Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Star-shaped Triarylamine-based Hole-transport Materials in Perovskite Solar Cells

Rosinda Fuentes Pineda[a], Yaroslav Zems[a,c], Joel Troughton[b], Muhammad R. Niazi,[c] Dmitrii F. Perepichka[c], Trystan Watson[b] and Neil Robertson[a*]

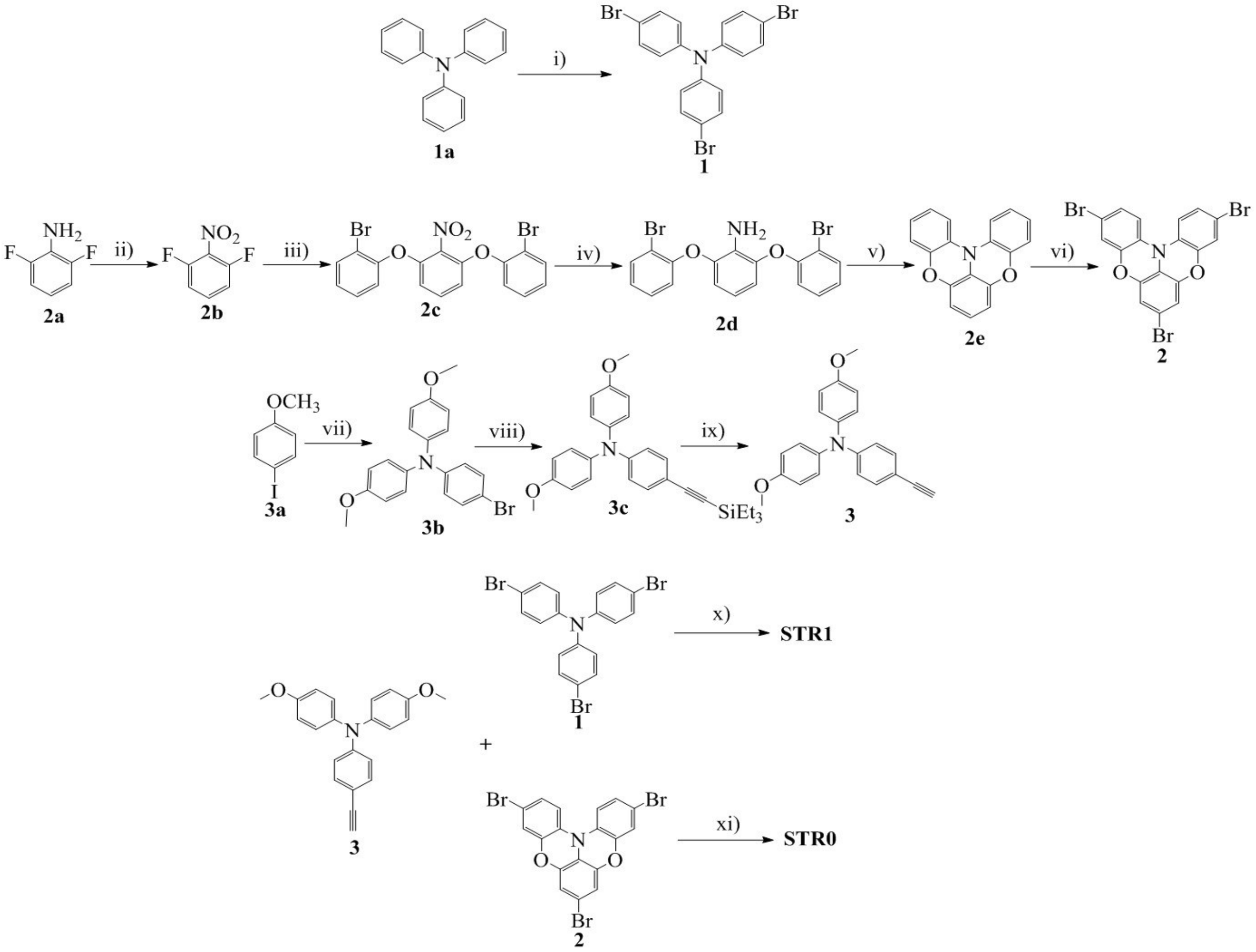
[a]EaStCHEM School of Chemistry, The University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, EH9 3FJ, United Kingdom. Email: neil.robertson@ed.ac.uk

[b]Swansea University Bay Campus, Fabian Way, Swansea, SA1 8EN, United Kingdom.
Email:T.M.Watson@swansea.ac.uk

[c]McGill University, Montreal, Quebec, Canada

Contents

1. Synthetic Procedure



Scheme S1. Complete synthetic procedure for all HTMs. Reaction conditions: i)NBS, DMF, rt, 4hrs, N_2; ii) PBS-2, ACOH, 65-70 °C; iii) NaH, 2-bromophenol, DMSO, 130 °C, N_2; iv) Fe, AcOH/EtOH, 70 °C, N_2; v) $Pd_2(dba)_3CHCl_3$, $P(^tBu)_3$, NaO^tBu, MePh, 120 °C; vi)$C_5H_6Br_3N$, C_6H_6/ETOH, 80 °C; vii) CuI, 1,10-phenantroline, KOH, MePh, 4-bromoaniline, N_2, 120 °C; viii) $C_8H_{16}Si$, CuI, piperidine, $(PPh_3)_2PdCl_2$, PPh_3,PhMe, N_2, 90 °C; ix) 1 M TBAF, DCM, rt, N_2; x)$PdCl_2(PPh_3)_2$, CuI, PPh_3, piperidine, MePh, N_2, 90 °C; xi) $Pd(PPh_3)_4$, CuI, piperidine, MePh, 60 °C, N_2.

*Tris (4-bromophenyl)amine***(1).**

To a solution of triphenylamine (2.0 g, 8.2 mmol) in DMF (15 mL), NBS (4.64 g, 26 mmol) in DMF (10 mL) was added drop-wise at 0°C and the mixture was stirred for 12 h at room temperature. 10 mL of distilled water was added to the reaction mixture, which was extracted with dichloromethane. The organic layer was washed with 10% solution of $Na_2S_2O_3$ and 5% solution of KOH, dried over anhydrous $MgSO_4$ and the solvent evaporated under vacuum. The crude was purified by column chromatography (SiO_2, Hexanes/DCM 90/10) to afford the product as white powder(3.5 g, 88%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 6H), 6.97 – 6.93 (m, 6H).

4-bromo-N,N-bis(4-methoxyphenyl)aniline **(3b)**

A mixture of 4-bromoaniline (58 mmol, 10.0 g), 1-iodo-4-methoxybenzene (145 mmol, 34 g), 1,10-phenantroline (11.6 mmol, 2.1 g) in toluene (200 mL) was heated and stirred under nitrogen atmosphere. CuI (11.6 mmol, 2.2 g) and KOH (465 mmol, 26 g) were added quickly at 110 °C. The mixture was stirred for 12 hrs at 135 °C under N_2 atmosphere. The cooled reaction was washed with 5% solution of HCl and 5% solution of KOH, dried over $MgSO_4$ and solvent evaporated under vacuum. The crude was passed through a quick silica plug in DCM and the product purified by column chromatography (SiO_2, Hexanes/DCM from 100 to 80: 20) to obtain a white powder (12 g, 55%). ^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.19 – 7.16 (m, 2H), 6.97 – 6.93 (m, 4H), 6.77 – 6.73 (m, 2H), 6.70 – 6.66 (m, 4H), 3.29 (s, 6H).

4-methoxy-N-(4-methoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)-phenyl)aniline **(3c)**

4-bromo-N-N-bis(4-methoxyphenyl)aniline (31 mmol, 12 g), $(PPh_3)_2PdCl_2$ (1.6 mmol, 1.1 g), CuI (6.3 mmol, 1.2 g), PPh_3 (2.5 mmol, 0.66 g) were added into a round bottom flask and dried under vacuum for 30 minutes. At the same time, a solution of piperidine (250 mmol, 25 mL) and triethylsilylacetylene (56 mmol, 10 mL) in toluene (200 mL) were stirred and degassed for 30 minutes, added to the first mixture and the mixture stirred at 100 ℃ for 12 hrs under nitrogen atmosphere. The reaction was stopped by the addition of 50 mL of NH_4Cl and washed with a 10% solution HCl and 10% solution KOH. The crude was passed through a quick silica plug in DCM and the product purified by column chromatography (SiO_2, Hex/DCM from 100 to 70:30) to obtain an orange oil (13 g, 93%).^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.44 – 7.40 (m, 2H), 6.98 – 6.94 (m, 4H), 6.89 – 6.85 (m, 2H), 6.68 – 6.64 (m, 4H), 3.27 (s, 6H), 1.14 (t, *J* = 7.9 Hz, 9H), 0.72 (q, *J* = 7.9 Hz, 6H).

4-ethynyl-N,N-bis(4-methoxyphenyl)aniline **(3)**

A mixture of 4-methoxy-N-(4-methoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)- phenyl)aniline (29.1 mmol, 12.9 g) in DCM (150 mL) was stirred under nitrogen for 10 minutes. TBAF (44 mL) was added to the previous solution and the mixture was stirred for 3 hrs under nitrogen atmosphere. The reaction was stopped by the addition of a saturated solution of NH_4Cl and the organic phase was extracted with DCM and dried over $MgSO_4$. The crude was passed through a short silica plug and DCM and the solvent removed under nitrogen to obtained a white powder (8.9 g, 93%).^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.38 – 7.34 (m, 2H), 6.99 – 6.91 (m, 4H), 6.86 – 6.83 (m, 2H), 6.69 – 6.65 (m, 4H), 3.28 (s, 6H), 2.77 (s, 1H).

1,3-difluoro-2-nitrobenzene **(2b)**

Sodium perborate tetrahydrate (3.90 mol, 600 g) and glacial acetic acid (4500 mL) were added to a 10000 mL flask equipped with a magnetic stir bar. The suspension was stirred vigorously and slowly (over 3 hours) brought to 65℃. The mixture became clearer until the contents of the flask were completely transparent. A solution of 2,6-difluoroaniline (0.774 mol, 100 g) in glacial acetic acid (500 mL) was added dropwise to the solution over 4 hours. The contents were brought to 70℃ and stirred for an additional 2 hours. The flask was brought back to room temperature and was allowed to stand overnight. The cooled reaction was filtered over Celite 545 (2.5 cm) to remove borate and unreacted perborate. The solvent was removed under reduced pressure (approx. 4L) and the rest was poured onto 3L of deionized water and extracted with diethyl ether (4 X 500 mL). The solvent was once again removed under reduced pressure and the residual oil re-dissolved in DCM (400 mL), and dried over sodium sulphate (50 g). The whole mixture was filtered over Celite 545 (5 cm) and the solvent removed under reduced pressure to yield a brown/dark yellow oil which was fractionally distilled (76℃, 756 microns) to afford a bright yellow oil which solidifies in the receiving flask into a bright yellow/white solid (86 g, 70%). ^{1}H NMR (500 MHz, Methylene Chloride-d$_2$) δ 7.56(tt, J=8.7, 5.9 Hz, 1H), 7.18-7.09(m, 2H).

