Novel carbonyl allylation mediated by $\text{SnCl}_2/\text{TiCl}_3$ in water

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Supporting information

Experimental method:

All reactions were carried out in water. TiCl_3 (15%, 1.5mL), SnCl_2 (20 mmol), allyl halide (20 mmol), water (10~20 mL) and aldehyde (18 mmol) were mixed in a flask. The mixture was stirred in room temperature for several hours. The mixture was then extracted with ether directly (3×30 mL). The combined organic layer was washed by water several times until the aqueous layer became colorless. After this operation, the organic layer which contains the crude product was dried over anhydrous MgSO_4 and the solvent was removed at low temperature. The residue was usually pure enough for NMR analyses. From the weight analyses the yield under this condition was calculated. In the cases when the residue is not sufficiently pure, flash column chromatography was used to purify it.

Spectroscopic characterization:

IR spectra were recorded on a FT/IR/410 JASCO instrument. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker DPX-300 at 300MHz. Elemental analysis was conducted using an Elementar Vario EL-III instrument.

Compound 1:

(mixed with dl and meso)

$C_8H_{14}O_2$ IR: (cm^{-1}) 3381, 1644, 1423. 1H NMR (300 MHz $CDCl_3$): δ (ppm) 5.81-5.90 (m, 2H), 5.08-5.27 (m, 4H), 3.50-3.80 (m, 2H), 2.10-2.40 (m, 4H), 1.68 (br, 2H).

^{13}C NMR (300M, $CDCl_3$): δ (ppm) 134.9, 134.5, 117.2, 73.2, 37.9, 36.1

Elemental analysis:

Found: C 67.48%, H 10.03%; Calc: C 67.57%, H 9.92%

Compound 2:

C₆H₁₂O IR: cm⁻¹ 3357, 3079, 1642. ¹H NMR (300 MHz □CDCl₃): δ(ppm) 5.78-5.88 (m, 1H), 5.15 (d, J = 12.5 Hz, 2H), 3.79 (m, 1H), 2.28 (m, 1H), 2.17 (m, 1H), 1.48 (m, 2H), 0.99 (t, J = 6.54 Hz, 3H).

¹³C NMR (300M, CDCl₃): δ(ppm) 135.0, 117.5, 72.1, 41.4, 28.8, 10.0

Elemental analysis:

Found: C 71.86%, H 11.99%; Calc: C 71.95%, H 12.08%

Compound 3:

C₅H₇Cl₃O IR: (cm⁻¹) 3417, 3081, 1644, 1089. ¹H NMR (300 MHz □ CDCl₃): δ(ppm) 5.90-6.00 (m, 1H), 5.19-5.27 (m, 2H), 4.09-4.19 (m, 1H), 2.85 (m, 1H), 2.8-2.6 (br, 1H), 2.46 (m, 1H).

C₇H₁₂O IR: (cm⁻¹) 3356, 3077, 1641, 1122. ¹H NMR (300 MHz, CDCl₃): δ(ppm) 5.81(m, 1H), 5.70-5.50 (m, 2H), 5.15 (m, 2H), 4.12 (m, 1H), 2.77 (m, 1H), 2.30 (m, 1H), 1.67 (d, J = 5.65, 2H), 1.25 (d, J=6.45, 1H).

¹³C NMR (300M, CDCl₃): δ(ppm) 136.3, 135.4, 134.5, 133.5, 117.2, 115.1, 71.6, 66.5, 41.8, 36.0, 23.2, 17.3

Elemental analysis:

Found: C 74.84%, H 10.90%; Calc: C 74.95%, H 10.78%

$C_6H_{10}O$ IR: (cm^{-1}) 3360, 3080, 1644. 1H NMR (300 MHz $\square$ $CDCl_3$): δ (ppm) 5.85 (m, 2H), 5.20(m, 4H), 4.19 (m, 1H), 2.33 (m, 2H), 1.72 (br, 1H).

^{13}C NMR (300M, $CDCl_3$): δ (ppm) 139.3, 133.4, 117.9, 115.2, 72.1, 41.0

Elemental analysis:

Found: C 73.45%, H 10.33%; Calc: C 73.43%, H 10.27%

Compound 5:

C₈H₁₆O IR: (cm⁻¹) 3356, 3078, 1641, 1138, 1027. ¹H NMR (300 MHz □ CDCl₃): 5.80-5.87 (m, 1H), 5.15 (d, J = 12.5 Hz, 2H), 3.75 (m, 1H), 2.26 (m, 1H), 2.13 (m, 1H), 1.77 (m, 2H), 1.40 (m, 1H), 1.30 (m, 1H), 0.92 (d, J = 2.7 Hz, 6H).

¹³C NMR(300M, CDCl₃): δ(ppm) 135.0, 117.5, 68.7, 45.9, 42.4, 24.5, 23.3, 22.0.

