Electronic Supplementary Information

Phthalate tethered strategy: carbohydrate nitrile oxide cycloaddition to 12-15 member chiral macrocycles with alkenyl chain length controlled orientation of bridged isoxazolines

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1. Experimental section

General: All reagents were purchased from best-known commercial sources and used without further purification unless otherwise stated. Flasks were oven or flame dried and cooled in a desiccator. Dry reactions were carried out under an atmosphere of nitrogen. Solvents were purified by standard methods. Thin layer chromatography was performed on E-Merck 250 Kieselgel 60 F254 silica gel plates. Silica gel 60-120 or 100-200 mesh size was used for chromatography. The spots were visualized by spraying Libermann reagents or by UV lamp. Melting points are recorded in open capillaries and are uncorrected. FTIR spectra were recorded using KBr plates or in neat. ^{1}H and ^{13}C NMR spectroscopic data were recorded at 300 or 600, and 75 or 150 MHz, respectively. Chemical shifts are reported relative to tetramethylsilaneδ = 0.00 ppm for ^{1}H, and $CDCl_3$ δ = 77.00 ppm (t) for ^{13}C NMR spectroscopy. High-resolution mass spectra (HRMS) were recorded on a quadrupole-TOF mass spectrometer using positive electrospray ionization. Optical rotations were measured using a digital polarimeter.

2. **General procedure for the preparation of 11a-b and 11d-f**: A mixture of diacetonide glucose (**9a**, 2.0 g, 7.7 mmol),) or allose (**9b**, 2.0 g, 7.7 mmol), phthalic anhydride (15.38 mmol) & pyridine (10 mL) was heated at 110-115 ℃ for 5 hr. Pyridine was removed under reduced pressure by co-evaporation with toluene after completion of the reaction. The residue was dissolved in ethyl acetate (50 mL), washed successively with 1% aqueous HCl solution (10 mL), washed with water (3x 10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure at room temperature to obtain phthalic acid half-ester (**10a-b**) which was used for the next step without further purification. To a stirred solution of phthalic acid half-ester (**10a** for **11a** and **11d-f**) and (**10b** for **11b**) (2.0 g, 4.9 mmol) in DMF (20 mL) was added K_2CO_3 (1.5 g, 10.87 mmol) &alkenylating agent (5.88 mmol) [allyl bromide for **10a-b**; 4-bromo butene for **10d**; 5-bromo pantene for **10e** and 6-bromo haxene for **10f**] were added and stirred magnetically at 60^{o}C for 2 h. The reaction mixture was cooled, filtered, washed the residue with ethyl acetate. To the filtrate, 5% aqueous acetic acid (20 mL) was added and the organic layer was separated, washed with brine (3 x 10 mL), dried and evaporated under reduced pressure at room temperature to provide a syrupy liquid, which was purified by column chromatography over silica gel (60-120 mesh) using 10-40% ethyl acetate in hexane as eluent.

Compound 11a: Yield 64% (2.20 g, in two steps); colorless syrup; $[\alpha]_D^{25}$–72.28 (*c* 1.01, $CHCl_3$); IR (neat) ν_{max} 3078, 2987, 1731, 1590, 1376, 1271, 1072 cm^{-1}; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 7.78 (d, *J* = 2.4 Hz, 1H), 7.70 (bs, 2H), 6.06-5.96 (m, 1H), 5.90 (bs, 1H), 5.42 (bs, 2H), 5.30 (d, *J* = 9.6 Hz, 1H), 4.81 (bs, 3H), 4.27-4.23 (m, 2H), 4.02 (bs, 2H), 1.49 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 166.4, 131.9, 131.7, 131.5, 131.4, 131.3, 127.1, 129.0, 118.8, 112.2, 109.3, 105.2, 82.7, 79.7, 77.5, 72.4, 67.2, 66.4, 26.9, 26.8, 26.3, 25.3; EI MS m/z 448, 433, 391, 375, 347, 289, 207, 189, 149, 113, 101; HRMS calculated for $C_{23}H_{28}O_9Na$ $[M + Na]^+$ m/z 471.1631, found m/z 471.1627.

Compound 11b: Yield 61% (2.102g, in two steps) colorless syrup; $[\alpha]_D^{25}$ + 68.00 (c 0.25, $CHCl_3$); IR (neat) ν_{max} 2991, 2925, 1732, 1601, 1377, 1273, 1069 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.73 (m, 2H), 7.59-7.54 (m, 2H), 6.08-5.95 (m, 1H), 5.88 (d, *J* = 3.9 Hz, 1H), 5.42-5.36 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.30-5.26 (dd, *J* = 10.5, 1.2 Hz,1H), 5.10-5.06 (dd, *J* = 8.7, 4.8 Hz, 1H), 4.96 (t, *J* = 4.8 Hz, 1H), 4.84-4.81 (m, 2H), 4.39-4.36 (m, 1H), 4.35-4.29 (dd, *J* = 15.7, 4.2 Hz, 1H), 4.10-4.06 (dd, *J* = 8.7, 6.9 Hz, 1H), 3.96-3.91 (dd, *J* = 8.4, 6.3 Hz, 1H), 1.68 (s,3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 166.6, 131.8, 131.7, 131.6, 131.2, 129.1, 128.8, 118.5, 113.2, 109.9, 104.1, 77.8, 77.4, 75.0, 73.4, 66.3, 65.4, 26.7, 26.2, 25.1; MS (ESI) m/z 471 (M+Na), 448, 433, 391; HRMS calculated for $C_{23}H_{28}O_9Na$ $[M + Na]^+$ m/z 471.1631, found m/z 471.1628

Compound 11d: Yield 63% (2.239 g, in two steps); colorless syrup; $[\alpha]_D^{25}$ + 85.83 (c 1.2, $CHCl_3$); IR (neat) ν_{max} 3077, 2987, 1728, 1599, 1382, 1278, 1072 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.67 (m, 2H), 7.58-7.52 (m, 2H), 5.93 (d, *J* = 3.6 Hz, 1H), 5.89-5.78 (m, 1H), 5.42 (d, *J* = 2.4 Hz, 1H), 5.20-5.10 (m, 2H), 4.81 (d, *J* = 3.6 Hz,1H), 4.43-4.33 (m, 2H), 4.31-4.21 (m, 2H), 4.06-3.98 (m, 2H), 2.50-2.48 (m, 2H), 1.55 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 166.4, 133.8, 131.8, 131.3, 131.3, 129.0, 129.0, 117.5, 112.3, 109.3, 105.2, 82.9, 79.7, 77.4, 72.4, 67.2, 64.7, 32.9, 26.8, 26.8, 26.3, 25.3; MS (ESI) m/z 485 (M+Na), 427, 405, 203, 149; HRMS calculated for $C_{24}H_{30}O_9Na$ $[M + Na]^+$ m/z 485.1788, found m/z 485.1787.

Compound 11e: Yield: 61% (2.233 g, in two steps); colorless syrup; $[\alpha]_D^{25}$ - 63.11 (c 1.03, $CHCl_3$); IR (neat) ν_{max} 3076, 2987, 2937, 1728, 1599, 1382, 1279, 1074 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.69 (m, 2H), 7.58-7.54 (m, 2H), 5.93 (d, *J* = 3.6 Hz,1H), 5.90-5.79 (m, 1H), 5.42 (d, *J* = 2.4 Hz, 1H), 5.10-5.03 (m, 2H), 4.81(d, *J* = 3.6 Hz,1H), 4.35-4.23 (m, 4H), 4.03-4.00 (m, 2H), 2.23-2.16 (m, 2H), 1.90-1.83 (m, 2H), 1.60(s, 3H), 1.55(s, 3H), 1.36(s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 166.3, 137.1, 131.8, 131.7, 131.1, 128.9,

115.4, 112.1, 109.2, 105.1, 82.6, 79.5, 77.3, 72.3, 67.1, 65.1, 29.9, 27.6, 26.7, 26.2, 25.2; MS (ESI) m/z 499 (M+Na); HRMS calculated for $C_{25}H_{32}O_9Na$ $[M+Na]^+$ m/z 499.1944, found m/z 499.1939.

Compound 11f: Yield 66% (2.488 g, in two steps) colorless syrup; $[\alpha]_D^{25}$+50.83 (c 1.2, $CHCl_3$); IR (neat) ν_{max} 3076, 2987, 1732, 1580, 1382, 1278, 1072 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82-7.67 (m, 2H), 7.58-7.46 (m, 2H), 5.92 (d, *J* = 3.6 Hz,1H), 5.85-5.68 (m, 1H), 5.42 (d, *J* = 2.4 Hz, 1H), 5.10-5.03 (m, 2H), 5.06-4.91 (m, 2H), 4.81(d, *J* = 3.6 Hz,1H), 4.39-4.14 (m, 4H), 4.06-3.98 (m, 1H), 2.17-1.99 (m, 2H), 1.82-1.70 (m, 2H), 1.67-1.60 (m, 1H), 1.58-1.51 (m, 5H), 1.49 (s, 3H), 1.35 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0,166.4, 138.2,131.8, 131.1, 128.9, 114.90, 112.2, 109.2, 105.2, 82.6, 79.6, 77.3, 72.4, 67.1, 65.6, 33.2, 27.9, 26.8, 26.2, 25.1; MS (ESI) m/z 513 (M+Na); HRMS calculated for $C_{26}H_{34}O_9Na$ $[M+Na]^+$ m/z 513.2101, found m/z 513.2100.

Compound 11c: To a solution of **10a** (2.75 g, 6.75 mmol, prepared from 1.75 gm of **9a**) in dry DCM (30 mL) HOBt (1.117g, 7.3 mmol) &EDCI.HCl (1.4g, 7.3 mmol) were added at 0℃. After stirring 30 min, DMAP (0.964g, 7.9 mmol) and *N*-allyl benzyl amine (0.87g, 6.08 mmol) were added successively. The resulting reaction mixture was warmed to room temperature and stirring was continued for 12 hr. The reaction mixture was diluted with DCM (25 mL) and successively washed with 2% aqueous-HCl solution (1 x 10 mL), saturated $NaHCO_3$ solution (1 x 10 mL), brine (3 x 10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated the filtrate under reduced pressure at room temperature which was subsequently chromatographed over silica gel (60-120 mesh, 3:7 ethyl acetate –hexane) to obtain **11c** as colorless syrup, yield: 66% (2.44g, in two steps); $[\alpha]_D^{25}$ + 95.15 (*c* 1.04, $CHCl_3$); IR (neat) ν_{max} 3068, 2987, 2936, 1732, 1645, 1259, 1048 cm-^{1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.98-7.94 (m, 1H), 7.61-7.55 (m, 1H), 7.53-7.40 (m, 2H), 7.39-7.30 (m, 4H), 7.28-7.15 (bd, 1H), 6.02-5.89 (m, 1H), 5.67-5.61 (m, 1H), 5.48 (d, *J* = 3.9 Hz,1H), 5.23-5.11 (m, 2H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.88 (d, *J* = 15 Hz, 1H), 4.77 (d, *J* = 14.7 Hz, 1H), 4.66-4.60 (m, 1H), 4.39-4.30 (m, 4H), 4.16-3.99 (m, 3H), 3.61 (d, *J* = 6.0 Hz, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 164.1, 139.0, 136.9, 136.1, 133.1, 132.9, 132.6, 130.2, 128.8, 128.6, 128.5, 12.4, 127.2, 127.0, 118.5, 112.3, 109.3, 105.1, 83.2, 79.9, 77.1, 72.4, 67.3, 50.7, 46.7, 26.8, 26.7, 26.2, 25.2; MS (ESI) m/z 560, 538, 502, 480, 422, 296, 278, 188, 148; HRMS calculated for $C_{30}H_{35}NO_8$ $[M+Na]^+$ m/z 537.2362 found m/z 537.2362.

3. **General procedure for the synthesis of 12a-f**: A solution of the di-*O*-isopropylidene phthalate derivatives **11a-f** (3.33 mmol) in 75% aqueous-acetic acid (v/v, 10mL) was stirred for overnight at ambient temperature. The reaction mixture was evaporated to dryness under reduced pressure and the residue was co-evaporated with dry toluene several times until complete removal of AcOH and H_2O. The residue was chromatographed over silica gel (60-120 mesh) to afford the diols**12a-f**.

Compound 12a: Yield 83% (1.127g); colorless syrup; $[\alpha]_D^{25}$ + 89.00 (*c* 1.00, $CHCl_3$); IR (neat) ν_{max} 3507, 2988, 2938, 1727, 1376, 1273, 1074 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90-7.86 (m, 1H), 7.65-7.54 (m, 3H), 6.06-5.96 (m, 1H), 5.91 (d, *J* = 3.9 Hz, 1H), 5.50 (d, *J* = 2.7 Hz, 1H), 5.42 (d, *J* =17.1 Hz, 1H), 5.32 (d, *J* =11.1 Hz, 1H), 4.83 (d, *J* =5.4 Hz, 2H), 4.70 (d, *J* =3.6 Hz, 1H), 4.31-4.28 (dd, *J* = 8.7Hz, 2.4 Hz, 1H), 3.86-3.77 (m, 2H), 3.72-3.66 (m, 1H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 166.7, 132.1, 131.8, 131.3, 131.0, 130.2, 129.2, 128.7, 118.9, 112.1, 104.9, 82.5, 78.7, 77.4, 68.0, 66.4, 63.9, 26.4, 26.0; MS (ESI) m/z 431 (M+Na), 409 (M+1); HRMS calculated for $C_{20}H_{24}O_9Na$ $[M + Na]^+$ m/z 431.1318, found m/z 431.1321.

Compound 12b: Yield 82% (1.113g); colorless syrup; $[\alpha]_D^{25}$ +49.96 (*c* 0.96, $CHCl_3$); IR (neat) ν_{max} 3428, 2988, 1728, 1580, 1375, 1280, 1075 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91-7.89 (m, 1H), 7.62-7.57 (m, 3H), 6.02-5.99 (m, 1H), 5.91(d, *J* = 1.8 Hz, 1H), 5.50 (d, *J* = 1.5 Hz, 1H), 5.44-5.40 (m, 1H), 5.33-5.31(m, 1H), 4.84-4.81 (m, 2H), 4.67 (d, *J* = 1.8 Hz, 1H), 4.30-4.28 (dd, *J* = 4.8, 1.5 Hz, 1H), 3.85-3.80 (m, 2H), 3.71-3.68 (m, 1H), 3.49 (bs, 1H), 2.20 (bs, 1H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 167.0, 133.1, 132.4, 131.5, 131.0, 130.0, 129.9, 128.9, 119.5, 112.6, 105.3, 83.1, 79.6, 77.9, 68.2, 66.9, 64.6, 26.9, 26.5; MS (ESI) m/z 431 (M+Na), 409 (M+1); HRMS calculated for $C_{20}H_{24}O_9Na$ $[M + Na]^+$ m/z 431.1318, found m/z 431.1320.

Compound 12c: Yield 88% (1.45g); colorless syrup; $[\alpha]_D^{25}$ + 78.90 (*c* 1.09, $CHCl_3$); IR (neat) ν_{max} 3420, 3068, 2987, 1726, 1621, 1263, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97-7.93 (m, 1H), 7.61-7.51 (m, 3H), 7.48-7.35 (m, 3H), 7.33-7.26 (m, 3H), 7.19-7.11(m, 1H), 6.02-5.89 (m, 1H), 5.79-5.49 (m, 2H), 5.48-5.02 (m, 1H), 4.72-4.64 (m, 1H), 4.44-4.10 (m, 2H), 4.09-3.96 (m, 2H), 3.81-3.78 (m, 2H), 3.66-3.61 (m, 2H), 1.97 (bs, 1H), 1.37 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 165.0, 138.1, 136.4, 132.9, 130.4, 129.2, 128.7, 127.7, 126.9, 119.1, 112.3, 105.0, 84.9, 83.0, 79.7, 74.9, 69.9, 68.0, 63.9, 46.9, 51.6, 26.7, 26.1; MS (ESI) m/z

520 (M+Na); 498 (M+1), 440, 296, 278; HRMS calcd $C_{27}H_{31}NO_8[M+Na]^+$ m/z 497.2049 found m/z 497.2049.

Compound 12d: Yield 84% (1.18g); colorless syrup; $[\alpha]_D^{25}$ + 81.95 (c 1.33, $CHCl_3$); IR (neat) ν_{max} 3486, 3077, 2985, 1727, 1599, 1384, 1279, 1072 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.61-7.55 (m, 2H), 5.92-5.90 (d, *J* = 3.6Hz, 1H), 5.89-5.80 (m, 1H), 5.57-5.56 (d, *J* = 2.4Hz, 1H), 5.20-5.11 (m, 2H), 4.69-4.67 (d, *J* = 3.6 Hz, 1H), 4.41-4.36 (m, 2H), 4.31-4.27 (m, 1H), 3.87-3.78 (m, 2H), 3.77-3.68 (m, 1H), 3.52-3.50 (m, 1H), 2.56-2.49 (m, 2H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 167.1, 133.5, 132.4, 131.9, 131.0, 130.3, 129.3, 128.7, 117.6, 117.5, 112.2, 105.0, 82.7, 79.0, 77.5, 68.1, 65.0, 64.1, 32.8, 26.5, 26.4; MS (ESI) m/z 461 (M+K), 445 (M+Na), 387; HRMS calcd $C_{21}H_{26}O_9Na$ $[M+Na]^+$ m/z 445.1475, found m/z 445.1472.

Compound 12e: Yield 87% (1.263g); colorless syrup; $[\alpha]_D^{25}$+91.21 (c 0.91, $CHCl_3$); IR (neat) ν_{max} 3424, 3079, 2991, 1724, 1578, 1384, 1281, 1071 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), 7.69-7.54 (m, 2H), 5.92-5.90 (d, *J* = 3.6 Hz, 1H), 5.88-5.76 (m, 1H), 5.57-5.56 (d, *J* = 2.4 Hz, 1H), 5.10-5.01 (dd, 2H), 4.69-4.68 (d, *J* = 3.6 Hz, 1H), 4.41-4.28 (m, 4H), 3.82-3.79 (m, 2H), 3.72-3.63 (m, 1H), 3.56-3.55 (m, 1H), 2.24-2.17 (m, 2H), 1.92-1.83 (m, 2H), 1.61 (bs, 4H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 167.1, 137.1, 132.7, 132.0, 131.0, 130.2, 129.4, 129.1, 128.7, 115.6, 117.5, 112.6, 105.1, 82.8, 79.2, 77.5, 68.1, 65.5, 64.3, 30.0, 27.6, 26.6, 26.2; MS (ESI) m/z 475 (M+K), 459 (M+Na); HRMS calcd $C_{22}H_{28}O_9Na$ [M + Na]$^+$ m/z 459.1631, found m/z 459.1633.

Compound 12f: Yield 89% (1.333g); colorless syrup; $[\alpha]_D^{25}$ – 68.18 (c 0.22, $CHCl_3$); IR (neat) ν_{max} 3467, 3075, 2935, 1725, 1580, 1384, 1279, 1071 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88-7.86 (m, 1H), 7.61-7.53 (m, 3H), 5.91-5.90 (d, *J* = 3.6 Hz,1H), 5.85-5.76 (m, 1H), 5.56-5.55 (d, *J* = 2.4 Hz, 1H), 5.06-4.96 (m, 2H), 4.69-4.68 (d, *J* = 3.6 Hz, 1H), 4.40-4.27 (m, 4H), 3.82-3.76 (m, 2H), 3.71-3.67 (m, 1H), 3.57-3.55 (m, 1H), 2.23 (bs, 1H), 2.16-2.09 (m, 2H), 1.83-1.70 (m, 4H), 1.68-1.47 (m, 5H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 167.1, 138.0, 132.4, 131.8, 131.0, 130.4, 129.2, 128.7, 114.9, 112.2, 105.0, 82.7, 78.9, 77.4, 68.1, 66.0, 64.1, 33.1, 27.8, 26.5, 26.1, 25.0; MS (ESI) m/z 489 (M+K), 473 (M+Na); HRMS calcd $C_{23}H_{30}O_9Na$ [M + Na]$^+$ m/z 473.1788, found m/z 473.1792.

4. **General procedure for synthesis of oxime 13a-f:** To a stirred solution of diols**12a-f** (3.0 mmol) in CH_3OH (20 mL) at 0^0C $NaIO_4$ (3.6 mmol) in H_2O (10 mL) was added drop wise for 30 minutes and stirring continued for 2 h at room temperature. The white ppt. was filtered, washed with methanol and the filtrate was concentrated under reduced pressure at room temperature. The residue was diluted with water (20 mL) and extracted with DCM (3 x 20 mL). The combined organic layers was washed with brine (2 x 10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford corresponding aldehyde as colorless syrup, which was used immediately without any further purification for the next step.

A solution of above aldehyde, hydroxylamine hydrochloride (4.5 mmol) in ethanol (15 mL) containing pyridine (3 mL) was heated at reflux for 2 hr. After removal of solvent the residue was extracted with DCM. The organic layer was washed with water, dried and evaporated. The residue was co-evaporated with toluene several times to give a syrupy liquid, which was chromatographed over silica gel (60-100 mesh) to give the oxime**13a-f**.

Compound 13a: Yield 81% (950 mg, in two steps) as light yellow oil; $[\alpha]_D^{25}$ + 104.67 (*c* 1.07, $CHCl_3$); IR (neat) ν_{max}3400, 3028, 2991, 2939, 1732, 1599, 1384, 1279, 1032 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.77 (m, 2H), 7.69-7.66 (m, 1H), 7.63-7.56 (m, 2H), 7.41 (d, *J* = 6.9 Hz, 1H), 6.07-5.99 (m, 2H), 5.44-5.30 (m, 3H), 4.96-4.93 (m, 1H), 4.83 (d, *J* = 4.8 Hz, 1H), 1.56 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$)(two isomer) δ 166.7, 166.6, 166.5, 166.4, 147.8, 146.0, 131.7, 131.6, 131.5, 131.4, 131.3, 131.2, 129.1, 129.0, 118.9, 118.8, 112.6, 112.4, 105.0, 104.7, 82.8, 82.8, 78.9, 77.8, 76.5, 74.1, 66.4, 26.7, 26.2; MS (ESI) *m/z* 414 (M +Na), 392, 334, 284, 189, 149, 128; HRMS calculated for $C_{19}H_{21}NO_8$ m/z 391.1267, found m/z 391.1269.

Compound 13b: Yield 79% (926 mg, in two steps), colorless syrup; $[\alpha]_D^{25}$ + 70.75 (*c* 1.06, $CHCl_3$); IR (neat) ν_{max}3433, 2990, 2729, 1449, 1277, 1074 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18-8.09 (bd, 1H), 7.80-7.71 (m, 2H), 7.59-7.51 (m, 2H), 7.45 (d, *J* = 6.6 Hz, 1H), 6.06-5.93 (m, 1H), 5.91 (d, *J* = 3.6 Hz, 1H), 5.44-5.38 (m, 1H), 5.36-5.10 (m, 1H), 5.03-4.91 (m, 2H), 4.83-4.73 (m, 3H), 1.56 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 166.7, 147.2, 131.7, 131.4, 131.3, 131.0, 129.1, 129.0, 118.5, 113.5, 104.2, 77.5, 77.1, 75.0, 74.8, 66.3, 26.6, 26.5; MS (ESI) m/z 414 (M +Na), 392 (M+1); HRMS calculated for $C_{19}H_{21}NO_8$ m/z 391.1267 found m/z 391.1263.

Compound 13c: Yield 80% (1.166g, in two steps); colorless foam; $[\alpha]_D^{25}$ – 72.58 (*c* 1.24, $CHCl_3$); IR (neat) ν_{max} 3267, 3084, 2994, 1729, 1618, 1260, 1076 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.75 (bs, 1H), 7.95-7.86 (m, 1H), 7.68-7.51 (m, 1H), 7.49-7.35 (m, 5H), 7.34-7.25 (m, 3H), 6.07-5.91 (m, 2H), 5.38-5.10 (m, 2H), 5.02-4.82 (m, 2H), 4.75-4.67 (m, 1H), 1.56 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 164.1, 146.9, 145.0, 138.5, 136.7, 135.9, 133.3, 132.9, 132.3, 130.4, 128.9, 128.6, 127.4, 126.7, 118.7, 112.3, 104.8, 104.5, 83.1, 77.5, 76.5, 50.8, 46.9, 26.7, 26.2; MS (ESI) m/z 503 (M+Na), 481 (M+1), 423, 296, 278; HRMS calculated for $C_{26}H_{28}N_2O_7$ m/z 480.1897 found m/z 480.1900

Compound 13d: Yield 81% (984 mg, in two steps), colorless foam; $[\alpha]_D^{25}$-71.86 (*c* 1.67, $CHCl_3$); IR (neat) ν_{max} 3419, 3079, 2988, 1732, 1599, 1380, 1281, 1074 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.10-8.01 (bs, 0.5H), 7.89-7.80 (bs, 0.5H), 7.78-7.71 (m, 1H), 7.68-7.61 (m, 1H), 7.60-7.51 (m, 2H), 7.40 (d, *J* = 6.9 Hz, 0.5H), 6.86 (d, *J* = 3.6 Hz, 1H), 6.01 (d, *J* = 3.6 Hz, 1H), 5.92-5.78 (m, 1H), 5.77 (d, *J* = 3.0 Hz, 1H), 5.44 (d, *J* = 3.0 Hz, 1H), 5.41-5.39 (m, 1H), 5.20-5.10 (m, 1H), 4.96-4.92 (m, 1H), 4.84 (d, *J* = 3.3 Hz, 1 H), 4.45-4.32 (m, 2H), 2.54-2.17 (m, 2H), 1.68 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 166.5, 166.4, 147.3, 145.6, 133.7, 131.3, 131.2, 128.9, 117.4, 112.5, 112.4, 104.9, 104.6, 82.6, 78.8, 77.7, 76.4, 74.0, 64.7, 32.7, 26.6, 26.5, 26.1; MS (ESI) m/z 428 (M+Na), 405, 370; HRMS calculated for $C_{20}H_{23}NO_8$ m/z 405.1424, found m/z 405.1428.