2,6-bis(2-bromophenoxy)nitrobenzene **(2c)**

NaH (223 mmol, 9 g, 60% in oil) was weighted directly in a round bottom flask and dried under vacuum for 30 min. Dry DMSO (160 mL) was added to the previous flask and the solution were heated at 70 ℃ for 1 hour under nitrogen. 2-bromophenol (22 mL, 203 mmol) was added to the NaH solution with a syringe and the mixture heated for 1 hour at the same temperature. After cooling to room temperature, 2,6-difluoronitrobenzene (14 g, 88 mmol) was added and the reaction was heated at 130 ℃ for 3 hours under nitrogen. The cooled mixture was poured in a saturated solution of ammonium chloride and mixture extracted with dichloromethane. The organic phase was dried over sodium sulphate, filtered and the solvent removed under reduced pressure. The crude solid was recrystallized in ethanol to obtain the product as white crystals (22 g, 55%). MS (ESI) m/z 463.91 $[M]^+$. ^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.22 (dd, *J* = 8.0, 1.5 Hz, 2H), 6.70 – 6.62 (m, 4H), 6.49 (ddd, *J* = 8.0, 7.2, 1.7 Hz, 2H), 6.41 (t, *J* = 8.5 Hz, 1H), 5.98 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.67, 149.97, 134.19, 133.88, 130.92, 129.03, 126.91, 122.22, 115.73, 110.94.

2,6-bis(2-bromophenoxy)aniline **(2d)**

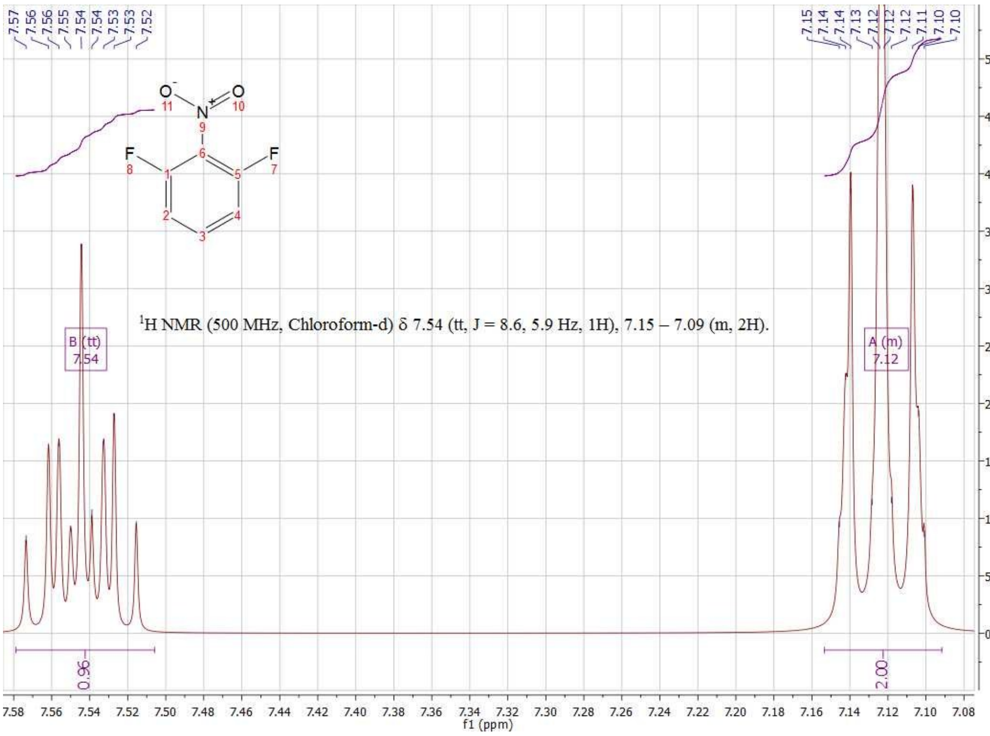
To a solution of 2,6-bis(2-bromophenoxy)nitrobenzene (26.8 mmol, 12.5 g) in glacial acetic acid (250 mL) and ethanol (250 mL) was added Fe powder (140 mmol, 7.7 g) at 0℃. The reaction was allowed to stir at 70 ℃ for 2 hrs. The reaction was concentrated under reduced pressured and the resulting material was diluted in distilled water and washed with a saturated solution of $NaHCO_3$ until the pH was basic. The mixture was extracted with ethyl acetate (3x300 mL), dried over $MgSO_4$ and the solvent removed under reduce pressure to give an oily product (10.6

g, 90%). MS (ESI) m/z 433.94 $[M]^+$. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.65 (dd, J = 7.9, 1.6 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.02 (td, J = 7.7, 1.5 Hz, 2H), 6.97 (dd, J = 8.2, 1.5 Hz, 2H), 6.66 (d, J = 3.8 Hz, 3H), 4.06 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 153.62 , 144.11 , 133.77 , 130.77 , 128.68 , 124.59 , 118.59 , 116.98 , 114.96 , 113.61.

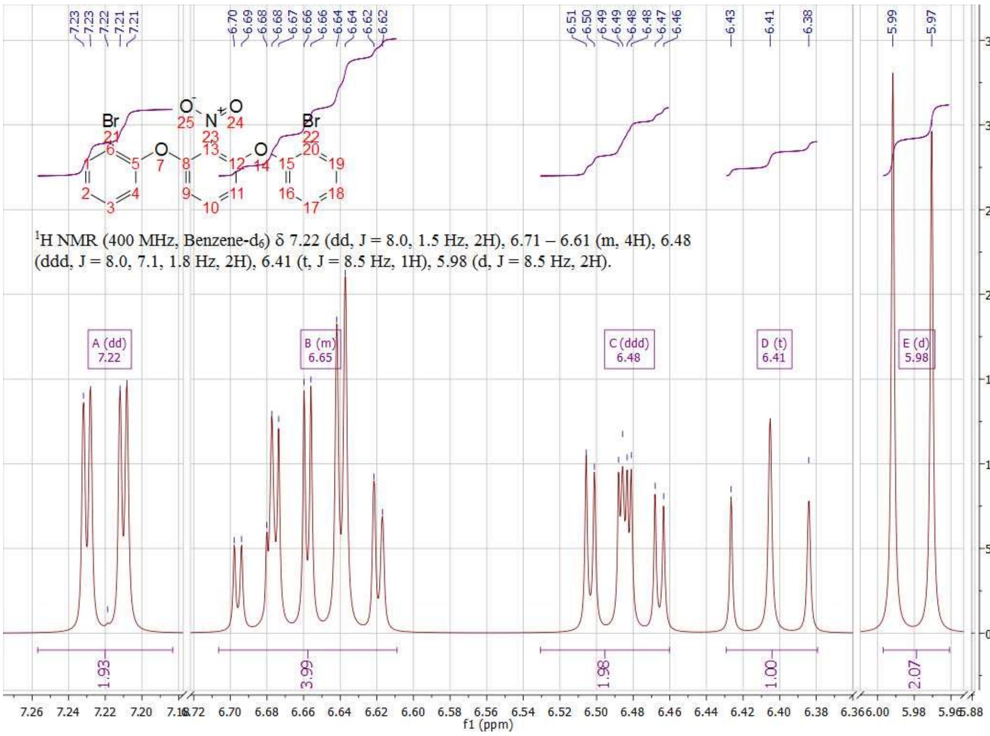
2,2':6'2''-dioxytriphenylamine **(2e)**
A mixture of tris(dibenzylideneacetone)dipalladium (0.262 mmol, 0.272 g), sodium t-butoxide (34.5 mmol, 3.31 g), tri-t-butylphosphine (1.15 mmol, 1.2 mL 0.1 M solution in toluene) and toluene (30 mL) was stirred under nitrogen atmosphere for 60 minutes. A solution of 2,6-bis(2-bromophenoxy)aniline (11.5 mmol, 10 g) in toluene (30 mL) was degassed and added to the previous solution. The reaction was stirred for 12 hrs at 120 ℃ under nitrogen atmosphere. The cooled reaction was passed through Celite 545 (2.5 cm) and a short silica plug using dichloromethane. The crude was recrystallized in hexane/DCM to afford a pale yellow powder. 1H NMR (500 MHz, Chloroform-d) δ 7.35 (dt, J = 7.9, 1.0 Hz, 2H), 6.99 – 6.93 (m, 2H), 6.93 – 6.91 (m, 4H), 6.77 (dd, J = 8.5, 7.9 Hz, 1H), 6.52 (d, J = 8.2 Hz, 2H).

*Tris-4-bromo(2,2':6'2''-dioxytriphenylamine)***(2)** Dioxytriphenylamine (0.94 g, 3.4 mmol) was dissolved in a mixed solvent of benzene (150 mL) and EtOH (100 mL) at refluxing temperature. Pyridinium bromide perbromide (33 g, 103 mmol) was added to the solution and the mixture was stirred for 3 hrs at refluxing temperature. During the first reaction a mixture of the tri-substitution and di-substitution product was obtained, therefore the reaction was done again under the same conditions. The crude product was recrystallized in ethanol to obtained a white powder (1.3 g, 74%).1H NMR (500 MHz, Benzene-d6) δ 6.79 (d, J = 2.2 Hz, 2H), 6.67 (dd, J = 8.6, 2.2 Hz, 2H), 6.40 (s, 1H), 6.36 (d, J = 8.6 Hz, 2H).

