Supplementary Material (ESI) for New Journal of Chemistry

Supporting information for

Addressing fluorescence and liquid crystal behaviour in multi-mesogenic BODIPY materials

S1: Experimental procedures

General

Transition temperatures and enthalpies were determined using a Mettler DSC822e differential scanning calorimeter with STARe software, under nitrogen/helium, at a rate of 10°C/min, calibrated with indium (156.6°C, 28.45J g^{-1}) and using an aluminium reference. Optical studies were carried out using an Olympus BH-2 optical polarising microscope equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Photographic images of the mesophases were taken using a JVC digital video camera connected to a PC. Software Studio Capture, supplied by Studio86Designs, was used for image capturing.

NMR spectra were recorded on a Jeol JNM ECP400 spectrometer, with TMS $\delta_H = 0$ as the internal standard or residual protic solvent. [$CDCl_3$, $\delta_H = 7.26$; CD_3OD, $\delta_H = 3.30$]. Chemical shifts are given in ppm (δ) and coupling constants (*J*) are given in Hertz (Hz). ^{1}H-NMR were recorded at 400 MHz; ^{13}C-NMR recorded at 100.5 MHz; ^{11}B-NMR recorded at 128.3 MHz.

UV-visible spectra were measured on a Varian Cary 50 Bio UV-visible Spectrophotometer. Fluorescence spectra were measured using a Varian Cary Eclipse Fluorescence Spectrophotometer. Fluorescence quantum yields were determined using an AMINCO-Bowman Series 2 Spectrofluorometer fitted with an integrating sphere.

Thin-layer chromatography (TLC) was performed using Merck aluminium plates coated with silica gel 60 F_{254} and visualised under UV light or potassium permanganate solution. Column chromatography was performed using MP Silica 32-63, 60 Å. All solvent mixtures are given in v/v ratios.

Materials and methods

4-Hydroxybenzoic acid, 11-bromoundecanol, *N,N'*-diisopropylethylamine, boron trifluoride diethyl etherate and DMAP were purchased from Alfa Aesar and used as received. Sodium hydroxide, potassium carbonate, potassium iodide, DCC, triethylamine, DDQ, pyrrole, TFA, chloranil and (2-biphenyl)di-*tert*-butylphosphine were purchased from Sigma Aldrich and used as received. 4'-(11-Hydroxyundecyl)-biphenyl-4-carbonitrile was purchased from TCI Europe and used as received. 4-Carboxyphenylboronic acid pinacol ester was purchased from Frontier Scientific and used as received. All solvents and desiccants were purchased from Fisher Scientific and used as received. Dibenzylideneacetone palladium (II) was purchased from Strem Chemicals and used as received.

The microwave-assisted reactions were carried out in a CEM Discover System.

Syntheses

4'-(11-Hydroxyundecyloxy)-biphenyl-4-carbonitrile:

4-Hydroxy-4'-cyanobiphenyl (7g, 0.036mol), 11-bromoundecanol (9.50g, 0.038mol), anhydrous potassium carbonate (7.46g, 0.054mol) and potassium iodide (0.60g, 0.0036mol) were added to acetone (150ml) and heated at reflux for 18hrs. The mixture was then cooled to r.t. and filtered. The solvent was removed *in vacuo* and the residue redissolved in dichloromethane (100ml). This solution was washed with 2% $HCl_{(aq)}$ (50ml) and water (2 x 50ml), dried over $MgSO_4$, filtered and evaporated. The residue was recrystallized from ethanol to give the product as an off-white solid (11.84g, 90%). Liquid crystal transitions: Cr 90 N 92 I (lit. Cr 89.8 N 92 I[1]).

^{1}H-NMR [$CDCl_3$, 400MHz] δ 1.29 (12H, m, CH_2's), 1.46 (4H, m, CH_2's), 1.79 (2H, m, CH_2), 3.63 (2H, t, CH_2OH, J = 6.72Hz), 3.99 (2H, t, CH_2O, J = 6.57Hz), 6.98 (2H, d, Ph-

H, *J* = 8.76Hz), 7.51 (2H, d, Ph-H, *J* = 8.44Hz), 7.62 (2H, d, Ph-H, *J* = 8.13Hz), 7.68 (2H, d, Ph-H, *J* = 8.44Hz).

^{13}C-NMR [$CDCl_3$, 100MHz] δ 25.7, 29.35, 29.40, 29.52, 29.56, 32.8, 63.1, 68.2, 110.0, 115.1, 119.1, 127.1, 128.3, 131.2, 132.6, 145.3, 159.8.

HRMS (ESI) = calc. 383.2693, found. 383.2698 ($M + NH_4^+$).

4'-(11-[4-Boronpinacolatephenylcarboxy]undecyloxy)-biphenyl-4-carbonitrile:

4'-(11-Hydroxyundecyl)-biphenyl-4-carbonitrile (0.90g, 2.47mmol) and 4-carboxyphenylboronic acid pinacol ester (0.60g, 2.42mmol) were mixed in dry dichloromethane (50ml). DMAP (0.30g, 2.49mmol) was then added followed by DCC (0.85g, 4.11mmol) and the mixture was stirred at r.t. for 18hrs. The mixture was then filtered and the filtrate washed with 2% $HCl_{(aq)}$ (50ml) and water (3 x 50ml), dried over $MgSO_4$ and evaporated. The residue was recrystallized from EtOAc to yield the pure product as a white solid (0.99g, 69%).

^{1}H-NMR [400MHz, $CDCl_3$] δ 1.31 (10H, m, CH_2's), 1.35 (12H, s, 4 x CH_3), 1.45 (4H, m, CH_2's), 1.78 (4H, m, CH_2's), 4.00 (2H, t, CH_2OPh, *J* = 6.60Hz), 4.31 (2H, t, CH_2O, *J* = 6.69Hz), 6.99 (2H, d, Ph-H, *J* = 8.80Hz), 7.52 (2H, d, Ph-H, *J* = 8.80Hz), 7.63 (2H, d, Ph-H, *J* = 8.80Hz), 7.69 (2H, d, Ph-H, *J* = 8.61Hz), 7.86 (2H, d, Ph-H, *J* = 8.25Hz), 8.01 (2H, d, Ph-H, *J* = 8.43Hz).

^{13}C-NMR [100MHz, $CDCl_3$] δ 24.9, 26.0, 28.7, 29.2, 29.3, 29.5, 29.5, 65.2, 68.2, 84.2, 110.0, 115.1, 119.1, 127.1, 128.3, 128.5, 131.2, 132.6, 132.7, 134.6, 145.3, 159.8, 166.7.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ 29.59.

HRMS (ESI) = calc. 596.3524, found. 596.3548 ($M - H^+$).

4-(11-Hydroxyundecyloxy)-benzoic acid:

4-Hydroxybenzoic acid (6g, 0.043mol) and sodium hydroxide (3.44g in 21ml water) was dissolved in ethanol (100ml) and heated to reflux. 11-Bromoundecanol (8.25g, 0.033mol) in ethanol (25ml) was then added dropwise. Once addition was complete, the mixture was heated at reflux for 16hrs. The mixture was then cooled to r.t. and the ethanol was removed by evaporation *in vacuo*. Water (150ml) was then added and the solution acidified with conc. $HCl_{(aq)}$ and the resulting precipitate filtered off and recrystallized from isopropanol to yield the pure product as a white solid (7.28g, 72%) m.p. 108-110°C (lit. 110°C[2]).

^{1}H-NMR [CD_3OD, 400MHz] δ 1.32 (12H, m, CH_2's), 1.50 (4H, m, CH_2's) 1.78 (2H, m, CH_2), 3.53 (2H, t, CH_2OH, J = 6.57Hz), 4.03 (2H, t, CH_2O, J = 6.57Hz), 6.96 (2H, d, Ph-H, J = 9.07Hz), 7.95 (2H, d, Ph-H, J = 9.07Hz).

^{13}C-NMR [CD_3OD, 100MHz] δ 26.9, 30.59, 30.64, 30.68, 33.7, 63.0, 69.3, 115.1, 123.8, 132.8, 164.6, 169.9.

HRMS (ESI) = calc. 309.2060, found 309.2063 ($M + H^+$).

4-(11-Hydroxyundecyloxy)-phenyl-4'-cyano-4-biphenyl carboxylate:

4-(11-Hydroxyundecyloxy)benzoic acid (2g, 6.48mmol) and 4'-(11-hydroxyundecyl)-biphenyl-4-carbonitrile (1.29g, 6.61mmol) were dissolved in dry dichloromethane (80ml). DCC (2.27g, 0.088mol) and DMAP (0.82g, 6.68mmol) were then added and the mixture was stirred under nitrogen for 20hrs. The mixture was then filtered and the filtrate washed with 2% $HCl_{(aq)}$ (50ml), sat. $Na_2CO_{3(aq)}$ (50ml) and water (2 x 50ml), dried over $MgSO_4$, filtered and evaporated. The residue was recrystallized from ethyl acetate to yield the pure product as a white solid (2.11g, 67%), Cr 125 N 175 I.

^{1}H-NMR [$CDCl_3$, 400MHz] δ 1.29 (12H, m, CH_2), 1.46 (4H, m, CH_2), 1.81 (2H, m, CH_2), 3.63 (2H, t, CH_2OH, *J* = 6.72Hz), 4.03 (2H, t, CH_2OPh, *J* = 6.72Hz), 6.96 (2H, d, Ph-H, *J* = 9.07Hz), 7.31 (2H, d, Ph-H, *J* = 8.76Hz), 7.62 (2H, d, Ph-H, *J* = 8.76Hz), 7.68 (2H, d, Ph-H, *J* = 8.44Hz), 7.71 (2H, d, Ph-H, *J* = 8.76Hz), 8.14 (2H, d, Ph-H, *J* = 8.76Hz).

^{13}C-NMR [$CDCl_3$, 100MHz] δ 25.7, 29.47, 29.50, 29.55, 32.8, 63.1, 68.3, 111.0, 114.4, 118.9, 121.2, 122.6, 127.7, 128.3, 132.3, 132.6, 136.7, 144.9, 151.6, 163.7, 164.8.

HRMS (ESI) = calc. 503.2904, found 503.2899 ($M + NH_4^+$).

4-(11-Carboxy-(4-[boronic acid pinacolate]-phenyl))-phenyl-4'-cyano-4-biphenyl carboxylate (Meso-1):

4-(11-Hydroxyundecyloxy)-phenyl-4'-cyano-4-biphenyl carboxylate (0.80g, 1.64mmol), 4-carboxyphenylboronic acid pinacol ester (0.40g, 1.61mmol), DCC (0.56g, 2.74mmol) and DMAP (0.20g, 1.66mmol) were dissolved in dry dichloromethane (50ml) and the solution was stirred at r.t. for 16hrs. The precipitate was then filtered off and the filtrate was washed with 2% $HCl_{(aq)}$ (40ml) and water (2 x 40ml), dried over $MgSO_4$ and evaporated. The residue was then recrystallized from ethyl acetate to yield the pure product as a white crystalline solid (0.80g, 78%).

