Supplementary Information for
Convergent Total Synthesis of (+)-Calcipotriol: A Scalable, Modular Approach to Vitamin D Analogs

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Summary of failed approaches

1.1 Abandoned route on A ring synthesis

1.2 Original racemic route and optimization

2. Failed approach on enantioselective desymmetrization

2.1 Synthesis of Feringa’s chiral phosphorus amidite ligands
2.2 Screening of the conjugate alkynylation (Table S1)

| Ligand Temperature | Yield [%] | ee [%] | Ligand Temperature | Yield [%] | ee [%] |
|--------------------|-----------|--------|--------------------|-----------|--------|
| L1 0 °C            | trace     | <5     | L3 0 °C            | trace     | <5     |
| L1 -40 °C          | trace     | <5     | L3 -40 °C          | trace     | <5     |
| L1 -78 °C          | -         | -      | L3 -78 °C          | -         | -      |
| L2 0 °C            | trace     | <5     | L4 0 °C            | trace     | <5     |
| L2 -40 °C          | trace     | <5     | L4 -40 °C          | trace     | <5     |
| L2 -78 °C          | -         | -      | L4 -78 °C          | -         | -      |

**Zinc reagent:**
- A1: from Et$_2$Zn, 70 °C for 4 hrs, 1 M
- A2: from EtMgBr, 60 °C for 1 hr, add to ZnCl$_2$ solution, stir at r.t. for 1 hr, 0.33 M

**Rxn procedure**
- B1: Add Cu+Ligand solution to zinc at -78 °C, add SM solution
- B2: Add Cu+Ligand solution to SM, cool to -78 °C, add zinc

| Entry | Zinc reagent | Rxn concentration | Rxn procedure | Solvent | Temp. | Yield | ee. |
|-------|--------------|--------------------|---------------|---------|-------|-------|-----|
| 1     | A1           | 0.15 M             | B1            | toluene/hexane | -78°C to 0 °C | trace | 40% |
| 2     | A1           | 0.15 M             | B1            | toluene/hexane | -78°C to -20 °C | trace | 38% |
| 3     | A2           | 0.1 M              | B2            | toluene/THF   | -78°C to 0 °C  | trace | 1%  |
| 4     | A2           | 0.1 M              | B2            | toluene/THF   | -78°C to -20 °C| trace | 5%  |

**Zinc reagent:**
- A1: from Et$_2$Zn, 70 °C for 4 hrs, 1 M
- A2: from Et$_2$Zn, 70 °C for 4 hrs, tightly sealed with teflon, 1 M
- A3: from Et$_2$Zn, 70 °C for 4 hrs, 0.5 M
- A4: from Et$_2$Zn, 70 °C for 4 hrs, then sonicate, 0.5 M

**Rxn procedure**
- B1: Add Cu+Ligand solution to zinc at -78 °C, add SM solution
- B2: Add Cu+Ligand solution to SM, cool to -78 °C, add zinc

| Entry | R       | Zinc reagent | Rxn concentration | Rxn procedure | Yield | ee. |
|-------|---------|--------------|--------------------|---------------|-------|-----|
| 1     | TMS     | A1           | 0.12 M             | B1            | trace | -   |
| 2     | TMS     | A2           | 0.12 M             | B1            | trace | -   |
| 3     | TMS     | A3           | 0.10 M             | B1            | trace | -   |
| 4     | TMS     | A4           | 0.10 M             | B1            | trace | -   |
| 5     | TMS     | A1           | 0.15 M             | B2            | trace | -   |
| 6     | TMS     | A2           | 0.15 M             | B2            | trace | 3%  |
| 7     | TMS     | A3           | 0.13 M             | B2            | trace | 49% |
| 8     | TMS     | A4           | 0.13 M             | B2            | trace | 15% |
| 9     | TIPS    | A1           | 0.12 M             | B1            | trace | -   |
| 10    | TIPS    | A4           | 0.10 M             | B1            | trace | -   |
| 11    | TIPS    | A1           | 0.15 M             | B2            | trace | -   |
| 12    | TIPS    | A4           | 0.13 M             | B2            | trace | -   |
| Entry | R   | Zinc equiv. | Rxn concentration | Rxn procedure | Yield | e.e. |
|-------|-----|-------------|-------------------|---------------|-------|------|
| 1     | TMS | 2.0         | 0.12 M            | B2            | -     | -    |
| 2     | TMS | 5.0         | 0.12 M            | B2            | -     | -    |
| 3     | TMS | 10.0        | 0.10 M            | B2            | -     | -    |
| 4     | TMS | 2.0         | 0.10 M            | B1            | -     | -    |
| 5     | TMS | 5.0         | 0.15 M            | B1            | -     | -    |
| 6     | TMS | 10.0        | 0.15 M            | B1            | -     | -    |
| 7     | TIPS| 2.0         | 0.13 M            | B2            | 5.0%  | racemic |
| 8     | TIPS| 5.0         | 0.13 M            | B2            | 10.0% | racemic |
| 9     | TIPS| 10.0        | 0.12 M            | B2            | 4.5%  | racemic |

| entry | R     | Cu         | Alkyne            | additive      | solvent | yield |
|-------|-------|------------|-------------------|---------------|---------|-------|
| 1     | H     | -          | dialkynyl zinc reagent | -             | toluene | -     |
| 2     | Me    | -          | dialkynyl zinc reagent | -             | toluene | -     |
| 3     | H     | Cu(OAc)₂  | TIPS acetylene    | sodium ascorbate | H₂O/MeCN | -     |
| 4     | Me    | Cu(OAc)₂  | TIPS acetylene    | sodium ascorbate | H₂O/MeCN | -     |
| 5     | H     | Cu(OAc)₂  | TIPS acetylene    | sodium ascorbate | H₂O     | -     |
| 6     | Me    | Cu(OAc)₂  | TIPS acetylene    | sodium ascorbate | H₂O     | -     |
| 7     | H     | (CuOTf)₂  | dialkynyl zinc reagent | -             | toluene | -     |
| 8     | Me    | (CuOTf)₂  | dialkynyl zinc reagent | -             | toluene | -     |
| 9     | H     | (CuOTf)₂  | TIPS acetylene    | Zn(OAc)₂/Et₃N | toluene | -     |
| 10    | Me    | (CuOTf)₂  | TIPS acetylene    | Zn(OAc)₂/Et₃N | toluene | -     |

| entry | R    | ligand   | yield | e.e. |
|-------|------|----------|-------|------|
| 1     | H    | Taniaphos| 12%   | racemic |
| 2     | Me   | Taniaphos| 1,2 addition | - |
| 3     | H    | Josiphs  | n.d.  | - |
| 4     | Me   | Josiphs  | 1,2 addition | - |
| 5     | H    | -        | n.d.  | - |
| 6     | Me   | -        | 1,2 addition | - |

Control Experiments

| entry | R     | ligand     | Result |
|-------|------|------------|--------|
| 1     | TIPS acetylene | Taniaphos | 1,2 addition (69%) |
| 2     | Ethyl Grignard | Taniaphos | 1,4 addition |
| 3     | TIPS acetylene | Josiphs  | 1,2 addition (34%) |
| 4     | Ethyl Grignard | Josiphs  | 1,4 addition |
| 5     | TIPS acetylene | stol. Cu | 1,2 addition (13%) |
| 6     | Ethyl Grignard | stol. Cu | 1,4 addition |
2.3 Zard alkyne synthesis approach

![Chemical reaction diagram]

| conditions | conversion |
|------------|------------|
| Et$_3$N (10 mol%), LiCl (1 equiv.), toluene | N.R. |
| Et$_3$N (3 equiv.), LiCl (1 equiv.), toluene | trace conversion |
| PPY (50 mol%), thiourea (50 mol%), toluene | 36% (2:5 d) |
| NaH, THF | 62% (1:5 d) |
| Allyl-BINOL (10 mol%), LiHMDS (9 mol%), THF | N.R. |

| conditions | conversion |
|------------|------------|
| Et$_3$N (10 mol%), LiCl (1 equiv.), toluene | N.R. |
| Et$_3$N (3 equiv.), LiCl (1 equiv.), toluene | N.R. |
| NaH, THF | N.R. |
| LDA | N.R. |
| Δ, neat | decompose at 125 - 150 °C |
| Allyl-BINOL (10 mol%), LiHMDS (9 mol%), THF | N.R. |
| LDA, TMSCl; then TiCl$_4$, DCM | N.R. |
| LDA, TMSCl; then SnCl$_4$, DCM | N.R. |
| TMSOTf, Et$_3$N, DCM | N.R. |
2.4 Attempted synthesis of oxa-Michael precursor (Table S2)

| entry | oxidant | solvent | additive | yield |
|-------|---------|---------|----------|-------|
| 1     | PIDA    | MeCN    | -        | 0.3   |
| 2     | PIDA    | MeCN    | DBU, 0.5 equiv | -     |
| 3     | PIDA    | MeCN    | DTBMP, 0.5 equiv | 0.3   |
| 4     | PIDA    | MeCN    | DIPA, 0.5 equiv | -     |
| 5     | PIDA    | MeCN    | TMG, 0.5 equiv | -     |
| 6     | PIFA    | MeCN    | -        | 3.0   |
| 7     | PIFA    | MeCN    | DBU, 0.5 equiv | 2.4   |
| 8     | PIFA    | MeCN    | DTBMP, 0.5 equiv | 3.6   |
| 9     | PIFA    | MeCN    | DIPA, 0.5 equiv | 1.5   |
| 10    | PIFA    | MeCN    | TMG, 0.5 equiv | 2.4   |
| 11    | PIDA    | THF     | -        | -     |
| 12    | PIDA    | DMF     | -        | -     |
| 13    | PIDA    | DCM     | -        | 2.7   |
| 14    | PIDA    | toluene | -        | 1.8   |
| 15    | PIDA    | TFE     | -        | -     |
| 16    | PIDA    | HFP     | -        | -     |
| 17    | PIDA    | MeCN    | DM-tartrate, 50 equiv | 6.6   |
2.5 Epoxidation screening of cyclohexanedienone (Table S3)

| conditions                        | results |
|-----------------------------------|---------|
| Ph₃COOH, NaHMDS, L-DIPT, MS₄A, toluene, -40°C | N.R. |
| Ti(OIPr)₄, D-DIPT, TBHP, MS₄A, DCM, 0°C | 2.5% yield racemic |
| VO(acac)₂, TBHP, benzene, reflux | 30% yield racemic |

2.5.1 Initial asymmetric conjugate borylation (Table S4)

| conditions                        | results |
|-----------------------------------|---------|
| CuCO₃, PPh₃, H₂O                  | N.R.    |
| CuCl, NaOtBu, BInAP, MeOH/THF     | N.R.    |
| NiCl-Imidazolium, DBU, MeOH/THF   | 9% yield |
| Cu(OAc)₂, 2,2'-bipyridine, MeOH/Et₂O | 30% yield |

3. Failed routes on racemic CD ring synthesis

3.1 Giese addition approach
3.2 Reduction approach

3.2.1 Aldol approach

| Solvent | E/Z (%conversion) |
|---------|-------------------|
| THF     | 1.0/3.0 (100 on 30 mg scale) |
| PhMe    | no reaction       |
| EtO     | trace conversion  |
| MTBE    | trace conversion  |
| MeTHF   | 1.0/3.6 (45)      |
| dioxane | 1.0/4.6 (65)      |
| gyline  | 1.0/3.7 (82)      |

| Conditions | Results |
|------------|---------|
| Pd₂dba₂, dpbb, Et₃N, DMA, 100 °C | proto deOTf, two unidentified byproducts, neither of them showed cyclohexane derived peak patterns, cyclohexanol recovery |
| Pd(OAc)₂, TBAB, K₂CO₃, Et₃N, DMA, 100 °C | proto deOTf, cyclohexanol recovery |
| Pd₂dba₂, ligands below, MS3A, DMA, rt | no reaction |

| Conditions | Results |
|------------|---------|
| Pd(OAc)₂, TBAB, K₂CO₃, Et₃N, DMA, 100 °C | proto deOTf, cyclohexanol recovery |
| Pd(TFA)₂, Pyox, DCE, 60 °C | no reaction |
3.2.2 Heck approach

Substrates | Conditions | Results
--- | --- | ---
allylic OH | NiCl₂·6H₂O, dtBubpy, TBABF₄, DMF; (+)-Mg(II)·RVC, 6 mA, 2.0 F/mol | vinyl I recovery
enone | NiCl₂·6H₂O, dtBubpy, TBABF₄, DMF; (+)-Mg(II)·RVC, 6 mA, 2.0 F/mol | vinyl I recovery (major) + unidentified byproduct (C147)
enone | Ni(glym)Br₂, bpy, Mn, MgBr₂·OEt₂, DMF/THF = 1:1 | vinyl I recovery
enone | Ni(glym)Br₂, bpy, DMF, MgBr₂·OEt₂, DMF; (+)-Al(II)·RVC, 10 mA, 2.0 F/mol | vinyl I recovery (major) + unidentified byproduct (C147)

3.2.3 Sigman-Heck approach

pTBOH, MeSO₄, 100 °C; ethyl acrylate, K₂CO₃, -45 °C (no reaction @ -78 °C)

MeLi, Et₂O, 0 °C/rt
MeMgBr, DMC/PhMeTHF

B(OH)₂, B(OOMe)₂, nBuLi

THF, -78 °C

B(OH)₂, (B(OOMe)₂)₂, Pd(MeCN)₂·OTf₂, PyrOx (12 mol%)

THF, 0 °C

70%
3.2.4 Reduction condition screening (Table S5)

| Conditions | Results (dr determined by GC) |
|------------|------------------------------|
| Pt/C, H₂   | Only cis pdt                |
| PADA, pyridine, AcOH, THF | Fast decomposition |
| PADA, pyridine, AcOH, DCM | Slow and messy rxn, desired Pdt dr ~ 1:1 |
| Mn(dpdm)₂, PhSH₂, TBHP, iPrOH | Desired Pdt dr ~ 3:1 (cis:trans) |
| L-selectride, THF | 1,2 & 1,4 reduction, only cis Pdt |
| Rh(PPPh₃)₂Cl, H₂, MeOH | Very slow rxn, only cis Pdt |
| [IPh₂P(C₆H₅)₂]₂, H₂O, toluene | Mostly cis Pdt dr ~ 39:1 (cis:trans) |

| Conditions | Results |
|------------|---------|
| Mn(dpdm)₂, PhSH₂, TBHP, iPrOH | dr ~ 4:1 |
| Mn(dpdm)₂, Ph([P(oPr)₂]SiH₂)₂, TBHP, hexane | dr ~ 4:1 |
| Co([acac]₂), Ph([P(oPr)₂]SiH₂)₂, TBHP, hexane | only cis detected, other pdt detected |
| Fe(dpdm)₂, PhSH₂, TBHP, iPrOH | dr ~ 4:1 |
| Fe(dpdm)₂, Ph([P(oPr)₂]SiH₂)₂, TBHP, hexane | dr ~ 4:1 |
| Mn(dpdm)₂, Ph([P(O)]SiH₂)₂, TBHP, iPrOH | dr ~ 7:1 |

| Conditions | Results |
|------------|---------|
| 2-nitrobenzenesulfonylhydrazide, THF/iPrOH (3:1), r.t. | messy rxn, cis domain |
| Tris[NH₂]₂, Et₂O, 36 °C | not fully reacted in 21 hrs cis:trans~1:1 (bzt) |

| Conditions | Results |
|------------|---------|
| 2-nitrobenzenesulfonylhydrazide, THF/iPrOH (3:1), r.t. | NR at r.t., 45°C |
| Tris[NH₂]₂, Et₂O, 36 °C | Only hydrazine condensation |
| PADA, AcOH, pyridine, DCM, 0 °C to r.t. | NR at r.t., 40°C |
3.3 Meinwald-HAT approach via epoxy-olefin (Table S6)
4. Failed strategies for the enantioselective synthesis of the CD ring

From racemic to asymmetric synthesis

Possible solutions

Related precedents

Precedents in total synthesis

Precedents in total synthesis

First pass conditions, R = Me

| Entry | [Fe] (mol%) | Conditions | solvent | Result |
|-------|-------------|------------|---------|--------|
| 1     | Fe(acac)₃ (0.3) | PhSiH₃, 60 °C, 30 min | EtOH/CH₂OH₂ | Intractable mix |
| 2     | Fe(acac)₃ (1.0) | PhSiH₃, 60 °C, 10 min | EtOH | Intractable mix |
| 3     | Fe(acac)₃ (0.3) | PhSiH₃(OPr)₃, rt, 15 min | DCE/(CH₂OH)₂ | TBD |
| 4     | Fe(acac)₃ (0.3) | PhSiH₃(OPr)₃, 6 °C, 1 min | DCE/(CH₂OH)₂ | TBD |
| 5     | Fe(acac)₃ (0.3) | PhSiH₃(OPr)₃, rt, 1 h | DCE/(CH₂OH)₂ | TBD - rigorous O₂ removal |

Overall: glycol/EtOH not most likely unwanted side reaction with epoxide. Ruben silane better

Aprotic solvents:

| Entry | [M] (0.5 mol%) | Conditions | solvent | Result |
|-------|---------------|------------|---------|--------|
| 1     | Fe(acac)₃ | PhSiH₃(OPr)₃, rt, 1.5 h | hexane | Fe not really soluble |
| 2     | Fe(dpdt)₃ | PhSiH₃(OPr)₃, rt, 1.5 h | hexane | mainly racem |
| 3     | Mn(dpdt)₃ | PhSiH₃(OPr)₃, rt, 1 h | hexane | 1:1 SM:A |
| 4     | Mn(dpdt)₃ | PhSiH₃(OPr)₃, 60 °C, 1 h | cyclohexane | 1:3 SM:A |

Overall: Epoxide survives and desired initial M-H add/don but unproductive pathway. Enolate untouched

Asymmetric CD Ring

Current shortest route: 11 steps, 30% overall yield

Eur. J. Org. Chem. 2002, 2727

Corey, JACS. 1993, 9327

56%

Snyder, JOC, 1990, 5008

95% 2:1 dr

AD-mix-r MeSO₂NH₂ NaHCO₃

99% ee
4.1 Chiral auxiliary approach (Table S7)

Failed Conditions
2-methoxypropene, cat. PPTS, toluene, r.t. — triphosgene, pyridine, DCM, r.t.
2-methoxypropene, Amberlyst 15, toluene, r.t. — biphosgene, pyridine, r.t.
2-methoxypropene, cat. CSA, DMF, r.t. — trimethoxy orthoformate, cat. TsOH, r.t.
2-methoxypropene, cat. TsOH, DCM, r.t. — tBuS(OTf)₂, 2,6-lutidine, DCE, r.t.
2-methoxypropene, cat. TsOH, 3AMS, DMF, r.t. — tBuS(OTf)₂, 2,6-lutidine, DCE, 50 °C
AlCl₃, acetone, r.t. — 2-methoxypropene cat. TsOH, 3AMS, DMF, 70 °C
trimethyl(isopropenylxoy)silane, CCl₄(TBD) — tBuS(OTf)₂, 2,6-lutidine, DCE, 100 °C

4.2 Enzymatic approach

Enzymatic approach

Bakers Yeast

For review see: Chem. Rev. 1991, 91, 49–97

75% yield
in accordance with lit.

Substrate Preparation

Conditions
TBSCI, Et,N; mCPBA
PhMe, O₂ (1 atm)
(COCl)₂, DMF. PhMe; NaOMe, MeOH; mCPBA
CeCl₃·7H₂O, PhOH, O₂ (1 atm)
mCPBA, DCM, 0 °C

Conditions
DMP, SiO₂, DCM
IBX
(COCl)₂, DMF, Et,N, DCM -78 °C

Swern conditions: R = SH

Reduction most likely taking place
from same side in enzyme pocket

observed product

10% glucose
2 d
4.3 Asymmetric borylation approach

4.3 Epoxy opening approach, enabled by CBS, to access enantiopure diol

For epoxide ring openings of this type see: *Tetrahedron* 59, 7949.
5. Optimization of CD ring synthesis

5.1 Dihydroxylation of Enone 41

*Precedent on electron deficient olefins with AD-mix α or β:*

*with AD-mix:*

| Structure | Yield | ee  |
|-----------|-------|-----|
| ![Structure 1](image1) | 79%  | 82% ee |
| ![Structure 2](image2) | 74%  | 92% ee |
| ![Structure 3](image3) | 78%  | 50% ee |
| ![Structure 4](image4) | >60% | >90% ee |
| ![Structure 5](image5) | 73%  | 98% ee |
**With AD-mix (Table S8)**

![Chemical reaction diagram]

| Entry | Conditions | solvent | Result |
|-------|------------|---------|--------|
| 1     | OsO₄ (cat.), NMO, citric acid | BuOH/H₂O/acetone | 81% y |
| 2     | ad-mix α (0.2M) | BuOH/H₂O (1:1) | 100% rcs, precipitate |
| 3     | ad-mix α (0.2M) + MeSO₄NH₂ | BuOH/H₂O (1:1) | 100% rcs, precipitate |
| 4     | ad-mix α (0.2M) + MeSO₂NH₂ | BuOH/H₂O/acetone | 100% rcs |
| 5     | ad-mix α (0.1M) | BuOH/H₂O (1:1) | 100% rcs |
| 6     | ad-mix α (0.1M) + MeSO₂NH₂ | BuOH/H₂O (1:1) | 100% rcs |
| 7     | ad-mix α - (0.05M) | BuOH/H₂O (1:1) | 100% rcs |
| 8     | ad-mix α - (0.05M) - another 0.5 equiv ad-mix | BuOH/H₂O (1:1) | 100% rcs |
| 9     | ad-mix β - (0.2M) | BuOH/H₂O (1:1) | 100% rcs, precipitate |
| 10    | ad-mix β - (0.1M) | BuOH/H₂O (1:1) | 100% rcs |
| 11    | ad-mix β - (0.05M) | BuOH/H₂O (1:1) | 100% rcs |
| 12    | ad-mix β - (0.05M) - another 0.5 equiv ad-mix | BuOH/H₂O (1:1) | 100% rcs |

![Chemical reaction diagram]

| Entry | Conditions | solvent | Result |
|-------|------------|---------|--------|
| 1     | ad-mix α (0.2M) | BuOH/H₂O (1:1) | 100% rcs, precipitate |
| 2     | ad-mix α (0.2M) + MeSO₂NH₂ | BuOH/H₂O (1:1) | 100% rcs, precipitate |
| 3     | ad-mix α (0.2M) + MeSO₂NH₂ | BuOH/H₂O/acetone | 100% rcs |
| 4     | ad-mix α (0.1M) | BuOH/H₂O (1:1) | 100% rcs |
| 5     | ad-mix α (0.1M) + MeSO₂NH₂ | BuOH/H₂O (1:1) | 100% rcs |
| 6     | ad-mix α (0.05M) | BuOH/H₂O (1:1) | 100% rcs |
| 7     | ad-mix α (0.05M) + MeSO₂NH₂ | BuOH/H₂O (1:1) | 100% rcs |
**Sharpless conditions revisited:**

**Hat Approach to CD Ring**

At a glance summary:

- **[O]:** NMO, K$_3$Fe(CN)$_6$, R$_2$NO, O$_2$, NaClO$_2$
- NMO: full conv./ no ee
- K$_3$Fe(CN)$_6$: 63% ee

L: (DHQD)$_2$-PHAL, -AQN, -PYR

Additive: • NaHCO$_3$ > K$_2$CO$_3$
- AD-mix-q has K$_2$CO$_3$-No Rxn
- MeSO$_3$NH$_2$: critical
- Me$_3$N$_2$NOAc helps catalyst turnover

Solvant: tBuOH/H$_2$O: up to 80% ee
- conv: 2:1 SM: Pd at 0 °C

---

**Entry** | **Ligand (L)** | **time** | **Result** |
--- | --- | --- | --- |
1 | (DHQD)$_2$-PTHAL | 5 h | 14% yield, 55% ee |
2 | (DHQD)$_2$-PTHAL | 15 h | 42% yield, 57% ee |
3 | (DHQD)-p-Cl-benzoate | 15 h | 32% yield, 37% ee |
4 | (DHQD)$_2$-AQN | 15 h | yield ND, 30% ee |
5 | (DHQ)$_2$PYR | 15 h | yield ND, 30% ee |
6 | (DHQ)$_2$PYR: + HFIP | 15 h | 100% rcsm
7 | (DHQ)$_2$PYR @ -95 °C | 15 h | ND |
8 | (DHQD)$_2$-PTHAL @ -95 °C | 15 h | ND |

**For absolute stereochemistry but not crystalline**

- **RCO$_2$H DCC DCM**
- R = p-NO$_2$-C$_6$H$_4$

**Currently scaling up**

- Solid
- For enantioenrichment
**Optimization (Table S9)**

### Initial and Oxidant Screening

**AD on Enone**

\[ \text{K}_2\text{OsO}_3(\text{OH})_3, \text{ Ox. , L} \rightarrow \text{MeSO}_2\text{NH}_2, \text{ solvent } 14 \text{ h} \]

| Entry | (L)         | Oxidant          | Conditions                  | Result                  |
|-------|-------------|------------------|-----------------------------|-------------------------|
| 1     | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone (1:3)      | full consumption, 6% ee  |
| 2     | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone (1:3)      | full consumption, -6% ee |
| 3     | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone-NaHCO\(_3\) buffered (1:3) | 1:4 prod:SM, 11% ee |
| 4     | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone-NaHCO\(_3\) buffered (1:3) | full consumption, -7% ee |
| 5     | (DHQD)_2PHAL | NMO              | H\(_2\)O/THF (1:1)          | 1:1 prod:SM, 5% ee      |
| 6     | (DHQD)_2PYR  | NMO              | H\(_2\)O/THF (1:1)          | full consumption, -3% ee |
| 7     | (DHQD)_2PHAL | NMO              | H\(_2\)O/MBUOH (1:1)        | full consumption, 0% ee  |
| 8     | (DHQD)_2PHAL | NMO              | H\(_2\)O/MBUOH (1:1)        | full consumption, -2% ee |
| 9     | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone (1:3)-slow add'n enone | 1:2 prod:SM, 19% ee |
| 10    | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone (1:3)-slow add'n NMO | TBD                      |
| 11    | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone-K\(_2\)CO\(_3\) (3 eq) (1:3) | 1:10 prod SM, TBD ee |
| 12    | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O/acetone (1:3)      | No rxn                  |
| 13    | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O/acetone(1:3)+NaHCO\(_3\) | 1:10 prod:SM, 63% ee  |
| 14    | (DHQD)_2PHAL | NaClO\(_2\)      | H\(_2\)O/acetone (1:3)      | No rxn                  |
| 15    | (DHQD)_2PHAL | NaClO\(_2\)      | H\(_2\)O/acetone(1:3)+NaHCO\(_3\) | <5% prod, 0% ee        |
| 16    | (DHQD)_2PHAL | Me\(_3\)NO       | H\(_2\)O/acetone (1:3)      | <5% prod                |
| 17    | (DHQD)_2PHAL | O\(_2\) (1 atm)  | H\(_2\)O/acetone pH = 10.4 (1:3) | No rxn                  |

