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Gold(III) (C^N) complex-catalyzed synthesis of propargylamines via a three-component coupling reaction of aldehydes, amines and alkynes

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ABSTRACT

Propargylamines are synthesized in high yields via a gold(III) (C^N) complex-catalyzed three-component coupling reaction of aldehydes, amines and alkynes in water at 40 °C. Excellent diastereoselectivities (up to 99:1) have been achieved when chiral prolinol derivatives are employed as the amine component. Notably, the [Au(C^N)Cl_2] complex (N^CH = 2-phenylpyridine) could be repeatedly used for 10 reaction cycles, leading to an overall turnover number of 812.

1. Introduction

Propargylamines are versatile building blocks for organic synthesis. They are generally used as precursors for the synthesis of N-containing heterocyclic compounds such as pyrrolidines, oxazoles and pyrroles [1], and as key intermediates for natural product synthesis [2]. Conventionally, propargylamines are synthesized by nucleophilic attack of lithium acetylides or Grignard reagents to imines or their derivatives [3,4]. However, these methods require the use of stoichiometric amount of organometallic reagents and strictly controlled reaction conditions. In addition, protection of sensitive functional groups, such as aldehyde, is necessary. Thus, there has been an ongoing interest to develop transition metal catalysts for C–H bond activation of terminal alkynes under mild reaction conditions [5]. Complexes of iridium [6], indium [7], zinc [8], copper [1c,9] and silver [10] have been developed as catalysts for the activation of acetylides for subsequent nucleophilic attack to imines or iminium ions to give propargylamines.

Recently, gold catalysis has emerged to be an active research area in organic synthesis [11]. The $AuBr_3$-catalyzed synthesis of propargylamines via a three-component coupling reaction of aldehydes, amines and alkynes in water was firstly reported by Li's group [12,13]. To extend and broaden the practical applications of gold catalysis, gold(III) complexes have been employed as catalysts for organic transformations. Furthermore, by changing the substituents on the ligand, the electronic and steric properties, and thus the catalytic activity, of the gold(III) complexes can be fine-tuned [14].

As part of our ongoing program to develop gold-catalyzed organic transformation reaction [15], we have employed gold(III) salen complexes as catalysts for the synthesis of chiral propargylamines [15b]. For the search of more stable gold(III) catalysts, gold(III) (C^N) complex [Au(C^N)Cl_2] (N^CH = 2-phenylpyridine) was found to be catalytically active towards this three-component coupling reaction. Here we report the first use of a gold(III) (C^N) complex [Au(C^N)Cl_2] as a recyclable catalyst for the synthesis of propargylamines via a three-component coupling reaction of aldehydes, amines and alkynes in water at 40 °C. By employing chiral prolinol derivatives as the amine component, excellent diastereoselectivities (99:1) have been achieved. The [Au(C^N)Cl_2] complex could be repeatedly used for 10 consecutive cycles leading to 812 product turnovers in total.

2. Results and discussion

2.1. Synthesis of [Au(C^N)Cl_2]

Gold(III) (C^N) complex [Au(C^N)Cl_2] (N^CH = 2-phenylpyridine) was synthesized according to a reported procedure [16]. In brief, $KAuCl_4$ and 2-phenylpyridine were stirred in 1:1 CH_3CN/H_2O at room temperature for 30 min. [Au(HC^N)Cl_3] complex was isolated as a yellow precipitate, which was refluxed overnight

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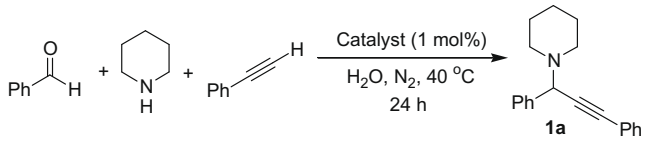
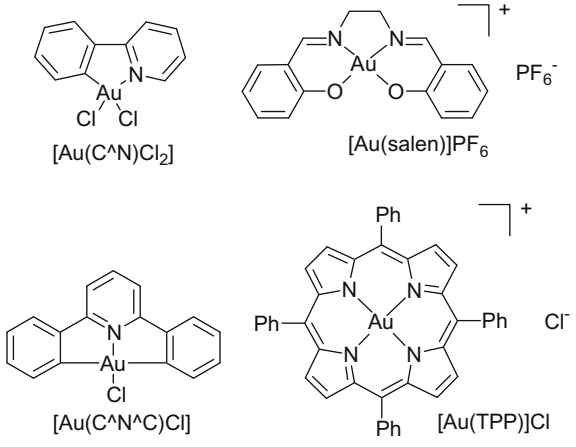
Table 1
Effects of different gold(III) catalysts on the synthesis of propargylamines.[a]



Entry	Catalyst	Conversion[b]	Yield[c]
1	[Au(C^N)Cl$_2$]	99	82
2	[Au(salen)PF$_6$]	99	94
3	[Au(C^N^C)Cl]	10	–
4	[Au(TPP)Cl]	0	–

[a] Reaction conditions: 1 mmol of benzaldehyde, 1.1 mmol of piperidine, 1.5 mmol of phenylacetylene, 1 mL of H_2O, 40 °C, 24 h.
[b] Determined by ^{1}H NMR analysis of crude reaction mixture based on benzaldehyde conversion.
[c] Isolated yield based on benzaldehyde conversion.



in 1:1 CH_3CN/H_2O solution. The product [Au(C^N)Cl$_2$] was filtered as a pale yellow solid, and was identified by ^{1}H NMR spectroscopy.

2.2. Ligand effects on the synthesis of propargylamines

The catalytic activities of a panel of gold(III) complexes with different *N*-donor ligands towards the three-component coupling reaction of benzaldehyde, piperidine and phenylacetylene in water at 40 °C were examined. As depicted in Table 1, [Au(C^N)Cl$_2$] was found to have a comparable activity as that of [Au(salen)PF$_6$], leading to 99% aldehyde conversion and 82% product yield (Table 1, entry 1).

