**Supporting Information** 

For the article entitled

# Bidentate Auxiliary-Directed Alkenyl C-H Allylation *via exo*-Palladacycles: Synthesis of Branched 1,4-dienes

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#### **Supporting Information**

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**General Methods** 

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were recorded on Bruker AMX 400 spectrophotometer (CDCl<sub>3</sub> as solvent), and Bruker AMX 500 spectrophotometer (CDCl<sub>3</sub> as solvent). Chemical shifts for <sup>1</sup>H NMR spectra are reported as  $\delta$  in units of parts per million (ppm) downfield from SiMe<sub>4</sub> ( $\delta$  0.0) and relative to the signal of chloroform-*d* ( $\delta$  7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (<sup>13</sup>C NMR) are reported as  $\delta$  in units of parts per million (ppm) downfield from SiMe<sub>4</sub> ( $\delta$  0.0) and relative to the signal of chloroform-d ( $\delta$  77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm<sup>-1</sup>). Pd(OAc)<sub>2</sub> were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification.



**General Procedure for Wittig Olefination**: Phosphonium salt **(S1)** was suspended in THF (0.5 M) and cooled to 0 °C. A solution of NaHMDS (1.3 equiv) in THF (2.0 M) was added dropwise. The mixture was stirred for 1 h until an orange suspension formed. The mixture was then further cooled to -78 °C, and the appropriate aldehyde (1.0 equiv) was added over 20 min. After addition was completed, the reaction was gradually warmed to room temperature and stirred overnight. The reaction was quenched with sat. NH<sub>4</sub>Cl (aq.) solution, then extracted with EA. The combined organic layers were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo, and the resulting residue was purified on silica gel column chromatography (PE / EA = 10 / 1). In some cases, complete separation of the product and unreacted aldehyde was unsuccessful, and in these cases the mixed fractions were combined, concentrated, and used directly in the next step.

**General Procedure for Ester Hydrolysis:** The appropriate alkenyl ester **(S2)** was dissolved in a 1 : 1 mixture of MeOH and H<sub>2</sub>O, and LiOH<sup>·</sup>H<sub>2</sub>O was added (5.0 equiv). The reaction was stirred vigorously at 100 °C for 2 h, and reaction progress was monitored by GC-MS. When full conversion was observed, the resulting mixture was diluted with water and washed with EA. The organic layer was discarded. The aqueous layer was acidified with 2 M HCl solution and extracted with EA. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo, and the resulting alkenyl carboxylic acid **(S3)** was used in the next step without further purification.

General Procedure for AQ Amide Preparation: The appropriate alkenyl carboxylic acid (1.0 equiv), 8-aminoquinoline (0.6 equiv), EDC (1.2 equiv) and TEA (1.1 equiv) were dissolved in DCM (1 M) and stirred at room temperature, and reaction progress was monitored by GC-MS. After 8-aminoquinoline was fully consumed (approximately 16 h), the resulting mixture was washed with 1 M HCl (aq.) solution, and the organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo, and the resulting residue was purified by silica gel column chromatography (PE/EA = 4/1).

For the preparation of the remaining substrates, see the reference 1.



**General Procedure for The Cross-Coupling Between Amides and Carbonates** 

An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), DMSO (0.35 mL) and MeOH (0.7 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol), amide **1** (1.0 equiv, 0.1 mmol) and carbonate **2** (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA = 4/1).

#### **Characterization Data**

0.

MeO

#### AQ (E)-4-benzylidene-N-(quinolin-8-yl)hept-6-enamide (3aa)

Following the general procedure, **3aa** was obtained as a colourless oil (25.3 mg, 74% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.77 (s, 1H), 8.77 – 8.74 (m, 2H), 8.11 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 (dd, *J* = 8.5, 4.0 Hz, 1H), 7.30 – 7.24 (m, 4H), 7.18 – 7.15 (m, 1H), 6.39 (s, 1H), 5.96 – 5.88 (m, 1H), 5.20 – 5.12 (m, 2H), 3.00 (dd, *J* = 7.0, 1.0 Hz, 2H), 2.81 – 2.78 (m, 2H), 2.71– 2.68 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.81, 147.00, 138.36, 137.21, 136.74, 135.26, 135.12, 133.39, 127.47, 127.23, 126.83, 126.57, 126.33, 125.29, 120.51, 120.34, 115.84, 115.31, 40.79, 35.43, 25.85; **HRMS** (ESI): m/z for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 343.1805, found: 343.1809; **FTIR** (KBr, cm<sup>-1</sup>): 3564.60, 3473.24, 3416.72, 1684.11, 1633.64, 1616.82, 1525.01, 1482.24.

### O AQ (E)-4-(4-fluorobenzylidene)-N-(quinolin-8-yl)hept-6enamide (3ba)

Following the general procedure, **3ba** was obtained as a yellow oil (33.4 mg, 93% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.76 (s, 1H), 8.77 – 8.74 (m, 2H), 8.13 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.43 (dd, J = 8.0, 4.0 Hz, 1H), 7.20 (q, J = 5.5 Hz, 2H), 6.96 (t, J = 9.0 Hz, 2H), 6.33 (s, 1H), 5.95 – 5.87 (m, 1H), 5.20 – 5.13 (m, 2H), 2.99 (d, J = 8.0 Hz, 2H), 2.77 – 2.73 (m, 2H), 2.70 – 2.66 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.70, 160.30 (d,  $J_{C-F} = 243.8$  Hz), 147.03, 138.43, 137.17, 135.31, 134.99, 133.32, 132.74, 132.71, 129.03 (d,  $J_{C-F} = 7.8$  Hz), 126.84, 126.33, 125.48, 120.48 (d,  $J_{C-F} = 18.5$  Hz), 115.95, 115.32, 114.06 (d,  $J_{C-F} = 21.1$  Hz), 40.61, 35.33, 25.77; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  –116.00; HRMS (ESI): m/z for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>OF [M+H]<sup>+</sup>: 361.1711, found: 361.1722; FTIR (KBr, cm<sup>-1</sup>): 3473.06, 3416.17, 2957.01, 2926.17, 1681.31, 1611.21, 1525.21, 823.36, 789.72.

### O AQ (E)-4-(4-methoxybenzylidene)-N-(quinolin-8-yl)hept-6enamide (3ca)

Following the general procedure, **3ca** was obtained as a yellow oil (28.0 mg, 76% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.79 (s, 1H), 8.79 – 8.75 (m, 2H), 8.15 (dd, J = 8.5, 1.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.44 (dd, J = 8.5,

4.5 Hz, 1H), 7.20 (d, J = 9.0 Hz, 2H), 6.84 – 6.82 (m, 2H), 6.33 (s, 1H), 5.96 – 5.88 (m, 1H), 5.20 – 5.12 (m, 2H), 3.76 (s, 3H), 2.98 (d, J = 8.0 Hz, 2H), 2.81 – 2.78 (m, 2H), 2.72 – 2.69 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.97, 156.99, 147.04, 137.24, 136.95, 135.33, 135.29, 133.42, 129.29, 128.62, 126.86, 126.37, 126.04, 120.54, 120.36, 115.70, 115.34, 112.67, 54.15, 40.96, 35.45, 25.86; **HRMS** (ESI): m/z for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 373.1911, found: 373.1918; **FTIR** (KBr, cm<sup>-1</sup>): 3478.50, 3416.68, 1658.88, 1636.45, 1616.82, 624.30.

