

Supporting information

Design, Synthesis and Biological Evaluation of New Generation Taxoids

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Characterization data for 9a, 9b and 9d-f:

7,10,13-Tris(triethylsilyl)-2-debenzoyl-2-(3-methylbenzoyl)-10-deacetyl baccatin III (9a).

White solid; 90%; mp 198-200 °C ^1H (300 MHz, CDCl_3) δ 0.68 (m, 18 H), 0.93 (m, 27 H), 1.11 (s, 3 H), 1.18 (s, 3 H), 1.59 (bs, 1 H), 1.64 (s, 3 H), 1.88 (m, 1 H), 1.98 (s, 3 H), 2.14 (m, 2 H), 2.27 (s, 3 H), 2.40 (s, 3 H) 2.50 (m, 1 H), 3.83 (d, $J = 7.2$ Hz, 1H), 4.12 (d, $J = 8.4$ Hz, 1 H), 4.29 (d, $J = 8.4$ Hz, 1 H), 4.40 (m, 1 H), 4.92 (m, 2 H), 5.19 (s, 1 H), 5.57 (d, $J = 6.9$ Hz, 1 H), 7.35 (m, 2 H), 7.88 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 5.34, 5.73, 6.45, 7.35, 7.38, 7.43, 10.9, 15.0, 21.1, 21.8, 22.8, 26.8, 37.8, 40.4, 43.5, 47.4, 58.7, 68.8, 73.2, 75.8, 77.9, 80.1, 81.3, 84.5, 127.7, 128.9, 130.1, 131.2, 134.6, 136.3, 138.7, 139.8, 167.7, 170.4, 206.1.

7,10,13-Tri(triethylsilyl)-2-debenzoyl-2-(3-methoxybenzoyl)-10-deacetyl baccatin III (9b).

White solid; 71%; mp 201-202 °C; $[\alpha]_{\text{D}}^{20}$ -40 (c 0.32, CHCl_3); ^1H NMR (CDCl_3) δ 0.60 (m, 18 H), 0.98 (m, 27 H), 1.11 (s, 3 H), 1.18 (s, 3 H), 1.57 (bs, 1 H), 1.62 (s, 3 H), 1.85 (m, 1 H), 1.96 (s, 3 H), 2.14 (m, 2 H), 2.26 (s, 3 H), 2.50 (m, 1 H), 3.83 (m, 4 H), 4.13 (d, $J = 7.9$ Hz, 1 H), 4.30 (d, $J = 8.1$ Hz, 1 H), 4.39 (dd, $J = 10.4, 6.9$ Hz, 1 H), 4.92 (m, 2 H), 5.17 (s, 1 H), 5.59 (d, $J = 6.9$ Hz, 1 H), 7.10 (m, 1 H), 7.35 (t, $J = 7.9$ Hz, 1 H), 7.61 (s, 1 H), 7.66 (d, $J = 7.7$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ 4.9, 5.2, 6.0, 6.9, 10.4, 14.6, 20.6, 22.4, 26.3, 37.3, 39.9, 43.0, 46.9, 55.3, 58.3, 68.3, 72.6, 75.5, 75.8, 76.6, 79.5, 80.9, 84.0, 114.3, 120.2, 122.5, 129.5, 130.9, 135.8, 139.4, 159.6, 167.0, 169.9, 205.7. HRMS: m/e calcd for $\text{C}_{48}\text{H}_{80}\text{O}_{11}\text{Si}_3\cdot\text{H}^+$: 917.5087. Found: 917.5084 ($\Delta = 0.3$ ppm).

7,10,13-Tri(triethylsilyl)-2-debenzoyl-2-(3-chlorobenzoyl)-10-deacetyl baccatin III (9d).

White solid; 81%; mp 175-177 °C; $[\alpha]_{\text{D}}^{20}$ -26 (c 0.27, CHCl_3); ^1H NMR (CDCl_3) δ 0.60 (m, 18 H), 0.98 (m, 27 H), 1.09 (s, 3 H), 1.16 (s, 3 H), 1.50 (bs, 1 H), 1.64 (s, 3 H), 1.85 (m, 1 H), 1.97 (s, 3 H), 2.14 (m, 2 H), 2.26 (s, 3 H), 2.57 (m, 1 H), 3.83 (d, $J = 7.0$ Hz, 1 H), 4.12 (d, $J = 8.3$ Hz, 1 H), 4.24 (d, $J = 8.2$ Hz, 1 H), 4.39 (dd, $J = 10.3, 6.5$ Hz, 1 H), 4.92 (m, 2 H), 5.17 (s, 1 H), 5.55 (d, $J = 7.1$ Hz, 1 H), 7.39 (m, 1 H), 7.43 (m, 1 H), 7.94 (d, $J = 7.8$ Hz, 1 H), 8.09 (m, 1 H); ^{13}C NMR (CDCl_3) δ 4.8, 5.2, 5.9, 6.9, 10.4, 14.6, 20.6, 22.3, 26.3, 37.2, 39.9, 42.9, 46.9, 58.2, 68.3, 72.7, 75.7, 76.0, 79.7, 80.7, 84.0, 87.6, 128.2, 128.6, 129.9, 130.2, 131.5, 133.4, 134.7, 135.7, 139.5, 165.7, 169.9, 205.5. HRMS: m/e calcd for $\text{C}_{47}\text{H}_{77}\text{O}_{10}\text{ClSi}_3\cdot\text{H}^+$: 921.4591. Found: 921.4588 ($\Delta = 0.4$ ppm).

7,10,13-Tris(triethylsilyl)-2-debenzoyl-2-(3-azidobenzoyl)-10-deacetyl baccatin III (9e).

White solid; 85 %: ^1H NMR (CDCl_3) δ 0.62 (m, 18 H), 1.01 (m, 27 H), 1.04 (s, 3 H), 1.20 (s, 3 H), 1.57 (bs, 1 H), 1.66 (s, 3 H), 1.88 (ddd, $J = 2.1, 10.5$ Hz, 1 H), 2.00 (s, 3 H), 2.17 (m, 2 H), 2.31 (s, 3 H), 2.55 (ddd, $J = 3.0, 6.6$ Hz, 1 H), 3.88 (d, $J = 6.9$ Hz, 1 H), 4.15 (d, $J = 8.1$ Hz, 1 H), 4.29 (d, $J = 8.1$ Hz, 1 H), 4.43 (dd, $J = 3.9, 10.8$ Hz, 1 H), 4.95 (m, 2 H), 5.21 (s, 1 H), 5.63 (d, $J = 6.9$ Hz, 1 H), 7.22 (d, $J = 8.1$ Hz, 1 H), 7.47 (t, $J = 8.1$ Hz, 1 H), 7.79 (s, 1 H), 7.86 (d, $J = 7.5$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 5.1, 5.5, 6.2, 7.1, 7.2, 10.7, 14.9, 20.8, 22.7, 26.6, 37.5, 40.0, 43.2, 47.1, 58.5, 68.5, 72.9, 76.0, 76.2, 76.8, 79.8, 81.0, 84.3, 120.2, 124.5, 126.9, 130.3, 131.6, 135.9, 139.8, 140.9, 166.4, 170.3, 205.9.

7,10,13-Tri(triethylsilyl)-2-debenzoyl-2-(3-ethenylbenzoyl)-10-deacetylbaecatin III (9f).

White solid; 54%; ¹H NMR (250 MHz, CDCl₃) δ 0.63 (m, 18 H), 0.97 (m, 27 H), 1.06 (s, 3 H), 1.10 (s, 3 H), 1.49 (bs, 1 H), 1.58 (s, 3 H), 1.86 (m, 1 H), 1.93 (s, 3 H), 2.00 (s, 1 H), 2.04 (s, 1 H), 2.16 (s, 3 H), 2.46 (m, 1 H), 3.84 (d, *J* = 7.0 Hz, 1 H), 4.14 (d, *J* = 7.8 Hz, 1 H), 4.28 (dd, *J* = 6.6, 10.4 Hz, 1 H), 4.40 (d, *J* = 7.9 Hz, 1 H), 4.91-4.95 (m, 2 H), 5.20 (s, 1 H), 5.30 (d, *J* = 16.0 Hz, 1 H), 5.60 (m, 1 H), 5.80 (d, *J* = 17.5 Hz, 1 H), 6.72 (m, 1 H), 7.40 (m, 1 H), 7.95 (d, 1 H), 8.15 (d, 1 H); ¹³C NMR (62.9 MHz, CDCl₃) δ 0.3, 0.7, 1.4, 2.3, 2.4, 5.9, 10.0, 16.1, 17.9, 21.8, 32.8, 38.5, 42.4, 53.7, 63.8, 68.1, 71.0, 72.1, 72.5, 72.9, 75.0, 76.3, 79.5, 110.6, 123.1, 124.2, 125.4, 126.7, 131.3, 131.5, 133.5, 134.9, 163.5, 165.3, 201.1.

Characterization data for 11a, 11b and 11d-I:

2-Debenzoyl-2-(3-methylbenzoyl)-7-triethylsilylbaecatin III (11a). White solid; 94%; mp 100-104 °C; ¹H (300 MHz, CDCl₃) δ 0.55 (m, 6 H), 0.88 (m, 9 H), 1.08 (s, 6 H), 1.67 (m, 1 H), 1.76(s, 3 H), 1.90 (m, 1 H), 2.12 (s, 3 H), 2.15 (s, 3 H), 2.21 (m, 2 H), 2.24 (s, 3 H), 2.41 (s, 3 H) 2.54 (m, 1 H), 3.90 (d, *J* = 6.6 Hz, 1H), 4.12 (d, *J* = 8.4 Hz, 1 H), 4.26 (d, *J* = 8.4 Hz, 1 H), 4.40 (m, 1 H), 4.81 (t, *J* = 6.6 Hz, 1 H), 4.95 (d, *J* = 8.4 Hz, 1 H), 5.54 (d, *J* = 7.2 Hz, 1 H), 6.45 (s, 1 H), 7.35 (m, 2 H), 7.88 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 5.18, 5.29, 6.70, 9.88, 15.1, 19.5, 20.1, 20.9, 21.3, 22.5, 26.8, 37.2, 38.6, 42.6, 47.0, 57.8, 67.8, 72.9, 74.6, 78.7, 80.7, 84.2, 127.2, 128.4, 129.3, 130.7, 134.3, 134.5, 138.3, 143.9, 167.3, 170.7, 205.1.

2-Debenzoyl-2-(3-methoxybenzoyl)-7-triethylsilylbaecatin III (11b). White solid; 77%, mp 100-104 °C; ¹H (300 MHz, CDCl₃) δ 0.55 (m, 6 H), 0.88 (m, 9 H), 1.08 (s, 6 H), 1.67 (m, 1 H), 1.76(s, 3 H), 1.90 (m, 1 H), 2.12 (s, 3 H), 2.15 (s, 3 H), 2.21 (m, 2 H), 2.24 (s, 3 H), 2.41 (s, 3 H) 2.54 (m, 1 H), 3.90 (d, *J* = 6.6 Hz, 1H), 4.12 (d, *J* = 8.4 Hz, 1 H), 4.26 (d, *J* = 8.4 Hz, 1 H), 4.40 (m, 1 H), 4.81 (t, *J* = 6.6 Hz, 1 H), 4.95 (d, *J* = 8.4 Hz, 1 H), 5.54 (d, *J* = 7.2 Hz, 1 H), 6.45 (s, 1 H), 7.35 (m, 2 H), 7.88 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 5.18, 5.29, 6.70, 9.88, 15.1, 19.5, 20.1, 20.9, 21.3, 22.5, 26.8, 37.2, 38.6, 42.6, 47.0, 57.8, 67.8, 72.9, 74.6, 78.7, 80.7, 84.2, 127.2, 128.4, 129.3, 130.7, 134.3, 134.5, 138.3, 143.9, 167.3, 170.7, 205.1.

7-Triethylsilyl-2-debenzoyl-2-(3-chlorobenzoyl)-10-deacetyl-10-propanoylbaecatin III (11d). White solid; 77%; mp 110-112 °C; [α]_D²⁰ -59 (c 0.22, CHCl₃); ¹H NMR (CDCl₃) δ 0.56 (q, *J* = 7.8 Hz, 6 H), 0.89 (t, *J* = 7.8 Hz, 9 H), 1.00 (s, 3 H), 1.20 (m, 7 H), 1.64 (s, 3 H), 1.83 (m, 1 H), 2.16 (s, 3 H), 2.25 (m, 3 H), 2.40 (m, 4 H), 3.85 (d, *J* = 6.8 Hz, 1 H), 4.09 (d, *J* = 8.2 Hz, 1 H), 4.25 (d, *J* = 8.2 Hz, 1 H), 4.45 (dd, *J* = 10.2, 6.7 Hz, 1 H), 4.79 (t, *J* = 7.5 Hz, 1 H), 4.94 (d, *J* = 8.9 Hz, 1 H), 5.55 (d, *J* = 7.1 Hz, 1 H), 6.45 (s, 1 H), 7.39 (t, *J* = 7.9 Hz, 1 H), 7.54 (d, *J* = 8.1 Hz, 1 H), 7.95 (d, *J* = 7.6 Hz, 1 H), 8.08 (s, 1 H); ¹³C NMR (CDCl₃) δ 5.3, 6.7, 9.2, 9.9, 14.9, 20.1, 22.5, 26.8, 27.7, 37.2, 38.3, 42.7, 47.2, 58.5, 67.8, 72.3, 75.2, 75.5, 76.4, 78.8, 80.7, 84.2, 128.2, 129.9, 130.2, 131.2, 132.5, 133.5, 134.7, 144.1, 165.6, 170.6, 172.7, 202.2. HRMS: *m/e* calcd for C₃₈H₅₃O₁₁ClSi·H⁺: 749.3124. Found: 749.3127 (Δ = - 0.4 ppm).

7-Triethylsilyl-2-debenzoyl-2-(3-azidobenzoyl)-10-deacetyl-10-propanoylbaccatin III (11e).

White solid; 84%; mp 105-108 °C; $[\alpha]_D^{20}$ -56 (c 0.090, CHCl₃); ¹H NMR (CDCl₃) δ 0.54 (q, J = 7.8 Hz, 6 H), 0.90 (t, J = 7.8 Hz, 9 H), 0.94 (s, 3 H), 1.20-1.22 (m, 9 H), 1.64 (s, 3 H), 1.83 (m, 1 H), 2.02 (s, 3 H), 2.18 (m, 3 H), 2.40 (m, 4 H), 3.87 (d, J = 6.9 Hz, 1 H), 4.09 (d, J = 8.2 Hz, 1 H), 4.25 (d, J = 8.2 Hz, 1 H), 4.47 (dd, J = 10.2, 6.7 Hz, 1 H), 4.79 (t, J = 7.5 Hz, 1 H), 4.92 (d, J = 8.7 Hz, 1 H), 5.60 (d, J = 7.0 Hz, 1 H), 6.45 (s, 1 H), 7.23 (m, 1 H), 7.44 (t, J = 7.9 Hz, 1 H), 7.78 (s, 1 H), 7.85 (d, J = 7.7 Hz, 1 H); ¹³C NMR (CDCl₃) δ 5.3, 6.7, 9.2, 9.9, 14.9, 20.1, 22.6, 26.7, 27.6, 37.2, 38.3, 42.7, 47.2, 58.5, 67.8, 72.3, 75.2, 75.5, 76.4, 78.7, 80.8, 84.2, 120.1, 124.2, 126.6, 130.1, 131.1, 132.6, 140.7, 144.0, 166.1, 170.7, 172.7, 202.2. HRMS: *m/e* calcd for C₃₈H₅₃N₃O₁₁Si·H⁺: 756.3528. Found: 756.3531 (Δ = - 0.4 ppm).

2-Debenzoyl-2-(3-vinylbenzoyl)-7-triethylsilyl-10-deacetyl-10-propanoylbaccatin III (11f).

White solid; 67%, mp 108-110 °C; ¹H (300 MHz, CDCl₃) δ 0.58 (m, 6 H), 0.91 (m, 9 H), 1.03 (s, 3 H), 1.19 (s, 3 H), 1.20 (t, J = 7.5 Hz, 3 H), 1.67 (s, 3 H), 1.87 (m, 1 H), 2.20 (s, 3 H), 2.26 (m, 2 H), 2.28 (s, 3 H), 2.47 (m, 1 H), 3.89 (d, J = 7.1 Hz, 1 H), 4.14 (d, J = 8.0 Hz, 1 H), 4.31 (d, J = 8.2 Hz, 1 H), 4.49 (dd, J = 6.9, 10.4 Hz, 1 H), 4.83 (t, J = 8.2 Hz, 1 H), 4.96 (d, J = 8.2 Hz, 1 H), 5.35 (d, J = 11.0 Hz, 1 H), 5.63 (d, J = 6.9 Hz, 1 H), 5.84 (d, J = 17.6 Hz, 1 H), 6.47 (s, 1 H), 6.75 (dd, J = 11.0, 17.0 Hz, 1 H), 7.43 (t, J = 7.7 Hz, 1 H), 7.61 (d, J = 7.7 Hz, 1 H), 7.97 (d, J = 7.7 Hz, 1 H), 8.18 (s, 1 H); ¹³C NMR (75.0 MHz, CDCl₃) δ 5.3, 6.7, 9.2, 14.9, 19.5, 20.1, 22.7, 26.8, 27.7, 37.2, 38.2, 42.8, 47.3, 58.6, 68.0, 72.3, 74.8, 78.7, 80.9, 84.2, 115.3, 127.7, 128.8, 129.7, 131.3, 135.9, 138.0, 143.8, 167.0, 170.6, 172.7, 202.2.

7-Triethylsilyl-2-debenzoyl-2-(3-methoxybenzoyl)-10-deacetyl-10-propanoylbaccatin III (11g).

White solid; 95%; mp 105-107 °C; $[\alpha]_D^{20}$ -85 (c 0.13, CHCl₃); ¹H NMR (CDCl₃) δ 0.56 (q, J = 7.8 Hz, 6 H), 0.85 (t, J = 7.8 Hz, 9 H), 0.99 (s, 3 H), 1.20 (m, 7 H), 1.64 (s, 3 H), 1.83 (m, 1 H), 2.00 (s, 3 H), 2.16 (s, 3 H), 2.23 (m, 3 H), 2.40 (m, 3 H), 3.85 (m, 4 H), 4.09 (m, 2 H), 4.29 (d, J = 8.3 Hz, 1 H), 4.45 (dd, J = 10.2, 6.7 Hz, 1 H), 4.79 (t, J = 7.9 Hz, 1 H), 4.94 (d, J = 8.9 Hz, 1 H), 5.57 (d, J = 6.9 Hz, 1 H), 6.45 (s, 1 H), 7.09 (dd, J = 8.3, 2.2 Hz, 1 H), 7.33 (t, J = 8.1 Hz, 1 H), 7.60 (s, 1 H), 7.66 (d, J = 7.7 Hz, 1 H); ¹³C NMR (CDCl₃) δ 5.3, 6.7, 9.2, 9.9, 14.2, 14.9, 20.1, 22.5, 26.8, 27.7, 37.2, 38.3, 42.7, 47.2, 55.3, 58.6, 60.4, 67.8, 72.3, 74.8, 75.6, 76.4, 78.7, 80.8, 84.2, 114.7, 119.9, 122.5, 129.6, 130.6, 132.6, 144.1, 159.6, 166.9, 170.6, 172.7, 202.4. HRMS: *m/e* calcd for C₃₉H₅₆O₁₂Si·H⁺: 745.3619. Found: 745.3617 (Δ = 0.3 ppm).

2-Debenzoyl-2-(3-methoxybenzoyl)-7-triethylsilyl-10-(cyclopropanecarbonyl)baccatin III (11h).

White solid; 32 mg, 84%; mp 145-147 °C; $[\alpha]_D^{25}$ -61 (c 0.77, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 0.55 (m, 6H), 0.91 (m, 9H), 1.04 (s, 3H), 1.19 (s, 3H), 1.63 (m, 4H), 1.66 (s, 3H), 1.86 (m, 2H), 2.18 (s, 3H), 2.25 (s, 3H), 2.27 (m, 2H), 2.51 (m, 1H), 3.86 (s, 3H), 3.88 (d, J = 6.9 Hz, 1H), 4.13 (d, J = 7.8 Hz, 1H), 4.33 (d, J = 8.4 Hz, 1H), 4.47 (dd, J = 6.6, 10.2 Hz, 1H), 4.82 (t, J = 8.1 Hz, 1H), 4.95 (d, J = 8.4 Hz, 1 H), 5.61 (d, J = 6.9 Hz, 1H), 6.45 (s, 1H), 7.13 (dd, J = 2.4, 8.1 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.63 (s, 1H), 7.70 (d, J = 7.5 Hz, 1H); ¹³C NMR (75.0 MHz, CDCl₃) δ 5.3, 6.7, 8.5, 9.9, 13.0, 14.9, 20.1, 22.6, 26.8, 37.2, 38.3, 42.7, 47.2, 55.4, 58.6, 67.9, 72.3, 74.8, 75.5, 78.7, 80.9, 84.2, 114.7, 120.0, 122.5, 129.6, 130.6, 132.7, 143.9, 159.6, 166.9, 170.7, 173.1, 202.3.

2-Debenzoyl-2-(3-methoxybenzoyl)-7-triethylsilyl-10-deacetyl-10-(methoxycarbonyl)-

baccatin III (11i): White solid; 92%, mp 110 °C; ¹H (300 MHz, CDCl₃) δ 0.55 (m, 6 H), 0.90 (m, 9 H), 1.08 (s, 3 H), 1.12 (s, 3 H), 1.62 (s, 3 H), 1.68 (m, 4 H), 1.90 (m, 1 H), 2.12 (s, 3 H), 2.21 (m, 2 H), 2.24 (s, 3 H), 2.59 (m, 1 H), 3.85 (m, 7 H), 4.07 (m, 2 H), 4.31 (d, *J* = 8.1 Hz, 1 H), 4.49 (dd, *J* = 10.2, 6.7 Hz, 1 H), 4.84 (m, 1 H), 4.94 (d, *J* = 8.1 Hz, 1 H), 5.60 (d, *J* = 6.9 Hz, 1 H), 6.28 (s, 1 H), 7.11 (dd, *J* = 8.3, 2.2 Hz, 1 H), 7.36 (t, *J* = 8.3 Hz, 1 H), 7.63 (s, 1 H), 7.68 (d, *J* = 7.5 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 5.3, 6.7, 9.9, 15.0, 19.5, 22.7, 26.7, 35.2, 37.1, 41.3, 47.2, 55.0, 55.4, 58.1, 67.9, 72.4, 74.7, 78.7, 79.2, 81.5, 84.2, 114.7, 120.0, 122.5, 129.6, 130.3, 134.5, 144.7, 154.6, 159.9, 168.5, 173.2, 204.3.

2-Debenzoyl-2-(3-methoxybenzoyl)-7-triethylsilyl-10-deacetyl-10-(benzyloxycarbonyl)-

baccatin III (11j): White solid; 94%, mp 112-120 °C; ¹H (300 MHz, CDCl₃) δ 0.55 (m, 6 H), 0.90 (m, 9 H), 1.08 (s, 3 H), 1.12 (s, 3 H), 1.62 (s, 3 H), 1.68 (m, 4 H), 1.90 (m, 1 H), 2.12 (s, 3 H), 2.21 (m, 2 H), 2.24 (s, 3 H), 2.59 (m, 1 H), 3.85 (m, 6 H), 4.07 (m, 2 H), 4.31 (d, *J* = 8.1 Hz, 1 H), 4.49 (dd, *J* = 10.2, 6.7 Hz, 1 H), 4.84 (m, 1 H), 4.94 (d, *J* = 8.1 Hz, 1 H), 5.60 (d, *J* = 6.9 Hz, 1 H), 6.29 (s, 1 H), 7.11 (dd, *J* = 8.3, 2.2 Hz, 1 H), 7.34 (m, 6 H), 7.63 (s, 1 H), 7.68 (d, *J* = 7.5 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 5.3, 6.8, 9.9, 15.1, 19.9, 22.7, 26.6, 37.2, 38.2, 42.6, 47.2, 55.4, 58.5, 67.9, 69.9, 72.3, 74.5, 76.5, 78.7, 79.2, 80.6, 84.2, 144.6, 120.0, 122.5, 128.3, 128.4, 128.5, 129.6, 130.6, 132.3, 135.2, 144.7, 154.3, 159.6, 166.9, 170.7, 201.5.

2-Debenzoyl-2-(3-methoxybenzoyl)-7-triethylsilyl-10-deacetyl-10-(2-methoxybenzoyl)-

baccatin III (11k): White solid; 40% (80% at 50% conversion); ¹H (300 MHz, CDCl₃) δ 0.58 (m, 6 H), 0.91 (q, *J* = 7.8 Hz, 9 H), 1.10 (s, 3 H), 1.12 (s, 3 H), 1.37 (s, 3 H), 1.92 (m, 2 H), 1.97 (bs, 1 H), 2.19 (s, 3 H), 2.30 (s, 3 H), 2.55 (m, 1 H), 3.54 (m, 1 H), 3.85 (m, 7 H), 3.94 (d, *J* = 6.9 Hz, 1 H), 4.15 (d, *J* = 7.8 Hz, 1 H), 4.34 (d, *J* = 7.8 Hz, 1 H), 4.53 (dd, *J* = 6.6 Hz, 3.6 Hz, 1 H), 4.84 (m, 1H), 4.97 (d, *J* = 7.8 Hz, 1 H), 5.66 (d, *J* = 6.9 Hz, 1 H), 6.69 (s, 1 H), 6.95-7.07 (m, 2 H), 7.14-7.19 (m, 1 H), 7.28-7.42 (m, 2 H), 7.65-7.73 (m, 2 H), 8.01 (m, 1 H).

2-Debenzoyl-2-(3-methoxybenzoyl)-7-triethylsilyl-10-deacetyl-10-(4-methoxyphenylacetyl)-

baccatin III (11l): White solid; 82%; ¹H NMR (400 MHz, CDCl₃) δ 0.55 (m, 6 H), 0.89 (m, 9 H), 0.92 (s, 3 H), 1.09 (s, 3 H), 1.27 (s, 3 H), 1.68 (s, 3 H), 1.87 (m, 1 H), 2.17 (s, 3 H), 2.24 (m, 2 H), 2.25 (s, 3 H), 2.50 (m, 1 H), 3.69 (d, *J* = 3.6 Hz, 1 H), 3.78 (s, 1 H), 3.85 (dd, *J* = 7.2, 1.6 Hz, 1 H), 3.86 (s, 3 H), 4.14 (d, *J* = 8.4 Hz, 1 H), 4.33 (d, *J* = 8.0 Hz, 1 H), 4.47 (dd, *J* = 10.8, 6.8 Hz, 1 H), 4.78 (t, *J* = 7.9 Hz, 1 H), 4.95 (d, *J* = 9.6 Hz, 1 H), 5.60 (d, *J* = 6.8 Hz, 1 H), 6.85 (dt, *J* = 6.8, 2.8 Hz, 2 H), 7.13 (dt, *J* = 8.4, 0.8 Hz, 1 H), 7.24 (d, *J* = 8.8 Hz, 2 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.64 (t, *J* = 1.2 Hz, 1 H), 7.70 (dd, *J* = 6.4, 0.8 Hz, 1 H).

Characterization data (¹H NMR) for 16a-g

(3R,4S)-1-Cyclopentyloxycarbonyl-3-triisopropylsiloxy-4-(2-methylprop-1-enyl)-azetid-2-one (16a): White solid; 80%; mp: 54-56 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.05 (m, 21 H), 1.5-1.7 (m, 14 H), 4.77 (dd, *J* = 10.0, 6.0 Hz, 1 H), 4.99 (d, *J* = 6.0 Hz, 1 H), 5.18 (m, 1 H), 5.29 (d, *J* = 10.0 Hz); ¹³C NMR (CDCl₃) δ 11.8, 17.5, 18.2, 23.5, 26.0, 32.7, 56.7, 77.4, 79.6, 118.0, 140.1, 149.1, 166.1.

(3R,4S)-1-Cyclohexyloxycarbonyl-3-*tert*-butyldimethylsiloxy-4-(2-methylprop-1-enyl)azetid-2-one (16b). Colorless viscous oil; 80%; ¹H NMR (300 MHz, CDCl₃) δ 0.060 (s, 3 H), 0.119 (s, 3 H), 0.873 (s, 9 H), 1.2-1.6 (m, 6 H), 1.65-1.9 (m, 10 H), 4.76 (m, 2 H), 4.88 (d, *J* = 5.7 Hz, 1 H), 5.24 (d, *J* = 9.6 Hz).

(3R,4S)-1-(Cyclopent-1-enylcarbonyl)-3-triisopropylsiloxy -4-(2-methylprop-1-enyl)azetid-2-one (16c). Colorless viscous oil; 95%; ¹H NMR (300 MHz, CDCl₃) δ 1.05 (s, 21 H), 1.76 (s, 3 H), 1.82 (s, 3 H), 1.85-2.02 (m, 2 H), 2.55-2.61 (m, 4 H), 4.88-4.97 (m, 2 H), 5.26 (d, *J* = 11.1 Hz, 1 H), 7.30 (s, 1 H).

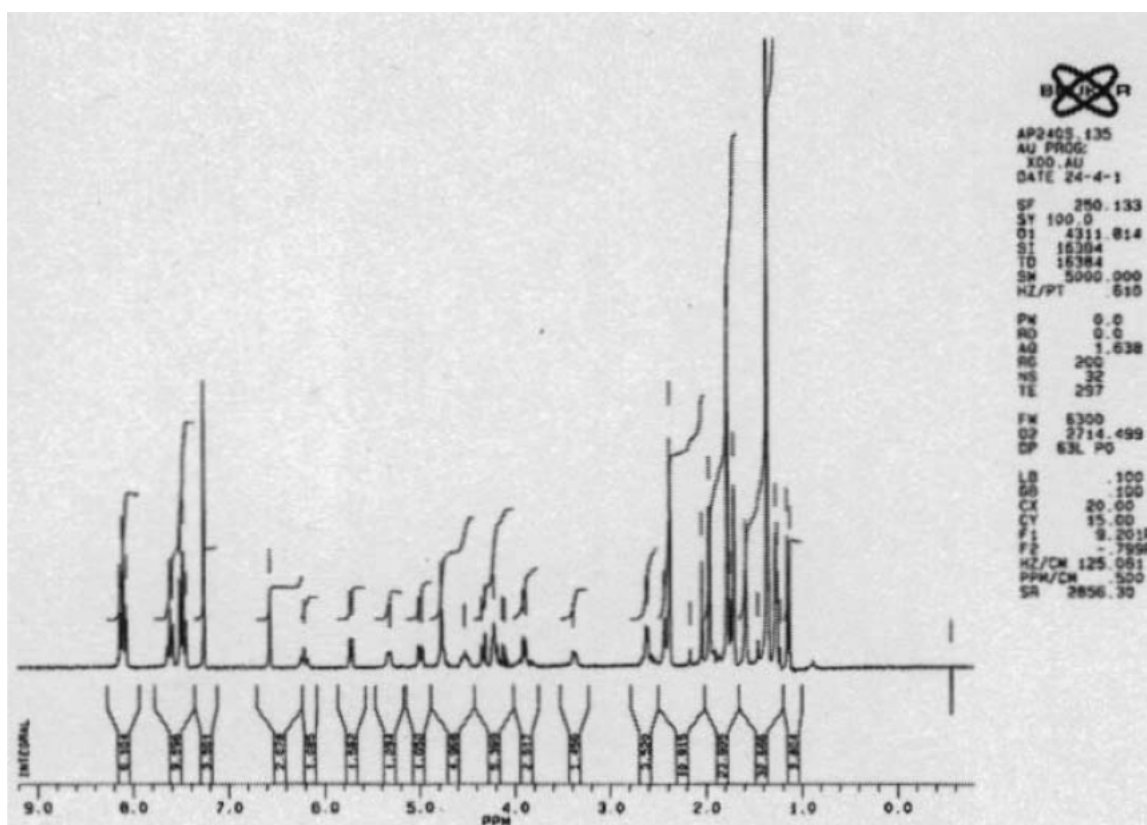
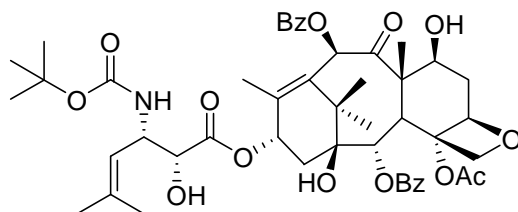
(3R,4S)-1-(Cyclohex-1-enylcarbonyl)-3-triisopropylsiloxy-4-(2-methylprop-1-enyl)azetid-2-one (16d). Colorless viscous oil; 97%; ¹H NMR (300 MHz, CDCl₃) δ 1.05 (s, 21 H), 1.76 (s, 3 H), 1.82 (s, 3 H), 1.85-2.02 (m, 2 H), 2.55-2.61 (m, 4 H), 4.88-4.97 (m, 2 H), 5.26 (d, *J* = 11.1 Hz, 1 H), 7.30 (s, 1 H).

(3R,4S)-1-Cyclopropanecarbonyl-3-triisopropylsiloxy-4-(2-methylprop-1-enyl)azetid-2-one (16e). Colorless viscous oil; 100%; ¹H NMR (300 MHz, CDCl₃) δ 1.05 (m, 25 H), 1.78 (s, 6 H), 2.57 (m, 1 H), 4.82 (dd, *J* = 6.3 Hz, *J* = 9.9 Hz, 1 H), 5.04 (d, *J* = 6.3 Hz, 1 H), 5.25 (d, *J* = 9.9 Hz, 1 H).

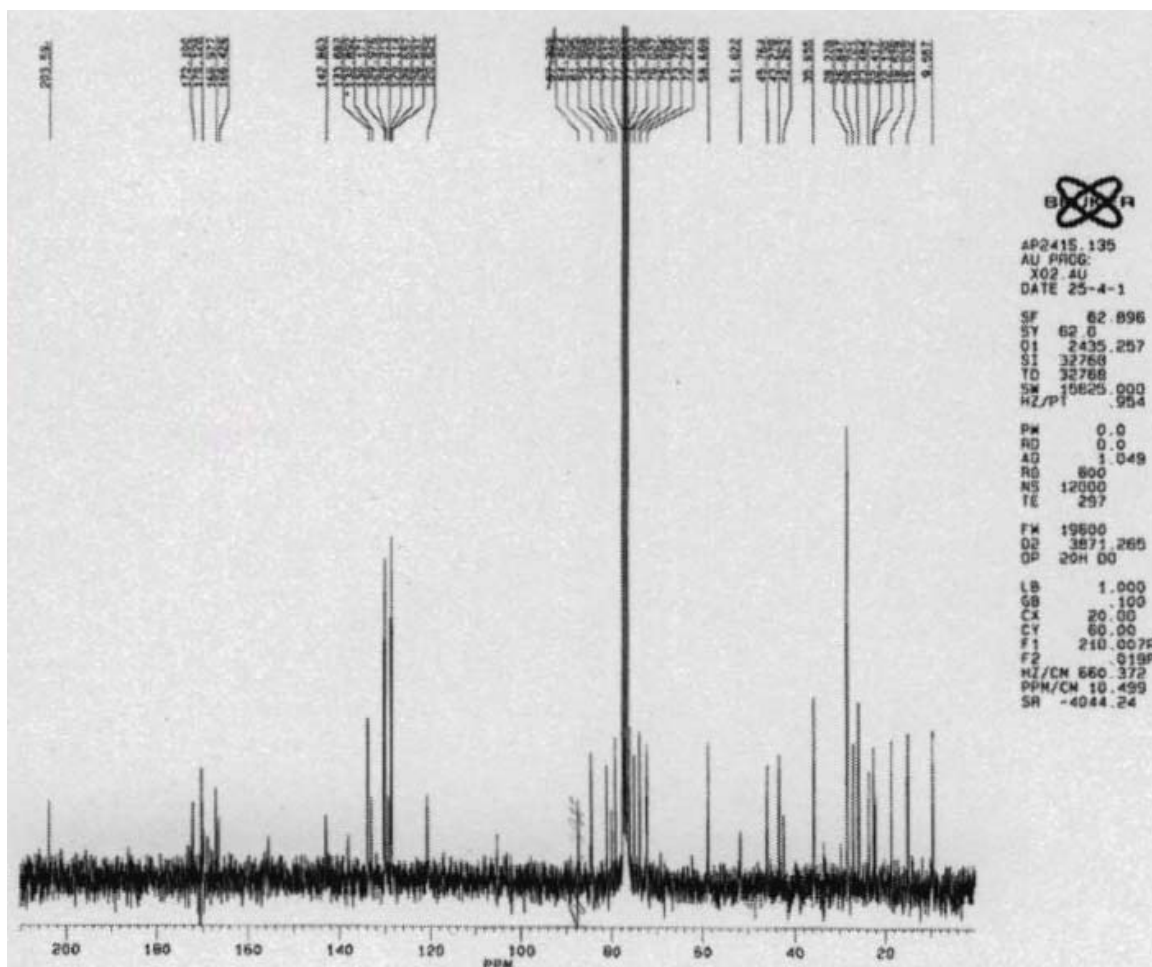
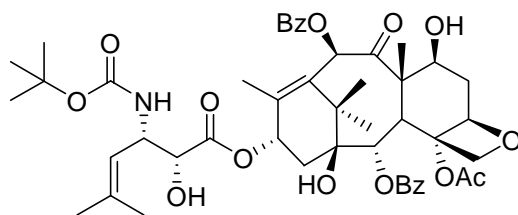
(3R,4S)-1-Cyclobutanecarbonyl-3-triisopropylsiloxy-4-(2-methylprop-1-enyl)azetid-2-one (16f). Colorless oil; 91%; ¹H NMR (300 MHz, CDCl₃) δ 1.05 (m, 21 H), 1.77 (s, 3 H), 1.80 (s, 3 H), 1.97 (m, 2 H), 2.21 (m, 4 H), 3.69 (m, 1 H), 4.79 (dd, *J* = 6.0 Hz, *J* = 9.6 Hz, 1 H), 4.98 (d, *J* = 6.0 Hz, 1 H), 5.21 (d, *J* = 9.6 Hz, 1 H).

(3R,4S)-1-Cyclopentanecarbonyl-3-triisopropylsiloxy-4-(2-methylprop-1-enyl)azetid-2-one (16g). Colorless oil; 80%; ¹H NMR (300 MHz, CDCl₃) δ 1.09 (m, 21 H), 1.56-1.77 (m, 6 H), 1.79 (s, 3 H), 1.80 (s, 3 H), 1.83-1.99 (m, 2 H), 3.36 (m, 1 H), 4.81 (dd, *J* = 6.0 Hz, *J* = 9.6 Hz, 1 H), 5.00 (d, *J* = 6.0 Hz, 1 H), 5.22 (dt, *J* = 9.6, 1.5 Hz, 1 H).

