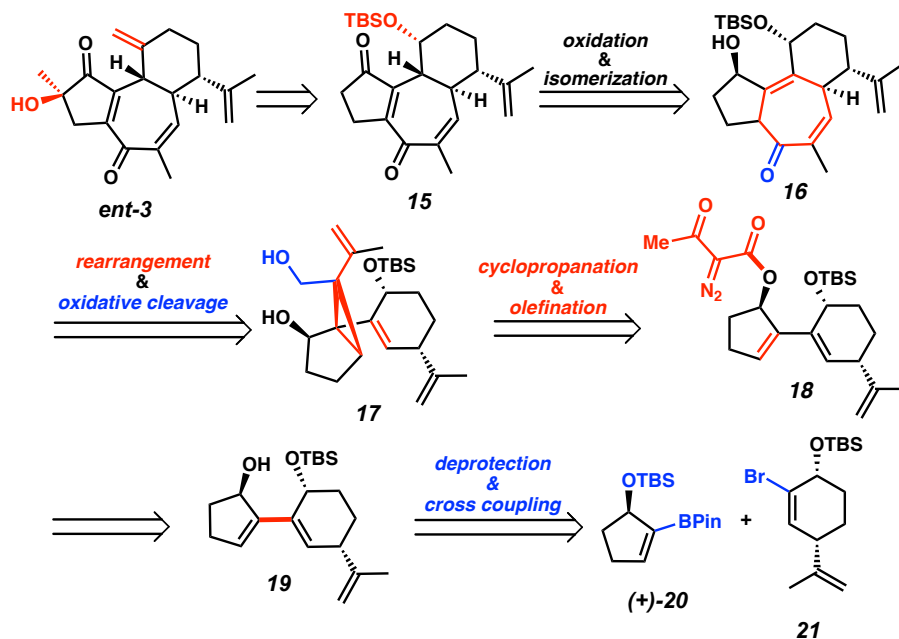
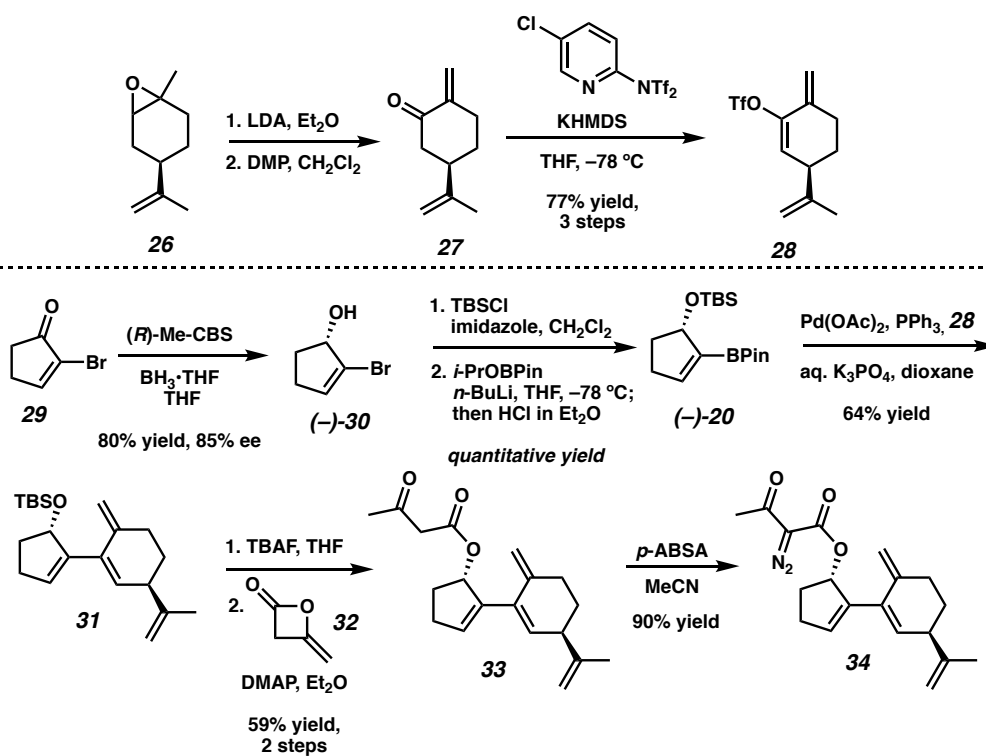
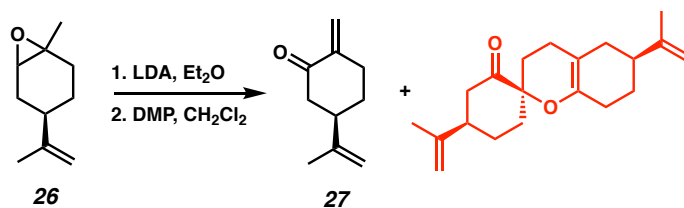
