First Example of a Total Axial to Centered Chirality Transfer in the [2+2+2] Cycloadditions of Allenediynes

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Abstract: The cobalt-mediated [2+2+2] cycloaddition of allenediynes bearing a phosphine oxide group at one alkyne terminus is a completely regio-, chemo- and diastereoselective high yielding process. Moreover, a total transfer of chiral information from axial to centered chirality is evident, which makes this reaction a new and powerful tool for the preparation of enantiomerically enriched tricyclic derivatives.

Key words: alkynes, allenes, chirality, cycloadditions, cobalt

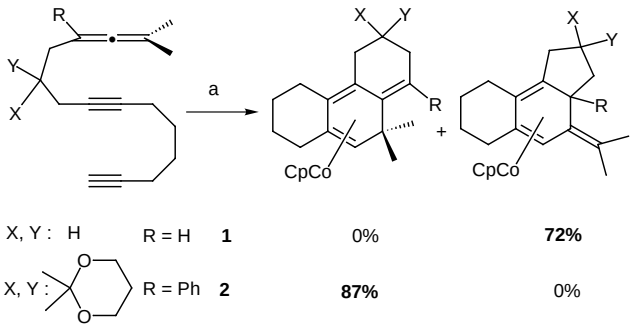
Chiral allenes are versatile precursors in asymmetric synthesis that efficiently transfer the axial to centered chirality and their reactivity has recently attracted much attention.[1] In addition, transition metal-promoted carbon-carbon bond forming reactions based on allenes have been extensively investigated.[2] These reactions include, for instance, co-oligomerizations,[3] intramolecular cyclizations,[4] [4+2], [5+1] and [5+2] cyclizations,[5] inter- and intramolecular Pauson−Khand reactions,[6] formation and electrocyclizations of π-allyl metal complexes[7] and formal Alder ene reaction.[8]

Although allenes are good ligands in organometallic chemistry, only few examples involving this moiety have been reported in nickel(II)/(0)[9] and palladium(0)[10] mediated [2+2+2] cycloadditions or homo Diels−Alder reactions.[11]

Recently, we disclosed that the cobalt(I) complex, $CpCo(CO)_2$, was able to mediate the intramolecular [2+2+2] cyclizations of allenediynes with pronounced regio- and diastereoselectivity.[12] Depending on the substitution of the allene, the regioselectivity of the cycloaddition was quite different leading either to the η^4-complexed tricyclic [6.6.6] or [6.6.5] compounds (Scheme 1). At this point of our studies, we were attracted to determine whether this cobalt-mediated [2+2+2] cyclization can be performed with a high degree of chirality transfer.

In this paper, we report that optically active allenediynes undergo intramolecular cobalt(I)- mediated [2+2+2] cyclization with a total axial to centered chirality transfer.

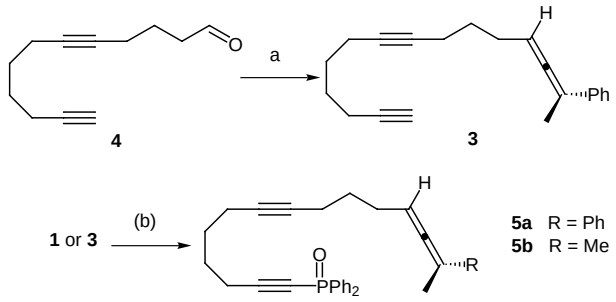
In order to determine the level of the stereoselectivity of the cyclization of chiral allenediynes, we first checked the behavior of racemic precursor **3**. The latter has been judiciously selected considering that the cyclization of **1** led to [6.6.5] complex as a sole diastereomer and in addition, that the double bond bearing a phenyl group in **2** was not reactive. By improving the procedure already described,



Reagents and conditions: a, $CpCo(CO)_2$ (1 equiv), xylenes, Δ, hν

Scheme 1

the allenediyne **3** was obtained from the dodeca-5,11-diynal **4**[13] (Scheme 2).