Compound 13e: Yield 83%, colorless foam (1.04g, in two steps); $[\alpha]_D^{25}$ - 140.31 (*c* 1.29, $CHCl_3$); IR (neat) ν_{max} 3418, 3077, 2989, 1728, 1580, 1385, 1279 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (bs, 1H), 7.95 (bs, 1H), 7.78-7.72 (m, 1H), 7.68-7.52 (m, 3H), 6.00 (d, *J* = 3.6 Hz, 1H), 5.91-5.79 (m, 2H), 5.77 (d, *J* = 3.0 Hz, 1H), 5.44-5.39 (m, 1H), 5.10-5.00 (m, 2H), 4.85 (d, *J* = 3.6 Hz, 1H), 4.40-4.28 (m, 2H), 2.23-2.16 (m, 2H), 1.90-1.77 (m, 2H), 1.68 (bs, 1H), 1.56 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 166.6, 147.5, 145.8, 137.3, 131.7, 131.4, 128.9, 115.5, 112.6, 105.0, 104.7, 82.8, 78.9, 76.5, 74.2, 65.3, 29.9, 27.6, 26.8, 26.2; MS (ESI) *m/z* 442.12 (M + Na); HRMS calculated for $C_{21}H_{25}NO_8$ m/z 419.1580, found m/z 419.1584.

Compound 13f: Yield 82%, (1.065 g in two steps); colorless syrup; $[\alpha]_D^{25}$ + 96.4 (*c* 1.11, $CHCl_3$); IR (neat) ν_{max} 3415, 3077, 2988, 1727, 1580, 1384, 1281 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24-8.21 (bs, 1H), 8.01 (bs, 1H), 7.77-7.71 (m, 1H), 7.68-7.60 (m, 1H), 7.58-7.51 (m, 2H), 6.00 (d, *J* = 3.6Hz, 1H), 5.88-5.74 (m, 1H), 5.44-5.39 (m, 1H), 5.06-4.92 (m, 3H), 4.85 (d, *J* = 3.6 Hz, 1H), 4.39-4.30 (m, 2H), 2.17-2.08 (m, 2H), 1.81-1.72 (m, 3H), 1.56-1.48 (s, 5H), 1.36

(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 166.6, 147.5, 145.7, 138.2, 131.6, 131.2, 128.9, 114.2, 112.5, 105.0, 104.6, 82.7, 78.9, 76.4, 74.1, 65.8, 33.2, 27.8, 26.7, 26.2, 25.1; MS (ESI) m/z 456 (M+Na), 433, 398, 331, 235, 149; HRMS $C_{22}H_{27}NO_8$ m/z 433.1737, found m/z 433.1741.

5. General procedure for synthesis of isoxazoline bridged macrocycle 15a-f.

To a stirred solution of oxime**13a-f** (1mmol) with 4-5 drops Et_3N in DCM (10 mL) at 0 ^oC 4% NaOCl solution (10 mL, excess) was added dropwise over 30 min. The reaction medium was stirred for additional 30 min at the same temperature and stirring was continued for overnight at room temperature. The organic phase was separated and the aqueous phase was extracted with DCM (2 x 10mL). The combined organic layer was washed with 2% aqueous HCl solution (20 mL), brine (2 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure at ambient remperature. The crude product was chromatographed using silica gel (100-200 mesh) to give the isoxazoline**15a-f**.

Macrocycle 15a: Yield 59% (230 mg), colorless solid, m. p. 176-178 ^0C; $[\alpha]_D^{25}$ + 93.20 (*c* 1.03, $CHCl_3$); IR (KBr) ν_{max} 2989, 2940, 1726, 1598, 1447, 1382, 1287, 1076 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.57 (m, 3H), 6.03 (d, *J* = 3.3 Hz, 1H), 5.83 (d, *J* = 3.3 Hz ,1H), 5.44 (d, *J* = 2.7 Hz, 1H), 4.96 (d, *J* = 10.5 Hz, ,1H), 4.69 (d, *J* = 3.3 Hz, 1H), 4.53 - 4.48 (dd, *J* = 12.6, 2.1 Hz, 1H), 4.439 (d, *J* = 12.6 Hz, 1H), 3.34-3.14 (m, 2H), 1.56 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 166.5, 154.6, 132.1, 132.0, 130.8, 128.6, 128.3, 112.7, 105.1, 83.6, 80.2, 76.6, 75.7, 68.6, 36.6, 26.7, 26.2; MS (ESI) 412 (M+Na), 390 (M+1), 332, 314*;* HRMS calculated for $C_{19}H_{19}NO_8$ m/z 389.1110, found m/z 389.1106.

Macrocycle 15b: Yield 58% (225 mg), colourless solid, m. p. 133-135 ^0C; $[\alpha]_D^{25}$ + 88.57 (*c* 1.05, $CHCl_3$); IR (KBr) ν_{max} 2989, 2940, 1731, 1580, 1376, 1277, 1074 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 3.3 Hz, 1H), 7.63-7.56 (m, 3H), 6.03 (d, *J* = 3.6 Hz, 1H), 5.69-5.67 (dd, *J* = 9.6, 4.2 Hz, 1H), 5.02-4.97 (m, 1H), 4.85 (t, *J* = 4.2 Hz, 1H), 4.76 (d, *J* = 9.6 Hz, 1H), 4.52 (d, *J* = 13.2 Hz, 1H), 4.34-4.32 (dd, *J* = 13.2, 3.6 Hz, 1H), 3.37-3.33 (d, *J* = 17.4, 11.4 Hz, 1H), 3.02-2.99 (d, *J* = 17.4, 3.0 Hz, 1H), 1.60 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 166.8, 166.7, 154.4, 132.4, 132.2, 131.3, 130.9, 129.2, 128.1, 113.7, 104.9, 78.3, 77.2, 76.8, 70.8, 69.7, 38.3, 26.4, 26.0; MS (ESI) m/z 412 (M+Na), 390 (M+1), 332, 314*;* HRMS calculated for $C_{19}H_{19}NO_8$ m/z 389.1110 found m/z 389.1105.

Macrocycle 15c: Yield 61% (291mg), colourless solid, m. p. 157-159 ^{0}C; $[\alpha]_D^{25}$ + 84.17 (*c* 1.20, $CHCl_3$); IR (KBr) ν_{max} 2990, 2929, 1720, 1634, 1386, 1279, 1042 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.26-7.21 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.01 (d, *J*= 3.6 Hz ,1H), 5.65 (d, *J* = 4.8 Hz, 1H), 5.46 (d, *J* = 4.2 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.69 (d, *J* = 3.6 Hz, 1H), 4.45 (d, *J* = 15.6 Hz, 1H), 4.34 (d, *J* = 15.6 Hz, 1H), 4.28 (d, *J* = 14.4 Hz, 1H), 3.91-3.88 (dd, *J* = 18.6, 3.0 Hz, 1H), 3.32-3.27 (dd, *J* = 18.6, 12.0 Hz, 1H), 3.10-3.07 (dd, *J* = 14.4, 2.4 Hz, 1H), 1.57 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$)δ 172.0, 165.8, 158.0, 136.5, 135.6, 133.8, 132.2, 129.3, 128.6, 128.5, 127.7, 127.5, 125.6, 112.7, 104.9, 83.8, 82.4, 80.1, 74.4, 52.7, 47.0, 38.4, 26.8, 26.3; MS (ESI) m/z 501.19 (M+ Na), 478 (M+1), 421; HRMS calculated for $C_{26}H_{26}N_2O_7$ m/z 478.1740 found m/z 478.1744.

Macrocycle 15d: Yield 52% (209mg), colourless solid, m. p. 199-201^{0}C; $[\alpha]_D^{25}$ +78.13 (*c* 0.64, $CHCl_3$); IR (KBr) ν_{max} 2991, 1726, 1599, 1382, 1280, 1073 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.65-7.48 (m, 3H), 6.19 (d, *J* = 3.6 Hz, 1H), 5.64 (d, *J* = 2.7 Hz, 1H), 5.11 (d, *J* = 2.4 Hz, 1H), 5.01-4.90 (m, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 4.64-4.58 (m, 1H), 4.35-4.21 (m, 1H), 3.25-3.16 (dd, *J* = 16.8, 10.2 Hz, 1H), 2.99-2.89 (dd, *J* = 17.7, 12.0 Hz,1H), 2.53-2.44 (m, 1H), 1.99-1.93 (dd, *J* = 16.5, 3.9 Hz, 1H), 1.58 (s, 5H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 165.6, 152.0, 134.2, 132.5, 130.5, 129.3, 128.9, 112.5, 104.5, 83.1, 78.3, 76.2, 61.2, 53.4, 37.1, 29.6, 26.7, 26.1; MS (ESI) m/z 426.22 (M + Na); HRMS calculated for $C_{20}H_{21}NO_8Na$ $[M + Na]^+$ m/z 426.1165, found m/z 426.1160.

Macrocycle 15e: Yield 52% (216 mg), colorless solid, m. p. 191-193 ^{0}C; $[\alpha]_D^{25}$ - 74.00 (*c* 0.5, $CHCl_3$); IR (KBr) ν_{max}2990, 1723, 1448, 1293, 1075 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.58-7.50 (m, 2H), 6.16 (d, *J* = 3.6Hz, 1H), 5.69 (d, *J* = 3.3 Hz, 1H), 5.11 (d, *J* = 3.0 Hz, 1H), 5.09-4.86 (m, 1H), 4.81(d, *J* = 3.6 Hz, 1H), 4.38-4.34 (m, 2H), 3.27-3.14 (m, 2H), 1.76-1.71 (m, 2H), 1.57 (bs, 5H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 165.6, 152.1, 134.3, 132.6, 132.0, 130.5, 129.9, 128.9, 112.7, 104.7, 83.1, 79.4, 77.7, 75.9, 65.1, 39.7, 30.0, 26.7, 26.2 22.6; MS (ESI) m/z 440.23 (M+Na); HRMS calculated for $C_{21}H_{23}NO_8Na$ $[M + Na]^+$ m/z 440.1321, found m/z 440.1329.

Macrocycle 15f: Yield 54% (232 mg), colorless solid, m. p. 227-229 ^{o}C; $[\alpha]_D^{25}$ - 77.5 (*c* 0.40, $CHCl_3$); IR (KBr) ν_{max} 2987, 2929, 1728, 1581, 1384, 1263, 1075 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.93 (m, 1H), 7.64-7.59 (m, 1H), 7.51-7.47 (m, 2H), 6.23 (d, *J* = 3.6 Hz, 1H),

5.64 (d, *J* = 2.4 Hz, 1H), 5.03 (d, *J* = 2.1 Hz, 1H), 4.81 (d, *J* = 3.6 Hz, 1H), 4.61-4.58 (m, 1H), 4.46-4.33 (m, 2H), 3.07-2.86 (m, 2H), 1.79 (dbs, 2H), 1.71-1.57 (m, 7H), 1.37 (s, 3H), 1.28-1.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 164.3, 150.9, 135.8, 133.2, 130.3, 127.7, 126.2, 112.6, 104.6, 83.0, 80.3, 76.3, 67.7, 39.9, 34.1, 30.9, 26.9, 26.6, 26.1, 23.2; MS (ESI) m/z 454.17 (M+Na); HRMS calculated for $C_{22}H_{25}NO_8Na$ $[M + Na]^+$ m/z 454.1478, found m/z 454.1482

Removal of phthalate template.A solution of $LiOH.H_2O$ (269.7mg, 6.45 mmol) in water (20 mL) was added drop wise to a solution **15a** or **15f** (1.29 mmol) taken in dioxane (20 mL) and the reaction mixture was stirred at room temperature for overnight. The solution was neutralized with 2M aq. HCl, evaporated to dryness under reduced pressure. The residue was taken in DCM (10 mL). It was successively washed with water (2 x 10 mL), brine (2 x 10 mL), dried over Na_2SO_4 and concentrated under reduced pressure at room temperature and the crude product was chromatographed over silica-gel (60-120) using ethyl acetate –hexane (3:2) to obtain diol**16** or **17** (79%, 309 mg).

Compound16: Yield 81% (271 mg), colorless oil; $[\alpha]_D^{25}$–83.33 (*c* 0.2, $CHCl_3$); IR (neat) 3464, 3340, 2989, 2941, 1717, 1637, 1382, 1221, 1064 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 (d, *J* = 3.3, 1H), 4.98 (s, 1H), 4.75-4.70 (m, 1H), 4.58 (d, *J* = 3.3Hz, 1H), 4.40 (s, 1H), 3.88-3.84 (d, *J* = 12.0 Hz, 1H), 3.57-3.53 (m, 2H), 3.26-3.05 (m, 2H), 1.51 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 112.1, 105.3, 84.6, 80.1, 77.3, 76.9, 64.3, 37.4, 26.8, 26.1; MS (ESI) *m/z* 282.10 (M + Na); HRMS calculated for $C_{11}H_{17}NO_6$ m/z 259.1056, found m/z 259.1051.

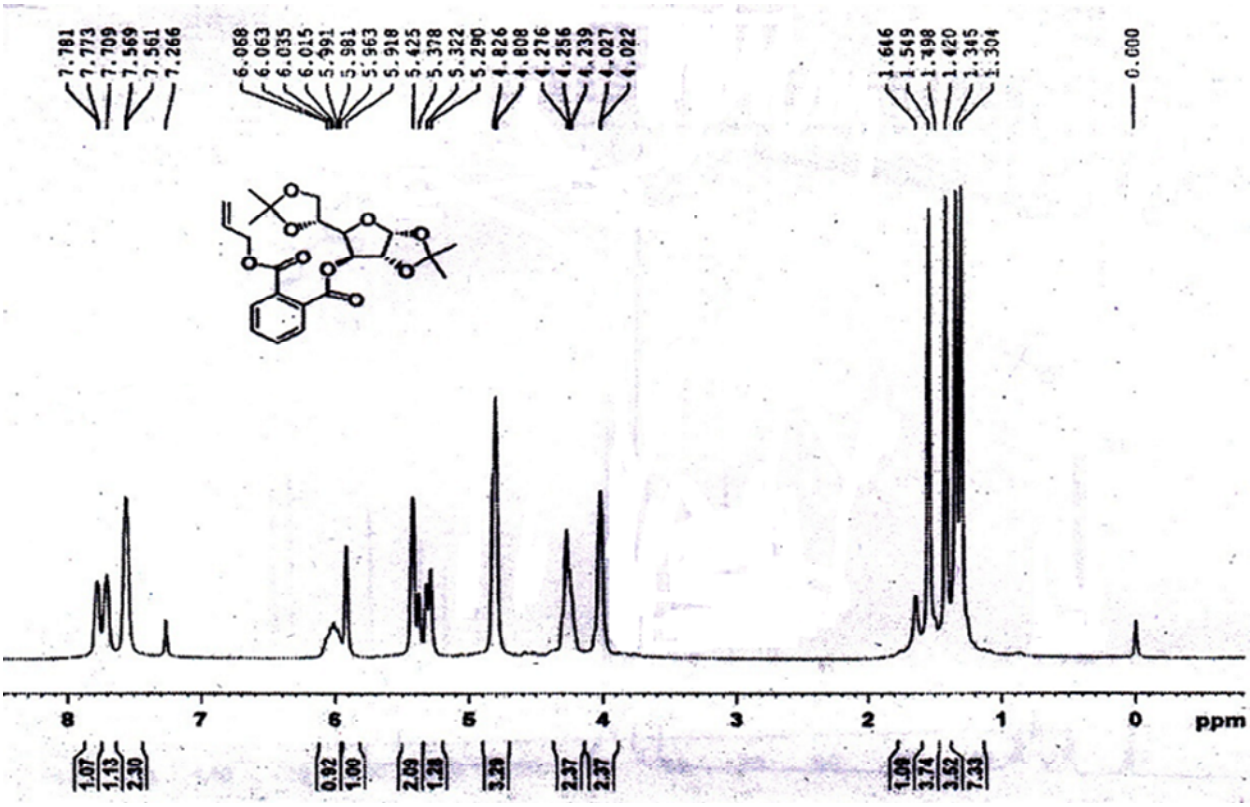
Compound 17: Yield 79% (309 mg), colorless solid, m. p. 82-84^{o}C; $[\alpha]_D^{25}$ + 82.05 (*c* 0.78, $CHCl_3$); IR (KBr) 3368, 2928, 1739, 1629, 1375, 1217, 1073 cm-^{1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.01 (d, *J* = 3.6, 1H), 4.82 (d, *J* = 1.5 Hz ,1H), 4.67-4.60 (m, 2H), 4.47 (bs, 1H), 3.66 (d, *J* = 6.0 Hz, 2H), 3.31-3.21 (dd, *J* = 17.1, 10.2 Hz,1H), 3.20 - 3.10 (m, 1H), 2.78 - 2.69 (dd, *J* = 17.4, 8.4 Hz, 1H), 1.80 - 1.70 (m, 8H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 111.9, 105.0, 84.6, 80.7, 76.6, 75.9, 62.6, 41.2, 34.7, 32.3, 29.7, 26.8, 26.0, 21.6; MS (ESI) *m/z* 324.20 (M+Na); HRMS calcd for $C_{14}H_{23}NO_6$ m/z 301.1525, found m/z 301.1520.

Synthesis of amino sugar derivative 18: Pd/C (10%, 100 mg) was added to a solution of diol**16** (250 mg, 1.275 mmol) in dry ethyl acetate (20 mL) and hydrogenated with H_2 under 1 atmospheric pressure at room temperature for 12 h. The catalyst was filtered, washed with ethyl acetate and the combined filtrate was concentrated under reduced pressure at room temperature. The crude product was dissolved in solution containing pyridine (2 mL), Ac_2O (1.0 mL, 10.2

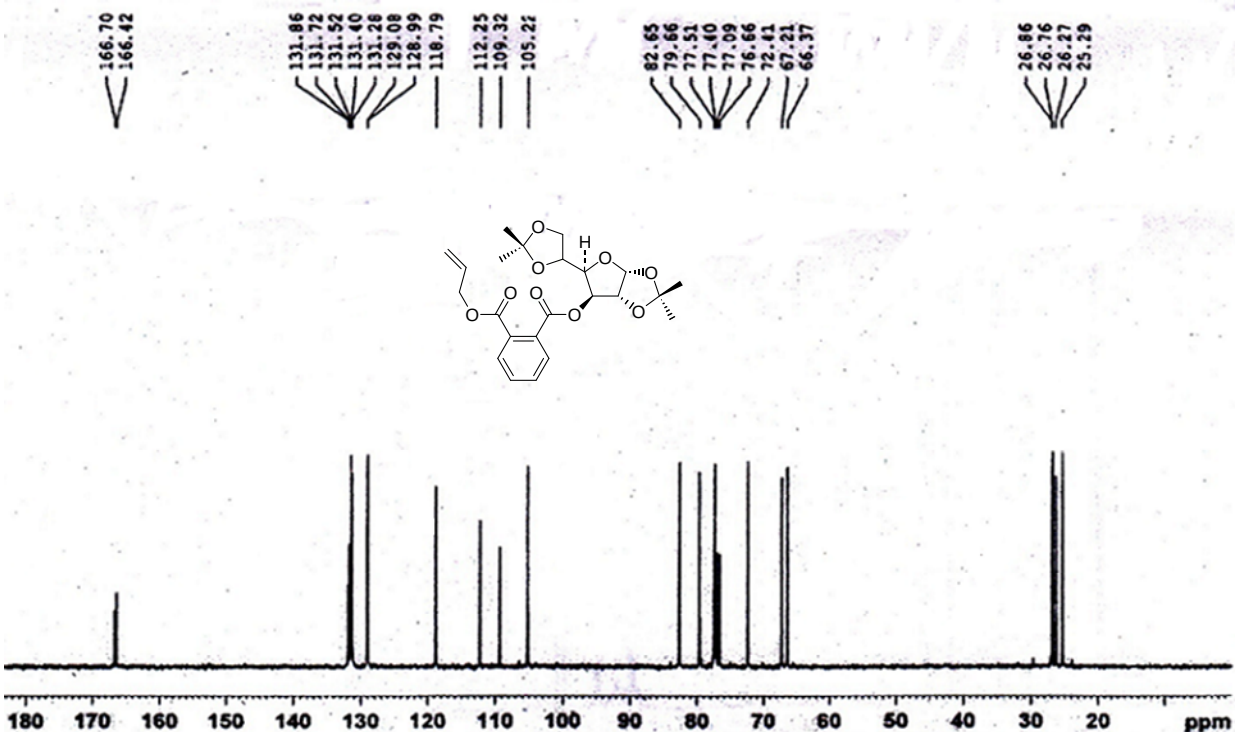
mmol) and DMAP (10 mg) kept at 0^{o}C. The reaction mixture was stirred at room temperature for 12 h. The post reaction mixture was extracted with EtOAc (3 x 20 mL) and the organic layer was washed with brine (2 x 10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (100–200 mesh) using hexane–ethyl acetate (1:4) as eluent to afford the tetraacetate**18**.

Compound 18: Yield 350 mg (72% in two steps, 300 mg), colorless thick oil; $[\alpha]_D^{25}$ + 74.75 (*c* 0.99, $CHCl_3$); IR (neat) 2990, 2926, 1742, 1653, 1375, 1231, 1048 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94-5.89 (m, 2H), 5.21 (d, *J* = 3.0 Hz, 1H), 5.07 (d, *J* = 3.0 Hz, 1H), 4.47 (d, *J* = 3.0 Hz, 1H), 4.32-4.25 (m, 2H), 4.20 - 4.17 (m, 1H), 4.07-4.01 (dd, *J* = 11.7, 5.7 Hz, 1H), 2.18-2.05 (4s, 12H), 2.00-1.87 (m, 1H), 1.77-1.68 (m, 1H), 1.29 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 170.6, 169.8, 112.0, 104.3, 83.3, 78.9, 76.4, 68.4, 64.3, 44.8, 33.4, 26.5, 25.9, 23.3, 21.1 20.8, 20.7; MS (ESI) *m/z* 454.12 (M+Na); HRMS calculated for $C_{19}H_{29}NO_{10}$ m/z 431.1791, found m/z 431.1796.

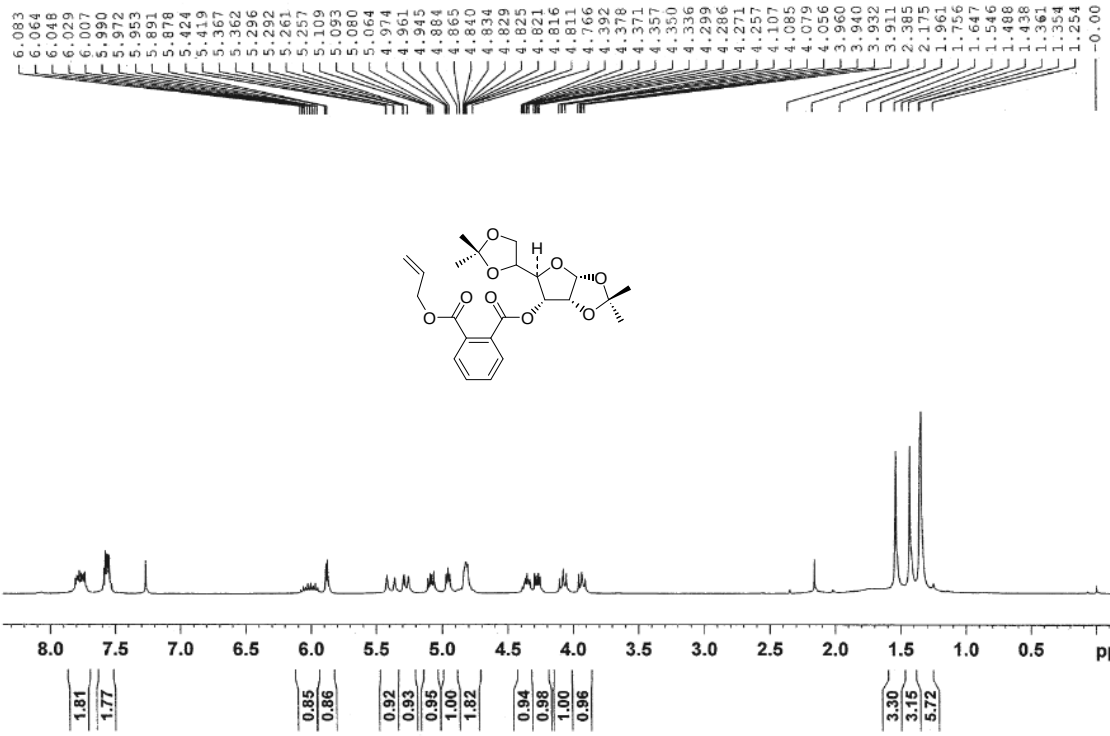
^{1}H NMR Spectra of 11a (300 MHz, $CDCl_3$)



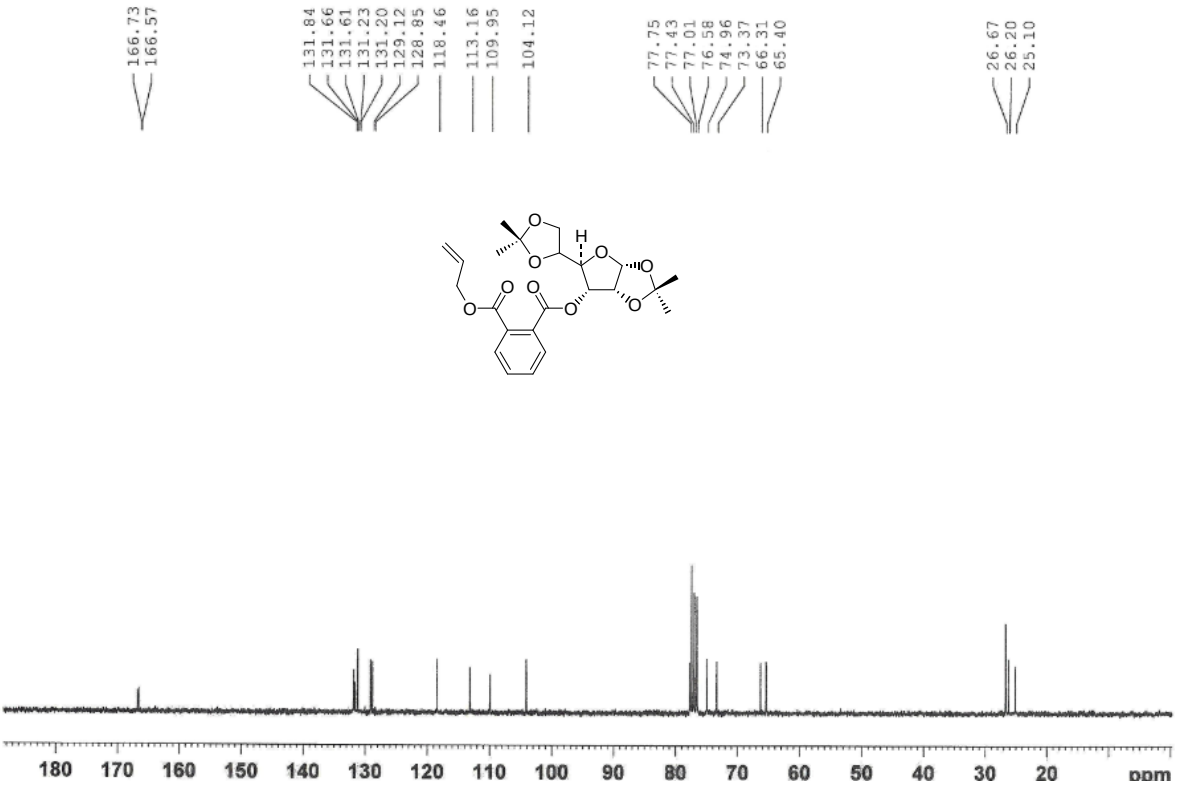
^{13}C NMR Spectra of 11a (75 MHz, $CDCl_3$)



