Evaluation of the Tubulin-Bound Paclitaxel Conformation: Synthesis, Biology and SAR Studies of C-4 to C-3′ Bridged Paclitaxel Analogs

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Characterization Data for Azetidinones 7b-d, 7f-g.

(3*R*,4*S*)-1-Benzoyl-3-*O*-triisopropylsilyloxy-4-(*m*-vinylphenyl)azetidin-2-one (7b): $[\alpha]_D$ +129.9 (*c* = 0.52, $CHCl_3$). ^1H NMR (400 MHz) δ = 8.03 (2H, d, *J* = 7.6 Hz), 7.59 (1H, t, *J* = 7.3 Hz), 7.48 (2H, m) 7.26-7.41 (4H, m), 6.70 (1H, dd, *J* = 17, 10.8 Hz), 5.72 (1H, d, *J* = 18 Hz), 5.43 (1H, d, *J* = 6 Hz), 5.25 (1H, d, *J* =10.8 Hz), 5.23 (1H, d, *J* =6 Hz), 1.00 (3H, m), 0.9 (m, 18H). ^{13}C NMR (100 MHz) δ = 166.5, 165.6, 137.7, 136.8, 134.4, 133.6, 132.2, 130.1, 128.5, 128.4, 127.8, 126.4, 114.3, 76.8, 61.3, 17.6, 17.5, 11.8. HRFABMS: *m/z* calcd for $C_{27}H_{36}NO_3Si^+$ 450.2464, found 450.2447 (Δ = 3.7 ppm).

(3*R*,4*S*)-1-Benzoyl-3-*O*-triisopropylsilyloxy-4-(*o*-allyloxyphenyl)azetidin-2-one (7c): $[\alpha]_D$ + 90 (*c* = 0.7, $CHCl_3$). ^1H NMR (500 MHz) δ = 8.03 (2H, d, *J* = 7.3 Hz), 7.56 (1H, t, *J* = 7.3 Hz), 7.47 (2H, t, *J* = 7.8 Hz), 7.29 (1H, dd, *J* = 7.5, 1.6 Hz), 7.24 (1H, dd, *J* = 7.6, 1.6 Hz), 6.94 (1H, t, *J* = 7.6 Hz), 6.86 (1H, d, *J* = 8.2 Hz), 6.07 (1H, m), 5.86 (1H, d, *J* = 6.4 Hz), 5.40 (1H, dd, *J* = 17.1, 1.6 Hz), 5.27 (1H, dd, *J* = 10.5, 1.6 Hz), 5.26 (1H, d, *J* = 6.2 Hz), 4.55 (2H, qd, *J* = 13.4, 5 Hz), 1.0 (3H, m), 0.89 (18H, d, *J* = 6.8 Hz). ^{13}C NMR (125 MHz) δ = 166.4, 165.8, 157.0, 133.4, 133.2, 132.5, 129.9, 129.1, 128.2, 128.1, 122.3, 120.5, 117.6, 111.5, 76.8, 69.2, 57.1, 17.53, 17.48, 12.0. HRFABMS *m/z* calcd for $C_{28}H_{38}NO_4Si^+$ 480.2570, found 480.2567 (Δ = 0.6 ppm).

(3*R*,4*S*)-1-Benzoyl-3-*O*-triisopropylsilyloxy-4-(*o*-(but-3-enyloxyphenyl)azetidin-2-one (7d): $[\alpha]_D$ + 130 (*c* = 3, $CHCl_3$). ^1H NMR (400 M Hz, $CDCl_3$) δ = 8.03 (2H, d, *J* = 7.3 Hz), 7.58 (1H, m), 7.48 (2H, m), 7.24 (2H, m), 6.95 (1H, t, *J* = 7.6 Hz), 6.87 (1H, d, *J* = 8.4 Hz), 5.90 (1H, m), 5.82 (1H, d, *J* = 6.4 Hz), 5.26 (1H, d, *J* = 6.4 Hz), 5.18 (1H, dd, *J* = 17, 1.6 Hz), 5.10 (1H, dd, *J* =10.3, 1.6 Hz), 4.03 (2H, m), 2.57 (2H, m), 1.0 (3H, m), 0.91 (2 br s, 18H). ^{13}C NMR (100 MHz) δ = 166.5, 166.0, 157.4, 134.6, 133.4, 132.6, 130.0, 129.3, 128.38, 128.32, 122.2, 120.4, 117.3, 111.4,

76.7, 67.5, 57.2, 33.9, 17.65, 17.62, 12.0. HRFABMS *m/z* calcd for $C_{29}H_{39}NO_4Si^+$ 494.2727, found 494.2754 (Δ = 5.5 ppm).

(3*R*,4*S*)-1-Benzoyl-3-*O*-triisopropylsilyloxy-4-(*o*-vinylphenyl)azetidin-2-one (7f): $[\alpha]_D$ + 172.4 (*c* = 2.5, $CHCl_3$). ^{1}H NMR (400 MHz) δ = 8.06 (2H, d, *J* = 7.3 Hz), 7.60 (1H, t, *J* = 7.3 Hz), 7.48 (3H, m) 7.35 (1H, m), 7.28 (2H, m), 7.12 1H, dd, *J* = 17.2, 10.8Hz), 5.77 (1H, d, *J* = 6Hz), 5.64 (1H, dd, *J* =17.2, 1.2 Hz), 5.39 (1H, d, *J* = 11, 1.6 Hz), 5.30 (1H, d, *J* = 6.4 Hz), 1.00 (3H, m), 0.9 (m, 18H). ^{13}C NMR (100 MHz) δ = 166.4, 165.4, 138.2, 134.6, 133.6, 132.2, 131.0, 130.1, 128.4, 128.3, 127.6, 127.2, 126.9, 117.6, 76.9, 58.0, 17.7, 17.6, 12.1. HRFABMS *m/z* calcd for $C_{27}H_{36}NO_3Si^+$ 450.2464, found 450.2472. (Δ = 1.8 ppm).

(3*R*,4*S*)-1-Benzoyl-3-*O*-triisopropylsilyloxy-4-(*o*-allylphenyl)azetidin-2-one (7g): $[\alpha]_D$ + 183.4 (c = 0.35, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.0 (2H, d, *J* = 8 Hz), 7.60 (1H, t, *J* = 7.2 Hz), 7.49 (2H, t, *J* = 7.6 Hz), 7.37 (1H, m), 7.22 (3H, m), 6.05 (1H, m), 5.72 (1H, d, *J* = 6.4 Hz), 5.31 (1H, d, *J* = 6 Hz), 5.16 (1H, dd, *J* = 11.6, 1.2 Hz), 5.12 (1H, dd, *J* = 17, 1.6 Hz), 3.60 (2H, m), 1.0 (3H, m), 0.94 (18H, m). ^{13}C NMR (100 MHz) δ = 166.4, 165.5, 138.5, 136.8, 133.5, 132.3, 132.1, 130.1, 129.8, 128.4, 128.3, 127.4, 126.3, 116.6, 76.7, 57.6, 37.6, 17.77, 17.74, 12.2. HRFABMS *m/z* calcd for $C_{28}H_{38}NO_3Si^+$ 464.2621, found 464.2645 (Δ = 5.2 ppm).

Characterization Data for Baccatins 11b-d.

4-Deacetyl-4-(pent-4-enoyl)-7-*O*-triethylsilylbaccatin III (11b): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (2H, d, *J* = 7.3 Hz), 7.60 (1H, t, *J* = 7.2 Hz), 7.42 (2H, t, *J* = 7.3 Hz), 6.42 (1H, s), 5.90 (1H, m), 5.64 (1H, d, *J* = 7.1 Hz), 5.08 (1H, dd, *J* = 16, 1.8 Hz), 5.04 (1H, dd, *J* = 10, 1.6 Hz), 4.98 (1H, d, *J* = 8 Hz), 4.80 (1H, m), 4.50 (1H, dd, *J* = 10, 6.8 Hz), 4.30 (1H, d, *J* = 8 Hz), 4.18 (1H, d, *J* = 8 Hz), 3.88 (1H, d, *J* = 6.9 Hz), 2.62 (2H, m), 2.50 (3H, m), 2.22 (2H, m), 2.20 (6H, s), 1.82

(1H, m), 1.62 (3H, s), 1.18 (3H, s), 1.00 (3H, s), 0.98 (9H, m), 0.60 (6H, m). ^{13}C NMR (100 MHz) δ = 202.4, 172.6, 169.6, 167.3, 144.2, 136.8, 133.8, 132.8, 130.3, 129.6, 128.7, 116.0, 84.5, 81.0, 78.9, 76.7, 76.0, 74.9, 72.5, 68.1, 58.8, 47.5, 42.9, 38.5, 37.4, 34.8, 28.9, 27.0, 21.7, 20.3, 15.1, 10.1, 6.9, 5.4. HRFABMS *m/z* calcd for $C_{40}H_{56}O_{11}SiLi$ 747.3752, found 747.3747 (Δ = 0.7 ppm).

4-Deacetyl-4-(hex-5-enoyl)-7-*O*-triethylsilylbaccatin III (11c): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (2H, d, *J* = 7.2 Hz), 7.59 (1H, t, *J* = 7.3 Hz), 7.45 (2H, t, *J* = 7.6 Hz), 6.46 (1H, s), 5.84 (1H, m), 5.60 (1H, d, *J* = 7.1 Hz), 5.08 (1H, dd, *J* = 17.6, 1.8 Hz), 5.02 (1H, dd, *J* = 10, 1.6 Hz), 4.92 (1H, d, *J* = 8 Hz), 4.81 (1H, m), 4.80 (1H, m), 4.28 (1H, d, *J* = 8 Hz), 4.15 (1H, d, *J* = 8 Hz), 3.82 (1H, d, *J* = 6.8 Hz), 2.58 (3H, m), 2.55 (2H, s), 2.15 (6H, s), 2.14 (1H, m), 1.84 (3H, m), 1.64 (4H, s), 1.20 (3H, s), 1.00 (3H, s), 0.98 (9H, m), 0.60 (6H, m). ^{13}C NMR (100 MHz) δ = 202.4, 173.1, 169.6, 167.3, 144.2, 137.8, 133.8, 132.8, 130.3, 129.5, 128.7, 115.8, 84.5, 80.9, 78.9, 76.8, 76.0, 74.9, 72.5, 68.1, 58.8, 47.4, 43.0, 38.5, 37.4, 35.0, 33.3, 27.0, 24.0, 21.1, 20.3, 15.1, 10.1, 6.9, 5.4. HRFABMS *m/z* calcd for $C_{41}H_{59}O_{11}Si^{+}$ 755.3827, found: 755.3834 (Δ = 1 ppm).

4-Deacetyl-4-(hept-6-enoyl)-7-*O*-triethylsilyl baccatin III (11d): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.11 (2H, d, *J* = 7.2 Hz), 7.59 (1H, t, *J* = 7.3 Hz), 7.45 (2H, t, *J* = 7.6 Hz), 6.44 (1H, s), 5.82 (1H, m), 5.62 (1H, d, *J* = 7.1 Hz), 5.05 (1H, dd, *J* = 17, 1.8 Hz), 4.92 (1H, dd, *J* = 10, 1.6 Hz), 4.90 (1H, d, *J* = 8 Hz), 4.81 (1H, m), 4.80 (1H, m), 4.48 (1H, dd, *J* = 10.4, 6.6 Hz), 4.28 (1H, d, *J* = 8 Hz), 4.13 (1H, d, *J* = 8 Hz), 3.86 (1H, d, *J* = 6.8 Hz), 2.56 (3H, m), 2.16 (6H, s), 2.13 (2H, m), 2.03 (1H, d, *J* = 5 Hz), 1.85 (1H, m), 1.74 (2H, s), 1.67 (3H, s), 1.62 (3H, s), 1.52 (1H, m), 1.18 (3H, s), 1.0 (3H, s), 0.91 (9H, m), 0.58 (6H, m). ^{13}C NMR (125 MHz) δ = 202.2, 173.1, 169.4, 167.2, 144.0, 138.4, 133.7, 132.7, 130.2, 129.4, 128.6, 115.0, 84.4, 80.8, 78.8, 76.6, 75.8, 74.8, 72.4, 68.0, 58.7, 47.3, 42.8, 38.3, 37.3, 35.5, 33.4, 28.5, 26.8, 24.1, 21.0, 20.1, 14.9, 10.0, 6.8, 5.3. HRFABMS *m/z* calcd for $C_{42}H_{61}O_{11}Si^{+}$ 769.3983, found 769.3973 (Δ = 1.3 ppm).

Characterization Data for Paclitaxels 12b-k

3'-Dephenyl-3'-(*m*-vinylphenyl)-4-deacetyl-4-acryloyl-7-*O*-triethylsilyl-2'-O-triisopropylsilylpaclitaxel (12b): ^{1}H NMR (400 MHz) δ = 8.15 (2H, d, *J* = 7.3 Hz), 8.07 (1H, m), 7.70 (2H, d, *J* = 7.6 Hz), 7.62-7.26 (9H, m), 7.08 (1H, d, *J* = 8.4 Hz), 6.74 (1H, dd, *J* = 17.6, 10.8 Hz), 6.61(1H, d, *J* = 17.6 Hz), 6.52 (1H, dd, *J* = 17.6, 10.8 Hz), 6.48 (1H, s), 6.13 (1H, t, *J* = 9.2 Hz), 5.88 (1H, d, *J* = 10.8 Hz), 5.79 (1H, s), 5.72 (1H, dd, *J* = 9.2, 6.8 Hz), 5.61 (1H, d, *J* = 8.8 Hz), 5.30 (1H, d, *J* = 10.4 Hz), 4.90 (1H, d, *J* = 9.6 Hz), 4.86 (1H, s), 4.58 (1H, dd, *J* = 11.4, 7.2 Hz), 4.34 (1H, d, *J* = 8.4 Hz), 4.25 (1H, d, *J* = 8.4 Hz), 3.90 (1H, d, *J* = 7.2 Hz), 2.58 (1H, m), 2.40 (1H, m), 2.20 (1H, m), 2.19 (3H, s), 2.08 (3H, m), 1.90 (1H, m), 1.70 (3H, s), 1.68 (3H, s), 1.25 (3H, s), 0.93 (30H, m), 0.60 (6H, m). ^{13}C NMR (100 MHz) δ = 201.9, 172.1, 169.5, 167.2, 167.1, 165.1, 140.5, 139.0, 138.2, 136.7, 134.3, 133.8, 133.7, 132.7, 131.9, 130.4, 129.6, 129.3, 129.0, 128.9, 127.1, 126.1, 125.9, 124.6, 114.7, 84.4, 81.6, 79.0, 77.4, 76.8, 75.3, 75.2, 72.4, 71.8, 58.6, 56.1, 47.0, 43.5, 37.4, 36.0, 29.9, 26.7, 21.7, 21.1, 18.07, 18.03, 14.5, 12.8, 10.3, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{65}H_{87}NO_{14}Si_2Na^+$ 1184.5563, found 1184.5529 (Δ = 3 ppm).

3'-Dephenyl-3'-(*o*-allyloxyphenyl)-4-deacetyl-4-acryloyl-7-*O*-triethylsilyl-2'-*O*-triisopropylsilylpaclitaxel (12c): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.12 (2H, d, *J* = 7.1 Hz), 7.73 (2H, d, *J* = 7.1 Hz), 7.54 (1H, t, *J* = 7.3 Hz), 7.44 (4H, m), 7.33 (2H, t, *J* = 7.8 Hz), 7.27 (1H, m), 7.05 (1H, d, *J* = 9 Hz), 6.94 (2H, m), 6.65 (1H, dd, *J* = 17, 10 Hz), 6.57 (1H, dd, *J* = 17.4, 1.2 Hz), 6.47 (1H, s), 6.35 (1H, m), 6.22 (1H, t, *J* = 7.4 Hz), 5.95 (1H, dd, *J* = 10, 1.2 Hz), 5.88 (1H, dd, *J* = 10, 1.1 Hz), 5.68 (1H, d, *J* = 7.3 Hz), 5.53 (1H, dd, *J* = 17.4, 1.4 Hz), 5.35 (2H, 2 singlets), 4.90 (1H, d, *J* = 7 Hz), 4.80 (1H, dd, *J* = 7.4, 5 Hz), 4.60 (2H, m), 4.30 (1H, d, *J* = 8.2 Hz), 4.21 (1H, d, *J* = 8.2 Hz), 3.84 (1H, d, *J* = 7.4 Hz), 2.55 (1H, m), 2.30 (1H, m), 2.17 (3H, s), 2.06 (3H, s), 1.98 (1H, m),

1.71 (3H, s), 1.65 (3H, s), 1.20 (3H, s), 1.06 (1H, m), 0.98 (27H, m), 0.60 (9H, m). ^{13}C NMR (100 MHz) δ = 201.8, 172.4, 169.3, 166.3, 165.6, 155.4, 140.7, 138.5, 134.4, 133.4, 133.2, 132.8, 131.5, 130.2, 129.4, 129.0, 128.7, 128.6, 128.2, 126.9, 125.9, 121.1, 119.0, 111.5, 84.2, 80.8, 79.4, 77.2, 75.2, 74.9, 72.9, 72.3, 71.0, 69.4, 58.3, 53.2, 47.0, 43.3, 37.1, 36.0, 29.7, 26.7, 22.0, 20.9, 17.8, 14.2, 12.5, 10.0, 6.7, 5.3. HRFABMS *m/z* calcd for $C_{66}H_{89}NO_{15}Si_2Na^+$ 1214.5668, found 1214.5667 (Δ = 0.1 ppm).

3'-Dephenyl-3'-(*o*-[but-3-enyloxy]phenyl)-4-deacetyl-4-acryloyl-7-*O*-triethylsilyl-2'-*O*-triisopropylsilylpaclitaxel (12d): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (2H, d, *J* = 7.3 Hz), 7.70 (2H, d, *J* = 7.2 Hz), 7.53 (1H, m), 7.45 (3H, m), 7.30 (4H, m), 7.03 (1H, d, *J* = 8.8 Hz), 6.95 (2H, m), 6.70 (1H, dd, *J* = 17.2, 10.4 Hz), 6.55 (1H, dd, *J* = 17.2, 1.2 Hz), 6.46 (1H, s), 6.26 (1H, t, *J* = 8.8 Hz), 5.95 (2H, m), 5.85(1H, d, *J* = 8.8 Hz), 5.68 (1H, d, *J* = 7.2 Hz), 5.39 (1H, d, *J* = 2 Hz), 5.25 (1H, dd, *J* = 17.4, 1.6 Hz), 5.14 (1H, dd, *J* = 10.4, 1.6 Hz), 4.92 (1H, d, *J* = 7.6 Hz), 4.58 (1H, dd, *J* = 10.8, 6.8 Hz), 4.30 (1H, d, *J* = 8.4 Hz), 4.23-4.1 (3H, m), 3.84 (1H, d, *J* = 7.2 Hz), 2.85 (1H, m), 2.74 (1H, m), 2.54 (1H, m), 2.30 (1H, dd, *J* = 15.2, 10Hz), 2.17 (3H, s), 2.06 (3H, s), 2.0-1.88 (2H, m), 1.72 (3H, s), 1.22 (6H, s), 0.98-0.88 (30H, m), 0.60 (9H, m). ^{13}C NMR (100 MHz) δ = 202.0, 172.5, 169.6, 167.3, 166.5, 165.9, 155.8, 140.8, 134.6, 134.0, 133.6, 133.5, 133.1, 131.7, 130.4, 129.6, 129.2, 128.9, 128.8, 128.3, 127.1, 125.8, 121.1, 117.8, 111.3, 84.4, 81.0, 79.7, 76.7, 75.3, 75.1, 73.1, 72.5, 71.0, 67.7, 58.4, 53.6, 47.2, 43.5, 37.3, 36.2, 33.7, 26.9, 22.2, 21.1, 18.0,17.9, 14.4, 12.6, 10.5, 6.9, 5.3. HRFABMS *m/z* calcd for $C_{67}H_{91}NO_{15}Si_2^+$ 1206.6006, found: 1206.5958 (Δ = 4 ppm).

3'-Dephenyl-3'-(*o*-vinylphenyl)-4-deacetyl-4-acryloyl-7-*O*-triethylsilyl-2'-*O*-triisopropylsilylpaclitaxel (12e): ^{1}H NMR (400 MHz) δ = 8.14 (2H, d, *J* = 7.3 Hz), 7.72 (2H, d, *J* = 7 Hz), 7.60 (2H, m), 7.45 (4H, m), 7.31 (6H, m), 7.02 (1H, d, *J* = 8.8 Hz), 6.48 (1H, s), 6.41 (1H, d,

J = 6.5 Hz), 6.39 (1H, d, *J* = 1.2 Hz), 6.06 ((1H, t, *J* = 9 Hz), 5.84 (1H, broad d, *J* = 7.6 Hz), 5.80 (1H, d, *J* = 1.4 Hz), 5.73 (1H, d, *J* =7.2 Hz), 5.48 (3H, m), 4.90 (1H, broad d, *J* = 8 Hz), 4.83 (1H, d, *J* = 1.2 Hz), 4.56 (1H, dd, *J* = 10.4, 6.8 Hz), 4.32 (1H, d, *J* = 8.4 Hz), 4.24 (1H, d, *J* = 8.4 Hz), 3.88 (1H, d, *J* = 7.2 Hz), 2.52 (1H, m), 2.42 (1H, m), 2.35 (1H, m), 2.10 (1H, m), 2.07 (3H, s), 1.90 (1H, m), 1.78 (1H, m), 1.72 (3H, s), 1.22 (3H, s), 1.20 (3H, s), 0.95 (30H, m), 0.60 (6H, m). ^{13}C NMR (100 MHz) δ = 201.9, 172.4, 169.5, 167.1, 166.7, 165.5, 140.7, 136.26, 136.20, 134.7, 134.3, 133.7, 133.5, 132.5, 131.8, 130.3, 129.7, 129.3, 128.8, 128.5, 128.2, 127.1, 127.0, 126.8, 117.0, 84.3, 81.4, 79.3, 75.3, 75.2, 74.3, 72.5, 58.6, 52.8, 47.2, 43.5, 37.3, 36.1, 26.8, 21.9, 21.1, 18.1, 18.0, 14.4, 12.9, 10.4, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{65}H_{87}NO_{14}Si_2Na^+$ 1184.5563, found 1184.5588 (Δ = 2.2 ppm).