The complex [Au(C^N^C)Cl] (CH^N^CH = 2,6-diphenylpyridine) is much less reactive and only 10% aldehyde conversion was found (entry 3). Interestingly, a stable [Au(C^N^C)] acetylide complex was collected after the coupling reaction by flash column chromatography, and its ^{1}H NMR spectrum is consistent with its chemical formulation [17]. We have also examined the catalytic activity of gold(III) porphyrin complex [Au(TPP)Cl] (H_2TPP = *meso*-tetraphenylporphyrin), but no substrate conversion was observed (entry 4).

2.3. Substrate scope

To examine the scope of this gold(III) (C^N) complex-catalyzed three-component coupling reaction, we extended the catalysis to different combinations of aldehydes, amines and alkynes. As depicted in Table 2, coupling of benzaldehyde with piperidine and phenylacetylene led to propargylamine **1a** in 82% yield based on 99% benzaldehyde conversion (entry 1). Reducing the catalyst loading of [Au(C^N)Cl$_2$] to 0.25 mol% gave **1a** with complete benzaldehyde conversion in 24 h. Further reducing the catalyst loading to 0.1 mol% led to 74% benzaldehyde conversion within 24 h and 97% conversion (70% yield) when the reaction time was extended to 48 h, representing a turnover number of 970 within 48 h. The reaction also worked well for aliphatic cyclohexylaldehyde (86% yield; entry 2), pyrrolidine (76% yield; entry 3), and trimethylsilyl (TMS) substituted alkyne (69% yield; entry 4).

Coupling reactions using chiral prolinol derivatives as the amine component were studied, and excellent diastereoselectivities (up to 99:1) were obtained. As depicted in Table 3, the α-substituents of the prolinol derivatives play a key role on the diastereoselectivities. With prolinol methyl ether as the amine component, propargylamine **2a** was obtained with a diastereomeric ratio of 94:6 in 83% yield (entry 1). The absolute configuration of **2a** was assigned with reference to the literature data [18], and that of others were assigned accordingly. Improved diastereoselectivity (96:4) was obtained when prolinol coupled with benzaldehyde and phenylacetylene to give **2b** (62% yield; entry 2). Chiral propargylamine **2c** was obtained in high diastereoselectivity by using prolinol of opposite chirality (75% yield, dr = 96:4, entry 3). Apart from prolinol derivatives, the coupling reaction involving 1-(2-pyrrolidinylmethyl)-pyrrolidine was also performed, giving **2d** in 94% yield with 97:3 dr (entry 4). The coupling of bulky α,α-diphenylprolinol gave the highest diastereoselectivity (99:1) where propargylamine **2e** was synthesized in good yield (83% yield based on 69% aldehyde conversion; entry 5). These experiments revealed that the chiral substituents on the prolinol derivatives are able to transfer chirality to the newly formed sp^3 carbon center. In addition, the methoxy, the hydroxyl and tertiary amine groups remained intact after the coupling reactions.

We extended our study to the coupling reaction of prolinol with aldehydes and acetylenes bearing various functionalities (Table 4). The coupling of benzaldehydes bearing various *p*-substituents with prolinol and phenylacetylene were performed. Excellent diastereoselectivities were observed in all attempts (entries 1–4). Propargylamines **2f–i** bearing different substituents in the *p*-position were obtained in up to 99% yield and up to 98:2 dr (entries 1–4). Propargylamine **2j** bearing *m*-Cl substituent was obtained in 85% yield with good diastereoselectivity (96:4; entry 5).

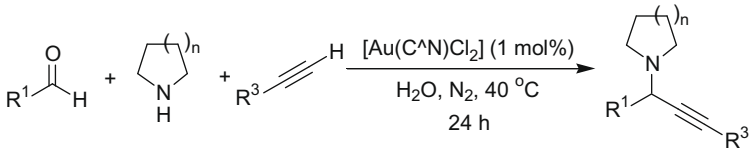
The [Au(C^N)Cl$_2$]-catalyzed three-component coupling reaction also worked well for various alkynes. Coupling of benzaldehyde, prolinol and 1-ethynylcyclohexene led to the formation of **2k** in 84% yield with diastereoselectivity of 96:4 (Table 4, entry 6). Changing the alkyne component to 1-ethynyl-5-methoxynaphthalene gave propargylamine **2l** in 71% yield with 96:4 dr (entry 7). The coupling reaction of *p*-methylphenylacetylene with benzaldehyde and prolinol proceeded smoothly and gave propargylamine **2m** in 92% yield with diastereoselectivity of 95:5 (entry 8).

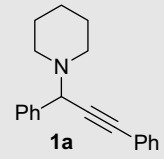
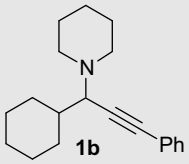
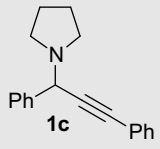
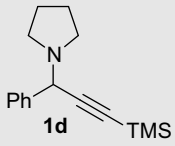
By reacting isophthalaldehyde bearing two aldehyde groups with prolinol and 1-ethynylcyclohexene, propargylamine **2n** was obtained in 87% yield with dr = 93:7 based on 75% aldehyde conversion (entry 9). When phenylacetylene was used, propargylamines **2o** and **2p** in a ratio of 1.7:1 in 83% total yield were obtained (entry 10).

