Supporting Information

Cu(II)-Mediated Oxyamination of Alkenylimines and Alkenylamidines with TEMPO

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1. General

$^1$H NMR spectra were measured on Bruker Avance 300 or 400 MHz spectrometers in CDCl$_3$ [using TMS (for $^1$H, $\delta = 0.00$) as internal standard]. $^{13}$C NMR spectra were measured on Bruker AVIII 400MHz spectrometers in CDCl$_3$ [using CDCl$_3$ (for $^{13}$C, $\delta = 77.0$) as internal standard]. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, dd = doublets of doublets, dddd = doublets of doublets of doublets of doublets, t = triplet, m = multiplet. IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR Spectrometer. High-resolution mass spectra were obtained with a Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus.

Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. Diisopropylamine was purchased from Alfa Aesar, distilled from KOH and stored over KOH. Tetrahydrofuran (THF), acetonitrile, and diethyl ether (Et$_2$O) were taken from a solvent purification system (PS-400-5, Innovative Technology, Inc.). Methanol (MeOH) was distilled from sodium and stored over MS 3Å. Anhydrous DMF (99.8%), AlCl$_3$ (99.99% trace metals basis), Cu(OAc)$_2$ (98% trace metals basis), and TEMPO (free radical, 98%) were purchased from Sigma-Aldrich Co., Inc.

All liquid starting materials were Kugelrohr distilled before use. 4-Pentenenitrile (1g) was purchased from Sigma Aldrich, Pte. Ltd., and was distilled with Kugelrohr before use (27 mm Hg/50 °C). All solid compounds were recrystallized over hexane/ethyl acetate.
2. Synthesis of alkenyl carbonitriles 2

Synthesis of alkenyl carbonitriles 1a-b, 1d-i: 1 A typical procedure for synthesis of 1e: To a 100 mL round-bottom flask was added diisopropylamine (2.20 mL, 15.4 mmol) and n-BuLi (9.20 mL, 14.7 mmol) in THF (18 mL), and the reaction mixture was stirred at 0 °C for 30 min. The mixture was then cooled down to -78 °C and isobutyronitrile (1.30 mL, 14.0 mmol) was slowly added. After stirring for 1 h, 1-bromo-3-methylbut-2-ene (1.80 mL, 15.4 mmol) was added dropwise and the reaction mixture was allowed to warm up to room temperature while stirring overnight. The reaction was quenched with saturated aqueous NH₄Cl solution. Organic materials were then extracted three times with 50 mL of Et₂O. The organic phase was washed with water and brine, and dried over MgSO₄. After filtration, the solvent was evaporated to give a crude mixture, which was purified by Kugelrohr distillation to provide 2,2,5-trimethylhex-4-enenitrile (1e) (1.52 g, 11.1 mmol) for 79% yield (5 mm Hg/86-88 °C).

2,2,4-Trimethylpent-4-enenitrile (1a):

Yield 90%; Colorless oil; 1H NMR (400 MHz, CDCl₃) δ 1.36 (6H, s), 1.90 (3H, s), 2.26 (2H, s), 4.84 (1H, s), 4.98 (1H, s); 13C NMR (100 MHz, CDCl₃) δ 23.6, 27.0, 31.3, 48.5, 116.1, 125.4, 140.6; distillation: 26 mm Hg/70-72 °C.
2,2-Dimethylpent-4-enenitrile (1b):

\[
\text{Me} \quad \text{CN} \\
\text{Me} \quad \text{Me}
\]

Yield 60%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.34 (6H, s), 2.28 (2H, d, \(J = 7.3\) Hz), 5.16-5.24 (2H, m), 5.82-5.92 (1H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.2, 32.1, 45.0, 119.9, 124.7, 132.2; distillation: 26 mm Hg/70-75 °C.

1-Allylcyclohexanecarbonitrile (1d):

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\text{CN}
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Yield 87%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.12-1.28 (3H, m), 1.56-1.64 (2H, m), 1.66-1.75 (3H, m), 1.96 (2H, d, \(J = 12.9\) Hz), 2.28 (2H, d, \(J = 7.4\) Hz), 5.15-5.22 (2H, m), 5.84-5.94 (1H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.0, 25.3, 35.3, 38.8, 44.6, 119.6, 123.3, 131.9; distillation: 5 mm Hg/95-100 °C.

2-Allyl-2-phenylpent-4-enenitrile (1e):

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\text{CN}
\]

Yield 38%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.65-2.75 (4H, m), 5.12-5.17 (4H, m), 5.60-5.71 (2H, m), 7.29-7.33 (1H, m), 7.37-7.43 (4H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 44.1, 47.6, 120.1, 121.6, 126.2, 127.8, 128.8, 131.6, 137.6.
2,2,5-Trimethylhex-4-enitrile (1f):

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.32 (6H, s), 1.65 (3H, s), 1.77 (3H, s), 2.23 (2H, d, \(J = 7.6\) Hz), 5.25 (1H, ddt, \(J = 1.3, 1.3, 7.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 18.1, 25.9, 26.2, 32.8, 39.1, 118.2, 125.3, 136.4; distillation: 5 mm Hg/86-88 °C.

**Synthetic procedure of 1c:**\(^2\) To a 200 mL round-bottom flask was added diisopropylamine (11.3 mL, 80.6 mmol) and \(n\)-BuLi (50 mL, 80 mmol) in THF (120 mL) and the reaction mixture was stirred at 0 °C. The lithium diisopropylamide (LDA) formed was used in three portions. Meanwhile, to a 300 mL round-bottomed flask was added acetonitrile (1.40 mL, 26 mmol) in THF (15 mL) and cooled down to -78 °C. After the first 1/3 portion of LDA was added dropwise, the mixture was stirred for 15 min. Allyl bromide (2.40 mL, 27.3 mmol) was then added dropwise and stirred for 30 min and allowed to warm up to room temperature. The reaction mixture was again cooled down to -78 °C for second addition. Second 1/3 portion of LDA was added and the mixture was stirred for 15 min. Allyl bromide (2.40 mL, 27.3 mmol) was then added dropwise and stirred for 30 min and allowed to warm up to room temperature. The reaction mixture was again cooled down to -78 °C for third addition. The last 1/3 portion of LDA was added and stirred for 15 min. Allyl bromide (2.40 mL, 27.3 mmol) was then added dropwise and the mixture was stirred overnight while warming up to room temperature.

