Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

1. Synthesis

Materials and Synthesis

All reagents were purchased from either Sigma-Aldrich or Alfa-Aesar, and they were used as received without further purification unless otherwise stated.

4-bromo-*N,N*-bis(4-ethoxyphenyl)aniline 4-bromoaniline (6.98 mmol, 1.2 g), CuI (0.35 mmol, 66 mg), 1,10-phenantroline (0.35 mmol, 63 mg), KOH (35 mmol, 2 g) were added into a Schlenk tube and dried under high vacuum for 30 min. A degassed solution of dried toluene (20 ml) and 4-iodoethoxybenzene (17.5 mmol, 4.3 g) was added to the previous mixture via cannula transfer. The reaction mixture was heated at 120°C overnight under N_2. The cooled reaction mixture was washed with 5% HCl and 5% NaOH solution respectively, dried with $MgSO_4$ and solvent evaporated under vacuum. The residue was passed through a short silica plug in DCM and solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2, Hexanes/EtA 90/10) to afford the product as a light yellow oil (1.2 g, 42% yield). ^{1}H NMR (500 MHz, Benzene-d6) δ 7.00 – 6.94 (m, 4H), 6.79 – 6.75 (m, 2H), 6.73 – 6.70 (m, 4H), 3.57 (q, J = 7.0 Hz, 4H), 1.11 (t, J = 6.9 Hz, 6H).

4-ethoxy-N-(4-ethoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)phenyl)aniline $(PPh_3)_2PdCl_2$ (102 mg, 0.15 mmol), CuI (0.58 mmol, 110 mg), PPh_3 (0.23 mmol, 61 mg) were added into a Schlenck tube and dried under vacuum for 30 minutes. 4-bromo-N,N-bis(4-ethoxyphenyl)aniline (2.91 mmol,1.2 g), piperidine (2.3 mL), triethylsilylacetylene (5.8 mmol, 1 mL) and toluene (15 ml) were all degassed and added to the previous mixture via cannula transfer. The solution was stirred under N_2 at 90°C overnight. The cooled reaction mixture was passed through a short silica plug in DCM and solvent was removed. The crude mixture was purified by column chromatography (SiO_2, Hexanes/EtA 95/5) to afford the product as a transparent yellow oil (1.3 g, 95%). ^{1}H NMR (500 MHz, Benzene-d6) δ 7.45 – 7.38 (m, 2H), 7.00 – 6.96 (m, 4H), 6.90 – 6.86 (m, 2H), 6.72 – 6.68 (m, 4H), 3.56 (q, J = 6.9 Hz, 4H), 1.18 – 1.07 (m, 15H), 0.72 (q, J = 7.9 Hz, 6H).

4-ethynyl-N,N-bis(4-ethoxyphenyl)aniline 4-ethoxy-N-(4-ethoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)phenyl)aniline (2.54 mmol, 1.2 g) and 10 mL of DCM were placed into a round bottom flask, and the mixture was stirred under N_2 for 10 minutes. TBAF (4 mL) was then added to the previous solution, and the reaction was stirred for 2 hours under N_2 at room temperature. The reaction was washed three times with a solution of 10% ammonium chloride (20 mL) , dried with $MgSO_4$ and the solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2, PE/DCM 100 to 90/10) to afford the product as a yellow oil (0.86 g, 95% yield). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.38 (m, 2H), 7.07 – 7.03 (m, 4H), 6.96 – 6.92 (m, 2H), 6.80 – 6.77 (m, 4H), 3.64 (q, J = 7.0 Hz, 4H), 2.85 (s, 1H), 1.18 (t, J = 7.0 Hz, 6H).

4,4'-(buta-1,3-diyne-1,4-diyl)bis(N,N-bis(4-ethoxyphenyl)aniline) (EtO-DATPA) CuCl (0.23g, 2.4 mmol) was weighed out directly into a round-bottomed flask, TMEDA (1.1 mL) was combined in one portion and later DCM (15 mL) was added slowly while stirring. 4 Å molecular sieves (5 g) were added to the mixture, and after 5 min of stirring, a solution of 4-ethynyl-N,N-bis(4-ethoxyphenyl)aniline (0.86 g, 2.4 mmol) in DCM (8 mL) was added to the previous solution and the mixture stirred for 1.5 hours at room temperature. The reaction was washed three times with a solution of 10% ammonium chloride (20 mL) , dried with $MgSO_4$ and the solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2, PE/EtA 98/2) to afford the product as a yellow powder. Finally, the product was recrystallized in Hexane/DCM (0.62 g. 73% yield). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.35 – 7.30 (m, 4H), 6.98 – 6.94 (m, 8H), 6.85 – 6.78 (m, 4H), 6.75 – 6.67 (m, 8H), 3.56 (q, J = 7.0 Hz, 8H), 1.10 (t, J = 6.9 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.91 , 149.35 , 139.69 , 133.26, 127.33 , 118.52 , 115.39 , 112.07 , 82.16 , 73.10 , 63.68 , 14.89 . MS EI (m/z): $[M]^+$ 713.3348. Anal. Calcd for $C_{48}H_{44}N_2O_4$: C. 80.87; H: 6.22; N. 3.93 analysed C, 80.83; H, 6.15; N, 4.04.

1-iodo-4-isopropoxybenzene 4-iodophenol (22.73 mmol, 5 g), K_2CO_3 (68.19 mmol, 9.4 g), 18-crown-6 (0.227 mmol, 0.6 g) and DMF (40 ml) were all added into a round bottom flask and stirred under N_2 to which 2-bromopropane (45.19 mmol, 4.26 mL) was added. The mixture was stirred and refluxed for 4 hrs under N_2 at 90°C. A silica plug (PE/DCM 90/10) was run to afford the product as a transparent oil (6 g, 97% yield). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.42 (m, 2H), 6.46 – 6.43 (m, 2H), 4.04 (hept, J = 6.0 Hz, 1H), 1.07 (d, J = 6.0 Hz, 6H).

4-bromo-N,N-bis(4-isopropoxyphenyl)aniline 4-bromoaniline (8.14 mmol, 1.4 g), CuI (0.4 mmol, 78 mg), 1, 10-phenantroline (0.4 mmol, 72 mg), KOH (40.7 mmol, 2.3 g) were added into a Schlenk tube and dried under high vacuum for 30 min. A degassed solution of dried toluene (20 ml) and 4-iodoisopropoxybenzene (20.35 mmol, 5.33 g) were added into the previous mixture via cannula transfer. The reaction mixture was heated at 120°C overnight under N_2. The cooled reaction mixture was washed with 5% HCl and 5% NaOH solution respectively, dried with $MgSO_4$ and solvent evaporated under vacuum. The residue was passed through a short silica in DCM and solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2,

Hexanes/EtA 90/10) to afford the product as a light yellow oil (1.3 g, 36% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.16 (d, J = 4.0 Hz, 9H), 6.99 – 6.94 (m, 2H), 6.80 – 6.73 (m, 2H), 6.77 – 6.70 (m, 4H), 4.12 (h, J = 6.0 Hz, 2H), 1.11 (d, J = 6.0 Hz, 12H).

4-isopropoxy-N-(4-isopropoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)phenyl)aniline $(PPh_3)_2PdCl_2$ (81 mg, 0.12 mmol), CuI (0.46 mmol, 88 mg), PPh_3 (0.18 mmol, 48 mg) were added into a Schlenck tube and dried under vacuum for 30 minutes. 4-bromo-N,N-bis(4-isopropoxyphenyl)aniline (2.3 mmol,1 g), piperidine (1.8 mL), triethylsilylacetylene (4.6 mmol, 0.83 mL) and toluene (15 ml) were all degassed and added to the previous mixture via cannula transfer. The solution was stirred under N_2 at 90°C overnight. The cooled reaction mixture was passed through a short silica plug in DCM and solvent was removed. The crude was purified by column chromatography (SiO_2, Hexanes/EtA 95/5) to afford the product as a transparent yellow oil (1.06 g, 92%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.43 – 7.37 (m, 2H), 7.02 – 6.94 (m, 4H), 6.92 – 6.85 (m, 2H), 6.80 – 6.68 (m, 4H), 4.11 (hept, J = 6.0 Hz, 2H), 1.13 (t, J = 7.9 Hz, 9H), 1.10 (d, J = 6.0 Hz, 12H), 0.71 (q, J = 7.9 Hz, 6H).

4-ethynyl-N,N-bis(4-isopropoxyphenyl)aniline 4-isopropoxy-N-(4-isopropoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)phenyl) aniline (1.6 mmol, 0.8 g) and 10 mL of DCM were placed into a round bottom flask, and the mixture was stirred under N_2 for 10 minutes. TBAF (2.5 mL) was then added to the previous solution, and the reaction was stirred for 2 hours under N_2 at room temperature. The reaction was washed three times with a solution of 10% ammonium chloride (20 mL) , dried with $MgSO_4$ and the solvent removed under vacuum. The crude product was purified by column chromatography ((SiO_2,PE/DCM 100 to 90/10) to afford the product as a yellow oil (0.57 g, 94%)^{1}H NMR (500 MHz, Benzene-d_6) δ 7.36 – 7.33 (m, 2H), 6.99 – 6.96 (m, 4H), 6.88 – 6.84 (m, 2H), 6.75 – 6.68 (m, 4H), 4.11 (h, J = 6.0 Hz, 2H), 2.77 (s, 1H), 1.10 (d, J = 6.1 Hz, 12H).

4,4'-(buta-1,3-diyne-1,4-diyl)bis(N,N-bis(4-isopropoxyphenyl)aniline) (iPrO-DATPA) CuCl (0.15 g, 1.5 mmol) was weighed out directly into a round bottomed flask, TMEDA (0.7 mL) was combined in one portion and later DCM (15 mL) was added slowly while stirring. 4 Å molecular sieves (3 g) were added to the mixture and after 5 min of stirring, a solution of 4-ethynyl-N,N-bis(4-isopropoxyphenyl)aniline (0.57 g , 1.5 mmol) in DCM (5 mL) were added to the previous solution and the mixture stirred for 1.5 hours at room temperature. The reaction was washed three times with a solution of 10% ammonium chloride (10 mL) , dried with $MgSO_4$ and the solvent remove under vacuum. The crude product was purified by column chromatography (SiO_2,PE/EtA 98/2) to afford the product as a yellow powder and was later recrystallized in DCM/Hexane (0.48 g, 84%) ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.33 – 7.30 (m, 4H), 6.98 – 6.95 (m, 8H), 6.83 – 6.80 (m, 4H), 6.73 – 6.70 (m, 8H), 4.12 (p, J = 6.0 Hz, 4H), 1.10 (d, J = 6.0 Hz, 24H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.82 , 149.36 , 139.57 , 133.25 , 127.33 , 118.55 , 116.75 , 112.03 , 82.19 , 77.22 , 73.09 , 70.18 , 22.13 . MS EI (m/z): $[M]^+$ 768.3911. Anal. Calcd for $C_{52}H_{52}N_2O_4$: C. 81.22; H: 6.82; N. 3.64 analysed C, 81.09; H, 6.90; N, 3.48.

1-iodo-4-propoxybenzene 4-iodophenol (22.7 mmol, 5 g), K_2CO_3 (67.5 mmol, 9.3 g), 18-crown-6 (2.25 mmol, 0.6 g) and acetone (45 ml) were all added into a round bottom flask and stirred under N_2 to which 2-bromopropane (33.8 mmol, 3.2 ml) was added. The mixture was stirred and refluxed overnight under N_2 at 70°C. The product was obtained through gravimetric filtration and purified using column chromatography (SiO_2; PE: DCM; 90:10). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.38 – 7.35 (m, 2H), 6.42 – 6.33 (m, 2H), 3.38 (t, *J* = 6.5 Hz, 2H), 1.55 – 1.44 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

4-bromo-N,N-bis(4-propoxyphenyl)aniline 4-bromoaniline (15.7 mmol, 2.7 g), CuI (0.79 mmol, 150 mg), 1, 10-phenantroline (0.79 mmol, 142 mg), KOH (78.5 mmol, 4.4 g) were added into a Schlenk tube and dried under high vacuum for 30 min. A degassed solution of dried toluene (40 ml) and 4-iodopropoxybenzene (39.25 mmol, 10.3 g) was added into the previous mixture via cannula transfer. The reaction mixture was heated at 120°C for 48 hrs under N_2. The cooled reaction mixture was washed with 5% HCl and 5% NaOH solution respectively, dried with $MgSO_4$ and solvent evaporated under vacuum. The residue was passed through a short silica in DCM and solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2, Hexanes/EtA 90/10) to afford the product as a light yellow oil (3.5 g, 50.7% yield). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.19 – 7.17 (m, 2H), 7.00 – 6.97 (m, 4H), 6.82 – 6.77 (m, 2H), 6.75 – 6.72 (m, 4H), 3.53 (t, J = 6.4 Hz, 4H), 1.60 – 1.53 (m, 4H), 0.85 (t, J = 7.4 Hz, 6H).

4-propoxy-N-(4-propoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)phenyl)aniline $(PPh_3)_2PdCl_2$ (240 mg, 34 mmol), CuI (1.36 mmol, 259 mg), PPh_3 (0.54 mmol, 142 mg) were added into a Schlenck tube and dried under vacuum for 30 minutes. 4-bromo-N,N-bis(4-propoxyphenyl)aniline (6.81 mmol, 3 g), piperidine (5.4 mL), triethylsilylacetylene (13.63 mmol, 2.4 mL) and toluene (30 ml) were all degassed and added to the previous mixture via cannula transfer. The solution was stirred under N_2 at 90°C overnight. The cooled reaction mixture was passed through a short silica plug in DCM and solvent was removed. The crude was purified by column chromatography (SiO_2, Hexanes/EtA 95/5) to afford the product as a transparent yellow oil (3.22 g, 95%). ^{1}H

NMR (500 MHz, Benzene-d_6) δ 7.43 – 7.40 (m, 2H), 7.01 – 6.98 (m, 4H), 6.91 – 6.88 (m, 2H), 6.74 – 6.70 (m, 4H), 3.52 (t, J = 6.5 Hz, 4H), 1.56 (dtd, J = 13.7, 7.4, 6.4 Hz, 4H), 1.13 (t, J = 7.9 Hz, 9H), 0.85 (t, J = 7.4 Hz, 6H), 0.72 (q, J = 7.9 Hz, 6H).

4-ethynyl-N,N-bis(4-propoxyphenyl)aniline 4-propoxy-N-(4-propoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)phenyl)aniline (6.08 mmol, 3.04 g) and 25 mL of DCM were placed into a round bottom flask, and the mixture was stirred under N_2 for 10 minutes. TBAF (9 mL) was then added to the previous solution, and the reaction was stirred for 2 hours under N_2 at room temperature. The reaction was washed three times with a solution of 10% ammonium chloride (30 mL) , dried with $MgSO_4$ and the solvent removed under vacuum. The crude product was purified by column chromatography ((SiO_2,PE/DCM 100 to 90/10) to afford the product as a yellow oil (2.22 g, 95%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.38 – 7.35 (m, 2H), 7.03 – 6.96 (m, 4H), 6.91 – 6.85 (m, 2H), 6.74 – 6.70 (m, 4H), 3.52 (t, *J* = 6.4 Hz, 4H), 2.77 (s, 1H), 1.61 – 1.50 (m, 4H), 0.85 (t, *J* = 7.4 Hz, 6H).

4,4'-(buta-1,3-diyne-1,4-diyl)bis(N,N-bis(4-isopropoxyphenyl)aniline) (nPrO-DATPA) CuCl (0.57 g, 5.7 mmol) was weighed out directly into a round bottomed flask, TMEDA (2.6 mL) was combined in one portion and later DCM (20 mL) was added slowly while stirring. 4 Å molecular sieves (5 g) were aggregated to the mixture and after 5 min of stirring, a solution of 4-ethynyl-N,N-bis(4-propoxyphenyl)aniline (2.2 g, 5.7 mmol) in DCM (15 mL) were added to the previous solution and the mixture stirred for 1.5 hours at room temperature. The reaction was washed three times with a solution of 10% ammonium chloride (10 mL) , dried with $MgSO_4$ and the solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2,PE/EtA 95/5) to afford the product as a yellow powder and was later recrystallized in DCM/Hexane (2 g, 91%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.37 – 7.30 (m, 4H), 7.00 – 6.95 (m, 8H), 6.84 – 6.80 (m, 4H), 6.74 – 6.70 (m, 8H), 3.52 (t, *J* = 6.4 Hz, 8H), 1.56 (h, *J* = 7.3 Hz, 8H), 0.85 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.12 , 149.38 , 139.64 , 133.26 , 127.33 , 118.48 , 115.40 , 112.02 , 82.17 , 77.21 , 73.09 , 69.76 , 22.64 , 10.55 . MS EI (m/z): $[M]^+$ 768.3887. Anal. Calcd for $C_{52}H_{52}N_2O_4$: C. 81.22; H: 6.82; N. 3.64 analysed C, 81.05; H, 6.95; N, 3.72.

1-iodo-4-butoxybenzene 4-iodophenol (22.73 mmol, 5 g), K_2CO_3 (68.19 mmol, 9.4 g), 18-crown-6 (0.227 mmol, 0.6 g) and DMF (20 ml) were all added into a round bottom flask and stirred under N_2 to which 1-bromobutane (45.19 mmol, 4.71 mL) was added. The mixture was stirred and refluxed for 4 hrs under N_2 at 90°C. A silica plug (PE/DCM 90/10) was run to afford the product as a transparent oil (5.57 g, 94% yield) ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.41 – 7.33 (m, 2H), 6.39 – 6.36 (m, 2H), 3.42 (t, *J* = 6.4 Hz, 2H), 1.51 – 1.41 (m, 2H), 1.25 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

4-bromo-*N,N*-bis(4-butoxyphenyl)aniline 4-bromoaniline (11.6 mmol, 2 g), CuI (0.58 mmol, 111 mg), 1, 10-phenantroline (0.58 mmol, 105 mg), KOH (58 mmol, 3.2 g) were added into a Schlenk tube and dried under high vacuum for 30 min. A degassed solution of dried toluene (20 ml) and 1-iodo-4-butoxybenzene (29 mmol, 8 g) was added into the previous mixture via cannula transfer. The reaction mixture was heated at 120°C for 48 hrs under N_2. The cooled reaction mixture was washed with 5% HCl and 5% NaOH solution respectively, dried with $MgSO_4$ and solvent evaporated under vacuum. The residue was passed through a short silica in DCM and solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2, Hexanes/EtA 90/10) to afford the product as a light yellow oil (2.97 g, 55% yield). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.19 – 7.16 (m, 2H), 7.01 – 6.97 (m, 4H), 6.80 – 6.74 (m, 6H), 3.60 (t, *J* = 6.4 Hz, 4H), 1.61 – 1.51 (m, 4H), 1.34 (h, *J* = 7.4 Hz, 4H), 0.82 (t, *J* = 7.4 Hz, 6H).

