Supplementary Materials: Enantioselective Bioreduction of Prochiral Pyrimidine Base Derivatives by Boni Protect Fungicide Containing Live Cells of *Aureobasidium pullulans*

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Characterization of the Compounds 1-3 and 1a-3a

1-Allyl-5-methyl-3-(2-oxo-2-phenylethyl)pyrimidine-2,4(1*H*,3*H*)-dione (**1**) HPLC (Lux® 5µ Cellulose-3, LC Column 250x4.6 mm *n*-hexane (99 % HPLC)/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}; retention time: **1** 25.2 min. *n*-hexane (95 % HPLC)/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}; retention time: **1** 26.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (d, *J*=1.2 Hz, 3H, C^5-CH_3), 4.37-4.38 (m, 2H, CH_2=CHCH_2), 5.26–5.33 (m, 2H, CH_2=CHCH_2), 5.43 (s, 2H, N^3-$CH_2COC_6H_5$), 5.85–5.94 (m, 1H, CH_2=CHCH_2), 7.05 (q, *J*=1.2 Hz, 1H, C^6-H), 7.48–7.52 (m, 2H, N^3-$CH_2COC_6H_5$), 7.61–7.63 (m, 1H, N^3-$CH_2COC_6H_5$), 8.00–8.02 (m, 2H, N^3-$CH_2COC_6H_5$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13.01 (CH_3), 47.26 (CH_2), 50.87 (CH_2), 110.04 (C), 119.03 (CH_2), 128.11 (2 CH), 128.75 (2 CH), 131.79 (CH), 133.70 (CH), 135.04 (C), 138.34 (CH), 151.23 (C=O), 163.38 (C=O), 192.01 (C=O) ppm.

1-Ethyl-5-methyl-3-(2-oxo-2-phenylethyl)pyrimidine-2,4(1*H*,3*H*)-dione (**2**) HPLC (Lux® 5µ Cellulose-3, LC Column 250x4.6 mm *n*-hexane (99 % HPLC)/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}; retention time: **2** 24.4 min. *n*-hexane (95 % HPLC)/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}; retention time: **2** 25.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, *J*=7.2 Hz, 3H, N^1-CH_2CH_3), 1.97 (d, *J*=1.2 Hz, 3H, C^5-CH_3), 3.81 (q, *J*= 7.2 Hz, 2H, N^1-CH_2CH_3), 5.43 (s, 2H, N^3-$CH_2COC_6H_5$), 7.07 (q, *J*=1.2 Hz, 1H, C^6-H), 7.48–7.52 (m, 2H, N^3-$CH_2COC_6H_5$), 7.59–7.63 (m, 1H, N^3-$CH_2COC_6H_5$), 8.01-8.03 (m, 2H, N^3-$CH_2COC_6H_5$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13.03 (CH_3), 14.35 (CH_3), 44.62 (CH_2), 47.17 (CH_2), 109.90 (C), 128.12 (2 CH), 128.74 (2 CH), 133.67 (CH), 135.10 (C), 138.54 (CH), 151.08 (C=O), 163.48 (C=O), 192.10 (C=O) ppm.

1,5-Dimethyl-3-(2-oxo-2-phenylethyl)pyrimidine-2,4(1*H*,3*H*)-dione (**3**) HPLC (Lux® 5µ Cellulose-3, LC Column 250x4.6 mm *n*-hexane (99 % HPLC)/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}; retention time: **3** 27.6 min. *n*-hexane (95 % HPLC)/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}; retention time: **3** 30.8 min. ^{1}H NMR (400 MHz,$CDCl_3$): δ = 1.96 (d, *J*=1.2 Hz, 3H, C^5-CH_3), 3.39 (s, 3H, N^1-CH_3), 5.42 (s, 2H, N^3-$CH_2COC_6H_5$), 7.07 (q, *J*=1.2 Hz, 2H, C^6-H), 7.48–7.52 (m, 2H, N^3-$CH_2COC_6H_5$), 7.59–7.63 (m, 1H, N^3-$CH_2COC_6H_5$), 8.01-8.03 (m, 2H, N^3-$CH_2COC_6H_5$) ppm. ^{13}C NMR(400 MHz, $CDCl_3$): δ = 12.94 (CH_3), 36.65 (CH_3), 47.18 (CH_2), 109.69 (C), 128.12 (2 CH), 128.76 (2 CH), 133.72 (CH), 135.04 (C), 139.73 (CH), 151.55 (C=O), 163.52 (C=O), 192.06 (C=O) ppm.

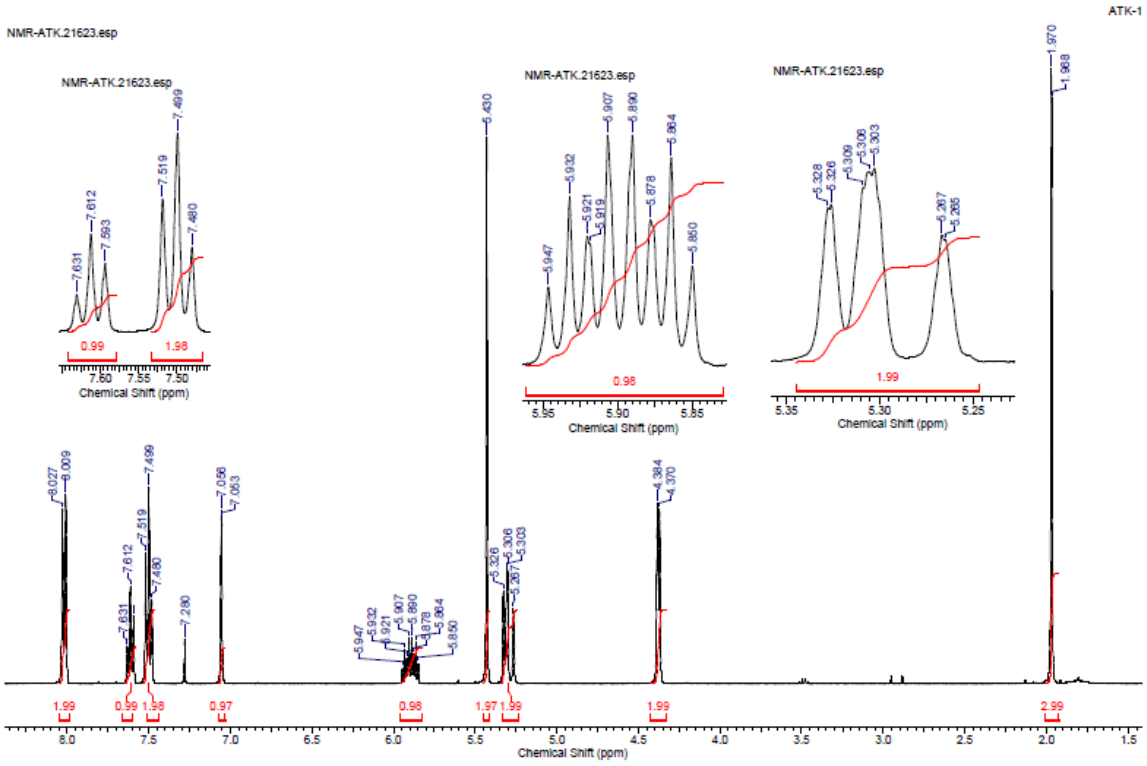
1-Allyl-3-(2-hydroxy-2-phenylethyl)-5-methylpyrimidine-2,4-(1*H*,3*H*)-dione (**1a**) Isolated yield: 49%. HPLC (Lux® 5µ Cellulose-3, LC Column 250x4.6 mm; *n*-hexane/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}); retention time: (*S*)-**1a** 14.3 min, (*R*)-**1a** 15.4 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (d, *J*=1.2 Hz, 3H, C^5-CH_3), 4.10 (m, 1H, OH), 4.29-4.33 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$), 4.39–4.40 (m, 2H, CH_2=CHCH_2), 5.04-5.07 (dd, *J*=8.4 3.6, 1H, N^3-$CH_2CH(OH)C_6H_5$), 5.25-5.29 (ddd, *J*=17.2 2.8 2.4 1.2 Hz, 1H, CH_AH_B=CHCH_2), 5.31-5.35 (ddd, *J*=10.4 2.4 1.2 Hz, 1H, CH_AH_B=CHCH_2), 5.84–5.94 (m, 1H, CH_2=CHCH_2), 7.01 (q, *J*=1.2 Hz, 1H, C^6-H), 7.28–7.32 (m, 1H, N^3-$CH_2CH(OH)C_6H_5$), 7.36–7.40 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$), 7.49–7.51 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13.00 (CH_3), 49.51 (CH_2), 51.09 (CH_2), 73.60 (CH), 110.45 (C), 119.37 (CH_2), 125.77 (2 CH), 127.71 (CH), 128.44 (2 CH), 131.60 (CH), 138.27 (C), 141.92 (CH), 152.31 (C=O), 164.85 (C=O) ppm.

