Electronic Supplementary Information

TEMPO-Mediated Allylic C-H Amination with Hydrazones

Xu Zhu and Shunsuke Chiba*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore.

E-mail: shunsuke@ntu.edu.sg

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1. General

$^1$H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 or 300 spectrometers in CDCl$_3$ [using CDCl$_3$ (for $^1$H, $\delta = 7.26$) as the internal standard unless otherwise stated]. $^{13}$C NMR (100 MHz) spectra on a Bruker Avance 400 or 300 spectrometers in CDCl$_3$ [using CDCl$_3$ (for $^{13}$C, $\delta = 77.00$) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, tt = triplet of triplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, tdd = triplet of doublet of doublet, dddd = doublet of doublet of doublet of doublet, m = multiplet, br = broad. IR spectra were recorded on a Shimazu IR Prestige-21 FT-IR Spectrometer on NaCl plate. High-resolution mass spectra were obtained with a Q-Tof Premier LC HR mass spectrometer (Waters). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractometer. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Flash column chromatography was performed using either Merck silica gel 60 or with distilled solvents. DMF (anhydrous), 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), diisopropyl azodicarboxylate (DIAD) and K$_2$CO$_3$ were purchased from Sigma-Aldrich Co., Inc. In the case that hydrazones (3l, 3m) were obtained as a mixture of E/Z-isomers, the stereochemistry was assigned using $^{13}$C NMR (the chemical shift of $\alpha$-carbon with syn to the NH is farther to the higher field than that with anti to the NH).$^1$

2. Synthesis of oximes 1 and hydrazones 3

2.1 Synthesis of oximes 1

General procedure:$^2$

$$\begin{align*}
&\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{O} \\
&\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{NH} \quad \text{HCl (1.5 equiv)} \\
&\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{OH} \quad \text{Pyridine (2.5 equiv)} \\
&\text{EtOH, 60 °C} \\
&\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{HO} \quad \text{N} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R}
\end{align*}$$

To a solution of corresponding ketone (1.0 equiv) and hydroxylamine hydrochloride (1.5 equiv) in EtOH (1.0 M) was added pyridine (2.5 equiv) under a nitrogen atmosphere. The reaction mixture was warmed to 60 °C and kept stirring until the ketone was consumed. After the mixture was cooled down to room temperature, the solvent was removed under vacuum. The residue was diluted with water and extracted with ethyl acetate. The combined extracts were washed with brine and dried over MgSO$_4$, followed by filtration and evaporation to give the crude oxime product. Purification of the crude product by flash column chromatography (silica gel;ethyl acetate: hexane = 5:95) afforded the oxime.

---

(Z)-2,2-Dimethyl-1,3-diphenylpropan-1-one oxime (1a):\(^2\)

![Chemical structure](image)

57% yield as a white solid (single Z-isomer) from 2,2-dimethyl-1,3-diphenylpropan-1-one.\(^3\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.08 (6H, s), 2.87 (2H, s), 7.09 (2H, d, \(J = 7.6\) Hz), 7.15 (2H, d, \(J = 7.2\) Hz), 7.20 - 7.28 (3H, m), 7.35 - 7.44 (3H, m), 7.56 (1H, s br); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 25.6, 41.0, 46.1, 126.2, 127.7, 127.8, 128.0, 128.1, 130.9, 133.6, 138.1, 166.6.

(Z)-(1-benzylocyclohexyl)(phenyl)methanone oxime (1b):\(^2\)

![Chemical structure](image)

81% yield as a white solid (single Z isomer) from (1-benzylocyclohexyl)(phenyl)methanone.\(^2\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.24 - 1.39 (3H, m), 1.45 - 1.56 (5H, m), 1.73 - 1.77 (2H, m), 2.93 (2H, s), 7.02 (2H, d, \(J = 7.2\) Hz), 7.18 - 7.39 (8H, m), 8.09 (1H, s); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 22.5, 25.8, 34.1, 44.8, 45.3, 126.2, 127.7, 127.8, 127.9, 128.0, 131.0, 133.5, 137.9, 163.9.

2.2 Synthesis of hydrazones 3

**General procedure: modified by the reported method\(^4\)**

\[
\begin{align*}
R - R' & + ArNHNH_2 \\ (1.5 \text{ equiv})
\end{align*}
\]

\[\xrightarrow{\text{AcOH (1.0 equiv)}}\]

\[
\begin{align*}
\text{EtOH, } 60^\circ C & \rightarrow \text{N}^+\text{NHAr} \\
R - R' & \text{N}^+\text{NHAr}
\end{align*}
\]

To a solution of ketone (1.0 equiv) and arylhydrazine (1.5 equiv) in EtOH (1.0 M) was added AcOH (1.0 equiv) under nitrogen atmosphere. The reaction mixture was then warmed to 60 °C and kept stirring until the ketone was consumed. After the mixture was cooled down to room temperature, the solvent was removed under vacuum and the resulting crude product was purified immediately by flash column chromatography under N\(_2\) protection (as the hydrazones are unstable and can be oxidized by oxygen to give the peroxide species\(^5\)) afforded the corresponding hydrazones which was used immediately or stored under -20 °C with N\(_2\) protection.

*All the hydrazones were obtained as a pure single isomer except for 3l and 3m.*

---

(Z)-1-((1-Benzylcyclohexyl)(phenyl)methylene)-2-phenylhydrazine (3a):

\[
\begin{align*}
\text{Ph} & \quad \text{N} \\
\text{Ph} & \quad \text{N} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

68% yield as a yellow viscous liquid (single Z-isomer) from (1-benzylcyclohexyl)(phenyl)methanone.\(^2\)

IR (NaCl) 3337, 3053, 2934, 1647, 1601, 1503, 1452, 1308, 1265 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.19-1.35 (1H, m), 1.40-1.49 (4H, m), 1.53-1.56 (3H, m), 1.81-1.86 (2H, m), 2.99 (2H, s), 6.78 (1H, t, J = 8.0 Hz), 6.90-6.92 (5H, m), 7.17-7.26 (7H, m), 7.35-7.43 (3H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 22.7, 26.0, 26.9, 34.4, 45.6, 112.5, 119.2, 125.9, 127.8, 128.39, 128.41, 129.0, 129.1, 131.1, 133.7, 138.9, 145.4, 151.5; ESIHRMS: Found: m/z 369.233. Calcd for C\(_{26}\)H\(_{29}\)N\(_2\): (M+H)\(^+\) 369.2331.

(Z)-1-(2,2-Dimethyl-1-phenylpent-4-en-1-ylidene)-2-phenylhydrazine (3b):

\[
\begin{align*}
\text{Ph} & \quad \text{N} \\
\text{Ph} & \quad \text{N} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

91% yield as a pale yellow oil (single Z-isomer) from 2,2-dimethyl-1-phenylpent-4-en-1-one.\(^5\)

IR (NaCl) 3335, 3068, 2928, 1639, 1601, 1265, 1252, 1101, 1066, 1016 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.17 (6H, s), 2.33 (2H, d, J = 7.2 Hz), 5.06 (1H, d, J = 16.8 Hz), 5.07 (1H, d, J = 11.2 Hz), 5.94 (1H, tdd, J = 7.2, 11.2, 16.8 Hz), 6.73 (1H, s br), 6.76 (1H, t, J = 7.6 Hz), 6.91 (2H, d, J = 8.4 Hz), 7.13 (2H, d, J = 7.6 Hz), 7.18 (2H, t, J = 7.6 Hz), 7.42 (1H, dd, J = 7.2, 7.6 Hz), 7.48 (1H, d, J = 7.6 Hz), 7.50 (1H, d, J = 7.2 Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.3, 41.0, 44.9, 112.5, 117.0, 119.3, 128.5, 128.6, 129.06, 130.10, 133.5, 135.7, 145.4, 153.2; ESIHRMS: Found: m/z 279.1861. Calcd for C\(_{19}\)H\(_{23}\)N\(_2\): (M+H)\(^+\) 279.1861.

(Z)-1-(2,2-Dimethyl-1-phenylpent-4-en-1-ylidene)-2-(4-methoxyphenyl)hydrazine (3c):

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Ph} & \quad \text{N} \\
\text{OMe} & \quad \text{N}
\end{align*}
\]

98% yield (purity >95%) as a yellow viscous oil (single Z-isomer) from 2,2-dimethyl-1-phenylpent-4-en-1-one. This compound was easily oxidized by atmospheric oxygen to form peroxide species, and thus should be used immediately after purification.