### O AQ (E)-4-(4-bromobenzylidene)-N-(quinolin-8-yl)hept-6enamide (3da)

Br

Following the general procedure, **3da** was obtained as a white solid (27.0 mg, 64% yield), m.p. = 74.6 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.76 (s, 1H), 8.79 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.74 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.16 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.46 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.30 (s, 1H), 5.95 – 5.88 (m, 1H), 5.25 – 5.07 (m, 2H), 3.04 – 2.95 (m, 2H), 2.79 – 2.72 (m, 2H), 2.72 – 2.64 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.63, 147.06, 139.32, 137.13, 135.65, 135.40, 134.83, 133.29, 130.31, 129.17, 126.88, 126.39, 125.42, 120.59, 120.45, 119.15, 116.10, 115.41, 40.67, 35.30, 25.87; HRMS (ESI): m/z for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>OBr [M+H]<sup>+</sup>: 421.091, found: 421.0917; FTIR (KBr, cm<sup>-1</sup>): 3592.19, 3418.18, 1653.27, 1633.64, 1418.23, 1394.35, 655.47.

### O AQ (E)-4-(4-methylbenzylidene)-N-(quinolin-8-yl)hept-6enamide (3ea)

Following the general procedure, **3ea** was obtained as a yellow oil (25.7 mg, 70% yield). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.77 (s, 1H), 8.78 (dd, J = 4.0, 1.5 Hz, 1H), 8.76 (dd, J = 7.5, 1.5 Hz, 1H), 8.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.36 (s, 1H), 5.96 – 5.88 (m, 1H), 5.20 – 5.12 (m, 2H), 2.99 (dd, J = 7.0, 1.0 Hz, 2H), 2.81 – 2.78 (m, 2H), 2.71 – 2.68 (m, 2H), 2.29 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.94, 147.01, 137.71, 137.26, 135.30, 135.27, 134.91, 133.84, 133.44, 127.95, 127.38, 126.87, 126.47, 126.38, 120.52, 120.34, 115.74, 115.36, 40.92, 35.48, 25.88, 20.09; **HRMS** (ESI): m/z for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 357.1961, found: 357.1969;

### O AQ (E)-4-(4-chlorobenzylidene)-N-(quinolin-8-yl)hept-6enamide (3fa)

Following the general procedure, **3fa** was obtained as a white solid (23.4 mg, 62% yield), m.p. = 107.0 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.75 (s, 1H), 8.78 (dd, J = 5.5, 1.0 Hz, 1H), 8.74 (dd, J = 7.5, 1.5 Hz, 1H), 8.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 7.24 – 7.22 (m, 2H), 7.17 (d, J = 8.5 Hz, 2H), 6.33 (s, 1H), 5.95 – 5.87 (m, 1H), 5.21 – 5.13 (m, 2H), 3.01 – 2.99 (m, 2H), 2.77 – 2.74 (m, 2H), 2.71 – 2.67 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.63, 147.09, 139.23, 137.21, 135.33, 135.20, 134.88, 133.34, 131.01, 128.82, 127.37, 126.88, 126.36, 125.42, 120.59, 120.44, 116.07, 115.35, 40.68, 35.33, 25.87; HRMS (ESI): m/z for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>OCl [M+H]<sup>+</sup>: 377.1415, found: 377.1422; FTIR (KBr, cm<sup>-1</sup>): 3416.41, 2959.81, 2923.36, 2853.27, 1633.64, 1614.02, 615.89.

#### $O_{\infty}$ AQ (E)-N-(quinolin-8-yl)-4-(4-

F<sub>3</sub>C

CI

#### (trifluoromethyl)benzylidene)hept-6-enamide (3ga)

Following the general procedure, **3ga** was obtained as a colorless oil (29.2 mg, 71% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.76 (s, 1H), 8.77 (dd, *J* = 4.0, 2.0 Hz, 1H), 8.74 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 – 7.49 (m, 4H), 7.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 5.96 – 5.88 (m, 1H), 5.23 – 5.16 (m, 2H), 3.04 – 3.02 (m, 2H), 2.80 – 2.76 (m, 2H), 2.72 – 2.69 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.49, 147.08, 140.65, 140.43 (d, *J*<sub>C-F</sub> = 1.1 Hz), 137.20, 135.35, 134.64, 133.29, 127.77, 127.26 (q, *J*<sub>C-F</sub> = 32.3 Hz), 126.89, 126.36, 125.37, 124.15 (q, *J*<sub>C-F</sub> = 3.6 Hz),123.203 (q, *J*<sub>C-F</sub> = 270.3 Hz), 120.55 (d, *J*<sub>C-F</sub> = 13.6 Hz), 116.29, 115.38, 40.59, 35.27, 25.94; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -62.38; HRMS (ESI): m/z for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>OF<sub>3</sub> [M+H]<sup>+</sup>: 327.1382, found: 327.1387; FTIR (KBr, cm<sup>-1</sup>): 3417.58, 1639.25, 1619.63, 1325.23, 624.30.

### O AQ (E)-4-(2-fluorobenzylidene)-N-(quinolin-8-yl)hept-6-enamide (3ha)

Following the general procedure, 3ha was obtained as a yellow

oil (22.8 mg, 63% yield). <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.77 (s, 1H), 8.78 (dd, J = 4.0, 1.5 Hz, 1H), 8.76 – 8.70 (d, J = 8.5 Hz, 1H), 8.15 (dd, J = 8.5, 1.5 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.16 (q, J = 5.5 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.33 (s, 1H), 5.98 – 5.90 (m, 1H), 5.23 – 5.15 (m, 2H), 3.04 (d, J = 6.5 Hz, 2H), 2.69 (s, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.82, 158.99 (d,  $J_{C-F} = 244.1$  Hz), 147.03, 140.81, 137.26, 135.30, 134.86, 133.41, 129.48 (d,  $J_{C-F} = 3.4$  Hz), 127.22 (d,  $J_{C-F} = 8.1$  Hz), 126.87, 126.37, 124.38 (d,  $J_{C-F} = 15.0$  Hz), 122.76 (d,  $J_{C-F} = 3.5$  Hz), 120.53, 120.36, 119.22, 116.06, 115.35, 114.36 (d,  $J_{C-F} = 22.3$  Hz), 40.23, 35.23, 26.25; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -114.84; HRMS (ESI): m/z for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>OF [M+H]<sup>+</sup>: 361.1711, found: 361.1719; FTIR (KBr, cm<sup>-1</sup>): 3416.39, 3237.38, 2959.81, 2923.36, 2856.07, 2357.01, 1633.64, 1614.02, 1527.10, 1400.93, 615.89.