1-Ethyl-3-(2-hydroxy-2-phenylethyl)-5-methylpyrimidine-2,4-(1*H*,3*H*)-dione (**2a**) Isolated yield: 42%. HPLC (Lux® 5µ Cellulose-3, LC Column 250x4.6 mm; *n*-hexane/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}); retention time: (*S*)-**2a** 14.4 min, (*R*)-**2a** 15.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (dd, *J*=7.2 8.0 Hz, 3H, N^1-CH_2CH_3), 1.98 (d, *J*=1.2 Hz, 3H, C^5-CH_3), 3.78–3.84 (dq, *J*=7.2 2.0 Hz, 2H, N^1-CH_2CH_3),

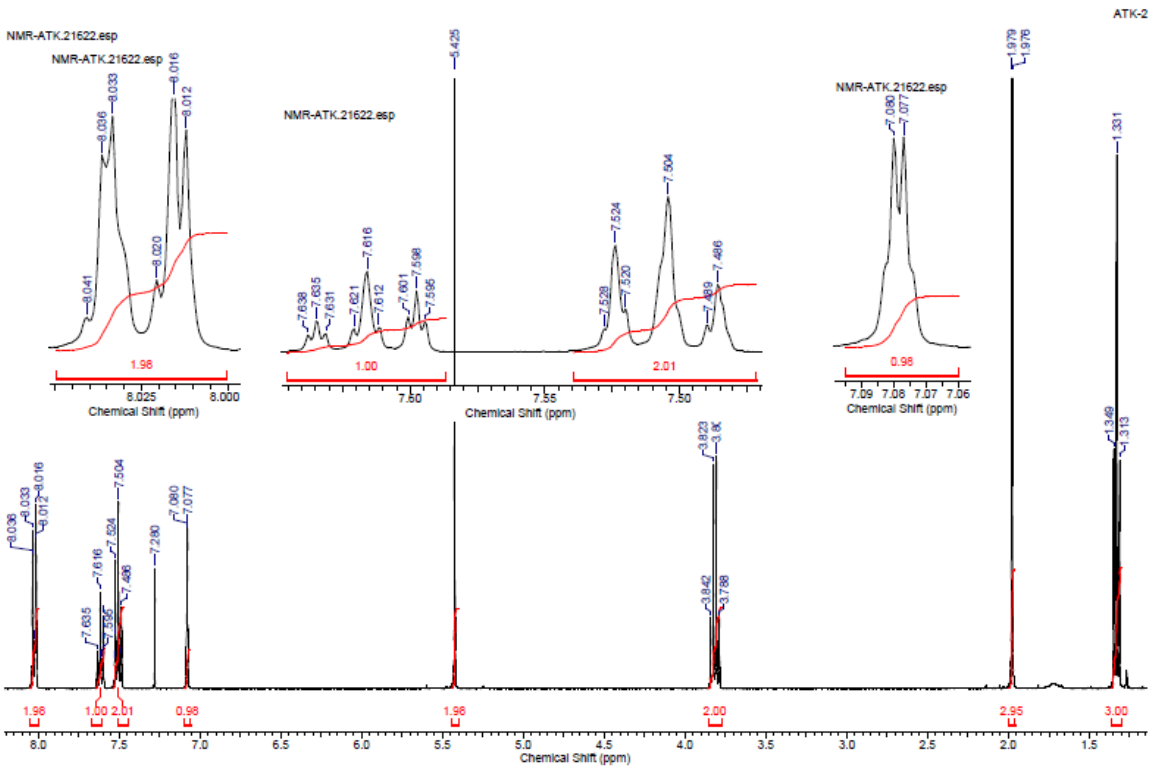
4.30 (m, 1H, OH), 4.27–4.35 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$), 5.03-5.06 (dd, *J* = 7.2 4.8 Hz, 1H, N^3-$CH_2CH(OH)C_6H_5$), 7.03 (q, *J*=1.2 Hz, 1H, C^6-H), 7.28–7.32 (m, 1H, N^3-$CH_2CH(OH)C_6H_5$), 7.36-7.41 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$), 7.49-7.52 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$) ppm. ^{13}C NMR(400 MHz, $CDCl_3$): δ = 12.99 (CH_3), 14.29 (CH_3), 44.86 (CH_2), 49.46 (CH_2), 73.65 (CH), 110.27 (C), 125.76 (2 CH), 128.12 (CH), 128.42 (2 CH), 138.59 (C), 141.98 (CH), 152.15 (C=O), 163.40 (C=O) ppm.

3-(2-Hydroxy-2-phenylethyl)-1,5-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (**3a**) Isolated yield: 34% HPLC (Lux® 5µ Cellulose-3, LC Column 250x4.6 mm; *n*-hexane/propan-2-ol, 60:40 (v/v); flow rate 0.5 mL min^{-1}); retention time: (*S*)-**3a** 16.4 min, (*R*)-**3a** 17.7 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (d, *J*=1.2 Hz, 3H, C^5-CH_3), 3.40 (s, 3H, N^1-CH_3), 3.77 (s, 1H, OH), 4.25–4.34 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$), 5.02-5.05 (dd, *J*=8.0 4.0 Hz, 1H, N^3- $CH_2CH(OH)$ C_6H_5), 7.03 (d, *J*=1.2 Hz, 1H, C^6-H), 7.28–7.32 (m, 1H, N^3-$CH_2CH(OH)C_6H_5$), 7.37–7.41 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$), 7.49–7.52 (m, 2H, N^3-$CH_2CH(OH)C_6H_5$) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12.93 (CH_3), 36.82 (CH_3), 49.48 (CH_2), 73.61 (CH), 110.11 (C), 125.76 (2 CH), 127.71 (CH), 128.45 (2 CH), 139.68 (C), 141.99 (CH), 152.67 (C=O), 164.97 (C=O) ppm.

