

## Supporting Information

### Novel syntheses of aryl quinoxaline C-nucleoside analogs by mild and efficient three-component sequential reactions

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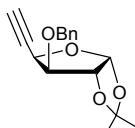
## General

Infrared spectra were recorded on a Shimadzu IR-435 instrument in the 400–4000 cm<sup>-1</sup> region. NMR spectra were recorded with a Bruker DPX-400 spectrometer. Chemical shifts are given as  $\delta$  values and are referenced to Me<sub>4</sub>Si or to the residual solvent signal 7.26 for CDCl<sub>3</sub>. Data were given as follows: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant (J/Hz). <sup>13</sup>C NMR spectra were recorded at 100 MHz. Internal references of carbon 77.16 was used for CDCl<sub>3</sub>. HRMS-ESI spectra were recorded on Waters Micromass Q-Tof Micro™ spectrometer with samples dissolved in CH<sub>3</sub>OH. Optical rotations were measured at the sodium D line (589 nm) in a microcell (10 cm, 1 mL) at 20 °C and are in units of degree·mL/(g·dm). Thin-layer chromatography (TLC) was carried out on glass plates coated with Silica Gel F<sub>254</sub>. The zones were detected with UV light when possible, or by charring with 1:9 concd H<sub>2</sub>SO<sub>4</sub>–EtOH followed by heating. Flash chromatography was performed with silica gel 60.

### General procedure for the preparation of terminal sugar alkynes 1a-1e<sup>1</sup>

To a mixture of zinc (3 eq), PPh<sub>3</sub> (3 eq) and dry CH<sub>2</sub>Cl<sub>2</sub> at 0°C, a solution of CBr<sub>4</sub> (2 eq) in dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise for 15 min with stirring and then a solution of sugar aldehyde<sup>2</sup> (1.0 eq) in dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise for 10min. The mixture was stirred at rt for 6 to 8 h until TLC indicated the complete conversion of sugar aldehyde. The mixture was evaporated. Flash chromatography on silica gel (6:1 - 3:1 petroleum ether-EtOAc) gave a syrup. A dry THF solution of the syrup (1.0 eq) was treated with *n*-butyllithium (2.5 eq) at -45 °C until TLC indicated the completion of the reaction. The solution was quenched by water and then evaporated. The residue was dissolved in EtOAc, then washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. Flash chromatography on silica gel (5:1 - 3:1 petroleum ether-EtOAc) gave 1a-1e.

### 3-O-Benzyl-5,6-dideoxy-1,2-O-isopropylidene- $\alpha$ -D-xylo-hex-5-ynofuranose (1a)<sup>3</sup>



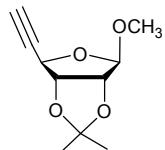
Colourless oil, 72% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40-7.27 (m, 5H, ArH), 5.96 (d, 1H,  $J_{1,2}$  = 3.6 Hz, H-1), 4.83 (t, 1H,  $J_{4,6}$  = 2.4 Hz,  $J_{4,3}$  = 2.8 Hz, H-4), 4.81 (d, B of AB, 1H,  $J$  = 12.4 Hz, PhCH<sub>B</sub>), 4.74 (d, A of AB, 1H,  $J$  = 12.4 Hz, PhCH<sub>A</sub>), 4.58 (d, 1H,  $J_{2,1}$  = 3.6 Hz, H-2), 4.02 (d, 1H,  $J_{3,4}$  = 2.8 Hz, H-3), 2.64 (d, 1H,  $J_{6,4}$  = 2.4 Hz, H-6), 1.49, 1.31 (2 s, each 3H, 2CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.37 (aromatic C), 128.47, 127.95, 127.80 (5 aromatic CH), 111.97 (isopropylidene C), 104.74 (C-1), 82.83 (C-2), 82.43 (C-3), 77.62 (C-5), 76.58 (C-6), 72.60 (PhCH<sub>2</sub>O), 70.70 (C-4), 26.82, 26.17 (2 CH<sub>3</sub>).

### 6,7-Dideoxy-1,2:3,4-di-O-isopropylidene- $\alpha$ -D-galacto-hept-6-ynopyranose (1b)<sup>3</sup>



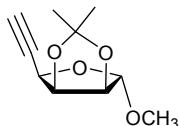
Colourless oil, 76%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.51 (d, 1H,  $J_{1,2}$  = 4.8 Hz, H-1), 4.60-4.58 (m, 2H, H-3, H-5), 4.29-4.25 (m, 2H, H-2, H-4), 2.51 (d, 1H,  $J$  = 2.0 Hz, H-7), 1.48, 1.47, 1.32, 1.27 (4 s, each 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  109.88, 108.87, 96.35, 78.78, 74.49, 72.56, 70.59, 70.11, 59.97, 26.06, 25.92, 24.74, 24.33.

### 1-O-Methyl-5,6-dideoxy-2,3-O-isopropylidene- $\beta$ -D-ribo-hex-5-ynofuranoside (1c)<sup>3</sup>



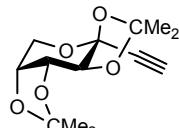
White solid, 63%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.97 (s, 1H, H-1), 4.78 (d, 1H,  $J_{3,2} = 6.0$  Hz, H-3), 4.68 (d, 1H,  $J_{4,6} = 2.8$  Hz, H-4), 4.58 (d, 1H,  $J_{2,3} = 6.0$  Hz, H-2), 3.27 (s, 3H,  $\text{OCH}_3$ ), 1.34, 1.20 (2 s, each 3H, 2 $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  112.48 (isopropylidene C), 109.22 (C-1), 85.28 (C-3), 85.09 (C-2), 81.46 (C-5), 74.59 (C-4), 74.07 (C-6), 54.14 ( $\text{OCH}_3$ ), 26.15, 24.81 (2 $\text{CH}_3$ ).

### **1-O-Methyl-5,6-dideoxy-2,3-O-isopropylidene- $\alpha$ -D-lyxo-hex-5-ynofuranoside (1d)<sup>3</sup>**



Yellow solid, 74%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.90 (s, 1H, H-1), 4.72 (d,  $J_{4,3} = 4$  Hz, 1H, H-4), 4.60 (dd, 1H,  $J_{3,2} = 5.6$  Hz,  $J_{3,4} = 4$  Hz, H-3), 4.53 (d, 1H,  $J_{2,3} = 5.6$  Hz, H-2), 3.32 (s, 3H,  $\text{OCH}_3$ ), 1.50, 1.32 (2 s, each 3H, 2 $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  113.43 (isopropylidene C), 107.17 (C-1), 84.82 (C-2), 80.57 (C-4), 77.36 (C-5), 76.60 (C-6), 70.63 (C-3), 54.98 ( $\text{OCH}_3$ ), 26.29, 25.30 (2 $\text{CH}_3$ ).

### **1,2-Dideoxy-3,4:5,6-di-O-isopropylidene- $\beta$ -D-arabino-hept-1-yn-3-ulohex-3,7-pyranose (1e)**

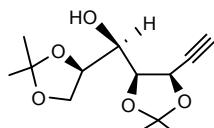


Colourless oil, 80%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.53 (dd, 1H,  $J_{5,4} = 2.0$  Hz,  $J_{5,6} = 8.0$  Hz, H-5), 4.43 (d, 1H,  $J_{4,5} = 2.0$  Hz, H-4), 4.18-4.15 (m, 1H, H-6), 3.73-3.67 (m, 2H, H-7), 2.58 (s, 1H, H-1), 1.46, 1.45, 1.40, 1.29 (4 s, each 3H, 4 $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  109.59, 109.54 (2 isopropylidene C), 95.79 (C-3), 81.82 (C-2), 75.72 (C-4), 72.40 (C-1), 70.44 (C-5), 70.16 (C-6), 61.16 (C-7), 26.12, 25.99, 24.63, 24.23 (4 $\text{CH}_3$ ); HRMS (ESI)  $m/z$  Calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_5\text{Na} [\text{M}+\text{Na}]^+$ : 277.1052. Found: 277.1058.

### **General procedure for the preparation of terminal sugar alkynes 1f-1g<sup>4</sup>**

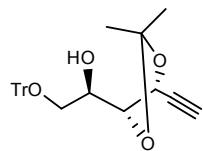
A mixture of sugar hemiacetal (10.0 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (3.0 eq) and  $\text{MeOH}$  (20 ml) was refluxed, to which Ohira's reagent (3.5 eq) is added dropwise for 6-8 h. TLC indicated the completion of the reaction. The mixture was evaporated to dryness and water (25 ml) was added. The solution was extracted with  $\text{EtOAc}$ , dried over  $\text{Na}_2\text{SO}_4$  and evaporated. Flash chromatography on silica gel (6:1 - 4:1 petroleum ether-EtOAc) gave 1f-1g.

### **3,4:6,7-Di-O-isopropylidene-1,2-dideoxy-D-manno-hex-1-ynitol (1f)<sup>5,6</sup>**



Colourless oil, 86%;  $^1\text{H}$  NMR (400 Hz,  $\text{CDCl}_3$ )  $\delta$  4.68 (dd, 1H,  $J_{3,1} = 1.4$  Hz,  $J_{3,4} = 7.6$  Hz, H-3), 4.30 (dd, 1H,  $J_{4,3} = 7.6$  Hz,  $J_{4,5} = 1.6$  Hz, H-4), 4.02-4.14 (m, 3H, H-6, H-7), 3.58 (brs, 1H, H-5), 2.56 (d, 1H,  $J_{1,3} = 1.4$  Hz, H-1), 2.23 (d, 1H,  $J_{\text{OH},5} = 7.6$  Hz, OH), 1.53, 1.45, 1.44, 1.38 (4 s, each 3H, 4 $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  110.01, 109.53 (2 isopropylidene C), 80.81 (C-4), 80.56 (C-2), 76.16 (C-6), 74.88 (C-1), 69.84 (C-5), 66.81 (C-7), 66.64 (C-3), 26.82, 26.65, 26.15, 25.27 (4 $\text{CH}_3$ ).

**3,4-Isopropylidene-6-O-triphenylmethyl-1,2-dideoxy-D-ribo-hex-1-yntol (1g)<sup>6,7</sup>**



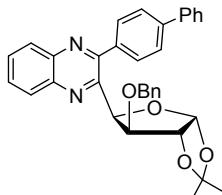
Colourless oil, 85%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50-7.28 (m, 15H, ArH), 4.72 (dd, 1H, J<sub>3,1</sub> = 2.0 Hz, J<sub>3,4</sub> = 6.2Hz, H-3), 4.25-4.22 (m, 1H, H-4), 3.92-3.90 (m, 1H, H-5), 3.35-3.34 (m, 2H, H-6), 2.52 (d, 1H, J<sub>OH,5</sub> = 3.6 Hz, OH), 2.49 (d, 1H, J<sub>1,3</sub> = 2.0 Hz, H-1), 1.52, 1.40 (2 s, each 3H, CH<sub>3</sub>).

**General procedure for the syntheses of aryl quinoxaline C-nucleoside analogs (2aa-2gg)**

A solution of aryl Iodide (0.81 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5 mol %), CuI (5 mol %) and Et<sub>3</sub>N (3 ml) was degassed for 5 min, to which **1a-1g** (0.80 mmol) in Et<sub>3</sub>N (4 ml) was added dropwise. The solution was stirred at rt until TLC indicated the completion of the sugar alkyne. The solution was evaporated and CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added, washed with water. RuCl<sub>3</sub>·H<sub>2</sub>O (1.3 mol %), NaIO<sub>4</sub> (2.4 mmol) and MeCN (5 ml) was added, and 1, 2- phenylenediamine (0.81 mol) was added later. The solution was stirred at rt until TLC indicated the completion of the reaction. The solution was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. Flash chromatography on silica gel (4:1-2:1 petroleum ether-EtOAc) gave the products **2aa-2gg**.

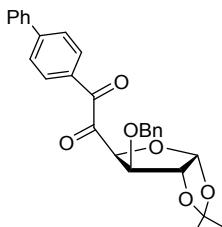
During the synthesis of **2aa**, the intermediate **5** was isolated according the similar procedure except that 1, 2- phenylenediamine was not added.

**2-(3-O-Benzyl-1,2-O-isopropylidene- $\alpha$ -D-xylo-tetrofuranos-4-yl)-3-biphenylquinoxaline (2aa)**



Pale yellow oil, 88%; R<sub>f</sub> 0.35 (3:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> -70.9 (c 1.6, CHCl<sub>3</sub>); FTIR (thin film): 3061, 3029, 2986, 2931, 1617, 1601, 1580, 1564, 1483, 1454, 766, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35-8.31 (m, 1H, ArH), 8.19-8.15 (m, 1H, ArH), 7.82-7.78 (m, 2H, ArH), 7.65-7.62 (m, 4H, ArH), 7.48 (t, 2H, J = 7.6 Hz, ArH), 7.41-7.31 (m, 3H, ArH), 7.19 (t, 1H, J = 7.4 Hz, ArH), 7.09 (t, 2H, J = 7.6 Hz, ArH), 6.75 (d, 2H, J = 7.4 Hz, ArH), 6.30 (d, 1H, J<sub>1',2'</sub> = 4.0 Hz, H-1'), 5.87 (d, 1H, J<sub>4',3'</sub> = 4.0 Hz, H-4'), 4.71 (d, 1H, J<sub>2',1'</sub> = 4.0 Hz, H-2'), 4.46 (d, B of AB, 1H, J = 12.4 Hz, PhCH<sub>B</sub>), 4.13 (d, A of AB, 1H, J = 12.4 Hz, PhCH<sub>A</sub>), 3.86 (d, 1H, J<sub>3',4'</sub> = 4.0 Hz, H-3'), 1.43, 1.33 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.44 (C-3), 149.43 (C-2), 141.99, 141.44, 140.35, 137.03 (6 aromatic C), 130.23, 130.00, 129.61, 129.13, 129.07, 128.93, 128.30, 127.94, 127.78, 127.59, 127.27, 127.22 (18 aromatic CH), 112.08 (isopropylidene C), 105.29 (C-1'), 83.05 (C-3'), 83.01 (C-2'), 80.03 (C-4'), 71.50 (PhCH<sub>2</sub>O), 26.96, 26.66 (2 CH<sub>3</sub>); HRMS (ESI) m/z Calcd for C<sub>34</sub>H<sub>31</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 531.2284. Found: 531.2296.

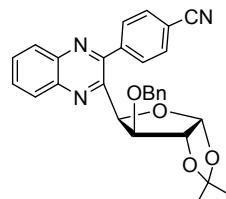
**1-(3-O-Benzyl-1,2-O-isopropylidene- $\alpha$ -D-xylo-tetrofuranos-4-yl)-2-biphenyl-1,2-diketone (5)**



Pale yellow oil, 90%;  $R_f$  0.30 (4:1 petroleum ether-EtOAc); FTIR (thin film): 3134, 2991, 2928, 2861, 1791, 1730 (CO), 1667, 1604, 1453, 1399, 746, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d, 2H,  $J$  = 8.0 Hz, ArH), 7.61 (d, 2H,  $J$  = 7.6 Hz, ArH), 7.55 (d, 2H,  $J$  = 8.4 Hz, ArH), 7.49 (t, 2H,  $J$  = 7.2 Hz, ArH), 7.43 (d, 1H,  $J$  = 6.8 Hz, ArH), 7.19-7.09 (m, 3H, ArH), 6.95 (d, 2H,  $J$  = 7.2 Hz, ArH), 6.14 (d, 1H,  $J_{1',2'}=3.2$  Hz, H-1'), 5.70 (d, 1H,  $J_{4',3'}=4.2$  Hz, H-4'), 4.68 (d, 1H,  $J_{2',1'}=3.2$  Hz, H-2'), 4.62 (d, 1H,  $J_{3',4'}=4.2$  Hz, H-3'), 4.53 (d, B of AB, 1H,  $J$  = 11.2 Hz,  $\text{PhCH}_B$ ), 4.25 (d, A of AB, 1H,  $J$  = 11.2 Hz,  $\text{PhCH}_A$ ), 1.55, 1.36 (2 s, each 3H, 2  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.64 (C-1), 189.88 (C-2), 147.21, 139.70, 135.97 (4 aromatic C), 131.33, 129.14, 128.67, 128.38, 128.29, 128.14, 127.41, 127.26 (14 aromatic CH), 112.89 (isopropylidene C), 105.87 (C-1'), 83.87 (C-4'), 83.75 (C-3'), 82.14 (C-2'), 72.67 ( $\text{PhCH}_2\text{O}$ ), 27.33, 26.65 (2  $\text{CH}_3$ ); HRMS (ESI)  $m/z$  Calcd for  $\text{C}_{28}\text{H}_{27}\text{O}_6$  [M+H] $^+$ : 459.1808. Found: 459.1813.

**2-(3-O-Benzyl-1,2-O-isopropylidene- $\alpha$ -D-xylo-tetrofuranos-4-yl)-3-(4-cyanophenyl)quinoxaline**

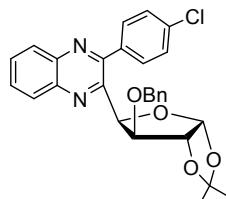
**(2ab)**



Pale yellow oil, 73%;  $R_f$  0.28 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -59.5 ( $c$  1.4,  $\text{CHCl}_3$ ); FTIR (thin film): 2986, 2956, 2933, 2227 (CN), 1606, 1483, 1455, 848, 749  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24-8.21 (m, 1H, ArH), 8.13-8.10 (m, 1H, ArH), 7.84-7.79 (m, 2H, ArH), 7.63 (d, 2H,  $J$  = 8.0 Hz, ArH), 7.32 (d, 2H,  $J$  = 8.0 Hz, ArH), 7.18 (t, 1H,  $J$  = 7.6 Hz, ArH), 7.06 (t, 2H,  $J$  = 7.6 Hz, ArH), 6.70 (d, 2H,  $J$  = 7.6 Hz, ArH), 6.03 (d, 1H,  $J_{1',2'}=4.0$  Hz, H-1'), 5.64 (d, 1H,  $J_{4',3'}=4.0$  Hz, H-4'), 4.68 (d, 1H,  $J_{2',1'}=4.0$  Hz, H-2'), 4.48 (d, B of AB, 1H,  $J$  = 12.4 Hz,  $\text{PhCH}_B$ ), 4.12 (d, A of AB, 1H,  $J$  = 12.4 Hz,  $\text{PhCH}_A$ ), 3.93 (d, 1H,  $J_{3',4'}=4.0$  Hz, H-3'), 1.42, 1.32 (2 s, each 3H, 2  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.11 (C-3), 149.29 (C-2), 143.32, 141.08, 140.75, 136.69 (4 aromatic C), 131.76, 130.64, 129.75, 129.37, 129.15, 128.89, 128.35, 128.14, 127.84 (13 aromatic CH), 118.51 (CN), 112.49 (aromatic C), 112.34 (isopropylidene C), 105.38 (C-1'), 83.18 (C-3'), 82.75 (C-2'), 81.14 (C-4'), 71.63 ( $\text{PhCH}_2\text{O}$ ), 27.02, 26.51 (2  $\text{CH}_3$ ); HRMS (ESI)  $m/z$  Calcd for  $\text{C}_{29}\text{H}_{26}\text{N}_3\text{O}_4$  [M+H] $^+$ : 480.1923. Found: 480.1920.

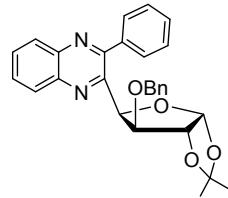
**2-(3-O-Benzyl-1,2-O-isopropylidene- $\alpha$ -D-xylo-tetrofuranos-4-yl)-3-(4-chlorophenyl)quinoxaline**

**(2ac)**



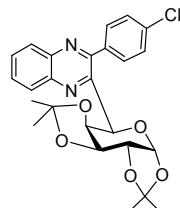
Pale yellow foam, 75%;  $R_f$  0.30 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -66.6 ( $c$  1.4, CHCl<sub>3</sub>); FTIR (thin film): 3108, 2990, 2953, 2932, 1623, 1610, 1578, 1485, 1447, 757 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29-8.27 (m, 1H, ArH), 8.12-8.10 (m, 1H, ArH), 7.81-7.76 (m, 2H, ArH), 7.34 (d, 2H,  $J$  = 8.4 Hz, ArH), 7.19-7.04 (m, 5H, ArH), 6.69 (d, 2H,  $J$  = 7.2 Hz, ArH), 6.22 (d, 1H,  $J_{1',2'}=4.0$  Hz, H-1'), 5.71 (d, 1H,  $J_{4',3'}=4.0$  Hz, H-4'), 4.69 (d, 1H,  $J_{2',1'}=4.0$  Hz, H-2'), 4.45 (d, B of AB, 1H,  $J$  = 12.4 Hz, PhCH<sub>B</sub>), 4.09 (d, A of AB, 1H,  $J$  = 12.4 Hz, PhCH<sub>A</sub>), 3.81 (d, 1H,  $J_{3',4'}=4.0$  Hz, H-3'), 1.42, 1.32 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.28 (C-3), 149.31 (C-2), 141.10, 140.96, 136.89, 136.75, 135.22 (5 aromatic C), 130.32, 130.17, 130.08, 129.55, 129.06, 128.62, 128.30, 127.99, 127.66 (13 aromatic CH), 112.16 (isopropylidene C), 105.31 (C-1'), 82.93 (C-3'), 82.89 (C-2'), 80.24 (C-4'), 71.43 (PhCH<sub>2</sub>O), 26.98, 26.59 (2 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>28</sub>H<sub>26</sub>ClN<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 489.1581. Found: 489.1585.

**2-(3-O-Benzyl-1,2-O-isopropylidene- $\alpha$ -D-xylo-tetrofuranos-4-yl)-3-phenylquinoxaline (2ad)**



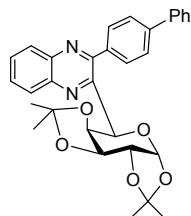
Brown oil, 86%;  $R_f$  0.35 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -60.6 ( $c$  1.4, CHCl<sub>3</sub>); FTIR (thin film): 3082, 3001, 2976, 2934, 1647, 1572, 1453, 1395, 745, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.37-8.33 (m, 1H, ArH), 8.18-8.14 (m, 1H, ArH), 7.83-7.79 (m, 2H, ArH), 7.46-7.40 (m, 3H, ArH), 7.24-7.17 (m, 3H, ArH), 7.09 (t, 2H,  $J$  = 7.6 Hz, ArH), 6.74 (d, 2H,  $J$  = 7.3 Hz, ArH), 6.29 (d, 1H,  $J_{1',2'}=4.0$  Hz, H-1'), 5.78 (d, 1H,  $J_{4',3'}=3.6$  Hz, H-4'), 4.69 (d, 1H,  $J_{2',1'}=4.0$  Hz, H-2'), 4.44 (d, B of AB, 1H,  $J$  = 12.4 Hz, PhCH<sub>B</sub>), 4.11 (d, A of AB, 1H,  $J$  = 12.4 Hz, PhCH<sub>A</sub>), 3.74 (d, 1H,  $J_{3',4'}=3.6$  Hz, H-3'), 1.41, 1.33 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.67 (C-3), 149.32 (C-2), 141.15, 141.06, 138.08, 137.02 (4 aromatic C), 130.17, 129.94, 129.63, 129.16, 129.09, 128.58, 128.49, 128.26, 127.89, 127.52 (14 aromatic CH), 111.97 (isopropylidene C), 105.20 (C-1'), 82.98 (C-3'), 82.88 (C-2'), 79.90 (C-4'), 71.44 (PhCH<sub>2</sub>O), 26.88, 26.61 (2 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 455.1971. Found: 455.1980.

**2-(1,2:3,4-di-O-isopropylidene- $\alpha$ -D-galaacto-pentopyranos-5-yl)-3-(4-chlorophenyl)quinoxaline (2ba)**



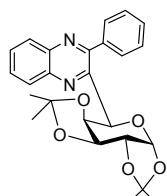
Brown oil, 76%;  $R_f$  0.40 (2:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -153.2 ( $c$  1.4, CHCl<sub>3</sub>); FTIR (thin film): 3064, 2985, 2935, 1737, 1609, 1533, 1494, 1383, 892, 762 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.29-8.26 (m, 1H, ArH), 8.09-8.06 (m, 1H, ArH), 8.77-8.72 (m, 2H, ArH), 7.55 (d, 2H,  $J$  = 8.4 Hz, ArH), 7.48 (d, 2H,  $J$  = 8.4 Hz, ArH), 5.83 (d, 1H,  $J_{1',2'}=5.2$  Hz, H-1'), 5.46 (d, 1H,  $J_{5',4'}=2.4$  Hz, H-5'), 4.53 (dd, 1H,  $J_{3',2'}=2.6$  Hz, J<sub>3',4'</sub> = 7.4 Hz, H-3'), 4.39 (dd, 1H,  $J_{2',3'}=2.6$  Hz, J<sub>2',1'</sub> = 5.2 Hz, H-2'), 4.12 (dd, 1H,  $J_{4',3'}=7.4$  Hz, J<sub>4',5'</sub> = 2.4 Hz, H-4'), 1.43 (s, 6H, 2 CH<sub>3</sub>), 1.32, 1.17 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.06 (C-3), 149.92 (C-2), 141.33, 140.86, 137.36, 135.32 (4 aromatic C), 130.21, 130.14, 130.05, 129.57, 129.08, 128.88 (8 aromatic CH), 110.10, 108.72 (2 isopropylidene C), 97.10 (C-1'), 72.22 (C-4'), 71.17 (C-3'), 70.13 (C-2'), 68.64 (C-5'), 25.93, 25.80, 24.85, 24.71 (4 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>25</sub>H<sub>26</sub>ClN<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 469.1530. Found: 469.1526.

### **2-(1,2:3,4-di-O-isopropylidene- $\alpha$ -D-galaacto-pentopyranos-5-yl)-3-biphenylquinoxaline (2bb)**



White foam, 89%;  $R_f$  = 0.30 (2:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -123.4 ( $c$  1.7, CHCl<sub>3</sub>); FTIR (thin film): 3077, 2999, 2934, 1727, 1606, 1550, 1486, 760, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34-8.31 (m, 1H, ArH), 8.14-8.10 (m, 1H, ArH), 7.79-7.75 (m, 4H, ArH), 7.70-7.64 (m, 4H, ArH), 7.50-7.47 (m, 2H, ArH), 7.40-7.38 (m, 1H, ArH), 5.90 (d, 1H,  $J_{1',2'}=5.2$  Hz, H-1'), 5.60 (d, 1H,  $J_{5',4'}=2.4$  Hz, H-5'), 4.54 (dd, 1H,  $J_{3',2'}=2.6$  Hz, J<sub>3',4'</sub> = 7.6 Hz, H-3'), 4.41 (dd, 1H,  $J_{2',3'}=2.6$  Hz, J<sub>2',1'</sub> = 5.2 Hz, H-2'), 4.19 (dd, 1H,  $J_{4',3'}=7.6$  Hz, J<sub>4',5'</sub> = 2.4 Hz, H-4'), 1.49, 1.44, 1.32, 1.20 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.97 (C-3), 150.05 (C-2), 142.06, 141.40, 141.03, 140.36, 137.66 (5 aromatic C), 130.02, 129.83, 129.67, 129.17, 129.15, 128.95, 127.81, 127.53, 127.21 (13 aromatic CH), 110.13, 108.75 (2 isopropylidene C), 97.27 (C-1'), 72.25 (C-4'), 71.24 (C-3'), 70.17 (C-2'), 68.41 (C-5'), 25.88, 24.92, 24.83 (4 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>31</sub>H<sub>31</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 511.2233. Found: 511.2239.

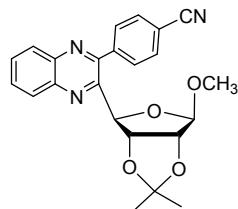
### **2-(1,2:3,4-di-O-isopropylidene- $\alpha$ -D-galaacto-pentopyranos-5-yl)-3-phenylquinoxaline (2bc)**



Pale yellow oil, 88%;  $R_f$  = 0.40 (4:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -154.2 ( $c$  1.3, CHCl<sub>3</sub>); FTIR (KBr): 3069, 3003, 2956, 1738, 1619, 1528, 1480, 748, 703 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.31-8.28 (m, 1H, ArH), 8.10-8.08 (m, 1H, ArH), 7.76-7.69 (m, 2H, ArH), 7.59-7.56 (m, 2H, ArH), 7.52-

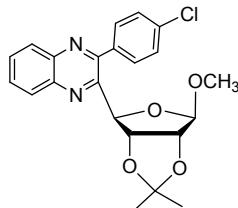
7.26 (m, 3H, ArH), 5.86 (d, 1H,  $J_{1',2'} = 5.2$  Hz, H-1'), 5.50 (d, 1H,  $J_{5',4'} = 2.4$  Hz, H-5'), 4.47 (dd, 1H,  $J_{3',2'} = 2.6$  Hz,  $J_{3',4'} = 7.4$  Hz, H-3'), 4.38 (dd, 1H,  $J_{2',3'} = 2.6$  Hz,  $J_{2',1'} = 5.2$  Hz, H-2'), 4.06 (dd, 1H,  $J_{4',3'} = 7.4$  Hz,  $J_{4',5'} = 2.4$  Hz, H-4'), 1.45, 1.39, 1.29, 1.16 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.18 (C-3), 150.00 (C-2), 141.38, 140.94, 138.70 (aromatic C), 129.96, 129.78, 129.64, 129.20, 129.10, 128.81, 128.61 (9 aromatic CH), 110.08, 108.71 (2 isopropylidene C), 97.22 (C-1'), 72.13 (C-4'), 71.19 (C-3'), 70.11 (C-2'), 68.35 (C-5'), 25.84, 24.89, 24.80 (4 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 457.1739. Found: 457.1742.

**2-(2,3-*O*-isopropylidene-1-*O*-methyl-β-D-ribo-tetrofuranos-4-yl)-3-(4-cyanophenyl)quinoxaline (2ca)**



Brown oil, 72%; *R<sub>f</sub>* 0.50 (3:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> +1.8 (*c* 1.0, CHCl<sub>3</sub>); FTIR (thin film): 3064, 2986, 2926, 2853, 2229 (CN), 1607, 1457, 1377, 865, 762 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13-8.10 (m, 2H, ArH), 7.98 (d, 2H, *J* = 8.4 Hz, ArH), 7.83-7.79 (m, 4H, ArH), 5.85 (d, 1H,  $J_{3',2'} = 6.0$  Hz, H-3'), 5.52 (s, 1H, H-4'), 5.00 (s, 1H, H-1'), 4.92 (d, 1H,  $J_{2',3'} = 6.0$  Hz, H-2'), 2.91 (s, 3H, OCH<sub>3</sub>), 1.50, 1.39 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.56 (C-3), 151.32 (C-2), 142.82, 141.24, 140.55 (3 aromatic C), 132.30, 130.85, 130.58, 130.32, 129.49, 129.18, (8 aromatic CH), 118.56 (CN), 112.93 (aromatic C), 112.32 (isopropylidene C), 110.91 (C-1'), 86.37 (C-2'), 84.96 (C-4'), 82.22 (C-3'), 54.79 (OCH<sub>3</sub>), 26.59, 25.05 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 404.1610. Found: 404.1616.

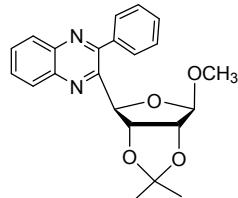
**2-(2,3-*O*-isopropylidene-1-*O*-methyl-β-D-ribo-tetrofuranos-4-yl)-3-(4-chlorophenyl)quinoxaline (2cb)**



Pale yellow oil, 76%; *R<sub>f</sub>* 0.30 (6:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> -7.7 (*c* 1.6, CHCl<sub>3</sub>); FTIR (thin film): 3065, 2992, 2935, 2854, 1613, 1450, 1379, 857, 758 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12-8.10 (m, 2H, ArH), 7.82-7.75 (m, 4H, ArH), 7.51 (d, 2H, *J* = 8.8 Hz, ArH), 5.84 (d, 1H,  $J_{3',2'} = 5.6$  Hz, H-3'), 5.58 (s, 1H, H-4'), 5.02 (s, 1H, H-1'), 4.95 (d, 1H,  $J_{2',3'} = 5.6$  Hz, H-2'), 2.93 (s, 3H, OCH<sub>3</sub>), 1.52, 1.40 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.47 (C-3), 151.52 (C-2), 141.33, 140.39,

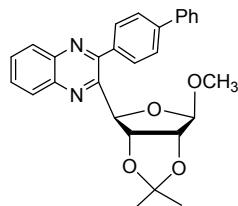
136.79, 135.53 (4 aromatic C), 130.95, 130.56, 130.03, 129.45, 129.11, 128.83 (8 aromatic CH), 112.24 (isopropylidene C), 110.89 (C-1'), 86.51 (C-2'), 85.01 (C-4'), 82.42 (C-3'), 54.70 (OCH<sub>3</sub>), 26.64, 25.10 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>22</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup>: 435.1088. Found: 435.1091

**2-(2,3-*O*-isopropylidene-1-*O*-methyl-β-D-*ribo*-tetrofuranos-4-yl)-3-phenylquinoxaline (2cc)**



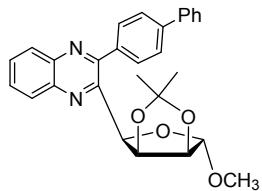
Yellow oil, 86%; *R*<sub>f</sub> 0.40 (5:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> -4.5 (*c* 1.5, CHCl<sub>3</sub>); FTIR (thin film): 3071, 3000, 2933, 2864, 1615, 1458, 1361, 860, 758, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18-8.13 (m, 2H, ArH), 7.88-7.86 (m, 2H, ArH), 7.82-7.75 (m, 2H, ArH), 7.60-7.51 (m, 3H, ArH), 5.86 (d, 1H, *J*<sub>3',2'</sub>= 6.0 Hz, H-3'), 5.68 (s, 1H, H-4'), 5.06 (s, 1H, H-1'), 5.00 (d, 1H, *J*<sub>2',3'</sub>= 6.0 Hz, H-2'), 2.98 (s, 3H, OCH<sub>3</sub>), 1.54, 1.43 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.75 (C-3), 151.77 (C-2), 141.40, 140.37, 138.37 (3 aromatic C), 130.39, 129.79, 129.48, 129.45, 129.18, 129.17, 128.61 (9 aromatic CH), 112.16 (isopropylidene C), 110.86 (C-1'), 86.59 (C-2'), 85.00 (C-4'), 82.56 (C-3'), 54.67 (OCH<sub>3</sub>), 26.64, 25.12 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup>: 401.1477. Found: 401.1481.

**2-(2,3-*O*-isopropylidene-1-*O*-methyl-β-D-*ribo*-tetrofuranos-4-yl)-3-biphenylquinoxaline (2cd)**



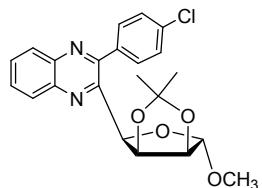
Pale yellow oil, 88%; *R*<sub>f</sub> 0.38 (5:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> -2.8 (*c* 2.0, CHCl<sub>3</sub>); FTIR (thin film): 3048, 2995, 2937, 2861, 1601, 1450, 1382, 750, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18-8.13 (m, 2H, ArH), 7.97 (d, 2H, *J*= 8.4 Hz, ArH), 7.80-7.75 (m, 4H, ArH), 7.69 (d, 2H, *J*= 7.4 Hz, ArH), 7.49 (t, 2H, *J*= 7.4 Hz, ArH), 7.40 (t, 1H, *J*= 7.4 Hz, ArH), 5.87 (d, 1H, *J*<sub>3',2'</sub>= 6.0 Hz, H-3'), 5.74 (s, 1H, H-4'), 5.09 (s, 1H, H-1'), 5.02 (d, 1H, *J*<sub>2',3'</sub>= 6.0 Hz, H-2'), 2.99 (s, 3H, OCH<sub>3</sub>), 1.55, 1.43 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.42 (C-3), 151.77 (C-2), 141.99, 141.48, 140.59, 140.38, 137.28 (5 aromatic C), 130.45, 130.02, 129.82, 129.47, 129.19, 128.90, 127.68, 127.39, 127.27 (13 aromatic CH), 112.20 (isopropylidene C), 110.94 (C-1'), 86.63 (C-2'), 85.08 (C-4'), 82.63 (C-3'), 54.71 (OCH<sub>3</sub>), 26.69, 25.14 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 455.1971, found: 455.1973.

**2-(2,3-*O*-isopropylidene-1-*O*-methyl- $\alpha$ -D-*lyxo*-tetrofuranos-4-yl)-3-biphenylquinoxaline (2da)**



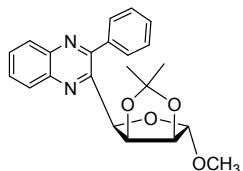
Pale yellow solid, 88%;  $R_f$  0.30 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -46.4 ( $c$  1.9, CHCl<sub>3</sub>); FTIR (KBr): 3031, 2985, 2855, 1642, 1588, 1484, 1381, 832, 769, 695 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36-8.34 (m, 1H, ArH), 8.15-8.13 (m, 1H, ArH), 7.79-7.74 (m, 4H, ArH), 7.69-7.65 (m, 4H, ArH), 7.48 (t, 2H,  $J$  = 7.4 Hz, ArH), 7.39 (t, 1H,  $J$  = 7.4 Hz, ArH), 5.51 (d, 1H,  $J_{4',3'}=4.2$  Hz, H-4'), 5.32 (s, 1H, H-1'), 4.59 (dd, 1H,  $J_{3',2'}=6.0$  Hz,  $J_{3',4'}=4.2$  Hz, H-3'), 4.55 (d, 1H,  $J_{2',3'}=6.0$  Hz, H-2'), 3.42 (s, 3H, OCH<sub>3</sub>), 1.28, 1.16 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.48 (C-3), 149.54 (C-2), 142.08, 141.21, 141.04, 140.36, 137.40 (5 aromatic C), 129.96, 129.82, 129.54, 129.16, 129.01, 128.96, 127.80, 127.51, 127.22 (13 aromatic CH), 113.39 (isopropylidene C), 106.83 (C-1'), 84.69 (C-2'), 81.23 (C-3'), 80.60 (C-4'), 55.34 (OCH<sub>3</sub>), 25.78, 25.25 (2 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> M<sup>+</sup>: 454.1893. Found: 454.1897.

**2-(2,3-O-isopropylidene-1-O-methyl-alpha-D-lyxo-tetrofuranos-4-yl)-3-(4-chlorophenyl)quinoxaline (2db)**



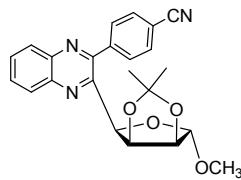
Brown oil, 75%;  $R_f$  = 0.50 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -44.3 ( $c$  1.7, CHCl<sub>3</sub>); FTIR (thin film): 2932, 2854, 1651, 1599, 1487, 1382, 827, 774 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32-8.29 (m, 1H, ArH), 8.10-8.07 (m, 1H, ArH), 7.77-7.72 (m, 2H, ArH), 7.50 (br s, 4H, ArH), 5.36 (d, 1H,  $J_{4',3'}=4.4$  Hz, H-4'), 5.27 (s, 1H, H-1'), 4.53 (d, 1H,  $J_{2',3'}=6.0$  Hz, H-2'), 4.47 (dd, 1H,  $J_{3',2'}=6.0$  Hz,  $J_{3',4'}=4.4$  Hz, H-3'), 3.38 (s, 3H, OCH<sub>3</sub>), 1.21, 1.13 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.51 (C-3), 149.35 (C-2), 141.22, 140.89, 136.96, 135.46 (4 aromatic C), 130.07, 130.01, 129.51, 129.08, 129.00 (8 aromatic CH), 113.41 (isopropylidene C), 106.74 (C-1'), 84.59 (C-2'), 81.07 (C-3'), 80.49 (C-4'), 55.30 (OCH<sub>3</sub>), 25.70, 25.18 (2 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>22</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup>: 435.1088. Found: 435.1093.

**2-(2,3-O-isopropylidene-1-O-methyl-alpha-D-lyxo-tetrofuranos-4-yl)-3-phenylquinoxaline (2dc)**



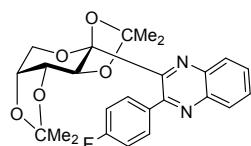
Pale yellow oil, 86%;  $R_f$  0.40 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -35.8 ( $c$  1.5, CHCl<sub>3</sub>); FTIR (thin film): 3052, 2961, 2867, 1629, 1593, 1485, 1386, 844, 760, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33-8.30(m, 1H, ArH), 8.12-8.10 (m, 1H, ArH), 7.76-7.71 (m, 2H, ArH), 7.57-7.50 (m, 5H, ArH), 5.41 (d, 1H,  $J_{4',3'} = 4.4$  Hz, H-4'), 5.48 (s, 1H, H-1'), 4.50 (d, 1H,  $J_{2',3'} = 6.0$  Hz, H-2'), 4.45 (dd, 1H,  $J_{3',2'} = 6.0$  Hz  $J_{3',4'} = 4.4$  Hz, H-3'), 3.38 (s, 3H, OCH<sub>3</sub>), 1.24, 1.13 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.69 (C-3), 149.52 (C-2), 141.18, 140.95, 138.50 (3 aromatic C), 129.90, 129.76, 129.52, 129.19, 129.12, 128.75, 128.49 (9 aromatic CH), 113.31 (isopropylidene C), 106.78 (C-1'), 84.64 (C-2'), 81.13 (C-3'), 80.56 (C-4'), 55.28 (OCH<sub>3</sub>), 25.75, 25.18 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 379.1658. Found: 379.1664.

**2-(2,3-*O*-isopropylidene-1-*O*-methyl- $\alpha$ -D-lyxo-tetrofuranos-4-yl)-3-(4-cyanophenyl)quinoxaline (2dd)**



White solid, 73%;  $R_f$  0.50 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -26.1 ( $c$  2.0, CHCl<sub>3</sub>); FTIR (KBr): 3063, 2987, 2931, 2854, 2229 (CN), 1607, 1482, 1383, 844, 762 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32-8.29 (m, 1H, ArH), 8.10-8.07 (m, 1H, ArH), 7.83-7.69 (m, 6H, ArH), 5.33 (d, 1H,  $J_{4',3'} = 4.4$  Hz, H-4'), 5.25 (s, 1H, H-1'), 4.53 (d, 1H,  $J_{2',3'} = 5.6$  Hz, H-2'), 4.44 (dd, 1H,  $J_{3',2'} = 5.6$  Hz,  $J_{3',4'} = 4.4$  Hz, H-3'), 3.37 (s, 3H, OCH<sub>3</sub>), 1.20, 1.13 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.66 (C-3), 148.92 (C-2), 143.11, 141.35, 140.76 (3 aromatic C), 132.45, 130.50, 130.40, 129.59, 129.52, 129.11 (8 aromatic CH), 118.30 (CN), 113.52 (isopropylidene C), 113.18 (aromatic C), 106.75 (C-1'), 84.55 (C-2'), 81.05 (C-3'), 80.47 (C-4'), 55.35 (OCH<sub>3</sub>), 25.65, 25.11 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>Na[M+Na]<sup>+</sup>: 426.1430. Found: 426.1436

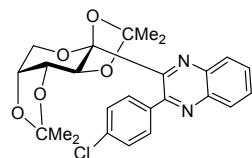
**2-(1,2:3,4-di-*O*-isopropylidene- $\beta$ -D-arabino-pent-1,5-pyranos-1-yl)-3-(4-fluorophenyl)quinoxaline (2ea)**



Brown oil, 71%;  $R_f$  0.55 (4:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  +22.8 ( $c$  0.6, CHCl<sub>3</sub>); FTIR (thin film): 3063, 2995, 2946, 1608, 1550, 1457, 1375, 862, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18-8.14 (m, 2H, ArH), 7.83-7.76 (m, 2H, ArH), 7.74-7.71 (m, 2H, ArH), 7.14-7.09 (m, 2H, ArH), 5.88 (d, 1H,  $J_{2',3'} = 2.2$  Hz, H-2'), 4.73 (dd, 1H,  $J_{3',2'} = 2.2$  Hz,  $J_{3',4'} = 7.4$  Hz, H-3'), 4.26 (dd, 1H,  $J_{4',3'} = 7.4$  Hz,  $J_{4',5'a} = 1.6$  Hz, H-4'), 3.89 (dd, 1H,  $J_{5'a,4'} = 1.6$  Hz,  $J_{5'a,5'b} = 13.0$  Hz, H-5'a), 3.53 (d, 1H,  $J_{5'b,5'a} = 13.0$  Hz, H-5'b),

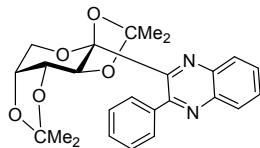
1.50 (s, 3H,  $CH_3$ ), 1.31 (d, 6H, 2  $CH_3$ ), 1.16 (s, 3H,  $CH_3$ );  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  162.80 (C-F, d,  $^1J_{C-F}$  = 245.0 Hz), 153.90 (C-3), 151.29 (C-2), 140.71 (C-8a), 139.12 (C-4a), 137.07 (aromatic C, d,  $^4J_{C-F}$  = 4.0 Hz), 131.28 (2 aromatic CH, d,  $^3J_{C-F}$  = 8.0 Hz), 130.46, 129.74, 129.34, 128.93 (4 aromatic CH), 114.04 (2 aromatic CH, d,  $^2J_{C-F}$  = 21.0 Hz), 109.05, 108.68 (2 isopropylidene C), 103.97 (C-1'), 72.11 (C-2'), 71.30 (C-3'), 70.43 (C-4'), 60.83 (C-5'), 26.15, 25.92, 25.31, 24.64 (4  $CH_3$ ); HRMS (ESI)  $m/z$  Calcd for  $C_{25}H_{25}N_2O_5Na$  [M+Na] $^+$ : 475.1645. Found: 475.1648.

