Supporting Information

Improved dynamics and positional bias with a second generation palladium(II)-complexed molecular shuttle

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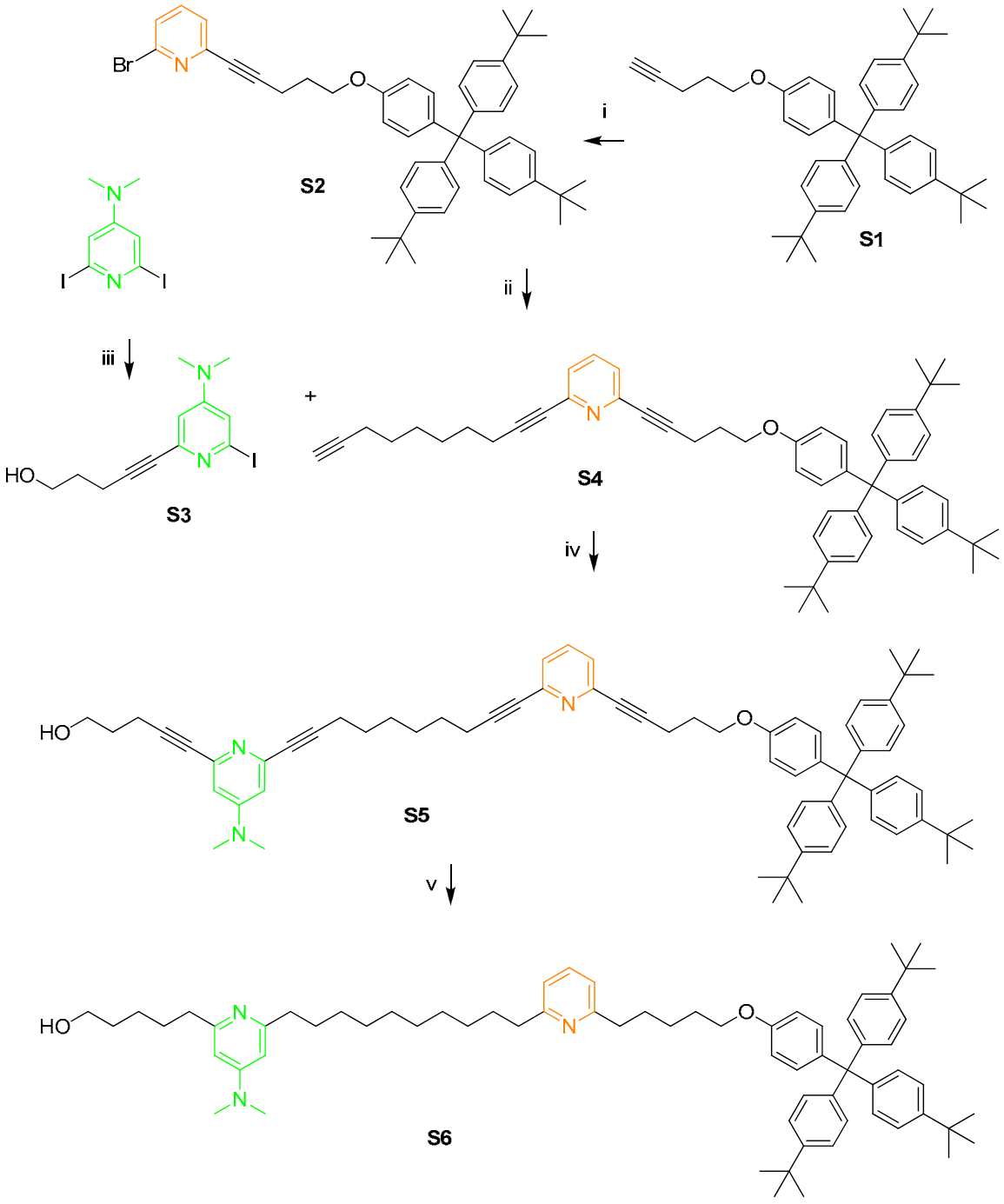
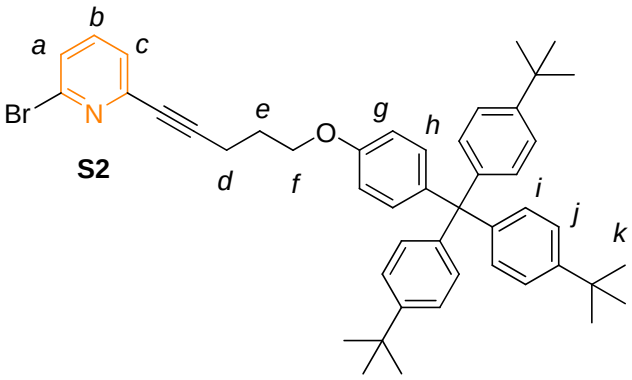
General Experimental Section

Unless stated otherwise, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification, tetrahydrofuran, dichloromethane, acetonitrile and *N*,*N*-dimethylformamide were dried using a solvent purification system manufactured by Innovative Technology, Newburyport, MA, USA. **L3**Pd(MeCN),[1] 1-(bis(4-tert-butylphenyl)(4-(pent-4-ynyloxy)phenyl)methyl)-4-tert-butylbenzene (**S1**),[2] 2,6-diiodo-(4-*N*,*N*-dimethylamino)pyridine[3] and 4-[tris-(4-*tert*-butylphenyl)methyl]-phenol (**S7**)[4] were prepared according to literature procedures. Unless stated otherwise, all reactions were carried out under an atmosphere of nitrogen. Column chromatography was carried out using Silica 60A (particle size 35-70 μm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany) and observed under UV light. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument, with the exception of the ^{13}C NMR spectrum of compound **S9** which was recorded on a Bruker AV 800 instrument at 298 K. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to residual solvent. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Melting points (m.p.) were determined using a Sanyo Gallenkamp apparatus. Mass spectrometry data was obtained from the EPSRC National Mass Spectrometry Service Centre (Swansea, U.K.) and the services at The University of Edinburgh.

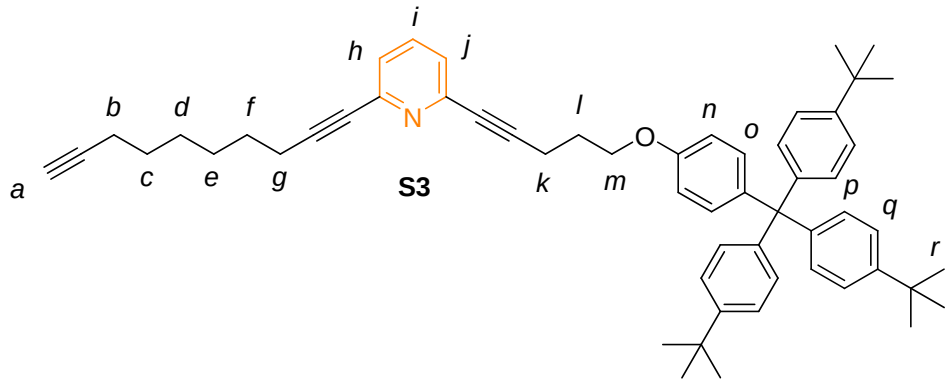
Synthesis and Experimental Section



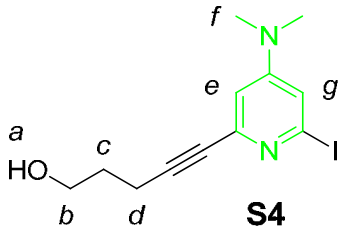
Scheme S1: Synthesis of pre-thread **S6**. Reagents and conditions: (i) 2,6-dibromopyridine, $Pd(PPh_3)_4$, CuI, THF/Et_3N, 18 h, RT, 39%; (ii) 1,9-decadiyne, $Pd(PPh_3)_4$, CuI, THF/Et_3N, 18 h, RT, 87%; (iii) pent-4-yne-1-ol, $Pd(PPh_3)_2Cl_2$, CuI, THF/Et_3N, 18 h, RT, 65%; (iv) $Pd(PPh_3)_2Cl_2$, CuI, THF/Et_3N, 18 h, RT, 30%; (v) $Pd(OH)_2/C$, H_2, THF/EtOH, 18 h, RT, 71%.



To a solution of 2,6-dibromopyridine (1.78 g, 7.51 mmol, 1.0 equiv.) in THF (50 mL) and Et_3N (25mL) was added **S1** (4.29 g, 7.51 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (0.867g, 0.751 mmol, 0.1 equiv.) and CuI (0.293 g, 1.54 mmol, 0.2 equiv.). The resulting mixture was stirred at RT for 18 h. The solvent was then removed under reduced pressure and the residue redissolved in CH_2Cl_2 (100 mL) and washed with a saturated aqueous solution of NH_4Cl (3 x 50 mL) and brine (100 mL). The organic layer was dried ($MgSO_4$), concentrated under reduced pressure and the crude residue purified by column chromatography (1:7 Et_2O:hexane) and then recrystallised from a hot CH_2Cl_2/CH_3CN solution to yield the title compound as a tan solid (2.12 g, yield = 39%). m.p. = 193 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 27H, H_k), 2.06-2.10 (m, 2H, H_e), 2.65 (t, J = 7.0, 2H, H_d), 4.07 (t, J = 5.9, 2H, H_f), 6.77 (d, J = 8.9, 2H, H_g), 7.06-7.09 (m, 8H, $H_{h,i}$), 7.23 (d, J = 8.5, 6H, H_j), 7.30 (d, J = 7.7, 1H, H_c), 7.38 (d, J = 7.7, 1H, H_a), 7.45 (t, J = 7.7, 1H, H_b); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 16.2, 28.1, 31.4, 34.3, 63.0, 66.0, 79.7, 91.9, 113.0, 124.0, 125.7, 127.1, 130.7, 132.3 (x 2), 138.3, 139.7, 141.5, 144.1, 148.3, 156.6; LREI-MS (3-NOBA matrix): m/z = 725 $[M]^+$; HREI-MS (reference compound: perfluorotributylamine): m/z = 725.3229 (calcd. for $C_{47}H_{52}{}^{79}BrNO$ 725.3227, $[M]^+$).

