179. Regioselective Radical Additions to 7-Oxabicyclo[2.2.1]hept-5-en-2-one

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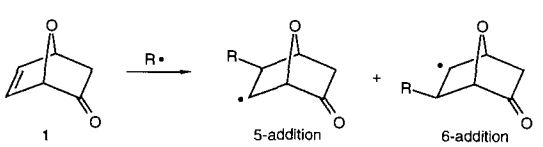
Radical addition to 7-oxabicyclo[2.2.1]hept-5-en-2-one (**1**) was examined from a regiochemical point of view, and despite the small electronic anisotropy of the double bond, electrophilic radicals were found to add preferentially at C(5) with selectivities of up to 5:1. We also report the first case of an inversion of the regioselectivity of a radical reaction using *Lewis* acids.

Introduction. – Enantiomerically pure 7-oxabicyclo[2.2.1]hept-5-en-2-one (**1**), easily prepared from furan in both enantiomeric forms, is a precursor for the synthesis of a variety of biologically interesting compounds [1]. Introduction of C-moieties into this system was mainly limited to the 3-position by aldol-type reactions [2]. Addition of C-residues to C(5) and C(6) is desirable, since it may open a new route to *C*-glycosides, *C*-branched carbohydrates and other products of biological interest. Therefore, we decided to investigate the direct radical addition to this system[2]). The bicyclic nature of the substrate was expected to insure complete *exo*-stereoselectivity[3]), the only remaining anticipated problem was the control of regioselectivity[4]) (*Scheme 1*). We report here a study of the regioselectivity of the addition of electrophilic and nucleophilic radicals to **1**.

Scheme 1



Results. – We looked first for efficient reactions which would allow us to test the regioselectivity of the addition of radicals possessing different electronic demand. Direct addition of simple alkyl iodides and thiohydroxamates to **1** gave only low yields of addition products and were, therefore, not suitable for our purpose. The absence of direct

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[2]) *Diels-Alder* reactions were reported to be sluggish [3]. Photochemically induced addition of phenylselenenyl phenyl sulfone was also reported [3], but isolation of the adduct was not possible due to its instability. We already published the introduction of a C-residue at C(6) by a radical cyclization based strategy [4].

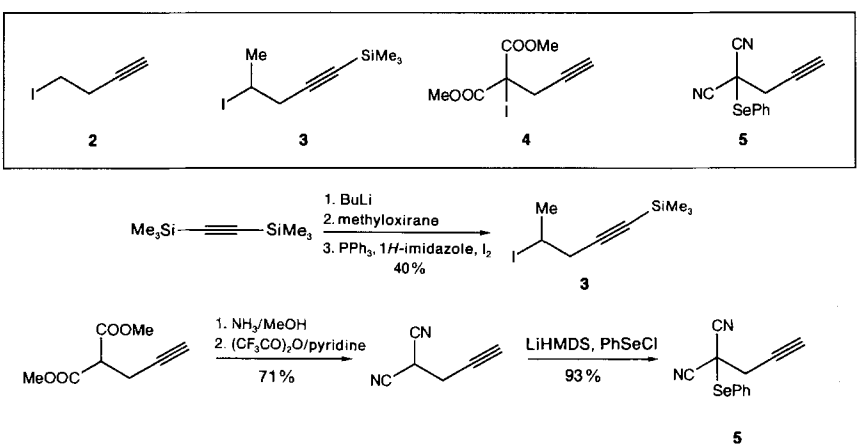
[3]) Radical additions to norbornene are *exo*-face selective [5]. For a discussion of the origin of *exo*-face selectivity, see [6].

[4]) Regioselective electrophilic additions [7a] and 1,3-dipolar cycloadditions [7b] were reported.

activation of **1**[5]) and the similarity between the starting alkyl radical and radical adduct probably explains this result. Therefore, we turned our attention to the annulation procedure developed by *Curran* and coworkers [8] and a modified version based on a phenylselenenyl-transfer reactions[6]). Using such methodologies, we were able to obtain satisfactory yields of addition products with nucleophilic and electrophilic radicals.

The radical precursors **2** [10] and **4** [8b] were prepared according to literature procedures. Iodide **3** was obtained from bis(trimethylsilyl)acetylene, and the selenenylated malonodinitrile derivative **5** was prepared by phenylselenenylation of 2-(prop-2-yn-1-yl)malonodinitrile (*Scheme 2*). Synthesis of the latter was carried out by ammonolysis (NH_3/MeOH) of dimethyl 2-(prop-2-yn-1-yl)malonate followed by dehydration (($(CF_3CO)_2O$/pyridine). This method was more convenient than the reported one[7]).

Scheme 2



The nucleophilic alkyl radicals generated from iodides **2** and **3** added preferentially at C(5) of **1** with low selectivity (→ **6** and **7**, resp.; *Table 1, Entries 1–2*; *Scheme 3*). The malonate- and malonodinitrile-derived radicals obtained from **4** and **5**, respectively, gave a higher selectivity (4.0:1 and 4.2:1, resp.) in favor of the addition at C(5) (→ **8** and **9**, resp.; *Table 1, Entries 3* and *4*). The regioselectivities were determined with compounds **10**–**13** obtained by acetalization of the ketones **6**–**9** followed by either ozonolysis (→ **10**–**12**) or by reaction with Bu_3SnH to a vinylstannane[8]) which was protodestannylated[9]) (→ **13**).

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[5]) The double bond is not directly substituted by an electron-withdrawing or -releasing group.

[6]) Phenylselenenyl transfer was more convenient than the I-atom transfer because of the greater stability and ease of preparation of the radical precursor [8d]. Moreover, such transfers do not require the presence of hexaalkylditin. Formation of C–C bonds *via* a phenylselenenyl transfer was already reported [9].

[7]) Substitution of commercially available malonodinitrile by a prop-2-yn-1-yl group gave a mixture of mono- and dialkylated products which were difficult to separate by chromatography [8d].

[8]) This reaction is presumably occurring through addition of a tin radical followed by β-elimination of a phenylselenenyl radical.

[9]) Similar reactions were performed with 2,2-(ethylenedioxy)-7-oxabicyclo[2.2.1]hept-5-ene (prepared by acetalization of **1** with ethylene glycol). Nucleophilic and electrophilic radicals generated from **2** to **4** added without regioselectivity to this acetal (**a**/**b** 1.2:1 in all three cases).