4-butoxy-N-(4-butoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)phenyl)aniline $(PPh_3)_2PdCl_2$ (187 mg, 0.27 mmol), CuI (1.07 mmol, 203 mg), PPh_3 (0.43 mmol, 112 mg) were added into a Schlenck tube and dried under vacuum for 30 minutes. 4-bromo-N,N-bis(4-butoxyphenyl)aniline (5.33 mmol, 2.5 g), piperidine (5.4 mL), triethylsilylacetylene (10.7 mmol, 2 mL) and toluene (30 ml) were all degassed and added to the previous mixture via cannula transfer. The solution was stirred under N_2 at 90°C overnight. The cooled reaction mixture was passed through a short silica plug in DCM and solvent was removed. The crude was purified by column chromatography (SiO_2, Hexanes/EtA 90/10) to afford the product as a transparent yellow oil (2.63 g, 93%). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.48 – 7.38 (m, 2H), 7.02 – 6.98 (m, 4H), 6.92 – 6.88 (m, 2H), 6.75 – 6.72 (m, 4H), 3.59 (t, *J* = 6.4 Hz, 4H), 1.61 – 1.49 (m, 4H), 1.41 – 1.26 (m, 4H), 1.14 (t, *J* = 7.9 Hz, 9H), 0.82 (t, *J* = 7.4 Hz, 6H), 0.72 (q, *J* = 7.8 Hz, 6H).

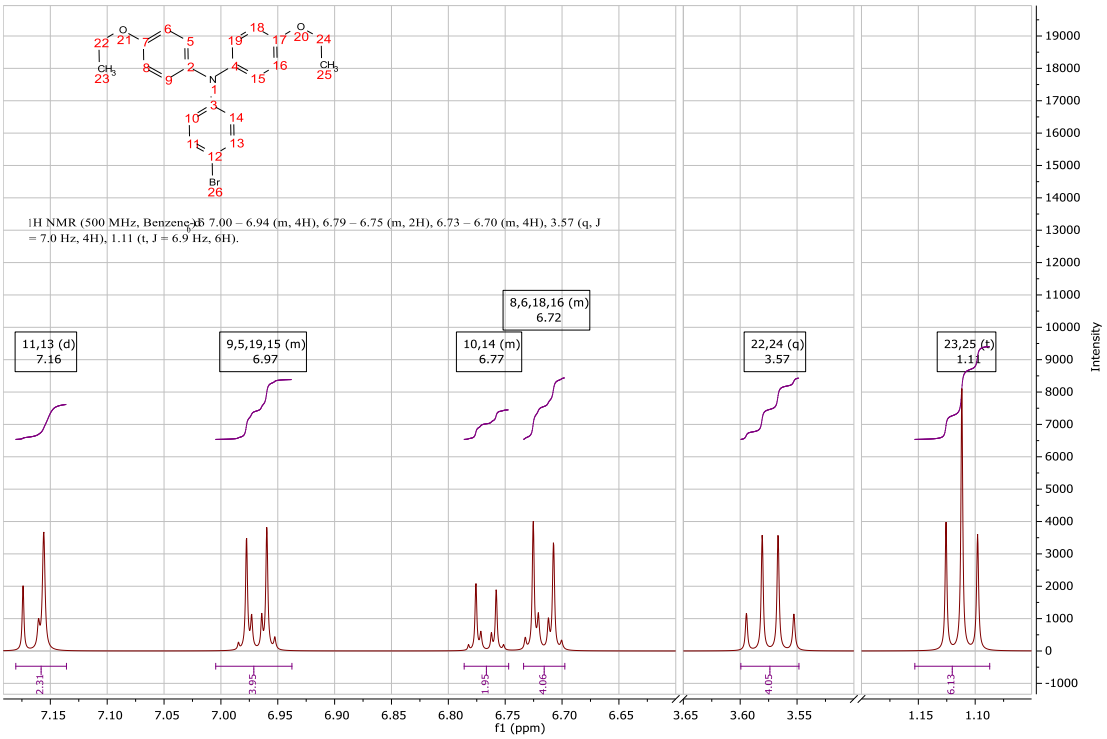
4-ethynyl-N,N-bis(4-butoxyphenyl)aniline 4-butoxy-N-(4-butoxyphenyl)-N-(4-((triethyllsilyl)ethynyl)phenyl)aniline (4.87 mmol, 2.5 g) and 20 mL of DCM were placed into a round bottom flask, and the mixture was stirred under N_2 for 10 minutes. TBAF (7 mL) was then added to the previous solution, and the reaction was stirred for 2 hours under N_2 at room temperature. The reaction was washed three times

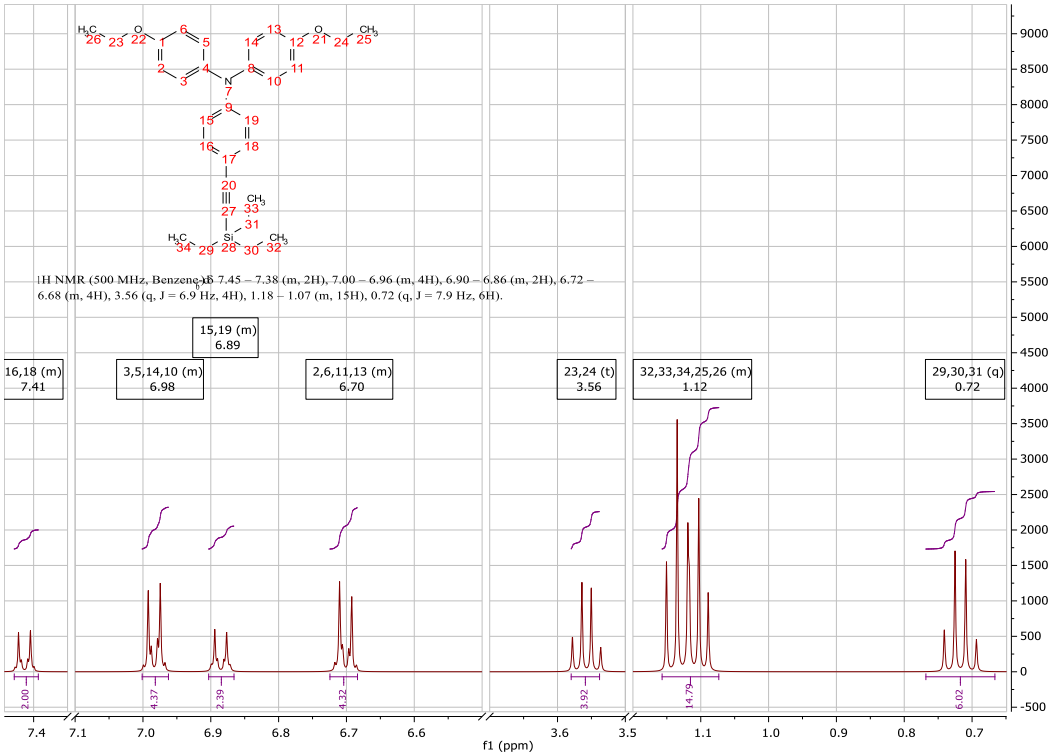
with a solution of 10% ammonium chloride (30 mL) , dried with $MgSO_4$ and the solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2,PE/DCM 100 to 90/10) to afford the product as a yellow oil (1.82 g, 92%). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.40 – 7.34 (m, 2H), 7.03 – 6.97 (m, 4H), 6.91 – 6.85 (m, 2H), 6.76 – 6.69 (m, 4H), 3.59 (t, *J* = 6.4 Hz, 4H), 2.77 (s, 1H), 1.59 – 1.51 (m, 4H), 1.39 – 1.28 (m, 4H), 0.82 (t, *J* = 7.4 Hz, 6H).

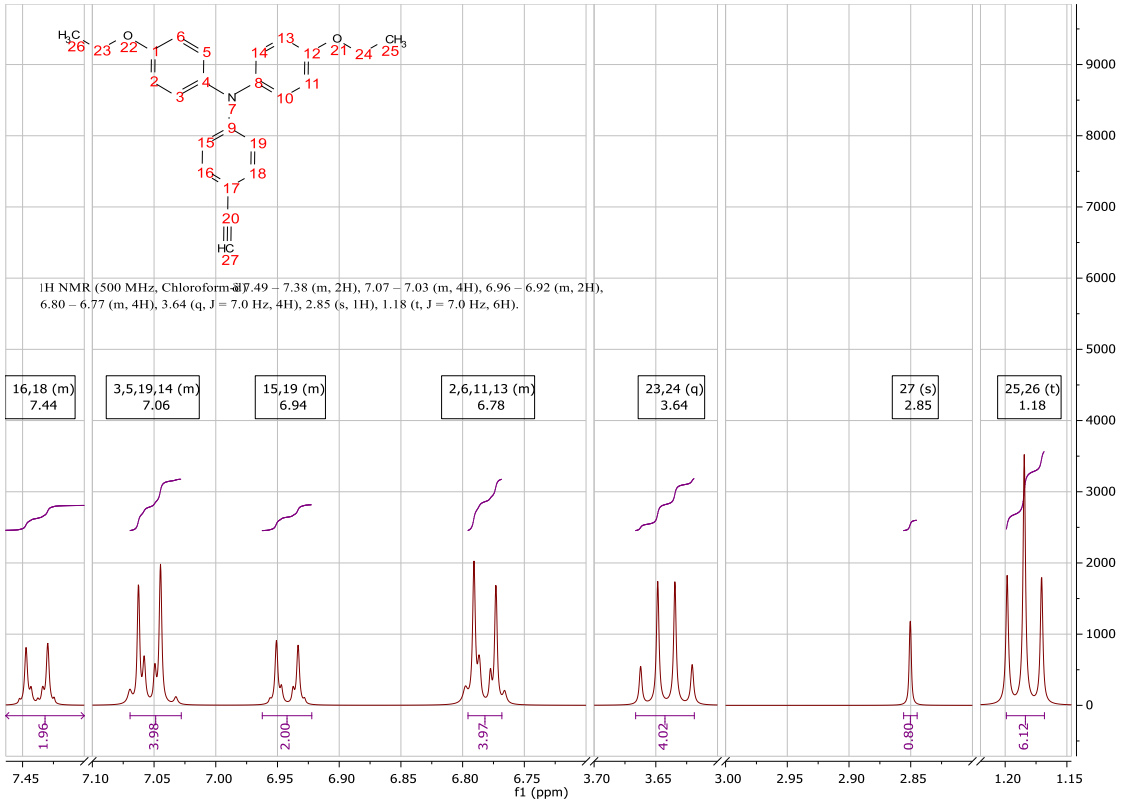
4,4'-(buta-1,3-diyne-1,4-diyl)bis(N,N-bis(4-butoxyphenyl)aniline) (BuO-DATPA)

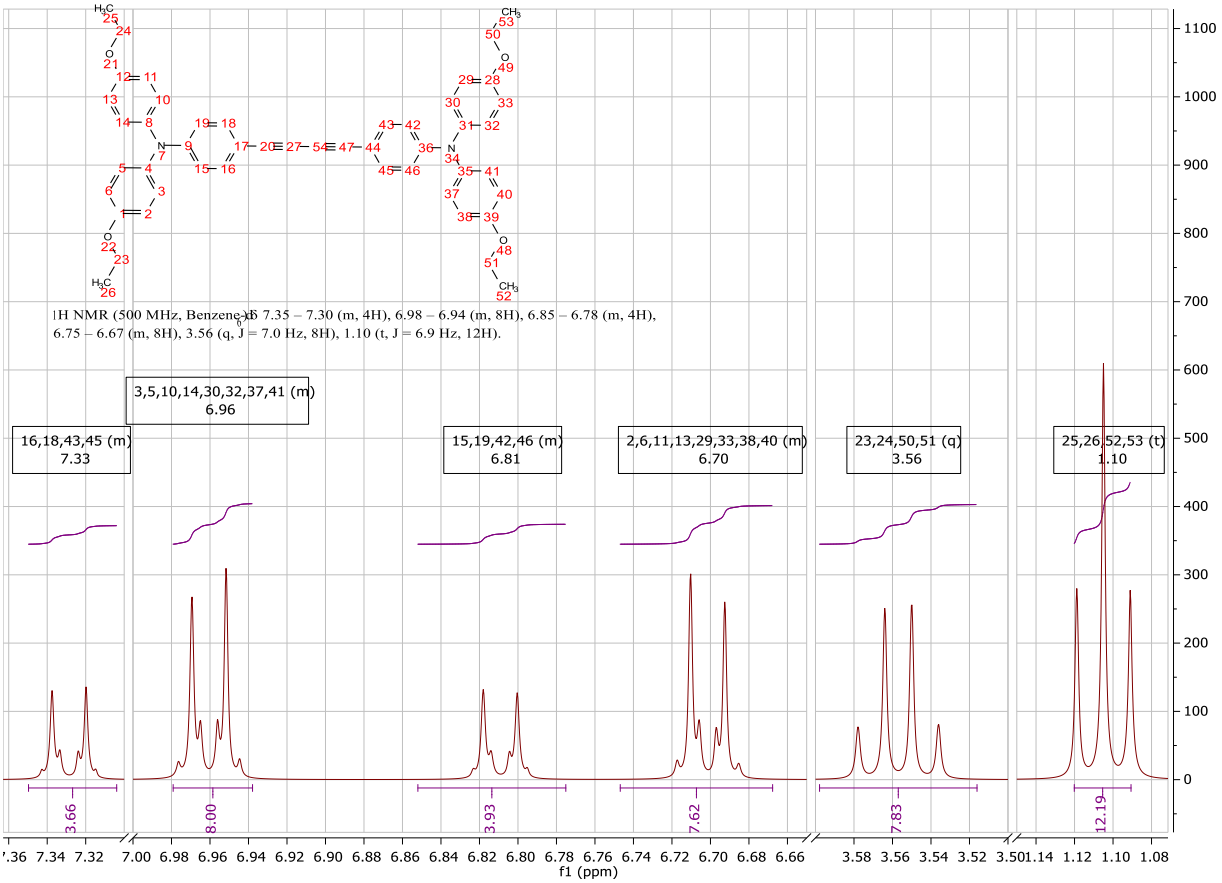
CuCl (0.41 g, 4.12 mmol) was weighed out directly into a round-bottomed flask, TMEDA (1.8 mL) was combined in one portion, and later DCM (20 mL) was added slowly while stirring. 4 Å molecular sieves (5 g) were aggregated to the mixture, and after 5 min of stirring, a solution of 4-ethynyl-N,N-bis(4-butoxyphenyl)aniline (1.7 g, 4.12 mmol) in DCM (10 mL) were added to the previous solution and the mixture stirred for 1.5 hours at room temperature. The reaction was washed three times with a solution of 10% ammonium chloride (20 mL) , dried with $MgSO_4$ and the solvent removed under vacuum. The crude product was purified by column chromatography (SiO_2, PE/EtA 90/10) to afford the product as a yellow powder. Finally, the product was recrystallized in Hexane/DCM (1.5 g. 88 % yield). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.38 – 7.30 (m, 4H), 7.00 – 6.97 (m, 8H), 6.85 – 6.81 (m, 4H), 6.76 – 6.71 (m, 8H), 3.60 (t, *J* = 6.4 Hz, 8H), 1.61 – 1.51 (m, 8H), 1.40 – 1.28 (m, 8H), 0.82 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.14 , 149.38 , 139.62 , 133.26 , 127.33 , 118.47 , 115.39 , 112.01 , 82.18 , 77.22 , 73.10 , 67.93 , 65.86 , 31.39 , 19.27 , 15.29 , 13.86. MS EI (m/z): $[M]^+$ 824.4507. Anal. Calcd for $C_{56}H_{60}N_2O_4$: C. 81.52; H: 7.33; N. 3.40 analysed C, 81.39; H, 7.40; N, 3.42.