The reaction may not have completed as two spots were observed on TLC after being stained with KMnO\(_4\). A fourth 1/3 equivalent of LDA mixture was prepared as stated above [diisopropylamine (4.00 mL, 28.6 mmol) and \(n\)-BuLi (17.1 mL, 27.3 mmol, 1.6 M in hexane)]
in THF (25 mL) and added to the reaction mixture at -78 °C. Allyl bromide (2.40 mL, 27.3 mmol) was then added dropwise and stirred for 1 h and allowed to warm up to room temperature. The reaction mixture was quenched with saturated aqueous NH₄Cl solution at room temperature. Organic materials were then extracted three times with 100 mL of Et₂O. The organic phase was washed with water and brine, and dried over MgSO₄. After filtration, the solvent was evaporated to give a crude mixture, which was purified by Kugelrohr distillation, affording product 1c (3.41 g, 21.1 mmol) for 81% yield.

2,2-Diallylpent-4-enenitrile (1c):

![Diagram of 2,2-Diallylpent-4-enenitrile (1c)]

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.27 (6H, d, J = 7.3 Hz), 5.20 (3H, d, J = 17.0 Hz), 5.25 (3H, d, J = 10.2 Hz), 5.85 (ddd, J = 7.3, 10.2, 17.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 40.0, 40.2, 120.3, 122.6, 131.6; distillation: 5 mm Hg/90-95 °C.

3. Synthesis of 3,4-dihydro-2H-pyrroles 3

![Diagram of Reaction Scheme]

To a 10 mL Schlenk tube with a Teflon valve was added carbonitrile 1a (48.2 mg, 0.39 mmol) in Et₂O (0.4 mL) and p-tolylmagnesium bromide (2a) (0.53 mL, 0.47 mmol, 0.88 M in Et₂O) was added slowly. The reaction was then heated at 60 °C under sealed conditions for 4 h. The mixture was quenched with distilled MeOH (60 µL) at 0 °C, and DMF (4 mL),
Cu(OAc)$_2$ (72.2 mg, 0.40 mmol), and TEMPO (91.7 mg, 0.59 mmol) were added immediately. The mixture was further stirred at room temperature for 2 h under an inert atmosphere. The reaction was quenched with pH 9 ammonium buffer solution and extracted thrice with Et$_2$O. The organic phase was then washed with water and brine, and dried over MgSO$_4$. The solvent was evaporated to give a crude mixture, which was purified by flash column chromatography (hexane/ethyl acetate = 95:5) to provide product 3aa (98.7 mg, 0.27 mmol) for 68% yield.

2,2,6,6-Tetramethyl-1-((2,4,4-trimethyl-5-p-tolyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)piperidine (3aa):

Colourless oil; IR (NaCl) 2968, 2932, 2870, 1609, 1468, 1360, 1244, 1132, 1070, 1053, 752, 731 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.07 (3H, s), 1.13 (3H, s), 1.20 (3H, s), 1.24 (3H, s), 1.32 (3H, s), 1.36 (3H, s), 1.44 (3H, s), 1.27-1.51 (6H, m), 1.68 (1H, d, $J = 12.8$ Hz), 2.34 (1H, d, $J = 12.8$ Hz), 2.36 (3H, s), 3.79 (1H, d, $J = 8.4$ Hz), 3.89 (1H, d, $J = 8.4$ Hz), 7.16 (2H, d, $J = 8.2$ Hz), 7.60 (2H, d, $J = 8.2$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 15.3, 18.6, 18.9, 19.6, 25.0, 26.3, 28.0, 31.4, 31.5, 38.0, 47.4, 50.0, 58.3, 70.5, 81.0, 126.3, 127.0, 130.6, 137.2, 175.8; ESIHRMS: Found: m/z 371.3053. Calcd for C$_{24}$H$_{39}$N$_2$O: (M+H)$^+$ 371.3062.
1-((5-(4-Methoxyphenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)-2,2,6,6-tetramethylpiperidine (3ab):

![Chemical Structure of 3ab](image)

Colourless oil; IR (NaCl) 2965, 2932, 2870, 1607, 1512, 1308, 1250, 1167, 1038, 991, 752 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.06 (3H, s), 1.13 (3H, s), 1.20 (3H, s), 1.24 (3H, s), 1.32 (3H, s), 1.37 (3H, s), 1.46 (3H, s), 1.06-1.51 (6H, m), 1.68 (1H, d, \(J = 12.9\) Hz), 2.34 (1H, d, \(J = 12.9\) Hz), 3.78 (1H, d, \(J = 8.4\) Hz), 3.82 (3H, s), 3.88 (1H, d, \(J = 8.4\) Hz), 6.88 (2H, d, \(J = 8.7\) Hz), 7.70 (2H, d, \(J = 8.7\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 17.0, 20.2, 20.5, 26.2, 28.1, 29.8, 33.1, 33.2, 39.7, 49.4, 51.5, 55.2, 60.0, 72.0, 82.2, 113.2, 127.5, 129.6, 160.3, 176.7; ESIHRMS: Found: m/z 387.3009. Calcd for C\(_{24}\)H\(_{39}\)N\(_2\)O\(_2\): (M+H)\(^{+}\) 387.3012.

2,2,6,6-Tetramethyl-1-((2,4,4-trimethyl-5-(4-phenoxphenyl)-3,4-dihydro-2H-pyrrol-2-yl)methoxy)piperidine (3ac):

![Chemical Structure of 3ac](image)

Colourless oil; IR (NaCl) 2968, 2932, 2870, 1587, 1489, 1373, 1308, 1238, 1165, 1132, 1053, 993, 750 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.07 (3H, s), 1.13 (3H, s), 1.19 (3H x 2, s, overlapped), 1.24 (3H, s), 1.32 (3H, s), 1.37 (3H, s), 1.44-1.51 (6H, m), 1.69 (1H, d, \(J = 13.2\) Hz), 2.35 (1H, d, \(J = 13.2\) Hz), 3.79 (1H, d, \(J = 8.4\) Hz), 3.89 (1H, d, \(J = 8.4\) Hz), 6.98 (2H, d, \(J = 8.6\) Hz), 7.03 (2H, d, \(J = 8.2\) Hz), 7.12 (1H, t, \(J = 7.4\) Hz), 7.34 (2H, dd, \(J = 7.4, 8.2\) Hz), 7.69 (2H, d, \(J = 8.6\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 16.5, 19.8, 20.1, 26.2, 27.5, 29.3,
32.6, 32.7, 39.2, 48.7, 51.2, 59.5, 71.8, 82.2, 117.5, 118.7, 123.0, 129.3, 129.6, 156.2, 157.7, 176.3; ESIHRMS: Found: m/z 449.3169. Calcd for C_{29}H_{41}N_2O_2: (M+H)^+ 449.3168.

