

# **An Umpolung Approach to Alkene Carboamination: Palladium Catalyzed 1,2-Amino-Acylation, -Carboxylation, -Arylation, -Vinylolation and –Alkynylation**

Adele Faulkner<sup>†</sup>, James S. Scott<sup>‡</sup>, and John F. Bower<sup>\*†</sup>

<sup>†</sup>*School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom*

<sup>‡</sup>*AstraZeneca, Alderley Park, Macclesfield, Cheshire, SK10 4TG, United Kingdom*

## **Supporting Information**

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## **General Experimental Details**

All reactions involving air-sensitive reagents were performed under a dry nitrogen atmosphere. Anhydrous DMF was purchased from Sigma Aldrich or obtained by distillation from  $\text{CaH}_2$ . Anhydrous  $\text{CH}_2\text{Cl}_2$  and THF were obtained by passage through a column of anhydrous alumina using equipment from Anhydrous Engineering, based on the Grubbs' design. Removal of solvents *in vacuo* was achieved using a Büchi rotary evaporator with bath temperatures up to 50 °C. Flash column chromatography (FCC) was carried out using Fluorochem 60 silica: 230-400 mesh (40-63  $\mu\text{m}$ ). Reactions were monitored by thin layer chromatography (TLC) analysis using Merck Kieselgel 60F<sub>254</sub> aluminium backed plates. Spots were visualized by UV light ( $\lambda_{\text{max}} = 254\text{nm}$ ) and were stained with  $\text{KMnO}_4$ , vanillin or anisaldehyde solutions as required.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a 400 MHz JEOL Eclipse 400 or Varian 400-MR spectrometer in  $\text{CDCl}_3$  and referenced to  $\text{CDCl}_3$  or tetramethylsilane. Chemical shifts are quoted in parts per million (ppm) and coupling constants ( $J$ ) are quoted to the nearest 0.5 Hz. Splittings are recorded as singlet (s), doublet (d), triplet (t), quartet (q) and broad singlet (br s). Assignments were based upon DEPT, COSY, HMBC and HSQC experiments. Where mixtures of isomers (*e.g.* diastereomers) are characterized together, integrals are normalized to the major isomer. nOe experiments (performed using a Varian VNMR S500b spectrometer) were used where appropriate.

Infrared spectroscopy was performed on a Perkin Elmer Spectrum RX/FT-IR System Spectrometer and recorded in the range 4000-600  $\text{cm}^{-1}$  as a thin film. IR absorbances are quoted in wavenumbers ( $\text{cm}^{-1}$ ) with the abbreviations br. (broad), s (strong), m (medium) or w (weak).

Mass spectra were recorded using either electrospray ionisation ( $\text{ESI}^+$ ), performed on a Bruker Daltonics 7.0 Telsa Apex 4 Fourier Transform Ion Cyclotron Resonance (FT-ICR) or chemical ionisation ( $\text{CI}^+$ ), performed on a Perkin Elmer Turbo Mass Gold Quadrupole.

$\text{PhB}(\text{OH})_2$ ,  $\text{PhBPin}$ ,  $\text{Ph}_4\text{B}^-\text{Na}^+$ ,  $\text{Ph}_4\text{B}^-\text{K}^+$ ,  $\text{Ph}_4\text{B}^-\text{NH}_4$  utilized were obtained from Sigma Aldrich or Alfa Aesar. All stannanes and boronic acid pinacol esters were obtained from commercial sources or synthesized as described below.

## **Experimental Procedures and Data**

**General Procedure A** for the preparation of ketone precursors via the corresponding  $\beta$ -keto ester. **Part A:** To NaH (100 mol%, 60% dispersion in mineral oil), the appropriate  $\beta$ -keto ester (100 mol%) was added at 0 °C. Anhydrous DMF (5 mL/mmol) was added to the reaction *via* cannula. The mixture was stirred at room temperature until gas evolution ceased (*ca.* 15 minutes). The appropriate chloride/bromide (110 mol%) was then added *via* syringe and the mixture was heated at 70 °C for 16 hours. The mixture was cooled to room temperature and the solvent removed by concentration *in vacuo* to afford the alkylated product which was used without further purification unless otherwise stated. **Part B:** The crude product from Part A was dissolved in THF (2 mL/mmol), MeOH (1 mL/mmol) and water (1 mL/mmol), and KOH (500 mol%) was added. The mixture was then heated at 75 °C until complete consumption of intermediate ester was observed by TLC (*ca.* 6-16 hours). After cooling to room temperature, the mixture was acidified with aq. 1 M HCl (8 mL/mmol) and extracted with Et<sub>2</sub>O (20 mL/mmol). The organic extracts were washed with brine (10 mL/mmol), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Purification of the residue by FCC, under the conditions noted, afforded the corresponding alkylated ketone.

**General Procedure B** for oxime ester formation: **Part A:** H<sub>2</sub>NOH.HCl (120 mol%) and NaOAc (120 mol%) were added to a solution of the appropriate ketone (100 mol%) in MeOH (3 mL/mmol). The mixture was heated at 75 °C for the specified time. After cooling to room temperature, the mixture was diluted with EtOAc (10 mL/mmol), washed with brine (10 mL/mmol), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The oxime obtained in this way was used in the next stage without further purification, unless otherwise stated. **Part B:** To a solution of the appropriate oxime (100 mol%) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (3 mL/mmol) at 0 °C was added, *via* syringe, Et<sub>3</sub>N (200 mol%) and then ClC(O)C<sub>6</sub>F<sub>5</sub> (120 mol %). The mixture was then warmed to room temperature and stirred for the specified time. MeOH (0.5 mL/mmol) and then EtOAc (15 mL/mmol) were added. The mixture was then washed with saturated aq. Na<sub>2</sub>CO<sub>3</sub> (2 × 15 mL/mmol) and brine (15 mL/mmol), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was purified by FCC, under the conditions noted, to afford the corresponding oxime ester.

**General procedure C** for the preparation of sodium tetraarylborates: A crystal of iodine was added to magnesium turnings (660 mol%), which were then stirred vigorously for 10 minutes. The mixture was then suspended in anhydrous THF or Et<sub>2</sub>O (1 mL/mmol). The corresponding bromide (600 mol%) was added slowly over approximately 1 hour. The resulting mixture was stirred for an additional 1.5 hours. Sodium tetrafluoroborate (100 mol%) was added and the mixture was stirred for 24-63 hours at room temperature. The reaction mixture was poured into a solution of Na<sub>2</sub>CO<sub>3</sub> (2.5 g/mmol) in water (25 mL/mmol) and stirred for 30 minutes. The resulting suspension was filtered through celite and the solids were washed sequentially with Et<sub>2</sub>O (30 mL/mmol) and EtOAc (30 mL/mmol). The organic phase was isolated and the aqueous phase was extracted with EtOAc (30 mL/mmol). The combined organic extracts were concentrated *in vacuo*. The resulting solid was washed with CHCl<sub>3</sub>/hexane and dried under vacuum to afford the corresponding sodium tetraarylborate.

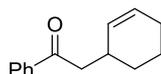
**General procedure D for counterion exchange of tetraarylborates:** The appropriate tetraarylborate was suspended in H<sub>2</sub>O:MeOH (1:1) (3 mL/mmol) and additional H<sub>2</sub>O:MeOH (1:1) (3 mL/mmol) was added portionwise until a solution was obtained. A 2.5 wt% solution of amine (150 mol%) was then added. Upon addition of the amine, a precipitate formed, and this was isolated by filtration, washed with H<sub>2</sub>O (10 mL/mmol) and dried under vacuum to afford the corresponding tetraarylborate.

**General procedure E for the  $\alpha$ -methylenation of aldehydes:** To a solution of formaldehyde (37% in water, 100 mol%) and aldehyde (100 mol%) in *i*-PrOH (1 mL/mmol) was added propionic acid (10 mol%) and pyrrolidine (10 mol%). The reaction mixture was stirred at 45 °C for 1-25 hours. NaHCO<sub>3</sub> (3 mL/mmol) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 2 mL/mmol). The combined organic extracts were washed with brine (3 mL/mmol), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated *in vacuo*. Purification of the residue by FCC, under the conditions noted, afforded the corresponding aldehyde.

**General procedure F for the preparation of alcohol precursors from  $\alpha$ -substituted acroleins:** To a solution of  $\alpha$ -substituted acrolein (100 mol%) in MeOH (0.5 mL/mmol) at 0 °C was added sodium borohydride (105 mol%) portionwise. The reaction was stirred at 0 °C for approximately 30 minutes (until complete consumption of starting material was observed). The reaction was then quenched with NH<sub>4</sub>Cl (0.5 mL/mmol). The mixture was diluted with water (1 mL/mmol) and extracted with Et<sub>2</sub>O (3 × 2 mL/mmol). The organic extracts were carefully concentrated *in vacuo*. Purification of the residue by FCC, under the conditions noted, afforded the corresponding alcohol.

**General Procedure G for the preparation of bromide precursors from the corresponding alcohol:** To a solution of the appropriate alcohol (100 mol%) in Et<sub>2</sub>O (2 mL/mmol) at 0 °C was added PBr<sub>3</sub> (50 mol%). The solution was warmed to room temperature and stirred for 16 hours. The reaction was cooled to 0 °C and water (1 mL/mmol) and 5% aq. K<sub>2</sub>CO<sub>3</sub> (1 mL/mmol) were added. The organic phase was isolated, washed with brine (1 mL/mmol), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo* to afford the corresponding bromide, which was used in the next stage without further purification, unless otherwise stated.

## 2-(Cyclohex-2-en-1-yl)-1-phenylethanone



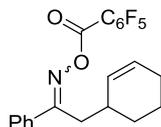
**General Procedure A:** Ethyl benzoylacetate (4.00 mL, 23.10 mmol) was employed. FCC (hexanes-EtOAc 20:1) afforded the title compound (4.01 g, 87%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.00-7.95 (m, 2H, ArH), 7.85-7.53 (m, 1H, ArH), 7.49-7.43 (m, 2H, ArH), 5.76-5.70 (m, 1H, HC=CHCH<sub>2</sub>), 5.60 (dddd, *J* = 10.0, 2.0, 2.0 and 2.0 Hz, 1H, HC=CHCH<sub>2</sub>), 3.00-2.92 (m, 2H, Ar(CO)CH<sub>2</sub>), 2.88- 2.78 (m, 1H, Ar(CO)CH<sub>2</sub>CH), 2.03-1.97 (m, 2H, CH<sub>2</sub>), 1.92-1.83 (m, 1H, CH<sub>2</sub>), 1.77-1.67 (m, 1H, CH<sub>2</sub>), 1.64-1.53 (m, 1H, CH<sub>2</sub>), 1.36-1.26 (m, 1H, CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.6 (C=O), 137.3 (ArC), 132.9 (ArCH), 130.8 (HC=CHCH<sub>2</sub>), 128.6, 128.1 (2 × ArCH), 128.0 (HC=CHCH<sub>2</sub>), 44.8 (Ar(CO)CH<sub>2</sub>), 31.6 (Ar(CO)CH<sub>2</sub>CH), 29.1, 25.1, 21.1 (3 × CH<sub>2</sub>).

*The spectroscopic properties of this compound were consistent with data available in the literature.*<sup>1</sup>

## 2-(Cyclohex-2-enyl)-1-phenylethanone-*O*-perfluorobenzoyl oxime (3)



**General Procedure B:** Part A: 2-(Cyclohex-2-en-1-yl)-1-phenylethanone (2.00 g, 10.00 mmol) was used and H<sub>2</sub>NOH.HCl (120 mol%) and NaOAc (120 mol%) were employed. The mixture was heated at 60 °C for 2 hours to afford the corresponding oxime (2.15 g, 99%) as a colorless solid. Part B: The corresponding oxime (1.00 g, 4.65 mmol) was employed and the reaction was run for 22 hours. FCC (hexane:EtOAc 5:1) afforded oxime ester **3** (1.53 g, 81%, 1:0.1 mixture of oxime isomers) as a colorless solid.

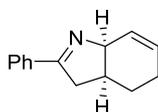
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Data for the major isomer:* 7.78-7.73 (m, 2H, ArH), 7.52-7.40 (m, 3H, ArH), 5.74-5.68 (m, 1H, HC=CHCH<sub>2</sub>), 5.49 (dddd, *J* = 10.0, 2.0, 2.0 and 2.0 Hz, 1H, HC=CHCH<sub>2</sub>), 2.92 (d, *J* = 3.0 Hz, 2H, Ar(CN)CH<sub>2</sub>), 2.46-2.37 (m, 1H, Ar(CN)CH<sub>2</sub>CH), 1.99-1.91 (m, 2H, CH<sub>2</sub>), 1.76-1.63 (m, 2H, CH<sub>2</sub>), 1.50-1.39 (m, 1H, CH<sub>2</sub>), 1.32-1.23 (m, 1H, CH<sub>2</sub>). *Characteristic signal for the minor isomer:* 5.55 (dddd, *J* = 10.0, 2.0, 2.0 and 2.0 Hz, 0.1H, HC=CHCH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): *Data for major isomer only:* 168.2 (C=N), 156.8 (C=O), 133.6 (ArC), 131.1 (ArCH), 129.6 (HC=CHCH<sub>2</sub>), 128.9 (ArCH), 128.7 (HC=CHCH<sub>2</sub>), 127.7 (ArCH), 34.8 (Ar(CN)CH<sub>2</sub>), 33.6 (Ar(CN)CH<sub>2</sub>CH), 28.9, 25.1, 21.0 (3 × CH<sub>2</sub>). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

The spectroscopic properties of this compound were consistent with data available in the literature.<sup>1</sup>

