DOI: 10.1002/adsc.200505136

Improved Turnover Numbers in Palladium-Catalyzed Bisdiene Cyclization-Trapping using N-Heterocyclic Carbene Ligands

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Received: April 1, 2005; Accepted: August 30, 2005

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: An optimized palladium-N-heterocyclic carbene catalyst system effects the palladium-catalyzed bisdiene cyclization-trapping with phenol at the 0.01% catalyst loading level with a TON of 7.6×10^3 and TOF of $280\ h^{-1}$, values much higher than typically found for this and related carbocyclizations. The reaction scales well and the *trans*-substituted six-membered ring product is obtained in excellent yield on a 10-mmole scale without further optimization of the catalyst system or reaction conditions.

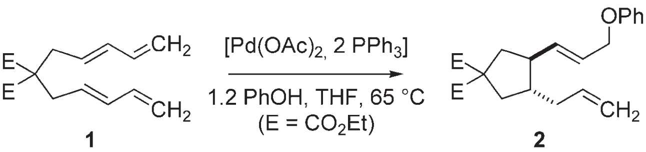
Keywords: C–C coupling; cyclization; homogeneous catalysis; N-heterocyclic carbenes; palladium

Metal-catalyzed carbocyclization reactions of α,ω-unsaturated substrates have attracted much interest in recent years and a number of useful strategy-level bond constructions have been developed for use in synthesis. We are interested in the palladium-catalyzed carbocyclization reactions of bisdienes, atom-economical reactions that can afford a variety of interesting ring systems. Recently, our efforts have been directed toward developing its potential for diversity-oriented synthesis by improving the control over several related cyclization modes (e.g., cyclization-trapping, cycloisomerization, or cycloaddition)[1] and improving the scope with respect to substrate and trapping reagent.[2] We now turn our attention toward improving the catalyst efficiency [i.e., turnover number (TON) and turnover frequency (TOF)] and, herein, describe catalyst optimization studies which led to a palladium-N-heterocyclic carbene (NHC) catalyst system exhibiting much improved turnover numbers for the bisdiene cyclization-trapping with a prototypical pronucleophile.

The current state of the art for palladium-catalyzed bisdiene cyclization-trapping is illustrated in Table 1. Using 5–10 mole percent of a catalyst such as a 1:2 mixture of $Pd(OAc)_2{:}PPh_3$, bisdiene **1** undergoes efficient cyclization-trapping to afford the substituted cyclopentane **2** (74–82% yield). However, under more practical catalyst loading levels, the yield drops off precipitously. For example, at 0.01% catalyst loading, the reaction gives only traces of **2** even after a prolonged reaction time (entry 5).

The palladium-catalyzed cyclization-trapping of bisdienes is related to the linear dimerization-trapping (telomerization) of simple acyclic dienes. The latter is an atom-economical reaction that can be used to exploit several cheap, readily available dienes (e.g., 1,3-butadiene, isoprene, etc.) for the preparation of useful industrial intermediates[3] and, therefore, is industrially attractive and of significant interest in the catalysis community.[4] Phosphines have often been employed for palladium-catalyzed linear diene dimerizations, but such ligands are typically air-sensitive and susceptible to decomposition at higher temperatures.[5] For example, $[Pd(OAc)_2/PPh_3]$ can give a very efficient catalyst system for the linear dimerization of butadiene with trapping by methanol, but only when a large excess of

Table 1. The influence of catalyst loading on the palladium-catalyzed bisdiene cyclization-trapping of bisdiene **1** with phenol.



Entry[a]	% catalyst	Time [h]	Yield [%]
1	10	4	82
2	5	4	74
3	1	4	30
4	0.1	4	26
5	0.01	22	trace

[a] The reaction is run using the indicated amount of $[(Pd(OAc)_2/2\ PPh_3]$ in THF at 65 °C.