2.4. Mechanism

To provide insight on the gold(III) (C^N) complex-catalyzed three-component coupling reaction, the conversion of aldehyde against reaction time was monitored. The study was conducted as follows: coupling reaction of benzaldehyde, piperidine and phenylacetylene was performed under the reaction conditions as depicted in entry 1 of Table 1. An aliquot amount of reaction mixture was taken out at regular time interval for the determination of aldehyde conversion by ^{1}H NMR analysis.

Table 2
Synthesis of propargylamines catalyzed by [Au(C^N)Cl_2].[a]



Entry	R^1	*n*	R^3	Product	Conversion[b]	Yield[c]
1	Ph	2	Ph	 **1a**	99	82
2	C_6H_{11}	2	Ph	 **1b**	100	86
3	Ph	1	Ph	 **1c**	98	76
4	Ph	1	TMS	 **1d**	95	69

[a] Reaction conditions: 1 mmol of aldehyde, 1.1 mmol of amine, 1.5 mmol of alkyne, 1 mL of H_2O, 40 °C, 24 h.
[b] Determined by ^1H NMR analysis of crude reaction mixture based on aldehyde conversion.
[c] Isolated yields based on aldehyde conversion.

As depicted in Fig. 1, the plot of aldehyde conversion against time showed that an induction period of around 2 h was required for the [Au(C^N)Cl_2] catalyst to become catalytically active. The addition of NaCl or $AgNO_3$ did not significantly affect the induction period of the catalysis with [Au(C^N)Cl_2] as catalyst.

We next examined the recyclability of [Au(C^N)Cl_2], and experiments were conducted as follows: coupling reaction of benzaldehyde, piperidine and phenylacetylene was performed under the reaction conditions as depicted in entry 1 of Table 1. After 24 h, the substrate conversion based on benzaldehyde was determined by ^1H NMR analysis of an aliquot of reaction mixture taken out from the reaction flask. An additional portion of starting materials was added into the reaction mixture. Then, the reaction continued for an additional 24 h.

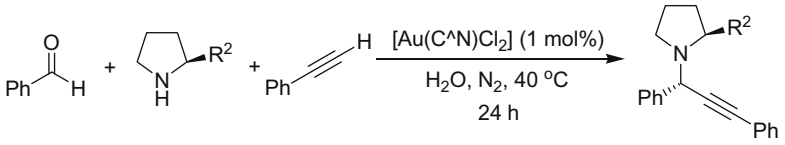
As depicted in Table 5, [Au(C^N)Cl_2] could be repeatedly used for 10 cycles leading to 812 product turnovers in total. In addition, the reaction remained clean without the formation of side product. These experiments demonstrated the recyclability of [Au(C^N)Cl_2]. Comparing to the results obtained from gold(III) salen complex (Fig. 2) [15b], [Au(C^N)Cl_2] exhibited a higher stability.

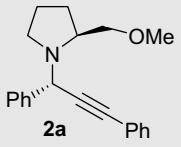
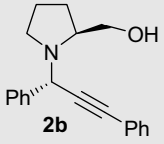
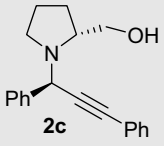
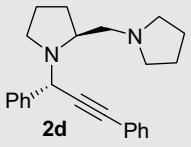
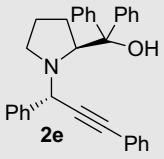
A proposed mechanism for the three-component coupling reaction of aldehyde, amine and alkyne is illustrated in Scheme 1. Aldehyde is first condensed *in situ* with the secondary amine to give an iminium ion, while the gold(III) (C^N) complex activates the C-H bond of terminal alkyne to generate a gold acetylide intermediate. The gold acetylide intermediate undergoes a nucleophilic attack on the iminium ion to give propargylamine.

3. Conclusion

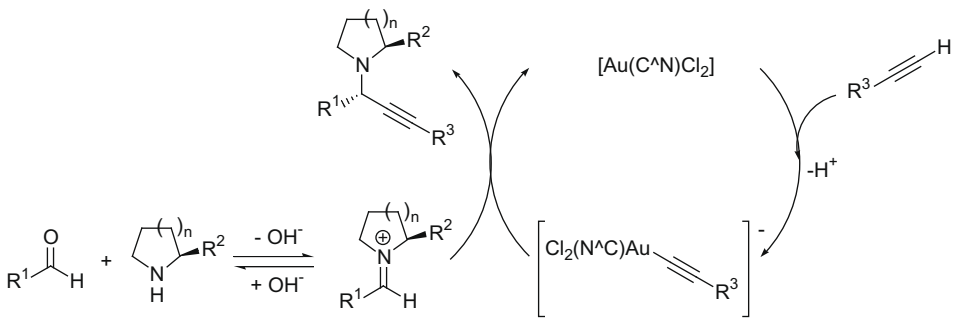
In summary, we have developed a three-component coupling reaction of aldehydes, amines and alkynes catalyzed by [Au(C^N)Cl_2] in water at 40 °C. A variety of propargylamines were synthesized in good to excellent yields. Using chiral prolinol derivatives as the amine component, diastereoselectivities up to 99:1 could be achieved. It was observed that [Au(C^N)Cl_2] was able to catalyze 10 successive reaction cycles, leading to an overall turnover number of 812.