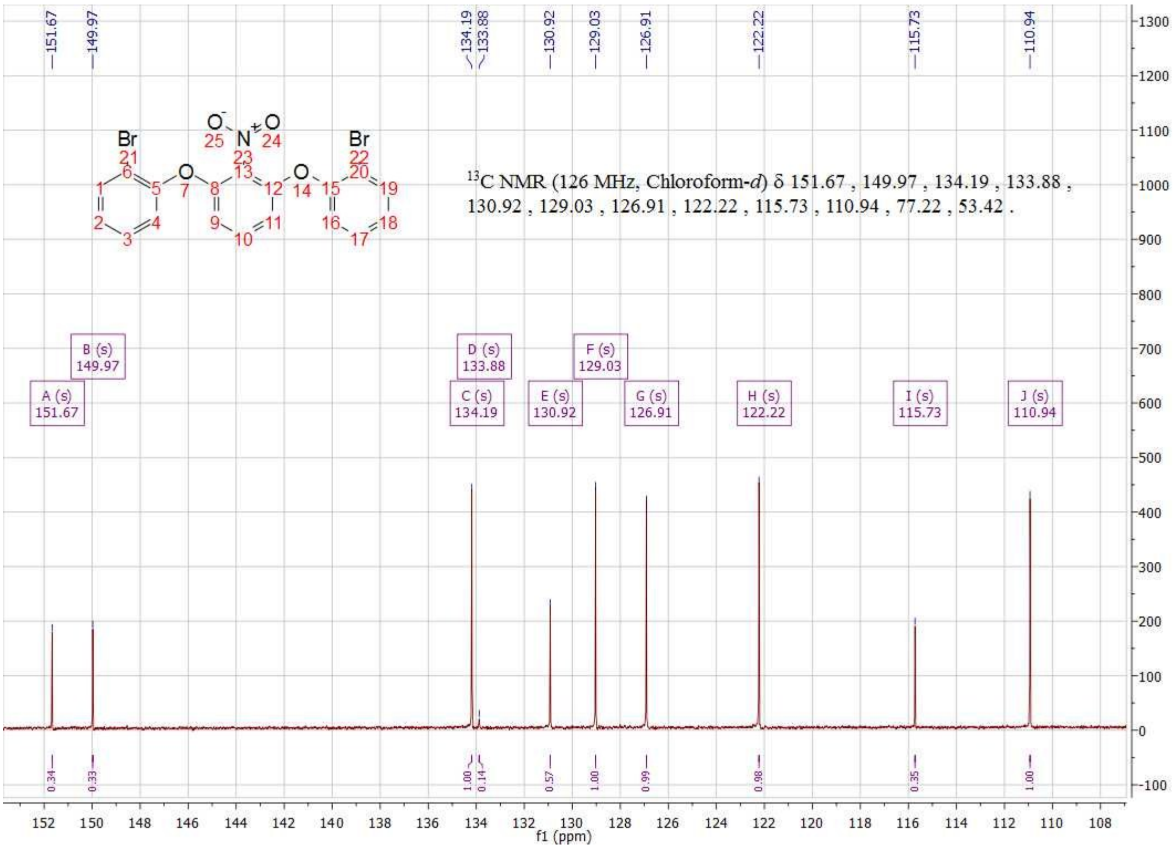
2. ^{1}H and ^{13}C NMR



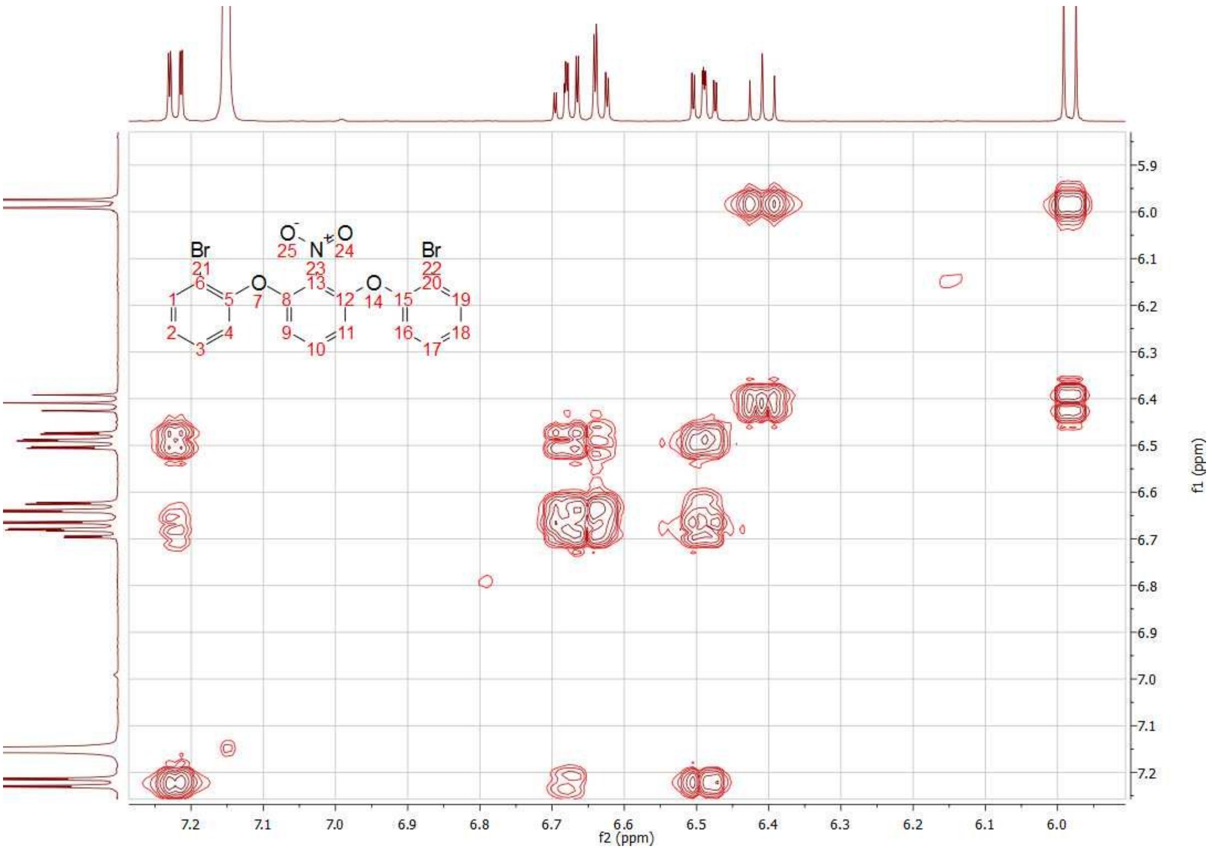
^{1}H NMR (500 MHz, Chloroform-d) δ 7.54 (tt, J = 8.6, 5.9 Hz, 1H), 7.15 – 7.09 (m, 2H).

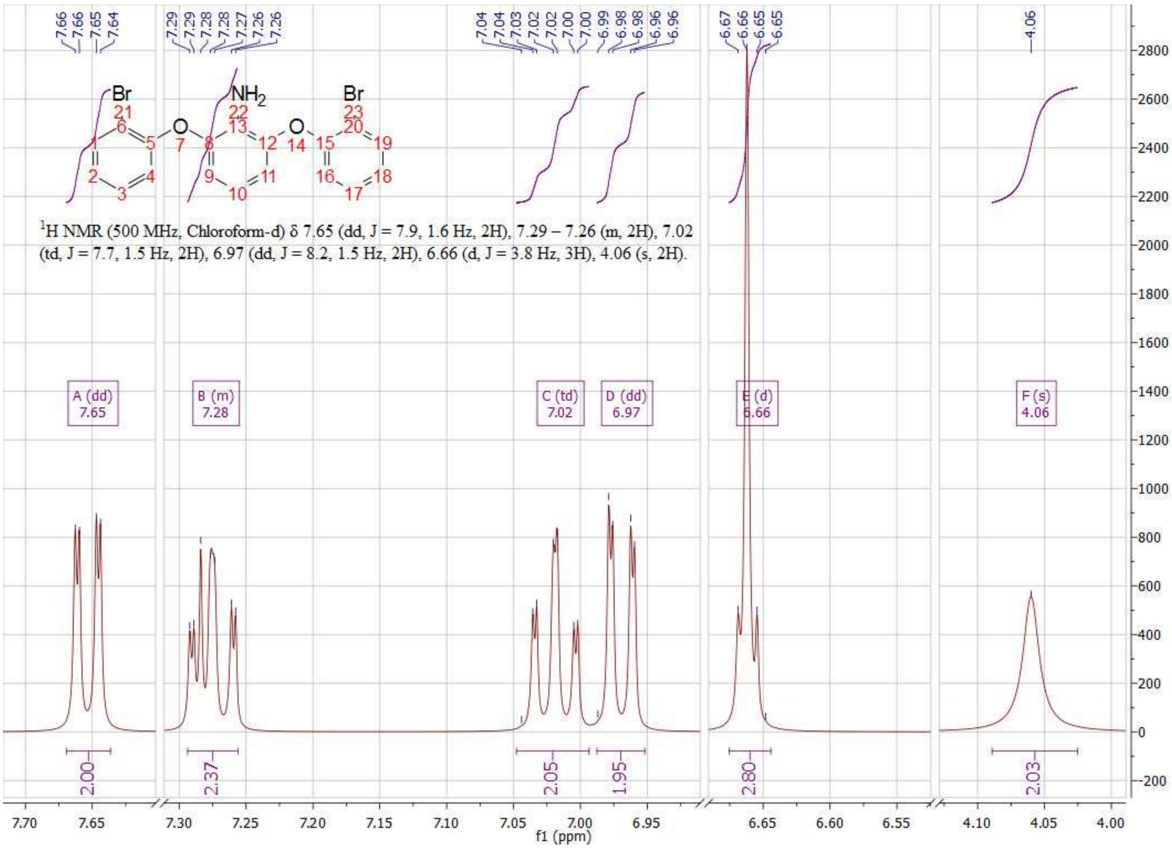


^{1}H NMR (400 MHz, Benzene-d$_6$) δ 7.22 (dd, J = 8.0, 1.5 Hz, 2H), 6.71 – 6.61 (m, 4H), 6.48 (ddd, J = 8.0, 7.1, 1.8 Hz, 2H), 6.41 (t, J = 8.5 Hz, 1H), 5.98 (d, J = 8.5 Hz, 2H).