2,2,6,6-Tetramethyl-1-((2,4,4-trimethyl-5-\alpha-tolyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)piperidine (3ad):

Colourless oil; IR (NaCl) 2965, 2932, 1634, 1470, 1450, 1375, 1360, 1132, 1053, 993, 908, 756, 729 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.15 (3H, s), 1.17 (3H, s), 1.19 (3H, s), 1.22 (3H, s), 1.24 (3H, s), 1.25 (3H, s), 1.35 (3H, s), 1.22-1.56 (6H, m), 1.69 (1H, d, \(J = 12.8\) Hz), 2.33 (3H, s), 2.36 (1H, d, \(J = 12.8\) Hz), 3.84 (1H, d, \(J = 8.8\) Hz), 3.92 (1H, d, \(J = 8.8\) Hz), 7.12-7.17 (2H, m), 7.19-7.23 (2H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 16.8, 19.8, 20.2, 20.4, 27.0, 27.4, 28.3, 32.9, 33.0, 39.6, 46.5, 53.6, 59.8, 73.5, 82.4, 124.4, 127.4, 127.5, 130.0, 135.2, 135.9, 179.0; ESIHRMS: Found: m/z 371.3064. Calcd for C_{24}H_{39}N_{2}O: (M+H)^+ 371.3062.

2,2,6,6-Tetramethyl-1-((2,4,4-trimethyl-5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)methoxy)piperidine (3ae):

Colourless oil; IR (NaCl) 2968, 2932, 2870, 1607, 1470, 1449, 1373, 1360, 1306, 1261, 1132, 1053, 908, 750, 731 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.09 (3H, s), 1.15 (3H, s), 1.19 (3H, s), 1.22 (3H, s), 1.29 (3H, s), 1.37 (3H, s), 1.44 (3H, s), 1.53 (3H, s), 1.32-1.53 (6H, m), 1.74 (1H, d, \(J =

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12.8 Hz), 2.41 (1H, d, J = 12.8 Hz), 3.84 (1H, d, J = 8.6 Hz), 3.96 (1H, d, J = 8.6 Hz), 7.45-7.50 (2H, m), 7.81-7.89 (4H, m), 8.16 (1H, s); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.7, 20.0, 20.3, 26.4, 27.8, 29.6, 32.8, 33.0, 39.4, 48.9, 51.7, 59.7, 72.2, 82.4, 125.6, 125.8, 126.2, 127.2, 127.3, 128.2, 132.3, 132.5, 133.2, 177.3; ESIHRMS: Found: m/z 407.3061. Calcd for C$_{27}$H$_{39}$N$_2$O: (M+H)$^+$ 407.3062.

1-((5-(4-Chlorophenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)-2,2,6,6-tetramethylpiperidine (3af):

Colourless oil; IR (NaCl) 2968, 2932, 2870, 1611, 1468, 1373, 1306, 1261, 1132, 1094, 1053, 993, 908, 756, 731 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.06 (3H, s), 1.13 (3H, s), 1.20 (3H, s), 1.23 (3H, s), 1.32 (3H, s), 1.35 (3H, s), 1.43 (3H, s), 1.30-1.51 (6H, m), 1.69 (1H, d, J = 13.0 Hz), 2.36 (1H, d, J = 13.0 Hz), 3.78 (1H, d, J = 8.6 Hz), 3.91 (1H, d, J = 8.6 Hz), 7.33 (2H, d, J = 8.6 Hz), 7.63 (2H, d, J = 8.6 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.9, 20.2, 20.5, 26.5, 27.7, 29.5, 33.0, 33.2, 39.6, 48.9, 51.8, 59.9, 72.5, 82.5, 128.2, 129.4, 133.6, 135.0, 176.6; ESIHRMS: Found: m/z 391.2524. Calcd for C$_{23}$H$_{36}$ClN$_2$O: (M+H)$^+$ 391.2516.

2,2,6,6-Tetramethyl-1-((2,4,4-trimethyl-5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)methoxy)piperidine (3ag):

![Diagram](image-url)
Colourless oil; IR (NaCl) 2972, 2930, 2870, 1601, 1447, 1360, 1308, 1261, 1231, 1186, 1132, 1053, 930, 729, 718 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.00 (3H, s), 1.12 (3H, s), 1.19 (3H, s), 1.24 (3H, s), 1.31 (3H, s), 1.48 (3H, s), 1.51 (3H, s), 1.28-1.48 (6H, m), 1.69 (1H, d, \(J = 12.8\) Hz), 2.35 (1H, d, \(J = 12.8\) Hz), 3.77 (1H, d, \(J = 8.4\) Hz), 3.87 (1H, d, \(J = 8.4\) Hz), 7.04 (1H, dd, \(J = 3.6, 5.0\) Hz), 7.34 (1H, dd, \(J = 0.8, 5.0\) Hz), 7.45 (1H, dd, \(J = 0.8, 3.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 16.9, 20.1, 20.4, 26.5, 27.8, 29.5, 32.8, 33.1, 39.5, 49.4, 51.3, 59.8, 72.8, 82.5, 127.0, 127.2, 127.8, 138.3, 171.0; ESIHRMS: Found: m/z 363.2474. Calcd for C\(_{21}\)H\(_{35}\)N\(_2\)OS: (M+H\(^+\)) 363.2470.