### Initial and Oxidant Screening

**AD on Enone**

\[ \text{K}_2\text{OsO}_3(\text{OH})_3, \text{ L [O]} \rightarrow \text{MeSO}_2\text{NH}_2, \text{ solvent } 14 \text{ h} \]

| Entry | (L)         | Oxidant          | Conditions                  | Result                  |
|-------|-------------|------------------|-----------------------------|-------------------------|
| 1     | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone (1:3)      | full consumption, 6% ee  |
| 2     | (DHQD)_2PHAL | NMO              | H\(_2\)O/acetone (1:3)-slow add'n enone | 1:2 prod:SM, 26% ee |
| 3     | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O/acetone-slow add'n enone, NaHCO\(_3\) | 1:8 prod:SM, TBD% ee |
| 4     | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O/pH = 10/acetone (1:3) | <5% prod, TBD% ee |
| 5     | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O/pH = 12/acetone (1:3) | 1:8 prod:SM, 63% ee  |
| 6     | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O/acetone(1:3)+K\(_2\)CO\(_3\)/ Os(5 mol%) | No rxn                  |
| 7     | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O/acetone(1:3)+NaHCO\(_3\)/ Os(5 mol%) | 1:8 prod:SM, 54% ee  |
| 8     | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | AD-mix β + Os(5 mol%) | <5% prod, TBD% ee |
| 9     | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O(pH=12)/acet/NaHCO\(_3)/Os(5 mol%) | 1:5 prod:SM, 65% ee  |
| 10    | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O(pH=12)/acet/NaHCO\(_3)/Os(10 mol%) | 1:3 prod:SM, 68% ee |
| 11    | (DHQD)-benzotriazolate | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O(pH=12)/acet/NaHCO\(_3)/Os(10 mol%) | 1:8 prod:SM, TBD% ee |
| 12    | (DHQD)_2-QQ | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O(pH=12)/acet/NaHCO\(_3)/Os(10 mol%) | 1:15 prod:SM, TBD% ee |
| 13    | (DHQD)_2PYR | K\(_3\)Fe(CN)\(_6\) | H\(_2\)O(pH=12)/acet/NaHCO\(_3)/Os(10 mol%) | 1:8 prod:SM, TBD% ee |
| 14    | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | as above, + 2,6-lutidine | no real rate enhancement |
| 15    | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | as above, + N-Me-Morpholine | no real rate enhancement |
| 16    | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | as above, + DBU | no real rate enhancement |
| 17    | (DHQD)_2PHAL | K\(_3\)Fe(CN)\(_6\) | as above, + Et\(_3\)N | no real rate enhancement |
5.2 Optimization of methylation (Table S10)

| Entry | Oxidant | Conditions | Result |
|-------|---------|------------|--------|
| 1     | K2[Fe(CN)6]3 | neutral pH (H2O) | 3:1 SM:Prod, 73% ee |
| 2     | K2[Fe(CN)6]3 | H2O(pH=10) | 3:1 SM:Prod, 77% ee |
| 3     | K2[Fe(CN)6]3 | H2O(pH=12) | 10:1 SM:Prod, 72% ee |
| 4     | K2[Fe(CN)6]3 | H2O(pH=14) | trace prod, ee ND |
| 5     | K2[Fe(CN)6]3 | neutral pH (H2O) + Me3NOAc | 2:1 SM:Prod, ee TBD |
| 6     | K2[Fe(CN)6]3 | H2O(pH=12) + Me3NOAc | 2:1 SM:Prod, 76% ee |
| 7     | K2[Fe(CN)6]3 | H2O(pH=12) + Me3NOAc, 0 °C | 3:1 SM:Prod, 81% ee |
| 8     | K2[Fe(CN)6]3 | neutral pH (H2O), 0 °C | 3:1 SM:Prod, 77% ee |
| 9     | K2[Fe(CN)6]3 | H2O(pH=12) | trace prod, 32% ee |
| 10    | K2[Fe(CN)6]3 | H2O(pH=12) | 5:1 (solvol?) SM:Prod, 52% ee |
| 11    | K2[Fe(CN)6]3 | H2O(pH=12) | 3:1 SM:Prod, 34% ee |
| 12    | K2[Fe(CN)6]3 | H2O(pH=12) + Me3NOAc, 0 °C + O2 | no enhancement |
| 13    | K2[Fe(CN)6]3 | H2O(pH=12) + Me3NOAc, 0 °C + H2O2 | no enhancement |
| 14    | K2[Fe(CN)6]3 | tBuOH/H2O/Acetone | 10:1 SM:Prod,  |
| 15    | K2[Fe(CN)6]3 | tBuOH/H2O/PhMe | 1:1 SM:Prod, ee TBD |
| 16    | K2[Fe(CN)6]3 | tBuOH/H2O/DCM | 1:1 SM:Prod, ee TBD |
| 17    | K2[Fe(CN)6]3 | H2O(pH=10) + Citric acid | No rxn |

**Conditions**

- **MePh2PBr, LDA, THF, r.t.** No reaction after 3 hrs
- **MePh2PBr, LDA, THF, 60 °C** Poor mass balance, messy mixture
- **MePh2PBr, LDA, THF, 80 °C** Poor mass balance, cleaner reaction, 6% yield
- **MePh2Br (3 equiv), nBuLi, THF, r.t.** SM all consumed, no product detected
- **MePh2Br (3 equiv), nBuLi, THF, 80 °C** SM all consumed, no product detected
- **Me3PPPh3 (2.1 equiv), KO8Bu, THF, r.t.** No reaction
- **Lambardo’s Rgnt, THF/DCM, 0 °C to r.t.** No reaction
- **TiCl4, CH3I, Zn, THF, 0 °C to r.t.** No reaction
- **Tebbe’s Rgnt, THF, -78 °C to r.t.** Methylation of ethyl ester
- **Cp2TiMe3 (1 equiv), toluene, 65 °C** 1,2 addition went on smoothly, elimination gave messy mixture, no desired product detected
- **Cp2TiMe3 (3 equiv), toluene, 65 °C** SM not fully consumed, desired product detected
- **SM fully consumed**
5.2 Optimization of HAT reductive annulation (Table S11)

| Conditions                                              | Yield* |
|---------------------------------------------------------|--------|
| Fe(acac)₃(0.4 equiv), PhSi(OrPr)H₂, DCE/CH₂OH2(2:1)     | 38%    |
| Fe(acac)₃(0.4 equiv), PhSi(OrPr)H₂, EtOAc/PrOH           | N.D.   |
| Fe(acac)₃(0.4 equiv), PhSi(OrPr)H₂, EtOH                | 35%    |
| Fe(acac)₃(0.4 equiv), PhSi(OrPr)H₂, THF/EtOH(15:1)      | 34%    |
| Fe(acac)₃(0.4 equiv), PhSi(OrPr)H₂, Na₂HPO₄, EtOH       | 34%    |
| Fe(dpmp)(0.4 equiv), PhSi(OrPr)H₂, DCE/CH₂OH2(2:1)      | 52%    |
| Fe(acac)₃(0.4 equiv), PhSH₂, DCE/CH₂OH2(2:1)            | N.D.   |
| Fe(acac)₃(0.4 equiv), PhSH₂, DCE/CH₂OH2(2:1)            | N.D.   |
| Fe(acac)₃(0.4 equiv), PhSH₂, EtOH                       | N.D.   |
| Fe(acac)₃(0.4 equiv), PhSH₂, THF/EtOH(10:1)             | N.D.   |
| Fe(acac)₃(0.4 equiv), PhSH₂, Na₂HPO₄(2.5 equiv), EtOH   | N.D.   |
| Fe(dpmp)(0.4 equiv), PhSH₂, DCE/CH₂OH2(2:1)             | N.D.   |
| Fe(acac)₃(2.0 equiv), PhSi(OrPr)H₂, DCE/CH₂OH2(2:1)     | 66%    |
| Mn(acac)₃(2.0 equiv), PhSi(OrPr)H₂, EtOH                | 20%    |
| Co(acac)₃(2.0 equiv), PhSi(OrPr)H₂, EtOH                | N.D.   |
| Fe(acac)₃(0.4 equiv), PhSi(OrPr)H₂, styrene(1.0 equiv), DCE/CH₂OH2(2:1) | 55% |
| Fe(dpmp)(0.4 equiv), PhSi(OrPr)H₂, styrene(1.0 equiv), DCE/CH₂OH2(2:1) | N.D. |
| Fe(acac)₃(0.4 equiv), PhSH₂, styrene(1.0 equiv), DCE/CH₂OH2(2:1) | 12% |
| Fe(dpmp)(0.4 equiv), PhSi(OrPr)H₂, DCE/CH₂OH2(2:1)      | 57%    |
| Fe(acac)₃(2.0 equiv), PhSi(OrPr)H₂, styrene(1.0 equiv), DCE/CH₂OH2(2:1) | 29% |
| Fe(acac)₃(0.4 equiv), PhSi(OrPr)H₂, styrene(0.4 equiv), DCE/CH₂OH2(2:1) | 42%b |

*5 mg scale, NMR yield unless specified; b) 100 mg scale isolated yield

6. Decarboxylative cross coupling screening

**[M] sources:** NiCl₂-glyme, Ni(TMHD)₂, Fe(acac)₃

**Ligand:** bipy, bipy-derivatives, bathophen, dpz

**Solvent:** THF/McCN, DMF, DMA, NMP, DMFU, DMSO, DMI

**Temp:** rt, 0 °C, 60 °C

OA*: TCHP, NiHPI, HATU (in situ activation)
Optimization (Table S12)

**Model substrates**

- 40% yield, dr = 2:1
- <5% yield, dr = 3:1
- 11% yield, dr > 20:1
- <5% yield, dr = 1:1

**In-situ generation**

1. ZnCl₂, ZnCl₂, Dibal
2. ZnCl₂

**[M] sources:** NiCl₂·6H₂O, NiCl₂·glyme, Ni(acac)₂, Ni(TMHD)₂, FeBr₃, Fe(acac)₃, CoBr₂

**Ligand:** bipy, bipy-derivatives, bathophen, dppz

**Solvent:** NMP, DMF, DMA, THF, PhMe, MeNO₂

**Temp:** rt, 30 °C, 0 °C, 50 °C, 80 °C

**OA·**: TCNHP, NHPI

| [M] (mol%) | Ligand | Variations | Yield | d.r. |
|------------|--------|------------|-------|------|
| NiCl₂ (20) | 2,2'-bipy | zinc reagent (2:0) | 24% | 2:1 |
| NiCl₂ (20) | 2,2'-bipy | zinc reagent (2:0), 50 °C | 28% | 2:1 |
| NiCl₂ (40) | 2,2'-bipy | zinc reagent (4:0), rt | 41% | 2:1 |
| CoBr₂ | - | zinc reagent (4:0), rt | - | - |
| Fe(acac)₃ | dppz | zinc reagent (4:0), rt | - | - |

**[M] (mol%)** | Variations | solvent | Yield | d.r. |
|------------|------------|---------|-------|------|
| NiCl₂ (40) | zinc reagent (4:0), rt, MgBr₂·OEt₂, 12 h | THF/NMP | 5% | 2:1 |
| NiCl₂ (40) | zinc reagent (4:0), 50 °C, MgBr₂·OEt₂, 12 h | THF/NMP | 9% | 2:1 |
| NiCl₂ (30) | zinc reagent (3:0), MgBr₂·OEt₂, rt 12 h | THF/DMF | 32% | 2:1 |
| NiCl₂ (30) | zinc reagent (3:0), 50 °C, MgBr₂·OEt₂, 12 h | THF/DMF | 28% | 2:1 |
| NiCl₂ (30) | zinc reagent (3:0), MgBr₂·OEt₂, 12 h | THF/MeCN | trace | - |
Model Studies – Probing C20 Diastereoselectivity (Table S13)

<5% yield
dr not determined

42% yield
dr = 1.4:1

13% yield
dr = 1:1.4

<5% yield
dr not determined
7. Experimental Procedures

General remarks

All reactions were carried out under an inert argon atmosphere with dry solvents under anhydrous conditions unless otherwise stated. Dry acetonitrile (MeCN), dichloromethane (DCM), diethyl ether (Et2O), tetrahydrofuran (THF), toluene (PhMe), dimethylformamide (DMF), benzene, and triethylamine (TEA) were obtained by passing the previously degassed solvents through activated alumina columns. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (1H NMR or LCMS) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F254), using UV light as the visualizing agent and/or phosphomolybdic acid and heat as a developing agent. Flash silica gel chromatography was performed using E. Merck silica gel (60, particle size 0.043 – 0.063 mm). NMR spectra were recorded on Bruker DRX600 and AMX-400 instruments and were calibrated using residual undeuterated solvent as an internal reference (chloroform-d: 1H NMR δ = 7.26 ppm, 13C NMR δ = 77.16 ppm). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time-of-flight (ESI-TOF) reflectron experiments.
To a stirring solution of \( p \)-cresol (10.8 g, 100 mmol) in MeCN/H\( \text{H}_2\text{O} \) (530 mL, 0.2 M, 3:1 mixture) at 0 °C was added Ph\( \text{I(OAc)}_2 \) (35.6 g, 110 mmol, 1.1 equiv.). The reaction was stirred at 0 °C until complete consumption of starting material was observed by TLC (approx. 3 hours), after which EtOAc (200 mL) and sat. NaHCO\( _3 \) (200 mL) were added. The layers were separated, followed by extraction of the aqueous layer with EtOAc (4 \times 150 mL). The combined organics were washed with brine (200 mL), dried over Na\( \text{2SO}_4 \), filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash chromatography eluting with hexanes/ethyl acetate (5:1 to 2:1) to provide 9.08 g (69.8 mmol, 70% yield) of SI-1 as an orange solid. SI-1 is in accordance with literature values.\(^1\)

**Physical State**: orange-yellow solid.

**TLC**: \( R_f = 0.2 \) (3:1 hexanes:EtOAc, UV/Vis).

\(^1\)H NMR (600 MHz, CDCl\( _3 \)) \( \delta \) 6.88 (d, \( J = 10.1 \) Hz, 1H), 6.13 (d, \( J = 10.1 \) Hz, 1H), 1.48 (s, 2H).

\(^{13}\)C NMR (151 MHz, CDCl\( _3 \)) \( \delta \) 185.4, 152.0, 127.5, 67.4, 26.9.

\(^1\)Chem. Commun., 2010, 46, 701–703.
To a stirring solution of SI-1 (9.08 g, 69.8 mmol) in DMF (228 mL, 0.3 M) was added imidazole (11.9 g, 174.5 mmol, 2.5 equiv.) followed by triethylchlorosilane (12.9 mL, 76.8 mmol, 1.1 equiv.) at rt. The reaction was heated and stirred at 40 °C until complete consumption of starting material was observed by TLC (approx. 4 h). The reaction was quenched by the addition of hexane (200 mL) followed by saturated NaHCO₃ aqueous solution (200 mL). The layers were separated, and the aqueous phase was extracted with hexane (3 x 150 mL). The combined organic extracts were then washed with 5% LiCl aqueous solution (1 x 200 mL), dried (Na₂SO₄), and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (1:0 to 20:1) to give 28a (13.3 g, 80%) as a pale-yellow oil.

**Physical State**: pale-yellow oil.

**TLC**: Rₜ = 0.92 (1:1 hexanes:EtOAc, UV/Vis).

**¹H NMR (600 MHz, CDCl₃)** δ 6.86 (d, J = 10 Hz, 1H), 6.11 (dd, J = 10 Hz, 1H), 1.43 (s, 3H), 0.91 (t, J = 7.9 Hz, 1H), 0.54 (q, J = 7.9 Hz, 1H).

**¹³C NMR (151 MHz, CDCl₃)** δ 185.6, 153.6, 126.9, 69.4, 29.7, 6.9, 6.2.

**HRMS (ESI-TOF)**: calc’d for C₁₃H₂₃O₂Si [M+H]⁺: 239.1467, found 239.1463.
Representative Graphical Supporting Information for the Synthesis of 28a (5 mmol scale).

(Left) Reagents used in the reaction. (Center) Reaction vessel was flame-dried under vacuum and put under Ar. (Right) Addition of 4-hydroxy dienone (5 mmol) was then added.

(Left) Dry DMF was then added to reaction mixture. (Center) Imidazole was then quickly added to the reaction mixture. (Right) Dropwise addition of triethylchlorosilane at rt.
The reaction mixture was then heated to 40 °C. (Center) After 4 hours the reaction was diluted with EtOAc. (Left) The reaction was subsequently quenched with NaHCO₃.

The layers were separated, and the organic layer was washed with H₂O (3 x 20 mL). (Center) Reaction mixture was filtered over a small pad of Na₂SO₄. (Right) Monitoring the reaction by TLC: Rₜ = 0.92 (1:1 hexanes:EtOAc): Left lane: Center lane: Co-spot, Right lane: Crude reaction mixture.
To a flame-dried 500 mL round-bottom flask was added Cu(OAc)$_2$·H$_2$O (363 mg, 2.0 mmol, 5 mol%) and pybox ligand L1 (723 mg, 2.4 mmol, 6 mol%). The flask was placed under vacuum and backfilled with Ar (repeated 3x) after which Et$_2$O (200 mL, 0.2 M) was added and the reaction mixture stirred for 20 min at rt. B$_2$pin$_2$ (30.5 g, 120 mmol, 3.0 equiv.) was then added and the reaction mixture was stirred for an addition 30 min until a brown color was observed (see graphical guide). A solution of enone 28a (9.54 g, 40 mmol) in Et$_2$O (10 mL) was added (over 5 min) followed by a bolus addition of MeOH (4.1 mL, 100 mmol, 2.5 equiv.) The reaction stirred at rt for 48 h after which additional MeOH (2 mL) was added and allowed to stir for additional 24 h. To this brown suspension was added 1 M HCl aqueous solution (90 mL) until the organic phase became a yellow solution. The layers were separated, and the aqueous phase extracted with EtOAc (3 x 100 mL). The combined organic layer was washed with saturated NaHCO$_3$ aqueous solution (100 mL) followed by a saturated aqueous NaCl solution (100 mL), then dried (Na$_2$SO$_4$). The solvent was removed under reduced pressure to obtain yellow oil. The product 29 is semi-stable for storage and was utilized in the next step immediately.

Physical State: colorless oil.

TLC: R$_f$ = 0.39 (9:1 hexanes:EtOAc, UV/Vis).

$^1$H NMR (600 MHz, CDCl$_3$) δ 6.76 (d, $J$ = 8.1 Hz, 1H), 2.42 (m, 1H), 5.79 (d, $J$ = 8.1 Hz, 1H), 2.63 (dd, $J$ = 13.8, 3.6 Hz, 1H), 2.38 (dd, $J$ = 13.8, 8.8 Hz, 1H), 1.96 (dd, $J$ = 8.8, 3.6 Hz, 1H), 1.47 (s, 3H), 1.21 (s, 12H), 0.94 (t, $J$ = 6.4 Hz, 9H), 0.61 (q, $J$ = 6.4 Hz, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 199.7, 156.8, 127.1, 83.6, 72.7, 37.3, 26.5, 24.9, 24.8, 7.2, 6.9.

HRMS (ESI-TOF): calc’d for C$_{19}$H$_{35}$BO$_4$Si [M+H]: 367.2470, found 367.2481.
Representative Graphical Supporting Information for Bpin 29 (5 gram scale).

(Left) Reagents used in the reaction. (Center) Reaction vessel was flame-dried under vacuum and put under Ar. (Right) Pybox ligand and Cu(OAc)$_2$ were put under Ar and Et$_2$O was added.

(Left) After stirring for 15 min, B$_2$pin$_2$ was quickly added. (Center) Reaction mixture stirring after 5 min. (Right) Stirring after 10 min.

(Left) Reaction mixture after stirring for 30 min. (Center) Enone 28a was added as a solution in Et$_2$O. (Right) Subsequent bolus addition of MeOH.
(Left) After completion, EtOAc was added. (Center) Addition of H₂O and 1 M HCl. (Right) Initial reaction color prior to mixing.

(Left) Color of reaction mixture after mixing followed by extraction with EtOAc. (Right) Monitoring the reaction by TLC: Rᵣ = 0.39 (9:1 hexanes:EtOAc): Left lane: Enone 28a, Center lane: Co-spot, Right lane: Crude reaction mixture.
A solution of 29 (theoretical quantity 81.8 mmol) in THF (400 mL, 0.2 M) was cooled to 0 °C. To this solution was added a suspension of NaBO₃·4H₂O (25.2 g, 164 mmol, 2.0 equiv.) in H₂O (400 mL, 0.4 M) in a portionwise manner. The reaction was warmed rt and vigorously stirred at rt until complete consumption of starting material was observed by TLC (approx. 1.5 h), after which the reaction mixture was diluted with EtOAc (200 mL). The layers were separated, and the organic phase was extracted with EtOAc (3 x 100 mL). The combined organic layer was washed with a saturated aqueous NaCl solution (150 mL), then dried (Na₂SO₄). The solvent was removed under reduced pressure to obtain yellow oil. The product is unstable for storage and was utilized in the next step immediately.

The yellow oil was dissolved in anhydrous THF (500 mL). To this yellow solution was added a solution of TBAF (98.2 mL, 98.2 mmol, 1.0 M in THF) at rt. Complete consumption of the starting material was observed in 3 h. The reaction mixture was concentrated under reduced pressure to obtain orange oil. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (1:1 to 1:3) to give 30 (5.21 g, 46% over 3 steps) as a white solid.

**Physical State:** colorless oil.

**TLC:** Rₛ = 0.19 (1:2 hexanes/EtOAc, UV/Vis).

**¹H NMR (600 MHz, CDCl₃)** δ 6.83 (d, J = 10.1 Hz, 1H), 5.93 (d, J = 10.1 Hz, 1H), 4.13 (dd, J = 12.1, 5.1 Hz, 1H), 2.81 (dd, J = 17.0, 5.1 Hz, 1H), 2.45 (dd, J = 17.0, 12.1 Hz, 1H), 2.34 (s, 1H), 1.62 (s, 1H), 1.42 (s, 3H).

**¹³C NMR (151 MHz, CDCl₃)** δ 197.5, 154.6, 128.3, 73.7, 73.3, 43.3, 20.6.

**HRMS (ESI-TOF):** calc’d for C₇H₁₁O₃ [M+H]⁺: 143.0703, found 143.0704.
Representative Graphical Supporting Information for the Synthesis of Diol 30 (1 mmol scale).

(Left) Addition of NaBO₃ (aq.) to a stirring THF solution of Diol 30 at rt. (Center) Diluting the reaction with brine after consumption of 29 (30 min). (Right) Dilution via addition of THF.

(Left) The layers were separated, and organic layer kept, and transferred to a separate reaction flask. (Center) Addition of TBAF to the oxidation product of 29. (Right) Monitoring the reaction by TLC: Left TLC plate: Left lane: BPin 29, Center lane: Co-spot, Right lane: crude reaction mixture showing intermediate alcohol Rₖ = 0.37 (4:1 hexanes/EtOAc). Right TLC plate: Left and Center lane: Crude reaction mixture after addition of TBAF indicating full conversion of alcohol intermediate and diol formation.
Chiral SFC analysis of diol 30

**Fig. 1.** Racemic Sample of 30

**Fig. 2.** Undesired Enantiomer of 30 with (S,S)-Pybox (94% ee).
Fig. 3. Desired Enantiomer of 30 with \((R,R)\)-Pybox (93% ee). Conditions: Diol 30 was analyzed on a Waters UPC2 SFC with a Daicel IA column (3 mm, 4.6x250 mm) under isocratic conditions (4 mL/min, 15% MeOH / CO\(_2\), 1600 psi backpressure) at 30 °C. The enantiomers were detected by UV light (220 nm).
Preparation of alkynyl Grignard: A flame-dried 500 mL round-bottom flask was put under vacuum and backfilled with Ar (repeated 3X). THF (134 mL, 0.2 M) was added followed by trimethylsilylacetylene (3.8 mL, 27 mmol, 3.8 equiv.). The reaction mixture was cooled to 0 °C after which EtMgBr (9.2 mL, 27 mmol, 3.8 equiv.) was dropwise added and stirred for 10 min. The ice bath was removed, and the reaction mixture stirred for 5 min at rt and then heated (pre-set oil bath) to 50 °C for 1 h (note: or until gas evolution ceases). The reaction mixture was cooled to rt by removal of the oil bath, stirred for 5 min, then cooled to 0 °C after which a solution of enone 30 (1 g, 7 mmol, 1.0 equiv.) in THF (36 mL, 0.2 M) was dropwise added over 15 min. The reaction mixture was allowed to reach ambient temperature in the ice-bath and stirred for an additional 1 h at rt. The reaction mixture was quenched by the addition of 1 M HCl (50 mL) and diluted by the addition of EtOAc (100 mL). The layers were separated, and the aqueous phase extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with saturated aqueous NaCl (10 mL), dried (Na2SO4), and concentrated under reduced pressure to give 31 (1.5 g, 91%) as a colorless oil which was used without further purification.

Physical State: yellow oil.

TLC: Rf = 0.74 (1:1 hexanes:EtOAc, PMA).

1H NMR (600 MHz, CDCl3) δ 4.12 (t, J = 3.9 Hz, 1H), 3.16 (dd, J = 11.3, 5.1 Hz, 1H), 3.03 (dd, J = 14.9, 3.7 Hz, 1H), 2.68 (dd, J = 14.9, 11.3 Hz, 1H), 2.49 (ddd, J = 14.9, 5.1, 2.2 Hz, 1H), 2.32 (ddd, J = 14.9, 4.4, 2.2, Hz, 1H), 2.11 (s, 1H), 1.86 (s, 1H), 1.48 (s, 3H), 0.18 (s, 9H).

13C NMR (151 MHz, CDCl3) δ 207.6, 104.6, 90.2, 75.0, 71.8, 45.4, 42.8, 37.4, 24.3, 0.17.

HRMS (ESI-TOF): calc’d for C14H23O3 [M+H]+: 241.1260, found 241.1255.
Representative Graphical Supporting Information of Ketone 31 (0.1 mmol scale).

(Left) Reagents used in the reaction. (Center) Addition of EtMgBr to ethynyltrimethylsilane. (Right) After 5 min, at rt, the reaction mixture was heated to 50 °C.

(Left) Gas evolution is initially observed. (Center) A new reaction vessel was flame dried. (Right) 0.3 mL of the freshly prepared alkynyl Grignard (0.33 M) was transferred under Ar.

(Left) Addition of diol 30 in THF over 5 min at 0 °C. (Center) After reaching rt, H₂O was added (1.0 mL) followed by 1 M HCl (1.0 mL, not shown). (Right) EtOAc (3 mL) was then added.
To a stirring solution of 31 (1.68 g, 7 mmol, 1 equiv.) in MeOH (200 mL 0.04M) at 0 °C was added NaBH₄ (530 mg, 14 mmol, 2.0 equiv.). The reaction was stirred at 0 °C until complete consumption of starting material was observed by TLC (approx. 2h), after which the reaction mixture was carefully quenched by the addition of H₂O (100 mL). The biphasic solution was concentrated under reduced pressure to remove any organic, after which 150 mL was added. The layers were separated after which the aqueous phase was extracted with EtOAc (3 x 50 mL). (Note: Due to the high polarity of 32, multiple extractions with EtOAc are recommended). The combined organic extracts were washed with saturated aqueous NaCl (10 mL), dried (Na₂SO₄), and concentrated under reduced pressure to give 32 (1.7 g, 90%) as a white amorphous solid which was used without further purification.

**Physical State**: white amorphous solid.

**TLC**: Rᵣ = 0.14 (1:2 hexanes:EtOAc, PMA).

**¹H NMR (600 MHz, CDCl₃)** δ 3.97 (ddt, J = 13.4, 8.8, 3.9 Hz, 1H), 3.90 (dd, J = 5.2, 3.0 Hz, 1H), 2.80 (dd, J = 10.7, 4.2 Hz, 1H), 2.01 – 1.95 (m, 2H), 1.87 – 1.80 (m, 2H), 1.33 (s, 3H), 0.17 (s, 9H).

**¹³C NMR (151 MHz, CDCl₃)** δ 106.5, 89.13, 73.09, 71.71, 65.64, 37.86, 36.76, 36.46, 23.89, 0.19.
Representative Graphical Supporting Information for the Synthesis of Triol 32 (0.1 mmol scale).

(Left) Addition of MeOH to ketone 31. (Center) NaBH₄ was added to the reaction mixture at 0 °C. (Right) After stirring for 2 h, H₂O was added followed by 1 M HCl (not shown).

