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Synthesis of a Simplified Version of Stable Bulky and Rigid Cyclic (Alkyl)(Amino)Carbenes (CAACs), and Catalytic Activity of the Ensuing Gold(I) Complex in the Three-Component Preparation of 1,2-Dihydroquinoline Derivatives

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Abstract

A 95/5 mixture of *cis* and *trans* 2,4-dimethyl-3-cyclohexenecarboxaldehyde (trivertal), a common fragrance and flavor material produced in bulk quantities, serves as the precursor for the synthesis of a stable spirocyclic (alkyl)(amino)carbene, in which the 2-methyl-substituted cyclohexenyl group provides steric protection to an ensuing metal. The efficiency of this carbene as ligand for transition metal based catalysts is first illustrated by the gold(I) catalyzed hydroamination of internal alkynes with secondary dialkyl amines, a process with little precedent. The feasibility of this reaction allows for significantly enlarging the scope of the one-pot three-component synthesis of 1,2-dihydroquinoline derivatives, and related nitrogen-containing heterocycles. Indeed, two different alkynes were used, which include an internal alkyne for the first step.

Keywords

Carbenes; Gold; Hydroamination; Catalysis; Nitrogen-heterocycles

Introduction

In the last few years, spectacular results in homogeneous catalysis have been achieved using bulky phosphines[1] and cyclic diaminocarbenes (NHCs)[2] as strong donor ligands. Recently, we have uncovered a novel family of stable carbenes,[3] the cyclic (alkyl)(amino)carbenes (CAACs) **1** (Fig. 1).[4] The replacement of one of the nitrogen by a carbon center makes CAACs slightly more nucleophilic, but considerably more electrophilic than NHCs.[5] Moreover, due to the presence of a quaternary carbon in a position α to the carbene center, CAACs feature steric environments that differentiate them dramatically from other ligands, including NHCs. Of particular interest, we have shown that spirocyclic CAACs **1a** and **1b** allow the preparation of low-coordinate metal complexes,[6] hitherto not isolable with any other ligands,[7] including the closely related CAAC **1c**. Since low-coordinate metal complexes often play a key role in

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BRIEFS. A gold(I) complex, bearing a stable spirocyclic (alkyl)(amino)carbene, built from a very cheap aldehyde precursor, allows for the one-pot three-component synthesis of 1,2-dihydroquinoline derivatives from secondary (aryl(alkyl) amines, internal and terminal alkynes.

Supporting Information Available. Crystallographic data for **2d** (CCDC number: 723865) and **11a** (CCDC number: 723864), and ^{1}H and ^{13}C NMR spectra for compounds **1d, 2d, 5, 7**, and **11a,b,e,i,j**. This material is available free of charge via the internet at http://pubs.acs.org.

catalytic processes, it is not surprising that, with a few exceptions,[8] CAACs **1a** and 1**b** lead to the best promoters. For example, in the presence of a stoichiometric amount of $KB(C_6F_5)_4$, (CAAC)AuCl complex **2a** efficiently catalyzed hydroamination of alkynes and allenes with ammonia[9a] and basic secondary amines,[9b] and the formation of allenes by coupling enamines and terminal alkynes.[9b, c] In contrast, all attempts to isolate the corresponding (CAAC)AuCl **2c** bearing the flexible CAAC **1c** failed, instead the cationic di(carbene) complex **3c** was obtained,[10] and the latter is of course not catalytically active. The striking differences observed using CAAC **1a,b** versus **1c** are due to the hindrance provided by the adamantyl and menthyl substituents, which are locked in the most sterically demanding conformation with respect to the metal center. In contrast the non-substituted cyclohexyl ring of **1c** can undergo a ring-flip that prevents the protection of the metal. This clearly demonstrates the importance of preventing the ring-flip and forcing the ring to be oriented such as it can protect the metal.

An obvious drawback for many catalytic processes is the cost of the catalyst. Although the flexible CAAC **1c** is conveniently prepared from the commercially available cyclohexane carboxaldehyde, rigid CAACs **1a** and **1b** have to be prepared from the more expensive 2-adamantanone and (−)-menthone, respectively, and an additional homologation step is required. Here we report the synthesis of CAAC **1d**, which is build from a very cheap aldehyde. We show that in the presence of $KB(C_6F_5)_4$, the corresponding gold(I) complex **2d** is as efficient as the analogous complexes bearing **1a** and **1b** for the hydroamination[11–13] of internal alkynes with secondary dialkyl amines, a process which has very rare precedent.[9b,14] Moreover, we demonstrate that **2d** allows for the one-pot synthesis of a variety of 1,2-dihydroquinolines, a family of compounds that have been recognized as important synthetic intermediates, and which exhibit interesting biological activities and potential pharmaceutical applications.[15]

Results

In order to construct a readily available spiro-CAAC bearing a rigid ring oriented in the desired direction, we reasoned that the presence of a single substituent in position β of the aldehyde would be sufficient. Indeed, a reactant should attack *trans* to the substituent, and based on the well-known propensity of electrophiles to approach a ring from the equatorial direction, the substituent should also end up in an equatorial position. The other chair conformation would be highly adverse, and therefore the ring would be locked in the right conformation (Scheme 1). As an economically viable precursor, we chose a 95/5 mixture of *cis* and *trans* 2,4-dimethyl-3-cyclohexenecarboxaldehyde **4**, also named “trivertal”, a common fragrance and flavor material produced in bulk quantities. Enamine **5** was readily prepared in 94% yield, then treated with LDA, and after addition of 3-chloro-2-methyl-1-propene, compound **6** was isolated as a single diastereomer in 90% yield. A hydroiminiumation reaction [4b] using a large excess of HCl gave rise to the cyclic aldiminium salt **7** (74% yield), and subsequent deprotonation with LDA afforded the desired carbene **1d** in 95% yield. Lastly, complex **2d** [(**1d**)AuCl] was prepared in 87% yield by ligand exchange from $(Me_2S)AuCl$. A single crystal X-ray diffraction study demonstrated that, as hypothesized, the cyclohexene ring was in the desired conformation and orientation to protect the metal center (Fig. 2).

We first tested the catalytic activity of **2d**, in the presence of one equivalent $KB(C_6F_5)_4$, for the addition of diethylamine to three representative internal alkynes. These reactions were chosen because, although numerous catalytic systems promote the hydroamination of alkynes,[11–13] so far, only complex **2a**[9a–b] has been reported to catalyze the intermolecular addition of dialkylamines to internal alkynes. We were pleased to find that **2d** was as efficient as **2a** (Table 1).

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Having in hand a readily available precatalyst, we wanted to take advantage of its unusual ability to promote hydroamination of *internal* alkynes with secondary amines. Inspired by the recent works of Yi *et al*.,[16] and Che *et al.*,[17,18] we chose to study the one-pot three-component synthesis of 1,2-dihydroquinoline derivatives. Yi and co-workers reported a ruthenium based catalytic system leading to quinoline derivatives from an aryl amine and excess terminal alkyne, via hydroamination and C-H bond activation reactions. For the hydroamination step, only *terminal* alkynes can be used, since a ruthenium acetylide complex is involved, and therefore the C^2 substituent can only be a methyl group; moreover the second molecule of alkyne reacts quickly, and therefore the C^2 and C^4 substituents are the same (Scheme 2, Eq. 1). The same limitations apply for the reaction developed by Che *et al.*, also a tandem hydroamination-hydroarylation protocol, but microwave assisted, and using a gold(I) catalyst of type (NHC) AuCl/$AgSbF_6$.

Since the gold(I) catalytic system[19] based on **1d** allows for the hydroamination of internal alkynes, even with strongly basic amines, it became clear that the only serious limitation, for the three component cyclization, would be the use of a terminal alkyne for the second step. Consequently the dihydroquinoline skeleton could be readily decorated with three different R^1, R^2 and R^3 substituents (Scheme 2, Eq. 2). The process was initially tested with N-methylaniline (**9a**), 3-hexyne (**8b**), and phenyl acetylene (**10a**) (Table 2). Using 5 mol% of complex **2d** and one equivalent of $KB(C_6F_5)_4$ in C_6D_6, the hydroamination of the internal alkyne **8b** was monitored by NMR spectroscopy. After complete conversion of the reactants, the terminal alkyne **10a** was added. As shown in Table 2, the 2-ethyl-2-propyl-4-phenyl trisubstituted derivative **11a** was obtained in 70% yield, and its structure was unambiguously confirmed by single crystal X-ray analysis. Note, that despite the formation of two regioisomers in the hydroamination of **8b**, only one dihydroquinoline is formed, as expected based on previous studies.[16,17]

The scope of the reaction was surveyed using different arylamines (**9a–e**), and internal (**8b,c**) and terminal alkynes (**10a,b**). Aryl amines featuring *p*-Cl (**9b**) and *p*-OMe (**9c**) substituents are well tolerated. Benzocyclic amines **9d,e** can also be used, giving rise to tricyclic quinoline derivatives, which are important synthetic intermediates and common substructures found in a variety of complex natural products.[20] Both aryl- (**10a**) and alkyl-substituted terminal acetylenes (**10b**) are suitable for the reaction. Lastly, it is interesting to note that the hydroamination of the unsymmetrical internal alkyne **8c** leads to only one cyclization product (**11c,d,f,h,k,l**), although the hydroamination step gives rise to the Markovnikov and anti-Markovnikov regioisomers in 85/15 to 60/40 ratios, depending on the amine. Examination of the crude reaction mixture reveals that, probably because of steric hindrance, only one enamine regioisomer undergoes the cyclization, the other remaining unchanged.