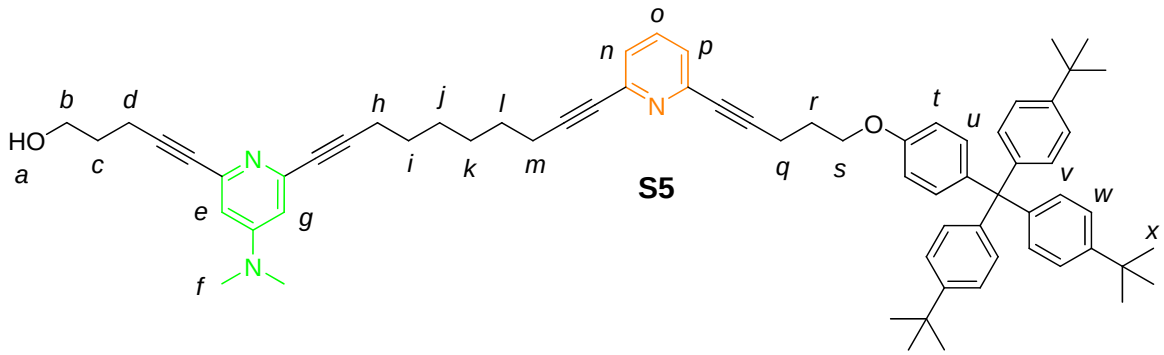


To a solution of **S2** (2.06 g, 2.83 mmol, 1.0 equiv.) in THF (20 mL) and Et_3N (10 mL) was added 1,9-decadiyne (3.80 g, 28.3 mmol, 10.0 equiv.), $Pd(PPh_3)_4$ (0.323 g, 0.280 mmol, 0.1 equiv.) and CuI (0.106 g, 0.560 mmol, 0.2 equiv.). The resulting mixture was stirred at RT for 18 h. The solvent was then removed under reduced pressure and the residue was redissolved in CH_2Cl_2 (50 mL) and washed with a saturated aqueous solution of NH_4Cl (3 x 25 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$), concentrated under reduced pressure and the crude residue purified by column chromatography (1:4 Et_2O:hexane) to give the title compound as tan solid (1.92 g, yield = 87 %). m.p. = 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 27H, H_r), 1.42-1.46 (m, 4H, $H_{e,d}$), 1.51-1.55 (m, 2H, H_c), 1.62-1.65 (m, 2H, H_f), 1.93 (t, J = 2.6, 1H, H_a), 2.06-2.10 (m, 2H, H_l), 2.17-2.21 (m, 2H, H_b), 2.42 (t, J = 7.1, 2H, H_g), 2.64 (t, J = 7.0, 2H, H_k), 4.07 (t, J = 6.0, 2H, H_m), 6.77 (d, J = 8.9, 2H, H_n), 7.07-7.10 (m, 8H, $H_{o,p}$), 7.22-7.24 (m, 8H, $H_{h,j,q}$), 7.51 (t, J = 7.8, 1H, H_i); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 16.2, 18.4, 19.1, 19.2, 27.9, 28.2 (x 2), 28.3, 31.4, 34.3, 63.1, 66.2, 68.2, 80.2, 80.6, 84.5, 90.1, 91.2, 113.0, 124.0, 125.4 (x 2), 130.7, 132.2, 136.2, 139.6, 143.8, 144.0, 144.2, 148.3, 156.7; LREI-MS: *m/z* = 780 $[M]^+$; HREI-MS (reference compound: perfluorotributylamine): *m/z* = 779.5061 (calcd. for $C_{57}H_{65}ON$, 779.5061, $[M]^+$).



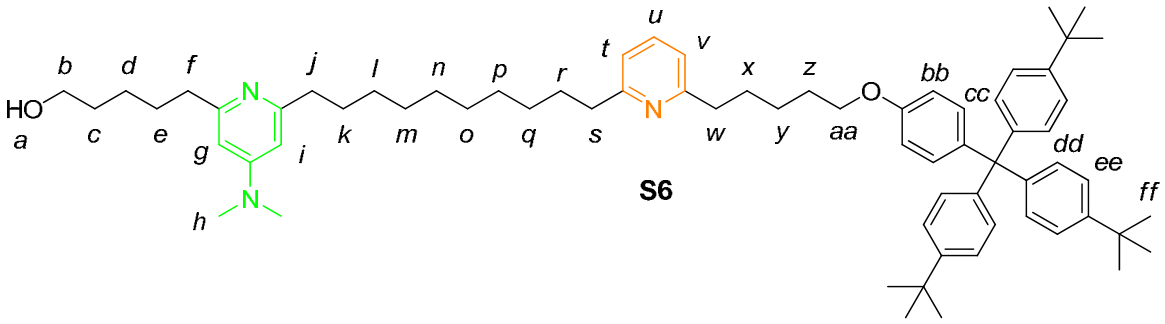
S4

To a solution of 2,6-diiodoDMAP (4.01 g, 10.7 mmol, 1.0 equiv.) in THF (60 mL) and Et_3N (30 mL) was added pent-4-yne-1-ol (0.902 g, 1.00 mL, 10.7 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (0.751 g, 1.07 mmol, 0.1 equiv.) and CuI (0.407 g, 2.14 mmol, 0.2 equiv.). The resulting mixture was stirred at RT for 18 h. The solvent was removed under reduced pressure and the residue was redissolved in EtOAc (50 mL) and washed with a saturated aqueous solution of NH_4Cl (3 x 25 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$), concentrated under reduced pressure and the crude residue purified by column chromatography (1:9 Me_2CO:CH_2Cl_2) to give the title compound as a yellow oil (2.30 g, yield = 65 %). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.83-1.87 (m, 2H, H_c), 2.17 (s, 1H, H_a), 2.52 (t, J = 7.0, 2H, H_d), 2.96 (s, 6H, H_f), 3.80-3.83 (m, 2H, H_b), 6.57 (d, J = 2.4, 1H, H_e), 6.82 (d, J = 2.4, 1H, H_g); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 15.9, 30.9, 39.2, 61.6, 80.5, 89.6, 109.7, 115.8, 118.3, 143.2, 154.5; LREI-MS: *m/z* = 330 $[M]^+$; HREI-MS (ref. comp.: perfluorotributylamine): *m/z* = 330.0225 (calcd. for $C_{12}H_{15}ON_2I$, 330.0224, $[M]^+$).



To a solution of **S3** (2.98 g, 3.82 mmol, 1.0 equiv.) and **S4** (1.89 g, 5.72 mmol, 1.5 equiv.) in THF (30 mL) and Et_3N (15 mL) was added $Pd(PPh_3)_2Cl_2$ (0.267 g, 0.382 mmol, 0.1 equiv.) and CuI (0.145 g, 0.764 mmol, 0.2 equiv.). The resulting mixture was stirred at RT for 18 h. The solvent was removed under reduced pressure and the residue was redissolved in EtOAc (40 mL) and washed with a saturated aqueous solution of NH_4Cl (3 x 20 mL) and brine (40 mL). The organic layer was dried ($MgSO_4$), concentrated under reduced pressure and the crude residue purified by column chromatography (1:19 Me_2CO:CH_2Cl_2) and then recrystallized from hot MeCN to yield the title compound as an off-white solid (1.12 g, yield = 30%). m.p. = 144 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.29 (s, 27H, H_x), 1.44-1.48 (m, 4H, $H_{j,k}$), 1.59-1.63 (m, 4H, $H_{i,l}$), 1.83-1.87 (m, 2H, H_c), 2.05-2.09 (m, 2H, H_r), 2.25 (br, 1H, H_a), 2.39-2.42 (m, 4H, $H_{h,m}$), 2.52 (t, J = 7.0, 2H, H_d), 2.63 (t, J = 7.0, 2H, H_q), 2.97 (s, 6H, H_f), 3.80 (t, J = 6.1, 2H, H_b), 4.06 (t, J = 6.0, 2H, H_s), 6.52-6.53 (m, 2H, $H_{e,g}$), 6.76 (d, J = 8.9, 2H, H_t), 7.06-7.10 (m, 8H, $H_{u,v}$), 7.20-7.24 (m, 8H, $H_{n,p,w}$), 7.51 (t, J = 7.8, 1H, H_o); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 13.9, 14.3, 17.2, 17.4 (x 2), 26.2, 26.3 (x 2), 26.6, 29.1, 29.5, 32.4, 37.3, 59.7, 61.1, 64.2, 78.2, 78.6, 79.0, 79.5, 86.2, 87.2, 88.1, 89.4, 106.7, 106.8, 111.1, 122.1, 123.5, 123.7, 128.8, 130.3, 134.3, 137.7, 141.5, 141.8, 142.0, 142.1, 142.2, 146.3, 152.4, 154.7; LRES-MS: m/z = 983 $[M+H]^+$; HRES-MS (reference