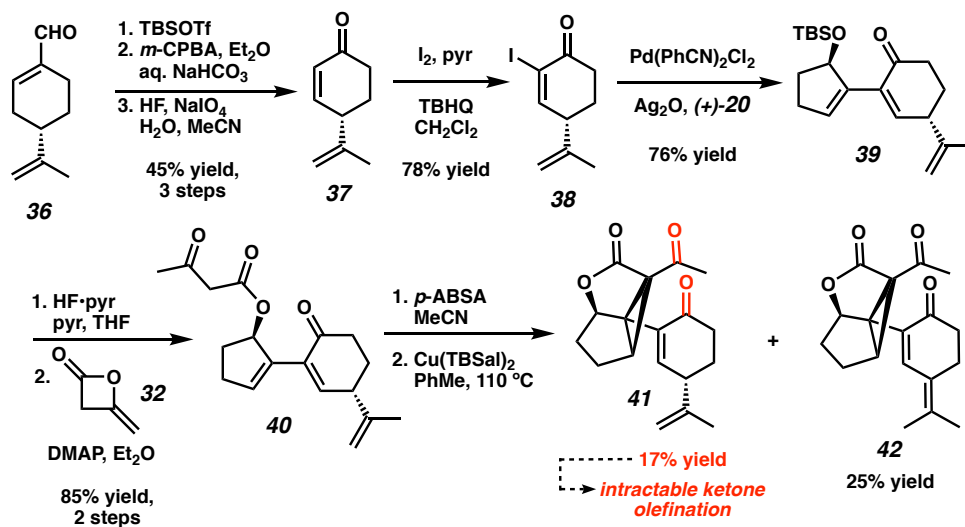
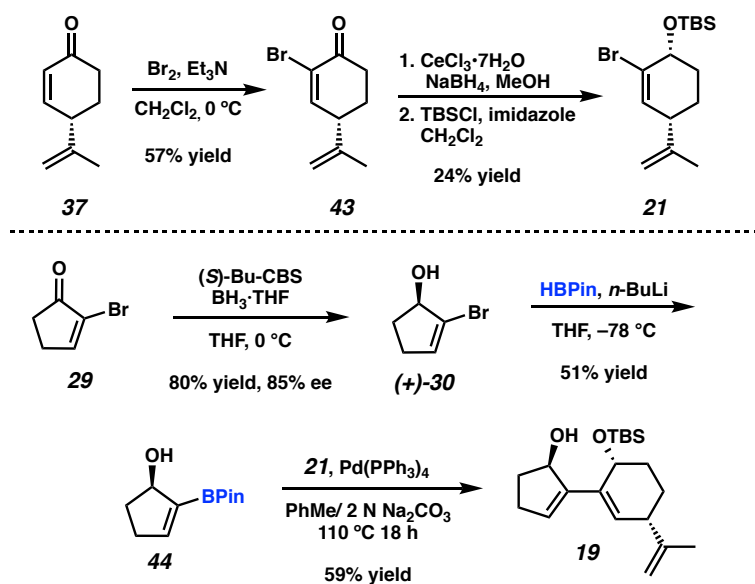