Summary

This study shows that a stable CAAC, which provides steric protection to an ensuing metal, is readily available, from a cheap aldehyde precursor. Its efficiency as a ligand for transition metal based catalysts is illustrated. The corresponding gold(I) complex allows the addition of secondary dialkyl amines to internal alkynes, a process that has little precedent. The feasibility of this reaction allows for significantly enlarging the scope of the one-pot three-component synthesis of 1,2-dihydroquinoline derivatives, and related nitrogen-containing heterocycles. Indeed, two different alkynes can be used, which includes an internal alkyne for the first step.

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Experimental Section

General Considerations

All reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques. Solvents were dried over Na metal or CaH_2. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ^{1}H NMR, and ^{13}C NMR spectra were obtained with a Bruker Advance 300 spectrometer at 298 K. ^{1}H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) referenced to TMS, and were measured relative to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants J are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus system. The Bruker X8-APEX (S^{xvii}) X-ray diffraction instrument with Mo-radiation was used for data collection.

Arylamines and alkynes are commercially available from Sigma-Aldrich and Acros Organics. Gold complex **2a** and $KB(C_6F_5)_4$ were prepared according to the literature.[9c] The spectroscopic data observed for the products of hydroamination of internal alkynes with Et_2NH (Table 1) are identical to those reported in the literature. [9b]

Synthesis of compound 5

2,6-Diisopropylaniline (10.00 mL, 9.40 g, 53.0 mmol) was added at room temperature to a reaction flask containing molecular sieves (15 g) and a toluene solution (25 mL) of trivertal **4** (8.05 mL, 7.54 g, 54.6 mmol). The reaction mixture was stirred for 16 h at 100 °C. Molecular sieves were removed by filtration, and toluene was removed under vacuum. Excess of trivertal **4** was removed by a short path distillation at 60 °C under high vacuum to afford 14.57 g of imine **5** as a yellow oil (94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, ^{3}J = 5.6 Hz, 1H, NCH^{trans}), 7.73 (d, ^{3}J = 5.4 Hz, 1H, NCH^{cis}), 7.29-7.18 (m, 3H, CH), 5.52 (s, 1H, CH^{trans}), 5.46 (s, 1H, CH^{cis}), 3.13 (sept, ^{3}J = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.63-2.55 (m, 1H, CH), 2.46-2.41 (m, 1H, CH), 2.21-2.14 (m, 4H, CH_2), 1.87 (s, 3H, CH_3^{cis}), 1.83 (s, 3H, CH_3^{trans}), 1.44 (d, ^{3}J = 6.7 Hz, 3H, CH_3^{trans}), 1.33 (d, ^{3}J = 6.8 Hz, 12H, CH_3^{cis}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9 (NCH^{cis}), 170.2 (NCH^{trans}), 149.1 (C^q), 137.7 (C^q), 133.3 (C^q), 127.0 (CH^{trans}), 126.5 (CH^{cis}), 124.0 (CH^{cis}), 123.7 (CH^{trans}), 122.9 (CH), 48.0 (CH^{cis}), 44.6 (CH^{trans}), 32.8 (CH^{cis}), 32.2 (CH^{trans}), 29.1 (CH$_2^{cis}$), 28.4 (CH$_2^{trans}$), 28.0 (CH^{trans}), 27.7 (CH^{cis}), 25.8 (CH$_2$), 23.6 (CH$_3^{cis}$), 22.6 (CH$_3^{trans}$), 20.8 (CH$_3^{cis}$), 18.1 (CH$_3^{trans}$); HRMS (ESI): *m/z* calcd for $C_{21}H_{32}N$: 298.2535 $[(M+H)]^+$; found: 298.2537.

Synthesis of compound 6

A solution of **5** (7.07 g, 23.8 mmol) in Et_2O (15 mL) was added slowly to a solution of lithium diisopropylamine (LDA) (2.62 g, 24.5 mmol) in Et_2O (30 mL) at −78 °C. The mixture was stirred and allowed to warm-up to room temperature, then stirred for an additional 3 h. All volatiles were removed under vacuum, and Et_2O (30 mL) was added. After the solution was cooled to −78 °C, 3-chloro-2-methyl-1-propene (2.22 g, 2.40 mL, 24.5 mmol) was slowly added under stirring. After stirring for 2 h, all volatiles were removed under vacuum. Hexanes (20 mL) was added and the suspension was filtered via a filter-cannula. The solvent was evaporated to give 7.52 g of compound **6** as a pale yellow oil (90% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.70 (s, 1H, NCH), 7.19-7.09 (m, 3H, CH), 5.22 (s, 1H, CH), 4.99 (s, 1H, CH_2), 4.84 (s, 1H, CH_2), 3.15 (sept, ^{3}J = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.61 (s, 2H, CH_2), 2.50-2.48 (m, 1H, CH), 1.94-1.84 (m, 4H, CH_2), 1.77 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 1.23 (d, ^{3}J = 6.8 Hz, 12H, CH_3), 1.04 (d, ^{3}J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 171.0 (NCH), 150.1 (C^q), 142.9 (C^q), 137.9 (C^q), 133.7 (C^q), 127.2 (CH), 124.6 (CH), 123.6 (CH), 116.2 (CH$_2$), 45.9 (C^q), 43.8 (CH$_2$), 35.8 (CH), 31.3 (CH$_2$), 28.8 (CH$_2$), 28.1 (CH), 24.2 (CH$_3$), 23.6

(CH_3), 21.3 (CH_3), 17.2 (CH_3); HRMS (ESI): *m/z* calcd for $C_{25}H_{38}N$: 352.3004 $[(M+H)]^+$; found: 352.2996.

Synthesis of iminium salt 7

To a solution of **6** (7.52 g, 23.8 mmol) in hexanes (10 mL) was added a solution of HCl in Et_2O (2M, 25.0 mL, 50.0 mmol) at −78 °C. Precipitation of a white powder was immediately observed. The mixture was warmed to room temperature and stirred for 30 min. Filtration of the precipitate, washing with hexanes (20 mL), and drying under vacuum afforded a white powder. Toluene (25 mL) was added and the reaction mixture heated for 16 h at 110 °C. Volatiles were removed under vacuum to afford **7** as a white powder (7.45 g, 74%). Mp: 218 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.67 (br, HCl_2), 10.07 (s, 1H, NC*H*), 7.40 (t, ^3J = 7.7 Hz, 1H, C*H*), 7.21 (d, ^3J = 7.7 Hz, 2H, C*H*), 5.25 (s, 1H, C*H*), 2.53 (sept, ^3J = 6.6 Hz, 2H, $CH(CH_3)_2$), 2.49-2.46 (m, 1H), 2.36 (s, 2H), 2.01 (t, ^3J = 6.2 Hz, 2H, CH_2), 1.89-1.80 (m, 2H), 1.62 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.24 (d, ^3J = 6.6 Hz, 6H, CH_3), 1.18-1.13 (m, 6H, CH_3), 1.09 (d, ^3J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.3 (N*C*H), 144.6 (C^q), 144.0 (C^q), 134.0 (C^q), 131.9 (*C*H), 129.1 (C^q), 125.4 (*C*H), 125.3 (*C*H), 123.9 (*C*H), 83.0 (C^q), 55.1 (C^q), 46.1 (CH_2), 39.7 (*C*H), 30.4 (CH_2), 30.0 (CH_3), 29.9 (CH_3), 29.2 (*C*H), 28.3, 26.8 (CH_3), 26.7 (CH_3), 26.3 (CH_2), 23.4 (CH_3), 22.2 (CH_3), 18.8 (CH_3); HRMS (ESI): *m/z* calcd for $C_{25}H_{38}N$: 352.3004 $[M]^+$; found: 352.3000.

Synthesis of CAAC 1d

To an Et_2O solution (10 mL) of iminium salt **7** (1.00 g, 2.36 mmol) was added at −78 °C a solution of LDA (0.51 g, 4.72 mmol) in Et_2O (10 mL). The mixture was warmed to room temperature and stirred for 2 h. The solvent was removed in vacuo, and the residue was extracted twice with hexane (10 mL). Removal of the solvent under vacuum afforded 0.79 g of carbene **1d** as a white solid (95% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.27-7.12 (m, 3H), 5.61 (m, 1H, C*H*), 3.17 (sept, ^3J = 6.8 Hz, 2H, $CH(CH_3)_2$), 3.16 (sept, ^3J = 6.7 Hz, 1H, $CH(CH_3)_2$), 2.45-2.37 (m, 1H), 2.32-2.24 (m, 2H), 2.08-1.92 (m, 2H), 1.79 (s, 2H), 1.62 (m, 3H), 1.38 (d, ^3J = 7.2 Hz, 3H, CH_3), 1.26 (d, ^3J = 6.9 Hz, 6H, CH_3), 1.20 (d, ^3J = 6.7 Hz, 3H, CH_3), 1.16-1.14 (m, 9H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 320.3 (N*C*C), 146.4 (C^q), 146.3 (C^q), 138.8 (C^q), 133.1 (C^q), 128.4 (*C*H), 128.1 (*C*H), 124.1 (*C*H), 81.0 (C^q), 65.2 (C^q), 48.7 (CH_2), 41.1, 33.7 (CH_2), 30.0, 29.8, 29.7, 29.4 (CH_2), 26.7, 26.6, 24.4, 22.3, 19.3.

