created: 30th August 2002 with: L^AT_EX 2 ϵ (pdfTeX (Web2C 7.3.1) 3.14159-0.14f-released-20000525)

An Improved Catalyst for Ring Closing Alkyne Metathesis Based on Molybdenum Hexacarbonyl/2-Fluorophenol

Supplementary Information

Karol Grela,^{*a} and Jolanta Ignatowska^b^aInstitute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.^bFaculty of Chemistry, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

grela@icho.edu.pl

1. Best Eight Phenols

Figure 1. The Catalytic Activity of Selected Phenols in the Cyclisation of Diyne **2a**

2. Screening of of Phenols **1a** and **1b**

Figure 2. Screening of the Catalytic Activity of Phenols **1a** and **1b** in the Cyclisation of Diyne **2a**.

3. General

Unless otherwise noted, all reactions were carried out under air using commercially grade solvents. *Flash column chromatography*: Merck silica gel 60 (230–400 mesh). *NMR*: Spectra were recorded on Bruker AVANCE 500 and Varian Gemini 200 spectrometers in CDCl₃;

chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. *IR*: Perkin-Elmer Spectrum 2000 FT-IR, wavenumbers in cm⁻¹. *MS* (EI, LSIMS): AMD 604 Intectra GmbH. *MS* (ESI): Mariner Perceptive Biosystems, Inc. All chemicals and reagents were either obtained from commercial sources or prepared according to literature procedures.

4. General Procedure for Ring Closing Alkyne Metathesis

A solution of diyne **2a–g** (0.4 mmol), Mo(CO)₆ (5–10 mg, 0.04–0.02 mmol, 5–10 mol%)¹ and 2-fluorophenol (45 mg, 0.4 mmol) in chlorobenzene (20 mL)² was refluxed for 2–6 h using electric heating mantle. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (*c*-hexane/ethyl acetate 4:1) to give cycloalkyne **3a–g**.

4.1. 1,6-dioxacyclodec-9-yne-2,5-dione (**3a**)

Yellow solid: MS (EI) *m/z*: 196 ([M⁺], 1); 166 (1); 101 (20); 78 (100); 66 (75); 55 (20); 39 (35); ¹H NMR (ppm): 2,47 (4H, t, J=3,9 Hz); 2,7 (4H, s); 4,27 (4H, t, J=5,7 Hz); ¹³C NMR (ppm): 171,7; 78,7; 61,3; 29,9; 19,6. Analytical data are in agreement with those published in literature.³

4.2. 1,8-dioxacyclotetradec-11-yne-2,7-dione (**3b**)

White solid: MS (EI) *m/z*: 224 ([M⁺], 1); 101 (10); 78 (100); 55 (50); 39 (50); ¹H NMR (ppm): 1,73–1,78 (4H, m); 2,37–2,41 (4H, m); 2,52 (4H, t, J = 5,6 Hz); 4,14 (4H, t, J = 5,5 Hz); ¹³C NMR (ppm): 173,1; 77,8; 62,4; 34,9; 24,9; 19,0; Analytical data are in agreement with those published in literature.³

4.3. 5,6-didehydro-3,4,7,8-tetrahydro-2,9-benzodioxacyclododecine-1,10-dione (**3c**)

White solid: MS (EI) *m/z*: 244 ([M⁺], 1); 149 (42); 78 (100); 66 (35); IR (KBr, 1/cm): 2970 (w); 2909 (w); 1736 (s); 1719 (s); 1598 (w); 1578(w); 1485 (w); 1454 (w); 1377 (w); 1341 (w); 1288 (s); 1132 (s); 744(m); ¹³C NMR (ppm): 167,7; 133,1; 130,9; 128,3; 78,9; 62,6; 19,7; ¹H NMR (ppm): 2,54 (4 H, m); 4,45 (4 H, t, J=5,5 Hz); 7,53 (2 H, dd, J=5,7 Hz and 3,3 Hz); 7,69 (2 H, dd, J=5,7 Hz and 3,3 Hz); HRMS ([M+Na]⁺; C₁₄H₁₂O₄Na): calcd: 267,0633; found: 267,0644. Analytical data are in agreement with those published in literature.³

4.4. 1,6-dioxacyclododec-3-en-9-yne-2,5-dione (**3d**)