(Left) Addition of EtOAc. (Center) Layers separated and multiple extractions with EtOAc. (Right) Concentration of organics and carried through to subsequent step.
To a stirring solution of triol 32 (1.7 g, 7 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (70 mL, 0.1 M) under argon at 0 °C, was dropwise added 2,6-lutidine (2.4 mL, 21 mmol, 3.0 equiv.), followed by freshly distilled TBSOTf dropwise (4.1 mL, 21 mmol, 3.0 equiv.). The reaction mixture was allowed to warm to room temperature by removal of the ice-bath and stirred for an additional 1 h after which NMR analysis of an aliquot (50 µL) revealed full consumption of 32 (note: reaction color changed to yellow). The mixture was then diluted with CH$_2$Cl$_2$ (50 mL) and quenched by the addition of the reaction mixture to ice-cold saturated NaHCO$_3$ (50 mL) at 0 °C. The layers were separated, followed by extraction with CH$_2$Cl$_2$ (3 x 20 mL). The combined organic extracts were washed with saturated aqueous NaCl (10 mL), dried (Na$_2$SO$_4$), and concentrated under reduced pressure to provide 33 (90%) as a colorless oil. 

**Physical State:** colorless oil.

**TLC:** R$_f$ = 0.4 (10:1 hexanes:EtOAc, Stained by p-Anisaldehyde, pink).

**$^1$H NMR (600 MHz, CDCl$_3$)** δ 3.91 (tt, $J$ = 11.1, 4.5 Hz, 1H), 3.73 (dd, $J$ = 3.5, 2.2 Hz, 1H), 2.74 (dd, $J$ = 13.0, 4.0 Hz, 1H), 1.90 – 1.67 (m, 4H), 1.28 (s, 3H), 0.89 (s, 9H), 0.87 (s, 9H), 0.16 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 107.1, 87.7, 74.6, 71.7, 65.6, 38.4, 37.2, 35.8, 26.0, 25.9, 18.2, 18.0, 0.3, -4.2, -4.5, -4.5, -5.0.
To a stirring solution of 33 (1.65 g, 3.5 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (50 mL, 0.07 M) at 0 °C was added a solution of pyridine (35, 0.2 M), followed by the addition of thionyl chloride (5 mL, 35 mmol, 10 equiv.) and stirred overnight at 0 °C (note: reaction mixtures changes to red color). Reaction mixture was then diluted with CH$_2$Cl$_2$ (50 mL) and quenched by the addition of the reaction mixture to an ice-cold saturated NaHCO$_3$ solution (50 mL) at 0 °C (note: after 30 min, gas evolution ceased). The reaction mixture was extracted with CH$_2$Cl$_2$ (3 x 50mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (50:1) to give SI-2 as a yellow oil. SI-2 is in accordance with all literature values\(^2\).

**Physical State:** yellow oil.

**TLC:** R$_f$ = 0.7 (10:1 hexanes:EtOAc, UV/Vis).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 4.19 – 4.16 (m, 1H), 4.07 (dddd, J = 11.2, 8.4, 5.2, 3.2 Hz, 1H), 2.40 (dd, J = 16.7, 5.2 Hz, 1H), 2.10 – 2.03 (m, 1H), 1.91 (s, 3H), 1.82 (dt, J = 13.0, 3.5, 1.3 Hz, 1H), 1.65 (ddd, J = 12.9, 10.6, 4.4 Hz, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.19 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.06 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 143.3, 115.2, 105.5, 96.6, 70.0, 64.2, 41.3, 39.5, 26.0, 25.9, 19.32, 18.3, 18.2, 0.3, -4.2, -4.5, -4.6, -4.7.

[$\alpha$]$_D^{21}$ = -45.1 (c = 1.0, CHCl$_3$).

HRMS (ESI-TOF): calc’d for C$_{24}$H$_{46}$O$_2$Si$_3$ [M+H]$^+$: 241.1260, found 241.1255.

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\(^2\)J. Org. Chem., 1997, 62(19), 6692.
SI-2 was prepared according to a known literature procedure.\(^2\) To a stirring solution of SI-2 (1.1 g, 2.5 mmol, 1.0 equiv.) in MeOH (66 mL, 0.04 M) at rt was added a K\(_2\)CO\(_3\) (0.75 g, 5.4 mmol, 2.2 equiv.). The reaction was stirred at rt until complete consumption of starting material was observed by NMR (approx. 2h), after which the reaction mixture was diluted with EtOAc (100 mL), and 1 M HCl was added (15 mL). The organic layer was separated, washed with brine (100 mL), dried over MgSO\(_4\), filtered, and concentrated under reduced pressure to afford \(\text{SI-2}\) (76% over 2 steps from \text{33}) as a yellow oil. \(\text{SI-2}\) is in accordance with all literature values.\(^1\)

**Physical State:** yellow oil.

**TLC:** \(R_f = 0.7\) (10:1 hexanes:EtOAc, UV/Vis).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 4.20 (t, \(J = 4.2\) Hz, 1H), 4.09 (dtd, \(J = 10.8, 5.1, 3.4\) Hz, 1H), 3.05 (s, 1H), 2.41 (ddq, \(J = 16.8, 5.4, 1.4\) Hz, 1H), 2.08 (dd, 15.4, 7.8 Hz, 1H), 1.92 (s, 3H), 1.83 (dddd, \(J = 13.0, 4.4, 3.2, 1.4\) Hz, 1H), 1.69 (ddd, \(J = 12.9, 10.2, 4.4\) Hz, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.06 (s, 6H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 143.7, 114.2, 84.0, 79.7, 69.9, 64.2, 41.2, 39.6, 26.0, 25.9, 19.1, 18.3, 18.2, -4.2, -4.5, -4.6, -4.7.

\([\alpha]_D^{21} = -48.4\) (c = 1.0, CHCl\(_3\)).

\(^2\)J. Org. Chem., 1997, 62(19), 6692.
Experimental Procedures for the Synthesis of CD Ring Containing Keto-ester 37

![Chemical Structure](image)

Prepared according to an adapted literature procedure.\(^3\) To a stirring solution of 2-cyclohexenone (1.80 g, 17.5 mmol) in DMF (32 mL, 0.55 M) was added tert-butyl acrylate (3.3 mL, 22.7 mmol) followed by DBU (0.52 mL, 3.5 mmol). The reaction vessel was sealed and heated to 185 °C for 36 h. The sealed tube was cooled to rt and poured into ice-water (100 mL). EtOAc was added (50 mL), the layers were separated, followed by extraction of the aqueous layer with EtOAc (3 × 15 mL). The combined organics were washed with water (5 × 100 mL), brine (15 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash chromatography eluting with hexanes/ethyl acetate (4:1) to provide 3.7 g of 41 (81%) as a colorless oil.

**Physical State**: colorless oil.

**TLC**: \(R_f = 0.25\) (9:1 hexanes:EtOAc, UV/Vis).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 6.88-6.68 (m, 1H), 2.56-2.42 (m, 4H), 2.42-2.30 (m, 4H), 1.99 (dq, \(J = 7.9, 6.1\) Hz, 2H), 1.44 (s, 9H).

\(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 199.3, 172.6, 146.2, 138.4, 80.3, 38.6, 34.6, 28.3, 26.2, 25.8, 23.2.

**GCMS (EI)**: calc’d for C\(_{13}\)H\(_{21}\)O\(_3\) [M]\(^+\): 224.1, found 224.1, 169.1.

\(^3\)J. Org. Chem. 2011, 76, 10173–10186.
To a 100 mL round-bottom flask was added K$_2$OsO$_2$(OH)$_4$ (164 mg, 0.45 mmol, 0.1 equiv.), and (DHQ)$_2$PHAL (486 mg, 0.62 mmol, 0.14 equiv.) followed by tBuOH/H$_2$O (1:1, 64 mL, 0.07M). The mixture was stirred for 15 min after which NaHCO$_3$ (1.1 g, 13.4 mmol, 3.0 equiv.), MeSO$_2$NH$_2$ (636 mg, 7.7 mmol, 1.5 equiv.) were added followed by K$_3$[Fe(CN)$_6$] (2.5 g, 7.7 mmol, 1.5 equiv.), and lastly 41 (1.03 g, 4.5 mmol, 1.0 equiv.). The reaction mixture was stirred for 36 hours after which a sodium bisulfite solution (4 g in 10 mL) was added and stirred for 1h. Sat. NaHCO$_3$ (10 mL) was then added (caution: slight exotherm) and stirred for 30 min after which EtOAc (100 mL) was added. The layers were separated, and the aqueous phase extracted with EtOAc (3 x 20 mL). The combined organic extracts were then washed with brine (100 mL), dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (1:1) to give 42 (484 mg, 42%, 87% brsm) as an off-white solid. Recrystallization from Et$_2$O (slow evaporation) gave colorless blocks which were determined to be up to 93% ee by SFC analysis of benzoylated 42. Typical benzoylation conditions: 42 (1 equiv.), BzCl (3 equiv.), Et$_3$N (3.5 equiv.), DMAP (1.5 equiv.) in DCM (0.1 M) rt, 1.5 h.

Physical State: off-white solid.

TLC: $R_f$ = 0.48 (1:1 hexanes:EtOAc, KMnO$_4$).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 4.25 (s, 1H), 4.05 (t, $J = 2.9$ Hz, 1H), 2.80 (dd, $J = 2.2$, 0.9 Hz, 1H), 2.63 (td, $J = 14.0$, 6.7 Hz, 1H), 2.47 (ddt, $J = 14.0$, 4.4, 2.0 Hz, 1H), 2.31 (ddd, $J = 16.4$, 8.9, 5.8 Hz, 1H), 2.21-1.90 (m, 7H), 1.42 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 213.2, 172.3, 81.0, 80.8, 76.4, 37.4, 30.8, 29.1, 28.2, 27.7, 21.6.

$[\alpha]_D^{21} = -77.91$ (c = 1.0, CHCl$_3$).

m.p. = 73 °C.

Fig. 4. The following picture shows the white solid obtained from flash chromatography (KR6-3) and the colorless crystalline after recrystallization (KR6-10).
To a stirring solution of 42 (6.72 g, 26 mmol, 1.0 equiv.) in PhMe (320 mL, 0.08 M) was added 2-methoxyprop-1-ene (14.3 mL, 149 mmol, 5.8 equiv.) followed by p-TsOH·H₂O (486 mg, 0.1 mmol, 0.1 equiv.) and 3Å m.s. (4.6 g). The reaction mixture was stirred overnight after which 10% NaHCO₃ (25 mL) was added. The layers were separated, and the aqueous phase extracted with EtOAc (3 x 150 mL). The combined organic extracts were then washed with brine (150 mL), dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (1:4) to give SI-3 (7.5 g, 97%) as a yellow oil.

**Physical State:** light-yellow oil.

**TLC:** Rₜ = 0.47 (4:1 hexanes:EtOAc, UV/Vis).

**1H NMR (600 MHz, CDCl₃)** δ 4.22-4.18 (m, 1H), 2.48-2.44 (m, 1H), 2.47-2.42 (m, 1H), 2.44-2.39 (m, 1H), 2.33 (ddd, J = 17.0, 9.0, 6.2 Hz, 1H), 2.27 – 2.18 (m, 1H), 2.07 (ddd, J = 15.1, 9.0, 6.2 Hz, 1H), 2.05-1.93 (m, 2H), 1.95-1.89 (m, 1H), 1.91-1.86 (m, 1H), 1.43 (s, 9H), 1.38 (d, J = 5.9 Hz, 6H).

**13C NMR (151 MHz, CDCl₃)** δ 211.1, 172.4, 108.6, 85.7, 80.8, 80.8, 40.3, 29.7, 28.1, 28.0, 27.1, 26.8, 26.1, 20.8.

**GCMS (EI):** calc’d for C₁₆H₂₆O₅ [M]⁺: 298.2, found 298.1, 242.1.

[α]D²¹ = -19.1 (c = 1.0, CHCl₃).

![Chemical structure](image-url)
Ti(O\textsubscript{i}Pr\textsubscript{2})Cl\textsubscript{2} was prepared according to a literature procedure\textsuperscript{2}. To a stirring solution of Nysted reagent (35 mL, 20\% by wt, 15.7 mmol, 4.7 equiv.) under Ar at 0 °C was dropwise added SI-3 (1.0 g, 3.3 mmol, 1.0 equiv.) as a solution in THF (33 mL, 0.1 M) over 5 min. (note: slight bubbling occurs upon addition). The reaction was stirred for 5 min, after which freshly prepared Ti(O\textsubscript{i}Pr\textsubscript{2})Cl\textsubscript{2} (13.3 mL, 1 M solution in DCM) was dropwise added over 15 min. (note: reaction turns milk chocolate brown during addition). The reaction mixture was allowed to warm to rt and stirred overnight, after which complete consumption of starting material was observed by TLC (approximately 22 h). Et\textsubscript{2}O (200 mL) was added, and the mixture was filtered through a pad of celite. To the organics was slowly added ice (note: precipitate forms) followed by careful addition of 1M HCl (50 mL) after which two visible layers is formed. The layers were separated, and the aqueous phase extracted with Et\textsubscript{2}O (3 x 50 mL). The combined organic extracts were then washed with brine (50 mL), dried (Na\textsubscript{2}SO\textsubscript{4}), filtered and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (9:1) to give 43 (625 mg, 64\%) as an off-yellow oil.

**Physical State:** yellow oil.

**TLC:** R\textsubscript{f} = 0.32 (9:1 hexanes:EtoAc, KMnO\textsubscript{4}).

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ 5.11 (dd, J = 2.3, 1.5 Hz, 1H), 4.94 (t, J = 2.2 Hz, 1H), 3.91 (t, J = 2.9 Hz, 1H), 2.41-2.25 (m, 3H), 2.12 (dt, J = 14.3, 2.7 Hz, 1H), 2.01-1.88 (m, 2H), 1.84-1.56 (m, 4H), 1.43 (s, 3H), 1.43 (s, 9H), 1.35 (s, 3H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 173.3, 148.9, 112.3, 107.8, 82.6, 80.2, 79.5, 33.7, 30.6, 30.5, 28.2, 27.9, 27.5, 27.1, 21.9.

**HRMS (ESI-TOF):** calc'd for C\textsubscript{17}H\textsubscript{28}O\textsubscript{4} [M+Na]\textsuperscript{+}: 319.1885, found 319.1893.

[\textalpha]\textsubscript{D} = -15.8 (c = 1.0, CHCl\textsubscript{3}).
To a stirring solution of 43 (731 mg, 2.5 mmol, 1.0 equiv.) in THF/MeOH/H$_2$O (4:1:1, 14.5 mL, 0.17 M) was added LiOH·H$_2$O (311 mg, 7.4 mmol, 3 equiv.) and heated to 60 °C. The reaction was stirred for 3.5 h, after which it was cooled to rt by removal of the oil bath. 1M HCl (15 mL) was dropwise added followed by EtOAc (75 mL). H$_2$O was then added (20 mL), the layers were separated, and the aqueous phase extracted with EtOAc (3 x 50 mL). The combined organic extracts were then washed with brine (25 mL), dried (Na$_2$SO$_4$), filtered and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (1:1) to give 44 (600 mg, quantitative) as a colorless oil.

**Physical State:** colorless oil.

**TLC:** $R_f = 0.48$ (1:1 hexanes:EtOAc, KMnO$_4$).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 5.15 (dt, $J = 2.5, 1.3$ Hz, 1H), 5.00 (q, $J = 2.0$ Hz, 1H), 3.95 (t, $J = 3.0$ Hz, 1H), 2.58-2.44 (m, 2H), 2.33 (dt, $J = 13.9, 3.1$ Hz, 1H), 2.16 (dp, $J = 14.2, 2.9$ Hz, 1H), 2.11-1.90 (m, 2H), 1.86 (dddd, $J = 14.0, 9.5, 6.2, 1.3$ Hz, 1H), 1.81-1.58 (m, 3H), 1.46 (s, 3H), 1.37 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 179.7, 148.5, 112.6, 108.1, 82.4, 79.7, 33.6, 30.1, 29.2, 27.8, 27.4, 27.1, 21.9.

**HRMS (ESI-TOF):** calc’d for C$_{13}$H$_{20}$O$_4$ [M-H]$^-$: 239.1283, found 239.1281.

[$\alpha$]$^D_{21}$ = -12.9 (c = 1.0, CHCl$_3$).
Gram-scale electrochemical reductive coupling of acid 44 and vinyl iodide 45

To a flame-dried culture tube containing 44 (1 g, 4.1 mmol, 1.0 equiv.) and NHPI (836 mg, 5.2 mmol, 1.25 equiv.) under Ar was added THF (3 mL, 1.4 M) followed by N,N-diisopropylcarbodiimide (0.7 mL, 4.5 mmol, 1.1 equiv.) at rt and stirred for an additional 1 h at this temperature. In another flame-dried culture tube was added NiCl$_2$·6H$_2$O (98 mg, 0.41 mmol, 0.1 equiv.), 2,2’-bipyridine (64 mg, 0.41 mmol, 0.1 equiv.), NaI (185 mg, 1.2 mmol, 0.3 equiv.), placed under vacuum and backfilled with Ar (repeated 3 x). DMF (12 mL, 0.33 M w/r to 44) was then added and stirred for 5 min at rt (or until homogenous), after which neat vinyl iodide 45 (1.2 g, 5 mmol, 1.2 equiv.) was added. In a separate flame-dried electrasyn vial was added AgNO$_3$ (210 mg, 1.2 mmol, 0.3 equiv.), placed under vacuum and backfilled with Ar (repeated 3 x). The entire DMF/Ni solution was then added to the freshly generated RAE/THF solution, stirred 1 min, and then all contents were transferred to the electrasyn vial containing AgNO$_3$ and immediately electrolyzed using an electrasyn device (conditions: 120 mA, 3.3 F/mol). Note: reaction changes from green to red to black towards the end of electrolysis. The reaction mixture was then transferred to a 100 mL round-bottom flask, diluted with EtOAc (20 mL), and 1M HCl (15 mL) was slowly added. The layers were separated, and the aqueous phase extracted with EtOAc (3 x 20 mL). The combined organic extracts were then washed with brine (15 mL), dried (Na$_2$SO$_4$), filtered and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (9:1) to give 40 (800 mg, 63% yield) as a pale-yellow oil.

Physical State: pale yellow oil.

TLC: R$_f$ = 0.48 (1:1 hexanes:EtOAc, KMnO$_4$).

$^1$H NMR (600 MHz, CDCl$_3$) δ 5.93 (td, J = 7.5, 1.5 Hz, 1H), 5.12 (dd, J = 2.4, 1.6 Hz, 1H), 4.94 (t, J = 2.2 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.96 (t, J = 2.8 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.32 (dq, J = 13.6, 3.1 Hz, 1H), 2.16 – 2.09 (m, 1H), 1.95 (tdd, J = 13.2, 4.2, 2.1 Hz, 1H), 1.88 (q, J = 1.4 Hz, 3H), 1.75 – 1.59 (m, 5H), 1.45 (d, J = 0.7 Hz, 3H), 1.36 (d, J = 0.7 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 168.3, 149.5, 142.4, 111.8, 107.7, 83.2, 78.9, 60.2, 35.4, 33.8, 27.9, 27.5, 27.2, 24.8, 21.9, 20.8, 14.4.

HRMS (ESI-TOF): calc’d for C$_{13}$H$_{20}$O$_4$ [M-H]$^-$: 239.1283, found 239.1281.
Fe-mediated HAT coupling of enoate 40

To a flame dried tube was added iron(III) acetylacetonate (45.9 mg, 0.13 mmol), styrene (13.5 mg, 0.13 mmol), anhydrous 1,2-dichloroethane (4.4 mL), and anhydrous ethylene glycol (2.2 mL). The mixture was degassed using freeze-pump-thaw technique for three cycles after which (isopropoxy)phenylsilane (23 µL, 0.13 mmol) was added at room temperature. The mixture was stirred for 30 minutes, after which 40 (97 mg, 0.33 mmol), (isopropoxy)phenylsilane (0.15 ml, 0.85 mmol) was added sequentially at 0 °C. The reaction was stirred at 0 °C until complete consumption of starting material was observed by TLC. The reaction mixture was diluted with Et₂O, and quenched by addition of 0.5 N aqueous HCl. The mixture was then stirred until the organic layer appeared colorless. The layers were separated, and the organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by flash chromatography afforded 39 as a colorless oil.

**Physical State:** colorless oil.

**TLC:** Rf = 0.21 (10:1 hexanes:EtOAc, PMA)

**H NMR (600 MHz, CDCl₃)** δ 4.17 – 4.05 (m, 2H), 3.97 (t, J = 6.0 Hz, 1H), 2.48 (dq, J = 9.6, 6.8 Hz, 1H), 1.92 (ddd, J = 10.7, 9.5, 8.1 Hz, 1H), 1.83 – 1.72 (m, 4H), 1.66 (dtd, J = 13.3, 7.8, 5.5 Hz, 1H), 1.56 – 1.53 (m, 2H), 1.51 – 1.44 (m, 5H), 1.34 (d, J = 0.8 Hz, 3H), 1.27 - 1.24 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.19 (d, J = 6.8 Hz, 3H), 0.97 (s, 3H).

**C NMR (151 MHz, CDCl₃)** δ 176.7, 107.3, 90.8, 76.5, 60.1, 53.5, 46.0, 40.2, 34.9, 29.5, 26.4, 26.2, 25.9, 25.0, 24.4, 18.1, 16.0, 14.4.

**HRMS(ESI-TOF):** calc’d for C13H20O4 [M+Na]⁺: 333.2042, found 333.2049.
Semi-pinacol rearrangement of 39 towards keto-ester 37

A solution of 39 (6.5 mg, 20.9 µmol) in AcOH/THF/H$_2$O (4:1:1, 0.32 mL) was stirred at 40 °C for 12 h (or complete consumption of 2-81 observed by crude NMR), after which it was cooled to rt, diluted with dichloromethane and quenched with sat. NaHCO$_3$ at 0 °C. The layers were separated, and the aqueous phase was extracted with dichloromethane 3 times. The combined organic extracts were then washed with sat. NaHCO$_3$ and brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the diol SI-6. The product is unstable for storage and was utilized in the next step immediately.

To a flame dried tube containing triphenylphosphine (27.8 mg, 0.11 mmol) under argon was added MeCN (0.4 mL), followed by hexachloroethane (25.1 mg, 0.11 mmol) in one portion. The reaction mixture was stirred for 20 min, after which DIPEA (36.8 µL, 0.21 mmol) was added. The mixture was cooled to 0 °C and a solution of diol SI-6 (11 mg, 0.041 mmol) in MeCN (0.4 mL) was added dropwise over 5 min. Upon complete consumption of SI-6 observed by crude NMR, the reaction mixture was heated to reflux for 2 h until the phosphorane intermediate was fully consumed indicated by NMR. The reaction mixture was cooled, diluted with Et$_2$O and washed with water. The combined aqueous fractions were extracted with Et$_2$O. The organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by flash chromatography afforded ketone 37 (4.5 mg, 44% yield over 2 steps) as a colorless oil.

**Physical State:** colorless oil.

**TLC:** Rf = 0.15 (10:1 hexanes:EtOAc, PMA)

$^1$H NMR (600 MHz, CDCl$_3$) δ 4.12 (qd, $J = 7.1, 3.0$ Hz, 2H), 2.49 (dd, $J = 11.4, 7.4$ Hz, 1H), 2.40 (dq, $J = 10.4, 6.9$ Hz, 1H), 2.34 – 2.20 (m, 2H), 2.04 (dtq, $J = 14.3, 7.1, 2.3$ Hz, 2H), 1.98 – 1.86 (m, 2H), 1.84 – 1.72 (m, 2H), 1.68 (td, $J = 13.2, 4.9$ Hz, 1H), 1.59 – 1.50 (m, 1H), 1.44 – 1.35 (m, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.22 (d, $J = 6.9$ Hz, 3H), 0.65 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 211.5, 176.5, 61.6, 60.4, 53.5, 49.8, 42.5, 41.1, 38.9, 26.7, 24.1, 19.4, 17.3, 14.4, 12.8.

**HRMS (ESI-TOF):** calc’d for C$_{15}$H$_{24}$O$_3$ [M-H]$: 253.1798, found 253.1794.

$[\alpha]_D^{21}$ = +8.4 (c = 1.0, CHCl$_3$).
Synthesis of Vinyl Iodide 45

To a stirring solution of (Z)-3-iodo-2-methylprop-2-en-1-ol (1 g, 5 mmol, 1 equiv.) in MeCN/phosphate buffer (1M, pH = 7) (8.5 mL) at 0 °C was added TEMPO (158 mg, 1 mmol, 0.20 equiv.) and PIDA (163 mg, 0.5 mmol, 0.10 equiv.). Next, sodium chlorite (1.4 g, 15.2 mmol, 3 eq.) was slowly added after which the reaction turned a deep purple and was allowed to slowly warm to room temperature and stirred 12 h. The reaction mixture was cooled to 0 °C and quenched with water (5 mL) and excess solid sodium sulfite until the reaction became colorless. The reaction was diluted with Et₂O (10 mL) and washed with 1N HCl (3 X 5 mL) before being extracted into the aqueous phase using 1N NaOH (4X 20 mL). The collected basic phase was then acidified with concentrated HCl to pH 1 at which point the aqueous phase was extracted with diethyl ether (4X 50 mL), the organics combined, washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated to provide 721 mg (68%) of SI-5 as an off-white solid. Note: stored in a -20 °C freezer.

Physical State: white amorphous solid.

TLC: Rf = 0.63 (9:1 hexanes:EtOAc, UV/Vis).

¹H NMR (600 MHz, CDCl₃) δ 7.10 (d, J = 1.5 Hz, 1H), 2.11 (d, J = 1.5 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.5, 137.8, 86.2, 22.6.

HRMS (ESI-TOF): calc’d for C₉H₁₄OSi [M+H]⁺: 212.9412, found 212.9405.
To a stirring solution of SI-4 (684 mg, 3.2 mmol, 1 equiv.) in EtOH (5.4 mL, 0.6 M) was added 2 H₂SO₄ (0.1 mL). The reaction mixture was heated to 70 °C and stirred for 4 h after which TLC analysis showed full consumption of acid SI-4. The reaction mixture was cooled to rt by removal of the oil bath, diluted with EtOAc (5 mL) and quenched by the addition of saturated NaHCO₃ (2 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The organics were combined, washed with brine (10 mL), dried over Na₂SO₄, filtered, and concentrated and filtered through a small plug of SiO₂ to provide 736 mg (95%) of SI-5 as a yellow liquid. Note: stored in a 20 °C freezer.

Physical State: yellow liquid.

TLC: Rf = 0.93 (9:1 hexanes:EtOAc, UV/Vis).

¹H NMR (600 MHz, CDCl₃) δ 6.80 (q, J = 1.6 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.06 (d, J = 1.6 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 166.2, 139.3, 82.4, 61.3, 22.6, 14.3.

HRMS (ESI-TOF): calc'd for C₉H₁₄OSi [M+H]⁺: 240.9725, found 240.9724.
To a flame-dried reaction flask under Ar was added LiHMDS (1.2 mL, 1.2 mmol, 1 M solution in THF) and cooled to -78 °C after which a solution of ketone 37 (252 mg, 1 mmol) in THF (3 mL, 0.33 M) was dropwise added over 10 min. The reaction mixture was stirred for 45 min after which a solution of PhNTf₂ (429 mg, 1.2 mmol) in THF (1.5 mL, 0.8 M) was dropwise added (over 5 min) and stirred for an additional 15 min at -78 °C. The dry ice/acetone bath was removed, and the reaction mixture was warmed to rt and stirred for an additional 15 min. The mixture was subsequently quenched by the addition of H₂O (5 mL) and then diluted with EtOAc (5 mL) followed by addition of brine (5 mL). The organic layer was passed through a column of Na₂SO₄ and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (20:1) to give 45 (349 mg, 91%) as a colorless oil.