Synthesis of complex 2d

A THF solution (5 mL) of the free carbene **1d** (390 mg, 1.11 mmol) was added to a THF solution (5 mL) of $AuCl(SMe_2)$ (324 mg, 1.10 mmol). The reaction mixture was stirred at room temperature in darkness for 12 h. The solvent was removed under vacuum, and the residue was washed twice with hexane (5 mL). The residue was extracted twice with methylene chloride (10 mL), and the solvent was removed under vacuum, affording complex **2d** as a white solid (564 mg, 87% yield). Mp: 240 °C; ^{1}H NMR (300 MHz, C_6D_6): δ = 7.11 (m, 1H), 7.01 (m, 2H), 5.37 (s, 1H, C*H*), 2.68 (sept, ^3J = 6.6 Hz, 2H, $CH(CH_3)_2$), 2.49 (m, 1H, $CH(CH_3)_2$), 2.11 (s, 1H), 2.09 (m, 2H), 1.83 (s, 3H, CH_3), 1.77-1.61 (m, 2H), 1.53 (d, ^3J = 6.5 Hz, 3H, CH_3), 1.47 (d, ^3J = 6.6 Hz, 3H, CH_3), 1.43-1.38 (m, 1H), 1.23 (d, ^3J = 7.0 Hz, 3H, CH_3), 1.12 (d, ^3J = 6.4 Hz, 3H, CH_3), 1.10 (d, ^3J = 6.5 Hz, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.88 (s, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 240.1 (N*C*C), 145.5 (C^q), 145.4 (C^q), 135.8 (C^q), 134.1 (C^q), 130.4 (*C*H), 127.0 (*C*H), 125.5 (*C*H), 125.3 (*C*H), 78.1 (C^q), 60.3 (C^q), 48.1 (CH_2), 40.0 (*C*H), 35.2 (CH_2), 29.8 (*C*H), 29.7 (CH_2), 29.6 (CH_3), 29.5 (*C*H), 29.3 (CH_3), 27.4 (CH_3), 27.3 (CH_3), 23.7 (CH_3), 23.4 (CH_3), 23.0 (CH_3), 19.1 (CH_3); HRMS (ESI; CH_3CN): *m/z* calcd for $C_{27}H_{40}AuN_2$: 589.2857 $[M{-}Cl{+}CH_3CN]^+$; found: 589.2865.

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General catalytic procedure for the hydroamination of internal alkynes with Et_2NH

In a dried J-Young-Tube, CAAC(AuCl) complex **2a** or **2d** (0.025 mmol) and $KB(C_6F_5)_4$ (0.025 mmol) were loaded under an argon atmosphere. C_6D_6 (0.4 mL) and the internal standard, benzyl methyl ether, were added and after shaking the tube, the internal alkyne **8** (0.5 mmol) and Et_2NH (0.5 mmol) were loaded. The tube was sealed, placed in an oil bath behind a blast shield, and heated at the specified temperature (Table 1). The reaction was monitored by NMR spectroscopy. The products were purified by removal of the solvent and extraction with *n*-hexane.

General catalytic procedure for the three-component coupling reaction of arylamines 9, internal alkynes 8, and terminal alkynes 10

In a dried J-Young-Tube, complex **2d** (0.025 mmol) and $KB(C_6F_5)_4$ (0.025 mmol) were loaded under an argon atmosphere. C_6D_6 (0.4 mL) and the internal standard benzyl methyl ether were added and after shaking the tube, internal alkyne **8** (0.55 mmol) and arylamine **9** (0.5 mmol) were loaded. The tube was sealed, placed in an oil bath behind a blast shield, heated at the corresponding temperature, and the reaction was monitored by NMR spectroscopy. After complete conversion of the reactants, a terminal alkyne **10** (0.5 mmol) was added, and the reaction mixture heated at 100 °C for 24 h. The products were purified by column chromatography.

Characterization of heterocycles 11 resulting from the three-component coupling reactions

11a—^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.36 (m, 5H, C*H*), 7.09 (td, ^3J = 6.8 Hz, ^4J = 1.5 Hz, 1H, C*H*), 6.80 (d, ^3J = 7.4 Hz, 1H, C*H*), 6.49 (t, ^3J = 7.0 Hz, 2H, C*H*), 5.08 (s, 1H, C*H*), 2.80 (s, 3H, CH_3), 1.36-1.27 (m, 6H, CH_2), 1.00 (t, ^3J = 7.4 Hz, 3H, CH_3), 0.94 (t, ^3J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8 (C^q), 140.3 (C^q), 138.5 (C^q), 129.3 (*C*H), 129.2 (*C*H), 128.3 (*C*H), 128.1 (*C*H), 127.3 (*C*H), 125.8 (*C*H), 121.0 (C^q), 114.9 (*C*H), 108.8 (*C*H), 64.1 (C^q), 44.2 (CH_2), 34.3 (CH_2), 30.2 (CH_3), 18.2 (CH_2), 14.7 (CH_3), 9.1 (CH_3); HRMS (ESI): *m/z* calcd for $C_{21}H_{26}N$: 292.2065 $[M+H]^+$; found: 292.2064. Mp: 93–94 °C; Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a hexane solution.

11b—^{1}H NMR (300 MHz, C_6D_6): δ = 7.14 (t, *J* = 1.7 Hz, 1H, C*H*), 7.12 (t, *J* = 1.5 Hz, 1H, C*H*), 6.68 (dd, ^3J = 7.5 Hz, *J* = 0.8 Hz, 1H, C*H*), 6.39 (d, ^3J = 7.1 Hz, 1H, C*H*), 4.78 (s, 1H, C*H*), 2.38 (s, 3H, CH_3), 2.34 (t, ^3J = 7.7 Hz, 2H, CH_2), 1.62-1.48 (m, 6H, CH_2), 1.39-1.22 (m, 4H, CH_2), 1.03-0.81 (m, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.6 (C^q), 135.8 (C^q), 129.6 (*C*H), 125.5 (*C*H), 123.8 (*C*H), 121.3 (C^q), 115.9 (*C*H), 109.4 (*C*H), 63.9 (C^q), 44.7 (CH_2), 34.8 (CH_2), 32.7 (CH_2), 31.6 (CH_2), 30.2 (CH_3), 23.4 (CH_2), 18.6 (CH_2), 15.1 (CH_3), 14.5 (CH_3), 9.4 (CH_3); HRMS (ESI): *m/z* calcd for $C_{19}H_{30}N$: 272.2378 $[M+H]^+$; found: 272.2381.

11c—^{1}H NMR (300 MHz, C_6D_6): δ = 7.37 (dd, ^3J = 7.9 Hz, *J* = 1.6 Hz, 4H, C*H*), 7.19-7.03 (m, 7H, C*H*), 6.60 (t, ^3J = 7.5 Hz, 2H, C*H*), 6.52 (d, ^3J = 8.2 Hz, 1H, C*H*), 5.18 (s, 1H, C*H*), 2.89 (d, ^2J = 12.9 Hz, 1H, CH_2), 2.54 (s, 3H, CH_3), 2.49 (d, ^2J = 12.9 Hz, 1H, CH_2), 1.26 (s, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 146.5 (C^q), 140.8 (C^q), 138.2 (C^q), 137.5 (C^q), 131.4 (*C*H), 129.8 (*C*H), 129.7 (*C*H), 129.7 (*C*H), 128.8 (*C*H), 128.6 (*C*H), 128.2 (*C*H), 127.8 (*C*H), 126.7 (*C*H), 120.7 (C^q), 117.1 (*C*H), 112.0 (*C*H), 59.9 (C^q), 44.3 (CH_2), 31.4 (CH_3), 27.5 (CH_3); HRMS (ESI): *m/z* calcd for $C_{24}H_{24}N$: 326.1909 $[M+H]^+$; found: 326.1913.

11d—^{1}H NMR (300 MHz, C_6D_6): δ = 7.28 (dd, ^3J = 7.9 Hz, ^4J = 1.9 Hz, 2H, C*H*), 7.14-7.06 (m, 4H, C*H*), 6.73 (td, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 2H, C*H*), 6.48 (d, *J* = 8.3 Hz, 1H, C*H*), 5.04 (s, 1H, C*H*), 2.90 (d, ^2J = 12.8 Hz, 1H, CH_2), 2.51 (s, 3H, CH_3), 2.45 (d, ^2J = 12.3 Hz, 1H, C*H*$_2$), 2.28 (t, ^3J = 7.8 Hz, 2H, C*H*$_2$), 1.49-1.43 (m, 4H, C*H*$_2$), 1.24 (s, 3H, C*H*$_3$), 0.84 (t, ^3J = 7.2 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, C_6D_6): δ = 146.4 (*C*^{q}), 138.5 (*C*^{q}), 134.0 (*C*^{q}), 131.3 (*C*H), 129.3 (*C*H), 128.2 (*C*H), 127.7 (*C*H), 126.6 (*C*H), 123.8 (*C*H), 121.9 (*C*^{q}), 116.9 (*C*H), 111.7 (*C*H), 59.9 (*C*^{q}), 45.1 (*C*H$_2$), 32.4 (*C*H$_2$), 31.4 (*C*H$_3$), 31.3 (*C*H$_2$), 27.5 (*C*H$_3$), 23.4 (*C*H$_2$), 14.5 (*C*H$_3$); HRMS (ESI): *m*/*z* calcd for $C_{22}H_{28}N$: 306.2222 [*M*+*H*]$^+$; found: 306.2217.