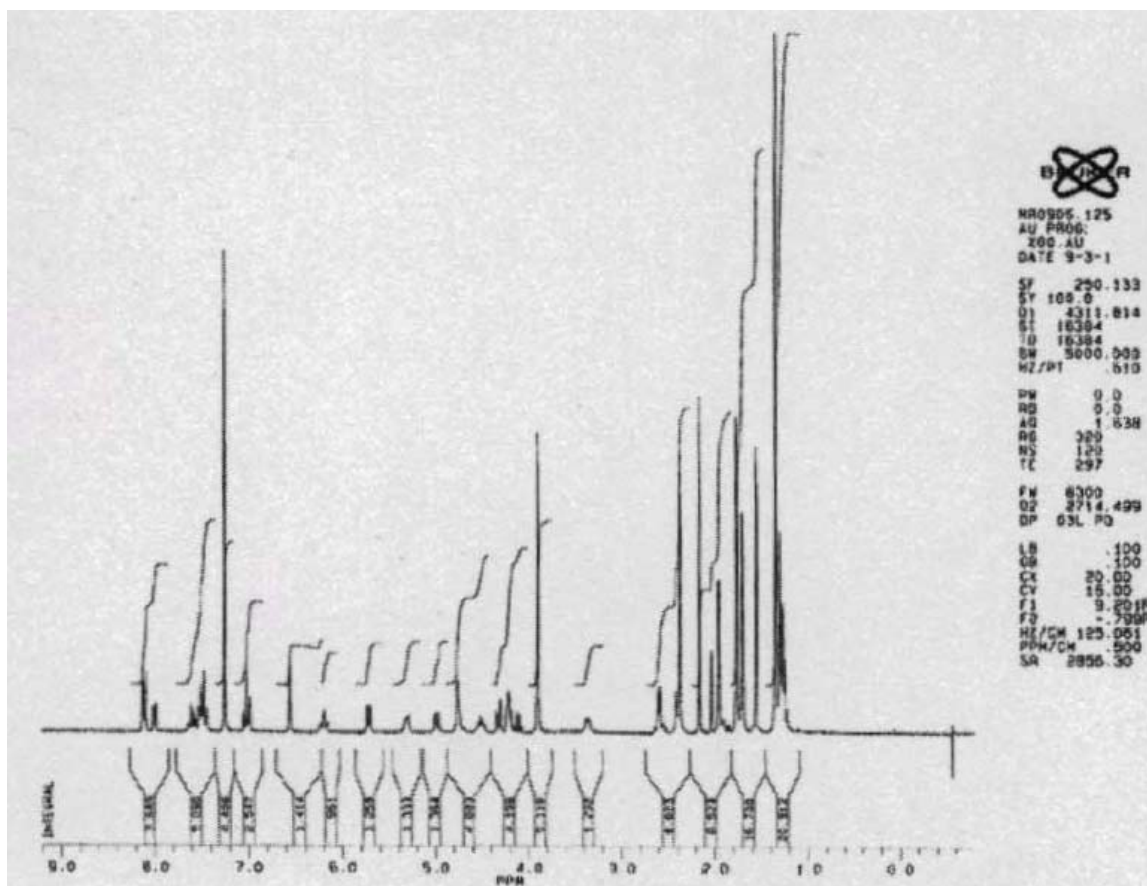
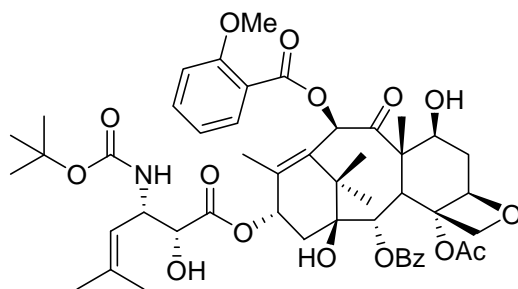
¹H NMR Spectrum of 6a



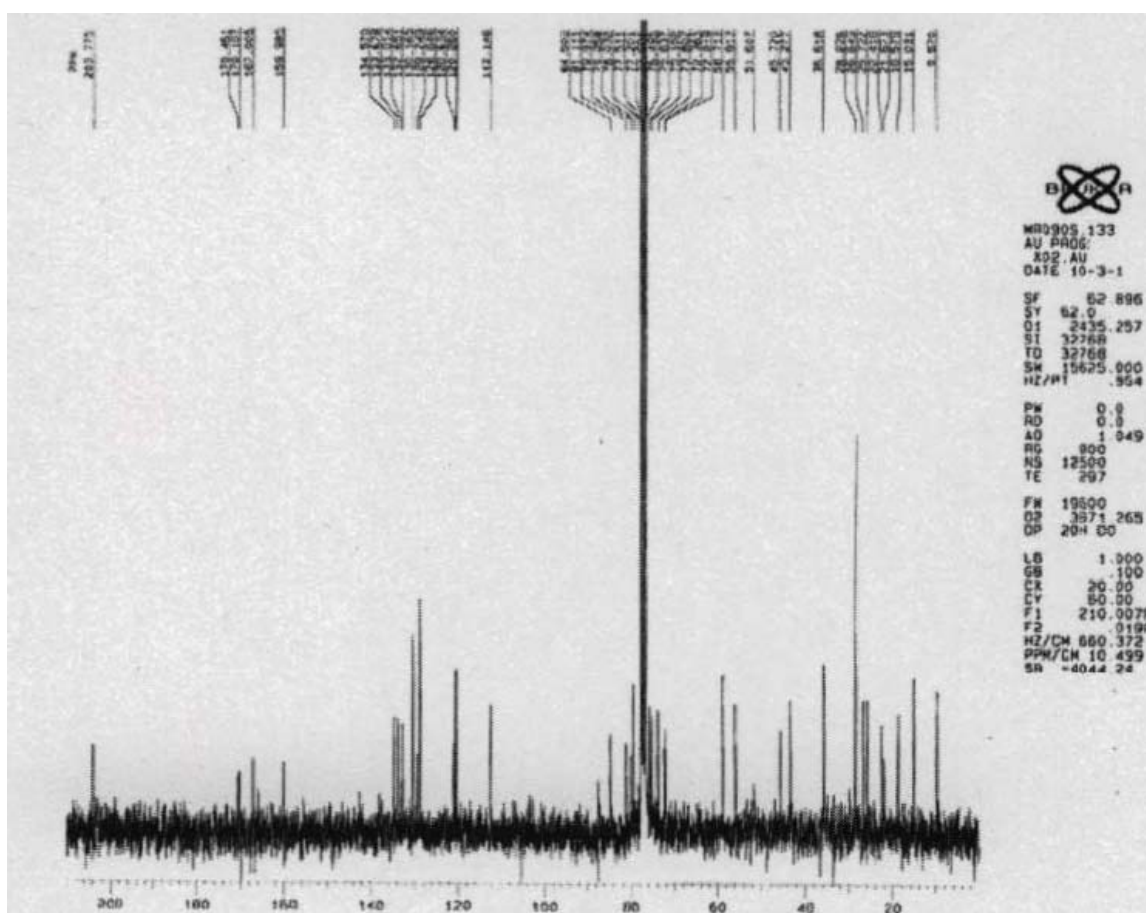
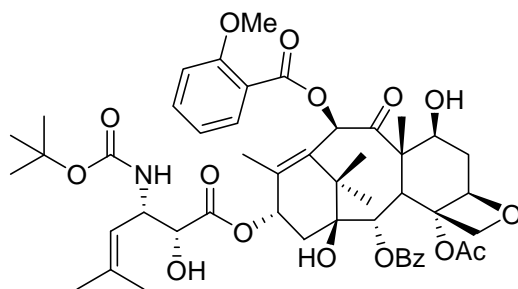
¹³C NMR Spectrum of **6a**



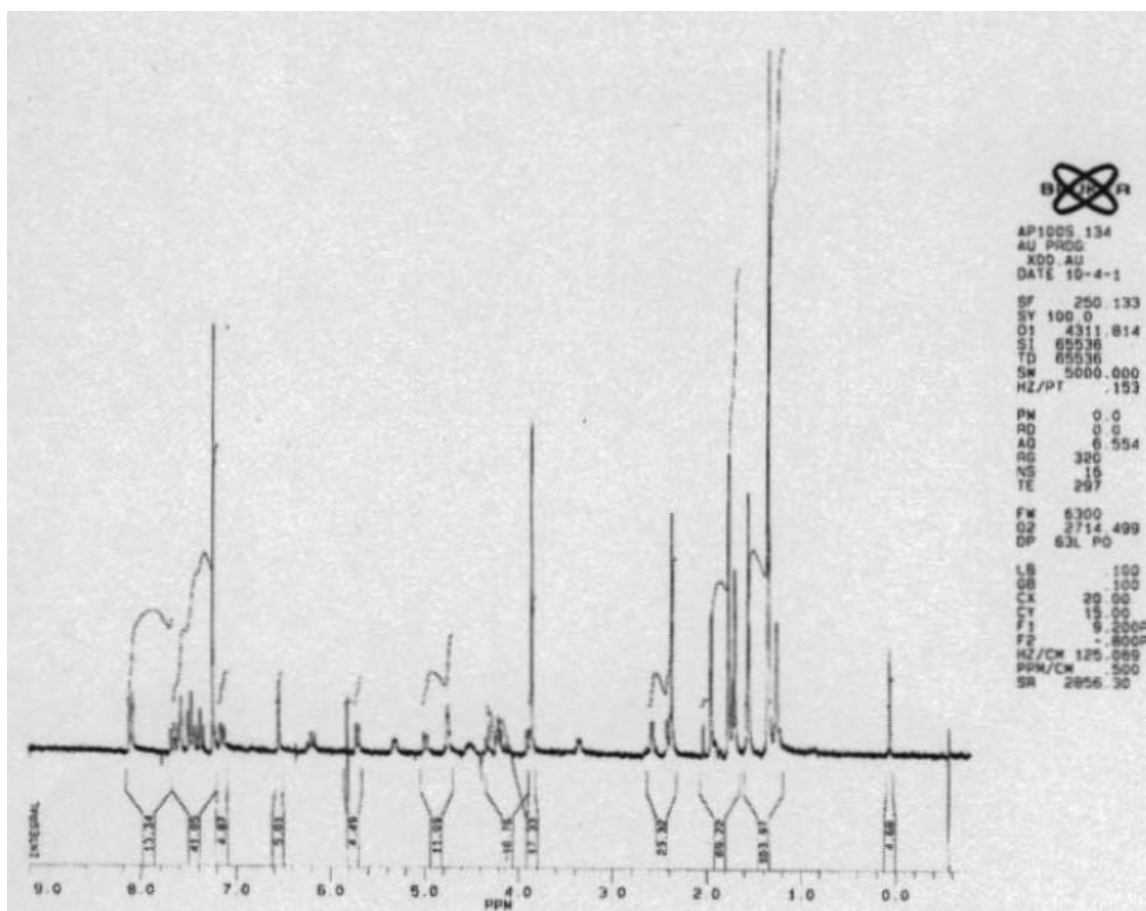
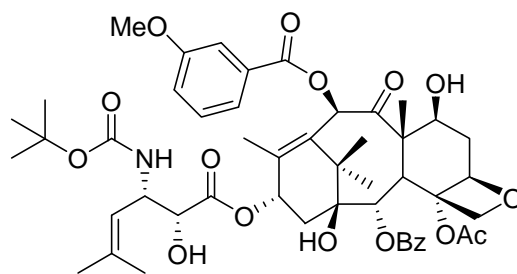
^1H NMR Spectrum of **6b**



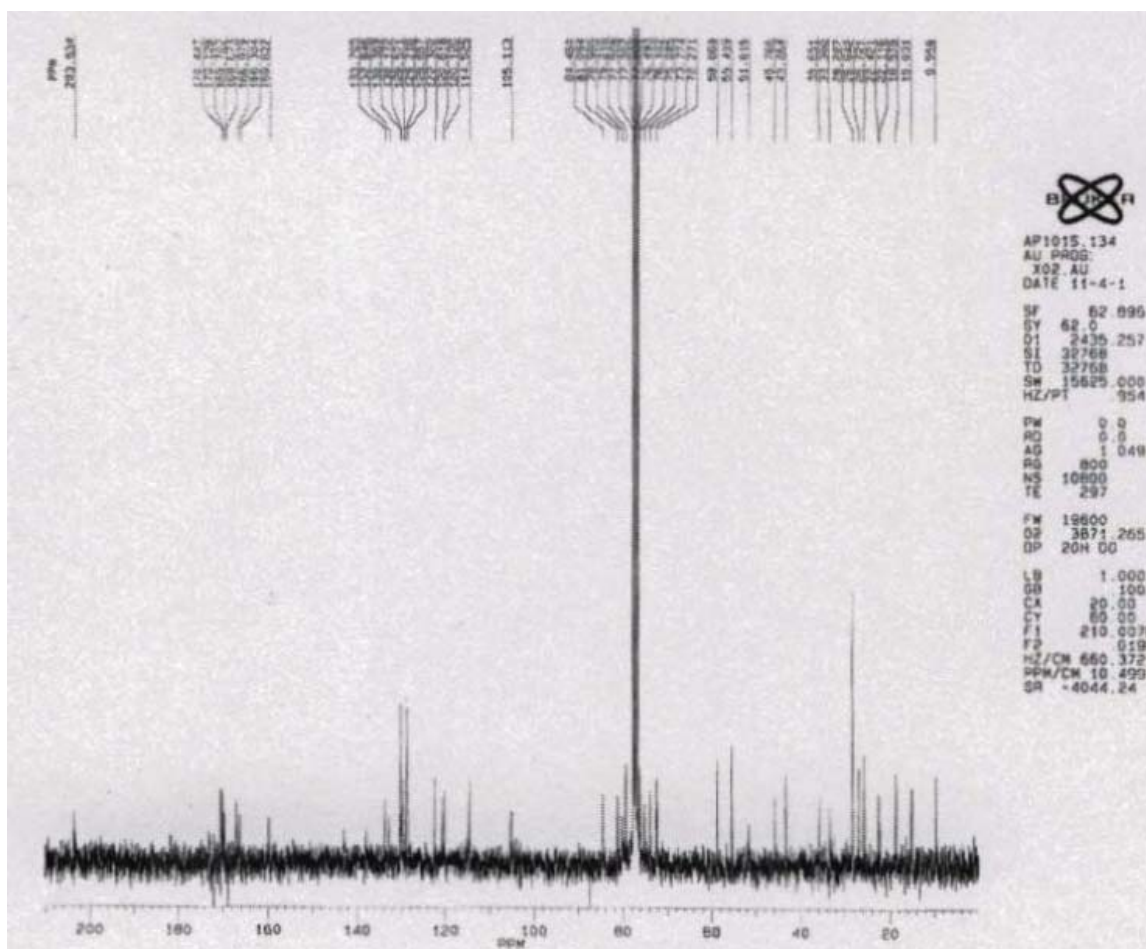
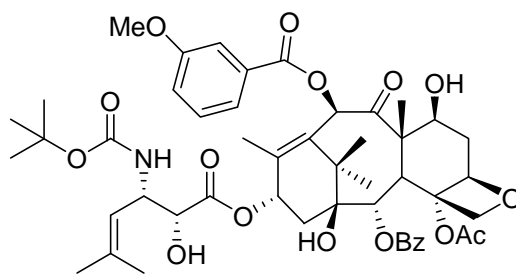
^{13}C NMR Spectrum of **6b**



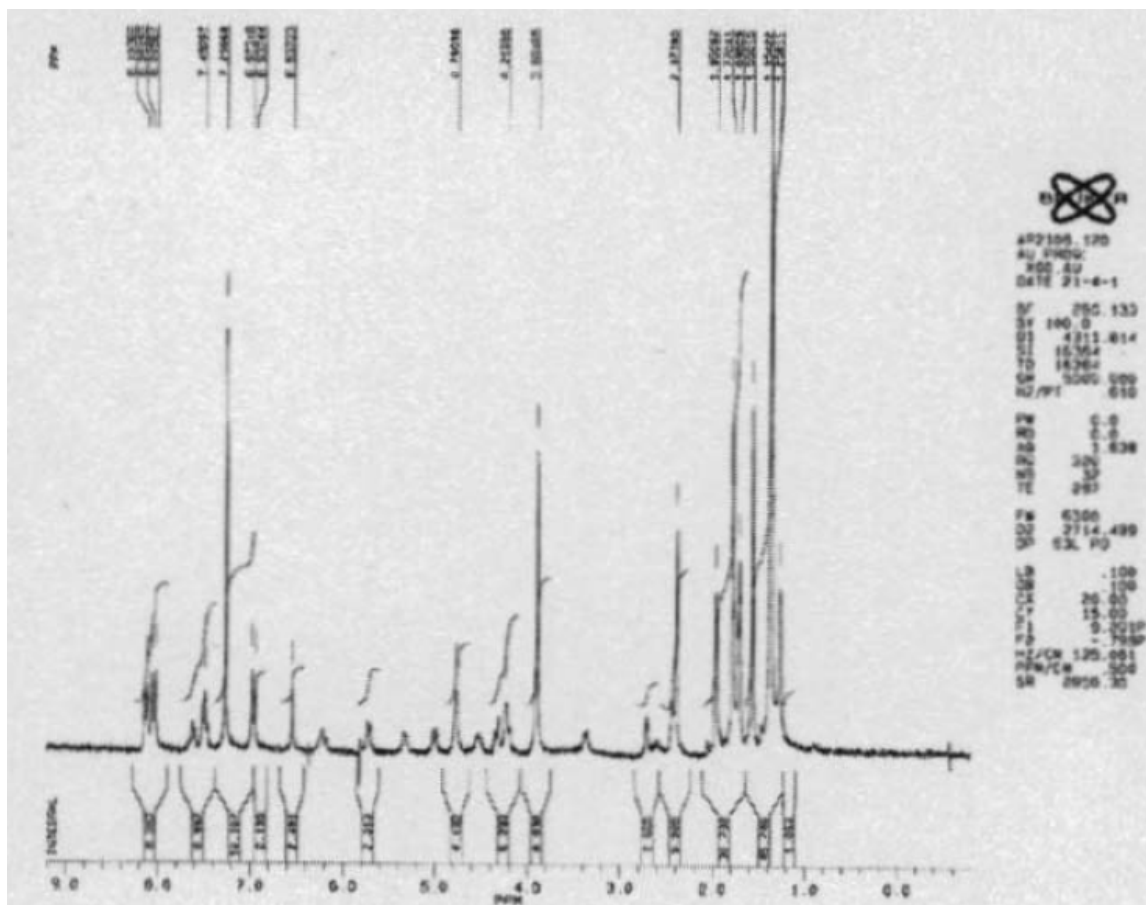
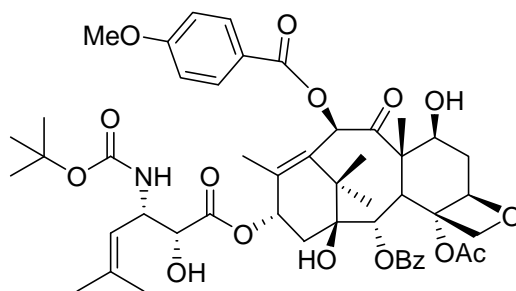
^1H NMR Spectrum of **6c**



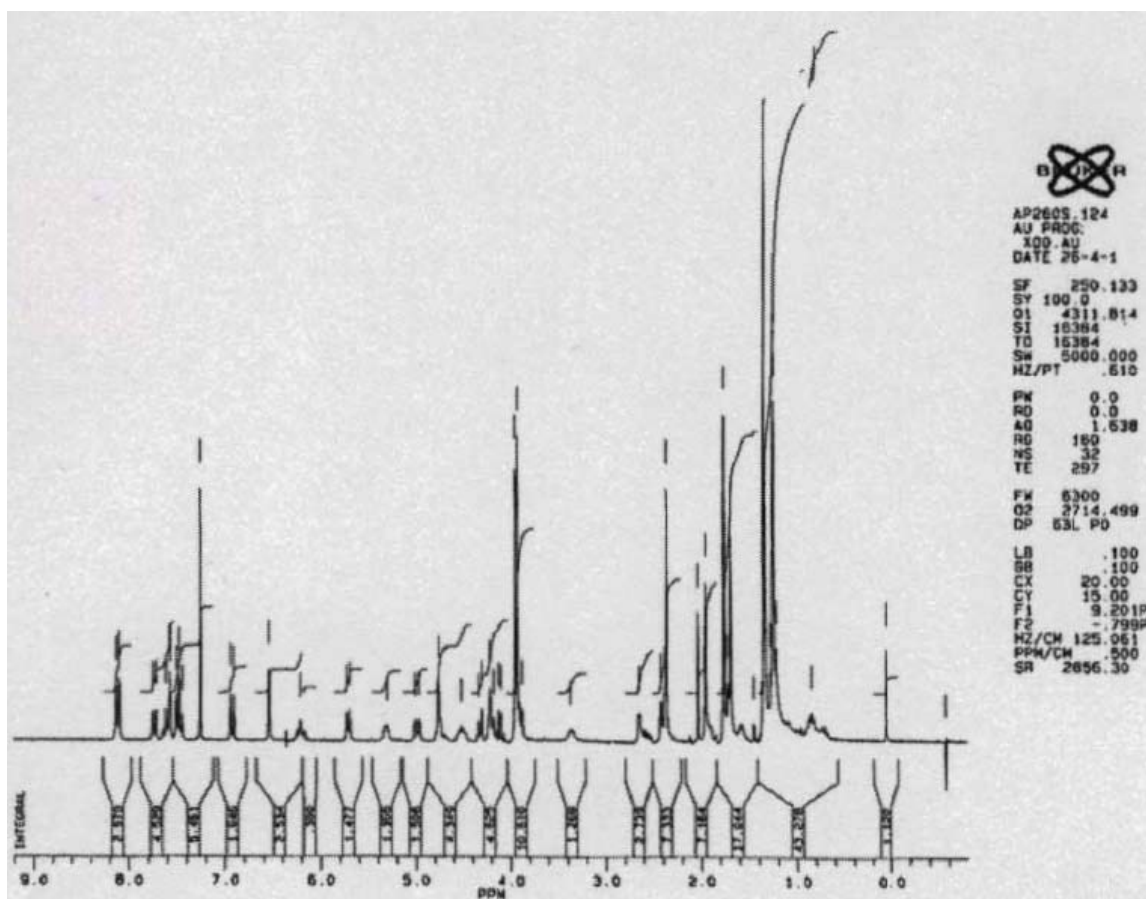
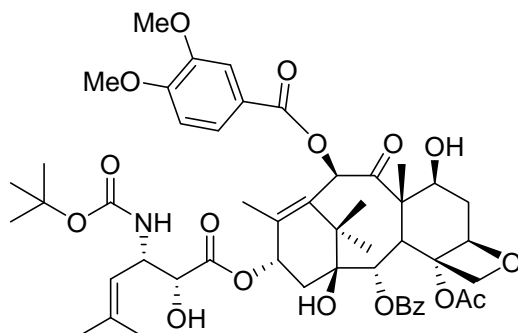
^{13}C NMR Spectrum of **6c**



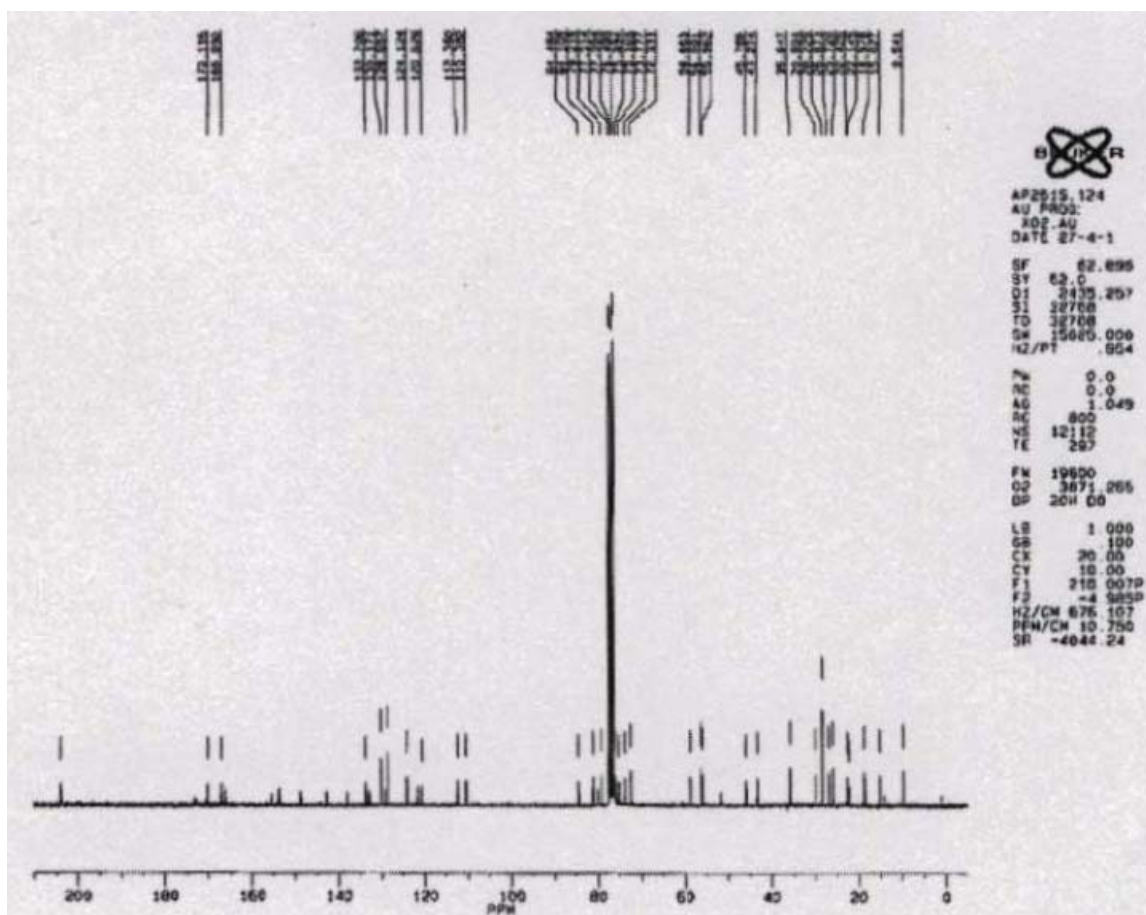
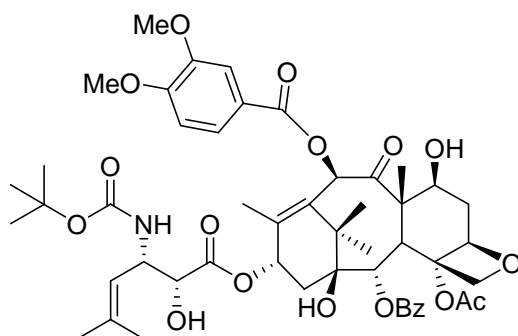
¹H NMR Spectrum of **6d**



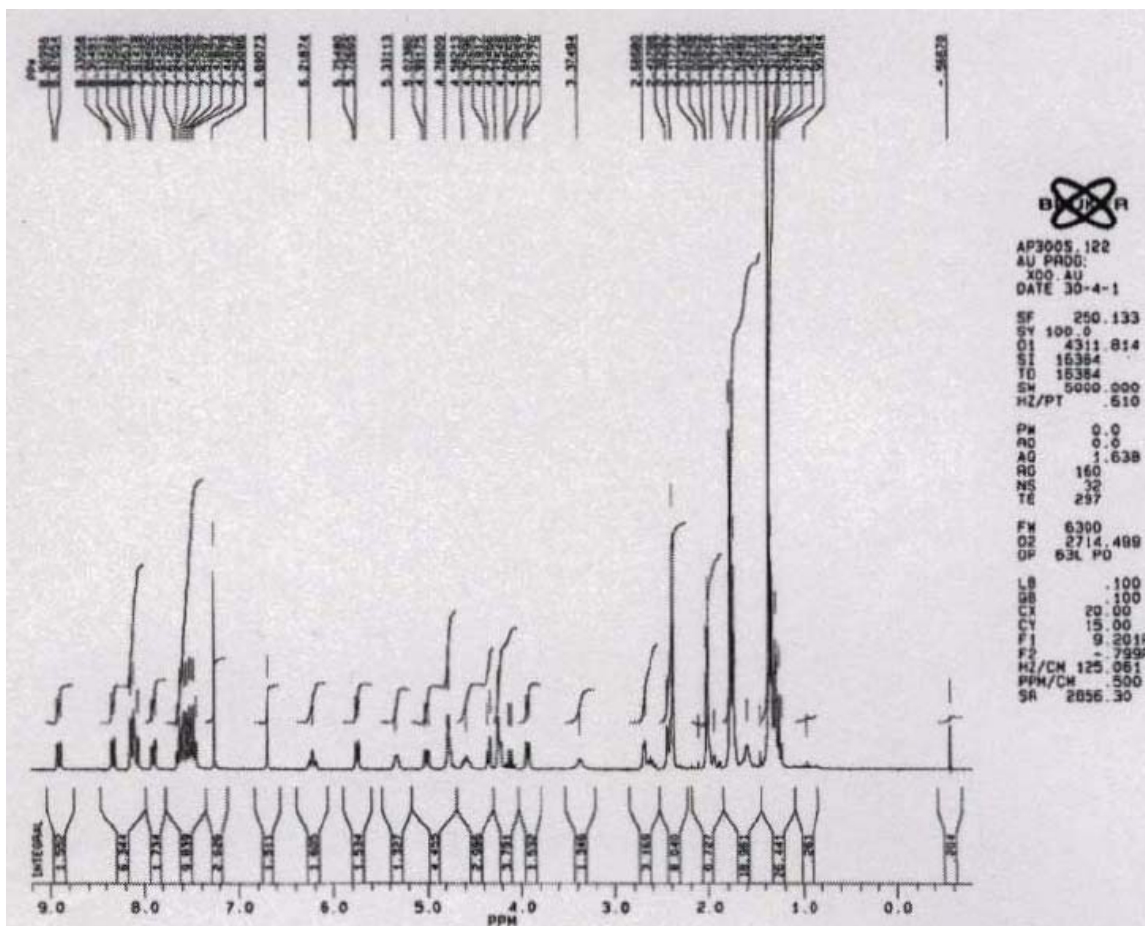
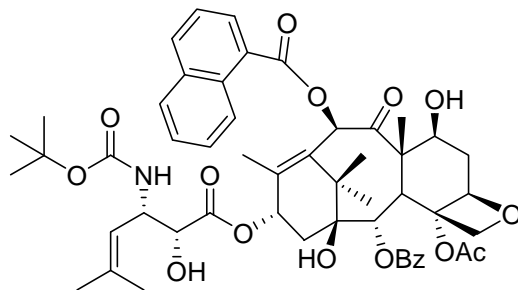
^1H NMR Spectrum of **6e**



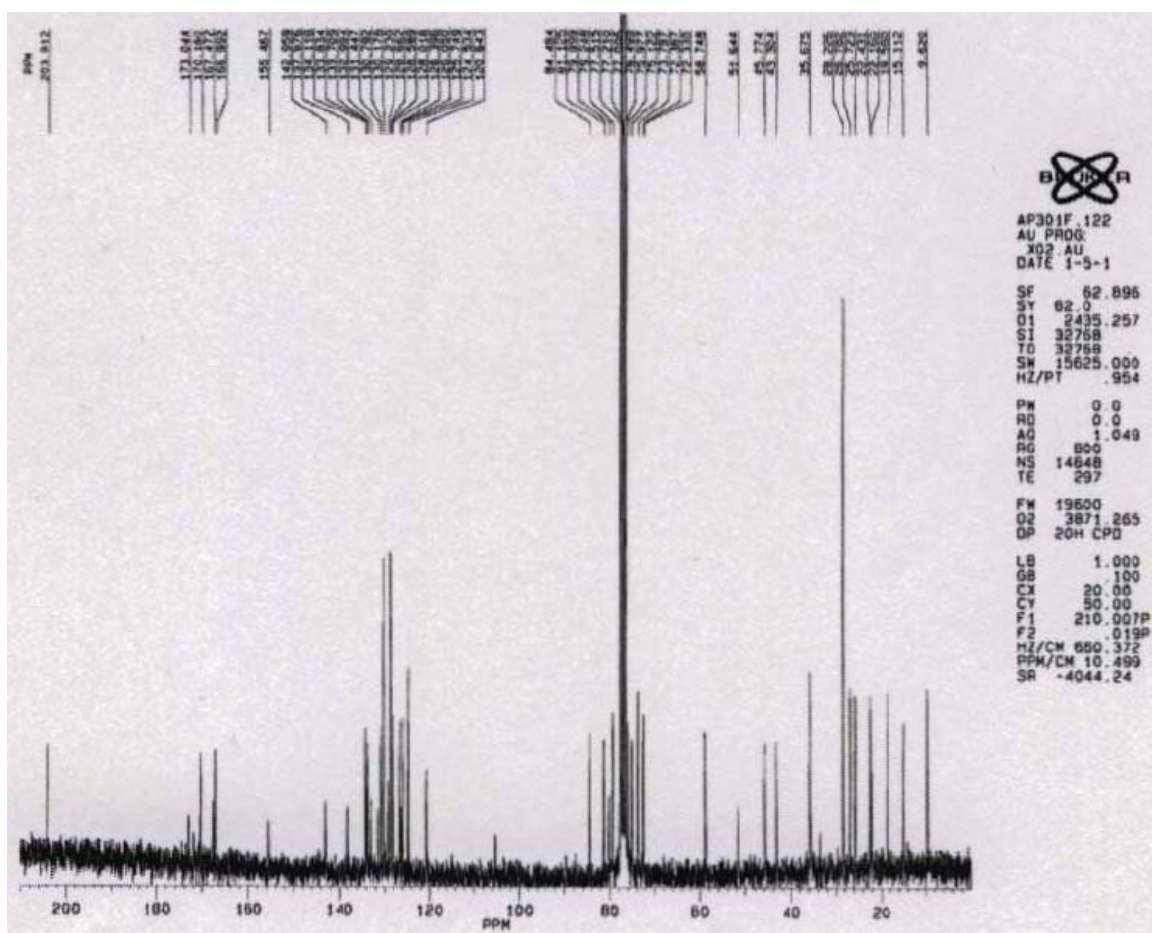
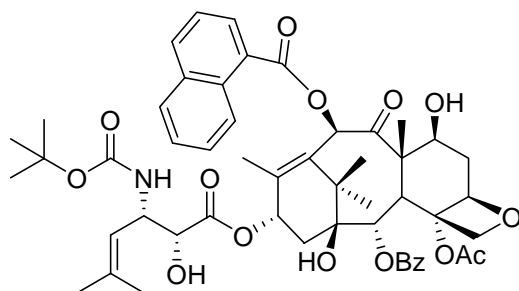
^{13}C NMR Spectrum of **6e**



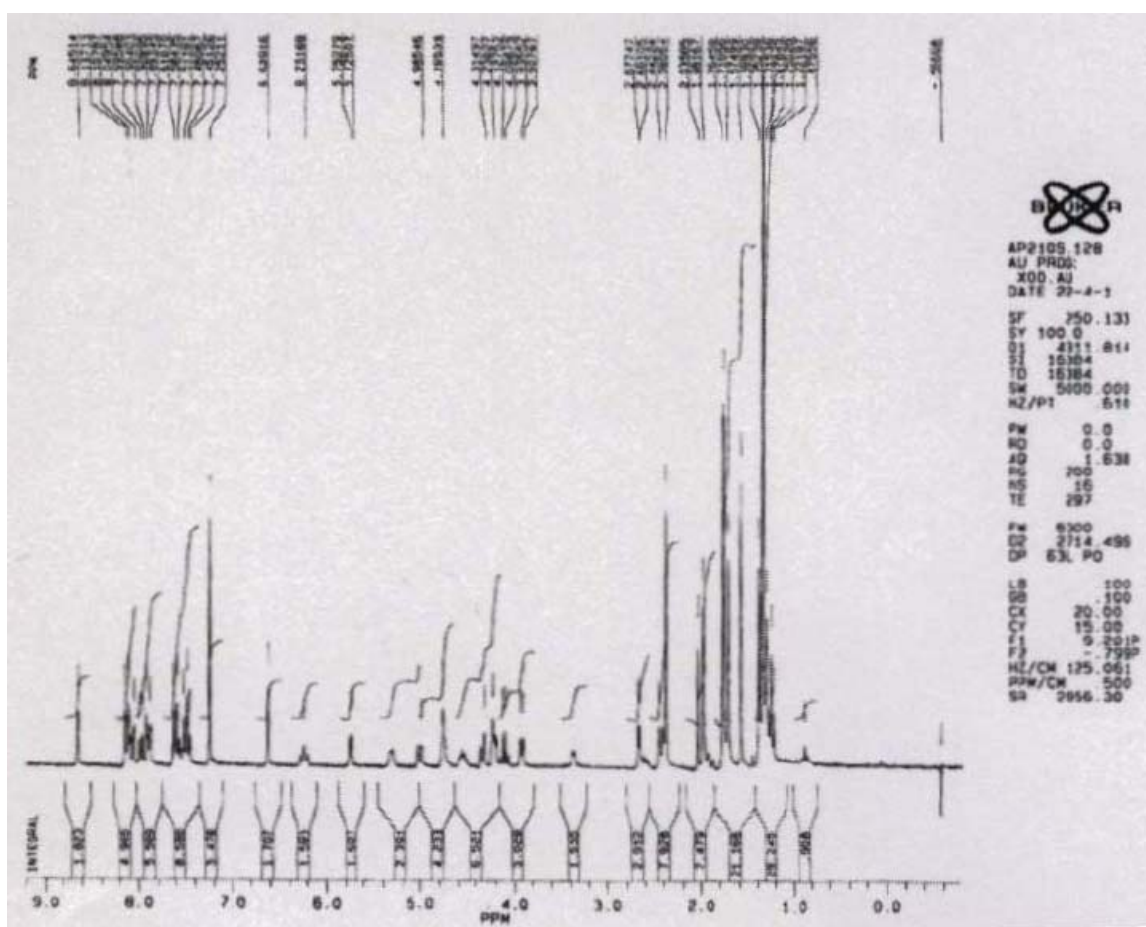
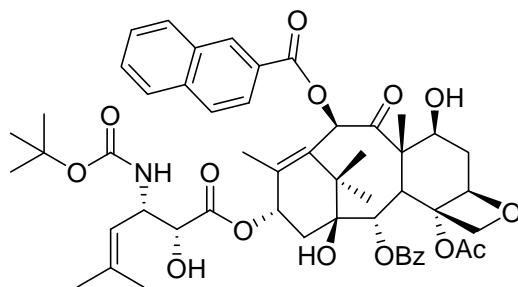
¹H NMR Spectrum of **6f**



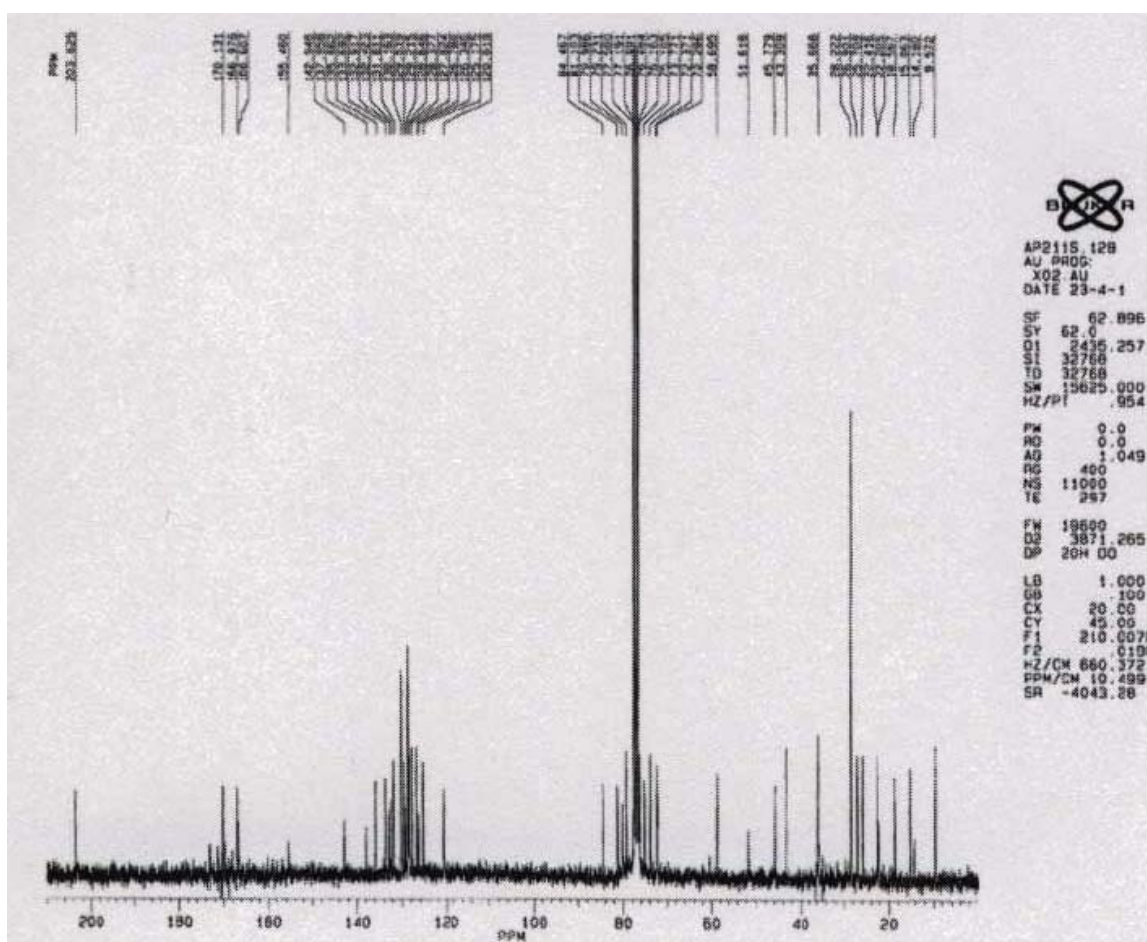
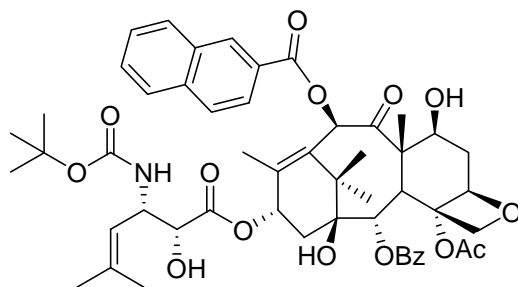
¹³C NMR Spectrum of **6f**