3'-Dephenyl-3'-(*o*-allylphenyl)-4-deacetyl-4-acryloyl-7-*O*-triethylsilyl-2'-*O*-triisopropylsilylpaclitaxel (12f): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (2H, d, *J* = 8 Hz), 7.70 (2H, d, *J* = 7.6 Hz), 7.60 (1H, t, *J* = 7.6 Hz), 7.44-7.52 (4H, m), 7.38 (2H, t, *J* = 7.6 Hz), 7.24-7.31 (3H, m), 6.95 (1H, d, *J* = 9.2 Hz), 6.48 (1H, s), 6.44 (1H, d, *J* = 1.6 Hz), 6.32 (1H, dd, *J* = 10, 6.1 Hz), 6.08 (1H, m), 5.95 (1H, t, *J* = 9.6 Hz), 5.80 (1H, d, *J* = 9.6 Hz), 5.75 (1H, d, *J* = 7.2 Hz), 5.57 (1H, dd, *J* = 10, 1.6 Hz), 5.18 (1H, dd, *J* = 16.8, 1.6 Hz), 5.12 (1H, dd, *J* = 10, 1.6 Hz), 4.90 (1H, d, *J* = 7.6 Hz), 4.74 (1H, d, *J* = 1.6 Hz), 4.54 (1H, dd, *J* = 10.4, 6.4 Hz), 4.34 (1H, d, *J* = 8 Hz), 4.25 (1H, d, *J* = 8.4 Hz), 3.90 (1H, d, *J* = 7.2 Hz), 3.72 (1H, dd, *J* = 15, 6.4 Hz), 3.52 (1H, dd, *J* = 15.4, 6.8 Hz), 2.56 (1H, m), 2.40 (2H, m), 2.18 (3H, s), 2.03 (3H, s), 1.71 (3H, s), 1.23 (3H, s), 1.18 (3H, s), 1.00-1.07 (11H, m), 0.94 (9H, t, *J* = 8 Hz), 0.60 (6H, m). ^{13}C NMR (100 MHz) δ = 202.8, 172.8, 169.5, 167.0, 165.0, 140.9, 137.4, 136.8, 136.2, 134.3, 133.7, 133.5, 132.0, 131.8, 130.29, 130.23, 129.7, 129.4, 128.8, 128.8, 128.5, 127.7, 127.6, 127.0, 126.8, 117.3, 84.4, 81.7, 78.9, 75.2, 74.4, 73.4, 72.3,

58.6, 52.4, 46.9, 43.5, 37.4, 37.1, 36.1, 26.6, 21.8, 21.0, 18.2, 18.1, 14.4, 13.0, 10.3, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{60}H_{89}NO_{14}Si_2Na^+$ 1198.5719, found 1198.5742 (Δ = 1.9 ppm).

Synthesis of 3'-Dephenyl-3'-(*m*-allyloxyphenyl)-4-deacetyl-4-acryloyl-7-*O*-triethylsilyl-2'-*O*-triisopropylsilylpaclitaxel (12g). To a solution of sodium hydride (95 mg, 20 eq) in THF (5 mL) was added **11b** (150 mg, 0.2 mmol) in THF (2.5 mL) at 0 °C, and the resulting solution was stirred for 15 min. A solution of **7a** (115 mg, 0.24 mmol, 1.2eq) in tetrahydrofuran (1.2 mL) was added to the above reaction mixture at 0 °C, and the resulting solution was brought to room temperature over 24 h. Saturated brine (5 mL) was added to quench the reaction, and usual work-up gave crude mass which was purified by preparative TLC using 20% EtOAc in hexane as solvent to furnish **12g** (168 mg, 62%). **(12g):** ^{1}H NMR (400 MHz) δ = 8.15 (2H, d, *J* = 7.3 Hz), 7.76 (2H, d, *J* = 7.2 Hz), 7.60 (1H, m), 7.52 (3H, m), 7.39 (1H, t, *J* = 7.6 Hz), 7.27 (1H, m), 7.08 (1H, d, *J* = 8.8 Hz), 6.90 (1H, d, *J* = 8 Hz), 6.85 (1H, dd, *J*= 9, 1.2 Hz), 6.45 (1H, s), 6.14 (1H, t, *J* = 8 Hz), 6.02 (1H, m), 5.85 (1H, m), 5.70 (1H, d, *J* = 7.2 Hz), 5.64 (1H, d, *J* = 7.2 Hz), 5.40 (1H, d, *J* = 17.2, 1.2 Hz), 5.28 (1H, dt, *J* = 10.8, 1.2 Hz), 5.14 (1H, d, *J* = 16.8 Hz), 5.03 (1H, d, *J* = 10.4 Hz), 4.90 (1H, m), 4.86 (1H, d, *J* = 9.6 Hz), 4.54 (1H, d, *J* = 5.2 Hz), 4.47 (1H, dd, *J* = 10.6, 6.4 Hz), 4.30 (1H, d, *J* = 8 Hz), 4.21 (1H, d, *J* = 8 Hz), 3.83 (1H, d, *J* = 6.8 Hz), 2.65-2.40 (4H, m), 2.20 (1H, m), 2.19 (3H, s), 2.05 (3H, m), 1.70 (1H, m), 1.69 (3H, s), 1.21 (3H, s), 1.16 (3H, s), 0.94 (30H, m), 0.5 (6H, m). ^{13}C NMR (100 MHz) δ = 202.0, 172.2, 172.1, 169.5, 167.1, 159.2, 140.4, 140.1, 135.9, 134.2, 133.8, 133.3, 132.0, 130.4, 129.9, 129.5, 128.9, 127.1, 119.1, 117.9, 117.0, 114.6, 113.2, 84.6, 81.4, 78.9, 75.6, 75.1, 72.4, 72.2, 71.7, 69.1, 58.6, 56.1, 46.9, 43.5, 37.4, 29.9, 26.7, 21.7, 21.1, 18.1, 18.0, 14.4, 12.8, 10.3, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{68}H_{93}NO_{15}Si_2Na^+$ 1242.5981, found 1242.5980 (Δ = 0.1 ppm).

3'-Dephenyl-3'-(*m*-vinylphenyl)-4-deacetyl-4-(pent-4-enoyl)-7-O-triethylsilyl-2'-O-triisopropylsilylpaclitaxel (12h): ^{1}H NMR (400 MHz) δ = 8.15 (2H, d, *J* = 7.3 Hz), 7.75 (2H, d, *J* = 7.3 Hz), 7.61 (1H, m), 7.52 (2H, m), 7.36 (6H, m), 7.25 (3H, m), 7.12 (1H, d, *J* = 8.8 Hz), 6.70 (1H, dd, *J* = 17.6, 10.8 Hz), 6.45 (1H, s), 6.16 (1H, t, *J* = 9 Hz), 5.83-5.65 (4H, m), 5.30 (1H, d, *J* = 10.8 Hz), 5.12 (1H, d, *J* = 17.2 Hz), 5.02 (1H, d, *J* = 10.4 Hz), 4.90 (1H, s), 4.88 (1H, d, *J* = 9.6 Hz), 4.85 (1H, dd, *J* = 10.6, 6.8 Hz), 4.31 (1H, d, *J* = 8.4 Hz), 4.21 (1H, d, *J* = 8.4 Hz), 4.12 (1H, d, *J* = 7.2 Hz), 3.84 (1H, d, *J* = 7.2 Hz), 3.24 (1H, m), 2.65 (1H, m), 2.58 (2H, m), 2.40 (1H, m), 2.19 (1H, m), 2.16 (3H, s), 2.04 (3H, m), 1.88 (1H, m), 1.71 (3H, s), 1.70 (3H, s), 1.16 (3H, s), 0.94 (30H, m), 0.55 (6H, m). ^{13}C NMR (100 MHz) δ = 201.9, 172.1, 169.5, 167.1, 140.4, 138.8, 138.3, 136.7, 135.8, 134.2, 133.8, 132.0, 130.4, 129.5, 129.1, 128.9, 127.1, 126.2, 126.0, 124.7, 117.1, 114.7, 84.6, 81.5, 78.9, 75.6, 75.2, 75.1, 72.4, 72.2, 58.6, 56.3, 46.9, 43.5, 37.4, 35.9, 29.9, 26.7, 21.7, 21.1, 18.1, 18.0, 14.4, 12.8, 10.3, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{67}H_{92}NO_{14}Si_2^+$ 1190.6056, found 1190.6060 (Δ = 0.3 ppm).

3'-Dephenyl-3'-(*o*-allyloxyphenyl)-4-deacetyl-4-(pent-4-enoyl)-7-*O*-triethylsilyl-2'-*O*-triisopropylsilylpaclitaxel (12i): ^{1}H NMR (500 MHz) = δ 8.17 (2H, d, *J* = 7.1 Hz), 7.69 (2H, d, *J* = 7.1 Hz), 7.56 (1H, t, *J* = 7 Hz), 7.50-7.40 (4H, m), 7.30 (3H, m), 7.11 (1H, d, *J* = 8.7 Hz), 6.93 (2H, m), 6.44 (1H, s), 6.34 (1H, m), 6.26 (1H, t, *J* = 8.5 Hz), 5.99 (1H, dd, *J* = 10.2, 1.8 Hz), 5.74 (1H, m), 5.65 (1H, d, *J* = 7.3 Hz), 5.49 (1H, d, *J* = 16.7 Hz), 5.33 (1H, dd, *J* = 16.7, 10.3 Hz), 5.31 (1H, d, *J* = 2.2 Hz), 4.99 (1H, d, *J* = 16.9 Hz), 4.86 (2H, m), 4.73 (1H, dd, *J* = 11.6, 4.3 Hz), 4.54 (2H, m), 4.26 (1H, d, *J* = 8 Hz), 4.18 (1H, d, *J* = 8 Hz), 3.80 (1H, d, *J* = 7.3 Hz), 3.24 (1H, m), 2.82 (1H, m), 2.50 (3H, m), 2.32 (1H, m), 2.22 (1H, m), 2.16 (3H, s), 2.03 (3H, s), 1.98 (1H, m), 1.70 (3H, s), 1.57 (3H, s), 1.19 (3H, s), 0.91 (30H, m), 0.59 (6H, m). ^{13}C NMR (100 MHz) δ = 202.0, 173.2, 172.5, 169.5, 167.2, 166.6, 155.6, 140.8, 136.5, 134.4, 133.6, 133.15, 133.11, 131.7, 130.6, 129.6, 129.2,

128.9, 128.86, 128.83, 128.36, 127.2, 127.1, 126.2, 121.2, 119.2, 116.0, 111.7, 84.7, 80.9, 79.6, 77.4, 76.7, 75.3, 75.1, 73.5, 72.5, 71.2, 69.7, 58.4, 53.0, 47.1, 43.5, 37.3, 36.2, 34.9, 30.2, 26.8, 22.3, 21.1, 18.0, 17.9, 17.7, 14.3, 12.7, 12.3, 10.5, 7.0, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{68}H_{93}NO_{15}Si_2Na^+$ 1242. 5981, found 1242.5944 (Δ = 3 ppm).

3'-Dephenyl-3'-(*o*-allyloxyphenyl)-4-deacetyl-4-(hex-5-enoyl)-7-*O*-triethylsilyl-2'-*O*-triisopropylsilylpaclitaxel (12j): ^{1}H NMR (400 MHz) δ = 8.18 (2H, d, *J* = 8.4 Hz), 7.69 (2H, d, *J* = 8.4 Hz), 7.56 (1H, m), 7.42 (4H, m), 7.28 (3H, m), 7.09 (1H, d, *J* = 9.6 Hz), 6.93 (3H, m), 6.52 (1H, m), 6.45 (1H, s), 6.38 (1H, m), 6.25 (1H, t, *J* = 9.2 Hz), 6.00 (1H, d, *J* = 9.2 Hz), 5.67 (2H, m), 5.49 (1H, d, *J* = 17.2 Hz), 5.34 (1H, d, *J* = 9.2 Hz), 5.33 (1H, d, *J* = 1.2 Hz), 4.88 (1H, d, *J* = 6 Hz), 4.86 (1H, d, *J* = 1.2 Hz), 4.83(1H, d, *J* = 6.8 Hz), 4.76 (1H, m), 4.59 (2H, m), 4.26 (1H, d, *J* = 8 Hz), 4.19 (1H, d, *J* = 8 Hz), 3.80 (1H, d, *J* = 7.6 Hz), 3.20 (1H, m), 2.82 (1H, m), 2.78 (1H, m), 2.58 (3H, m), 2.38 (1H, m), 2.20 (1H, m), 2.17 (3H, s), 2.02 (3H, s), 1.98 (2H, m), 1.90 (1H, m), 1.71 (3H, s), 1.61 (3H, s), 1.26 (1H, m), 1.20 (3H, s), 0.93 (30H, m), 0.59 (6H, m). ^{13}C NMR (100 MHz) δ = 202.0, 173.7, 172.4, 169.6, 167.2, 166.4, 155.5, 140.9, 137.8, 134.4, 133.6, 133.1, 133.0, 131.7, 130.6, 130.2, 129.5, 129.2, 128.9, 128.86, 128.81, 128.3, 127.7, 127.2, 127.1, 126.3, 121.2, 119.3, 115.4, 111.7, 84.8, 80.7, 79.7, 76.7, 75.3, 75.1, 73.4, 72.5, 71.1, 69.8, 58.4, 53.0, 47.1, 43.5, 37.3, 36.3, 35.2, 33.2, 26.8, 25.5, 22.3, 21.1, 18.0, 17.9, 14.3, 12.7, 10.5, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{69}H_{96}NO_{15}Si_2^+$ 1234. 6319, found 1234.6331 (Δ = 1 ppm).

3'-Dephenyl-3'-(*o*-allyloxyphenyl)-4-deacetyl-4-(hept-6-enoyl)-7-*O*-triethylsilyl-2'-*O*-triisopropylsilylpaclitaxel (12k): ^{1}H NMR (400 MHz) δ = 8.20 (2H, d, *J* = 7.6 Hz), 7.68 (2H, d, *J* = 7.6 Hz), 7.54 (1H, m), 7.48 (4H, m), 7.28 (3H, m), 7.08 (1H, d, *J* = 9.2 Hz), 6.93 (2H, m), 6.52 (1H, s), 6.45 (1H, s), 6.37 (1H, m), 6.26 (1H, t, *J* = 8.4 Hz), 6.00 (1H, dd, *J* = 9.2, 1.6 Hz), 5.58-5.68 (2H, m), 5.50 (1H, d, *J* = 17.2 Hz), 5.36 (1H, d, *J* = 2.4 Hz), 5.34 (1H, d, *J* = 10.6, 1.6 Hz), 4.88 (3H,

m), 4.75 (1H, dd, *J* = 12, 4.8 Hz), 4.55 (2H, m), 4.26 (1H, d, *J* = 8.4 Hz), 4.20 (1H, d, *J* = 8.4 Hz), 3.80 (1H, d, *J* = 7.6 Hz), 3.20 (1H, m), 2.71 (1H, m), 2.54 (3H, m), 2.35 (1H, m), 2.17 (3H, s), 2.03 (3H, s), 1.90 (3H, m), 1.71 (3H, s), 1.61(3H, s), 1.20 (3H, s), 1.05 (1H, m), 0.92 (30H, m), 0.59 (6H, m). ^{13}C NMR (100 MHz) δ = 202.0, 173.9, 172.4, 169.6, 167.3, 166.4, 155.5, 140.9, 138.5, 134.4, 133.6, 133.1, 133.0, 131.7, 130.6, 130.29, 130.21, 129.6, 129.2, 128.88, 128.81, 128.2, 127.1, 126.3, 121.3, 119.3, 114.8, 111.6, 84.8, 80.7, 79.7, 76.7, 75.3, 75.1, 73.4, 72.5, 71.1, 69.7, 58.4, 53.0, 47.1, 43.5, 37.3, 36.3, 35.6, 33.2, 28.5, 26.8, 25.7, 22.3, 21.1, 18.0, 14.3, 12.7, 10.5, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{70}H_{97}NO_{15}Si_2Na^+$ 1270. 6294, found 1270.6277 (Δ = 1.3 ppm).

Characterization Data for Paclitaxels 13b-j

3'-Dephenyl-3'-(*m*-vinylphenyl)-4-deacetyl-4-acryloylpaclitaxel (13b): ^{1}H NMR (400 MHz) δ = 8.20 (2H, d, *J* = 7.2 Hz), 7.74 (2H, d, *J* = 7.2 Hz), 7.68 (1H, m), 7.55 (4H, m), 7.44 (5H, m), 6.88 (1H, d, *J* = 9.2 Hz), 6.80 (1H, dd, *J* = 17.4, 10.8 Hz), 6.53 (1H, dd, *J* = 17.6, 1.2 Hz), 6.38 (1H, dd, *J* = 13.8, 10.4 Hz), 6.33 (1H, s), 6.20 (1H, m), 5.86 (1H, dd, *J* = 17.2, 1.2 Hz), 5.80 (1H, d, *J* = 1.6 Hz), 5.73 (1H, d, *J* = 7.2 Hz), 5.68 (1H, dd, *J* = 10.4, 1.2 Hz), 5.35 (1H, d, *J* = 11.2 Hz), 4.96 (1H, dd, *J* = 7.6, 1 Hz), 4.79 (1H, m), 4.52 (1H, m), 4.39 (1H, d, *J* = 8.4 Hz), 4.28 (1H, d, *J* = 8.4 Hz), 3.91 (1H, d, *J* = 6.8 Hz), 3.40 (1H, d, *J* = 4.4 Hz), 2.60 (1H, m), 2.52-2.34 (3H, m), 2.28 (3H, s), 1.93 (1H, m), 1.87 (3H, s), 1.74 (3H, s), 1.26 (3H, s), 1.18 (3H, s). ^{13}C NMR (100 MHz) δ = 203.6, 173.0, 171.3, 167.0, 166.9, 165.2, 142.0, 138.7, 138.4, 136.4, 133.7, 133.2, 132.1, 131.9, 130.2, 129.3, 129.2, 128.7, 127.0, 126.4, 126.0, 125.1, 114.8, 84.4, 81.4, 79.0, 77.2, 76.5, 75.6, 75.1, 72.6, 72.19, 72.14, 58.6, 54.4, 45.8, 43.1, 35.7, 35.6, 29.7, 26.8, 21.8, 20.8, 14.8, 9.6. HRFABMS *m/z* calcd for $C_{50}H_{54}NO_{14}^+$ 892.3544, found 892.3555 (Δ = 1.2 ppm).

3'-Dephenyl-3'-(*o*-allyloxyphenyl)-4-deacetyl-4-acryloylpaclitaxel (13c): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (2H, d, *J* = 8 Hz), 7.75 (2H, d, *J* = 8 Hz), 7.60 (1H, t, *J* = 7 Hz), 7.51 (4H, m), 7.40 (3H, m), 7.05 (3H, m), 6.55 (1H, dd, *J* = 17.4, 1.2 Hz), 6.40 (1H, dd, *J* = 17.2, 10.4 Hz), 6.33 (1H, s), 6.15 (2H, m), 5.97 (1H, dd, *J* = 9, 3.6 Hz), 5.82 (1H, dd, *J* = 10.4, 1.2 Hz), 5.73 (1H, d, *J* = 7.2 Hz), 5.55 (1H, dd, *J* = 17.2, 1.2 Hz), 5.36 (1H, dd, *J* = 10.6, 1.2 Hz), 4.98 (1H, d, *J* = 7.6 Hz), 4.79 (1H, dd, *J* = 6.4, 3.6 Hz), 4.72 (2H, dd, *J* = 5.4, 1.6 Hz), 4.54 (1H, m), 4.37 (1H, d, *J* = 8.4 Hz), 4.26 (1H, d, *J* = 9.2 Hz), 3.88 (1H, d, *J* = 7.2 Hz), 3.51 (1H, d, *J* = 6.4 Hz), 2.60 (1H, m), 2.53 (1H, d, *J* = 4 Hz), 2.36 (1H, dd, *J* = 15.4, 8.8 Hz), 2.28 (3H, s), 2.24 (1H, dd, *J* = 15.4, 8.8 Hz), 1.93 (1H, m), 1.89 (3H, s), 1.73 (3H, s), 1.28 (3H, s), 1.18 (3H, s). ^{13}C NMR (100 MHz) δ = 204.0, 173.3, 171.5, 167.3, 167.1, 165.4, 156.1, 142.8, 134.2, 133.8, 133.0, 132.6, 132.5, 131.9, 130.3, 129.9, 129.5, 129.2, 129.0, 128.8, 127.2, 126.1, 121.6, 118.7, 112.5, 84.6, 81.4, 79.3, 77.4, 76.6, 75.8, 75.3, 72.8, 72.36, 72.31, 69.4, 58.7, 52.6, 45.8, 43.4, 35.9, 35.7, 29.9, 27.0, 22.2, 21.1, 15.0, 9.8. HRFABMS *m/z* calcd for $C_{51}H_{56}NO_{15}^{+}$ 922.3650, found 922.3641 (Δ = 1.0 ppm).