### Procedure for investigating the effects of additives on the cyclization of 3 to 5

#### (3a*S*\*,7a*R*\*)-2-Phenyl-3a,4,5,7a-tetrahydro-3*H*-indole

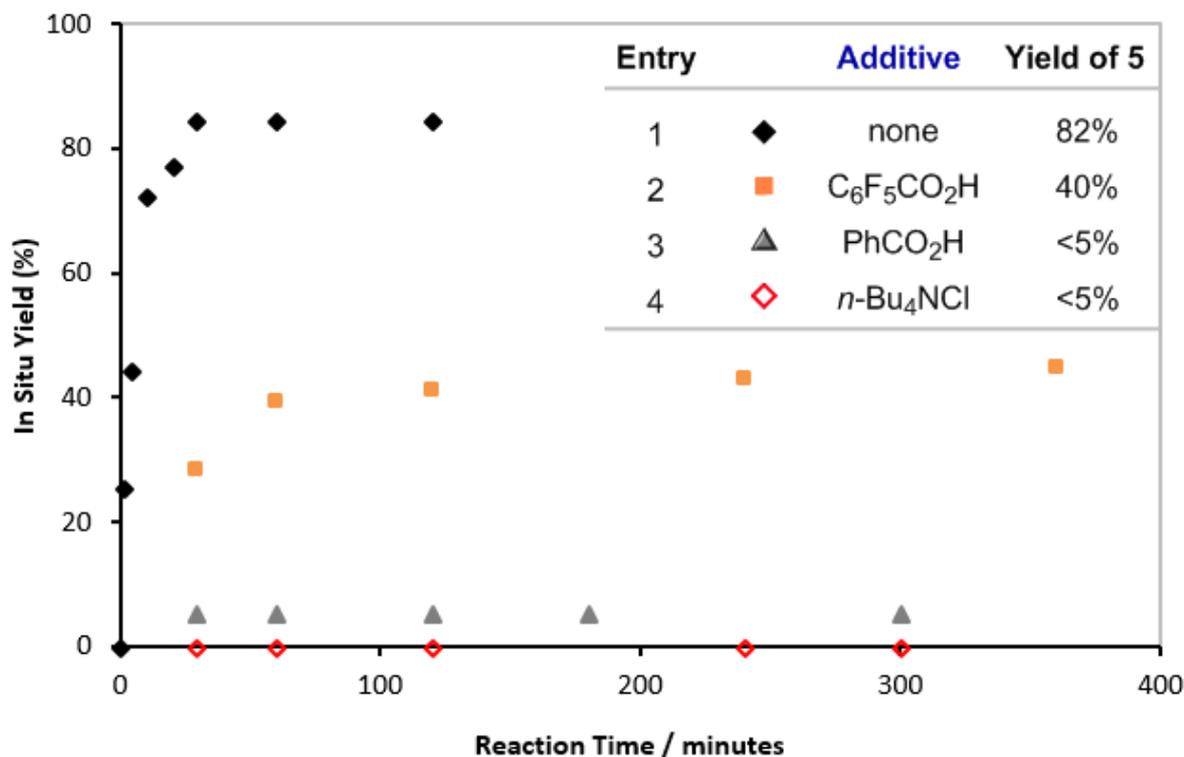


An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (2.8 mg, 3.06 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>Ph)<sub>3</sub> (8.2 mg, 0.012 mmol), oxime ester substrate (50 mg, 0.122 mmol) and additive (100 mol%). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.2 mL) and then reagent grade Et<sub>3</sub>N (68 μL, 0.488 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 90 °C. After the desired time the mixture was immediately cooled in an ice bath. The reaction was concentrated *in vacuo*. The *in situ* yield was determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard. For entry 1, FCC (hexane:EtOAc 10:1) afforded the title compound (19.5 mg, 80%) as a colorless oil.

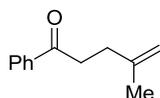
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.76-7.65 (m, 2H, ArH), 7.31-7.21 (m, 3H, ArH), 6.17 (m, 1H, HC=CHCH<sub>2</sub>), 5.94-5.87 (m, 1H, HC=CHCH<sub>2</sub>), 4.38-4.31 (m, 1H, (NC)HCH), 3.05 (dddd, *J* = 16.5, 8.5, 8.0 and 2.5 Hz, 1H, Ar(CN)CH<sub>2</sub>), 2.76 (dddd, *J* = 16.5, 2.5, 2.5 and 2.0 Hz, 1H, Ar(CN)CH<sub>2</sub>), 2.55-2.44 (m, 1H, Ar(CN)CH<sub>2</sub>CH), 2.00-1.83 (m, 2H, HC=CHCH<sub>2</sub>), 1.64-1.56 (m, 1H, HC=CHCH<sub>2</sub>CH<sub>2</sub>), 1.24-1.14 (m, 1H, HC=CHCH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.4 (C=N), 134.9 (ArC), 130.4 (ArCH), 129.9 (HC=CHCH<sub>2</sub>), 128.3, 127.6 (2 × ArCH), 127.4 (HC=CHCH<sub>2</sub>), 70.1 ((NC)HCH), 42.0 (Ar(CN)CH<sub>2</sub>), 35.2 (Ar(CN)CH<sub>2</sub>CH), 25.5 (HC=CHCH<sub>2</sub>CH<sub>2</sub>), 23.3 (HC=CHCH<sub>2</sub>).

The spectroscopic properties of this compound were consistent with the data in the literature.<sup>1</sup>



#### 4-Methyl-1-phenylpent-4-en-1-one



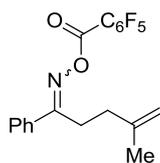
**General Procedure A:** Ethyl benzoylacetate (2.01 mL, 11.60 mmol) and 3-chloro-2-methylprop-1-ene (1.25 mL, 12.07 mmol) were employed. FCC (hexane:EtOAc 20:1) afforded the title compound (1.52 g, 76%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.00-7.96 (m, 2H, ArH), 7.60-7.55 (m, 1H, ArH), 7.51-7.45 (m, 2H, ArH), 4.79-4.77 (m, 1H, C=CH<sub>2</sub>), 4.74-4.72 (m, 1H, C=CH<sub>2</sub>), 3.16-3.10 (m, 2H, Ar(CO)CH<sub>2</sub>), 2.46 (t, *J* = 8.0 Hz, 2H, Ar(CO)CH<sub>2</sub>CH<sub>2</sub>), 1.80 (d, *J* = 0.5 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.7 (C=O), 144.7 (C=CH<sub>2</sub>), 136.9 (ArC), 133.0, 128.6, 128.0 (3 × ArCH), 110.2 (C=CH<sub>2</sub>), 36.8 (Ar(CO)CH<sub>2</sub>), 31.9 (Ar(CO)CH<sub>2</sub>CH<sub>2</sub>), 22.8 (CH<sub>3</sub>C=CH<sub>2</sub>).

*The spectroscopic properties were consistent with the data in the literature.*<sup>2</sup>

#### 4-Methyl-1-phenylpent-4-en-1-one-*O*-perfluorobenzoyl oxime (6a)



**General Procedure B:** Part A: 4-Methyl-1-phenylpent-4-en-1-one (1.40 g, 8.04 mmol) was employed. The reaction was heated to 75 °C for 16 hours to afford the corresponding oxime (1.21 g, 80%) as a colorless solid. Part B: The corresponding oxime (0.65 g, 3.43 mmol) was employed and the reaction was left stirring for 16 hours. FCC (hexane:EtOAc 25:1) afforded the title compound (1.12 g, 85%, 1:0.05 mixture of oxime isomers) as a colorless solid.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Signals for the major isomer:* 7.79-7.73 (m, 2H, ArH), 7.53-7.42 (m, 3H, ArH), 4.80-4.76 (m, 1H, C=CH<sub>2</sub>), 4.74-4.70 (m, 1H, C=CH<sub>2</sub>), 3.08-3.01 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.28 (t, *J* = 8.5 Hz, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.74 (d, *J* = 0.5 Hz, 3H, CH<sub>3</sub>). *Characteristic signals of the minor isomer:* 4.68-4.65 (m, 0.05H, C=CH<sub>2</sub>), 2.91-2.86 (m, 0.1H, Ar(CN)CH<sub>2</sub>).

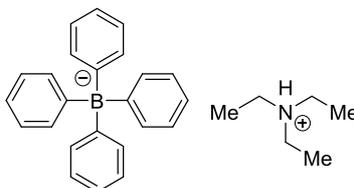
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 168.4 (C=N), 156.6 (C=O), 143.6 (C=CH<sub>2</sub>), 133.0 (ArC), 131.1, 128.8, 127.4 (3 × ArCH), 111.2 (C=CH<sub>2</sub>), 34.3 (Ar(CN)CH<sub>2</sub>), 27.4 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 22.2 (CH<sub>3</sub>C=CH<sub>2</sub>). *No signals corresponding to the perfluorobenzoyl ester moiety were observed due to the anticipated weak intensity of these signals.*

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): *Signals for the major isomer:* -137.0 (2F), -147.3 (1F), -159.6 (2F). *Signals for the minor isomer:* -137.2 (0.1F), -147.9 (0.05F), -160.0 (0.1F).

**FTIR:** 1753, 1652, 1496, 1321, 1192 cm<sup>-1</sup>.

**MS:** (Cl<sup>+</sup>) Found [M+H]<sup>+</sup>: 384.1037, C<sub>19</sub>H<sub>15</sub>F<sub>5</sub>NO<sub>2</sub> requires 384.1023.

#### Triethylammonium tetraphenylborate



**General Procedure D:** Sodium tetraphenylborate (3.66 g, 10.70 mmol), 34 mL H<sub>2</sub>O:MeOH (1:1) and Et<sub>3</sub>N (16.10 mmol) were employed. The precipitate was filtered and washed with H<sub>2</sub>O (50 mL) to afford the title compound (4.00 g, 89%) as a colorless solid.

**M.P.:** 195-198 °C (MeOH:H<sub>2</sub>O). [Lit.: 197-198 °C (MeOH:H<sub>2</sub>O)]

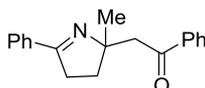
**<sup>1</sup>H NMR** (400 MHz, d<sub>6</sub>-acetone): 7.37-7.30 (m, 8H, ArH), 6.92 (t, *J* = 7.5 Hz, 8H, ArH), 6.80-6.74 (m, 4H, ArH), 3.43 (q, *J* = 7.5 Hz, 6H, (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>)), 1.39 (t, *J* = 7.5 Hz, 9H, (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>)).

**<sup>13</sup>C NMR** (125 MHz, d<sub>6</sub>-acetone): 165.0 (q, *J* = 50.0 Hz, B-C), 137.1-137.0 (m, ArCH), 126.0 (q, *J* = 2.0 Hz, ArCH), 122.3 (ArCH), 47.9 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 9.5 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

**<sup>11</sup>B NMR** (128 MHz, d<sub>6</sub>-acetone): -7.5.

The spectroscopic properties of this compound were consistent with the data in the literature.<sup>3</sup>

### 2-(2-Methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (10a)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and triethylammonium tetraphenylborate (60.5 mg, 0.143 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 7 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 6:1 to 4:1) afforded imine **10a** (22.5 mg, 62%) as a pale yellow oil.

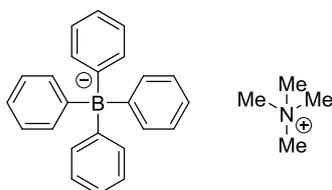
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.03-7.96 (m, 2H, ArH), 7.79-7.73 (m, 2H, ArH), 7.57-7.34 (m, 6H, ArH), 3.51 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.28 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.13-2.97 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.32-2.22 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.12-2.02 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.45 ((NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 199.2 (C=O), 170.9 (C=N), 137.9, 134.5 (2 × ArC), 132.8, 130.3, 128.4 (2 signals), 128.3, 127.7 (6 × ArCH), 75.2 (quaternary C), 49.1 ((CO)CH<sub>2</sub>), 35.5 (Ar(CN)CH<sub>2</sub>), 34.2 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.5 ((NC)CH<sub>3</sub>).

**FTIR**: 1682, 1447, 1351, 1338, 1192 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 278.1544, C<sub>19</sub>H<sub>20</sub>NO requires 278.1539.

## Tetramethylammonium tetraphenylborate



To a solution of sodium tetraphenylborate (0.27 g, 0.80 mmol) in CH<sub>3</sub>CN (80 mL) was added Me<sub>4</sub>NCl (0.09 g, 0.80 mmol) in CH<sub>3</sub>CN (80 mL). The reaction was stirred at room temperature for 1 hour 30 minutes. The reaction was concentrated *in vacuo* to afford the title compound (0.30 g, 95%) as a colorless solid.

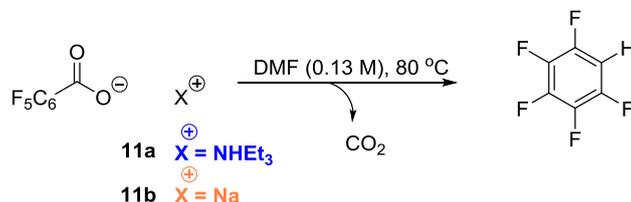
**M.P.** : > 220 °C (CH<sub>3</sub>CN:H<sub>2</sub>O). [Lit. 368-370 °C (CH<sub>3</sub>CN:H<sub>2</sub>O)].

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>CN): 7.29-7.22 (m, 8H, ArH), 6.98 (t, *J* = 7.5 Hz, 8H, ArH), 6.83 (t, *J* = 7.5 Hz, 4H, ArH), 3.01 (s, 12H, CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>CN): 136.7, 126.6, 122.8 (3 × ArCH), 56.2 (CH<sub>3</sub>). No C-B signal was observed due to quadrupolar relaxation.

The spectroscopic properties of this compound were consistent with the data in the literature.<sup>4</sup>

## Decarboxylation Experiments



Data for pentafluorobenzene:

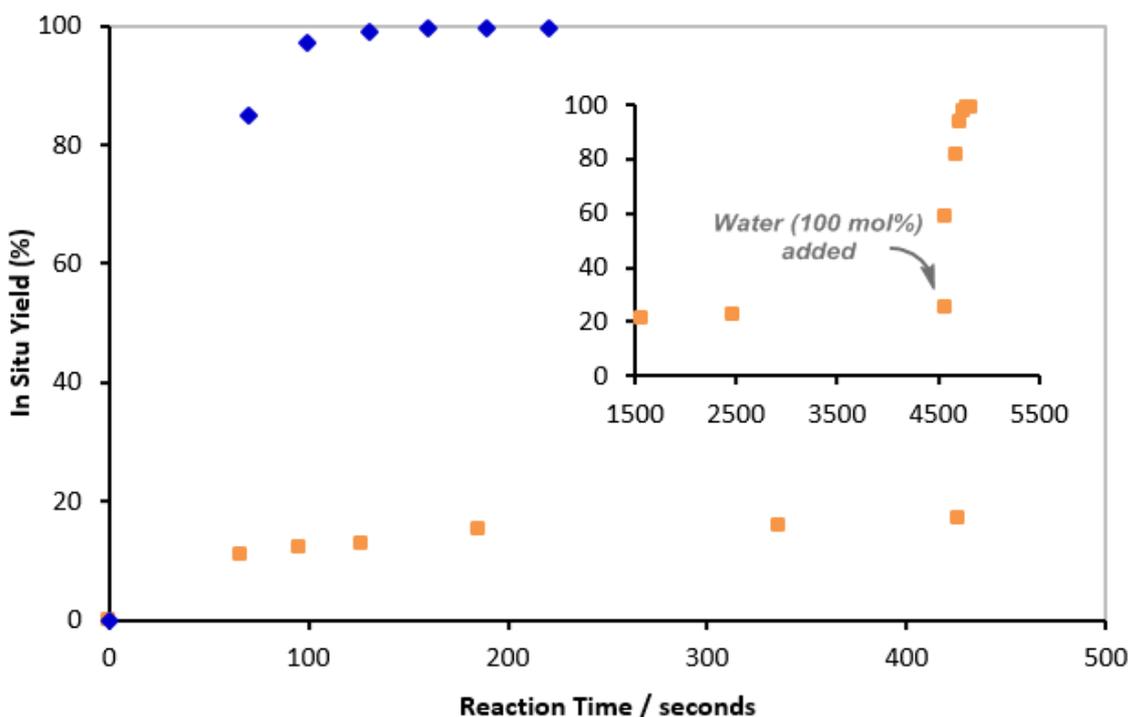
**<sup>1</sup>H NMR** (400 MHz, d<sub>7</sub>-DMF): 7.86-7.73 (m, 1H, H).