11e—^{1}H NMR (300 MHz, C_6D_6): δ = 7.19 (d, *J* = 1.7 Hz, 1H, C*H*), 7.07 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H, C*H*), 6.07 (d, *J* = 8.6 Hz, 1H, C*H*), 4.72 (s, 1H, C*H*), 2.23 (s, 3H, C*H*$_3$), 2.14 (t, ^3J = 7.5 Hz, 2H, C*H*$_2$), 1.49-1.35 (m, 6H, C*H*$_2$), 1.28-1.16 (m, 4H, C*H*$_2$), 0.96-0.82 (m, 9H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0 (*C*^{q}), 134.9 (*C*^{q}), 129.7 (*C*^{q}), 128.7 (*C*H), 126.8 (*C*H), 123.7 (*C*H), 123.0 (*C*^{q}), 110.3 (*C*H), 64.1 (*C*^{q}), 44.6 (*C*H$_2$), 34.7 (*C*H$_2$), 32.2 (*C*H$_2$), 31.1 (*C*H$_2$), 30.2 (*C*H$_3$), 23.2 (*C*H$_2$), 18.5 (*C*H$_2$), 15.0 (*C*H$_3$), 14.4 (*C*H$_3$), 9.3 (*C*H$_3$); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{29}NCl$: 306.1989 [*M*+*H*]$^+$; found: 306.1987.

11f—^{1}H NMR (300 MHz, C_6D_6): δ = 7.19 (t, *J* = 2.4 Hz, 2H, C*H*), 7.13-7.12 (m, 4H, C*H*), 6.97 (d, ^3J = 7.8 Hz, 2H, C*H*), 4.98 (s, 1H, C*H*), 2.76 (d, ^2J = 13.1 Hz, 1H, C*H*$_2$), 2.41 (d, ^2J = 13.1 Hz, 1H, C*H*$_2$), 2.37 (s, 3H, C*H*$_3$), 2.09 (t, ^3J = 6.7 Hz, 2H, C*H*$_2$), 1.39-1.30 (m, 4H, C*H*$_2$), 1.17 (s, 3H, C*H*$_3$), 0.79 (t, *J* = 7.2 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, C_6D_6): δ = 144.9 (*C*^{q}), 138.1 (*C*^{q}), 133.4 (*C*^{q}), 131.2 (*C*H), 128.8 (*C*H), 128.6 (*C*H), 128.3 (*C*H), 127.6 (*C*^{q}), 126.8 (*C*H), 123.6 (*C*H), 124.6 (*C*^{q}), 112.5 (*C*H), 60.1 (*C*^{q}), 45.3 (*C*H$_2$), 31.9 (*C*H$_2$), 31.4 (*C*H$_3$), 30.8 (*C*H$_2$), 27.5 (*C*H$_3$), 23.2 (*C*H$_2$), 14.4 (*C*H$_3$); HRMS (ESI): *m*/*z* calcd for $C_{22}H_{27}NCl$: 340.1832 [*M*+*H*]$^+$; found: 340.1836.

11g—^{1}H NMR (300 MHz, C_6D_6): δ = 6.97 (d, *J* = 2.9 Hz, 1H, C*H*), 6.72 (dd, *J* = 8.7 Hz, *J* = 2.9 Hz, 1H, C*H*), 6.31 (d, *J* = 8.7 Hz, 1H, C*H*), 4.86 (s, 1H, C*H*), 3.48 (s, 3H, C*H*$_3$), 2.42 (s, 3H, C*H*$_3$), 2.31 (t, ^3J = 7.5 Hz, 2H, C*H*$_2$), 1.66-1.56 (m, 2H, C*H*$_2$), 1.54-1.46 (m, 4H, C*H*$_2$), 1.35-1.26 (m, 4H, C*H*$_2$), 0.91 (t, ^3J = 7.2 Hz, 3H, C*H*$_3$), 0.84 (t, ^3J = 7.3 Hz, 6H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.7 (*C*^{q}), 142.3 (*C*^{q}), 135.5 (*C*^{q}), 127.2 (*C*H), 122.8 (*C*^{q}), 113.6 (*C*H), 111.7 (*C*H), 109.6 (*C*H), 63.5 (*C*^{q}), 55.8 (*C*H$_3$), 44.3 (*C*H$_2$), 34.4 (*C*H$_2$), 32.7 (*C*H$_2$), 31.5 (*C*H$_2$), 30.4 (*C*H$_3$), 23.3 (*C*H$_2$), 18.6 (*C*H$_2$), 15.1 (*C*H$_3$), 14.5 (*C*H$_3$), 9.5 (*C*H$_3$); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{32}NO$: 302.2484 [*M*+*H*]$^+$; found: 302.2479.

11h—^{1}H NMR (300 MHz, C_6D_6): δ = 7.32 (d, ^3J = 7.0 Hz, 1H, C*H*), 7.12-7.05 (m, 5H, C*H*), 7.01 (d, *J* = 2.8 Hz, 1H, C*H*), 6.84 (d, *J* = 8.7 Hz, 1H, C*H*), 5.11 (s, 1H, C*H*), 3.48 (s, 3H, C*H*$_3$), 2.91 (d, ^2J = 13.2 Hz, 1H, C*H*$_2$), 2.54 (s, 3H, C*H*$_3$), 2.48 (d, ^2J = 13.2 Hz, 1H, C*H*$_2$), 2.30 (t, ^3J = 7.1 Hz, 2H, C*H*$_2$), 1.53-1.41 (m, 4H, C*H*$_2$), 1.26 (s, 3H, C*H*$_3$), 0.78 (t, ^3J = 7.2 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, C_6D_6): δ = 152.4 (*C*^{q}), 145.5 (*C*^{q}), 138.7 (*C*^{q}), 133.9 (*C*^{q}), 131.3 (*C*H), 129.0 (*C*H), 128.2 (*C*H), 127.4 (*C*^{q}), 126.9 (*C*H), 121.0 (*C*H), 115.5 (*C*H), 114.1 (*C*H), 59.5 (*C*^{q}), 55.6 (*C*H$_3$), 44.0 (*C*H$_2$), 32.4 (*C*H$_2$), 31.6 (*C*H$_3$), 31.2 (*C*H$_2$), 26.8 (*C*H$_3$), 23.3 (*C*H$_2$), 14.5 (*C*H$_3$); HRMS (ESI): *m*/*z* calcd for $C_{23}H_{30}NO$: 336.2327 [*M*+*H*]$^+$; found: 336.2324.

11i—^{1}H NMR (300 MHz, C_6D_6): δ = 7.37 (d, *J* = 1.8 Hz, 1H, C*H*), 7.35 (d, *J* = 1.4 Hz, 1H, C*H*), 7.20-7.17 (m, 3H, C*H*), 6.90 (d, ^3J = 7.5 Hz, 1H, C*H*), 6.81 (dd, ^3J = 7.3 Hz, ^4J = 0.7 Hz, 1H, C*H*), 6.44 (t, ^3J = 7.4 Hz, 1H, C*H*), 4.88 (s, 1H, C*H*), 2.84 (t, *J* = 5.4 Hz, 2H, C*H*$_2$), 2.56 (t, *J* = 5.3 Hz, 2H, C*H*$_2$), 1.71-1.60 (m, 6H, C*H*$_2$), 1.49-1.42 (m, 2H, C*H*$_2$), 1.04-0.98 (m, 3H, C*H*$_3$), 0.88 (t, ^3J = 7.1 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, C_6D_6): δ = 143.7 (*C*^{q}), 141.4 (*C*^{q}), 139.7 (*C*^{q}), 130.3 (*C*H), 129.8 (*C*H), 128.8 (*C*H), 127.7 (*C*H), 127.5 (*C*H), 125.4 (*C*H), 121.1 (*C*^{q}), 120.3 (*C*^{q}), 115.5 (*C*H), 63.7 (*C*^{q}), 43.7 (*C*H$_2$), 41.8 (*C*H$_2$), 33.7 (*C*H$_2$), 29.1 (*C*H$_2$), 22.4 (*C*H$_2$), 18.8 (*C*H$_2$), 15.2 (*C*H$_3$), 9.6 (*C*H$_3$); HRMS (ESI): *m*/*z* calcd for $C_{23}H_{28}N$: 318.2222 [*M*+*H*]$^+$; found: 318.2215.

11j—^{1}H NMR (300 MHz, C_6D_6): δ = 6.98 (d, ^3J = 7.5 Hz, 1H, C*H*), 6.81 (d, ^3J = 7.2 Hz, 1H, C*H*), 6.56 (t, ^3J = 7.4 Hz, 1H, C*H*), 4.74 (s, 1H, C*H*), 2.83 (t, *J* = 5.4 Hz, 2H, CH_2), 2.55 (t, *J* = 6.2 Hz, 2H, CH_2), 2.33 (t, ^3J = 7.4 Hz, 2H, CH_2), 1.69-1.49 (m, 8H, CH_2), 1.41-1.27 (m, 4H, CH_2), 1.02-0.94 (m, 6H, CH_3), 0.87 (t, ^3J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 143.8 (C^q), 135.9 (C^q), 130.0 (*C*H), 125.0 (*C*H), 122.5 (*C*H), 120.6 (C^q), 119.9 (C^q), 115.4 (*C*H), 63.5 (C^q), 44.1 (CH_2), 41.8 (CH_2), 34.0 (CH_2), 33.1 (CH_2), 31.7 (CH_2), 29.3 (CH_2), 23.5 (CH_2), 22.4 (CH_2), 18.6 (CH_2), 15.2 (CH_3), 14.5 (CH_3), 9.6 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{21}H_{32}N$: 298.2535 $[M+H]^+$; found: 298.2527.

