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Vinylogous Nicholas Reactions in the Synthesis of Bi- and Tricyclic Cycloheptynedicobalt Complexes

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Abstract

The Lewis acid mediated intramolecular Nicholas reactions of allylic acetate enyne-$Co_2(CO)_6$ complexes afford cycloheptenyne-$Co_2(CO)_6$ complexes in three manifestations. Electron rich aryl substituted alkyne complexes give tricyclic 6,7,x- benzocycloheptenyne complexes, with x = 5, 6, or 7. Allylsilane substituted complexes afford exo methylene bicyclic x,7- cycloheptenyne complexes (x = 6,7). The allyl acetate function may also be replaced by a benzylic acetate, to afford dibenzocycloheptyne-$Co_2(CO)_6$ complexes. Following reductive complexation, the methodology may be applied to the synthesis of the icetexane diterpene carbon framework.

Introduction

The chemistry of cycloheptyne-$Co_2(CO)_6$ complexes is of interest from several aspects.[1] The ca. 140 ^{o} bond angle of the alkynedicobalt complex[2] renders stable complexes of otherwise unstable alkyne functions. The intermediacy of these complexes has proved central in the synthesis of several groups of seven- membered ring containing compounds.[3] In addition, its presence in compounds with adjacent π- systems have raised important questions in bonding.[4]

Synthesis of this class of compounds has been accomplished in a limited number of cases via ring closing methathesis,[5] a carbonylative Heck reaction,[6] Diels-Alder reactions,[7] Hososmi-Sakurai reactions,[8] ene- reaction chemistry,[3e] Mukaiyama aldol reactions,[9] and Michael chemistry,[10] but most often by intramolecular nucleophilic attack on propargyldicobalt cations (Nicholas reaction chemistry).[11,12] In some cases they have provided an excellent way of favouring cyclization to the seven- membered ring system over the five membered ring isomer. The potential use of vinylogous Nicholas reaction chemistry for access to cycloheptynedicobalt complexes, however, has not been investigated previously. The use of vinylogous propargyl

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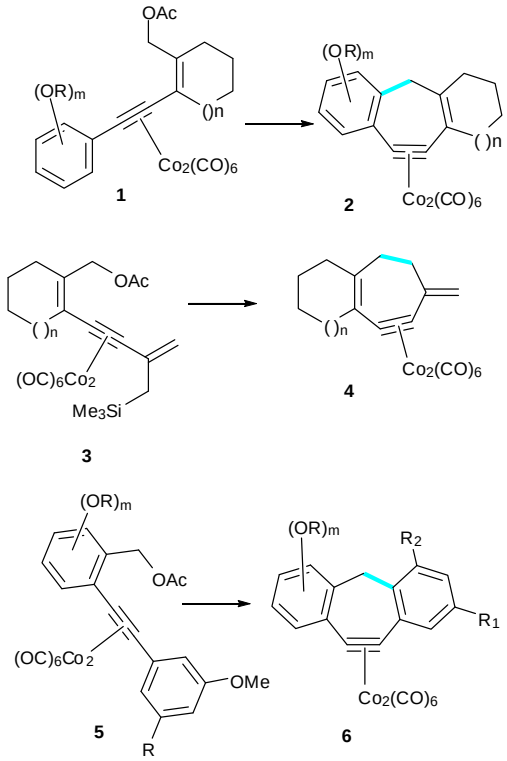
†Electronic supplementary information (ESI) available: Experimental details and spectroscopic data, ^{1}H and ^{13}C NMR spectra for new compounds.

cation complexes in reactions with nucleophiles not only favour remote attack with most nucleophiles,[13] but competitive proximal attack in substrates such as **1** would result in a prohibitively angle strained cyclopentynedicobalt complex. As a result, there is a good likelihood of success for the vinylogous Nicholas reactions (**1** → **2**) of allyl propargyl cation complexes to result in the preparation of cycloheptyne complexes (Scheme 1).



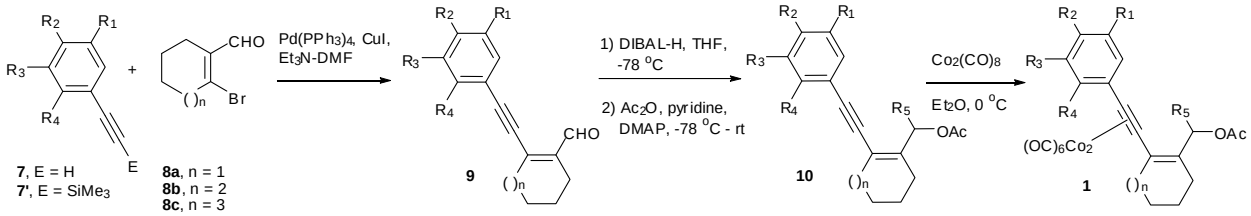
Scheme 1. Intramolecular vinylogous Nicholas reactions.

Of the tricyclic systems reflected in **2**, the 6,7,6- system that would result from cyclization reactions with arene nucleophiles, the n = 1 systems are heavily encountered in the icetexane and faveline diterpenes.[14] These classes of compounds have been the subject of a number of different synthetic tactics,[15,16,17,18,19,20,21,22] but have not been approached by Nicholas reaction chemistry; consequently we were interested in the application of these vinylogous Nicholas reactions in the construction of the icetexane ring system. In addition, we have interest in the viability of nucleophiles other than arenes, particular allylsilane nucleophiles (**3**), in accomplishing analogous chemistry, to afford bicyclic complexes **4**. Finally, it is in principle possible for the use of arenes as opposed to cyclic alkenes as the spacers between the alkynedicobalt complex and leaving group (**5**) to give dibenzocycloheptyne complexes **6**; we wished to determine the viability of this transformation, particularly given the occurrence of

dibenzo[a,d]cycloheptenes in tricyclic antidepressants.[23] We have reported on some aspects of the chemistry in preliminary fashion[24] and now describe a complete report.

Results and discussion

The initial attempts at vinylogous Nicholas reaction chemistry involved the choice of electron rich arene nucleophiles (**1**), with the intent of generation 6,7,x- systems upon cyclization (**2**). The starting materials for the cyclization precursors were alkynylarenes **7**, which were subjected to Sonogashira coupling reactions with 2-bromocyclopentenecarbaldehyde (**8a**), 2-bromocyclohexenecarbaldehyde (**8b**), or 2-bromocycloheptenecarbaldehyde (**8c**), to give aryl substituted cyclic enynecarbaldehydes **9** (Scheme 2, Table 1). In three cases, the corresponding(trimethylsilyl)alkynylarene (**7'd, 7'i**) was employed instead, with a desilylative Sonogashira coupling[25] giving **9e**, **9f** and **9p** in straightforward fashion. Reduction of the aldehyde function and acetylation of resultant alcohol gave acetates **10**, which underwent ready complexation reactions with $Co_2(CO)_8$ to form the enyne/allylic acetate complexes **1** in good to excellent yields.



Scheme 2. Preparation of aryl substituted allylic acetate alkyne-$Co_2(CO)_6$ complexes.

Table 1. Preparation of aryl substituted allylic acetate alkyne-$Co_2(CO)_6$ complexes.

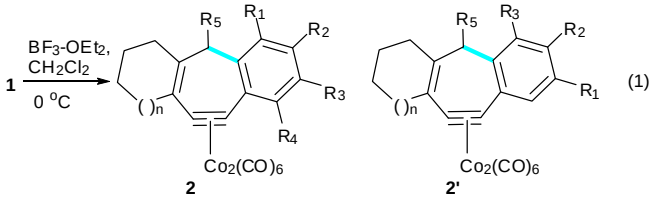
7	R^1	R^2	R^3	R^4	R^5	n	9, 10, 1	Yield of 9 (%)	Yield of 10 (%)	Yield of 1 (%)
a	H	H	H	H	H	0	**a**	72	89	90
a	H	H	H	H	H	1	**b**	82	86	89
b	H	H	OMe	H	H	1	**c**	74	89	92
c	H	OMe	OMe	H	H	1	**d**	80	89	93
7'd	OMe	H	OMe	H	H	0	**e**	91[b]	88	86
7'd	OMe	H	OMe	H	H	1	**f**	90[b]	91	92
e	OMe	H	H	OMe	H	0	**g**	79	90	91
e	OMe	H	H	OMe	H	1	**h**	85	90	83
e	OMe	H	H	OMe	H	2	**i**	74	85	85
f	H	OMe	OMe	OMe	H	0	**j**	86	92	87
f	H	OMe	OMe	OMe	H	1	**k**	82	89	94
f	H	OMe	OMe	OMe	Me	1	**kk**	–	89[b]	91
g	OMe	OMe	OMe	H	H	0	**l**	83	89	89

g	OMe	OMe	OMe	H	H	1	**m**	85	88	86
g	OMe	OMe	OMe	H	H	2	**n**	86	90	92
g	OMe	OMe	OMe	H	Ph	1	**mm**	–	80[c]	87
h	*i*-Pr	OMe	OMe	H	H	1	**o**	86	90	89
7'i	3-thienyl			H	H	1	**p**	80	94	91

[a] *n*-Bu_4NF (TBAF) added in reaction mixture. [b] Use of MeLi in pace of DIBAL-H. [c] Use of PhMgBr in place of DIBAL-H.

