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Cobalt-Catalyzed Cycloisomerization of *N*,*N*-Diallylanilines

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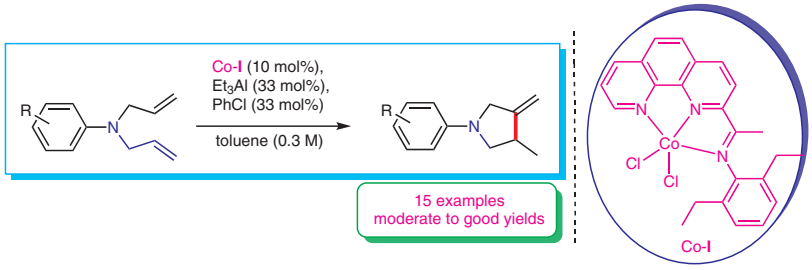

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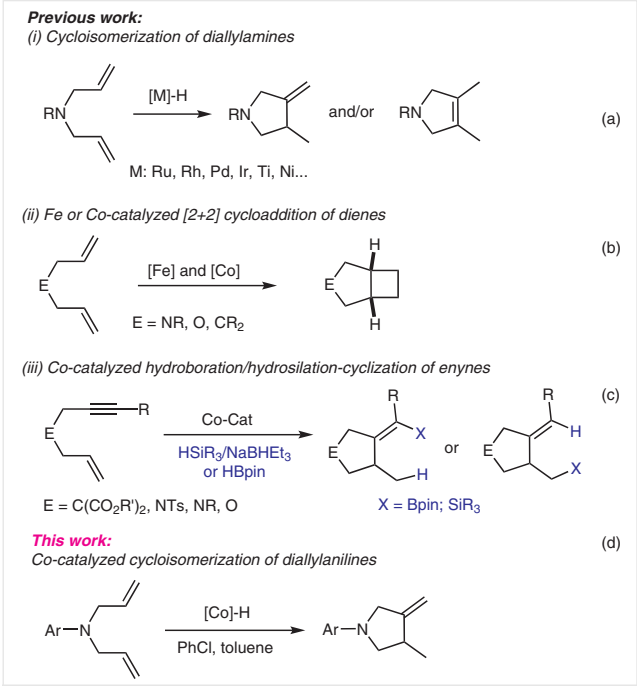
Abstract Cobalt catalysts bearing 2-imino-1,10-phenanthroline ligands are quite efficient bench-stable catalysts for the oligomerization of ethylenes. Herein, their further application was developed in the catalytic transformation of *N*,*N*-diallylanilines to pyrrolidines through a cycloisomerization process. In this protocol, chlorobenzene is a vital additive to promote reaction efficiency.

Key words cycloisomerization, cobalt-catalyzed, pyrrolidine, *N*,*N*-diallylaniline, phenanthroline ligand

Pyrrolidines are fundamental chemical feedstocks in nature and drugs.[1] One of the general procedures for the synthesis of pyrrolidines is designed through the transition-metal-catalyzed cycloisomerization of diallylamines, as typical 1,6-diene analogues.[2] Generally, precious metals, like Ru,[3] Rh,[4] and Pd,[5] are highly efficient pre-catalysts in this transformation, while metal hydrides are active catalysts (Scheme 1a). Moreover, first-row, earth-abundant metal catalysts, like Ti,[6] Ni,[7] and Fe,[8] also serve as sustainable alternatives in recent decade, and have been further explored in the asymmetric cycloisomerization synthesis.[9] However, there is still no example for the cycloisomerization of dienes under the catalysis of the earth-abundant cobalt catalysts.

Due to the fact of low costs and toxicity, economical cobalt catalyst-mediated transformations have gained continuous attention during the last two decades.[10] Chirik and Thomas observed [2π+2π] cycloaddition of dienes under the catalysis of iron or cobalt complexes bearing bis(iminopyridine) ligands, respectively (Scheme 1b).[11] Moreover, Lu reported the cobalt-iminopyridine complex-catalyzed hydroboration or hydrosilation/cyclization of 1,6-enynes,[12a,b] while Ge reported the cobalt-catalyzed hydroboration/cyclization of 1,6-enynes with catalysts generated from $Co(acac)_2$ and chiral bisphosphine ligands (Scheme 1c).[12c,d] Recently, one of us[13] and Sun's group[14] developed iron and cobalt catalysts bearing the 2-imino-1,10-phenanthroline ligands as efficient bench-stable catalysts for the oligomerization of ethylene.



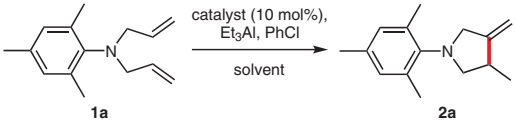
Scheme 1 Transition-metal-catalyzed transformations of diallylamines and related analogues

As we know, before ethylene oligomerization/polymerization, metal hydrides (M-Hs) are in-situ generated from metal halides, triethylaluminum, and imino-1,10-phenanthroline ligands. The M-Hs and co-catalyst methylalumi-

noxane (MAO) then promote the ethylene oligomerization through a stepwise intermolecular 1,2-insertion and end up with a β-hydride elimination. For the further study, we thus surmise that an intramolecular insertion of dienes may also be realized under similar conditions. Hence, herein we have developed the cycloisomerization of *N*,*N*-diallylanilines under the catalysis of bench-stable cobalt-imino-1,10-phenanthroline complexes.

