` Electronic Supplementary Material (ESI)

Synthesis and insecticidal activity of 5-deoxyavermectin B2a oxime ester derivatives

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1. Experimental Section

*5-(benzoyloxyimino)-5-deoxyavermectin B2a (**8a**)*: yield, 63% ; white solid; mp: 146-148 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02~8.19 (m, 2H, Ar-H), 7.56~7.69 (m, 1H, Ar-H), 7.41~7.54 (m, 2H, Ar-H), 6.08~6.17 (m, 1H, H3), 5.92~6.06 (m, 1H, H9), 5.70~5.89 (m, 2H, H10, H11), 5.22~5.51 (m, 2H, H1″, H19), 5.01 (t, *J* = 7.2 Hz, 1H, H15), 4.71~4.91 (m, 4H, H1′, H8ax2, H6), 3.99 (s, 1H, 7-OH), 3.72~3.93 (m, 4H, H23, H13, H5″, H5′), 3.41~3.71 (m, 11H, H2, H25, H17, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.28 (t, *J* = 9.0 Hz, 1H, H4′), 3.19 (t, 1H, *J* = 9.1 Hz, H4″), 2.50~2.65 (m, 1H, H12), 1.92~2.46 (m, 10H, H24, H18, H16x2, H2′, H2″, Me4a, H20), 1.43~1.85 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.25~1.39 (m, 6H, Me6′, Me6″), 1.21 (d, *J* = 6.9 Hz, 3H, Me12a), 0.77~1.07 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.37, 163.06, 157.35, 138.75, 137.57, 135.60, 133.35, 131.84, 129.77, 129.71, 128.68, 128.47, 124.64, 121.89, 117.52, 99.57, 98.42, 94.79, 81.60, 80.33, 79.22, 79.04, 78.11, 77.20, 75.96, 74.35, 70.77, 69.75, 68.97, 68.26, 68.08, 67.95, 67.21, 56.37, 56.29, 46.36, 41.83, 41.08, 39.86, 36.31, 35.62, 35.04, 34.39, 34.16, 27.19, 26.89, 24.87, 20.03, 18.29, 17.59, 17.51, 15.08, 13.67, 12.33, 11.72; HRMS (ESI) calcd for $C_{55}H_{78}NO_{16}$ $(M + H)^+$ 1008.5321, found 1008.5328.

*5-(phenylacetyloxyimino)-5-deoxyavermectin B2a (**8b**):* yield, 61% ; white solid; mp: 103-105 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77~7.62 (m, 5H, Ar-H), 5.87~6.02 (m, 1H, H3), 5.80~5.86 (m, 1H, H9), 5.68~5.80 (m, 2H, H10, H11), 5.23~5.46 (m, 2H, H1″, H19), 4.99 (t, *J* = 7.1 Hz, 1H, H15), 4.60~4.86 (m, 4H, H1′, H8ax2, H6), 3.71~4.05 (m, 6H, 7-OH, 23-OH, H23, H13, H5″, H5′), 3.37~3.72 (m, 13H, $PhCH_2$, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.27 (t, 1H, *J* = 9.0 Hz, H4′), 3.19 (t, 1H, *J* = 9.1 Hz, H4″), 2.47~2.63 (m, 1H, H12), 2.14~2.45 (m, 4H, H24, H16x2, H2′), 1.75~2.13 (m, 6H, H2″, Me4a, H18, H20), 1.36~1.75 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.24~1.36 (m, 6H, Me6′, Me6″), 1.19 (d, *J* = 6.9 Hz, 3H, Me12a), 0.77~1.07 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.21, 172.91, 150.88, 138.23, 138.08, 135.61, 134.67, 132.13, 129.30, 128.94, 127.34, 124.82, 124.73, 121.27, 117.45, 99.58, 98.43, 94.77, 81.66, 80.37, 79.25, 78.63, 78.32, 77.20, 75.77, 72.96, 70.75, 69.85, 68.56, 68.31, 68.12, 67.63, 67.20, 56.40, 56.36, 46.35, 43.09, 41.04, 40.70, 39.83, 36.28, 35.61, 35.03, 34.39, 34.17, 34.00, 27.18, 20.06, 18.28, 17.60, 17.47, 15.05, 13.67, 12.33, 11.72; HRMS (ESI)

calcd for $C_{56}H_{80}NO_{16}$ $(M + H)^+$ 1022.5477, found 1022.5479.

*5-((2-fluorobenzoyl)oxyimino)-5-deoxyavermectin B2a (**8c**):* yield, 65% ; pale yellow solid; mp: 124-136 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95~8.13 (m, 1H, Ar-H), 7.42~7.72 (m, 2H, Ar-H), 7.12~7.26 (m, 1H, Ar-H), 6.08~6.22 (m, 1H, H3), 5.93~6.03 (m, 1H, H9), 5.68~5.87 (m, 2H, H10, H11), 5.32~5.46 (m, 2H, H1″, H19), 5.00 (t, *J* = 7.2 Hz, 1H, H15), 4.67~4.89 (m, 4H, H1′, H8ax2, H6), 3.72~4.04 (m, 6H, 7-OH, 23-OH, H23, H13, H5″, H5′), 3.40~3.70 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.27 (t, *J* = 9.0 Hz, 1H, H4′), 3.18 (t, 1H, *J* = 9.1 Hz, H4″), 2.74 (s, 1H, 4′-OH), 2.46~2.64 (m, 1H, H12), 1.94~2.44 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.40~1.76 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.24~1.35 (m, 6H, Me6′, Me6″), 1.20 (d, *J* = 6.9 Hz, 3H, Me12a), 0.77~1.06 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.41, 163.57 (d, *J* = 260.0 Hz), 161.29 (d, *J* = 4.0 Hz), 157.64, 138.58, 137.79, 135.63, 135.01 (d, *J* = 8.9 Hz), 132.49, 132.07 (d, *J* = 9.9 Hz), 131.72, 130.15, 128.47 (d, *J* = 12.1 Hz), 124.71, 124.16 (d, *J* = 3.7 Hz), 121.74, 117.54, 117.11, 116.81, 99.58, 98.45, 94.81, 81.62, 80.37, 79.24, 79.15, 78.14, 77.20, 76.00, 74.29, 70.79, 69.77, 68.28, 68.09, 67.95, 67.23, 56.38, 56.30, 46.43, 40.72, 39.85, 36.33, 35.65, 35.06, 34.17, 29.58, 27.21, 20.04, 18.30, 17.60, 17.49, 15.08, 13.68, 12.34, 11.73; HRMS (ESI) calcd for $C_{55}H_{77}FNO_{16}$ $(M + H)^+$ 1026.5226, found 1026.5233.

*5-((2-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a (**8d**):* yield, 70% ; white solid; mp: 184-186 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89~7.97 (m, 1H, Ar-H), 7.46~7.56 (m, 2H, Ar-H), 7.33~7.45 (m, 1H, Ar-H), 6.08~6.18 (m, 1H, H3), 5.94~6.02 (m, 1H, H9), 5.68~5.84 (m, 2H, H10, H11), 5.32~5.47 (m, 2H, H1″, H19), 5.01 (t, *J* = 7.0 Hz, 1H, H15), 4.68~4.86 (m, 4H, H1′, H8ax2, H6), 3.99 (s, 1H, 7-OH), 3.94 (s, 1H, 23-OH), 3.72~3.91 (m, 4H, H23, H13, H5″, H5′), 3.41~3.71 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.28 (t, *J* = 9.0 Hz, 1H, H4′), 3.20 (t, 1H, *J* = 9.1 Hz, H4″), 2.47~2.66 (m, 2H, 4″-OH, H12), 1.94~2.45 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.45~1.78 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.23~1.36 (m, 6H, Me6′, Me6″), 1.20 (d, *J* = 6.9 Hz, 3H, Me12a), 0.86~1.04 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.32, 162.43, 157.57, 138.65, 137.41, 135.57, 133.86, 132.95, 131.74, 131.61, 131.04, 130.22, 128.59, 126.60, 124.58, 121.79, 117.38, 99.53, 98.36, 94.71, 81.51, 80.19, 79.18, 79.06, 78.06, 75.87, 74.23, 70.70, 69.75, 68.89, 68.20, 68.02, 67.92, 67.14, 56.38, 56.29, 46.32, 41.00, 40.62, 39.76, 36.24, 35.56, 34.98, 34.34, 34.08, 33.97, 27.16, 20.03,

18.28, 17.59, 17.52, 15.06, 13.67, 12.34, 11.69; HRMS (ESI) calcd for $C_{55}H_{77}ClNO_{16}$ $(M + H)^+$ 1042.4931, found 1042.4940.

*5-((2-bromobenzoyl)oxyimino)-5-deoxyavermectin B2a (**8e**):* yield, 62% ; white solid; mp: 185-187 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82~7.96 (m, 1H, Ar-H), 7.63~7.79 (m, 1H, Ar-H), 7.35~7.53 (m, 2H, Ar-H), 6.08~6.16 (m, 1H, H3), 5.93~6.02 (m, 1H, H9), 5.71~5.88 (m, 2H, H10, H11), 5.35~5.51 (m, 2H, H1″, H19), 5.01 (t, *J* = 7.0 Hz, 1H, H15), 4.64~4.86 (m, 4H, H1′, H8ax2, H6), 3.99 (s, 1H, 7-OH), 3.93 (s, 1H, 23-OH), 3.71~3.89 (m, 4H, H23, H13, H5″, H5′), 3.39~3.71 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.28 (t, *J* = 9.0 Hz, 1H, H4′), 3.20 (t, 1H, *J* = 9.0 Hz, H4″), 2.49~2.63 (m, 2H, 4″-OH, H12), 1.96~2.45 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.44~1.82 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.25~1.36 (m, 6H, Me6′, Me6″), 1.20 (d, *J* = 6.8 Hz, 3H, Me12a), 0.83~1.05 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$), δ 172.30, 162.85, 157.64, 138.68, 137.47, 135.60, 134.31, 132.86, 131.66, 131.57, 130.83, 130.19, 127.12, 124.61, 121.84, 117.49, 99.55, 98.40, 94.77, 81.58, 80.32, 79.21, 79.08, 78.11, 77.20, 75.95, 74.24, 70.76, 69.74, 68.88, 68.25, 68.07, 67.96, 67.19, 56.36, 56.28, 46.36, 41.06, 40.69, 39.83, 36.29, 35.61, 35.03, 34.37, 34.15, 33.99, 27.18, 20.01, 18.28, 17.58, 17.48, 15.06, 13.66, 12.32, 11.71; HRMS (ESI) calcd for $C_{55}H_{77}BrNO_{16}$ $(M + H)^+$ 1086.4426, found 1086.4451.

*5-((2-trifluoromethylbenzoyl)oxyimino)-5-deoxyavermectin B2a (**8f**) :* yield, 72%; white solid; mp: 183-186 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86~7.93 (m, 1H, Ar-H), 7.76~7.81 (m, 1H, Ar-H), 7.48~7.73 (m, 2H, Ar-H), 6.08~6.15 (m, 1H, H3), 5.92~6.02 (m, 1H, H9), 5.65~5.89 (m, 2H, H10, H11), 5.25~5.47 (m, 2H, H1″, H19), 5.00 (t, *J* = 7.1 Hz, 1H, H15), 4.68~4.83 (m, 3H, H1′, H8ax2), 4.65 (s, 1H, H6), 3.98 (s, 1H, 7-OH), 3.91 (s, 1H, 23-OH), 3.72~3.88 (m, 4H, H23, H13, H5″, H5′), 3.40~3.69 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.27 (t, *J* = 9.0 Hz, 1H, H4′), 3.19 (t, 1H, *J* = 9.1 Hz, H4″), 2.64 (s, 1H, 4″-OH), 2.47~2.60 (m, 1H, H12), 1.95~2.44 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.43~1.80 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.24~1.35 (m, 6H, Me6′, Me6″), 1.18 (d, *J* = 6.9 Hz, 3H, Me12a), 0.85~1.04 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.28, 163.33, 157.77, 138.64, 137.45, 135.61, 131.75, 131.59, 131.51, 130.49, 129.11 (q, *J* = 7.1 Hz), 128.58 (q, *J* = 8.1 Hz), 126.67 (q, *J* = 5.2 Hz), 124.60, 121.78, 121.29 (q, *J* = 272.0 Hz), 117.49, 99.56, 98.41, 94.77, 81.58, 80.34, 79.22, 79.09, 78.12, 75.96, 73.98, 70.76, 69.75, 68.79, 68.26, 68.07, 67.98,

67.20, 56.36, 56.27, 46.34, 41.07, 40.69, 39.82, 36.28, 35.61, 35.04, 34.38, 34.15, 33.99, 27.19, 20.00, 18.28, 17.58, 17.46, 15.05, 13.66, 12.32, 11.71; HRMS (ESI) calcd for $C_{56}H_{77}F_3NO_{16}$ $(M + H)^+$ 1076.5194, found 1076.5206.

5-((3-methylbenzoyl)oxyimino)-5-deoxyavermectin B2a ***(8g)*** : yield, 62%; white solid; mp: 147-149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81~8.00 (m, 2H, Ar-H), 7.31~7.60 (m, 2H, Ar-H), 6.08~6.13 (m, 1H, H3), 5.96~6.04 (m, 1H, H9), 5.69~5.89 (m, 2H, H10, H11), 5.25~5.47 (m, 2H, H1″, H19), 5.01 (t, *J* = 7.2 Hz, 1H, H15), 4.68~4.90 (m, 4H, H1′, H8ax2, H6), 4.05 (s, 1H, 7-OH), 3.99 (s, 1H, 23-OH), 3.71~3.92 (m, 4H, H23, H13, H5″, H5′), 3.40~3.68 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.27 (t, *J* = 9.0 Hz, 1H, H4′), 3.18 (t, 1H, *J* = 9.1 Hz, H4″), 2.76 (s, 1H, 4″-OH), 2.53~2.63 (m, 1H, H12), 2.44 (s, 3H, $PhCH_3$), 1.97~2.41 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.44~1.83 (m, 11H, H18, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.24~1.34 (m, 6H, Me6′, Me6″), 1.20 (d, *J* = 6.9 Hz, 3H, Me12a), 0.81~1.06 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.32, 163.20, 157.27, 138.70, 138.21, 137.62, 135.57, 134.10, 132.01, 131.88, 131.79, 130.27, 129.74, 128.55, 128.43, 128.31, 128.27, 126.78, 124.63, 121.88, 117.51, 99.54, 98.39, 94.77, 81.58, 80.31, 79.19, 79.03, 78.10, 77.20, 75.93, 74.37, 70.73, 69.73, 68.24, 68.07, 67.19, 56.34, 56.27, 46.36, 41.05, 39.83, 35.59, 35.02, 34.15, 27.17, 21.24, 19.99, 18.27, 17.57, 17.50, 15.04, 13.64, 12.30, 11.70; HRMS (ESI) calcd for $C_{56}H_{80}NO_{16}$ $(M + H)^+$ 1022.5477, found 1022.5491.

5-((4-methoxybenzoyl)oxyimino)-5-deoxyavermectin B2a ***(8h)*** *:* yield, 65%; white solid; mp: 158-161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.97 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.05~6.16 (m, 1H, H3), 5.95~6.04 (m, 1H, H9), 5.71~5.90 (m, 2H, H10, H11), 5.31~5.48 (m, 2H, H1″, H19), 5.01 (t, *J* = 7.2 Hz, 1H, H15), 4.69~4.90 (m, 4H, H1′, H8ax2, H6), 3.99 (s, 1H, 7-OH), 3.97 (s, 1H, 23-OH), 3.90 (s, 3H, $PhOCH_3$), 3.72~3.87 (m, 4H, H23, H13, H5″, H5′), 3.41~3.70 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.27 (t, *J* = 9.0 Hz, 1H, H4′), 3.19 (t, 1H, *J* = 9.1 Hz, H4″), 2.69 (s, 1H, 4″-OH), 2.52~2.62 (m, 1H, H12), 1.96~2.40 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.43~1.86 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.23~1.34 (m, 6H, Me6′, Me6″), 1.20 (d, *J* = 6.9 Hz, 3H, Me12a), 0.83~1.06 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.20, 163.63, 162.74, 156.90, 138.58, 137.59, 135.53, 131.74, 129.56, 124.62, 121.82, 120.77, 117.47, 113.74, 99.50, 98.35, 94.73, 81.56, 80.27, 79.15, 78.98, 78.05, 75.87, 74.31, 70.67, 69.69, 68.84, 68.21, 68.03, 67.83, 67.14, 56.29,

56.23, 55.28, 46.27, 40.99, 40.64, 39.80, 36.21, 35.54, 34.97, 34.32, 34.12, 33.93, 27.12, 19.97, 18.22, 17.53, 17.45, 15.00, 13.60, 12.25, 11.65; HRMS (ESI) calcd for $C_{56}H_{80}NO_{17}$ $(M + H)^+$ 1038.5426, found 1038.5468.

5-((4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a ***(8i)*** *:* yield, 64%; white solid; mp: 163-165 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 2H, Ar-H), 7.48 (d, J = 8.5 Hz, 2H, Ar-H), 6.08~6.16 (m, 1H, H3), 5.97~6.04 (m, 1H, H9), 5.72~5.91 (m, 2H, H10, H11), 5.32~5.51 (m, 2H, H1″, H19), 5.01 (t, J = 7.0 Hz, 1H, H15), 4.77~4.89 (m, 3H, H1′, H8ax2), 4.76 (s, 1H, H6), 3.71~4.09 (m, 6H, 7-OH, 23-OH, H23, H13, H5″, H5′), 3.41~3.70 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.28 (t, J = 9.0 Hz, 1H, H4′), 3.20 (t, 1H, J = 9.1 Hz, H4″), 2.52~2.68 (m, 2H, 4″-OH, H12), 1.96~2.43 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.45~1.84 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.26~1.37 (m, 6H, Me6′, Me6″), 1.21 (d, J = 6.8 Hz, 3H, Me12a), 0.85~1.05 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.22, 162.22, 157.58, 139.83, 138.82, 137.33, 135.58, 131.62, 131.03, 130.11, 128.84, 127.10, 124.57, 121.98, 117.48, 99.53, 98.37, 94.75, 81.55, 80.28, 79.18, 78.98, 78.09, 77.20, 75.90, 74.36, 70.73, 69.72, 68.95, 68.23, 68.06, 67.95, 67.18, 56.33, 56.26, 46.32, 41.02, 40.66, 39.83, 36.26, 35.57, 35.00, 34.35, 34.14, 33.96, 27.15, 20.00, 18.26, 17.57, 17.44, 15.04, 13.63, 12.29, 11.68; HRMS (ESI) calcd for $C_{55}H_{77}ClNO_{16}$ $(M + H)^+$ 1042.4931, found 1042.4970.

5-((4-nitrobenzoyl)oxyimino)-5-deoxyavermectin B2a ***(8j)*** *:* yield, 66%; pale yellow solid; mp: 195-198 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22~8.36 (m, 4H, Ar-H), 6.09~6.14 (m, 1H, H3), 5.94~6.02 (m, 1H, H9), 5.67~5.88 (m, 2H, H10, H11), 5.32~5.47 (m, 2H, H1″, H19), 4.98 (t, J = 7.0 Hz, 1H, H15), 4.63~4.88 (m, 4H, H1′, H8ax2, H6), 3.99 (s, 1H, 7-OH), 3.97 (s, 1H, 23-OH), 3.70~3.86 (m, 4H, H23, H13, H5″, H5′), 3.40~3.67 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.25 (t, J = 9.0 Hz, 1H, H4′), 3.16 (t, 1H, J = 9.3 Hz, H4″), 2.50~2.62 (m, 2H, 4″-OH, H12), 1.93~2.38 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.40~1.82 (m, 11H, H18, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.21~1.30 (m, 6H, Me6′, Me6″), 1.18 (d, J = 6.9 Hz, 3H, Me12a), 0.76~1.04 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.07, 161.19, 158.25, 150.59, 138.97, 137.00, 135.55, 134.10, 131.29, 130.80, 130.74, 124.48, 123.57, 122.11, 117.43, 99.48, 98.31, 94.70, 81.48, 80.22, 79.14, 78.94, 78.05, 75.84, 74.42, 70.69, 69.67, 68.99, 68.19, 68.02, 67.13, 56.28, 56.23, 46.28, 40.97, 40.61, 39.80, 36.21, 35.52, 34.95, 34.30, 34.11,

33.92, 27.11, 19.95, 18.21, 17.53, 17.36, 15.00, 13.59, 12.25, 11.64; HRMS (ESI) calcd for $C_{55}H_{77}N_2O_{18}$ $(M + H)^+$ 1053.5171, found 1053.5178.

*5-((2,4-dichlorobenzoyl)oxyimino)-5-deoxyavermectin B2a (**8k**):* yield, 63%; white solid; mp: 176-179 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 1H, Ar-H), 7.50 (d, J = 2.0 Hz, 1H, Ar-H), 7.33 (dd, J = 8.5 Hz, 2.0 Hz, 1H, Ar-H), 6.06~6.12 (m, 1H, H3), 5.90~5.98 (m, 1H, H9), 5.67~5.84 (m, 2H, H10, H11), 5.30~5.44 (m, 2H, H1″, H19), 4.98 (t, J = 7.0 Hz, 1H, H15), 4.68~4.79 (m, 3H, H1′, H8ax2), 4.67 (s, 1H, H6), 3.95 (s, 1H, 7-OH), 3.92 (s, 1H, 23-OH), 3.70~3.87 (m, 4H, H23, H13, H5″, H5′), 3.38~3.66 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.24 (t, J = 8.9 Hz, 1H, H4′), 3.16 (t, 1H, J = 9.1 Hz, H4″), 2.46~2.67 (m, 2H, 4″-OH, H12), 1.93~2.40 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20), 1.38~1.82 (m, 11H, H18, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.22~1.33 (m, 6H, Me6′, Me6″), 1.17 (d, J = 6.9 Hz, 3H, Me12a), 0.82~1.02 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.11, 161.48, 157.79, 138.71, 137.27, 135.56, 134.99, 132.72, 131.41, 130.93, 130.53, 127.04, 126.94, 124.55, 121.90, 117.44, 99.50, 98.34, 94.72, 81.52, 80.26, 79.16, 79.04, 78.07, 75.87, 74.31, 70.70, 69.69, 68.84, 68.21, 68.04, 67.94, 67.15, 56.31, 56.25, 46.31, 40.99, 40.64, 39.78, 36.21, 35.55, 34.98, 34.33, 34.13, 33.93, 27.13, 19.97, 18.23, 17.55, 17.40, 15.01, 13.61, 12.27, 11.67; HRMS (ESI) calcd for $C_{55}H_{76}Cl_2NO_{16}$ $(M + H)^+$ 1076.4541, found 1076.4559.

*5-((3-trifluoromethyl-4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a (**8l**) :* yield, 59%; white solid; mp: 142-145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, J = 1.7 Hz, 1H, Ar-H), 8.19 (dd, J = 8.3 Hz, 1.9 Hz, 1H, Ar-H), 7.64 (d, J = 8.4 Hz, 1H, Ar-H), 6.07~6.13 (m, 1H, H3), 5.93~6.02 (m, 1H, H9), 5.67~5.87 (m, 2H, H10, H11), 5.30~5.52 (m, 2H, H1″, H19), 4.98 (t, J = 6.9 Hz, 1H, H15), 4.74~4.82 (m, 3H, H1′, H8ax2), 4.70 (s, 1H, H6), 4.00 (s, 1H, 7-OH), 3.97 (s, 1H, 23-OH), 3.72~3.88 (m, 4H, H23, H13, H5″, H5′), 3.39~3.68 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.25 (t, J = 8.9 Hz, 1H, H4′), 3.16 (t, 1H, J = 9.1 Hz, H4″), 2.47~2.64 (m, 2H, 4″-OH, H12), 1.94~2.40 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.41~1.78 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.22~1.32 (m, 6H, Me6′, Me6″), 1.19 (d, J = 6.8 Hz, 3H, Me12a), 0.81~1.02 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.36, 161.08, 158.10, 139.07, 137.14, 135.65, 133.88, 131.99, 131.56, 130.54, 128.89 (q, J = 13.3 Hz), 127.69, 124.55, 124.07 (q, J = 271.9 Hz), 122.19, 117.48, 99.57, 98.42, 94.78, 81.56, 80.31, 79.24, 78.98, 78.13, 75.97, 74.69, 70.80, 69.76, 69.05, 68.27, 68.09, 68.04, 67.23, 56.38, 56.30, 46.44, 41.08, 40.68, 39.86, 36.35, 35.64, 35.05, 34.41, 34.16, 34.02, 27.21, 20.00, 18.31, 17.60, 17.44, 15.07, 13.67, 12.34, 11.72; HRMS (ESI) calcd for

$C_{56}H_{76}ClF_3NO_{16}$ $(M + H)^+$ 1110.4805, found 1110.4845.

*5-((3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a (**8m**) :* yield, 68%; white solid; mp: 162-164 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.18~9.34 (m, 1H, Ar-H), 8.79~8.83 (m, 1H, Ar-H), 8.33~8.38 (m, 1H, Ar-H), 7.40~7.47 (m, 1H, Ar-H), 6.05~6.15 (m, 1H, H3), 5.92~6.01 (m, 1H, H9), 5.66~5.89 (m, 2H, H10, H11), 5.31~5.46 (m, 2H, H1″, H19), 4.97 (t, *J* = 6.9 Hz, 1H, H15), 4.65~4.90 (m, 4H, H1′, H8ax2, H6), 3.96 (s, 1H, 7-OH), 3.94 (s, 1H, 23-OH), 3.69~3.88 (m, 4H, H23, H13, H5″, H5′), 3.40~3.66 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.24 (t, *J* = 9.0 Hz, 1H, H4′), 3.16 (t, 1H, *J* = 9.2 Hz, H4″), 2.47~2.65 (m, 2H, 4″-OH, H12), 1.92~2.40 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.42~1.83 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.22~1.33 (m, 6H, Me6′, Me6″), 1.18 (d, *J* = 6.8 Hz, 3H, Me12a), 0.81~1.01 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.04, 161.69, 158.03, 153.57, 150.62, 138.82, 137.27, 137.15, 135.59, 131.34, 130.69, 124.91, 124.56, 123.46, 122.11, 117.43, 99.51, 98.34, 94.72, 81.53, 80.23, 79.18, 79.01, 78.08, 77.20, 75.88, 74.44, 70.70, 69.71, 68.94, 68.23, 68.06, 67.98, 67.15, 56.32, 56.28, 46.29, 40.67, 39.82, 36.22, 35.55, 34.98, 34.34, 34.14, 33.94, 27.13, 19.98, 18.24, 17.56, 17.40, 15.04, 13.62, 12.28, 11.67; HRMS (ESI) calcd for $C_{54}H_{77}N_2O_{16}$ $(M + H)^+$ 1009.5273, found 1009.5289.

*5-((2-chloro-3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a (**8n**):* yield, 64%; white solid; mp: 188-191 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.8 Hz, 2.0 Hz, 1H, Ar-H), 8.23 (dd, *J* = 7.7 Hz, 2.0 Hz, 1H, Ar-H), 7.36 (dd, *J* = 4.8 Hz, 7.7 Hz, 1H, Ar-H), 6.04~6.16 (m, 1H, H3), 5.91~6.00 (m, 1H, H9), 5.66~5.86 (m, 2H, H10, H11), 5.31~5.45 (m, 2H, H1″, H19), 4.97 (t, *J* = 7.2 Hz, 1H, H15), 4.66~4.81 (m, 4H, H1′, H8ax2, H6), 3.96 (s, 1H, 7-OH), 3.91 (s, 1H, 23-OH), 3.70~3.88 (m, 4H, H23, H13, H5″, H5′), 3.40~3.68 (m, 11H, H17, H25, H2, H3″, H3′, 3″-OCH_3, 3′-OCH_3), 3.24 (t, *J* = 9.0 Hz, 1H, H4′), 3.16 (t, 1H, *J* = 9.1 Hz, H4″), 2.46~2.62 (m, 2H, 4″-OH, H12), 1.93~2.39 (m, 10H, H24, H16x2, H2′, H2″, Me4a, H20, H18), 1.41~1.82 (m, 11H, Me14a, H20, H26, H27x2, H22x2, H2′, H2″), 1.21~1.31 (m, 6H, Me6′, Me6″), 1.17 (d, *J* = 6.9 Hz, 3H, Me12a), 0.79~1.04 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.92, 161.35, 158.13, 152.06, 149.79, 140.55, 138.69, 137.10, 135.51, 131.10, 130.99, 125.65, 124.48, 122.05, 121.94, 117.36, 99.45, 98.26, 94.66, 81.45, 80.17, 79.10, 79.03, 78.01, 75.79, 74.27, 70.62, 69.64, 68.82, 68.15, 67.99, 67.91, 67.08, 56.25, 56.22, 46.25, 40.92, 40.59, 39.72, 36.13, 35.48, 34.91, 34.27, 34.09, 33.86, 27.06, 19.91, 18.18, 17.51, 17.33, 14.95, 13.57, 12.22, 11.61; HRMS (ESI) calcd for $C_{54}H_{76}ClN_2O_{16}$ $(M + H)^+$ 1043.4883, found 1043.4896.

*5-(benzoyloxyimino)-5-deoxyavermectin B2a monosaccharide (**11a**)*: yield, 68% ; white solid; mp: 244-247 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03~8.15 (m, 2H, Ar-H), 7.54-7.66 (m, 1H, Ar-H), 7.41~7.52 (m, 2H, Ar-H), 6.05~6.10 (m, 1H, H3), 5.93~6.03

(m, 1H, H9), 5.72~5.85 (m, 2H, H10, H11), 5.32~5.49 (m, 1H, H19), 4.98 (t, *J* = 6.7 Hz, 1H, H15), 4.68~4.89 (m, 4H, H1′, H8ax2, H6), 3.98 (s, 1H, 7-OH), 3.71~3.92 (m, 4H, 23-OH, H23, H13, H5′), 3.43~3.63 (m, 7H, H17, H25, H2, H3′, 3′-OCH_3), 3.17 (t, 1H, *J* = 9.2 Hz, H4′), 2.51~2.58 (m, 2H, H12, H24), 2.2 2~2.40 (m, 3H, H16x2, H2′), 2.15 (s, 3H, Me4a), 1.93~2.07 (m, 2H, H18, H20), 1.43~1.78 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.28 (d, *J* = 6.2 Hz, 3H, Me6′), 1.17 (d, *J* = 6.9 Hz, 3H, Me12a), 0.83~1.02 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) 172.20, 163.02, 157.34, 138.68, 137.50, 135.51, 133.32, 131.70, 129.88, 129.66, 128.63, 128.44, 124.60, 121.92, 117.48, 99.54, 94.91, 81.47, 79.02, 78.18, 75.89, 74.35, 70.69, 69.73, 68.90, 68.24, 68.08, 67.87, 56.43, 46.32, 41.01, 40.67, 39.82, 36.25, 35.56, 35.00, 33.95, 33.85, 27.14, 20.00, 17.59, 17.48, 15.04, 13.64, 12.29, 11.69 ; HRMS (ESI) calcd for $C_{48}H_{66}NO_{13}$ $(M + H)^+$ 864.4534, found 864.4540.

*5-(phenylacetyloxyimino)-5-deoxyavermectin B2a monosaccharide (**11b**):* yield, 75% ; white solid; mp: 196-199 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.24~7.38 (m, 5H, Ar-H), 5.98~6.07 (m, 1H, H3), 5.87~5.98 (m, 1H, H9), 5.68~5.84 (m, 2H, H10, H11), 5.25~5.43 (m, 1H, H19), 4.97 (t, *J* = 7.2 Hz, 1H, H15), 4.81(d, *J* = 3.3 Hz, 1H, H1′), 4.65(t, *J* = 2.1 Hz, 2H, H8ax2), 4.48 (s, 1H, H6), 3.98 (s, 1H, 7-OH), 3.71~3.90 (m, 6H, 23-OH, H23, H13, H5′, $PhCH_2$), 3.46~3.62 (m, 6H, H17, H25, H3′, 3′-OCH_3), 3.35~3.41(m, 1H, H2),3.17 (t, 1H, *J* = 9.1 Hz, H4′), 2.50~2.63 (m, 2H, H12, H24), 2.20~2.39 (m, 3H, H16x2, H2′), 1.95~2.07 (m, 5H, Me4a, H18, H20), 1.39~1.80 (m, 10H, Me14a, H20, H26, H27x2, H22x2, H2′), 1.29 (d, *J* = 6.2 Hz, 3H, Me6′), 1.17 (d, *J* = 6.9 Hz, 3H, Me12a), 0.82~1.07 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*13C NMR (75 MHz, CDCl3) *δ* 172.14, 168.15, 156.83, 138.56, 137.39, 135.48, 132.99, 131.46, 129.88, 129.22, 128.40, 127.04, 124.52, 121.73, 117.43, 99.49, 94.86, 81.41, 78.94, 78.17, 75.85, 73.80, 70.65, 69.68, 68.64, 68.20, 68.07, 67.81, 56.41, 46.22, 40.98, 40.63, 39.96, 39.77, 36.21, 35.53, 34.97, 33.93, 33.84, 27.11, 19.99, 17.58, 17.36, 15.00, 13.61, 12.26, 11.66; HRMS (ESI) calcd for $C_{49}H_{68}NO_{13}$ $(M + H)^+$ 878.4691, found 878.4693.

*5-((2-fluorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (**11c**):* yield, 74% ; white solid; mp: 238-240 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.94~8.13 (m, 1H, Ar-H), 7.49~7.64 (m, 1H, Ar-H), 7.08~7.29 (m, 2H, Ar-H), 6.04~6.13 (m, 1H, H3), 5.88~6.01 (m, 1H, H9), 5.69~5.83 (m, 2H, H10, H11), 5.32~5.44 (m, 1H, H19), 4.98 (t, *J* = 7.2 Hz, 1H, H15), 4.70~4.83 (m, 4H, H1′, H8ax2, H6), 3.98 (s, 1H, 7-OH),

3.72~3.91 (m, 4H, 23-OH, H23, H13, H5′), 3.37~3.62 (m, 7H, H17, H25, H2, H3′, 3′-OCH_3), 3.17 (t, *J* = 9.1 Hz, 1H, H4′), 2.47~2.64 (m, 2H, H12, H24), 2.20~2.39 (m, 3H, H16x2, H2′), 2.13 (s, 3H, Me4a), 1.92~2.07 (m, 2H, H18, H20), 1.43~1.76 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.28 (d, *J* = 6.2 Hz, 3H, Me6′), 1.16 (d, *J* = 7.0 Hz, 3H, Me12a), 0.79~1.01 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$), *δ*13C NMR (75 MHz, CDCl3) *δ* 172.18, 161.23(d, *J* = 259.1 Hz), 160.04, 157.63, 138.47, 137.68, 135.51, 134.87 (d, *J* = 8.8 Hz), 132.40, 131.51, 130.32, 124.64, 124.06 (d, *J* = 3.6 Hz), 121.77, 117.46, 117.06, 116.76, 99.53, 94.89, 81.45, 79.12, 78.18, 75.89, 74.28, 70.68, 69.73, 68.85, 68.24, 68.07, 67.84, 56.42, 46.36, 41.01, 40.67, 39.78, 36.23, 35.56, 34.99, 33.86, 32.19, 27.13, 19.99, 17.58, 17.44, 15.02, 13.62, 12.28, 11.68; HRMS (ESI) calcd for $C_{48}H_{65}FNO_{13}$ $(M + H)^+$ 882.4440, found 882.4467.

*5-((2-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (**11d**):* yield, 67% ; white solid; mp: 236-239 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.85~7.95 (m, 1H, Ar-H), 7.42~7.52 (m, 2H, Ar-H), 7.30~7.39 (m, 1H, Ar-H), 6.05~6.17 (m, 1H, H3), 5.87~6.02 (m, 1H, H9), 5.62~5.85 (m, 2H, H10, H11), 5.31~5.48 (m, 1H, H19), 4.97 (t, *J* = 7.4 Hz, 1H, H15), 4.63~4.83 (m, 4H, H8ax2, H1′, H6), 3.97 (s, 1H, 7-OH), 3.68~3.93 (m, 4H, 23-OH, H23, H13, H5′), 3.39~3.64 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.16 (t, 1H, *J* = 9.1 Hz, H4′), 2.45~2.64 (m, 2H, H12, H24), 2.22~2.37 (m, 3H, H16x2, H2′), 2.13 (s, 3H, Me4a), 1.94~2.05 (m, 2H, H18, H20), 1.40~1.78 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, *J* =5.7 Hz, 3H, Me6′), 1.15 (d, *J* = 6.9 Hz, 3H, Me12a), 0.78~1.02 (m, 10H, H28, Me 24a, Me26a, H18; ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 172.22, 162.39, 157.62, 138.63, 137.46, 135.54, 133.88, 132.91, 131.72, 131.61, 131.03, 130.25, 128.67, 126.58, 124.59, 121.85, 117.47, 99.55, 94.91, 81.46, 79.09, 78.21, 75.90, 74.31, 70.71, 69.75, 68.86, 68.25, 68.08, 67.91, 56.44, 46.36, 41.03, 40.68, 39.81, 36.26, 35.58, 35.02, 33.97, 33.85, 27.16, 20.00, 17.61, 17.48, 15.06, 13.65, 12.31, 11.71; HRMS (ESI) calcd for $C_{48}H_{64}ClNO_{13}$ $(M + H)^+$ 898.4144, found 898.4164.

*5-((2-bromobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (**11e**):* yield, 66% ; white solid; mp: 239-242 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.81~7.89 (m, 1H, Ar-H), 7.64~7.71 (m, 1H, Ar-H), 7.32~7.43 (m, 2H, Ar-H), 6.06~6.11 (m, 1H, H3), 5.90~6.01 (m, 1H, H9), 5.66~5.83 (m, 2H, H10, H11),5.32~5.46 (m, 1H, H19), 4.97 (t, *J* = 7.2 Hz, 1H, H15), 4.66~4.85 (m, 4H, H8ax2, H1′, H6), 3.97 (s, 1H, 7-OH), 3.70~3.91 (m, 4H, 23-OH, H23, H13, H5′), 3.42~3.61 (m, 7H, H17, H25, H3′, H2,

3′-OCH_3), 3.17 (t, 1H, *J* = 9.2 Hz, H4′), 2.47~2.60 (m, 2H, H12, H24), 2.19~2.39 (m, 3H, H16x2, H2′), 2.13 (s, 3H, Me4a), 1.94~2.06 (m, 2H, H18, H20), 1.38~1.79 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, *J* =6.1 Hz, 3H, Me6′), 1.15 (d, *J* = 6.9 Hz, 3H, Me12a), 0.80~1.03 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$), *δ*13C NMR (75 MHz, CDCl3) *δ*13C NMR (75 MHz, CDCl3) *δ* 172.18, 162.80, 157.63, 138.63, 137.42, 135.52, 134.30, 132.85, 131.56, 130.76, 130.26, 127.11, 124.58, 121.83, 117.45, 99.54, 94.90, 81.45, 79.07, 78.19, 75.88, 74.26, 70.69, 69.73, 68.84, 68.23, 68.07, 67.90, 56.43, 46.33, 41.02, 40.67, 39.80, 36.24, 35.57, 35.00, 33.96, 33.84, 27.15, 19.98, 17.60, 17.47, 15.05, 13.65, 12.30, 11.70; HRMS (ESI) calcd for $C_{48}H_{65}BrNO_{13}$ $(M + H)^+$ 942.3639, found 942.3673.

*5-((2-trifluoromethylbenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide **(11f)** :* yield, 70%; white solid; mp: 222-225 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.83~7.90 (m, 1H, Ar-H), 7.75~7.81 (m, 1H, Ar-H), 7.61~7.69 (m, 2H, Ar-H), 6.06~6.13 (m, 1H, H3), 5.89~5.97 (m, 1H, H9), 5.64~5.83 (m, 2H, H10, H11), 5.32~5.44 (m, 1H, H19), 4.97 (t, *J* = 7.2 Hz, 1H, H15), 4.60~4.83 (m, 4H, H8ax2, H1′, H6), 3.96 (s, 1H, 7-OH), 3.70~3.93 (m, 4H, 23-OH, H23, H13, H5′), 3.40~3.63 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.17 (t, 1H, *J* = 9.1 Hz, H4′), 2.45~2.62 (m, 2H, H12, H24), 2.20~2.37 (m, 3H, H16x 2, H2′), 2.12 (s, 3H, Me4a), 1.95~2.05 (m, 2H, H18, H20), 1.37~1.76 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, *J* = 6.9 Hz, 3H, Me6′), 1.14 (d, *J* = 7.0 Hz, 3H, Me12a), 0.80~1.04 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 172.02, 163.23, 157.78, 138.53, 137.37, 135.49, 131.71, 131.49, 131.36, 130.59, 130.43, 128.64 (q, *J* = 32.6 Hz), 126.58 (q, *J* = 5.2 Hz), 124.54, 121.81, 121.23 (q, *J* = 271.9 Hz), 117.43, 99.51, 94.87, 81.43, 79.08, 78.17, 75.84, 74.00, 70.65, 69.71, 68.69, 68.22, 68.04, 67.87, 56.38, 46.27, 40.97, 40.65, 39.76, 36.18, 35.52, 34.97, 33.83, 27.11, 19.92, 17.54, 17.40, 14.98, 13.59, 12.24, 11.65; HRMS (ESI) calcd for $C_{49}H_{65}F_3NO_{13}$ $(M + H)^+$ 932.4408, found 932.4420.

*5-((3-methylbenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide **(11g)** :* yield, 81%; white solid; mp: 208-211C; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.82~7.94 (m, 2H, Ar-H), 7.30~7.44 (m, 2H, Ar-H), 6.04~6.11 (m, 1H, H3), 5.93~6.03 (m, 1H, H9), 5.70~5.85 (m, 2H, H10, H11), 5.30~5.45 (m, 1H, H19), 4.97 (t, *J* = 7.1 Hz, 1H, H15), 4.70~4.85 (m, 4H, H8ax2, H1′, H6), 3.70~4.00 (m, 5H, 7-OH, 23-OH, H23, H13, H5′), 3.43~3.61 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.16 (t, 1H, *J* = 9.1 Hz, H4′), 2.48~2.71 (m, 2H, H12, H24), 2.41 (s, 3H, $PhCH_3$), 2.19~2.37 (m, 3H, H16x2, H2′),

2.14 (s, 3H, Me4a), 1.88~2.04 (m, 2H, H18, H20), 1.42~1.79 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, *J* = 6.2 Hz, 3H, Me6′), 1.16 (d, *J* = 7.0 Hz, 3H, Me12a), 0.82~1.01 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) 172.16, 163.17, 157.26, 138.64, 138.18, 137.54, 135.48, 134.08, 131.66, 130.21, 129.84, 128.49, 128.29, 126.74, 124.59, 121.91, 117.45, 99.51, 94.88, 81.44, 79.01, 78.16, 75.86, 74.36, 70.65, 69.70, 68.86, 68.22, 68.07, 67.82, 56.41, 46.31, 40.98, 40.64, 39.79, 36.22, 35.54, 34.93, 33.85, 27.11, 24.78, 21.21, 19.96, 17.58, 17.47, 15.00, 13.62, 12.26, 11.66; HRMS (ESI) calcd for $C_{49}H_{68}NO_{13}$ $(M + H)^+$ 878.4691, found 878.4713.

5-((4-methoxybenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide ***(11h)*** *:* yield, 65%; white solid; mp: 198-200 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.94 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.03~6.10 (m, 1H, H3), 5.92~6.03 (m, 1H, H9), 5.69~5.86 (m, 2H, H10, H11), 5.32~5.47 (m, 1H, H19), 4.98 (t, *J* = 7.0 Hz, 1H, H15), 4.68~4.88 (m, 4H, H8ax2, H1′, H6), 3.98 (s, 1H, 7-OH), 3.71~3.93 (m, 7H, 23-OH, H23, H13, H5′, $PhOCH_3$), 3.43~3.62 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.17 (t, 1H, *J* = 9.1 Hz, H4′), 2.46~2.68 (m, 2H, H12, H24), 2.21~2.39 (m, 3H, H16x2, H2′), 2.14 (s, 3H, Me4a), 1.94~2.07 (m, 2H, H18, H20), 1.42~1.76 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.28 (d, *J* = 6.2 Hz, 3H, Me6′), 1.16 (d, *J* = 6.9 Hz, 3H, Me12a), 0.81~1.04 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) 13C NMR (75 MHz, CDCl3) δ 172.26, 163.67, 162.80, 156.93, 138.64, 137.58, 135.52, 131.83, 131.78, 129.54, 124.63, 121.89, 120.82, 117.50, 113.78, 99.55, 94.92, 81.49, 79.01, 78.20, 75.90, 74.36, 70.70, 69.75, 68.88, 68.26, 68.09, 67.87, 56.44, 55.33, 46.32, 41.02, 40.68, 39.84, 36.26, 35.58, 35.01, 33.96, 33.86, 27.15, 20.01, 17.60, 17.50, 15.06, 13.65, 12.30, 11.70; HRMS (ESI) calcd for $C_{49}H_{68}NO_{14}$ $(M + H)^+$ 894.4640, found 894.4668.

5-((4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide ***(11i)*** *:* yield, 73%; white solid; mp: 182-185 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.44 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.05~6.12 (m, 1H, H3), 5.94~6.04 (m, 1H, H9), 5.69~5.86 (m, 2H, H10, H11), 5.30~5.47 (m, 1H, H19), 4.98 (t, *J* = 7.4 Hz, 1H, H15), 4.69~4.87 (m, 4H, H8ax2, H1′, H6), 3.98 (s, 1H, 7-OH), 3.70~3.94 (m, 4H, 23-OH, H23, H13, H5′), 3.42~3.63 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.17 (t, 1H, *J* = 9.1 Hz, H4′), 2.47~2.67 (m, 2H, H12, H24), 2.19~2.39 (m, 3H, H16x2, H2′), 2.13 (s, 3H, Me4a), 1.94~2.08 (m, 2H, H18, H20), 1.42~1.75 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, *J* = 6.2 Hz, 3H, Me6′), 1.16 (d, *J* = 6.9 Hz, 3H,

Me12a), 0.78~1.04 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.98, 162.16, 157.58, 139.76, 138.71, 137.27, 135.48, 131.43, 130.98, 130.27, 128.79, 127.06, 124.53, 122.01, 117.44, 99.49, 94.86, 81.42, 78.97, 78.15, 75.81, 74.38, 70.64, 69.67, 68.85, 68.20, 68.06, 67.86, 56.38, 46.26, 40.95, 40.63, 39.78, 36.17, 35.51, 34.95, 33.84, 27.09, 19.94, 17.55, 17.39, 14.99, 14.00, 13.59, 12.23, 11.64; HRMS (ESI) calcd for $C_{48}H_{65}ClNO_{13}$ $(M + H)^+$ 898.4144, found 898.4159.

