Supporting Information

An NMR Study on a Pseudo-Intramolecular Transacylation of α-Aryl-β-keto Ester

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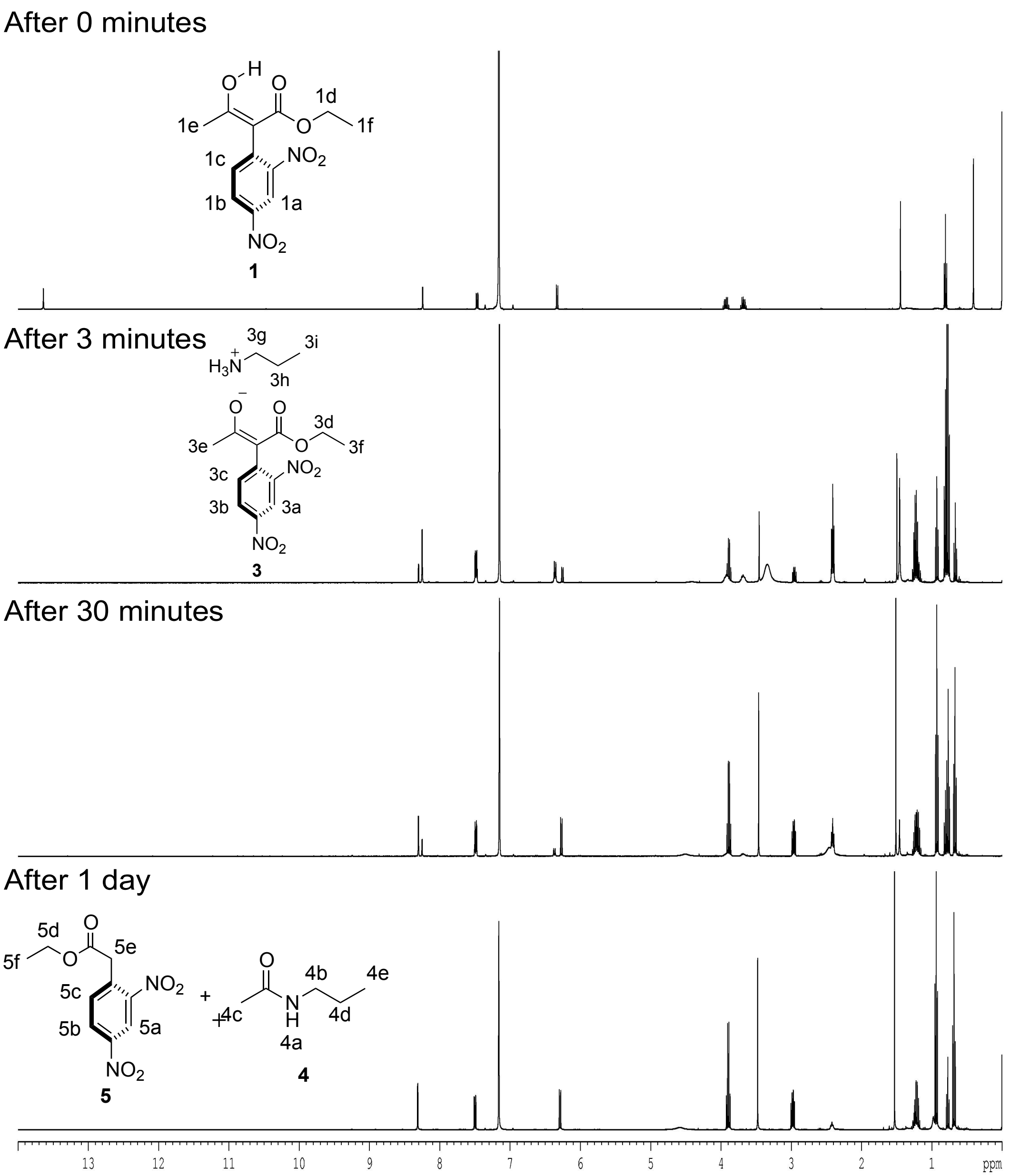
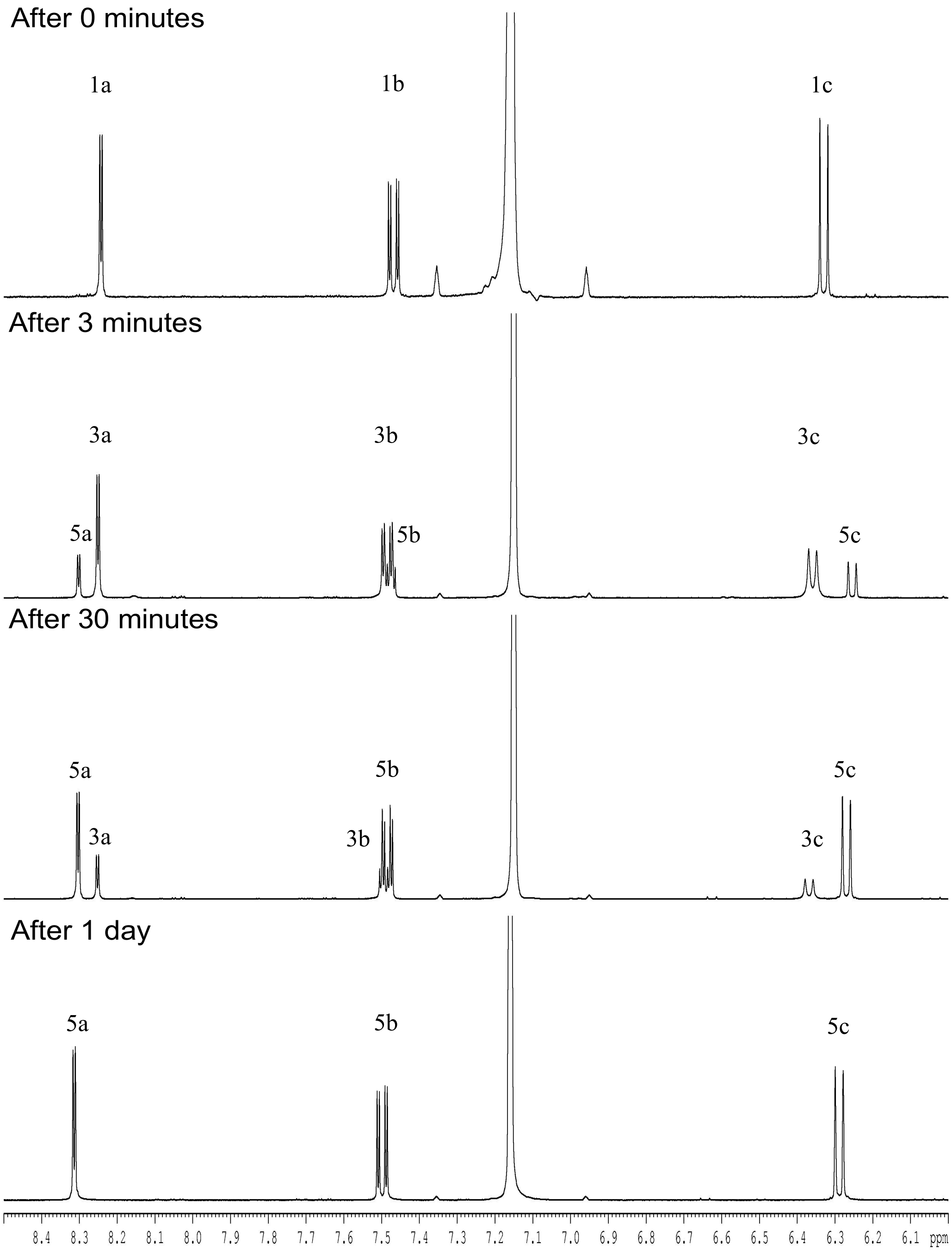
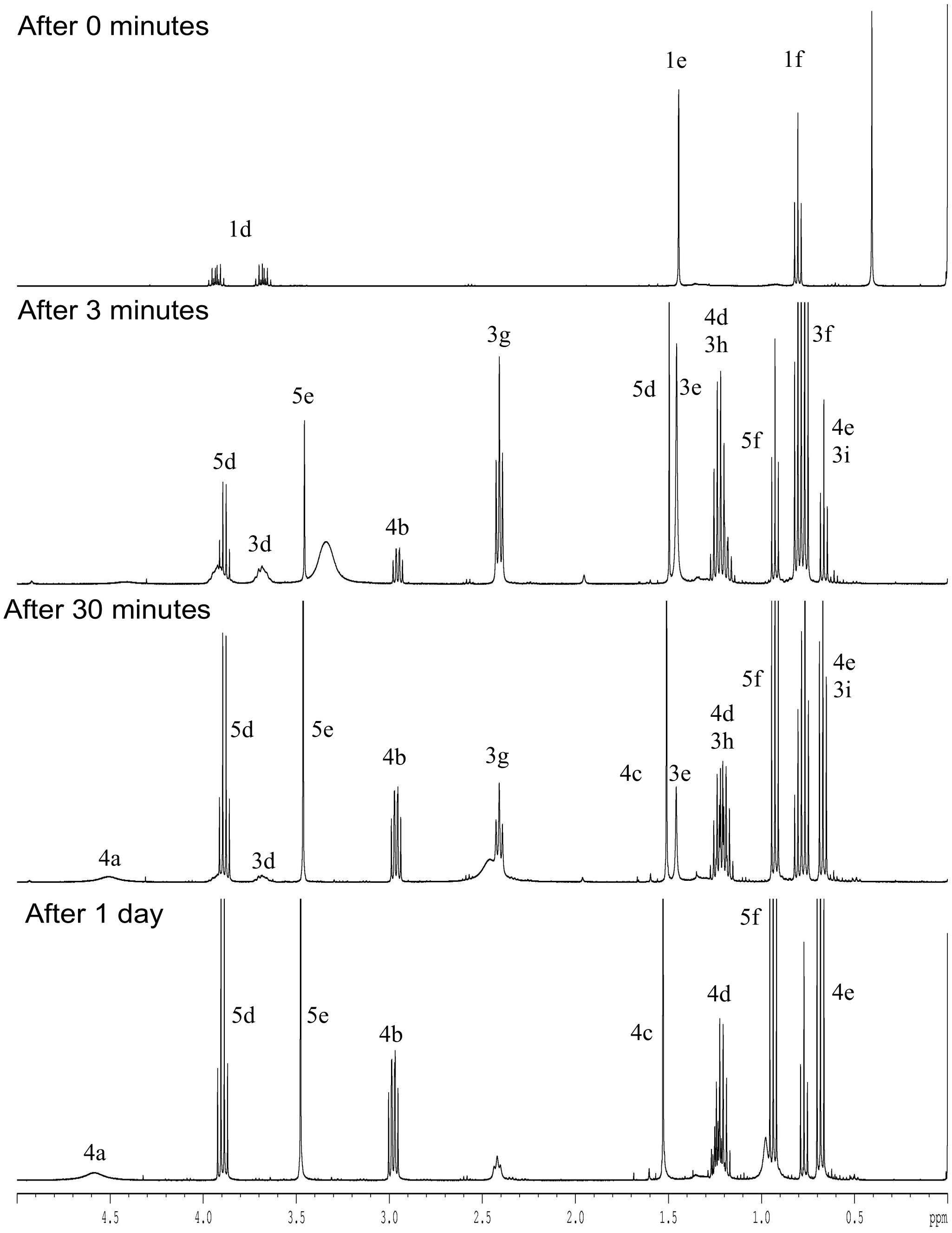
1. General

