Supplementary Information

Palladium on layered double hydroxide: a heterogeneous system for the enol phosphate carbon-oxygen bond activation in aqueous media

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Spectroscopic data for the products

*N-acetyl-4-methoxyaniline (**2a**)*. Yellow solid, 80%. ^{1}H NMR ($CDCl_3$, 400MHz, δ ppm): 7.38 (d, *J* = 7.4 Hz, 2H), 6.83 (d, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 2.13 (s, 3H).

N-acetyl, N'-carboxybenzyl-4-methoxyaniline (**3a**). Pale yellow oil, 64%. ^{1}H NMR ($CDCl_3$, 400MHz, δ ppm): 7.38 (m, 3H), 7.19 (d, *J* = 8.7 Hz, 2H) 7.1 (d, *J* = 7.4 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.22 (d, 2H), 3.81 (s, 3H), 2.63 (s, 3H).

N-acetyl, N'-carboxybenzyl-2-bromoaniline (**3b**). Pale yellow oil, 45%. ^{1}H NMR ($CDCl_3$, 400MHz, δ ppm): 7.66 (d, *J* = 7.9 Hz, 1H), 7.4 – 7.19 (m, 8H), 2.68 (s, 3H).

N-acetyl, N'-tert-butyloxycarbonyl-2-bromoaniline (**3c**). Pale yellow solid, 88%. ^{1}H NMR ($CDCl_3$, 400MHz, δ ppm): 7.62 (d, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 7.8 Hz, *J* = 7.5 Hz, 1H), 7.28 – 7.13 (m, 3H), 2.63 (s, 3H), 1.38 (s, 9H).

Enol phosphate **4a**. Pale yellow oil, 72%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.35–7.06 (m, 9H), 6.80 (d, *J* = 12.1 Hz, 2H), 5.26 (s, 1H), 5.15 (s, 2H), 4.89 (dd, *J* = 3.0 Hz, *J* = 2.0 Hz, 1H), 3.79–3.76 (s, 3H).

Enol phosphate **4c**. Pale yellow solid, 78%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.58 (d, *J* = 7.6 Hz, 1H), 7.39–7.1 (m, 13H), 5.11 (s, 1H), 4.99 (d, *J* = 2.0 Hz, 1H), 1.43 (s, 3H).

Product **6a**. Pale yellow oil, 72%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.29 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 2H), 7.4 – 7.05 (m, 8H), 6.89 (d, *J* = 7.0 Hz, 2H), 5.31 (d, 2H), 5.19 (s, 2H), 5.15 (d, *J* = 3.0 Hz, 1H), 3.8 (s, 3H).