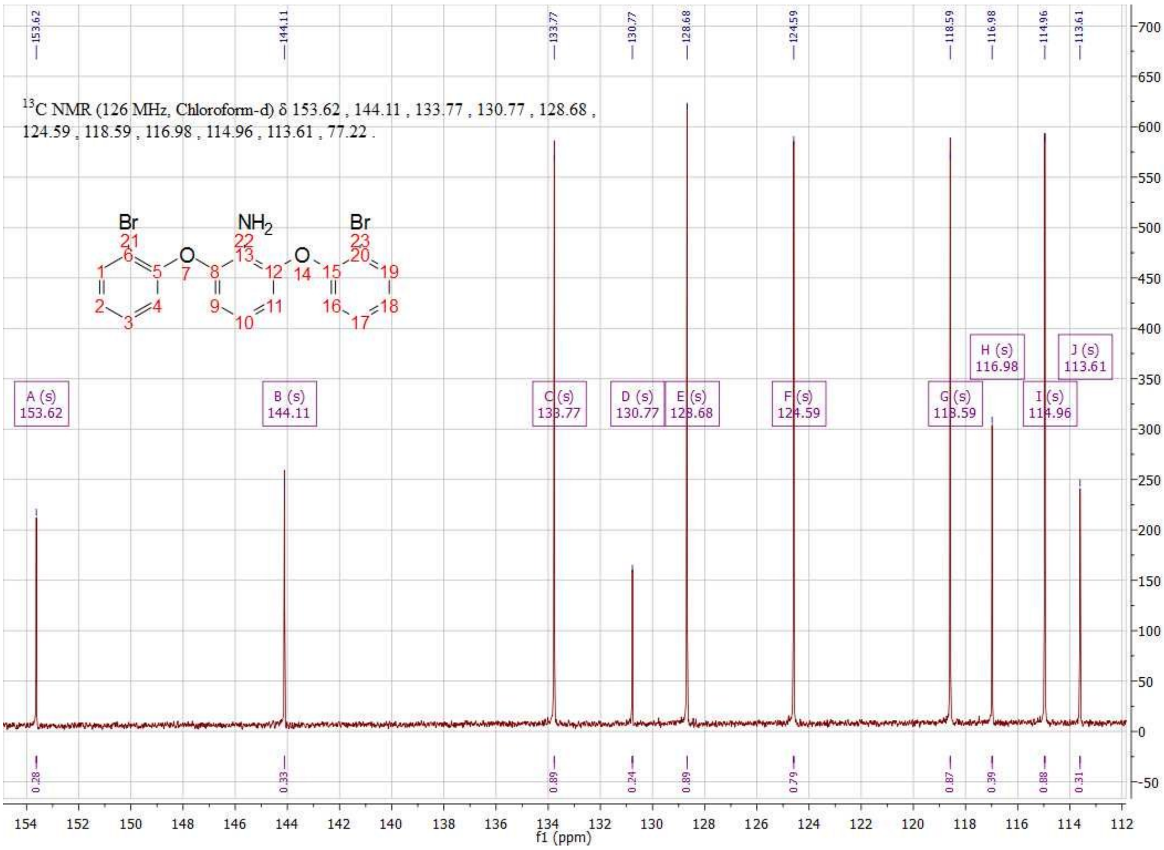


^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.67 , 149.97 , 134.19 , 133.88 , 130.92 , 129.03 , 126.91 , 122.22 , 115.73 , 110.94 , 77.22 , 53.42 .

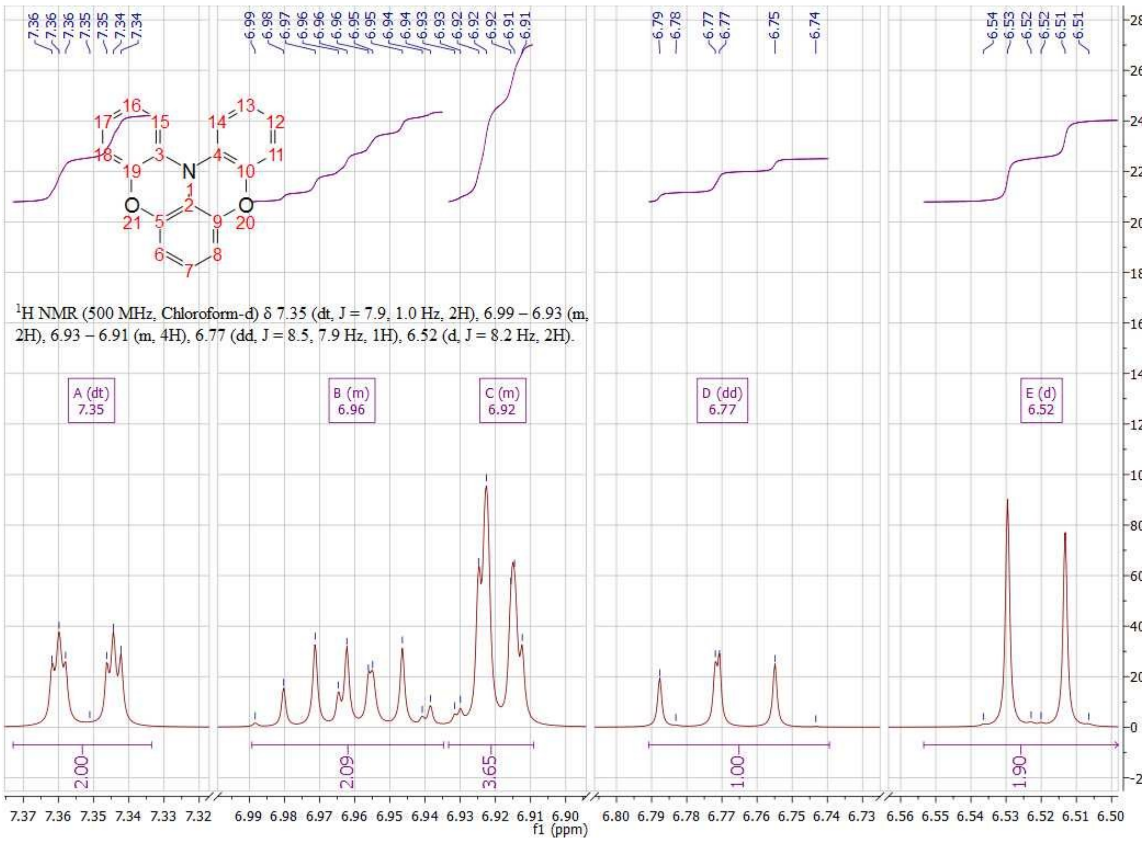




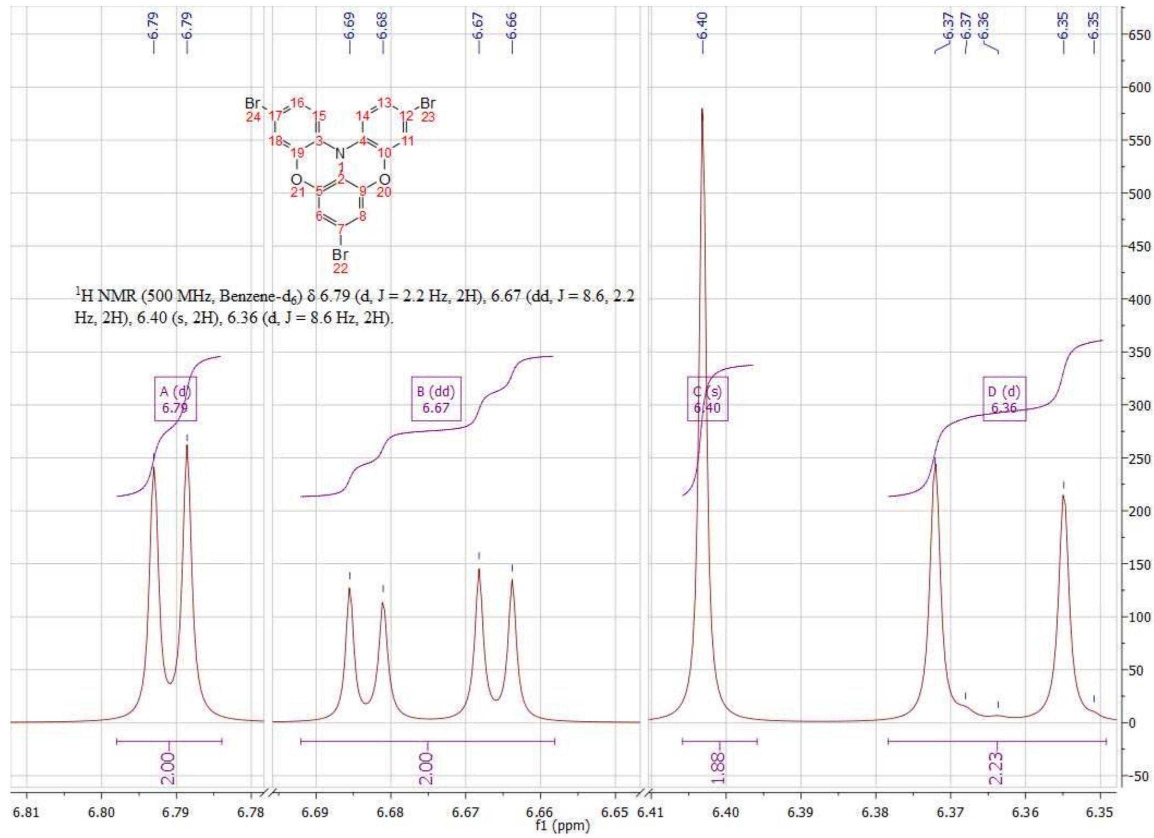
^{1}H NMR (500 MHz, Chloroform-d) δ 7.65 (dd, J = 7.9, 1.6 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.02 (td, J = 7.7, 1.5 Hz, 2H), 6.97 (dd, J = 8.2, 1.5 Hz, 2H), 6.66 (d, J = 3.8 Hz, 3H), 4.06 (s, 2H).