**2-(1,2:3,4-di-O-isopropylidene- $\beta$ -D-arabino-pent-1,5-pyranos-1-yl)-3-(4-chlorophenyl)quinoxaline (2eb)**



Yellow oil, 71%;  $R_f$  0.33 (5:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  +21 ( $c$  0.5,  $CHCl_3$ ); FTIR (thin film): 3055, 3037, 2986, 2930, 1608, 1552, 1465, 1387, 851, 767 cm $^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.16-8.11 (m, 2H, ArH), 7.81-7.75 (m, 2H, ArH), 7.66 (d, 2H,  $J$  = 8.6 Hz, ArH), 7.38 (d, 2H,  $J$  = 8.6 Hz, ArH), 5.86 (d, 1H,  $J_{2',3'}=2.3$  Hz, H-2'), 4.71 (dd, 1H,  $J_{3',2'}=2.3$  Hz,  $J_{3',4'}=7.6$  Hz, H-3'), 4.24 (br d, 1H,  $J$  = 7.6 Hz, H-4'), 3.85 (dd, 1H,  $J_{5'a,4'}=1.8$  Hz,  $J_{5'a,5'b}=13.0$  Hz, H-5'a), 3.51 (dd, 1H,  $J_{5'b,4'}=2.4$  Hz,  $J_{5'b,5'a}=13.0$  Hz, H-5'b), 1.48, 1.30, 1.29, 1.18 (4 s, each 3H, 4  $CH_3$ );  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  152.69 (C-3), 150.18 (C-2), 139.69, 138.52, 138.13, 132.95 (4 aromatic C), 129.80, 129.44, 128.79, 128.31, 127.94, 126.30 (8 aromatic CH), 108.01, 107.73 (2 isopropylidene C), 102.87 (C-1'), 71.05 (C-2'), 70.25 (C-3'), 69.43 (C-4'), 59.84 (C-5'), 25.13, 24.88, 24.29, 23.59 (4  $CH_3$ ); HRMS (ESI)  $m/z$  Calcd for  $C_{25}H_{25}ClN_2O_5Na$  [M+Na] $^+$ : 491.1350. Found: 491.1356.

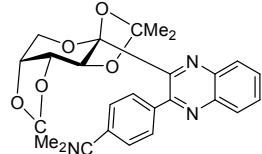
**2-(1,2:3,4-di-O-isopropylidene- $\beta$ -D-arabino-pent-1,5-pyranos-1-yl)-3-phenylquinoxaline (2ec)**



Yellow oil, 83%;  $R_f$  0.52 (4:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  +19.8 ( $c$  0.5,  $CHCl_3$ ); FTIR (thin film): 3051, 2985, 2938, 2867, 1611, 1554, 1459, 1382, 872, 761, 697 cm $^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.18-8.16 (m, 2H, ArH), 7.82-7.76 (m, 2H, ArH), 7.72-7.70 (m, 2H, ArH), 7.45-7.41 (m, 3H, ArH), 5.88 (d, 1H,  $J_{2',3'}=2.1$  Hz, H-2'), 4.73 (dd, 1H,  $J_{3',2'}=2.1$  Hz,  $J_{3',4'}=7.6$  Hz, H-3'), 4.25 (br d, 1H,  $J_{4',3'}=7.6$  Hz, H-4'), 3.86 (dd, 1H,  $J_{5'a,4'}=2.0$  Hz,  $J_{5'a,5'b}=13.0$  Hz, H-5'a), 3.51 (d, 1H,  $J_{5'b,5'a}=13.0$  Hz, H-5'b), 1.48 (s, 3H,  $CH_3$ ), 1.32 (s, 6H, 2  $CH_3$ ), 1.18 (s, 3H,  $CH_3$ );  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  154.99 (C-3), 151.40 (C-2), 141.08 (C-8a), 140.77 (C-4a), 139.13 (aromatic C), 130.33, 129.60, 129.32, 127.78, 127.09 (9 aromatic CH), 109.05, 108.60 (2 isopropylidene C), 104.00 (C-1'), 72.17 (C-2'),

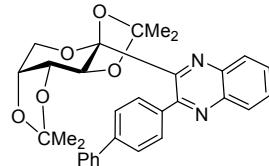
71.39 (C-3'), 70.47 (C-4'), 60.81 (C-5'), 26.15, 25.96, 25.32, 24.70 (4 CH<sub>3</sub>). HRMS (ESI) *m/z* Calcd for C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 457.1739. Found: 457.1741.

**2-(1,2:3,4-di-*O*-isopropylidene- $\beta$ -D-*arabino*-pent-1,5-pyranos-1-yl)-3-(4-cyanophenyl)quinoxaline (2ed)**



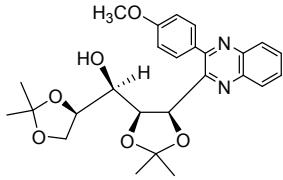
Yellow oil, 70%; *R*<sub>f</sub> 0.42 (5:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> +15.7 (*c* 0.5, CHCl<sub>3</sub>); FTIR (thin film): 3064, 3000, 2986, 2939, 2229 (CN), 1605, 1549, 1458, 1385, 860, 772 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19-8.12 (m, 2H, ArH), 7.83-7.81 (m, 4H, ArH), 7.72 (d, 2H, *J* = 8.4 Hz, ArH), 5.86 (d, 1H, *J*<sub>2',3'</sub> = 2.2 Hz, H-2'), 4.71 (dd, 1H, *J*<sub>3',2'</sub> = 2.2 Hz, *J*<sub>3',4'</sub> = 8.0 Hz, H-3'), 4.23 (dd, 1H, *J*<sub>4',5'b</sub> = 1.5 Hz, *J*<sub>4',3'</sub> = 8.0 Hz, H-4'), 3.83 (dd, 1H, *J*<sub>5'a,4'</sub> = 1.5 Hz, *J*<sub>5'a,5'b</sub> = 13.2 Hz, H-5'a), 3.45 (d, 1H, *J*<sub>5'b,5'a</sub> = 13.2 Hz, H-5'b), 1.49, 1.32, 1.28, 1.10 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.84 (C-3), 151.06 (C-2), 145.66, 140.57, 139.37 (3 aromatic C), 131.04, 130.85, 130.40, 130.12, 129.42, 128.99 (8 aromatic CH), 119.18 (CN), 111.44 (aromatic C), 109.03, 108.98 (2 isopropylidene C), 103.65 (C-1'), 71.99 (C-2'), 71.07 (C-3'), 70.35 (C-4'), 60.91 (C-5'), 26.16, 25.89, 25.34, 24.53 (4 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>26</sub>H<sub>25</sub>N<sub>3</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 482.1692. Found: 482.1696.

**2-(1,2:3,4-di-*O*-isopropylidene- $\beta$ -D-*arabino*-pent-1,5-pyranos-1-yl)-3-biphenylquinoxaline (2ee)**



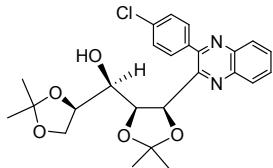
Brown oil, 81%; *R*<sub>f</sub> 0.36 (4:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> +8.0 (*c* 1.0, CHCl<sub>3</sub>); FTIR (thin film): 3065, 2988, 2935, 1601, 1546, 1456, 1383, 844, 766, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17-8.15 (m, 2H, ArH), 7.82-7.76 (m, 4H, ArH), 7.47 (t, 2H, *J* = 7.6 Hz, ArH), 7.36 (t, 1H, *J* = 7.6 Hz, ArH), 5.89 (d, 1H, *J*<sub>2',3'</sub> = 2.4 Hz, H-2'), 4.72 (dd, 1H, *J*<sub>3',2'</sub> = 2.4 Hz, *J*<sub>3',4'</sub> = 8.2 Hz, H-3'), 4.25 (br d, 1H, *J* = 6.8 Hz, H-4'), 3.88 (dd, 1H, *J*<sub>5'a,4'</sub> = 1.8 Hz, *J*<sub>5'a,5'b</sub> = 13.2 Hz, H-5'a), 3.53 (d, 1H, *J*<sub>5'b,5'a</sub> = 13.2 Hz, H-5'b), 1.50, 1.33, 1.30, 1.17 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.63 (C-3), 151.38 (C-2), 141.16, 140.83, 140.47, 140.18, 139.11 (5 aromatic C), 130.38, 129.85, 129.64, 129.34, 129.03, 128.77, 127.25, 127.17, 125.92 (13 aromatic CH), 109.07, 108.72 (2 isopropylidene C), 104.04 (C-1'), 72.21 (C-2'), 71.38 (C-3'), 70.50 (C-4'), 60.87 (C-5'), 26.22, 25.98, 25.38, 24.70 (4 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>31</sub>H<sub>31</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 511.2233. Found: 511.2236.

**2-(1,2:4,5-di-*O*-isopropylidene-D-manno-1,2,3,4,5-pentahydroxypentyl)-3-(4-methoxyphenyl)quinoxaline (2fa)**



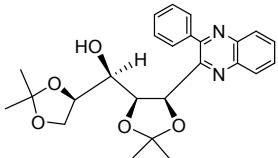
Pale yellow foam, 90%;  $R_f$  0.55 (2:1 petroleum ether-EtOAc);  $[\alpha]_D^{20} +57.5$  ( $c$  0.5, CHCl<sub>3</sub>); FTIR (thin film): 3431 (OH), 2997, 2926, 2858, 1628, 1457, 1395, 849, 768 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16-8.11 (m, 2H, H-5, H-8), 7.92 (d, 2H,  $J$  = 8.8 Hz, ArH), 7.81-7.74 (m, 2H, H-6, H-7), 7.06 (d, 2H,  $J$  = 8.8 Hz, ArH), 5.36-5.27 (m, 2H, H-1', H-2'), 3.96-3.81 (m, 6H, H-4', H-5', OCH<sub>3</sub>), 3.46-3.42 (m, 1H, H-3'), 2.47 (d, 1H,  $J_{OH,3'} = 6.0$  Hz, OH), 1.64, 1.55, 1.15, 1.02 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.76 (aromatic C), 155.38 (C-3), 149.39 (C-2), 141.76 (C-8a), 140.78 (C-4a), 131.37 (2 aromatic CH), 130.56 (aromatic CH), 130.33 (aromatic C), 129.57, 129.35, 129.16 (3 aromatic CH), 114.00 (2 aromatic CH), 110.48, 109.26 (2 isopropylidene C), 79.79 (C-2'), 76.06 (C-1'), 71.50 (C-3'), 66.98 (C-5'), 55.51 (OCH<sub>3</sub>), 27.42, 27.18, 26.64, 25.21 (4 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>26</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>Na [M+Na]<sup>+</sup>: 489.2002. Found: 489.2008.

**2-(1,2:4,5-di-O-isopropylidene-D-manno-1,2,3,4,5-pentahydroxypentyl)-3-(4-chlorophenyl)quinoxaline (2fb)**



Yellow solid, 77%;  $R_f$  0.65 (2:1 petroleum ether-EtOAc);  $[\alpha]_D^{20} +37.1$  ( $c$  0.5, CHCl<sub>3</sub>); FTIR (KBr): 3418 (OH), 2989, 2938, 2847, 1609, 1455, 1388, 852, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16-8.14 (m, 2H, H-5, H-8), 7.91 (d, 2H,  $J$  = 8.4 Hz, ArH), 7.85-7.77 (m, 2H, H-6, H-7), 7.53 (d, 2H,  $J$  = 8.8 Hz, ArH), 5.37 (dd, 1H,  $J_{2',3'} = 4.4$  Hz,  $J_{2',1'} = 8.0$  Hz, H-2'), 5.20 (d, 1H,  $J_{1',2'} = 8.0$  Hz, H-1'), 3.98-3.84 (m, 3H, H-4', H-5'), 3.46 (br s, 1H, H-3'), 2.40 (br s, 1H, OH), 1.62, 1.53, 1.16, 1.02 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.51 (C-3), 149.18 (C-2), 141.54 (C-8a), 140.93 (C-4a), 136.28, 135.70 (2 aromatic C), 131.14, 130.73, 130.05, 129.30, 129.15, 128.64 (8 aromatic CH), 110.50, 109.17 (2 isopropylidene C), 79.49 (C-2'), 76.25 (C-4'), 75.95 (C-1'), 71.39 (C-3'), 66.94 (C-5'), 27.26, 27.06, 26.59, 25.12 (4 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>25</sub>H<sub>28</sub>ClN<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 471.1687. Found: 471.1689.

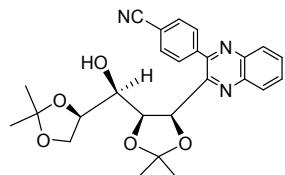
**2-(1,2:4,5-di-O-isopropylidene-D-manno-1,2,3,4,5-pentahydroxypentyl)-3-phenylquinoxaline (2fc)**



Pale yellow oil, 85%;  $R_f$  0.35 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20} +32.6$  ( $c$  0.6, CHCl<sub>3</sub>); FTIR (thin

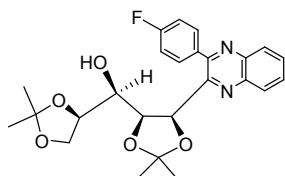
film): 3425 (OH), 3018, 2984, 2950, 2853, 1610, 1458, 1382, 846, 750, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16-8.13 (m, 2H, H-5, H-8), 7.92-7.89 (m, 2H, ArH), 7.79-7.76 (m, 2H, H-6, H-7), 7.92-7.89 (m, 2H, ArH), 7.53-7.51 (m, 3H, ArH), 5.32-5.25 (m, 2H, H-1', H-2'), 3.94-3.81 (m, 3H, H-4', H-5'), 3.45-3.42 (m, 1H, H-3'), 2.38 (br d, 1H, J<sub>OH,3'</sub>= 6.4 Hz, OH), 1.61, 1.50, 1.13, 1.02 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.72 (C-3), 149.58 (C-2), 141.73 (C-4a), 141.05 (C-8a), 137.93 (aromatic C), 130.68, 129.92, 129.83, 129.41, 129.32, 128.53 (9 aromatic CH), 110.55, 109.30 (2 isopropylidene C), 79.83 (C-2'), 76.10 (C-4'), 75.98 (C-1'), 71.45 (C-3'), 66.97 (C-5'), 27.40, 27.16, 26.64, 25.25 (4 CH<sub>3</sub>); HRMS (ESI) m/z Calcd for C<sub>25</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 459.1896. Found: 459.1898.

**2-(1,2:4,5-di-O-isopropylidene-D-manno-1,2,3,4,5-pentahydroxypentyl)-3-(4-cyanophenyl)quinox-aline (2fd)**



Pale yellow foam, 72%; R<sub>f</sub>= 0.32 (3:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup>+27.3 (c 0.7, CHCl<sub>3</sub>); FTIR (thin film): 3440 (OH), 2986, 2926, 2854, 2230 (CN), 1607, 1546, 1457, 1383, 855, 763cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19-8.14 (m, 2H, H-5, H-8), 8.08 (d, 2H, J= 8.4 Hz, ArH), 7.86-7.83 (m, 4H, H-6, H-7, ArH), 5.38 (dd, 1H, J<sub>2',3'</sub>= 4.4 Hz, J<sub>2',1'</sub>= 8.0 Hz, H-2'), 5.15 (d, 1H, J<sub>1',2'</sub>= 8.0 Hz, H-1'), 4.01-3.85 (m, 3H, H-4', H-5'), 3.48 (br s, 1H, H-3'), 2.42 (d, 1H, J<sub>OH,3'</sub>= 6.0 Hz, OH), 1.59, 1.51, 1.17, 1.03 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.50 (C-3), 149.16 (C-2), 142.35 (aromatic C), 141.44 (C-8a), 141.10 (C-4a), 132.10, 131.04, 130.66, 130.47, 129.34, 129.25 (8 aromatic CH), 118.59 (CN), 113.01 (aromatic C), 110.61, 109.18 (2 isopropylidene C), 79.33 (C-2'), 75.94 (C-4'), 75.66 (C-1'), 71.32 (C-3'), 66.98 (C-5'), 27.18, 27.05, 26.66, 25.13 (4 CH<sub>3</sub>); HRMS (ESI) m/z Calcd for C<sub>26</sub>H<sub>28</sub>N<sub>3</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 462.2029. Found: 462.2036.

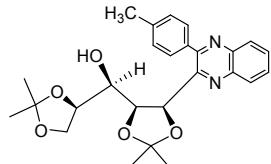
**2-(1,2:4,5-di-O-isopropylidene-D-manno-1,2,3,4,5-pentahydroxypentyl)-3-(4-fluorophenyl)quinox-aline (2fe)**



Yellow foam, 74%; R<sub>f</sub> 0.43 (3:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup>+55.3 (c 0.5, CHCl<sub>3</sub>); FTIR (thin film): 3416 (OH), 2988, 2928, 1606, 1514, 1379, 845, 769 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17-8.14 (m, 2H, H-5, H-8), 7.98-7.93 (m, 2H, ArH), 7.84-7.77 (m, 2H, H-6, H-7), 7.26-7.21 (m, 2H, ArH), 5.37 (dd, 1H, J<sub>2',3'</sub>= 4.4 Hz, J<sub>2',1'</sub>= 8.0 Hz, H-2'), 5.22 (d, 1H, J<sub>1',2'</sub>= 8.0 Hz, H-1'), 3.99-3.83 (m, 3H, H-4', H-5'), 3.46 (br d, 1H, H-3'), 2.42 (d, 1H, J<sub>OH,3'</sub>= 5.6 Hz, OH), 1.62, 1.53, 1.16, 1.03 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.72 (C-3), 149.58 (C-2), 141.73 (C-4a), 141.05 (C-8a), 137.93 (aromatic C), 130.68, 129.92, 129.83, 129.41, 129.32, 128.53 (9 aromatic CH), 110.55, 109.30 (2 isopropylidene C), 79.83 (C-2'), 76.10 (C-4'), 75.98 (C-1'), 71.45 (C-3'), 66.97 (C-5'), 27.40, 27.16, 26.64, 25.25 (4 CH<sub>3</sub>); HRMS (ESI) m/z Calcd for C<sub>26</sub>H<sub>28</sub>F<sub>2</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 479.1946. Found: 479.1946.

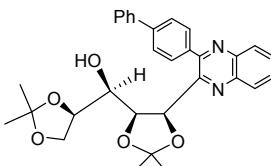
<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) δ 163.64 (C-F, d, <sup>1</sup>J<sub>C-F</sub> = 249.5 Hz), 154.57 (C-3), 149.22 (C-2), 141.53 (C-4a), 140.88 (C-8a), 133.92 (aromatic C, d, <sup>4</sup>J<sub>C-F</sub> = 3.0 Hz), 131.76 (2 aromatic CH, d, <sup>3</sup>J<sub>C-F</sub> = 8.0 Hz), 130.69, 129.93, 129.30, 129.12 (4 aromatic CH), 115.46 (2 aromatic CH, d, <sup>2</sup>J<sub>C-F</sub> = 22.1 Hz), 110.46, 109.17 (2 isopropylidene C), 79.48 (C-2'), 75.97 (C-1'), 75.81 (C-4'), 71.36 (C-3'), 66.91 (C-5'), 27.27, 27.04, 26.92, 26.58 (4 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 477.1802. Found: 477.1809.

**2-(1,2:4,5-di-*O*-isopropylidene-D-*manno*-1,2,3,4,5-pentahydroxypentyl)-3-(4-methylphenyl)quinoxaline (2ff)**



Yellow oil, 89%; *R*<sub>f</sub> 0.60 (3:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> +30 (*c* 0.5, CHCl<sub>3</sub>); FTIR (KBr): 3426 (OH), 3035, 2989, 2945, 2853, 1606, 1545, 1456, 1387, 852, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17-8.13 (m, 2H, H-5, H-8), 7.83 (d, 2H, *J* = 8.0 Hz, ArH), 7.80-7.75 (m, 2H, H-6, H-7), 7.35 (d, 2H, *J* = 8.0 Hz, ArH), 5.34-5.28 (m, 2H, H-1', H-2'), 3.96-3.87 (m, 3H, H-4', H-5'), 3.44 (br s, 1H, H-3'), 2.47 (s, 3H, PhCH<sub>3</sub>), 2.41 (br s, 1H, OH), 1.64, 1.54, 1.15, 1.03 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.67 (C-3), 149.41 (C-2), 141.66 (C-4a), 140.84 (C-8a), 139.33, 134.94 (2 aromatic C), 130.46, 129.66, 129.60, 129.27, 129.14 (8 aromatic CH), 110.42, 109.17 (2 isopropylidene C), 79.73 (C-2'), 76.00 (C-4'), 75.92 (C-1'), 71.33 (C-3'), 66.84 (C-5'), 27.31, 27.07, 26.51, 25.11 (4 CH<sub>3</sub>), 21.38 (PhCH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>26</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 473.2052. Found: 473.2060.

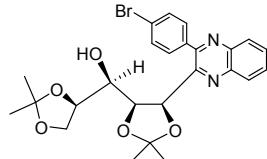
**2-(1,2:4,5-di-*O*-isopropylidene-D-*manno*-1,2,3,4,5-pentahydroxypentyl)-3-biphenylquinoxaline (2fg)**



Pale yellow foam, 84%; *R*<sub>f</sub> 0.62 (3:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> +29.5 (*c* 0.7, CHCl<sub>3</sub>); FTIR (thin film): 3431 (OH), 3025, 2988, 2935, 2862, 1608, 1545, 1456, 1382, 847, 758, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20-8.15 (m, 2H, H-5, H-8), 8.04 (d, 2H, *J* = 8.4 Hz, ArH), 7.85-7.77 (m, 4H, H-6, H-7, ArH), 7.72-7.68 (m, 3H, ArH), 7.53-7.49 (m, 2H, ArH), 5.40-5.34 (m, 2H, H-1', H-2'), 3.98-3.84 (m, 3H, H-4', H-5'), 3.49 (br s, 1H, H-3'), 2.43 (d, 1H, *J* = 5.6 Hz, OH), 1.66, 1.56, 1.17, 1.05 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.30 (C-3), 149.43 (C-2), 142.13 (C-4a), 141.69 (C-8a), 140.62, 140.54, 136.74 (aromatic C), 130.59, 130.24, 129.81, 129.62, 129.31, 129.21, 128.89, 127.82, 127.70, 127.24, 127.17 (13 aromatic CH), 110.50, 109.20 (2 isopropylidene C), 79.72 (C-2'), 76.01 (C-

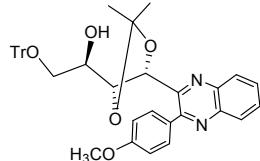
1'), 75.95 (C-4'), 71.43 (C-3'), 66.90 (C-5'), 27.32, 27.12, 26.55, 25.14 (4 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>31</sub>H<sub>33</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 513.2389. Found: 513.2381

**2-(1,2:4,5-di-*O*-isopropylidene-D-manno-1,2,3,4,5-pentahydroxypentyl)-3-(4-bromophenyl)quinoxaline (2fh)**



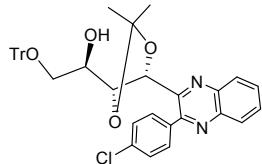
Pale yellow foam, 75%; *R<sub>f</sub>* = 0.53 (2:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> +60.1 (*c* 0.6, CHCl<sub>3</sub>); FTIR (thin film): 3419 (OH), 2992, 2935, 2847, 1608, 1450, 1384, 855, 758 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14-8.11 (m, 2H, ArH), 7.83-7.78 (m, 4H, ArH), 7.66 (d, 2H, *J* = 8.4 Hz, ArH), 5.34 (dd, 1H, *J*<sub>2,3'</sub> = 4.4 Hz, *J*<sub>2,1'</sub> = 8.2 Hz, H-2'), 5.18 (d, 1H, *J*<sub>1',2'</sub> = 8.2 Hz, H-1'), 3.97 - 3.81 (m, 3H, H-4', H-5'), 3.44 (m, 1H, H-3'), 2.40 (br d, 1H, OH), 1.60, 1.51, 1.42, 1.00 (4 s, each 3H, 4 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.56 (C-3), 149.25 (C-2), 141.66 (C-4a), 141.05 (C-8a), 136.84 (aromatic C), 131.70, 131.51, 130.87, 130.20, 129.43, 129.26 (8 aromatic CH), 124.19 (aromatic C), 110.62, 109.29 (2 isopropylidene C), 79.60 (C-2'), 76.04 (C-4'), 75.88 (C-1'), 71.49 (C-3'), 67.06 (C-5'), 27.38, 27.19, 26.72, 25.23 (4 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>25</sub>H<sub>27</sub>BrN<sub>2</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 537.1001. Found: 537.1008.

**2-(1,2-*O*-isopropylidene-4-*O*-triphenylmethyl-D-ribo-1,2,3,4-butahydroxybutyl)-3-(4-methoxyphenyl)quinoxaline (2ga)**



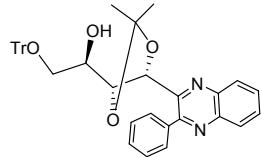
Yellow oil, 84%; *R<sub>f</sub>* = 0.43 (4:1 petroleum ether-EtOAc); [α]<sub>D</sub><sup>20</sup> -19.6 (*c* 0.5, CHCl<sub>3</sub>); FTIR (thin film): 3428 (OH), 3061, 2982, 2925, 2860, 1608, 1515, 1450, 1382, 763, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, 1H, *J* = 8.0 Hz, ArH), 8.10 (d, 1H, *J* = 8.0 Hz, ArH), 7.82-7.74 (m, 2H, ArH), 7.70 (d, 2H, *J* = 8.8 Hz, ArH), 7.28-7.18 (m, 15H, ArH), 7.03 (d, 2H, *J* = 8.8 Hz, ArH), 5.33-5.28 (m, 2H, H-1', H-2'), 4.04 (br d, 1H, *J* = 4.8 Hz, H-3'), 3.91 (s, 3H, OCH<sub>3</sub>), 3.06 (dd, 1H, *J*<sub>4a,3'</sub> = 6.0 Hz, *J*<sub>4a,4b'</sub> = 9.6 Hz, H-4'a), 2.85 (dd, 1H, *J*<sub>4b,3'</sub> = 4.2 Hz, *J*<sub>4b,4a'</sub> = 9.6 Hz, H-4'b), 2.35 (br s, 1H, OH), 1.66, 1.50 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.41 (aromatic C), 155.10 (C-3), 150.07 (C-2), 143.54 (3 aromatic C), 141.62 (C-8a), 140.98 (C-4a), 130.40 (aromatic C), 131.07, 129.48, 129.36, 129.08, 128.45, 127.83, 127.75, 126.97 (21 aromatic CH), 113.92 (2 aromatic CH), 110.59 (isopropylidene C), 86.65 (ph<sub>3</sub>CO), 79.71 (C-2'), 76.28 (C-1'), 70.94 (C-3'), 64.65 (C-4'), 55.38 (OCH<sub>3</sub>), 27.19, 27.12 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>41</sub>H<sub>39</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 639.2859. Found: 639.2852.

**2-(1,2-*O*-isopropylidene-4-*O*-triphenylmethyl-D-*ribo*-1,2,3,4-butahydroxybutyl)-3-(4-chlorophenyl)quinoxaline 2gb)**



Yellow oil, 74%;  $R_f$  0.0.48 (4:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -20.6 ( $c$  0.5, CHCl<sub>3</sub>); FTIR (thin film): 3437 (OH), 3050, 2989, 2926, 2856, 1615, 1458, 1384, 851, 762 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18-8.11 (m, 2H, H-5, H-8), 7.86-7.77 (m, 2H, H-6, H-7), 7.66 (d, 2H,  $J$  = 8.4 Hz, ArH), 7.48 (d, 2H,  $J$  = 8.4 Hz, ArH), 7.28-7.18 (m, 15H, ArH), 5.31 (dd, 1H,  $J_{2',3'} = 6.0$  Hz,  $J_{2',1'} = 8.0$  Hz, H-2'), 5.20 (d, 1H,  $J_{1',2'} = 8.0$  Hz, H-1'), 4.05-4.01 (m, 1H, H-3'), 3.08 (dd, 1H,  $J_{4'a,3'} = 6.0$  Hz,  $J_{4'a,4'b} = 9.6$  Hz, H-4'a), 2.85 (dd, 1H,  $J_{4'b,3'} = 6.0$  Hz,  $J_{4'b,4'a} = 9.6$  Hz, H-4'b), 2.36 (br s, 1H, OH), 1.64, 1.48 (2 s, each 3H, 2 CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.20 (C-3), 149.97 (C-2), 143.49 (3 aromatic C), 141.49 (C-8a), 141.25 (C-4a), 136.36, 135.41 (2 aromatic C), 130.98, 130.70, 129.91, 129.54, 129.14, 128.65, 128.43, 127.77, 127.70 (23 aromatic CH), 110.78 (isopropylidene C), 86.66 (Ph<sub>3</sub>CO), 79.62 (C-2'), 76.22 (C-1'), 70.94 (C-3'), 64.59 (C-4'), 27.12 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>40</sub>H<sub>35</sub>ClN<sub>2</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup>: 665.2183. Found: 665.2186.

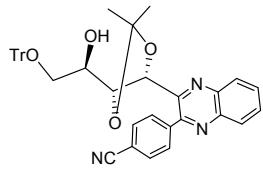
**2-(1,2-*O*-isopropylidene-4-*O*-triphenylmethyl-D-*ribo*-1,2,3,4-butahydroxybutyl)-3-phenylquinoxaline(2gc)**



Pale yellow oil, 80%;  $R_f$  = 0.52 (4:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -24.8 ( $c$  0.5, CHCl<sub>3</sub>); FTIR (thin film): 3430 (OH), 3039, 2986, 2935, 2852, 1609, 1450, 1382, 851, 760, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (d, 1H,  $J$  = 8.0 Hz, H-8), 8.09 (d, 1H,  $J$  = 8.0 Hz, H-5), 7.81-7.73 (m, 2H, H-6, H-7), 7.68-7.66 (m, 2H, ArH), 7.48-7.46 (m, 3H, ArH), 7.24-7.15 (m, 15H, ArH), 5.28-5.22 (m, 2H, H-1', H-2'), 4.01-3.97 (m, 1H, H-3'), 3.05 (dd, 1H,  $J_{4'a,3'} = 5.6$  Hz,  $J_{4'a,4'b} = 9.6$  Hz, H-4'a), 2.83 (dd, 1H,  $J_{4'b,3'} = 4.0$  Hz,  $J_{4'b,4'a} = 9.6$  Hz, H-4'b), 2.26 (br s, 1H, OH), 1.62, 1.43 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.52 (C-3), 150.29 (C-2), 143.64 (3 aromatic C), 141.60 (C-8a), 141.34 (C-4a), 137.99 (aromatic C), 130.64, 129.79, 129.63, 129.27, 129.14, 128.85, 128.55, 128.51, 127.10 (24 aromatic CH), 110.74 (isopropylidene C), 86.75 (Ph<sub>3</sub>CO), 79.84 (C-2'), 76.41 (C-1'), 71.08 (C-3'), 64.76 (C-4'), 27.26, 27.20 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>40</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup>: 631.2573, found: 631.2578.

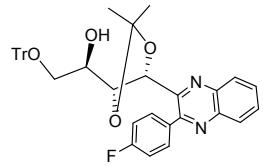
**2-(1,2-*O*-isopropylidene-4-*O*-triphenylmethyl-D-*ribo*-1,2,3,4-butahydroxybutyl)-3-(4-cyanophenyl-**

**D)quinoxaline (2gd)**



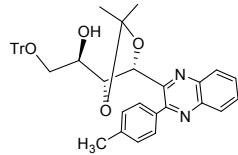
Brown oil, 70%;  $R_f$  0.4 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -4.2 ( $c$  1.0, CHCl<sub>3</sub>); FTIR (thin film): 3441 (OH), 3038, 2995, 2929, 2858, 2227 (CN), 1622, 1454, 1387, 862, 762 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16-8.11 (m, 2H, H-5, H-8), 7.83-7.75 (m, 4H, H-6, H-7, ArH), 7.66 (d, 2H,  $J$  = 8.0 Hz, ArH), 7.29-7.17 (m, 15H, ArH), 5.34-5.30 (m, 1H, H-2'), 5.13 (d, 1H,  $J_{1',2'} = 7.6$  Hz, H-1'), 4.02 (d, 1H,  $J$  = 4.4 Hz, H-3'), 3.11-3.06 (m, 1H, H-4'a), 2.87-2.82 (m, 1H, H-4'b), 2.36 (br s, 1H, OH), 1.60, 1.45 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.30 (C-3), 149.93 (C-2), 143.45 (3 aromatic C), 142.27 (C-8a), 141.43(C-4a), 141.40 (aromatic C), 132.31, 132.15, 130.37, 129.65, 128.64, 128.43, 127.83, 127.79, 127.04 (23 aromatic CH), 118.65 (CN), 112.80 (aromatic C), 110.97 (isopropylidene C), 86.67 (Ph<sub>3</sub>CO), 79.57 (C-2'), 76.23 (C-1'), 70.96 (C-3'), 64.56 (C-4'), 27.13, 27.07 (2 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>41</sub>H<sub>36</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 634.2706. Found: 634.2712.

**2-(1,2-O-isopropylidene-4-O-triphenylmethyl-D-ribo-1,2,3,4-butahydroxybutyl)-3-(4-fluorophenyl)quinoxaline (2ge)**



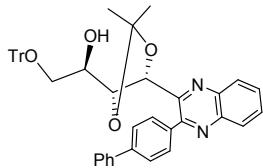
Brown oil, 73%;  $R_f$  = 0.45 (4:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -22.3 ( $c$  0.6, CHCl<sub>3</sub>); FTIR (thin film): 3447 (OH), 3061, 2979, 2925, 2857, 1602, 1450, 1378, 847, 764 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19-8.11 (m, 2H, H-5, H-8), 7.85-7.76 (m, 2H, ArH), 7.73-7.69 (m, 2H, H-6, H-7), 7.38-7.32 (m, 2H, ArH), 7.28-7.17 (m, 15H, ArH), 5.32 (dd, 1H,  $J_{2',3'} = 6.4$  Hz,  $J_{2',1'} = 8.0$  Hz, H-2'), 5.21 (d, 1H,  $J_{1',2'} = 8.0$  Hz, H-1'), 4.06-4.02 (m, 1H, H-3'), 3.09 (dd, 1H,  $J_{4'a,3'} = 6.0$  Hz,  $J_{4'a,4'b} = 9.6$  Hz, H-4'a), 2.85 (dd, 1H,  $J_{4'b,3'} = 6.0$  Hz,  $J_{4'b,4'a} = 9.6$  Hz, H-4'b), 2.38 (br s, 1H, OH), 1.65, 1.45 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.44 (C-F, d,  $^1J_{C-F} = 248.5$  Hz), 154.38 (C-3), 150.02 (C-2), 143.50 (3 aromatic C), 141.18 (C-8a), 141.20 (C-4a), 133.97 (aromatic C, d,  $^4J_{C-F} = 3.4$  Hz), 131.52 (2 aromatic CH, d,  $^3J_{C-F} = 8.0$  Hz), 130.67, 129.64, 129.54, 129.11, 128.44, 127.77, 127.01 (19 aromatic CH), 115.47 (aromatic CH, d,  $^2J_{F-C} = 21.10$  Hz), 110.73 (isopropylidene C), 86.66 (ph<sub>3</sub>CO), 79.61 (C-2'), 76.21 (C-1'), 70.94 (C-3'), 64.61 (C-4'), 27.15, 27.11 (2 CH<sub>3</sub>); HRMS (ESI)  $m/z$  Calcd for C<sub>40</sub>H<sub>35</sub>FN<sub>2</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup>: 649.2479. Found: 649.2486.

**2-(1,2-O-isopropylidene-4-O-triphenylmethyl-D-ribo-1,2,3,4-butahydroxybutyl)-3-(4-methylphenyl)quinoxaline (2gf)**



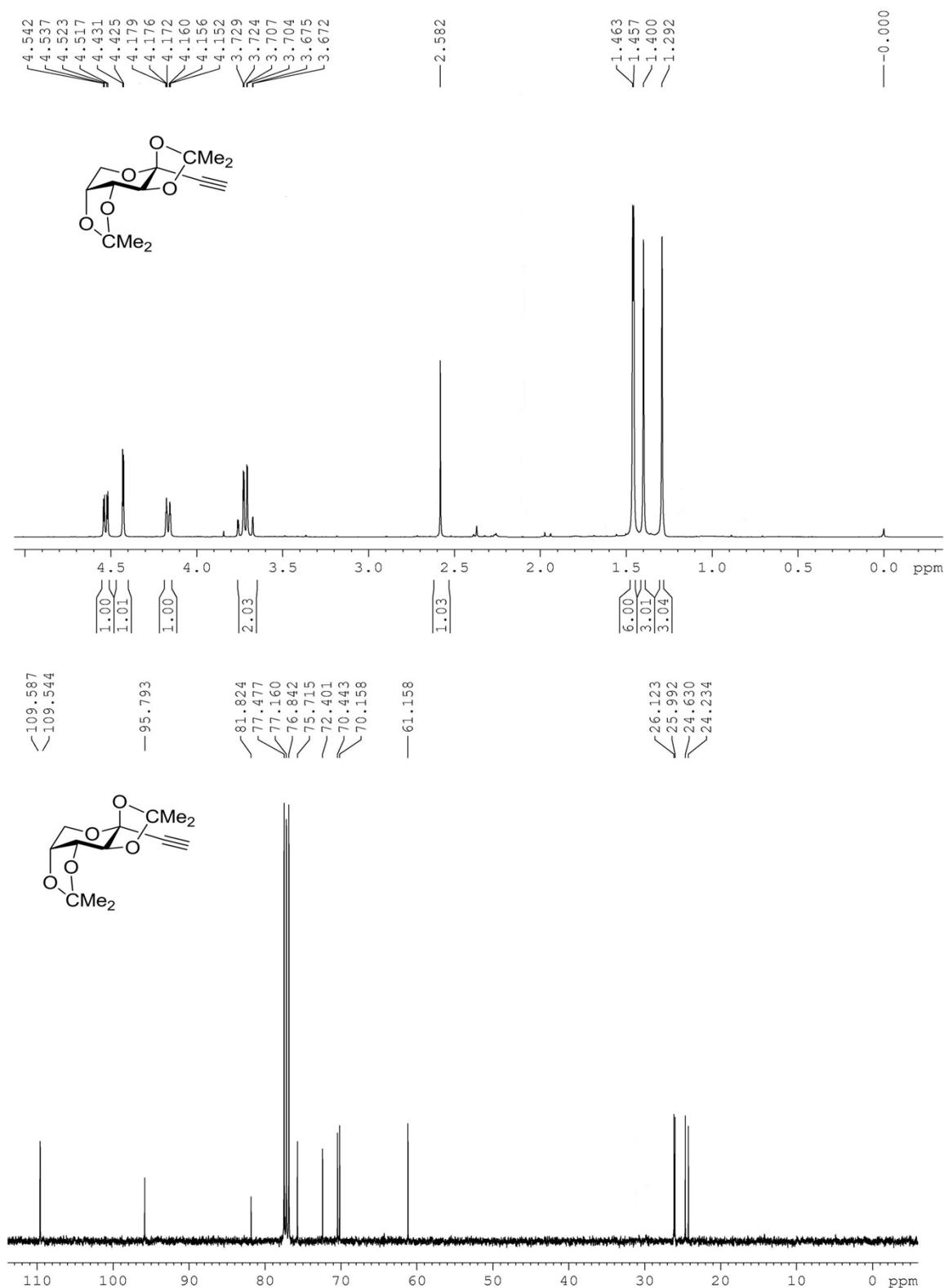
Brown oil, 83%;  $R_f$  0.55 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -14.2 ( $c$  0.5, CHCl<sub>3</sub>); FTIR (thin film): 3438 (OH), 3057, 2990, 2927, 2855, 1626, 1456, 1381, 862, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18-8.09 (m, 2H, H-5, H-8), 7.83-7.74 (m, 2H, H-6, H-7, ArH), 7.60 (d, 2H,  $J$  = 8.0 Hz, ArH), 7.36 (d, 2H,  $J$  = 8.0 Hz, ArH), 7.26-7.17 (m, 15H, ArH), 5.29-5.26 (m, 2H, H-1', H-2'), 4.02 (br s, 1H, H-3'), 3.06 (dd, 1H,  $J_{4'a,3'}=$  6.0 Hz,  $J_{4'a,4'b}=$  9.6 Hz, H-4'a), 2.83 (dd, 1H,  $J_{4'b,3'}=$  4.0 Hz,  $J_{4'b,4'a}=$  9.6 Hz, H-4'b), 2.46 (s, 3H, PhCH<sub>3</sub>), 2.33 (br s, 1H, OH), 1.65, 1.48 (2 s, each 3H, 2 CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.48 (C-3), 150.13 (C-2), 143.53 (3 aromatic C), 141.60 (C-8a), 141.10 (C-4a), 138.96, 135.03 (2 aromatic C), 130.42, 129.64, 129.47, 129.13, 128.65, 128.44, 127.82, 127.74, 126.97 (23 aromatic CH), 110.59 (isopropylidene C), 86.63 (ph<sub>3</sub>CO), 79.76 (C-2'), 76.26 (C-1'), 70.94 (C-3'), 64.63 (C-4'), 27.17, 27.11 (2 CH<sub>3</sub>), 21.54 (PhCH<sub>3</sub>); .HRMS (ESI) *m/z* Calcd for C<sub>41</sub>H<sub>39</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 623.2910, found: 623.2918.