PPh_3 is employed; for example, using a 50-fold excess of phosphine, the TON approaches 10^5 with the TOF approaching $1.6 \times 10^3\ h^{-1}$.[6]

N-Heterocyclic carbenes (NHC) derived from hindered imidazolium salts mimic phosphines as sigma donors and have emerged as a useful class of ligands for catalysis.[7] NHC-complexed catalysts have been used for a variety of metal-catalyzed reactions and, in particular, in many variants of palladium-catalyzed cross-coupling reactions. In contrast to many phosphines, the NHC precursors are generally more stable to air, water, and higher reaction temperatures.[8] NHC-metal catalysts can usually be prepared *in situ via* the combination of a metal complex, the imidazolium salt NHC-precursor, and a suitable base, although preformed NHC-metal complexes can often be isolated as well.

NHCs have recently been examined in the palladium-catalyzed linear dimerization-trapping of butadiene with simple amines[9] and alcohols.[10] A series of studies by the groups of Beller and Nolan recently culminated in their joint finding that palladium-carbene complex **3** exhibits outstanding activity in the reaction of butadiene with methanol; the TON obtained with **3** is greater than 10^6 for that reaction with the TOF approaching $10^5\ h^{-1}$.[11] Very impressive TONs ($10^4 - 10^5$) were observed with a series of other alcohols and substituted phenols. However, phenol itself is somewhat of an exception; its TON is lower, 7.6×10^3 (TOF $= 475\ h^{-1}$).

The use of NHCs in metal-catalyzed carbocyclization reactions of α,ω-polyunsaturated substrates is still rather limited.[12] However, the successful applications of NHCs to the linear diene dimerization discussed above and to palladium-catalyzed allylations[13] led us to investigate their use in palladium-catalyzed bisdiene cyclizations. The cyclization-trapping of bisdiene **5** with phenol was selected as a relatively demanding test case, demanding, in part, because it leads to the formation of a six-membered ring (i.e., **6**). As is typical of most related carbocyclizations, five-membered ring formation *via* bisdiene cyclization-trapping is usually more facile than other ring sizes, especially when aided by the *gem*-dialkyl effect or the presence of a heteroatom within the nearly formed five-membered ring.[14] As indicated above, phenol is not a particularly favorable trapping reagent, and, thus, it is expected that the data obtained from the cyclization-trapping of a bisdiene **5** with phenol should give a good indication of the potential effectiveness of NHCs for a range of bisdiene cyclization-trapping reactions.

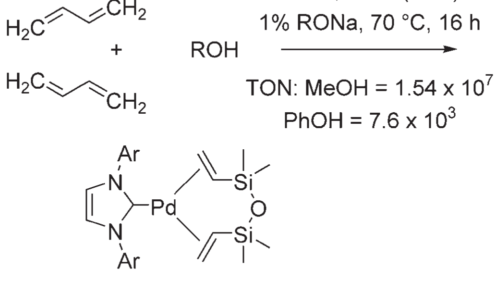
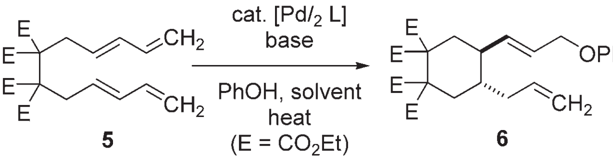


Figure 1. The efficient linear dimerization-trapping of 1,3-butadiene catalyzed by NHC-Pd complex **3** as reported by Beller, Nolan, et al.