1-((4,4-Dimethyl-5-p-tolyl-3,4-dihydro-2H-pyrrol-2-yl) methoxy)-2,2,6,6-tetramethylpiperidine (3ba):

![Chemical Structure](image)

Colourless oil; IR (NaCl) 2970, 2932, 2870, 1601, 1466, 1452, 1373, 1244, 1132, 1045, 908, 822, 754, 731 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.09 (3H, s), 1.13 (3H, s), 1.22 (3H, s), 1.28 (3H, s), 1.37 (3H, s), 1.38 (3H, s), 1.44-1.51 (6H, m), 1.87 (1H, dd, \(J = 10.4, 16.4\) Hz), 2.05 (1H, dd, \(J = 10.4, 16.4\) Hz), 2.36 (3H, s), 3.94 (1H, dd, \(J = 8.4, 11.2\) Hz), 4.12 (1H, dd, \(J = 6.2, 11.2\) Hz) 4.12-4.24 (1H, m), 7.17 (2H, d, \(J = 8.0\) Hz), 7.63 (2H, d, \(J = 8.0\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 16.3, 19.3, 19.4, 20.4, 25.8, 26.4, 32.3, 36.8, 38.8, 44.1, 49.4, 59.0, 66.4, 78.5, 127.0, 127.9, 131.1, 138.4, 178.6; ESIHRMS: Found: m/z 357.2900. Calcd for C\(_{23}\)H\(_{37}\)N\(_2\)O: (M+H\(^+\)) 357.2906.
1-((4,4-Diallyl-5-p-tolyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)-2,2,6,6-

tetramethylpiperidine (3ca):

Colourless oil; IR (NaCl) 2974, 2928, 2870, 1639, 1512, 1470, 1449, 1373, 1360, 1261,
1182, 1132, 993, 914, 820, 754 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.09 (3H, s), 1.12 (3H, s),
1.20 (3H, s), 1.25 (3H, s), 1.30-1.49 (6H, m), 1.99 (1H, dd, \(J = 8.0, 13.2\) Hz), 2.09 (1H, dd, \(J = 8.0, 13.2\) Hz), 2.34-2.44 (2H, m), 2.37 (3H, s), 2.56 (1H, dd, \(J = 6.0, 14.2\) Hz), 2.62 (1H, dd, \(J = 6.4, 14.2\) Hz), 3.98 (1H, dd, \(J = 5.6, 8.8\) Hz), 4.04 (1H, dd, \(J = 4.4, 8.8\) Hz), 4.06-4.13 (1H, m), 5.99 (1H, d, \(J = 9.9\) Hz), 5.00 (1H, d, \(J = 17.2\) Hz), 5.05 (1H, d, \(J = 10.1\) Hz), 5.12 (1H, d, \(J = 16.8\) Hz), 5.57-5.67 (1H, m), 5.70-5.80 (1H, m), 7.18 (2H, d, \(J = 8.0\) Hz), 7.66 (2H, d, \(J = 8.0\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 17.1, 20.1, 20.3, 21.3, 33.1, 36.8, 39.6, 42.8, 43.6,
58.4, 59.9, 68.5, 79.0, 118.17, 118.21, 127.8, 128.9, 132.3, 134.0, 134.3, 139.4, 176.0;
ESIHRMS: Found: m/z 409.3216. Calcd for C\(_{27}\)H\(_{41}\)N\(_2\)O: (M+H)\(^+\) 409.3219.

3-((2,2,6,6-Tetramethylpiperidin-1-yloxy)methyl)-1-p-tolyl-2-azaspiro[4.5]dec-1-ene

(3da):

Colourless oil; IR (NaCl) 2970, 2930, 2859, 1601, 1512, 1470, 1449, 1373, 1298, 1184, 1132,
1057, 993, 908, 754, 731 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.11-1.22 (12H, m), 1.34-1.42
(2H, m), 1.45-1.51 (5H, m), 1.56-1.58 (2H, m), 1.70-1.77 (7H, m), 1.81 (1H, dd, J = 7.2, 12.8 Hz), 2.23 (1H, dd, J = 8.0, 12.8 Hz), 2.36 (3H, s), 3.95 (1H, dd, J = 6.0, 8.4 Hz), 4.10 (1H, dd, J = 4.4, 8.4 Hz), 4.18-4.24 (1H, m), 7.17 (2H, d, J = 8.0 Hz), 7.48 (2H, d, J = 8.0 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 17.0, 20.2, 21.2, 23.1, 23.3, 25.6, 32.9, 33.1, 34.9, 37.6, 39.6, 56.3, 59.8, 68.1, 79.3, 127.9, 28.5, 133.0, 138.6, 180.4; ESIHRMS: Found: m/z 397.3217. Calcd for C$_{26}$H$_{41}$N$_2$O: (M+H)$^+$ 397.3219.

1-((4-Allyl-4-phenyl-5-p-tolyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)-2,2,6,6-tetramethylpiperidine (3ea-trans (major)):

![Structural diagram]

Colourless oil; IR (NaCl) 2974, 2930, 2872, 1611, 1470, 1445, 1373, 1360, 1182, 1132, 1055, 1020, 908, 822, 731 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.10 (3H, s), 1.12 (3H, s), 1.22 (3H, s), 1.29 (3H, s), 1.26-1.58 (6H, m), 2.08 (1H, dd, J = 7.6, 13.0 Hz), 2.29 (3H, s), 2.42 (1H, dd, J = 8.8, 13.0 Hz), 2.89-2.99 (2H, m), 4.06 (1H, dd, J = 6.0, 8.6 Hz), 4.13 (1H, dd, J = 4.8, 8.6 Hz), 4.27-4.34 (1H, m), 4.99 (1H, d, J = 18.3 Hz), 5.00 (1H, d, J = 10.3 Hz), 5.55 (1H, dddd, J = 6.0, 8.1, 10.3, 18.3 Hz), 7.03 (2H, d, J = 8.2 Hz), 7.23-7.27 (1H, m), 7.30-7.34 (4H, m), 7.38 (2H, d, J = 8.2 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 17.0, 20.0, 20.2, 21.2, 33.0, 39.6, 40.2, 42.2, 59.8, 61.3, 68.7, 78.8, 118.8, 125.4, 126.5, 128.2, 128.7, 128.8, 131.5, 134.1, 139.6, 145.6, 175.5; ESIHRMS: Found: m/z 445.3215. Calcd for C$_{30}$H$_{41}$N$_2$O: (M+H)$^+$ 445.3219.
NOE experiments of 3ea-trans:

Fig. S1

Fig. S2

1-((4-Allyl-4-phenyl-5-p-tolyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)-2,2,6,6-tetramethylpiperidine (3ea-cis (minor)):
Colourless oil; IR (NaCl) 2974, 2930, 1609, 1472, 1373, 1360, 1184, 1132, 908, 754, 731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.08 (3H, s), 1.09 (3H, s), 1.16 (3H, s), 1.23 (3H, s), 1.29-1.57 (6H, m), 2.26 (3H, s), 2.34 (1H, dd, J = 7.6, 13.2 Hz), 2.47 (1H, dd, J = 7.6, 13.2 Hz), 2.91 (1H, dd, J = 8.8, 13.6 Hz), 3.03 (1H, dd, J = 6.0, 13.6 Hz), 4.05-4.09 (1H, m), 4.18-4.23 (2H, m), 5.05 (1H, d, J = 10.2 Hz), 5.12 (1H, d, J = 16.6 Hz), 5.69 (1H, m), 6.99 (2H, d, J = 8.2 Hz), 7.19 (1H, t, J = 7.3 Hz), 7.29 (2H, dd, J = 7.3, 7.7 Hz), 7.40 (2H, d, J = 7.7 Hz), 7.46 (2H, d, J = 8.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 17.6, 20.3, 20.4, 21.2, 32.9, 33.1, 39.7, 41.0, 44.9, 59.9, 61.9, 70.0, 78.4, 118.7, 126.2, 126.4, 128.5, 128.7, 128.8, 130.5, 133.6, 139.6, 147.5, 173.7; ESIHRMS: Found: m/z 445.3224. Calcd for C₃₀H₄₁N₂O: (M+H)⁺ 445.3219.

**NOE experiments of 3ea-cis:**

Although the NOE experiment by irradiation to the proton Hₙ was examined, the signal from Hₙ was very obscure (the proton Hₙ was overlapped with another proton).
1-(2-(4,4-Dimethyl-5-p-tolyl-3,4-dihydro-2\textsubscript{H}-pyrrol-2-yl)propan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (3fa):

Colourless oil; IR (NaCl) 3007, 2924, 1670, 1603, 1564, 1512, 1464, 1373, 1136, 1061, 1011, 908, 822, 756, 731 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 1.08 (3H, s), 1.10 (3H, s), 1.13 (3H, s), 1.18 (3H, s), 1.19 (3H, s), 1.30-1.56 (6H, m), 1.32 (3H, s), 1.39 (3H, s), 1.62 (3H, s), 1.94 (1H, dd, \( J = 9.3, 13.2 \) Hz), 2.00 (1H, dd, \( J = 7.4, 13.2 \) Hz), 2.36 (3H, s), 4.31 (1H, dd, \( J = 7.4, 9.3 \) Hz), 7.16 (2H, d, \( J = 7.8 \) Hz), 7.60 (2H, d, \( J = 7.8 \) Hz); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 17.2, 20.4, 20.8, 21.3, 22.9, 24.7, 26.4, 26.9, 34.7, 34.8, 40.9, 43.3, 49.9, 59.29, 59.32, 80.6, 127.8, 128.8, 132.3, 139.2, 178.7; ESIHRMS: Found: m/z 385.3221. Calcd for C\textsubscript{25}H\textsubscript{41}N\textsubscript{2}O: (M+H)\textsuperscript{+} 385.3219.

2,2,6,6-Tetramethyl-1-((5-p-tolyl-3,4-dihydro-2\textsubscript{H}-pyrrol-2-yl)methoxy)piperidine (3ga):

Colourless oil; IR (NaCl) 2972, 2930, 2870, 1614, 1470, 1454, 1373, 1360, 1337, 1261, 1132, 1053, 907, 754, 731 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 0.95 (3H, s), 1.10 (3H, s), 1.15 (3H, s), 1.21 (3H, s), 1.26-1.48 (6H, m), 1.97-2.06 (1H, m), 2.08-2.17 (1H, m), 2.38 (3H, s), 2.89-3.04 (2H, m), 3.94 (1H, dd, \( J = 5.2, 8.8 \) Hz), 4.07 (1H, dd, \( J = 4.4, 8.8 \) Hz), 4.41-4.43 (1H, m), 7.20 (2H, d, \( J = 8.2 \) Hz), 7.74 (2H, d, \( J = 8.2 \) Hz); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 17.0, 20.0,
20.2, 21.4, 25.9, 33.0, 33.2, 35.3, 39.6 59.8, 72.2, 79.1, 127.6, 129.0, 132.0, 140.3, 173.2;
ESIHRMS: Found: m/z 329.2596. Calcd for C_{21}H_{33}N_{2}O: (M+H)^+ 329.2953.

4. Synthesis of N-Allylamidines 4

\[
\begin{align*}
\text{\text{-}} & \quad \text{NH} \\
\text{\text{-}} & \quad \text{NC} \\
\text{\text{-}} & \quad \text{AlCl}_3 \\
\text{\text{-}} & \quad \text{NH} \\
\text{\text{-}} & \quad \text{phenylbenzimidamide} \\
\end{align*}
\]

Synthesis of N-allylamidines 4a-f: \(^3\) A typical procedure for the synthesis of 4a: To a 50 mL sealed tube was added benzonitrile (3.00 mL, 29.3 mmol), N-allylaniline (4.80 mL, 35.4 mmol) and AlCl\(_3\) (3.92 g, 29.4 mmol). The reaction was then heated at 120 °C for 1 h. Saturated NaOH solution was then added drop wise into the hot melt while maintaining vigorous stirring until pH 14 was reached. The mixture was then cooled down to rt and extracted thrice with 80 mL of CH\(_2\)Cl\(_2\). The organic phase was then washed with water, brine and finally dried over MgSO\(_4\). The organic extract was filtered and the solvent was evaporated to give crude mixture, which was purified by flash column chromatography (100% ethyl acetate then ethyl acetate/Et\(_3\)N = 95:5) to provide product 4a (4.20 g, 17.8 mmol) for 61% yield.