*5-((4-nitrobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (**11j**) :* yield, 66%; pale yellow solid; mp: 186-188 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16~8.43 (m, 4H, Ar-H), 6.09~6.16 (m, 1H, H3), 5.94~6.04 (m, 1H, H9), 5.70~5.88 (m, 2H, H10, H11), 5.31~5.47 (m, 1H, H19), 4.98 (t, *J* = 7.4 Hz, 1H, H15), 4.71~4.87 (m, 4H, H8ax2, H1′, H6), 3.72~4.01 (m, 5H, 7-OH, 23-OH, H23, H13, H5′), 3.43~3.62 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.17 (t, 1H, *J* = 9.1 Hz, H4′), 2.49~2.63 (m, 2H, H12, H24), 2.19~2.40 (m, 3H, H16x2, H2′), 2.14 (s, 3H, Me4a), 1.95~2.08 (m, 2H, H18, H20), 1.43~1.72 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, *J* = 6.2 Hz, 3H, Me6′), 1.17 (d, *J* = 6.9 Hz, 3H, Me12a), 0.80~1.02 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.01, 161.20, 158.28, 150.60, 138.94, 137.01, 135.51, 134.12, 131.27, 130.86, 130.74, 124.48, 123.58, 122.16, 117.44, 99.50, 94.88, 81.42, 78.96, 78.15, 75.85, 74.46, 70.67, 69.69, 68.98, 68.21, 68.08, 67.97, 56.39, 46.29, 40.97, 40.63, 39.81, 36.22, 35.53, 34.96, 33.85, 27.11, 19.95, 17.56, 17.36, 15.02, 13.60, 12.25, 11.65; HRMS (ESI) calcd for $C_{48}H_{65}N_2O_{15}$ $(M + H)^+$ 909.4385, found 909.4395.

*5-((2,4-dichlorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (**11k**):* yield, 75%; white solid; mp: 199-201 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.50 (d, *J* = 1.9 Hz, 1H, Ar-H), 7.33 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, Ar-H), 6.05~6.13 (m, 1H, H3), 5.90~6.01 (m, 1H, H9), 5.65~5.85 (m, 2H, H10, H11), 5.30~5.45 (m, 1H, H19), 4.98 (t, *J* = 6.7 Hz, 1H, H15), 4.63~4.85 (m, 4H, H8ax2, H1′, H6), 3.97 (s, 1H, 7-OH), 3.70~3.92 (m, 4H, 23-OH, H23, H13, H5′), 3.41~3.61 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.17 (t, 1H, *J* = 9.4 Hz, H4′), 2.48~2.64 (m, 2H, H12, H24), 2.20~2.39 (m, 3H, H16x2, H2′), 2.12 (s, 3H, Me4a), 1.89~2.06 (m, 2H, H18, H20), 1.41~1.75 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, *J* = 6.2 Hz, 3H, Me6′), 1.15 (d, *J* = 6.9 Hz, 3H, Me12a), 0.81~1.04 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.17, 161.52, 157.82, 138.76, 137.31, 135.55, 135.04, 132.76, 131.50, 130.99, 130.49, 127.07, 126.99, 124.56, 121.95, 117.47, 99.55, 94.92, 81.45, 79.07, 78.20, 75.92, 74.36, 70.72, 69.74, 68.89,

68.25, 68.09, 67.95, 56.44, 46.35, 41.05, 40.69, 39.83, 36.28, 35.59, 35.02, 33.98, 33.87, 33.78, 27.17, 20.00, 17.61, 17.45, 15.06, 13.66, 12.31, 11.71; HRMS (ESI) calcd for $C_{48}H_{64}Cl_2NO_{13}$ $(M + H)^+$ 932.3755, found 932.3794.

*5-((3-trifluoromethyl-4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (**11l**) :* yield, 72%; white solid; mp: 183-186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, J = 1.8 Hz, 1H, Ar-H), 8.19 (dd, J = 8.4 Hz, 1.9 Hz, 1H, Ar-H), 7.64 (d, J = 8.4 Hz, 1H, Ar-H), 6.06~6.17 (m, 1H, H3), 5.93~6.04 (m, 1H, H9), 5.69~5.88 (m, 2H, H10, H11), 5.31~5.49 (m, 1H, H19), 4.98 (t, J = 7.3 Hz, 1H, H15), 4.64~4.85 (m, 4H, H8ax2, H1′, H6), 3.71~4.01 (m, 5H, 7-OH, 23-OH, H23, H13, H5′), 3.40~3.61 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.17 (t, 1H, J = 9.2 Hz, H4′), 2.52~2.64 (m, 2H, H12, H24), 2.21~2.38 (m, 3H, H16x2, H2′), 2.13 (s, 3H, Me4a), 1.88~2.06 (m, 2H, H18, H20), 1.44~1.75 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.28 (d, J = 6.2 Hz, 3H, Me6′), 1.17 (d, J = 7.0 Hz, 3H, Me12a), 0.82~1.02 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.21, 161.06, 158.12, 139.00, 137.12, 135.58, 133.85, 131.97, 131.45, 130.65, 128.87 (q, J = 13.3 Hz), 127.68, 124.54, 122.23, 120.42 (q, J = 271.9 Hz) 117.47, 99.56, 94.93, 81.46, 78.99, 78.22, 75.93, 74.71, 70.74, 69.75, 68.99, 68.27, 68.12, 67.98, 56.45, 46.41, 41.05, 40.68, 39.85, 36.31, 35.61, 35.03, 33.99, 33.88, 33.80, 27.18, 24.82, 19.98, 17.62, 17.43, 15.06, 13.66, 12.31, 11.71; HRMS (ESI) calcd for $C_{49}H_{64}ClF_3NO_{13}$ $(M + H)^+$ 966.4018, found 966.4029.

*5-((3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (**11m**) :* yield, 74%; white solid; mp: 210-212 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.27 (s, 1H, Ar-H), 8.81 (d, J = 3.6 Hz, 1H, Ar-H), 8.31~8.40 (m, 1H, Ar-H), 7.38~7.49 (m, 1H, Ar-H), 6.07~6.16 (m, 1H, H3), 5.92~6.03 (m, 1H, H9),5.67~5.86 (m, 2H, H10, H11), 5.28~5.49 (m, 1H, H19), 4.97 (t, J = 7.2 Hz, 1H, H15), 4.67~4.88 (m, 4H, H8ax2, H1′, H6), 3.70~4.01 (m, 5H, 7-OH, 23-OH, H23, H13, H5′), 3.43~3.62 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.17 (t, 1H, J = 9.1 Hz, H4′), 2.49~2.70 (m, 2H, H12, H24), 2.20~2.39 (m, 3H, H16x2, H2′), 2.13 (s, 3H, Me4a), 1.90~2.09 (m, 2H, H18, H20), 1.40~1.73 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, J = 6.2 Hz, 3H, Me6′), 1.16 (d, J = 6.9 Hz, 3H, Me12a), 0.83~1.02 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.82, 161.65, 158.05, 153.52, 150.57, 138.75, 137.22, 137.14, 135.50, 131.18, 130.86, 124.53, 123.43, 122.17, 117.44, 99.50, 94.87, 81.42, 79.03, 78.16, 75.85, 74.48, 70.64, 69.69, 68.88, 68.22, 68.09, 67.90, 56.41, 46.26, 40.98, 40.68, 39.80, 36.18, 35.52, 34.96, 33.89, 27.10, 20.83, 19.94, 17.57, 17.37, 15.01, 13.60, 12.24, 11.65; HRMS (ESI) calcd for $C_{47}H_{65}N_2O_{13}$ $(M + H)^+$ 865.4487, found 865.4491.

*5-((2-chloro-3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a monosaccharide **(11n)**:* yield, 76%; white solid; mp: 226-229 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55

(dd, *J* = 4.8 Hz, 2.0 Hz, 1H, Ar-H), 8.22 (dd, *J* = 7.7 Hz, 2.0 Hz, 1H, Ar-H), 7.36 (dd, *J* = 4.8 Hz, 7.7 Hz, 1H, Ar-H), 6.07~6.15 (m, 1H, H3), 5.89~6.01 (m, 1H, H9), 5.65~5.84 (m, 2H, H10, H11), 5.27~5.46 (m, 1H, H19), 4.97 (t, *J* = 7.1 Hz, 1H, H15), 4.65~4.83 (m, 4H, H8ax2, H1′, H6), 3.97 (s, 1H, 7-OH), 3.70~3.93 (m, 4H, 23-OH, H23, H13, H5′), 3.42~3.62 (m, 7H, H17, H25, H3′, H2, 3′-OCH_3), 3.16 (t, 1H, *J* = 9.1 Hz, H4′), 2.47~2.65 (m, 2H, H12, H24), 2.20~2.37 (m, 3H, H16x2, H2′), 2.11 (s, 3H, Me4a), 1.95~2.05 (m, 2H, H18, H20), 1.41~1.69 (m, 10H, Me14a, H20, H2′, H26, H27x2, H22x2), 1.27 (d, *J* = 5.6 Hz, 3H, Me6′), 1.15 (d, *J* = 6.9 Hz, 3H, Me12a), 0.80~1.02 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 171.95, 161.37, 158.15, 152.09, 149.86, 140.56, 138.72, 137.13, 135.50, 131.18, 125.69, 124.50, 122.06, 122.00, 117.41, 99.49, 94.86, 81.40, 79.07, 78.15, 75.84, 74.34, 70.65, 69.68, 68.86, 68.20, 68.05, 67.92, 56.40, 46.30, 40.98, 40.64, 39.76, 36.19, 35.52, 34.95, 33.91, 33.84, 27.10, 19.93, 17.56, 17.37, 15.00, 14.02, 13.60, 12.25, 11.66; HRMS (ESI) calcd for $C_{47}H_{64}ClN_2O_{13}$ $(M + H)^+$ 899.4097, found 899.4106.

*5-(benzoyloxyimino)-5-deoxyavermectin B2a aglycone (**14a**)*: yield, 75% ; white solid; mp: 230-233 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.02-8.14 (m, 2H, Ar-H), 7.53-7.65 (m, 1H, Ar-H), 7.40-7.53 (m, 2H, Ar-H), 6.03-6.10 (m, 1H, H3), 5.87-5.96 (m, 1H, H9), 5.69-5.85 (m, 2H, H10, H11), 5.27-5.38 (m, 2H, H19, H15), 4.68-4.88 (m, 3H, H8ax2, H6), 4.01 (s, 1H, 7-OH), 3.92 (s, 1H, 23-OH), 3.65-3.83 (m, 2H, H23, H13), 3.39-3.61 (m, 2H, H17, H25), 3.37-3.45 (m, 1H, H2), 2.45-2.59 (m, 1H, H12), 1.86-2.40 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.36-1.75 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.17 (d, *J* = 7.0 Hz, 3H, Me12a), 0.80-1.04 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 172.15, 163.11, 157.42, 139.14, 138.11, 137.55, 133.36, 131.69, 129.97, 129.72, 128.70, 128.48, 124.53, 121.99, 116.47, 99.53, 78.95, 77.36, 74.39, 71.33, 69.86, 69.02, 68.35, 67.90, 46.34, 41.10, 40.81, 40.18, 36.15, 35.64, 35.10, 34.12, 27.41, 19.03, 17.52, 14.52, 13.73, 12.44, 11.41 ; HRMS (ESI) calcd for $C_{41}H_{54}NO_{10}$ $(M + H)^+$ 720.3748, found 720.3752.

*5-(phenylacetyloxyimino)-5-deoxyavermectin B2a aglycone (**14b**):* yield, 76% ; white solid; mp: 189-191 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*7.20-7.42 (m, 5H, Ar-H), 5.99-6.08 (m, 1H, H3), 5.84-5.93 (m, 1H, H9), 5.68-5.82 (m, 2H, H10, H11), 5.24-5.37 (m, 2H, H19, H15), 4.65(d, *J* = 1.9 Hz, 2H, H8ax2), 4.47 (s, 1H, H6), 4.01 (s, 1H, 7-OH), 3.88 (s, 1H, 23-OH), 3.67-3.84 (m, 4H, H23, H13, PhCH2), 3.49-3.62 (m, 2H, H17, H25), 3.30-3.40 (m, 1H, H2), 2.44-2.62 (m, 1H, H12), 1.90-2.41 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.39-1.74 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.19 (d, *J* = 6.9 Hz, 3H, Me12a), 0.78-1.04 (m, 10H, H28, Me24a, Me26a,

H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.99, 168.25, 156.88, 139.12, 138.01, 137.36, 133.01, 131.34, 130.02, 129.24, 128.42, 127.06, 124.39, 121.79, 116.36, 99.44, 78.85, 77.21, 73.81, 71.24, 69.79, 68.71, 68.29, 67.79, 46.20, 41.01, 40.73, 40.11, 39.99, 36.05, 35.55, 35.03, 34.08, 27.33, 19.01, 17.37, 14.44, 13.66, 12.37, 11.36; HRMS (ESI) calcd for $C_{42}H_{56}NO_{10}$ $(M + H)^+$ 734.3904, found 734.3904.

*5-((2-fluorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (**14c**):* yield, 75%; white solid; mp: 206-209 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94~8.07 (m, 1H, Ar-H), 7.48~7.61 (m, 1H, Ar-H), 7.07~7.32 (m, 2H, Ar-H), 6.04~6.11 (m, 1H, H3), 5.86~5.96 (m, 1H, H9), 5.67~5.85 (m, 2H, H10, H11), 5.20~5.39 (m, 2H, H19, H15), 4.65~4.81 (m, 3H, H8ax2, H6), 4.00 (s, 1H, 7-OH), 3.94 (s, 1H, 23-OH), 3.67~3.83 (m, 2H, H23, H13), 3.49~3.66 (m, 2H, H17, H25), 3.38~3.48 (m, 1H, H2), 2.46~2.61 (m, 1H, H12), 1.86~2.41 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.39~1.69 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.17 (d, J = 6.9 Hz, 3H, Me12a), 0.81~1.04 (m, 10H, H28, Me24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.05, 163.52 (d, J = 259.0 Hz), 161.24 (d, J = 4.0 Hz), 157.68, 139.15, 137.66 (d, J = 21.6 Hz), 134.90 (d, J = 8.9 Hz), 132.42, 131.39, 130.46, 124.52, 124.09 (d, J = 3.8 Hz), 121.83, 117.08, 117.00 (d, J = 10.6 Hz), 116.79, 116.39, 99.48, 79.03, 77.25, 74.29, 71.28, 69.83, 68.93, 68.33, 67.84, 46.34, 41.03, 40.77, 40.12, 36.07, 35.57, 35.05, 34.08, 27.36, 19.00, 17.45, 14.46, 13.68, 12.40, 11.36; HRMS (ESI) calcd for $C_{41}H_{53}FNO_{10}$ $(M + H)^+$ 738.3654, found 738.3658.

*5-((2-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (**14d**):* yield, 80%; white solid; mp: 212-214 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86~7.94 (m, 1H, Ar-H), 7.42~7.54 (m, 2H, Ar-H), 7.30~7.40 (m, 1H, Ar-H), 6.07~6.13 (m, 1H, H3), 5.85~5.95 (m, 1H, H9), 5.69~5.83 (m, 2H, H10, H11),5.23~5.43 (m, 2H, H19, H15), 4.65~4.79 (m, 3H, H8ax2, H6), 4.02 (s, 1H, 7-OH), 3.91 (s, 1H, 23-OH), 3.67~3.83 (m, 2H, H23, H13), 3.49~3.62 (m, 2H, H17, H25), 3.39~3.46 (m, 1H, H2), 2.46~2.60 (m, 1H, H12), 1.83~2.41 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.39~1.72 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.18 (d, J = 7.0 Hz, 3H, Me12a), 0.80~1.06 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.07, 162.47, 157.70, 139.16, 138.05, 137.48, 133.90, 132.92, 131.75, 131.48, 131.05, 130.42, 128.71, 126.60, 124.49, 121.90, 116.42, 99.50, 79.01, 77.30, 74.32, 71.31, 69.85, 68.94, 68.34, 67.89, 46.34, 41.08, 40.79, 40.14, 36.11, 35.61, 35.08, 34.11, 27.39, 19.01, 17.48, 14.49, 13.71, 12.42, 11.39; HRMS (ESI) calcd for $C_{41}H_{53}ClNO_{10}$ $(M + H)^+$ 754.3358, found 754.3361.

*5-((2-bromobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (**14e**):* yield, 81% ; white solid; mp: 207-210 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79~7.93 (m, 1H, Ar-H), 7.65~7.75 (m, 1H, Ar-H), 7.32~7.46 (m, 2H, Ar-H), 6.05~6.17 (m, 1H, H3), 5.86~5.97 (m, 1H, H9), 5.69~5.83 (m, 2H, H10, H11), 5.25~5.40 (m, 2H, H19, H15), 4.64~4.79 (m, 3H, H8ax2, H6), 4.02 (s, 1H, 7-OH), 3.91 (s, 1H, 23-OH), 3.68~3.83 (m, 2H, H23, H13), 3.47~3.62 (m, 2H, H17, H25), 3.38~3.45 (m, 1H, H2), 2.44~2.62 (m, 1H, H12), 1.78~2.39 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.37~1.73 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.18 (d, J = 7.0 Hz, 3H, Me12a), 0.81~1.06 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.01, 162.88, 157.72, 139.15, 138.07, 137.42, 134.31, 132.87, 131.58, 131.42, 130.45, 127.12, 124.45, 121.91, 121.83, 116.39, 99.48, 78.99, 77.25, 74.27, 71.29, 69.83, 68.91, 68.32, 67.88, 46.31, 41.05, 40.77, 40.13, 36.08, 35.58, 35.06, 33.77, 27.37, 24.82, 19.00, 17.46, 14.48, 13.70, 12.41, 11.37 ; HRMS (ESI) calcd for $C_{41}H_{53}BrNO_{10}$ $(M + H)^+$ 798.2853, found 798.2855.

*5-((3-methylbenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (**14f**) :* yield, 63%; white solid; mp: 201-204 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85~7.96 (m, 2H, Ar-H), 7.29~7.45 (m, 2H, Ar-H), 6.04~6.12 (m, 1H, H3), 5.89~5.99 (m, 1H, H9), 5.71~5.86 (m, 2H, H10, H11), 5.26~5.41 (m, 2H, H19, H15), 4.70~4.88 (m, 3H, H8ax2, H6), 4.02 (s, 1H, 7-OH), 4.00 (s, 1H, 23-OH), 3.68~3.85 (m, 2H, H23, H13), 3.37~3.64 (m, 3H, H17, H25, H2), 2.47~2.61 (m, 1H, H12), 2.42 (s, 3H, PhCH3), 1.82~2.38 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.41~1.73 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.19 (d, J = 6.8 Hz, 3H, Me12a), 0.80~1.04 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.35, 162.50, 158.54, 139.48, 138.40, 138.07, 134.40, 134.14, 129.62, 128.86, 128.22, 127.89, 126.35, 124.34, 122.56, 116.47, 98.84, 79.40, 75.77, 74.21, 69.81, 68.32, 68.15, 67.72, 45.81, 40.35, 40.08, 35.36, 35.19, 34.73, 26.77, 20.84, 20.63, 19.25, 17.07, 14.17, 14.00, 13.57, 12.11, 11.82 ; HRMS (ESI) calcd for $C_{42}H_{56}NO_{10}$ $(M + H)^+$ 734.3904, found 734.3911.

*5-((4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (**14g**) :* yield, 76%; white solid; mp: 192-195 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.7 Hz, 2H, Ar-H), 7.43 (d, J = 8.7 Hz, 2H, Ar-H), 6.05~6.15 (m, 1H, H3), 5.88~5.97 (m, 1H, H9), 5.71~5.85 (m, 2H, H10, H11), 5.25~5.38 (m, 2H, H19, H15), 4.69~4.85 (m, 3H, H8ax2, H6), 3.94~4.04 (m, 2H, 7-OH, 23-OH), 3.68~3.82 (m, 2H, H23, H13), 3.39~3.62 (m, 3H, H17, H25, H2), 2.47~2.61 (m, 1H, H12), 1.85~2.39 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.38~1.74 (m, 9H, Me14a, H20, H26, H27x2,

H22x2), 1.18 (d, *J* = 6.9 Hz, 3H, Me12a), 0.80~1.04 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.06, 162.29, 157.69, 139.88, 139.15, 138.25, 137.35, 131.54, 131.06, 130.28, 128.88, 127.18, 124.47, 122.11, 116.48, 99.52, 78.93, 77.33, 74.43, 71.34, 69.85, 69.03, 68.35, 67.94, 46.33, 41.10, 40.82, 40.19, 36.15, 35.63, 35.10, 34.13, 33.79, 27.40, 24.83, 19.03, 17.47, 14.51, 13.72, 12.42, 11.41; HRMS (ESI) calcd for $C_{41}H_{53}ClNO_{10}$ $(M + H)^+$ 754.3358, found 754.3360.

*5-((4-nitrobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (**14h**):* yield, 70%; pale yellow solid; mp: 189-191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19~8.38 (m, 4H, Ar-H), 6.08~6.18 (m, 1H, H3), 5.89~5.96 (m, 1H, H9), 5.69~5.87 (m, 2H, H10, H11), 5.23~5.41 (m, 2H, H19, H15), 4.68~4.86 (m, 3H, H8ax2, H6), 4.01 (s, 1H, 7-OH), 3.67~3.82 (m, 2H, H23, H13), 3.35~3.64 (m, 3H, H17, H25, H2), 2.47~2.62 (m, 1H, H12), 1.82~2.39 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.35~1.73 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.18 (d, *J* = 6.9 Hz, 3H, Me12a), 0.79~1.04 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.71, 161.21, 158.36, 150.58, 139.10, 138.42, 136.93, 134.13, 131.13, 130.71, 124.30, 123.55, 122.25, 116.36, 99.42, 78.88, 77.14, 74.47, 71.22, 69.77, 68.99, 68.29, 67.91, 48.86, 46.24, 40.95, 40.72, 40.12, 36.00, 35.49, 34.99, 34.03, 33.62, 27.29, 24.71, 18.94, 17.31, 14.40, 13.62, 12.31, 11.30; HRMS (ESI) calcd for $C_{41}H_{53}N_2O_{12}$ $(M + H)^+$ 765.3599, found 765.3604.

*5-((2,4-dichlorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (**14i**):* yield, 65%; white solid; mp: 196-199 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.88 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.52 (d, *J* = 1.9 Hz, 1H, Ar-H), 7.34 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H, Ar-H), 6.07~6.13 (m, 1H, H3), 5.88~5.96 (m, 1H, H9), 5.70~5.84 (m, 2H, H10, H11), 5.24~5.42 (m, 2H, H19, H15), 4.65~4.78 (m, 3H, H8ax2, H6), 4.03 (s, 1H, 7-OH), 3.92 (s, 1H, 23-OH), 3.68~3.84 (m, 2H, H23, H13), 3.36~3.61 (m, 3H, H17, H25, H2), 2.46~2.61 (m, 1H, H12), 1.85~2.42 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.42~1.79 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.19 (d, *J* = 7.0 Hz, 3H, Me12a), 0.82~1.06 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.98, 161.57, 157.89, 139.15, 138.77, 138.15, 137.30, 135.04, 132.77, 131.35, 130.99, 130.66, 127.07, 124.43, 122.01, 116.42, 99.49, 78.98, 77.27, 74.38, 71.30, 69.83, 68.94, 68.33, 67.91, 46.33, 40.79, 40.15, 36.10, 35.59, 35.07, 34.11, 33.77, 27.38, 24.81, 19.00, 17.43, 14.48, 13.69, 12.40, 11.39; HRMS (ESI) calcd for $C_{41}H_{52}Cl_2NO_{10}$ $(M + H)^+$ 788.2968, found 788.2977.

5-((3-trifluoromethyl-4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone

(14j) *:* yield, 73%; white solid; mp: 203-206 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, J = 1.7 Hz, 1H, Ar-H), 8.21 (dd, J = 8.4 Hz, 1.9 Hz, 1H, Ar-H), 7.65 (d, J = 8.4 Hz, 1H, Ar-H), 6.08~6.13 (m, 1H, H3), 5.90~6.00 (m, 1H, H9), 5.73~5.85 (m, 2H, H10, H11), 5.28~5.42 (m, 2H, H19, H15), 4.79(d, J =1.9 Hz, 2H, H8ax2), 4.71 (s, 1H, H6), 4.04 (s, 1H, 7-OH), 4.02 (s, 1H, 23-OH), 3.70~3.86 (m, 2H, H23, H13), 3.38~3.62 (m, 3H, H17, H25, H2), 2.51~2.63 (m, 1H, H12), 1.88~2.43 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.42~1.76 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.21 (d, J = 7.0 Hz, 3H, Me12a), 0.82~1.09 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.16, 161.13, 158.20, 139.17, 138.38, 137.81, 137.20, 133.90, 132.02, 131.46, 130.74, 128.93(q, J = 18.7 Hz), 127.77, 124.50, 122.30, 120.49 (q, J = 272.0 Hz), 116.52, 99.56, 78.92, 74.76, 71.40, 69.88, 69.12, 68.38, 68.01, 49.08, 46.46, 40.84, 40.21, 36.23, 35.69, 35.14, 33.86, 27.46, 25.57, 24.87, 19.03, 17.47, 14.53, 13.75, 12.46, 11.45; HRMS (ESI) calcd for $C_{42}H_{52}ClF_3NO_{10}$ $(M + H)^+$ 822.3232, found 822.3236.

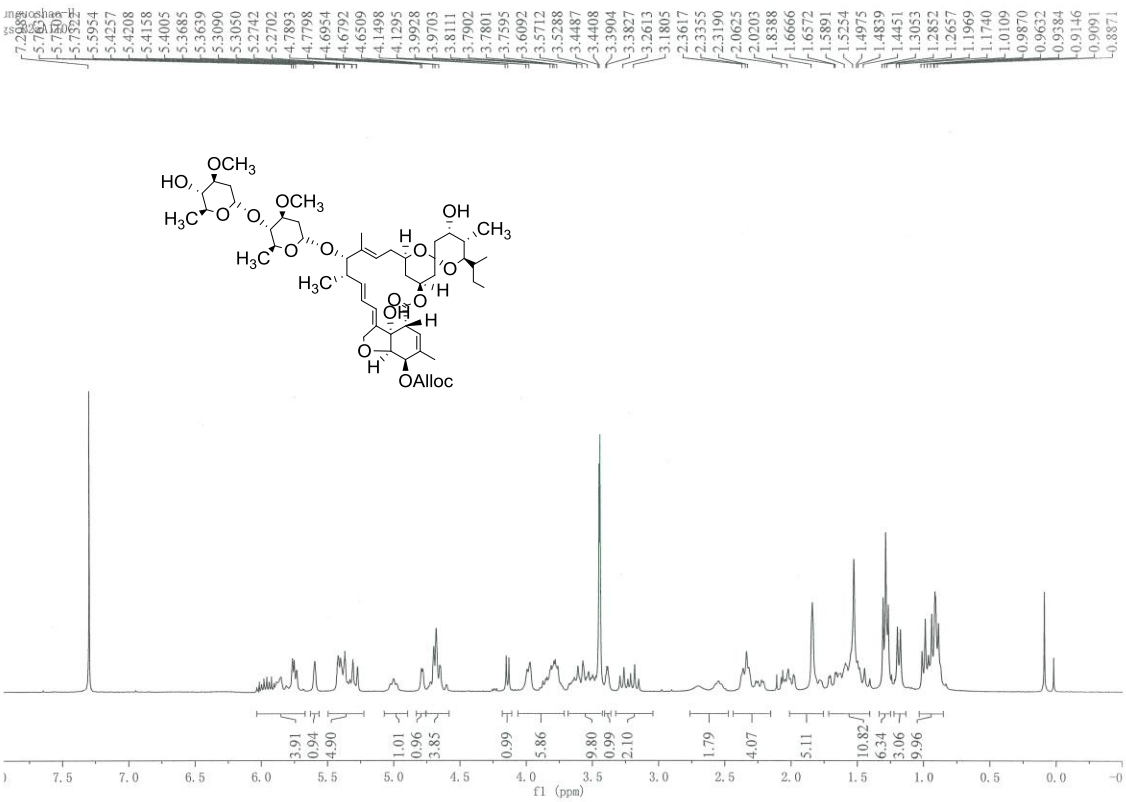
5-((3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a aglycone ***(14k)*** *:* yield, 75%; white solid; mp: 220-223 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.25~9.29 (m, 1H, Ar-H), 8.74~8.87 (m, 1H, Ar-H), 8.30~8.44 (m, 1H, Ar-H), 7.37~7.49 (m, 1H, Ar-H), 6.08~6.16 (m, 1H, H3), 5.90~5.98 (m, 1H, H9), 5.70~5.86 (m, 2H, H10, H11), 5.24~5.43 (m, 2H, H19, H15), 4.68~4.90 (m, 3H, H6, H8ax2), 4.03 (s, 1H, 7-OH), 3.70~3.85 (m, 2H, H23, H13), 3.38~3.66 (m, 3H, H17, H25, H2), 2.48~2.64 (m, 1H, H12), 1.94~2.41 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.38~1.74 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.19 (d, J = 6.9 Hz, 3H, Me12a), 0.80~1.06 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.77, 161.66, 158.14, 153.39, 150.46, 139.17, 138.28, 137.42, 137.14, 131.14, 130.97, 125.05, 124.40, 123.55, 122.25, 116.43, 99.47, 78.96, 77.21, 74.51, 71.25, 69.83, 68.99, 68.33, 67.94, 46.29, 41.02, 40.79, 40.19, 36.05, 35.56, 35.04, 34.08, 27.33, 19.02, 17.39, 14.49, 13.67, 12.37, 11.37; HRMS (ESI) calcd for $C_{40}H_{53}N_2O_{10}$ $(M + H)^+$ 721.3700, found 721.3709 .

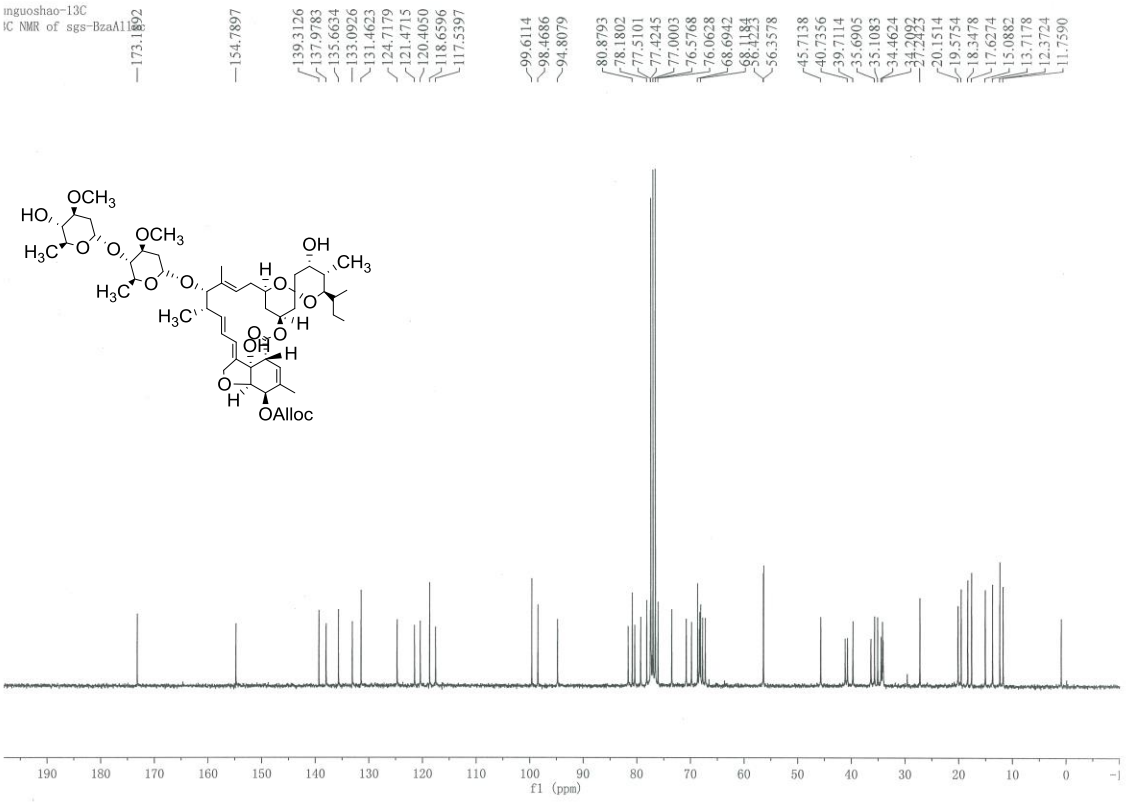
5-((2-chloro-3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a aglycone ***(14l)****:* yield, 77%; white solid; mp: 210-213 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (dd, J = 4.8 Hz, 2.0 Hz, 1H, Ar-H), 8.23 (dd, J = 7.7 Hz, 2.0 Hz, 1H, Ar-H), 7.37 (dd, J = 4.8 Hz, 7.7 Hz, 1H, Ar-H), 6.05~6.17 (m, 1H, H3), 5.87~6.00 (m, 1H, H9), 5.69~5.82 (m, 2H, H10, H11), 5.24~5.43 (m, 2H, H19, H15), 4.63~4.76 (m, 3H, H6, H8ax2), 4.02 (s, 1H, 7-OH), 3.94 (s, 1H, 23-OH), 3.66~3.83 (m, 2H, H23, H13), 3.48~3.65 (m, 2H,

H17, H25), 3.37~3.46 (m, 1H, H2), 2.46~2.62 (m, 1H, H12), 1.92~2.39 (m, 8H, H16x2, H24, Me4a, H18, H20), 1.39~1.72 (m, 9H, Me14a, H20, H26, H27x2, H22x2), 1.19 (d, J = 6.9 Hz, 3H, Me12a), 0.78~1.06 (m, 10H, H28, Me 24a, Me26a, H18); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.81, 161.42, 158.22, 152.08, 149.86, 140.61, 139.14, 138.19, 137.12, 131.07, 125.73, 124.37, 122.08, 116.35, 99.44, 78.98, 77.19, , 74.36, 71.23, 69.79, 68.93, 68.29, 67.90, 46.28, 41.00, 40.74, 40.10, 36.03, 35.53, 35.01, 34.05, 27.31, 18.96, 17.36, 14.44, 13.65, 12.36, 11.36; HRMS (ESI) calcd for $C_{40}H_{52}ClN_2O_{10}$ $(M + H)^+$ 755.3310, found 755.3312.

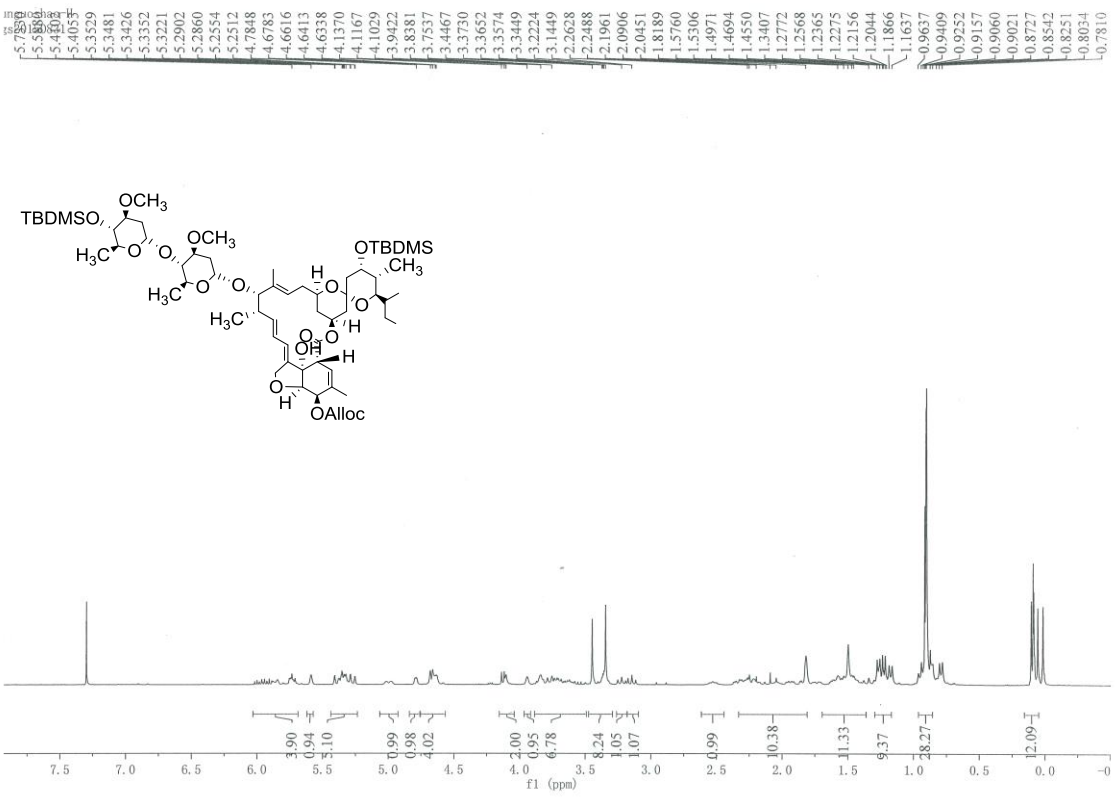
2. ^{1}H NMR and ^{13}C NMR spectra

5-o-alloc avermectin B2a (2)





1 5-o-alloc-4",23-bis-o-(tert-butyldimethysilyl) avermectin B2a (3)



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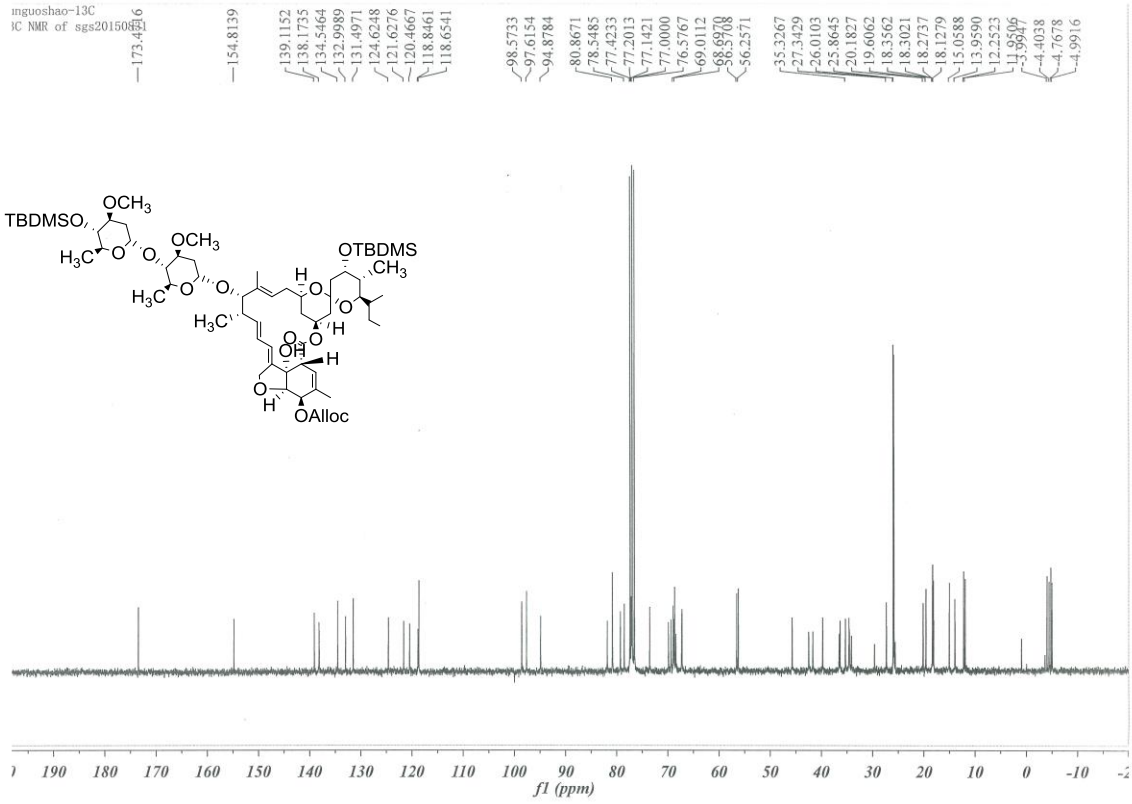

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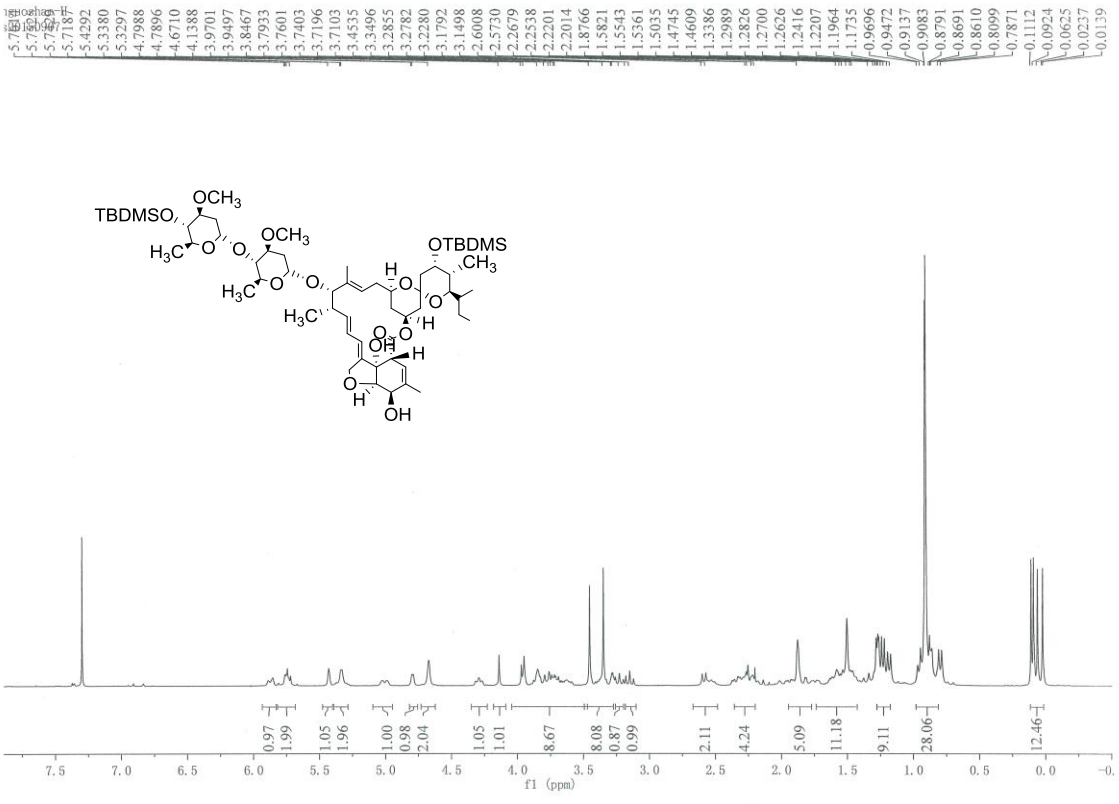
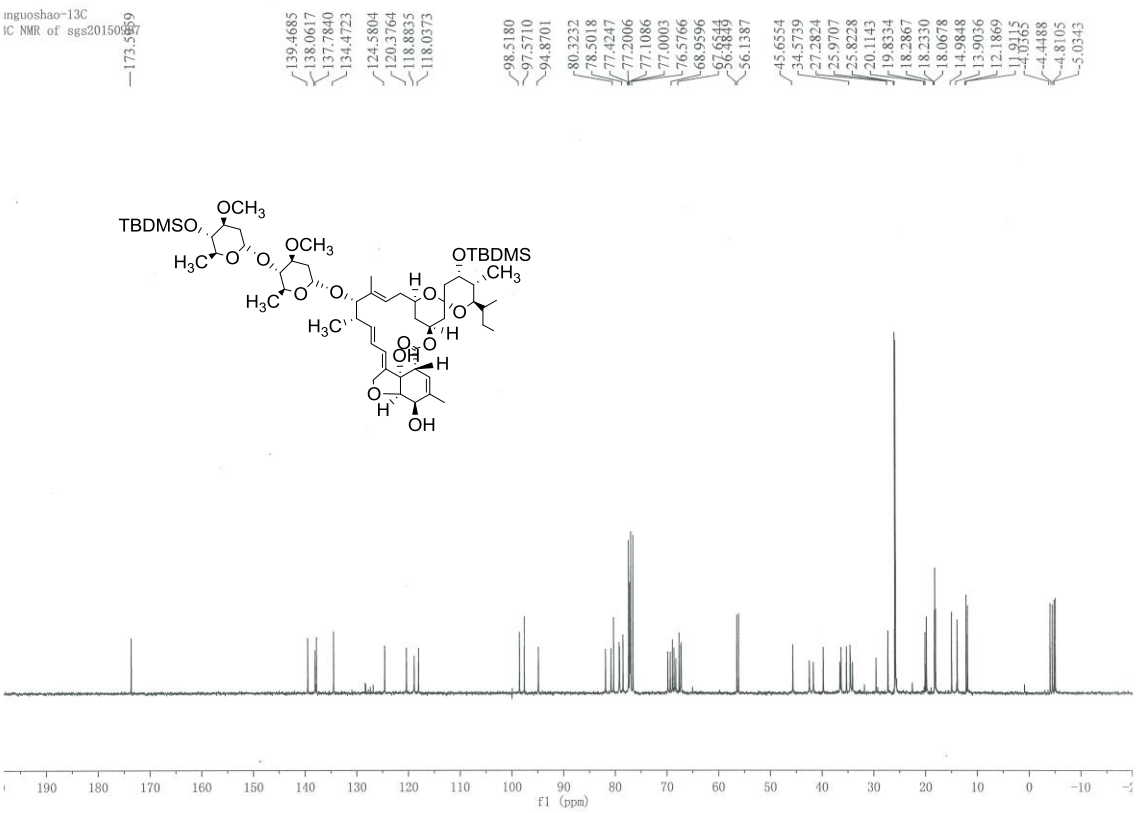
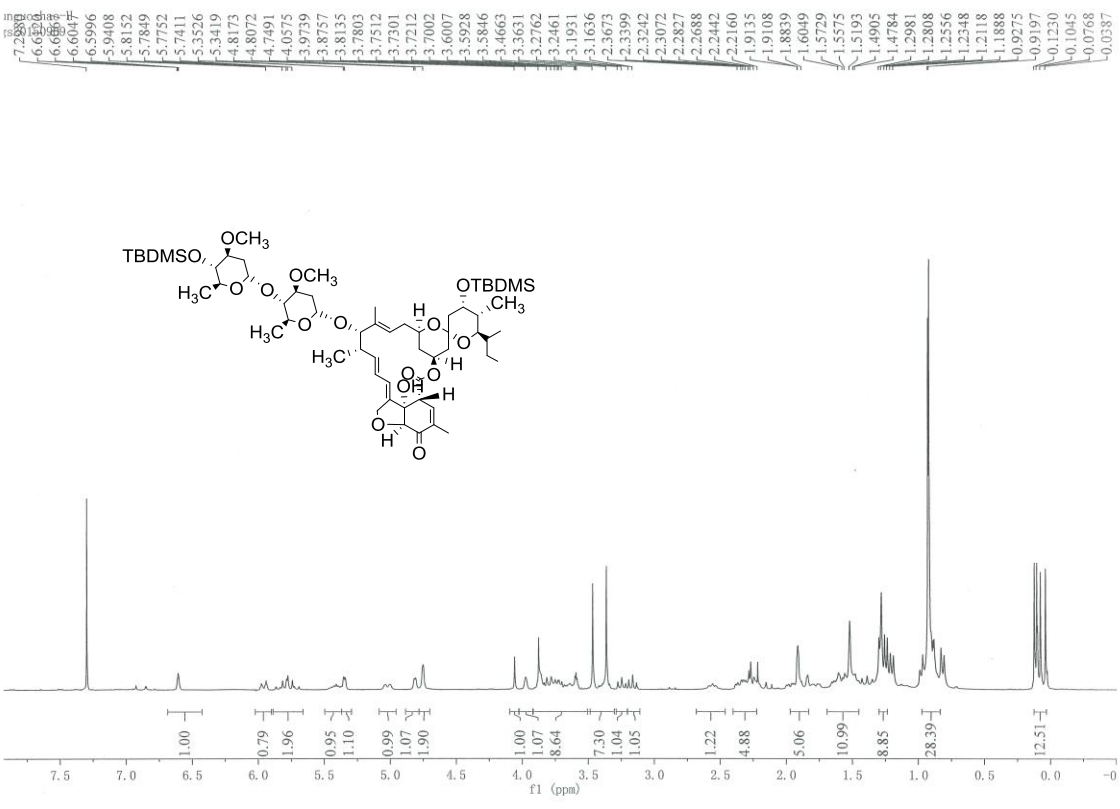
4",23-bis-o-(tert-butyldimethysilyl) avermectin B2a (4)





