

## Supplemental Information

### **Design and Electro-optic investigations of de Vries smectics for exhibiting broad temperature ranges of SmA\* and SmC\* phases and fast electro-optic switching**

V. Swaminathan<sup>1</sup>, V. P. Panov<sup>1</sup>, A. Panov<sup>2</sup>, D. Rodriguez-Lojo<sup>2</sup> and P. J. Stevenson<sup>2</sup> E. Gorecka<sup>3</sup>  
and Jagdish K. Vij<sup>1,\*</sup>

<sup>1</sup>*Department of Electronic and Electrical Engineering, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland.*

<sup>2</sup>*School of Chemistry and Chemical Engineering, Queens University, Belfast, U. K.*

<sup>3</sup>*Department of Chemistry, Warsaw University, Al. Zwirki i Wigury 101, 02089 Warsaw, Poland.*

\*Author of correspondence email [jvij@tcd.ie](mailto:jvij@tcd.ie)

## APPENDIX A: SYNTHETIC PROCEDURE OF COMPOUNDS

### (a) DR118

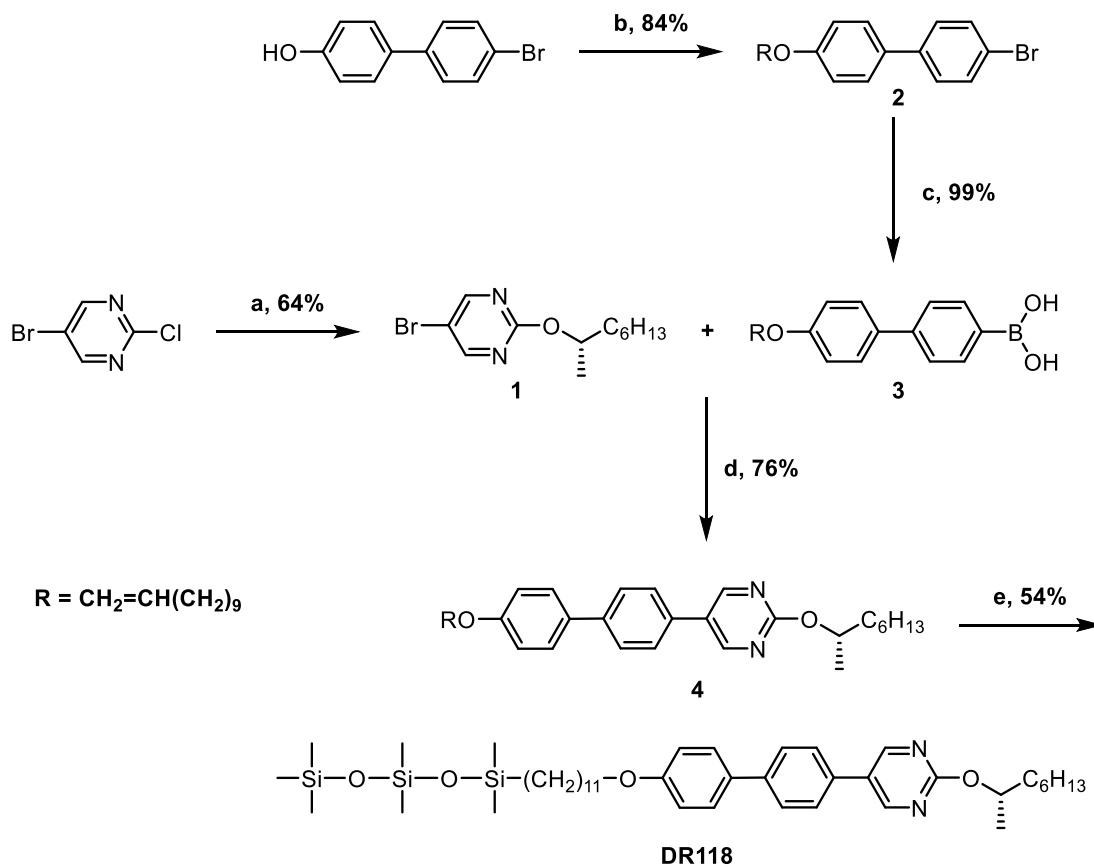


Figure 10 Scheme of synthesis of DR118

*Reagents and conditions:* a) (*S*)-(+)-2-octanol, Na, toluene, 55 °C; b)  $\text{K}_2\text{CO}_3$ , 11-bromo-1-undecene, DMF, 80 °C; c)  $n\text{BuLi}$ , trimethylborate, THF, -78 °C; d)  $\text{K}_2\text{CO}_3$ ,  $\text{Pd}(\text{PPh}_3)_4$ , toluene/MeOH/ $\text{H}_2\text{O}$ , reflux; e) 1,1,1,3,3,5,5-heptamethyltrisiloxane, Karstedt's catalyst, THF.

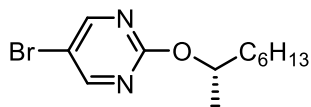


Figure 11 Chemical formula of [1] (*S*)-5-bromo-2-(octan-2-yloxy)pyrimidine

## Compound 1

Toluene washed sodium (0.09 g, 3.91 mmol) was quickly added to a solution of (*S*)-(+)-2-octanol (0.50 g, 3.84 mmol) in dry toluene (10 mL) in a Schlenk under N<sub>2</sub>. The resulting mixture was magnetically stirred at 55 °C overnight. 5-Bromo-2-chloropyrimidine (0.68 g, 3.52 mmol) was added to the solution as a solid and the reaction was stirred for 1 hr at 55 °C. The solution was diluted with EtOAc (20 mL) and filtered. The crude was concentrated in vacuo and water (30 mL) was added. The product was extracted with EtOAc (3 x 20 mL), the combined organic phases were dried with MgSO<sub>4</sub> and concentrated. The product was purified by column chromatography (EtOAc: hexane 1:19, R<sub>f</sub> = 0.45) to give the titled compound as a colourless oil (0.64 g, 2.23 mmol, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.47 (s, 2H), 5.07 (m, 1H), 1.76 (m, 1H), 1.57 (m, 1H), 1.48 – 1.14 (m, 11H), 0.83 (t, *J* = 6.8, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 163.87, 159.69, 111.26, 74.95, 36.12, 31.90, 29.33, 25.54, 22.73, 19.73, 14.21. IR (film):  $\tilde{\nu}$  = 3039, 2929, 2858, 1569, 1541, 1427, 1328, 1273, 1120, 794 cm<sup>-1</sup>. HRMS (EI): calcd for C<sub>12</sub>H<sub>19</sub>BrN<sub>2</sub>O [M<sup>+</sup>] 286.0681, found: 286.0704. [ $\alpha$ ]<sub>D</sub><sup>20</sup>: +9.00 (c 3.00, Ethanol).

