (dd, *J*= 7.9, 1.6 Hz, 1H). $^{13}$C NMR 100 MHz ($CDCl_3$) δ (ppm): 24.1; 32.9; 80.8; 113.2; 114.8; 121.5; 128.3; 133.5; 154.70.






**3.2.3 1-bromo-2-(cycloheptyloxy)benzene:** This precursor was synthesized and purified according to general procedure 1 and obtained as a colorless oil (Y = 92%). $^{1}$H NMR 400 MHz ($CDCl_3$) δ (ppm): 1.41-1.51 (m, 2H); 1.55-1.68 (m, 5H); 1.73-1.82 (m, 2H); 1.84-1.93 (m, 2H); 1.96-2.03 (m, 2H); 4.47 (hept, *J*= 4.5 Hz, 1H); 6.80 (td, *J*= 7.6, 1.4 Hz, 1H); 6.87 (dd, *J*= 8.3, 1.3 Hz, 1H); 7.22 (ddd, *J*= 8.3, 7.4, 1.6 Hz, 1H); 7.53 (dd, *J*= 7.9, 1.6 Hz, 1H). $^{13}$C NMR 100 MHz ($CDCl_3$) δ (ppm): 22.9; 28.4; 33.7; 79.6; 113.8; 115.6; 121.7; 128.3; 133.6; 154.5.




Br
O
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm
8.0
7.5
7.0
6.5
6.0
5.5
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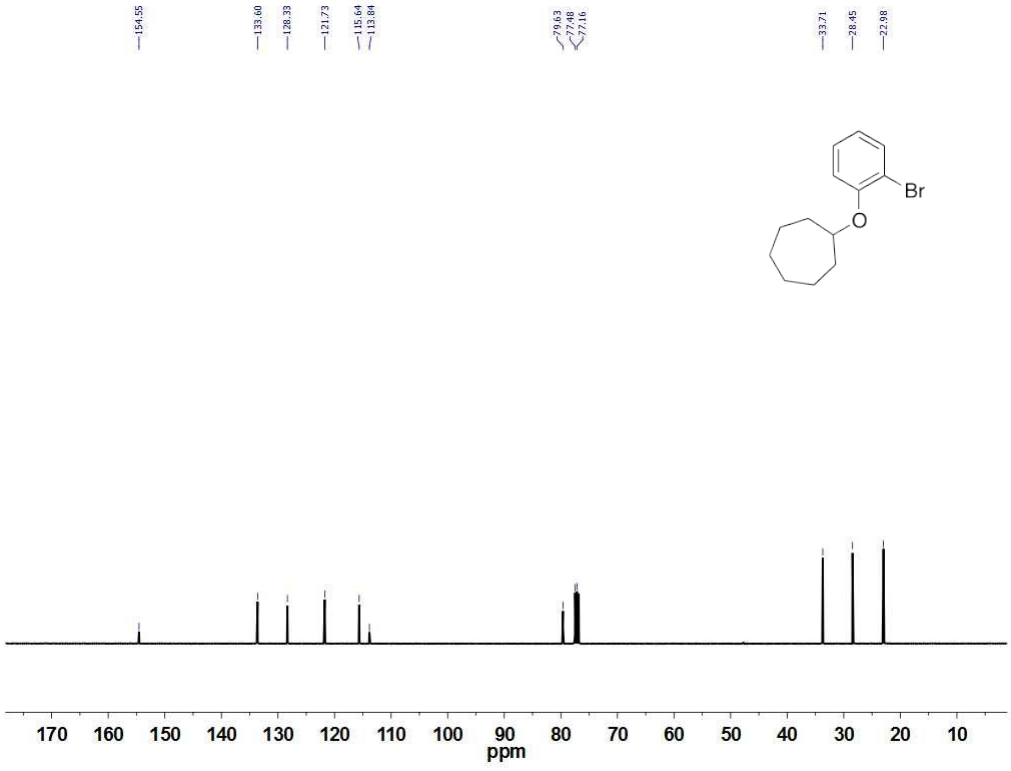
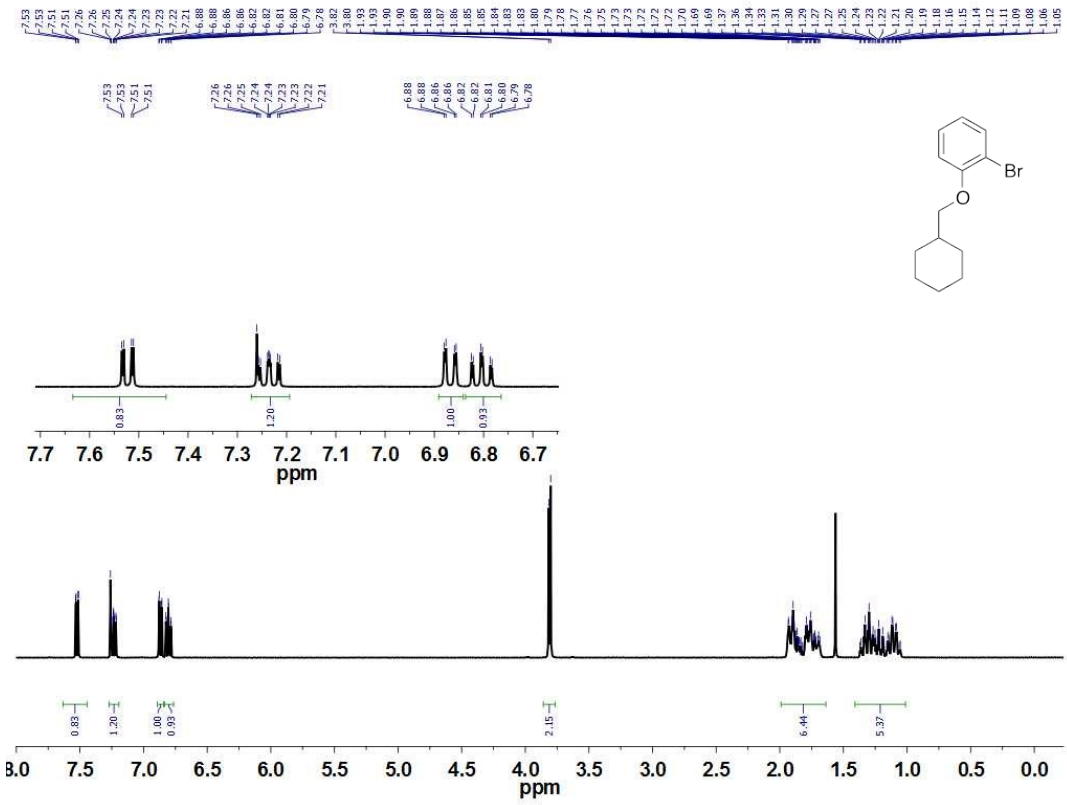
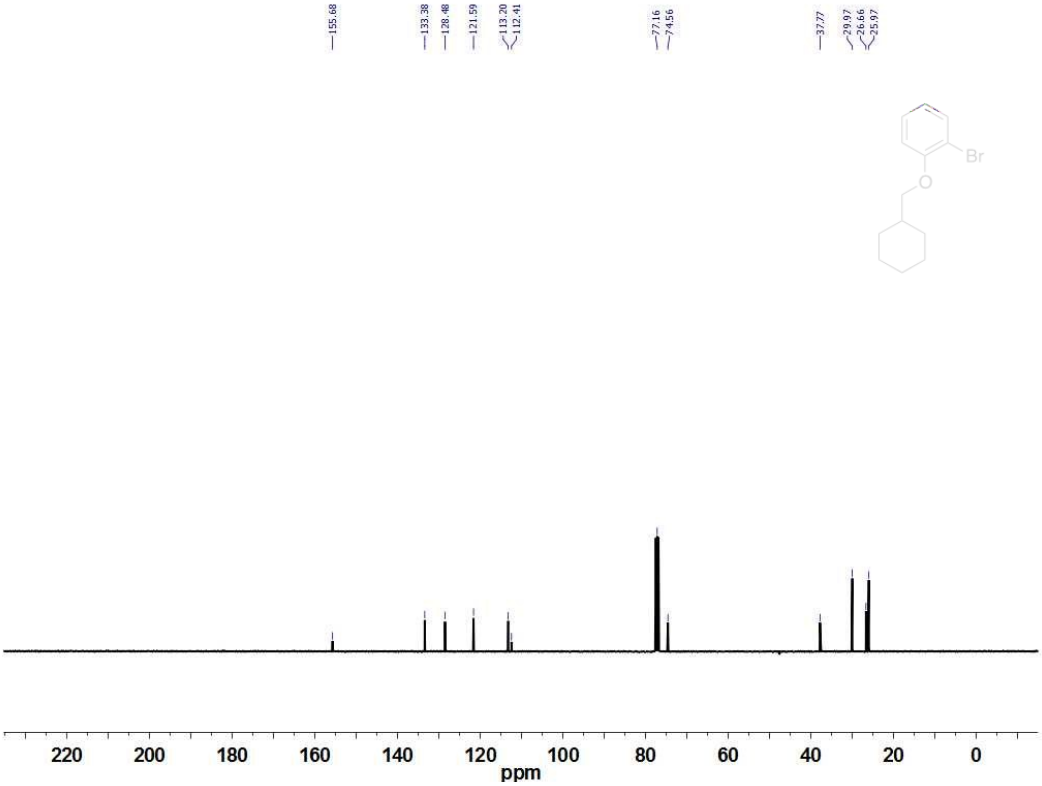
3.5
3.0
2.5
2.0
1.5
ppm


154.55
133.60
128.33
121.73
115.64
113.04
79.63
77.48
77.16
33.71
28.45
22.98
Br
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

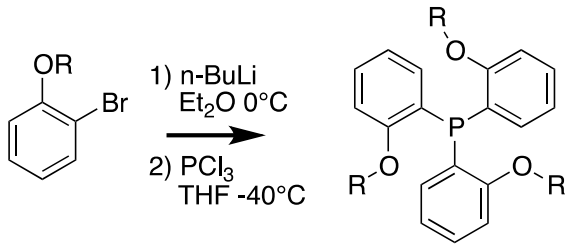
**3.2.4 1-bromo-2-(cyclohexylmethoxy)benzene:** This precursor was synthesized and purified according to general procedure 1 and obtained as a colorless oil (Y = 82%). $^{1}$H NMR 400 MHz ($CDCl_3$) δ (ppm): 1.05-1.36 (m, 5H); 1.69-1.93 (m, 6H); 3.81 (d, *J*= 6.2 Hz, 2H); 6.81 (td, *J*= 7.7, 1.4 Hz, 1H); 6.87 (dd, *J*= 8.3, 1.4 Hz, 1H), 7.25 (ddd, *J*= 7.8, 1.6, 1 Hz, 1H), 7.52 (dd, *J*= 7.9, 1.6 Hz, 1H). $^{13}$C NMR 100 MHz ($CDCl_3$) δ (ppm): 25.9; 26.6; 29.9; 37.7; 74.5; 112.4; 113.2; 121.6; 128.5; 133.4; 155.7.



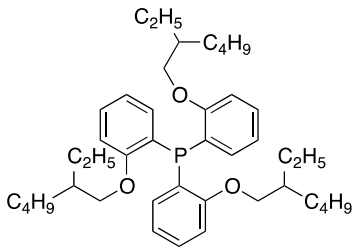

155.68
133.38
128.48
121.59
113.20
112.41
77.16
74.56
37.77
29.97
26.66
25.97
Br
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

### 3.3 General procedure 2 for the synthesis of Ligand.

All the ligands (**L1-L5**) were synthesized according to procedure described in literature.[6]

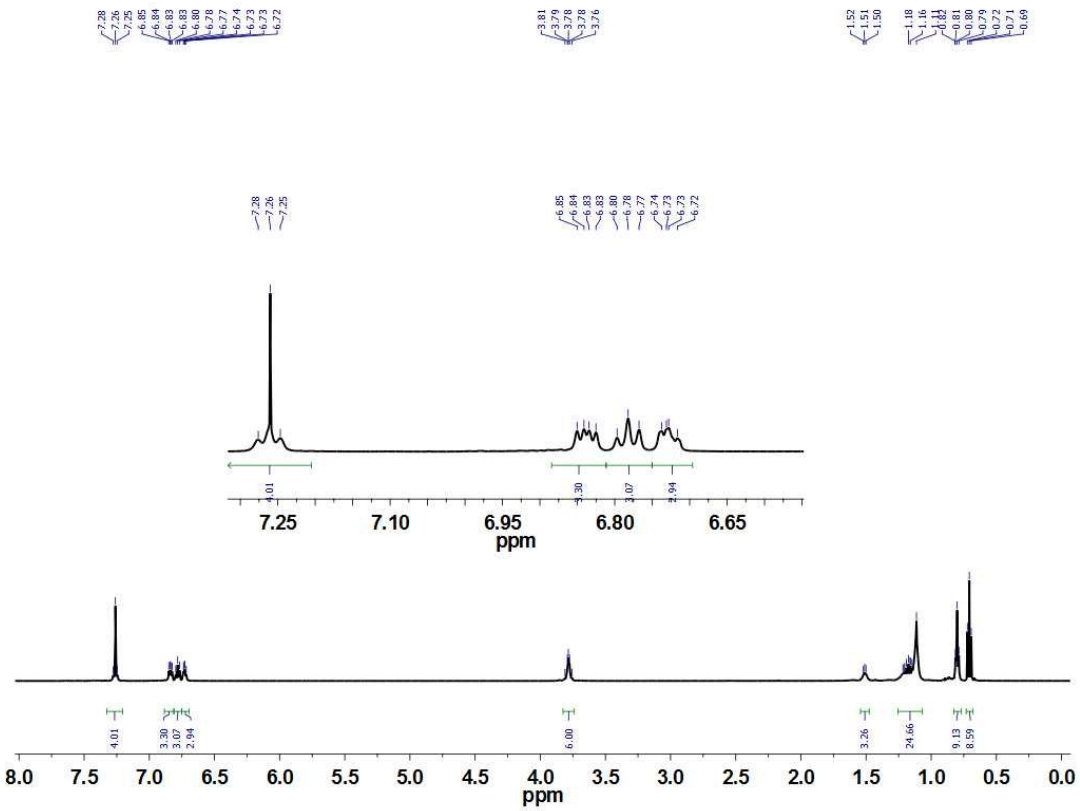


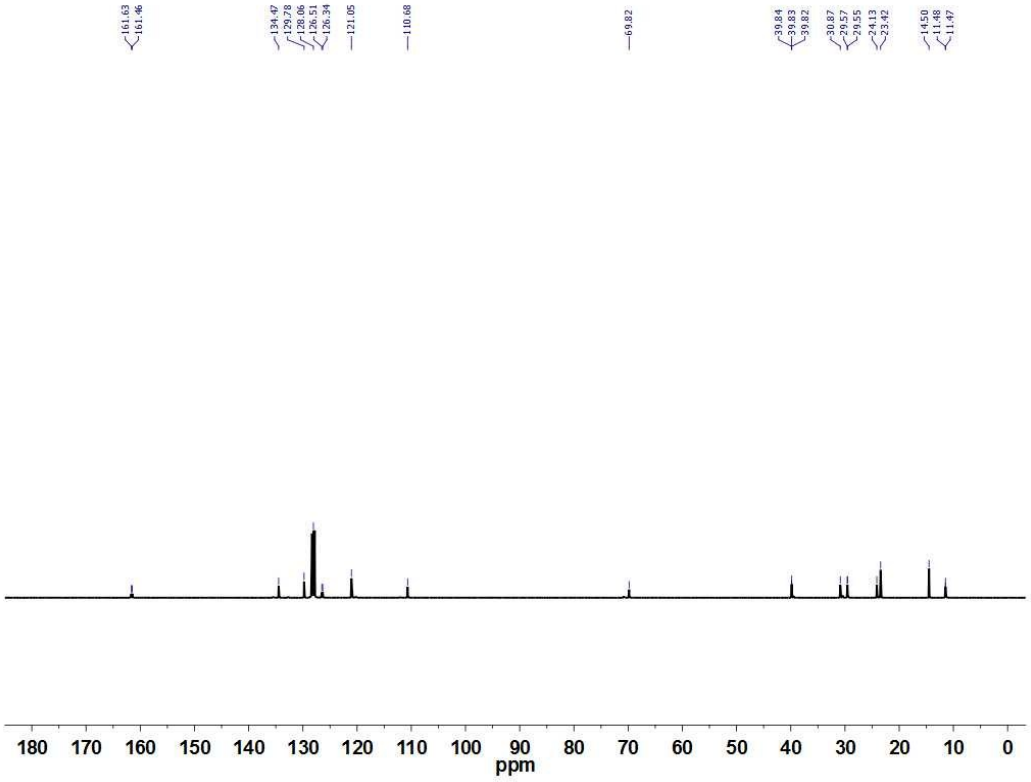

**3.3.1 Synthesis of tris(2-(2-ethylhexyloxy)phenyl)phosphine (L2) :** To a diethyl

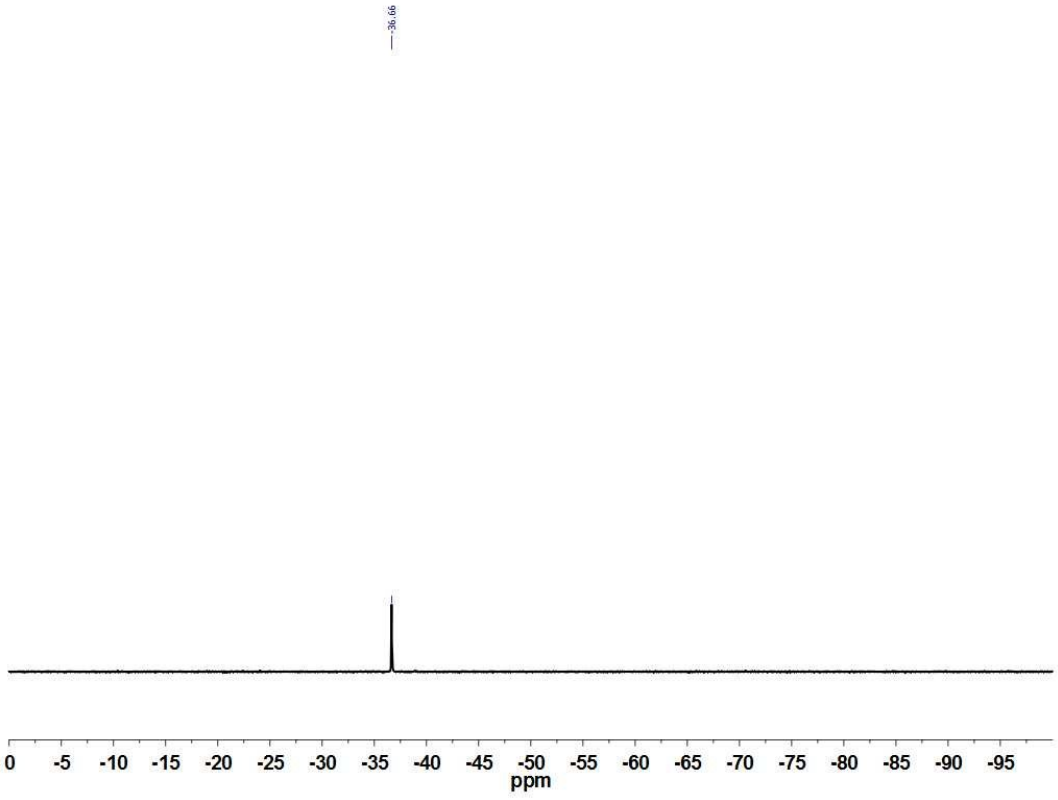



ether solution (20 mL) of 1-bromo-2-isopropoxybenzene (3.44 g, 12.06 mmol) was added at 0°C *n*-butyllithium (1.5 M in hexane, 8.45 mL, 12.66 mmol). After stirring at 0° C for 1 h, diethyl ether was removed under reduced pressure. Then anhydrous THF (20mL) was added and the solution was cooled at -40°C followed by the slow addition of phosphorus trichloride (0.315 mL, 3.6 mmol). After the addition of $PCl_3$, the cooling bath was removed and the reaction mixture was allowed to stir overnight at room temperature. A saturated aqueous solution of $NH_4Cl$ was added to the mixture and then extracted with diethyl ether. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography (aluminum oxide) with $CHCl_3$/hexanes as eluent (30/70) to afford the desired phosphine as a colorless oil (**L2**, 1g, 1.545 mmol, Y = 42%). The product was then crystalized in a mixture of ether/methanol by slow evaporation. $^1H$ NMR 500 MHz ($CDCl_3$) δ (ppm): 0.71 (t, $J$ = 7.5 Hz, 9H); 0.80 (t, $J$ = 7.4 Hz, 9H);

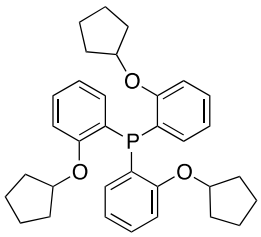
1.11-1.22 (m, 24H); 1.50-1.52 (m, 3H); 3.76-3.81 (m, 6H); 6.72-6.74 (m, 3H); 6.77-6.80 (m, 3H); 6.83-6.85 (m, 3H); 7.25-7.28 (m, 3H overlap with solvent). $^{31}$P NMR 202 MHz ($CDCl_3$) δ (ppm): -36.66. $^{13}$C NMR 100 MHz ($C_6D_6$): 11.4; 14.5; 23.4; 24.1; 29.5; 30.8; 39.8; 69.8; 110.7; 121.1; 126.4 (d, *J*= 17.3 Hz), 129.8; 134.4; 161.5 (d, *J*= 16.9 Hz). Anal. Calcd for $C_{42}H_{63}O_3P$: C, 77.98; H, 9.82 found: C, 77.76; H, 9.73



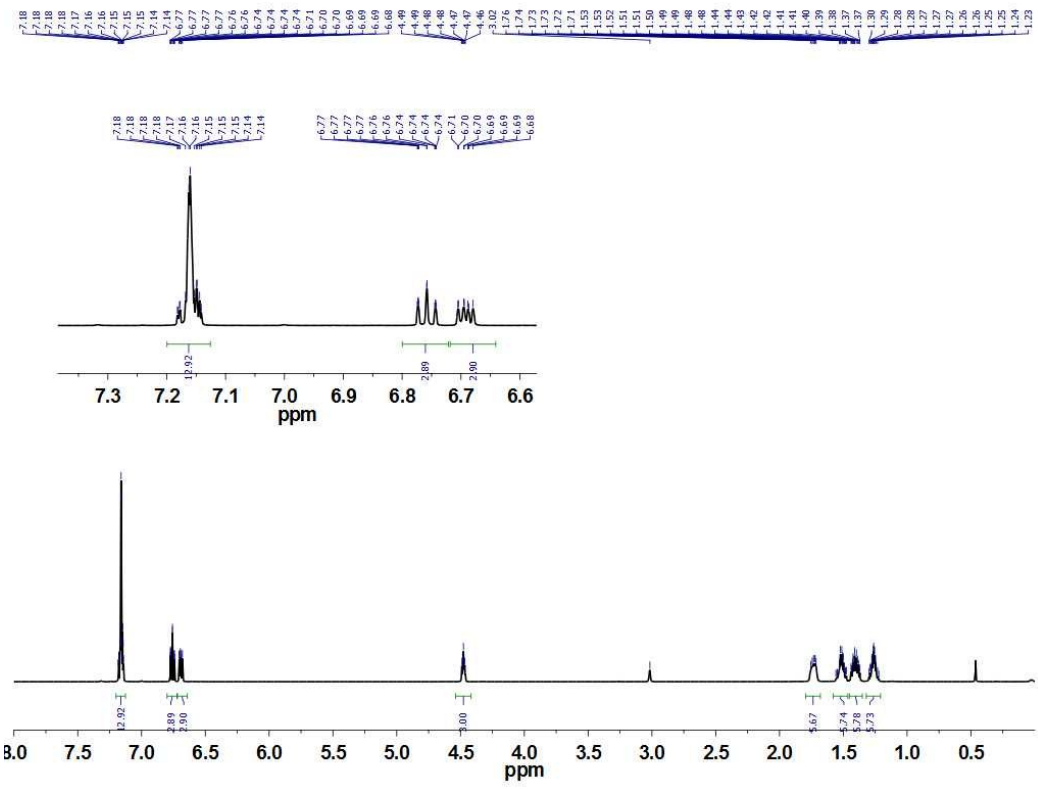

161.63
161.46
134.47
129.78
128.06
126.51
126.34
121.05
110.68
69.82
39.84
39.83
39.82
30.87
29.57
29.55
24.13
23.42
14.50
11.48
11.47
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

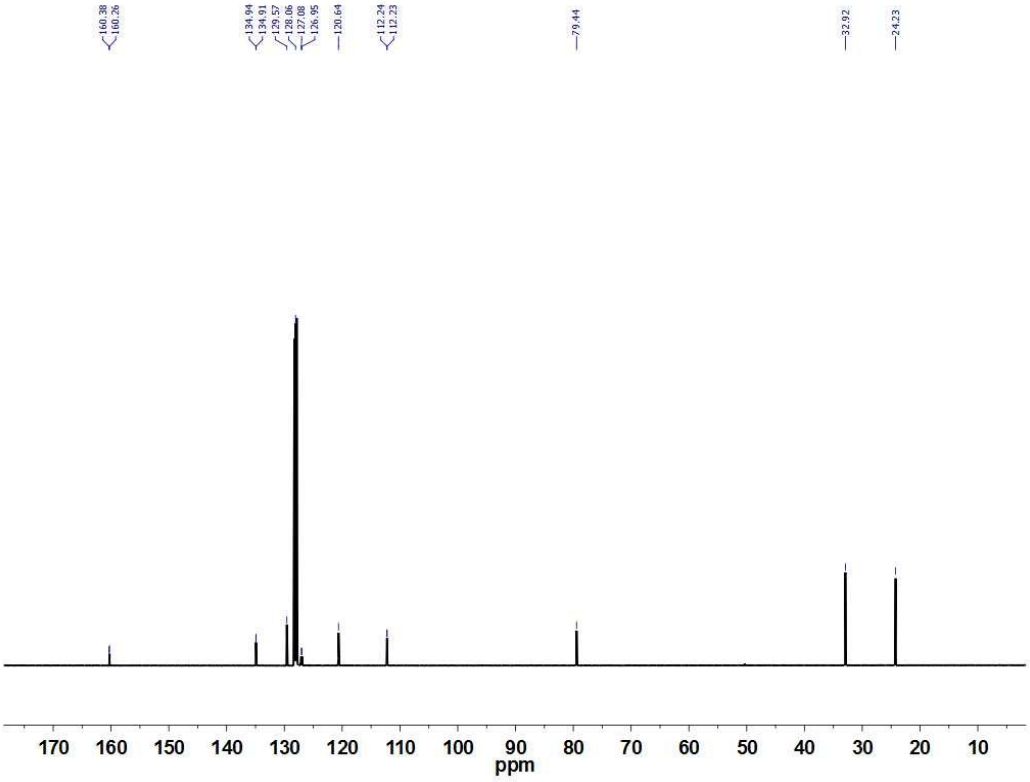

-36.66
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
ppm

**3.3.2 Synthesis of tris(2-cyclopentyloxyphenyl)phosphine (L3) :** L3 was synthesized and purified according to general procedure 2.



Colorless crystals (Y = 53%). $^{1}$H NMR 500 MHz ($C_6D_6$) δ (ppm): 1.22-1.30 (m, 6H); 1.37-1.44 (m, 6H); 1.48-1.56 (m, 6H); 1.71-1.76 (m, 6H); 4.46-4.49 (m, 3H); 6.68-6.71 (m, 3H); 6.74-6.77 (m, 3H); 7.14-7.18 (m, 6H, overlap with solvent). $^{31}$P NMR 202 MHz ($C_6D_6$) δ (ppm): -34.13. $^{13}$C NMR 100 MHz ($C_6D_6$) δ (ppm): 24.2; 32.9; 79.4; 112.2 (d, *J*= 1.2 Hz); 120.6; 127 (d, *J*= 16.7 Hz); 129.5; 134.9 (d, *J*= 3.2 Hz); 160.3 (d, *J*= 16.1 Hz). Anal. Calcd for $C_{33}H_{39}O_3P$: C, 77.02; H, 7.64 found: C, 77.09; H, 7.72.

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134.91
129.57
128.06
127.08
126.95
120.64
112.24
112.23
79.44
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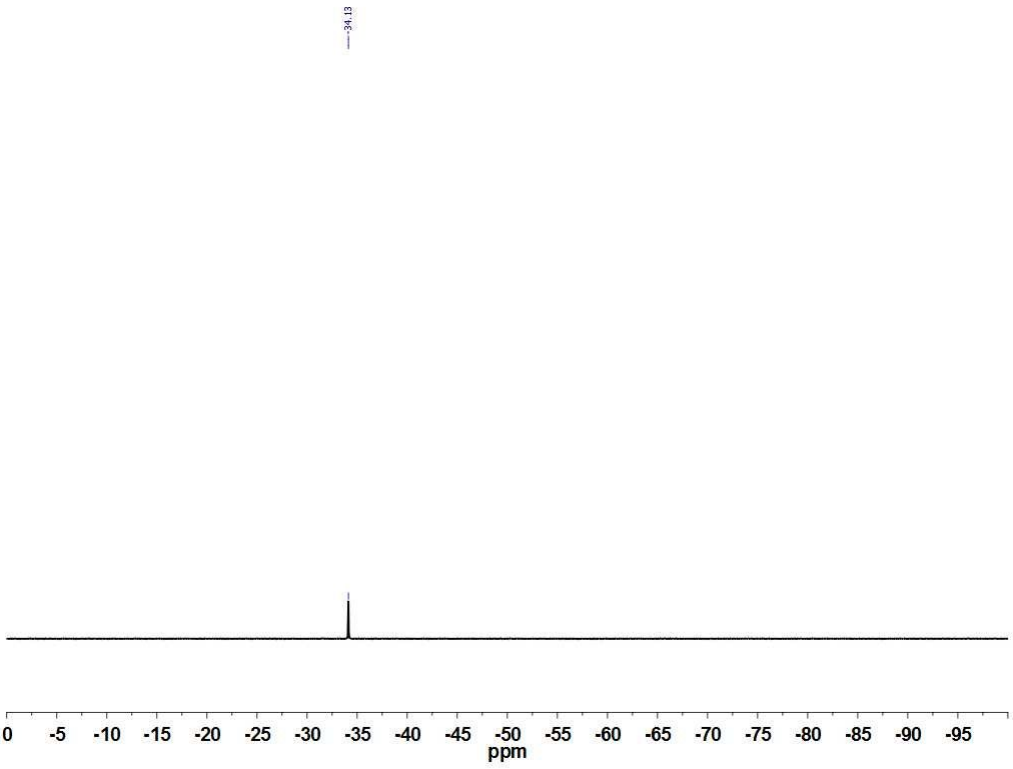
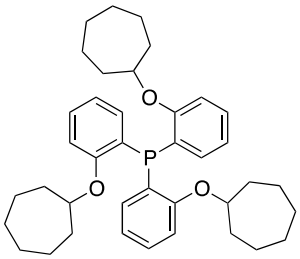
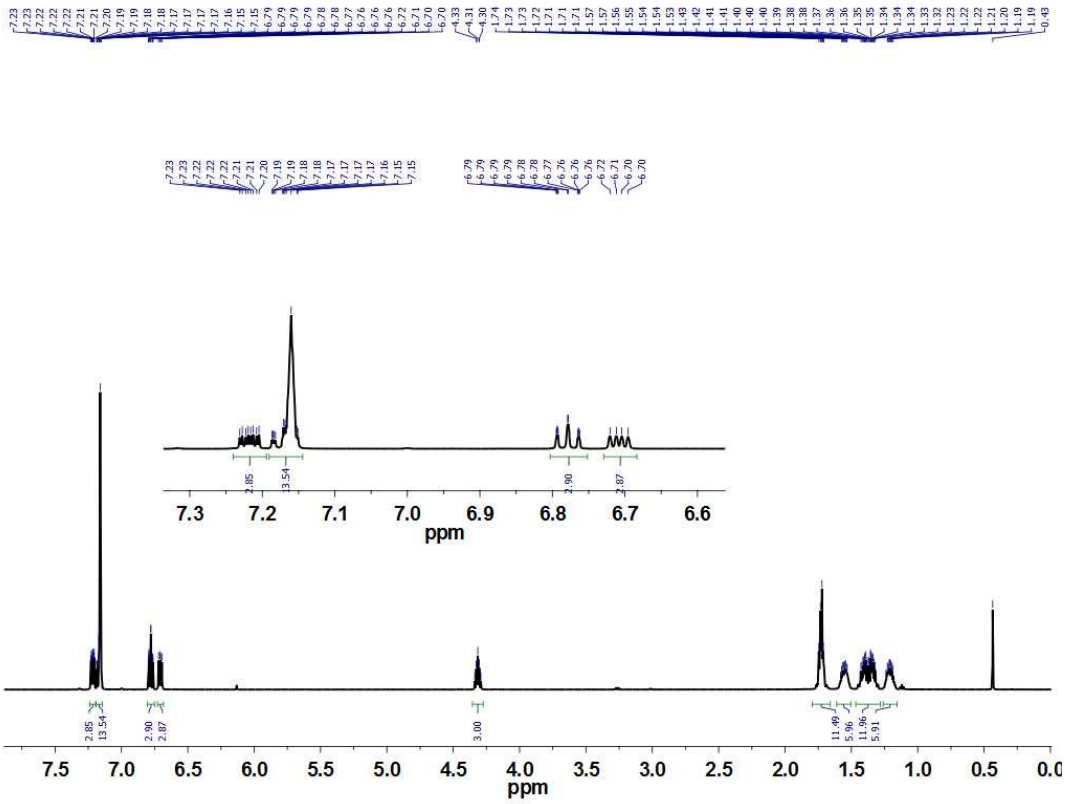
24.23
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

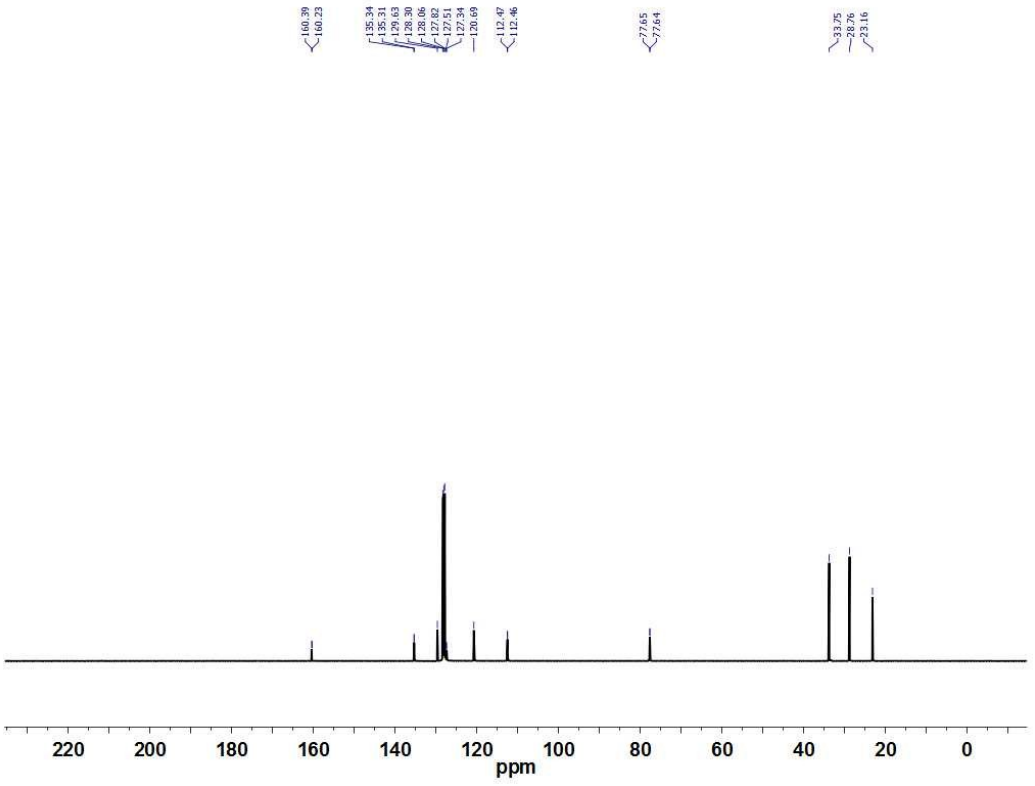

-34.13
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
ppm

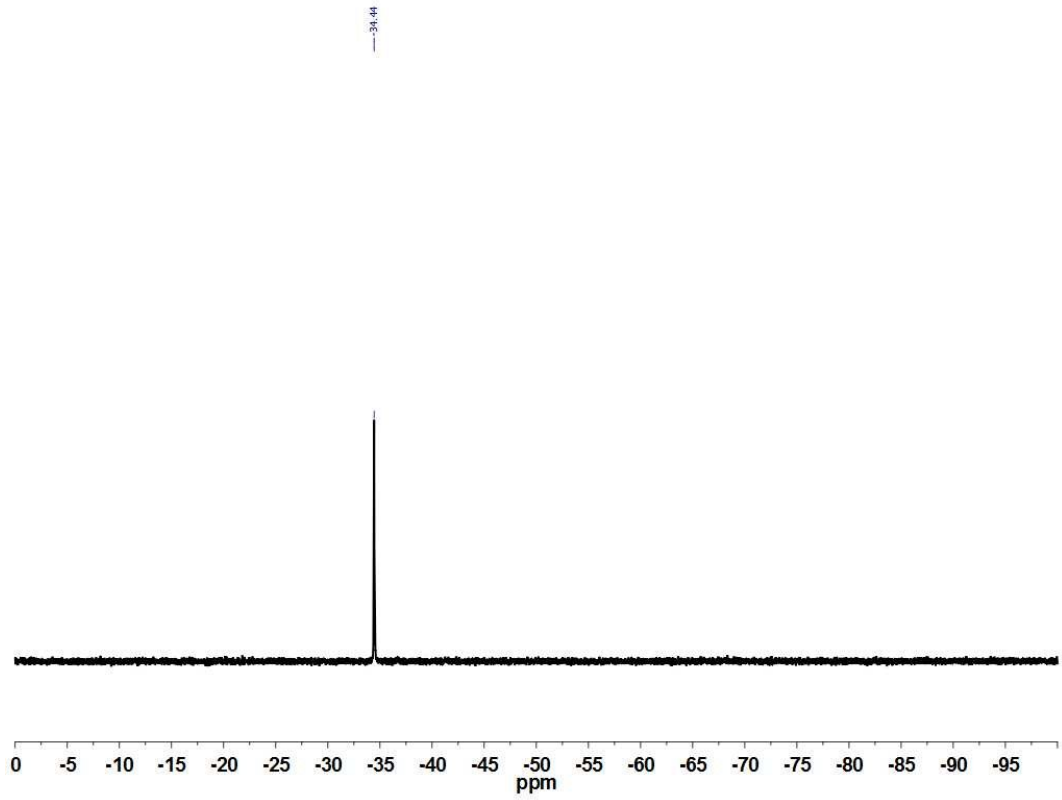
**3.3.3 Synthesis of tris(2-cycloheptyloxyphenyl)phosphine (L4) : L4** was



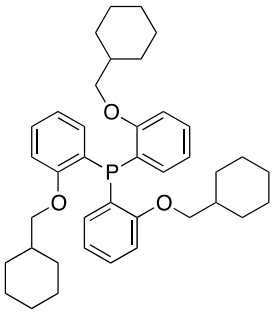
synthesized and purified according to general procedure 2. Colorless crystals (Y = 58%). $^{1}$H NMR 500 MHz ($C_6D_6$) δ (ppm): 1.19-1.24 (m, 6H); 1.32-1.41 (m, 12H); 1.53-1.58 (m, 6H), 1.71-1.74 (m, 12H); 4.32 (m, 3H); 6.70-6.72 (m, 3H); 6.76-6.79 (m, 3H); 7.15-7.19 (m, 3H, overlap with solvent) 7.20-7.23 (m, 3H). $^{31}$P NMR 202 MHz ($C_6D_6$) δ (ppm): -34.44. $^{13}$C NMR 100 MHz ($C_6D_6$) δ (ppm): 23.1; 28.7; 33.7; 77.6; 112.4 (d, *J*= 1.6 Hz); 120.7; 127.4 (d, *J*= 16.6 Hz); 129.6; 135.3 (d, *J*= 2.7 Hz); 160.3 (d, *J*= 16.4 Hz). Anal. Calcd for $C_{39}H_{51}O_3P$: C, 78.23; H, 8.58 found: C, 78.43; H, 8.69.