1 5-oxo-4",23-bis-o-(tert-butyldimethysilyl) avermectin B2a (5)



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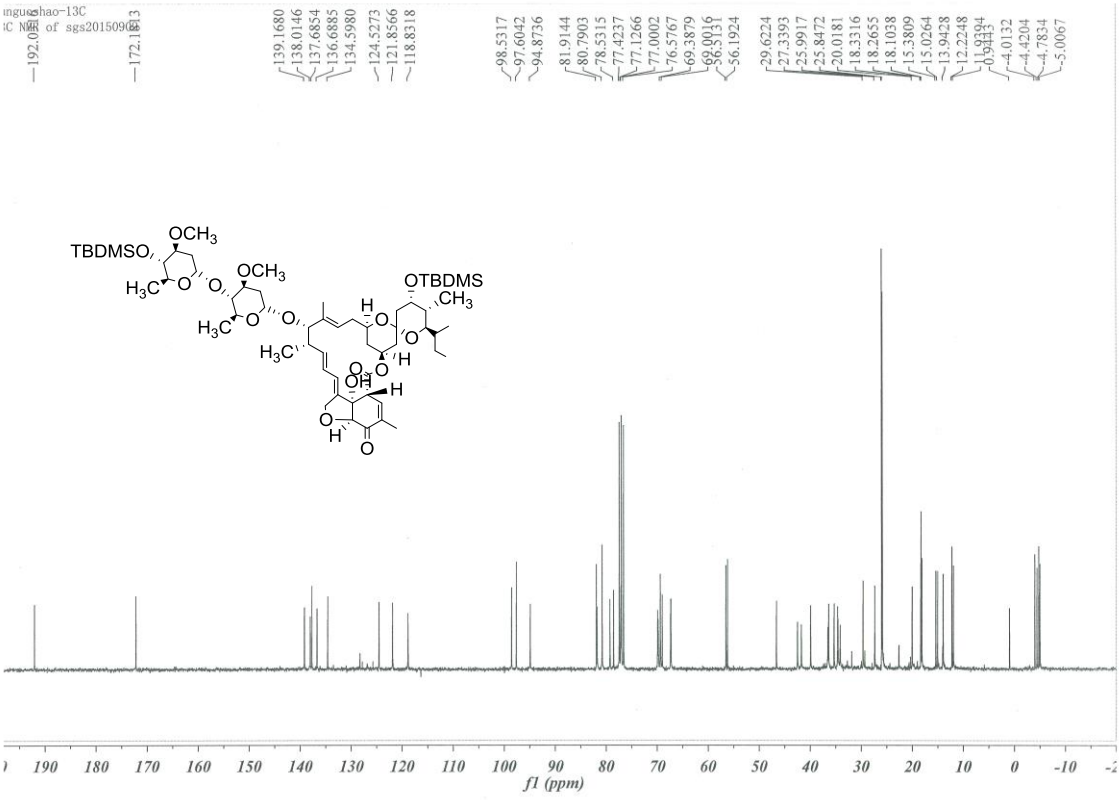

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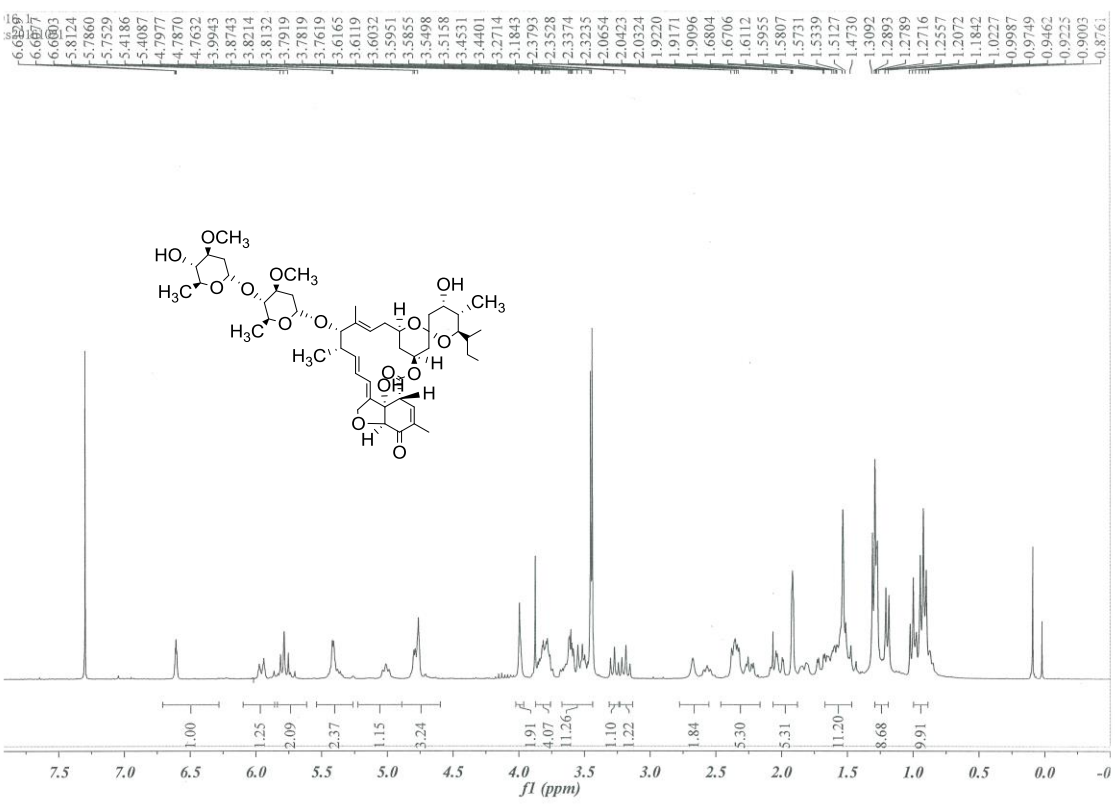
1 5-oxo avermectin B2a (6)



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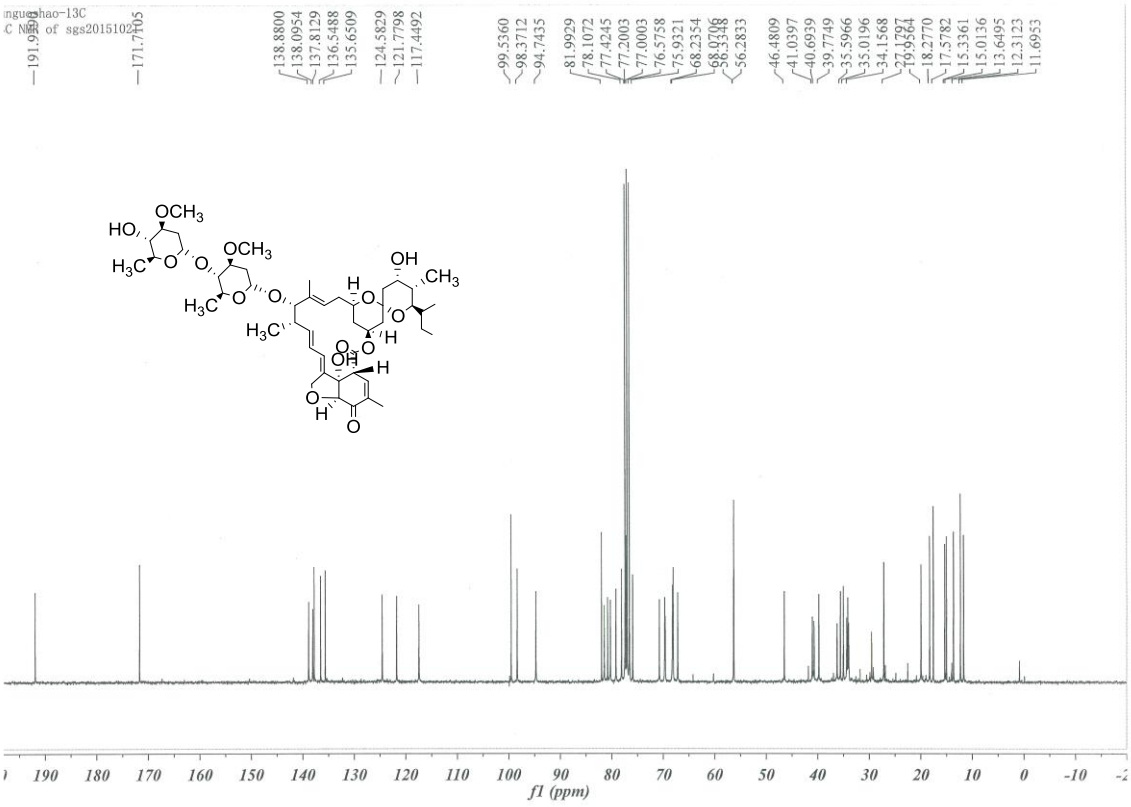

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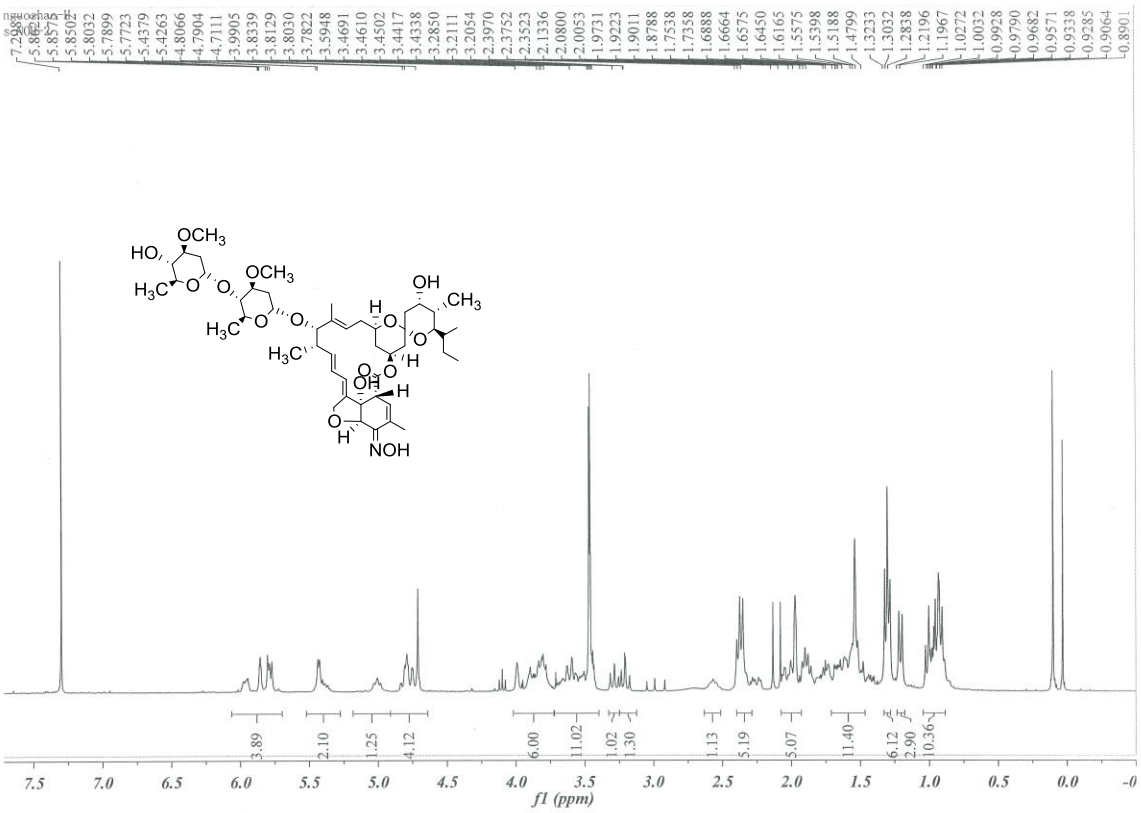
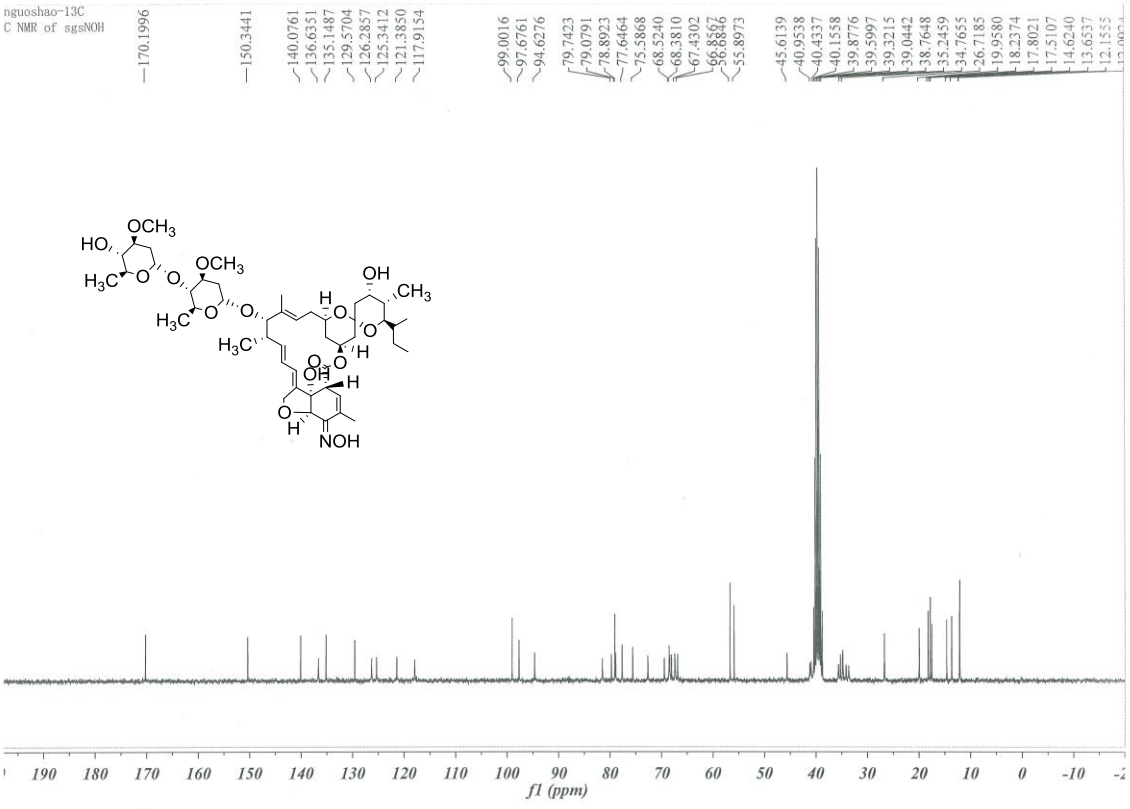
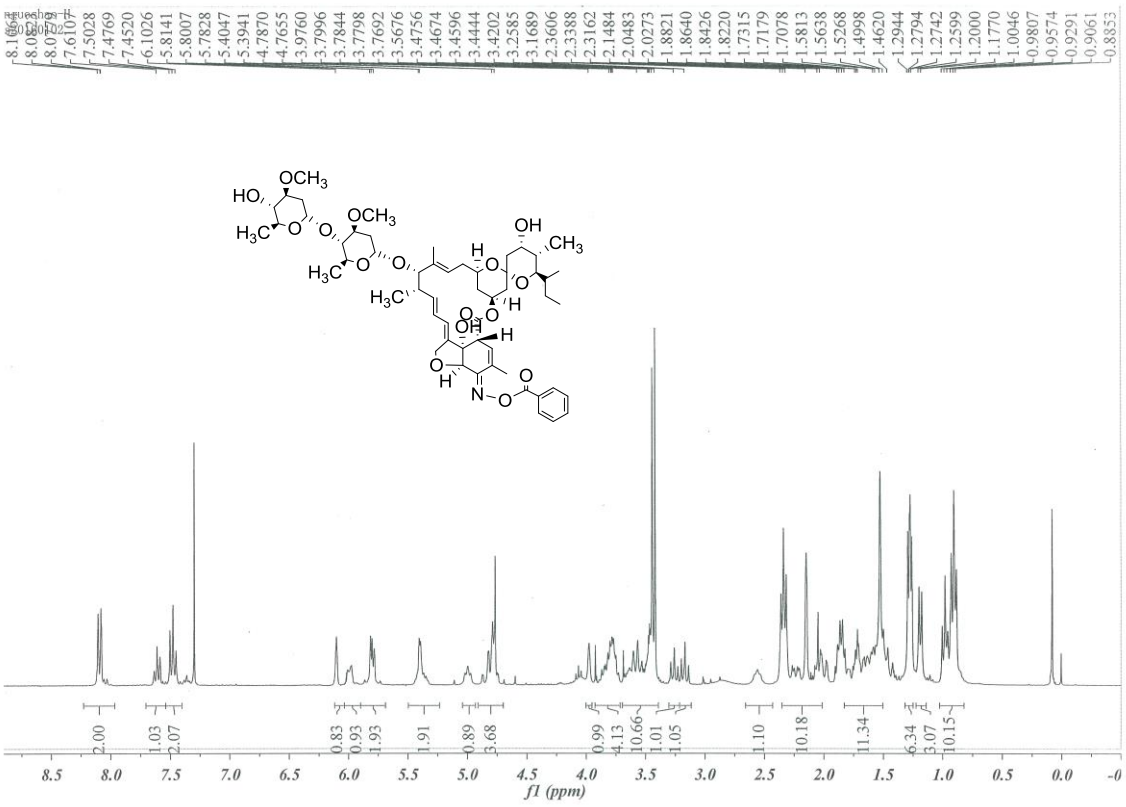
5-oximino-5-deoxyavermectin B2a (7)





1 5-(benzoyloxyimino)-5-deoxyavermectin B2a (8a).



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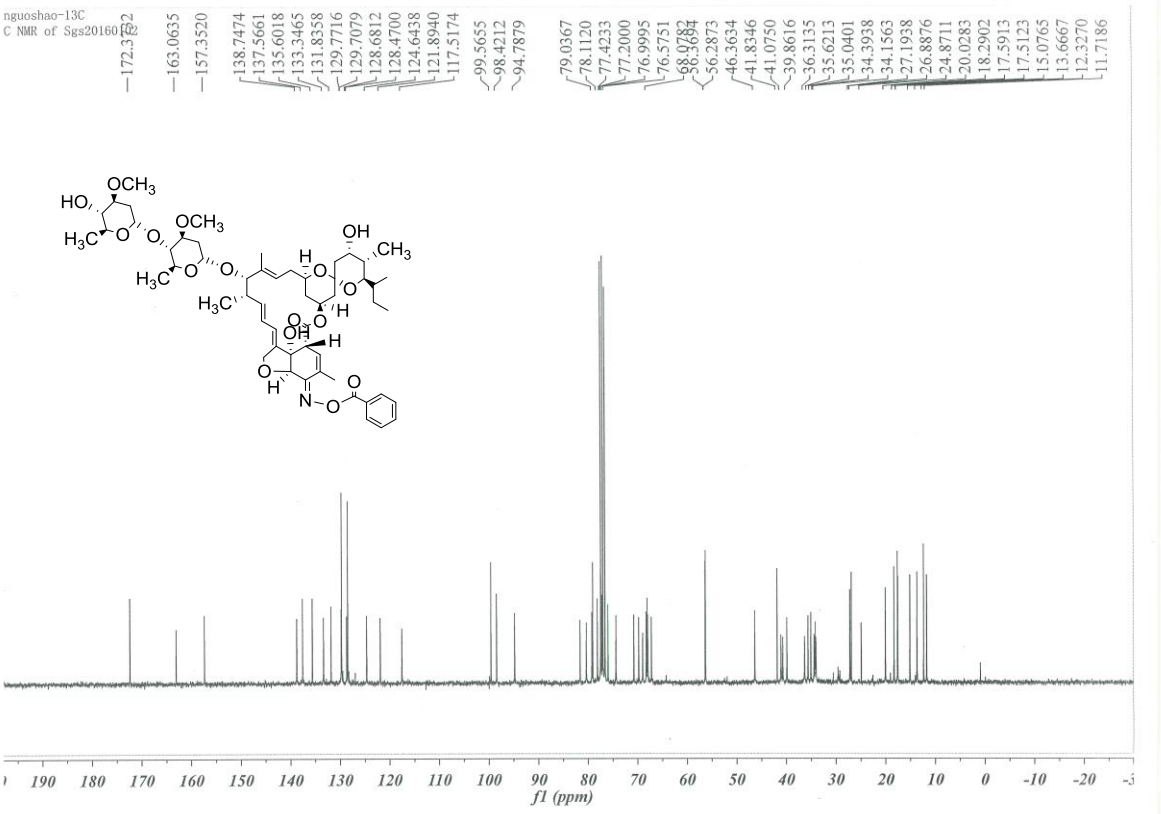

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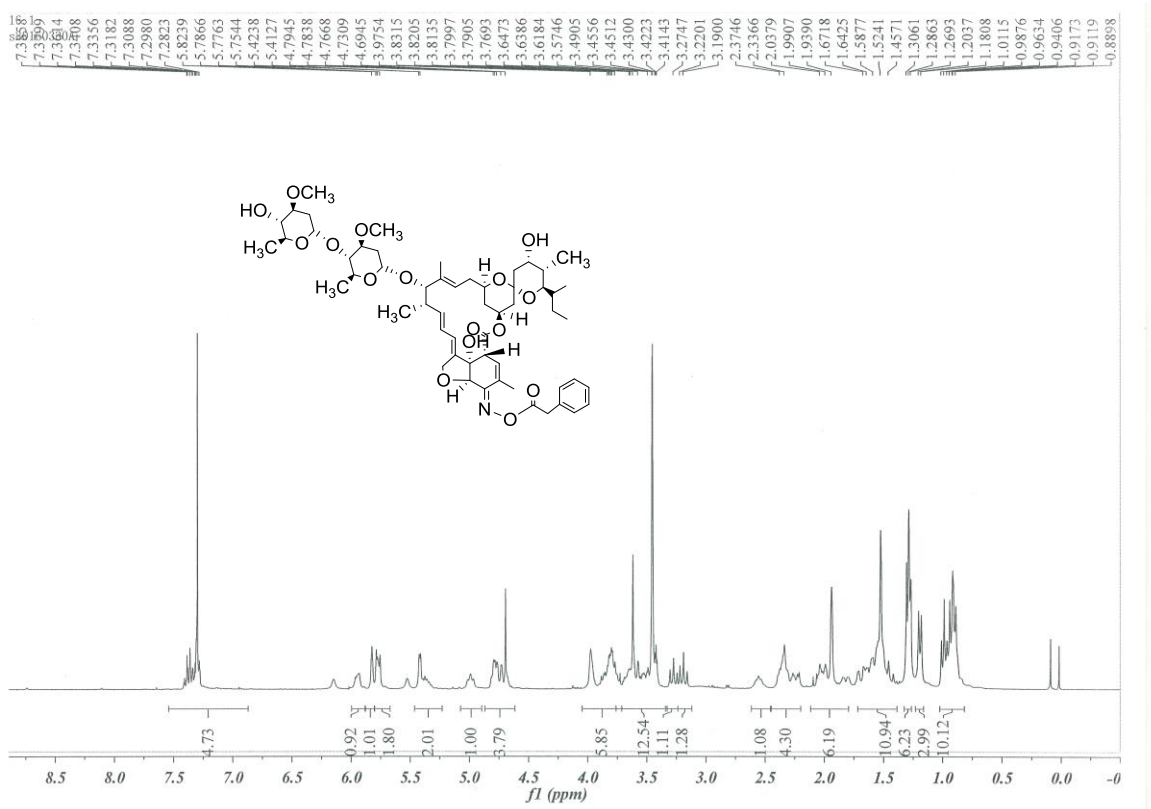
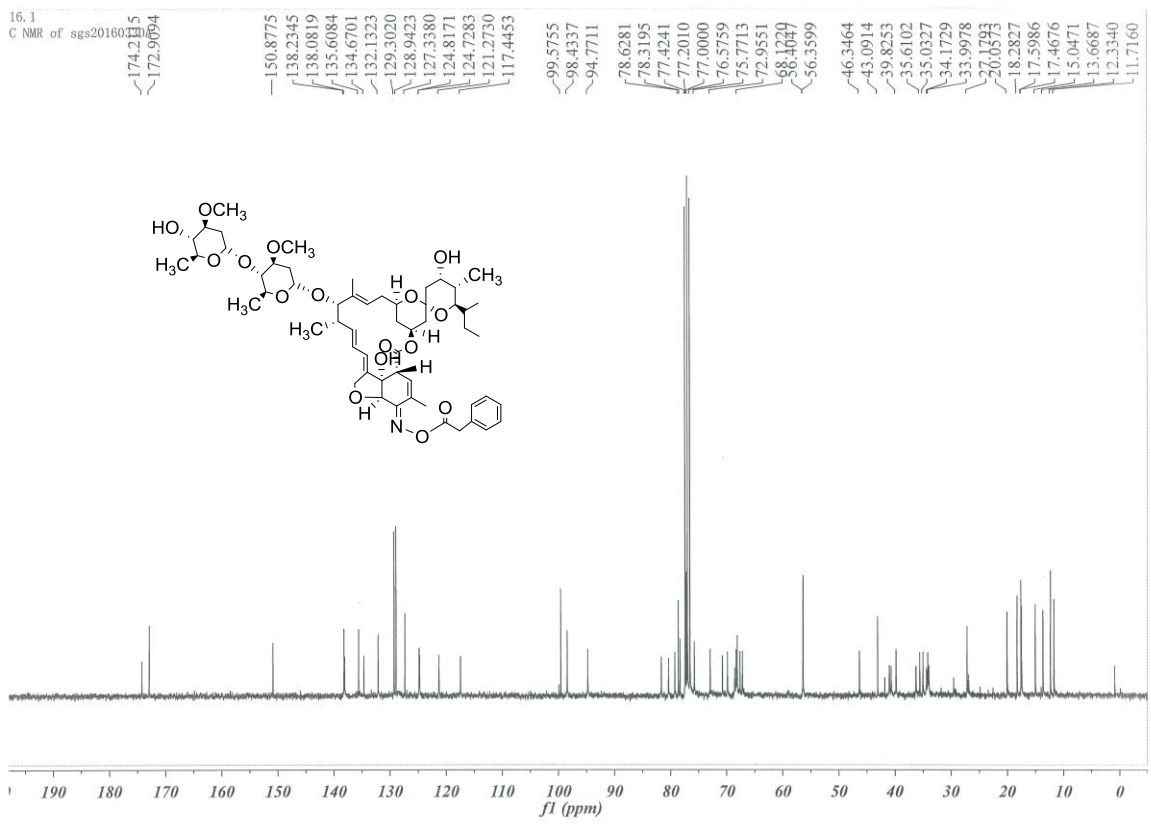
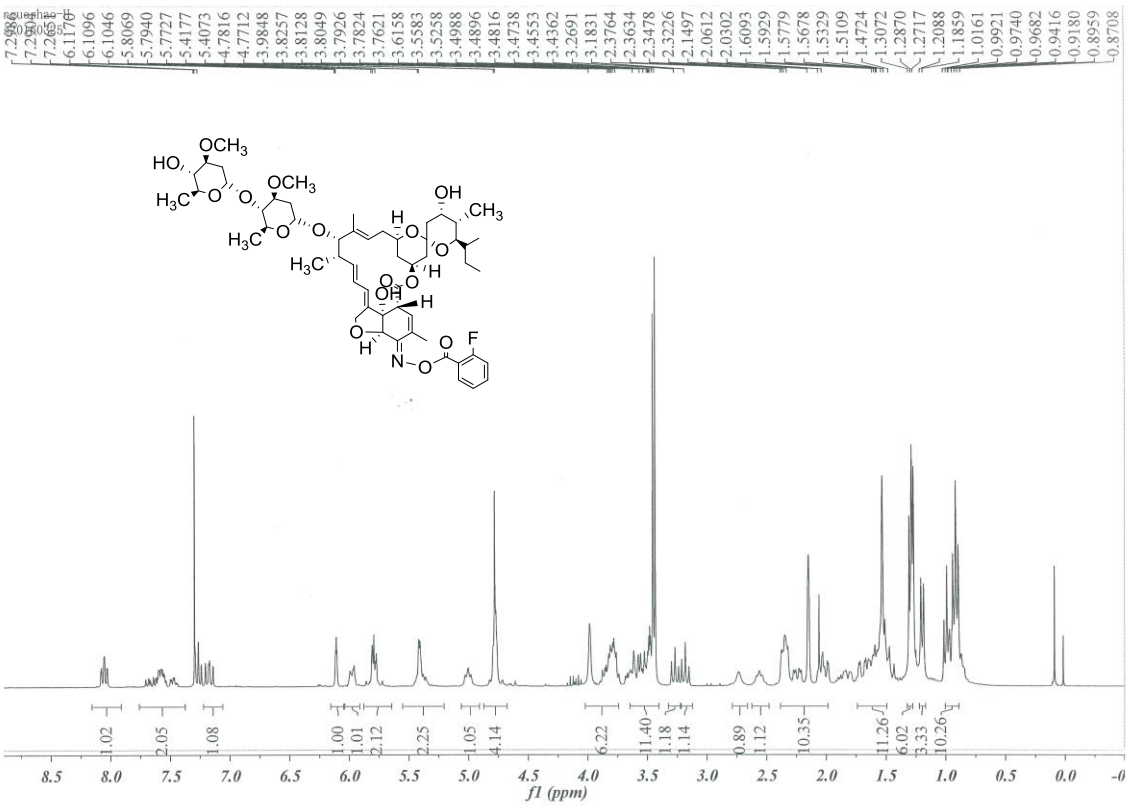
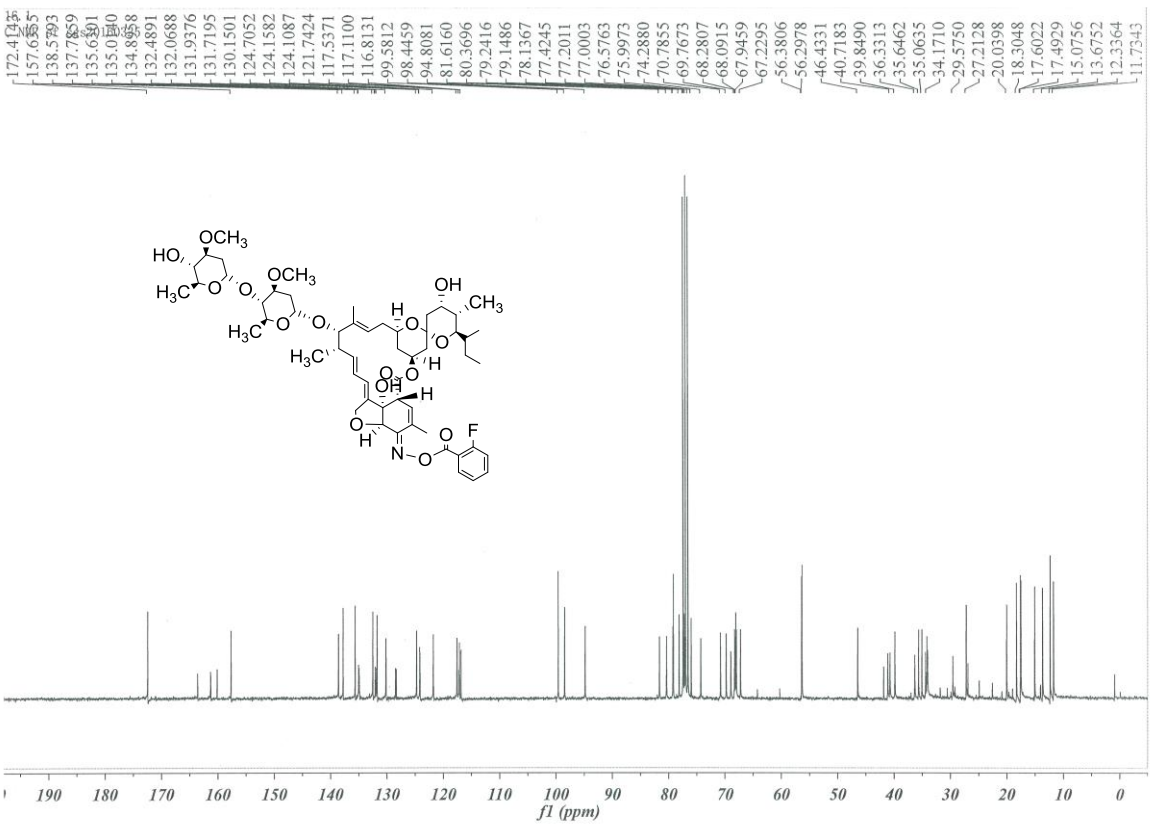
5-(phenylacetyloxyimino)-5-deoxyavermectin B2a (8b)



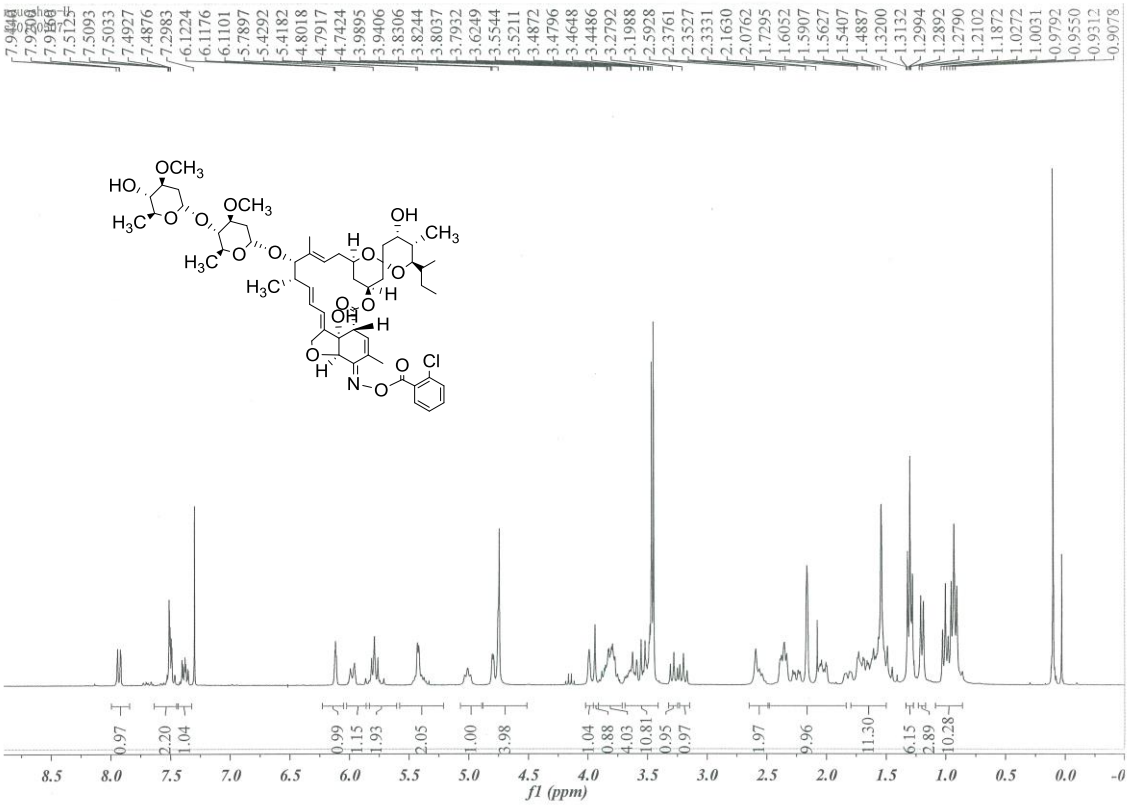


5-((2-fluorobenzoyl)oxyimino)-5-deoxyavermectin B2a (8c)





1 5-((2-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a (8d)



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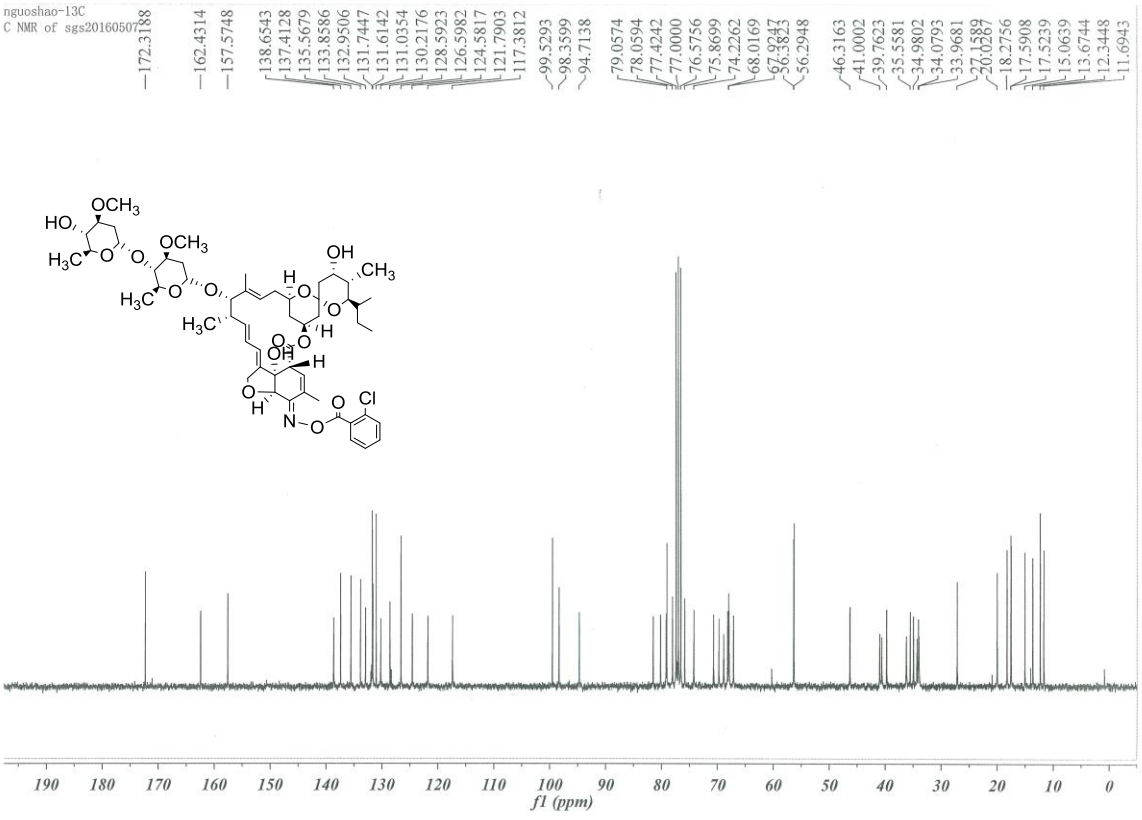