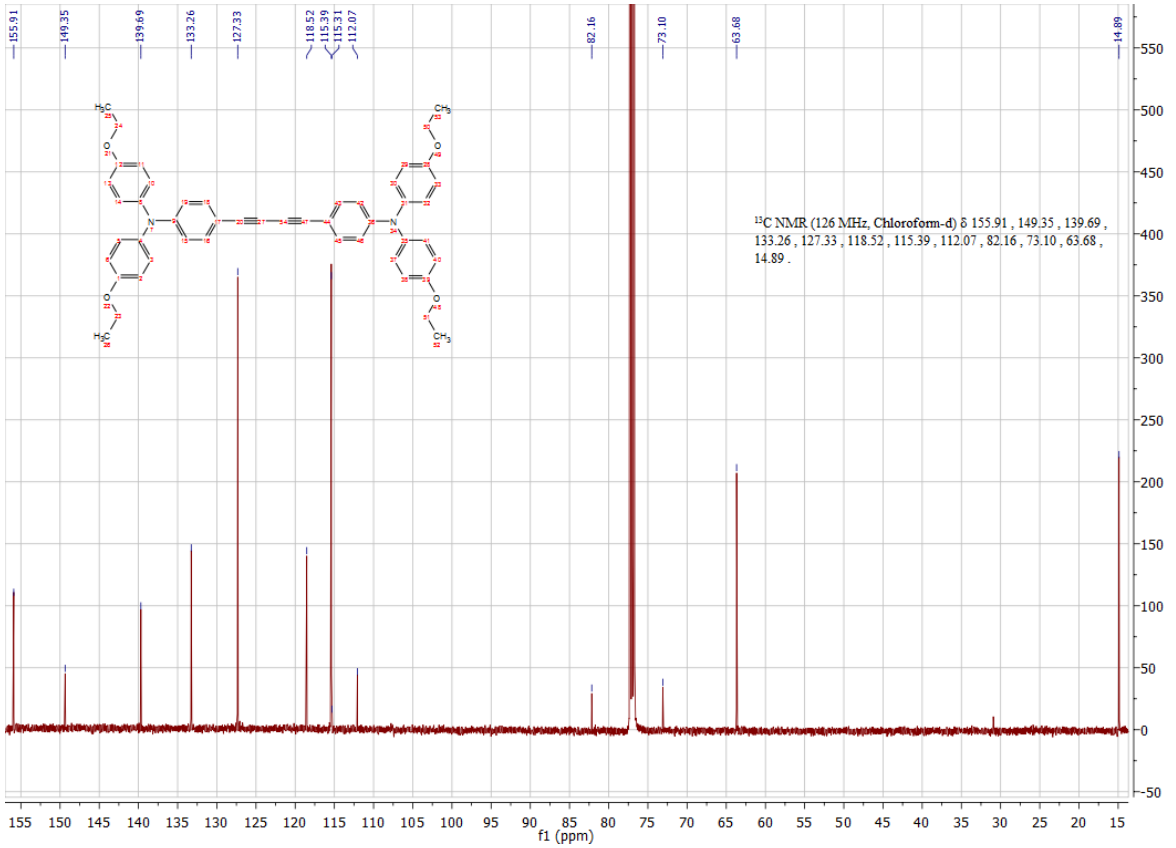
2. ^{1}H and ^{13}C NMR

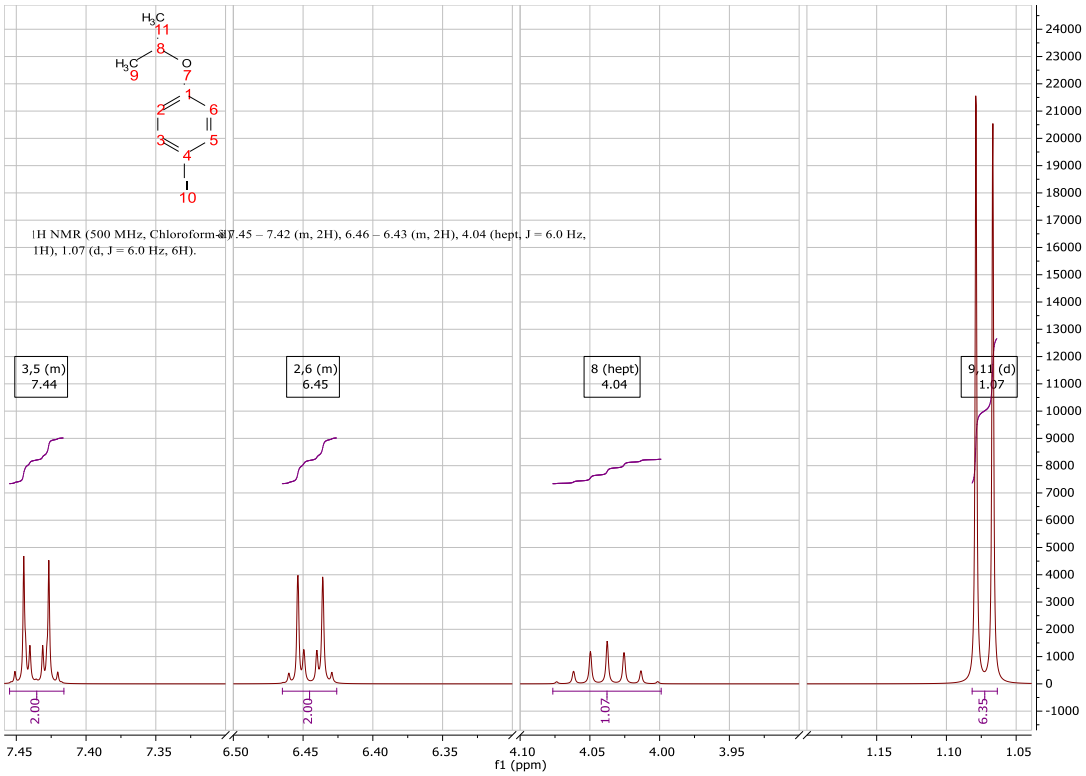


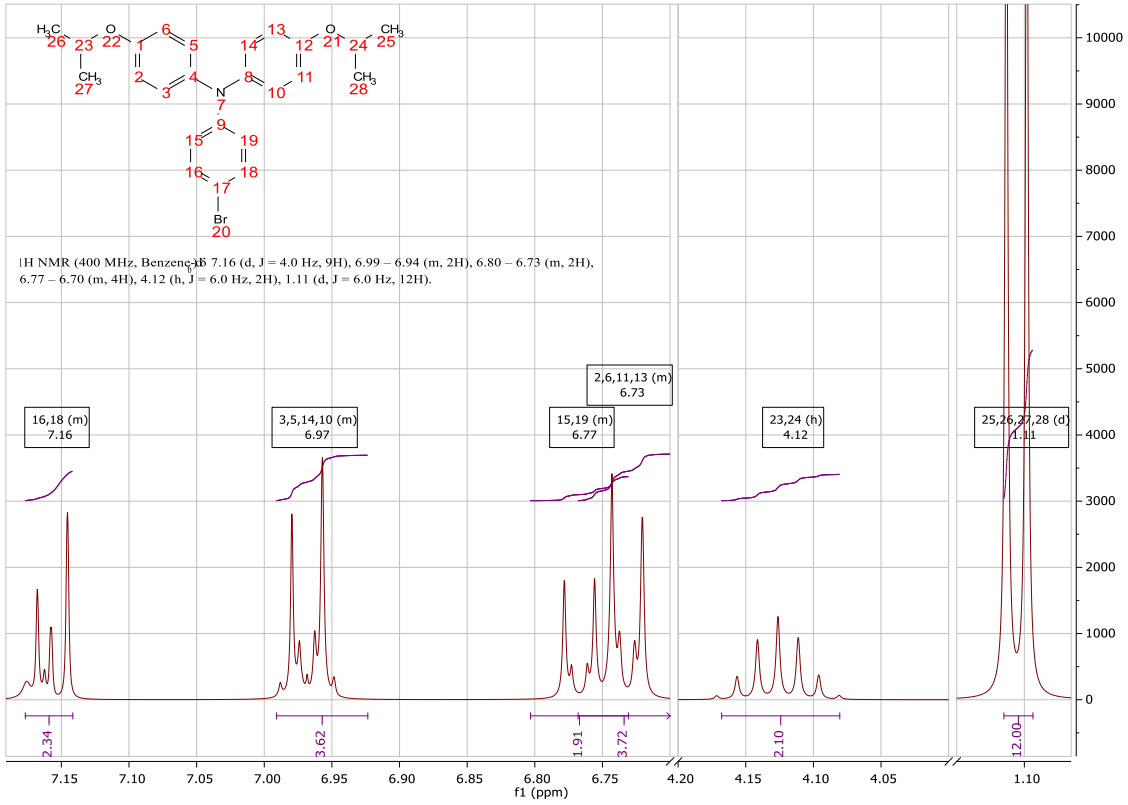


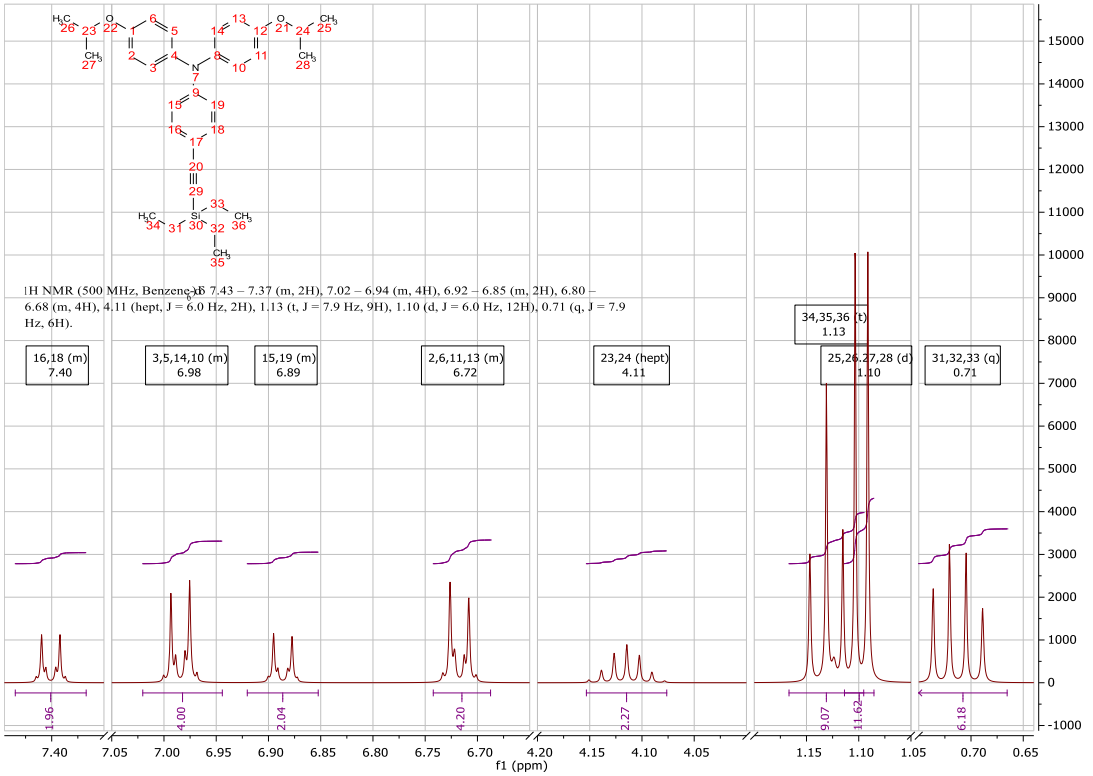

1H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.38 (m, 2H), 7.07 – 7.03 (m, 4H), 6.96 – 6.92 (m, 2H), 6.80 – 6.77 (m, 4H), 3.64 (q, J = 7.0 Hz, 4H), 2.85 (s, 1H), 1.18 (t, J = 7.0 Hz, 6H).
16,18 (m) 7.44
3,5,19,14 (m) 7.06
15,19 (m) 6.94
2,6,11,13 (m) 6.78
23,24 (q) 3.64
27 (s) 2.85
25,26 (t) 1.18
1.96
3.98
2.00
3.97
4.02
0.80
6.12
f1 (ppm)

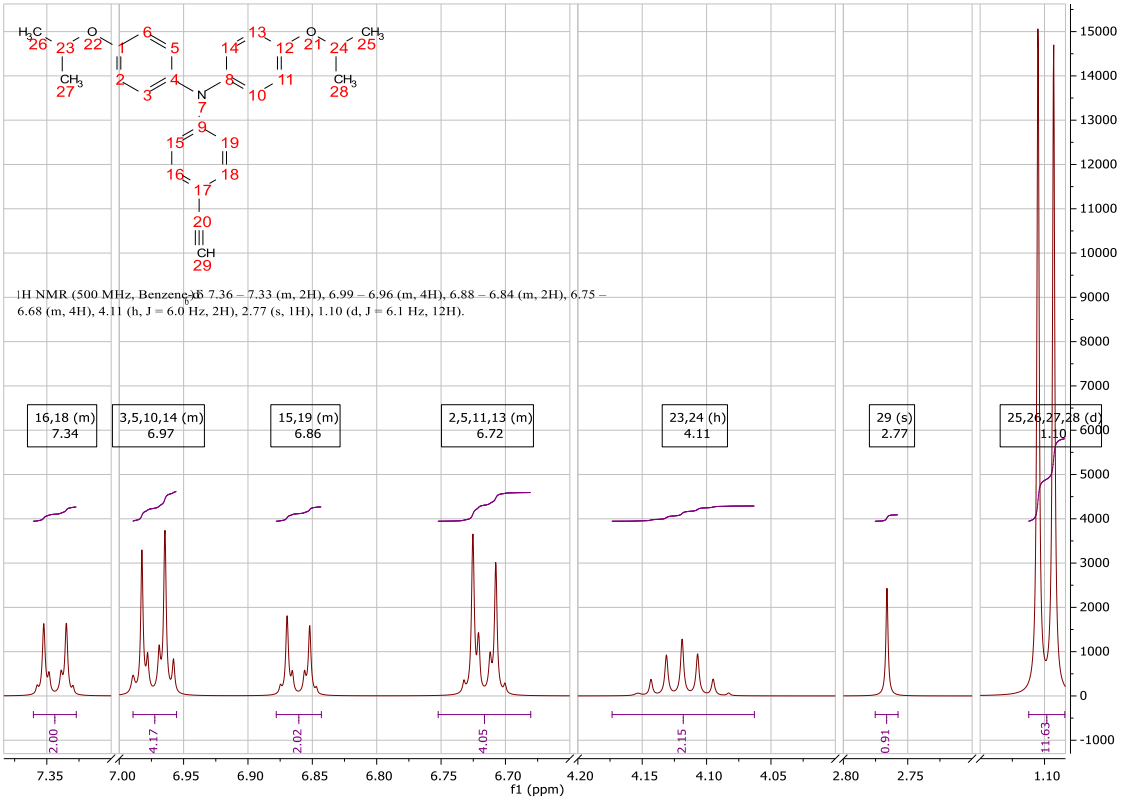

1H NMR (500 MHz, Benzene-d6) δ 7.35 – 7.30 (m, 4H), 6.98 – 6.94 (m, 8H), 6.85 – 6.78 (m, 4H), 6.75 – 6.67 (m, 8H), 3.56 (q, J = 7.0 Hz, 8H), 1.10 (t, J = 6.9 Hz, 12H).
3,5,10,14,30,32,37,41 (m) 6.96
16,18,43,45 (m) 7.33
15,19,42,46 (m) 6.81
2,6,11,13,29,33,38,40 (m) 6.70
23,24,50,51 (q) 3.56
25,26,52,53 (t) 1.10
3.66
8.00
3.93
7.62
7.83
12.19
f1 (ppm)

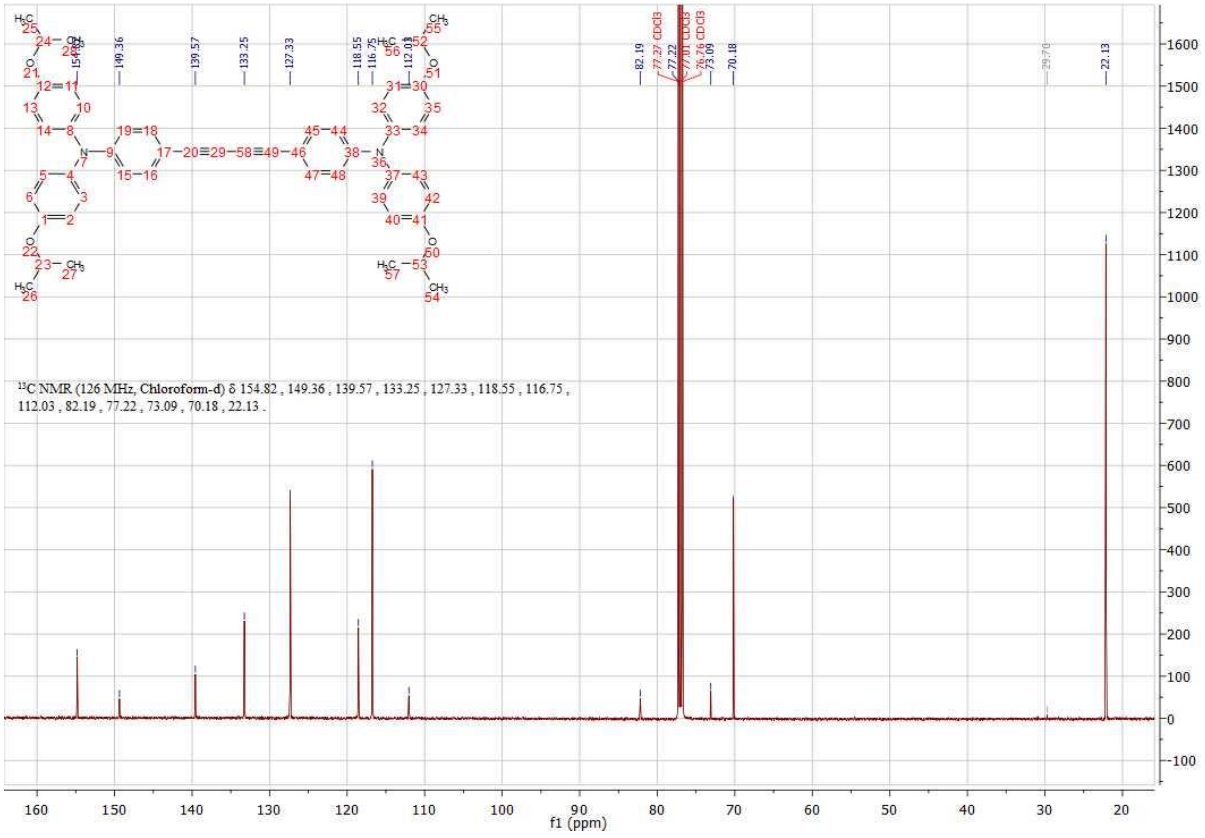

155.91
149.35
139.69
133.26
127.33
118.52
115.39
115.31
112.07
82.16
73.10
63.68
14.89
^{13}C NMR (126 MHz, Chloroform-d) δ 155.91 , 149.35 , 139.69 , 133.26 , 127.33 , 118.52 , 115.39 , 112.07 , 82.16 , 73.10 , 63.68 , 14.89 .
f1 (ppm)

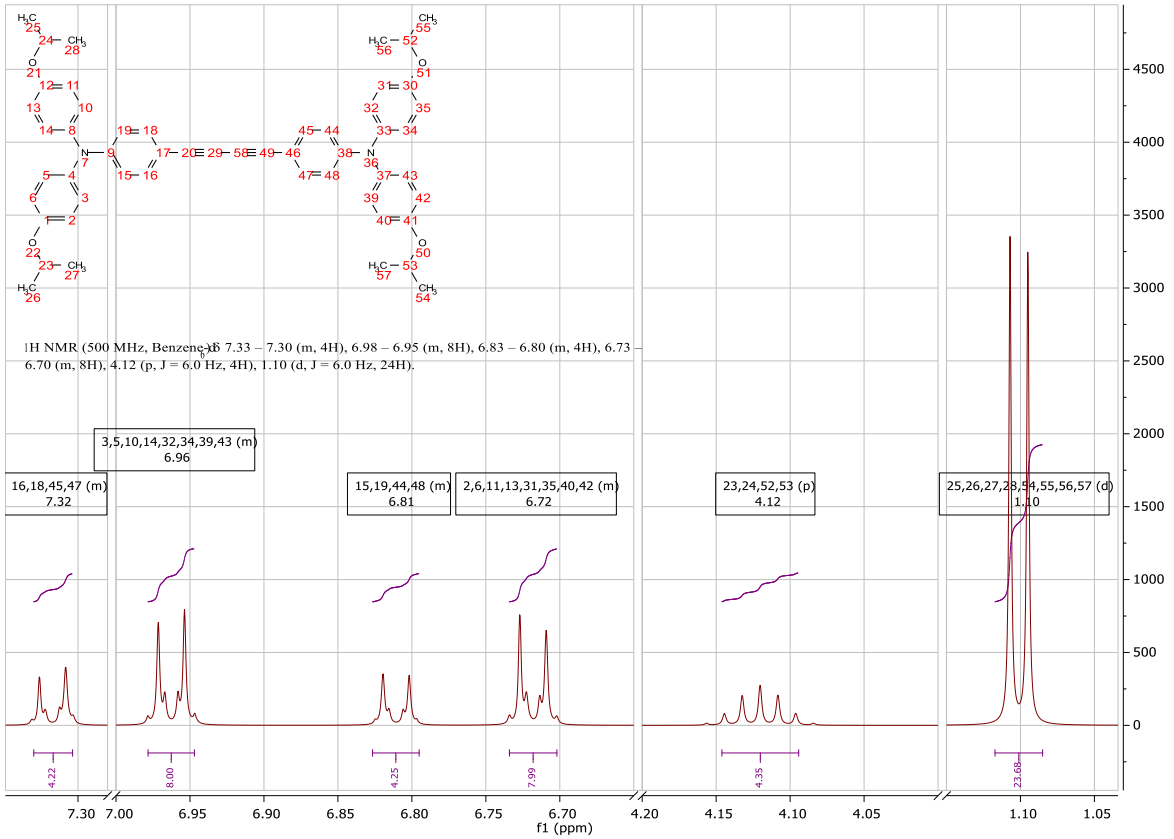

1H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.42 (m, 2H), 6.46 – 6.43 (m, 2H), 4.04 (hept, J = 6.0 Hz, 1H), 1.07 (d, J = 6.0 Hz, 6H).
3,5 (m) 7.44
2,6 (m) 6.45
8 (hept) 4.04
9,11 (d) 1.07
2.00
2.00
1.07
6.35
f1 (ppm)