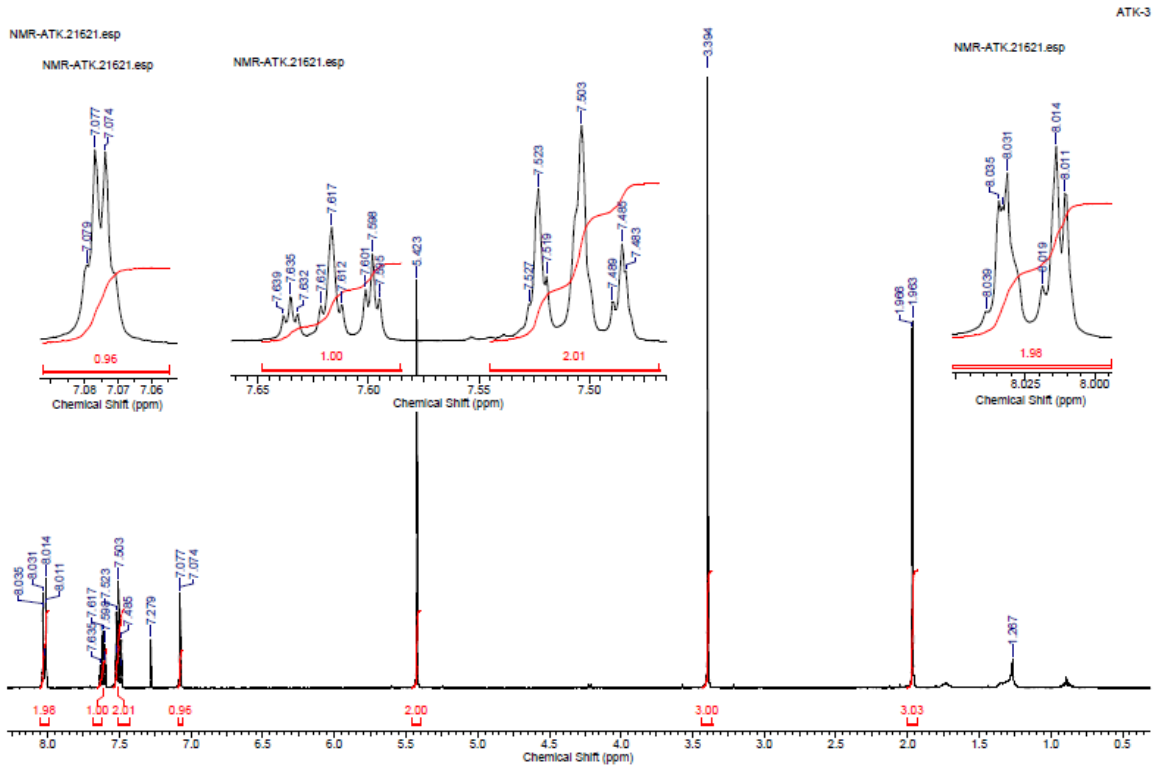
^{1}H NMR Spectra



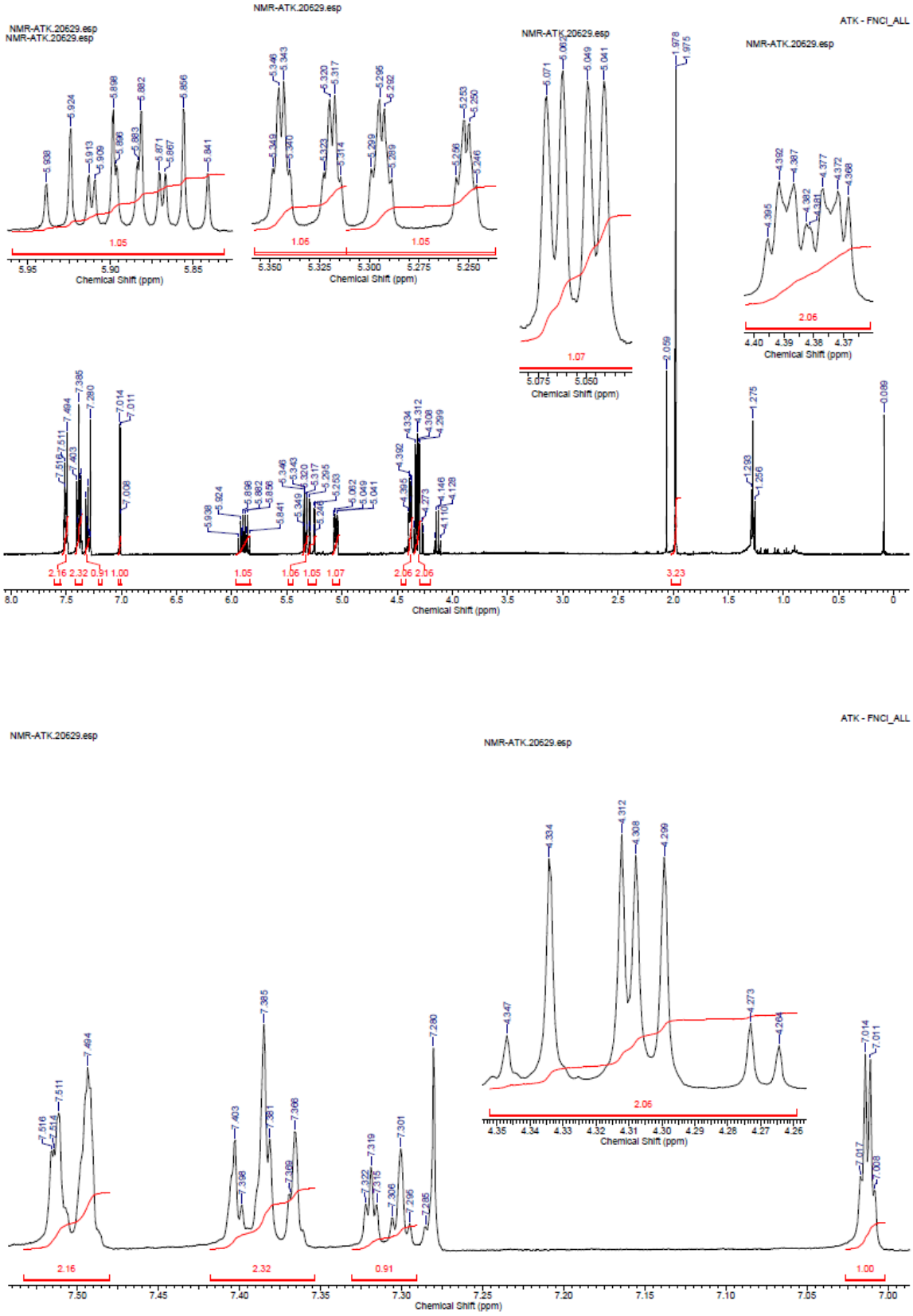
Supplemental Figure 1. ^{1}H NMR spectra of **1**.



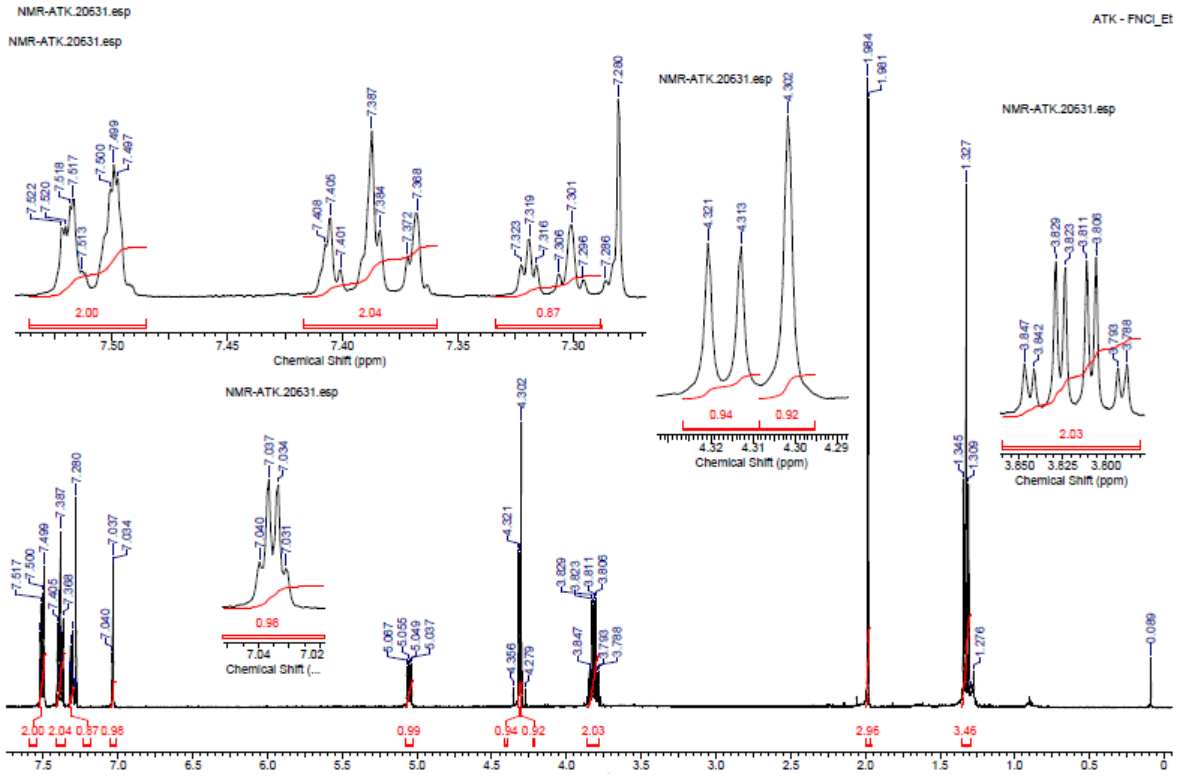
Supplemental Figure 2. ^{1}H NMR spectra of **2**.