11k—^{1}H NMR (300 MHz, C_6D_6): δ = 7.41 (d, ^3J = 6.9 Hz, 2H, C*H*), 7.19-7.14 (m, 5H, C*H*), 7.08-7.03 (m, 4H, C*H*), 6.87 (d, ^3J = 7.3 Hz, 1H, C*H*), 6.56 (t, ^3J = 7.4 Hz, 1H, C*H*), 5.16 (s, 1H, C*H*), 2.99 (d, ^2J = 12.7 Hz, 1H, CH_2), 2.91-2.86 (m, 2H, CH_2), 2.61 (d, ^2J = 12.7 Hz, 1H, CH_2), 2.53 (t, ^3J = 7.0 Hz, 2H, CH_2), 1.66 (t, ^3J = 7.8 Hz, 2H, CH_2), 1.27 (s, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 142.5 (C^q), 141.2 (C^q), 138.4 (C^q), 137.6 (C^q), 131.5 (*C*H), 129.7 (*C*H), 129.6 (*C*H), 129.2 (*C*H), 128.8 (*C*H), 128.3 (*C*H), 127.8 (*C*H), 127.5 (C^q), 126.7 (*C*H), 125.5 (*C*H), 123.2 (C^q), 116.6 (*C*H), 59.2 (C^q), 43.1 (2CH_2), 28.9 (CH_2), 26.6 (CH_3), 22.8 (CH_2); HRMS (ESI): *m*/*z* calcd for $C_{26}H_{26}N$: 352.2065 $[M+H]^+$; found: 352.2060.

11l—^{1}H NMR (300 MHz, C_6D_6): δ = 7.15-7.05 (m, 6H, C*H*), 6.87 (d, ^3J = 6.8 Hz, 1H, C*H*), 6.68 (t, ^3J = 7.5 Hz, 1H, C*H*), 5.03 (s, 1H, C*H*), 3.00–2.89 (m, 3H, CH_2), 2.62-2.51 (m, 3H, CH_2), 2.32 (t, *J* = 8.0 Hz, 2H, CH_2), 1.63-1.57 (m, 4H, CH_2), 1.51-1.44 (m, 2H, CH_2), 1.26 (s, 3H, CH_3), 0.84 (t, ^3J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 142.4 (C^q), 138.7 (C^q), 134.2 (C^q), 131.4 (*C*H), 128.6 (*C*H), 128.2 (*C*H), 127.6 (C^q), 127.3 (C^q), 127.1 (*C*H), 126.5 (*C*H), 122.6 (*C*H), 116.5 (*C*H), 59.2 (C^q), 44.0 (CH_2), 42.9 (CH_2), 32.7 (CH_2), 31.3 (CH_2), 29.0 (CH_2), 26.6 (CH_3), 23.4 (CH_2), 22.6 (CH_2), 14.5 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{24}H_{30}N$: 332.2378 $[M+H]^+$; found: 332.2373.

11m—^{1}H NMR (300 MHz, C_6D_6): δ = 7.41 (d, ^3J = 7.8 Hz, 2H, C*H*), 7.21-7.17 (m, 3H, C*H*), 6.92 (d, ^3J = 7.6 Hz, 1H, C*H*), 6.85 (d, ^3J = 7.2 Hz, 1H, C*H*), 6.46 (t, ^3J = 7.1 Hz, 1H, C*H*), 4.89 (s, 1H, C*H*), 3.12 (t, ^3J = 7.1 Hz, 2H, CH_2), 2.73 (t, ^3J = 6.9 Hz, 2H, CH_2), 1.63-1.49 (m, 4H, CH_2), 1.10-1.05 (m, 2H, CH_2), 1.01 (t, ^3J = 6.9 Hz, 3H, CH_3), 0.87 (t, ^3J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 150.9 (C^q), 140.1 (C^q), 139.2 (C^q), 129.3 (*C*H), 128.9 (*C*H), 127.9 (*C*H), 127.3 (C^q), 127.0 (*C*H), 125.3 (C^q), 124.9 (*C*H), 123.3 (*C*H), 116.3 (*C*H), 62.7 (C^q), 45.3 (CH_2), 43.3 (CH_2), 33.4 (CH_2), 28.6 (CH_2), 18.8 (CH_2), 15.2 (CH_3), 9.7 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{22}H_{26}N$: 304.2065 $[M+H]^+$; found: 304.2062.

11n—^{1}H NMR (300 MHz, C_6D_6): δ = 6.92 (d, ^3J = 7.6 Hz, 1H, C*H*), 6.86 (dd, ^3J = 7.3 Hz, ^4J = 1.0 Hz, 1H, C*H*), 6.57 (t, ^3J = 7.4 Hz, 1H, C*H*), 4.70 (s, 1H, C*H*), 3.10 (t, *J* = 8.7 Hz, 2H, CH_2), 2.71 (t, *J* = 8.5 Hz, 2H, CH_2), 2.34 (t, ^3J = 7.1 Hz, 2H, CH_2), 1.61-1.50 (m, 6H, CH_2), 1.38-1.30 (m, 4H, CH_2), 0.99 (t, ^3J = 7.1 Hz, 3H, CH_3), 0.88 (t, ^3J = 7.3 Hz, 3H, CH_3), 0.86 (t, ^3J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 151.0 (C^q), 136.3 (C^q), 127.2 (C^q), 125.0 (C^q), 124.5 (*C*H), 124.1 (*C*H), 121.3 (*C*H), 116.1 (*C*H), 62.3 (C^q), 45.2 (CH_2), 43.5 (CH_2), 33.5 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 28.6 (CH_2), 23.3 (CH_2), 18.7 (CH_2), 15.2 (CH_3), 14.5 (CH_3), 9.7 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{30}N$: 284.2378 $[M+H]^+$; found: 284.2371.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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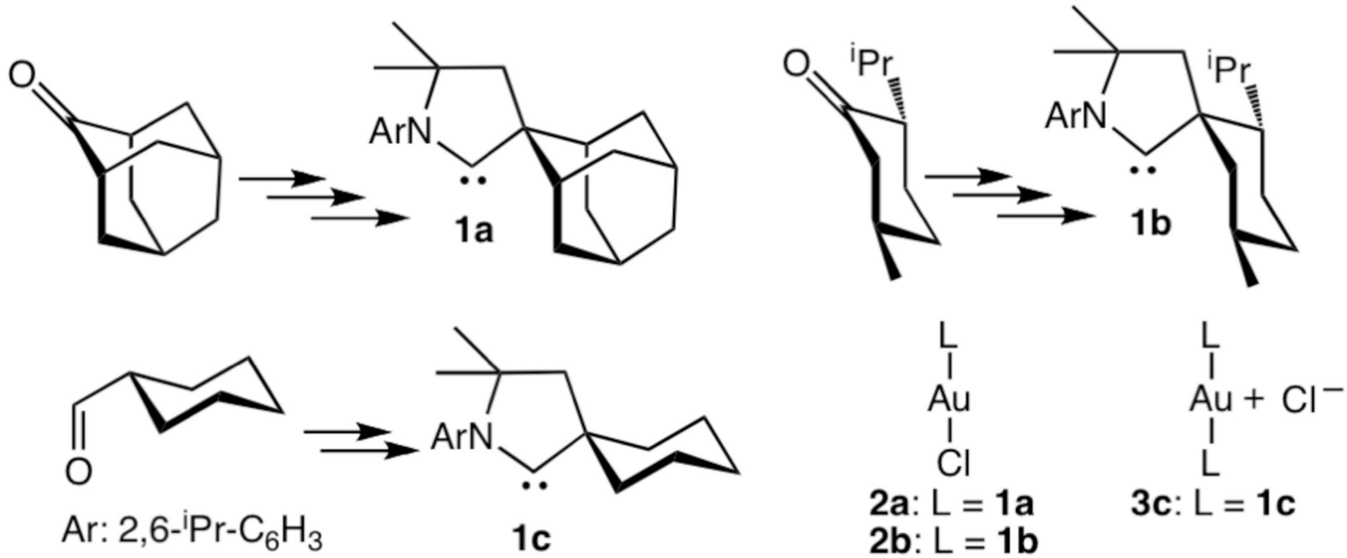


Figure 1.
CAACs **1a–c** and their precursors, and the corresponding gold complexes **2a,b** and **3c**.