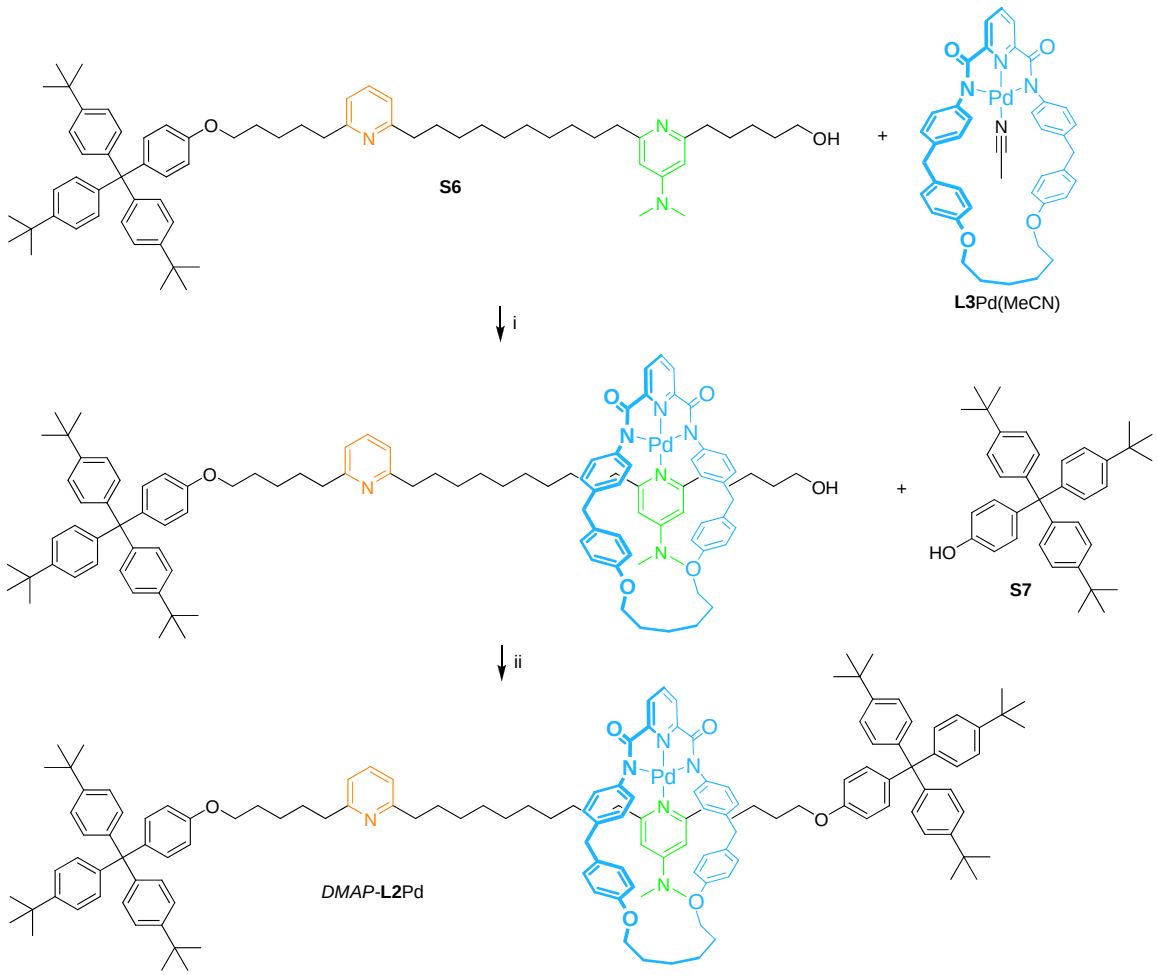
compound: caffeine): *m/z* = 982.6252 $[M+H]^+$ (calcd. for $C_{69}H_{80}O_2N_3$, 982.6245, $[M+H]^+$).



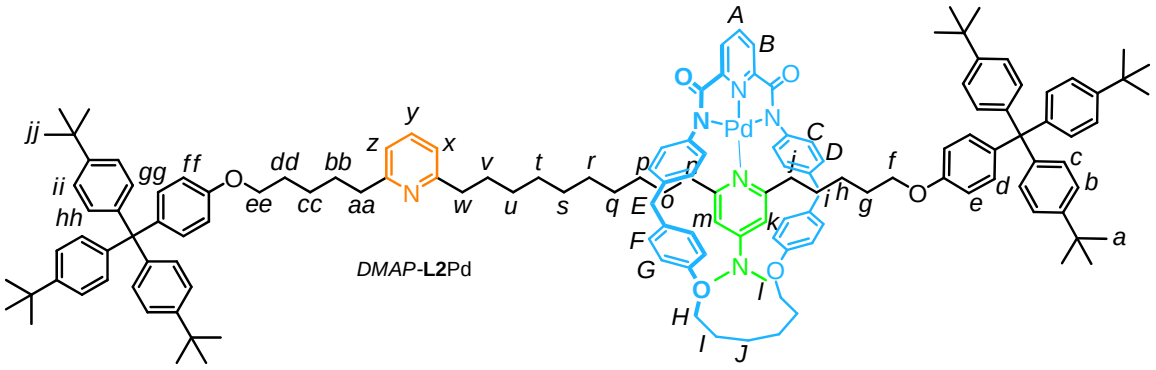
S6

To a solution of **S5** (0.670 g, 0.682 mmol) in THF (5 mL) and EtOH (5 mL) was added 10% w/w $Pd(OH)_2/C$ (0.268 g, 40% b/w). The suspension was repeatedly degassed and purged with N_2 before being repeatedly degassed and purged with H_2 and then stirred for 18 h at RT under an atmosphere of H_2. The reaction mixture was then purified by column chromatography (1:4 MeOH:Me_2CO) to yield the title compound as a white solid (0.486 g, yield = 71%). m.p. = 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.20-1.27 (m, 8H, $H_{m,n,o,p}$), 1.29 (s, 27H, H_{ff}), 1.34-1.38 (m, 4H, $H_{l,q}$), 1.50.1.54 (m, 4H, $H_{d,y}$), 1.61-1.90 (m, 13H, $H_{a,c,e,k,r,x,z}$), 2.73-2.77 (m, 4H, $H_{s,w}$), 3.00-3.04 (m, 4H, $H_{f,j}$), 3.16 (s, 6H, H_h), 3.67 (t, *J* = 6.2, 2H, H_b), 3.92 (t, *J* = 6.5, 2H, H_{aa}), 6.27-6.29 (m, 2H, $H_{g,i}$), 6.74 (d, *J* = 8.8, 2H, H_{bb}), 6.92-6.95 (m, 2H, $H_{t,v}$), 7.06 (d, *J* = 8.8, 2H, H_{cc}), 7.07 (d, *J* = 8.6, 6H, H_{dd}), 7.22 (d, *J* = 8.6, 6H, H_{ee}), 7.48 (t, *J* = 7.6, 1H, H_u); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.0, 26.0, 29.0, 29.2, 29.3 (x 2), 29.4, 29.5 (x 2), 29.7 (x 2), 30.0, 30.2, 31.4, 31.6, 33.1, 34.3, 38.5, 38.6 (x 2), 40.0, 62.1, 63.0, 67.6, 103.4, 103.5, 112.9, 119.6, 119.7, 124.0, 130.7, 132.2, 136.5, 139.3, 144.1, 144.2, 148.2, 148.3, 156.8, 160.0, 161.1, 162.3;

LRES-MS: *m/z* = 999 $[M+H]^+$; HRES-MS (reference compound: caffeine): *m/z* = 998.7509 $[M+H]^+$ (calcd. for $C_{69}H_{96}O_2N_3$, 998.7497, $[M+H]^+$).

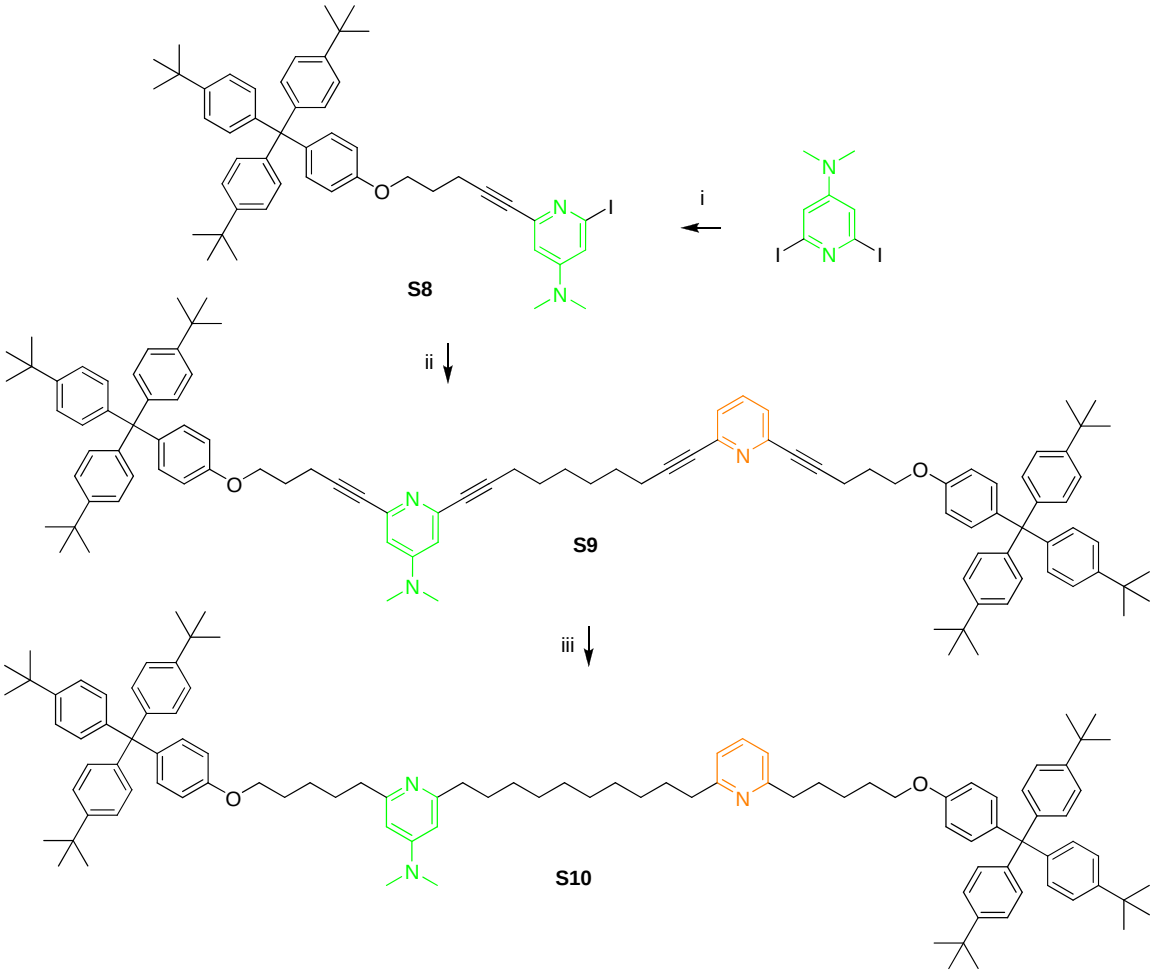


Scheme S2: Synthesis of molecular shuttle *DMAP*-**L2**Pd. Reagents and conditions: (i) CH_2Cl_2, 30 mins, RT; (ii) PPh_3, DIAD, toluene, 24 h, RT, 15%.