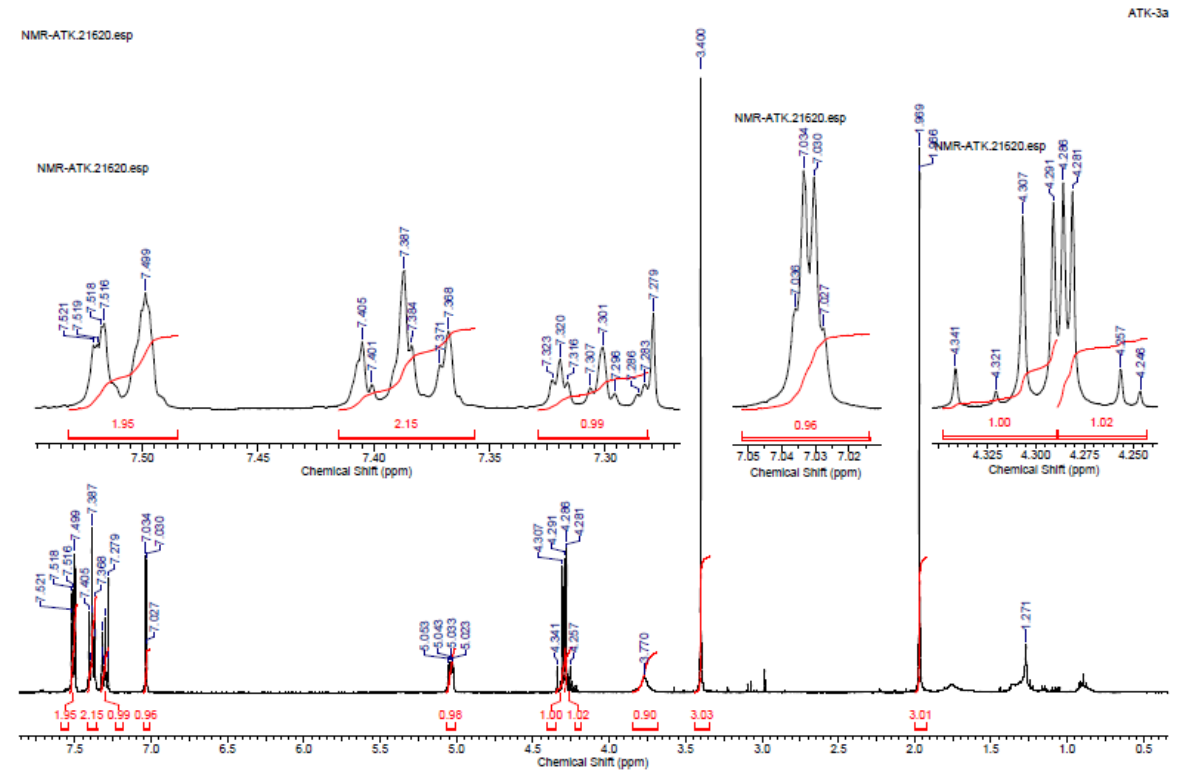
Supplemental Figure 3. ^{1}H NMR spectra of **3**.



Supplemental Figure 4. ^{1}H NMR spectra of **1a**.

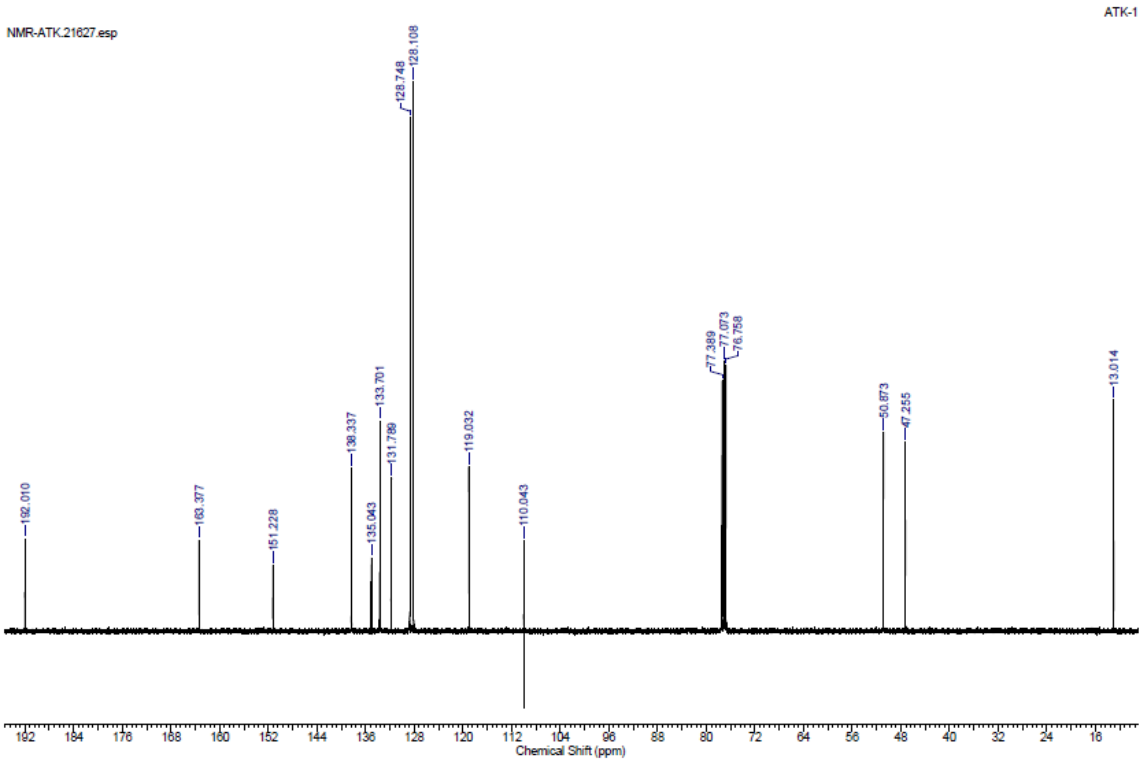


Supplemental Figure 5. ^{1}H NMR spectra of **2a**.