Reagents and conditions : a, one-pot i. PhC≡CLi, THF, −78 °C, ii. CH_3SO_2Cl, iii. 2 LiCl, MeCuCNMgBr, 74%; b, i. *n*-BuLi, THF, −78 °C, 30 min, ii. $Ph_2P(O)Cl$, −78°to 50 °C, 10 min, **5a**:90%; **5b**:87%

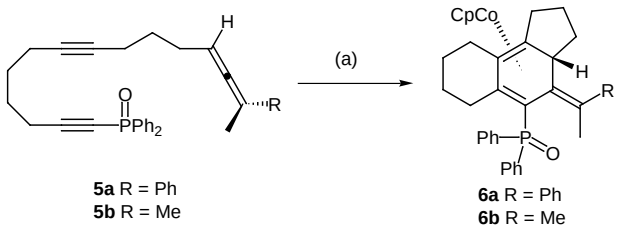
Scheme 2

Indeed, aldehyde **4** was treated in THF, at −78 °C, in a one-pot operation, subsequently with phenyl lithiumacetylide, methanesulfonylchloride and methylcyanocuprate (generated from methyl Grignard, copper(I) cyanide and lithium chloride) affording the allenediyne **3** in 74% yield. The latter was exposed to one equivalent of (η^5-cylopentadienyl)cobalt dicarbonyl in refluxing xylenes under irradiation and was consumed after 30 minutes. Surprisingly, despite many attempts, we were unable to isolate η^4-cobalt complexes in pure form, even when oxygen-free conditions were used during the purification.

On the basis of the ^{1}H NMR spectrum of the crude mixture, we could safely assume that the cyclization had occurred but, probably, the existence of strong allylic strains in the resulting complexes associated with their high sensitivity caused their degradation.

Recently, we disclosed that the substitution of the triple bond of an enediyne with a phosphine oxide group greatly enhances the stability of the corresponding complex and thus, the yield of the cyclization.[13a, 14] Furthermore, we have decided to exploit the property of such substituents in the cyclization of allenediynes.

Thus, deprotonation of **3** or **1** with *n*-butyllithium followed by the alkylation of the corresponding lithium-acetylide with diphenylphosphinic chloride afforded the allenediyne **5a** and **5b** in 90% and 87% yields, respectively. Gratifyingly, addition of one equivalent of $CpCo(CO)_2$ to **5a** in boiling THF under irradiation yielded complex **6a** quantitatively as a single diastereomer (Scheme 3). Compound **6a** crystallizes spontaneously from a 1:3 mixture of dichloromethane/hexane and the assigned structure was unambiguously secured by a single crystal X-ray analysis (Figure).



Reagents and conditions: a, $CpCo(CO)_2$ (1 equiv), THF, Δ, hν, **6a**:quantitative; **6b**:66%

Scheme 3

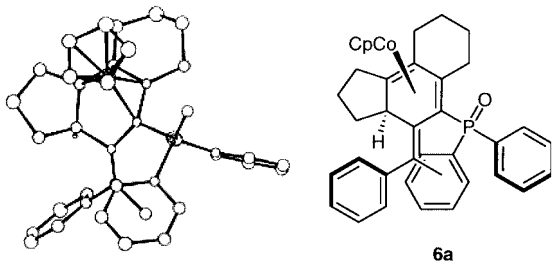
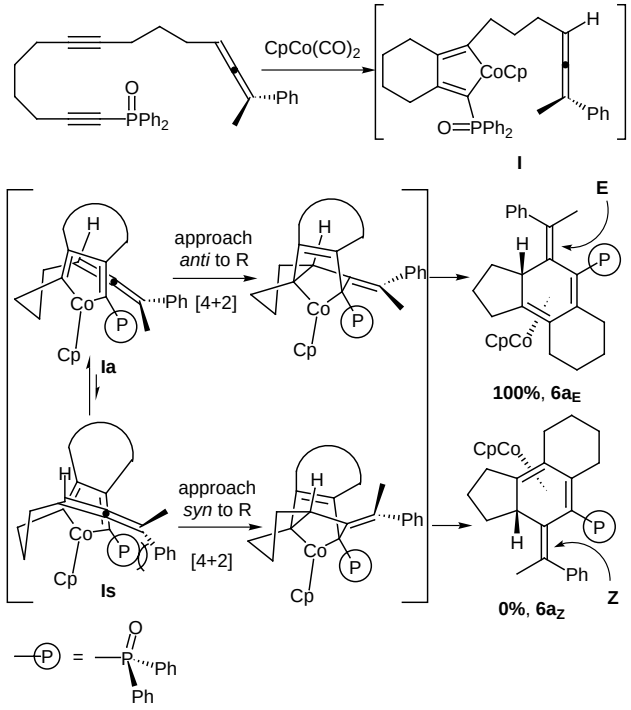