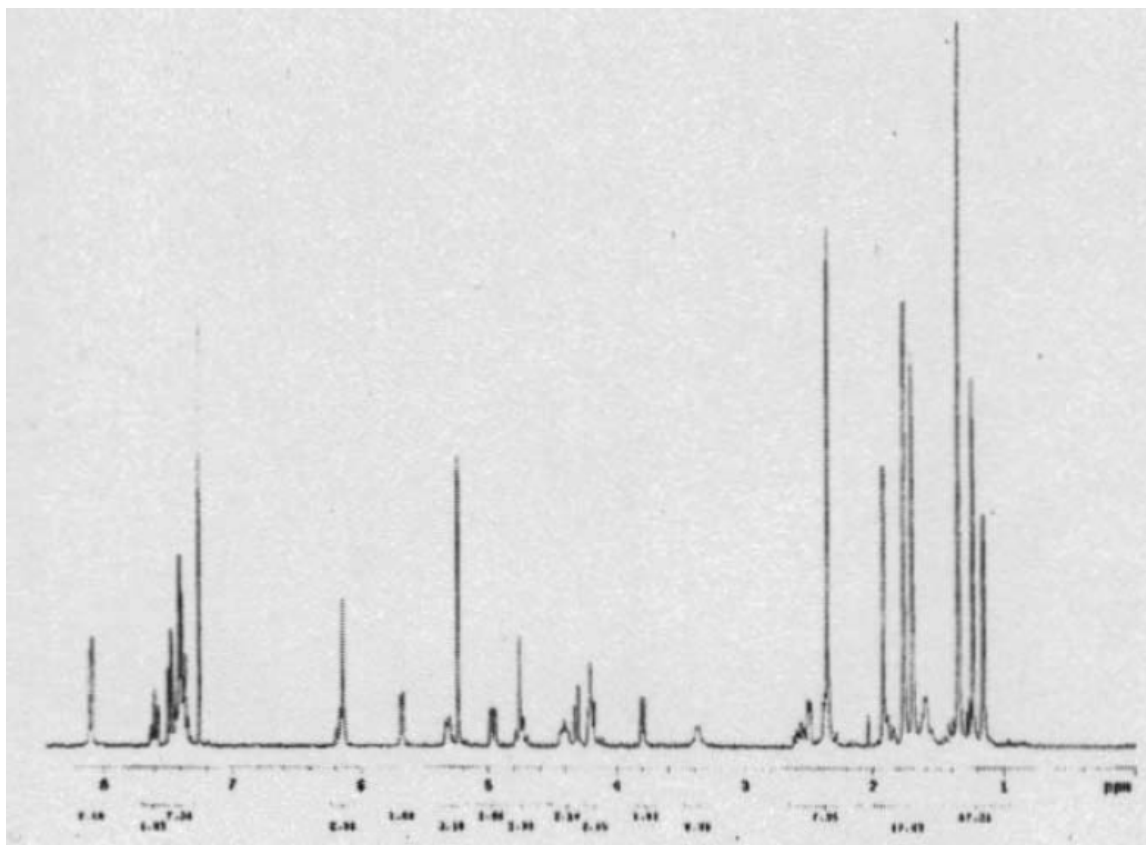
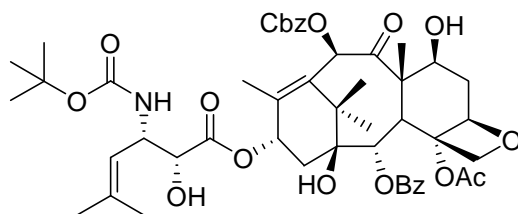
¹H NMR Spectrum of **6g**



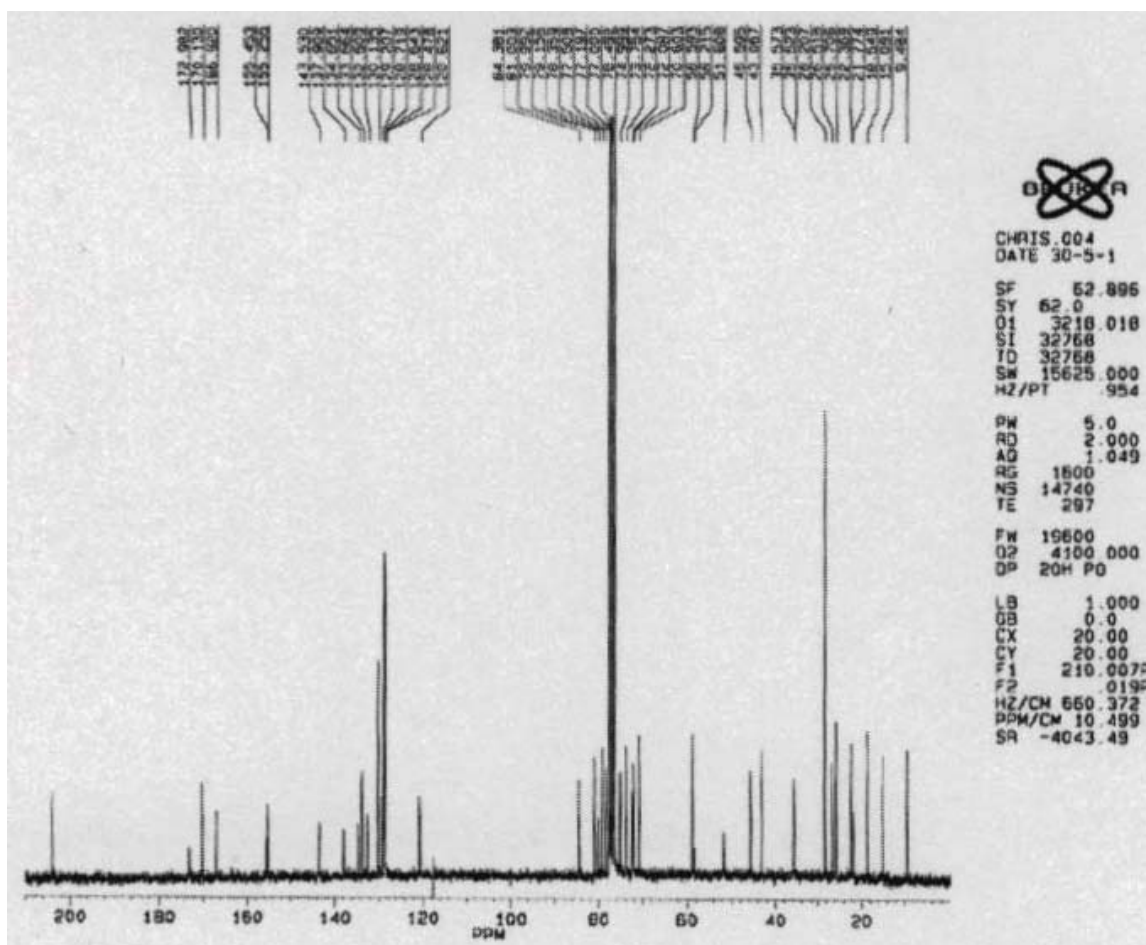
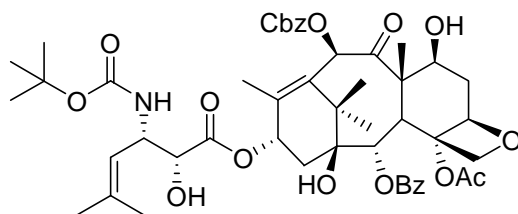
^{13}C NMR Spectrum of **6g**



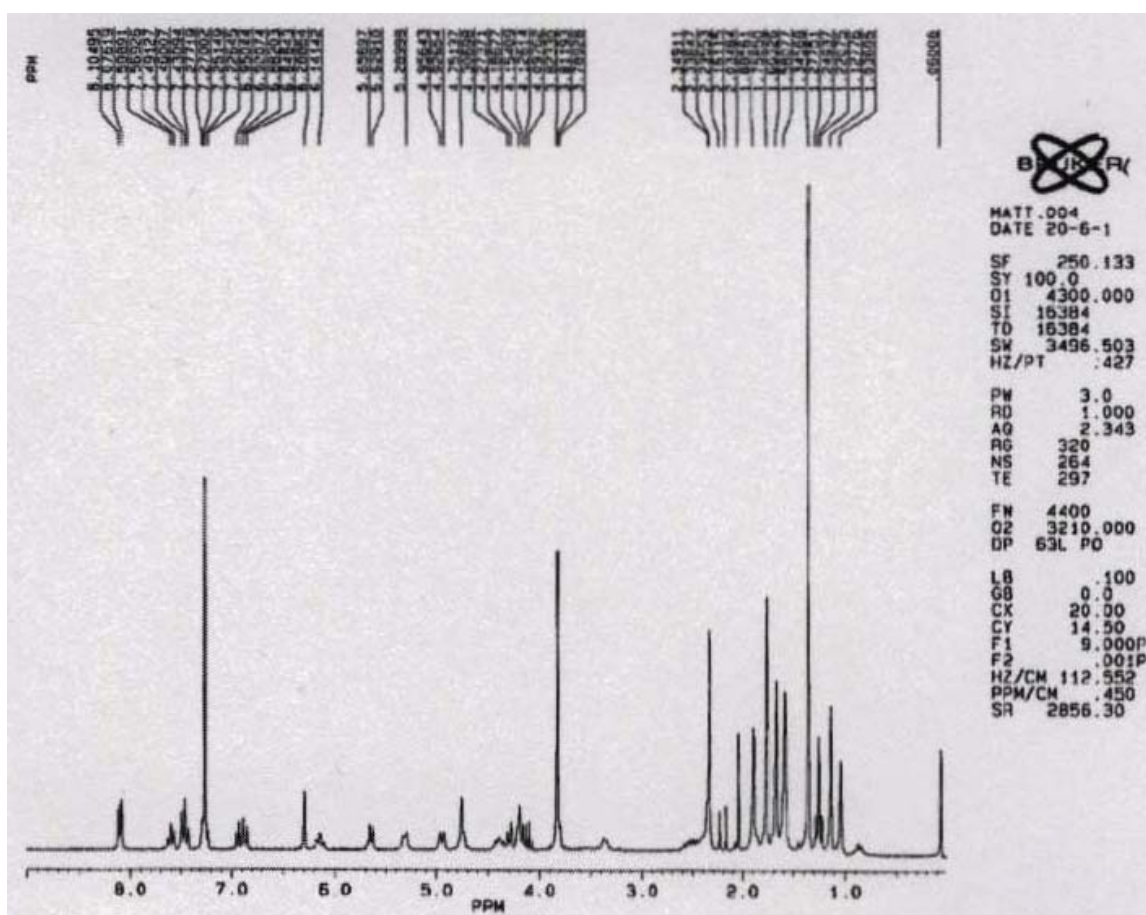
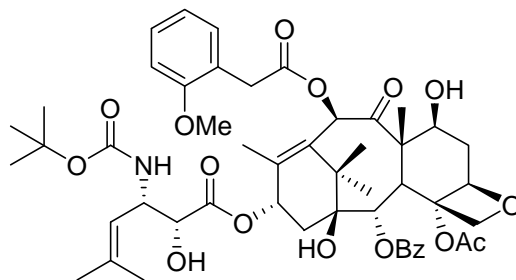
¹H NMR Spectrum of 6h



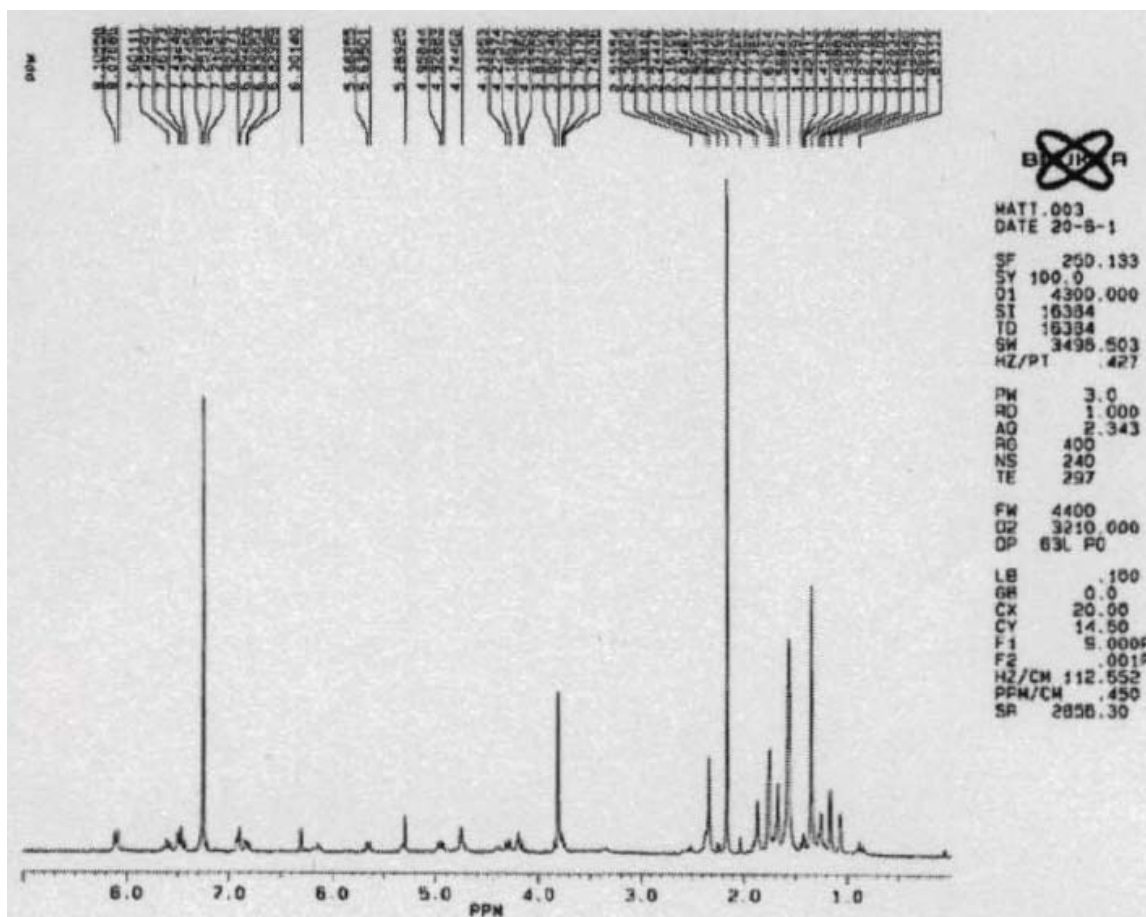
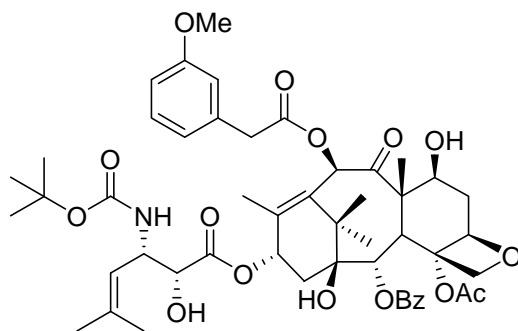
^{13}C NMR Spectrum of **6h**



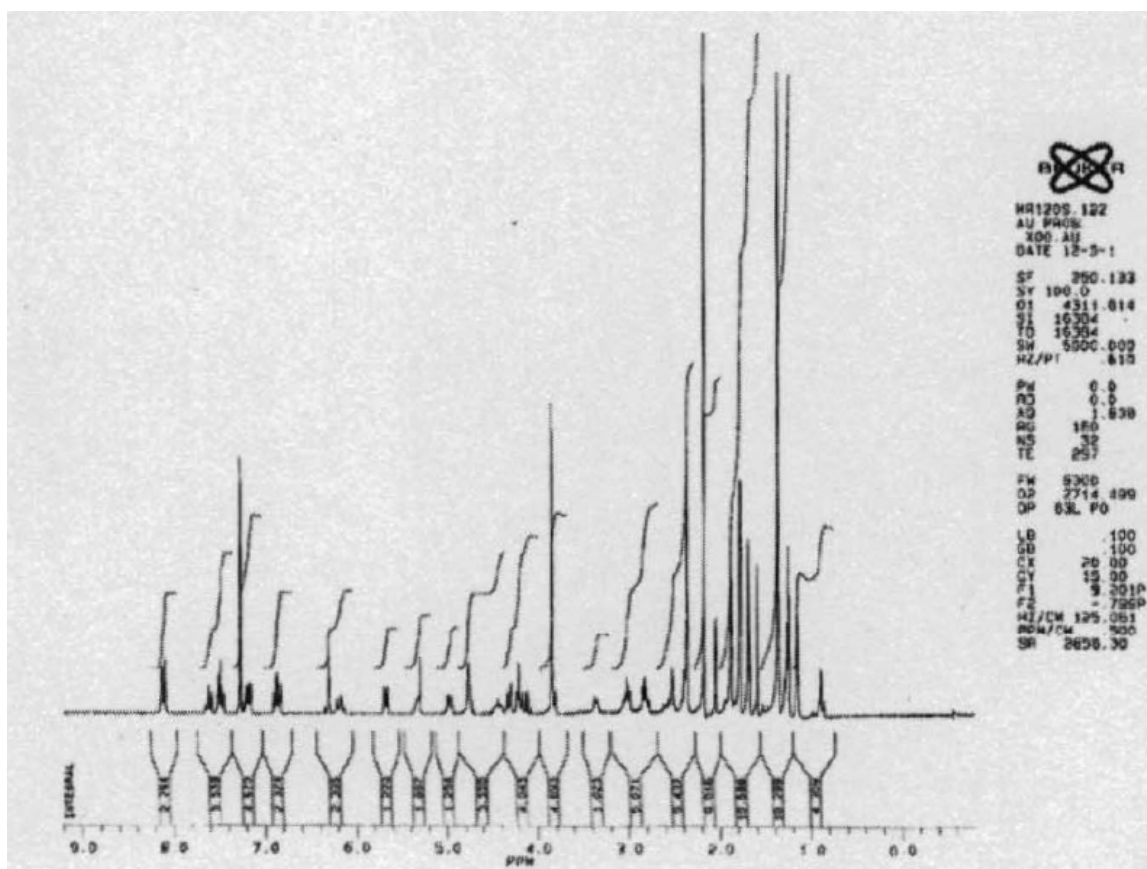
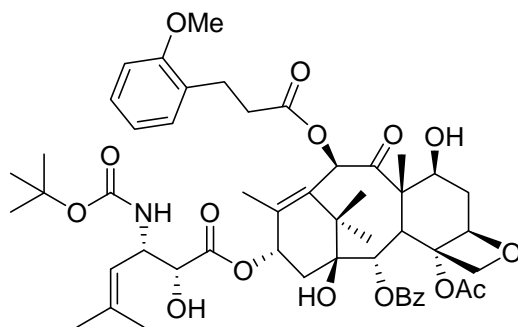
^1H NMR Spectrum of **6i**



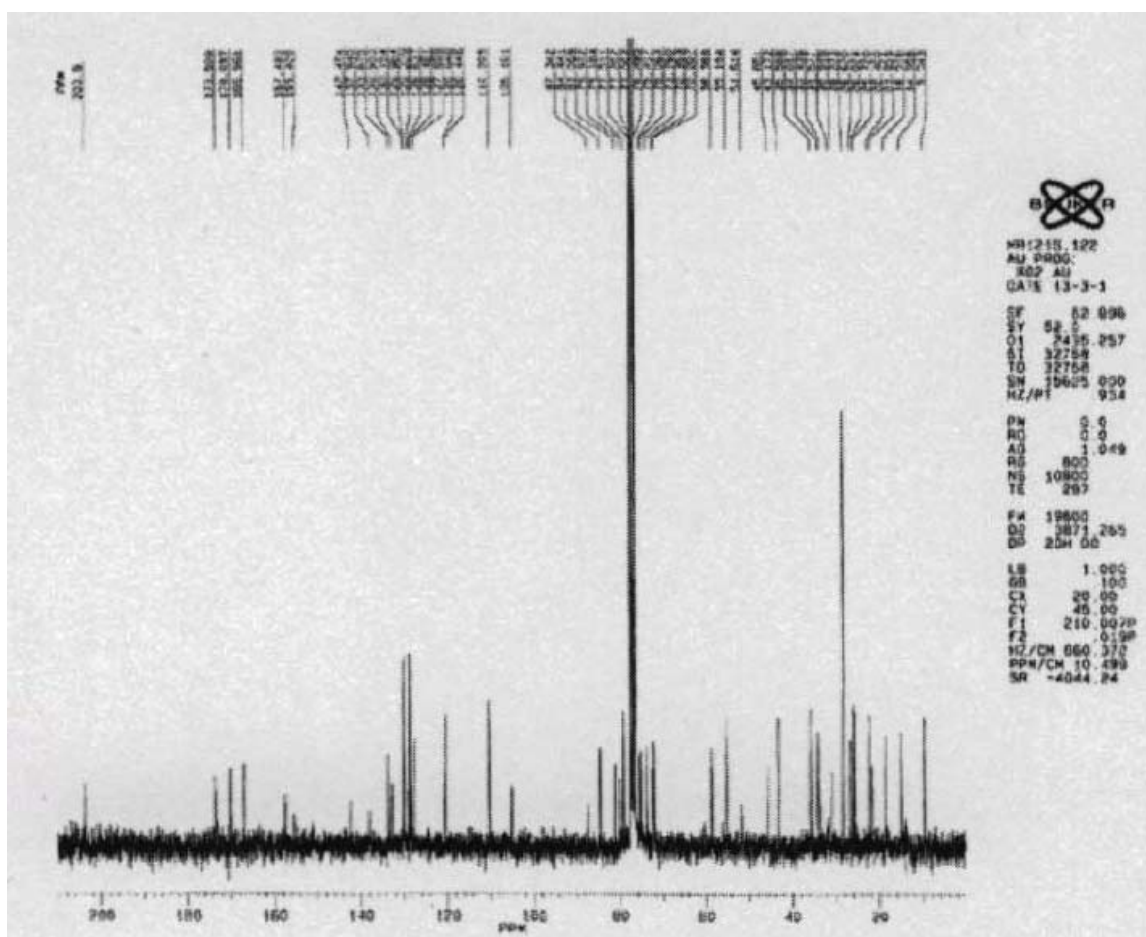
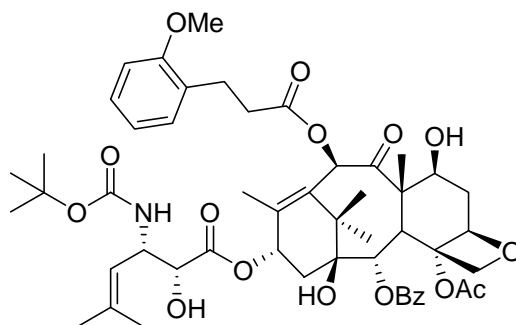
¹H NMR Spectrum of 6j



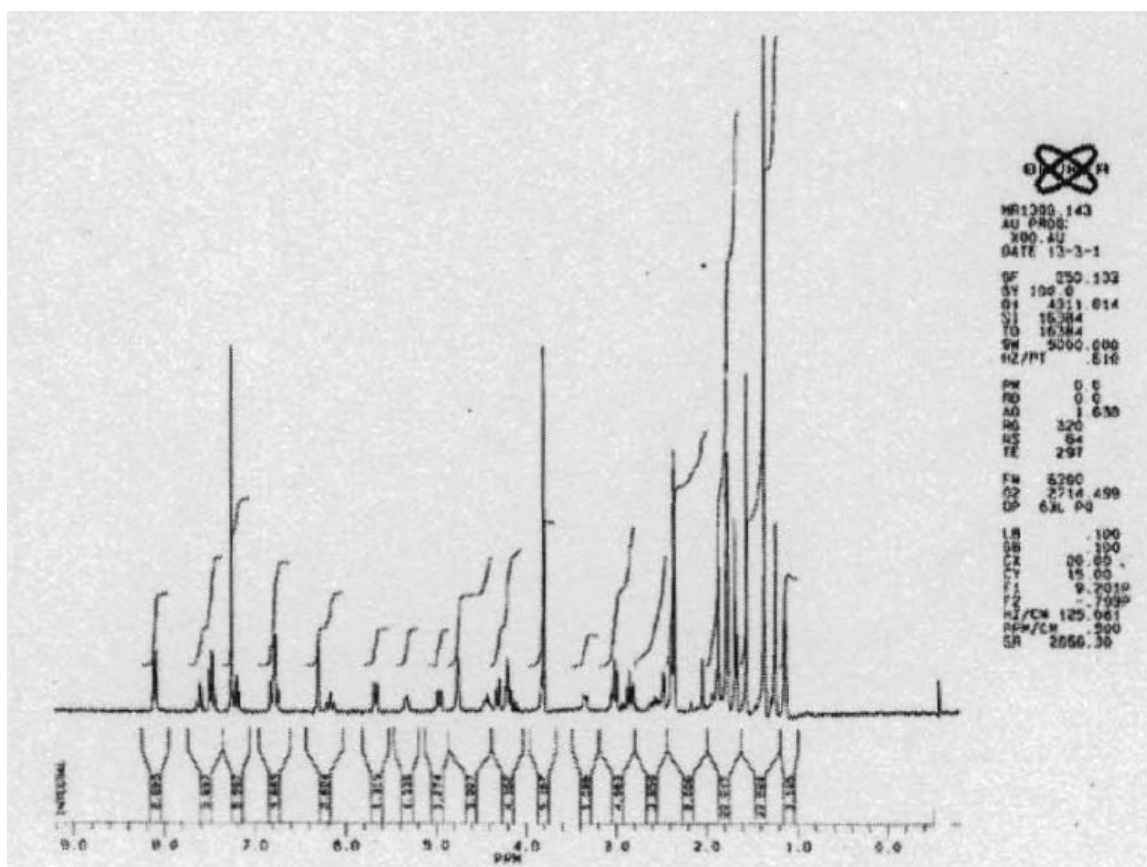
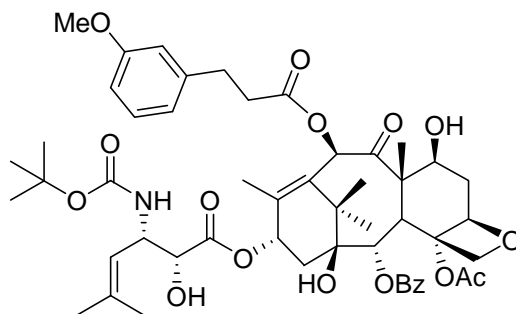
¹H NMR Spectrum of **6m**



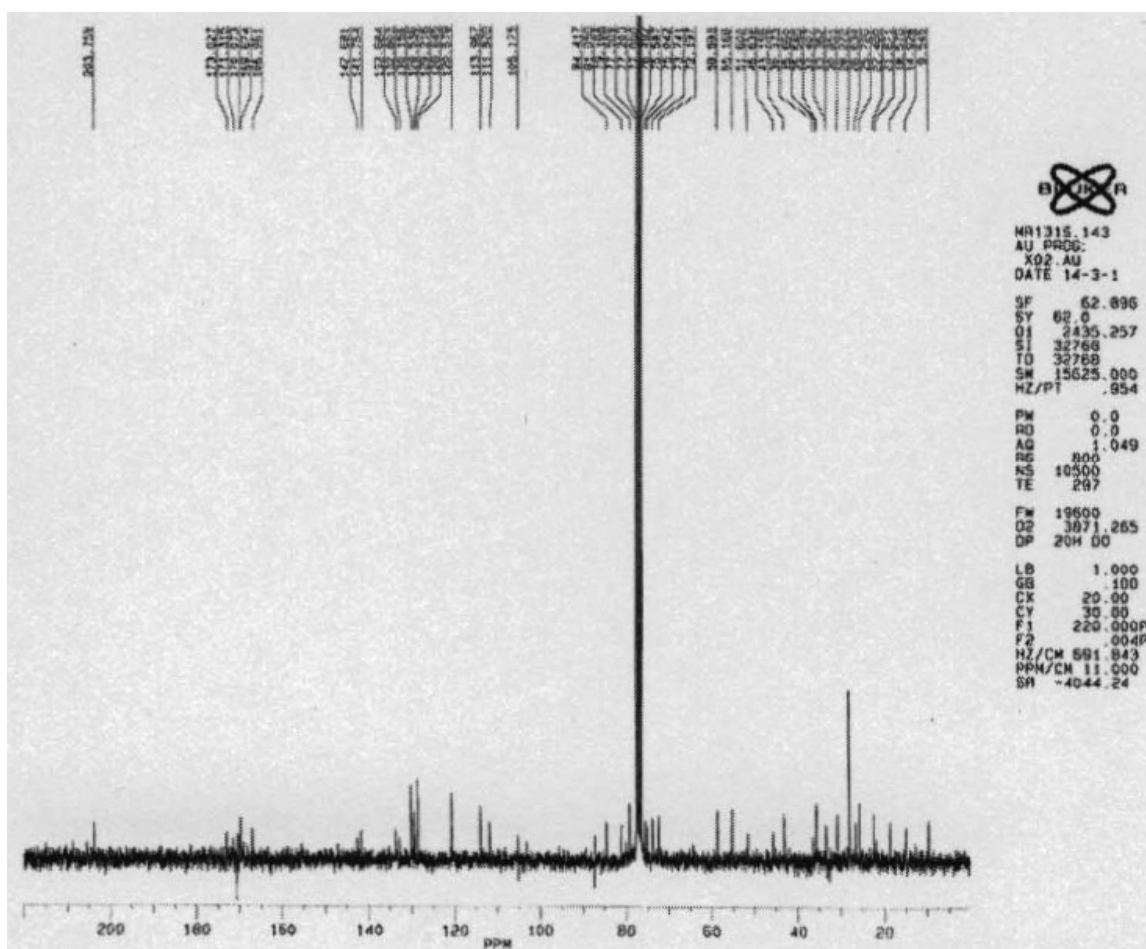
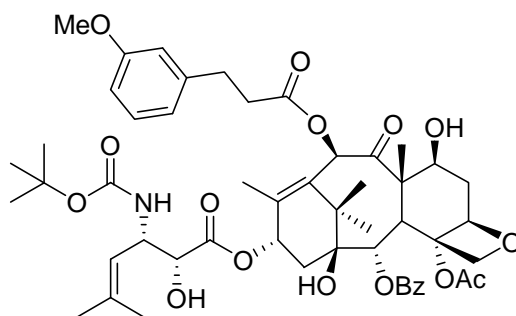
^{13}C NMR Spectrum of **6m**



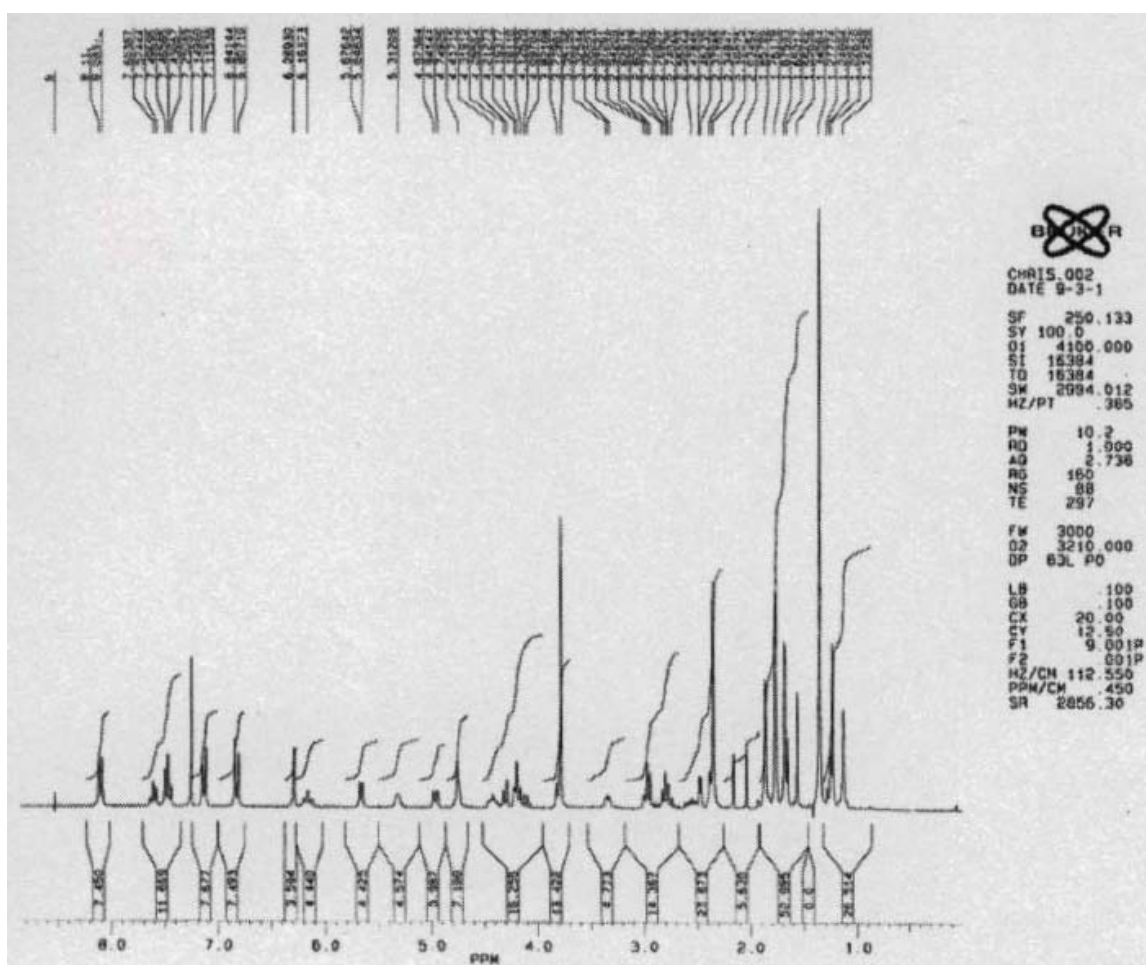
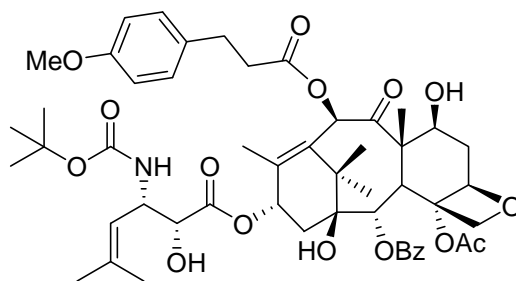
^1H NMR Spectrum of **6n**



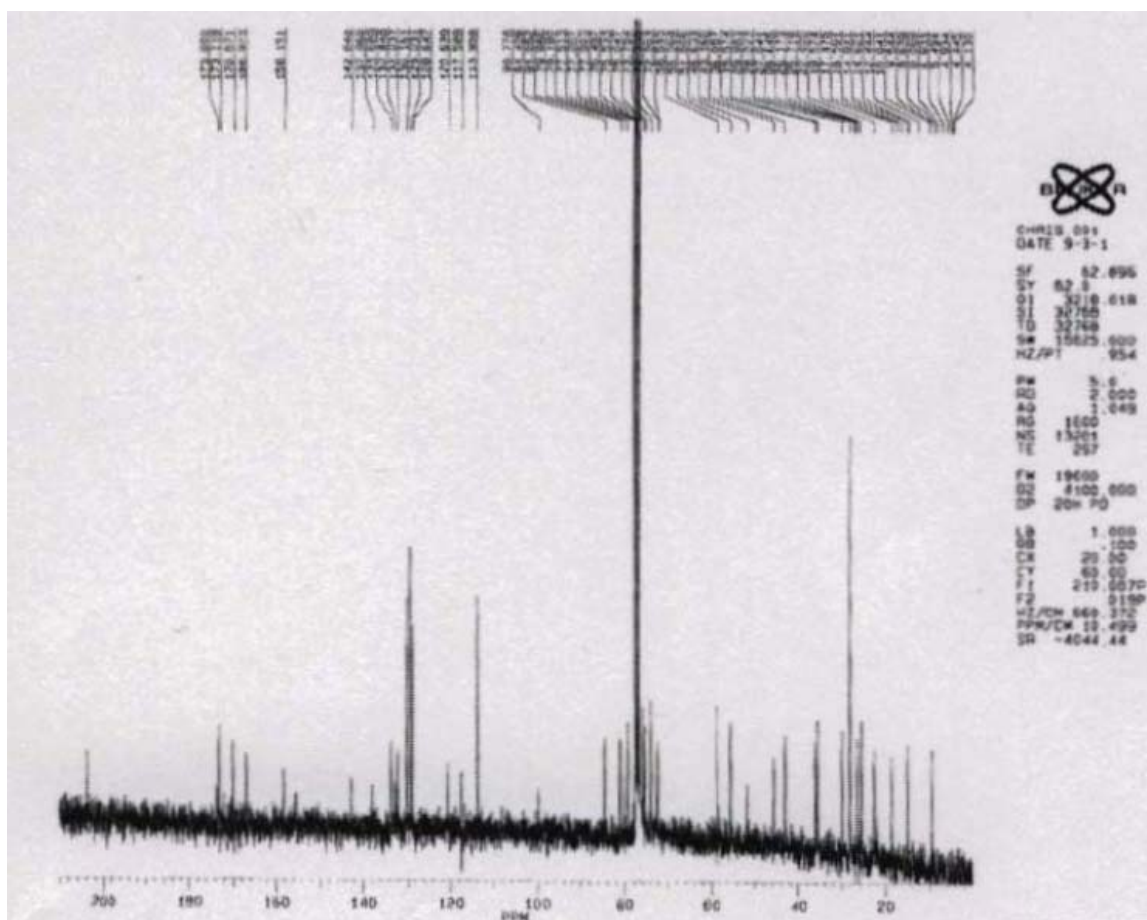
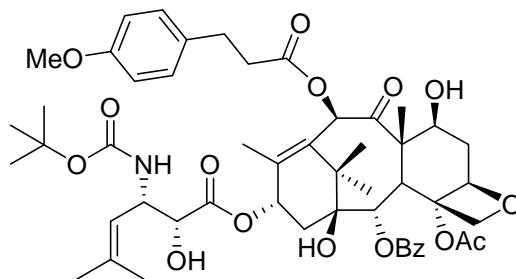
^{13}C NMR Spectrum of **6n**