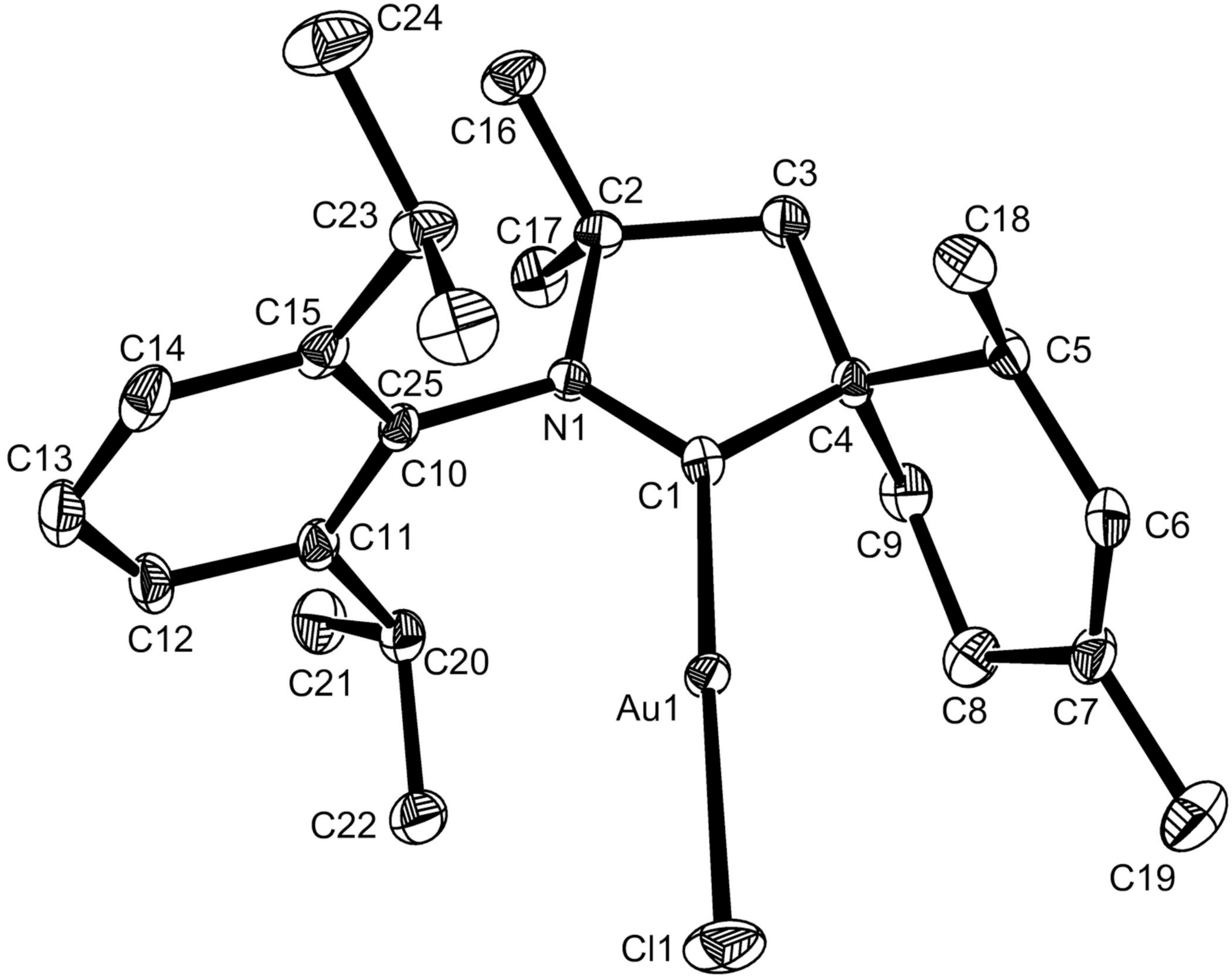
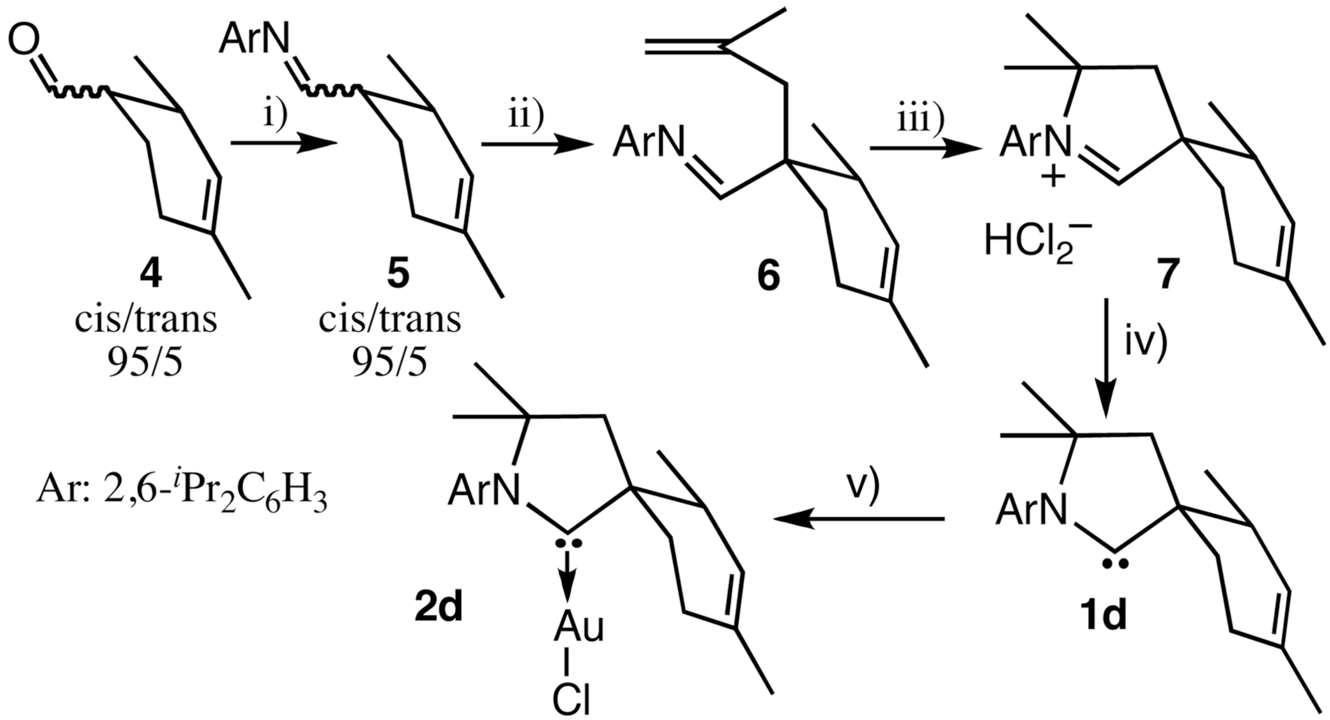


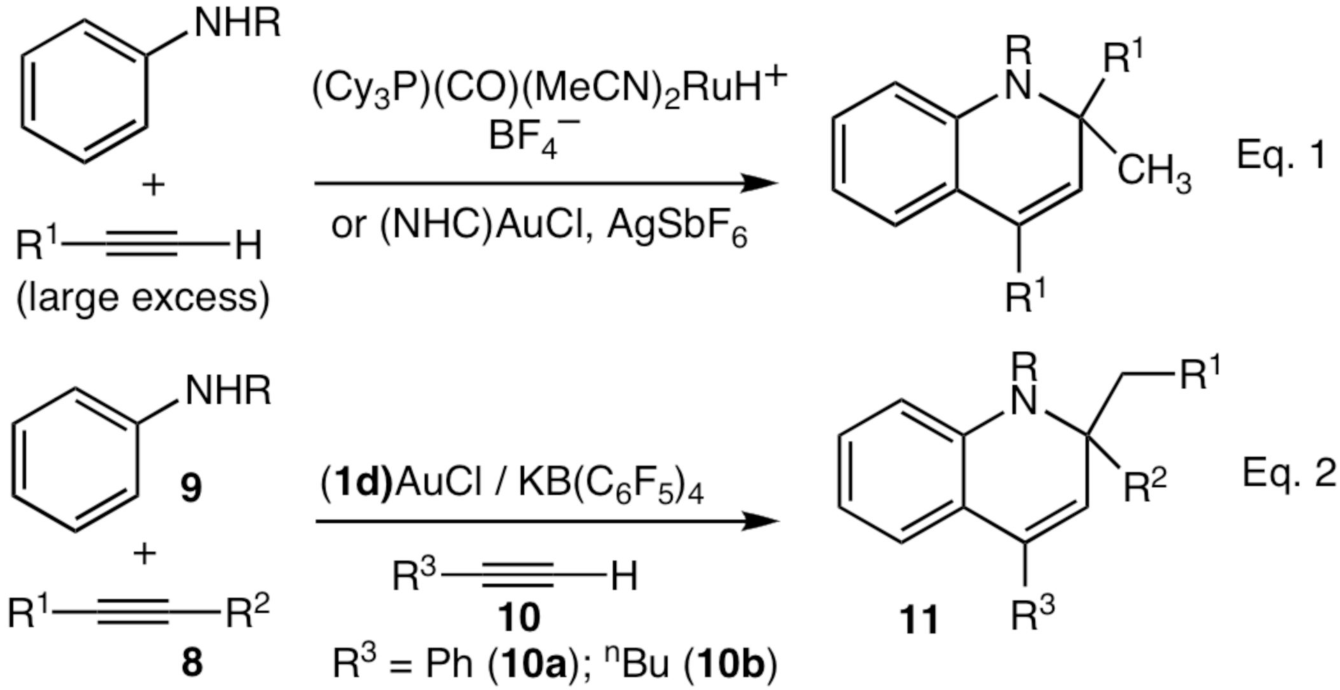
Figure 2.
Molecular structure of one enantiomer of **2d** (50% thermal ellipsoids are shown). Hydrogen atoms have been omitted for clarity.



Scheme 1.

