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Synthesis of *a*,*b*-unsaturated Amides by Olefin Cross-Metathesis

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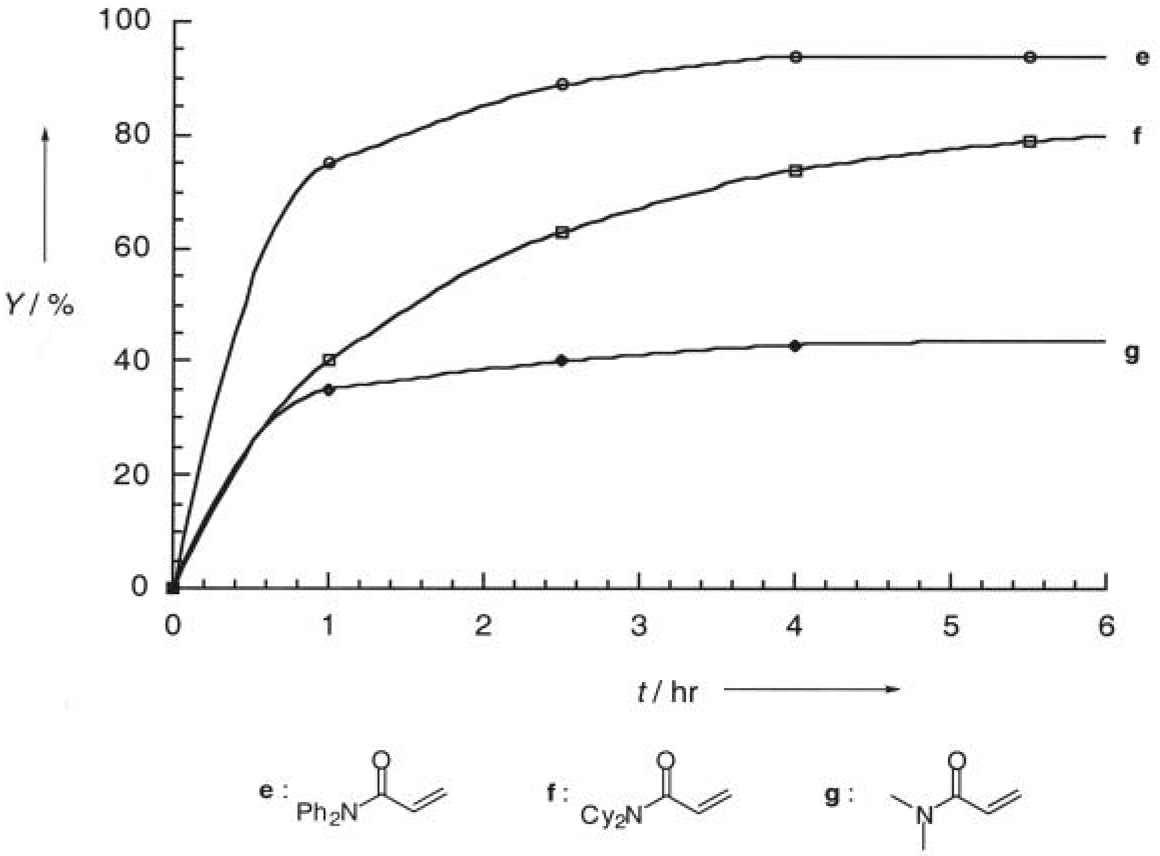
Kinetic Studies of Various Amides with Terminal Olefin **II**



General Experimental Section. NMR spectra were recorded on Varian-300 NMR. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and multiplet (m). The reported ^{1}H NMR data refer to the major olefin isomer unless stated otherwise. The reported ^{13}C NMR data include all peaks observed and no peak assignments were made. High-resolution mass spectra (EI and FAB) were provided by the UCLA Mass Spectrometry Facility (University of California, Los Angeles).

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. All other chemicals were purchased from the Aldrich, Strem, or Nova Biochem Chemical Companies, and used as delivered unless noted otherwise. CH_2Cl_2 was purified by passage through a solvent column prior to use.[i]

General Procedure: To a flask charged with amide (1.0 equiv) in CH_2Cl_2 (0.2 M), catalyst **1** (0.05 equiv in CH_2Cl_2) was added by cannulation followed by addition of either terminal olefin (1.25

equiv), or styrene (1.9 equiv) via syringe. The flask was fitted with a condenser and refluxed under argon for 15 hours. The reaction was monitored by TLC. After the solvent was evaporated, the product was purified directly on a silica gel column.