Experiments on the Lewis acid mediated cyclization reactions were conducted in CH_2Cl_2 (0.007 M) at 0 °C, with BF_3-OEt_2 (3 equiv). The substrates with simple phenyl substituents (**1a,b**) on the alkynedicobalt unit failed to give any cyclization products (**2**); **1a** underwent complete decomposition, and the use of $TiCl_4$ or $SnCl_4$ did not give any improvement. In the case of **1b**, $TiCl_4$ and $SnCl_4$ did give the elimination product **11b**, with $SnCl_4$ giving **11b** in 52% yield (Equation 1, Figure 1, Table 2). These results were not entirely surprising, as the Mayr electrophilicity (propargyldicobalt cation) and nucleophilicity (benzene) values suggest a too slow reaction of unactivated arenes with propargyldicobalt cations.[26] In the presence of more electron rich aryls, the cyclizations were much more successful. 3-Methoxy- substituted **1c** gave **2c** in 82% yield as 4.9:1 separable mixture of isomers (**2c**, **2c'**) stemming from reaction at C-6 and C-2 respectively; this isomer ratio improved noticeably with minimal loss in yield when cooling the reaction successively to -40 °C and -78 °C. Similarly, 3,4-dimethoxy- substituted **1d** gave **2d** and **2d'** as a separable regioisomeric mixture (90% yield, **2d:2d'** = 8.8:1). Amongst the other dimethoxyaryl- substituted substrates, the 3,5-dimethoxyphenyl- substituted cases afforded excellent yields of cyclization products for both cyclopentene- and cyclohexene- containing cases (**2e**, 85%**; 2f**, 85%), while the less electron rich 2,5-dimethoxyphenyl- substituted cases worked poorly with BF_3-OEt_2, $SnCl_4$, or $TiCl_4$ in the cyclopentene- containing case (**2g**, 6% with BF_3-OEt_2) but very well in the cyclohexene- and cycloheptene- substituted cases (**2h** 82%; **2i**, 85%). The trimethoxyphenyl- substituted substrates showed an analogous trend. The less electron rich 2,3,4-trimethylphenyl- cases gave very poor yields in the cyclopentene- cases (**2j**, 8%), and better but still modest yields for the cyclohexene- spacer (**2k**, 39%; **2kk**, 39%); these substrates required $SnCl_4$ rather than BF_3-OEt_2 as Lewis acid to give any products whatsoever. Conversely, the more electron rich 3,4,5-trimethoxyphenyl- substituted cases cyclized readily and in good yields regardless of the ring size in which the alkene spacer was present (**2l** 85%; **2m**, 86%; **2n**, 84%). Substitution of the reactive site was somewhat detrimental here, however, as allylic benzylic acetate **1mm** gave only 34% of, along with elimination product **11mm** (40%).

However, switching the Lewis acid to $SnCl_4$, under otherwise identical conditions gave **2mm** as the sole tractable product in 79% yield. Isopropyldimethoxy- substituted **1o** underwent cyclization quite smoothly to give a 79% yield of a mixture of isomers, with the site p- to the methoxy function reacting preferentially to that p- to the isopropyl (**2o**:**2o'** = 14:1). Finally, 3-thienyl substituted **1p** gave excellent yields of **2p** (90%), with cyclization occurring solely through C-2 of the thiophene unit.



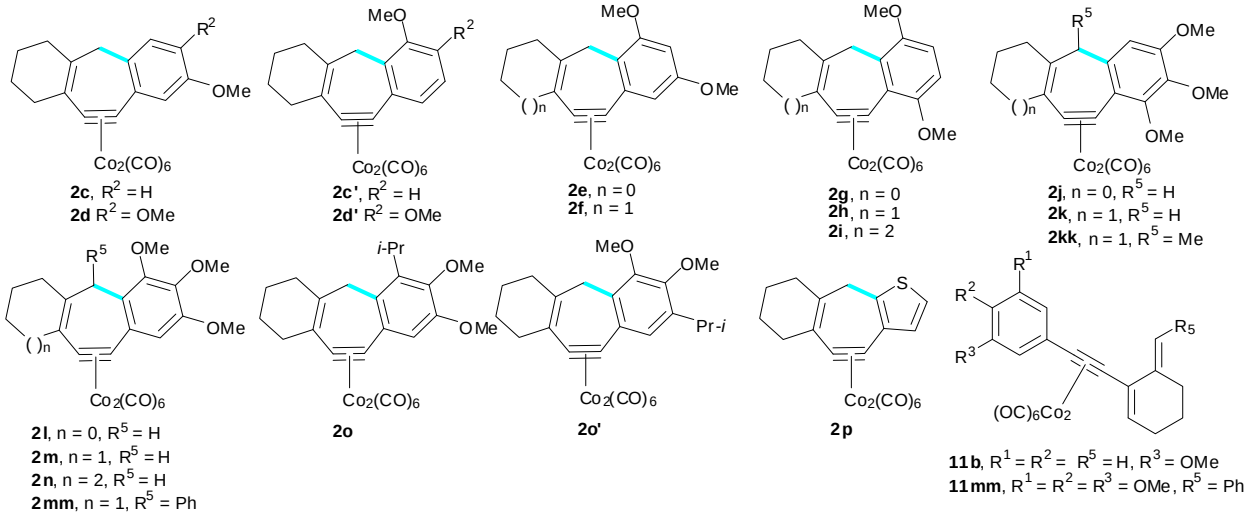
(1)

Table 2. Intramolecular vinylogous Nicholas reactions of **1**

Starting material	Time (h)	Product	Yield (%)
1b	2	**11b**	52[a]
1c	1.5	**2c** **2c'**	68 14
1c	2[b]	**2c** **2c'**	69 10
1c	3[c]	**2c** **2c'**	72 9
1d		**2** **2d'**	81 9
1e	0.75	**2e**	85
1f	0.75	**2f**	85
1g	2	**2g**	6
1h	1	**2h**	82
1i	1	**2i**	85
1j	1	**2j**	8[a]
1k	1	**2k**	39[a]
1kk		**2kk**	39[a]
1l	0.5	**2l**	85
1m	0.5	**2m**	86
1mm	1	**2mm**	79[a]
1n	0.5	**2n**	84
1o		**2o** **2o'**	74 5
1p	0.67	**2p**	90

[a] $SnCl_4$ as Lewis acid. [b] at -40 °C. [c] at -78 °C, 2.15 h; warmed to 0 °C

Figure 1. Tricyclic 6,7,x- benzocycloheptenyne complexes prepared via Equation 1

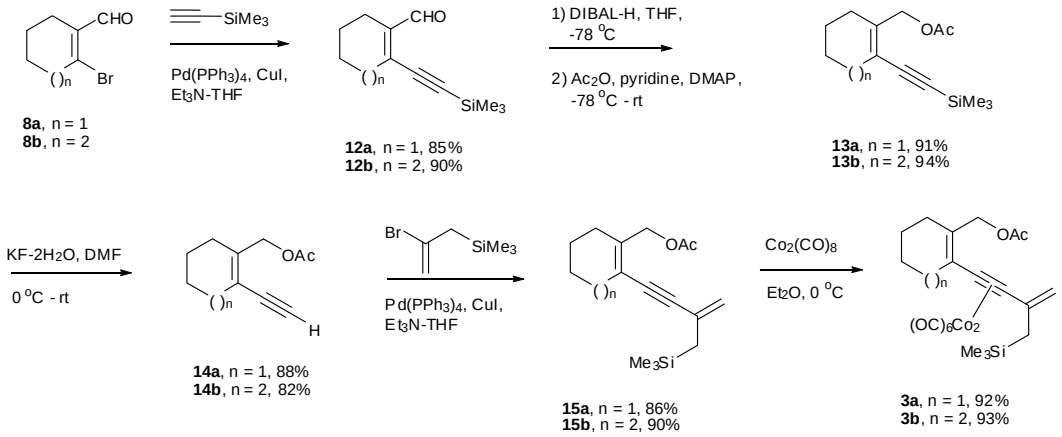


Some trends become apparent among the above results. The intramolecular Nicholas reactions can succeed with each of 5-, 6- and 7- membered cycloalkene spacers separating the allylic acetate and alkynedicobalt function, but the yields of cyclopentene- containing products become compromised more readily as the arene nucleophiles become less electron rich. This is likely due to greater angle strain caused by the five membered ring on the incipient cycloheptyne complexes relative to the six- and seven- membered homologues.

Secondly, the results with the allylic phenyl- substituted **1mm** were of additional interest. Reactions conducted with BF_3-OEt_2 at lower temperature (-50 - -60 ^oC) revealed greater amounts of elimination product **11mm** relative to **2mm**. This suggests that **11mm** is actually the dominant initial product of reaction of **1mm** in all cases, but in the presence of liberated acid during the reaction it may be in equilibrium with the allyl propargyl cation complex, which can in turn ultimately funnel towards **2mm**. The stronger acid generated in the $SnCl_4$ mediated cases then allows this latter process to go to completion. The use of enyne-$Co_2(CO)_6$ complexes as propargyldicobalt cation precursors is well established, particularly by Smit and Caple.[27]

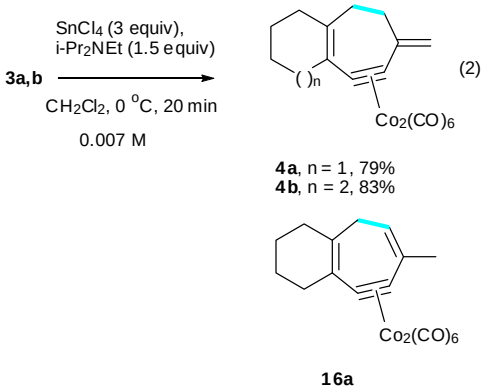
We wished to demonstrate the ability of allylsilanes to participate in this type of intramolecular vinylogous Nicholas reactions chemistry (**3** → **4**, Scheme 1), and as a result targeted complexes **3a** and **3b** as potential substrates (Scheme 3). These cyclization precursors could be prepared from bromocycloalkene carbaldehydes **8a,b**. The Sonogashira reactions of **8** with trimethylsilylacetylene afforded 2-alkynylcyclohexenecarbaldehyde **12a** (85% yield) and 2-alkynylcycloheptenecarbaldehyde **12b** (90% yield) readily. Attempts to desilylate **12a,b** at this point gave materials which decomposed rapidly after isolation, and consequently the aldehyde

functions of **12** were reduced with DIBAL-H and the products immediately acetylated, to give allylic alcohols **13a** (91% yield) and **13b** (94%). Desilylation of these intermediates with KF-$2H_2O$ then gave terminal alkynes **14a** (88% yield) and **14b** (82% yield), which were subjected to Sonogashira coupling with 2-bromoallyltrimethylsilane, affording **15a** (86% yield) and **15b** (90% yield) in excellent yields. Complexation of alkyne functions of **15** then gave **3a** (92% yield) and **3b** (93% yield).