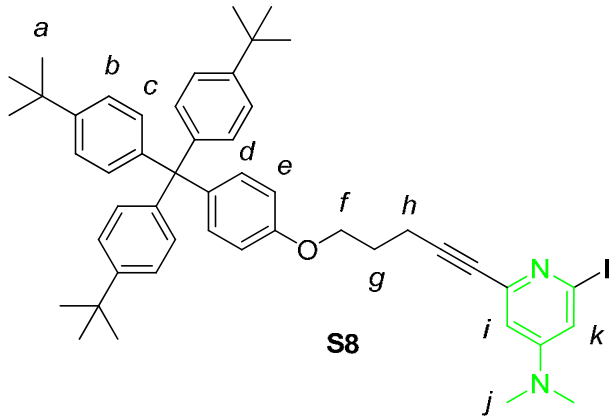


To a solution of **S6** (0.050 g, 50 μmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) was added **L3**Pd(MeCN) (0.038 g, 50 μmol, 1.0 equiv.) and the yellow solution stirred at RT for 30 minutes. After this time, TLC analysis (2% MeOH in CH_2Cl_2) showed that no free **S6** remained in solution. The solvent was then removed under reduced pressure and the yellow residue redissolved in toluene (10 mL) and cooled to 0 ˚C. To this cooled solution were added sequentially PPh_3 (0.066 g, 0.25 mmol, 5.0 equiv.), **S7** (0.13 g, 0.25 mmol, 5.0 equiv.) and finally DIAD (0.051 g, 0.049 mL, 0.25 mmol, 5.0 equiv.) and the mixture stirred at RT for 24 h. After this time, the reaction was concentrated under reduced pressure and the orange residue subjected to column chromatography on silica (2% MeOH in CH_2Cl_2) to give a yellow solid, which was precipitated from CH_2Cl_2 by addition of MeOH to give the title compound as a yellow powder (0.017 g, yield = 15%). m.p. = 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.18-1.41 (m, 66H, $H_{a,p,q,r,s,t,u,jj}$), 1.43-1.58 (m, 12H, $H_{h,i,o,cc,J}$), 1.64-1.85 (m, 12H, $H_{g,v,bb,dd,I}$), 2.66 (s, 6H, H_l), 2.71-2.80 (m, 4H, $H_{w,aa}$), 3.06-3.21 (m, 4H, $H_{j,n}$), 3.64 (s, 4H, H_E), 3.79-3.88 (m, 6H, $H_{f,H}$), 3.92 (t, J = 6.5, 2H, H_{ee}), 5.59 (d, J = 2.3, 1H, $H_{(m \text{ or } k)}$), 5.67 (d, J = 2.3, 1H, $H_{(m \text{ or } k)}$), 6.56-6.62 (m, 4H, $H_{e,ff}$), 6.65-6.77 (m, 16H, $H_{d,gg,D,F,(C \text{ or } G)}$), 6.92-6.97 (m, 2H, $H_{x,z}$), 7.05-7.11 (m, 16H, $H_{c,hh,(C \text{ or } G)}$), 7.20-7.25 (m, 12H, $H_{b,ii}$), 7.48 (t, J = 7.6, 1H, H_y), 7.89 (d, J = 7.8, 2H, H_B), 8.00-8.04 (m, 1H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ =

25.8, 25.9, 26.0, 27.8, 27.9, 28.3, 29.0, 29.1, 29.2, 29.5 (x 3), 29.6 (x 2), 29.7, 29.9, 30.2, 31.3 (x 2), 34.2, 38.4, 38.6, 38.7, 38.9, 39.1, 40.3, 63.0 (x 2), 67.3, 67.4, 67.6, 103.3, 103.5, 112.8 (x 2), 113.7, 119.6 (x 2), 123.9, 124.0, 125.4, 125.6, 128.6, 129.3, 130.6 (x 3), 132.1, 134.5, 136.4, 136.8, 139.3, 139.4, 140.1, 144.1 (x 2), 144.7, 148.2 (x 2), 152.8, 154.9, 156.7, 156.8, 157.0, 159.9, 160.3, 161.4, 161.9, 169.4. LRFAB-MS (3-NOBA matrix): *m/z* = 2200 $[M^{104}Pd+H]^+$. HRFAB-MS (3-NOBA matrix): *m/z* = 2200.2534 $[M+H]^+$ (calcd. for $C_{145}H_{173}O_6N_6{}^{104}Pd$, 2200.2446, $[M+H]^+$).

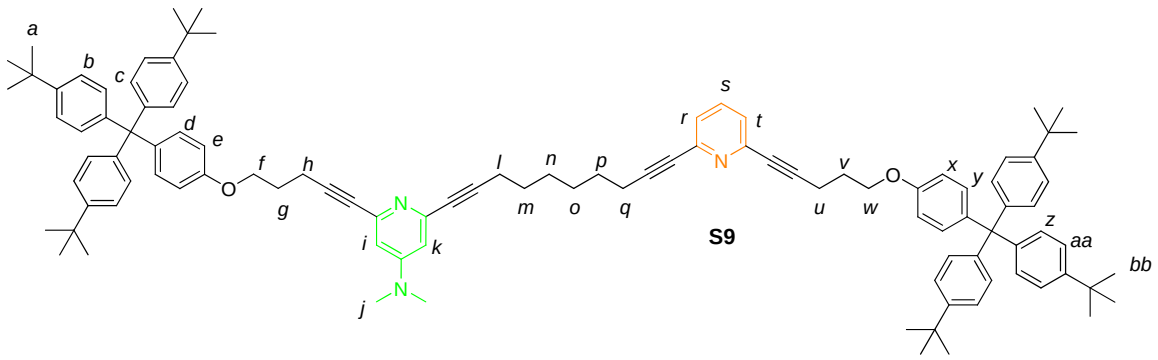


Scheme S3: Synthesis of thread **S10**. Reagents and conditions: (i) **S1**, $Pd(PPh_3)_4$, CuI, THF/Et_3N, 18 h, RT, 44%; (ii) **S3**, $Pd(PPh_3)_2Cl_2$, CuI, THF/Et_3N, 18 h, RT, 32%; (iii) $Pd(OH)_2/C$, H_2, THF, 18 h, RT, 83%.



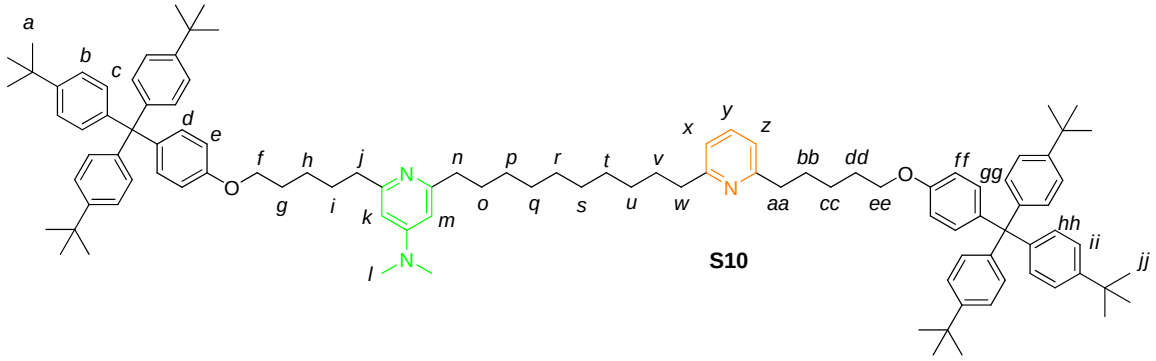
S8

To a solution of 2,6-diiodoDMAP (1.11 g, 2.96 mmol, 1.0 equiv.) and **S1** (1.69 g, 2.96 mmol, 1.0 equiv.) in THF (20 mL) and Et_3N (10 mL) was added $Pd(PPh_3)_4$ (1.03 g, 0.89 mmol, 0.3 equiv.) and CuI (0.338 g, 1.78 mmol, 0.6 equiv.). The resulting mixture was stirred at RT for 18 h. The solvent was removed under reduced pressure and the residue redissolved in EtOAc (50 mL) and washed with a saturated aqueous solution of NH_4Cl (3 x 25 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$), concentrated under reduced pressure and the crude residue purified by column chromatography (1:3 petroleum ether 40-60:CH_2Cl_2) to yield the title compound as a white solid (1.07 g, yield = 44%). m.p. = 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 27H, H_a), 2.04-2.08 (m, 2H, H_g), 2.61 (t, J = 7.0, 2H, H_h), 2.95 (s, 6H, H_j), 4.05 (t, J = 6.0, 2H, H_f), 6.57 (d, J = 2.3, 1H, H_i), 6.77 (d, J = 8.9, 2H, H_e), 6.82 (d, J = 2.3, 1H, H_k), 7.06-7.10 (m, 8H, $H_{c,d}$), 7.23 (d, J = 8.5, 6H, H_b); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 16.2, 28.1, 31.4, 34.3, 39.2, 63.0, 66.1, 80.4, 89.4, 109.7, 113.0, 115.8, 118.3, 124.0, 130.4, 132.2, 139.6, 143.2, 144.1, 148.3, 154.5, 156.6; LREI-MS (3-NOBA matrix): m/z = 816 $[M]^+$; HREI-MS (3-NOBA matrix): m/z = 816.3508 (calcd. for $C_{49}H_{57}INO_2$ 816.3510, $[M]^+$).