Scheme 3

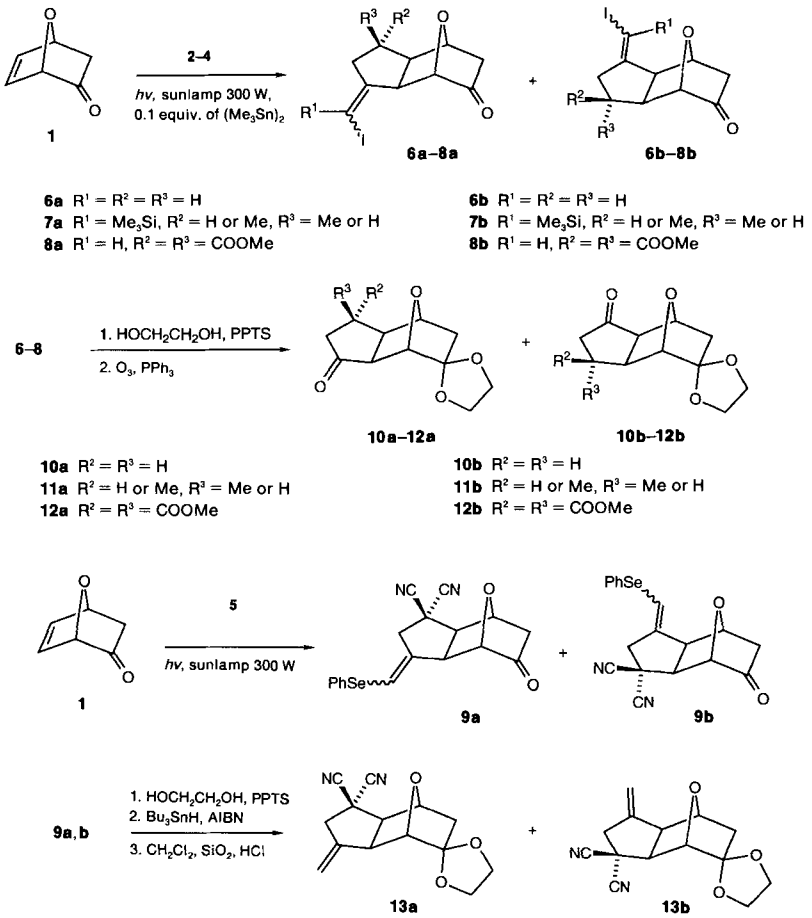


Table 1. *Annulation Reaction between* **1** *and Radical Precursors* **2–5**

Entry	Radical precursor	Product	Yield[a]) [%]	**a**/**b**[b])
1	**2**	**6**	60	2.0:1
2	**3**	**7**	82	2.6:1
3	**4**	**8**	76	4.0:1
4	**5**	**9**	80	4.2:1

[a]) Mixture of isomers. [b]) Determined after conversion to **10**–**13**.

The structures of **10a**–**13a** were difficult to deduce from their ^{1}H-NMR spectra due to the lack of coupling between the protons of the newly formed five-membered ring and the rest of the molecule. Therefore, they were unambiguously assigned by X-ray crystal-structure analysis of **10a** and (*Fig. 1*) **12a**[10]).

[10]) The structures data of **10a** and **12a** were deposited at the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EW, England.

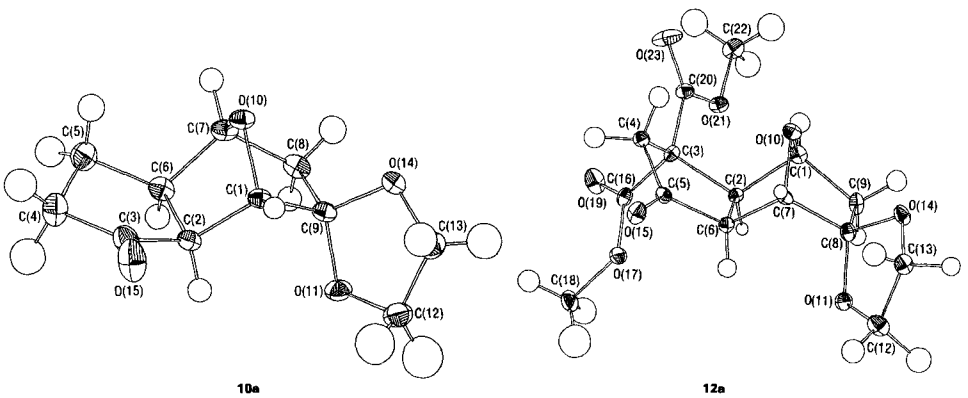


Fig. 1. *X-Ray crystal structure of* **10a** *and* **12a** (ORTEP plots)

Preferential addition at C(5) may be rationalized by the frontier molecular orbitals (FMO) theory. Nucleophilic alkyl radicals interact with the LUMO and electrophilic radicals with the HOMO of the olefin. Both the LUMO and HOMO of **1** possess a larger coefficient at C(5) as shown by *ab initio* calculations (*Fig. 2*) [7b]. It is of interest to notice that even a very small difference in the coefficients, 0.42 *vs.* 0.39 for the HOMO at C(4) and C(5), respectively, may lead to substantial regioselectivity.

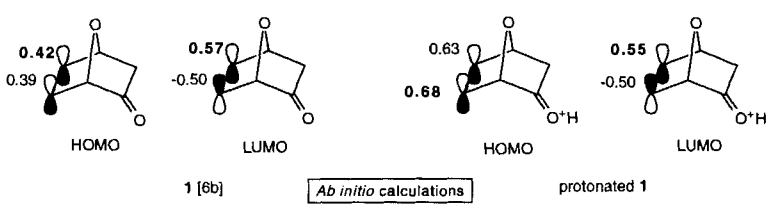


Fig. 2. *HOMO and LUMO of* **1** *and protonated* **1**

By analogy to *Diels-Alder* reactions [11], we decided to investigate the effect of *Lewis* acids on the control of regioselectivity[11]). Only small effects were observed for nucleophilic radicals. *E.g.*, the reaction of **1** with but-3-ynyl iodide (**2**) gave a 3.0:1 mixture **6a**/**6b** in the presence of 1 equiv. of titanium triisopropoxide monochloride (a 2.0:1 mixture **6a**/**6b** was formed in the absence of *Lewis* acid, *Table 1, Entry 1*). The use of stronger *Lewis* acids was not possible because of the instability of alkyl iodides under such conditions.