Scheme 3. Preparation of allylsilane substituted allylic acetate alkyne-$Co_2(CO)_6$ complexes.

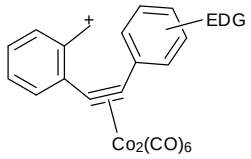
The attempts at Lewis acid mediated cyclizations were less straightforward than the best cases of the **1** → **2** transformation. The use of BF_3-OEt_2 in cyclization of **3a** gave **4a** contaminated with double bond isomer **16a** (Equation 2). The use of $TiCl_4$ and $SnCl_4$ gave successively smaller amounts of impurity **16a**, and the use of $SnCl_4$ (3 equiv) in the presence of *i*-Pr_2NEt (1.5 equiv) afforded **4a** (79% yield) devoid of any **16a** impurity. Employing analogous reaction conditions on **3b** resulted in the formation of **4b** (83%) as the sole isolable product.



(2)

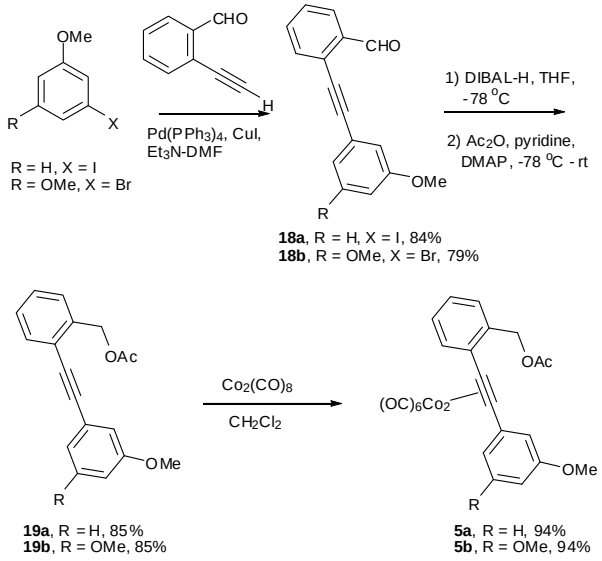
As an extension to the ability of vinylogous propargyldicobalt cations to undergo intramolecular Nicholas reaction chemistry, a more stringent test would be to determine whether

the analogous benzylic cations, i.e., **17**, could lead to dibenzocycloheptynedicobalt complexes (**5** → **6**, Scheme 1). While it is highly unlikely that such cations would have the same stability as simple propargyldicobalt cations, alkynedicobalt complexes are known as activating groups in electrophilic aromatic substitution,[28] and benzylic cation generation under reasonably mild conditions has become a subject of recent interest.[29]



17

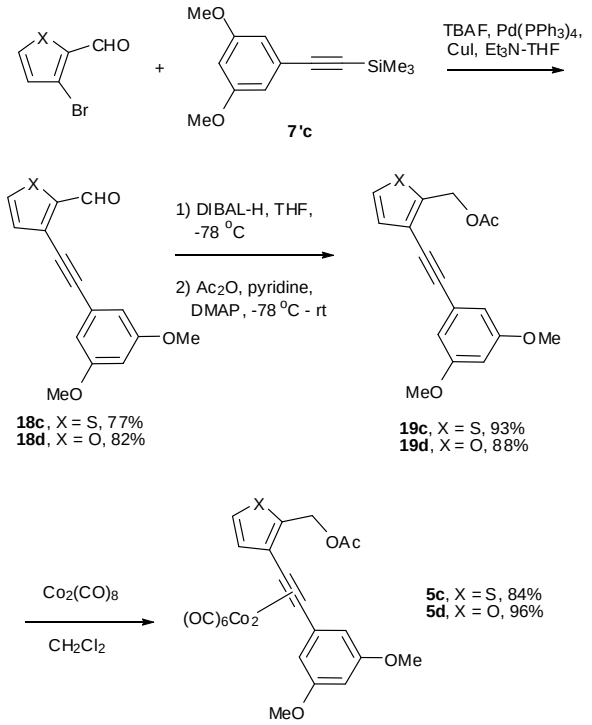
For investigation of this possibility, a number of ortho- arylalkynylbenzyl acetates **5a-d** were targeted. Beginning with 2-ethynylbenzaldehyde (Scheme 4), Sonogashira reaction with 3-iodoanisole then afforded **18a** (84% yield), while the use of 1-bromo-3,5-dimethoxybenzene gave **18b** (79% yield). Reduction with DIBAL-H followed by acetylation produced **19a** (85% yield) and **19b** (85% yield) from **18a** and **18b**, respectively. Finally, complexation of **19a** and **19b** with $Co_2(CO)_8$ resulted the production of **5a** (94% yield) and **5b** (94% yield), respectively.



Scheme 4. Preparation of benzylic acetates complexes.

Substrates with thiophene and furan spacers between the potential acetate leaving group and the alkynedicobalt complex were prepared in a similar manner, starting with 3-bromothiophene-2-carbaldehyde or 3-bromofurancarbaldehyde. Desilylative Sonogashira reactions with **7'd** gave **18c** (77% yield) and **18d** (82% yield) (Scheme 5). DIBAL-H reduction and acetylation afforded benzylic acetates **19c** (93% yield) and **19d** (88% yield), and

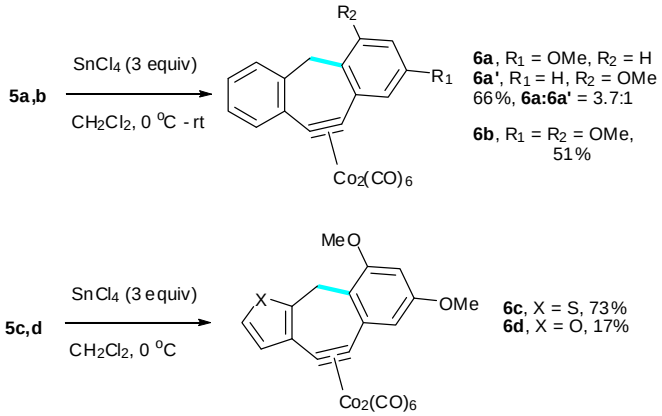
complexation of these alkynes with $Co_2(CO)_8$ gave **5c** (84% yield) and **5d** (96% yield), respectively.



Scheme 5. Preparation of heterocyclic benzylic acetate complexes.

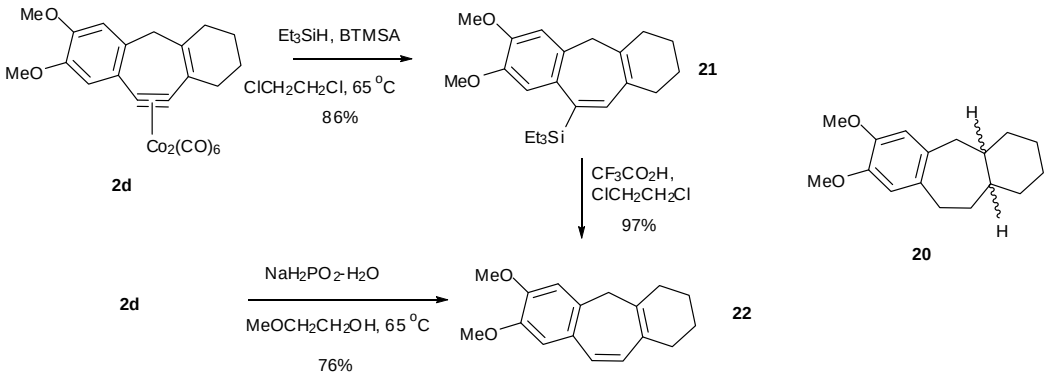
Initial attempts at the Lewis acid mediated cyclization of **5a** were unsuccessful. The use of BF_3-OEt_2 (3 equiv, CH_2Cl_2) gave complete decomposition of the substrate, and the additional presence of *i*-Pr_2NEt, the use of a Bronsted acid (H_2SO_4) in place of BF_3-OEt_2, or the employment of 1,1,1,3,3,3-hexafluoroisopropanol as solvent did not improve the results. Conversely, the use of $SnCl_4$ as Lewis acid (3 equiv, CH_2Cl_2, 0 °C – rt) induced the conversion of **5a** into **6a** (66% yield), as a mixture of regioisomers resulting from reactions para- (**6a**) and ortho- (**6a'**) to the methoxy group (**6a**:**6a'** = 3.7:1) (Scheme 6). Under these conditions, **5b** also transformed into **6b**, in moderate yield (51%).

The thienyl- and furyl- analogues **5c,d** were also subjected to these reaction conditions, and underwent starting material consumption somewhat more rapidly. Thienyl substrate **5c** gave tricyclic complex **6c** in good yield (73%), but even under these condition the furyl substrate **5d** gave significant amounts of decomposition; nevertheless, a small amount of tricycle **6d** (17% yield) could be isolated.



Scheme 6. Intramolecular vinylogous Nicholas reactions of benzylic acetate complexes (**5**).

