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Abstract: The intramolecular vinylogous Nicholas reactions of aryl substituted acetoxy enyne-$Co_2(CO)_6$ complexes afford tricyclic 6,7,6- ring systems and related systems in good yield.

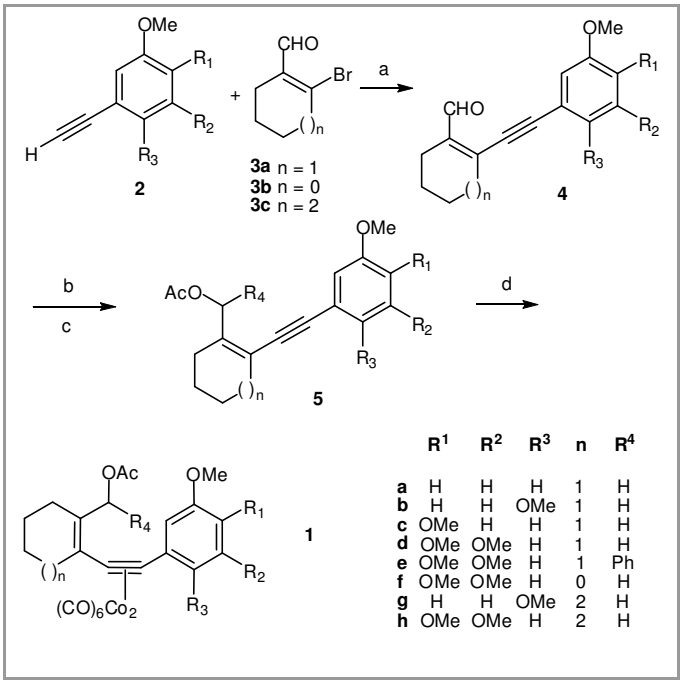
Key words: carbocations, alkyne complexes, electrophilic aromatic substitution, cyclization, fused-ring systems.

The reactions of alkynedicobalt complexes have proven useful in the synthesis of seven membered ring systems[1] by way of ring closing metathesis,[2] carbonylative Heck reactions,[3] Diels-Alder reactions,[4] Hosomi-Sakurai and Mukaiyama aldol reactions,[5] Michael reaction,[6] and particularly by Nicholas reactions.[7,8] In the latter case, the combination of ready generation of the propargyldicobalt cations with the sufficient reactivity of the cations for electron rich arenes has allowed preparation of benzo- and dibenzocycloheptyne complexes.[9] By contrast, a more limited amount is known regarding vinylogous Nicholas reactions, which are the reactions of cations generated from dicobalt complexes of propargyl-allyl alcohol derivatives. Although the preference for attack by carbon nucleophiles at the allyl terminus remote to cobalt is known[10] and they have been shown to be useful in dehydrooxepane synthesis (through proximal attack)[8a] and a macrocyclization,[10b] vinylogous Nicholas reactions have never been employed in the formation of cycloheptynedicobalt ring systems.

The 6,7,6- systems of the icetexane diterpenes and related compounds such as the favelines have become the object of recent increased synthetic attention.[11] In addition to both modified and traditional Friedel-Crafts approaches to the system,[12] successful access to these systems have been accomplished by way of Bronsted or Lewis acid mediated conjugate additions,[13] Diels-Alder, carbonyl ylide and benzopyrylium ion cycloadditions,[14] radical cyclization chemistry,[15] palladium catalyzed Heck and enolate arylation reactions,[16] aldol type ring closures,[17] Barbier type reactions,[18] and cycloisomerization and ring expansion reactions.[19]

Given the normal reactivity pattern of vinylogous propargyldicobalt cations and the fact that cyclopentynedicobalt complexes appear to be prohibitively strained, we considered it a reasonable possibility that intramolecular vinylogous Nicholas reaction chemistry would readily give access to these 6,7,6- systems and other 6,7,n- systems. This letter reports our preliminary findings in this effort.

The precursors to the cyclization reactions were envisioned as allylic acetate complexes **1**, the endocyclic alkene being advantageous in imposing an *anti* geometry on any resulting allyl cation. The complexes could be prepared beginning with ethynylarenes **2**[20] and 2-bromocycloalkenecarboxaldehydes **3**, which were subjected to Sonogashira coupling to afford alkynals **4** (Scheme 1, Table 1). Reduction of the aldehyde function in **4** with acetylation of the alcohol gave acetates **5** in good yield, which then underwent complexation with $Co_2(CO)_8$ to give **1** in straightforward fashion (Table 1).[21] For compound **4d**, an additional case involving replacement of the reduction step by a PhMgBr reaction with the aldehyde afforded benzylic acetates **5e** and **1e** without incident.