3'-Dephenyl-3'-(*o*-[but-3-enoyloxy]phenyl)-4-deacetyl-4-acryloylpaclitaxel (13d): ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.16 (2H, d, *J* = 7.3 Hz), 7.75 (2H, d, *J* = 7.3 Hz), 7.63 (1H, t, *J* = 7 Hz), 7.53-7.34 (7H, m), 7.12(1H, d, *J* = 8.8 Hz), 7.02 (2H, m), 6.55 (1H, d, *J* = 17.2 Hz), 6.43 (1H, dd, *J* = 17.2, 10 Hz), 6.33 (1H, s), 6.16 (1H, t, *J* = 8.8 Hz), 5.90 (2H, m), 5.82 (1H, d, *J* = 10 Hz), 5.73 (1H, d, *J* = 10 Hz), 5.18 (1H, d, *J* = 17.2 Hz), 5.06 (1H, d, *J* = 10.4 Hz), 4.98 (1H, d, *J* = 9.6 Hz), 4.78 (1H, bs), 4.53 (1H, m), 4.38 (1H, d, *J* = 8.4 Hz), 4.26 (1H, d, *J* = 8.4 Hz), 4.19 (2H, m), 3.91 (1H, d, *J* = 6.8 Hz), 3.59 (1H, m), 2.66 (3H, m), 2.35 (m, 2H), 2.27 (3H, s), 1.93 (1H, m), 1.88 (3H, s), 1.73 (3H, s), 1.29 (3H, s), 1.18 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 172.8, 171.3, 167.1, 167.0, 165.1, 156.3, 142.7, 134.0, 133.6, 132.8, 131.7, 130.0, 129.7, 129.3, 129.2, 128.8, 128.65, 128.62, 127.0, 125.8, 121.2, 117.9, 111.9, 84.4, 81.2, 79.2, 76.4, 75.6, 75.1, 72.9, 72.1, 71.9, 67.6,

58.6, 52.7, 45.7, 43.1, 35.7, 35.5, 33.7, 26.8, 21.9, 20.8, 14.9, 9.6. HRFABMS *m/z* calcd for $C_{52}H_{58}NO_{15}^{+}$ 936.3806, found 936.3770 (Δ = 3.9 ppm).

3'-Dephenyl-3'-(*o*-vinylphenyl)-4-deacetyl-4-acryloylpaclitaxel (13e): ^{1}H NMR (400 MHz) δ = 8.12 (2H, d, *J* = 7.3 Hz), 7.80 (1H, m), 7.65 (3H, m), 7. 49 (3H, m), 7.40 (3H, m), 7.08 (1H, d, *J* = 11.2 Hz), 7.05 (1H, d, *J* = 11.2 Hz), 6.47 (1H, d, *J* = 9.2 Hz), 6.32 (1H, s), 6.29 (1H, dd, *J* = 17.2, 1.2 Hz), 6.17 (1H, m), 6.07 (1H, dd, *J* = 17.6, 10.4 Hz), 5.83 (1H, d, *J* = 9.2 Hz), 5.78 (1H, dd, *J* = 17.2, 1.2 Hz), 5.72 (1H, d, *J* = 7.2 Hz), 5.40 (1H, dd, *J* = 10.8, 1.2 Hz), 5.04 (1H, d, *J* = 11.2 Hz), 4.89 (1H, d, *J* = 7.6 Hz), 4.67 (1H, d, *J* = 6.7 Hz) , 4.48 (1H, m), 4.32 (1H, d, *J* = 8.2 Hz), 4.24 (1H, d, *J* = 8.2 Hz), 3.89 (1H, d, *J* = 6.8 Hz), 3.43(1H, d, *J* = 5.Hz), 2.65-2.45 (3H, m), 2.25 (3H, s), 1.93 (1H, m), 1.83 (3H, s), 1.70 (3H, s), 1.27 (3H, s), 1.17 (3H, s). HRFABMS *m/z* calcd for $C_{50}H_{54}NO_{14}^{+}$ 892.3544, found 892.3546 (Δ = 0.2 ppm).

3'-Dephenyl-3'-(*o*-allylphenyl)-4-deacetyl-4-acryloylpaclitaxel (13f): ^{1}H NMR (400 MHz) δ = 8.11 (2H, d, *J* = 7.2 Hz), 7.77 (1H, d, *J* = 6.6 Hz), 7.65 (2H, d, *J* = 7.2 Hz), 7.61 (2H, t, *J* = 7.6 Hz), 7. 48 (3H, t, *J* = 7.6 Hz), 7.31-7.40 (5H, m), 6.50 (1H, d, *J* = 8.8 Hz), 6.34 (1H, dd, *J*= 17.2, 1.2 Hz), 6.31 (1H, s), 6.13 (2H, m), 5.97 (1H, m), 5.82 (1H, dd, *J* = 8.8, 1.2 Hz), 5.72 (1H, d, *J* = 6.8Hz), 5.17 (1H, dd, *J* = 10.4, 1.2 Hz), 5.09 (1H, dd, *J* = 8, 1.6 Hz), 5.05 (1H, s), 4.90 (1H, d, *J* = 8 Hz), 4.64 (1H, d, *J* = 1.6 Hz) , 4.4 (1H, dd, *J* = 10.8, 6.4 Hz), 4.34 (1H, d, *J* = 8.4 Hz), 4.25 (1H, d, *J* = 8.4 Hz), 3.89 (1H, d, *J* = 6.8 Hz), 3.52 (1H, d, *J* = 6.4 Hz), 2.60 (2H, m), 2.46 (1H, m), 2.25 (3H, s), 1.90 (1H, m), 1.86 (3H, s), 1.71 (3H, s), 1.26 (3H, s), 1.18 (3H, s). ^{13}C NMR (100 MHz) δ = 203.9, 173.6, 171.5, 167.1, 167.0, 165.2, 142.6, 138.9, 137.0, 136.7, 133.9, 133.7, 133.3, 132.1, 131.9, 130.8, 130.2, 129.6, 129.2, 129.0, 128.8, 128.80, 127.6, 127.4, 127.2, 116.9, 84.6, 81.7, 79.0, 76.7, 75.9, 75.3, 73.1, 72.3, 71.9, 58.9, 51.6, 45.9, 43.4, 36.9, 35.9, 35.7, 27.0, 21.9, 21.1, 15.2, 9.7. HRFABMS *m/z* calcd for $C_{51}H_{56}NO_{14}$ 906.3701, found 906.3692 (Δ = 1 ppm).

3'-Dephenyl-3'-(*m*-allyoxylphenyl)-4-deacetyl-4-(pent-4-enoyl)paclitaxel (13g): ^{1}H NMR (400 MHz) δ = 8.14 (2H, d, *J* = 8 Hz), 7.72 (2H, d, *J* = 8 Hz), 7.60 (1H, t, *J* = 8 Hz), 7.49 (3H, m), 7.40 (2H, t, *J* = 7.2 Hz), 7.33 (2H, t, *J* = 7.2 Hz), 7.07 (2H, broad d, *J* = 7.2 Hz), 6.89 (2H, m), 6.26 (1H, s), 6.19 (1H, t, *J* = 8.4 Hz), 6.03 (1H, m), 5.78-5.66 (3H, m), 5.40 (1H, dd, *J* = 17.4, 1.2 Hz), 5.29 (1H, dd, *J* = 10.8, 1.2 Hz), 5.06 (1H, d, *J* = 17.2 Hz), 4.98 (1H, d, *J* = 10.4 Hz), 4.88 (1H, d, *J* = 8.8 Hz), 4.74 (1H, m), 4.54 (2H, m), 4.42 (1H, m), 4.30 (1H, d, *J* = 8.2 Hz), 4.19 (1H, d, *J* = 8.2 Hz), 3.80 (1H, d, *J* = 7.2 Hz), 3.42 (1H, d, *J* = 6.8 Hz), 2.80 (1H, m), 2.60-2.40 (5H, m), 2.25 (1H, m), 2.23 (3H, s), 1.86 (1H, m), 1.80 (3H, s), 1.68 (3H, s), 1.25 (3H, s), 1.14 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 173.1, 172.5, 171.5, 167.2, 167.1, 159.3, 142.2, 139.7, 135.9, 133.9, 133.7, 133.3, 132.1, 132.2, 130.4, 130.0, 129.4, 128.9, 127.7, 127.2, 119.6, 118.2, 116.8, 114.6, 114.2, 84.7, 81.4, 79.2, 76.6, 75.7, 75.2, 73.0, 72.8, 72.3, 69.1, 58.8, 55.2, 45.8, 43.4, 35.9, 35.7, 35.0, 29.9, 29.5, 27.0, 22.1, 21.0, 15.0, 9.8. HRFABMS *m/z* calcd for $C_{53}H_{60}NO_{15}^{+}$ 950.3963, found 950.3970 (Δ = 0.7 ppm).

3'-Dephenyl-3'-(*m*-vinylphenyl)-4-deacetyl-4-(pent-4-enoyl)paclitaxel (13h): ^{1}H NMR (400 MHz) δ = 8.14 (2H, d, *J* = 7.2 Hz), 7.73 (2H, d, *J* = 7.2 Hz), 7.62 (1H, d, *J* = 7.2 Hz), 7.50 (4H, m), 7.40 (5H, m), 6.90 (1H, d, *J* = 8.8 Hz), 6.74 (1H, dd, *J* = 17.4, 10.8 Hz), 6.27 (1H, s), 6.19 (1H, t, *J* = 8.8 Hz), 5.76 (1H, d, *J* = 18 Hz), 5.71 (3H, m), 5.31 (1H, d, *J* = 11.2 Hz), 5.04 (1H, dd, *J* = 17.2, 1.2 Hz), 4.96 (1H, dd, *J*=10.8, 1 Hz), 4.88 (1H, d, *J* = 8 Hz), 4.77 (1H, bs), 4.41 (1H, m), 4.30 (1H, d, *J* = 8 Hz), 4.19 (1H, d, *J* = 8.4 Hz), 3.80 (1H, d, *J* = 6.8 Hz), 3.49 (1H, bs), 2.80 (1H, m), 2-60-2.36 (7H, m), 2.23 (3H, s), 1.88 (1H, m), 1.80 (3H, s), 1.68 (3H, s), 1.24 (3H, s), 1.14 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 173.2, 172.5, 171.5, 167.3, 167.1, 142.2, 138.6, 138.5, 136.5, 135.8, 133.9, 133.7, 133.3, 132.1, 132.2, 130.4, 129.46, 129.41, 128.95, 128.92, 127.2, 126.7, 126.3, 125.4, 116.8, 115.1, 84.7, 81.4, 79.2, 76.6, 75.7, 75.1, 72.9, 72.3, 58.8, 55.2, 45.8, 43.4, 35.9, 35.7, 35.0,

29.5, 27.0, 22.1, 21.0, 15.0, 9.8. HRFABMS *m/z* calcd for $C_{52}H_{58}NO_{14}^{+}$ 920.3857, found 920.3834 (Δ = 2.5 ppm).

3'-Dephenyl-3'-(*o*-allyoxylphenyl)-4-deacetyl-4-(pent-4-enoyl)paclitaxel (13i): ^{1}H NMR (500 MHz) δ = 8.12 (2H, d, *J* = 7.1 Hz), 7.71 (2H, d, *J* = 7.1 Hz), 7.60 (1H, t, *J* = 7.6 Hz), 7.48 (3H, m), 7.40 (4H, m), 7.30 (1H, m), 7.01 (1H, m), 6.96 (1H, d, *J* = 8 Hz), 6.25 (1H, s), 6.17 (1H, t, *J* = 8.4 Hz), 6.15 (1H, m), 5.95 (1H, m), 5.77 (1H, m), 5.65(1H, d, *J* = 7.1 Hz), 5.52 (1H, dd, *J* = 16.8, 1.2 Hz), 5.34 (1H, dd, *J* = 9.2, 1.2 Hz), 5.07 (1H, d, *J* = 16, 1.2 Hz), 4.95 (1H, d *J* = 10.3 Hz), 4.88 (1H, d, *J* = 8 Hz), 4.77 (1H, m), 4.66 (2H, m), 4.42 (1H, m), 4.29 (1H, d, *J* = 8 Hz), 4.18 (1H, d, *J* = 8 Hz), 3.78 (1H, d, *J* = 5.6 Hz), 3.66 (1H, d, *J* = 6 Hz), 2.80 (1H, m), 2.69 (1H, m), 2.55-2.40 (3H, m), 2.26 (1H, m), 2.25 (3H, s), 2.14 (1H, m), 1.88 (1H, m), 1.81 (3H, s), 1.66 (3H, s), 1.26 (3H, s), 1.12 (3H, s). ^{13}C NMR (100 MHz) δ = 204.0, 173.2, 172.7, 171.5, 167.4, 167.1, 156.0, 142.8, 136.2, 134.0, 133.9, 132.9, 132.6, 132.0, 130.4, 129.9, 129.5, 129.0, 128.8, 127.2, 125.8, 121.7, 118.9, 116.4, 112.5, 84.8, 81.2, 79.5, 77.4, 76.6, 75.7, 75.3, 73.5, 72.3, 72.2, 69.5, 58.7, 53.0, 45.7, 43.4, 35.9, 35.7, 34.5, 29.9, 29.5, 27.0, 22.4, 21.0, 14.9, 9.8. HRFABMS *m/z* calcd for $C_{53}H_{60}NO_{15}^{+}$ 950.3963, found 950.3967 (Δ = 0.5 ppm).

3'-Dephenyl-3'-(*o*-allyoxylphenyl)-4-deacetyl-4-(hex-5-enoyl)paclitaxel (13j): ^{1}H NMR (500 MHz):δ = 8.12 (2H, d, *J* = 7.1 Hz), 7.71 (2H, d, *J* = 7.1 Hz), 7.60 (1H, t, *J* = 7.6 Hz), 7.48 (3H, m), 7.45-7.35 (3H, m), 7.30 (1H, m), 7.21 (1H, d, *J* = 8.9 Hz), 7.00 (1H, t, *J* = 7.3 Hz), 6.95 (1H, d, *J* = 8 Hz), 6.25 (1H, s), 6.19 (1H, t, *J* = 8 Hz), 6.11 (1H, m), 5.96 (1H, dd, *J* = 10, 4Hz), 5.72 (1H, m), 5.65 (1H, d, *J* = 7.1Hz), 5.50 (1H, dd, *J* = 17.2, 1.2 Hz), 5.33 (1H, dd, *J* = 10.8, 1.2 Hz), 4.96 (1H, m), 4.94 (1H, d, *J* = 1.2 Hz), 4.90 (1H, d, *J* = 6.8 Hz), 4.76 (1H, dd, *J* = 10.4, 4 Hz), 4.66 (2H, m), 4.43 (1H, m), 4.28 (1H, d, *J* = 8.5 Hz), 4.18 (1H, d, *J* = 8.5 Hz), 3.78 (1H, d, *J* = 7.1 Hz), 3.64 (1H, d, *J* = 6.8 Hz), 2.71 (1H, m), 2.56 (2H, m), 2.47 (1H, d, *J* = 4Hz), 2.28 (1H, m), 2.23 (3H, s), 2.16

(1H, m), 2.02 (2H, m), 1.89 (1H, m), 1.81 (3H, s), 1.72 (1H, m), 1.66 (3H, s), 1.58(1H, m), 1.24 (3H, s), 1.12 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 173.0, 172.9, 171.3, 167.1, 166.9, 155.8, 142.6, 137.3, 133.8, 133.6, 132.7, 132.4, 131.8, 130.2, 129.7, 129.3, 128.8, 128.6, 127.0, 125.7, 121.5, 118.6, 115.6, 112.3, 84.7, 80.9, 79.3, 77.2, 76.5, 75.5, 75.1, 73.2, 72.1, 72.0, 69.3, 58.5, 52.7, 45.5, 43.2, 35.7, 35.5, 34.5, 32.9, 29.7, 26.9, 24.5, 22.2, 20.8, 14.7, 9.6. HRFABMS *m/z* calcd for $C_{54}H_{62}NO_{15}^+$ 964.4119, found 964.4060 (Δ = 6.2 ppm).

Characterization Data for 7-O-Triethylsilyl-2'-O-triisopropylsilyl Bridged Paclitaxels 14c-d and 14f-k.

7-*O*-Triethylsilyl-2'-*O*-triisopropylsilyl Bridged Paclitaxel 14c: ^{1}H NMR (500 MHz) δ = 8.06 (2H, d, *J* = 7.1 Hz), 7.75 (2H, d, *J* = 7.1 Hz), 7.60 (1H, t, *J* = 7.3 Hz), 7.48 (2H, m), 7.44 (2H, t, *J* = 6 Hz), 7.32 (2H, m), 7.17 (1H, d, *J* = 9 Hz), 7.0 (2H, m), 6.64 (1H, d, *J* = 15.8 Hz), 6.45 (1H, s), 6.11 (1H, t, *J* = 5.5 Hz), 5.81 (1H, d, *J* = 8.9 Hz), 5.73 (1H, d, *J* = 7 Hz), 5.14 (1H, s), 5.12 (1H, d, *J* = 7.8 Hz), 4.84 (1H, ABq, *J* = 10, 1 Hz), 4.83 (1H, ABq, *J* = 10, 1 Hz), 4.48 (1H, d, *J* = 8 Hz), 4.46 (1H, d, *J* = 8 Hz), 4.27 (1H, d, *J* = 8.2 Hz), 3.78 (1H, d, *J* = 6.8 Hz), 2.54 (2H, m), 2.16 (3H, s), 2.12 (1H, m), 2.0 (3H, s), 1.95 (1H, m), 1.70 (3H, s), 1.2 (3H, s), 1.14 (3H, s), 0.91 (30H, m), 0.5 (6H, m). ^{13}C NMR (125 MHz) δ = 201.7, 172.8, 169.3, 167.6, 167.0, 164.7, 155.4, 141.9, 140.4, 134.2, 133.8, 133.6, 131.8, 130.0, 129.5, 129.2, 128.8, 128.7, 127.1, 127.0, 124.6, 122.8, 115.1, 83.8, 81.4, 78.9, 76.2, 75.2, 74.9, 73.3, 72.2, 67.8, 58.2, 52.6, 47.1, 43.4, 37.1, 35.7, 29.7, 26.5, 21.8, 20.9, 17.9, 17.7, 14.2, 12.4, 10.3, 6.8, 5.3. HRFABMS *m/z* calcd for $C_{64}H_{86}NO_{15}Si_2^+$ 1164.5536, found 1164.5469 (Δ = 5.7 ppm).

7-*O*-Triethylsilyl-2'-*O*-triisopropylsilyl Bridged Paclitaxel 14d: ^{1}H NMR (500 MHz) δ = 8.10 (2H, d, *J* = 7.3 Hz), 7.75 (2H, d, *J* = 7.2 Hz), 7.61 (1H, t, *J* = 7.2 Hz), 7.49 (3H, m), 7.39 (2H,

m), 7.36 (1H, m), 7.25-7.22 (1H, m), 7.17 (1H, d, *J* = 8.4 Hz), 6.95 (2H, m), 6.49 (1H, s), 6.24 (1H, d, *J* = 16 Hz), 6.10 (1H, t, *J* = 9 Hz), 5.83 (1H, dd, *J* = 8.4, 1.9 Hz), 5.68 (1H, d, *J* = 6.9 Hz), 4.94 (1H, d, *J* = 2 Hz), 4.91 (1H, d, *J* = 8 Hz), 4.53 (1H, dd, *J* = 10, 6.8 Hz), 4.46 (2H, m), 4.31 (1H, d, *J* = 8.2 Hz), 4.28 (1H, d, *J* = 8.2 Hz), 3.90 (1H, d, *J* = 6.8 Hz), 3.05 (1H, m), 2.70 (1H, m), 2.53 (1H, m), 2.43 (1H, m), 2.16 (3H, s), 2.08 (1H, m), 2.06 (3H, s), 1.93 (1H, m), 1.71 (3H, s), 1.24 (3H, s), 1.11 (3H, s), 0.95-0.82 (30H, m), 0.57 (6H, m). ^{13}C NMR (125 MHz) δ = 202.0, 173.1, 169.4, 166.9, 166.6, 164.6, 155.2, 146.8, 140.6, 134.3, 133.6, 133.4, 131.7, 130.1, 129.6, 129.0, 128.8, 128.6, 128.5, 127.0, 126.9, 122.8, 121.1, 111.8, 84.2, 80.9, 78.6, 75.3, 75.1, 73.0, 72.4, 72.0, 64.9, 58.6, 52.0, 46.7, 43.3, 37.3, 35.4, 32.0, 31.3, 26.4, 21.3, 20.9, 18.1, 17.8, 14.4, 12.8, 10.0, 6.8, 5.4. HRFABMS *m/z* calcd for $C_{65}H_{88}NO_{15}Si_2^+$ 1178.5693, found 1178.5702 (Δ = 0.8 ppm).