**<sup>19</sup>F NMR** (376 MHz, d<sub>7</sub>-DMF): -139.8 (2F), -155.8 (1F), -163.6 (2F).

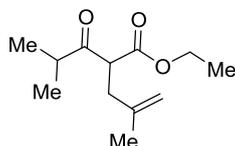
**Decarboxylation of 11a:** An oven-dried schlenk flask was purged with nitrogen and charged with pentafluorobenzoic acid (59.6 mg, 0.28 mmol). Anhydrous DMF (2.0 mL) and anhydrous Et<sub>3</sub>N (39 μl, 0.28 mmol) was added *via* syringe. A portion of this solution (0.5 mL) was transferred under nitrogen to a Young's tap NMR tube containing powdered 4 Å molecular sieves (20 mg). The reaction was then immediately placed in the NMR machine which was preheated to 80 °C and the reaction was monitored by <sup>19</sup>F NMR.

**Decarboxylation of 11b:** An oven-dried schlenk flask was purged with nitrogen and charged with NaH (56.0 mg, 1.40 mmol, 60% dispersion in mineral oil). The solid was washed with anhydrous hexane (2 × 1.5 mL) *via* syringe. The schlenk was placed under vacuum for 1 hour

to remove any residual hexane. Pentafluorobenzoic acid (298 mg, 1.40 mmol) was added followed by anhydrous DMF (10.0 mL). After approximately 3 minutes gas evolution ceased and a portion of the solution (0.5 mL) was transferred under nitrogen to a Young's tap NMR tube containing powdered 4 Å molecular sieves (20 mg). The reaction was then immediately placed in the NMR machine which was preheated to 80 °C and the reaction was monitored by <sup>19</sup>F NMR. After 4500 seconds, H<sub>2</sub>O (5 μl, 100 mol%) was added to the NMR tube and returned immediately to the NMR machine. The results from this experiment suggest that under "anhydrous" conditions, protodecarboxylation of **11b** is promoted by adventitious water.



### Ethyl 2-isobutyryl-4-methylpent-4-enoate



**General Procedure A: Part A:** Ethyl 4-methyl-3-oxopentanoate (4.80 mL, 30.00 mmol) and 3-chloro-2-methylprop-1-ene (3.30 mL, 33.30 mmol) were employed. FCC (toluene:EtOAc 4:1) afforded the title compound (4.02 g, 63%) as a colorless oil.

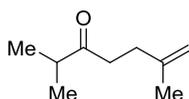
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 4.80-4.76 (m, 1H, C=CH<sub>2</sub>), 4.73-4.68 (m, 1H, C=CH<sub>2</sub>), 4.17 (q, *J* = 7.0 Hz, 2H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 3.84 (dd, *J* = 7.0 and 7.0 Hz, 1H, (CO)CH(CO)), 2.79 (sept. *J* = 7.0 Hz, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), 2.61-2.48 (m, 2H, (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 1.74 (s, 3H, CH<sub>3</sub>C=CH<sub>2</sub>), 1.25 (t, *J* = 7.0 Hz, 3H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 1.11 (d, *J* = 7.0 Hz, 3H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.10 (d, *J* = 7.0 Hz, 3H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 208.4 ((CH<sub>3</sub>)<sub>2</sub>CH(C=O)), 169.4 ((C=O)OCH<sub>2</sub>CH<sub>3</sub>), 142.0 (C=CH<sub>2</sub>), 112.3 (C=C<sub>H</sub>), 61.3 ((CO)OCH<sub>2</sub>CH<sub>3</sub>), 55.6 (CO)CH(CO)), 40.5 (CH<sub>3</sub>)<sub>2</sub>CH), 35.9 ((CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 22.5 CH<sub>3</sub>C=CH<sub>2</sub>), 18.4, 18.1 (CH<sub>3</sub>)<sub>2</sub>CH), 14.1 ((CO)OCH<sub>2</sub>CH<sub>3</sub>).

**FTIR**: 2973, 1740, 1713, 1466, 1447, 1245, 1155 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 235.1301, C<sub>12</sub>H<sub>20</sub>NaO<sub>3</sub> requires 235.1305.

### 2,6-Dimethylhept-6-en-3-one



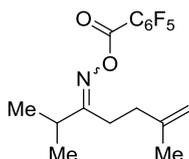
**General Procedure A: Part B:** Ethyl 2-isobutyryl-4-methylpent-4-enoate (2.50 g, 11.80 mmol) was employed. FCC (pentane:Et<sub>2</sub>O 25:1) afforded the title compound (1.20 g, 74%) as a colorless oil. *N.B. Concentration in vacuo should be performed using an ice bath due to the volatility of the product.*

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 4.76-4.64 (m, 2H, C=CH<sub>2</sub>), 2.69-2.56 (m, 3H, (CO)CH<sub>2</sub>) and (CH<sub>3</sub>)<sub>2</sub>CH), 2.27 (t, *J* = 7.5 Hz, 2H, (CO)CH<sub>2</sub>CH<sub>2</sub>), 1.74 (s, 3H, CH<sub>3</sub>C=CH<sub>2</sub>), 1.11 (d, *J* = 7.0 Hz, 6H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 214.1 (C=O), 144.8 (C=CH<sub>2</sub>), 109.9 (C=C<sub>H</sub>), 40.8 (CH<sub>3</sub>)<sub>2</sub>CH), 38.5 ((CO)CH<sub>2</sub>), 31.4 ((CO)CH<sub>2</sub>CH<sub>2</sub>), 22.7 CH<sub>3</sub>C=CH<sub>2</sub>), 18.3 (CH<sub>3</sub>)<sub>2</sub>CH).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>5</sup>

### 2,6-Dimethylhept-6-en-3-one-*O*-perfluorobenzoyl oxime (6b)



**General Procedure B: Part A:** 2,6-Dimethylhept-6-en-3-one (1.20 g, 8.50 mmol) was employed. The reaction was heated to 75 °C for 3 hours. FCC (pentane:Et<sub>2</sub>O 10:1) afforded the corresponding oxime (1.07 g, 81%, 1:0.2 mixture of oxime isomers). **Part B:** The corresponding oxime (1.06 g, 6.84 mmol) was employed and the reaction was left stirring for 16 hours. FCC (hexane:EtOAc 30:1) afforded oxime ester **6b** (2.03 g, 85%, 1:0.2 mixture of oxime isomers) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Signals for both isomers:* 4.76-4.64 (m, 2.4H, maj. and min. C=CH<sub>2</sub>), 3.35 (sept. *J* = 7.0 Hz, 0.2H, min. (CH<sub>3</sub>)<sub>2</sub>CH), 2.76 (sept. *J* = 7.0 Hz, 1H, maj. (CH<sub>3</sub>)<sub>2</sub>CH), 2.54-2.44 (m, 2.4H, maj. and min. (CN)CH<sub>2</sub>), 2.40-2.31 (m, 0.4H, min. (CN)CH<sub>2</sub>CH<sub>2</sub>), 2.23 (t, *J* = 7.5 Hz, 2H, maj. (CN)CH<sub>2</sub>CH<sub>2</sub>), 1.76 (s, 0.6H, min. CH<sub>3</sub>C=CH<sub>2</sub>), 1.72 (s, 3H, maj. CH<sub>3</sub>C=CH<sub>2</sub>), 1.21 (d, *J* = 7.0 Hz, 6H, maj. (CH<sub>3</sub>)<sub>2</sub>CH), 1.14 (d, *J* = 7.0 Hz, 1.2H, min. (CH<sub>3</sub>)<sub>2</sub>CH).

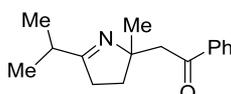
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): Signals for the major isomer only: 175.3 (C=N), 144.0 (C=CH<sub>2</sub>), 110.9 (C=CH<sub>2</sub>), 34.2, 34.1 ((CN)CH<sub>2</sub>CH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CH), 26.9 ((CN)CH<sub>2</sub>), 22.1 (CH<sub>3</sub>C=CH<sub>2</sub>), 19.7 (CH<sub>3</sub>)<sub>2</sub>CH). No signals corresponding to the perfluorobenzoyl ester moiety were observed due to the anticipated weak intensity of these signals.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): Signals for both isomers: -137.4 (2.4F), -148.1 (1.2F), -160.0 (2.4F).

**FTIR**: 1757, 1651, 1495, 1324, 1193, 995 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 372.1002, C<sub>16</sub>H<sub>16</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 372.0993.

### 2-(5-Isopropyl-2-methyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (10b)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.6 mg, 7.2×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (19.2 mg, 0.029 mmol) oxime ester **6b** (50.0 mg, 0.143 mmol) and triethylammonium tetraphenylborate (66.0 mg, 0.157 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.6 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 8:1 to 2:1) afforded imine **10b** (21.0 mg, 61%) as a colorless oil.

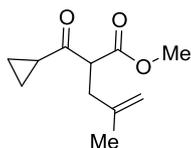
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.00-7.95 (m, 2H, ArH), 7.56-7.50 (m, 1H, ArH), 7.47-7.40 (m, 2H, ArH), 3.31 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.22 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 2.62-2.46 (m, 3H, Ar(CN)CH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CH), 2.16-2.04 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.88-1.78 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.34 (s, 3H, (NC)CH<sub>3</sub>), 1.03 (d, *J* = 7.0 Hz, 6H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.5 (C=O), 180.7 (C=N), 137.9 (ArC), 132.8, 128.5, 128.4 (3 × ArCH), 74.2 (quaternary C), 48.9 ((CO)CH<sub>2</sub>), 34.7 (Ar(CN)CH<sub>2</sub>), 33.6 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 32.5 ((CH<sub>3</sub>)<sub>2</sub>CH), 27.9 ((NC)CH<sub>3</sub>), 20.0 ((CH<sub>3</sub>)<sub>2</sub>CH).

**FTIR**: 2964, 2929, 1639, 1673, 1448 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 244.1691, C<sub>16</sub>H<sub>22</sub>NO requires 244.1696.

### Methyl 2-(cyclopropanecarbonyl)-4-methylpent-4-enoate



**General Procedure A: Part A:** Methyl 3-cyclopropyl-3-oxopropanoate (1.50 g, 10.60 mmol) and 3-chloro-2-methylprop-1-ene (1.14 mL, 11.60 mmol) were employed. FCC (hexane:EtOAc 20:1) afforded the title compound (1.01 g, 48%) as a colorless oil.

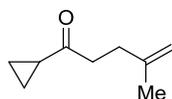
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 4.80-4.76 (m, 1H, C=CH<sub>2</sub>), 4.73-4.69 (m, 1H, C=CH<sub>2</sub>), 3.84 (t, *J* = 7.5 Hz, 1H, (CO)CH(CO)), 3.74 (s, 3H, CH<sub>3</sub>C=CH<sub>2</sub>), 2.68-2.56 (m, 2H, (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 2.13-2.04 (m, 1H, (CH<sub>2</sub>)<sub>2</sub>CH), 1.75 (s, 3H, (CO)OCH<sub>3</sub>), 1.11-1.02 (m, 2H, (CH<sub>2</sub>)<sub>2</sub>CH), 0.97-0.90 (m, 2H, (CH<sub>2</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 204.6 ((CH<sub>2</sub>)<sub>2</sub>CH(C=O)), 170.0 ((C=O)OCH<sub>3</sub>), 141.9 (C=CH<sub>2</sub>), 112.1 (C=CH<sub>2</sub>), 58.3 (CO)CH(CO)), 52.4 ((CO)OCH<sub>3</sub>), 35.8 ((CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 22.5 CH<sub>3</sub>C=CH<sub>2</sub>), 19.7 (CH<sub>2</sub>)<sub>2</sub>CH), 11.9, 11.7 (CH<sub>2</sub>)<sub>2</sub>CH).

**FTIR:** 1739, 1700, 1381, 1159 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 219.1000, C<sub>11</sub>H<sub>16</sub>NaO<sub>3</sub> requires 219.0992.

### 1-Cyclopropyl-4-methylpent-4-en-1-one



**General Procedure A: Part B:** Methyl 2-(cyclopropanecarbonyl)-4-methylpent-4-enoate (0.92 g, 4.72 mmol) was employed. FCC (hexane:EtOAc 5:1) afforded the title compound (0.34 g, 52%) as a colorless oil. *N.B. Concentration in vacuo should be performed using an ice bath due to the volatility of the product, therefore pentane:Et<sub>2</sub>O solvent system should be used for FCC.*

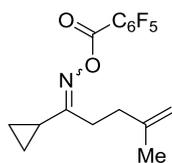
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 4.76-4.72 (m, 1H, C=CH<sub>2</sub>), 4.70-4.66 (m, 1H, C=CH<sub>2</sub>), 2.74-2.67 (m, 2H, (CO)CH<sub>2</sub>), 2.32 (t, *J* = 7.5 Hz, 2H, (CO)CH<sub>2</sub>CH<sub>2</sub>), 1.99-1.89 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.75 (s, 3H, CH<sub>3</sub>C=CH<sub>2</sub>), 1.06-0.99 (m, 2H, (CH<sub>2</sub>)<sub>2</sub>CH), 0.91-0.83 (m, 2H, (CH<sub>2</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 210.4 (C=O), 144.6 (C=CH<sub>2</sub>), 110.0 (C=CH<sub>2</sub>), 41.7 ((CO)CH<sub>2</sub>), 31.6 ((CO)CH<sub>2</sub>CH<sub>2</sub>), 22.6 (CH<sub>3</sub>C=CH<sub>2</sub>), 20.4 (CH<sub>2</sub>)<sub>2</sub>CH), 10.6 (CH<sub>2</sub>)<sub>2</sub>CH).