Pale yellow oil: MS (ESI) *m/z*: 217 ([M+Na]⁺, 100); IR (KBr, 1/cm): 2965 (m); 1732 (s); 1632 (m); 1395 (m); 1273 (s); 1297 (s); 1026 (m); 832 (m); ¹H NMR

(ppm): 2,41–2,53 (4 H, m); 4,32 (4H, t, J=5,5 Hz); 6,28 (2H, s); ¹³C NMR (ppm): 164,9; 129,6; 79,4; 62,4; 19,6; HRMS ([M+Na]⁺; C₁₀H₁₀O₄Na): calcd 217,0471; found: 214,0481. Analytical data are in agreement with those published in literature.³

4.5. 2,2-dimethyl-7,10,21,24-tetraoxatricyclo-[23.2.2.2^{3,6}]hentriaconta-1(27),3,5,25,28,30-hexaen-15-yne-11,20-dione (**3e**)

White solid: MS (EI) *m/z*: 478 ([M⁺], 28); 463 (28); 165 (9); 152 (11); 99 (100); 55 (9); 43 (17); IR (KBr, 1/cm): 2969 (m); 1726 (s); 1607 (m); 1511 (m); 1456 (m); 1297 (s); 1246–1234 (s); 1060 (m); ¹³C NMR (ppm): 172,9; 156,6; 143,7; 127,4; 114,8; 79,5; 66,6; 63,3; 41,4; 33,0; 30,3; 24,2; 18,0; ¹H NMR (ppm): 1,63–1,71 (4H, m); 1,66 (6H, s); 2,05–2,09 (4H, m); 2,26 (4H, t, J = 7,1 Hz); 4,22–4,24 (4H, AA'XX'); 4,38–4,4 (4H, AA'XX'); 6,80–6,84 (4H, AA'XX'); 7,08–7,12 (4H, AA'XX'); HRMS ([M⁺]): calcd 478,2355; found: 478,2368.

4.6. N¹-(2,5-dioxo-1,6-dioxo-9-cyclododecynyl)-2,2,2-trifluoroacetamide (**3f**)

Pale yellow syrup: MS (ESI) *m/z*: 330 ([M+Na]⁺, 100); IR (KBr, 1/cm): 2968 (m); 1752 (s); 1734 (s); 1542 (m); 1210 (s); 1175 (s); 1045 (m); ¹H NMR (ppm): 2,25–2,40 (1H, m); 2,47–2,65 (3H, m); 4,93 (1H, m); 5,28 (1H, m); 5,87–5,95 (1H, m); 6,10–6,15 (1H, m); 6,35–6,46 (1H, m); 6,85–7,00 (2H, m); 7,51 (1H, br); ¹³C NMR (ppm): 18,7; 20,09; 35,85; 48,83; 61,34; 63,99; 78,19; 78,52; 115,5 (q, ¹J=287 Hz); 156,7 (q, ²J=38 Hz); 168,7; 170,8; HRMS ([M+Na]⁺; C₁₂H₁₂NO₅F₃Na): calcd 330,0560; found: 330,0550.

4.7. 1-Oxycyclotridec-10-yno-2-one (**3g**)

Pale yellow, fruity odoured oil: MS (EI) *m/z*: 194 ([M⁺], 1); 107 (18); 94 (14); 93 (36); 91 (23); 81 (23); 80 (100); 67 (27); 65 (18); 55 (36); 41 (50); IR (film, 1/cm): 2931 (s); 2858 (s); 1737 (s); 1449 (m); 1379 (m); 1338 (m); 1259 (s); ¹H NMR (ppm): 1,2–1,56 (8H, m); 1,64–1,79 (2H, m); 2,14 (m); 2,36 (2H, t, J=6 Hz); 2,45–2,54 (2H, m); 4,15 (2 H, t, J=5,5 Hz); ¹³C NMR (ppm): 173,8; 82,7; 62,6; 34,5; 27,6; 27,2; 27,0; 26,7; 24,7; 19,4; 18,8. Analytical data are in agreement with those published in literature.³

¹ Purchased from Fluka

² Purchased from Polskie Odczynniki Chemiczne S.A.; p.a.

³ Fürstner, A.; Guth, O.; Rumbo, A.; Seidel, G. *J. Am. Chem. Soc.* **1999**, *121*, 11108–11113.