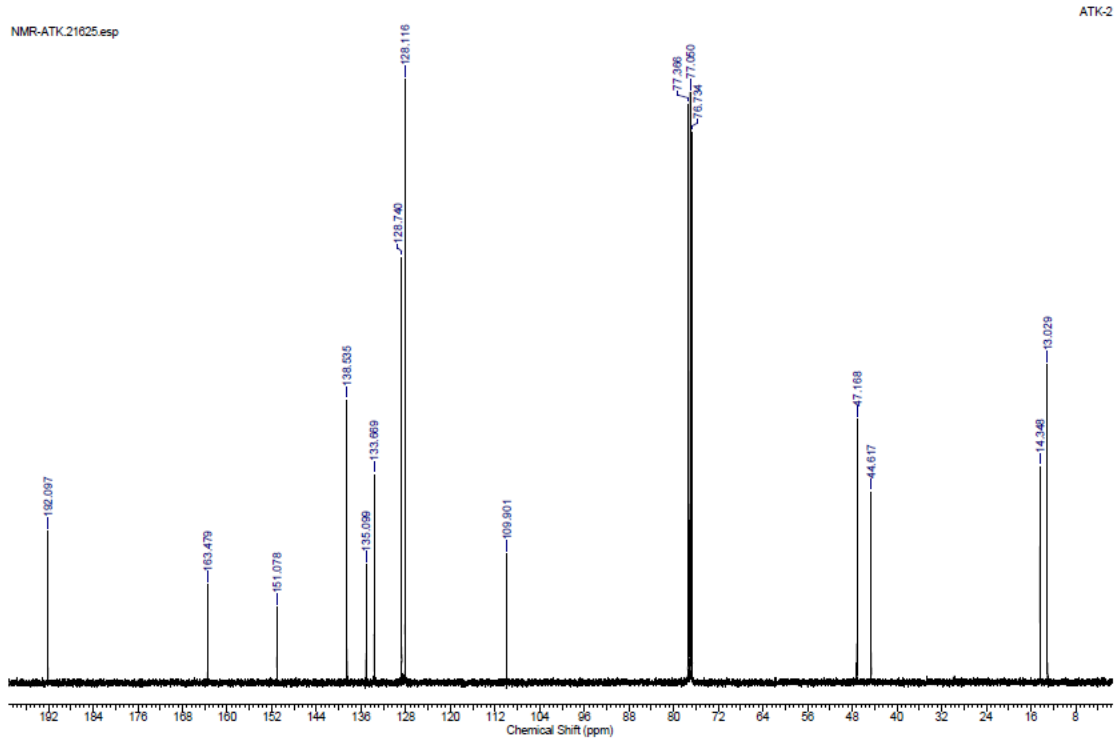


Supplemental Figure 6. ^{1}H NMR spectra of **3a**.

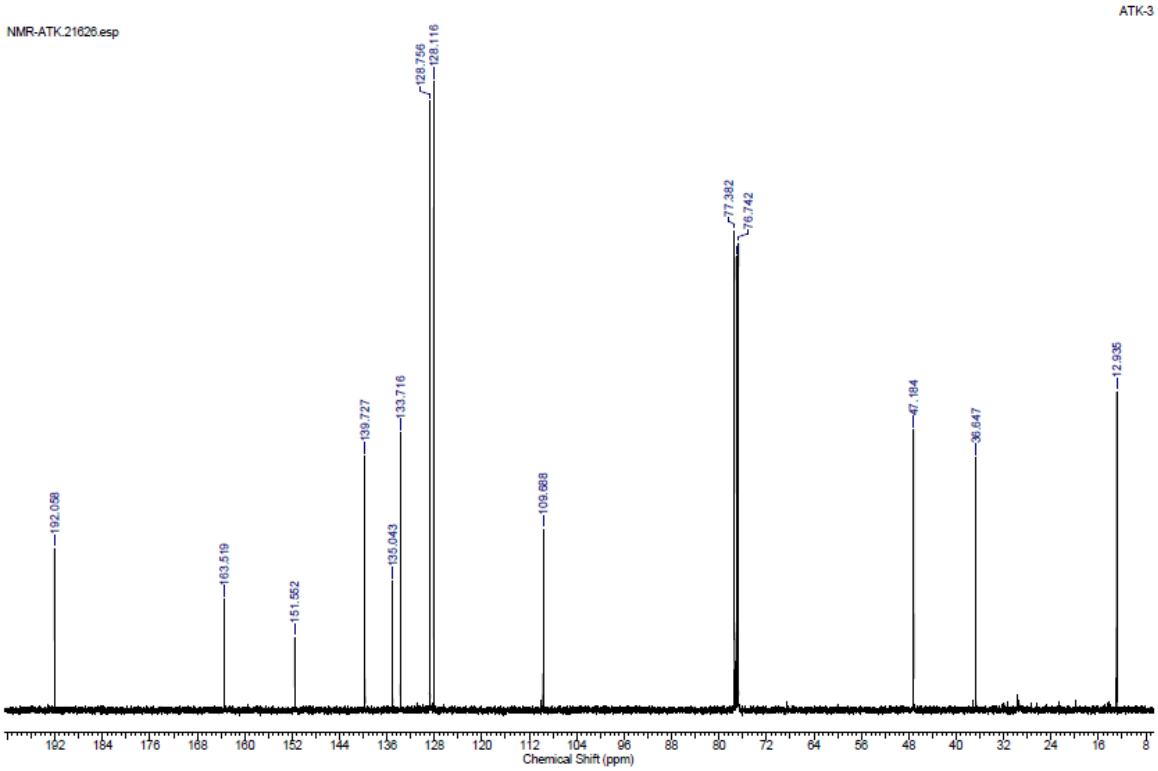
^{13}C NMR Spectra



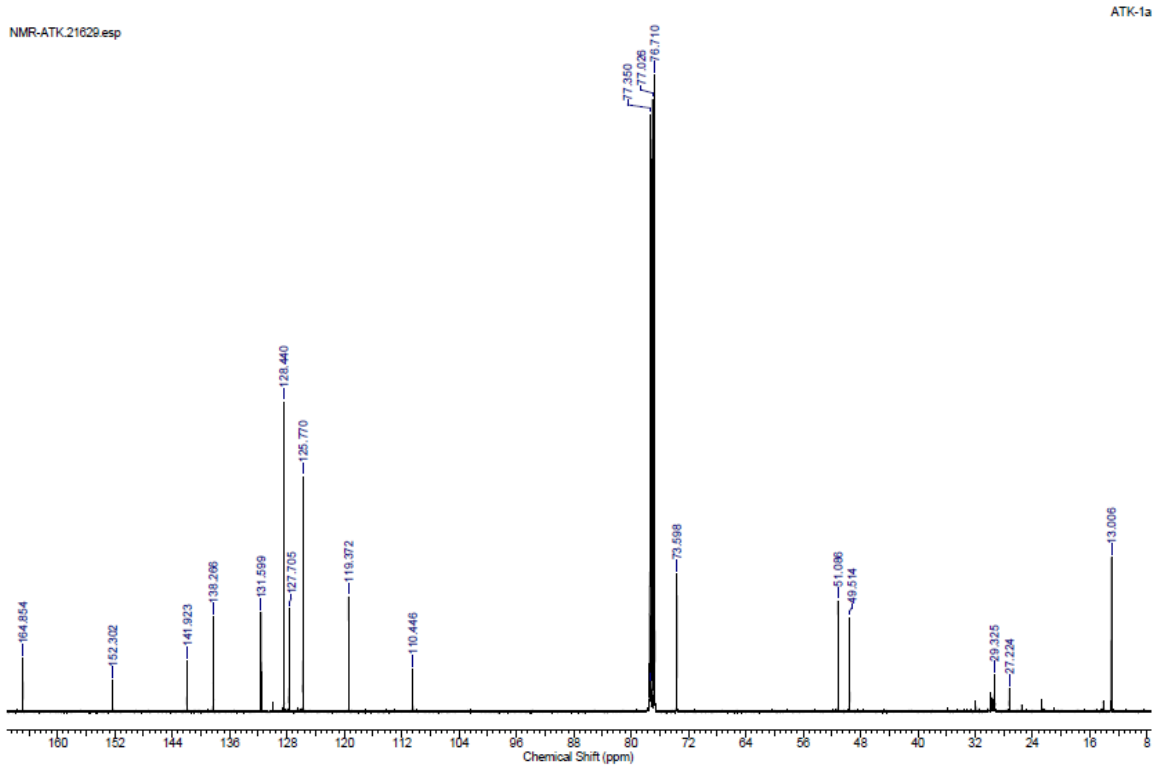
Supplemental Figure 7. ^{13}C NMR spectra of **1**.