**FTIR:** 1698, 1445, 1386 cm<sup>-1</sup>.

**MS:** (CI<sup>+</sup>) Found [M+H]<sup>+</sup>: 139.1127, C<sub>9</sub>H<sub>15</sub>O requires 139.1123.

#### 4-Methyl-1-(naphthalene-2-yl)pent-4-en-1-one-O-perfluorobenzoyl oxime (**6c**)



**General Procedure B: Part A:** 1-Cyclopropyl-4-methylpent-4-en-1-one (0.32 g, 2.32 mmol) was employed. The reaction was heated to 75 °C for 16 hours. FCC (hexane:Et<sub>2</sub>O 4:1 to 1:1) afforded the corresponding oxime (0.27 g, 75%, 1:0.5 mixture of oxime isomers) as a colorless oil. **Part B:** The corresponding oxime (0.27 g, 1.76 mmol) was employed and the reaction was left stirring for 16 hours. FCC (hexane:EtOAc 10:1) afforded oxime ester **6c** (0.50 g, 82%, 1:0.5 mixture of oxime isomers) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Signals for both isomers:* 4.81-4.67 (m, 3H, maj. and min. C=CH<sub>2</sub>), 2.46-2.39 (m, 2H, maj. (CN)CH<sub>2</sub>), 2.36-2.23 (m, 3.5H, min. (CH<sub>2</sub>)<sub>2</sub>CH and maj. and min. (CN)CH<sub>2</sub>CH<sub>2</sub>), 2.15-2.08 (m, 1H, min. (CN)CH<sub>2</sub>), 1.77-1.68 (m, 5.5H, maj. and min. CH<sub>3</sub>C=CH<sub>2</sub> and maj. (CH<sub>2</sub>)<sub>2</sub>CH), 1.06-0.83 (m, 6H, maj. and min. (CH<sub>2</sub>)<sub>2</sub>CH).

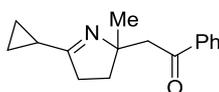
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): *Signals for both isomers:* 173.0, 171.6 (2 × C=N), 144.2, 143.8 (2 × C=CH<sub>2</sub>), 111.0, 110.6 (2 × C=CH<sub>2</sub>), 34.6, 34.1 (2 × (CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6, 27.4 (2 × (CN)CH<sub>2</sub>), 22.5, 22.2 (2 × CH<sub>3</sub>C=CH<sub>2</sub>), 14.2, 10.2 (2 × (CH<sub>2</sub>)<sub>2</sub>CH), 6.8, 6.6 (2 × (CH<sub>2</sub>)<sub>2</sub>CH). *No signals corresponding to the perfluorobenzoyl ester moiety were observed due to the anticipated weak intensity of these signals.*

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): *Signals for both isomers:* -137.3 (3F), -148.0 (1.5F), -159.9 (3F).

**FTIR:** 2972, 1756, 1523, 1495, 1324, 1197 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 370.0834, C<sub>16</sub>H<sub>14</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 370.0837.

#### 2-(5-Cyclopropyl-2-methyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (**10c**)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.6 mg, 7.2×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (19.3 mg, 0.029 mmol) oxime ester **6c** (50.0 mg, 0.144 mmol) and triethylammonium tetraphenylborate (66.0 mg, 0.158 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.6 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (× 2; 1<sup>st</sup> column hexane:EtOAc 8:1 to 1:1; 2<sup>nd</sup> column EtOAc to EtOAc:MeOH 1:1) afforded imine **10c** (21.0 mg, 60%) as a colorless oil.

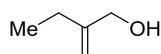
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.99-7.93 (m, 2H, ArH), 7.54 (tt, *J* = 7.5 and 1.0 Hz, 1H, ArH), 7.48-7.41 (m, 2H, ArH), 7.35 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.16 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 2.49-2.32 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.12-2.02 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.90-1.80 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.74-1.64 (m, 1H, (CH<sub>2</sub>)<sub>2</sub>CH), 1.33 (s, 3H, (NC)CH<sub>3</sub>), 0.83-0.66 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.4 (C=O), 177.3 (C=N), 137.9 (ArC), 132.8, 128.4, 128.3 (3 × ArCH), 74.2 (quaternary C), 49.0 ((CO)CH<sub>2</sub>), 34.8 (Ar(CN)CH<sub>2</sub>), 33.6 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6 ((NC)CH<sub>3</sub>), 14.1 (CH<sub>2</sub>)<sub>2</sub>CH, 7.1, 7.0 (CH<sub>2</sub>)<sub>2</sub>CH.

**FTIR**: 2969, 2923, 1690, 1630, 1449 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 242.1534, C<sub>16</sub>H<sub>20</sub>NO requires 242.1539.

### 3-Methylenebutan-1-ol



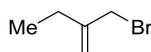
**General Procedure F**: 2-Methylenebutanal (2.50 g, 29.70 mmol) was employed. The reaction was stirred at 0 °C for 30 minutes. FCC (pentane:Et<sub>2</sub>O 10:1 to 1:1) afforded the corresponding aldehyde (2.04 g, 80%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 5.03-4.99 (m, 1H, C=CH<sub>2</sub>), 4.90-4.85 (m, 1H, C=CH<sub>2</sub>), 4.09 (s, 2H, CH<sub>2</sub>OH), 2.09 (q, *J* = 7.5 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>) 1.08 (t, *J* = 7.5 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 150.7 (C=CH<sub>2</sub>), 108.0 (C=CH<sub>2</sub>), 66.0 (CH<sub>2</sub>OH), 25.7 (CH<sub>2</sub>CH<sub>3</sub>), 12.1 (CH<sub>2</sub>CH<sub>3</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>6</sup>

### 2-(Bromomethyl)but-1-ene



**General Procedure G**: 3-Methylenebutan-1-ol (2.00 g, 23.20 mmol) was employed to afford bromide (1.05 g, 31%) as a colorless oil. *N.B. Due to the volatility of the title compound concentration in vacuo should be performed in an ice bath.*

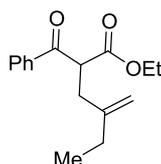
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 5.17 (s, 1H, C=CH<sub>2</sub>), 4.98 (s, 1H, C=CH<sub>2</sub>), 4.00 (s, 2H, CH<sub>2</sub>Br), 2.25 (q, *J* = 7.5 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.09 (t, *J* = 7.5 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 147.1 (C=CH<sub>2</sub>), 113.8 (C=CH<sub>2</sub>), 36.9 (CH<sub>2</sub>Br), 26.2 (CH<sub>2</sub>CH<sub>3</sub>), 11.9 (CH<sub>2</sub>CH<sub>3</sub>).

**FTIR**: 2959, 1195 cm<sup>-1</sup>.

*Mass spectrometry data was not obtained using either EI, CI and ESI techniques due to high volatility of this bromide.*

### Ethyl 2-benzoyl-4-methylenehexanoate



**General Procedure A: Part A:** Ethyl benzoylacetate (1.07 mL, 6.20 mmol) and 2-(bromomethyl)but-1-ene (1.00 g, 6.80 mmol) were employed. FCC (hexane:EtOAc 30:1) afforded the title compound (1.52 g, 94%) as a colorless oil.

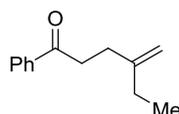
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.05-7.99 (m, 2H, ArH), 7.62-7.45 (m, 3H, ArH), 4.81-4.77 (m, 1H, C=CH<sub>2</sub>), 4.75-4.71 (m, 1H, C=CH<sub>2</sub>), 4.57 (dd, *J* = 8.0 and 8.0 Hz, 1H, (CO)CH(CO)), 4.15 (q, *J* = 7.0 Hz, 2H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 2.83-2.67 (m, 2H, (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 2.16-1.99 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>), 1.18 (t, *J* = 7.0 Hz, 3H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 1.04 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 194.7 (Ar(C=O)), 169.5 ((C=O)OCH<sub>2</sub>CH<sub>3</sub>), 147.7 (C=CH<sub>2</sub>), 136.2 (ArC), 133.4, 128.7, 128.6 (3 × ArCH), 109.6 (C=CH<sub>2</sub>), 61.4 ((CO)OCH<sub>2</sub>CH<sub>3</sub>), 52.8 (CO)CH(CO), 34.9 ((CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 29.0 (CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>), 14.0 (CO)OCH<sub>2</sub>CH<sub>3</sub>, 12.2 (CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>).

**FTIR:** 2967, 1733, 1685, 1447 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 283.1296, C<sub>16</sub>H<sub>20</sub>NaO<sub>3</sub> requires 283.1305.

### 4-Methylene-1-phenylhexan-1-one



**General Procedure A: Part B:** Ethyl 2-benzoyl-4-methylenehexanoate (1.50 g, 5.77 mmol) was employed. FCC (hexane:EtOAc 15:1) afforded the title compound (1.00 g, 92%) as a colorless oil.

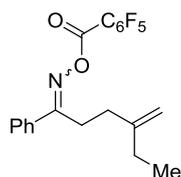
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.01-7.95 (m, 2H, ArH), 7.60-7.44 (m, 3H, ArH), 4.80-4.73 (m, 2H, C=CH<sub>2</sub>), 3.16-3.10 (m, 2H, Ar(CO)CH<sub>2</sub>), 2.48 (t, *J* = 7.5 Hz, 2H, Ar(CO)CH<sub>2</sub>CH<sub>2</sub>), 2.11 (q, *J* = 7.5 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>), 1.07 (t, *J* = 7.5 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.8 (C=O), 150.3 (C=CH<sub>2</sub>), 137.0 (ArC), 133.0, 128.6, 128.0 (3 × ArCH), 107.9 (C=CH<sub>2</sub>), 37.0 (Ar(CO)CH<sub>2</sub>), 30.3 (Ar(CO)CH<sub>2</sub>CH<sub>2</sub>), 29.1 (CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>), 12.3 (CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>).

**FTIR:** 2966, 1685, 1448, 1203 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 211.1080, C<sub>13</sub>H<sub>16</sub>NaO requires 211.1093.

#### 4-Methylene-1-phenylhexan-1-one-*O*-perfluorobenzoyl oxime (**6d**)



**General Procedure B: Part A:** 4-Methylene-1-phenylhexan-1-one (1.00 g, 5.32 mmol) was employed. The reaction was heated to 75 °C for 10 hours. FCC (hexane:EtOAc 15:1) afforded the corresponding oxime (0.98 g, 91%) as a colorless oil.

*Data for the intermediate oxime:*

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.66-7.57 (m, 2H, ArH), 7.46-7.36 (m, 3H, ArH), 4.79 (s, 2H, C=CH<sub>2</sub>), 3.01-2.92 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.29 (t, *J* = 7.5 Hz, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.10 (q, *J* = 7.5 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>), 1.04 (t, *J* = 7.5 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 159.6 (C=N), 150.5 (C=CH<sub>2</sub>), 135.5 (ArC), 129.2, 128.6, 126.3 (3 × ArCH), 108.1 (C=CH<sub>2</sub>), 32.4 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 28.8 (CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>), 25.0 (Ar(CN)CH<sub>2</sub>), 12.3 (CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>).

**FTIR:** 3229, 2965, 1646, 1462, 1436 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 204.1380, C<sub>13</sub>H<sub>18</sub>NO requires 204.1383.

**General Procedure B: Part B:** The corresponding oxime (0.45 g, 2.20 mmol) was employed and the reaction was left stirring for 16 hours. FCC (hexane:EtOAc 15:1) afforded oxime ester **6d** (0.65 g, 74%) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.79-7.72 (m, 2H, ArH), 7.54-7.41 (m, 3H, ArH), 4.81-4.73 (m, 2H, C=CH<sub>2</sub>), 3.08-3.00 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.29 (t, *J* = 8.0 Hz, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.03 (q, *J* = 7.5 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>), 1.00 (t, *J* = 7.5 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>).

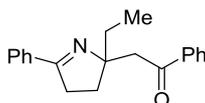
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 168.5 (C=N), 149.3 (C=CH<sub>2</sub>), 133.1 (ArC), 131.1, 128.8, 127.4 (3 × ArCH), 108.9 (C=CH<sub>2</sub>), 32.8 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 28.6 (CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>), 27.6 (Ar(CN)CH<sub>2</sub>), 12.1 (CH<sub>3</sub>CH<sub>2</sub>C=CH<sub>2</sub>). *No signals corresponding to the perfluorobenzoyl ester moiety were observed due to the anticipated weak intensity of these signals.*

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -137.0 (2F), -147.4 (1F), -159.7 (2F).

**FTIR:** 2971, 1768, 1651, 1495, 1325, 1193 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 420.0991, C<sub>20</sub>H<sub>16</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 420.0993.

## 2-(2-Ethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (10d)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (5.8 mg, 6.3×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.0 mg, 0.025 mmol) oxime ester **6d** (50.0 mg, 0.126 mmol) and triethylammonium tetraphenylborate (69.0 mg, 0.164 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 10:1 to 7:1) afforded imine **10d** (23.0 mg, 63%) as a colorless oil.

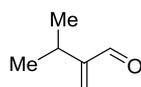
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.01-7.95 (m, 2H, ArH), 7.76-7.68 (m, 2H, ArH), 7.51-7.48 (m, 1H, ArH), 7.45-7.32 (m, 5H, ArH), 3.42 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.36 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.09-2.93 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.29-2.19 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.14-2.04 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.88 (q, *J* = 7.5 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 0.91 (t, *J* = 7.5 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.6 (C=O), 171.5 (C=N), 138.0, 134.3 (2 × ArC), 132.7, 130.4, 128.4, 128.3 (2 signals), 127.8 (6 × ArCH), 78.7 (quaternary C), 47.8 ((CO)CH<sub>2</sub>), 36.3 (Ar(CN)CH<sub>2</sub>), 33.6 (CH<sub>2</sub>CH<sub>3</sub>), 30.5 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 8.4 (CH<sub>2</sub>CH<sub>3</sub>).