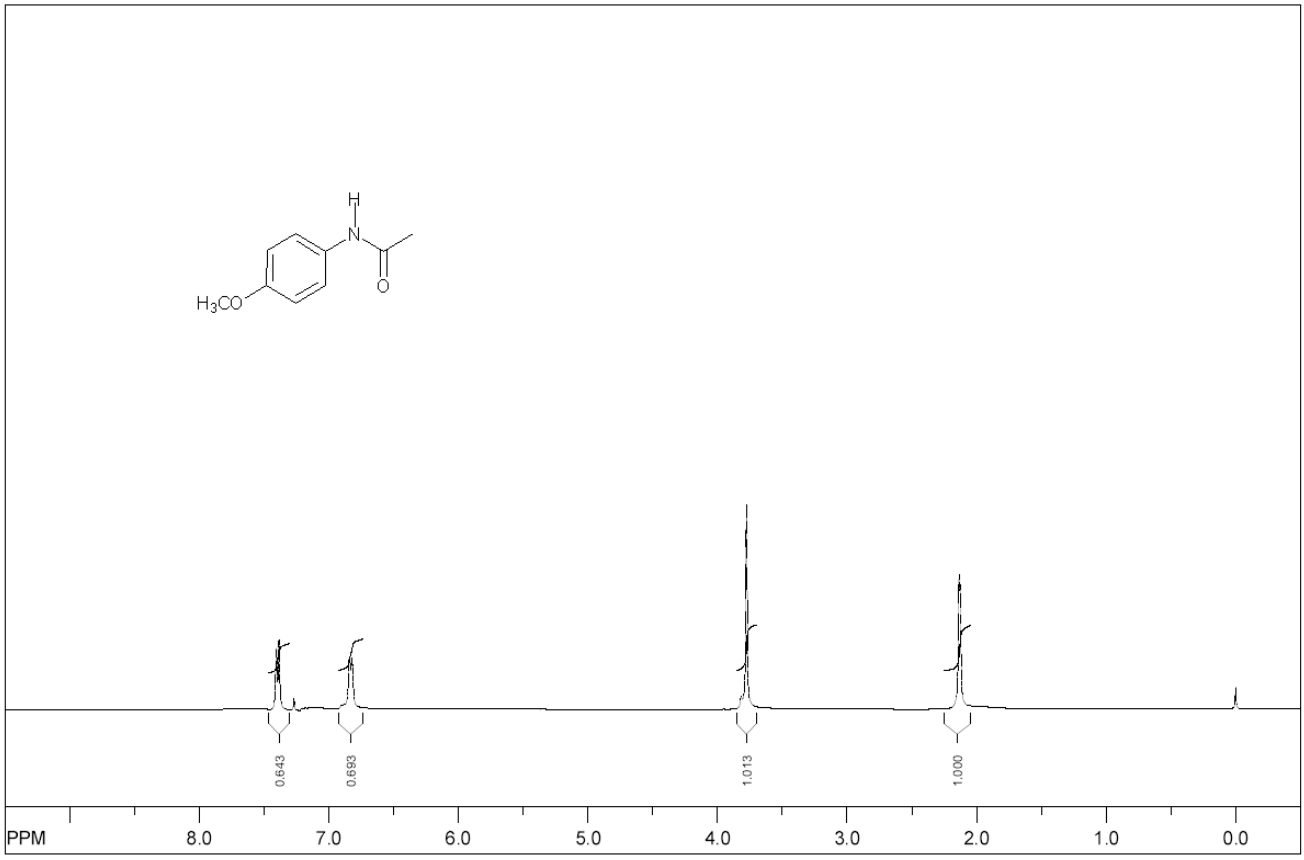
Product **8**. Pale yellow solid, 64%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.2 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.20 (m, 8H), 6.56 (s, 1H), 1.55 (s, 9H).

References

[1] H. Fuwa; M. Sasaki, "Synthesis of 2-Substituted Indoles and Indolines via Suzuki-Miyaura Coupling/5-endo-trig Cyclization Strategies", The Journal of Organic Chemistry, vol. 74, pp. 212–221, 2009.

[2] A. B. C. Simas, D. L. Sales, K. C. Pais, "Acyclic ketene aminal phosphates derived from N,N-diprotected acetamides: stability and cross-couplings", Tetrahedron Letters, vol. 50, pp. 6977–6980, 2009.