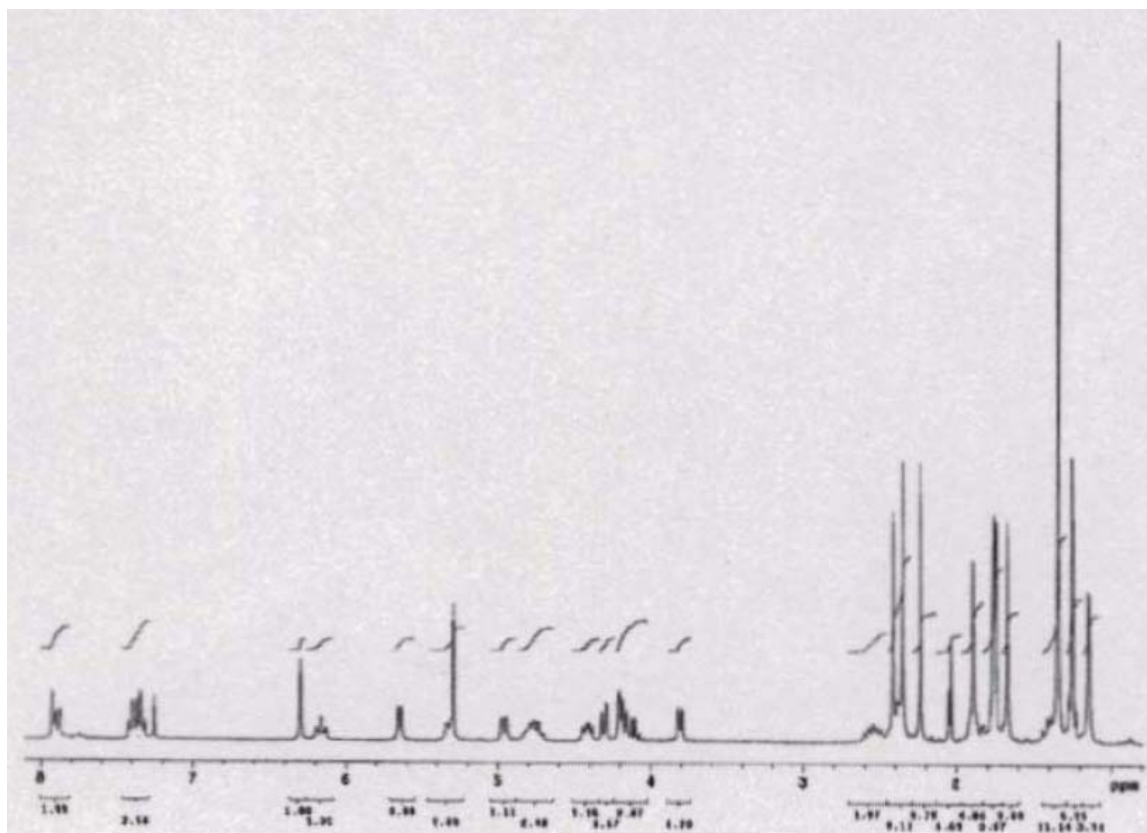
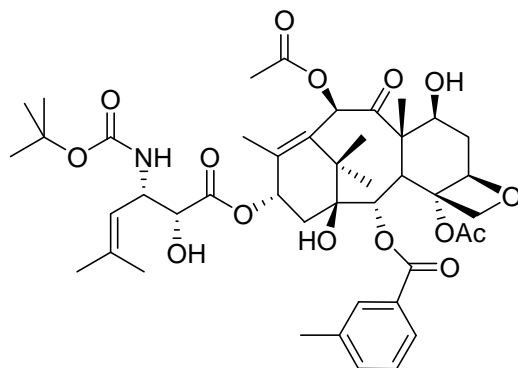
¹H NMR Spectrum of **60**



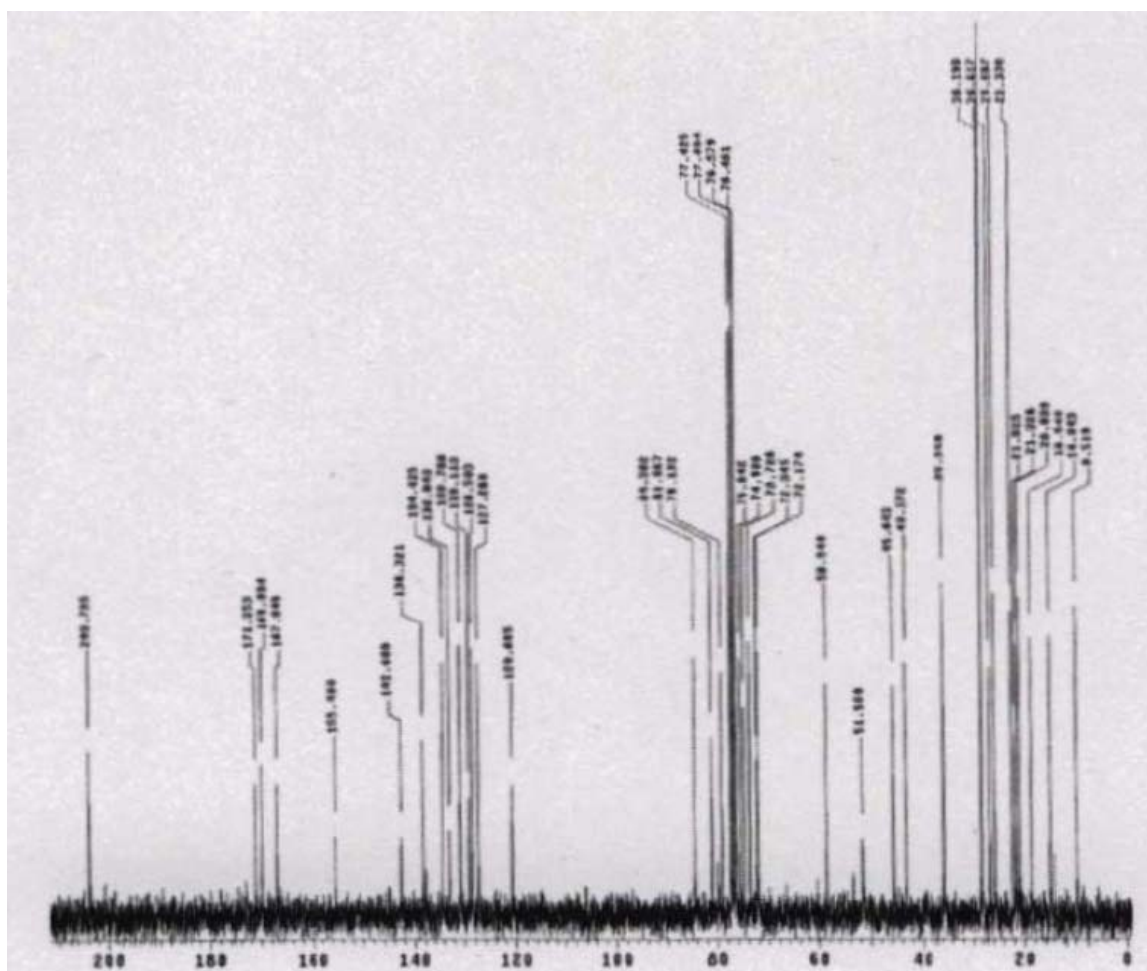
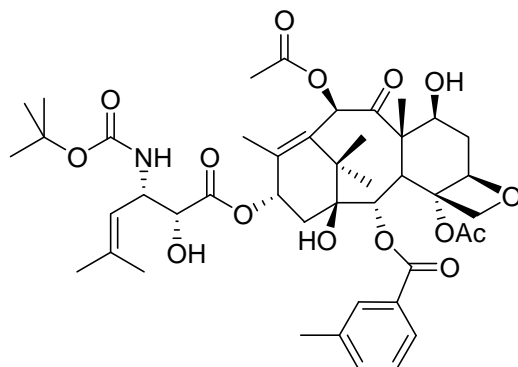
^{13}C NMR Spectrum of **60**



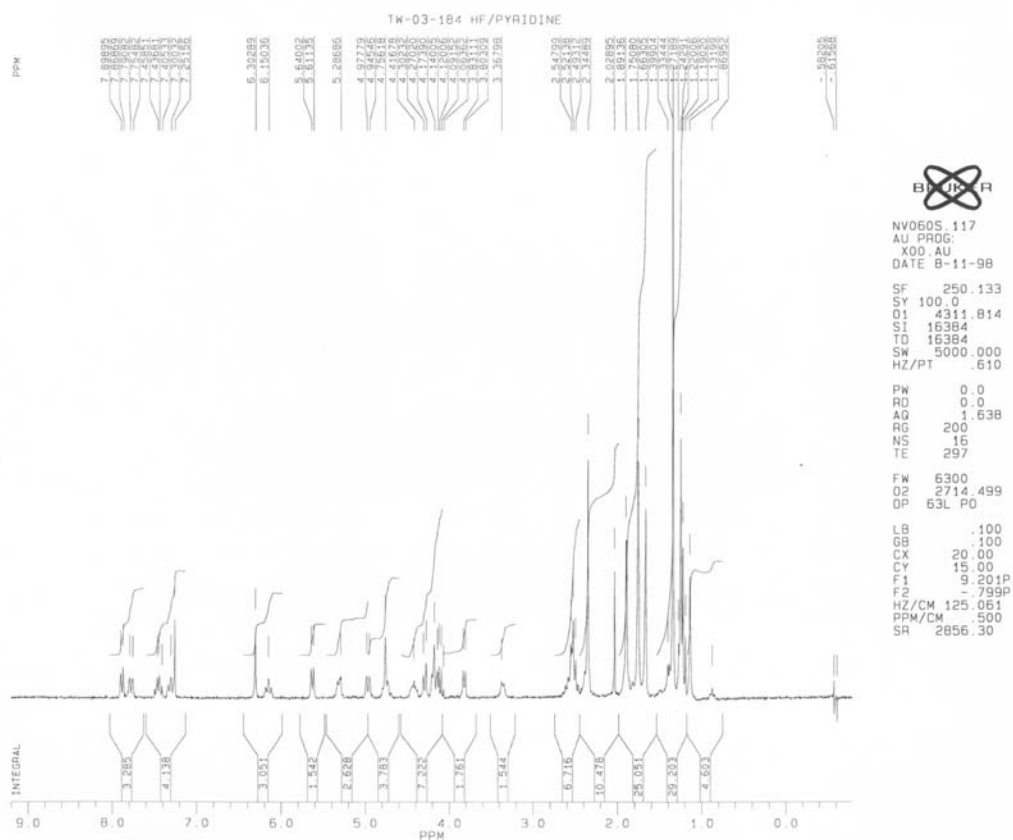
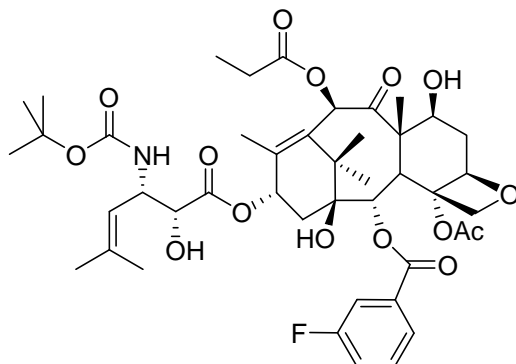
^1H NMR Spectrum of **14a**



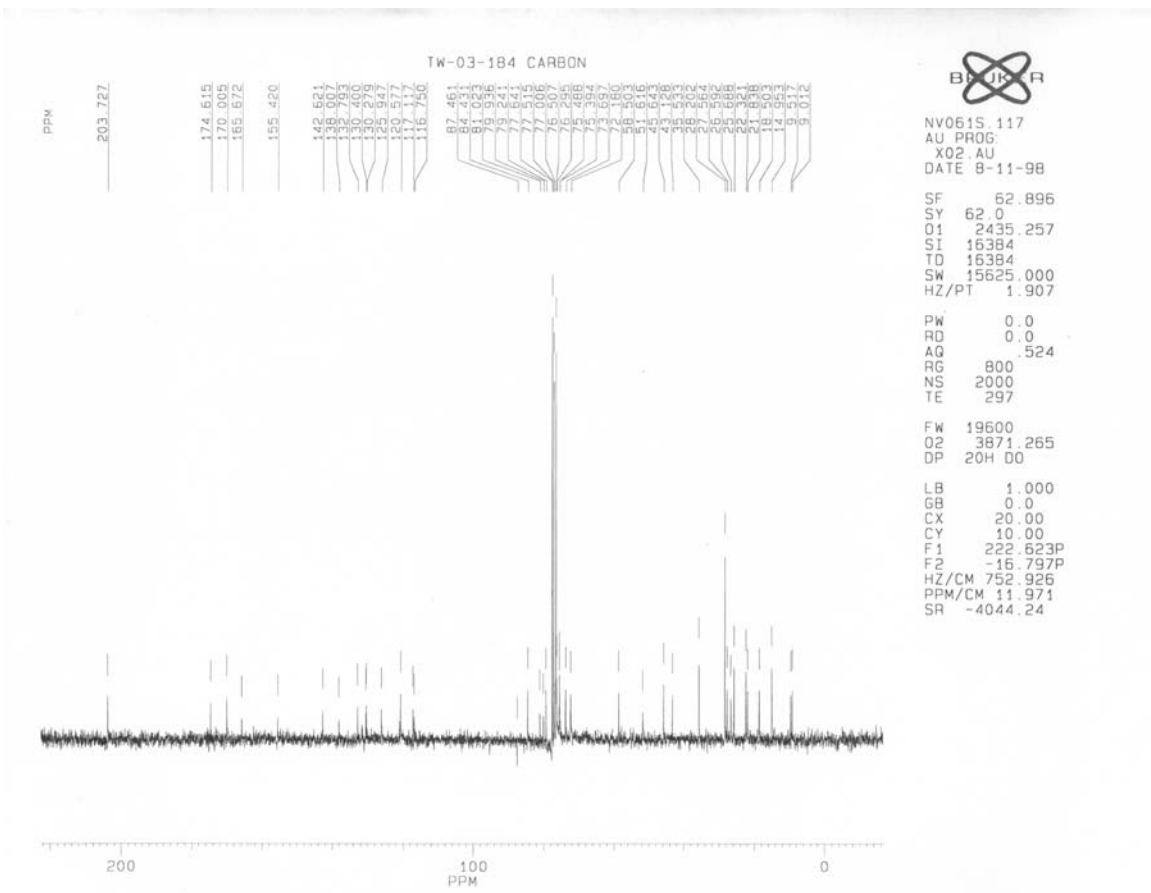
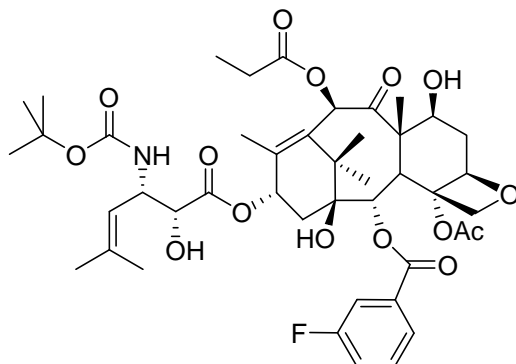
¹³C NMR Spectrum of 14a



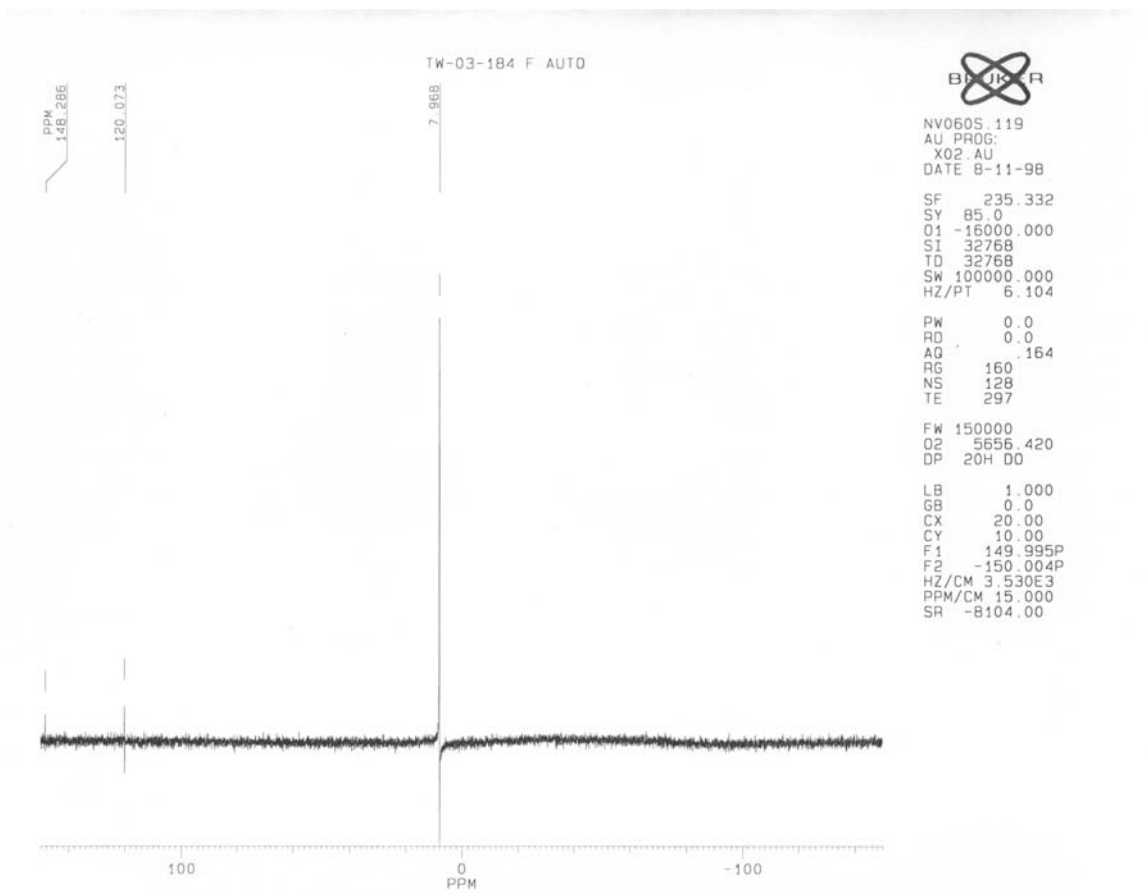
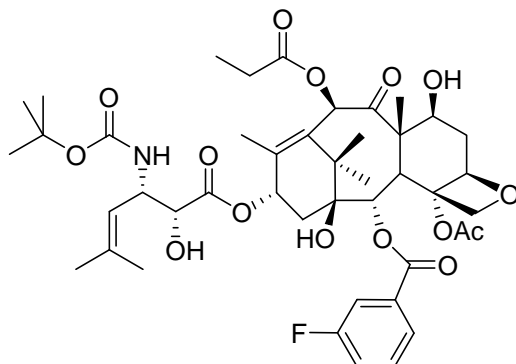
¹H NMR Spectrum of 14c



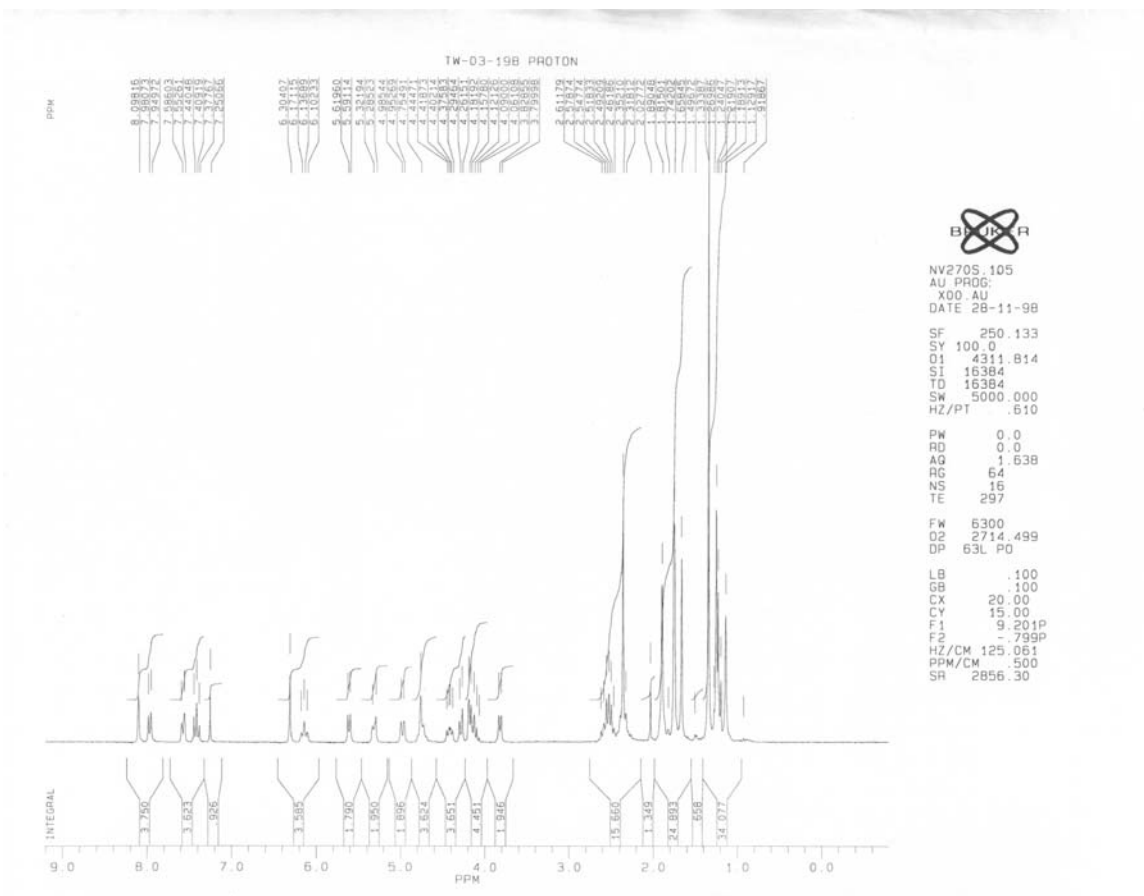
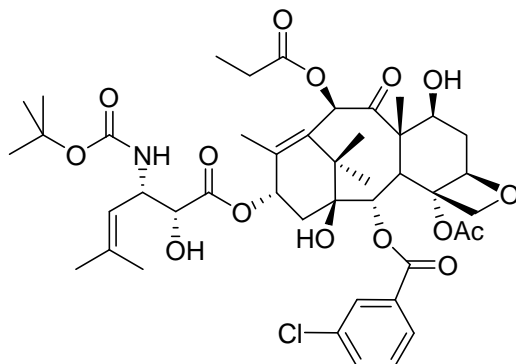
¹³C NMR Spectrum of 14c



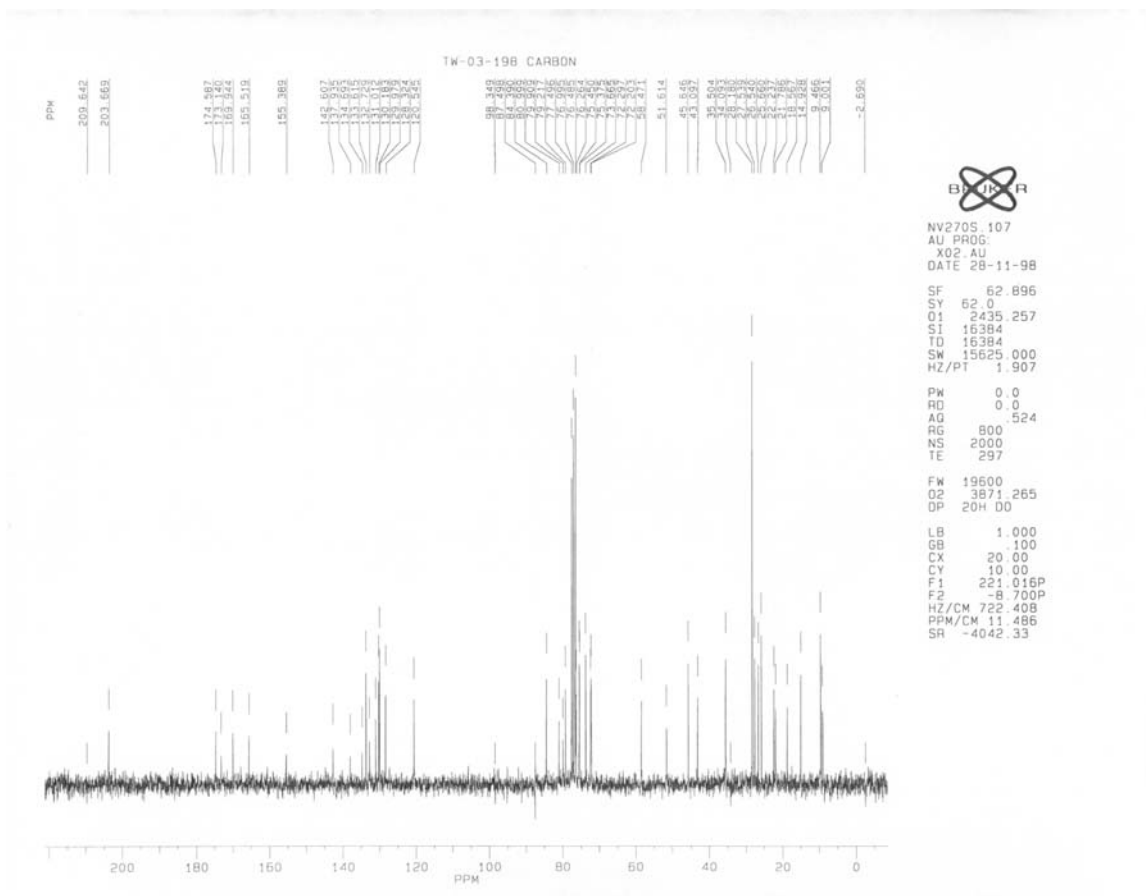
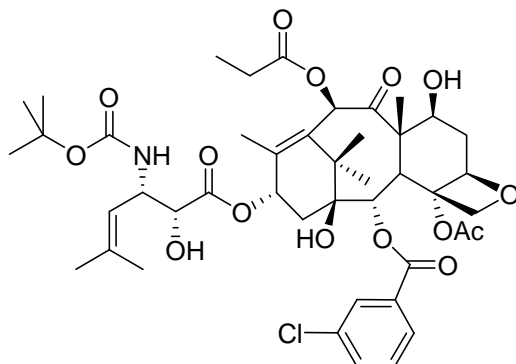
^{19}F NMR Spectrum of **14c**



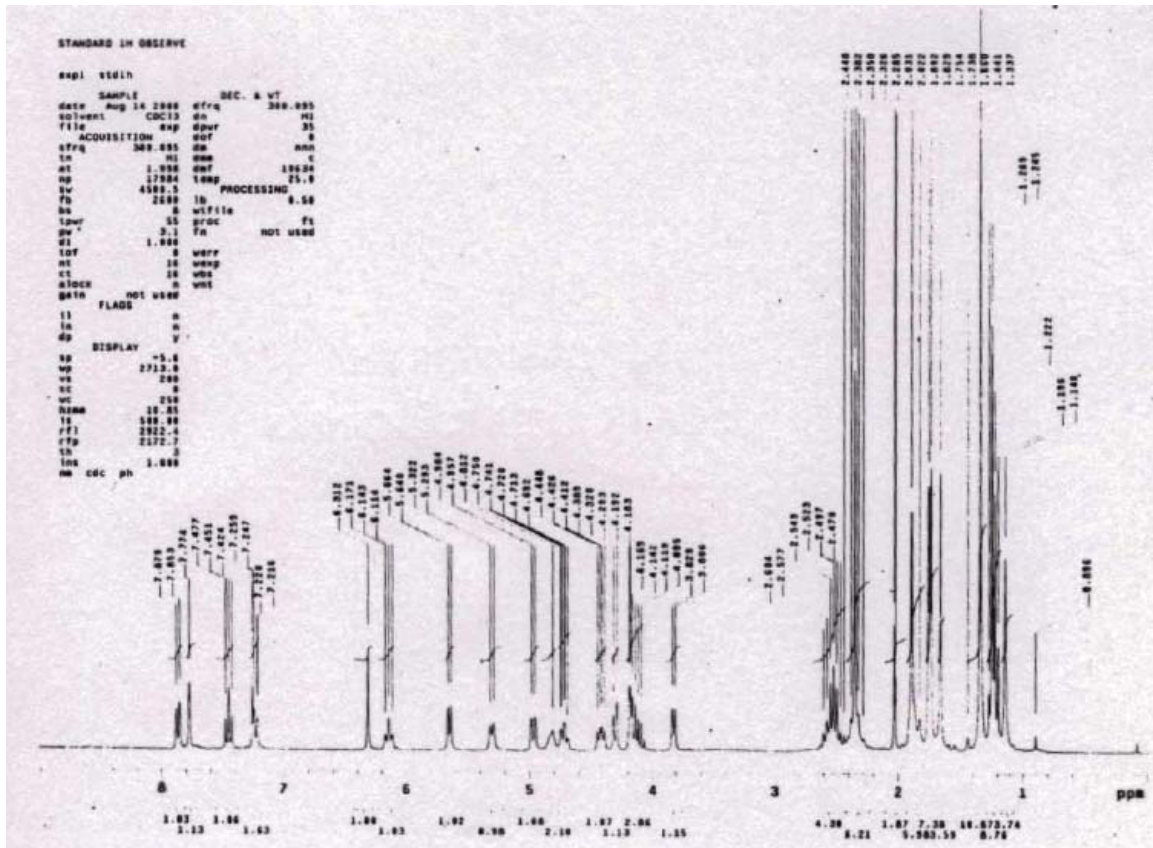
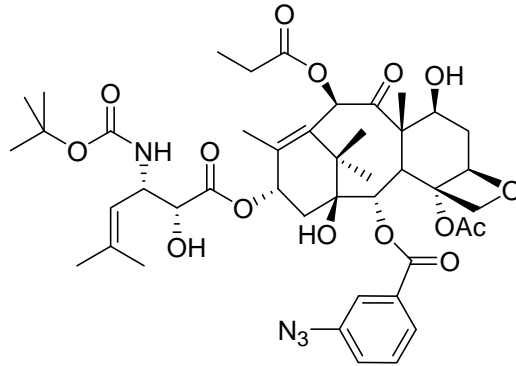
¹H NMR Spectrum of 14d



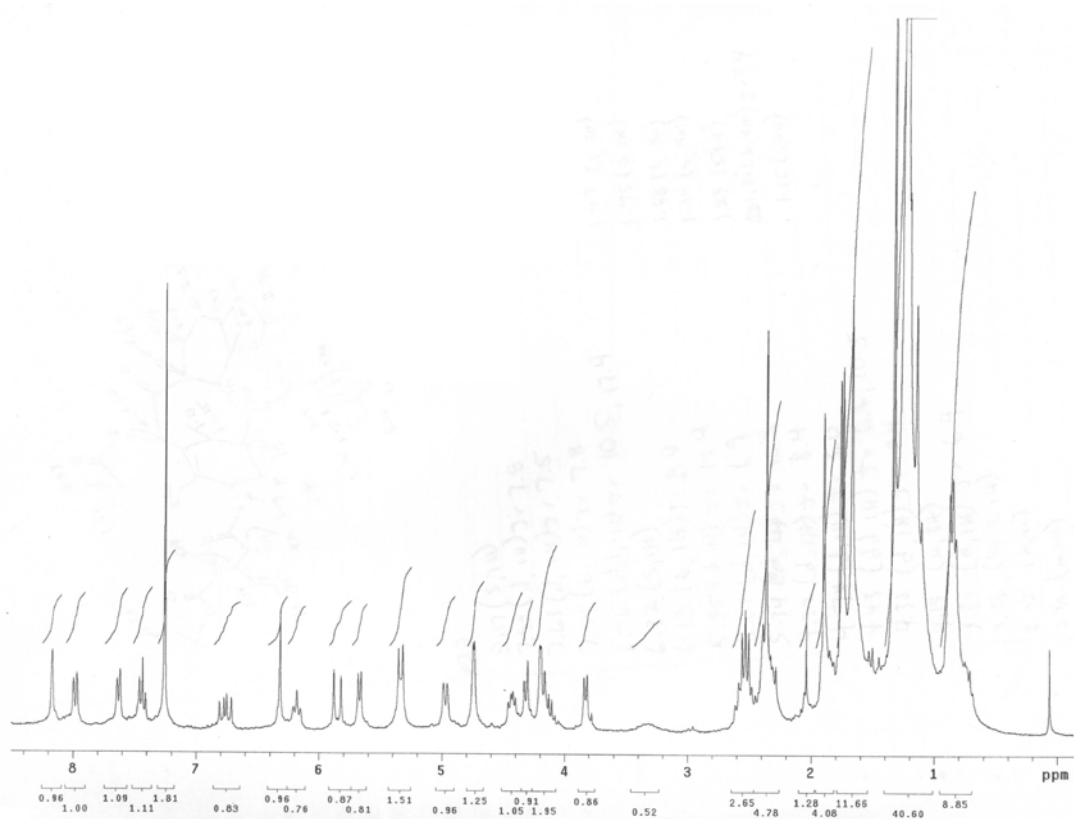
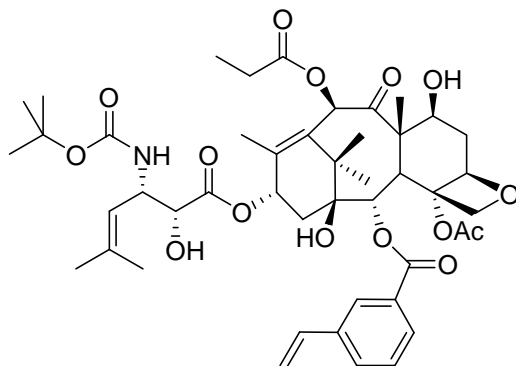
¹³C NMR Spectrum of **14d**



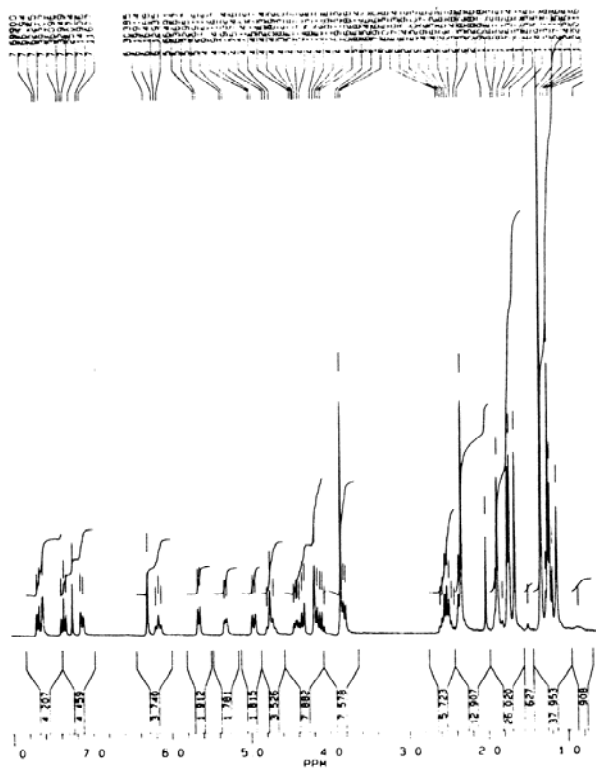
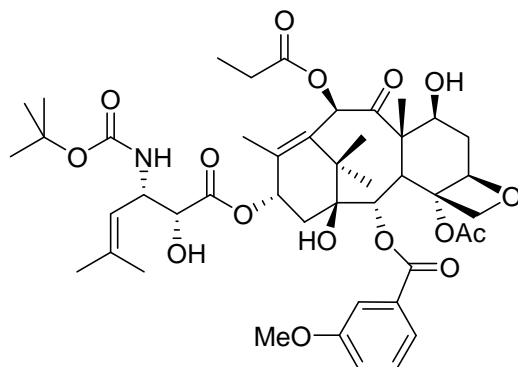
¹H NMR Spectrum of 14e



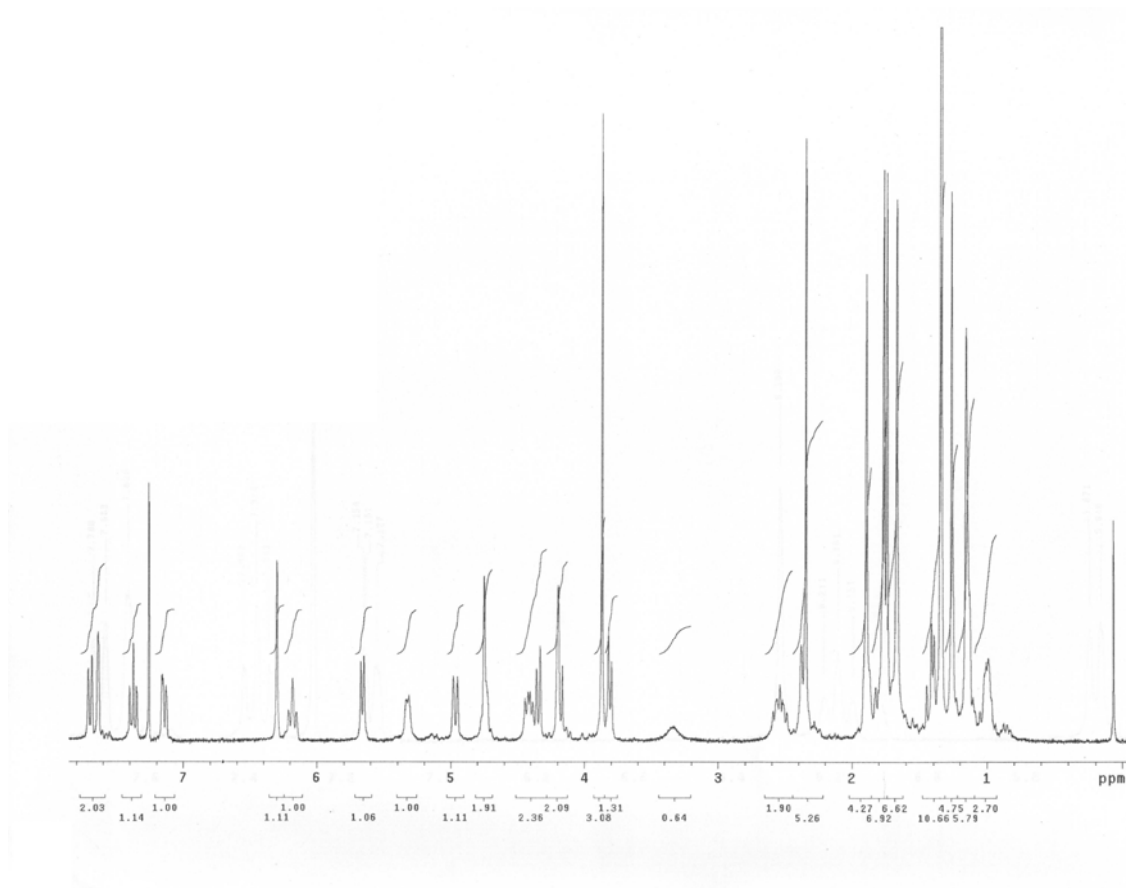
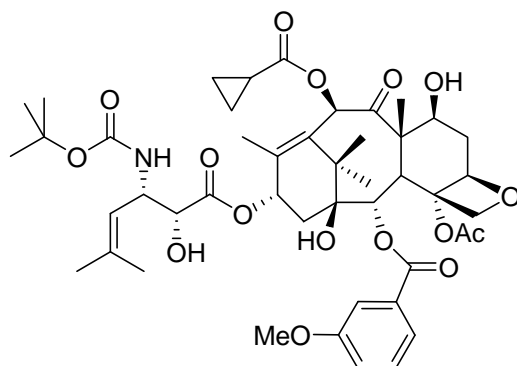
^1H NMR Spectrum of **14f**