**FTIR**: 2964, 1672, 1684 1447 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 292.1698, C<sub>20</sub>H<sub>22</sub>NO requires 292.1696.

## 3-Methyl-2-methylenebutanal



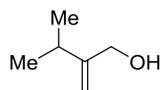
**General Procedure E**: Isovaleraldehyde (12.80 mL, 120.00 mmol) was employed. The reaction was heated to 45 °C for 20 hours. FCC (pentane:Et<sub>2</sub>O 19:1) afforded the corresponding aldehyde (4.70 g, 40%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 9.54 (s, 1H, (CO)H), 6.25 (d, *J* = 1.0 Hz, 1H, C=CH<sub>2</sub>), 5.95 (s, 1H, C=CH<sub>2</sub>), 2.81 (sept. d, *J* = 7.0 and 1.0 Hz, ((CH<sub>3</sub>)<sub>2</sub>CH), 1.09 (d, *J* = 7.0 Hz, 6H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 194.6 (C=O), 156.5 (C=CH<sub>2</sub>), 132.1 (C=CH<sub>2</sub>), 26.1 ((CH<sub>3</sub>)<sub>2</sub>CH), 21.3 ((CH<sub>3</sub>)<sub>2</sub>CH).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>7</sup>

### 3-Methyl-2-methylenebutan-1-ol



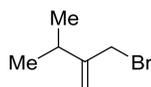
**General Procedure F:** 3-Methyl-2-methylenebutanal (2.00 g, 20.40 mmol) was employed. The reaction was stirred at 0 °C for 30 minutes. FCC (pentane:Et<sub>2</sub>O 1:1) afforded the corresponding aldehyde (1.75 g, 86%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 5.02-4.99 (m, 1H, C=CH<sub>2</sub>), 4.91-4.88 (m, 1H, C=CH<sub>2</sub>), 4.13 (s, 2H, CH<sub>2</sub>OH), 2.33 (sept. *J* = 7.0 Hz, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.07 (d, *J* = 7.0 Hz, 6H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 155.2 (C=CH<sub>2</sub>), 106.9 (C=CH<sub>2</sub>), 54.9 (CH<sub>2</sub>OH), 31.0 ((CH<sub>3</sub>)<sub>2</sub>CH), 21.8 ((CH<sub>3</sub>)<sub>2</sub>CH).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>8</sup>

### 2-(Bromomethyl)-3-methylbut-1-ene



**General Procedure G:** 3-Methyl-2-methylenebutan-1-ol (1.75 g, 17.50 mmol) was employed to afford bromide (1.86 g, 78%) as a pale yellow oil.

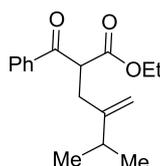
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 5.17 (s, 1H, C=CH<sub>2</sub>), 5.01 (s, 1H, C=CH<sub>2</sub>), 4.04 (s, 2H, CH<sub>2</sub>Br), 2.57 (sept. *J* = 7.0 Hz, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.11 (d, *J* = 7.0 Hz, 6H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 151.6 (C=CH<sub>2</sub>), 113.1 (C=CH<sub>2</sub>), 36.3 (CH<sub>2</sub>Br), 30.9 ((CH<sub>3</sub>)<sub>2</sub>CH), 21.7 ((CH<sub>3</sub>)<sub>2</sub>CH).

**FTIR:** 2962, 1209 cm<sup>-1</sup>.

*Mass spectrometry data was not obtained using either EI, CI and ESI techniques due to high volatility of this bromide.*

### Ethyl 2-benzoyl-5-methyl-4-methylenehexanoate



**General Procedure A: Part A:** Ethyl benzoylacetate (1.70 mL, 9.80 mmol) and 2-(bromomethyl)-3-methylbut-1-ene (1.75 g, 10.80 mmol) were employed. FCC (hexane:EtOAc 25:1) afforded the title compound (2.58 g, 96%) as a colorless oil.

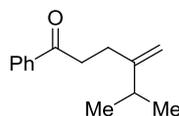
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.05-8.00 (m, 2H, ArH), 7.62-7.45 (m, 3H, ArH), 4.81 (s, 1H, C=CH<sub>2</sub>), 4.69 (s, 1H, C=CH<sub>2</sub>), 4.60 (dd, *J* = 7.5 and 7.5 Hz, 1H, (CO)CH(CO)), 4.15 (q, *J* = 7.0 Hz, 2H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 2.83-2.70 (m, 2H, (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 2.28 (sept. *J* = 7.0 Hz, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.18 (t, *J* = 7.0 Hz, 3H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 1.06 (d, *J* = 7.0 Hz, 3H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.04 (d, *J* = 7.0 Hz, 3H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 194.8 (Ar(C=O)), 169.5 ((C=O)OCH<sub>2</sub>CH<sub>3</sub>), 152.3 (C=CH<sub>2</sub>), 136.2 (ArC), 133.5, 128.7, 128.6 (3 × ArCH), 108.0 (C=CH<sub>2</sub>), 61.4 ((CO)OCH<sub>2</sub>CH<sub>3</sub>), 52.9 (CO)CH(CO), 34.1 ((CH<sub>3</sub>)<sub>2</sub>CH), 33.1 (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>, 21.7, 21.6 ((CH<sub>3</sub>)<sub>2</sub>CH), 14.0 ((CO)OCH<sub>2</sub>CH<sub>3</sub>).

**FTIR**: 2962, 1735, 1686, 1448 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 297.1460, C<sub>17</sub>H<sub>22</sub>NaO<sub>3</sub> requires 297.1461.

### 5-Methyl-4-methylene-1-phenylhexan-1-one



**General Procedure A: Part B:** Ethyl 2-benzoyl-5-methyl-4-methylenehexanoate (2.50 g, 9.10 mmol) was employed. FCC (hexane:EtOAc 30:1) afforded the title compound (1.56 g, 85%) as a colorless oil.

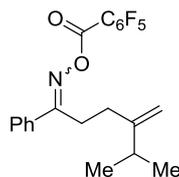
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.02-7.96 (m, 2H, ArH), 7.61-7.43 (m, 3H, ArH), 4.84-4.81 (m, 1H, C=CH<sub>2</sub>), 4.74-4.70 (m, 1H, C=CH<sub>2</sub>), 3.19-3.09 (m, 2H, (CO)CH<sub>2</sub>), 2.49 (t, *J* = 7.5 Hz, 2H, (CO)CH<sub>2</sub>CH<sub>2</sub>), 2.31 (sept. *J* = 7.0 Hz, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.08 (d, *J* = 7.0 Hz, 6H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.9 (C=O), 154.8 (C=CH<sub>2</sub>), 137.0 (ArC), 133.0, 128.6, 128.0 (3 × ArCH), 106.6 (C=CH<sub>2</sub>), 37.3 ((CO)CH<sub>2</sub>), 34.3 ((CH<sub>3</sub>)<sub>2</sub>CH), 28.3 ((CO)CH<sub>2</sub>CH<sub>2</sub>), 21.8 ((CH<sub>3</sub>)<sub>2</sub>CH).

**FTIR**: 2961, 1684, 1448 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 225.1257, C<sub>14</sub>H<sub>18</sub>NaO requires 225.1250.

### 5-Methyl-4-methylene-1-phenylhexan-1-one-*O*-perfluorobenzoyl oxime (6e)



**General Procedure B: Part A:** 5-Methyl-4-methylene-1-phenylhexan-1-one (1.56 g, 7.72 mmol) was employed. The reaction was heated to 75 °C for 10 hours. FCC (hexane:EtOAc 20:1 to 10:1) afforded the corresponding oxime (1.31 g, 79%) as a colorless oil.

Data for the intermediate oxime:

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.66-7.57 (m, 2H, ArH), 7.43-7.36 (m, 3H, ArH), 4.82 (s, 1H, C=CH<sub>2</sub>), 4.79 (s, 1H, C=CH<sub>2</sub>), 2.99-2.91 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.36-2.23 (m, 3H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CH), 1.03 (d, *J* = 7.0 Hz, 6H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 159.9 (C=N), 155.0 (C=CH<sub>2</sub>), 135.4 (ArC), 129.3, 128.6, 126.4 (3 × ArCH), 106.9 (C=CH<sub>2</sub>), 33.8 ((CH<sub>3</sub>)<sub>2</sub>CH), 30.5 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 25.3 (Ar(CN)CH<sub>2</sub>), 21.8 ((CH<sub>3</sub>)<sub>2</sub>CH).

**FTIR**: 3233, 1640, 1462 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 218.1540, C<sub>14</sub>H<sub>20</sub>NO requires 218.1539.

**General Procedure B: Part B**: The corresponding oxime (0.35 g, 1.61 mmol) was employed and the reaction was left stirring for 16 hours. FCC (hexane:EtOAc 15:1) afforded oxime ester **6e** (0.46 g, 70%) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.78-7.73 (m, 2H, ArH), 7.53-7.42 (m, 3H, ArH), 4.84-4.83 (m, 1H, C=CH<sub>2</sub>), 4.74-4.73 (m, 1H, C=CH<sub>2</sub>), 3.07-3.00 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.33-2.17 (m, 3H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CH), 0.98 (d, *J* = 7.0 Hz, 6H, (CH<sub>3</sub>)<sub>2</sub>CH).

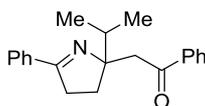
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 168.6 (C=N), 153.9 (C=CH<sub>2</sub>), 133.1 (ArC), 131.1, 128.8, 127.4 (3 × ArCH), 107.6 (C=CH<sub>2</sub>), 33.8 ((CH<sub>3</sub>)<sub>2</sub>CH), 30.8 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.9 (Ar(CN)CH<sub>2</sub>), 21.6 ((CH<sub>3</sub>)<sub>2</sub>CH). No signals corresponding to the perfluorobenzoyl ester moiety were observed due to the anticipated weak intensity of these signals.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -137.0 (2F), -147.4 (1F), -159.7 (2F).

**FTIR**: 2966, 2900, 1760, 1493, 1323, 1203 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 434.1144, C<sub>21</sub>H<sub>18</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 434.1150.

## 2-(2-Isopropyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (10e)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (5.6 mg, 6.1 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (16.5 mg, 0.024 mmol) oxime ester **6e** (50.0 mg, 0.121 mmol) and triethylammonium tetraphenylborate (57.0 mg, 0.133 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.45 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (×

2; 1<sup>st</sup> column hexane:EtOAc 10:1 ; 2<sup>nd</sup> column toluene:Et<sub>2</sub>O 40:1 to 30:1) afforded imine **10e** (21.5 mg, 58%) as a colorless oil.

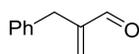
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.97-7.91 (m, 2H, ArH), 7.65-7.58 (m, 2H, ArH), 7.49-7.26 (m, 6H, ArCH), 3.56 (d, *J* = 14.0 Hz, 1H, (CO)CH<sub>2</sub>), 3.20 (d, *J* = 14.0 Hz, 1H, (CO)CH<sub>2</sub>), 3.02 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.29-2.16 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>CH), 2.10-1.96 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.05 (d, *J* = 7.0 Hz, 3H, (CH<sub>3</sub>)<sub>2</sub>CH), 0.90 (d, *J* = 7.0 Hz, 3H, (CH<sub>3</sub>)<sub>2</sub>CH).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 200.6 (C=O), 171.1 (C=N), 138.3, 134.5 (2 × ArC), 132.5, 130.1, 128.6, 128.2, 128.1, 127.6 (6 × ArCH), 82.3 (quaternary C), 46.2 ((CO)CH<sub>2</sub>), 37.2 ((CH<sub>3</sub>)<sub>2</sub>CH), 36.5 (Ar(CN)CH<sub>2</sub>), 27.6 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 17.7, 17.4 ((CH<sub>3</sub>)<sub>2</sub>CH).

**FTIR**: 2961, 1670, 1621, 1448, 1340 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 306.1838, C<sub>21</sub>H<sub>24</sub>NO requires 306.1853.

## 2-Benzylacrylaldehyde



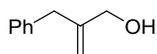
**General Procedure E**: 3-Phenylpropanal (13.10 mL, 100.00 mmol) was employed. The reaction was heated to 45 °C for 20 hours. FCC (hexane:EtOAc 30:1) afforded the corresponding aldehyde (10.30 g, 71%) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 9.58 (s, 1H, (CO)H), 7.34-7.11 (m, 5H, ArH), 6.11-6.03 (m, 2H, C=CH<sub>2</sub>), 3.56 (s, 2H, ArCH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 193.9 (C=O), 149.7 (C=CH<sub>2</sub>), 138.1 (ArC), 135.2 (C=CH<sub>2</sub>), 129.1, 128.5, 126.4 (3 × ArCH), 34.1 (ArCH<sub>2</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>9</sup>

## 2-Benzylprop-2-en-1-ol



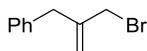
**General Procedure F**: 2-Benzylacrylaldehyde (2.50 g, 17.00 mmol) was employed. The reaction was stirred at 0 °C for 30 minutes. FCC (hexane:EtOAc 10:1 to 5:1) afforded the corresponding aldehyde (2.40 g, 95%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.34-7.14 (m, 5H, ArH), 5.16-5.11 (m, 1H, C=CH<sub>2</sub>), 4.94-4.89 (m, 1H, C=CH<sub>2</sub>), 4.06 (s, 2H, CH<sub>2</sub>OH), 3.43 (s, 2H, ArCH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 148.2 (C=CH<sub>2</sub>), 139.0 (ArC), 128.9, 128.4, 126.3 (3 × ArCH), 111.4 (C=CH<sub>2</sub>), 65.3 (CH<sub>2</sub>OH), 39.9 (ArCH<sub>2</sub>).

The spectroscopic properties of this compound were consistent with the data in the literature.<sup>10</sup>

### (2-(Bromomethyl)allyl)benzene



**General Procedure G:** 2-Benzylprop-2-en-1-ol (0.24 g, 16.20 mmol) was employed to afford bromide (0.24 g, 71%) as a pale yellow oil.

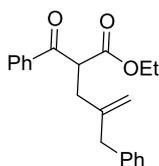
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.36-7.19 (m, 5H, ArH), 5.27-5.23 (m, 1H, C=CH<sub>2</sub>), 5.01-4.97 (m, 1H, C=CH<sub>2</sub>), 3.90 (s, 2H, CH<sub>2</sub>Br), 3.57 (s, 2H, ArCH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 145.0 (C=CH<sub>2</sub>), 138.4 (ArC), 129.1, 128.5, 126.5 (3 × ArCH), 116.7 (C=CH<sub>2</sub>), 40.0 (CH<sub>2</sub>Br), 35.9 (ArCH<sub>2</sub>).