Synthesis of carbene **1d** and gold chloride complex **2d**a (**2d** has been redrawn)

[a] Reagents and conditions: i) $ArNH_2$, molecular sieves, toluene, 100 °C, 16 h, 94%; ii) LDA, Et_2O, −78 °C to rt, 3 h, then 3-chloro-2-methyl-1-propene, −78 °C to rt, 2 h, 90%; iii) HCl (2.1 eqs), toluene, 110 °C, 16 h, 74%; iv) LDA, Et_2O, −78 °C to rt, 2 h, 95%; v) $AuCl(SMe_2)$, THF, rt, 12h, 87%.

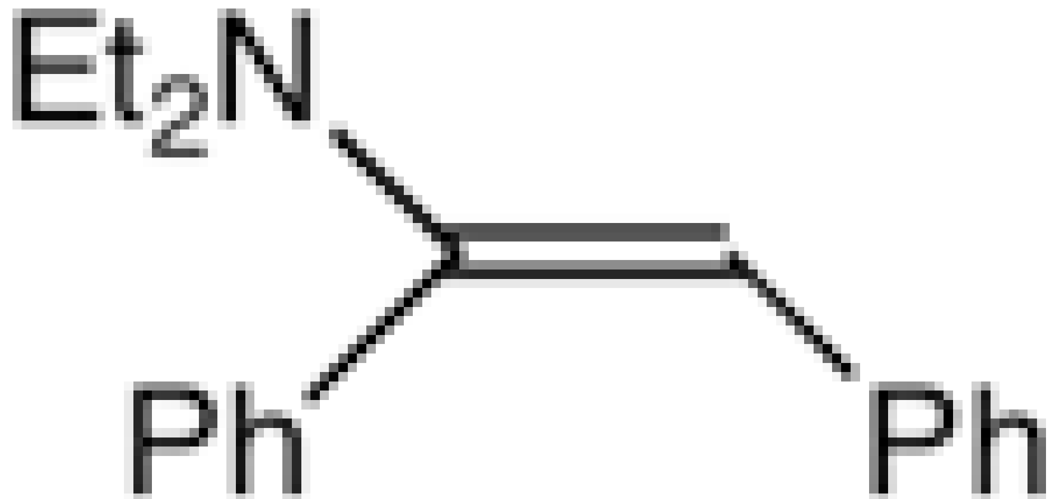
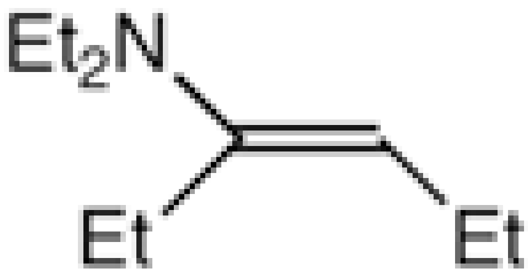
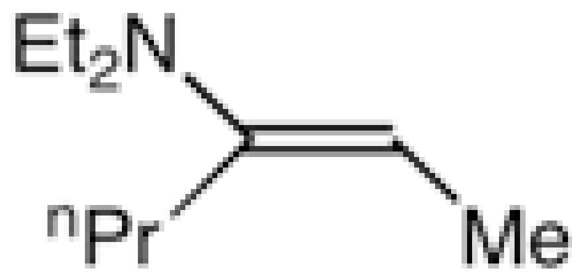


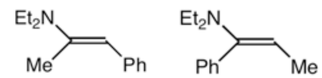
Scheme 2.

Scope of previously reported catalytic systems (Eq.1),[16,17] compared to the one described here (Eq. 2)

Table 1

Compared efficiency of Gold(I) complexes **2**, bearing CAAC ligand **1a** and **1d** for the hydroamination of internal alkynes with Et_2NH[a]

Alkyne	L	*T* (°C)	*t* (h)	Products		Yield[b](%)
PhCCPh	**1a**	90	20			98
8a	**1d**	90	20			92
EtCCEt						
8b	**1a**	110	16	43%	57%	94
	1d	110	20	39%	61%	93

Alkyne	L	*T* (°C)	*t* (h)	Products		Yield[b](%)
PhCCMe						
8c	**1a**	120	20	57%	43%	89
	1d	120	20	52%	48%	92

[a](L)AuCl complex (5 mol%), $KB(C_6F_5)_4$ (5 mol%), Et_2NH (0.5 mmol), alkyne (0.5 mmol), C_6D_6 (0.4 mL).

[b]Yields are determined by ^1H NMR using benzylmethyl ether as an internal standard.

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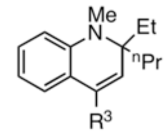
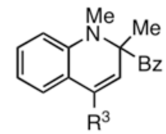
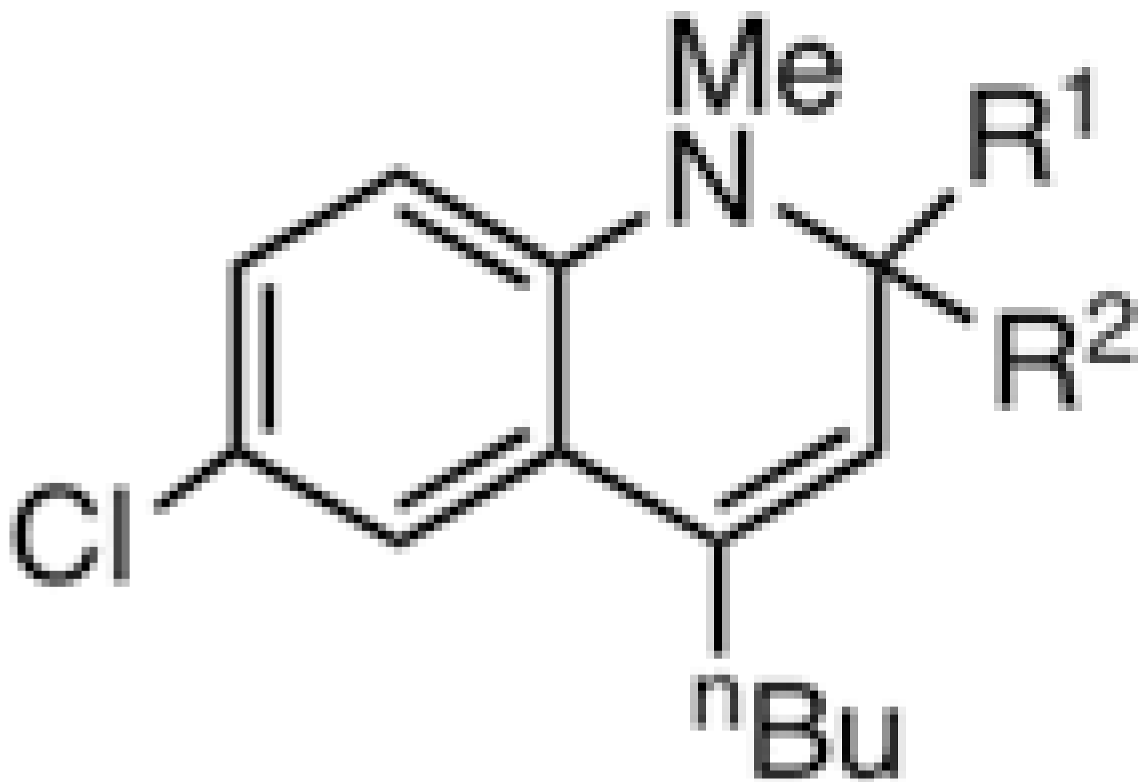
l alkynes[a]

Internal alkyne	Terminal alkyne	Products		Yield[b]%
8b	**10a**		R^3 = Ph, **11a**	70
	10b		R^3 = ^{n}Bu, **11b**	77
8c	**10a**		R^3 = Ph, **11c**	83
	10b		R^3 = ^{n}Bu, **11d**	71
8b	**10b**		R^1 = Et, R^2 = ^{n}Pr, **11e**	68

Internal alkyne	Terminal alkyne	Products	Yield[b]%
8c		R^1 = Me, R^2 = Bz, **11f**	79[c]