IR (NaCl) 3333, 3055, 2967, 2932, 1640, 1512, 1466, 1265, 1233, 1115, 1092 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.16 (6H, s), 2.32 (2H, d, \(J = 7.2\) Hz), 3.74 (3H, s), 5.05 (1H, d, 16.4 Hz), 5.06 (1H, d, \(J = 10.8\) Hz), 5.94 (1H, tdd, \(J = 7.2, 10.8, 16.4\) Hz), 6.57 (1H, s br), 6.76-6.79 (2H, m), 6.85-6.88 (2H, m), 7.11-7.13 (2H, m), 7.39-7.43 (1H, dd, \(J = 7.2, 7.6\) Hz), 7.47 (1H, d, \(J = 7.6\) Hz), 7.49 (1H, d, \(J = 7.2\) Hz); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.4, 40.9, 44.9, 55.8, 113.7, 114.6, 117.0, 128.4, 128.7, 129.1, 135.8, 139.8, 152.7, 153.2; ESIHRMS: Found: \(m/z\) 309.1967. Calcd for C\(_{20}\)H\(_{25}\)N\(_2\)O: (M+H\(^+\)) 309.1967.

\((Z)-1-(4-Bromophenyl)-2-(2,2-dimethyl-1-phenylpent-4-en-1-ylidene)hydrazine (3d):\)

\[\begin{array}{c}
\text{Br} \\
\text{HN} \\
\text{N} \\
\text{Ph} \\
\text{Me} \\
\text{Me} \\
\end{array}\]

98% yield as a yellow viscous oil (single Z-isomer) from 2,2-dimethyl-1-phenylpent-4-en-1-one.

IR (NaCl) 3337, 3075, 2968, 2928, 1638, 1595, 1493, 1250, 1171, 1116, 1069 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.60 (6H, s), 2.32 (2H, d, \(J = 7.2\) Hz), 5.06 (1H, dd, \(J = 0.8, 17.6\) Hz), 5.07 (1H, dd, \(J = 0.8, 9.6\) Hz), 5.3 (1H, tdd, \(J = 7.2, 9.6, 17.6\) Hz), 6.72 (1H, s br), 6.79 (2H, d, \(J = 8.8\) Hz), 7.10-7.13 (2H, m), 7.23-7.27 (2H, m), 7.41-7.51 (3H, m); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.3, 41.1, 44.9, 110.9, 114.2, 117.2, 128.5, 128.7, 129.2, 131.8, 133.2, 135.5, 144.4, 154.1; ESIHRMS: Found: \(m/z\) 357.0966. Calcd for C\(_{19}\)H\(_{22}\)BrN\(_2\): (M+H\(^+\)) 357.0966.

\((Z)-1-((1-Allylcyclohexyl)(phenyl)methylene)-2-phenylhydrazine (3e):\)

\[\begin{array}{c}
\text{Ph} \\
\text{HN} \\
\text{N} \\
\text{Ph} \\
\end{array}\]

93% yield as a yellow viscous oil (single Z-isomer) from (1-allylcyclohexyl)(phenyl)methanone (III).

IR (NaCl) 3337, 3074, 2928, 1635, 1601, 1504, 1452, 1254, 1112, 1069 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.35-1.66 (8H, m), 1.86-1.92 (2H, m), 2.29 (2H, d, \(J = 6.9\) Hz), 5.04-5.09 (2H, m), 5.84-5.98 (1H, m), 6.74-6.81 (2H, m), 6.91 (2H, d, \(J = 7.5\) Hz), 7.15-7.20 (4H, m), 7.39-7.43 (1H, dd, \(J = 7.2, 7.6\) Hz), 7.47 (1H, d, \(J = 7.6\) Hz), 7.49 (1H, d, \(J = 7.2\) Hz).
7.39-7.51 (3H, m); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 22.5, 26.3, 34.1, 42.6, 44.3, 112.5, 116.8, 119.2, 128.5 (overlapped), 129.1 (overlapped), 133.4, 135.2, 145.5, 150.9; ESIHRMS: Found: m/z 319.2174. Caled for C$_{22}$H$_{27}$N$_{2}$: (M+H)$^+$ 319.2174.

Synthesis of (1-allylcyclohexyl)(phenyl)methanone (III) (for synthesis of 3e):

To a freshly prepared LDA (from 11.0 mmol n-BuLi and 12.0 mmol diisopropyl amine at 0 °C for 30 min) in THF (20 mL) was added cyclohexane carbonitrile I (1.2 mL, 10.0 mmol) dropwise at -78 °C. The resulting mixture was stirred at the same temperature for 30 min. Allyl bromide (1.2 mL, 14.0 mmol) was added to the reaction mixture dropwise before allowing the reaction mixture to warm up to room temperature. After stirring for overnight, the reaction mixture was quenched with water at 0 °C and extracted with ethyl acetate. The combined extracts was washed with brine, dried over MgSO$_4$, and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 5: 95) afforded compound II (1.40 g, 9.38 mmol) in 94% yield.

In a flame-dried schlenk tube was placed compound II (667 mg, 4.54 mmol) and ether (5 mL) under N$_2$ atmosphere. After the mixture was cooled down to 0 °C, PhMgBr (2.3 mL, 3.0 M in ether) was added via syringe. The schlenk tube was sealed and the reaction mixture was stirred for overnight at 60 °C. The reaction was quenched with 6 N HCl before cooling down to 0 °C. The resulting mixture was kept stirring and heating until the hydrolysis finished. After dilution with water and ether, the reaction mixture was extracted with ether. The combined extracts were washed with brine, dried over MgSO$_4$, and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 1: 99) afforded (1-allylcyclohexyl)(phenyl)methanone (III) (580 mg, 2.54 mmol) in 56% yield as a colorless oil.

(1-Allylcyclohexyl)(phenyl)methanone (III) (for synthesis of 3e):

IR (NaCl) 3053, 2936, 1668, 1452, 1265, 1219, 1001 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.32 (6H, s), 1.82-1.86 (2H, m), 1.97-2.03 (2H, m), 4.90-4.99 (2H, m), 5.70-5.80 (1H, m), 7.37-7.41 (2H, m), 7.44-7.48 (1H, m), 7.64-7.66 (2H, m); $^{13}$C NMR (100 MHz,
(E)-1-(1,2-Diphenylpent-4-en-1-ylidene)-2-phenylhydrazine (3f):

99% yield as a yellow viscous oil (single E-isomer) from 1,2-diphenylpent-4-en-1-one.\(^6\)

IR (NaCl) 3339, 3057, 3026, 1639, 1601, 1504, 1252, 1130, 1067 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.66 (1H, ddd,\(\ J = 7.6, 8.4, 14.4 \text{ Hz}\)), 3.05 (1H, ddd,\(\ J = 6.8, 7.6, 14.4 \text{ Hz}\)), 3.80 (1H, dd,\(\ J = 7.6, 7.6 \text{ Hz}\)), 4.99 (1H, dd,\(\ J = 1.2, 10.4 \text{ Hz}\)), 5.09 (1H, dd,\(\ J = 1.2, 16.8 \text{ Hz}\)), 5.89 (1H, dddd,\(\ J = 6.8, 8.4, 10.4, 16.8 \text{ Hz}\)), 6.81 (1H, t,\(\ J = 7.2 \text{ Hz}\)), 6.92-6.95 (2H, m), 6.99-7.02 (2H, m), 7.15-7.24 (8H, m), 7.31-7.36 (3H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 38.0, 53.8, 112.7, 116.1, 119.5, 126.8, 128.3, 128.4, 128.6, 129.1, 129.2, 134.5, 137.2, 141.5, 145.3, 147.6; ESI-HRMS: Found: \(m/z\) 327.1860. Calcd for C\(_{23}\)H\(_{23}\)N\(_2\): (M+H)\(^+\) 327.1861.