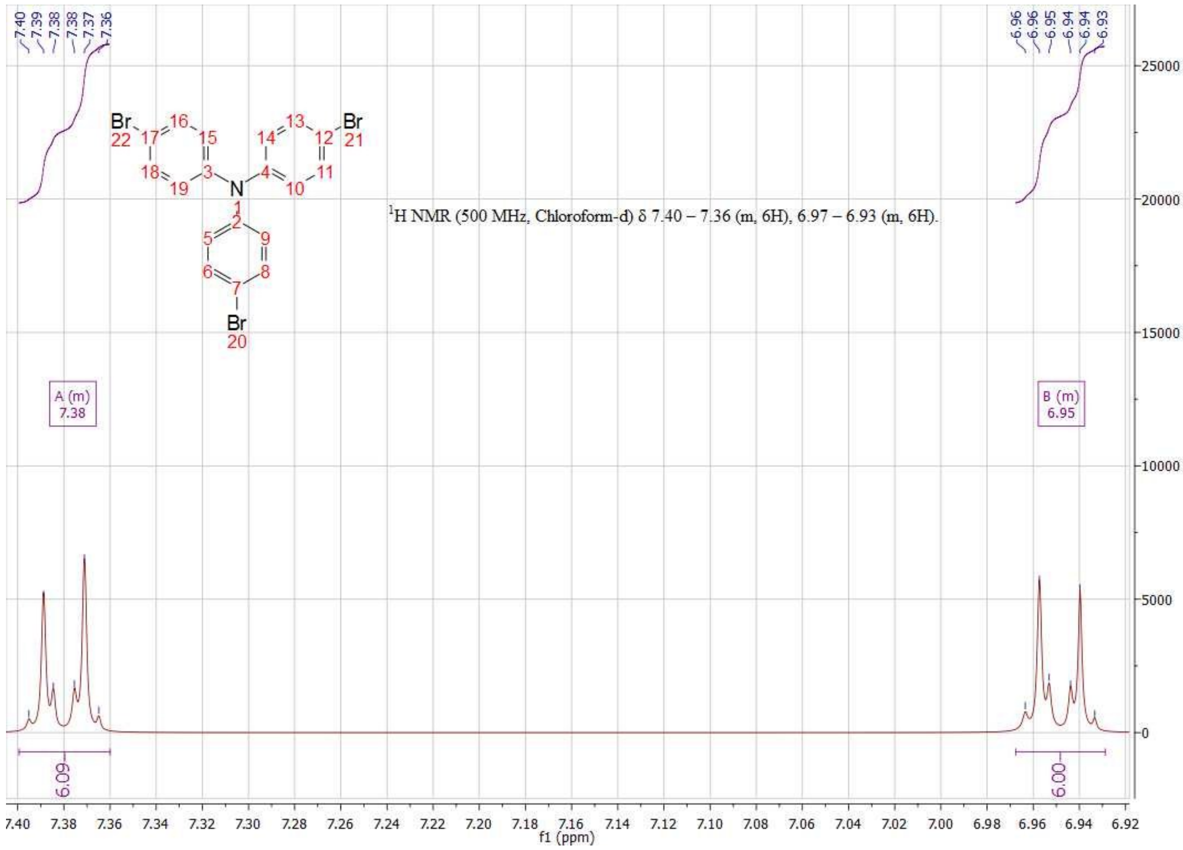
^{13}C NMR (126 MHz, Chloroform-d) δ 153.62 , 144.11 , 133.77 , 130.77 , 128.68 , 124.59 , 118.59 , 116.98 , 114.96 , 113.61 , 77.22 .



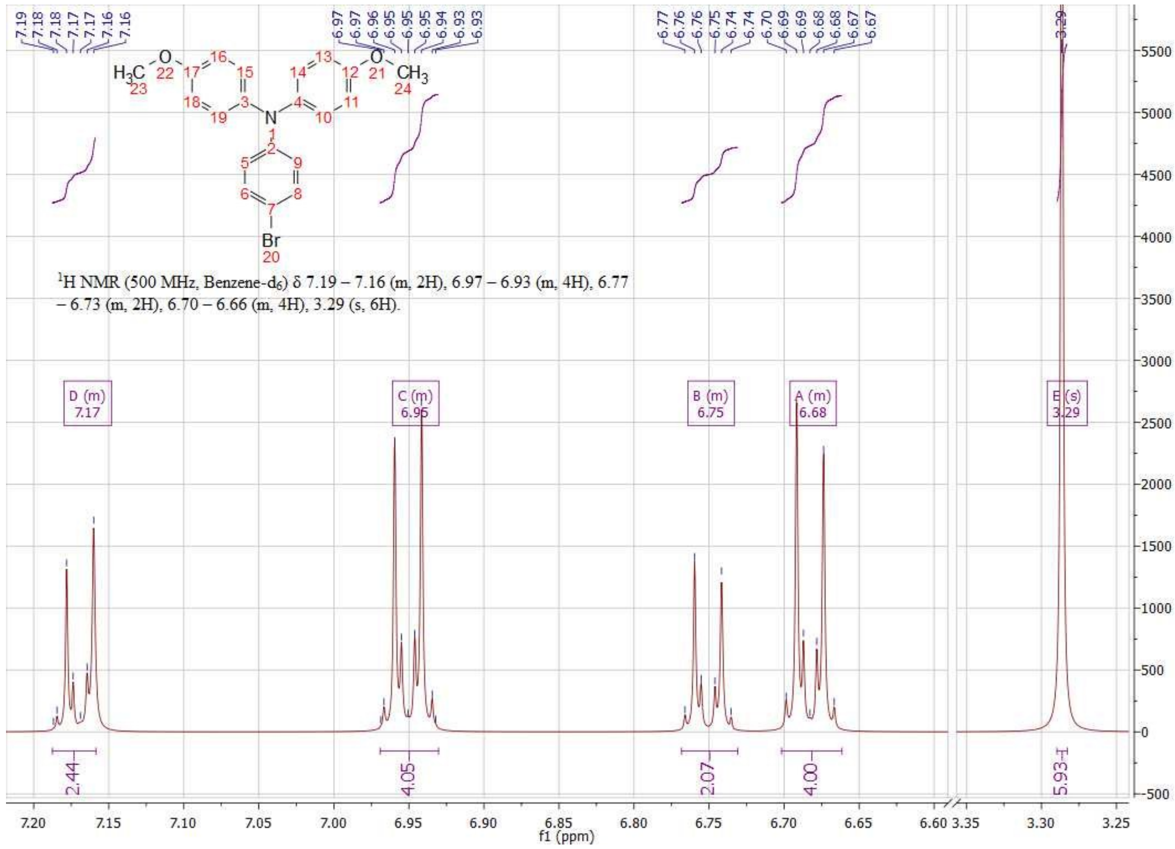
^{1}H NMR (500 MHz, Chloroform-d) δ 7.35 (dt, J = 7.9, 1.0 Hz, 2H), 6.99 – 6.93 (m, 2H), 6.93 – 6.91 (m, 4H), 6.77 (dd, J = 8.5, 7.9 Hz, 1H), 6.52 (d, J = 8.2 Hz, 2H).



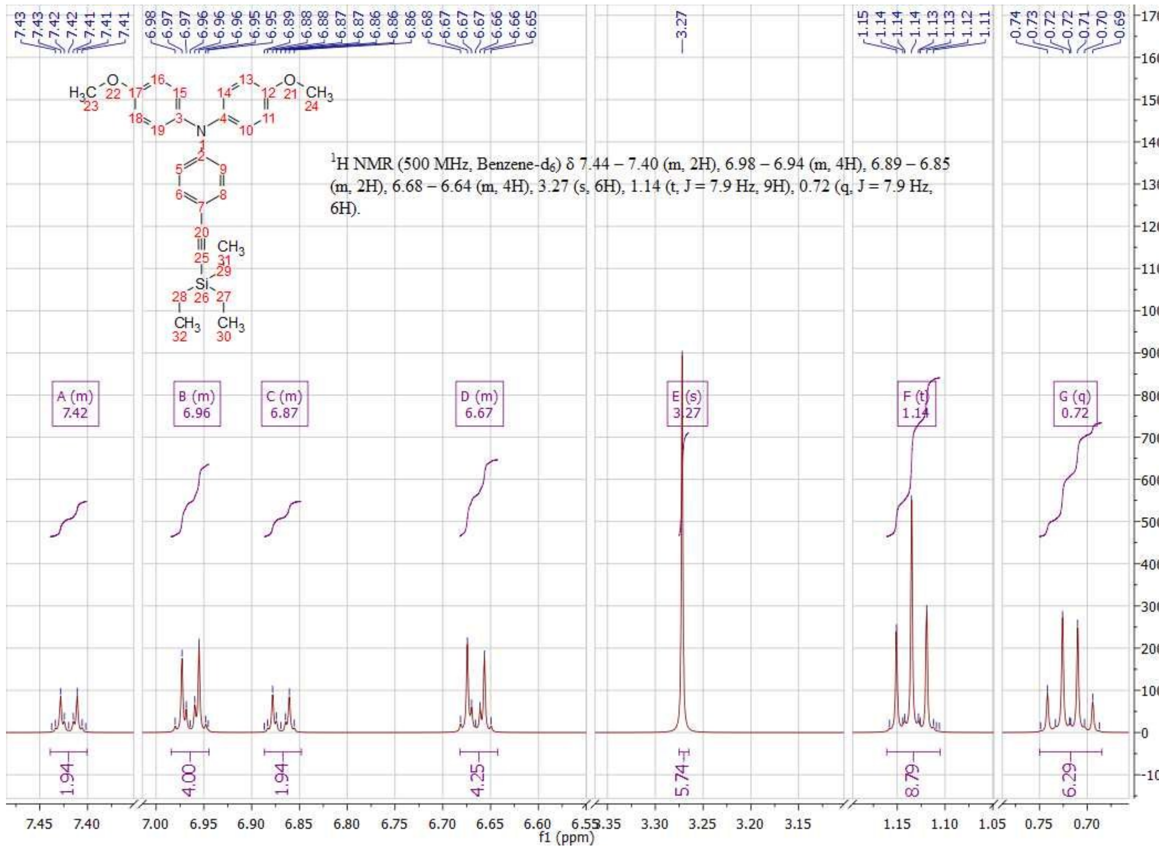
^{1}H NMR (500 MHz, Benzene-d_6) δ 6.79 (d, J = 2.2 Hz, 2H), 6.67 (dd, J = 8.6, 2.2 Hz, 2H), 6.40 (s, 2H), 6.36 (d, J = 8.6 Hz, 2H).