Cobalt and iron catalysts **I** to **VI** were easily prepared from the corresponding 2-imino-1,10-phenanthroline ligands with $CoCl_2$ and $FeCl_2$ by following the references.[13,14] At the beginning, both heptan-1,6-diene and diallyl ether were attempted in toluene under the catalysis of catalyst Co-**I** and triethylaluminum, but none of the desired cyclized products was generated (see SI). *N*,*N*-Diallylanilines were next investigated. In order to facilitate the analysis, *N*,*N*-diallylmesitylamine (**1a**) was chosen as the substrate to opti-

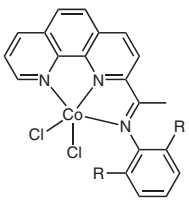
Table 1 Optimization of the Transformation[a]



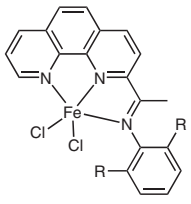
1a **2a**

Entry	Catalyst	Cocatalyst (mol%)	Additive (mol%)	Solvent	Temp (°C)	Yield (%)[b]
1	Co-**I**	Et_3Al (100)	–	toluene	0–25	28
2	Co-**I**	MAO (100)	–	toluene	0–25	0
3	Co-**I**	AmMgCl (100)	–	toluene	0–25	0
4	Co-**I**	Me_3Al (100)	–	toluene	0–25	0
5	Co-**I**	$EtAlCl_2$ (100)	–	toluene	0–25	0
6	Co-**II**	Et_3Al (100)	–	toluene	0–25	messy
7	Fe-**III**	Et_3Al (100)	–	toluene	0–25	messy
8	Fe-**IV**	Et_3Al (100)	–	toluene	0–25	messy
9	Fe-**V**	Et_3Al (100)	–	toluene	0–25	messy
10	Fe-**VI**	Et_3Al (100)	–	toluene	0–25	messy
11	Co-**I**	Et_3Al (100)	–	THF	0–25	17
12	Co-**I**	Et_3Al (100)	–	*n*-Hexane	0–25	0
13	Co-**I**	Et_3Al (100)	–	DCM	0–25	0
14	Co-**I**	Et_3Al (100)	–	PhCl	0–25	trace
15	Co-**I**	Et_3Al (100)	PhCl (40)	toluene	0–25	72
16	Co-**I**	Et_3Al (250)	PhCl (40)	toluene	0–25	0
17	Co-**I**	Et_3Al (50)	PhCl (40)	toluene	0–25	70
18	Co-**I**	Et_3Al (33)	PhCl (40)	toluene	0–25	78
19	Co-**I**	Et_3Al (20)	PhCl (40)	toluene	0–25	50
20	Co-**I**	Et_3Al (33)	PhCl (33)	toluene	0–40	52
21	Co-**I**	Et_3Al (33)	PhCl (33)	toluene	0–60	25

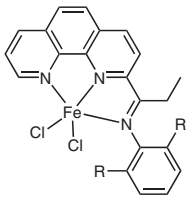
[a] Reaction conditions: **1a** (0.6 mmol), catalyst (0.06 mmol), and cocatalyst in solvent (2 mL) under N_2 at 0 °C for 1 h and then at 25 °C for 4 h.
[b] Yields are determined by ^1H NMR analysis with the internal standard of 1,3,5-trimethoxybenzene.



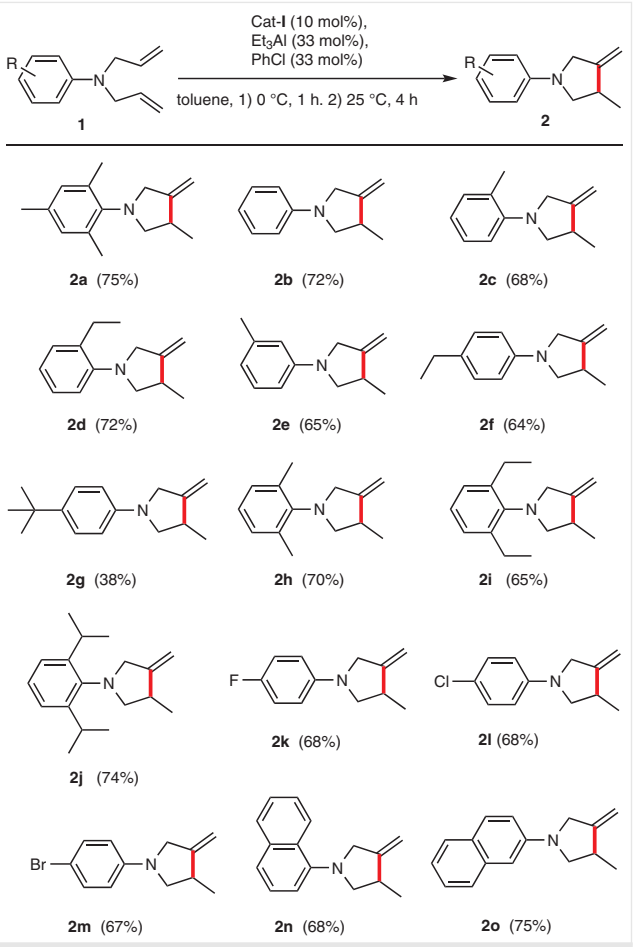
(Co-**I**) R = Et
(Co-**II**) R = *i*-Pr