Scheme 1. *Reagents and conditions:* (a) $Pd(PPh_3)_4$ (3 mol%), CuI (6 mol%), Et_3N-THF, 40-80 °C; (b) DIBAL-H, Et_2O, -78 °C (PhMgBr, THF, -78 °C for **5e**); (c) Ac_2O, pyridine; (d) $Co_2(CO)_8$, CH_2Cl_2.

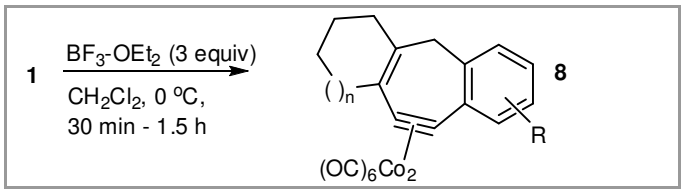
Table 1 Preparation of Allyl Acetate Complexes **1**

2	R^1	R^2	R^3	**3**	R^4	**4** (Yield, %)	**5** (Yield, %)	**1** (Yield, %)
2a	H	H	H	**3a** (n = 1)	H	**4a** (74)	**5a** (88)	**1a** (92)
2b	H	H	OMe	**3a** (n = 1)	H	**4b** (76)	**5b** (82)	**1b** (82)

2c	OMe	H	H	**3a** (n = 1)	H	**4c** (81)	**5c** (80)	**1c** (85)
2d	OMe	OMe	H	**3a** (n = 1)	H	**4d** (85)	**5d** (83)	**1c** (86)
2d	OMe	OMe	H	**3a** (n = 1)	Ph	**-**	**5e** (80)	**1e** (87)
2d	OMe	OMe	H	**3b** (n = 0)	H	**4f** (80)	**5f** (80)	**1f** (85)
2b	H	H	OMe	**3c** (n = 2)	H	**4g** (76)	**5g** (83)	**1g** (84)
2d	OMe	OMe	H	**3c** (n = 2)	H	**4h** (79)	**5h** (84)	**1h** (83)

Compound **1a** was tested for its ability to undergo Lewis acid based Nicholas type cyclization reactions. An excess of BF_3-OEt_2 (3 equiv) mediated a relatively rapid consumption of **1a** at 0 °C. After 1 h, this compound had disappeared completely, and separable compounds **8a** and **8a'** could be isolated in a combined 81% yield (**8a**:**8a'** = 4.9:1) (Table 2). The addition of *i*-Pr_2NEt, which was beneficial in Nicholas based cyclizations toward dibenzocycloheptyne complexes, showed no advantage in the reaction of **1a**. Reducing the reaction temperature to -40 °C still allowed the reaction to progress (1.5 h), giving an enhanced amount of the substitution *para*- to the methoxy function (79% yield, **8a**:**8a'** = 6.8:1).[22] 2,6-Dimethoxy substituted **1b** reacted at a similar rate to **1a**, and at 0 °C afforded **8b** in 78% yield. 3,4-Dimethoxy substituted **1c** afforded a separable mixture of regioisomeric products **8c** and **8c'** favouring the less sterically hindered site, and in overall excellent yield (90% yield, **8c**:**8c'** = 8:1). Trimethoxy substituted **1d** gave the corresponding 6,7,6- system in a straightforward fashion (**8d**, 82%), in 0.5 h. Substitution at the reacting centre however, was detrimental to the Nicholas reaction; benzylic acetate complex **1e** afforded **8e** in modest yield (40%, entry 6) due to competitive elimination (**9**, 40%).

The size of the cycloalkene ring in **1** could be varied with no noticeable effect on the cyclization. Cyclopentene containing **1f** transformed to 6,7,5- tricycle **8f** under the standard conditions (87% yield, entry 7) in 45 min, while cycloheptene containing **1g** and **1h** similarly afforded 6,7,7- tricycles **8g** and **8h** in 81% yield (entry 8) and 77% yield (entry 9), respectively, each over 1 h.[23]