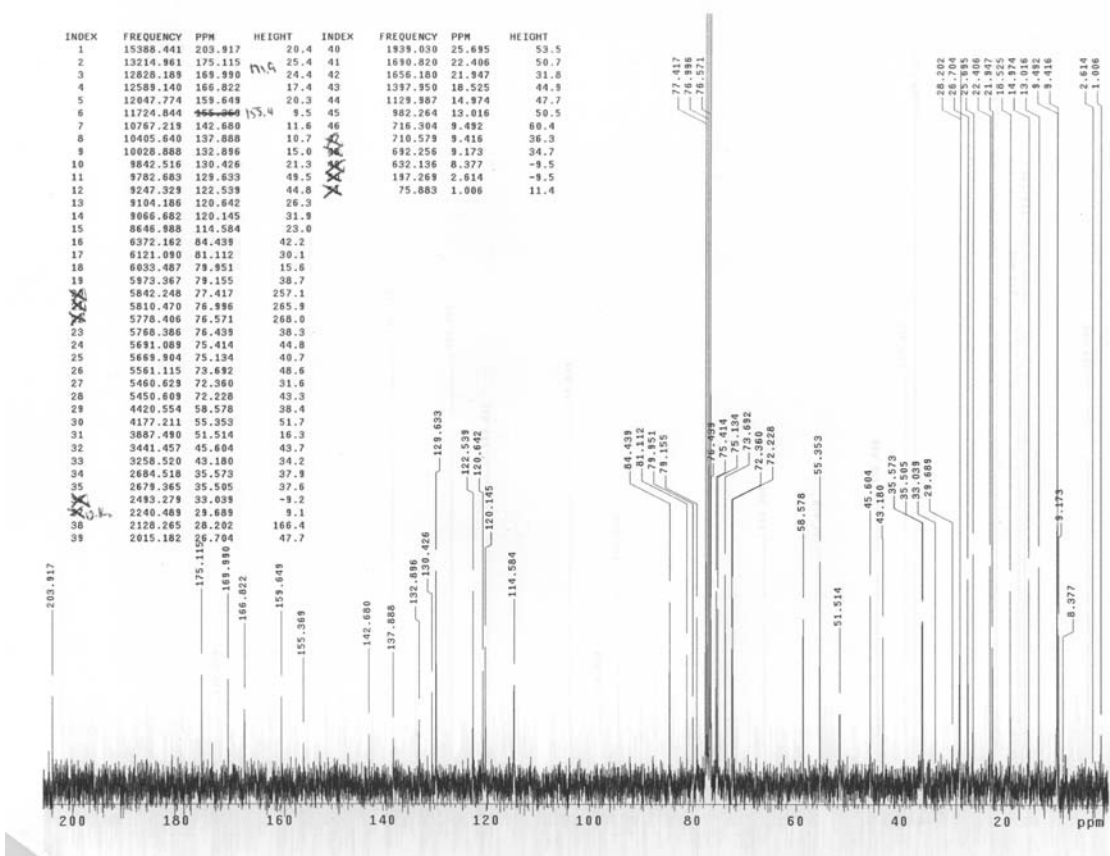
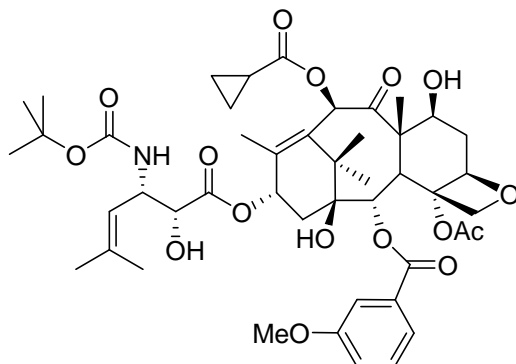
^1H NMR Spectrum of **14g**



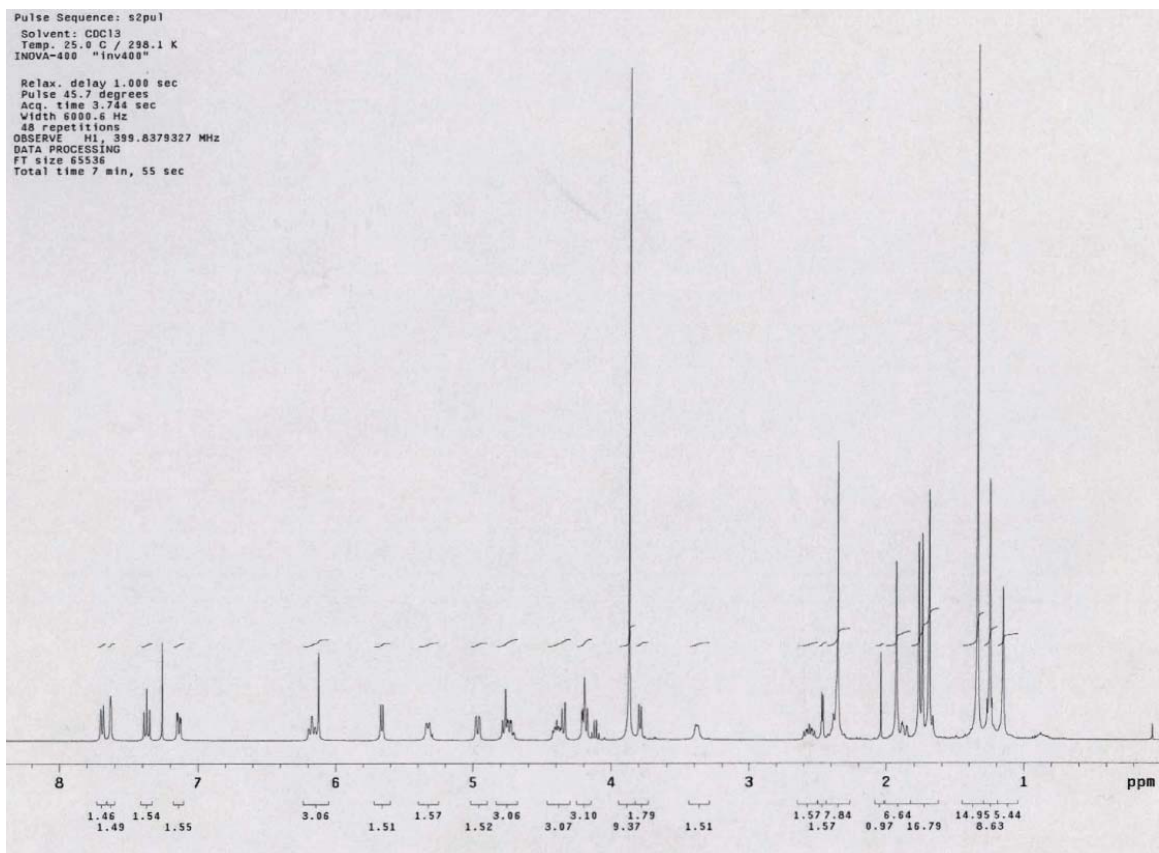
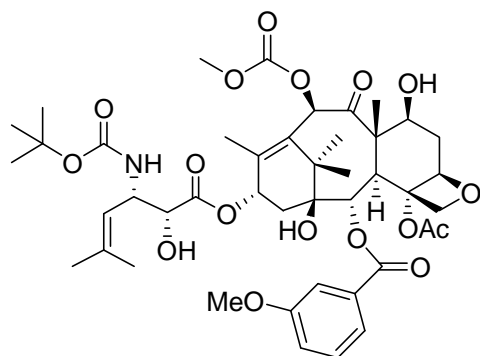
¹H NMR Spectrum of **14h**



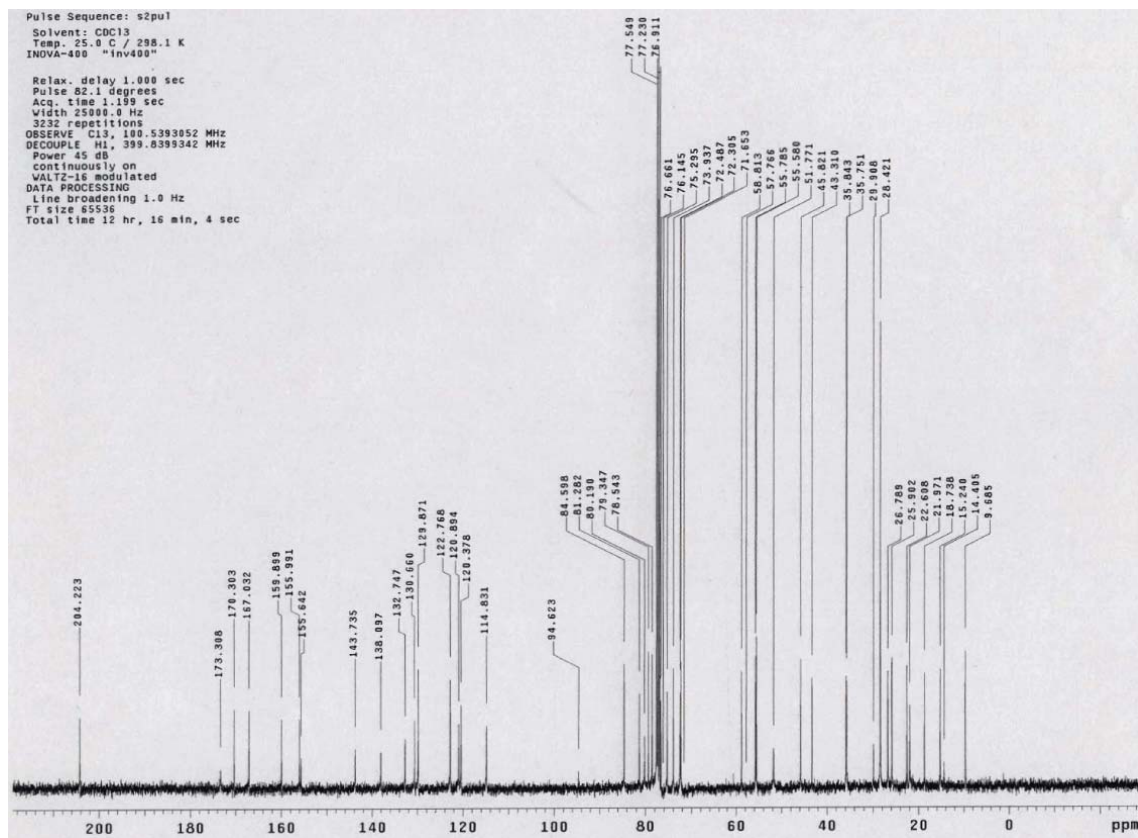
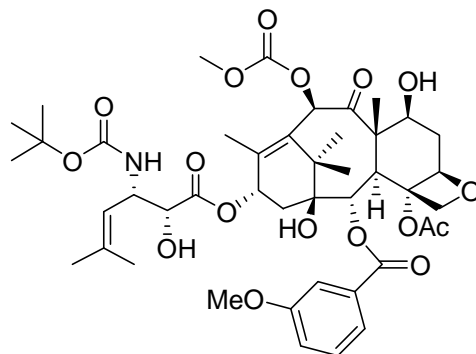
¹H NMR Spectrum of 14h



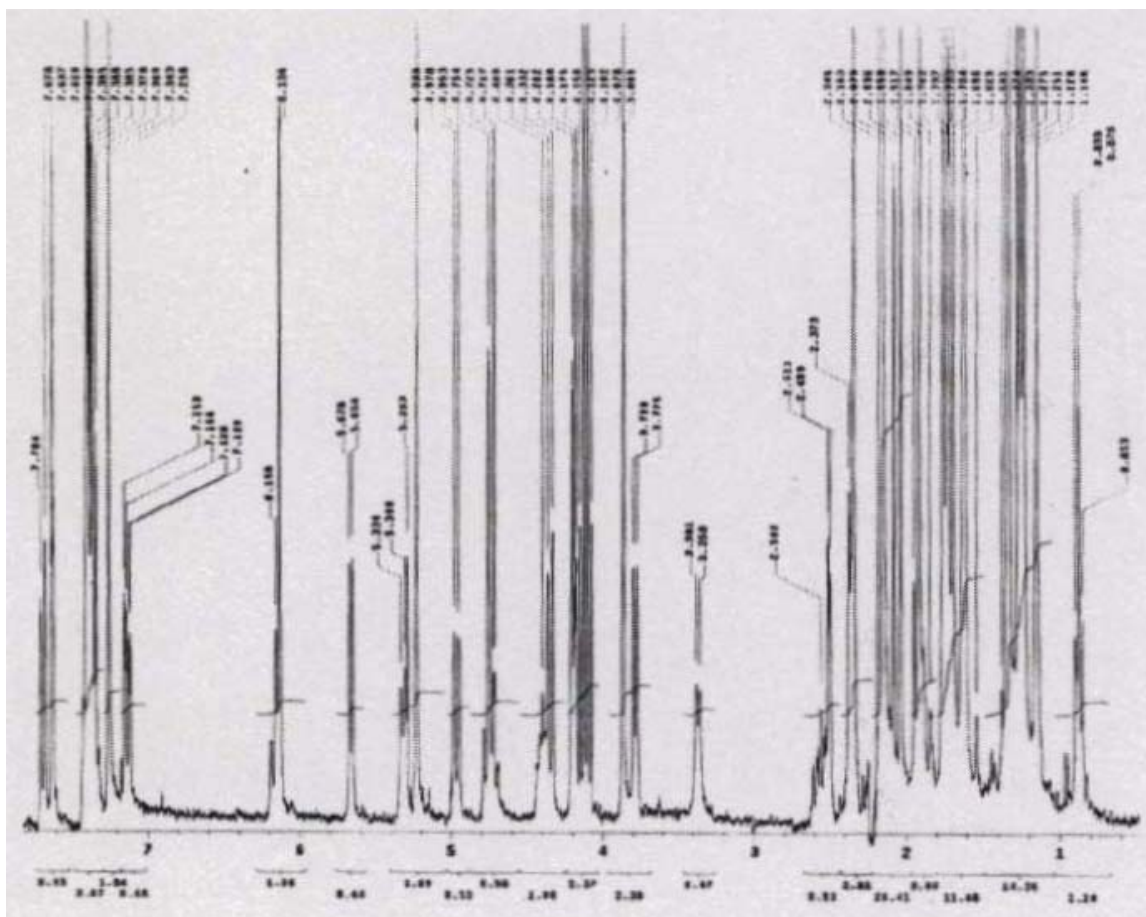
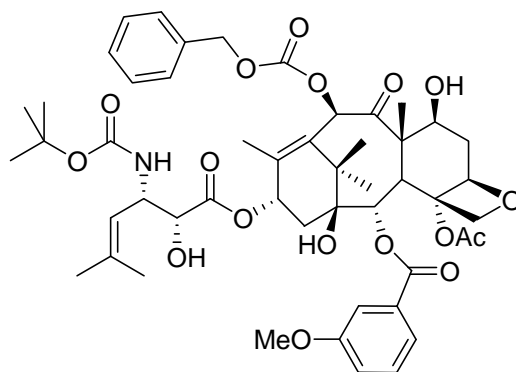
^1H NMR Spectrum of **14i**



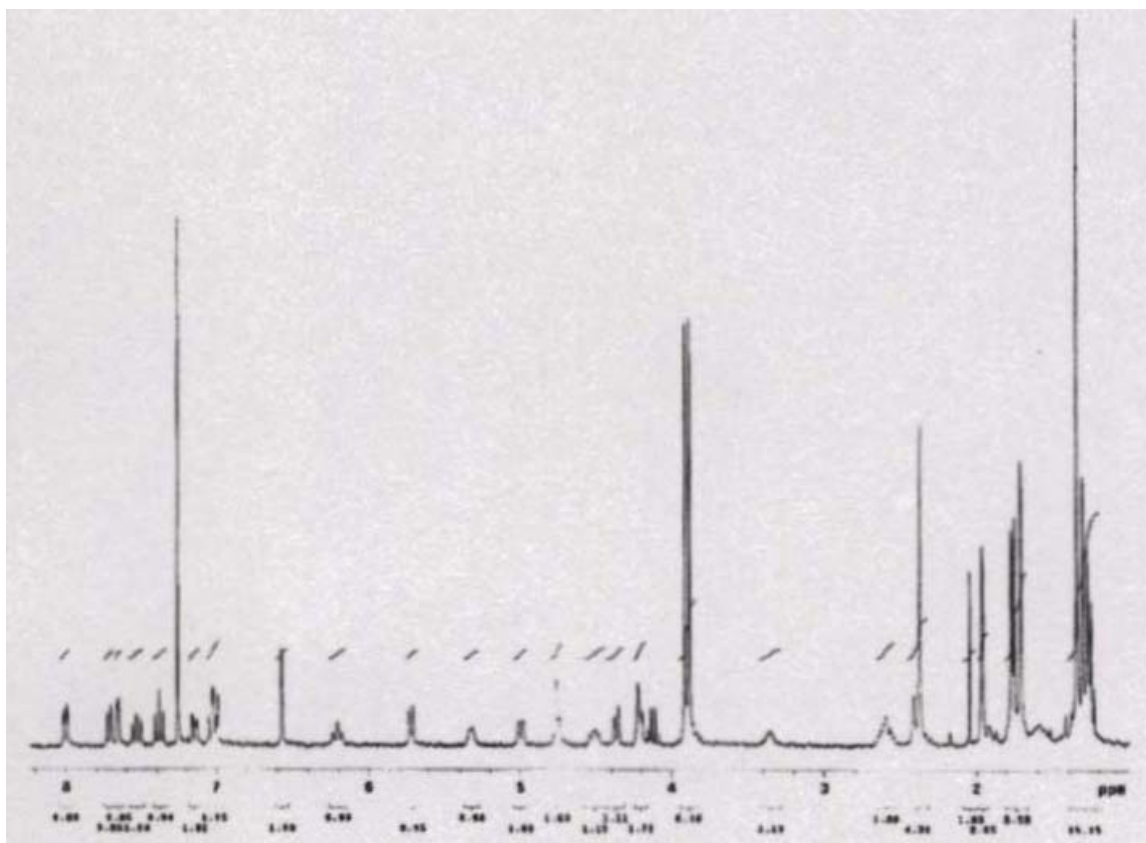
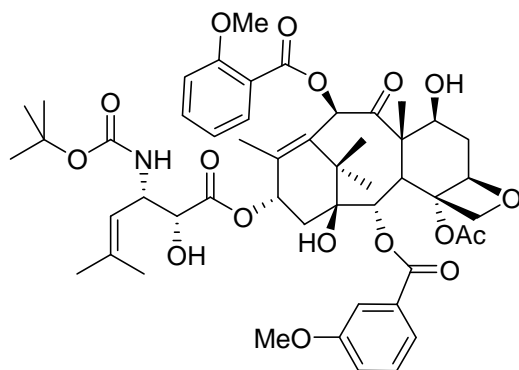
¹³C NMR Spectrum of 14i



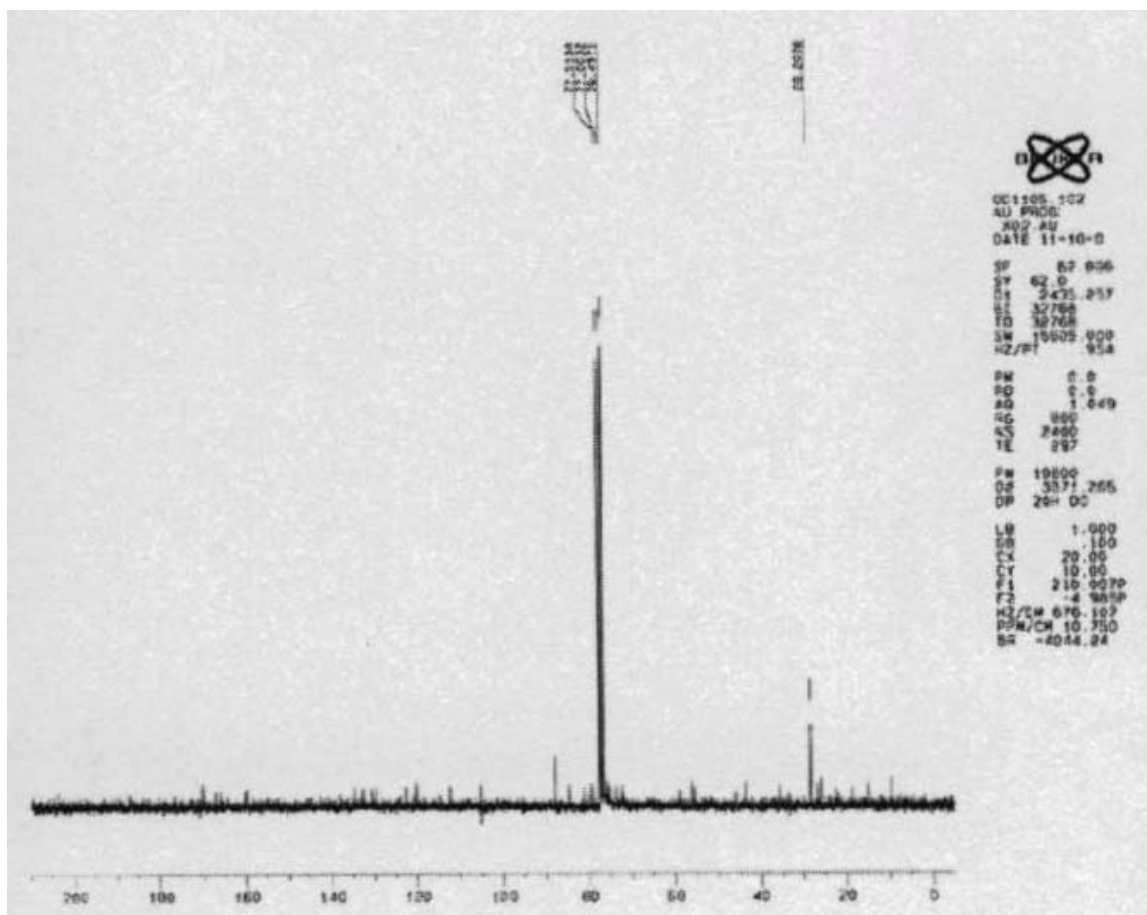
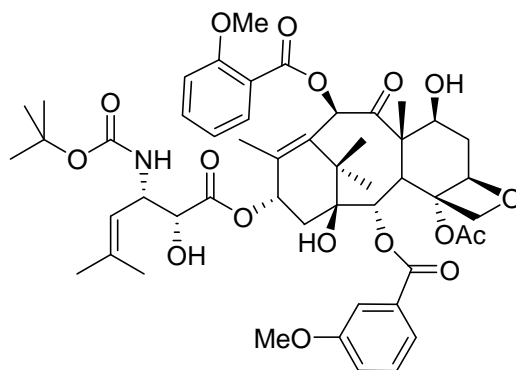
¹H NMR Spectrum of **14j**



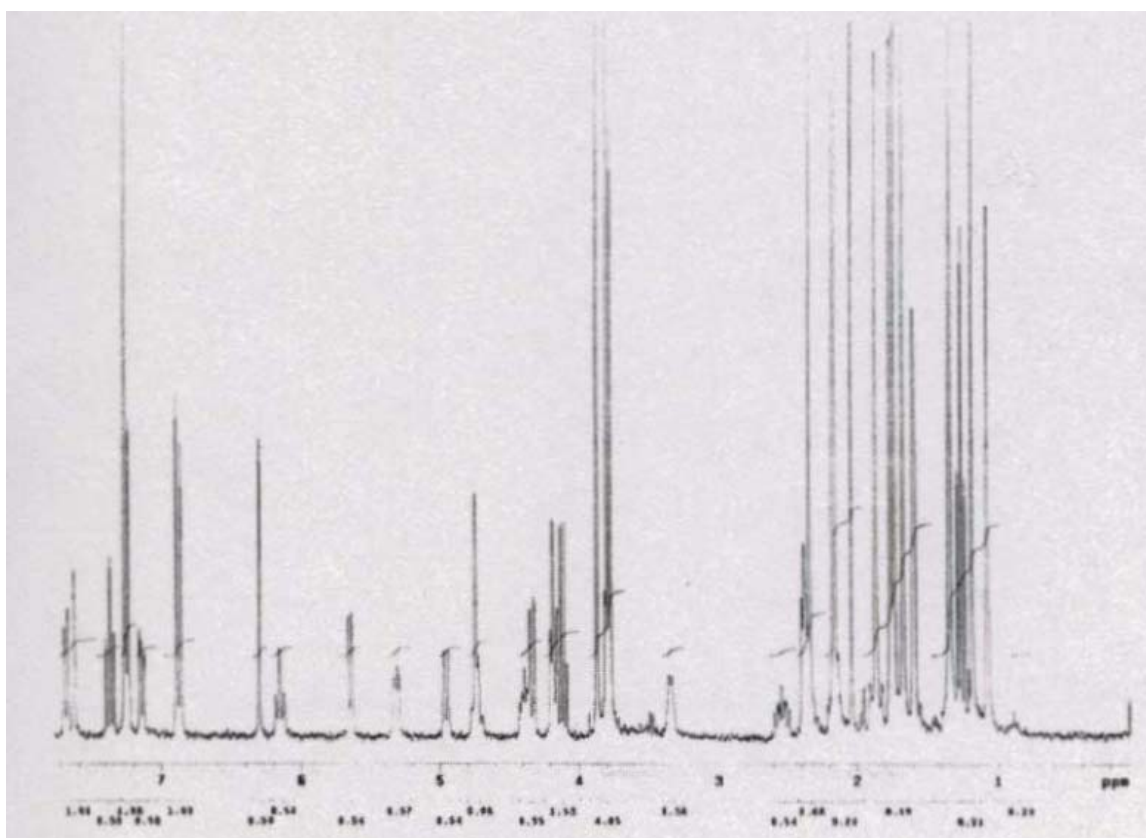
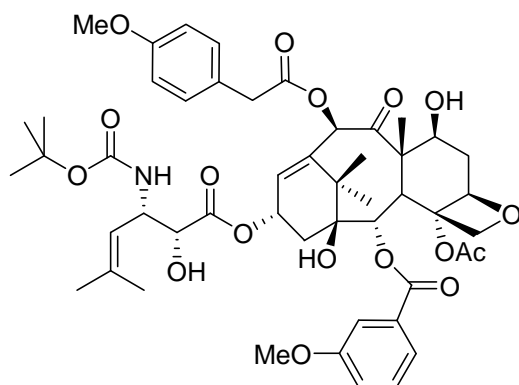
^1H NMR Spectrum of **14k**



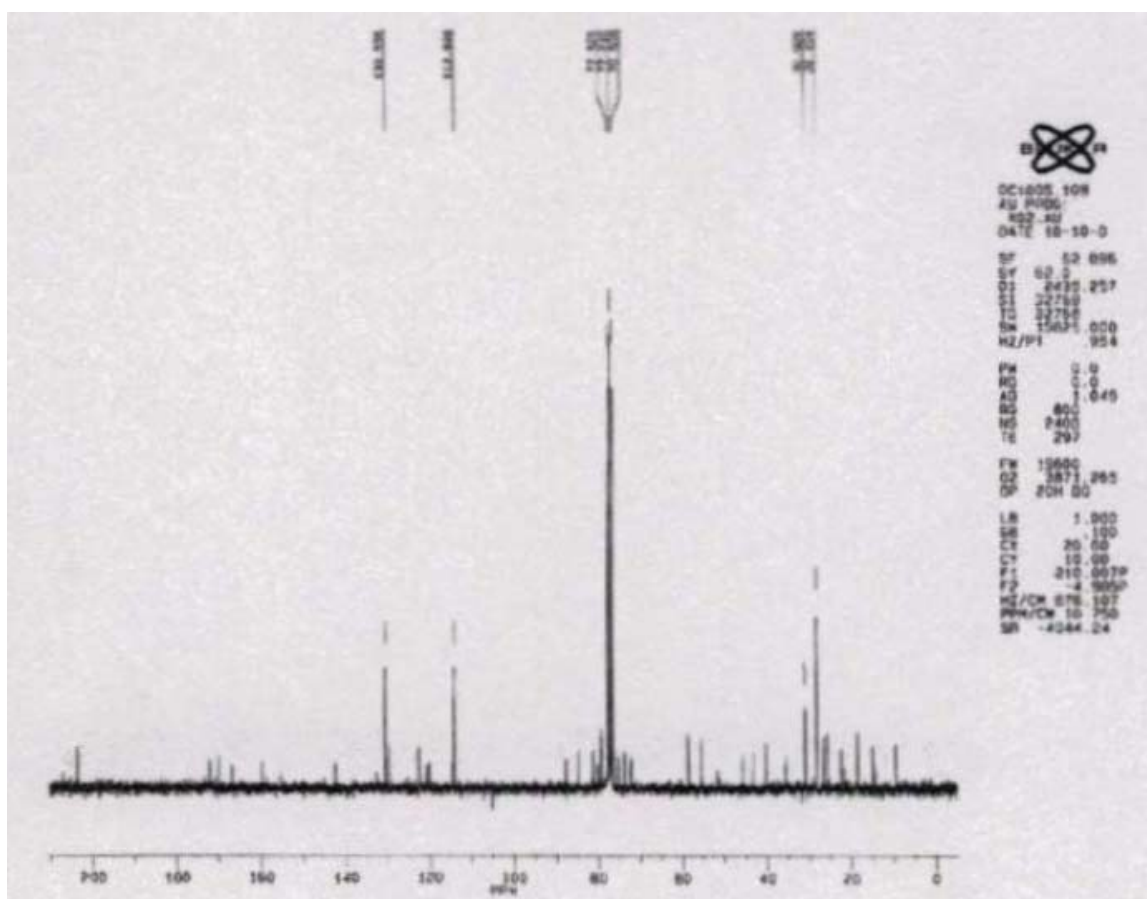
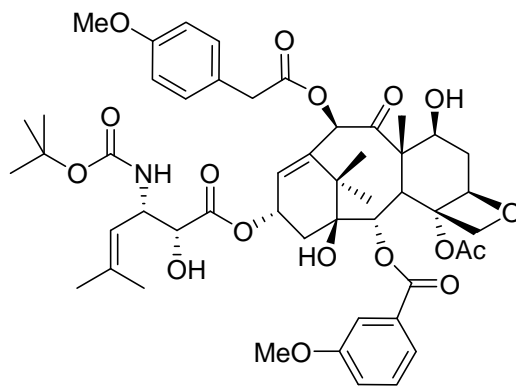
^{13}C NMR Spectrum of **14k**



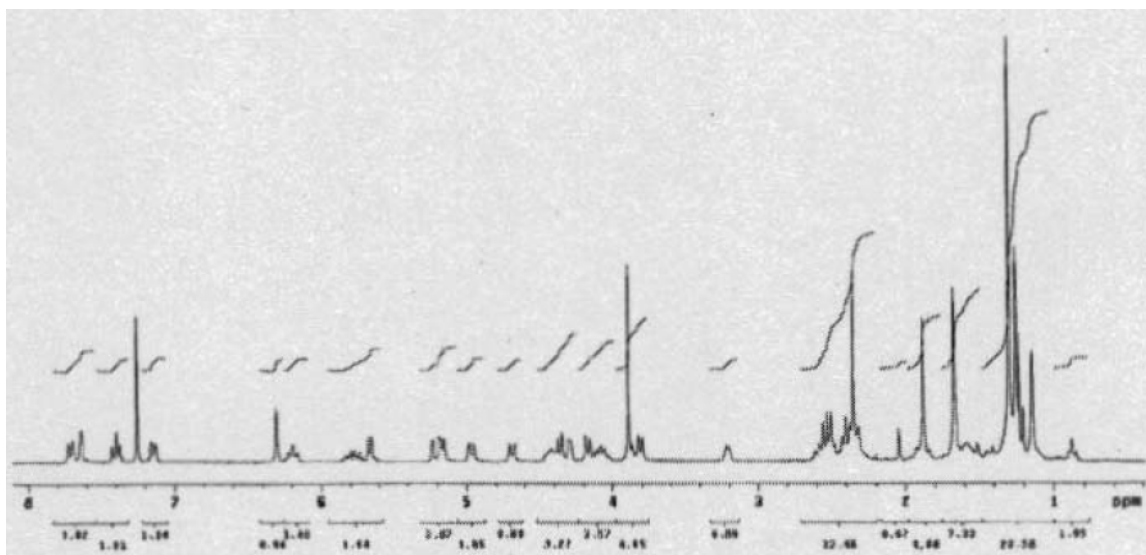
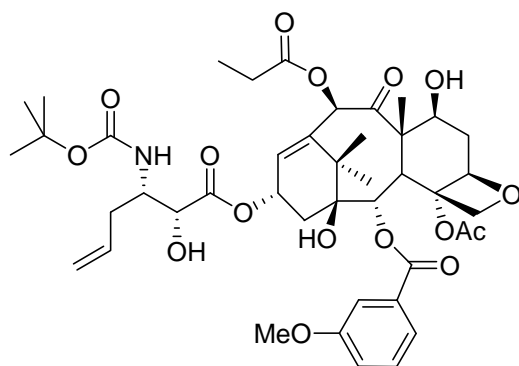
^1H NMR Spectrum of **14l**



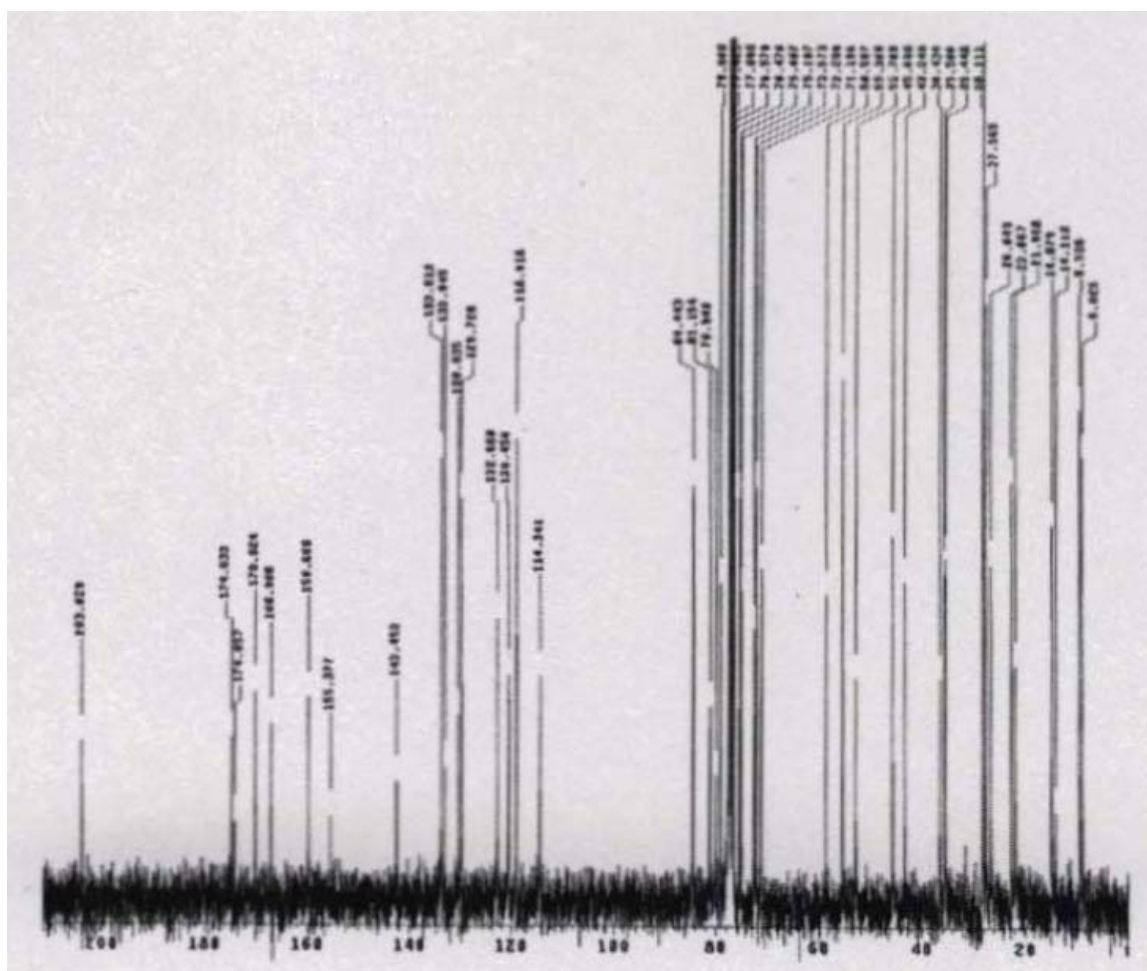
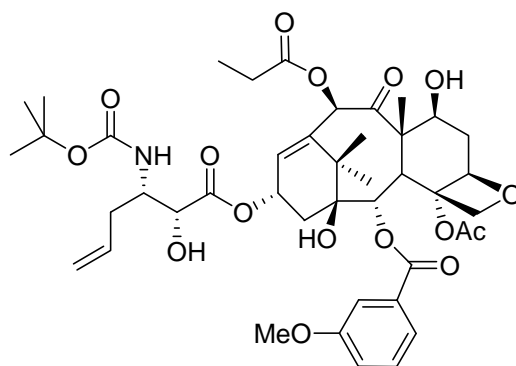
^{13}C NMR Spectrum of **14l**



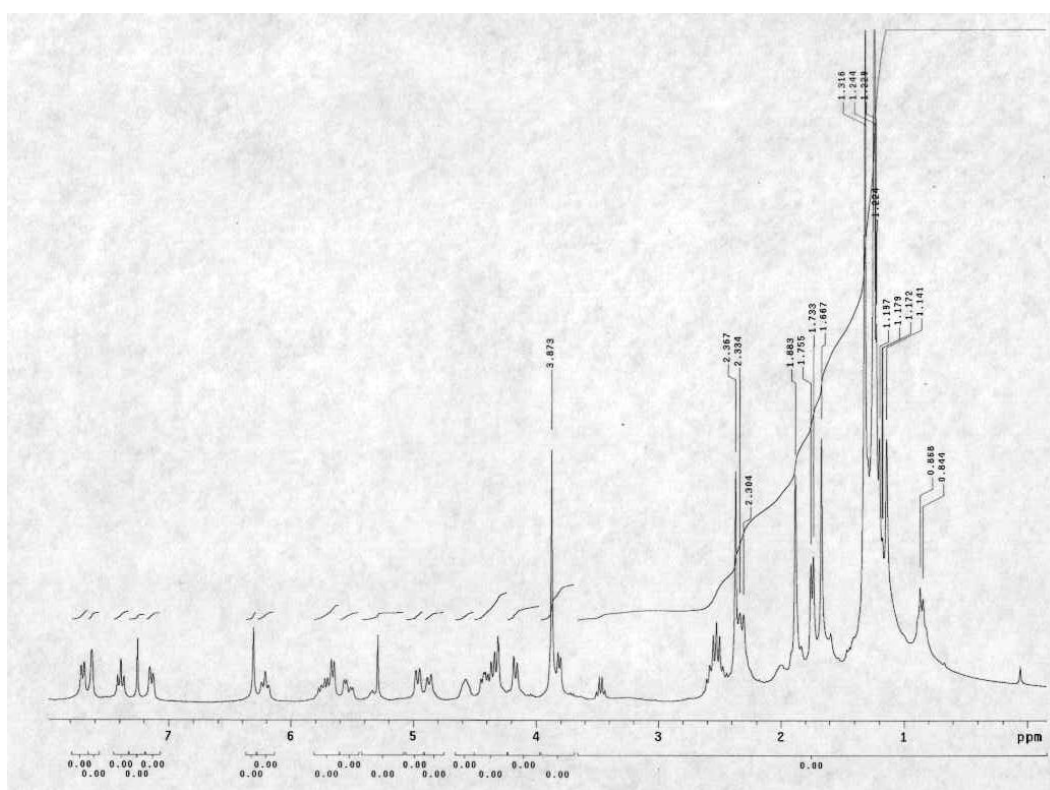
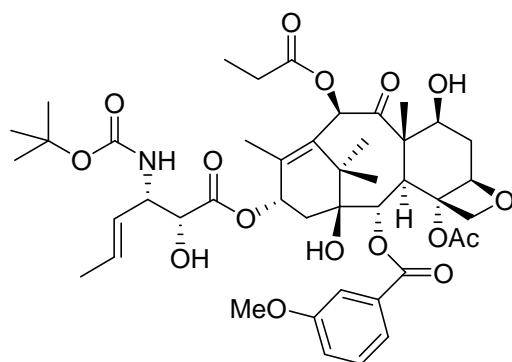
^1H NMR Spectrum of **14m**