### AQ (E)-4-(3-fluorobenzylidene)-N-(quinolin-8-yl)hept-6-enamide (3ia)

Following the general procedure, **3ia** was obtained as a yellow oil (23.0 mg, 64% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.77 (s, 1H), 8.78 (dd, *J* = 4.5, 2.0 Hz, 1H), 8.74 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 10.5 Hz, 1H), 6.86 (td, *J* = 8.5, 2.0 Hz, 1H), 6.34 (s, 1H), 5.95 – 5.87 (m, 1H), 5.21 – 5.14 (m, 2H), 3.00 – 3.00 (dd, *J* = 6.5, 0.5 Hz, 2H), 2.80 – 2.77 (m, 2H), 2.71 – 2.68 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.61, 161.71 (d, *J*<sub>C-F</sub> = 243.9 Hz), 147.06, 139.03 (d, *J*<sub>C-F</sub> = 7.6 Hz), 137.24, 135.31, 134.82, 133.36, 128.64 (d, *J*<sub>C-F</sub> = 8.5 Hz), 126.88, 126.37, 125.53, 123.22, 120.48 (d, *J*<sub>C-F</sub> = 17.6 Hz), 116.11, 115.37, 114.33 (d, *J* = 21.1Hz), 112.18 (d, *J*<sub>C-F</sub> = 20.9 Hz), 40.64, 35.31, 25.84; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -113.50; HRMS (ESI): m/z for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>OF [M+H]<sup>+</sup>: 361.1711, found: 361.1718; FTIR (KBr, cm<sup>-1</sup>): 3473.03, 3444.56, 3417.72, 2954.21, 2926.17, 2853.27, 2359.81, 2331.78, 1653.27, 1633.64, 1538.32, 1403.74.

### AQ (*E*)-4-(3-methoxybenzylidene)-N-(quinolin-8-yl)hept-6enamide (3ja)

Following the general procedure, 3ja was obtained as a yellow oil

0

OMe

(25.0 mg, 67% yield). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.77 (s, 1H), 8.77 (dd, J = 4.5, 2.0 Hz, 1H), 8.75 (dd, J = 7.0, 1.0 Hz, 1H), 8.14 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 (dd, J = 8.5, 4.5 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 6.79 (s, 1H), 6.73 (dd, J = 8.0, 2.0 Hz, 1H), 6.37 (s, 1H), 5.96 – 5.88 (m, 1H), 5.20 – 5.13 (m, 2H), 3.76 (s, 3H), 3.00 (dd, J = 7.0, 1.5 Hz, 2H), 2.82 – 2.78 (m, 2H), 2.72 – 2.68 (m, 2H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.82, 158.49, 147.04, 138.67, 138.22, 137.29, 135.29, 135.12, 133.45, 128.21, 126.89, 126.55, 126.38, 120.53, 120.36, 119.98, 115.87, 115.39, 112.82, 111.23, 54.13, 40.80, 35.53, 26.00; **HRMS** (ESI): m/z for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 373.1911, found: 373.1918; **FTIR** (KBr, cm<sup>-1</sup>): 3441.75, 2957.01, 2926.17, 2351.40, 1650.47, 1633.64, 1535.51, 1398.13, 465.24, 431.38.

### O AQ (E)-4-(2-methylbenzylidene)-N-(quinolin-8-yl)hept-6-enamide (3ka)

Following the general procedure, **3ka** was obtained as a yellow oil (28.9 mg, 81% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.70 (s, 1H), 8.76 (dd, J = 4.0, 1.5 Hz, 1H), 8.72 (d, J = 7.0 Hz, 1H), 8.14 (dd, J = 8.0, 1.0 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 (dd, J = 8.0, 4.0 Hz, 1H), 7.16 (d, J = 6.5 Hz, 1H), 7.12 – 7.08 (m, 3H), 6.35 (s, 1H), 5.99 – 5.90 (m, 1H), 5.21 – 5.13 (m, 2H), 3.03 (d, J = 6.5 Hz, 2H), 2.62 (s, 4H), 2.19 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.91, 147.00, 138.00, 137.24, 136.11, 135.33, 135.27, 135.21, 133.42, 128.67, 127.84, 126.85, 126.36, 125.99, 125.65, 124.51, 120.50, 120.30, 115.69, 115.32, 39.99, 35.56, 25.82, 18.90; HRMS (ESI): m/z for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 357.1961, found: 357.1969; FTIR (KBr, cm<sup>-1</sup>): 3472.65, 3417.43, 2957.01, 2926.17, 2853.274, 2354.21, 2331.78, 1653.27, 1636.45, 1614.82, 1538.32, 1504.67, 1504.67, 1403.74.

### O AQ (E)-4-(furan-3-ylmethylene)-N-(quinolin-8-yl)hept-6enamide(3la)

Following the general procedure, **3la** was obtained as a yellow solid (22.1 mg, 66% yield), m.p. = 51.3 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.91 (s, 1H), 8.81 – 8.79 (m, 2H), 8.16 (dd, J = 8.0, 1.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.46 – 7.44 (m, 2H), 6.39 (dd, J = 3.0, 1.5 Hz, 1H), 6.31 (d, J = 3.5 Hz, 1H), 6.14 (s, 1H),

5.91 – 5.83 (m, 1H), 5.17 – 5.11 (m, 2H), 2.98 – 2.33 (m, 4H), 2.77 – 2.74 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.32, 151.91, 147.03, 140.52, 137.55, 137.32, 135.35, 134.70, 133.54, 126.92, 126.42, 120.55, 120.38, 116.14, 115.44, 114.65, 110.09, 107.49, 41.70, 36.01, 27.60; **HRMS** (ESI): m/z for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 333.1598, found: 333.1606; **FTIR** (KBr, cm<sup>-1</sup>): 3473.06, 3416.71, 1633.64, 1614.02, 1538.32, 1389.72, 618.69.

### AQ (E)-N-(quinolin-8-yl)-4-(thiophen-2-ylmethylene)hept-6enamide (3ma)

Following the general procedure, **3ma** was obtained as a yellow solid (22.9 mg, 66% yield), m.p. = 74.4 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.90 (s, 1H), 8.81 – 8.78 (m, 2H), 8.16 (dd, J = 8.5, 1.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.00 (d, J = 3.5 Hz, 2H), 6.49 (s, 1H), 5.93 – 5.84 (m, 1H), 5.19 – 5.12 (m, 2H), 3.00 (dd, J = 7.0, 1.0 Hz, 2H), 2.95 – 2.92 (m, 2H), 2.78 – 2.75 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.83, 147.06, 139.23, 137.47, 137.31, 135.31, 134.77, 133.48, 126.90, 126.40, 125.90, 125.73, 123.44, 120.56, 120.40, 119.37, 116.14, 115.41, 41.66, 35.03, 26.95; HRMS (ESI): m/z for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>: 349.1369, found: 349.1374; FTIR (KBr, cm<sup>-1</sup>): 3472.84, 3417.08, 1650.47, 1636.45, 1616.82.