**2-(1,2-O-isopropylidene-4-O-triphenylmethyl-D-ribo-1,2,3,4-butahydroxybutyl)-3-(4-biphenylyl)-quinoxaline (2gg)**

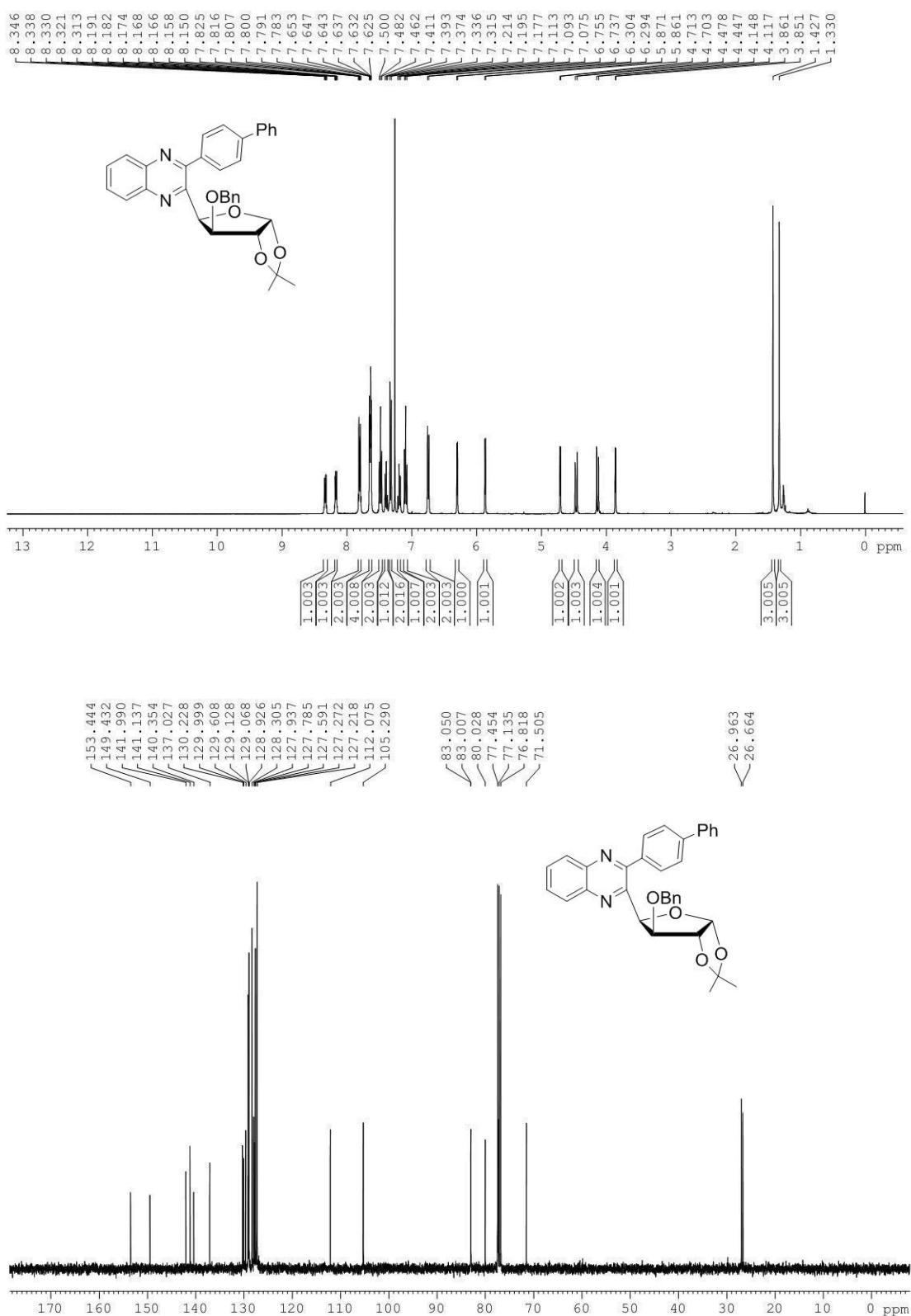


Pale yellow oil, 83%;  $R_f$  0.52 (3:1 petroleum ether-EtOAc);  $[\alpha]_D^{20}$  -7.3 ( $c$  0.5, CHCl<sub>3</sub>); FTIR (thin film): 3438 (OH), 3204, 3062, 2986, 2925, 2855, 1634, 1485, 1449, 1393, 849, 765, 700 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20-8.15 (m, 2H, H-5, H-8), 7.84-7.78 (m, 4H, H-6, H-7, ArH), 7.75-7.70 (m, 4H, ArH), 7.54-7.47 (m, 3H, ArH), 7.28-7.19 (m, 15H, ArH), 5.36-5.31 (m, 2H, H-1', H-2'), 4.06 (br d, 1H, H-3'), 3.10 (dd, 1H,  $J_{4'a,3'}=$  6.0 Hz,  $J_{4'a,4'b}=$  9.6 Hz, H-4'a), 2.88 (dd, 1H,  $J_{4'b,3'}=$  4.4 Hz,  $J_{4'b,4'a}=$  9.6 Hz, H-4'b), 2.36 (br s, 1H, OH), 1.67, 1.50 (2 s, each 3H, 2 CH<sub>3</sub>). <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.12 (C-3), 150.14 (C-2), 143.54 (3 aromatic C), 141.83 (C-8a), 141.63 (C-4a), 141.20, 140.64, 136.85 (3 aromatic C), 130.55, 130.05, 129.68, 129.54, 129.21, 128.89, 128.68, 128.46, 127.77, 127.25, 127.20, 127.00 (28 aromatic CH), 110.71, 110.53 (2 isopropylidene C), 86.67 (ph<sub>3</sub>CO), 79.74 (C-2'), 76.36 (C-1'), 70.99 (C-3'), 64.66 (C-4'), 27.18, 27.15 (2 CH<sub>3</sub>); HRMS (ESI) *m/z* Calcd for C<sub>46</sub>H<sub>41</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 685.3066. Found: 685.3074.

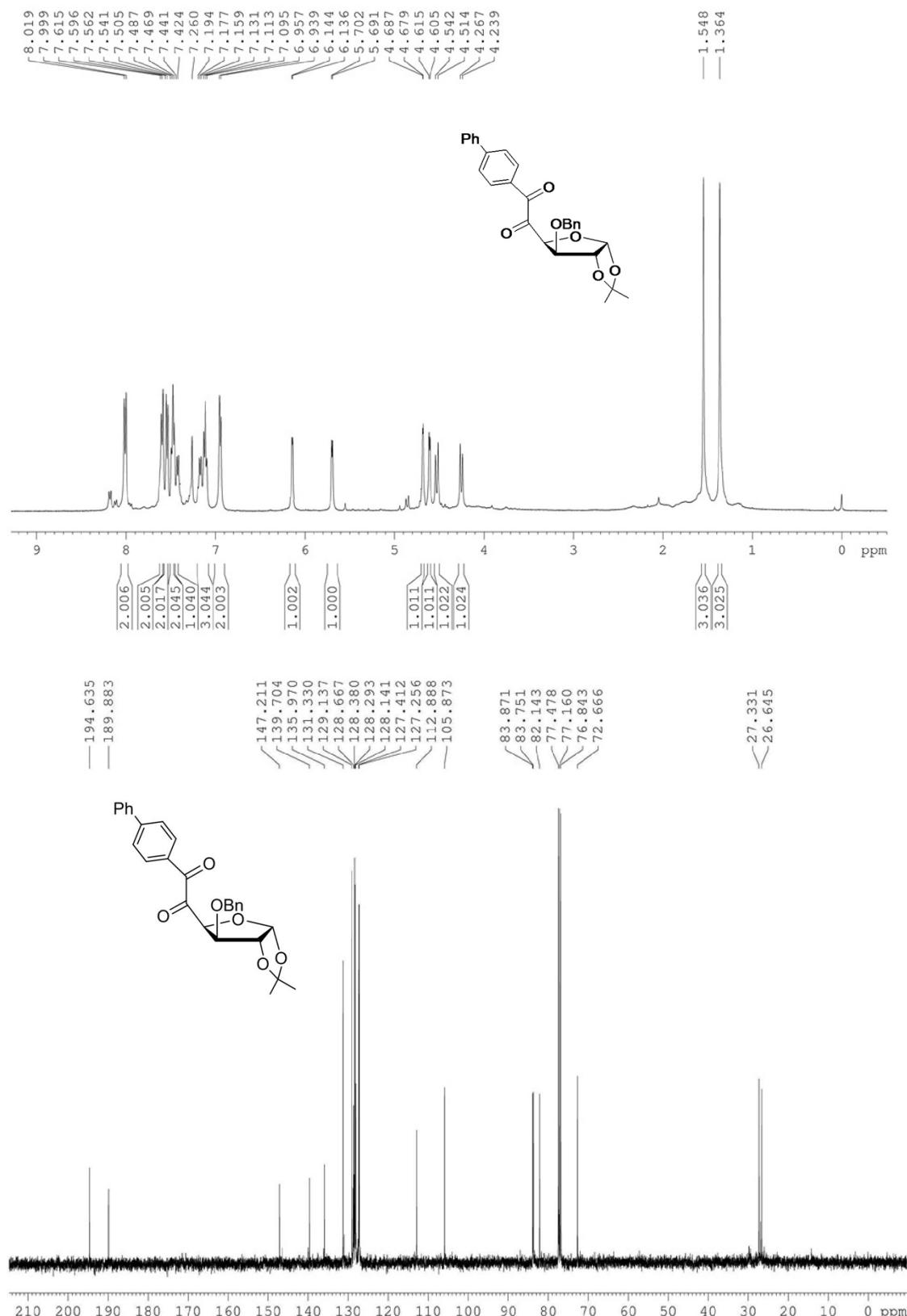
<sup>1</sup>H NMR and <sup>13</sup>C NMR of **1e**

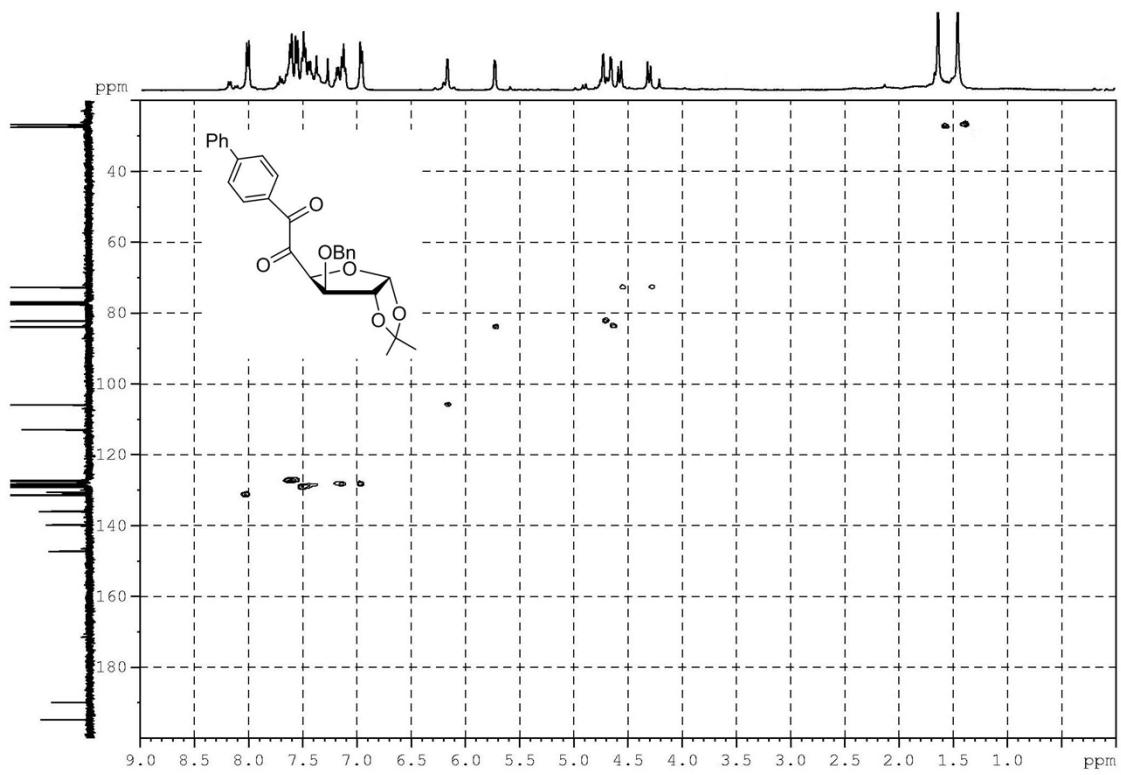
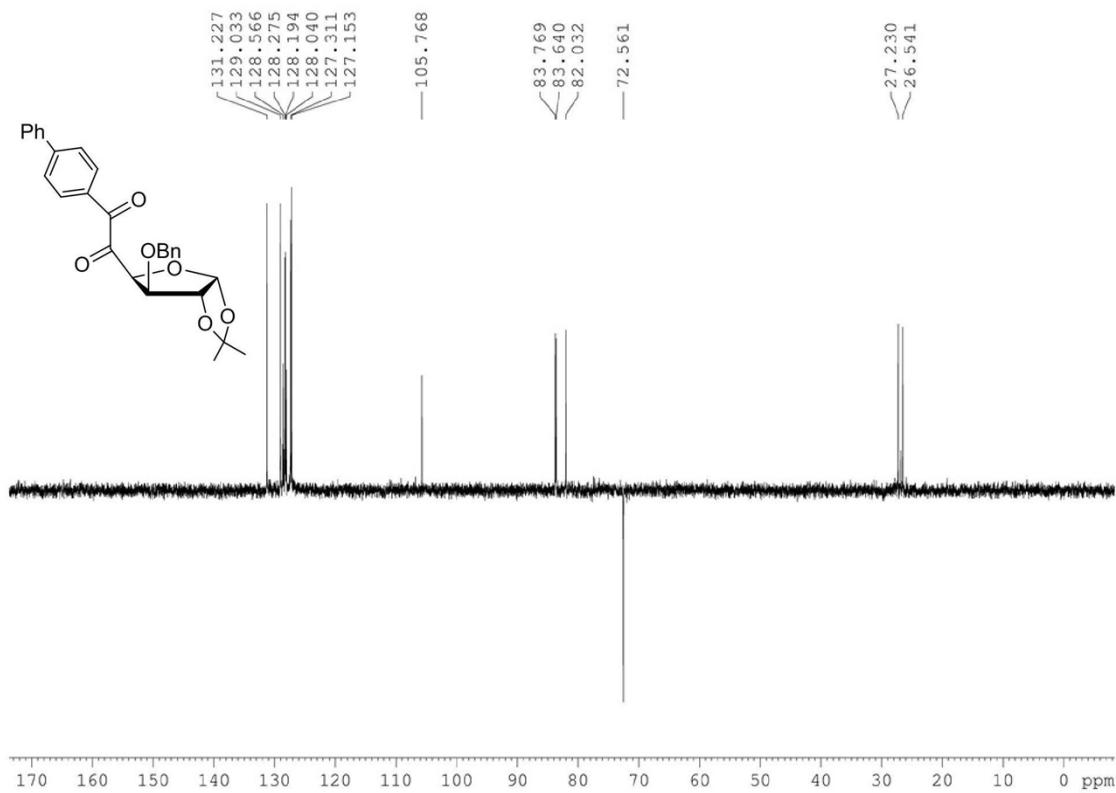


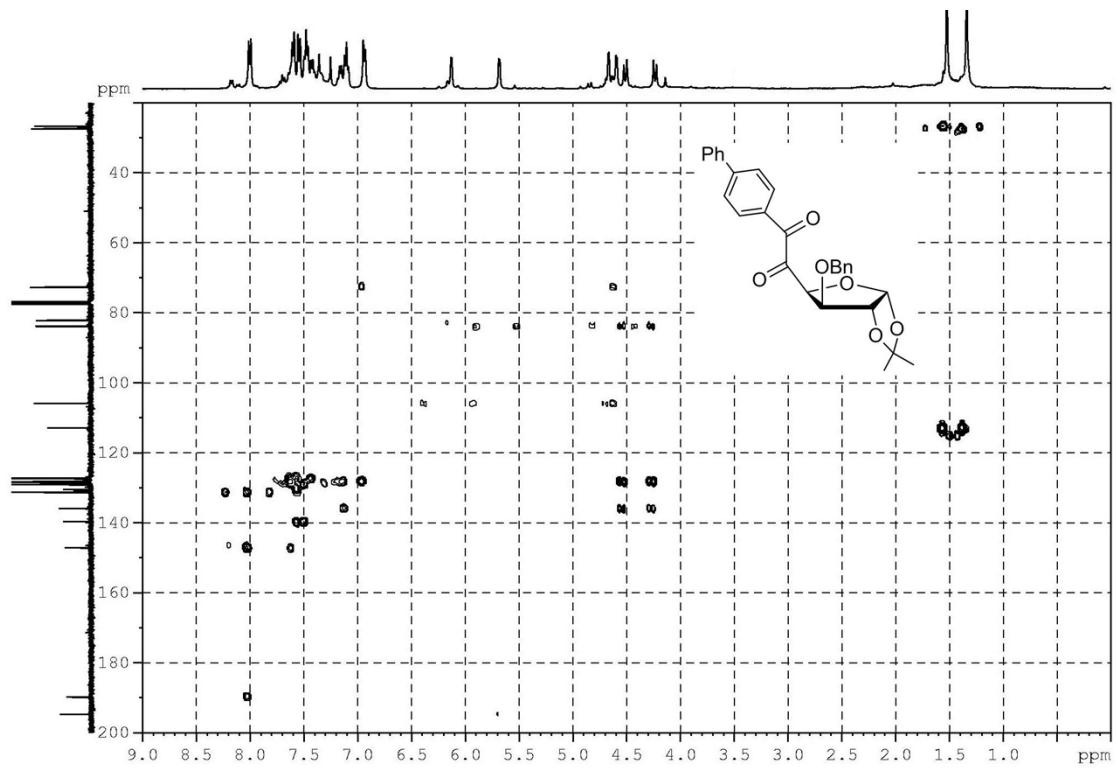
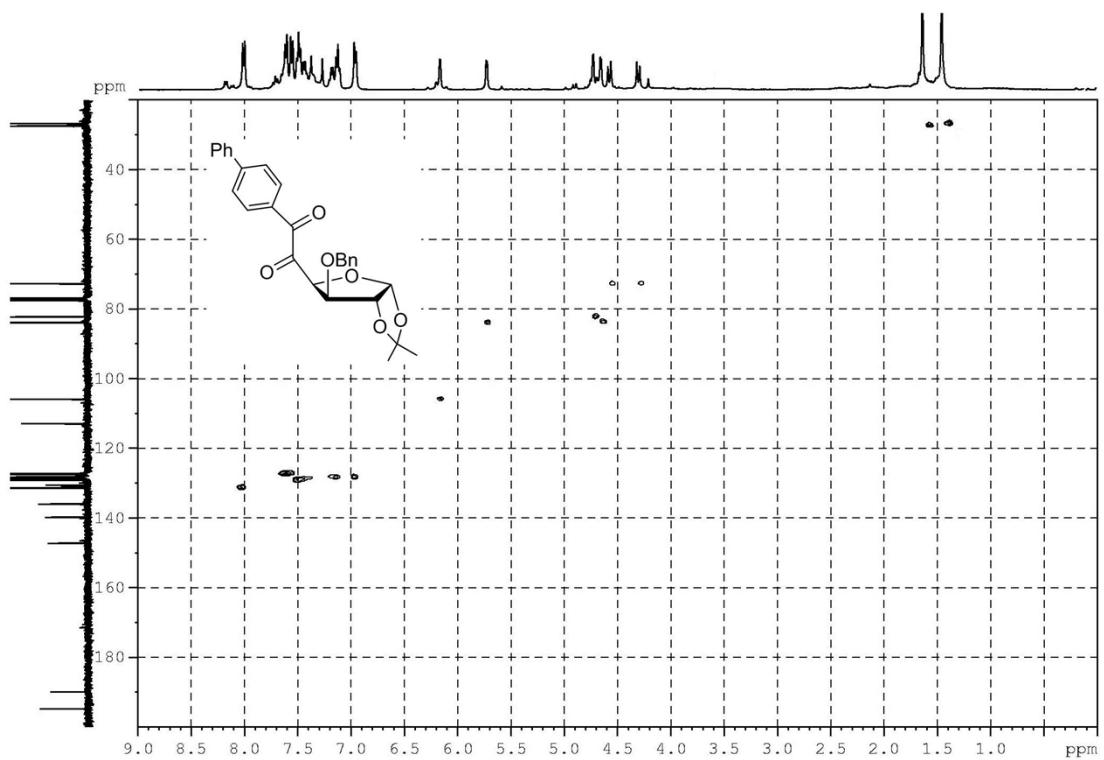
<sup>1</sup>H NMR and <sup>13</sup>C NMR of **2aa**



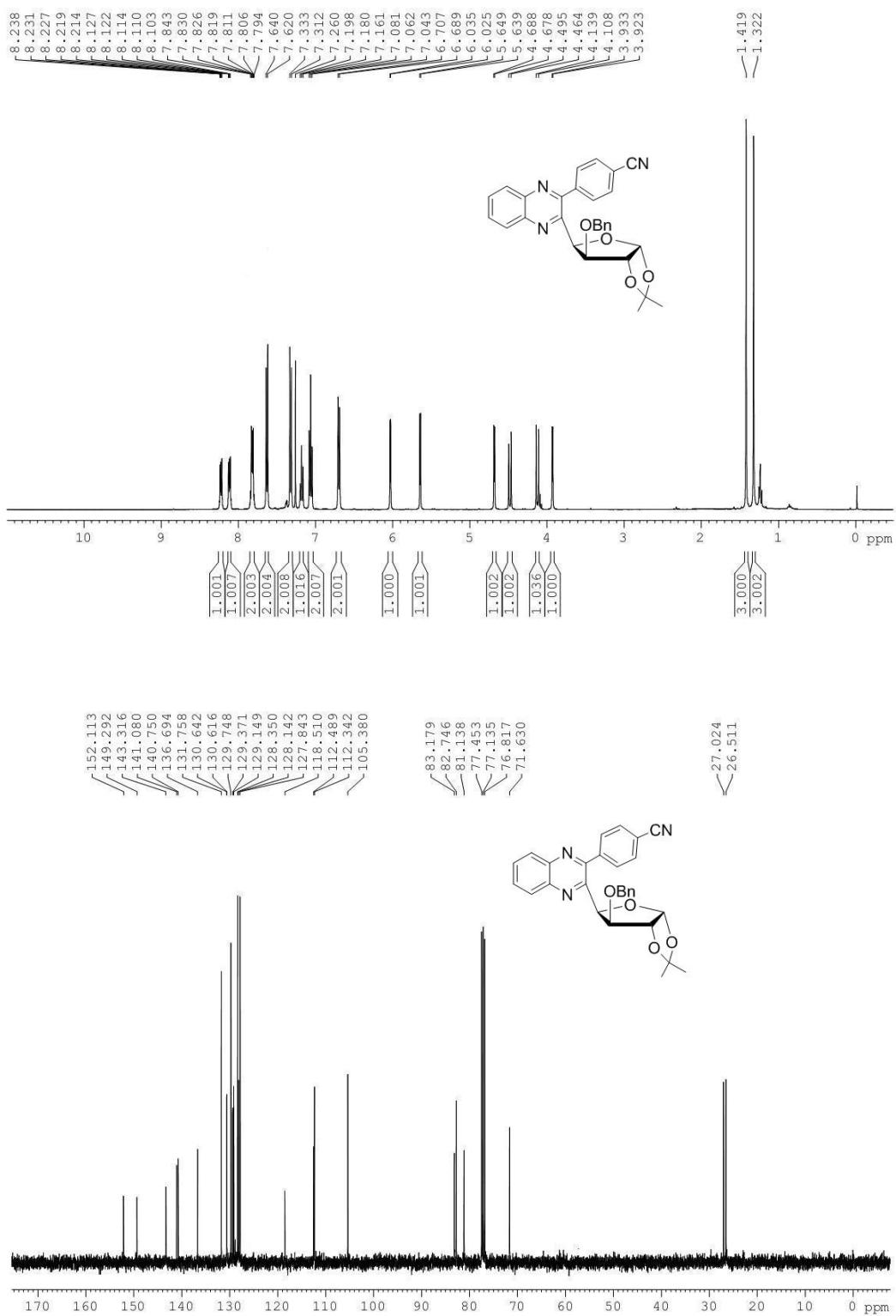
<sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT-135, <sup>1</sup>H-<sup>1</sup>H COSY, HSQC and HMBC of intermediate **5**

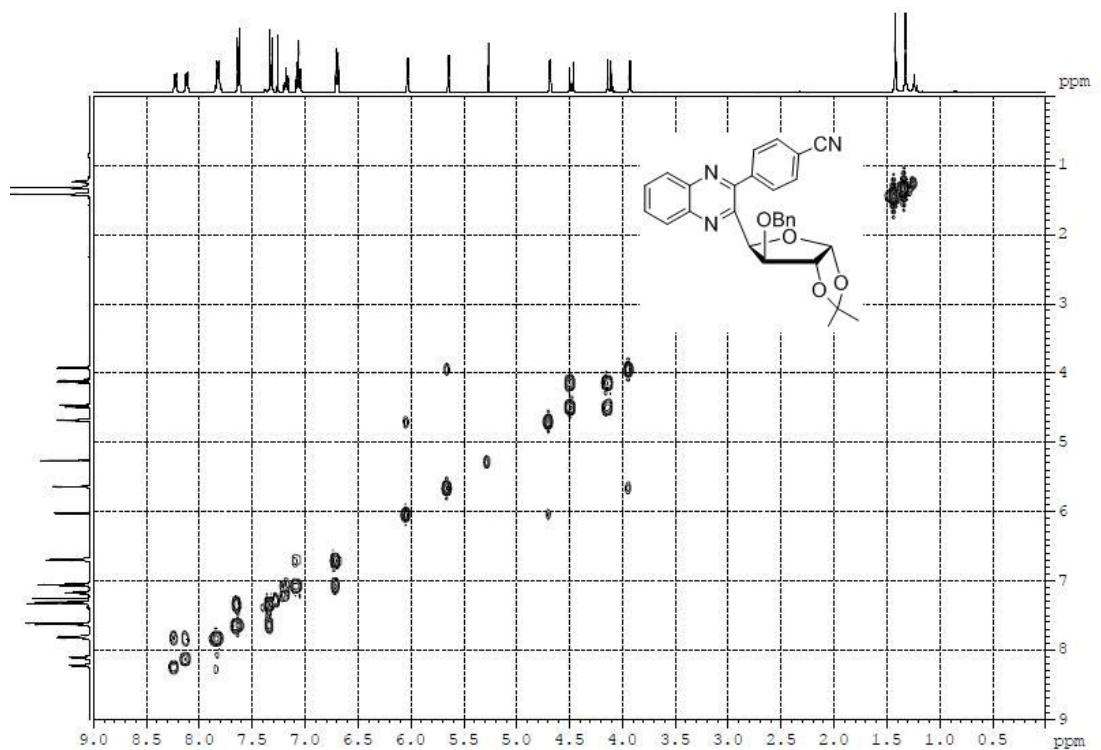
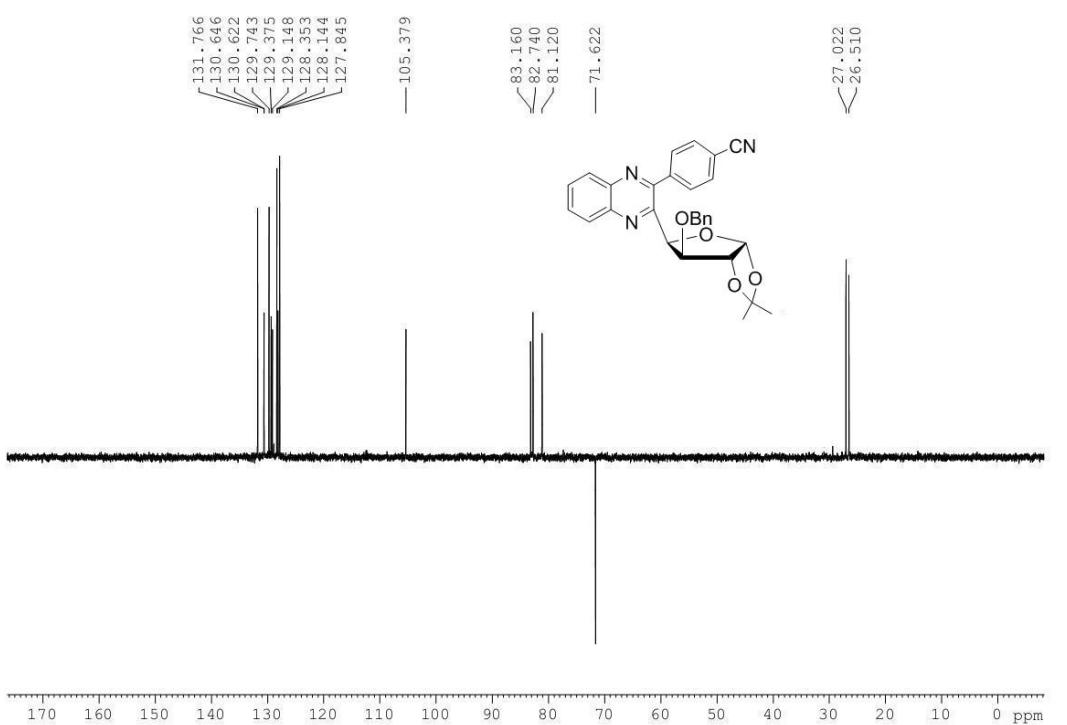


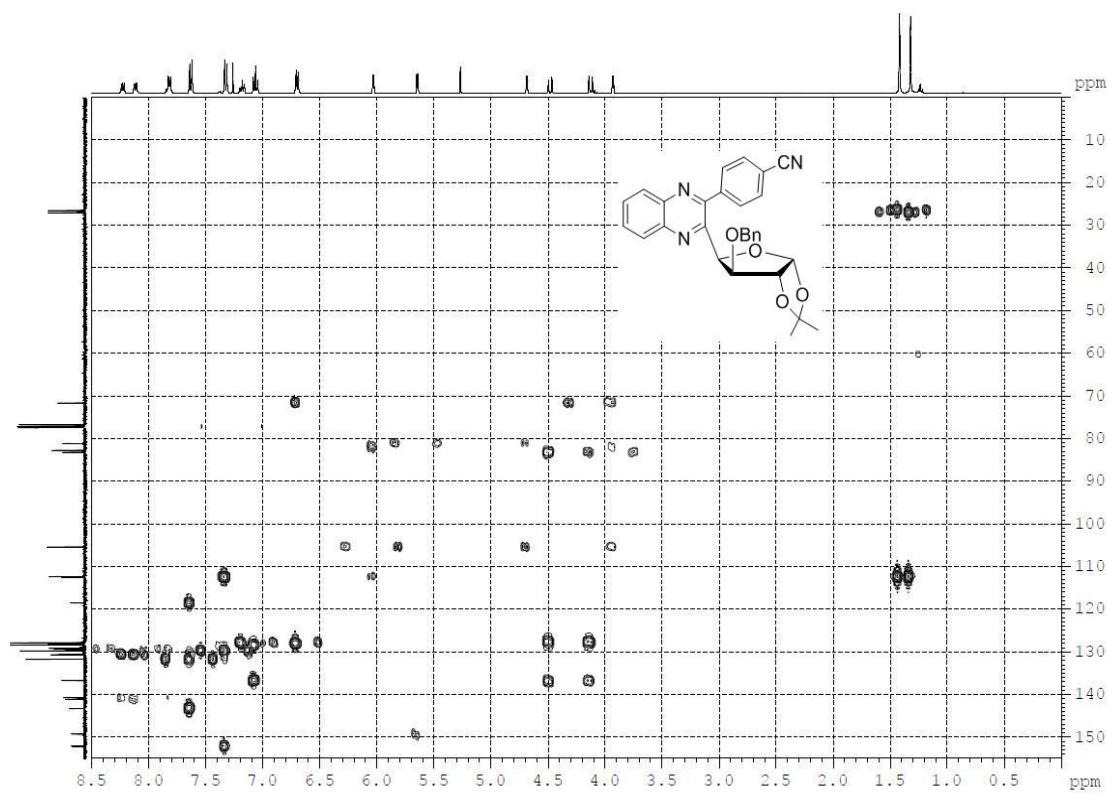
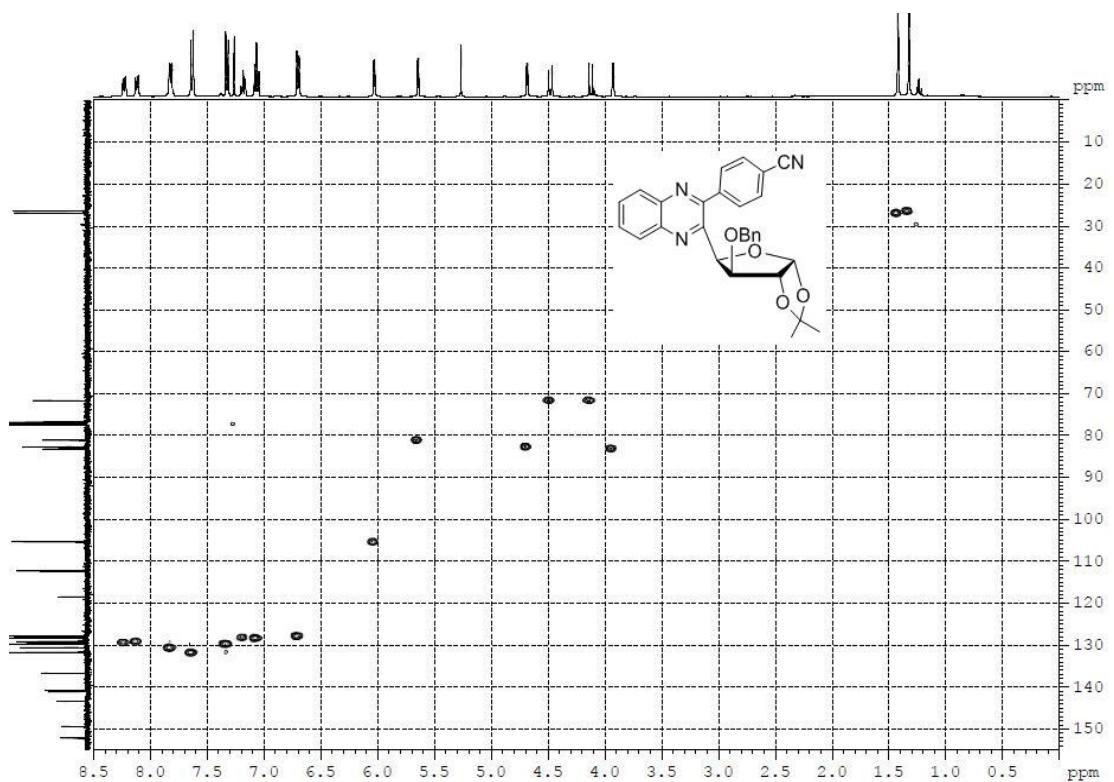




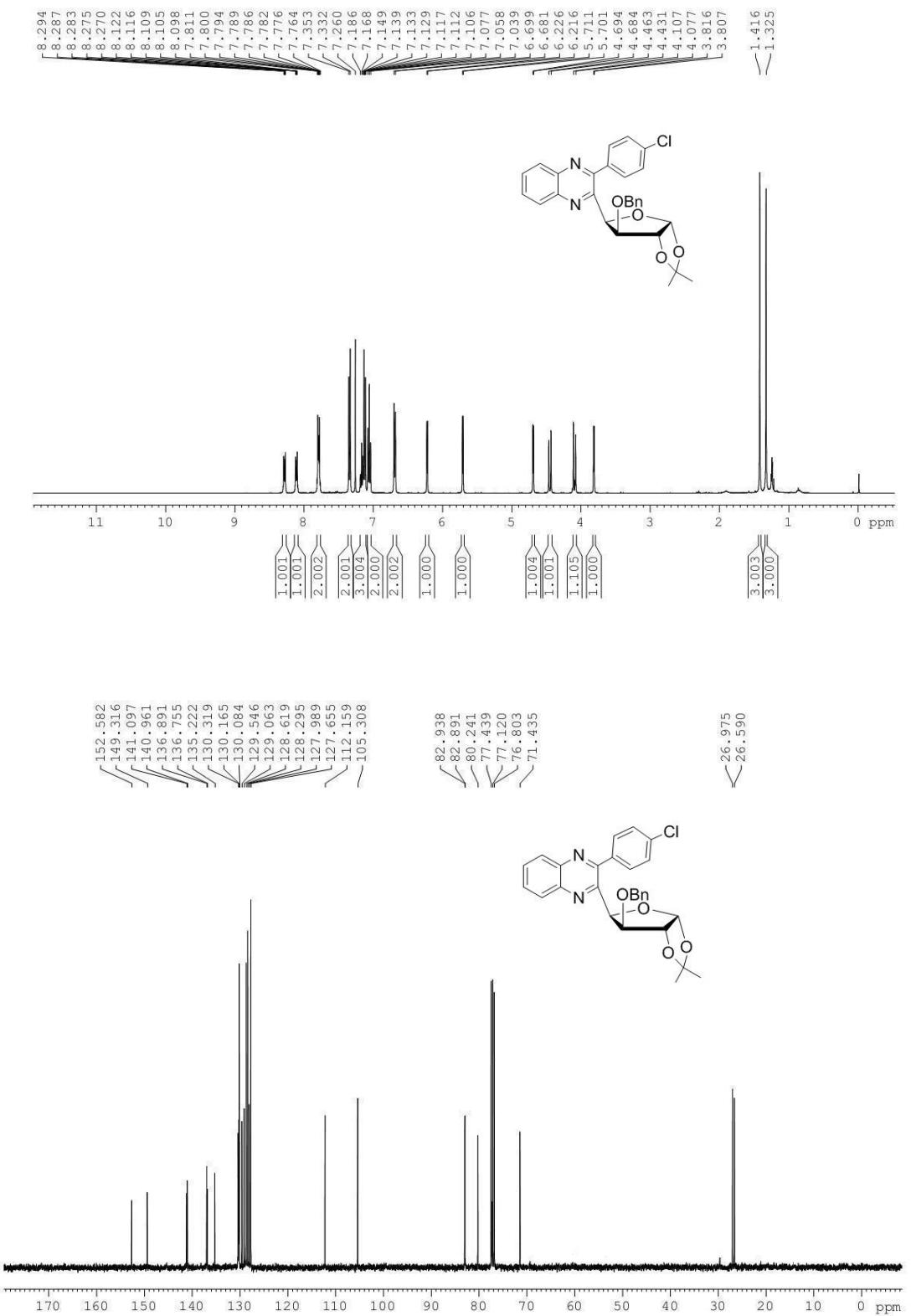
<sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT-135, <sup>1</sup>H-<sup>1</sup>H COSY, HSQC and HMBC of **2ab**



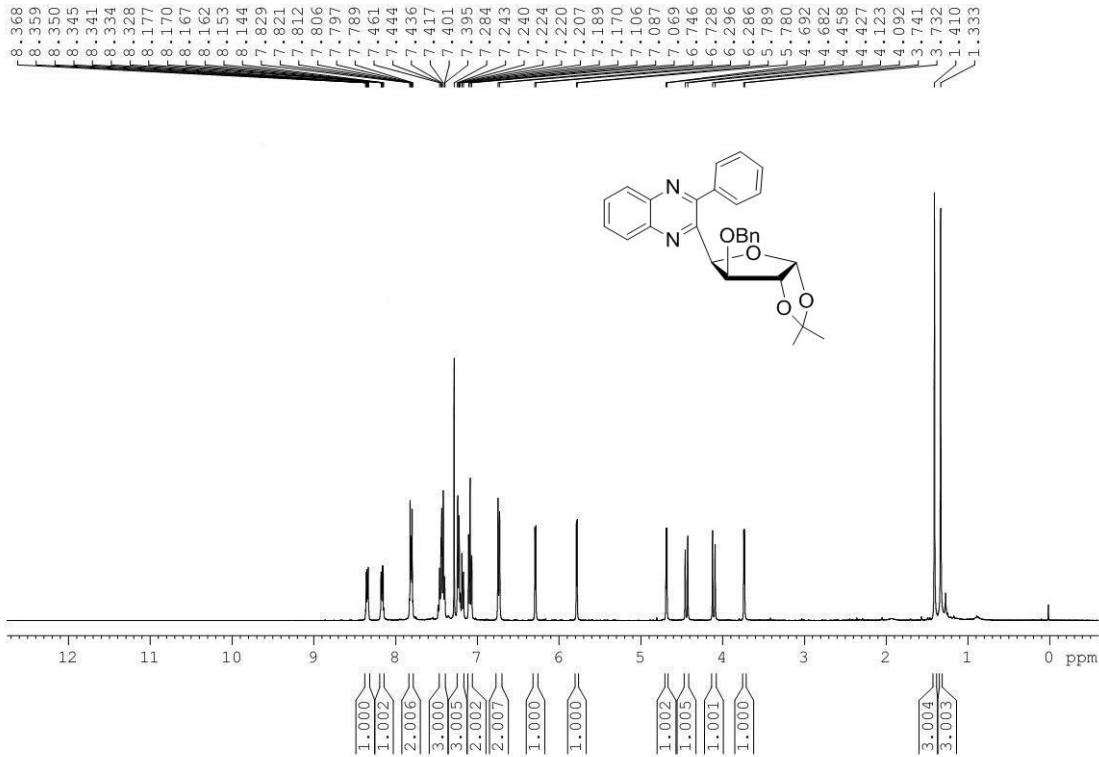


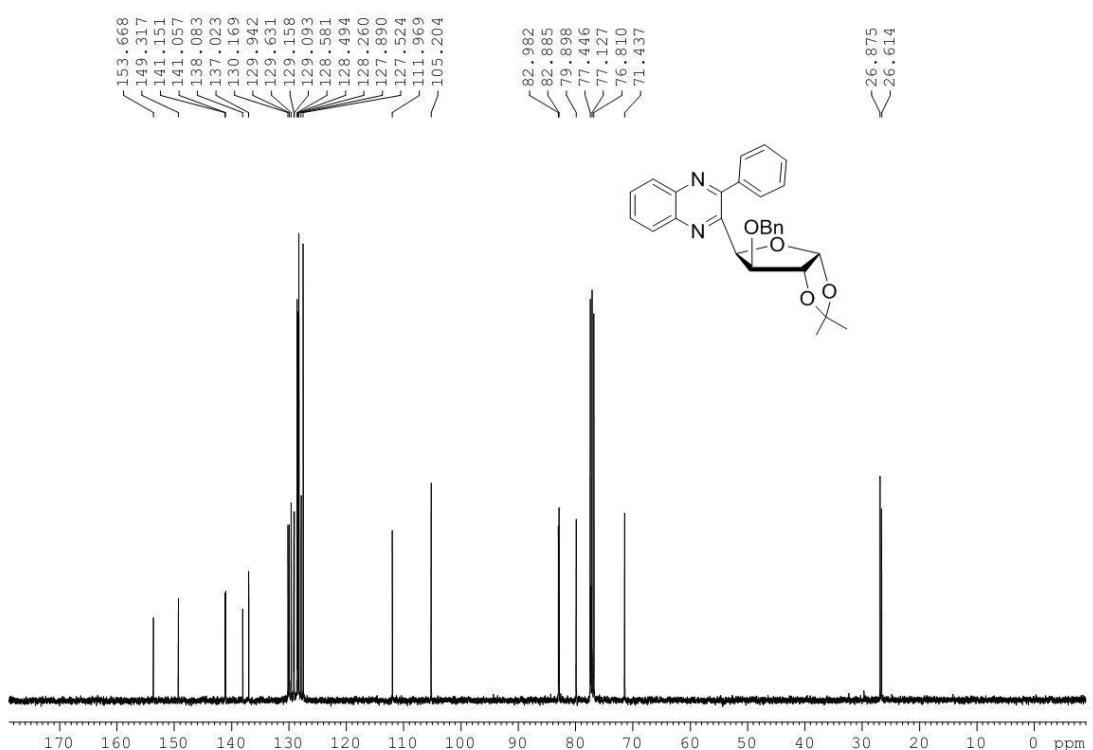


**<sup>1</sup>H NMR and <sup>13</sup>C NMR of 2ac**

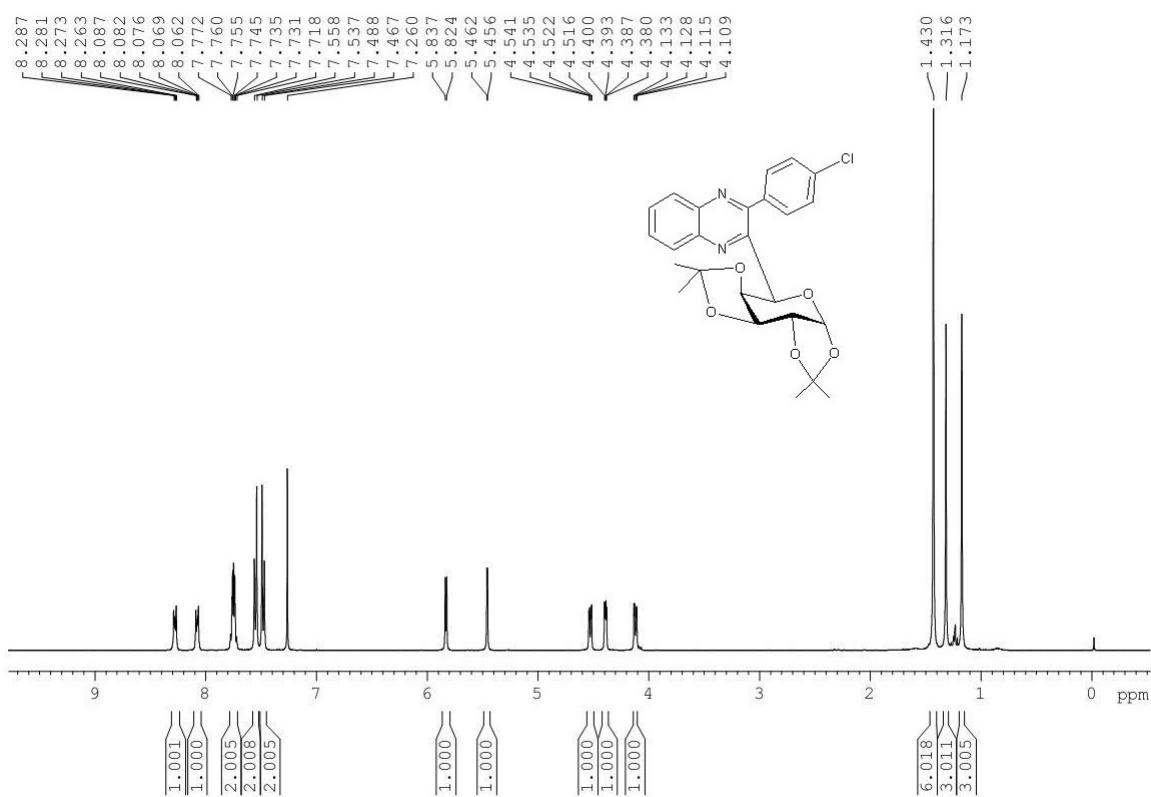


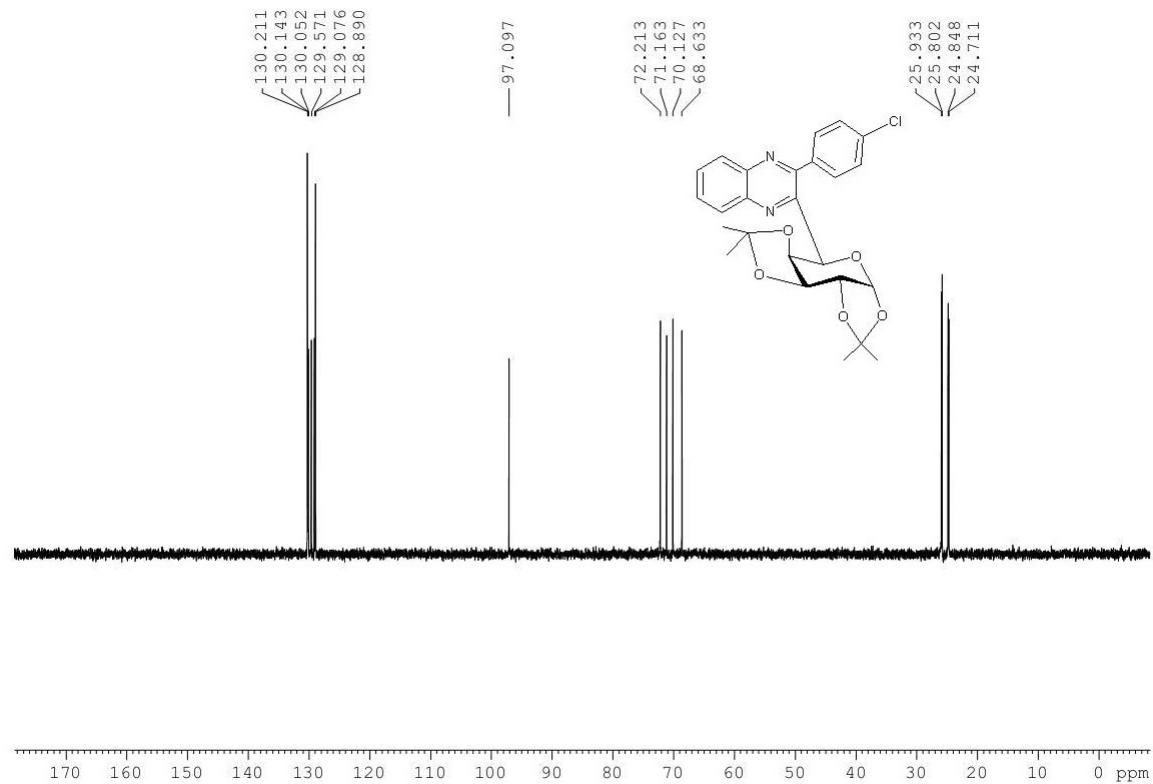
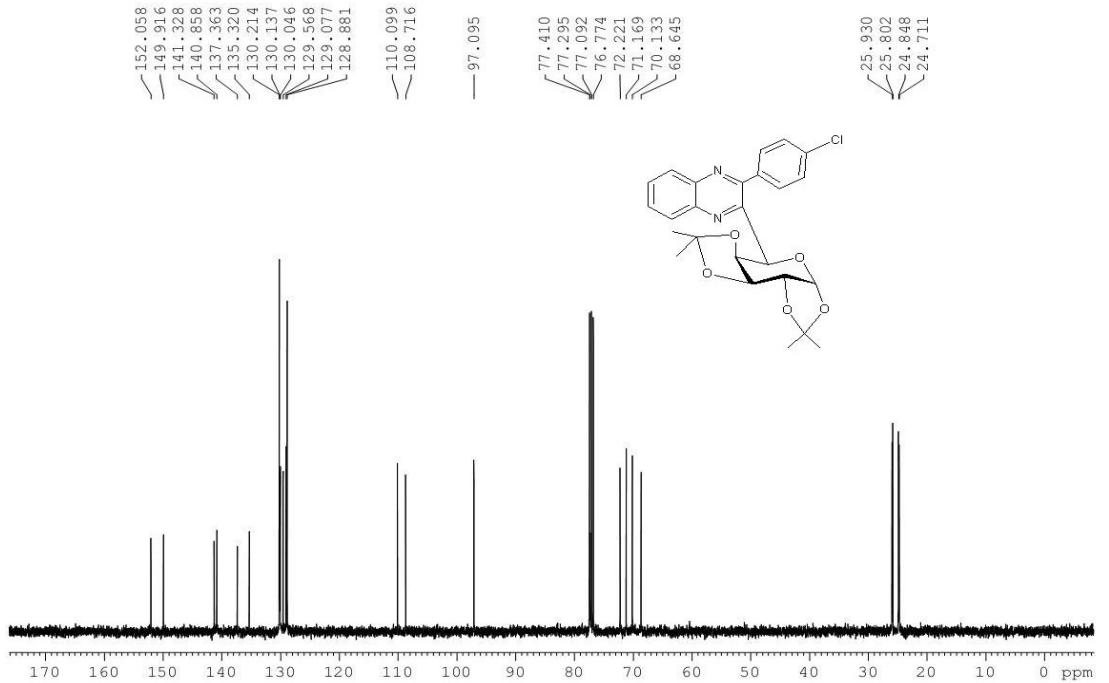
### <sup>1</sup>H NMR and <sup>13</sup>C NMR of **2ad**