(Fe-**III**) R = Et
(Fe-**IV**) R = *i*-Pr



(**Fe-V**) R = Et
(**Fe-VI**) R = *i*-Pr

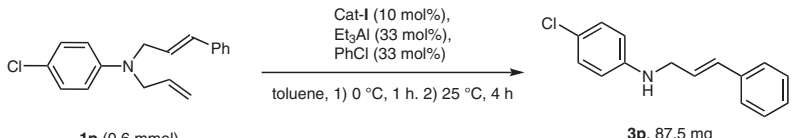


Scheme 2 Scope of *N*,*N*-diallylanilines. *Reagents and conditions*: **1** (0.6 mmol), Co-**I** (0.06 mmol), Et_3Al (0.2 mmol), and PhCl (0.2 mmol) in toluene (2.0 mL) under N_2 at 0 °C for 1 h and then at 25 °C for 4 h.

mize the conditions in toluene owing to its typical singlet aromatic proton signal in the ^1H NMR spectrum (Table 1). A co-catalyst was indispensable to activate the precatalyst to afford the active metal hydride. Methylaluminoxane, pentylmagnesium chloride (AmMgCl), trimethylaluminum (Me_3Al), triethylaluminum (Et_3Al), and ethyl aluminum dichloride ($EtAlCl_2$) were subsequently investigated, while only Et_3Al gave the corresponding cycloisomerization product **2a** in a moderate yield (entries 1–5). A variety of precatalysts Co-**II** and Fe-**III** to **VI** were then explored, but only Co-**I** could promote the reaction, and all of the rest of catalysts produced very complicated systems (entries 1 vs 6–10).

We next screened the solvents, including toluene, *n*-hexane, dichloromethane (DCM), tetrahydrofuran (THF), and chlorobenzene (PhCl) (entries 1 vs 11–14). Most of the solvents showed no efficiency, but the reactions were carried out smoothly in toluene (28%) and THF (17%). Interestingly, all raw materials were totally converted when the reaction was performed in chlorobenzene, but only trace of **2a** was detected. Inspired by this, we thus explored to use toluene as the solvent with PhCl as additive to promote the reaction efficiency. To our great delight, when PhCl (40 mol%) was added as additive, the yield of the isolated product **2a** was raised directly to 72% in toluene (entry 15). The loading of Et_3Al was then investigated (entries 15–19) and the best yield was obtained when decreasing the loading to 33 mol% (entry 18). Generally, the reaction was first conducted at 0 °C when Et_3Al was added, and then slowly raised up to 25 °C (room temperature). The yield dropped dramatically when the reaction temperature was raised up to 40 and 60 °C (entries 20 and 21).

We next investigated the scope of the reaction. *N*,*N*-Diallylaniline (**1b**) gave the corresponding pyrrolidine **2b** in 72% yield under the optimized conditions. A variety of *ortho*-, *meta*-, and *para*-alkyl mono- and disubstituted anilines were tested, affording the desired products in good yields (Scheme 2). First, *o*-methyl and *o*-ethyl *N*,*N*-diallylanilines **1c** and **1d** gave the desired pyrrolidines **2c** and **2d** in good yields. Moreover, *m*-methyl *N*,*N*-diallylaniline **1e**, *p*-ethyl and *tert*-butyl *N*,*N*-diallylanilines **1f** and **1g** also provided the desired products **2e–g** in 65%, 64%, and 38% yields, respectively. Notably, the yield of **2g** was relatively low because some unknown by-products with similar polarity were accompanied with **2g** so that the isolation of **2g** was less effective during the column chromatography. Comparing the *ortho*-substituents with *meta*- and *para*-ones, the above results also demonstrated that the steric hindrance on the arene ring did not affect the reaction transformation. Further evidences were obtained by introducing 2,6-dimethyl **1h**, diethyl **1i**, and especially bulky diisopropyl **1j** substituents to *N*,*N*-diallylanilines, all of which gave the corresponding pyrrolidines **2h–j** in good yields. Moreover, the current conditions were also well tolerant with halogens. Fluoro **1k**, chloro **1l**, and bromo **1m** substrates afforded the desired products **2k–m** in 68%, 68%, and 67% yields, respectively. It is worthy to mention that both 1-