Figure ORTEP Representation of **6a**

The ORTEP representation showed: (i) the [6.6.5] framework, confirming that the internal double bond of the allene had reacted in the process, (ii) the *anti* relationship between the angular H and the cobalt moiety, (iii) the *E* configuration of the exocyclic double bond, (iv) the vinylic aromatic ring is not conjugated with the exocyclic double bond (the strong allylic strain, of the styrene moiety, evidently forces an out of plane rotation of the phenyl group), and (v) the vinylic methyl is placed in the anisotropic cone of one of the two phenyls on phosphorus. The latter effect is particularly helpful for the stereochemical assignment of the double bond. As observed in the ^{1}H NMR spectrum, the vinylic methyl in **6a** is strongly shielded (δ 0.83 ppm) relative to the classical chemical shift. This anisotropic effect was also found with the cycloadduct **6b**, obtained by the cyclization of the compound **5b**, which bears two vinylic methyl groups: one at δ 0.62 ppm and the other at δ 1.32 ppm. Finally, the cyclization is totally chemo- and diastereoselective.

These results could be explained by the most probable mechanism of the [2+2+2] cyclization which may involve a cobaltacyclopentadiene **I**. The latter could react with the internal double bond of the allene moiety following two pathways in the intramolecular [4+2] cycloaddition process which will deliver the tricyclic cobalt complex (Scheme 4).

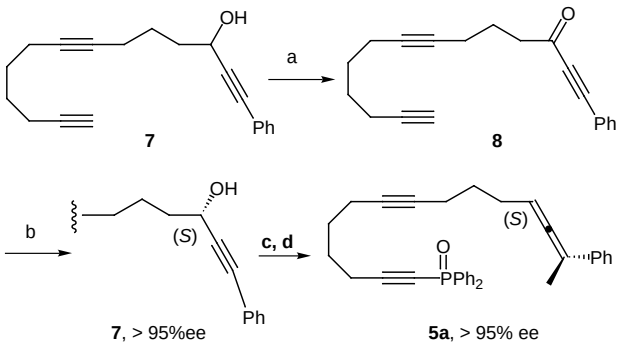


Scheme 4

The most favored approach of the polyunsaturated partners in which the non-bonded interactions and $A_{1,3}$ strains were minimized is the *exo* approach in which the tether is in a chair-like conformation. However, the cobaltacyclopentadiene **I** could approach one or the other face of the allene. The approach *anti* to R (**Ia**) would lead to an intermediary-bridged polycyclic cobaltacyclopentene complex in which the relative configuration of all stereogenic centers is set. After reductive elimination, the final [6.6.5] tricyclic η^4-cobalt complex would have an *E* exocyclic double bond (compound $\mathbf{6a_E}$). An approach *syn* to R (**Is**) would also lead to a [6.6.5] tricyclic compound. However, this compound would possess the *Z* configured exocyclic

double bond ($\mathbf{6a_Z}$). Such an approach is strongly disfavored due to the non-bonding interactions between R, the metallacyclopentadiene, and the phosphine oxide group and in fact, the sole product $\mathbf{6a_E}$ was obtained in the reaction of **5a**.