**Physical State:** colorless oil.

**TLC:** Rf = 0.60 (9:1 hexanes:EtOAc, PMA).

**¹H NMR (600 MHz, CDCl₃)** δ 5.59 (q, J = 3.5 Hz, 1H), 4.12 (qd, J = 7.1, 1.5 Hz, 3H), 2.55-2.50 (m, 1H), 2.49-2.42 (m, 1H), 2.36-2.27 (m, 2H), 1.96-1.86 (m, 2H), 1.80 (tdd, J = 9.4, 8.0, 4.2 Hz, 2H), 1.59-1.46 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.21 (d, J = 6.9 Hz, 3H), 0.78 (s, 3H).

**¹³C NMR (151 MHz, CDCl₃)** δ 176.4, 149.6, 116.3, 60.4, 51.1, 49.9, 45.3, 42.9, 34.8, 27.4, 23.9, 21.7, 17.3, 14.4, 11.7.

**¹⁹F NMR (376 MHz, CDCl₃)** δ -77.0.

**HRMS (ESI-TOF):** calc’d for C₁₆H₂₃F₃O₅S [M+H]⁺: 385.1291, found 385.1288.

[α]D²¹ = +6.4 (c = 1.0, CHCl₃).
To a stirring solution of vinyl triflate 45 (461 mg, 1.2 mmol, 1.0 equiv.) in \( i\text{Pr}_2\text{NH/DMF} \) (4:1) (3 mL, 0.4 M) under argon was added \( \text{Pd(PPh}_3)_2\text{Cl}_2 \) (17 mg, 2 mol\%). and CuI (6.8 mg, 3 mol\%). The resulting solution was degassed for 10 min, followed by addition of 22 (503 mg, 1.32 mmol, 1.1 equiv.) in DMF (0.5 mL). The reaction mixture was stirred for 3 h \( \text{(or until TLC indicated full conversion of triflate)} \) after which the reaction mixture was diluted with EtOAc (10 mL) and sat. \( \text{NH}_4\text{Cl} \) (5 mL) was added. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over \( \text{Na}_2\text{SO}_4 \), filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash chromatography eluting with hexanes/ethyl acetate (20:1) to provide 576 mg (78\%) yield of 48 as a light-yellow oil.

**Physical State:** light-yellow oil.

**TLC:** \( R_f = 0.72 \) (9:1 hexanes:EtOAc, UV/Vis).

**\(^1\)H NMR (600 MHz, CDCl\textsubscript{3})** \( \delta 5.99 \) (q, \( J = 3.4 \text{ Hz}, 1H \)), 4.21 (t, \( J = 3.9 \text{ Hz}, 1H \)), 4.19 – 4.11 (m, 2H), 4.14 – 4.07 (m, 1H), 2.48 (dq, \( J = 10.5, 6.9 \text{ Hz}, 1H \)), 2.42 (dd, \( J = 16.8, 5.2 \text{ Hz}, 1H \)), 2.29 (d, \( J = 12.9 \text{ Hz}, 1H \)), 2.27 (s, 3H), 1.95 (dd, \( J = 12.6, 6.1 \text{ Hz}, 1H \)), 1.92 – 1.90 (m, 3H), 1.90 – 1.85 (m, 1H), 1.85 (ddt, \( J = 6.9, 3.4, 1.3 \text{ Hz}, 2H \)), 1.79 – 1.73 (m, 1H), 1.69 (ddd, \( J = 12.9, 10.5, 4.3 \text{ Hz}, 1H \)), 1.59 (s, 1H), 1.61 – 1.53 (m, 1H), 1.52 – 1.41 (m, 2H), 1.30 (s, 1H), 1.32 – 1.21 (m, 7H), 0.96 – 0.87 (m, 20H), 0.74 (s, 3H), 0.10 (dd, \( J = 19.4, 1.3 \text{ Hz}, 13H \)).

**\(^{13}\)C NMR (151 MHz, CDCl\textsubscript{3})** \( \delta 176.8, 140.7, 133.2, 122.4, 115.6, 92.3, 88.5, 70.2, 64.4, 60.2, 51.6, 49.9, 43.1, 42.1, 41.4, 39.9, 35.9, 27.1, 26.1, 26.0, 25.2, 24.4, 19.3, 18.3, 18.2, 17.3, 14.4, 11.4, -4.2, -4.5, -4.6, -4.7.

**HRMS (ESI-TOF):** calc’d for \( \text{C}_{36}\text{H}_{62}\text{O}_{4}\text{Si}_2 \) [M+H]+: 615.4260, found 615.4262.

\( [\alpha]_D^{21} = -31.0 \) (\( c = 1.0, \text{CHCl}_3 \)).
To a stirring solution of 48 (450 mg, 0.75 mmol, 1.0 equiv.) in THF/MeOH/H$_2$O (15 mL, 0.05 M (4:1:1)) was added LiOH·H$_2$O (126 mg, 3 mmol, 4 equiv.) The reaction mixture was heated to 60 °C and stirred for 12 h, after which it was cooled to rt by removal of the oil bath. 1M HCl (10 mL) was dropwise added followed by EtOAc (20 mL). H$_2$O was then added (10 mL), the layers were separated, and the aqueous phase extracted with EtOAc (3 x 15 mL). The combined organic extracts were then washed with brine (25 mL), dried (Na$_2$SO$_4$), filtered and concentrated under reduced pressure.

To a stirring solution of crude acid in DCM (3.8 mL, 0.2 M) was added NHPI (135 mg, 0.83 mmol, 1.1 equiv.) followed by DIC (130 uL, 0.83 mmol, 1.1 equiv.) The mixture was stirred for 2 h, after which full consumption of starting material was observed by TLC analysis. The crude reaction mixture was filtered through a small pad of SiO$_2$/celite and rinsed with 10 mL of EtOAc into a 100 mL round-bottom flask and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (10:1) to give RAE 49 (461 mg, 84% over 2 steps) as a white foam.

**Physical State:** white foam.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.91 (dt, $J$ = 5.3, 2.6 Hz, 2H), 7.81 (dt, $J$ = 5.3, 2.6 Hz, 2H), 6.00 (q, $J$ = 3.5 Hz, 1H), 4.22 (d, $J$ = 4.1 Hz, 1H), 4.16-4.08 (m, 1H), 2.89 (dq, $J$ = 10.4, 6.8 Hz, 1H), 2.43 (dd, $J$ = 16.3, 5.1 Hz, 1H), 2.29 (dd, $J$ = 7.1, 3.5 Hz, 1H), 2.21-2.06 (m, 2H), 2.02-1.83 (m, 4H), 1.91 (s, 3H), 1.70 (ddd, $J$ = 12.8, 10.4, 4.3 Hz, 1H), 1.68-1.61 (m, 1H), 1.58 (dd, $J$ = 12.4, 6.3 Hz, 1H), 1.47 (t, $J$ = 5.2 Hz, 3H), 0.97-0.85 (m, 18H), 0.82 (s, 3H), 0.81 (s, 1H), 0.13 (s, 3 H), 0.13 (s, 3 H), 0.09 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 172.5, 162.20, 140.9, 134.8, 133.1, 129.2, 124.1, 122.4, 115.5, 92.2, 88.7, 70.2, 64.4, 51.3, 49.9, 42.4, 41.4, 40.73, 39.9, 35.9, 27.2 26.1, 26.0, 25.2, 24.5, 19.3, 18.3, 18.2, 17.4, 11.5, -4.2, -4.5, -4.5, -4.6.

**HRMS (ESI-TOF):** calc’d for C$_{42}$H$_{61}$NO$_6$Si$_2$ [M+H]$^+$: 732.4116, found 732.4111.

**TLC:** $R_f$ = 0.38 (10:1 hexanes:EtOAc).

$[\alpha]_D^{21} = +34.2$ ($c = 0.5$, CHCl$_3$).
Synthesis of vinyl bromide 50

Prepared according to a literature procedure. To a stirring solution of AlCl$_3$ (3.2 g, 18.7 mmol, 0.9 equiv.) in DCM (20 mL) at -20 °C was dropwise added a solution of cyclopropanecarbonyl chloride (2.1 g, 20.2 mmol) and 1,2-bis(trimethylsilyl)ethyne (4.06 g, 30.5 mmol, 1.5 equiv.) in DCM (10 mL) over 5 min. The reaction was stirred for 2 h and quenched by the addition of 1M HCl (20 mL), slightly exothermic. The layers were separated, followed by extraction of the aqueous layer with DCM (3 x 50 mL). The combined organics were washed with water (5 x 100 mL), brine (15 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash chromatography eluting with hexanes/ethyl acetate (9:1) to provide 2.72 g (81% yield) of SI-7 as a light-yellow oil.

Physical State: light yellow oil.

TLC: $R_f = 0.63$ (9:1 hexanes:EiOAc, UV/Vis).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 2.09-2.00 (m, 1H), 1.25-1.18 (m, 2H), 1.03 (ddd, $J = 7.9$, 5.4, 2.1 Hz, 2H), 0.22 (dt, $J = 2.6$, 1.3 Hz, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 188.3, 100.4, 97.6, 24.5, 11.3, -0.6.

HRMS (ESI-TOF): calc’d for C$_9$H$_{14}$OSi [M+H]$^+$: 167.0892, found 167.0891.
Prepared according to a literature procedure. To a stirring solution of ketone SI-7 (500 mg, 3.0 mmol, 1.0 equiv.) in THF (15 mL, 0.2 M) was added 4 Å m.s. and dried for 1 h. In a separate 100 mL round-bottom flask was added CBS catalyst (1.25 g, 4.5 mmol, 1.5 equiv.) followed by THF (15 mL). Ketone SI-7 was then added, and the reaction mixture was cooled to -30 °C after which BH$_3$ (3 mL, 6 mmol, 2 M solution in SMe$_2$) was dropwise added over 15 min. The reaction mixture was stirred for 15 min after which full conversion of the starting material was observed by TLC analysis. The reaction mixture was slowly quenched by the addition of MeOH (10 mL, caution: exotherm!) until bubbles have ceased and allowed to reach rt by removal of the dry-ice/acetone bath. The reaction mixture was then concentrated under reduced vacuum pressure. The crude reaction mixture was purified by flash chromatography eluting with hexanes/ethyl acetate (4:1) to provide 442 mg (88% yield) of SI-8 as a colorless oil.

**Physical State:** colorless oil.

**TLC:** $R_f = 0.39$ (9:1 hexanes:EtOAc, KMnO$_4$).

**$^1$H NMR (600 MHz, CDCl$_3$)** $\delta$ 4.23 (d, $J = 6.4$ Hz, 1H), 2.04 (bs, 1H), 1.22 (tt, $J = 8.0, 6.4, 5.0$ Hz, 1H), 0.57-0.44 (m, 3H), 0.42 (t, $J = 8.9, 5.9, 3.1$ Hz, 1H), 0.15 (s, 9H).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** $\delta$ 104.3, 89.8, 66.1, 16.9, 3.3, 1.5, 0.0.

**HRMS (ESI-TOF):** calc’d for C$_9$H$_{16}$OSi [M+H$^+$]: 169.1049, found 169.1044.

$[\alpha]_{D}^{21} = +38.5$ (c = 1.0, CHCl$_3$).

**Conditions:** Propargyl alcohol SI-8 was analyzed on a Waters UPC2 SFC with a Daicel IBN column (3 um, 4.6x250 mm) under isocratic conditions (4 mL/min, 2% MeOH / CO$_2$, 1600 psi backpressure) at 30 °C. The enantiomers were detected by UV light (211 nm).

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$^4$J. Org. Chem. 1996, 61, 9021-9025.
To a stirring solution of **SI-7** (505 mg, 3 mmol) in MeOH/THF (6 mL, 0.5 M, 1:1 mixture) was added K$_2$CO$_3$ (2.1 g, 15 mmol, 5.0 equiv). The reaction mixture was vigorously stirred at rt until complete consumption of starting material was observed by TLC (~1.5 h). EtOAc (20 mL) was then added followed by the addition of 1M HCl (20 mL). The layers were separated, and the aqueous phase extracted with EtOAc (3 x 20 mL). The combined organic extracts were then washed with brine (100 mL), dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The resulting crude mixture was carried on to the next step without further purification.

To a stirring solution of crude unprotected alkyne was added DCM (5 mL, 0.6 M) followed by lutidine (0.5 mL, 4.2 mmol, 1.4 equiv.), DMAP (550 mg, 4.5 mmol, 1.5 equiv.), and lastly TBSCl (543 mg, 3.6 mmol). The reaction mixture was stirred at rt for 2 h after which full consumption of the starting material was consumed as indicated by TLC analysis. The mixture was diluted with DCM (10 mL) after which saturated NaHCO$_3$ (10 mL) was slowly added. The layers were separated, followed by extraction of the aqueous layer with DCM (3 x 50 mL). The combined organics were washed with brine (15 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was filtered through a small pad of SiO$_2$ (1:9 EtOAc/hexanes), concentrated and carried through to the next step without further purification. **Note:** the crude TBS protected alcohol was dried under high vacuum for ~1 h prior to use in the subsequent step.

Vinyl bromide **50** was prepared according to an adapted literature protocol.$^5$ To a stirring solution of ZrCp$_2$Cl$_2$ (0.55 mmol, 1.1 equiv.) in THF (0.44 M) was added DIBAL (0.55 mL, 1.1 equiv. 1 M solution in DCM). **Note:** Aluminum foil was wrapped around the reaction mixture at this time. The reaction mixture was stirred for 30 min after which a white precipitate was formed indicating Schwartz reagent was generated. A solution of protected alkyne (0.5 mmol, 2 M in THF) was then added, the ice-bath removed, and the reaction mixture stirred at rt for an additional 30 min. **Note:** After 30 min, a light-yellow homogenous mixture was observed. The reaction mixture was then cooled to -78 °C using a dry-ice/acetone bath after which a solution of NBS (120 mg, 0.7 mmol, 1.3 equiv. in THF (0.8 M)) was added. The reaction mixture stirred at -78 °C for 1 h and then quenched by transferring the entire mixture to a separate flask containing ice-cold 1 M HCl (100 mL). The layers were separated, followed by extraction of the aqueous layer with DCM (3 x 50 mL). The combined organics were washed with Na$_2$S$_2$O$_3$ (2 x 50 mL), water (50 mL), brine (50 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash chromatography eluting with hexanes/ethyl acetate (50:1) to provide 0.6 g (59% yield over 3 steps) of **50** as a colorless oil.

**Physical State:** colorless oil.

**TLC:** $R_f = 0.43$ (50:1 hexanes:EtOAc, PMA).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.34 – 6.23 (m, 2H), 3.66 (dd, $J = 6.7$, 4.7 Hz, 1H), 1.29 (t, $J = 7.4$ Hz, 1H), 0.98 – 0.91 (m, 1H), 0.91 (s, 9H), 0.55 – 0.44 (m, 2H), 0.39 – 0.32 (m, 1H), 0.30 – 0.22 (m, 1H), 0.07 (d, $J = 12.7$ Hz, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 140.6, 105.7, 75.9, 26.0, 18.3, 17.4, 3.1, 1.9, -4.4.
HRMS (ESI-TOF): calc’d for C₁₂H₂₅BrOSi [M+H]+: 291.0780, found 291.0767.

[α]₀²¹ = -7.2 (c = 1.0, CHCl₃).

⁵Org. Lett., 2006, 8, 3675-3678.
Experimental Procedure for the Synthesis of Calcipotriol (7)

To a flame-dried culture tube was added 49 (128 mg, 0.17 mmol, 1.0 equiv.), NiCl₂·6H₂O (20.2 mg, 0.09 mmol, 0.5 equiv.), and 2,2'-bipyridine (13.3 mg, 0.09 mmol, 0.5 equiv.). The contents were placed under vacuum and backfilled with Ar (repeated 3 x). DMF (2.5 mL) and THF (0.5 mL) was then added and stirred for 5 min at rt (or until homogenous), after which neat vinyl bromide 50 (75 mg, 0.26 mmol, 1.5 equiv.) was added. In a separate flame-dried electrasyn vial was added AgNO₃ (10mg mg, 0.05 mmol, 0.3 equiv.), placed under vacuum and backfilled with Ar (repeated 3 x). The entire contents containing 49/DMF/Ni solution were then transferred to the electrasyn vial containing AgNO₃ and immediately electrolyzed using an electrasyn device (conditions: 6 mA, 3.3 F/mol). Note: reaction changes from green to red towards the end of electrolysis. The reaction mixture was then diluted with EtOAc (5 mL), and 1M HCl (5 mL) was slowly added. The layers were separated, and the aqueous phase extracted with EtOAc (3 × 5 mL). The combined organic extracts were then washed with brine (10 mL), dried (Na₂SO₄), filtered and concentrated under reduced pressure. The resulting crude mixture containing 51 was filtered through a small plug of SiO₂ eluting with hexanes/EtOAc (20 mL, 50:1) and concentrated under reduced pressure which was used to the subsequent step without any further purification. NMR yield of combined C20-51 diastereomers (48%).

To a flame-dried vial was added 51 (theoretical amount 7.5 mg, 0.01 mmol) followed by 0.4 mL of EtOAC. Quinoline (4 µL, 3 mol%) was added followed by Pd/BaSO₄ (2.6 mg, 10 mol%) after which the contents were placed under a H₂ atmosphere. The reaction mixture stirred until TLC analysis showed full consumption of 51. The reaction mixture was then put under an Ar atmosphere after which the contents were filtered through a small plug of celite with 0.5 mL of hexanes into a new reaction vial. The reaction mixture was purged with Ar and then heated to 40 °C in an oil bath, which stirred overnight to induce the thermal isomerization. The crude reaction mixture was concentrated under reduced pressure after which the contents were placed under vacuum and backfilled with Ar (repeated 3 x). THF was added (0.2 mL, 0.05 M) at ambient temperature followed by TBAF (40 µL, 0.04 mmol, 1 M THF solution) and subsequently heated to 50 °C in an oil bath 1 h. The reaction mixture was allowed to reach rt by removal of the oil bath after which the mixture was diluted with EtOAc (0.5 mL), and 1 M HCl (0.5 mL) was added. The layers were separated, followed by extraction of the aqueous layer with EtOAc (3 × 0.5 mL). The combined organics were washed with brine (1 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by pTLC eluting with hexanes/ethyl acetate (1:2) to provide 1.1 mg (13% yield over 3 steps) of calcipotriol 7 as a white amorphous solid.

Physical State: white foam.

TLC: Rₜ = 0.27 (1:2 hexanes:EtOAc).
$^1$H NMR (500 MHz, CDCl$_3$)  $\delta$ 6.40 (d, $J = 11.2$ Hz, 1H), 6.04 (d, $J = 11.2$ Hz, 1H), 5.51-5.48 (2H, m), 5.35 (s, 1H), 5.02 (1H, s), 4.45 (1H, bs), 4.26 (1H, bs), 3.47-3.45 (1H, m),

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 147.8, 143.2, 138.2, 133.1, 129.1, 125.1, 117.2, 111.9, 70.1, 67.0, 56.5, 56.2, 46.0, 45.4, 43.0, 40.5, 40.0, 29.9, 27.8, 23.7, 22.4, 20.6, 17.8, 12.4, 3.2, 2.0.

HRMS (ESI-TOF): calc’d for C$_{27}$H$_{39}$O$_2$ [M-OH]$^+$: 395.2944, found 395.2944.

Spectroscopic data matched the literature.$^6$

$^6$WO 03/087048PCT/PL03/00037
### 1H NMR Data

| Literature Calcipotriol (7) | Synthetic 7 (600 MHz) | Δδ  |
|-----------------------------|-----------------------|-----|
| 6.37 (1H, J = 11.2 Hz)      | 6.40 (1H, J = 11.2 Hz) | +0.03 |
| 6.02 (1H, J = 11.2 Hz)      | 6.04 (1H, J = 11.2 Hz) | +0.02 |
| 5.47 (2H, m)                | 5.51-5.48 (2H, m)     | -   |
| 5.32 (1H, bs)               | 5.35 (1H, s)          | +0.03 |
| 5.00 (1H, bs)               | 5.02 (1H, s)          | +0.02 |
| 4.43 (1H, bs)               | 4.45 (1H, bs)         | +0.02 |
| 4.23 (1H, bs)               | 4.26 (1H, bs)         | +0.03 |
| 3.44 (1H, m)                | 3.47-3.45 (1H, m)     | -   |
| -                           | 2.87-2.85 (1H, m)     | -   |
| -                           | 2.63-2.61 (1H, m)     | -   |
| 1.05 (3H, J = 6.6 Hz)       | 1.07 (3H, J = 6.6 Hz) | +0.02 |
| 0.57 (3H, s)                | 0.59 (3H, s)          | +0.02 |
| 0.51 (2H, m)                | 0.57-0.50 (2H, m)     | -   |
| 0.32 (1H, m)                | 0.36-0.35 (1H, m)     | -   |
| 0.22 (1H, m)                | 0.25-0.23 (1H, m)     | -   |

### 13C NMR Data

| Literature Calcipotriol (7) | Synthetic 7 (151 MHz) | g   |
|-----------------------------|-----------------------|-----|
| 147.67                      | 147.79                | +0.12 |
| 142.96                      | 143.17                | +0.21 |
| 137.96                      | 138.16                | +0.20 |
| 132.97                      | 133.08                | +0.11 |
| 128.98                      | 129.09                | +0.11 |
| 124.94                      | 125.12                | +0.18 |
| 117.11                      | 117.24                | +0.13 |
| 111.73                      | 111.92                | +0.19 |
| 76.99 missing (buried in CHCl3) | -                |    |
| 70.82                       | 70.99                 | +0.17 |
| 66.86                       | 67.02                 | +0.16 |
| 56.36                       | 56.51                 | +0.15 |
| 56.07                       | 56.19                 | +0.12 |
| 45.88                       | 46.04                 | +0.16 |
| 45.28                       | 45.42                 | +0.14 |
| 42.89                       | 43.01                 | +0.12 |
| 40.35                       | 40.50                 | +0.15 |
| 39.88                       | 40.01                 | +0.13 |
| 29.05                       | 29.85                 | +0.8 |
| 27.62                       | 27.80                 | +0.18 |
| 23.54                       | 23.70                 | +0.16 |
| 22.24                       | 22.40                 | +0.16 |
| 20.49                       | 20.64                 | +0.15 |
| 17.65                       | 17.83                 | +0.18 |
| 12.27                       | 12.43                 | +0.16 |
| 3.04                        | 3.21                  | +0.17 |
| 1.83                        | 1.99                  | +0.16 |

6WO 03/087048PCT/PL03/00037
To a stirring solution of 48 (93 mg, 0.15 mmol, 1.0 equiv.) in hexanes (15 mL, 0.01 M) was added Pd/BaSO₄ (102 mg, 10 mol%) followed by 1.8 mL of a 0.5% quinoline solution in hexane. The reaction mixture was degassed with H₂ and allowed to stir at rt for 3 h, after which full consumption of starting material was observed by NMR. The crude reaction mixture was filtered through a small pad of SiO₂/celite and rinsed with 15 mL of hexane/EtOAc (20:1) into a 100 mL round-bottom flask. The reaction mixture was placed under Ar and heated to 50 °C after which full consumption of starting material was observed by NMR. The reaction mixture was concentrated under reduced pressure and used without further purification. To the crude triene was added THF/MeOH/H₂O (4:1:1, 0.9 mL, 0.2 M) after which LiOH·H₂O (72 mg, 1.7 mmol, 10 equiv.) was added and heated to 65 °C. The reaction was stirred for 15 h, after which it was cooled to rt by removal of the oil bath. 1M HCl (1 mL) was dropwise added followed by EtOAc (20 mL). H₂O was then added (10 mL), the layers were separated, and the aqueous phase extracted with EtOAc (3 x 15 mL). The combined organic extracts were then washed with brine (25 mL), dried (Na₂SO₄), filtered and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (4:1) to give 51 (46 mg, 46% over 2 steps) as a white foam.

**Physical State:** white foam.

**TLC:** Rₜ = 0.33 (4:1 hexanes:EtOAc).

**¹H NMR (500 MHz, CDCl₃)** δ 6.25 (d, J = 11.1 Hz, 1H), 6.05 (d, J = 11.2 Hz, 1H), 5.20 (s, 1H), 4.88 (d, J = 2.6 Hz, 1H), 4.39 (dd, J = 6.9, 3.5 Hz, 1H), 4.21 (dp, J = 7.5, 3.6 Hz, 1H), 2.86 (dd, J = 14.0, 5.1 Hz, 1H), 0.94-0.89 (m, 26H), 0.58 (s, 3H), 0.08 (d, J = 6.0 Hz, 15H).

**¹³C NMR (151 MHz, CDCl₃)** δ 181.4, 148.4, 140.3, 135.6, 123.1, 118.4, 111.5, 72.2, 67.7, 56.0, 53.0, 46.2, 45.9, 45.0, 42.8, 40.6, 32.1, 29.9, 28.9, 26.9, 26.0, 23.5, 22.4, 18.4, 18.3, 17.4, 14.3, 12.3, -4.5, -4.6, -4.9.

**HRMS (ESI-TOF):** calc’d for C₃₄H₆₀O₄Si₂ [M+H]⁺: 589.4108, found 589.4107.

[α]₂¹ = +34.2 (c = 0.5, CHCl₃).
General Experimental Procedure for the Synthesis of Vitamin D Analogs.

To a flame-dried culture tube was weighed out triene acid 52 (28 mg, 0.05 mmol, 1.0 equiv) and HATU (19 mg, 0.05 mmol, 1.05 equiv.). The contents were put under vacuum and backfilled with Ar (repeated 3X). THF (0.2 mL, 0.25 M) was then added followed by Et3N (7 uL, 0.05 mmol, 1.05 equiv.) at rt. The reaction mixture stirred at rt after which acid 52 was fully consumed as indicated by TLC. A solution of Fe(acac)3 (3.53 mg, 20 mol%), and dppz (8.9 mg, 40 mol%) in THF (0.15 mL) was subsequently added followed by a bolus addition of the corresponding ZnR2 (2.5 equiv.) at rt. The reaction mixture stirred overnight after which 1M HCl (3 mL) was added followed by EtOAc (3 mL). The layers were separated, and the aqueous phase extracted with EtOAc (3 x 5 mL). The combined organic extracts were then washed with brine (5 mL), dried (Na2SO4), filtered and concentrated under reduced pressure. The resulting crude mixture was filtered through a pad of SiO2 eluting with hexanes/EtOAc (20 mL, 20:1), concentrated under reduced pressure and carried through the subsequent step without further purification.

The crude reaction was placed in flame-dried culture tube, put under vacuum, and backfilled with Ar (repeated 3x). THF (0.5 mL, 0.05 M) was then added followed by the addition of TBAF (0.15 mL, 3.0 equiv., 1.0 M solution) at rt. The reaction mixture was then subsequently heated to 50 °C and stirred for 1h after which the mixture was cooled to rt by removal of the oil bath. 1M HCl (1 mL) was added followed by EtOAc (3 mL). The layers were separated, and the aqueous phase extracted with EtOAc (3 x 3 mL). The combined organic extracts were then washed with brine (5 mL), dried (Na2SO4), filtered and concentrated under reduced pressure. The reaction mixture was purified by flash chromatography eluting with hexanes/EtOAc (50:1) to give the desired arylated vitamin D analogs 53-57 as a statistical mixture of diastereomers.
Physical State: white foam.