7-*O*-Triethylsilyl-2'-*O*-triisopropylsilyl Bridged Paclitaxel 14f: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (2H, d, *J* = 7.8 Hz), 7.78 (2H, d, *J* = 7.1 Hz), 7.58 (1H, t, *J* = 7.3 Hz), 7.5 (3H, m), 7.38-7.42 (3H, m), 7.23-7.31 (3H, m), 6.72 (1H, td, *J* = 10, 2.8 Hz), 6.5 (1H, s), 6.41 (1H, t, *J* = 8 Hz) 6.30 (1H, dd, *J* = 11.2, 1.6 Hz), 5.74 (1H, d, *J* = 4.4 Hz), 5.78 (1H, d, *J* = 3.2 Hz), 5.01(1H, d, *J* = 8 Hz), 4.86 (1H, dd, *J* = 20, 9.2 Hz), 4.67 (1H, d, *J* = 0.8 Hz), 4.46 (1H, dd, *J* = 10.4, 7.8 Hz), 4.33 (1H, d, *J* = 8 Hz), 4.24 (1H, d, *J* = 8.4 Hz), 3.82 (1H, d, *J* = 6.4 Hz) 3.67 (1H, dt, *J* = 19.2, 3.2 Hz), 2.6 (1H, m), 2.21 (1H, m), 2.20 (3H, s), 2.08 (1H, m), 2.05 (3H, s), 1.99 (1H, m), 1.75 (3H, s), 1.26 (3H, s), 1.24 (3H, s), 0.94 (30H, m), 0.6 (6H, m). ^{13}C NMR (100 MHz) δ = 202, 171.4, 169.6, 167.3, 166.6, 165.1, 153.3, 140.5, 138.2, 137.2, 134.1, 133.9, 133.5, 132.0, 130.7, 130.4, 129.2, 128.9, 128.5, 127.5, 127.16, 127.10, 120.6, 84.2, 81.1, 78.8, 75.4, 74.8, 74.4, 72.9, 70.6, 59.2, 53.5, 47.0, 43.8, 37.9, 35.7, 34.9, 29.9, 27, 21.4, 21.1, 18.2, 17.9, 14.9, 12.9, 10.2, 7.0, 5.5. HRFABMS *m/z* calcd for $C_{64}H_{85}NO_{14}Si_2Na^+$ 1170.5406, found 1170.5426 (Δ = 1.7 ppm).

7-*O*-Triethylsilyl-2'-*O*-triisopropylsilyl Bridged Paclitaxel 14g: ^{1}H NMR (400 MHz) δ = 8.14 (2H, d, *J* = 7.3 Hz), 7.76 (2H, d, *J* = 7.2 Hz), 7.66 (1H, t, *J* = 7.2 Hz), 7.54 (3H, m), 7.44 (2H, m), 7.22 (2H, m), 7.0 (1H, d, *J* = 7.2 Hz), 6.92 (1H, dd, *J* = 8.2, 2 Hz), 6.46 (1H, s), 6.07 (1H, t, *J* = 8.8 Hz), 5.90 (2H, m), 5.72 (1H, d, *J* = 7.2 Hz), 5.38 (1H, d, *J* = 8.4 Hz), 4.90 (1H, d, *J* = 8 Hz), 4.68 (3H, m), 4.47 (1H, dd, *J* = 10, 6.8 Hz), 4.35 (1H, d, *J* = 8.4 Hz), 4.22 (1H, d, *J* = 8 Hz), 3.78 (1H, d, *J* = 6.8 Hz), 2.82 (1H, m), 2.78 (1H, m), 2.58 (1H, m), 2.5-2.4 (2H, m), 2.30 (1H, m), 2.16 (3H, s), 2.0 (3H, s), 1.69 (3H, s), 1.64 (3H, s), 1.17 (3H, s), 0.96 (30H, m), 0.57 (6H, m). ^{13}C NMR (100 MHz) δ = 202.2, 172.3, 171.0, 169.5, 167.2, 167.0, 159.8, 141.9, 140.4, 134.2, 133.8, 133.6, 131.8, 130.0, 129.5, 129.2, 128.8, 128.7, 124.4, 124.1, 122.8, 115.1, 84.5, 81.4, 78.9, 77.2, 75.4, 75.2, 75.0, 72.8, 72.5, 71.7, 58.5, 57.1, 47.0, 43.5, 38.2, 37.3, 35.8, 29.9, 29.2, 26.7, 21.0, 18.2, 17.9, 14.4, 13.0, 10.2, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{66}H_{89}NO_{15}Si_2Na^+$ 1214.5668, found 1214.5717 (Δ = 4 ppm).

7-*O*-Triethylsilyl-2'-*O*-triisopropylsilyl Bridged Paclitaxel 14h: ^{1}H NMR (400 MHz) δ = 8.13 (2H, d, *J* = 7.6 Hz), 7.85 (2H, d, *J* = 7.2 Hz), 7.61 (1H, t, *J* = 7.2 Hz), 7.50 (8H, m), 7.30 (1H, m), 7.14 (2H, m), 6.58 (1H, d, *J* = 12 Hz), 6.45 (1H, s), 6.23 (1H, m), 5.83 (1H, m), 5.73 (1H, d, *J* = 7.2 Hz), 5.32 (1H, d, *J* = 7.2 Hz), 4.88 (1H, d, *J* = 9.2 Hz), 4.79 (1H, s), 4.43 (1H, dd, *J* =10, 6.8 Hz), 4.31 (1H, d, *J* = 8.4 Hz), 4.24 (1H, d, *J* = 8.4 Hz), 3.76 (1H, d, *J* = 6.4 Hz), 3.08 (1H, m), 2.90 (2H, m), 2.58 (1H, m), 2.40 (1H, m), 2.20 (3H, s), 1.92 (3H, m), 1.78 (1H, m), 1.70 (3H, s), 1.63 (6H, s), 1.25 (3H, s), 0.94 (30H, m), 0.57 (6H, m). ^{13}C NMR (100 MHz) δ = 201.8, 172.2, 169.5, 167.3, 140.5, 137.2, 134.1, 133.9, 132.0, 130.3, 129.3, 129.1, 128.9, 127.3, 123.5, 84.7, 77.4, 75.1, 72.6, 58.8, 43.6, 37.5, 36.1, 34.2, 29.9, 27.1, 23.7, 21.1, 18.1, 17.8, 12.7, 10.4, 6.9, 5.5. HRFABMS *m/z* calcd for $C_{65}H_{88}NO_{14}Si_2^+$ 1162.5743, found 1162.5741 (Δ = 0.2 ppm).

7-*O*-Triethylsilyl-2'-*O*-triisopropylsilyl Bridged Paclitaxel 14i: ^{1}H NMR (500 MHz: δ = 8.15 (2H, d, *J* = 7.3 Hz), 7.68 (2H, d, *J* = 7.3 Hz), 7.60 (1H, t, *J* = 7.2 Hz), 7.50 (2H, m), 7.45 (1H, m), 7.35 (2H, m), 7.23 (2H, d, *J* = 6.6 Hz), 6.93 (2H, m), 6.43 (1H, s), 6.30 (1H, m), 6.16 (1H, m), 6.00 (1H, m), 5.67 (1H, d, *J* = 7.1 Hz), 5.06 (1H, s), 4.88 (1H, d, *J* = 8 Hz), 4.86 (1H, t, *J* = 7 Hz), 4.60 (1H, m), 4.51 (1H, m), 4.31 (1H, d, *J* = 8.2 Hz), 4.24 (1H, d, *J* = 8.2 Hz), 3.80 (1H, d, *J* = 6 Hz), 3.02 (1H, m), 2.75 (2H, m), 2.51 (2H, m), 2.15 (1H, m), 2.14 (3H, s), 1.99 (3H, s), 1.64 (6H, s), 1.17 (3H, s), 0.92 (30H, m), 0.57 (6H, m). ^{13}C NMR (100 MHz) δ = 201.8, 173.1, 169.3, 167.2, 167.0, 140.7, 137.0, 133.6, 133.4, 131.6, 130.2, 129.6, 128.8, 128.7, 128.6, 126.9, 124.9, 120.0, 111.0, 84.7, 81.2, 79.0, 76.4, 75.3, 74.9, 72.5, 72.0, 61.8, 58.2, 46.6, 43.4, 37.1, 36.9, 26.5, 23.4, 21.9, 20.9, 18.0, 17.9, 17.7, 14.1, 12.59, 12.51, 10.3, 6.8, 5.4. HRFABMS *m/z* calcd for $C_{66}H_{89}NO_{15}Si_2Na^+$ 1214.5668, found 1214.5702 (Δ = 2.7 ppm).

7-*O*-Triethylsilyl-2'-O-triisopropylsilyl Bridged Paclitaxel 14j: ^{1}H NMR (400 MHz) δ = 8.15 (2H, d, *J* = 7.3 Hz), 7.79 (2H, d, *J* = 7.3 Hz), 7.65 (1H, t, *J* = 7.3 Hz), 7.60-7.40 (4H, m), 7.24 (2H, m), 7.05 (1H, d, *J* = 8 Hz), 6.98 (2H, m), 6.50 (1H, s), 5.99 (2H, m), 5.7 (2H, m), 5.28 (1H, d, *J* = 3.2 Hz), 4.98 (1H, m), 4.58 (1H, d, *J* = 5.6 Hz), 4.52 (1H, m), 4.33 (1H, d, *J* = 8.4 Hz), 4.25 (1H, d, *J* = 8.4 Hz), 3.80 (1H, d, *J* = 6.4 Hz), 2.60 (1H, m), 2.56 (1H, m), 2.40 (1H, m), 2.20 (3H, s), 2.04 (3H, s), 1.98 (1H, m), 1.77 (3H, s), 1.70 (3H, s), 1.20 (3H, s), 0.98 (30H, m), 0.60 (6H, m). ^{13}C NMR (100 MHz) δ = 201.8, 174.6, 173.1, 169.1, 166.7, 164.4, 155.4, 141.0, 134.5, 133.5, 133.1, 131.7, 130.1, 129.5, 129.0, 128.9, 128.77, 128.72, 128.6, 128.2, 127.0, 126.9, 126.8, 125.4, 120.6, 110.6, 84.6, 81.0, 79.0, 76.5, 75.2, 75.0, 74.7, 73.1, 71.9, 67.8, 58.1, 52.4, 46.2, 43.5, 37.1, 35.9, 33.9, 31.4, 26.4, 23.7, 22.5, 20.8, 18.0, 17.8, 17.7, 13.8, 12.6, 12.5, 10.2, 6.7, 5.3. HRFABMS *m/z* calcd for $C_{67}H_{92}NO_{15}Si_2^+$ 1206.6006, found 1206.6036 (Δ = 2.4 ppm).

7-*O*-Triethylsilyl-2'-*O*-triisopropylsilyl Bridged Paclitaxel 14k: ^{1}H NMR (400 MHz) δ = 8.19 (2H, d, *J* = 7.2 Hz), 7.70 (2H, d, *J* = 7.3 Hz), 7.36 (1H, t, *J* = 7.3 Hz), 7.45-7.40 (4H, m), 7.30 (3H, m), 7.25 (1H, d, *J* = 7.2 Hz), 7.0 (3H, m), 6.48 (1H, s), 6.25 (1H, m), 6.12 (1H, m), 5.99 (1H, dd, *J* = 9.6, 1.6Hz), 5.90 (1H, m), 5.64 (1H, d, *J* = 7.2 Hz), 5.27 (1H, s), 4.99 (1H, d, *J* = 8.4 Hz), 4.80 (2H, m), 4.58 (1H, m), 4.30 (1H, d, *J* = 8 Hz), 4.22 (1H, d, *J* = 8 Hz), 3.88 (1H, d, *J* =7.6 Hz), 3.0 (1H, m), 2.58 (2H, m), 2.21 (2H, m), 2.20 (3H, s), 2.05 (3H, s), 1.98 (3H, m), 1.71 (3H, s), 1.61 (3H, s), 1.25 (2H, m), 1.20 (3H, s), 0.91 (30H, m), 0.65 (6H, m). ^{13}C NMR (100 MHz) δ = 201.8, 173.2, 172.9, 169.2, 166.9, 166.3, 155.3, 140.5, 137.5, 134.2, 133.5, 133.1, 131.6, 130.2, 130.1, 129.4, 128.9, 128.6, 128.5, 126.8, 123.5, 120.6, 111.2, 84.6, 80.4, 79.2, 77.2, 76.5, 75.1, 74.8, 73.2, 72.0, 71.7, 62.9, 58.2, 46.3, 43.3, 37.2, 35.8, 33.2, 29.7, 26.6, 25.4, 25.3, 23.1, 22.1, 20.9, 17.9, 17.8, 13.9, 12.6, 12.5, 10.2, 6.7, 5.3. HRFABMS *m/z* calcd for $C_{68}H_{93}NO_{15}Si_2Na$+ 12426.5981, found 1242.5994 (Δ = 1.0 ppm).

Characterization Data for Bridged Paclitaxels 15c-d and 15f-k.

Bridged Paclitaxel 15c: ^{1}H NMR (500 MHz) δ = 8.10 (2H, d, *J* = 7.1 Hz), 7.72 (2H, d, *J* = 7.1 Hz), 7.60 (1H, t, *J* = 6.5 Hz), 7.52 (3H, m), 7.40 (1H, t, *J* = 6 Hz), 7.35-7.28 (4H, m), 7.11 (1H, d, *J* = 7.8 Hz), 7.05 (1H, m), 6.66 (1H, d, *J* = 15.5 Hz), 6.26 (1H, s), 6.15 (1H, t, *J* =5.5 Hz) 5.98 (1H, d, *J* = 7.8 Hz), 5.69 (1H, d, *J* = 7 Hz), 5.08 (1H, d, *J* = 7.5 Hz), 4.97 (1H, ABq, *J* = 10 Hz), 4.87 (1H, ABq, *J* = 10 Hz), 4.76 (1H, t, *J* = 4.1Hz), 4.46 (1H, m), 4.45 (1H, d, *J* = 8.4 Hz), 4.26 (1H, d, *J* = 8.5 Hz), 3.74 (1H, d, *J* = 7.3 Hz), 3.19 (1H, bs), 2.56 (1H, m), 2.47 (1H, d, *J* = 4 Hz), 2.23 (3H, s), 1.92 (1H, m), 1.86 (3H, s), 1.78 (1H, m), 1.68 (3H, s), 1.53 (1H, m), 1.24 (1H, m),1.22 (3H, s), 1.12 (3H, s). ^{13}C NMR (125 MHz) δ = 203.7, 173.9, 171.4, 167.2, 167.1, 164.9, 155.4, 142.5, 142.3, 133.9, 133.8, 133.2, 132.0, 130.1, 129.5, 129.4, 128.8, 127.0, 123.3, 116.1, 84.1, 81.3, 79.4, 76.1,

75.5, 75.4, 72.9, 72.4, 72.1, 58.3, 45.9, 43.3, 35.7, 35.3, 29.7, 26.8, 22.6, 20.9, 14.7, 9.8. HRFABMS *m/z* calcd for $C_{49}H_{52}NO_{15}^{+}$ 894.3337, found 894.3343 (Δ = 0.6 ppm).

Bridged Paclitaxel 15d: ^{1}H NMR (400 MHz) δ = 8.14 (2H, d, *J* = 7.2 Hz), 7.71 (2H, d, *J* = 7.2 Hz), 7.62 (1H, t, *J* = 7.2 Hz), 7.54-7.46 (3H, m), 7.40-7.28 (4H, m), 7.02 (2H, m), 6.96 (d, *J* = 8.8 Hz), 6.32 (1H, s), 6.26 (1H, d, *J* = 16 Hz), 6.22 (1H, t, *J* =7.6 Hz) 5.98 (1H, dd, *J* = 8.8, 2.8 Hz), 5.68 (1H, d, *J* = 7.2 Hz), 4.91 (1H, dd, *J* = 8, 1.2 Hz), 4.68 (1H, d, *J* = 2.8 Hz), 4.48 (2H, m), 4.32 (1H, d, *J* = 8.4 Hz), 4.26 (1H, d, *J* = 8.4 Hz), 3.91 (1H, d, *J* = 6.8 Hz), 3.00 (2H, m), 2.72 (1H, m), 2.58 (1H, m), 2.42 (2H, m), 2.24 (3H, s), 2.08 (1H, m), 1.92 (1H, m), 1.90 (3H, s), 1.70 (3H, s), 1.22 (3H, s), 1.13 (3H, s). ^{13}C NMR (100 MHz) δ = 204.0, 173.7, 171.5, 167.1, 165.1, 155.3, 147.1, 142.8, 134.2, 133.9, 133.0, 132.0, 130.4, 129.66, 129.60, 128.3, 127.2, 126.7, 123.1, 121.6, 112.3, 84.6, 81.1, 79.2, 77.4, 75.8, 75.4, 72.4, 72.3, 72.0, 65.4, 58.7, 58.8, 50.8, 45.8, 43.4, 38.3, 35.8, 35.6, 32.1, 31.4, 27.0, 22.3, 21.0, 14.9, 9.7. HRFABMS *m/z* calcd for $C_{50}H_{54}NO_{15}^{+}$ 908.3493, found 908.3508 (Δ = 1.6 ppm).

Bridged Paclitaxel 15f: ^{1}H NMR (400 MHz) δ = 8.14 (2H, d, *J* = 8 Hz), 7.76 (2H, d, *J* = 7.6 Hz), 7.60 (1H, t, *J* = 7.2 Hz), 7.42-7.52 (6H, m), 7.30 (3H, m), 7.13 (1H, d, *J* = 8 Hz), 6.76 (1H, td, *J* = 9.2, 2 Hz), 6.49 (1H, t, *J* = 8.8 Hz) 6.36 (1H, s), 6.29 (1H, dd, *J* =11.4, 2 Hz), 5.93 (1H, d, *J* = 8 Hz), 5.73 (1H, d, *J* = 6.8 Hz), 5.01 (1H, d, *J* = 7.6 Hz), 4.88 (1H, dd, *J* = 19.2, 9.2 Hz), 4.46 (1H, d, *J* = 9.2 Hz), 4.35 (1H, s), 4.34 (1H, d, *J* = 8.4 Hz), 4.24 (1H, d, *J* = 8 Hz), 3.89 (1H, d, *J* = 6.8 Hz), 3.66 (1H, td, *J* = 19.2, 2.8 Hz), 3.25 (1H, d, *J* = 2 Hz), 2.66 (1H, m), 2.48 (2H, m), 2.24 (3H, s), 2.24-2.26 (1H, m), 1.94-1.96 (1H, m), 1.95 (3H, s), 1.75 (3H, s), 1.3 (3H, s), 1.19 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 173.3, 171.4, 167.3, 166.8, 165.6, 153.2, 142.4, 138.6, 137.0, 134.0, 133.3, 132.1, 131.0, 130.5, 129.2, 129.0, 128.9, 128.6, 127.9, 127.3, 126.5, 120.5, 84.6, 81.3, 79.2, 75.7,

75.0, 72.9, 72.6, 72.2, 59.1, 51.0, 46.2, 43.6, 36.3, 35.6, 35.1, 27.2, 22.0, 21.0, 15.5, 9.7. HRFABMS *m/z* calcd for $C_{49}H_{52}NO_{14}$ 878.3388, found 878.33820 (Δ = 0.7 ppm).

Bridged Paclitaxel 15g: ^{1}H NMR (400 MHz) δ = 8.18 (2H, d, *J* = 7.2 Hz), 7.69 (2H, d, *J* = 7.2 Hz), 7.65 (1H, t, *J* = 7.2 Hz), 7.51 (3H, m), 7.39 (2H, t, *J* = 8.3 Hz), 7.32 (1H, t, *J*=8.2 Hz), 7.27 (1H, m), 7.05 (1H, bs), 6.95 (1H, d, *J*= 8 Hz), 6.85 (1H, d, *J*= 8.8 Hz) 6.27 (1H, s), 6.26(1H, m), 5.85 (1H, m), 5.77 (1H, m), 5.71 (1H, d, *J* = 7.2 Hz), 5.56 (1H, d, *J* = 8.8 Hz), 4.89 (1H, d, *J* = 7.6 Hz), 4.77 (1H, dd, *J* = 15.8, 3.6 Hz), 4.69 (1H, dd, *J* = 15.8, 3.6 Hz), 4.56 (1H, s), 4.40 (1H, m), 4.34 (1H, d, *J* = 8 Hz), 4.22 (1H, d, *J* = 8 Hz), 3.77 (1H, d, *J* = 6.8 Hz), 3.47 (1H, bs), 2.86 (m, 1H), 2.68 (1H, m), 2.58-2.38 (5H, m), 2.24 (s, 3H), 1.90 (1H, m, 1H), 1.84 (3H, s), 1.69 (3H, s), 1.60 (2H, m), 1.29 (3H, s), 1.16 (3H, s). ^{13}C NMR (100 MHz) δ = 203.7, 173.3, 171.3, 167.0, 158.4, 142.4, 139.2, 133.9 133.8, 133.7, 133.1, 132.0, 130.4, 130.2, 129.3, 128.8, 128.7, 127.8, 127.1, 119.5, 119.0, 116.3, 84.6, 81.1, 79.4, 76.3, 75.5, 75.1, 72.8, 72.7, 72.2, 70.0, 58.5, 55.5, 45.7, 43.3, 37.5, 36.0, 35.7, 35.5, 29.7, 29.2, 26.7, 22.3, 20.9, 14.7, 9.6. HRFABMS *m/z* calcd for $C_{51}H_{56}NO_{15}$ 922.3650, found 922.3603 (Δ = 5 ppm).

Bridged paclitaxel 15h: ^{1}H NMR (400 MHz) δ = 8.07 (2H, d, *J* = 7.2 Hz), 7.8 (2H, d, *J* = 7.2 Hz), 7.61 (1H, t, *J* = 7.2 Hz), 7.51-7.34 (7H, m), 7.27 (1H, m), 7.19 (1H, t, *J* = 7.6 Hz), 7.05 (1H, d, *J* = 7.2 Hz), 6.70 (1H, d, *J* = 11.2 Hz), 6.27 (1H, m), 6.25 (1H, s), 5.88 (1H, m), 5.69 (1H, d, *J* = 7.2 Hz), 5.60 (1H, m), 4.87 (1H, d, *J* = 9.2 Hz), 4.52 (1H, bs), 4.36 (1H, m), 4.29 (1H, dd, *J* = 8.4 Hz), 4.20 (1H, d, *J* = 8.4 Hz), 3.78 (1H, bs), 3.70 (1H, d, *J* = 6.8 Hz), 2.88-2.7 (3H, m), 2.58 (3H, m), 2.23 (3H, s), 2.26-2.04 (2H, m), 1.88 (1H, m), 1.77 (3H, s), 1.69 (3H, s), 1.31 (3H, s), 1.14 (3H, s). ^{13}C NMR (100 MHz) δ = 203.7, 173.2, 172.1, 171.6, 168.2, 167.3, 142.8, 138.8, 138.1, 134.0 133.7, 132.8, 132.3, 131.4, 130.3, 129.7, 129.3, 128.94, 128.91, 128.7, 127.3, 126.4, 125.1, 84.9,

82.0, 79.5, 77.0, 75.9, 75.6, 75.3, 72.4, 71.7, 58.7, 56.6, 46.1, 43.5, 35.9, 35.8, 34.9, 27.4, 24.0, 22.8, 21.0, 14.5, 9.8. HRFABMS *m/z* calcd for $C_{50}H_{54}NO_{14}^+$ 892.3544, found 892.3541 (Δ = 0.3 ppm).