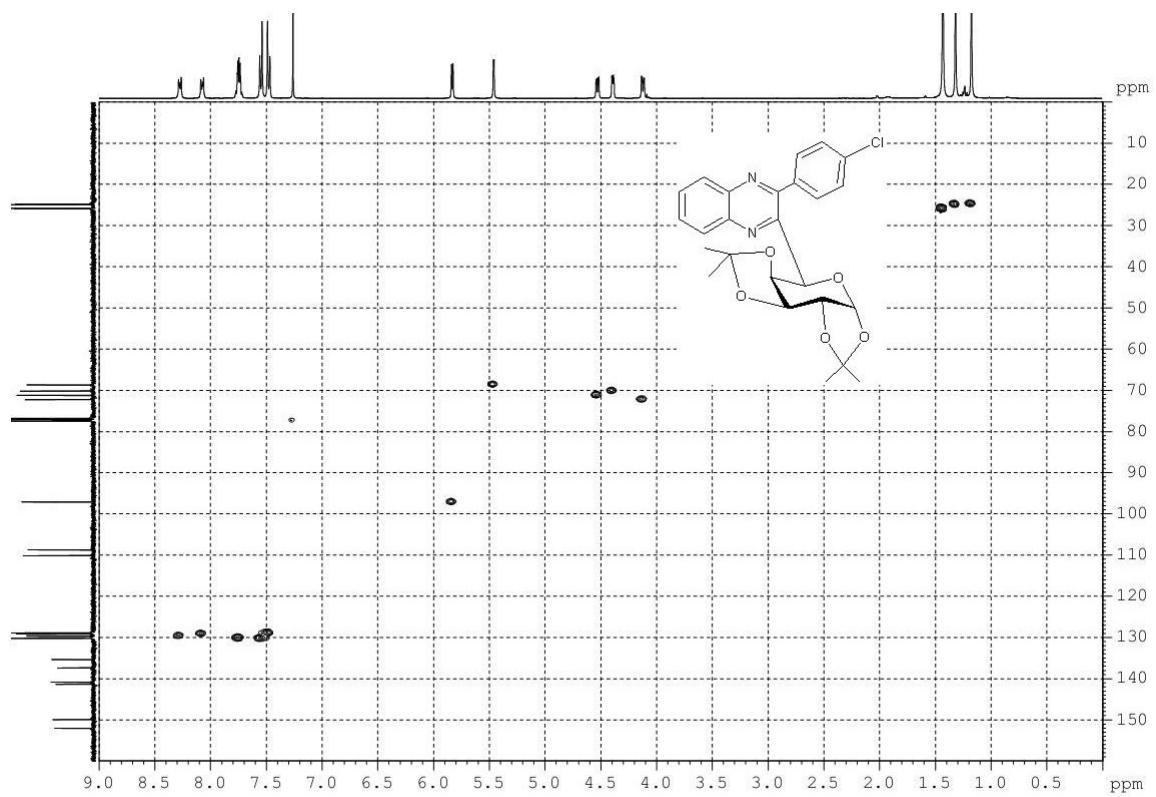
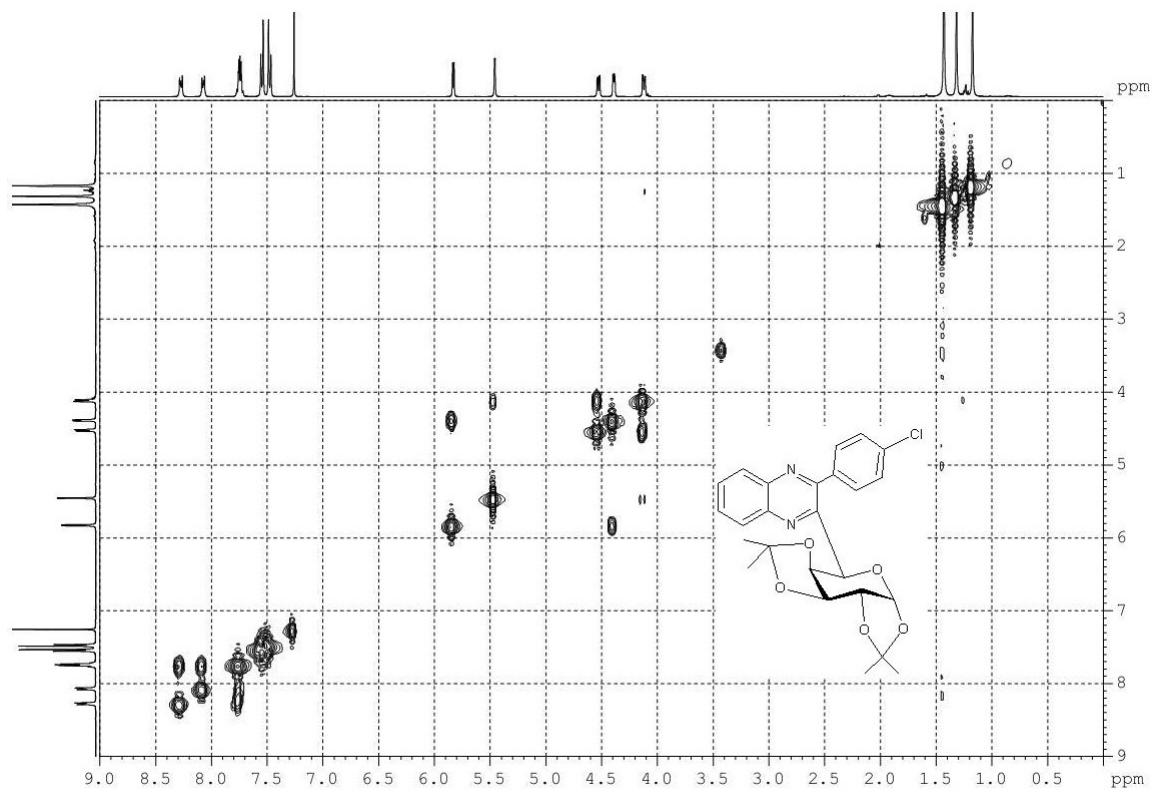


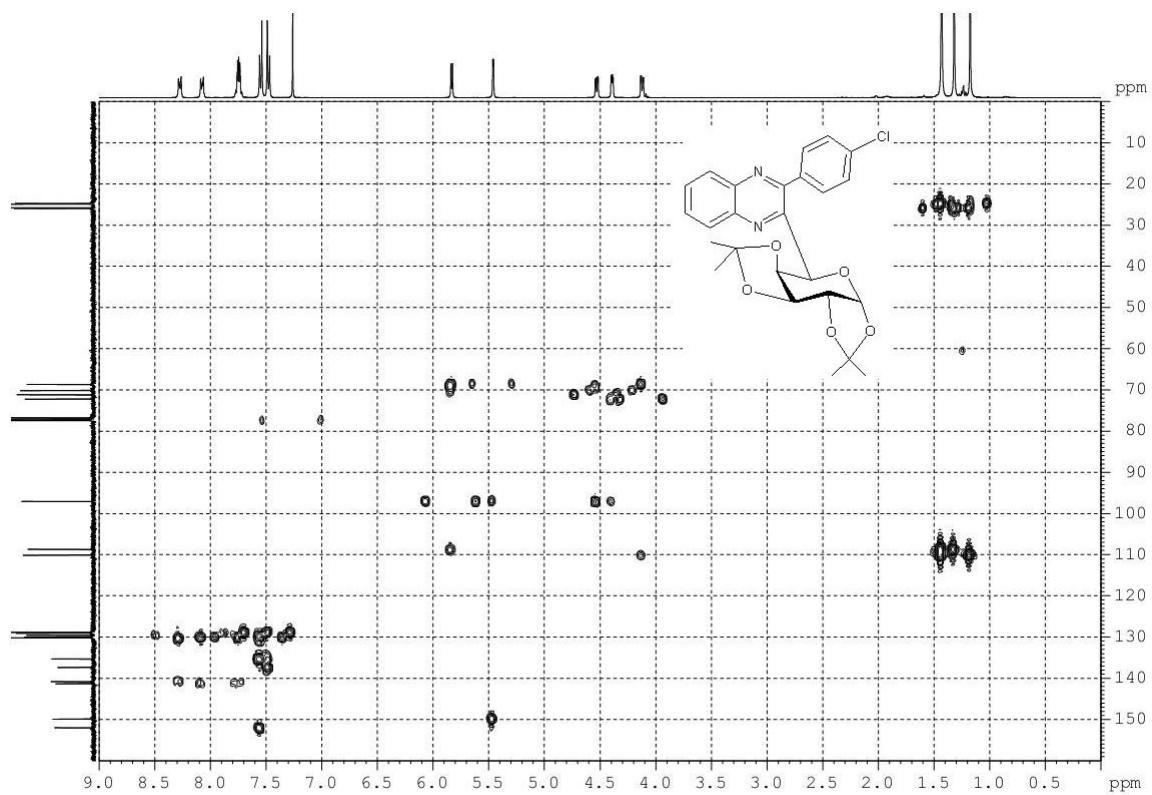


<sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT-135, <sup>1</sup>H-<sup>1</sup>H COSY, HSQC and HMBC of **2ba**

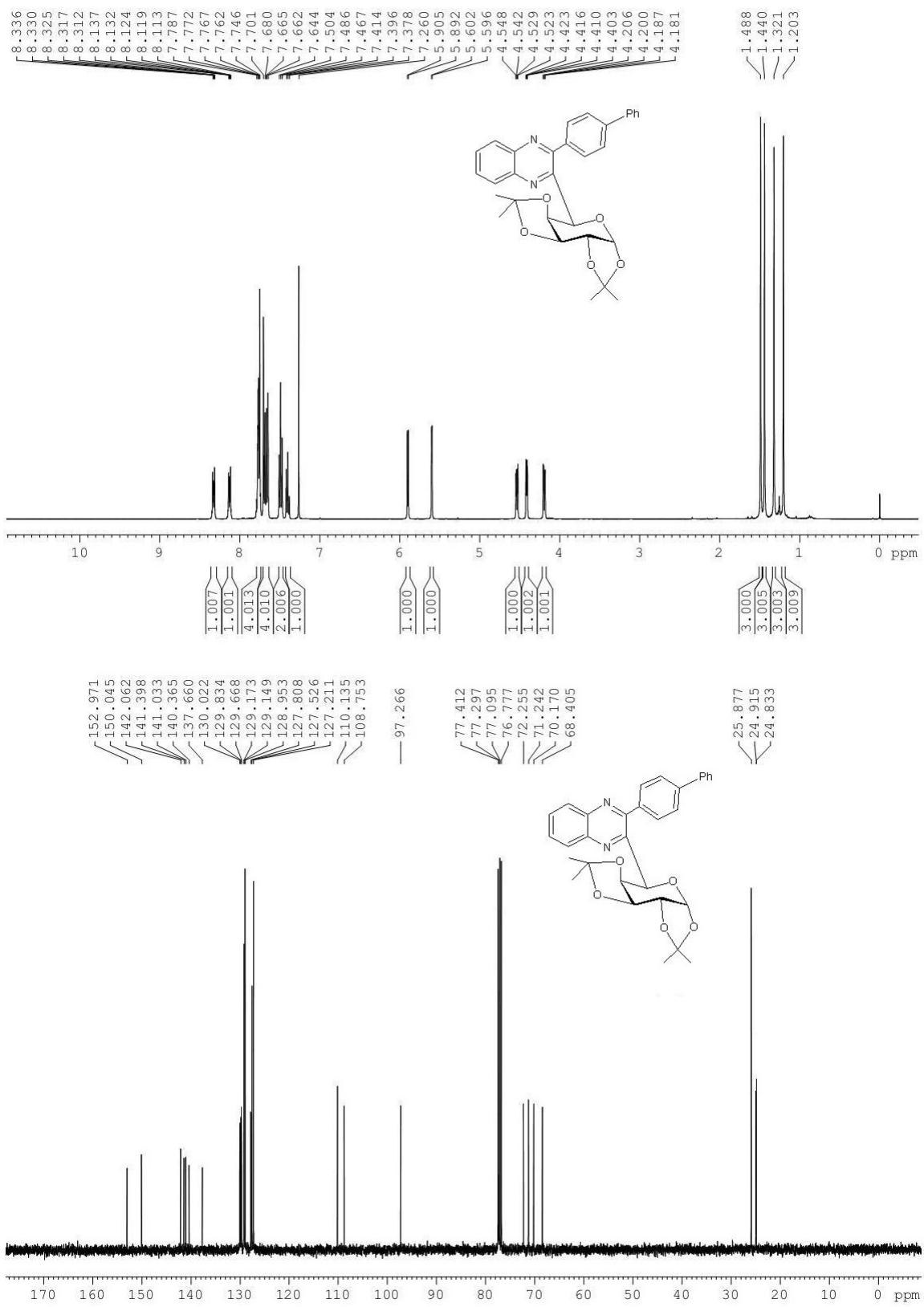




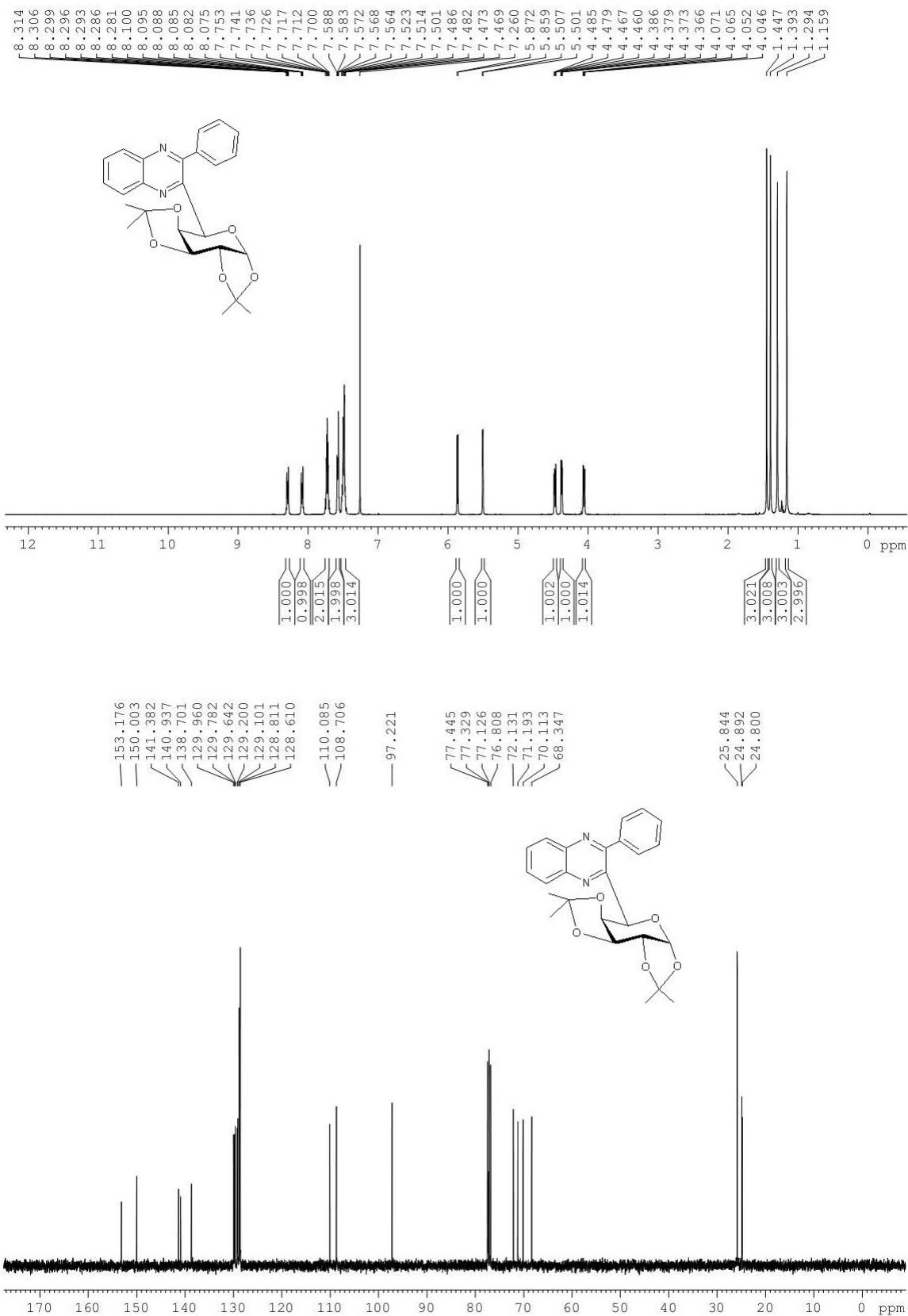




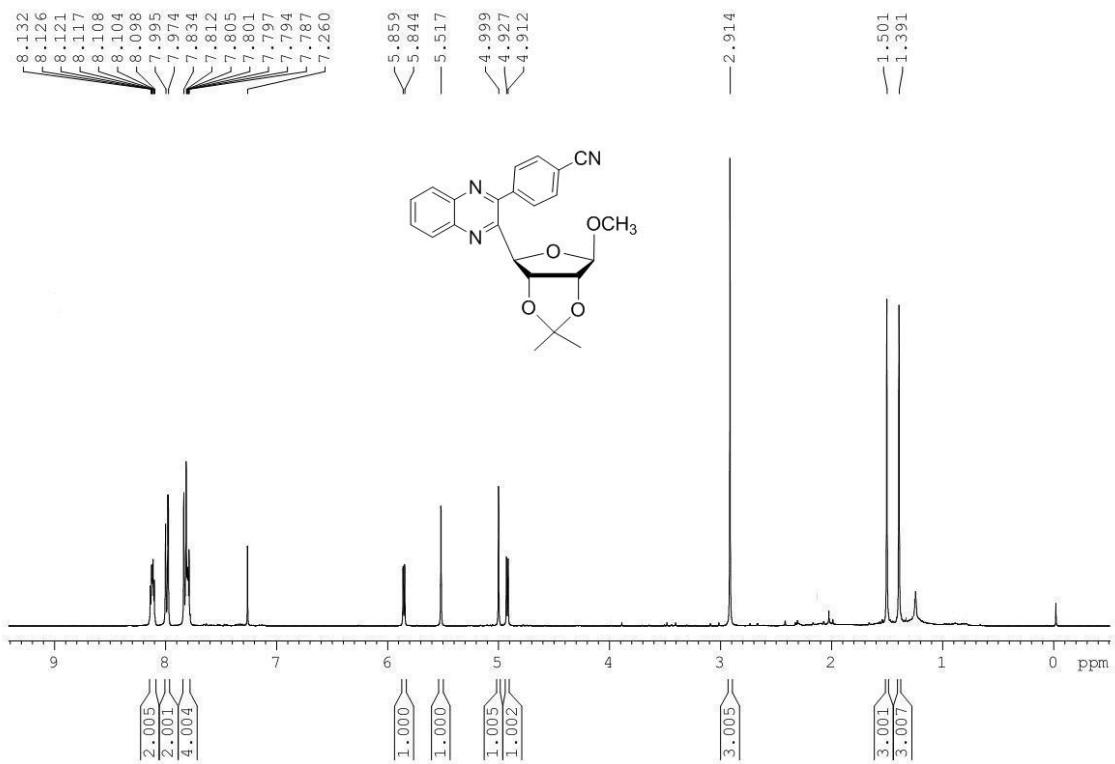
<sup>1</sup>H NMR and <sup>13</sup>C NMR of **2bb**

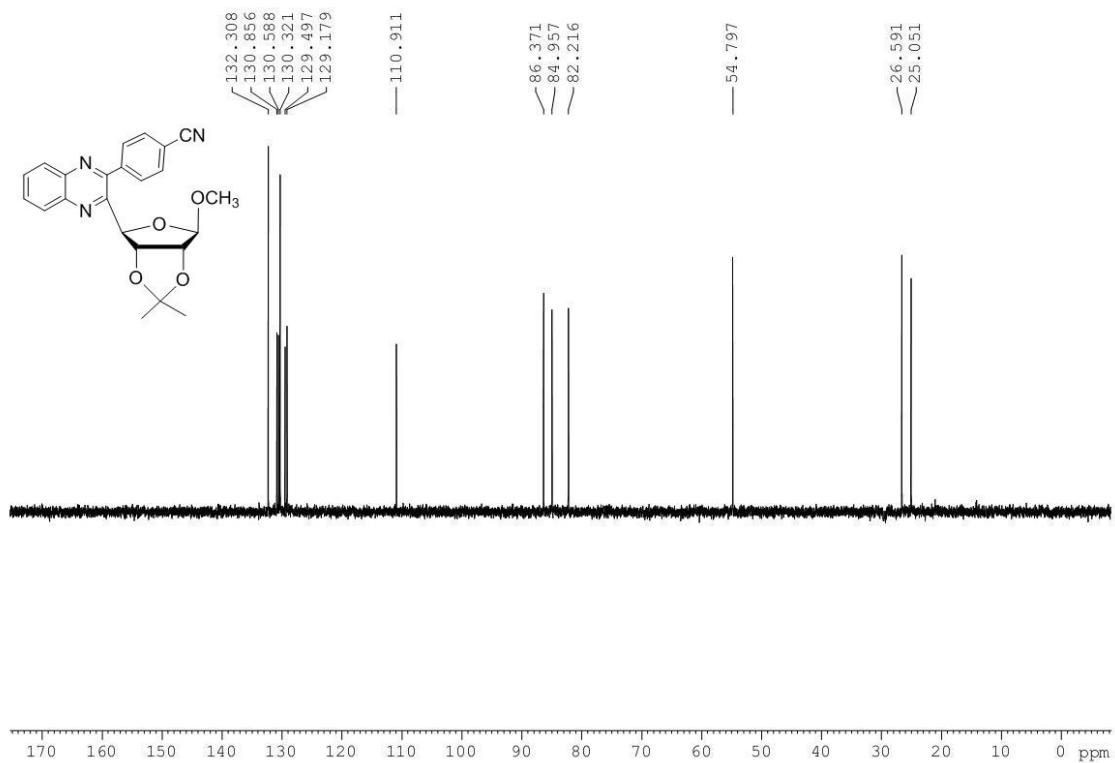
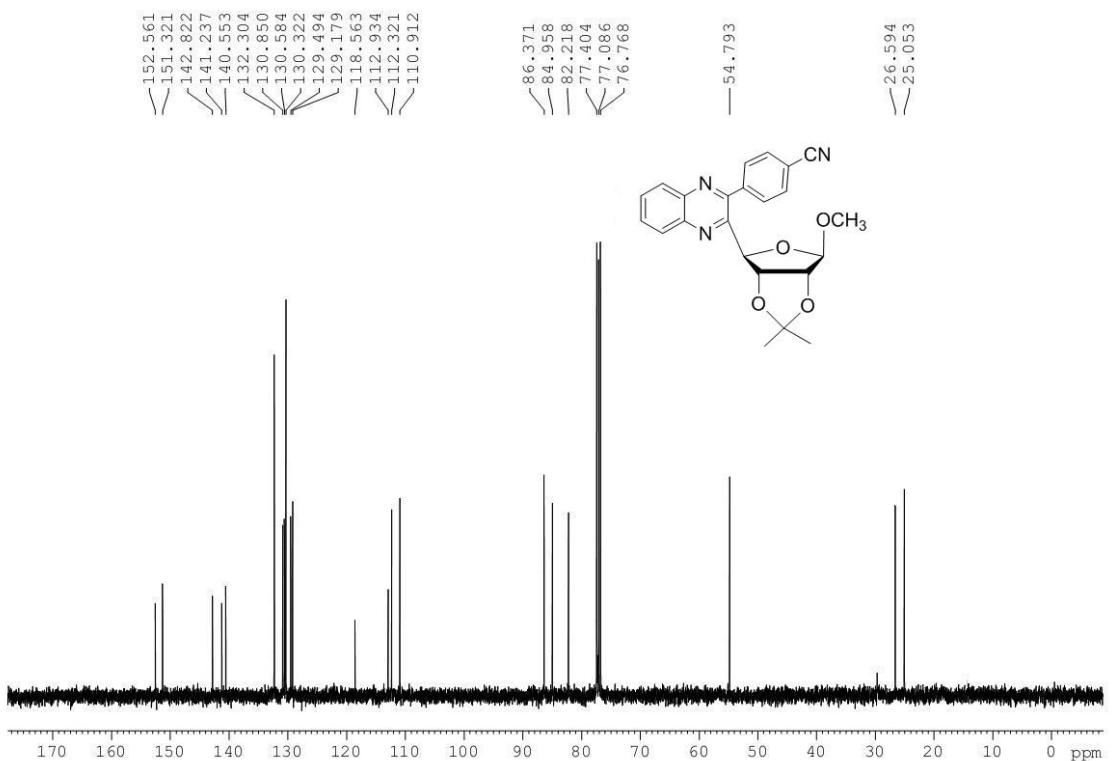


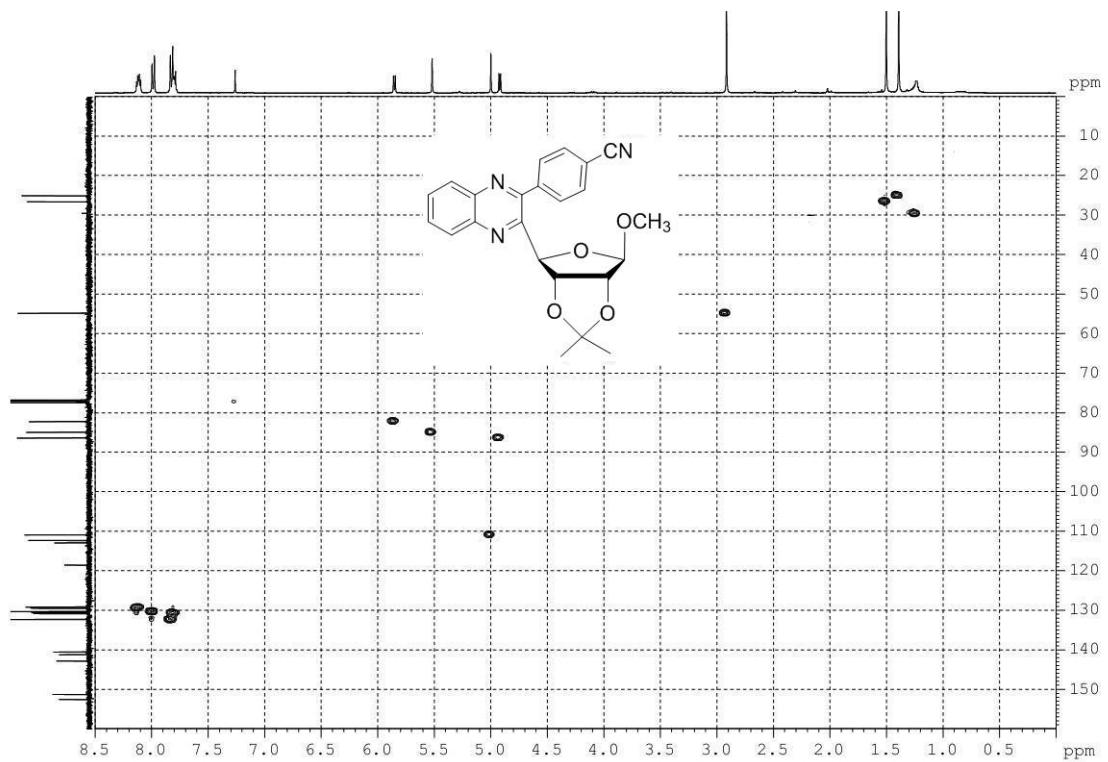
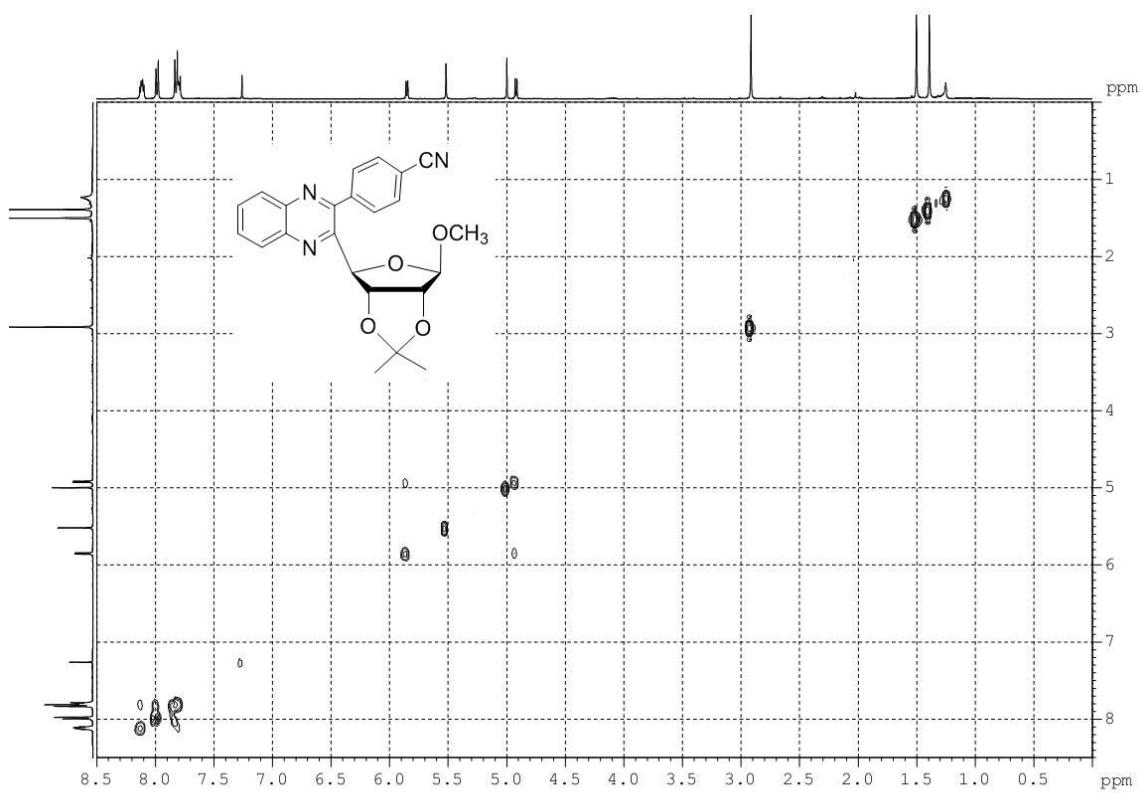
### <sup>1</sup>H NMR and <sup>13</sup>C NMR of **2bc**

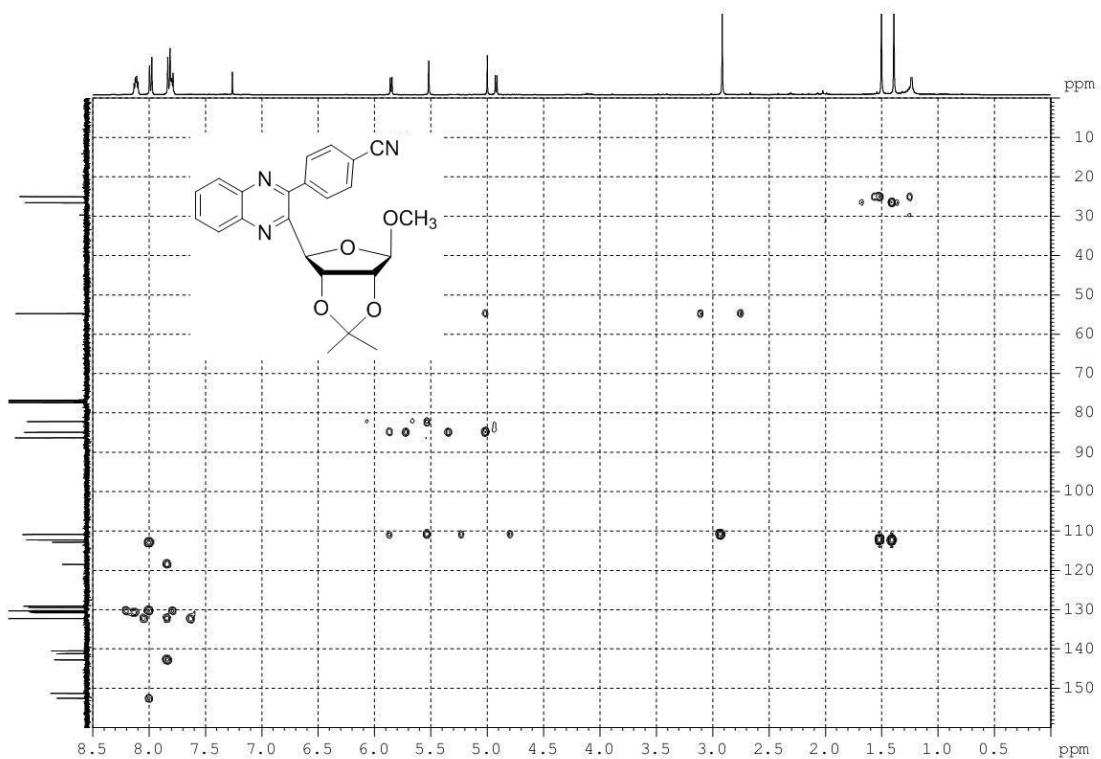


<sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT-135, <sup>1</sup>H-<sup>1</sup>H COSY, HSQC and HMBC of **2ca**

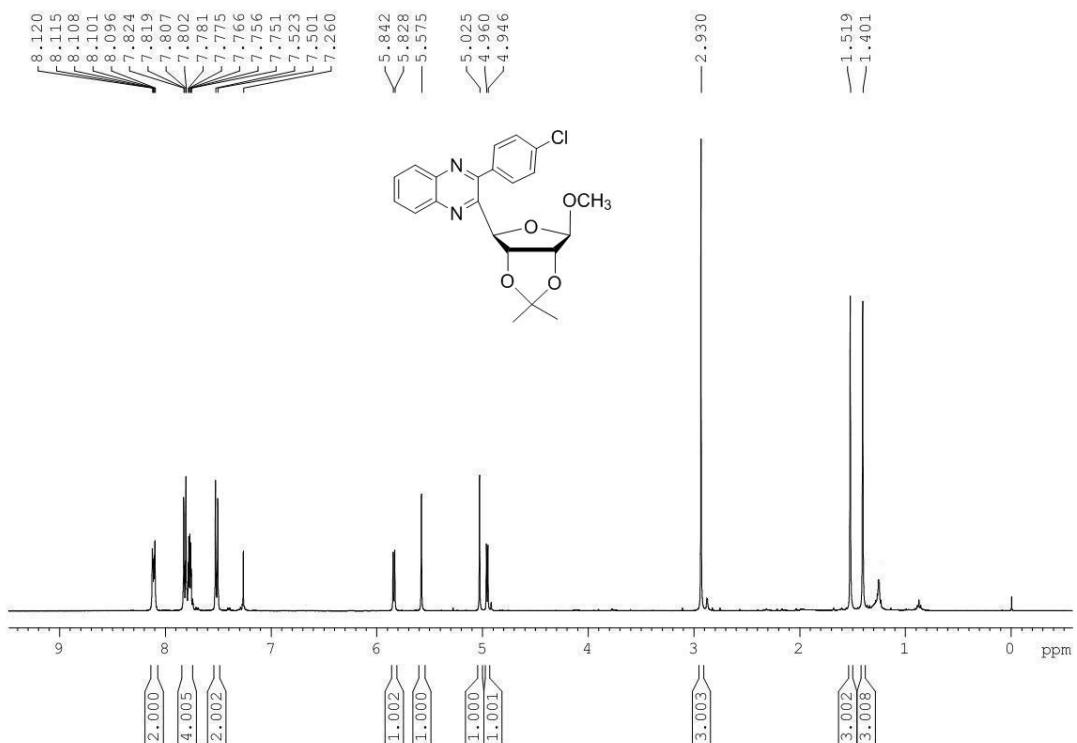


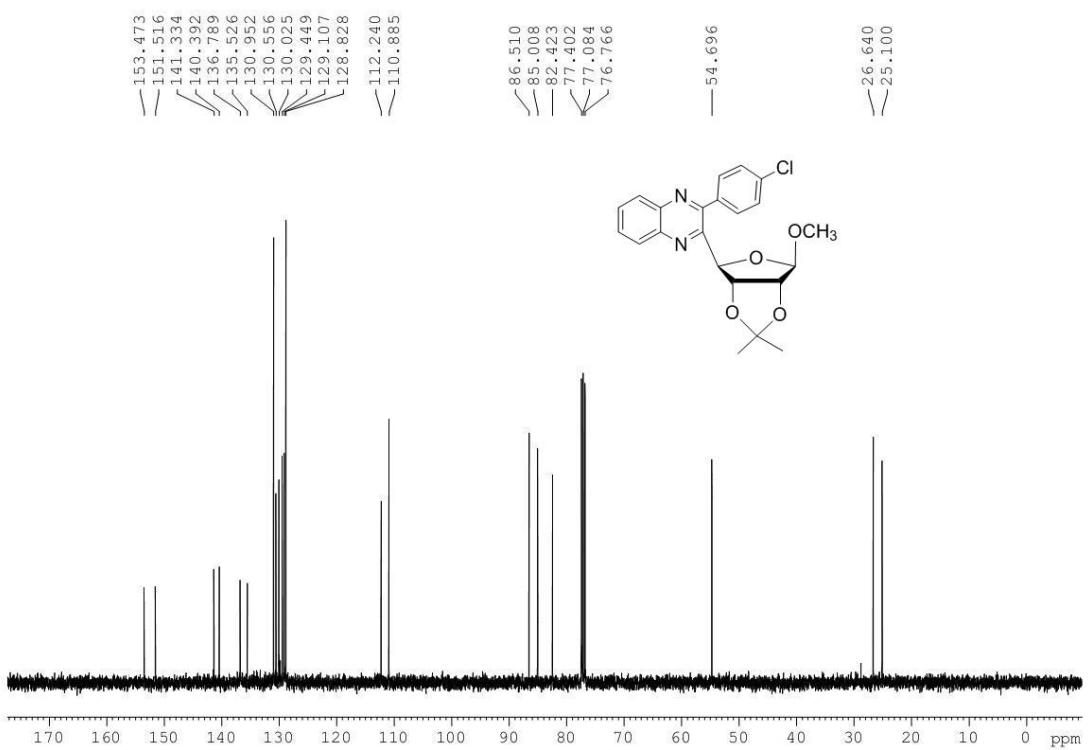




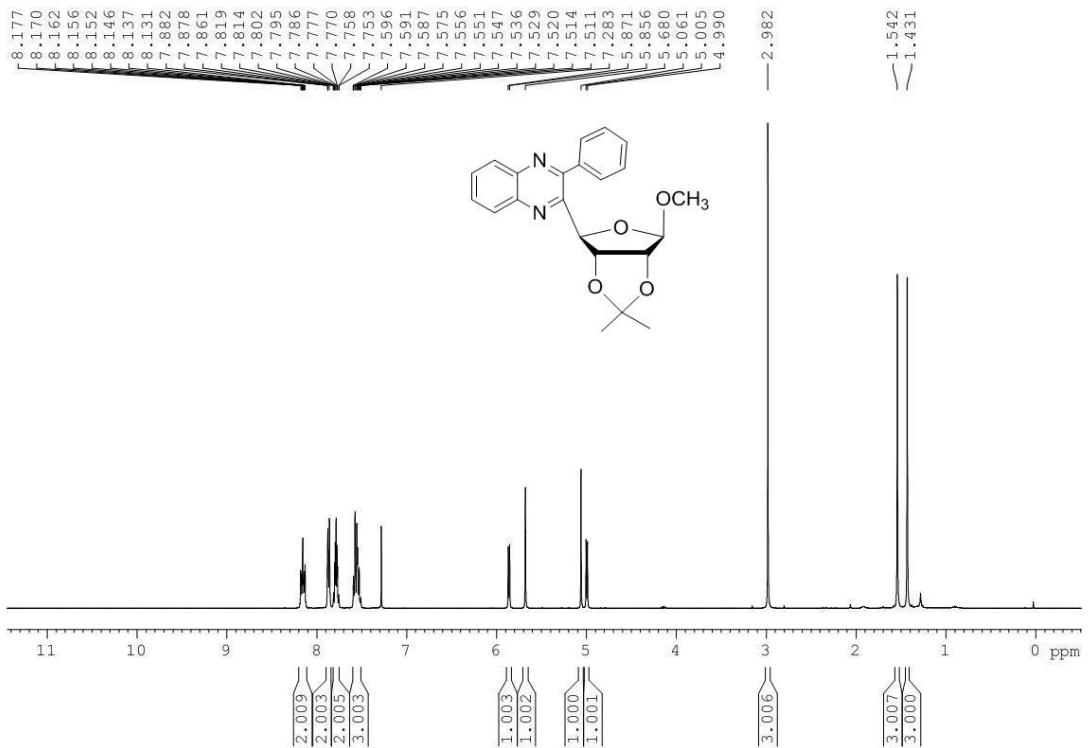


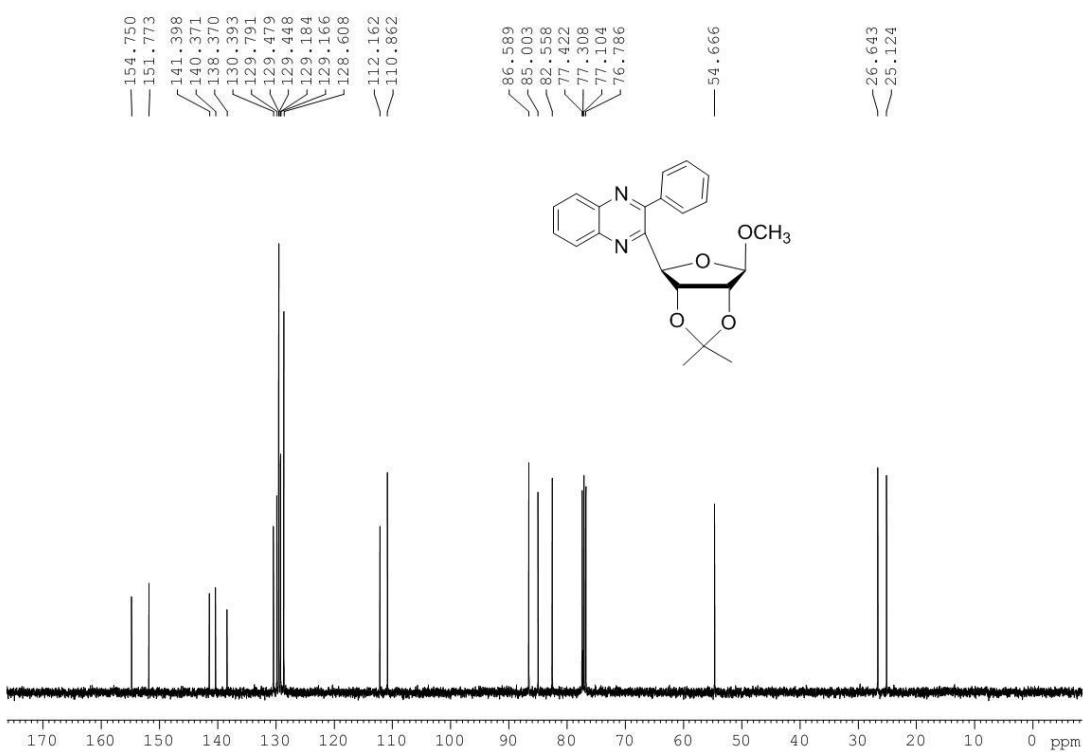
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of **2cb**