TLC: $R_f = 0.20$ (1:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.17 (t, $J = 7.8$ Hz, 1H), 6.79 (dt, $J = 7.8$, 1.2 Hz, 1H), 6.74 (t, $J = 2.1$ Hz, 1H), 6.71 (ddd, $J = 8.1$, 2.6, 0.9 Hz, 1H), 6.34 (d, $J = 11.2$ Hz, 1H), 6.00 (d, $J = 11.2$ Hz, 1H), 5.33 (t, $J = 1.7$ Hz, 1H), 5.00 (t, $J = 1.6$ Hz, 1H), 4.43 (dd, $J = 7.6$, 4.8 Hz, 1H), 4.22 (tt, $J = 6.8$, 3.6 Hz, 1H), 3.80 (s, 3H), 2.72 (d, $J = 13.6$ Hz, 1H), 2.58 (dd, $J = 13.6$, 3.8 Hz, 1H), 2.53 (dd, $J = 10.9$, 6.8 Hz, 1H), 2.29 (dd, $J = 13.4$, 6.7 Hz, 1H), 2.01 (ddd, $J = 11.6$, 7.0, 4.0 Hz, 2H), 1.99 – 1.94 (m, 1H), 1.94 – 1.89 (m, 1H), 1.83 (q, $J = 9.7$ Hz, 1H), 1.54 – 1.48 (m, 2H), 1.41 (ddd, $J = 13.6$, 9.4, 4.9 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.27 – 1.24 (m, 1H), 1.21 (dt, $J = 13.6$, 4.4 Hz, 1H), 1.17 (d, $J = 6.8$ Hz, 3H), 0.76 (td, $J = 13.2$, 4.4 Hz, 1H), 0.54 (m, 1H), 0.52 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.5, 149.7, 147.8, 143.5, 132.9, 129.1, 125.2, 120.4, 117.1, 113.7, 111.9, 110.9, 71.0, 67.0, 57.4, 56.2, 46.1, 45.4, 43.0, 42.8, 39.4, 29.2, 27.6, 23.6, 22.9, 22.1, 12.5.

HRMS (ESI-TOF): calc’d for C$_{28}$H$_{38}$O$_3$ [M+H]$^+$: 423.2899, found 423.2899.

$[\alpha]_D^{21} = -28.1$ (c = 0.01, CHCl$_3$).

Physical State: white foam.

TLC: $R_f = 0.20$ (1:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.21 – 7.16 (m, 1H), 6.80 – 6.75 (m, 1H), 6.74 – 6.67 (m, 2H), 6.39 (d, $J = 11.3$ Hz, 1H), 6.00 (d, $J = 11.3$ Hz, 1H), 5.31 (t, $J = 1.7$ Hz, 1H), 4.99 (t, $J = 1.7$ Hz, 1H), 4.42 (m, 1H), 4.23 (m, 1H), 3.80 (s, 3H), 2.88 – 2.80 (m, 1H), 2.60 (d, $J = 13.8$ Hz, 1H), 2.56 (dd, $J = 10.7$, 6.8 Hz, 1H), 2.32 (dd, $J = 13.4$, 6.6 Hz, 1H), 2.10 (d, $J = 12.2$ Hz, 1H), 2.01 (dd, $J = 11.9$, 5.0 Hz, 2H), 1.95 – 1.87 (m, 1H), 1.81 – 1.76 (m, 1H), 1.76 – 1.70 (m, 2H), 1.50 – 1.46 (m, 1H), 1.46 – 1.39 (m, 1H), 1.37 – 1.32 (m, 1H), 1.32 – 1.28 (m, 2H), 1.27 – 1.24 (m, 3H), 1.11 (q, $J = 12.3$, 11.5 Hz, 1H), 0.65 (s, 3H).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 159.7, 150.4, 147.8, 143.1, 133.1, 129.3, 125.1, 119.9, 117.3, 113.4, 112.0, 110.7, 71.0, 67.0, 57.1, 56.5, 55.3, 46.2, 45.4, 43.7, 43.0, 40.7, 29.9, 28.4, 26.8, 24.7, 23.8, 12.3.

HRMS (ESI-TOF): calc’d for C$_{28}$H$_{38}$O$_3$ [M+H]$^+$: 423.2899, found 423.2899.

[α]$_D^{21}$ = +11.4 (c = 0.01, CHCl$_3$).

Physical State: white foam.

TLC: R$_f$ = 0.31 (1:1 hexanes:EtOAc).

$^{1}$H NMR (600 MHz, CDCl$_3$) δ 7.25 – 7.22 (m, 2H), 7.16 (d, $J$ = 7.1 Hz, 3H), 6.39 (d, $J$ = 11.3 Hz, 1H), 6.00 (d, $J$ = 11.2 Hz, 1H), 5.31 (s, 1H), 4.99 (s, 1H), 4.42 (m, 1H), 4.23 (m, 1H), 2.90 – 2.76 (m, 1H), 2.65 – 2.54 (m, 2H), 2.32 (dd, $J$ = 13.4, 6.6 Hz, 1H), 2.11 (d, $J$ = 13.0 Hz, 1H), 2.03 (td, $J$ = 12.0, 6.4 Hz, 2H), 1.97 – 1.87 (m, 1H), 1.79 (q, $J$ = 9.4 Hz, 1H), 1.74 (m, 2H), 1.48 (d, $J$ = 5.8 Hz, 1H), 1.46 – 1.39 (m, 1H), 1.35 (d, $J$ = 9.7 Hz, 1H), 1.31 (d, $J$ = 21.6 Hz, 2H), 1.27 (d, $J$ = 7.7 Hz, 3H), 1.13 – 1.03 (m, 1H), 0.66 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 148.6, 147.8, 143.1, 133.1, 128.3, 127.4, 125.8, 125.1, 117.3, 112.0, 71.0, 67.0, 57.2, 56.5, 46.2, 45.4, 43.6, 43.0, 40.7, 30.1, 29.2, 28.4, 23.8, 22.5, 12.3.

HRMS (ESI-TOF): calc’d for C$_{27}$H$_{36}$O$_2$ [M+H]$^+$: 393.2794, found 393.2790

[α]$_D^{21}$ = -18.1 (c = 0.01, CHCl$_3$).

Physical State: white foam.

TLC: R$_f$ = 0.31 (1:1 hexanes:EtOAc).

$^{1}$H NMR (600 MHz, CDCl$_3$) δ 7.24 (d, $J$ = 7.6 Hz, 2H), 7.21 – 7.15 (m, 3H), 6.33 (d, $J$ = 11.2 Hz, 1H), 6.00 (d, $J$ = 11.2 Hz, 1H), 5.33 (s, 1H), 5.00 (s, 1H), 4.64 – 4.36 (m, 1H), 4.25 – 4.18 (m, 1H), 2.71 (d, $J$ = 15.1 Hz, 1H), 2.63 – 2.52 (m, 2H), 2.29 (dd, $J$ = 13.7, 6.6 Hz, 1H), 2.02 (dt, $J$ = 14.6, 7.0 Hz, 2H), 1.96 (t, $J$ = 9.6 Hz, 1H), 1.94 – 1.89 (m, 1H), 1.84 (q, $J$ = 9.8 Hz, 1H), 1.49 (m, 2H),
1.47 (m, 1H), 1.45 – 1.40 (m, 1H), 1.34 – 1.28 (m, 1H), 1.20 (m, 1H), 1.18 (d, J = 6.9 Hz, 3H), 0.71 (td, J = 13.7, 5.0 Hz, 1H), 0.51 (s, 3H), 0.42 (d, J = 13.2 Hz, 1H).

\(^1\text{H NMR (600 MHz, CDCl}_3\) \(\delta 7.09 (d, J = 1.3 Hz, 4H), 6.34 (d, J = 11.3 Hz, 1H), 6.00 (d, J = 11.3 Hz, 1H), 5.33 (t, J = 1.7 Hz, 1H), 5.00 (s, 1H), 4.53 – 4.31 (m, 1H), 4.30 – 0.9 (m, 1H) 2.87 (p, J = 6.9 Hz, 1H), 2.71 (d, J = 13.7 Hz, 1H), 2.58 (d, J = 13.2 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.29 (dd, J = 13.5, 6.6 Hz, 1H), 2.01 (dd, J = 12.6, 7.5 Hz, 2H), 1.98 – 1.89 (m, 2H), 1.81 (q, J = 9.7 Hz, 1H), 1.55 – 1.50 (m, 2H), 1.50 – 1.45 (m, 1H), 1.45 – 1.38 (m, 1H), 1.31 (m, 1H), 1.23 (d, J = 6.9 Hz, 6H), 1.16 (d, J = 6.9 Hz, 3H), 0.89 (q, J = 7.9 Hz, 1H), 0.70 (td, J = 13.3, 4.5 Hz, 1H), 0.50 (s, 3H), 0.43 (d, J = 13.0 Hz, 1H).

\(^{13}\text{C NMR (151 MHz, CDCl}_3\) \(\delta 147.9, 147.8, 143.5, 132.9, 128.21, 127.7, 126.0, 125.2, 117.1, 111.9, 71.0, 67.0, 57.5, 56.2, 46.1, 45.4, 43.0, 42.8, 39.4, 29.2, 27.7, 23.6, 22.9, 22.1, 12.5.

HRMS (ESI-TOF): calc’d for C\(_{27}\)H\(_{36}\)O\(_2\) [M+H]\(^+\): 393.2794, found 393.2790.

\([\alpha]\)_D\(^{21}\) = +14.2 (c = 0.01, CHCl\(_3\)).

Physical State: white foam.

TLC: R\(_f\) = 0.29 (1:1 hexanes:EtOAc).

\(^1\text{H NMR (600 MHz, CDCl}_3\) \(\delta 7.16 – 6.95 (m, 4H), 6.39 (d, J = 11.2 Hz, 1H), 6.00 (d, J = 11.2 Hz, 1H), 5.31 (d, J = 1.8 Hz, 1H), 4.99 (t, J = 1.6 Hz, 1H), 4.42 (dd, J = 8.0, 4.3 Hz, 1H), 4.23 (dd, J = 6.7, 3.4 Hz, 1H), 2.86 (td, J = 12.4, 10.8, 5.7 Hz, 2H), 2.60 (d, J = 11.5 Hz, 1H), 2.55 (dd, J = 10.7,
6.8 Hz, 1H), 2.32 (dd, J = 13.4, 6.5 Hz, 1H), 2.11 (d, J = 12.7 Hz, 1H), 2.06 – 1.98 (m, 2H), 1.91 (ddd, J = 12.9, 8.4, 3.4 Hz, 1H), 1.81 – 1.69 (m, 3H), 1.49 – 1.45 (m, 1H), 1.45 – 1.39 (m, 1H), 1.38 – 1.27 (m, 3H), 1.25 (d, J = 6.7 Hz, 3H), 1.24 (d, J = 6.9 Hz, 6H), 1.15 – 1.00 (m, 1H), 0.65 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 147.8, 146.2, 145.9, 143.3, 133.07, 127.2, 126.3, 125.1, 117.2, 111.9, 71.0, 67.0, 57.4, 56.5, 46.1, 45.4, 43.2, 43.0, 40.7, 33.7, 29.3, 28.5, 24.2, 24.2, 23.8, 22.5, 22.3, 12.3.

HRMS (ESI-TOF): calc'd for C$_{30}$H$_{42}$O$_2$ [M+H]$^+$: 435.3263, found 435.3261.

$[\alpha]_D^{21} = +16.4$ (c = 0.01, CHCl$_3$).

Physical State: white foam.

TLC: $R_f = 0.30$ (1:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.06 – 7.78 (m, 2H), 7.28 – 7.26 (m, 1H), 7.26 – 7.25 (m, 1H), 6.32 (d, J = 11.2 Hz, 1H), 6.00 (d, J = 11.3 Hz, 1H), 5.33 (t, J = 1.7 Hz, 1H), 5.08 – 4.89 (m, 1H), 4.53 – 4.36 (m, 1H), 4.28 – 4.16 (m, 1H), 3.90 (s, 3H), 2.70 (d, J = 13.7 Hz, 1H), 2.66 – 2.60 (m, 1H), 2.57 (d, J = 12.2 Hz, 1H), 2.29 (dd, J = 13.5, 6.6 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.96 (t, J = 9.5 Hz, 1H), 1.91 (ddd, J = 13.7, 8.6, 4.0 Hz, 1H), 1.86 (q, J = 9.6 Hz, 1H), 1.51 – 1.50 (m, 1H), 1.50 – 1.47 (m, 2H), 1.46 – 1.40 (m, 1H), 1.34 – 1.28 (m, 1H), 1.19 (d, J = 6.9 Hz, 3H), 1.16 – 1.12 (m, 1H), 0.70 (td, J = 13.3, 4.6 Hz, 1H), 0.50 (s, 3H), 0.38 (d, J = 12.8 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 167.4, 153.6, 147.8, 143.1, 133.1, 129.7, 128.0, 127.8, 125.1, 117.2, 111.9, 71.0, 67.0, 57.3, 56.2, 52.1, 46.0, 45.4, 43.0, 42.9, 39.6, 29.1, 27.6, 23.5, 22.7, 22.0, 12.6.

HRMS (ESI-TOF): calc'd for C$_{29}$H$_{38}$O$_4$ [M+H]$^+$: 451.2848, found 451.2845.

$[\alpha]_D^{21} = -26.9$ (c = 0.01, CHCl$_3$).

Physical State: white foam.

TLC: $R_f = 0.30$ (1:1 hexanes:EtOAc).
\[1^H\text{ NMR (600 MHz, CDCl}_3\] } \delta 7.94 (d, \(J = 8.3 \text{ Hz}, 2\)H), 7.25 – 7.21 (m, 2H), 6.38 (d, \(J = 11.2 \text{ Hz}, 1\)H), 6.00 (d, \(J = 11.2 \text{ Hz}, 1\)H), 5.31 (t, \(J = 1.7 \text{ Hz}, 1\)H), 4.99 (dd, \(J = 2.0, 1.2 \text{ Hz}, 1\)H), 4.42 (m, 1H), 4.23 (m, 1H), 3.90 (s, 3H), 2.90 – 2.82 (m, 1H), 2.69 – 2.63 (m, 1H), 2.63 – 2.57 (m, 1H), 2.32 (dd, \(J = 13.4, 6.6 \text{ Hz}, 1\)H), 2.11 (d, \(J = 12.2 \text{ Hz}, 1\)H), 2.02 (ddd, \(J = 18.6, 12.2, 5.9 \text{ Hz}, 2\)H), 1.91 (dd, \(J = 17.6, 8.3, 4.3 \text{ Hz}, 1\)H), 1.80 (q, \(J = 9.7 \text{ Hz}, 1\)H), 1.77 – 1.69 (m, 2H), 1.62 (m, 1H), 1.48 (m, 2H), 1.46 – 1.40 (m, 1H), 1.37 – 1.32 (m, 1H), 1.27 (d, \(J = 6.8 \text{ Hz}, 3\)H), 1.06 (q, \(J = 10.3 \text{ Hz}, 1\)H), 0.66 (s, 3H).

\[13^C\text{ NMR (151 MHz, CDCl}_3\] } \delta 167.3, 154.0, 147.8, 142.8, 133.3, 129.9, 127.9, 127.5, 125.0, 117.4, 112.0, 71.0, 67.0, 56.92, 56.4, 52.1, 46.2, 45.4, 43.7, 43.0, 40.7, 29.2, 28.3, 23.7, 22.3, 22.2, 12.3.

HRMS (ESI-TOF): calc’d for C\(_{29}\)H\(_{38}\)O\(_4\) [M+H]\(^+\): 451.2848, found 451.2845.

\([\alpha]\)\(_D\)\(^{21}\) = +17.8 (c = 0.01, CHCl\(_3\)).

Physical State: white foam.

TLC: \(R_f = 0.19\) (1:1 hexanes:EtOAc).

\[1^H\text{ NMR (600 MHz, CDCl}_3\] } \delta 7.61 – 7.58 (m, 2H), 7.46 – 7.39 (m, 4H), 7.36 – 7.30 (m, 2H), 7.17 (dt, \(J = 7.6, 1.5 \text{ Hz}, 1\)H), 6.33 (d, \(J = 11.2 \text{ Hz}, 1\)H), 6.01 (d, \(J = 11.5 \text{ Hz}, 1\)H), 5.33 (t, \(J = 1.7 \text{ Hz}, 1\)H), 5.00 (t, \(J = 1.6 \text{ Hz}, 1\)H), 4.43 (dt, \(J = 8.9, 4.7 \text{ Hz}, 1\)H), 4.28 – 4.17 (m, 1H), 2.71 (d, \(J = 13.7 \text{ Hz}, 1\)H), 2.63 (dq, \(J = 10.7, 6.9 \text{ Hz}, 1\)H), 2.58 (dd, \(J = 13.4, 3.8 \text{ Hz}, 1\)H), 2.29 (dd, \(J = 13.5, 6.6 \text{ Hz}, 1\)H), 2.09 – 2.02 (m, 1H), 2.02 – 1.97 (m, 2H), 1.94 – 1.88 (m, 2H), 1.56 – 1.55 (m, 1H), 1.55 – 1.51 (m, 2H), 1.44 (ddt, \(J = 14.4, 10.0, 9.6, 4.9 \text{ Hz}, 1\)H), 1.36 – 1.30 (m, 1H), 1.23 (d, \(J = 6.8 \text{ Hz}, 3\)H), 1.22 – 1.17 (m, 1H), 0.77 (td, \(J = 13.2, 4.4 \text{ Hz}, 1\)H), 0.54 (s, 3H), 0.54 – 0.51 (m, 1H).

\[13^C\text{ NMR (151 MHz, CDCl}_3\] } \delta 148.4, 147.8, 143.4, 141.7, 141.0, 133.0, 128.9, 128.6, 127.3, 127.3, 126.9, 126.5, 125.1, 124.9, 117.1, 111.9, 71.0, 67.0, 57.5, 56.2, 46.1, 45.4, 43.0, 42.9, 39.6, 29.2, 27.7, 23.6, 23.0, 22.1, 12.6.

HRMS (ESI-TOF): calc’d for C\(_{33}\)H\(_{40}\)O\(_2\) [M-OH]\(^+\): 451.3001, found 451.2995.

\([\alpha]\)\(_D\)\(^{21}\) = -19.5 (c = 0.01, CHCl\(_3\)).
Physical State: white foam.

TLC: $R_f = 0.19$ (1:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.62 – 7.57 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.41 – 7.38 (m, 2H), 7.36 – 7.31 (m, 2H), 7.15 (dt, $J = 7.6$, 1.5 Hz, 1H), 6.39 (d, $J = 11.2$ Hz, 1H), 6.01 (d, $J = 11.2$ Hz, 1H), 5.31 (t, $J = 1.8$ Hz, 1H), 4.99 (t, $J = 1.6$ Hz, 1H), 4.44 – 4.40 (m, 1H), 4.26 – 4.20 (m, 1H), 2.90 – 2.83 (m, 1H), 2.66 (dq, $J = 10.7$, 6.8 Hz, 1H), 2.60 (dd, $J = 13.2$, 3.7 Hz, 1H), 2.32 (dd, $J = 13.4$, 6.6 Hz, 1H), 2.13 (dd, $J = 12.4$, 3.2 Hz, 1H), 2.03 (ddd, $J = 25.7$, 12.2, 5.4 Hz, 2H), 1.92 (ddd, $J = 11.9$, 7.9, 3.1 Hz, 1H), 1.84 (q, $J = 9.8$ Hz, 1H), 1.76 – 1.70 (m, 2H), 1.61 – 1.59 (m, 1H), 1.52 – 1.50 (m, 1H), 1.48 – 1.41 (m, 1H), 1.40 – 1.34 (m, 2H), 1.32 (d, $J = 6.9$ Hz, 3H), 1.14 (q, $J = 11.2$, 10.8 Hz, 1H), 0.68 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 149.1, 147.8, 143.1, 141.7, 141.3, 133.2, 128.8, 128.8, 127.4, 127.3, 126.4, 126.3, 125.1, 124.7, 117.3, 112.0, 71.0, 67.0, 57.2, 56.5, 46.2, 45.4, 43.7, 43.0, 40.8, 29.2, 28.5, 23.8, 22.5, 22.3, 12.3.

HRMS (ESI-TOF): calc’d for C$_{33}$H$_{40}$O$_2$ [M-OH]$^+$: 451.3001, found 451.2995.

$[\alpha]_D^{21} = +22.6$ ($c = 0.01$, CHCl$_3$).
8. Biological Testing

Testing vitamin D analogues for inhibition of IL-17A secretion from human PBMC:

Peripheral blood mononuclear cells (PBMC) were isolated from human buffy coats. A total of four donors were used for the experiment. The cells were suspended in RPMI1640 with 10% foetal calf serum, pen/strep and glutamax and supplemented with 20 ng/mL of IL-23 (R&D systems, cat. no 1290-IL-010).

Test compounds were dissolved and diluted in DMSO and added in duplicates to 384 well plates to give a final concentration of 0.1% DMSO in all wells.

The cells were mixed with antiCD3/antiCD28-coated beads ((1 cell pr bead) (Milteney T-cell expansion kit), and immediately thereafter the cells were pipetted to the plates at 130,000 cells per well. The plates were incubated for 3 days at 37°C with 5% CO₂.

On day 3 the level of IL-17A in the culture supernatants was measured using an alpha-LISA kit (Perkin Elmer cat. No AL219F).

Cell viability was measured by adding PrestoBlue® (Life technologies, cat. no A13262) and incubated for 4 hours at 37°C. Live cells reduce resazurin to resorufin which is highly fluorescent and this was measured (Ex535/Em615).

Compounds Evaluated (Table S12)

| LEO number | Structure | IL-17A inh, hPBMC, bead (1321) GMean Rel EC50 (nM) | IL-17A inh, hPBMC, bead (1321) Mean Emax (%) | Viability, hPBMC, bead (1322) GMean Rel EC50 (nM) | Viability, hPBMC, bead (1322) Mean Emax (%) |
|------------|-----------|--------------------------------------------------|---------------------------------------------|-----------------------------------------------|---------------------------------------------|
| MC2220A    | ![Structure](image) | 5.90                                              | 96.6                                         | >10000                                        |                                             |
| LEO174129A | ![Structure](image) | 104                                               | 90.8                                         | >10000                                        |                                             |
| Compound       | Code    | Value1 | Value2 | Value3 |
|---------------|---------|--------|--------|--------|
| LEO174130A    |         | 12.4   | 92.8   | >10000 |
| LEO174135A    |         | 852    | 109    | >10000 |
| MC903A        |         | 0.287  | 84.8   | >10000 |
| EB895A        |         | 0.325  | 91.2   | >10000 |
| LEO174131A    |         | 750    | 84     | >10000 |
| LEO174132A    |         | 411    | 90.4   | >10000 |
| LEO174133A    |         | >10000 | 16.1   | >10000 |
| LEO174134A | ![Molecule Image](image1) | 469 | 72.6 | >10000 |
|-------------|--------------------------|-----|------|--------|
| LEO174136A | ![Molecule Image](image2) | 9.37| 92.6 | >10000 |
| LEO174137A | ![Molecule Image](image3) | 2770| 100  | >10000 |
9. NMR Spectra
HSQC
HMBC

32

HMBC
32 NOESY
38
53b
57a

HSQC
57a
COSY
57b
COSY
10. X-ray Crystallographic Data for Diol 30
Table 1. Crystal data and structure refinement for Baran776.

| Property                          | Value                        |
|----------------------------------|------------------------------|
| Report date                      | 2021-01-22                   |
| Identification code              | baran776                     |
| Empirical formula                | C7 H10 O3                    |
| Molecular formula                | C7 H10 O3                    |
| Formula weight                   | 142.15                       |
| Temperature                      | 100.0 K                      |
| Wavelength                       | 1.54178 Å                    |
| Crystal system                   | Orthorhombic                 |
| Space group                      | P2,2,2                       |
| Unit cell dimensions             | a = 12.7070(2) Å, b = 15.0443(2) Å, c = 7.40520(10) Å |
|                                 | â = 90°, â = 90°, â = 90°    |
| Volume                           | 1415.64(3) Å³                |
| Z                                | 8                            |
| Density (calculated)             | 1.334 Mg/m³                  |
| Absorption coefficient           | 0.875 mm⁻¹                   |
| F(000)                           | 608                          |
| Crystal size                     | 0.22 x 0.2 x 0.2 mm³         |
| Crystal color, habit             | colorless block              |
| Theta range for data collection  | 4.555 to 70.138°             |
| Index ranges                     | -15<=h<=15, -18<=k<=18, -9<=l<=8 |
| Reflections collected            | 19402                        |
| Independent reflections          | 2679 [R(int) = 0.0298]        |
| Completeness to theta = 67.500° | 100.0 %                      |
| Absorption correction            | Semi-empirical from equivalents |
| Max. and min. transmission       | 0.7533 and 0.6238             |
| Refinement method                | Full-matrix least-squares on F² |
| Data / restraints / parameters   | 2679 / 0 / 188               |
| Goodness-of-fit on F²            | 1.058                         |
| Description                                      | Value               |
|-------------------------------------------------|---------------------|
| Final R indices [I>2sigma(I)]                  | R1 = 0.0238, wR2 = 0.0615 |
| R indices (all data)                           | R1 = 0.0243, wR2 = 0.0618 |
| Absolute structure parameter                   | -0.01(3)            |
| Extinction coefficient                         | 0.0024(3)           |
| Largest diff. peak and hole                    | 0.158 and -0.127 e Å^-3 |
Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Baran776. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|      | x     | y     | z     | $U(\text{eq})$ |
|------|-------|-------|-------|----------------|
| O(1) | 2472(1) | 3763(1) | 7313(2) | 26(1)         |
| O(2) | 3498(1) | 5498(1) | 7407(2) | 34(1)         |
| O(3) | 3579(1) | 5234(1) | 13758(2) | 43(1)        |
| C(1) | 2396(1) | 4355(1) | 8813(2) | 23(1)         |
| C(2) | 3398(1) | 4918(1) | 8913(2) | 25(1)         |
| C(3) | 3431(2) | 5490(1) | 10602(2) | 30(1)        |
| C(4) | 3249(1) | 4966(1) | 12306(2) | 29(1)        |
| C(5) | 2638(1) | 4140(1) | 12149(2) | 28(1)        |
| C(6) | 2264(1) | 3860(1) | 10570(2) | 26(1)        |
| C(7) | 1402(1) | 4897(1) | 8455(2) | 33(1)         |
| O(1')| 3657(1) | 2275(1) | 8001(1) | 24(1)         |
| O(2')| 5838(1) | 2754(1) | 7226(2) | 25(1)         |
| O(3')| 4871(1) | 2556(1) | 1012(2) | 45(1)         |
| C(1')| 4232(1) | 2020(1) | 6413(2) | 20(1)         |
| C(2')| 5026(1) | 2742(1) | 5911(2) | 20(1)         |
| C(3')| 5486(1) | 2588(1) | 4031(2) | 24(1)         |
| C(4')| 4666(1) | 2432(1) | 2612(2) | 27(1)         |
| C(5')| 3633(1) | 2112(1) | 3194(2) | 25(1)         |
| C(6')| 3431(1) | 1934(1) | 4927(2) | 22(1)         |
| C(7')| 4742(1) | 1116(1) | 6751(2) | 26(1)         |
Table 3. Bond lengths [Å] and angles [°] for Baran776.