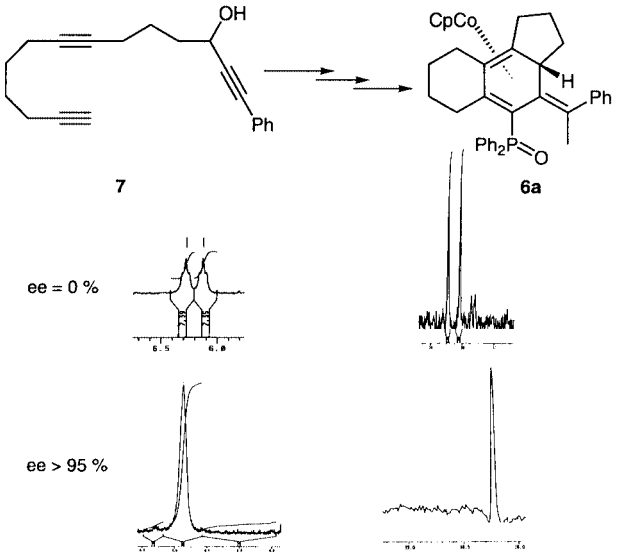
Then, we turned our attention to the cyclization of the optically active allenediyne **5a**. Its straightforward preparation is outlined in Scheme 5.



Reagents and conditions: a, PCC (1.4 equiv), Al_2O_3, CH_2Cl_2, r.t., 60%; b, [Ru]* (5 mol%) = $[(p\text{-cymene})RuCl_2]_2$, (*S*,*S*)-TsDPEN (2 equiv/Ru), *i*-PrOH, 80 °C, 20 min, then KOH (20 equiv/Ru), **8**, *i*-PrOH, r.t., 30 min, 75%; c, i. *n*-BuLi, THF, −78 °C, ii. MsCl, iii. MeCuCNMgBr, 71%; d, i. *n*-BuLi, THF, −78 °C, ii. $Ph_2P(O)Cl$, −78°to 50 °C, 78%

Scheme 5

The propargylic alcohol **7**, obtained as previously described by addition of phenyl lithiumacetylide to aldehyde **4**, was oxidized with PCC on alumina in dichloromethane to afford the ketone **8**. Its enantioselective reduction was of **8** carried out by following two methods. The first one[15] was run in ether in the presence of $LiAlH_4$ and Chirald to afford the chiral alcohol **7** in 73% yield and with an enantiomeric excess of 70% (the ee was determined by ^{1}H NMR by using chiral europium salts). The second method[16] involved a transfer hydrogenation from 2-propanol to the ketone under the action of a chiral ruthenium (II) catalyst. The chiral catalyst was generated in situ by adding KOH into a mixture of $[p\text{-cymeneRuCl}_2]_2$ and (*S*,*S*)-N-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine [(*S*,*S*)-TsDPEN]. Thus, in presence of 5 mol% of catalyst in 2-propanol, **7** was obtained from **8** in 75% yield and with 95% ee.[17] Each step, particularly the addition of the methylcyanocuprate being stereoselective,[18] the optically active allenediyne **5a** was obtained similarly as the racemic one in 55% overall yield. However, the titration of the enantiomers was impossible by using classical methods (GC, HPLC), nevertheless the optically active allenediyne **5a** was submitted to the cyclization protocol and furnished the complex **6a** in 95% yield. But, at this point, the major problem remained the determination of the enantiomeric excess. Indeed, to our knowledge no methods have been reported for the titration of the enantiomeric cobalt complexes. The classical ones have been tried without any success and the ^{1}H NMR chiral resolution reagents were totally ineffective. In our laboratory, we disclosed that the titration of the enantiomeric cobalt complexes bearing a phosphine oxide substituent is possible with ^{31}P NMR in presence of (+) zinc taddolate,[19] obtained by the reaction of dimethylzinc with the (+)-taddol. Thus, in the presence of one equivalent of (+) zinc taddolate, the enantiomers of complex **6a** are totally discriminated by ^{31}P NMR. In fact, the cyclization of the allenediyne **5a** (70% ee) provided the adduct **6a** in 70% ee and the enantiopure **5a** afforded the enantiomerically pure cycloadduct **6a** meaning a total retention of the optical activity during the cyclization.