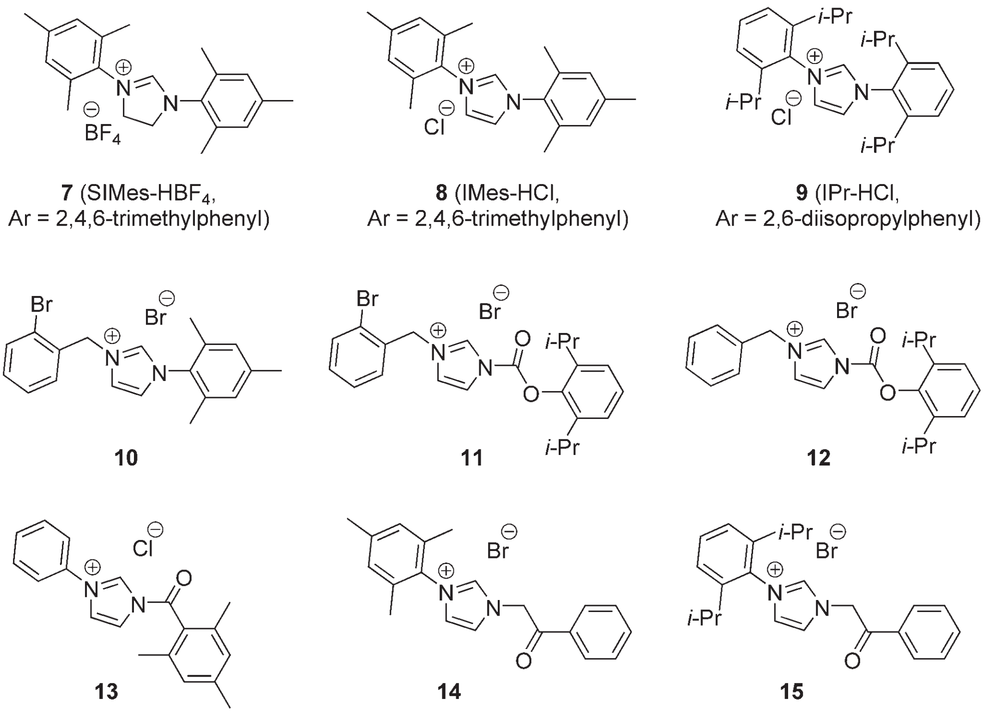


(1)

The NHC-precursors selected are illustrated in Figure 2. Included are the three most commonly used and commercially available imidazolium salts, SIMes·HBF_4 (**7**), IMes·HCl (**8**) and IPr·HCl (**9**), as well as a number of more exotic NHC-precursors. We recently became interested in chelated *N*-acyl-NHC-palladium catalysts, and although it is unproven whether these function as the chelate in catalysis or simply as a reservoir for Pd(0),[15] we recently reported that precursor **11** gives a remarkably effective catalyst for the Suzuki-Miyaura coupling reaction (TON $> 10^7$).[16] Its relative effectiveness compared to **10**[17] suggests that the *N*-carbamoyl substituent may be playing a key role in its success, perhaps due to its electronic influence or as a hemilabile ligating group. It is possible that *N*-acyl-NHC derivatives can contribute to further expanding the rich chemistry of NHCs, and the present study asks whether **11** and/or the *N*-acylimidazolium derivatives **12** and **13** are effective in the bisdiene cyclization-trapping reaction. The recently reported keto-imidazolium derivative **14**[18] and its analogue **15** were included for further comparison.

To establish whether an NHC-Pd complex would catalyze the bisdiene cyclization-trapping reaction, bisdiene **5** and phenol were treated with the presumed *in situ* generated IMes-Pd complex derived from 10% $[Pd(OAc)_2/2$ IMes·HCl] and Cs_2CO_3 in dioxane (75 °C). Figure 3 shows the time course for the formation of product **6** under those conditions. The graph shows a very typical rate profile and complete reaction under these conditions of high catalyst loading within about 3 hours. In other experiments, the amount of NHC-precursor was varied from 0.5 to 2.0 equivalents relative to palladium, and while a lower ratio is often acceptable, the 2:1 ratio generally gives higher yields and thus was used throughout this study.

Ultimately, it is the relative effectiveness of the NHC-precursors in Figure 2 that is to be evaluated. However, our previous studies on bisdiene cyclization-trapping show that the reaction efficiency can be highly depen-



7 (SIMes-HBF$_4$, Ar = 2,4,6-trimethylphenyl)

8 (IMes-HCl, Ar = 2,4,6-trimethylphenyl)

9 (IPr-HCl, Ar = 2,6-diisopropylphenyl)

10

11

12

13

14

15

Figure 2. Collection of NHC-precursors examined.