| Bond                  | Length [Å] | Angle [°]   |
|-----------------------|------------|-------------|
| O(1)-H(1)             | 0.8400     | C(2’)-C(3’) | 1.527(2)   |
| O(1)-C(1)             | 1.4273(18) | C(3’)-H(3’A) | 0.9900     |
| O(2)-H(2)             | 0.8400     | C(3’)-H(3’B) | 0.9900     |
| O(2)-C(2)             | 1.4218(18) | C(3’)-C(4’)  | 1.498(2)   |
| O(3)-C(4)             | 1.222(2)   | C(4’)-C(5’)  | 1.463(2)   |
| C(1)-C(2)             | 1.531(2)   | C(5’)-H(5’)  | 0.9500     |
| C(1)-C(6)             | 1.509(2)   | C(5’)-C(6’)  | 1.336(2)   |
| C(1)-C(7)             | 1.526(2)   | C(6’)-H(6’)  | 0.9500     |
| C(2)-H(2A)            | 1.0000     | C(7’)-H(7’A) | 0.9800     |
| C(2)-C(3)             | 1.519(2)   | C(7’)-H(7’B) | 0.9800     |
| C(3)-H(3A)            | 0.9900     | C(7’)-H(7’C) | 0.9800     |
| C(3)-H(3B)            | 0.9900     |             |            |
| C(3)-C(4)             | 1.507(2)   | C(1)-O(1)-H(1) | 109.5      |
| C(4)-C(5)             | 1.469(2)   | C(2)-O(2)-H(2) | 109.5      |
| C(5)-H(5)             | 0.9500     | O(1)-C(1)-C(2) | 109.08(13) |
| C(5)-C(6)             | 1.331(2)   | O(1)-C(1)-C(6) | 111.71(12) |
| C(6)-H(6)             | 0.9500     | O(1)-C(1)-C(7) | 104.75(13) |
| C(7)-H(7A)            | 0.9800     | C(6)-C(1)-C(2) | 108.90(13) |
| C(7)-H(7B)            | 0.9800     | C(6)-C(1)-C(7) | 108.71(14) |
| C(7)-H(7C)            | 0.9800     | C(7)-C(1)-C(2) | 113.68(13) |
| O(1’)-H(1’)           | 0.8400     | O(2)-C(2)-C(1) | 112.05(13) |
| O(1’)-C(1’)           | 1.4371(18) | O(2)-C(2)-H(2A) | 108.5      |
| O(2’)-H(2’)           | 0.8400     | O(2)-C(2)-C(3) | 107.15(13) |
| O(2’)-C(2’)           | 1.4180(17) | C(1)-C(2)-H(2A) | 108.5      |
| O(3’)-C(4’)           | 1.228(2)   | C(3)-C(2)-C(1) | 112.08(13) |
| C(1’)-C(2’)           | 1.528(2)   | C(3)-C(2)-H(2A) | 108.5      |
| C(1’)-C(6’)           | 1.505(2)   | C(2)-C(3)-H(3A) | 109.0      |
| C(1’)-C(7’)           | 1.527(2)   | C(2)-C(3)-H(3B) | 109.0      |
| C(2’)-H(2’A)          | 1.0000     | H(3A)-C(3)-H(3B) | 107.8      |
| Bond                        | Length (Å) | Bond                        | Length (Å) |
|-----------------------------|------------|-----------------------------|------------|
| C(4)-C(3)-C(2)             | 112.85(13) | C(3')-C(2')-H(2'A)          | 108.7      |
| C(4)-C(3)-H(3A)            | 109.0      | C(2')-C(3')-H(3'A)          | 108.9      |
| C(4)-C(3)-H(3B)            | 109.0      | C(2')-C(3')-H(3'B)          | 108.9      |
| O(3)-C(4)-C(3)             | 120.76(15) | H(3'A)-C(3')-H(3'B)         | 107.7      |
| O(3)-C(4)-C(5)             | 122.01(15) | C(4')-C(3')-C(2')          | 113.43(13) |
| C(5)-C(4)-C(3)             | 117.20(14) | C(4')-C(3')-H(3'A)          | 108.9      |
| C(4)-C(5)-H(5)             | 119.1      | C(4')-C(3')-H(3'B)          | 108.9      |
| C(6)-C(5)-C(4)             | 121.78(15) | O(3')-C(4')-C(3')          | 120.36(15) |
| C(6)-C(5)-H(5)             | 119.1      | O(3')-C(4')-C(5')          | 121.67(15) |
| C(1)-C(6)-H(6)             | 117.9      | C(5')-C(4')-C(3')          | 117.96(15) |
| C(5)-C(6)-C(1)             | 124.14(15) | C(4')-C(5')-H(5')          | 119.3      |
| C(5)-C(6)-H(6)             | 117.9      | C(6')-C(5')-C(4')          | 121.41(15) |
| C(1)-C(7)-H(7A)            | 109.5      | C(6')-C(5')-H(5')          | 119.3      |
| C(1)-C(7)-H(7B)            | 109.5      | C(1')-C(6')-H(6')          | 118.1      |
| C(1)-C(7)-H(7C)            | 109.5      | C(5')-C(6')-C(1')          | 123.76(15) |
| H(7A)-C(7)-H(7B)           | 109.5      | C(5')-C(6')-H(6')          | 118.1      |
| H(7A)-C(7)-H(7C)           | 109.5      | C(1')-C(7')-H(7'A)         | 109.5      |
| H(7B)-C(7)-H(7C)           | 109.5      | C(1')-C(7')-H(7'B)         | 109.5      |
| C(1')-O(1')-H(1')          | 109.5      | C(1')-C(7')-H(7'C)         | 109.5      |
| C(2')-O(2')-H(2')          | 109.5      | H(7'A)-C(7')-H(7'B)        | 109.5      |
| O(1')-C(1')-C(2')          | 110.17(12) | H(7'A)-C(7')-H(7'C)        | 109.5      |
| O(1')-C(1')-C(6')          | 106.11(12) | H(7'B)-C(7')-H(7'C)        | 109.5      |
| O(1')-C(1')-C(7')          | 108.65(12) |                            |            |
| C(6')-C(1')-C(2')          | 109.26(12) |                            |            |
| C(6')-C(1')-C(7')          | 109.29(13) |                            |            |
| C(7')-C(1')-C(2')          | 113.12(13) |                            |            |
| O(2')-C(2')-C(1')          | 108.82(12) |                            |            |
| O(2')-C(2')-H(2'A)         | 108.7      |                            |            |
| O(2')-C(2')-C(3')          | 110.51(12) |                            |            |
| C(1')-C(2')-H(2'A)         | 108.7      |                            |            |
| C(3')-C(2')-C(1')          | 111.49(12) |                            |            |
Table 4. Anisotropic displacement parameters ($\AA^2 \times 10^3$) for Baran776. The anisotropic displacement factor exponent takes the form: $-\frac{1}{2} \sum h^2 a^* a^* U_{11} + ... + 2h k a^* b^* U_{12}$

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|---------|---------|---------|---------|---------|---------|
| O(1)  | 30(1)   | 24(1)   | 26(1)   | -4(1)   | -4(1)   | 1(1)    |
| O(2)  | 56(1)   | 29(1)   | 16(1)   | 0(1)    | 5(1)    | -14(1)  |
| O(3)  | 66(1)   | 45(1)   | 18(1)   | -2(1)   | -1(1)   | -9(1)   |
| C(1)  | 26(1)   | 20(1)   | 23(1)   | -1(1)   | 2(1)    | 1(1)    |
| C(2)  | 30(1)   | 26(1)   | 18(1)   | 0(1)    | 3(1)    | -5(1)   |
| C(3)  | 41(1)   | 28(1)   | 20(1)   | -1(1)   | 2(1)    | -8(1)   |
| C(4)  | 35(1)   | 30(1)   | 20(1)   | -2(1)   | 5(1)    | 3(1)    |
| C(5)  | 35(1)   | 26(1)   | 23(1)   | 6(1)    | 9(1)    | 3(1)    |
| C(6)  | 26(1)   | 21(1)   | 31(1)   | 2(1)    | 7(1)    | 1(1)    |
| C(7)  | 32(1)   | 30(1)   | 38(1)   | 1(1)    | -2(1)   | 6(1)    |
| O(1') | 24(1)   | 31(1)   | 18(1)   | -1(1)   | 1(1)    | 2(1)    |
| O(2') | 27(1)   | 27(1)   | 20(1)   | 0(1)    | -6(1)   | -4(1)   |
| O(3') | 40(1)   | 77(1)   | 18(1)   | 2(1)    | 0(1)    | -10(1)  |
| C(1') | 23(1)   | 20(1)   | 17(1)   | -1(1)   | 0(1)    | 2(1)    |
| C(2') | 23(1)   | 21(1)   | 17(1)   | -1(1)   | -2(1)   | 1(1)    |
| C(3') | 22(1)   | 32(1)   | 19(1)   | 1(1)    | 1(1)    | -2(1)   |
| C(4') | 31(1)   | 32(1)   | 19(1)   | -2(1)   | 0(1)    | 1(1)    |
| C(5') | 26(1)   | 26(1)   | 23(1)   | -3(1)   | -6(1)   | 0(1)    |
| C(6') | 21(1)   | 21(1)   | 25(1)   | -2(1)   | -1(1)   | -1(1)   |
| C(7') | 28(1)   | 22(1)   | 28(1)   | 2(1)    | -1(1)   | 2(1)    |
Table 5. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for Baran776.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| H(1) | 2851  | 3326  | 7595  | 40    |
| H(2) | 3518  | 5198  | 6451  | 51    |
| H(2A) | 4019  | 4509  | 8930  | 30    |
| H(3A) | 4125  | 5787  | 10676 | 36    |
| H(3B) | 2886  | 5959  | 10506 | 36    |
| H(5)  | 2507  | 3797  | 13202 | 34    |
| H(6)  | 1889  | 3314  | 10548 | 31    |
| H(7A) | 1450  | 5175  | 7261  | 50    |
| H(7B) | 1332  | 5359  | 9380  | 50    |
| H(7C) | 787   | 4505  | 8494  | 50    |
| H(1') | 4078  | 2350  | 8862  | 36    |
| H(2') | 6044  | 3279  | 7381  | 38    |
| H(2'A) | 4661  | 3330  | 5924  | 24    |
| H(3'A) | 5911  | 3112  | 3686  | 29    |
| H(3'B) | 5962  | 2068  | 4074  | 29    |
| H(5') | 3094  | 2029  | 2321  | 30    |
| H(6') | 2743  | 1742  | 5239  | 27    |
| H(7'A) | 5204  | 1153  | 7809  | 39    |
| H(7'B) | 5157  | 943   | 5692  | 39    |
| H(7'C) | 4193  | 671   | 6970  | 39    |
Table 6. Hydrogen bonds for Baran776 [Å and °].

| D-H...A       | d(D-H) | d(H...A) | d(D...A)     | <(DHA) |
|---------------|--------|----------|--------------|--------|
| O(1)-H(1)...O(1') | 0.84   | 1.91     | 2.7449(16)   | 173.8  |
| O(2)-H(2)...O(3)#1 | 0.84   | 2.00     | 2.7332(17)   | 145.9  |
| O(1')-H(1')...O(3')#2 | 0.84   | 1.91     | 2.7438(16)   | 172.3  |
| O(2')-H(2')...O(2)#3  | 0.84   | 1.93     | 2.7649(16)   | 172.7  |

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z-1  #2 x,y,z+1  #3 -x+1,-y+1,z
11. X-ray Crystallographic Data for Keto-Diol 42
Table 1. Crystal data and structure refinement for Baran782.

| Description                                      | Value                                      |
|--------------------------------------------------|--------------------------------------------|
| Report date                                      | 2021-09-28                                 |
| Identification code                              | baran782                                   |
| Empirical formula                               | C13 H22 O5                                 |
| Molecular formula                                | C13 H22 O5                                 |
| Formula weight                                   | 258.30                                     |
| Temperature                                      | 100.0 K                                    |
| Wavelength                                       | 1.54178 Å                                  |
| Crystal system                                   | Orthorhombic                               |
| Space group                                      | P2,2,2_1                                   |
| Unit cell dimensions                             | a = 12.6035(3) Å, b = 16.5398(4) Å, c = 20.3896(4) Å |
| Volume                                           | 4250.40(17) Å³                            |
| Z                                                | 12                                         |
| Density (calculated)                             | 1.211 Mg/m³                                |
| Absorption coefficient                           | 0.763 mm⁻¹                                 |
| F(000)                                           | 1680                                       |
| Crystal size                                     | 0.21 x 0.18 x 0.175 mm³                    |
| Crystal color, habit                             | colorless block                            |
| Theta range for data collection                  | 3.441 to 69.845°.                          |
| Index ranges                                     | -15<=h<=15, -19<=k<=19, -23<=l<=24          |
| Reflections collected                            | 38350                                      |
| Independent reflections                          | 7940 [R(int) = 0.0453]                     |
| Completeness to theta = 67.500°                  | 100.0 %                                    |
| Absorption correction                            | None                                       |
| Max. and min. transmission                       | 0.6600 and 0.6105                          |
| Refinement method                                | Full-matrix least-squares on F²            |
| Data / restraints / parameters                    | 7940 / 1 / 510                             |
| Goodness-of-fit on F²                             | 1.024                                      |
Final R indices [I>2sigma(I)] \[ R1 = 0.0276, \text{wR}2 = 0.0663 \]
R indices (all data) \[ R1 = 0.0301, \text{wR}2 = 0.0678 \]
Absolute structure parameter \[ 0.01(5) \]
Largest diff. peak and hole \[ 0.152\text{ and }-0.161\text{ e.Å}^{-3} \]
Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for Baran782. U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

|      | x      | y      | z      | U(eq) |
|------|--------|--------|--------|-------|
| O(1) | 3154(1)| 4490(1)| 2813(1)| 26(1) |
| O(2) | 2935(1)| 5951(1)| 3253(1)| 20(1) |
| O(3) | 4926(1)| 5584(1)| 3752(1)| 23(1) |
| O(4) | -813(1)| 4992(1)| 3760(1)| 22(1) |
| O(5) | -40(1)| 5430(1)| 4694(1)| 26(1) |
| C(1) | 3184(1)| 4528(1)| 3408(1)| 18(1) |
| C(2) | 3026(2)| 5343(1)| 3745(1)| 17(1) |
| C(3) | 4024(2)| 5510(1)| 4164(1)| 19(1) |
| C(4) | 4260(2)| 4819(1)| 4637(1)| 21(1) |
| C(5) | 4389(2)| 4016(1)| 4276(1)| 22(1) |
| C(6) | 3417(2)| 3824(1)| 3845(1)| 20(1) |
| C(7) | 2005(2)| 5354(1)| 4154(1)| 19(1) |
| C(8) | 1039(2)| 5080(1)| 3764(1)| 21(1) |
| C(9) | 15(2)| 5191(1)| 4135(1)| 20(1) |
| C(10) | -1921(2)| 5072(1)| 4004(1)| 22(1) |
| C(11) | -2082(2)| 4573(1)| 4622(1)| 26(1) |
| C(12) | -2562(2)| 4728(1)| 3442(1)| 29(1) |
| C(13) | -2177(2)| 5959(1)| 4110(1)| 27(1) |
| O(1") | 1206(1)| 3637(1)| 4941(1)| 25(1) |
| O(2") | 912(1)| 4758(1)| 5869(1)| 20(1) |
| O(3") | 3019(1)| 4464(1)| 6087(1)| 23(1) |
| O(4") | -2552(1)| 3519(1)| 6188(1)| 22(1) |
| O(5") | -1653(1)| 3238(1)| 7118(1)| 25(1) |
| C(1") | 1418(1)| 3421(1)| 5496(1)| 19(1) |
|      |            |            |            |            |
|------|------------|------------|------------|------------|
| C(2")| 1208(2)    | 3976(1)    | 6078(1)    | 17(1)      |
| C(3")| 2245(2)    | 4062(1)    | 6475(1)    | 19(1)      |
| C(4")| 2713(2)    | 3250(1)    | 6668(1)    | 25(1)      |
| C(5")| 2923(2)    | 2726(1)    | 6065(1)    | 28(1)      |
| C(6")| 1906(2)    | 2613(1)    | 5654(1)    | 26(1)      |
| C(7")| 310(1)     | 3629(1)    | 6508(1)    | 19(1)      |
| C(8")| -708(2)    | 3516(1)    | 6115(1)    | 21(1)      |
| C(9")| -1673(2)   | 3405(1)    | 6541(1)    | 19(1)      |
| C(10")| -3633(1)  | 3446(1)    | 6470(1)    | 21(1)      |
| C(11")| -3860(2)  | 2562(1)    | 6606(1)    | 28(1)      |
| C(12")| -4306(2)  | 3772(2)    | 5912(1)    | 32(1)      |
| C(13")| -3765(2)  | 3974(1)    | 7072(1)    | 26(1)      |
| O(1') | 4854(1)    | 8176(1)    | 2192(1)    | 23(1)      |
| O(2') | 5090(1)    | 7080(1)    | 3133(1)    | 19(1)      |
| O(3') | 3089(1)    | 7622(1)    | 3412(1)    | 24(1)      |
| O(4') | 8790(1)    | 7873(1)    | 3479(1)    | 23(1)      |
| O(5') | 8015(1)    | 8806(1)    | 4131(1)    | 28(1)      |
| C(1') | 4797(1)    | 8442(1)    | 2746(1)    | 18(1)      |
| C(2') | 4980(1)    | 7898(1)    | 3342(1)    | 16(1)      |
| C(3') | 3965(2)    | 7938(1)    | 3766(1)    | 20(1)      |
| C(4') | 3677(2)    | 8800(1)    | 3950(1)    | 24(1)      |
| C(5') | 3517(2)    | 9320(1)    | 3340(1)    | 26(1)      |
| C(6') | 4504(2)    | 9303(1)    | 2898(1)    | 22(1)      |
| C(7') | 5964(1)    | 8150(1)    | 3738(1)    | 18(1)      |
| C(8') | 6981(1)    | 8052(1)    | 3343(1)    | 19(1)      |
| C(9') | 7969(2)    | 8295(1)    | 3705(1)    | 19(1)      |
| C(10')| 9896(2)    | 8027(1)    | 3693(1)    | 27(1)      |
| C(11')| 10211(2)   | 8878(2)    | 3513(2)    | 47(1)      |
| C(12')| 10501(2)   | 7398(2)    | 3305(1)    | 47(1)      |
| C(13')| 10014(2)   | 7861(2)    | 4419(1)    | 37(1)      |
Table 3. Bond lengths [Å] and angles [°] for Baran782.

| Bond          | Length  | Bond          | Length  |
|---------------|---------|---------------|---------|
| O(1)-C(1)     | 1.215(2)| C(10)-C(12)   | 1.512(3)|
| O(2)-H(2)     | 0.860(19)| C(10)-C(13)   | 1.517(3)|
| O(2)-C(2)     | 1.425(2)| C(11)-H(11A)  | 0.9800  |
| O(3)-H(3)     | 0.8400  | C(11)-H(11B)  | 0.9800  |
| O(3)-C(3)     | 1.419(2)| C(11)-H(11C)  | 0.9800  |
| O(4)-C(9)     | 1.335(2)| C(12)-H(12A)  | 0.9800  |
| O(4)-C(10)    | 1.488(2)| C(12)-H(12B)  | 0.9800  |
| O(5)-C(9)     | 1.210(2)| C(12)-H(12C)  | 0.9800  |
| C(1)-C(2)     | 1.526(2)| C(13)-H(13A)  | 0.9800  |
| C(1)-C(6)     | 1.497(3)| C(13)-H(13B)  | 0.9800  |
| C(2)-C(3)     | 1.545(3)| C(13)-H(13C)  | 0.9800  |
| C(2)-C(7)     | 1.535(3)| O(1")-C(1")  | 1.216(2)|
| C(3)-H(3A)    | 1.0000  | O(2")-H(2")  | 0.85(3) |
| C(3)-C(4)     | 1.525(3)| O(2")-C(2")  | 1.413(2)|
| C(4)-H(4A)    | 0.9900  | O(3")-H(3")  | 0.87(3) |
| C(4)-H(4B)    | 0.9900  | O(3")-C(3")  | 1.420(2)|
| C(4)-C(5)     | 1.527(3)| O(4")-C(9")  | 1.335(2)|
| C(5)-H(5A)    | 0.9900  | O(4")-C(10") | 1.483(2)|
| C(5)-H(5B)    | 0.9900  | O(5")-C(9")  | 1.209(2)|
| C(5)-C(6)     | 1.540(3)| C(1")-C(2")  | 1.523(3)|
| C(6)-H(6A)    | 0.9900  | C(1")-C(6")  | 1.506(3)|
| C(6)-H(6B)    | 0.9900  | C(2")-C(3")  | 1.544(3)|
| C(7)-H(7A)    | 0.9900  | C(2")-C(7")  | 1.542(2)|
| C(7)-H(7B)    | 0.9900  | C(3")-H(3")  | 1.0000  |
| C(7)-C(8)     | 1.523(3)| C(3")-C(4")  | 1.519(3)|
| C(8)-H(8A)    | 0.9900  | C(4")-H(4")  | 0.9900  |
| C(8)-H(8B)    | 0.9900  | C(4")-H(4")  | 0.9900  |
| C(8)-C(9)     | 1.507(3)| C(4")-C(5")  | 1.527(3)|
| C(10)-C(11)   | 1.522(3)| C(5")-H(5")  | 0.9900  |
C(5")-H(5"B)  0.9900  C(1')-C(6')  1.504(3)
C(5")-C(6")  1.542(3)  C(2')-C(3')  1.546(2)
C(6")-H(6"A)  0.9900  C(2')-C(7')  1.537(2)
C(6")-H(6"B)  0.9900  C(3')-H(3'A)  1.0000
C(7")-H(7"A)  0.9900  C(3')-C(4')  1.519(3)
C(7")-H(7"B)  0.9900  C(4')-H(4'A)  0.9900
C(7")-C(8")  1.524(3)  C(4')-H(4'B)  0.9900
C(8")-H(8"A)  0.9900  C(4')-C(5')  1.526(3)
C(8")-H(8"B)  0.9900  C(5')-H(5'A)  0.9900
C(8")-C(9")  1.505(3)  C(5')-H(5'B)  0.9900
C(10")-C(11")  1.517(3)  C(5')-C(6')  1.536(3)
C(10")-C(12")  1.518(3)  C(6')-H(6'A)  0.9900
C(10")-C(13")  1.516(3)  C(6')-H(6'B)  0.9900
C(11")-H(11D)  0.9800  C(7')-H(7'A)  0.9900
C(11")-H(11E)  0.9800  C(7')-H(7'B)  0.9900
C(11")-H(11F)  0.9800  C(7')-C(8')  1.522(3)
C(12")-H(12D)  0.9800  C(8')-H(8'A)  0.9900
C(12")-H(12E)  0.9800  C(8')-H(8'B)  0.9900
C(12")-H(12F)  0.9800  C(8')-C(9')  1.503(3)
C(13")-H(13D)  0.9800  C(10')-C(11')  1.508(3)
C(13")-H(13E)  0.9800  C(10')-C(12')  1.513(3)
C(13")-H(13F)  0.9800  C(10')-C(13')  1.513(3)
O(1')-C(1')  1.214(2)  C(11')-H(11G)  0.9800
O(2')-H(2')  0.8400  C(11')-H(11H)  0.9800
O(2')-C(2')  1.425(2)  C(11')-H(11I)  0.9800
O(3')-H(3')  0.86(3)  C(12')-H(12G)  0.9800
O(3')-C(3')  1.418(2)  C(12')-H(12H)  0.9800
O(4')-C(9')  1.330(2)  C(12')-H(12I)  0.9800
O(4')-C(10')  1.482(2)  C(13')-H(13G)  0.9800
O(5')-C(9')  1.213(2)  C(13')-H(13H)  0.9800
C(1')-C(2')  1.530(2)  C(13')-H(13I)  0.9800
C(2)-O(2)-H(2) 103.3(16)  C(1)-C(6)-C(5) 109.54(15)
C(3)-O(3)-H(3) 109.5  C(1)-C(6)-H(6A) 109.8
C(9)-O(4)-C(10) 121.47(14)  C(5)-C(6)-H(6A) 109.8
O(1)-C(1)-C(2) 119.51(16)  C(5)-C(6)-H(6B) 109.8
O(1)-C(1)-C(6) 124.07(17)  H(6A)-C(6)-H(6B) 108.2
C(6)-C(1)-C(2) 116.37(15)  C(2)-C(7)-H(7A) 109.1
O(2)-C(2)-C(1) 108.43(14)  C(2)-C(7)-H(7B) 109.1
O(2)-C(2)-C(3) 109.21(14)  H(7A)-C(7)-H(7B) 107.8
O(2)-C(2)-C(7) 107.88(14)  C(8)-C(7)-C(2) 112.47(15)
C(1)-C(2)-C(3) 107.49(14)  C(8)-C(7)-H(7A) 109.1
C(1)-C(2)-C(7) 111.43(14)  C(8)-C(7)-H(7B) 109.1
C(7)-C(2)-C(3) 112.33(14)  C(7)-C(8)-H(8A) 109.1
O(3)-C(3)-C(2) 109.85(15)  C(7)-C(8)-H(8B) 109.1
O(3)-C(3)-H(3A) 109.5  H(8A)-C(8)-H(8B) 107.8
O(3)-C(3)-C(4) 106.46(15)  C(9)-C(8)-C(7) 112.67(15)
C(2)-C(3)-H(3A) 109.5  C(9)-C(8)-H(8A) 109.1
C(4)-C(3)-C(2) 112.02(15)  C(9)-C(8)-H(8B) 109.1
C(4)-C(3)-H(3A) 109.5  O(4)-C(9)-C(8) 110.69(15)
C(3)-C(4)-H(4A) 109.3  O(5)-C(9)-O(4) 125.11(18)
C(3)-C(4)-H(4B) 109.3  O(5)-C(9)-C(8) 124.20(17)
C(3)-C(4)-C(5) 111.54(15)  O(4)-C(10)-C(11) 110.63(15)
H(4A)-C(4)-H(4B) 108.0  O(4)-C(10)-C(12) 102.46(15)
C(5)-C(4)-H(4A) 109.3  O(4)-C(10)-C(13) 109.49(15)
C(5)-C(4)-H(4B) 109.3  C(12)-C(10)-C(11) 110.57(16)
C(4)-C(5)-H(5A) 109.3  C(12)-C(10)-C(13) 111.03(17)
C(4)-C(5)-H(5B) 109.3  C(13)-C(10)-C(11) 112.24(17)
C(4)-C(5)-C(6) 111.72(16)  C(10)-C(11)-H(11A) 109.5
H(5A)-C(5)-H(5B) 107.9  C(10)-C(11)-H(11B) 109.5
C(6)-C(5)-H(5A) 109.3  C(10)-C(11)-H(11C) 109.5
C(6)-C(5)-H(5B) 109.3  H(11A)-C(11)-H(11B) 109.5
| Bond/Angle | Value          | Bond/Angle     | Value          |
|------------|----------------|----------------|----------------|
| H(11A)-C(11)-H(11C) | 109.5          | C(4")-C(3")-H(3"A) | 109.3          |
| H(11B)-C(11)-H(11C) | 109.5          | C(3")-C(4")-H(4"A) | 109.4          |
| C(10)-C(12)-H(12A)  | 109.5          | C(3")-C(4")-H(4"B) | 109.4          |
| C(10)-C(12)-H(12B)  | 109.5          | C(3")-C(4")-C(5") | 111.13(16)     |
| C(10)-C(12)-H(12C)  | 109.5          | H(4"A)-C(4")-H(4"B) | 108.0          |
| H(12A)-C(12)-H(12B) | 109.5          | C(5")-C(4")-H(4"A) | 109.4          |
| H(12A)-C(12)-H(12C) | 109.5          | C(5")-C(4")-H(4"B) | 109.4          |
| H(12B)-C(12)-H(12C) | 109.5          | C(4")-C(5")-H(5"A) | 109.4          |
| C(10)-C(13)-H(13A)  | 109.5          | C(4")-C(5")-H(5"B) | 109.4          |
| C(10)-C(13)-H(13B)  | 109.5          | C(4")-C(5")-C(6") | 111.27(16)     |
| C(10)-C(13)-H(13C)  | 109.5          | H(5"A)-C(5")-H(5"B) | 108.0          |
| H(13A)-C(13)-H(13B) | 109.5          | C(6")-C(5")-H(5"A) | 109.4          |
| H(13A)-C(13)-H(13C) | 109.5          | C(6")-C(5")-H(5"B) | 109.4          |
| H(13B)-C(13)-H(13C) | 109.5          | C(1")-C(6")-C(5") | 110.35(15)     |
| C(2")-O(2")-H(2")  | 108.7(17)      | C(1")-C(6")-H(6"A) | 109.6          |
| C(3")-O(3")-H(3")  | 111.0(18)      | C(1")-C(6")-H(6"B) | 109.6          |
| C(9")-O(4")-C(10") | 122.90(14)     | C(5")-C(6")-H(6"A) | 109.6          |
| O(1")-C(1")-C(2")  | 120.72(17)     | C(5")-C(6")-H(6"B) | 109.6          |
| O(1")-C(1")-C(6")  | 123.24(17)     | H(6"A)-C(6")-H(6"B) | 108.1          |
| C(6")-C(1")-C(2")  | 116.03(16)     | C(2")-C(7")-H(7"A) | 109.3          |
| O(2")-C(2")-C(1")  | 111.18(15)     | C(2")-C(7")-H(7"B) | 109.3          |
| O(2")-C(2")-C(3")  | 107.25(14)     | H(7"A)-C(7")-H(7"B) | 108.0          |
| O(2")-C(2")-C(7")  | 108.60(14)     | C(8")-C(7")-C(2") | 111.40(15)     |
| C(1")-C(2")-C(3")  | 108.46(15)     | C(8")-C(7")-H(7"A) | 109.3          |
| C(1")-C(2")-C(7")  | 110.28(15)     | C(8")-C(7")-H(7"B) | 109.3          |
| C(7")-C(2")-C(3")  | 111.03(15)     | C(7")-C(8")-H(8"A) | 109.0          |
| O(3")-C(3")-C(2")  | 109.45(15)     | C(7")-C(8")-H(8"B) | 109.0          |
| O(3")-C(3")-H(3"A) | 109.3          | H(8"A)-C(8")-H(8"B) | 107.8          |
| O(3")-C(3")-C(4")  | 106.95(16)     | C(9")-C(8")-C(7") | 113.03(16)     |
| C(2")-C(3")-H(3"A) | 109.3          | C(9")-C(8")-H(8"A) | 109.0          |
| C(4")-C(3")-C(2")  | 112.46(15)     | C(9")-C(8")-H(8"B) | 109.0          |
| Bond                  | Angle (deg) | Bond                  | Angle (deg) |
|----------------------|-------------|----------------------|-------------|
| O(4")-C(9")-C(8")   | 110.04(16)  | O(1')-C(1')-C(6')    | 123.35(17)  |
| O(5")-C(9")-O(4")   | 125.00(18)  | C(6')-C(1')-C(2')    | 115.55(16)  |
| O(5")-C(9")-C(8")   | 124.97(17)  | O(2')-C(2')-C(1')    | 109.64(14)  |
| O(4")-C(10")-C(11") | 108.81(15)  | O(2')-C(2')-C(3')    | 106.71(14)  |
| O(4")-C(10")-C(12") | 101.24(15)  | O(2')-C(2')-C(7')    | 109.70(14)  |
| O(4")-C(10")-C(13") | 111.59(15)  | C(1')-C(2')-C(3')    | 107.06(14)  |
| C(11")-C(10")-C(12")| 111.98(18)  | C(1')-C(2')-C(7')    | 112.29(14)  |
| C(13")-C(10")-C(11")| 112.69(17)  | C(7')-C(2')-C(3')    | 111.26(14)  |
| C(13")-C(10")-C(12")| 109.97(17)  | O(3')-C(3')-C(2')    | 110.18(15)  |
| C(10")-C(11")-H(11D)| 109.5       | O(3')-C(3')-H(3'A)   | 109.3       |
| C(10")-C(11")-H(11E)| 109.5       | O(3')-C(3')-C(4')    | 106.59(15)  |
| C(10")-C(11")-H(11F)| 109.5       | C(2')-C(3')-H(3'A)   | 109.3       |
| H(11D)-C(11")-H(11E)| 109.5       | C(4')-C(3')-C(2')    | 112.09(15)  |
| H(11D)-C(11")-H(11F)| 109.5       | C(4')-C(3')-H(3'A)   | 109.3       |
| H(11E)-C(11")-H(11F)| 109.5       | C(3')-C(4')-H(4'A)   | 109.4       |
| C(10")-C(12")-H(12D)| 109.5       | C(3')-C(4')-H(4'B)   | 109.4       |
| C(10")-C(12")-H(12E)| 109.5       | C(3')-C(4')-C(5')    | 111.09(16)  |
| C(10")-C(12")-H(12F)| 109.5       | H(4'A)-C(4')-H(4'B)  | 108.0       |
| H(12D)-C(12")-H(12E)| 109.5       | C(5')-C(4')-H(4'A)   | 109.4       |
| H(12D)-C(12")-H(12F)| 109.5       | C(5')-C(4')-H(4'B)   | 109.4       |
| H(12E)-C(12")-H(12F)| 109.5       | C(4')-C(5')-H(5'A)   | 109.4       |
| C(10")-C(13")-H(13D)| 109.5       | C(4')-C(5')-H(5'B)   | 109.4       |
| C(10")-C(13")-H(13E)| 109.5       | C(4')-C(5')-C(6')    | 111.17(16)  |
| C(10")-C(13")-H(13F)| 109.5       | H(5'A)-C(5')-H(5'B)  | 108.0       |
| H(13D)-C(13")-H(13E)| 109.5       | C(6')-C(5')-H(5'A)   | 109.4       |
| H(13D)-C(13")-H(13F)| 109.5       | C(6')-C(5')-H(5'B)   | 109.4       |
| H(13E)-C(13")-H(13F)| 109.5       | C(1')-C(6')-C(5')    | 109.67(16)  |
| C(2')-O(2')-H(2')    | 109.5       | C(1')-C(6')-H(6'A)   | 109.7       |
| C(3')-O(3')-H(3')    | 108.7(18)   | C(1')-C(6')-H(6'B)   | 109.7       |
| C(9')-O(4')-C(10')   | 122.68(15)  | C(5')-C(6')-H(6'A)   | 109.7       |
| O(1')-C(1')-C(2')    | 121.07(17)  | C(5')-C(6')-H(6'B)   | 109.7       |
| Bond                         | Angle (°) | Bond                         | Angle (°) |
|------------------------------|-----------|------------------------------|-----------|
| H(6'A)-C(6')-H(6'B)         | 108.2     | H(12G)-C(12')-H(12H)        | 109.5     |
| C(2')-C(7')-H(7'A)          | 109.3     | H(12G)-C(12')-H(12I)        | 109.5     |
| C(2')-C(7')-H(7'B)          | 109.3     | H(12H)-C(12')-H(12I)        | 109.5     |
| H(7'A)-C(7')-H(7'B)         | 107.9     | C(10')-C(13')-H(13G)        | 109.5     |
| C(8')-C(7')-C(2')           | 111.83(15)| C(10')-C(13')-H(13H)        | 109.5     |
| C(8')-C(7')-H(7'A)          | 109.3     | C(10')-C(13')-H(13I)        | 109.5     |
| C(8')-C(7')-H(7'B)          | 109.3     | H(13G)-C(13')-H(13H)        | 109.5     |
| C(7')-C(8')-H(8'A)          | 108.7     | H(13G)-C(13')-H(13I)        | 109.5     |
| C(7')-C(8')-H(8'B)          | 108.7     | H(13H)-C(13')-H(13I)        | 109.5     |
| H(8'A)-C(8')-H(8'B)         | 107.6     | H(11G)-C(11')-H(11H)        | 109.5     |
| C(9')-C(8')-C(7')           | 114.12(15)| H(11G)-C(11')-H(11I)        | 109.5     |
| C(9')-C(8')-H(8'A)          | 108.7     | H(11H)-C(11')-H(11I)        | 109.5     |
| C(9')-C(8')-H(8'B)          | 108.7     | H(12G)-C(12')-H(12I)        | 109.5     |
| O(4')-C(9')-C(8')           | 109.54(15)| C(10')-C(12')-H(12G)        | 109.5     |
| O(5')-C(9')-O(4')           | 125.14(17)| C(10')-C(12')-H(12H)        | 109.5     |
| O(5')-C(9')-C(8')           | 125.32(17)| C(10')-C(12')-H(12I)        | 109.5     |
| O(4')-C(10')-C(11')         | 109.64(17)| C(10')-C(11')-H(11G)        | 109.5     |
| O(4')-C(10')-C(12')         | 101.66(16)| C(10')-C(11')-H(11H)        | 109.5     |
| O(4')-C(10')-C(13')         | 110.44(17)| C(10')-C(11')-H(11I)        | 109.5     |
| C(11')-C(10')-C(12')        | 112.4(2)  | H(11G)-C(11')-H(11H)        | 109.5     |
| C(11')-C(10')-C(13')        | 112.5(2)  | H(11G)-C(11')-H(11I)        | 109.5     |
| C(13')-C(10')-C(12')        | 109.7(2)  | H(11H)-C(11')-H(11I)        | 109.5     |
| C(10')-C(11')-H(11G)        | 109.5     | C(10')-C(12')-H(12G)        | 109.5     |
| C(10')-C(11')-H(11H)        | 109.5     | C(10')-C(12')-H(12H)        | 109.5     |
| C(10')-C(11')-H(11I)        | 109.5     | C(10')-C(12')-H(12I)        | 109.5     |
Table 4. Anisotropic displacement parameters (Å$^2 \times 10^3$) for Baran782. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^* a^* U_{11} + \ldots + 2hk a^* b^* U_{12}]$