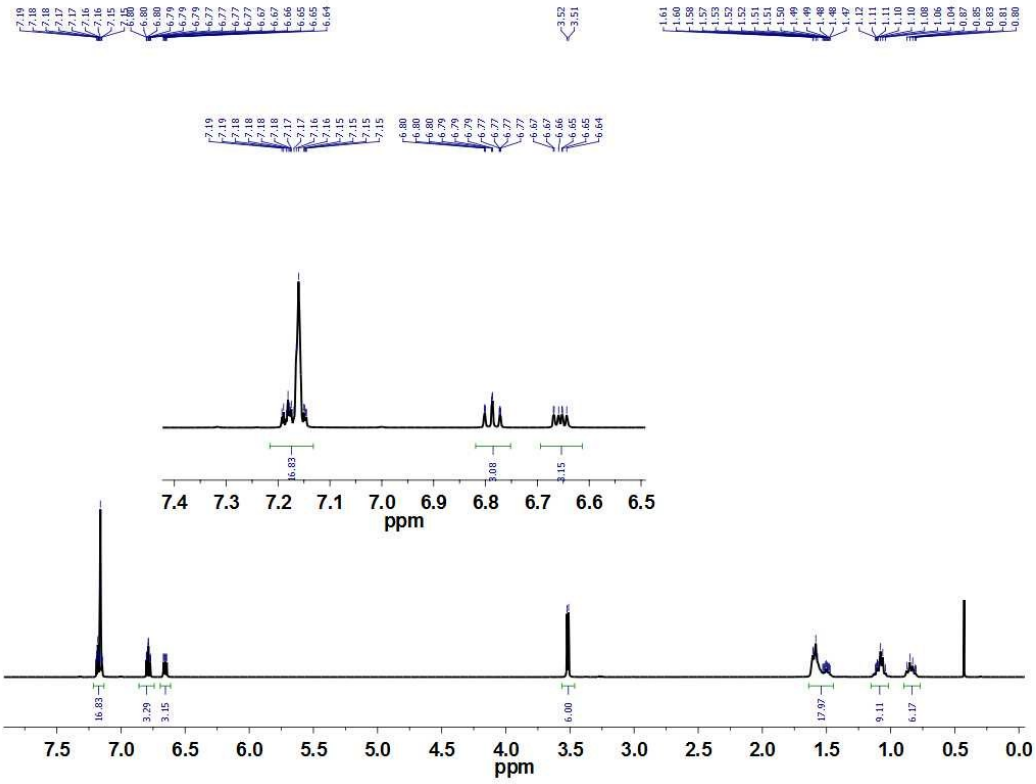

160.39
160.23
135.34
135.31
129.63
128.30
128.06
127.82
127.51
127.34
120.69
112.47
112.46
77.65
77.64
33.75
28.76
23.16
220
200
180
160
140
120
100
80
60
40
20
0
ppm

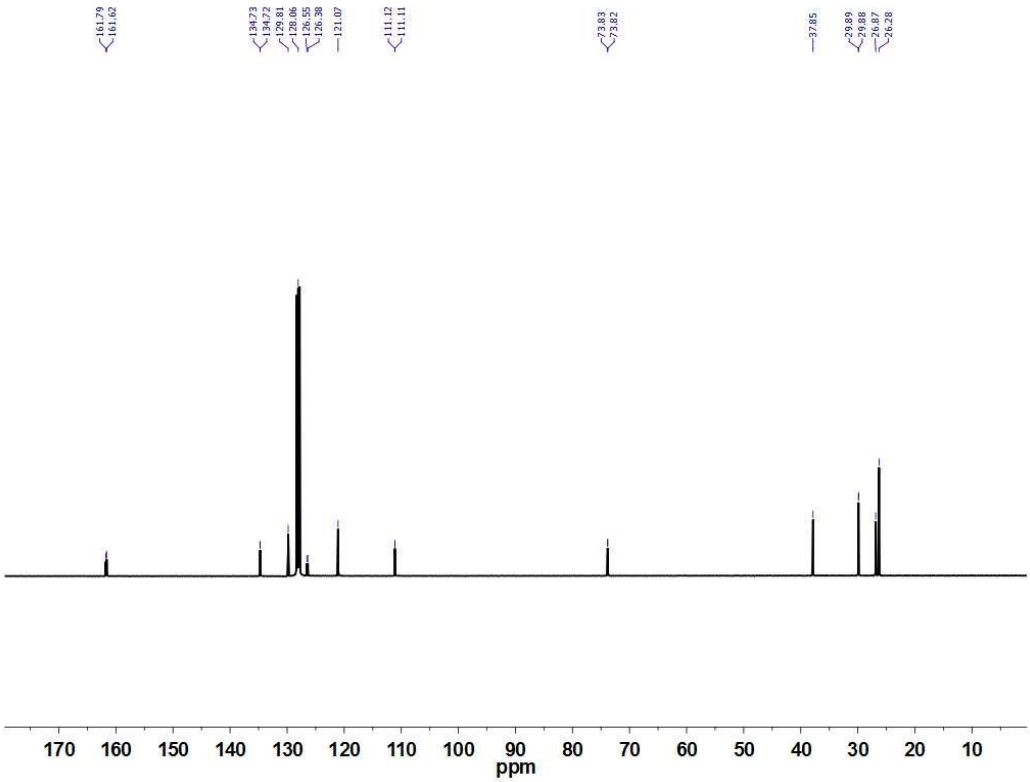

-34.44
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

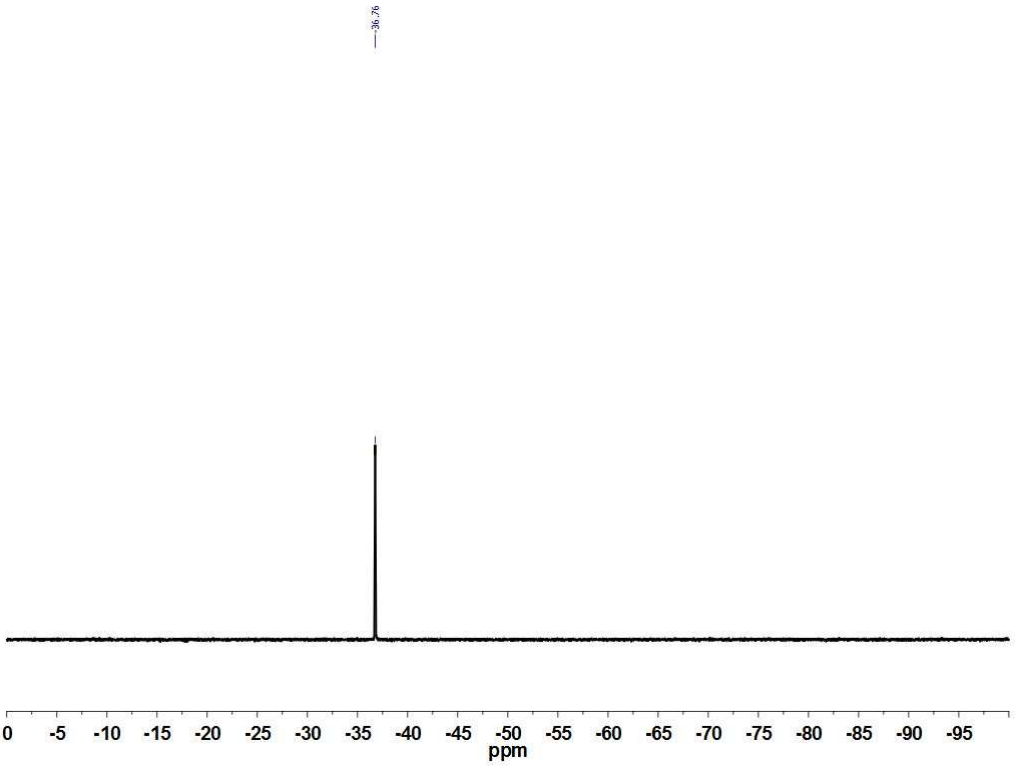
**3.3.4 Synthesis of tris(2-cyclohexylmethoxyphenyl)phosphine (L5) : L5** was



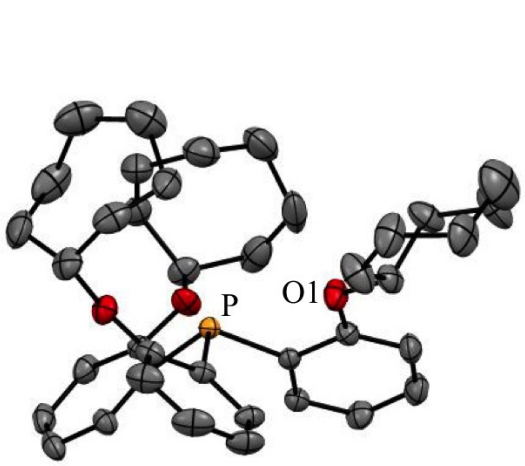
synthesized and purified according to general procedure 2. Colorless crystals (Y = 68%). $^{1}$H NMR 500 MHz ($C_6D_6$) δ (ppm): 0.80-0.87 (m, 6H), 1.04-1.12 (m, 9H), 1.41-1.61 (m, 18H); 3.52 (d, $^{3}$J = 6.1 Hz, 1H); 6.64-6.67 (m, 3H); 6.77-6.80 (m, 3H); 7.15-7.19 (m, 6H, overlap with solvent). $^{31}$P NMR 202 MHz ($C_6D_6$) δ (ppm): -36.76. $^{13}$C NMR 100 MHz ($C_6D_6$) δ (ppm): 26.3; 26.8; 29.9; 37.8; 73.8; 111.1 (d, *J*= 1.3 Hz); 121.1; 126.4 (d, *J*= 16.9 Hz); 129.8; 134.7 (d, *J*= 1.7 Hz); 161.7 (d, J= 16.7 Hz). Anal. Calcd for $C_{39}H_{51}O_3P$: C, 78.23; H, 8.58 found: C, 78.33; H, 8.69



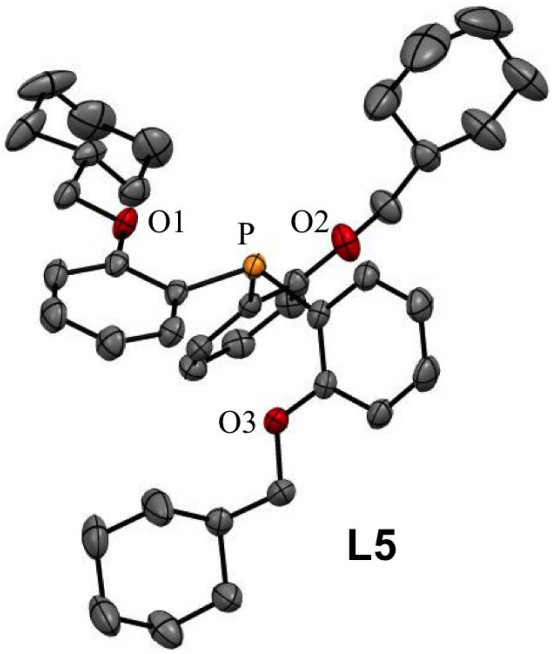

161.79
161.62
134.73
134.72
129.81
128.06
126.55
126.38
121.07
111.12
111.11
73.83
73.82
37.85
29.89
29.88
26.87
26.28
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


-36.76
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
ppm

**3.3.5** ORTEP drawing of **L4** and **L5** with thermal ellipsoids (50% probability). Hydrogen atoms are omitted for clarity.



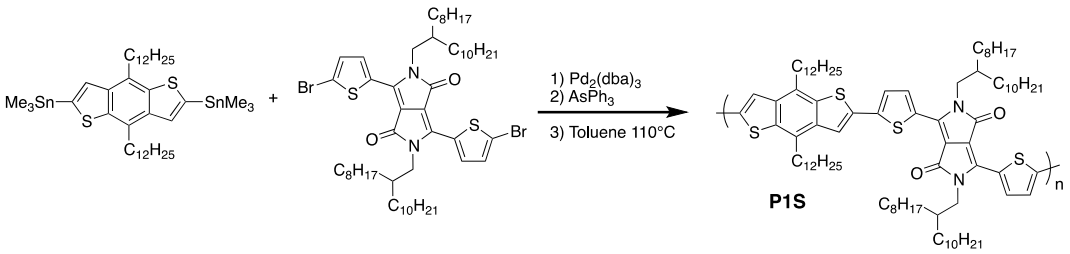

**L4**



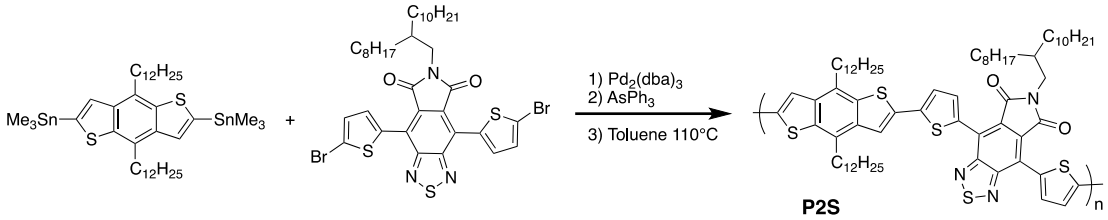

**L5**

### 3.4 General procedure 3 for the synthesis of polymer obtained by Migita-Stille coupling.

A 10 mL oven-dry microwave vial was charged with 1 equivalent of dibromo compound, 1 equivalent of bis(trimethylstannyl) compound, 0.02 eq. of $Pd_2(dba)_3$, 0.08 eq. of triphenylarsine ($AsPh_3$). The vial was sealed and purged through vacuum/nitrogen filling (3 times). Then, degassed toluene ([0.1]) was added and the reaction mixture was vigorously stirred in a pre-heated oil bath (110°C) until gelation of the reaction mixture. The reaction was then stopped by the addition of 5mL of *o*-dichrolobenzene (ODCB) and stirred for an additional 20 min. The reaction was cooled at room temperature and the polymer was precipitated in methanol, filtered through a 0.45 µm nylon filter and washed by Soxhlet extraction using acetone, hexanes and then chloroform. The chloroform fraction was reduced to 20-30 mL and then poured in methanol. The precipitate was filtered through 0.45 µm nylon filter and air-dry to give of the desired polymer.




**3.4.1 P1S** was prepared from (3,6-bis(5-bromo-thiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]-pyrrole-1,4-dione and 4,8-bis(didodecyl)-2,6-bis-trimethylstannanyl-benzo[1,2-b ;4,5-b']dithiophene following the general procedure **3**: reaction time 1h, Y = 59 % , $\bar{M}_n$= 56 kDa; $\bar{M}_w$ = 179 kDa; $Đ_M$ = 3.2 .

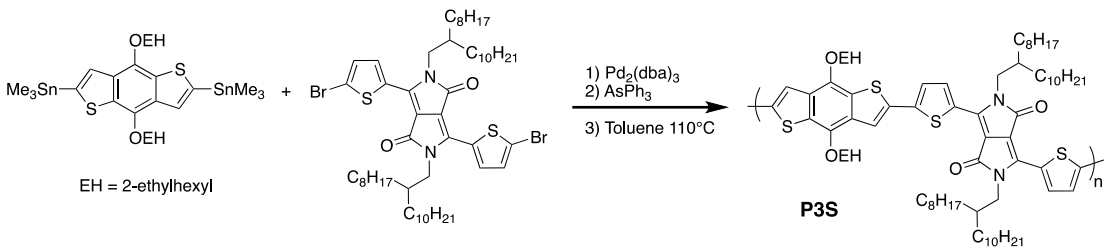



**3.4.2 P2S** was prepared from 4,8-Bis(5-bromo-thiophen-2-yl)-6-(2-octyldodecyl)-[1,2,5]thiadiazolo[3,4-e]isoindole-5,7-Dione and 4,8-bis(didodecyl)-2,6-bis-trimethylstannanyl-benzo[1,2-b ;4,5-b']dithiophene following the general procedure **3**: Reaction time 48h, Y = 90%. $\bar{M}_n$= 22 kDa; $\bar{M}_w$= 42 kDa; $Đ_M$ = 1.9.

$^1$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.16 (s, br), 7.78 (s, br), 7.61 (s, br), 3.78 (s, br), 3.30 (s, br), 2.10-2.01 (m, br), 1.64-1.36 (m, br), 0.95 (s, br).

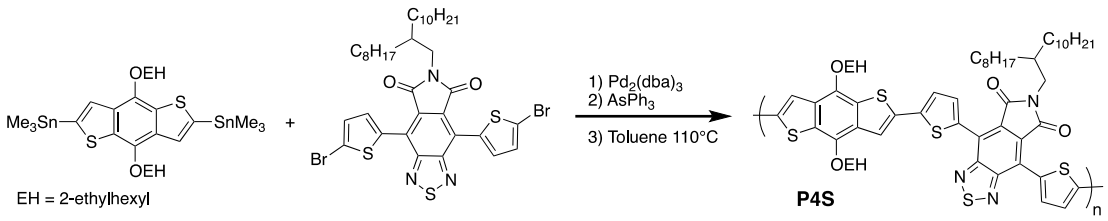
**3.4.3 P2S-HC (HC stand for Homocoupling)** was prepared from 4,8-Bis(5-bromo-thiophen-2-yl)-6-(2-octyldodecyl)-[1,2,5]thiadiazolo[3,4-e]isoindole-5,7-Dione (O.8 equivalent), 4,8-bis(didodecyl)-2,6-bis-trimethylstannanyl-benzo[1,2-b ;4,5-b']dithiophene (1 equivalent), and 2,6-Dibromo-4,8-bis(didodecyl)benzo[1,2-*b*:4,5-*b*′]dithiophene (0.2 equivalent) following the general procedure **3**: Reaction time 5h, Y = 90 %. $\bar{M}_n$= 20 kDa; $\bar{M}_w$= 42 kDa; $Đ_M$ = 2.1.

$^1$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.16 (s, br), 7.78 (s, br), 7.61 (s, br), 3.79 (s, br), 3.30 (s, br), 2.10-2.02 (m, br), 1.64-1.37 (m, br), 0.95 (s, br).



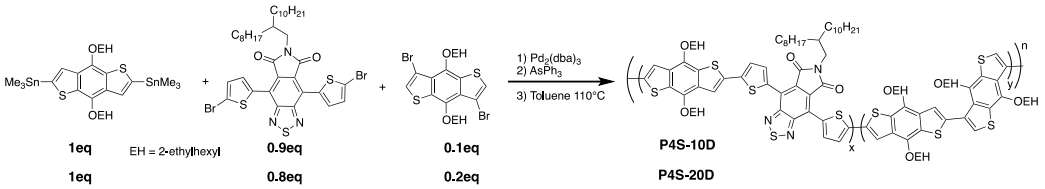

**3.4.4 P3S** was prepared from (3,6-bis(5-bromo-thiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]-pyrrole-1,4-dione and 2,6-Bis(trimethyltin)-4,8-bis(2-

ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′] dithiophene following the general procedure **3**: Reaction time 5h, Yield = 90%. $\bar{M}_n$= 57 kDa; $\bar{M}_w$ = 165 kDa; $Đ_M$ = 2.9.



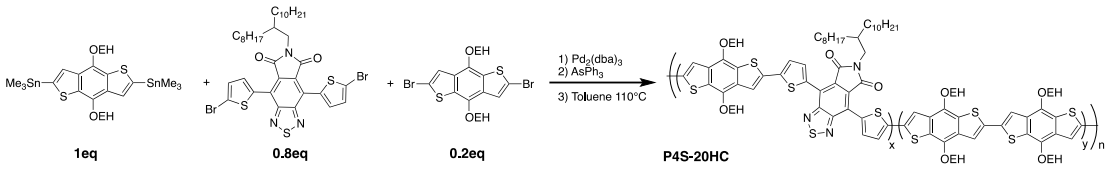

**3.4.5 P4S-High** was prepared from 4,8-Bis(5-bromo-thiophen-2-yl)-6-(2-octyldodecyl)-[1,2,5]thiadiazolo[3,4-e]isoindole-5,7-Dione and 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′] dithiophene following the general procedure **3**: Reaction time 3h, Yield = 90%. $\bar{M}_n$= 30 kDa; $\bar{M}_w$ = 60 kDa; $Đ_M$ = 2.0. $^1$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.17 (s, br), 7.79-7.76 (m, br), 7.58 (s, br), 4.38 (s, br), 3.78 (s, br), 2.11-2.0 (m, br), 1.78-1.10 (m, br), 0.95 (s, br).

**3.4.6 P4S-Low** was prepared from 4,8-Bis(5-bromo-thiophen-2-yl)-6-(2-octyldodecyl)-[1,2,5]thiadiazolo[3,4-e]isoindole-5,7-Dione and 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene following the general procedure **3**: Reaction time 3h, Yield = 90%. $\bar{M}_n$= 16 kDa; $\bar{M}_w$ = 32 kDa; $Đ_M$ = 2. $^1$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.16 (s, br), 7.79-7.76 (m, br), 7.58 (s, br), 4.38 (s, br), 3.78 (s, br), 2.11-2.0 (m, br), 1.78-1.10 (m, br), 0.99-0.95 (m, br).



**3.4.7 P4S-10D and P4S-20D** were prepared from 4,8-Bis(5-bromo-thiophen-2-yl)-6-(2-octyldodecyl)-[1,2,5]thiadiazolo[3,4-e]isoindole-5,7-Dione (0.9 eq. for **P4S-10D** and 0.8 eq. for **P4S-20D**), 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene (1 eq.) and 3,7-Dibromo-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene (0.1 eq. for **P4S-10D** and 0.2 eq. for **P4S-20D**) following the general procedure **3**: **P4S-10D** : Reaction time 3h, Yield = 90%. $\bar{M}_n$= 22 kDa; $\bar{M}_w$ = 40 kDa; $Đ_M$ = 1.8. **P4S-20D :** Reaction time 3h, Yield = 90%. $\bar{M}_n$= 20 kDa; $\bar{M}_w$ = 36 kDa; $Đ_M$ = 1.8.

$^1$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.16 (s, br), 7.83-7.76 (m, br), 7.59 (s, br), 4.38 (s, br), 3.78 (s, br), 2.10-2.01 (m, br), 1.84-1.34 (m, br), 1.20-1.17 (m, br), 1.09 (s, br), 0.95 (s, br).




**3.4.8 P4S-20HC** were prepared from 4,8-Bis(5-bromo-thiophen-2-yl)-6-(2-octyldodecyl)-[1,2,5]thiadiazolo[3,4-e]isoindole-5,7-Dione (0.8 eq.) 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene (1 eq.) and 2,6-Dibromo-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene (0.2 eq.) following the general procedure **3**: **P4S-20HC :** Reaction time 3h, Yield = 90%. $\bar{M}_n$= 30 kDa; $\bar{M}_w$ = 63 kDa; $Đ_M$ = 2.1.

$^1$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.16 (s, br), 7.83-7.76 (m, br), 7.59 (s, br), 4.38 (s, br), 3.78 (s, br), 2.10-2.01 (m, br), 1.79-1.11 (m, br), 0.95 (s, br).

### 3.5 General procedure 4 for the synthesis of P1H, P2H, P3H and P4H by Direct Heteroarylation polymerization.

**3.5.1 Polymer P1H**: $Br_2$-BDT-C12 (0.150 mmol, 1eq.), DPP (0.150 mmol, 1eq.), $Pd(OAc)_2$ (5 % mol), Phosphine (20 % mol), $Cs_2CO_3$ (3eq.) and pivalic acid (1eq.) were put in a microwave vial with a magnetic stirring bar. The vial was sealed with a cap and then purged with nitrogen to remove the oxygen (3X). Degassed and anhydrous toluene was added (C = 0.5 $mol.l^{-1}$, 0.3ml) and the reaction was heated with an oil bath pre-heated at 125 °C (reaction under pressure) until gelation of the reaction mixture. The reaction was cooled to 65 °C and then 1 ml of TCB was added. The mixture was poured in methanol/acidified water (10 % HCl) (9:1), and the solid was recovered by filtration using a 0.45 μm nylon filter. The polymer was washed using a Soxhlet apparatus with acetone, hexanes and then chloroform. The chloroform fraction was reduced to 5-10 mL and then poured in methanol. The polymer was recovered by filtration over a 0.45 μm nylon filter and dry under vacuum.

All polymers P2H, P3H, P4H, P1H', P2H', P3H' were synthesized according to this general procedure 4 with different phosphine.

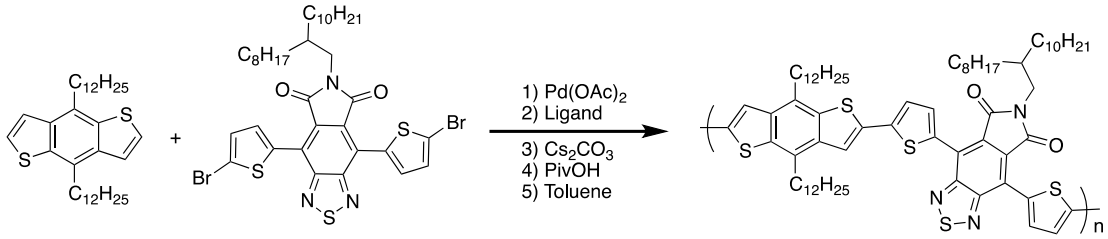
**3.5.2 P2H-L1:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br), 7.78 (s, br); 7.61 (s, br); 3.79 (s, br), 3.29 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br).

**3.5.3 P2H-L2:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.17 (s, br); 7.78 (s, br); 7.61 (s, br); 3.79 (s, br); 3.30 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br).

**3.5.4 P2H-L3:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br); 3.77 (s, br); 3.30 (s, br); 2.10-2.01 (m, br); 1.64-1.37 (m, br); 0.95 (s, br).

**3.5.5 P2H-L4:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br); 3.77 (s, br); 3.30 (s, br); 2.10-2.01 (m, br); 1.64-1.37 (m, br); 0.95 (s, br).

**3.5.6 P2H-L5:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br); 3.78 (s, br); 3.30 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br).




**3.5.7 P2H'-Lref:**.$^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br), 7.55 (s, br); 3.79 (s, br); 3.29 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br).

**3.5.8 P2H'-L1:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br); 7.55 (s, br); 3.79 (s, br); 3.29 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br).

**3.5.9 P2H'-L2:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br); 7.55 (s, br); 3.79 (s, br); 3.29 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br).

**3.5.10 P2H'-L3:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br); 7.55 (s, br); 3.79 (s, br); 3.29 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br).

**3.5.11 P2H'-L4:** $^1$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br); 7.55 (s, br); 3.79 (s, br); 3.29 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br).

**3.5.12 P2H'-L5:** $^{1}$H NMR (TCE 90°C) δ (ppm) = 8.16 (s, br); 7.78 (s, br); 7.61 (s, br); 7.55 (s, br); 3.79 (s, br); 3.29 (s, br); 2.10-2.01 (m, br); 1.64-1.36 (m, br); 0.95 (s, br)

**3.5.13 P4H-Lref:** $^{1}$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.15 (s, br), 7.80 (s, br), 7.59 (s, br), 4.38 (s, br), 3.75 (s, br), 2.09-1.99 (m, br), 1.76-1.33 (m, br), 1.18 (s, br) 1.09 (s, br), 0.95 (s, br).

**3.5.14 P4H-L1:** $^{1}$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.16 (s, br), 7.80 (s, br), 7.59 (s, br), 4.38 (s, br), 3.78 (s, br), 2.10-2.0 (m, br), 1.84-1.34 (m, br), 1.19 (s, br) 1.09 (s, br), 0.95 (s, br).

**3.5.15 P4H-L2:** $^{1}$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.18 (s, br), 7.82 (s, br), 7.57 (s, br), 4.40 (s, br), 3.81 (s, br), 2.12-2.02 (m, br), 1.88-1.36 (m, br), 1.21 (s, br) 1.12 (s, br), 0.97 (s, br).

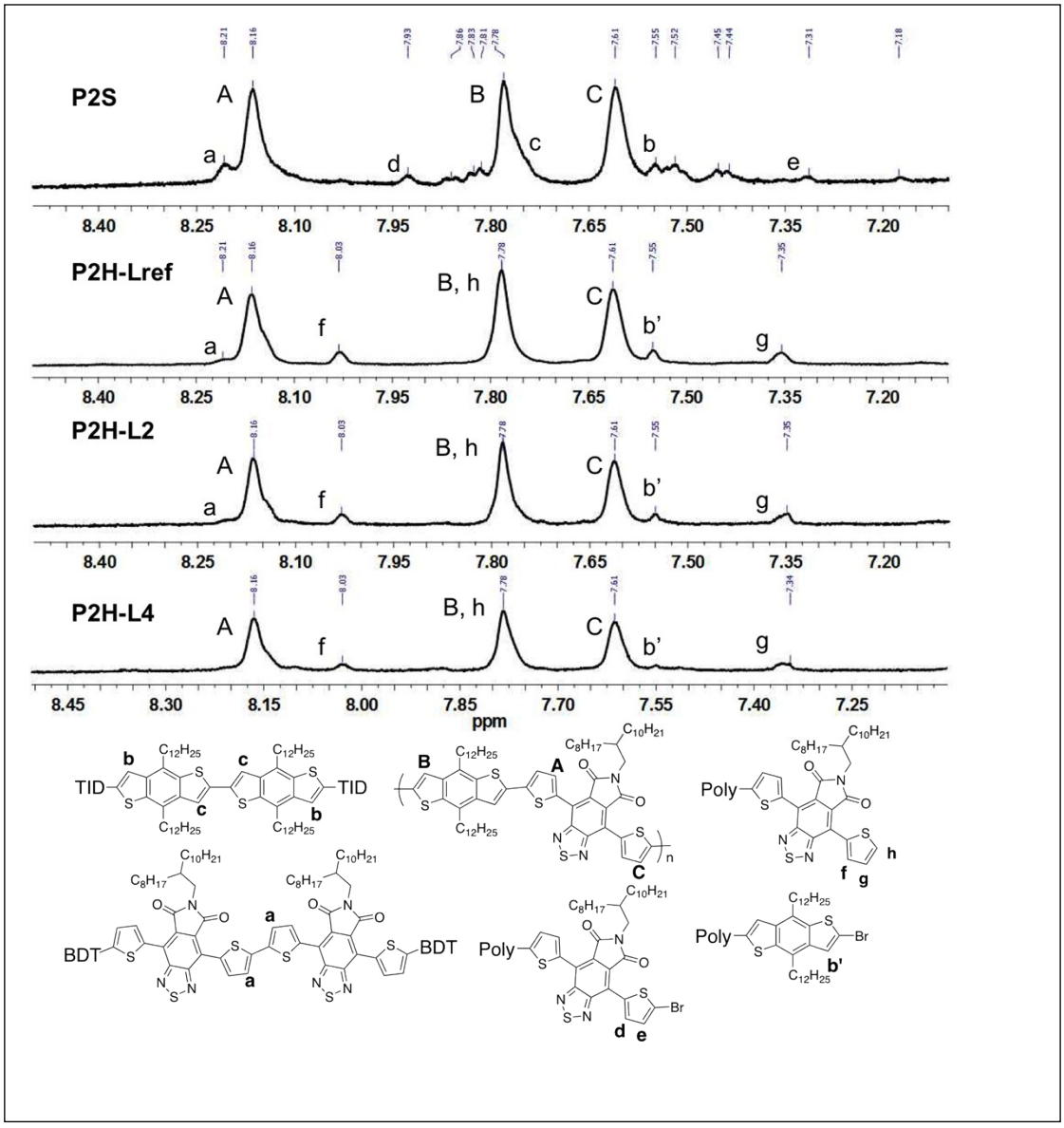
**3.5.16 P4H-L3:** $^{1}$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.18 (s, br), 7.82 (s, br), 7.61 (s, br), 4.40 (s, br), 3.80 (s, br), 2.12-2.01 (m, br), 1.85-1.36 (m, br), 1.21 (s, br) 1.12 (s, br), 0.97 (s, br).

**3.5.17 P4H-L4:** $^{1}$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.16 (s, br), 7.79 (s, br), 7.59 (s, br), 4.40 (s, br), 3.80 (s, br), 2.12-2.01 (m, br), 1.85-1.36 (m, br), 1.21 (s, br) 1.11 (s, br), 0.97 (s, br).

**3.5.18 P4H-L5:** $^{1}$H NMR 500 MHz (TCE at 90°C) δ (ppm): 8.18 (s, br), 7.82 (s, br), 7.61 (s, br), 4.40 (s, br), 3.80 (s, br), 2.13-2.02 (m, br), 1.85-1.36 (m, br), 1.21 (s, br) 1.12 (s, br), 0.97 (s, br).