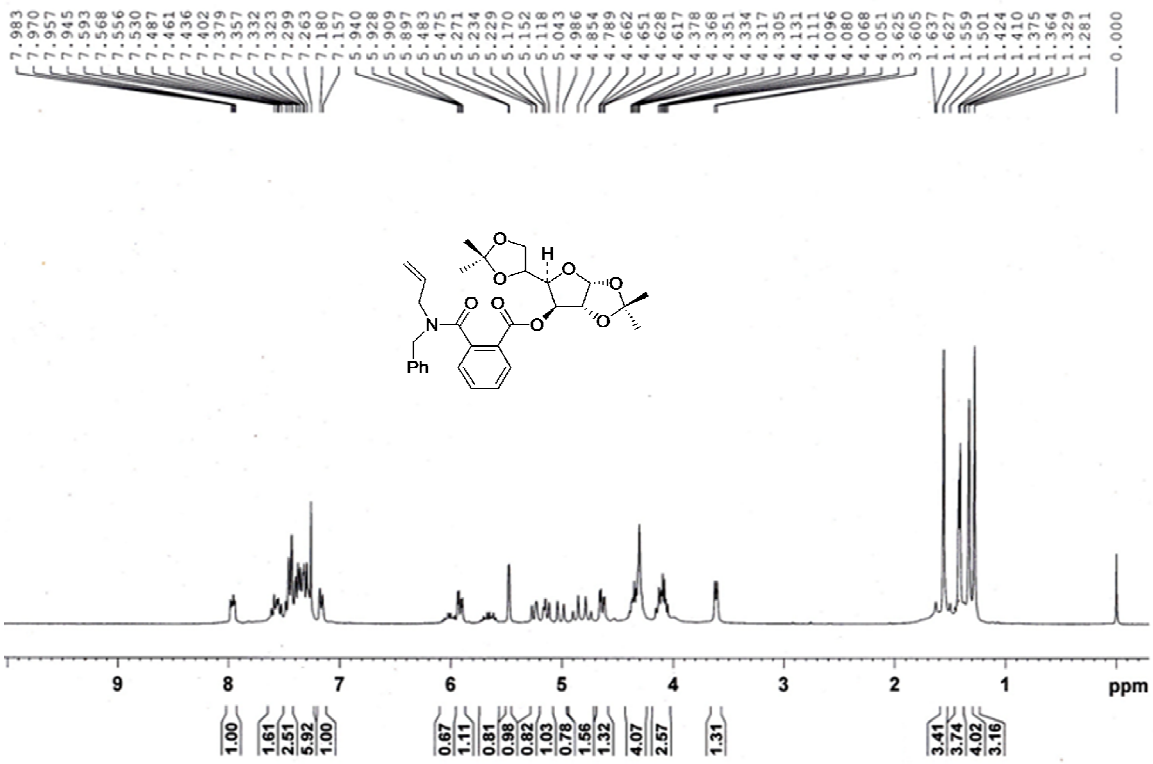
^{1}H NMR Spectra of 11b (300 MHz, $CDCl_3$)



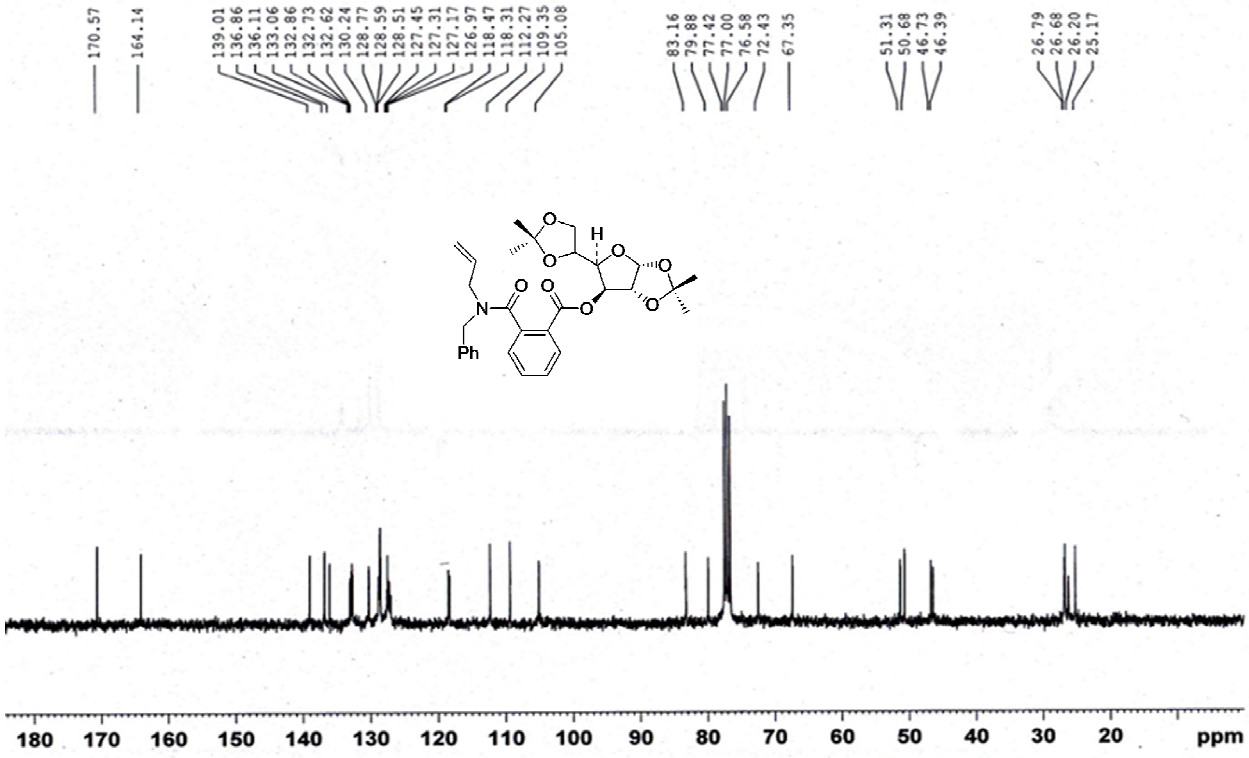
^{13}C NMR Spectra of 11b (75 MHz, $CDCl_3$)



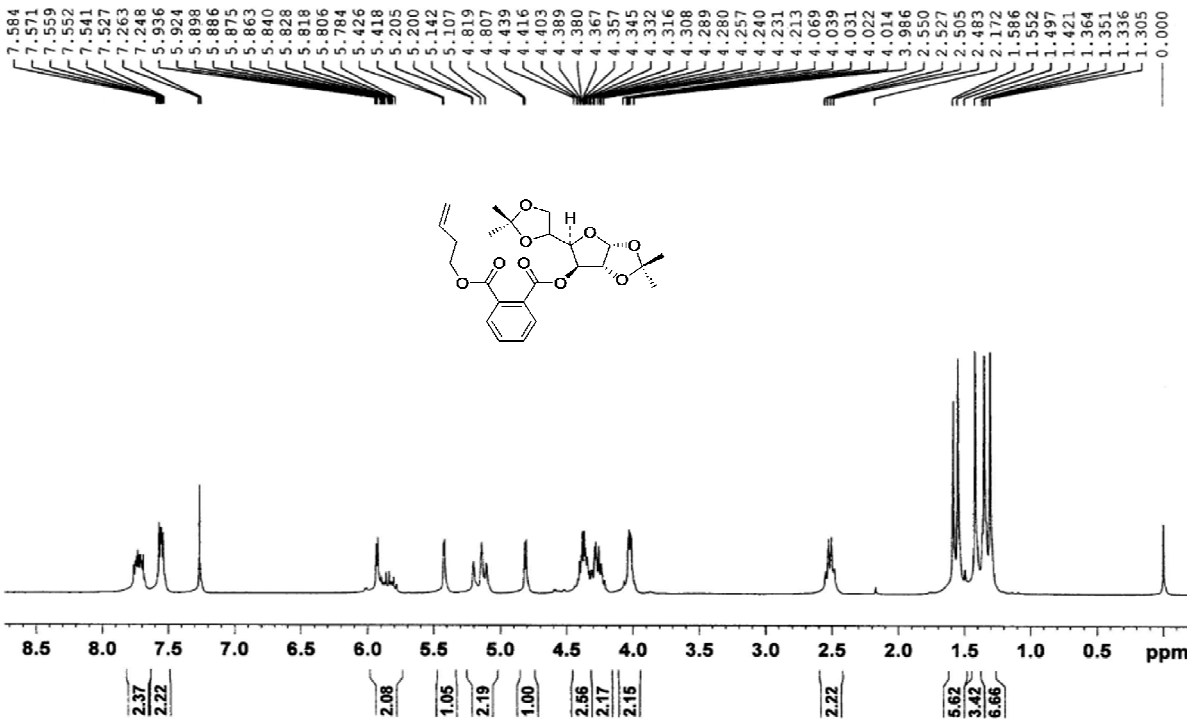
^{1}H NMR Spectra of 11c (300 MHz, $CDCl_3$)



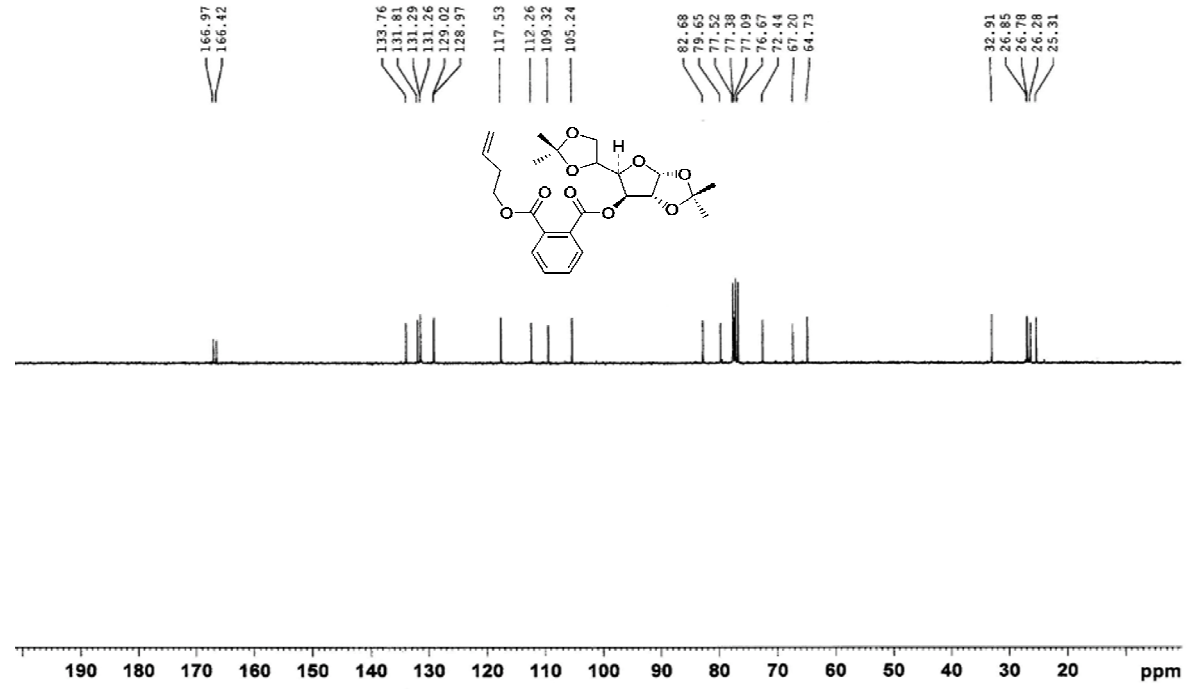
^{13}C NMR Spectra of 11c (75 MHz, $CDCl_3$)



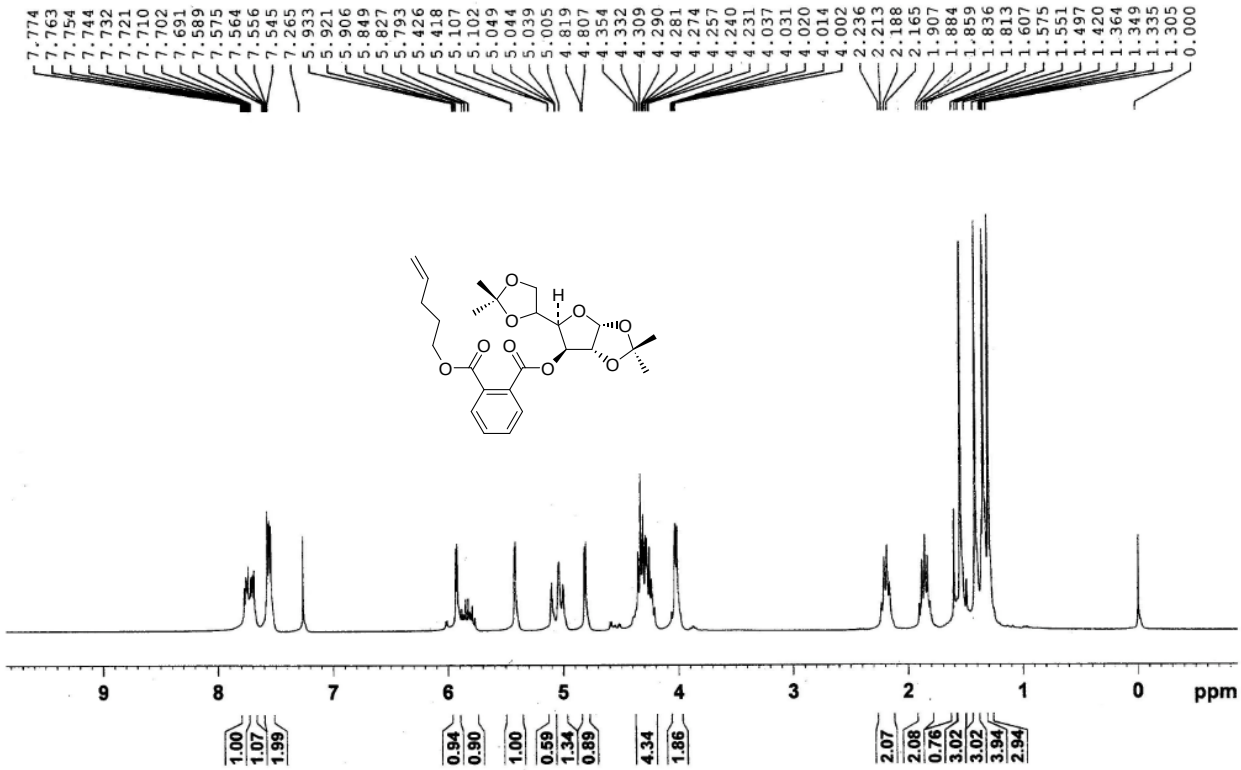
^{1}H NMR Spectra of 11d (300 MHz, $CDCl_3$)



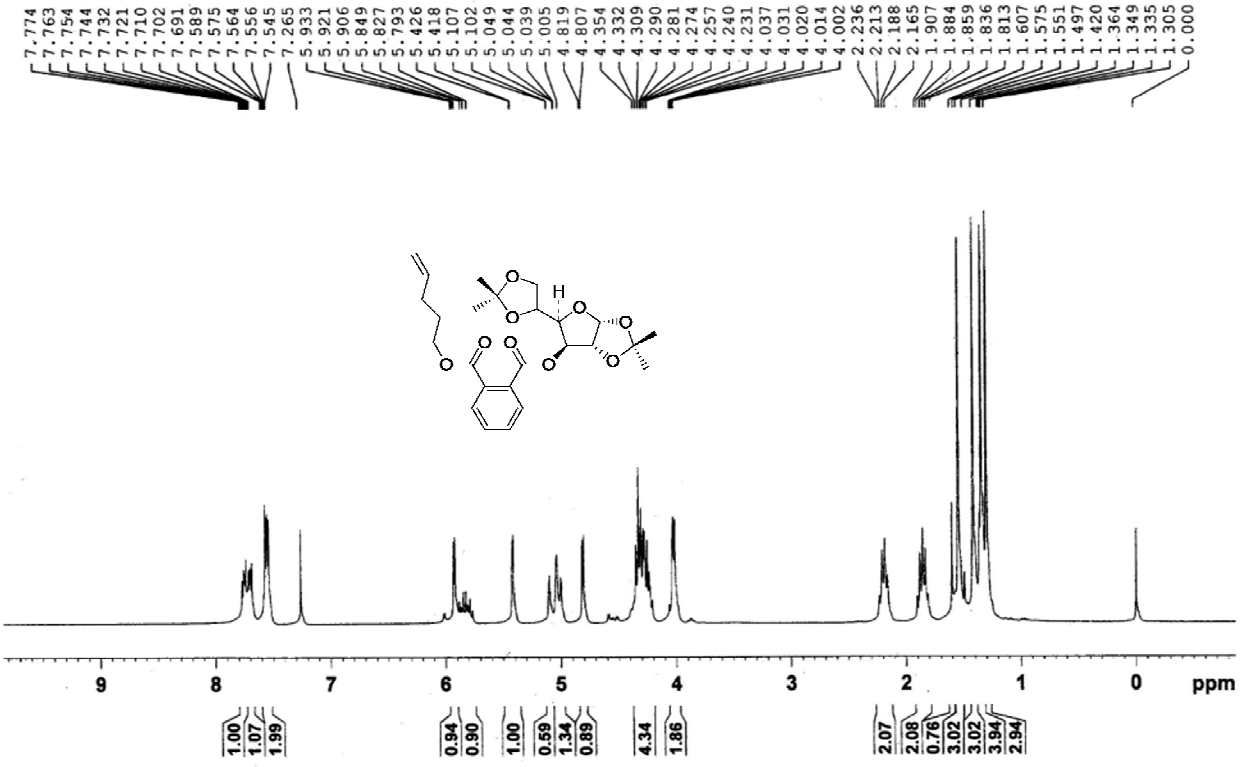
^{13}C NMR Spectra of 11d (75 MHz, $CDCl_3$)



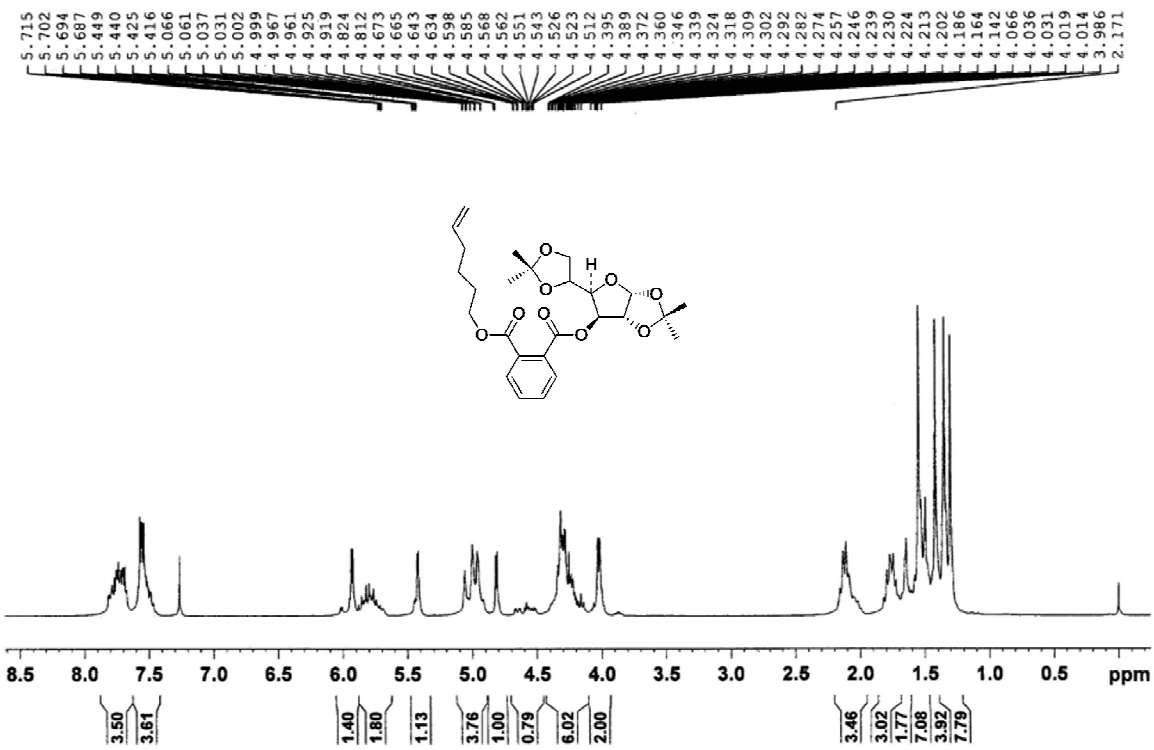
^{1}H NMR Spectra of 11e (300 MHz, $CDCl_3$)



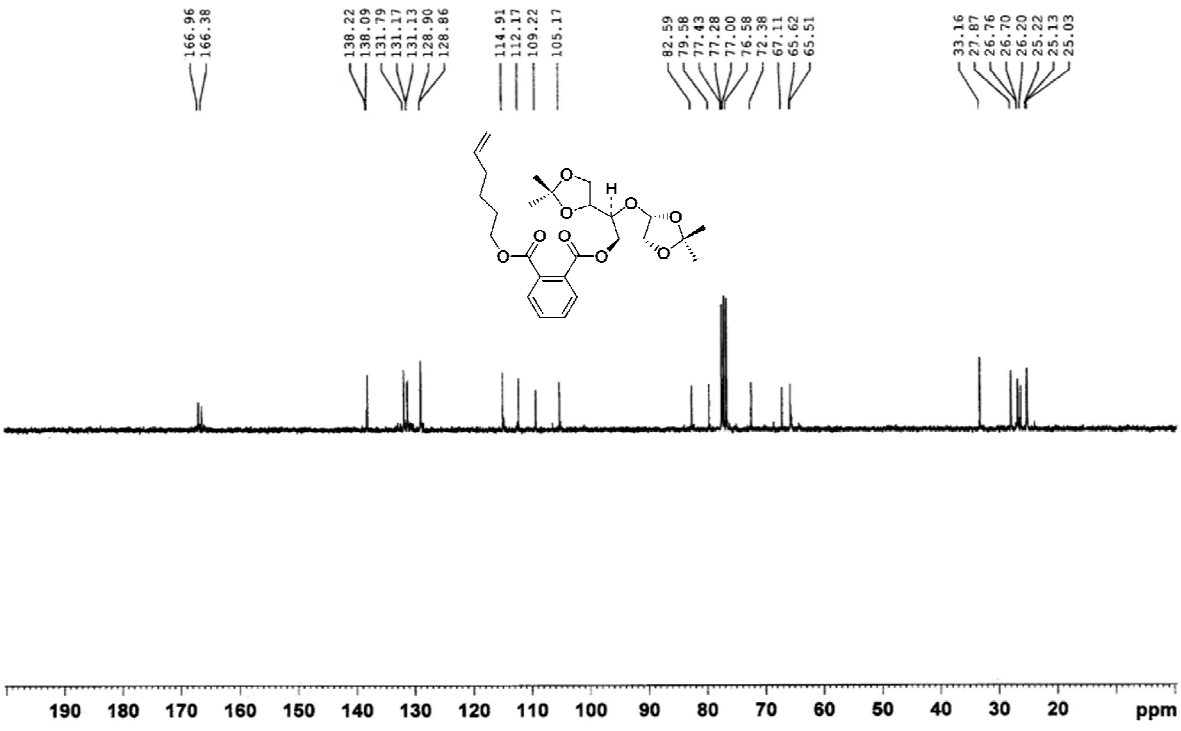
^{1}H NMR Spectra of 11e (300 MHz, $CDCl_3$)



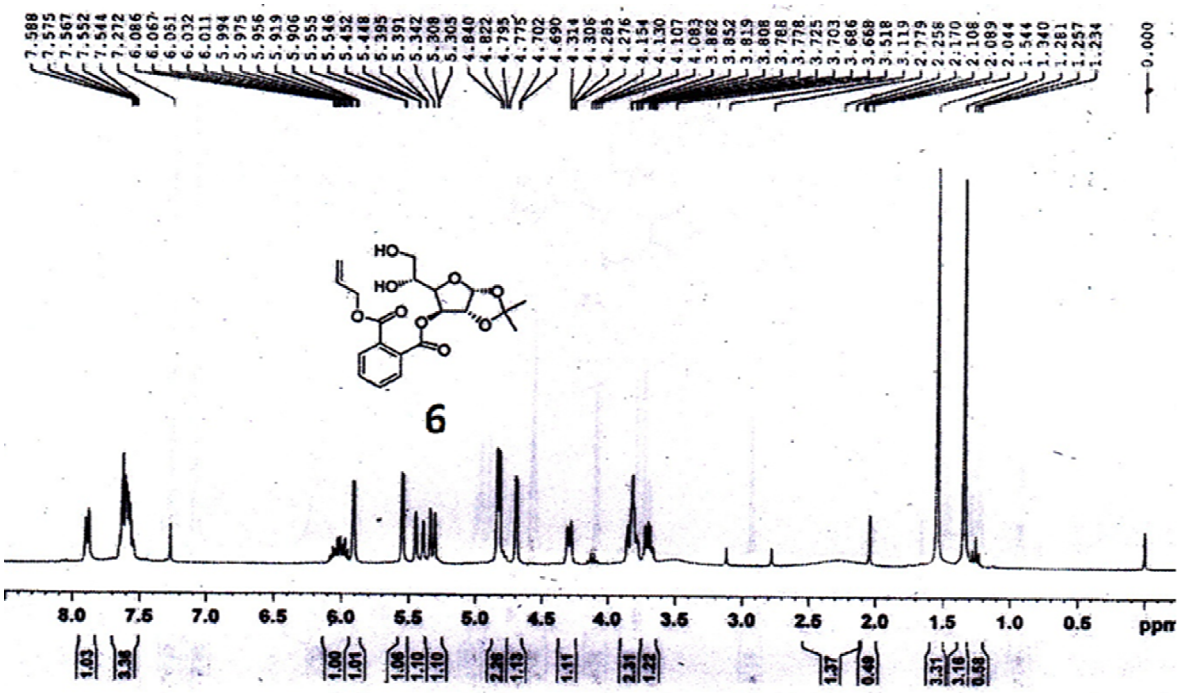
^{1}H NMR Spectra of 11f (300 MHz, $CDCl_3$)