Equation 1

Table 2 Vinylogous Nicholas Reaction Based Cyclizations

Entry	R^1	R^2	R^3	n	R^4	**8** (Yield, %)
1	H	H	H	1	H	**8a + 8a'** 81 (4.9:1)[a]
2	H	H	H	1	H	**8a + 8a'** 79 (6.8:1)[b]
3	H	H	OMe	1	H	**8b** 78
4	OMe	H	H	1	H	**8c + 8c'** 90 (8.0:1)
5	OMe	OMe	H	1	H	**8d** 82
6	OMe	OMe	H	1	Ph	**8e** 40[c]
7	OMe	H	H	0	H	**8f** 87
8	H	H	OMe	2	H	**8g** 81
9	OMe	OMe	OMe	2	H	**8h** 77

[a] Product ratios in parentheses
[b] Reaction conducted at -40 °C
[c] In addition, 40% of **9** was isolated

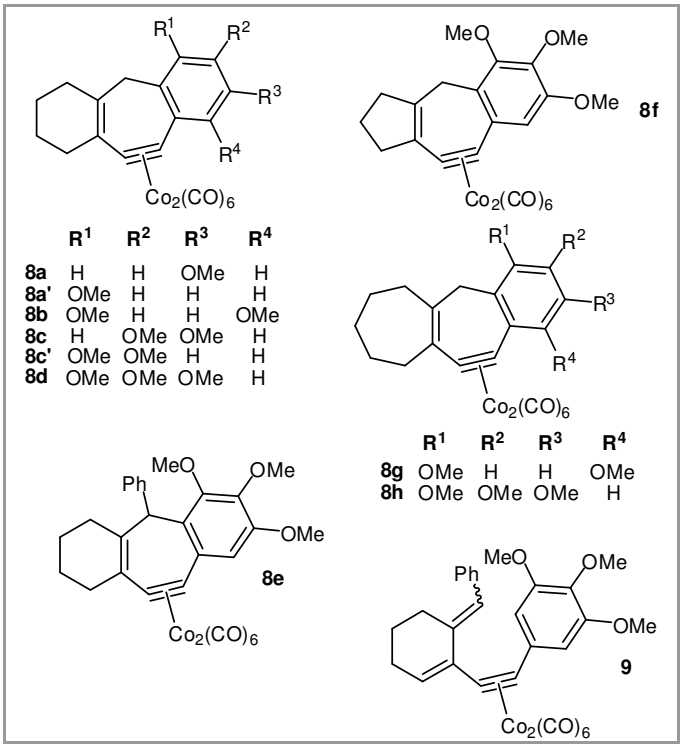
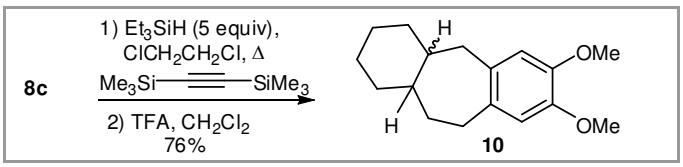


Figure 1

In order to demonstrate the ability to remove the $Co_2(CO)_6$ unit from the cyclization products, compound **8c** was chosen for study. Reductive decomplexation was facile on this compound. Subjecting **8c** to the hydrosilylation conditions developed by Isobe,[24] followed by *in situ* protodesilylation with TFA,[9b] gave an overall reductive decomplexation that included reduction of the alkene functions, to give benzocycloheptene **10** in 76 % yield (1:1 diastereomeric mixture).



Equation 2

In summary, aryl substituted allylic acetoxy enyne-$Co_2(CO)_6$ complexes readily undergo intramolecular vinylogous Nicholas reactions to afford 6,7,6-, 6,7,5- and 6,7,7- ring systems. Yields are in general good and removal of the $Co_2(CO)_6$ unit is facile, although the possi-

bility for competitive elimination compromises the cyclization yields in some cases. Work on biasing the regioselectivity of cyclization onto the aryl ring, the use of other nucleophilic functions, and on systems with A ring substitution leading to specific icetexanes or faveline, is in progress, and will be reported in due course.

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(20) These compounds were prepared from the corresponding iodoarenes, by known Sonogashira reactions with trimethylsilylacetylene followed by desilylation. See, for example: Montalbetti, C.; Savignac, M.; Bonnefis, F.; Genet, J. P. *Tetrahedron Lett.* **1995**, *36*, 5891.