S9

To a solution of **S3** (1.12 g, 1.43 mmol, 1.0 equiv.) and **S8** (1.17 g, 1.43 mmol, 1.0 equiv.) in THF (10 mL) and Et_3N (5 mL) was added $Pd(PPh_3)_2Cl_2$ (0.100 g, 0.143 mmol, 0.1 equiv.) and CuI (54.0 mg, 0.286 mmol, 0.2 equiv.). The resulting mixture was stirred at RT for 18 h. The solvent was removed under reduced pressure and the residue was redissolved in EtOAc (30 mL) and washed with a saturated aqueous solution of NH_4Cl (3 x 15 mL) and brine (30 mL). The organic layer was dried ($MgSO_4$), concentrated under reduced pressure and the crude residue purified by column chromatography (1:1 Et_2O:hexane) to yield the title compound as an off-white solid (0.674 g, yield = 32%). m.p. = 164 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.29 (s, 54H, $H_{a,bb}$), 1.42-1.48 (m, 4H, $H_{n,o}$), 1.60-1.64 (m, 4H, $H_{m,p}$), 2.04-2.08 (m, 4H, $H_{g,v}$), 2.38-2.42 (m, 4H, $H_{l,q}$), 2.59-2.63 (m, 4H, $H_{h,u}$), 2.96 (s, 6H, H_j), 4.06 (t, J = 5.6, 4H, $H_{f,w}$), 6.51-6.55 (m, 2H, $H_{i,k}$), 6.74-6.78 (m, 4H, $H_{e,x}$), 7.04-7.12 (m, 16H, $H_{c,d,y,z}$), 7.18-7.25 (m, 14H, $H_{b,r,t,aa}$), 7.51 (t, J = 7.8, 1H, H_s); ^{13}C NMR (200 MHz, $CDCl_3$, 298 K): δ = 16.0, 19.1, 27.8, 27.9 (x 4), 28.2 (x 3), 29.1, 31.1, 33.2, 34.0, 39.1, 62.8, 65.8, 65.9 (x 2), 79.9, 80.0, 80.3 (x 2), 80.4 (x 2), 89.8, 89.9, 108.4, 108.6, 112.7 (x 2), 123.8 (x 2), 125.2, 125.3, 130.5 (x 2), 132.0 (x 2), 136.0, 139.3, 139.4, 143.9 (x 2), 148.0 (x 2), 148.1, 156.3 (x 2), 156.4 (x 2), 160.6 (x 2). LRFAB-MS (3-NOBA matrix): *m/z* = 1469 $[M+H]^+$; HRFAB-MS (3-NOBA matrix): *m/z* = 1468.9521 $[M+H]^+$ (calcd. for $C_{106}H_{122}O_2N_3$, 1468.9532, $[M+H]^+$).



S10

To a solution of **S9** (0.641 g, 0.436 mmol) in THF (10 mL) was added 10% w/w $Pd(OH)_2/C$ (0.256 g, 60% b/w). The suspension was repeatedly degassed and purged with N_2 before being repeatedly degassed and purged with H_2 and then stirred for 18 h at RT under an atmosphere of H_2. The reaction mixture was purified by column chromatography (EtOAc) to yield the title compound as a white solid (0.539 g, yield = 83%). m.p. = 97-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.23-1.38 (m, 66H, $H_{a,p,q,r,s,t,u,jj}$), 1.50-1.54 (m, 4H, $H_{h,cc}$), 1.65-1.84 (m, 12H, $H_{g,i,o,v,bb,dd}$), 2.63-2.67 (m, 4H, $H_{n,j}$), 2.73-2.77 (m, 4H, $H_{w,aa}$), 2.96 (s, 6H, H_l), 3.90-3.94 (m, 4H, $H_{f,ee}$), 6.21 (s, 2H, $H_{k,m}$), 6.72-6.76 (m, 4H, $H_{e,ff}$), 6.93 (d, J = 7.7, 2H, $H_{x,z}$), 7.03-7.10 (m, 16H, $H_{c,d,gg,hh}$), 7.22 (d, J = 8.6, 12H, $H_{b,ii}$), 7.46 (t, J = 7.7, 1H, H_y); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.9 (x 2), 29.1 (x 3), 29.4 (x 2), 29.5 (x 4), 29.6, 29.9, 30.0, 30.1, 30.3, 31.3 (x 2), 34.2 (x 2), 38.4, 38.5, 39.2, 62.9 (x 2), 67.5 (x 2), 102.8 (x 2), 112.8 (x 2), 119.6 (x 2), 123.9 (x 2), 130.6 (x 2), 132.1 (x 2), 136.4, 139.2 (x 2), 144.1 (x 3), 148.1 (x 2), 155.4, 155.7, 155.8, 161.4 (x 2), 161.9; LRFAB-MS (3-NOBA matrix): *m/z* = 1485 $[M+H]^+$. HRFAB-MS (3-NOBA matrix): *m/z* = 1485.0761 $[M+H]^+$ (calcd. for $C_{106}H_{138}O_2N_3$, 1485.0784, $[M+H]^+$).

References:

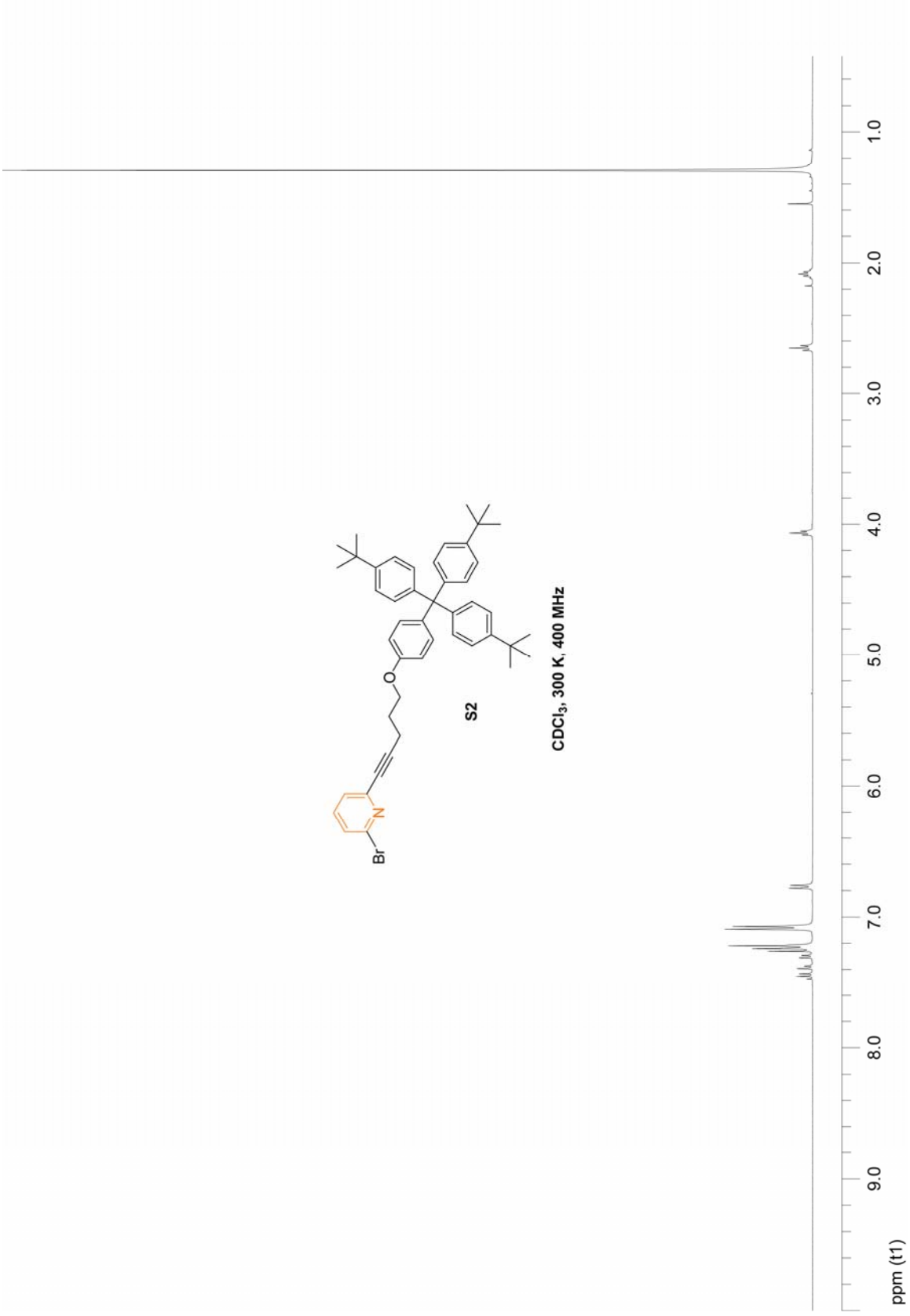
[1] S. M. Goldup, D. A. Leigh, P. J. Lusby, R. T. McBurney, A. M. Z. Slawin, *Angew. Chem. Int. Ed.* 2008, **47**, 3381-3384.