### AQ (*E*)-4-((1-methyl-1H-pyrrol-2-yl)methylene)-N-(quinolin-8yl)hept-6-enamide (3na-1)

Following the general procedure, **3na-1** was obtained as a brown solid (6.7 mg, 20% yield), m.p. = 87.0 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.83 (s, 1H), 8.80 – 8.78 (m, 2H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.58 – 6.57 (m, 1H), 6.32 (d, *J* = 3.5 Hz, 1H), 6.14 – 6.13 (m, 2H), 5.93 – 5.85 (m, 1H), 5.18 – 5.11 (m, 2H), 3.56 (s, 3H), 3.00 (dd, *J* = 7.0, 1.0 Hz, 2H), 2.88 – 2.85 (m, 2H), 2.76 – 2.72 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.10, 147.06, 137.31, 136.75, 135.29, 135.23, 133.50, 128.73, 126.89, 126.40, 120.96, 120.53, 120.34, 115.77, 115.39, 114.98, 107.29, 106.61, 41.46, 35.02, 33.06, 26.65; HRMS (ESI): m/z for C<sub>22</sub>H<sub>24</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 346.1914, found: 346.1923; FTIR (KBr, cm<sup>-1</sup>): 3564.63, 3473.04, 3454.93, 3417.45, 2917.76, 1653.27, 1633.64,

0.



# (*Z*)-4-((1-methyl-1H-pyrrol-2-l)methylene)-N-(quinolin-8-yl)hept-6-enamide (3na-2)

Following the general procedure, **3na-2** was obtained as a brown solid (13.5 mg, 40% yield), m.p. = 100.5 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.85 (s, 1H), 8.79 (dd, J = 7.5, 1.5 Hz, 1H), 8.77 (dd, J = 4.0, 1.5 Hz, 1H), 8.16 (dd, J = 8.0, 1.5 Hz, 1H), 7.55 –

7.49 (m, 2H), 7.45 (dd, J = 8.5, 4.5 Hz, 1H), 6.55 – 6.54 (m, 1H), 6.26 (s, 1H), 6.18 – 6.17 (m, 1H), 6.09 – 6.08 (m, 1H), 5.96 – 5.88 (m, 1H), 5.20 – 5.12 (m, 2H), 3.45 (s, 3H), 3.17 (d, J = 4.0 Hz, 2H), 2.80 – 2.76 (m, 2H), 2.73 – 2.70 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.02, 147.09, 137.29, 136.09, 135.33, 134.47, 133.45, 128.80, 126.90, 126.38, 120.94, 120.57, 120.40, 115.41, 115.25, 115.16, 107.39, 106.21, 35.95, 35.23, 32.94, 32.31; HRMS (ESI): m/z for C<sub>22</sub>H<sub>24</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 346.1914, found: 346.1923; FTIR (KBr, cm<sup>-1</sup>): 3478.50, 3417.29, 2959.81, 2926.17, 2856.07, 1650.47, 1636.45, 1616.82, 1535.51.



#### (*E*)-4-(naphthalen-1-ylmethylene)-N-(quinolin-8-yl)hept-6-enamide (30a)

Following the general procedure, **30a** was obtained as a yellow oil (21.0 mg, 54% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.61 (s, 1H), 8.70 (dd, J = 4.0, 1.5 Hz, 1H), 8.66 (dd, J = 7.0,

1.0 Hz, 1H), 8.11 (dd, J = 8.0, 1.5 Hz, 1H), 7.93 – 7.91 (m, 1H), 7.76 (dd, J = 6.0, 2.5 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.49 – 7.32 (m, 7H), 6.77 (s, 1H), 6.09 – 6.01 (m, 1H), 5.29 – 5.19 (m, 2H), 3.14 (d, J = 7.0 Hz, 2H), 2.67 – 2.64 (m, 2H), 2.61 – 2.58 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.81, 146.92, 139.91, 137.15, 135.21, 134.18, 133.33, 132.45, 130.99, 127.17, 126.79, 126.32, 126.03, 125.24, 124.79, 124.65, 124.60, 124.36, 123.95, 120.45, 120.25, 115.97, 115.26, 40.03, 35.69, 26.22; HRMS (ESI): m/z for C<sub>27</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 393.1961, found: 393.1969; FTIR (KBr, cm<sup>-1</sup>): 3416.98, 3240.19, 2923.36, 2850.47, 2354.21, 1644.86, 1636.45, 1616.82, 1400.93.

#### (*E*)-4-allyl-N-(quinolin-8-yl)hept-4-enamide (3pa)



Following the general procedure, **3pa** was obtained as a yellow oil SI-11

(23.5 mg, 80% yield). <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.80 (s, 1H), 8.80 – 8.77 (m, 2H), 8.14 (dd, J = 8.0, 1.5 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 5.87–5.79 (m, 1H), 5.26 (t, J = 7.0 Hz, 1H), 5.11 – 5.04 (m, 2H), 2.81 (d, J = 8.0 Hz, 2H), 2.63 – 2.60 (m, 2H), 2.57 – 2.53 (m, 2H), 2.12 – 2.06 (m, 2H), 0.95 (t, J = 8.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.24, 147.05, 137.28, 135.98, 135.30, 133.99, 133.50, 128.69, 126.88, 126.39, 120.53, 120.31, 115.35, 115.02, 76.28, 76.02, 75.77, 40.42, 35.89, 25.05, 20.13, 13.47; **HRMS** (ESI): m/z for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 295.1805, found: 295.1813; **FTIR** (KBr, cm<sup>-1</sup>): 3626.83, 3616.94, 3411.23, 2954.21, 2928.97, 2357.03, 1651.66, 1634.59, 1615.62.

#### O AQ (E)-4-ethylidene-N-(quinolin-8-yl)hept-6-enamide (3qa)

Following the general procedure, **3qa** was obtained as a colorless oil Me (23.7 mg, 85% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.80 (s, 1H), 8.81 – 8.77 (m, 2H), 8.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 5.86 – 5.78 (m, 1H), 5.35 (q, J = 6.5 Hz, 1H), 5.11 – 5.04 (m, 2H), 2.82 (d, J = 7.0 Hz, 2H), 2.64 – 2.61 (m, 2H), 2.58 – 2.55 (m, 2H), 1.66 (d, J = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.33, 147.06, 137.30, 135.92, 135.49, 135.33, 133.50, 126.90, 126.42, 120.71, 120.54, 120.34, 115.40, 115.03, 40.50, 35.51, 24.78, 12.37; HRMS (ESI): m/z for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 281.1648, found: 281.1652; FTIR (KBr, cm<sup>-1</sup>): 3646.02, 3626.52, 3454.21, 1660.29, 1651.50, 1644.61, 1634.03.

 $Me \qquad (E)-4-ethylidene-N-(quinolin-8-yl)dec-6-enamide (3ra)$ Following the general procedure, **3ra** was obtained as colorless oil (26.1 mg, 78% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.80 (s, 1H), 8.80 – 8.77 (m, 2H), 8.15 (d, J = 8.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.45 (dd, J = 8.5, 5.0 Hz, 1H), 5.87 – 5.79 (m, 1H), 5.26 (t, J = 7.0 Hz, 1H), 5.07 (dd, J = 19.5, 14.0 Hz, 2H), 2.82 (d, J = 6.5 Hz, 2H), 2.63 – 2.54 (m, 4H), 2.06 (q, J =7.0 Hz, 2H), 1.35 – 1.29(m, 6H), 0.85 (t, J = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.27, 147.03, 137.29, 136.02, 135.29, 134.37, 133.51, 127.19, 126.88, 126.40, 120.52, 120.29, 115.34, 114.98, 40.45, 35.90, 30.54, 28.59, 26.86, 25.17, 21.55, 13.03; **HRMS** (ESI): m/z for C<sub>22</sub>H<sub>29</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 337.2274, found: 337.2284; **FTIR** (KBr, cm<sup>-1</sup>): 3550.41, 3473.27, 3416.55, 1634.76, 1615.66.