|     | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-----|---------|---------|---------|---------|---------|---------|
| O(1) | 33(1)   | 27(1)   | 18(1)   | -3(1)   | -1(1)   | 4(1)    |
| O(2) | 24(1)   | 18(1)   | 18(1)   | 2(1)    | 0(1)    | 1(1)    |
| O(3) | 17(1)   | 22(1)   | 32(1)   | 6(1)    | 3(1)    | -1(1)   |
| O(4) | 16(1)   | 30(1)   | 20(1)   | -1(1)   | -1(1)   | -2(1)   |
| O(5) | 19(1)   | 38(1)   | 21(1)   | -6(1)   | -1(1)   | 4(1)    |
| C(1) | 14(1)   | 21(1)   | 19(1)   | -2(1)   | 1(1)    | -1(1)   |
| C(2) | 18(1)   | 15(1)   | 16(1)   | 2(1)    | 0(1)    | 1(1)    |
| C(3) | 18(1)   | 19(1)   | 19(1)   | -2(1)   | 1(1)    | -1(1)   |
| C(4) | 19(1)   | 27(1)   | 17(1)   | 1(1)    | -2(1)   | 0(1)    |
| C(5) | 21(1)   | 21(1)   | 24(1)   | 6(1)    | -1(1)   | 2(1)    |
| C(6) | 22(1)   | 16(1)   | 23(1)   | 0(1)    | 2(1)    | 0(1)    |
| C(7) | 18(1)   | 21(1)   | 18(1)   | -2(1)   | 1(1)    | 1(1)    |
| C(8) | 17(1)   | 24(1)   | 21(1)   | -2(1)   | 0(1)    | 1(1)    |
| C(9) | 20(1)   | 20(1)   | 20(1)   | 1(1)    | -3(1)   | 1(1)    |
| C(10)| 16(1)   | 27(1)   | 22(1)   | 2(1)    | 2(1)    | -1(1)   |
| C(11)| 26(1)   | 28(1)   | 25(1)   | 6(1)    | 0(1)    | -4(1)   |
| C(12)| 21(1)   | 40(1)   | 26(1)   | 3(1)    | -2(1)   | -7(1)   |
| C(13)| 21(1)   | 28(1)   | 33(1)   | 5(1)    | -1(1)   | 3(1)    |
| O(1")| 29(1)   | 26(1)   | 19(1)   | -2(1)   | 2(1)    | -2(1)   |
| O(2")| 27(1)   | 16(1)   | 17(1)   | 2(1)    | 1(1)    | 1(1)    |
| O(3")| 20(1)   | 21(1)   | 28(1)   | -1(1)   | 5(1)    | -4(1)   |
| O(4")| 14(1)   | 31(1)   | 20(1)   | 3(1)    | 1(1)    | 1(1)    |
| O(5")| 19(1)   | 32(1)   | 24(1)   | 10(1)   | -1(1)   | -1(1)   |
| C(1")| 14(1)   | 20(1)   | 24(1)   | -2(1)   | 2(1)    | -5(1)   |
| C(2")| 18(1)   | 15(1)   | 18(1)   | 2(1)    | 2(1)    | 1(1)    |
| C(3") | 18(1) | 21(1) | 18(1) | -1(1) | 3(1)  | -3(1) |
| C(4") | 18(1) | 26(1) | 30(1) | 4(1)  | -4(1) | -1(1) |
| C(5") | 22(1) | 21(1) | 40(1) | -2(1) | -2(1) | 4(1)  |
| C(6") | 25(1) | 19(1) | 35(1) | -4(1) | -1(1) | 1(1)  |
| C(7") | 17(1) | 19(1) | 21(1) | 3(1)  | 1(1)  | 0(1)  |
| C(8") | 16(1) | 24(1) | 23(1) | 1(1)  | 1(1)  | 0(1)  |
| C(9") | 17(1) | 16(1) | 24(1) | 2(1)  | -1(1) | 0(1)  |
| C(10")| 12(1) | 29(1) | 22(1) | 1(1)  | 2(1)  | 0(1)  |
| C(11")| 21(1) | 30(1) | 32(1) | -6(1) | 3(1)  | -4(1) |
| C(12")| 20(1) | 50(1) | 27(1) | 3(1)  | -2(1) | 5(1)  |
| C(13")| 20(1) | 28(1) | 28(1) | -3(1) | 2(1)  | 1(1)  |
| O(1') | 28(1) | 23(1) | 20(1) | -2(1) | 0(1)  | -3(1) |
| O(2') | 20(1) | 14(1) | 23(1) | -1(1) | 5(1)  | -1(1) |
| O(3') | 15(1) | 21(1) | 36(1) | -5(1) | 1(1)  | -2(1) |
| O(4') | 12(1) | 26(1) | 29(1) | -7(1) | -2(1) | 1(1)  |
| O(5') | 21(1) | 24(1) | 38(1) | -9(1) | -5(1) | 2(1)  |
| C(1') | 13(1) | 20(1) | 21(1) | -1(1) | -1(1) | -4(1) |
| C(2') | 16(1) | 13(1) | 20(1) | -2(1) | 1(1)  | 1(1)  |
| C(3') | 16(1) | 24(1) | 21(1) | 1(1)  | 1(1)  | -2(1) |
| C(4') | 16(1) | 29(1) | 27(1) | -10(1)| 3(1)  | 1(1)  |
| C(5') | 22(1) | 20(1) | 35(1) | -7(1) | -4(1) | 5(1)  |
| C(6') | 23(1) | 18(1) | 26(1) | 1(1)  | -7(1) | 0(1)  |
| C(7') | 16(1) | 20(1) | 20(1) | 0(1)  | 0(1)  | 0(1)  |
| C(8') | 15(1) | 22(1) | 21(1) | 1(1)  | -1(1) | 0(1)  |
| C(9') | 18(1) | 16(1) | 23(1) | 2(1)  | 0(1)  | 1(1)  |
| C(10')| 12(1) | 34(1) | 35(1) | -7(1) | -4(1) | 0(1)  |
| C(11')| 22(1) | 50(1) | 69(2) | 11(1) | -1(1) | -14(1)|
| C(12')| 18(1) | 69(2) | 56(2) | -30(1)| -5(1) | 9(1)  |
| C(13')| 24(1) | 49(1) | 37(1) | -4(1) | -10(1)| 5(1)  |
Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($\AA^2 x 10^3$) for Baran782.

|      | x      | y      | z      | U(eq)  |
|------|--------|--------|--------|--------|
| H(2) | 3060(20)| 5691(14)| 2895(10)| 30     |
| H(3) | 4911   | 6034   | 3561   | 35     |
| H(3A)| 3924   | 6022   | 4417   | 23     |
| H(4A)| 3674   | 4772   | 4958   | 26     |
| H(4B)| 4919   | 4940   | 4882   | 26     |
| H(5A)| 4490   | 3577   | 4600   | 26     |
| H(5B)| 5031   | 4040   | 3996   | 26     |
| H(6A)| 3560   | 3338   | 3577   | 24     |
| H(6B)| 2795   | 3711   | 4127   | 24     |
| H(7A)| 2095   | 4996   | 4539   | 22     |
| H(7B)| 1881   | 5910   | 4318   | 22     |
| H(8A)| 1004   | 5391   | 3350   | 25     |
| H(8B)| 1123   | 4502   | 3650   | 25     |
| H(11A)|-1766 | 4037   | 4562   | 40     |
| H(11B)|-2843 | 4515   | 4709   | 40     |
| H(11C)|-1741 | 4845   | 4994   | 40     |
| H(12A)|-2413 | 5034   | 3042   | 43     |
| H(12B)|-3320 | 4766   | 3546   | 43     |
| H(12C)|-2370 | 4159   | 3376   | 43     |
| H(13A)|-1759 | 6166   | 4478   | 41     |
| H(13B)|-2935 | 6019   | 4207   | 41     |
| H(13C)|-2004 | 6265   | 3712   | 41     |
| H(2")| 840(20)| 4753(15)| 5452(14)| 30     |
| H(3")| 2810(20)| 4952(17)| 5988(13)| 35     |
|    | H(3'A) | H(4'A) | H(5'A) | H(5'B) | H(6'A) | H(6'B) | H(7'A) | H(7'B) | H(8'A) | H(8'B) | H(11D) | H(11E) | H(11F) | H(12D) | H(12E) | H(12F) | H(13D) | H(13E) | H(13F) | H(2') | H(3') | H(3'A) | H(4'A) | H(4'B) | H(5'A) | H(5'B) | H(6'A) | H(6'B) | H(7'A) | H(7'B) |
|----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|
|    | 2104   | 2215   | 3386   | 3477   | 2081   | 1391   | 534    | 173    | -816   | -630   | -3729  | -4602  | -3395  | -4060  | -5049  | -4244  | -3360  | -4518  | -3504  | 5395  | 3190(20) | 4072  | 4250  | 3017  | 3369  | 2897  | 4357  | 5103  | 5890  | 6010  |
|    | 4387   | 2965   | 3336   | 2984   | 2326   | 2280   | 3101   | 4000   | 3995   | 3038   | 2244   | 2499   | 2370   | 4314   | 3799   | 3413   | 3743   | 4000   | 4519   | 7067  | 7115(17) | 7613  | 9035  | 8799  | 9885  | 9119  | 9598  | 9575  | 8722  | 7816  |
|    | 6879   | 6964   | 6908   | 5791   | 5241   | 5901   | 6690   | 6879   | 5831   | 5827   | 6208   | 6739   | 6959   | 5793   | 6051   | 5531   | 7437   | 7192   | 6977   | 2767  | 3351(13) | 4174  | 4222  | 4213  | 3473  | 3091  | 2485  | 3122  | 3873  | 4140  |
|     |  H(8'A) |  H(8'B) |  H(11G) |  H(11H) |  H(11I) |  H(12G) |  H(12H) |  H(12I) |  H(13G) |  H(13H) |  H(13I) |
|-----|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|     |  7048   |  6925   |  10044  |  10975  |  9821   |  10218  |  11254  |  10422  |  9610   |  10765  |  9745   |
|     |  7479   |  8382   |  8976   |  8947   |  9262   |  6860   |  7419   |  7508   |  8262   |  7893   |  7318   |
|     |  3208   |  2939   |  3050   |  3583   |  3787   |  3404   |  3424   |  2835   |  4669   |  4541   |  4518   |
|     |         |         |         |         |         |         |         |         |         |         |         |
|     |         |         |         |         |         |         |         |         |         |         |         |
Table 6. Hydrogen bonds for Baran782 [Å and °].

| D-H...A       | d(D-H) | d(H...A) | d(D...A)     | <(DHA) |
|---------------|--------|----------|--------------|--------|
| O(3')-H(3')...O(2') | 0.84   | 1.95     | 2.7837(18)   | 172.1  |
| O(2'')-H(2'')...O(5)  | 0.85(3) | 2.21(3)  | 2.8997(19)   | 138(2) |
| O(3'')-H(3'')...O(5')#1 | 0.87(3) | 2.08(3)  | 2.896(2)     | 155(2) |
| O(2'')-H(2'')...O(5'')#2 | 0.84   | 2.13     | 2.9058(18)   | 154.3  |
| O(3')-H(3')...O(2)    | 0.86(3) | 1.96(3)  | 2.7901(19)   | 162(3) |

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,-z+1  #2 -x+1/2,-y+1,z-1/2
Table 1. Crystal data and structure refinement for Baran783.

| Property                        | Value                        |
|--------------------------------|------------------------------|
| Report date                     | 2021-09-27                   |
| Identification code             | baran783                     |
| Empirical formula               | C13 H22 O5                   |
| Molecular formula               | C13 H22 O5                   |
| Formula weight                  | 258.30                       |
| Temperature                     | 100.0 K                      |
| Wavelength                      | 1.54178 Å                    |
| Crystal system                  | Orthorhombic                 |
| Space group                     | P2,2,2,1                     |
| Unit cell dimensions            | a = 12.6120(2) Å             |
|                                 | b = 16.5429(3) Å             |
|                                 | c = 20.4063(4) Å             |
|                                 | \( \alpha = 90^\circ \)     |
| Volume                          | 4257.55(13) Å³              |
| Z                               | 12                           |
| Density (calculated)            | 1.209 Mg/m³                  |
| Absorption coefficient          | 0.762 mm⁻¹                   |
| F(000)                          | 1680                         |
| Crystal size                    | 0.2 x 0.2 x 0.2 mm³          |
| Crystal color, habit            | colorless block              |
| Theta range for data collection | 3.439 to 70.084°             |
| Index ranges                    | \(-14 <= h <= 15, -19 <= k <= 20, -24 <= l <= 24\) |
| Reflections collected           | 50589                        |
| Independent reflections         | 8074 [R(int) = 0.0367]       |
| Completeness to theta = 67.500° | 100.0 %                      |
| Absorption correction           | Semi-empirical from equivalents |
| Max. and min. transmission      | 0.7534 and 0.6299            |
| Refinement method               | Full-matrix least-squares on \( F^2 \) |
| Data / restraints / parameters  | 8074 / 0 / 505               |
| Goodness-of-fit on \( F^2 \)    | 1.028                        |
| Parameter                                      | Value                           |
|-----------------------------------------------|---------------------------------|
| Final R indices [$I>\sigma(I)$]              | $R_1 = 0.0260$, $wR_2 = 0.0661$ |
| R indices (all data)                          | $R_1 = 0.0267$, $wR_2 = 0.0665$ |
| Absolute structure parameter                  | 0.01(4)                         |
| Extinction coefficient                        | 0.00014(4)                      |
| Largest diff. peak and hole                   | 0.207 and -0.138 e.Å$^{-3}$     |
Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Baran783. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|     | x     | y     | z     | $U(\text{eq})$ |
|-----|-------|-------|-------|---------------|
| O(1)| 8154(1)| 5509(1)| 2814(1)| 26(1)         |
| O(2)| 7936(1)| 4048(1)| 3254(1)| 20(1)         |
| O(3)| 9925(1)| 4416(1)| 3753(1)| 22(1)         |
| O(4)| 4962(1)| 4570(1)| 4694(1)| 26(1)         |
| O(5)| 4188(1)| 5007(1)| 3762(1)| 21(1)         |
| C(1)| 8186(1)| 5471(1)| 3408(1)| 17(1)         |
| C(2)| 8026(1)| 4657(1)| 3745(1)| 16(1)         |
| C(3)| 9026(1)| 4490(1)| 4165(1)| 18(1)         |
| C(4)| 9260(1)| 5180(1)| 4638(1)| 21(1)         |
| C(5)| 9390(1)| 5984(1)| 4277(1)| 21(1)         |
| C(6)| 8417(1)| 6176(1)| 3847(1)| 19(1)         |
| C(7)| 7006(1)| 4646(1)| 4155(1)| 18(1)         |
| C(8)| 6040(1)| 4919(1)| 3764(1)| 20(1)         |
| C(9)| 5015(1)| 4808(1)| 4136(1)| 19(1)         |
| C(10)|3080(1)| 4927(1)| 4004(1)| 21(1)        |
| C(11)|2438(2)| 5272(1)| 3442(1)| 28(1)        |
| C(12)|2826(2)| 4040(1)| 4110(1)| 27(1)        |
| C(13)|2918(2)| 5427(1)| 4623(1)| 26(1)        |
| O(1")|6207(1)| 6364(1)| 4943(1)| 24(1)        |
| O(2")|5913(1)| 5241(1)| 5869(1)| 19(1)        |
| O(3")|8019(1)| 5537(1)| 6089(1)| 22(1)        |
| O(4")|3347(1)| 6761(1)| 7118(1)| 24(1)        |
| O(5")|2449(1)| 6481(1)| 6188(1)| 21(1)        |
| C(1")|6418(1)| 6578(1)| 5496(1)| 18(1)        |
|   | C(2") | C(3") | C(4") | C(5") | C(6") | C(7") | C(8") | C(9") | C(10") | C(11") | C(12") | C(13") | O(1') | O(2') | O(3') | O(4') | O(5') | C(1') | C(2') | C(3') | C(4') | C(5') | C(6') | C(7') | C(8') | C(9') | C(10') | C(11') | C(12') | C(13') |
|---|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|   |       |       |       |       |       |       |       |       |        |        |        |        |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | 6207(1)| 6026(1)| 6079(1)| 16(1) | 7244(1)| 5936(1)| 6476(1)| 18(1) | 5310(1)| 6370(1)| 6508(1)| 18(1) | 4982(1)| 2897(1)| 6658(1)| 15(1) | 3966(1)| 2937(1)| 6234(1)| 19(1) | 3454(1)| 2640(1)| 5800(1)| 23(1) | 5090(1)| 2079(1)| 6867(1)| 18(1) | 4290(1)| 6484(1)| 6116(1)| 21(1) | 8015(1)| 3805(1)| 5870(1)| 27(1) | 3326(1)| 6595(1)| 6541(1)| 18(1) | 1367(1)| 6554(1)| 6470(1)| 20(1) | 694(2) | 6228(1)| 5912(1)| 32(1) | 13733(1)| 7072(1)| 1235(2)| 5090(1)| 2079(1)| 6867(1)| 18(1) | 3091(1)| 2624(1)| 6589(1)| 23(1) | 4290(1)| 6484(1)| 6116(1)| 21(1) | 5090(1)| 2079(1)| 6867(1)| 18(1) | 4290(1)| 6484(1)| 6116(1)| 21(1) | 4290(1)| 6484(1)| 6116(1)| 21(1) | 4290(1)| 6484(1)| 6116(1)| 21(1) | 4290(1)| 6484(1)| 6116(1)| 21(1) | 4290(1)| 6484(1)| 6116(1)| 21(1) |
Table 3. Bond lengths [Å] and angles [°] for Baran783.