Table 3
Effect of chiral prolinol derivatives on diastereoselectivity.[a]



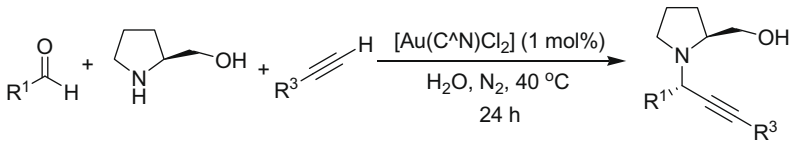
Entry	R^2	Product	Conversion[b]	Yield[c]	dr[d]
1	CH_2OMe	 **2a**	99	83	94:6
2	CH_2OH	 **2b**	78	62	96:4
3	CH_2OH	 **2c**	86	75	96:4
4	$CH_2N(C_4H_8)$	 **2d**	62	94	97:3
5	CPh_2OH	 **2e**	69	83	99:1

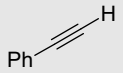
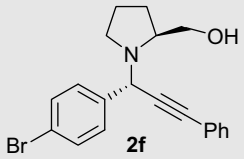
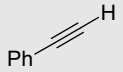
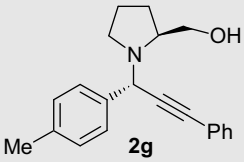
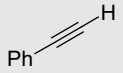
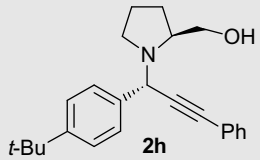
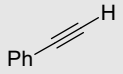
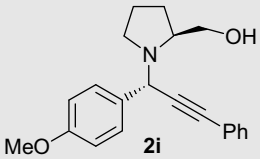
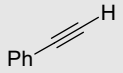
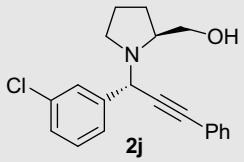
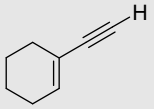
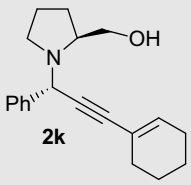
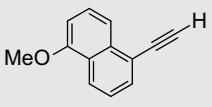
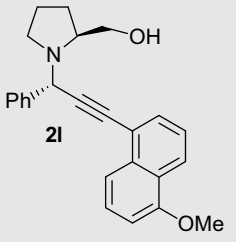
[a] Reaction conditions: 1 mmol of benzaldehyde, 1.1 mmol of amine, 1.5 mmol of phenylacetylene, 1 mL of H_2O, 40 °C, 24 h.
[b] Determined by ^1H NMR analysis of crude reaction mixture based on benzaldehyde conversion.
[c] Isolated yield based on benzaldehyde conversion.
[d] Determined by ^1H NMR analysis of crude reaction mixture.



Scheme 1. Proposed reaction mechanism for the three-component coupling reaction.

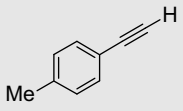
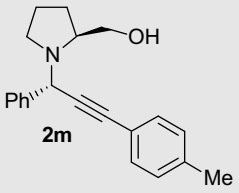
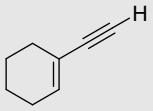
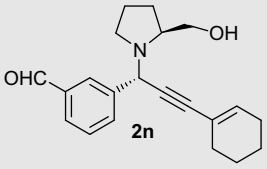
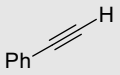
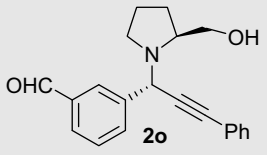
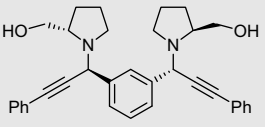
Table 4
Substrate scope on the synthesis of chiral propargylamines catalyzed by [Au(C^N)Cl_2].[a]



Entry	R^1	R^3	Product	Conversion[b]	Yield[c]	dr[d]
1	*p*-BrC_6H_4		 **2f**	100	68	98:2
2	*p*-MeC_6H_4		 **2g**	39	91	96:4
3	*p*-*t*-BuC_6H_4		 **2h**	87	70	97:3
4	*p*-$OMeC_6H_4$		 **2i**	18	99	96:4
5	*m*-ClC_6H_4		 **2j**	100	85	96:4
6	Ph		 **2k**	97	84	96:4
7	Ph		 **2l**	99	71	96:4

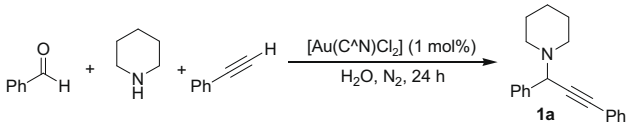
(continued on next page)

Table 4 (*continued*)

Entry	R^1	R^3	Product	Conversion[b]	Yield[c]	dr[d]
8	Ph		 **2m**	99	92	95:5
9	*m*-$CHOC_6H_4$		 **2n**	75	87	93:7
10	*m*-$CHOC_6H_4$		 **2o** and  **2p**	85[e]	83[f]	94:6[g]

[a] Reaction conditions: 1 mmol of aldehyde, 1.1 mmol of amine, 1.5 mmol of alkyne, 1 mL of H_2O, 40 °C, 24 h.
[b] Determined by ^1H NMR analysis of crude reaction mixture based on aldehyde conversion.
[c] Isolated yield based on aldehyde conversion.
[d] Determined by ^1H NMR analysis of crude reaction mixture.
[e] Determined by recovery of isophthalaldehyde.
[f] **2o**:**2p** = 1.7:1.

Table 5
Experiment on the recycling of $[Au(C^N)Cl_2]$.[a]



Cycle	1	2	3	4	5	6	7	8	9	10
Conversion[b]	100	100	92	89	84	76	73	70	67	60

[a] Reaction conditions: 1 mmol of benzaldehyde, 1.1 mmol of piperidine, 1.5 mmol of phenylacetylene, 1 mL of H_2O, 40 °C, 24 h.
[b] Determined by ^1H NMR analysis of crude reaction mixture based on benzaldehyde conversion.

4. Experimental

4.1. General

Gold(III) (C^N) complex $[Au(C^N)Cl_2]$ (N^CH = 2-phenylpyridine) was synthesized according to a reported procedure [16]. All reagents were commercially available and used without further purification. All experiments were carried out under an inert atmosphere of nitrogen. NMR spectra were recorded in $CDCl_3$ on Bruker DX300 or DX400 spectrometer at 25 °C with TMS as an internal standard. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer. IR spectra were recorded, using NaCl or KBr discs, on a Bio-Rad FTS-165 spectrometer.