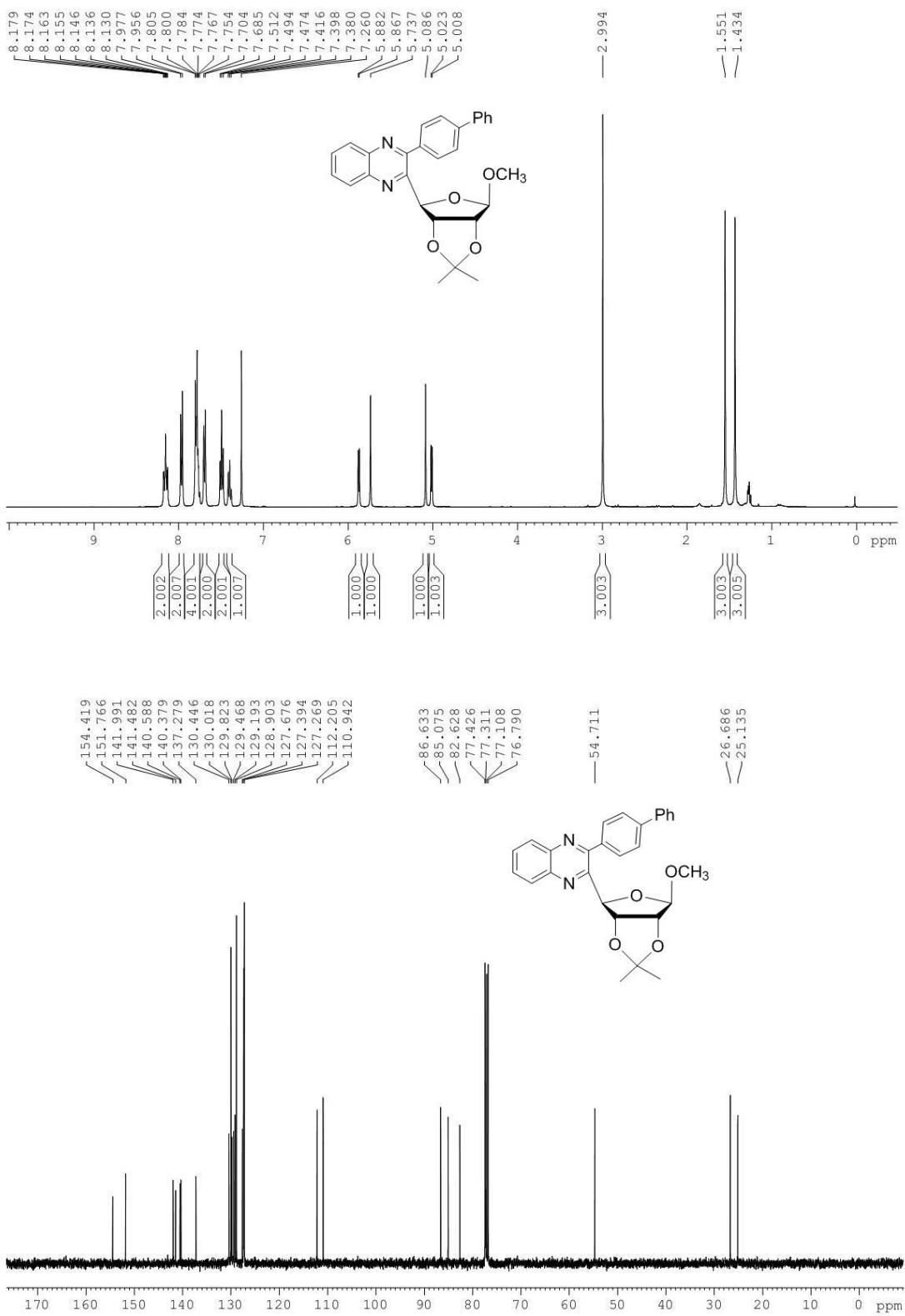


<sup>1</sup>H NMR and <sup>13</sup>C NMR of **2cc**

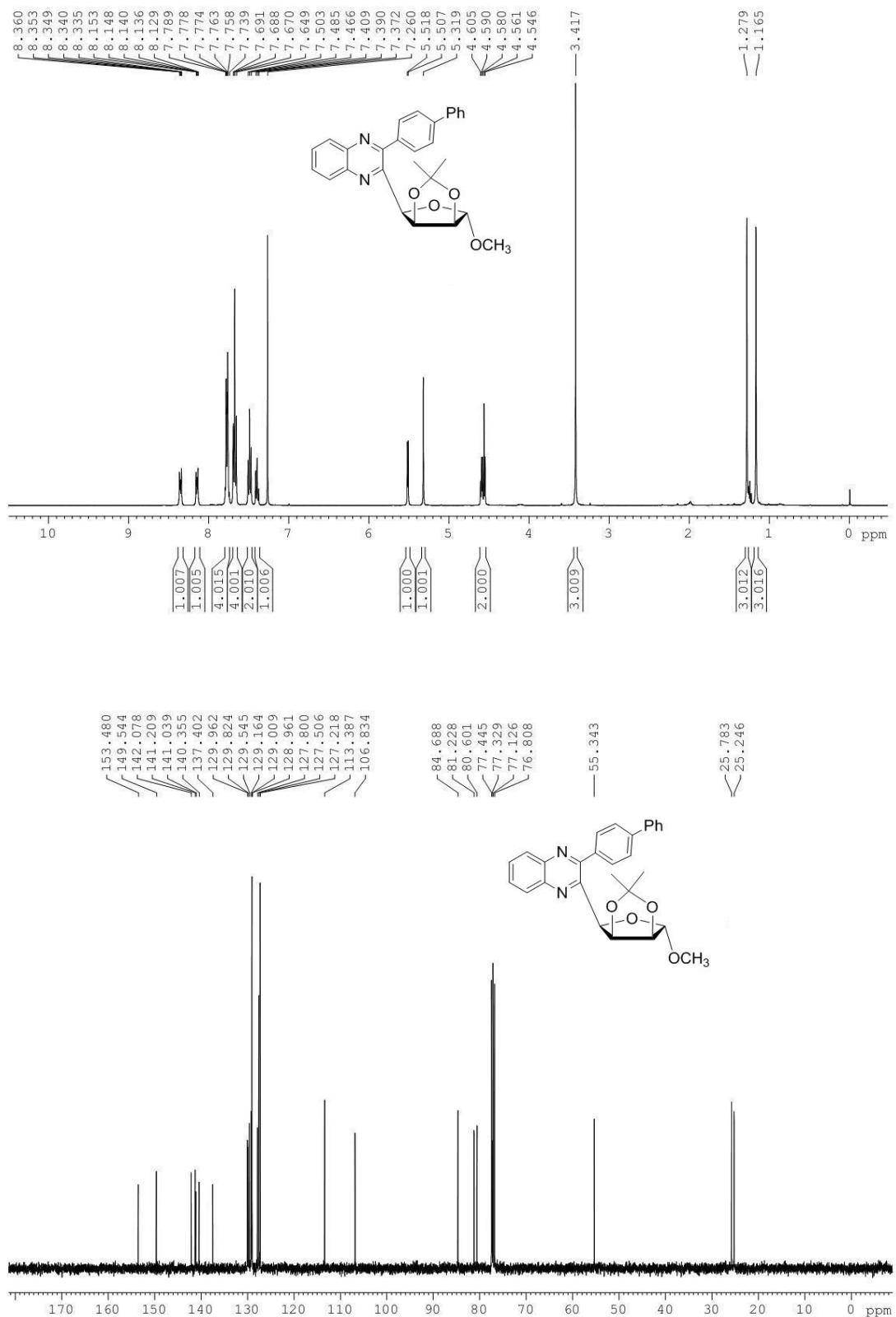


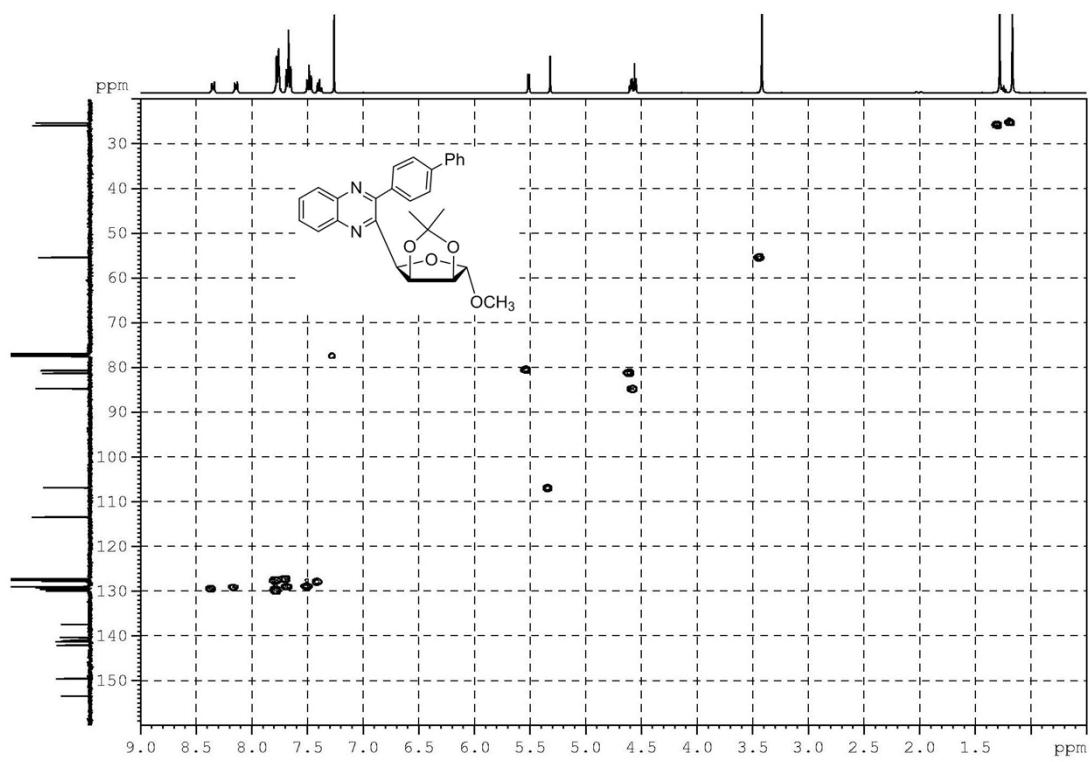
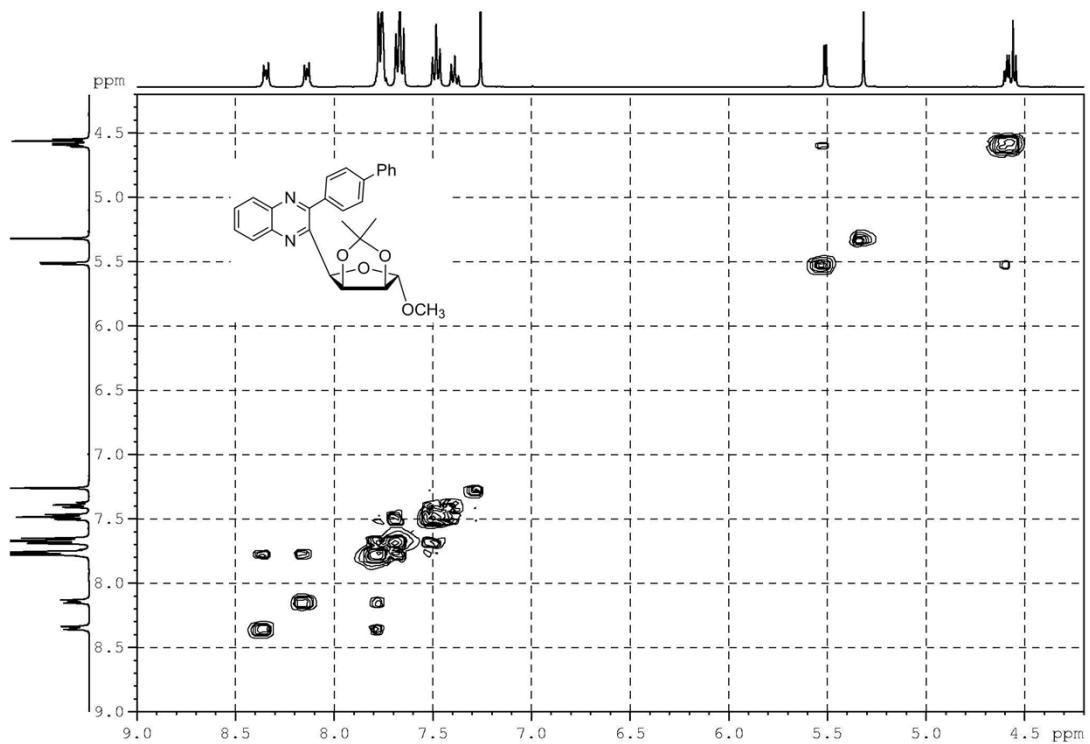


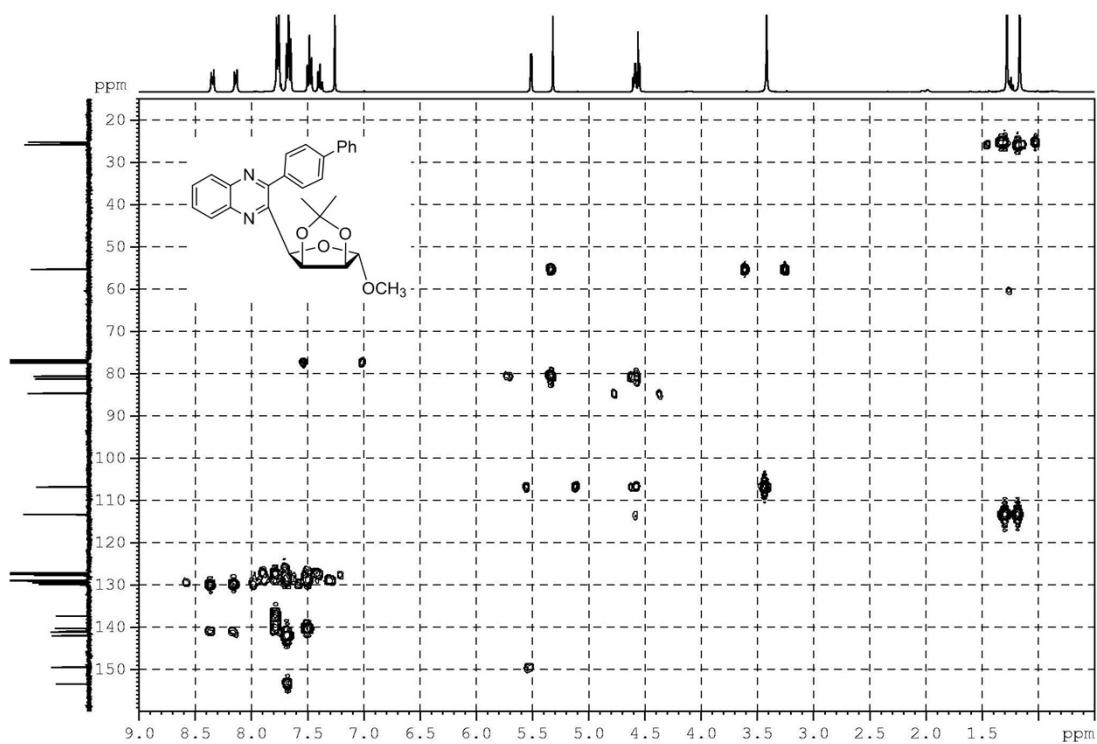
<sup>1</sup>H NMR and <sup>13</sup>C NMR of **2cd**



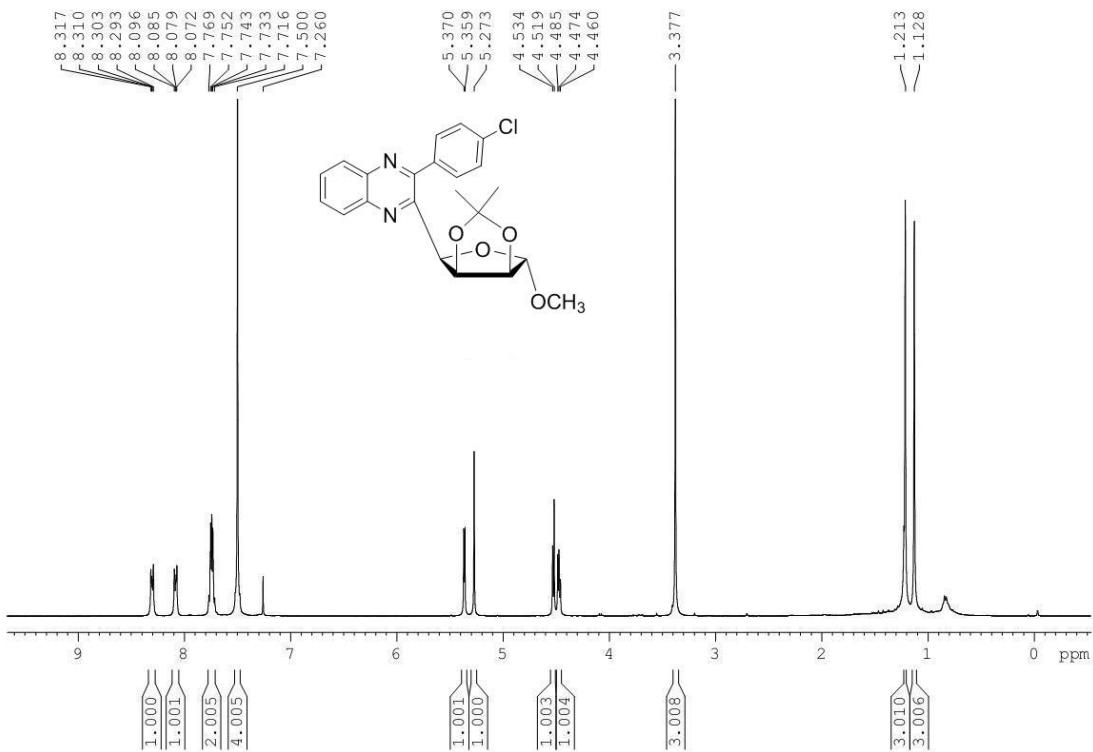
<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>1</sup>H-<sup>1</sup>H COSY, HSQC and HMBC of **2da**

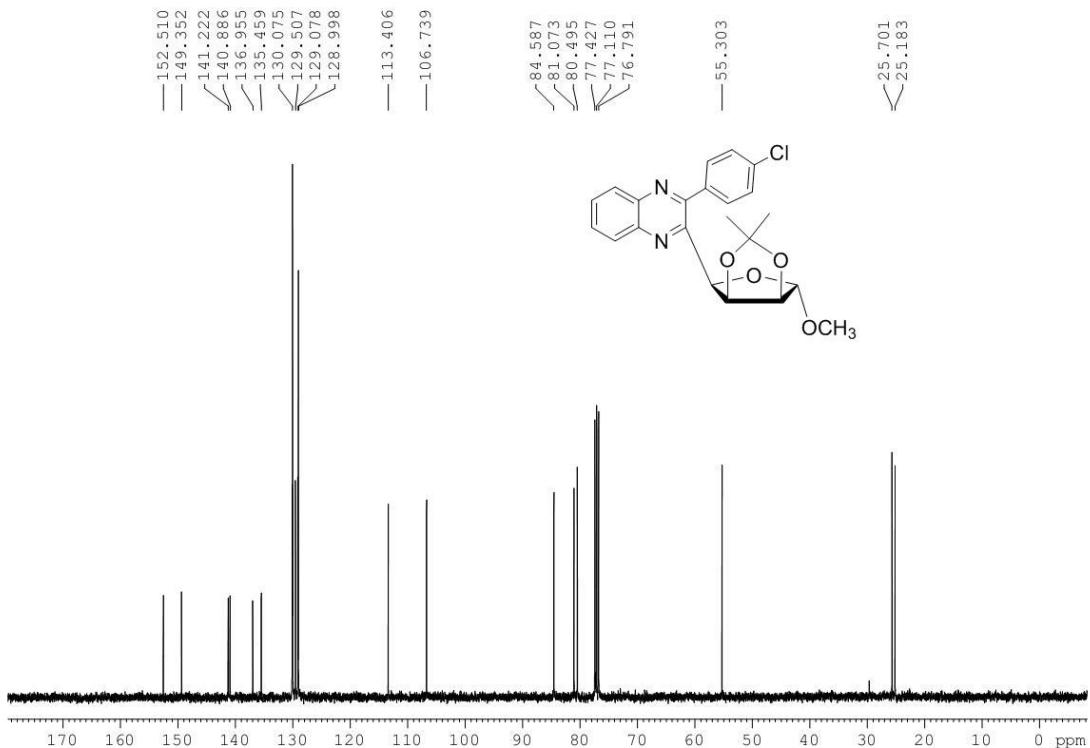




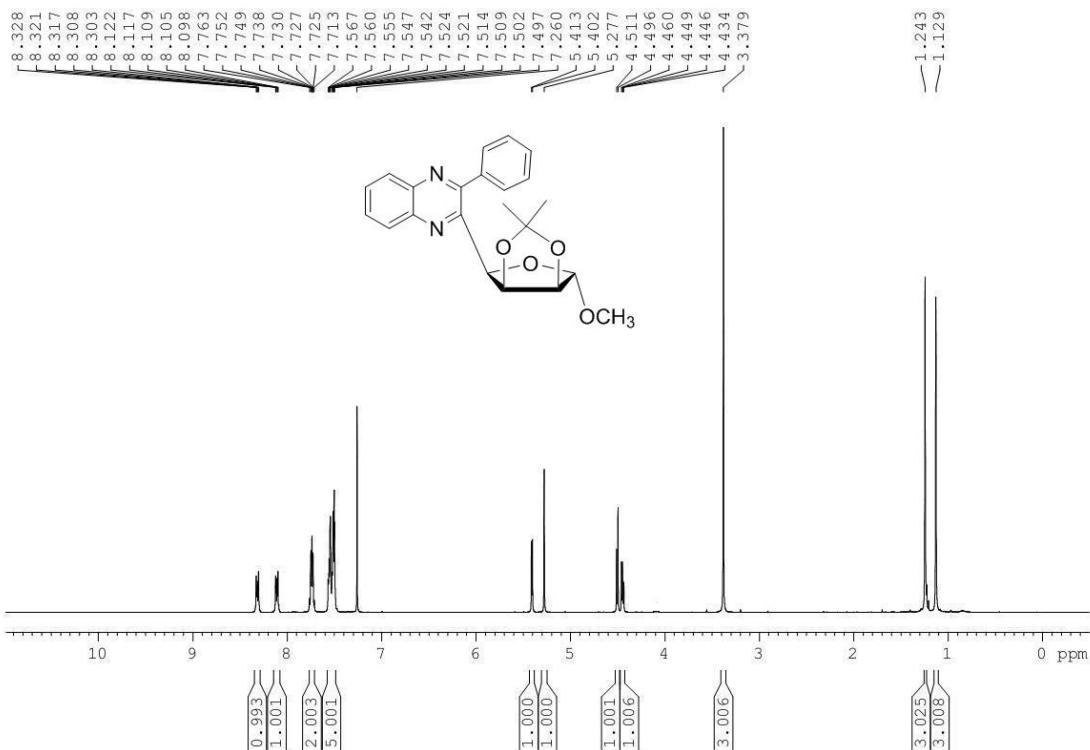


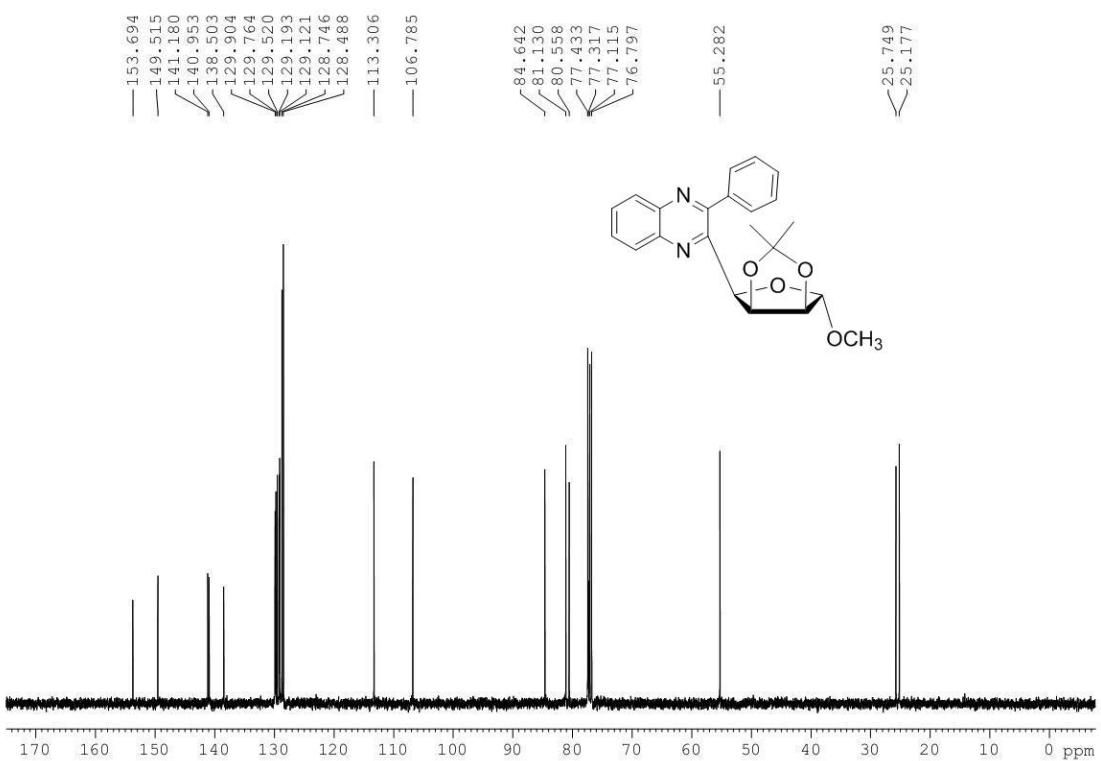
<sup>1</sup>H NMR and <sup>13</sup>C NMR of **2db**



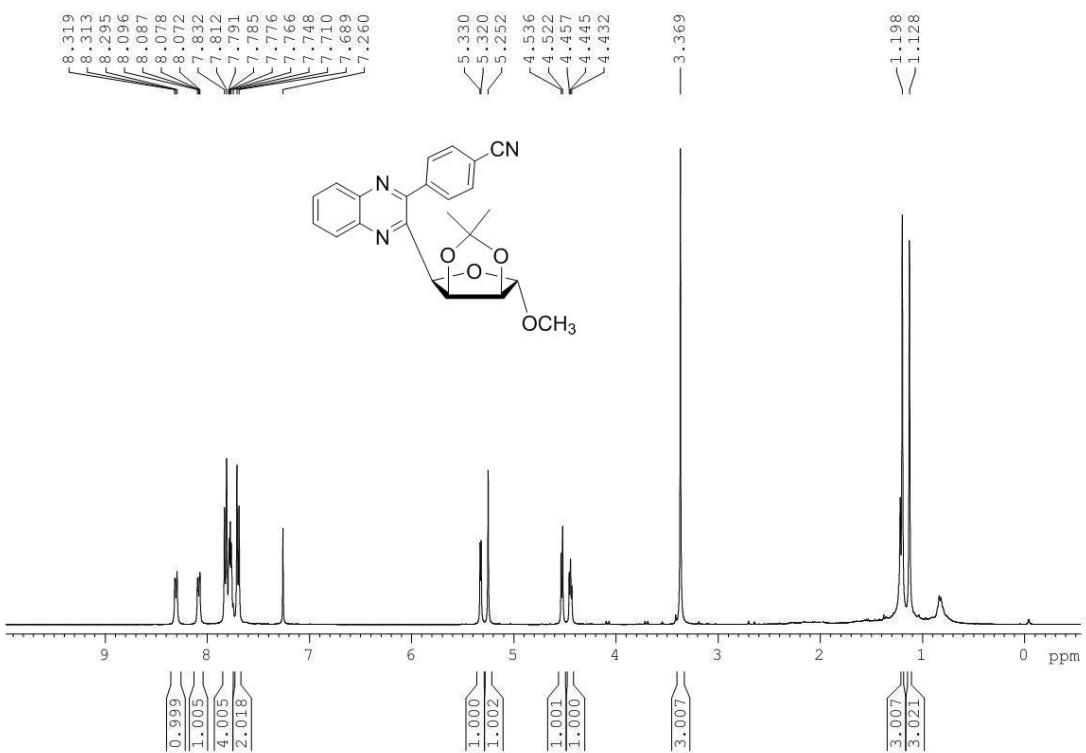


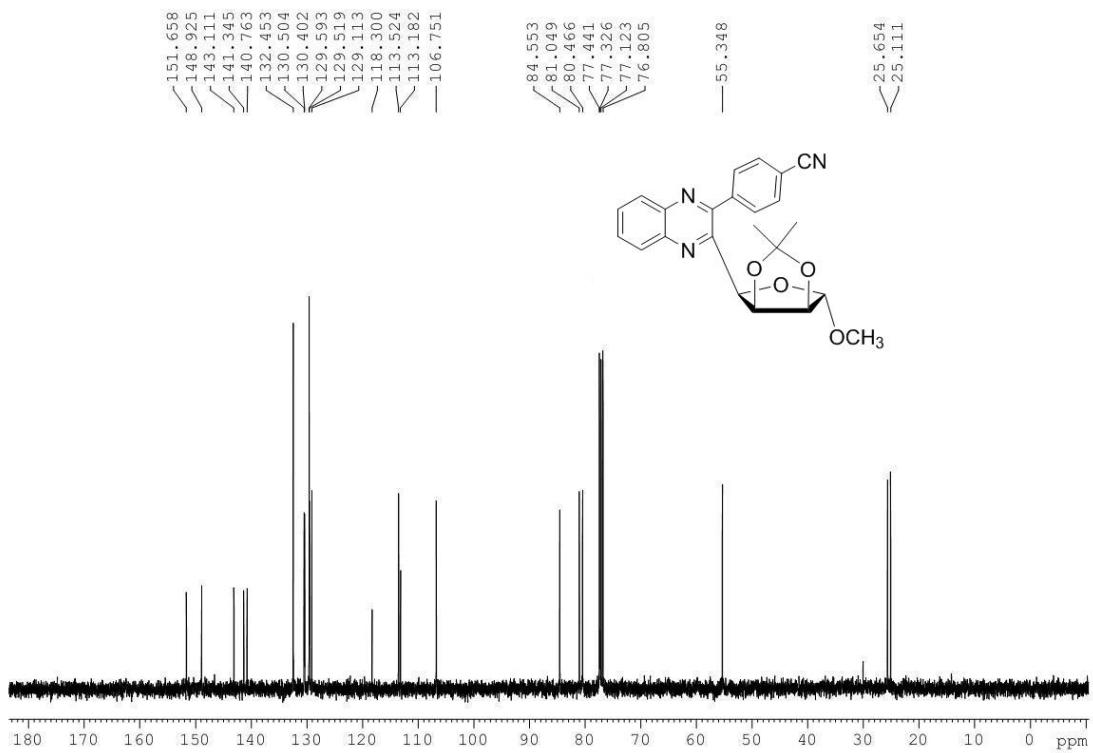
<sup>1</sup>H NMR and <sup>13</sup>C NMR of **2dc**



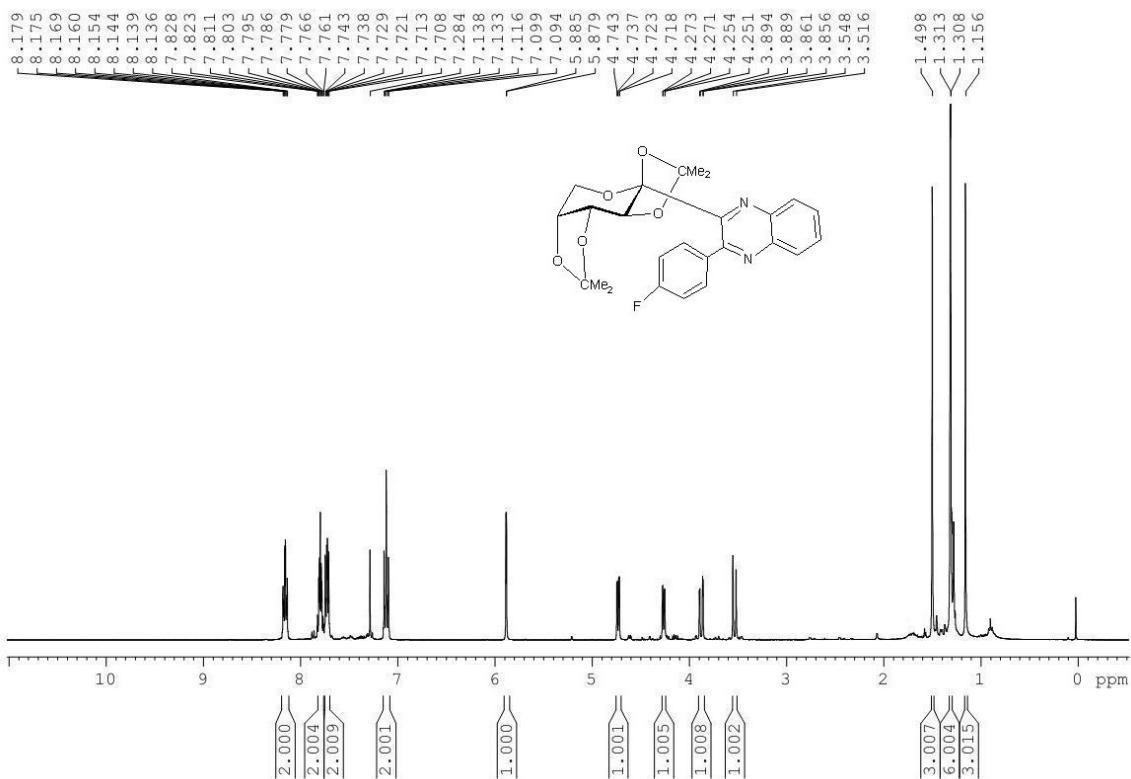


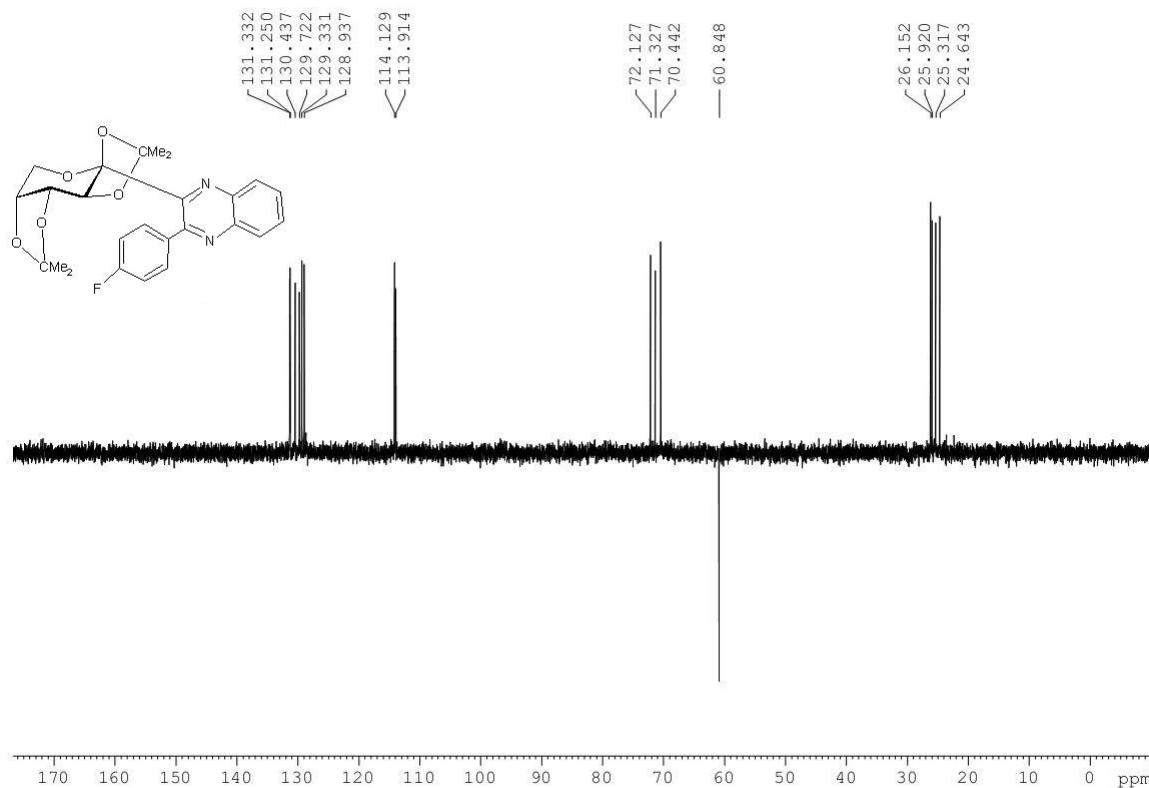
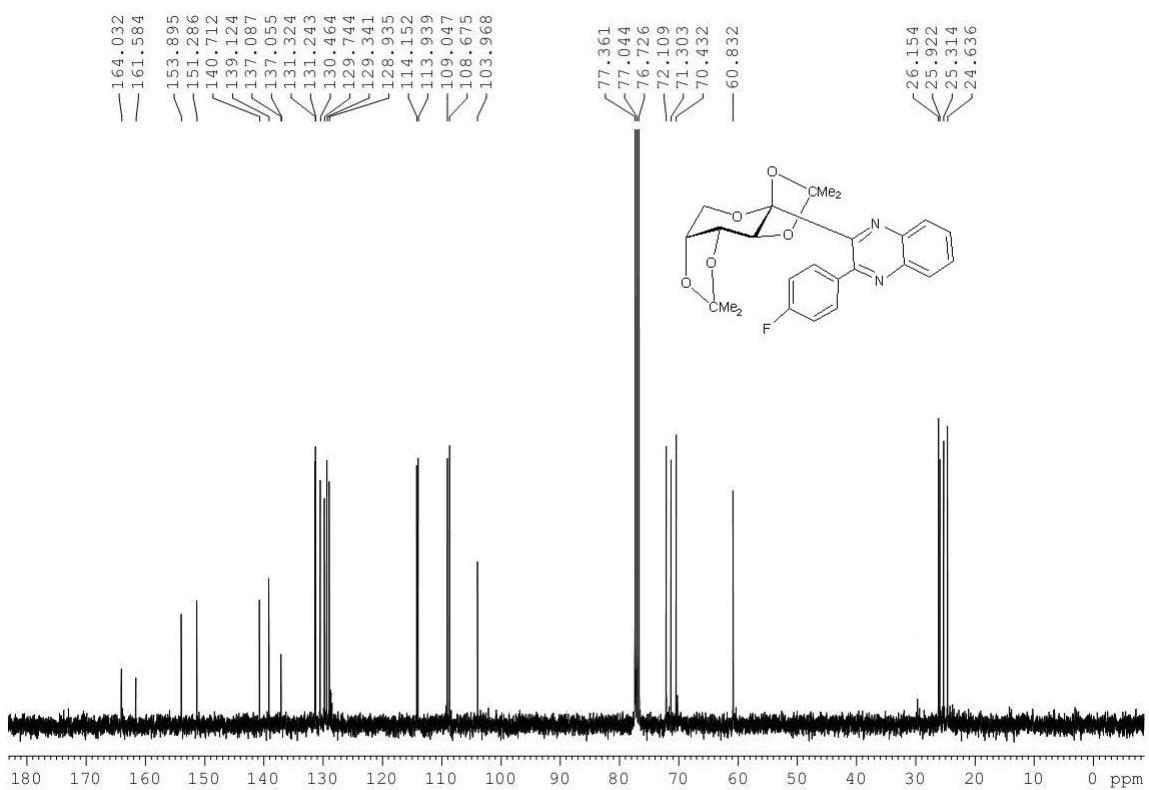
<sup>1</sup>H NMR and <sup>13</sup>C NMR of 2dd