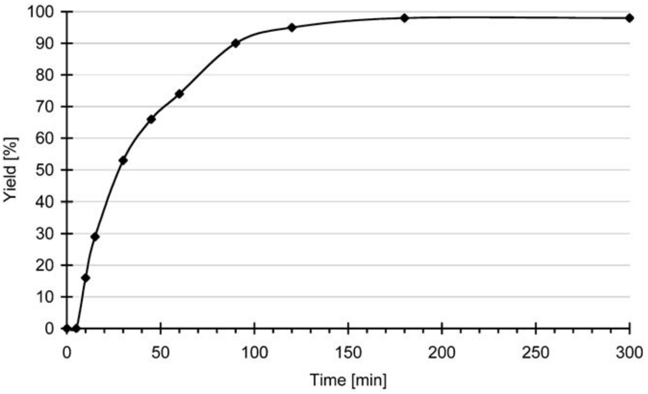


Figure 3. The time course of the reaction of bisdiene **5** with phenol catalyzed by 10% [Pd(OAc)$_2$/2 IMes · HCl] in dioxane (30% Cs_2CO_3, 75 °C).

dent upon the precise combination of catalyst precursor, ligand and solvent; that is, many of the key variables in this reaction prove to be highly interdependent.[2] Developing efficient strategies for optimizing catalyst systems when several reaction variables show strong interdependence is a challenging and timely problem in catalysis.[19] Using IPr · HCl (**9**) as the NHC-precursor, a collection of solvents, ranging from very non-polar (e.g., toluene) to very polar (e.g., DMSO), were screened with three commonly used bases (i.e., sodium *tert*-pentoxide, potassium *tert*-butoxide and cesium carbonate) and two frequently employed catalyst precursors [i.e., Pd(OAc)$_2$ and allylpalladium chloride dimer (APC)]. In line with our goal to identify catalyst systems exhibiting more practical TONs and TOFs, the catalyst loading used in this initial screening study was reduced from 10%, as had been used in for the reaction in Figure 2, to 1% palladium. To further bias the assay toward identifying the fastest catalyst systems and conditions, the reaction time was limited to 4 hours. The data obtained, summarized in Table 2, show considerable variation indicating that the reaction variables are indeed highly interdependent. Overall, the combination of Cs_2CO_2 in dioxane worked well for both catalyst precursors and, on that basis, was selected for the studies that follow.

In Table 3 are summarized the data obtained for the cyclization-trapping of bisdiene **5** with phenol as a function of catalyst precursor and ligand. Six catalyst precursors were selected: Pd_2dba_3; Pd(OAc)$_2$; allylpalladium chloride dimer (APC); and the combinations of APC with sodium tetrafluoroborate, hexafluorophosphate, and hexafluoroantimate. In separate experiments (not included in Table 3), the corresponding silver salts were compared to the sodium salts listed with little change. In addition to the nine NHC-precursors, PPh_3 is included for comparison. All reactions use 1% Pd with Cs_2CO_3 as the base and, with the exception of PPh_3, dioxane as the solvent. Preliminary experiments showed that PPh_3 in combination with several catalyst precursors gave much higher yields in THF than in dioxane. For example, the PPh_3-containing catalysts from Pd_2dba_3 and Pd(OAc)$_2$ gave 16% and 8% yield, respectively, in dioxane (75 °C), but 68% and 85% yield when

Table 2. Yields of **6** as a function of solvent and base for two catalyst precursors with the NHC-precursor, IPr·HCl.[a, b]

Pd source	Base	Toluene	THF	Dioxane	DME	MeCN	DMSO
$Pd(OAc)_2$	$NaOC_5H_{11}$	20	8	59	31	0	47
$Pd(OAc)_2$	KO-*t*-Bu	31	97	74	8	78	70
$Pd(OAc)_2$	Cs_2CO_3	20	98	**94**	10	31	35
$[(\eta^3\text{-}C_3H_5)PdCl]_2$	$NaOC_5H_{11}$	8	8	90	23	4	55
$[(\eta^3\text{-}C_3H_5)PdCl]_2$	KO-τ-Bu	4	4	90	50	59	34
$[(\eta^3\text{-}C_3H_5)PdCl]_2$	Cs_2CO_3	0	27	**94**	11	78	32

[a] Reaction conditions: 0.06 M solution of **5** in the solvent indicated with 1% [Pd/2 IPr·HCl], 3% base, and phenol (2 equivalents) at 75 °C (4 h).

