Enantioselective Azahelicenes via Intramolecular Hydroarylation of Alkynes

**Significance:** The authors report an enantioselective synthesis of azahelicenes and S-shaped double azahelicenes, promoted by gold/silver triflate co-catalyzed intramolecular hydroarylation of alkynes. The photophysical properties of both azahelicenes and S-shaped double azahelicenes were then evaluated by measuring the circularly polarized luminescence activity.

**Comment:** Azahelicenes and S-shaped double azahelicenes were successfully synthesized via catalytic enantioselective sequential hydroarylation of achiral diynes and tetranyes in high yields and moderate to high enantioselectivities. Interestingly, the chiroptical property of the S-shaped double azahelicenes is very promising, since the circularly polarized luminescence activity of double azahelicenes was amazingly much higher than that of the simple azahelicenes.

**Selected examples:**

1. \( \text{R}^1 = 2\text{-MeOC_6H_4} \), \( \text{R}^2 = \text{Bn} \)
   - 96\% yield, 69\% ee
2. \( \text{R}^1 = 2\text{-MeOC_6H_4} \), \( \text{R}^2 = \text{CH}_2\text{C_6H_4-4-OMe} \)
   - 83\% yield, 48\% ee
3. \( \text{R}^1 = 2\text{-MeOC_6H_4} \), \( \text{R}^2 = \text{Bn} \)
   - 97\% yield, 36\% ee

**Application:**

4. \( \text{S-shaped double azahelicene} \)
   - (-)-4 using (R)-BINAP: 56\% yield, >99\% ee
   - (+)-4 using (S)-BINAP: 60\% yield, >99\% ee