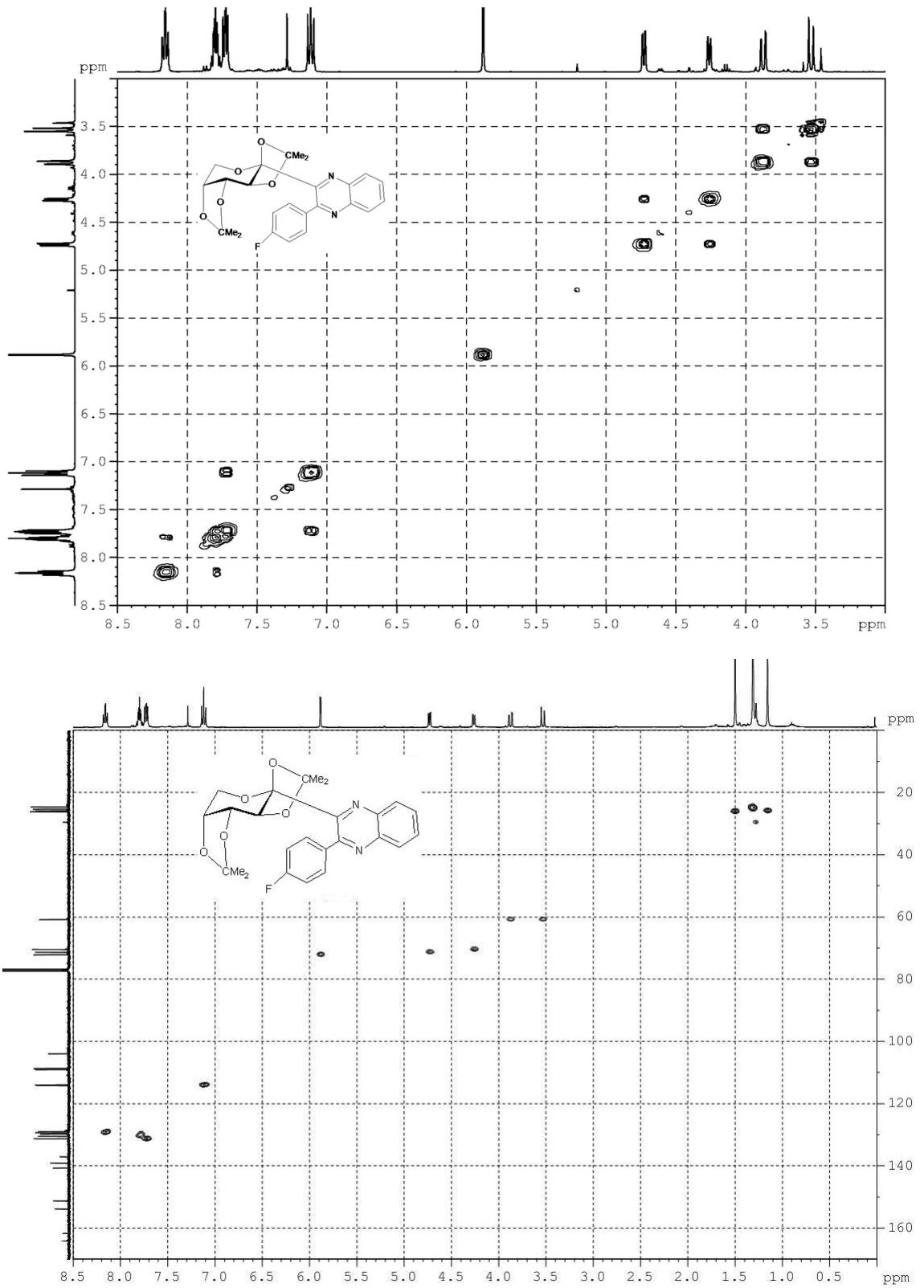


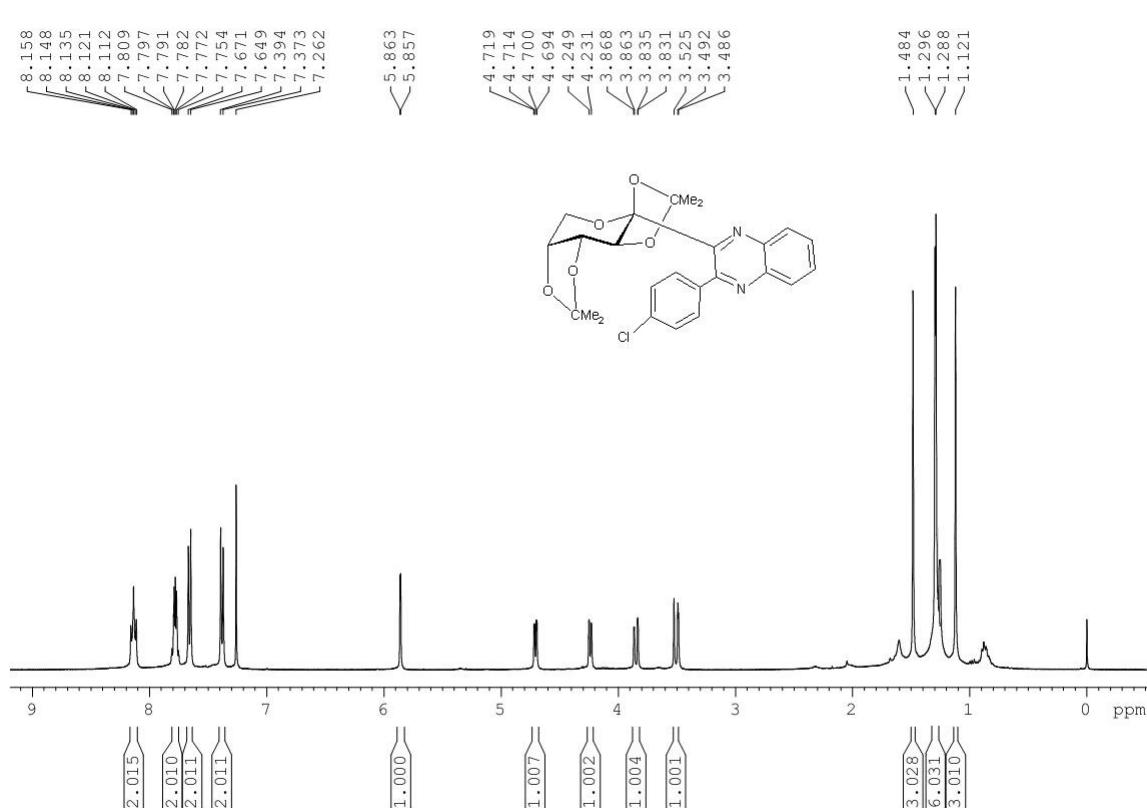
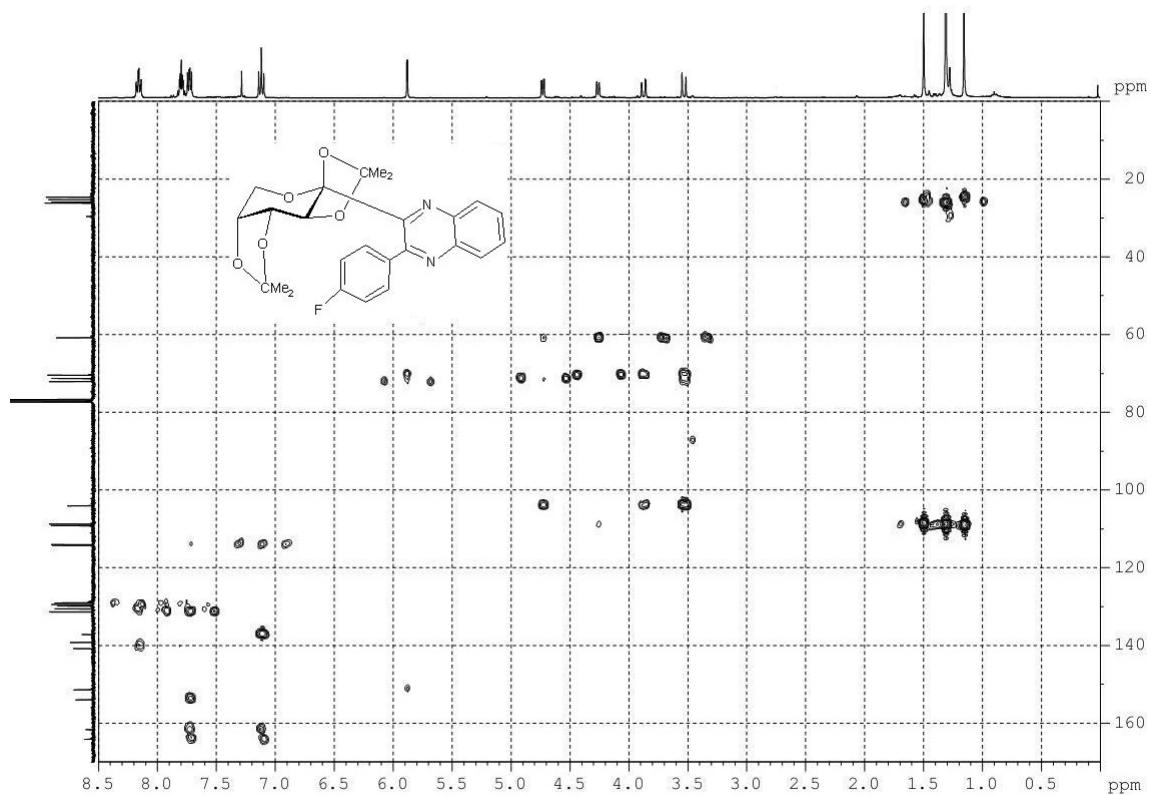


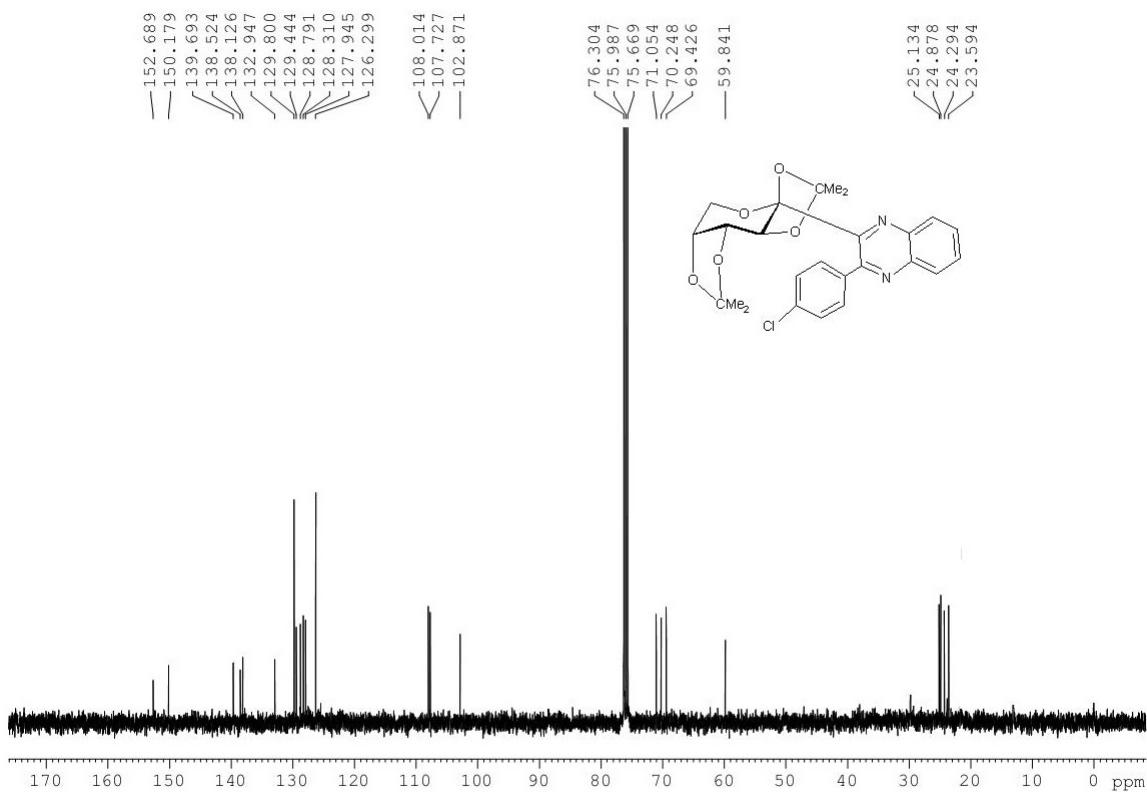
<sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT-135, <sup>1</sup>H-<sup>1</sup>H COSY, HSQC and HMBC of 2ea



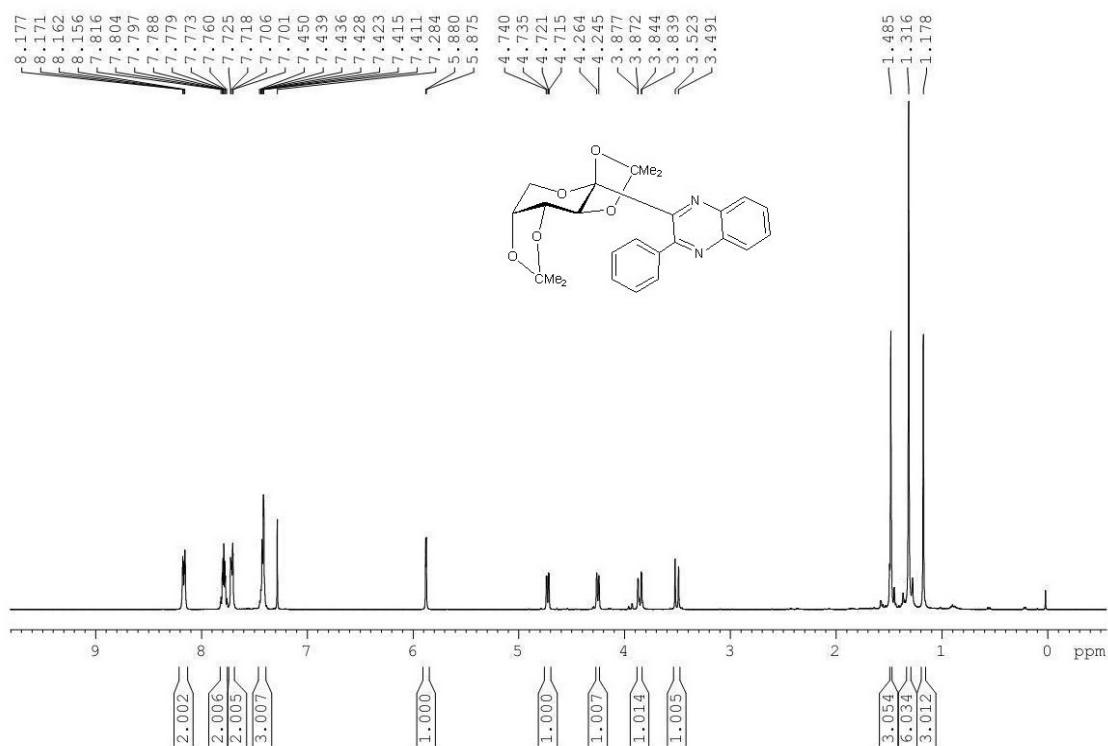


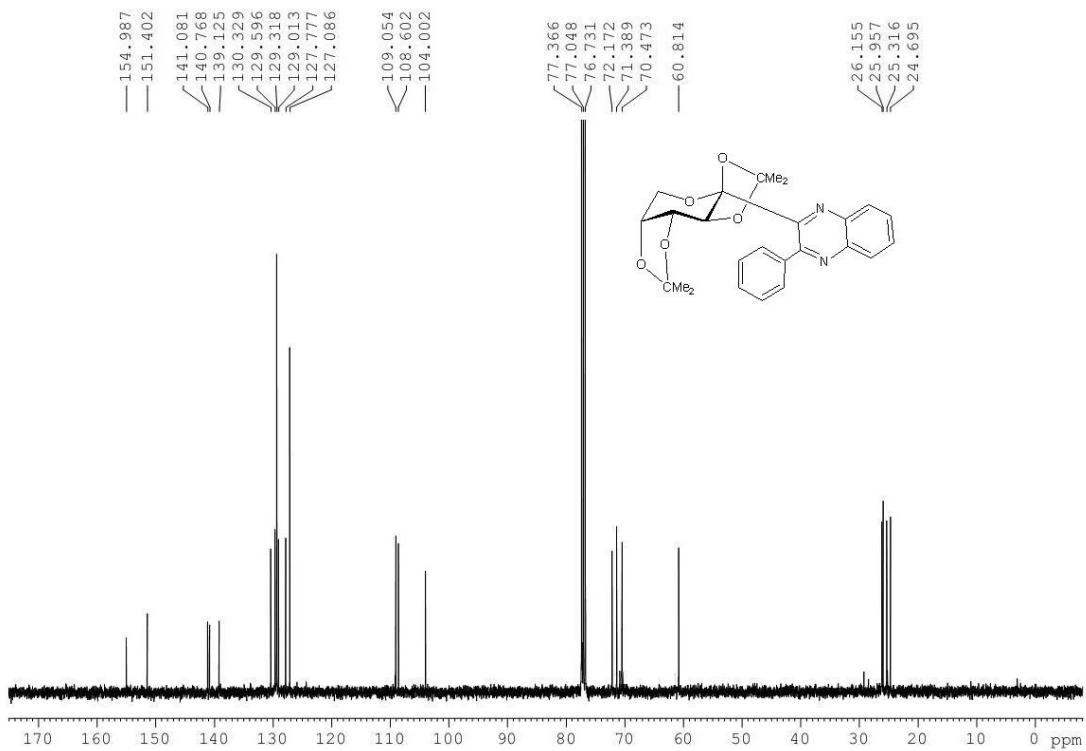




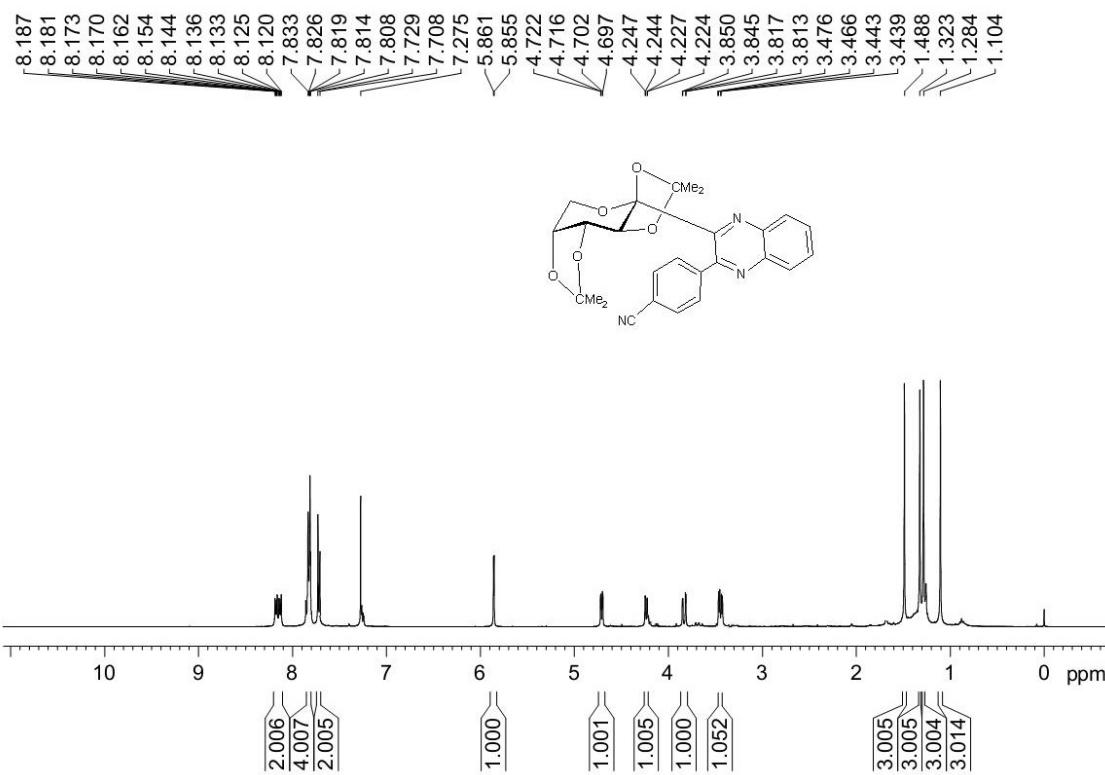


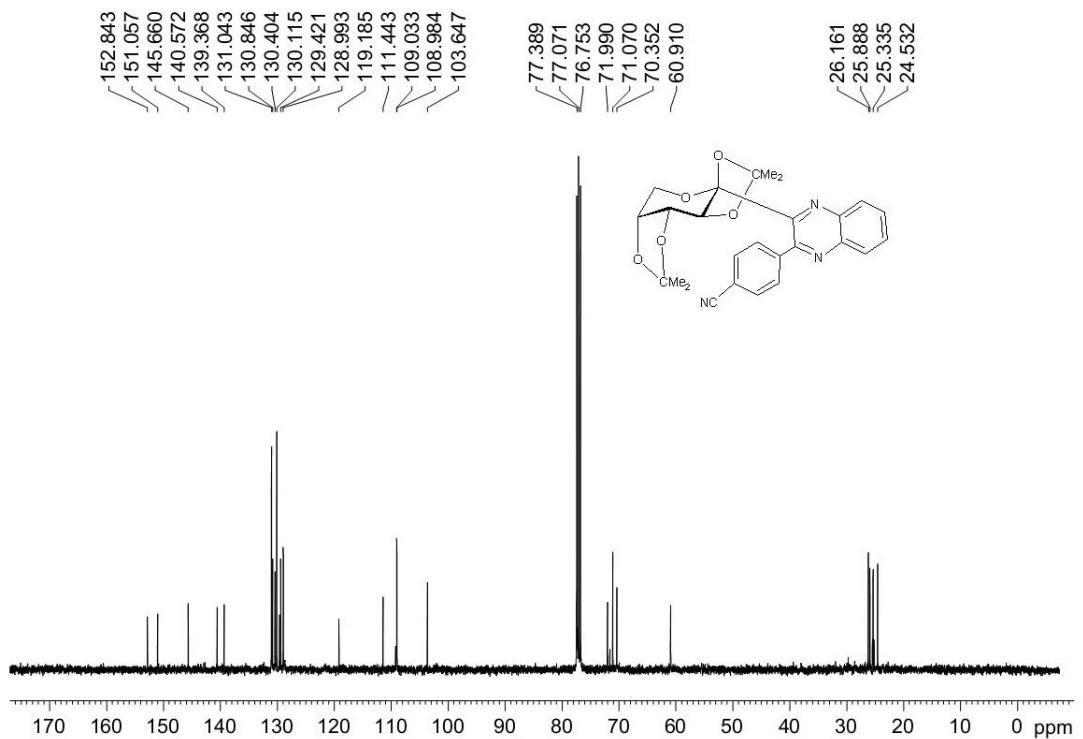
<sup>1</sup>H NMR and <sup>13</sup>C NMR of 2ec



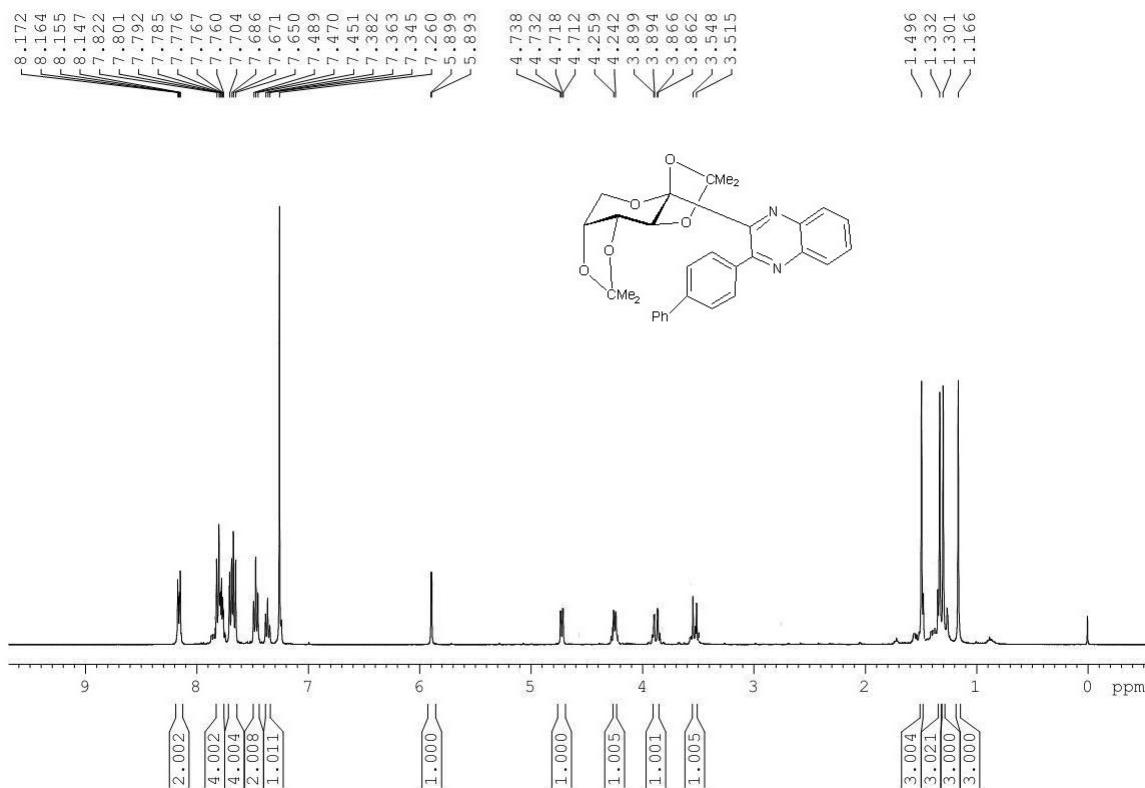


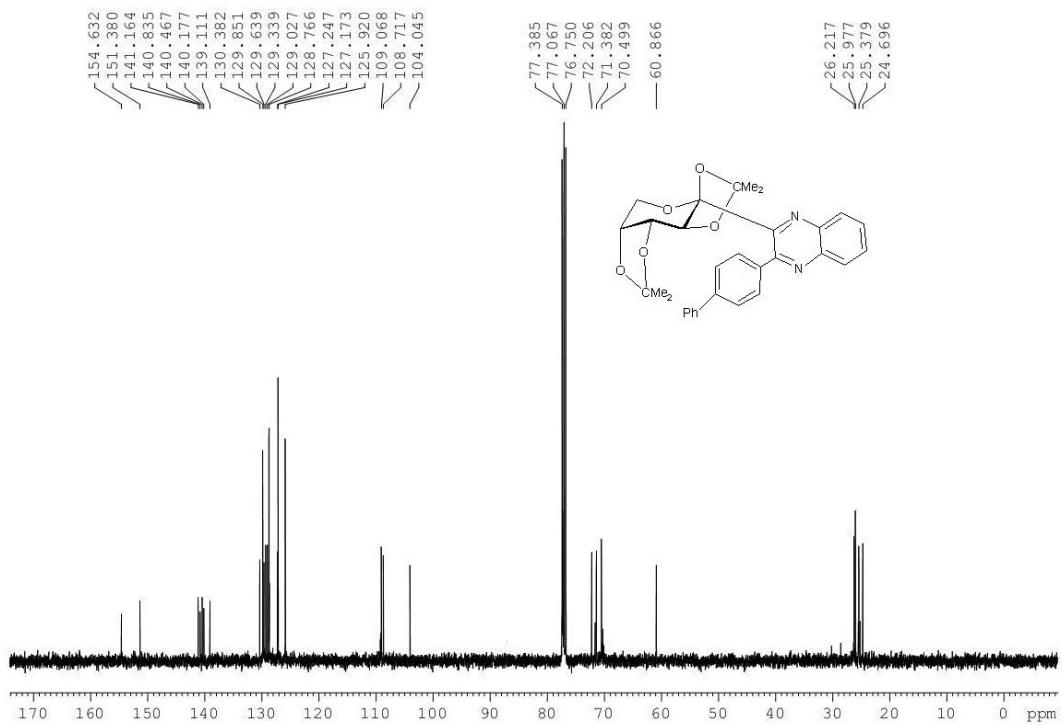
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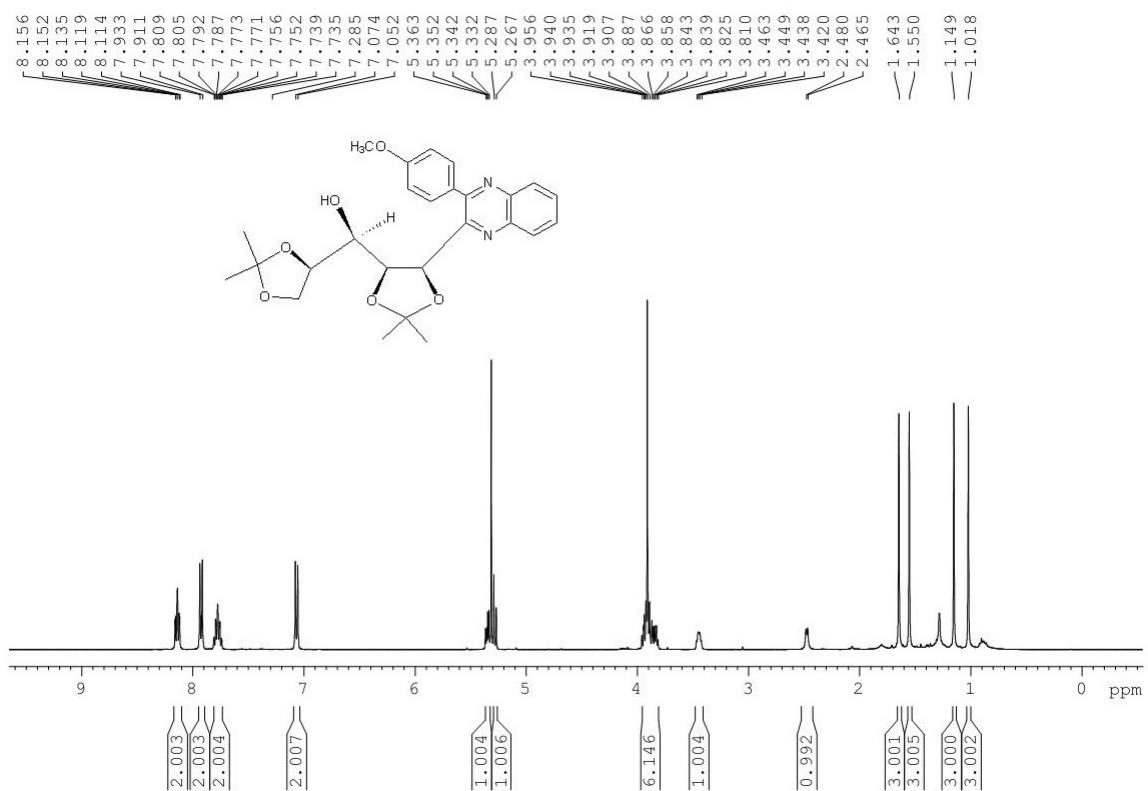


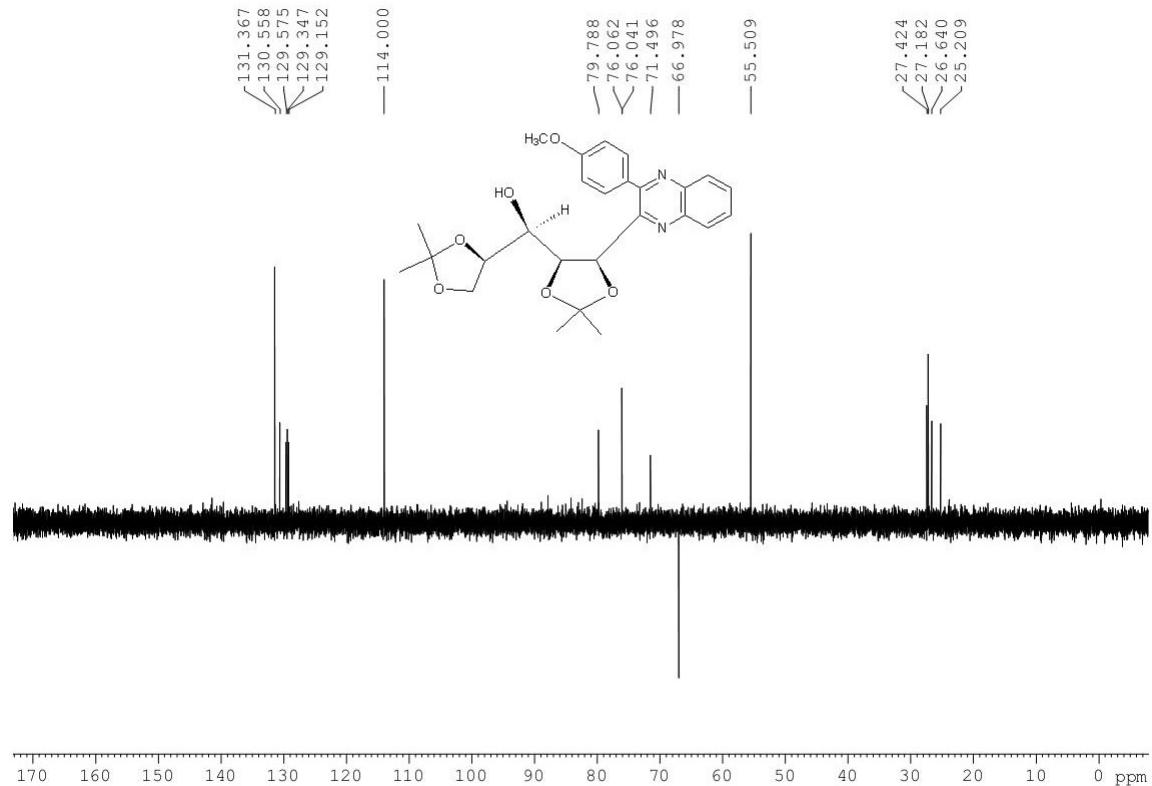
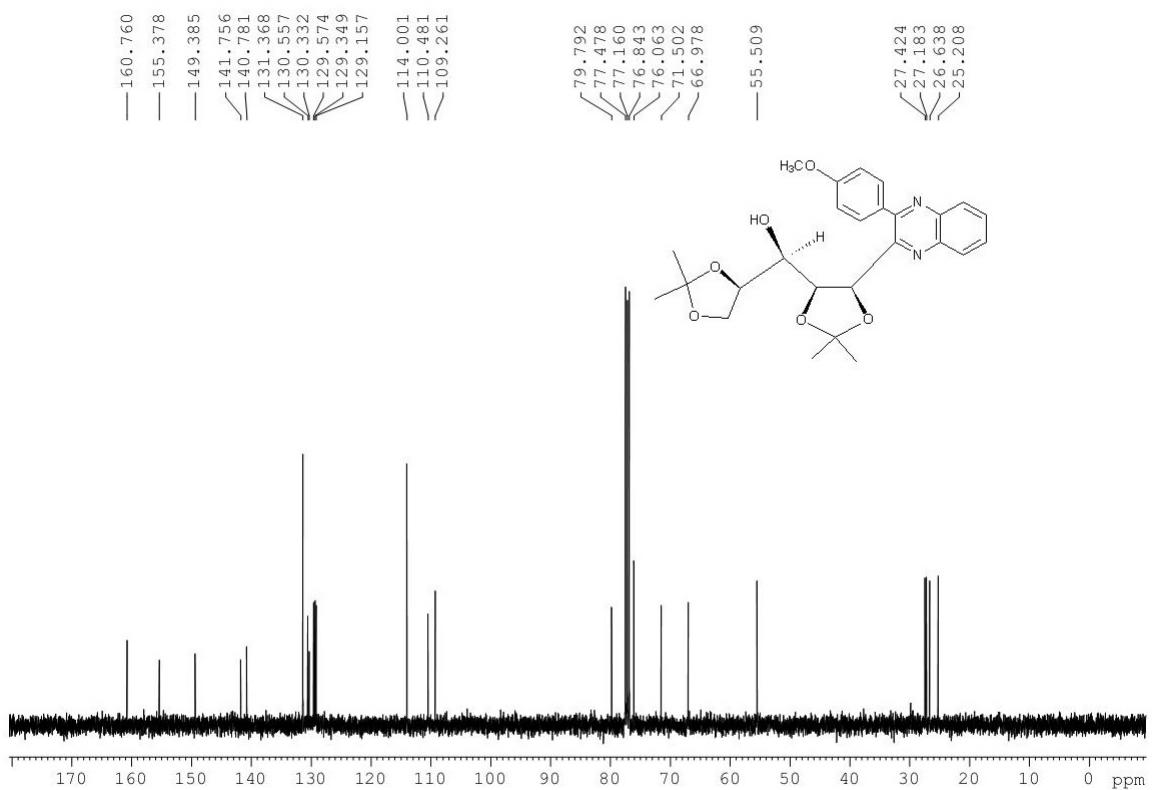
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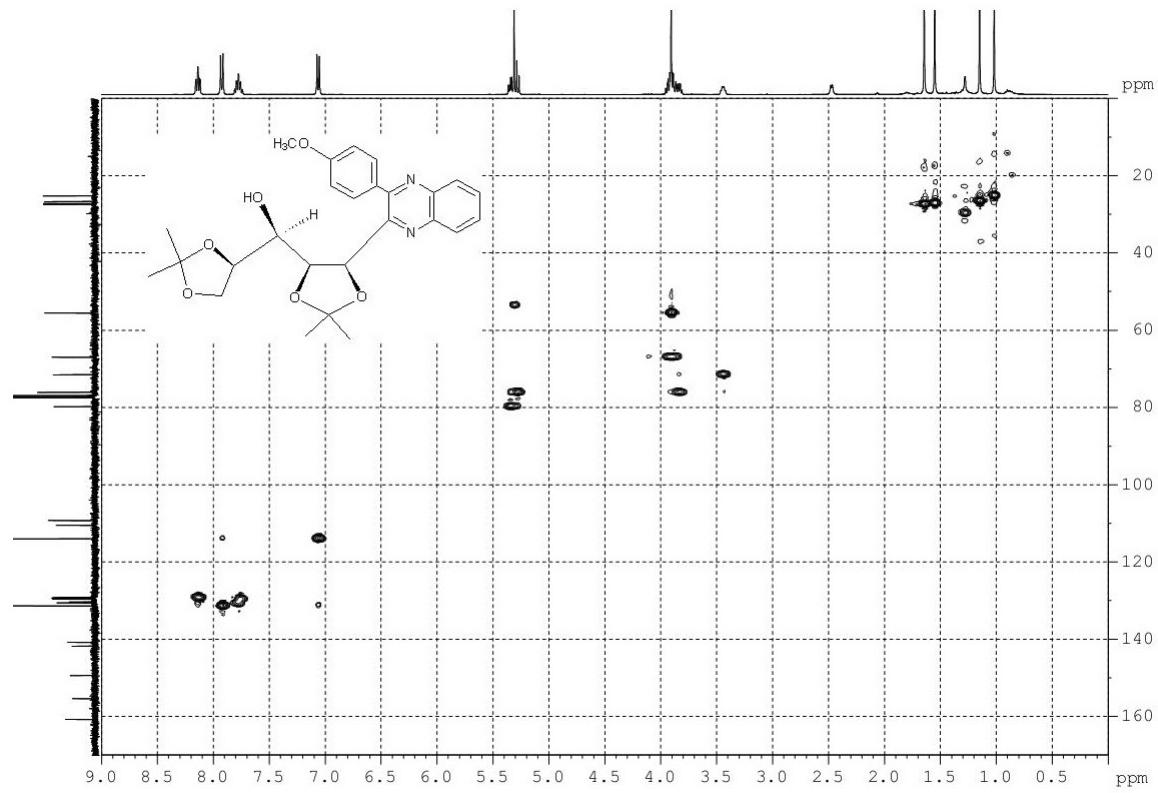
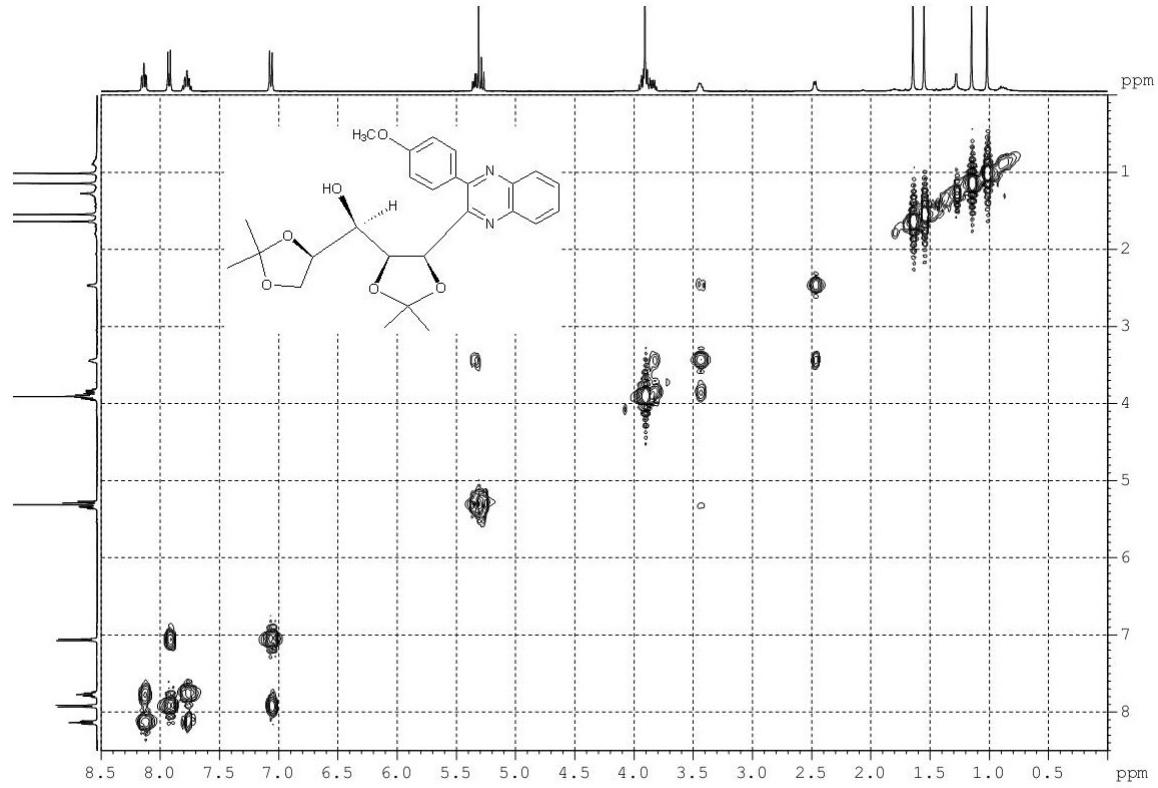


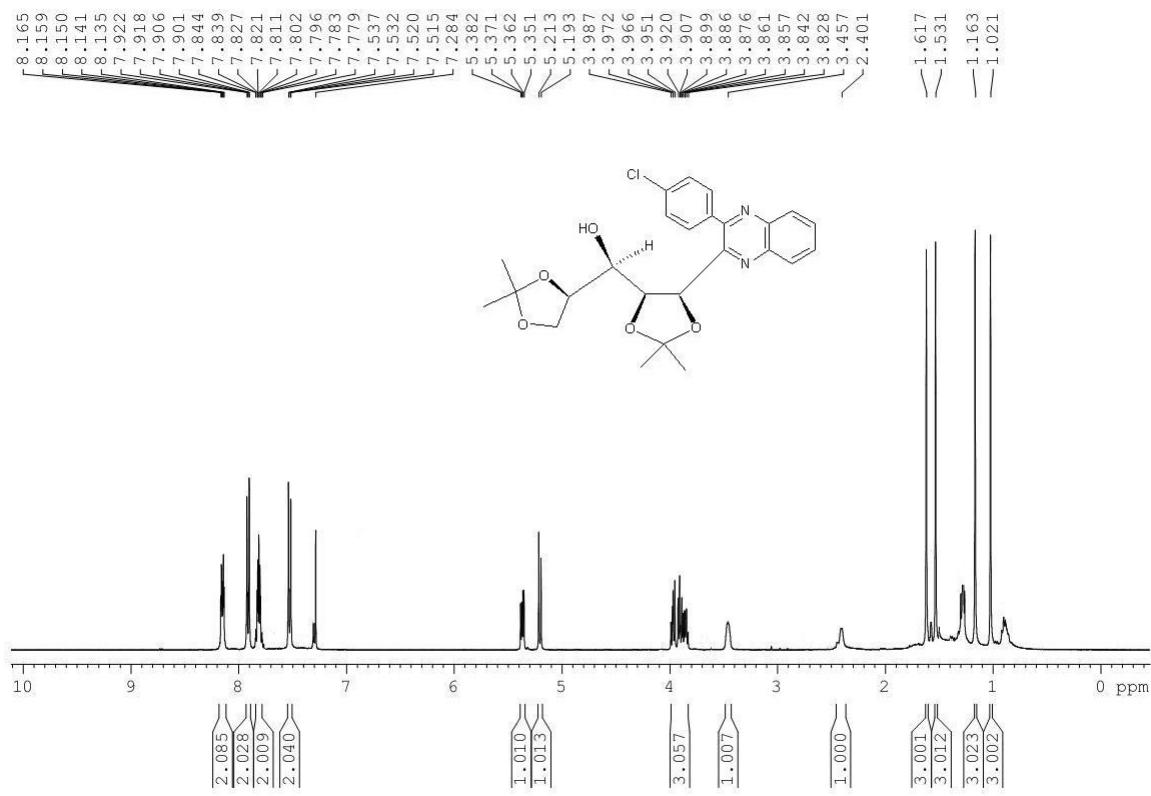
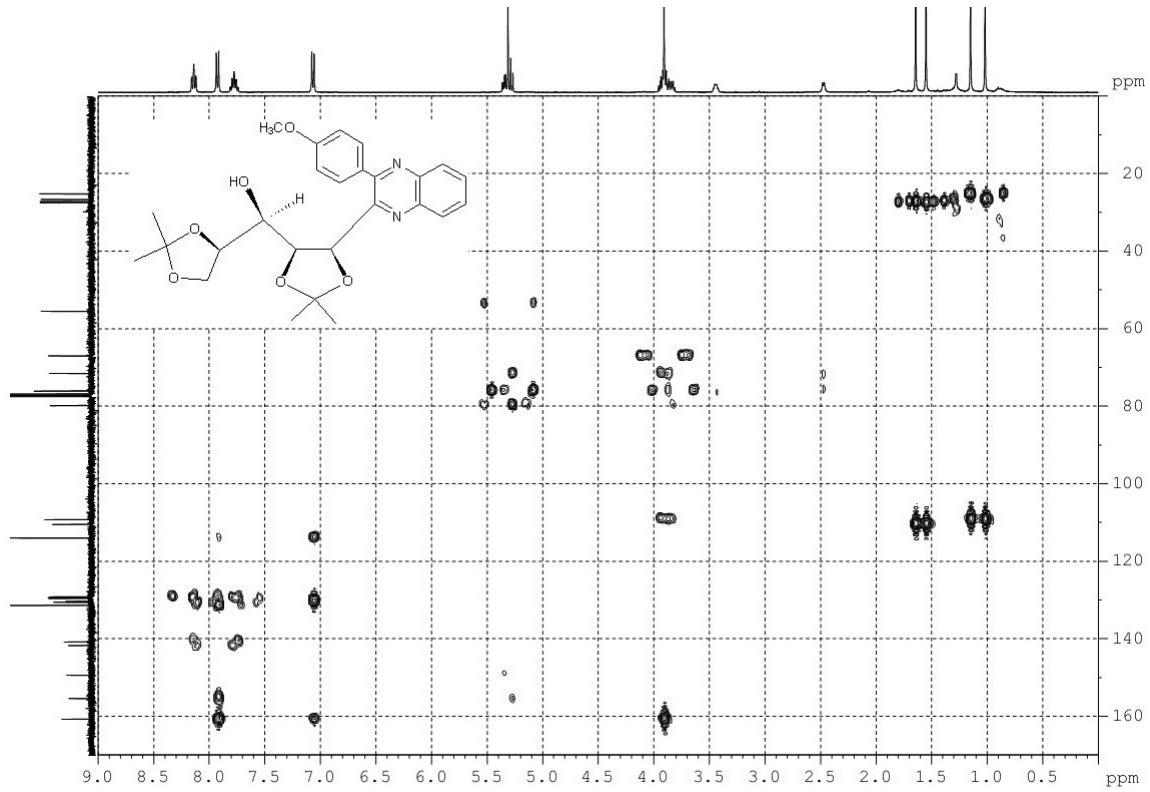