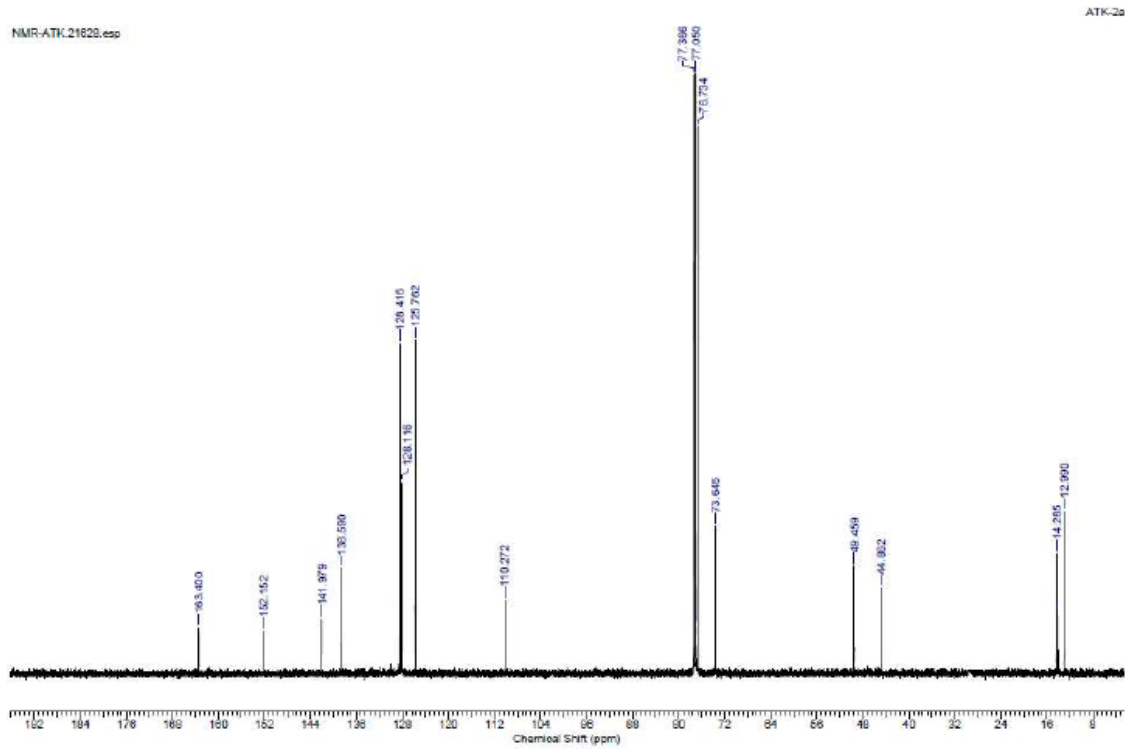
Supplemental Figure 8. ^{13}C NMR spectra of **2**.



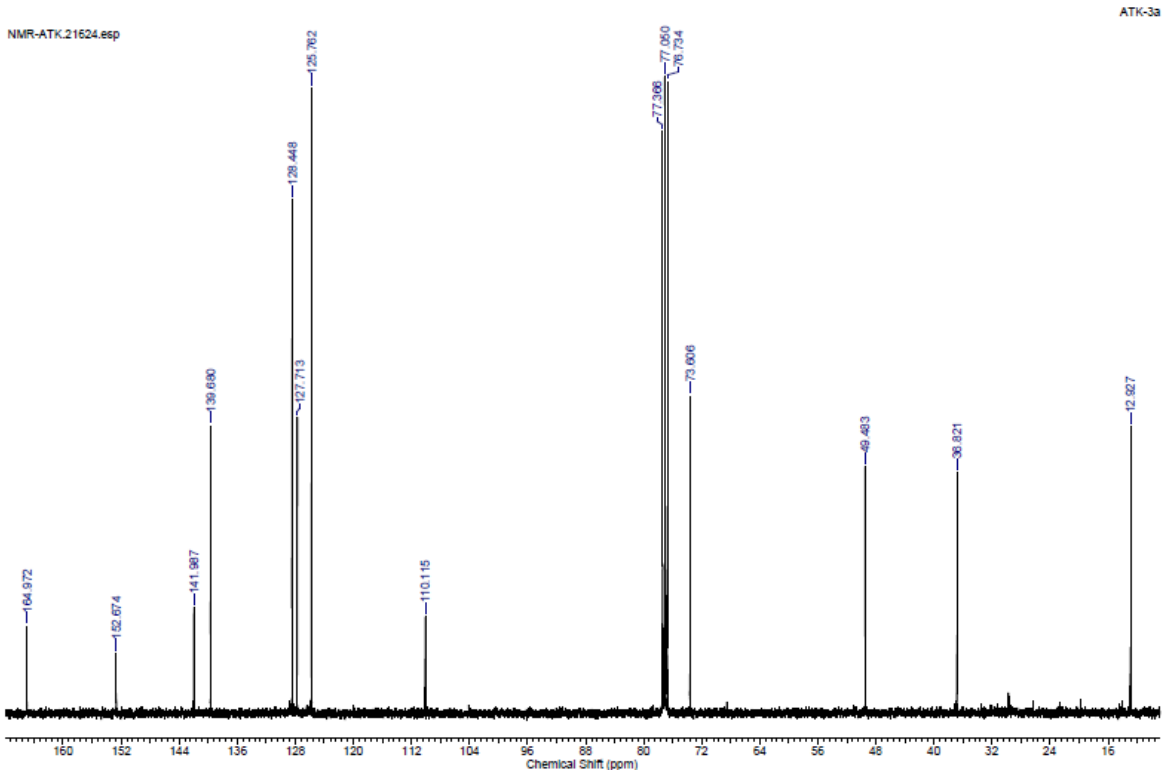
Supplemental Figure 9. ^{13}C NMR spectra of **3**.



Supplemental Figure 10. ^{13}C NMR spectra of **1a**.

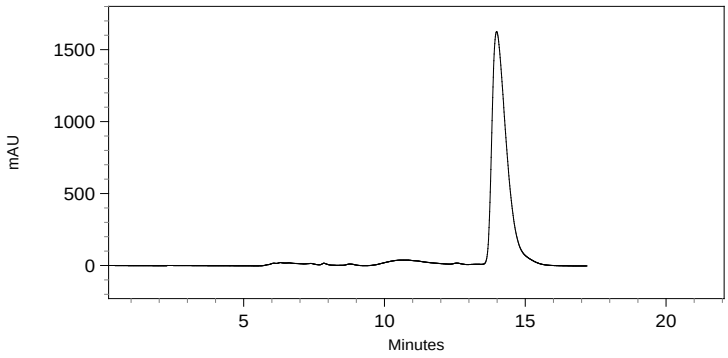


Supplemental Figure 11. ^{13}C NMR spectra of **2a**.

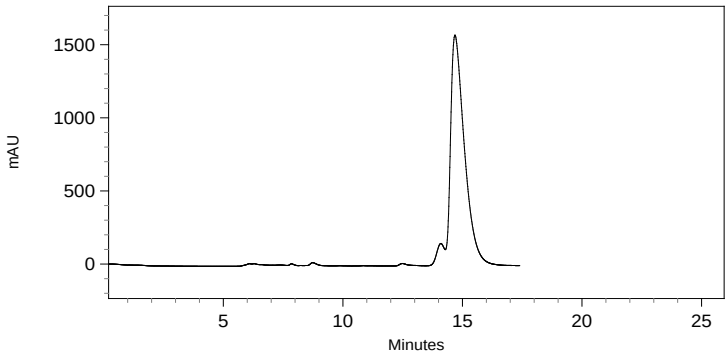


Supplemental Figure 12. ^{13}C NMR spectra of **3a**.