## 4. $^1$H NMR spectroscopy.

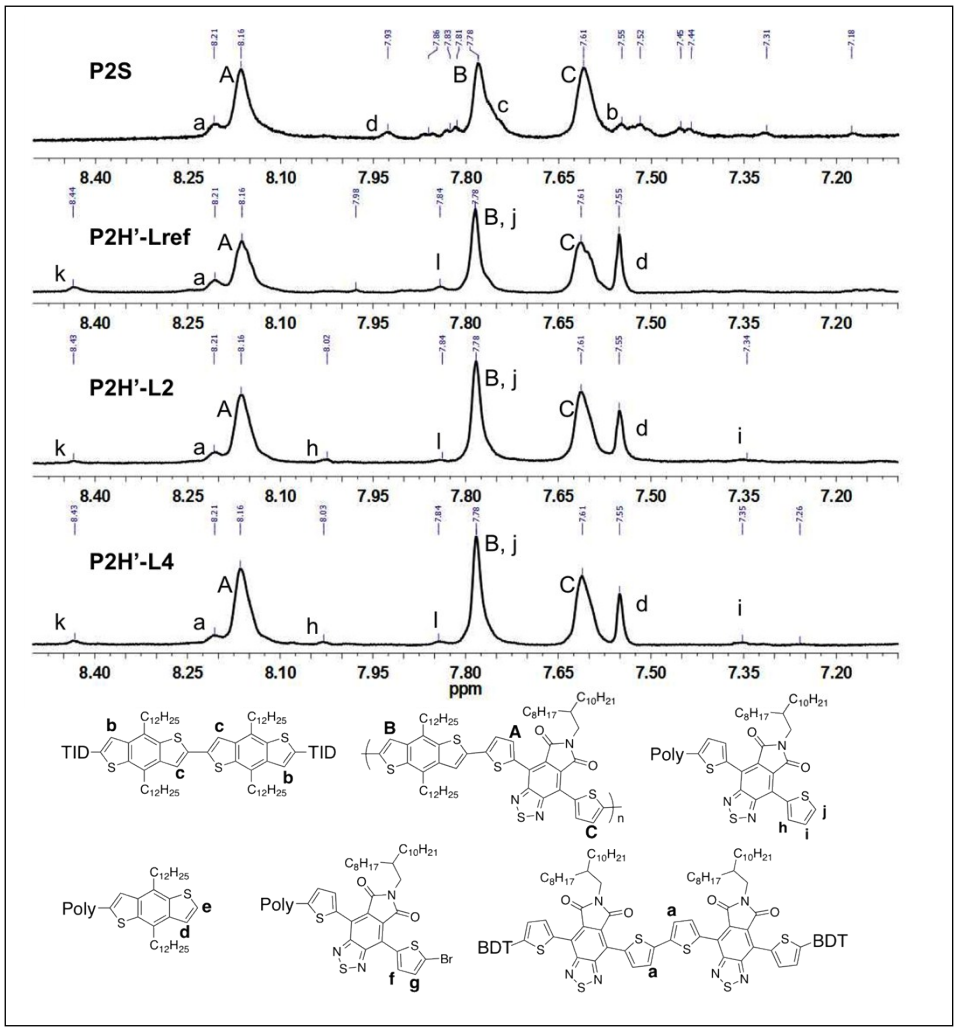
The $^1$H NMR spectra of each monomer and polymer were obtained in deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$) at 90 °C using the same acquisition parameters. Model compounds were prepared and characterized in order to assign the signals and to identify the structural defects generated during DHAP between BDT and TID. $^1$H NMR spectra of **P2S** and **P4S high** were used as benchmark. To lighten the main manuscript, the rational strategy used to identify the defects is reported here. $^1$H NMR spectra of **P2S** and **P2H** were compared, focusing on the aromatic part of the spectra (Figure 5 in the main text).



In addition to the main signals observed for **A** (8.16 ppm; TID), **B** (7.78 ppm; BDT) and **C** (7.61 ppm; TID), several unexpected resonances can be seen for **P2S.** The signal observed at 8.21 ppm (**a**) has the same chemical shift as a resonance found in the $^{1}$H NMR spectrum of poly(**P2S-HC**) (**SI 4.3**) indicating the presence of homocoupling of the TID units during the copolymerization of $(Me_3Sn)_2$-BDT-$C_{12}$ with $Br_2$-TID. Furthermore, two signals (**b**: 7.55 ppm and **c**: 7.75 ppm) are also found in the $^{1}$H NMR spectrum of poly(BDT) suggesting that BDT homocoupling is also possible during the polymerization of **P2S**. The signal at 7.55 ppm (**b**, **b'**) may also come from either Br-BDT-$C_{12}$, H-BDT-$C_{12}$ or BDT-BDT homocoupling which obfuscates its assignment (**SI 4.1**). The signals at 7.93 ppm (**d**) and 7.31 ppm (**e**) were assigned to the Br-TID terminus chain. We also observed other signals for **P2S** that could not be assigned based on the NMR data of our model compounds. These $^{1}$H NMR analyses clearly show that the Migita-Stille cross-coupling is not a defect-free polymerization method. For **P2H-$L_{REF}$**, in addition to the main signals for **A** (8.16 ppm; TID), **B** (7.78 ppm; BDT) and **C** (7.61 ppm; TID), other residual signals (**a**, **b'**, **f**, **g** and **h**) were observed. The lower intensity of the signal at 8.21 ppm (**a**) for **P2H-$L_{REF}$** compared to the one observed for **P2S** suggests that the DHAP may lead to a lower rate of TID homocoupling side-reactions. A resonance at 7.55 ppm (**b'**) was also observed as for **P2S**, but the absence of a broad peak at 7.75 ppm (**c**) for **P2H-$L_{REF}$** suggests that the signal (**b'**) is for the Br-BDT-$C_{12}$ terminus unit. To confirm this observation, we synthesized a copolymer with 20% of homocoupling and we found that the intensity of the peak at 7.75 ppm was higher than the one observed for **P2S (SI 4.4)**. Unlike **P2S**, no signal at 7.93 ppm (**d**) and 7.31 ppm (**e**) for the Br-TID terminus chain was detected which is in good agreement with the non-brominated TID comonomer used for the synthesis of the **P2H** series. Two new signals can be

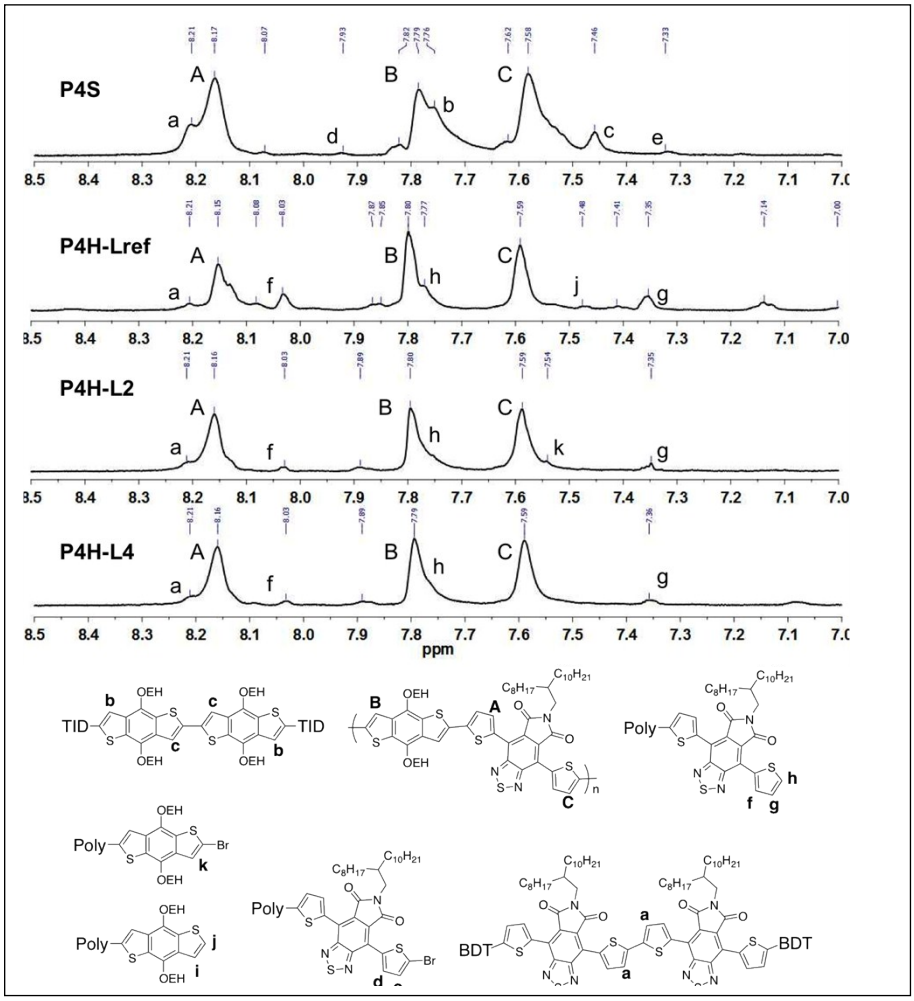
observed for **P2H-L$_{REF}$** at 8.03 ppm (**f**) and 7.35 ppm (**g**), both assigned to the H-TID terminus groups. **h** has the same chemical shift as the main peak B and therefore cannot be observed. Thus, we found that the use of **L$_{REF}$** in DHAP decreases homocoupling when compared to Migita-Stille polymerization. On the other hand, for **P2H-L2** and **P2H-L4,** a significant drop of the intensity of the peak at 8.21 ppm (**a**) (related to the homocoupling of TID) was observed while the other residual peaks (**b'**: 7.55 ppm; **f**: 8.03 ppm; **g**: 7.35) are almost the same indicating that the bulkier phosphines limit side reactions, particularly the homocoupling of the TID units.

The aromatic part of the well-defined $^{1}$H NMR spectra for **P2H'-L$_{REF}$**, **P2H'-L2** and **P2H'-L4** is shown below.



As for **P2S** and **P2H**, the main peaks **A, B** and **C** correspond to the protons of the main chain while the residual signals (**a-i**) are related to end groups or homocoupling motifs. The residual signal at 8.21 ppm (**a**) is related to the homocoupling of the TID units for each **P2H'**. No signal corresponding to the Br-TID units (peak **f** at 7.93 nm) in **P2H'** was found. Moreover, the signals found at 8.03 ppm (**h**) and 7.35 ppm (**i**) previously assigned to the H-TID end chains confirm a partial dehalogenation of the Br-TID unit during polymerization. It must be noted that the proton labeled **j** possesses the same chemical shift that the main peak B and cannot be observed. The signal observed at 7.55 is the most striking feature found in $^{1}$H NMR spectra of the **P2H'** series. Indeed, this resonance is coming either from Br-BDT end chain units and/or poly-BDT homopolymer (**b**). If the resonance peak is coming from poly-BDT, we must see a shoulder at 7.75 ppm (**c**). The absence of a broad peak (**c**; 7.75 ppm) for the **P2H'** series suggests therefore that the 7.55 ppm signal (**d**) is for Br-BDT-$C_{12}$ terminus unit. The resonance found at 8.43 ppm (**k**) and 7.84 ppm (**l**) could not be assigned.

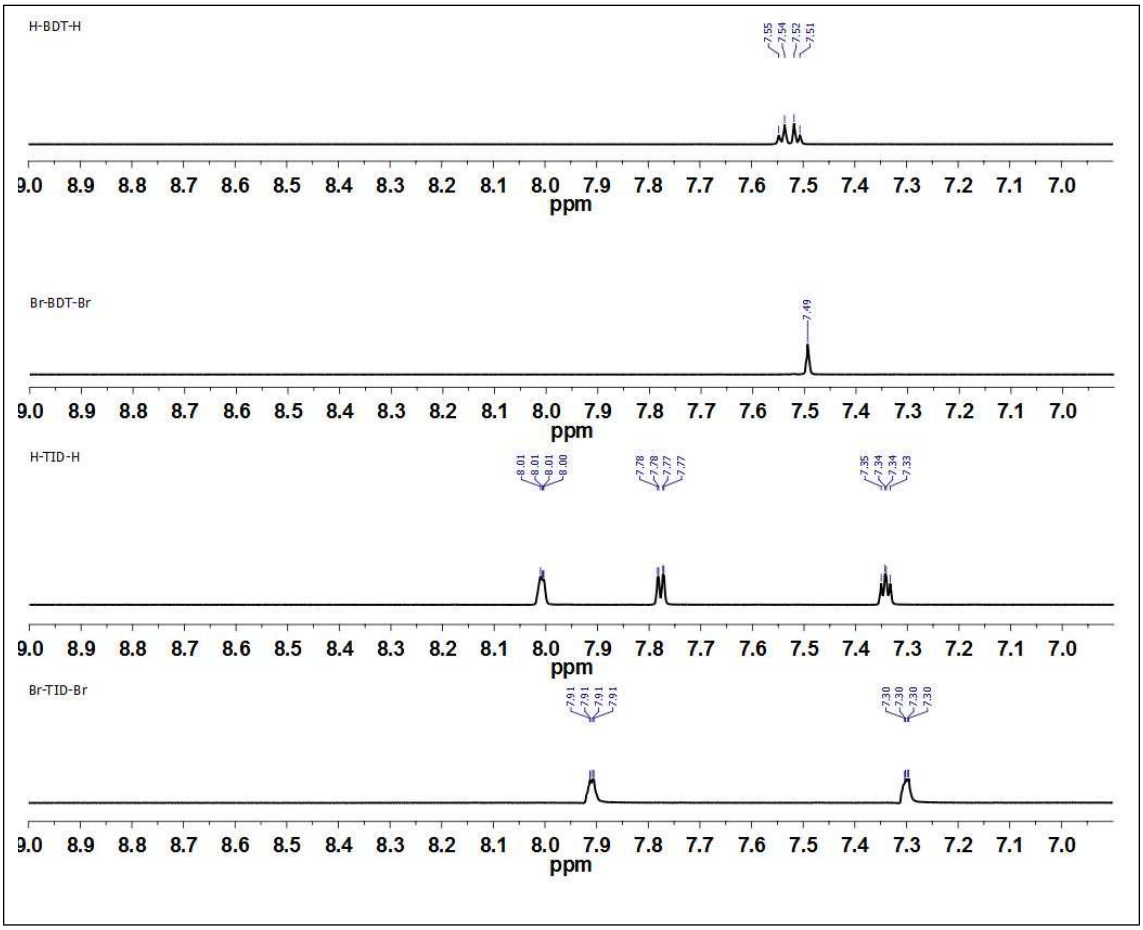
The aromatic part of the well-defined $^{1}$H NMR spectra for **P4S**, **P4H-L$_{REF}$**, **P4H-L2** and **P4H-L4** is shown below. The main peaks **A**, **B** and **C** correspond to the protons of the main chain while the residual signals (**a-k**) are related to end groups or homocoupling units. For **P4S,** in addition to the main signals observed for **A** (8.17 ppm; TID), **B** (7.79 ppm; BDT) and **C** (7.58 ppm; TID), several residual resonances can be observed**.** The signal found at 8.21 ppm (**a**) indicates the presence of homocoupling.



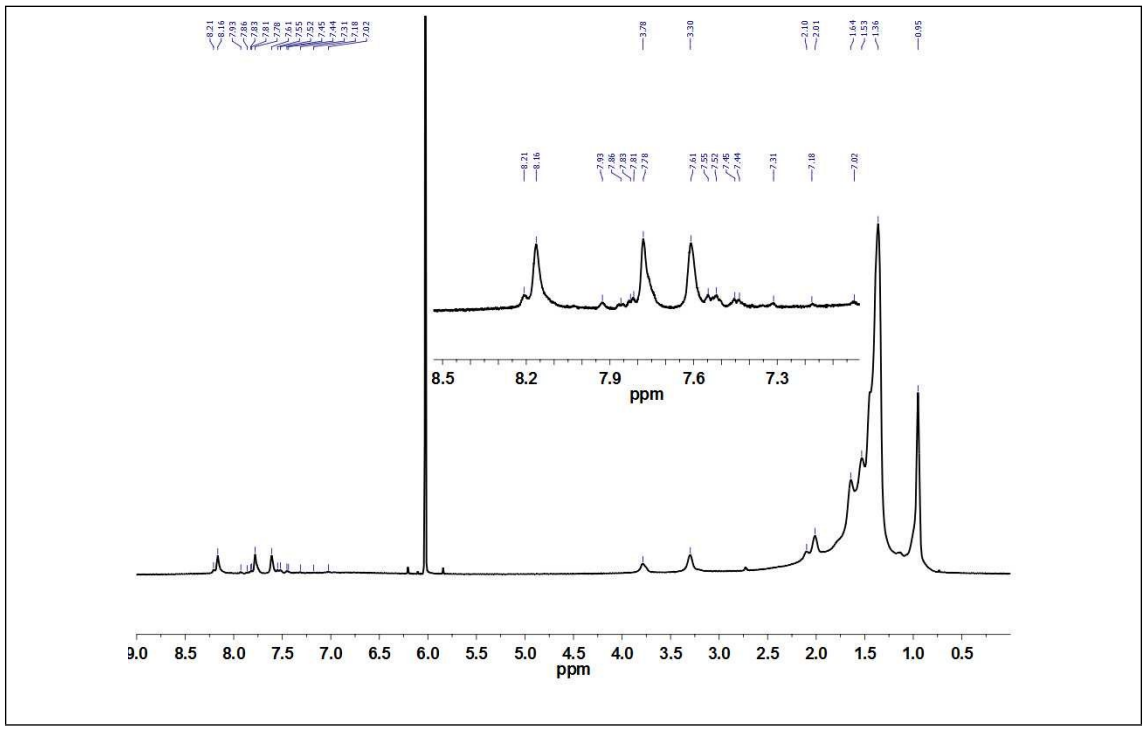

Two signals (**b**: 7.76 ppm and **c**: 7.46 ppm) are also found in the $^{1}$H NMR spectrum of poly(BDT) suggesting that BDT homocoupling is also possible during the polymerization of **P4S** and confirmed by the analysis of the $^{1}$H NMR of **P4S-20HC (SI 4.18)**. Indeed, the intensity of the resonance at 7.76 ppm (for 20% of BDT homocoupling) is higher than the intensity of the resonance observed for **P4S (4.15)**. Both signals at 7.93 ppm (**d**) and 7.33 ppm (**e**) were assigned to the Br-TID terminus chain. Two other signals (7.82 and 8.07 ppm) could not be assigned based on the NMR data of the model compounds. For **P4H-L$_{REF}$**, in addition to the main signals for **A** (8.15 ppm; TID), **B** (7.80 ppm; BDT) and **C** (7.59 ppm; TID), other residual signals (**a, f, h, j** and **g**) were observed. Although the exact integrations were difficult

to determine, the lower intensity of the signal at 8.21 ppm for **P4H-$L_{REF}$** compared to the one observed for **P4S** suggests that the DHAP may lead to lower amounts of TID homocoupling side-reactions. A resonance at 7.77 ppm (**h**) was also observed (as with **P4S**), but the absence of a broad peak at 7.46 ppm (**c**) in the spectrum of **P4H-$L_{REF}$** suggests that the signal (**h**) is for the H-TID terminus. This hypothesis was confirmed by the presence of the signals **f** and **g** at 8.03 and 7.35 ppm respectively. As expected, no resonance at 7.93 ppm (**d**) (Br-TID terminus chain) was detected for **P4H-$L_{REF}$** since the non-brominated TID comonomer was used during polymerization. According to the NMR spectrum, the utilization of **$L_{REF}$** in DHAP decreases the amount of homocoupling compared to Migita-Stille polymerization. Moreover, for **P4H-L2** and **P4H-L4,** a significant drop of the intensity of the peak at 8.21 ppm (**a**) (related to the homocoupling of TID) was observed compared to **P4S.** The other residual peaks (**h**: 7.77 ppm; **f**: 8.03 ppm; **g**: 7.35) for **P4H-L2** and **P4H-L4** are less intense compared to **P4H-$L_{REF}$** due to higher molecular weights. Despite similar NMR spectra for **P4H** series, the structural defects differ from those found in **P4S.**

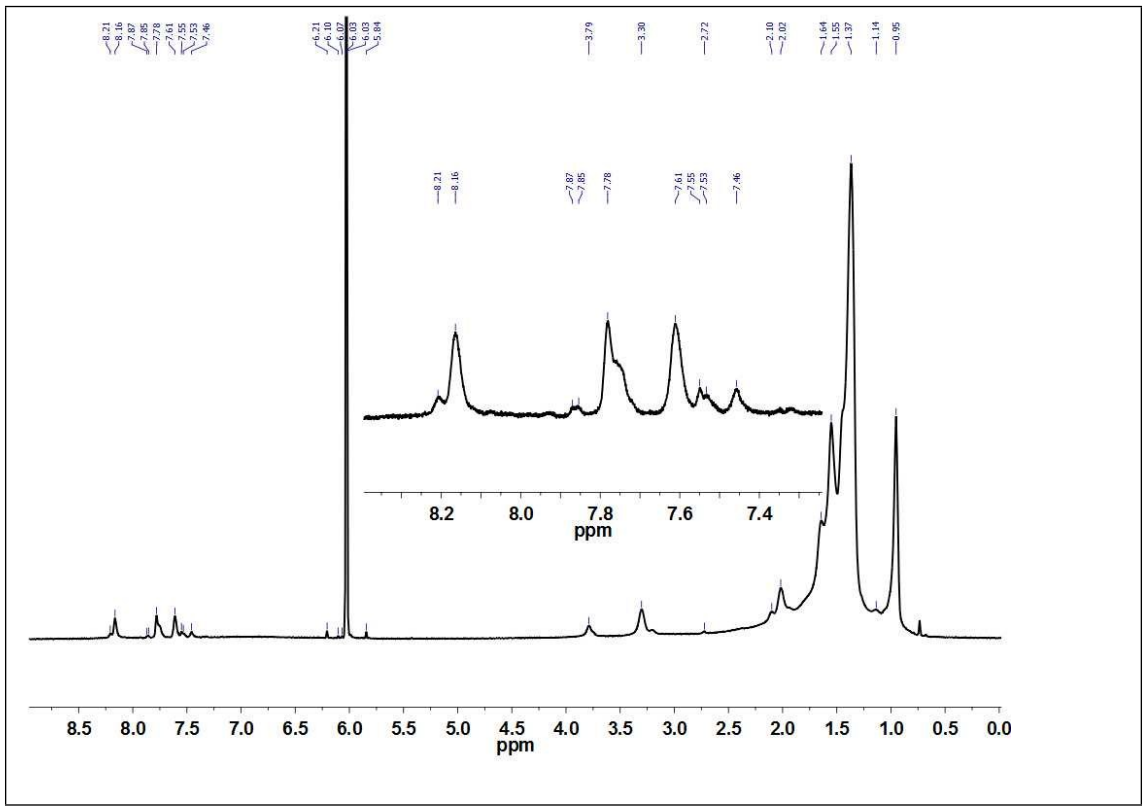
**4.1** $^{1}$H NMR spectra (500 MHz) in TCE at 90°C of all monomers used for DHAP



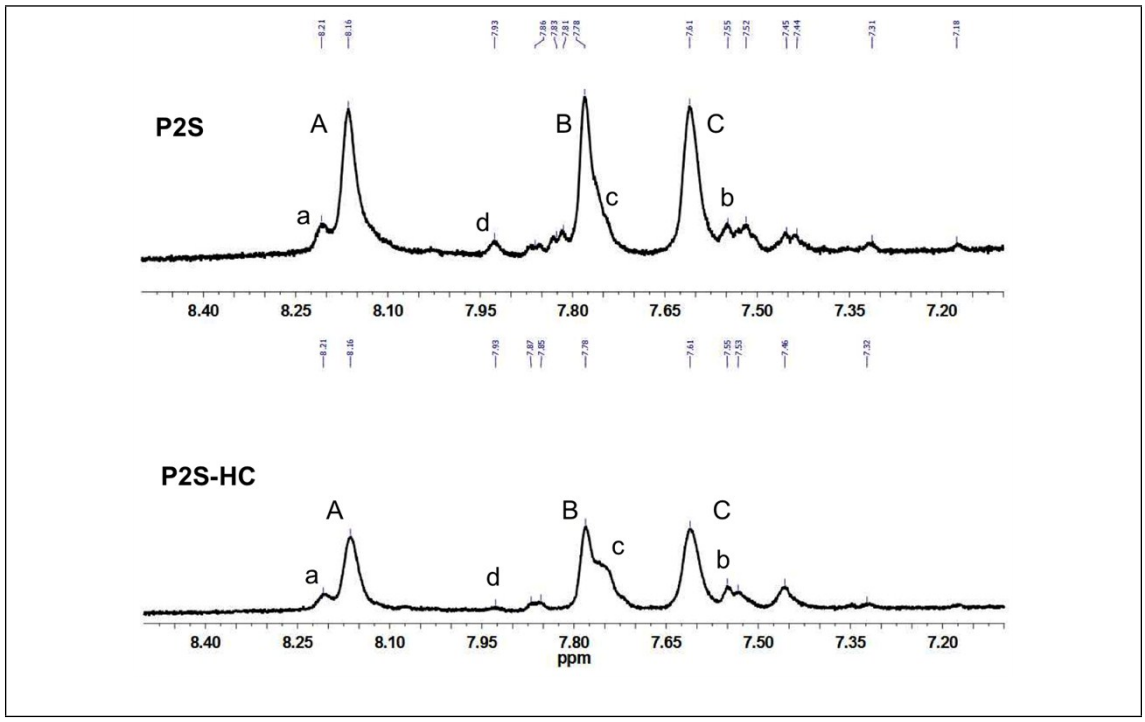
**4.2** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2S.**



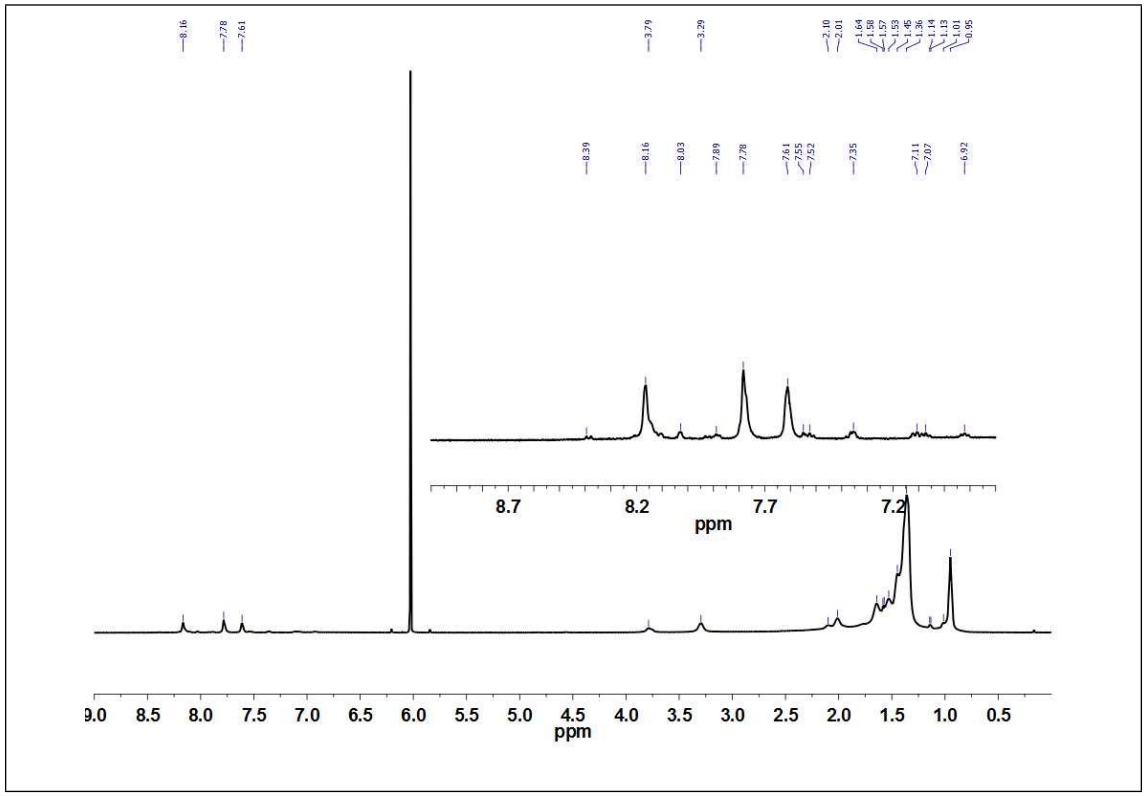

**4.3** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2S-HC.**



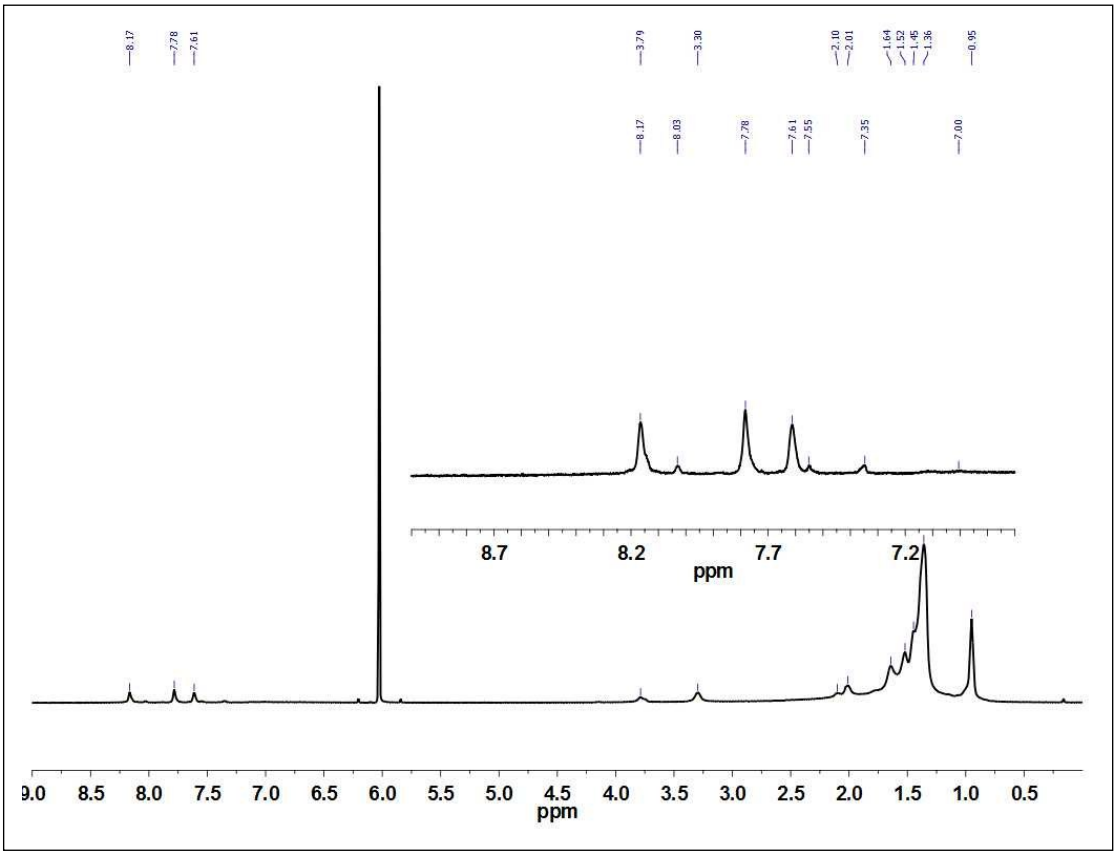
**4.4** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2S** and **P2S-HC** in aromatic part.



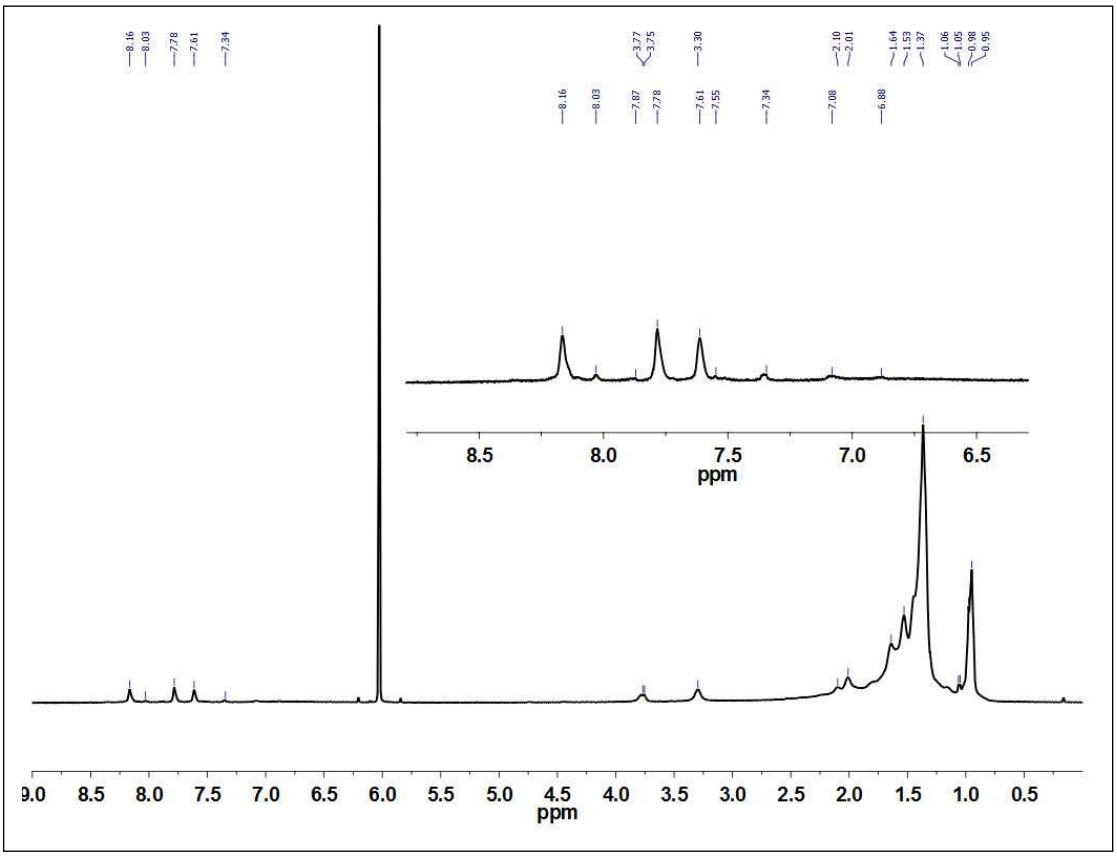

**4.5** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H-L1.**



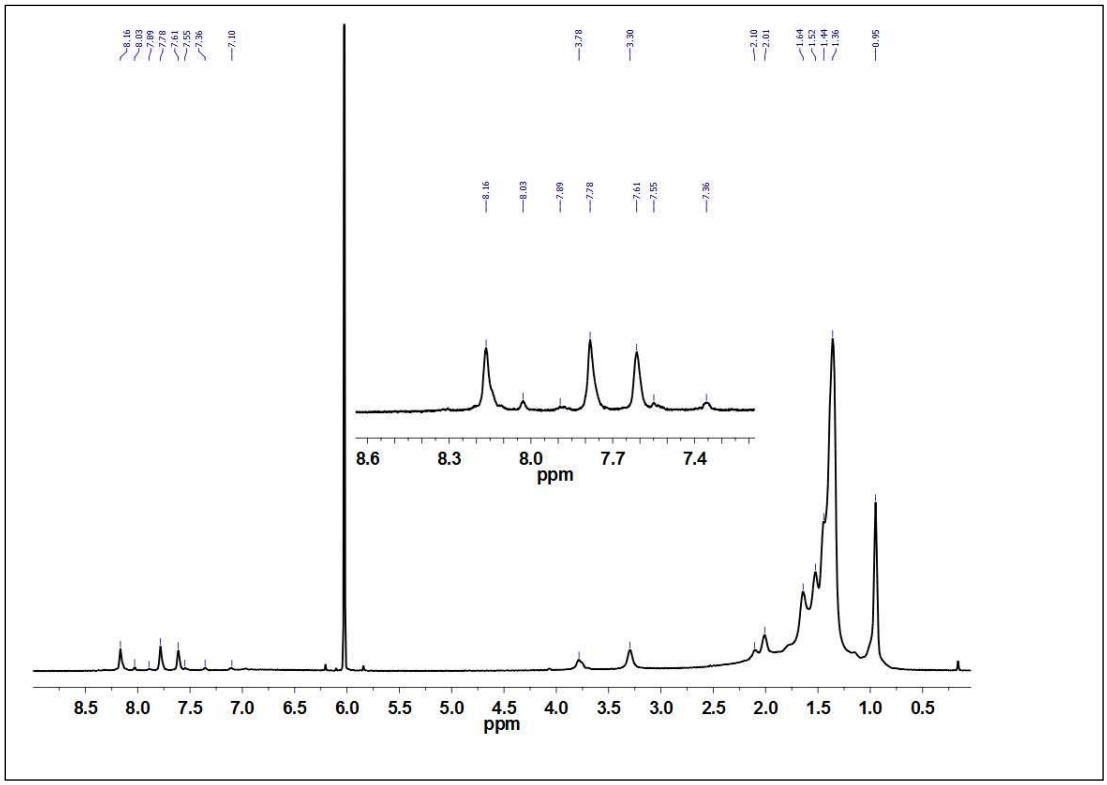
**4.6** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H-L2.**