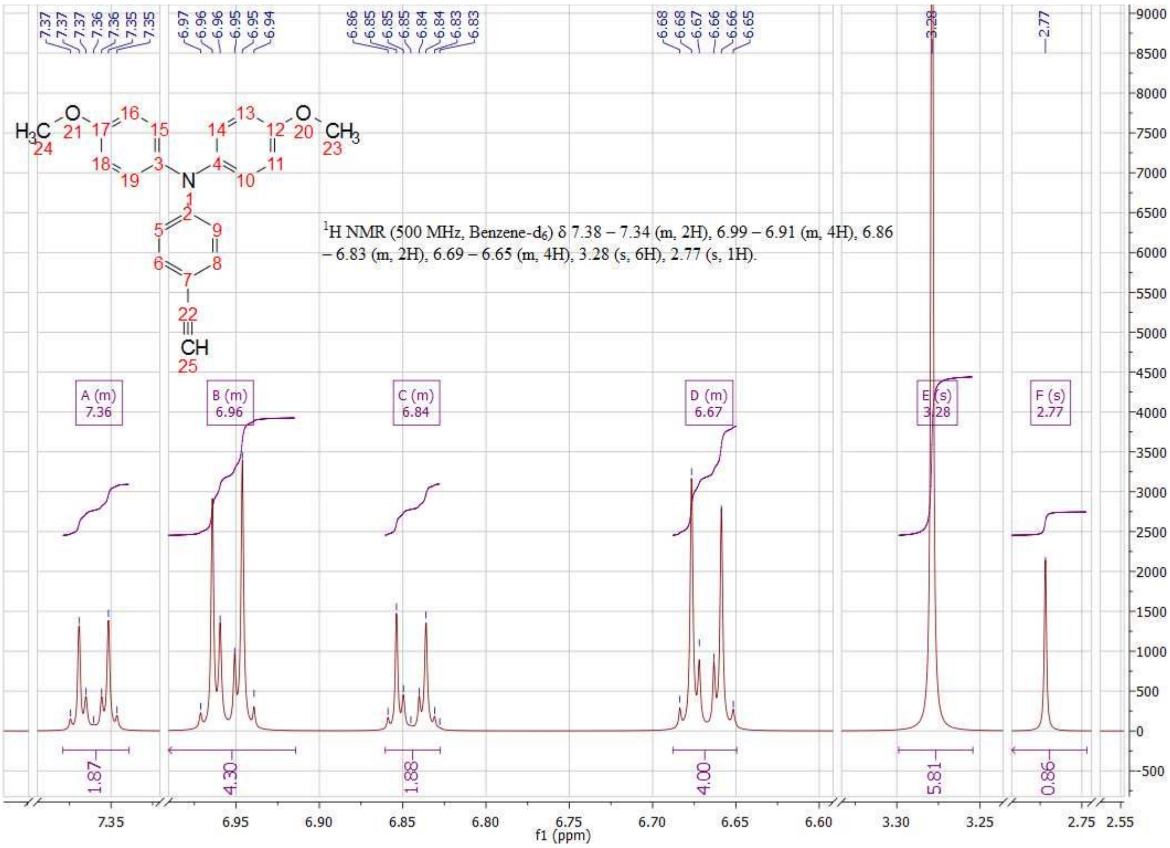
^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.36 (m, 6H), 6.97 – 6.93 (m, 6H).



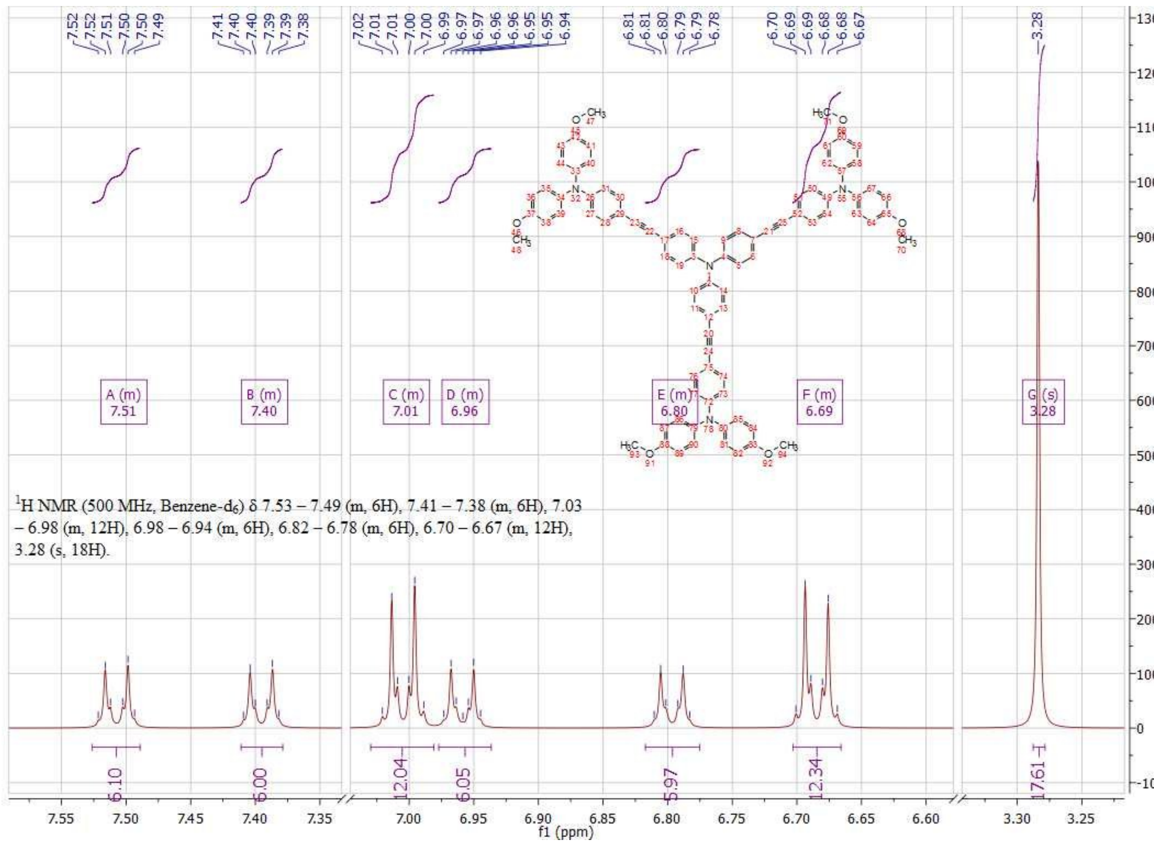
^{1}H NMR (500 MHz, Benzene-d_6) δ 7.19 – 7.16 (m, 2H), 6.97 – 6.93 (m, 4H), 6.77 – 6.73 (m, 2H), 6.70 – 6.66 (m, 4H), 3.29 (s, 6H).



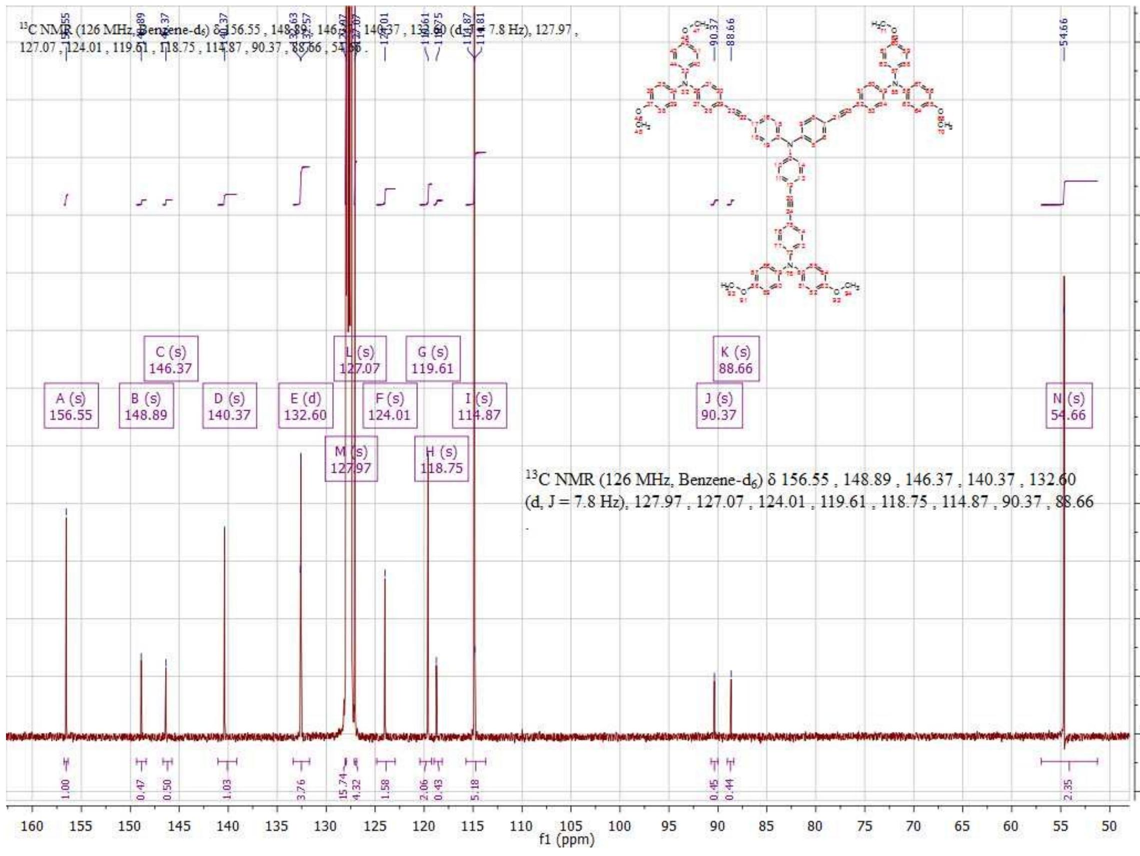
^{1}H NMR (500 MHz, Benzene-d_6) δ 7.44 – 7.40 (m, 2H), 6.98 – 6.94 (m, 4H), 6.89 – 6.85 (m, 2H), 6.68 – 6.64 (m, 4H), 3.27 (s, 6H), 1.14 (t, J = 7.9 Hz, 9H), 0.72 (q, J = 7.9 Hz, 6H).



^{1}H NMR (500 MHz, Benzene-d_6) δ 7.38 – 7.34 (m, 2H), 6.99 – 6.91 (m, 4H), 6.86 – 6.83 (m, 2H), 6.69 – 6.65 (m, 4H), 3.28 (s, 6H), 2.77 (s, 1H).