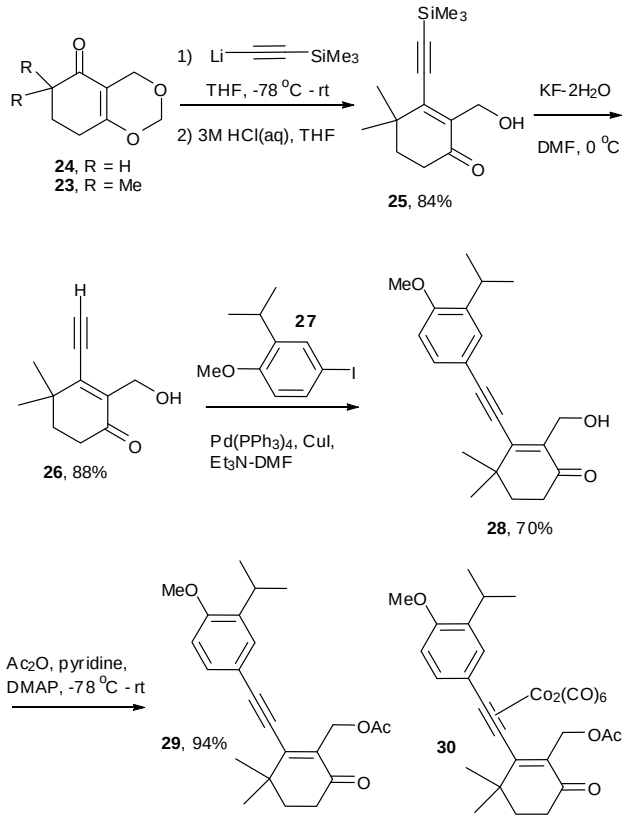
Studies on reductive removal of the $Co_2(CO)_6$ unit focused on **2d** (Scheme 7). The use of our hydrosilylation-protodesilylation modification[3c,d] of the Isobe hydrosilylation protocol[30] was investigated first. Addition of Et_3SiH/bis(trimethylsilylacetylene) (BTMSA) at 65 °C, followed by CF_3CO_2H at room temperature gave successful removal of the hexacarbonyldicobalt group, but resulted in overreduction of any initial alkene products and isolation of **20** (81% yield) as a ca. 1:1 diastereomeric mixture. Separation of the process in the two discrete steps was more successful, as the Et_3SiH/BTMSA/1,2-dichloroethane protocol gave vinylsilane **21** in 86% yield, as a (94:6) mixture of vinylsilane regioisomers (major shown); subjecting this compound mixture to CF_3CO_2H then afforded diene **22** in 97% yield. Alternatively, the use of NaH_2PO_2-H_2O/2-methoxyethanol[31] also gave **22** from **2d** in a one pot procedure (76% yield).



Scheme 7. Reductive decomplexation of **2d**.

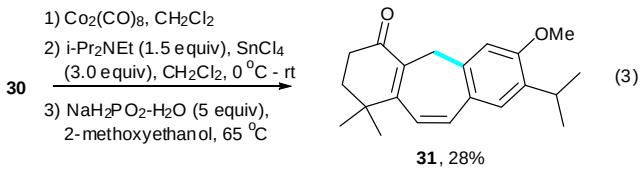
Application of this vinylogous Nicholas reaction chemistry to the synthesis of the icetexane framework of pisferin essentially originated with *gem*-dimethyltetrahydrobenzodioxinone **23**, itself prepared by dimethylation of **24**.[32] Addition of (trimethylsilyl)ethynyllithium to **23**, followed by acidic workup, afforded enynone **25** in 84%

yield (Scheme 8). Straightforward desilylation (**26**, 88% yield), followed by Sonogashira reaction with iodoisopropylanisole **27**, gave **28** (70% yield). Alcohol acetylation of **28** gave **29** (94% yield).



Scheme 8. Preparation of icetexane ring systems precursors.

Attempted $Co_2(CO)_8$ based complexation of **29** presumably resulted in the formation of **30**, but this material possessed very limited stability and decomposed by the concentration phase of a typical workup. Attempts at cyclization reactions with either BF_3-OEt_2, $SnCl_4$ or Bu_2BOTf without isolation and purification of **30** gave in turn material with a limited lifetime. As a result, we chose to adapt the one pot complexation-Nicholas reaction-decomplexation tactic employed by the Tyrrell group[33] to our needs. Reaction of a slight excess of $Co_2(CO)_8$ in CH_2Cl_2 with **29** for 3h was followed by addition of *i*-Pr_2NEt (1.5 equiv) and $SnCl_4$ (3 equiv) at 0 °C - rt. When monitoring by TLC indicated that the presumed **30** had been consumed (15 h), workup and filtration through a short plug of silica gel, with subsequent reductive decomplexation using NaH_2PO_2-H_2O in 2-methoxyethanol, gave icetexane framework structure **31** in a modest yield (28%) (Equation 3).



Conclusion

In conclusion, we have demonstrated the utility of vinylogous Nicholas reaction chemistry in the preparation of cycloheptynedicobalt complexes. Arene nucleophiles work well given sufficient electron richness, affording tricyclic 6,7,x- systems (x = 5,6,7), and allylsilanes also serve as acceptable nucleophiles to give bicyclic cycloheptynes. In some cases, aromatic spacers may be used in place of alkene spacers, although the yields are variable. Finally, the icetexane ring system may be constructed by the chemistry by way of a one pot complexation-Nicholas reaction-reductive decomplexation protocol, although the steric hindrance imposed by the *gem*-dimethyl groups appears to limit the yields in this construction.

Experimental Section

General Methods: All reaction solvents were used after passage through a solvent purification system. Commercial BF_3-OEt_2 was distilled and stored under nitrogen. All reactions were conducted under a nitrogen atmosphere unless otherwise noted. Flash chromatography was performed as described by Still using silica gel 60 (230-400 mesh).[34] All new compounds are >95% purity as determined by ^{1}H and ^{13}C NMR spectroscopy. NMR spectra were run on Bruker Avance 500 or 300 spectrometers at 500 MHz or 300 MHz for ^{1}H and 125 MHz or 75 MHz for ^{13}C in $CDCl_3$ unless otherwise stated; chemical shifts are given in ppm and coupling constants (*J*) are given in Hz. High resolution mass spectra were run on a Waters/Micromass GCT (time of flight) mass spectrometer, in EI mode, at 70 eV.

2-(Phenylethynyl)cyclopent-1-enecarbaldehyde (9a)

General Procedure A: To a mixture of $Pd(PPh_3)_4$ (0.1699 g, 0.147 mmol, 3 mol%) and CuI (0.0467 g, 0.245 mmol, 5 mol%) was added a solution of 2-bromocyclopent-1-ene-1-carbaldehyde (**8a**)[35] (1.2860 g, 7.3496 mmol) in DMF (5 mL), followed by a solution of phenylacetylene (**7a**) (0.5000 g, 4.900 mmol) in DMF (5 mL). Triethylamine (32 mL) was added, and the reaction mixture stirred at 75 °C for 20 h. The mixture was filtered through Celite® and subjected to a conventional extractive workup (Et_2O). Compound **9a** was isolated by preparative TLC (25:1 hexanes:Et_2O) as a yellow oil (0.6907 g, 3.522 mmol, 72%). ^{1}H-NMR (500 MHz, $CDCl_3$): 10.16 (s, 1H), 7.49 (apparent dd, 2H, J = 7.6, J = 1.8), 7.33-7.38 (m, 3H),

2.79 (t, 2H, J = 7.9), 2.64 (t, 2H, J = 7.9), 1.98 (apparent pentet, 2H, J = 7.9); ^{13}C-NMR (75 MHz, $CDCl_3$): 188.9, 148.1, 143.2, 132.0, 129.5, 128.7, 122.2, 100.8, 83.4, 39.1, 29.8, 22.3; IR (KBr): 3312, 3081, 2969, 2850, 2811, 2722, 2199, 1676, 1353; HRMS: m/e for $C_{14}H_{12}O$ calculated 196.0888 (M^+), found 196.0883.

2-[(3-Methoxyphenyl)ethynyl]cyclohex-1-enecarbaldehyde (9c)

Compound **9c** was synthesized according to General Procedure A from **7b**[36] (0.4596 g, 3.480 mmol) and 2-bromocyclohex-1-ene-1-carbaldehyde **8b** (0.9918 g, 5.220 mmol). The product was isolated as a yellow oil (0.6204 g, 2.584 mmol, 74%) via preparative TLC (20:1 hexanes:Et_2O). ^{1}H-NMR (500 MHz, $CDCl_3$): 10.32 (s, 1H), 7.26 (apparent t, 1H, J = 8.0), 7.07 (d of t, 1H, J = 7.6, J = 1.2), 6.99 (dd, 1H, J = 2.5, J = 1.4), 6.93 (ddd, 1H, J = 8.3, J = 2.6, J = 0.9), 3.82 (s, 3H), 2.50-2.53 (m, 2H), 2.30-2.33 (m, 2H), 1.66-1.75 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): 193.0, 159.5, 142.8, 140.0, 129.7, 124.3, 123.4, 116.4, 115.9, 98.6, 86.2, 55.4, 32.4, 22.2, 22.0, 21.2; IR (KBr): 2937, 2835, 2194, 1673, 1212; HRMS: m/e for $C_{16}H_{16}O_2$ calculated 240.1150 (M^+), found 240.1158.