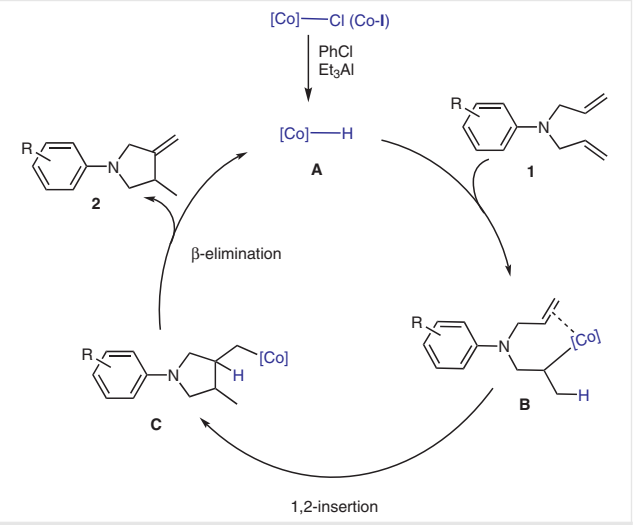


Scheme 3 Reaction of 4-chloro-*N*-cinnamylaniline under the optimal conditions

naphthyl and 2-naphthyl substrates provided the desired products **2n** and **2o** in 68% and 75% yields, respectively.

Other substrates with electron-withdrawing substituents on the nitrogen atom, such as *N*,*N*-diallyl-4-nitroaniline, ethyl 4-diallylaminobenzoate, and *N*,*N*-diallylbenzenesulfonamide, were also investigated, but all of them afforded the desired cyclized products in very low yields (<5%) possibly because the strong electron-withdrawing substituents inhibited the reactions. For substrate with *N*-alkyl substituent, *N*,*N*-diallylbenzylamine gave messy products under the optimal conditions. Finally, sterically demanding *N*-allyl-4-chloro-*N*-cinnamylaniline (**1p**) was also investigated, affording a deallylation product, 4-chloro-*N*-cinnamylaniline (**3p**), in 60% yield (Scheme 3).

The reaction mechanism is finally proposed in Scheme 4 by referring similar transition-metal-catalyzed transformations.[3–8] First, under the chlorobenzene promotion, cobalt hydride complex **A** is first generated from Co-**I** catalyst and triethylaluminum. Both Me_3Al and MAO [O–Al(Me)] are inefficient, supporting the formation of Co-H catalyst because Co-Et undergoes a β-H elimination to generate Co-H catalyst, but Co-Me cannot. The cobalt hydride **A** coordinates with diallylanilines **1** followed by an insertion step to form the intermediates **B**. The subsequent cycloisomerization of **B** through a 1,2-insertion is realized via a 5-*exo*-trig process to generate cyclized **C**. Finally, the β-hydride elimination of the complexes **C** affords the desired pyrrolidines **2** and regenerates the catalyst Co-H (**A**).



Scheme 4 Proposed reaction mechanism of the cycloisomerization of diallylanilines

In conclusion, we have developed an efficient way to prepare pyrrolidines from *N*,*N*-diallylanilines through a cycloisomerization process in the presence of earth-abundant cobalt catalyst. One of the quite inexpensive and bench-stable cobalt-2-imino-1,10-phenanthroline catalysts was verified as an effective catalyst for not only oligomerization of olefins, but also for the cyclization of *N*,*N*-diallylanilines. In this transformation, chlorobenzene was identified as the vital additive to promote reaction efficiency. Moreover, various alkyl- and halo-substituted *N*,*N*-diallylanilines were tolerated in these transformations. The current cobalt-catalyzed system is only suitable for electron-rich *N*,*N*-diallylanilines.

Unless otherwise noted, all materials were purchased from commercial suppliers. All reactions were performed in a Schlenk flask equipped with a magnetic stir bar under N_2 atmosphere. Flash column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemical Industry. Petroleum ether (PE) used for column chromatography is 60–90 °C fraction, and the removal of residue solvent was accomplished under rotovap. Reactions were monitored by TLC on silica gel GF254 coated 0.2 mm plates from Institute of Yantai Chemical Industry. The plates were visualized under UV light. All commercially available reactants are used directly. Anhydrous toluene was prepared by reflux with Na. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer in $CDCl_3$ and acetone-d_6 with TMS as an internal standard. IR spectra were recorded directly on a Nicolet AVATAR 330 FTIR spectrophotometer. HRMS spectra were recorded on an Agilent Liquid Chromatography/Mass Spectrometry/Data and Time-of-Flight (LC/MSD /TOF) mass spectrometer.