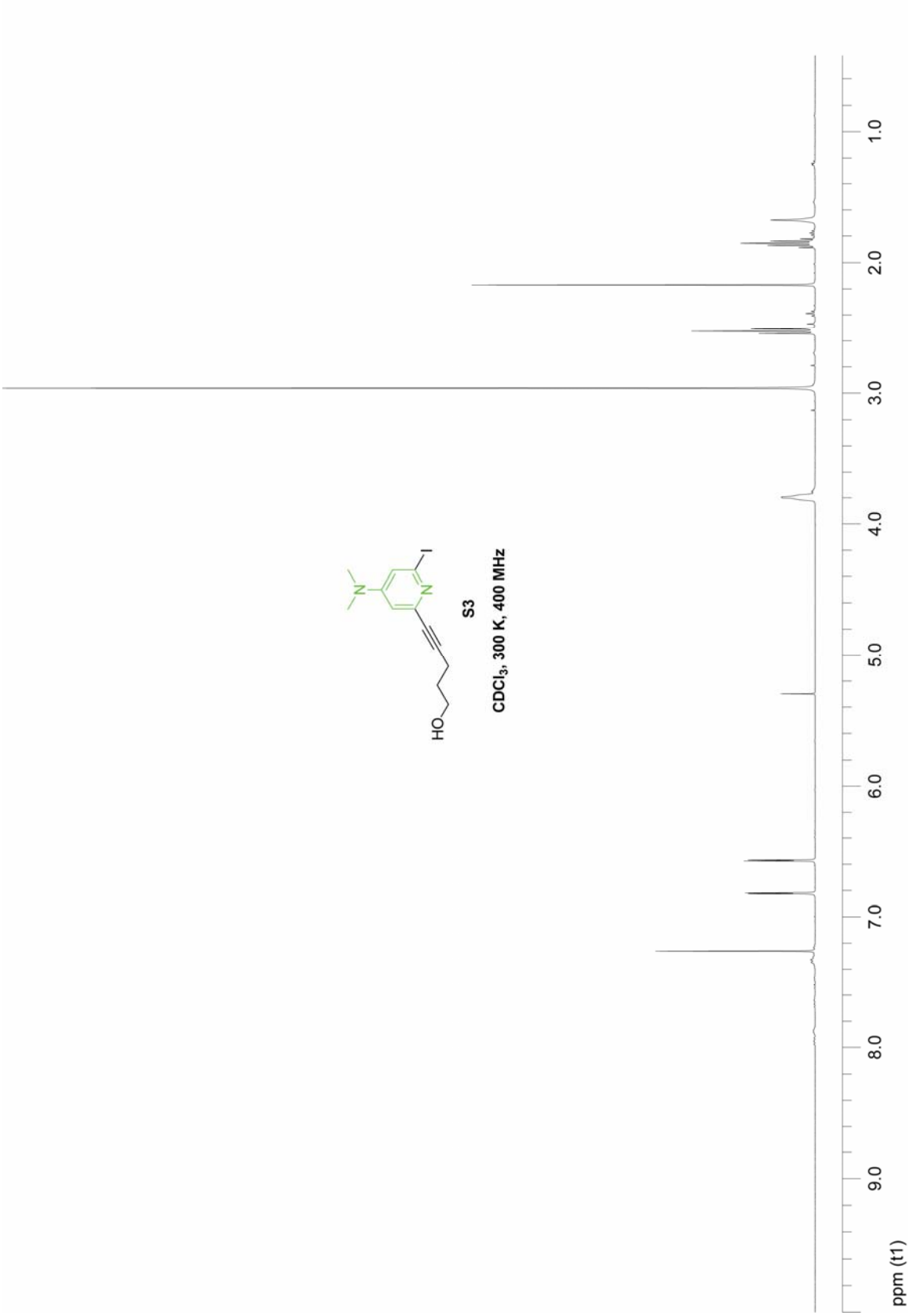
[2] J. Berná, J. D. Crowley, S. M. Goldup, K. D. Hänni, A.-L. Lee, D. A. Leigh, *Angew. Chem. Int. Ed.* 2007, **46**, 5709-5713.

[3] J. D. Crowley, D. A. Leigh, P. J. Lusby, R. T. McBurney, L.-E. Perret-Aebi, C. Petzold, A. M. Z. Slawin, M. D. Symes, *J. Am. Chem. Soc.* 2007, **129**, 15085-15090.

[4] H. W. Gibson, S. H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, *J. Org. Chem.* 1993, **58**, 3748-3756.