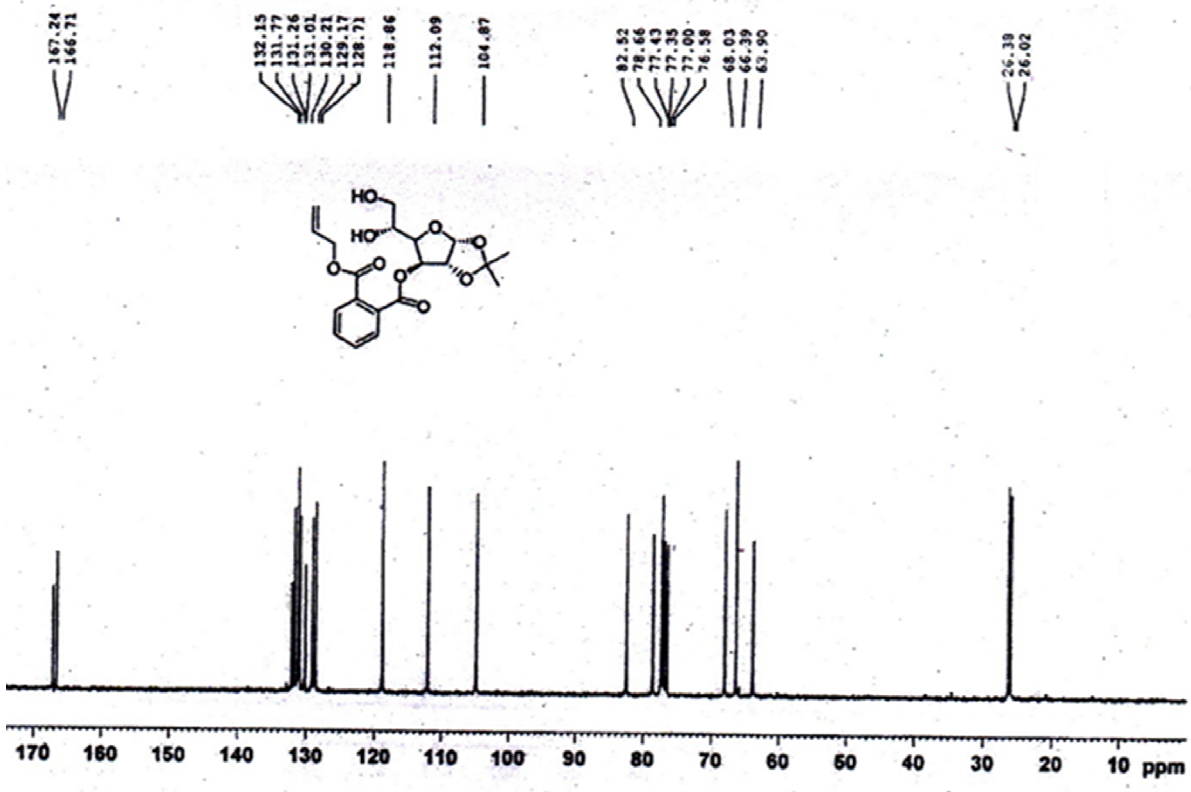
^{13}C NMR Spectra of 11f (75 MHz, $CDCl_3$)



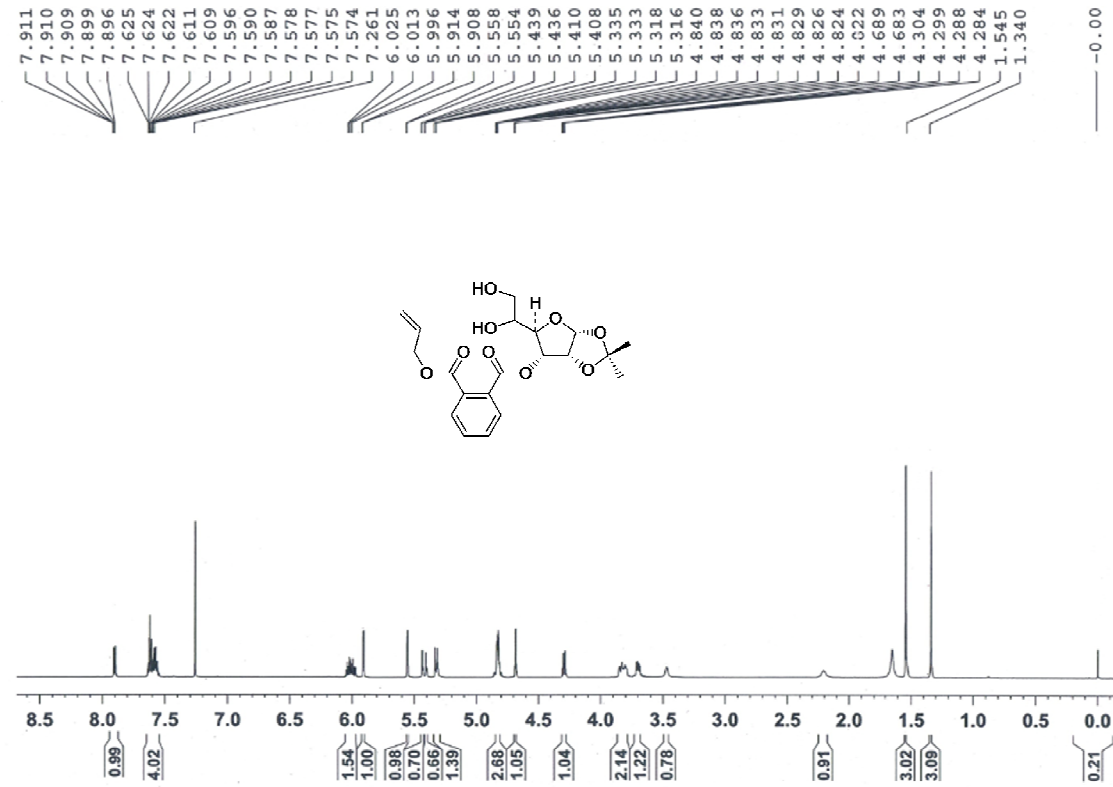
^{1}H NMR Spectra of 12a (300 MHz, $CDCl_3$)



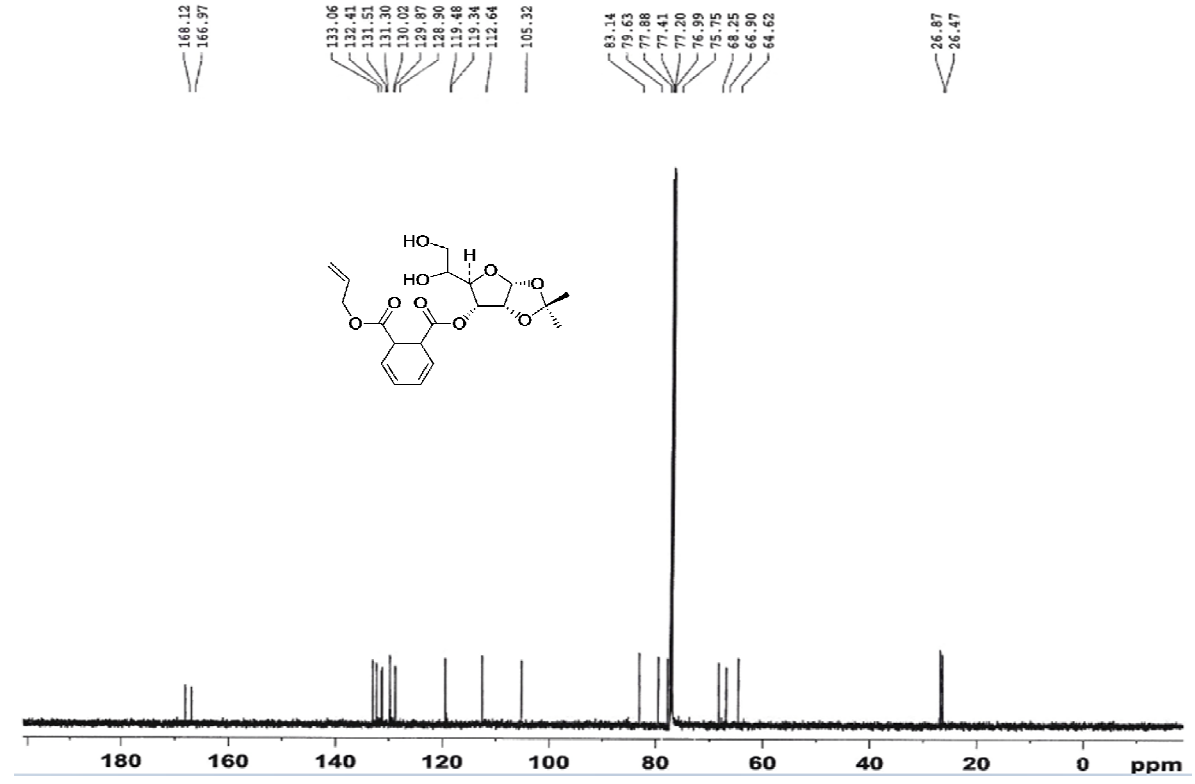
^{13}C NMR Spectra of 12a (75 MHz, $CDCl_3$)



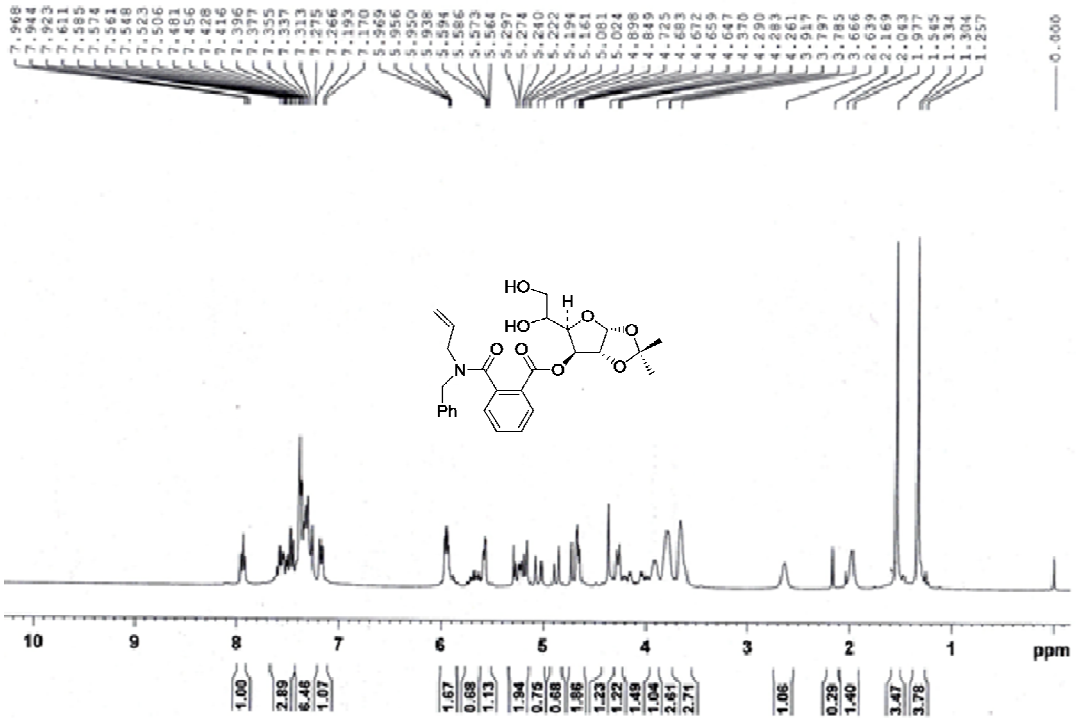
^{1}H NMR Spectra of 12b (300 MHz, $CDCl_3$)



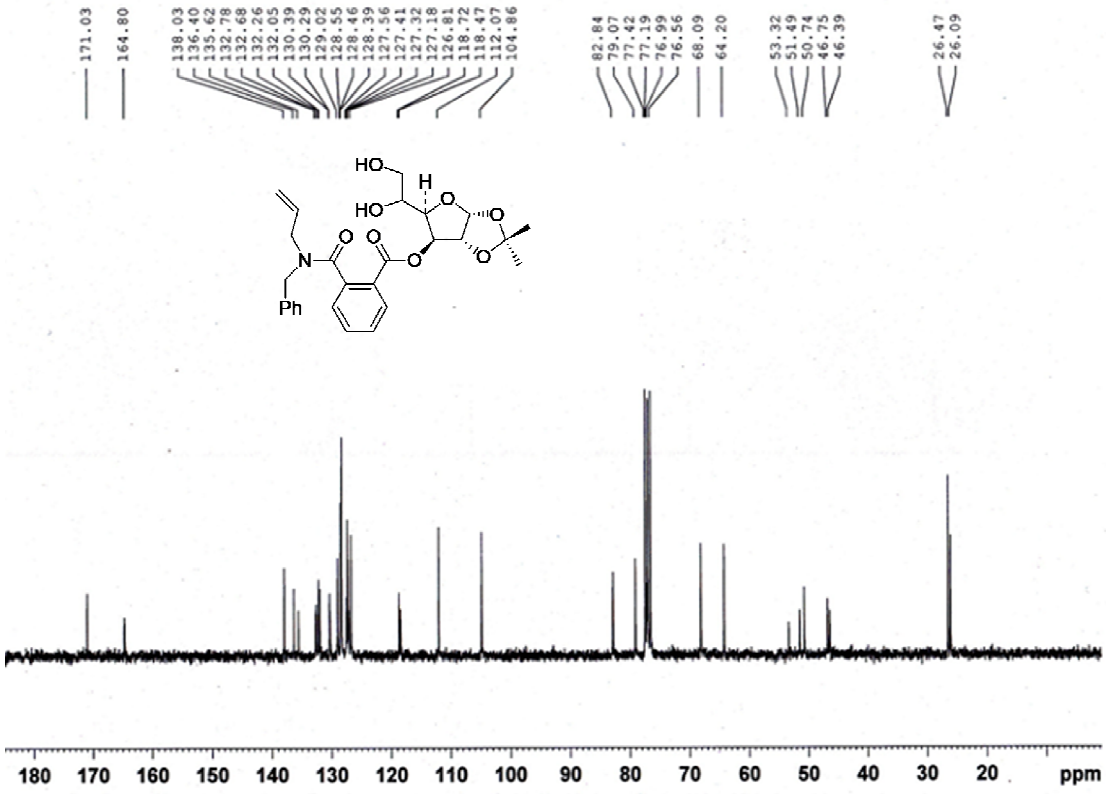
^{1}H NMR Spectra of 12b (75 MHz, $CDCl_3$)



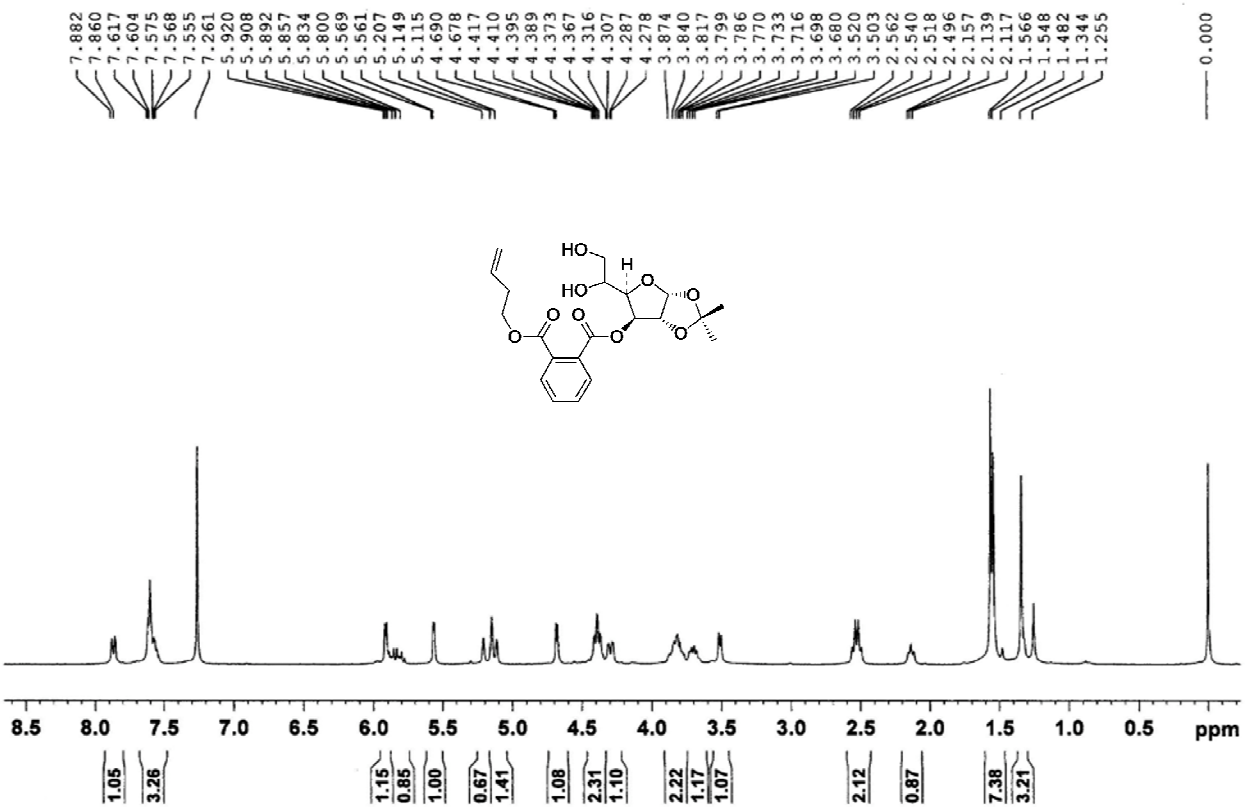
^{1}H NMR spectra of 12c (300 MHz, $CDCl_3$)



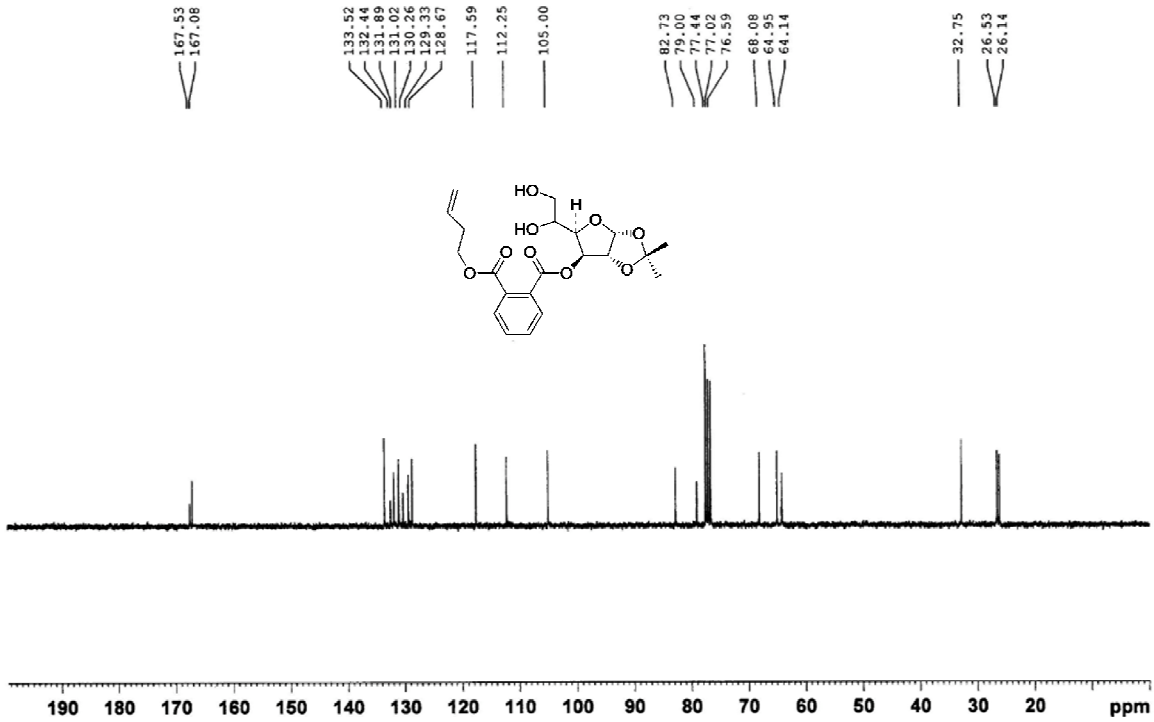
^{13}C NMR spectra of 12c (75 MHz, $CDCl_3$)



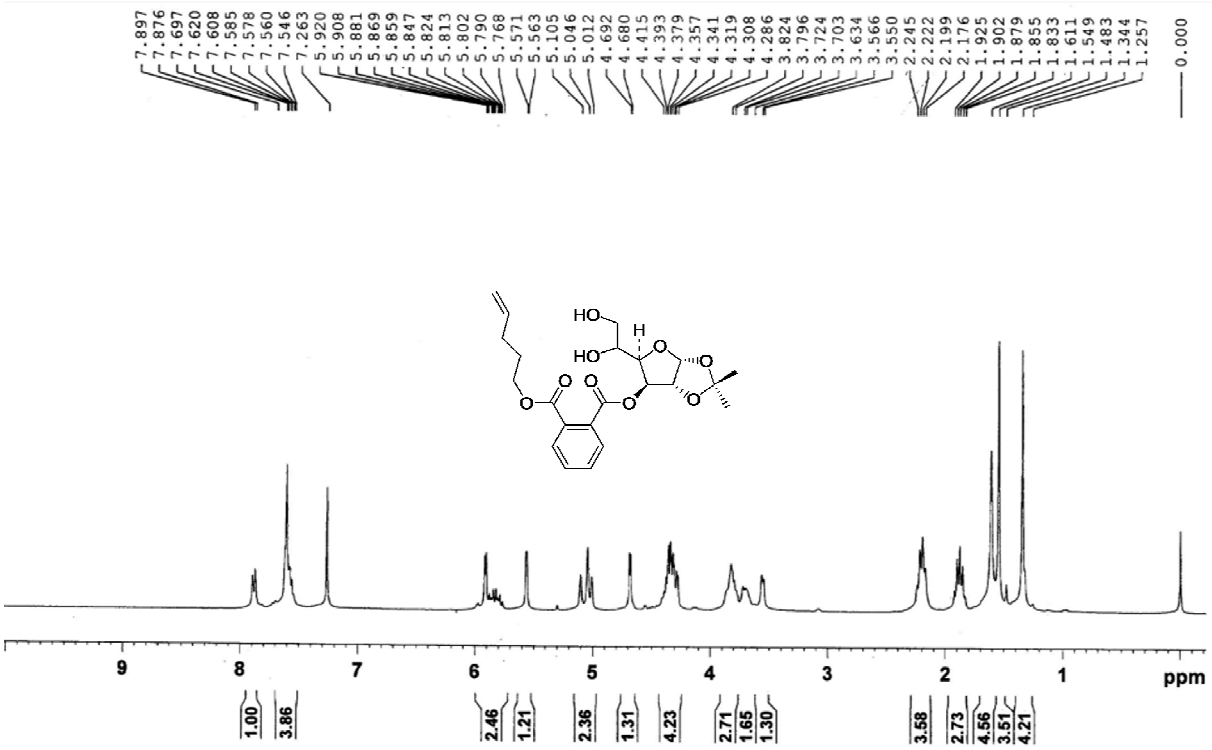
^{1}H NMR spectra of 12d (300 MHz, $CDCl_3$)



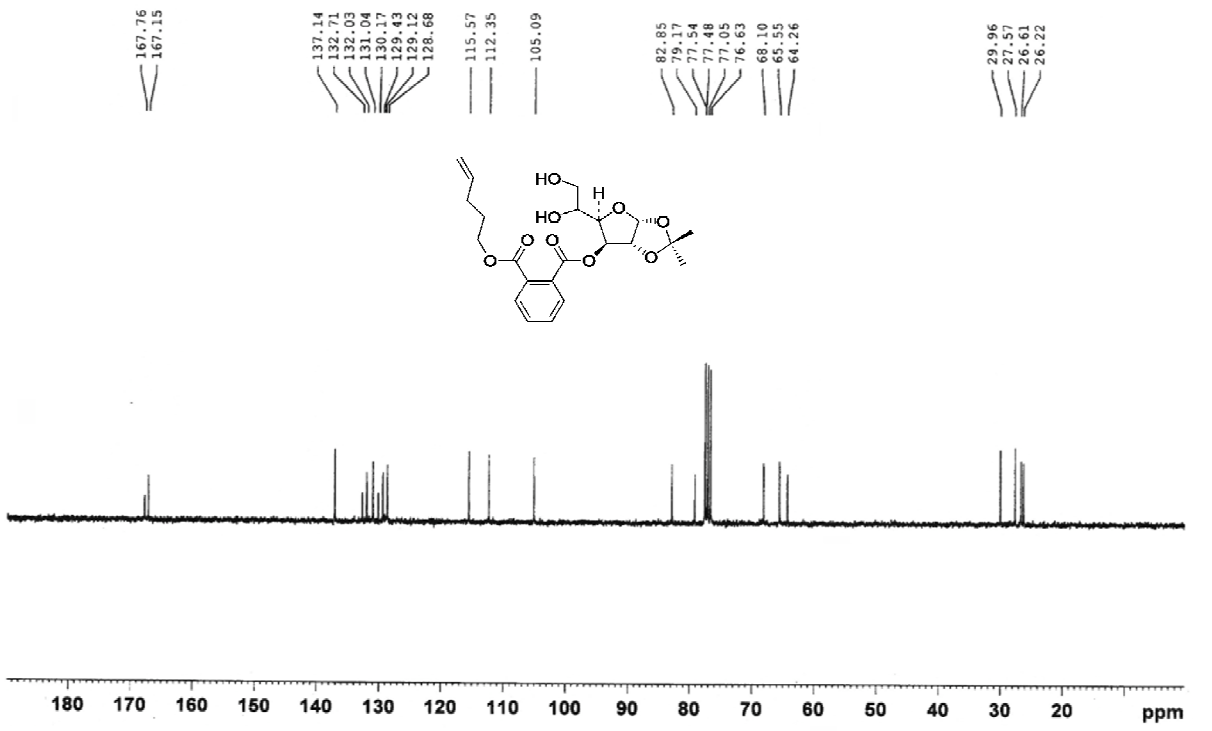
^{13}C NMR spectra of 12d (75 MHz, $CDCl_3$)