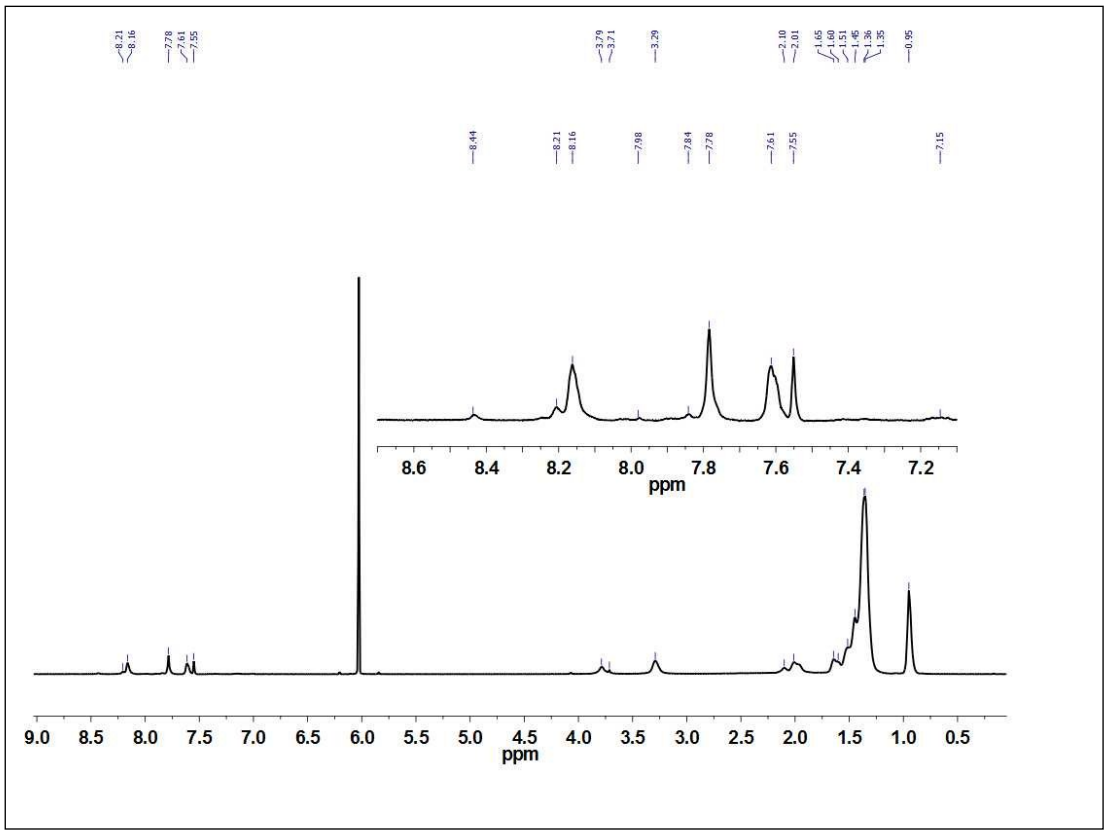

**4.7** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H-L4**



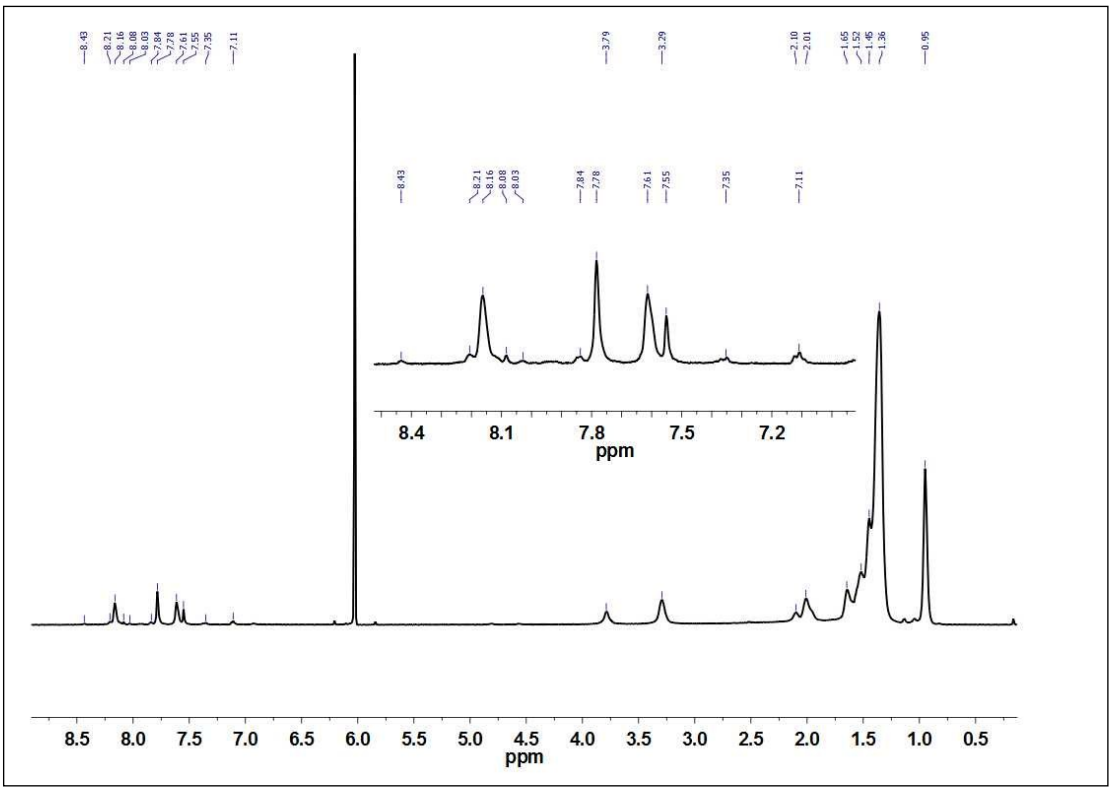
**4.8** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H-L5**



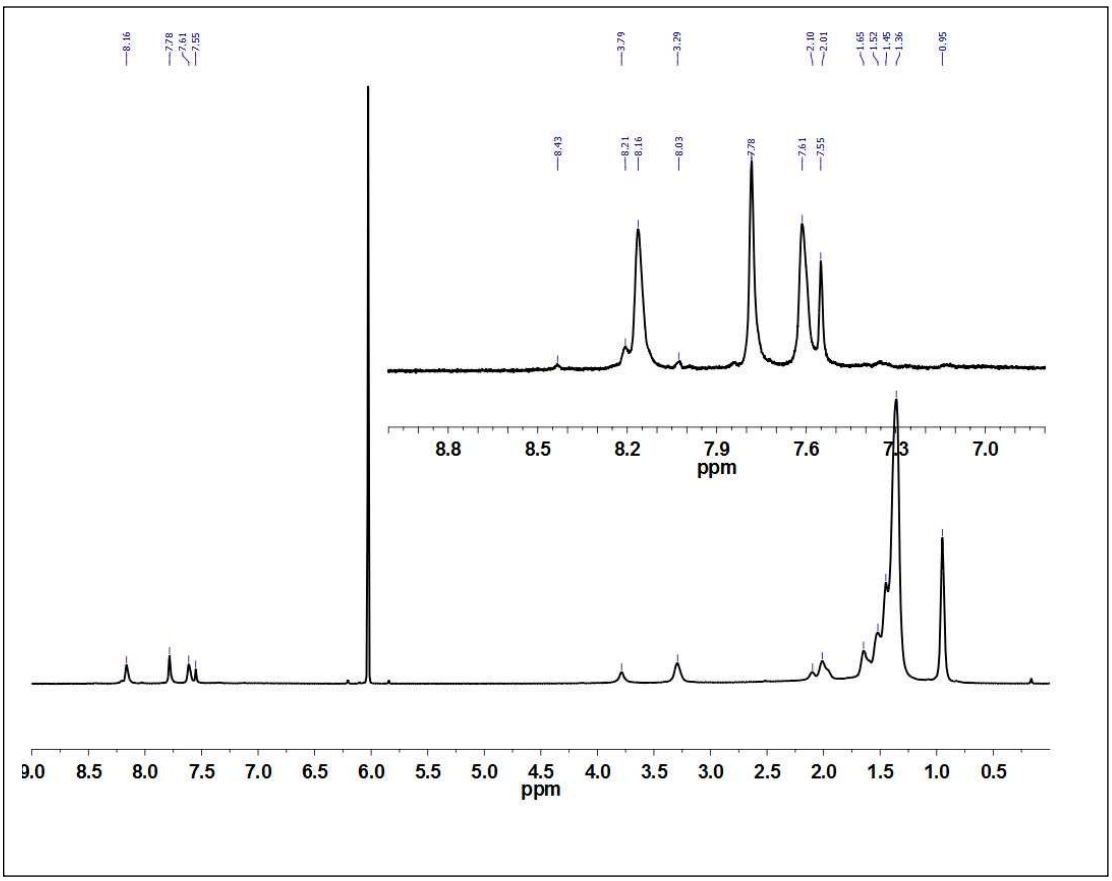

**4.9** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H'-Lref.**



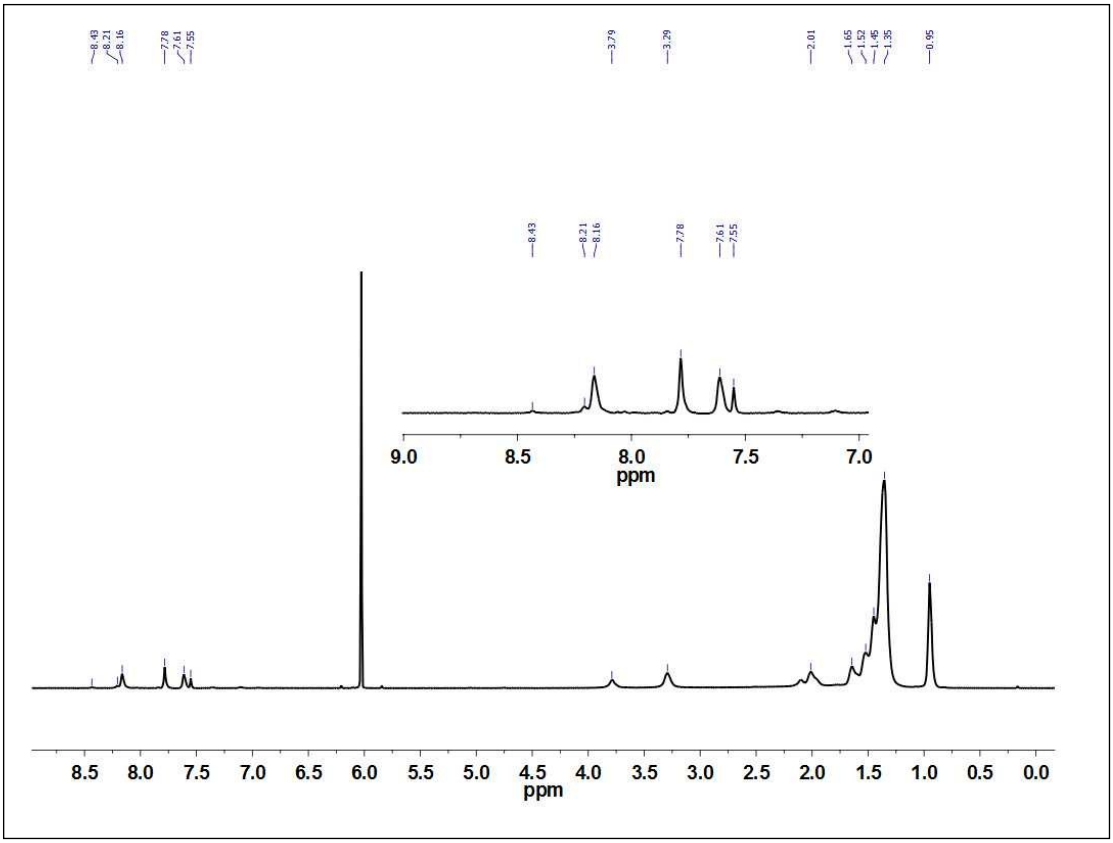
**4.10** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H'-L1.**



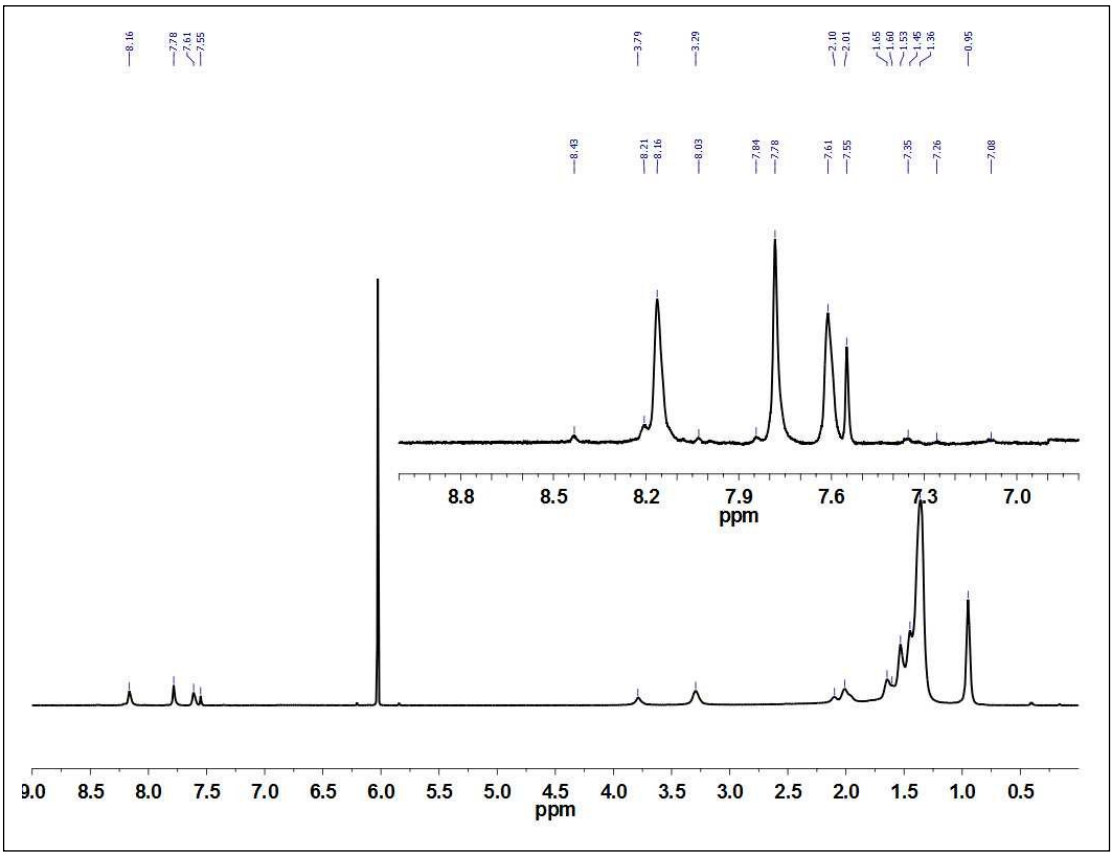

**4.11** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H'-L2.**



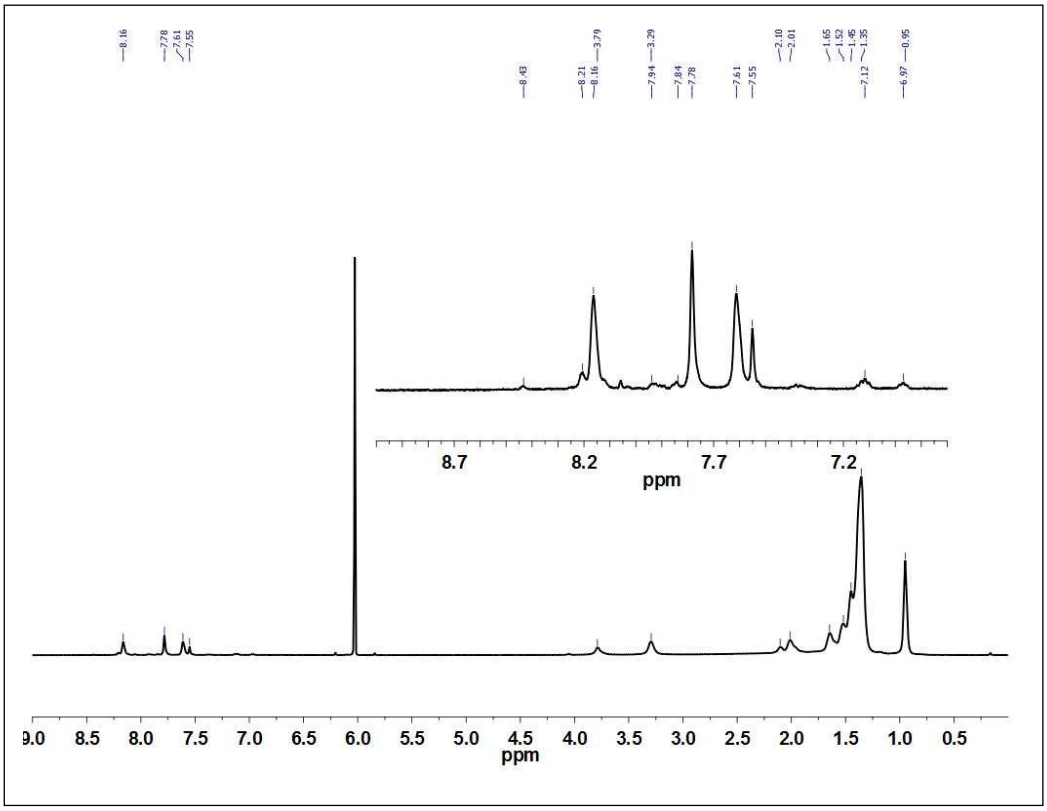
**4.12** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H'-L3.**



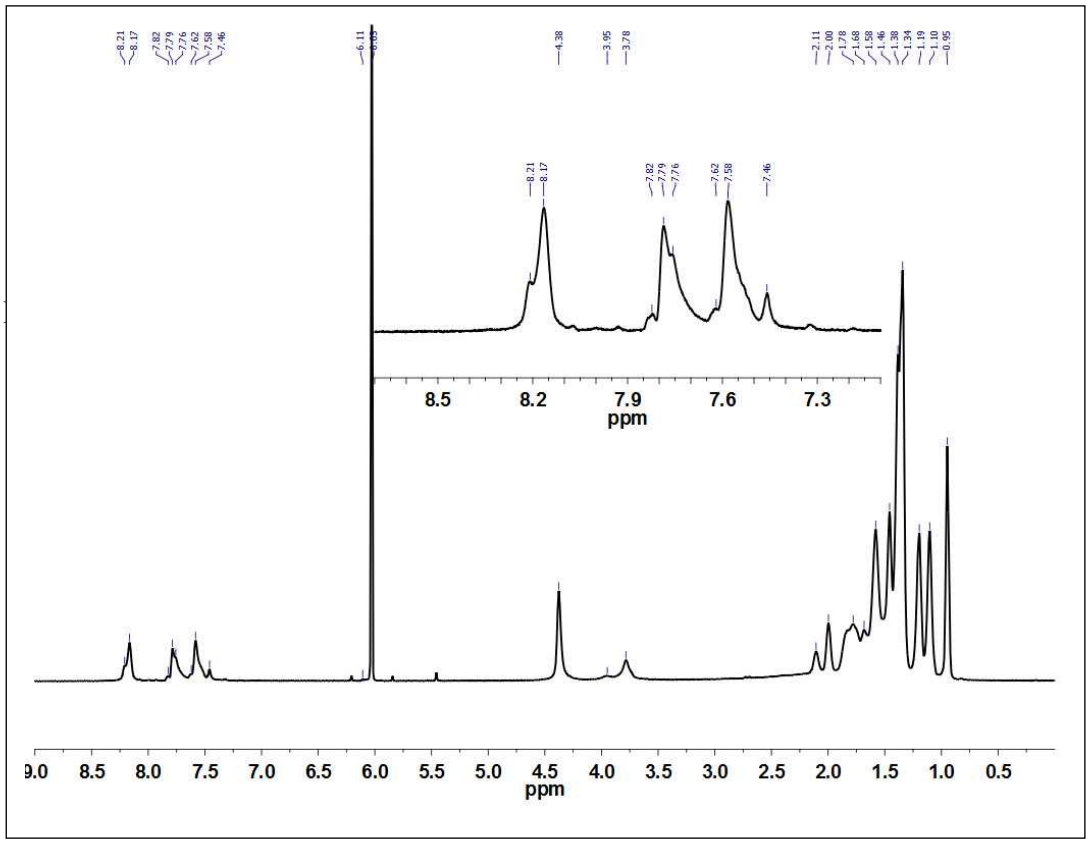

**4.13** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H'-L4.**



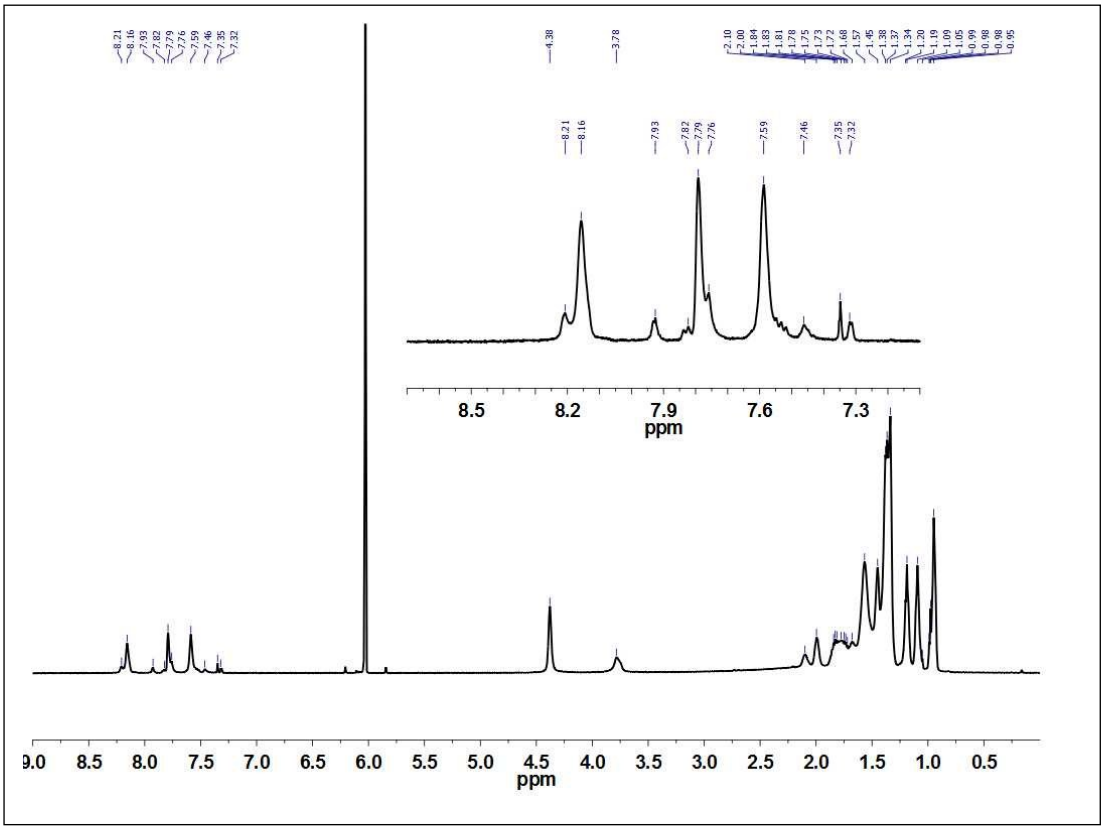
**4.14**. $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P2H'-L5**



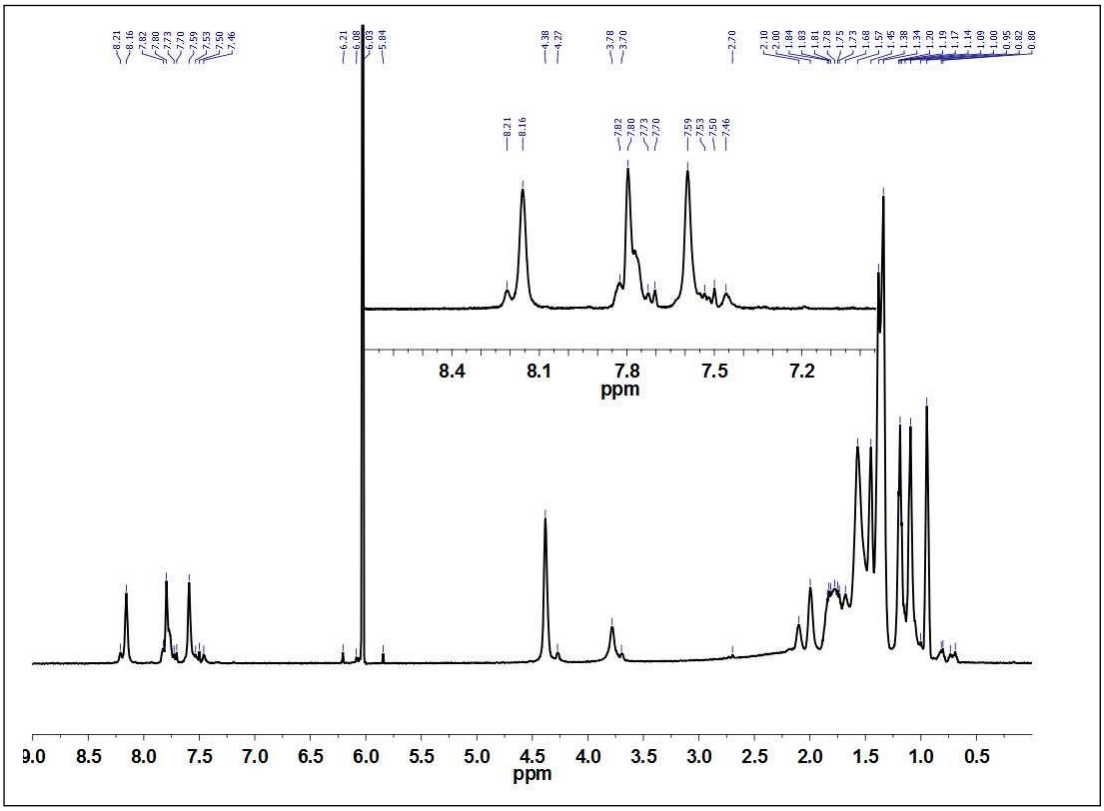

**4.15** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4S-High.**



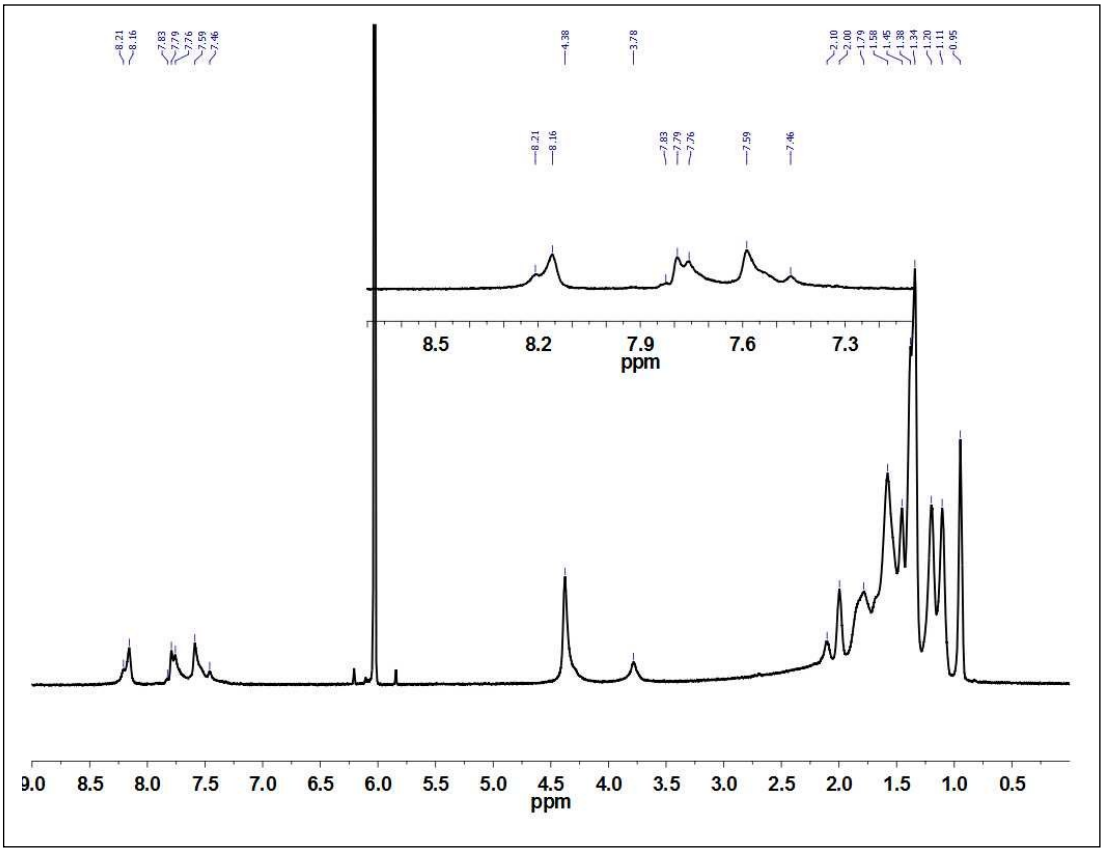
**4.16** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4S-Low.**



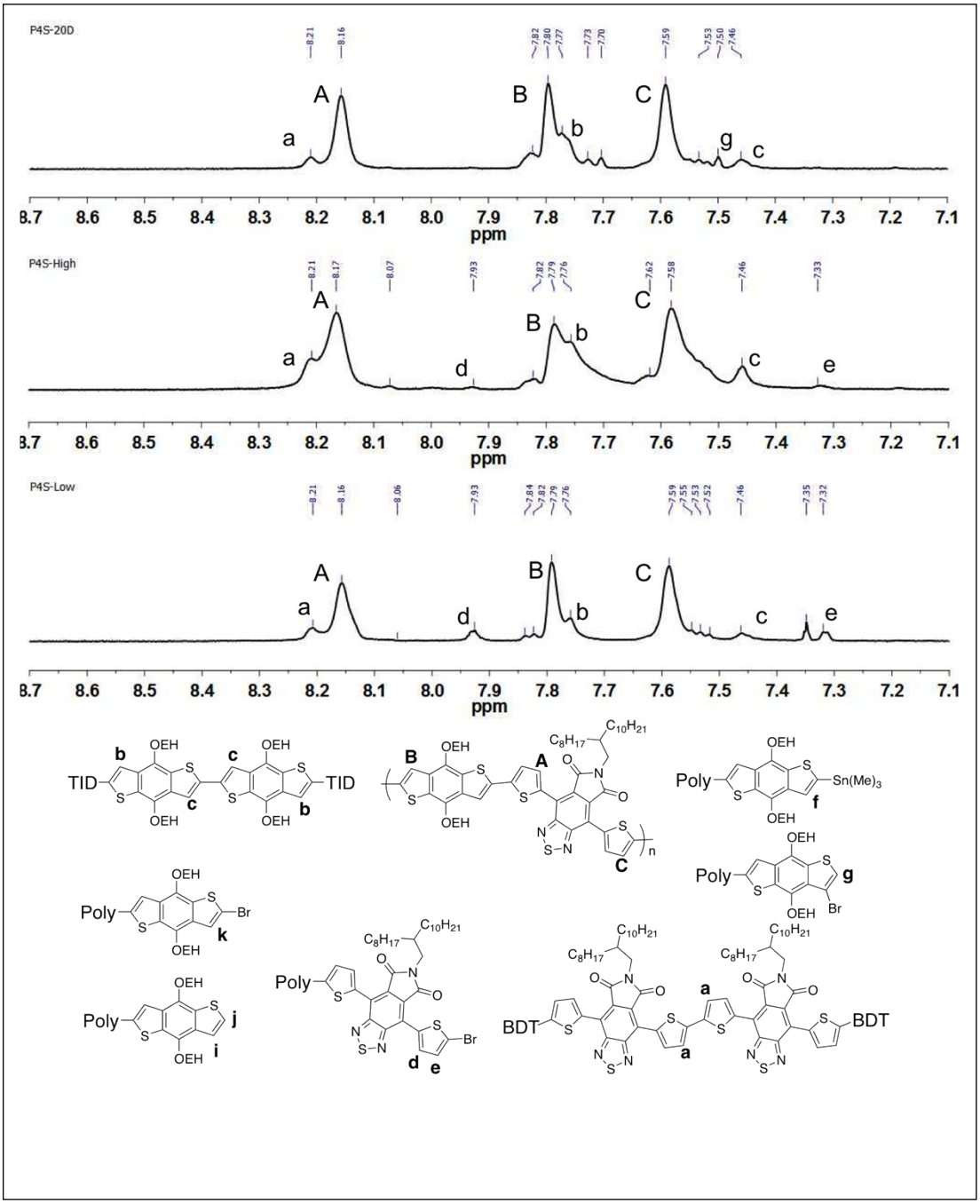

**4.17** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4S-20D.**



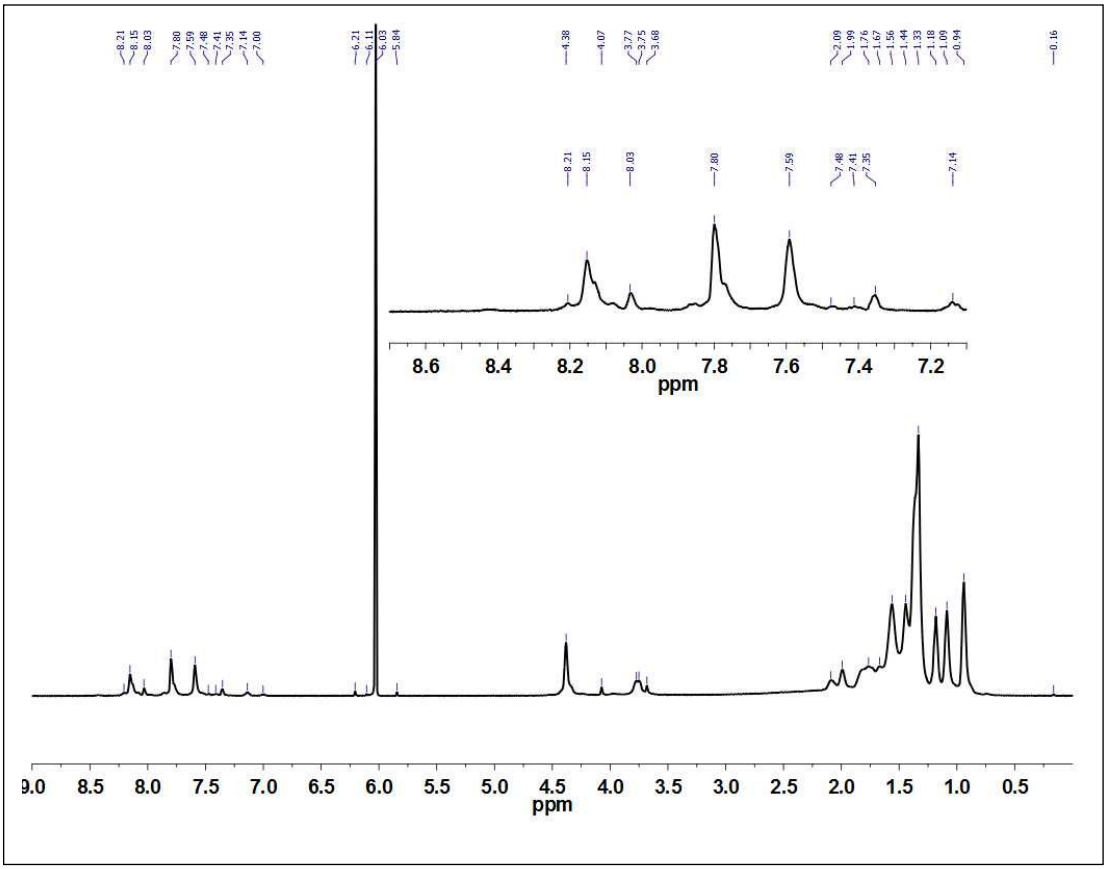
**4.18** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4S-20HC.**



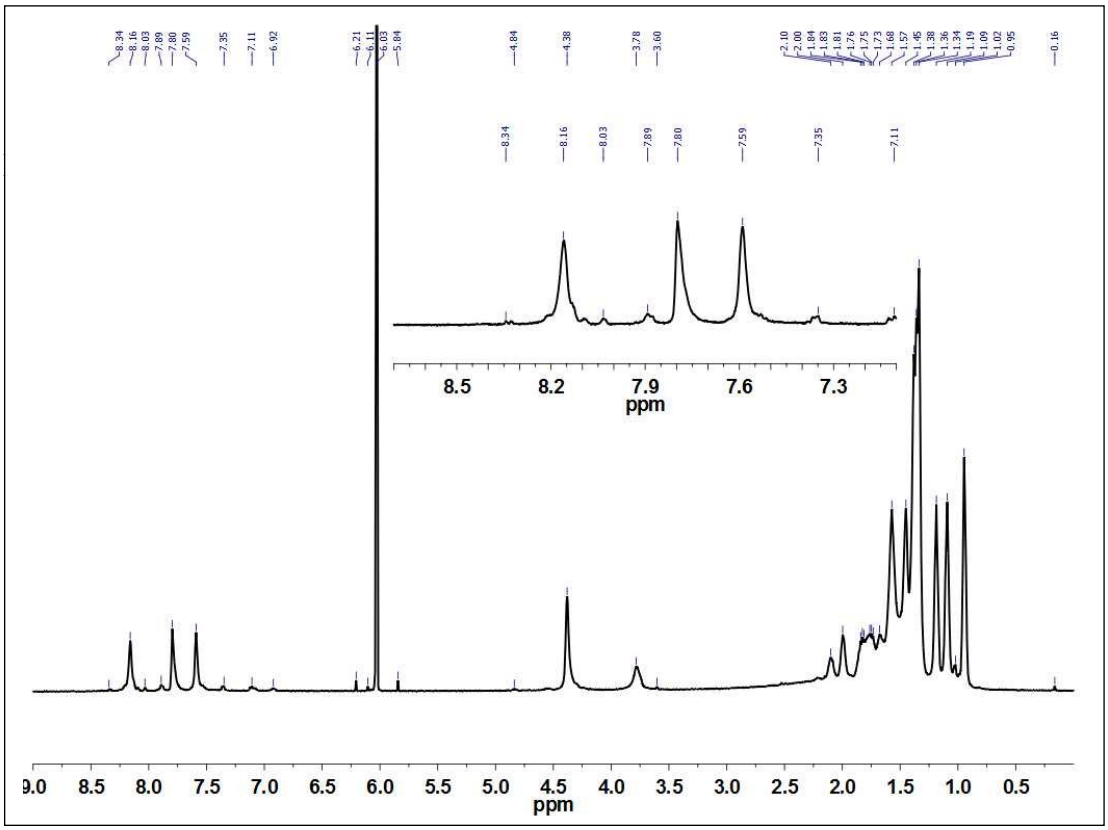
**4.19** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4S-20D, P4S-High** and **P4S-Low** in aromatic part.