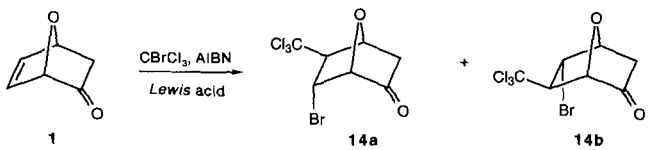
More interesting effects were expected for the addition of electrophilic radicals to **1** in the presence of *Lewis* acids. Calculations[12]) showed that protonation of **1** leads to an

[11]) *Lewis* acids have long been known to influence free-radical polymerizations. *E.g.*, the control of the alternance was efficiently performed by using *Lewis* acids [12a, b]. Complexation effects in non-polymerization radical chemistry are rather poorly documented. However, complexation of aminyl radicals with *Lewis* acids was reported for reactivity enhancement [12c]. It was also recently shown that stereoselectivity of a radical reaction may be controlled by *Lewis* acids [12d, e].

[12]) The shape of the frontier orbitals of **1** protonated on the carbonyl O-atom was calculated by *ab initio* calculations (STO 3G) on MNDO-optimized geometries.

inversion of the relative magnitude of the HOMO coefficient at C(5) and C(6) (*Fig. 2*). This suggests that in the presence of sufficiently strong *Lewis* acids, electrophilic radicals should preferentially add at C(6). To test this hypothesis, we looked for an electrophilic radical with weak affinity for *Lewis* acids to insure that only complexation of **1** would occur. We found that the well documented [13] addition of $CBrCl_3$ to alkenes was suitable for our study. The addition of $CBrCl_3$ to **1** at 15° in the absence of a *Lewis* acid led exclusively to the two regioisomers **14a** and **14b** in the ratio 2.8:1 (*Table 2, Entry 1*; *Scheme 4*). The CCl_3 radical added exclusively to the *exo*-face and the Br-atom was transferred to the *endo*-position. The ratio **14a**/**14b** was enhanced to 5.4:1 at −78° (*Table 2, Entry 2*). In the presence of 1 equiv. of titanium tetraisopropoxide ($Ti(i\text{-}PrO)_4$), a 3.7:1 mixture **14a**/**14b** was obtained (*Entry 3*). The use of $TiCl(i\text{-}PrO)_3$ lowered the regioselectivity to 2.2:1 (*Entry 4*). The anticipated inversion of selectivity was observed with stronger *Lewis* acids such as $TiCl_2(i\text{-}PrO)_2$ (**14a**/**14b** 1:2.9) and $BF_3 \cdot Et_2O$ (**14a**/**15b** 1:1.3) (*Entries 5* and *6*). The degree of inversion of the selectivity was dependant on the amount of *Lewis* acid used: with $TiCl_2(i\text{-}PrO)_2$ the inversion occurred when 0.3 equiv. were present (**14a**/**14b** 1:1.4).

Scheme 4



1 **14a** **14b**

Table 2. *Addition of Bromotrichloromethane to* **1**

Entry	*T* [°C]	*Lewis* acid	Yield [%]	**14a**/**14b**
1	15	–	94	2.8:1
2	−78	–	90[a])	5.4:1
3	15	$Ti(i\text{-}PrO)_4$	78	3.7:1
4	15	$Ti(i\text{-}PrO)_3Cl$	62	2.2:1
5	15	$Ti(i\text{-}PrO)_2Cl_2$	84[b])	1:2.9
6	15	$BF_3 \cdot Et_2O$	70[b])	1:1.3

[a]) 23% conversion. [b]) By GC.

In conclusion, we demonstrated that direct radical addition to 7-oxanorbornenone **1** using halogen-atom or phenylselenenyl transfer occur with low to good regioselectivities for nucleophilic and electrophilic radicals, respectively. By carrying out the reaction in the presence of *Lewis* acids, the regioselectivity of the addition of an electrophilic radical could be inverted. To our knowledge, such an inversion has no precedent for radical reactions. Moreover, the high synthetic potential of 7-oxabicyclo[2.2.1]hept-5-en-2-one, allied with the regioselective electrophilic radical-mediated introduction of C-moieties, opens new ways of synthesis for numerous biologically interesting compounds. Applications of this strategy are currently being investigated in our laboratory and will be reported in due course.

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Experimental Part

General. THF was freshly distilled from K under N_2, CH_2Cl_2 from P_2O_5, and benzene from CaH_2 under N_2. Irradiations were conducted using a sunlamp *Osram Ultra-Vitalux 300 W*. Compounds **1** (racemic) [14], **2** [10], and **4** [8b] were prepared according to literature procedures. Flash column chromatography (FC) and filtration: *Merck* silica gel *60* (70–230 mesh); elution with AcOEt and petroleum ether (p.e.) as TLC: *Merck* silica gel *60* F_{254} anal. plates; detection with UV, I_2, or by spraying with a soln. of phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot 4\,H_2O$ (10 g), conc. H_2SO_4 (60 ml) and H_2O (940 ml) with subsequent heating. M.p.: not corrected; *Büchi-Tottoli* apparatus. Bulb-to-bulb distillations: *Büchi-GKR-50* apparatus; b.p.'s refer to air-bath temp. GC: *Carlo Erba, DB-WAX*, 29-m capillary column. IR: *Perkin-Elmer-297* spectrophotometer. NMR: *Bruker AC-250 FT* (^{1}H 250 MHz, ^{13}C 62.9 MHz); unless otherwise indicated, $CDCl_3$ solns.; chemical shifts δ in ppm rel. to Me_4Si (= 0 ppm). MS: *Finnigan 1020* and *Nermag R10-10C*; CI, chemical ionisation with NH_3; EI, electron ionization at 70 eV. Elemental analysis: *Isle Beetz, Mikroanalytisches Laboratorium*, D–8640 Kronach.

General Procedure. Annulation Reaction via *Iodine-Atom Transfer* [8a]. A soln. of **1** (1.6 g, 15 mmol), iodobutyne derivative (16 mmol, 1.1 equiv.), and hexamethylditin (490 mg, 1.5 mmol) in benzene (30 ml) was irradiated at r.t. for 12 h with a 300-W sunlamp. Products were isolated by FC.

4-Iodo-1-(trimethylsilyl)pent-1-yne (**3**). A soln. of 5-(trimethylsilyl)pent-4-yn-2-ol [15] (1.0 g, 8.0 mmol) in CH_2Cl_2 (10 ml) was added at r.t. under N_2 to a soln. of PPh_3 (2.8 g, 10.9 mmol), 1*H*-imidazole (0.74 g, 10.9 mmol), and I_2 (2.8 g, 10.9 mmol) in CH_2Cl_2 (40 ml) [16]. The mixture was stirred at r.t. for 30 min and then evaporated. FC (pentane) of the crude product gave **3** (1.34 g, 71%). Pale yellow oil. ^{1}H-NMR (60 MHz): 4.1 (*m*, CHI); 2.75 (*d*, J = 6, CH_2); 1.89 (*d*, J = 7, MeC); 0.1 (*s*, MeSi).