Appendix A. ^{1}H NMR of all compounds and complexes

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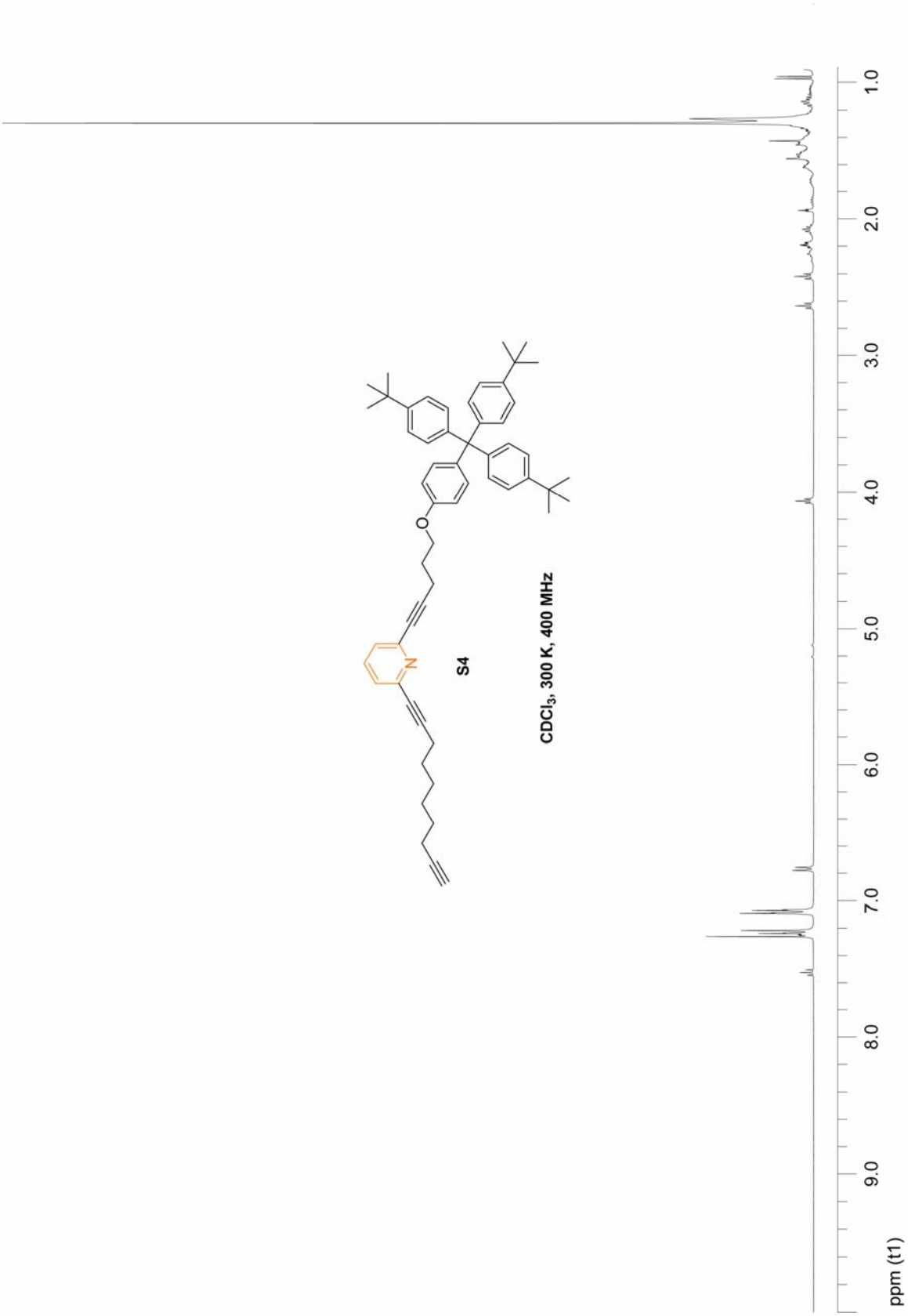
6.0
7.0
8.0
9.0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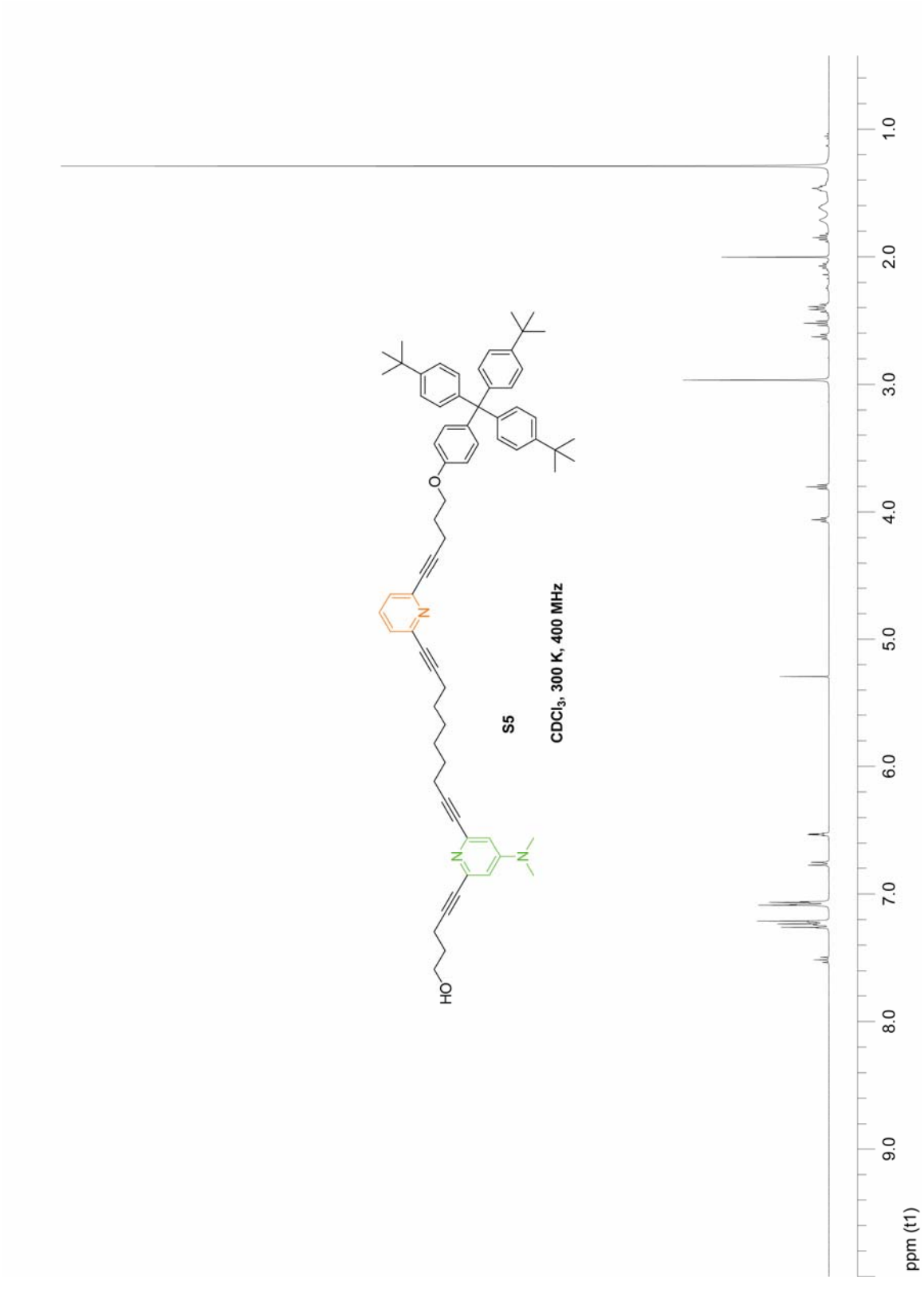
9.0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HO
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N
O
N
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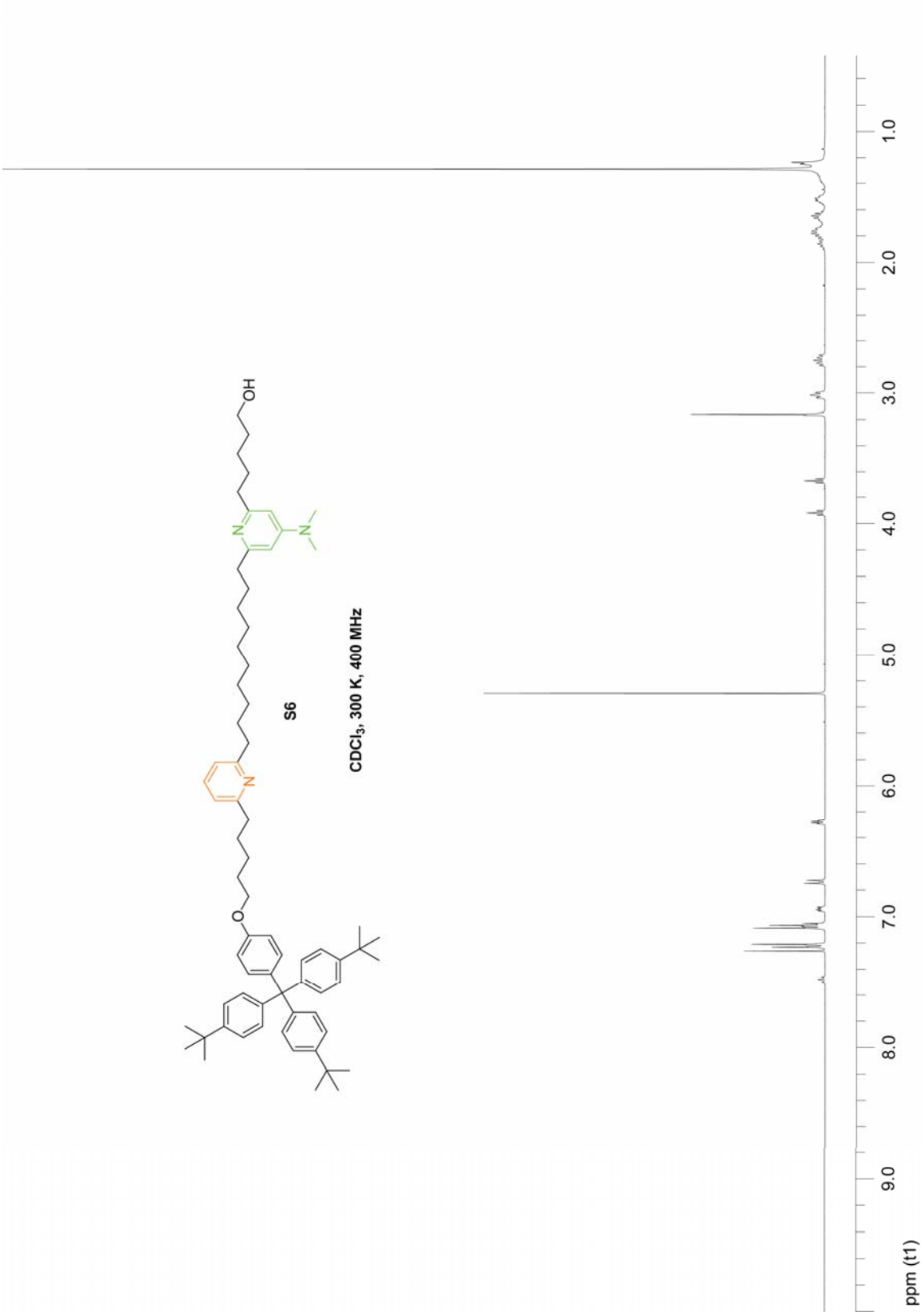
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)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N
N
N
O