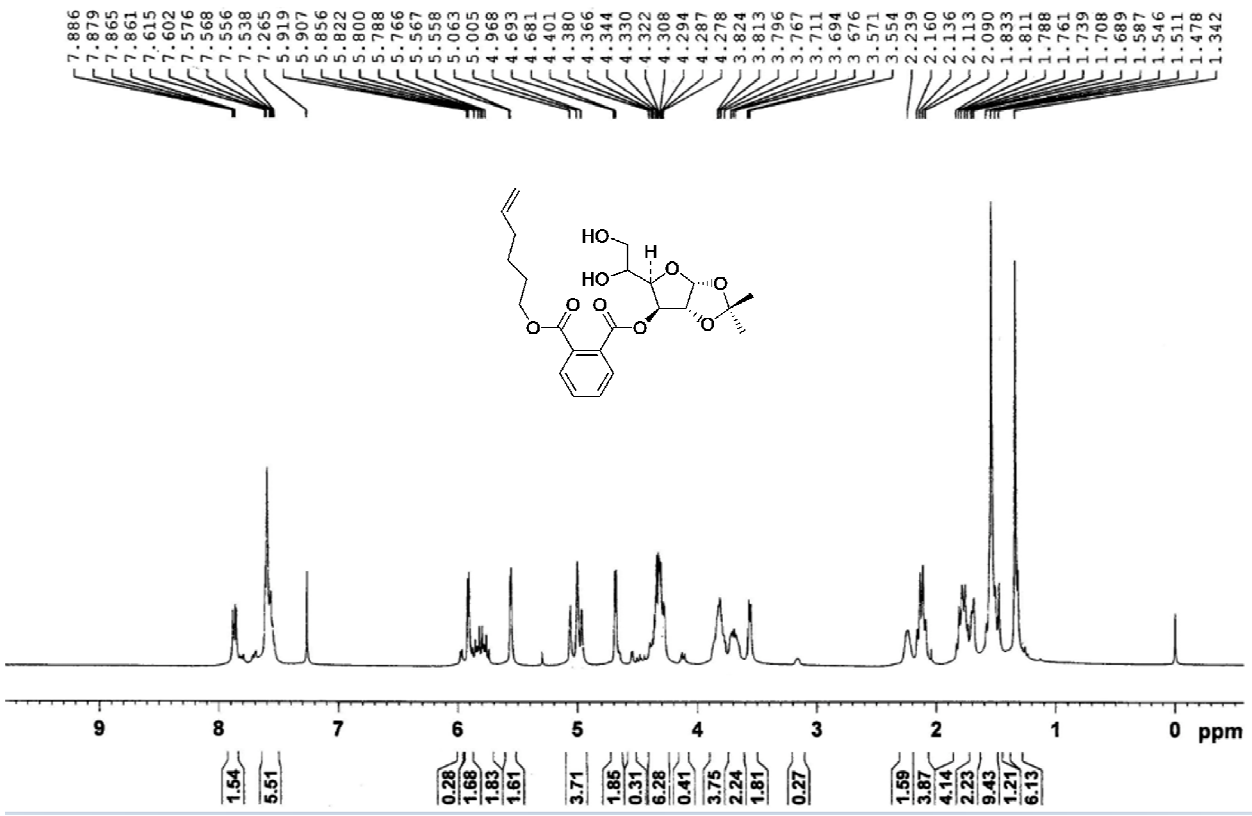
^{1}H NMR spectra of 12e (300 MHz, $CDCl_3$)



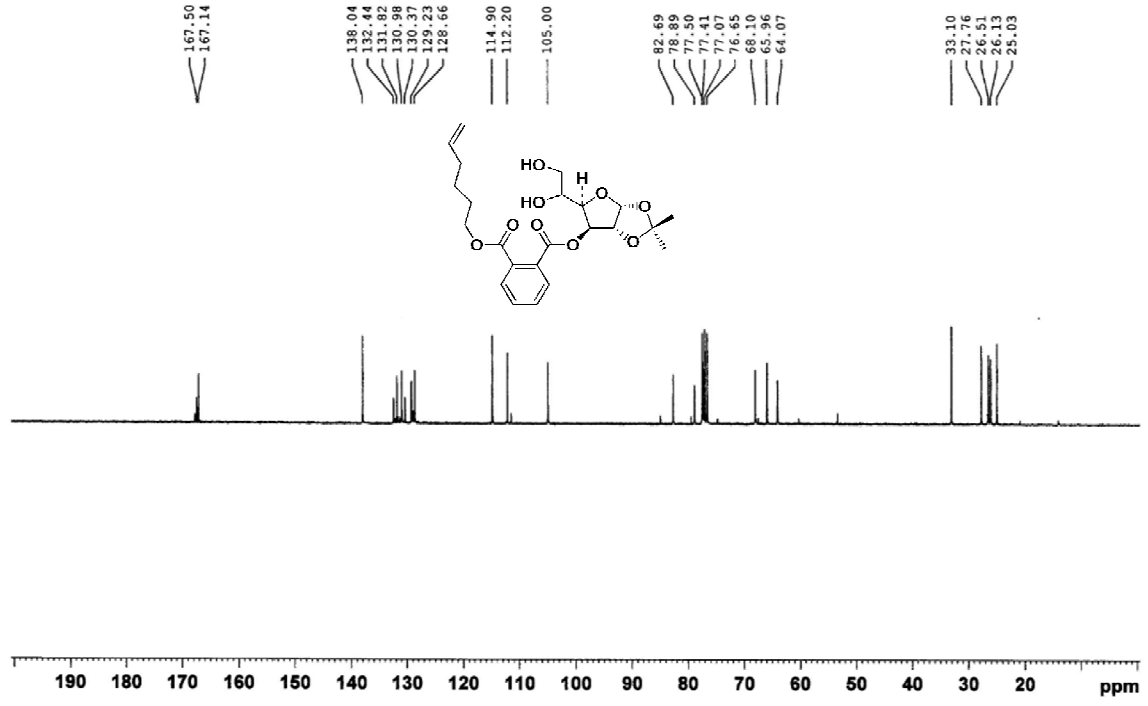
^{13}C NMR spectra of 12e (75 MHz, $CDCl_3$)



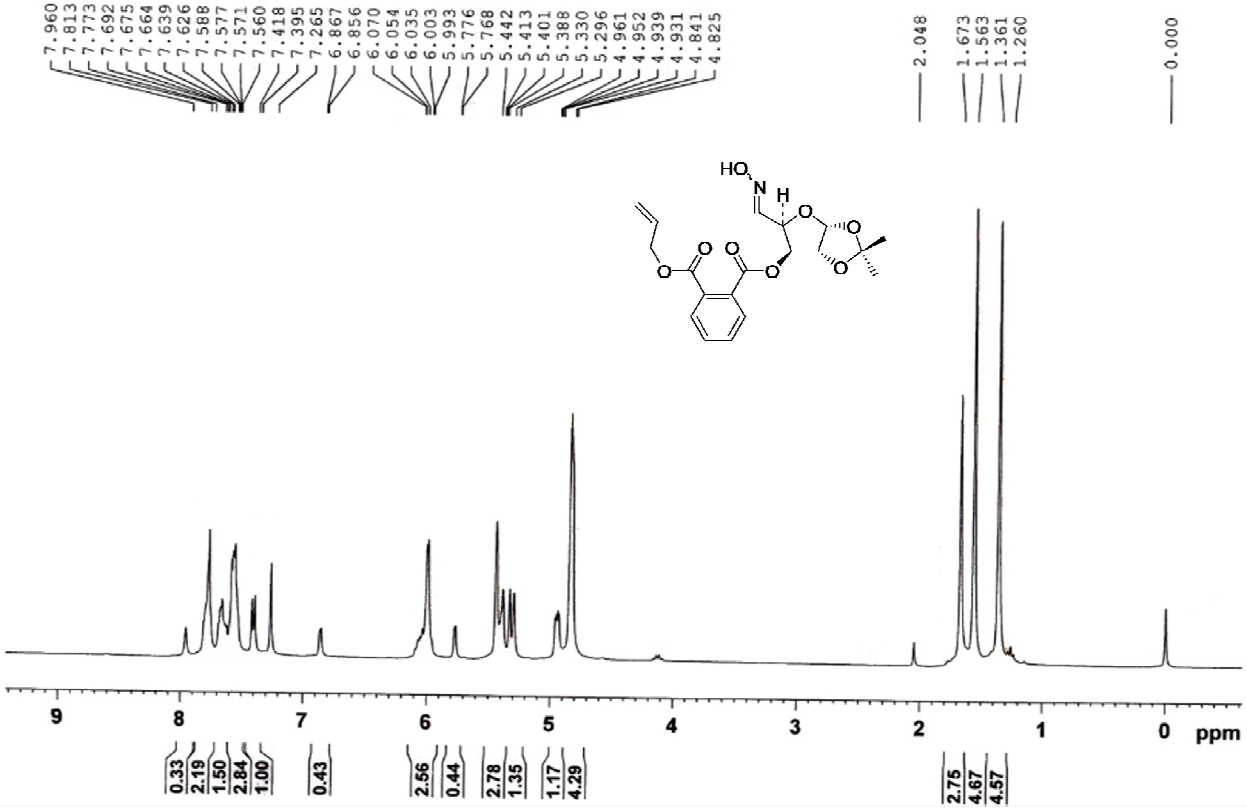
^{1}H NMR spectra of 12f (300 MHz, $CDCl_3$)



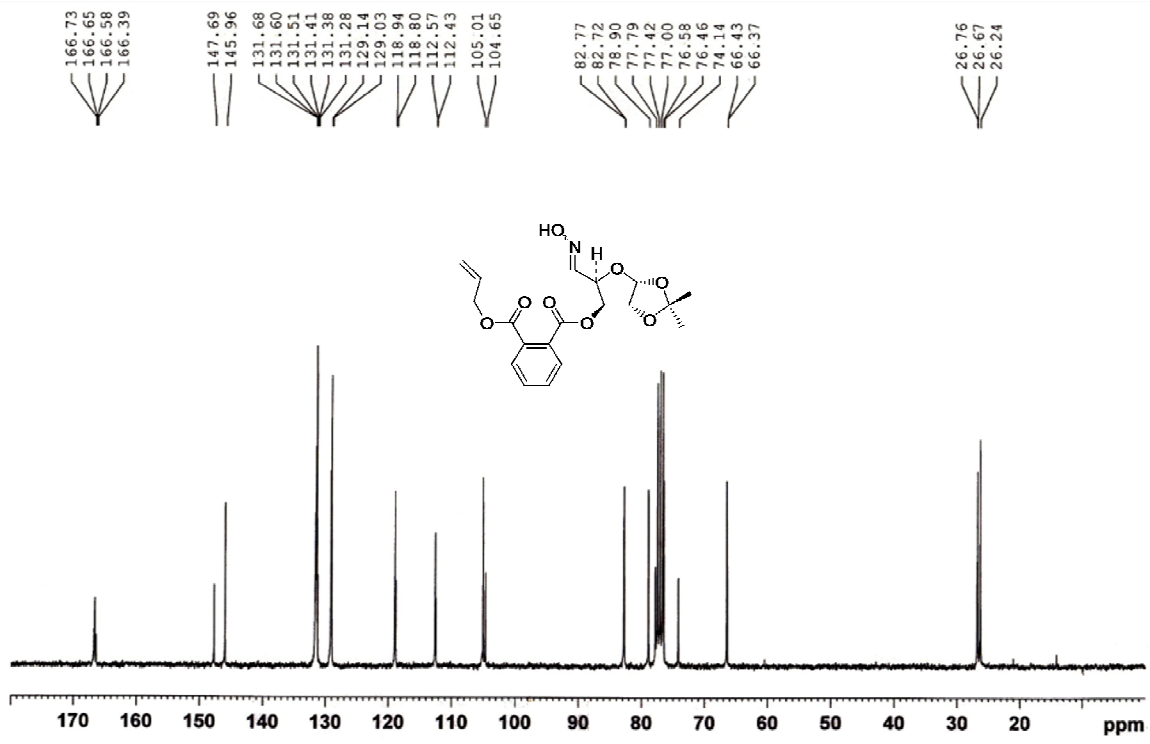
^{13}C NMR spectra of 12f (75 MHz, $CDCl_3$)



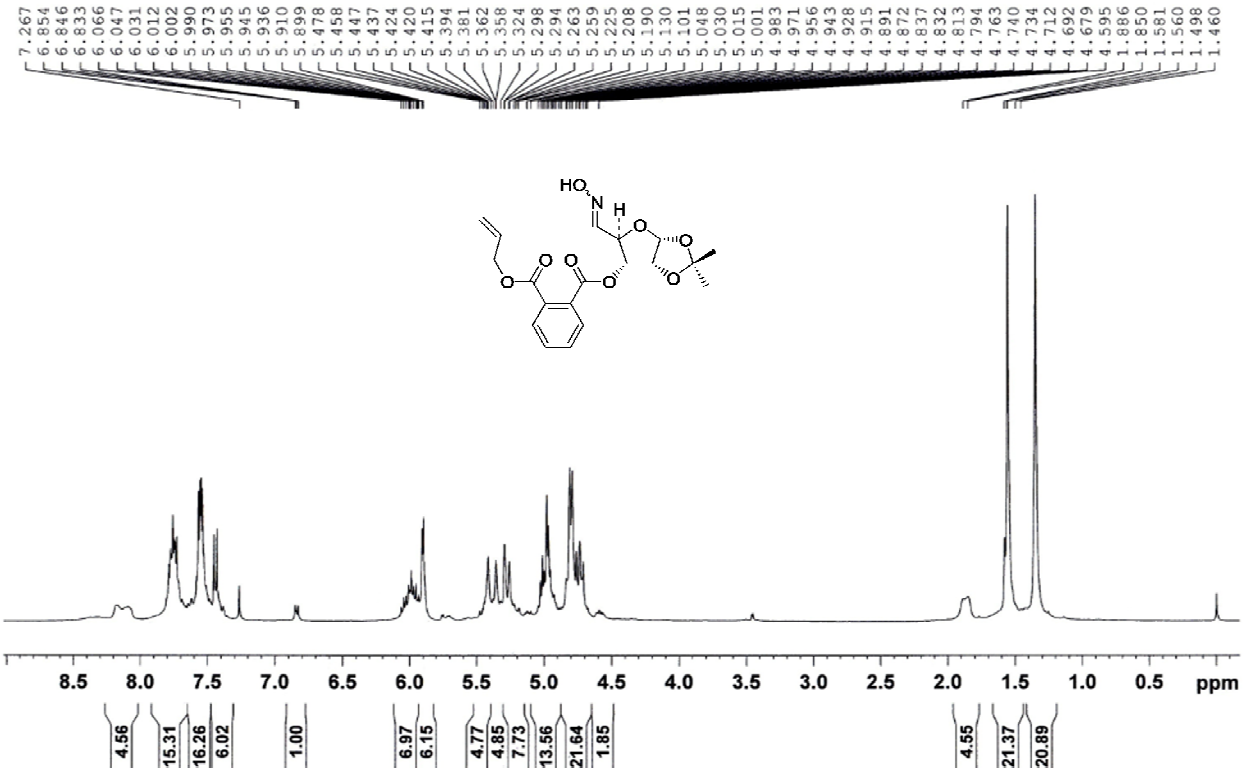
^{1}H NMR spectra of 13a (300 MHz, $CDCl_3$)



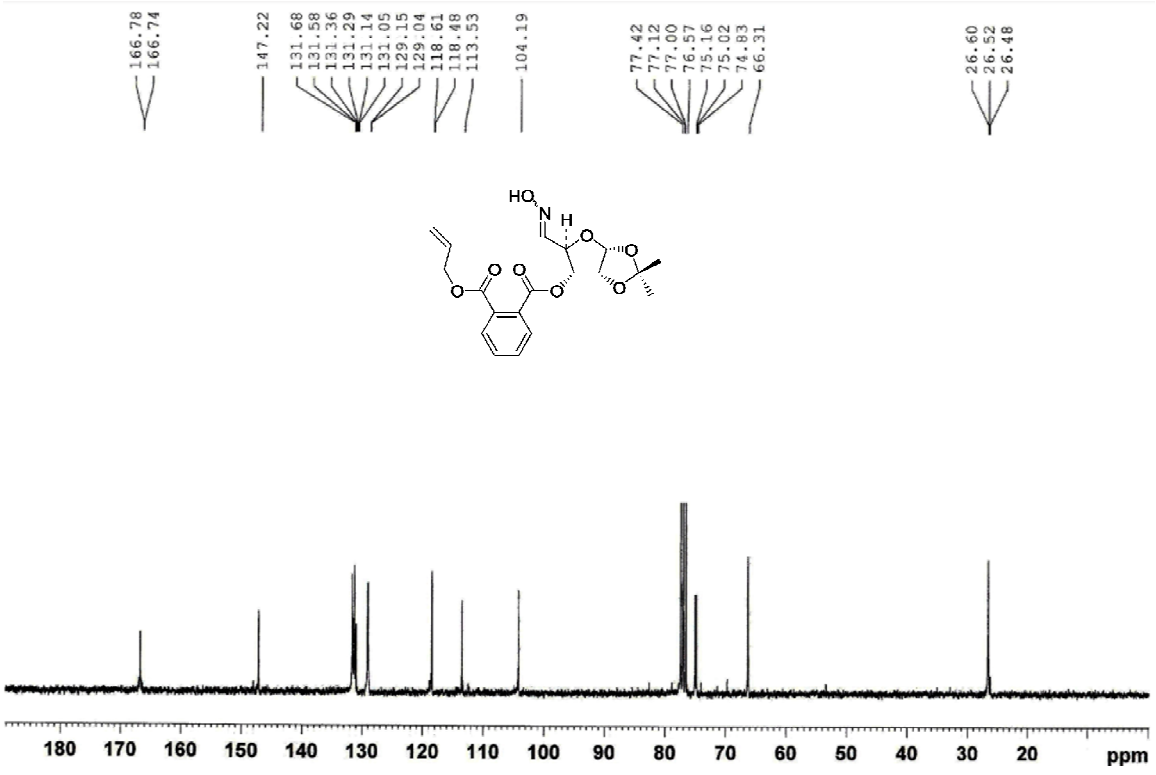
^{13}C NMR spectra of 13a (75 MHz, $CDCl_3$)



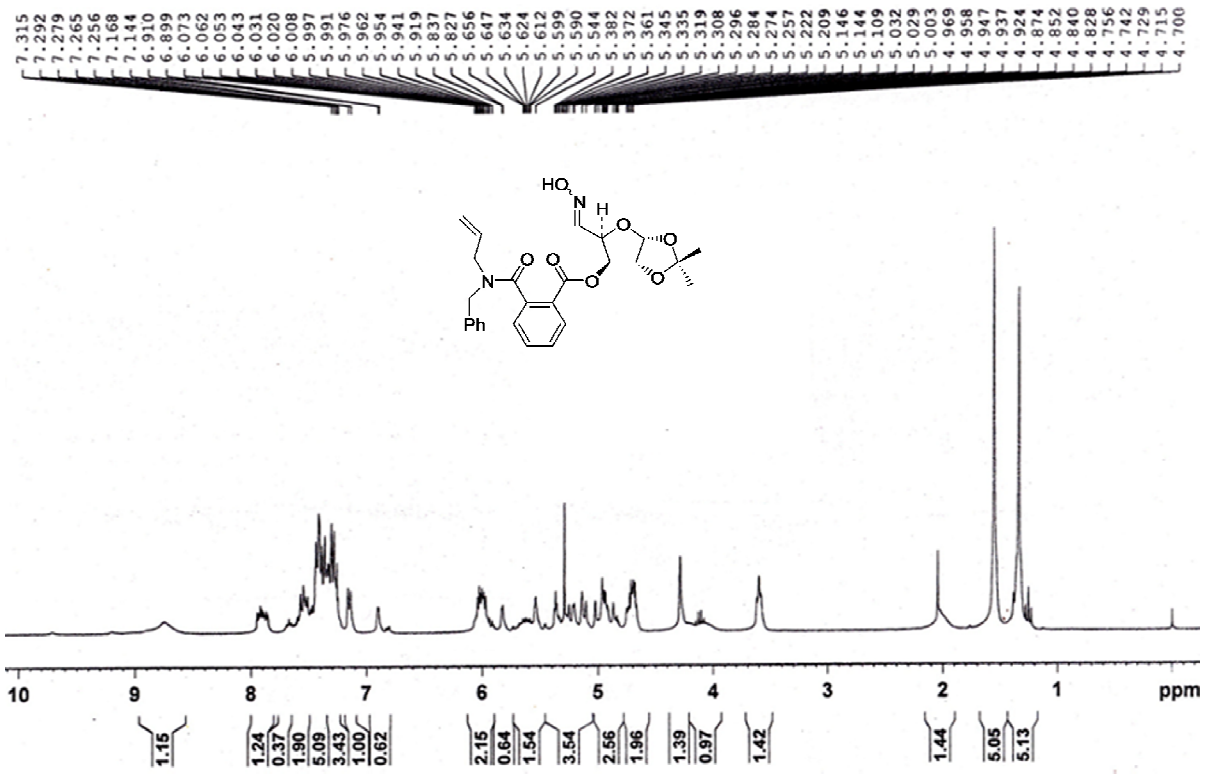
^{1}H NMR spectra of 13b (300 MHz, $CDCl_3$)



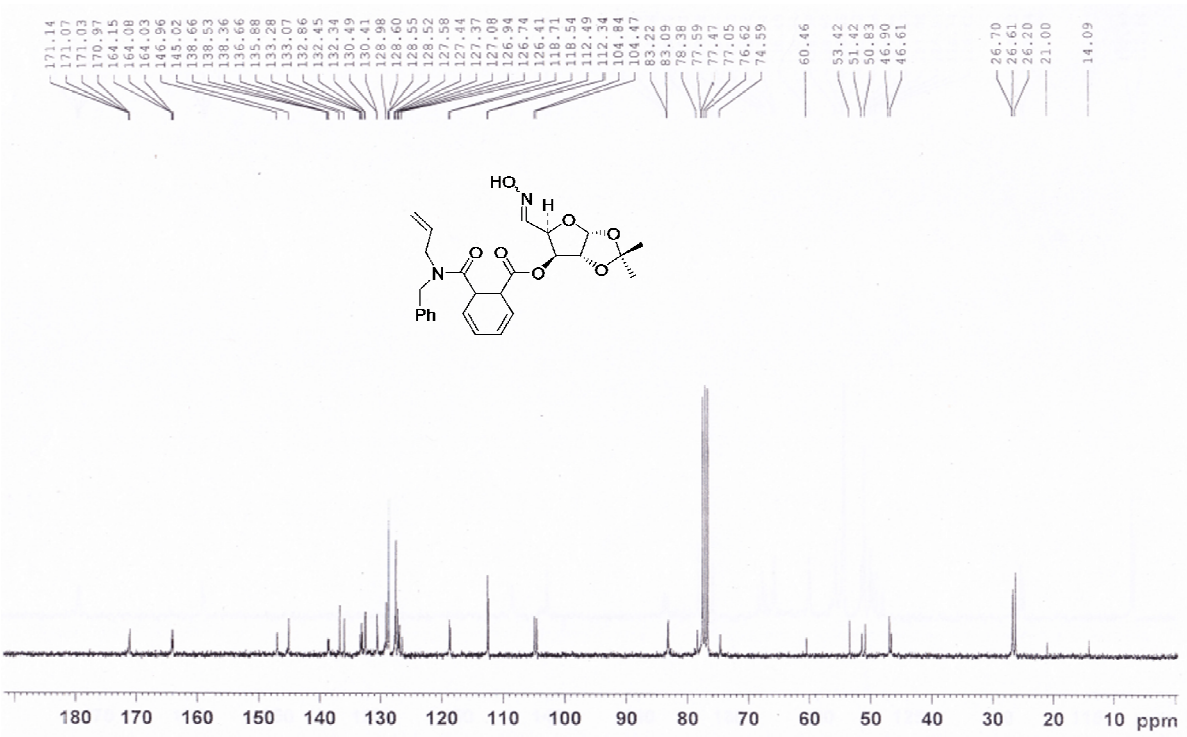
^{13}C NMR spectra of 13b (75 MHz, $CDCl_3$)



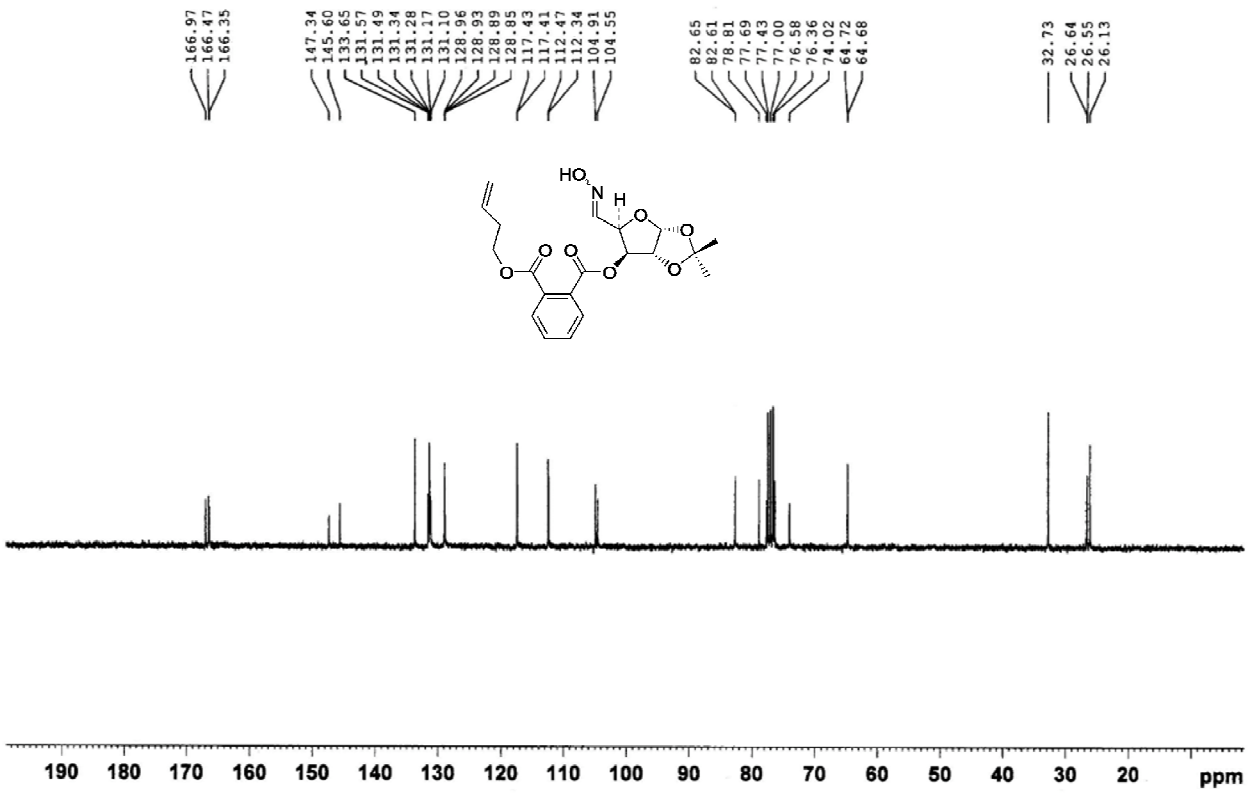
^{1}H NMR spectra of 13c (300 MHz, $CDCl_3$)