2-(Phenylselenenyl)-2-(prop-2-yn-1-yl)propanedinitrile (**5**). A soln. of dimethyl 2-(prop-2-yn-1-yl)malonate (15 g, 13 mmol) in MeOH (100 ml) was saturated with gas. NH_3 and stirred overnight. The precipitate of diamide was isolated by filtration. Recrystallization (MeOH) gave *2-(prop-2-yn-1-yl)propanediamide* (10.9 g, 87%). White crystals. M.p. 183–184°. IR (KBr): 3420*s* (br.), 3380*s*, 3300*s* (br.), 1670*s*, 1430*s*, 1410*m*, 1380*s*, 1320*m*, 1290*m*, 1280*w*, 1200*m*, 1130*w*, 970*w*, 830*m*, 700*m*, 660*s*. ^{1}H-NMR (D_2O): 3.5 (*t*, ^3J = 7.5, $CH(CONH_2)_2$); 2.68 (*dd*, ^3J = 7.5, ^4J = 2, CH_2); 2.38 (*m*, CH≡C). ^{13}C-NMR (D_2O): 173.81 (*s*); 81.48 (*s*); 72.32 (*d*); 52.45 (*d*); 19.63 (*t*). EI-MS: 141 (0.3, $[M + 1]^+$), 140 (0.8, M^+), 139 (1.2, $M + 1]^+$), 123 (14), 113 (2), 96 (100), 86 (1), 85 (2), 82 (3), 80 (17) 79 (20), 78 (42), 72 (5), 68 (70), 56 (13), 55 (31), 54 (25), 53 (24), 52 (56), 51 (26), 50 (25). Anal. calc. for $C_6H_8N_2O_2$ (140.14): C 51.42, H 5.75; found: C 51.37, H 5.70.

$(CF_3CO)_2O$ [17] (29 ml, 208 mmol) was added dropwise to a soln. of the diamide (10 g, 71 mmol) and pyridine (22.6 ml, 280 mmol) in dioxane (100 ml) at −15°. The red mixture was allowed to warm to 3° over 1 h, and H_2O (200 ml) was added and the mixture extracted with CH_2Cl_2 (2 × 100 ml). The org. phases were washed with H_2O (5 × 50 ml) and brine (2 × 50 ml), dried ($MgSO_4$), and evaporated. Distillation of the crude product under reduced pressure gave *(prop-2-yn-1-yl)propanedinitrile* (6.0 g, 81%). Colorless oil crystallizing slowly and melting at r.t. B.p. 110°/15 Torr. IR (film): 3300*s*, 2980*m*, 2920*s*, 2260*m*, 2140*w*, 1750*w*, 1670*w*, 1430*s*, 1330*m*, 1310*m*, 1220*m*, 1190*m*, 1040*s*, 940*m*, 870*w*, 800*m*, 660*s*. ^{1}H-NMR: 3.98 (*t*, ^3J = 6.5, $CH(CN)_2$); 2.94 (*dd*, ^3J = 6.5, ^4J = 2.5, CH_2); 2.41 (*t*, ^4J = 2.5, CH≡C). ^{13}C-NMR: 111.70 (*s*); 75.23 (*d*); 74.41 (*d*); 22.72 (*d*); 21.15 (*t*). EI-MS: 104 (75.99, $M^{+\cdot}$), 100 (4), 87 (47), 84 (6), 75 (100), 70 (93), 67 (3), 64 (76), 61 (91), 57 (28), 55 (22), 53 (23), 52 (5), 51 (15).

A soln. of dinitrile (1.0 g, 9.6 mmol) in THF (50 ml) was treated at −78° with 0.7M LiHMDS (13.7 ml, 9.6 mmol; prepared from hexamethyldisilazane (14.6 ml, 70 mmol) in THF (41.6 ml) and 1.6M BuLi (43.7 ml, 70 mmol) in hexane). After 5 min, a soln. of benzeneselenenyl chloride (1.84 g, 9.6 mmol) in THF (10 ml) was added. The mixture was allowed to warm to r.t, poured into 1M NH_4Cl (50 ml), and extracted with Et_2O (200 ml). The org. phase was washed with brine (50 ml), dried ($MgSO_4$), and evaporated. FC (AcOEt/p.e. 1:10) of the crude product gave **5** (2.3 g, 93%). Yellow oil. IR (film): 3300*s*, 3060*m*, 2960*m*, 2220*m*, 2120*w*, 1570*w*, 1480*m*, 1440*s*, 1430*m*, 1305*m*, 1280*w*, 1240*w*, 1180*w*, 1160*w*, 1070*m*, 1020*m*, 1000*m*, 800*w*, 750*s*, 690*s*, 670*s*. ^{1}H-NMR: 7.9 (*m*, 2 arom. H); 7.54 (*m*, 3 arom. H); 3.07 (*d*, ^4J = 2.7, CH_2); 2.51 (*t*, ^4J = 2.7, CH≡C). ^{13}C-NMR: 137.90 (*d*); 131.95 (*d*); 130.05 (*d*); 124.11 (*s*); 113.23 (*s*); 75.76 (*d*); 74.47 (*d*); 28.47 (*t*). EI-MS: 259 (12, $M^{+\cdot}$), 258 (5), 232 (6), 194 (17), 182 (7), 179 (16), 178 (17), 157 (7), 156 (14), 155 (64), 154 (5), 140 (7), 126 (6), 117 (8), 115 (5), 114 (44), 107 (4), 102 (11), 98 (5), 96 (12), 93 (7), 85 (9), 84 (9), 82 (11), 77 (22), 76 (100), 71 (22), 65 (23), 57 (36), 55 (27), 52 (12), 51 (98), 50 (19). Anal. calc. for $C_{12}H_8N_2Se$ (259.17): C 55.61, H 3.11, Se 30.47; found: C 55.74, H 3.21, Se 30.40.