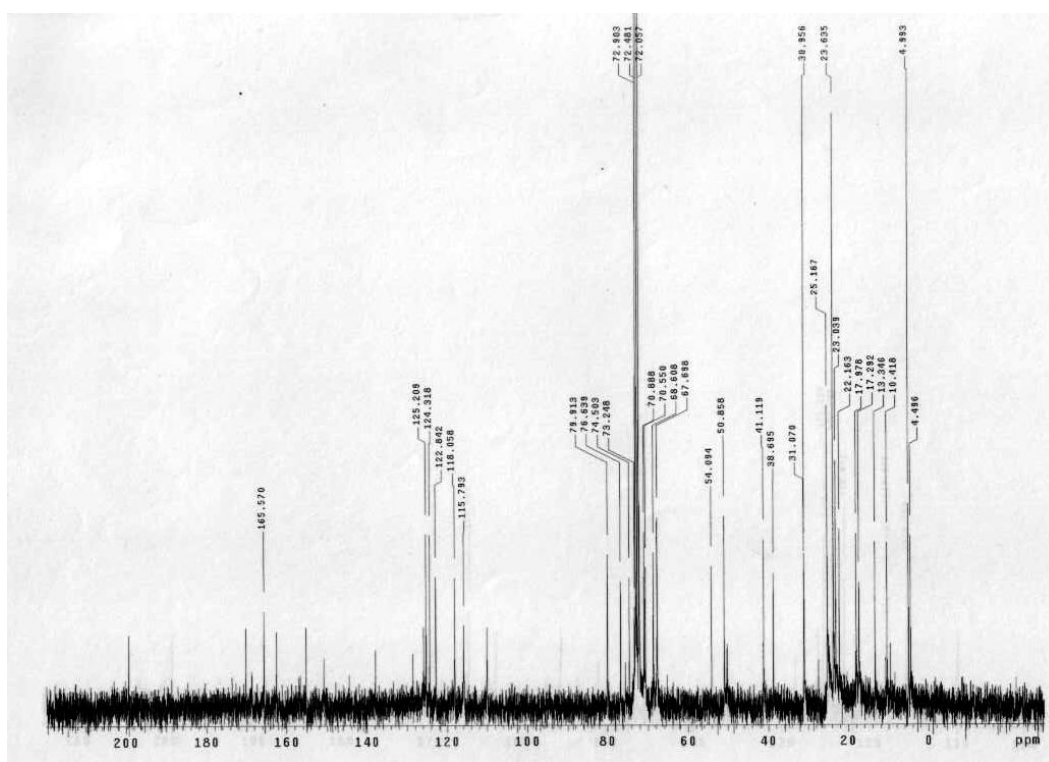
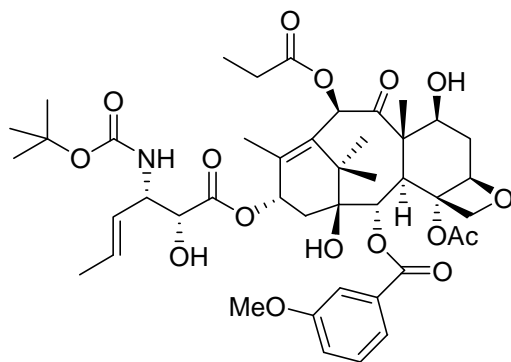
^{13}C NMR Spectrum of **14m**



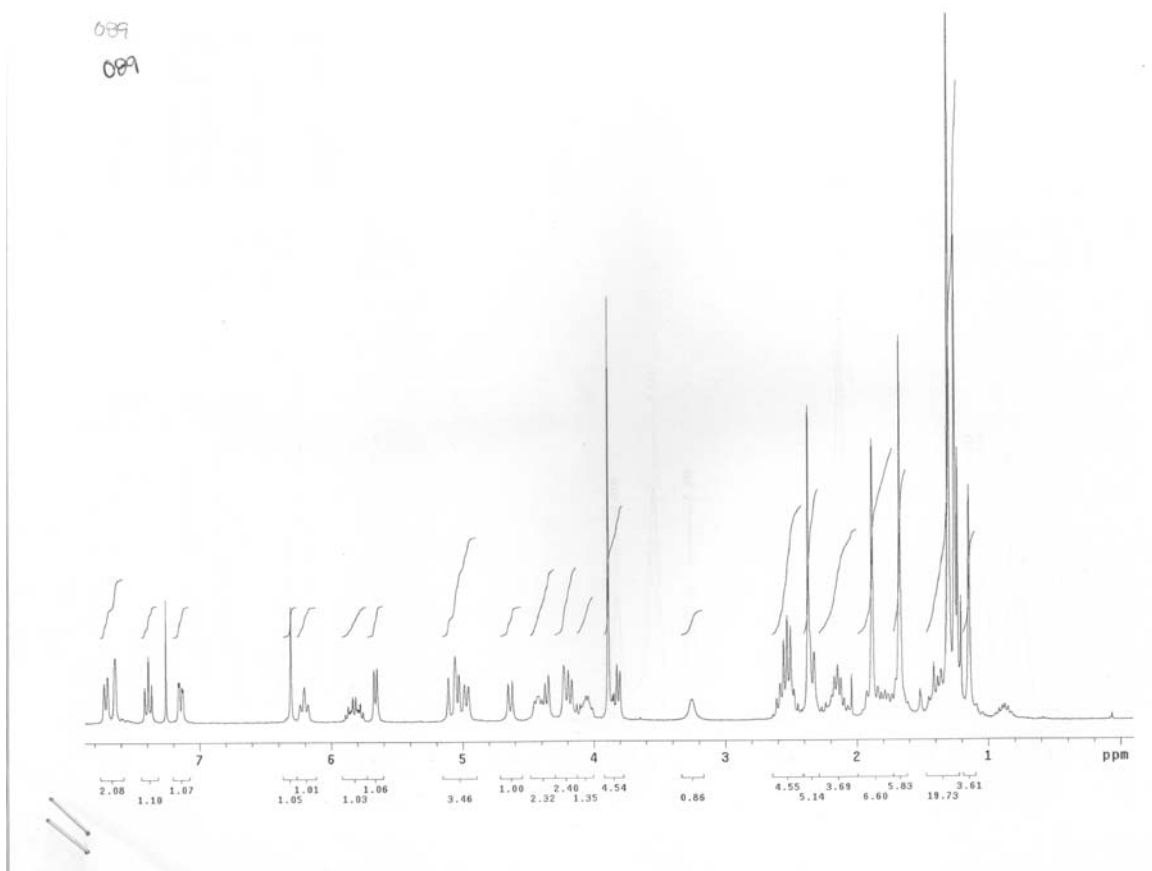
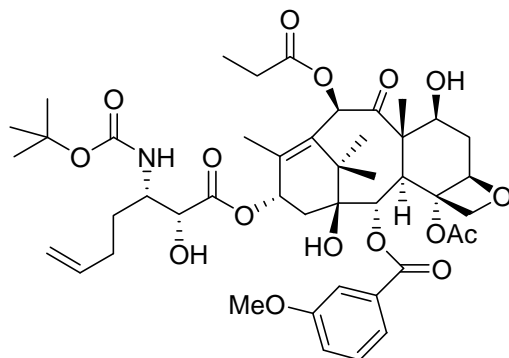
¹H NMR Spectrum NMR of **14n**



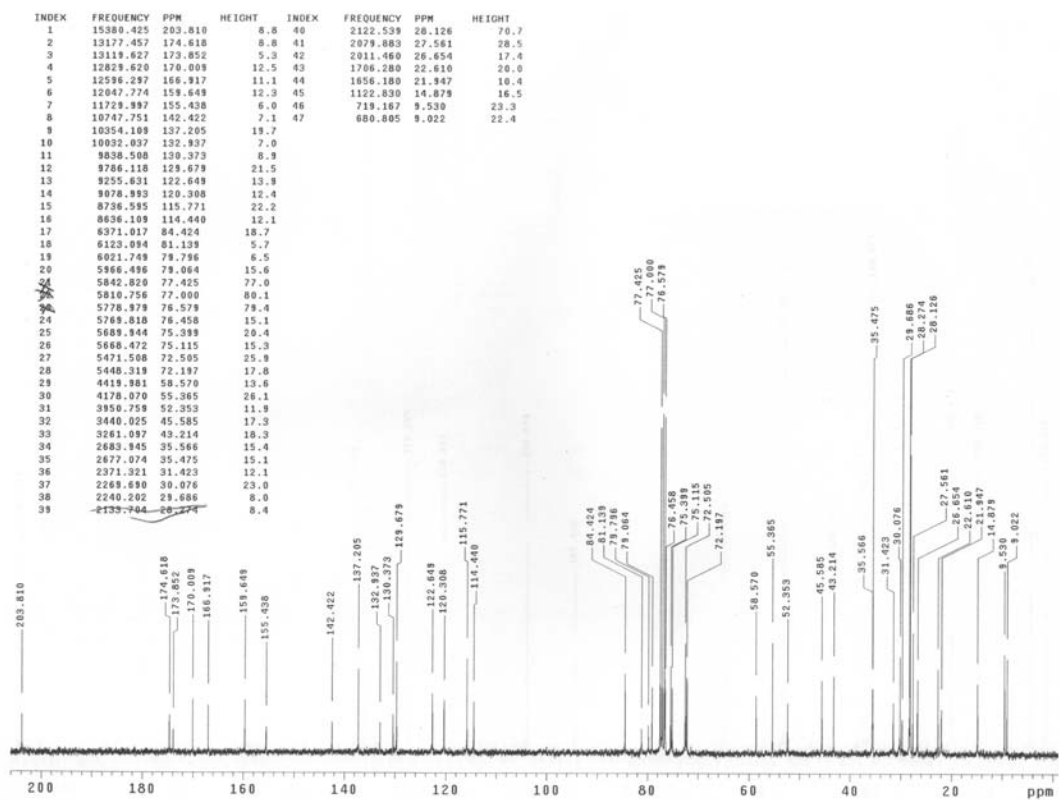
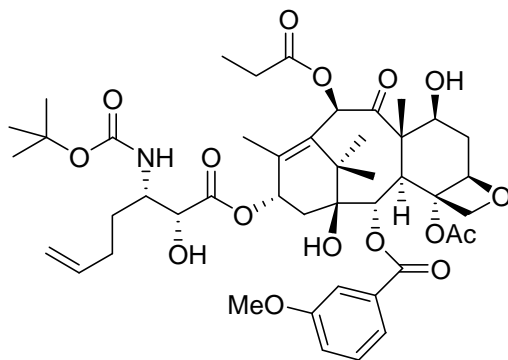
¹³C NMR Spectrum of 14n



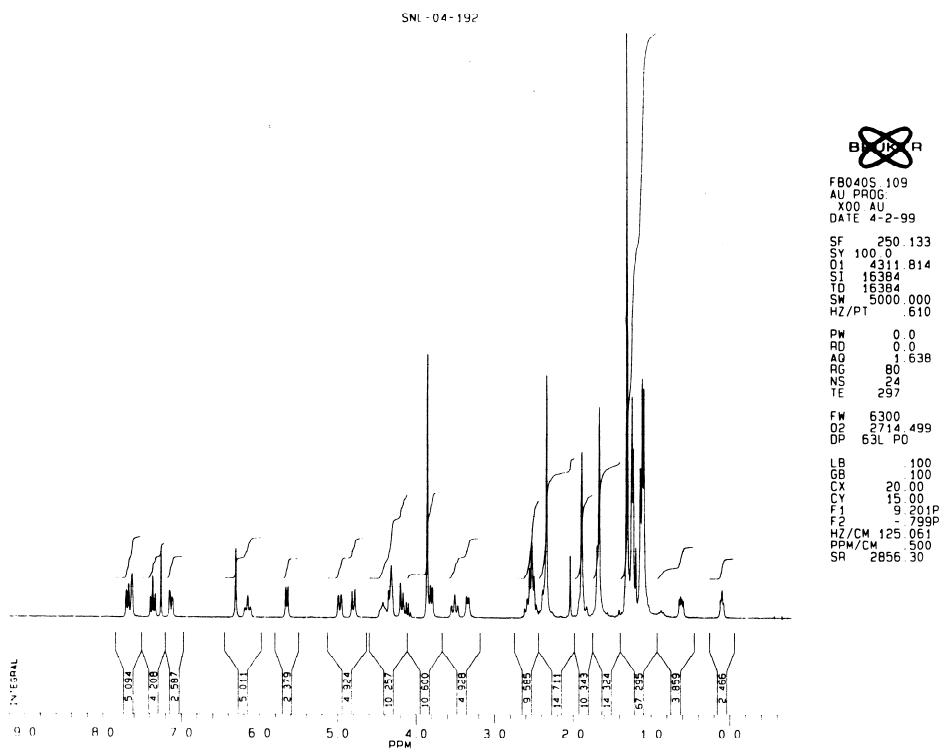
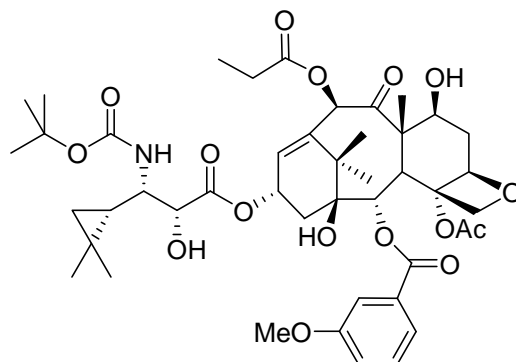
¹H NMR Spectrum of **14o**



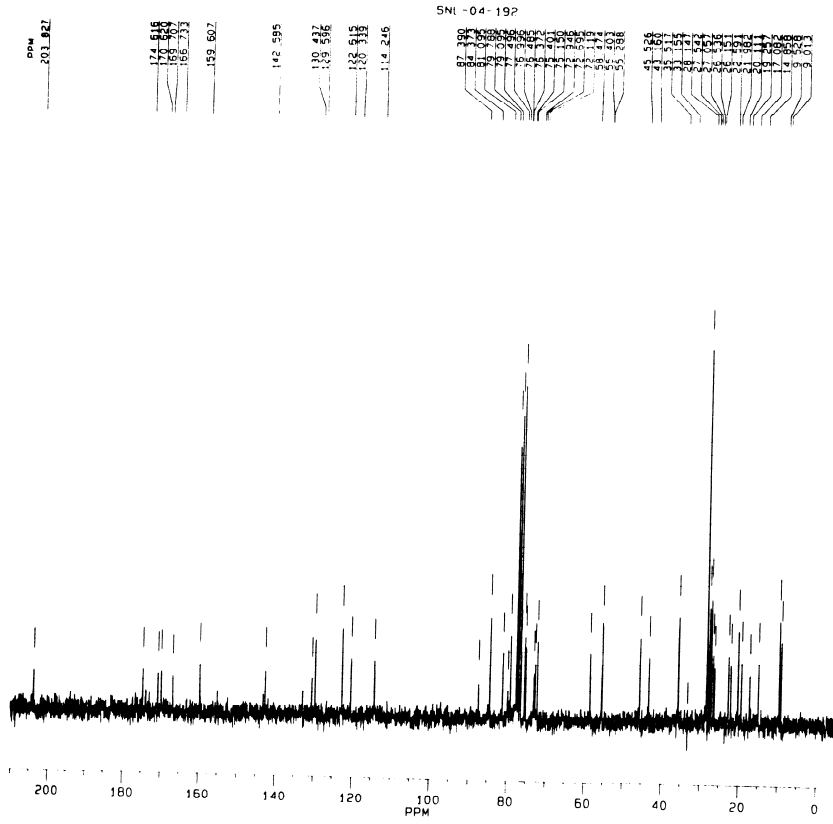
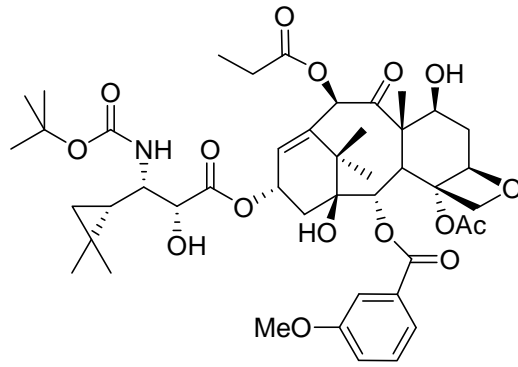
¹H NMR Spectrum of **14o**



¹H NMR Spectrum of **14p**



¹³C NMR Spectrum of **14p**



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AU PROG
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DATE 4-2-99

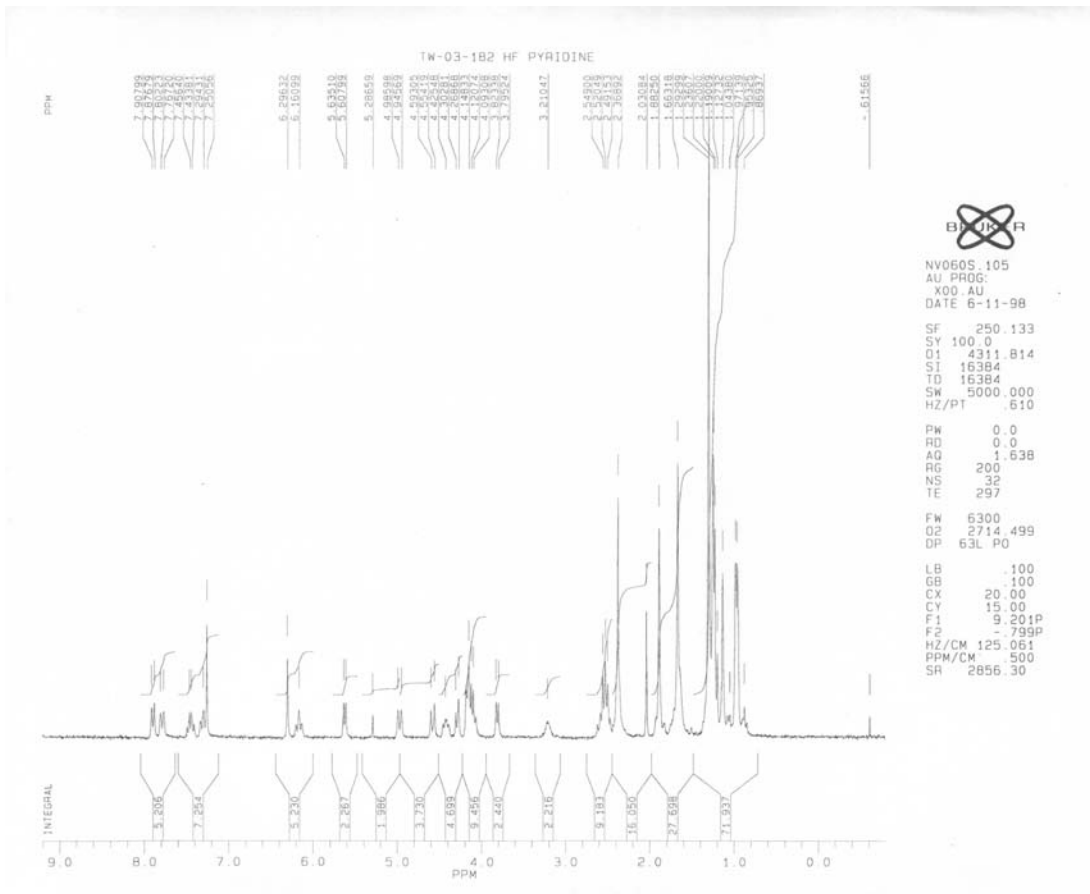
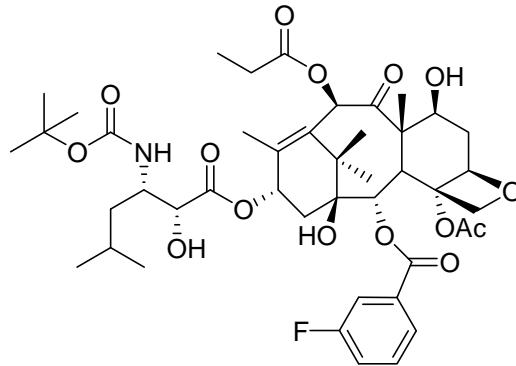
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NS 2000
TE 297

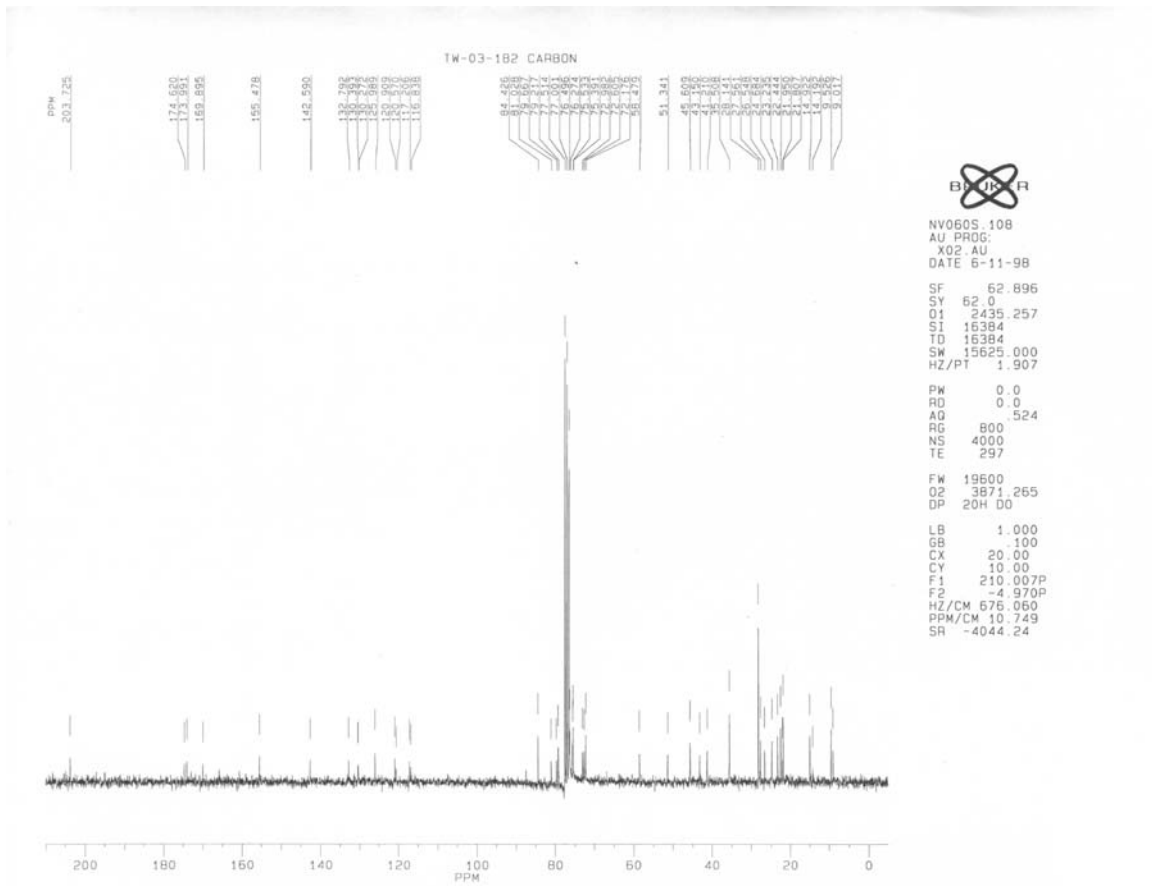
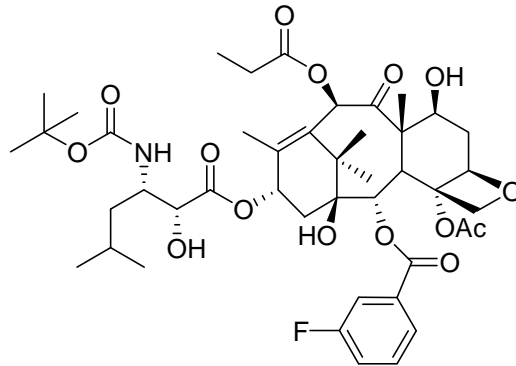
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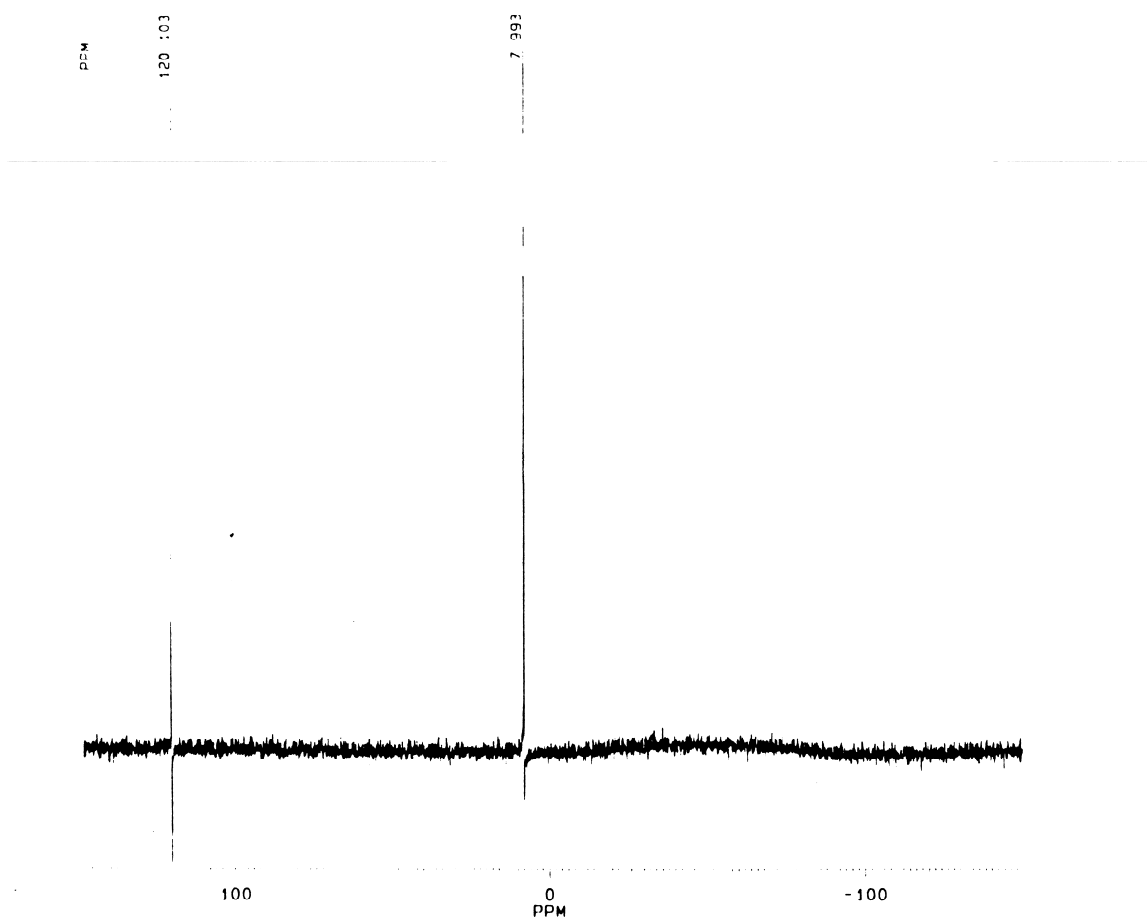
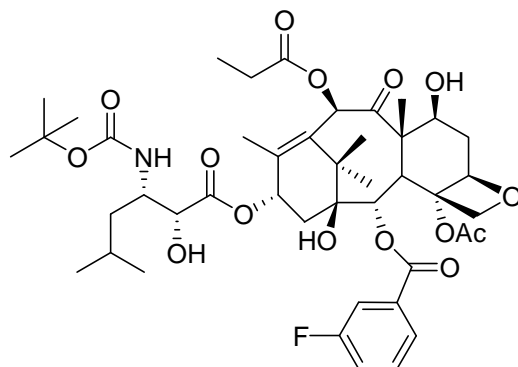
¹H NMR Spectrum of 15c



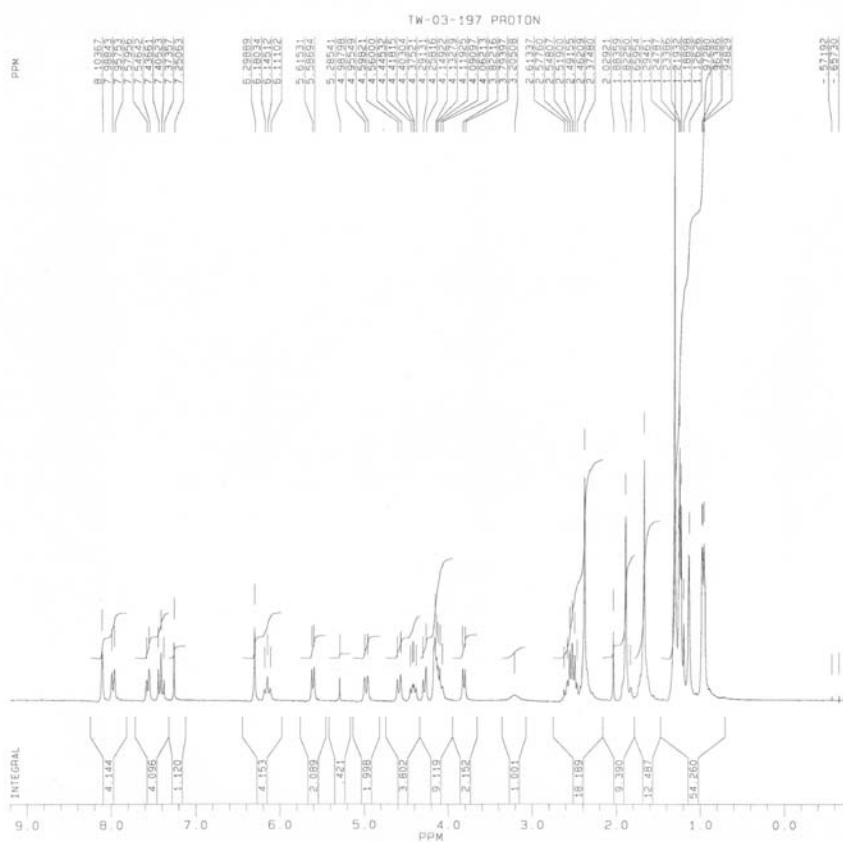
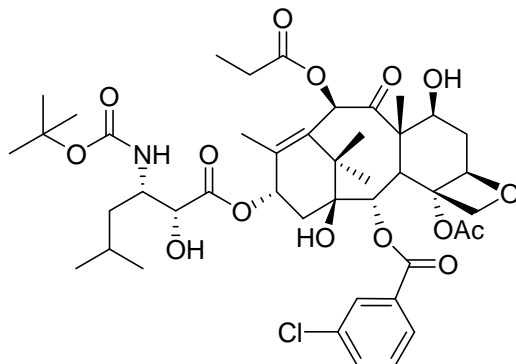
¹³C NMR Spectrum of 15c




^{19}F NMR Spectrum of **15c**

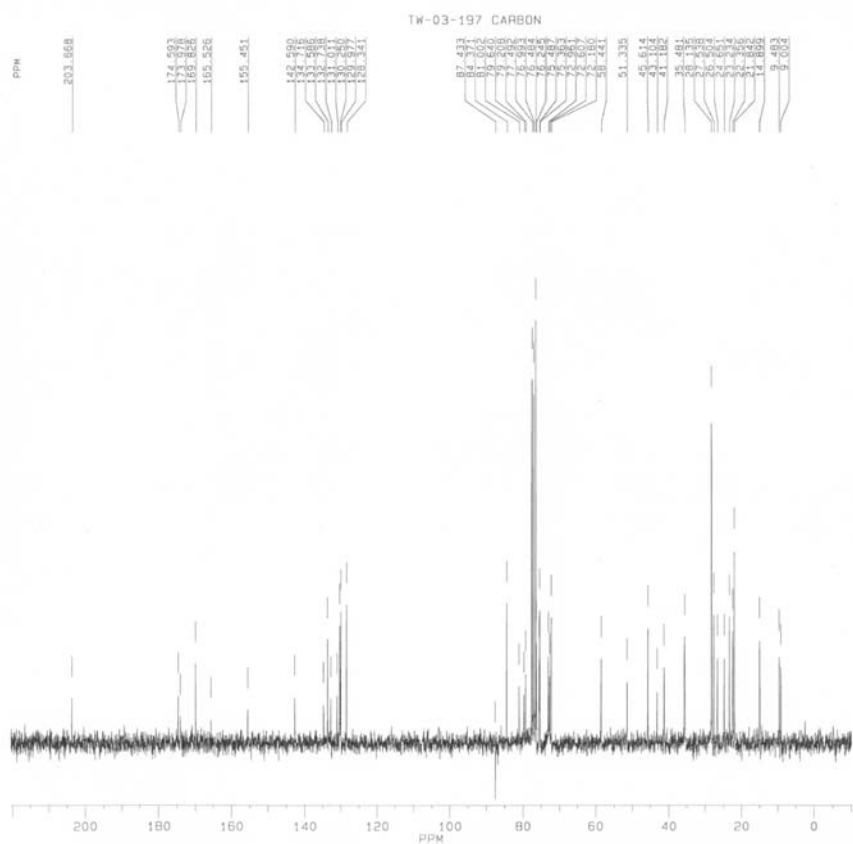
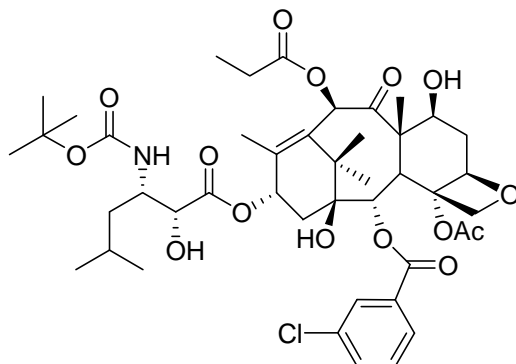


¹H NMR Spectrum of 15d




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 TE 297
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¹³C NMR Spectrum of 15d



NV2705.105
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 DATE 28-11-98

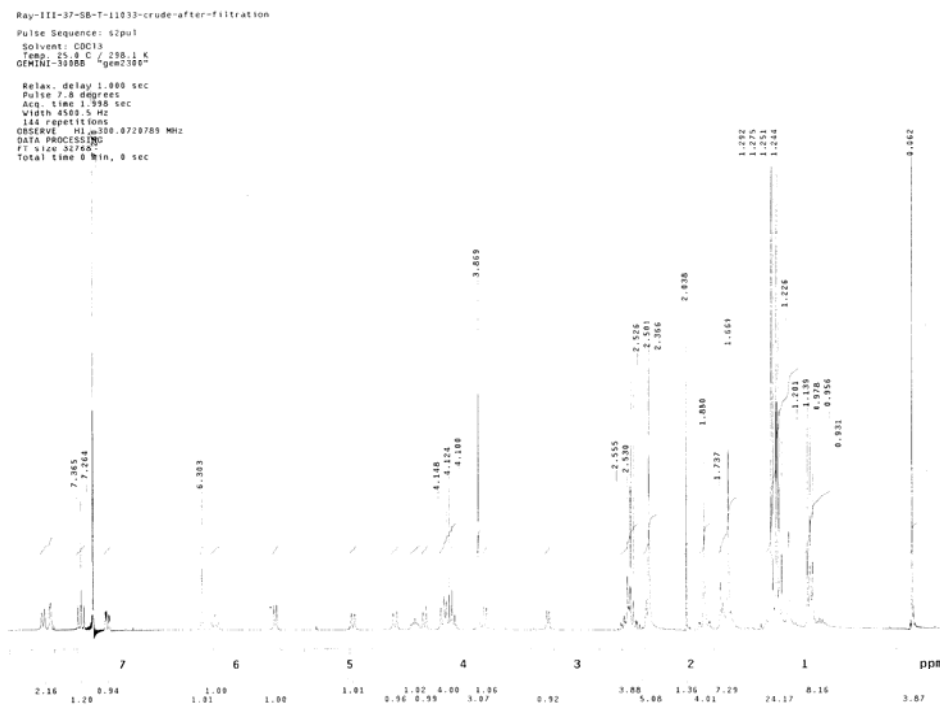
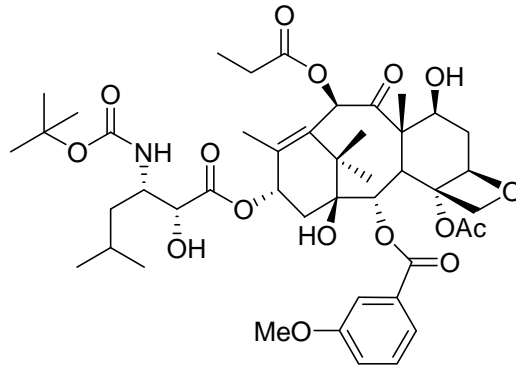
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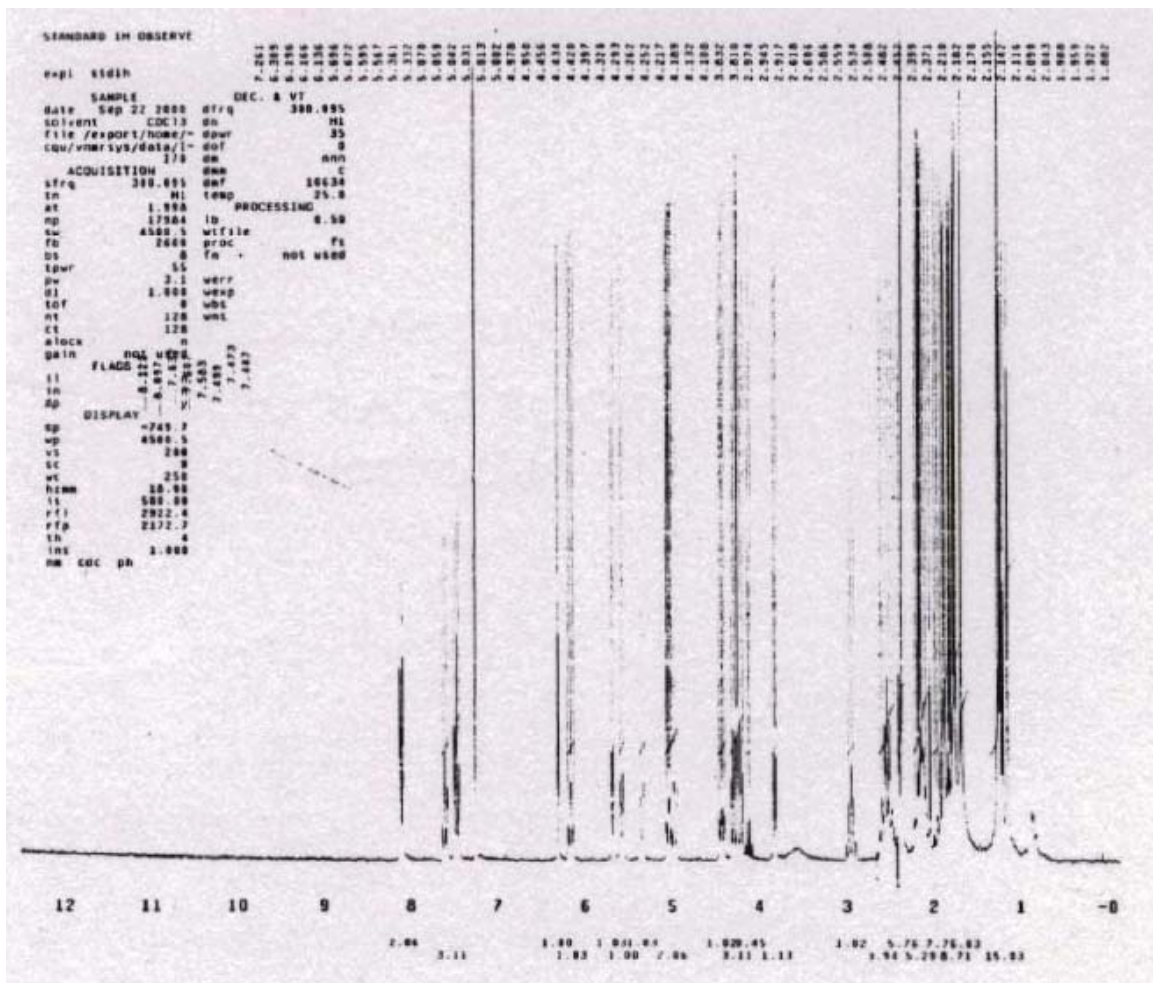
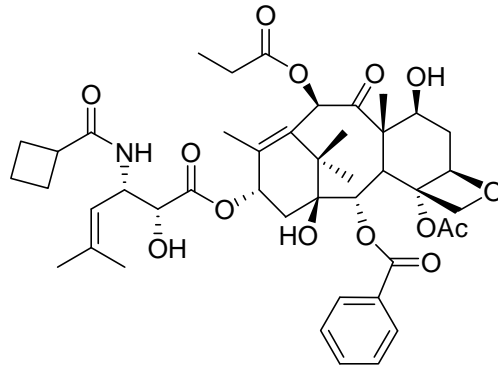
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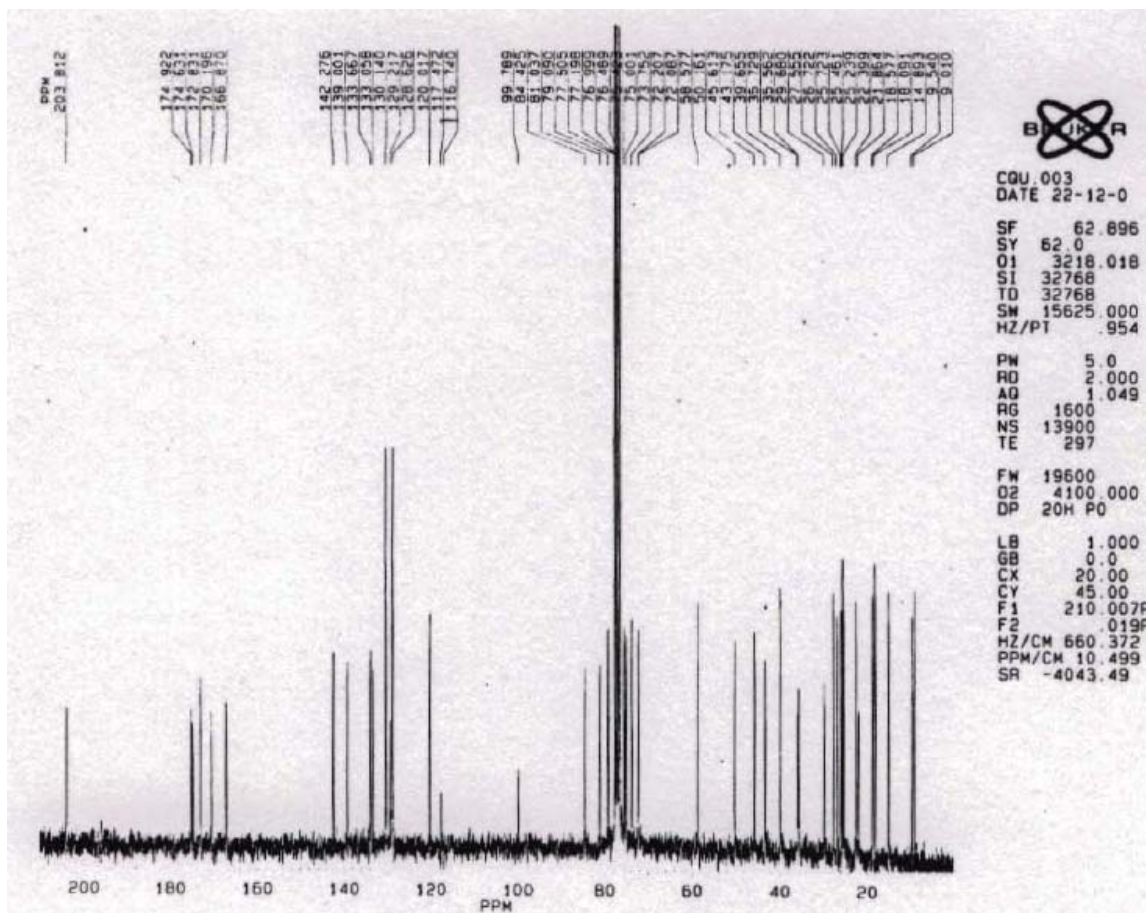
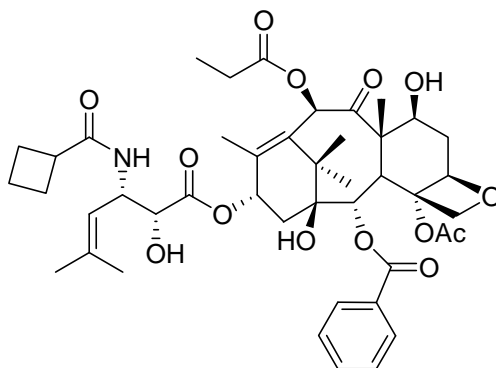
¹H NMR Spectrum of 15g