All the reagents and solvents were purchased from Wako Pure Chemicals and used as received. The ^{1}H spectra were measured on a Bruker Ascend-400 at 400 MHz with TMS as an internal standard.

2. Monitoring the transacylation from 1 to 2 by ^{1}H NMR by using benzene-d_6 as a solvent (0.06 M)




After 0 minutes
1a
1b
1c
After 3 minutes
3a
5a
3b
5b
3c
5c
After 30 minutes
5a
3a
5b
3b
5c
3c
After 1 day
5a
5b
5c
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
ppm


After 0 minutes
1d
1e
1f
After 3 minutes
5d
3d
5e
4b
3g
5d
3e
4d
3h
5f
3f
4e
3i
After 30 minutes
4a
5d
3d
5e
4b
3g
4c
3e
4d
3h
5f
4e
3i
After 1 day
4a
5d
5e
4b
4c
4d
5f
4e
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

3. Experimental procedure with results from NMR analysis for starting keto ester 1 and transacylated products 4 and 5

Ethyl 2-(2,4-dinitrophenyl)-3-hydroxy-2-butenoate (1)

To a solution of ethyl 3-oxobutanoate (1.30 g, 10 mmol) in THF (10 mL), sodium hydride (60 wt %, 0.80 g, 20 mmol) was gradually added, and the mixture was stirred at room temperature for 15 min. Then 1-chloro-2,4-dinitrobenzene (2.02 g, 10 mmol) was added, and the resultant reddish solution was stirred for 1 day. After addition of 3 M hydrochloric acid (10 mL), generated sodium chloride was filtered off, and the filtrate was concentrated. The extraction of the residue with hot hexane (30 mL × 3) followed by concentration afforded the keto ester **1** (2.70 g, 9.1 mmol, 91%). Further purification was performed with recrystallization from hexane (mp 93-94 °C, lit.[1] 93.5-95 °C).

^{1}H NMR (400 MHz, C_6D_6)

δ 0.81 (t, 3H, *J* = 7.2 Hz), 1.45 (s, 3H), 3.68 (dq, 1H, *J* = 7.2, 18.0 Hz), 3.93 (dq, 1H, *J* = 7.2, 18.0 Hz), 6.33 (d, 1H, *J* = 8.4 Hz), 7.47 (dd, 1H, *J* = 2.4, 8.4 Hz), 8.24 (d, 1H, *J* = 2.4 Hz), 13.64 (s, 1H).

***N*-propylacetamide (4)**

^{1}H NMR (400 MHz, C_6D_6)

δ 0.68 (t, 3H, *J* = 7.2 Hz), 1.22 (tq, 2H, *J* = 7.2, 7.2 Hz), 1.53 (s, 3H), 2.98 (dt, 2H, *J* = 6.0, 7.2 Hz), 4.5-4.7 (br, 1H).

Ethyl (2,4-dinitrophenyl)acetate (5)

^{1}H NMR (400 MHz, C_6D_6)

δ 0.94 (t, 3H, *J* = 7.2 Hz), 3.48 (s, 2H), 3.90 (q, 2H, *J* = 7.2 Hz), 6.29 (d, 1H, *J* = 8.4 Hz), 7.50 (dd, 1H, *J* = 2.4, 8.4 Hz), 8.31 (d, 1H, *J* = 2.4 Hz).

Reference

1 H. J. Shine, B.-J-. Zhao, J. N. Marx, T. Ould-Ely, K. H. Whitmire, *J. Org. Chem.* **2004**, *69*, 9255–9261.

4. The reaction of propylamine with acetone in benzene-d_6