(1RS,2SR,6SR,7RS)-5-[(E)- and (Z)-Iodomethylidene]-10-oxatricyclo[5.2.1.0^{2,6}]decan-8-one (**6a**) *and (1RS,2RS,6RS,7RS)-3-[(E)- and (Z)-Iodomethylidene]-10-oxatricyclo[5.2.1.0^{2,6}]decan-8-one* (**6b**). According to *General Procedure* from **1** (1.6 g, 15 mmol), 4-iodobut-1-yne (3.0 g, 16 mmol), and hexamethylditin (0.88 g, 1.5 mmol) in benzene (30 ml). Evaporation of the solvent and filtration through silica gel (AcOEt/p.e. 1:4) gave **6a**/**6b** (2.2 g, 51%) and unreacted **1** (0.25 g, 15%). Colorless oil.

(1RS,2RS,6SR,7RS)-9,9-(Ethylenedioxy)-10-oxatricyclo[5.2.1.0^{2,6}]decan-3-one (**10a**) *and (1RS,2SR,6RS, 7RS)-8,8-(Ethylenedioxy)-10-oxatricyclo[5.2.1.0^{2,6}]decan-3-one* (**10b**). A soln. of crude **6a**/**6b** (2.0 g, 6.9 mmol), ethylene glycol (2.0 g, 32 mmol) and pyridinium toluene-4-sulfonate (PPTS; 0.2 g, 0.8 mmol) in benzene (30 ml) was heated under reflux for 36 h in a *Dean-Stark* apparatus. The mixture was poured into Et_2O (100 ml), washed with H_2O (3 × 30 ml), and dried ($MgSO_4$). Evaporation gave the crude acetal (1.88 g, 82%). Viscous colorless oil. The acetal (1.5 g, 4.5 mmol) in CH_2Cl_2 (50 ml) was cooled to −78° and ozone bubbled through the soln. until appearance of a blue color (15 mn). The excess of ozone was purged off with N_2 and a soln. of PPh_3 (1.17 g, 4.5 mmol) in CH_2Cl_2 (10 ml) added. The mixture was allowed to warm to r.t. After removal of the solvent, the crude product was filtered through silica gel (AcOEt/p.e. 2:1): **10a**/**10b** 2.0:1. Regioselectivity by ^{1}H-NMR: 4.45 (*d*, H–C(7) of **10a**); 4.67 (*d*, H–C(1) of **10b**). FC (AcOEt/p.e. 2:1) and recrystallization (AcOEt/p.e.) gave pure **10** (0.78 g, 83%). White solid. M.p. 125–126°. IR (KBr): 2990*w*, 2960*w*, 2900*w*, 1730*s* (br.), 1475*w*, 1270*m*, 1250*m*, 1225*s*, 1190*m*, 1160*m*, 1120*m*, 1060*m*, 1040*m*, 1020*s*, 990*m*, 950*m*, 910*m*, 820*m*, 805*w*. ^{1}H-NMR: 4.45 (*d*, ^3J = 6, H–C(7)); 4.24 (*s*, H–C(1)); 4.12–3.75 (*m*, 2 CH_2O); 2.88 (*d*, ^3J = 8.5, H–C(2)); 2.66 (*m*, H–C(6)); 2.27–2.20 (*m*, H–C(4)); 2.33–2.19 (*m*, H–C(5)); 2.15 (*dd*, ^3J = 6, ^2J = 13, H_{exo}–C(8)); 1.8 (*m*, H–C(5)); 1.73 (*d*, ^2J = 13, H_{endo}–C(8)). ^{13}C-NMR: 219.85 (*s*); 113.95 (*s*); 83.67 (*d*); 83.00 (*d*); 65.17 (*t*); 64.59 (*t*); 50.36 (*d*); 43.91 (*d*); 42.44 (*t*); 39.18 (*t*); 25.84 (*t*). EI-MS: 210 (4, $M^{+\cdot}$), 153 (13), 126 (10), 125 (49), 112 (7), 100 (22), 99 (83), 95 (8), 86 (100), 81 (22), 67 (11), 55 (23), 53 (17). Anal. calc. for $C_{11}H_{14}O_4$ (210.23): C 62.85, H 6.71; found: C 62.62, H 6.73.

(1RS,2SR,3SR,6SR,7RS)- and (1RS,2SR,3RS,6SR,7RS)-5-[(E)- and (Z)-Iodo(trimethylsilyl)methylidene]-3-methyl-10-oxatricyclo[5.2.1.0^{2,6}]decan-8-one (**7a**) *and (1RS,2RS,5SR,6RS,7RS)- and (1RS,2RS, 5RS,6RS,7RS)-3-[(E)- and -(Z)-Iodo(trimethylsilyl)methylidene]-3-methyl-10-oxatricyclo[5.2.1.0^{2,6}]decan-8-one* (**7b**). According to *General Procedure* from **1** (280 mg, 2.5 mmol), **3** (740 mg, 2.8 mmol), and hexamethylditin (147 mg, 0.25 mmol) in benzene (6 ml). Evaporation and filtration through silica gel (AcOEt/p.e. 1:3) of the crude product gave **7a**/**7b** (860 mg, 82%).

(1RS,2RS,5SR,6SR,7SR,7RS)- and (1RS,2RS,5RS,6SR,7RS)-9,9-(Ethylenedioxy)-5-methyl-10-oxatricyclo[5.2.1.0^{2,6}]decan-3-one (**11a**) *and (1RS,2SR,5SR,6RS,7RS)- and (1RS,2SR,5RS,6RS,7RS)-8,8-(Ethylenedioxy)-5-methyl-10-oxatricyclo[5.2.1.0^{2,6}]decan-3-one* (**11b**). As described for **10a**/**10b**, with **7a**/**7b** (578 mg, 1.54 mmol), ethylene glycol (480 mg, 7.7 mmol), PPTS (100 mg, 0.4 mmol), and benzene (15 ml). Workup with AcOEt (50 ml) and H_2O (3 × 10 ml): crude acetal (0.52 g, 84%). Oxidation of the acetal (0.40 g, 1.1 mmol) in CH_2Cl_2 (20 ml) was described above, with ozone (5 min) and then PPh_3 (0.27 g, 1.1 mmol) in CH_2Cl_2 (5 ml). Filtration through silica gel (AcOEt/p.e. 1:1) gave **11a**/**11b** (2.6:1), 1:1 mixture of epimers at C(5). Regioselectivity by ^{1}H-NMR: 4.82 and 4.49 (*d*, H–C(7) of **11a**); 4.68 and 4.59 (*d*, H–C(1) of **11b**). Recrystallization (AcOEt/p.e.) gave pure **11a** (150 mg, 63%), epimers at C(5) not separable. White solid. M.p. 124–126°. IR (KBr): 2980*m*, 2960*m*, 2900*m*, 1735*s*, 1340*m*, 1310*m*, 1220*m*, 1120*m*, 1020*s*, 995*m*. ^{1}H-NMR: 4.82, 4.49 (*2d*, ^3J = 6, H–C(7)); 4.29, 4.17 (2*s*, H–C(1)); 4.08–3.80 (*m*, 2 CH_2O); 3.03–2.93 (*m*, 1 H); 2.60–1.90 (*m*, 5 H); 1.69, 1.71 (2*d*, *J* = 13, H_{endo}–C(8)); 1.22, 1.14 (2*d*, ^3J = 6.5, Me). CI-MS: 225 (7, $[M + 1]^+$), 224 (9, M^+), 196 (3), 167 (5), 139 (20), 125 (6), 99 (85), 86 (100). Anal. calc. for $C_{12}H_{16}O_4$ (224.25): C 64.27, H 7.19; found: C 64.56, H 6.88.