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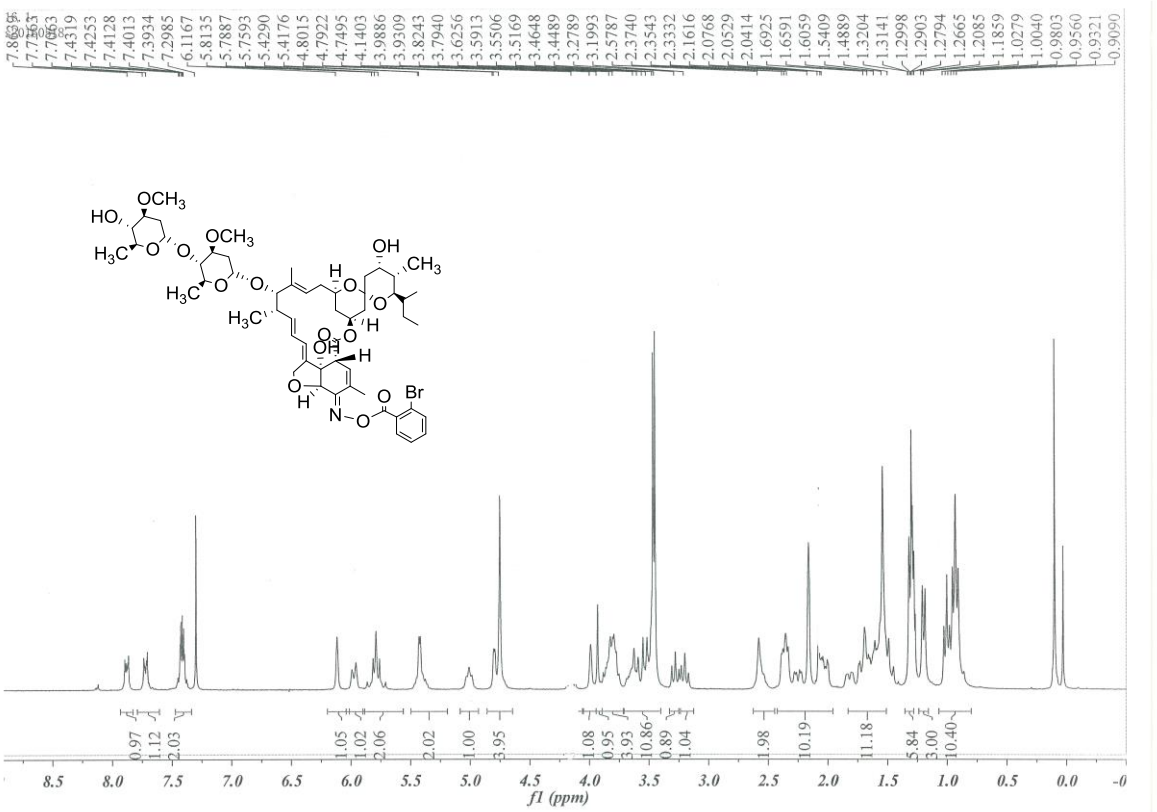
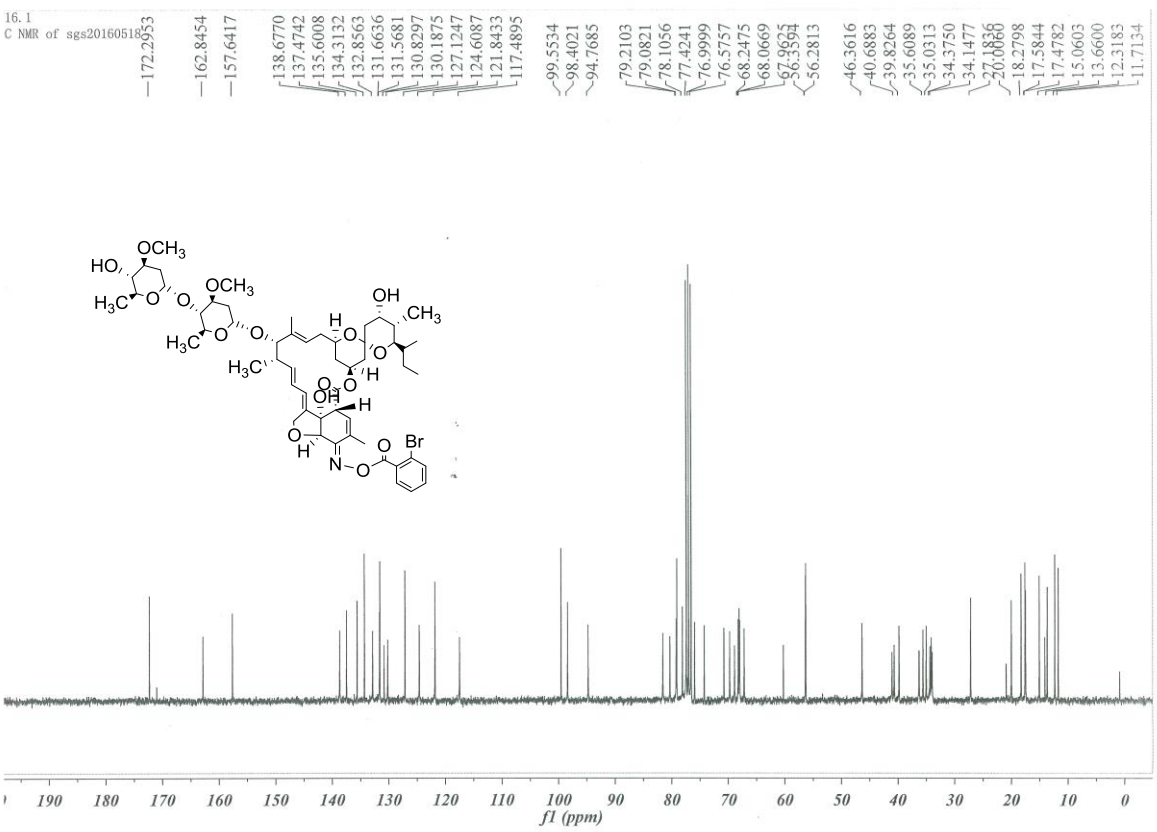
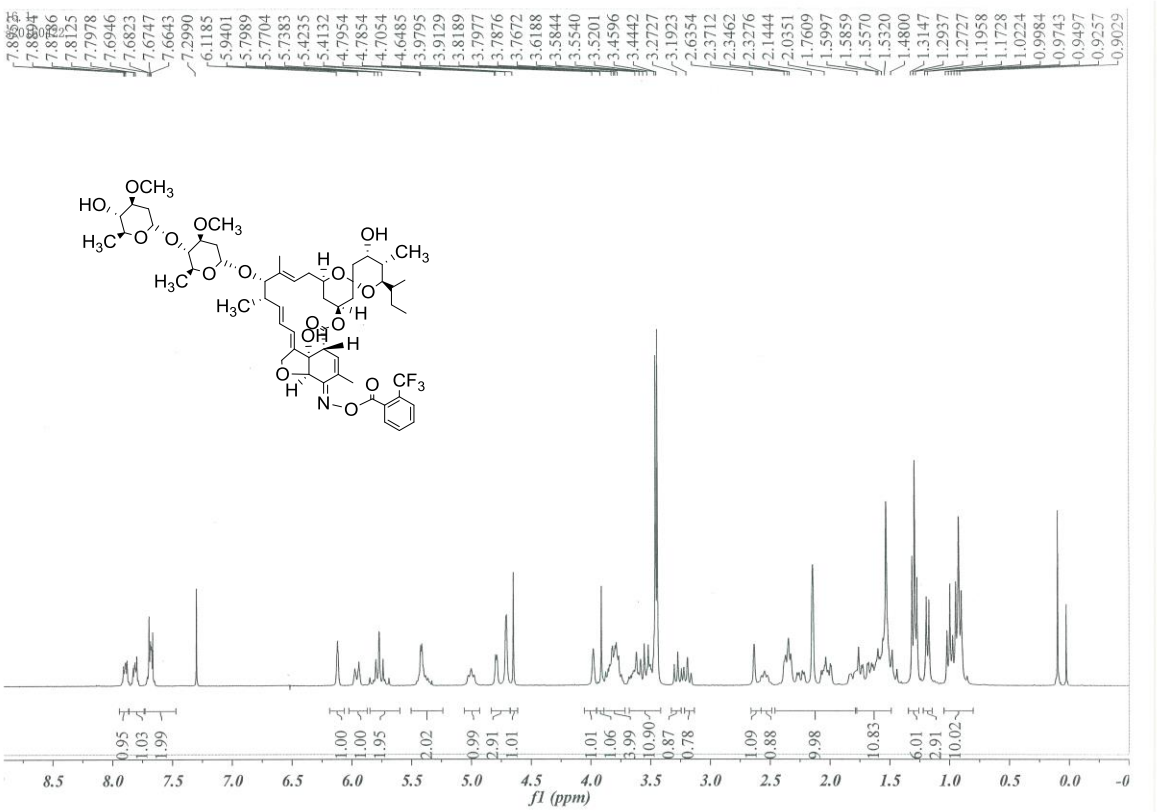
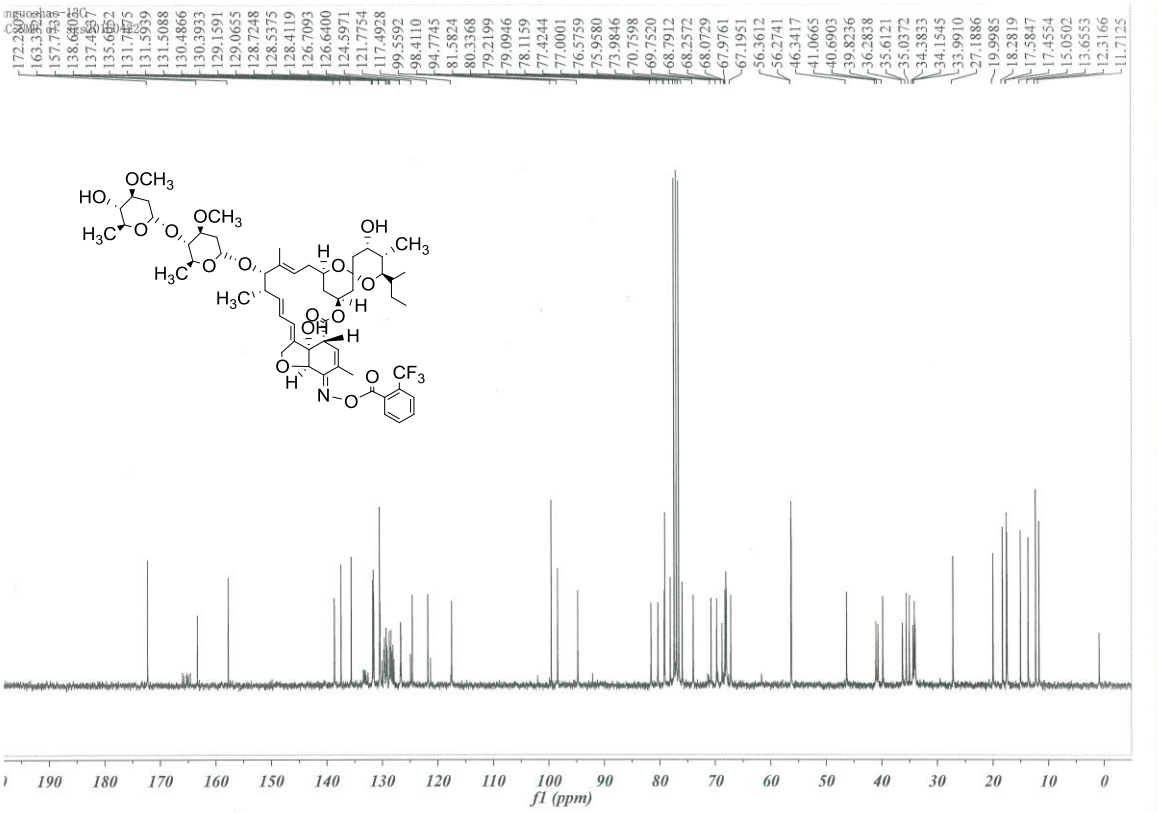
5-((2-bromobenzoyl)oxyimino)-5-deoxyavermectin B2a (8e)



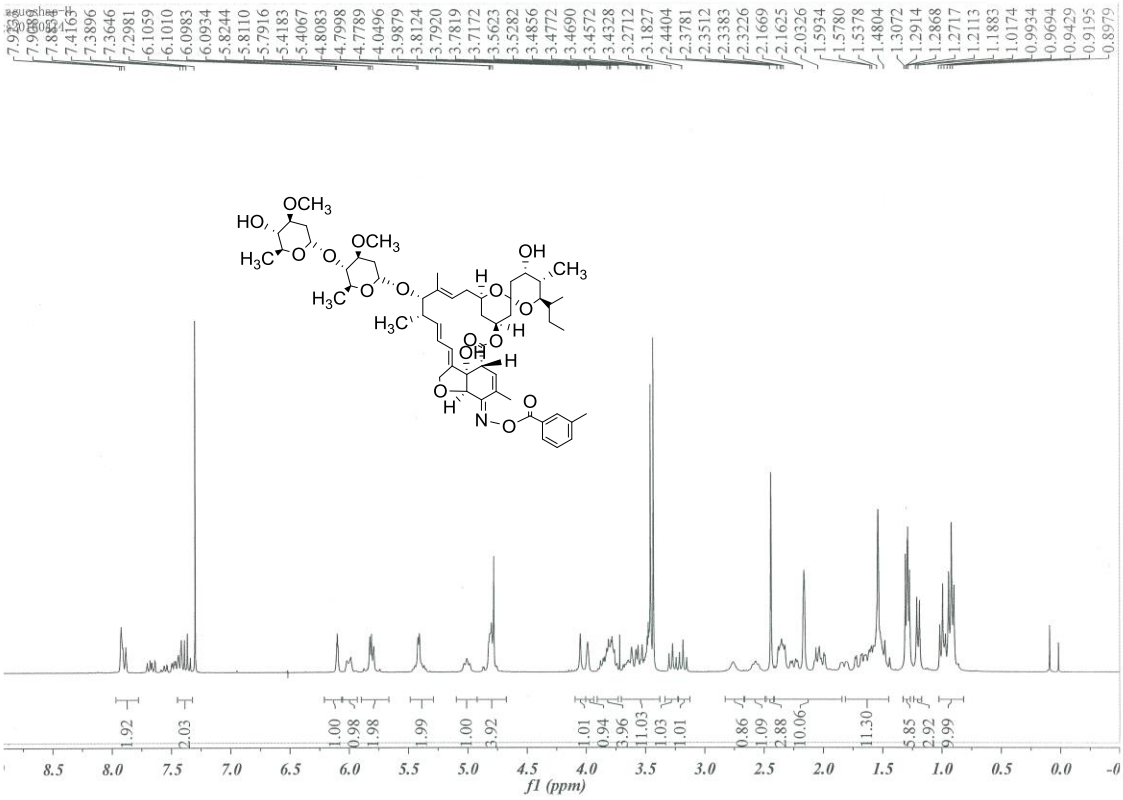


5-((2-trifluoromethylbenzoyl)oxyimino)-5-deoxyavermectin B2a (8f)





1 5-((3-methylbenzoyl)oxyimino)-5-deoxyavermectin B2a (8g)



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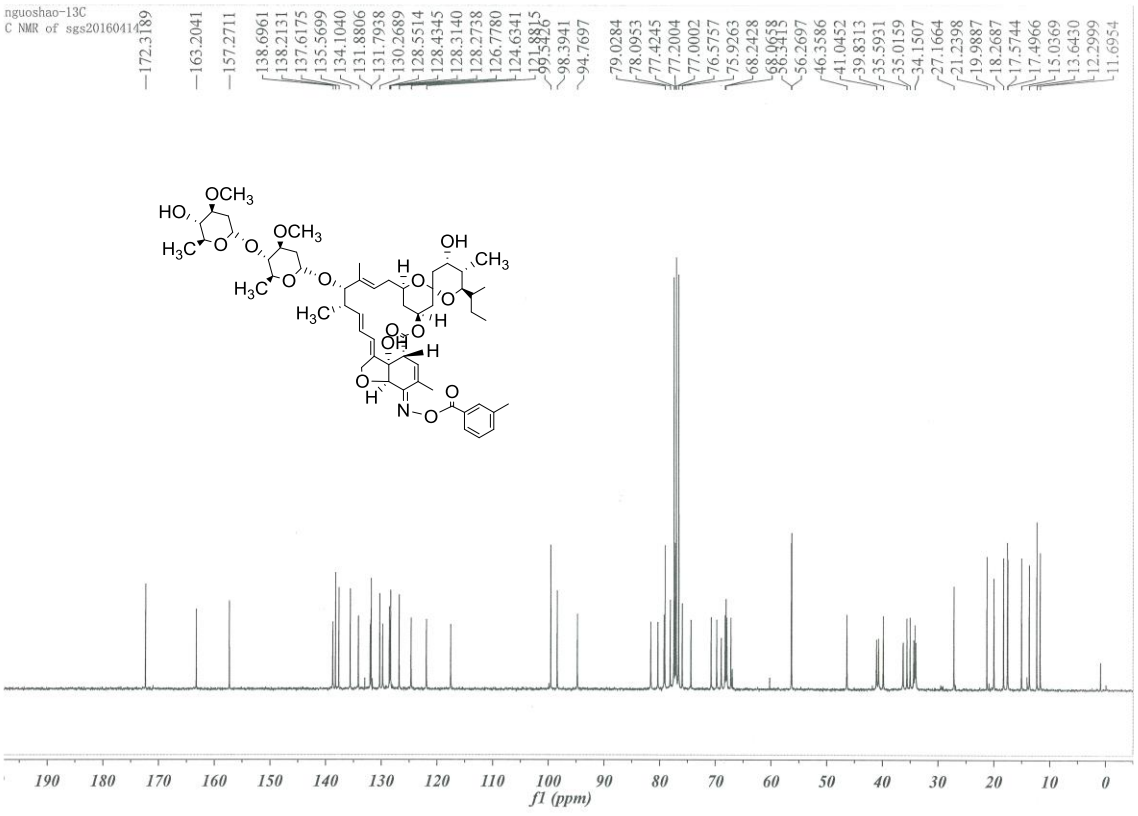

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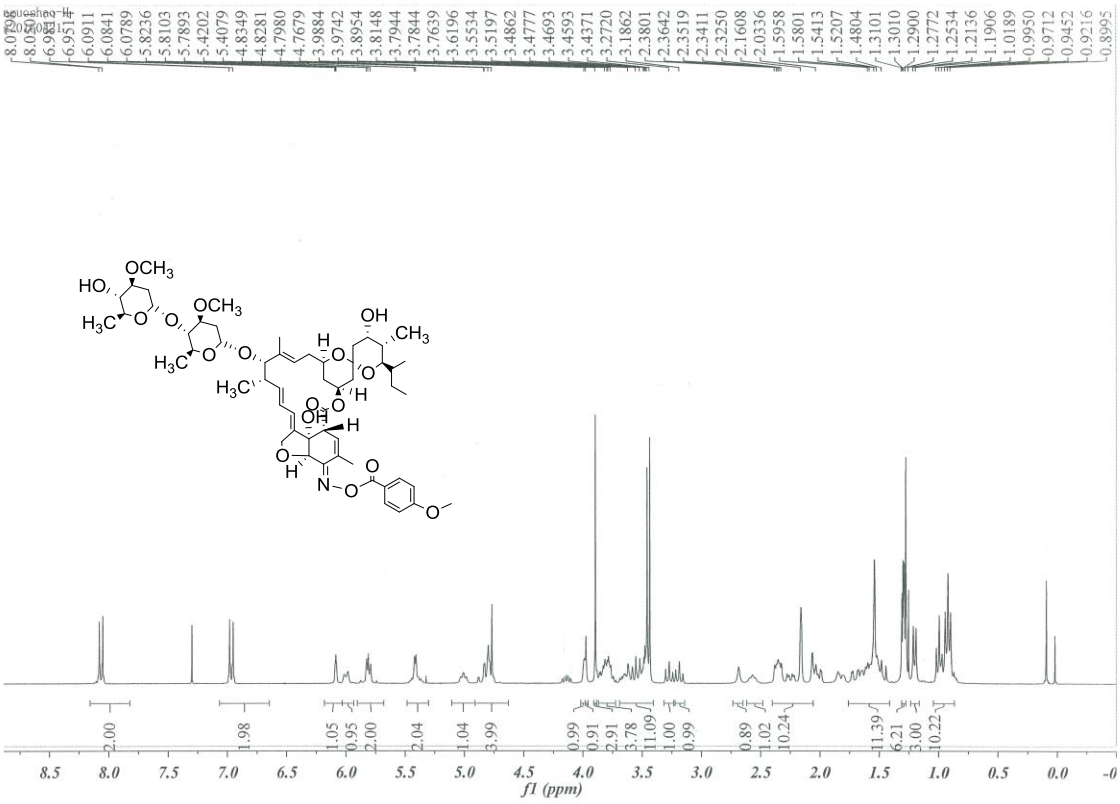
1 5-((4-methoxybenzoyl)oxyimino)-5-deoxyavermectin B2a (8h)



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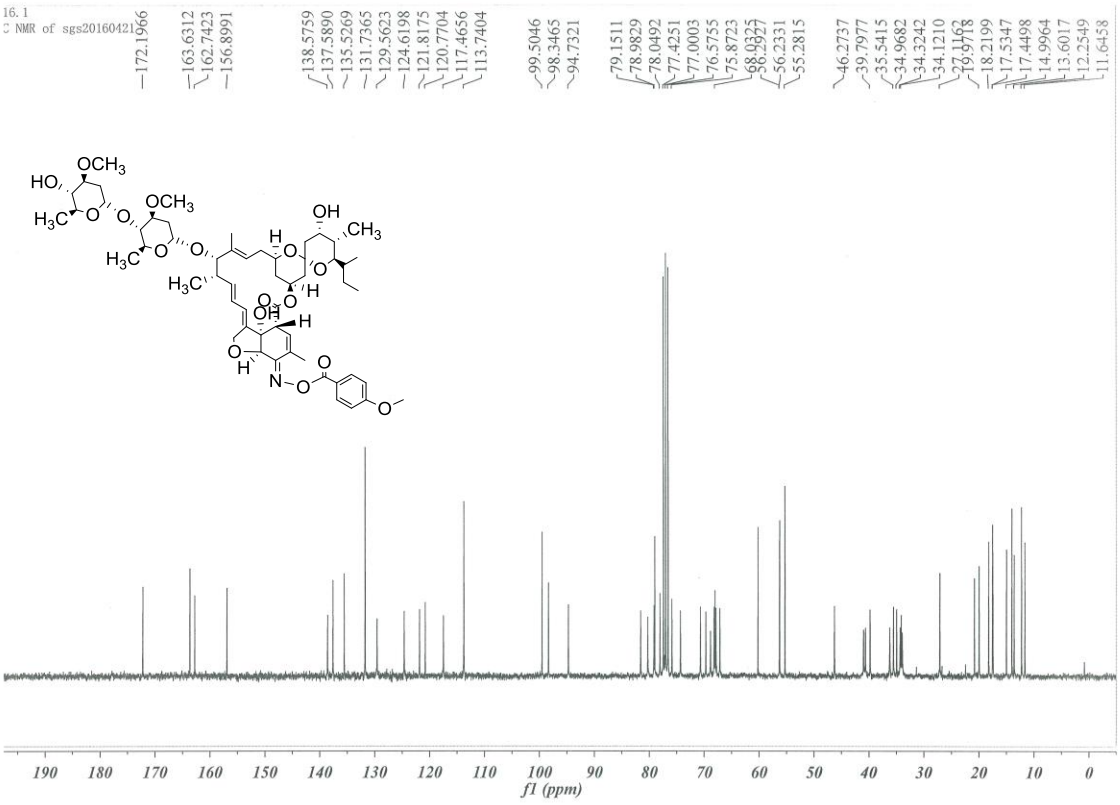

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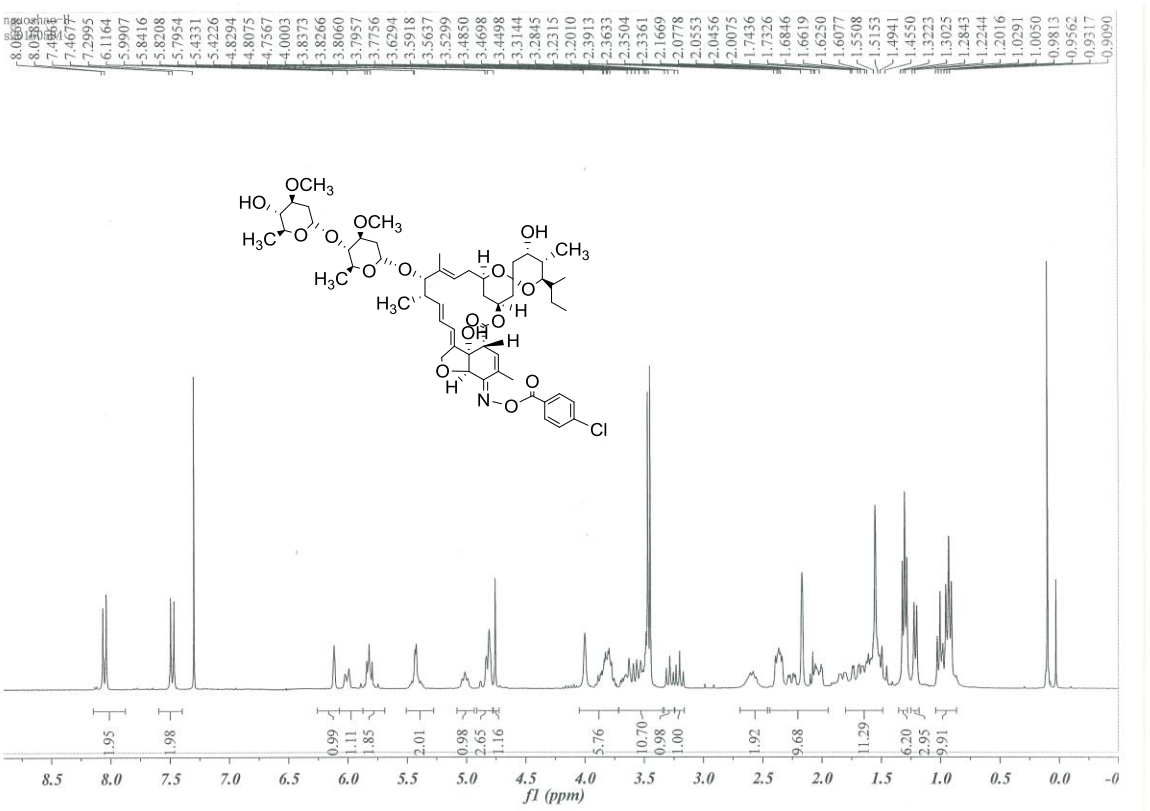
1 5-((4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a (8i)



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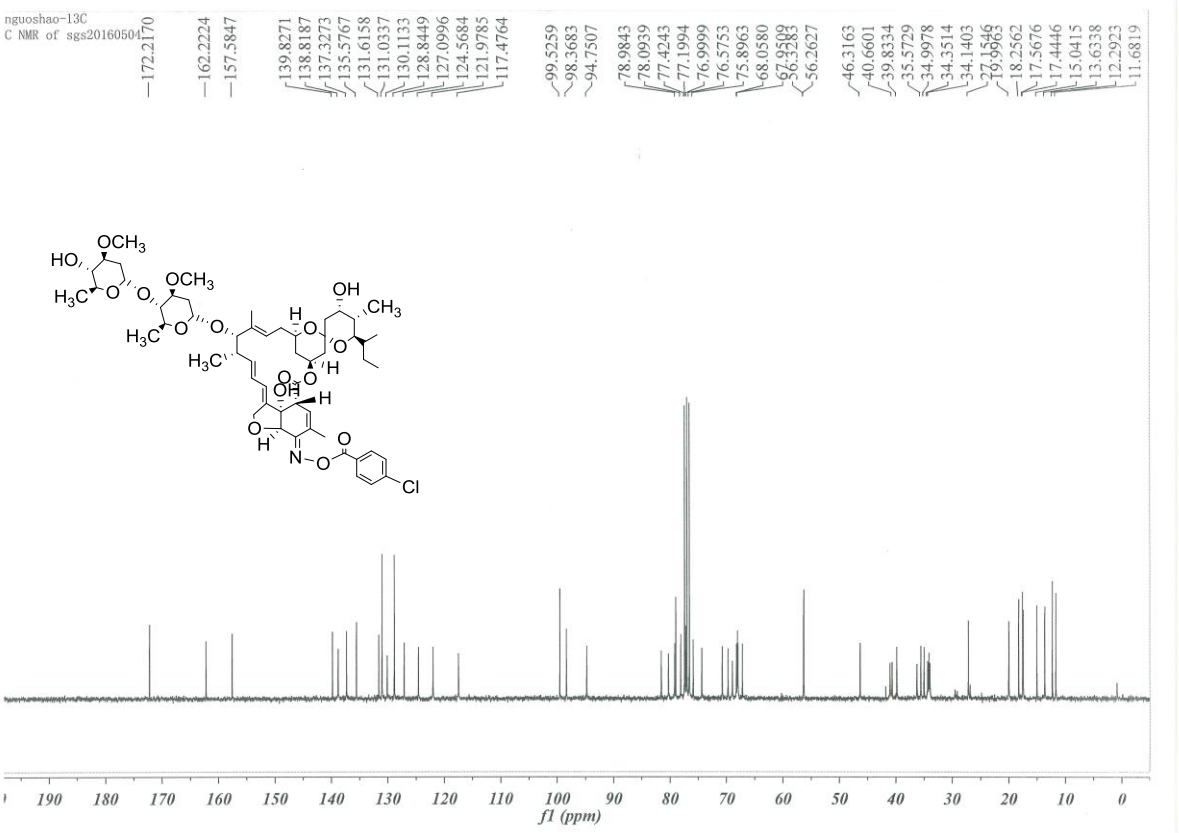

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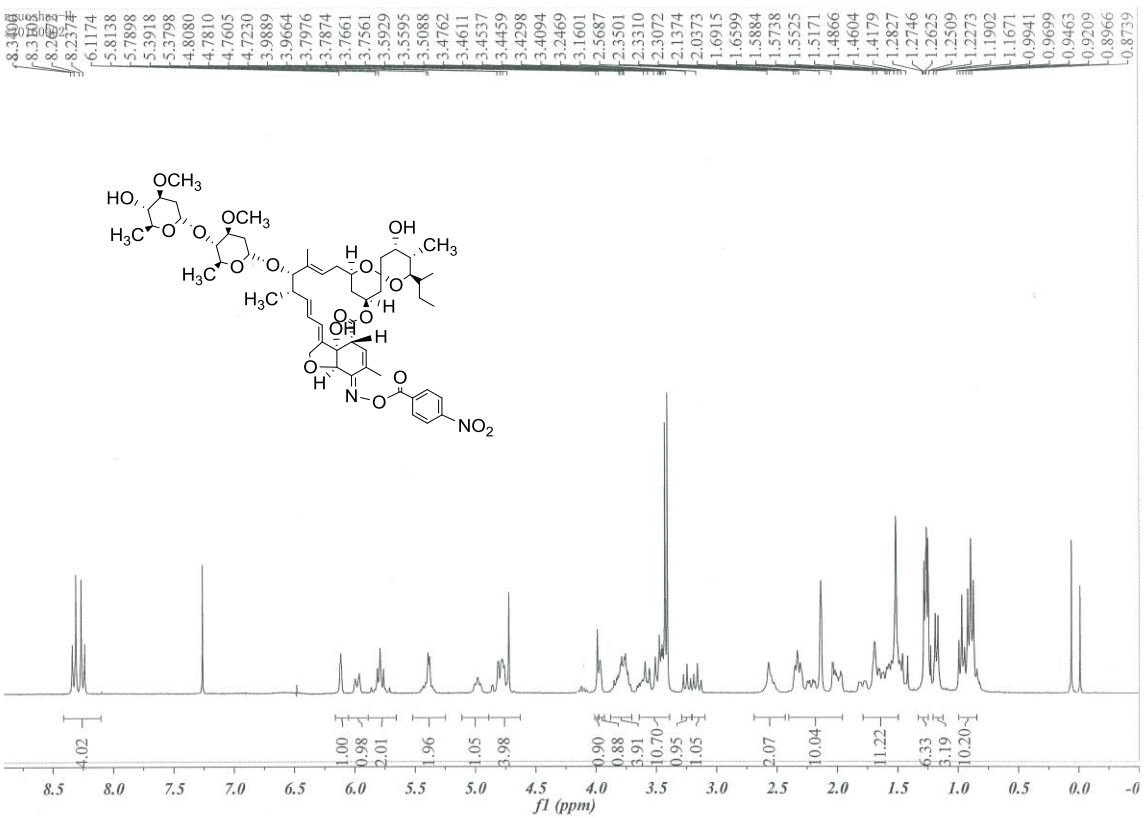
1 5-((4-nitrobenzoyl)oxyimino)-5-deoxyavermectin B2a (8j)



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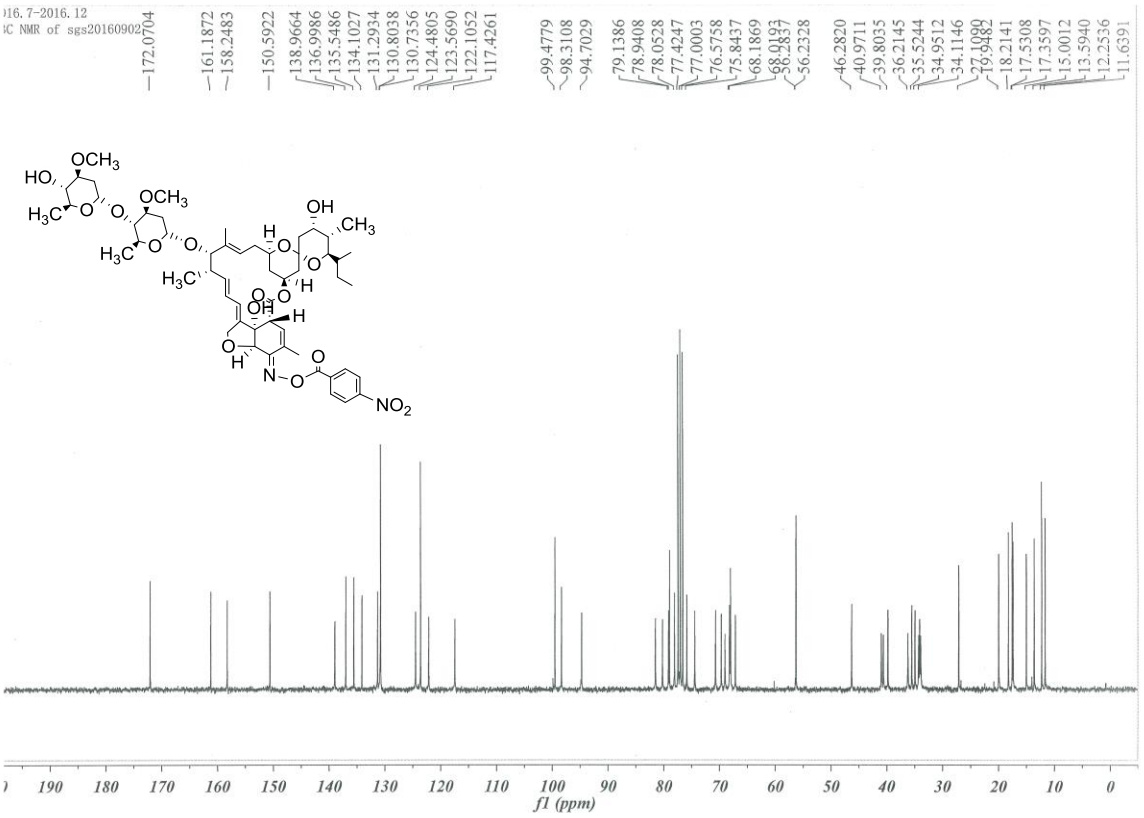

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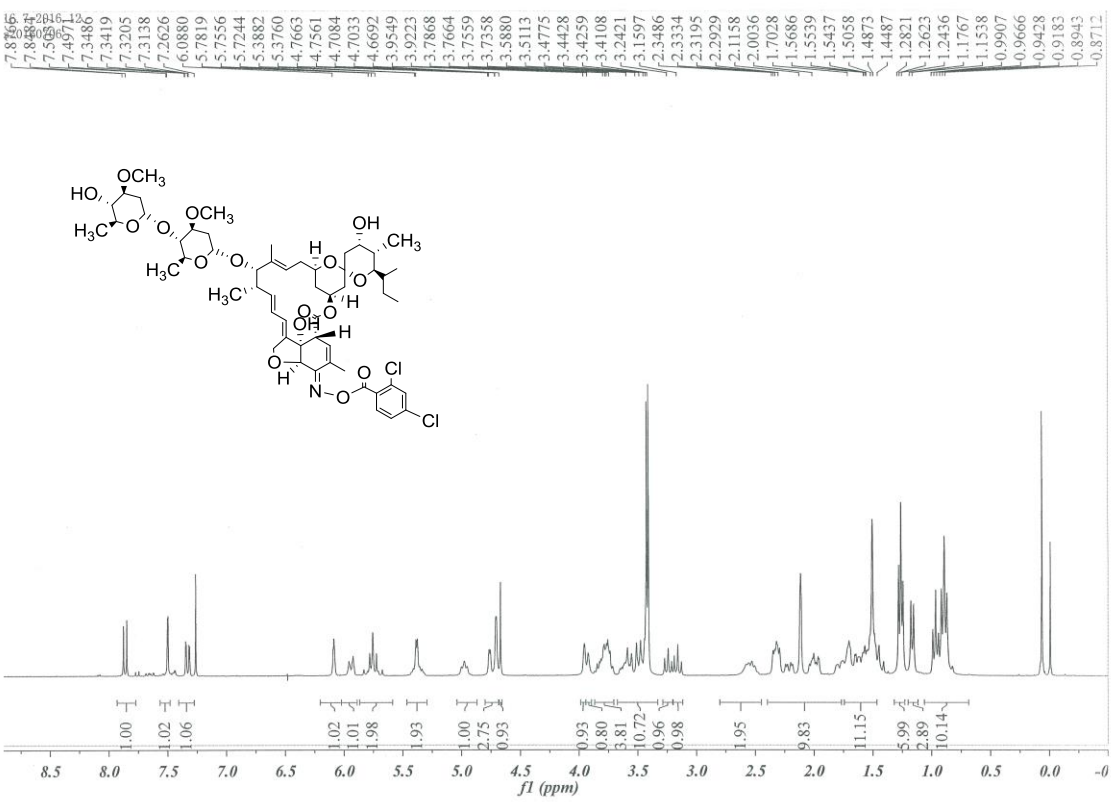
1 5-((2,4-dichlorobenzoyl)oxyimino)-5-deoxyavermectin B2a (8k)



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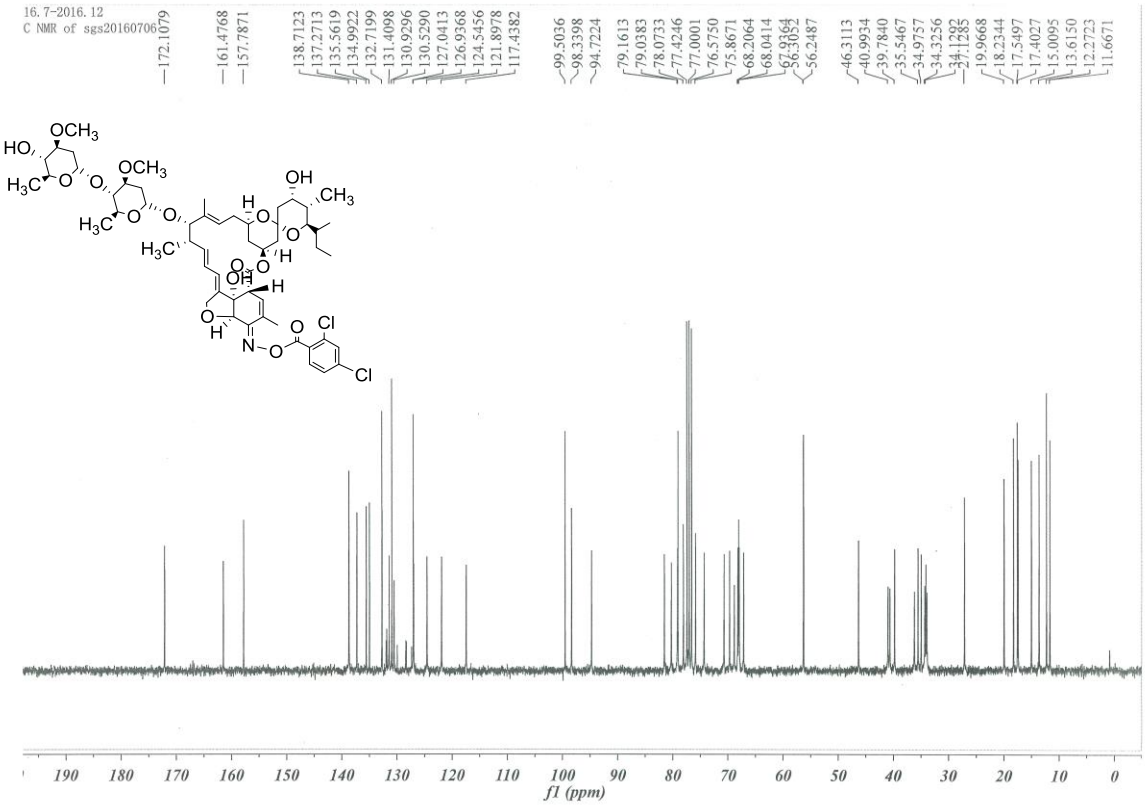

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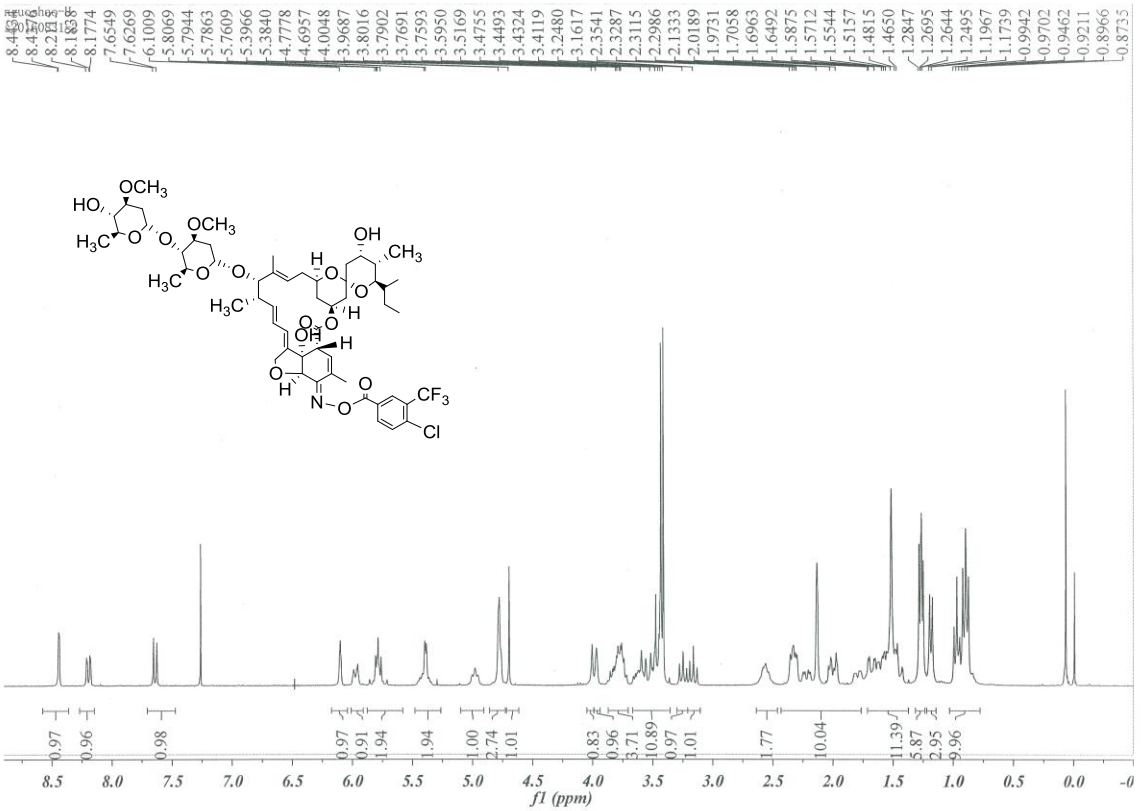
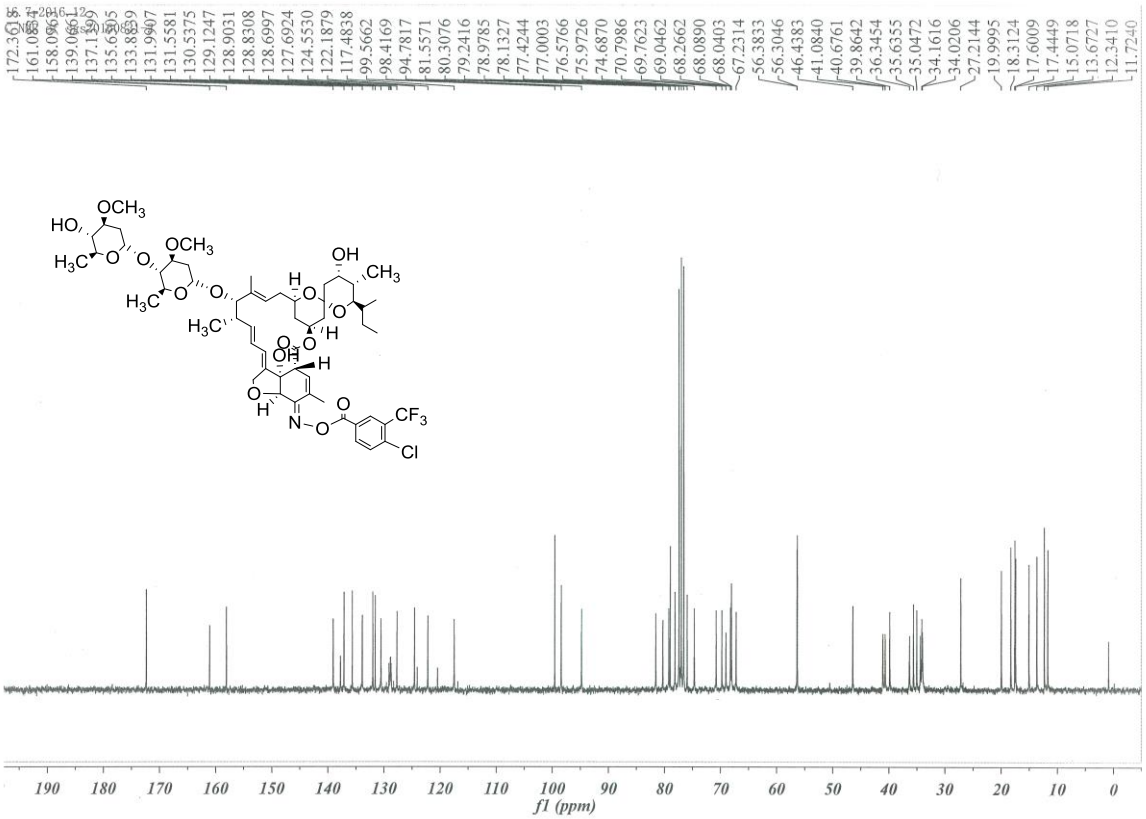
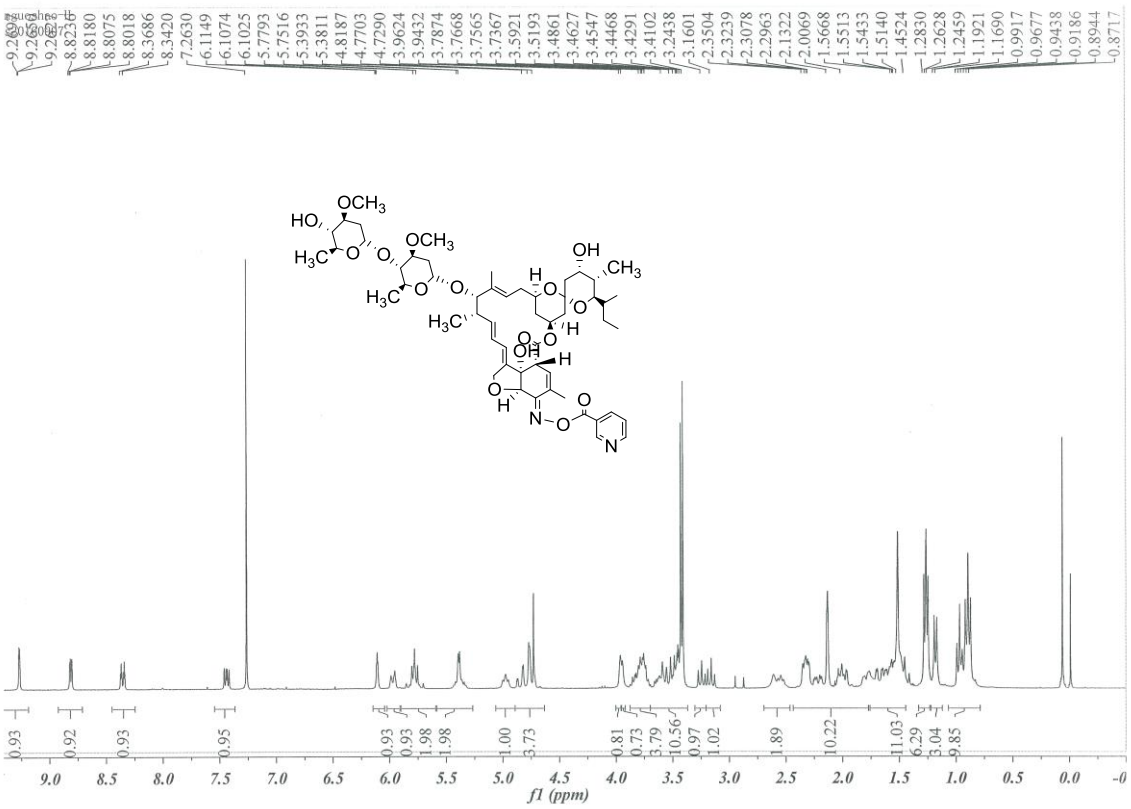
5-((3-trifluoromethyl-4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a (8l)





1 5-((3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a (8m)