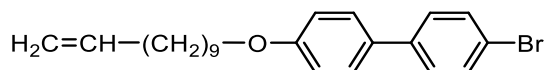


Figure 12 Chemical formula of [2] 4-bromo-4'-(undec-10-en-1-yloxy)-1,1'-biphenyl

4-Bromo-4'-hydroxybiphenyl (1.00 g, 4.01 mmol), 11-bromo-1-undecene (1.12 g, 4.82 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.83 g, 6.02 mmol) were dissolved in dry DMF (25 mL) under N<sub>2</sub>, the solution was magnetically stirred at 80 °C overnight. The DMF was concentrated and the product purified by column chromatography (hexane → EtOAc: hexane, 3:97, R<sub>f</sub> = 0.23 in 3:97) to give the titled

compound as a white powder (1.35 g, 3.37 mmol, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.53 (d,  $J = 8.7$ , 2H), 7.48 (d,  $J = 8.9$ , 2H), 7.42 (d,  $J = 8.7$ , 2H), 6.97 (d,  $J = 8.9$ , 2H), 5.83 (m, 1H), 4.98 (m, 2H), 4.00 (t,  $J = 6.6$ , 2H), 2.06 (m, 2H), 1.81 (m, 2H), 1.53-1.26 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.23, 140.02, 139.41, 132.44, 131.98, 128.47, 128.13, 120.92, 115.12, 114.35, 68.33, 34.01, 29.73, 29.64, 29.59, 29.49, 29.33, 29.14, 26.26. IR (film):  $\tilde{\nu} = 3082, 2920, 2850, 1606, 1483, 1289, 1255, 1199, 917, 810, 734\text{ cm}^{-1}$ .

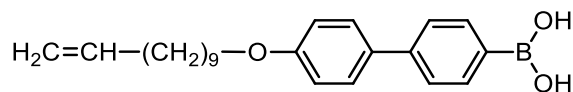


Figure 13 Chemical formula of [3] (4'-(undec-10-en-1-yloxy)-[1,1'-biphenyl]-4-yl)boronic acid

$n\text{BuLi}$  (2.87 mmol, 1.79 mL of 1.6M solution) was added dropwise to a solution of compound 2 (1.00 g, 2.49 mmol) in dry THF (35 mL) under  $\text{N}_2$  at  $-78\text{ }^\circ\text{C}$ . The solution was magnetically stirred for 1 hr at  $-78\text{ }^\circ\text{C}$  after which trimethylborate (0.91 g, 8.72 mmol) was added dropwise. The resulting solution was stirred for 2 hrs while warming to room temperature. Water (30 mL) was added and the solution was stirred for a further 15 minutes. The product was extracted with  $\text{Et}_2\text{O}$  (3 x 30 mL), the combined organic layers were washed with brine (20 mL), dried over  $\text{MgSO}_4$  and concentrated to give the titled compound and oligomers as a white powder (0.91 g, 2.48 mmol, 99%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.31 (d,  $J = 8.1$ ), 7.78 (d,  $J = 8.2$ ), 7.72 (d,  $J = 8.2$ ), 7.62 (m), 7.55 (d,  $J = 8.8$ ), 7.02 (d,  $J = 8.8$ ), 6.98 (d,  $J = 8.8$ ), 5.81 (m, 1H), 4.97 (m, 2H), 4.01 (m, 2H), 2.04 (m, 2H), 1.81 (m, 2H), 1.51-1.24 (m, 12H). IR (film):  $\tilde{\nu} = 3049, 3082, 2920, 2851, 1606, 1532, 1394, 1344, 1285, 1258, 992, 912, 815, 741\text{ cm}^{-1}$ .

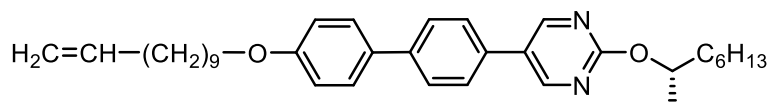


Figure 14 Chemical formula of [4] (*S*)-2-(octan-2-yloxy)-5-(4'-(undec-10-en-1-yloxy)-[1,1'-biphenyl]-4-yl)pyrimidine

Degassed MeOH (5 mL) was added to a solution of boronic acid 3 (0.26 g, 0.71 mmol) in degassed toluene (7 mL) under N<sub>2</sub> in a Schlenk. A solution of K<sub>2</sub>CO<sub>3</sub> (0.40 g, 2.90 mmol) in degassed water (2 mL) was added to the reaction flask.