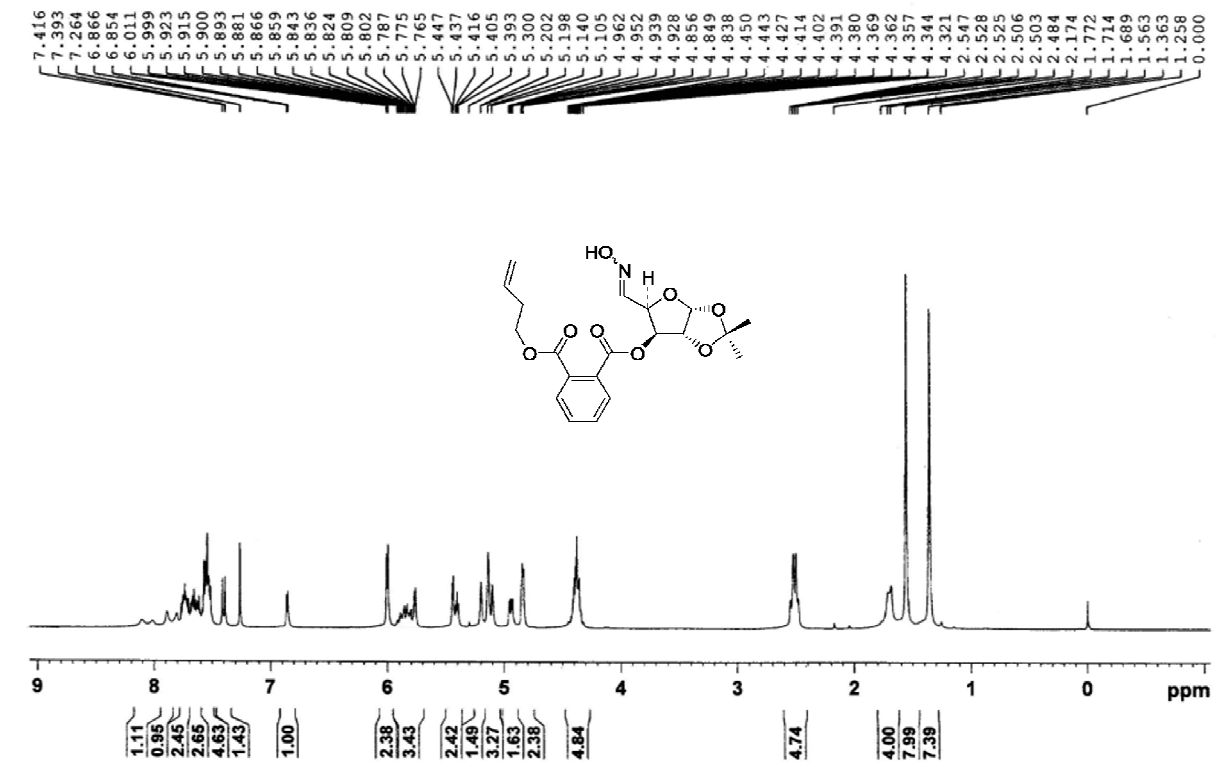
^{13}C NMR spectra of 13c (75 MHz, $CDCl_3$)



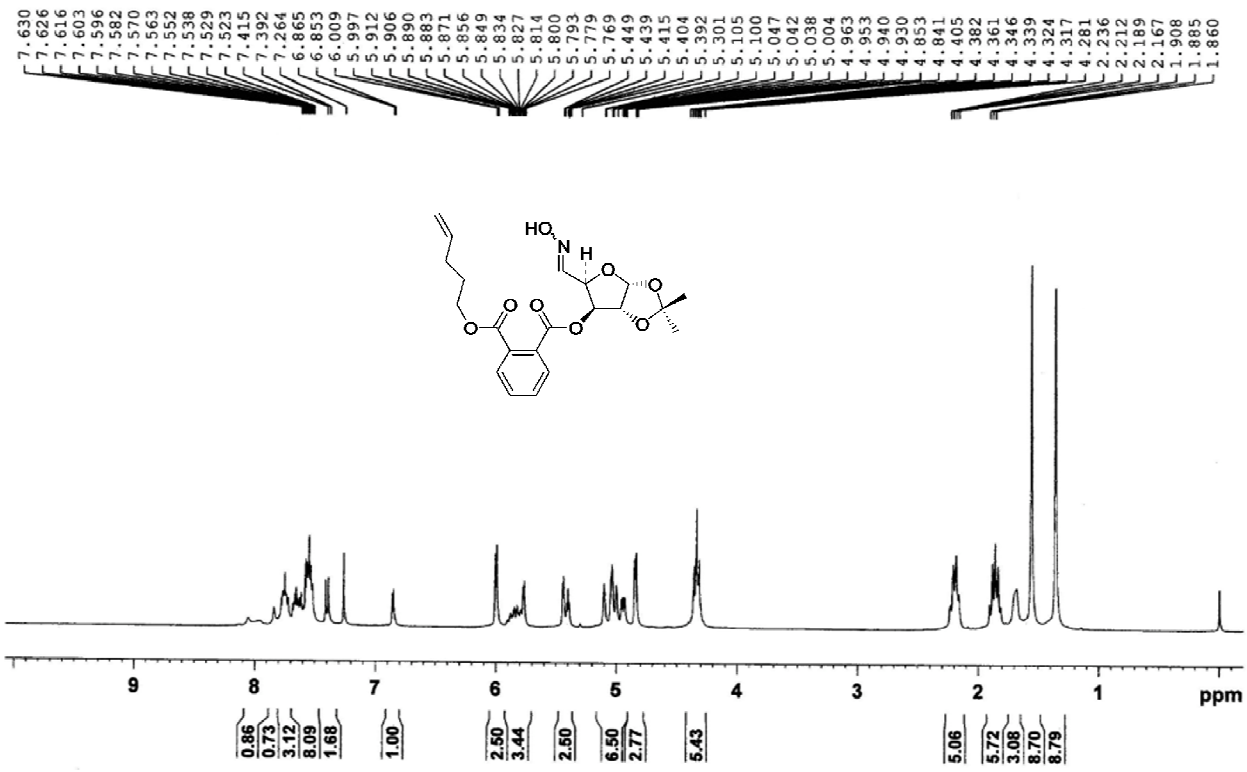
^{13}C NMR spectra of 13d (75 MHz, $CDCl_3$)



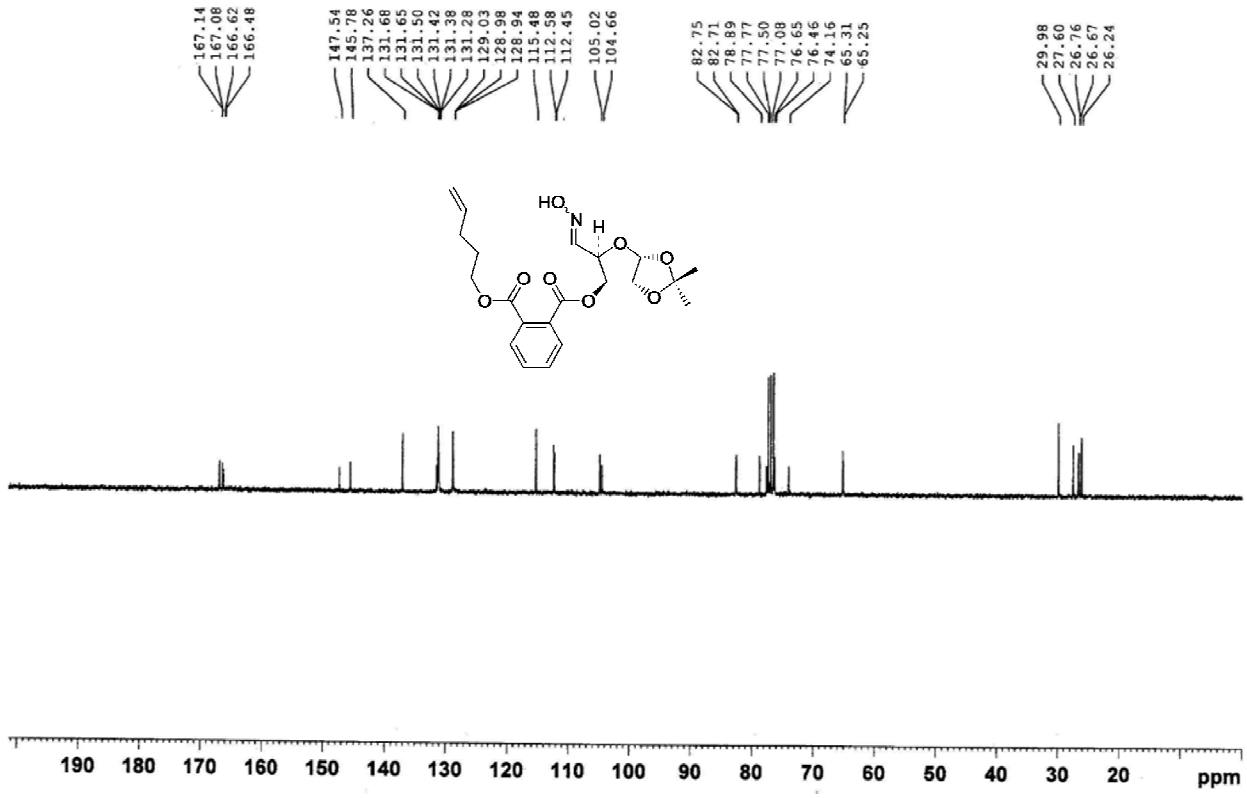
^{1}H NMR spectra of 13d (300 MHz, $CDCl_3$)



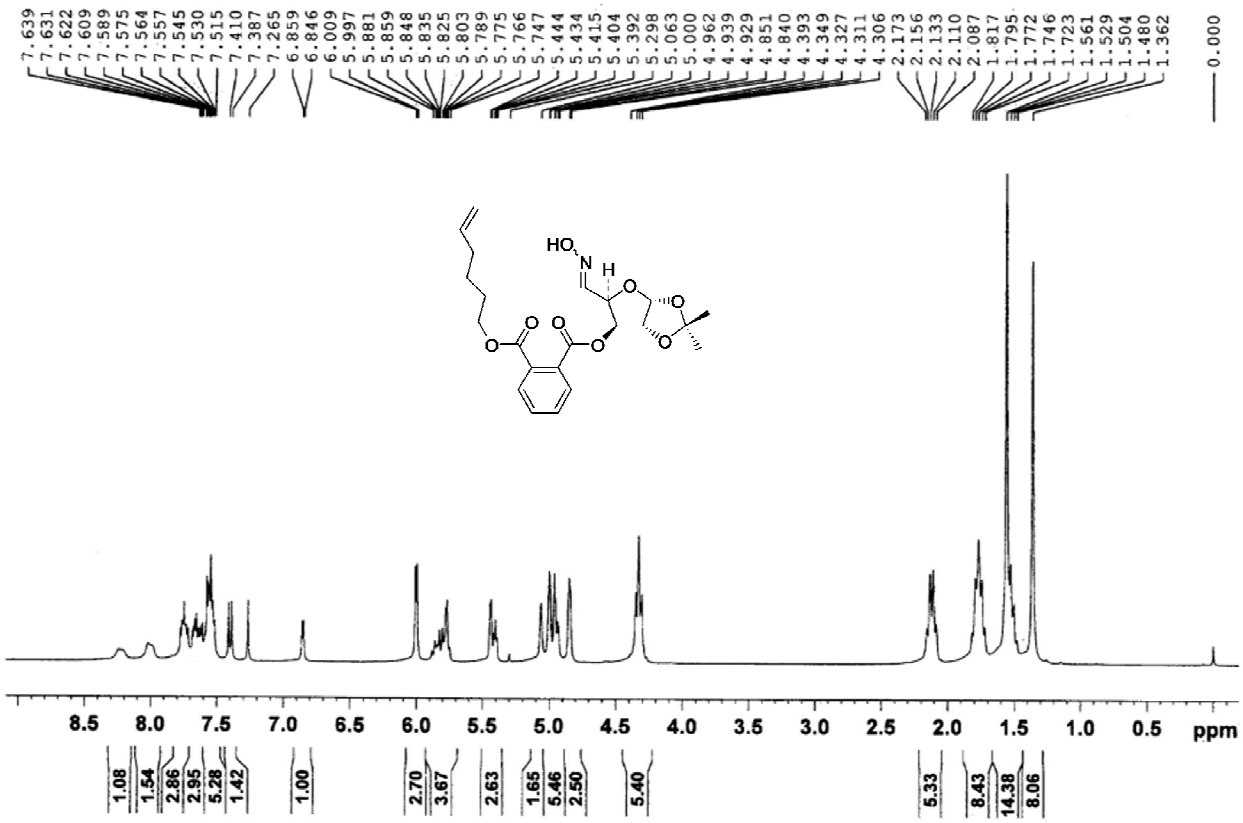
^{1}H NMR spectra of 13e (300 MHz, $CDCl_3$)



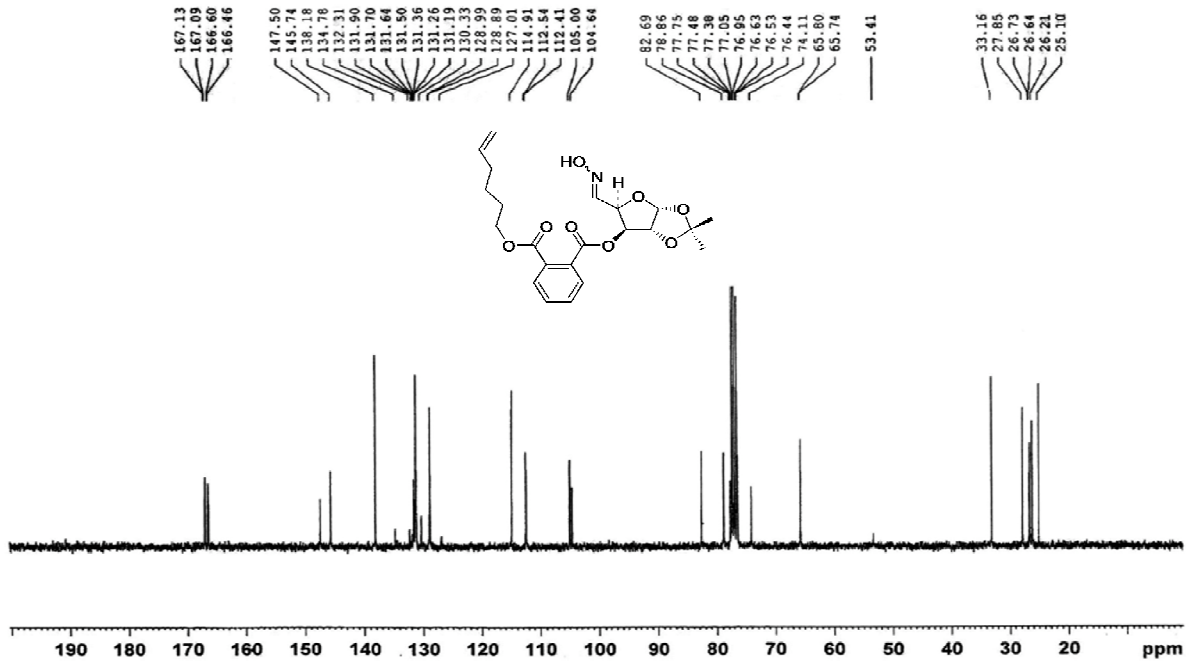
^{13}C NMR spectra of 13e (75 MHz, $CDCl_3$)



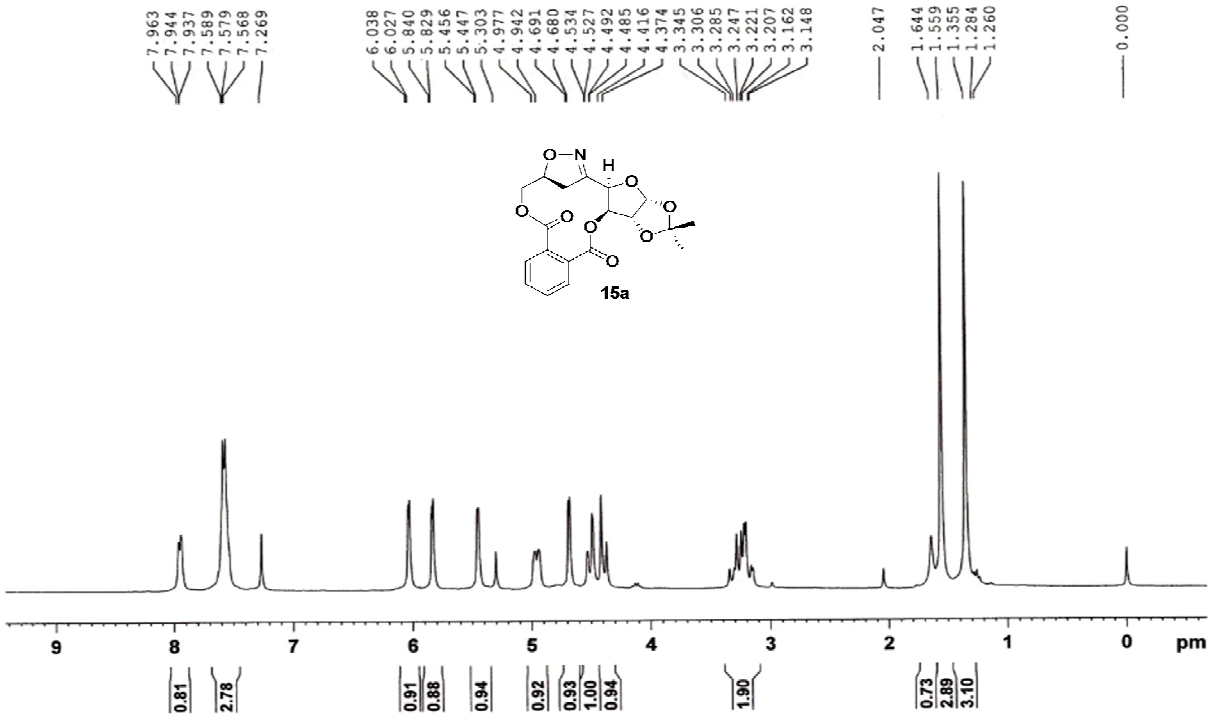
^{1}H NMR spectra of 13f (300 MHz, $CDCl_3$)



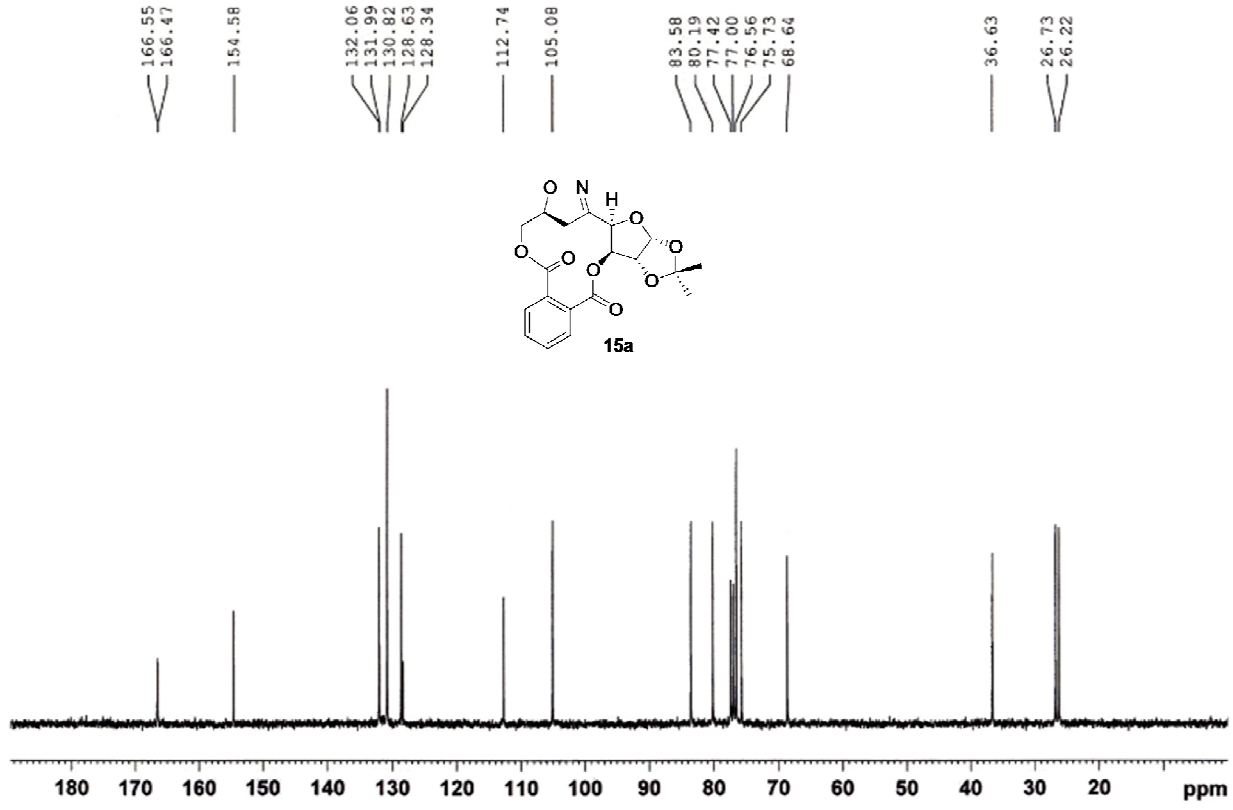
^{13}C NMR spectra of 13f (75 MHz, $CDCl_3$)



^{1}H NMR spectra of 15a (300 MHz, $CDCl_3$)



^{13}C NMR spectra of 15a (75 MHz, $CDCl_3$)