^{1}H-NMR [400MHz, $CDCl_3$] δ 1.33 (10H, m, CH_2's), 1.36 (12H, s, 4 x CH_3), 1.47 (4H, m, CH_2's), 1.80 (4H, m, CH_2's), 4.06 (2H, t, CH_2OPh, *J* = 6.51Hz), 4.33 (2H, t, CH_2O, *J* = 6.78Hz), 6.99 (2H, d, Ph-H, *J* = 8.98Hz), 7.34 (2H, d, Ph-H, *J* = 8.61Hz), 7.65 (2H, d, Ph-H, *J* = 8.80Hz), 7.70 (2H, d, Ph-H, *J* = 8.61Hz), 7.75 (2H, d, Ph-H, *J* = 8.61Hz), 7.87 (2H, d, Ph-H, *J* = 8.43Hz), 8.03 (2H, d, Ph-H, *J* = 8.43Hz), 8.16 (2H, d, Ph-H, *J* = 8.98Hz).

^{13}C-NMR [100MHz, $CDCl_3$] δ 24.9, 26.0, 28.7, 29.1, 29.2, 29.3, 29.5, 65.2, 68.4, 84.2, 111.0, 114.4, 118.9, 121.2, 122.6, 127.7, 128.3, 128.5, 132.3, 132.6, 132.7, 134.6, 136.7, 144.9, 151.6, 163.7, 164.8, 166.7.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ 29.74.

HRMS (ESI) = calc. 733.4026, found 733.4011 ($M + NH_4^+$).

8-(3,5-Dibromophenyl)-BODIPY (A):

3,5-Dibromobenzaldehyde (1.5g, 5.68mmol) was dissolved in freshly distilled pyrrole (15.8ml, 0.23mol) and the solution was degassed with argon for 20mins. TFA (0.1ml) was then added and the mixture stirred at r.t. under argon and protected from light for 15mins. The excess pyrrole was then removed by evaporation *in vacuo* and the oily residue was passed through a short silica column eluting with 1:4 hexane:CH_2Cl_2. The combined eluant was reduced by evaporated *in vacuo*. The residue was dissolved in THF (50ml) and chloranil (1.40g, 5.68mmol) was added. The mixture was stirred at r.t. for 16hrs. The THF was then removed by evaporation *in vacuo* and the residue redissolved in dichloromethane before filtering to remove the quinine species. The dichloromethane solution was concentrated *in vacuo* to 50ml before diisopropylethylamine (4.61ml, 26.5mmol) was added followed by boron trifluoride diethyl etherate (3.79ml, 29.9mmol) and the solution was stirred under nitrogen for 18hrs. The solution was then filtered through Celite then washed with water (6 x 50ml), dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography eluting with 1:4 hexane:toluene to yield the pure product as a shiny red solid (0.7g, 29%), m.p. 178-179°C, lit. 178-179°C[3].

^{1}H-NMR [400MHz, $CDCl_3$] δ 6.58 (2H, d, Py-H), 6.90 (2H, d, Py-H), 7.64 (2H, m, Ph-H), 7.89 (1H, m, Ph-H), 7.97 (2H, m, Py-H).

^{13}C-NMR [100MHz, $CDCl_3$] δ 119.2, 123.1, 131.2, 131.6, 134.5, 136.0, 136.8, 143.0, 145.36.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ -0.73.

HRMS (ESI) = calc. 426.9246, found. 426.9242 ($M + H^+$).

8-(3,5-Dibromophenyl)-1,3,5,7-tetramethyl-BODIPY (B):

3,5-Dibromobenzaldehyde (1.5g, 5.68mmol) and 2,4-dimethylpyrrole (1.17ml, 11.36mmol) were dissolved in dry dichloromethane (70ml) and degassed with argon for 20mins. TFA (0.1ml) was then added and the solution was stirred at r.t. under argon for 16hrs. DDQ (1.29g, 5.68mmol) was added and the mixture was stirred for 6hrs. Triethylamine (3.69ml, 26.5mmol) was then added followed by boron trifluoride diethyl etherate (3.79ml, 29.9mmol) and the solution was stirred under argon for 18hrs. The mixture was then filtered and washed with water (6 x 60ml), dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by column chromatography eluting with 1:1 hexane:CH_2Cl_2 to yield the pure product as a bright red solid (186mg, 7%), m.p. 257-258°C (decomp.).

^{1}H-NMR [400MHz, $CDCl_3$] δ 1.47 (6H, s, 2 x CH_3), 2.53 (6H, s, 2 x CH_3), 6.00 (2H, s, Py-H), 7.42 (2H, m, Ph-H), 7.80 (1H, m, Ph-H).

^{13}C-NMR [100MHz, $CDCl_3$] δ 14.6, 14.9, 121.7, 123.6, 130.1, 130.9, 134.7, 137.4, 138.4, 142.7, 156.5.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ -0.49.

HRMS (ESI) = calc. 482.9876, found. 482.9867 ($M + H^+$).

8-(3,5-Dibromophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-BODIPY (C):

3,5-Dibromobenzaldehyde (1.5g, 5.68mmol) and kryptopyrrole (1.53ml, 11.36mmol) were dissolved in dry dichloromethane (40ml) and degassed with argon for 20mins. TFA (0.1ml) was then added and the solution was stirred at r.t. under argon for 16hrs. DDQ (1.29g, 5.68mmol) was added and the mixture was stirred for 6hrs. Triethylamine

(3.69ml, 26.5mmol) was then added followed by boron trifluoride diethyl etherate (3.79ml, 29.9mmol) and the solution was stirred under argon for 18hrs. The mixture was filtered and washed with water (6 x 60ml), dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by column chromatography eluting with 3:2 toluene:hexane to yield the pure product as a bright red solid (384mg, 13%), m.p. 241-242°C.

^{1}H-NMR [400MHz, $CDCl_3$] δ 0.99 (6H, t, C**H$_3$**CH$_2$, *J* = 7.50Hz), 1.39 (6H, s, 2 x CH_3), 2.31 (4H, q, C**H$_2$**CH$_3$, *J* = 7.50Hz), 2.53 (6H, s, 2 x CH_3), 7.44 (2H, d, Ph-H), 7.81 (1H, t, Ph-H).

^{13}C-NMR [100MHz, $CDCl_3$] δ 12.2, 12.6, 14.6, 17.1, 123.5, 130.4, 133.4, 134.5, 135.9, 137.8, 139.3, 154.8.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ -0.24.

HRMS (ESI) = calc. 539.0503, found. 539.0495 ($M + H^+$).

8-(3,5-Bis[11-carboxyphenylundecyloxybiphenyl-4-carbonitrile]-phenyl)-BODIPY (1):

8-(3,5-Dibromophenyl)-BODIPY (40mg, 93.9μmol), 4'-(11-[4-boronpinacolatephenylcarboxy]undecyloxy)-biphenyl-4-carbonitrile (134mg, 0.225mmol), dibenzylideneacetone palladium (II) (34mg, 37.6μmol), (2-biphenyl)di-*tert*-butylphosphine (14mg, 47.0μmol) and potassium carbonate (65mg, 0.470mmol) were mixed in DMF (6ml) and the mixture was degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was removed *in vacuo* and the residue subjected to column chromatography eluting with 1:99 EtOAc:toluene. The residue was then precipitated from CH_2Cl_2 with cold MeOH to yield the pure product as a bright red solid (78mg, 69%), m.p. 78-79°C, R_f = 0.17 (toluene).

^{1}H-NMR [400MHz, $CDCl_3$] δ 1.32 (20H, m, CH_2's), 1.45 (8H, m, CH_2's), 1.80 (8H, m, CH_2's), 4.00 (4H, t, 2 x CH_2OPh, J = 6.57Hz), 4.36 (4H, t, 2 x CH_2O, J = 6.57Hz), 6.58 (2H, m, Py-H), 6.97 (4H, d, Ph-H, J = 8.76Hz), 7.01 (2H, m, Py-H), 7.51 (4H, d, Ph-H, J = 8.76Hz), 7.63 (4H, d, Ph-H, J = 8.44Hz), 7.68 (4H, d, Ph-H, J = 8.44Hz), 7.75 (4H, d, Ph-H, J = 8.44Hz), 7.82 (2H, d, Ph-H), 7.99 (2H, m, Py-H), 8.05 (1H, t, Ph-H), 8.18 (4H, d, Ph-H, J = 8.44Hz).

^{13}C-NMR [100MHz, $CDCl_3$] δ 26.0, 28.8, 29.2, 29.3, 29.5, 65.4, 68.2, 110.1, 115.1, 118.9, 119.1, 127.1, 127.3, 128.3, 128.5, 130.3, 130.4, 131.2, 131.3, 132.6, 134.9, 135.1, 141.3, 143.8, 144.8, 145.3, 159.8, 166.3.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ -0.49.

MS (MALDI) = calc. 1202.6, found. 1202.6 (M^+).

8-(3,5-Bis[11-carboxyphenylundecyloxybiphenyl-4-carbonitrile]-phenyl)-1,3,5,7-tetramethyl-BODIPY (2):

8-(3,5-Dibromophenyl)-1,3,5,7-tetramethyl-BODIPY (45mg, 93.4μmol), 4'-(11-[4-boronpinacolatephenylcarboxy]undecyloxy)-biphenyl-4-carbonitrile (134mg, 0.224mmol), dibenzylideneacetone palladium (II) (34mg, 37.4μmol), (2-biphenyl)di-*tert*-butylphosphine (14mg, 46.7μmol) and potassium carbonate (65mg, 0.467mmol) were mixed in DMF (6ml) and the mixture was degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was then removed by evaporation *in vacuo* and the residue subjected to column chromatography eluting with 1:99 EtOAc:toluene. The residue was then precipitated from CH_2Cl_2 with cold MeOH to yield the pure product as a bright red solid (30mg, 25%), m.p. 73-74°C, R_f = 0.18 (toluene).

^{1}H-NMR [400MHz, $CDCl_3$] δ 1.32 (20H, m, CH_2's), 1.46 (8H, m, CH_2's), 1.50 (6H, s, 2 x CH_3), 1.80 (8H, m, CH_2's), 2.58 (6H, s, 2 x CH_3), 3.99 (4H, t, 2 x CH_2OPh, J =

6.57Hz), 4.35 (4H, t, 2 x CH_2O, *J* = 6.57Hz), 6.01 (2H, s, Py-H), 6.98 (4H, d, Ph-H, *J* = 8.76Hz), 7.51 (4H, d, Ph-H, *J* = 8.76Hz), 7.62 (6H, m, Ph-H), 7.68 (4H, d, Ph-H, *J* = 8.60Hz), 7.72 (4H, d, Ph-H, *J* = 8.44Hz), 7.98 (1H, t, Ph-H), 8.14 (4H, d, Ph-H, *J* = 8.44Hz).

^{13}C-NMR [100MHz, $CDCl_3$] δ 14.6, 14.9, 26.0, 28.7, 29.21, 29.25, 29.4, 29.5, 65.3, 68.2, 110.0, 115.1, 119.1, 121.5, 126.5, 127.0, 127.1, 128.3, 129.3, 130.3, 131.3, 132.6, 141.8, 142.8, 143.9, 145.3, 156.0, 159.8, 166.3.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ 0.00.

MS (MALDI) = calc. 1258.7, found. 1258.6 (M^+).

8-(3,5-Bis[11-carboxyphenylundecyloxybiphenyl-4-carbonitrile]-phenyl)-1,3,5,7-tetramethyl-2,6-diethyl-BODIPY (3):

8-(3,5-Dibromophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-BODIPY (50mg, 92.9μmol), 4'-(11-[4-boronpinacolatephenylcarboxy]undecyloxy)-biphenyl-4-carbonitrile (133mg, 0.223mmol), dibenzylideneacetone palladium (II) (34mg, 37.2μmol), (2-biphenyl)di-*tert*-butylphosphine (14mg, 46.5μmol) and potassium carbonate (64mg, 0.465mmol) were mixed in DMF (6ml) and the mixture was degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was then removed by evaporation *in vacuo* and the residue subjected to column chromatography eluting with 1:99 EtOAc:toluene. The residue was then precipitated from CH_2Cl_2 with cold MeOH to yield the pure product as a bright red solid (56mg, 46%), m.p. 87-88°C, R_f = 0.18 (toluene).