Tetrakis(triphenylphosphine)palladium(0) (0.04 g, 0.04 mmol) and bromide 1 (0.18 g, 0.62 mmol) were added to the solution which was refluxed overnight. Water (30 mL) was added and the crude extracted with Et<sub>2</sub>O (3 x 30 mL), the combined organic phases were dried with MgSO<sub>4</sub> and concentrated. The product was purified by column chromatography (EtOAc: hexane 1:9, R<sub>f</sub> = 0.36) to give the titled compound as a white powder (0.26 g, 0.49 mmol, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.73 (s, 2H), 7.65 (d, *J* = 8.4, 2H), 7.54 (m, 4H), 6.98 (d, *J* = 8.8, 2H), 5.82 (m, 1H), 5.23 (m, 1H), 4.97 (m, 2H), 3.99 (t, *J* = 6.6, 2H), 2.05 (m, 2H), 1.84 (m, 3H), 1.65 (m, 1H), 1.57-1.21 (m, 23H), 0.89 (t, *J* = 6.9, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 164.68, 159.16, 157.21, 140.71, 139.25, 132.86, 132.56, 128.08, 127.53, 127.51, 126.79, 115.03, 114.28, 74.17, 68.20, 36.28, 33.92, 31.92, 29.65, 29.55, 29.51, 29.41, 29.38, 29.24, 29.05, 26.18, 25.61, 22.73, 19.90, 14.21. IR (film):  $\tilde{\nu}$  = 3080, 2962, 2925, 2855, 1601, 1533, 1453, 1337, 1261, 1097, 1021, 911, 814 cm<sup>-1</sup>. HRMS (EI): *m/z* calcd for C<sub>35</sub>H<sub>49</sub>N<sub>2</sub>O<sub>2</sub> [M + H<sup>+</sup>] 529.3794, found: 529.3787. [α]<sub>D</sub><sup>20</sup> +3.55 (c 2.73, CHCl<sub>3</sub>).

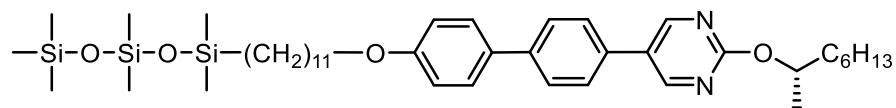


Figure 15 Chemical formula of [DR118] (*S*)-5-(4'-((11-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)undecyl)oxy)-[1,1'-biphenyl]-4-yl)-2-(octan-2-yloxy)pyrimidine

Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (0.22 mL of 0.05M solution, 0.01 mmol) was added to a solution of compound 4 (0.24 g, 0.45 mmol) and 1,1,1,3,3,5,5-heptamethyltrisiloxane (0.12 g, 0.53 mmol) in dry THF (15 mL) under N<sub>2</sub>, the solution was magnetically stirred for 1 hr at room temperature. The solution was concentrated and the product was purified by column chromatography (EtOAc: hexane, 1:19, where R<sub>f</sub> = 0.73 in EtOAc: hexane, 2:8) to give the titled compound as a white wax (0.18 g, 0.24 mmol, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.73 (s, 2H), 7.66 (d, *J* = 8.5, 2H), 7.56 (m, 4H), 6.99 (d, *J* = 8.8, 2H), 5.23 (m, 1H), 4.01 (t, *J* = 6.6, 2H), 1.84 (m, 3H), 1.66 (m, 1H), 1.55-1.22 (m, 27H), 0.89 (t, *J* = 6.9, 3H), 0.55 (m, 2H), 0.10 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 164.77, 159.25, 157.31, 140.83, 132.97, 132.67, 128.18, 127.63, 127.62, 126.89, 115.11, 74.26, 68.31, 36.35, 33.64, 31.99, 29.84, 29.79, 29.62, 29.60, 29.50, 29.45, 26.27, 25.68, 23.43, 22.79, 19.97, 18.49, 14.27, 2.01, 1.47, 0.41. IR (film):  $\tilde{\nu}$  = 2958, 2922, 2853, 1602, 1533, 1445, 1331, 1257, 1053, 841, 823, 795 cm<sup>-1</sup>. HRMS (EI): *m/z* calcd for C<sub>42</sub>H<sub>71</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>3</sub> [M + H<sup>+</sup>] 751.4722, found: 751.4758. [α]<sub>D</sub><sup>20</sup> + 1.30 (c 2.62, CHCl<sub>3</sub>).