Scheme 6

In summary, the [2+2+2] cyclization of allenediynes was shown to be completely regio-, chemo- and diastereoselective, the facial selectivity occurring on the less hindered face of the allene. Considering the rapid access to enantiopure allenediynes and the total transfer of the axial into the centered chirality, the cobalt-mediated [2+2+2] cylizations of allenediynes may be regarded as a powerful tool for the construction of enantiomerically pure polycyclic frameworks. Indeed, free ligands could be very interesting as constituting the BCD moiety of steroids bearing an oxidized C-11 position. Approaches to such compounds are under investigations in our laboratories.

14-Phenylpentadeca-12,13-dien-1,7-diyne (3)

In a one-pot operation, a solution of *n*-BuLi in hexane (2.2 M, 1.1 mL, 2.5 mmol) was added dropwise to a THF (10 mL) solution of phenylacetylene (0.255 g, 2.5 mmol) at −78 °C. After stirring for 5 min, a solution of dodeca-5,11-diynal **4**[13] (0.445g, 2.5 mmol) in THF (5 mL) was added. The mixture was stirred for 5 min and methanesulfonyl chloride (0.19 mL, 2.5 mmol) was added at once. The resulting mixture was transferred via a cannula to a solution of the methylcyanocuprate previously generated. To a cooled (−78 °C) THF (100 mL) solution of CuCN (1.34 g, 15 mmol) and

LiCl (1.27 g, 30 mmol) (dried overnight at 100 °C under vacuum 1 mm Hg) was added dropwise a solution of methylmagnesium bromide in Et_2O (2.4 M, 3.1 mL, 7.5 mmol), the mixture was stirred at −78 °C for 15 min. After being stirred at –40 °C for 1 h, the reaction mixture was hydrolyzed at −78 °C with a solution of NH_4Cl/NH_4OH (3:1), warmed to r.t. and diluted with Et_2O (150 mL). The organic layer was separated, washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography (petroleum ether/Et_2O, 95:5) of the crude mixture afforded **3** (0.51 g, 74%).

(*S*)-3: $[\alpha]_D^{25}$ +146.6 (*c* 1.3, $CHCl_3$).

IR (neat): ν = 3290, 2100, 1940, 1590, 1570, 1490, 1450, 1060, 1020 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, 2H, *J* = 7.7 Hz), 7.37 (t, 2H, *J* = 7.7 Hz), 7.24 (t, 1H, *J* = 7.6 Hz), 5.52−5.48 (tq, 1H, *J* = 6.4, 3.0 Hz), 2.32−2.20 (m, 8H), 2.15 (d, 3H, *J* = 3.0 Hz), 2.00 (t, 1H, *J* = 2.5 Hz), 1.72 (quint, 2H, *J* = 7.1 Hz), 1.69−1.59 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.4, 128.4, 137.7, 126.5 (2C), 125.7 (2C), 100.8, 92.5, 84.4, 80.2, 80.1, 68.6, 28.7, 28.2, 28.1, 27.7, 18.4, 18.1, 17.3.

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.10; H, 8.86.

Compound (5a)

To a cooled (−78 °C) THF (20 mL) solution of the allenediyne **3** (0.918 g, 3.3 mmol) was added dropwise a solution of *n*-BuLi in hexane (2.0 M, 1.65 mL, 3.3 mmol). After stirring the solution for 30 min, diphenylphosphinic chloride (0.7 mL, 3.3 mmol) was added. After the addition, the reaction mixture was warmed up quickly with a steam bath (50 °C) and was stirred for 10 min. Then, the mixture was hydrolyzed with sat. NH_4Cl and diluted with CH_2Cl_2 (40 mL). The organic layer was separated, washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography (petroleum ether/EtOAc, 20:80) of the crude mixture yielded **5a** (1.4 g, 90%).

(*S*)-5a $[\alpha]_D^{25}$ +34.7 (*c* 0.13, $CHCl_3$).