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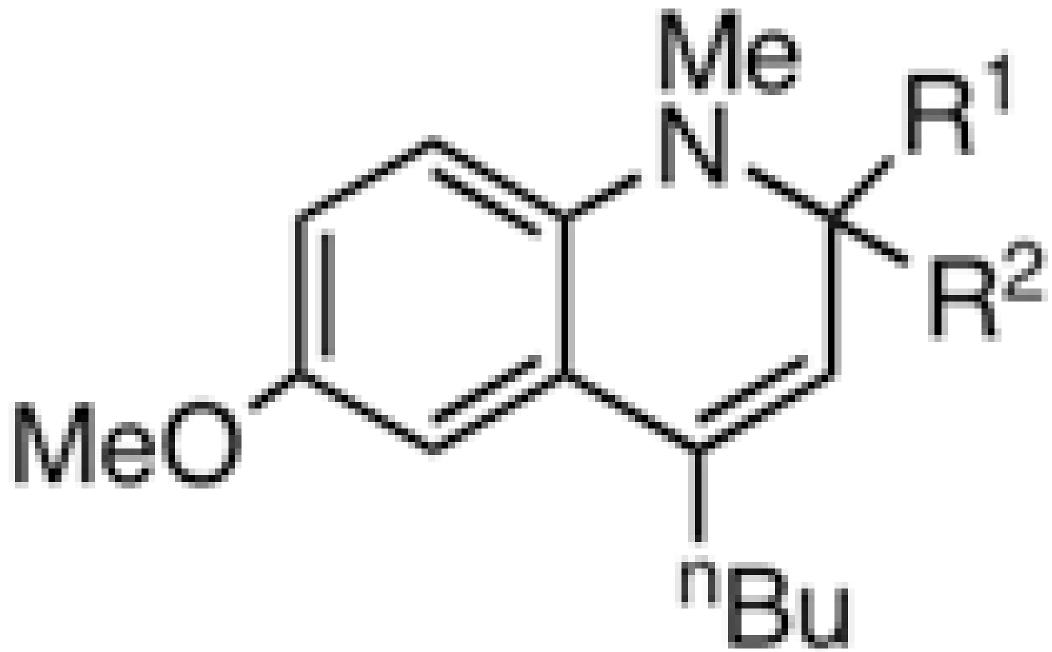
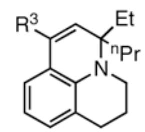
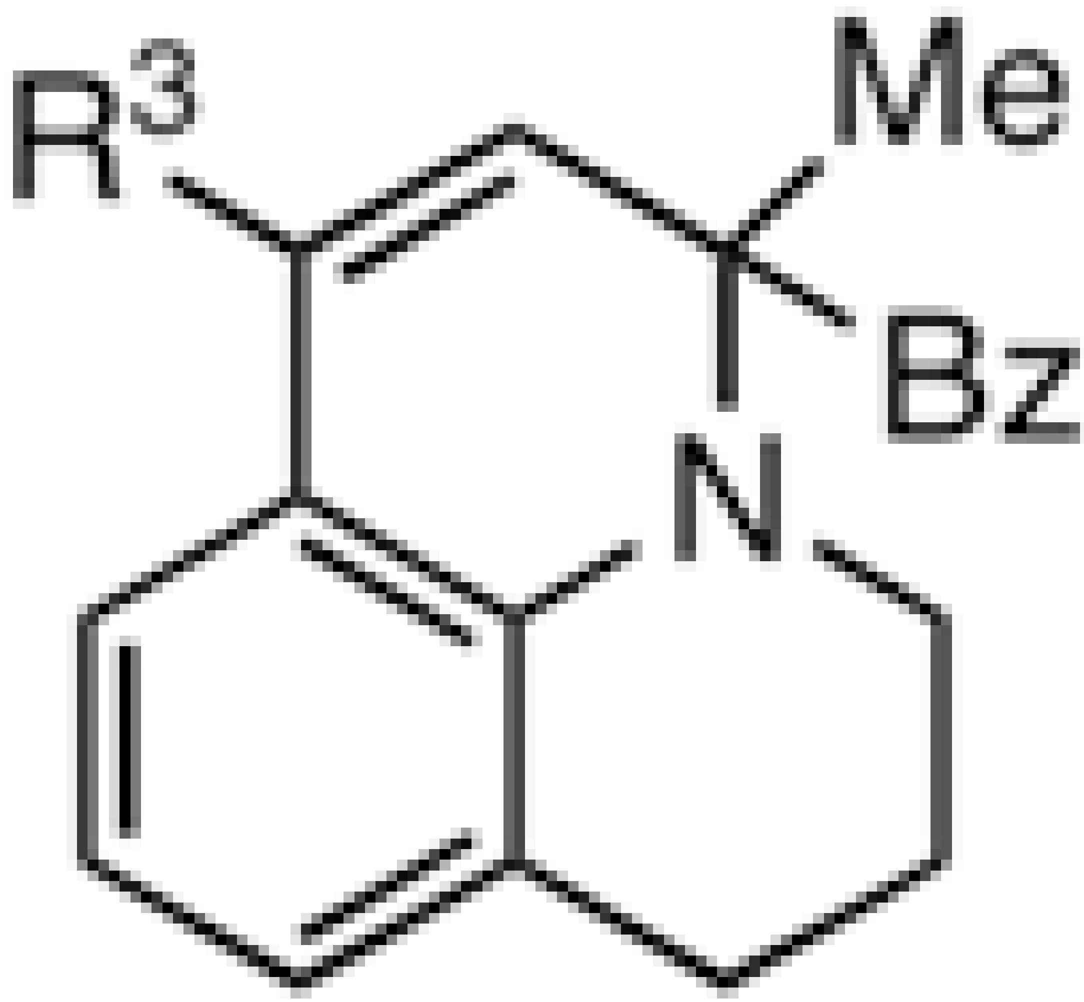
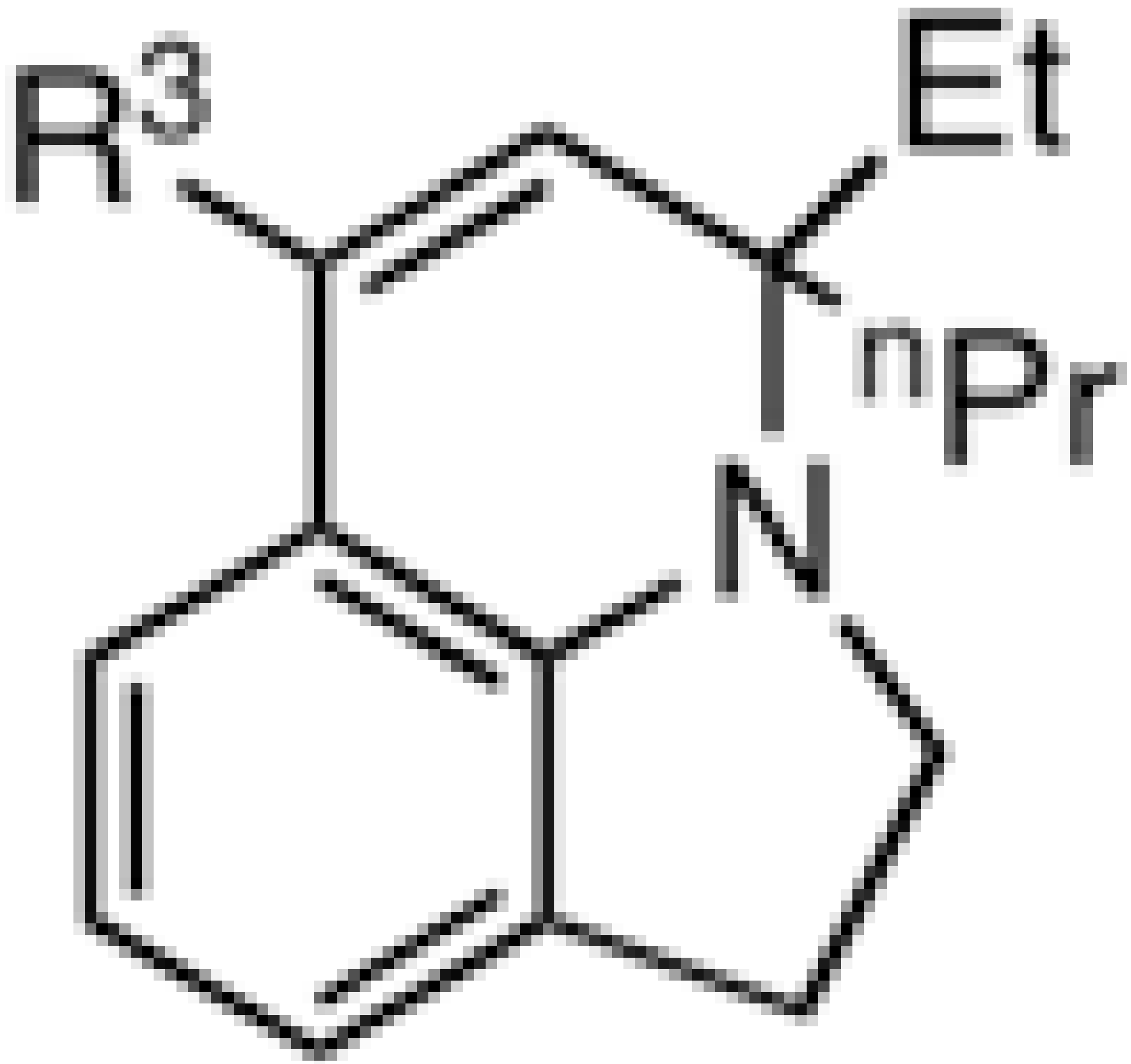
Internal alkyne	Terminal alkyne	Products		Yield[b]%
8b			R^1 = Et, R^2 = ^{n}Pr, **11g**	77
8c	**10b**		R^1 = Me, R^2 = Bz, **11h**	61[c]

Internal alkyne	Terminal alkyne	Products		Yield[b]%
	10a		R^3 = Ph, **11i**	76
8b	**10b**		R^3 = ^{n}Bu, **11j**	65[c]

Internal alkyne	Terminal alkyne	Products		Yield[b]%
8c	10a		R^3 = Ph, **11k**	53[c]
	10b		R^3 = ^{n}Bu, **11l**	56[c]

Internal alkyne	Terminal alkyne	Products		Yield[b]%
8b	10a		R^3 = Ph, **11m**	66[d]
	10b		R^3 = ^{n}Bu, **11n**	73[d]

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[a] **2d** complex (5 mol%), $KB(C_6F_5)_4$ (5 mol%), aryl amine **9** (0.5 mmol), internal alkyne **8** (0.55 mmol), C_6D_6 (0.4 mL). Reaction mixture heated at 120 °C till amine was completely consumed. Terminal alkyne **10** (0.5 mmol), 100 °C, 24 h.

[b] Yields are based on arylamine **9**, and determined by ^1H NMR using benzylmethyl ether as an internal standard.

[c] Hydroamination step at 100 °C.

[d] Hydroamination step at 88 °C