4.2. General procedure for $[Au(C^N)Cl_2]$-catalyzed three-component coupling reaction

A mixture of $[Au(C^N)Cl_2]$ (0.01 mmol), aldehyde (1.0 mmol), amine (1.1 mmol) and alkyne (1.5 mmol) in water (1 mL) was stirred at 40 °C for 24 h under N_2 atmosphere. The reaction mixture was extracted with diethyl ether or CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4 or $MgSO_4$, filtered, and

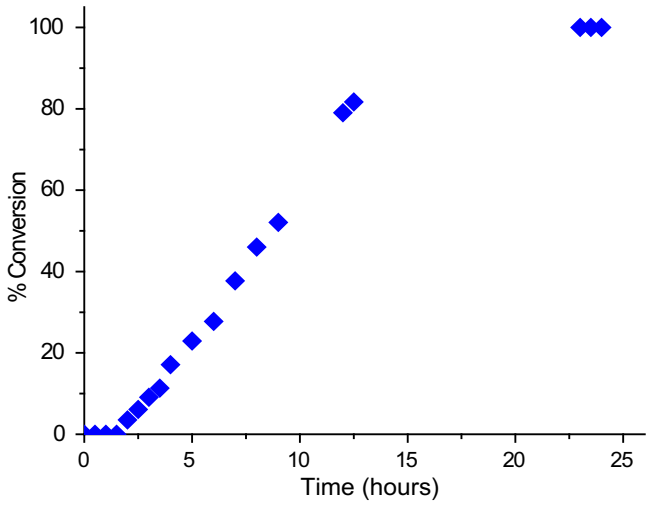


Fig. 1. Reaction profile of [Au(C^N)Cl_2]-catalyzed coupling of benzaldehyde, piperidine and phenylacetylene.

concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel using ethyl acetate–hexane as eluent.

4.3. Characterization

4.3.1. 1-(1,3-diphenylprop-2-ynyl)piperidine (**1a**) [12]

Yellowish oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.30; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2H), 7.53–7.50 (m, 2H), 7.37–7.24 (m, 6H), 4.79 (s, 1H), 2.57–2.54 (m, 4H), 1.61–1.55 (m, 4H), 1.45-1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.51, 131.81, 128.57, 128.27, 128.06, 127.43, 123.34, 87.86, 86.04, 62.36, 50.68, 26.14, 24.42; IR (NaCl, neat, cm^{-1}) 2314; EIMS *m/z* 275 (M^+); HRMS (EI) for $C_{20}H_{21}N$, Calc. 275.1674, found: 275.1672.

4.3.2. 1-(1-cyclohexyl-3-phenylprop-2-ynyl)piperidine (**1b**) [10a]

Yellowish oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.29–7.27 (m, 3H), 3.10 (d, *J* = 9.9 Hz, 1H), 2.63–2.61 (m, 2H), 2.41–2.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.72, 128.19, 127.62, 123.69, 87.94, 85.75, 64.39, 39.61, 31.34, 30.46, 39.72, 26.82, 26.30, 26.12, 24.73; IR (NaCl, neat, cm^{-1}) 2335; EIMS *m/z* 281 (M^+); HRMS (EI) for $C_{20}H_{27}N$, Calc. 281.2143, found: 281.2130.

4.3.3. 1-(1,3-diphenylprop-2-ynyl)pyrrolidine (**1c**) [10a]

Yellowish oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.50–7.47 (m, 2H), 7.39–7.28 (m, 6H), 4.89 (s, 1H), 2.71–2.67 (m, 4H), 1.80–1.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.32, 131.79, 128.32, 128.26, 128.10, 127.61, 123.19, 86.98, 86.56, 59.08, 50.23, 23.49; IR (NaCl, neat, cm^{-1}) 2333; EIMS *m/z* 261 (M^+); HRMS (EI) for $C_{19}H_{19}N$, Calc. 261.1517, found: 261.1506.

4.3.4. 1-(1-phenyl-3-trimethylsilylprop-2-ynyl)pyrrolidine (**1d**)

Yellowish oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.36; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.33–7.31 (m, 2H), 7.28–7.26 (m, 1H), 4.65 (s, 1H), 2.58 (t, *J* = 6.7 Hz, 4H), 1.76 (t, *J* = 6.3 Hz, 4H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.25, 128.26, 128.18, 127.48, 102.92, 91.23, 59.23, 50.06, 23.47, 0.18; IR (NaCl, neat, cm^{-1}) 2163; EIMS *m/z* 257 (M^+); HRMS (EI) for $C_{16}H_{23}NSi$, Calc. 257.1599, found: 257.1589.

4.3.5. (S)-1-((S)-1,3-diphenylprop-2-ynyl)-2-(methoxymethyl)pyrrolidine (**2a**) [18]

Pale yellow oil; analytical TLC (silica gel 60) (30% EtOAc in hexane), R_f = 0.24; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.53–7.48 (m, 2H), 7.40–7.30 (m, 6H), 5.12 (s, 1H), 3.84 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.54 (dd, *J* = 10.9, 2.2 Hz, 1H), 3.31–3.27 (m, 1H), 2.82 (dd, *J* = 9.2, 7.3 Hz, 1H), 2.63 (td, *J* = 8.0, 3.0 Hz, 1H), 1.97–1.92 (m, 1H), 1.87–1.75 (m, 1H), 1.73–1.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.18, 131.85, 128.46, 128.40, 128.37, 128.34, 128.31, 128.09, 127.62, 122.99, 87.83, 85.37, 61.83, 61.75, 56.25, 47.90, 28.04, 23.60; IR (NaCl, neat, cm^{-1}) 3436, 2361, 2341; EIMS *m/z* 291 (M^+); HRMS (EI) for $C_{20}H_{21}NO$, Calc. 291.1623, found: 291.1617.