Bridged Paclitaxel 15i: ^{1}H NMR (500 MHz) δ = 8.15 (2H, d, *J* = 7.1 Hz), 7.69 (2H, d, *J* = 7.1 Hz), 7.65 (1H, t, *J* = 7.2 Hz), 7.54-7.35 (7H, m), 7.15 (1H, m), 6.88 (2H, m), 6.30 (1H, m), 6.21 (1H, s), 6.10 (1H, m), 5.88 (1H, m), 5.84 (1H, dd, *J* = 10.4, 6.8 Hz), 5.59 (1H, d, *J* = 7.3 Hz), 4.90 (1H, d, *J* = 7.6 Hz), 4.79 (2H, m), 4.60 (1H, dd, *J* = 10, 6Hz), 4.42 (1H, m), 4.30 (1H, d, *J* = 8.2 Hz), 4.18 (1H, d, *J* = 8.2 Hz), 3.71 (1H, d, *J* = 6.8 Hz), 2.88-2.70 (2H, m), 2.50-2.40 (4H, m), 2.15 (3H, s), 1.98 (1H, m), 1.80 (1H, m), 1.72 (3H, s), 1.59 (3H, s), 1.30 (1H, m), 1.08 (3H, s), 1.02 (3H, s). ^{13}C NMR (100 MHz) δ = 203.6, 173.6, 171.6, 171.3, 167.4, 166.8, 155.8, 142.5, 137.4, 133.8, 133.7, 132.6, 131.7, 130.0, 139.9, 129.6, 124.4, 124.3, 121.4, 111.3, 84.7, 81.0, 79.2, 76.1, 75.3, 75.2, 73.8, 71.79, 71.74, 62.0, 60.3, 58.2, 45.3, 43.2, 43.0, 36.0, 35.2, 26.6, 23.2, 22.4, 21.0, 20.7, 14.3, 14.1, 9.6. HRFABMS *m/z* calcd for $C_{51}H_{55}NO_{15}Na^+$ 944.3469, found 944.34436 (Δ = 2.6 ppm).

Bridged Paclitaxel 15j: ^{1}H NMR (500 MHz) δ = 8.06 (2H, d, *J* = 7.2 Hz), 7.78 (2H, d, *J* = 7.2 Hz), 7.61 (1H, t, *J* = 7.6 Hz), 7.51-7.37 (7H, m), 7.29 (1H, m), 6.99 (2H, m), 6.25 (1H, s), 6.07 (1H, m), 5.91 (3H, m), 5.63 (1H, m), 4.85 (2H, m), 4.74 (1H, m), 4.66 (1H, m), 4.40 (1H, m), 4.28 (1H, d, *J* = 8.2 Hz), 4.17 (1H, d, *J* = 8.2 Hz), 4.00 (1H, d, *J* = 6.2 Hz), 3.78 (1H, d, *J* = 6.9Hz), 2.53-2.34 (5H, m), 2.22 (3H, s), 2.19 (1H, m), 2.1 (1H, m), 1.97 (2H, m), 1.85 (1H, m), 1.81 (3H, s), 1.67 (3H, s), 1.61 (2H, m), 1.19 (3H, s), 1.10 (3H, s). ^{13}C NMR (125 MHz) δ = 203.8, 173.0, 172.79, 172.74, 172.4, 171.4, 167.6, 166.9, 155.5, 143.2, 135.5, 133.8, 132.5, 131.9, 130.4, 130.1, 129.7, 129.3, 128.7, 128.6, 127.2, 127.1, 126.2, 125.7, 124.7, 121.6, 112.2, 84.8, 81.1, 79.2, 76.5, 75.6, 75.1, 73.4, 72.9, 72.2, 71.5, 68.3, 63.5, 58.6, 54.1, 45.6, 43.1, 35.7, 35.6, 34.0, 31.4, 29.7, 27.2, 26.9, 26.8, 25.0, 24.2, 22.0, 20.9, 14.8, 9.6. HRFABMS *m/z* calcd for $C_{52}H_{58}NO_{15}^+$ 936.3806, found 936.3773 (Δ = 3.5 ppm).

Bridged Paclitaxel 15k: ^{1}H N MR (500 MHz) δ = 8.11 (2H, d, *J* = 7.1 Hz), 7.71 (2H, d, *J* = 7.2 Hz), 7.62 (1H, t, *J* = 7.6 Hz), 7.52-7.33 (7H, m), 7.25 (1H, m), 6.98 (2H, m), 6.21 (1H, s), 6.16 (1H, t, *J* = 8.4 Hz), 6.05 (1H, m), 5.94 (1H, m), 5.88 (1H, m), 5.60 (1H, d, *J* = 7.3 Hz), 4.89 (1H, dd, *J* = 9, 1.2 Hz), 4.78 (2H, m), 4.63 (1H, dd, *J* = 10.4, 6.8 Hz), 4.45 (1H, m), 4.29 (1H, d, *J* = 8.2 Hz), 4.16 (1H, d, *J* = 8.2 Hz), 3.72 (1H, d, *J* = 6.8 Hz), 2.75 (2H, m), 2.55 (1H, m), 2.45 (2H, m), 2.35 (1H, m), 2.23 (1H, m), 2.22 (3H, s), 2.10 (1H, m), 1.88 (3H, s), 1.78 (3H, s), 1.63 (3H, s), 1.58 (4H, m), 1.20 (3H, s), 1.08 (3H, s). ^{13}C NMR (125 MHz) δ = 203.8, 173.4, 173.2, 171.4, 167.3, 167.0, 155.8, 142.7, 138.2, 133.9, 133.8, 132.7, 132.0, 130.3, 129.8, 129.4, 129.3, 128.7, 128.6, 127.0, 124.4, 123.2, 121.3, 111.4, 84.8, 80.7, 79.5, 76.4, 75.5, 75.3, 73.5, 71.9, 71.5, 62.8, 58.3, 53.8, 45.4, 43.2, 35.5, 35.4, 33.1, 29.7, 26.9, 26.3, 25.8, 23.0, 22.6, 20.9, 14.4, 9.7. HRFABMS *m/z* calcd for $C_{53}H_{60}NO_{15}^{+}$ 950.3963, found 950.4001 (Δ = 4.0 ppm).

Characterization Data for Dihydro Bridged Paclitaxels 16c-d, 16f-j.

Dihydro Bridged Paclitaxel 16c: ^{1}H NMR (400 MHz) δ = 8.12 (2H, d, *J* = 7.5 Hz), 7.74 (2H, d, *J* = 7.2 Hz), 7.59 (1H, t, *J* = 7.2 Hz), 7.51 (3H, m), 7.43 (2H, t, *J* = 7 Hz), 7.31 (1H, m), 6.99 (2H, m), 6.93 (1H, dd, *J* = 8, 1 Hz), 6.27 (2H, bs), 6.13 (1H, t, *J* = 10 Hz) 5.74 (1H, d, *J* = 7.2 Hz), 5.0 (1H, s), 4.99(1H, s), 4.47 (1H, m), 4.34 (1H, d, *J* = 8.4 Hz), m), 4.31 (1H, m), 4.24 (1H, d, *J* = 8.4 Hz), 4.10 (1H, m), 3.75 (1H, d, *J* = 7.6 Hz), 3.3 (1H, m), 3.06 (1H, bs), 2.90 (1H, m), 2.60 (1H, m), 2.48-2.30 (2H, m), 2.26 (1H, m), 2.24 (3H, s), 1.90 (1H, m), 1.86 (3H, s), 1.70 (3H, s), 1.30 (3H, s), 1.25 (3H, s). ^{13}C NMR (100 MHz) δ = 203.9, 174.3, 172.7, 171.6, 167.2, 155.0, 142.5, 134.1, 133.8, 133.3, 132.1, 130.3, 129.4, 129.0, 127.2, 127.0, 126.0, 121.3, 111.1, 84.8, 81.4, 79.4, 76.69, 76.61, 75.6, 75.5, 73.1, 72.2, 71.4, 65.5, 58.5, 45.6, 43.6, 36.1, 35.6, 31.8, 29.9, 27.3, 24.7,

23.1, 21.1, 14.5, 10.0. HRFABMS *m/z* calcd for $C_{49}H_{54}NO_{15}^{+}$ 896.3493, found 896.3515 (Δ = 2.2 ppm).

Dihydro Bridged Paclitaxel 16d: ^{1}H NMR (400 MHz) δ = 8.16 (2H, d, *J* = 7.6 Hz), 7.69 (2H, d, *J* = 7.6 Hz), 7.60 (1H, t, *J* = 7.6 Hz), 7.53-7.30 (7H, m), 6.99 (2H, m), 6.88 (1H, d, *J* = 8.8 Hz), 6.29 (1H, s), 6.25 (1H, m), 6.13 (1H, dd, *J* = 9.2, 2.8 Hz), 5.94 (1H, dd, *J* = 9.2, 2.4 Hz), 5.69 (1H, m), 4.90 (1H, d, *J* = 9.2Hz), 4.73 (1H, bs), 4.38 (2H, m), 4.31 (1H, d, *J* = 8.4 Hz), 4.23 (1H, d, *J* = 8.4 Hz), 3.82 (1H, d, *J* = 6.8 Hz), 3.10 (1H, bs), 3.00 (1H, m), 2.90 (2H, m), 2.58 (2H, m), 2.46 (2H, m), 2.24 (3H, s), 2.20 (1H, m), 2.10 (3H, s), 1.90 (1H, m), 1.88 (3H, s), 1.69 (3H, s), 1.26 (3H, s), 1.14 (3H, s). ^{13}C NMR (100 MHz) δ = 203.9, 173.9, 173.1, 171.5, 167.0, 155.5, 142.6, 134.2, 133.9, 133.1, 132.0, 130.4, 129.7, 129.5, 128.92, 128.88, 128.2, 127.2, 126.2, 121.2, 112.0, 84.8, 80.9, 79.4, 75.7, 75.3, 72.8, 72.3, 72.2, 69.1, 58.7, 50.2, 45.6, 43.4, 36.7, 35.7, 29.0, 27.1, 25.7, 24.2, 24.1, 22.6, 21.0, 14.8, 9.8. HRFABMS *m/z* calcd for $C_{50}H_{55}NO_{15}Na^{+}$ 932.3469, found 932.3432 (Δ = 4 ppm).

Dihydro Bridged Paclitaxel 16f: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (2H, d, *J* = 8 Hz), 7.77 (3H, m), 7.62 (1H, t, *J* = 7.6 Hz), 7.54 (3H, m), 7.38 (2H, t, *J* = 8 Hz), 7.26-7.30 (3H, m), 6.97 (1H, d, *J* = 8.8 Hz), 6.53 (1H, t, *J* = 8.4 Hz), 6.28 (1H, s), 5.95 (1H, d, *J* = 8.8 Hz), 5.74 (1H, d, *J* = 7.2 Hz), 4.95 (1H, d, *J* = 8 Hz), 4.57 (1H, d, *J* = 2.4 Hz), 4.38 (1H, dd, *J* = 10.4, 6.8 Hz), 4.32 (1H, d, *J* = 8.8 Hz), 4.22 (1H, d, *J* = 8.4 Hz), 3.74 (1H, d, *J* = 7.2 Hz), 3.47 (1H, d, *J* = 3.2 Hz), 3.22 (1H, m), 3.10 (1H, m), 2.76-2.90 (2H, m), 2.26-2.30 (5H, m), 2.23 (3H, s), 2.05 (1H, m), 1.98 (1H, m), 1.83 (3H, s), 1.71 (3H, s), 1.34 (3H, s), 1.18 (3H, s). ^{13}C NMR (100 MHz) δ = 203.6, 173.7, 172.3, 171.3, 167.1, 166.8, 142.2, 139.3, 138.7, 133.7, 133.6, 133.0, 131.9, 130.3, 130.1, 129.1, 128.8, 128.6, 128.4, 127.4, 127.1, 84.4, 80.9, 79.4, 75.4, 75.0, 73.1, 72.4, 72.2, 58.6, 49.4, 45.5, 43.4, 35.7,

35.0, 33.5, 27.3, 26.0, 22.6, 20.8, 14.7, 9.6. HRFABMS *m/z* calcd for $C_{49}H_{53}NO_{14}Na^+$ 902.3364, found 902.3419 (Δ = 6.1 ppm).

Dihydro Bridged Paclitaxel 16g: ^{1}H NMR (400 MHz) δ = 8.14 (2H, d, *J* = 7.6 Hz), 7.76 (2H, d, *J* = 7.6 Hz), 7.64 (1H, t, *J* = 8 Hz), 7.52 (3H, m), 7.41 (2H, t, *J* = 7.8Hz), 7.32 (1H, t, *J* = 7.6 Hz), 7.13 (1H, d, *J* = 7.6 Hz), 6.99 (1H, bs), 6.95 (1H, m), 6.92 (1H, d, *J* = 8.8 Hz), 6.28 (1H, s), 6.23 (1H, m), 5.69 (1H, d, *J* = 7.2 Hz) 5.61 (1H, dd, *J* = 8, 3.2 Hz), 4.83 (1H, d, *J* = 10 Hz), 4.56 (1H, t, *J* = 2.8 Hz), 4.39 (1H, m), 4.27 (1H, d, *J* = 8.4 Hz), 4.26 (2H, m), 4.21 (1H, d, *J* = 8.4 Hz), 3.80 (1H, d, *J* = 6.8 Hz), 3.48 (1H, bs), 2.62-2.48 (5H, m), 2.32 (1H, m), 2.24 (3H, s), 2.02 (1H, m), 1.90-1.82 (5H, m), 1.85 (3H, s), 1.78 (1H, m), 1.68 (3H, s), 1.29 (3H, s), 1.15 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 173.2, 172.9, 171.5, 167.8, 167.1, 158.7, 142.5, 139.7, 134.0, 133.9, 133.1, 132.2, 130.9, 130.4, 129.4, 128.9, 127.3, 119.9, 118.8, 114.7, 84.9, 81.4, 79.3, 77.4, 76.7, 75.7, 75.2, 74.1, 72.6, 72.3, 68.7, 58.7, 56.0, 45.8, 43.5, 35.8, 35.7, 35.6, 27.1, 26.2, 25.0, 24.9, 22.4, 21.0, 14.8, 9.8. HRFABMS *m/z* calcd for $C_{51}H_{58}NO_{15}$+ 924.3806, found 924.3823 (Δ = 1.8 ppm).

Dihydro Bridged Paclitaxel 16h: ^{1}HN MR (400 MHz) δ = 8.09 (2H, d, *J* = 7.8 Hz), 7.87 (2H, d, *J* = 7.8 Hz), 7.52 (1H, t, *J* = 8 Hz), 7.60 (3H, m), 7.51 (2H, t, *J* = 7.6 Hz), 7.43 (1H, bs), 7.20 (2H, d, *J* = 6.4 Hz), 7.14 (1H, d, *J* = 6.4 Hz), 6.90 (1H, bs), 6.27 (1H, m), 6.23 (1H, s), 5.64 (1H, d, *J* = 7.2 Hz) 5.28 (1H, dd, *J* = 10.2, 5.6 Hz), 4.83 (1H, d, *J* = 7.6 Hz), 4.37 (1H, m), 4.25 (2H, m), 4.14 (1H, d, *J* = 8.4 Hz), 3.95 (1H, m), 3.59 (1H, d, *J* = 6.8 Hz), 3.22 (1H, m), 2.72 (1H, m), 2.52 (2H, m), 2.28 (3H, s), 2.10-1.82 (5H, m), 1.80 (3H, s), 1.72 (2H, m), 1.67 (3H, s), 1.32 (3H, s), 1.16 (3H, s). ^{13}C NMR (100 MHz) δ = 203.6, 173.4, 172.0, 171.3, 168.8, 167.0, 142.6, 142.4, 137.4, 133.9, 133.6, 132.6, 132.1, 130.1, 129.6, 129.4, 129.3, 128.7, 128.5, 127.1, 126.7, 124.6, 84.5, 80.6, 79.2, 77.2, 76.2, 75.4, 75.0, 72.0, 70.8, 58.7, 58.3, 45.3, 43.1, 37.8, 35.7, 35.4, 35.2, 29.7, 27.5, 27.0,

25.3, 22.3, 20.8, 14.4, 9.5. HRFABMS *m/z* calcd for $C_{50}H_{55}NO_{14}Na^+$ 916.3520, found 916.3553 (Δ = 3.6 ppm).

Dihydro Bridged Paclitaxel 16i: ^{1}H NMR (500 MHz) δ = 8.15 (2H, d, *J* = 7.8 Hz), 7.67 (2H, d, *J* = 7.8 Hz), 7.61 (1H, t, *J* = 7.6 Hz), 7.51 (3H, m), 7.44 (1H, t, *J* = 7.8 Hz), 7.32 (3H, t, *J* = 7.6 Hz), 7.25 (2H, m), 6.96 (1H, t, *J* = 7.6 Hz), 6.91 (1H, d, *J* = 8.2 Hz), 6.23 (1H, s), 6.05 (1H, t, *J* = 8.8Hz), 5.99 (1H, dd, *J* = 10.2, 5.4 Hz) 5.61 (1H, d, *J* = 7.3 Hz), 4.90 (2H, m), 4.48 (1H, dd, *J* = 10.6, 6.8 Hz), 4.32 (1H, m), 4.30 (1H, d, *J* = 8.4 Hz), 4.22 (1H, m), 4.19 (1H, d, *J* = 8.4 Hz), 3.73 (1H, d, *J* = 6.8 Hz), 2.99 (1H, m), 2.82 (1H, m), 2.55 (2H, m), 2.25 (2H, m), 2.22 (3H, s), 2.0 (1H, m), 1.88 (3H, m),1.86 (1H, m), 1.64 (3H, s), 1.60 (2H, m), 1.24 (3H, s), 1.08 (3H, s). ^{13}C NMR (100 MHz) δ = 203.7, 172.7, 171.3, 167.2, 166.9, 155.4, 142.5, 133.6, 132.7, 131.8, 130.2, 129.6, 129.3, 128.8, 128.65, 128.60, 126.9, 124.4, 120.9, 111.4, 84.6, 80.7, 80.4, 79.5, 76.2, 75.3, 73.1, 72.4, 71.8, 66.0, 58.2, 53.0, 45.3, 43.1, 35.6, 35.2, 35.0, 34.0, 29.9, 28.0, 26.8, 26.2, 24.7, 22.8, 22.5, 20.8, 14.7, 9.7. HRFABMS *m/z* calcd for $C_{51}H_{58}NO_{15}^+$ 924.3806, found 924.3841 (Δ = 3.7 ppm).

Dihydro Bridged Paclitaxel 16j: ^{1}H NMR (400 MHz) δ = 8.09 (2H, d, *J* = 8 Hz), 7.75 (2H, d, *J* = 8 Hz), 7.61 (1H, t, *J* = 8 Hz), 7.50 (3H, m), 7.43 (4H, m), 7.29 (1H, m), 6.90 (1H, t, *J* = 8 Hz), 6.25 (1H, s), 6.14 (1H, t, *J* = 8.8Hz), 5.89 (1H, t, *J* = 8 Hz), 5.64 (1H, d, *J* = 7.2 Hz), 4.90 (1H, d, *J* = 9.2 Hz), 4.68 (1H, t, *J* = 7.2 Hz), 4.42 (1H, m), 4.29 (1H, m), 4.27 (1H, d, *J* = 8.2 Hz), 4.17 (1H, d, *J* = 8.2 Hz), 3.92 (1H, d, *J* = 7.6 Hz), 3.74 (1H, d, *J* = 7.6 Hz), 2.62-2.58 (3H, m), 2.52 (1H, m), 2.23 (3H, s), 2.20 (1H, m), 2.02 (2H, m), 1.89-1.84 (2H, m), 1.89 (3H, s), 1.76 (1H, m), 1.66 (3H, s), 1.26-1.20 (3H, m), 1.22 (3H, s), 1.11 (3H, s). ^{13}C NMR (100 MHz) δ = 204.0, 172.7, 172.4, 171.5, 168.4, 167.1, 156.4, 143.5, 134.1, 133.9, 132.6, 132.1, 131.0, 130.3, 130.0, 129.5, 128.9, 128.7, 127.2, 124.7, 121.5, 111.7, 84.8, 80.9, 79.6, 77.4, 76.5, 75.7, 75.3, 73.4, 72.3, 71.4, 66.6, 58.6, 54.4,

45.7, 43.3, 35.8, 35.6, 35.4, 29.9, 27.7, 27.3, 27.1, 24.5, 22.4, 21.0, 14.9, 9.7. HRFABMS *m/z* calcd for $C_{52}H_{60}NO_{15}^{+}$ 938.3963, found 938.3950 (Δ = 1.4 ppm).