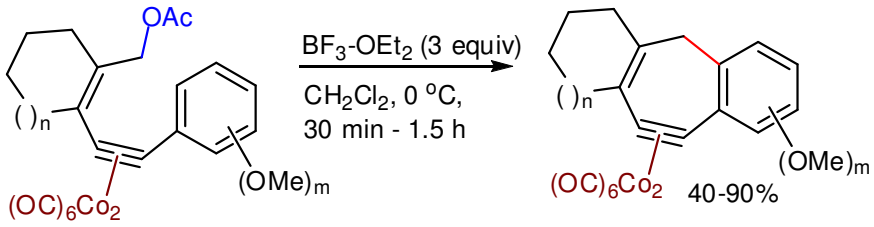
(21) Selected compounds: Compound **4g**: IR (KBr) υ_{max} 2954, 2833, 2187, 1673 cm^{-1}; ^1H NMR δ 10.35 (s, 1H), 6.96 (d, J = 3.1, 1H), 6.90 (dd, J = 9.1, 3.1, 1H), 6.83 (d, J = 9.1, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.73 (m, 2H), 2.55 (m, 2H), 1.83 (m, 2H), 1.70 (m, 1H), 1.48 (m, 1H); ^{13}C 193.0, 154.9, 153.2, 148.2, 145.9, 117.5, 116.8, 112.0, 111.9, 96.7, 91.9, 56.4, 55.8, 37.4, 32.3, 25.7, 24.2; MS m/e (M^+) 284; HRMS m/e calcd. for $C_{18}H_{20}O_3$ (M^+) 284.1412, found 284.1412. Compound **5g**: IR (KBr) υ_{max} 2964, 1746 cm^{-1}; ^1H NMR δ 6.93 (d, J = 2.9, 1H), 6.81 (d of ½ ABquartet, J = 2.9, 8.9, 1H), 6.78 (1/2 ABquartet, J = 8.9, 1H), 4.97 (s, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 2.51 (m, 2H), 2.32 (m, 2H), 2.09 (s, 3H), 1.79 (m, 2H), 1.62 (m, 2H), 1.53 (m, 2H); ^{13}C 171.2, 154.4, 153.1, 145.1, 126.0, 117.4, 115.4, 113.3, 111.9, 94.9, 89.9, 68.0, 56.4, 55.8, 34.6, 32.3, 31.2, 26.1, 26.0, 21.0; MS m/e (M^+) 328; HRMS m/e calcd. for $C_{20}H_{24}O_4$ (M^+) 328.1675, found 328.1683. Compound **1g**: IR (KBr) υ_{max} 2926, 2085, 2058, 2013, 1741 cm^{-1}; ^1H NMR δ 7.01 (d, J = 3.1, 1H), 6.86 (dd, J = 8.9, 3.1, 1H), 6.75 (d, J = 8.9, 1H), 4.53 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H), 2.61 (m, 2H), 2.31 (m, 2H), 1.95 (s, 3H), 1.83 (m, 2H), 1.55-1.64 (m, 4H); ^{13}C 199.8, 170.9, 153.5, 150.1, 139.1, 138.6, 127.7, 117.2, 113.5, 110.2, 95.8, 91.0, 65.6, 58.7, 54.4, 37.5, 32.6, 32.3, 26.6, 26.3, 20.8; MS m/e 558 (M^+-2CO), 530 (M^+-3CO), 446 (M^+-5CO); HRMS m/e for $C_{26}H_{24}Co_2O_{10}$ (M-2CO^+) 558.0106, found 558.0117.

(22) Compound **8a**: IR (KBr) υ_{max} 2930, 2087, 2046, 2017 cm^{-1}; ^1H NMR δ 7.20 (d, J = 2.7, 1H), 7.04 (d, J = 8.4, 1H), 6.84 (dd, J = 8.4, 2.7, 1H), 3.85 (s, 3H), 3.20 (s, 2H), 2.33-2.38 (m, 2H), 2.26-2.30 (m, 2H), 1.73-1.78 (m, 2H), 1.66-1.72 (m, 2H); ^{13}C 200.0, 159.0, 139.1, 137.2, 130.1, 129.9,