2-[(3,5-Dimethoxyphenyl)ethynyl]cyclopent-1-enecarbaldehyde (9e)

General Procedure B. To a mixture of $Pd(PPh_3)_4$ (0.1552 g, 0.1344 mmol, 3 mol%) and CuI (0.0427 g, 0.224 mmol, 5 mol%) was added 2-bromocyclopent-1-ene-1-carbaldehyde (**8a**) (1.1764 g, 6.7213 mmol) in THF (7.5 mL), followed by compound **7'd**[37] (1.0490 g, 4.4808 mmol) in THF (7.5 mL). After triethylamine (30 mL) was added, the mixture was cooled to 0 ^{o}C and tetra-n-butylammonium fluoride (TBAF) (1.0 M in THF, 9.0 mL, 9.0 mmol) was added. After stirring for 10 min, the mixture was warmed to 75 ^{o}C for 20 h. The reaction was filtered through Celite® and subjected to a conventional extractive workup (Et_2O). The product **9e** was isolated as a pale yellow solid (1.0474 g, 4.0896 mmol, 91%) following flash chromatography (10:1 hexanes:Et_2O). mp. 120-122 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$): 10.16 (s, 1H), 6.64 (d, 2H, J = 2.3), 6.50 (apparent t, 1H, J = 2.3), 3.79 (s, 6H), 2.80 (t, 2H, J = 7.6), 2.65 (t, 2H, J = 7.6), 2.00 (apparent pentet, 2H, J = 7.6); ^{13}C-NMR (75 MHz, $CDCl_3$): 188.9, 160.7, 148.2, 143.0, 123.3, 109.6, 102.9, 100.9, 82.8, 55.5, 38.9, 29.7, 22.2; IR (KBr): 3080, 2995, 2936, 2838, 2190, 1669, 1587, 1156; HRMS: m/e for $C_{16}H_{16}O_3$ calculated 256.1099 (M^+), found 256.1096.

[2-(Phenylethynyl)cyclopent-1-enyl]methyl acetate (10a)

General Procedure C. To a -78 ^{o}C solution of compound **9a** (0.5077 g, 2.589 mmol) in THF (30 mL) was added DIBAL-H (1.0 M in THF, 5.2 mL, 5.2 mmol) in a dropwise fashion. After 1

h at -78 ^{o}C, pyridine (6.2 mL, 78 mmol) was added, followed by acetic anhydride (12.2 mL, 130 mmol) and DMAP (1.577 g, 12.9 mmol). The reaction was allowed to warm to room temperature for 20 h. NH_4Cl (aq, sat) was added and the mixture subjected to a conventional extractive workup (Et_2O). Product **10a** was isolated by preparative TLC (15:1 hexanes:Et_2O) as a yellow oil (0.5531 g, 2.303 mmol, 89%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45 (apparent dd, 2H, J = 6.5, J = 3.1), 7.31-7.33 (m, 3H), 4.89 (s, 2H), 2.63 (t, 2H, J = 7.7), 2.52 (t, 2H, J = 7.9), 2.10 (s, 3H), 1.97 (apparent pentet, 2H, J = 7.7); ^{13}C-NMR (75 MHz, $CDCl_3$): 171.2, 144.8, 131.6, 128.4, 128.3, 123.4, 123.1, 95.0, 84.7, 62.1, 37.1, 34.2, 22.5, 21.0; IR (KBr): 2960, 2852, 1743, 1225; HRMS: m/e for $C_{16}H_{16}O_2$ calculated 240.1150 (M^+), found 240.1145.

[2-((3-Methoxyphenyl)ethynyl)cyclohex-1-enyl]methyl acetate (10c)

Compound **9c** (0.6204 g, 2.584 mmol) was subjected to General Procedure C. The product **10c** was isolated as a pale yellow oil (0.6542 g, 2.302 mmol, 89%) via preparative TLC (10:1 hexanes:Et_2O). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.22 (apparent t, 1H, J = 8.0), 7.03 (d of t, 1H, J = 7.6, J = 1.0), 6.96 (dd, 1H, J = 2.4, J = 1.4), 6.86 (ddd, 1H, J = 8.4, J = 2.6, J = 0.7), 4.90 (s, 2H), 3.81 (s, 3H), 2.31 (m, 2H), 2.17 (m, 2H), 2.10 (s, 3H), 1.65-1.71 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): 171.3, 159.4, 139.3, 129.4, 124.5, 124.1, 120.0, 116.2, 114.9, 93.1, 88.0, 66.6, 55.4, 30.3, 27.2, 22.2, 22.1, 21.1; IR (KBr): 3002, 2935, 2861, 2198, 1738, 1596, 1230; HRMS: m/e for $C_{18}H_{20}O_3$ calculated 284.1412 (M^+), found 284.1415.

Hexacarbonyl[μ-η^4(2-(Phenylethynyl)cyclopent-1-enyl]methyl acetate)]dicobalt (1a)

General Procedure D. Compound **10a** (0.5067 g, 2.110 mmol) and dicobalt octacarbonyl (excess) were dissolved in dry CH_2Cl_2 (25 mL). The mixture was allowed to stir at room temperature, for 2 h. The solvent was then removed under reduced pressure, and the solid loaded onto a column of silica. The column was washed with 100% hexanes to remove excess, uncomplexed dicobalt octacarbonyl. Subsequently, elution with 15:1 hexanes:Et_2O afforded product **1a**, which was isolated as a dark brown solid (1.002 g, 1.9051 mmol, 90%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.44-7.47 (m, 2H), 7.30-7.37 (m, 3H), 4.63 (s, 2H), 2.79 (t, 2H, J = 7.8), 2.56 (t, 2H, J = 7.9), 2.03 (apparent pentet, 2H, J = 7.9), 2.00 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 199.4, 170.8, 138.5, 137.6, 137.2, 129.3, 128.9, 127.9, 93.1, 84.7, 61.2, 39.9, 36.3, 21.9, 20.9; IR (KBr): 3077, 2957, 2848, 2089, 2050, 2021, 1745, 1231; HRMS: m/e for $C_{22}H_{16}Co_2O_8$ calculated 497.9560 (M-CO$^+$), found 497.9552.

Hexacarbonyl[μ-η^4(2-((3-methoxyphenyl)ethynyl)cyclohex-1-enyl]methyl acetate)]dicobalt (1c)

Compound **10c** (0.6542 g, 2.302 mmol) was subjected to complexation as outlined in General Procedure D. The complexed product **1c** was isolated as a dark brown solid (1.2123 g, 2.1269 mmol, 92%) by flash chromatography (10:1 hexanes:Et_2O), after washing through excess, uncomplexed $Co_2(CO)_8$ with 100% hexanes. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.26 (t, 1H, J = 7.9), 7.01 (apparent ddd, 1H, J = 7.6, J = 1.6, J = 0.9), 6.95 (dd, 1H, J = 2.4, J = 1.7), 6.85 (ddd, 1H, J = 8.3, J = 2.6, J = 0.9), 4.55 (s, 2H), 3.83 (s, 3H), 2.38 (t, 2H, J = 6.0), 2.13 (t, 2H, J = 6.1), 1.97 (s, 3H), 1.72-1.79 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): 199.6, 170.9, 159.6, 140.2, 133.5, 132.0, 129.8, 122.0, 115.2, 113.0, 93.5, 91.7, 65.3, 55.3, 33.3, 28.5, 23.4, 22.2, 20.8; IR (KBr): 2088, 2049, 2019, 1742, 1230; HRMS: m/e for $C_{24}H_{20}Co_2O_9$ calculated 430.0026 (M-5CO$^+$), found 430.0021.

Hexacarbonyl[μ-η^4([2-((3,5-dimethoxyphenyl)ethynyl)cyclopent-1-enylmethyl acetate)]dicobalt (1e)

Compound **10e** (1.0852 g, 3.6157 mmol) was subjected to complexation according to General Procedure D. The complexed compound **1e** was isolated via flash chromatography (5:1 hexanes:Et_2O) following removal of excess, uncomplexed $Co_2(CO)_8$ with 100% hexanes. The product was isolated as a dark brown solid (1.8212 g, 3.1080 mmol, 86%). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.62 (d, 2H, J = 2.2), 6.42 (t, 1H, J = 2.1), 4.67 (s, 2H), 3.81 (s, 6H), 2.79 (t, 2H, J = 7.8), 2.55 (t, 2H, J = 7.9), 2.02 (apparent pentet, 2H, J = 7.9), 2.02 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 199.9, 170.8, 160.8, 140.5, 137.7, 137.1, 107.6, 99.9, 93.1, 84.6, 61.1, 55.4, 39.8, 36.3, 21.9, 20.7; IR (Pt/diamond ATR): 3020, 2977, 2838, 2087, 2046, 2005, 1989, 1734, 1586, 1205; HRMS: m/e for $C_{24}H_{20}Co_2O_{10}$ calculated 473.9925 (M-4CO$^+$), found 473.9930.

Hexacarbonyl[μ-η^4-((10,11-η:10,11-η)-2,3,4,5-tetrahydro-8-methoxy-1*H*-dibenzo[*a,d*]cycloheptene)]dicobalt (2c) and Hexacarbonyl[μ-η^4-((10,11-η:10,11-η)-2,3,4,5-tetrahydro-6-methoxy-1*H*-dibenzo[*a,d*]cycloheptene)]dicobalt (2c')

General Procedure E. To a solution of complexed compound **1c** (0.0322 g, 0.0565 mmol) in CH_2Cl_2 (8 mL, 7 x 10^{-3} M) at 0 ^{o}C was added BF_3-OEt_2 (21 μL, 0.17 mmol). After 1.5 h, starting material consumption was complete and the reaction was subjected to a conventional extractive workup (CH_2Cl_2). The product regioisomers were separable by flash chromatography using 100% hexanes. The major product **2c** (0.0195 g, 0.0382 mmol, 68%) eluted as the second band,

and as a dark maroon solid. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.20 (d, 1H, J = 2.7), 7.04 (d, 1H, J = 8.3), 6.84 (dd, 1H, J = 8.4, J = 2.7), 3.58 (s, 3H), 3.20 (s, 2H), 2.36 (t, 2H, J = 5.8), 2.28 (t, 2H, J = 6.0), 1.67-1.78 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): 200.0, 159.0, 139.0, 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; IR (KBr): 2930, 2086, 2046, 2017, 1270; HRMS: m/e for $C_{22}H_{16}Co_2O_7$ calculated 481.9625 (M-CO$^+$), found 481.9634.