[b] Yields based on ^{1}H NMR analysis relative to 4-methoxybenzyl alcohol as an internal standard.

Table 3. Yields of **6** obtained as a function of palladium catalyst precursor, counterion, and NHC precursor or PPh_3.[a, b]

Pd source	Additive	SIMes·HCl	IMes·HCl	IPr·HCl	**10**	**11**	**12**	**13**	**14**	**15**	PPh_3
Pd_2dba_3	–	79	58	84	19	23	53	27	78	67	68
$Pd(OAc)_2$	–	79	86	**94**	35	12	22	32	**95**	**90**	85
APC	–	64	66	**94**	4	16	72	20	**92**	**92**	**99**
APC	$NaBF_4$	65	20	**90**	2	7	54	16	**94**	64	**98**
APC	$NaPF_6$	63	34	**90**	7	2	38	20	**96**	65	46
APC	$NaSbF_6$	26	16	40	4	2	28	20	70	54	**99**

[a] Reaction conditions: 0.06*M* solution of **5** in dioxane (except with PPh_3 which is run in THF) with 1% [Pd/2 IPr·HCl], 3% Cs_2CO_3, and phenol (2 equivalents) at 75 °C (4 h); APC = $[(\eta^3\text{-}C_3H_5)PdCl]_2$.

[b] Yields (%) based on ^{1}H NMR analysis relative to 4-methoxybenzyl alcohol as an internal standard.

run in THF (65 °C). Therefore, the reactions using PPh_3 were run in THF.

About 20% of the catalyst precursor-ligand combinations in Table 3 give product **6** in yields of 90% or greater. Comparing the three commercially available imidazolium salts, IPr·HCl (**9**) is often superior to IMes·HCl (**8**) and its dihydro derivative, SIMes·HBF_4 (**7**). This is somewhat surprising since studies on the linear dimerization of butadiene found the IMes derivative to be superior and, in some cases, the IPr derivative promoted dimerization without trapping.[20] Nonetheless, the combinations of IPr·HCl (**9**) with $Pd(OAc)_2$, APC, APC/$NaBF_4$, and APC/$NaPF_6$ are among the overall best catalyst systems. Neither of the two aryl bromide containing NHC-precursors (i.e., **10** and **11**) gives a good catalyst. This is perhaps not surprising since the current mechanistic model for the cyclization, adapted from the work of Jolly[21] on the linear dimerization of butadiene and discussed elsewhere,[1] supposes three open coordination sites on palladium during the catalytic cycle; the bromide is expected to facilitate the formation of an NHC-chelated palladacycle thus limiting the number of available sites. The *N*-carbamoyl analogue lacking the bromine (i.e., **12**) performs better but is still generally less successful than SIMes·HBF_4 or IMes·HCl. It was, of course, recognized that the *N*-acylimidazolium salt **13** is a potent acylating reagent[22] and could potentially react with phenol in preference to, or in competition with, the formation a Pd-carbene complex. It proved to be relatively ineffective as a cyclization catalyst. The most surprising results were those obtained with the keto derivatives **14** and **15**. NHC-precursor **14** was used by Waymouth[18] to synthesize an allylpalladium-**14** complex. The latter undergoes reversible deprotonation to give a conjugated anionic chelated NHC-Pd complex which was found to undergo allyl isomerization *via* an associative mechanism. We find these keto derivatives give very active cyclization catalysts. The mesityl derivative **14** is generally the better of the two giving yields above 90% with four of the six catalyst precursors screened. PPh_3 in combination with APC, or with APC plus $NaBF_4$ or $NaSbF_6$, give yields comparable or better than the best of the NHCs. Beller[10] reported a similar result in an early study comparing a preformed palladium(0)-carbene complex to $Pd(OAc)_2/PPh_3$ in the linear dimerization-trapping of butadiene with methanol; subsequent improvements to the carbene-complex ultimately rendered it far superior.