**FTIR** 3027, 1601, 1494, 1210 cm<sup>-1</sup>.

**MS:** (EI<sup>+</sup>) Found [M]<sup>+</sup>: 210.0036, C<sub>10</sub>H<sub>11</sub><sup>79</sup>Br requires 210.0044.

### Ethyl 2-benzoyl-4-benzylpent-4-enoate



**General Procedure A: Part A:** Ethyl benzoylacetate (1.71 mL, 10.00 mmol) and 2-(bromomethyl)allyl)benzene (2.30 g, 10.90 mmol) were employed. FCC (hexane:EtOAc 30:1) afforded the title compound (2.73 g, 85%) as a colorless oil.

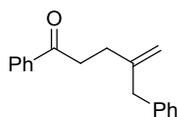
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.96-7.91 (m, 2H, ArH), 7.61-7.42 (m, 3H, ArH), 7.32-7.14 (m, 5H, ArH), 4.91-4.82 (m, 2H, C=CH<sub>2</sub>), 4.55-4.50 (m, 1H, (CO)CH(CO)), 4.13 (q, *J* = 7.0 Hz, 2H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 3.41 (d, *J* = 2.5 Hz, ArCH<sub>2</sub>C=CH<sub>2</sub>), 2.80-2.64 (m, 2H, (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 1.17 (t, *J* = 7.0 Hz, 3H, (CO)OCH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 194.5 (Ar(C=O)), 169.4 ((C=O)OCH<sub>2</sub>CH<sub>3</sub>), 145.2 (C=CH<sub>2</sub>), 138.9, 136.1 (2 × ArC), 133.5, 129.0, 128.7, 128.6, 128.4, 126.3 (6 × ArCH), 113.6 (C=CH<sub>2</sub>), 61.4 ((CO)OCH<sub>2</sub>CH<sub>3</sub>), 52.8 (CO)CH(CO)), 43.2 (ArCH<sub>2</sub>C=CH<sub>2</sub>), 34.3 (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 14.0 ((CO)OCH<sub>2</sub>CH<sub>3</sub>).

**FTIR:** 3290, 1713, 1687, 1270 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 345.1446, C<sub>21</sub>H<sub>22</sub>NaO<sub>3</sub> requires 345.1461.

#### 4-Benzyl-1-phenylpent-4-en-1-one



**General Procedure A: Part B:** Ethyl 2-benzoyl-4-benzylpent-4-enoate (2.70 g, 8.38 mmol) was employed. FCC (hexane:EtOAc 20:1) afforded the title compound (1.24 g, 60%) as a colorless oil.

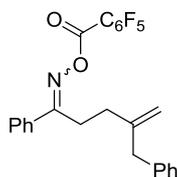
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.95-7.89 (m, 2H, ArH), 7.59-7.42 (m, 3H, ArH), 7.34-7.18 (m, 5H, ArH), 4.91-4.83 (m, 2H, C=CH<sub>2</sub>), 3.43 (s, 2H, ArCH<sub>2</sub>C=CH<sub>2</sub>), 3.13-3.07 (m, 2H, (CO)CH<sub>2</sub>), 2.44 (t, *J* = 7.5 Hz, 2H, (CO)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.5 (C=O), 147.8 (C=CH<sub>2</sub>), 139.4, 136.9 (2 × ArC), 133.0, 129.0, 128.6, 128.4, 128.0, 126.2 (6 × ArCH), 111.6 (C=CH<sub>2</sub>), 43.5 (ArCH<sub>2</sub>C=CH<sub>2</sub>), 36.9 ((CO)CH<sub>2</sub>), 29.7 ((CO)CH<sub>2</sub>CH<sub>2</sub>).

**FTIR:** 1683, 1448, 1203 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 273.1240, C<sub>18</sub>H<sub>18</sub>NaO requires 273.1250.

#### 4-Benzyl-1-phenylpent-4-en-1-one-*O*-perfluorobenzoyl oxime (6f)



**General Procedure B: Part A:** 4-Benzyl-1-phenylpent-4-en-1-one (1.20 g, 4.80 mmol) was employed. The reaction was heated to 75 °C for 2 hours. FCC (hexane:EtOAc 10:1) afforded the corresponding oxime (1.25 g, 98%) as a colorless oil.

*Data for the intermediate oxime:*

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 9.20-8.99 (s, 1H, OH), 7.57-7.48 (m, 2H, ArH), 7.42-7.33 (m, 3H, ArH), 7.32-7.14 (m, 5H, ArH), 4.94-4.77 (m, 2H, C=CH<sub>2</sub>), 3.40 (s, 2H, ArCH<sub>2</sub>C=CH<sub>2</sub>), 3.01-2.92 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.30-2.21 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 159.2 (C=N), 148.0 (C=CH<sub>2</sub>), 139.4, 135.5 (2 × ArC), 129.2, 129.1, 128.5, 128.3, 126.3, 126.1 (6 × ArCH), 111.9 (C=CH<sub>2</sub>), 42.9 (ArCH<sub>2</sub>C=CH<sub>2</sub>), 31.7 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 24.9 (Ar(CN)CH<sub>2</sub>).

**FTIR:** 3228, 1645, 1494, 1451, 1437 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 266.1543, C<sub>18</sub>H<sub>20</sub>NO requires 266.1539.

**General Procedure B: Part B:** The corresponding oxime (0.50 g, 1.89 mmol) was employed and the reaction was left stirring for 16 hours. FCC (hexane:EtOAc 15:1) afforded oxime ester **6f** (0.61 g, 71%) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.68-7.60 (m, 2H, ArH), 7.51-7.37 (m, 3H, ArH), 7.28-7.09 (m, 5H, ArH), 4.92-4.84 (m, 2H, C=CH<sub>2</sub>), 3.35 (s, 2H, ArCH<sub>2</sub>C=CH<sub>2</sub>), 3.05-2.97 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.30-2.20 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

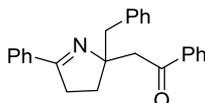
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 168.2 (C=N), 146.8 (C=CH<sub>2</sub>), 138.9, 132.9 (2 × ArC), 131.1, 128.8 (2 signals), 128.3, 127.4, 126.3 (6 × ArCH), 112.6 (C=CH<sub>2</sub>), 42.9 (ArCH<sub>2</sub>C=CH<sub>2</sub>), 31.9 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.5 (Ar(CN)CH<sub>2</sub>). No signals corresponding to the perfluorobenzoyl ester moiety were observed due to the anticipated weak intensity of these signals.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -137.0 (2F), -147.4 (1F), -159.6 (2F).

**FTIR:** 1767, 1503, 1323, 1189 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 482.1154, C<sub>25</sub>H<sub>18</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 482.1150.

### 2-(2-Benzyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (**10f**)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (5.5 mg, 6.0 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (16.0 mg, 0.024 mmol) oxime ester **6f** (55.0 mg, 0.120 mmol) and triethylammonium tetraphenylborate (56.0 mg, 0.132 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.42 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 8 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 6:1) afforded imine **10f** (26.0 mg, 62%) as a colorless oil.

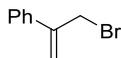
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.01-7.95 (m, 2H, ArH), 7.74-7.67 (m, 2H, ArH), 7.57-7.33 (m, 6H, ArH), 7.26-7.13 (m, 5H, ArH), 3.58 (d, *J* = 16.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.37 (d, *J* = 16.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.20 (d, *J* = 13.0 Hz, 1H, CH<sub>2</sub>Ar), 3.13 (d, *J* = 13.0 Hz, 1H, CH<sub>2</sub>Ar), 2.86-2.75 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.35-2.04 (m, 3H, Ar(CN)CH<sub>2</sub> and Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.2 (C=O), 172.1 (C=N), 137.9, 134.5 (2 × ArC), 132.9 (ArCH), 130.8 (2 signals) (ArC and ArCH), 130.3, 128.4, 128.3, 128.2, 127.7, 127.6, 126.1 (7 × ArCH), 78.6 (quaternary C), 48.3 ((CO)CH<sub>2</sub>), 45.9 (CH<sub>2</sub>Ar), 35.9 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 31.7 (Ar(CN)CH<sub>2</sub>).

**FTIR:** 2929, 2847, 2150, 1733, 1471 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 354.1844, C<sub>25</sub>H<sub>24</sub>NO requires 354.1852.

### (3-(Bromoprop-1-en-2-yl)benzene



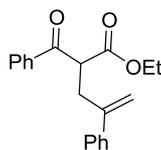
To a solution of  $\alpha$ -methylstyrene (3.30 mL, 25.4 mmol) in dry THF (60 mL) was added *N*-bromosuccinimide (4.75 g, 26.70 mmol) and TsOH (0.48 g, 2.540 mmol) were added. The reaction was stirred at 100 °C for 15 hours. The reaction was cooled to room temperature and diluted with petroleum (10 mL) and washed with H<sub>2</sub>O (3 × 15 mL). The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. FCC (petroleum) afforded the title compound (3.78 g, 76%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.55-7.48 (m, 2H, ArH), 7.44-7.31 (m, 3H, ArH), 5.60-5.57 (m, 1H, C=CH<sub>2</sub>), 5.54-5.50 (m, 1H, C=CH<sub>2</sub>), 4.41 (s, 2H, CH<sub>2</sub>Br).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 144.3 (C=CH<sub>2</sub>), 137.6 (ArC), 128.5, 128.3, 126.1 (3 × ArCH), 117.2 (C=CH<sub>2</sub>), 34.2 (CH<sub>2</sub>Br).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>11</sup>

### Ethyl 2-benzoyl-4-phenylpent-4-enoate



**General Procedure A: Part A:** Ethyl benzoylacetate (1.98 mL, 11.60 mmol) and (3-(bromoprop-1-en-2-yl)benzene (2.50 g, 12.76 mmol) were employed. FCC (toluene) afforded the title compound (1.88 g, 53%) as a colorless oil.

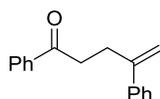
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.88 (d, *J* = 7.5 Hz, 2H, ArH), 7.56 (t, *J* = 7.5 Hz, 1H, ArH), 7.42 (t, *J* = 7.5 Hz, 2H, ArH), 7.38-7.26 (m, 5H, ArH), 5.28 (s, 1H, C=CH<sub>2</sub>), 5.14 (s, 1H, C=CH<sub>2</sub>), 4.46 (t, *J* = 7.5 Hz, 1H, (CO)CH(CO)), 4.10 (q, *J* = 7.0 Hz, 2H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 3.31-3.18 (m, 2H, (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 1.15 (t, *J* = 7.0 Hz, 3H, (CO)OCH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 194.8 (Ar(C=O)), 169.4 ((C=O)OCH<sub>2</sub>CH<sub>3</sub>), 145.0 (C=CH<sub>2</sub>), 140.2, 136.3 (2 × ArC), 133.4, 128.6 (2 signals), 128.4, 127.8, 126.4 (6 × ArCH), 115.1 (C=CH<sub>2</sub>), 61.4 ((CO)OCH<sub>2</sub>CH<sub>3</sub>), 52.8 (CO)CH(CO)), 34.7 (CO)CHCH<sub>2</sub>C=CH<sub>2</sub>), 14.0 ((CO)OCH<sub>2</sub>CH<sub>3</sub>).

**FTIR:** 1684, 1732, 1447, 1228 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 331.1303, C<sub>20</sub>H<sub>20</sub>NaO<sub>3</sub> requires 331.1305.

## 1,4-Diphenylpent-4-en-1-one



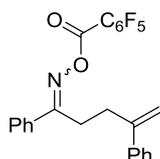
**General Procedure A: Part B:** Ethyl 2-benzoyl-4-phenylpent-4-enoate (1.80 g, 5.80 mmol) was employed. FCC (hexane:EtOAc 40:1) afforded the title compound (1.33 g, 97%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.95-7.90 (m, 2H, ArH), 7.54 (tt, *J* = 7.5 and 2.0 Hz, 1H, ArH), 7.47-7.27 (m, 7H, ArH), 5.36-5.33 (m, 1H, C=CH<sub>2</sub>), 5.16-5.12 (m, 1H, C=CH<sub>2</sub>), 3.16-3.09 (m, 2H, (CO)CH<sub>2</sub>), 3.00-2.93 (m, 2H, (CO)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.5 (C=O), 147.3 (C=CH<sub>2</sub>), 140.6, 136.9 (2 × ArC), 133.0, 128.5, 128.4, 128.0, 127.6, 126.1 (6 × ArCH), 112.9 (C=CH<sub>2</sub>), 37.5 ((CO)CH<sub>2</sub>), 29.7 ((CO)CH<sub>2</sub>CH<sub>2</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>12</sup>

## 1,4-Diphenylpent-4-en-1-one-*O*-perfluorobenzoyl oxime (6g)



**General Procedure B: Part A:** 1,4-Diphenylpent-4-en-1-one (1.33 g, 5.63 mmol) was employed. The reaction was heated to 75 °C for 3 hours. FCC (hexane:EtOAc 8:1) afforded the corresponding oxime (1.10 g, 78%, 1:0.1 mixture of oximer isomers) as a colorless oil.

*Data for the intermediate oxime:*

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Data for the major isomer:* 8.50 (s, 1H, OH), 7.62-7.52 (m, 2H, ArH), 7.47-7.21 (m, 8H, ArH), 5.34 (s, 1H, C=CH<sub>2</sub>), 5.18-5.13 (m, 1H, C=CH<sub>2</sub>), 3.01-2.93 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.82-2.75 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>). *Characteristic signals of the minor isomer:* 5.31 (s, 0.1H, C=CH<sub>2</sub>), 5.09 (s, 0.1H, C=CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 159.3 (C=N), 147.5 (C=CH<sub>2</sub>), 140.6, 135.5 (2 × ArC), 129.2, 128.6, 128.3, 127.5, 126.3, 126.1 (6 × ArCH), 112.7 (C=CH<sub>2</sub>), 31.6 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 25.7 (Ar(CN)CH<sub>2</sub>).

**FTIR:** 3229, 1627, 1494, 1440, 1326 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 252.1375, C<sub>17</sub>H<sub>18</sub>NO requires 252.1383.