*N-acetyl-4-methoxyaniline (**2a**)*



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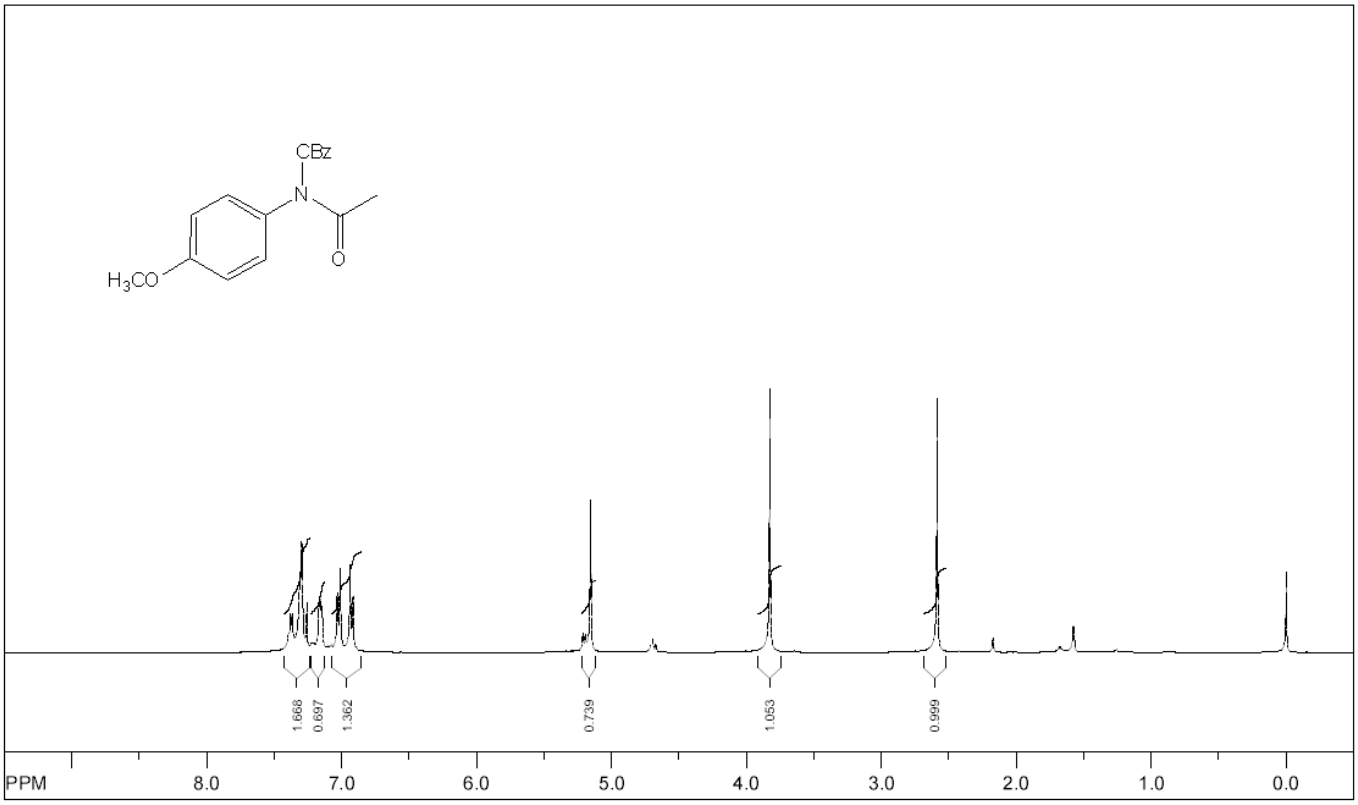
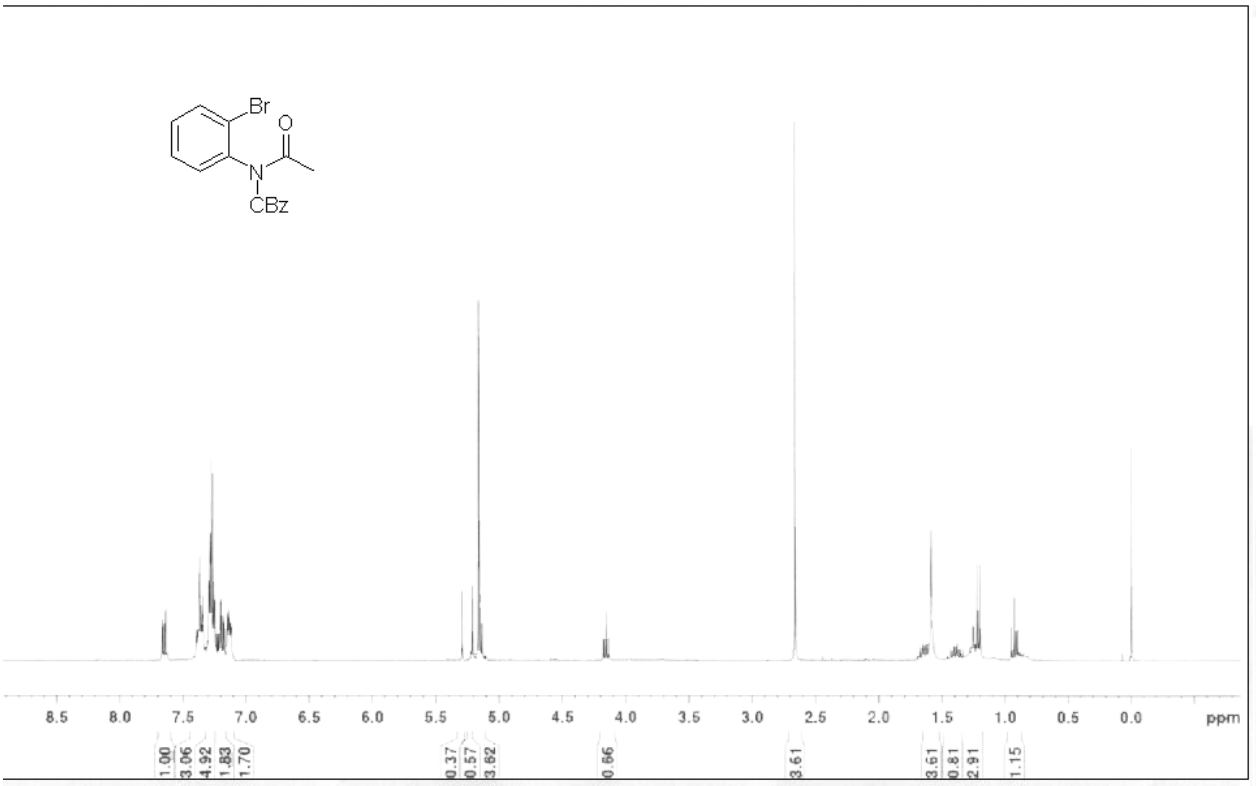
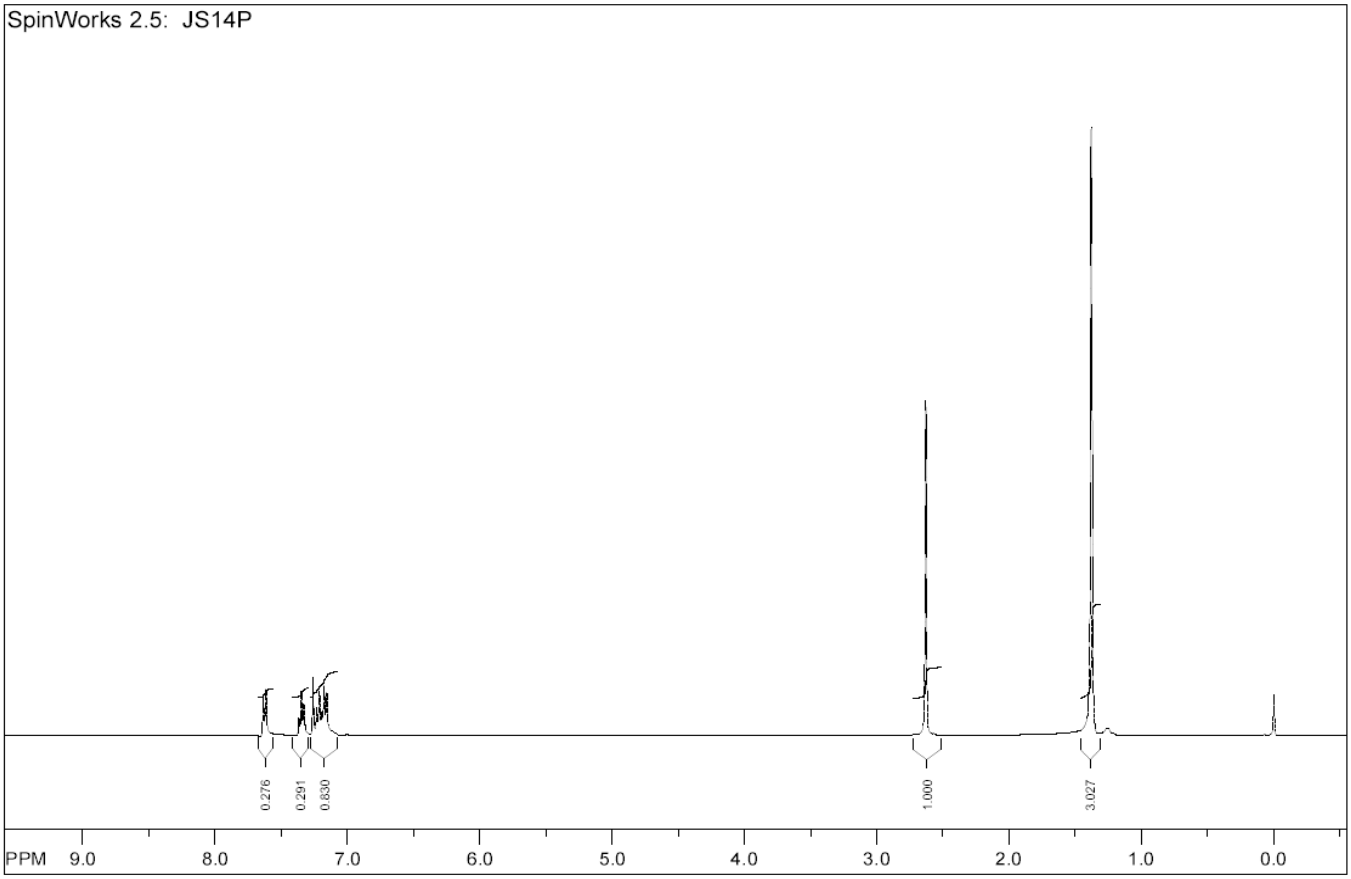