The three best NHC-precursors (i.e., IPr·HCl, **14**, and **15**) and PPh_3 were further examined for their effectiveness at lower catalyst loading (Table 4). Using APC as the palladium source, we were initially disappointed to find that the yields dropped considerably with the *N*-acyl-NHCs **14** and **15** at catalyst loading dropped below 1% palladium. The PPh_3-catalyst system gave a high yield (98%) at 0.1% catalyst loading, but the yield dropped precipitously at lower levels. In contrast, the combination of APC and IPr·HCl gave excellent yield (93%) at a catalyst loading as low as 0.025% (85 °C, 4 h). Several catalysts systems were active at even lower levels, but

Table 4. Comparing yields of **6** as a function of catalyst loading for PPh_3- and NHC-modified catalysts derived from allylpalladium chloride dimer (APC).[a]

% Pd	T [°C]	t [h]	APC IPr·HCl	APC **14**	APC **15**	APC PPh_3	APC/BF_4 IPr·HCl	APC/PF_6 IPr·HCl	APC/SbF_6 IPr·HCl	(IPr)Pd-(allyl)Cl (**16**)	$Pd(OAc)_2$ IPr·HCl	Pd_2dba_3 IPr·HCl
1	75	4	97	92	91	98	89	90	41	87	95	84
0.1	75	4	94	71	43	98	61	74	23	81	59	55
0.05	75	4	94	32	10	24	33	40	9	68	9	44
0.05	85	4	94	–	–	27	–	–	–	–	75	58
0.025	85	4	93	–	–	9	–	–	–	33[b]	9	36
0.01	95	6	40	12	6	–	25	31	0	–	5	26
0.01	95	27	76[c]	51	11	–	58	63	9	52	47	57

[a] Reaction conditions: 0.06 M solution of **5** in dioxane (except with PPh_3 which is run in THF) with 1% [Pd/2 IPr·HCl], 3% Cs_2CO_3, and phenol (2 equivalents); APC = $[(\eta^3\text{-}C_3H_5)PdCl]_2$. Yields based on ^1H NMR analysis relative to 4-methoxybenzyl alcohol as an internal standard.

[b] At 75 °C (4 h).

[c] Turnover number = 7.6×10^3; turnover frequency = 280 h^{-1}.

required higher temperatures and longer reaction times. The [APC/IPr·HCl] combination proved best overall, and at the 0.01% catalyst level, it gave a TON of 7.6×10^3 with a TOF of 280 h^{-1}.

We briefly examined other catalyst combinations with IPr·HCl. The chloride-exchanged catalysts, prepared *in situ via* exchange of APC with $NaBF_4$ or $NaPF_6$, give results similar to those obtained with **14**; the $NaSbF_6$-exchanged catalyst is inferior, consistent with data in Table 3. Using the procedure of Nolan,[23] we prepared and isolated the mononuclear (IPr)Pd(allyl)Cl complex (**16**). Unfortunately, this preformed complex did not prove better than the corresponding *in situ* preparation (Table 4); neither did the corresponding isolated (IPr)Pd(allyl)X complexes (X = BF_4, PF_6, SbF_6; data not shown). Similarly, the results obtained with IPr·HCl and two other catalyst precursors [i.e., ($Pd(OAc)_2$ and Pd_2dba_3) offer no improvement over APC.

The screening reactions were carried out on small scale (i.e., approximately 0.22 mmol of **5**), and encouraged by its success, the [APC/IPr·HCl] catalyst system was used in a larger scale preparative reaction. The cyclization-trapping of bisdiene **5** with phenol was carried out on a 10 mmol scale at a catalyst loading of 0.025% palladium. The reaction proceeds smoothly (0.5 M in dioxane, Cs_2CO_3, 85 °C, 10 h) to give cyclized product **6** in 84% yield after chromatographic purification. Product **6** is formed with high diastereoselectivity (>95%) with the *trans* relative stereochemistry between the two newly-formed side-chains and the *E*-disubstituted alkene geometry.