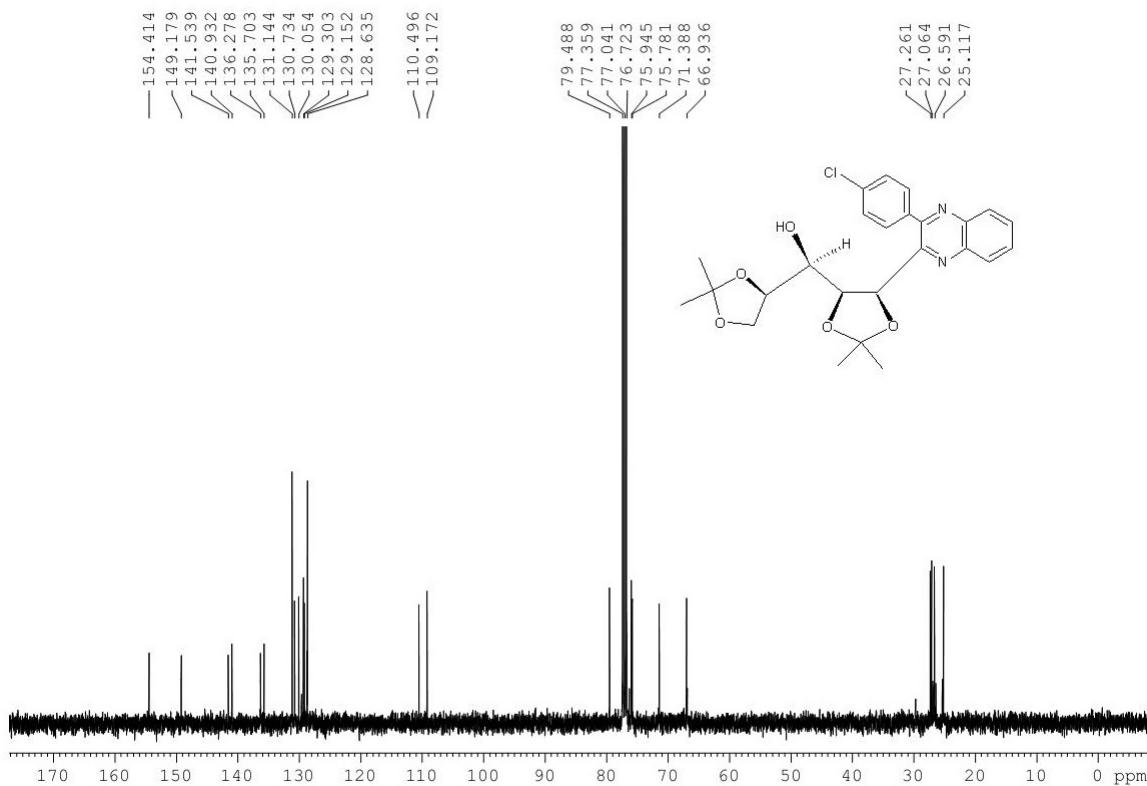
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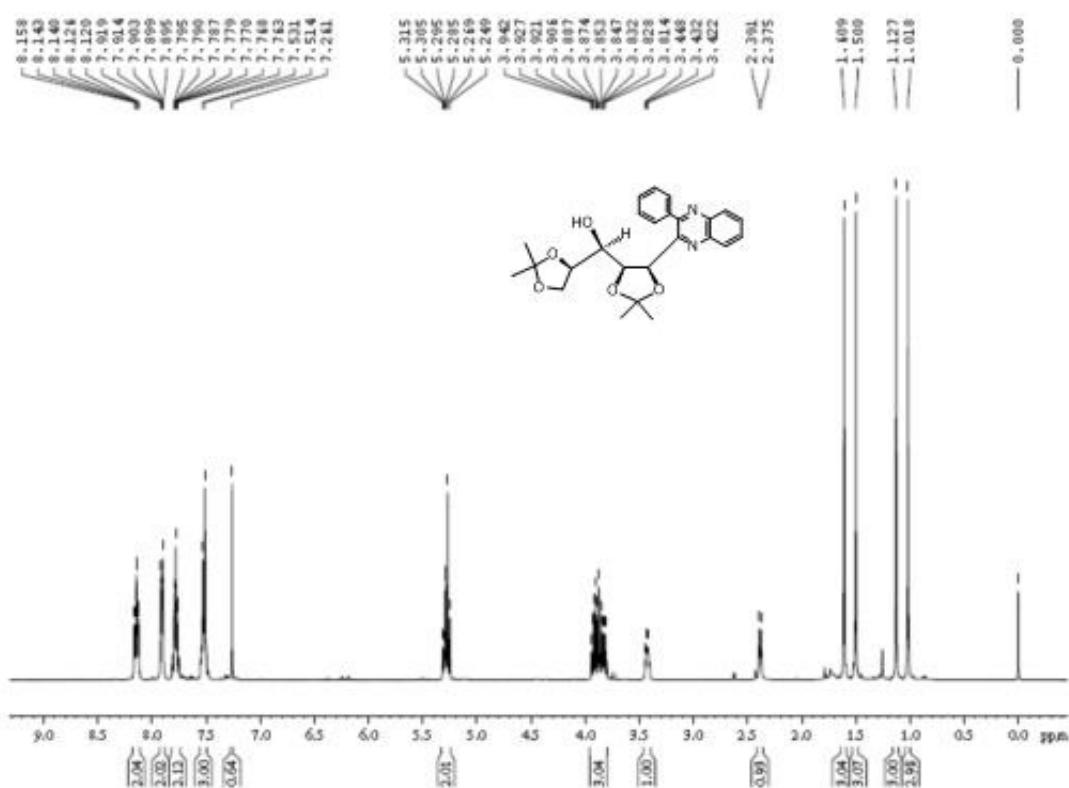


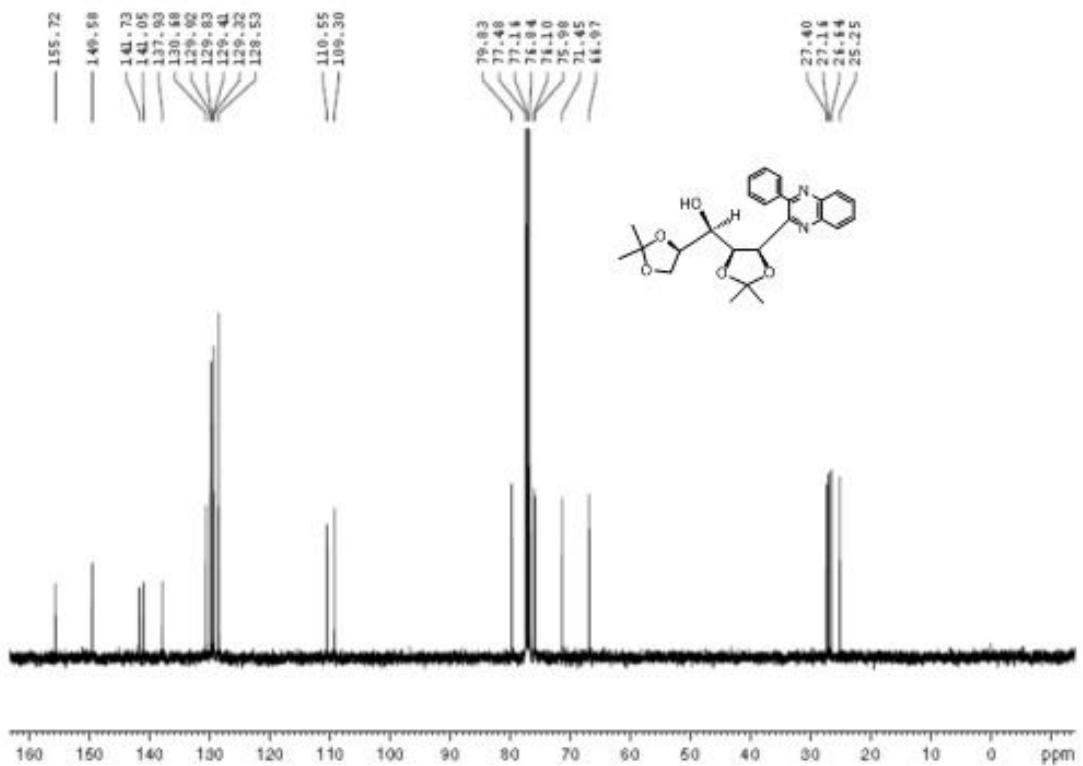




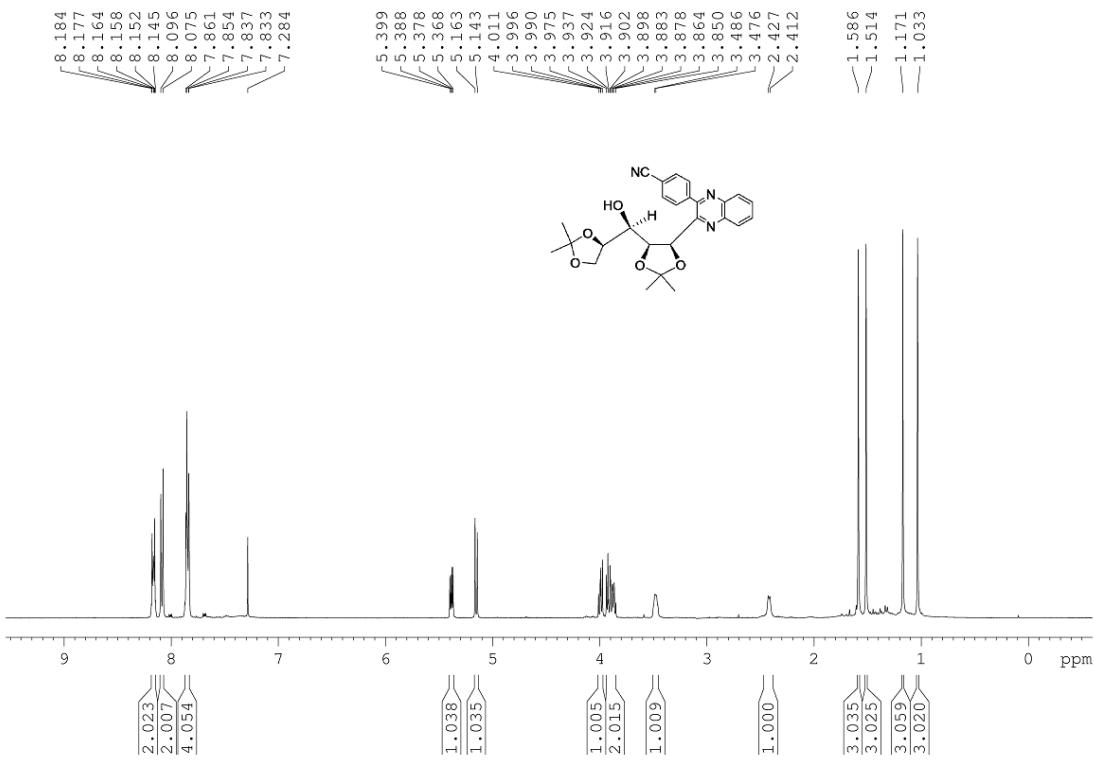


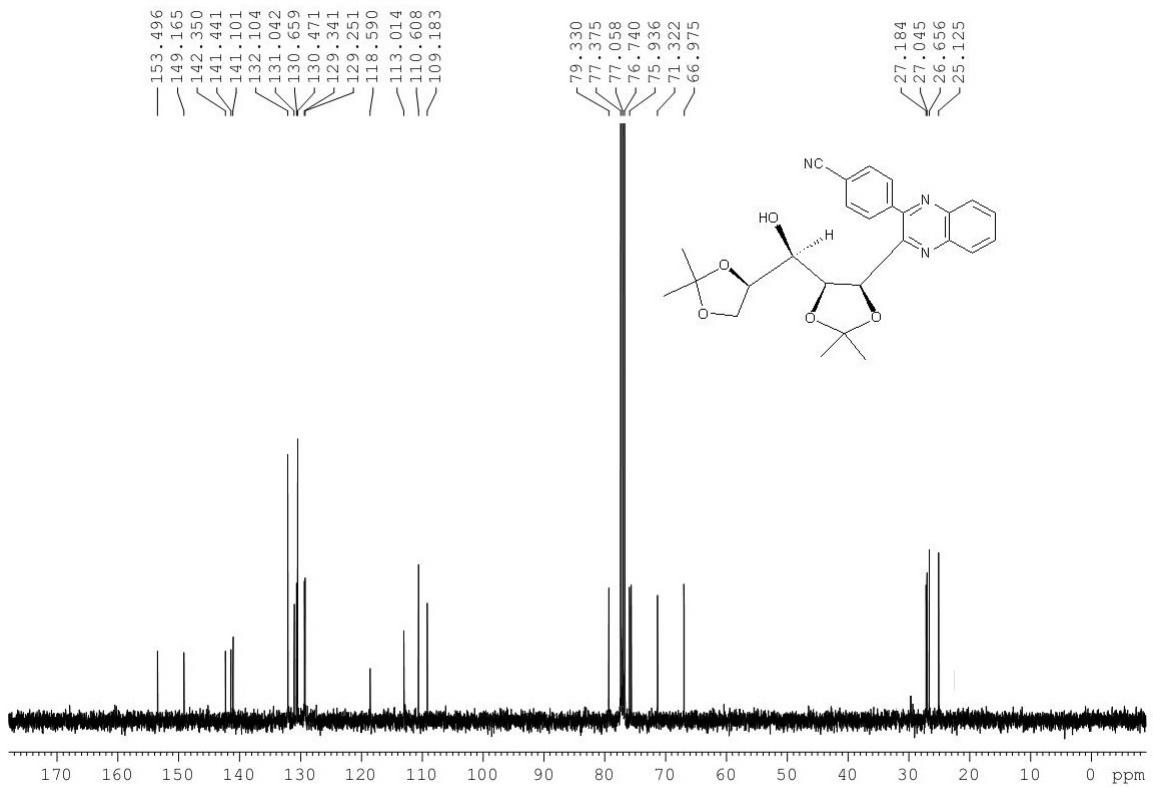
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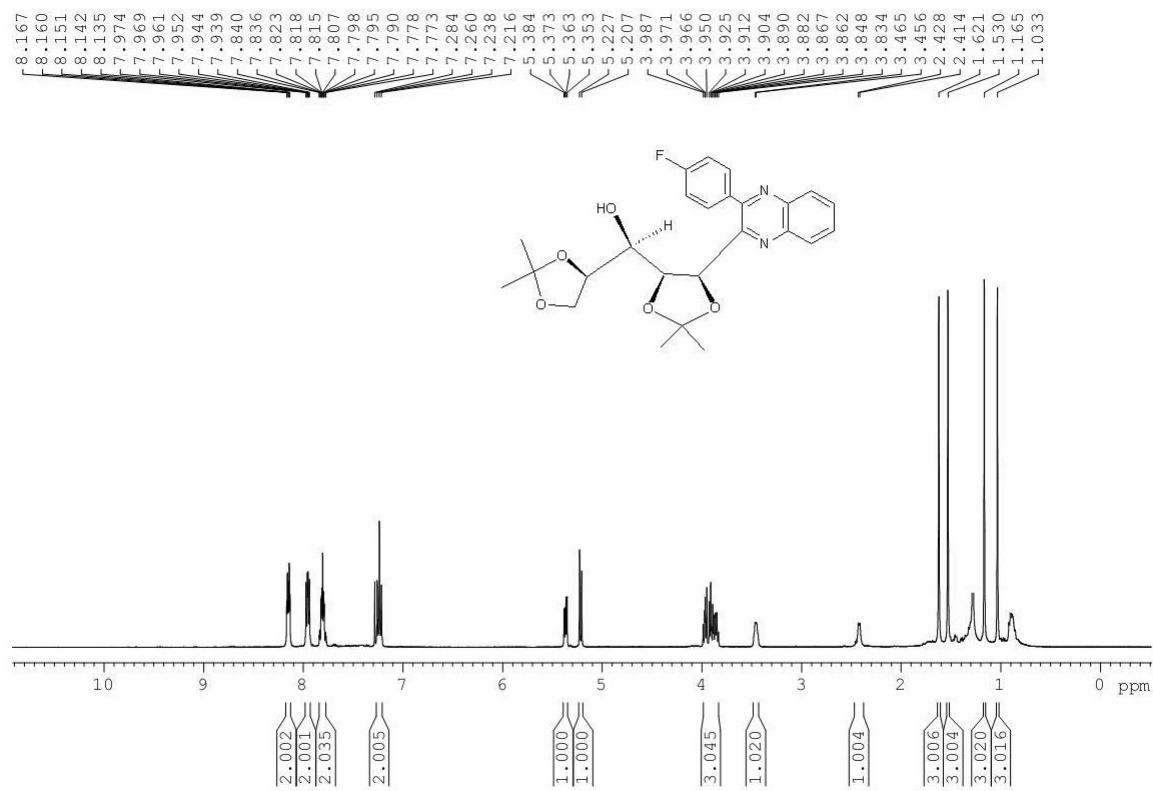


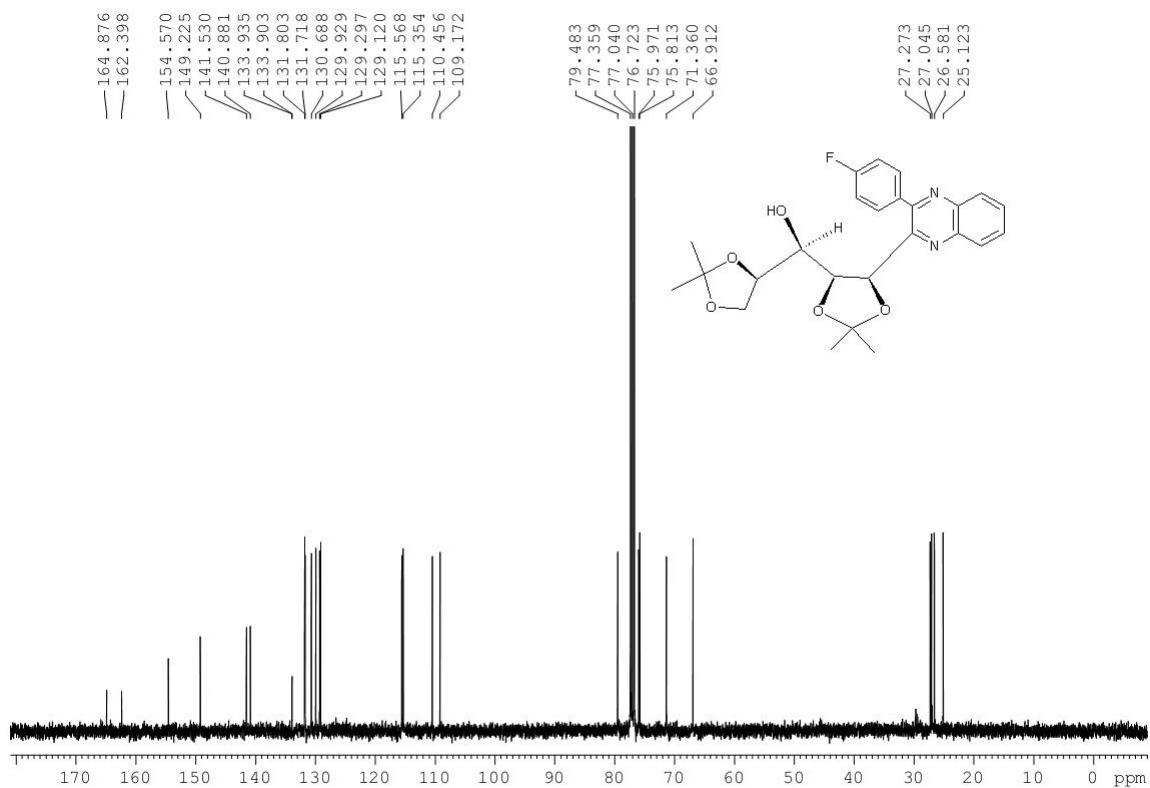
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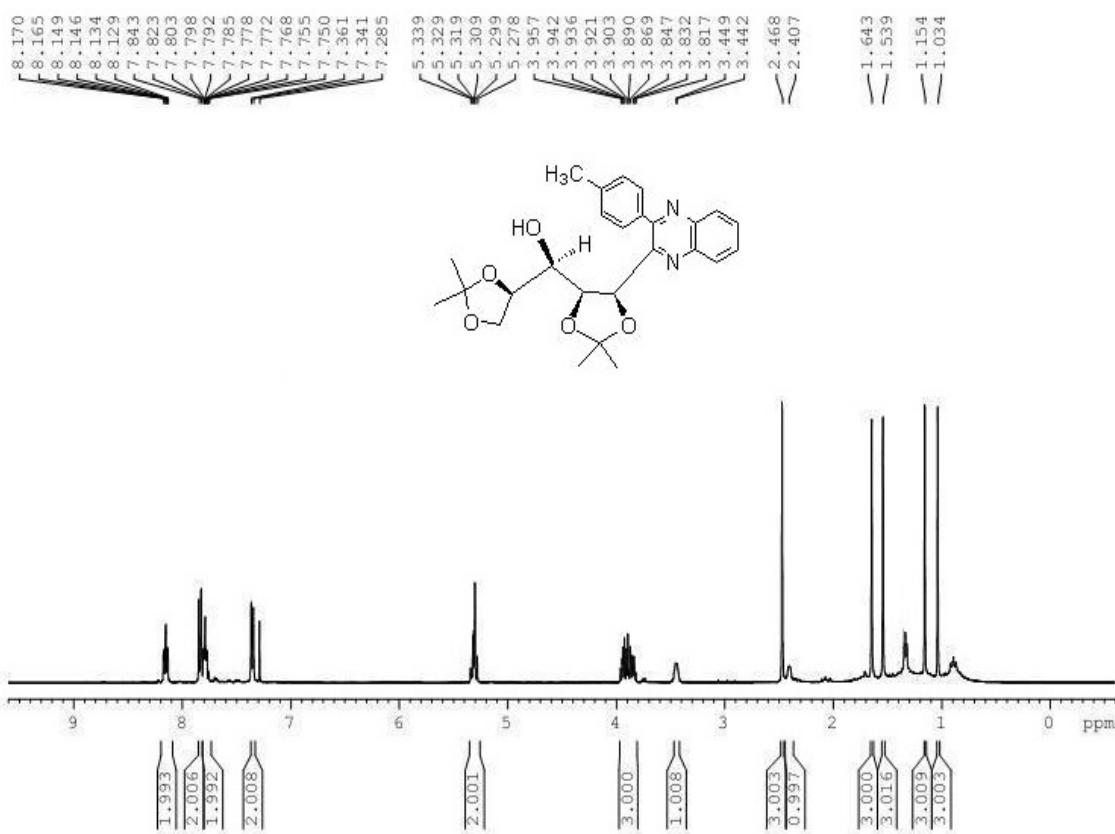


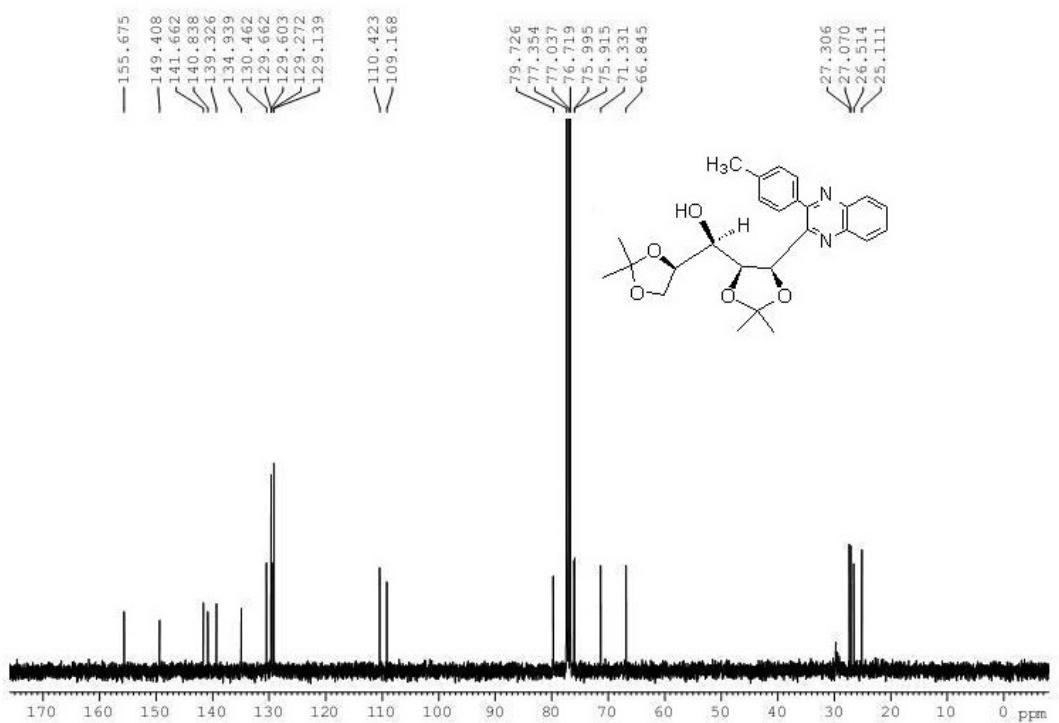
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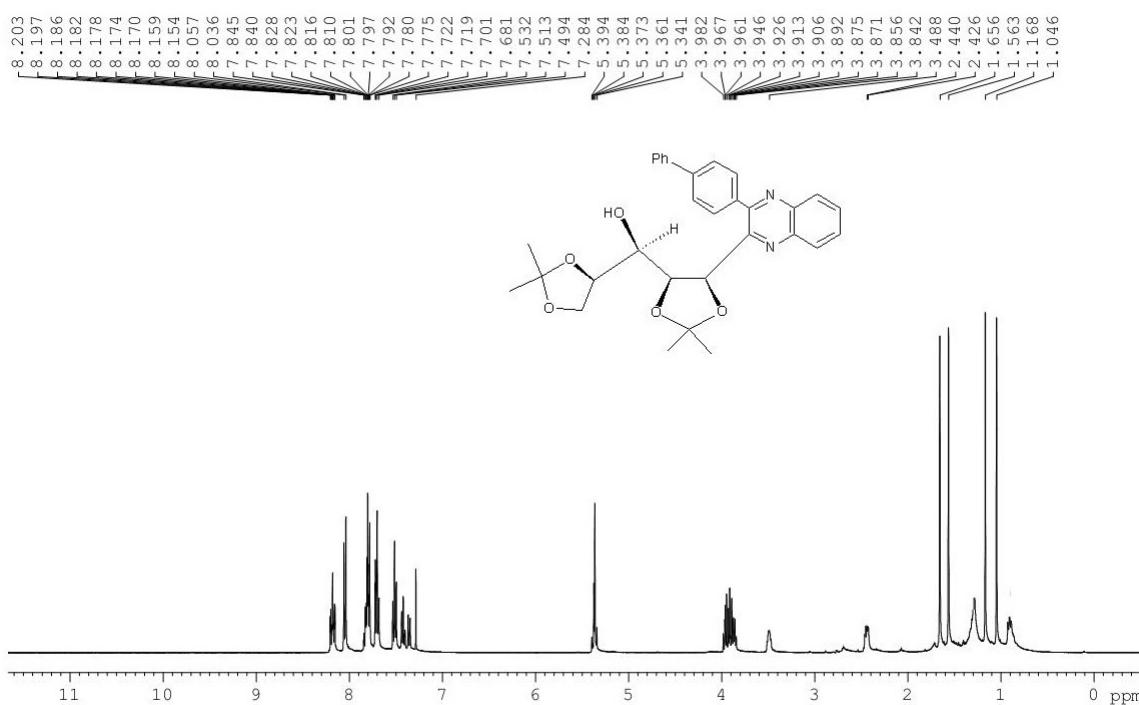


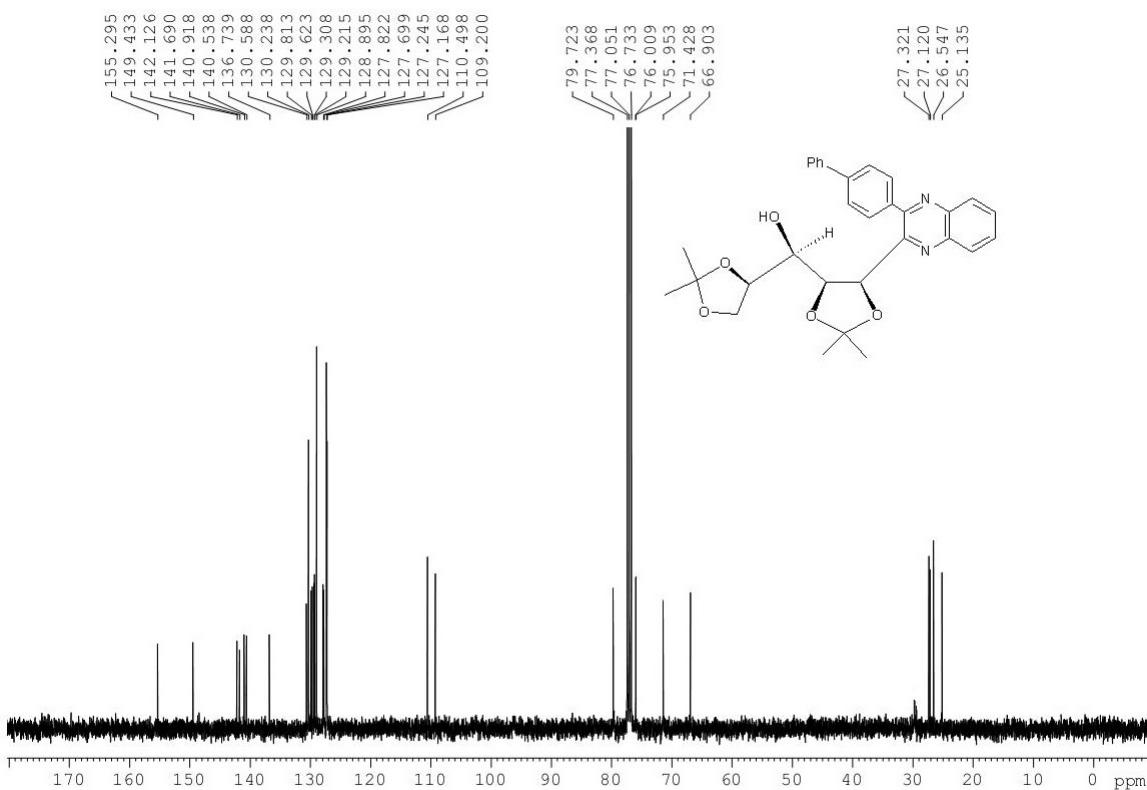
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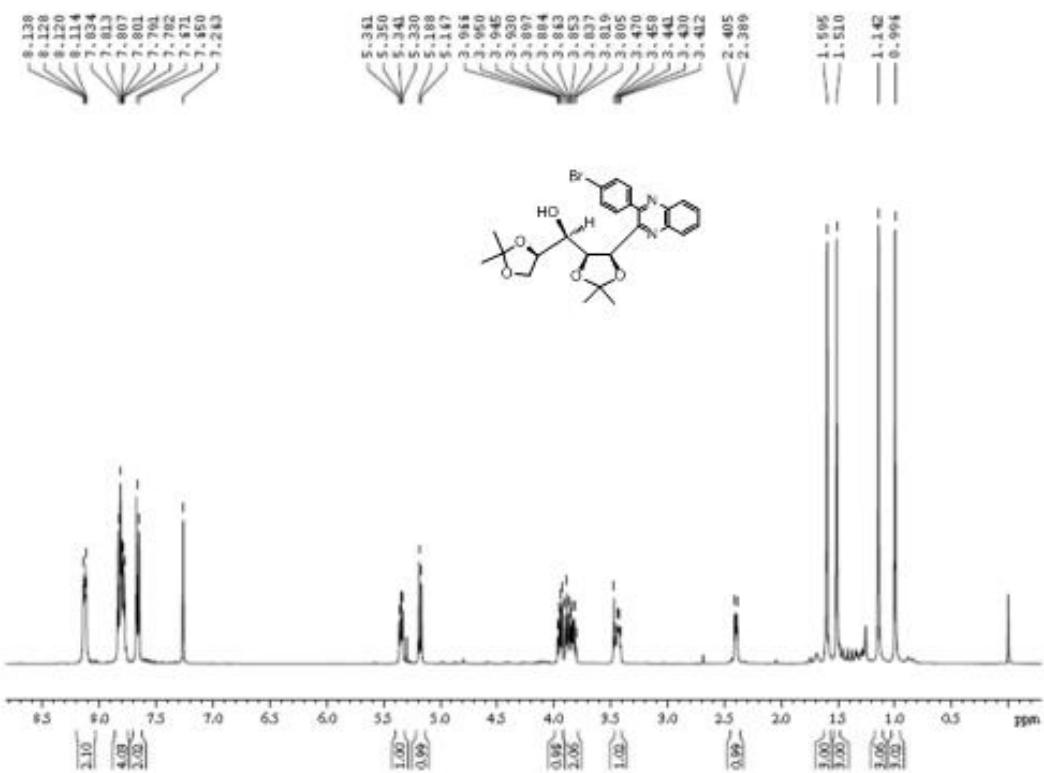


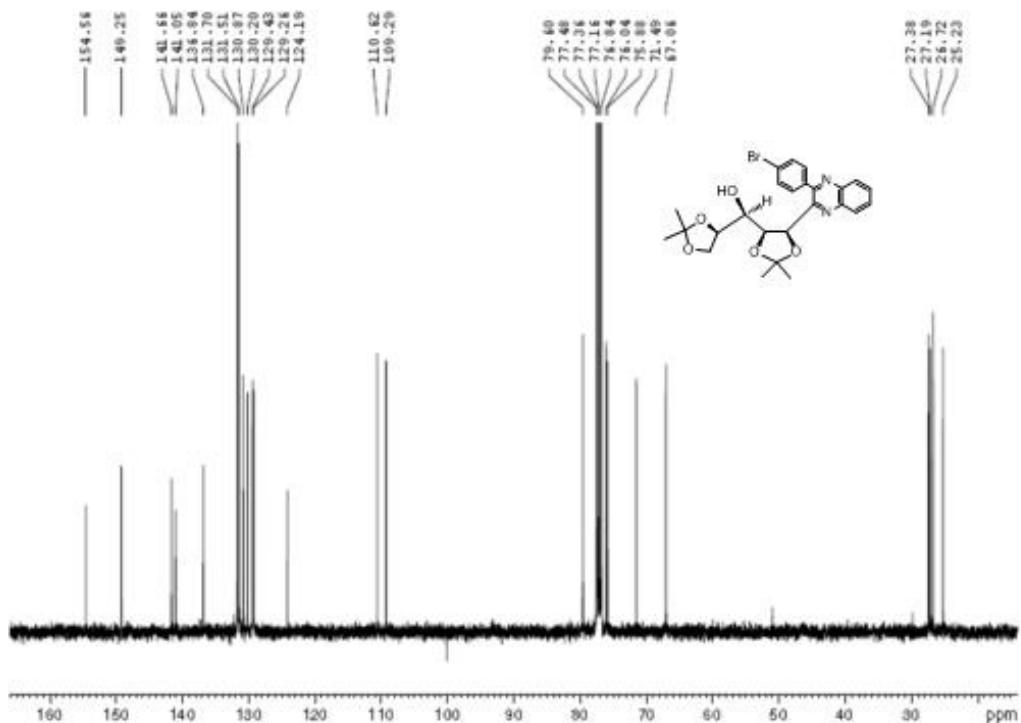
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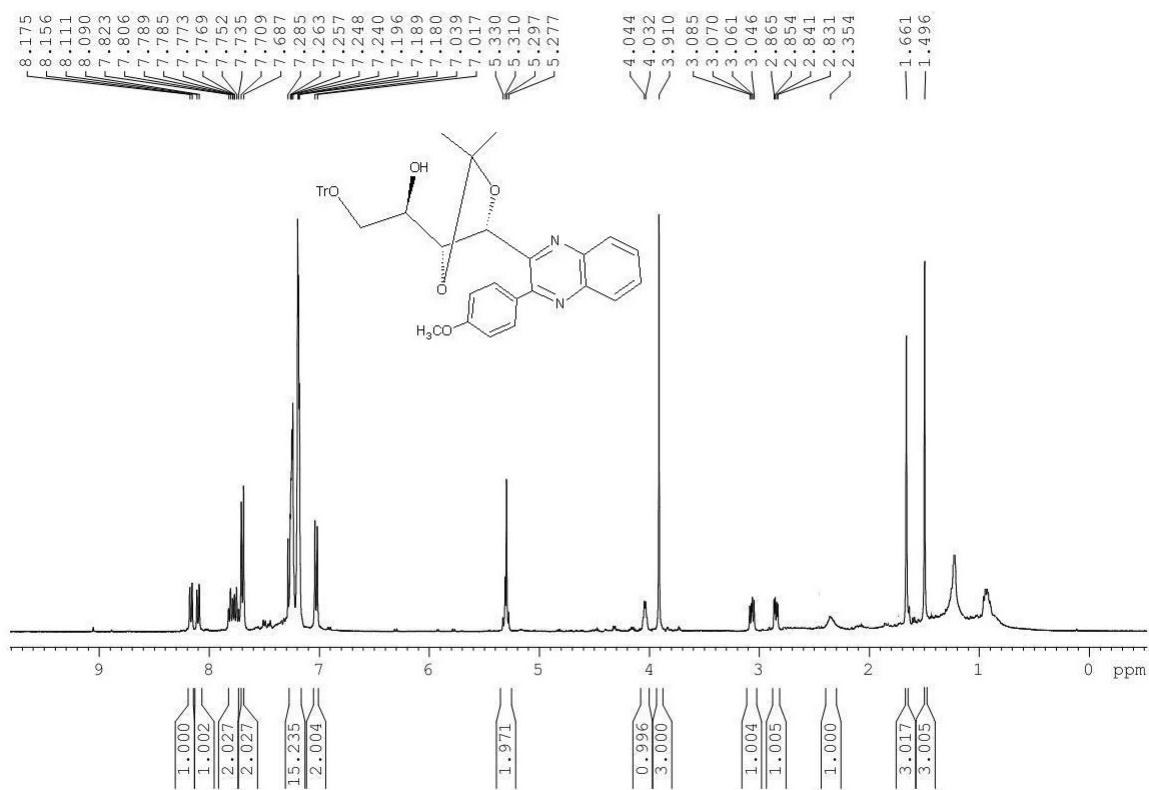