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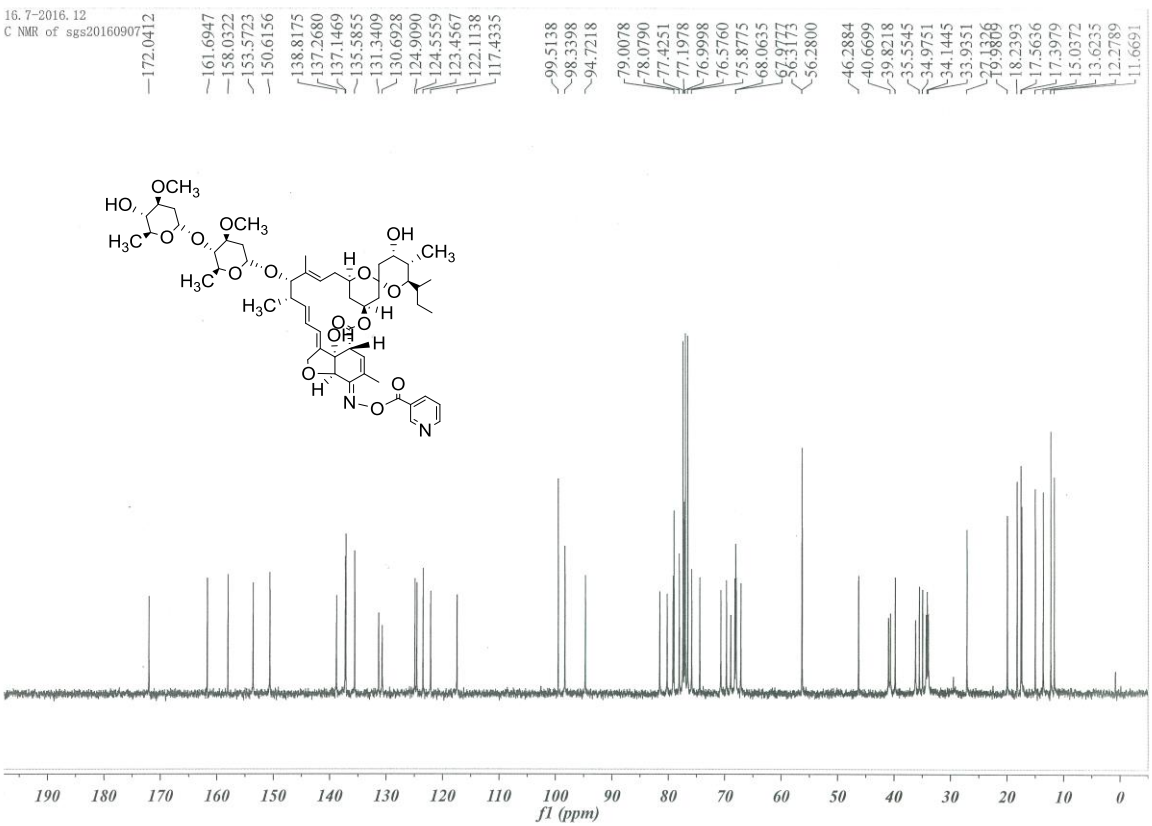

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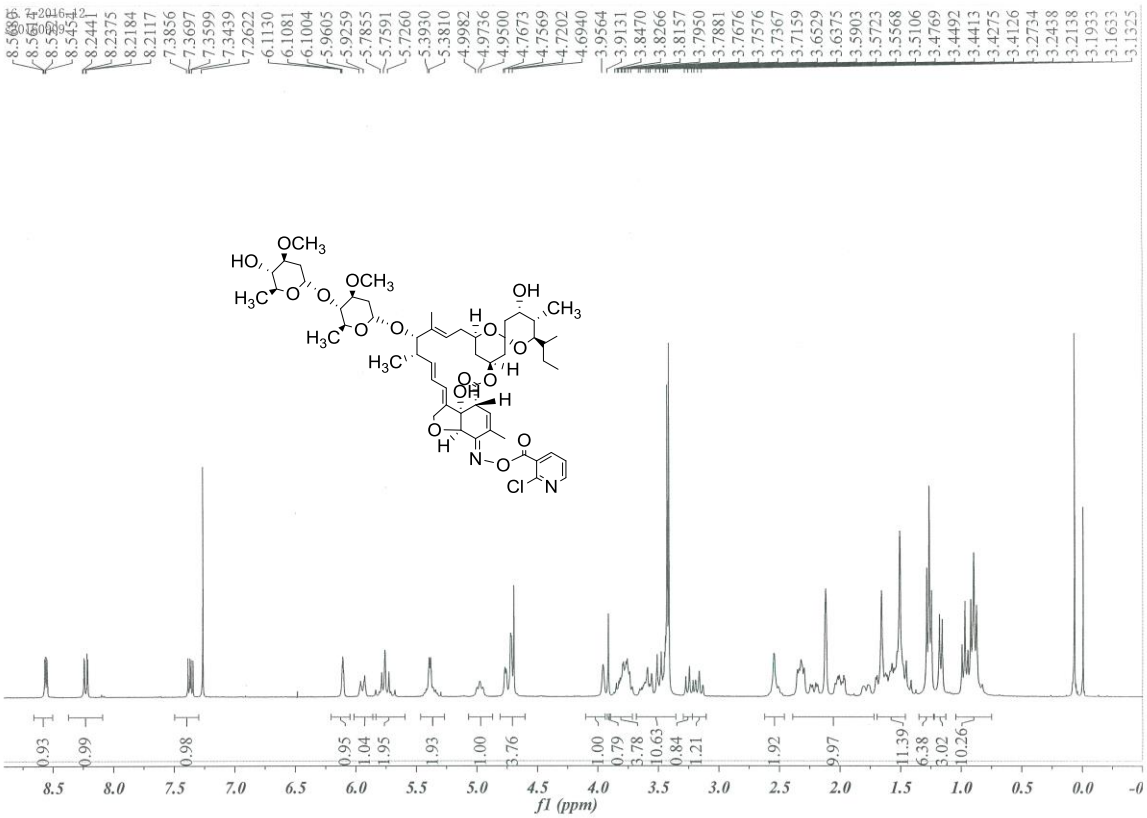
1 5-((2-chloro-3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a (8n)



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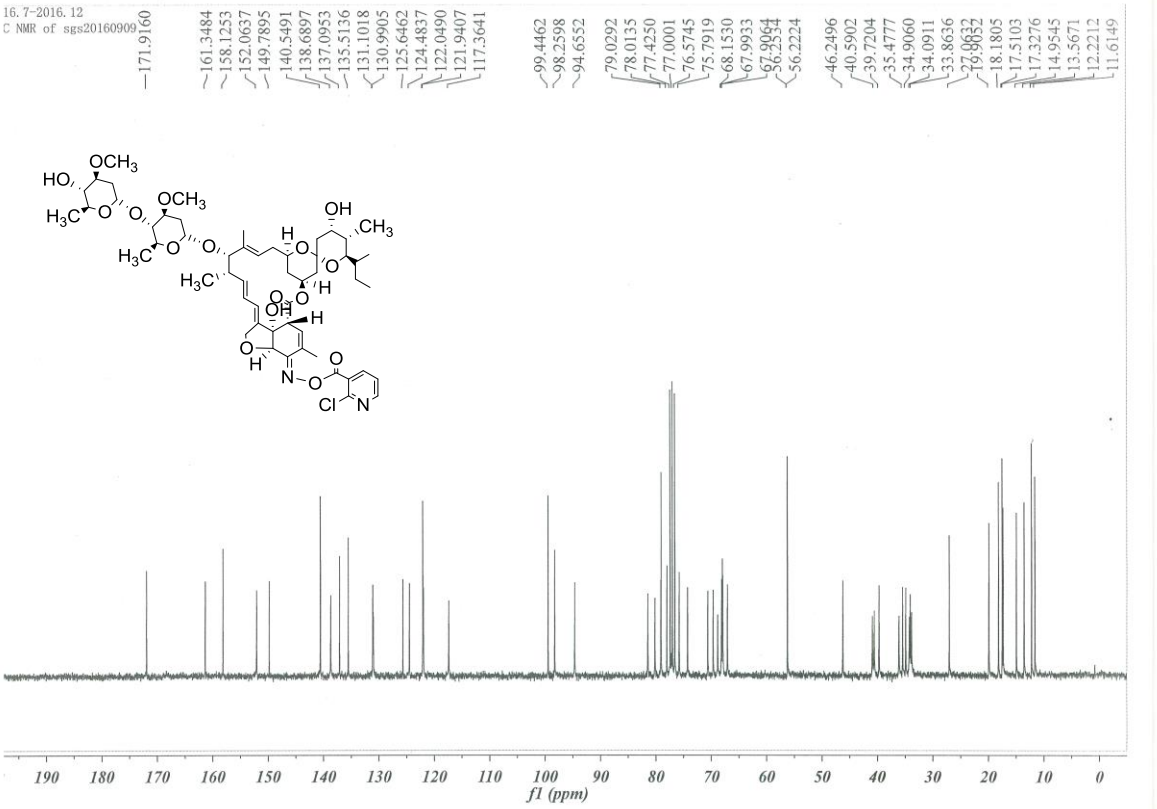

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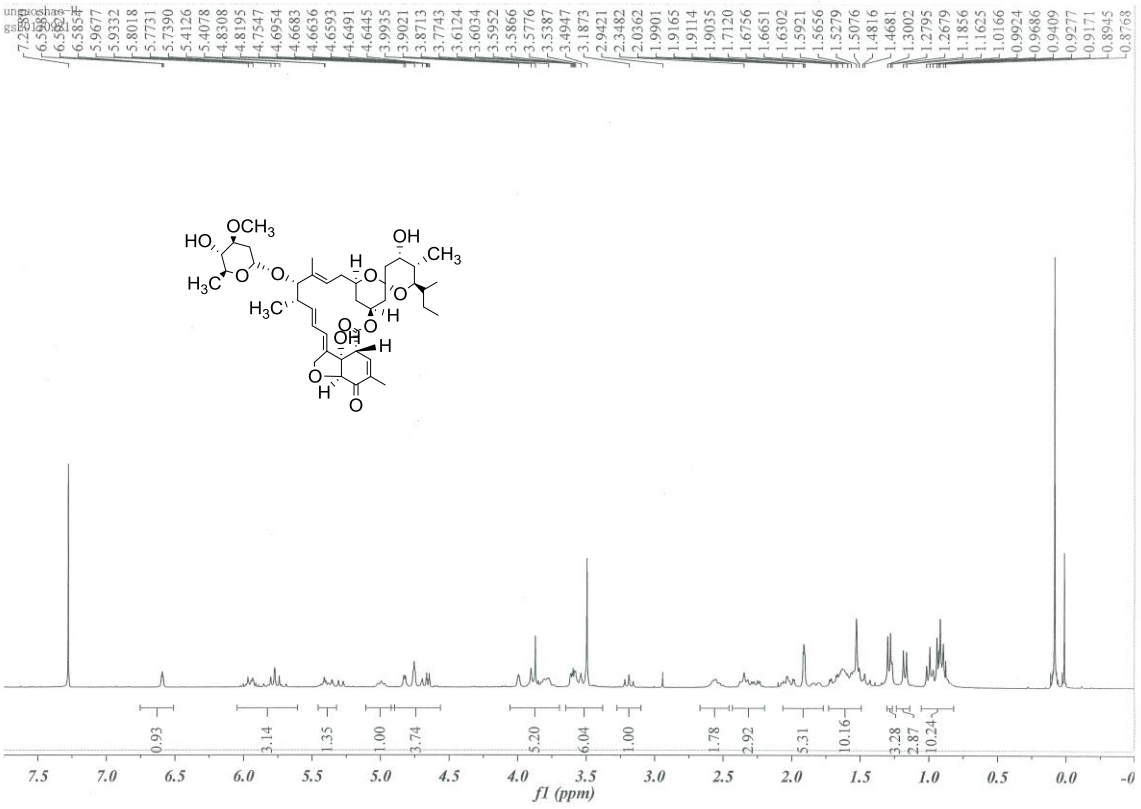
1 5-oxoavermectin B2a monosaccharide (9)



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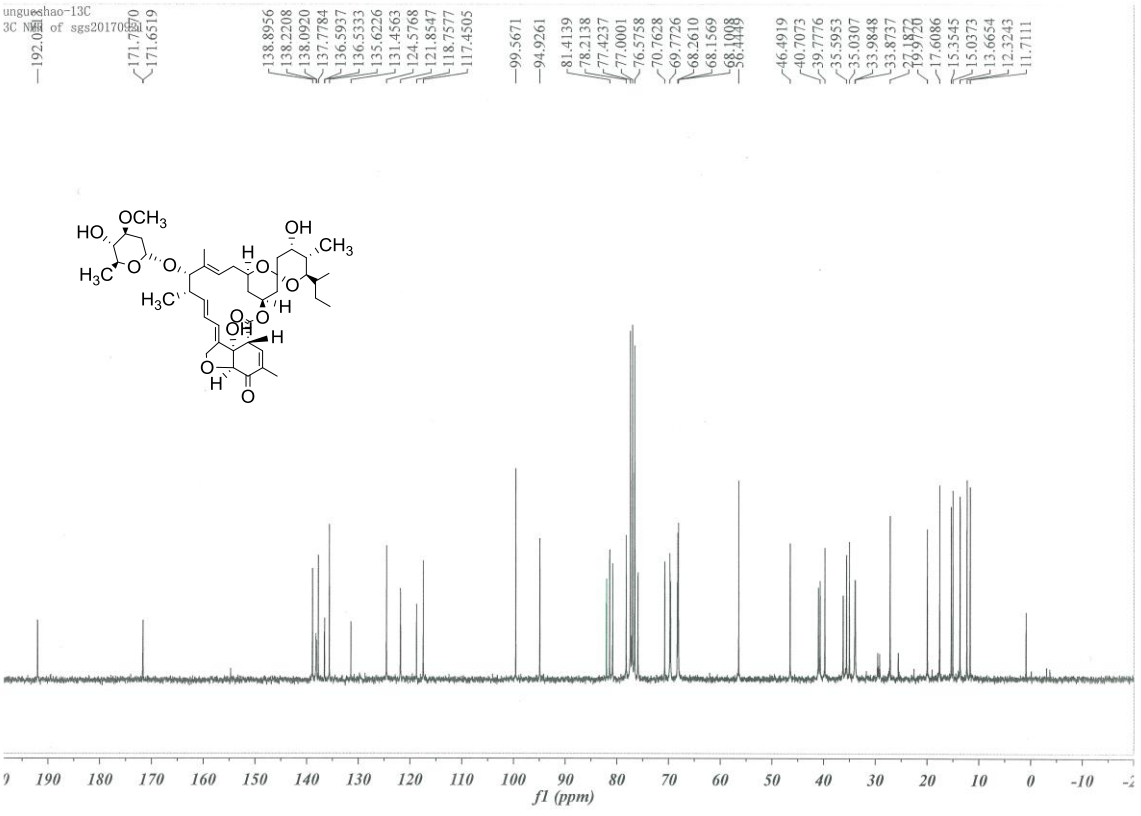

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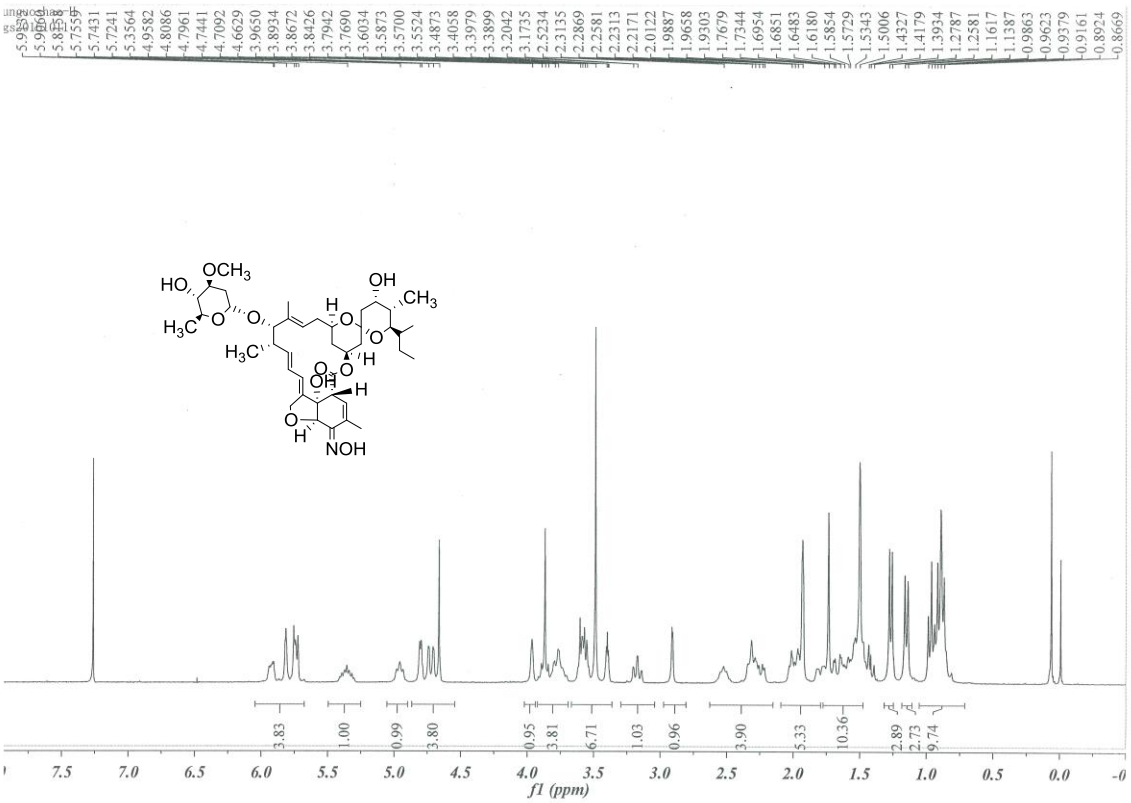
1 5-oximino-5-deoxyavermectin B2a monosaccharide (10)



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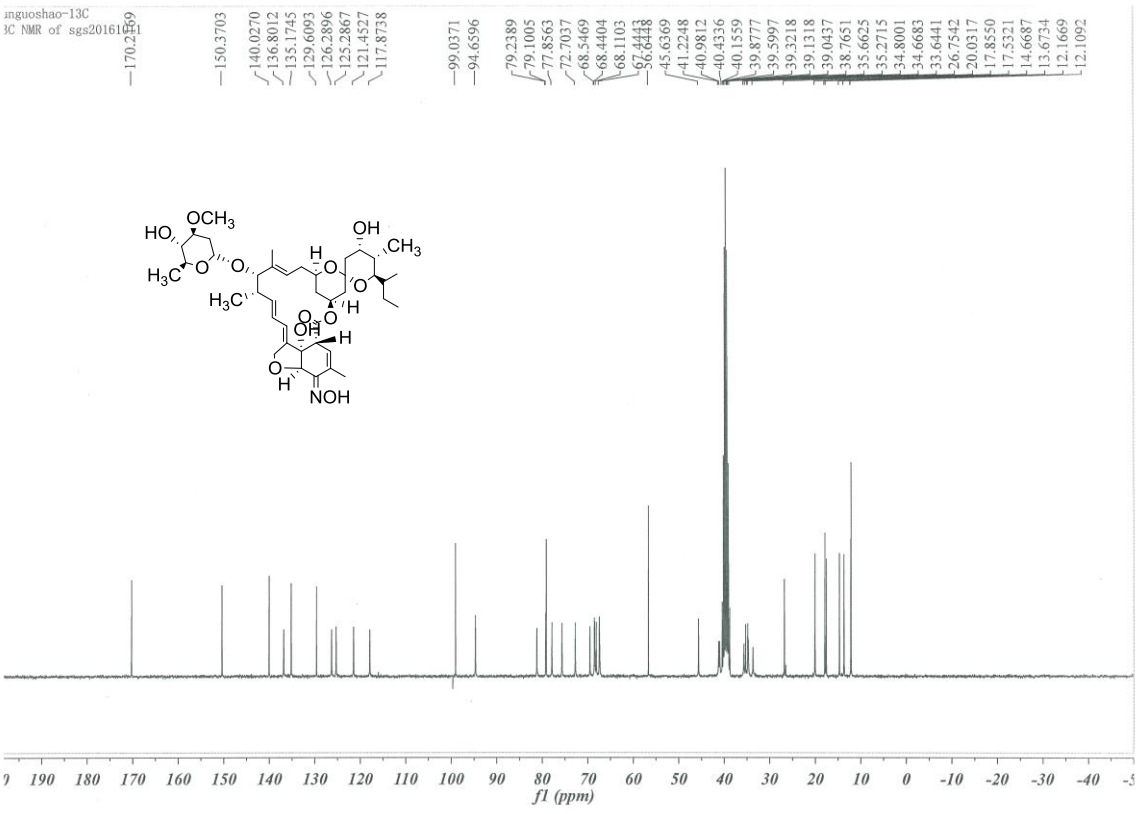

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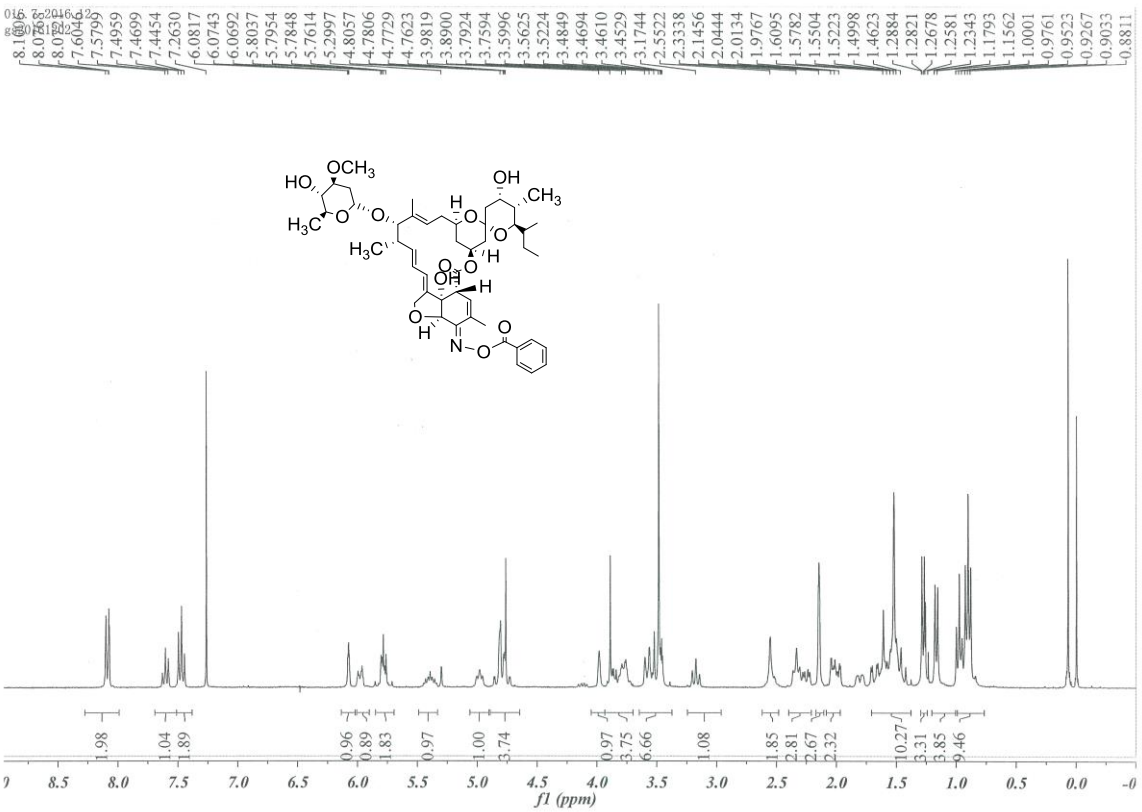
1 5-(benzoyloxyimino)-5-deoxyavermectin B2a monosaccharide (11a)



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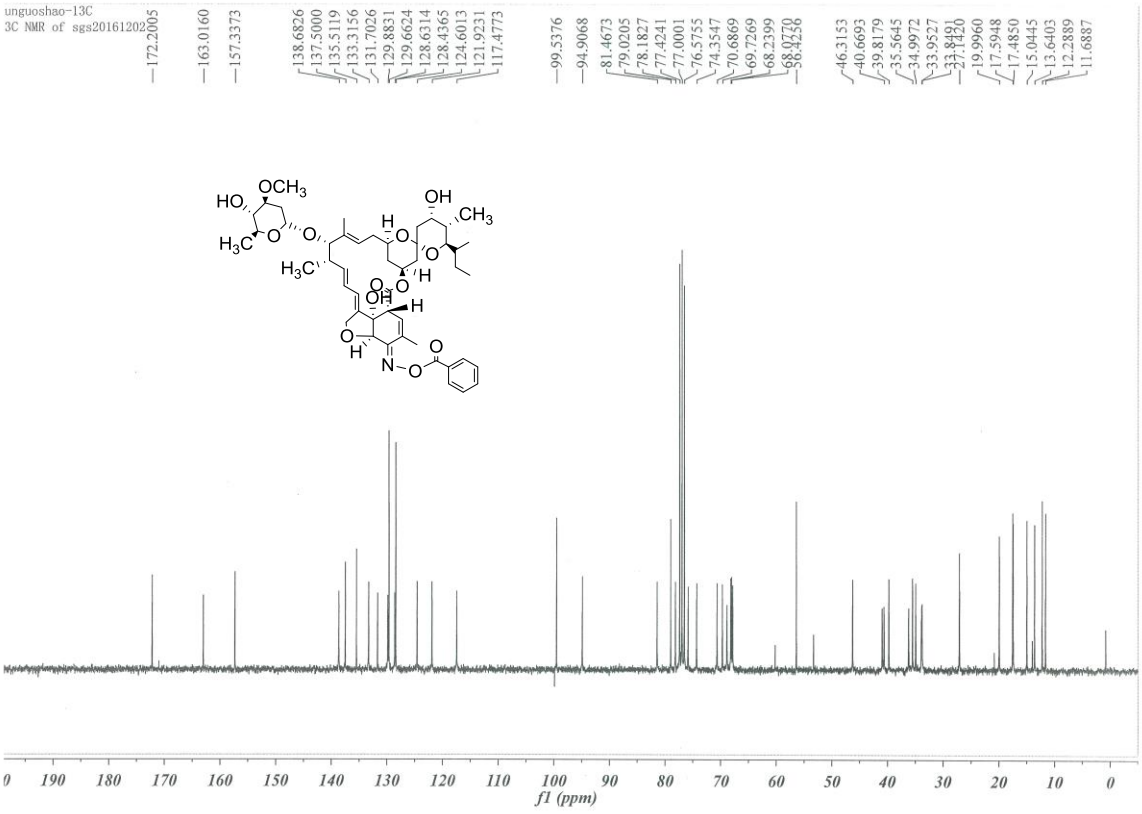

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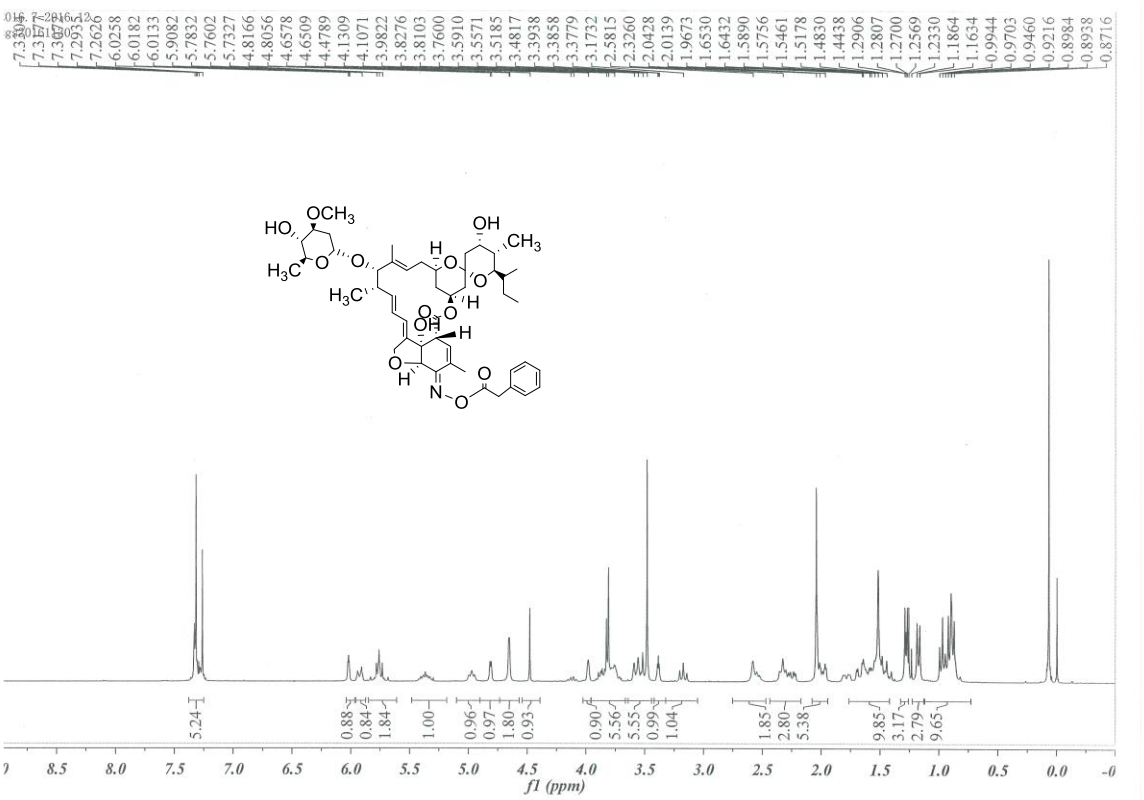
1 5-(phenylacetyloxyimino)-5-deoxyavermectin B2a monosaccharide (11b)



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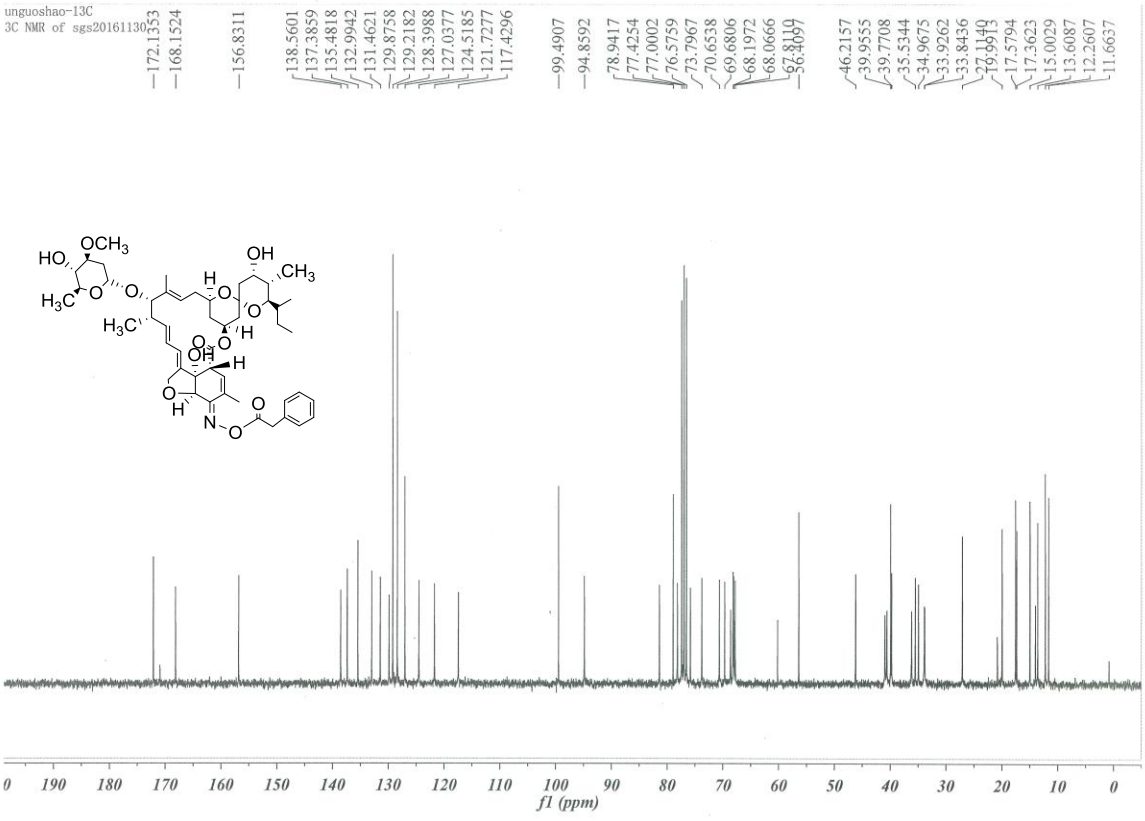

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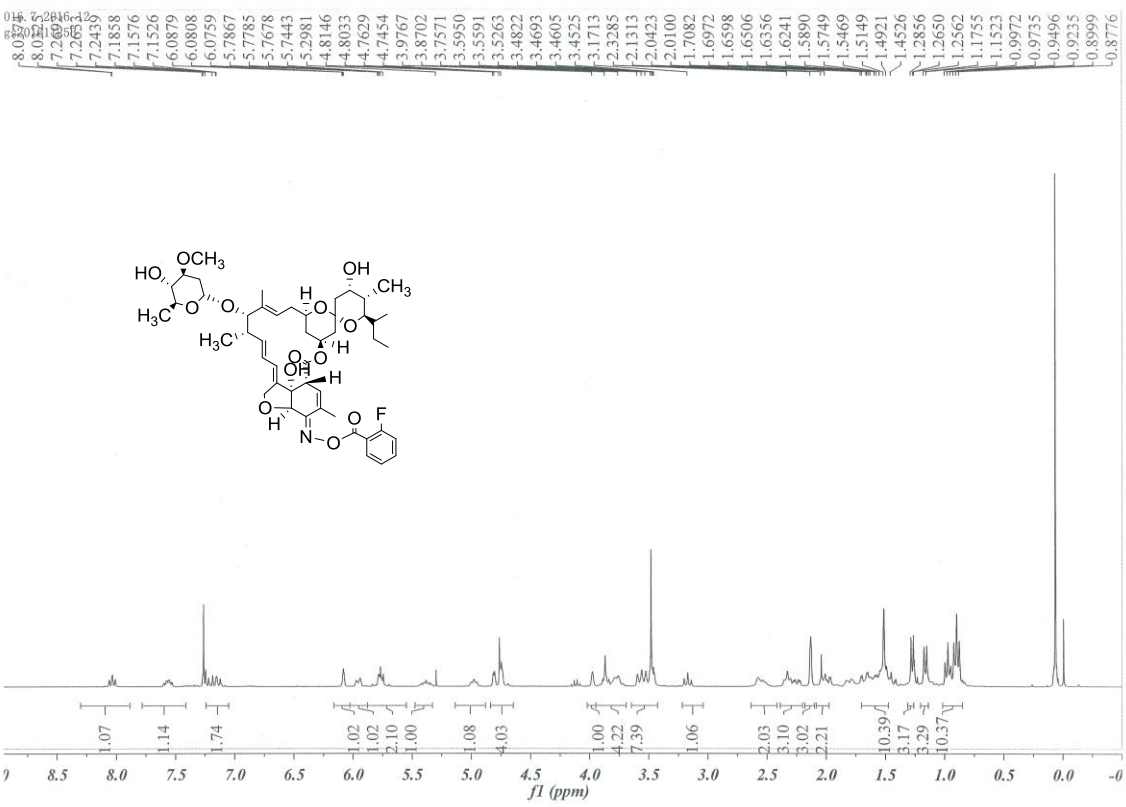
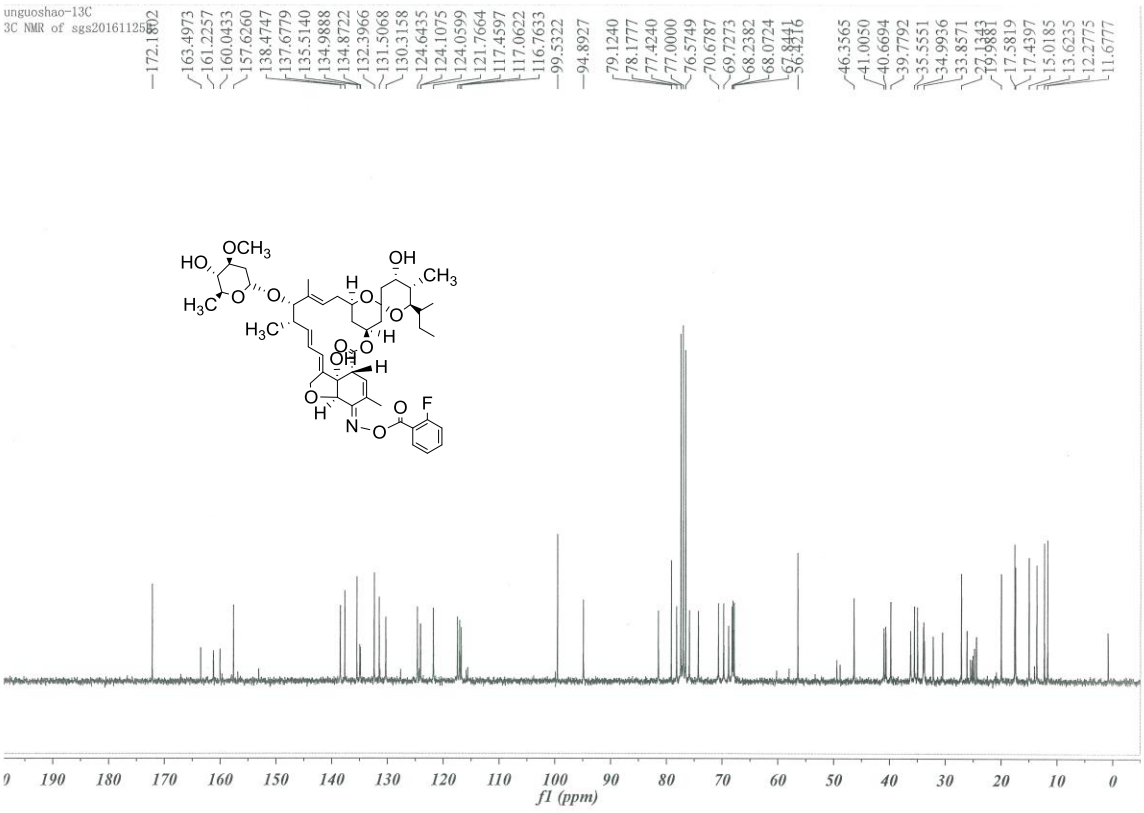
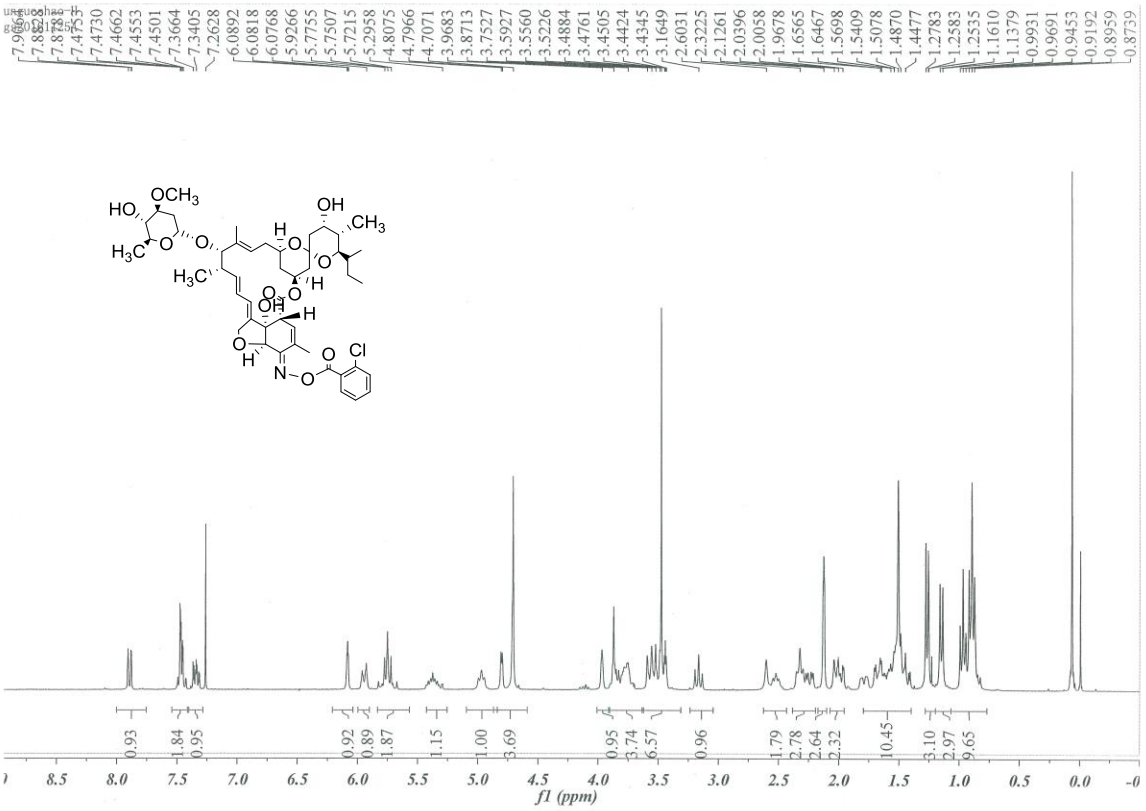
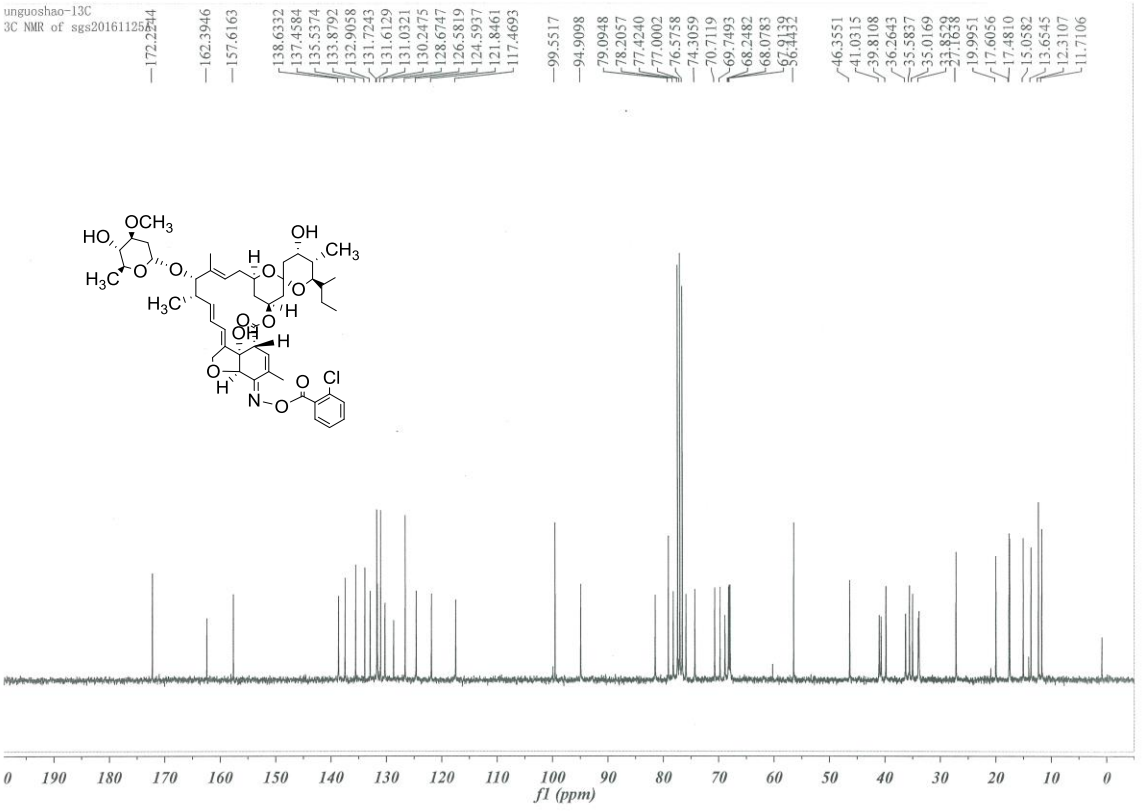
5-((2-fluorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11c)



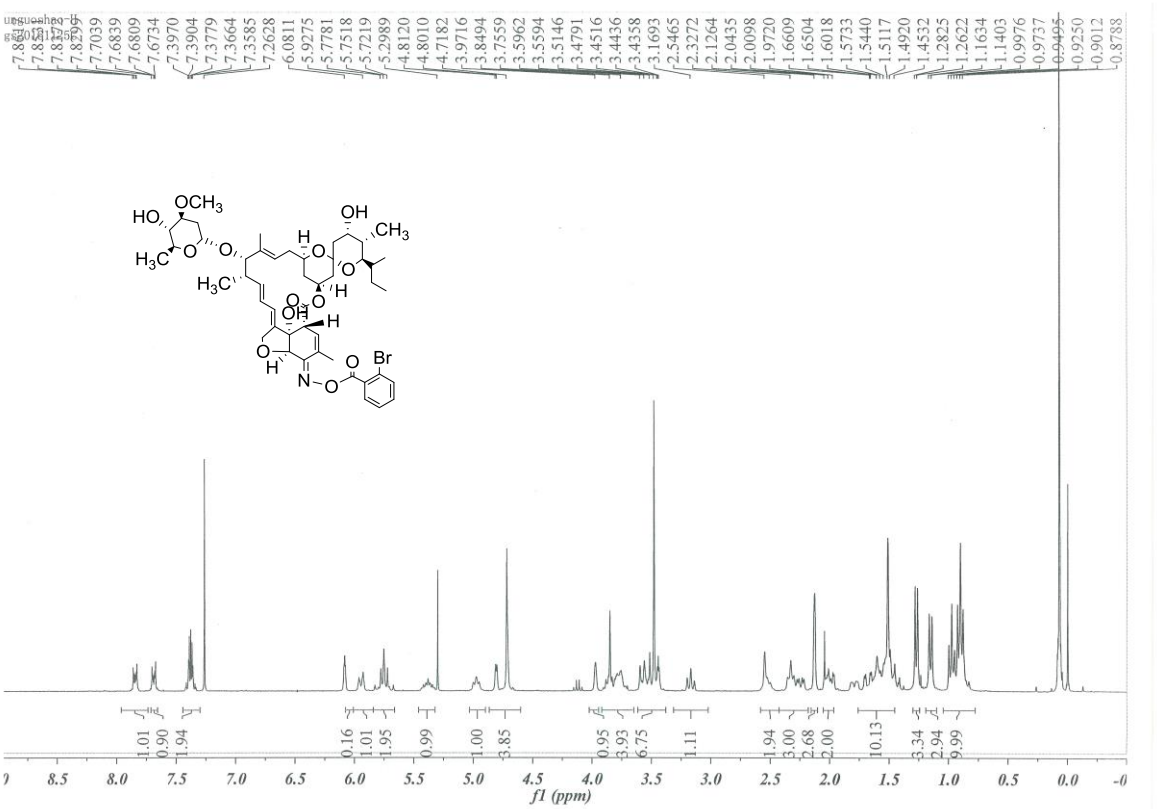


5-((2-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11d)