^{1}H-NMR [400MHz, $CDCl_3$] δ 0.99 (6H, t, 2 x C**H$_3$**CH_2, *J* = 7.52Hz), 1.32 (20H, m, CH_2's), 1.40 (6H, s, 2 x CH_3), 1.47 (8H, m, CH_2's), 1.80 (8H, m, CH_2's), 2.30 (4H, q, C**H$_2$**CH_3, *J* = 7.50Hz), 2.53 (6H, s, 2 x CH_3), 3.99 (4H, t, 2 x CH_2OPh, *J* = 6.42Hz), 4.35 (4H, t, 2 x CH_2O, *J* = 6.69Hz), 6.98 (4H, d, Ph-H, *J* = 8.80Hz), 7.52 (4H, d, Ph-H, *J* =

8.61Hz), 7.62 (6H, m, Ph-H), 7.69 (4H, d, Ph-H, J = 8.06Hz), 7.74 (4H, d, Ph-H, J = 8.43Hz), 7.98 (1H, t, Ph-H), 8.15 (4H, d, Ph-H, J = 8.25Hz).

^{13}C-NMR [100MHz, $CDCl_3$] δ 12.2, 12.6, 14.6, 17.1, 26.0, 28.7, 29.21, 29.25, 29.4, 29.5, 65.3, 68.2, 110.0, 115.1, 119.1, 126.8, 127.0, 127.1, 127.2, 128.3, 130.0, 130.3, 131.3, 132.5, 133.1, 137.3, 141.7, 144.0, 145.3, 154.3, 159.8, 166.3.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ 0.00.

MS (MALDI) = calc. 1314.7, found. 1314.6 (M^+).

8-(3,5-Bis[11-carboxyphenylundecyloxy-phenyl-4'-cyano-4-biphenyl-carboxylate]-phenyl)-BODIPY (4):

8-(3,5-Dibromophenyl)-BODIPY (35mg, 82.2μmol), 4-(11-[4-boronpinacolatephenylcarboxy]undecyloxy)-phenyl-4'-cyano-4-biphenyl carboxylate (125mg, 0.197mmol), dibenzylideneacetone palladium (II) (30mg, 32.9μmol), (2-biphenyl)di-*tert*-butylphosphine (12mg, 41.1μmol) and potassium carbonate (57mg, 0.411mmol) were mixed in DMF (6ml) and the mixture was degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was removed by evaporation *in vacuo* and the residue subjected to column chromatography eluting with 1:99 EtOAc:toluene. The residue was then precipitated from CH_2Cl_2 with cold MeOH to yield the pure product as a bright red solid (56mg, 47%), R_f = 0.19 (toluene).

^{1}H-NMR [400MHz, $CDCl_3$] δ 1.33 (20H, m, CH_2's), 1.47 (8H, m, CH_2's), 1.80 (8H, m, CH_2's), 4.04 (4H, t, 2 x CH_2OPh, J = 6.57Hz), 4.36 (4H, t, 2 x CH_2O, J = 6.72Hz), 6.58 (2H, m, Py-H), 6.97 (4H, d, Ph-H, J = 9.07Hz), 7.01 (2H, m, Py-H), 7.32 (4H, d, Ph-H, J = 8.76Hz), 7.63 (4H, d, Ph-H, J = 8.76Hz), 7.68 (4H, d, Ph-H, J = 8.44Hz), 7.74 (8H, m, Ph-H), 7.82 (2H, d, Ph-H), 7.99 (2H, m, Py-H), 8.05 (1H, t, Ph-H), 8.16 (8H, m, Ph-H).

^{13}C-NMR [100MHz, $CDCl_3$] δ 25.99, 26.04, 28.7, 29.1, 29.3, 29.4, 29.5, 65.4, 68.4, 111.0, 114.4, 118.9, 121.2, 122.6, 127.3, 127.7, 128.4, 130.3, 130.4, 131.5, 132.4, 132.7, 135.0, 135.3, 136.7, 141.3, 143.7, 144.7, 144.8, 151.5, 163.7, 164.8, 166.3.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ -0.67.

MS (MALDI) = calc. 1465.6, found. 1465.7 ($M + Na^+$).

8-(3,5-Bis[11-carboxyphenylundecyloxy-phenyl-4'-cyano-4-biphenyl-carboxylate]-phenyl)-1,3,5,7-tetramethyl-BODIPY (5):

8-(3,5-Dibromophenyl)-1,3,5,7-tetramethyl-BODIPY (40mg, 82.2μmol), 4-(11-[4-boronpinacolatephenylcarboxy]undecyloxy)-phenyl-4'-cyano-4-biphenyl carboxylate (125mg, 0.197mmol), dibenzylideneacetone palladium (II) (30mg, 32.9μmol), (2-biphenyl)di-*tert*-butylphosphine (12mg, 41.1μmol) and potassium carbonate (57mg, 0.411mmol) were mixed in DMF (6ml) and the mixture was degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was removed by evaporation *in vacuo* and the residue subjected to column chromatography eluting with 1:99 EtOAc:toluene. The residue was then precipitated from CH_2Cl_2 with cold MeOH to yield the pure product as a bright red solid (36mg, 29%), R_f = 0.52 (15:85 EtOAc:toluene).

^{1}H-NMR [400MHz, $CDCl_3$] δ 1.31 (24H, m, CH_2's), 1.44 (8H, m, CH_2's), 1.49 (6H, s, 2 x CH_3), 1.78 (8H, m, CH_2's), 2.56 (6H, s, 2 x CH_3), 4.02 (4H, t, 2 x CH_2OPh, J = 6.57Hz), 4.33 (4H, t, 2 x CH_2O, J = 6.73Hz), 6.00 (2H, s, Py-H), 6.95 (4H, d, Ph-H, J = 8.76Hz), 7.30 (4H, d, Ph-H, J = 8.44Hz), 7.61 (6H, m, Ph-H), 7.67 (4H, d, Ph-H, J = 8.44Hz), 7.71 (8H, m, Ph-H), 7.96 (1H, t, Ph-H), 8.13 (8H, d, Ph-H, J = 8.76Hz).

^{13}C-NMR [100MHz, $CDCl_3$] δ 14.9, 26.0, 28.7, 29.1, 29.26, 29.34, 29.5, 65.3, 68.4, 114.4, 118.9, 122.6, 127.0, 127.7, 128.3, 130.2, 130.3, 132.3, 132.7, 136.7, 143.9, 144.9, 151.6, 163.6, 164.8, 166.3.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ -0.24.

MS (MALDI) = calc. 1498.7, found. 1498.7 (M^+).

8-(3,5-Bis[11-carboxyphenylundecyloxy-phenyl-4'-cyano-4-biphenyl-carboxylate]-phenyl)-1,3,5,7-tetramethyl-2,6-diethyl-BODIPY (6):

8-(3,5-Dibromophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-BODIPY (44mg, 82.2μmol), 4-(11-[4-boronpinacolatephenylcarboxy]undecyloxy)-phenyl-4'-cyano-4-biphenyl carboxylate (125mg, 0.197mmol), dibenzylideneacetone palladium (II) (30mg, 32.9μmol), (2-biphenyl)di-*tert*-butylphosphine (12mg, 41.1μmol) and potassium carbonate (57mg, 0.411mmol) were mixed in DMF (6ml) and the mixture was degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was removed by evaporation *in vacuo* and the residue subjected to column chromatography eluting with 2:98 EtOAc:toluene. The residue was then precipitated from CH_2Cl_2 with cold MeOH to yield the pure product as a bright red solid (57mg, 45%), R_f = 0.63 (1:9 EtOAc:toluene).

^{1}H-NMR [400MHz, $CDCl_3$] δ 0.99 (6H, t, 2 x C**H$_3$**CH_2, J = 7.66Hz), 1.33 (20H, m, CH_2's), 1.41 (6H, s, 2 x CH_3), 1.46 (8H, m, CH_2's), 1.80 (8H, m, CH_2's), 2.30 (4H, q, 2 x C**H$_2$**CH_3, J = 7.50Hz), 2.55 (6H, s, 2 x CH_3), 4.04 (4H, t, 2 x CH_2OPh, J = 6.57Hz), 4.35 (4H, t, 2 x CH_2O, J = 6.73Hz), 6.98 (4H, d, Ph-H, J = 8.76Hz), 7.32 (4H, d, Ph-H, J = 8.76Hz), 7.63 (6H, m, Ph-H), 7.68 (4H, d, Ph-H, J = 8.44Hz), 7.74 (8H, d, Ph-H, J = 8.44Hz), 7.99 (1H, t, Ph-H), 8.15 (8H, d, Ph-H, J = 8.76Hz).

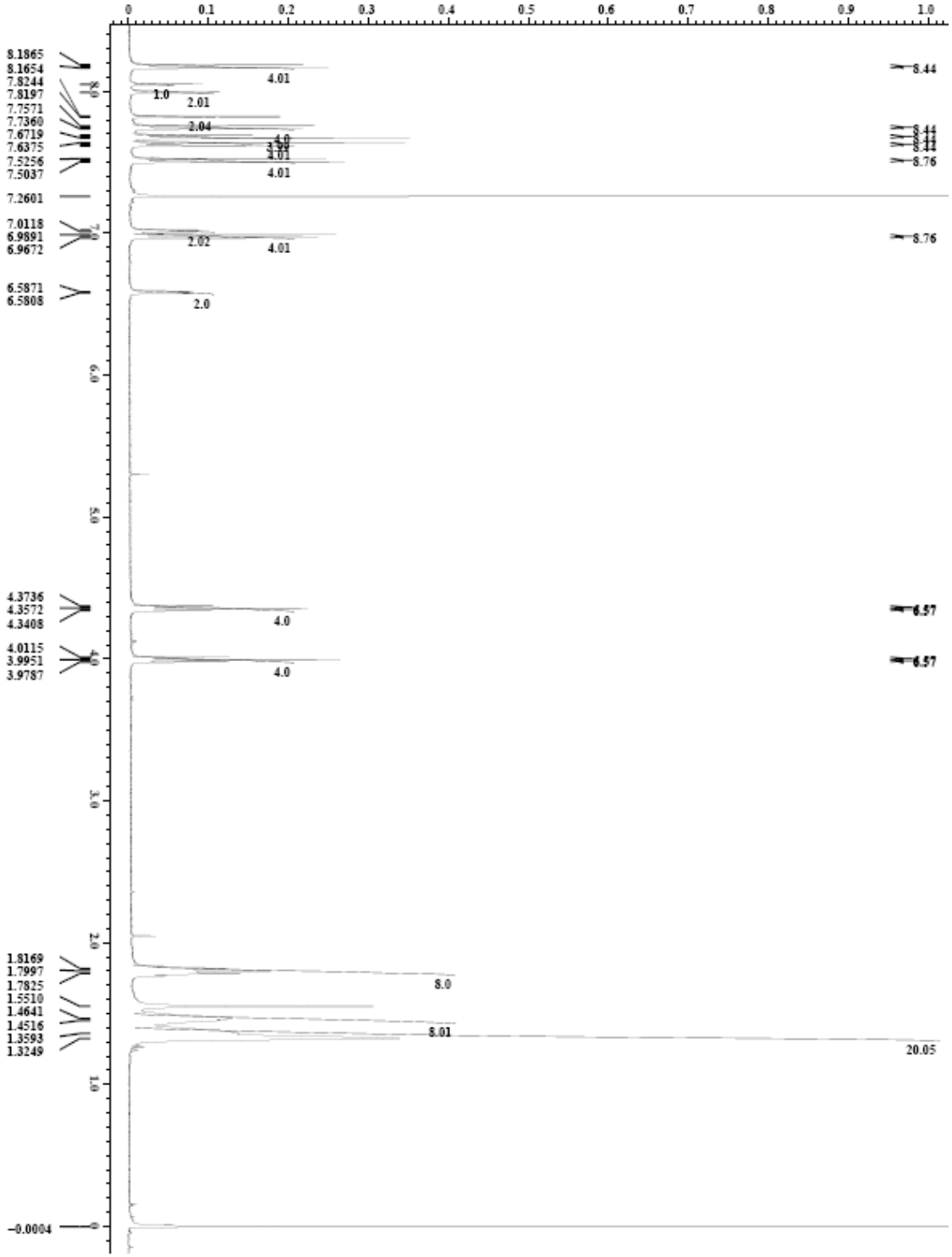
^{13}C-NMR [100MHz, $CDCl_3$] δ 12.2, 12.6, 14.6, 17.1, 26.00, 26.03, 28.7, 29.1, 29.3, 29.4, 29.5, 53.4, 65.3, 68.4, 111.0, 114.4, 118.9, 121.2, 122.6, 126.8, 127.0, 127.7, 128.4, 130.1, 132.4, 132.7, 133.1, 136.7, 138.0, 141.7, 144.1, 144.9, 151.6, 154.3, 163.7, 164.8, 166.3.