N-Allyl-N-phenylbenzimidamide (4a):

Yield 61%; Pale yellow solid; m.p. 32-34 °C; IR (NaCl) 3314, 3061, 2980, 1643, 1589, 1568, 1495, 1433, 1393, 1179 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 4.59\) (2H, d, \(J = 5.4\) Hz), 5.17 (1H, dd, \(J = 1.4, 10.3\) Hz), 5.24 (1H, dd, \(J = 1.5, 17.2\) Hz), 6.01-6.11 (1H, m), 6.96-7.00 (3H,
m), 7.12 (2H, d, J = dd, J = 7.8, 7.8 Hz), 7.18-7.30 (5H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 54.0, 116.4, 124.8, 126.7, 127.7, 128.0, 128.6, 128.8, 134.0, 138.6, 145.4, 167.7; ESIHRMS: Found: m/z 237.1391. Calcd for C$_{16}$H$_{17}$N$_2$: (M+H)$^+$ 237.1392.

$N$-Allyl-2-methyl-$N$-phenylbenzimidamide (4b):

\[
\begin{array}{c}
\text{NH} \\
\text{Me} \\
\text{C} \\
\text{H} \\
\text{Cl}
\end{array}
\]

Yield 30%; Yellow sticky oil; IR (NaCl) 3422, 3316, 2922, 1639, 1572, 1493, 1395, 1173, 1125, 1034 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.30 (3H, s), 4.50 (2H, s), 5.13-5.20 (2H, m), 5.99-6.09 (1H, m), 7.00-7.19 (9H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 19.5, 53.4, 116.8, 125.4, 125.5, 127.2, 127.9, 128.2, 128.5, 130.1, 133.9, 134.0, 138.4, 144.2, 167.1; ESIHRMS: Found: m/z 251.1551. Calcd for C$_{17}$H$_{19}$N$_2$: (M+H)$^+$ 251.1548.

$N$-Allyl-4-chloro-$N$-phenylbenzimidamide (4c):

\[
\begin{array}{c}
\text{NH} \\
\text{Cl}
\end{array}
\]

Yield 47%; Pale yellow solid; m.p. 53-55 °C; IR (NaCl) 3447, 3318, 2978, 1639, 1580, 1560, 1493, 1404, 1182, 1090, 1015, 754 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.56 (1H, d, J = 5.1 Hz), 5.17 (1H, d, J = 10.3 Hz), 5.23 (1H, d, J = 17.2 Hz), 5.99-6.09 (1H, m), 6.95 (2H, d, J = 7.7 Hz), 7.01 (1H, dd, J = 7.4, 7.4 Hz), 7.13-7.26 (6H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
N-Allyl-N-phenyl-2-naphthimidamide (4d):

Yield 43%; White solid; m.p. 80-82 °C; IR (NaCl) 3445, 3057, 2928, 1643, 1566, 1493, 1431, 1398, 1344, 1229, 1169, 1126, 1034 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.64 (2H, d, \(J = 4.8\) Hz), 5.19 (1H, d, \(J = 10.3\) Hz), 5.28 (1H, d, 17.2 Hz), 6.05-6.13 (1H, m), 6.94 (1H, d, \(J = 7.2\), 7.2 Hz), 7.03 (2H, d, \(J = 7.8\) Hz), 7.09 (2H, dd, \(J = 7.9, 7.9\) Hz), 7.33 (1H, d, \(J = 8.4\) Hz), 7.43-7.47 (2H, m), 7.62 (1H, d, \(J = 8.5\) Hz), 7.72-7.77 (2H, m), 7.87 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 54.2, 116.5, 124.9, 125.0, 126.4, 126.7, 127.5, 127.61, 127.67 (two carbons overlapped), 128.3, 128.7, 132.7, 133.2, 134.0, 136.2, 145.4, 167.7; ESIHRMS: Found: m/z 287.1549. Calcd for C\(_{20}\)H\(_{19}\)N\(_2\): (M+H)\(^+\) 287.1548.

N-Allyl-N-phenylthiophene-2-carboximidamide (4e):

Yield 66%; Yellow sticky oil; IR (NaCl) 3312, 3073, 2922, 1643, 1568, 1518, 1435, 1385, 1323, 1229, 1165, 1138, 1042, 1032 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.55 (2H, d, \(J = 6.2\) Hz), 5.16 (1H, dd, \(J = 1.4, 6.3\) Hz), 5.23 (1H, dd, \(J = 3.0, 17.2\) Hz), 5.98-6.06 (1H, m), 6.79 (1H, dd, \(J = 3.7, 4.6\) Hz), 6.98 (1H, dd, \(J = 1.1, 3.6\) Hz), 7.03-7.08 (3H, m), 7.17-7.21 (3H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 54.4, 116.6, 125.2, 126.4, 126.5, 127.3, 128.5, 128.7,
133.6, 140.2, 145.4, 160.4; ESIHRMS: Found: m/z 243.0955. Calcd for C_{14}H_{15}N_{2}S: (M+H)^+ 243.0956.

\[ \text{N,N-Diallylbenzimidamide (4f):} \]

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{H} \\
\text{N}
\end{array}
\]

Yield 47%; Yellow sticky oil; IR (NaCl) 3447, 3076, 2916, 1641, 1585, 1497, 1454, 1414, 1198, 1101, 1028 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.90 (4H, d, \(J = 3.8\) Hz), 5.14-5.19 (4H, m), 5.76-5.86 (2H, m), 7.32-7.37 (5H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 49.6, 116.7, 126.4, 128.4, 128.8, 133.8, 138.7, 169.2; ESIHRMS: Found: m/z 201.1391. Calcd for C_{13}H_{17}N_{2}: (M+H)^+ 201.1392.

5. **Synthesis of 4,5-dihydro-1\(H\)-imidazoles 5**

A typical procedure for the synthesis of 5a: To a 25 mL Schlenk tube was added amidine 4a (136.7 mg, 0.58 mmol), Cu(OAc)\(_2\) (113.0 mg, 0.62 mmol), and TEMPO (135.5 mg, 0.87 mmol) in DMF (6.0 mL). The reaction was then heated at 80 \(^\circ\)C for 24 h. The reaction was quenched with pH 9 ammonium buffer solution at rt. It was then extracted three times with ethyl acetate. The organic phase was then washed with water and brine, and dried over MgSO\(_4\). The solvent was removed in vacuo, affording crude residue, which was purified by
flash column chromatography (hexane/ethyl acetate = 80:20, gradually 20% ethyl acetate increment every time after 50 mL eluent, until 100% ethyl acetate was reached) to provide 5a (126.8 mg, 0.33 mmol) for 56% yield (all amidines were obtained as more than 90% purity along with inseparable unidentified impurities).