**General Procedure B: Part B:** The corresponding oxime (0.50 g, 2.00 mmol) was employed and the reaction was left stirring for 16 hours. FCC (hexane:EtOAc 15:1) afforded oxime ester **6g** (0.78 g, 88%, 1:0.1 mixture of oxime isomers) as a colorless solid.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Data for the major isomer:* 7.75-7.68 (m, 2H, ArH), 7.53-7.40 (m, 3H, ArH), 7.35-7.14 (m, 5H, ArH), 5.31-5.29 (m, 1H, C=CH<sub>2</sub>), 5.03-5.00 (m, 1H, C=CH<sub>2</sub>), 3.10-3.02 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.80-2.72 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>). *Characteristic signals of the minor isomer:* 5.11-5.09 (m, 0.2H, C=CH<sub>2</sub>), 2.93-2.87 (m, 0.2H, Ar(CN)CH<sub>2</sub>).

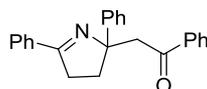
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 168.0 (C=N), 146.1 (C=CH<sub>2</sub>), 139.8, 132.9 (2 × ArC), 131.1, 128.8, 128.4, 128.2, 127.5, 125.9 (6 × ArCH), 113.8 (C=CH<sub>2</sub>), 32.2 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.8 (Ar(CN)CH<sub>2</sub>). *No signals corresponding to the perfluorobenzoyl ester moiety were observed due to the anticipated weak intensity of these signals.*

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): *Signals for the major isomer:* -136.9 (2F), -147.8 (1F), -159.8 (2F). *Signals for the minor isomer:* -137.2 (0.2F), -147.8 (0.1F), -160.0 (0.2F).

**FTIR:** 1759, 1650, 1490, 1319, 1192 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 468.0990, C<sub>24</sub>H<sub>16</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 468.0993.

### 2-(2,5-Diphenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (**10g**)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (5.7 mg, 6.2×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (16.6 mg, 0.025 mmol) oxime ester **6g** (55.0 mg, 0.124 mmol) and triethylammonium tetraphenylborate (57.0 mg, 0.136 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.45 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 20 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 30:1 to 20:1) afforded imine **10g** (22.5 mg, 54%) as a colorless oil.

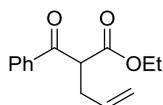
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.90-7.74 (m, 4H, ArH), 7.60-7.28 (m, 10H, ArH), 7.25-7.17 (m, 1H, ArH), 3.67 (d, *J* = 14.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.62 (d, *J* = 14.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.18-3.06 (m, 1H, Ar(CN)CH<sub>2</sub>), 3.05-2.94 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.91-2.81 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.51-2.41 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.1 (C=O), 172.2 (C=N), 147.9, 137.9, 134.7 (3 × ArC), 132.6, 130.4, 128.6, 128.3, 128.2 (2 signals), 127.9, 126.6, 125.9 (9 × ArCH), 80.6 (quaternary C), 50.3 ((CO)CH<sub>2</sub>), 35.7 (Ar(CN)CH<sub>2</sub>), 34.3 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**FTIR:** 1689, 1259, 1447, 1342 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 340.1695, C<sub>24</sub>H<sub>22</sub>NO requires 340.1696.

## Ethyl 2-benzoylpent-4-enoate



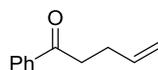
**General Procedure A: Part A:** Ethyl benzoylacetate (5.20 mL, 30.00 mmol) and allyl bromide (2.85 mL, 33.00 mmol) were employed. FCC (hexane:EtOAc 40:1) afforded the title compound (6.53 g, 94%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.00 (d,  $J = 7.5$  Hz, 2H, ArH), 7.62-7.56 (m, 1H, ArH), 7.48 (t,  $J = 7.5$  Hz, 2H, ArH), 5.89-5.75 (m, 1H, HC=CH<sub>2</sub>), 5.13 (dd,  $J = 17.0$  and 1.5 Hz, 1H, HC=CH<sub>2</sub>), 5.05 (dd,  $J = 10.0$  and 1.5 Hz, 1H, HC=CH<sub>2</sub>), 4.40 (t,  $J = 7.5$  Hz, 1H, Ar(CO)CH), 4.19-4.10 (m, 2H, (CO)OCH<sub>2</sub>CH<sub>3</sub>), 2.83-2.69 (m, 2H, Ar(CO)CHCH<sub>2</sub>), 1.17 (t,  $J = 7.5$  Hz, 3H, (CO)OCH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 194.5 (Ar(C=O)), 169.4 ((C=O)OCH<sub>2</sub>CH<sub>3</sub>), 136.2 (ArC), 134.5 (HC=CH<sub>2</sub>), 133.5, 128.7, 128.6 (3 × ArCH), 117.4 (HC=CH<sub>2</sub>), 61.4 ((CO)OCH<sub>2</sub>CH<sub>3</sub>), 53.9 (Ar(CO)CH), 33.0 (Ar(CO)CHCH<sub>2</sub>), 14.0 ((CO)OCH<sub>2</sub>CH<sub>3</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.<sup>13</sup>*

## 1-Phenylpent-4-en-1-one



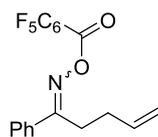
**General Procedure A: Part B:** Ethyl 2-benzoylpent-4-enoate (6.53 g, 28.10 mmol) was employed. FCC (hexane:EtOAc 20:1) afforded the title compound (3.22 g, 72%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.01-7.95 (m, 2H, ArH), 7.60-7.53 (m, 1H, ArH), 7.47 (t,  $J = 7.5$  Hz, 2H, ArH), 5.98-5.86 (m, 1H, HC=CH<sub>2</sub>), 5.10 (dddd,  $J = 17.0, 1.5, 1.5$  and 1.5 Hz, 1H, HC=CH<sub>2</sub>), 5.03 (dddd,  $J = 10.0, 1.5, 1.5$  and 1.5 Hz, 1H, HC=CH<sub>2</sub>), 3.09 (t,  $J = 7.5$  Hz, 2H, Ar(CO)CH<sub>2</sub>), 2.55-2.47 (m, 2H, Ar(CO)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.4 (C=O), 137.3, 136.9 (ArCH and HC=CH<sub>2</sub>), 133.0, 128.6, 128.0 (3 × ArCH), 115.3 (HC=CH<sub>2</sub>), 37.7 (Ar(CO)CH<sub>2</sub>), 28.1 (Ar(CO)CH<sub>2</sub>CH<sub>2</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.<sup>14</sup>*

## 1-Phenylpent-4-en-1-one-*O*-perfluorobenzoyl oxime (**6h**)



**General Procedure B: Part A:** 1-Phenylpent-4-en-1-one (0.90 g, 5.63 mmol) was used. The reaction was heated at 75 °C for 14 hours. FCC (hexane:EtOAc 10:1) afforded the corresponding oxime (0.84 g, 85%, 1:0.05 mixture of oxime isomers) as a colorless solid.

*Data for the intermediate oxime:*

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Signals for the major isomer:* 8.86 (s, 1H, OH), 7.65-7.58 (m, 2H, ArH), 7.45-7.36 (m, 3H, ArH), 5.94-5.80 (m, 1H, HC=CH<sub>2</sub>), 5.08 (dddd, *J* = 17.0, 1.5, 1.5 and 1.5 Hz, 1H, HC=CH<sub>2</sub>), 5.01 (dddd, *J* = 10.0, 1.5, 1.5 and 1.5 Hz, 1H, HC=CH<sub>2</sub>), 2.97 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.40-2.31 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>). *Characteristic signals only for the minor isomer:* 2.70-2.65 (m, 0.1H, Ar(CN)CH<sub>2</sub>), 2.30-2.23 (m, 0.1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): *Signals for the major isomer only:* 159.2 (C=N), 137.4 (HC=CH<sub>2</sub>), 135.6 (ArC), 129.2, 128.6, 126.3 (3 × ArCH), 115.2 (HC=CH<sub>2</sub>), 30.3 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 25.6 (Ar(CN)CH<sub>2</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>15</sup>

**General Procedure B: Part B:** 1-Phenylpent-4-en-1-one oxime (0.40 g, 2.28 mmol) was employed and the reaction was stirred for 2 hours. FCC (hexane:EtOAc 12:1) afforded oxime ester **6h** (0.59 g, 70%, 1:0.05 mixture of oxime isomers) as a colorless solid.

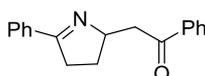
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Signals for the major isomer:* 7.78-7.72 (m, 2H, ArH), 7.54-7.40 (m, 3H, ArH), 5.88-5.74 (m, 1H, HC=CH<sub>2</sub>), 5.09-5.00 (m, 2H, HC=CH<sub>2</sub>), 3.04-2.97 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.40-2.31 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>). *Characteristic signals only for the minor isomer:* 2.89-2.83 (m, 0.1H, Ar(CN)CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): *Signals for the major isomer only:* 168.2 (C=N), 136.1 (HC=CH<sub>2</sub>), 133.0 (ArC), 131.1, 128.8, 127.5 (3 × ArCH), 116.2 (HC=CH<sub>2</sub>), 30.7 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 28.2 (Ar(CN)CH<sub>2</sub>). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): *Signals for the major isomer:* -137.0 (2F), -147.4 (1F), -159.7 (2F). *Signals for the minor isomer:* -137.2 (0.1F), -148.0 (0.05F), -160.0 (0.1F).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>16</sup>

### 1-Phenyl-2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethan-1-one (10h)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with  $\text{Pd}_2(\text{dba})_3$  (6.2 mg,  $6.8 \times 10^{-3}$  mmol),  $\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$  (18.2 mg, 0.027 mmol) oxime ester **6h** (50.0 mg, 0.136 mmol) and triethylammonium tetraphenylborate (63.0 mg, 0.150 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 8:1 to 4:1) afforded imine **10h** (15.0 mg, 42%) as a pale yellow oil.

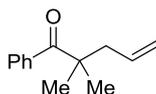
**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ): 8.05-7.99 (m, 2H, ArH), 7.88-7.79 (m, 2H, ArH), 7.62-7.35 (m, 6H, ArH), 4.84-4.72 (m, 1H, (CO)CH<sub>2</sub>CH), 3.78 (dd,  $J = 16.5$  and 4.0 Hz, 1H, (CO)CH<sub>2</sub>), 3.15-2.90 (m, 3H, Ar(CN)CH<sub>2</sub> and (CO)CH<sub>2</sub>), 2.53-2.40 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.75-1.63 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ ): 198.8 (C=O), 173.1 (C=N), 137.0, 134.3 (2 × ArC), 133.1, 130.6, 128.6, 128.4, 128.2, 127.7 (6 × ArCH), 69.4 (quaternary C), 45.5 ((CO)CH<sub>2</sub>), 35.2 (Ar(CN)CH<sub>2</sub>), 29.2 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**FTIR**: 1682, 1448, 1339, 1204  $\text{cm}^{-1}$ .

**MS**: ( $\text{Cl}^-$ ) Found  $[\text{M}+\text{H}]^+$ : 264.1386,  $\text{C}_{18}\text{H}_{18}\text{NO}$  requires 264.1388.

### 2,2-Dimethyl-1-phenylpent-4-en-1-one



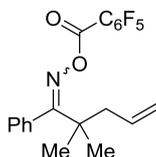
To a solution of *iso*-butyrophenone (2.02 mL, 17.00 mmol) in anhydrous *t*-butanol (25.0 mL) was added potassium *t*-butoxide (2.10 g, 18.70 mmol) and the mixture was stirred at room temperature for 5 minutes. Then allylbromide (1.64 mL, 18.70 mmol) was added *via* syringe and the mixture was heated at 90 °C for 16 hours. The mixture was cooled to room temperature and  $\text{H}_2\text{O}$  (5 mL) was added. The mixture was extracted with  $\text{Et}_2\text{O}$  (2 × 100 mL). The organic extracts were combined, washed with brine (100 mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*. <sup>1</sup>H NMR of the crude residue showed that *iso*-butyrophenone (~30%) remained and therefore the reaction was repeated. Purification of the residue by FCC (toluene:hexane 4:5) afforded the title compound (1.70 g, 53%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ): 7.70-7.62 (m, 2H, ArH), 7.50-7.36 (m, 3H, ArH), 5.80-5.67 (m, 1H, HC=CH<sub>2</sub>), 5.08-4.98 (m, 2H, HC=CH<sub>2</sub>), 2.50 (dt,  $J = 7.5$  and 1.0 Hz, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 1.33 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 208.8 (C=O), 139.1 (ArC), 134.1 (HC=CH<sub>2</sub>), 130.7, 128.1, 127.6 (3 × ArCH), 118.1 (HC=CH<sub>2</sub>), 47.6 (C(CH<sub>3</sub>)<sub>2</sub>), 44.9 (Ar(CO)CCH<sub>2</sub>), 25.7 (C(CH<sub>3</sub>)<sub>2</sub>).

The spectroscopic properties of this compound were consistent with the data in the literature.<sup>17</sup>

### 2,2-Dimethyl-1-phenylpent-4-en-1-one-O-perfluorobenzoyl oxime (6i)



**General Procedure C: Part A:** 2,2-Dimethyl-1-phenylpent-4-en-1-one (0.50 g, 2.66 mmol) was used and, in a modification to the general procedure, H<sub>2</sub>NOH.HCl (0.37 g, 5.32 mmol) and NaOAc (0.44 g, 5.32 mmol) were employed. The reaction was heated to 75 °C for 5 hours to afford the corresponding oxime (0.52 g, 96%) as a colorless solid. **Part B:** The corresponding oxime (0.52 g, 2.55 mmol) was employed and the reaction was stirred for 3 hours 30 minutes FCC (hexane:EtOAc 50:1) afforded oxime ester **6i** (0.85 g, 84%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.44-7.34 (m, 3H, ArH), 7.12-7.04 (m, 2H, ArH), 5.98-5.86 (m, 1H, HC=CH<sub>2</sub>), 5.21-5.07 (m, 2H, HC=CH<sub>2</sub>), 2.37 (d, *J* = 7.0 Hz, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 1.26 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>).

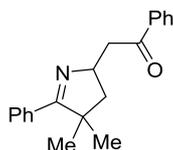
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 176.3 (C=N), 133.8 (HC=CH<sub>2</sub>), 132.4 (ArC), 128.6, 128.0, 126.4 (3 × ArCH), 118.5 (HC=CH<sub>2</sub>), 44.1 (Ar(CN)CCH<sub>2</sub>), 41.8 (C(CH<sub>3</sub>)<sub>2</sub>), 25.6 (C(CH<sub>3</sub>)<sub>2</sub>). Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -137.4 (2F), -148.4 (1F), -160.3 (2F).