^{11}B-NMR [128.3MHz, $CDCl_3$] δ 0.00.

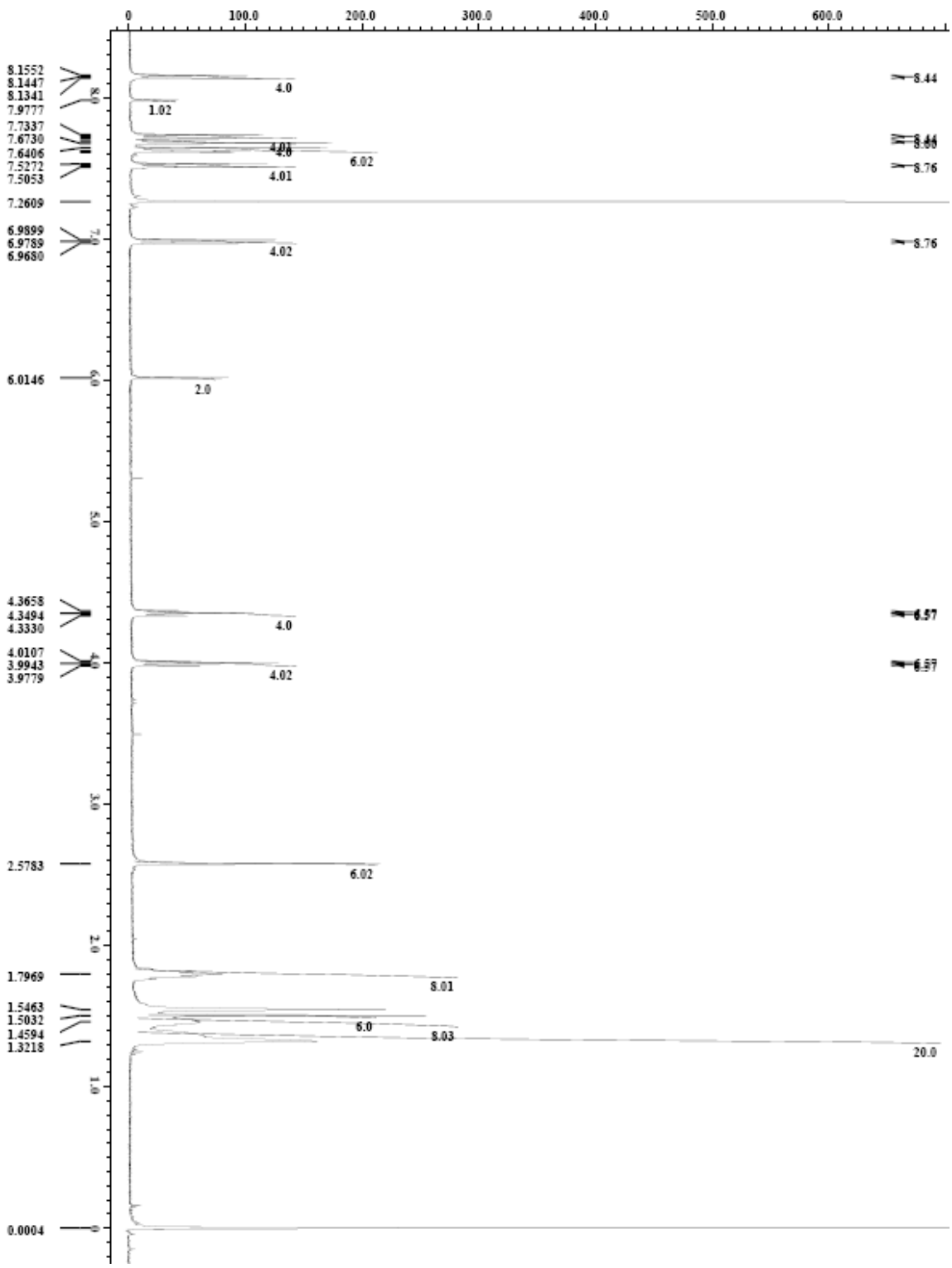
MS (MALDI) = calc. 1555.6, found. 1553.8 ($M - H^+$).

S2: ^{1}H-NMR spectra for compounds 1-6

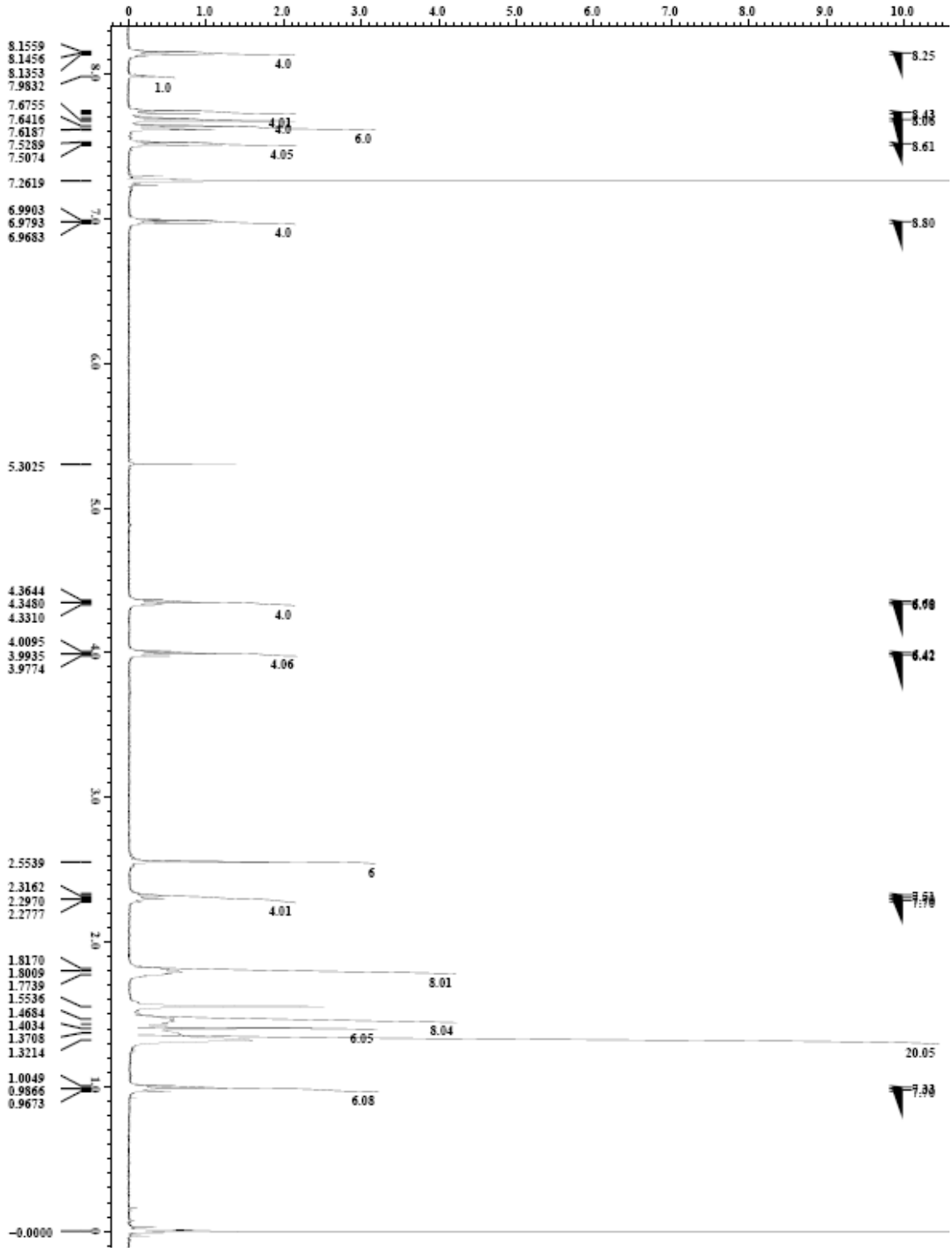
^{1}H-NMR spectrum for compound 1:



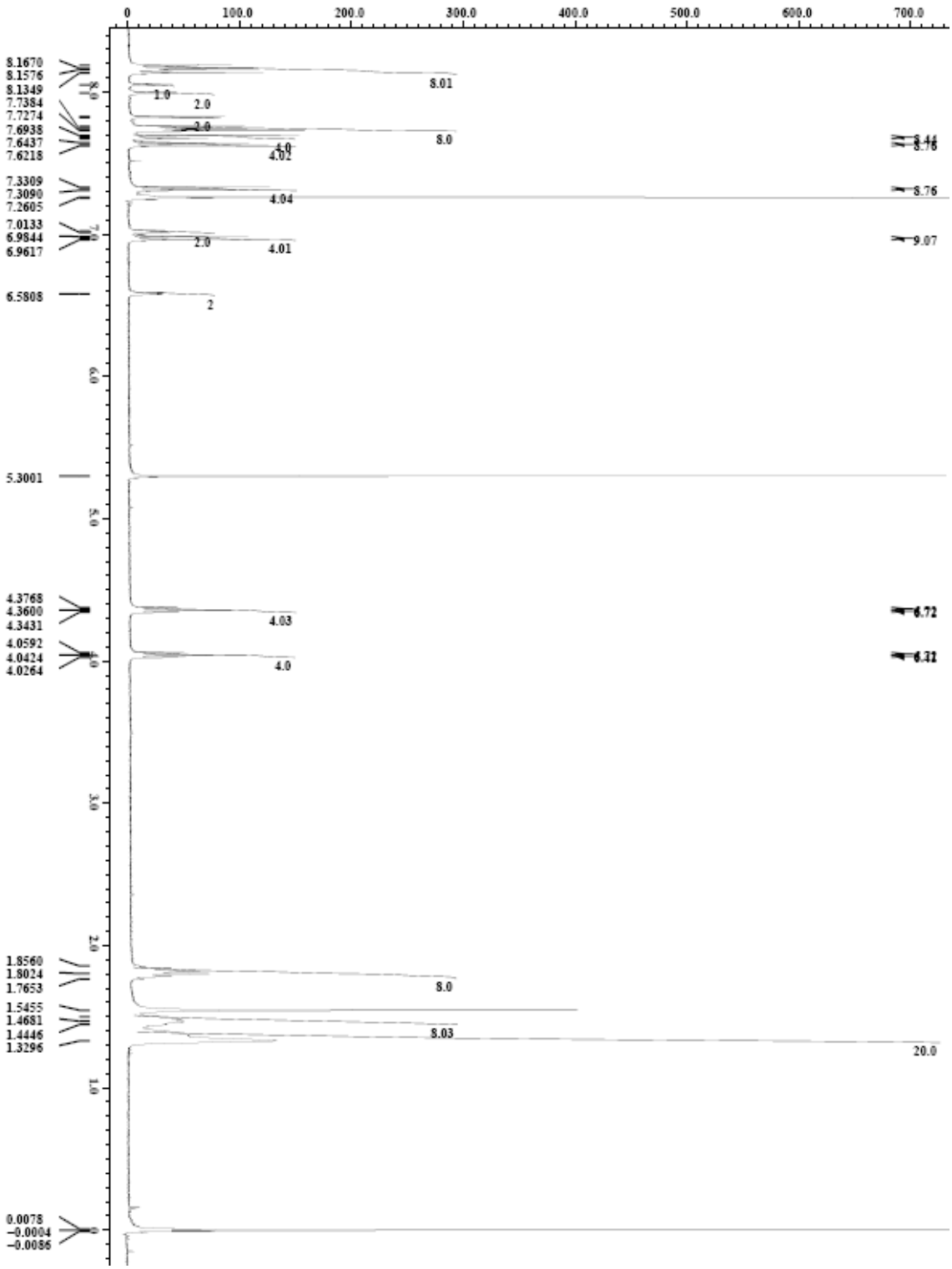
^{1}H-NMR spectrum for compound 2:



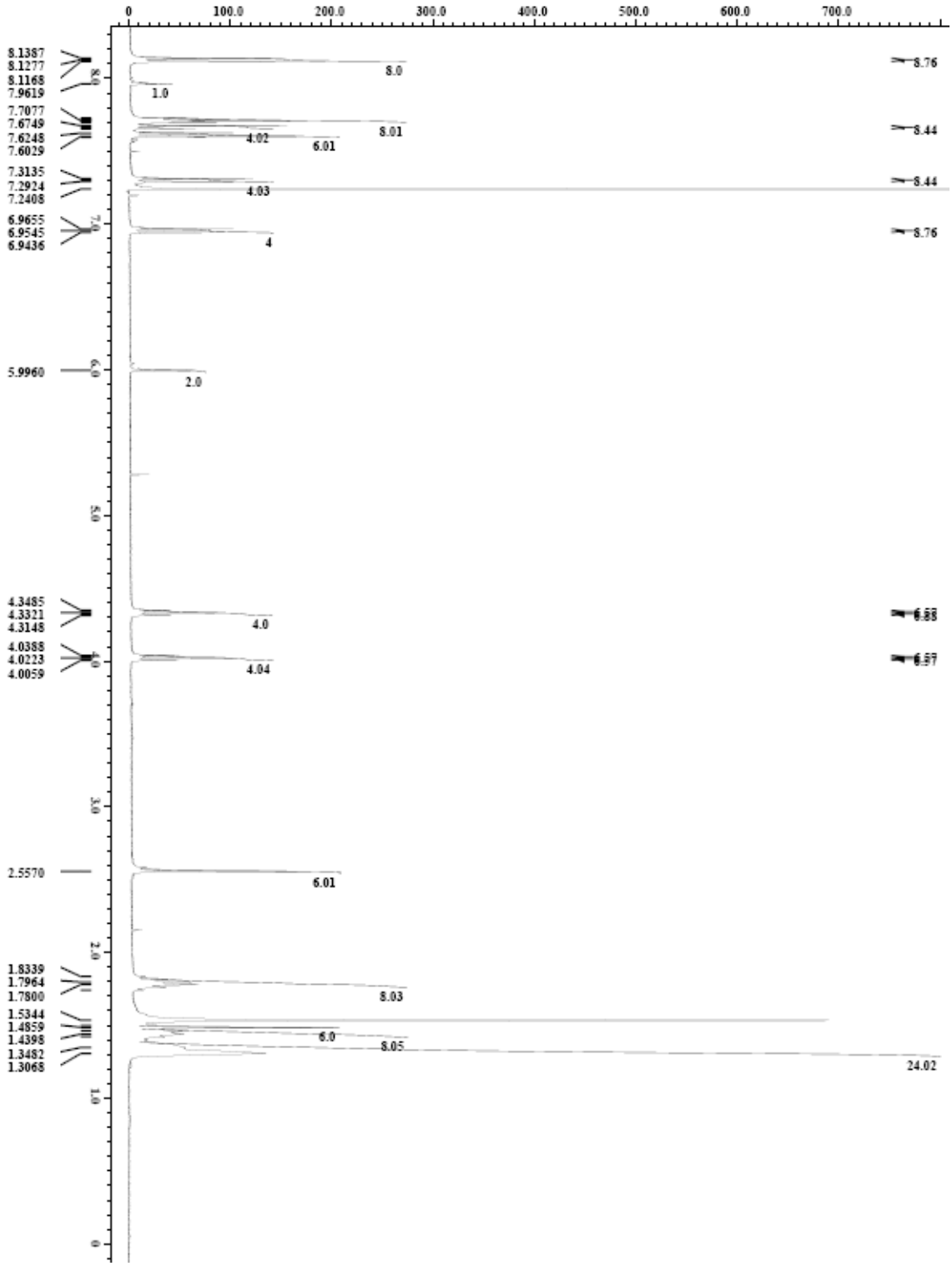
^{1}H-NMR spectrum for compound 3:



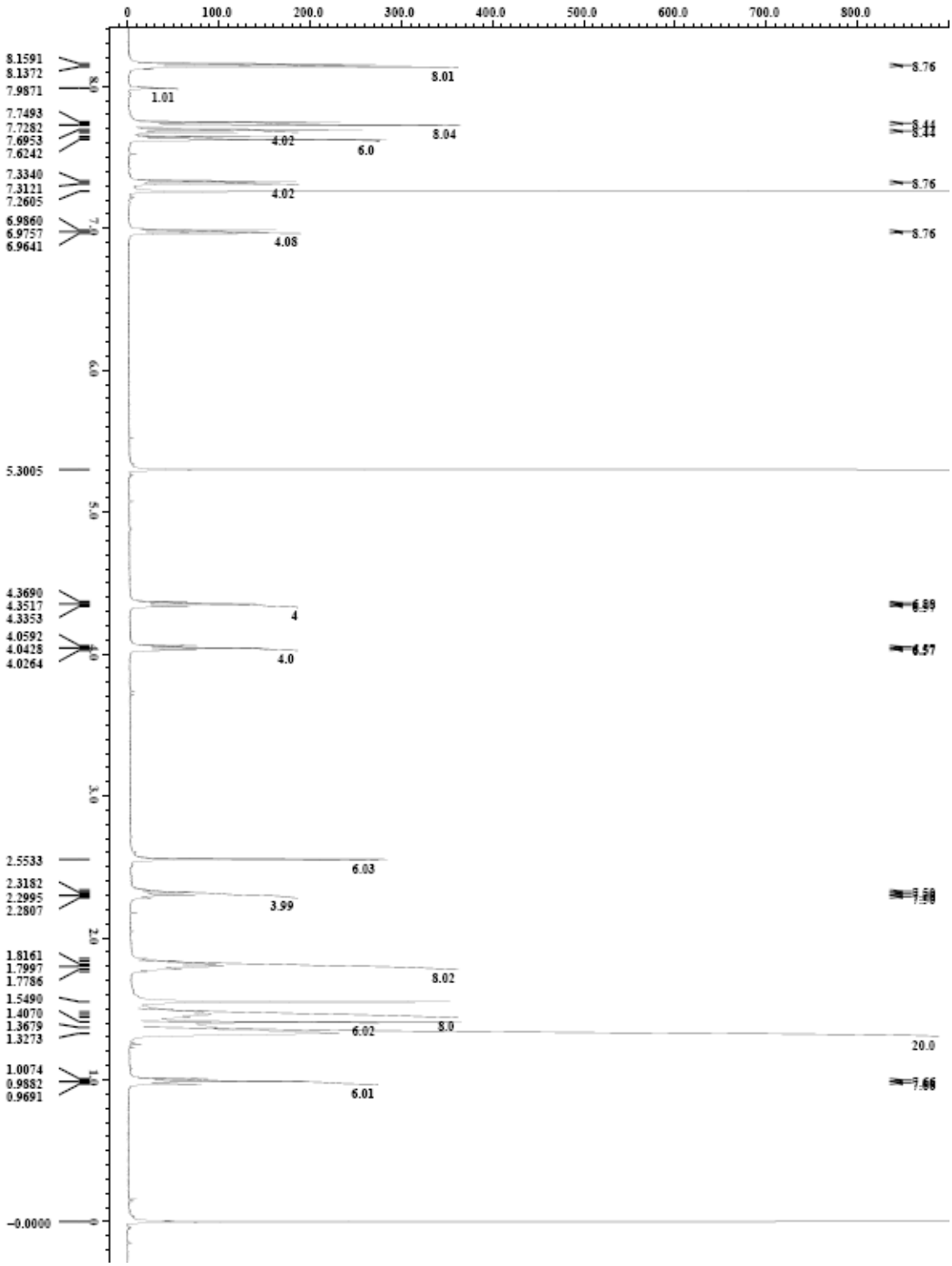
^{1}H-NMR spectrum for compound 4:



^{1}H-NMR spectrum for compound 5:

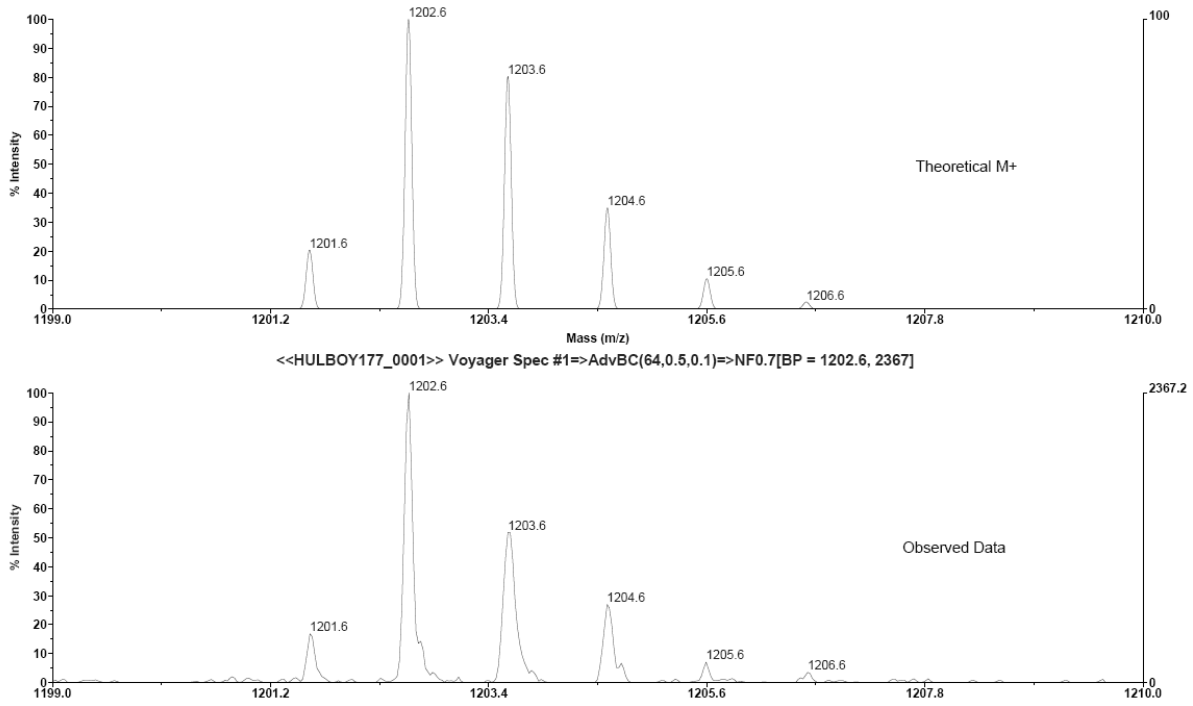


^{1}H-NMR spectrum for compound 6:

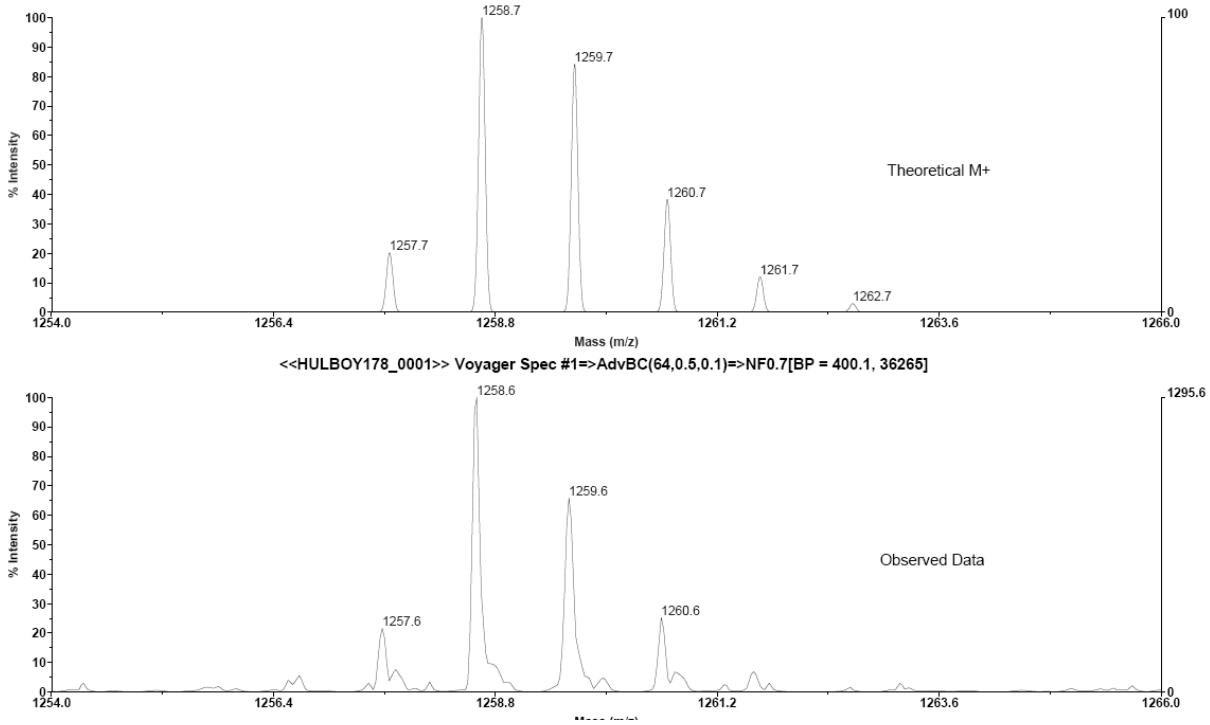


S3: MALDI-TOF for compounds 1-6

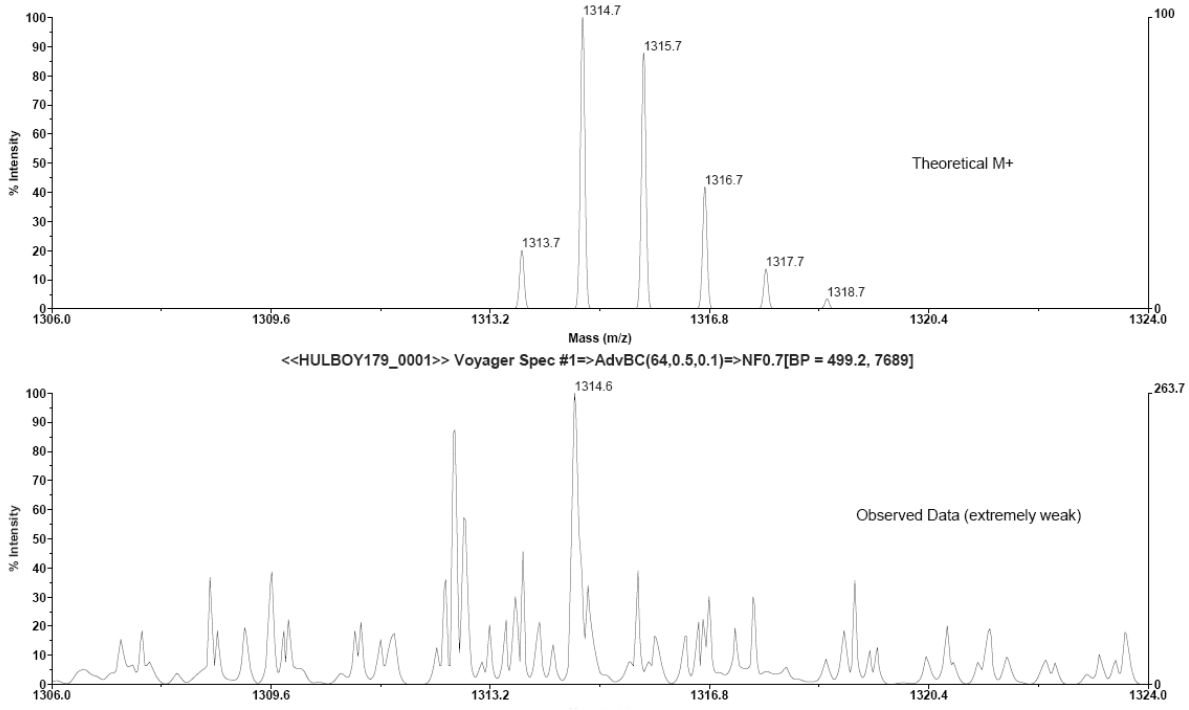
MALDI-TOF for compound 1:



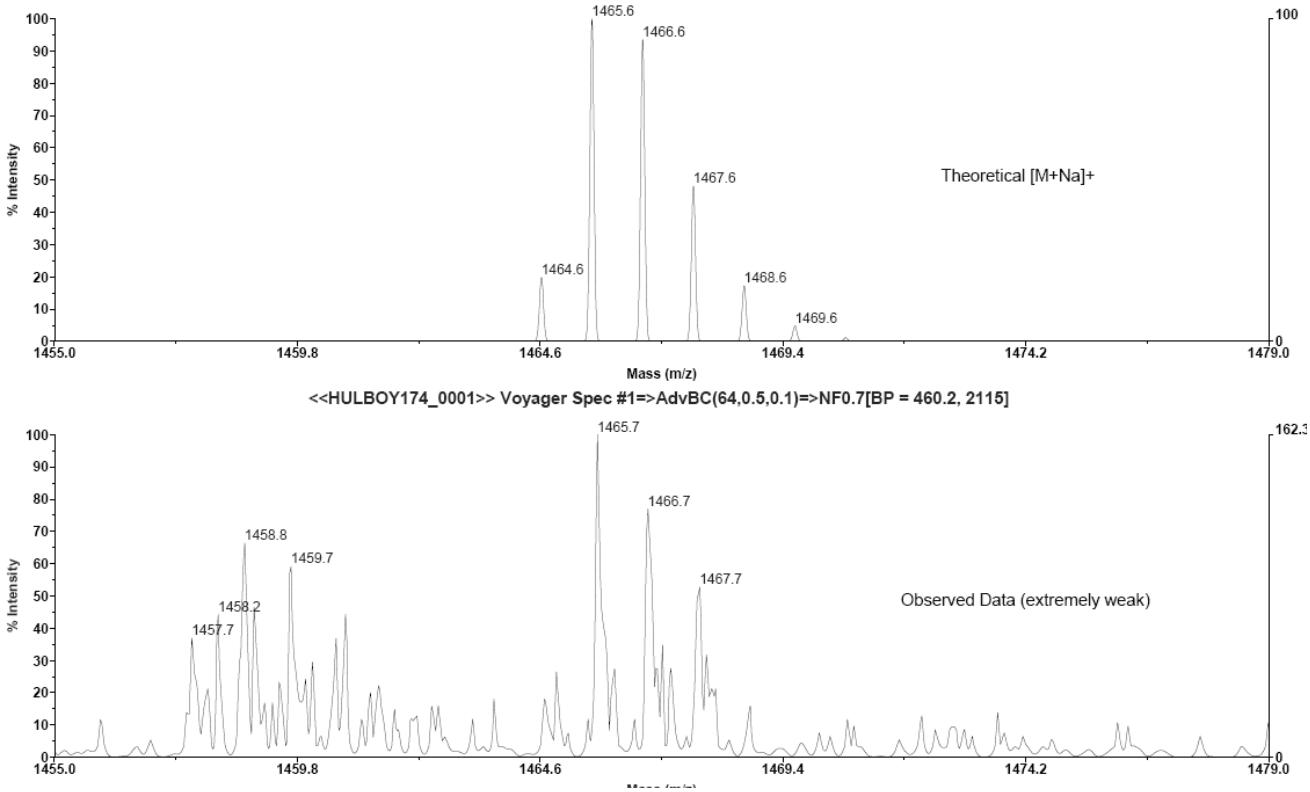
MALDI-TOF for compound 2:



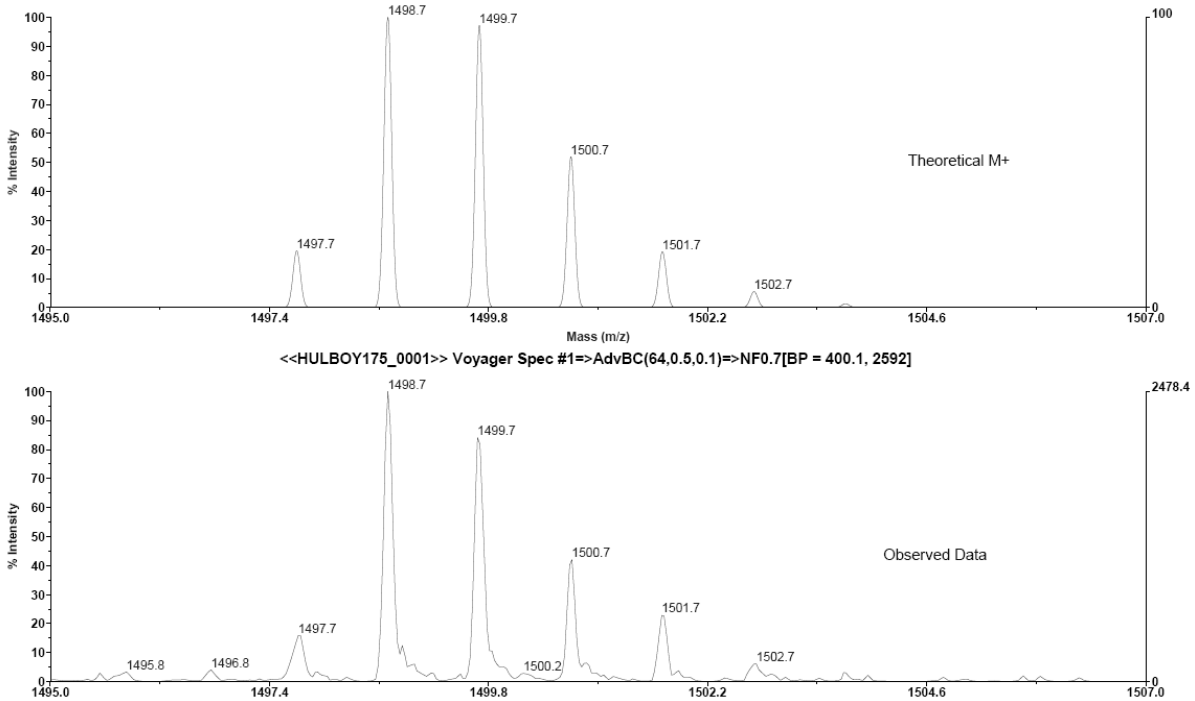
MALDI-TOF for compound 3:



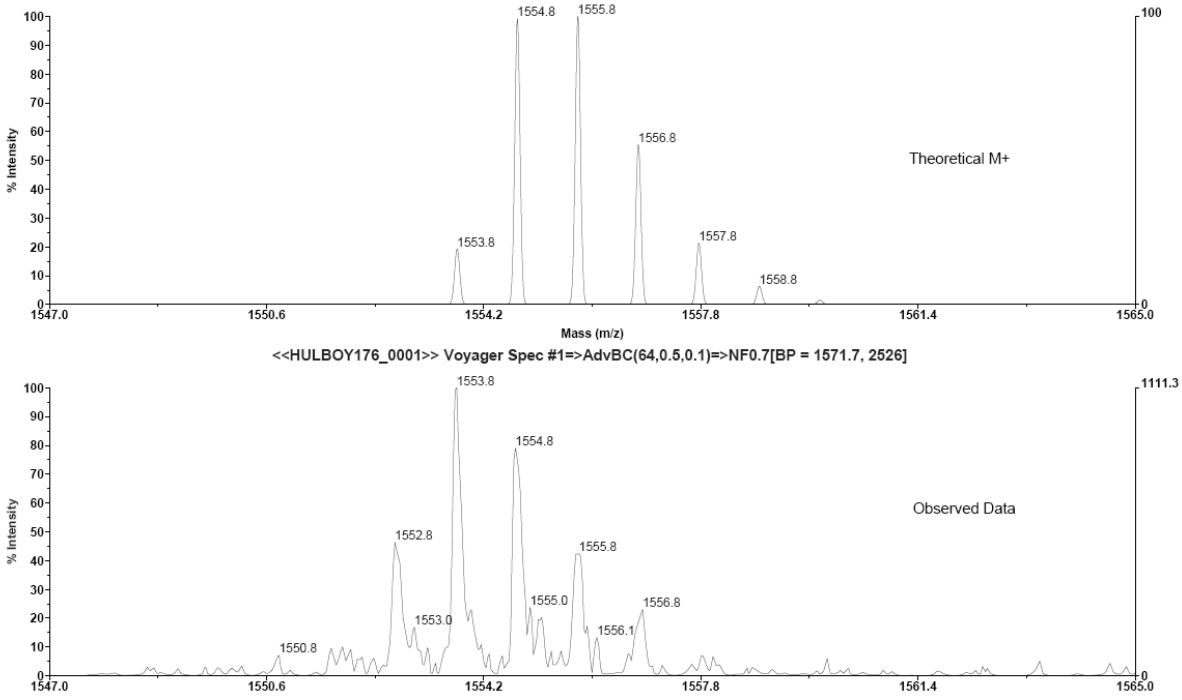
MALDI-TOF for compound 4:



MALDI-TOF for compound 5:

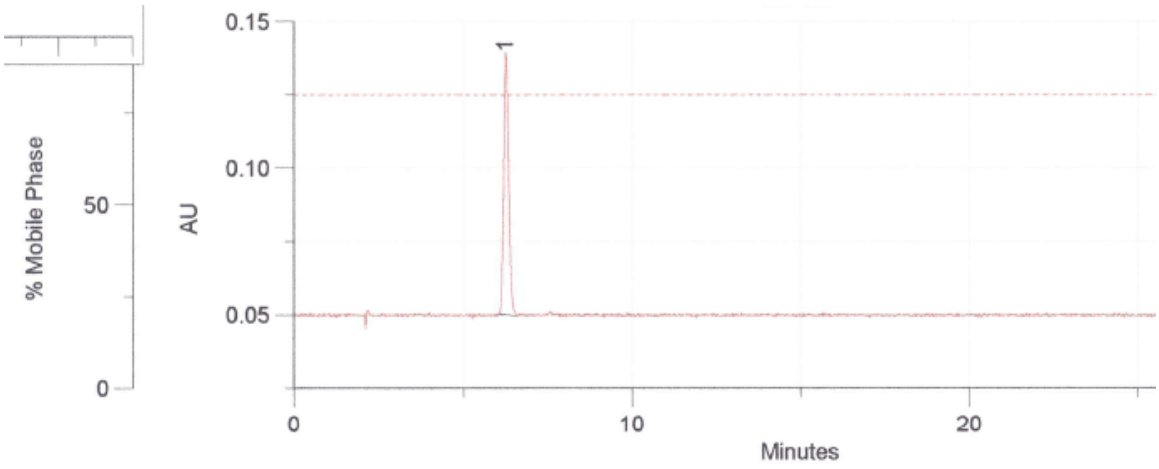


MALDI-TOF for compound 6:

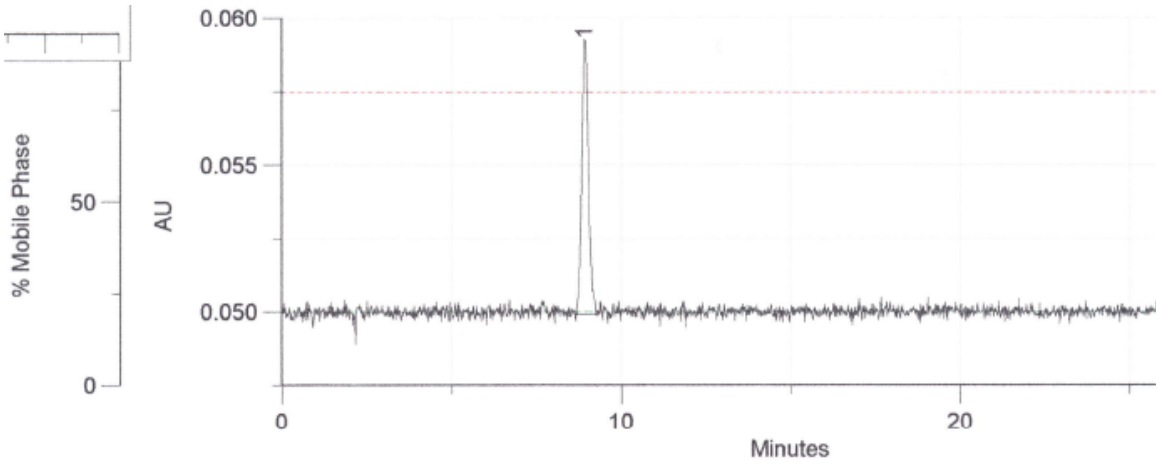


S4: HPLC traces for compounds 1-6

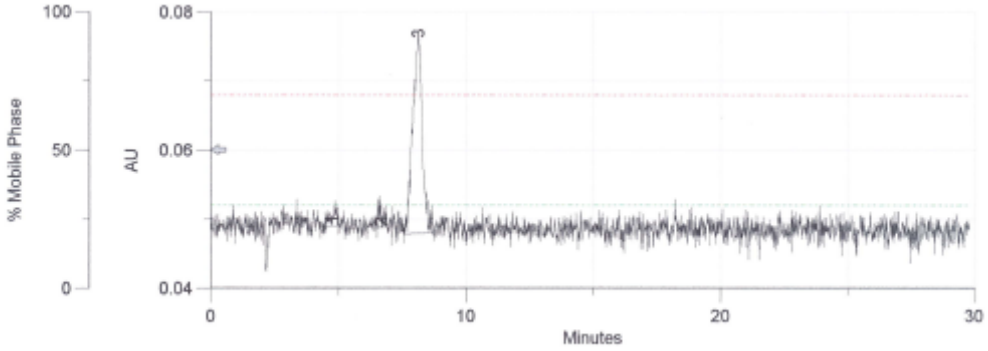
HPLC trace for compound 1 (4:1 MeCN:CH_2Cl_2):



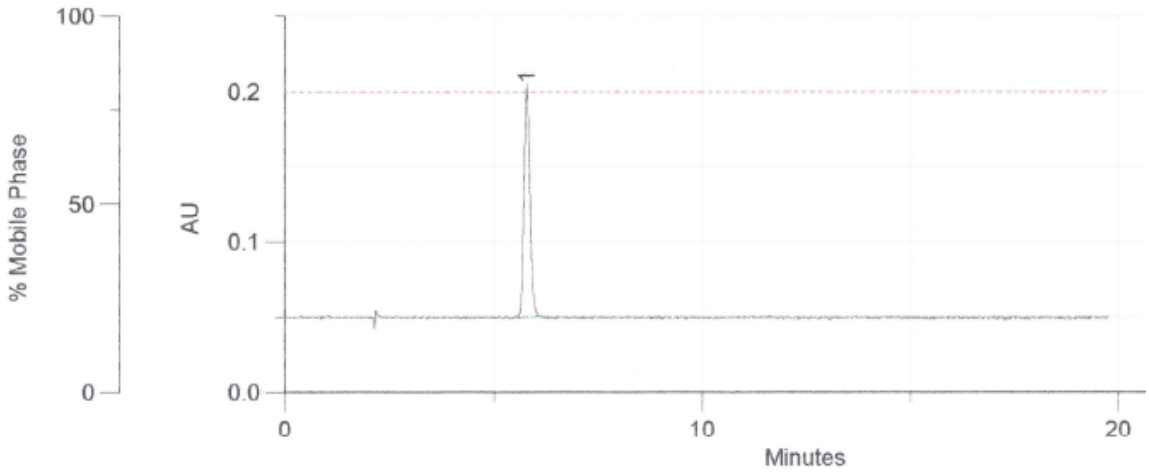
HPLC trace for compound 2 (4:1 MeCN:CH_2Cl_2):