Cobalt-Catalyzed Cycloisomerization of *N*,*N*-Diallylanilines; General Procedure

Cobalt-**I** (29.0 mg, 0.067 mmol) was added to a reaction tube (or a Schlenk tube) and the whole system was replaced with N_2 gas three times. PhCl (22.4 mg, 20 μL, 0.2 mmol), Et_3Al (1 M in *n*-hexane, 0.2 mL), and toluene (2 mL) were then introduced into the tube and the resulting solution was stirred for 10 min at 0 °C to activate the catalyst. The respective *N*,*N*-diallylaniline **1** (0.6 mmol) was added and the reaction mixture was first stirred for 1 h at 0 °C and then warmed up to 25 °C for 4 h. The reaction was quenched with aq 25% NaOH (1.0 mL) and filtered through Celite (1.0 g) to remove the aluminum complex. DCM (2.0 mL) was added to flush the Celite. The filtrate was separated and the aqueous phase was extracted with DCM (2 × 1.0 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under vacuum. The residue was finally purified by silica gel column chromatography with hexanes as eluent.

1-Mesityl-3-methyl-4-methylenepyrrolidine (2a)[7c]

Colorless liquid; yield: 78.0 mg (75%); R_f = 0.40 (hexanes).

IR (film): 2961, 2917, 2868, 1482, 1459, 1372, 1343, 1270, 1194, 1156, 1032, 947, 881, 850 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (s, 2 H), 4.93 (d, *J* = 2.2 Hz, 1 H), 4.91 (d, *J* = 2.2 Hz, 1 H), 4.01–3.70 (m, 2 H), 3.38 (dd, *J* = 7.6, 7.6 Hz, 1 H), 2.95 (dd, *J* = 7.6, 7.6 Hz, 1 H), 2.91–2.80 (m, 1 H), 2.25 (s, 3 H), 2.23 (s, 6 H), 1.20 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.9, 141.8, 138.1, 134.8, 129.4, 103.3, 58.6, 55.0, 38.7, 20.8, 18.7, 17.1.

3-Methyl-4-methylene-1-phenylpyrrolidine (2b)[6]

Colorless oil; yield: 74.7 mg (72%); R_f = 0.35 (hexanes).

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.18 (dd, *J* = 7.4, 7.4 Hz, 2 H), 6.64 (t, *J* = 7.3 Hz, 1 H), 6.59 (d, *J* = 7.9 Hz, 2 H), 5.06 (d, *J* = 2.3 Hz, 1 H), 4.98 (d, *J* = 2.3 Hz, 1 H), 4.05 (d, *J* = 14.0 Hz, 1 H), 3.84 (dd, *J* = 14.0, 1.7 Hz, 1 H), 3.66 (t, *J* = 8.0 Hz, 1 H), 2.98–2.87 (m, 1 H), 2.85 (d, *J* = 8.4 Hz, 1 H), 1.21 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (101 MHz, acetone-d_6): δ = 152.9, 149.0, 129.8, 117.0, 112.9, 105.0, 56.1, 53.9, 38.1, 17.1.

HRMS (APCI): *m*/*z* calcd for $C_{12}H_{16}N^+$ [M + H]$^+$: 174.1277; found: 174.1284.

3-Methyl-4-methylene-1-(*o*-tolyl)pyrrolidine (2c)

Colorless liquid; yield: 76.3 mg (68%); R_f = 0.35 (hexanes).

FT-IR (film): 3075, 3016, 2978, 2924, 2810, 1642, 1598, 1459, 1417, 1357, 1218, 919, 765, 729 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (t, *J* = 7.0 Hz, 2 H), 6.84–8.80 (m, 2 H), 4.89 (d, *J* = 0.8 Hz, 1 H), 4.83 (d, *J* = 1.2 Hz, 1 H), 3.95 (d, *J* = 13.6 Hz, 1 H), 3.56 (d, *J* = 13.6 Hz, 1 H), 3.34–3.28 (m, 1 H), 2.78–2.74 (m, 2 H), 2.25 (s, 3 H), 1.14 (d, *J* = 6.0 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.2, 148.6, 131.5, 129.9, 126.3, 121.3, 116.6, 103.7, 58.8, 56.4, 37.5, 20.0, 17.0.

HRMS (APCI): *m*/*z* calcd for $C_{13}H_{18}N^+$ [M + H]$^+$: 188.1443; found: 188.1434.

1-(2-Ethylphenyl)-3-methyl-4-methylenepyrrolidine (2d)

Colorless liquid; yield: 86.0 mg (72%); R_f = 0.45 (hexanes).

FT-IR (film): 3075, 3017, 2924, 2810, 1642, 1599, 1492, 1450, 1416, 1357, 1218, 919, 753 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.18 (d, *J* = 7.6 Hz, 1 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 7.01 (d, *J* = 7.6 Hz, 1 H), 6.94 (t, *J* = 7.4 Hz, 1 H), 4.97 (d, *J* = 1.6 Hz, 1 H), 4.92 (d, *J* = 2.0 Hz, 1 H), 3.90 (d, *J* = 13.6 Hz, 1 H), 3.63 (dt, *J* = 13.6, 2.0 Hz, 1 H), 3.37–3.31 (m, 1 H), 2.84–2.78 (m, 2 H), 2.73–2.65 (m, 2 H), 1.22 (t, *J* = 7.6 Hz, 3 H), 1.21 (t, *J* = 6.2 Hz, 3 H).