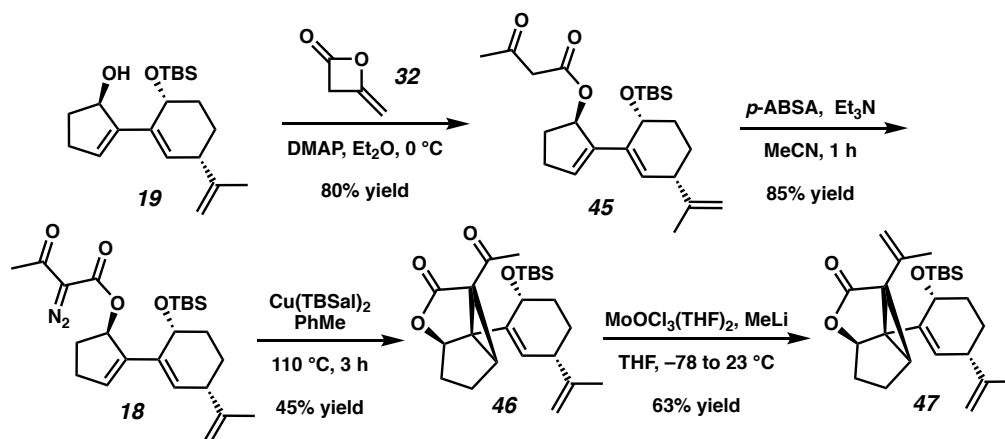
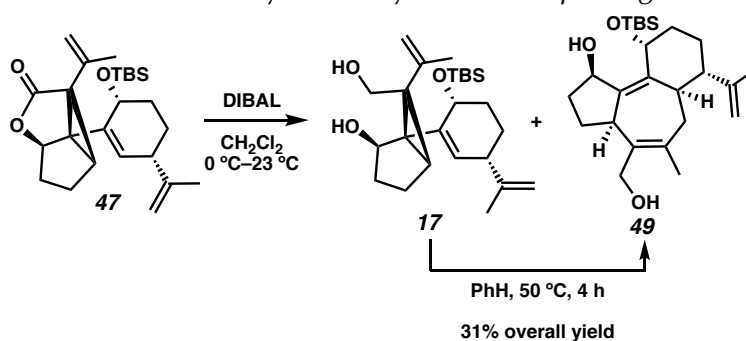
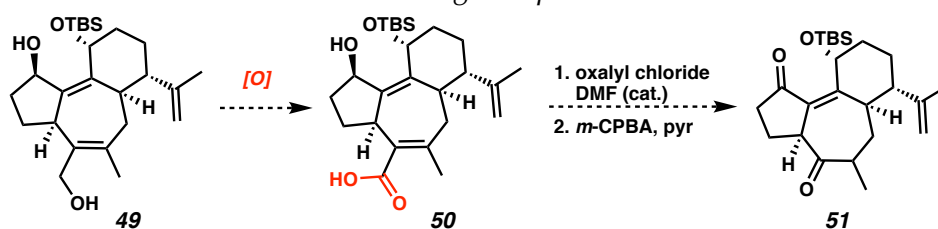
APPENDIX 1