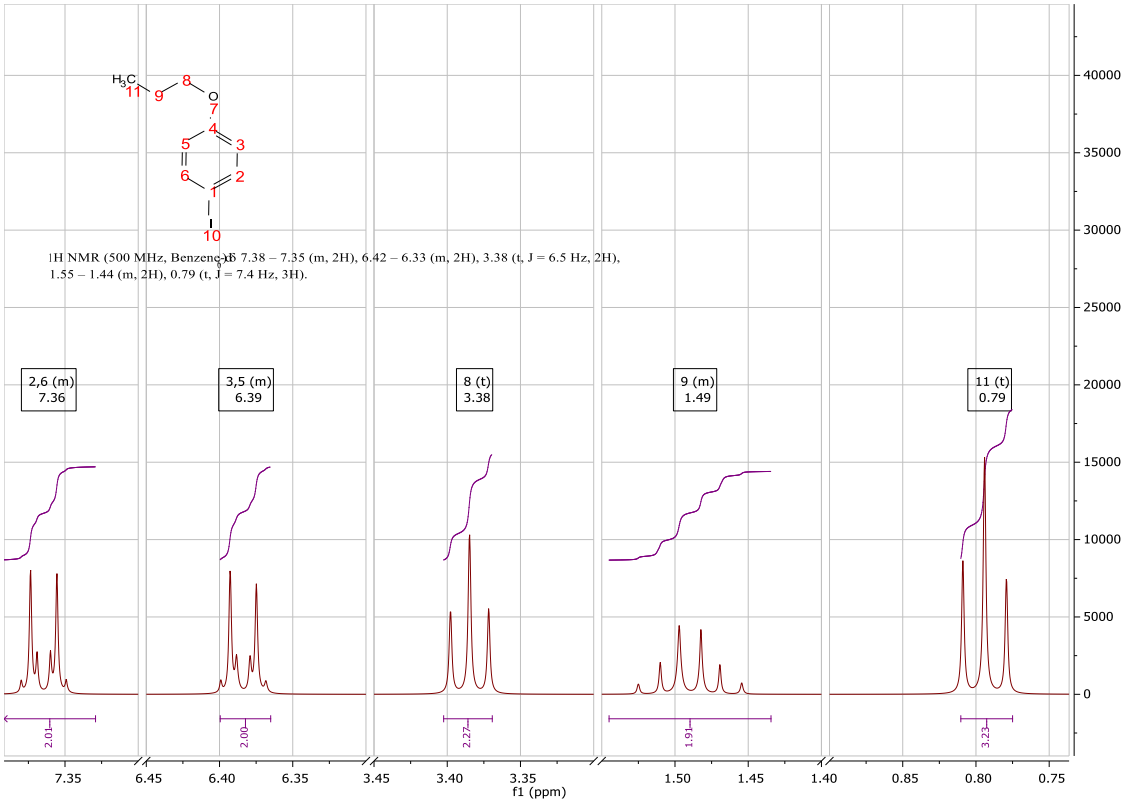

1H NMR (400 MHz, Benzene-d6) δ 7.16 (d, J = 4.0 Hz, 9H), 6.99 – 6.94 (m, 2H), 6.80 – 6.73 (m, 2H), 6.77 – 6.70 (m, 4H), 4.12 (h, J = 6.0 Hz, 2H), 1.11 (d, J = 6.0 Hz, 12H).
16,18 (m) 7.16
3,5,14,10 (m) 6.97
2,6,11,13 (m) 6.73
15,19 (m) 6.77
23,24 (h) 4.12
25,26,27,28 (d) 1.11
2.34
3.62
1.91
3.72
2.10
12.00
f1 (ppm)

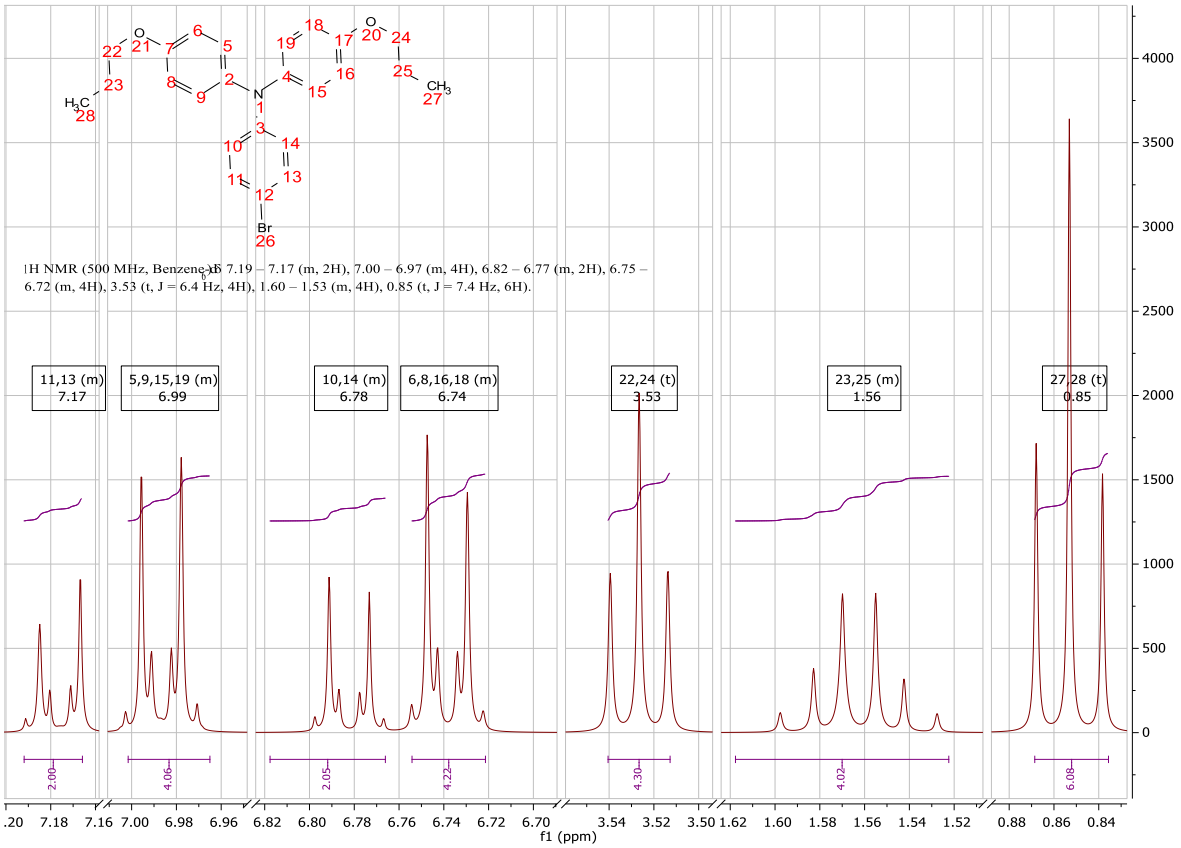

1H NMR (500 MHz, Benzene-d6) δ 7.43 – 7.37 (m, 2H), 7.02 – 6.94 (m, 4H), 6.92 – 6.85 (m, 2H), 6.80 – 6.68 (m, 4H), 4.11 (hept, J = 6.0 Hz, 2H), 1.13 (t, J = 7.9 Hz, 9H), 1.10 (d, J = 6.0 Hz, 12H), 0.71 (q, J = 7.9 Hz, 6H).
16,18 (m) 7.40
3,5,14,10 (m) 6.98
15,19 (m) 6.89
2,6,11,13 (m) 6.72
23,24 (hept) 4.11
34,35,36 (t) 1.13
25,26,27,28 (d) 1.10
31,32,33 (q) 0.71
1.96
4.00
2.04
4.20
2.27
9.07
11.62
6.18
f1 (ppm)

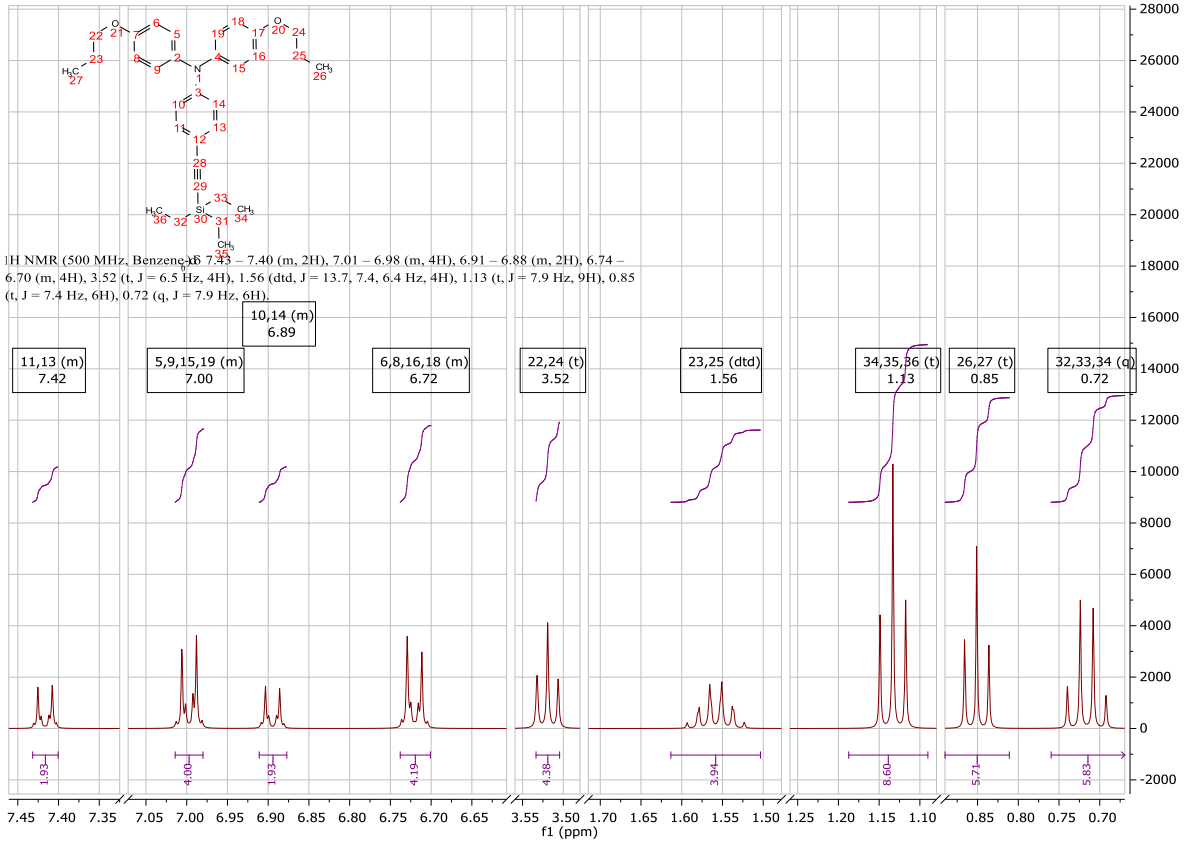

1H NMR (500 MHz, Benzene-d6) δ 7.36 – 7.33 (m, 2H), 6.99 – 6.96 (m, 4H), 6.88 – 6.84 (m, 2H), 6.75 – 6.68 (m, 4H), 4.11 (h, J = 6.0 Hz, 2H), 2.77 (s, 1H), 1.10 (d, J = 6.1 Hz, 12H).
16,18 (m) 7.34
3,5,10,14 (m) 6.97
15,19 (m) 6.86
2,5,11,13 (m) 6.72
23,24 (h) 4.11
29 (s) 2.77
25,26,27,28 (d) 1.10
2.00
4.17
2.02
4.05
2.15
0.91
11.63
f1 (ppm)

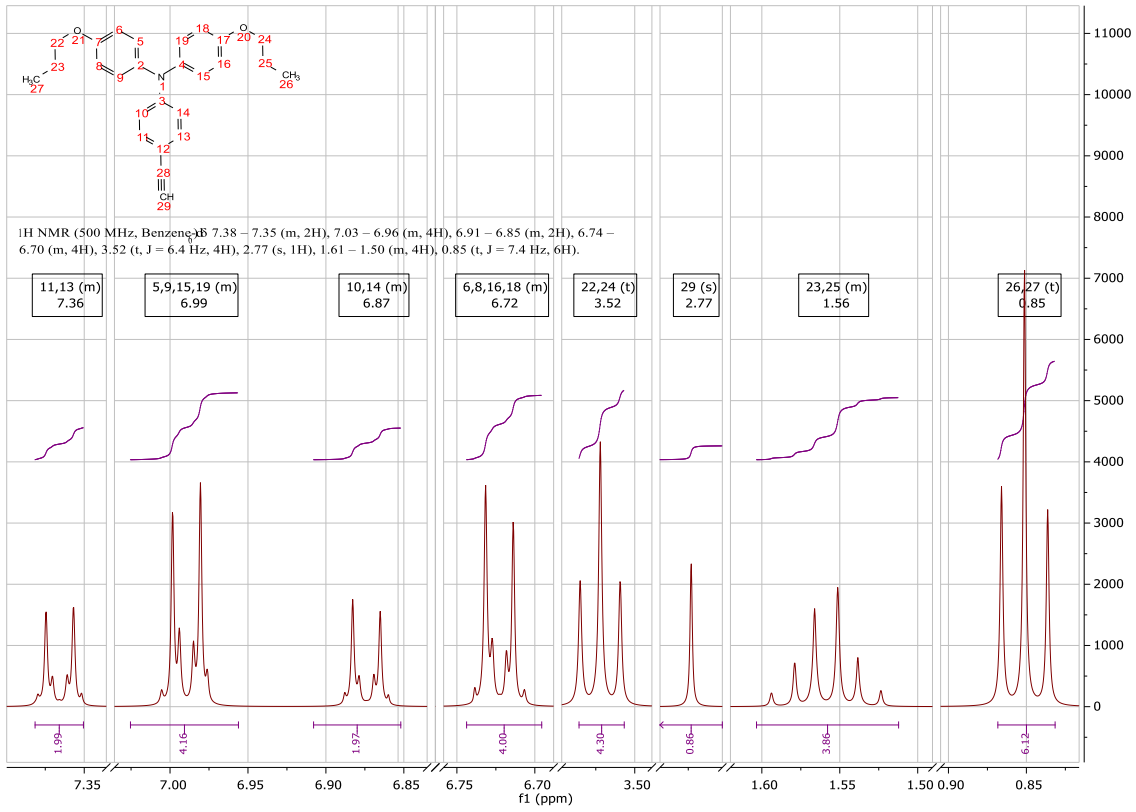

154.82
149.36
139.57
133.25
127.33
118.55
116.75
112.03
82.19
77.27 CDCl3
77.22
77.01 CDCl3
76.76 CDCl3
73.09
70.18
29.70
22.13
¹³C NMR (126 MHz, Chloroform-d) δ 154.82 , 149.36 , 139.57 , 133.25 , 127.33 , 118.55 , 116.75 , 112.03 , 82.19 , 77.22 , 73.09 , 70.18 , 22.13 .
f1 (ppm)

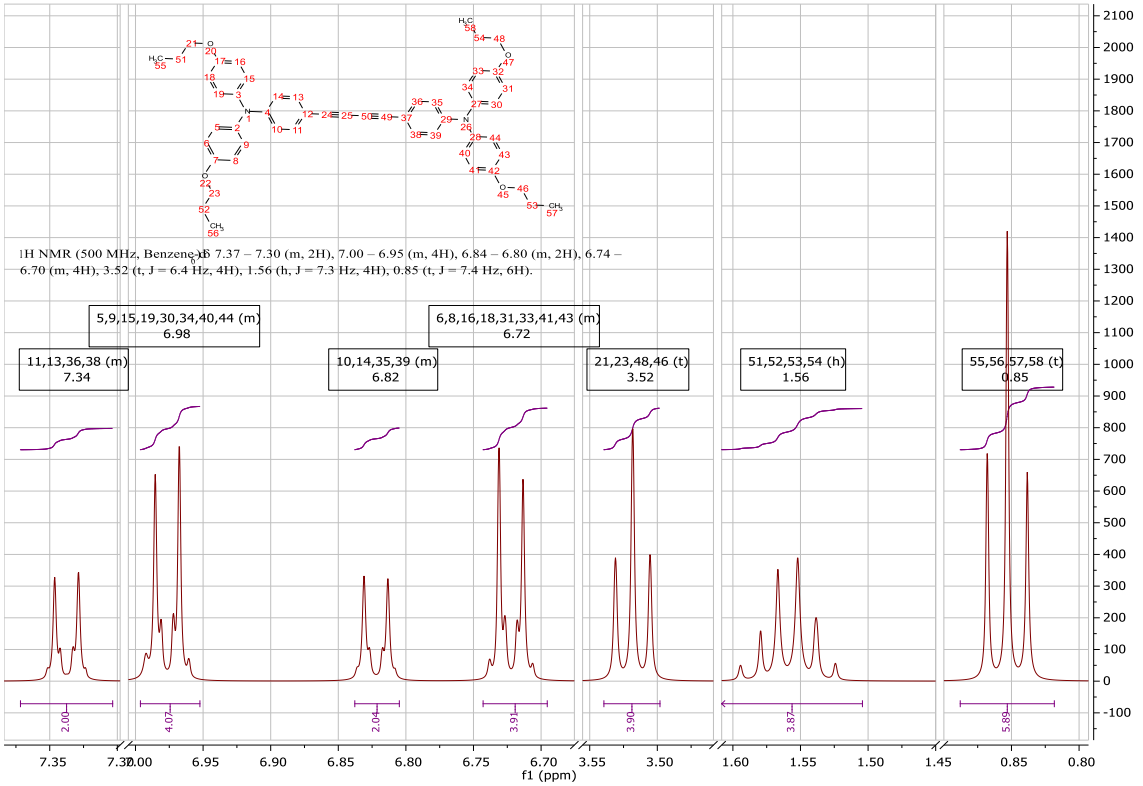

¹H NMR (500 MHz, Benzene-d6) δ 7.33 – 7.30 (m, 4H), 6.98 – 6.95 (m, 8H), 6.83 – 6.80 (m, 4H), 6.73 – 6.70 (m, 8H), 4.12 (p, J = 6.0 Hz, 4H), 1.10 (d, J = 6.0 Hz, 24H).
3,5,10,14,32,34,39,43 (m) 6.96
16,18,45,47 (m) 7.32
15,19,44,48 (m) 6.81
2,6,11,13,31,35,40,42 (m) 6.72
23,24,52,53 (p) 4.12
25,26,27,28,54,55,56,57 (d) 1.10
4.22
8.00
4.25
7.99
4.35
23.68
f1 (ppm)