^{13}C NMR (101 MHz, acetone-d_6): δ = 154.6, 149.0, 137.8, 130.0, 127.2, 123.2, 118.7, 104.2, 60.5, 58.0, 38.5, 17.7, 14.8.

HRMS (APCI): *m*/*z* calcd for $C_{14}H_{20}N^+$ [M + H]$^+$: 202.1590; found: 202.1596.

3-Methyl-4-methylene-1-(*m*-tolyl)pyrrolidine (2e)

Colorless liquid; yield: 73.0 mg (65%); R_f = 0.35 (hexanes).

FT-IR (film): 3075, 2978, 2924, 2810, 1642, 1599, 1492, 1463, 1385, 1218, 919, 837, 765, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (t, *J* = 8.1 Hz, 1 H), 6.46 (d, *J* = 7.4 Hz, 1 H), 6.32 (s, 1 H), 6.31 (d, *J* = 8.1 Hz, 1 H), 4.94 (s, 1 H), 4.87 (s, 1 H), 3.99 (d, *J* = 13.8 Hz, 1 H), 3.78 (d, *J* = 13.8 Hz, 1 H), 3.61–3.46 (m, 1 H), 2.88–2.71 (m, 2 H), 2.24 (s, 3 H), 1.13 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.7, 148.0, 138.8, 129.0, 117.2, 112.7, 109.2, 104.5, 55.3, 53.3, 37.3, 21.8, 16.8.

HRMS (APCI): *m*/*z* calcd for $C_{13}H_{18}N^+$ [M + H]$^+$: 188.1440; found: 188.1434.

1-(4-Ethylphenyl)-3-methyl-4-methylenepyrrolidine (2f)

Colorless liquid; yield: 77.2 mg (64%); R_f = 0.35 (hexanes).

FT-IR (film): 3078, 3007, 2961, 2925, 1615, 1519, 1384, 1232, 917, 813 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 8.3 Hz, 2 H), 6.55 (d, *J* = 8.3 Hz, 2 H), 5.02 (s, 1 H), 4.95 (s, 1 H), 4.07 (d, *J* = 13.8 Hz, 1 H), 3.85 (d, *J* = 13.8 Hz, 1 H), 3.64 (dd, *J* = 7.6, 7.6 Hz, 1 H), 2.96–2.81 (m, 2 H), 2.56 (q, *J* = 7.6 Hz, 2 H), 1.21 (d, *J* = 6.4 Hz, 3 H), 1.20 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.0, 146.2, 132.1, 128.5, 112.1, 104.5, 55.6, 53.6, 37.4, 27.9, 16.9, 16.0.

HRMS (APCI): *m*/*z* calcd for $C_{14}H_{20}N^+$ [M + H]$^+$: 202.1590; found: 202.1597.

1-[4-(*tert*-Butyl)phenyl]-3-methyl-4-methylenepyrrolidine (2g)

Colorless oil; yield: 52.0 mg (38%); R_f = 0.45 (hexanes).

FT-IR (film): 3078, 2961, 2864, 1613, 1520, 1391, 1363, 1233, 918, 813 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.23 (d, *J* = 8.7 Hz, 2 H), 6.55 (d, *J* = 8.7 Hz, 2 H), 5.04 (s, 1 H), 4.97 (s, 1 H), 4.03 (d, *J* = 14.0 Hz, 1 H), 3.82 (d, *J* = 14.0 Hz, 1 H), 3.64 (t, *J* = 8.0 Hz, 1 H), 2.91–2.89 (m, 1 H), 2.84–2.81 (m, 1 H), 1.26 (s, 9 H), 1.19 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (101 MHz, acetone-d_6): δ = 153.2, 147.0, 139.4, 126.4, 112.8, 104.9, 56.3, 54.1, 38.2, 34.3, 31.9, 17.2.

HRMS (APCI): *m*/*z* calcd for $C_{16}H_{24}N^+$ [M + H]$^+$: 230.1903; found: 230.1908.

1-(2,6-Dimethylphenyl)-3-methyl-4-methylenepyrrolidine (2h)

Colorless liquid; yield: 84.3 mg (70%); R_f = 0.40 (hexanes).

FT-IR (film): 3074, 3010, 2977, 2920, 1640, 1473, 1435, 1415, 1372, 1215, 990, 917, 768 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95–6.90 (m, 3 H), 4.98–4.93 (m, 2 H), 3.83 (dq, *J* = 13.5, 1.0 Hz, 1 H), 3.80 (dq, *J* = 13.5, 2.0 Hz, 1 H), 3.34 (t, *J* = 7.6 Hz, 1 H), 2.89 (t, *J* = 7.6 Hz, 1 H), 2.84–2.79 (m, 1 H), 2.19 (s, 6 H), 1.14 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.7, 144.5, 138.3, 128.6, 125.3, 103.3, 58.5, 54.9, 38.7, 18.9, 17.0.