(\(E\))-1-(2-Methyl-1-phenylpent-4-en-1-ylidene)-2-phenylhydrazine (3g):

97% yield as a pale yellow viscous oil (single E-isomer) from 2-methyl-1-phenylpent-4-en-1-one.\(^7\)

IR (NaCl) 3337, 3053, 2968, 2928, 1639, 1601, 1504, 1309, 1252, 1063 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.16 (3H, d,\(\ J = 7.2 \text{ Hz}\)), 2.13 (1H, ddd, 7.2, 7.2, 14.4 Hz), 2.50 (1H, ddd,\(\ J = 6.8, 7.2, 14.4 \text{ Hz}\)), 2.77 (1H, ddq,\(\ J = 7.2, 7.2, 7.2 \text{ Hz}\)), 5.02 (1H, dd,\(\ J = 1.2, 10.4 \text{ Hz}\)), 5.05 (1H, dd,\(\ J = 1.2, 17.6 \text{ Hz}\)), 5.87 (1H, dddd,\(\ J = 6.8, 7.2, 10.4, 14.4 \text{ Hz}\)), 6.77 (1H, t,\(\ J = 7.2 \text{ Hz}\)), 6.94 (2H, d,\(\ J = 8.0 \text{ Hz}\)), 7.13 (1H, s br), 7.16-7.23 (4H, m), 7.39-7.43 (1H, m), 7.47 (1H, d,\(\ J = 8.0 \text{ Hz}\)), 7.49 (1H, d,\(\ J = 7.2 \text{ Hz}\)); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 18.1, 38.6, 41.2, 112.6, 116.1, 119.3, 127.9, 128.7, 129.1, 129.3, 134.2, 137.1, 145.4, 150.4; ESIHRMS: Found: \(m/z\) 265.1706. Calcd for C\(_{18}\)H\(_{18}\)N\(_2\): (M+H)\(^+\) 265.1705.

---


(E)-1-(2-Benzyl-1-phenylpent-4-en-1-ylidene)-2-phenylhydrazine (3h):

\[
\begin{align*}
 &\text{Ph} \quad \text{N} \quad \text{Ph} \\
 &\text{Ph} \quad \equiv \quad \equiv \\
 &\text{Ph}
\end{align*}
\]

95% yield as a pale yellow viscous oil (single E-isomer) from 2-benzyl-1-phenylpent-4-en-1-one. 

IR (NaCl) 3339, 3078, 3053, 3026, 1639, 1601, 1504, 1443, 1265, 1253, 1128 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.26 (1H, ddd, \(J = 6.0, 6.8, 14.0\) Hz), 2.46 (1H, ddd, \(J = 7.2, 7.2, 14.0\) Hz), 2.80 (1H, dd, \(J = 6.8, 13.2\) Hz), 2.97 (1H, dddd, \(J = 6.0, 6.8, 7.2, 7.6\) Hz), 3.12 (1H, dd, \(J = 7.6, 13.2\) Hz), 5.01-5.07 (2H, m), 5.88 (1H, m), 6.76 (1H, dd, \(J = 7.2, 7.2\) Hz), 6.94 (2H, d, \(J = 7.6\) Hz), 7.01-7.03 (2H, m), 7.11-7.24 (8H, m), 7.30-7.39 (3H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 37.1, 38.9, 48.7, 112.6, 116.5, 119.3, 125.8, 127.6, 128.1, 128.6, 129.0, 129.2, 129.3, 134.7, 136.6, 140.7, 145.2, 147.9; ESIHRMS: Found: \(m/z\) 341.2017. Calcd for C\(_{24}\)H\(_{25}\)N\(_2\): (M+H)\(^+\) 341.2018.

(E)-1-Phenyl-2-(1-phenylpent-4-en-1-ylidene)hydrazine (3i):

\[
\begin{align*}
 &\text{Ph} \quad \text{N} \quad \text{Ph} \\
 &\text{Ph} \quad \equiv \quad \equiv \\
 &\text{Ph}
\end{align*}
\]

85% yield as a pale yellow viscous oil (single E-isomer) from 2-benzyl-1-phenylpent-4-en-1-one.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.38 (2H, td, \(J = 7.2, 7.6\) Hz), 2.78 (2H, t, \(J = 7.6\) Hz), 5.09 (1H, d, \(J = 10.0\) Hz), 5.17 (1H, d, \(J = 18.0\) Hz), 5.92 (1H, dddd, \(J = 7.6, 10.0, 18.0\) Hz), 6.87 (1H, t, \(J = 7.2\) Hz), 7.16-7.18 (2H, m), 7.26-7.31 (3H, m), 7.35-7.39 (3H, m), 7.78-7.80 (2H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 25.0, 29.8, 113.2, 116.1, 120.2, 125.5, 127.9, 128.4, 129.2, 137.1, 138.1, 144.1, 145.2.

(Z)-1-Phenyl-2-(2,2,4-trimethyl-1-phenylpent-4-en-1-ylidene)hydrazine (3j):

\[
\begin{align*}
 &\text{Ph} \quad \text{N} \quad \text{Ph} \\
 &\text{Me} \quad \equiv \quad \equiv \\
 &\text{Me}
\end{align*}
\]

99% yield as a pale yellow viscous oil (single Z-isomer) from 2,2,4-trimethyl-1-phenylpent-4-en-1-one.

IR (NaCl) 3335, 3051, 2967, 2928, 1639, 1601, 1504, 1468, 1310, 1252, 1101, 1067 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.20 (6H, s), 1.79 (3H, s), 2.34 (2H, s), 4.78 (1H, s), 4.89 (1H, s), 4.90 (1H, s),

6.73-6.77 (2H, m), 6.91 (2H, d, J = 8.0 Hz), 7.14-7.19 (4H, m), 7.40-7.44 (1H, m), 7.46-7.50 (2H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 25.4, 27.0, 41.1, 47.8, 112.5, 114.3, 119.2, 128.5, 128.6, 129.07, 129.09, 133.7, 143.5, 145.4, 153.6; ESIHRMS: Found: m/z 293.2018. Calcd for C\(_{20}\)H\(_{25}\)N\(_2\): (M+H)\(^{+}\) 293.2018.

The ketone was synthesized following the above procedure [see synthesis of (1-allylcyclohexyl)(phenyl)methanone (III)] from isobutyronitrile and 3-bromo-2-methylprop-1-ene.

2,2,4-Trimethyl-1-phenylpent-4-ene-1-one (for synthesis of 3j):

![Chemical structure of 2,2,4-Trimethyl-1-phenylpent-4-ene-1-one]

IR (NaCl) 3072, 2968, 2936, 1672, 1468, 1445, 1387, 1207 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 1.34 (6H, s), 1.65 (3H, s), 2.57 (2H, s), 4.66-4.66 (1H, m), 4.82-4.83 (1H, m), 7.37-7.41 (2H, m), 7.43-7.48 (1H, m), 7.68-7.70 (2H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 24.4, 26.8, 47.5, 48.4, 114.5, 127.9, 128.0, 130.8, 139.0, 142.4, 209.0; ESIHRMS: Found: m/z 203.1436. Calcd for C\(_{14}\)H\(_{19}\)O: (M+H)\(^{+}\) 203.1436.

(1Z)-1-(2,2-Dimethyl-1-phenylhex-4-en-1-ylidene)-2-phenylhydrazine (3k):

![Chemical structure of (1Z)-1-(2,2-Dimethyl-1-phenylhex-4-en-1-ylidene)-2-phenylhydrazine]

96% yield as a pale yellow viscous oil from 2,2-dimethyl-1-phenylhex-4-en-1-one (E/Z ratio of the alkenyl moiety = 6:1)

IR (NaCl) 3335, 3022, 2964, 2928, 1639, 1601, 1502, 1252, 1113 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 1.15 (6H, s), 1.67-1.69 (3H, m), 2.24 (2H, d, J = 6.8 Hz), 5.41-5.60 (2H, m), 6.72-6.73 (1H, s br), 6.76 (1H, t, J = 7.2 Hz), 6.91 (2H, d, J = 7.6 Hz), 7.12 (2H, d, J = 6.8 Hz), 7.18 (2H, dd, J = 7.6, 8.4 Hz), 7.40-7.43 (1H, m), 7.46-7.50 (2H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 18.1, 26.3, 41.2, 43.7, 112.5, 119.2, 127.5, 127.9, 128.5, 128.6, 128.7, 129.1, 133.7, 145.5, 153.6; ESIHRMS: Found: m/z 293.2016. Calcd for C\(_{20}\)H\(_{25}\)N\(_2\): (M+H)\(^{+}\) 293.2018.