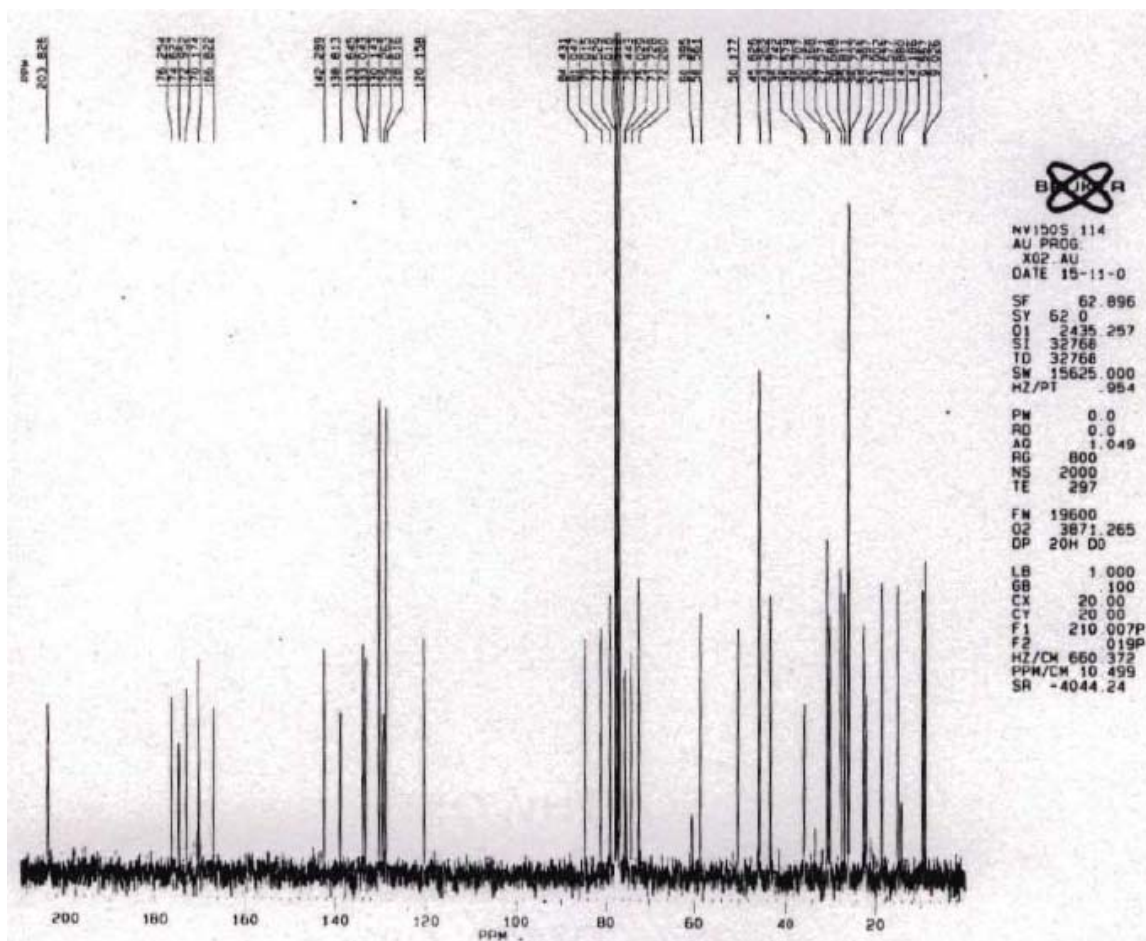
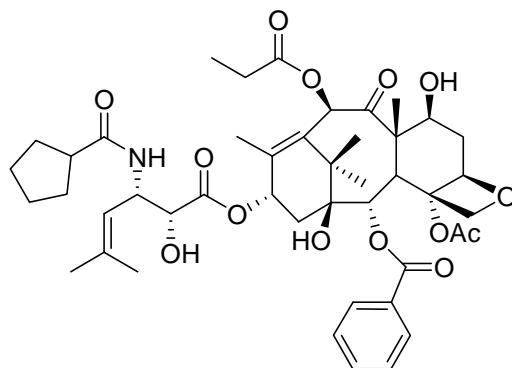
^1H NMR Spectrum of 17a



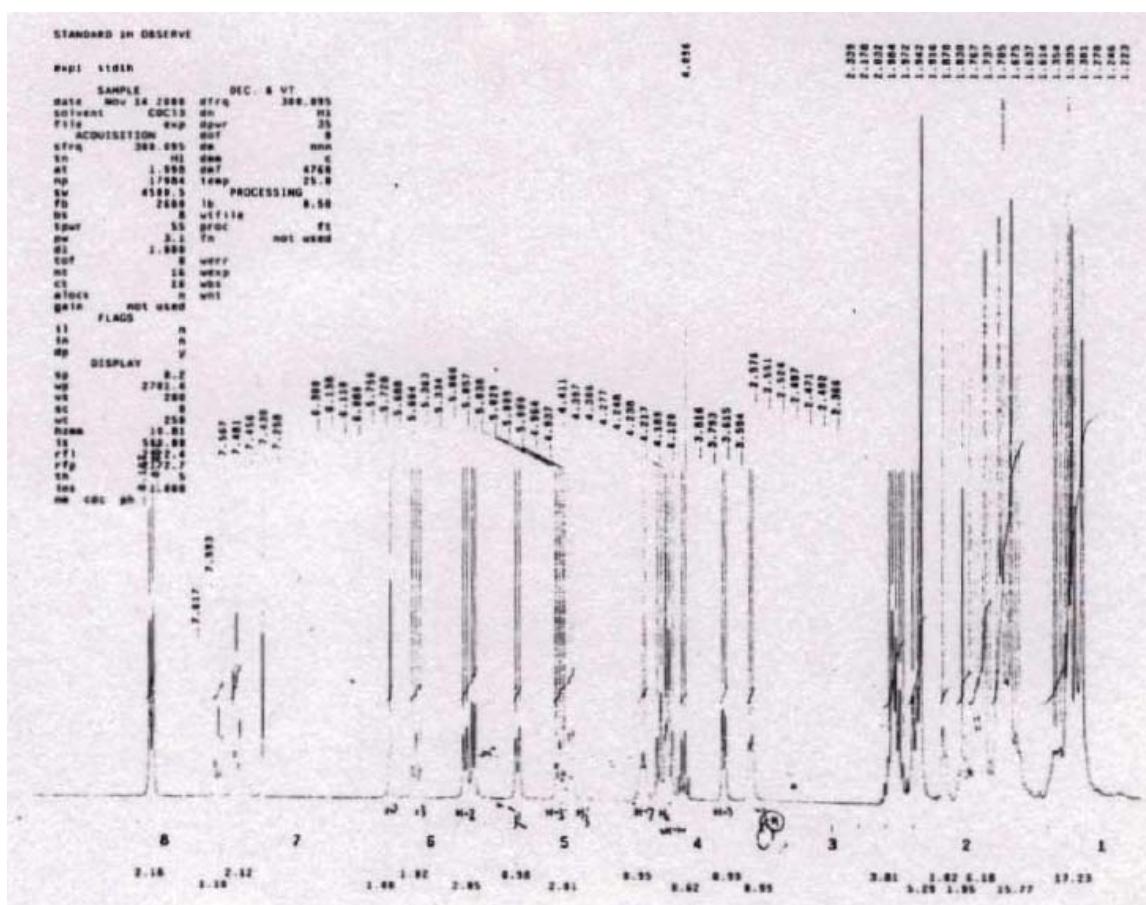
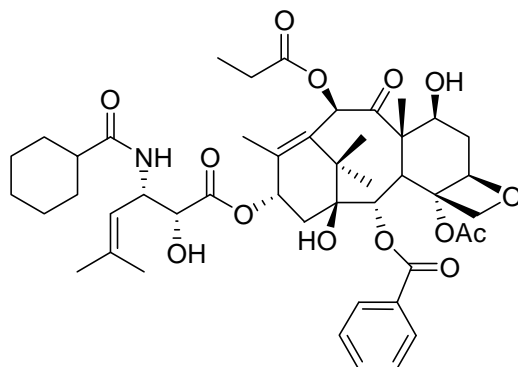
^{13}C NMR Spectrum of 17a



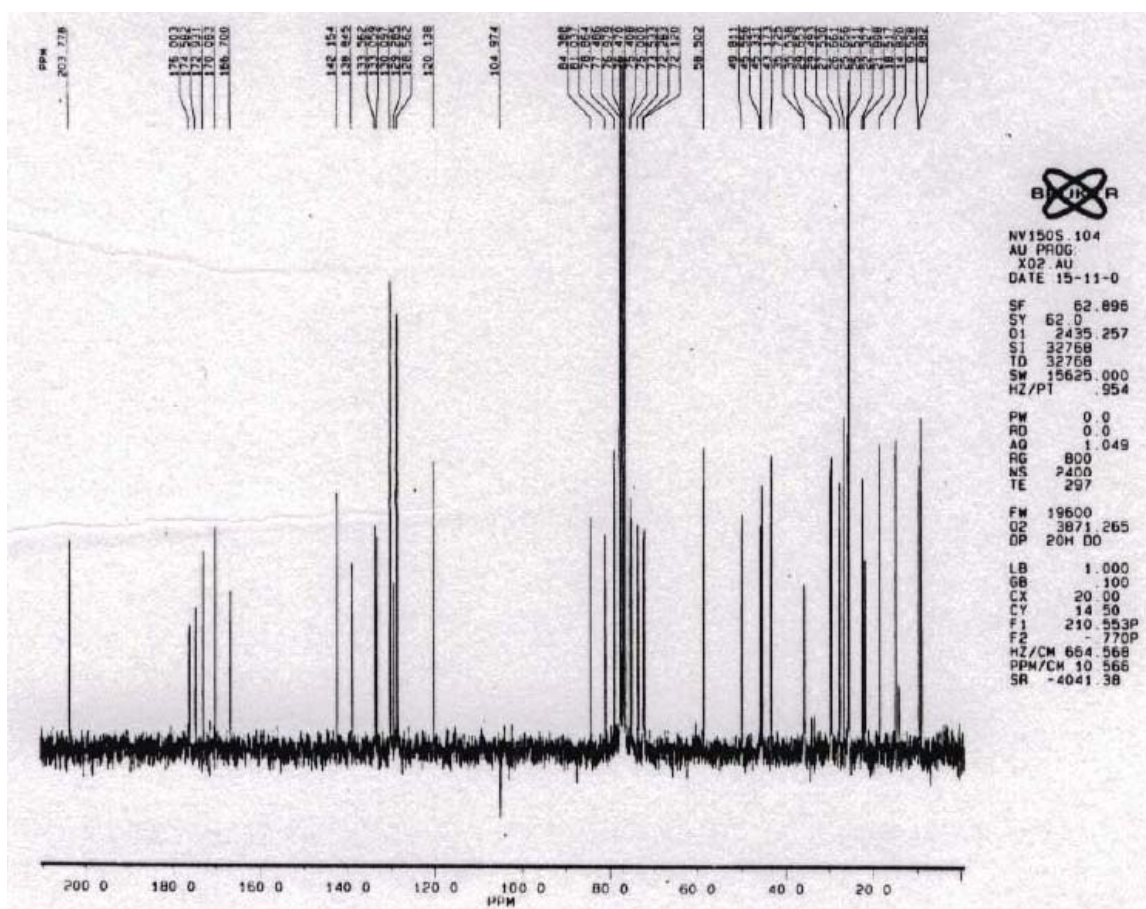
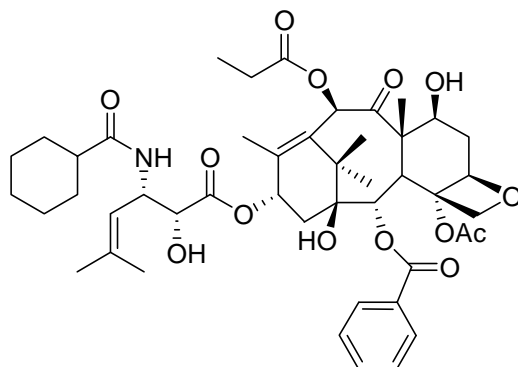
^{13}C NMR Spectrum of 17b



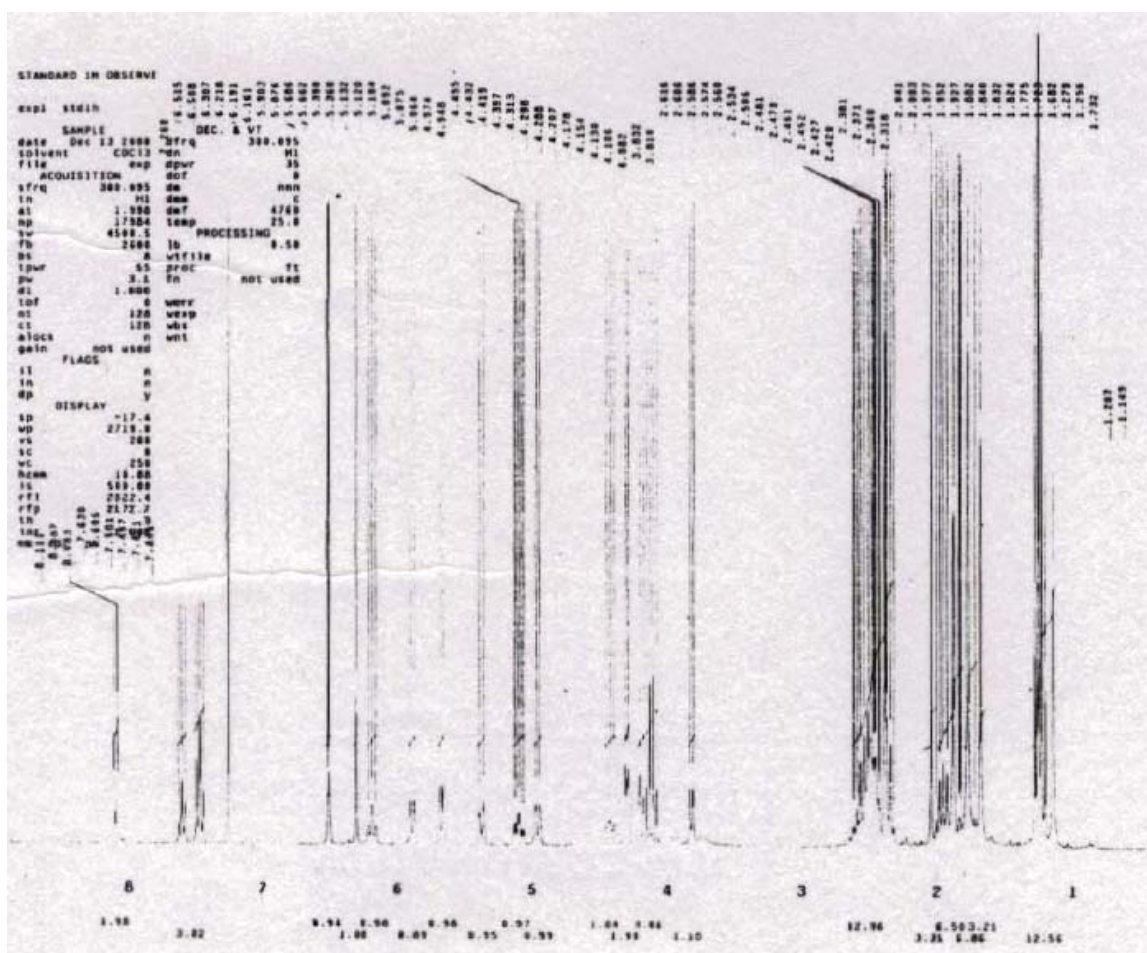
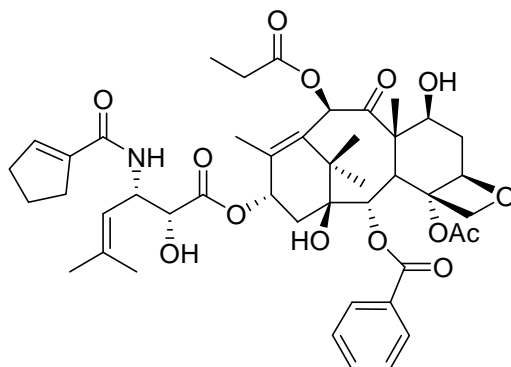
^1H NMR Spectrum of 17c



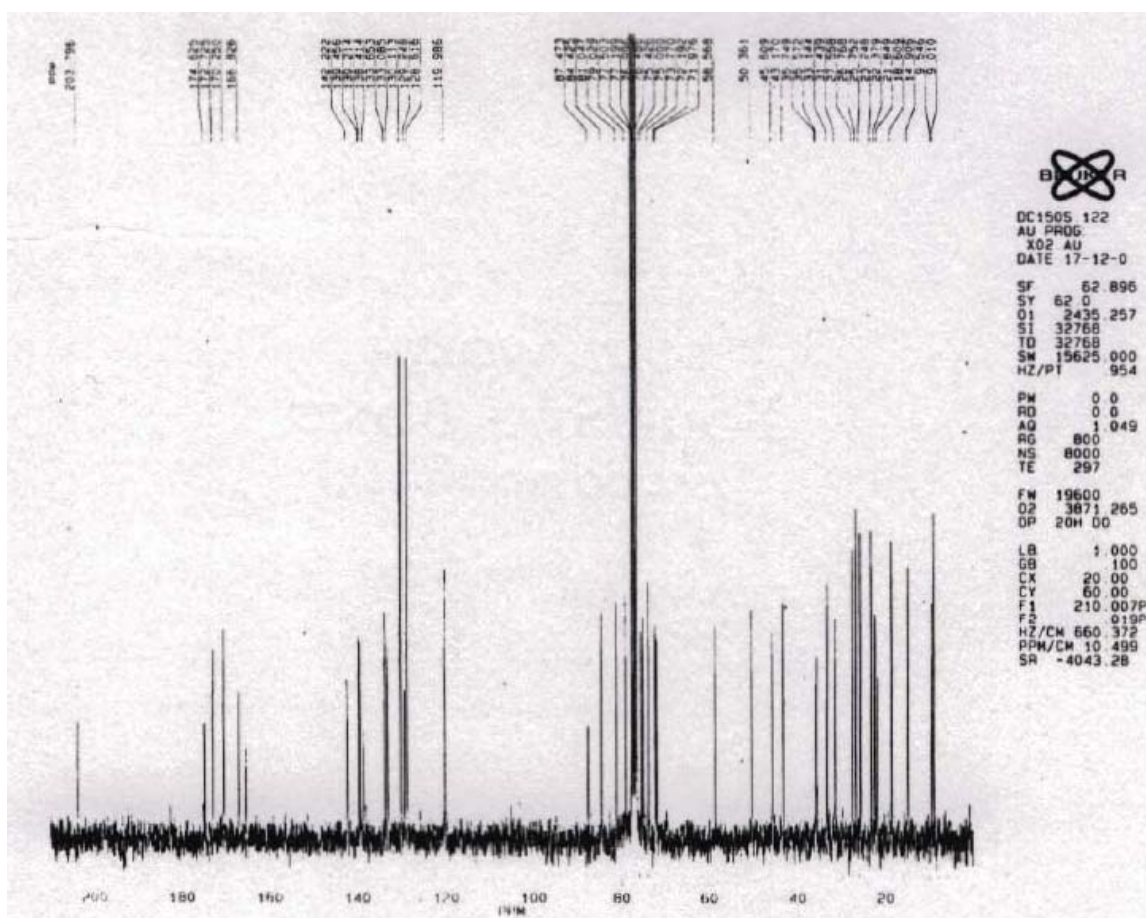
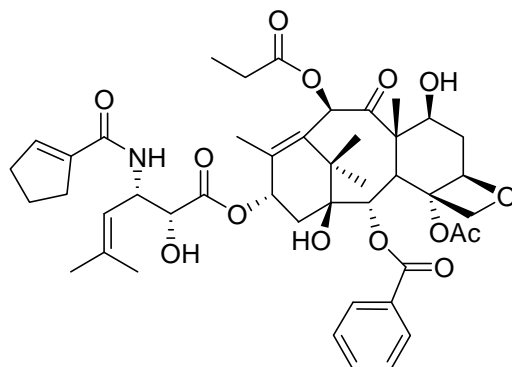
^{13}C NMR Spectrum of 17c



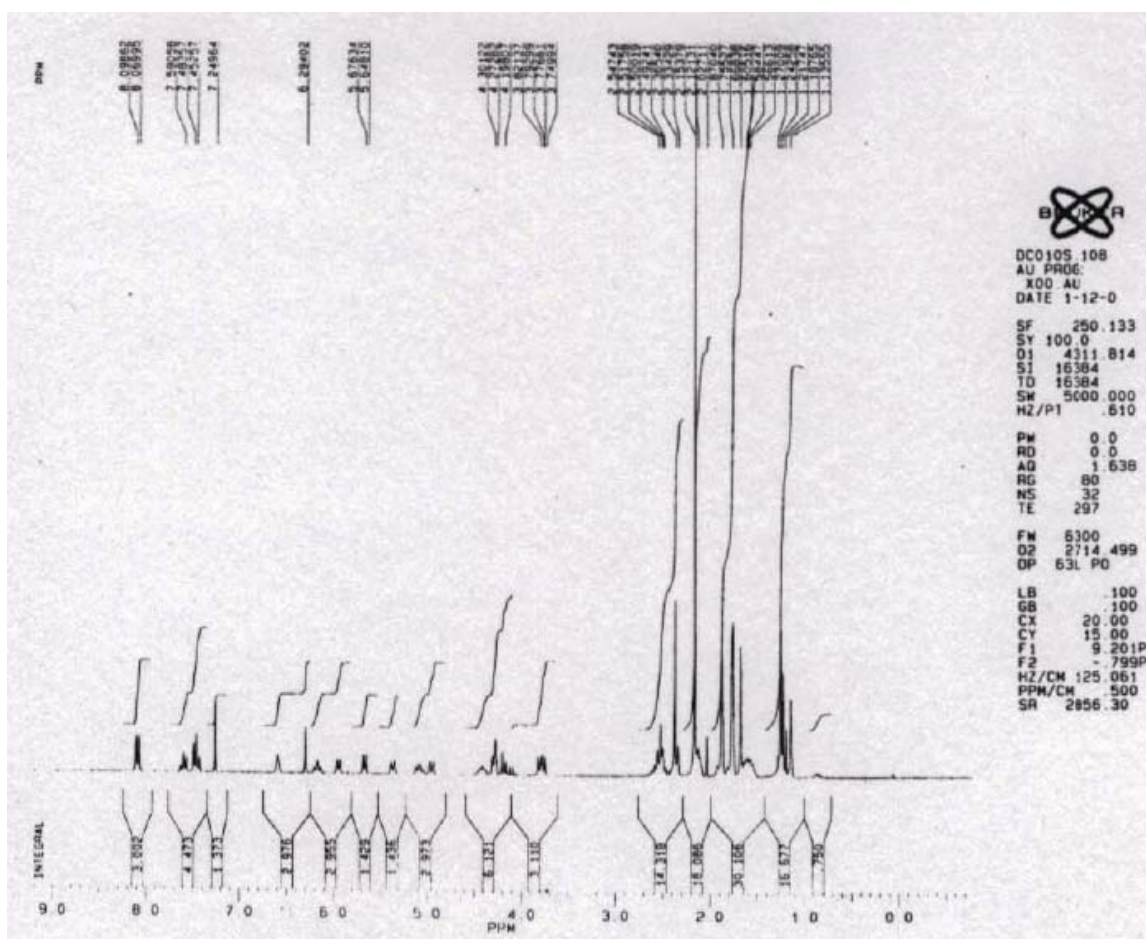
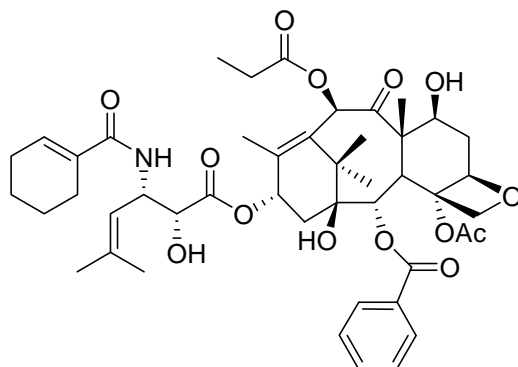
¹H NMR Spectrum of 17d



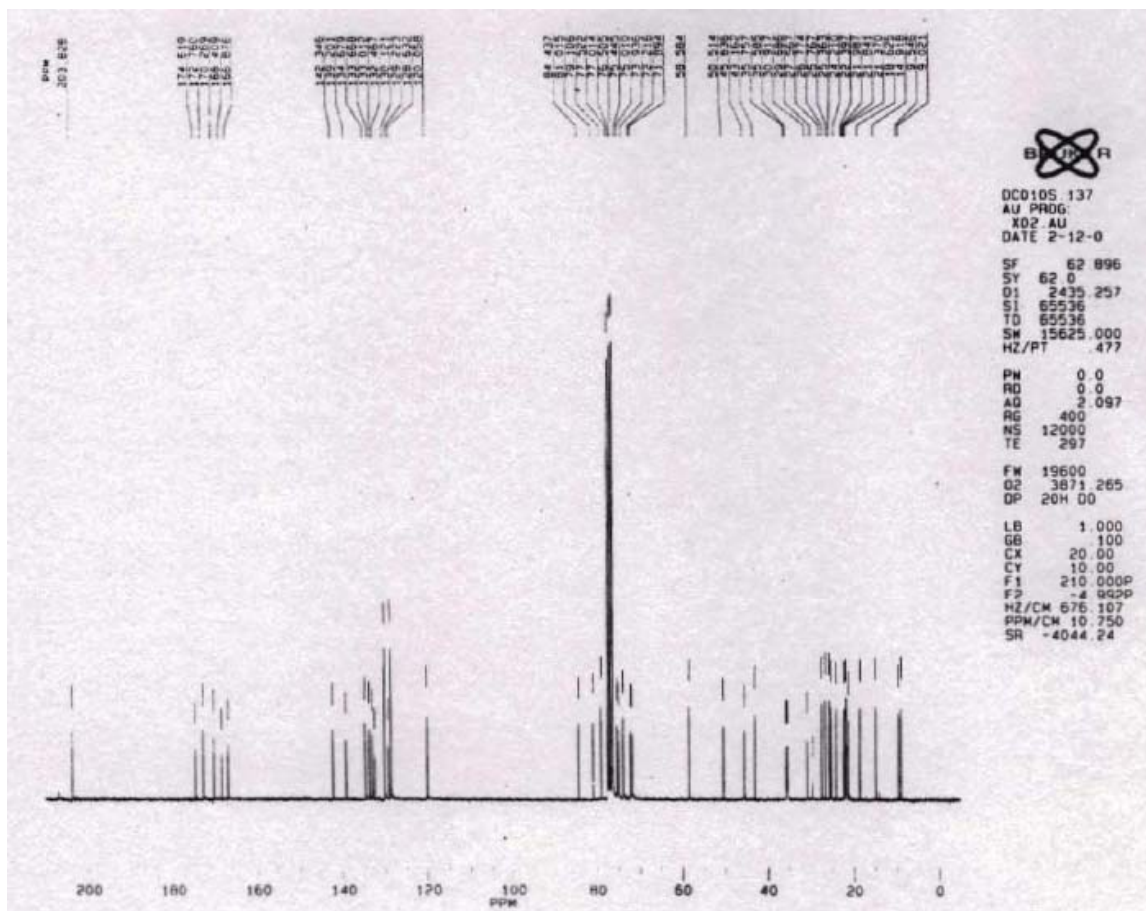
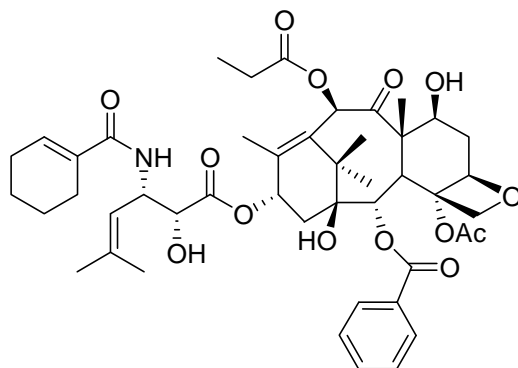
^{13}C NMR Spectrum of 17d



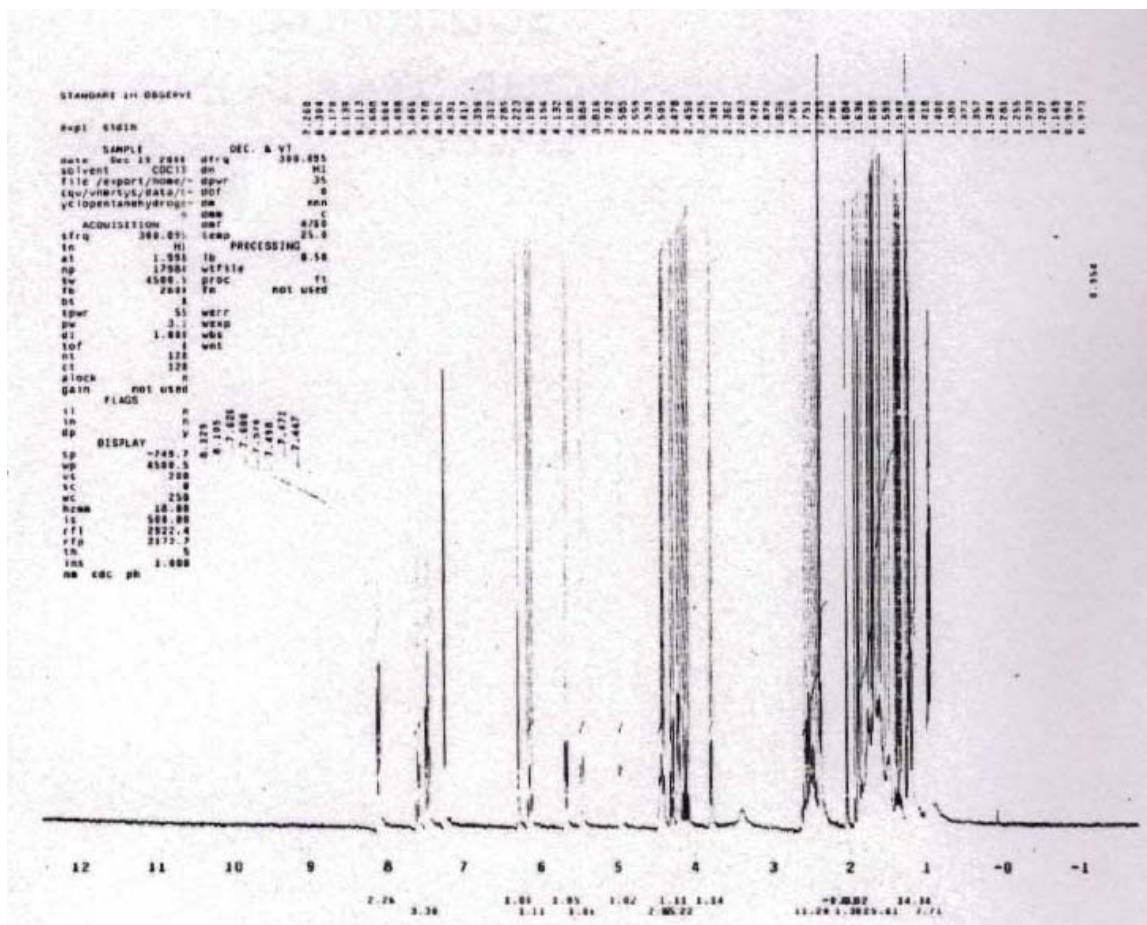
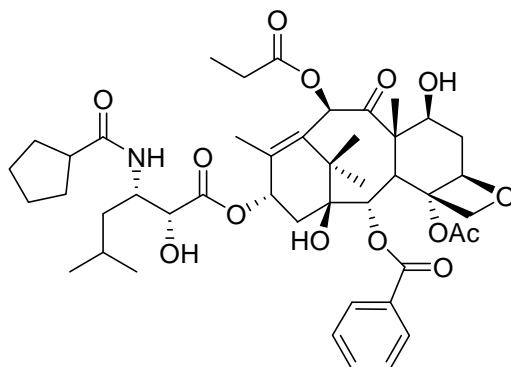
¹H NMR Spectrum of **17e**



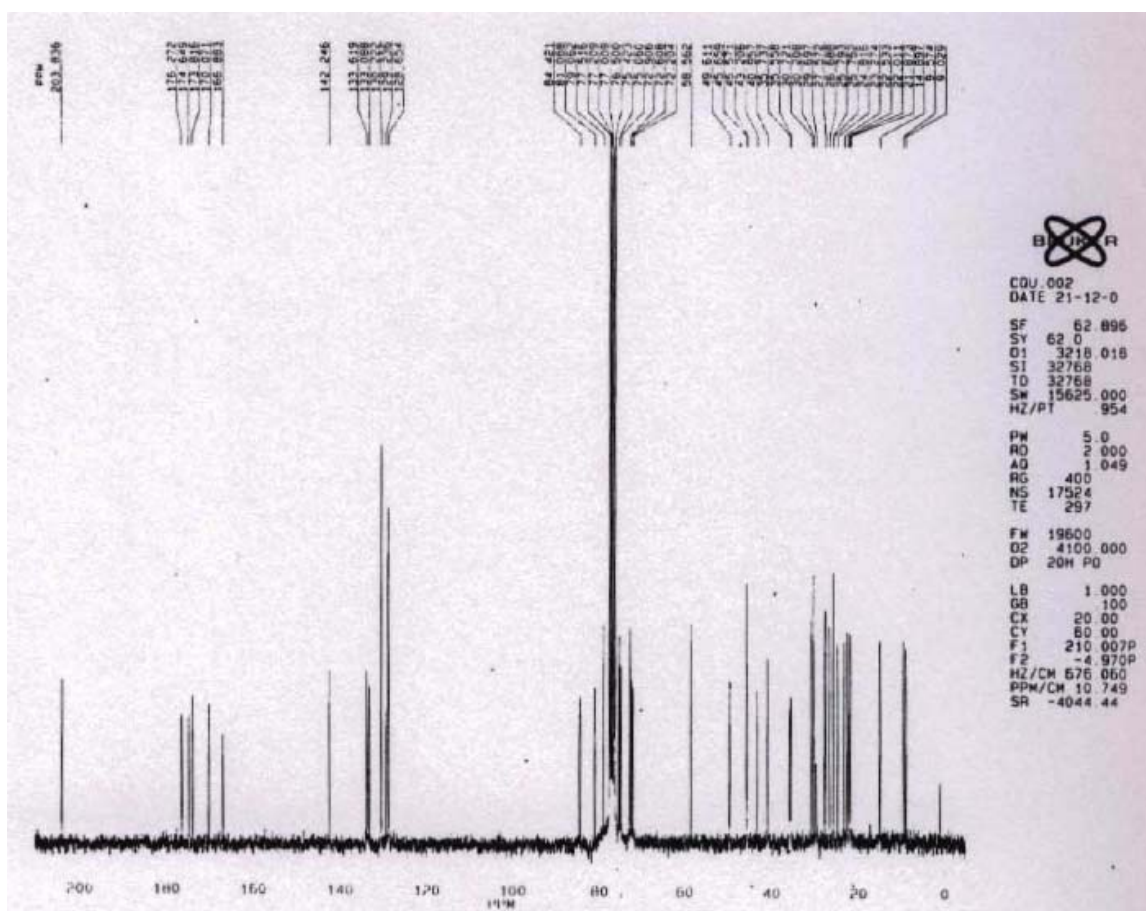
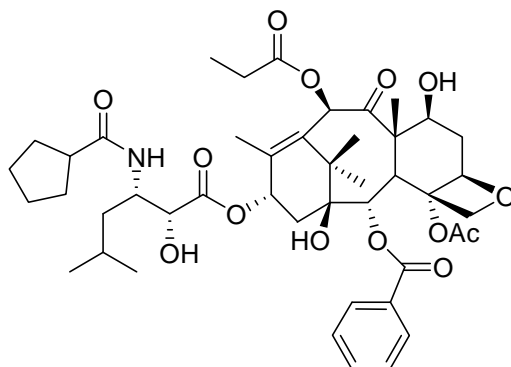
^{13}C NMR Spectrum of 17e