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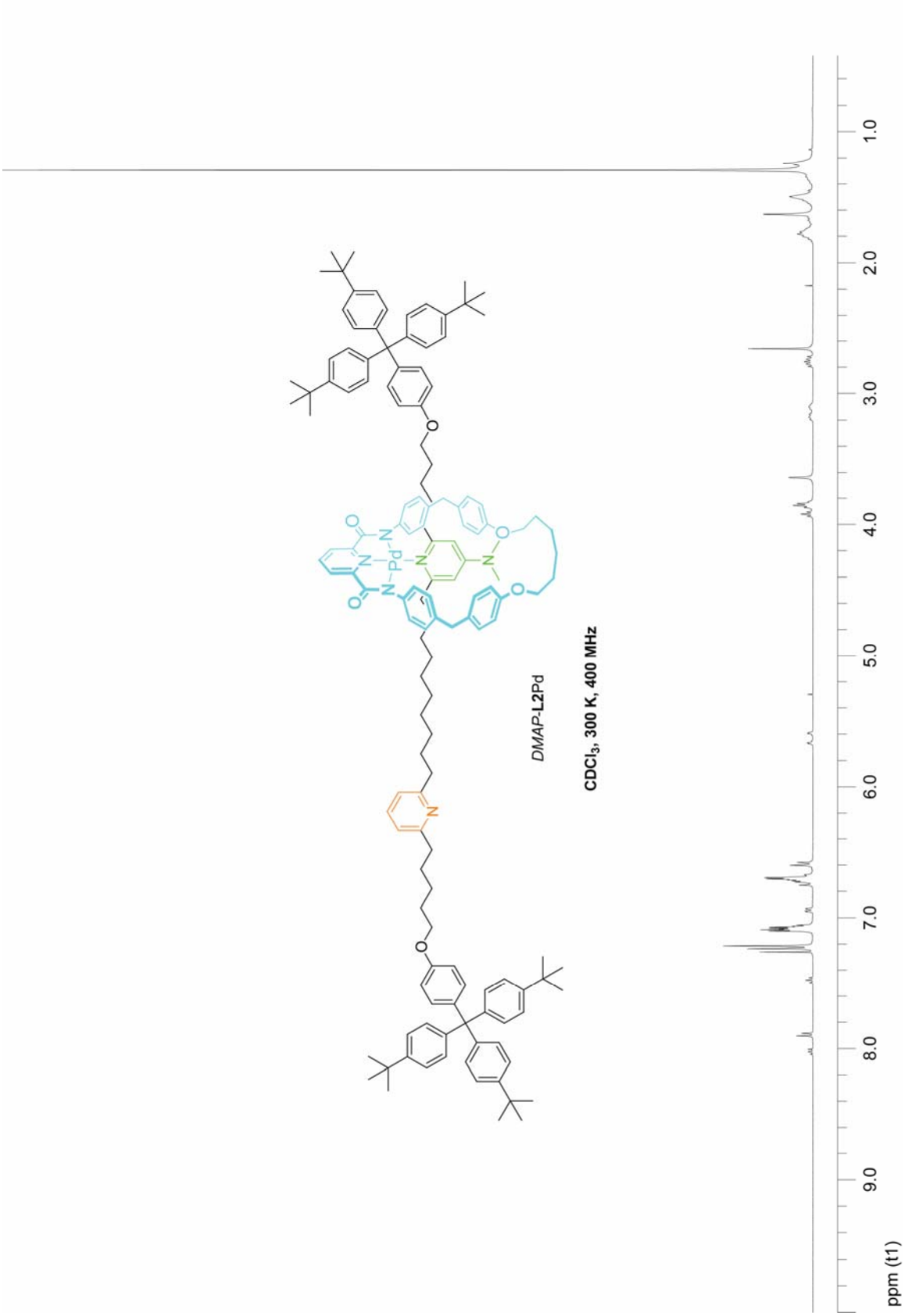
7.0
8.0
9.0
ppm (t1)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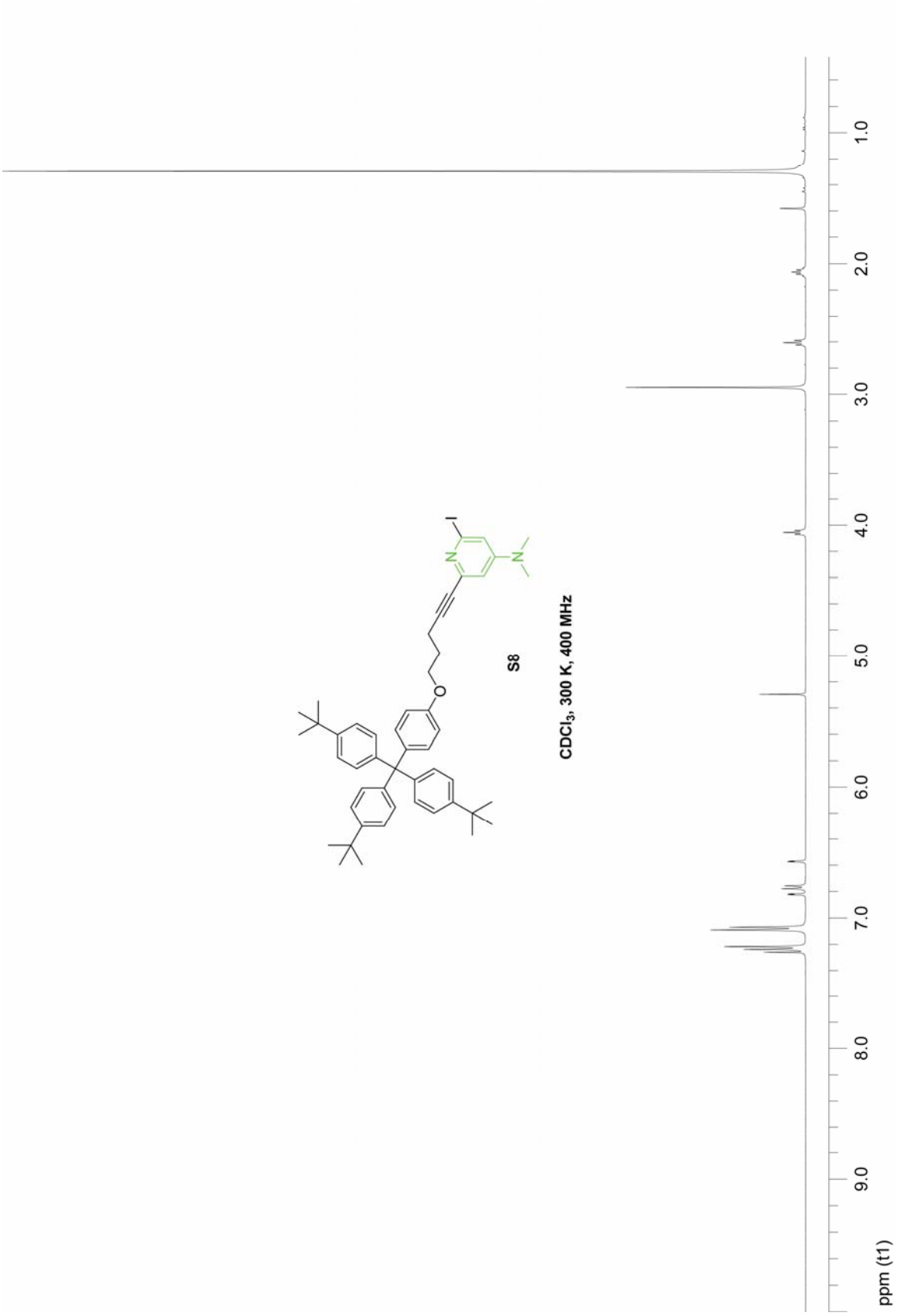
6.0
7.0
8.0
9.0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9.0
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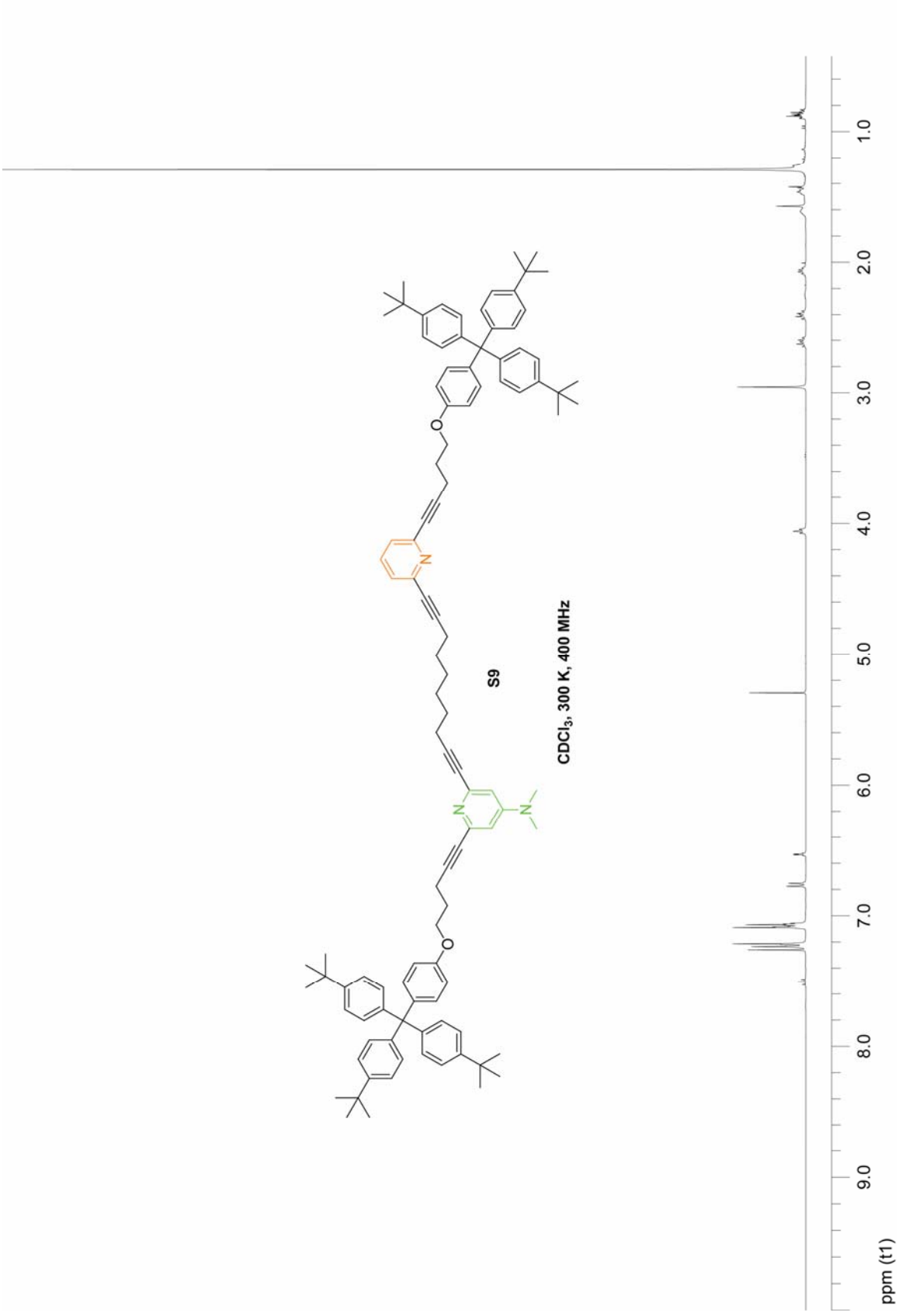
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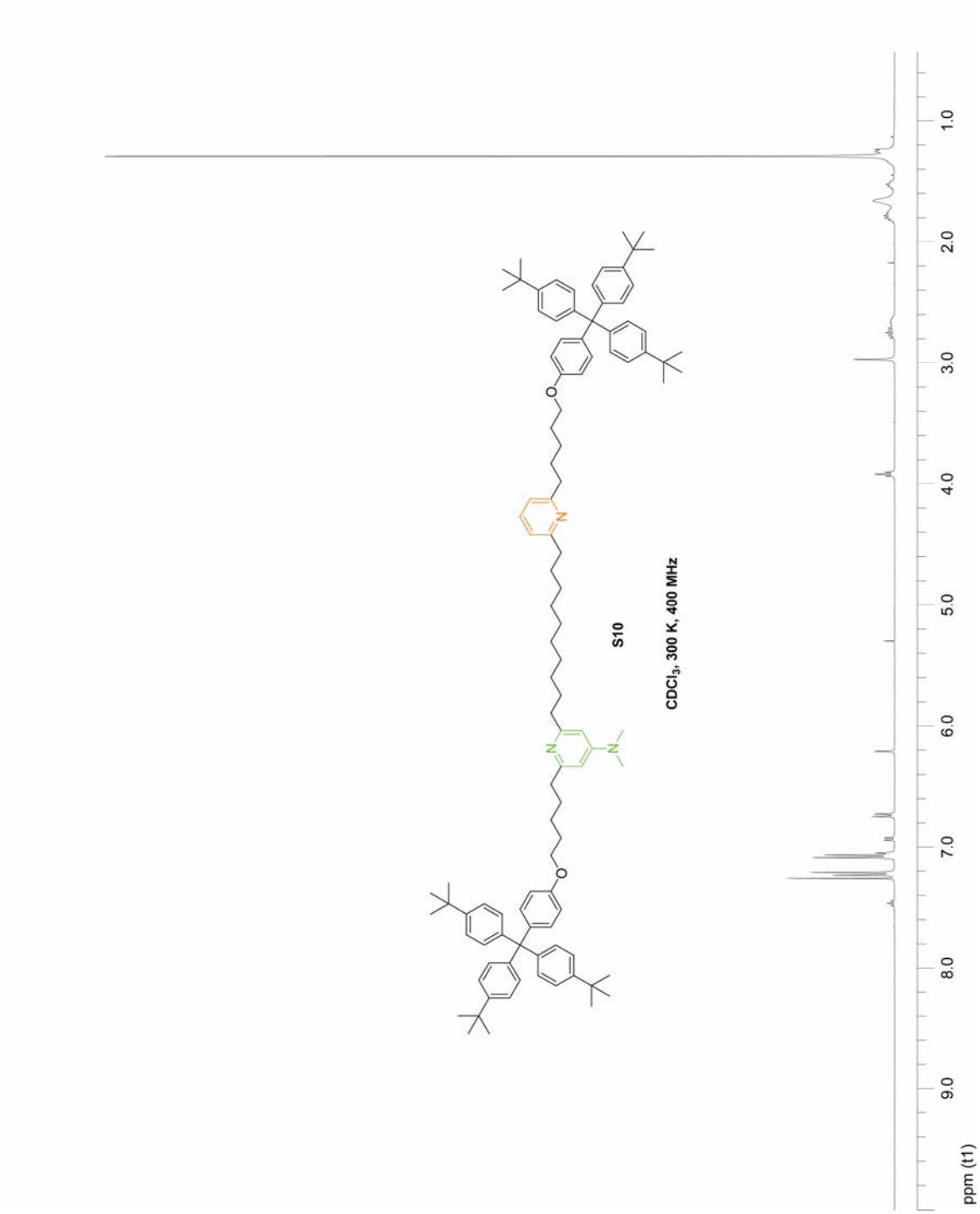
8.0
9.0
ppm (t1)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CDCl3, 300 K, 400 MHz
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6.0
7.0
8.0
9.0
ppm (t1)