N-acetyl, N'-carboxybenzyl-2-bromoaniline (**3b**)



N-acetyl, N'-tert-butyloxycarbonyl-2-bromoaniline (**3c**)



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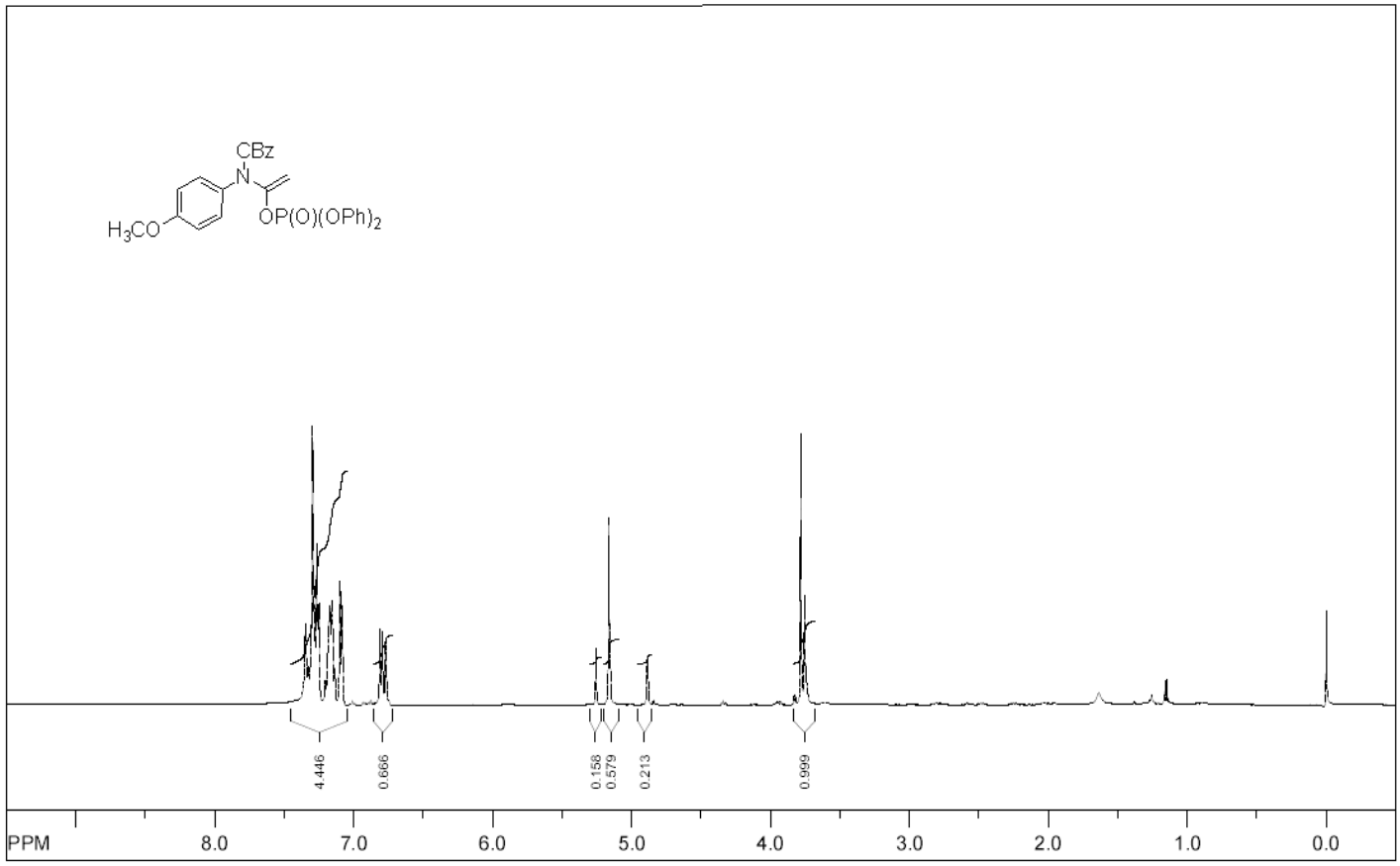
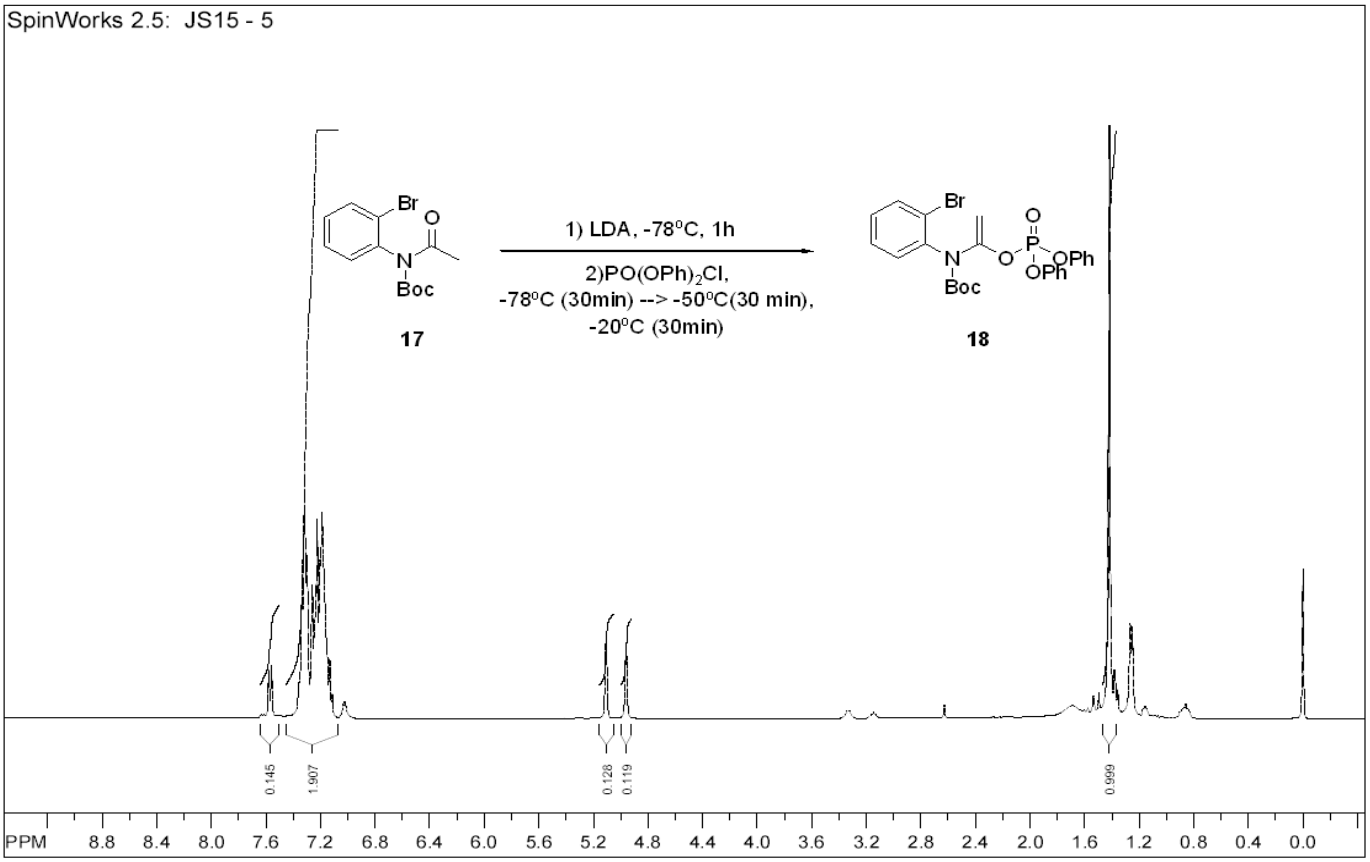
Enol phosphate **4a**