#### (E)-4-(cyclohexylmethylene)-N-(quinolin-8-yl)hept-6-



#### enamide(3sa)

Following the general procedure, **3sa** was obtained as a white oil (25.9 mg, 74% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.81 (s, 1H),

8.81 – 8.77 (m, 2H), 8.16 (dd, J = 8.5, 1.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.46 (dd, J = 8.0, 4.0 Hz, 1H), 5.86 – 5.77 (m, 1H), 5.11 – 5.03 (m, 3H), 2.79 (d, J = 8.0 Hz, 2H), 2.64 – 2.60 (m, 2H), 2.56 (dd, J = 10.5, 7.0 Hz, 2H), 2.30 – 2.23 (m, 1H), 1.67 – 1.56 (m, 6H), 1.25 – 1.21 (m, 2H), 1.16 – 1.11 (m, 1H), 1.06 – 0.98 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.35, 147.07, 137.28, 136.11, 135.34, 133.47, 133.30, 132.54, 126.90, 126.41, 120.54, 120.33, 115.38, 114.92, 40.28, 36.33, 35.88, 32.55, 25.37, 25.01, 24.88; **HRMS** (ESI): m/z for C<sub>23</sub>H<sub>30</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 349.2274, found: 349.2283; **FTIR** (KBr, cm<sup>-1</sup>): 3564.71, 3454.24, 3417.43, 2923.36, 2853.27, 2359.81, 2340.19, 1636.45, 1630.84, 1524.30.

(E)-4-allyl-6,6-dimethyl-N-(quinolin-8-yl)hept-4-enamide (3ta) 0 AQ Following the general procedure, **3ta** was obtained as a yellow oil Me Me (25.6 mg, 80% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.82 (s, 1H), Me 8.81 - 8.77 (m, 2H), 8.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.55 - 7.48 (m, 2H), 7.45 (dd, J =8.5, 4.5 Hz, 1H), 5.86 – 5.77 (m, 1H), 5.30 (s, 1H), 5.11 – 5.04 (m, 2H), 2.77 (dd, J = 7.0, 1.0 Hz, 2H), 2.71 – 2.63 (m, 4H), 1.16 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.22, 147.08, 137.33, 137.28, 136.37, 135.33, 133.74, 133.50, 126.92, 126.41, 120.54, 120.36, 115.44, 114.87, 41.54, 36.08, 31.50, 30.48, 25.43; HRMS (ESI): m/z for  $C_{21}H_{27}N_2O$  [M+H]<sup>+</sup>: 323.2118, found: 323.2125; FTIR (KBr, cm<sup>-1</sup>): 3564.95, 3507.74, 3473.06, 3453.67, 3417.70, 2959.81, 2354.21, 2331.78, 1653.27, 1639.25, 1525.09, 1487.85, 1392.52, 795.33.

#### O<sub>N</sub>AQ 2-(2-allylcyclopent-2-en-1-yl)-N-(quinolin-8-yl)acetamide (3ua)

Following the general procedure, **3ua** was obtained as a white solid (20.1 mg, 69% yield), m.p. = 44.8 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 9.84 (s, 1H), 8.81 – 8.79 (m, 2H), 8.16 (dd, J = 8.5, 2.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.45 (dd, J = 8.5, 4.5 Hz, 1H), 5.93 – 5.85 (m, 1H), 5.48 (d, J = 1.5 Hz , 1H), 5.12 – 5.04 (m, 2H), 3.21 (s, 1H), 2.94 – 2.79 (m, 3H), 2.40 – 2.33 (m, 2H), 2.31 – 2.23 (m, 2H), 1.77 – 1.70 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.08, 147.08, 143.37, 137.29, 135.31, 134.96, 133.49, 126.89, 126.40, 125.05, 120.54, 120.34, 115.38, 114.92, 43.02, 41.26, 32.82, 29.65, 29.43; **HRMS** (ESI): m/z for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 293.1648, found: 293.1656; FTIR (KBr, cm<sup>-1</sup>): 3472.98, 3415.96, 1633.64, 1619.63, 1403.74, 624.30.

#### 2-(2-allylcyclohex-2-en-1-yl)-N-(qunolin-8-yl)acetamide (3va) AQ 0

Following the general procedure, 3va was obtained as a white solid  $(22.4 \text{ mg}, 73\% \text{ yield}), \text{ m.p.} = 85.9 \text{ °C}. {}^{1}\text{H} \text{ NMR} (500 \text{ MHz}, \text{CDCl}_{3}) \delta$ 9.83 (s, 1H), 8.81 - 8.79 (m, 2H), 8.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.55 - 7.48 (m, 2H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 5.89 – 5.81 (m, 1H), 5.56 – 5.54 (m, 1H), 5.13 – 5.06 (m, 2H), 2.86 - 2.77 (m, 4H), 2.43 (dd, J = 14.0, 10.0 Hz, 1H), 2.05 - 2.02 (m, 2H), 1.81 – 1.74 (m, 1H), 1.72 – 1.64 (m, 2H), 1.62 – 1.55 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) § 170.11, 147.07, 137.28, 136.77, 135.84, 135.29, 133.50, 126.88, 126.40, 123.50, 120.54, 120.34, 115.35, 115.02, 40.66, 38.90, 33.29, 26.88, 24.43, 17.88; **HRMS** (ESI): m/z for  $C_{20}H_{23}N_2O$  [M+H]<sup>+</sup>: 307.1805, found: 307.1813; **FTIR** (KBr, cm<sup>-1</sup>): 3550.31, 3473.05, 3416.10, 2926.17, 1634.69, 1615.50, 618.69.

#### 4-methylene -N-(quinolin-8-yl)-hept-6-enamide (3wa) 0 AQ

Following the general procedure (at 100 °C), 3wa was obtained as a colorless oil (4.5 mg, 17% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)δ 9.84 (s, 1H), 8.81 (dd, J = 4.0, 1.5 Hz, 1H), 8.78 (dd, J = 7.5, 1.5 Hz, 1H), 8.17 (dd, J = 8.0, 1.5 Hz, 1H), 7.56 - 7.48 (m, 2H), 7.46 (dd, J = 8.5, 4.5 Hz, 1H), 5.90 - 5.82 (m, 1H), 5.13 - 5.07 (m, 2H), 4.90 (s, 1H), 4.86 (s, 1H), 2.86 (d, J = 7.0 Hz, 2H), 2.75 - 2.72(m, 2H), 2.57 - 2.54 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.08, 147.08, 145.55, 137.32, 135.35, 135.04, 133.47, 126.92, 126.42, 120.56, 120.38, 115.51, 115.44, 109.71, 40.04, 35.28, 30.32; **HRMS** (ESI): m/z for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 267.1492, found: 267.1495; FTIR (KBr, cm<sup>-1</sup>): 3562.62, 3416.44, 2926.17, 2853.27, 2359.81, 2328.97, 1636.45, 1616.82, 1266.36, 744.86, 621.50.