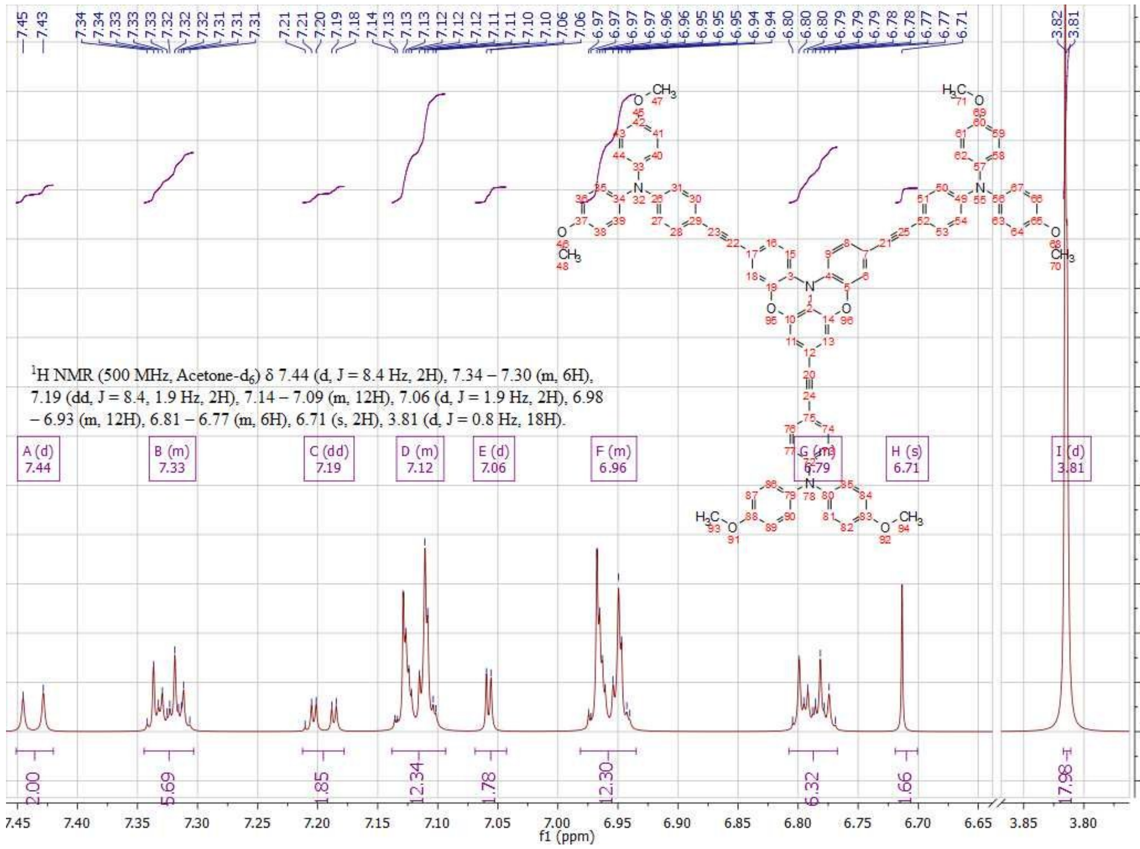


^{1}H NMR (500 MHz, Benzene-d_6) δ 7.53 – 7.49 (m, 6H), 7.41 – 7.38 (m, 6H), 7.03 – 6.98 (m, 12H), 6.98 – 6.94 (m, 6H), 6.82 – 6.78 (m, 6H), 6.70 – 6.67 (m, 12H), 3.28 (s, 18H).



^{13}C NMR (126 MHz, Benzene-d_6) δ 156.55 , 148.89 , 146.37 , 140.37 , 132.60 (d, J = 7.8 Hz), 127.97 , 127.07 , 124.01 , 119.61 , 118.75 , 114.87 , 90.37 , 88.66 , 54.66 .

^{13}C NMR (126 MHz, Benzene-d_6) δ 156.55 , 148.89 , 146.37 , 140.37 , 132.60 (d, J = 7.8 Hz), 127.97 , 127.07 , 124.01 , 119.61 , 118.75 , 114.87 , 90.37 , 88.66



^{1}H NMR (500 MHz, Acetone-d$_6$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.34 – 7.30 (m, 6H), 7.19 (dd, J = 8.4, 1.9 Hz, 2H), 7.14 – 7.09 (m, 12H), 7.06 (d, J = 1.9 Hz, 2H), 6.98 – 6.93 (m, 12H), 6.81 – 6.77 (m, 6H), 6.71 (s, 2H), 3.81 (d, J = 0.8 Hz, 18H).

3. Thermal properties

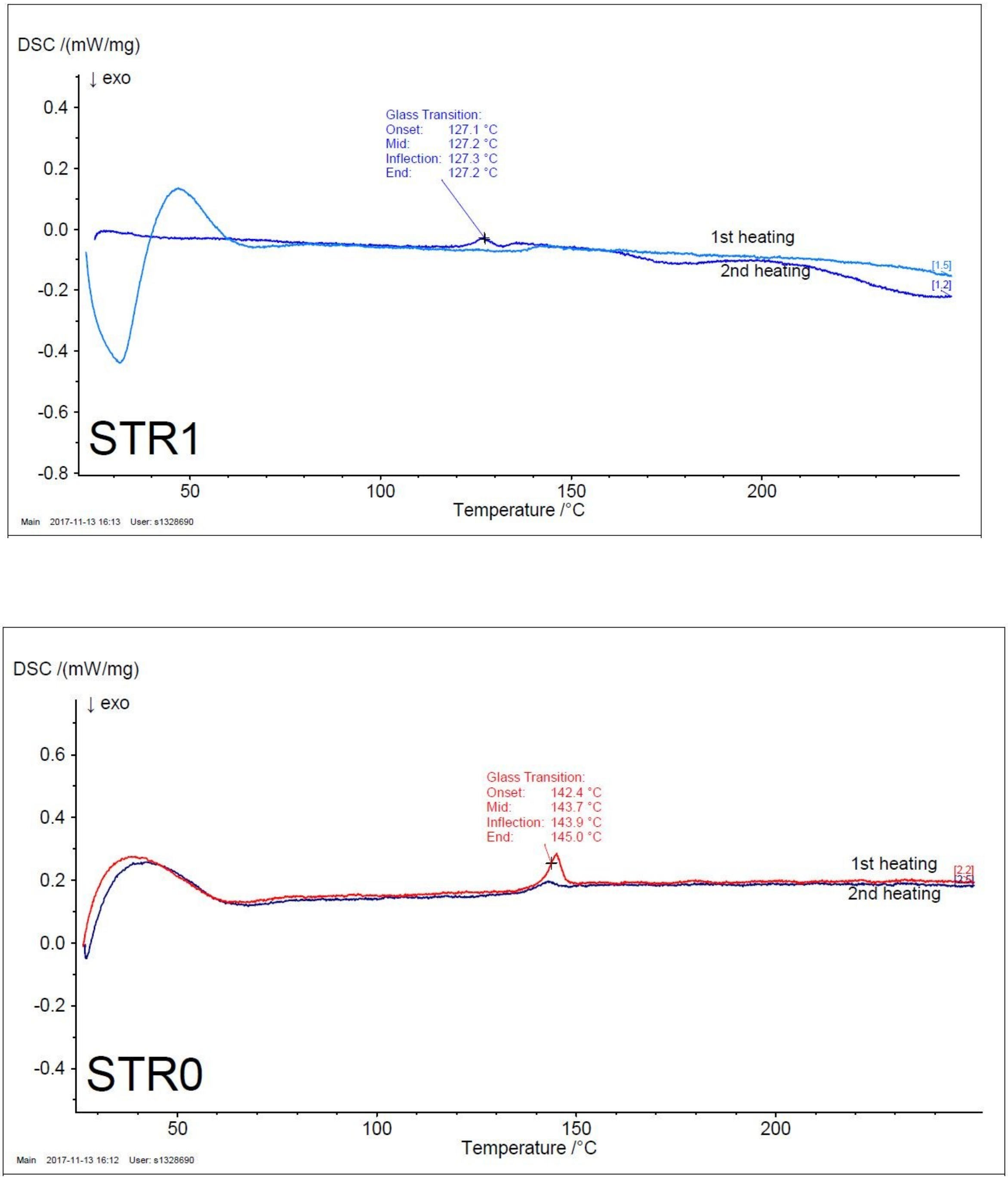


Figure S1 Differential scanning calorimetry curves

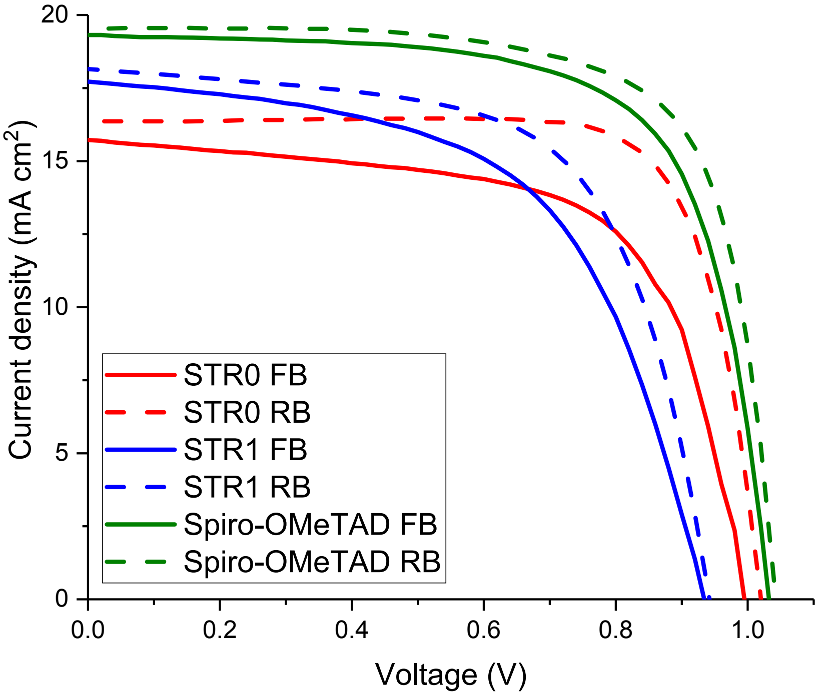
4. Solar Cells

Table S1. Summary of the PV parameters after fabrication

HTM	PCE (%)	Jsc (mA cm^{-2})	Voc (V)	FF (%)
STR0 Undoped	3.0±0.9	15.12±1.79	0.82±0.10	22.8±3.3
STR0 Doped	11.7±1.1	15.17±1.06	0.99±0.03	75.1±2.5
STR1 Undoped	0.3±0.2	3.26±1.54	0.56±0.12	19.4±7.6
STR1 Doped	7.9±3.3	15.53±2.13	0.93±0.02	51.1±16.1
Spiro-OMeTAD	13.7±1.0	19.09±1.03	1.02±0.02	68.4±3.0

Table S2. Summary of the PV parameters after two weeks of storing

HTM	PCE (%)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)
STR0 Undoped	5.62±1.17	13.06±1.45	0.90±0.01	47.97±12.76
STR0 Doped	7.93±1.84	12.53±2.06	0.92±0.05	67.03±2.02
STR1 Undoped	1.01±0.20	6.06±1.29	0.81±0.08	20.50±1.05
STR1 Doped	5.66±0.86	10.81±1.45	0.88±0.03	58.14±4.37
Spiro-OMeTAD	12.28±3.10	16.59±2.6	0.99±0.07	70.01±8.93