Compound **2c'** eluted as the first band, as a dark maroon solid, and as the minor product (0.0040 g, 0.0078 mmol, 14%). The product ratio of major:minor **2c**:**2c'** (i.e., para attack:ortho attack) was 4.9:1, with a combined yield of 82%. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.28 (dd, 1H, J = 7.9, J = 1.2), 7.23 (apparent t, 1H, J = 7.8), 6.90 (dd, 1H, J = 8.0, J = 1.1), 3.87 (s, 3H), 3.33 (s, 2H), 2.31-2.35 (m, 4H), 1.67-1.77 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): 200.2, 155.9, 139.6, 137.7, 130.9, 127.6, 125.4, 124.8, 110.7, 95.2, 90.0, 56.0, 33.8, 32.3, 30.5, 23.1, 22.8; IR (KBr): 2933, 2086, 2046, 2017, 1570, 1262; HRMS: m/e for $C_{22}H_{16}Co_2O_7$ calculated 481.9611 (M-CO$^+$), found 481.9624.

Hexacarbonyl[μ-η^4-(9,10-didehydro-5,7-dimethoxy-1,2,3,4-tetrahydrobenzo[f]azulene)]dicobalt (2e)

Compound **1e** (0.1874 g, 0.3198 mmol) was reacted according to General Procedure E using BF_3-OEt_2 (121 μL, 0.959 mmol). The reaction was complete within 45 minutes, as assessed by TLC analysis. The cyclized product (**2e**) was isolated by flash chromatography (15:1 hexanes:Et_2O) as a maroon solid (0.1433 g, 0.2724 mmol, 85%). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.82 (d, 1H, J = 2.2), 6.48 (d, 1H, J = 2.4), 3.85 (s, 3H), 3.83 (s, 3H), 3.50 (s, 2H), 2.71 (t, 2H, J = 7.6), 2.54 (t, 2H, J = 7.7), 2.05 (apparent pentet, 2H, J = 7.6); ^{13}C-NMR (75 MHz, $CDCl_3$): 199.8, 159.3, 157.3, 142.4, 139.6, 134.6, 116.3, 109.3, 99.0, 91.0, 87.8, 55.9, 55.4, 39.4, 35.4, 27.1, 22.6; IR (KBr): 3004, 2956, 2838, 2087, 2047, 2016, 1600, 1458, 1141; HRMS: m/e for $C_{22}H_{16}Co_2O_8$ calculated 525.9509 (M$^+$), found 525.9510.

Hexacarbonyl[μ–η^4-(10,11-didehydro-2,3,4,5-tetrahydro-7-methoxy-1*H*-dibenzo[*a,d*]cycloheptene)]dicobalt (2f)

Compound **1f** (see Supporting Information) (0.0783 g, 0.130 mmol) was reacted according to General Procedure E using BF_3-OEt_2 (50 μL, 0.39 mmol). The reaction was complete within 45 minutes, as assessed by TLC analysis. The cyclized product (**2f**) was isolated by flash chromatography (15:1 hexanes:Et_2O) as a maroon solid (0.0601 g, 0.111 mmol, 85%). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.80 (d, 1H, J = 2.2), 6.49 (d, 1H, J = 2.1), 3.84 (s, 3H), 3.83 (s, 3H), 3.25 (s,

2H), 2.30-2.34 (m, 4H), 1.66-1.78 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 200.0, 159.2, 156.7, 140.1, 138.2, 130.5, 118.2, 108.0, 98.8, 95.2, 90.4, 55.9, 55.4, 33.7, 31.8, 30.4, 23.0, 22.8; IR (KBr): 3020, 2086, 2046, 2015, 1600, 1279; HRMS: m/e for $C_{23}H_{18}Co_2O_8$ calculated 539.9666 (M^+), found 539.9669.

Hexacarbonyl[μ-η^4-((10,11-η:10,11-η)-10,11-didehydro-2,3,4,5-tetrahydro-6,9-dimethoxy-1*H*-dibenzo[*a,d*]cycloheptene)] dicobalt (2h)

Compound **1h** (see Supporting Information) (0.3248 g, 0.5413 mmol) was reacted according to General Procedure E using BF_3-OEt_2 (206 μL, 1.62 mmol). The reaction was complete after 1 h, as assessed by TLC analysis. The cyclized product (**2h**) was isolated by flash chromatography (15:1 hexanes:Et_2O) as a maroon solid (0.2405 g, 0.4454 mmol, 82%). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.92 (d, 1H, J = 9.0), 6.74 (d, 1H, J = 9.0), 3.87 (s, 3H), 3.82 (s, 3H), 3.34 (s, 2H), 2.30-2.36 (m, 4H), 1.73-1.78 (m, 2H), 1.66-1.71 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): 200.4, 154.0, 150.3, 136.3, 131.5, 127.4, 126.6, 112.2, 108.7, 96.0, 84.8, 56.7, 54.7, 33.6, 32.8, 30.5, 23.1, 22.9; IR (KBr): 2924, 2850, 2085, 2046, 2026, 1739, 1463, 1261; HRMS: m/e for $C_{23}H_{18}Co_2O_8$ calculated 539.9666 (M^+), found 539.9669.

[2-((Trimethylsilyl)ethynyl)cyclohex-1-enyl]methyl acetate (13a)

Compound **12a**[38] (1.4485 g, 7.0277 mmol) was subjected to General Procedure C. The product was isolated as a pale yellow oil (1.6033 g, 6.4096 mmol, 91%) via flash chromatography (10:1 hexanes:Et_2O). ^{1}H-NMR (500 MHz, C_6D_6): 4.94 (s, 2H), 2.08 (t, 2H, J = 6.1), 1.91 (t, 2H, J = 6.1), 1.66 (s, 3H), 1.26-1.33 (m, 4H), -0.15 (s, 9H); ^{13}C-NMR (75 MHz, C_6D_6): 169.6, 140.5, 119.7, 104.5, 97.7, 66.0, 29.9, 26.7, 21.9, 21.8, 20.1, -0.2; IR (ATR): 2933, 2861, 2140, 1741, 1366, 1227; HRMS: m/e for $C_{14}H_{22}O_2Si$ calculated 250.1389 (M^+), found 250.1386.

(2-Ethynylcyclohex-1-enyl)methyl acetate (14a)

General Procedure F. To a 0 ^{o}C solution of compound **13a** (1.6033 g, 6.4096 mmol) in DMF (5 mL) was added KF-2H_2O (0.7843 g, 8.332 mmol, 1.3 equiv). The mixture was allowed to warm to room temperature over 2 h at which point, TLC analysis showed the desilylation to be complete. The mixture was filtered and the filtrate was subjected to a conventional extractive workup (Et_2O). Compound **14a** was isolated as a yellow oil (1.0047 g, 5.6412 mmol, 88%) following flash chromatography (10:1 hexanes:Et_2O). ^{1}H-NMR (500 MHz, C_6D_6): 4.84 (s, 2H), 2.98 (s, 1H), 2.03 (t, 2H, J = 6.0), 1.89 (t, 2H, J = 6.0), 1.70 (s, 3H), 1.26-1.33 (m, 4H); ^{13}C-

NMR (75 MHz, C_6D_6): 169.8, 140.7, 118.7, 82.4, 81.4, 65.9, 29.9, 26.6, 21.8, 21.7, 20.1; IR (ATR): 3286, 2932, 2861, 1736, 1366, 1227; HRMS: m/e for $C_{11}H_{14}O_2$ calculated 178.0994 (M^+), found 178.0998.

[2-(3-((Trimethylsilyl)methyl)but-3-en-1-ynyl)cyclohex-1-enyl]methyl acetate (15a)

Compound **14a** (1.0047 g, 5.6412 mmol) was subjected to Sonogashira conditions according to General Procedure A with 2-bromo-3-(trimethylsilyl)-1-propene[39] (1.8413 g, 9.5901 mmol). The coupled compound **15a** was isolated as a yellow oil (1.4095 g, 4.8575 mmol, 86%) using flash chromatography (10:1 hexanes:Et_2O). ^{1}H-NMR (500 MHz, $CDCl_3$): 5.15 (d, 1H, J = 2.0), 4.98 (m, 1H), 4.77 (s, 2H), 2.18 (m, 2H), 2.10 (m, 2H), 2.05 (s, 3H), 1.66 (s, 2H), 1.58-1.65 (m, 4H), 0.04 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): 171.0, 138.3, 128.8, 120.1, 118.6, 95.3, 87.0, 66.5, 30.1, 28.3, 26.9, 22.1, 22.0, 20.9, -1.6; IR (KBr): 2934, 2894, 2862, 2195, 1743, 1594, 1376, 1232; HRMS: m/e for $C_{17}H_{26}O_2Si$ calculated 290.1702 (M^+), found 290.1708.

Hexacarbonyl[μ-η^4-(2-(3-((trimethylsilyl)methyl)but-3-en-1-ynyl)cyclohex-1-enyl)methyl acetate)]dicobalt (3a)

General Procedure G. Compound **15a** (1.4095 g, 4.8575 mmol) was dissolved in Et_2O (dry) (56.2 mL) along with excess $Co_2(CO)_8$. The solution was cooled to 0 ^{o}C, and allowed to stir for 1 h at that temperature under a nitrogen atmosphere. Following the hour, the solvent was removed under reduced pressure, and the residue was loaded onto a flash chromatographic column containing neutralized silica. The complexed compound (**3a**) was isolated by first washing the column with 100% hexanes to remove any excess, uncomplexed $Co_2(CO)_8$, followed by 10:1 hexanes:Et_2O to elute the product as a maroon solid (2.5800 g, 4.4791 mmol, 92%). ^{1}H-NMR (500 MHz, C_6D_6): 5.41 (s, 1H), 5.17 (s, 1H), 4.92 (s, 2H), 2.35 (t, 2H, J = 5.9), 1.98 (t, 2H, J = 6.1), 1.85 (s, 2H), 1.70 (s, 3H), 1.44-1.49 (m, 2H), 1.34-1.39 (m, 2H), 0.07 (s, 9H); ^{13}C-NMR (75 MHz, C_6D_6): 200.0, 169.8, 144.1, 133.8, 131.4, 116.0, 100.0, 93.9, 65.0, 33.4, 28.1, 26.8, 23.2, 22.0, 20.1, -1.1; IR (KBr): 2938, 2863, 2087, 2048, 2020, 1744, 1607, 1377, 1231; HRMS: m/e for $C_{23}H_{26}Co_2O_8Si$ calculated 408.0366 (M^+-6CO), found 408.0363.