1-((1,2-Diphenyl-4,5-dihydro-1H-imidazol-4-yl)methoxy)-2,2,6,6-tetramethylpiperidine (5a):

Yellow oil; IR 2932, 1614, 1574, 1495, 1470, 1385, 1360, 1300, 1283, 1134, 1051, 1028 (NaCl) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (3H, s), 1.08 (3H, s), 1.17 (3H, s), 1.24 (3H, s), 1.42-1.49 (6H, m), 3.95-3.98 (2H, m), 4.05-4.08 (1H, m), 4.22 (1H, dd, J = 9.4, 9.9 Hz), 4.33-4.43 (1H, m), 6.79 (2H, d, J = 8.1 Hz), 6.96 (1H, dd, J = 7.1, 7.4 Hz), 7.15 (2H, dd, J = 7.6, 7.8 Hz), 7.25-7.29 (2H, m), 7.35 (1H, dd, J = 7.1, 7.4 Hz), 7.51 (2H, d, J = 7.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 17.0, 19.9, 20.1, 33.1, 33.3, 39.6, 56.7, 60.0, 63.5, 78.6, 122.6, 123.1, 128.1, 128.2, 128.6, 128.7, 129.8, 131.3, 143.1; ESIHRMS: Found: m/z 392.2701. Calcd for C₂₅H₃₄N₃O: (M+H)⁺ 392.2702.

Yield: 56% with 6% of 6a (NMR yield)

4-Methyl-1,2-diphenyl-1H-imidazole (6a):⁴
Yellow oil; IR (NaCl) 2924, 1694, 1574, 1470, 1408, 1306, 1285, 1217, 1190, 1070 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.34 (3H, d, $J = 0.74$ Hz), 6.89 (1H, d, $J = 0.74$ Hz), 7.18-7.25 (5H, m), 7.34-7.39 (5H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.5, 119.4, 125.7, 127.8, 128.06, 128.12, 128.5, 129.3, 130.3, 138.0, 138.6, 145.8; ESIHRMS: Found: m/z 235.1236. Calcd for C$_{16}$H$_{15}$N$_2$: (M+H)$^+$ 235.1235.

2,2,6,6-Tetramethyl-1-((1-phenyl-2-(o-tolyl)-4,5-dihydro-1H-imidazol-4-yl)methoxy)piperidine (5b):

Yellow oil; IR (NaCl) 2932, 1614, 1597, 1574, 1487, 1470, 1454, 1385, 1360, 1321, 1263, 1146, 1132, 1047 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.07 (3H, s), 1.13 (3H, s), 1.21-1.23 (two singlets of 3H overlapped, total 6H), 1.42-1.51 (6H, m), 2.13 (3H, s), 3.95-4.03 (2H, m), 4.11-4.17 (2H, m), 4.37-4.44 (1H, m), 6.65 (2H, d, $J = 8.0$ Hz), 6.88 (1H, dd, $J = 7.4$, 7.4 Hz), 7.06-7.11 (3H, m), 7.18 (1H, dd, $J = 7.4$, 7.4 Hz), 7.25-7.28 (1H, m), 7.39 (1H, d, $J = 7.4$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 17.1, 19.5, 20.0, 20.2, 33.2, 33.3, 39.7, 54.4, 60.0, 63.2, 78.8, 119.4, 122.3, 125.9, 128.6, 129.0, 129.4, 130.3, 132.1, 136.2, 141.4, 161.9; ESIHRMS: Found: m/z 406.2860. Calcd for C$_{26}$H$_{36}$N$_3$O: (M+H)$^+$ 406.2858.

**Yield:** 77% with 4% of 6b (NMR yield)
1-((2-(4-Chlorophenyl)-1-phenyl-4,5-dihydro-1H-imidazol-4-yl)methoxy)-2,2,6,6-tetramethylpiperidine (5c):

Yellow oil; IR (NaCl) 2932, 1614, 1591, 1495, 1470, 1402, 1373, 1360, 1296, 1261, 1134, 1092, 1016, 835 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.96 (3H, s), 1.07 (3H, s), 1.16 (3H, s), 1.23 (3H, s), 1.39-1.49 (6H, m), 3.95 (2H, ddd, \(J = 6.4, 8.9, 15.6\) Hz), 4.04 (1H, dd, \(J = 3.7, 8.9\) Hz), 4.21 (1H, dd, \(J = 9.4, 10.3\) Hz), 4.32-4.39 (1H, m), 6.80 (2H, d, \(J = 7.7\) Hz), 7.00 (1H, dd, \(J = 7.4, 7.4\) Hz), 7.18 (2H, dd, \(J = 7.4, 7.7\) Hz), 7.25 (2H, d, \(J = 8.6\) Hz), 7.44 (2H, d, \(J = 8.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 16.9, 19.9, 20.1, 33.07, 33.14, 39.5, 56.8, 59.9, 63.5, 78.4, 122.7, 123.5, 128.3, 128.7, 129.6, 130.0, 135.8, 142.9, 161.4; ESIHRMS: Found: m/z 426.2314. Calcd for C\(_{25}\)H\(_{33}\)ClN\(_3\)O: (M+H)+ 426.2312.

**Yield**: 54% with 7% of 6c (NMR yield)

2,2,6,6-Tetramethyl-1-((2-(naphthalen-2-yl)-1-phenyl-4,5-dihydro-1H-imidazol-4-yl)methoxy)piperidine (5d):

Yellow oil; IR (NaCl) 2932, 1614, 1593, 1570, 1499, 1476, 1393, 1375, 1360, 1300, 1263, 1236, 1198, 1134, 1053, 1032 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.98 (3H, s), 1.09 (3H, s),
1.19 (3H, s), 1.27 (3H, s), 1.41-1.51 (6H, m), 3.99-4.04 (2H, m), 4.11 (1H, dd, J = 3.8, 8.8 Hz), 4.27 (1H, dd, J = 9.4, 10.3 Hz), 4.39-4.44 (1H, m), 6.84 (2H, d, J = 7.7 Hz), 6.95 (1H, dd, J = 7.3, 7.3 Hz), 7.13 (2H, dd, J = 7.6, 8.0 Hz), 7.44-7.53 (3H, m), 7.72 (1H, d, J = 8.5 Hz), 7.79 (2H, dd, J = 6.8, 7.2 Hz), 8.13 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 17.1, 20.0, 33.16, 33.20, 39.6, 58.0, 59.8, 63.7, 78.5, 124.7, 124.9, 126.9, 128.2, 128.9, 129.5, 133.3, 143.3, 157.1; ESIHRMS: Found: m/z 442.2857. Calcd for C\(_{29}\)H\(_{36}\)N\(_3\)O: (M+H)\(^{+}\) 442.2858.