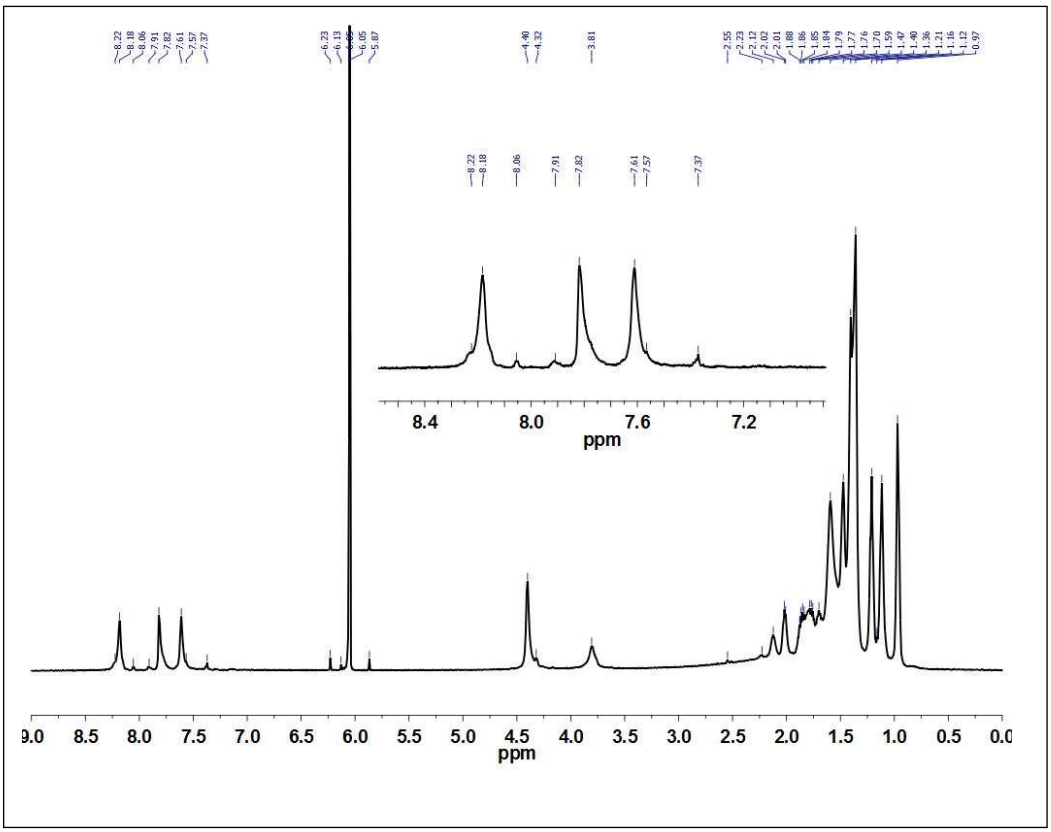
**4.20** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4H-Lref.**



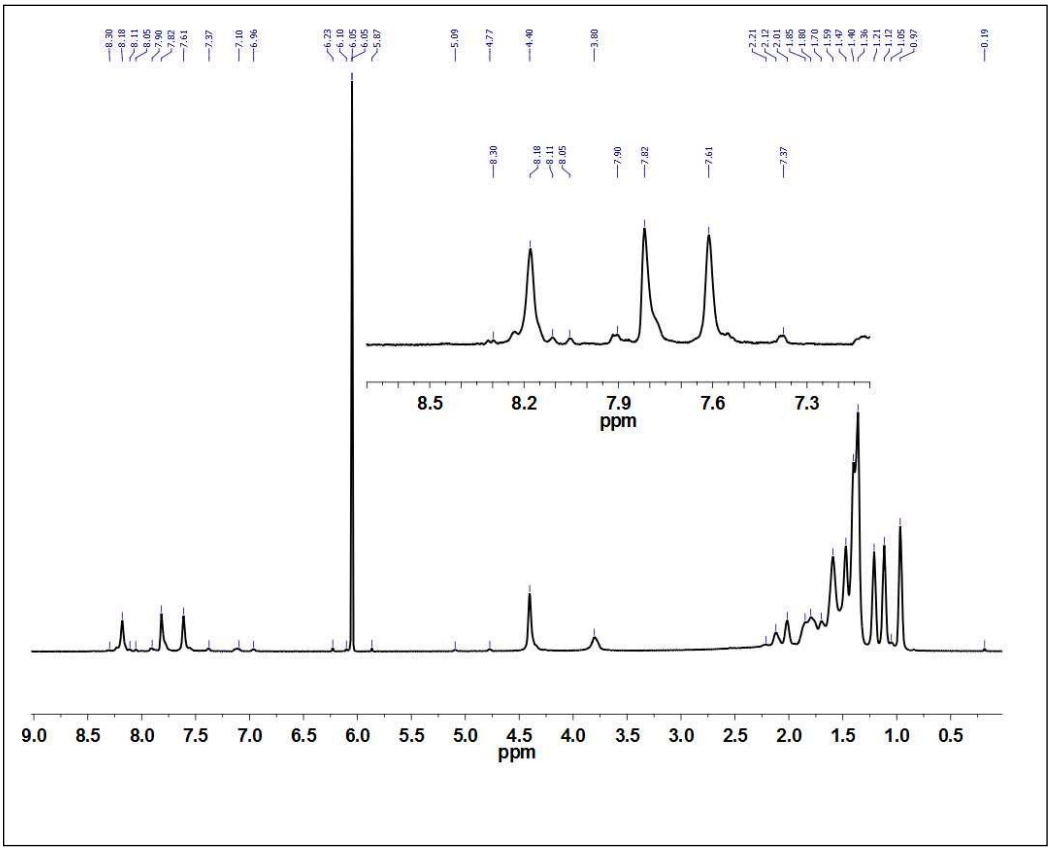

**4.21** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4H-Lref.**



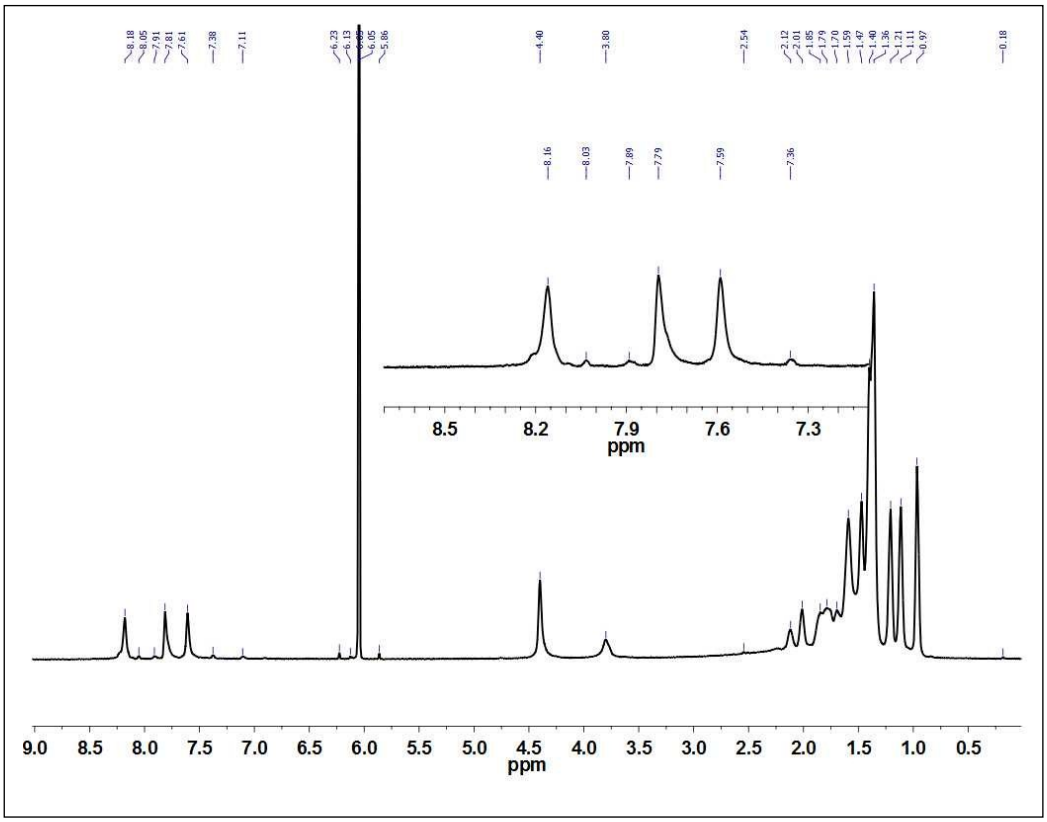
**4.22** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4H-L2.**



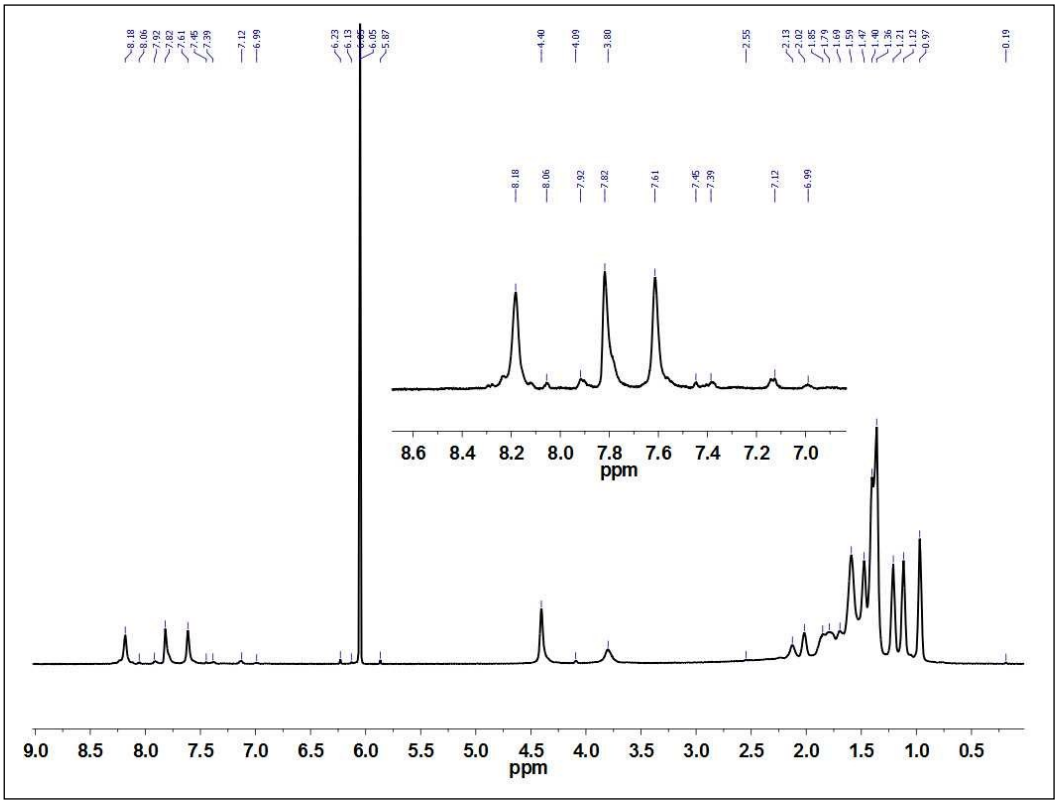

**4.23** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4H-L3.**



**4.24** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4H-L4.**




**4.25** $^{1}$H NMR spectrum (500 MHz) in TCE at 90°C of **P4H-L5.**

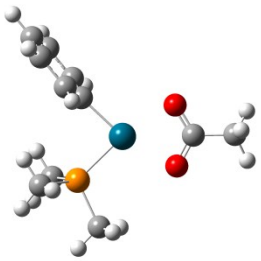


## 5. DFT calculations

All calculations were performed using the Gaussian 09 Suite of programs.[16] The B3LYP functional[17, 18] was used in combination with the TZVP basis set[19] for all atoms except Pd (DZVP).[20] This method was previously applied by Gorelski to elucidate the selectivity of palladium-catalyzed direct arylation.[21] The transition states were located and confirmed by frequency calculations (single imaginary frequency). The stationary points were characterized as minima by full vibration frequency calculations (no imaginary frequency). All geometry optimizations were carried out without any symmetry constraints. It is worth noting that methyl group was used as side chain on each comonomer (instead of linear or branched alkyl chains) to keep computational times reasonable. This approximation should not affect the results since alkyl chains are known to affect mostly the molecular packing, which is not considered here because all molecular calculations were done on single molecules in vacuum.

## Cartesian coordinates for calculated species

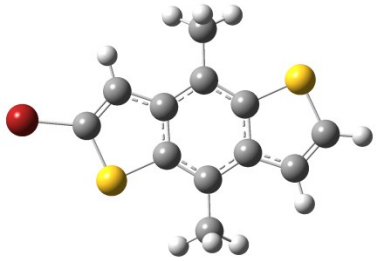
### a) Model catalyst



| | | | |
|---|---|---|---|
| Pd | 2.43414400 | 3.30462500 | 17.78838900 |
| P | 0.83172300 | 4.69522000 | 18.65852500 |
| C | 2.27207100 | 4.33427400 | 16.04987100 |
| C | 3.14732900 | 5.99637300 | 14.52211100 |
| H | 3.82868200 | 6.81650200 | 14.32555700 |
| C | 1.41936400 | 3.88190900 | 15.04248100 |
| H | 0.75003700 | 3.04828300 | 15.22213500 |
| C | 3.13120100 | 5.40071000 | 15.78328500 |
| H | 3.80827700 | 5.76401700 | 16.54794200 |
| C | 1.43675000 | 4.47918200 | 13.78192400 |
| H | 0.77733100 | 4.10933100 | 13.00483000 |
| C | 2.29806700 | 5.53952700 | 13.51927900 |
| H | 2.31116600 | 6.00241500 | 12.53996600 |
| O | 2.99815000 | 1.87017500 | 19.39475900 |
| O | 3.96313800 | 1.72794700 | 17.41625600 |
| C | 3.82307300 | 1.31128800 | 18.60467900 |
| C | 4.66124000 | 0.15509200 | 19.08795100 |
| H | 4.26164400 | -0.24921800 | 20.01610700 |
| H | 4.70606100 | -0.61899800 | 18.32186000 |
| H | 5.68122900 | 0.50541400 | 19.26284800 |
| C | 1.18202100 | 6.50502800 | 18.68740400 |
| H | 1.28140700 | 6.86965500 | 17.66606300 |
| H | 0.37881500 | 7.04480000 | 19.19282900 |
| H | 2.12095300 | 6.68379400 | 19.21140300 |
| C | -0.84910000 | 4.59127800 | 17.90811800 |
| H | -1.55152900 | 5.23570500 | 18.44034400 |
| H | -0.79681800 | 4.89272700 | 16.86269300 |
| H | -1.20055900 | 3.56052700 | 17.95451000 |
| C | 0.54980400 | 4.27281700 | 20.43224600 |
| H | -0.22198300 | 4.90954000 | 20.86957300 |
| H | 0.25349300 | 3.22715600 | 20.50983800 |
| H | 1.48234200 | 4.39468200 | 20.98258600 |

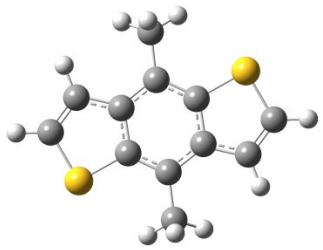
**b) Monomers**

**1) BDTBr**



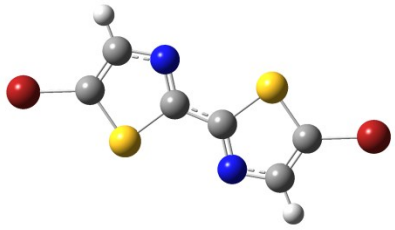
| | | | |
|---|---|---|---|
| C | -0.28175300 | 1.08152300 | 0.85004100 |
| C | 1.00800300 | 0.81260300 | 1.14192800 |
| S | -0.53245400 | 2.62718400 | 0.05102500 |
| C | 1.90304500 | 1.86507800 | 0.73330600 |
| H | 1.32155900 | -0.09975000 | 1.62558500 |
| C | 1.21200300 | 2.94411100 | 0.11489600 |
| C | 3.29804200 | 1.91118300 | 0.88267500 |
| C | 1.83575600 | 4.08647600 | -0.36808100 |
| C | 3.92540400 | 3.04764400 | 0.38257800 |
| C | 4.07542300 | 0.78756400 | 1.51274800 |
| C | 3.23416000 | 4.12653200 | -0.23213000 |
| C | 1.06682000 | 5.19969400 | -1.02659800 |
| S | 5.66732000 | 3.35678800 | 0.41793000 |
| H | 3.48664700 | 0.26001400 | 2.26288400 |
| H | 4.39035600 | 0.05517200 | 0.76278600 |
| H | 4.97597900 | 1.15851100 | 2.00507300 |
| C | 4.13626200 | 5.16748500 | -0.65233900 |
| H | 0.03614400 | 5.23680100 | -0.67016200 |
| H | 1.51712100 | 6.17159200 | -0.82352900 |
| H | 1.03424000 | 5.07037500 | -2.11289900 |
| C | 5.43165600 | 4.90084900 | -0.37570900 |
| H | 3.81886600 | 6.07448800 | -1.14619900 |
| H | 6.29136100 | 5.51596200 | -0.59072900 |
| Br | -1.76762800 | -0.03068200 | 1.21161800 |

**2) BDTH**



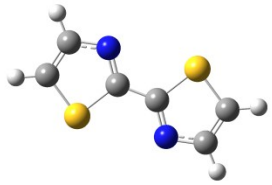
| | | | |
|---|---|---|---|
| H | -1.14704900 | 0.43747100 | 1.00306000 |
| C | -0.29001400 | 1.06477500 | 0.81407300 |
| C | 1.00219400 | 0.80717400 | 1.11158100 |
| S | -0.52491900 | 2.61159400 | 0.02441600 |
| C | 1.90409200 | 1.85975900 | 0.71822200 |
| H | 1.31860300 | -0.10640800 | 1.59369600 |
| C | 1.21369200 | 2.93889300 | 0.09985800 |
| C | 3.29863700 | 1.91036000 | 0.87706000 |
| C | 1.83943600 | 4.08601500 | -0.37403400 |
| C | 3.92623500 | 3.04997500 | 0.38709600 |
| C | 4.07481600 | 0.78602600 | 1.50779800 |
| C | 3.23565500 | 4.13010200 | -0.22815900 |
| C | 1.07005100 | 5.19857500 | -1.03340400 |
| S | 5.66801100 | 3.36429900 | 0.43584400 |
| H | 3.48109900 | 0.25397600 | 2.25085000 |
| H | 4.39675500 | 0.05729700 | 0.75710300 |
| H | 4.97123000 | 1.15669900 | 2.00809100 |
| C | 4.13886600 | 5.17534500 | -0.63742200 |
| H | 0.04586500 | 5.24723100 | -0.66010600 |
| H | 1.53164900 | 6.16909000 | -0.85057500 |
| H | 1.01728100 | 5.05590300 | -2.11738700 |
| C | 5.43287200 | 4.91163000 | -0.35299600 |
| H | 3.82267500 | 6.08361100 | -1.12979600 |
| H | 6.29208700 | 5.53036600 | -0.55953300 |

**3) BTABr**



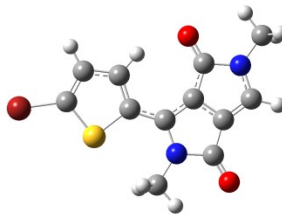
| | | | |
|---|---|---|---|
| C | -0.27455400 | 1.11830400 | 0.96641900 |
| C | 1.02919500 | 0.74912700 | 1.11808600 |
| S | -0.39630400 | 2.71749000 | 0.28037300 |
| H | 1.36250500 | -0.19488400 | 1.52208900 |
| C | 1.36711400 | 2.75423800 | 0.25651400 |
| C | 2.07773200 | 3.90955200 | -0.24220600 |
| S | 3.84115000 | 3.94630000 | -0.26606500 |
| C | 2.41565100 | 5.91466300 | -1.10377700 |
| C | 3.71940000 | 5.54548600 | -0.95211100 |
| H | 2.08234100 | 6.85867400 | -1.50778100 |
| N | 1.94227500 | 1.67894200 | 0.71543200 |
| N | 1.50257100 | 4.98484800 | -0.70112400 |
| Br | -1.79946500 | 0.10422700 | 1.40833000 |
| Br | 5.24431000 | 6.55956300 | -1.39402200 |

**4) BTAH**



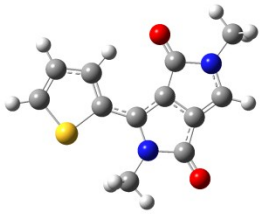
| | | | |
|---|---|---|---|
| H | -1.16813200 | 0.52079000 | 1.14359300 |
| C | -0.28384100 | 1.09454200 | 0.91935500 |
| C | 1.02071600 | 0.74644400 | 1.10176200 |
| S | -0.39331700 | 2.68406900 | 0.23331700 |
| H | 1.36000800 | -0.19252000 | 1.51435800 |
| C | 1.36818000 | 2.74887800 | 0.24903900 |
| C | 2.07666600 | 3.91491200 | -0.23473100 |
| S | 3.83816300 | 3.97972100 | -0.21900900 |
| C | 2.42413000 | 5.91734600 | -1.08745400 |
| C | 3.72868700 | 5.56924800 | -0.90504600 |
| H | 2.08483700 | 6.85631000 | -1.50004900 |
| H | 4.61297800 | 6.14300000 | -1.12928400 |
| N | 1.94373500 | 1.68078300 | 0.72316400 |
| N | 1.50111100 | 4.98300700 | -0.70885600 |

**5) DPPBr**



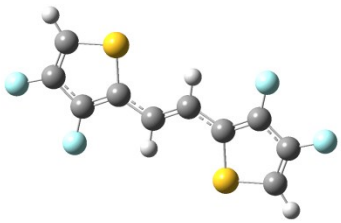
| | | | |
|---|---|---|---|
| C | -2.73912100 | -1.49314400 | 3.88795400 |
| C | -1.50222700 | -1.51715200 | 3.31082100 |
| S | -3.48616100 | -3.05980300 | 3.94378600 |
| C | -1.12747300 | -2.81321300 | 2.89776900 |
| H | -0.88493800 | -0.63984500 | 3.18745900 |
| C | -2.07549900 | -3.78544100 | 3.15701200 |
| Br | -3.63560200 | 0.01303100 | 4.58210900 |
| H | -0.18445900 | -3.04493900 | 2.41724300 |
| C | -1.93022700 | -5.17754500 | 2.83002600 |
| C | -0.84181800 | -5.77048300 | 2.20338600 |
| C | -2.39633700 | -7.46475900 | 2.62716400 |
| C | -1.09601500 | -7.16800100 | 2.06424600 |
| C | 0.45895900 | -5.48727700 | 1.63520500 |
| C | -0.02527200 | -7.74444100 | 1.44516200 |
| H | 0.15051700 | -8.77272400 | 1.16878300 |
| N | 0.90824100 | -6.77209500 | 1.18132600 |
| N | -2.86232800 | -6.17886400 | 3.08658000 |
| C | -4.15922800 | -6.07420400 | 3.72784300 |
| H | -4.07304000 | -5.71312600 | 4.75403800 |
| H | -4.83621200 | -5.42837300 | 3.16605300 |
| H | -4.57292300 | -7.08114500 | 3.74533300 |
| C | 2.18994800 | -6.96724800 | 0.53202200 |
| H | 2.06162100 | -7.36896800 | -0.47509100 |
| H | 2.67192100 | -5.99374500 | 0.46716300 |
| H | 2.82530000 | -7.64044000 | 1.11129300 |
| O | 1.12126200 | -4.46561200 | 1.51022800 |
| O | -3.04014900 | -8.48664300 | 2.74455200 |

**6) DPPH**



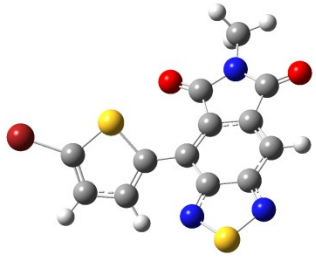
| | | | |
|---|---|---|---|
| C | -2.73835000 | -1.48868200 | 3.89618500 |
| C | -1.50053600 | -1.51973900 | 3.31913200 |
| S | -3.47335900 | -3.05191100 | 3.94282800 |
| C | -1.11723900 | -2.81200700 | 2.90013000 |
| H | -0.88005800 | -0.64338600 | 3.19696700 |
| C | -2.06815000 | -3.78288400 | 3.15774000 |
| H | -0.17489400 | -3.04439900 | 2.41992600 |
| C | -1.92477000 | -5.17556900 | 2.82863700 |
| C | -0.83871000 | -5.77125800 | 2.19992900 |
| C | -2.39668900 | -7.46188000 | 2.62538700 |
| C | -1.09660000 | -7.16846300 | 2.06072400 |
| C | 0.46254600 | -5.49203300 | 1.63040900 |
| C | -0.02903800 | -7.74850500 | 1.44027500 |
| H | 0.14287700 | -8.77736400 | 1.16358600 |
| N | 0.90684300 | -6.77876900 | 1.17468300 |
| N | -2.85849000 | -6.17590200 | 3.08612500 |
| C | -4.15449000 | -6.06965700 | 3.72882000 |
| H | -4.06626800 | -5.70597300 | 4.75370200 |
| H | -4.83058100 | -5.42252200 | 3.16776000 |
| H | -4.56883400 | -7.07627400 | 3.74769500 |
| C | 2.18841600 | -6.97829400 | 0.52707200 |
| H | 2.06046200 | -7.38145500 | -0.47960300 |
| H | 2.67221500 | -6.00572000 | 0.46111400 |
| H | 2.82206000 | -7.65184800 | 1.10796700 |
| O | 1.12989700 | -4.47399100 | 1.50456600 |
| O | -3.04246800 | -8.48291300 | 2.74282700 |
| H | -3.26879500 | -0.64073300 | 4.29969200 |

**7) FTVTH**



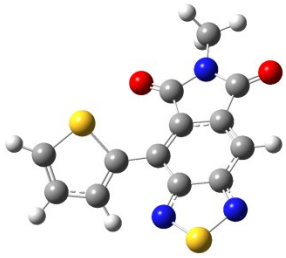
| | | | |
|---|---|---|---|
| C | -6.63377700 | -1.36733600 | -0.00019600 |
| C | -5.28176400 | -1.27217400 | -0.00051500 |
| C | -4.80848000 | 0.06406700 | 0.00020200 |
| C | -5.79203700 | 1.01808600 | 0.00105900 |
| S | -7.36157700 | 0.21595500 | 0.00092100 |
| H | -7.23793900 | -2.25853200 | -0.00059700 |
| C | -5.59672600 | 2.44210400 | 0.00191500 |
| H | -4.55372400 | 2.74443400 | 0.00180100 |
| C | -6.56415400 | 3.37983900 | 0.00282500 |
| H | -7.60714400 | 3.07746600 | 0.00296300 |
| C | -6.36888600 | 4.80387400 | 0.00369000 |
| C | -7.35247400 | 5.75786600 | 0.00447900 |
| S | -4.79937500 | 5.60606000 | 0.00389000 |
| C | -6.87923400 | 7.09412300 | 0.00522600 |
| C | -5.52722400 | 7.18932700 | 0.00504000 |
| H | -4.92310600 | 8.08052800 | 0.00549100 |
| F | -7.71930000 | 8.13628600 | 0.00603800 |
| F | -8.66247700 | 5.47475700 | 0.00454700 |
| F | -3.49846600 | 0.34714000 | 0.00004300 |
| F | -4.44173100 | -2.31436700 | -0.00138800 |

**8) NDPPBr**



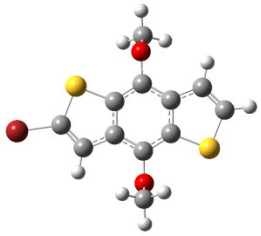
| | | | |
|---|---|---|---|
| C | -1.40624900 | 0.08258200 | 0.58891100 |
| C | -1.86680600 | 1.24869100 | 1.24137700 |
| C | -2.22460000 | -0.27914300 | -0.44191800 |
| C | -3.00706800 | 1.79227200 | 0.69419800 |
| S | -3.54290100 | 0.82173900 | -0.67299800 |
| H | -1.37382200 | 1.67472600 | 2.10092500 |
| C | -3.75996200 | 2.93551700 | 1.20343800 |
| C | -4.40929100 | 3.90494200 | 0.46376700 |
| C | -3.88905700 | 3.10720300 | 2.64153800 |
| C | -5.14281700 | 4.97902900 | 1.06077700 |
| C | -4.64495700 | 4.20830100 | 3.22233400 |
| C | -5.28575300 | 5.16933400 | 2.39544700 |
| H | -5.84229000 | 5.99752600 | 2.81148000 |
| N | -3.37369200 | 2.29442200 | 3.55831300 |
| N | -4.67006600 | 4.20336800 | 4.55213800 |
| S | -3.80155400 | 2.88811200 | 5.03432900 |
| C | -4.44353200 | 4.14235600 | -1.01508300 |
| C | -5.66983100 | 5.85788200 | -0.02110600 |
| O | -6.34719400 | 6.85391700 | 0.08059600 |
| O | -3.93088500 | 3.52174600 | -1.91654100 |
| N | -5.20858500 | 5.30000800 | -1.21210000 |
| C | -5.46861300 | 5.85620400 | -2.52763800 |
| H | -6.11228600 | 6.72303700 | -2.39826500 |
| H | -4.53486900 | 6.15519300 | -3.00471400 |
| H | -5.96101100 | 5.11590200 | -3.15816700 |
| H | -0.51955900 | -0.46487300 | 0.87132600 |
| Br | -2.00869700 | -1.76973100 | -1.58010700 |

**9) NDPPH**



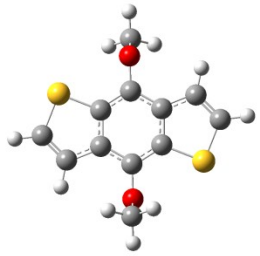
| | | | |
|---|---|---|---|
| C | -1.41311500 | 0.09524200 | 0.56497800 |
| C | -1.84844000 | 1.27038400 | 1.22104100 |
| C | -2.27366100 | -0.30852100 | -0.41626300 |
| C | -3.02251700 | 1.78246900 | 0.71760800 |
| S | -3.61214500 | 0.76788700 | -0.58713400 |
| H | -1.31787000 | 1.72824700 | 2.04147800 |
| H | -2.19448600 | -1.16908200 | -1.06149100 |
| C | -3.76612400 | 2.93409700 | 1.22269700 |
| C | -4.40900500 | 3.89947700 | 0.47460300 |
| C | -3.89371200 | 3.11661000 | 2.65794500 |
| C | -5.14851900 | 4.97493300 | 1.06217900 |
| C | -4.65365600 | 4.21896800 | 3.23077800 |
| C | -5.29704500 | 5.17163800 | 2.39552200 |
| H | -5.85811200 | 6.00015100 | 2.80484800 |
| N | -3.37332900 | 2.31192300 | 3.57915800 |
| N | -4.67749800 | 4.22404100 | 4.56067000 |
| S | -3.80159600 | 2.91581500 | 5.05090800 |
| C | -4.42395900 | 4.13446100 | -1.00555200 |
| C | -5.67270300 | 5.84567300 | -0.02761000 |
| O | -6.35643300 | 6.83874700 | 0.06452600 |
| O | -3.88852900 | 3.52387200 | -1.89984500 |
| N | -5.19901300 | 5.28571300 | -1.21244200 |
| C | -5.44452800 | 5.84062000 | -2.53109500 |
| H | -6.09686200 | 6.70232900 | -2.41090800 |
| H | -4.50643500 | 6.14733100 | -2.99471400 |
| H | -5.92175300 | 5.09684300 | -3.16914700 |
| H | -0.50384300 | -0.43223800 | 0.81581500 |

**10) OBDTBr**



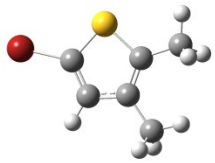
| | | | |
|---|---|---|---|
| H | 1.03703000 | -0.65110300 | 1.05517500 |
| C | 0.34617000 | -1.25474900 | 0.48676200 |
| C | 0.65766000 | -2.45370400 | -0.05114700 |
| C | -1.00686200 | -0.86459900 | 0.19665000 |
| S | -0.65415600 | -3.21511400 | -0.95074000 |
| C | -1.68586800 | -1.82627200 | -0.59751600 |
| C | -1.67874800 | 0.29828000 | 0.59127300 |
| C | -2.99247300 | -1.65396800 | -1.02725700 |
| C | -2.98808300 | 0.47139500 | 0.16191600 |
| C | -3.66672900 | -0.49072100 | -0.63165100 |
| S | -4.02410600 | 1.85346800 | 0.51228700 |
| C | -5.01878300 | -0.09270500 | -0.91599500 |
| C | -5.33900900 | 1.10644200 | -0.38048400 |
| H | -5.70917400 | -0.69777400 | -1.48533500 |
| H | -6.28307800 | 1.62444300 | -0.44652700 |
| O | -1.04697900 | 1.26634000 | 1.33593400 |
| O | -3.61435400 | -2.62774500 | -1.77356700 |
| C | -1.12870100 | 1.08642700 | 2.75782500 |
| H | -0.59842100 | 1.92653200 | 3.20160900 |
| H | -2.16830300 | 1.09190500 | 3.09569000 |
| H | -0.65348700 | 0.15078800 | 3.06485900 |
| C | -3.58553800 | -2.41434500 | -3.19271900 |
| H | -2.55737700 | -2.37392900 | -3.56220900 |
| H | -4.09839200 | -3.26415500 | -3.63850400 |
| H | -4.10360800 | -1.49092100 | -3.46456800 |
| Br | 2.32204400 | -3.34001300 | 0.08124500 |