The ketone was synthesized following the above procedure [see synthesis of (1-allylcyclohexyl)(phenyl)methanone (III)] from isobutyronitrile and 1-bromobut-2-ene.

2,2-Dimethyl-1-phenylhex-4-en-1-one (E/Z ratio of the alkenyl moiety = 6:1)
Major $E$ isomer: IR (NaCl) 3053, 2983, 1670, 1630, 1465, 1423, 1265 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.29 (6H, s), 1.62 (3H, dd, $J = 1.2, 6.0$ Hz), 2.41 (2H, d, $J = 6.8$ Hz), 5.29-5.45 (2H, m), 7.36-7.40 (2H, m), 7.42-7.47 (1H, m) 7.63-7.66 (2H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 17.9, 25.7, 43.7, 47.9, 126.3, 127.6, 128.0, 128.7, 130.6, 139.3, 209.0; ESIHRMS: Found: $m/z$ 203.1436. Calcd for C$_{14}$H$_{19}$O: (M+H)$^+$ 203.1436.

1-(3,3-Dimethyl-1-phenylhex-5-en-1-ylidene)-2-phenylhydrazine (3l):

99% yield as a pale yellow oil ($E/Z = 1:1$) from 3,3-dimethyl-1-phenylhex-5-en-1-one. The stereochemistry of each isomer was not assigned. Spectrum data were shown as a 1:1 mixture.

IR (NaCl) 3335, 3053, 2960, 2932, 1672, 1601, 1495, 1447, 1265, 1153 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (6H, s), 0.91 (6H, s), 2.02 (2H, d, $J = 7.2$ Hz), 2.08 (2H, d, $J = 7.6$ Hz), 2.56 (2H, s), 2.68 (2H, s), 4.89-5.12 (4H, m, overlapped), 5.71-5.96 (2H, m, overlapped), 6.78 (1H, t, $J = 7.2$ Hz), 6.86 (1H, t, $J = 7.2$ Hz), 6.95 (2H, d, $J = 8.0$ Hz), 7.14 (2H, d, $J = 7.6$ Hz), 7.20 (2H, dd, $J = 7.2$, 8.4 Hz), 7.23-7.42 (9H, m, overlapped), 7.45-7.54 (3H, m, overlapped), 7.71 (2H, d, $J = 7.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 27.6, 28.2, 34.8, 35.9, 36.0, 46.8, 48.3, 49.1, 112.6, 113.0, 117.1, 118.4, 119.4, 120.0, 126.3, 127.7, 127.8, 128.2, 128.7, 129.1, 129.2, 129.3, 134.8, 135.5, 135.8, 140.7, 144.2, 145.0, 145.2, 145.7; ESIHRMS: Found: $m/z$ 293.2019. Calcd for C$_{20}$H$_{25}$N$_2$: (M+H)$^+$ 293.2018.

Synthesis of 3,3-dimethyl-1-phenylhex-5-en-1-one (for synthesis of 3l):

Modified procedure from reported literature$^9$: A solution of TiCl$_4$ (4.8 mL, 1.0 M in CH$_2$Cl$_2$) was added dropwise to the solution of 3-methyl-1-phenylbut-2-en-1-one (769 mg, 4.80 mmol) in CH$_2$Cl$_2$ at -78 °C. After stirring for 5 min, allylsilane (1.0 mL, 6.24 mmol) in 5 mL CH$_2$Cl$_2$ was added dropwise and the resulting mixture was kept stirring for 5 min. The reaction was warmed to room temperature and stirred for 30 min followed by cooling down to 0 °C and quenched with H$_2$O. The reaction

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mixture was diluted with ether, the separated organic layer was washed with 10% HCl, satd. NaHCO₃, bine. The organic layer was dried over MgSO₄ and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 1: 99) afforded 3,3-dimethyl-1-phenylhex-5-en-1-one (500 mg, 2.47 mmol) in 51% yield as a colorless oil.

### 3,3-Dimethyl-1-phenylhex-5-en-1-one (for synthesis of 3l):

![Chemical Structure](image)

IR (NaCl) 3059, 2959, 2930, 1690, 1672, 1638, 1597, 1448, 1359, 1265 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.05 (6H, s), 2.18 (2H, d, J = 7.6 Hz), 2.85 (2H, s), 5.01-5.06 (2H, m), 5.79-5.90 (1H, m), 7.44 (2H, dd, J = 7.6, 7.6 Hz), 7.53 (1H, dd, J = 7.2, 7.6 Hz), 7.91-7.93 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 27.4, 34.1, 46.8, 47.7, 117.7, 128.1, 128.5, 132.7, 135.1, 138.6, 200.3; ESIHRMS: Found: m/z 203.1437. Calcd for C₁₄H₁₉O: (M+H)⁺ 203.1436.

### 1-(1-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-ylidene)-2-phenylhydrazine (3m):

99% yield as a pale yellow oil (E/Z = 1:0.8) from 1-(4-methoxyphenyl)-3,3-dimethylhex-5-en-1-one. The mixture of E/Z = 0.2:1 was partially isolated and was used in the next step. IR (NaCl) 3337, 3053, 2959, 2936, 1639, 1601, 1502, 1466, 1292, 1265, 1177, 1032 cm⁻¹; ¹H NMR (400 MHz, CDCl₃ for major Z-isomer): δ 0.87 (6H, s), 2.02 (2H, d, J = 7.6 Hz), 2.53 (2H, s), 3.86 (3H, s), 4.94 (1H, dd, J = 2.0, 17.2 Hz), 5.01 (1H, J = 2.0, 10.4 Hz), 5.84 (1H, tdd, J = 7.2, 10.4, 17.2 Hz), 6.78 (1H, t, J = 7.2 Hz), 6.95-7.00 (4H, m), 7.20 (2H, dd, J = 7.6, 8.0 Hz), 7.24-7.28 (2H, m), 7.45 (1H, s br); ¹³C NMR (100 MHz, CDCl₃ for major Z-isomer): δ 27.6, 34.8, 46.9, 49.3, 55.3, 112.6, 114.6, 117.0, 119.3, 129.1, 129.2 (overlapped), 135.6, 145.36, 145.42, 159.6; ESIHRMS: Found: m/z 323.2122. Calcd for C₂₁H₂₇N₂O: (M+H)⁺ 323.2123.

The ketone was synthesized following the above procedure [see synthesis of 3,3-dimethyl-1-phenylhex-5-en-1-one (for synthesis of 3l)] from 1-(4-methoxyphenyl)-3-methylbut-2-en-1-one and allylsilane.
1-(4-methoxyphenyl)-3,3-dimethylhex-5-en-1-one (for synthesis of 3m):

\[
\begin{align*}
\text{MeO} & \quad \text{Ph} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

24% yield; colorless oil; IR (NaCl) 3074, 2959, 2932, 1728, 1682, 1660, 1601, 1510, 1462, 1259 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.04 (6H, s), 2.17 (2H, d, \(J = 7.6\) Hz), 2.80 (2H, s), 3.87 (3H, s), 5.01-5.07 (2H, m), 5.80-5.89 (1H, m), 6.92 (2H, d, \(J = 8.8\) Hz), 7.92 (2H, d, \(J = 8.8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 27.5, 34.1, 46.9, 47.4, 55.4, 113.6, 117.6, 130.4, 131.7, 135.2, 163.2, 198.8; ESIHRMS: Found: \(m/z\) 233.1542. Calcd for C\(_{15}\)H\(_{21}\)O\(_2\): (M+H)\(^+\) 233.1542.

1-phenyl-2-(2,5,5-trimethyloct-7-en-3-ylidene)hydrazine (3n):

\[
\begin{align*}
\text{Ph} & \quad \text{HN} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

72% yield as a wine red oil (single isomer; the stereochemistry is not assigned) from 2,5,5-trimethyloct-7-en-3-one.\(^\text{10}\) This compound was easily oxidized by atmospheric oxygen to form peroxide species,\(^3\) and thus should be used immediately after purification.