4.3.6. ((S)-1-((S)-1,3-diphenylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2b**) [15b]

Pale yellow oil; analytical TLC (silica gel 60) (30% EtOAc in hexane), R_f = 0.24; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61–7.59 (d, *J* = 7.2 Hz, 2H), 7.53–7.48 (m, 2H), 7.40–7.30 (m, 6H), 5.12 (s, 1H), 3.86–3.81 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.56–3.51 (dd, *J* = 10.9, 2.2 Hz, 1H), 3.31–3.27 (m, 1H), 2.86–2.77 (dd, *J* = 9.2, 7.3 Hz, 1H), 2.66–2.59 (td, *J* = 8.0, 3.0 Hz, 1H), 1.97–1.92 (m, 1H), 1.87–1.75 (m, 1H), 1.73–1.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.18, 131.85, 128.46, 128.40, 128.37, 128.34, 128.31, 128.09, 127.62, 122.99, 87.83, 85.37, 61.83, 61.75, 56.25, 47.90, 28.04, 23.60; IR (KBr, neat, cm^{-1}) 3436, 2361, 2341; EIMS *m/z* 291 (M^+); HRMS (EI) for $C_{20}H_{21}NO$, Calc. 291.1623, found: 291.1617.

4.3.7. (S)-1-((S)-1,3-diphenylprop-2-ynyl)-2-(pyrrolidin-1-ylmethyl)pyrrolidine (**2d**)

Yellow oil; analytical TLC (silica gel 60) (80% EtOAc in hexane) R_f = 0.17; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.63 (m, 2H), 7.52–7.48 (m, 2H), 7.40–7.22 (m, 6H), 5.56 (s, 1H), 3.22–3.13 (m, 1H), 2.78 (dd, *J* = 12.0, 5.6 Hz, 1H), 2.71 (t, *J* = 8.4 Hz, 1H), 2.64–2.49 (m, 6H), 2.04–1.97 (m, 1H), 1.81–1.75 (m, 4H), 1.71–1.56 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.03, 131.80, 128.27, 128.17, 128.09, 127.96, 127.16, 123.43, 87.48, 86.46, 62.45, 59.57, 56.95,

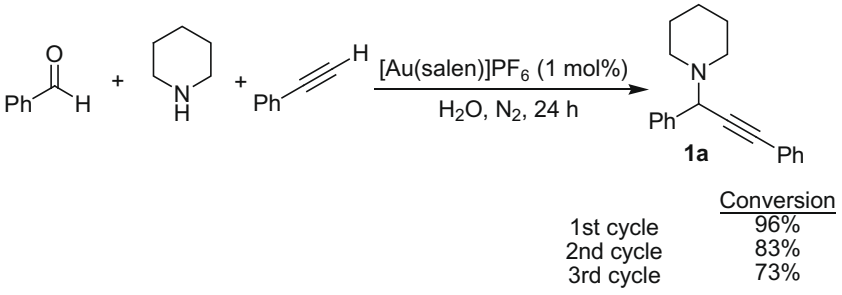


Fig. 2. Recyclability experiment for gold(III) salen complex [15b].

54.97, 47.84, 30.60, 29.69, 23.54, 22.78; IR (NaCl, neat, cm^{-1}) 3427, 2246; EIMS *m/z* 344 (M^+); HRMS (EI) for $C_{24}H_{28}N_2$, Calc. 344.2252, found: 344.2246.

4.3.8. ((S)-1-((S)-1,3-diphenylprop-2-ynyl)pyrrolidin-2-yl)diphenylmethanol (**2e**) [15b]

Pale yellow solid; analytical TLC (silica gel 60) (10% EtOAc in hexane), R_f = 0.39; ^1H NMR (300 MHz, $CDCl_3$) δ 7.86–7.83 (m, 2H), 7.64–7.61 (m, 2H), 7.57–7.54 (m, 2H), 7.40–7.37 (m, 3H), 7.32–7.29 (m, 6H), 7.26–7.21 (m, 3H), 7.20–7.12 (m, 2H), 4.69 (s, 1H), 4.51 (q, *J* = 5.0 Hz, 1H), 4.27 (s, 1H), 2.94 (td, *J* = 9.1, 7.1 Hz, 1H), 1.98–1.82 (m, 1H), 1.81–1.60 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.98, 146.53, 139.19, 131.89, 128.74, 128.43, 128.40, 128.32, 128.12, 128.11, 127.99, 127.90, 127.44, 127.02, 126.68, 126.28, 125.49, 125.46, 123.16, 87.58, 85.83, 77.89, 68.10, 57.90, 49.48, 30.92, 29.89, 24.26; IR (NaCl, neat, cm^{-1}) 3391, 2360; FAB-MS *m/z* 444 (M^++H).

4.3.9. ((S)-1-((S)-1-(4-bromophenyl)-3-phenylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2f**) [15f]

Light yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.09; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52–7.48 (m, 6H), 7.36–7.33 (m, 3H), 5.07 (s, 1H), 3.80 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.54 (dd, *J* = 11.0, 2.6 Hz, 1H), 3.30–3.16 (m, 1H), 2.79–2.75 (m, 1H), 2.00–1.65 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.26, 131.82, 131.52, 131.39, 129.96, 129.78, 128.44, 128.38, 122.68, 121.50, 88.15, 87.71, 62.05, 61.80, 55.83, 47.83, 27.93, 23.53; IR (NaCl, neat, cm^{-1}) 3430, 2359; EIMS *m/z* 369 (M^+); HRMS (EI) for $C_{20}H_{20}BrNO$, Calc. 369.0728, found: 369.0710.