Compound 3. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:2=ethyl acetate:hexane. A viscous oil (R_f=0.45 in 1:1=EA/Hx) was obtained (26 mg, 39% yield 1.0 mg of cis compound separated) ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.85 (1H, dt, J=7.0, 17.0 Hz), 6.20 (1H, d, J=17.0 Hz), 3.58 (2H, t, J=6.7 Hz), 3.00 (6H, s), 2.18 (2H, dt, J=6.7, 6.7Hz), 1.42 (4H, m), 1.30 (8H, m) 0.82 (9H, s), 0(6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm), δ 167.0, 146.5, 120.4, 63.5, 33.1, 33.8, 30.0, 29.6, 29.4, 29.0, 26.5, 26.1, 18.7, -4.99. HRMS (EI) calcd.for $C_{19}H_{39}NO_2Si$: 341.2750. Found: 341.2747.

Compound 4. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 2:1=EA:Hx. A solid was obtained (R_f=0.30 in 2:1=EA/Hx, 8.3 mg, 25% yield). Characterization by: Gill, G. etc. *J. Chem. Soc. Perkin Trans.1* 1994, 369-378

Compound 5. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:10=EA/Hx. A viscous oil was obtained (R_f**=**0.30 in 1:10:EA/Hx, 75.6 mg, 77% yield) ^{1}H NMR (300MHz, $CDCl_3$, ppm):δ 6.70 (1H, dt, J=7.0, 17.0 Hz), 6.16 (1H, d, J=17.0 Hz), 3.58 (2H, t, J=6.7 Hz), 3.00 (6H, s), 2.18 (2H, dt, J=6.7, 6.7Hz), 1.42 (4H, m), 1.30 (8H, m) 0.82 (9H, s), 0.0(6H, s). ^{13}C NMR (75MHz,$CDCl_3$,ppm), δ 166.7, 144.5, 123.4, 63.6, 33.2, 33.8, 32.1, 30.7, 29.8, 29.7, 29.5, 28.8, 26.82, 26.5, 26.3, 26.1, 25.8, 18.7, –4.9. HRMS (EI) calcd. for $C_{29}H_{55}NO_2Si$:477.4002. Found: 477.4018.

Compound 6. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:10=EA:Hx. Solid was obtained (R_f=0.30 in 1:10=EA:Hx, 20 mg, 35% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 7.76 (1H, d, J=17.0 Hz), 7.50 (2H, m), 7.35 (3H, m), 6.84 (1H, d, J=17.0 Hz), 3.56 (2H, broad), 2.15 (2H, broad), 1.80 (6H, broad), 1.65 (6H, broad), 1.20 (6H, broad). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 166.4, 140.9,136.0, 128.9, 127.8, 121.2, 56.1, 30.7, 26.9, 25.8. HRMS (EI) calcd. for $C_{21}H_{29}NO$: 311.2249. Found: 311.2254.

Compound 7. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:1=EA:Hx. Viscous oil was obtained (R_f=0.30 in 1:1=EA:Hx, 41.9 mg, 80% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.80 (1H, dt, J=7.0, 17 Hz), 5.70 (1H, d, J=17.0 Hz), 5.2 (1H, broad), 4.56 (1H, t J=4.0 Hz), 4.10 (1H, m), 3.82 (1H, m), 3.72(1H, m), 3.46 (1H, m), 3.38 (1H,m), 2.20 (2H, dt J=6.7, 6.7 Hz), 1.45-1.80 (10H, m), 1.18 (6H, d, J=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm)

165.3, 144.1, 124.3, 99.1, 67.5, 62.6, 41.5, 32.1, 31.1, 29.6, 25.8, 25.3, 23.1, 20.0 HRMS (EI) calcd for $C_{15}H_{27}NO_3$:269.1991. Found: 269.1997.