HRMS (APCI): *m*/*z* calcd for $C_{14}H_{20}N^+$ [M + H]$^+$: 202.1590; found: 202.1599.

1-(2,6-Diethylphenyl)-3-methyl-4-methylenepyrrolidine (2i)

Colorless liquid; yield: 89.3 mg (65%); R_f = 0.35 (hexanes).

FT-IR (film): 3075, 2965, 2931, 2873, 2813, 1639, 1456, 1415, 1371, 990, 917, 765 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–6.98 (m, 3 H), 4.86–4.84 (m, 2 H), 3.83 (d, *J* = 13.5, 1.0 Hz, 1 H), 3.80 (d, *J* = 13.5, 1.8 Hz, 1 H), 3.33 (t, *J* = 7.7 Hz, 1 H), 2.90 (t, *J* = 7.7 Hz, 1 H), 2.87–2.80 (m, 1 H), 2.56 (q, *J* = 7.5 Hz, 4 H), 1.13 (t, *J* = 7.5 Hz, 6 H), 1.12 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.8, 145.1, 143.7, 126.9, 126.1, 103.4, 60.3, 56.8, 38.8, 24.8, 17.0, 15.7.

HRMS (APCI): *m*/*z* calcd for $C_{16}H_{24}N^+$ [M + H]$^+$: 230.1903; found: 230.1912.

1-(2,6-Diisopropylphenyl)-3-methyl-4-methylenepyrrolidine (2j)[7c]

Colorless liquid; yield: 114.0 mg (74%); R_f = 0.45 (hexanes).

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.18–7.10 (m, 3 H), 4.97–4.95 (m, 2 H), 3.92 (dq, *J* = 13.4, 0.9 Hz, 1 H), 3.87 (dq, *J* = 13.4, 1.8 Hz, 1 H), 3.44 (t, *J* = 7.2 Hz, 1 H), 3.40–3.18 (m, 2 H), 2.99 (t, *J* = 7.4 Hz, 1 H), 2.98–2.87 (m, 1 H), 1.22 (d, *J* = 6.5 Hz, 3 H), 1.19 (d, *J* = 6.9 Hz, 6 H), 1.18 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (101 MHz, acetone-d_6): δ = 155.3, 150.6, 142.8, 127.6, 124.8, 104.8, 62.0, 58.4, 39.5, 28.8, 24.8, 24.6, 17.3.

HRMS (APCI): *m*/*z* calcd for $C_{18}H_{28}N^+$ [M + H]$^+$: 258.2216; found: 258.2221.

1-(4-Fluorophenyl)-3-methyl-4-methylenepyrrolidine (2k)

Colorless oil; yield: 77.9 mg (68%); R_f = 0.40 (hexanes).

FT-IR (film): 3081, 3007, 2980, 2915, 1642, 1519, 1387, 1229, 1181, 1227, 920, 813 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (t, *J* = 8.8 Hz, 2 H), 6.50 (dd, *J* = 8.8, 4.3 Hz, 2 H), 5.03 (q, *J* = 2.2 Hz, 1 H), 4.96 (q, *J* = 2.2 Hz, 1 H), 4.05 (d, *J* = 13.6 Hz, 1 H), 3.82 (dq, *J* = 13.6, 1.6 Hz, 1 H), 3.61 (t, *J* = 7.9 Hz, 1 H), 2.98–2.87 (m, 1 H), 2.84 (t, *J* = 8.1 Hz, 1 H), 1.22 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.3 (d, *J* = 234.3 Hz), 151.6, 144.7, 115.5 (d, *J* = 22.1 Hz), 112.6 (d, *J* = 7.3 Hz), 104.7, 55.9, 53.9, 37.4, 16.8.

^{19}F NMR (377 MHz, acetone-d_6): δ = –131.3.

HRMS (APCI): *m*/*z* calcd for $C_{12}H_{15}FN^+$ [M + H]$^+$: 192.1183; found: 192.1192.

1-(4-Chlorophenyl)-3-methyl-4-methylenepyrrolidine (2l)

Colorless oil; yield: 84.5 mg (68%); R_f = 0.30 (hexanes).

FT-IR (film): 3075, 2979, 2920, 1642, 1597, 1499, 1387, 1234, 920, 808 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 8.90 Hz, 2 H), 6.46 (d, *J* = 8.9 Hz, 2 H), 5.02 (q, *J* = 2.1 Hz, 1 H), 4.95 (q, *J* = 2.2 Hz, 1 H), 4.02 (d, *J* = 13.7 Hz, 1 H), 3.81 (dq, *J* = 13.7, 1.7 Hz, 1 H), 3.59 (t, *J* = 7.9 Hz, 1 H), 3.15–2.87 (m, 1 H), 2.83 (t, *J* = 8.2 Hz, 1 H), 1.20 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.2, 146.3, 128.9, 121.0, 112.9, 104.8, 77.3, 77.0, 76.7, 55.4, 53.3, 37.3, 16.6.

HRMS (APCI): *m*/*z* calcd for $C_{16}H_{24}ClN^+$ [M + H]$^+$: 208.0888; found: 208.0897.