129.3, 117.4, 113.6, 94.9, 89.5, 55.3, 42.1, 33.7, 30.5, 23.0, 22.7; MS m/e 510 (M^+), 482 (M^+-CO), 454 (M^+-2CO), 426 (M^+-3CO), 398 (M^+-4CO); HRMS m/e for $C_{22}H_{16}Co_2O_7$ calcd. (M-CO^+) 481.9611 , found 481.9634. Compound **8a'**: IR (KBr) υ_{max} 2933, 2087, 2046, 2017 cm^{-1}; ^1H NMR δ 7.28 (dd, obscured, 1H), 7.23 (apparent t, J = 7.8, 1H), 6.90 (dd, J = 8.0, 1.1, 1H), 3.86 (s, 3H), 3.33 (s, 2H), 2.30-2.38 (m, 4H), 1.73-1.79 (m, 2H), 1.65-1.71 (m, 2H); ^{13}C 200.1, 155.8, 139.5, 137.5, 130.8, 127.5, 125.3, 124.7, 110.5, 95.1, 89.9, 55.9, 33.7, 32.2, 30.4, 23.0, 22.7; MS m/e 510 (M^+), 482 (M^+-CO), 454 (M^+-2CO), 426 (M^+-3CO), 398 (M^+-4CO); HRMS m/e for $C_{22}H_{16}Co_2O_7$ calcd. (M^+-CO) 481.9611, found 481.9624. Compound **8b**: IR (KBr) υ_{max} 2964, 2085, 2046, 2026 cm^{-1}; ^1H NMR δ 6.92 (d, J = 8.9, 1H), 6.75 (d, J = 8.9, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.34 (s, 2H), 2.29-2.37 (m, 4H), 1.73-1.79 (m, 2H), 1.65-1.72 (m, 2H); ^{13}C 200.5, 153.9, 150.2, 136.2, 131.4, 127.3, 126.5, 112.0, 108.6, 95.9, 84.7, 56.6, 54.7, 33.5, 32.7, 30.5, 23.0, 22.6; MS m/e 512 (M^+-CO), 484 (M^+-2CO), 428 (M^+-4CO); HRMS m/e for $C_{23}H_{18}Co_2O_8$ calcd. 539.9666, found 539.9669. Compound **8c**: IR (KBr) υ_{max} 2935, 2085, 2043, 2012 cm^{-1}; ^1H NMR δ 7.13 (s, 1H), 6.64 (s, 1H), 3.92 (s, 6H), 3.19 (s, 2H), 2.34-2.39 (m, 2H), 2.26-2.31 (m, 2H), 1.74-1.79 (m, 2H), 1.68-1.73 (m, 2H); ^{13}C 200.1, 149.2, 148.4, 136.3, 130.4, 129.7, 114.6, 112.3, 95.1, 90.5, 56.0, 42.6, 33.8, 30.5, 23.0, 22.7; HRMS m/e for $C_{23}H_{18}Co_2O_8$ calcd. (M^+-CO) 511.9716, found 511.9711. Compound **8d**: IR (KBr) υ_{max} 2936, 2085, 2045, 2016 cm^{-1}; ^1H NMR δ 6.98 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.25 (s, 2H), 2.36 (m, 2H), 2.31 (m, 2H), 1.77 (m, 2H), 1.70 (m, 2H); ^{13}C 200.1, 152.4, 150.4, 142.8, 137.0, 133.7, 130.8, 123.3, 111.0, 95.2, 90.3, 61.6, 60.8, 56.0, 33.7, 32.8, 30.4, 23.0, 22.7; MS m/e 458 (M^+-4CO), 430 (M^+-5CO), 402 (M^+-6CO); HRMS m/e for $C_{24}H_{20}Co_2O_9$ calcd. (M^+-CO) 541.9822, found 541.9821. Compound **8e**: IR (KBr) υ_{max} 2931, 2084, 2049, 2015, 1638 cm^{-1}; ^1H NMR δ 7.14 (apparent t, J = 7.7, 2H), 7.09 (s, 1H), 7.06 (t, J = 6.9, 1H), 6.89 (d, J = 8.2, 2H), 5.32 (s, 1H), 3.98 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H), 2.63-2.72 (m, 1H), 2.50-2.60 (m, 1H), 2.27-2.48 (m, 2H), 1.82-1.95 (m, 2H), 1.68-1.77 (m, 2H); ^{13}C 199.7, 152.7, 151.6, 142.8, 141.0, 138.3, 132.7, 131.4, 128.4, 126.8, 126.3, 125.0, 112.2, 91.6, 61.7, 60.8, 55.7, 47.6, 35.8, 31.4, 23.4, 22.8; MS m/e 562 (M^+-3CO); 534 (M^+-4CO), 478 (M^+-6CO); HRMS m/e for $C_{30}H_{24}Co_2O_9$ calcd. (M^+-3CO) 562.0237, found 562.0240. Compound **8f**: IR (KBr) υ_{max} 2938, 2087, 2048, 2019 cm^{-1}; ^1H NMR δ 6.99 