| Bond                  | Length  | Bond                  | Length  |
|-----------------------|---------|-----------------------|---------|
| O(1)-C(1)             | 1.215(2)| C(10)-C(12)           | 1.517(2)|
| O(2)-H(2)             | 0.87(2) | C(10)-C(13)           | 1.523(2)|
| O(2)-C(2)             | 1.4255(19)| C(11)-H(11A)     | 0.9800  |
| O(3)-H(3)             | 0.8400  | C(11)-H(11B)          | 0.9800  |
| O(3)-C(3)             | 1.417(2)| C(11)-H(11C)          | 0.9800  |
| O(4)-C(9)             | 1.207(2)| C(12)-H(12A)          | 0.9800  |
| O(5)-C(9)             | 1.335(2)| C(12)-H(12B)          | 0.9800  |
| O(5)-C(10)            | 1.488(2)| C(12)-H(12C)          | 0.9800  |
| C(1)-C(2)             | 1.525(2)| C(13)-H(13A)          | 0.9800  |
| C(1)-C(6)             | 1.499(2)| C(13)-H(13B)          | 0.9800  |
| C(2)-C(3)             | 1.550(2)| C(13)-H(13C)          | 0.9800  |
| C(2)-C(7)             | 1.534(2)| O(1")-C(1")          | 1.214(2)|
| C(3)-H(3A)            | 1.0000  | O(2")-H(2")          | 0.8400  |
| C(3)-C(4)             | 1.523(2)| O(2")-C(2")          | 1.4158(19)|
| C(4)-H(4A)            | 0.9900  | O(3")-H(3")          | 0.8400  |
| C(4)-H(4B)            | 0.9900  | O(3")-C(3")          | 1.419(2)|
| C(4)-C(5)             | 1.529(2)| O(4")-C(9")          | 1.209(2)|
| C(5)-H(5A)            | 0.9900  | O(5")-C(9")          | 1.334(2)|
| C(5)-H(5B)            | 0.9900  | O(5")-C(10")         | 1.4865(19)|
| C(5)-C(6)             | 1.542(2)| C(1")-C(2")          | 1.524(2)|
| C(6)-H(6A)            | 0.9900  | C(1")-C(6")          | 1.506(2)|
| C(6)-H(6B)            | 0.9900  | C(2")-C(3")          | 1.545(2)|
| C(7)-H(7A)            | 0.9900  | C(2")-C(7")          | 1.540(2)|
| C(7)-H(7B)            | 0.9900  | C(3")-H(3"A)         | 1.0000  |
| C(7)-C(8)             | 1.526(2)| C(3")-C(4")          | 1.524(2)|
| C(8)-H(8A)            | 0.9900  | C(4")-H(4"A)         | 0.9900  |
| C(8)-H(8B)            | 0.9900  | C(4")-H(4"B)         | 0.9900  |
| C(8)-C(9)             | 1.510(2)| C(4")-C(5")          | 1.526(3)|
| C(10)-C(11)           | 1.516(2)| C(5")-H(5"A)         | 0.9900  |
| Bond                  | Length  | Bond                  | Length  |
|----------------------|---------|-----------------------|---------|
| C(5")-H(5"B)        | 0.9900  | C(1')-C(6')           | 1.505(2)|
| C(5")-C(6")         | 1.543(3)| C(2')-C(3')           | 1.548(2)|
| C(6")-H(6"A)        | 0.9900  | C(2')-C(7')           | 1.539(2)|
| C(6")-H(6"B)        | 0.9900  | C(3')-H(3'A)          | 1.0000  |
| C(7")-H(7"A)        | 0.9900  | C(3')-C(4')           | 1.520(2)|
| C(7")-H(7"B)        | 0.9900  | C(4')-H(4'A)          | 0.9900  |
| C(7")-C(8")         | 1.525(2)| C(4')-H(4'B)          | 0.9900  |
| C(8")-H(8"A)        | 0.9900  | C(4')-C(5')           | 1.528(3)|
| C(8")-H(8"B)        | 0.9900  | C(5')-H(5'A)          | 0.9900  |
| C(8")-C(9")         | 1.505(2)| C(5')-H(5'B)          | 0.9900  |
| C(10")-C(11")       | 1.519(2)| C(5')-C(6')           | 1.536(3)|
| C(10")-C(12")       | 1.517(2)| C(6')-H(6'A)          | 0.9900  |
| C(10")-C(13")       | 1.518(3)| C(6')-H(6'B)          | 0.9900  |
| C(11")-H(11D)       | 0.9800  | C(7')-H(7'A)          | 0.9900  |
| C(11")-H(11E)       | 0.9800  | C(7')-H(7'B)          | 0.9900  |
| C(11")-H(11F)       | 0.9800  | C(7')-C(8')           | 1.519(2)|
| C(12")-H(12D)       | 0.9800  | C(8')-H(8'A)          | 0.9900  |
| C(12")-H(12E)       | 0.9800  | C(8')-H(8'B)          | 0.9900  |
| C(12")-H(12F)       | 0.9800  | C(8')-C(9')           | 1.507(2)|
| C(13")-H(13D)       | 0.9800  | C(10')-C(11')         | 1.514(3)|
| C(13")-H(13E)       | 0.9800  | C(10')-C(12')         | 1.514(3)|
| C(13")-H(13F)       | 0.9800  | C(10')-C(13')         | 1.507(3)|
| O(1')-C(1')          | 1.211(2)| C(11')-H(11G)         | 0.9800  |
| O(2')-H(2')          | 0.8400  | C(11')-H(11H)         | 0.9800  |
| O(2')-C(2')          | 1.4248(18)| C(11')-H(11I)       | 0.9800  |
| O(3')-H(3')          | 0.8400  | C(12')-H(12G)         | 0.9800  |
| O(3')-C(3')          | 1.417(2)| C(12')-H(12H)         | 0.9800  |
| O(4')-C(9')          | 1.210(2)| C(12')-H(12I)         | 0.9800  |
| O(5')-C(9')          | 1.331(2)| C(13')-H(13G)         | 0.9800  |
| O(5')-C(10')         | 1.482(2)| C(13')-H(13H)         | 0.9800  |
| C(1')-C(2')          | 1.532(2)| C(13')-H(13I)         | 0.9800  |
C(2)-O(2)-H(2) 104.1(15)  C(1)-C(6)-C(5) 109.57(13)
C(3)-O(3)-H(3) 109.5  C(1)-C(6)-H(6A) 109.8
C(9)-O(5)-C(10) 121.44(13)  C(1)-C(6)-H(6B) 109.8
O(1)-C(1)-C(2) 119.47(14)  C(5)-C(6)-H(6A) 109.8
O(1)-C(1)-C(6) 124.20(15)  C(5)-C(6)-H(6B) 109.8
C(6)-C(1)-C(2) 116.29(13)  H(6A)-C(6)-H(6B) 108.2
O(2)-C(2)-C(1) 111.93(13)  C(2)-C(7)-H(7A) 109.1
O(2)-C(2)-C(3) 109.08(13)  C(2)-C(7)-H(7B) 109.1
O(2)-C(2)-C(7) 107.96(13)  C(7)-C(8)-C(2) 112.41(13)
C(1)-C(2)-C(3) 107.42(13)  C(8)-C(7)-H(7A) 109.1
C(1)-C(2)-C(7) 111.61(13)  C(8)-C(7)-H(7B) 109.1
C(7)-C(2)-C(3) 112.20(13)  C(7)-C(8)-H(8A) 109.1
O(3)-C(3)-C(2) 109.77(13)  C(7)-C(8)-H(8B) 109.1
O(3)-C(3)-H(3A) 109.5  H(8A)-C(8)-H(8B) 107.8
O(3)-C(3)-C(4) 106.56(14)  C(9)-C(8)-C(7) 112.66(13)
C(2)-C(3)-H(3A) 109.5  C(9)-C(8)-H(8A) 109.1
C(4)-C(3)-C(2) 111.93(13)  C(9)-C(8)-H(8B) 109.1
C(4)-C(3)-H(3A) 109.5  O(4)-C(9)-O(5) 125.32(16)
C(3)-C(4)-H(4A) 109.3  O(4)-C(9)-C(8) 124.12(15)
C(3)-C(4)-H(4B) 109.3  O(5)-C(9)-C(8) 110.56(13)
C(3)-C(4)-C(5) 111.62(14)  O(5)-C(10)-C(11) 102.48(13)
H(4A)-C(4)-H(4B) 108.0  O(5)-C(10)-C(12) 109.40(14)
C(5)-C(4)-H(4A) 109.3  O(5)-C(10)-C(13) 110.64(14)
C(5)-C(4)-H(4B) 109.3  C(11)-C(10)-C(12) 111.16(15)
C(4)-C(5)-H(5A) 109.3  C(11)-C(10)-C(13) 110.51(14)
C(4)-C(5)-H(5B) 109.3  C(12)-C(10)-C(13) 112.23(15)
C(4)-C(5)-C(6) 111.55(14)  C(10)-C(11)-H(11A) 109.5
H(5A)-C(5)-H(5B) 108.0  C(10)-C(11)-H(11B) 109.5
C(6)-C(5)-H(5A) 109.3  C(10)-C(11)-H(11C) 109.5
C(6)-C(5)-H(5B) 109.3  H(11A)-C(11)-H(11B) 109.5
| Bond | Angle | Bond | Angle |
|------|-------|------|-------|
| H(11A)-C(11)-H(11C) | 109.5 | C(4")-C(3")-H(3"A) | 109.4 |
| H(11B)-C(11)-H(11C) | 109.5 | C(3")-C(4")-H(4"A) | 109.4 |
| C(10)-C(12)-H(12A)  | 109.5 | C(3")-C(4")-H(4"B) | 109.4 |
| C(10)-C(12)-H(12B)  | 109.5 | C(3")-C(4")-C(5") | 111.01(14) |
| C(10)-C(12)-H(12C)  | 109.5 | H(4"A)-C(4")-H(4"B) | 108.0 |
| H(12A)-C(12)-H(12B) | 109.5 | C(5")-C(4")-H(4"A) | 109.4 |
| H(12A)-C(12)-H(12C) | 109.5 | C(5")-C(4")-H(4"B) | 109.4 |
| H(12B)-C(12)-H(12C) | 109.5 | C(4")-C(5")-H(5"A) | 109.4 |
| C(10)-C(13)-H(13A)  | 109.5 | C(4")-C(5")-H(5"B) | 109.4 |
| C(10)-C(13)-H(13B)  | 109.5 | C(4")-C(5")-C(6") | 111.35(15) |
| C(10)-C(13)-H(13C)  | 109.5 | H(5"A)-C(5")-H(5"B) | 108.0 |
| H(13A)-C(13)-H(13B) | 109.5 | C(6")-C(5")-H(5"A) | 109.4 |
| H(13A)-C(13)-H(13C) | 109.5 | C(6")-C(5")-H(5"B) | 109.4 |
| H(13B)-C(13)-H(13C) | 109.5 | C(1")-C(6")-C(5") | 110.25(14) |
| C(2")-O(2")-H(2")  | 109.5 | C(1")-C(6")-H(6"A) | 109.6 |
| C(3")-O(3")-H(3")  | 109.5 | C(1")-C(6")-H(6"B) | 109.6 |
| C(9")-O(5")-C(10") | 122.74(12) | C(5")-C(6")-H(6"A) | 109.6 |
| O(1")-C(1")-C(2")  | 120.86(15) | C(5")-C(6")-H(6"B) | 109.6 |
| O(1")-C(1")-C(6")  | 123.25(16) | H(6"A)-C(6")-H(6"B) | 108.1 |
| C(6")-C(1")-C(2")  | 115.89(14) | C(2")-C(7")-H(7"A) | 109.3 |
| O(2")-C(2")-C(1")  | 111.07(13) | C(2")-C(7")-H(7"B) | 109.3 |
| O(2")-C(2")-C(3")  | 107.02(13) | H(7"A)-C(7")-H(7"B) | 108.0 |
| O(2")-C(2")-C(7")  | 108.56(13) | C(8")-C(7")-C(2") | 111.60(13) |
| C(1")-C(2")-C(3")  | 108.55(13) | C(8")-C(7")-H(7"A) | 109.3 |
| C(1")-C(2")-C(7")  | 110.46(13) | C(8")-C(7")-H(7"B) | 109.3 |
| C(7")-C(2")-C(3")  | 111.13(13) | C(7")-C(8")-H(8"A) | 108.9 |
| O(3")-C(3")-C(2")  | 109.62(13) | C(7")-C(8")-H(8"B) | 108.9 |
| O(3")-C(3")-H(3"A) | 109.4 | H(8"A)-C(8")-H(8"B) | 107.7 |
| O(3")-C(3")-C(4")  | 106.79(14) | C(9")-C(8")-C(7") | 113.25(14) |
| C(2")-C(3")-H(3"A) | 109.4 | C(9")-C(8")-H(8"A) | 108.9 |
| C(4")-C(3")-C(2")  | 112.24(13) | C(9")-C(8")-H(8"B) | 108.9 |
O(4")-C(9")-O(5") 125.21(16) O(1')-C(1')-C(6') 123.43(15)
O(4")-C(9")-C(8") 124.84(15) C(6')-C(1')-C(2') 115.37(14)
O(5")-C(9")-C(8") 109.95(14) O(2')-C(2')-C(1') 109.54(12)
O(5")-C(10")-C(11") 101.17(13) O(2')-C(2')-C(3') 106.65(12)
O(5")-C(10")-C(12") 111.54(14) O(2')-C(2')-C(7') 109.82(13)
O(5")-C(10")-C(13") 108.70(14) C(1')-C(2')-C(3') 107.03(13)
C(12")-C(10")-C(11") 109.98(15) C(1')-C(2')-C(7') 112.34(13)
C(12")-C(10")-C(13") 112.84(15) C(7')-C(2')-C(3') 111.27(13)
C(13")-C(10")-C(11") 112.02(16) O(3')-C(3')-C(2') 110.09(13)
C(10")-C(11")-H(11D) 109.5 O(3')-C(3')-H(3'A) 109.4
C(10")-C(11")-H(11E) 109.5 O(3')-C(3')-C(4') 106.46(14)
C(10")-C(11")-H(11F) 109.5 C(2')-C(3')-H(3'A) 109.4
H(11D)-C(11")-H(11E) 109.5 C(4')-C(3')-C(2') 112.03(13)
H(11D)-C(11")-H(11F) 109.5 C(4')-C(3')-H(3'A) 109.4
H(11E)-C(11")-H(11F) 109.5 C(3')-C(4')-H(4'A) 109.4
C(10")-C(12")-H(12D) 109.5 C(3')-C(4')-H(4'B) 109.4
C(10")-C(12")-H(12E) 109.5 C(3')-C(4')-C(5') 111.16(14)
C(10")-C(12")-H(12F) 109.5 C(4')-C(5')-C(6') 111.01(14)
H(12D)-C(12")-H(12E) 109.5 H(4'A)-C(4')-H(4'B) 108.0
H(12D)-C(12")-H(12F) 109.5 C(5')-C(4')-H(4'A) 109.4
H(12E)-C(12")-H(12F) 109.5 C(5')-C(4')-H(4'B) 109.4
C(10")-C(13")-H(13D) 109.5 C(4')-C(5')-H(5'A) 109.4
C(10")-C(13")-H(13E) 109.5 C(4')-C(5')-H(5'B) 109.4
C(10")-C(13")-H(13F) 109.5 C(4')-C(5')-C(6') 111.01(14)
C(10")-C(13")-H(13D) 109.5 H(5'A)-C(5')-H(5'B) 108.0
H(13D)-C(13")-H(13E) 109.5 C(6')-C(5')-H(5'A) 109.4
H(13D)-C(13")-H(13F) 109.5 C(6')-C(5')-H(5'B) 109.4
H(13E)-C(13")-H(13F) 109.5 C(1')-C(6')-C(5') 109.79(14)
C(2')-O(2')-H(2') 109.5 C(1')-C(6')-H(6'A) 109.7
C(3')-O(3')-H(3') 109.5 C(1')-C(6')-H(6'B) 109.7
C(9")-O(5")-C(10") 122.68(13) C(5')-C(6')-H(6'A) 109.7
O(1')-C(1')-C(2') 121.16(15) C(5')-C(6')-H(6'B) 109.7
| Bond/Formula | Angle (°) | Bond/Formula | Angle (°) |
|--------------|----------|--------------|----------|
| H(6'A)-C(6')-H(6'B) | 108.2 | H(12G)-C(12')-H(12H) | 109.5 |
| C(2')-C(7')-H(7'A) | 109.3 | H(12G)-C(12')-H(12I) | 109.5 |
| C(2')-C(7')-H(7'B) | 109.3 | H(12H)-C(12')-H(12I) | 109.5 |
| H(7'A)-C(7')-H(7'B) | 107.9 | C(10')-C(13')-H(13G) | 109.5 |
| C(8')-C(7')-C(2') | 111.74(13) | C(10')-C(13')-H(13H) | 109.5 |
| C(8')-C(7')-H(7'A) | 109.3 | C(10')-C(13')-H(13I) | 109.5 |
| C(8')-C(7')-H(7'B) | 109.3 | H(13G)-C(13')-H(13H) | 109.5 |
| C(7')-C(8')-H(8'A) | 108.7 | H(13G)-C(13')-H(13I) | 109.5 |
| C(7')-C(8')-H(8'B) | 108.7 | H(13H)-C(13')-H(13I) | 109.5 |
| H(8'A)-C(8')-H(8'B) | 107.6 |          |          |
| C(9')-C(8')-C(7') | 114.03(13) |          |          |
| C(9')-C(8')-H(8'A) | 108.7 |          |          |
| C(9')-C(8')-H(8'B) | 108.7 |          |          |
| O(4')-C(9')-O(5') | 125.20(15) |          |          |
| O(4')-C(9')-C(8') | 125.29(15) |          |          |
| O(5')-C(9')-C(8') | 109.50(13) |          |          |
| O(5')-C(10')-C(11') | 101.66(14) |          |          |
| O(5')-C(10')-C(12') | 110.31(15) |          |          |
| O(5')-C(10')-C(13') | 109.51(16) |          |          |
| C(11')-C(10')-C(12') | 109.77(18) |          |          |
| C(13')-C(10')-C(11') | 112.6(2) |          |          |
| C(13')-C(10')-C(12') | 112.42(18) |          |          |
| C(10')-C(11')-H(11G) | 109.5 |          |          |
| C(10')-C(11')-H(11H) | 109.5 |          |          |
| C(10')-C(11')-H(11I) | 109.5 |          |          |
| H(11G)-C(11')-H(11H) | 109.5 |          |          |
| H(11G)-C(11')-H(11I) | 109.5 |          |          |
| H(11H)-C(11')-H(11I) | 109.5 |          |          |
| C(10')-C(12')-H(12G) | 109.5 |          |          |
| C(10')-C(12')-H(12H) | 109.5 |          |          |
| C(10')-C(12')-H(12I) | 109.5 |          |          |
Table 4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Baran783. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^*^2 U^{11} + \ldots + 2hkab^* U^{12} ]$

|       | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| O(1)  | 35(1)    | 24(1)    | 17(1)    | 3(1)     | -1(1)    | -4(1)    |
| O(2)  | 26(1)    | 16(1)    | 18(1)    | -3(1)    | -1(1)    | -1(1)    |
| O(3)  | 18(1)    | 19(1)    | 30(1)    | -7(1)    | 2(1)     | 1(1)     |
| O(4)  | 21(1)    | 37(1)    | 20(1)    | 5(1)     | -1(1)    | -4(1)    |
| O(5)  | 18(1)    | 28(1)    | 19(1)    | 1(1)     | -1(1)    | 2(1)     |
| C(1)  | 15(1)    | 18(1)    | 18(1)    | 1(1)     | 1(1)     | 1(1)     |
| C(2)  | 19(1)    | 13(1)    | 15(1)    | -2(1)    | 0(1)     | 0(1)     |
| C(3)  | 19(1)    | 17(1)    | 18(1)    | 1(1)     | 1(1)     | 1(1)     |
| C(4)  | 22(1)    | 24(1)    | 17(1)    | -2(1)    | -2(1)    | 0(1)     |
| C(5)  | 23(1)    | 19(1)    | 22(1)    | -6(1)    | -1(1)    | -2(1)    |
| C(6)  | 22(1)    | 14(1)    | 22(1)    | -1(1)    | 2(1)     | 1(1)     |
| C(7)  | 18(1)    | 18(1)    | 16(1)    | 2(1)     | 1(1)     | -1(1)    |
| C(8)  | 19(1)    | 22(1)    | 19(1)    | 2(1)     | 0(1)     | -1(1)    |
| C(9)  | 19(1)    | 18(1)    | 19(1)    | -1(1)    | -2(1)    | -1(1)    |
| C(10) | 15(1)    | 25(1)    | 22(1)    | -3(1)    | 1(1)     | 1(1)     |
| C(11) | 22(1)    | 38(1)    | 24(1)    | -3(1)    | -1(1)    | 6(1)     |
| C(12) | 23(1)    | 25(1)    | 32(1)    | -5(1)    | -1(1)    | -3(1)    |
| C(13) | 28(1)    | 27(1)    | 24(1)    | -6(1)    | 0(1)     | 4(1)     |
| O(1") | 31(1)   | 23(1)    | 19(1)    | 2(1)     | 2(1)     | 3(1)     |
| O(2") | 29(1)   | 14(1)    | 16(1)    | -3(1)    | 1(1)     | -1(1)    |
| O(3") | 21(1)   | 18(1)    | 28(1)    | 0(1)     | 5(1)     | 4(1)     |
| O(4") | 20(1)   | 30(1)    | 24(1)    | -11(1)   | -1(1)    | 0(1)     |
| O(5") | 15(1)   | 29(1)    | 19(1)    | -4(1)    | 1(1)     | -1(1)    |
| C(1") | 16(1)   | 17(1)    | 22(1)    | 1(1)     | 1(1)     | 5(1)     |
| C(2") | 19(1)   | 12(1)    | 17(1)    | -3(1)    | 1(1)     | -1(1)    |
|     | C(3") | C(4") | C(5") | C(6") | C(7") | C(8") | C(9") | C(10") | C(11") | C(12") | C(13") | O(1') | O(2') | O(3') | O(4') | O(5') | C(1') | C(2') | C(3') | C(4') | C(5') | C(6') | C(7') | C(8') | C(9') | C(10') | C(11') | C(12') | C(13') |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|     | 20(1) | 19(1) | 17(1) | 1(1)  | 2(1)  | 2(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(4")| 20(1) | 23(1) | 28(1) | -6(1) | -5(1) | 1(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(5")| 23(1) | 18(1) | 42(1) | 1(1)  | -3(1) | -3(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(6")| 26(1) | 16(1) | 35(1) | 4(1)  | -1(1) | -1(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(7")| 17(1) | 17(1) | 20(1) | -4(1) | 1(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(8")| 18(1) | 22(1) | 22(1) | -3(1) | 0(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(9")| 17(1) | 14(1) | 23(1) | -3(1) | 0(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(10")| 14(1) | 27(1) | 20(1) | -2(1) | 2(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(11")| 20(1) | 50(1) | 25(1) | -4(1) | -3(1) | -6(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(12")| 23(1) | 26(1) | 27(1) | 3(1)  | 1(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(13")| 24(1) | 27(1) | 32(1) | 4(1)  | 4(1)  | 4(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| O(1')| 29(1) | 20(1) | 19(1) | 2(1)  | 0(1)  | -4(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| O(2')| 21(1) | 12(1) | 22(1) | 1(1)  | -4(1) | -1(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| O(3')| 15(1) | 19(1) | 34(1) | 4(1)  | 0(1)  | -2(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| O(4')| 22(1) | 22(1) | 37(1) | 9(1)  | 5(1)  | 2(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| O(5')| 13(1) | 25(1) | 28(1) | 6(1)  | 2(1)  | 1(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(1')| 14(1) | 16(1) | 20(1) | 1(1)  | 1(1)  | -3(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(2')| 17(1) | 11(1) | 18(1) | 1(1)  | 0(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(3')| 17(1) | 21(1) | 19(1) | -1(1) | -1(1) | -1(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(4')| 18(1) | 26(1) | 26(1) | 10(1) | -3(1) | 2(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(5')| 23(1) | 18(1) | 34(1) | 7(1)  | 4(1)  | 6(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(6')| 25(1) | 14(1) | 25(1) | 0(1)  | 7(1)  | 1(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(7')| 17(1) | 17(1) | 18(1) | 0(1)  | 1(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(8')| 16(1) | 19(1) | 19(1) | -1(1) | 1(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(9')| 18(1) | 14(1) | 22(1) | -3(1) | 1(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(10')| 12(1) | 32(1) | 33(1) | 8(1)  | 3(1)  | 0(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(11')| 19(1) | 67(2) | 54(1) | 29(1) | 6(1)  | 10(1) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(12')| 25(1) | 47(1) | 38(1) | 4(1)  | 9(1)  | 4(1)  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C(13')| 25(1) | 48(1) | 68(2) | -11(1)| 2(1)  | -14(1)|       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
Table 5. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^{-3}$) for Baran783.

|     | x          | y          | z          | U(eq) |
|-----|------------|------------|------------|-------|
| H(2) | 8062(19)   | 4305(14)   | 2888(12)   | 30    |
| H(3) | 9904       | 3970       | 3557       | 34    |
| H(3A)| 8925       | 3977       | 4418       | 22    |
| H(4A)| 9917       | 5058       | 4884       | 25    |
| H(4B)| 8673       | 5226       | 4958       | 25    |
| H(5A)| 10032      | 5960       | 3998       | 26    |
| H(5B)| 9490       | 6423       | 4601       | 26    |
| H(6A)| 7795       | 6287       | 4129       | 23    |
| H(6B)| 8559       | 6663       | 3579       | 23    |
| H(7A)| 6884       | 4091       | 4320       | 21    |
| H(7B)| 7097       | 5005       | 4539       | 21    |
| H(8A)| 6122       | 5498       | 3650       | 24    |
| H(8B)| 6005       | 4608       | 3351       | 24    |
| H(11A)| 2626      | 5842       | 3378       | 42    |
| H(11B)| 1681      | 5230       | 3543       | 42    |
| H(11C)| 2592      | 4969       | 3040       | 42    |
| H(12A)| 2997      | 3734       | 3713       | 40    |
| H(12B)| 2070      | 3979       | 4210       | 40    |
| H(12C)| 3248      | 3833       | 4477       | 40    |
| H(13A)| 3267      | 5160       | 4993       | 39    |
| H(13B)| 2158      | 5477       | 4713       | 39    |
| H(13C)| 3225      | 5966       | 4560       | 39    |
| H(2")| 5836       | 5240       | 5460       | 29    |
| H(3")| 7804       | 5071       | 5993       | 34    |
|        |        |        |        |        |
|--------|--------|--------|--------|--------|
| H(3")A| 7103   | 5611   | 6879   | 22     |
| H(4")A| 8385   | 6665   | 6909   | 29     |
| H(4")B| 7215   | 7035   | 6964   | 29     |
| H(5")A| 8474   | 7013   | 5792   | 33     |
| H(5")B| 8190   | 7807   | 6205   | 33     |
| H(6")A| 6390   | 7719   | 5902   | 31     |
| H(6")B| 7079   | 7674   | 5243   | 31     |
| H(7")A| 5174   | 5998   | 6878   | 22     |
| H(7")B| 5534   | 6897   | 6691   | 22     |
| H(8")A| 4369   | 6962   | 5829   | 25     |
| H(8")B| 4182   | 6005   | 5832   | 25     |
| H(11D) | 758    | 6586   | 5531   | 48     |
| H(11E) | -50    | 6203   | 6050   | 48     |
| H(11F) | 938    | 5685   | 5794   | 48     |
| H(12D) | 1497   | 5480   | 6977   | 38     |
| H(12E) | 483    | 5999   | 7192   | 38     |
| H(12F) | 1640   | 6257   | 7437   | 38     |
| H(13D) | 1602   | 7629   | 6962   | 42     |
| H(13E) | 398    | 7505   | 6734   | 42     |
| H(13F) | 1283   | 7758   | 6210   | 42     |
| H(2")  | 5372   | 2067   | 7240   | 27     |
| H(3")  | 3181   | 2127   | 6654   | 34     |
| H(3")A | 4071   | 2612   | 5826   | 23     |
| H(4")A | 3019   | 3799   | 5788   | 28     |
| H(4")B | 4251   | 4035   | 5779   | 28     |
| H(5")A | 2898   | 4119   | 6910   | 30     |
| H(5")B | 3370   | 4885   | 6528   | 30     |
| H(6")A | 5104   | 4572   | 6877   | 26     |
| H(6")B | 4360   | 4598   | 7514   | 26     |
| H(7")A | 6012   | 2817   | 5861   | 21     |
| H(7")B | 5891   | 3722   | 6128   | 21     |
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|   |   |   |   |   |
|---|---|---|---|---|
| H(8'A) | 6922 | 3382 | 7061 | 22 |
| H(8'B) | 7046 | 2479 | 6792 | 22 |
| H(11G) | 10422 | 2507 | 7165 | 70 |
| H(11H) | 11252 | 2418 | 6576 | 70 |
| H(11I) | 10216 | 1860 | 6597 | 70 |
| H(12G) | 9748 | 2316 | 5484 | 55 |
| H(12H) | 10760 | 2899 | 5457 | 55 |
| H(12I) | 9599 | 3258 | 5333 | 55 |
| H(13G) | 9810 | 4261 | 6214 | 70 |
| H(13H) | 10969 | 3952 | 6411 | 70 |
| H(13I) | 10047 | 3977 | 6949 | 70 |