1-(4-Bromophenyl)-3-methyl-4-methylenepyrrolidine (2m)

Colorless oil; yield: 100.9 mg (67%); R_f = 0.30 (hexanes).

FT-IR (film): 3082, 3007, 2980, 2911, 2865, 1642, 1590, 1497, 1389, 1233, 1181, 920, 806 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.30 (d, *J* = 9.0 Hz, 2 H), 6.54 (d, *J* = 9.0 Hz, 2 H), 5.06 (q, *J* = 2.2 Hz, 1 H), 4.99 (q, *J* = 2.3 Hz, 1 H), 4.04 (d, *J* = 14.0 Hz, 1 H), 3.85 (dq, *J* = 14.0, 1.9 Hz, 1 H), 3.66 (t, *J* = 8.1 Hz, 1 H), 2.96–2.88 (m, 1 H), 2.85 (t, *J* = 8.2 Hz, 1 H), 1.21 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (101 MHz, acetone-d_6): δ = 152.5, 148.0, 132.4, 114.7, 108.3, 105.3, 56.0, 53.8, 38.1, 17.0.

HRMS (APCI): *m*/*z* calcd for $C_{12}H_{15}BrN^+$ [M + H]$^+$: 252.0382; found: 252.0384.

3-Methyl-4-methylene-1-(naphthalen-1-yl)pyrrolidine (2n)

Colorless oil; yield: 92.0 mg (68%); R_f = 0.35 (hexanes).

FT-IR (film): 3048, 3008, 2978, 2922, 2815, 1642, 1576, 1398, 918.9, 774 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 8.21 (dd, *J* = 5.6, 4.1 Hz, 1 H), 7.96–7.76 (m, 1 H), 7.52 (d, *J* = 8.2 Hz, 1 H), 7.50–7.42 (m, 2 H), 7.39 (t, *J* = 4.0 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 5.04 (q, *J* = 2.0 Hz, 1 H), 4.98 (q, *J* = 2.0 Hz, 1 H), 4.12 (dt, *J* = 13.6, 2.2 Hz, 1 H), 3.80 (dq, *J* = 13.8, 2.2 Hz, 1 H), 3.60–3.54 (m, 1 H), 3.06–2.88 (m, 2 H), 1.28 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (101 MHz, acetone-d_6): δ = 154.3, 147.9, 135.8, 129.5, 129.1, 126.8, 126.5, 125.6, 125.1, 123.3, 113.7, 104.5, 61.1, 58.8, 38.5, 17.7.

HRMS (APCI): *m*/*z* calcd for $C_{16}H_{18}N^+$ [M + H]$^+$: 224.1434; found: 224.1441.

3-Methyl-4-methylene-1-(naphthalen-2-yl)pyrrolidine (2o)

Colorless oil; yield: 108.0 mg (75%); R_f = 0.45 (hexanes).

FT-IR (film): 3057, 3008, 2978, 2915, 1628, 1599, 1510, 1392, 1220, 918, 824, 743 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.9 Hz, 1 H), 7.61 (d, *J* = 8.0 Hz, 1 H), 7.57 (d, *J* = 8.3 Hz, 1 H), 7.28 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1 H), 7.11 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H), 6.93 (dd, *J* = 8.9, 2.5 Hz, 1 H), 6.71 (d, *J* = 2.2 Hz, 1 H), 5.00 (q, *J* = 2.0 Hz, 1 H), 4.92 (q, *J* = 2.2 Hz, 1 H), 4.13 (d, *J* = 13.8 Hz, 1 H), 3.92 (dq, *J* = 13.8, 1.7 Hz, 1 H), 3.75–3.67 (m, 1 H), 2.94 (t, *J* = 7.9 Hz, 1 H), 2.92–2.85 (m, 1 H), 1.18 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (101 MHz, acetone-d_6): δ = 154.3, 147.9, 135.9, 129.5, 129.1, 126.8, 126.5, 125.6, 125.1, 123.3, 113.7, 104.5, 61.1, 58.8, 38.5, 17.7.

HRMS (APCI): *m*/*z* calcd for $C_{16}H_{18}N^+$ [M + H]$^+$: 224.1434; found: 224.1443.

4-Chloro-*N*-cinnamylaniline (3p)

White powder; yield: 87.5 mg (60%); mp 69–71 °C (Lit.[15] mp 77–79 °C); R_f = 0.50 (PE/DCM 1:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 4 H), 7.26–7.21 (m, 1 H), 7.11 (d, *J* = 8.8 Hz, 2 H), 6.60 (d, *J* = 15.9 Hz, 1 H), 6.57 (d, *J* = 8.8 Hz, 2 H), 6.28 (td, *J* = 15.9, 5.7 Hz, 1 H), 3.90 (dd, *J* = 5.7, 1.5 Hz, 2 H), 3.86 (br s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.5, 136.7, 131.8, 129.1, 128.6, 127.6, 126.4, 126.3, 122.2, 114.1, 46.2.

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Supporting Information

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