**11) OBDTH**



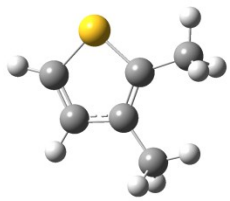
| | | | |
|---|---|---|---|
| H | 1.03535200 | -0.63801300 | 1.02672400 |
| C | 0.34573400 | -1.24435300 | 0.45772000 |
| C | 0.66901600 | -2.43947000 | -0.08426700 |
| C | -1.00996700 | -0.85117500 | 0.18222800 |
| S | -0.64747300 | -3.18981500 | -0.97352500 |
| H | 1.61587000 | -2.95326200 | -0.02508500 |
| C | -1.68878800 | -1.81362700 | -0.61146700 |
| C | -1.68590100 | 0.30683300 | 0.58606400 |
| C | -3.00137300 | -1.64477100 | -1.02946200 |
| C | -2.99843500 | 0.47566900 | 0.16807900 |
| C | -3.67734000 | -0.48688000 | -0.62548900 |
| S | -4.03966400 | 1.85209500 | 0.52974400 |
| C | -5.03297400 | -0.09352000 | -0.90132500 |
| C | -5.35616600 | 1.10172100 | -0.35961300 |
| H | -5.72251800 | -0.70009400 | -1.47018000 |
| H | -6.30293700 | 1.61565500 | -0.41883700 |
| O | -1.05578800 | 1.27677700 | 1.33192500 |
| O | -3.63163500 | -2.61452900 | -1.77543000 |
| C | -1.11716300 | 1.08133100 | 2.75166300 |
| H | -0.59353900 | 1.92422500 | 3.19850300 |
| H | -2.15257600 | 1.06849200 | 3.10257100 |
| H | -0.62532600 | 0.14937700 | 3.04370600 |
| C | -3.56895800 | -2.41968700 | -3.19524400 |
| H | -2.53327200 | -2.40764700 | -3.54533200 |
| H | -4.09276600 | -3.26243100 | -3.64214300 |
| H | -4.06000200 | -1.48752700 | -3.48795300 |

**12) ThioBr**



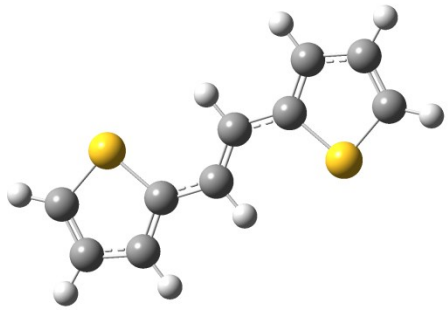
| | | | |
|---|---|---|---|
| C | -0.89121100 | 0.95317600 | 0.00014000 |
| C | 0.46568900 | 0.98336300 | -0.00060100 |
| C | 0.99584300 | 2.31494100 | -0.00016000 |
| C | 0.02177400 | 3.27524700 | 0.00086500 |
| S | -1.57975400 | 2.55351600 | 0.00139800 |
| H | 1.07885100 | 0.09279100 | -0.00146300 |
| C | 2.47293200 | 2.59279400 | -0.00061600 |
| H | 2.95612600 | 2.16239400 | 0.88080000 |
| H | 2.95632000 | 2.15811900 | -0.87979600 |
| H | 2.68270700 | 3.66199700 | -0.00317500 |
| C | 0.16565800 | 4.76832100 | 0.00159900 |
| H | 0.70814600 | 5.11645400 | 0.88433300 |
| H | 0.70706200 | 5.11741300 | -0.88142900 |
| H | -0.80631900 | 5.26246000 | 0.00246500 |
| Br | -1.99625800 | -0.58385100 | -0.00014900 |

**13) ThioH**



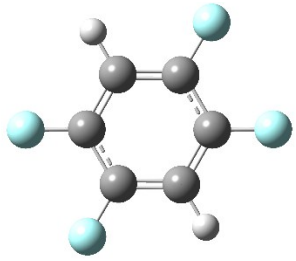
| | | | |
|---|---|---|---|
| C | -0.89543700 | 0.94364900 | 0.00013800 |
| C | 0.46309300 | 0.98683900 | -0.00053700 |
| C | 0.99912600 | 2.31492500 | -0.00017200 |
| C | 0.02170100 | 3.27364500 | 0.00089500 |
| S | -1.57187900 | 2.54383600 | 0.00170800 |
| H | -1.54099700 | 0.08032300 | -0.00004200 |
| H | 1.08203100 | 0.09872200 | -0.00142000 |
| C | 2.47551800 | 2.59737200 | -0.00068400 |
| H | 2.96060700 | 2.16859000 | 0.88073100 |
| H | 2.96086900 | 2.16351100 | -0.87943400 |
| H | 2.68401900 | 3.66703200 | -0.00371900 |
| C | 0.16626000 | 4.76657300 | 0.00163700 |
| H | 0.70937400 | 5.11520400 | 0.88401100 |
| H | 0.70848100 | 5.11616000 | -0.88091400 |
| H | -0.80590100 | 5.26030400 | 0.00239900 |

**14) TVTH**



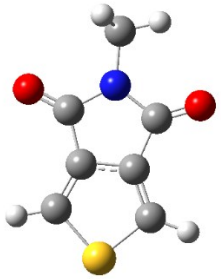
| | | | |
|---|---|---|---|
| C | -6.62294400 | -1.34950900 | -0.00015300 |
| C | -5.26258100 | -1.27432400 | -0.00052400 |
| C | -4.78361700 | 0.06158500 | 0.00031000 |
| C | -5.77809700 | 1.01249900 | 0.00099600 |
| S | -7.35579500 | 0.22848600 | 0.00077700 |
| H | -7.24731700 | -2.22837100 | -0.00050400 |
| H | -4.62063700 | -2.14416800 | -0.00121000 |
| H | -3.73414500 | 0.32382900 | 0.00030700 |
| C | -5.59725100 | 2.44157800 | 0.00180900 |
| H | -4.55610400 | 2.75364700 | 0.00178500 |
| C | -6.56264400 | 3.38158500 | 0.00265400 |
| H | -7.60378000 | 3.06947100 | 0.00274900 |
| C | -6.38184500 | 4.81069000 | 0.00359100 |
| C | -7.37635700 | 5.76157500 | 0.00459300 |
| S | -4.80418900 | 5.59478100 | 0.00372500 |
| C | -6.89744500 | 7.09750900 | 0.00522300 |
| H | -8.42581700 | 5.49929000 | 0.00473600 |
| C | -5.53708700 | 7.17275600 | 0.00503700 |
| H | -7.53942300 | 7.96732700 | 0.00593500 |
| H | -4.91274900 | 8.05164400 | 0.00551000 |

**15) 1,2,4,5-tetrafluorobenzene**



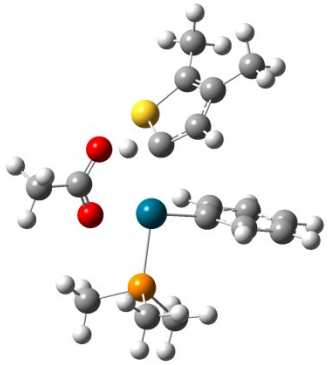
| | | | |
|---|---|---|---|
| C | -1.51498500 | 1.02019000 | 0.00006700 |
| C | -0.13037600 | 1.00691400 | 0.00048900 |
| C | 0.55051900 | 2.21252900 | -0.00001800 |
| C | -0.14399600 | 3.41555500 | -0.00101400 |
| C | -1.52855900 | 3.42882800 | -0.00144800 |
| C | -2.20947500 | 2.22317100 | -0.00093400 |
| H | 0.41009500 | 0.07047400 | 0.00127300 |
| H | -2.06911400 | 4.36522000 | -0.00224000 |
| F | -2.19536600 | -0.13630100 | 0.00057900 |
| F | -3.55119700 | 2.21234700 | -0.00136700 |
| F | 1.89223500 | 2.22344300 | 0.00041600 |
| F | 0.53645800 | 4.57199800 | -0.00152100 |

**16) TPD**



| | | | |
|---|---|---|---|
| C | 0.94323300 | -0.91293600 | 0.41207200 |
| C | 3.33880700 | -0.25868600 | -0.03561300 |
| S | 2.01399800 | -0.91241000 | -0.96706500 |
| C | 2.94566100 | -0.06574300 | 1.24833300 |
| C | 1.59706800 | -0.43420700 | 1.50025300 |
| H | 4.29368000 | -0.06875000 | -0.49876600 |
| C | 3.53767600 | 0.43511000 | 2.51468600 |
| C | 1.29814700 | -0.17758700 | 2.93158800 |
| N | 2.50030300 | 0.33536300 | 3.46050600 |
| O | 4.64796400 | 0.84786300 | 2.75022000 |
| O | 0.27919500 | -0.34879900 | 3.55646400 |
| C | 2.66127800 | 0.73063200 | 4.84775000 |
| H | 1.72987200 | 0.51094800 | 5.36457000 |
| H | 3.48004400 | 0.17549900 | 5.30597900 |
| H | 2.87911600 | 1.79698500 | 4.91861800 |
| H | -0.07286200 | -1.26072400 | 0.31798600 |

**TS for the CMD activation of the α protons of the H-derivatives**



**1) BDTH**

| | | | |
|---|---|---|---|
| Pd | -1.56544600 | -0.69137900 | -0.22769700 |
| C | 0.93388300 | -0.37495000 | -3.72704600 |
| C | -0.04639500 | -0.16027900 | -2.75800200 |
| C | -0.12475600 | -0.98189200 | -1.63370500 |
| C | 0.79731400 | -2.02141700 | -1.49729300 |
| C | 1.77958500 | -2.23389100 | -2.46501800 |
| C | 1.84910000 | -1.41304200 | -3.58613200 |
| O | -3.20980300 | -0.53486000 | 1.28813800 |
| C | -3.01755000 | 0.06965200 | 2.36979500 |
| P | -2.90047300 | -2.35463900 | -1.25387800 |
| O | -1.94233400 | 0.69103500 | 2.66277100 |
| H | -0.73597900 | 0.66608500 | -2.88010400 |
| H | 2.49149600 | -3.04207400 | -2.33764900 |
| H | 2.61177800 | -1.57662300 | -4.33791100 |
| H | 0.98284600 | 0.27790600 | -4.59147800 |
| H | 0.76839200 | -2.67086900 | -0.62918800 |
| C | -4.11318500 | 0.10036800 | 3.40994700 |
| H | -4.51714500 | 1.11344300 | 3.46570400 |
| H | -4.91080900 | -0.59249400 | 3.15238500 |
| H | -3.70129800 | -0.14000600 | 4.39015200 |
| H | -1.18233200 | 0.71933900 | 1.69173400 |
| C | -2.49612700 | -3.00559500 | -2.93033800 |
| H | -3.23197500 | -3.74898000 | -3.24299900 |
| H | -2.48261100 | -2.18280200 | -3.64466000 |

| | | | |
|---|---|---|---|
| H | -1.50308300 | -3.45293900 | -2.91909900 |
| C | -3.02634800 | -3.88085600 | -0.21986500 |
| H | -3.72921300 | -4.59620000 | -0.65230000 |
| H | -2.04400900 | -4.34679400 | -0.14014400 |
| H | -3.35965000 | -3.60118000 | 0.77914400 |
| C | -4.65672600 | -1.80799000 | -1.41352500 |
| H | -5.29666500 | -2.62697100 | -1.74849200 |
| H | -4.99375800 | -1.44303500 | -0.44420400 |
| H | -4.71599700 | -0.98925400 | -2.13098800 |
| C | -0.29307400 | 0.93066800 | 0.64338000 |
| C | 1.03094200 | 0.75159700 | 0.95789200 |
| S | -0.49542400 | 2.52286900 | -0.12834700 |
| C | 1.91592900 | 1.82270800 | 0.61883200 |
| H | 1.37408700 | -0.14963600 | 1.44931300 |
| C | 1.22200500 | 2.89906700 | -0.00256800 |
| C | 3.30617300 | 1.89804600 | 0.83699100 |
| C | 1.84650900 | 4.06963900 | -0.42407400 |
| C | 3.92685700 | 3.05767800 | 0.39823000 |
| C | 4.06515200 | 0.76979700 | 1.48102800 |
| C | 3.23351600 | 4.13843800 | -0.22124600 |
| C | 1.07819300 | 5.18155200 | -1.08602400 |
| S | 5.65992400 | 3.41394100 | 0.52442800 |
| H | 3.51829100 | 0.35765600 | 2.33055000 |
| H | 4.23557400 | -0.04605800 | 0.77213800 |
| H | 5.03866400 | 1.09915300 | 1.84552900 |
| C | 4.12836800 | 5.21248300 | -0.56881700 |
| H | 0.04818400 | 5.21352100 | -0.72739400 |
| H | 1.52670500 | 6.15549900 | -0.88910100 |
| H | 1.04192100 | 5.04671500 | -2.17191400 |
| C | 5.41611500 | 4.97262300 | -0.23769200 |
| H | 3.81098700 | 6.12480400 | -1.05280900 |
| H | 6.26655300 | 5.61766100 | -0.39472000 |

**2) BTAH**

| | | | |
|---|---|---|---|
| Pd | -1.61700300 | -0.59515000 | -0.24947900 |
| C | 0.86030500 | -0.15192200 | -3.75246900 |
| C | -0.11840600 | 0.02609900 | -2.77446500 |
| C | -0.19724000 | -0.84127000 | -1.68500500 |
| C | 0.71994700 | -1.88947200 | -1.59240800 |
| C | 1.69939800 | -2.06577900 | -2.56998400 |
| C | 1.77099000 | -1.19890300 | -3.65549800 |
| O | -3.22795000 | -0.50103400 | 1.30030900 |
| C | -3.02975500 | 0.05541500 | 2.40706800 |
| P | -2.95086500 | -2.20254800 | -1.35535700 |
| O | -1.95655300 | 0.66993400 | 2.71953800 |
| H | -0.80828900 | 0.85632200 | -2.86652800 |
| H | 2.40950400 | -2.87980400 | -2.47594900 |
| H | 2.53273500 | -1.33355900 | -4.41381800 |
| H | 0.91082400 | 0.53623100 | -4.58881000 |
| H | 0.69197900 | -2.57215600 | -0.75027800 |
| C | -4.11805500 | 0.03140400 | 3.45500100 |
| H | -3.69580300 | -0.23906800 | 4.42277400 |
| H | -4.53629200 | 1.03571000 | 3.55077700 |
| H | -4.90786600 | -0.66253100 | 3.17707700 |
| H | -1.19198500 | 0.73249200 | 1.74705000 |
| C | -2.68369700 | -2.58645700 | -3.13807000 |
| H | -3.39488500 | -3.34178800 | -3.47791500 |
| H | -2.80969600 | -1.67867700 | -3.72756400 |
| H | -1.66632300 | -2.94519300 | -3.28689000 |
| C | -2.85593500 | -3.85954400 | -0.54391000 |
| H | -3.54675600 | -4.56636400 | -1.00830800 |
| H | -1.83967200 | -4.24495200 | -0.62679800 |
| H | -3.10151100 | -3.75309300 | 0.51242600 |
| C | -4.74608200 | -1.78420300 | -1.26606300 |
| H | -5.36040400 | -2.60658300 | -1.63819700 |
| H | -4.99871700 | -1.56303000 | -0.23016900 |
| H | -4.93797600 | -0.89286600 | -1.86383500 |
| C | -0.30293800 | 0.95370900 | 0.71414800 |
| C | 1.03613700 | 0.72009600 | 0.98403300 |
| S | -0.38896000 | 2.56494300 | 0.01366200 |
| H | 1.39894200 | -0.18960700 | 1.44451600 |
| C | 1.34752800 | 2.72623000 | 0.14745500 |
| C | 2.05905000 | 3.90971500 | -0.28188400 |
| S | 3.81038400 | 4.02711100 | -0.08655700 |
| C | 2.43863900 | 5.91343200 | -1.11861800 |

| | | | |
|---|---|---|---|
| C | 3.72764400 | 5.60515200 | -0.79963600 |
| H | 2.11793800 | 6.83897100 | -1.57486800 |
| H | 4.61303100 | 6.20347200 | -0.94042500 |
| N | 1.94123700 | 1.68249400 | 0.67708200 |
| N | 1.50727400 | 4.95832000 | -0.82580000 |

**3) DPPH**

| | | | |
|---|---|---|---|
| Pd | -1.24479000 | -0.12469100 | -0.05795200 |
| C | -0.03036500 | 3.69522700 | 1.52647800 |
| C | -0.58445300 | 2.42576100 | 1.36262800 |
| C | -0.46854900 | 1.74933100 | 0.14731800 |
| C | 0.21016400 | 2.36865400 | -0.90247300 |
| C | 0.76292100 | 3.63926700 | -0.73914700 |
| C | 0.64257000 | 4.30799800 | 0.47446700 |
| O | -2.21576600 | -2.12246500 | -0.24863700 |
| C | -1.69395800 | -3.14374000 | 0.25880500 |
| P | -3.27700800 | 0.91761100 | -0.67239300 |
| O | -0.55041200 | -3.16011000 | 0.82506400 |
| H | -1.09452800 | 1.96353000 | 2.20037800 |
| H | 1.29314300 | 4.10200500 | -1.56397400 |
| H | 1.07554500 | 5.29267500 | 0.60192800 |
| H | -0.12175000 | 4.20065600 | 2.48134800 |
| H | 0.32704800 | 1.86199300 | -1.85309400 |
| C | -2.43526500 | -4.45942900 | 0.20802900 |
| H | -2.50949800 | -4.87610000 | 1.21331600 |
| H | -3.42654300 | -4.32840700 | -0.21920200 |
| H | -1.86470500 | -5.16819600 | -0.39501000 |
| C | 0.79408700 | -0.94904100 | 0.45493700 |
| C | 3.25911200 | -0.51500900 | -0.07498300 |
| H | 0.01386000 | -2.06597000 | 0.66922500 |
| S | 1.84092700 | -1.09338000 | -0.94149700 |
| C | 2.90928100 | -0.23759100 | 1.24122400 |
| C | 1.55735900 | -0.48068200 | 1.51784100 |
| C | -3.20470800 | 2.05572400 | -2.12272800 |
| H | -4.19242200 | 2.46520800 | -2.34322500 |
| H | -2.51063500 | 2.86769000 | -1.91080700 |
| H | -2.84024600 | 1.50941800 | -2.99297800 |
| C | -4.59016200 | -0.28906200 | -1.14544300 |
| H | -5.51204300 | 0.22840200 | -1.41786900 |
| H | -4.24102800 | -0.89039800 | -1.98369200 |
| H | -4.77369900 | -0.96350400 | -0.31078700 |
| C | -4.09312100 | 1.94346600 | 0.62701300 |

| | | | |
|---|---|---|---|
| H | -5.03619400 | 2.35341300 | 0.26029700 |
| H | -4.28662400 | 1.32799500 | 1.50582800 |
| H | -3.42918100 | 2.75781600 | 0.91377500 |
| H | 3.62928400 | 0.12295800 | 1.96489800 |
| H | 1.13260300 | -0.32662200 | 2.50141800 |
| C | 4.58251500 | -0.36031700 | -0.61027100 |
| C | 5.71553600 | 0.07666100 | 0.06882300 |
| C | 6.36257200 | -0.36491100 | -2.13447100 |
| C | 6.81928900 | 0.08338800 | -0.83554100 |
| C | 6.18958400 | 0.52260100 | 1.36310400 |
| C | 7.93122800 | 0.50530800 | -0.16687200 |
| H | 8.94496200 | 0.63776400 | -0.51263400 |
| O | 5.65603800 | 0.69104500 | 2.45066100 |
| O | 6.92129500 | -0.52230400 | -3.20178100 |
| C | 4.15140800 | -1.10547300 | -3.02685500 |
| H | 3.73266100 | -2.09036100 | -2.81615600 |
| H | 3.34293900 | -0.41157700 | -3.26077900 |
| H | 4.81544900 | -1.17926000 | -3.88640400 |
| C | 8.47571500 | 1.24165000 | 2.17876600 |
| H | 7.88292000 | 1.34494700 | 3.08564700 |
| H | 9.28164600 | 0.52722400 | 2.35998000 |
| H | 8.90533500 | 2.21250700 | 1.92237000 |
| N | 4.96366100 | -0.62464400 | -1.92533900 |
| N | 7.58694100 | 0.77171400 | 1.13529500 |

**4) FTVTH**

| | | | |
|---|---|---|---|
| Pd | -1.60136200 | -0.65632100 | -0.20311000 |
| C | 0.74808300 | -0.17249700 | -3.78763500 |
| C | -0.24295500 | -0.05937400 | -2.81190700 |
| C | -0.17211600 | -0.81414300 | -1.64107900 |
| C | 0.90486200 | -1.68296700 | -1.46177800 |
| C | 1.89532500 | -1.79448600 | -2.43793100 |
| C | 1.81797300 | -1.04278300 | -3.60606100 |
| O | -3.22072600 | -0.65432300 | 1.33915300 |
| C | -3.13107800 | 0.02165700 | 2.39338500 |
| P | -2.79636000 | -2.42957800 | -1.19936300 |
| O | -2.16960600 | 0.81408900 | 2.66128800 |
| H | -1.06111600 | 0.63337900 | -2.97000900 |
| H | 2.73049400 | -2.46714900 | -2.27813400 |
| H | 2.58783100 | -1.12828800 | -4.36338100 |

| | | | |
|---|---|---|---|
| H | 0.68164500 | 0.42626900 | -4.68918100 |
| H | 0.99456900 | -2.26492300 | -0.55181400 |
| C | -4.21852900 | -0.08766600 | 3.43744700 |
| H | -4.64206500 | 0.90017300 | 3.62463700 |
| H | -4.99900300 | -0.77224300 | 3.11423400 |
| H | -3.78301900 | -0.43605100 | 4.37542600 |
| H | -1.35164700 | 0.86233000 | 1.71873600 |
| C | -2.30070700 | -3.13190000 | -2.82852400 |
| H | -2.97886000 | -3.93509500 | -3.12288100 |
| H | -2.31486700 | -2.34628400 | -3.58324300 |
| H | -1.28291200 | -3.51478900 | -2.76536500 |
| C | -2.85609800 | -3.90239400 | -0.08772900 |
| H | -3.50544700 | -4.67954500 | -0.49619500 |
| H | -1.85039000 | -4.30360000 | 0.03828100 |
| H | -3.22929600 | -3.58818900 | 0.88644300 |
| C | -4.57556900 | -1.99574100 | -1.42798500 |
| H | -5.15556700 | -2.86540200 | -1.74385400 |
| H | -4.96116700 | -1.61524300 | -0.48299900 |
| H | -4.66420200 | -1.21200100 | -2.18056200 |
| C | -0.43775100 | 1.03334500 | 0.71997900 |
| C | 0.89480800 | 0.85632800 | 1.01126300 |
| S | -0.57432700 | 2.60640300 | -0.07717600 |
| C | 1.76438200 | 1.88999900 | 0.62531600 |
| C | 1.14267100 | 2.94971100 | 0.00351600 |
| F | 1.37213700 | -0.22909700 | 1.64068900 |
| F | 3.08754200 | 1.84254700 | 0.85515000 |
| C | 1.79075400 | 4.13599800 | -0.47843500 |
| H | 2.86198300 | 4.16490100 | -0.30113500 |
| C | 1.18857800 | 5.16800500 | -1.10447600 |
| H | 0.11918300 | 5.13265600 | -1.28795100 |
| C | 1.82797400 | 6.36347300 | -1.57853700 |
| C | 1.22409000 | 7.40596800 | -2.23226600 |
| S | 3.54449000 | 6.72441400 | -1.40000000 |
| C | 2.09565200 | 8.46633100 | -2.58537200 |
| C | 3.38161000 | 8.25824300 | -2.21065500 |
| H | 4.23023100 | 8.90402800 | -2.35878500 |
| F | 1.65300000 | 9.55448700 | -3.22854200 |
| F | -0.08344300 | 7.44299200 | -2.52560700 |

**5) NDPPH**

| | | | |
|---|---|---|---|
| Pd | -1.07281300 | 0.12461100 | -0.11817400 |
| C | -0.81024800 | 4.35432600 | 0.60472800 |
| C | -1.11475500 | 2.99474600 | 0.68075500 |
| C | -0.61255400 | 2.09992800 | -0.26604200 |
| C | 0.20119900 | 2.58355700 | -1.28963100 |
| C | 0.50158800 | 3.94406900 | -1.36442600 |
| C | -0.00469700 | 4.83455300 | -0.42274800 |
| O | -1.76334200 | -2.00117900 | 0.11361900 |
| C | -1.18606000 | -2.76099600 | 0.92560500 |
| P | -3.16046600 | 0.56414800 | -1.13655400 |
| O | -0.12527900 | -2.45310800 | 1.56892800 |
| H | -1.73833700 | 2.64236700 | 1.49526800 |
| H | 1.14224700 | 4.30222700 | -2.16242700 |
| H | 0.23269300 | 5.88991700 | -0.48374000 |
| H | -1.20302500 | 5.03433500 | 1.35268700 |
| H | 0.63551400 | 1.91060000 | -2.01823800 |
| C | -1.73940700 | -4.14392000 | 1.17682600 |
| H | -1.04959600 | -4.88160900 | 0.76166300 |
| H | -1.80388300 | -4.32727300 | 2.24959900 |
| H | -2.71594500 | -4.25965200 | 0.71268400 |
| H | 0.31885500 | -1.38698000 | 1.17425900 |
| C | -3.42767300 | 2.10066900 | -2.11863100 |
| H | -4.43913400 | 2.12379500 | -2.52885600 |
| H | -3.26660900 | 2.97166600 | -1.48506100 |
| H | -2.70377200 | 2.13942300 | -2.93216100 |
| C | -3.61795300 | -0.78617400 | -2.30842600 |
| H | -4.63980300 | -0.66404200 | -2.67339000 |
| H | -2.92968000 | -0.77499800 | -3.15384200 |
| H | -3.51373100 | -1.74031900 | -1.79390600 |
| C | -4.56159800 | 0.57659500 | 0.06812200 |
| H | -5.52156900 | 0.67704100 | -0.44276400 |
| H | -4.54805700 | -0.35336800 | 0.63607500 |
| H | -4.43601900 | 1.40836000 | 0.76137800 |
| C | 1.63378300 | 0.58090000 | 1.59300600 |
| C | 2.96772000 | 0.89438800 | 1.28260500 |
| C | 0.98985700 | -0.25170100 | 0.68765100 |
| C | 3.39668200 | 0.34178500 | 0.08972800 |
| S | 2.11022000 | -0.60936100 | -0.61044300 |
| H | 3.60330800 | 1.50655200 | 1.90469500 |
| C | 4.73675000 | 0.42262200 | -0.47993600 |
| C | 5.06135000 | 0.59842800 | -1.81163700 |

| | | | |
|---|---|---|---|
| C | 5.88819800 | 0.27494100 | 0.39425500 |
| C | 6.41226900 | 0.61195300 | -2.28558600 |
| C | 7.25252000 | 0.29185400 | -0.11489500 |
| C | 7.50904300 | 0.46545500 | -1.50158200 |
| H | 8.51542400 | 0.48623500 | -1.89582300 |
| N | 5.82772600 | 0.08391200 | 1.70786700 |
| N | 8.18112800 | 0.12754400 | 0.82318300 |
| S | 7.37655700 | -0.04578300 | 2.25328900 |
| C | 4.19608600 | 0.90845800 | -2.99489100 |
| C | 6.40220200 | 0.85566000 | -3.75476700 |
| O | 7.33983900 | 0.91441300 | -4.51691900 |
| O | 3.00174500 | 1.07517100 | -3.07683900 |
| N | 5.06171400 | 1.02098800 | -4.09517300 |
| C | 4.59394100 | 1.31980100 | -5.43544300 |
| H | 5.45877500 | 1.31870900 | -6.09480900 |
| H | 3.87600200 | 0.56658300 | -5.76039800 |
| H | 4.10984600 | 2.29674200 | -5.46134800 |
| H | 1.14119600 | 0.95120900 | 2.48276000 |

**6) OBDTH**

| | | | |
|---|---|---|---|
| Pd | -1.53217900 | -0.68699800 | -0.20642100 |
| C | 1.01976900 | -0.37917300 | -3.66903000 |
| C | 0.02761300 | -0.15928100 | -2.71330200 |
| C | -0.07823000 | -0.98835300 | -1.59674200 |
| C | 0.82805700 | -2.04134400 | -1.45470700 |
| C | 1.82136700 | -2.26000100 | -2.41019000 |
| C | 1.91859600 | -1.43090500 | -3.52338800 |
| O | -3.18763900 | -0.52183000 | 1.29403800 |
| C | -3.00629400 | 0.08945700 | 2.37395500 |
| P | -2.86405000 | -2.34355600 | -1.24450600 |
| O | -1.93571800 | 0.71643500 | 2.67208600 |
| H | -0.64832900 | 0.67762200 | -2.83922300 |
| H | 2.51830200 | -3.08092100 | -2.28064400 |
| H | 2.68903000 | -1.59963200 | -4.26607200 |
| H | 1.09049100 | 0.28046700 | -4.52661100 |
| H | 0.77656400 | -2.69800300 | -0.59299000 |
| C | -4.10991900 | 0.12128900 | 3.40532400 |
| H | -3.70602000 | -0.12348100 | 4.38781000 |
| H | -4.51079000 | 1.13552400 | 3.46143000 |
| H | -4.90760000 | -0.56846900 | 3.13988900 |
| H | -1.16737600 | 0.73911600 | 1.70973600 |
| C | -2.45020200 | -2.99109900 | -2.91978700 |

| | | | |
|---|---|---|---|
| H | -3.18987800 | -3.72663400 | -3.24177200 |
| H | -2.42340000 | -2.16560700 | -3.63061300 |
| H | -1.46147600 | -3.44760200 | -2.90182000 |
| C | -3.00686500 | -3.87128700 | -0.21537200 |
| H | -3.71089200 | -4.58089600 | -0.65526200 |
| H | -2.02816300 | -4.34370900 | -0.12944200 |
| H | -3.34607700 | -3.59229100 | 0.78182000 |
| C | -4.61471200 | -1.78367600 | -1.41597300 |
| H | -5.25747600 | -2.59715000 | -1.75871500 |
| H | -4.95664300 | -1.41960600 | -0.44807800 |
| H | -4.66249200 | -0.96225200 | -2.13119100 |
| C | -0.27245900 | 0.95005600 | 0.66479200 |
| C | 1.05511800 | 0.77379900 | 0.96278100 |
| S | -0.49529600 | 2.53783000 | -0.12026700 |
| C | 1.92636000 | 1.84495700 | 0.59478300 |
| H | 1.41962100 | -0.11078300 | 1.46819200 |
| C | 1.21766200 | 2.91915800 | -0.01226000 |
| C | 3.31883600 | 1.93252500 | 0.75819200 |
| C | 1.85772400 | 4.07989700 | -0.43123300 |
| C | 3.95087800 | 3.09096000 | 0.33852300 |
| C | 3.24432600 | 4.16867200 | -0.26207000 |
| S | 5.67550500 | 3.44686700 | 0.45868700 |
| C | 4.12251500 | 5.24771600 | -0.62439000 |
| C | 5.41461400 | 5.00604300 | -0.30898700 |
| H | 3.77930400 | 6.15074700 | -1.10765500 |
| H | 6.26266600 | 5.65230000 | -0.47443800 |
| O | 4.03191400 | 0.91975000 | 1.35561000 |
| O | 1.17294100 | 5.10433500 | -1.04648400 |
| C | 4.45779600 | -0.12259900 | 0.46477800 |
| H | 3.60412500 | -0.59394400 | -0.02815000 |
| H | 5.14279700 | 0.26708400 | -0.29326800 |
| H | 4.97721800 | -0.85458600 | 1.08052100 |
| C | 0.51378900 | 6.01225100 | -0.15395500 |
| H | -0.23795900 | 5.50017900 | 0.45182500 |
| H | 1.23548800 | 6.50475900 | 0.50447000 |
| H | 0.02665900 | 6.75665500 | -0.78117800 |

**7) ThioH**

| | | | |
|---|---|---|---|
| Pd | -1.53004100 | -0.66404200 | -0.24627800 |
| C | 0.94829400 | -0.36486500 | -3.76532000 |
| C | -0.02564900 | -0.14397500 | -2.79127400 |
| C | -0.08809800 | -0.94652400 | -1.65129200 |
| C | 0.84961500 | -1.97143300 | -1.50559800 |
| C | 1.82584100 | -2.19057700 | -2.47767200 |
| C | 1.87683500 | -1.38981300 | -3.61432900 |
| O | -3.16981200 | -0.50181200 | 1.28400800 |
| C | -2.99486700 | 0.11616500 | 2.35819900 |
| P | -2.86843000 | -2.35307600 | -1.24943300 |
| O | -1.93005800 | 0.75934500 | 2.65455000 |
| H | -0.72692000 | 0.67082700 | -2.92434200 |
| H | 2.54811400 | -2.98815700 | -2.34149800 |
| H | 2.63416500 | -1.55933100 | -4.37035100 |
| H | 0.98096900 | 0.27188900 | -4.64266300 |
| H | 0.83655700 | -2.60467500 | -0.62530300 |
| C | -4.09508600 | 0.14239100 | 3.39354500 |
| H | -3.68714500 | -0.10356600 | 4.37419700 |
| H | -4.49957200 | 1.15493100 | 3.45381700 |
| H | -4.89074800 | -0.55009900 | 3.12915300 |
| H | -1.16971000 | 0.77803500 | 1.71648700 |
| C | -2.46554200 | -3.02018300 | -2.92107500 |
| H | -3.19160400 | -3.77800000 | -3.22186800 |
| H | -2.46718100 | -2.20602500 | -3.64547500 |
| H | -1.46583200 | -3.45277600 | -2.90975800 |
| C | -2.97991700 | -3.87352700 | -0.20345900 |
| H | -3.67747300 | -4.59898300 | -0.62769500 |
| H | -1.99324100 | -4.33008500 | -0.12214700 |
| H | -3.31270800 | -3.58934100 | 0.79453700 |
| C | -4.63304700 | -1.83090400 | -1.41095600 |
| H | -5.26473600 | -2.66013500 | -1.73646100 |
| H | -4.97302900 | -1.46050000 | -0.44463000 |
| H | -4.70406000 | -1.01947200 | -2.13571000 |
| C | -0.26914600 | 0.92418900 | 0.62790600 |
| C | 1.06648700 | 0.75556300 | 0.95882400 |
| S | -0.41154700 | 2.51426700 | -0.12633300 |
| C | 1.94124000 | 1.82507200 | 0.64744200 |
| H | 1.41889900 | -0.14597800 | 1.44727800 |
| C | 1.27977100 | 2.87203800 | 0.04098300 |
| C | 3.41595600 | 1.82695400 | 0.94455800 |
| H | 3.70693400 | 2.68867100 | 1.55225200 |

| | | | |
|---|---|---|---|
| H | 3.70236300 | 0.92680400 | 1.48945900 |
| H | 4.01264500 | 1.86156000 | 0.02825500 |
| C | 1.86741000 | 4.16735800 | -0.42422000 |
| H | 2.39283100 | 4.67577500 | 0.38975800 |
| H | 2.59370300 | 4.00488700 | -1.22674200 |
| H | 1.10252500 | 4.84610700 | -0.80172500 |

**8) TVTH**

| | | | |
|---|---|---|---|
| Pd | -1.40794000 | -0.76238200 | -0.24114900 |
| C | 0.38947500 | 0.12912300 | -4.06127200 |
| C | -0.40187600 | 0.16729000 | -2.91299800 |
| C | -0.24053900 | -0.78542500 | -1.90685600 |
| C | 0.73201000 | -1.77386300 | -2.07084400 |
| C | 1.52474400 | -1.81065000 | -3.21808600 |
| C | 1.35381300 | -0.86064700 | -4.22009100 |
| O | -2.74461600 | -0.89996500 | 1.56284200 |
| C | -2.38402200 | -0.42550500 | 2.66417900 |
| P | -2.86563000 | -2.34584500 | -1.23628600 |
| O | -1.30162300 | 0.23005300 | 2.84664300 |
| H | -1.13357400 | 0.95868700 | -2.80503400 |
| H | 2.27906300 | -2.58271100 | -3.32350000 |
| H | 1.96978200 | -0.88747600 | -5.11089400 |
| H | 0.25248400 | 0.88182000 | -4.82976700 |
| H | 0.89126200 | -2.52018700 | -1.30025700 |
| C | -3.26305600 | -0.60474300 | 3.87977200 |
| H | -3.66416700 | 0.36749700 | 4.17321500 |
| H | -4.08292700 | -1.28663500 | 3.66694600 |
| H | -2.66780300 | -0.97555000 | 4.71460400 |
| H | -0.73060100 | 0.41883700 | 1.79399900 |
| C | -2.78939800 | -3.98996100 | -0.39592400 |
| H | -3.54866700 | -4.67154700 | -0.78529000 |
| H | -1.80263800 | -4.42848900 | -0.54580000 |
| H | -2.94446600 | -3.84328600 | 0.67265100 |
| C | -4.63303400 | -1.85214200 | -1.03018700 |
| H | -5.30830100 | -2.64930900 | -1.34803600 |
| H | -4.80264200 | -1.61593500 | 0.01951900 |
| H | -4.82932600 | -0.95752800 | -1.62156700 |
| C | -2.73941500 | -2.77177600 | -3.02536600 |
| H | -3.49690800 | -3.50730500 | -3.30288700 |
| H | -2.87155200 | -1.86916600 | -3.62129000 |
| H | -1.74680600 | -3.16736100 | -3.23717100 |
| C | -0.04367000 | 0.77361500 | 0.61002100 |

| | | | |
|---|---|---|---|
| C | 1.33597600 | 0.62583500 | 0.63760000 |
| S | -0.38933000 | 2.43098000 | 0.09845100 |
| C | 2.08248100 | 1.76035600 | 0.27276700 |
| C | 1.30275700 | 2.85319100 | -0.06245900 |
| C | 1.79400200 | 4.14268400 | -0.46913400 |
| H | 2.87786700 | 4.21498900 | -0.51127500 |
| C | 1.05362800 | 5.22298200 | -0.79257500 |
| H | -0.02962300 | 5.15002800 | -0.74858800 |
| C | 1.53907700 | 6.51264600 | -1.20763800 |
| C | 0.77497000 | 7.60960600 | -1.53578600 |
| S | 3.24945500 | 6.90547400 | -1.37084900 |
| C | 1.53219000 | 8.74899400 | -1.91221200 |
| C | 2.87641900 | 8.52829200 | -1.87365500 |
| H | 3.67597500 | 9.21260200 | -2.10766700 |
| H | 3.16438500 | 1.79446400 | 0.25548700 |
| H | 1.80159800 | -0.30650000 | 0.93215300 |
| H | -0.30612500 | 7.58952400 | -1.50459400 |
| H | 1.09434000 | 9.69460100 | -2.20008300 |