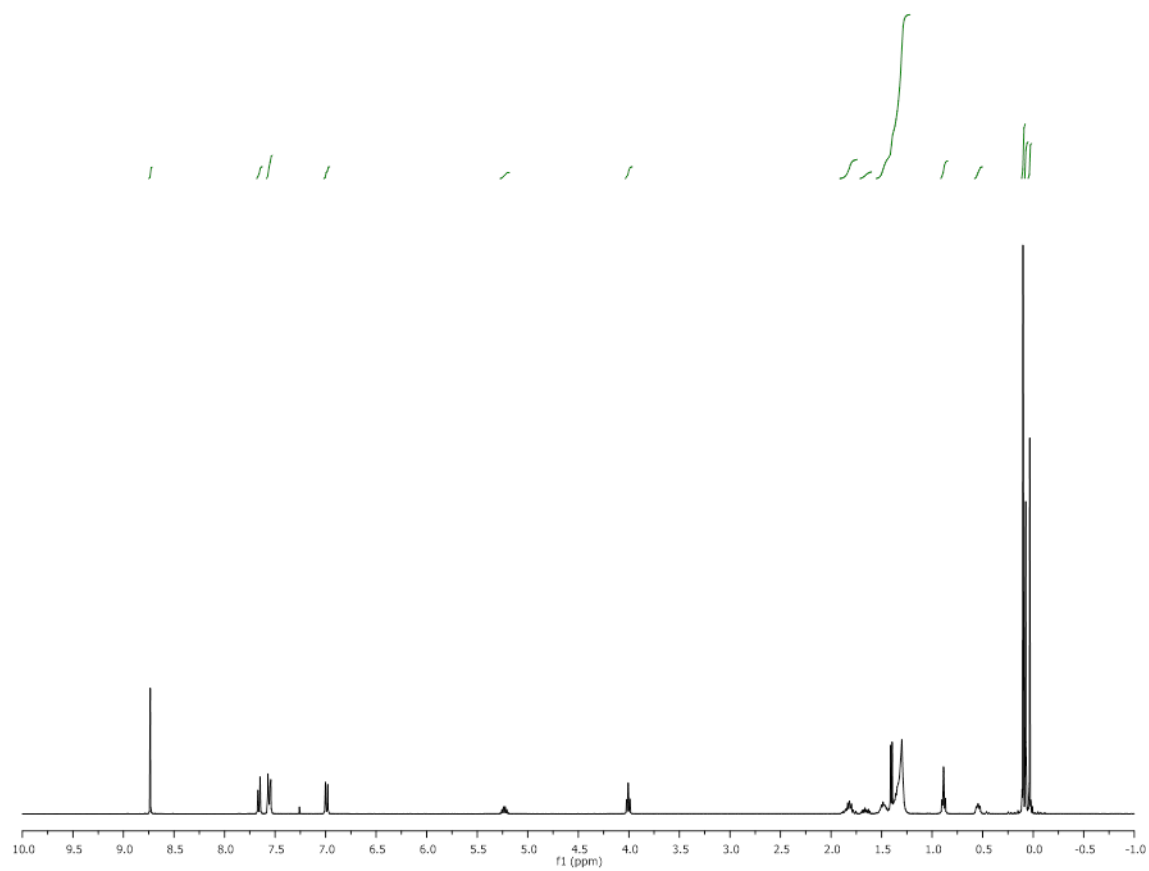


Figure 16  $^1\text{H}$  NMR spectra of DR118

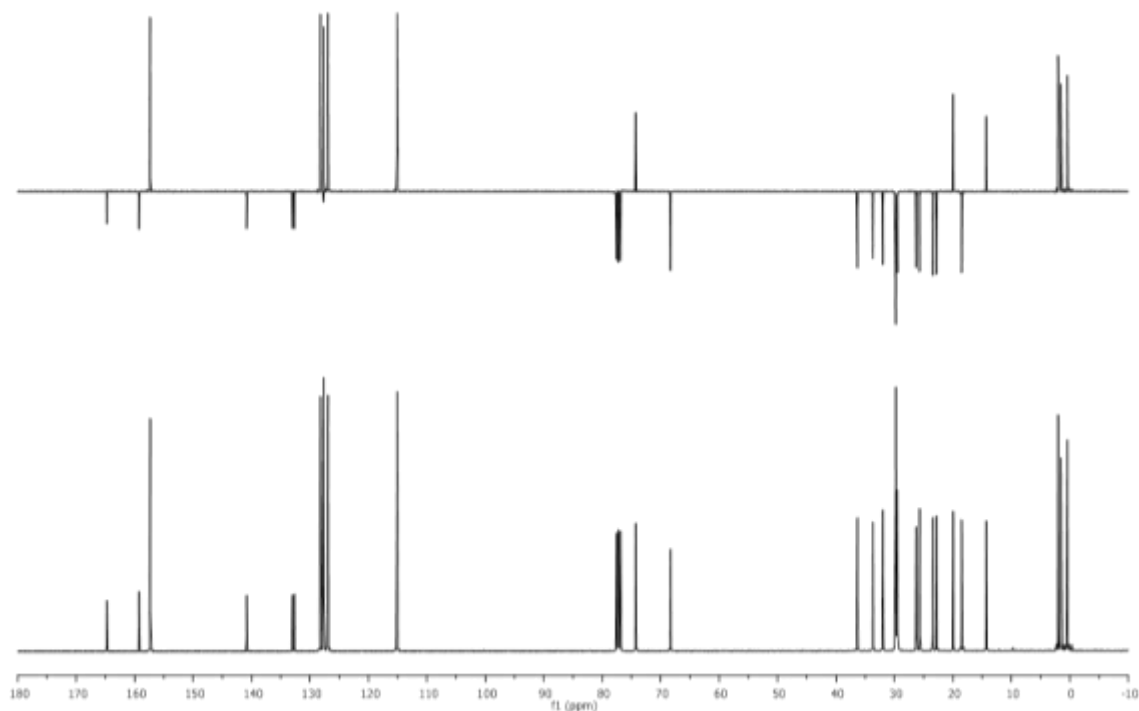


Figure 17  $^{13}\text{C}$  NMR spectrum of DR118.

## APPENDIX B: SYNTHETIC PROCEDURE OF DR133

All reagents were purchased from Sigma Aldrich, Fluorochem, Alfa Aesar, ABCR, Synthonix and used without any further purification. Solvents were purchased from Sigma Aldrich, DMF was purchased pre-dried, THF was dried using a sodium/benzophenone still under  $\text{N}_2$  and DCM was dried using  $\text{CaH}_2$ . All reactions were generally carried out under nitrogen using oven-dried glassware. TLC plates were performed on Merck silica gel 60  $\text{F}_{254}$  and were visualized using a 254 nm light source. Flash column chromatography was performed on Fluorochem silica gel 60 (40-63 micron).

IR spectra were recorded using a Perkin Elmer Spectrum Two FT-IR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded at 25  $^\circ\text{C}$  ( $\text{CDCl}_3$  as solvent and TMS as reference) using a Bruker 400



MHz Ultrashield (Avance 400). HRMS spectra were recorded using a Waters – TOF Electrospray micromass LCT premier. Optical rotations were recorded using a polarimeter Perkin Elmer: model 341 Polarimeter.

(b) **DR133:**

(SCHEME)