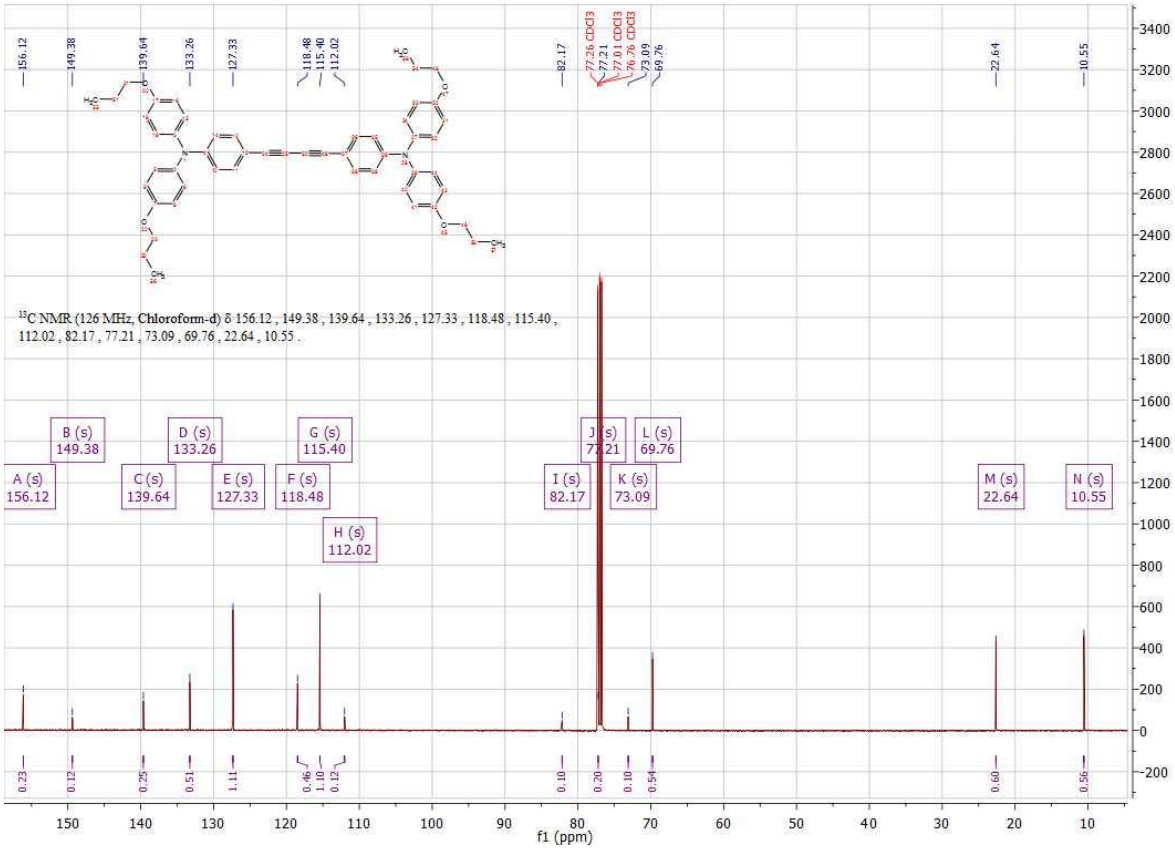

1H NMR (500 MHz, Benzene-d6) δ 7.38 – 7.35 (m, 2H), 6.42 – 6.33 (m, 2H), 3.38 (t, J = 6.5 Hz, 2H), 1.55 – 1.44 (m, 2H), 0.79 (t, J = 7.4 Hz, 3H).
2,6 (m) 7.36
3,5 (m) 6.39
8 (t) 3.38
9 (m) 1.49
11 (t) 0.79
f1 (ppm)

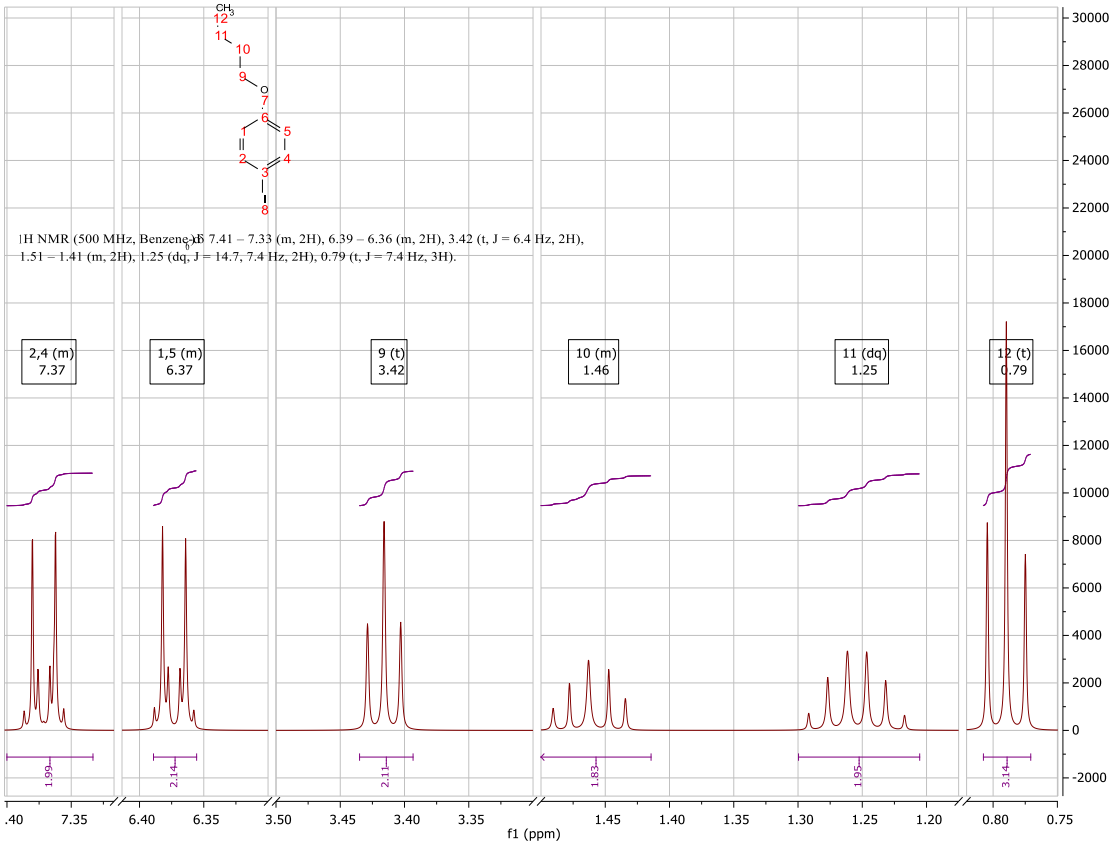

1H NMR (500 MHz, Benzene-d6) δ 7.19 – 7.17 (m, 2H), 7.00 – 6.97 (m, 4H), 6.82 – 6.77 (m, 2H), 6.75 – 6.72 (m, 4H), 3.53 (t, J = 6.4 Hz, 4H), 1.60 – 1.53 (m, 4H), 0.85 (t, J = 7.4 Hz, 6H).
11,13 (m) 7.17
5,9,15,19 (m) 6.99
10,14 (m) 6.78
6,8,16,18 (m) 6.74
22,24 (t) 3.53
23,25 (m) 1.56
27,28 (t) 0.85
f1 (ppm)

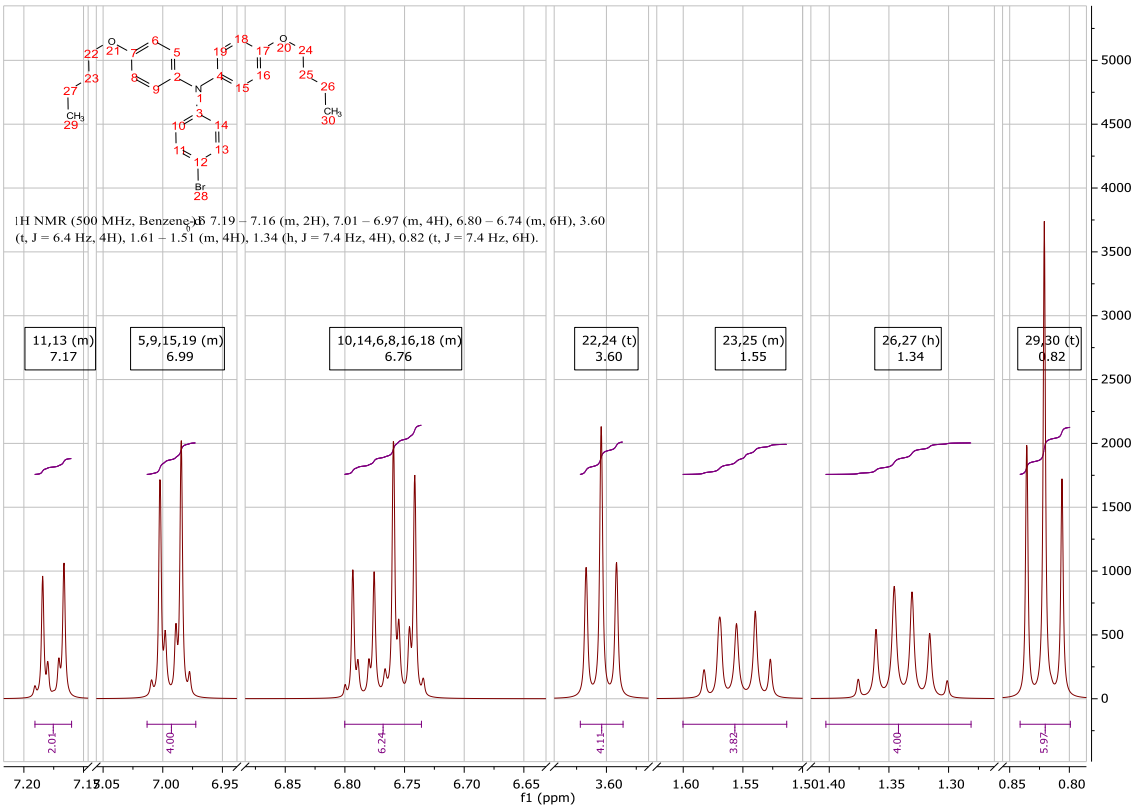

1H NMR (500 MHz, Benzene-d6) δ 7.43 – 7.40 (m, 2H), 7.01 – 6.98 (m, 4H), 6.91 – 6.88 (m, 2H), 6.74 – 6.70 (m, 4H), 3.52 (t, J = 6.5 Hz, 4H), 1.56 (dtd, J = 13.7, 7.4, 6.4 Hz, 4H), 1.13 (t, J = 7.9 Hz, 9H), 0.85 (t, J = 7.4 Hz, 6H), 0.72 (q, J = 7.9 Hz, 6H).
10,14 (m) 6.89
11,13 (m) 7.42
5,9,15,19 (m) 7.00
6,8,16,18 (m) 6.72
22,24 (t) 3.52
23,25 (dtd) 1.56
34,35,36 (t) 1.13
26,27 (t) 0.85
32,33,34 (q) 0.72
1.93
4.00
1.93
4.19
4.38
3.94
8.60
5.71
5.83
f1 (ppm)

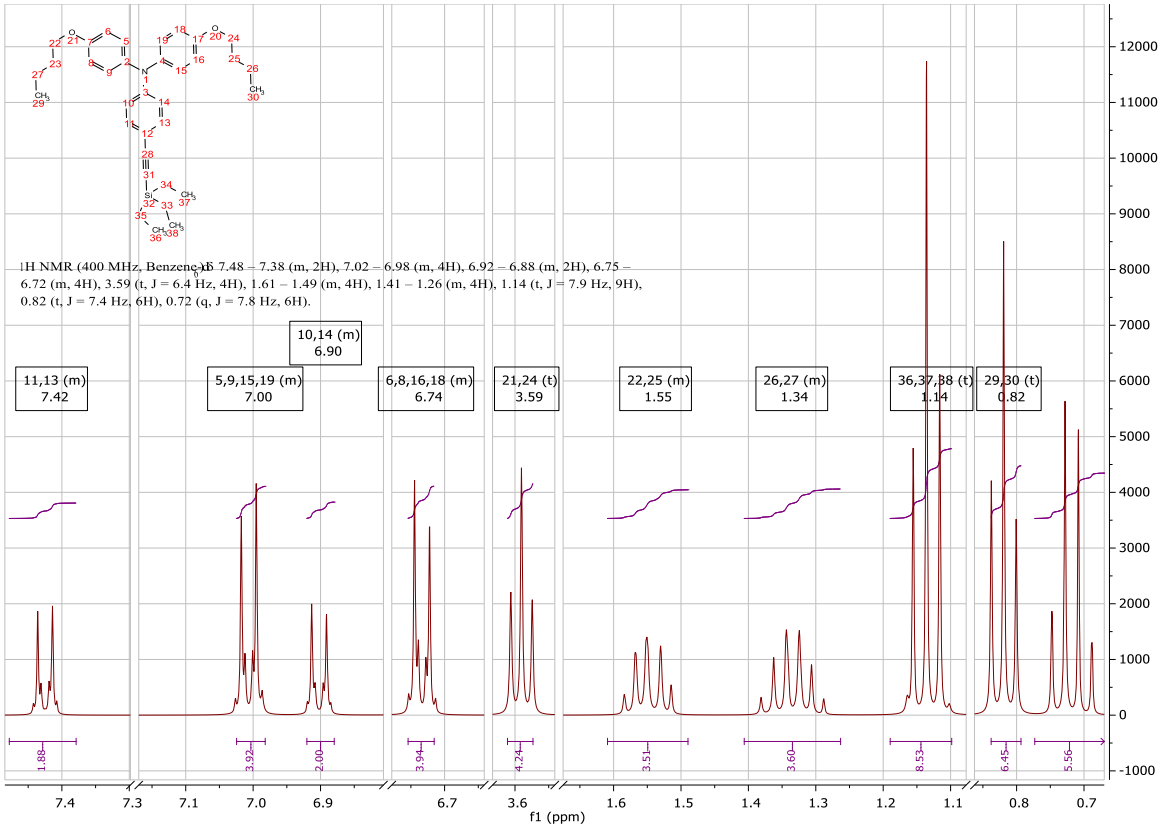

1H NMR (500 MHz, Benzene-d6) δ 7.38 – 7.35 (m, 2H), 7.03 – 6.96 (m, 4H), 6.91 – 6.85 (m, 2H), 6.74 – 6.70 (m, 4H), 3.52 (t, J = 6.4 Hz, 4H), 2.77 (s, 1H), 1.61 – 1.50 (m, 4H), 0.85 (t, J = 7.4 Hz, 6H).
11,13 (m) 7.36
5,9,15,19 (m) 6.99
10,14 (m) 6.87
6,8,16,18 (m) 6.72
22,24 (t) 3.52
29 (s) 2.77
23,25 (m) 1.56
26,27 (t) 0.85
1.99
4.16
1.97
4.00
4.30
0.86
3.86
6.12
f1 (ppm)

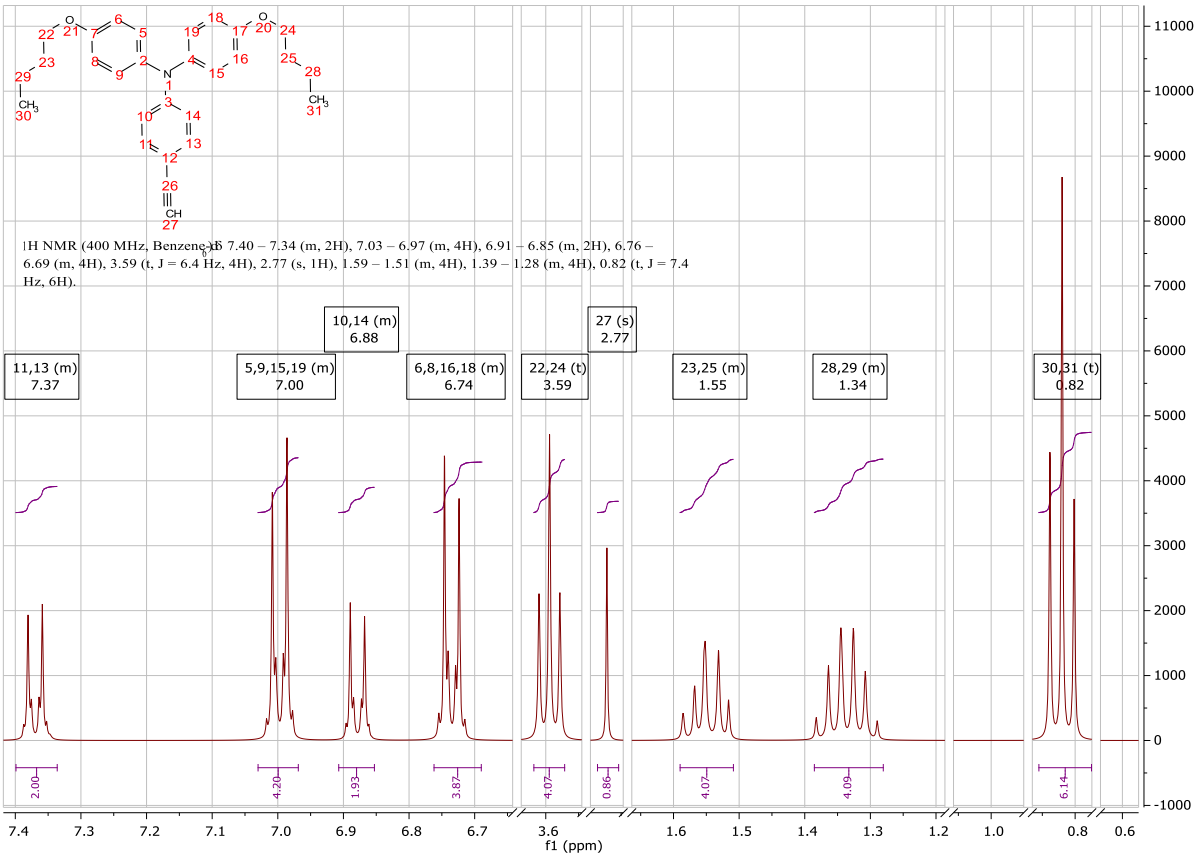

1H NMR (500 MHz, Benzene-d6) δ 7.37 – 7.30 (m, 2H), 7.00 – 6.95 (m, 4H), 6.84 – 6.80 (m, 2H), 6.74 – 6.70 (m, 4H), 3.52 (t, J = 6.4 Hz, 4H), 1.56 (h, J = 7.3 Hz, 4H), 0.85 (t, J = 7.4 Hz, 6H).
5,9,15,19,30,34,40,44 (m) 6.98
6,8,16,18,31,33,41,43 (m) 6.72
11,13,36,38 (m) 7.34
10,14,35,39 (m) 6.82
21,23,48,46 (t) 3.52
51,52,53,54 (h) 1.56
55,56,57,58 (t) 0.85
2.00
4.07
2.04
3.91
3.90
3.87
5.89
f1 (ppm)