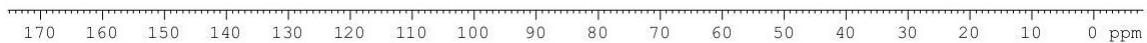
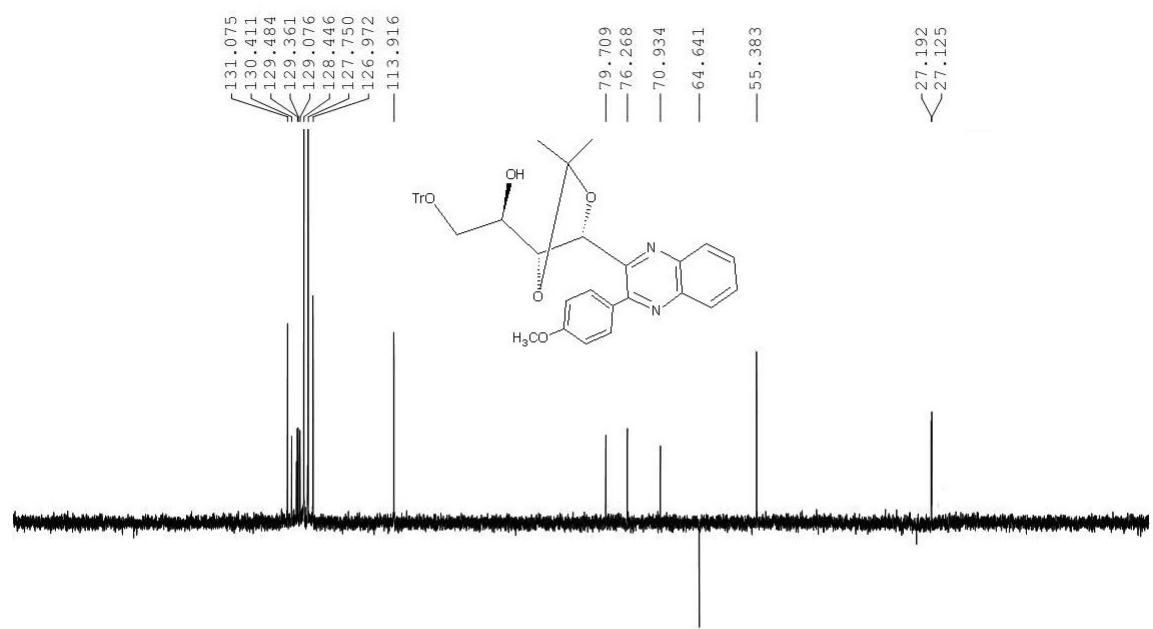
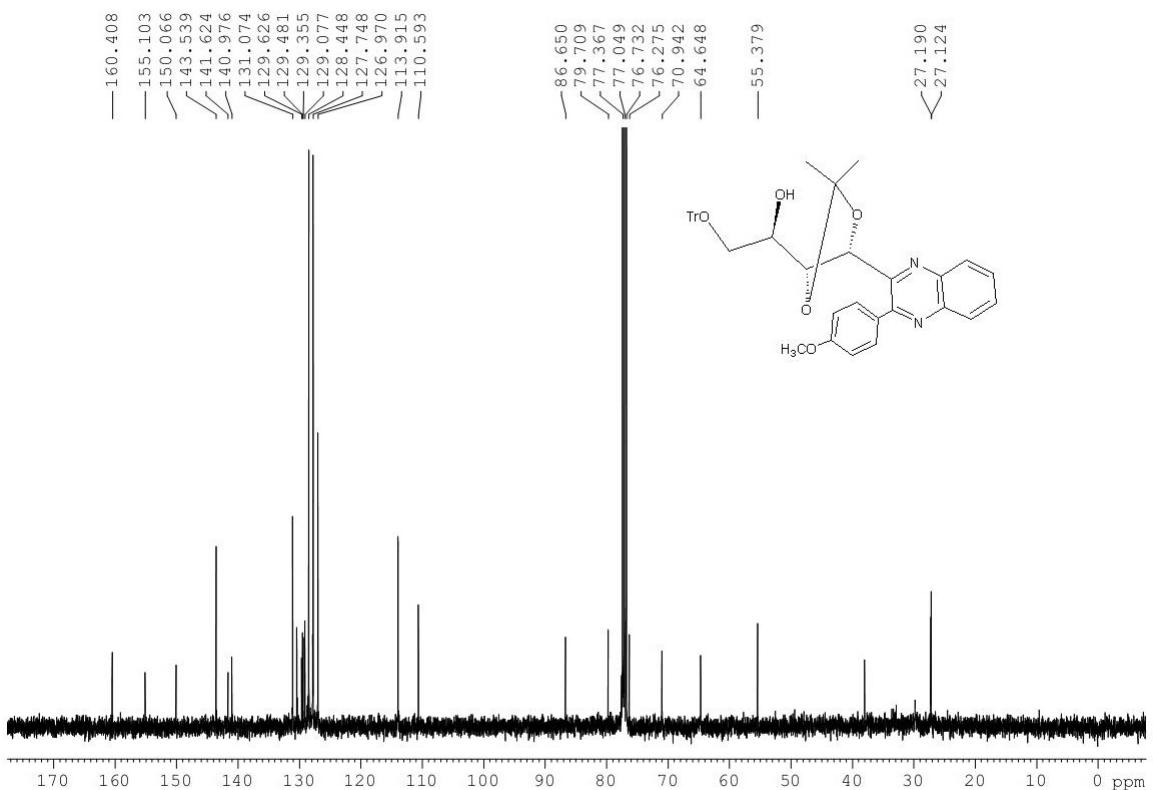
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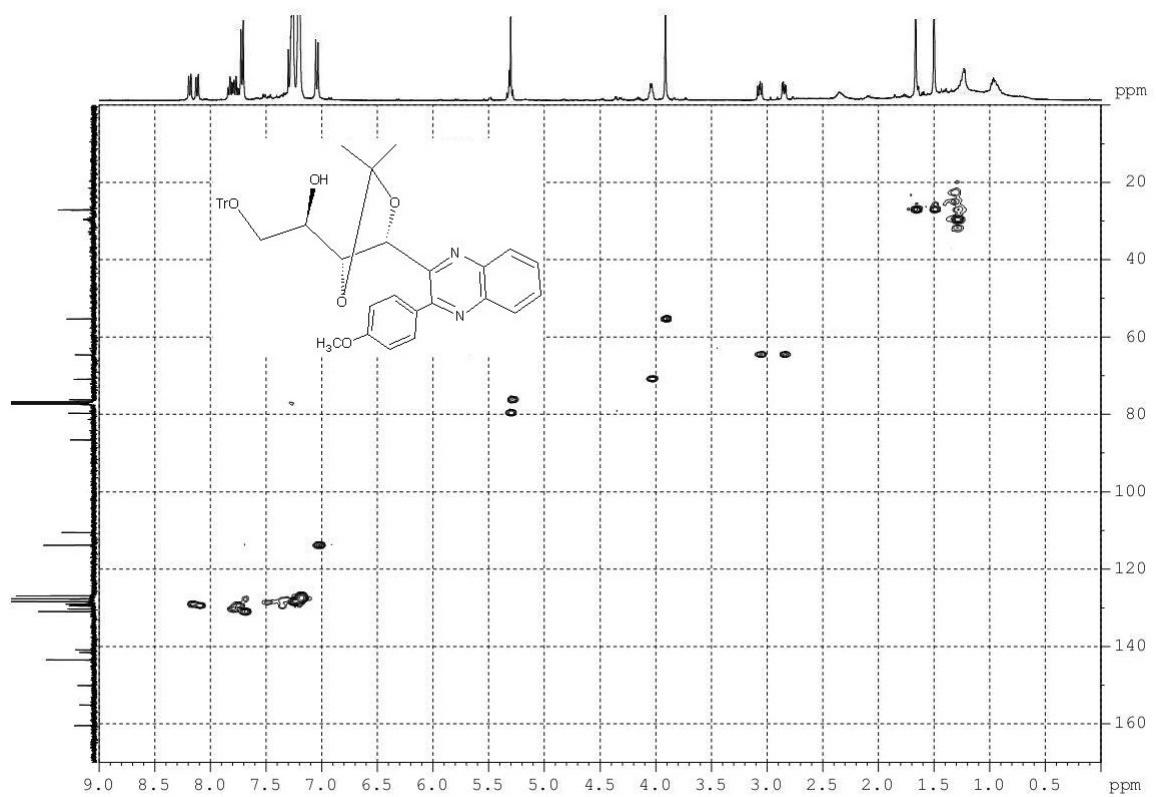
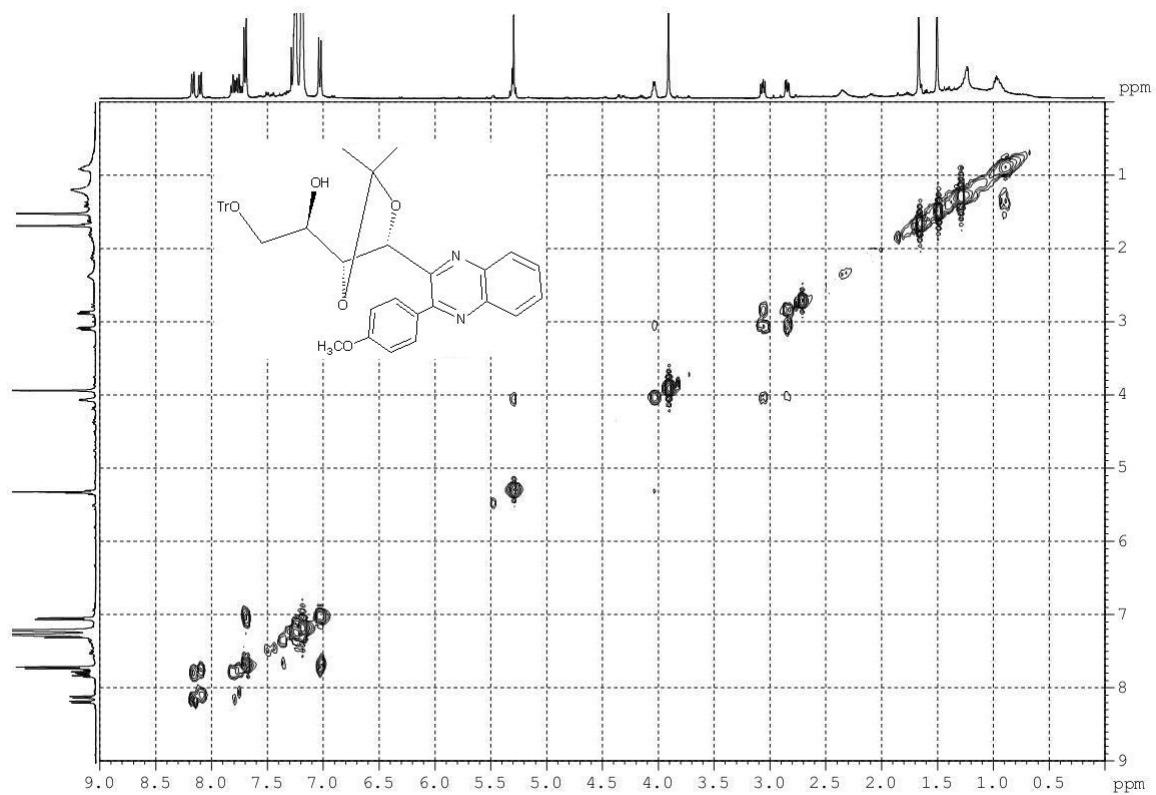


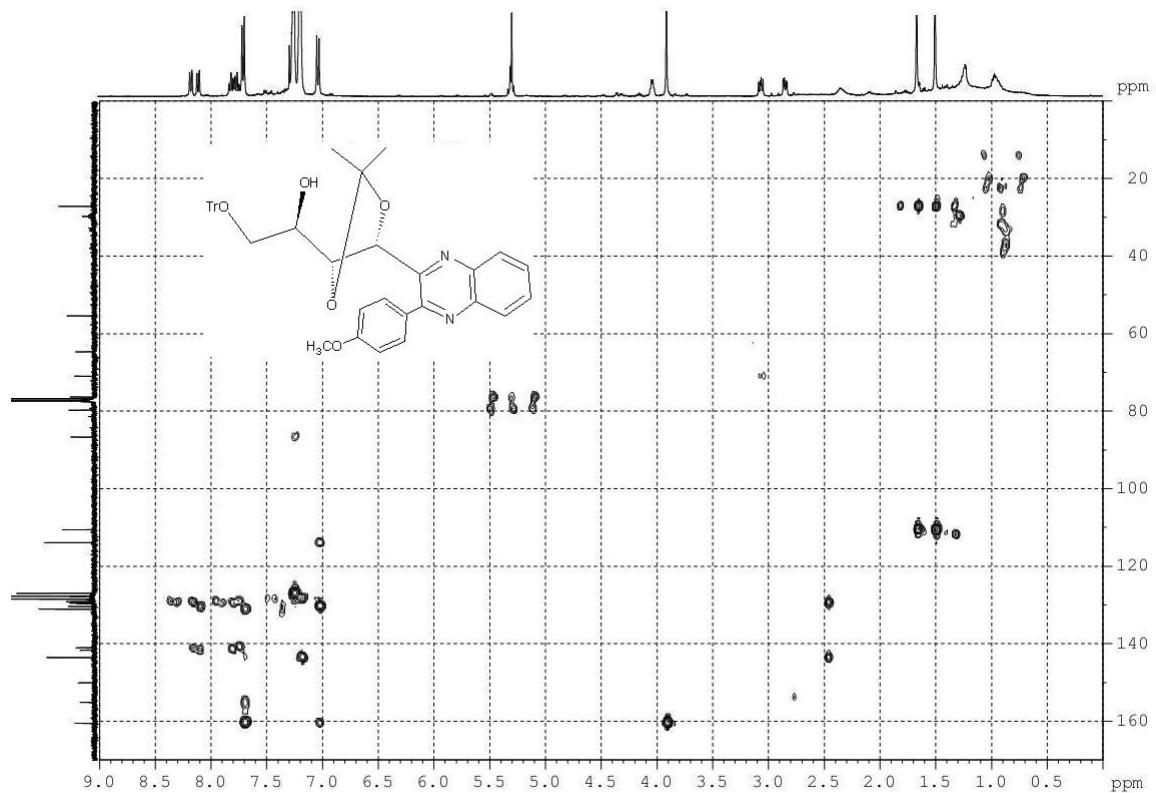


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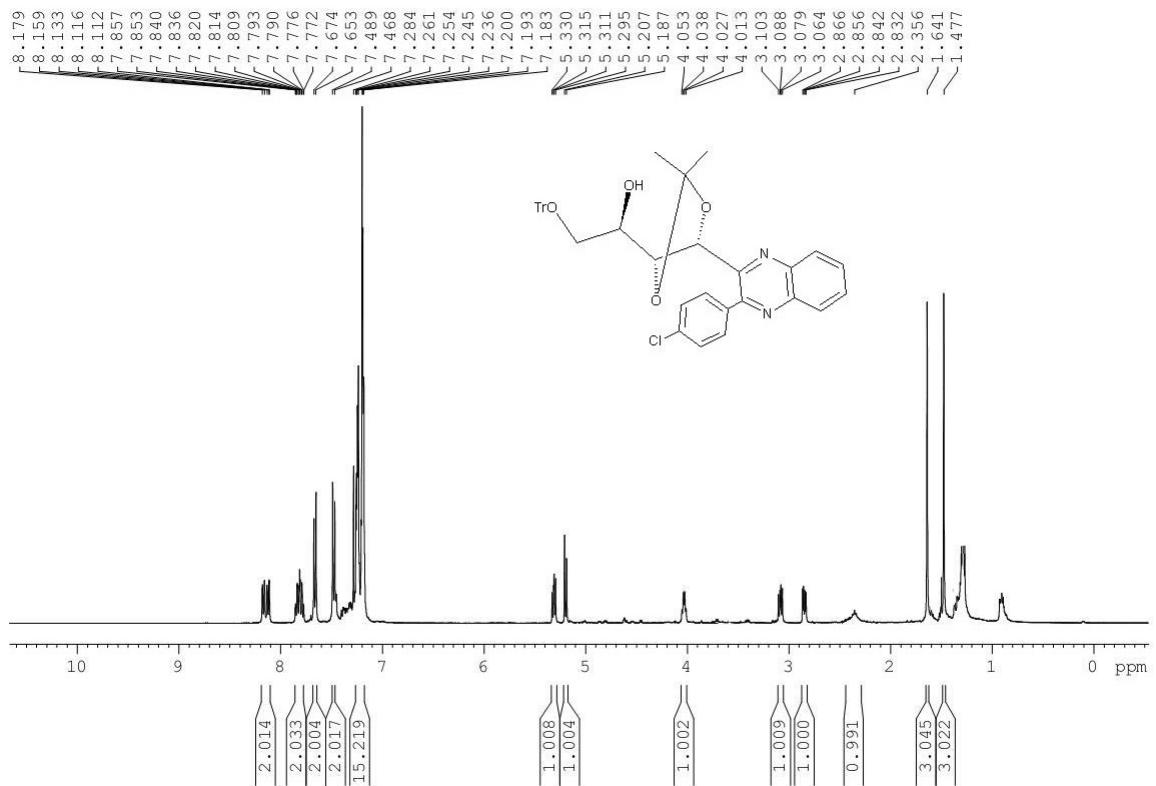


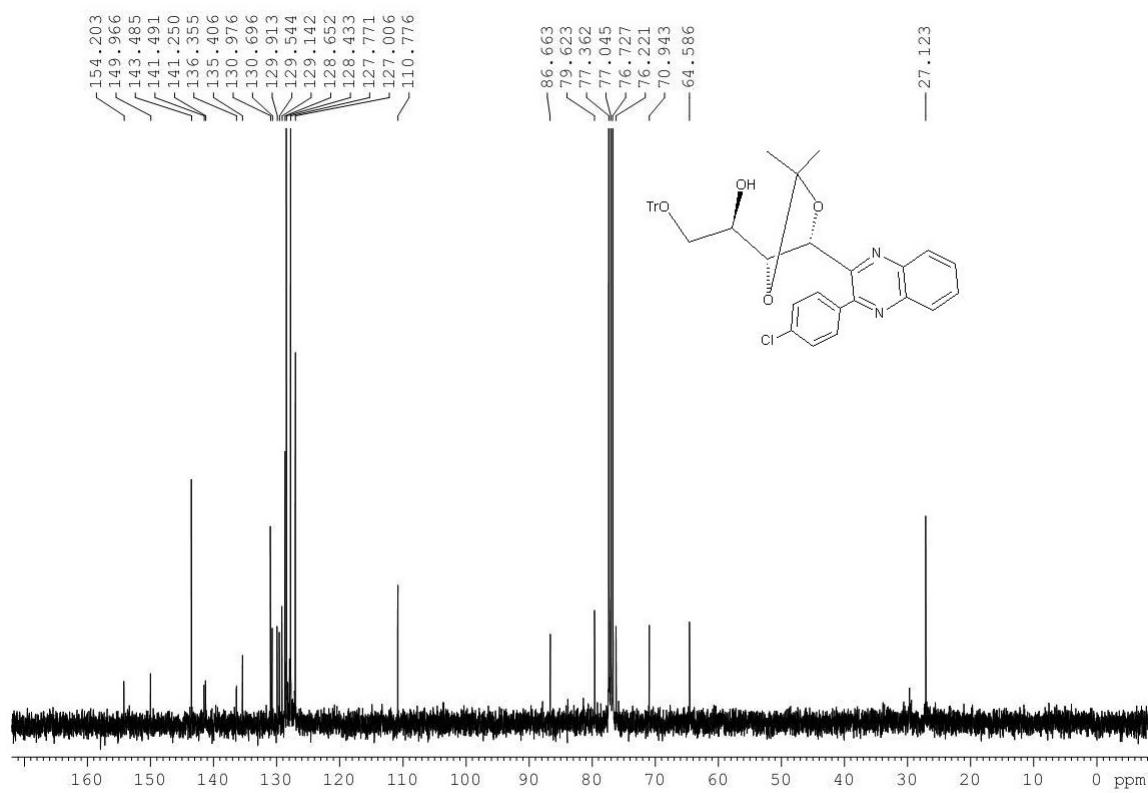




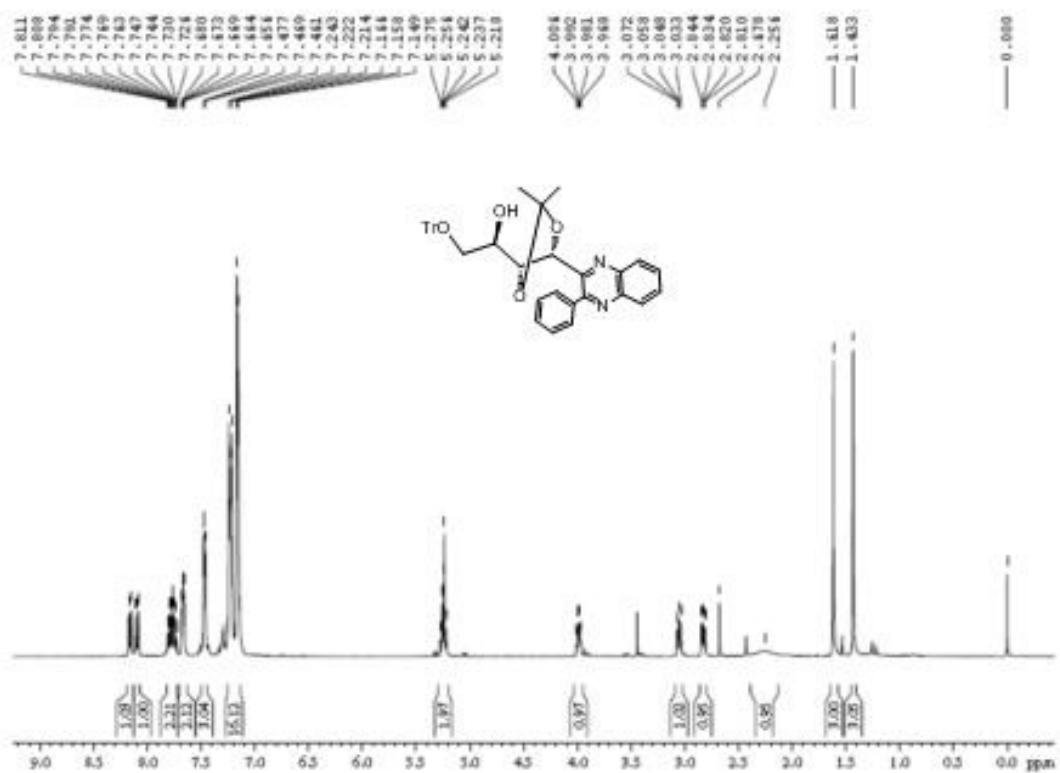


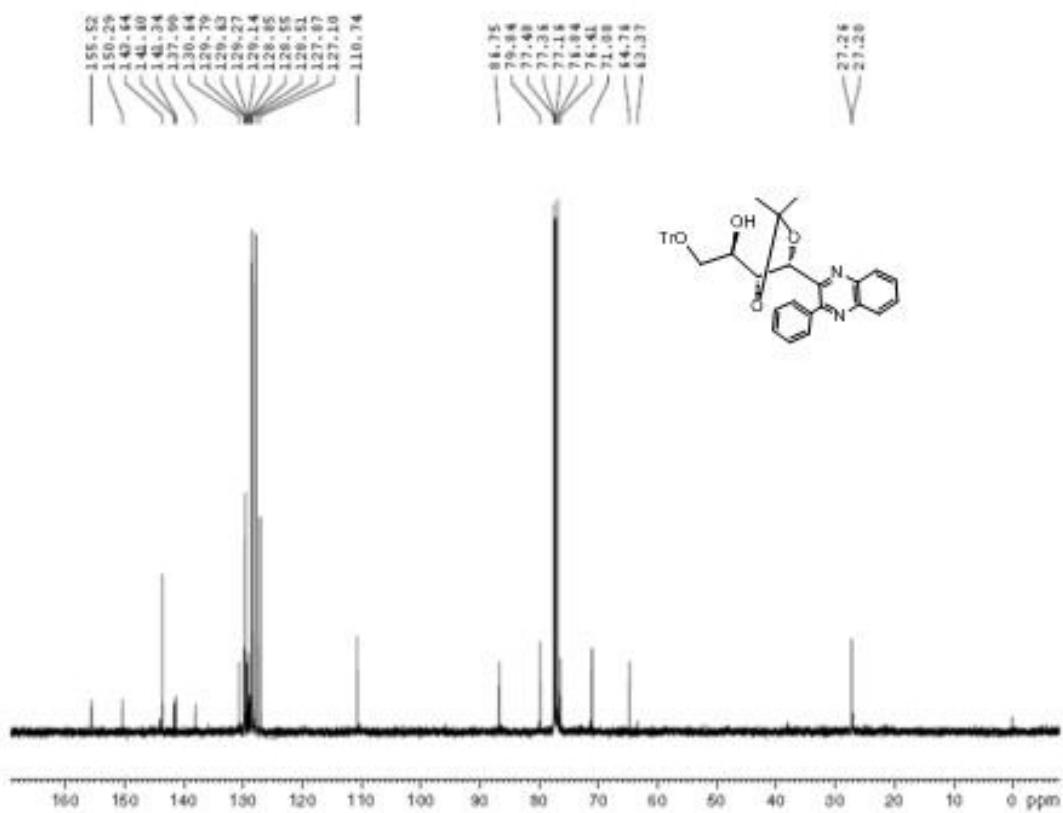
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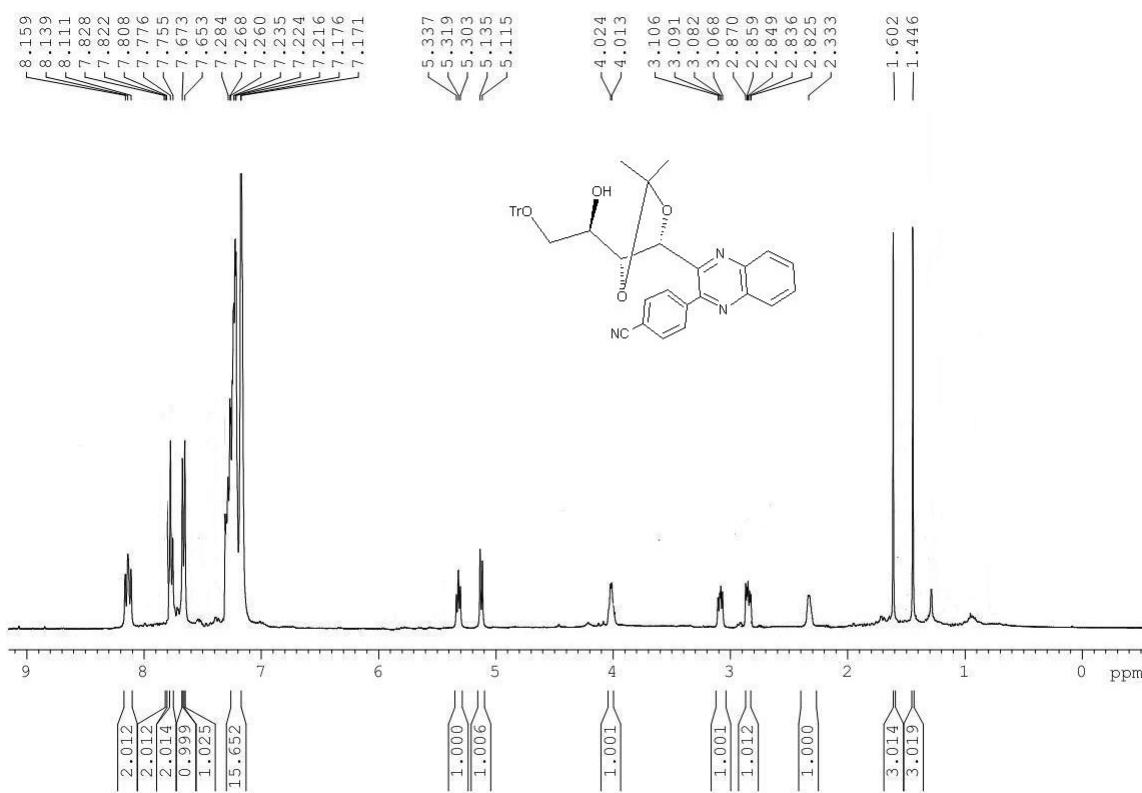


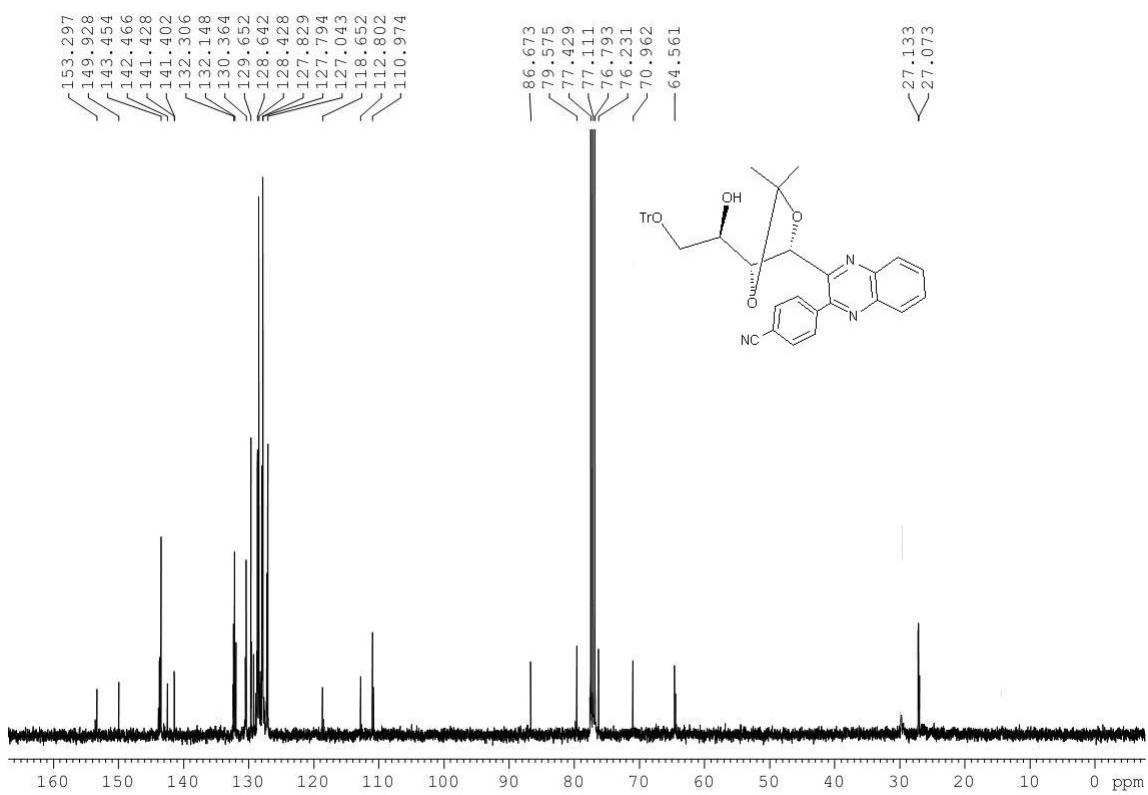
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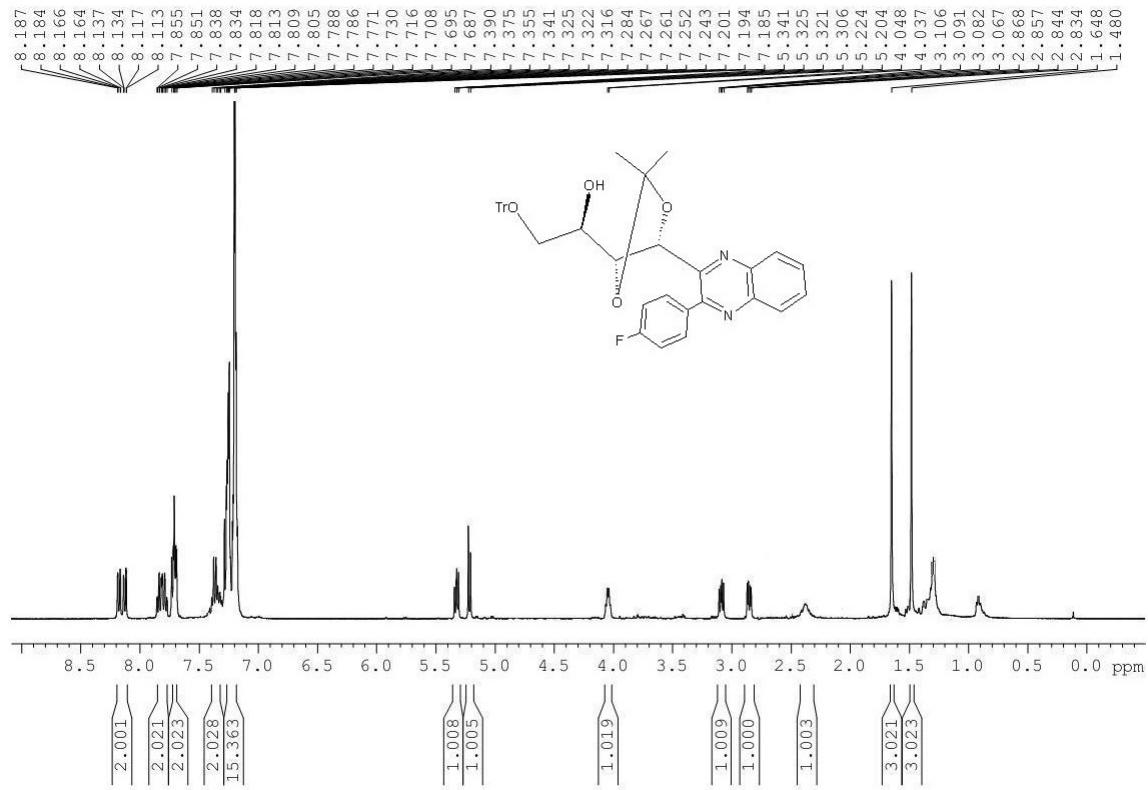


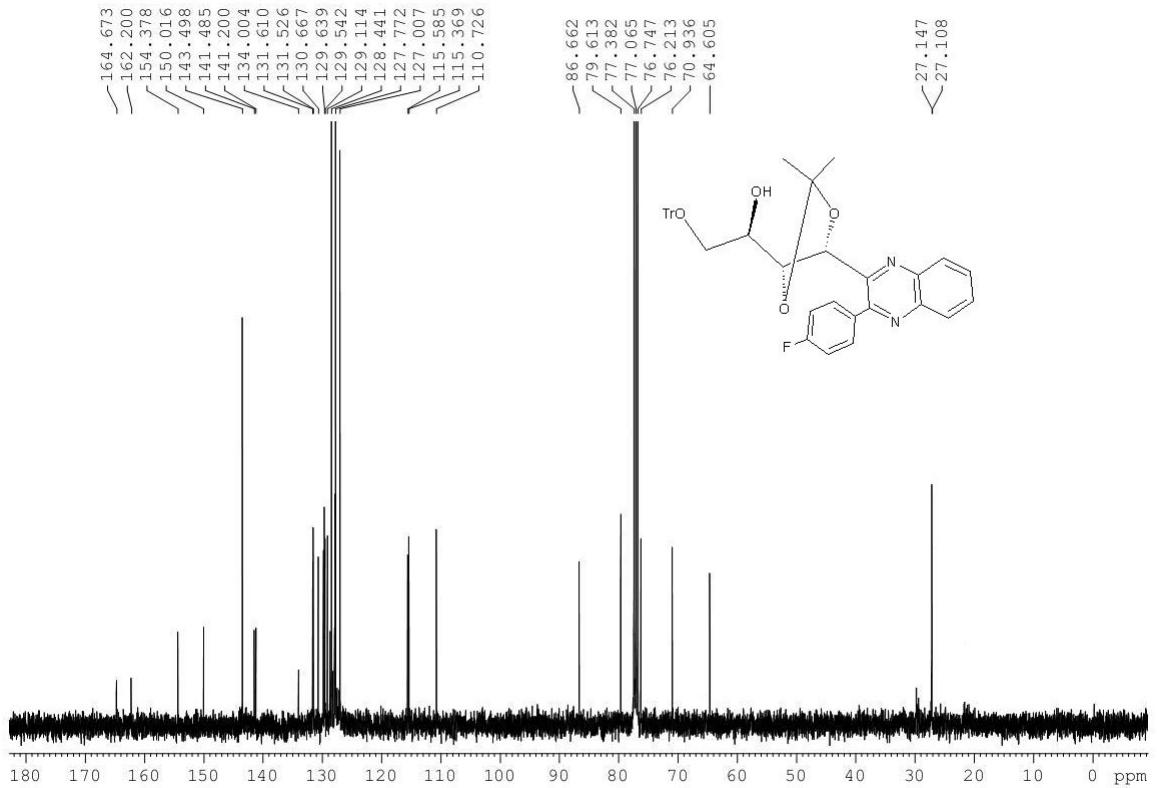
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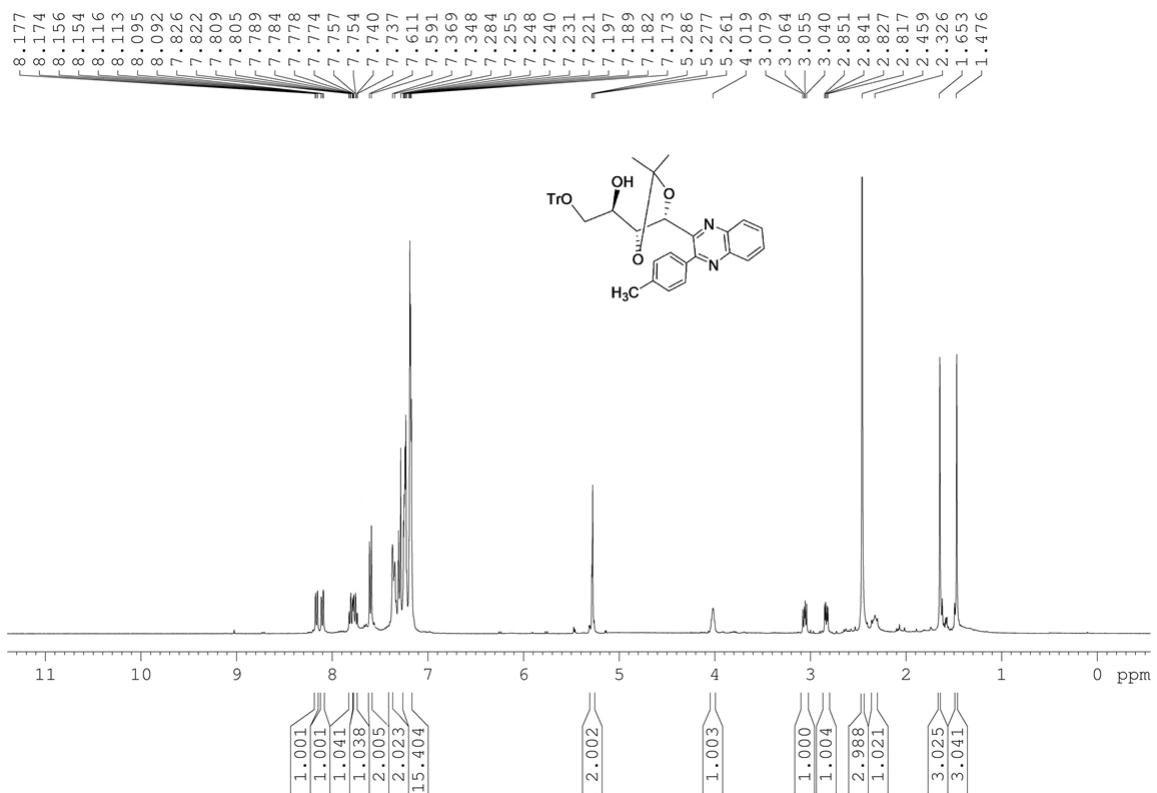


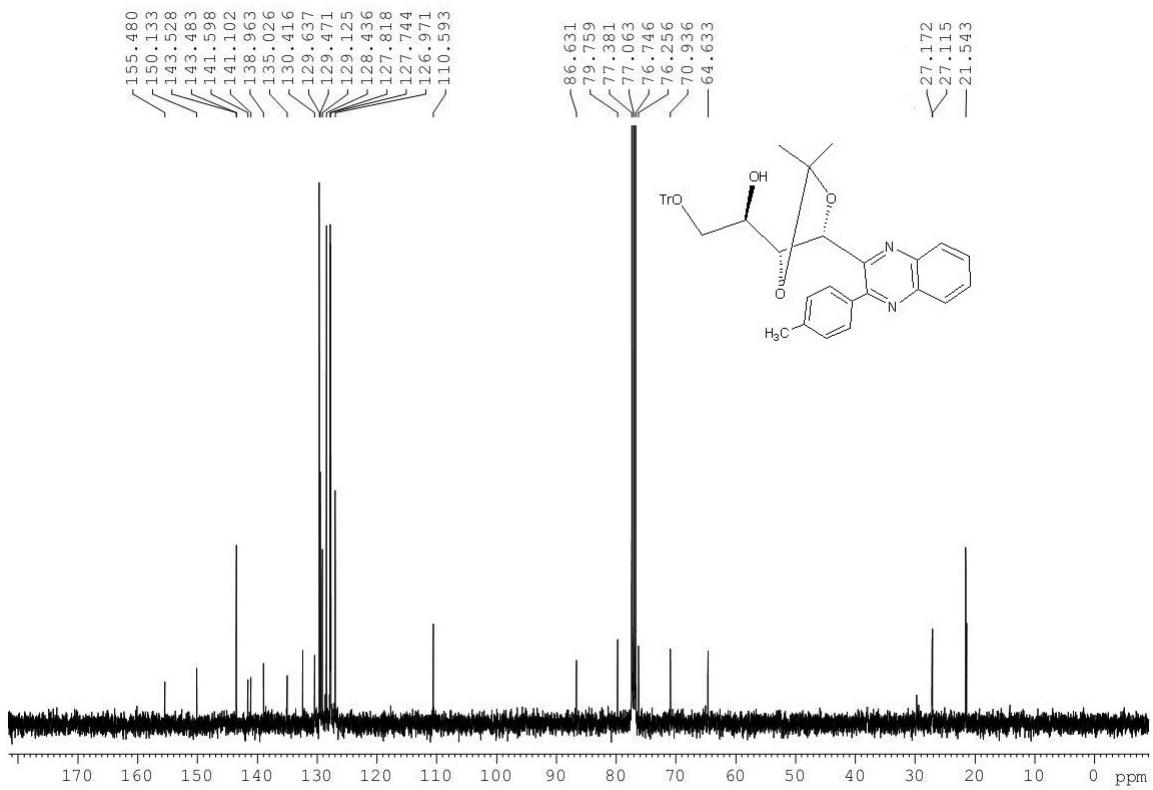
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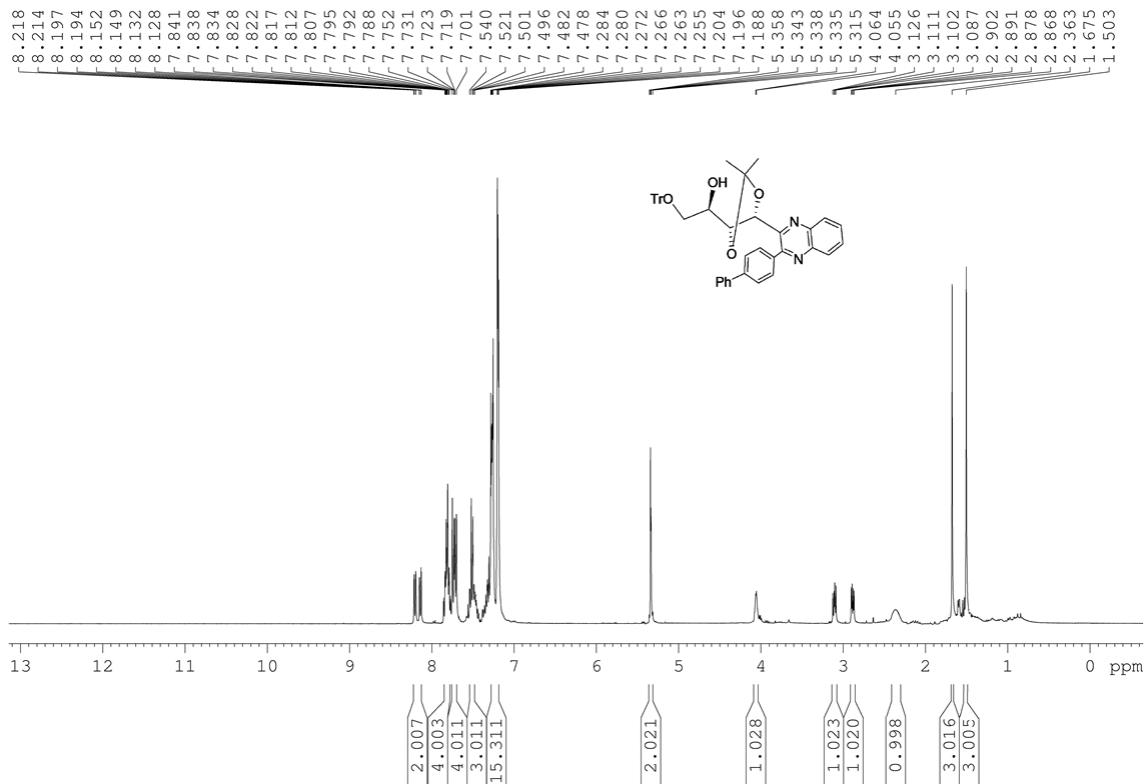


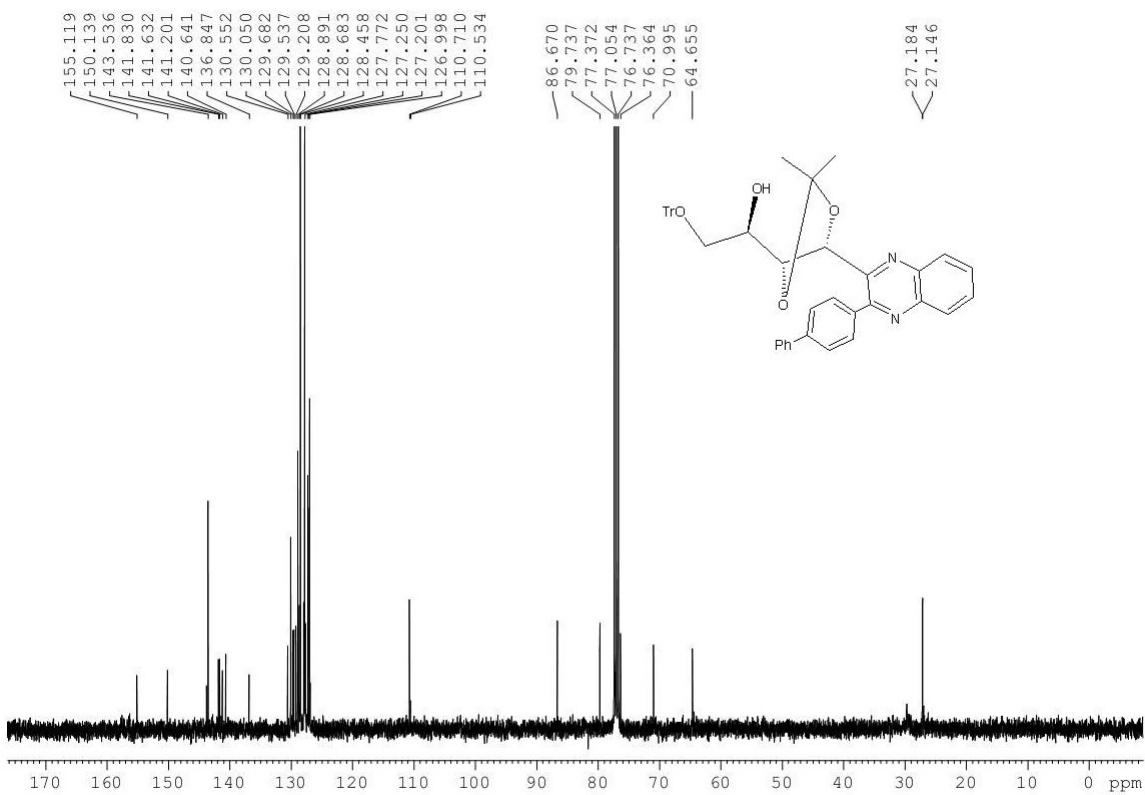
<sup>1</sup>H NMR and <sup>13</sup>C NMR of **2gf**





<sup>1</sup>H NMR and <sup>13</sup>C NMR of **2gg**





## References

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