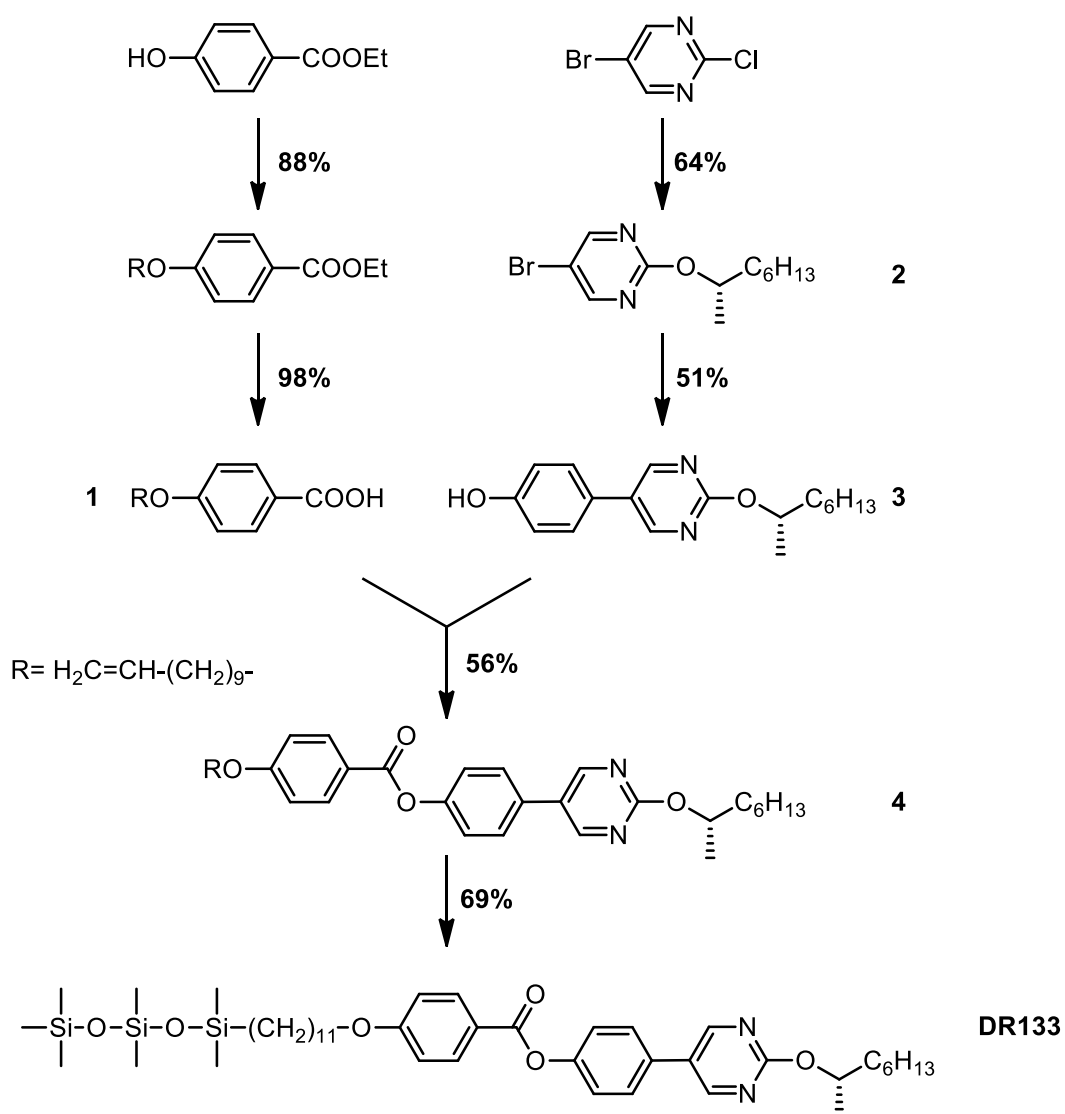


Figure 18 Scheme of synthesis of DR133

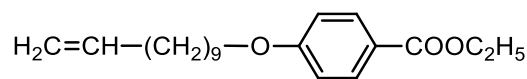


Figure 19 Chemical formula of compound Ethyl 4-(undec-10-en-1-yloxy) benzoate

Ethyl 4-hydroxybenzoate (3.57 g, 21.5 mmol), 11-bromo-1-undecene (5.00 g, 21.5 mmol) and potassium carbonate (4.44 g, 32.1 mmol) were dissolved in dry DMF (50 mL) under nitrogen. The solution was stirred overnight at room temperature. The DMF was removed under reduced pressure, water (50 mL) was added and this was extracted with DCM (3 x 50 mL). The combined organic extracts was dried over magnesium sulphate and concentrated to give a yellow oil (6.01 g, 88%). Spectral properties identical to literature values [48]

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ:** 7.98 (d, *J* = 8.8, 2H), 6.88 (d, *J* = 8.8, 2H), 5.80 (ddt, *J* = 13.4, 10.1, 6.7, 1H), 4.97 (m, 2H), 4.33 (q, *J* = 7.1, 2H), 3.98 (t, *J* = 6.5, 2H), 2.02 (m, 2H), 1.77 (m, 2H), 1.55 – 1.19 (m, 15H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ:** 166.53 (C), 163.03 (C), 139.27 (CH), 131.64 (2CH), 122.82 (C), 114.29 (CH<sub>2</sub>), 114.14 (2CH), 68.30 (CH<sub>2</sub>), 60.68 (CH<sub>2</sub>), 33.94 (CH<sub>2</sub>), 29.64 (CH<sub>2</sub>), 29.55 (CH<sub>2</sub>), 29.49 (CH<sub>2</sub>), 29.26 (2CH<sub>2</sub>), 29.07 (CH<sub>2</sub>), 26.13 (CH<sub>2</sub>), 14.53 (CH<sub>3</sub>).

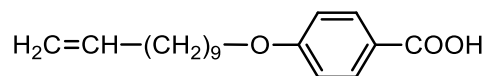


Figure 20 Chemical formula of compound 4-(Undec-10-en-1-yloxy) benzoic acid, **1** in Scheme

Ethyl 4-(undec-10-en-1-yloxy) benzoate (1.00 g, 3.28 mmol), was dissolved in methanol: water (24 mL: 6 mL), lithium hydroxide monohydrate (1.00 g, 23.8 mmol) was added and the solution

was boiled under reflux for 2 hours. The mixture was brought to pH 3 using 1M HCl and the precipitate was filtered. The product was purified using column chromatography (ethyl acetate: hexane 1:9  $\rightarrow$  100% ethyl acetate upon elution of the top impurity, where  $R_f = 0.13$  in ethyl acetate: hexane 1:9) to yield a white powder (0.89 g, 3.06 mmol, 98%). Spectral properties identical to literature values. [49]

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 8.06 (d,  $J = 8.7$ , 2H), 6.93 (d,  $J = 8.8$ , 2H), 5.81 (m, 1H), 4.96 (m, 2H), 4.02 (t,  $J = 6.5$ , 2H), 2.03 (m, 2H), 1.80 (m, 2H), 1.52 – 1.19 (m, 12H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 171.96 (C), 163.92 (C), 139.42 (CH), 132.56 (2CH), 121.59 (C), 114.42 (2CH), 114.35 ( $\text{CH}_2$ ), 68.50 ( $\text{CH}_2$ ), 34.01 ( $\text{CH}_2$ ), 29.70 ( $\text{CH}_2$ ), 29.62 ( $\text{CH}_2$ ), 29.54 ( $\text{CH}_2$ ), 29.31 (2 $\text{CH}_2$ ), 29.14 ( $\text{CH}_2$ ), 26.18 ( $\text{CH}_2$ ).