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.48 (s, 2H), 2.71 (m, 2H), 2.56 (m, 2H), 2.06 (apparent quintet, J = 7.5, 2H); ^{13}C 199.7, 152.3, 150.8, 142.9, 141.5, 135.2, 133.4, 121.5, 112.2, 90.9, 87.9, 61.2, 60.8, 55.9, 39.2, 35.4, 27.4, 22.5; MS m/e 472 (M^+-3CO), 444 (M^+-4CO), 416 (M^+-5CO), 388 (M^+-6CO) ; HRMS m/e for $C_{23}H_{18}Co_2O_9$ calcd. (M^+-CO) 527.9654, found 527.9666. Compound **8g**: IR (KBr) υ_{max} 2937, 2085, 2051, 2029 cm^{-1}; ^1H NMR δ 6.92 (d, J = 8.9, 1H), 6.74 (d, J = 8.9, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.40 (s, 2H), 2.76 (m, 1H), 2.51-2.57 (m, 4H), 2.29 (m, 1H), 1.75-1.81 (m, 2H), 1.61-1.72 (m, 2H); ^{13}C 200.0, 153.8, 150.1, 141.6, 136.7, 130.9, 126.7, 112.2, 108.5, 97.6, 56.8, 54.6, 38.5, 35.5, 34.6, 31.4, 29.7, 26.2; MS m/e 526 (M^+-CO), 498 (M^+-2CO), 442 (M^+-4CO); HRMS m/e for $C_{24}H_{20}Co_2O_8$ calcd. (M^+) 553.9822, found 553.9802. Compound **8h**: IR (KBr) υ_{max} 2918, 2085, 2046, 2016 cm^{-1}; ^1H NMR δ 6.97 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.31 (s, 2H), 2.56 (m, 4H), 1.79 (m, 2H), 1.65 (m, 2H), 1.59 (m, 2H); ^{13}C 200.1, 152.4, 150.3, 142.89, 142.85, 136.3, 133.5, 123.3, 110.7, 97.1, 90.9, 61.7, 60.9, 56.0, 39.0, 35.4, 34.9, 31.6, 26.24, 26.19; MS m/e 584 (M^+), 556 (M^+-CO), 528 (M^+-2CO), 500 (M^+-3CO), 472 (M^+-4CO), 444 (M^+-5CO), 414 (M^+-6CO); HRMS m/e for $C_{25}H_{22}Co_2O_9$ calcd. (M^+-2CO) 528.0029, found 528.0030. Compound **10**: IR (KBr) υ_{max} 3035, 2919, 1607, 1516 cm^{-1}; ^1H NMR δ 6.66 (s, 1H), 6.65 (s, 1H), 6.64 (s, 1H), 6.60 (s, 1H), 3.861 (s, 3H), 3.860 (s, 6H), 3.85 (s, 3H), 2.86 (apparent t, J = 13.1, 1H), 2.76 (dd, J = 14.2, 10.6, 1H), 2.62-2.75 (m, 3H), 2.61 (dd, J = 14.2, 6.9, 1H)), 2.32 (d, J = 14.2, 1H), 1.97 (m, 1H), 1.89 (m, 1H), 1.80 (m, 1H), 0.95-1.75 (m, 22H) ; ^{13}C 146.51, 146.45, 146.44, 146.3, 135.4, 135.1, 134.3, 113.8, 113.1, 112.5, 112.4, 56.00, 55.95, 55.90, 48.5, 43.9, 43.7, 38.0, 36.3, 35.8, 35.4, 34.9, 26.7, 26.4; MS m/e 260 (M^+); HRMS for $C_{17}H_{24}O_2$ calcd. 260.1776, found 260.1775.

(23) Typical Experimental: To a solution of **1f** (0.406 g, mmol) in CH_2Cl_2 (9 mL) at 0 °C was added BF_3-OEt_2 (25 μL, 0.20 mmol). After stirring for 45 min, $NH_4Cl_{(aq)}$ was added and the mixture subjected to a conventional extractive workup (CH_2Cl_2). Flash chromatography (1:1 petroleum ether:Et_2O) afforded **8f** (0.0319 g, 87% yield) as a viscous red-brown oil.

(24) (a) Kira, K.; Tanda, H.; Hamajima, A.; Baba, T.; Takai, S.; Isobe, M. *Tetrahedron* **2002**, *58*, 6485; (b) For related examples, see: Hosokawa, S.; Isobe, M. *Tetrahedron Lett.* **1998**, *39*, 2609; (c) Takai, S.; Ploypradith, P.; Hamajima, A.; Kira, K.; Isobe, M. *Synlett* **2002**, 588.



Vinylogous Nicholas reactions in the synthesis of icetexane, faveline, and related ring systems