**9) 1,2,4,5-tetrafluorobenzene**

| | | | |
|---|---|---|---|
| Pd | -1.24960700 | -0.10701600 | -0.17512300 |
| C | 0.13231200 | 3.54807400 | 1.63421200 |
| C | -0.45857900 | 2.30413900 | 1.40981600 |
| C | -0.42904400 | 1.72670500 | 0.14037400 |
| C | 0.19497000 | 2.41251200 | -0.90174200 |
| C | 0.78511400 | 3.65651100 | -0.67530300 |
| C | 0.75241000 | 4.22953800 | 0.59188300 |
| O | -2.32352000 | -2.01468000 | -0.56456300 |
| C | -1.74192900 | -3.11900200 | -0.40903200 |
| P | -3.28918200 | 0.92156100 | -0.69005800 |
| O | -0.53270600 | -3.24478200 | -0.03717000 |
| H | -0.92613600 | 1.78559400 | 2.23900000 |
| H | 1.27398700 | 4.17321400 | -1.49353200 |
| H | 1.21126000 | 5.19506700 | 0.76691800 |
| H | 0.10932400 | 3.97948500 | 2.62858300 |
| H | 0.24067400 | 1.98080800 | -1.89509200 |
| C | -2.50148700 | -4.39651700 | -0.68113000 |
| H | -2.44035400 | -5.04967400 | 0.19013800 |
| H | -3.54113900 | -4.18684100 | -0.92082300 |
| H | -2.02980500 | -4.92124200 | -1.51393800 |
| C | 0.81967700 | -1.04380700 | 0.34825800 |
| C | 3.44859700 | -0.24164100 | 1.02539200 |

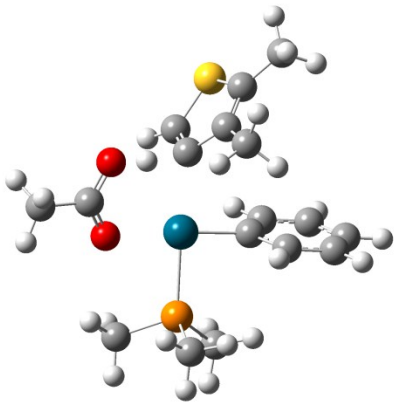
| | | | |
|---|---|---|---|
| H | 0.01689300 | -2.11609000 | 0.13021300 |
| C | 2.49858500 | -0.45583800 | 2.01010900 |
| C | 1.21575800 | -0.85150600 | 1.66747000 |
| C | -3.86594100 | 0.41409200 | -2.36651400 |
| H | -4.88002300 | 0.77094200 | -2.55827900 |
| H | -3.19223700 | 0.82038600 | -3.12099200 |
| H | -3.83880700 | -0.67326200 | -2.42468400 |
| C | -4.62552300 | 0.32298400 | 0.43135800 |
| H | -5.60099900 | 0.69557800 | 0.11212900 |
| H | -4.62455700 | -0.76623600 | 0.41929800 |
| H | -4.42602700 | 0.66076800 | 1.44833900 |
| C | -3.48445600 | 2.75197000 | -0.68211500 |
| H | -4.50642300 | 3.02834400 | -0.94838900 |
| H | -3.24534900 | 3.13960700 | 0.30730900 |
| H | -2.78734900 | 3.19587700 | -1.39165500 |
| H | 4.45037200 | 0.07275300 | 1.28355800 |
| C | 1.79762500 | -0.83003600 | -0.61714400 |
| C | 3.08633700 | -0.43400100 | -0.29741300 |
| F | 3.99476100 | -0.22968400 | -1.27150700 |
| F | 1.49546200 | -1.00898300 | -1.92168100 |
| F | 0.32636300 | -1.04902700 | 2.66463200 |
| F | 2.82918200 | -0.27223200 | 3.30333400 |

**10) TPD**

| | | | |
|---|---|---|---|
| Pd | -1.19607400 | -0.14086800 | -0.04913100 |
| C | 0.00449300 | 3.70694000 | 1.46625100 |
| C | -0.53339000 | 2.42678900 | 1.32960100 |
| C | -0.46162700 | 1.75494700 | 0.10845900 |
| C | 0.15373000 | 2.38545200 | -0.97323100 |
| C | 0.69123000 | 3.66573800 | -0.83490400 |
| C | 0.61546900 | 4.33198100 | 0.38373700 |
| O | -2.14485700 | -2.14243800 | -0.18576600 |
| C | -1.54448600 | -3.18482400 | 0.17810700 |
| P | -3.26271100 | 0.85886300 | -0.56440400 |
| O | -0.33261900 | -3.21802800 | 0.56382800 |
| H | -0.98811500 | 1.94973900 | 2.19017100 |
| H | 1.17211600 | 4.13865500 | -1.68384700 |
| H | 1.03392800 | 5.32537200 | 0.49064700 |
| H | -0.05252200 | 4.21155300 | 2.42422700 |
| H | 0.23160800 | 1.88212300 | -1.92965400 |
| C | -2.29208200 | -4.49862500 | 0.18375000 |
| H | -2.47466100 | -4.79282400 | 1.21960800 |

| | | | |
|---|---|---|---|
| H | -3.24226300 | -4.40550100 | -0.33699200 |
| H | -1.68079500 | -5.27645800 | -0.27351800 |
| C | 0.90844200 | -0.93184100 | 0.40682700 |
| C | 3.35298700 | -0.25081700 | -0.04184800 |
| H | 0.18052700 | -2.06082800 | 0.49552200 |
| S | 2.03699500 | -0.91986200 | -0.95804900 |
| C | 2.95235100 | -0.05680700 | 1.24499300 |
| C | 1.61036000 | -0.43460900 | 1.48154800 |
| C | -3.29353500 | 2.04750400 | -1.97457100 |
| H | -4.30705900 | 2.41664800 | -2.14320200 |
| H | -2.62990700 | 2.88392800 | -1.76091500 |
| H | -2.93941300 | 1.54798800 | -2.87659300 |
| C | -4.54810300 | -0.38030600 | -1.02350300 |
| H | -5.50365200 | 0.11103500 | -1.21646800 |
| H | -4.22487800 | -0.92266700 | -1.91101100 |
| H | -4.65169200 | -1.10264800 | -0.21606700 |
| C | -4.05033200 | 1.80353500 | 0.81024300 |
| H | -5.02614600 | 2.18625900 | 0.50473800 |
| H | -4.17335000 | 1.14944000 | 1.67353000 |
| H | -3.40603200 | 2.63435600 | 1.09407600 |
| H | 4.31332600 | -0.05233100 | -0.49165400 |
| C | 3.54175000 | 0.43850600 | 2.51155300 |
| C | 1.30493300 | -0.17594400 | 2.91235900 |
| N | 2.50463800 | 0.32839800 | 3.45566400 |
| O | 4.65056000 | 0.85551200 | 2.75452400 |
| O | 0.27799600 | -0.32793900 | 3.53408100 |
| C | 2.65745500 | 0.72209300 | 4.84247900 |
| H | 1.72333700 | 0.50029900 | 5.35379000 |
| H | 3.47415200 | 0.16781300 | 5.30602900 |
| H | 2.87428400 | 1.78874700 | 4.91740100 |

**TS for the CMD activation of the β protons of the H-derivatives**



**1) BDTH**

| | | | |
|---|---|---|---|
| Pd | 2.06012800 | 0.44217400 | 0.15899800 |
| C | 1.75272600 | 0.08609500 | -4.13152100 |
| C | 2.12717000 | -0.06644500 | -2.79660400 |
| C | 1.50041300 | 0.67060800 | -1.78968700 |
| C | 0.48669200 | 1.55985500 | -2.14797800 |
| C | 0.11155900 | 1.71329500 | -3.48293600 |
| C | 0.74561900 | 0.98003400 | -4.48038000 |
| O | 2.78559800 | 0.26129700 | 2.26926100 |
| C | 2.19945900 | -0.46258700 | 3.10329400 |
| P | 3.70436900 | 2.11177900 | -0.23166800 |
| O | 1.16617500 | -1.17080300 | 2.83987400 |
| H | 2.90665100 | -0.77842500 | -2.55005900 |
| H | -0.68433200 | 2.40398700 | -3.73809000 |
| H | 0.45213900 | 1.09713200 | -5.51660500 |
| H | 2.24729800 | -0.50173600 | -4.89690400 |
| H | -0.03416700 | 2.13253700 | -1.38974900 |
| C | 2.70564100 | -0.53344100 | 4.52436000 |
| H | 3.60135000 | 0.07083700 | 4.64490500 |
| H | 1.92643200 | -0.18131500 | 5.20258300 |
| H | 2.91584700 | -1.57173100 | 4.78482300 |
| H | 0.88189200 | -1.07345900 | 1.68023200 |
| C | 5.00604100 | 1.70211700 | -1.47586700 |
| H | 5.71764000 | 2.52379300 | -1.57804400 |

| | | | |
|---|---|---|---|
| H | 5.53725100 | 0.80385700 | -1.16023400 |
| H | 4.53529800 | 1.50509200 | -2.43807200 |
| C | 3.07853200 | 3.74851700 | -0.81304400 |
| H | 3.90164300 | 4.45080700 | -0.95905800 |
| H | 2.53957600 | 3.61584400 | -1.75036900 |
| H | 2.38729100 | 4.15413200 | -0.07388500 |
| C | 4.69002000 | 2.55022000 | 1.26728700 |
| H | 5.43824200 | 3.30993500 | 1.03233300 |
| H | 4.02087300 | 2.91907100 | 2.04354900 |
| H | 5.17677600 | 1.65494600 | 1.65102800 |
| C | 0.41751800 | -1.09476400 | 0.32335900 |
| C | 0.73160500 | -2.27021200 | -0.29592800 |
| C | -0.99512300 | -0.78104400 | 0.11746000 |
| S | -0.57754900 | -3.04857900 | -1.15433400 |
| H | 1.69196200 | -2.76614700 | -0.30312900 |
| C | -1.67814200 | -1.74880200 | -0.67341600 |
| C | -1.71383900 | 0.31332100 | 0.62885600 |
| C | -3.02642500 | -1.68851100 | -1.00452600 |
| C | -3.06375200 | 0.38054300 | 0.29561500 |
| C | -1.08782700 | 1.34581900 | 1.52623300 |
| C | -3.73118900 | -0.57945500 | -0.50942600 |
| C | -3.68426800 | -2.73391200 | -1.86490800 |
| S | -4.18384100 | 1.65412800 | 0.80978600 |
| H | -0.02252800 | 1.45726600 | 1.31952900 |
| H | -1.56185600 | 2.32174200 | 1.39983800 |
| H | -1.18897800 | 1.06354900 | 2.57862700 |
| C | -5.11985900 | -0.24520400 | -0.70044900 |
| H | -3.59005300 | -2.48918500 | -2.92773400 |
| H | -3.22695300 | -3.71361200 | -1.71518100 |
| H | -4.74664200 | -2.82976700 | -1.64056700 |
| C | -5.49248300 | 0.89162400 | -0.07287600 |
| H | -5.80456500 | -0.83615500 | -1.29164900 |
| H | -6.46975100 | 1.34835000 | -0.06179600 |

**2) BTAH**

| | | | |
|---|---|---|---|
| Pd | 1.86292400 | 0.53003100 | 0.25422400 |
| C | 3.37424500 | -1.27661700 | -3.35844000 |
| C | 3.21030700 | -0.85187700 | -2.03949700 |
| C | 2.10166300 | -0.08786500 | -1.66983000 |
| C | 1.16065000 | 0.24418000 | -2.64456100 |
| C | 1.32649000 | -0.17811500 | -3.96365600 |

| | | | |
|---|---|---|---|
| C | 2.43427100 | -0.93791900 | -4.32635200 |
| O | 1.75310700 | 1.27724600 | 2.36091500 |
| C | 1.24974000 | 0.53999500 | 3.24090600 |
| P | 3.33084300 | 2.33227600 | -0.16720700 |
| O | 0.73066400 | -0.60203400 | 3.00506600 |
| H | 3.95306900 | -1.13509400 | -1.30160300 |
| H | 0.58153300 | 0.08412200 | -4.70660700 |
| H | 2.55978400 | -1.26844200 | -5.35032300 |
| H | 4.23792600 | -1.87574900 | -3.62530700 |
| H | 0.28230400 | 0.82116800 | -2.38014600 |
| C | 1.22159200 | 1.00662600 | 4.67687400 |
| H | 1.51668000 | 0.19360000 | 5.33982500 |
| H | 1.87114000 | 1.86766900 | 4.81588500 |
| H | 0.19684500 | 1.28355300 | 4.93418000 |
| H | 0.67155700 | -0.79821900 | 1.79423100 |
| C | 2.75311900 | 3.87417500 | 0.66555900 |
| H | 3.50259400 | 4.66521700 | 0.59678200 |
| H | 1.82890100 | 4.21057000 | 0.19514000 |
| H | 2.54179000 | 3.64424000 | 1.70879000 |
| C | 5.01384100 | 2.06546200 | 0.54763200 |
| H | 5.63699300 | 2.95489300 | 0.43243500 |
| H | 4.91470900 | 1.82639200 | 1.60619800 |
| H | 5.49260200 | 1.22477200 | 0.04547600 |
| C | 3.68008400 | 2.87617400 | -1.89316400 |
| H | 4.36529800 | 3.72602900 | -1.89826800 |
| H | 4.11165700 | 2.05023800 | -2.45671700 |
| H | 2.74592400 | 3.15966600 | -2.37741600 |
| C | 0.34188100 | -1.12382000 | 0.46949100 |
| C | 0.59354200 | -2.42128500 | 0.08689100 |
| S | -0.74042700 | -3.14004800 | -0.74933400 |
| C | -1.60192100 | -1.60892200 | -0.53827400 |
| C | -2.95099200 | -1.43476000 | -1.03779200 |
| S | -3.80898300 | 0.08939500 | -0.79712600 |
| C | -4.87312000 | -1.87816900 | -2.02321800 |
| C | -5.15912300 | -0.60301900 | -1.64111500 |
| H | -5.54562700 | -2.52955400 | -2.56264200 |
| N | -3.63130400 | -2.33935100 | -1.68165200 |
| N | -0.92982000 | -0.70016800 | 0.09708300 |
| H | -6.06600400 | -0.04303100 | -1.80098600 |
| H | 1.49343000 | -2.99249800 | 0.25439600 |

**3) DPPH**

| | | | |
|---|---|---|---|
| Pd | 0.53773000 | -0.11972600 | 0.14559400 |
| C | 0.59035200 | 3.51814500 | -2.16685500 |
| C | 0.55378400 | 2.17918200 | -1.77633300 |
| C | 0.59460000 | 1.83202300 | -0.42530000 |
| C | 0.67468000 | 2.84642000 | 0.52918600 |
| C | 0.71411500 | 4.18487700 | 0.13687000 |
| C | 0.67487200 | 4.52573500 | -1.21140400 |
| O | 0.65807900 | -2.27777300 | 0.72716200 |
| C | -0.39459900 | -2.93268000 | 0.91004700 |
| P | 2.88369100 | -0.24705900 | -0.07546900 |
| O | -1.56795800 | -2.43806600 | 0.81652500 |
| H | 0.48349900 | 1.41160000 | -2.53914000 |
| H | 0.76969400 | 4.96077500 | 0.89221500 |
| H | 0.70249800 | 5.56556800 | -1.51414000 |
| H | 0.55088400 | 3.77022600 | -3.22089100 |
| H | 0.68960500 | 2.60691100 | 1.58604700 |
| C | -0.30996400 | -4.39392300 | 1.28095500 |
| H | -1.00805300 | -4.97252900 | 0.67608100 |
| H | 0.70368300 | -4.76630700 | 1.15360800 |
| H | -0.60903400 | -4.50931900 | 2.32497200 |
| H | -1.51114900 | -1.23164400 | 0.61341200 |
| C | 3.88593500 | 1.20650100 | -0.60232800 |
| H | 4.94745300 | 0.95293200 | -0.62949300 |
| H | 3.56175300 | 1.53575900 | -1.58881000 |
| H | 3.72307300 | 2.02934600 | 0.09280300 |
| C | 3.65758800 | -0.75788500 | 1.52025700 |
| H | 4.72772900 | -0.93776300 | 1.39832400 |
| H | 3.50490300 | 0.02252900 | 2.26576200 |
| H | 3.16735100 | -1.66724200 | 1.86582900 |
| C | 3.40189400 | -1.58303900 | -1.24045600 |
| H | 4.48375900 | -1.73002800 | -1.21626100 |
| H | 2.89889900 | -2.50554000 | -0.95268100 |
| H | 3.09738000 | -1.32203800 | -2.25417900 |
| C | -1.68731800 | 0.15940500 | 0.49024500 |
| C | -2.03509500 | 0.87703800 | 1.67365200 |
| C | -2.51741400 | 0.53264700 | -0.54341600 |
| C | -3.08644300 | 1.76368800 | 1.54764100 |
| S | -3.69822300 | 1.71941500 | -0.11255700 |
| H | -1.51438100 | 0.76329900 | 2.61602900 |

| | | | |
|---|---|---|---|
| C | -3.57004100 | 2.61850000 | 2.59546800 |
| C | -2.97886500 | 2.83475300 | 3.83597200 |
| C | -4.92352000 | 4.13245500 | 3.76476700 |
| C | -3.77915300 | 3.76203100 | 4.57084900 |
| C | -1.81510700 | 2.51151900 | 4.63066800 |
| C | -3.16705100 | 4.02054000 | 5.76122200 |
| H | -3.46030300 | 4.66969300 | 6.57185400 |
| N | -4.72948500 | 3.38957000 | 2.54704000 |
| N | -2.00297800 | 3.29137400 | 5.82262600 |
| O | -0.84649200 | 1.78008000 | 4.46226800 |
| O | -5.87242700 | 4.86602800 | 3.95629200 |
| C | -5.72626500 | 3.46278900 | 1.49535700 |
| H | -5.32341900 | 3.91649000 | 0.58848700 |
| H | -6.13063200 | 2.47755400 | 1.25987300 |
| H | -6.52637700 | 4.09572800 | 1.87541100 |
| C | -1.06948400 | 3.26215400 | 6.92965000 |
| H | -0.25003300 | 2.60522200 | 6.64396700 |
| H | -0.67263300 | 4.25877400 | 7.13503500 |
| H | -1.54013500 | 2.86938800 | 7.83391300 |
| H | -2.51692600 | 0.16655500 | -1.55971300 |

**4) NDPPH**

| | | | |
|---|---|---|---|
| Pd | 0.88748400 | -0.13712600 | 0.11393000 |
| C | 0.53706300 | 3.79199100 | -1.63758200 |
| C | 0.47488900 | 2.41680600 | -1.41686400 |
| C | 0.98712200 | 1.86242000 | -0.24361000 |
| C | 1.56055400 | 2.71151700 | 0.70539200 |
| C | 1.62289400 | 4.08808700 | 0.48404700 |
| C | 1.11438500 | 4.63257200 | -0.69043800 |
| O | 0.90934500 | -2.32081000 | 0.62525100 |
| C | 0.15328500 | -2.71077700 | 1.54476600 |
| P | 3.13240900 | -0.31128900 | -0.61526000 |
| O | -0.74656400 | -1.98202700 | 2.08892900 |
| H | 0.00174600 | 1.78685800 | -2.16019900 |
| H | 2.06666700 | 4.73219400 | 1.23521600 |
| H | 1.16003000 | 5.70122100 | -0.86252100 |
| H | 0.12033300 | 4.20481100 | -2.54916000 |
| H | 1.95261100 | 2.31254900 | 1.63457800 |
| C | 0.27199500 | -4.12285000 | 2.06578100 |
| H | 1.11130000 | -4.63648900 | 1.60333500 |
| H | 0.39211900 | -4.10366500 | 3.14972300 |
| H | -0.65275000 | -4.66214800 | 1.85255500 |

| | | | |
|---|---|---|---|
| H | -0.87758800 | -0.95869300 | 1.45324700 |
| C | 3.74526700 | 0.82816000 | -1.92937700 |
| H | 4.78417600 | 0.60548700 | -2.18054000 |
| H | 3.12657000 | 0.71845900 | -2.81990000 |
| H | 3.66186900 | 1.85823800 | -1.58630500 |
| C | 4.37786000 | -0.10022200 | 0.73393200 |
| H | 5.39267000 | -0.24739100 | 0.35834600 |
| H | 4.29211400 | 0.90324400 | 1.15039900 |
| H | 4.17783100 | -0.82240700 | 1.52540000 |
| C | 3.51682200 | -1.98640300 | -1.28944400 |
| H | 4.58343700 | -2.09252400 | -1.49682500 |
| H | 3.19460500 | -2.73722200 | -0.56971900 |
| H | 2.95334200 | -2.13918700 | -2.21023400 |
| C | -1.28040200 | 0.14163400 | 0.63112100 |
| C | -1.81000100 | 1.30291000 | 1.27468400 |
| C | -2.11425300 | -0.23112700 | -0.40364000 |
| C | -2.96840200 | 1.80601200 | 0.73348200 |
| S | -3.47083000 | 0.81268800 | -0.63010400 |
| H | -1.33635400 | 1.76739900 | 2.12628200 |
| H | -2.01778300 | -1.08901600 | -1.05374000 |
| C | -3.74988900 | 2.93628100 | 1.22354100 |
| C | -4.38701700 | 3.90269900 | 0.46839100 |
| C | -3.92342500 | 3.10227700 | 2.65769700 |
| C | -5.15439800 | 4.96312900 | 1.04878000 |
| C | -4.70977300 | 4.19092600 | 3.22190100 |
| C | -5.33937200 | 5.14623500 | 2.37940800 |
| H | -5.92004200 | 5.96472000 | 2.78126700 |
| N | -3.42648400 | 2.28936300 | 3.58391100 |
| N | -4.77292300 | 4.18005500 | 4.55041600 |
| S | -3.90192400 | 2.87010600 | 5.04972500 |
| C | -4.37169500 | 4.15213200 | -1.00714600 |
| C | -5.66245900 | 5.84001400 | -0.04303900 |
| O | -6.35970800 | 6.82530400 | 0.04288900 |
| O | -3.81315600 | 3.55912900 | -1.89976000 |
| N | -5.15582300 | 5.29835800 | -1.22117600 |
| C | -5.37951700 | 5.86153200 | -2.53907100 |
| H | -6.04361300 | 6.71516000 | -2.42502400 |
| H | -4.43568100 | 6.18266000 | -2.98119700 |
| H | -5.83529800 | 5.11867500 | -3.19393700 |

**5) OBDTH**

| | | | |
|---|---|---|---|
| Pd | 2.08278700 | 0.36506000 | 0.05557900 |
| C | 1.34643500 | 0.48280100 | -4.19103800 |
| C | 1.84108400 | 0.16041700 | -2.92692100 |
| C | 1.34345900 | 0.79354300 | -1.78740500 |
| C | 0.34041000 | 1.75254200 | -1.93286800 |
| C | -0.15208000 | 2.07503700 | -3.19786800 |
| C | 0.35149500 | 1.44520700 | -4.33171100 |
| O | 3.03584000 | 0.01126100 | 2.06555100 |
| C | 2.49624900 | -0.75169900 | 2.89358000 |
| P | 3.73056800 | 2.04444300 | -0.22155400 |
| O | 1.40873900 | -1.39420100 | 2.67272800 |
| H | 2.61178500 | -0.59705200 | -2.84202100 |
| H | -0.93616700 | 2.81820200 | -3.29169600 |
| H | -0.03267200 | 1.69563800 | -5.31336400 |
| H | 1.74013500 | -0.02403300 | -5.06529300 |
| H | -0.07713500 | 2.24273400 | -1.06131300 |
| C | 3.12837600 | -0.96858700 | 4.24724400 |
| H | 2.40052400 | -0.75538200 | 5.03124800 |
| H | 3.41230700 | -2.01780500 | 4.34670000 |
| H | 4.00518200 | -0.33724400 | 4.36799100 |
| H | 1.03775900 | -1.22234900 | 1.55127100 |
| C | 5.44030200 | 1.39535900 | 0.04188500 |
| H | 6.17537500 | 2.20301200 | 0.04469700 |
| H | 5.46828700 | 0.86763400 | 0.99450800 |
| H | 5.68571300 | 0.68963100 | -0.75209200 |
| C | 3.87342300 | 3.00438900 | -1.78853800 |
| H | 4.68321500 | 3.73367000 | -1.72342900 |
| H | 4.06038800 | 2.32241200 | -2.61729500 |
| H | 2.93274100 | 3.51669200 | -1.98704900 |
| C | 3.58141200 | 3.35698800 | 1.07085800 |
| H | 4.40040300 | 4.07637200 | 1.00368900 |
| H | 2.63239400 | 3.87912200 | 0.94789900 |
| H | 3.59091600 | 2.88318500 | 2.05203100 |
| C | 0.47663300 | -1.20264900 | 0.21756600 |
| C | 0.74242200 | -2.38103600 | -0.41818500 |
| C | -0.93474900 | -0.87118000 | 0.06365900 |
| S | -0.61966000 | -3.15281200 | -1.21021400 |
| H | 1.69133600 | -2.89715800 | -0.45919800 |
| C | -1.66133500 | -1.82525900 | -0.70244200 |
| C | -1.62607400 | 0.23703900 | 0.57041100 |
| C | -3.01195200 | -1.70071400 | -0.99256600 |

| | | | |
|---|---|---|---|
| C | -2.97821700 | 0.36985400 | 0.27530000 |
| C | -3.69297500 | -0.58757500 | -0.48723200 |
| S | -4.03006200 | 1.70191500 | 0.76173100 |
| C | -5.07876200 | -0.23368400 | -0.63905500 |
| C | -5.39448000 | 0.93450700 | -0.03792200 |
| H | -5.79129500 | -0.84760400 | -1.17060900 |
| H | -6.35801500 | 1.41856700 | -0.00359900 |
| O | -0.97418000 | 1.22099000 | 1.28372300 |
| O | -3.67984500 | -2.66552200 | -1.71553400 |
| C | -1.06624500 | 1.09764000 | 2.71082700 |
| H | -0.50120000 | 1.93163800 | 3.12417600 |
| H | -2.10447500 | 1.16415700 | 3.04682700 |
| H | -0.63020000 | 0.15575100 | 3.04917000 |
| C | -3.67327900 | -2.46423600 | -3.13507800 |
| H | -2.65326900 | -2.45209100 | -3.52774900 |
| H | -4.21761600 | -3.30321500 | -3.56486900 |
| H | -4.17346300 | -1.52880800 | -3.40184200 |

**6) ThioH**

| | | | |
|---|---|---|---|
| Pd | 2.01818900 | 0.56302500 | 0.27132100 |
| C | 1.44464900 | -0.12474900 | -3.95355100 |
| C | 1.83352500 | -0.24107600 | -2.61979100 |
| C | 1.41538800 | 0.69274700 | -1.66966300 |
| C | 0.59595200 | 1.74418200 | -2.08772000 |
| C | 0.20318000 | 1.85958700 | -3.42210800 |
| C | 0.62925800 | 0.92678300 | -4.36152500 |
| O | 2.71222200 | 0.58278800 | 2.40810100 |
| C | 1.98339500 | 0.09253100 | 3.29908500 |
| P | 3.65443800 | 2.22983900 | -0.17374000 |
| O | 0.89730400 | -0.54300500 | 3.06770700 |
| H | 2.45516900 | -1.07729700 | -2.32460700 |
| H | -0.43759500 | 2.68117800 | -3.72327600 |
| H | 0.32543800 | 1.01469100 | -5.39772100 |
| H | 1.77568900 | -0.86519500 | -4.67337500 |
| H | 0.24724800 | 2.48353800 | -1.37523400 |
| C | 2.37688100 | 0.22726500 | 4.75089900 |
| H | 3.25862300 | 0.85476700 | 4.85549600 |
| H | 1.54550500 | 0.64692500 | 5.31857100 |
| H | 2.58032000 | -0.76426700 | 5.15961300 |
| H | 0.76632300 | -0.70611300 | 1.88167000 |
| C | 4.33000200 | 2.41592800 | -1.88026200 |
| H | 5.08538200 | 3.20350500 | -1.91453300 |

| | | | |
|---|---|---|---|
| H | 4.77529000 | 1.47268200 | -2.19628100 |
| H | 3.51995900 | 2.65204600 | -2.56880800 |
| C | 3.09768600 | 3.94373800 | 0.24137900 |
| H | 3.89878300 | 4.66924100 | 0.08459300 |
| H | 2.24696200 | 4.20890500 | -0.38623400 |
| H | 2.78150200 | 3.97440200 | 1.28404000 |
| C | 5.17016000 | 2.02138100 | 0.86084900 |
| H | 5.84498600 | 2.87242600 | 0.74962700 |
| H | 4.86875600 | 1.91064100 | 1.90123500 |
| H | 5.68700700 | 1.11008900 | 0.55875700 |
| C | 0.53029500 | -1.08696600 | 0.51970500 |
| C | 1.05600400 | -2.32101700 | 0.22329200 |
| C | -0.86464600 | -1.01641800 | 0.12619500 |
| S | -0.08829700 | -3.39134300 | -0.52099300 |
| C | -1.34304000 | -2.16340300 | -0.44250000 |
| C | -2.70512500 | -2.45342600 | -0.99463500 |
| H | -3.45832600 | -1.83660500 | -0.50181800 |
| H | -2.75923400 | -2.24099800 | -2.06702400 |
| H | -2.98809300 | -3.49804400 | -0.85160800 |
| C | -1.69881400 | 0.21567100 | 0.34707600 |
| H | -1.68678900 | 0.86625600 | -0.53192200 |
| H | -2.74154700 | -0.02622300 | 0.56229500 |
| H | -1.30812900 | 0.79315800 | 1.18626300 |
| H | 2.05195800 | -2.68686900 | 0.42554700 |

**7) TVTH**

| | | | |
|---|---|---|---|
| Pd | 2.01550000 | 0.51182300 | 0.28792100 |
| C | 1.15953200 | -0.05623900 | -3.90369900 |
| C | 1.66588000 | -0.19492200 | -2.61172400 |
| C | 1.29070600 | 0.69251000 | -1.60293600 |
| C | 0.39913700 | 1.72145500 | -1.91278500 |
| C | -0.10778400 | 1.85970600 | -3.20533900 |
| C | 0.27337800 | 0.97283800 | -4.20672500 |
| O | 2.82196400 | 0.48528400 | 2.38371100 |
| C | 2.05455000 | 0.12590800 | 3.30647600 |
| P | 3.66701000 | 2.13393300 | -0.21104200 |
| O | 0.89038300 | -0.36766600 | 3.11700700 |
| H | 2.34325500 | -1.01252200 | -2.39621300 |
| H | -0.80429400 | 2.66135900 | -3.42503600 |
| H | -0.12153100 | 1.07744300 | -5.21001400 |
| H | 1.45531700 | -0.76136200 | -4.67252300 |
| H | 0.08027800 | 2.42060300 | -1.14742300 |

| | | | |
|---|---|---|---|
| C | 2.49926000 | 0.25330400 | 4.74379400 |
| H | 2.63492800 | -0.74561800 | 5.16322000 |
| H | 3.43317400 | 0.80598200 | 4.81186600 |
| H | 1.72218400 | 0.74704400 | 5.32793000 |
| H | 0.72558200 | -0.59145800 | 1.93641600 |
| C | 4.09614700 | 2.53738000 | -1.95804000 |
| H | 4.88485700 | 3.29118800 | -1.99913400 |
| H | 4.43067200 | 1.63331000 | -2.46624600 |
| H | 3.21026300 | 2.90297100 | -2.47570700 |
| C | 3.29020200 | 3.78686300 | 0.52485100 |
| H | 4.11161400 | 4.48857600 | 0.36507900 |
| H | 2.38361900 | 4.18682100 | 0.07059600 |
| H | 3.11769800 | 3.66734600 | 1.59420300 |
| C | 5.29370800 | 1.69627600 | 0.54471500 |
| H | 6.01002200 | 2.51453300 | 0.44709600 |
| H | 5.13380600 | 1.46032800 | 1.59586500 |
| H | 5.69178500 | 0.80940700 | 0.05097200 |
| C | 0.48071000 | -1.09292100 | 0.62086500 |
| C | 0.97750200 | -2.36081100 | 0.42459400 |
| C | -0.86658400 | -1.02085400 | 0.13281000 |
| S | -0.15014000 | -3.44974700 | -0.33119500 |
| C | -1.37196000 | -2.17733700 | -0.40510400 |
| H | -1.46321500 | -0.11850700 | 0.17888200 |
| C | -2.68743200 | -2.36779200 | -0.95966200 |
| H | -3.30342900 | -1.47228500 | -0.94372300 |
| C | -3.19762200 | -3.50377400 | -1.47448000 |
| H | -2.58325300 | -4.40004400 | -1.48877800 |
| C | -4.51319500 | -3.68827800 | -2.03342100 |
| C | -5.02680800 | -4.85309800 | -2.55504300 |
| S | -5.71652500 | -2.40522500 | -2.13966000 |
| C | -6.35816600 | -4.73457400 | -3.03395700 |
| H | -4.45491200 | -5.77068200 | -2.59027900 |
| C | -6.86728300 | -3.48042300 | -2.88066700 |
| H | -6.91389100 | -5.55065800 | -3.47455200 |
| H | -7.84344500 | -3.11335500 | -3.15374300 |
| H | 1.94673500 | -2.74667600 | 0.70517000 |