**IR (film):**  $\tilde{\nu} = 3082, 2930, 2850, 1681, 1602, 1513, 1468, 1434, 1332, 1254, 1171, 845 \text{ cm}^{-1}$ .

**HRMS (EI):**  $m/z$  calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_3\text{Na}$  [ $\text{M} + \text{Na}^+$ ] 313.1780, found: 313.1798.

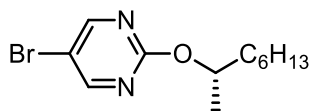


Figure 21 Chemical formula of compound (*S*)-5-bromo-2-(octan-2-yloxy) pyrimidine, **2** in

#### Scheme

(*S*)-(+)-2-Octanol (0.50 g, 3.84 mmol) was sealed in a 25 mL Schlenk under nitrogen. 10 mL of dry toluene was added and the solution stirred. Sodium (0.09 g, 3.91 mmol) was washed with dry toluene and then weighed in dried toluene before quickly being added to the solution. The sodium was stirred at 55 °C overnight. 5-Bromo-2-chloropyrimidine (0.68 g, 3.52 mmol) was added to the solution as a solid and the reaction was stirred for 1 hour at 55 °C. The solution was diluted with ethyl acetate (20 mL) and filtered to remove any remaining sodium. The crude was

concentrated and water (30 mL) was added before extraction with ethyl acetate (3 x 20 mL). The organic phase was dried, concentrated and purified by column chromatography (ethyl acetate: hexane 1:19,  $R_f$  = 0.45) to yield a colourless oil (0.64 g, 64%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 8.47 (s, 2H), 5.07 (m, 1H), 1.76 (m, 1H), 1.57 (m, 1H), 1.48 – 1.14 (m, 11H), 0.83 (t,  $J$  = 6.8, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 163.87 (C), 159.69 (2CH), 111.26 (C), 74.95 (CH), 36.12 (CH<sub>2</sub>), 31.90 (CH<sub>2</sub>), 29.33 (CH<sub>2</sub>), 25.54 (CH<sub>2</sub>), 22.73 (CH<sub>2</sub>), 19.73 (CH<sub>3</sub>), 14.21 (CH<sub>3</sub>).

**IR (film):**  $\tilde{\nu}$  = 3039, 2929, 2858, 1569, 1541, 1427, 1328, 1273, 1120, 794  $\text{cm}^{-1}$ .

**HRMS (EI):** calcd for  $\text{C}_{12}\text{H}_{20}\text{N}_2\text{OBr}$  [ $\text{M} + \text{H}^+$ ] 286.0681, found 286.0704.

$[\alpha]_{\text{D}}^{20} + 9.00$  (c 0.03, Ethanol).

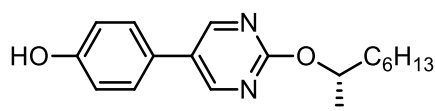


Figure 22 Chemical formula of compound (*S*)-4-(2-(Octan-2-yloxy) pyrimidin-5-yl) phenol, **3** in Scheme

4-Hydroxyphenylboronic acid (0.32 g, 2.32 mmol) was added to a Schlenk tube under nitrogen. Toluene (12 mL) was added and the solution degassed for 5 minutes. Degassed methanol (7 mL) and potassium carbonate (1.21 g, 8.75 mmol) dissolved in degassed water (3 mL) were added to the solution. Tetrakis(triphenylphosphine)palladium(0) (0.11 g, 0.10 mmol) and (**2**) (0.55 g, 1.91 mmol) were added to the solution which was boiled under reflux overnight. Water (30 mL) was added and the residue was extracted with DCM (3 x 30 mL) before being dried with magnesium

sulfate and concentrated. The product was purified by column chromatography (ethyl acetate: hexane 3:7, where  $R_f = 0.36$  in ethyl acetate: hexane 2:8) to yield a white wax (0.29 g, 51%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 8.65 (s, 2H), 8.21 (s, 1H), 7.36 (d,  $J = 8.6$ , 2H), 7.04 (d,  $J = 8.6$ , 2H), 5.22 (m, 1H), 1.81 (m, 1H), 1.63 (m, 1H), 1.51-1.19 (m, 11H), 0.84 (t,  $J = 6.8$ , 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 163.98 (C), 157.21 (C), 156.96 (2CH), 128.17 (C), 127.88 (2CH), 126.33 (C), 116.76 (2CH), 74.57 (CH), 36.28 ( $\text{CH}_2$ ), 31.95 ( $\text{CH}_2$ ), 29.41 ( $\text{CH}_2$ ), 25.60 ( $\text{CH}_2$ ), 22.76 ( $\text{CH}_2$ ), 19.94 ( $\text{CH}_3$ ), 14.24 ( $\text{CH}_3$ ).

**IR (film):**  $\tilde{\nu} = 3165, 3020, 2930, 2857, 1600, 1553, 1435, 1379, 1328, 1272, 1178, 1120, 835, 733, \text{cm}^{-1}$ .

**HRMS (EI):**  $m/z$  calcd for  $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_2$  [ $\text{M} + \text{H}^+$ ] 301.1916, found: 301.1910.

$[\alpha]_D^{20} +6.3$  (c 0.017,  $\text{CHCl}_3$ ).