7-*O*-Triethylsilyl-2'-*O*-triisopropylsilyl Bridged Paclitaxel 17f: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (2H, d, *J* = 7.2 Hz), 7.78 (2H, m), 7.30 (2H, d, *J* = 7.2 Hz), 7.64 (1H, m), 7.55 (3H, m), 7.42 (3H, m), 7.30 (1H, m), 7.20 (1H, m), 6.48 (1H, m), 6.46 (1H, s), 6.19 (1H, t, *J* = 8.8 Hz), 5.73 (1H, d, *J* = 6.8 Hz), 5.59 (1H, d, *J* = 15.6 Hz), 5.41(1H, d, *J* = 8 Hz), 4.99 (1H, d, *J* = 8.4 Hz), 4.70 (1H, s), 4.62 (1H, dd, *J* = 20, 4.8 Hz), 4.50 (1H, dd, *J* = 10.4, 6.8 Hz), 4.39 (1H, d, *J* = 8 Hz), 4.24 (1H, d, *J* = 8 Hz) 3.77 (1H, d, *J* = 6.8 Hz), 3.65 (1H, dt, *J* = 19.6, 1.2 Hz), 2.56 (1H, m), 2.42 (1H, m), 2.28 (1H, m), 2.20 (1H, m), 2.18 (3H, s), 2.01 (3H, s), 1.90 (1H, m), 1.72 (3H, s), 1.27 (3H, s), 1.16 (3H, s), 1.21-1.10 (21H, m), 0.99 (12H, m), 0.56 (6H, m). ^{13}C NMR (DEPT, 100 MHz) δ = 149.2, 133.7, 131.7, 131.2, 130.0, 128.7, 128.6, 127.9, 127.8, 126.9, 123.3, 83.8, 76.6, 75.3, 74.8, 74.6, 72.6, 70.4, 51.3, 47.3, 37.5, 37.2, 35.1, 27.5, 20.9, 20.4, 18.3, 18.0, 15.0, 13.3, 9.9, 6.7, 5.3. HRFABMS *m/z* calcd for $C_{64}H_{85}NO_{14}Si_2Na^{+}$ 1170.5406, found 1170.5427 (Δ = 1.8 ppm).

Bridged Paclitaxel 18f: ^{1}H NMR (400 MHz) δ = 8.21 (2H, d, *J* = 7.6 Hz), 8.00 (1H, d, *J* = 7.6 Hz), 7.70 (2H, d, *J* = 7.6 Hz), 7.63 (1H, m), 7.60-7.40 (3H, m), 7.42-7.36 (5H, m), 7.22 (1H, d, *J* = 7.2 Hz), 6.72 (1H, d, *J* = 9.2 Hz), 6.33 (1H, t, *J* = 9.6 Hz), 6.29 (1H, s), 5.88 (1H, d, *J* = 16 Hz), 5.74 (1H, d, *J* = 6.8 Hz), 5.59 (1H, d, *J* = 16Hz), 4.97 (1H, d, *J* = 8.8 Hz), 4.61 (1H, bs), 4.45 (1H, dd, *J* = 10.6, 6.4 Hz), 4.38 (1H, d, *J* = 8.4 Hz), 4.29 (1H, d, *J* = 8.4 Hz), 4.26 (1H, d, *J* = 4.8 Hz), 3.81 (1H, d, *J* = 6.8 Hz), 3.60 (1H, d, *J* = 19.2 Hz), 3.49 (1H, bs), 2.60 (2H, m), 2.46 (2H, m), 2.24 (3H, s), 2.21 (1H, m), 1.90 (1H, m), 1.82 (3H, s), 1.73 (3H, s), 1.25 (3H, s), 1.17 (3H, s). ^{13}C NMR (125 MHz) δ = 203.9, 173.5, 171.4, 167.3, 166.9, 164.4, 149.3, 142.2, 140.0, 134.6, 133.9, 133.7, 133.5, 132.1, 131.4, 130.4, 129.7, 129.3, 128.9, 128.8, 128.1, 127.3, 123.4, 84.4, 80.8, 79.3, 76.6,

75.8, 75.5, 72.5, 72.4, 72.1, 58.1, 49.9, 46.1, 43.3, 37.4, 35.8, 35.7, 27.0, 21.8, 21.0, 15.2, 9.7. HRFABMS *m/z* calcd for $C_{49}H_{52}NO_{14}^{+}$ 878.3388, found: 878.3362 (Δ = 3.0 ppm).

Characterization Data for Bridged Paclitaxels with Substituted C2 benzoyl Groups

2-Debenzoyl-2-(*m*-methoxybenzoyl) Bridged Paclitaxel 25: ^{1}H NMR (400 MHz) δ = 8.00 (1H, d, *J* = 7.6 Hz), 7.80 (1H, d, *J* = 7.6 Hz), 7.73-7.65 (3H, m), 7.50-7.35 (6H, m), 7.20 (1H, m), 7.16 (1H, m), 6.69 (1H, d, *J* = 9.2 Hz), 6.33 (1H, t, *J* = 9.4 Hz), 6.29 (1H, s), 5.85 (1H, d, *J* = 9.2 Hz), 5.72 (1H, dd, *J* = 7.2 Hz), 5.55 (1H, d, *J* = 16.0 Hz), 4.97 (1H, d, *J* = 7.6 Hz), 4.59 (1H, s), 4.44 (1H, dd, *J* = 10.8, 6.8 Hz), 4.41 (1H, d, *J* = 8.0 Hz), 4.28 (1H, d, *J* = 8.2 Hz), 3.87 (3H, s), 3.80 (1H, d, *J* = 6.8 Hz), 3.58 (1H, d, *J* = 19.2 Hz), 3.50 (1H, brs), 2.62-2.42 (3H, m), 2.24 (3H, s), 1.98-1.80 (2H, m), 1.83 (3H, s), 1.72 (3H, s), 1.26 (1H, m), 1.24 (3H, s), 1.16 (3H, s). ^{13}C NMR (100 MHz) δ = 204.0, 173.6, 171.5, 167.1, 167.0, 164.5, 160.0, 149.4, 142.3, 140.0, 134.6, 133.8, 133.7, 133.6, 132.1, 131.5, 131.0, 130.0, 129.4, 129.0, 128.9, 128.1, 127.3, 123.3, 122.7, 119.5, 115.8, 84.4, 80.9, 77.4, 76.9, 75.9, 75.5, 58.9, 55.8, 50.1, 46.2, 43.4, 37.4, 35.8, 35.7, 27.0, 21.8, 21.1, 15.3, 9.7. HRFABMS *m/z* calcd for $C_{50}H_{54}NO_{15}^{+}$ 908.3493, found 908.3516 (Δ = 2.5 ppm).

2-Debenzoyl-2-(*m*-methoxybenzoyl) Dihydro Bridged Paclitaxel 26: ^{1}H NMR (400 MHz) δ = 7.77 (1H, d, *J* = 7.2 Hz), 7.66-7.63 (2H, m), 7.50-7.36 (4H, m), 7.31-7.15 (3H, m), 6.95 (1H, d, *J* = 8.8Hz), 6.53 (1H, t, *J* = 8.6 Hz), 6.27 (1H, s), 5.94 (1H, d, *J* = 8.8 Hz), 5.74 (1H, d, *J* = 7.2 Hz), 4.96 (1H, d, *J* = 8.0 Hz), 4.56 (1H, bs), 4.40-4.33 (2H, m), 4.23 (1H, d, *J* = 8.4 Hz), 3.90 (3H, s), 3.73 (1H, d, *J* = 6.8 Hz), 3.11-2.96 (2H, m), 2.86-2.68 (2H, m), 2.56 (1H, m), 2.35 (1H, m), 2.28-2.24 (1H, m), 2.24 (3H, s), 2.11-1.98 (2H, m), 1.94-1.88 (1H, m), 1.82 (3H, s), 1.72 (3H, s), 1.34 (3H, s), 1.18 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 174.0, 172.4, 171.5, 167.2, 167.0, 160.0, 142.5, 139.4, 138.9, 133.8, 133.2, 130.5, 130.3, 130.1, 128.9, 128.8, 128.6, 127.7, 127.3, 122.9,

120.7, 114.6, 84.6, 81.1, 79.6, 77.4, 75.6, 75.3, 73.4, 72.6, 72.4, 58.8, 55.7, 50.7, 49.5, 45.7, 43.6, 40.0, 35.4, 33.8, 30.0, 27.5, 25.9, 22.8, 21.1, 14.9, 9.8.

2-Debenzoyl-2-(*m*-methoxybenzoyl) Bridged Paclitaxel 28: ^{1}H NMR (400 MHz) δ = 7.76 (2H, d, *J* = 8.0 Hz), 7.6 (1H, m), 7.52 (1H, t, *J* = 7.2 Hz), 7.46-7.37 (4H, m), 7.31 (3H, m), 7.13 (2H, d, *J* = 8.4 Hz), 6.74 (1H, t, *J* = 10.4 Hz), 6.50 (1H, t, *J* = 9.0 Hz), 6.36 (1H, s), 6.28 (1H, d, *J* = 11.6 Hz), 5.93 (1H, d, *J* = 8.4 Hz), 5.73 (1H, d, *J* = 6.8 Hz), 5.03 (1H, d, *J* = 8.0 Hz), 4.86 (1H, dd, *J* = 10.8, 7.2 Hz), 4.44 (1H, s) 4.37 (1H, d, *J* = 8.0 Hz), 4.25 (1H, d, *J* = 8.4 Hz), 3.89 (1H, d, *J* = 6.8 Hz), 3.86 (3H, s), 3.65 (1H, d, *J* = 18.8 Hz), 2.69-2.61 (1H, m), 2.25 (3H, s), 2.23 (1H, m), 1.96 (1H, m), 1.95 (3H, s), 1.76 (3H, s), 1.30 (3H, s), 1.19 (3H, s). ^{13}C NMR (100 MHz) δ = 203.9, 173.3, 171.5, 167.3, 166.7, 165.6, 159.9, 153.3, 142.4, 138.6, 137.0, 134.0 133.3, 132.2, 131.0, 130.4, 130.1, 128.9, 128.6, 127.9, 127.3, 126.5, 122.9, 120.8, 120.5, 114.6, 84.6, 81.3, 79.1, 77.2, 75.8, 75.1, 73.0, 72.6, 72.1, 58.2, 55.8, 51.0, 46.2, 43.6, 36.3, 35.7, 35.1, 29.9, 27.3, 22.0, 21.1, 15.5, 9.7 HRFABMS *m/z* calcd for $C_{50}H_{54}NO_{15}^{+}$ 908.3493, found 908.3516 (Δ = 2.5).

***N*-Debenzoyl-*N*-Boc Bridged Paclitaxel 31a:** ^{1}H NMR (400 MHz) δ = 8.17 (2H, d, *J* = 7.2 Hz), 7.88 (2H, d, *J* = 7.6 Hz), 7.64 (1H, t, *J* = 6.8 Hz), 7.52 (3H, m), 7.38-7.30 (2H, m), 7.19 (1H, dd, *J* = 7.2, 1.6 Hz), 6.33 (1H, t, *J* = 8.4 Hz), 6.28 (1H, s), 6.15 (1H, t, *J* =5.5 Hz), 5.69 (1H, d, *J* = 7.2 Hz), 5.61 (1H, d, *J* = 16 Hz), 5.40 (1H, d, *J* = 9.6 Hz), 5.15 (1H, d, *J* = 10.0, Hz), 4.95 (1H, d, *J* = 8.0 Hz), 4.47 (1H, s), 4.44 (1H, dd, *J* = 10.8, 6.8 Hz), 4.34 (1H, d, *J* = 8.4 Hz), 4.26 (1H, d, *J* = 8.4 Hz), 4.15 (1H, m), 3.79 (1H, d, *J* = 7.2 Hz), 3.56 (1H, m), 3.39 (1H, bs), 2.56 (1H, m), 2.35 (1H, m), 2.24 (3H, s), 1.88 (1H, m), 1.82 (3H, s), 1.71 (3H, s), 1.65 (1H, m), 1.35 (9H, s), 1.27 (1H, m),1.25 (3H, s), 1.16 (3H, s). ^{13}C NMR (100 MHz) δ = 204.0, 173.6, 171.5, 167.5, 164.5, 155.3, 149.3, 142.5, 140.4, 134.3, 133.9, 133.4, 131.3, 130.4, 129.9, 129.0, 128.9, 128.7, 128.1, 123.3, 84.4, 80.8,

80.1, 79.4, 77.4, 76.7, 75.9, 75.5, 72.5, 71.7, 58.8, 51.0, 46.2, 43.3, 37.5, 35.8, 35.6, 29.9, 28.4, 21.9, 21.1, 15.3, 9.7.

***N*-Debenzoyl-*N*-Boc-2-debenzoyl-2-(*m*-methoxybenzoyl) Bridged Paclitaxel 31b:** ^{1}H NMR (400 MHz) δ = 7.88 (1H, d, *J* = 7.2 Hz), 7.76 (1H, d, *J* = 7.6 Hz), 7.70 (1H, dd, *J* = 1.6, 2.4 Hz), 7.60 (1H, dd, *J* = 3.6, 5.6 Hz), 7.56 (1H, dd, *J* = 3.6, 5.6 Hz), 7.43 (1H, t, *J* = 8.0 Hz) 7.38-7.30 (2H, m), 7.19-7.14 (2H, m), 6.32 (t, *J* = 9.0 Hz), 6.28 (1H, s), 5.69 (1H, d, *J* = 7.2 Hz), 5.57 (1H, d, *J* = 16.0 Hz), 5.36 (1H, d, *J* = 9.6 Hz), 5.13 (1H, d, *J* = 9.6 Hz), 4.96 (1H, d, *J* = 8.0 Hz), 4.46 (1H, s), 4.43 (1H, dd, *J* = 6.8, 10.8 Hz), 4.32 (1H, d, *J*= 8.4 Hz), 4.25 (1H, d, *J* = 8.4 Hz), 4.14 (1H, m), 3.89 (3H, s), 3.78 (1H, d, *J* = 7.2 Hz), 3.55 (1H, d, *J* = 19.2 Hz), 3.39 (1H, bs), 2.58-2.48 (3H, m), 2.35 (2H, m), 2.34 (3H, s), 1.86 (2H, m), 1.81 (3H, s), 1.70 (3H, s), 1.34 (9H, s), 1.25 (3H, s), 1.15 (3H, s). ^{13}C NMR (100 MHz) δ = 204.0, 173.6, 171.4, 167.3, 164.5, 160.0, 155.3, 149.4, 142.5, 140.4, 134.3, 133.4, 131.3, 131.0, 129.0, 128.8, 128.1, 123.2, 122.6, 119.6, 115.6, 84.4, 80.8, 80.1, 79.3, 77.4, 76.7, 75.9, 75.5, 72.5, 71.7, 58.8, 55.8, 51.0, 46.2, 43.3, 37.4, 35.8, 35.5, 28.4, 27.0, 21.8, 21.1, 15.3, 9.7. HRFABMS *m/z* calcd for $C_{48}H_{58}NO_{16}^{+}$ 904.3756, found 904.3729 (Δ = 2.9 ppm).

***N*-Debenzoyl-*N*-Boc Dihydro Bridged Paclitaxel 32a:** ^{1}H NMR (400 MHz) δ = 8.15 (2H, d, *J* = 7.6 Hz), 7.63 (2H, t, *J* = 5.6 Hz), 7.52 (2H, t, *J* = 7.6 Hz), 7.31-7.19 (3H, m), 6.52 (1H, t, *J* = 9.0 Hz), 6.27 (1H, s), 5.72 (1H, d, *J* = 7.2 Hz), 5.42 (2H, m), 4.93 (1H, d, *J* = 8.0 Hz), 4.44 (1H, d, *J* = 3.2 Hz), 4.37 (1H, dd, *J* = 10.8, 6.8 Hz), 4.30 (1H, d, *J* = 8.4 Hz), 4.19 (1H, d, *J* = 8.4 Hz), 3.73 (1H, d, *J* = 7.2 Hz), 3.35 (1H, bs) 3.11-2.98 (2H, m), 2.88-2.68 (2H, m), 2.56 (1H, m), 2.35 (1H, m), 2.23 (3H, s), 2.28-2.22 (1H, m), 2.11-1.98 (2H, m), 1.94-1.88 (1H, m), 1.82 (3H, s), 1.71 (3H, s), 1.35 (3H, s), 1.33 (9H, s), 1.18 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 174.0, 172.5, 171.5, 167.4, 155.3, 142.7, 139.1, 134.0, 133.0, 130.5, 130.2, 129.3, 129.0, 128.4, 127.4, 84.6, 81.1, 79.7, 7.4,

75.6, 75.2, 73.5, 72.6, 72.1, 58.8, 50.7, 45.8, 43.6, 35.9, 35.8, 33.7, 28.4, 27.4, 26.0, 22.7, 21.1, 14.9, 9.8. HRFABMS *m/z* calcd for $C_{47}H_{58}NO_{15}^{+}$ 876.3806, found 876.3795 (Δ = 1.3 ppm).

***N*-Debenzoyl-*N*-Boc-2-debenzoyl-2-*m*-methoxybenzoyl Dihydro Bridged Paclitaxel 32b:** ^{1}H NMR (400 MHz) δ = 7.76 (1H, d, *J* = 7.6 Hz), 7.66-7.63 (2H, m), 7.43 (1H, t, *J* = 8.0 Hz), 7.31-7.15 (5H, m), 6.52 (1H, t, *J* = 9.2 Hz), 6.27 (1H, s), 5.72 (1H, d, *J* = 7.2 Hz), 5.42 (2H, m), 4.95 (1H, d, *J* = 7.6 Hz), 4.43 (1H, bs), 4.38 (1H, dd, *J* = 10.8, 6.8 Hz), 4.34 (1H, d, *J* = 8.0 Hz), 4.20 (1H, d, *J* = 8.0 Hz), 3.90 (3H, s), 3.73 (1H, d, *J* = 6.8 Hz), 3.35 (1H, bs) 3.11-2.96 (2H, m), 2.86-2.68 (2H, m), 2.56 (1H, m), 2.35 (1H, m), 2.28-2.24 (1H, m), 2.24 (3H, s), 2.11-1.98 (2H, m), 1.94-1.88 (1H, m), 1.82 (3H, s), 1.71 (3H, s), 1.35 (3H, s), 1.32 (9H, s), 1.18 (3H, s). ^{13}C NMR (100 MHz) δ = 203.8, 174.0, 172.5, 171.5, 167.3, 160.0, 155.3, 142.7, 139.2, 139.0, 133.0, 130.5, 130.2, 130.1, 128.4, 127.6, 127.5, 122.9, 120.7, 114.6, 84.6, 81.1, 80.2, 79.7, 77.4, 75.6, 75.3, 73.5, 72.6, 72.1, 58.8, 55.7, 50.7, 45.8, 43.6, 35.9, 35.8, 35.3, 33.7, 28.4, 27.4, 25.9, 22.7, 21.1, 14.9, 9.8. HRFABMS *m/z* calcd for $C_{48}H_{59}NO_{16}Na^{+}$ 928.3732, found 928.3690 (Δ = 6.3 ppm).

^{1}H NMR spectra of compounds 15c, 15d, 15f, 15f (expanded), 15f (COSY), 16c, 16f, 25, 31a, 31b, 32a, & 32b.