4.3.10. ((S)-1-((S)-1-(4-methylphenyl)-3-phenylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2g**)

Light yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.31; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51–7.46 (m, 4H), 7.33–7.29 (m, 3H), 7.17–7.15 (d, *J* = 7.9 Hz, 2H), 5.07 (s, 1H), 3.82–3.77 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.54–3.49 (dd, *J* = 10.9, 2.4 Hz, 1H), 3.29–3.22 (m, 1H), 2.85–2.76 (td, *J* = 9.2, 7.3 Hz, 1H), 2.66–2.60 (m, 1H), 2.34 (s, 3H), 2.00–1.65 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.19, 136.18, 131.76, 128.94, 128.28, 128.17, 127.93, 122.99, 87.54, 85.61, 61.85, 61.64, 55.94, 47.84, 28.02, 23.51, 21.03; IR (NaCl, neat, cm^{-1}) 3418, 2358; EIMS *m/z* 305 (M^+); HRMS (EI) for $C_{21}H_{23}NO$, Calc. 305.1780, found: 305.1770.

4.3.11. ((S)-1-((S)-1-(4-tert-butylphenyl)-3-phenylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2h**) [15f]

Yellowish oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.10; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54–7.48 (m, 4H), 7.39–7.36 (m, 2H), 7.32–7.30 (m, 3H), 5.08 (s, 1H), 3.80 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.52 (dd, *J* = 10.9, 2.2 Hz, 1H), 3.29–3.23 (m, 1H), 2.87–2.78 (m, 1H), 2.69–2.62 (m, 1H), 1.96-1.67 (m, 4H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.45, 136.14, 131.76, 128.27, 128.15, 127.95, 127.70, 125.16, 123.03, 87.49, 85.68, 61.90, 61.67, 55.88, 47.88, 34.44, 31.32, 28.02, 23.53; IR (NaCl, neat, cm^{-1}) 3430, 2361; EIMS *m/z* 347 (M^+); HRMS (EI) for $C_{24}H_{29}NO$, Calc. 347.2249, found: 347.2243.

4.3.12. ((S)-1-((S)-1-(4-methoxyphenyl)-3-phenylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2i**)

Yellowish oil; analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.20; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52–7.48 (m, 4H), 7.35–7.30 (m, 3H), 6.90–6.87 (d, *J* = 8.7 Hz, 2H), 5.06 (s, 1H), 3.81–3.76 (m, 1H), 3.80 (s, 3H), 3.54–3.50 (dd, *J* = 10.9, 2.4 Hz, 1H), 3.27–3.21 (m, 1H), 2.84–2.59 (m, 2H), 1.99–1.66 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.94, 131.70, 131.28, 129.09, 128.24, 128.13, 122.93, 113.54, 87.50, 85.70, 61.97, 61.58, 55.62, 55.15, 47.78, 28.01, 23.43; IR (NaCl, neat, cm^{-1}) 3430, 2202; EIMS *m/z* 321 (M^+); HRMS (EI) for $C_{21}H_{23}NO_2$, Calc. 321.1729, found: 321.1722.

4.3.13. ((S)-1-((S)-1-(3-chlorophenyl)-3-phenylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2i**) [15f]

Pale yellow oil; analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.31; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.52–7.50 (m, 3H), 7.35–7.34 (m, 3H), 7.29–7.25 (m, 2H), 5.10 (s, 1H), 3.81 (dd, *J* = 11.0, 3.6 Hz, 1H), 3.55 (dd, *J* = 11.0, 1.9 Hz, 1H), 3.29–3.24 (m, 1H), 2.81–2.75 (m, 1H), 2.63–2.58 (m, 2H), 1.98–1.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.28, 134.20, 131.85, 129.56, 128.46, 128.38, 128.14, 127.77, 126.27, 122.64, 88.20, 84.53, 62.07, 61.81, 55.91, 47.87, 28.89, 23.55; IR (KBr, neat cm^{-1}) 3431, 2362; EIMS *m/z* 294 (M^+-CH_2OH); HRMS (EI) for $C_{19}H_{17}NCl$, Calc. 294.1049, found: 294.1046.

4.3.14. ((S)-1-((S)-cyclohexenyl-1-phenylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2k**) [15f]

Yellowish oil; analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.26; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.32–7.28 (m, 2H), 7.24–7.21 (m, 1H), 6.16–6.13 (m, 1H), 4.99 (s, 1H), 3.73 (dd, *J* = 10.9, 3.8 Hz, 1H), 3.49 (dd, *J* = 10.9, 2.5 Hz, 1H), 3.19–3.13 (m, 1H), 2.89 (br, s, 1H), 2.73–2.67 (m, 1H), 2.55–2.50 (m, 1H), 2.19–2.18 (m, 2H), 2.10–2.08 (m, 2H), 1.96–1.76 (m, 2H), 1.67–1.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.34, 134.32, 127.99, 127.94, 127.15, 120.25, 89.43, 82.14, 61.90, 61.49, 56.01, 47.49, 29.46, 27.85, 25.39, 23.30, 22.14, 13.91; IR (NaCl, neat, cm^{-1}) 3412, 2361, 1602; EIMS *m/z* 264 (M^+–CH_2OH).