Compound 8. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:1=EA:Hx. Solid was obtained (R_f=0.40 in 1:1=EA:Hx, 24.0 mg, 62% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm) δ 7.60 (1H, d, J=17.0Hz), 7.48 (2H, m), 7.38 (3H, m), 6.26 (1H, d, J=17.0 Hz), 5.40 (1H, broad), 1.19(6H, d, J=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 165.2, 140.7, 135.1, 129.2, 127.7, 121.3, 41.8, 23.5, 22.9. HRMS (EI) calcd. for $C_{12}H_{15}NO$: 189.1154. Found: 189.1152.

Compound 9. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:2=EA.Hx. Viscous oil was obtained (R_f=0.30 in 1:2=EA:Hx, 64.1 mg, 89% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm) δ 6.90 (1H, dt, J=7.0, 17 Hz), 6.30 (1H, d, J=17.0 Hz), 4.50 (1H, t, J=4.o Hz), 3.82 (1H, m), 3.72(1H, m), 3.61 (3H, s) 3.46 (1H, m), 3.38 (1H,m), 3.17 (1H, s), 2.20 (2H, dt J=6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 167.0, 147.6, 119.0, 99.0, 67.4, 62.5, 61.9, 32.6, 31.0, 29.6, 25.8, 25.4, 20.0. HRMS (EI) calcd. for $C_{14}H_{25}NO_4$: 271.1784. Found: 271.1791.

Compound 10. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with

1:2=EA:Hx. Viscous oil was obtained (R_f=0.35 in 1:2=EA:Hx, 25.2 mg, 66% yield). Characterization by: Solladie. G. etc.*J. Org. Chem* **1999**, 64, 2309-2314

Compound 11. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 2:1=EA:Hx. Solid was obtained (R_f=0.30 in 3:1=EA:Hx, 72 mg, 89% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.78 (1H, dt, J=7.3, 17 Hz), 6.22 (2H, broad) 5.83 (1H, d, J=17.0 Hz), 4.01 (2H, t, J=7.0 Hz), 2.20 (2H, m), 2.00 (3H, s), 1.60 (2H, m), 1.50 (2H, m), ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 171.4, 168.4, 145.5, 123.6, 64.4, 31.8, 28.4, 24.9, 21.4 HRMS (EI) calcd. for $C_9H_{15}NO_3$:185.1052. Found: 185.1061.

Compound 12. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 4:1=EA:Hx. Solid was obtained (R_f=0.35 in 4:1=EA:Hx, 20.3 mg, 69% yield). Characterization by: Moriarty, R.M. etc.*J. Org. Chem* **1993**, 58,2478-2482

Compound 13. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:3=EA:Hx. Solid was obtained (R_f=0.35 in 1:3=EA:Hx, 55.4 mg, 90% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 7.58 (2H, d, J=11 Hz), 7.25 (2H, m), 7.10 (1H, t, J=11 Hz) 6.95 (1H, dt, J=7.3, 17 Hz), 5.93 (1H, d, J=17.0 Hz), 4.58 (1H, t J=4.0 Hz), 3.82 (1H, m), 3.72(1H, m), 3.61 (3H, s) 3.46 (1H, m), 3.38 (1H,m), 3.17 (1H, s), 2.22 (2H, dt J=6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 166.3, 147.9, 140.6,130.9,126.3, 126.1, 122.0, 101.2, 69.4, 64.6, 34.1, 33.1, 31.6, 27.8, 27.2, 22.1 HRMS (EI) calcd.for $C_{18}H_{25}NO_3$:303.1834. Found: 303.1840.

Compound 14. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:3=EA:Hx. Solid was obtained (R_f**=**0.35 in 1:3=EA:Hx, 30.5 mg, 69% yield). Characterization by: Wang, T. etc. *Synthesis* **1997**, 87-90

Compound 15. See **General Procedure**. The product was purified directly on a silica gel column (1X15 cm), eluting with 1:2 = EA:Hx. Viscous oil was obtained (R_f=0.30 in 1:2=EA:Hx, 62 mg, 97% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.40 (3h, m), 7.16 (2H, d, J=11 Hz), 6.83 (1H, dt, J=7.3, 17 Hz), 5.70 (1H, d, J=17.0 Hz), 4.52 (1H, t, J=4.0 Hz), 3.80 (1H, m), 3.62 (1H, m), 3.44 (1H, m), 3.38 (1H, m), 3.35 (3H, s), 2.06 (2H, dt, J=6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 166.3, 145.8, 143.9, 129.7, 127.6, 127.5, 121.7, 98.9, 67.4, 62.5, 37.7, 32.3, 31.0, 29.5, 25.8, 25.4, 19.9, HRMS (EI) calcd. for $C_{19}H_{27}N{=}_3$: 317.1991. Found: 317.1996.