#### (E)-4-((Z)-3-phenylallyl)-N-(quinolin-8-yl)hept-4-enamide (3pb-Z)

Following the general procedure, **3pb-Z** was obtained as a SI-14

white oil (16.7 mg, 45% yield). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.80 (s, 1H), 8.78 (m, 2H), 8.16 (dd, J = 8.5, 1.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H), 6.43 (d, J = 15.5 Hz, 1H), 6.25 – 6.19 (m, 1H), 5.31 (t, J = 7.0 Hz, 1H), 2.97 (d, J =6.5 Hz, 2H), 2.67 – 2.58 (m, 4H), 2.14 – 2.09 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.20, 147.07, 137.32, 136.61, 135.31, 134.27, 133.52, 130.25, 128.97, 127.81, 127.42, 126.91, 126.43, 125.93, 125.06, 120.53, 120.33, 115.39, 39.49, 36.02, 25.30, 20.20, 13.48; HRMS (ESI): m/z for C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 371.2118, found: 371.2120; FTIR (KBr, cm<sup>-1</sup>): 3444.86, 2968.22, 2920.56, 2858.88, 1681.31, 1651.70, 1541.12, 1504.67, 1400.93, 1260.75, 1022.43, 806.54.



(*E*)-4-cinnamyl-N-(quinolin-8-yl)hept-4-enamide (3pb-E) Following the general procedure, **3pb-E** was obtained as a brown oil (11.2 mg, 30% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.75 (s, 1H), 8.80 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.76 (dd, *J* =

7.5, 1.5 Hz, 1H), 8.16 (dd, J = 8.0, 1.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.47 – 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 7.30 – 7.27 (m, 4H), 7.21 – 7.17 (m, 1H), 6.57 (d, J = 11.5 Hz, 1H), 5.78 – 5.72 (m, 1H), 5.33 (t, J = 7.0 Hz, 1H), 3.06 (d, J = 7.5 Hz, 2H), 2.60 – 2.53 (m, 4H), 2.15 – 2.09 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.16, 147.04, 137.32, 136.35, 135.31, 134.34, 133.51, 129.32, 128.26, 127.57, 127.13, 126.91, 126.42, 125.62, 120.54, 120.32, 116.32, 115.41, 35.75, 34.51, 25.69, 20.15, 13.49; **HRMS** (ESI): m/z for C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 371.2118, found: 371.2117; **FTIR** (KBr, cm<sup>-1</sup>): 3646.22, 3564.54, 3417.91, 2920.56, 1681.31, 1653.27, 1541.12, 1506.54, 1263.55, 1095.33, 1016.82, 795.33.

### • AQ 4-((*E*)-benzylidene)-7-phenyl-N-(quinolin-8-yl)hept-6enamide (3ab)

<sup>Ph</sup> Following the general procedure, **3ab** was obtained as a white oil (34.3 mg, 82% yield, E/Z = 55:45). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.79 (s, 0.55H), 9.72 (s, 0.45H), 8.78 – 8.73 (m, 2H), 8.16 – 8.13 (m, 1H), 7.54 – 7.48 (m, 2H), 7.46 – 7.42 (m, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.32 – 7.25 (m, 7H), 7.21 – 7.16 (m, 2H), 6.66 (d, J = 11.5 Hz, 0.45H), 6.52 (d, J = 15.5 Hz, 0.55H), 6.47 (d, J = 9.0 Hz, 1H), 6.34 –

6.29 (m, 0.55H), 5.88 – 5.83 (m, 0.45H), 3.25 (d, J = 7.5 Hz, 0.9H), 3.16 (d, J = 7.0 Hz, 1.1H), 2.86 – 2.80 (m, 2H), 2.75 – 2.72 (m, 1.1H), 2.65 – 2.61 (m, 0.9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.83, 169.76, 147.05, 147.02, 138.81, 138.72, 137.32, 136.85, 136.79, 136.45, 136.21, 135.30, 133.46, 131.04, 130.10, 128.42, 127.59, 127.57, 127.53, 127.46, 127.28, 127.26, 127.23, 126.91, 126.90, 126.85, 126.40, 126.25, 126.10, 125.80, 125.37, 125.33, 125.13, 120.53, 120.36, 115.43, 39.94, 35.62, 35.39, 35.02, 30.91, 30.61, 30.49, 30.42, 29.20, 29.14, 28.68, 28.64, 28.49, 28.34, 28.14, 27.95, 26.46, 26.12, 21.67, 13.09; HRMS (ESI): m/z for C<sub>29</sub>H<sub>27</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 419.2118, found: 419.2127; FTIR (KBr, cm<sup>-1</sup>): 3417.56, 2962.62, 2917.76, 2850.47, 2357.01, 2320.56, 1681.31, 1650.47, 1630.84, 1518.69, 1400.93, 1260.75, 1103.74, 1025.23, 789.13.



#### (4*E*)-4-propylidene-N-(quinolin-8-yl)tridec-6enamide (3pc)

Following the general procedure, **3pc** was obtained as a brown oil (22.0 mg, 58% yield,

E/Z = 63:37). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.80 (s, 1H), 8.80 – 8.78 (m, 2H), 8.16 (d, J = 8.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.46 – 7.43 (m, 1H), 5.51 – 5.46 (m, 1H), 7.44 – 7.37 (m, 1H), 5.24 (q, J = 6.5 Hz, 1H), 2.81 (d, J = 7.0 Hz, 1.25H), 2.75 (d, J = 6.5 Hz, 0.75H), 2.64 – 2.59 (m, 2H), 2.56 – 2.49 (m, 2H), 2.11 – 2.05 (m, 2.5H), 2.04 – 1.99 (m, 1.5H), 1.42 – 1.26 (m, 8H), 0.96 – 0.92 (m, 3H), 0.86 – 0.84 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.16, 147.04, 137.32, 136.35, 135.31, 134.34, 133.51, 129.32, 128.26, 127.57, 127.13, 126.91, 126.42, 125.62, 120.54, 120.32, 116.32, 115.41, 35.75, 34.51, 25.69, 20.15, 13.49; HRMS (ESI): m/z for C<sub>25</sub>H<sub>35</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 379.2744, found: 379.2754; FTIR (KBr, cm<sup>-1</sup>): 3473.08, 3444.69, 3417.28, 2959.81, 2928.97 2856.07, 2359.81, 2328.97, 1698.13, 1684.11, 1650.47, 1525.19, 1389.72, 1319.63, 826.17, 789.72.