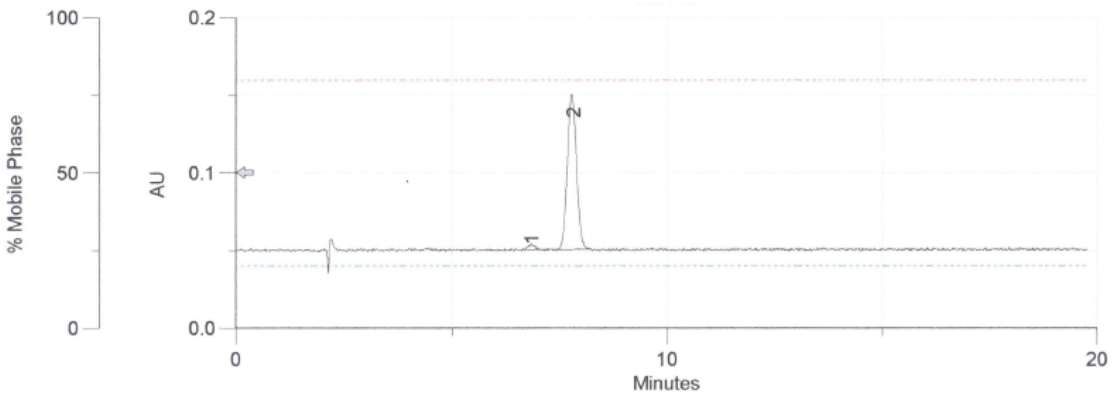
HPLC trace for compound 3 (7:3 MeCN:CH_2Cl_2):



HPLC trace for compound 4 (4:1 MeCN:CH_2Cl_2):

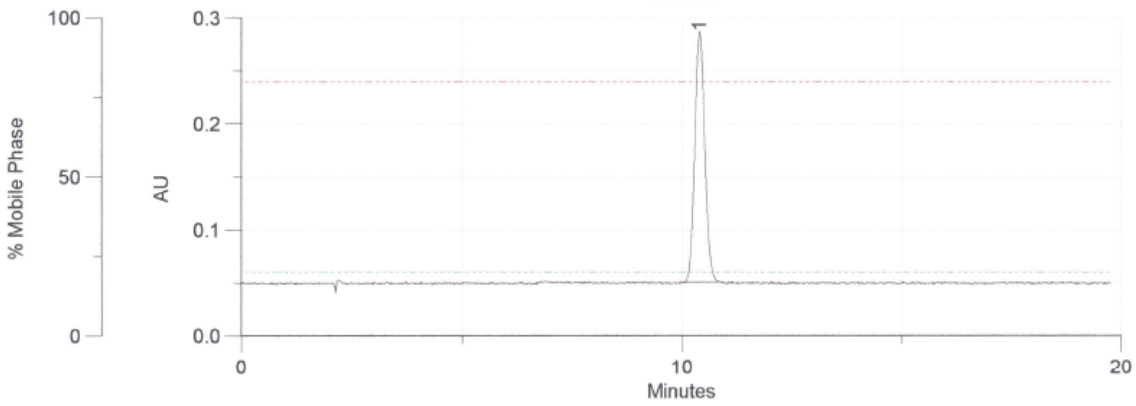


HPLC trace for compound 5 (4:1 MeCN:CH_2Cl_2):



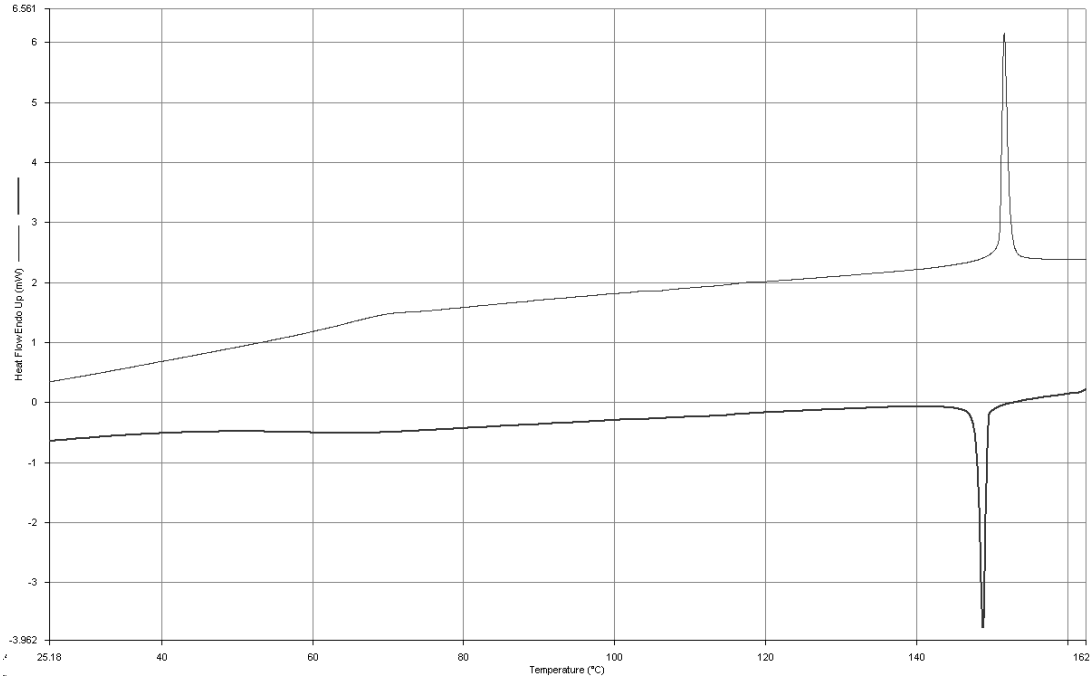
	Inj. Number	Peak Name	R. Time	Area	Area %
1	2.00	*1	6.84	700535.69	2.73
2	2.00	*2	7.78	24922242.00	97.27

HPLC trace for compound 6 (4:1 MeCN:CH_2Cl_2):

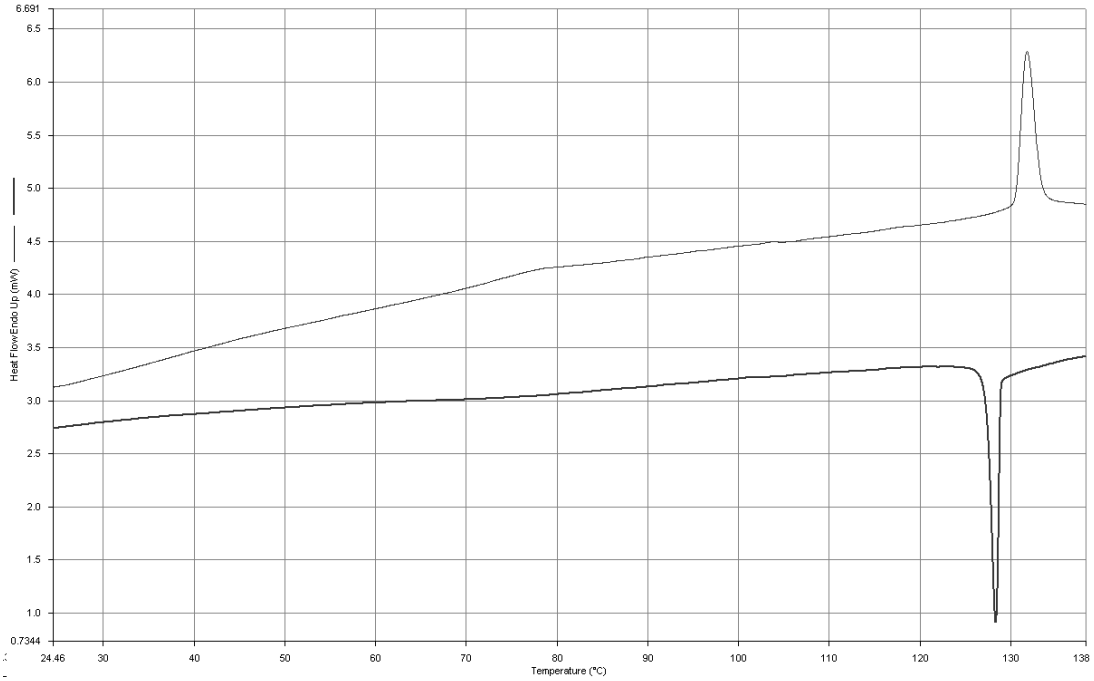


S5: DSC thermograms for compounds 4-6

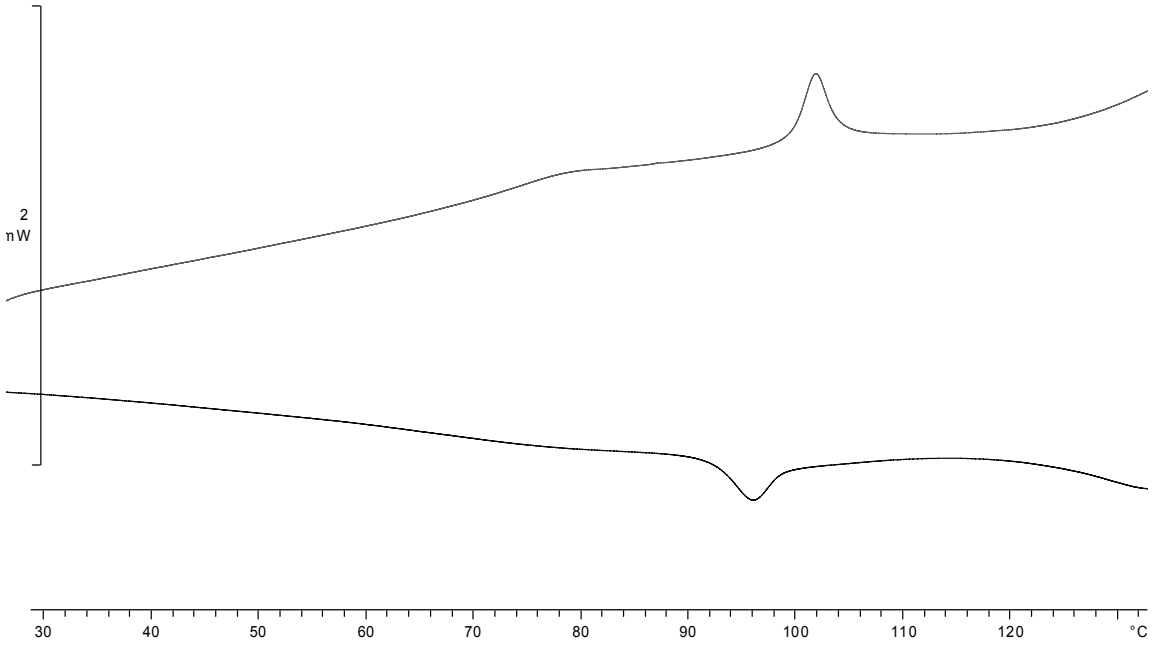
DSC thermogram for compound 4:



DSC thermogram of compound 5:



DSC thermogram of compound 6:



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2. H. Yu, A. Shishido, J. Li, K. Kamata, T. Iyoda and T. Ikeda, *J. Mater. Chem.*, 2007, **17**, 3485-3488.
3. E. Lager, J. Liu, A. Aguilar-Aguilar, B. Z. Tang and E. Pena-Cabrera, *J. Org. Chem.*, 2009, **74**, 2053-2058.