Dimethyl (1RS,2RS,6SR,7RS)-5-[(E)- and (Z)-Iodomethylidene]-8-oxo-10-oxatricyclo[5.2.1.0^{2,6}]decane-3,3-dicarboxylate (**8a**) *and Dimethyl (1RS,2SR,6RS,7RS)-5-[(E)- and (Z)-iodomethylidene]-9-oxo-10-oxatricyclo[5.2.1.0^{2,6}]decane-3,3-dicarboxylate* (**8b**). According to *General Procedure* from **1** (1.6 g, 15 mmol), **4** (5.0 g, 16 mmol), and hexamethylditin (0.58 g, 1.6 mmol) in benzene (30 ml). The crude product was filtered through silica gel (AcOEt/p.e. 1:2): **8a**/**8b** (4.7 g, 76%). Colorless oil, partially crystallizing.

Dimethyl (1RS,2RS,6RS,7RS)-8,8-(Ethylenedioxy)-5-oxo-10-oxatricyclo[5.2.1.0^{2,6}]decane-3,3-dicarboxylate (**12a**) *and Dimethyl (1RS,2SR,6SR,7RS)-9,9-(Ethylenedioxy)-5-oxo-10-oxatricyclo[5.2.1.0^{2,6}]decane-3,3-dicarboxylate* (**12b**). As described for **10a**/**10b** with crude **8a**/**8b** (2.1 g, 5.2 mmol), ethylene glycol (1.6 g, 25.8 mmol), and PPTS (200 mg, 0.8 mmol) in benzene (30 ml). Workup with AcOEt (100 ml) and H_2O (3 × 50 ml): crude acetal (2.1 g, 90%). Oxidation of the acetal (2.1 g, 4.7 mmol) in CH_2Cl_2 (20 ml) as described above with ozone (5 min) and then PPh_3 (1.2 g, 4.7 mmol) in CH_2Cl_2 (5 ml). Filtration through silica gel (AcOEt/p.e. 1:1) gave **12a**/**12b** (4.0:1; 1.34 g, 76%). Regioselectivity by ^{1}H-NMR: 4.56 (*d*, H–C(1) of **12a**); 4.65 (*d*, H–C(7) of **12b**). Colorless crystallizing oil. The major isomer **12a** was isolated by recystallization (AcOEt/p.e.). White solid. M.p. 122–123°. IR (KBr): 3010*m*, 2980*w*, 2960*m*, 2900*m*, 1740*s*, 1430*m*, 1405*m*, 1350*m*, 1300*s*, 1260*s*, 1240*s*, 1230*s*, 1220*s*, 1180*s*, 1160*s*, 1130*s*, 1080*s*, 950*m*, 930*m*, 870*m*, 820*m*, 790*m*. ^{1}H-NMR: 4.56 (*d*, ^3J = 6, H–C(1)); 4.12 (*s*, H–C(7)); 4.08–3.70 (*m*, 2 CH_2O); 3.82, 3.72 (2*s*, 2 MeO); 3.17 (*s*, 2 H–C(4)); 3.02 (*A* of *ABX*, $^3J_{AB}$ = 17.5, H–C(6)); 2.57 (*B* of *ABX*, $^3J_{BA}$ = 17.5, $^3J_{BX}$ = 1.0, H–C(2)); 2.18 (*dd*, ^3J = 6.1, ^2J = 13, H_{exo}–C(9)); 1.78 (*d*, ^2J = 13, H_{endo}–C(9)). ^{13}C-NMR: 213.52 (*s*); 171.42 (*s*); 169.18 (*s*); 113.49 (*s*); 83.47 (*d*); 79.85 (*d*); 65.26 (*t*); 64.70 (*t*); 58.88 (*s*); 53.24 (*q*); 52.91 (*q*); 51.48 (*d*); 49.41 (*d*); 46.03 (*t*), 43.61 (*t*). CI-MS: 328 (1, $[M + 2]^+$), 327 (5, $[M + 1]^+$), 326 (0.8, $M^{+\cdot}$), 298 (10), 267 (2), 239 (3), 154 (10), 153 (4), 115 (2), 113 (7), 101 (3), 100 (12), 99 (36), 93 (9), 86 (100), 81 (13), 79 (5), 77 (6), 73 (3), 71 (3), 70 (1). Anal. calc. for $C_{15}H_{18}O_8$ (326.30): C 55.21, H 5.56; found: C 55.27, H 5.61.

(1RS,2RS,6SR,7RS)-5-[(E)- and (Z)-(Phenylselenenyl)methylidene]-8-oxo-10-oxatricyclo[5.2.1.0^{2,6}]-decane-3,3-dicarbonitrile (**9a**) *and (1RS,2SR,6RS,7RS)-5-[(E)- and (Z)-(Phenylselenenyl)methylidene]-9-oxo-10-oxatricyclo[5.2.1.0^{2,6}]decane-3,3-dicarbonitrile* (**9b**). A soln. of **1** (1.36 g, 12.4 mmol) and **5** (3.90 g, 14.9 mmol) in benzene (40 ml) was irradiated for 12 h at 50° under N_2 with a 300-W sunlamp. Evaporation and filtration through silica gel (AcOEt/p.e. 1:10→1:4) gave **9a**/**9b** (4.0 g, 87%), mixture of four isomers. Yellow oil.