1 5-((2-bromobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11e)



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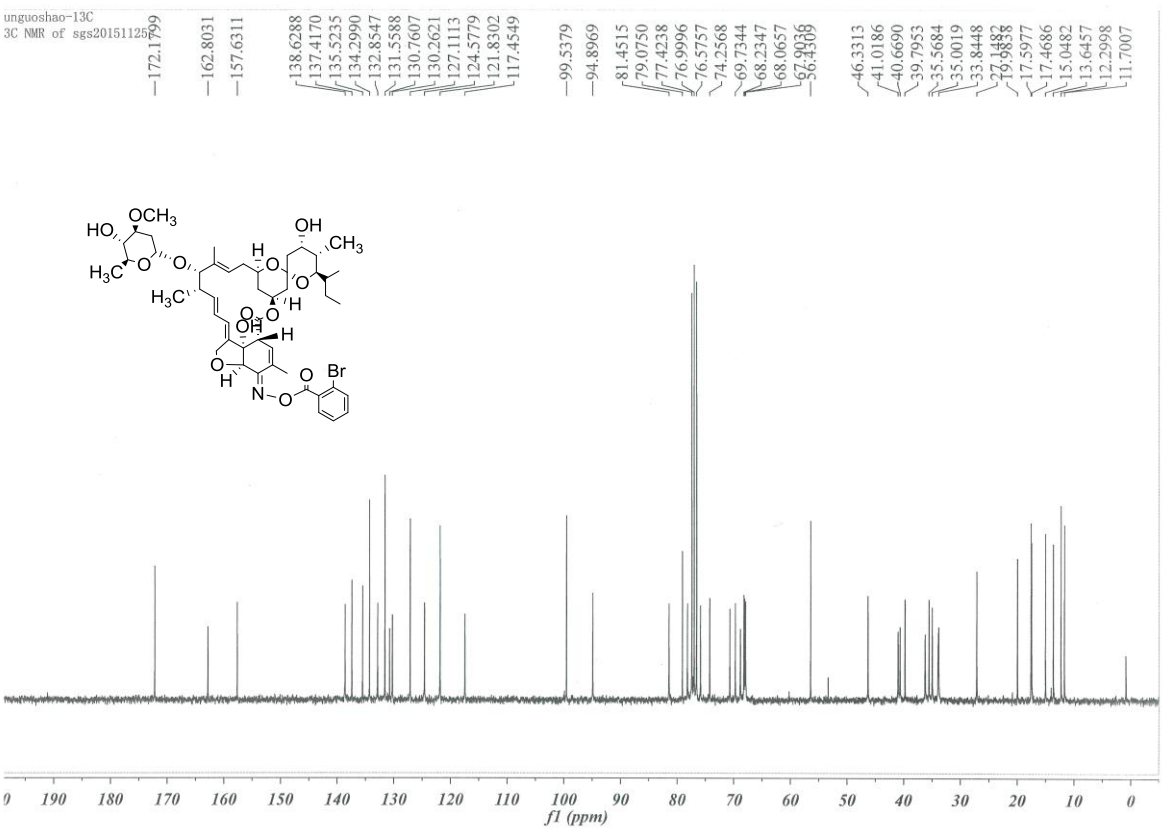

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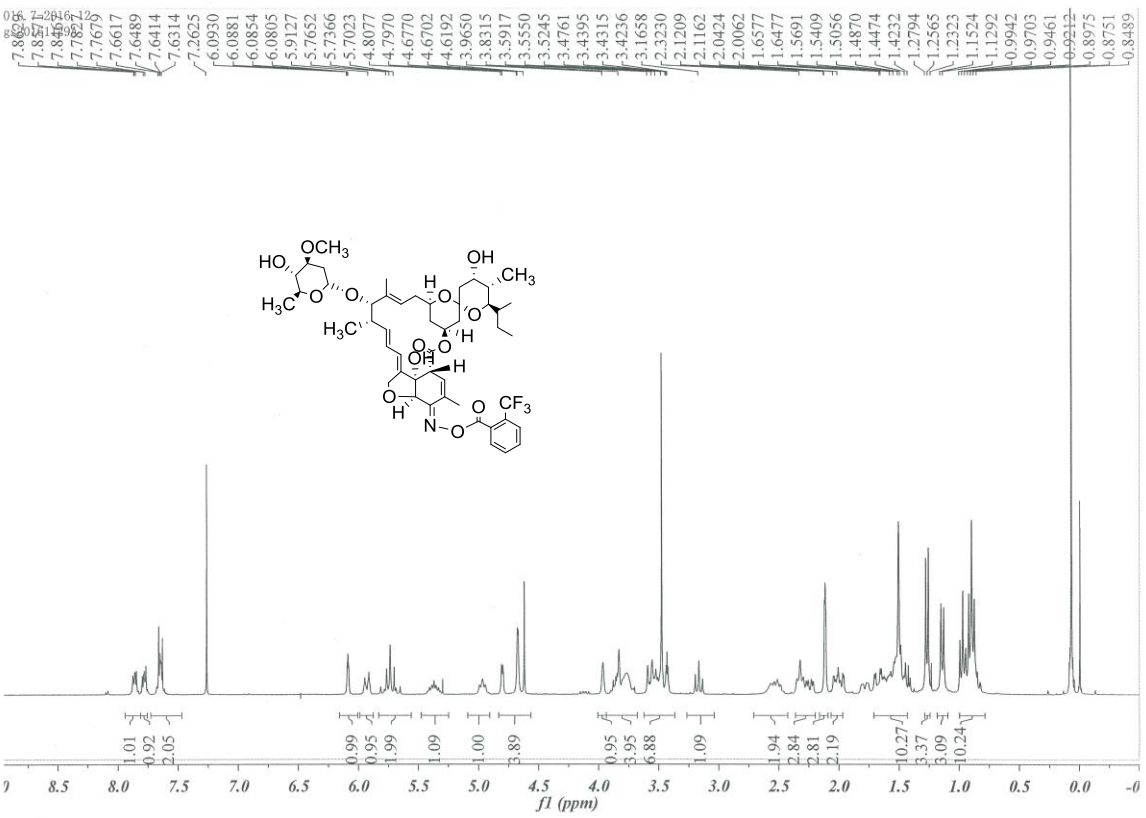
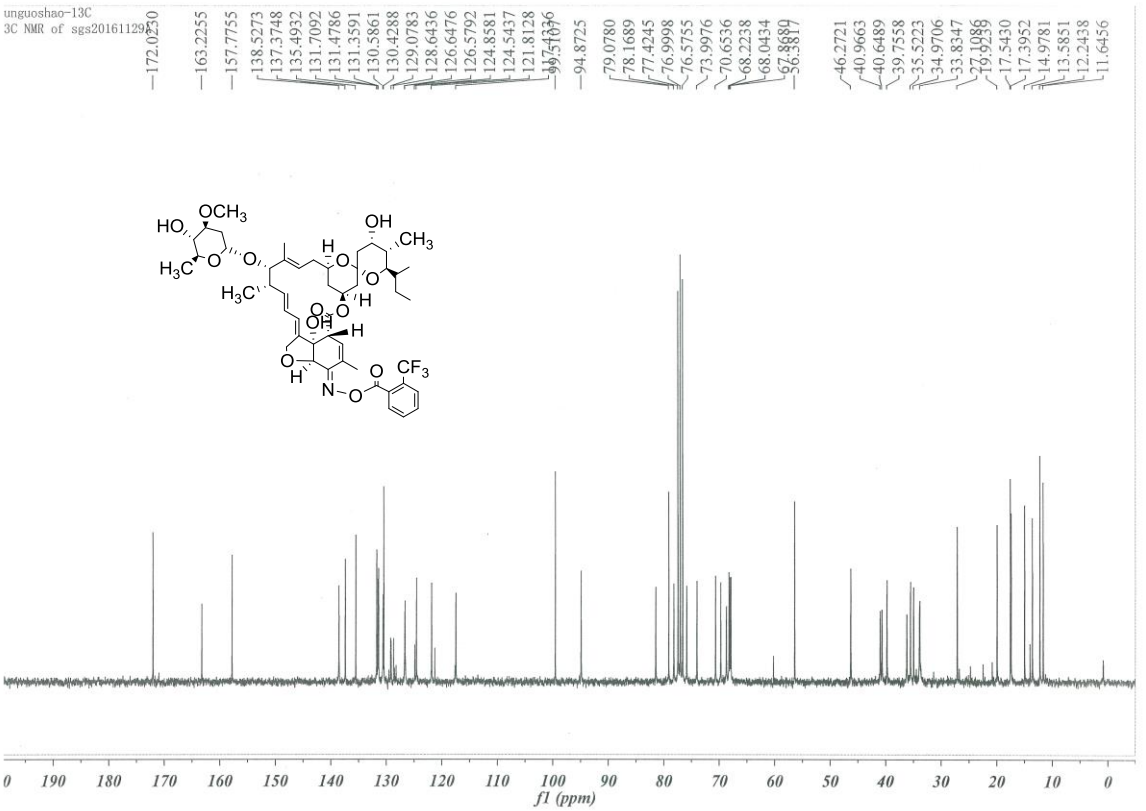
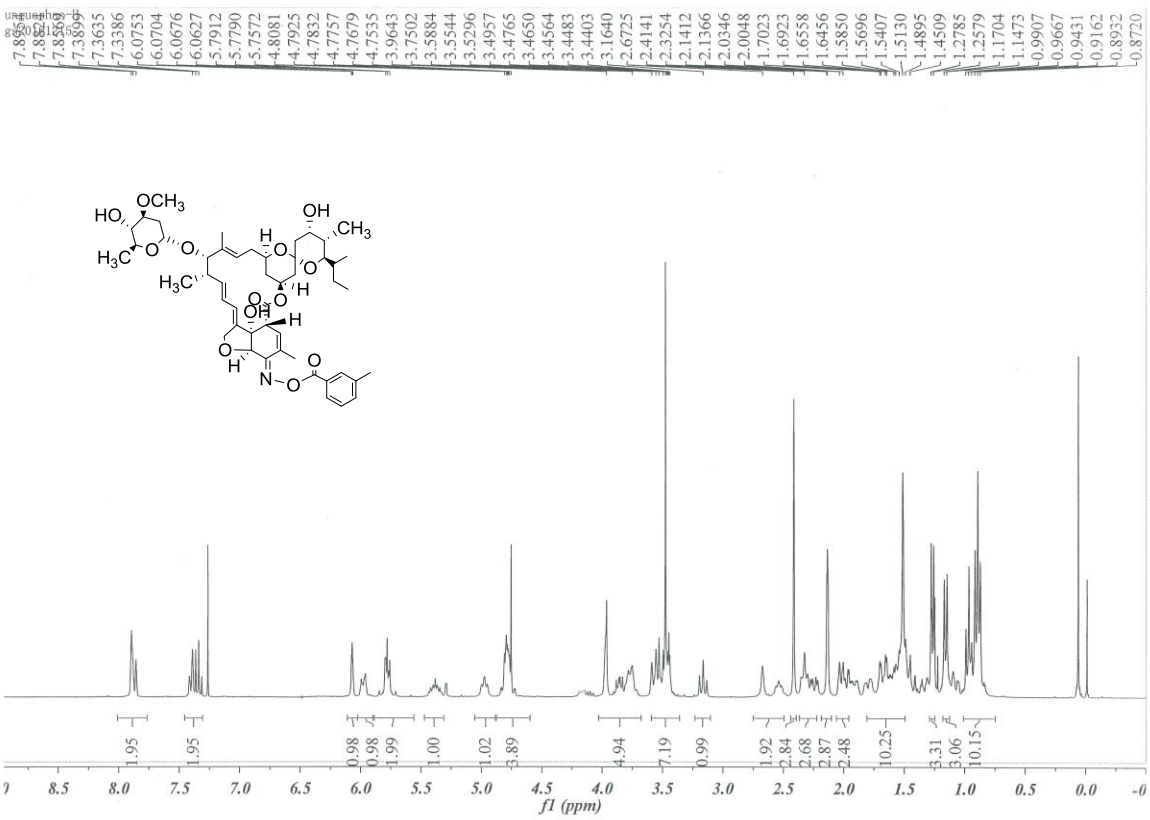
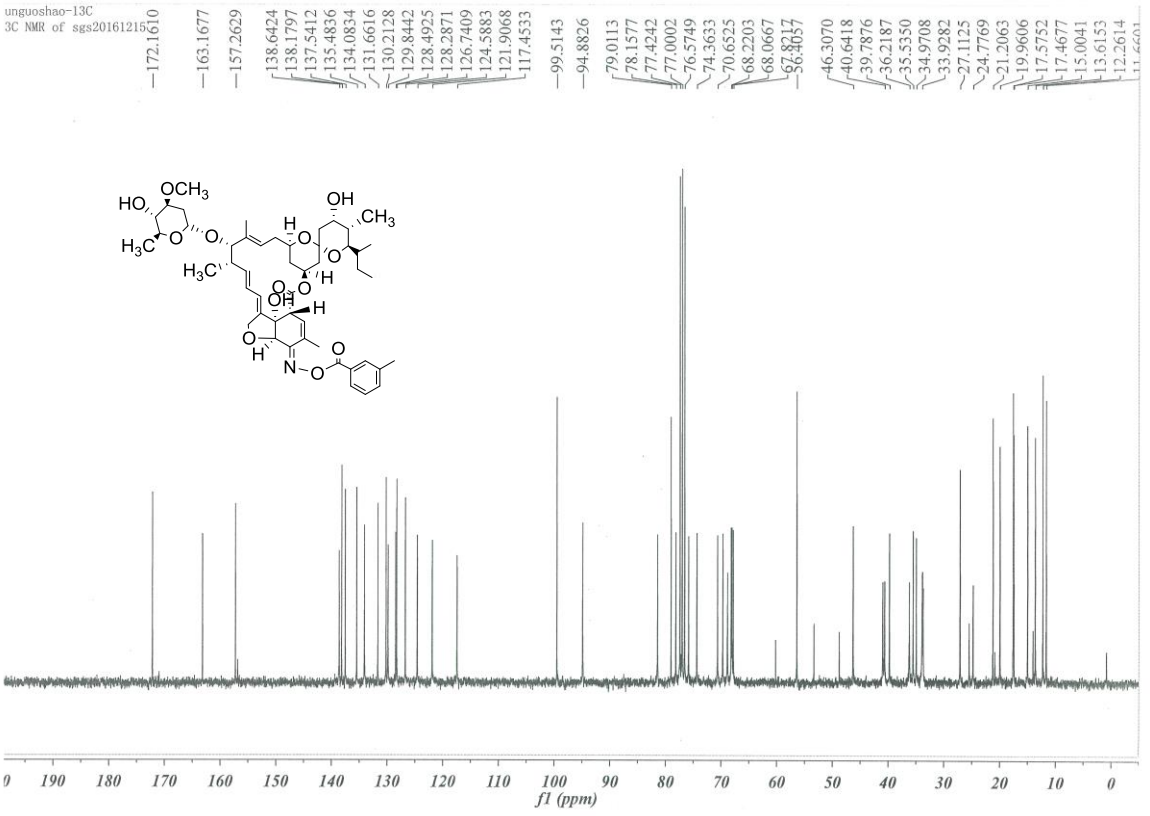
5-((2-trifluoromethylbenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11f)



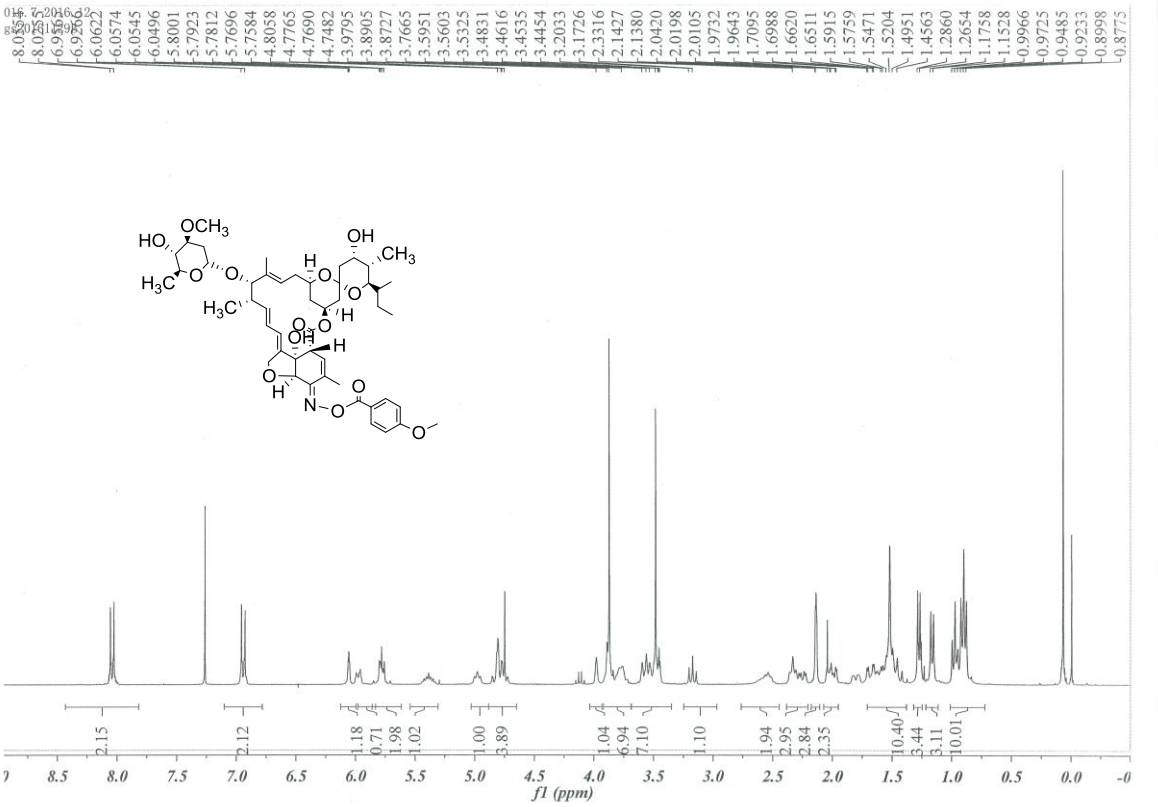


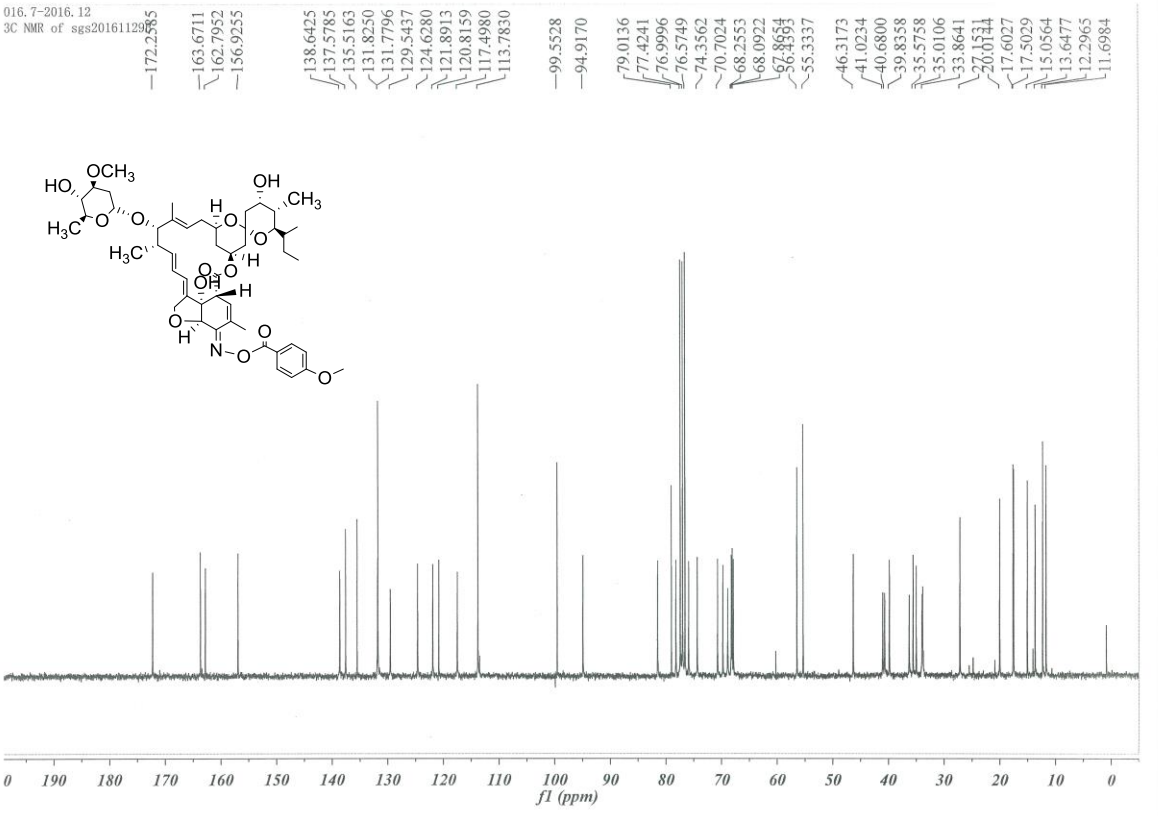
5-((3-methylbenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11g)



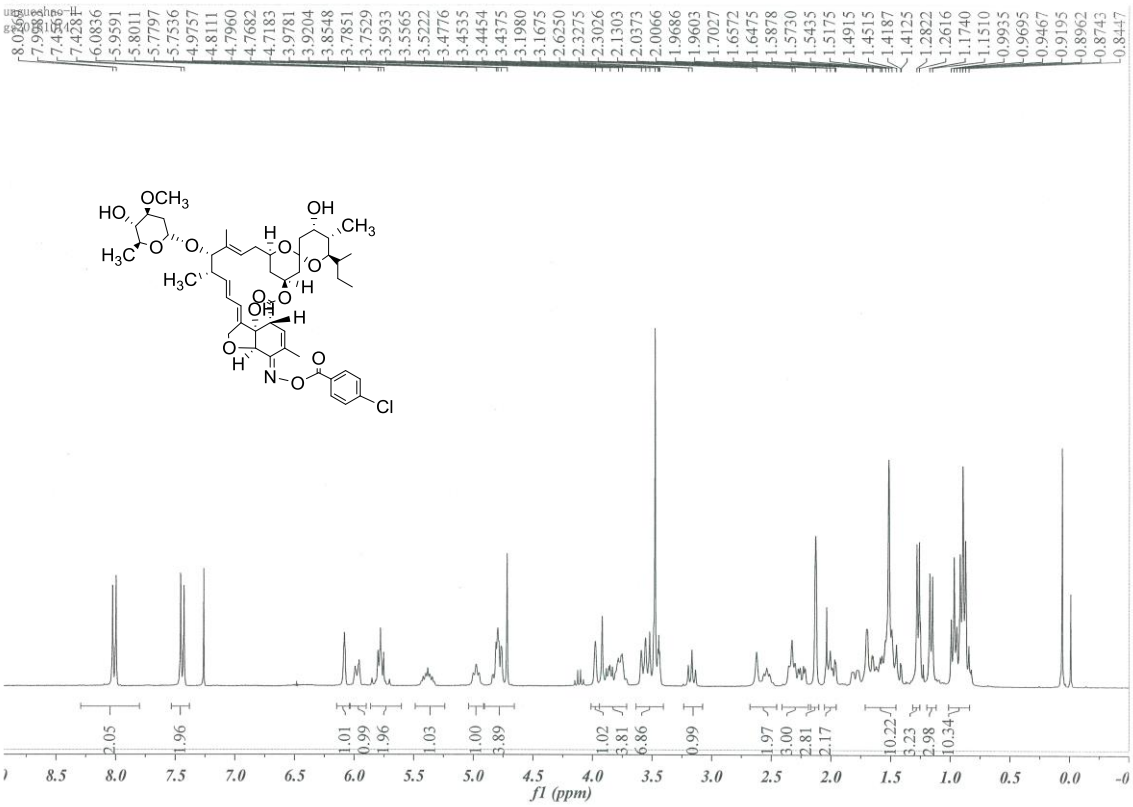


5-((4-methoxybenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11h)





1 5-((4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11i)



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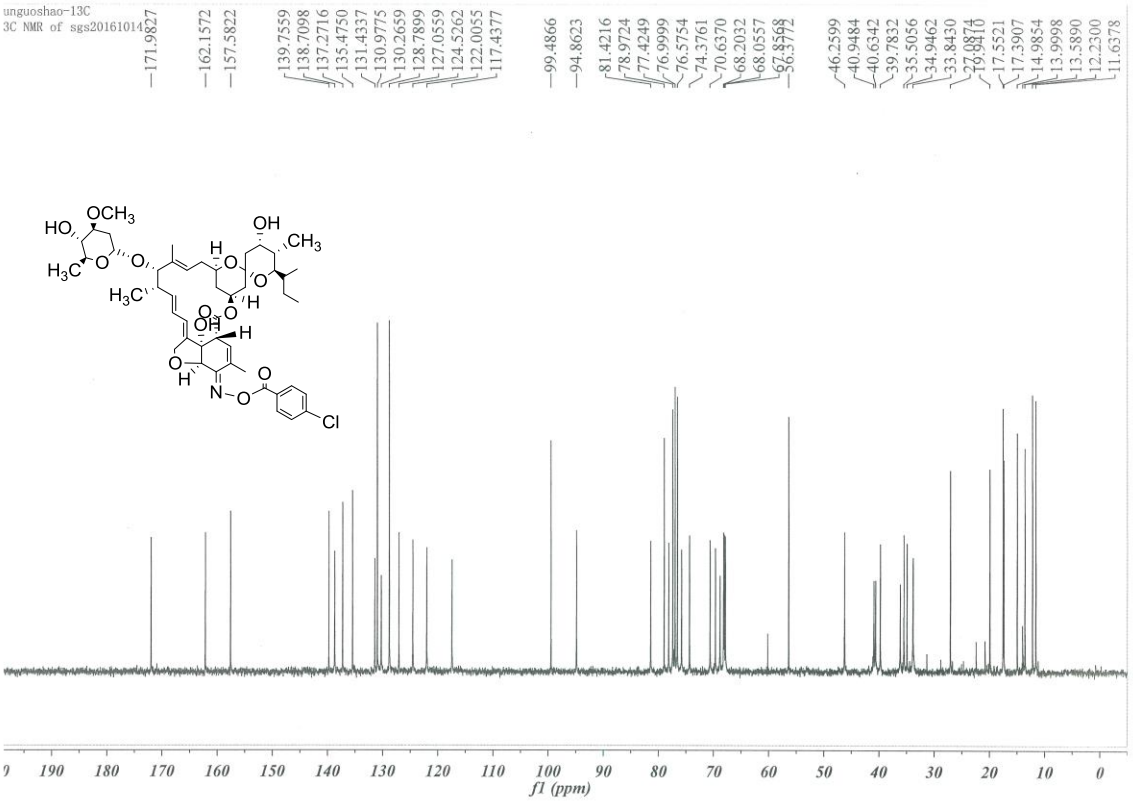

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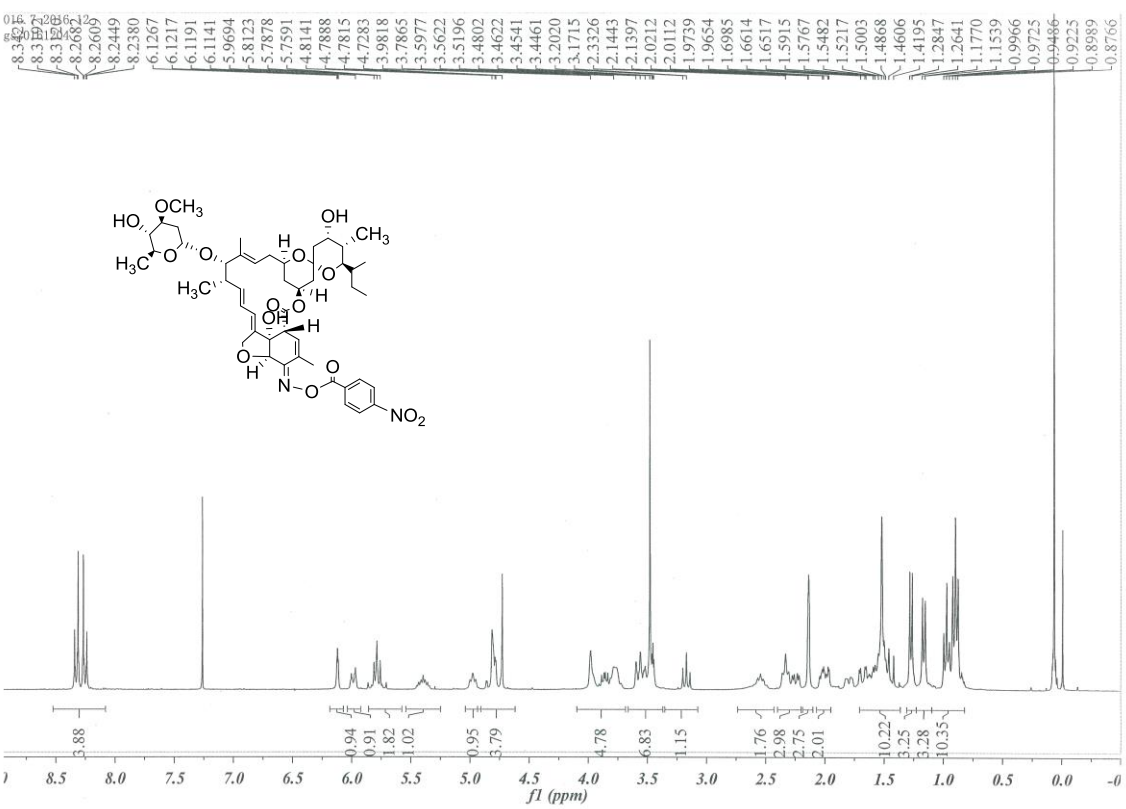
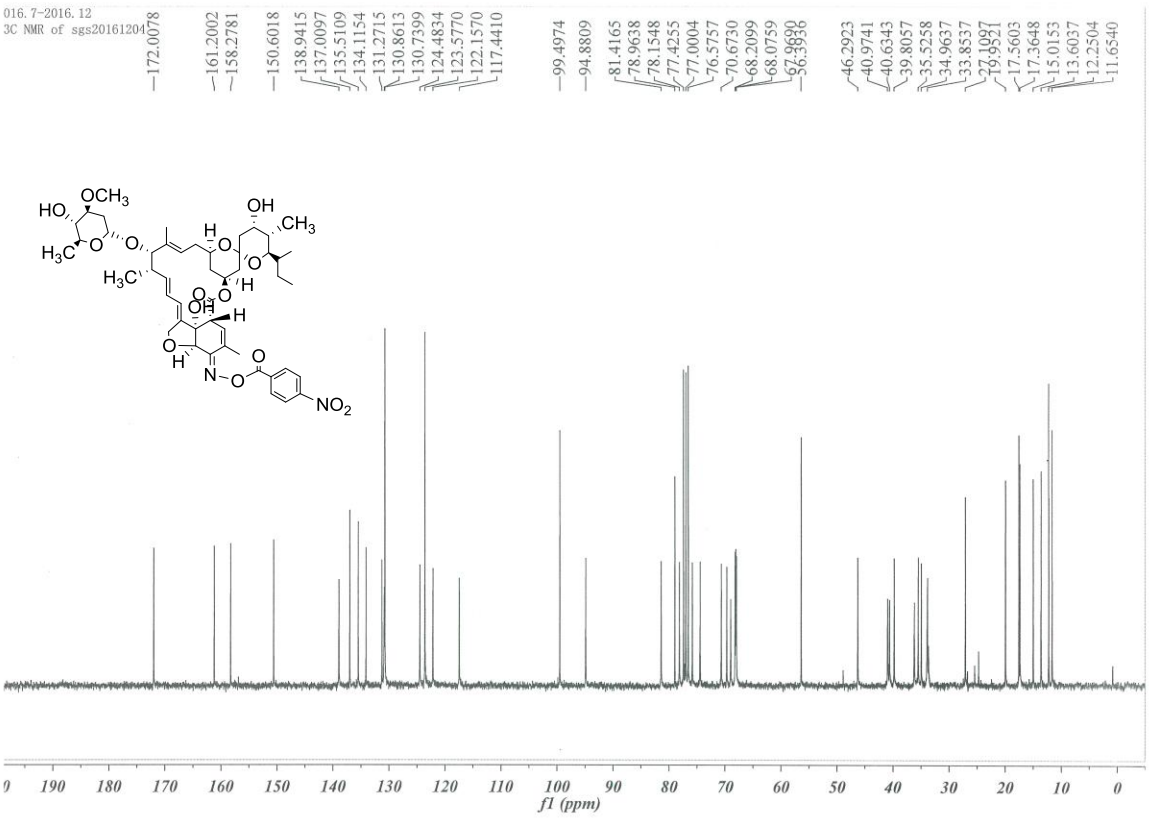
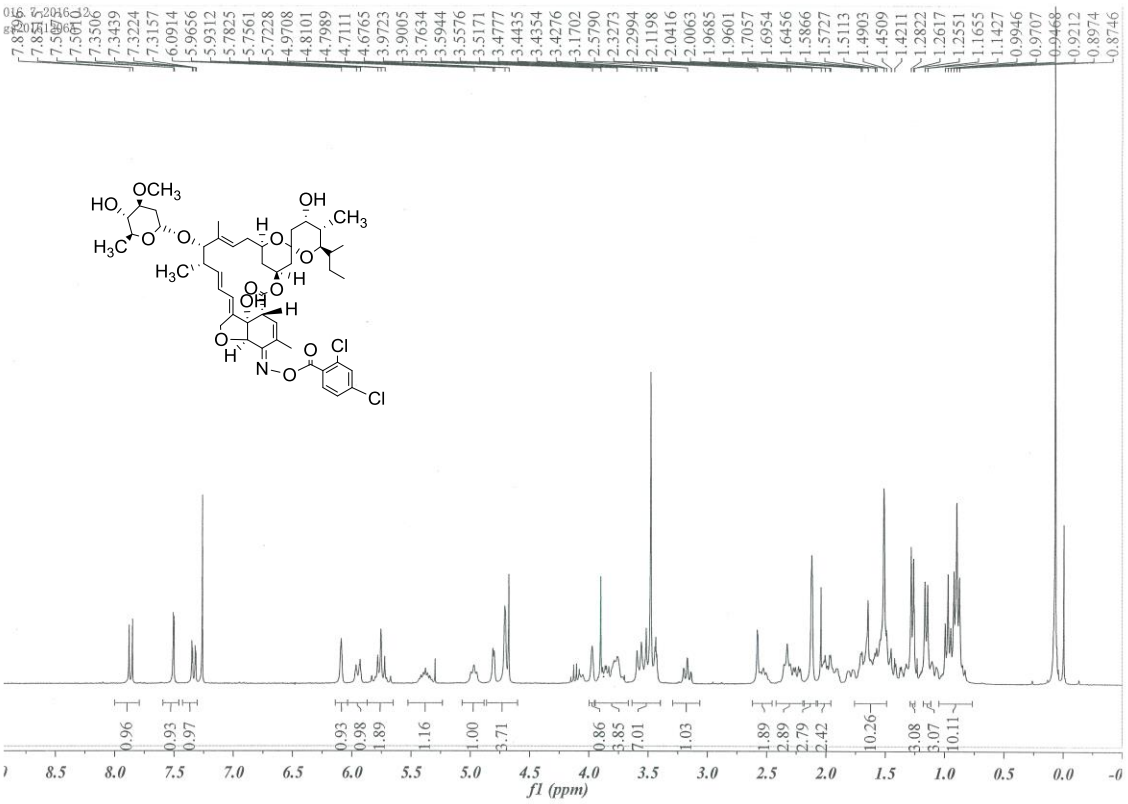
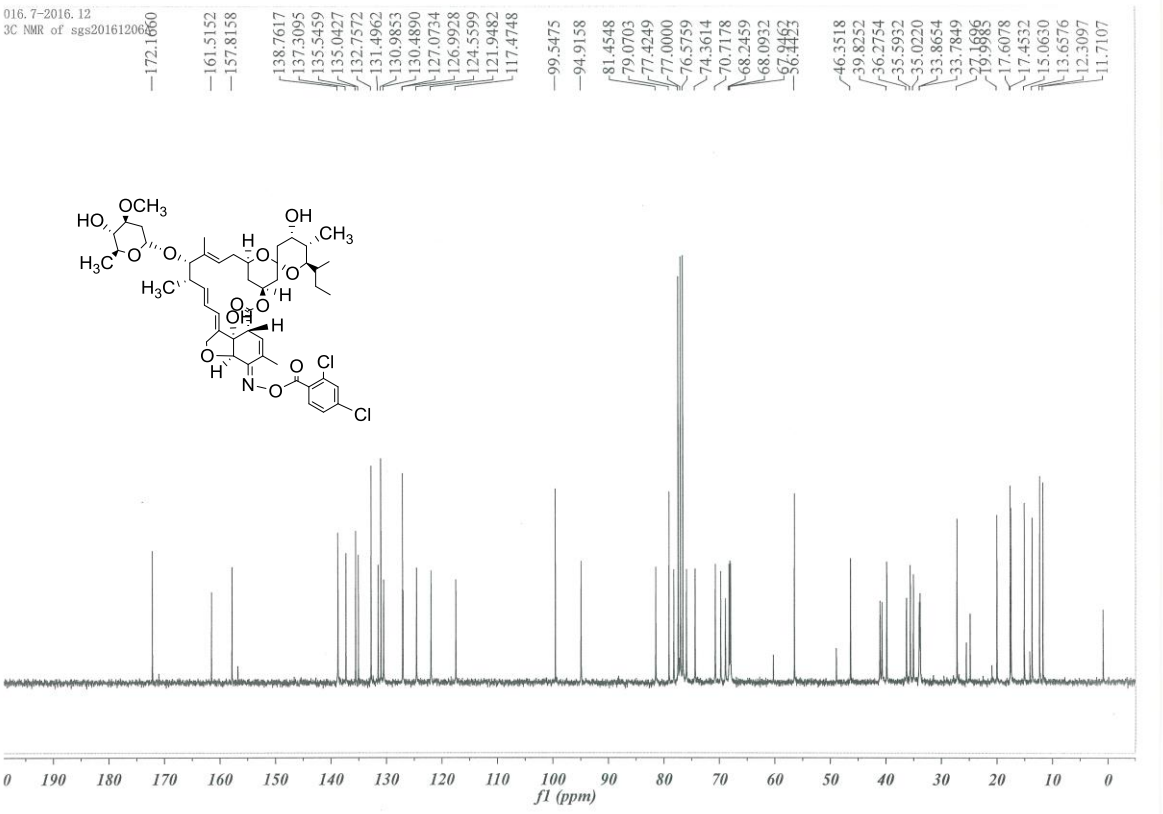
5-((4-nitrobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11j)



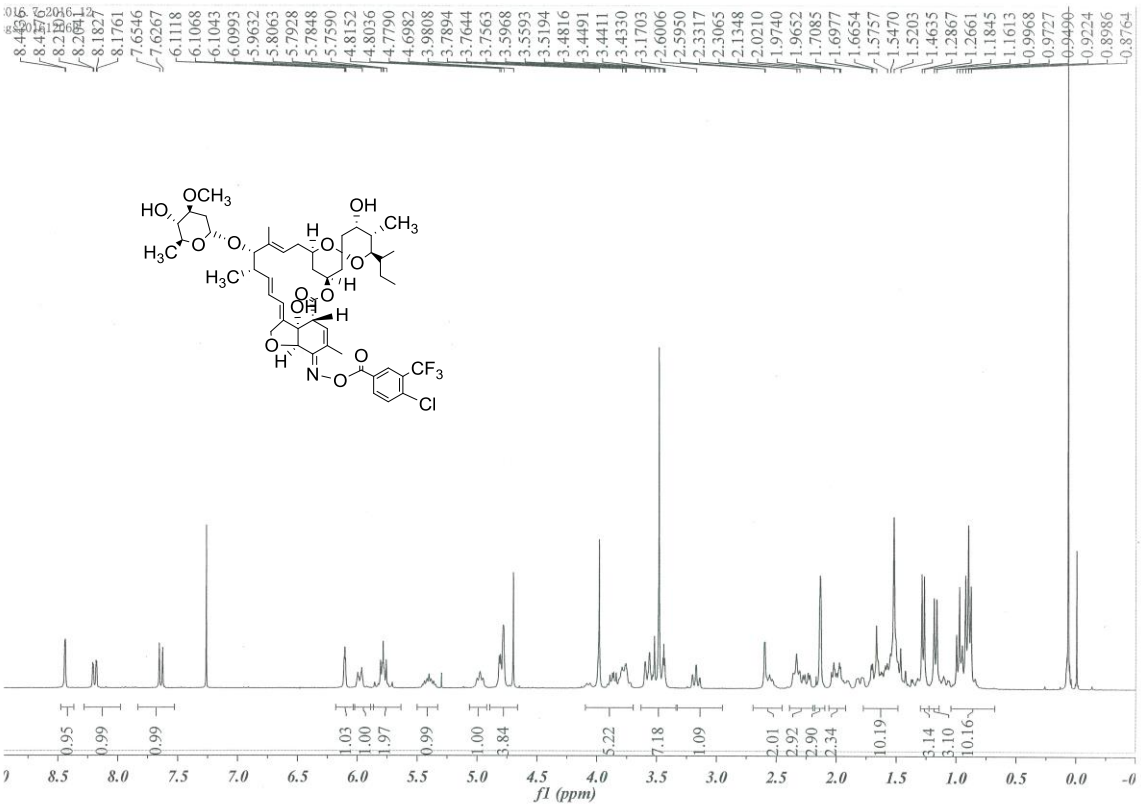


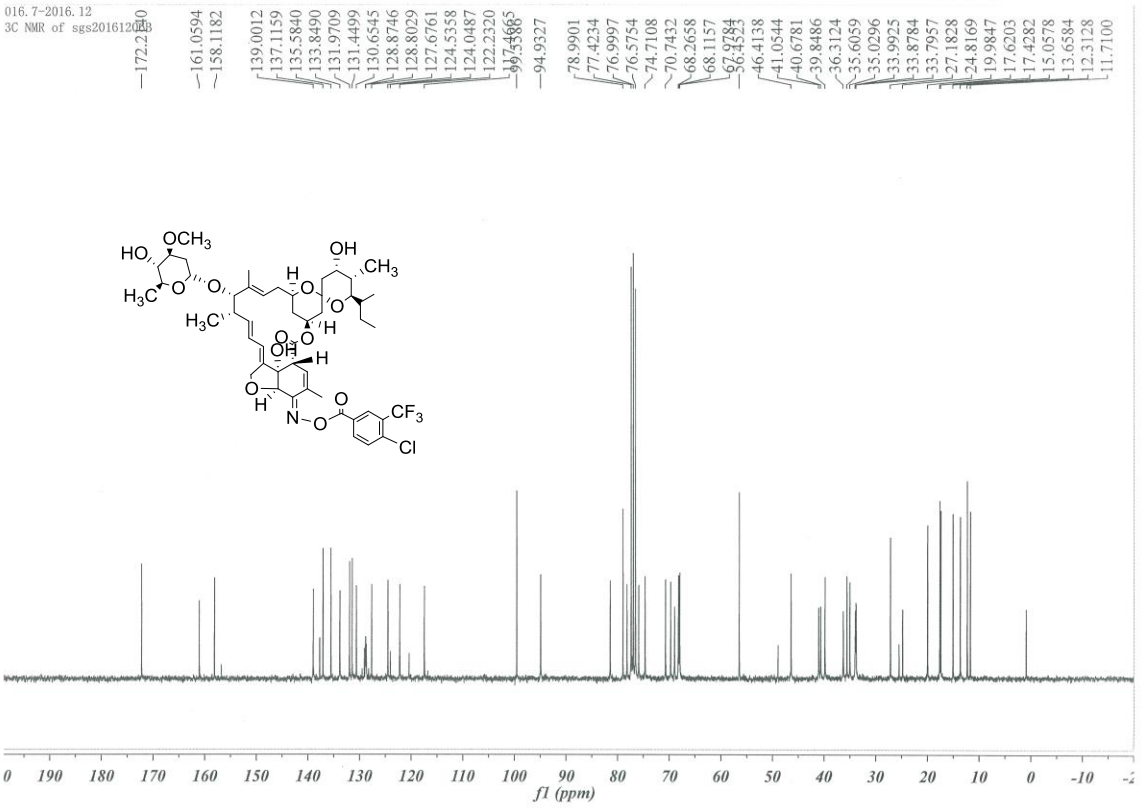
5-((2,4-dichlorobenzoyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11k)