**TS for the CMD activation of the β protons of the Br-derivatives**

**1) BDTBr**

| | | | |
|---|---|---|---|
| Pd | 2.07771300 | 0.40797400 | -0.13976300 |
| C | 1.09862000 | 1.08024200 | -4.28146400 |
| C | 1.66856200 | 0.60814200 | -3.09887100 |
| C | 1.23966900 | 1.09231400 | -1.86293600 |
| C | 0.23415700 | 2.05806600 | -1.82977300 |
| C | -0.33467800 | 2.53053500 | -3.01282600 |
| C | 0.09820500 | 2.04632300 | -4.24291700 |
| O | 3.12061500 | -0.20976200 | 1.74990800 |
| C | 2.65935100 | -1.12841600 | 2.46495400 |
| P | 3.74093600 | 2.07599200 | -0.29172800 |
| O | 1.58883100 | -1.77410000 | 2.20055300 |
| H | 2.43739000 | -0.15398900 | -3.15250900 |
| H | -1.12221400 | 3.27444100 | -2.96741000 |
| H | -0.34541000 | 2.41164400 | -5.16128600 |
| H | 1.43686200 | 0.68530300 | -5.23302000 |
| H | -0.12807900 | 2.44219100 | -0.88348800 |
| C | 3.39132900 | -1.53804600 | 3.72070900 |
| H | 4.19241100 | -0.83806600 | 3.94575700 |
| H | 2.69257700 | -1.59822200 | 4.55526500 |
| H | 3.81056700 | -2.53569500 | 3.57450700 |
| H | 1.12931700 | -1.42872800 | 1.13077100 |
| C | 3.83676700 | 3.09048800 | 1.24847200 |
| H | 4.70404300 | 3.75386300 | 1.23088500 |
| H | 2.93048000 | 3.68799500 | 1.34927400 |
| H | 3.90561500 | 2.41599700 | 2.10111800 |
| C | 5.42519400 | 1.32685700 | -0.40368600 |
| H | 6.20113300 | 2.09412000 | -0.35968100 |
| H | 5.55145700 | 0.62830300 | 0.42286400 |
| H | 5.51597900 | 0.77629000 | -1.34006500 |
| C | 3.73338500 | 3.33234700 | -1.63935000 |
| H | 4.58381800 | 4.00923400 | -1.53823100 |
| H | 3.77527700 | 2.83080000 | -2.60538700 |
| H | 2.80500200 | 3.90111100 | -1.60052200 |
| C | 0.46055100 | -1.19350600 | -0.08953300 |
| C | 0.63840000 | -2.18712400 | -1.00113200 |
| C | -0.96549600 | -0.87759900 | -0.00156700 |

| | | | |
|---|---|---|---|
| S | -0.79348000 | -2.78157800 | -1.81716000 |
| C | -1.78123100 | -1.64959700 | -0.87719300 |
| C | -1.57548700 | 0.05207600 | 0.85735400 |
| C | -3.16264200 | -1.54759700 | -0.96704400 |
| C | -2.96130500 | 0.16100400 | 0.76918400 |
| C | -0.79701900 | 0.86397700 | 1.85599400 |
| C | -3.76291500 | -0.60195400 | -0.11907400 |
| C | -3.96488700 | -2.38073800 | -1.93025100 |
| S | -3.96674500 | 1.24899800 | 1.74068800 |
| H | -1.29966900 | 1.80731700 | 2.07841700 |
| H | -0.67967500 | 0.31977400 | 2.79778000 |
| H | 0.20409600 | 1.09393000 | 1.48673300 |
| C | -5.15978900 | -0.27129800 | 0.00068000 |
| H | -4.96992500 | -2.57285600 | -1.55449000 |
| H | -4.06254500 | -1.88225500 | -2.89984900 |
| H | -3.49152100 | -3.34830000 | -2.10732000 |
| C | -5.41083900 | 0.67763300 | 0.92915000 |
| H | -5.93871900 | -0.72751200 | -0.59312000 |
| H | -6.36755700 | 1.09217500 | 1.20584100 |
| Br | 2.29161500 | -3.01779000 | -1.45507800 |

**2) BATBr**

| | | | |
|---|---|---|---|
| Pd | 1.75294800 | 0.73623100 | 0.37056300 |
| C | 3.31487400 | -1.51447600 | -2.96124700 |
| C | 3.11265700 | -0.96112900 | -1.69635400 |
| C | 2.06137800 | -0.07194100 | -1.47133500 |
| C | 1.21610700 | 0.25503100 | -2.53169700 |
| C | 1.42124600 | -0.29643700 | -3.79661100 |
| C | 2.47371800 | -1.17923300 | -4.01715900 |
| O | 1.54513100 | 1.73466200 | 2.35404600 |
| C | 0.74198200 | 1.27811700 | 3.20353100 |
| P | 3.30867000 | 2.42934700 | -0.13108200 |
| O | 0.01312800 | 0.24950000 | 3.01768700 |
| H | 3.77427800 | -1.24691500 | -0.88650400 |
| H | 0.75108700 | -0.03623600 | -4.60834100 |
| H | 2.63097600 | -1.60845500 | -4.99926400 |
| H | 4.13134500 | -2.21099600 | -3.11623000 |
| H | 0.37992100 | 0.92671900 | -2.37753400 |
| C | 0.60120100 | 1.96711000 | 4.54030300 |
| H | 0.79931300 | 1.25210900 | 5.33999900 |
| H | 1.28380600 | 2.81003500 | 4.61564800 |
| H | -0.42758800 | 2.31074700 | 4.66034500 |

| | | | |
|---|---|---|---|
| H | 0.20851400 | -0.22743000 | 1.88968600 |
| C | 4.80286500 | 2.31287800 | 0.94752500 |
| H | 5.46172500 | 3.17108400 | 0.79936900 |
| H | 4.48003200 | 2.27407600 | 1.98745200 |
| H | 5.34774800 | 1.39710300 | 0.71849100 |
| C | 4.00469000 | 2.62637400 | -1.82528300 |
| H | 4.71254800 | 3.45694300 | -1.85469600 |
| H | 4.50315000 | 1.70589500 | -2.12622200 |
| H | 3.19462100 | 2.81201900 | -2.52980700 |
| C | 2.63256700 | 4.10071500 | 0.26214200 |
| H | 3.40180100 | 4.86899000 | 0.15998400 |
| H | 1.80629600 | 4.32623800 | -0.41224700 |
| H | 2.25335300 | 4.08760600 | 1.28306500 |
| C | 0.21833900 | -0.92049900 | 0.69268400 |
| C | 0.62109700 | -2.23555800 | 0.74028500 |
| S | -0.41389600 | -3.31357900 | -0.15367600 |
| C | -1.38107100 | -1.88731300 | -0.55747000 |
| Br | 2.11035500 | -2.91797000 | 1.67979900 |
| C | -2.56696800 | -2.00253000 | -1.37826300 |
| S | -3.53230800 | -0.57360600 | -1.75977600 |
| C | -4.14844700 | -2.91548100 | -2.62232200 |
| C | -4.58356200 | -1.62574900 | -2.67318100 |
| H | -4.63014200 | -3.75171700 | -3.10654900 |
| N | -3.01301400 | -3.11381100 | -1.89040000 |
| N | -0.94152300 | -0.77523200 | -0.05752600 |
| Br | -6.10388800 | -0.97669300 | -3.57985500 |

**3) DPPBr**

| | | | |
|---|---|---|---|
| Pd | 2.03668700 | 0.36166100 | 0.17970900 |
| C | 1.02067100 | -0.14466900 | -3.97562200 |
| C | 1.60961000 | -0.26225300 | -2.71596500 |
| C | 1.18986400 | 0.54737700 | -1.66077600 |
| C | 0.17514600 | 1.47893400 | -1.88168500 |
| C | -0.40978000 | 1.59635300 | -3.14300000 |
| C | 0.01276300 | 0.78875800 | -4.19436600 |
| O | 3.11245300 | 0.28025400 | 2.13782400 |
| C | 2.68295100 | -0.45018400 | 3.06286200 |
| P | 3.70079600 | 1.89260600 | -0.46049200 |
| O | 1.63688900 | -1.17400200 | 2.97485300 |
| H | 2.38766800 | -1.00181300 | -2.56503500 |
| H | -1.20311300 | 2.31905900 | -3.29764800 |
| H | -0.44410800 | 0.88081100 | -5.17237100 |

| | | | |
|---|---|---|---|
| H | 1.35202100 | -0.78740600 | -4.78364800 |
| H | -0.18517100 | 2.10446600 | -1.07323500 |
| C | 3.41764500 | -0.49099400 | 4.38183600 |
| H | 2.78626500 | -0.04585800 | 5.15339800 |
| H | 3.60048400 | -1.52669300 | 4.66927600 |
| H | 4.35583200 | 0.05508300 | 4.31928300 |
| H | 1.10159400 | -1.04167900 | 1.86776400 |
| C | 5.38562400 | 1.14332300 | -0.36896800 |
| H | 6.15980500 | 1.89544100 | -0.53472200 |
| H | 5.51378700 | 0.69534600 | 0.61577800 |
| H | 5.47753800 | 0.36067300 | -1.12215200 |
| C | 3.67737300 | 2.72037300 | -2.10573100 |
| H | 4.52428800 | 3.40234400 | -2.20276600 |
| H | 3.71810900 | 1.96917500 | -2.89343300 |
| H | 2.74586000 | 3.27330900 | -2.22143300 |
| C | 3.78778100 | 3.29225000 | 0.73810800 |
| H | 4.64162700 | 3.93968900 | 0.52745200 |
| H | 2.86887400 | 3.87571700 | 0.67963200 |
| H | 3.87415600 | 2.88017900 | 1.74276500 |
| C | 0.29713100 | -1.02249900 | 0.73778700 |
| C | -0.97114300 | -0.37559600 | 0.84494600 |
| C | 0.12839100 | -2.22697700 | 0.10119300 |
| C | -2.04914900 | -1.05130400 | 0.31199400 |
| S | -1.50331700 | -2.59482400 | -0.36762700 |
| H | -1.09648400 | 0.59916300 | 1.29935800 |
| C | -3.39208000 | -0.54634200 | 0.26390400 |
| C | -3.80618500 | 0.74716800 | 0.56214600 |
| C | -5.71293000 | -0.46547500 | -0.04299000 |
| C | -5.21974300 | 0.83063600 | 0.37497600 |
| C | -3.31794700 | 2.05959300 | 0.92218500 |
| C | -5.61384400 | 2.11690500 | 0.59676800 |
| H | -6.59294400 | 2.56732600 | 0.54219800 |
| N | -4.52253100 | -1.27450700 | -0.09705500 |
| N | -4.50730200 | 2.86436000 | 0.92453500 |
| O | -2.20980800 | 2.51022500 | 1.18846900 |
| O | -6.82038200 | -0.88887100 | -0.30474000 |
| C | -4.62518600 | -2.68563300 | -0.41849700 |
| H | -4.12224100 | -2.92467700 | -1.35711600 |
| H | -4.22025000 | -3.30710600 | 0.38132400 |
| H | -5.68700200 | -2.89774200 | -0.53186400 |
| C | -4.49655100 | 4.27294100 | 1.26297700 |
| H | -3.45996300 | 4.55618100 | 1.43563900 |
| H | -4.89996200 | 4.87495700 | 0.44600500 |

| | | | |
|---|---|---|---|
| H | -5.07255100 | 4.46640200 | 2.17082400 |
| Br | 1.47321500 | -3.51076000 | -0.26458800 |

**4) NDPPBr**

| | | | |
|---|---|---|---|
| Pd | 0.93269900 | -0.00477600 | -0.06433400 |
| C | 2.18003800 | 3.10283800 | -2.77527700 |
| C | 1.82795600 | 1.87523600 | -2.21321600 |
| C | 1.41876800 | 1.79469400 | -0.88171200 |
| C | 1.36538900 | 2.96301400 | -0.12158300 |
| C | 1.72072300 | 4.18925300 | -0.68410900 |
| C | 2.13404800 | 4.26372000 | -2.01038500 |
| O | 0.58921500 | -2.04028100 | 0.80099600 |
| C | -0.55225600 | -2.55794300 | 0.76788700 |
| P | 3.22603400 | -0.42846700 | 0.29236400 |
| O | -1.59301300 | -1.96791500 | 0.32414100 |
| H | 1.86074700 | 0.98616800 | -2.83229600 |
| H | 1.66723200 | 5.08910900 | -0.08126300 |
| H | 2.40797900 | 5.21709000 | -2.44589000 |
| H | 2.48770500 | 3.14734100 | -3.81408900 |
| H | 1.02343000 | 2.93531100 | 0.90555700 |
| C | -0.74746200 | -3.96834500 | 1.27175700 |
| H | -1.09657500 | -4.59681200 | 0.45055900 |
| H | 0.18082000 | -4.36786400 | 1.67283700 |
| H | -1.52311500 | -3.97788000 | 2.03857000 |
| H | -1.32692200 | -0.82168000 | -0.02193500 |
| C | 4.48446200 | 0.90886500 | 0.13890200 |
| H | 5.48385700 | 0.52017800 | 0.34370100 |
| H | 4.45052400 | 1.33005100 | -0.86480600 |
| H | 4.25195600 | 1.70683500 | 0.84350900 |
| C | 3.53312700 | -1.12210700 | 1.97504200 |
| H | 4.56585100 | -1.46154300 | 2.07822700 |
| H | 3.33024400 | -0.35654200 | 2.72428900 |
| H | 2.84869900 | -1.95379100 | 2.13598000 |
| C | 3.85644900 | -1.74929300 | -0.83412000 |
| H | 4.88687400 | -2.01759900 | -0.59141200 |
| H | 3.21843200 | -2.62733800 | -0.73731600 |
| H | 3.80997900 | -1.39897600 | -1.86533300 |
| C | -1.25435800 | 0.53351900 | -0.35831700 |
| C | -1.80687600 | 1.44059200 | 0.59928000 |
| C | -1.73529200 | 0.87277100 | -1.60149400 |
| C | -2.66873500 | 2.39933600 | 0.11600300 |
| S | -2.84198100 | 2.20182000 | -1.63139000 |

| | | | |
|---|---|---|---|
| H | -1.57487400 | 1.37325700 | 1.65129100 |
| C | -3.29946500 | 3.47137000 | 0.87689400 |
| C | -4.54205300 | 4.04341300 | 0.65772800 |
| C | -2.57849300 | 4.05986300 | 2.00034700 |
| C | -5.06507800 | 5.10682600 | 1.46125100 |
| C | -3.14097100 | 5.14022800 | 2.80212700 |
| C | -4.42519300 | 5.67236200 | 2.51310500 |
| H | -4.85791500 | 6.46899200 | 3.10176400 |
| N | -1.36069400 | 3.70829400 | 2.39980000 |
| N | -2.34625500 | 5.55972700 | 3.78207900 |
| S | -0.97181000 | 4.65373600 | 3.69250800 |
| C | -5.62500600 | 3.68426200 | -0.31132200 |
| C | -6.43332100 | 5.44763900 | 0.97974000 |
| O | -7.18623400 | 6.30020300 | 1.39179000 |
| O | -5.66631700 | 2.82219100 | -1.15745800 |
| N | -6.69168500 | 4.56142200 | -0.06097000 |
| C | -7.93347400 | 4.52090000 | -0.81073600 |
| H | -8.57362800 | 5.31424100 | -0.43201300 |
| H | -7.73805700 | 4.67379500 | -1.87226300 |
| H | -8.42293400 | 3.55506100 | -0.68245600 |
| Br | -1.37373800 | -0.02756800 | -3.23073700 |

**5) OBDTBr**

| | | | |
|---|---|---|---|
| Pd | 2.00070700 | 0.57220300 | 0.26316000 |
| C | 1.90612100 | -0.31787500 | -3.95147600 |
| C | 2.22514700 | -0.30333200 | -2.59326600 |
| C | 1.54319800 | 0.53939600 | -1.71555200 |
| C | 0.53889400 | 1.36864800 | -2.21598300 |
| C | 0.22260700 | 1.35376500 | -3.57485000 |
| C | 0.90730200 | 0.51405000 | -4.44773500 |
| O | 2.63296500 | 0.74069800 | 2.41675800 |
| C | 2.03095400 | 0.09090800 | 3.29884700 |
| P | 3.56744800 | 2.28246200 | -0.14640100 |
| O | 1.04387300 | -0.69036200 | 3.06569300 |
| H | 3.00057400 | -0.96610400 | -2.22673400 |
| H | -0.56495200 | 1.99953100 | -3.94713200 |
| H | 0.66108300 | 0.50366100 | -5.50282900 |
| H | 2.44039800 | -0.98459400 | -4.61932300 |
| H | -0.01615200 | 2.01916500 | -1.55027500 |
| C | 2.47101900 | 0.19278300 | 4.73963300 |
| H | 1.60544000 | 0.34290400 | 5.38506300 |
| H | 2.93563000 | -0.75102700 | 5.03280600 |

| | | | |
|---|---|---|---|
| H | 3.18583500 | 1.00213000 | 4.86770100 |
| H | 0.84166500 | -0.78807500 | 1.87463700 |
| C | 3.94927600 | 2.86811500 | -1.85152700 |
| H | 4.69576700 | 3.66440700 | -1.82608500 |
| H | 4.32175100 | 2.03594400 | -2.44786600 |
| H | 3.03830400 | 3.23374500 | -2.32388700 |
| C | 3.11541200 | 3.83212000 | 0.75157900 |
| H | 3.89815400 | 4.58780000 | 0.65698700 |
| H | 2.18262800 | 4.22614400 | 0.34814700 |
| H | 2.96368900 | 3.59181700 | 1.80342000 |
| C | 5.22313000 | 1.85983400 | 0.55182800 |
| H | 5.90456300 | 2.71152500 | 0.49946800 |
| H | 5.08948800 | 1.55398700 | 1.58864900 |
| H | 5.64801900 | 1.02368800 | -0.00384600 |
| C | 0.47526300 | -1.09261900 | 0.54033800 |
| C | 0.85272800 | -2.34305500 | 0.16115200 |
| C | -0.91378500 | -0.88749200 | 0.14486700 |
| S | -0.34992300 | -3.33417800 | -0.65526800 |
| C | -1.49429600 | -1.99817800 | -0.52776600 |
| C | -1.70407400 | 0.25086700 | 0.34815100 |
| C | -2.79192100 | -2.00625600 | -1.01194800 |
| C | -3.00650400 | 0.25056500 | -0.14249400 |
| C | -3.57660300 | -0.86479500 | -0.80515900 |
| S | -4.16029000 | 1.58312500 | -0.04592800 |
| C | -4.94045500 | -0.62549400 | -1.19324600 |
| C | -5.37555800 | 0.60954800 | -0.85938100 |
| H | -5.55427400 | -1.36341600 | -1.68908000 |
| H | -6.35129400 | 1.03450100 | -1.03591400 |
| Br | 2.55180500 | -3.14413900 | 0.47074200 |
| O | -3.30327200 | -3.12436100 | -1.63323800 |
| O | -1.18634900 | 1.37695500 | 0.94932400 |
| C | -1.51004500 | 1.53000700 | 2.34060300 |
| H | -1.11214600 | 0.69790100 | 2.92431800 |
| H | -1.03986400 | 2.45875300 | 2.65945600 |
| H | -2.59040200 | 1.60371200 | 2.48897100 |
| C | -3.21567000 | -3.10874500 | -3.06513400 |
| H | -3.63633600 | -4.05269500 | -3.40656500 |
| H | -3.78936600 | -2.27897000 | -3.48710200 |
| H | -2.17622000 | -3.03127500 | -3.39452300 |

**6) ThioBr**

| | | | |
|---|---|---|---|
| Pd | 1.98400500 | 0.58573500 | 0.22237200 |
| C | 1.75336000 | -0.21256600 | -4.01059900 |
| C | 2.07902400 | -0.25880100 | -2.65515900 |
| C | 1.49878100 | 0.63405700 | -1.75333700 |
| C | 0.59126100 | 1.57771100 | -2.23855200 |
| C | 0.26314400 | 1.62237800 | -3.59410000 |
| C | 0.84543200 | 0.72839300 | -4.48635300 |
| O | 2.60234100 | 0.70870200 | 2.37685700 |
| C | 1.99206300 | 0.04229100 | 3.24412600 |
| P | 3.56730800 | 2.30489700 | -0.12333800 |
| O | 1.02851300 | -0.75594200 | 2.98770100 |
| H | 2.77989400 | -1.00906700 | -2.30865900 |
| H | -0.44883900 | 2.35947100 | -3.94911300 |
| H | 0.59201200 | 0.76196900 | -5.53912700 |
| H | 2.20938500 | -0.92070200 | -4.69357900 |
| H | 0.12487000 | 2.28781900 | -1.56487600 |
| C | 2.40216900 | 0.14968600 | 4.69380800 |
| H | 1.52049700 | 0.28002100 | 5.32135900 |
| H | 2.88079600 | -0.78496400 | 4.99371000 |
| H | 3.09708900 | 0.97355800 | 4.83817600 |
| H | 0.85812200 | -0.84911000 | 1.78063400 |
| C | 3.97441500 | 2.92975200 | -1.80907300 |
| H | 4.73684200 | 3.70941800 | -1.75644800 |
| H | 4.33605900 | 2.10612100 | -2.42386000 |
| H | 3.07576300 | 3.32615700 | -2.27997500 |
| C | 3.14831300 | 3.83945200 | 0.81679900 |
| H | 3.95407500 | 4.57424100 | 0.75694800 |
| H | 2.23439400 | 4.27657800 | 0.41416500 |
| H | 2.97481400 | 3.57086300 | 1.85839600 |
| C | 5.20952900 | 1.82521600 | 0.56951800 |
| H | 5.91198900 | 2.66070800 | 0.53889100 |
| H | 5.06512300 | 1.49787600 | 1.59827900 |
| H | 5.61483300 | 0.99200800 | -0.00494200 |
| C | 0.52457400 | -1.12522000 | 0.44397100 |
| C | 0.95660300 | -2.34736700 | 0.01011500 |
| C | -0.89304300 | -0.97902100 | 0.14751900 |
| S | -0.26591200 | -3.32086500 | -0.74908500 |
| C | -1.45785700 | -2.04952600 | -0.48330300 |
| Br | 2.70781000 | -3.07235600 | 0.20145500 |
| C | -2.85903800 | -2.25267200 | -0.97163200 |
| H | -3.53441800 | -1.53740600 | -0.50203400 |

| | | | |
|---|---|---|---|
| H | -2.93363600 | -2.11249400 | -2.05422000 |
| H | -3.22789200 | -3.25505900 | -0.74273500 |
| C | -1.64411000 | 0.26494200 | 0.53690700 |
| H | -1.51638200 | 1.05325800 | -0.20982600 |
| H | -2.71427400 | 0.08452100 | 0.64487500 |
| H | -1.27186800 | 0.65138800 | 1.48731800 |

**7) TVTBr**

| | | | |
|---|---|---|---|
| Pd | 2.00845900 | 0.51826300 | 0.24644600 |
| C | 1.86627300 | -0.26215000 | -3.99001600 |
| C | 2.21703700 | -0.25877400 | -2.63974100 |
| C | 1.49790800 | 0.50712700 | -1.72239400 |
| C | 0.42310400 | 1.27046400 | -2.17968900 |
| C | 0.07234200 | 1.26618200 | -3.52994300 |
| C | 0.79525000 | 0.50270000 | -4.44074100 |
| O | 2.65426400 | 0.70973400 | 2.38316000 |
| C | 2.12835000 | -0.01367700 | 3.26238200 |
| P | 3.39547700 | 2.38651500 | -0.13072900 |
| O | 1.24483600 | -0.90178800 | 3.02370400 |
| H | 3.04779800 | -0.87190600 | -2.31003100 |
| H | -0.77076500 | 1.85944300 | -3.86623700 |
| H | 0.52199600 | 0.49797500 | -5.48898700 |
| H | 2.43142000 | -0.87023600 | -4.68760000 |
| H | -0.16034700 | 1.86759300 | -1.48785100 |
| C | 2.55188700 | 0.13990400 | 4.70421200 |
| H | 3.08431500 | -0.76141500 | 5.01445500 |
| H | 3.19924000 | 1.00492200 | 4.82707600 |
| H | 1.67096700 | 0.23176000 | 5.34001600 |
| H | 1.03744000 | -0.99894300 | 1.81088000 |
| C | 3.65838000 | 3.07895500 | -1.81769300 |
| H | 4.33659400 | 3.93361200 | -1.78072600 |
| H | 4.07470200 | 2.30895200 | -2.46620600 |
| H | 2.70209600 | 3.38654800 | -2.23892400 |
| C | 2.86206200 | 3.84925100 | 0.86228900 |
| H | 3.58825000 | 4.66149400 | 0.78809400 |
| H | 1.89350700 | 4.19938700 | 0.50514200 |
| H | 2.75911400 | 3.54253200 | 1.90257800 |
| C | 5.10509200 | 2.06119300 | 0.48375200 |
| H | 5.71628900 | 2.96553700 | 0.45149900 |
| H | 5.03640000 | 1.69569000 | 1.50758000 |
| H | 5.57023300 | 1.28942600 | -0.12976700 |
| C | 0.66890700 | -1.29908300 | 0.50227400 |

| | | | |
|---|---|---|---|
| C | 1.12893100 | -2.50106400 | 0.03138100 |
| C | -0.73317200 | -1.19785500 | 0.20333800 |
| S | -0.06865100 | -3.49302800 | -0.75852000 |
| C | -1.29730200 | -2.25652700 | -0.45996100 |
| Br | 2.89522900 | -3.18222000 | 0.18863400 |
| H | -1.32624200 | -0.33807100 | 0.49014300 |
| C | -2.67102700 | -2.38817900 | -0.86783900 |
| H | -3.28784700 | -1.53242100 | -0.60501600 |
| C | -3.23350600 | -3.42753800 | -1.51553500 |
| H | -2.61750500 | -4.28330800 | -1.77884200 |
| C | -4.61015500 | -3.55229900 | -1.92216800 |
| C | -5.17662500 | -4.61737300 | -2.58354700 |
| S | -5.83016100 | -2.31593500 | -1.62540700 |
| C | -6.56126100 | -4.45934300 | -2.85387600 |
| H | -4.60522600 | -5.49134000 | -2.86617300 |
| C | -7.05818700 | -3.27454900 | -2.40096400 |
| H | -7.16262700 | -5.19831300 | -3.36485700 |
| H | -8.06607400 | -2.89823300 | -2.47000700 |

**6.** Table S1. Several conditions tested reported in literature.

| Entry | Catalytic system | Solvent Conc. Temp (°C) | time | yield Mn/Mw PDI |
|---|---|---|---|---|
| **S1**[11] | Pd(Herrmann) (2.5%); $P(o\text{-}NMe_2Ph)_3P$ (10%); $Cs_2CO_3$ (3eq) ; NDA (1eq) | THF, 0.5M, 120 | 24h | No Polymerisation |
| **S2**[12] | Pd(Herrmann) (2.5%); $P(o\text{-}NMe_2Ph)_3P$ (10%); $Cs_2CO_3$ (3eq) ; | THF, 0.5M, 120 | 24h | No Polymerisation |
| **S3**[11] | Pd(Herrmann) (4%); $P(o\text{-}NMe_2Ph)_3P$ (16%); $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |
| **S4**[11] | Pd(Herrmann) (2.5%); $P(o\text{-}OMeC_6H_4)_3$ (10%); $Cs_2CO_3$ (3eq) ; PivOH (1eq) | 1,4-dioxane, 0.5M, 125 | 48h | No Polymerisation |
| **S5**[13] | $Pd_2dba_3$ (1%); $K_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M 100 | 24h | No Polymerisation |
| **S6** [11,14] | Pd(2-2'bipy)$Cl_2$ (10%) $Cs_2CO_3$ (3 eq) ; NDA (1 eq) | Chloro-benzene | | No Polymerisation |
| **S7** | $Pd(PPh_3)_2Cl_2$ (5%); $P(o\text{-}OMeC_6H_4)_3$ (10%); $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | 1,4-dioxane, 0.5M, 125 | 48h | No Polymerisation |
| **S8** | $Pd(OAc)_2$ (5%); $Cs_2CO_3$ (2 eq) | DMAC, 0.5M, 125 | 24h | Monomers degradation |
| **S9** [15] | $Pd_2dba_3$ (2.5%); $P(o\text{-}OMeC_6H_4)_3$ (10%); $K_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |
| **S10** | $Pd(PPh_3)_2Cl_2$ (5%); $P(o\text{-}NMe_2Ph)_3P$ (10%); $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |

| | | | | |
|---|---|---|---|---|
| **S11** | $Pd(PPh_3)_2Cl_2$ (5%); Xphos (10%) $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |
| **S12** | $Pd(PPh_3)_2Cl_2$ (5%); Davephos (10%) $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |
| **S13** | $Pd(PPh_3)_2Cl_2$ (5%); Sphos (10%) $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |
| **S14** | $Pd(OAc)_2$ (5%); 1,2bis(dicyclohexylphosphino)ethane (20%) $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |
| **S15** | $Pd(OAc)_2$ (5%); $(2\text{-}4\text{-}6\text{-}OMeC_6H_2)_3P$ (20%) $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |
| **S16** | $Pd(OAc)_2$ (5%); 2-(Di-t-butylphosphino)biphenyl (20%) $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |
| **S17** | $Pd(OAc)_2$ (5%); tri-2-pyridyl phosphine (20%) $Cs_2CO_3$ (3 eq) ; PivOH (1 eq) | Toluene, 0.5M, 125 | 24h | No Polymerisation |

Table S2. Properties of reference polymers by Migita-Stille coupling.

| | $\bar{M}_n$ (kg/mol) | Đ | Yield (%) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|
| P1S | 56 | 3.2 | 59 | 754/690 |
| P2S | 22 | 1.9 | 89 | 690/425 |
| P3S | 57 | 2.9 | 85 | 748/685 |
| P4S | 30 | 2.0 | 90 | 639/418 |

Table S3. Effect of the ligand for the synthesis of **P1H.**

| | Phosphine | Time (h) | $\bar{M}_n$(kg/mol) | Đ | Yield (%) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| P1S | | 1 | 56 | 3.2 | 59 | 754/690 |
| P1H-$L_{REF}$ | $L_{REF}$ | 0.5 | 21 | 2.7 | 75 | 753/690 |
| P1H-L1 | L1 | 1 | 16 | 2.5 | 73 | 753/690 |
| P1H-L2 | L2 | 1 | 39 | 2.6 | 73 | 757/690 |
| P1H-L3 | L3 | 1 | 47 | 2.7 | 74 | 758/690 |
| P1H-L4 | L4 | 1 | 43 | 2.6 | 75 | 758/690 |
| P1H-L5 | L5 | 1 | 42 | 3.0 | 65 | 758/690 |

Table S4. Effect of the ligand for the synthesis of **P2H**.

| | Phosphine | Time (h) | $\bar{M}_n$ (kg/mol) | Đ | Yield (%) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| P2S | | 48 | 22 | 1.9 | 89 | 690/425 |
| P2H-$L_{REF}$ | $L_{REF}$ | 12 | 14 | 2.2 | 39 | 678/411 |
| P2H-L1 | L1 | 2 | 14 | 2.3 | 91 | 686/410 |
| P2H-L2 | L2 | 2 | 20 | 2.6 | 70 | 686/412 |
| P2H-L3 | L3 | 2 | 21 | 2.7 | 75 | 692/419 |
| P2H-L4 | L4 | 2 | 21 | 2.7 | 72 | 692/419 |
| P2H-L5 | L5 | 2 | 18 | 2.7 | 61 | 691/415 |

Table S5. Effect of the ligand for the synthesis of **P3H**.

| | Phosphine | Time (h) | $\bar{M}_n$ (kDa) | Đ | Yield (%) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| P3S | | 5 | 57 | 2.9 | 85 | 748/685 |
| P3S | | 6 | 67 | 3.2 | 90 | 748/685 |
| P3H-$L_{REF}$ | $L_{REF}$ | 2 | 27 | 3.0 | 53 | 740/677 |
| P3H-L1 | L1 | 2 | 28 | 3.5 | 67 | 748/685 |
| P3H-L2 | L2 | 2 | 35 | 2.7 | 60 | 749/685 |
| P3H-L3 | L3 | 3 | 21 | 2.9 | 75 | 746/685 |
| P3H-L4 | L4 | 3 | 34 | 3.3 | 66 | 748/685 |
| P3H-L5 | L5 | 3 | 39 | 2.9 | 50 | 750/685 |

Table S6. Effect of the ligand for the synthesis of **P4H.**

| | Phosphine | Time (h) | $\bar{M}_n$ (kDa) | Đ | Yield (%) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| P4S-High | | 3 | 30 | 2 | 90 | 639/418 |
| P4S-Low | | 1 | 16 | 2 | 90 | 617/414 |
| P4S-20HC | | 3 | 30 | 2.1 | 90 | 627/428 |
| P4S-20D | | 3 | 20 | 1.8 | 90 | 616/413 |
| P4S-10D | | 3 | 22 | 1.8 | 90 | 621/414 |
| P4H-$L_{REF}$ | $L_{REF}$ | 12 | 10 | 2.2 | 35 | 583/407 |
| P4H-L1 | L1 | 12 | 17 | 2.2 | 90 | 616/411 |
| P4H-L2 | L2 | 12 | 27 | 2.9 | 92 | 623/412 |
| P4H-L3 | L3 | 12 | 19 | 2.4 | 90 | 613/411 |
| P4H-L4 | L4 | 12 | 30 | 3.2 | 95 | 625/414 |
| P4H-L5 | L5 | 12 | 22 | 2.4 | 93 | 618/413 |

Table S7. Effect of the ligand for the synthesis of **P1H'**

| | Phosphine | Time (h) | $\bar{M}_n$ (kDa) | Đ | Yield (%) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| P1S | | 1 | 56 | 3.2 | 59 | 754/690 |
| P1H'-$L_{REF}$ | $L_{REF}$ | 12 | 21 | 5.1 | 34 | 674/731 |
| P1H'-L1 | L1 | 12 | 21.5 | 4.3 | 32 | 677/738 |
| P1H'-L2 | L2 | 12 | 17.5 | 4.1 | 24 | 743/681 |
| P1H'-L3 | L3 | 12 | 12.5 | 2.8 | 26 | 740/678 |
| P1H'-L4 | L4 | 12 | 29 | 2.7 | 11 | 740/677 |
| P1H'-L5 | L5 | 12 | 13 | 2.9 | 35 | 746/682 |

Table S8. Effect of the ligand for the synthesis of **P2H'**

| | Phosphine | Time (h) | $\bar{M}_n$ (kDa) | Đ | Yield (%) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| P2S | | 48 | 22 | 1.9 | 89 | 690/425 |
| P2H'-$L_{REF}$ | $L_{REF}$ | 20 | 15 | 5 | 67 | 596/399 |
| P2H'-L1 | L1 | 20 | 11 | 3 | 35 | 606/404 |
| P2H'-L2 | L2 | 20 | 15 | 3 | 60 | 616/407 |
| P2H'-L3 | L3 | 4 | 16 | 2.5 | 71 | 607/403 |
| P2H'-L4 | L4 | 4 | 17 | 2.5 | 94 | 627/407 |
| P2H'-L5 | L5 | 4 | 13 | 2.2 | 73 | 619/406 |

Table S9. Effect of the ligand for the synthesis of **P3H'**

| | Phosphine | Time (h) | $\bar{M}_n$ (kDa) | **Đ** | Yield (%) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| P3S | | 6 | 67 | 3.2 | 90 | 748/685 |
| P3H'-$L_{REF}$ | $L_{REF}$ | 2 | 18 | 3 | 23 | 676/739 |
| P3H'-L1 | L1 | 2 | 10 | 2.7 | 12 | 678/742 |
| P3H'-L2 | L2 | 2 | 10 | 3.8 | 20 | 678/744 |
| P3H'-L3 | L3 | 2 | 26 | 4.1 | 46 | 679/743 |
| P3H'-L4 | L4 | 2 | 13 | 3.4 | 10 | 677/741 |
| P3H'-L5 | L5 | 2 | 12 | 4.4 | 39 | 680/745 |

## 7. Additional crystallographic data for L4.

### Datablock: tb0909_a_a

Bond precision: C-C = 0.0029 A Wavelength=0.71073

Cell: a=10.2109(13) b=18.659(2) c=35.308(4)
alpha=90 beta=94.153(2) gamma=90
Temperature: 150 K

| | Calculated | Reported |
|---|---|---|
| Volume | 6709.4(14) | 6709.2(14) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C38.93 H49 O3 P, C39 H51 O3 P, 1.71(H) | 2(C38.93 H50.7 O3 P) |
| Sum formula | C77.93 H101.71 O6 P2 | C78 H102 O6 P2 |
| Mr | 1196.39 | 1197.53 |
| Dx,g cm-3 | 1.184 | 1.186 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.118 | 0.118 |
| F000 | 2589.1 | 2592.0 |
| F000' | 2590.95 | |
| h,k,lmax | 14,26,49 | 14,26,49 |
| Nref | 19261 | 19234 |
| Tmin,Tmax | 0.958,0.971 | 0.679,0.746 |
| Tmin' | 0.954 | |

Correction method= # Reported T Limits: Tmin=0.679 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 29.829

R(reflections)= 0.0578( 14710) wR2(reflections)= 0.1548( 19234)

S = 1.022 Npar= 835

**Additional crystallographic data for L5.**

## Datablock: tb20160923_0m_a

```
Bond precision:  C-C = 0.0032 A          Wavelength=0.71073

Cell:          a=10.8957(14)      b=13.0496(16)     c=13.9607(17)
               alpha=101.403(2)   beta=109.481(2)   gamma=104.921(2)
Temperature:   150 K

                 Calculated                 Reported
Volume           1718.4(4)                  1718.4(4)
Space group      P -1                       P -1
Hall group       -P 1                       -P 1
Moiety formula   C39 H50.15 O3 P, 0.836(H)  C39 H50.99 O3 P
Sum formula      C39 H50.99 O3 P            C39 H51 O3 P
Mr               598.76                     598.76
Dx,g cm-3        1.157                      1.157
Z                2                          2
Mu (mm-1)        0.115                      0.115
F000             648.0                      648.0
F000'            648.43
h,k,lmax         15,18,19                   15,18,19
Nref             9738                       9684
Tmin,Tmax        0.946,0.955                0.676,0.746
Tmin'            0.944

Correction method= # Reported T Limits: Tmin=0.676 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.994          Theta(max)= 29.664

R(reflections)= 0.0542( 7182)     wR2(reflections)= 0.1506( 9684)

S = 1.052                 Npar= 427
```

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