Hexacarbonyl[μ-η^4-(8,9-dehydro-2,3,4,5,6,7-hexahydro-7-methylene-1H-benzo[7]annulene)]dicobalt (4a)

General Procedure H. Complexed compound **3a** (0.1836 g, 0.3187 mmol) was placed in a round bottom flask, and placed under vacuum for 5 minutes. The flask was then purged with nitrogen. This was repeated two times more. Dry CH_2Cl_2 (45.5 mL) was added to the reaction

flask, and the solution was cooled to 0 °C. *N*,*N*-Diisopropylethylamine (83 μL, 0.48 mmol) was added to the solution, followed by the dropwise addition of $SnCl_4$ (112 μL, 0.956 mmol). The reaction was allowed to stir for 20 minutes under nitrogen, at which point TLC analysis showed complete starting material consumption. NH_4Cl (aq, sat) was added, and the mixture was subjected to a conventional extractive workup (CH_2Cl_2). Flash chromatography on neutralized silica using 100% hexanes eluted compound **4a** (0.1115 g, 0.2512 mmol, 79%) as a maroon solid. ^{1}H-NMR (300 MHz, C_6D_6): 5.63-5.64 (m, 1H), 5.24 (apparent q, 1H, J = 1.3), 2.34-2.38 (m, 2H), 2.27-2.30 (m, 2H), 1.99-2.02 (m, 2H), 1.68-1.72 (m, 2H), 1.42-1.50 (m, 2H), 1.30-1.39 (m, 2H); ^{13}C-NMR (75 MHz, C_6D_6): 200.3, 147.7, 140.5, 128.4, 118.9, 94.2, 89.1, 35.9, 33.7, 33.2, 30.2, 22.9, 22.6; IR (KBr): 2933, 2863, 2087, 2053, 1612, 1432, 1237; HRMS: m/e for $C_{18}H_{14}Co_2O_6$ calculated 415.9505 ($M\text{-}CO^+$), found 415.9513.

2-[(Methoxyphenyl)ethynyl]benzyl acetate (19a)

Compound **18a** (0.8583 g, 3.646 mmol) was subjected to General Procedure C. Flash chromatography (15:1 hexanes:Et_2O) afforded compound **19a** as a pale yellow oil (0.8677 g, 3.098 mmol, 85%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.59 (dd, 1H, J = 7.4, J = 1.6), 7.44 (dd, 1H, J = 7.3, J = 1.2), 7.31-7.37 (m, 2H), 7.72 (apparent t, 1H, J = 8.0), 7.18 (d of apparent t, 1H, J = 7.6, J = 1.2), 7.11-7.12 (m, 1H), 6.92 (ddd, 1H, J = 8.3, J = 2.6, J = 1.0), 5.40 (s, 2H), 3.81 (s, 3H), 2.13 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 170.8, 159.5, 137.6, 132.3, 129.6, 128.6, 128.5, 128.2, 124.2, 124.1, 122.7, 116.4, 115.2, 94.4, 86.5, 64.8, 55.3, 21.0; IR (ATR): 3002, 2938, 1737, 1573, 1492; HRMS: m/e for $C_{18}H_{16}O_3$ calculated 280.1099 (M^+), found 280.1100.

Hexacarbonyl[μ-η^4-(2-((methoxyphenyl)ethynyl)benzyl acetate)]dicobalt (5a)

Compound **19a** (0.8677 g, 3.098 mmol) was subjected to General Procedure D. Following flash chromatography (15:1 hexanes:Et_2O) compound **5a** was isolated as a dark brown solid (1.6404 g, 2.8985 mmol, 94%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.67 (dd, 1H, J = 7.8, J = 1.4), 7.43 (dd, 1H, J = 7.4, J = 1.4), 7.34-7.40 (m, 2H), 7.30 (apparent t, 1H, J = 8.0), 7.07 (ddd, 1H, J = 7.6, J = 1.6, J = 0.9), 7.01-7.02 (m, 1H), 6.91 (ddd, 1H, J = 8.2, J = 2.5, J = 0.9), 5.13 (s, 2H), 3.83 (s, 3H), 2.04 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): 199.1, 170.5, 159.8, 140.0, 136.1, 134.5, 132.4, 129.9, 129.6, 128.8, 128.4, 121.8, 115.0, 113.4, 95.0, 88.9, 63.6, 55.2, 20.8; IR (ATR): 3019, 2905, 2087, 2048, 2010, 1993, 1748, 1584, 1231; HRMS: m/e for $C_{24}H_{16}Co_2O_9$ calculated 509.9560 ($M\text{-}2CO^+$), found 509.9543.

3-[(3,5-Dimethoxyphenyl)ethynyl]thiophene-2-carbaldehyde (18c)

[(3,5-Dimethoxyphenyl)ethynyl]trimethylsilane **7'd** (0.7501 g, 3.204 mmol) was subjected to tandem desilylation/Sonogashira chemistry according to General Procedure B with 3-bromothiophene-2-carbaldehyde (1.0648 g, 5.6071 mmol), with the exception that the reaction was warmed to rt. The product **18c** was isolated via flash chromatography (7:1 hexanes:Et_2O) as a colourless solid (0.6715 g, 2.468 mmol, 77%). mp. 94.5-95 ^oC; ^1H-NMR (300 MHz, $CDCl_3$): 10.21 (d, 1H, J = 0.7), 7.67 (dd, 1H, J = 0.7, J = 5.0), 7.23 (d, 1H, J = 5.0), 6.68 (d, 2H, J = 2.3), 6.50 (t, 1H, J = 2.2), 3.79 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): 183.0, 160.7, 143.7, 134.0, 131.6, 130.8, 123.2, 109.6, 102.7, 96.2, 81.1, 55.5; IR (ATR): 3008, 2964, 2835, 2209, 1659, 1585, 1203; HRMS: m/e for $C_{15}H_{12}O_3S$ calculated 272.0507 (M^+), found 272.0512.

[3-((3,5-Dimethoxyphenyl)ethynyl)thiophen-2-yl]methyl acetate (19c)

Compound **18c** (0.6715 g, 2.468 mmol) was reduced and acetylated according to General Procedure C. The product **19c** was isolated as a yellow oil (0.7250 g, 2.294 mmol, 93%) using flash chromatography (5:1 hexanes:Et_2O). ^1H-NMR (500 MHz, $CDCl_3$): 7.29 (d, 1H, J = 5.0), 7.12 (d, 1H, J = 5.0), 6.69 (m, 2H), 6.48 (m, 1H), 5.42 (s, 2H), 3.81 (s, 6H), 2.12 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): 170.7, 160.6, 140.5, 129.7, 125.8, 124.2, 122.4, 109.3, 101.9, 92.9, 82.3, 59.4, 55.4, 20.9; IR (ATR): 3000, 2838, 1736, 1586, 1419, 1155; HRMS: m/e for $C_{17}H_{16}O_4S$ calculated 316.0769 (M^+), found 316.0756.

Hexacarbonyl[μ-η^4-(3-((3,5-dimethoxyphenyl)ethynyl)thiophen-2-ylmethyl acetate)]dicobalt (5c)

Compound **19c** (0.7250 g, 2.294 mmol) was subjected to complexation according to General Procedure D. The product **5c** was isolated as a dark brown solid (1.1616 g, 1.9298 mmol, 84%) using flash chromatography (5:1 hexanes:Et_2O), after removing excess, uncomplexed $Co_2(CO)_8$ with 100% hexanes. ^1H-NMR (500 MHz, $CDCl_3$): 7.31 (d, 1H, J = 5.2), 7.15 (d, 1H, J = 5.2), 6.67 (d, 2H, J = 2.3), 6.46 (t, 1H, J = 2.2), 5.23 (s, 2H), 3.80 (s, 6H), 2.03 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): 199.0, 170.5, 160.9, 140.3, 136.5, 134.9, 130.5, 126.1, 107.5, 99.9, 93.3, 82.4, 58.6, 55.3, 20.6; IR (ATR): 2966, 2840, 2086, 2044, 1990, 1741, 1579, 1227; HRMS: m/e for $C_{23}H_{16}Co_2O_{10}S$ calculated 517.9281 (M-3CO$^+$), found 517.9290.

Hexacarbonyl[μ-η^4-(10,11-dehydro-2-methoxy-5*H*-dibenzo[*a*,*d*]cycloheptene)]dicobalt (6a) and Hexacarbonyl[μ-(10,11-dehydro4-methoxy-5*H*-dibenzo[*a*,*d*]cycloheptene)]dicobalt (6a')

Compound **5a** (0.2279 g, 0.4027 mmol) was reacted according to General Procedure E, using $SnCl_4$ (141 μL, 1.21 mmol). The reaction mixture was allowed to warm to room temperature over the course of 15 h, at which point the reaction was complete (as determined by TLC). Flash chromatography (15:1 hexanes:Et_2O) on neutralized silica afforded compound **6a** as the major product (and the second band on the column) as a dark maroon solid (0.1060 g, 0.2095 mmol, 52%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.69-7.71 (m, 1H), 7.32-7.36 (m, 2H), 7.27-7.31 (m, 1H), 7.26 (d, 1H, J = 2.8), 7.22 (d, 1H, J = 8.6), 6.89 (dd, 1H, J = 8.5, J = 2.8), 3.87 (s, 2H), 3.86 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 199.4, 159.2, 138.4, 137.7, 137.1, 132.1, 130.4, 130.0, 129.3, 128.6, 127.7, 117.4, 113.8, 90.8, 55.3, 42.1; IR (ATR): 2942, 2843, 2087, 2048, 2034, 2019, 1995, 1270; HRMS: m/e for $C_{22}H_{12}Co_2O_7$ calculated 449.9349 (M-2CO$^+$), found 449.9361.