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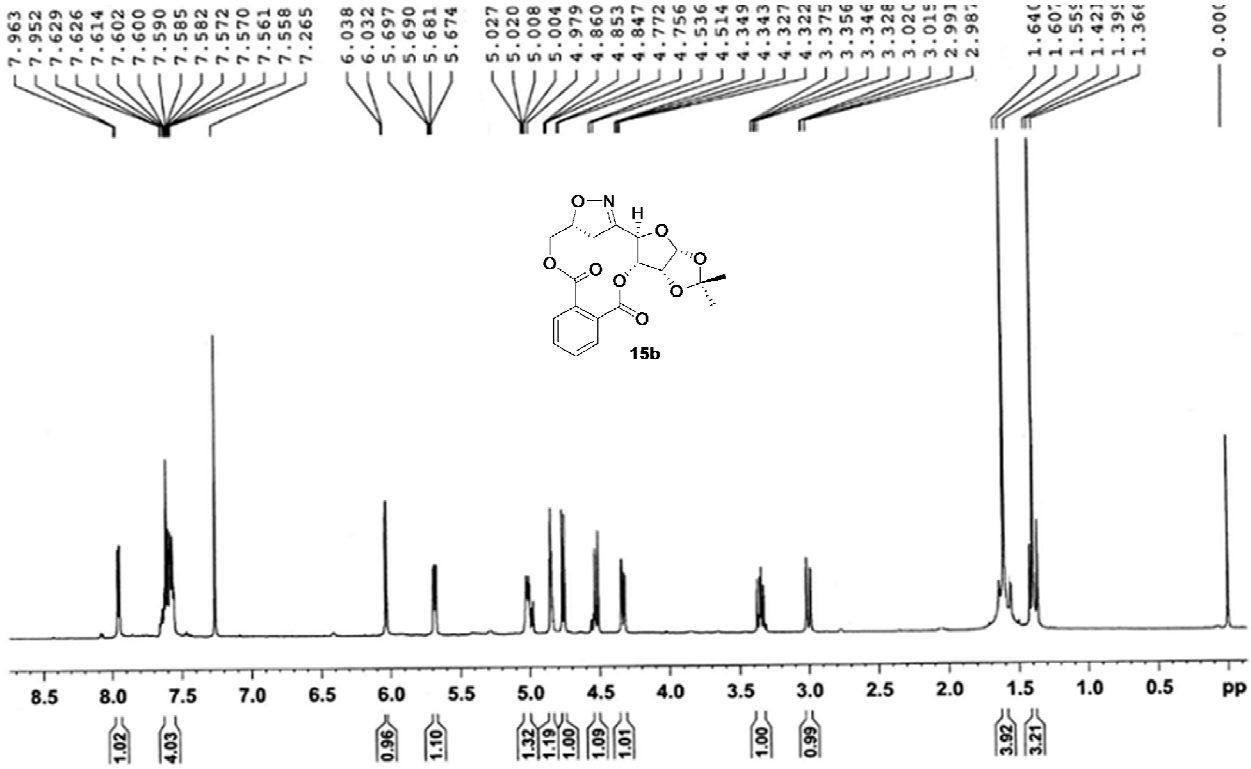
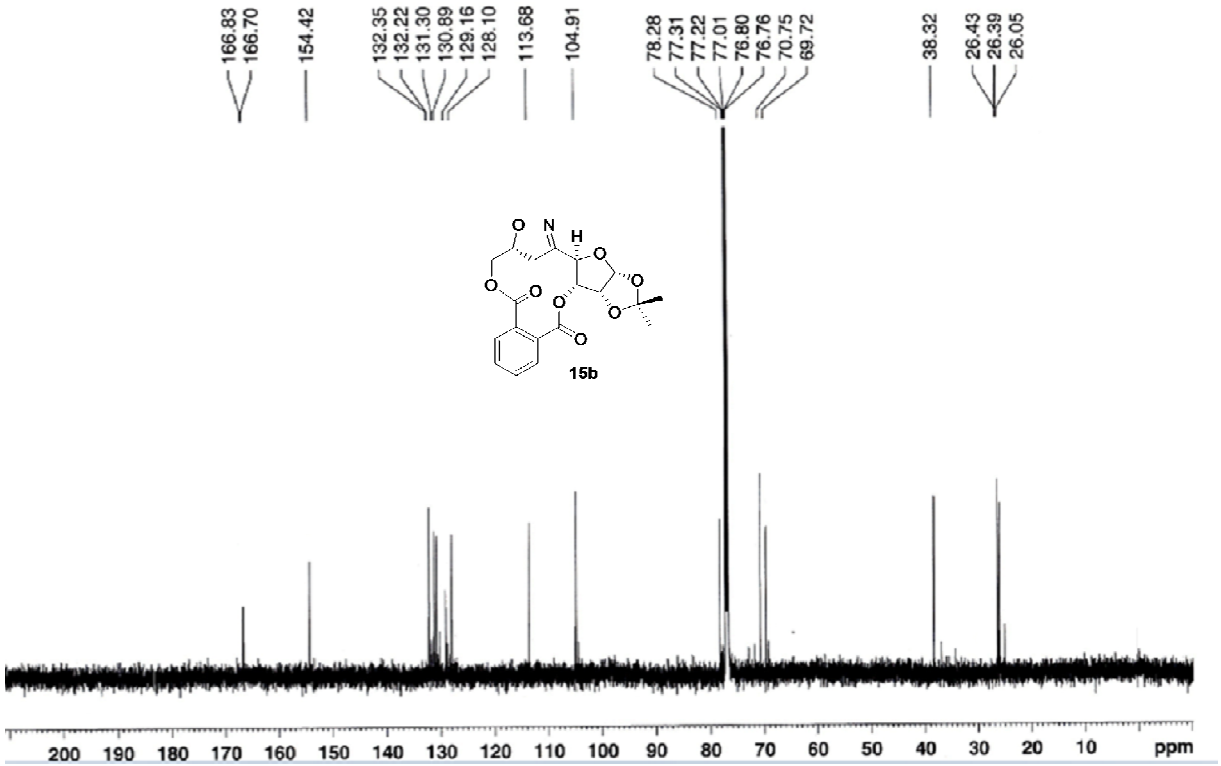
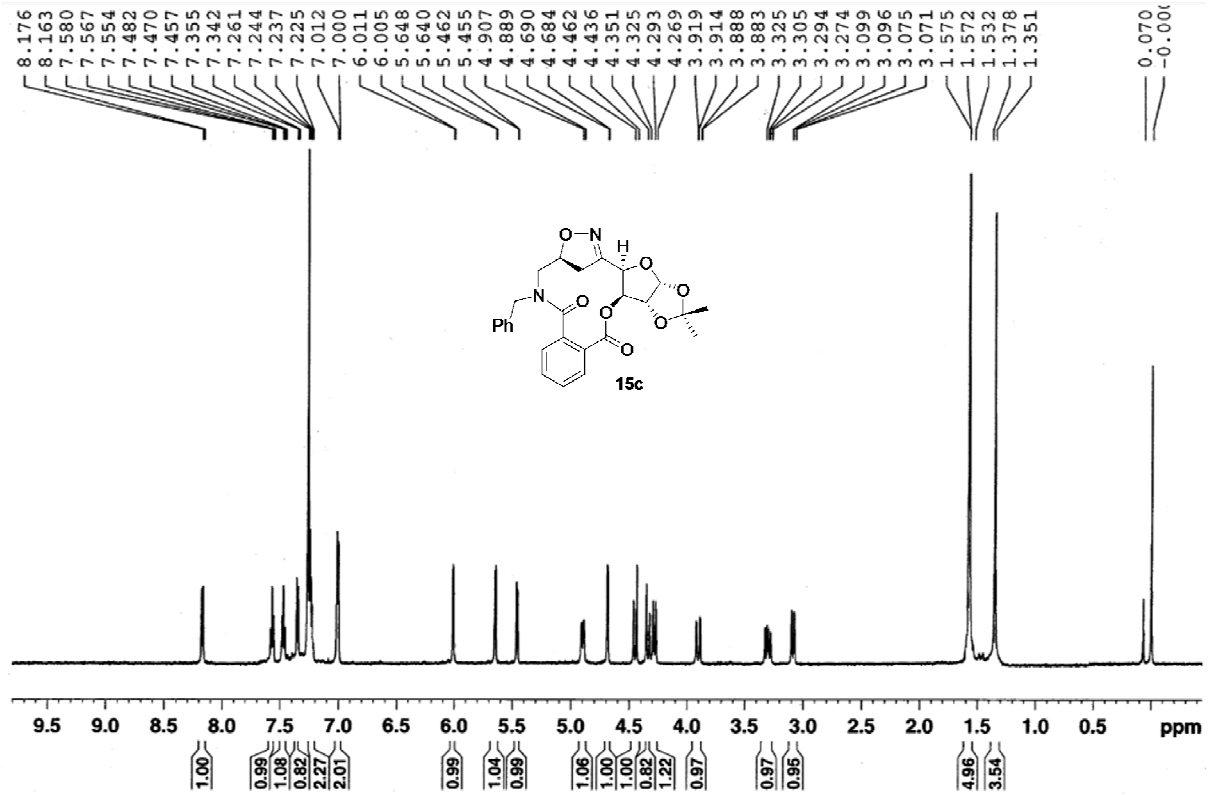


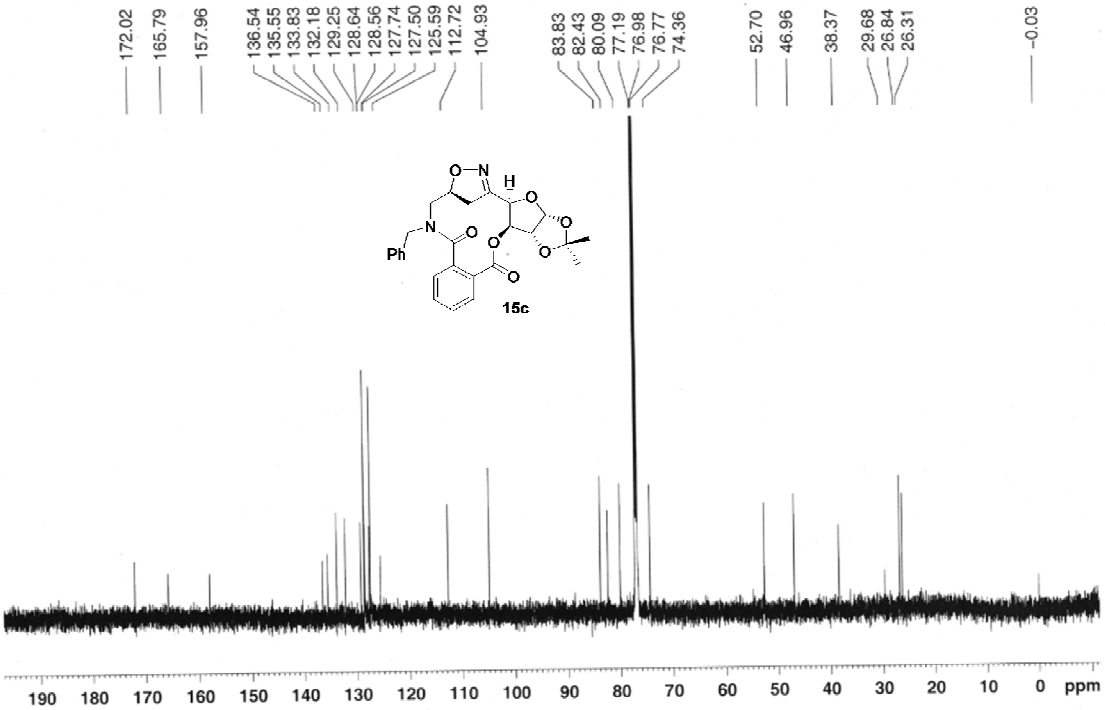
^{13}C NMR spectra of 15b (75 MHz, $CDCl_3$)



^{1}H NMR spectra of 15c (300 MHz, $CDCl_3$)



^{13}C NMR spectra of 15c (75 MHz, $CDCl_3$)



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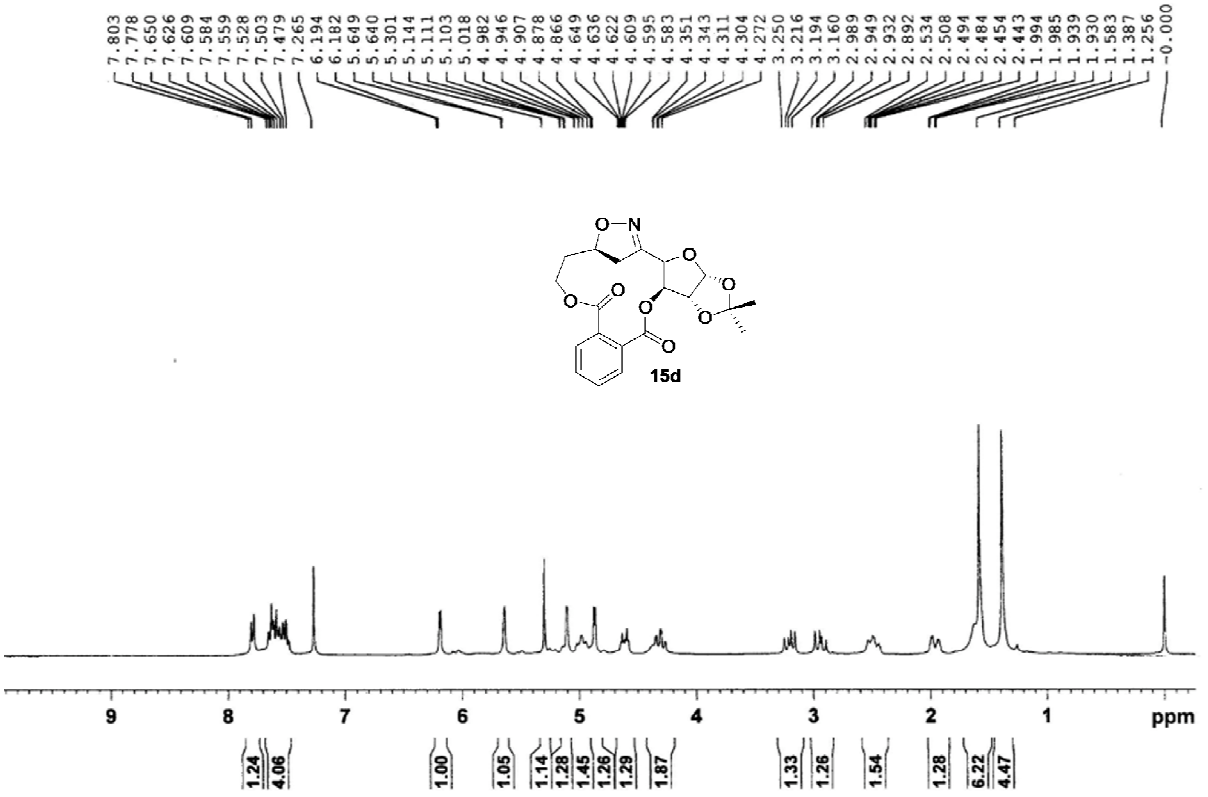
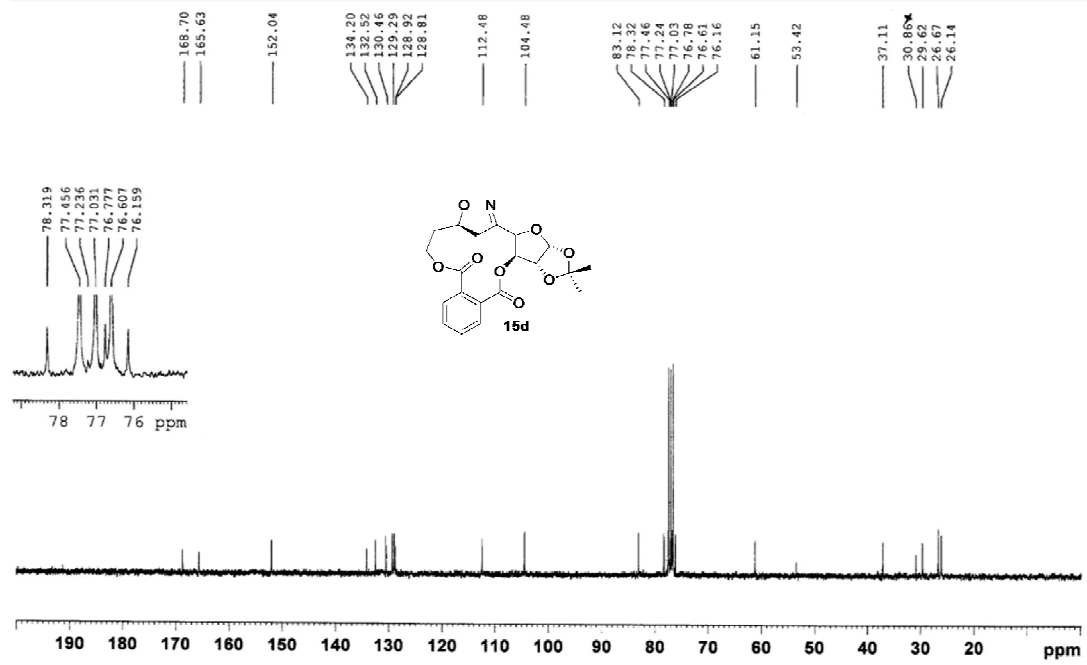
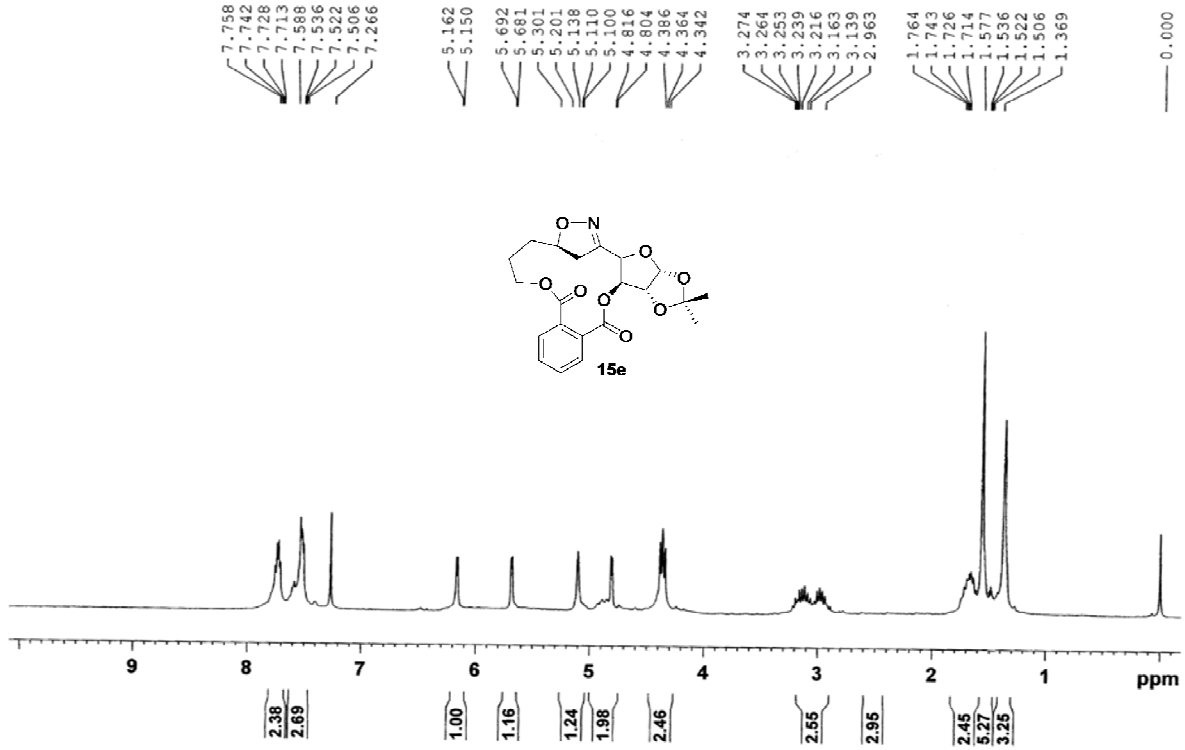


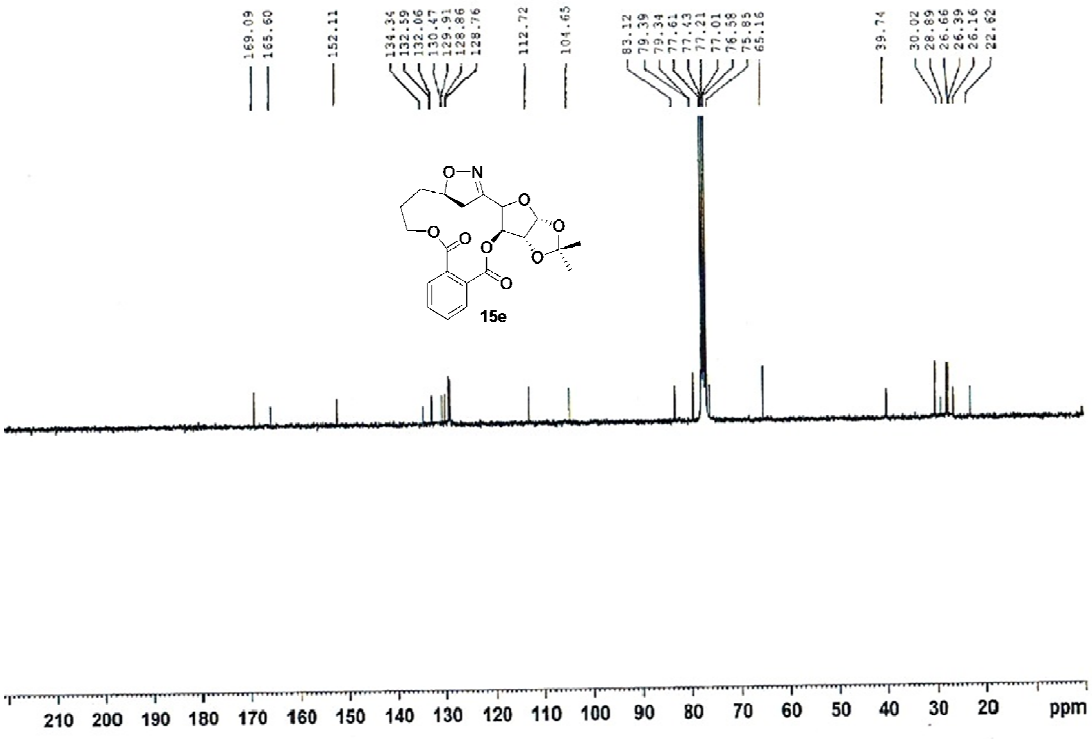
^{13}C NMR spectra of 15d (75 MHz, $CDCl_3$)



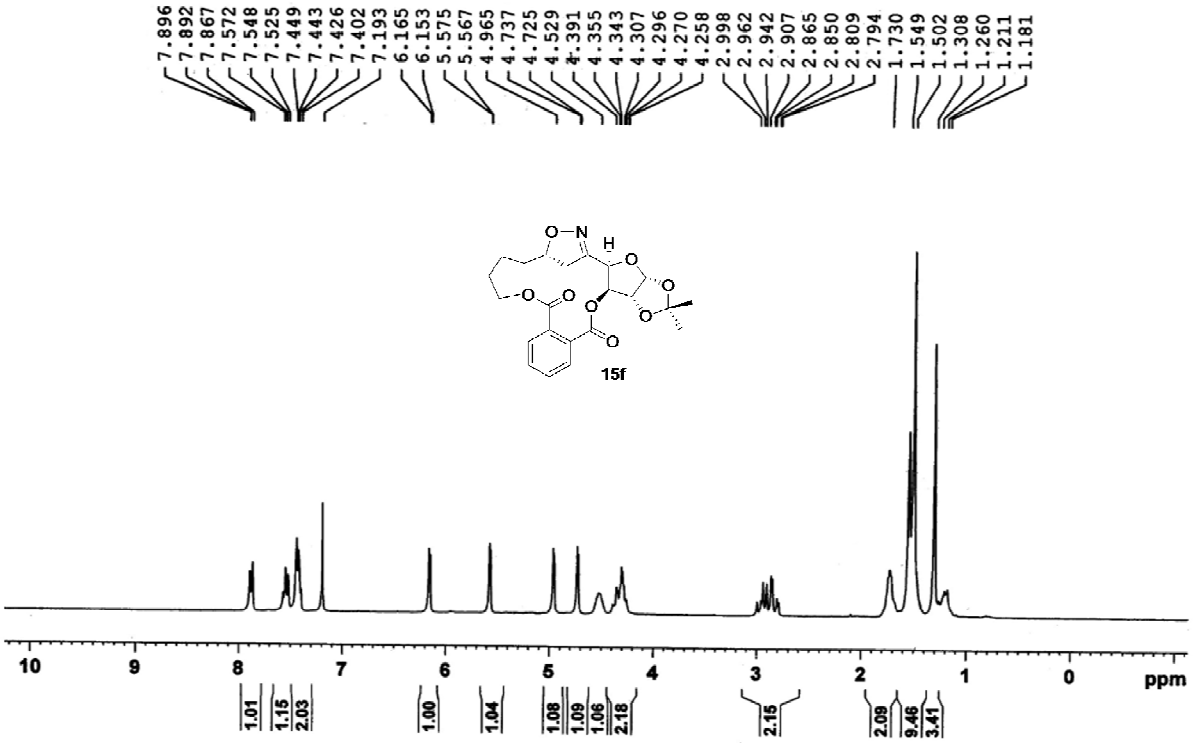
^{1}H NMR spectra of 15e (300 MHz, $CDCl_3$)



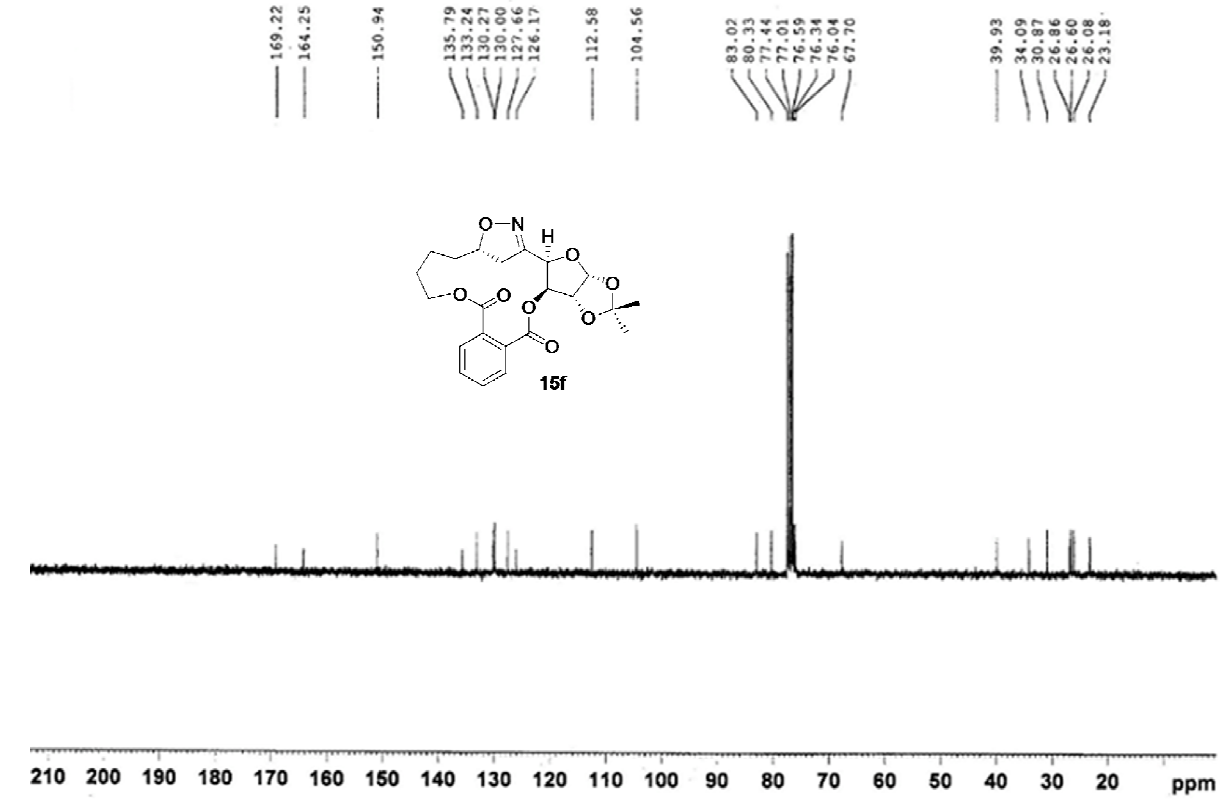
^{13}C NMR spectra of 15e (75 MHz, $CDCl_3$)