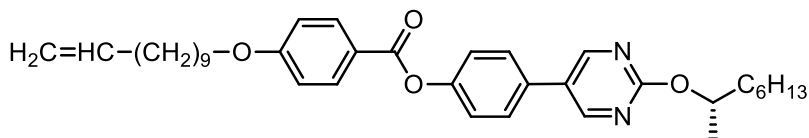


Figure 23 Chemical formula of compound (*S*)-4-(2-(Octan-2-yloxy) pyrimidin-5-yl) phenyl 4-(undec-10-en-1-yloxy)benzoate, **4** in Scheme

(**1**) (0.21 g, 0.72 mmol), (**3**) (0.20 g, 0.65 mmol), and 4-dimethylaminopyridine (0.01 g, 0.08 mmol) were dissolved in dry DCM (15 mL) under nitrogen. *N,N'*-dicyclohexylcarbodiimide (0.16 g, 0.79 mmol) was dissolved in dry DCM (10 mL) under nitrogen and added dropwise to the reaction flask. The resulting solution was stirred at room temperature overnight. The solvent

was evaporated and the product purified by column chromatography (ethyl acetate: hexane 1:9, where  $R_f = 0.56$  in ethyl acetate: hexane 2:8) to yield a white wax (0.21 g, 56%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 8.70 (s, 2H), 8.15 (d,  $J = 9.0$ , 2H), 7.56 (d,  $J = 8.7$ , 2H), 7.32 (d,  $J = 8.7$ , 2H) 6.98 (d,  $J = 9.0$ , 2H), 5.82 (m, 1H), 5.22 (m, 1H), 4.96 (m, 2H), 4.05 (t,  $J = 6.6$ , 2H), 2.04 (m, 2H), 1.83 (m, 3H), 1.66 (m, 1H), 1.55-1.22 (m, 23H), 0.88 (t,  $J = 6.9$ , 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 165.08 (C), 164.83 (C), 163.90 (C), 157.48 (2CH), 151.34 (C), 139.39 (CH), 132.55 (2CH), 132.45 (C), 127.78 (2CH), 127.38 (C), 122.95 (2CH), 121.47 (C), 114.57 (2CH), 114.36 ( $\text{CH}_2$ ), 74.36 (CH), 68.56 ( $\text{CH}_2$ ), 36.34 ( $\text{CH}_2$ ), 34.00 ( $\text{CH}_2$ ), 31.99 ( $\text{CH}_2$ ), 29.69 ( $\text{CH}_2$ ), 29.61 ( $\text{CH}_2$ ), 29.54 ( $\text{CH}_2$ ), 29.45 ( $\text{CH}_2$ ), 29.31 ( $\text{CH}_2$ ), 29.29 ( $\text{CH}_2$ ), 29.12 ( $\text{CH}_2$ ), 26.18 ( $\text{CH}_2$ ), 25.69 ( $\text{CH}_2$ ), 22.80 ( $\text{CH}_2$ ), 19.97 ( $\text{CH}_3$ ), 14.28 ( $\text{CH}_3$ ).

**IR (film):**  $\tilde{\nu} = 3076, 2926, 2855, 1732, 1605, 1546, 1439, 1326, 1260, 1207, 1167, 1071, 846, 763 \text{ cm}^{-1}$ .

**HRMS (EI):**  $m/z$  calcd for  $\text{C}_{36}\text{H}_{49}\text{N}_2\text{O}_4$  [ $\text{M} + \text{H}^+$ ] 573.3692, found: 573.3701.

$[\alpha]_D^{20} +1.26$  (c 0.028,  $\text{CHCl}_3$ ).

Chemical formula of compound (*S*)-4-(2-(octan-2-yloxy) pyrimidin-5-yl) phenyl 4-((11-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)undecyl)oxy) benzoate, DR133 in Scheme)

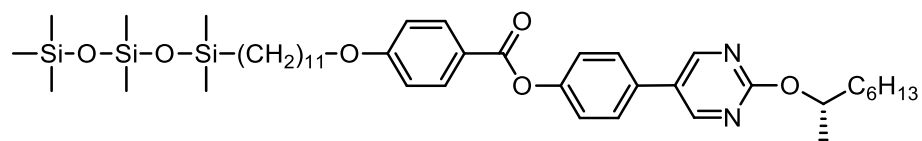


Figure 24 Chemical formula of compound (*S*)-4-(2-(octan-2-yloxy) pyrimidin-5-yl) phenyl 4-((11-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)undecyl)oxy) benzoate, DR133 in Scheme)

(4) (0.15 g, 0.26 mmol), and 1,1,1,3,3,5,5-Heptamethyltrisiloxane (0.07 g, 0.31 mmol) were dissolved in dry THF (10 mL) under nitrogen. Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (0.13 mL of 0.05M solution, 0.006 mmol) was added to the flask and the solution was stirred for 2 hours at room temperature. The solution was concentrated and the product was purified by column chromatography (ethyl acetate: hexane, 3:47, where  $R_f = 0.60$  in ethyl acetate: hexane, 2:8) to yield a white wax (0.14 g, 69%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 8.69 (s, 2H), 8.15 (d, 2H,  $J = 8.8$ ), 7.55 (d,  $J = 8.6$ , 2H), 7.32 (d,  $J = 8.6$ , 2H), 6.98 (d,  $J = 8.9$ , 2H), 5.22 (m, 1H), 4.05 (t,  $J = 6.5$ , 2H), 1.82 (m, 3H), 1.64 (m, 1H), 1.52-1.22 (m, 27 H), 0.88 (t,  $J = 6.8$ , 3H), 0.52 (m, 2H), 0.09 (s, 9H), 0.06 (s, 6H), 0.02 (s, 6H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ :** 165.04 (C), 164.82 (C), 163.89 (C), 157.46 (2CH), 151.34 (C), 132.53 (2CH), 132.43 (C), 127.75 (2CH), 127.37 (C), 122.93 (2CH), 121.46 (C), 114.55 (2CH), 74.33 (CH), 68.56 ( $\text{CH}_2$ ), 36.33 ( $\text{CH}_2$ ), 33.63 ( $\text{CH}_2$ ), 31.98 ( $\text{CH}_2$ ), 29.82 ( $\text{CH}_2$ ), 29.77 ( $\text{CH}_2$ ), 29.76 ( $\text{CH}_2$ ), 29.59 ( $\text{CH}_2$ ), 29.58 ( $\text{CH}_2$ ), 29.44 ( $\text{CH}_2$ ), 29.30 ( $\text{CH}_2$ ), 26.19 ( $\text{CH}_2$ ), 25.67 ( $\text{CH}_2$ ), 23.42 ( $\text{CH}_2$ ), 22.79 ( $\text{CH}_2$ ), 19.96 ( $\text{CH}_3$ ), 18.49 ( $\text{CH}_2$ ), 14.27 ( $\text{CH}_3$ ), 2.01 (3 $\text{CH}_3$ ), 1.47 (2 $\text{CH}_3$ ), 0.41 (2 $\text{CH}_3$ ).