Synthetic Summary Toward the Total Synthesis of Curcusone C

Scheme A1.1. Retrosynthetic Analysis of ent-Curcusone C (ent-3) via Rearrangement

Scheme A1.2. 1st Generation Synthesis of Diazo 34

Scheme A1.3. Undesired Hetero-Diels–Alder of Enone **27**Scheme A1.4. 2nd Generation Approach toward *ent*-**1–4**Scheme A1.5. 3rd Generation Assembly of Bicycle **19**

Scheme A1.6. 3rd Generation Synthesis of Divinylcyclopropane **47**SCHEME A1.7. Construction of Tricycle **49** by Lactone Opening and RearrangementScheme A1.8. Envisioned Oxidative Cleavage Sequence on Diol **49**

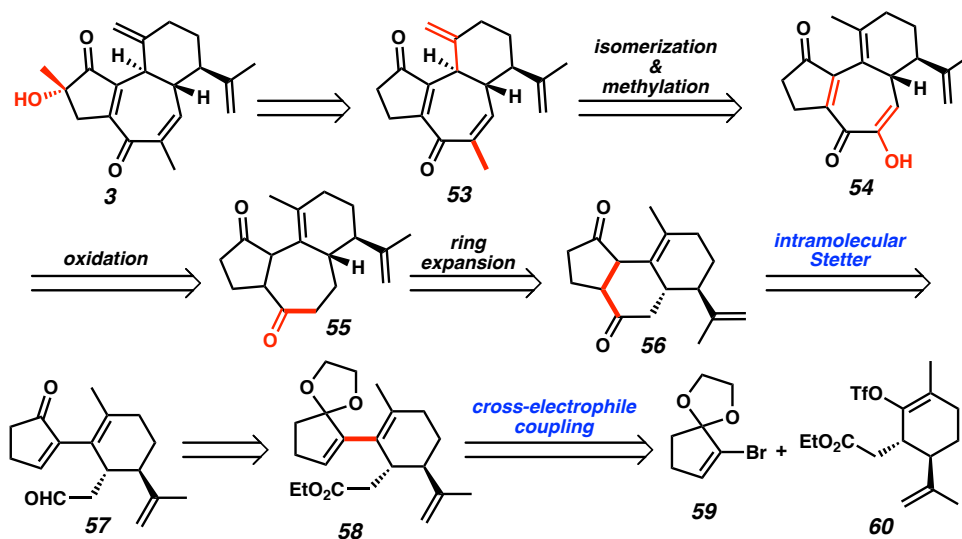
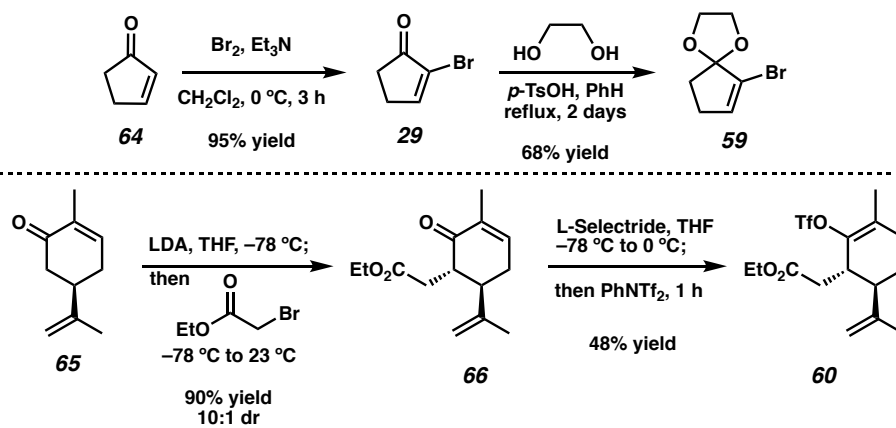
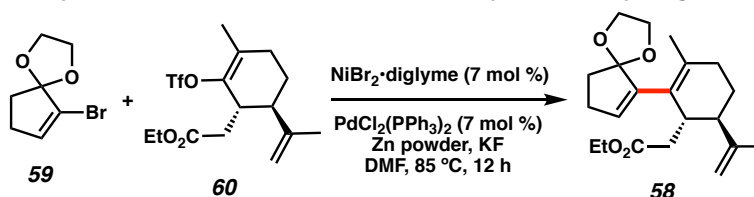
Scheme A1.9. 2nd Generation Retrosynthesis of **3**Scheme A1.10. Synthesis of Coupling Partners **59** and **60**

Table A1.1. Initial Optimization of the Cross-Electrophile Coupling



Entry	Deviation from standard procedure	Result
1	none	23% yield
2	No Pd	no product
3	No Ni	no product
4	dioxane instead of DMF	no product
5	Nal instead of KF	trace 58
6	no KF	trace 58
7	TDAE* instead of Zn	no product
8	4 equiv of 59	32% yield
9	syringe pump addition of 59	60% yield