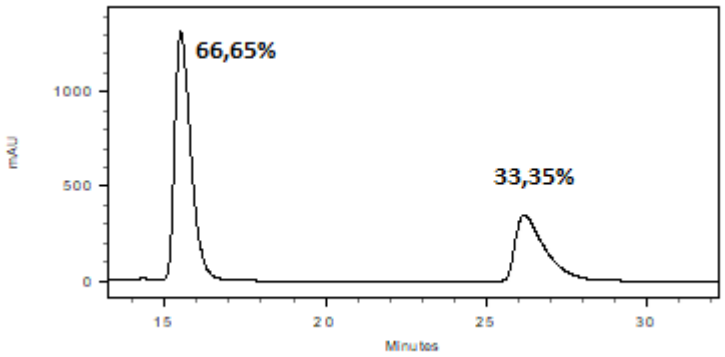
HPLC Spectra



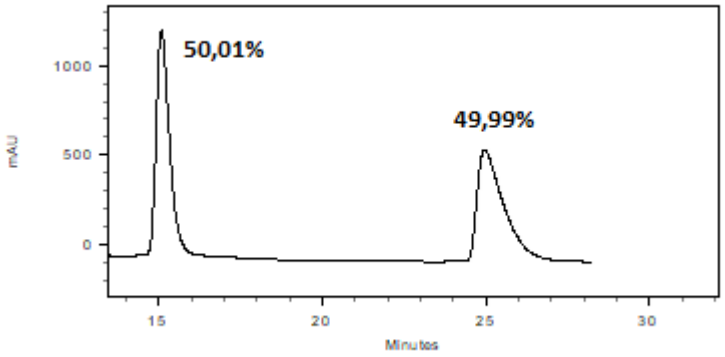
Supplemental Figure 13. (*S*)-**1a** (99% ee).



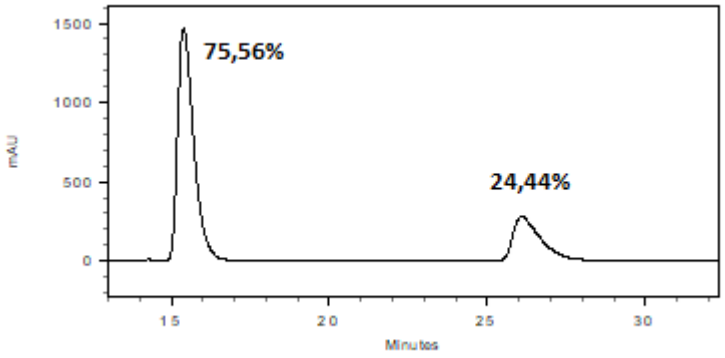
Supplemental Figure 14. (*R*)-**1a** (96% ee).



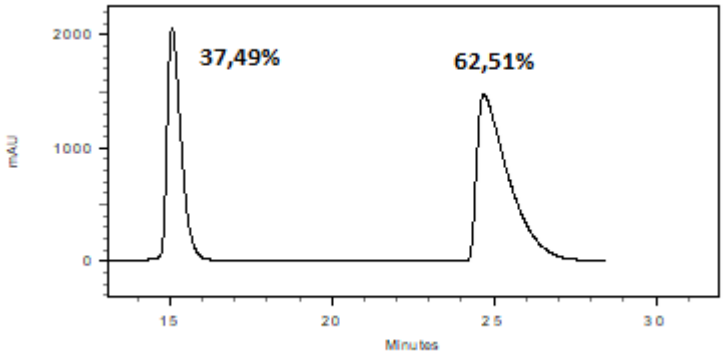
Supplemental Figure 15. Reduction of **1** in phosphate buffer solution (pH = 6.5) with glucose at 30 °C.



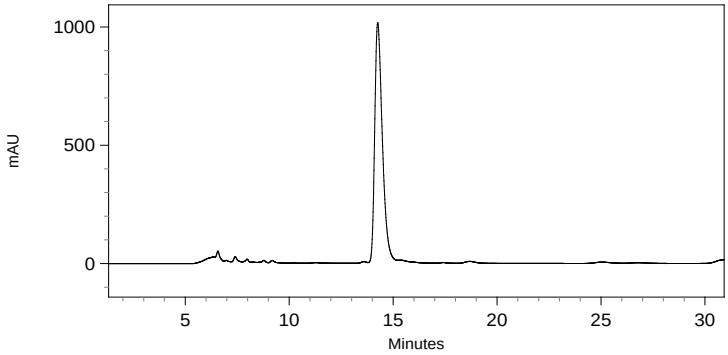
Supplemental Figure 16. Reduction of **1** in phosphate buffer solution (pH = 6.5) with glucose at 33 °C.



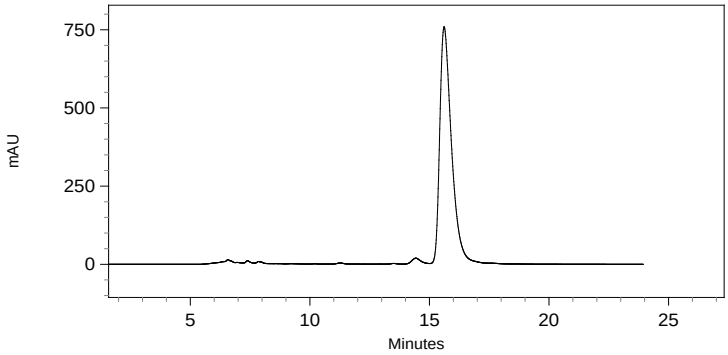
Supplemental Figure 17. Reduction of **1** in phosphate buffer solution (pH = 7.0) with sucrose at 30 °C.



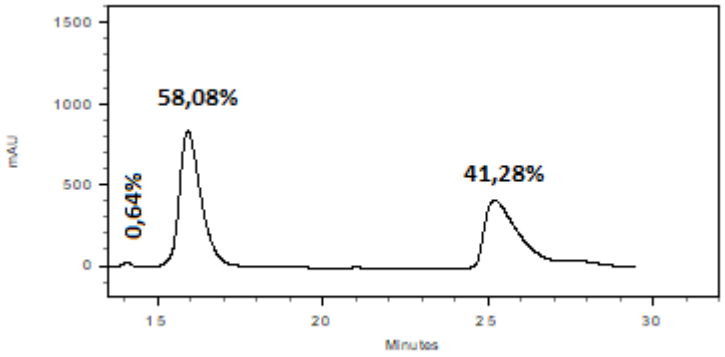
Supplemental Figure 18. Reduction of **1** in phosphate buffer solution (pH = 7.0) with sucrose at 33 °C.



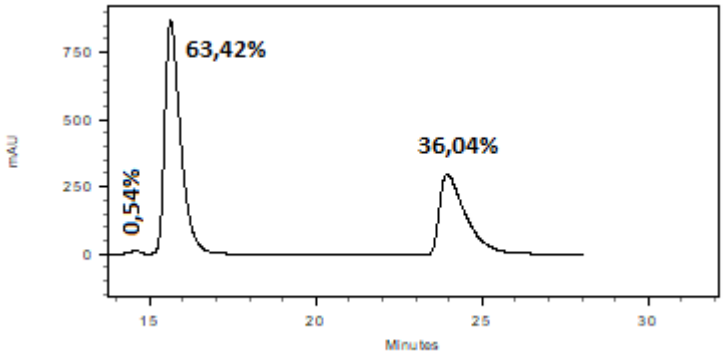
Supplemental Figure 19. (*S*)-**2a** (99% ee).