Elemental analysis:

Found: C 74.78%, H 12.70%; Calc: C 74.94%, H 12.58%

Compound 6:

$\text{C}_{11}\text{H}_{22}\text{O}$ IR: (cm^{-1}) 3355, 3077, 1643, 1101. ^1H NMR (300 MHz CDCl_3): δ (ppm) 5.80 (m, 1H), 5.13 (d, $J = 12.9$ Hz, 2H), 3.64 (m, 1H), 2.30 (m, 1H), 2.16 (m, 1H), 1.48-1.21 (m, 12H), 0.88 (s, 3H).

^{13}C NMR (300M, CDCl_3): δ (ppm) 135.0, 117.7, 70.8, 42.0, 36.9, 31.9, 29.7, 29.3, 25.7, 22.7, 14.1.

Elemental analysis:

Found: C 77.73%, H 13.15%; Calc: C 77.58%, H 13.02%

Compound 7:

C₁₁H₁₄O IR: (cm⁻¹) 3362, 3062, 1641, 1603, 1495, 1454, 1045. ¹H NMR (300 MHz □ CDCl₃): δ(ppm) 7.32-7.20 (m, 5H), 5.82 (m, 1H), 5.15 (d, J = 11.1 Hz), 3.87 (m, 1H), 2.80 (m, 2H), 2.20-2.40 (m, 2H), 1.68 (br, 1H).

¹³C NMR (300M, CDCl₃): δ(ppm) 138.5, 134.7, 129.3, 128.3, 126.2, 117.6, 71.6, 43.1, 41.0

Elemental analysis:

Found: C 81.42%, H 8.66%; Calc: C 81.44%, H 8.70%

Compound 8:

C₁₀H₁₂O IR: (cm⁻¹) 3400, 3070, 1641, 1600, 1496, 1446, 1049. ¹H NMR (300 MHz, CDCl₃): δ(ppm) 7.40-7.25 (m, 5H), 5.90-5.75 (m, 1H), 5.18 (q, J = 4.95 Hz, 2H), 4.75 (q, J = 3.2 Hz, 1H), 2.50 (m, 2H), 2.20-1.85 (br, 1H).

¹³C NMR (300M, CDCl₃): δ(ppm) 144.0, 134.5, 128.2, 127.3, 125.9, 117.6, 73.4, 43.6.

Elemental analysis:

Found: C 81.12%, H 8.33%; Calc: C 81.04%, H 8.16%

Compound 9:

C₁₁H₁₄O IR: (cm⁻¹) 3385, 3080, 1644, 1594, 1577, 1450. ¹H NMR (300MHz □ CDCl₃): δ(ppm) 7.25 (d, J = 5.7 Hz, 2H), 7.16 (d, J = 7.6 Hz, 2H), 5.80 (m, 1H), 5.15 (q, J = 5.0 Hz, 2H), 4.71 (t, J = 3.96 Hz, 1H), 2.50 (t, J = 8.18 Hz, 2H), 2.35 (s, 3H), 1.98 (br, 1H).

¹³C NMR (300M, CDCl₃): δ(ppm) 141.0, 136.6, 134.6, 128.7, 125.7, 117.3, 73.1, 43.3, 20.8.

Elemental analysis:

Found: C 81.56%, H 8.66%; Calc: C 81.44%, H 8.70%

Compound 10:

C₁₀H₁₁ClO IR: (cm⁻¹) 3384, 3074, 1641, 1595, 1573, 1473, 1107, 1033. ¹H NMR (300 MHz, CDCl₃): δ(ppm) 7.56 (d, J = 7.76 Hz, 1H), 7.34-7.20 (m, 3H), 5.80 (m, 1H), 5.20 (m, 3H), 2.62 (m, 1H), 2.40 (m, 1H), 2.10-2.00 (br, 1H).

¹³C NMR (300M, CDCl₃): δ(ppm) 141.4, 134.2, 131.6, 129.3, 128.3, 127.2, 126.9, 118.1, 69.7, 41.9.

Elemental analysis:

Found: C 65.59%, H 6.10%; Calc: C 65.76%, H 6.07%

Compound 11:

C₁₀H₁₂O₂ IR: (cm⁻¹) 3390, 3077, 1642, 1608, 1450, 1106. ¹H NMR (300 MHz, CDCl₃): δ(ppm) 8.00 (s, 1H), 7.18 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 7.0 Hz, 1H), 6.85 (m, 2H), 5.85 (m, 1H), 5.22 (d, J = 13.0 Hz, 2H), 4.88 (s, 1H), 2.68 (s, 1H), 2.61 (s, 2H).

¹³C NMR (300M, CDCl₃): δ(ppm) 155.2, 134.1, 128.7, 128.3, 127.0, 119.6, 118.5, 116.9, 74.2, 41.9.