In summary, building upon the very successful work by Beller and Nolan on the linear dimerization-trapping of 1,3-butadiene, we carried out a study of the bisdiene cyclization-trapping reaction and are very pleased to report that NHC-Pd complexes catalyze the cyclization-trapping reaction, give the same product as the phosphine-promoted reactions, and the diastereoselectivity observed in the cyclization is high (>95%). At the 0.01% catalyst level the [APC/IPr·HCl] *in situ* generated catalyst gave a TON of 7.6×10^3 with a TOF of 280 h^{-1}, values that are (i) significantly higher that usually seen in this and related carbocyclization reactions, and (ii) almost identical to those obtained by Beller, Nolan et al. with an optimized preformed NHC-Pd(0) complex in the linear dimerization-trapping of butadiene with phenol. Furthermore, the reaction scales well and a very good isolated yield (84%) was obtained on a 10 mmole scale without further optimization of the catalyst system or reaction conditions. The extensions of these studies to other substrates and trapping reagents are in progress.

Experimental Section

General Remarks

All solvents were purchased from Aldrich and degassed by the freeze-pump-thaw method prior to use. All palladium salts and available NHC ligands were purchased from Strem Chemicals. DMSO was dried over calcium hydride and distilled prior to use. DME was distilled prior to use.

Palladium-Catalyzed Cyclization-Trapping of Bisdiene (5) with Phenol

To a solution of bisdiene **5** (4.50 g, 10.0 mmol) and phenol (1.84 g, 20.0 mmol) in dioxane (20 mL) was added Cs_2CO_3 (122.2 mg, 0.38 mmol) and IPr·HCl (212.5 mg , 0.50 mmol). The resulting mixture was stirred (0.5 h, room temperature) and then a solution of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (45.7 mg, 0.125 mmol) in dichloromethane (DCM, 2.0 mL) was added. The reaction mixture was heated at 85 °C for 10 h. Afterwards, the mixture was cooled to room temperature and filtered through a plug of silica gel (DCM) to remove the precipitated palladium. The filtrate was washed sequentially with 1 M aqueous NaOH (twice), brine, and water. The organic layer was dried (anhydrous Na_2SO_4) and concentrated *via* rotovap. Flash chromatography on silica (90:10 hexanes/ethyl acetate) gave the substituted cyclohexane **6** as a light yellow oil; yield: 5.32 g (84%). TLC analysis (90:10 hexanes/ethyl acetate) showed one spot (UV visualization) at $R_f = 0.3$; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.23–1.33 (overlapping t's, 12H), 1.46–1.55 (m, 1H), 1.78–1.84 (m, 1H), 2.04–2.39 (m, 6H), 4.13–4.25 (overlapping q's, 8H), 4.94 (d, J = 10 Hz, 2H), 5.01 (overlapping d's, 2H), 5.57 (dd, J = 7, 15 Hz, 1H), 5.6–5.77 (m, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.94 (t, J = 7 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.80, 13.82, 13.92, 13.93, 33.7, 35.2, 36.3, 37.8, 40.8, 58.1, 59.2, 61.3, 61.5, 61.60, 61.62, 68.3, 114.8, 116.7, 120.8, 126.9, 129.4, 135.8, 137.0, 158.6, 169.32, 169.37, 170.5, 170.7; IR (neat): ν = 1730 (C=O), 1596 cm^{-1} (C=C); HR-MS (EI): *m/z* = 544.2680; calcd. for $C_{30}H_{40}O_9$ (M^+): 544.2672.

Acknowledgements

Support from the NSF (CHE-0316825) is gratefully acknowledged. The NMR spectrometers used in this study were purchased with shared instrument grants (NIH SIG-1-510-RR-06307, NSF CHE-0091975 and NSF MRI-0079750).

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