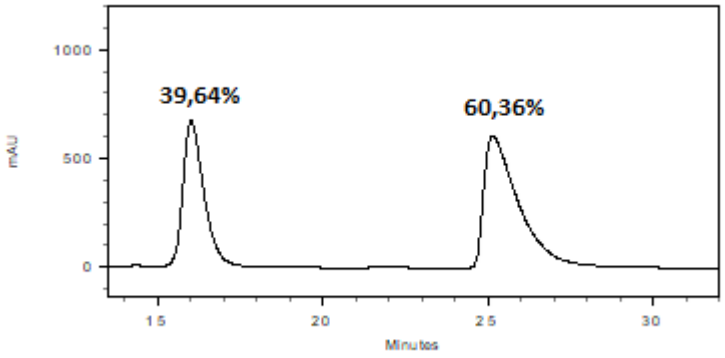
Supplemental Figure 20. (*R*)-**2a** (97% ee).



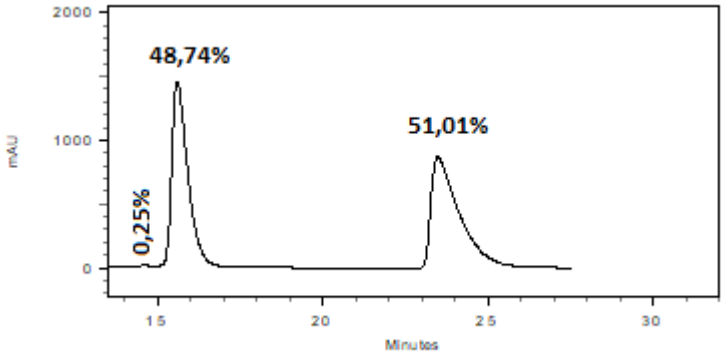
Supplemental Figure 21. Reduction of **2** in phosphate buffer solution (pH = 7.0) with glucose at 30 °C.



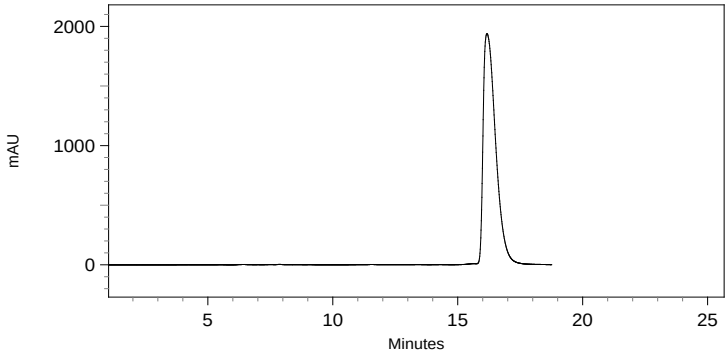
Supplemental Figure 22. Reduction of **2** in phosphate buffer solution (pH = 7.0) with glucose at 33 °C.



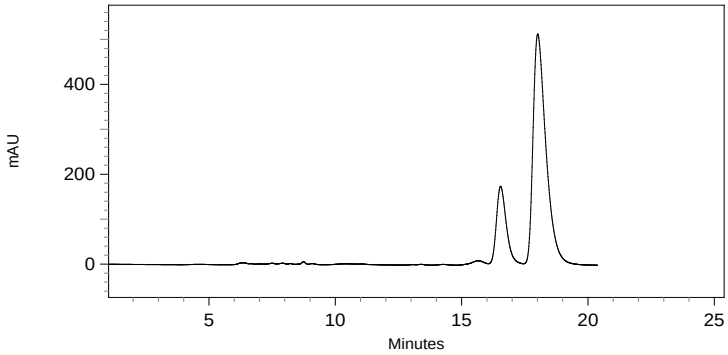
Supplemental Figure 23. Reduction of **2** in phosphate buffer solution (pH = 6.5) with glucose at 30 °C.



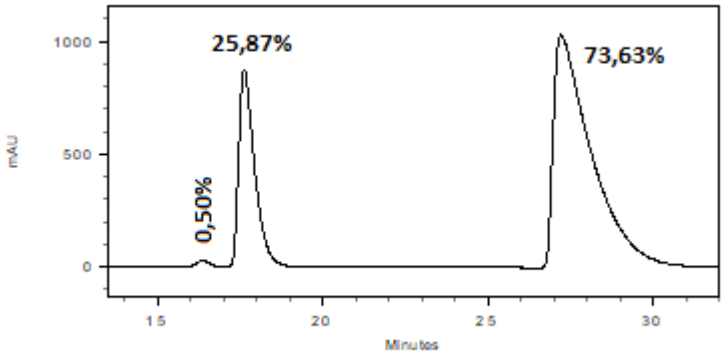
Supplemental Figure 24. Reduction of **2** in phosphate buffer solution (pH = 6.5) with glucose at 33 °C.



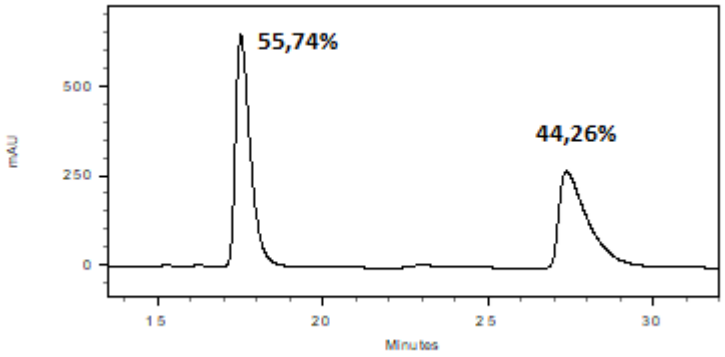
Supplemental Figure 25. (*S*)-**3a** (99% ee).



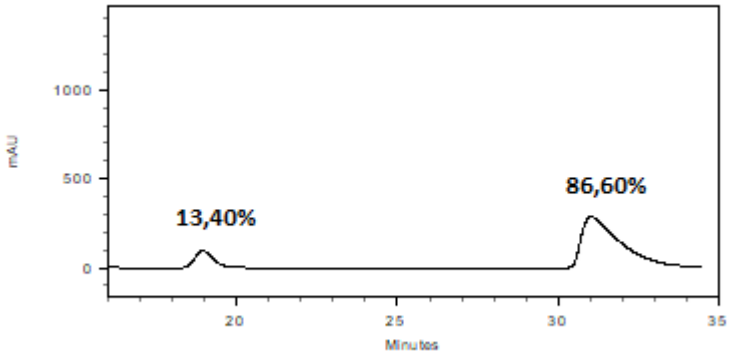
Supplemental Figure 26. (*R*)-**3a** (62% ee).



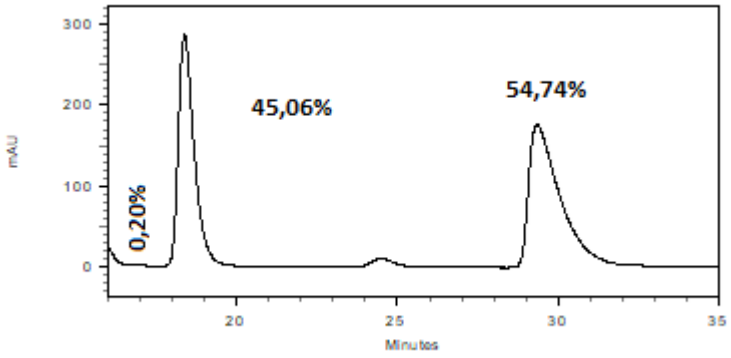
Supplemental Figure 27. Reduction of **3** in phosphate buffer solution (pH = 7.0) with glucose at 30 °C.



Supplemental Figure 28. Reduction of **3** in phosphate buffer solution (pH = 7.0) with glucose at 33 °C.



Supplemental Figure 29. Reduction of **3** in phosphate buffer solution (pH = 7.0) with sucrose at 30 °C.



Supplemental Figure 30. Reduction of **3** in phosphate buffer solution (pH = 7.0) with sucrose at 33 °C.