(Millions)
0
100.0
200.0
300.0
X : parts per Million : 1H
8.1108
8.0966
8.0938
7.7219
7.7077
7.5377
7.5222
7.4191
7.4035
7.2899
7.2546
7.1108
7.0952
6.6898
6.6587
6.2689
6.1589
5.9972
5.9817
5.7027
5.6885
5.1040
5.0889
4.8832
4.8786
4.7682
4.7600
4.4512
4.4343
4.2794
4.2625
3.7458
3.7311
3.1915
2.5685
2.5493
2.4778
2.4700
2.2726
2.2373
2.2021
2.0381
1.8663
1.8645
1.7527
1.6899
1.6551
1.6011
1.2465
1.2378
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6.0
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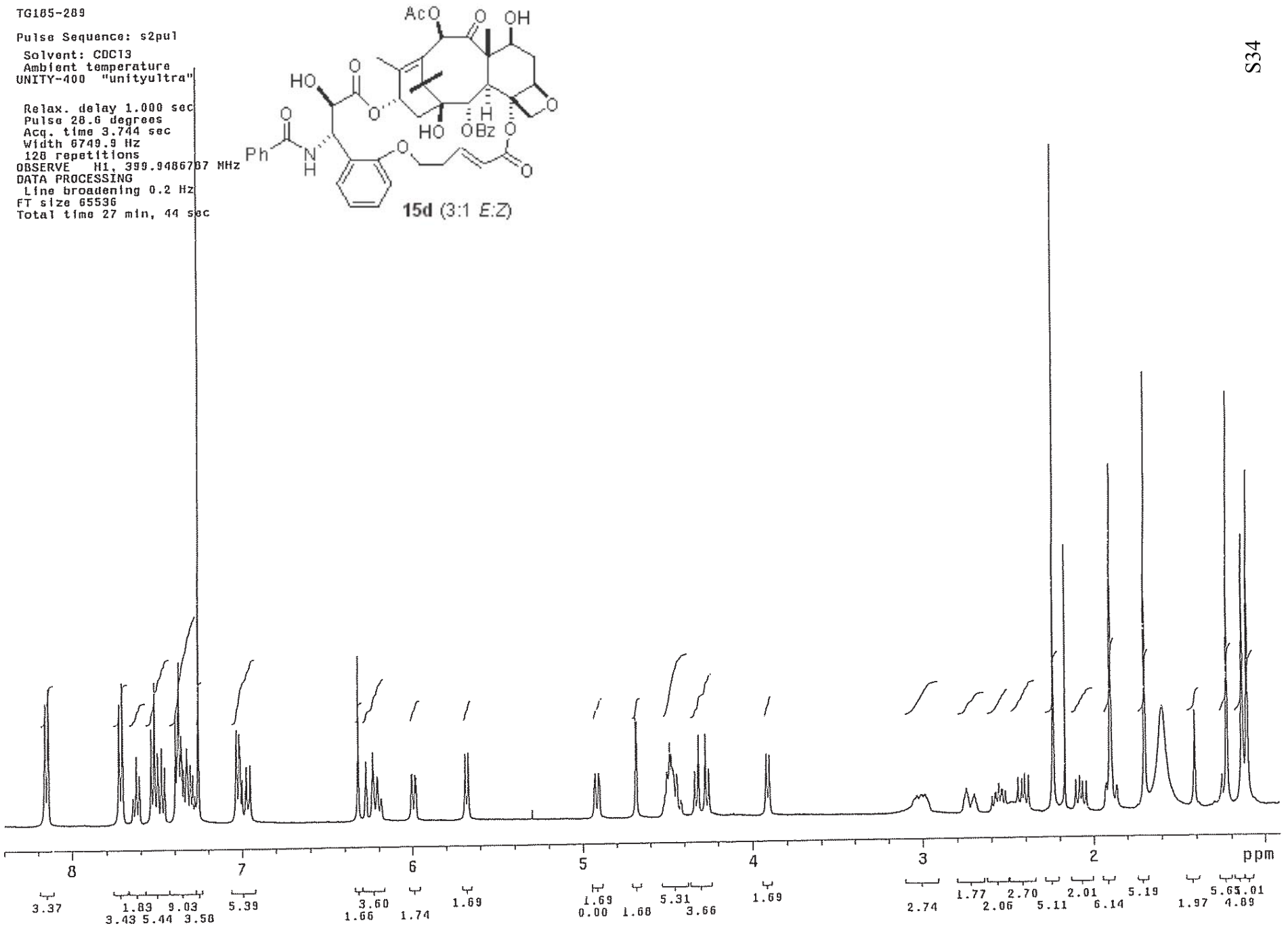
4.0
3.0
2.0
1.0
15c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Ambient temperature
UNITY-400 "unityultra"
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Width 6749.9 Hz
128 repetitions
OBSERVE H1, 399.9486787 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 27 min, 44 sec
AcO
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OH
HO
O
HO
H
OBz
O
O
Ph
N
H
O
O
O
15d (3:1 E:Z)
8
7
6
5
4
3
2
ppm
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3.60
1.69
1.69
5.31
1.69
2.74
1.77
2.70
2.01
5.19
5.65
1.01
3.43
5.44
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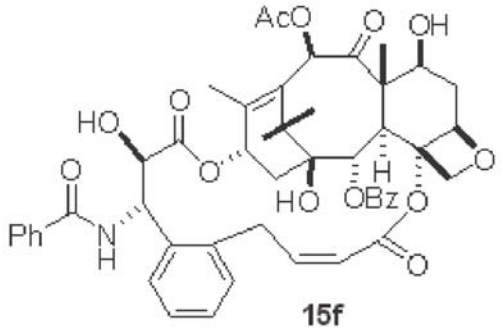
0.00
1.68
3.66
2.06
5.11
6.14
1.97
4.89

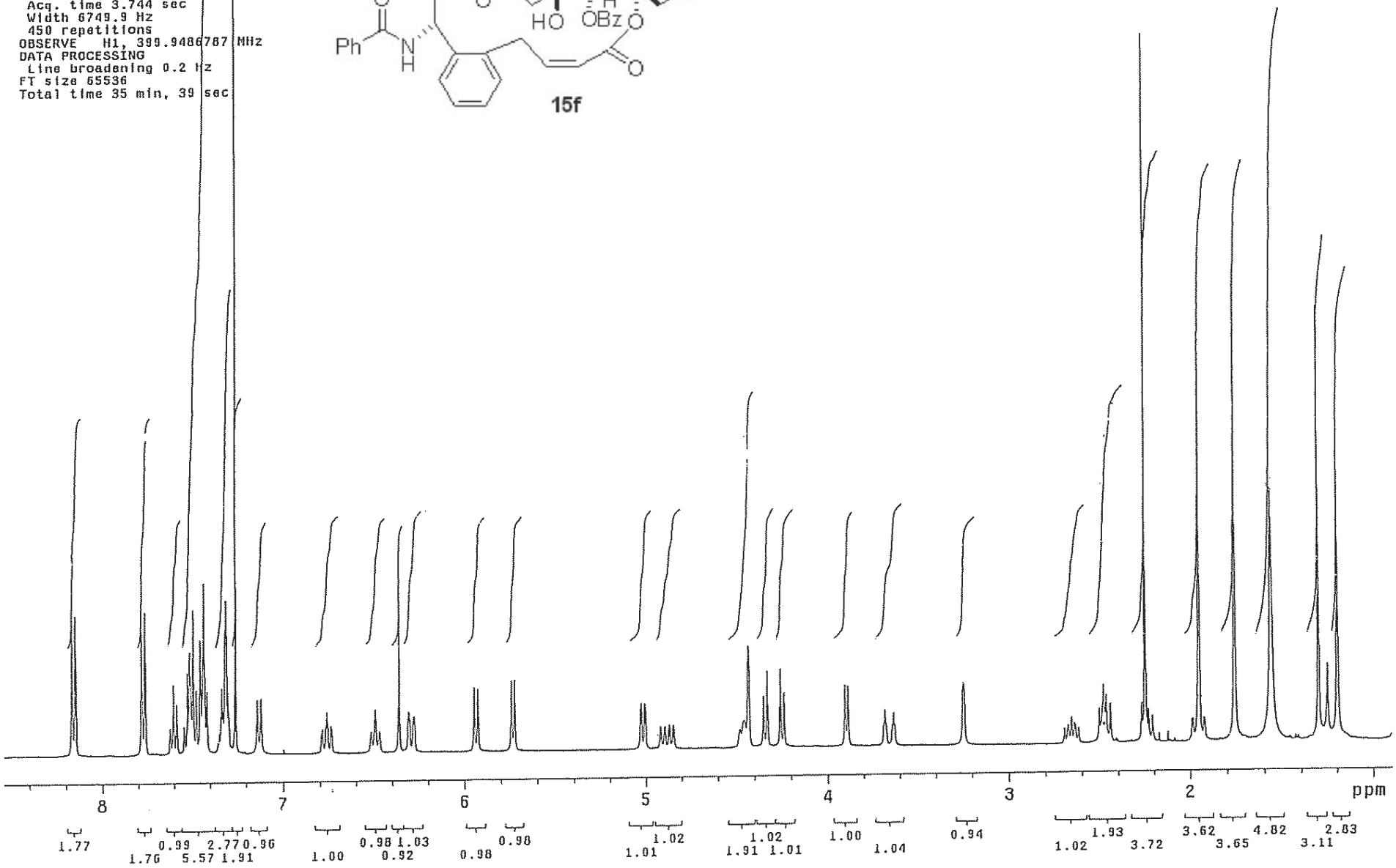
TG185-258

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-400 "unityultra"

Relax. delay 1.000 sec
Pulse 28.6 degrees
Acq. time 3.744 sec
Width 6749.9 Hz
450 repetitions
OBSERVE H1, 399.9486787 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 35 min, 39 sec



15f



TG185-258

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-400 "unityultra"

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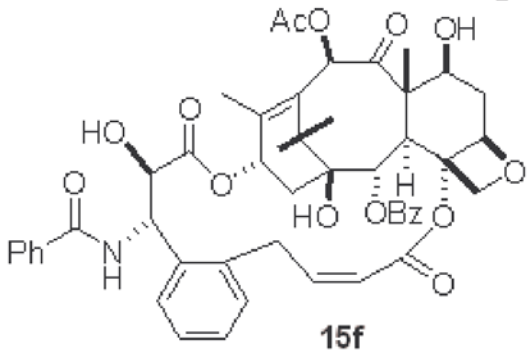
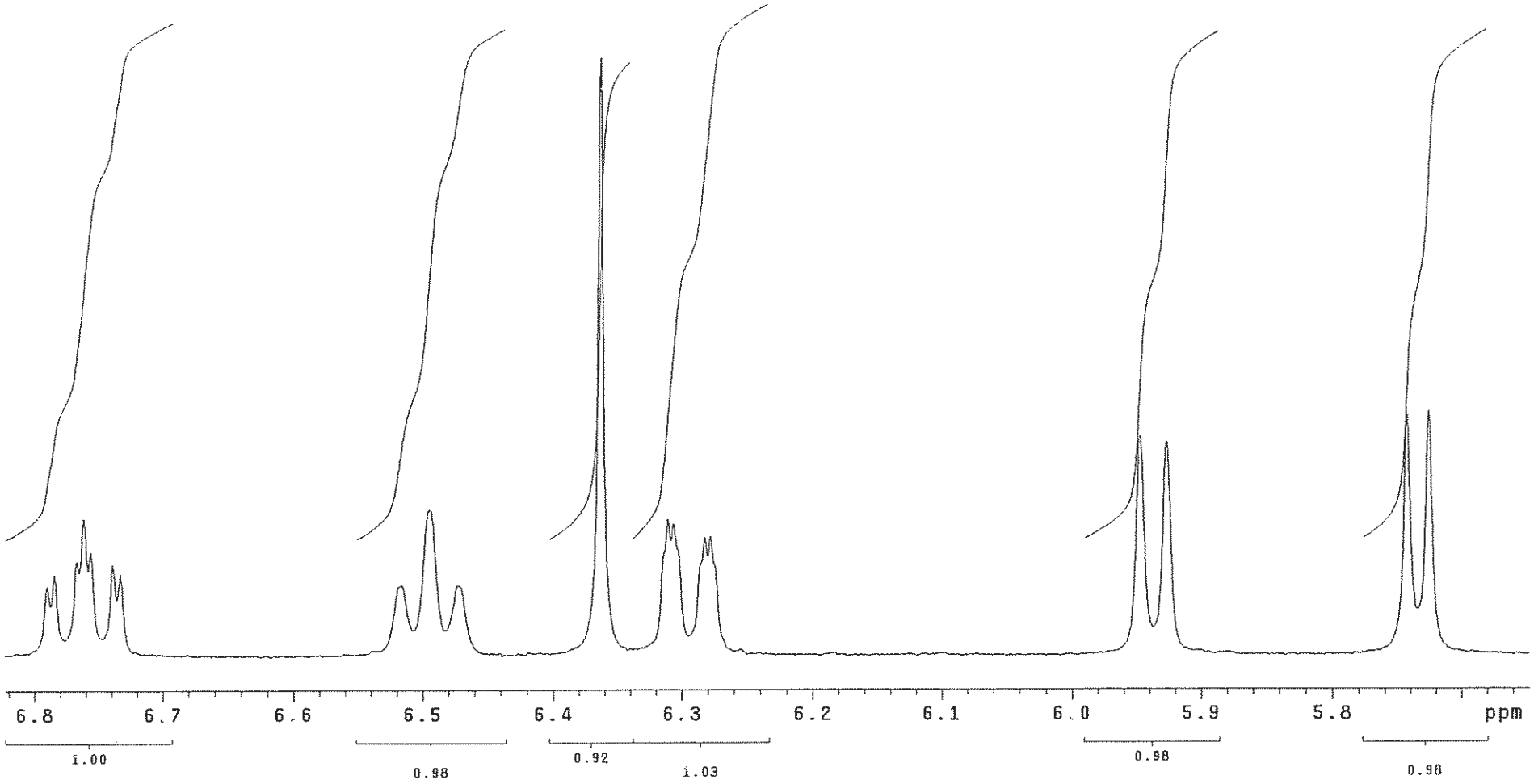
Pulse 28.6 degrees
Acq. time 3.744 sec
Width 6749.9 Hz
450 repetitions
OBSERVE H1, 399.9486787 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 35 min, 39 sec



15f



STANDARD 1H OBSERVE

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Solvent: CDCl3
Ambient temperature
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2D Width 6499.8 Hz
4 repetitions
128 increments
OBSERVE H1, 399.9441186 MHz
DATA PROCESSING
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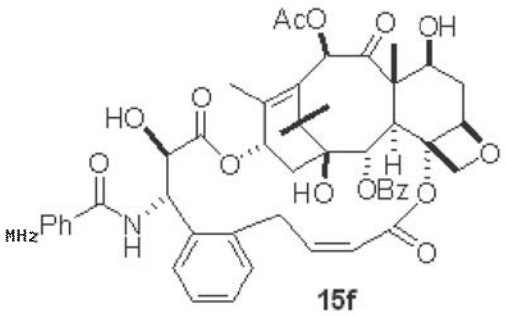
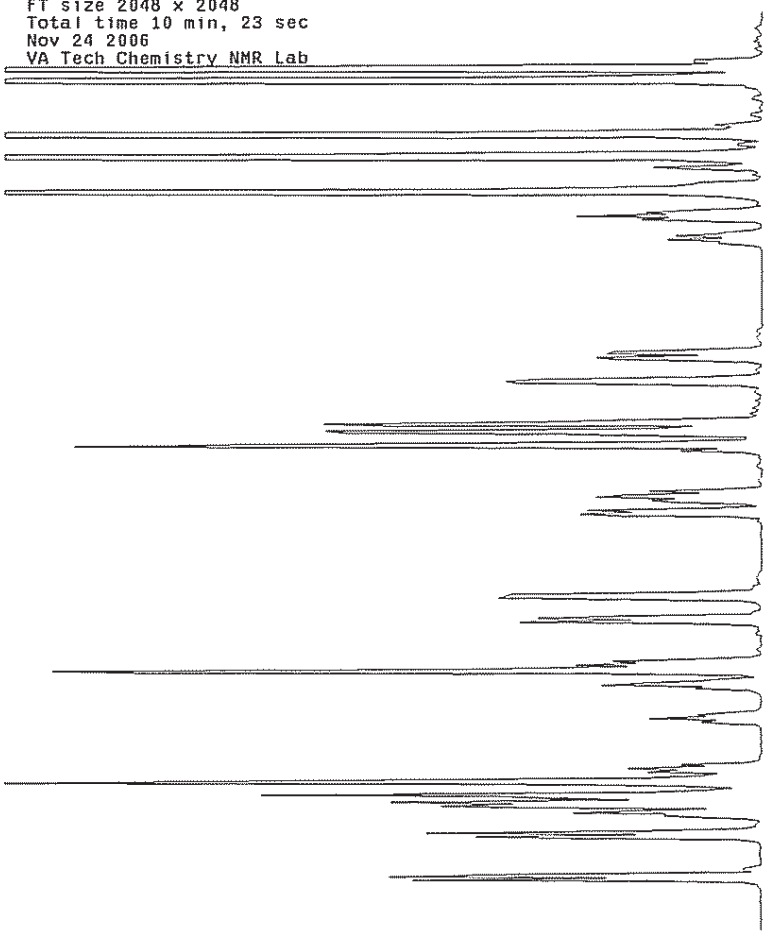
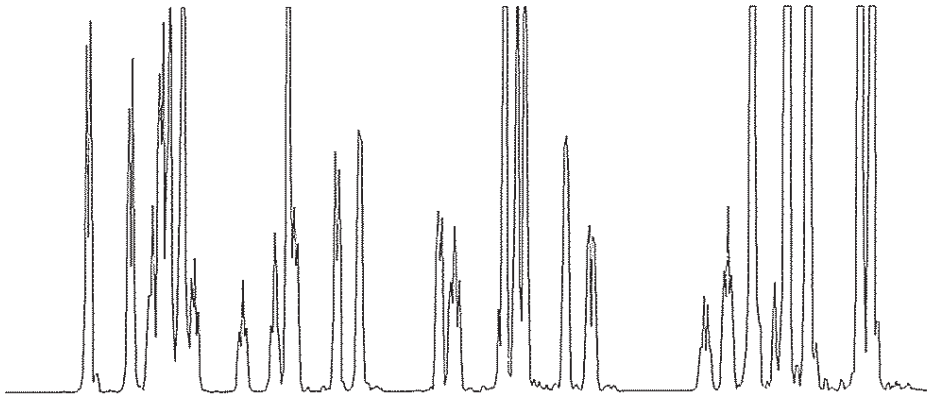
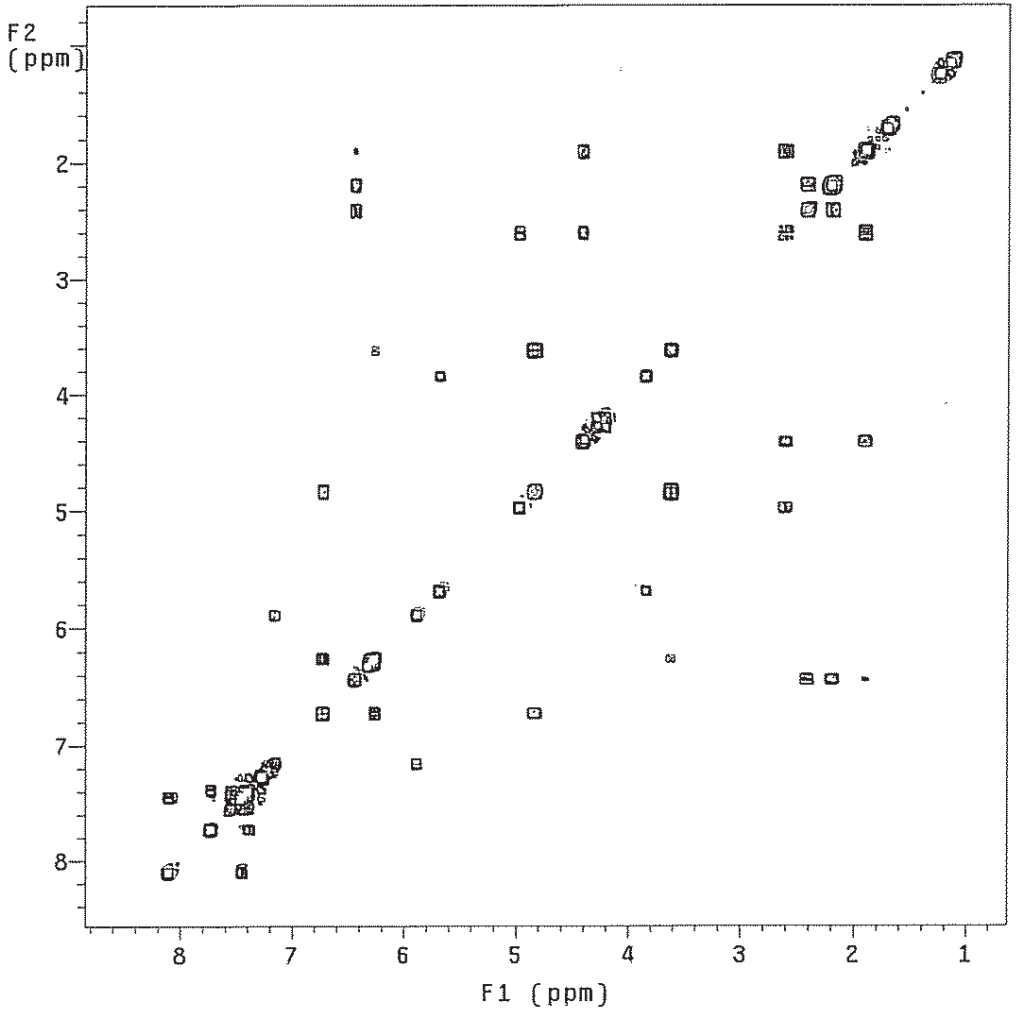
F1 DATA PROCESSING
Sq. sine bell 0.020 sec
FT size 2048 x 2048
Total time 10 min, 23 sec
Nov 24 2006
VA Tech Chemistry NMR Lab



15f







STANDARD 1H OBSERVE

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Solvent: CDCl3
Ambient temperature
UNITY-400 "unityultra"

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Pulse 28.6 degrees
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Width 6749.9 Hz
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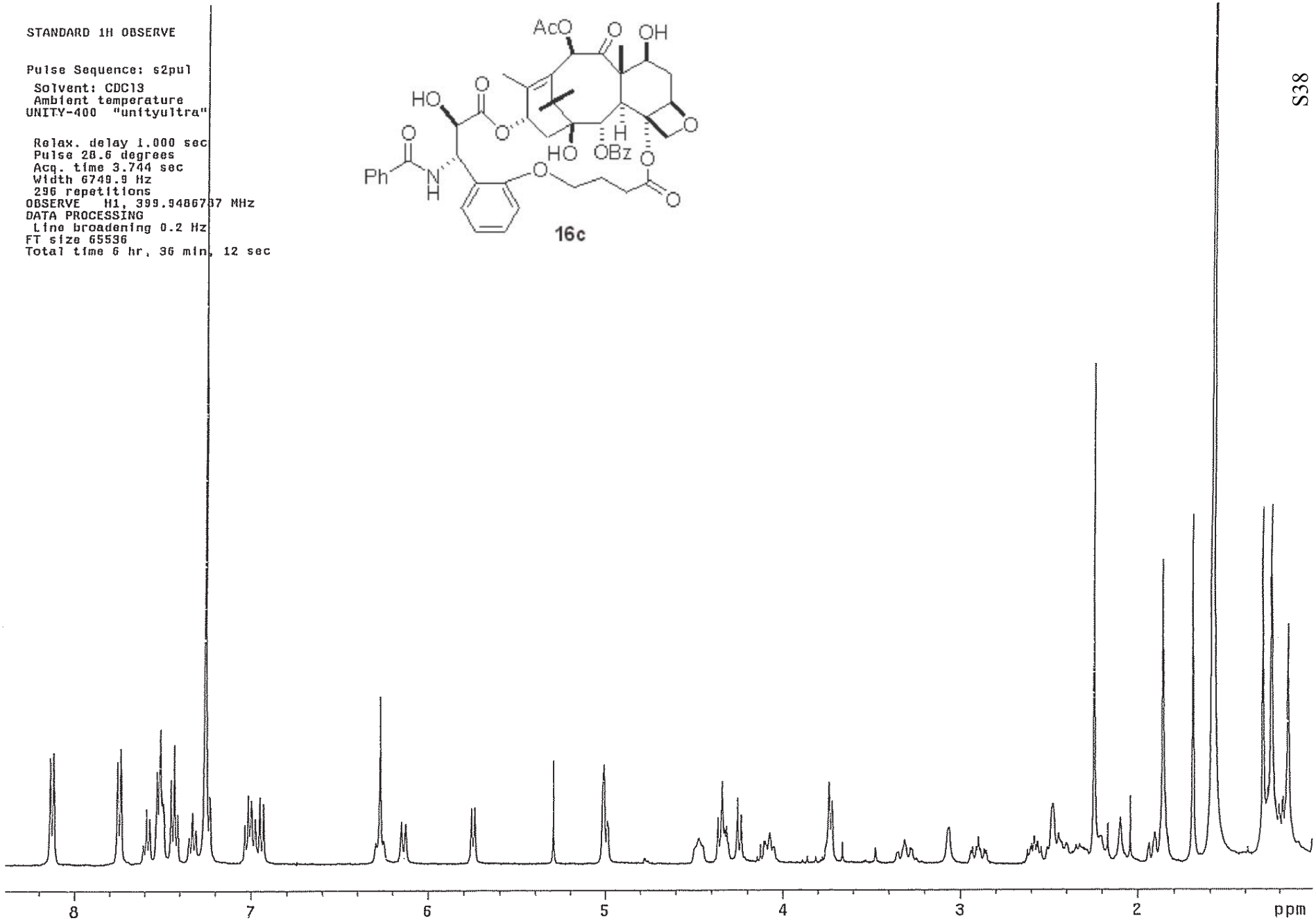
16c