IR (NaCl) 3374, 2963, 2930, 1638, 1601, 1503, 1468, 1265, 1142 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.01 (6H, s), 1.16 (6H, d, \(J = 7.2\) Hz), 2.09 (2H, d, \(J = 7.2\) Hz), 2.18 (2H, s), 2.45 (1H, septet, \(J = 7.2\) Hz), 5.06-5.16 (2H, m), 5.84-5.94 (1H, m), 6.79 (1H, t, \(J = 7.2\) Hz), 7.01-7.03 (2H, m), 7.17 (1H, s br), 7.20-7.25 (2H, m); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 21.0, 28.1, 35.8, 36.8, 38.9, 48.3, 112.6, 118.2, 119.2, 129.1, 134.8, 146.0, 152.3; ESIHRMS: Found: \(m/z\) 259.2172. Calcd for C\(_{17}\)H\(_{27}\)N\(_2\): (M+H)\(^+\) 259.2174.

\((E)-1-(1-(2-Allylphenyl)propylidene)-2-phenylhydrazine (3o):

\[
\begin{align*}
\text{Ph} & \quad \text{HN} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

86% yield as a pale yellow oil (single E isomer) from 1-(2-allylphenyl)propan-1-one.

IR (NaCl) 3333, 3051, 2974, 1638, 1601, 1503, 1429, 1265, 1126 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.18 (3H, t, \(J = 7.2\) Hz), 2.56 (2H, dq, \(J = 2.0, 7.2\) Hz), 3.25 (2H, d, \(J = 6.4\) Hz), 4.99-5.05 (2H, m), 5.84-5.94 (1H, m), 6.78 (1H, t, \(J = 7.2\) Hz), 6.86 (1H, s br), 6.94 (2H, d, \(J\)

= 7.6 Hz), 7.09 (1H, d, J = 7.6 Hz), 7.19 (2H, dd, J = 7.2, 7.6 Hz), 7.31-7.41 (3H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 11.0, 31.5, 37.0, 112.6, 116.5, 119.3, 127.2, 127.9, 129.0, 129.1, 130.0, 134.4, 136.6, 137.6, 145.3, 148.8; ESIHRMS: Found: m/z 265.1704. Caled for C$_{13}$H$_{21}$N$_2$: (M+H)$^+$ 265.1705.

Synthesis of 1-(2-allylphenyl)propan-1-one (for synthesis of 3o):

To a solution of 2-allylbenzaldehyde (1.14 g, 7.79 mmol) in THF (15 mL) was added EtMgBr (5.1 mL, 2.3 M in THF, 11.68 mmol) dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 1 hour before quenching with Satd. NH$_4$Cl at the same temperature. The reaction mixture was extracted with ether. The combined extracts were washed with brine, dried over MgSO$_4$, and concentrated. The resulting crude alcohol was used directly for the next step.

To a solution of obtained crude alcohol (1.13 g, 6.39 mmol) in CH$_2$Cl$_2$ (18 mL) was added celite (1.0 g) and then PCC (2.07 g, 9.58 mmol) portionwise at room temperature. The reaction mixture was stirred for 2 hours and filtered. The filtrate was evaporated and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 5: 95) afforded 1-(2-allylphenyl)propan-1-one (0.924 g, 5.30 mmol) in 83% yield.

1-(2-Allylphenyl)propan-1-one (for synthesis of 3o):

IR (NaCl) 3073, 2978, 2938, 1690, 1638, 1599, 1445, 1222 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.18 (3H, t, J = 7.2 Hz), 2.90 (2H, q, J = 7.2 Hz), 3.60 (2H, d, J = 6.8 Hz), 4.97-5.03 (2H, m), 5.92-6.02 (1H, m), 7.26-7.29 (2H, m), 7.37-7.41 (1H, m), 7.55-7.57 (1H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 8.30, 35.1, 37.8, 115.7, 126.1, 127.9, 131.0, 131.1, 137.5, 138.8, 139.1, 205.6; ESIHRMS: Found: m/z 175.1122. Caled for C$_{12}$H$_{15}$O: (M+H)$^+$ 175.1123
3. TEMPO and DIAD-mediated reactions with oximes 1 (Scheme 1-b) and hydrazones 3a (Scheme 3)

A typical procedure for synthesis of hemiacetal 2a from oxime 1a:

To a solution of oxime 1a (74.3 mg, 0.293 mmol), TEMPO (137.5 mg, 0.880 mmol), and K$_2$CO$_3$ (81.1 mg, 0.587 mmol) in DMF was added DIAD (diisopropyl diazene-1,2-dicarboxylate) (173.0 µL, 0.880 mmol) via a micro syringe under an Ar atmosphere. The reaction mixture was kept stirring at 120 °C for 4 hours before cooling down to room temperature. After dilution with water and ethyl acetate, the mixture was extracted with ethyl acetate. The combined extracts were washed with water for three times (to remove DMF) and brine, dried over MgSO$_4$, and concentrated. Purification of the crude product by flash column chromatography (silica gel; ethyl acetate: hexane = 20: 80) afforded hemiacetal 2a (57.1 mg, 0.214 mmol) in 73% yield as a white solid.

**4,4-Dimethyl-3,5-diphenyl-4,5-dihydroisoxazol-5-ol (2a):**

Colourless crystal (CCDC 926979); mp: 162-164 °C; IR (NaCl) 3422, 3053, 2986, 1638, 1551, 1491, 1422, 1265 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.89 (3H, s), 1.46 (3H, s), 3.01 (1H, s br), 7.40-7.43 (6H, m), 7.65-7.69 (4H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 17.6, 25.1, 55.4, 110.1, 126.7, 127.7, 128.2, 128.6, 129.0, 129.4, 129.9, 137.8, 166.2; ESI-HRMS: Found: m/z 268.1339. Calcd for C$_{17}$H$_{16}$NO$_2$: (M+H)$^+$ 268.1338.

**1,4-Diphenyl-2-oxa-3-azaspiro[4.5]dec-3-en-1-ol (2b):**
55%; White solid; mp: 165-167 °C; IR (NaCl) 3421, 3053, 2986, 1639, 1551, 1491, 1265 cm⁻¹;¹H NMR (400 MHz, CDCl₃) δ 0.30-0.40 (1H, m), 0.99-1.12 (2H, m), 1.21-1.27 (1H, m), 1.43-1.60 (4H, m), 1.74-1.81 (1H, m), 2.29-2.40 (1H, m), 3.05 (1H, s br), 7.38-7.47 (6H, m), 7.49-7.54 (2H, m), 7.74-7.77 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.2, 21.5, 24.9, 26.4, 31.2, 58.9, 109.4, 127.8, 128.1, 128.3, 128.9, 129.0, 129.4, 130.3, 139.0, 167.1; ESIHRMS: Found: m/z 308.1644. Calcd for C₂₀H₂₂NO₂: (M+H)⁺ 308.1651.

3-(1-Benzylcyclohexyl)-1-phenyl-1H-indazole (4a):  

54%; Yellow thick viscous liquid; IR (NaCl) 3053, 2986, 1638, 1597, 1506, 1422, 1267 cm⁻¹;¹H NMR (400 MHz, CDCl₃) δ 1.32-1.38 (1H, m), 1.47-1.56 (3H, m), 1.62-1.73 (4H, m), 2.56-2.59 (2H, m), 3.09 (2H, s), 6.67-7.70 (2H, m), 7.01-7.12 (4H, m), 7.26-7.37 (2H, m), 7.47 (2H, d, J = 8.0 Hz), 7.59-7.62 (2H, m), 7.72 (1H, d, J = 8.0 Hz), 7.76 (1H, d, J = 8.0 Hz);¹³C NMR (100 MHz, CDCl₃) δ 22.8, 26.3, 35.8, 42.9, 49.2, 110.4, 120.4, 122.4, 122.8, 123.8, 125.8, 126.0, 126.1, 127.3, 129.2, 130.3, 138.1, 140.2, 140.5, 150.8; ESIHRMS: Found: m/z 367.2175. Calcd for C₂₆H₂₇N₂: (M+H)⁺ 367.2174.