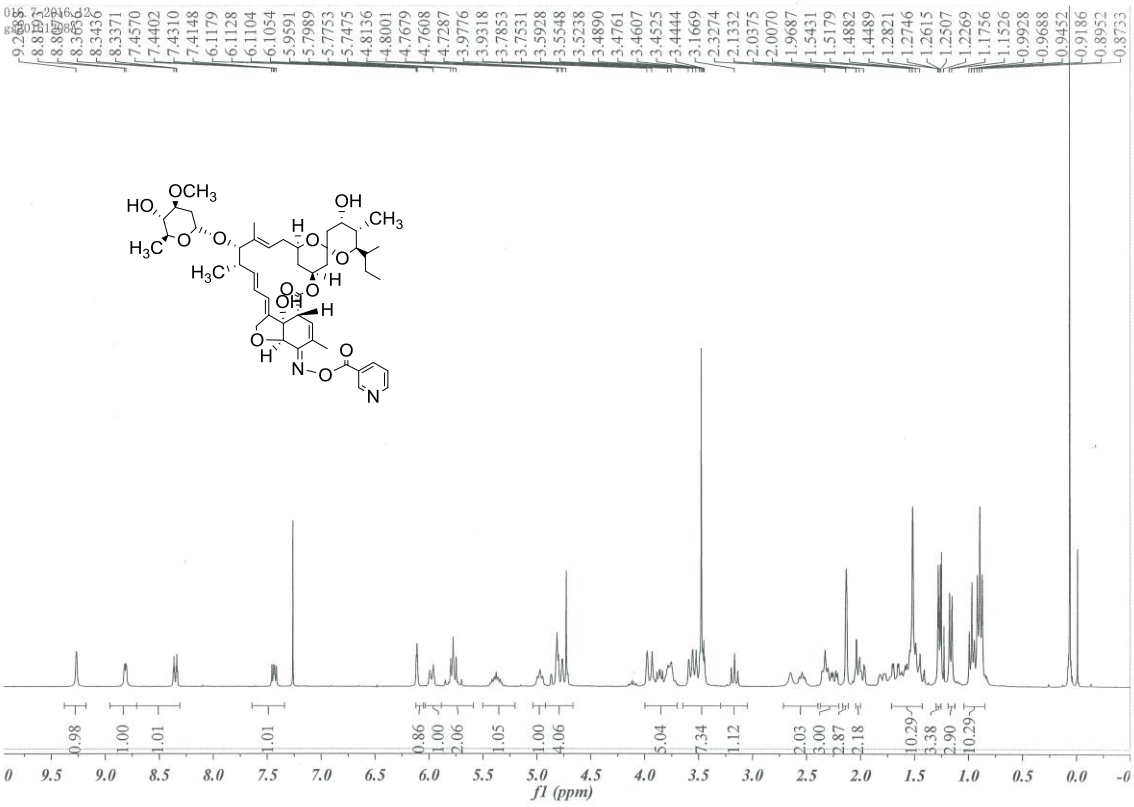


5-((3-trifluoromethyl-4-chlorobenzoyl)oxyimino)-5-deoxyavermectin monosaccharide (11l) B2a





1 5-((3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11m)



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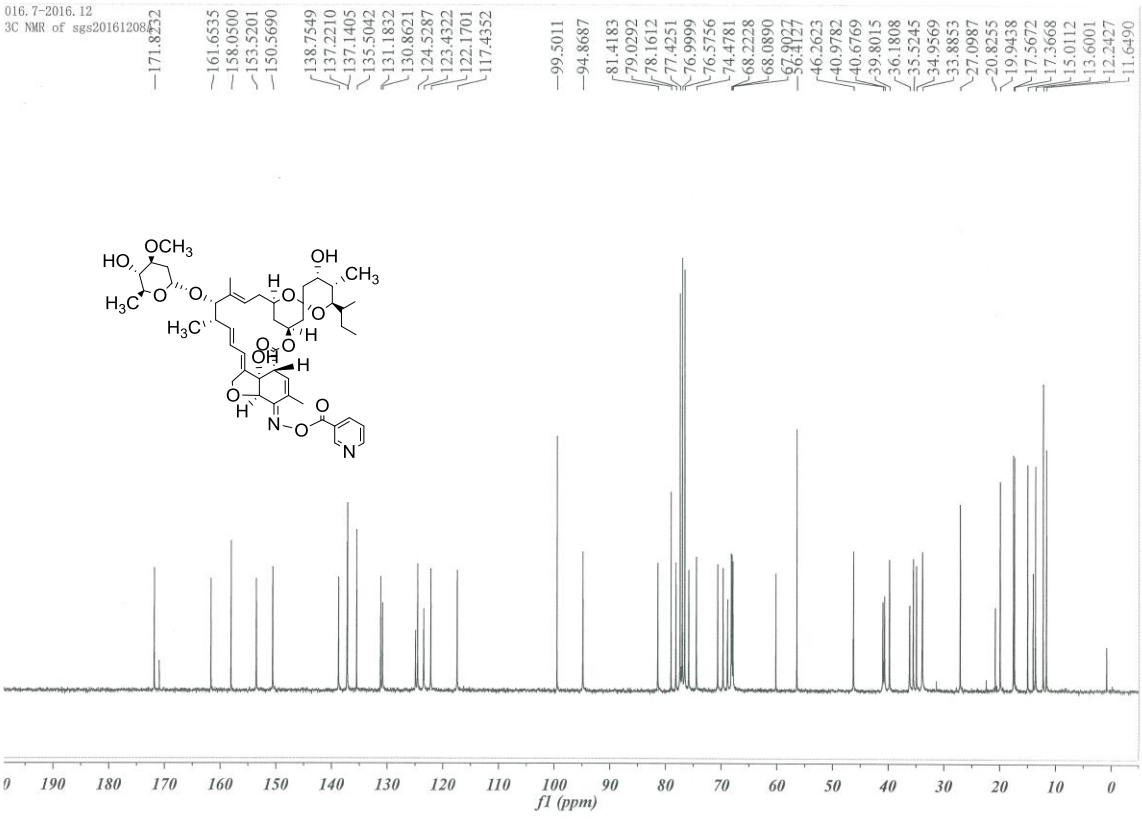

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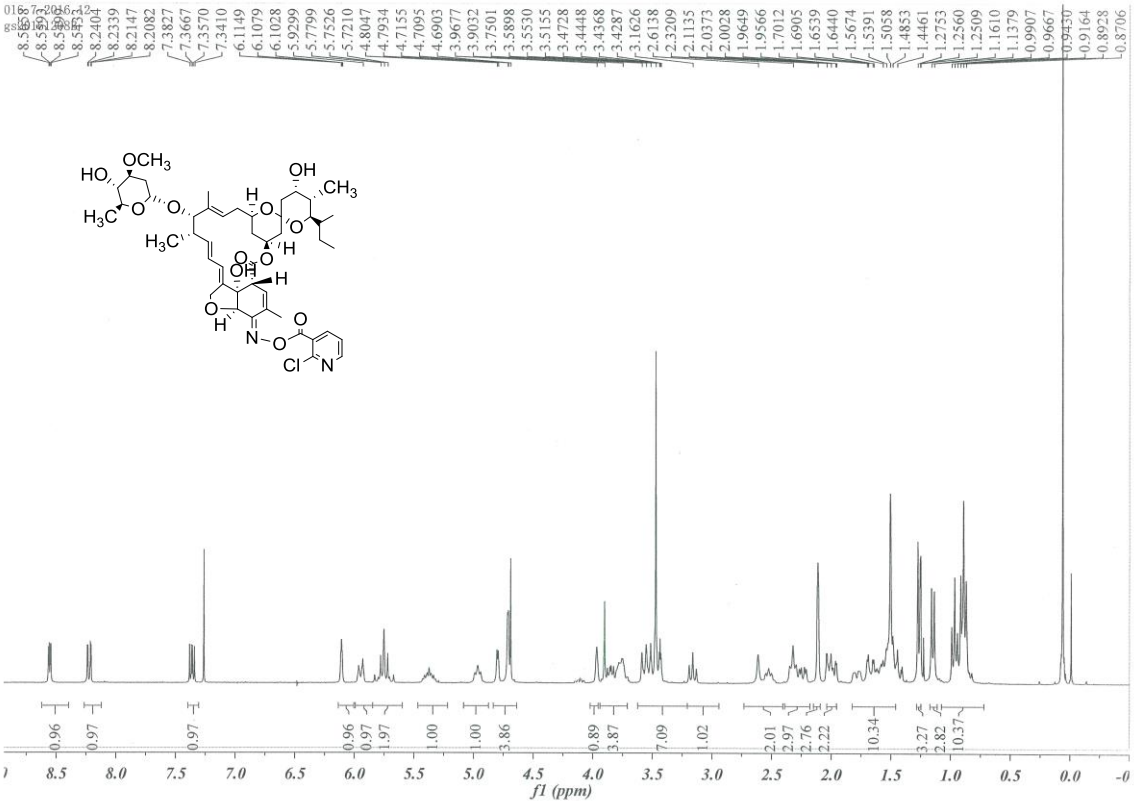
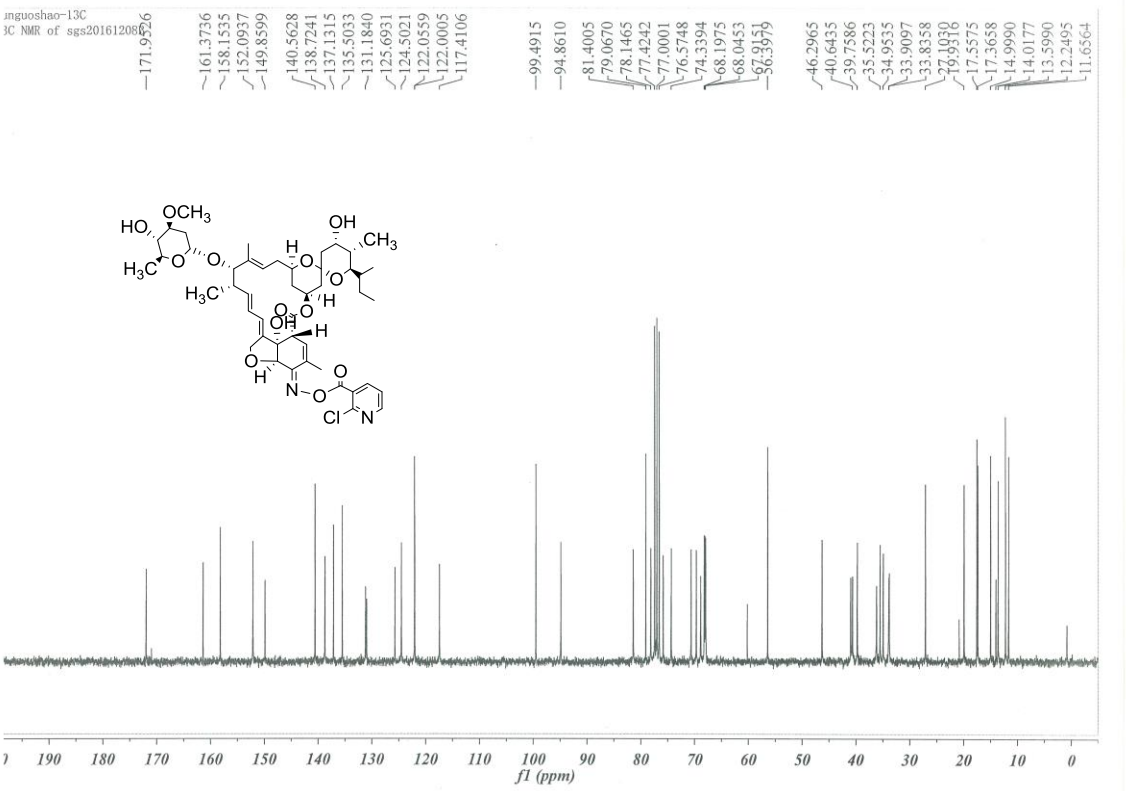
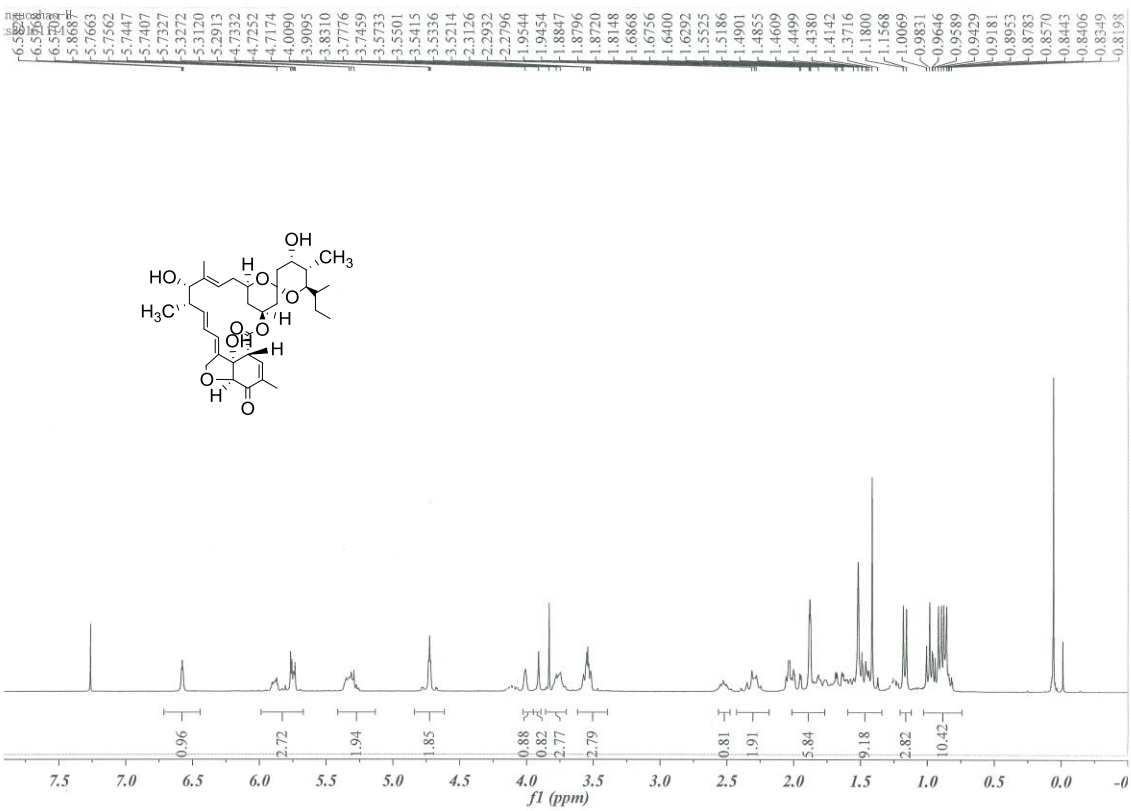
5-((2-chloro-3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a monosaccharide (11n)





1 5-oxoavermectin B2a aglycone (12)



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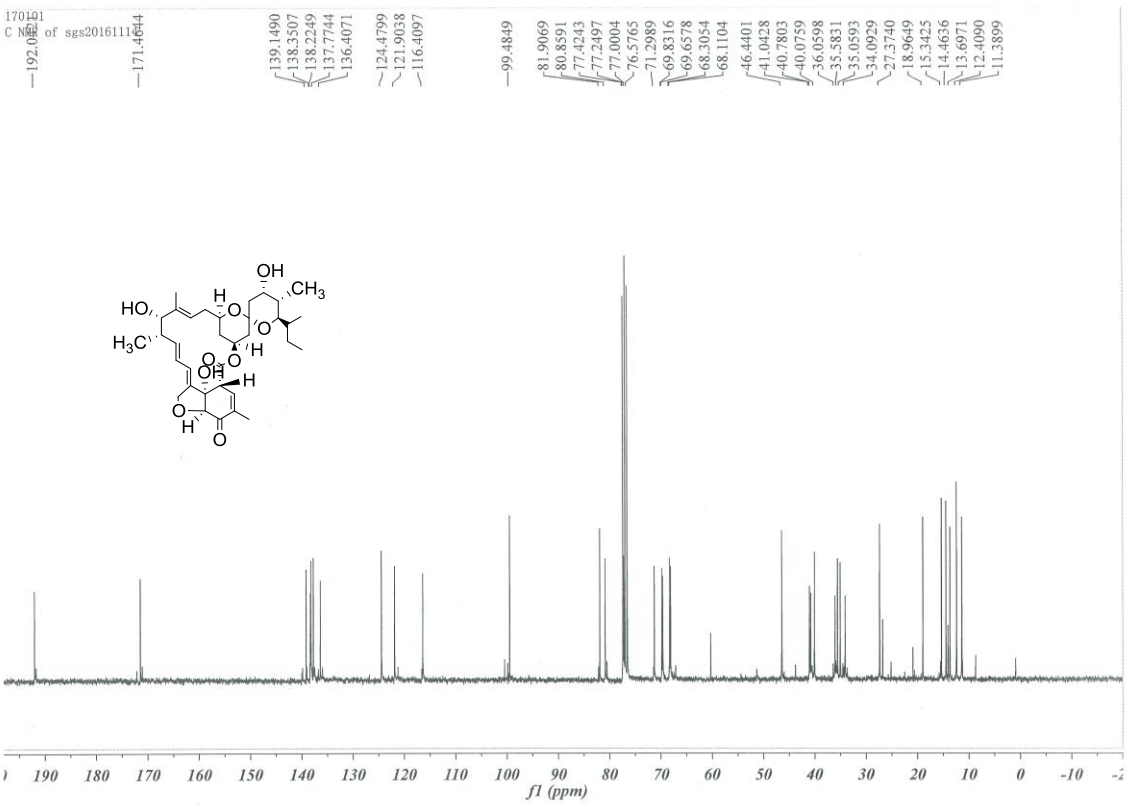

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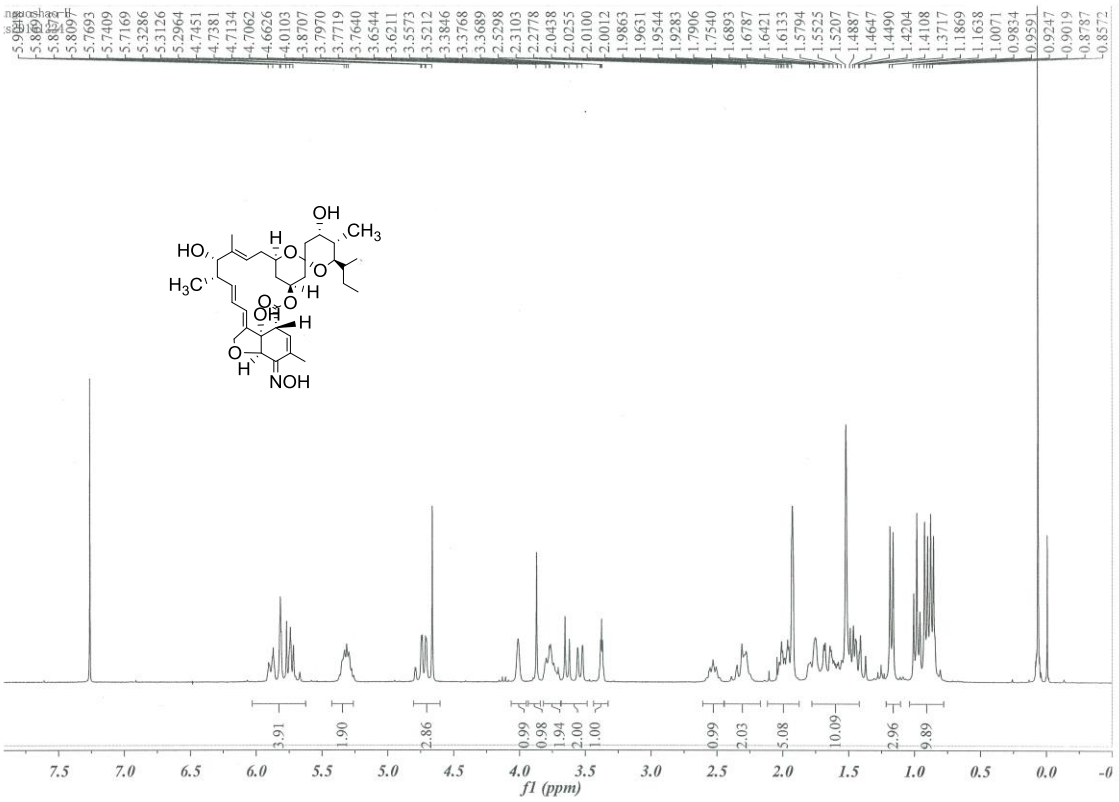
1 5-oximino-5-deoxyavermectin B2a aglycone (13)



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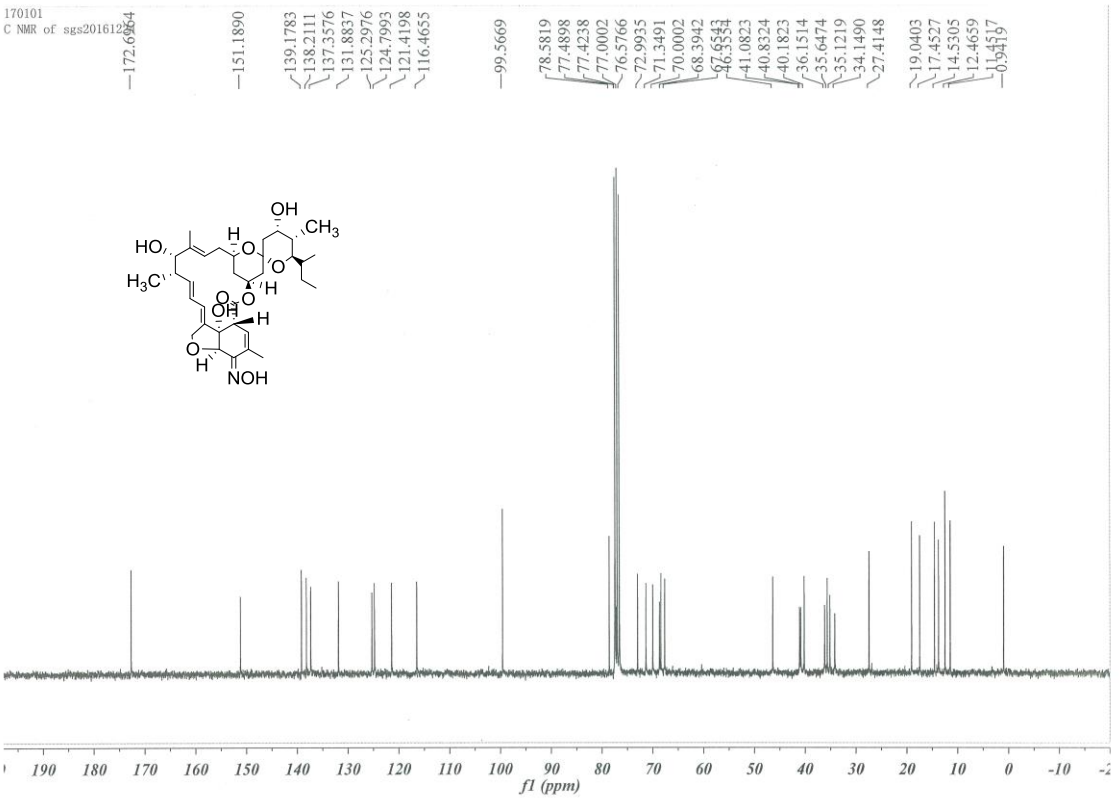

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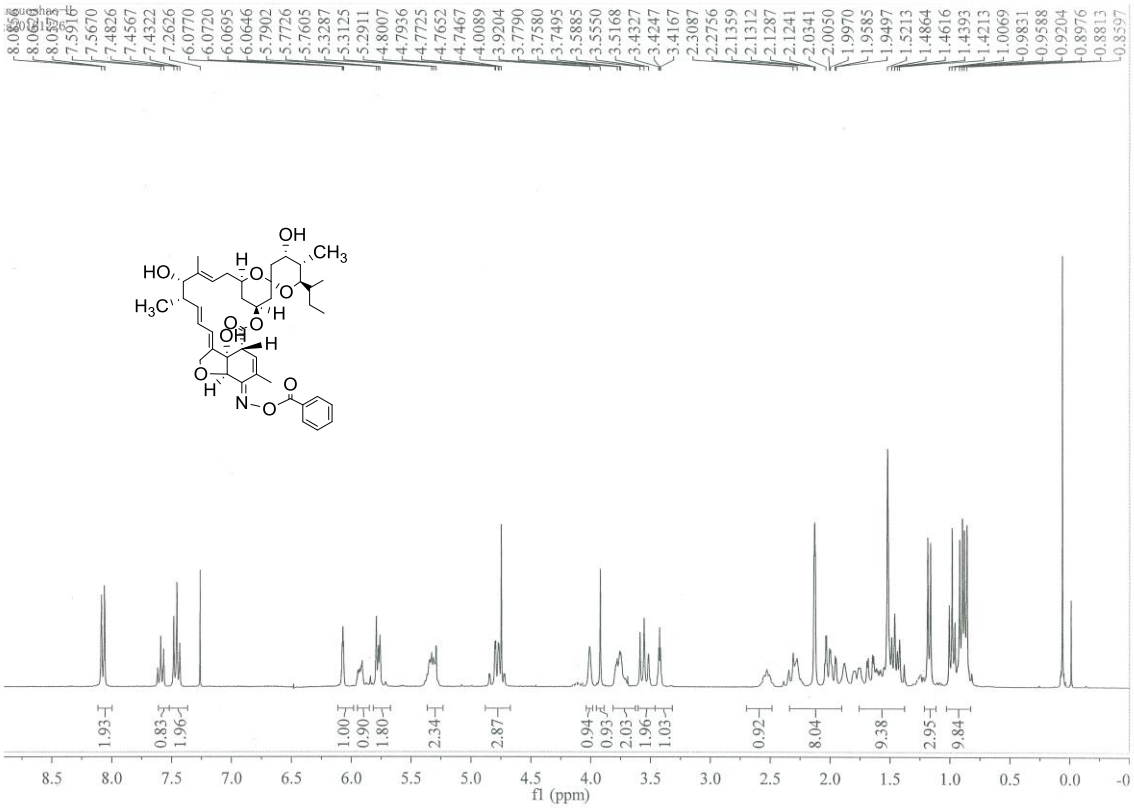
1 5-(benzoyloxyimino)-5-deoxyavermectin B2a aglycone (14a)



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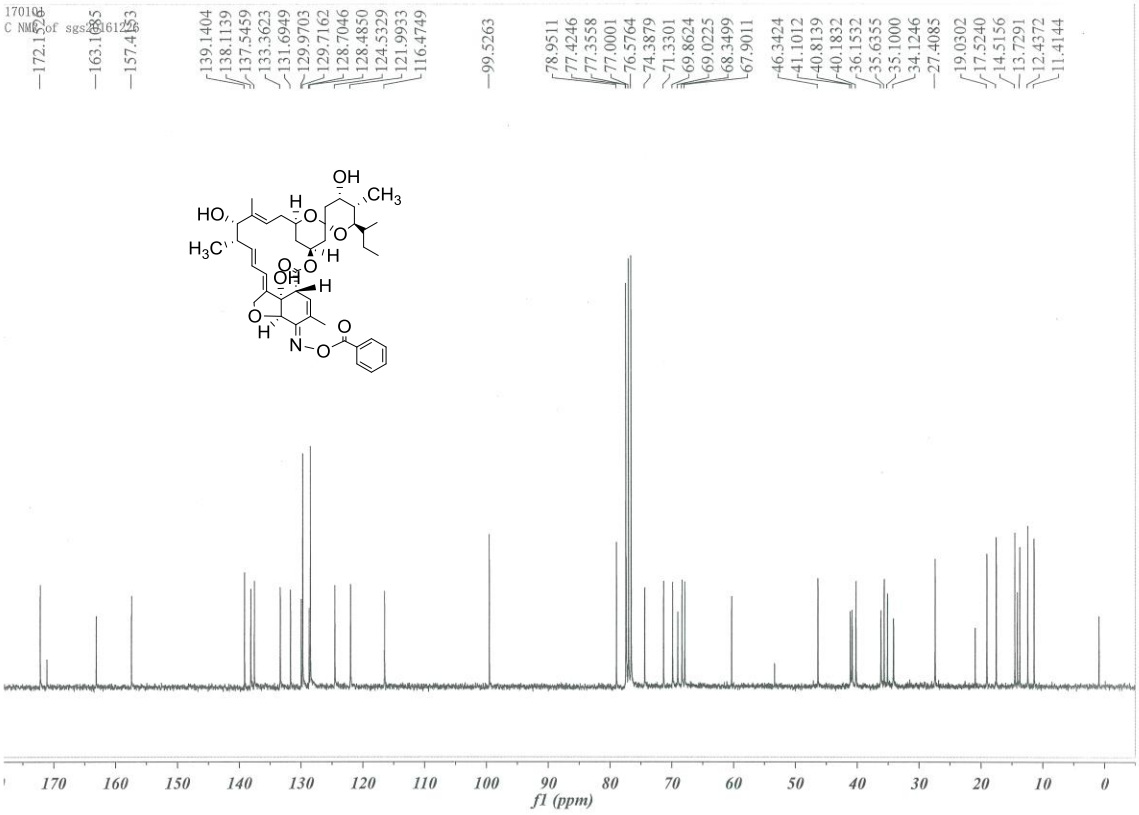

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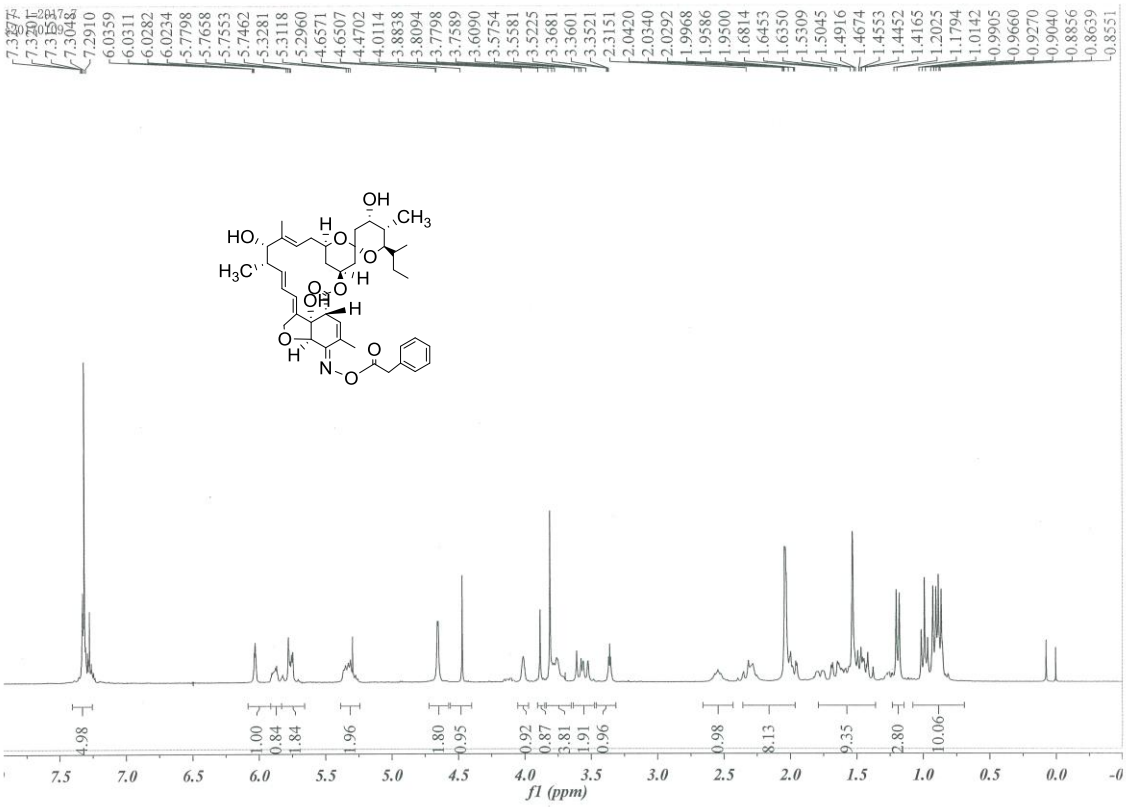
1 5-(phenylacetyloxyimino)-5-deoxyavermectin B2a aglycone (14b)



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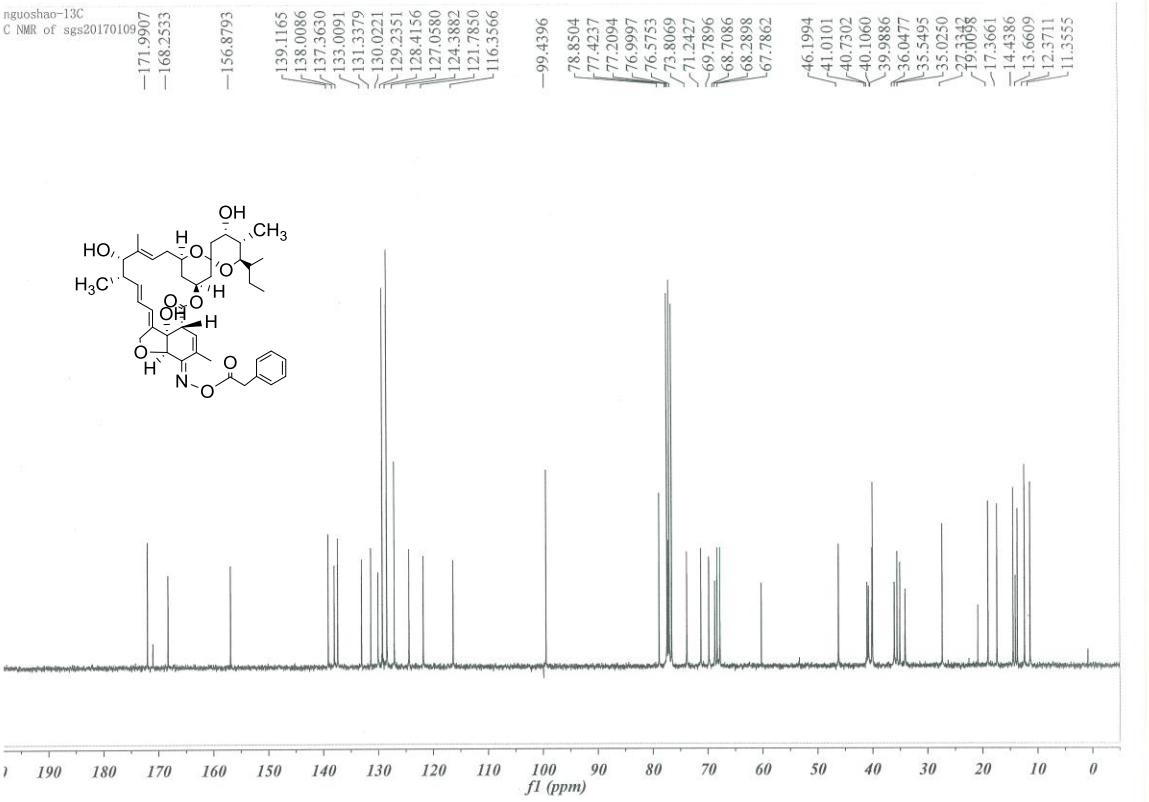

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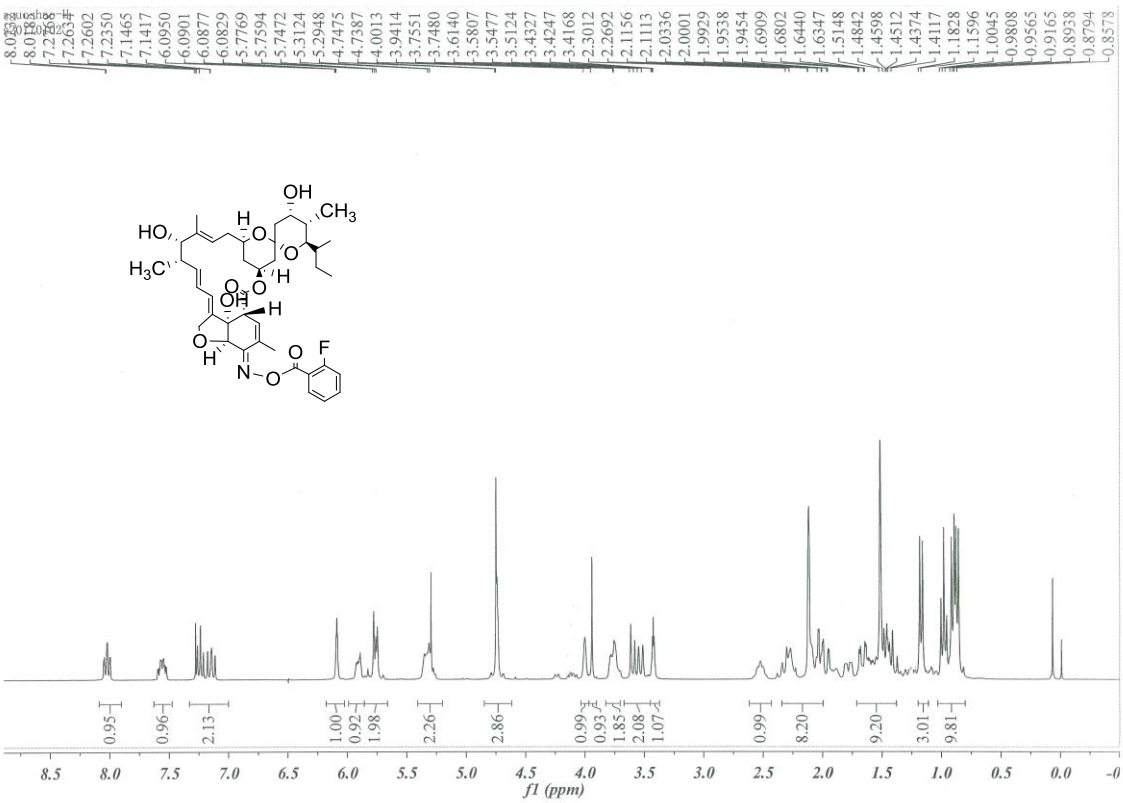
1 5-((2-fluorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (14c)



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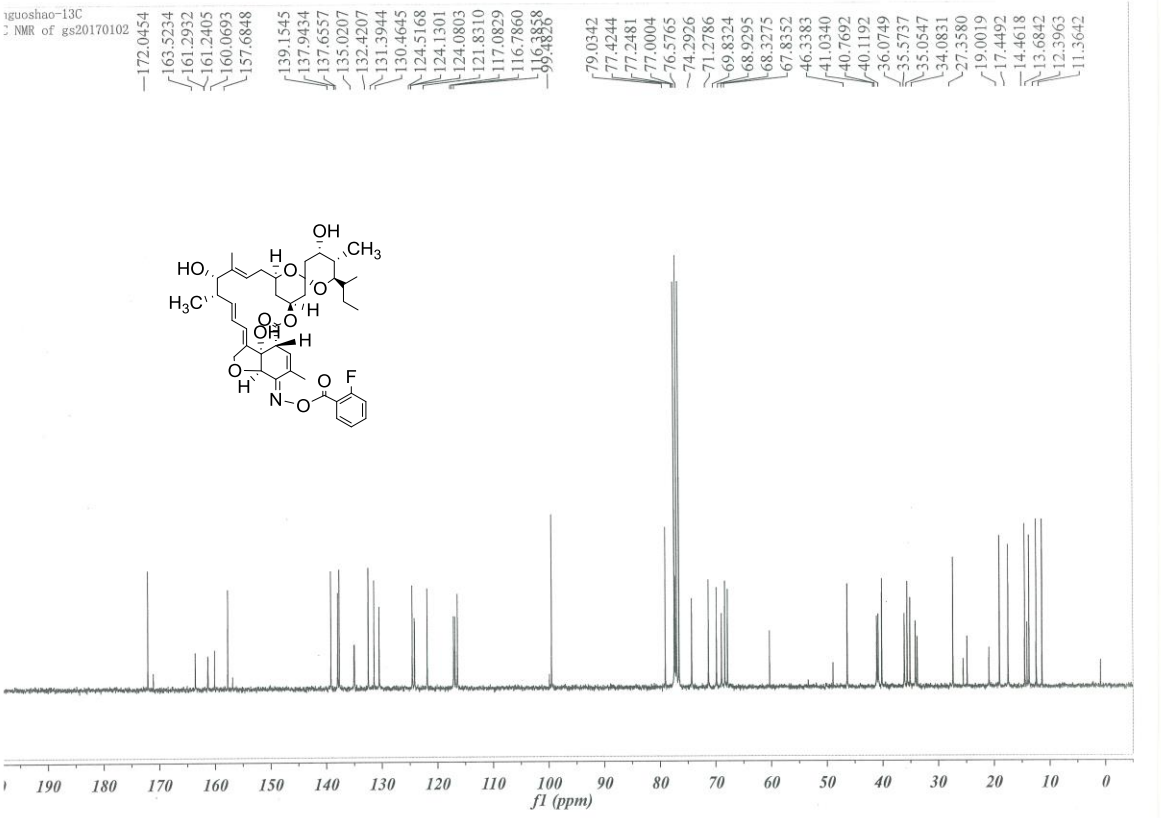

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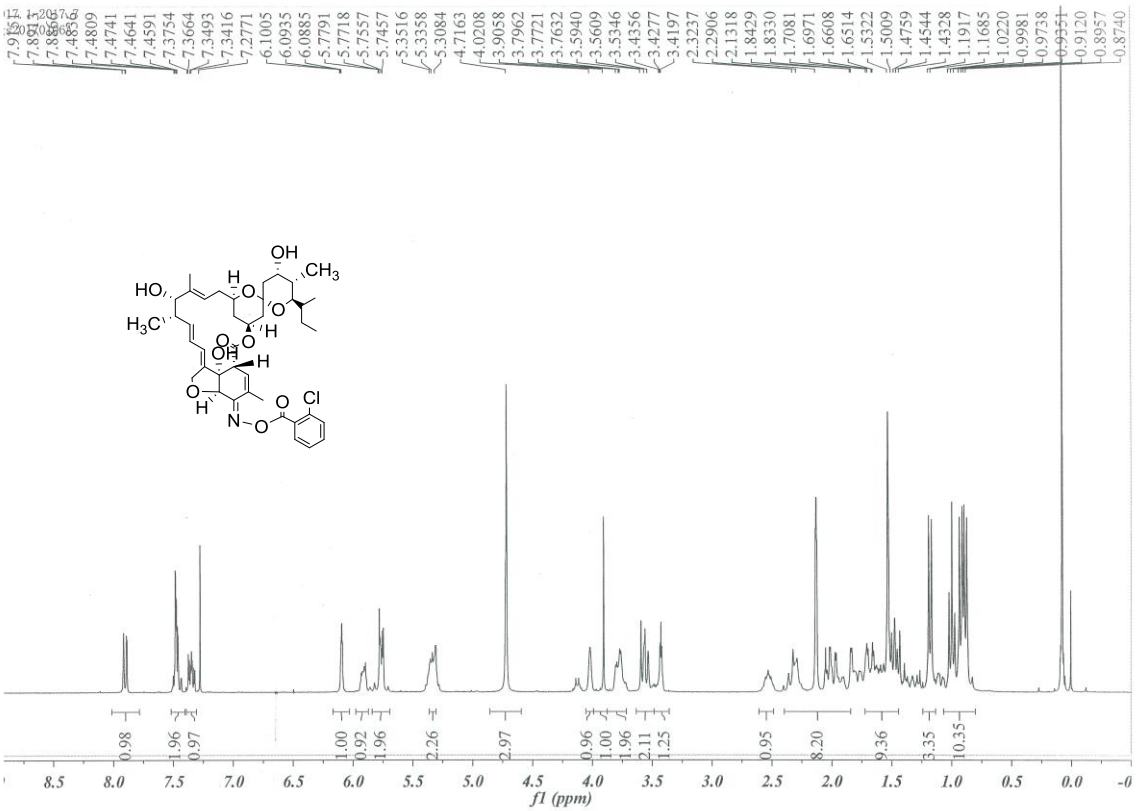
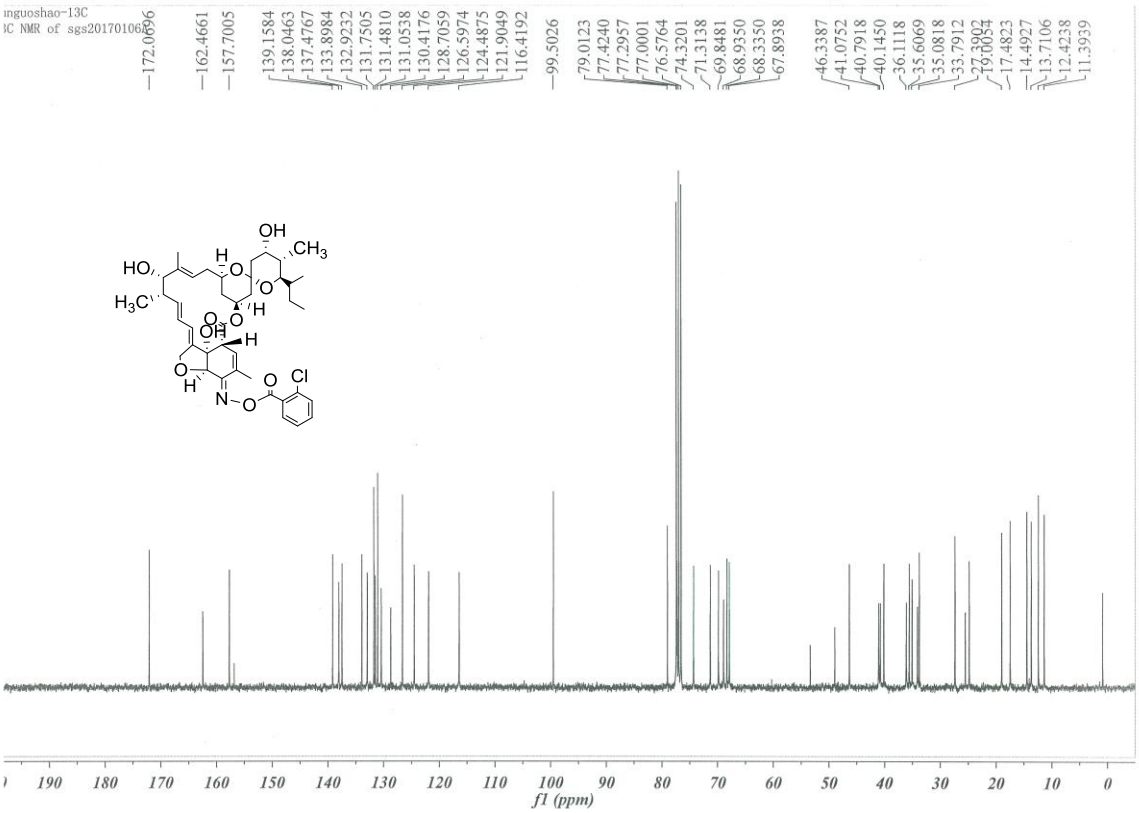
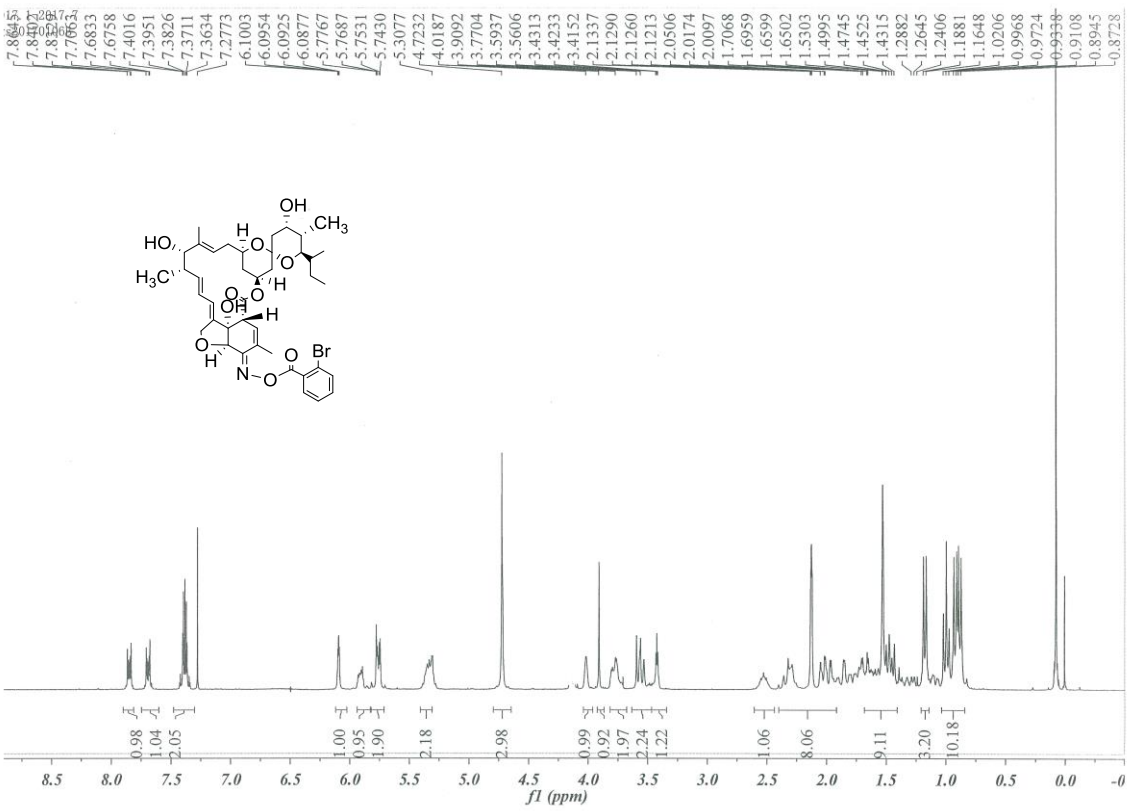
5-((2-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (14d)