**Yield:** 59% with 6% of 6e (NMR yield)

\[2,2,6,6\text{-Tetramethyl-1-}\left(1\text{-phenyl-2-(thiophen-2-yl)-4,5-dihydro-1H-imidazol-4-yl}\right)\text{methoxy)piperidine (5e):}\]

![Structure of 2,2,6,6-Tetramethyl-1-((1-phenyl-2-(thiophen-2-yl)-4,5-dihydro-1H-imidazol-4-yl)methoxy)piperidine (5e)](image)

Yellow oil; IR (NaCl) 2932, 1593, 1520, 1495, 1470, 1435, 1373, 1360, 1298, 1263, 1132, 1105, 1047, 1030 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.00 (3H, s), 1.07 (3H, s), 1.17 (3H, s), 1.23 (3H, s), 1.41-1.52 (6H, m), 3.89 (1H, dd, J = 6.8, 9.1 Hz), 3.95 (1H, dd, J = 6.5, 8.8 Hz), 4.05 (1H, dd, J = 3.8, 8.8 Hz), 4.14 (1H, dd, J = 9.3, 10.2 Hz), 4.32-4.39 (1H, m), 6.85-6.87 (2H, m), 7.05 (2H, d, J = 7.4 Hz), 7.13 (1H, dd, J = 7.4, 7.4 Hz), 7.25-7.31 (3H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 17.1, 20.0, 20.2, 33.16, 33.20, 39.6, 58.0, 59.8, 63.7, 78.5, 124.7, 124.9, 126.9, 128.2, 128.9, 129.5, 133.3, 143.3, 157.1; ESIHRMS: Found: m/z 398.2264. Calcd for C\(_{23}\)H\(_{32}\)N\(_3\)OS: (M+H)\(^{+}\) 398.2266.

**Yield:** 56% with 6% of 6f (NMR yield)
1-((1-Allyl-2-phenyl-4,5-dihydro-1H-imidazol-4-yl)methoxy)-2,2,6,6-tetramethylpiperidine (5f):

Yellow oil; IR (NaCl) 2930, 1614, 1595, 1499, 1470, 1447, 1402, 1373, 1360, 1246, 1132, 1047, 1028 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.10 (3H, s), 1.12 (3H, s), 1.20 (3H, s), 1.24 (3H, s), 1.39-1.61 (6H, m), 3.43 (1H, dd, \(J = 8.0, 8.4\) Hz), 3.57-3.68 (2H, m), 3.76 (1H, dd, \(J = 4.8, 16.3\) Hz), 3.89 (1H, dd, \(J = 6.9, 7.8\) Hz), 4.02 (1H, d, \(J = 5.7\) Hz), 4.21-4.31 (1H, m), 5.23 (2H, dd, \(J = 10.2, 17.1\) Hz), 5.74-5.83 (1H, m), 7.56 (2H, d, \(J = 7.1\) Hz), 7.35-7.41 (3H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 17.0, 20.1, 20.2, 33.1, 33.2, 39.6, 51.4, 53.6, 59.8, 63.8, 78.8, 116.5, 128.1, 128.3, 129.8, 131.2, 134.3, 166.9; ESIHRMS: Found: m/z 356.2703. Calcd for C\(_{22}\)H\(_{34}\)N\(_3\)O: (M+H)\(^+\) 356.2702.

Yield: 35% with 6% of 6g (NMR yield)

\((1,2\text{-Diphenyl-1H-imidazol-4-yl})\text{methyl acetate (6a')}:\)

Yellow oil; IR (NaCl) 2957, 1732, 1597, 1499, 1472, 1456, 1447, 1410, 1362, 1246, 1233, 1070, 1028 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.13 (3H, s), 5.16 (2H, s), 7.20-7.27 (5H, m), 7.37-7.40 (5H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.1, 60.4, 122.4, 125.8, 128.2, 128.3,
128.6, 128.7, 129.5, 129.9, 136.7, 138.2, 147.0, 171.1; ESIHRMS: Found: m/z 293.1293.

Calcd for C$_{18}$H$_{17}$N$_2$O$_2$: (M+H)$_+^+$ 293.1290.
$^1$H NMR spectrum of 3aa (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3aa (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3ab (300MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3ab (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3ac (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3ac (400MHz, CDCl$_3$)
\(^1\)H NMR spectrum of 3ad (400MHz, CDCl\(_3\))

\(^{13}\)C NMR spectrum of 3ad (400MHz, CDCl\(_3\))
$^1$H NMR spectrum of 3ae (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3ae (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3af (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3af (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3ag (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3ag (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3ba (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3ba (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3ca (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3ca (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3da (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3da (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3ea-trans (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3ea-trans (400MHz, CDCl$_3$)
$^1$H NMR spectrum of $3\text{ea-cis}$ (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of $3\text{ea-cis}$ (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3fa (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3fa (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 3ga (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3ga (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 4b (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 4b (100MHz, CDCl$_3$)
$^1$H NMR spectrum of 4c (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 4c (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 4d (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 4d (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 4e (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 4e (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 4f (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 4f (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 5a (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 5a (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 5b (400MHz, CDCl$_3$)

13C NMR spectrum of 5b (400MHz, CDCl$_3$)
\( ^1H \) NMR spectrum of 5e (400MHz, CDCl\(_3\))

\[ \text{Diagram of the } ^1H \text{ NMR spectrum} \]

\( ^{13}C \) NMR spectrum of 5e (400MHz, CDCl\(_3\))

\[ \text{Diagram of the } ^{13}C \text{ NMR spectrum} \]
$^1$H NMR spectrum of 5d (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 5d (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 5e (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 5e (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 5f (400MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 5f (400MHz, CDCl$_3$)
\(^1\)H NMR spectrum of 6a\(^*\) (400MHz, CDCl\(_3\))

\(^{13}\)C NMR spectrum of 6a\(^*\) (400MHz, CDCl\(_3\))
References