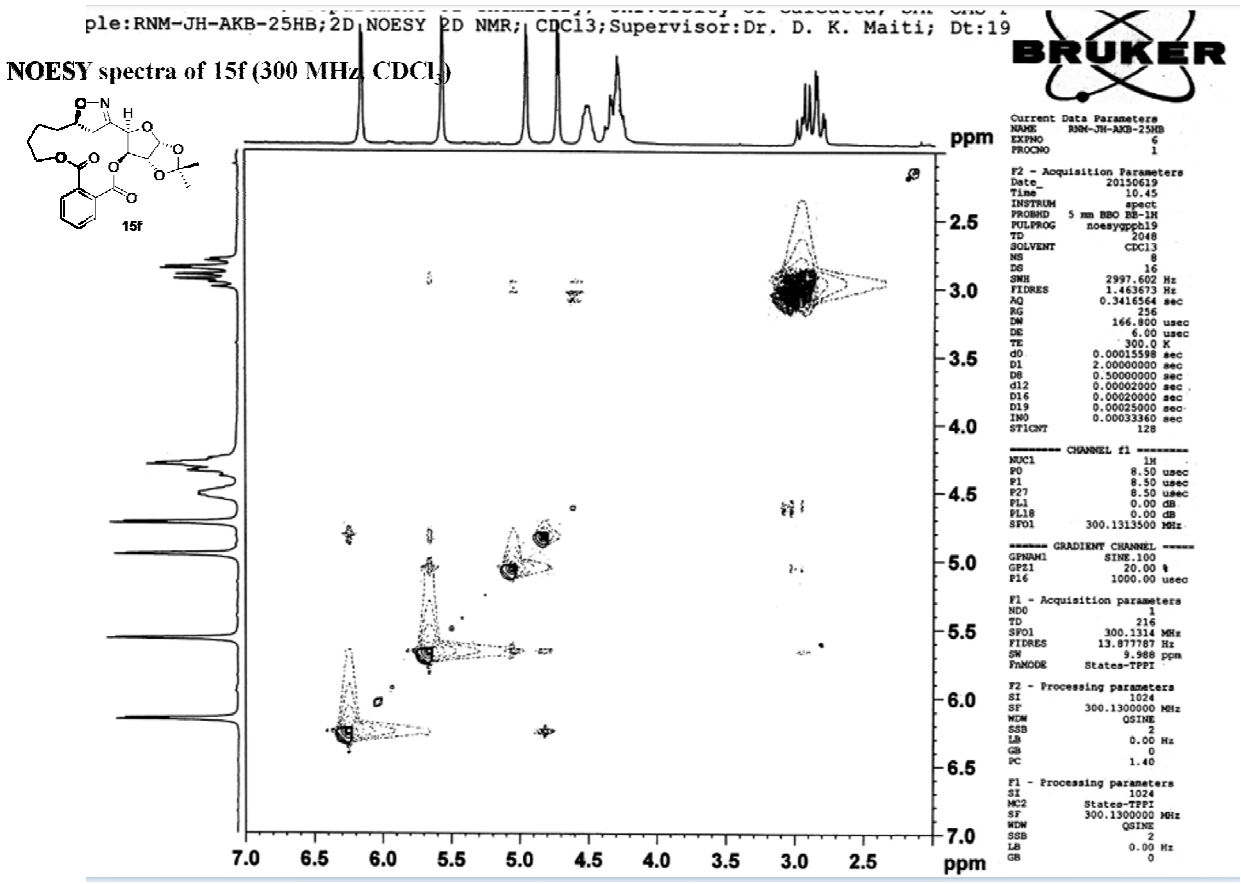
^{1}H NMR spectra of 15f (300 MHz, $CDCl_3$)



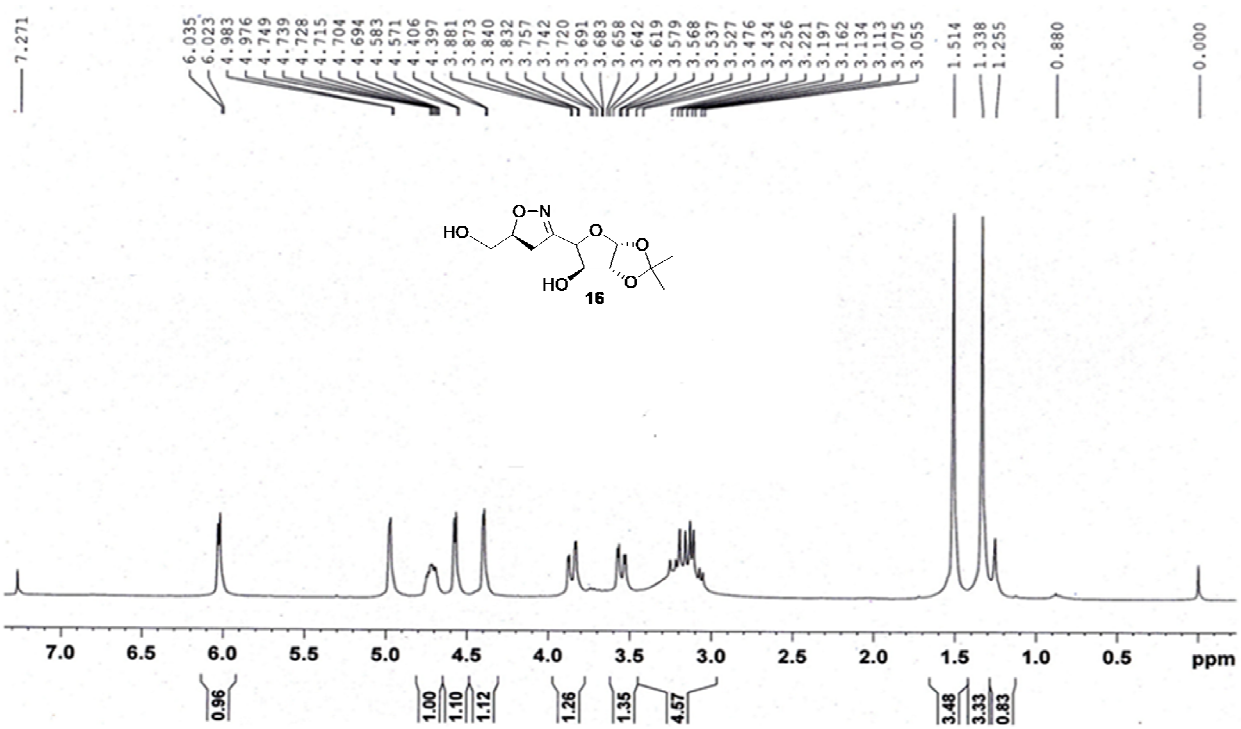
^{13}C NMR spectra of 15f (75 MHz, $CDCl_3$)



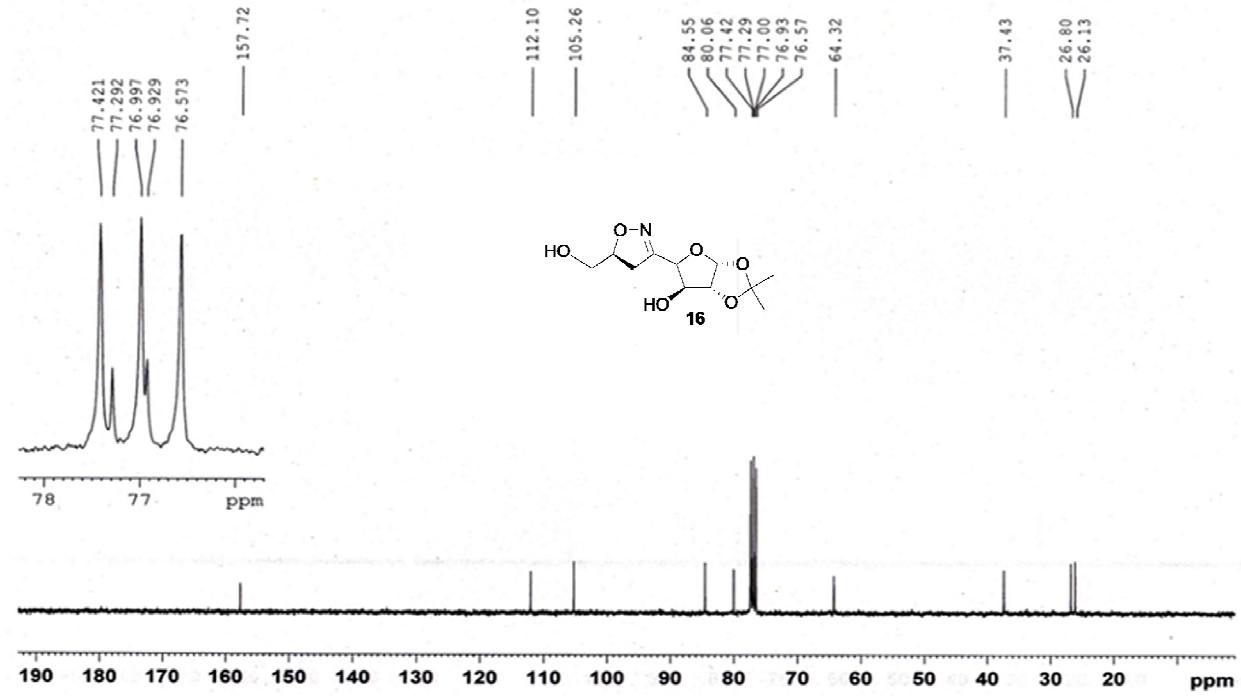
NOESY spectra of 15f (300 MHz, $CDCl_3$)



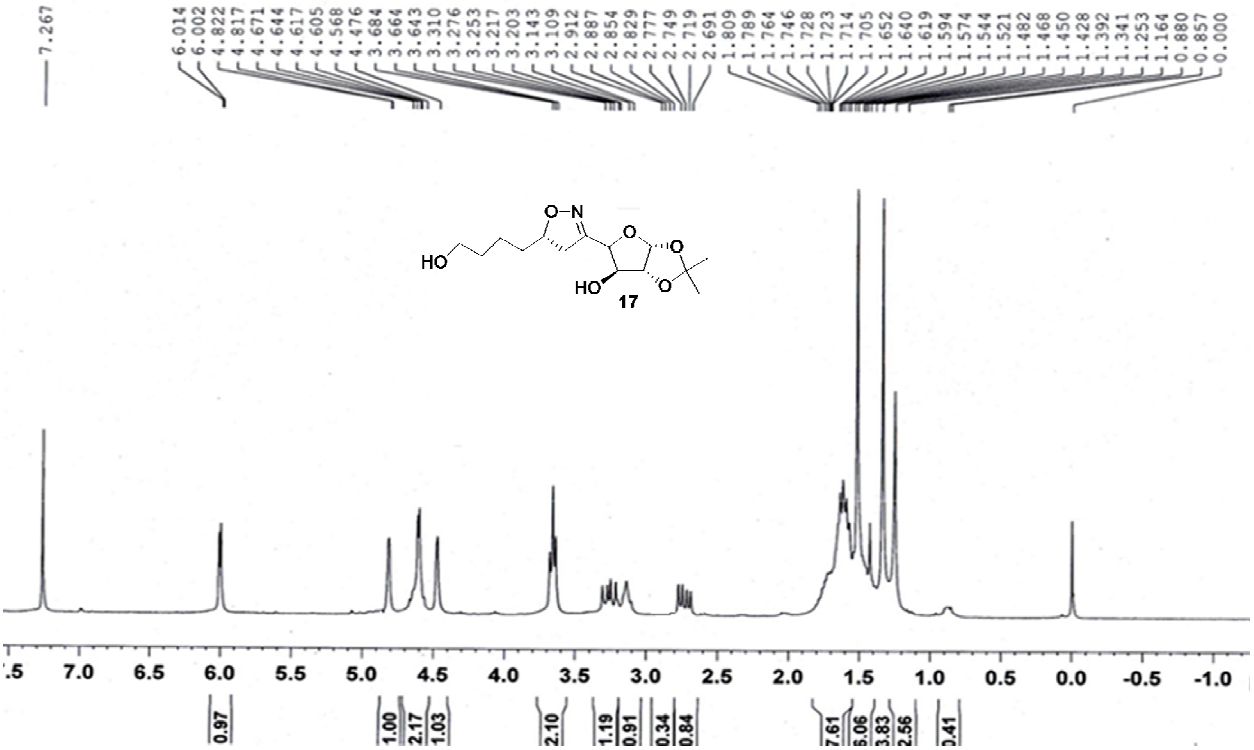
^{1}H NMR spectra of 16 (300 MHz, $CDCl_3$)



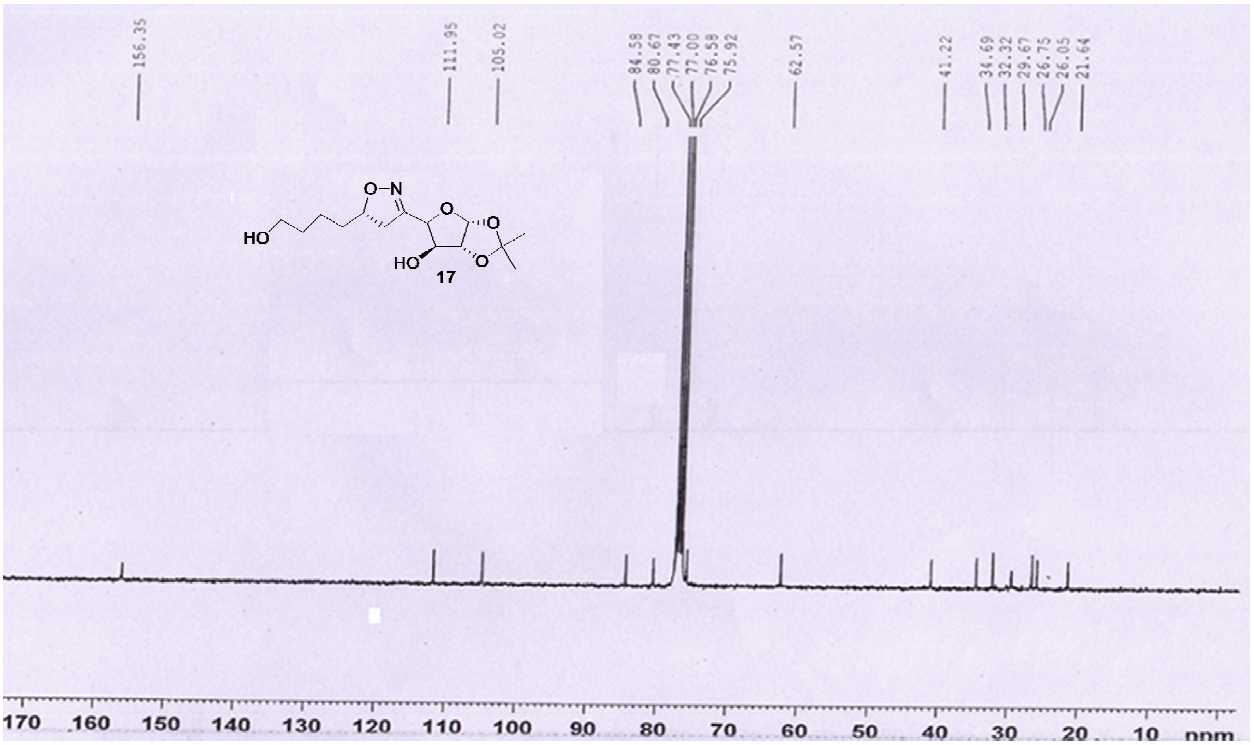
^{13}C NMR spectra of 16 (75 MHz, $CDCl_3$)



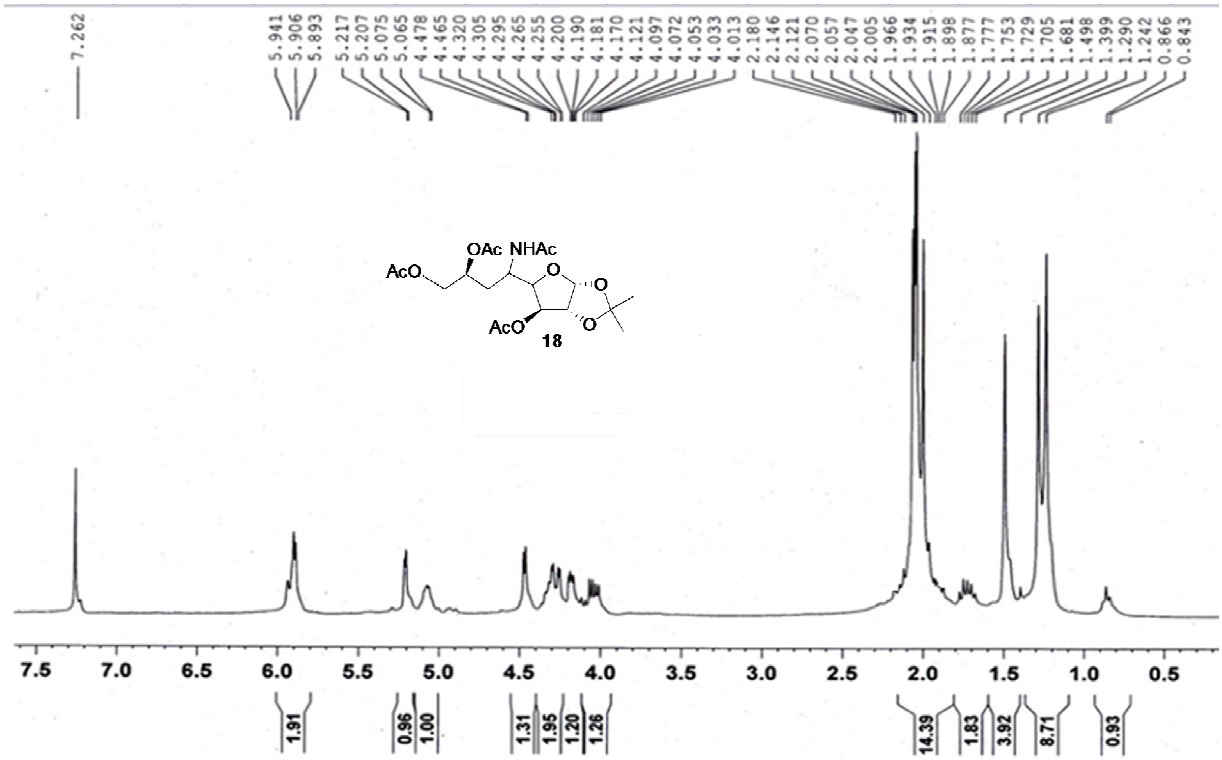
^{1}H NMR spectra of 17 (300 MHz, $CDCl_3$)



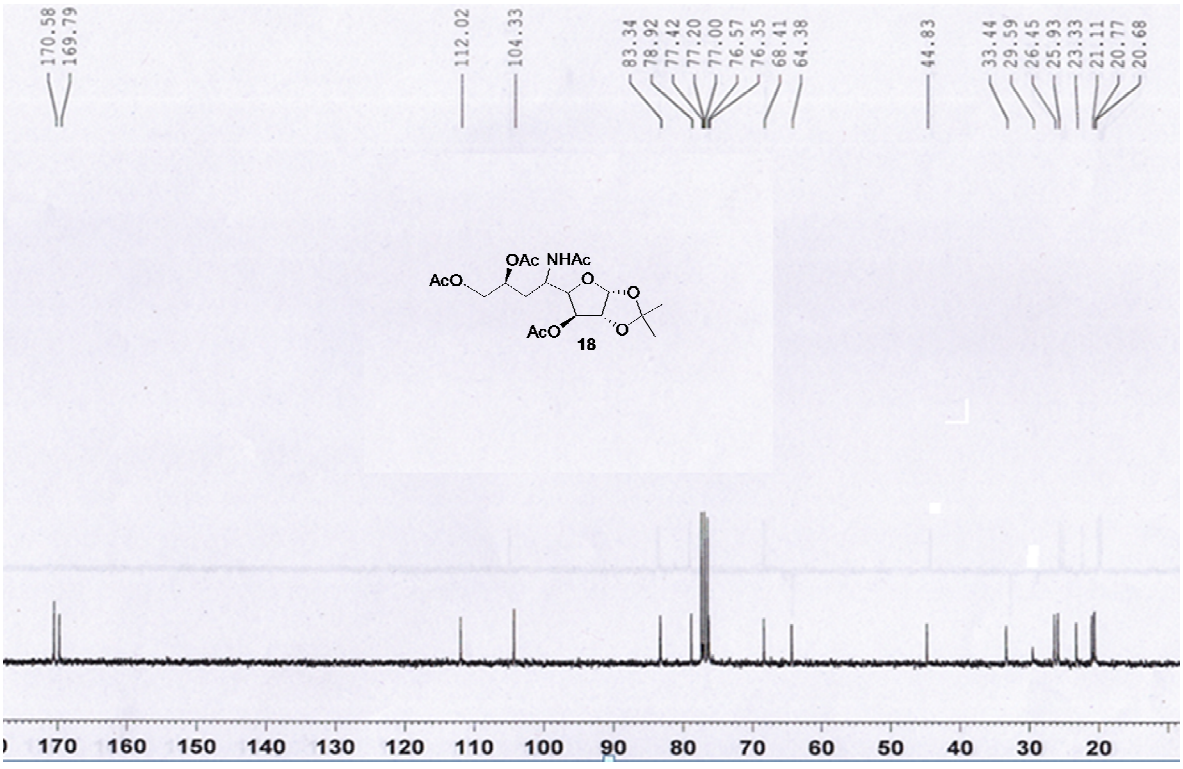
^{13}C NMR spectra of 16 (75 MHz, $CDCl_3$)



^{1}H NMR spectra of 18 (300 MHz, $CDCl_3$)

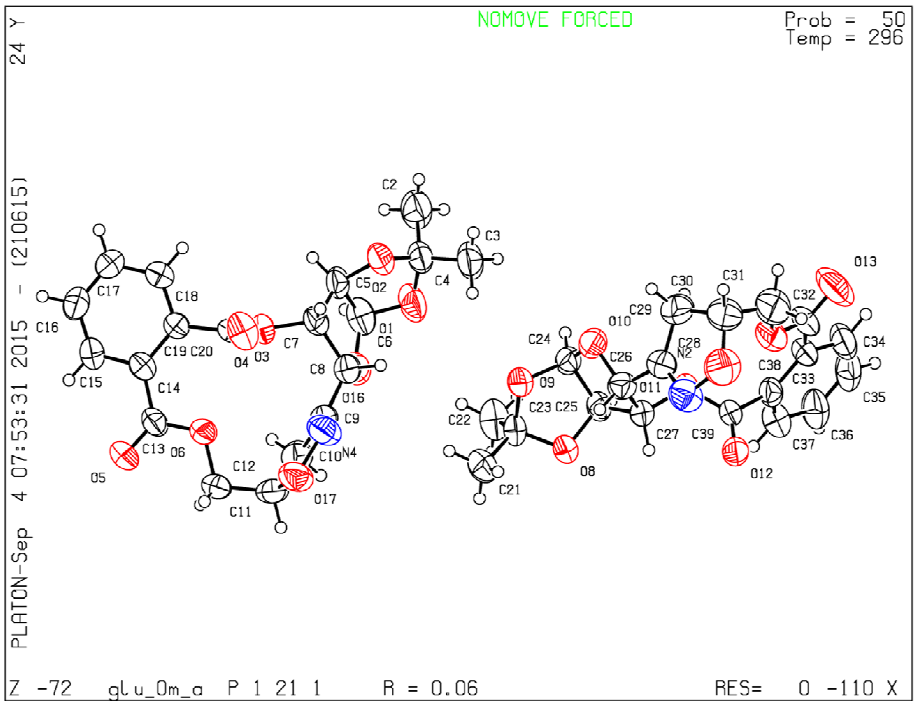


^{13}C NMR spectra of 18 (75 MHz, $CDCl_3$)



Crystallographic data of 15a (CCDC deposition no. 1418502)

ellipsoid plot of 15a



Thermal ellipsoid plot of **15a** at the probability level 50%

Datablock of 15a

Bond precision: C-C = 0.0101 A Wavelength=0.71073

Cell: a=7.7477(17) b=11.018(2) c=21.427(5)
alpha=90 beta=90.865(4) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1828.9(7)	1829.0(7)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C19 H19 N O8	C19 H19 N O8
Sum formula	C19 H19 N O8	C19 H19 N O8
Mr	389.35	389.35
Dx,g cm-3	1.414	1.414
Z	4	4
Mu (mm-1)	0.112	0.112
F000	816.0	816.0
F000'	816.51	
h,k,lmax	10,14,28	10,14,28
Nref	9452[4964]	8752
Tmin,Tmax	0.969,0.978	0.618,0.746
Tmin'	0.969	

Correction method= # Reported T Limits: Tmin=0.618
Tmax=0.746 AbsCorr = MULTI-SCAN

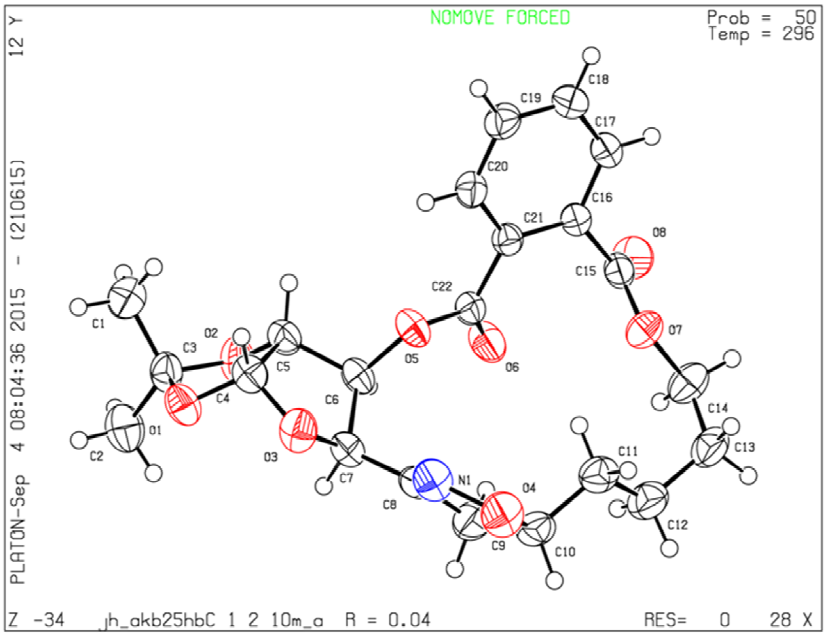
Data completeness= 1.76/0.93 Theta(max)= 28.693

R(reflections)= 0.0640(3849) wR2(reflections)= 0.2038(8752)

S = 0.896 Npar= 509

Crystallographic data of 15f (CCDC deposition no. 1418503)

ellipsoid plot of **15f**



Thermal ellipsoid plot of **15f** at the probability level 50%

Data block of 15f

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=21.5800(14) b=7.9030(4) c=12.3258(7)
alpha=90 beta=92.122(4) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	2100.7(2)	2100.7(2)
Space group	C 2	C 1 2 1
Hall group	C 2y	C 2y
Moiety formula	C22 H25 N O8	C22 H25 N O8
Sum formula	C22 H25 N O8	C22 H25 N O8
Mr	431.43	431.43
Dx,g cm-3	1.364	1.364
Z	4	4
Mu (mm-1)	0.104	0.104
F000	912.0	912.0
F000'	912.54	
h,k,lmax	28,10,16	28,10,15
Nref	4808[2579]	4366
Tmin,Tmax	0.949,0.968	0.663,0.746
Tmin'	0.936	

Correction method= # Reported T Limits: Tmin=0.663
Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 1.69/0.91 Theta(max)= 27.492

R(reflections)= 0.0382(3931) wR2(reflections)= 0.1182(4366)

S = 0.909 Npar= 282