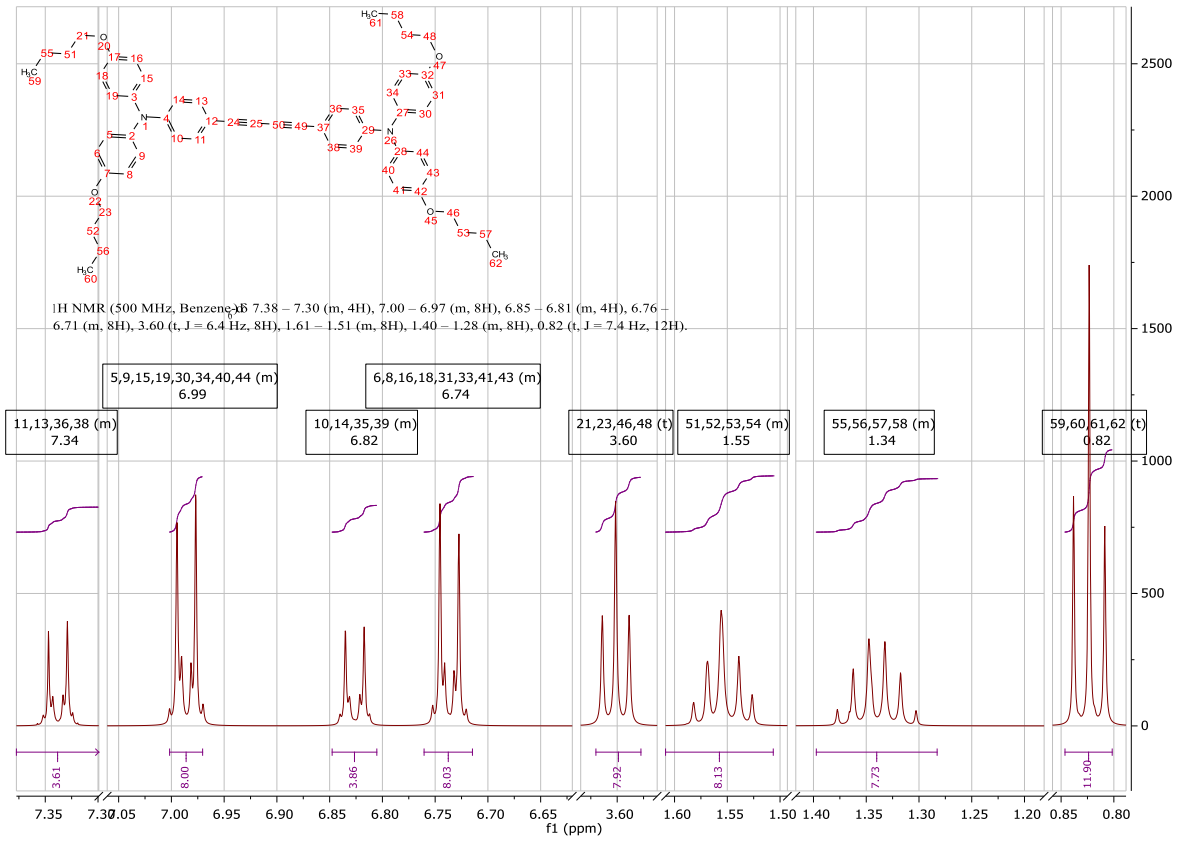

156.12
149.38
139.64
133.26
127.33
118.48
115.40
112.02
82.17
77.26 CDCl3
77.21
77.01 CDCl3
76.76 CDCl3
73.09
69.76
22.64
10.55
13C NMR (126 MHz, Chloroform-d) δ 156.12 , 149.38 , 139.64 , 133.26 , 127.33 , 118.48 , 115.40 , 112.02 , 82.17 , 77.21 , 73.09 , 69.76 , 22.64 , 10.55 .
A (s) 156.12
B (s) 149.38
C (s) 139.64
D (s) 133.26
E (s) 127.33
F (s) 118.48
G (s) 115.40
H (s) 112.02
I (s) 82.17
J (s) 77.21
K (s) 73.09
L (s) 69.76
M (s) 22.64
N (s) 10.55
f1 (ppm)

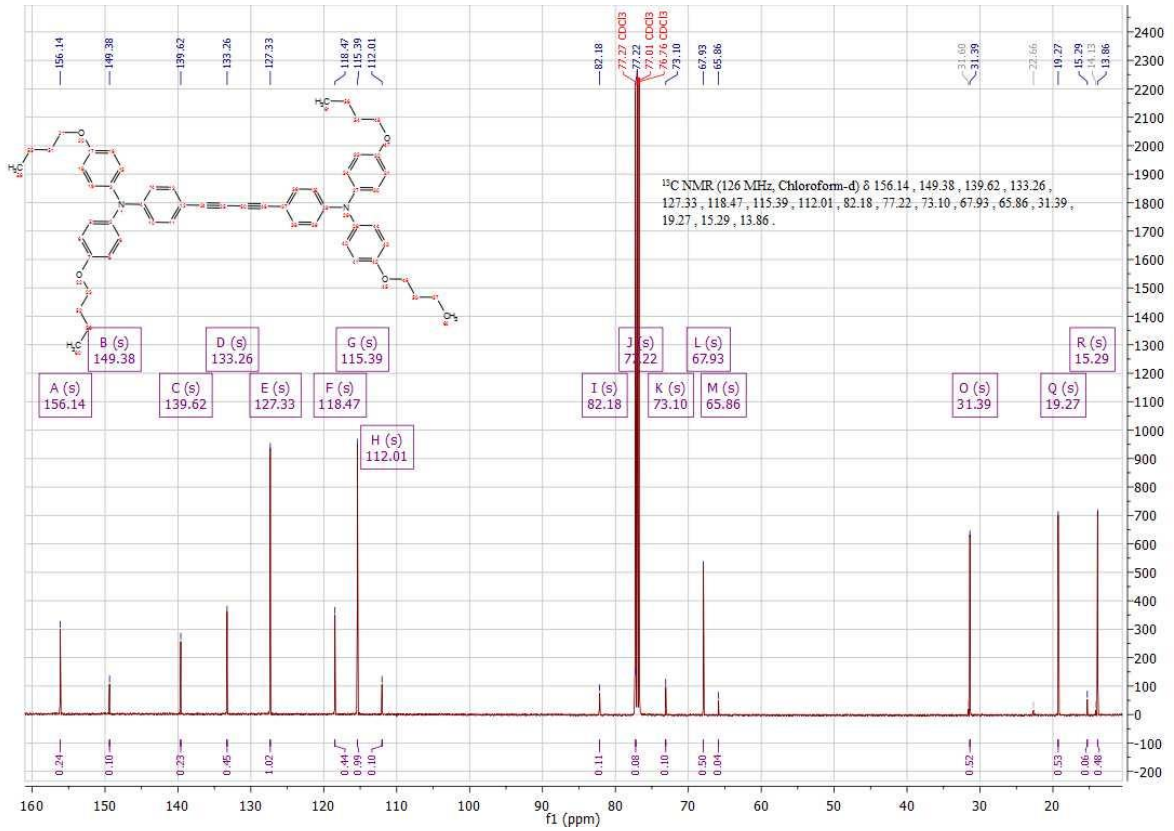

1H NMR (500 MHz, Benzene-d6) δ 7.41 – 7.33 (m, 2H), 6.39 – 6.36 (m, 2H), 3.42 (t, J = 6.4 Hz, 2H), 1.51 – 1.41 (m, 2H), 1.25 (dq, J = 14.7, 7.4 Hz, 2H), 0.79 (t, J = 7.4 Hz, 3H).
2,4 (m) 7.37
1,5 (m) 6.37
9 (t) 3.42
10 (m) 1.46
11 (dq) 1.25
12 (t) 0.79
1.99
2.14
2.11
1.83
1.95
3.14
f1 (ppm)


1H NMR (500 MHz, Benzene-d6) δ 7.19 – 7.16 (m, 2H), 7.01 – 6.97 (m, 4H), 6.80 – 6.74 (m, 6H), 3.60 (t, J = 6.4 Hz, 4H), 1.61 – 1.51 (m, 4H), 1.34 (h, J = 7.4 Hz, 4H), 0.82 (t, J = 7.4 Hz, 6H).
11,13 (m) 7.17
5,9,15,19 (m) 6.99
10,14,6,8,16,18 (m) 6.76
22,24 (t) 3.60
23,25 (m) 1.55
26,27 (h) 1.34
29,30 (t) 0.82
2.01
4.00
6.24
4.11
3.82
4.00
5.97
f1 (ppm)


1H NMR (400 MHz, Benzene-d6) δ 7.48 – 7.38 (m, 2H), 7.02 – 6.98 (m, 4H), 6.92 – 6.88 (m, 2H), 6.75 – 6.72 (m, 4H), 3.59 (t, J = 6.4 Hz, 4H), 1.61 – 1.49 (m, 4H), 1.41 – 1.26 (m, 4H), 1.14 (t, J = 7.9 Hz, 9H), 0.82 (t, J = 7.4 Hz, 6H), 0.72 (q, J = 7.8 Hz, 6H).
11,13 (m) 7.42
5,9,15,19 (m) 7.00
10,14 (m) 6.90
6,8,16,18 (m) 6.74
21,24 (t) 3.59
22,25 (m) 1.55
26,27 (m) 1.34
36,37,38 (t) 1.14
29,30 (t) 0.82
f1 (ppm)


1H NMR (400 MHz, Benzene-d6) δ 7.40 – 7.34 (m, 2H), 7.03 – 6.97 (m, 4H), 6.91 – 6.85 (m, 2H), 6.76 – 6.69 (m, 4H), 3.59 (t, J = 6.4 Hz, 4H), 2.77 (s, 1H), 1.59 – 1.51 (m, 4H), 1.39 – 1.28 (m, 4H), 0.82 (t, J = 7.4 Hz, 6H).
11,13 (m) 7.37
5,9,15,19 (m) 7.00
10,14 (m) 6.88
6,8,16,18 (m) 6.74
22,24 (t) 3.59
27 (s) 2.77
23,25 (m) 1.55
28,29 (m) 1.34
30,31 (t) 0.82
f1 (ppm)


1H NMR (500 MHz, Benzene-d6) δ 7.38 – 7.30 (m, 4H), 7.00 – 6.97 (m, 8H), 6.85 – 6.81 (m, 4H), 6.76 – 6.71 (m, 8H), 3.60 (t, J = 6.4 Hz, 8H), 1.61 – 1.51 (m, 8H), 1.40 – 1.28 (m, 8H), 0.82 (t, J = 7.4 Hz, 12H).
5,9,15,19,30,34,40,44 (m) 6.99
6,8,16,18,31,33,41,43 (m) 6.74
11,13,36,38 (m) 7.34
10,14,35,39 (m) 6.82
21,23,46,48 (t) 3.60
51,52,53,54 (m) 1.55
55,56,57,58 (m) 1.34
59,60,61,62 (t) 0.82
3.61
8.00
3.86
8.03
7.92
8.13
7.73
11.90
f1 (ppm)


13C NMR (126 MHz, Chloroform-d) δ 156.14 , 149.38 , 139.62 , 133.26 , 127.33 , 118.47 , 115.39 , 112.01 , 82.18 , 77.22 , 73.10 , 67.93 , 65.86 , 31.39 , 19.27 , 15.29 , 13.86 .
A (s) 156.14
B (s) 149.38
C (s) 139.62
D (s) 133.26
E (s) 127.33
F (s) 118.47
G (s) 115.39
H (s) 112.01
I (s) 82.18
J (s) 77.22
K (s) 73.10
L (s) 67.93
M (s) 65.86
O (s) 31.39
Q (s) 19.27
R (s) 15.29
f1 (ppm)

3. Computational results

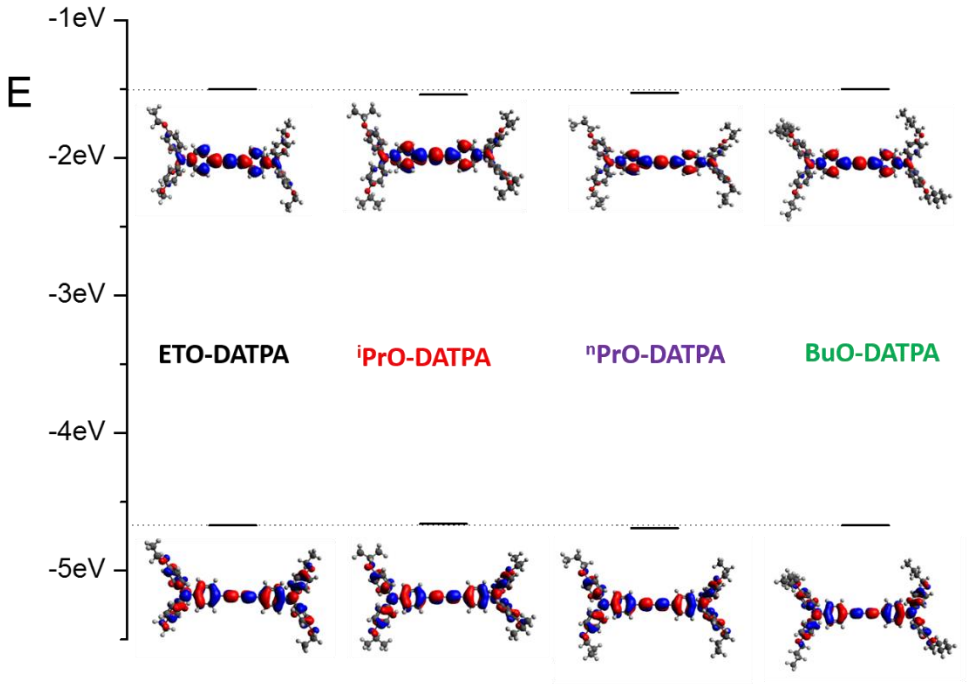
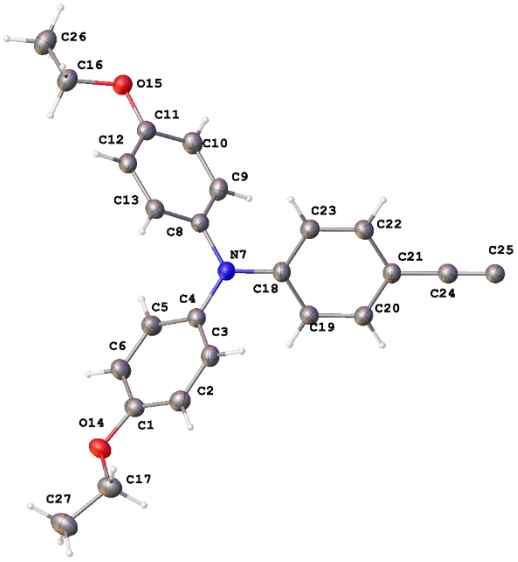
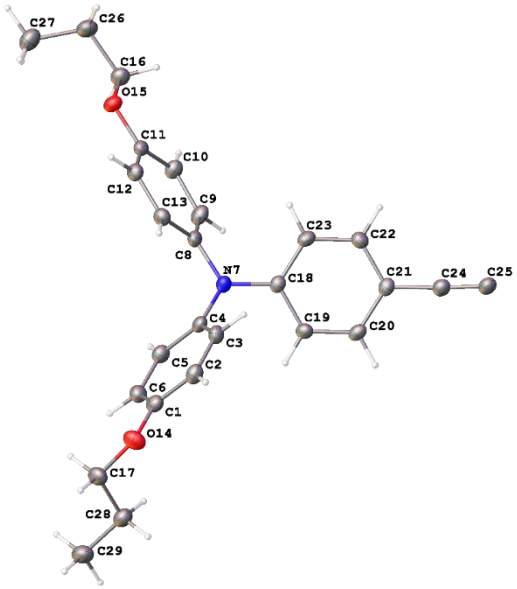


Figure S1 Molecular Orbital distribution of HOMO (bottom) and LUMO (top) for DATPA derivatives at B3LYP/6-31G(d) level of theory

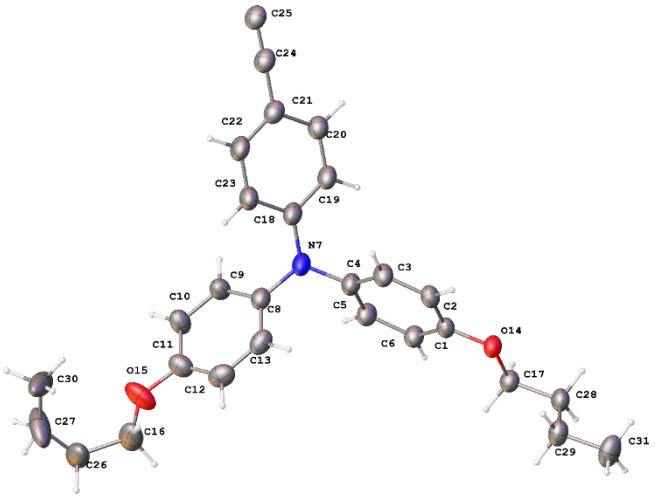
4. X-ray Crystallography



EtO-DATPA

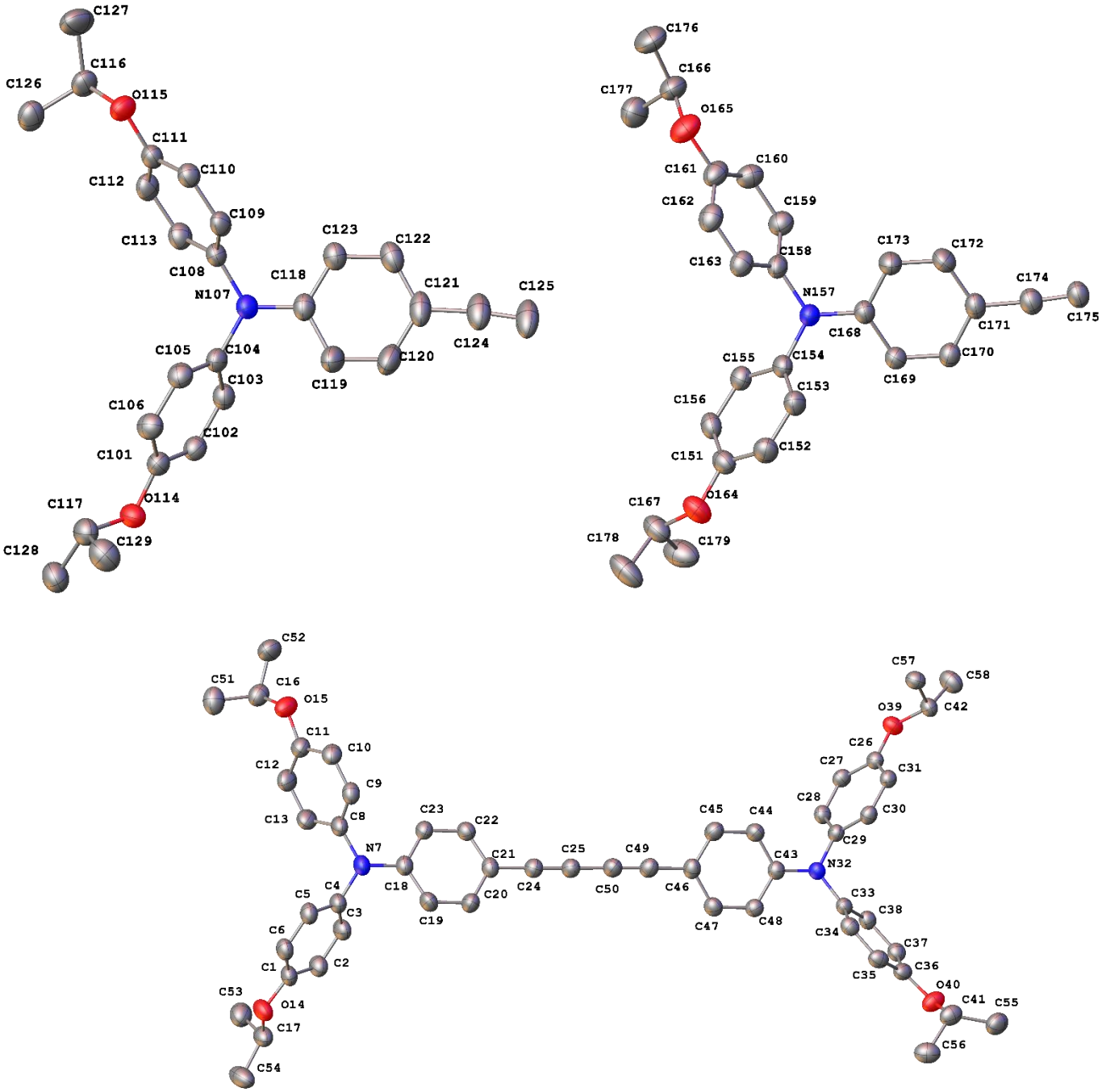


^{n}PrO-DATPA



BuO-DATPA

Figure S2 The asymmetric portion of the molecular structure of EtO-DATPA, ^{n}PrO-DATPA and BUO-DATPA.



