Enantioselective Total Syntheses of Grayanoid (-)-Mollfoliagein A and (-)-Rhodomollein XXV

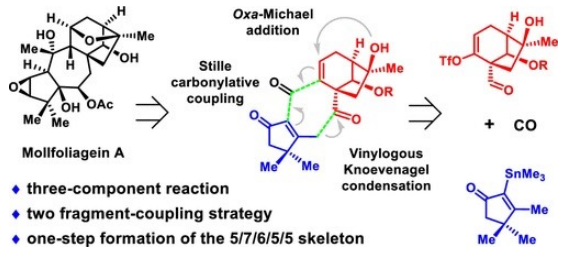
Shu-Fei Du, Yi-Peng Zhang* Quan-Lin Wu, and Hongbin Zhang*

J. Am. Chem. Soc. 2026, 148, 15410-15416.

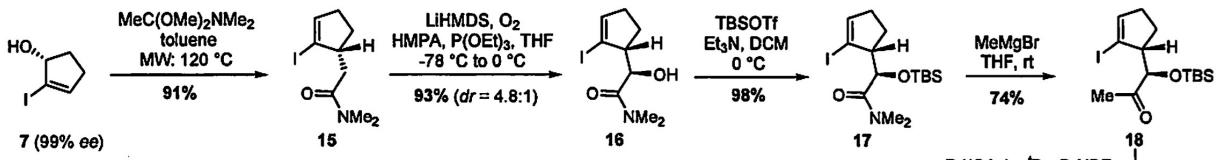
a Stille carbonylative coupling/transannular oxa-Michael addition/ vinylogous Knoevenagel condensation cascade