(1RS,2RS,6SR,7RS)-8,8-(Ethylenedioxy)-5-methylidene-10-oxatricyclo[5.2.1.0^{2,6}]decane-3,3-dicarbonitrile (**13a**) *and (1RS,2SR,6RS,7RS)-9,9-(Ethylenedioxy)-5-methylidene-10-oxatricyclo[5.2.1.0^{2,6}]decane-3,3-dicarbonitrile* (**13b**). A soln. of crude **9a**/**9b** (4.0 g, 10.7 mmol), ethylene glycol (3.1 g, 50 mmol), and PPTS (0.2 g, 0.8 mmol) in benzene (30 ml) was heated under reflux for 24 h in a *Dean-Stark* apparatus. The mixture was poured into Et_2O (100 ml), washed with H_2O (3 × 30 ml) and dried ($MgSO_4$). FC (AcOEt/p.e. 1:4) gave the acetal (3.7 g, 84%). Colorless oil. A soln. of the acetal (1.0 g, 2.4 mmol), Bu_3SnH (1.4 g, 4.8 mmol), and 2,2′-azobis(isobutyronitrile) (= 2,2′-dimethyl-2,2′-azobis(propanenitrile); AIBN; 40 mg, 0.24 mmol) in benzene (10 ml) was heated under reflux for 12 h with addition of AIBN (40 mg) every 4 h. Evaporation and filtration through silica gel (AcOEt/p.e. 1:6) gave the 5-(tributylstannyl)methylidene derivatives (1.1 g, 83%) which were dissolved in CH_2Cl_2 (5 ml). Silica gel (1.0 g) and 1M aq. HCl (1.0 ml) were added, and the mixture was stirred at r.t. for 4 days and poured into CH_2Cl_2 (100 ml). The org. phase was washed with H_2O (2 × 50 ml), dried ($MgSO_4$), and evaporated and the crude product filtered through silica gel (AcOEt/p.e. 1:4): **13a**/**13b** (4.2:1, 440 mg, 94%). Regioselectivity by ^{1}H-NMR: 4.90 (*d*, 1 H, H–C(1) of **13a**); 4.50 (*d*, 1 H, H–C(7) of **13b**). Colorless oil. The major isomer **13a** was isolated by FC (AcOEt/p.e. 1:4) and recrystallization (Et_2O/p.e.). M.p. 112–113°. IR ($CHCl_3$): 3000*s*, 2960*s*, 2920*s*, 2890*s*, 2260*w*, 1730*w*, 1670*w*, 1430*m*, 1350*m*, 1330*m*, 1310*m*, 1290*m*, 1270*s*, 1250*m*, 1230*m*, 1170*m*, 1130*s*, 1070*s*, 1060*s*, 1020*s*, 1010*m*, 970*w*, 950*m*, 940*m*, 920*m*, 910*s*, 850*m*, 660*m*. ^{1}H-NMR: 5.21 (*m*, CH_2=C); 4.90 (*d*, ^3J = 6.5, H–C(1)); 4.08 (*s*, H–C(7)); 4.10–3.81 (*m*, 2 CH_2O); 3.49 (*d*, ^3J = 7, ^4J = 1.5, H–C(2)); 3.15 (*A* of *ABMX*, ^4J = 1.5, 3, $^2J_{AB}$ = 14.5, H–C(4)); 3.0 (*d*, ^3J = 7, H–C(6)); 2.93 (*B* of *ABMX*, ^4J = 1.0, $^2J_{AB}$ = 14.5, H–C(4)); 2.21 (*dd*, ^2J = 13.5, ^3J = 6.5, H_{exo}–C(9)); 1.75 (*d*, ^2J = 13.5, H_{endo}–C(9)). ^{13}C-NMR: 145.34 (*s*); 115.85 (*s*); 114.11 (*s*); 113.17 (*s*); 112.72 (*t*); 87.17 (*d*); 79.73 (*d*); 65.38 (*t*); 64.79 (*t*); 56.00 (*d*); 46.77 (*d*); 45.74 (*t*); 42.85 (*t*); 37.60 (*s*). EI-MS: 259 (1, $M + 1]^+$), 258 (2, $M^{+\cdot}$), 230 (3), 229 (13), 165 (4), 130 (4), 128 (5), 125 (14), 116 (6), 115 (10), 104 (7), 103 (8), 101 (10), 100 (5), 99 (15), 91 (13), 89 (8), 87 (9), 86 (100), 81 (10), 79 (24), 78 (18), 77 (40), 76 (9), 73 (17), 66 (11), 65 (22), 57 (6), 53 (18), 52 (13), 51 (14), 50 (7). Anal. calc. for $C_{14}H_{14}N_2O_3$ (258.28): C 65.11, H 5.46; found: C 65.01, H 5.52.

(1RS,4SR,5RS,6RS)-6-Bromo-5-(trichloromethyl)-7-oxabicyclo[2.2.1]heptan-2-one (**14a**) *and (1RS,4RS,5RS,6SR)-5-Bromo-6-(trichloromethyl)-7-oxabicyclo[2.2.1]heptan-2-one* (**14b**). A soln. of **1** (330 mg, 3.0 mmol) and AIBN (50 mg, 0.3 mmol) in $CBrCl_3$ (5 ml) was heated to 60–65° for 10 h. Removal of excess $CBrCl_3$ under reduced pressure gave crude **14a**/**14b** (2.0:1). Purification by FC (AcOEt/p.e. 1:4) yielded **14a**/**14b** (860 mg, 93%), unseparable isomer mixture. Colorless oil. B.p. 115°/10^{-1} Torr. IR (KBr): 2990*w*, 2940*w*, 1170*s*, 1400*m*, 1305*w*, 1270*w*, 1230*m*, 1200*w*, 1170*m*, 1140*w*, 1100*m*, 1080*m*, 1040*w*, 1000*s*, 960*m*, 910*s*, 820*m*, 790*s*, 780*s*, 770*s*, 740*s*, 730*m*, 700*m*, 680*m*. ^{1}H-NMR: **14a**: 5.11 (*d*, ^3J = 6.5, H–C(4)); 4.51 (*d*, ^3J = 5.5, H–C(1)); 4.22 (*dd*, ^3J = 5.5, 4.5, H–C(6)); 3.32 (*d*, ^3J = 4.5, H–C(5)); 2.72 (*dd*, ^3J = 6.5, ^2J = 17.5, H_{exo}–C(3)); 2.29 (*d*, ^2J = 17.5, H_{endo}–C(3)); **14b**: 5.07 (*t*, ^3J = 5.5, 5, H–C(4)); 4.6 (*s*, H–C(1)); 4.44 (*dd*, ^3J = 5.1, 5, H–C(5)); 3.23 (*d*, ^3J = 5.1, H–C(6)); 3.02 (*d*, ^2J = 18, H_{endo}–C(3)); 2.65 (*dd*, ^3J = 5.5, ^2J = 18, H_{exo}–C(3)). EI-MS: 310 (1, $[M + 2]^+$), 308 (1, $M^{+\cdot}$), 306 (1), 274 (2), 272 (4), 270 (3), 231 (3), 229 (6), 227 (6), 201 (6), 199 (5), 191 (8), 189 (12), 187 (12), 185 (13), 163 (6), 151 (4), 149 (8), 135 (24), 123 (6), 121 (13), 119 (13), 117 (13), 115 (5), 111 (5), 109 (16), 107 (5), 101 (14), 99 (34), 87 (15), 85 (32), 83 (26), 81 (100), 75 (15), 73 (22), 71 (30), 68 (10), 65 (13), 62 (15), 57 (8), 55 (11), 53 (24), 51 (34), 50 (14). Anal. calc. for $C_7H_6BrCl_3O_2$ (308.39): C 27.26, H 1.96, Br 25.91, Cl 34.49; found: C 27.29, H 1.99, Br 25.87, Cl 34.48.