# O AQ 4-((E)-benzylidene)-N-(quinolin-8-yl)tridec-6 enamide (3ac)

Ph Me Following the general procedure, **3ac** was obtained as a white oil (21.2 mg, 46% yield, E/Z = 50:50). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.78 (s, 1H), 8.78 (d, J = 4.0 Hz, 1H), 8.76 (d, J = 7.5 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.45 (dd, J = 8.0, 3.5 Hz, 1H), 7.30 – 7.24 (m, 5H), 7.16 (t, J = 6.5 Hz, 1H), 6.39 (d, J = 6.5 Hz, 1H), 5.59 – 5.55 (m, 1H), 5.54 – 5.47 (m, 1H), 3.00 (d, J = 6.5 Hz, 1H), 2.94 (d, J = 6.5 Hz, 1H), 2.79 – 2.77 (m, 2H), 2.72 – 2.68 (m, 2H), 2.13 – 2.09 (m, 1H), 2.06 – 2.02 (m, 1H), 1.39 – 1.26 (m, 8H), 0.86 – 0.86 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.90, 147.03, 139.38, 139.12, 137.31, 137.02, 136.99, 135.30, 133.49, 132.25, 131.29, 127.51, 127.23, 126.90, 126.40, 126.28, 126.05, 125.82, 125.54, 125.20, 125.19, 120.53, 120.34, 120.33, 115.38, 39.72, 35.68, 35.56, 34.12, 31.54, 30.53, 30.42, 28.31, 28.12, 26.27, 25.91, 21.55, 21.49, 13.03; HRMS (ESI): m/z for C<sub>29</sub>H<sub>35</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 427.2744, found: 427.2750; FTIR (KBr, cm<sup>-1</sup>): 3453.27, 3417.57, 2920.56, 2853.27, 2359.81, 2326.17, 1698.13, 1689.72, 1653.27, 1636.45, 1630.84, 1541.12, 1406.54.

#### (4*E*)-8-phenyl-4-propylidene-N-(quinolin-8-yl)oct-6enamide (3pd)

Following the general procedure, **3pd** was obtained as a Me Ph white oil (23.0 mg, 60% yield, E/Z = 55:45). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.80 (s, 1H), 8.78 – 8.77 (m, 2H), 8.16 – 8.14 (m, 1H), 7.55 – 7.48 (m, 2H), 7.45 - 7.42 (m, 1H), 7.27 - 7.22 (m, 2H), 7.19 - 7.13 (m, 3H), 5.71 -5.63 (m, 1H), 5.60 – 5.49 (m, 1H), 5.30 – 7.22 (m, 1H), 3.43 (d, J = 7.0 Hz, 1.1H), 3.37 (d, J = 6.5 Hz, 0.9H), 2.93 (d, J = 7.5 Hz, 1.1H), 2.79 (d, J = 6.5 Hz, 0.9H), 2.65 -5.53 (m, 4H), 2.13 -2.06 (m, 2H), 0.95 (t, J = 7.5, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) & 171.26, 148.10, 140.95, 140.83, 138.38, 136.34, 135.59, 135.33, 134.56, 130.66, 129.93, 129.58, 129.47, 129.27, 128.50, 128.39, 128.38, 128.36, 127.96, 127.46, 125.89, 125.84, 121.56, 121.37, 121.34, 116.44, 40.21, 39.00, 37.09, 36.99, 34.62, 33.48, 29.71, 29.37, 26.60, 26.16, 22.70, 21.17, 14.51, 14.11; HRMS (ESI): m/z for C<sub>26</sub>H<sub>29</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 385.2274, found: 385.2277; FTIR (KBr, cm<sup>-1</sup>): 3416.82, 3360.75, 2965.42, 2923.83, 2856.07, 2551.40, 1681.31, 1687.29, 1653.07, 1525.13, 1485.05, 1261.02, 1096.14, 1019.98, 800.68.



0<sub>>></sub>

AQ

4-((*E*)-benzylidene)-8-phenyl-N-(quinolin-8-yl)oct-6enamide (3ad)

Following the general procedure, **3ad** was obtained as a white oil (17.0 mg, 40% yield, E/Z = 50:50). <sup>1</sup>H NMR (500

MHz, CDCl<sub>3</sub>)  $\delta$  9.78 (d, J = 4.0 Hz, 1H), 8.77 – 8.75 (m, 2H), 8.16 – 8.14 (m, 1H), 7.54 – 7.48 (m, 2H), 7.46 – 7.43 (m, 1H), 7.31 – 7.25 (m, 7H), 7.21 – 7.14 (m, 4H), 6.43 (s, 0.5H), 6.40 (s, 0.5H), 5.80 – 5.73 (m, 1H), 5.71 – 5.66 (m, 0.5H), 5.64 – 5.58 (m, 0.5H), 3.49 (d, J = 7.0 Hz, 1H), 3.40 (d, J = 6.5 Hz, 1H), 3.12 (d, J = 7.5 Hz, 1H), 2.99 (d, J = 6.5 Hz, 1H), 2.84 – 2.78 (m, 2H), 2.73 – 2.68 (m, 2H); <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.89, 147.06, 139.74, 139.63, 139.03, 138.78, 138.26, 137.33, 136.90, 135.30, 133.49, 130.54, 129.37, 128.05, 127.52, 127.50, 127.42, 127.38, 127.26, 126.92, 126.67, 126.41, 126.35, 126.18, 125.29, 124.93, 124.89, 120.54, 120.36, 115.42, 39.62, 38.01, 35.66, 35.54, 34.08, 32.80, 32.54, 30.91, 30.61, 30.43, 29.20, 28.68, 28.64, 28.34, 26.34, 25.96, 21.67, 13.09; **HRMS** (ESI): m/z for C<sub>30</sub>H<sub>29</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 433.2274, found: 433.2282; **FTIR** (KBr, cm<sup>-1</sup>): 3444.65, 3417.51, 2968.22, 2926.17, 2856.07, 1695.33, 1681.31, 1650.47, 1406.54, 1257.94, 1103.74, 1019.63, 798.13.

#### **Pd-Catalyzed H/D Exchange**



An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), amide **1a** (1.0 equiv, 0.1 mmol),  $(CD_3)_2SO$  (0.35 mL) and  $CD_3OD$  (0.7 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 12 h. After cooling down, the mixture was

directly applied to a flash column chromatography (PE / EA = 4 / 1).



An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), amide **1a** (1.0 equiv, 0.1 mmol),  $(CD_3)_2SO$  (0.35 mL) and  $CD_3OD$  (0.7 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol) and carbonate **2a** (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 10 min. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA = 4 / 1).



An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), amide **1a** (1.0 equiv, 0.1 mmol), **1a**- $d_2$  (1.0 equiv, 0.1 mmol), DMSO (0.35 mL) and MeOH (0.7 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol) and carbonate **2a** (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 3 min. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA = 4 / 1), We calculated the yield by NMR with 0.1 mmol 1,3,5-trimethoxybenzene as the interior label.



An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), DMSO (0.7 mL) and MeOH (1.4 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol), amide 1c (1.0 equiv, 0.1 mmol), 1g (1.0 equiv, 0.1 mmol) and carbonate 2a (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 10 min. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA = 4 / 1). We calculated the yield by NMR with 0.1 mmol 1,3,5-trimethoxybenzene as the internal standard.



An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), DMSO (0.7 mL) and MeOH (1.4 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol), amide **1a** (1.0 equiv, 0.1 mmol), **1r** (1.0 equiv, 0.1 mmol) and carbonate **2a** (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated

to 40 °C with stirring for 10 min. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA = 4 / 1). We calculated the yield by NMR with 0.1 mmol 1,3,5-trimethoxybenzene as the interior label.