IR (neat): ν = 3040, 2180, 1940, 1890, 1810, 1770, 1570, 1480, 1430, 1200, 1140, 1020, 840, 750, 720, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.81 (m, 4H), 7.55−7.40 (m, 6H), 7.33−7.28 (m, 4H), 7.19 (t, 1H, *J* = 7.2 Hz), 5.45 (tq, 1H, *J* = 6.2, 2.8 Hz), 2.46 (dt, 2H, *J* = 6.9, 2.9 Hz), 2.25−2.13 (m, 6H), 2.09 (d, 3H, *J* = 2.8 Hz), 1.77−1.46 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.4, 137.6, 133.5 (d, 2C, *J* = 121 Hz), 132.2 (2C), 131.5 (d, 4C, *J* = 11 Hz), 128.6 (d, 4C, *J* = 14 Hz), 128.4 (2C), 126.5, 125.7 (2C), 109.3 (d, *J* = 30 Hz), 100.7, 92.4, 80.7, 79.6, 75.2 (d, *J* = 173 Hz), 28.5, 28.2, 28.1, 26.7, 19.4, 18.3, 18.2, 17.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.83.

Compound (6a)

$CpCo(CO)_2$ (120 μL, 1 mmol) was added to a refluxing solution of **5a** (0.476 g, 1 mmol) in THF (20 mL), degassed by three freeze-pump-thaw cycles and was irradiated (light from a projector lamp ELW, 240W, 80% of its power). The reaction was monitored by TLC and after its completion, the solvent was removed in vacuo. The residue was purified by flash chromatography to give **6a** (0.598 g, quantitative).

IR (CH_2Cl_2): ν = 2860, 1700,1600, 1160, 1110, 910, 820 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.31−8.27 (m, 4H), 8.13−8.09 (m, 4H), 7.51 (br s, 6H), 7.18−7.09 (m, 3H), 6.79 (d, 2H, *J* = 7.0 Hz), 4.81 (s, 5H), 3.33−3.17 (m, 1H), 2.43 (tq, 2H, *J* = 20.3, 5.6 Hz), 2.19−1.53 (m, 5H), 1.38−1.19 (m, 3H), 0.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 138.1−125.8 (19C), 97.5 (d, *J* = 5 Hz), 88.1 (d, *J* = 11 Hz), 84.9 (5C), 75.7, 53.8 (d, *J* = 8 Hz), 50.0 (d, *J* = 143 Hz), 34.1, 32.9, 30.9, 27.7, 24.2, 23.1, 22.1, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.56.

(*S*)-1-Phenyltetradeca-1,7,13-triyn-3-ol [(*S*)-7]

In a flame-dried flask, under Ar, [*p*-(cymene)$RuCl_2]_2$ (0.196 g, 0.32 mmol) and (*S*,*S*)-TsDPEN (0.234 g, 0.64 mmol) were charged and dissolved in *i*-PrOH (10 mL), and degassed by three freeze-pump-thaw cycles. The mixture was heated at 80 °C for 20 min, the reaction mixture turned from orange to red. KOH (flame-dried under vacuum) (0.09 g, 1.6 mmol) was then added and the mixture was held under fast stirring; the color turned quickly to purple. A degassed solution of the ketone **8** (1.76 g, 6.4 mmol) in *i*-PrOH (50 mL) was added slowly via a cannula at r.t.. After being stirred for 30 min, the reaction mixture was concentrated and subjected to flash chromatography (petroleum ether/EtOAc, 85:15) to yield **(*S*)-7** (1.33 g, 75%, ≥ 90% ee).

$[\alpha]_D^{25}$ +5.36 (*c* 1.35, $CHCl_3$).

IR (neat): ν = 3300, 3290, 2200, 2100, 1950, 1880, 1800, 1440, 1330 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.40 (m, 2H), 7.36−7.20 (m, 3H), 4.63 (t, 1H, *J* = 6.1 Hz), 2.30−2.13 (m, 6H), 1.97 (t, 1H, *J* = 2.5Hz), 1.95−1.86 (m, 2H), 1.79−1.68 (m, 2H), 1.68−1.54 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.8 (2C), 128.5, 128.4 (2C), 122.7, 90.1, 85.0, 84.4, 80.4, 80.1, 68.6, 52.7, 37.0, 28.1, 27.6, 24,9, 18.6, 18.5, 18.4.

Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.28; H, 8.08.

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