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Chemical reaction scheme showing the synthesis of (-)-Psathyrin A. The scheme starts with a complex polycyclic intermediate on the left, which undergoes a series of transformations (indicated by arrows) to form (-)-Psathyrin A on the right. The final product is a complex polycyclic molecule with a highlighted blue region.

Reagents and conditions:

- 6/4/5/5/ tetracyclic skeleton
- 3 all-carbon quaternary centers
- Suzuki-Miyaura coupling
- Au-catalyzed Conia-Ene cyclization
- Baran reductive olefin coupling

16 $\xrightarrow[1\text{-bromo-2-butyne (18), 12 h}]{1. \text{Cu(OTf)}_2, \text{19}, i\text{-PrMgBr, Et}_2\text{O, 4 h; then HMPA, 30 min}}$ **20** $\xrightarrow[Comins' \text{ reagent, THF, 10 min}]{2. \text{KHMDS}}$ **15** $\xrightarrow[PdCl_2(dppf), K_3PO_4, DMF/H_2O, 4 h]{3. \text{21}}$ **22**

22 $\xrightarrow[CH_2Cl_2, 30 \text{ min}]{4. m\text{-CPBA}}$ **23** $\xrightarrow[p\text{-TsOH, 10 min}]{\text{Meinwald rearrangement}}$ **24** $\xrightarrow[toluene, 30 \text{ min}]{5. \text{AuCl(PPh}_3\text{)}, AgOTf}$ **25**

25 $\xrightarrow[EtOH, 1.5 \text{ h}]{10. \text{Fe(acac)}_3, PhSiH_3}$ **26** $\xrightarrow[then \text{OsO}_4, 30 \text{ min}]{11. \text{TBAF (2 mol\%), HMDS, TMS-imidazole, THF, 2 h}}$ **27**

27 $\xrightarrow[CH_2Cl_2, 30 \text{ min}]{12. \text{TBSOTf, 2,6-lutidine}}$ **28** $\xrightarrow[then \text{H}_2\text{O}_2, 30 \text{ min}]{13. \text{LiHMDS, CNCO}_2\text{Me, Et}_2\text{O, 30 min; 14. PhSeBr, pyridine, CH}_2\text{Cl}_2, 1 \text{ h}}$ **29**

29 $\xrightarrow[MeOH, 10 \text{ min}]{15. \text{CeCl}_3 \cdot 7\text{H}_2\text{O, NaBH}_4}$ **30** $\xrightarrow[30 \text{ min}]{16. \text{NaH, CS}_2, \text{THF; then MeI, 30 min; 17. AIBN, } n\text{-Bu}_3\text{SnH, toluene}}$ **31**

31 $\xrightarrow[then \text{HF} \cdot \text{pyridine, THF, 30 min}]{19. \text{IBX, DMSO, 30 min}}$ **32**

32 $\xrightarrow[then \text{potassium sodium tartrate, 1 h}]{18. \text{DIBAL-H, CH}_2\text{Cl}_2, 10 \text{ min; then TBSCl, imidazole, 30 min}}$ **33**

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66 $\xrightarrow[then \text{HF} \cdot \text{pyridine, THF, 30 min}]{19. \text{IBX, DMSO, 3$

28 → 1 nine steps,
just 2 days due to the short reaction time and high efficiency of each step