Current density (mA cm^2)
Voltage (V)
0
5
10
15
20
0.0
0.2
0.4
0.6
0.8
1.0
STR0 FB
STR0 RB
STR1 FB
STR1 RB
Spiro-OMeTAD FB
Spiro-OMeTAD RB

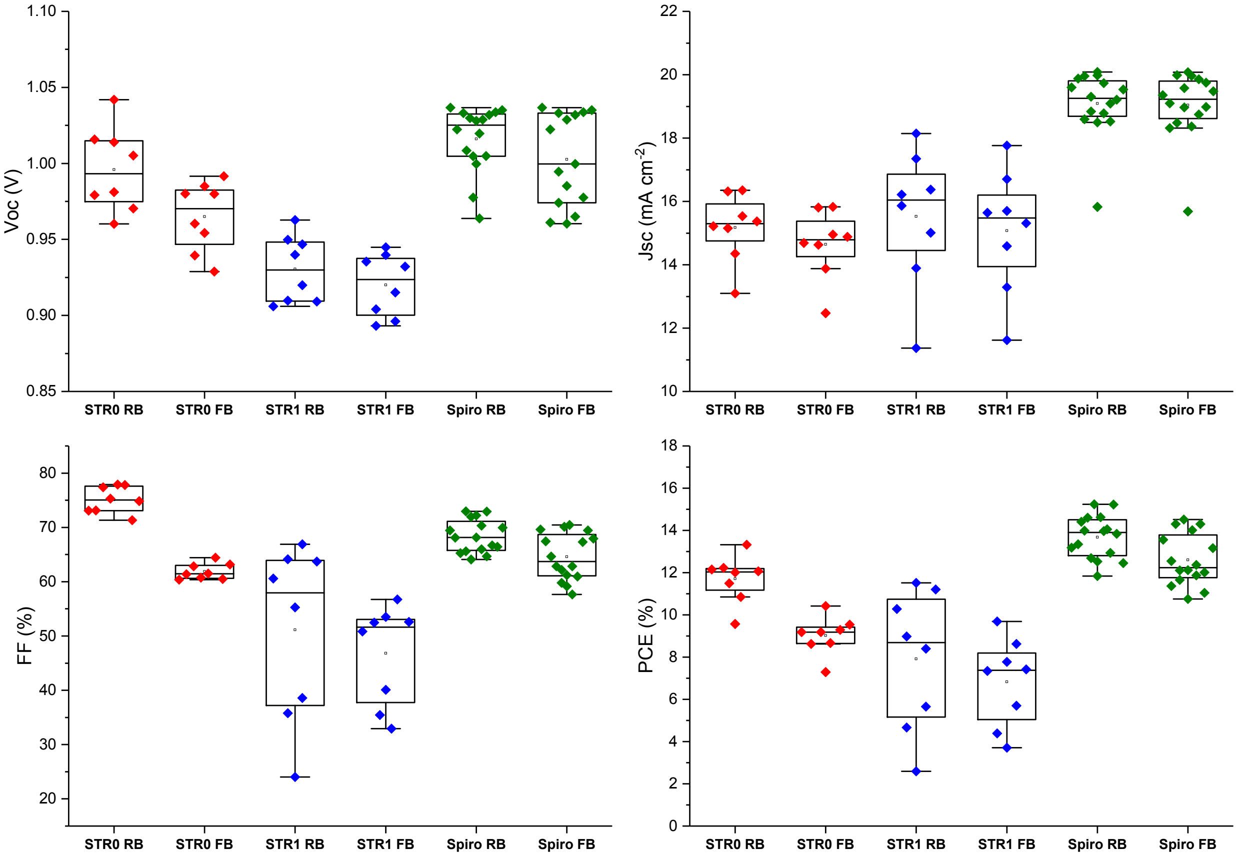


Figure S2 Hysteresis: JV curves and box plot

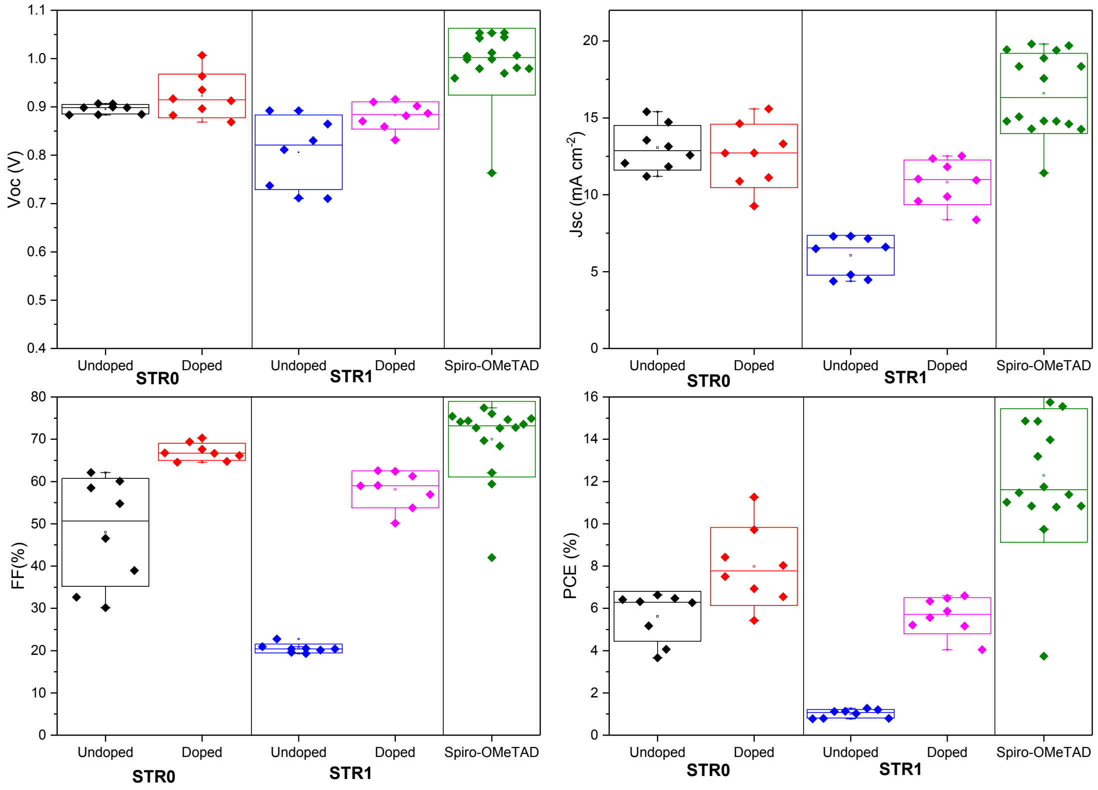


Figure S3 Box plot of photovoltaic parameters of PSCs with STR1, STR0 and spiro-OMeTAD measured after two weeks of storage.

5. Water Contact Angle

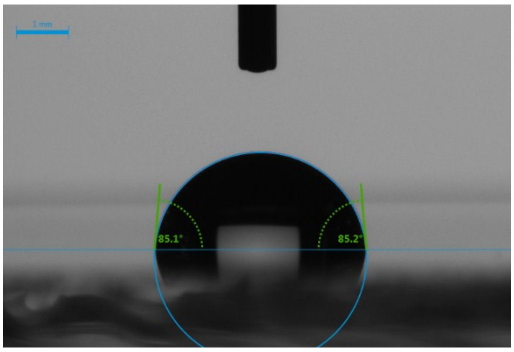
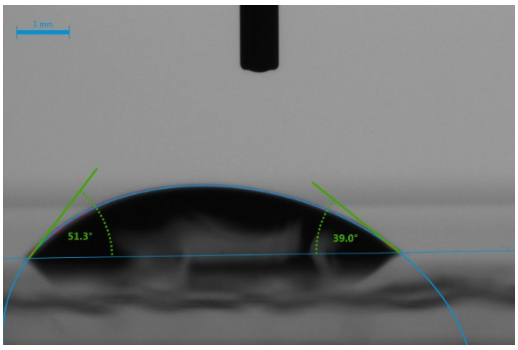
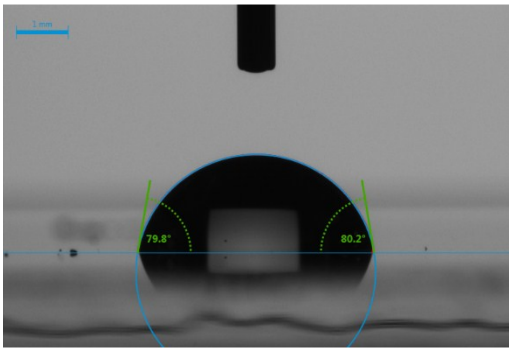
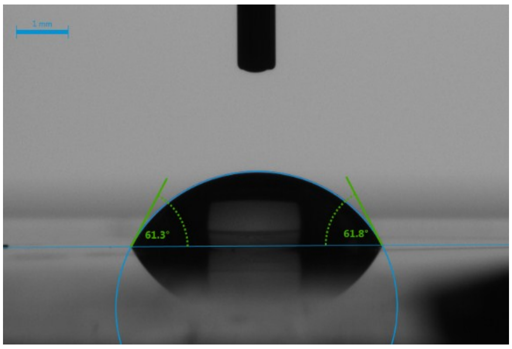
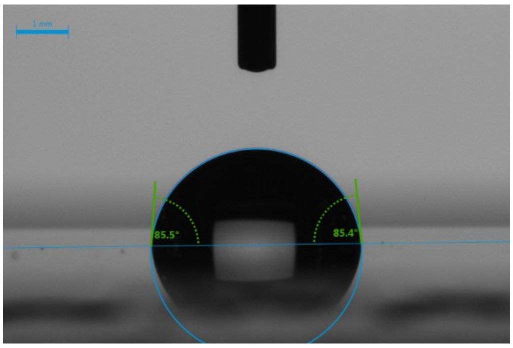
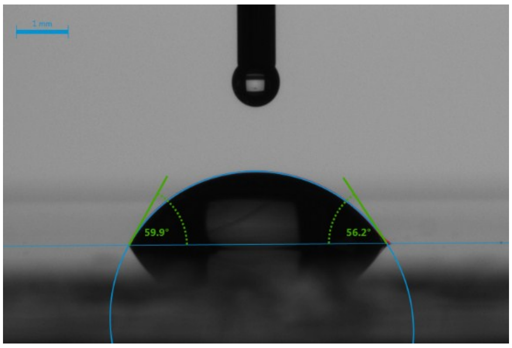
HTM	**Without additives**	**With additives**
Spiro-OMeTAD		
STR1		
STR0		

Figure S4 Water contact angle of the HTMs with and without additives.