Reaction of **1** *with $CBrCl_3$ in the Presence of* Lewis *Acids*. A soln. of **1** (330 mg, 3 mmol), *Lewis* acid (3 mmol), and AIBN (50 mg, 0.3 mmol) in $CBrCl_3/CH_2Cl_2$ 3:1 (9 ml) was irradiated for 6 h with a 300-W sunlamp keeping the temp. at 10°. The mixture was poured into CH_2Cl_2 (50 ml) and washed with sat. Na_2CO_3 soln. (20 ml) and H_2O (20 ml). After drying ($MgSO_4$) and evaporation, the crude product was purified by FC (AcOEt/p.e. 1:4). The diastereoselectivity was determined on the crude product by GC (100° (2 min)–220° (10 min), 20°/min): t_R 13.0 (**14a**), 10.9 min (**14b**).

X-Ray Structure Analysis of **10a** *and* **12a**. Suitable crystals were obtained by slow crystallization from AcOEt/p.e. Experimental parameters are given in *Tables 3* and *4*, resp. Atomic coordinates are deposited with the *Cambridge Crystallographic Data Centre*.

Table 3. *X-Ray Structure Determination of* **10a**

Crystal Data	
Chemical formula	$C_{11}H_{14}O_4$
Formula weight	210.2
Color, habit	Colorless-transparent platelets
Crystal system	Monoclinic
Unit-cell dimensions	$a = 7.645(2)$ Å $b = 5.870(2)$ Å $c = 22.261(4)$ Å $\beta = 91.13(2)°$
Space group	$P2_1/n$
Volume	998.8(5) Å^3
Z	4
Density (calc.)	1.398 Mg/m^3
Absorption coefficient	0.887 mm^{-1}
$F(000)$	448
Data Collection	
Diffractometer used	*Siemens R3m/V*
Radiation	CuK_α ($\lambda = 1.54178$ Å)
Temperature (K)	293
Monochromator	highly oriented graphite crystal
2θ Range	0.0–110.0°
Scan type	2θ–θ
Scan speed	variable; 3.00–10.00°/min in ω
Scan range (ω)	1.50° plus K_α separation
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard reflections	3 measured every 97 reflections
Index ranges	$-8 \leq h \leq , -6 \leq k \leq 3$, $-23 \leq l \leq 23$
Reflections collected	3844
Independent reflections	1258 ($R_{int} = 1.70\%$)
Observed reflections	1258 ($F > 0.0\, s(F)$)
Absorption correction	*N/A*
Solution and Refinement	
System used	*Siemens* SHELXTL PLUS (VMS)
Solution	direct methods
Refinement method	full-matrix least-squares
Quantity minimized	$\Sigma w (F_o - F_c)^2$
Absolute structure	*N/A*
Extinction correction	$\chi = 0.024(7)$, where $F^* = F[1 + 0.002 \cdot F^2/\sin(2\theta)]^{-1/4}$
H-Atom	riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000\, F^2$
Number of parameters refined	193
Final R indices (obs. data)	$R = 3.81\%$, $wR = 4.39\%$
R Indices (all data)	$R = 0.00\%$, $wR = 0.00\%$
Goodness-of-fit	5.96
Largest and mean Δ/σ	0.002, 0.000
Data-to-parameter ratio	6.5:1
Largest difference peak	0.00 eÅ^{-3}
Largest difference hole	0.00 eÅ^{-3}

Table 4. *X-Ray Structure Determination of* **12a**

Crystal Data	
Chemical formula	$C_{15}H_{18.4}O_{8.2}$
Crystal system	triclinic
Unit-cell dimensions	$a = 7.412$ Å $\alpha = 89.53°$ $b = 10.1620(10)$ Å $\beta = 76.54°$ $c = 10.3710(10)$ Å $\gamma = 85.42°$
Space group	$P\bar{1}$
Volume	757.23(10) Å^3
Z	2
Density	1.431 Mg/m^3
Absorption coefficient	1.002 mm^{-1}
$F(000)$	344
Data Collection	
Diffractometer used	*Siemens R3m/V*
Radiation	CuK_α ($\lambda = 1.54178$ Å)
Temperature (K)	293 (2)
2θ Range	4.36–57.19°
Index ranges	$-8 \leq h \leq 8$, $-10 \leq k \leq 11$, $-10 \leq l \leq 11$
Reflections collected	40091
Independant reflections	2046 ($R_{int} = 0.018$)
Solution and Refinement	
System used	*Siemens* SHELXTL PLUS (VMS)
Solution	direct methods
Refinement method	full-matrix least-squares on F^2
Extinction coefficient	0.047(3)
Final R indices ($l > 2\sigma(I)$)	$R_1 = 0.0554$, $wR_2 = 0.1300$
R indices (all data)	$R_1 = 0.0594$, $wR_2 = 0.1372$
Goodness-of fit on F^2	7.289
Largest difference peak	0.371 eÅ^{-3}
Largest difference hole	0.290 eÅ^{-3}
Data/restraints/parameters	2046/0/292

An intriguing residue near atom C(4) emerged during the refinement of **12a** (two different crystals were measured). It was interpreted as 0.2 H_2O molecules forming H-bonds to four surrounding O-atoms (O–O from 2.79–3.08 Å). The additional 0.2 O-atoms lowered the R_F value from 0.075 to 0.055. We did not seek any deeper understanding of this problem. It is noteworthy that there exist superstructures along all three vectors. But since the difference reflections turned out to be extremely weak, these features were neglected for the structure determination.

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