**IR (film):**  $\tilde{\nu} = 3071, 2957, 2922, 2853, 1726, 1604, 1546, 1442, 1323, 1258, 1206, 1167, 1049, 842, 793, 764 \text{ cm}^{-1}$ .

**HRMS (EI):**  $m/z$  calcd for  $\text{C}_{43}\text{H}_{71}\text{N}_2\text{O}_6\text{Si}_3$  [ $\text{M} + \text{H}^+$ ] 795.4620, found: 795.4636.

$[\alpha]_{\text{D}}^{20} +1.41$  (c 0.024,  $\text{CHCl}_3$ ).

## THE NMR SPECTRA OF DR133:

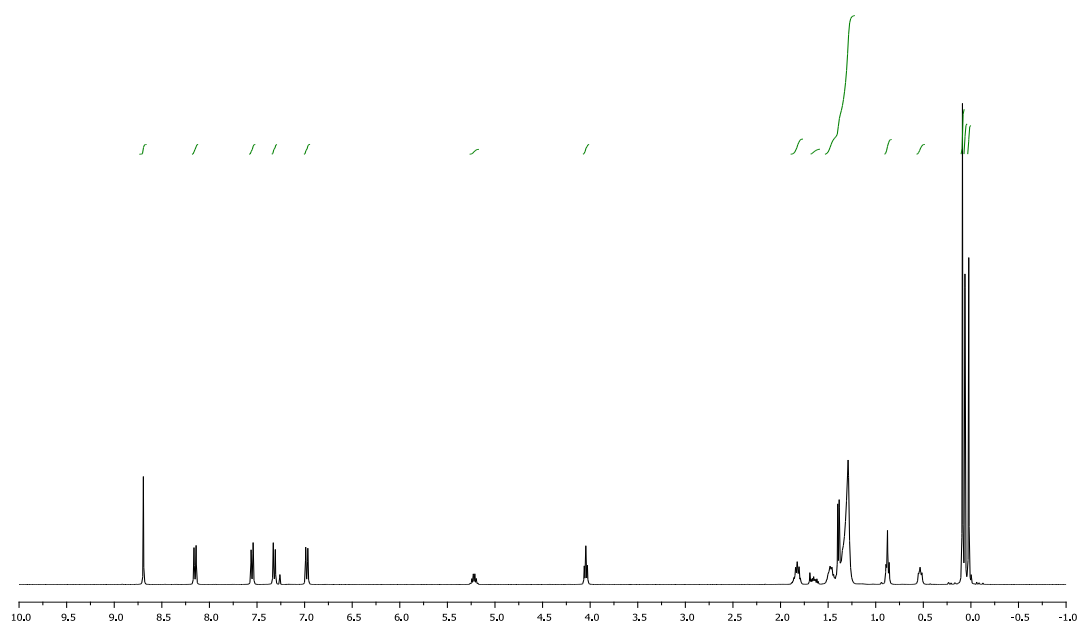


Figure 25  $^1\text{H}$  NMR spectra of DR133.



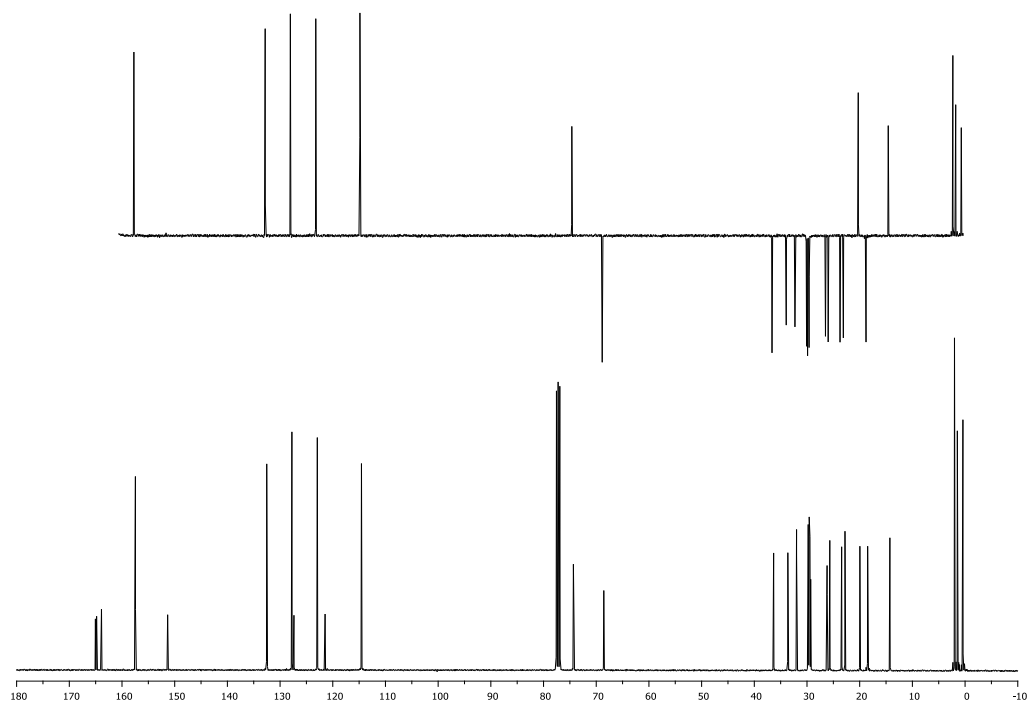


Figure 26  $^{13}\text{C}$  NMR spectra of DR133.