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: CY-196-94
UNITY-400 "unityultra"

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Acq. time 3.744 sec
Width 6000.6 Hz
300 repetitions
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DATA PROCESSING
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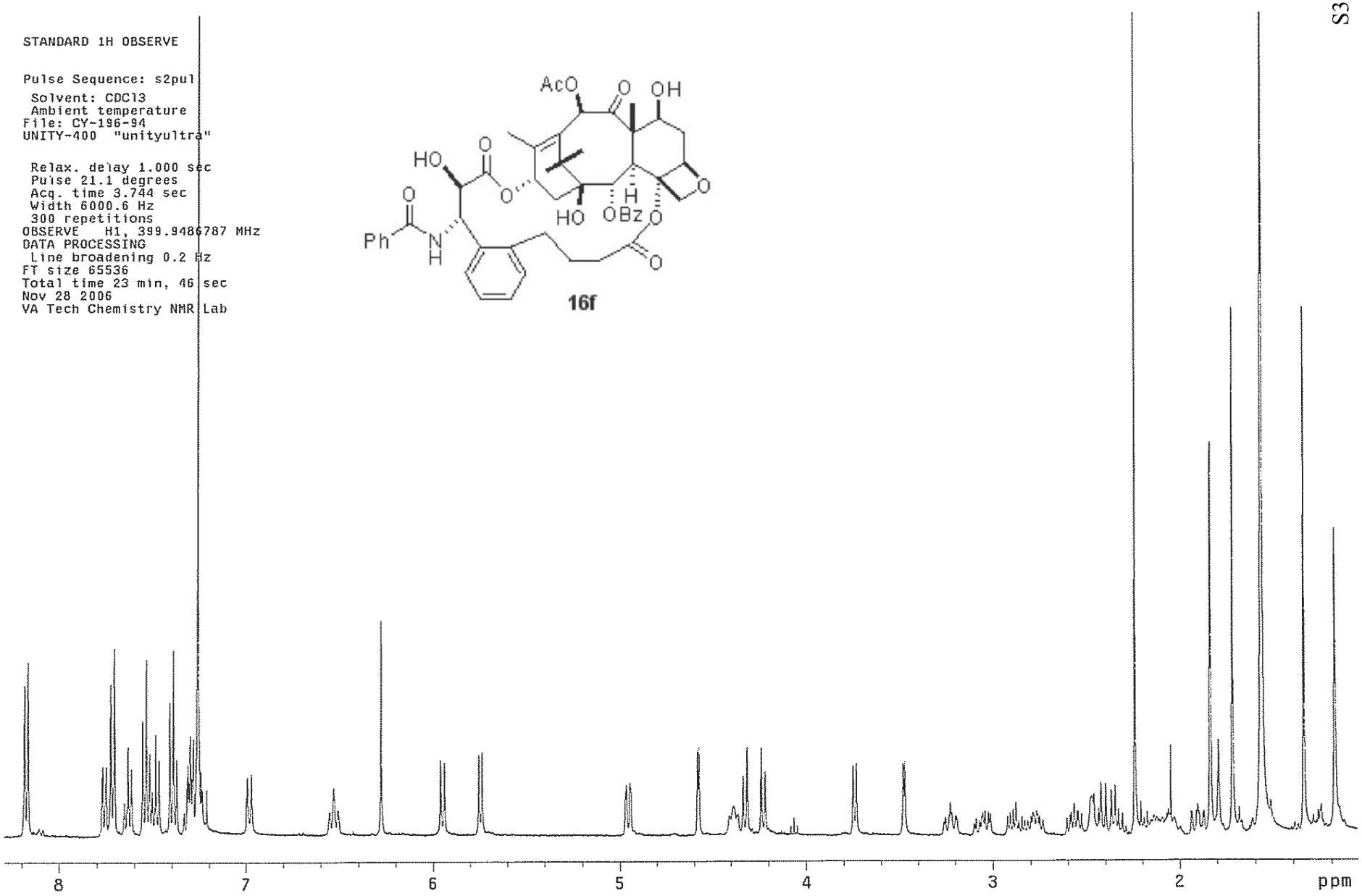
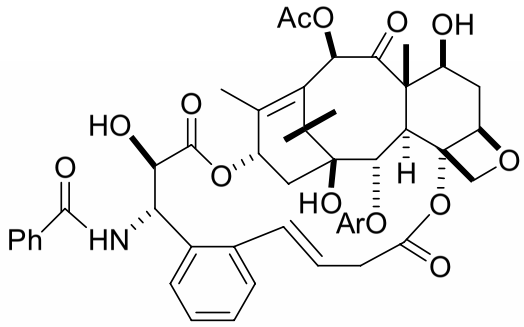
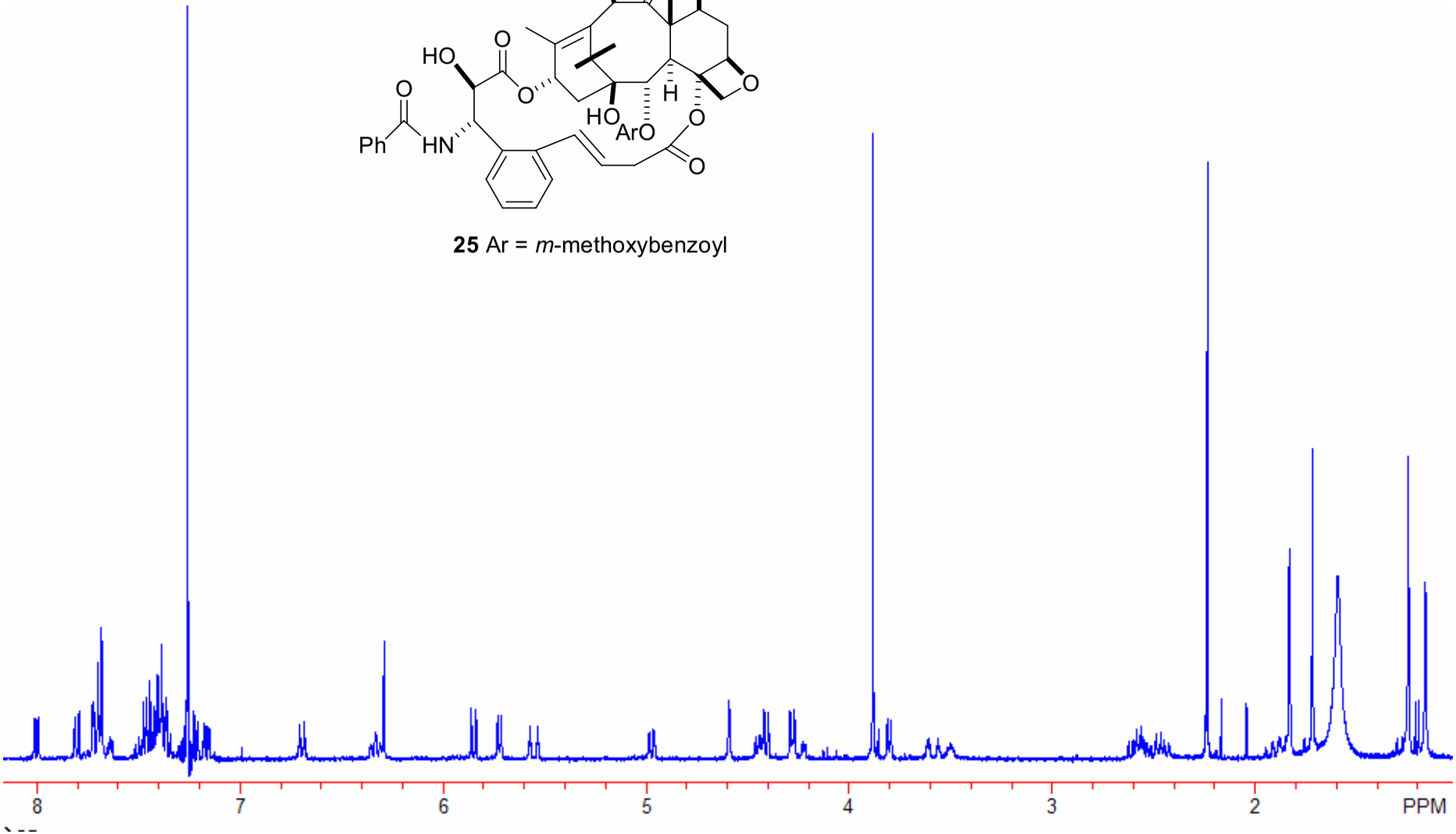
FT size 65536
Total time 23 min, 46 sec
Nov 28 2006
VA Tech Chemistry NMR Lab

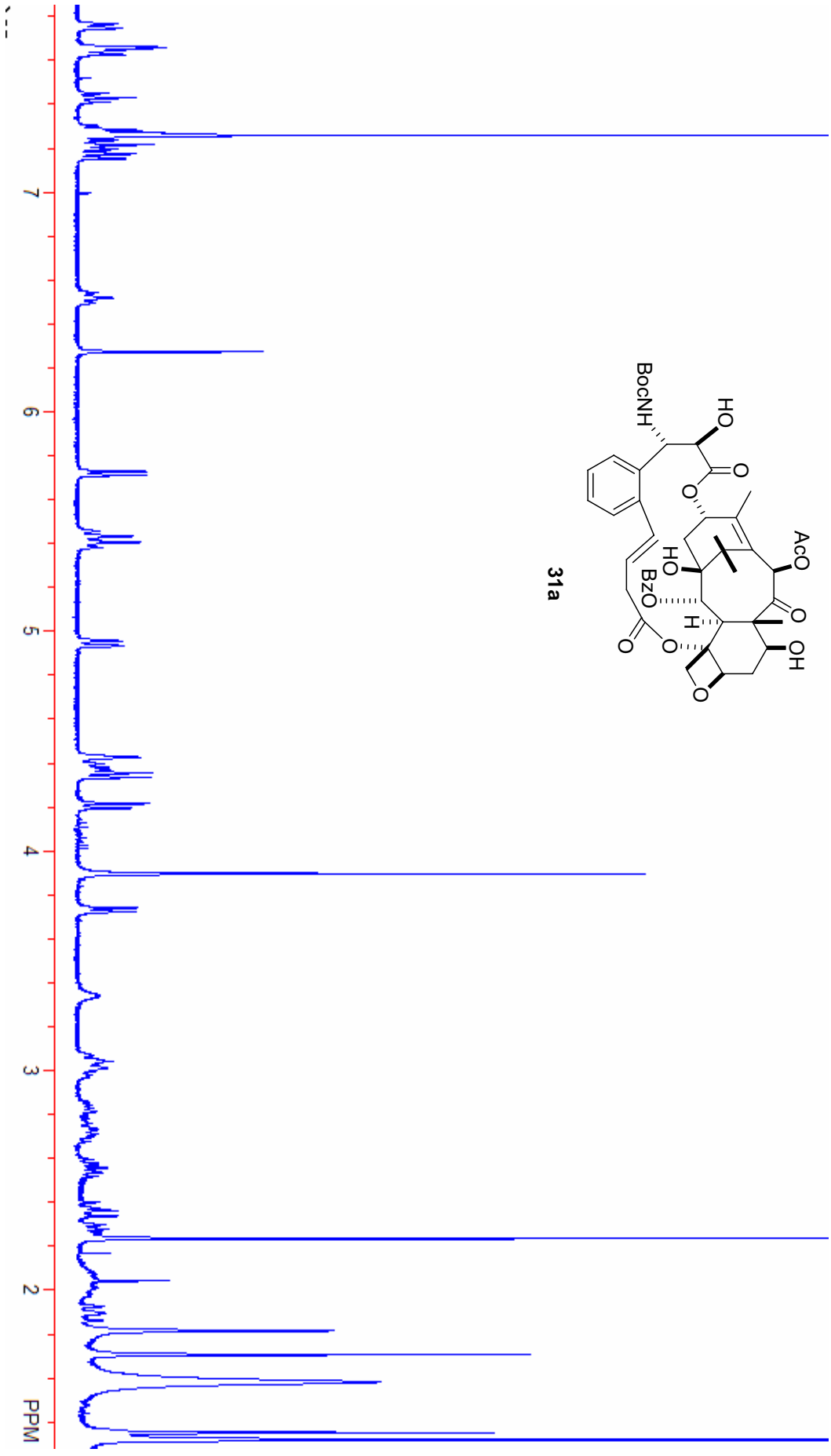
16f





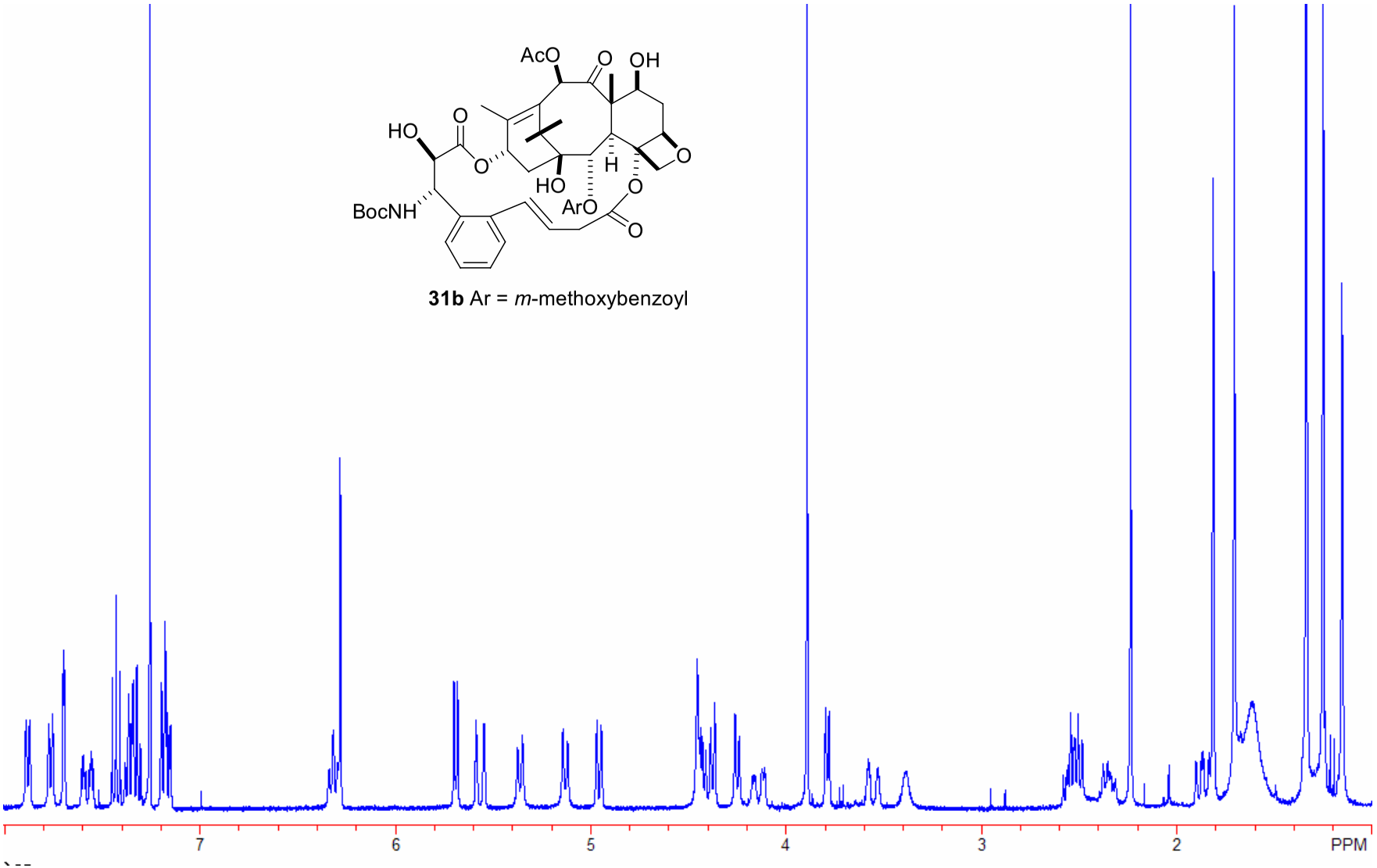
25 Ar = *m*-methoxybenzoyl

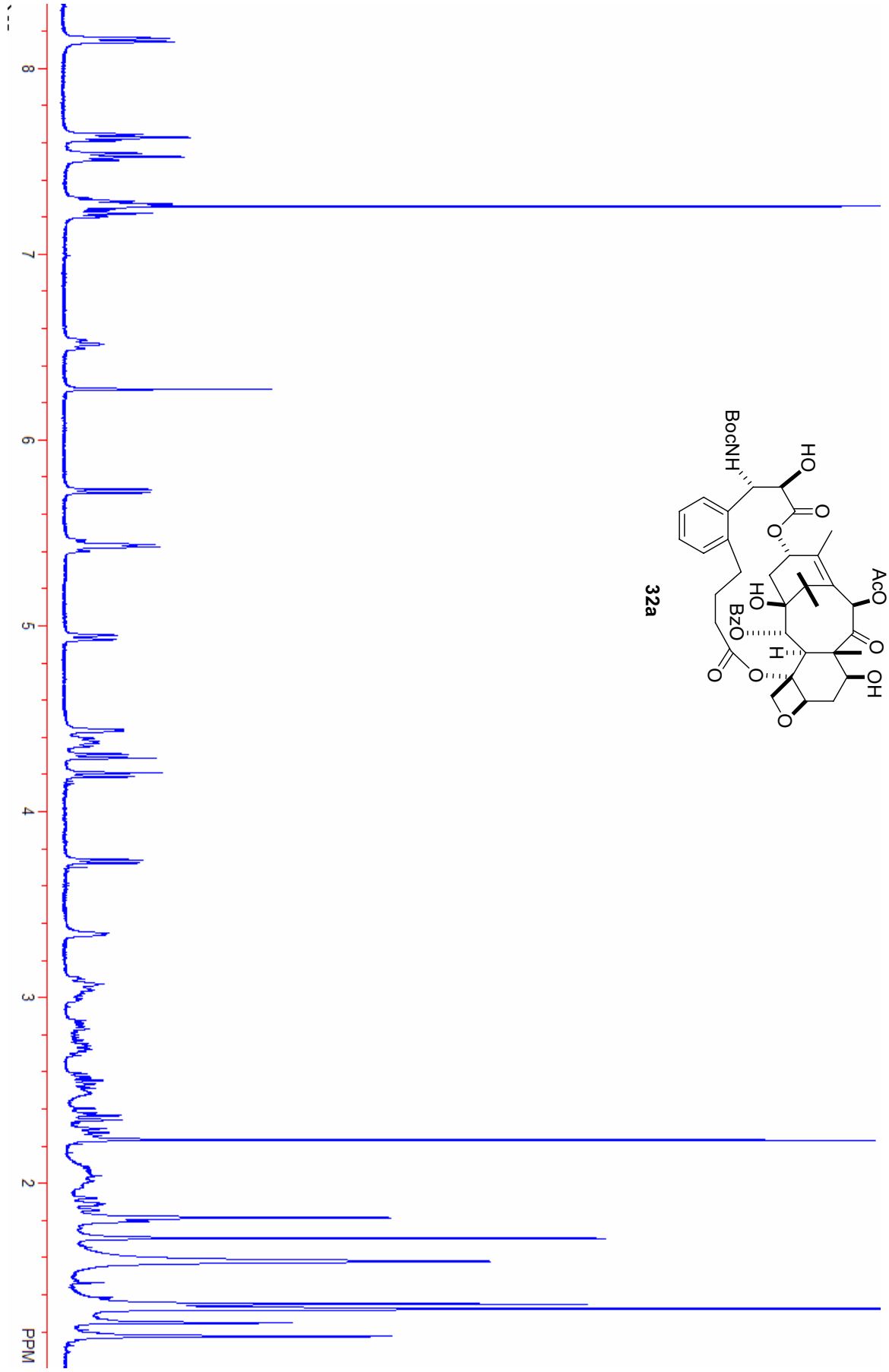




31a

31b Ar = *m*-methoxybenzoyl





32a

32b Ar = *m*-methoxybenzoyl