4. TEMPO-mediated reactions with hydrazones 3b-3k (Table 1-entry 1, Table 2)

A typical procedure for synthesis of dihydropyrazole 5b from hydrazone 3b:

The mixture of hydrazine 3b (56.0 mg, 0.201 mmol) and TEMPO (78.5 mg, 0.503 mmol) in anhydrous DMF (0.1 M) was heated at 130 °C for 24 hours under an Ar atmosphere. The mixture was then cooled down to room temperature and diluted with water. The resulting mixture was extracted with ethyl acetate and the combined extracts were washed with water for 3 times (to remove DMF) and then washed with brine. The organic phase was dried over MgSO₄, and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 1: 99) afforded 5b (42.8 mg, 0.155 mmol) in 77% yield. (In table 1, entry 4, the byproduct 5b' was formed in 11% yield.)
4,4-Dimethyl-1,3-diphenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5b):

77%; Pale yellow crystal (CCDC 996573); mp: 99-100 °C; IR (NaCl) 3053, 2976, 1636, 1597, 1495, 1265, 1138 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (3H, s), 1.26 (3H, s), 4.13 (1H, d, J = 8.4 Hz), 5.36 (1H, d, J = 12.4 Hz), 5.37 (1H, d, J = 16.4 Hz), 5.86 (1H, ddd, J = 8.4, 12.4, 16.4 Hz), 6.85-6.89 (1H, m), 7.23-7.28 (4H, m), 7.30-7.39 (3H, m), 7.76-7.79 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.8, 25.9, 51.3, 76.4, 115.2, 118.9, 120.0, 126.8, 128.2, 128.4, 128.7, 132.5, 134.7, 146.0, 155.4; ESIHRMS: Found: m/z 277.1706. Calcd for C₁₉H₂₁N₂ (M+H)⁺ 277.1705.

1,1'-(1-(1-(4,4-dimethyl-1,3-diphenyl-4,5-dihydro-1H-pyrazol-5-yl)ethane-1,2-diyl)bis(oxy))bis(2,2,6,6-tetramethylpiperidine) (5b’, Table 1, entry 4):

11%; ¹H NMR (400 MHz, CDCl₃) δ 0.78 (3H, s), 0.82 (3H, s), 1.00 (3H, s), 1.09 (3H, s), 1.22-1.26 (14 H, m), 1.31-1.37 (4H, m), 1.46-1.55 (9H, m), 1.73 (3H, s), 3.97-4.02 (1H, m), 4.27-4.30 (2H, m), 4.62 (1H, dd, J = 4.0, 10.8 Hz), 6.72-6.76 (1H, m), 7.21-7.29 (4H, m), 7.31-7.38 (3H, m), 7.71-7.73 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 17.1, 17.2, 20.0, 20.2, 20.3, 26.8, 30.1, 32.9, 33.5, 33.7, 34.2, 39.5, 40.1, 41.1, 49.5, 59.0, 59.7, 60.7, 70.6, 74.5, 79.1, 112.5, 117.6, 127.1, 127.8, 128.0, 129.0, 132.9, 144.1, 155.6.

1-(4-Methoxyphenyl)-4,4-dimethyl-3-phenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5c):

73%; Pale yellow solid; mp: 63-65 °C; IR (NaCl) 3053, 2982, 2934, 1636, 1508, 1464, 1265, 1242 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.26 (3H, s), 1.44 (3H, s), 3.77 (3H, s), 3.97 (1H, d, J = 8.8 Hz), 5.34 (1H, d, J = 18.0 Hz), 5.35 (1H, d, J = 10.4 Hz), 5.92 (1H, ddd, J = 8.8, 10.4, 18.0 Hz), 6.81-6.86 (2H, m), 7.19-7.24 (2H, m), 7.29-7.38 (3H, m), 7.75-7.78 (2H, m); ¹³C
NMR (100 MHz, CDCl₃) δ 20.5, 25.3, 51.3, 55.6, 76.7, 114.1, 117.5, 119.2, 126.7, 128.2, 128.3, 132.6, 134.9, 140.6, 154.2, 155.4; ESIHRMS: Found: m/z 307.1810. Calcd for C₂₀H₂₂N₂O: (M+H)⁺ 307.1810.

1-(4-Bromophenyl)-4,4-dimethyl-3-phenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5d):

74%; Yellow thick viscous liquid; IR (NaCl) 3051, 2980, 1597, 1572, 1491, 1368, 1265, 1094 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.28 (3H, s), 1.46 (3H, s), 4.09 (1H, d, J = 8.4 Hz), 5.35 (1H, d, J = 17.2 Hz), 5.37 (1H, d, J = 10.0 Hz), 5.82 (1H, ddd, J = 8.4, 10.0, 17.2 Hz), 7.11-7.14 (2H, m), 7.31-7.40 (5H, m), 7.74-7.77 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.8, 25.9, 51.5, 76.3, 112.1, 116.7, 119.3, 126.8, 128.4, 128.6, 131.5, 132.2, 134.2, 144.9, 156.0; ESIHRMS: Found: m/z 355.0808. Calcd for C₁₉H₂₀N₂Br: (M+H)⁺ 355.0810.

1,3-Diphenyl-4-vinyl-2,3-diazaspiro[4.5]dec-1-ene (5e):

62%; Yellow thick viscous liquid; IR (NaCl) 3053, 2980, 2936, 1630, 1597, 1576, 1501, 1302, 1265 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.30-1.36 (2H, m), 1.62-1.70 (2H, m), 1.73-1.80 (3H, m), 1.85-1.99 (3H, m), 4.71 (1H, d, J = 8.4 Hz), 5.29 (1H, d, J = 10.8 Hz), 5.30 (1H, d, J = 17.2 Hz), 5.66 (1H, ddd, J = 8.4, 10.8, 17.2 Hz), 6.80 (1H, tt, J = 0.8, 7.2 Hz), 7.11-7.14 (2H, m), 7.22-7.26 (2H, m), 7.32-7.40 (3H, m), 7.67-7.70 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 22.4, 23.0, 25.4, 28.2, 31.9, 55.8, 69.7, 113.7, 118.6, 119.3, 127.5, 128.2 (overlapped), 128.8, 131.4, 133.0, 144.4, 155.3; ESIHRMS: Found: m/z 317.2019. Calcd for C₂₂H₂₅N₂: (M+H)⁺ 317.2018.

(4S,5S)-1,3,4-Triphenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5f):
80%; Pale yellow crystal (CCDC 995494); IR (NaCl) 3061, 3028, 1641, 1597, 1553, 1493, 1445, 1387, 1336, 1138 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.38 (1H, d, \(J = 4.8\) Hz), 4.59 (1H, dd, \(J = 4.8, 6.8\) Hz), 5.24 (1H, d, \(J = 10.4\) Hz), 5.25 (1H, d, \(J = 17.2\) Hz), 5.96 (1H, ddd, \(J = 6.8, 10.4, 17.2\) Hz), 6.84 (1H, t, \(J = 7.2\) Hz), 7.18-7.30 (12H, m), 7.63-7.65 (2H, m); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 59.3, 72.9, 113.7, 117.1, 119.3, 126.2, 127.4, 127.5, 128.2, 128.4, 128.9, 129.2, 132.2, 136.4, 140.2, 144.5, 148.9; ESIHRMS: Found: m/z 325.1705. Calcd for C\(_{23}\)H\(_{21}\)N\(_2\): (M+H\(^{+}\)) 325.1705.

\((4S,5S)-4\)-Methyl-1,3-diphenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5g):

53%; Yellow thick viscous liquid; IR (NaCl) 3053, 2982, 2930, 1641, 1597, 1557, 1504, 1391, 1265 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.33 (3H, d, \(J = 7.2\) Hz), 3.37 (1H, dq, \(J = 4.0, 7.2\) Hz), 4.36 (1H, dd, \(J = 4.0, 6.8\) Hz), 5.17 (1H, d, \(J = 10.4\) Hz), 5.25 (1H, d, \(J = 17.2\) Hz), 5.83 (1H, ddd, \(J = 6.8, 10.4, 17.2\) Hz), 6.82 (1H, t, \(J = 7.2\) Hz), 7.18 (2H, d, \(J = 8.0\) Hz), 7.23-7.32 (3H, m), 7.37 (2H, dd, \(J = 7.2, 7.6\) Hz), 7.74 (2H, d, \(J = 7.6\) Hz); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 18.1, 47.1, 71.0, 113.5, 116.6, 118.9, 126.0, 128.3, 128.6, 128.9, 132.1, 136.2, 144.7, 151.6; ESIHRMS: Found: m/z 263.1548. Calcd for C\(_{18}\)H\(_{19}\)N\(_2\): (M+H\(^{+}\)) 263.1548.