An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), **5** (1.0 equiv, 0.1 mmol), DMSO (0.35 mL) and MeOH (0.7 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol) and carbonate **2a** (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column  $\frac{SI-22}{2}$ 

chromatography (PE / EA = 4 / 1). Compound **5a** was obtained as a colorless oil (14.5 mg, 52% yield).



#### (E)-4-benzylidene-N-(pyridin-2-yl)hept-6-enamide (5a)

Following the general procedure, **5a** was obtained as a colorless oil (14.5 mg, 52% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 – 8.52 (m, 1H), 8.18 (d, J = 8.5 Hz, 1H), 8.03 (s, 1H), 7.84 (td, J =

7.5, 1.5 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.26 – 7.23 (m, 3H), 7.20 – 7.18 (m, 2H), 7.16 – 7.13 (m, 1H), 6.35 (s, 1H), 5.92 – 5.83 (m, 1H), 5.15 – 5.08 (m, 2H), 3.43 (q, J = 7.0 Hz, 2H), 2.93 (dd, J = 7.0, 1.0 Hz, 2H), 2.37 – 2.34 (m, 2H), 1.84 – 1.78 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  163.21, 148.92, 146.93, 139.37, 137.08, 136.27, 135.35, 127.49, 127.13, 125.89, 125.00, 121.11, 115.57, 40.57, 38.22, 28.68, 27.02; HRMS (ESI): m/z for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 307.1819, found: 307.1825; FTIR (KBr, cm<sup>-1</sup>): 3444.62, 2957.01, 2839.25, 2354.21, 1684.11, 1672.90, 1650.47, 1633.64, 1557.94, 1541.12, 1507.48, 1022.43.



An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), DMSO (0.35 mL) and MeOH (0.7 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol), amide **6** (1.0 equiv, 0.1 mmol) and carbonate **2a** (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA = 1 / 1). Compound **6** was recovered as a yellow oil (11.5 mg, 82% recovered).

#### **Synthetic Applications**



An screw-cap vial was charged with  $Pd(OAc)_2$  (15 mol%, 0.59 mmol), DMSO (13.8 mL) and MeOH (27.5 mL). Then, pivalic acid (2.0 equiv, 7.86 mmol), amide **1p** (1.0 g, 3.93 mmol) and carbonate **2a** (4.0 equiv, 15.7 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 16 h. After cooling down, the reaction was diluted with water and extracted with EA (×3). The combined organic layers were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo, and the resulting residue was purified using silica gel column chromatography (PE/EA = 4/1). Product **3pa** was obtained as a



A screw-cap vial was charged with Ni(tmhd)<sub>2</sub> (50 mol%, 0.1 mmol), MeOH (1.0 ml), Then **3pa** (1.0 equiv, 0.2 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 100 °C with stirring for 24 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA = 10 / 1). Compound **7** was obtained as a yellow oil (26.2 mg, 71% yield), compound **8** was obtained as a yellow solid (16.7 mg, 58% yield).

O<sub>>></sub>OMe Methyl (*E*)-4-allyl-hept-4-enoate (7)

Following the general procedure, **7** was obtained as a yellow oil, (25.8 mg, 71% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  5.80 – 5.72 (m, 1H), 5.21 (t, *J* = 7.0 Hz, 1H), 5.06 – 5.00 (m, 2H), 3.67 (s, 3H), 2.73 – 2.71 (m, 2H), 2.36 (s, 3H), 2.06 – 1.99 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  173.74, 136.90, 134.88, 129.59, 115.92, 51.53, 41.21, 32.98, 25.43, 21.04, 14.46; **HRMS** (ESI): m/z for C<sub>11</sub>H<sub>19</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 183.138, found : 183.1389; **FTIR** (KBr, cm<sup>-1</sup>): 3564.63, 3473.04, 3454.93, 3417.45, 2917.76, 1653.27, 1633.64, 1616.82.



An screw-cap vial was charged with  $Pd(OAc)_2$  (20 mol%, 0.02 mmol), amide 1a-Z (1.0 equiv, 0.1 mmol), amide 1a-E (1.0 equiv, 0.1 mmol), DMSO (0.35 mL) and

MeOH (0.7 mL). Then, pivalic acid (2.0 equiv, 0.2 mmol) and carbonate **2a** (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA = 4 / 1). Compound **3aa** was recovered as a yellow solid (27.2 mg, 80% yield), mixture **1a**-*Z*/**1a**-*E* was recovered as a yellow oil (32.5mg, 108% yield, Z/E = 10/90).



A falsk was charged with Pd/C (20 wt %), MeOH (1.0 ml), Then **3ab** (1.0 equiv, 0.1 mmol) was added into the solution. The flask was equipped with hydrogen balloon (1 atm) and stirring at room temperature for 3.0 h. After the reaction is complete, the mixture was directly applied to a flash column chromatography (PE / EA = 4 / 1). Compound **9** was obtained as a colorless oil (35.0 mg, 83% yield).

#### (*R*)-4-benzyl-7-phenyl-N-(quinolin-8-yl)heptanamide (9)



### Following the general procedure, the compound **9** was obtained as a colorless oil, (35.0 mg, 83% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) $\delta$ 9.75 (s, 1H), 8.78 (dd, *J* = 4.5, 2.0 Hz, 1H), 8.76 (dd, *J*

= 7.0, 1.0 Hz, 1H), 8.15 (dd, J = 8.5, 2.0 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 7.25 – 7.23 (m, 4H), 7.18 – 7.13 (m, 6H), 2.62 (d, J = 6.5 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 2.54 – 2.48 (m, 2H), 1.84 – 1.79 (m, 3H), 1.74 – 1.65 (m, 2H), 1.42 – 1.37 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  171.83, 148.09, 142.55, 140.92, 138.34, 136.38, 134.54, 129.20, 128.42, 128.28, 128.28, 127.95, 127.46, 125.82, 125.67, 121.58, 121.36, 116.42, 40.38, 39.26, 36.15, 35.59, 32.56, 29.11, 28.35; HRMS (ESI): m/z for C<sub>29</sub>H<sub>31</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 423.2431, found: 423.2422; FTIR (KBr, cm<sup>-1</sup>): 3472.97, 3444.68, 3417.96, 2354.21, 1692.52, 1681.31, 1653.27, 1633.64, 1555.14, 1538.32, 1406.54, 1028.04.

#### Plausible catalytic cycle



A plausible catalytic cycle for this reaction is shown below. Following substrate and metal coordination to give a  $\pi$ -alkene palladium complex I,  $\gamma$ -C(alkenyl)–H activation takes place to generate the six-membered palladacycle II. Coordination of the allyl carbonate, followed by alkene insertion and  $\beta$ -oxygen elimination, produced 1,4-diene **3**.

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#### <sup>1</sup>H / <sup>13</sup>C NMR Charts













 $\geq$ 











≫ (3ga)



--62.38

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)















SI-41































0~ AQ <sup>≫</sup>(3wa)











Ph Ph (3ab)







Me (3ac)