4.3.15. ((S)-1-((S)-3-(5-methoxynaphthalen-1-yl)-1-phenylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2l**)

Pale yellow solid; analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.25; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.69–7.63 (m, 4H), 7.52–7.50 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.39–7.35 (m, 2H), 7.31–7.27 (t, *J* = 2.4 Hz, 1H), 7.16–7.14 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.09–7.08 (d, *J* = 2.4 Hz, 1H), 5.15 (s, 1H), 3.88 (s, 3H), 3.84–3.70 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.57–3.53 (dd, *J* = 10.9, 2.5 Hz, 1H), 3.34–3.29 (m, 1H), 2.89–2.83 (td, *J* = 9.3, 7.3 Hz, 1H), 2.67–2.62 (m, 1H), 2.04–1.94 (m, 1H), 1.90–1.82 (m, 1H), 1.78–1.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.24, 139.21, 134.08, 131.33, 129.18, 129.14, 128.41, 128.27, 128.08, 127.54, 126.79, 119.42, 117.75, 105.28, 88.26, 84.87, 61.93, 61.78, 56.37, 55.24, 47.90, 28.50, 23.53; IR (NaCl, neat cm^{-1}) 3436, 2361, 2214; EIMS *m/z* 371 (M^+); HRMS (EI) for $C_{25}H_{25}NO_2$, Calc. 371.1885, found: 371.1874.

4.3.16. ((S)-1-((S)-1-phenyl-3-p-tolylprop-2-ynyl)pyrrolidin-2-yl)methanol (**2m**)

Yellowish oil; Analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.40; ^1H NMR (300 MHz, $CDCl_3$) δ 7.61–7.59 (d, *J* = 7.3 Hz, 2H), 7.40–7.38 (d, *J* = 8.0 Hz, 2H), 7.34–7.30 (m, 2H), 7.26–7.21 (m, 1H), 7.10–7.07 (d, *J* = 7.9 Hz, 2H), 5.10 (s, 1H), 3.78–3.73 (dd, *J* = 10.9, 3.9 Hz, 1H), 3.54–3.50 (dd, *J* = 10.9, 2.6 Hz, 1H), 3.27–3.20 (m, 1H), 2.84–2.75 (m, 1H), 2.62–2.59 (m, 1H), 2.30 (s, 3H), 1.98–1.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.13, 138.05, 131.48, 128.85, 128.03, 127.88, 127.27, 119.73, 87.67, 84.55, 62.11, 61.63, 56.23, 47.67, 27.86, 23.31, 21.19; IR (NaCl, neat, cm^{-1}) 3426, 2209; EIMS *m/z* 305 (M^+); HRMS (EI) for $C_{21}H_{23}NO$, Calc. 305.1779, found: 305.1781.

4.3.17. 3-((S)-3-cyclohexenyl-1-((S)-2-(hydroxymethyl)pyrrolidin-1-yl)prop-2-ynyl)benzaldehyde (**2n**)

Yellow oil; analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.29; ^1H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.07 (s, 1H), 7.84–7.80 (m, 2H), 7.53–7.49 (m, 1H), 6.22–6.19 (m, 1H), 5.09 (s, 1H), 3.80 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.55 (dd, *J* = 11.0, 2.7 Hz, 1H),

3.24–3.19 (m, 1H), 2.74–2.67 (m, 1H), 2.52–2.47 (m, 1H), 2.22–2.19 (m, 2H), 2.14–2.12 (m, 2H), 1.96–1.55 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.32, 140.79, 136.37, 135.23, 134.23, 129.44, 128.90, 128.71, 120.10, 90.31, 80.25, 62.09, 61.73, 55.89, 47.63, 29.51, 27.81, 25.55, 23.42, 22.21, 21.39; IR (KBr, neat, cm^{-1}) 3435, 2365, 2219, 1698; EIMS *m/z* 323 (M^+); HRMS (EI) for $C_{21}H_{25}NO_2$, Calc. 323.1885, found: 323.1881.

4.3.18. 3-((S)-1-((S)-2-(hydroxymethyl)pyrrolidin-1-yl)-3-phenylprop-2-ynyl)benzaldehyde (**2o**) [15f]

Yellowish oil; analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.19; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.14 (s, 1H), 7.90 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.56–7.51 (m, 3H), 7.36–7.34 (m, 3H), 5.24 (s, 1H), 3.84 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.60 (dd, *J* = 11.0, 2.8 Hz, 1H), 3.34–3.27 (m, 1H), 2.85–2.77 (m, 1H), 2.61–2.55 (m, 2H), 1.91–1.64 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.15, 140.50, 136.48, 134.15, 131.81, 129.33, 128.97, 128.82, 128.44, 128.34, 122.55, 88.39, 84.45, 62.42, 61.94, 56.12, 47.83, 27.84, 23.45; IR (NaCl, neat, cm^{-1}) 3421, 2361, 1699; EIMS *m/z* 319 (M^+); HRMS (EI) for $C_{21}H_{21}NO_2$, Calc. 319.1572, found: 319.1570.

4.3.19. Compound **2p** [15f]

Pale yellow solid; analytical TLC (silica gel 60) (30% EtOAc in hexane) R_f = 0.03; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.54–7.51 (m, 2H), 7.48–7.45 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.33–7.24 (m, 4H), 5.14 (s, 2H), 3.82 (dd, *J* = 10.9, 3.5 Hz, 2H), 3.54 (dd, *J* = 11.0, 2.3 Hz, 2H), 3.31–3.26 (m, 2H), 2.85–2.79 (m, 2H), 2.67–2.56 (m, 2H), 2.00–1.83 (m, 5H), 1.76–1.64 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.35, 131.82, 128.32, 128.22, 127.68, 127.33, 122.89, 87.84, 85.40, 62.02, 61.81, 56.35, 48.01, 28.03, 23.61; IR (NaCl, neat, cm^{-1}) 3435, 2336; EIMS *m/z* 473 (M^+-CH_2OH); HRMS (EI) for $C_{33}H_{33}N_2O$, Calc. 473.2593, found: 473.2599.

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