Compound **6a'** was isolated as the minor product (and the first band off the column) as a dark maroon solid (0.0286 g, 0.0565 mmol, 14%). The combined yield was 66%, with a 3.7:1 para:ortho attack (i.e., major:minor products). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.68-7.70 (m, 1H), 7.36-7.38 (m, 1H), 7.32-7.34 (m, 3H), 7.29 (apparent t, 1H, J = 8.0), 6.94 (d, 1H, J = 8.3), 4.01 (s, 2H), 3.92 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 199.6, 156.3, 138.8, 137.7, 137.6, 131.9, 129.9, 128.6, 127.9, 127.6, 125.7, 124.6, 111.1, 91.2, 90.8, 56.1, 32.2; IR (ATR): 2920, 2839, 2091, 2047, 2018, 2002, 1568, 1254; HRMS: m/e for $C_{22}H_{12}Co_2O_7$ calculated 477.9298 (M-CO$^+$), found 477.9301.

Hexacarbonyl[μ-η^4-(4,5-dehydro-7,9-dimethoxy-10*H*-benzo[5,6]cyclohepta[1,2-*b*] thiophene)]dicobalt (6c)

Compound **5c** (0.1291 g, 0.2145 mmol) was subjected to Nicholas reaction chemistry according to General Procedure E, using $SnCl_4$ (75 μL, 0.64 mmol). The reaction was complete after 10 minutes, as determined by TLC, and the product (**6c**) was isolated as a dark maroon solid (0.0851 g, 0.157 mmol, 73%) using flash chromatography (15:1 hexanes:Et_2O). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.24 (½ ABq, 1H, J = 13.7), 7.18 (½ ABq, 1H, J = 5.4), 6.86 (d, 1H, J = 2.6), 6.53 (d, 1H, J = 2.6), 4.11 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 199.5, 159.7, 157.1, 134.0, 137.4, 135.8, 129.4, 123.8, 116.0, 109.4, 99.1, 91.2, 84.6, 56.1, 55.4, 25.0; IR (ATR): 2963, 2832, 2086, 2035, 2004, 1567, 1210; HRMS: m/e for $C_{21}H_{12}Co_2O_8S$ calculated 513.8968 (M-CO$^+$), found 513.8949.

2,3,4,5-Tetrahydro-7,8-dimethoxy-10-triethylsilyl-1*H*-dibenzo[*a,d*]cycloheptene (21)

To a stirred solution of compound **2d** (0.1437 g, 0.2661 mmol) dissolved in degassed 1,2-dichloroethane (4.1 mL) was added bis(trimethylsilyl)acetylene (121 μL, 0.532 mmol) and triethylsilane (213μL, 1.33 mmol). The reaction was placed in an oil bath set at 65 ^{o}C, and allowed to stir for 6 h under a nitrogen atmosphere. Following the 6 h, the reaction was cooled, dissolved in Et_2O (75 mL) and subjected to a conventional extractive workup (Et_2O). Preparative TLC (15:1 hexanes:Et_2O) afforded compound **21** as the major isomer, and as a colourless solid (0.0862 g, 0.233 mmol, 86% combined yield). mp. 95-97 ^{o}C; ^{1}H-NMR (500 MHz, $CDCl_3$): 6.88 (s, 1H), 6.62 (s, 1H), 6.52 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.76 (s, 2H), 2.33 (m, 2H), 2.08 (m, 2H), 1.60 (m, 4H), 0.96 (t, 9H, J = 7.8), 0.78 (q, 6H, J = 7.8); NOE (500 MHz, $CDCl_3$): Irradiation of the 0.96 ppm ($SiEt_3$) resonance gave enhancement of the 6.88 ppm (1.0%) and 6.51 ppm (1.0%) resonances; ^{13}C-NMR (125 MHz, $CDCl_3$): 148.2, 146.1, 142.4, 138.4, 135.5, 131.8, 131.6, 128.4, 110.5, 110.4, 55.9, 55.8, 40.4, 30.9, 28.8, 22.9, 22.8, 7.6, 4.5; IR (KBr): 2950, 2932, 2873, 1604, 1508, 1463, 1262; HRMS: m/e for $C_{23}H_{24}O_2Si$ calculated 370.2328 (M^+), found 370.2325.

2,3,4,5-Tetrahydro-7,8-dimethoxy-1*H*-dibenzo[*a,d*]cycloheptene (22)

METHOD 1: To a stirred solution of **21** (0.0849 g, 0.229 mmol) in degassed 1,2-dichoroethane (3.5 mL) was added trifluoroacetic acid (88 μL, 1.2 mmol), and the solution was allowed to stir for 3 h at room temperature under a nitrogen atmosphere. The mixture was dissolved in Et_2O (75 mL) and subjected to a conventional extractive workup (Et_2O). Preparative TLC (15:1 hexanes:Et_2O) afforded compound **22** as a colourless solid (0.0570 g, 0.222 mmol, 97%). mp. 88-90 ^{o}C.

METHOD 2: To a stirred solution of **2d** (0.3209 g, 0.5943 mmol) in degassed 2-methoxyethanol (9.1 mL) was added sodium hypophosphite monohydrate (0.3149 g, 2.972 mmol). The solution was placed in an oil bath set at 65 ^{o}C, and allowed to stir overnight (18 h) under a nitrogen atmosphere. The reaction mixture was filtered through Celite® and subjected to a conventional extractive workup (EtOAc). Preparative TLC afforded compound **22** as colourless crystals (0.1164 g, 0.4544 mmol, 76%). ^{1}H-NMR (300 MHz, $CDCl_3$): 6.84 (d, 1H, J = 11.6), 6.81 (s, 1H), 6.65 (s, 1H), 6.24 (d, 1H, J = 11.5), 3.91 (s, 3H), 3.88 (s, 3H), 2.89 (s, 2H), 2.35 (m, 2H), 2.12 (m, 2H), 1.56-1.66 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): 149.7, 146.9, 132.2, 129.8, 129.5, 128.8, 128.1, 110.4, 110.1, 56.1, 40.5, 31.6, 29.4, 23.1, 23.0; IR (KBr): 2998, 2930,

2833, 1605, 1510, 1353, 1263; HRMS: m/e for $C_{17}H_{20}O_2$ calculated 256.1463 (M^+), found 256.1457.

1,2,3,5,-Tetrahydro-8-isopropyl-7-methoxy-1,1,8-trimethyl-4*H*-Dibenzo[*a*,*d*]cyclohepten-4-one (31)

Compound **29** (0.2507 g, 0.6809 mmol) was dissolved in dry CH_2Cl_2 (97.2 mL) along with a slight excess of $Co_2(CO)_8$. The solution was allowed to stir at room temperature under a nitrogen atmosphere for 2 h. The reaction flask was cooled 0 ^oC. $SnCl_4$ (238 μL, 2.04 mmol) was added dropwise into the reaction, followed by *N*,*N*-diisoproplyethylamine (178 μL, 1.02 mmol). The reaction was then allowed to stir under a nitrogen atmosphere for another 15 h, while warming to room temperature. Following the 15 h, TLC analysis showed complete starting material consumption, and $NH_4^+Cl^-$ (aq., sat., 75 mL) was added. The organic portion was rinsed once more with $NH_4^+Cl^-$ (aq., sat., 75 mL) in a separatory funnel, and then with brine (75 mL). The organic fraction was then dried over $MgSO_4$, filtered, removed under reduced pressure, and the remaining residue quickly passed through a short column of silica to remove any excess impurities (100% hexanes, then 3:1 hexanes:Et_2O). The collected fraction (~0.16 g, ~0.27 mmol) was dissolved in degassed 2-methoxyethanol (4.1 mL) along with 5 equivalents of NaH_2PO_2-H_2O (0.1185 g, 1.347 mmol). The solution was allowed to stir at 65 ^oC for 20 h under a nitrogen atmosphere. The reaction mixture was filtered through Celite®, and the collected fraction subjected to a conventional extractive workup (EtOAc). Preparative TLC chromatography (2:1 hexanes:Et_2O) isolated the product as a yellow oil (0.0592 g, 0.191 mmol, 28%). ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.30 (d, 1H, J = 12.0), 7.15 (s, 1H), 6.77 (s, 1H), 6.67 (d, 1H, J = 11.9), 3.85 (s, 3H), 3.22-3.30 (m, 3H), 2.42 (t, 2H, J = 6.8), 1.82 (t, 2H, J = 6.8), 1.20 (s, 9H), 1.18 (s, 3H); NOE (500 MHz, $CDCl_3$): Irradiation at δ 7.14 resonance gave enhancement of doublet further downfield and isopropyl protons at δ 1.21. Irradiation at δ 6.79 resonance gave enhancement of methoxy protons at δ 3.87; ^{13}C-NMR (75 MHz, CD_2Cl_2): 196.3, 158.8, 155.9, 138.4, 137.1, 134.6, 128.3, 126.0, 125.8, 109.3, 55.5, 37.2, 34.8, 34.4, 30.5, 27.6, 26.6, 22.4; IR (ATR): 2957, 2923, 2866, 1657, 1496, 1255; HRMS: m/e for $C_{21}H_{26}O_2$ calculated 310.1933 (M^+), found 310.1932.

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