highly oxygenated grayananes

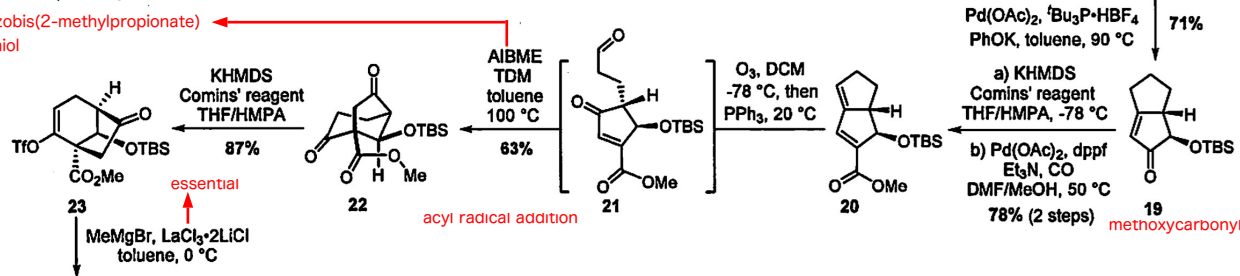
oxa-tricyclo[3.3.1.0^{3,7}]nonane

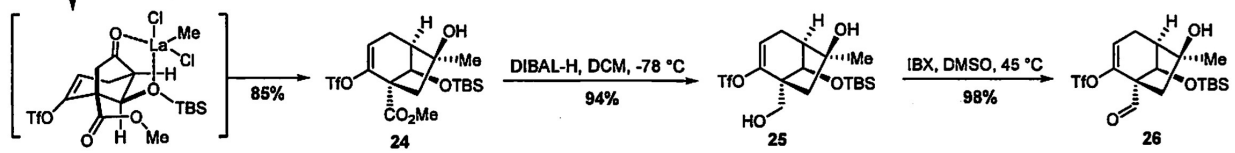


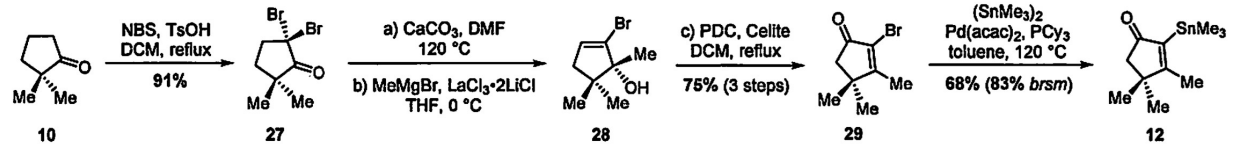
Eschenmoser-Claisen rearrangement

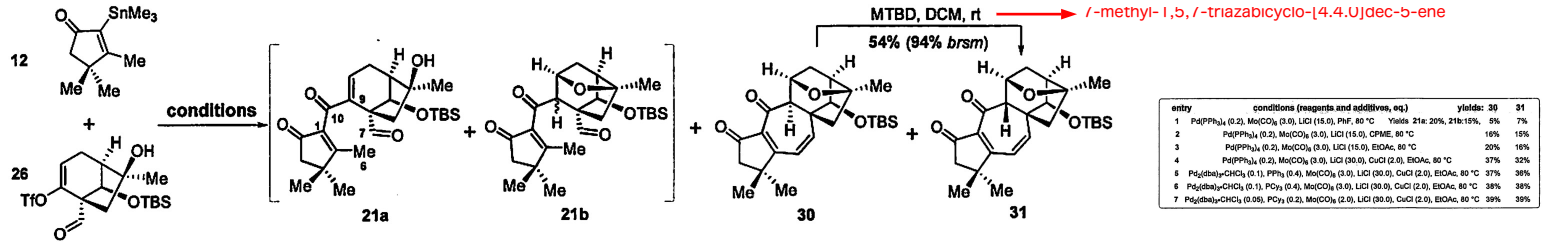


Dimethyl 2,2'-azobis(2-methylpropionate)
tert-dodecanethiol







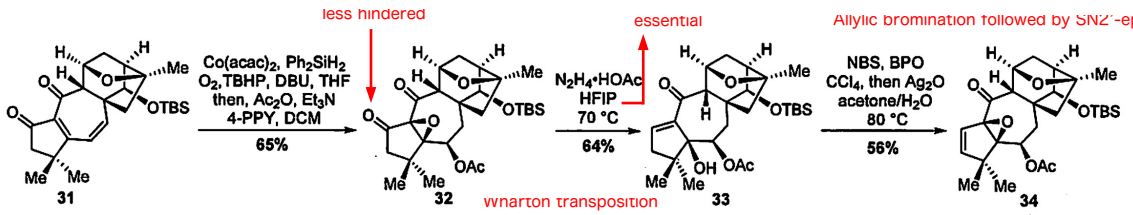


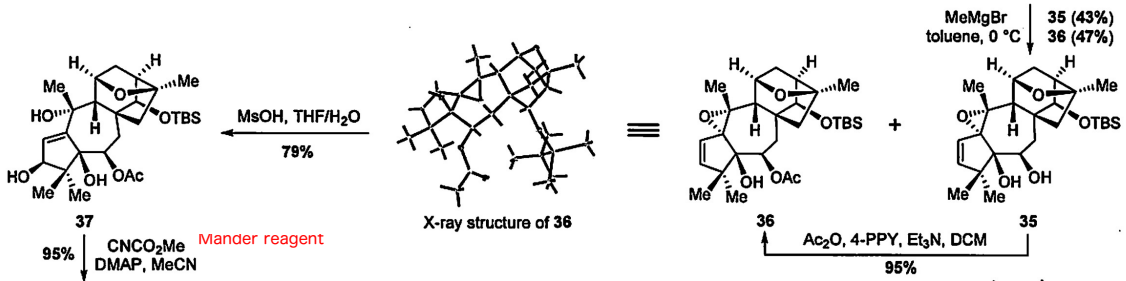
entry	conditions (reagents and additives, eq.)	yields: 30	31
1	$Pd(PPh_3)_4$ (0.2), $Mo(CO)_6$ (3.0), LiCl (15.0), PhF, 80 °C Yields 21a: 20%, 21b:15%,	5%	7%
2	$Pd(PPh_3)_4$ (0.2), $Mo(CO)_6$ (3.0), LiCl (15.0), CPME, 80 °C	16%	15%
3	$Pd(PPh_3)_4$ (0.2), $Mo(CO)_6$ (3.0), LiCl (15.0), EtOAc, 80 °C	20%	16%
4	$Pd(PPh_3)_4$ (0.2), $Mo(CO)_6$ (3.0), LiCl (30.0), CuCl (2.0), EtOAc, 80 °C	37%	32%
5	$Pd_2(dba)_3$•$CHCl_3$ (0.1), PPh_3 (0.4), $Mo(CO)_6$ (3.0), LiCl (30.0), CuCl (2.0), EtOAc, 80 °C	37%	36%
6	$Pd_2(dba)_3$•$CHCl_3$ (0.1), PCy_3 (0.4), $Mo(CO)_6$ (3.0), LiCl (30.0), CuCl (2.0), EtOAc, 80 °C	38%	36%
7	$Pd_2(dba)_3$•$CHCl_3$ (0.05), PCy_3 (0.2), $Mo(CO)_6$ (2.0), LiCl (30.0), CuCl (2.0), EtOAc, 80 °C	39%	39%

less hindered

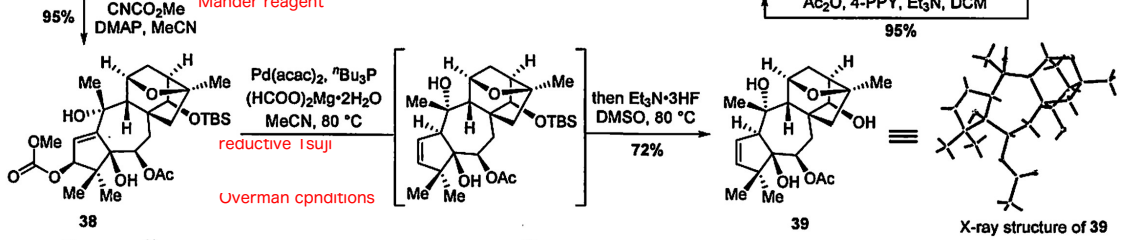
essential

Allylic bromination followed by SN2'-epoxidation



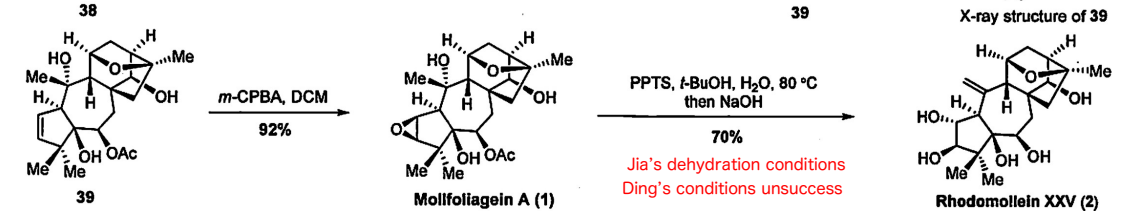


Mander reagent



reductive Tsuji

Overman conditions



Jia's dehydration conditions

Ding's conditions unsuccess