^{i}PrO-DATPA

Figure S3 The asymmetric units of the molecular structure of ^{i}PrO-DATPA.

Table S4 Summary of X-ray crystallographic data for all DATPA derivatives

	EtO-DATPA	**^{n}PrO-DATPA**	**^{i}PrO-DATPA**	**BuO-DATPA**
Formula	$C_{48}H_{44}N_2O_4$	$C_{52}H_{52}N_2O_4$	$C_{52}H_{52}N_2O_4$	$C_{56}H_{60}N_2O_4$
$D_{calc.}$/ g cm^{-3}	1.233	1.228	1.154	1.181
μ/mm^{-1}	0.078	0.077	0.072	0.572
Formula Weight	712.85	768.95	768.95	825.06
Colour	Yellow	yellow	orange	orange
Shape	block	plate	block	block
Max Size/mm	0.24	0.55	0.51	0.25
Mid Size/mm	0.16	0.29	0.23	0.24
Min Size/mm	0.14	0.09	0.10	0.14
T/K	120.0	120.0	120.0	120.0
Crystal System	monoclinic	monoclinic	triclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$	P-1	$P2_1/c$
a/Å	9.8398(3)	12.0510(4)	12.4603(2)	11.82431(7)
b/Å	18.2197(5)	10.2594(3)	14.8711(4)	13.11889(7)
c/Å	10.8932(3)	17.3214(5	24.3863(6)	14.97854(9)
α/°	90	90	100.569(2)	90
β/°	100.468(3)	103.750(3)	90.6323(17)	93.5009(5)
γ/°	90	90	94.7035(18)	90
V/Å^3	1920.41(10)	2080.17(12)	4425.56(18)	2319.16(2)
Z	2	2	4	2
Z'	0.5	0.5	2	0.5
Θ_{min}/°	3.071	0.71073	2.992	3.745
Θ_{max}/°	29.756	MoK_α	28.282	76.172
Measured Refl.	34735	43687	88294	56181
Independent Refl.	5021	4742	21939	4833
Reflections Used	4479	3662	16792	4563
R_{int}	0.0308	0.0557	0.0382	0.0378
Parameters	332	367	1061	320
Restraints	0	0	0	45
Largest Peak	0.249	0.208	0.565	0.472
Deepest Hole	-0.216	-0.173	-0.259	-0.389
GooF	1.080	1.051	1.059	1.028
wR_2 (all data)	0.1211	0.0994	0.2062	0.1559
wR_2	0.1174	0.0943	0.1920	0.1536
R_1 (all data)	0.0540	0.0578	0.0996	0.0598
R_1	0.0475	0.0405	0.0783	0.0578

5. Cyclic voltammetry of DATPA derivatives

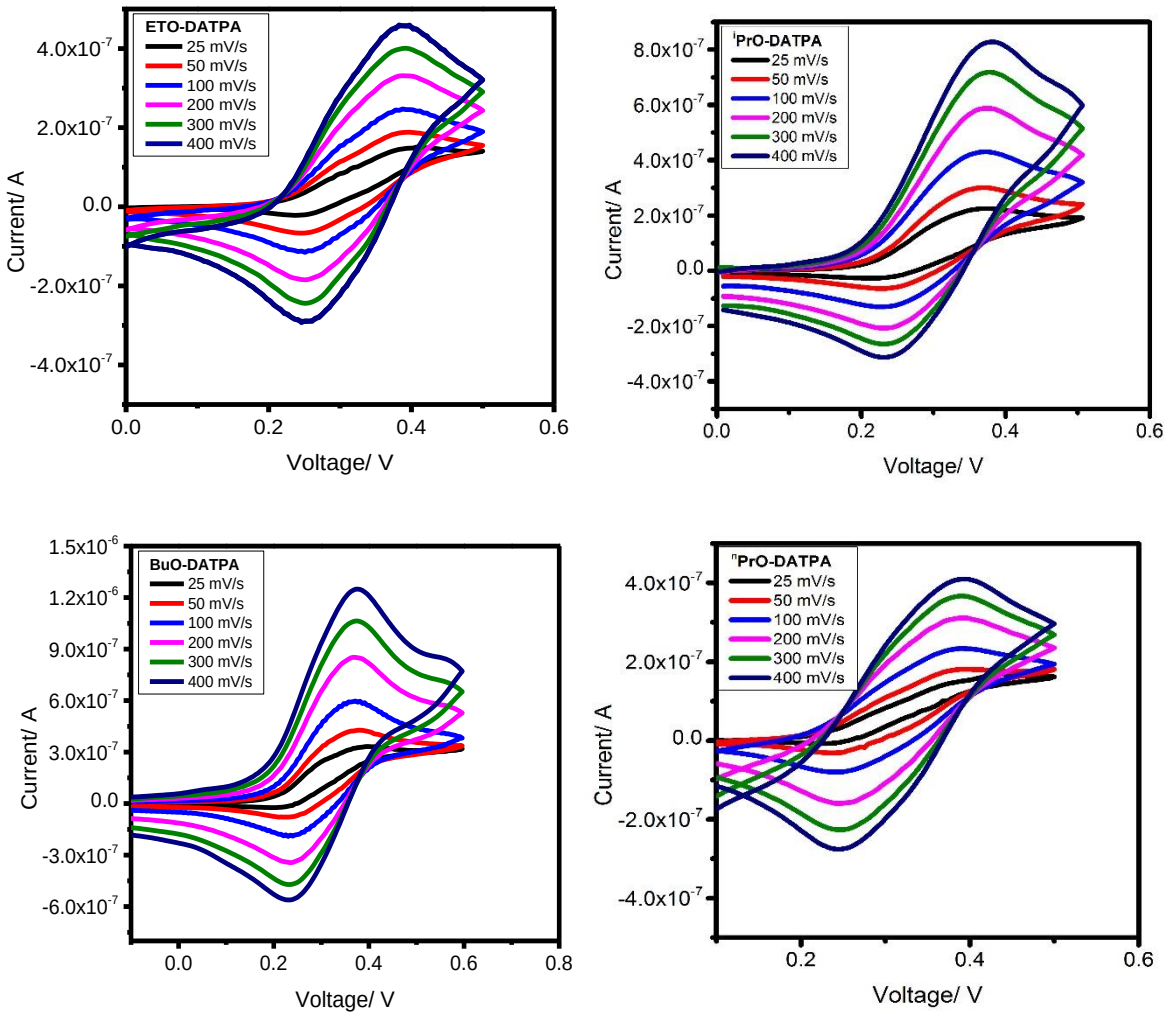


Figure S5. Cyclic voltammetry traces at different scan rates of EtO-DATPA, ^{i}PrO-DATPA, ^{n}PrO-DATPA and BuO-DATPA

6. Powder Difraction

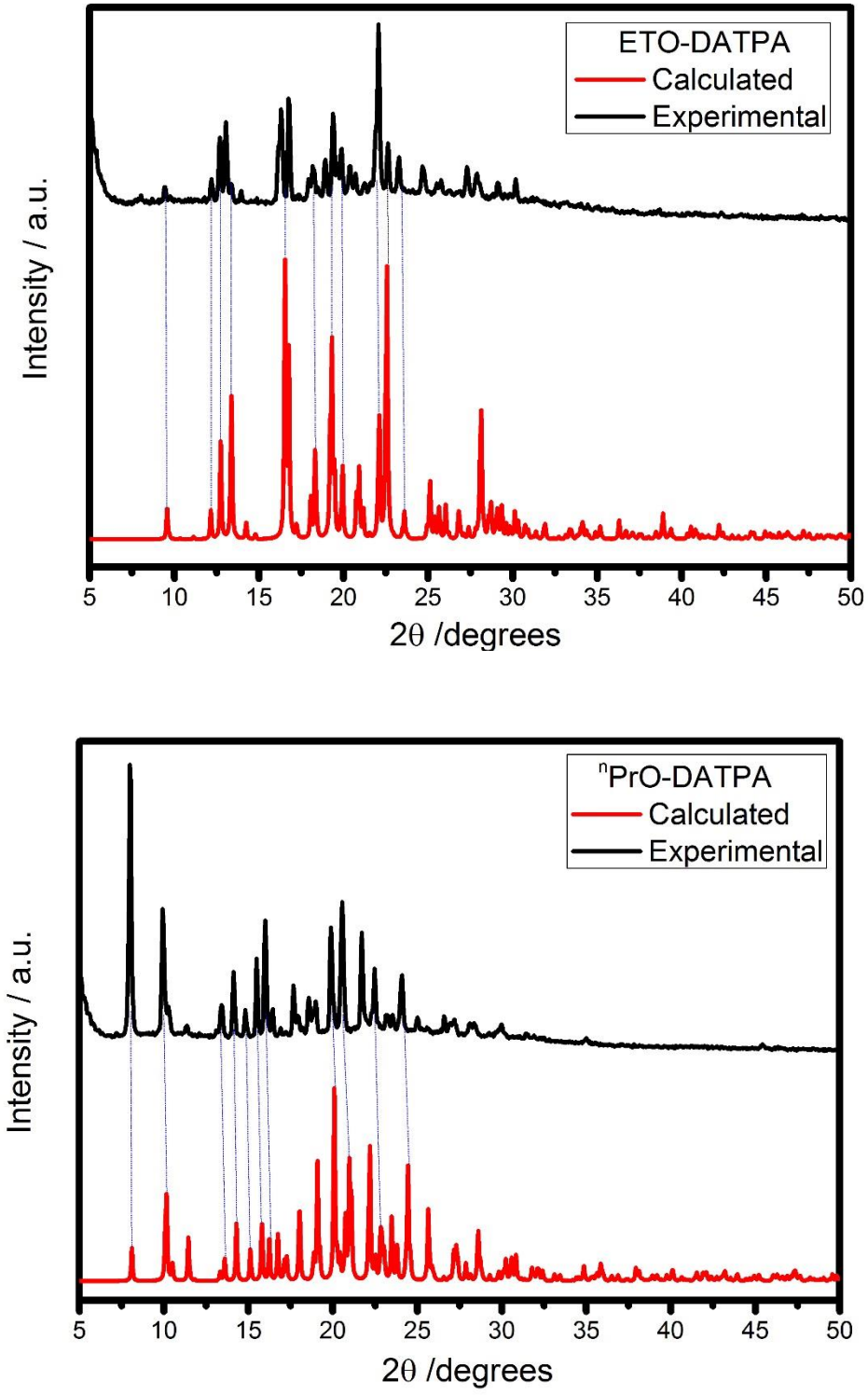


Figure S6 XRD powder patterns: simulated from single-crystal structures (red) and experimental (black).

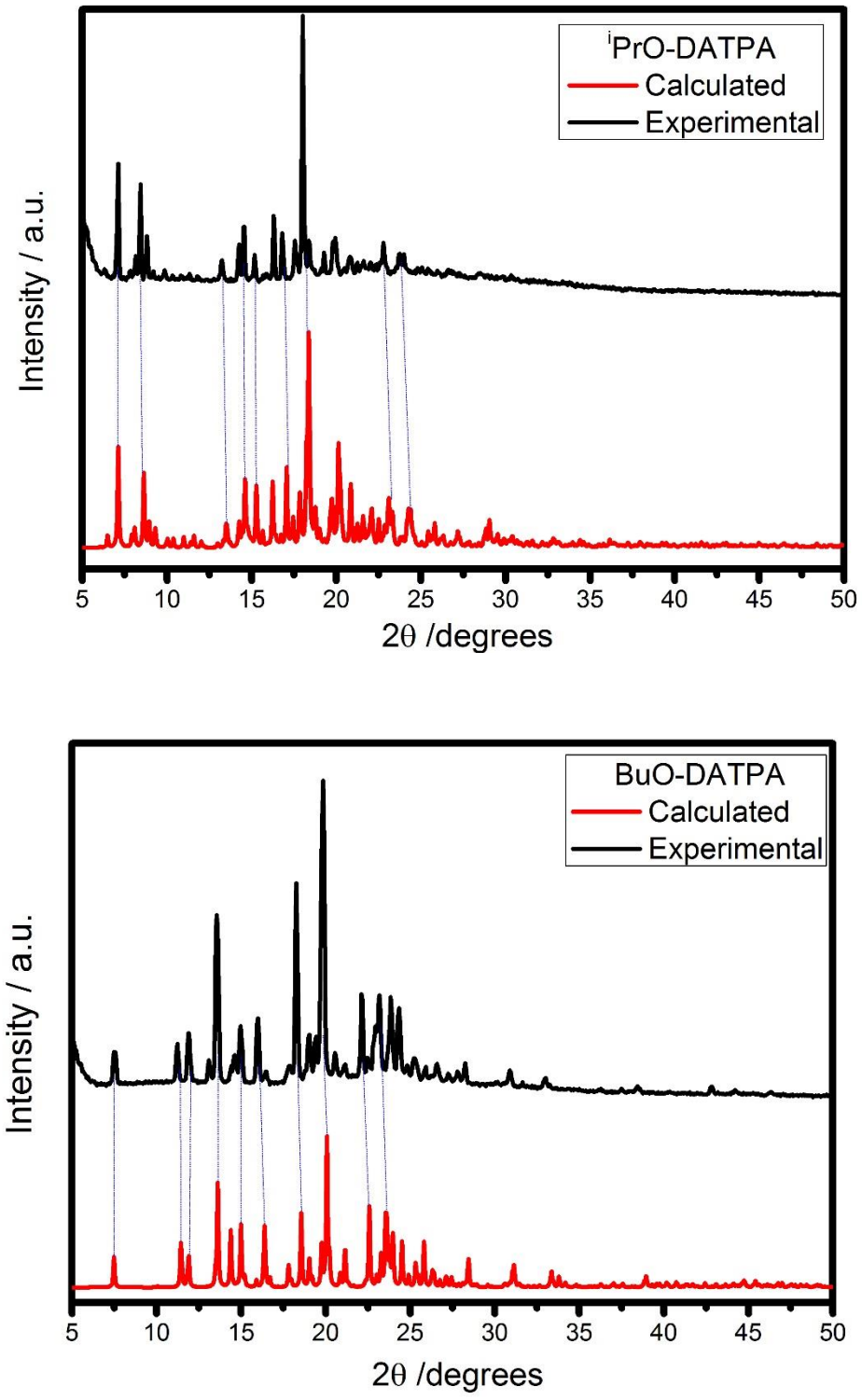


Figure S7 XRD powder patterns: simulated from single-crystal structures (red) and experimental (black).