Enol phosphate **4c**



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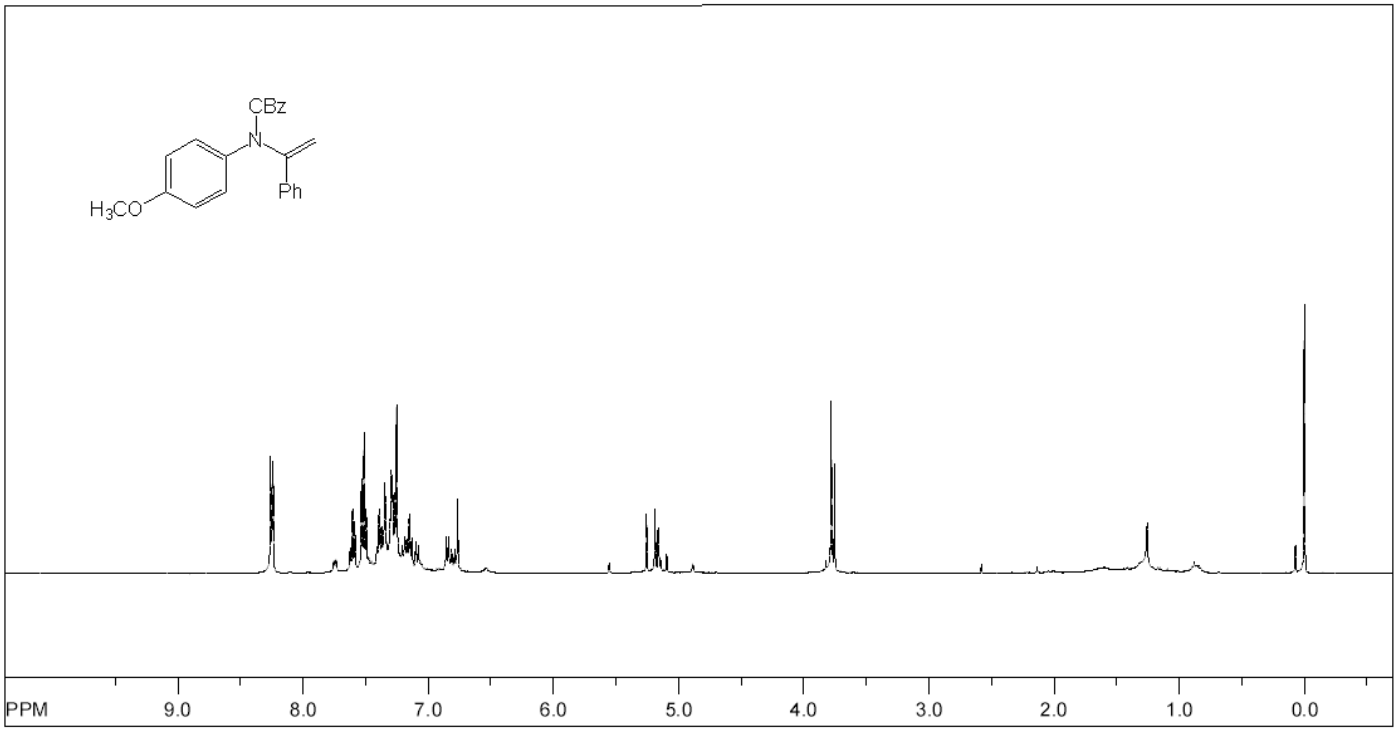
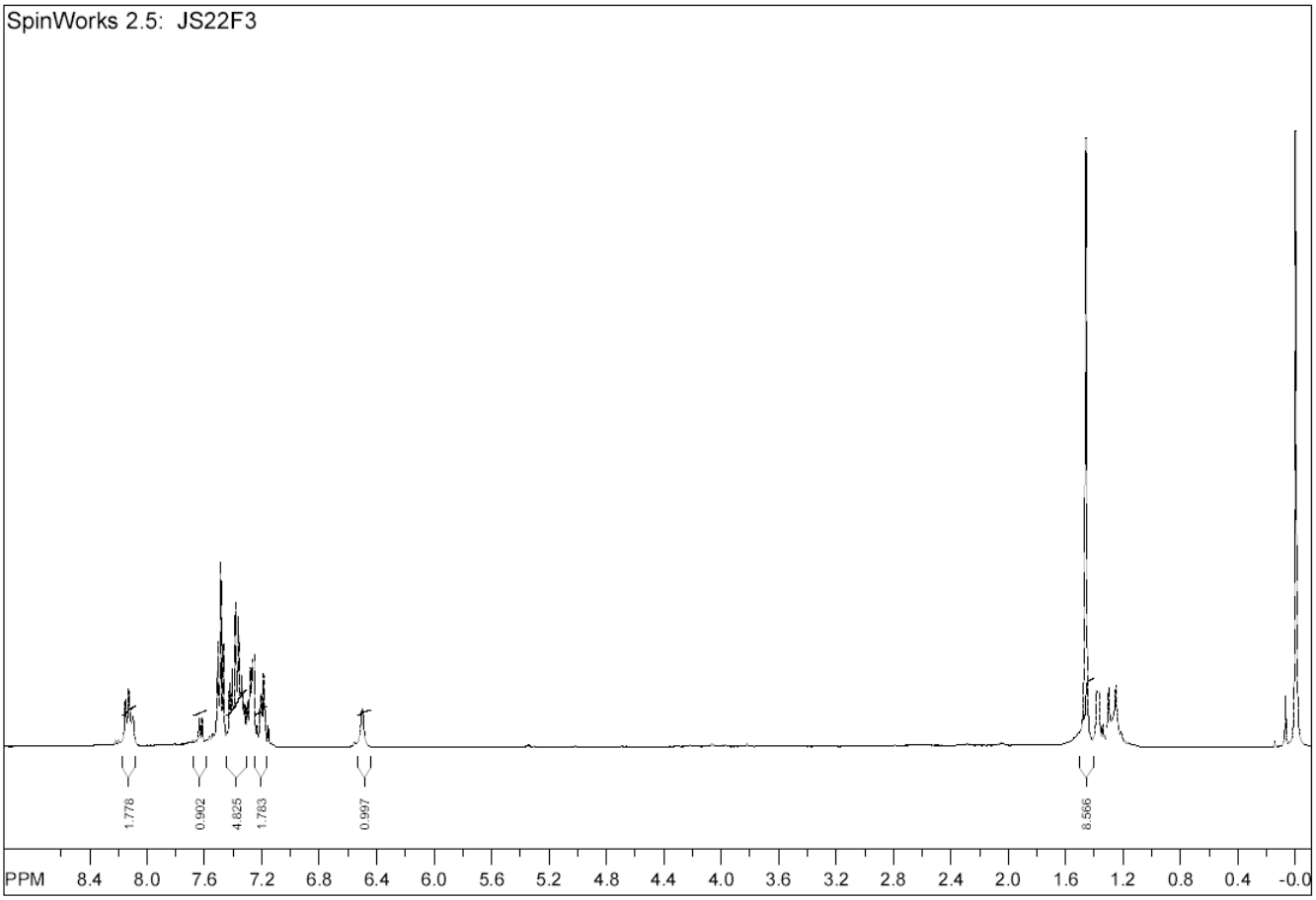
Product 6a



Product 8



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time domain size: 32768 points LB: 0.000 GB: 0.0000
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number of scans: 256