1 5-((2-bromobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (14e)



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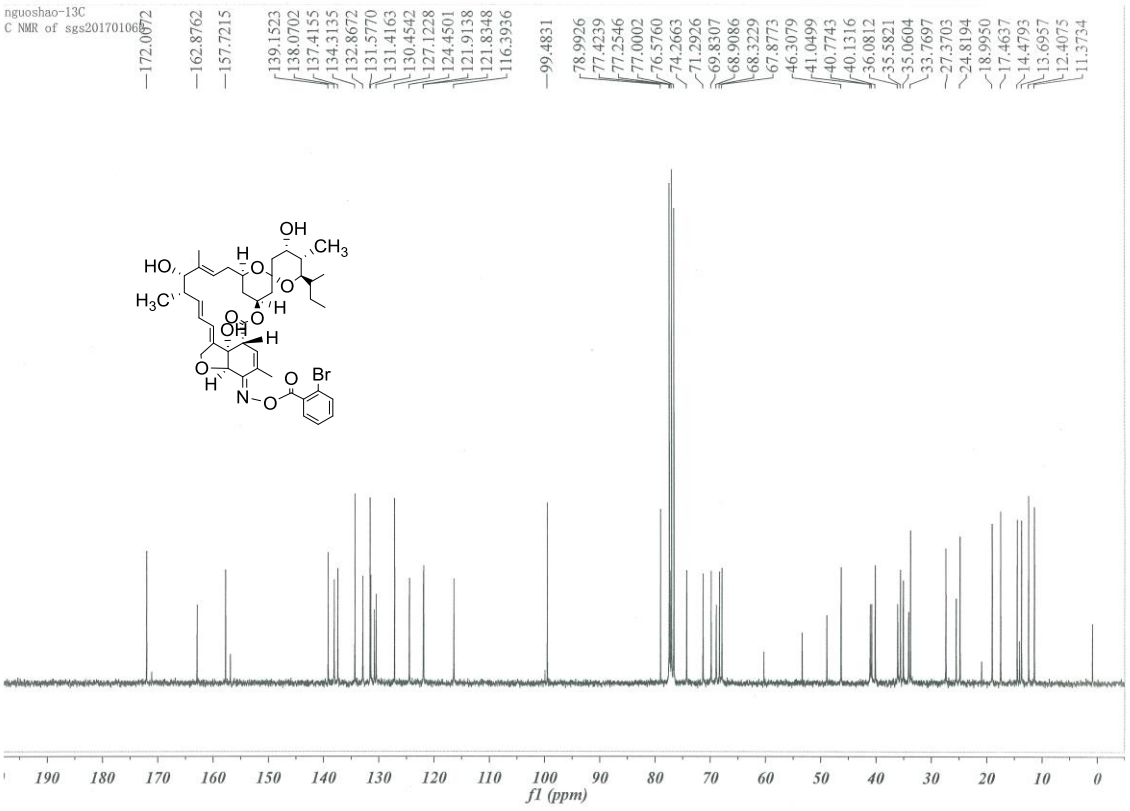

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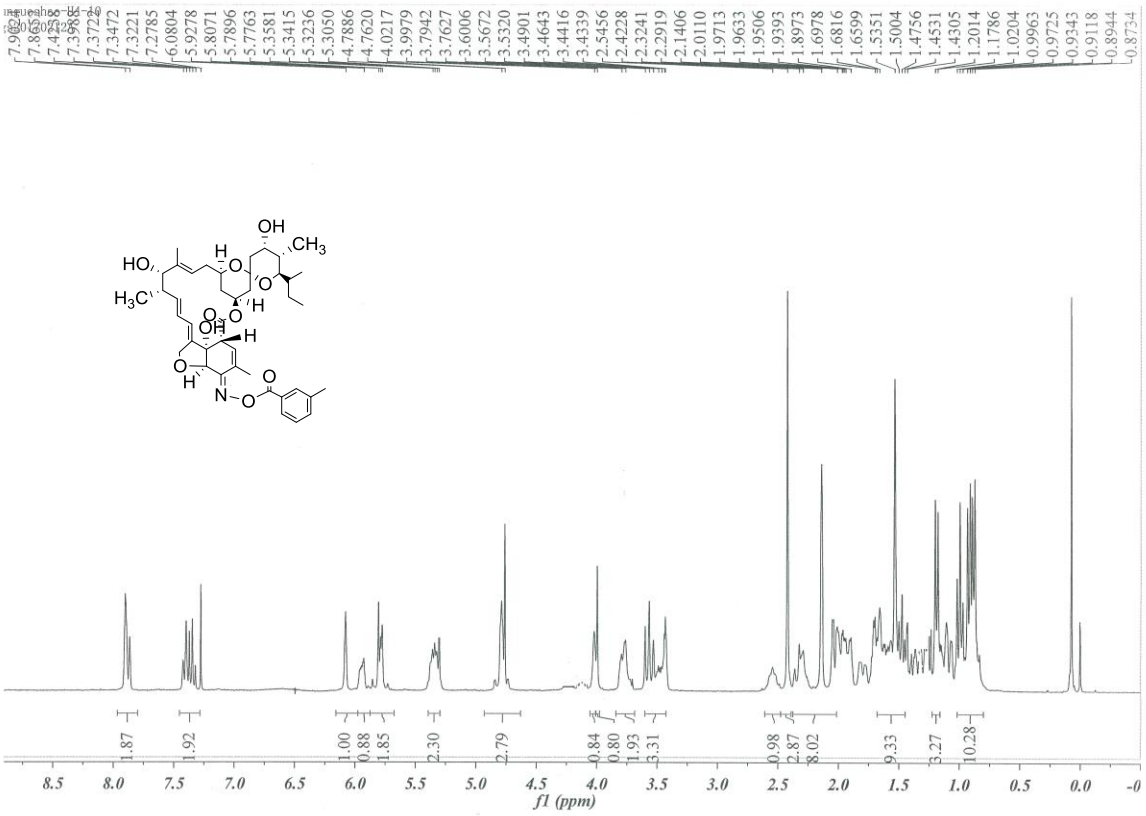
1 5-((3-methylbenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (14f)



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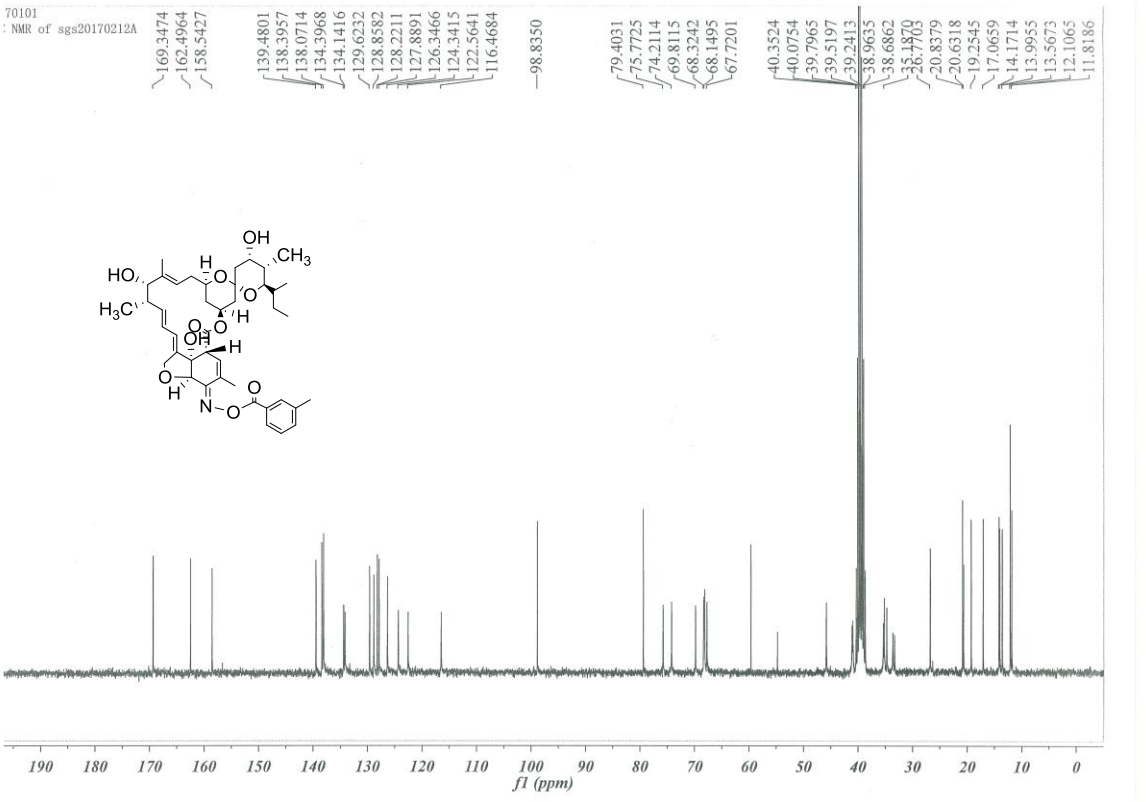

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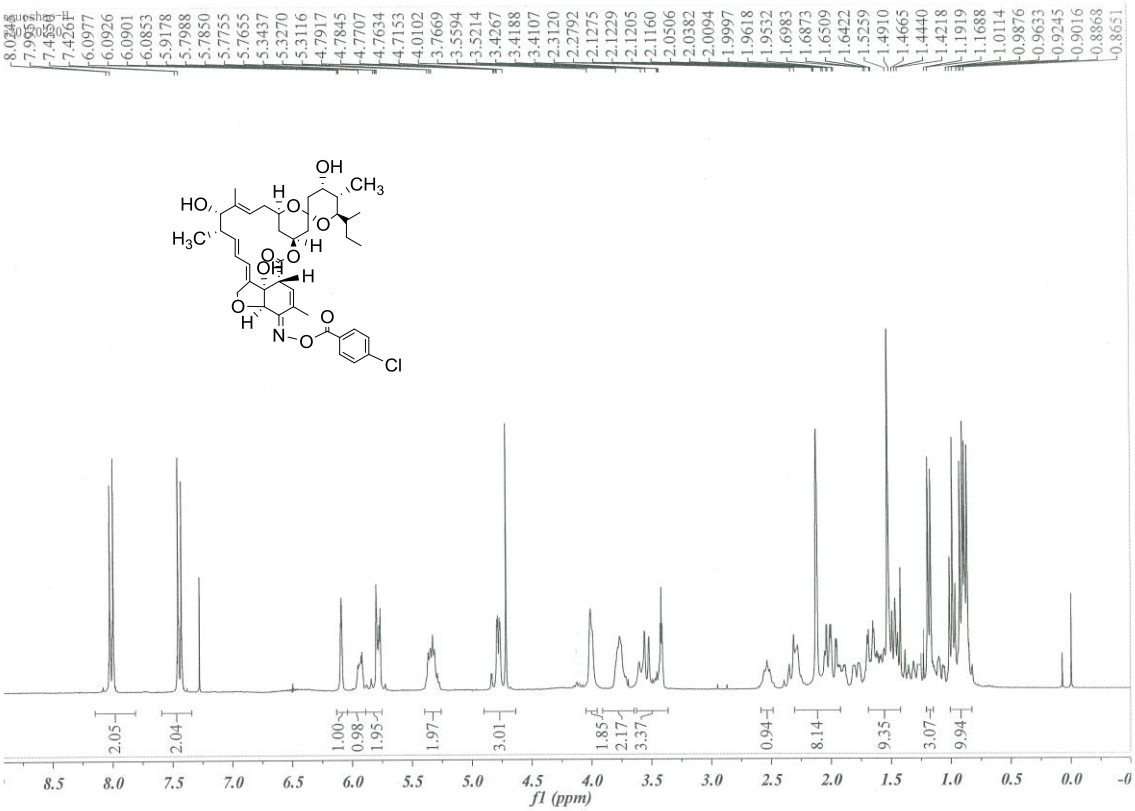
1 5-((4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (14g)



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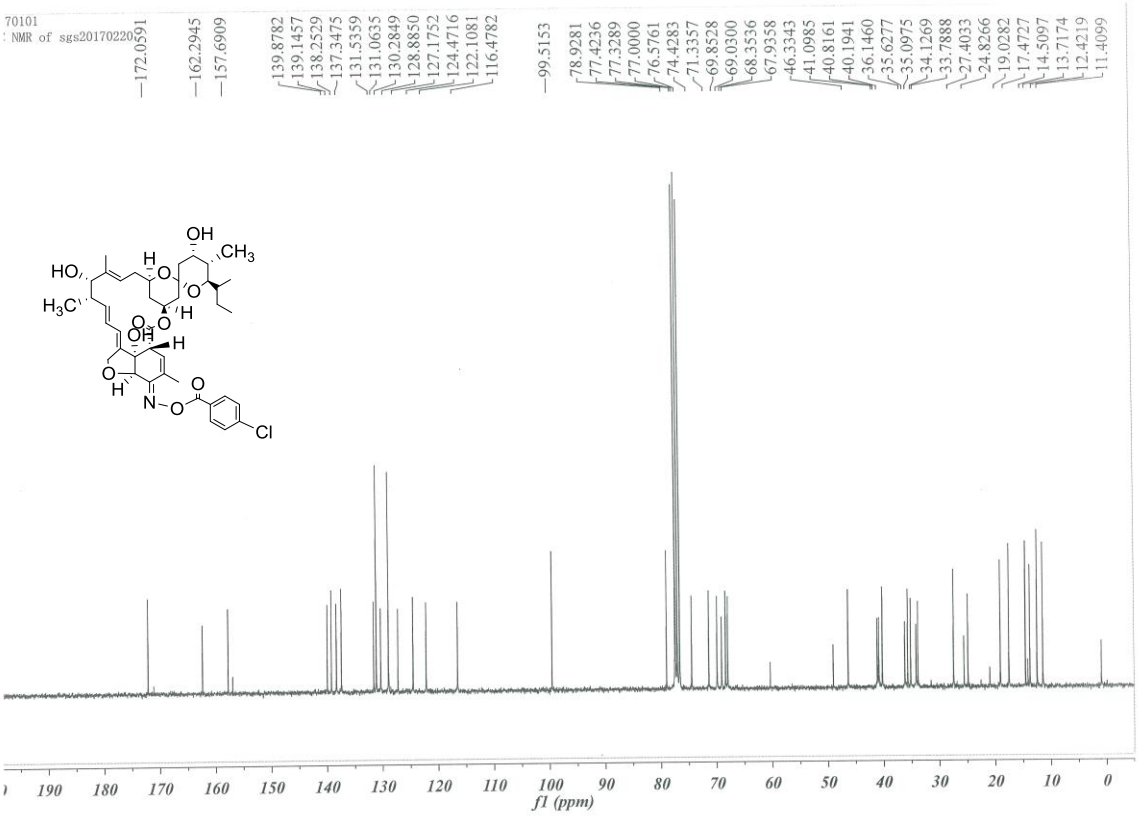

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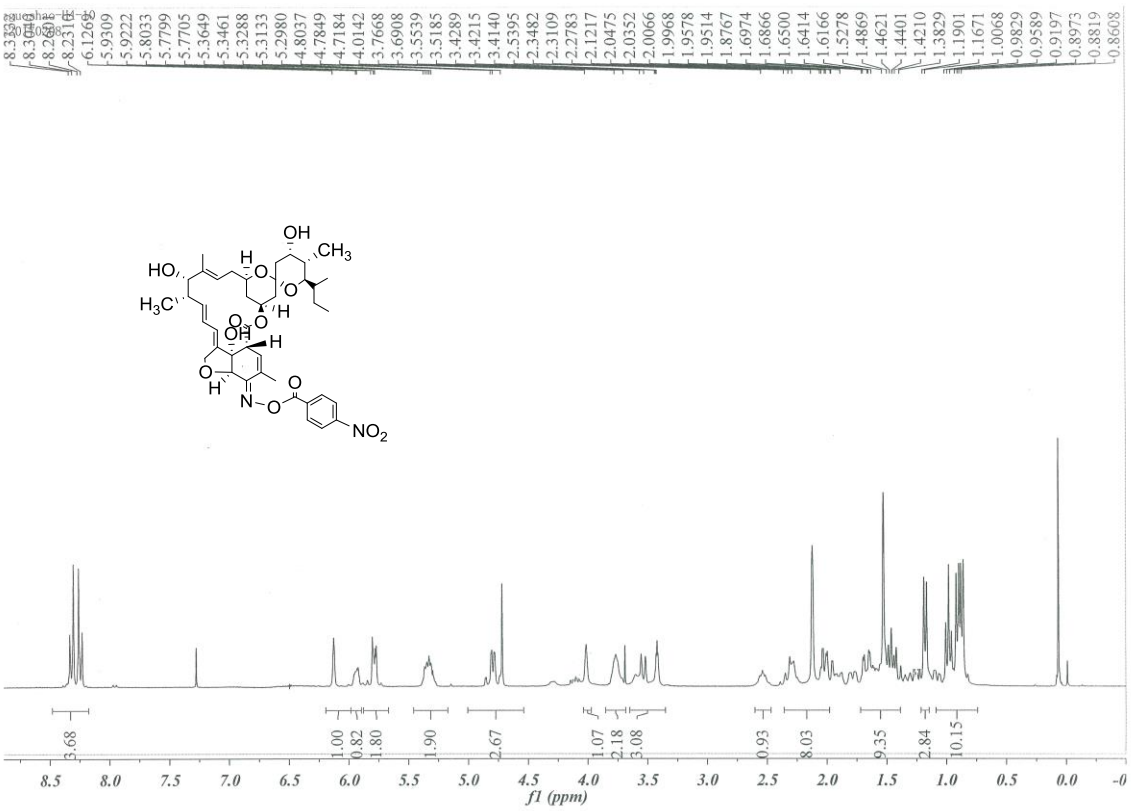
1 5-((4-nitrobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (14h)



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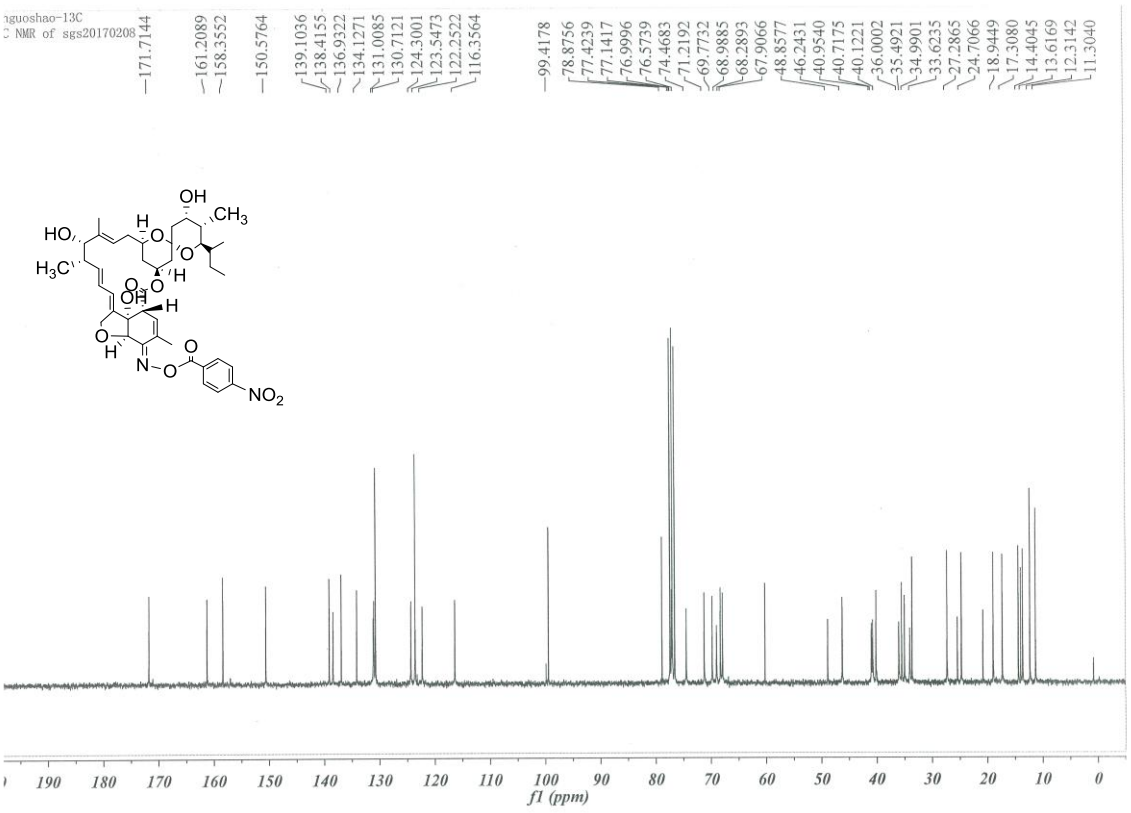

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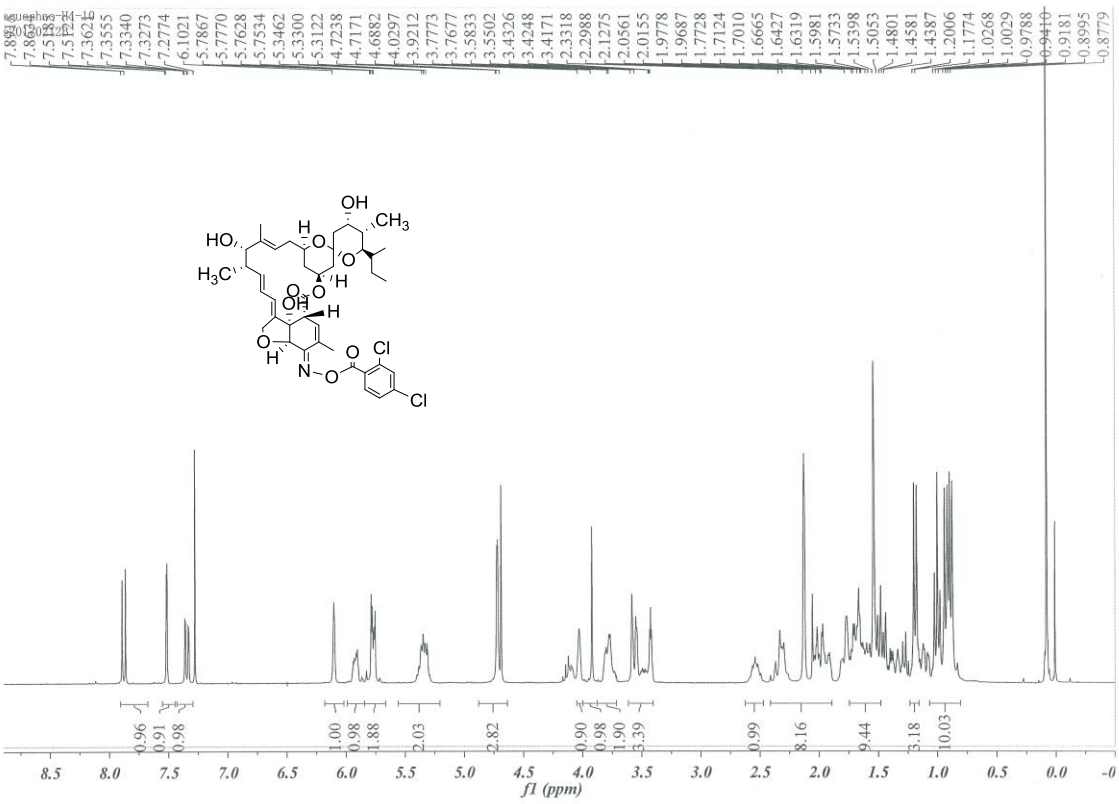
1 5-((2,4-dichlorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (14i)



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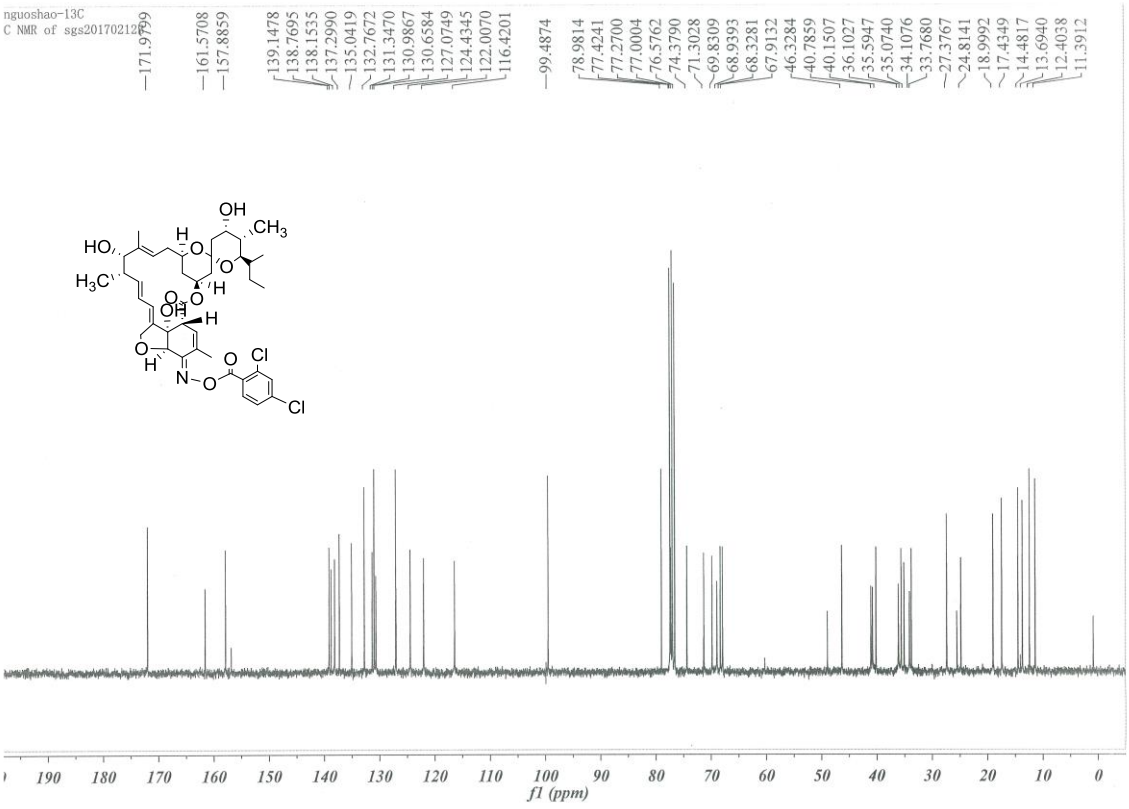

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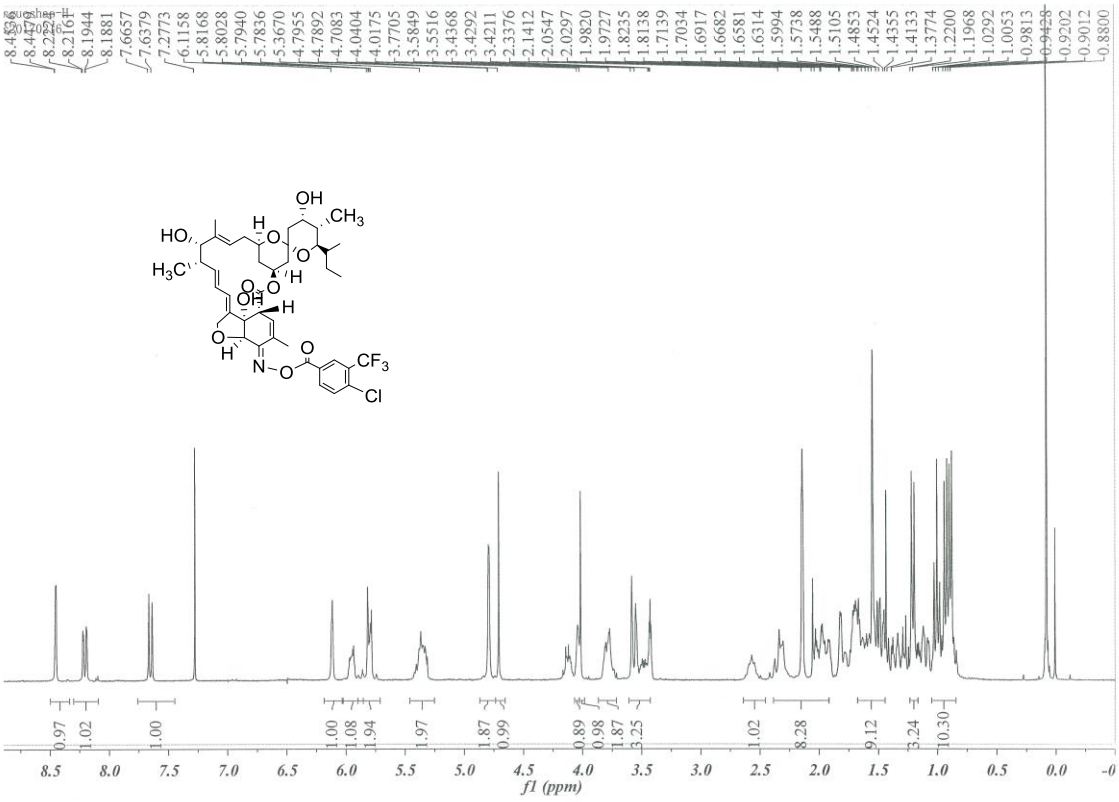
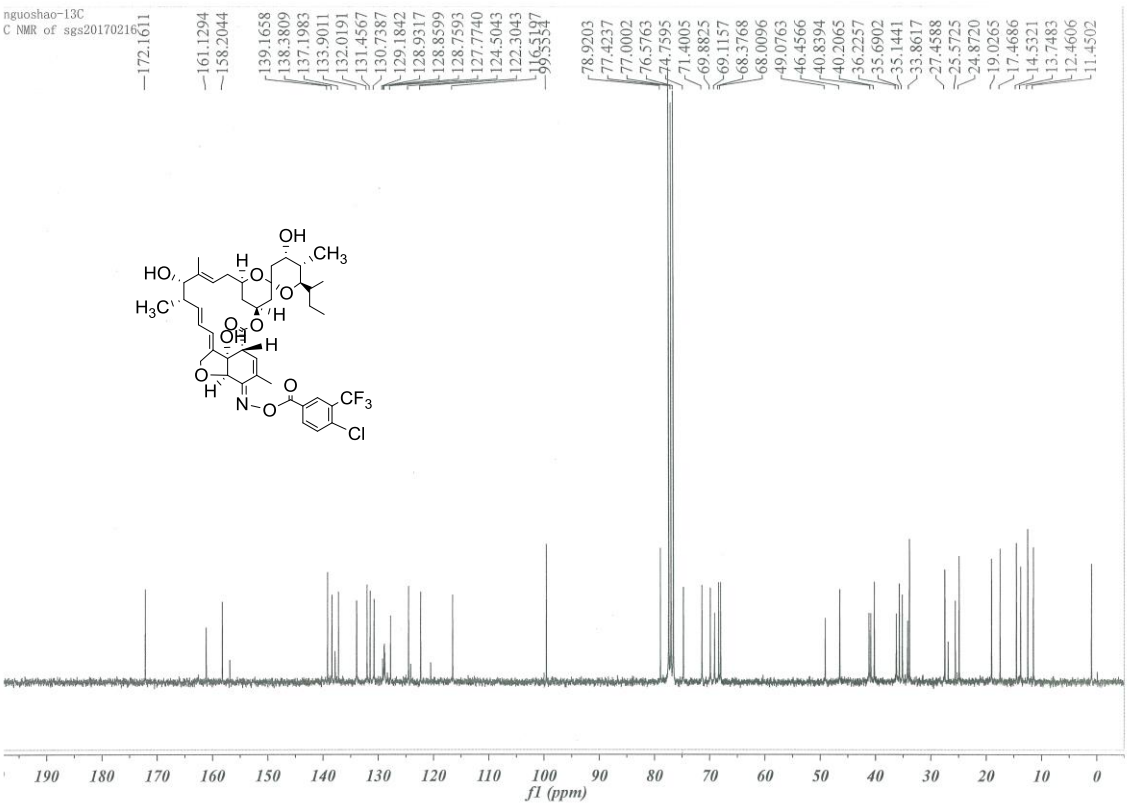
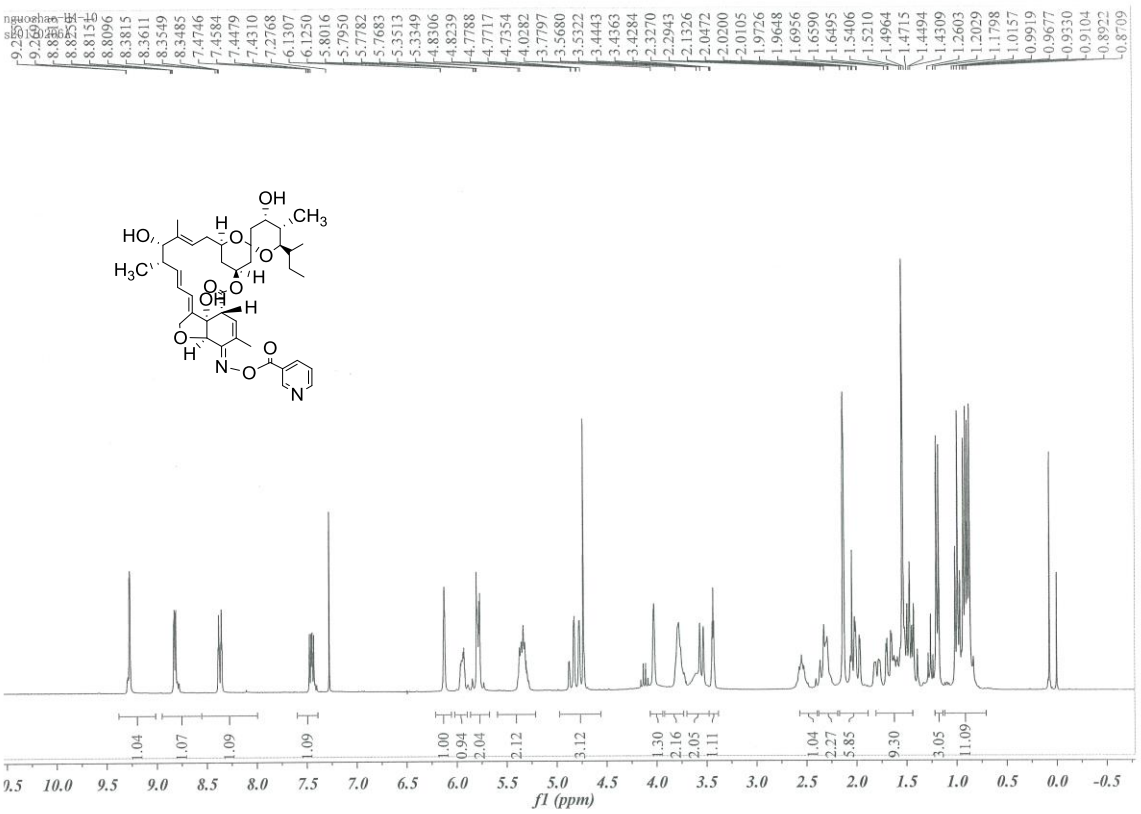
5-((3-trifluoromethyl-4-chlorobenzoyl)oxyimino)-5-deoxyavermectin B2a aglycone (14j)





1 5-((3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a aglycone (14k)



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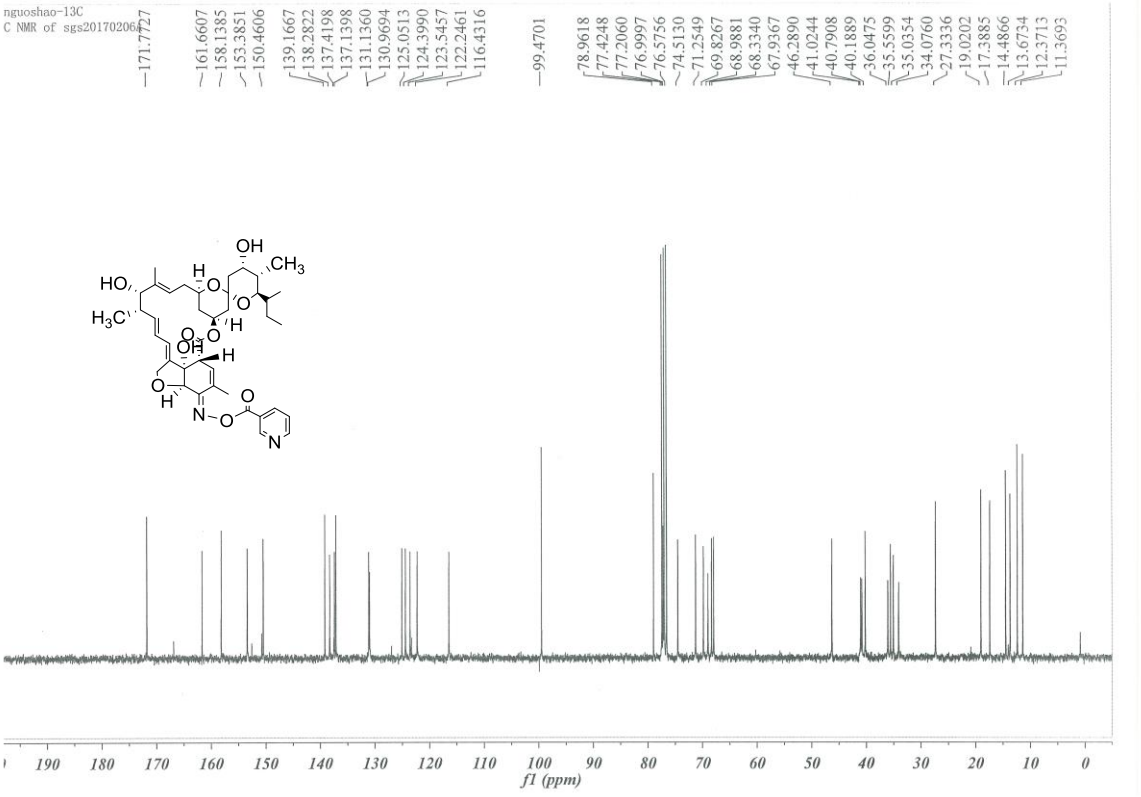

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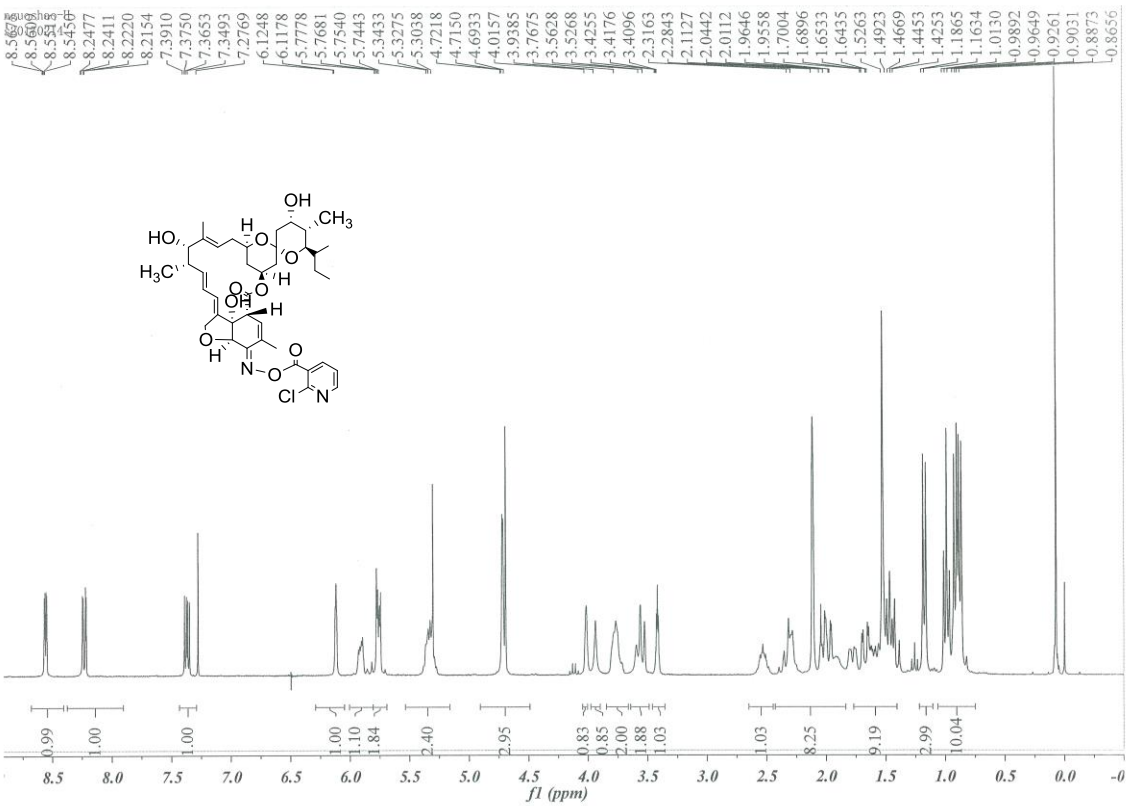
1 5-((2-chloro-3-pyridinylcarbonyl)oxyimino)-5-deoxyavermectin B2a aglycone (14l)



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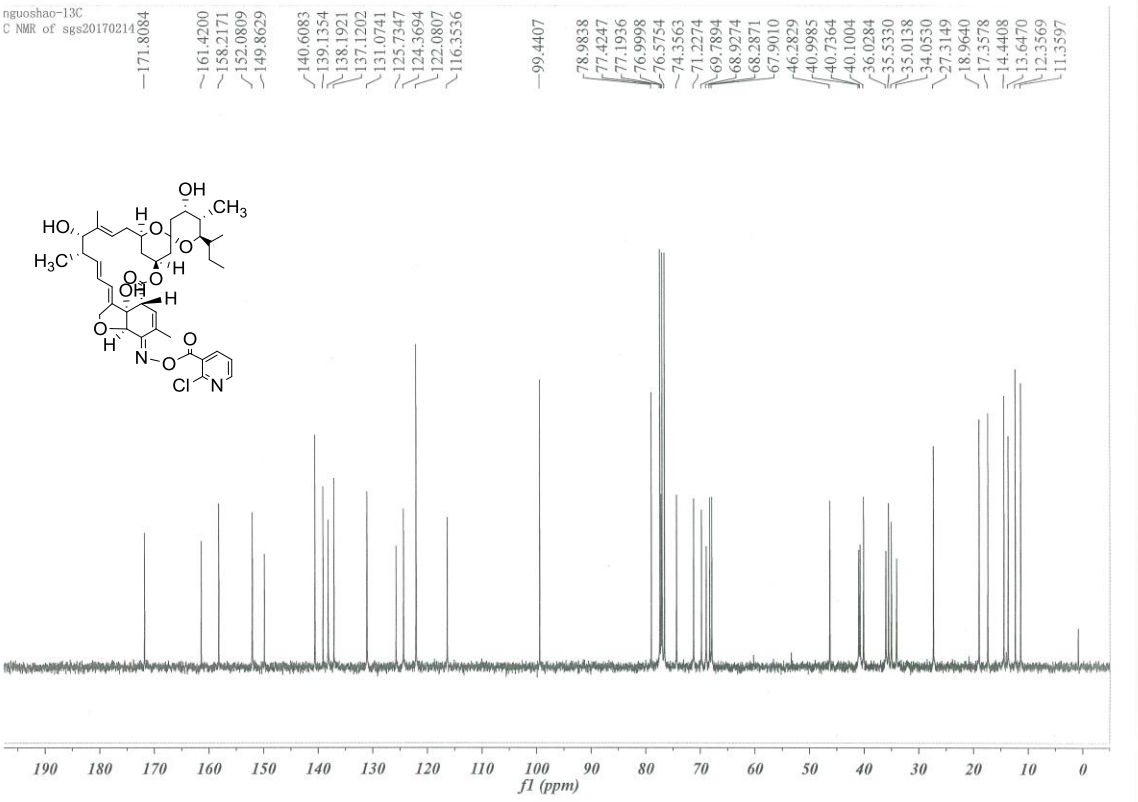

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