7. Charge transport parameters

Organic Field Effect Transistor (OFETs)

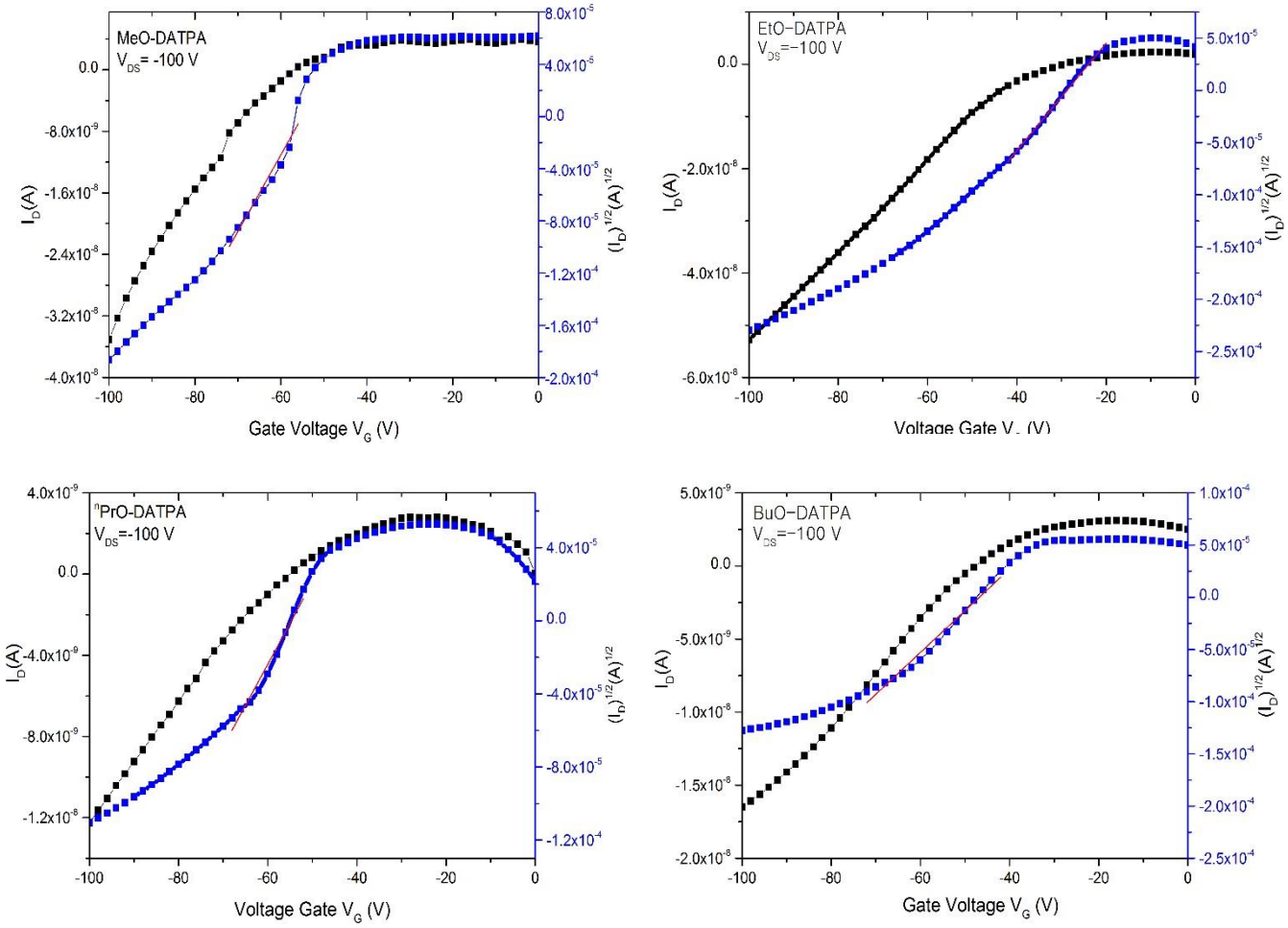
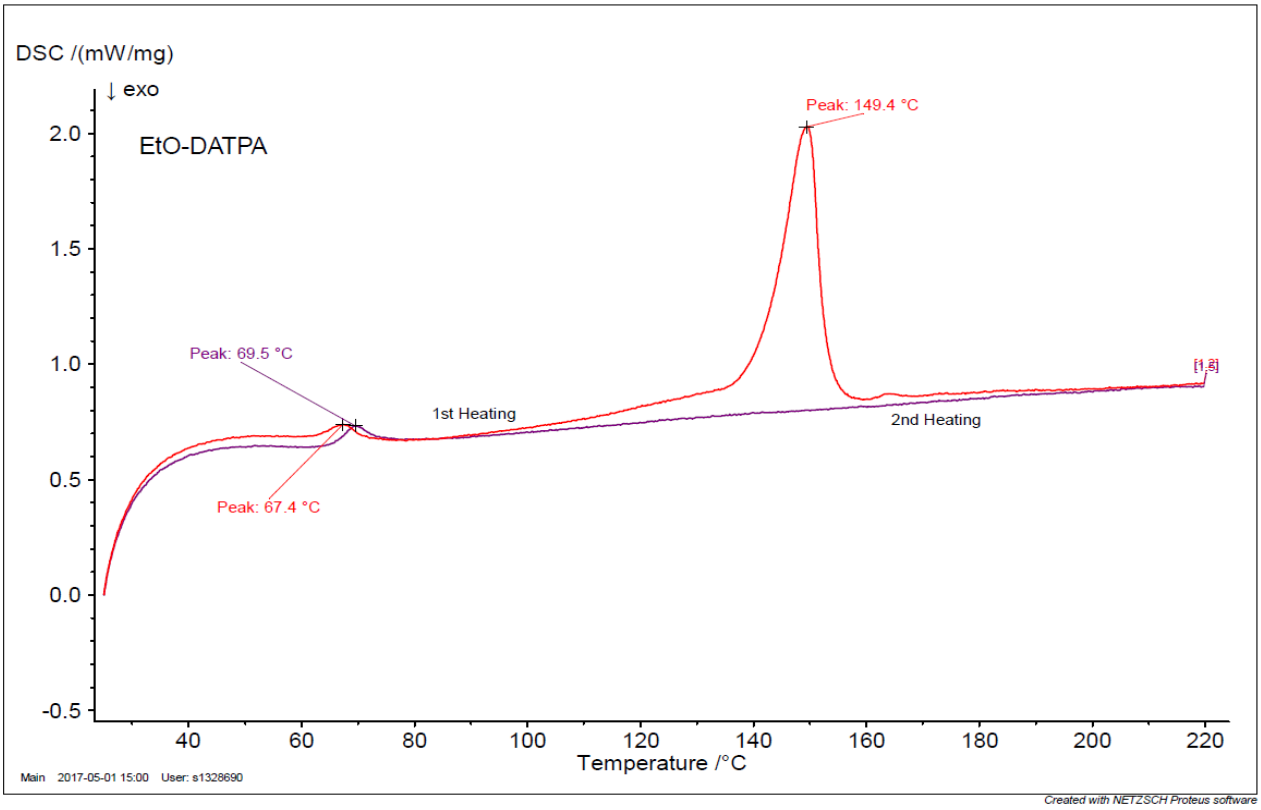


Figure S8 Transfer Characteristic Curves of MeO-DATPA, EtO-DATPA, ^{n}PrO-DATPA and BuO-DATPA (left to right) on a bottom gate/bottom contact device.

8. Thermal properties



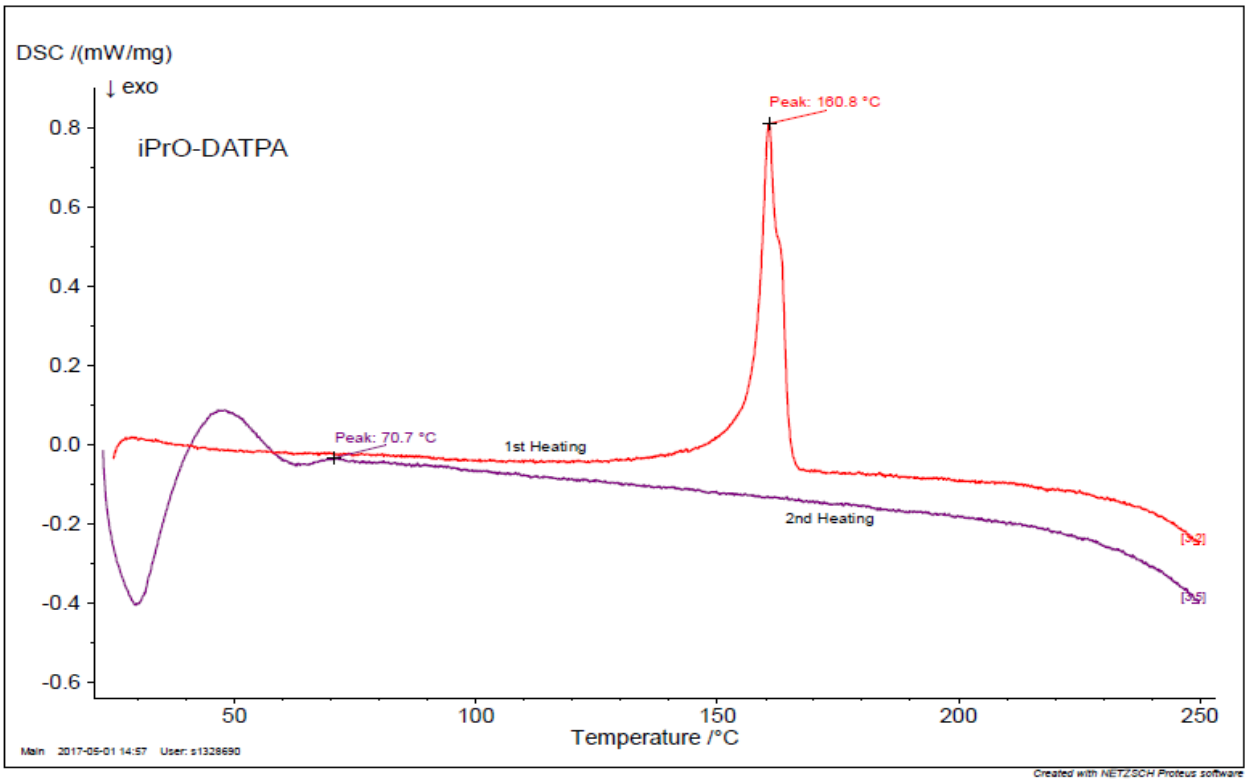
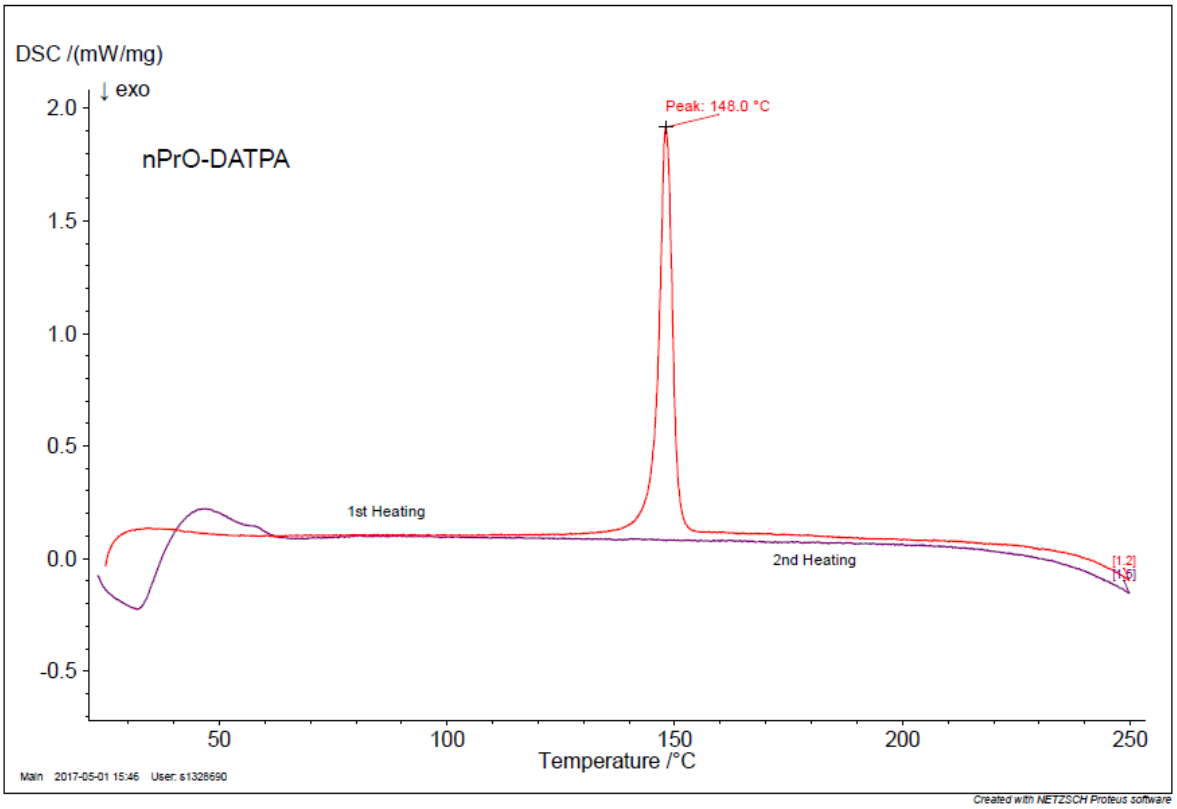


Figure S9 Differential scanning calorimetry curves of EtO-DATPA and ^{i}PrO-DATPA



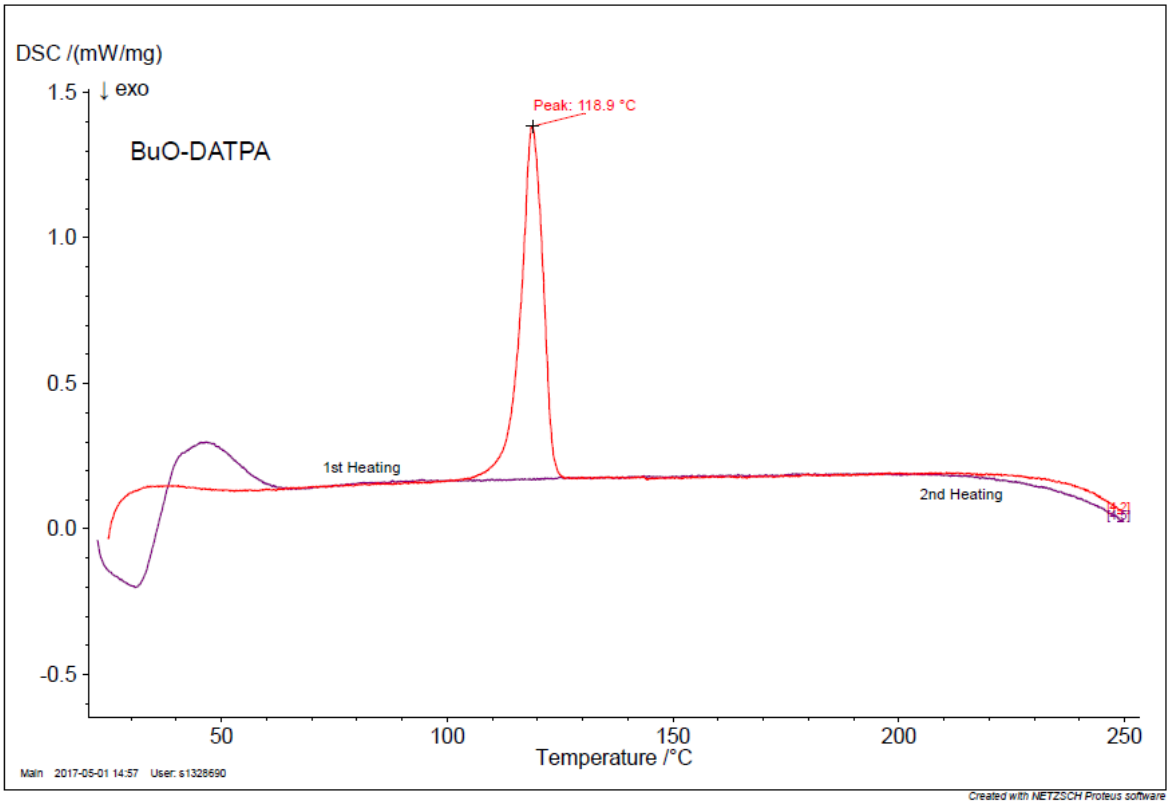


Figure S10 Differential scanning calorimetry curves of ^{n}PrO-DATPA and BuO-DATPA

9. Transient Absorption Spectroscopy

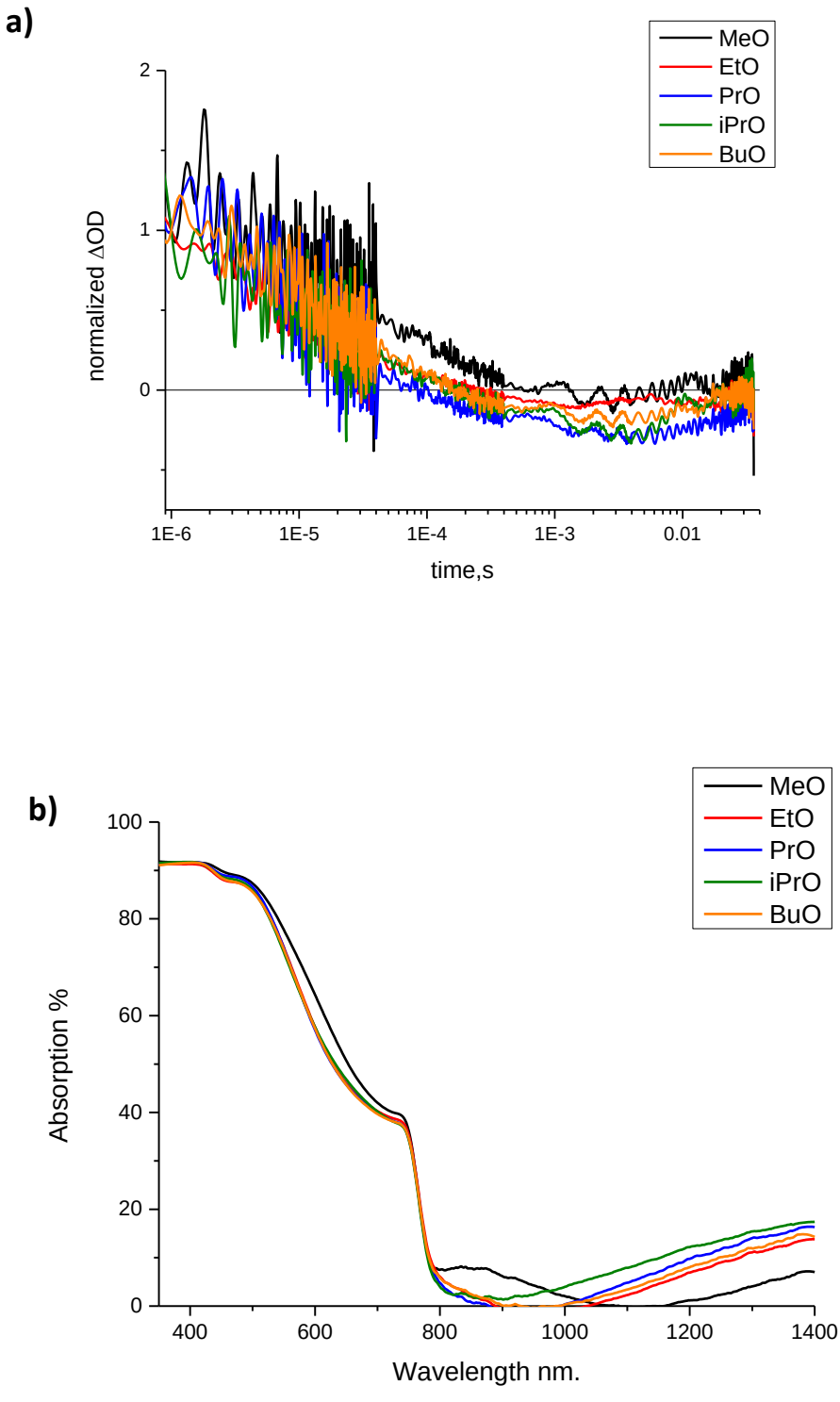


Figure S11. **a)** Normalized Transient Absorption spectra and **b)** UV-Vis spectra of mp-TiO_2/$CH_3NH_3PbI_3$/HTM for all DATPA derivatives

Device performance

HTM	PCE (%)	Jsc (mA cm^{-2})	Voc (V)	FF (%)
MeO-DATPA	4.87±0.82	10.79±0.56	0.84±0.0054	54.10±8.01
EtO-DATPA	0.77±0.22	3.13±0.82	0.79±0.022	31.83±1.01
^{n}PrO-DATPA	4.07±0.54	10.07±0.65	0.78±0.021	51.98±6.19
^{i}PrO-DATPA	2.46±0.51	7.99±1.27	0.79±0.0079	38.41±2.50
BuO-DATPA	2.43±0.47	5.88±0.87	0.75±0.024	56.59±8.01
Spiro-OMeTAD	14.51±0.87	19.19±0.71	0.99±0.0079	73.74±4.13

Table S12. Summary of the solar cell parameters over 7 repeat devices