Compound 16. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:5=EA:Hx. Solid was obtained (R_f=0.30 in 1:3=EA:Hx, 43.2 mg, 83%

yield). Characterization by: Froeyen, P. etc. *Synth. Commun* 1995, 25, 959-968.

Compound 17. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:5=EA:Hx. Viscous was obtained (R_f=0.35 in 1:3=EA:Hx, 76.7 mg, 100% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 7.35 (6H, m), 7.23 (8H, m), 7.00 (1H, dt, J=7.3, 17 Hz), 5.82 (1H, d, J=17.0 Hz), 4.56 (1H, t J=4.0 Hz), 3.80 (1H, m), 3.62(1H, m), 3.44 (1H, m), 3.38 (1H,m), 2.18 (2H, dt J=6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 166.3, 147.1, 143.0, 129.4, 127.6, 126.8, 122.9, 99.0, 67.4, 62.5, 32.5, 31.1, 29.6, 25.8, 25.4, 20.0 HRMS (EI) calcd. for $C_{24}H_{29}NO_3$: 379.2147. Found: 379.2144.

Compound 18. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:1=toluene:methylene chloride. Solid was obtained (R_f=0.30 in 1:1=toluene:methylene chloride, 52.3 mg, 87% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 7.81(2H, 2, J=16 Hz), 7.23-7.42 (10H, m), 6.50 (1H, d, J=16 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 166.3, 142.9, 135.3, 123.0,129.5,129.0,128.2, 127.1, 120.0. HRMS (EI) calcd. for $C_{21}H_{17}NO$:299.1310. Found: 299.1301.

Compound 19. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:3=EA:Hx. Viscous oil was obtained (R_f=0.40 in 1:5=EA:Hx, 66.4 mg, 87% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 7.24 (1H, d, J=17

Hz), 7.17 (1H, dt, J=6.7, 17 Hz), 4.41 (2H, t, J= 12 Hz), 4.08 (2H, t, J=12 Hz), 3.57 (2H, t, J=11 Hz), 2.25 (2H, m), 1.50 (4H, m), 1.25 (8H, m), .0.84 (9H, s),), 0.00 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 165.6, 154.8, 152.1, 120.2, 63.6, 62.4, 43.1, 33.2, 33.1, 29.8, 29.7, 29.5, 28.4, 26.4, 26.1, 18.8, -4.85. HRMS (EI) calcd. for $C_{20}H_{37}NO_4Si$:383.2492. Found: 383.2496.

Compound 20. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:2=EA:Hx. Solid was obtained (R_f=0.35). However, product could not be isolated from starting material. Yield was estimated by NMR ratio. Compound 20 is known compound. Kanemasa, S etc.*J. Am.. Chem. Soc* **1998**, 120,3074

Compound 21. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:2=EA:Hx. Viscous oil was obtained (R_f=0.25 in 1:2=EA:Hx, 46 mg, 100% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 11.2 (1H, broad), 7.07 (1H, dt, J=7.7, 17.3 Hz), 5.82 (1H, d, J=17.3 Hz), 4.58 (1H, t J=4.0 Hz), 3.82 (1H, m), 3.72(1H, m), 3.46 (1H, m), 3.38 (1H,m), 3.17 (1H, s), 2.24 (2H, dt J=6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 171.9, 151.9, 121.1, 99.0, 67.4, 62.6, 32.4, 31.0, 29.5, 25.8,25.0,19.9. HRMS (EI) calcd. for $C_{12}H_{20}O_4$:228.1362. Found:228.1369.

Compound 22. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with

1:2=EA:Hx. Viscous oil was obtained (R_f=0.30 in 1:2=EA/Hx, 19.0 mg, 63% yield). Characterization by: Kim, T. etc. *J. Chem. Soc. Perkin Trans.1* **1995**, 2257-2262.

(i) The solvent columns are composed of activated alumina (A-2) and supported copper redox catalyst (Q-5 reactant). See: Pangborn, A. B.; Giard410 ello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.