*TDAE = tetrakis(dimethylamino)ethylene

Scheme A1.11. Further Optimization of the Reductive Coupling on Multigram Scale

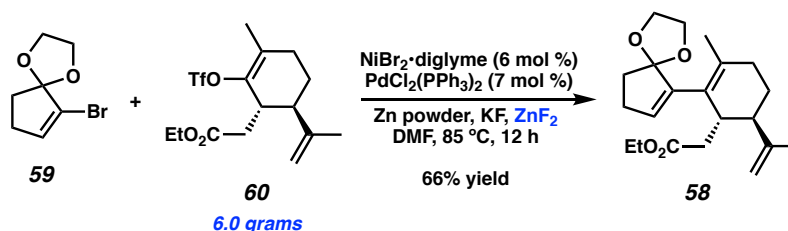
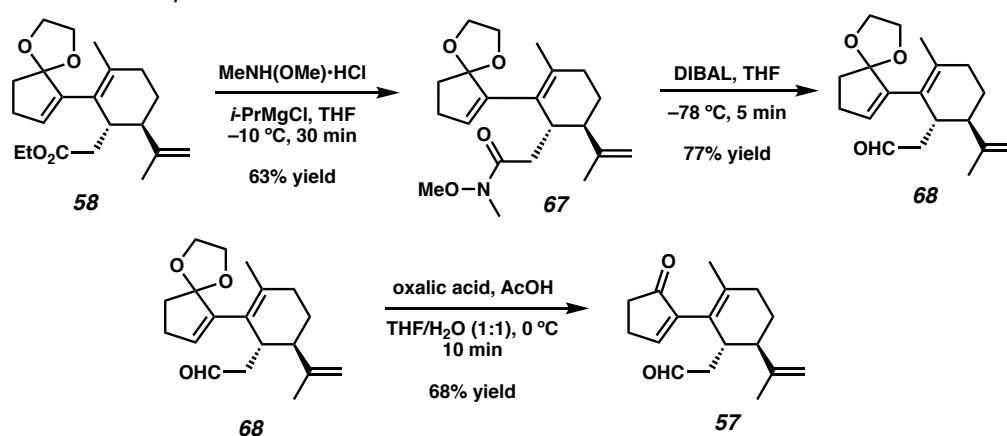
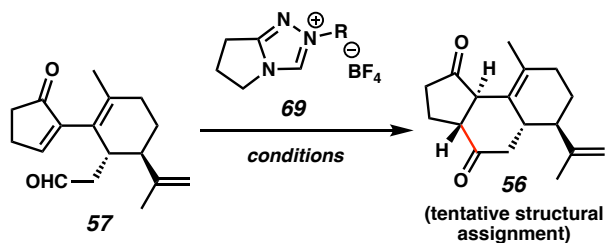
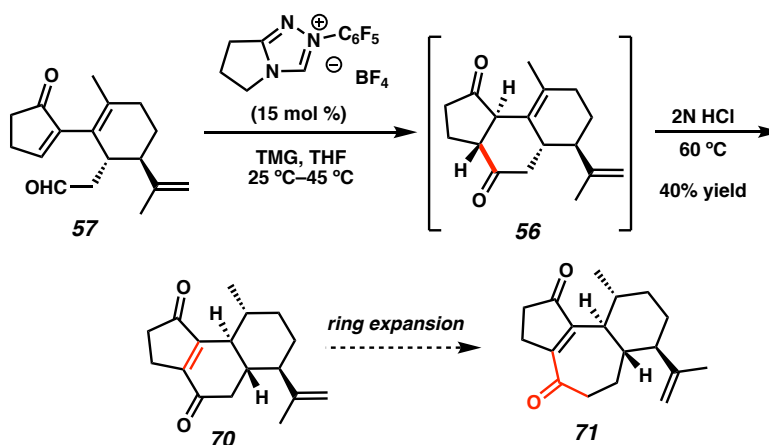
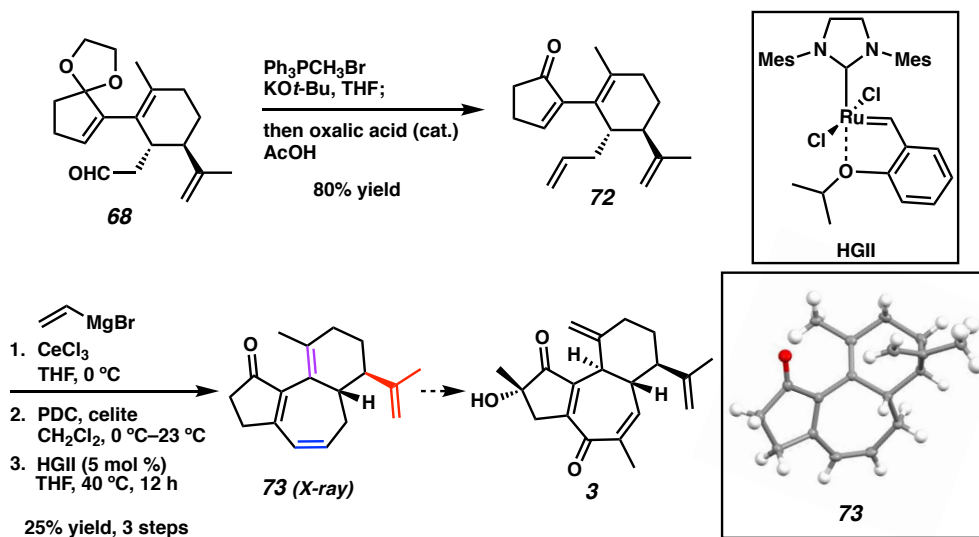
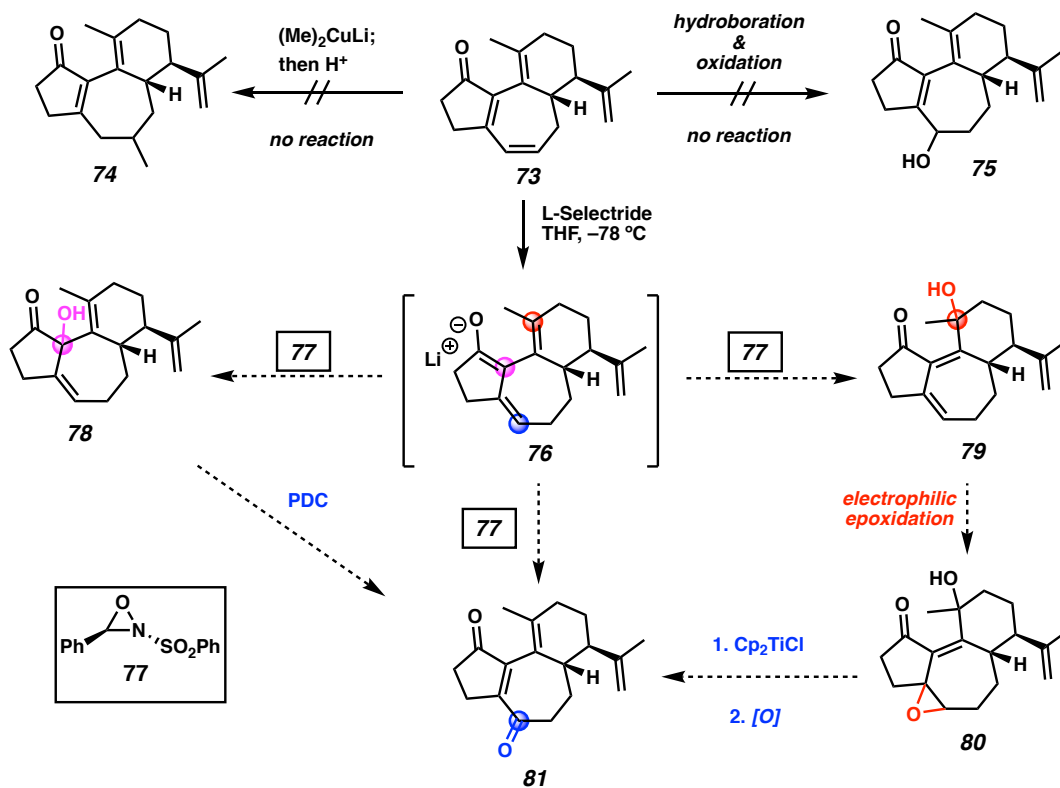
Scheme A1.12. Preparation of Stetter Precursor **57**

Table A1.2. Optimization of the Catalytic Stetter Reaction on Ketoaldehyde **57**

entry	R	catalyst loading	conditions	result*
1	Ph	30 mol %	DBU, dioxane 80 °C, 12 h	17% yield 1:1 dr
2	C ₆ F ₅	30 mol %	LiHMDS, PhMe 70 °C, 12 h	1,2-adduct
3	C ₆ F ₅	20 mol %	DBU, THF 30 °C, 30 min	24% yield 5:1 dr
4	C ₆ F ₅	5 mol %	DBU, THF, 0 °C–23 °C 12 h	incomplete conversion
5	C ₆ F ₅	15 mol %	TMG, THF 23 °C–45 °C	50–60% yield 2:1 dr

*Relative stereochemistry at the 5–6 juncture was identified by ¹H NMR, however the absolute stereochemistry could not be determined.

Scheme A1.13. Unsuccessful Ring Expansion of Ene-dione **70**

Scheme A1.14. Construction of Tricycle **73** via an RCM ApproachScheme A1.15. Divergent Oxidation Strategies to Form Ene-dione **81**

Scheme A1.16. Divergent Advancement of **81** to Curcusones A–D