Elemental analysis:

Found: C 73.22%, H 7.39%; Calc: C 73.15%, H 7.37%

Compound 12:

C₁₁H₁₄O₂ IR: (cm⁻¹) 3400, 3078, 1643, 1612, 1513, 1463, 1248, 1175. ¹H NMR (300 MHz, CDCl₃): δ(ppm) 7.27 (d, J = 7.16 Hz, 2H), 6.88 (d, J = 4.95 Hz, 2H), 5.80 (m, 1H), 5.15 (d, J = 13.2 Hz, 2H), 4.68 (t, J = 6.52 Hz, 1H), 3.79 (s, 3H), 2.50 (m, 2H), 2.10-1.90 (br, 1H).

¹³C NMR (300M, CDCl₃): δ(ppm) 159.1, 135.2, 134.1, 128.3, 116.5, 113.7, 77.5, 55.1, 42.9.

Elemental analysis:

Found: C 74.20%, H 8.02%; Calc: C 74.13%, H 7.92%

Compound 13:

C₁₀H₁₃NO IR: (cm⁻¹) 3381, 3077, 2974, 1642, 1610, 1510, 1450. ¹H NMR (300 MHz, CDCl₃): δ(ppm) 7.15 (d, J = 8.3 Hz, 2H), 6.65 (d, J = 8.22 Hz, 2H), 5.85 (m, 1H), 5.17 (m, 2H), 4.60 (t, J=6.53Hz, 1H), 3.67 (br, 2H), 2.52 (t, J=6.9Hz, 2H), 1.90 (br, 1H).

¹³C NMR (300M, CDCl₃): δ(ppm) 145.2, 134.9, 134.1, 126.9, 117.3, 115.0, 73.1, 43.3.

Elemental analysis:

Found: C 73.60%, H 8.12%, N 8.55%; Calc: C 73.59%, H 8.03%, N 8.58%

Compound 14:

C₁₀H₁₀Cl₂O IR: (cm⁻¹) 3280, 3079, 1638, 1590, 1564, 1470, 1102, 1070. ¹H NMR (300 MHz, CDCl₃): δ(ppm) 7.51 (d, J = 8.23 Hz, 1H), 7.35 (s, 1H), 7.27 (d, J = 8.5 Hz, 1H), 5.85 (m, 1H), 5.20 (d, J = 12.9 Hz, 2H), 5.12 (t, J = 4.44 Hz, 1H), 2.60 (m, 1H), 2.27 (m, 1H), 2.16 (br, 1H).

¹³C NMR (300M, CDCl₃): δ(ppm) 139.9, 133.9, 133.5, 132.3, 129.1, 128.2, 127.4, 119.0, 69.3, 42.0.

Elemental analysis:

Found: C 55.36%, H 4.66%; Calc: C 55.33%, H 4.64%

Compound 15:

C₆H₁₂O IR: (cm⁻¹) 3374, 3077, 1641, 1151. ¹H NMR (300 MHz, CDCl₃): δ(ppm) 5.86

Current Data Parameters

NAME	1m027
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20030402
Time	18.29
INSTRUM	av300
PROBHD	5 mm BBO BB-1H
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SMH	11990.407 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	256
DW	41.700 usec
DE	8.00 usec
TE	300.0 K
D1	2.00000000 sec

***** CHANNEL f1 *****

NUC1	1H
P1	4.00 usec
PL1	-3.00 dB
SFO1	300.1320000 MHz

F2 - Processing parameters

SI	16384
SF	300.1300001 MHz
WDW	no
SGB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.00 cm
CY	0.00 cm
F1P	12.000 ppm
F1	3601.56 Hz
F2P	-0.200 ppm
F2	-60.03 Hz
PPHMC	0.55455 ppm/c
HCN	166.43573 Hz/c

1a

CDCl₃

Current Data Parameters

NAME	1a1c17-1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20030403
Time	8.52
INSTRUM	av300
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	501
DS	2
SWH	18832.393 Hz
FIDRES	0.514719 Hz
AQ	0.8705404 sec
RG	3649.1
DW	26.550 usec
DE	6.00 usec
TE	300.2 K
D1	2.0000000 sec
d11	0.03000000 sec

===== CHANNEL f1 =====

NUC1	¹ H
P1	10.00 usec
PL1	-6.00 dB
SFO1	75.4705588 MHz

===== CHANNEL f2 =====

CHRG2	h11z116
NUC2	¹³ C
PCPD2	80.00 usec
PL2	120.00 dB
PL12	16.00 dB
SFO2	300.1315007 MHz

F2 - Processing parameters

SF	131072
SR	75.4677480 MHz
WDW	EM
SGB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CH	22.00 cm
CT	0.00 cm
CF	200.000.000 ppm
F1	15083.55 Hz
F2P	-6.000 ppm
F2	-0.000 Hz
PCWH	9.08053 ppm/cm
HCWH	686.0763 Hz/cm

Found: C 71.88%, H 12.10%; Calc: C 71.95%, H 12.08%

For allyl chloride: dl:meso = 69 :31

For allyl bromide: dl:meso = 70:30