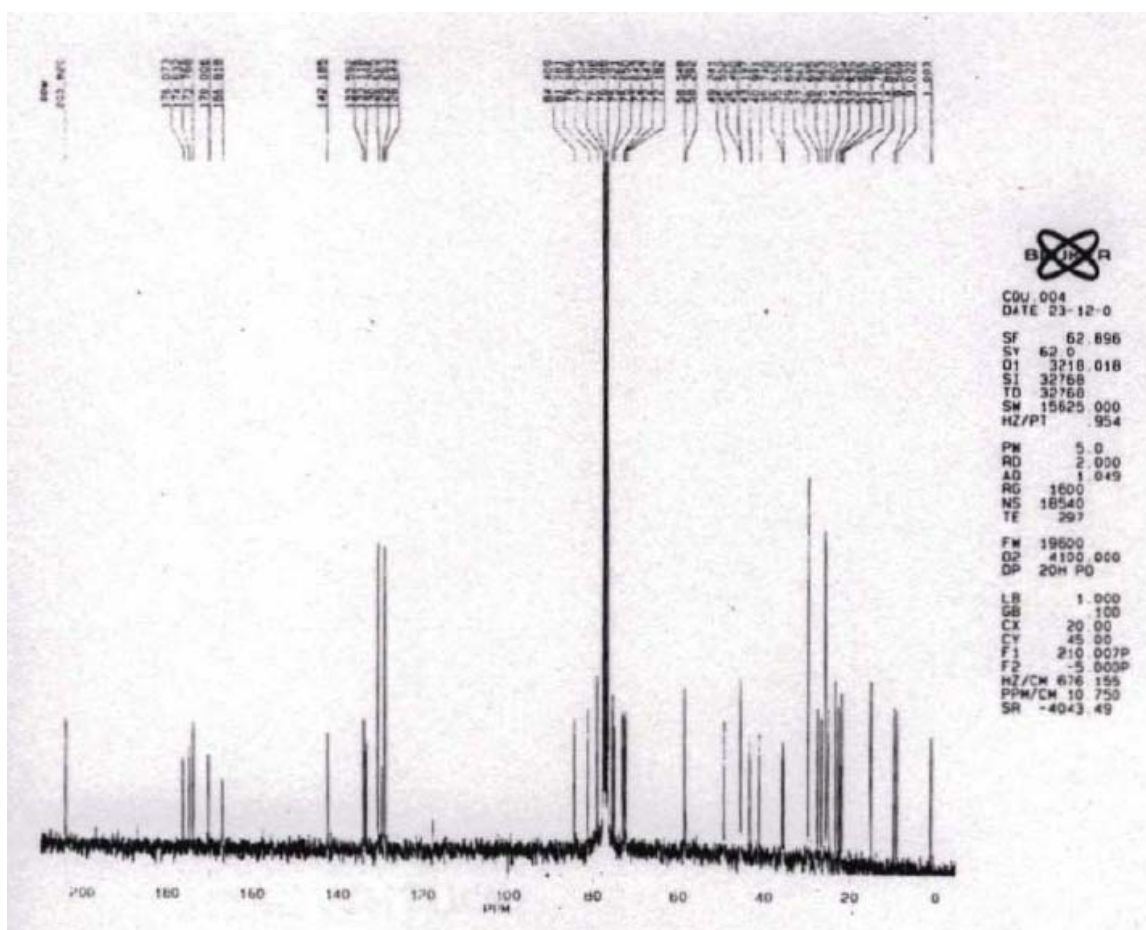
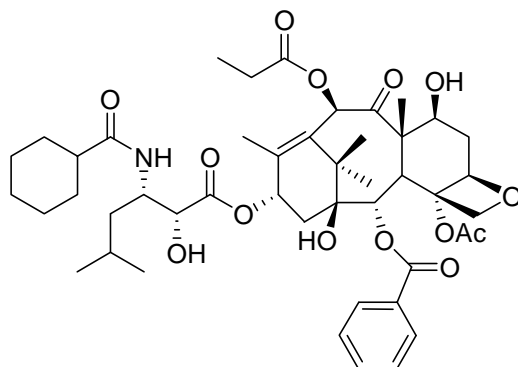
¹H NMR Spectrum of **18b**



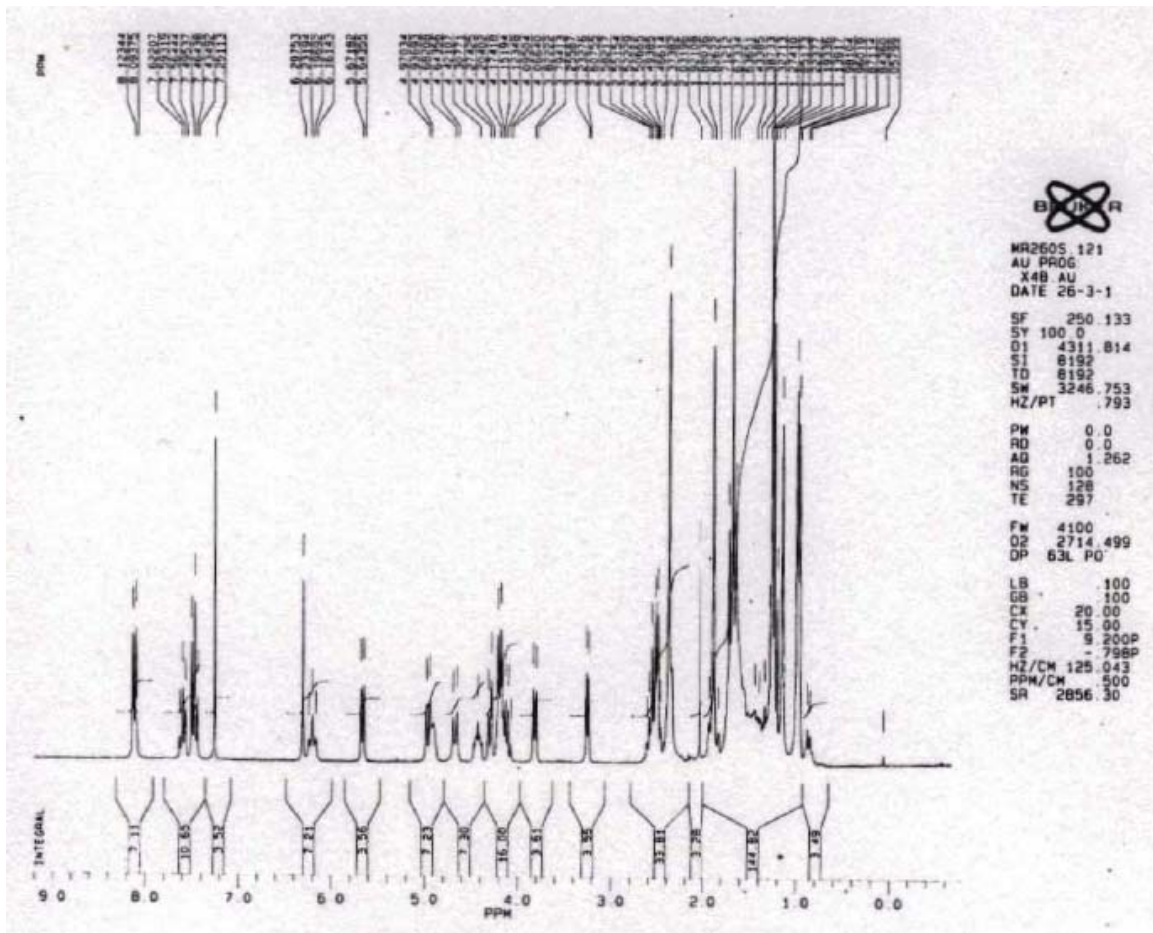
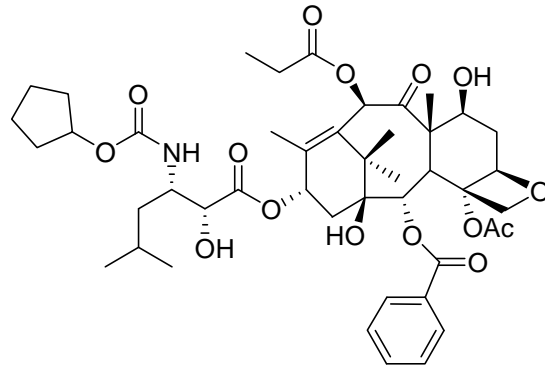
^{13}C NMR Spectrum of **18b**



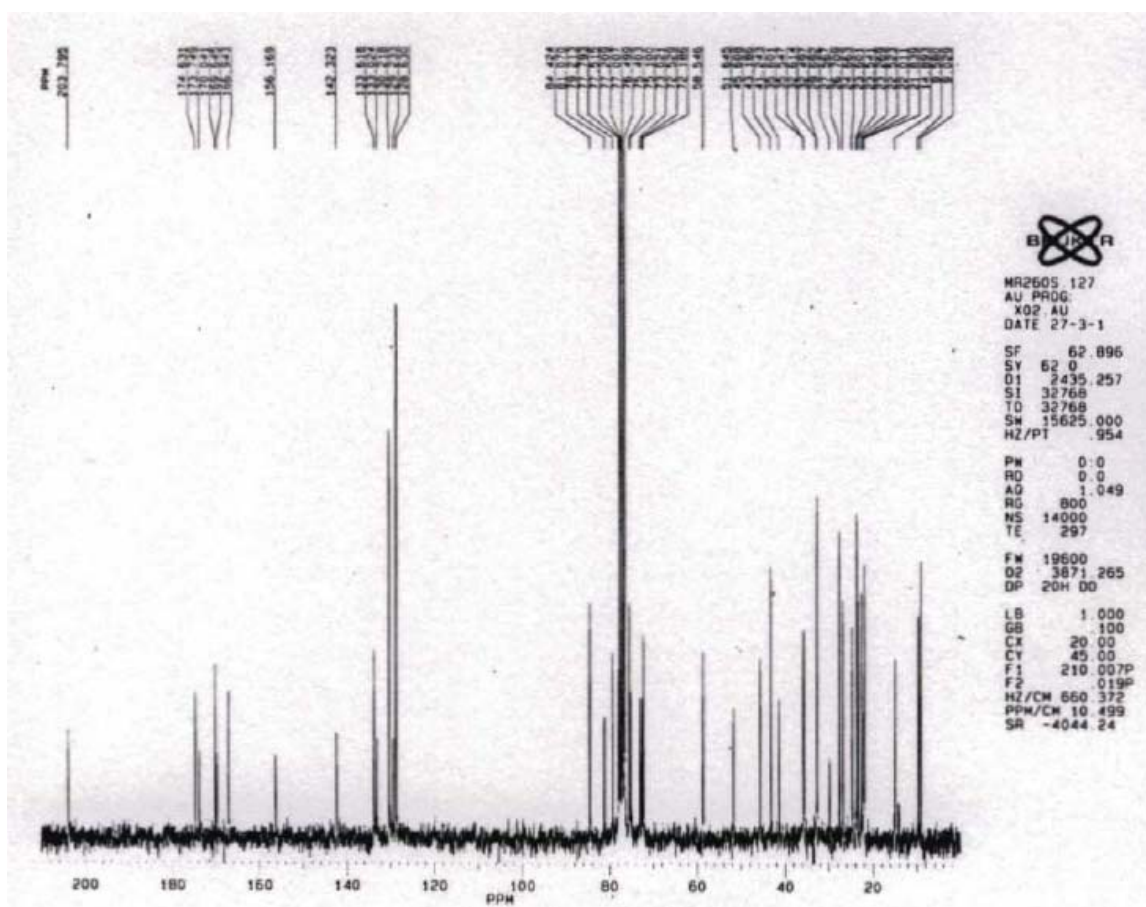
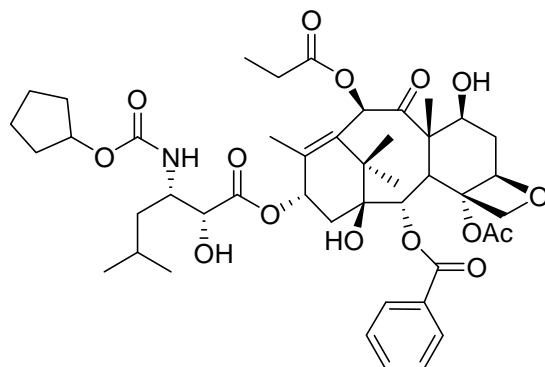
^{13}C NMR Spectrum of 18c



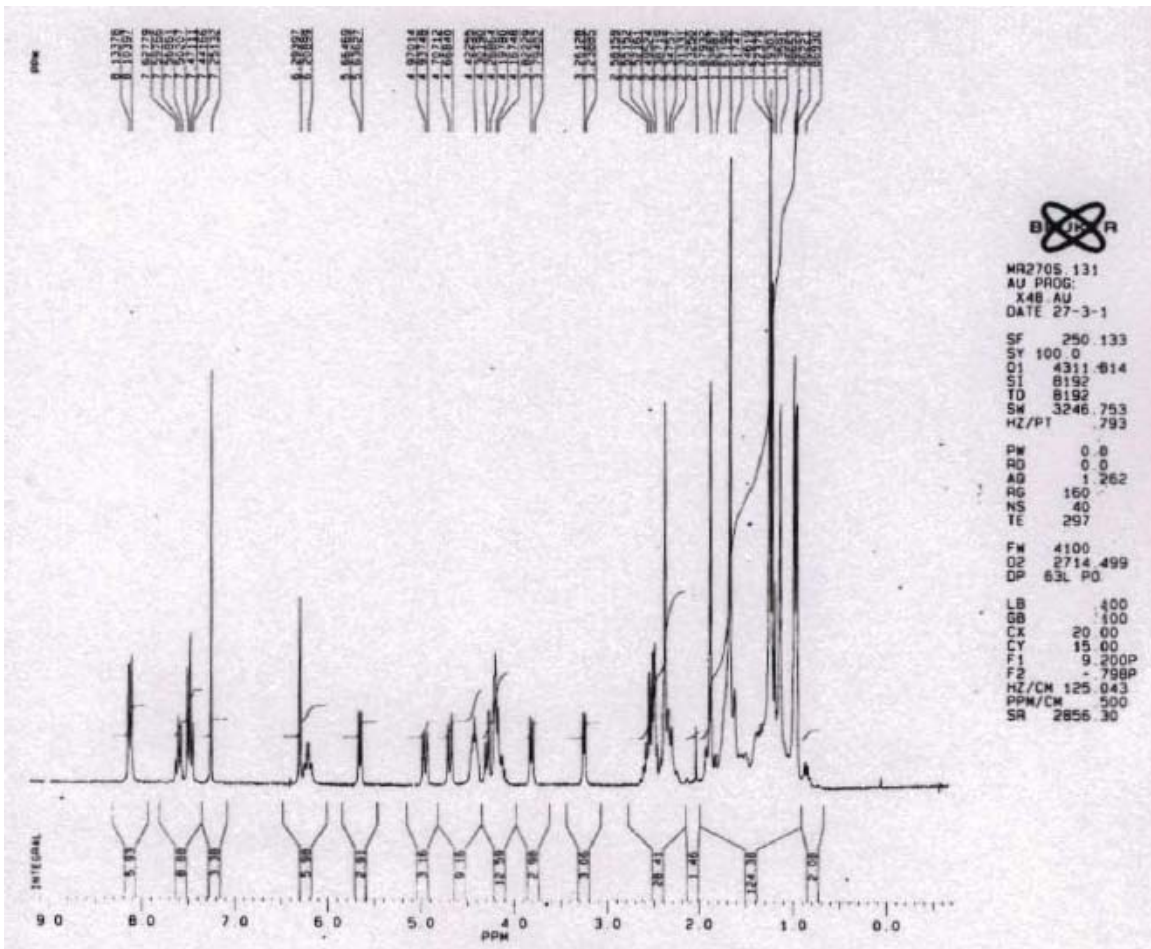
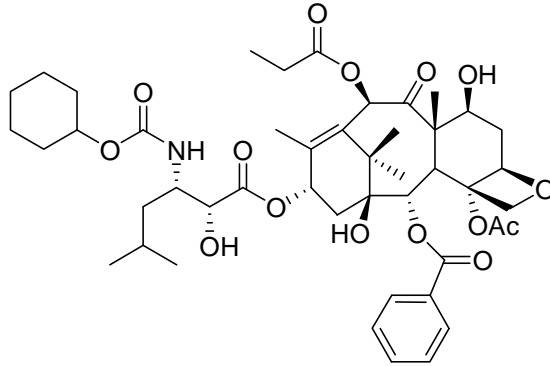
¹H NMR Spectrum of **18f**



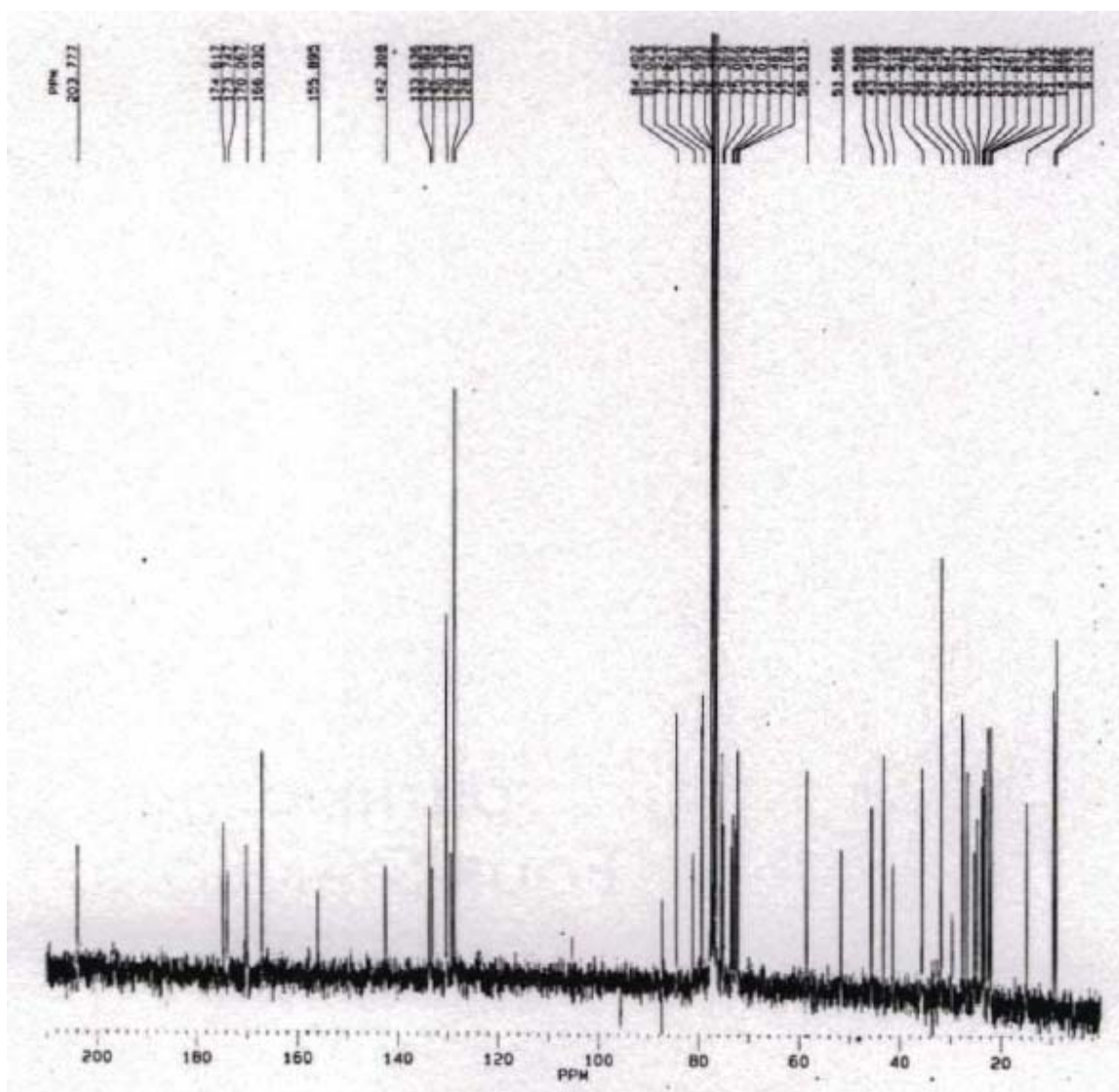
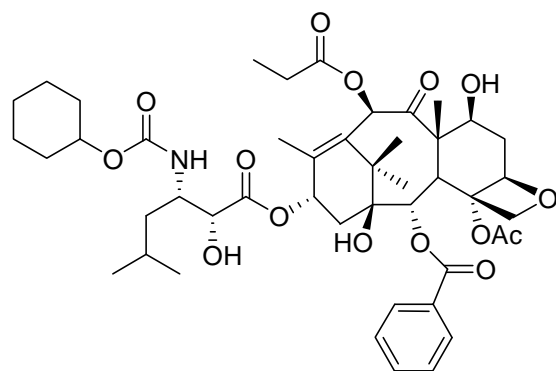
^{13}C NMR Spectrum of **18f**



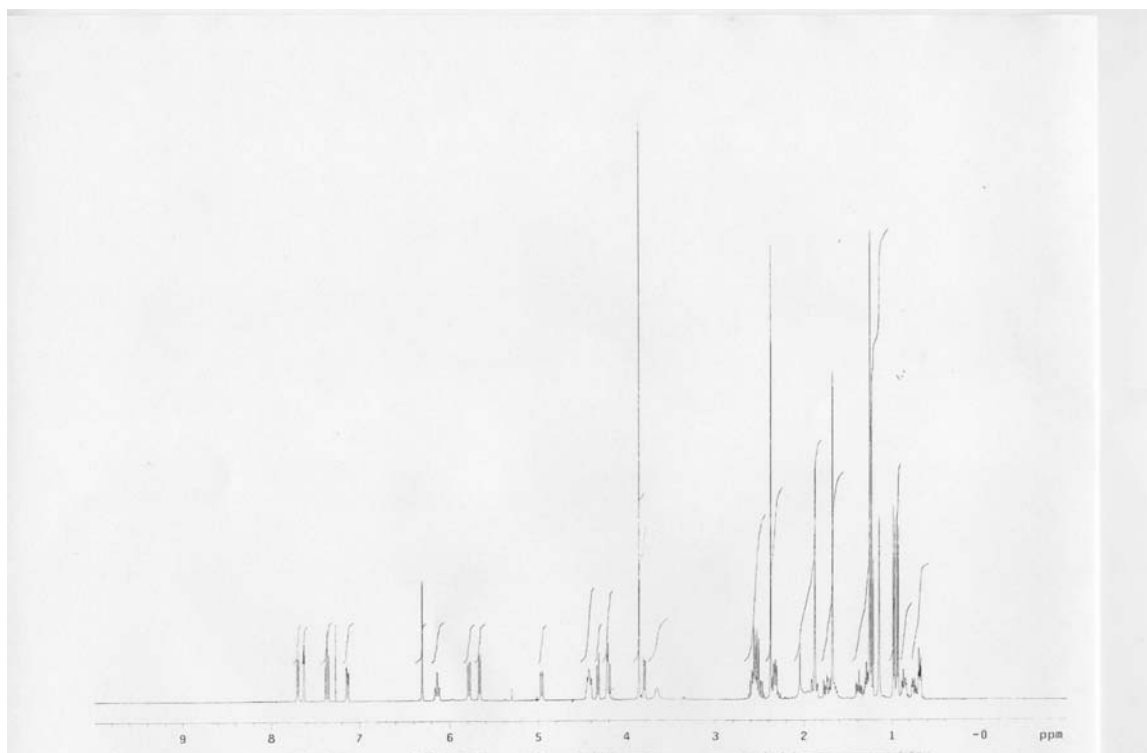
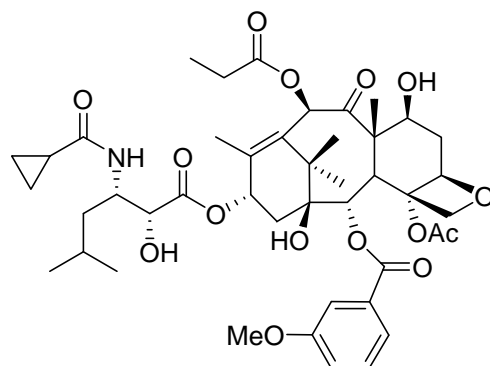
¹H NMR Spectrum of **18g**



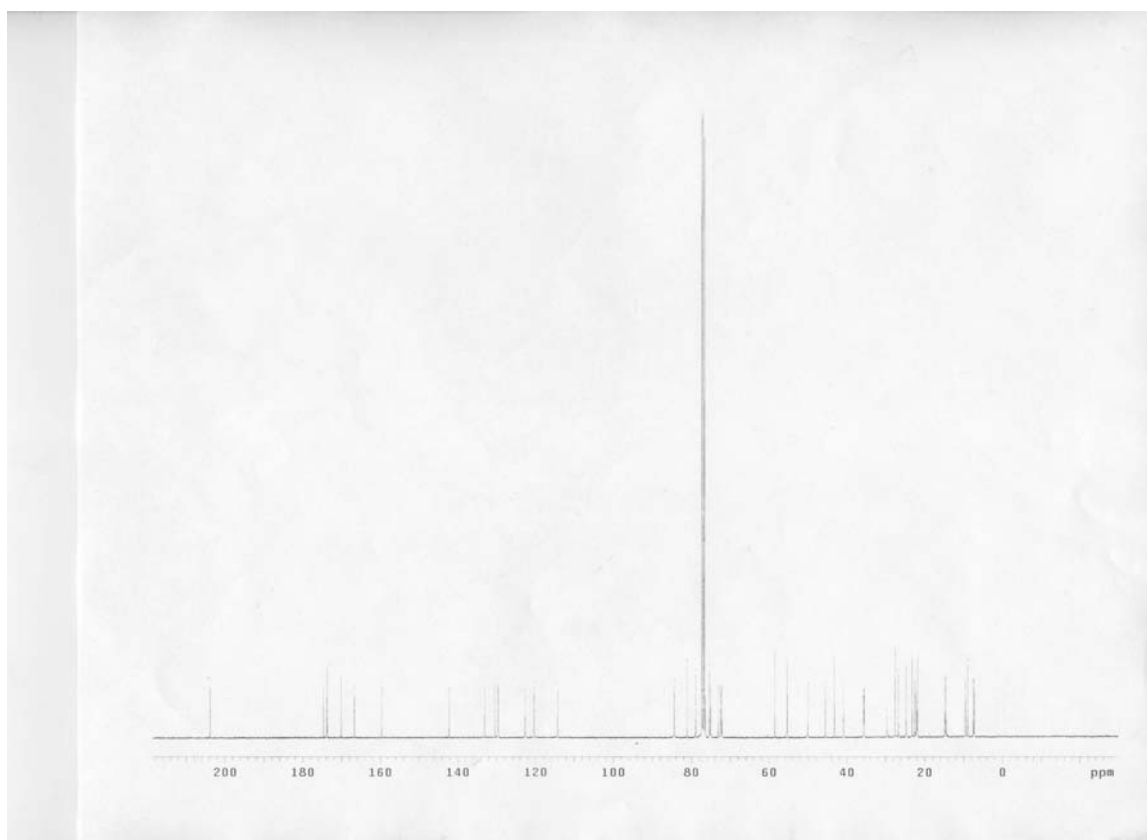
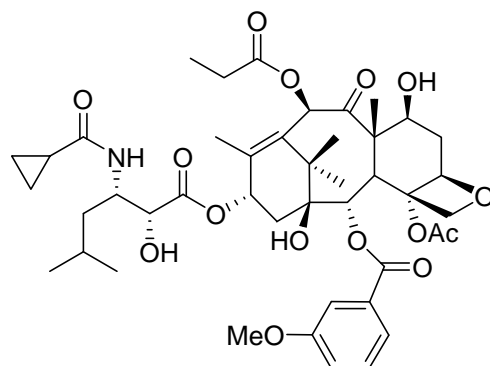
^{13}C NMR Spectrum of 18g



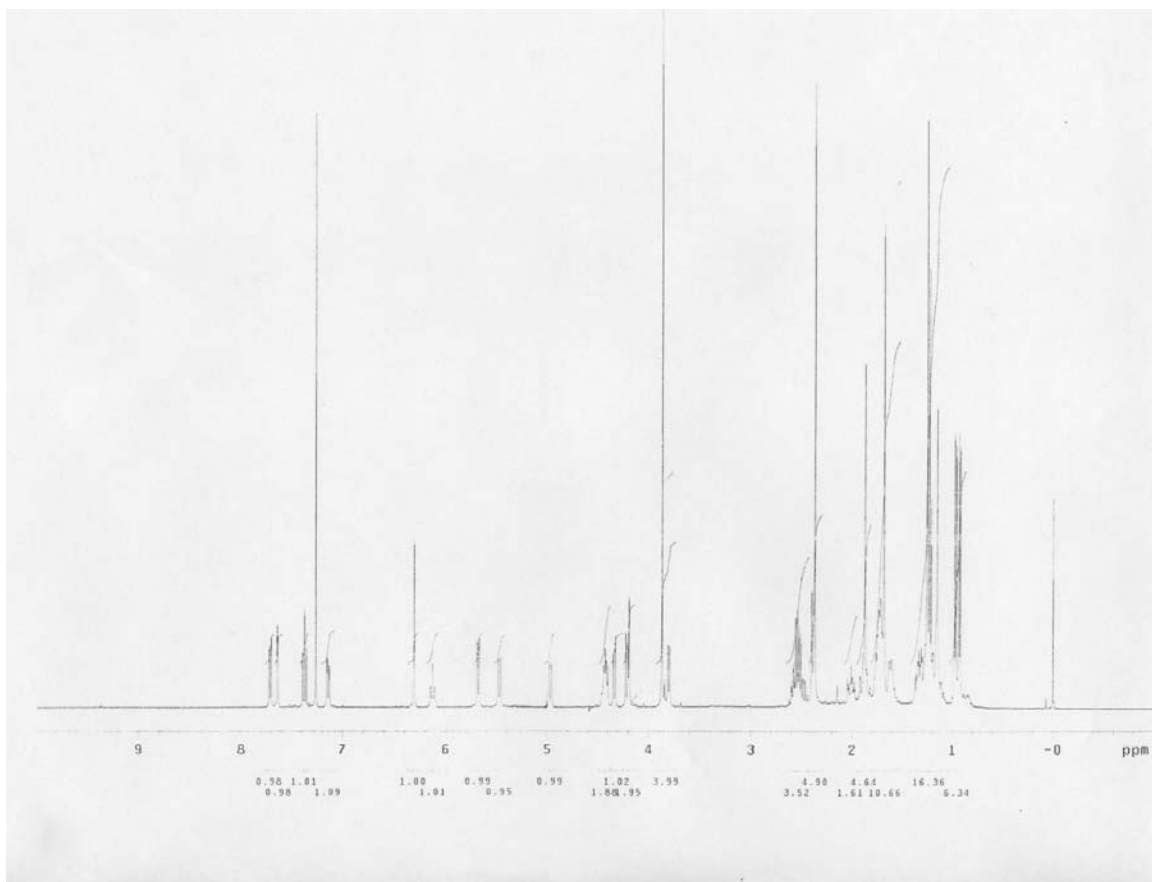
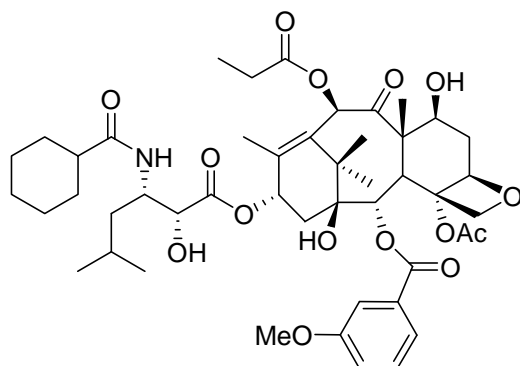
¹H NMR Spectrum of **18h**



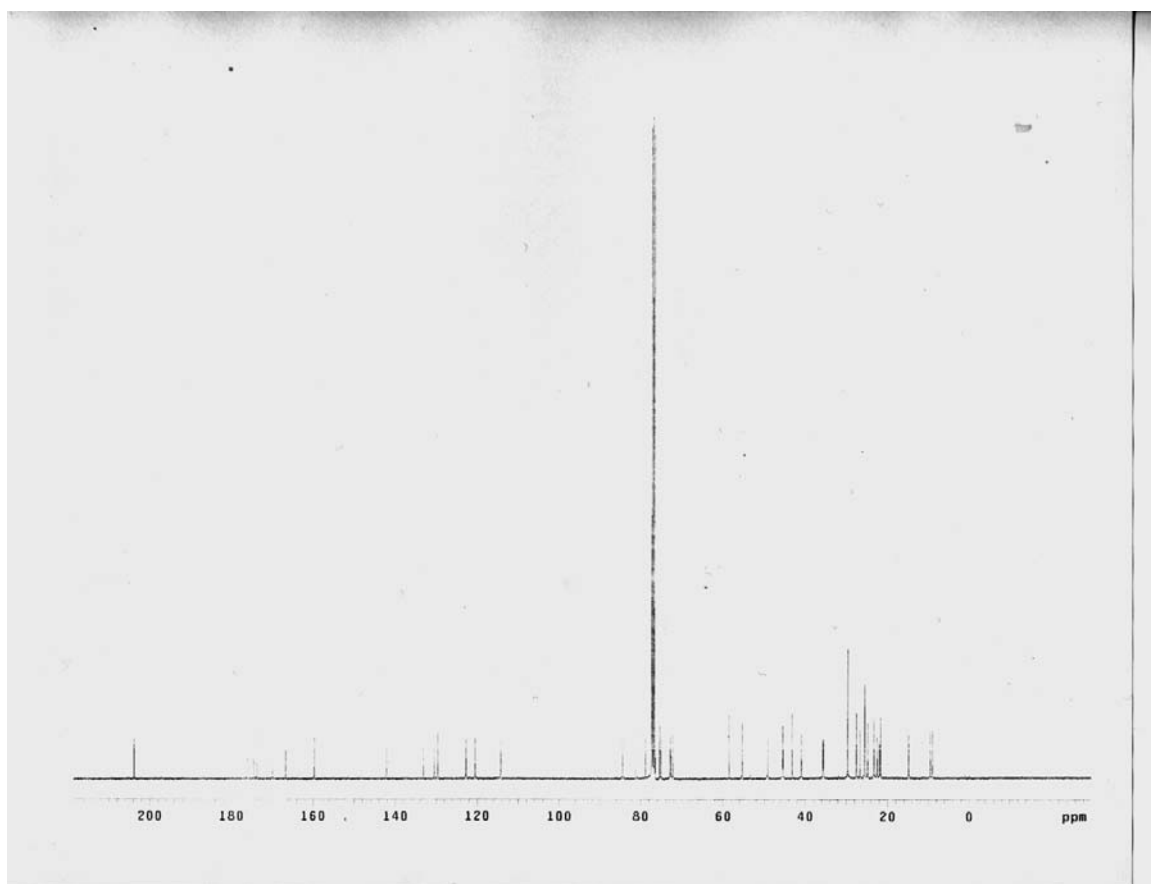
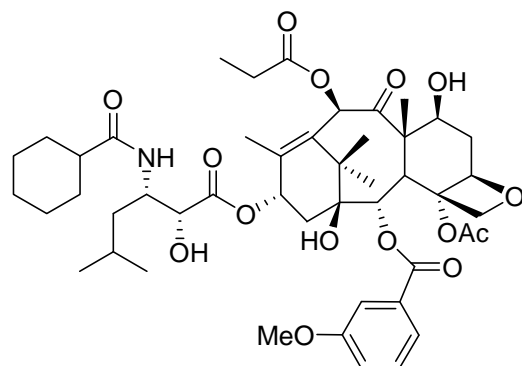
^{13}C NMR Spectrum of **18h**



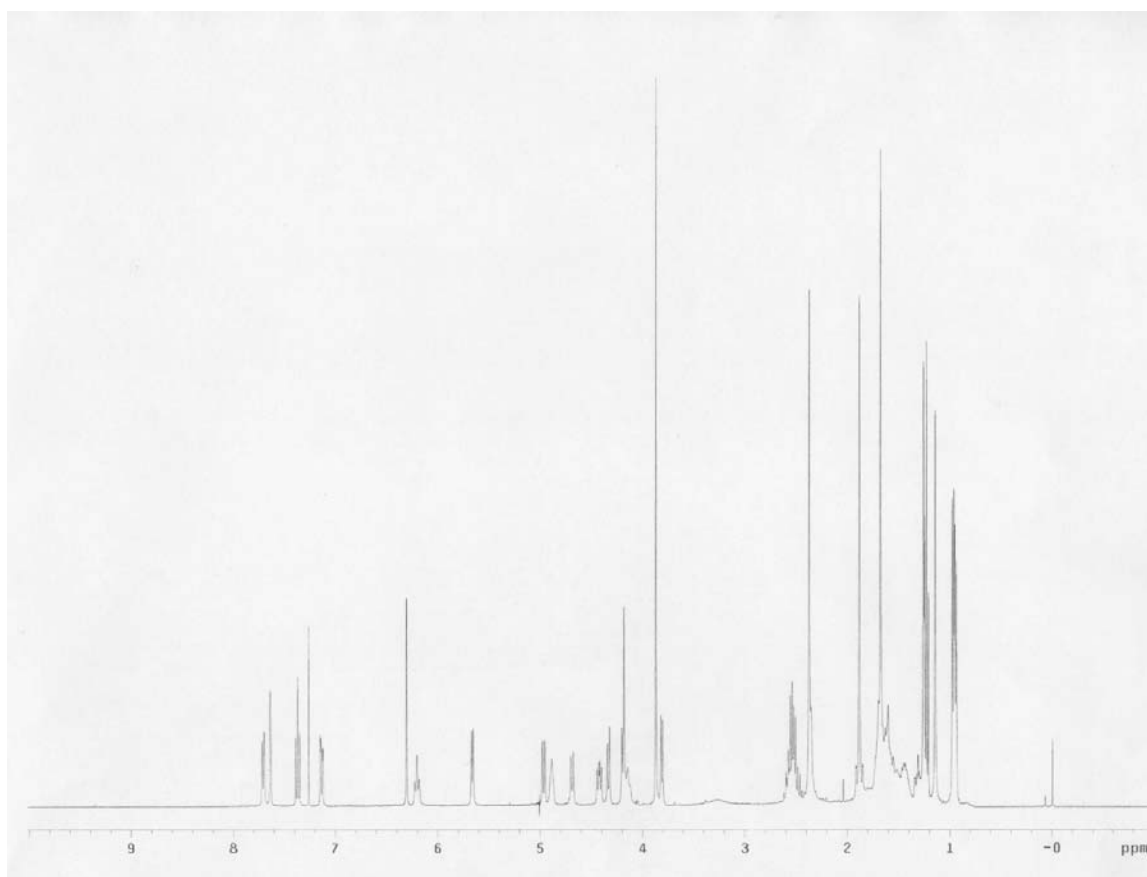
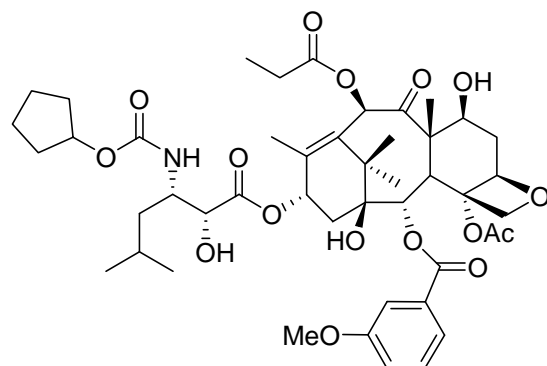
¹H NMR Spectrum of **18k**



^{13}C NMR Spectrum of **18k**



^1H NMR Spectrum of **18m**



^{13}C NMR Spectrum of **18m**