\((4S,5S)-4\)-Benzy1-1,3-diphenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5h):

72%; Yellow thick viscous liquid; IR (NaCl) 3053, 2981, 2928, 1635, 1590, 1546, 1500, 1389, 1265 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.64 (1H, dd, \(J = 10.8, 14.0\)), 3.19 (1H, dd, \(J = 10.8, 14.0\)), 3.19 (1H, dd, \(J = 10.8, 14.0\)).
= 3.6, 14.0 Hz), 3.63 (1H, ddd, J = 3.2, 3.6, 10.8 Hz), 4.53 (1H, dd, J = 3.2, 6.4 Hz), 4.92 (1H, d, J = 17.2 Hz), 5.01 (1H, d, J = 10.0 Hz), 5.61 (1H, ddd, J = 6.4, 10.0, 17.2 Hz), 6.80 (1H, t, J = 7.2 Hz), 7.11 (2H, d, J = 8.4 Hz), 7.21-7.24 (5H, m), 7.30-7.34 (3H, m), 7.40 (2H, dd, J = 7.6, 7.6 Hz), 7.81 (2H, d, J = 7.6 Hz); 13C NMR (100 MHz, CDCl3) δ 37.3, 53.8, 66.8, 113.3, 116.4, 118.9, 125.9, 126.6, 128.4, 128.69, 128.9, 129.0, 132.1, 135.7, 138.3, 144.2, 149.7; ESIHRMS: Found: m/z 339.1861. Calcd for C24H23N2: (M+H)+ 339.1861.

1,3-Diphenyl-5-vinyl-1H-pyrazole (5i): 2

80%; 1H NMR (400 MHz, CDCl3) δ 5.35 (1H, d, J = 11.2 Hz), 5.79 (1H, d, J = 17.2 Hz), 6.56 (1H, dd, J = 17.2, 11.2 Hz), 6.89 (1H, s), 7.30-7.34 (1H, m), 7.39-7.43 (3H, m), 7.47-7.53 (4H, m), 7.89 (2H, d, J = 8.0 Hz); 13C NMR (100 MHz, CDCl3) δ 101.3, 117.5, 124.6, 125.5, 125.8, 127.9, 128.6, 129.1 (overlapped), 133.0, 139.5, 142.6, 151.8.

4,4-Dimethyl-1,3-diphenyl-5-(prop-1-en-2-yl)-4,5-dihydro-1H-pyrazole (5j): 3

86%; Yellow thick viscous liquid; IR (NaCl) 3051, 2978, 2938, 1647, 1595, 1545, 1503, 1465, 1443, 1383, 1265 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 1.33 (3H, s), 1.51 (3H, s), 1.57 (3H, s), 4.28 (1H, s), 5.06 (2H, s), 6.83 (1H, t, J = 6.8 Hz), 7.17-7.19 (2H, m), 7.24-7.28 (2H, m), 7.31-7.39 (3H, m), 7.77 (2H, d, J = 6.8 Hz); 13C NMR (100 MHz, CDCl3) δ 19.3, 20.5, 28.3, 50.3, 78.8, 113.6, 115.9, 119.0, 126.8, 128.2, 128.4 (overlapped), 128.8, 132.5, 145.1, 154.7; ESIHRMS: Found: m/z 291.1861. Calcd for C20H23N2: (M+H)+ 291.1861.

4,4-Dimethyl-1,3-diphenyl-5-(prop-1-en-1-yl)-4,5-dihydro-1H-pyrazole (5k) (alkene: E/Z = 25:1): 4

56%; Yellow thick viscous liquid; IR (NaCl) 3053, 2982, 1670, 1595, 1545, 1495, 1464, 1379, 1265 cm⁻¹; 1H NMR (400 MHz, CDCl3 for major E-isomer) δ 1.28 (3H, s), 1.43 (3H, s),
1.78 (3H, d, $J = 5.6$ Hz), 4.08 (1H, d, $J = 8.4$ Hz), 5.51 (1H, dd, $J = 8.4, 15.6$ Hz), 5.79 (1H, qd, $J = 5.6, 15.6$ Hz), 6.85-6.89 (1H, m), 7.24-7.30 (4H, m), 7.32-7.39 (3H, m), 7.79 (2H, d, $J = 7.2$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$ for major $E$-isomer) $\delta$ 17.9, 20.8, 25.8, 51.1, 75.9, 115.2, 119.7, 126.7, 127.4, 128.2, 128.6, 130.0, 132.7, 146.1, 155.4; ESIHRMS: Found: $m/z$ 291.1861. Calcd for C$_{20}$H$_{23}$N$_2$: (M+H)$^+$ 291.1861.

5. TEMPO-mediated reactions with hydrozones 3l-3o (Scheme 5)

A typical procedure for synthesis of tetrahydropyridazine 5l from hydrazone 3l:

```
Ph
HN
N
HN
Ph
Ph
5l
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The mixture of hydrazine 3l (87.4 mg, 0.299 mmol) and TEMPO (140 mg, 0.897 mmol) in anhydrous DMF (0.1 M) was heated at 130 °C for 6 hours under an Ar atmosphere. The mixture was then cooled down to room temperature and diluted with water. The resulting mixture was extracted with ethyl acetate and the combined extracts were washed with water for 3 times (to remove DMF) and then washed with brine. The organic phase was dried over MgSO$_4$, and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 1: 99) afforded 5l (79.0 mg, 0.272 mmol) in 91% yield as a yellow thick viscous liquid.

IR (NaCl) 3053, 2970, 2930, 1639, 1589, 1564, 1491, 1445, 1265 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.97 (3H, s), 1.18 (3H, s), 2.34 (2H, s), 4.12 (1H, d, $J = 6.0$ Hz), 5.08 (1H, ddd, $J = 1.2, 1.2, 17.2$ Hz), 5.19 (1H, ddd, $J = 1.2, 1.2, 10.4$ Hz), 5.79 (1H, ddd, $J = 6.0, 10.4, 17.2$ Hz), 6.88 (1H, t, $J = 7.2$ Hz), 7.25-7.32 (3H, m), 7.35-7.39 (4H, m), 7.81-7.84 (2H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 27.1, 27.6, 29.9, 33.2, 64.3, 114.0, 118.3, 119.7, 124.6, 127.5, 128.2, 128.8, 132.0, 138.1, 138.9, 147.2; ESIHRMS: Found: $m/z$ 291.1860. Calcd for C$_{20}$H$_{23}$N$_2$: (M+H)$^+$ 291.1861.

3-(4-Methoxyphenyl)-5,5-dimethyl-1-phenyl-6-vinyl-1,4,5,6-tetrahydropyridazine (5m):

```
O
Ph
HN
N
HN
Ph
Me
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S20
87%; Yellow thick viscous liquid; IR (NaCl) 3053, 2974, 2936, 1625, 1595, 1512, 1495, 1375, 1265 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (3H, s), 1.17 (3H, s), 2.31 (2H, s), 3.82 (3H, s), 4.11 (1H, d, J = 6.0 Hz), 5.08 (1H, d, J = 17.2 Hz), 5.18 (1H, d, J = 10.4 Hz), 5.78 (1H, ddd, J = 6.0, 10.4, 17.2 Hz), 6.85 (1H, t, J = 7.2 Hz), 6.89-6.92 (2H, m), 7.28 (2H, dd, J = 7.6, 8.4 Hz), 7.30-7.35 (2H, m), 7.76 (2H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 27.1, 27.6, 29.9, 33.2, 55.3, 64.2, 113.6, 113.9, 118.2, 119.3, 125.8, 128.8, 131.9, 132.0, 138.1, 147.3, 159.3; ESIHRMS: Found: m/z 321.1968. Calcd for C₂₁H₂₅N₂O: (M+H)⁺ 321.1967.

3-Isopropyl-5,5-dimethyl-1-phenyl-6-vinyl-1,4,5,6-tetrahydropyridazine (5n):

87%; Yellow thick viscous liquid; IR (NaCl) 3053, 2974, 2936, 1625, 1595, 1512, 1495, 1375, 1265 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (3H, s), 1.17 (3H, s), 2.31 (2H, s), 3.82 (3H, s), 4.11 (1H, d, J = 6.0 Hz), 5.08 (1H, d, J = 17.2 Hz), 5.18 (1H, d, J = 10.4 Hz), 5.78 (1H, ddd, J = 6.0, 10.4, 17.2 Hz), 6.85 (1H, t, J = 7.2 Hz), 6.89-6.92 (2H, m), 7.28 (2H, dd, J = 7.6, 8.4 Hz), 7.30-7.35 (2H, m), 7.76 (2H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 27.1, 27.6, 29.9, 33.2, 55.3, 64.2, 113.6, 113.9, 118.2, 119.3, 125.8, 128.8, 131.9, 132.0, 138.1, 147.3, 159.3; ESIHRMS: Found: m/z 321.1968. Calcd for C₂₁H₂₅N₂O: (M+H)⁺ 321.1967.

4-Ethyl-2-phenyl-1-vinyl-1,2-dihydropthalazine (5o):

41%; Yellow thick viscous liquid; IR (NaCl) 3061, 2970, 2934, 1636, 1595, 1495, 1454, 1265 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.30 (3H, t, J = 7.2 Hz), 2.80 (1H, qd, J = 7.2, 15.2 Hz), 2.83 (1H, qd, J = 7.2, 15.2 Hz), 4.94 (1H, ddd, J = 1.2, 1.2, 16.8 Hz), 5.06 (1H, ddd, J = 1.2, 1.2, 10.4 Hz), 5.70 (1H, d, J = 4.8 Hz), 5.80 (1H, ddd, J = 4.8, 10.4, 16.8 Hz), 6.92 (1H, t, J = 7.2 Hz), 7.19-7.21 (1H, m), 7.29-7.44 (7H, m); ¹³C NMR (100 MHz, CDCl₃) δ 12.2, 25.3, 57.9, 114.6, 116.2, 120.2, 122.9, 125.1, 126.3, 128.0, 128.9, 130.1, 132.4, 133.8, 146.5, 146.6; ESIHRMS: Found: m/z 263.1548. Calcd for C₁₈H₁₉N₂: (M+H)⁺ 263.1548.
$^1$H NMR spectrum of 2a (400 MHz, CDCl$_3$)
$^{13}\text{C}$ NMR spectrum of 2a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 2b (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 2b (100 MHz, CDCl$_3$)
${}^{1}$H NMR spectrum of 3a (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3b (400 MHz, CDCl$_3$)

ppm (t1)

6.70
6.80
6.90
7.00
7.10
7.20
7.30
7.40
7.50

2.05
2.00
1.98
1.95
1.90
1.80
1.70
1.60
1.50

0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00

0.00000
0.50000
1.00000
1.50000
2.00000
2.50000
3.00000
3.50000
4.00000
4.50000
5.00000
5.50000
6.00000

ppm (t1)
$^{13}$C NMR spectrum of 3b (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3c (400 MHz, CDCl$_3$)

**Chemical Shifts (ppm):**
- Ph 7.477
- N 7.132
- Me 7.128
- OMe 5.990

**Other Observations:**
- Ph 7.832, 7.809
- N 7.495, 7.477
- Me 7.394
- OMe 6.573, 5.990
$^{13}$C NMR spectrum of 3c (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3d (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3d (100 MHz, CDCl₃)
$^1$H NMR spectrum of 3e (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3e (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3f (400 MHz, CDCl$_3$)

ppm (t$_1$)
$^{13}$C NMR spectrum of 3f (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3g (400 MHz, CDCl$_3$)

ppm (t1)

$^{13}$C NMR spectrum of 3g (100 MHz, CDCl$_3$)

- Ph
- N
- Me

ppm (t1)
$^1$H NMR spectrum of 3h (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3h (100 MHz, CDCl$_3$)

![NMR spectrum diagram]
$^1$H NMR spectrum of 3j (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3j (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3k (400 MHz, CDCl$_3$)

Ph
\[ \begin{array}{c}
\text{Ph} \\
\text{Me} \\
\text{Me} \\
\text{Me}
\end{array} \]

$E/Z = 6:1$

Ph
\[ \begin{array}{c}
\text{Ph} \\
\text{Me} \\
\text{Me} \\
\text{Me}
\end{array} \]

$E/Z = 6:1$
$^{13}$C NMR spectrum of 3k (100 MHz, CDCl$_3$)

$E/Z = 6:1$
$^1$H NMR spectrum of 3 I (400 MHz, CDCl$_3$)
\textsuperscript{13}C NMR spectrum of 3l (100 MHz, CDCl\textsubscript{3})
$^1$H NMR spectrum of 3m (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3m (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3n (400 MHz, CDCl$_3$)

![NMR spectrum diagram]
$^{13}$C NMR spectrum of 3n (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3o (400 MHz, CDCl$_3$)
\(^{13}\text{C} \text{NMR spectrum of } 3\text{a} (100 \text{ MHz, CDCl}_3)\)
$^1$H NMR spectrum of 4a (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 4a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5b (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 5b (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5c (400 MHz, CDCl₃)
$^{13}$C NMR spectrum of 5c (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5d (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 5d (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5e (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 5e (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5f (400 MHz, CDCl₃)
$^{13}$C NMR spectrum of 5f (100 MHz, CDCl$_3$)
$\text{H NMR spectrum of 5g (400 MHz, CDCl)}_3$

0.0 5.0 10.0 ppm (t1)

7.396 7.378 7.359 7.321 7.303 7.278 7.258 7.239 7.234 7.188 7.168 6.837 6.819 6.801 5.873 5.855 5.847 5.830 5.812 5.804 5.786 5.271 5.228 5.183 5.157 4.373 4.363 4.356 4.346 3.397 3.387 3.379 3.369 3.362 3.351 3.344 3.334 1.341 1.323 0.00 0.00 0.00 0.00 1.03 1.00 2.03 2.00 3.29 2.04 3.11 ppm (t1)
$^{13}$C NMR spectrum of 5g (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5h (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 5h (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5i (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 5i (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5j (400 MHz, CDCl$_3$)

![NMR Spectrum](image-url)
$^{13}$C NMR spectrum of 5j (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5k (400 MHz, CDCl$_3$)

$E/Z = 25:1$
$^{13}$C NMR spectrum of 5k (100 MHz, CDCl$_3$)
$^1\text{H NMR}$ spectrum of 5I (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 5I (100 MHz, CDCl$_3$)
\(^1\)H NMR spectrum of 5m (400 MHz, CDCl\(_3\))
$^{13}$C NMR spectrum of 5m (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5n (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 5n(100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5o (400 MHz, CDCl$_3$)

N

N

Ph

Me

NPh
$^{13}$C NMR spectrum of 5o (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of (1-allylcyclohexyl)(phenyl)methanone (for synthesis of 3e) (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of (1-allylcyclohexyl)(phenyl)methanone (for synthesis of 3e) (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 2,2,4-trimethyl-1-phenylpent-4-en-1-one (for synthesis of 3j) (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 2,2,4-trimethyl-1-phenylpent-4-en-1-one (for synthesis of 3j) (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 2,2-dimethyl-1-phenylhex-4-en-1-one (for synthesis of 3k) (400 MHz, CDCl$_3$)

$E/Z = 6:1$
$^{13}$C NMR spectrum of 2,2-dimethyl-1-phenylhex-4-en-1-one (for synthesis of 3k) (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3,3-dimethyl-1-phenylhex-5-en-1-one (for synthesis of 3I) (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3,3-dimethyl-1-phenylhex-5-en-1-one (for synthesis of 3l) (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 1-(4-methoxyphenyl)-3,3-dimethylhex-5-en-1-one (for synthesis of 3m) (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 1-(4-methoxyphenyl)-3,3-dimethylhex-5-en-1-one (for synthesis of 3m) (100 MHz, CDCl₃)
$^1$H NMR spectrum of 1-(2-allylphenyl)propan-1-one (for synthesis of 3o) (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 1-(2-allylphenyl)propan-1-one (for synthesis of 3o) (100 MHz, CDCl$_3$)