**FTIR:** 1761, 1523, 1497, 1326, 1190 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 420.1012, C<sub>20</sub>H<sub>16</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 420.0993.

### 2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (10i)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.2 mg, 6.5 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (18.0 mg, 0.026 mmol) oxime ester **6i** (50.0 mg, 0.126 mmol) and triethylammonium tetraphenylborate (61.0 mg, 0.139 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon

pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.45 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 85 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 6:1 to 4:1) afforded imine **10i** (28.0 mg, 78%) as a colorless oil.

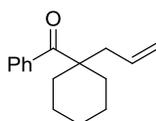
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.07-7.99 (m, 2H, ArH), 7.74-7.66 (m, 2H, ArH), 7.62-7.45 (m, 3H, ArH), 7.43-7.34 (m, 3H, ArH), 4.67-4.54 (m, 1H, (CO)CH<sub>2</sub>CH), 3.84 (dd, *J* = 16.0 and 4.0 Hz, 1H, (CO)CH<sub>2</sub>), 3.07 (dd, *J* = 16.0 and 10.0 Hz, 1H, (CO)CH<sub>2</sub>), 2.36 (dd, *J* = 13.0 and 6.5 Hz, 1H, Ar(CN)CCH<sub>2</sub>), 1.61 (dd, *J* = 13.0 and 8.5 Hz, 1H, Ar(CN)CCH<sub>2</sub>), 1.39 (s, 3H, (CH<sub>3</sub>)<sub>2</sub>), 1.37 (s, 3H, (CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 198.8 (C=O), 180.2 (C=N), 137.1, 134.6 (2 × ArC), 133.1, 129.5, 128.6, 128.2 (2 signals), 127.9 (6 × ArCH), 64.4 ((CO)CH<sub>2</sub>CH), 50.8 (C(CH<sub>3</sub>)<sub>2</sub>), 48.7 ((CO)CH<sub>2</sub>), 45.9 (Ar(CN)CCH<sub>2</sub>), 27.4, 25.9 ((CH<sub>3</sub>)<sub>2</sub>).

**FTIR**: 1684, 1598, 1448, 1365 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 292.1703, C<sub>20</sub>H<sub>22</sub>NO requires 292.1696.

#### (1-Allylcyclohexyl)(phenyl)methanone



To a solution of cyclohexyl phenyl ketone (1.88 g, 10.00 mmol) in anhydrous *t*-butanol (10.0 mL) was added potassium *t*-butoxide (1.34 g, 12.00 mmol) and the mixture was stirred at room temperature for 5 minutes. Then allylbromide (0.95 mL, 11.00 mmol) was added *via* syringe and the mixture was heated at 90 °C for 16 hours. The mixture was cooled to room temperature and H<sub>2</sub>O (5 mL) was added. The mixture was extracted with Et<sub>2</sub>O (2 × 60 mL). The organic extracts were combined, washed with brine (30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. <sup>1</sup>H NMR of the crude residue showed that iso-butyrophenone (~70%) remained and therefore the reaction was repeated three more times until less than 50% cyclobutyl phenyl ketone remained. Purification of the residue by FCC (hexane:toluene 5:1) afforded the title compound (0.52 g, 23%) as a colorless oil.

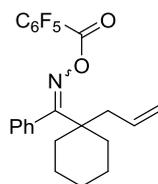
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.67-7.60 (m, 2H, ArH), 7.49-7.36 (m, 3H, ArH), 5.79-5.66 (m, 1H, HC=CH<sub>2</sub>), 5.09-4.99 (m, 2H, HC=CH<sub>2</sub>), 2.56 (dt, *J* = 7.5 and 1.0 Hz, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 2.26-2.16 (m, 2H, CH<sub>2</sub>), 1.64-1.22 (m, 8H, 4 × CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 208.8 (C=O), 140.0 (ArC), 133.4 (HC=CH<sub>2</sub>), 130.5, 128.0, 127.3 (3 × ArCH), 118.0 (HC=CH<sub>2</sub>), 52.4 (Ar(CO)C), 43.3 (CH<sub>2</sub>CH=CH<sub>2</sub>), 34.3, 25.9, 22.8 (3 × CH<sub>2</sub>).

**FTIR**: 2930, 1672, 1452, 1217 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 229.1587, C<sub>16</sub>H<sub>21</sub>O requires 229.1587.

**(1-Allylcyclophenyl)(phenyl)methanone-*O*-perfluorobenzoyl oxime (6j)**



**General Procedure C: Part A:** (1-Allylcyclophenyl)(phenyl)methanone (0.50 g, 2.19 mmol) was used and, in a modification to the general procedure, H<sub>2</sub>NOH.HCl (0.60 g, 8.76 mmol) and NaOAc (0.72 g, 8.76 mmol) were employed. The reaction was heated to 75 °C for 36 hours to afford the corresponding oxime (0.50 g, 94%) as a colorless solid. **Part B:** The corresponding oxime (0.90 g, 2.06 mmol) was employed and the reaction was stirred for 1 hour. FCC (hexane:EtOAc 40:1) afforded oxime ester **6j** (0.70 g, 78%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.43-7.35 (m, 3H, ArH), 7.15-7.08 (m, 2H, ArH), 6.00 (m, 1H, HC=CH<sub>2</sub>), 5.22-5.11 (m, 2H, HC=CH<sub>2</sub>), 2.37 (d, *J* = 7.0Hz, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 1.98-1.87 (m, 2H, CH<sub>2</sub>), 1.72-1.36 (m, 8H, 4 × CH<sub>2</sub>).

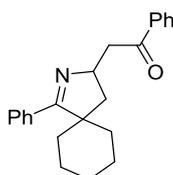
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 174.9 (C=N), 133.4 (HC=CH<sub>2</sub>), 132.2 (ArC), 128.6, 128.0, 126.4 (3 × ArCH), 118.2 (HC=CH<sub>2</sub>), 45.5 (Ar(CN)C), 41.2 (CH<sub>2</sub>CH=CH<sub>2</sub>), 33.5, 25.9, 22.2 (3 × CH<sub>2</sub>). Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -137.4 (2F), -148.5 (1F), -160.3 (2F).

**FTIR:** 1759, 1522, 1497, 1325, 1190 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 460.1309, C<sub>23</sub>H<sub>20</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 460.1306.

**1-Phenyl-2-(1-phenyl-2-azaspiro[4.5]dec-1-en-3-yl)ethan-1-one (10j)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (5.8 mg, 6.3×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (16.9 mg, 0.025 mmol) oxime ester **6j** (55.0 mg, 0.126 mmol) and triethylammonium tetraphenylborate (62.0 mg, 0.139 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.46 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 6:1 to 3:1) afforded imine **10j** (30.0 mg, 72%) as a colorless oil.

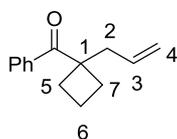
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.05-8.00 (m, 2H, ArH), 7.62-7.34 (m, 8H, ArH), 4.66-4.55 (m, 1H, (CO)CH<sub>2</sub>CH), 3.84 (dd, *J* = 16.5 and 4.0 Hz, 1H, (CO)CH<sub>2</sub>), 3.06 (dd, *J* = 16.5 and 10.0 Hz, 1H, (CO)CH<sub>2</sub>), 2.64 (dd, *J* = 13.0 and 7.5 Hz, 1H, Ar(CN)CCH<sub>2</sub>CH), 1.91-1.06 (m, 11H, Ar(CN)CCH<sub>2</sub>CH and 5 × CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 198.8 (C=O), 181.2 (C=N), 137.0, 135.7 (2 × ArC), 133.1, 129.0, 128.6, 128.2, 128.0, 127.2 (6 × ArCH), 65.2 ((CO)CH<sub>2</sub>CH), 56.8 (Ar(CN)C), 46.3 ((CO)CH<sub>2</sub>), 41.8 (Ar(CN)CCH<sub>2</sub>CH), 36.0, 31.9, 25.6, 23.3, 23.1 (5 × CH<sub>2</sub>).

**FTIR**: 1683, 1598, 1448 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 332.2012, C<sub>23</sub>H<sub>26</sub>NO requires 332.2009.

### (1-Allylcyclobutyl)(phenyl)methanone



To a solution of cyclobutyl phenyl ketone (1.52 mL, 10.00 mmol) in anhydrous *t*-butanol (10.00 mL) was added potassium *t*-butoxide (1.34 g, 12.00 mmol) and the mixture was stirred at room temperature for 5 minutes. Then allylbromide (0.95 mL, 11.00 mmol) was added *via* syringe and the mixture was heated at 90 °C for 16 hours. The mixture was cooled to room temperature and H<sub>2</sub>O (5 mL) was added. The mixture was extracted with Et<sub>2</sub>O (2 × 60 mL). The organic extracts were combined, washed with brine (30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. <sup>1</sup>H NMR of the crude residue showed that iso-butyrophenone (~40%) remained and therefore the reaction was repeated until less than 10% cyclobutyl phenyl ketone remained. Purification of the residue by FCC (hexane:toluene 2:1) afforded the title compound (1.48 g, 74%) as a colorless oil.

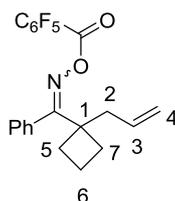
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.86-7.80 (m, 2H, ArH), 7.52 (tt, *J* = 7.5 and 1.5 Hz, 1H, ArH), 7.47-7.40 (m, 2H, ArH), 5.71-5.60 (m, 1H, C3-H), 5.04-4.91 (m, 2H, C4-H<sub>2</sub>), 2.72-2.64 (m, 4H, C2-H<sub>2</sub> and C5/7-H<sub>2</sub>), 2.21-2.12 (m, 2H, C5/7-H<sub>2</sub>), 2.12-1.98 (m, 1H, C6-H<sub>2</sub>), 1.89-1.78 (m, 1H, C6-H<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 204.1 (C=O), 134.8 (ArC), 133.2 (C3), 132.4, 129.0, 128.3 (3 × ArCH), 117.9 (C4), 52.6 (C1), 42.8 (C2), 30.2 (C5&7), 15.4 (C6).

**FTIR**: 1672, 1447, 1219 cm<sup>-1</sup>.

**MS**: (CI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 223.1093, C<sub>14</sub>H<sub>16</sub>NaO requires 223.1093.

**(1-Allylcyclobutyl)(phenyl)methanone-O-perfluorobenzoyl oxime (6k)**



**General Procedure C: Part A:** (1-Allylcyclobutyl)(phenyl)methanone (0.90 g, 4.50 mmol) was used and, in a modification to the general procedure, H<sub>2</sub>NOH.HCl (0.62 g, 9.00 mmol) and NaOAc (0.74 g, 9.00 mmol) were employed. The reaction was heated to 75 °C for 20 hours to afford the corresponding oxime (0.90 g, 93%) as a colorless solid. **Part B:** The corresponding oxime (0.90 g, 4.19 mmol) was employed and the reaction was stirred for 1 hour. FCC (hexane:EtOAc 60:1) afforded oxime ester **6k** (1.14 g, 67%, 1:0.8 mixture of oxime isomers) as a colorless solid.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Signals for both isomers:* 7.54-7.34 (m, 7.2H, ArH), 7.20-7.12 (m, 1.8H, ArH), 6.07-5.73 (m, 1.8H, maj. and min. C3-H), 5.29-5.04 (m, 3.6H, min. and maj. C4-H<sub>2</sub>), 2.83 (d, *J* = 7.0 Hz, 1.6H, min. C2-H<sub>2</sub>), 2.80-2.69 (m, 2H, maj. C5/7-H<sub>2</sub>), 2.45 (d, *J* = 7.0 Hz, 2H, maj. C2-H<sub>2</sub>), 2.38-2.25 (m, 1.6H, min. C5/7-H<sub>2</sub>), 2.20-2.09 (m, 1.6H, min. C5/7-H<sub>2</sub>), 2.09-1.64 (m, 5.6H, maj. C5/7-H<sub>2</sub>, min. and maj. C6-H<sub>2</sub>).

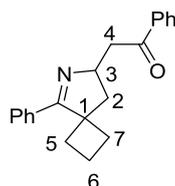
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): *Signals for both isomers:* 174.3 (min. C=N), 173.4 (maj. C=N), 134.1 (min. C<sub>3</sub>), 133.5 (maj. C<sub>3</sub>), 133.0, 131.9 (2 × ArC), 130.1, 129.1, 128.5, 128.4, 128.1, 126.5 (6 × ArCH), 118.9 (min. C<sub>4</sub>), 118.3 (maj. C<sub>4</sub>), 47.5 (maj. C<sub>1</sub>), 47.1 (min. C<sub>1</sub>), 41.7 (min. C<sub>2</sub>), 40.8 (maj. C<sub>2</sub>), 32.9 (min. C<sub>5/7</sub>), 29.9 (maj. C<sub>5/7</sub>), 16.2 (maj. C<sub>6</sub>), 15.4 (min. C<sub>6</sub>). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): *Signals for both isomers:* -137.3 (3.6F), -147.9 (0.8F), -148.4 (1F), -159.6 (1.6F), -160.2 (2F).

**FTIR:** 1762, 1523, 1501, 1326, 1193 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 432.0992, C<sub>21</sub>H<sub>16</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 432.0993.

**1-Phenyl-2-(5-phenyl-6-azaspiro[3.4]oct-5-en-7-yl)ethan-1-one (10k)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (5.6 mg, 6.1 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (16.5 mg, 0.024 mmol) oxime ester **6k** (50.0 mg, 0.122 mmol) and triethylammonium tetraphenylborate (60.0 mg, 0.134 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via*

syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.45 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 10:1 to 4:1) afforded imine **10k** (24.0 mg, 65%) as a colorless oil.

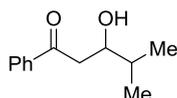
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.05-8.00 (m, 2H, ArH), 7.81-7.74 (m, 2H, ArH), 7.61-7.40 (m, 6H, ArH), 4.58-4.48 (m, 1H, C3-H), 3.79 (dd, *J* = 16.0 and 4.0 Hz, 1H, C4-H<sub>2</sub>), 3.00 (dd, *J* = 16.0 and 10.0 Hz, 1H, C4-H<sub>2</sub>), 2.82-2.68 (m, 2H, C2-H<sub>2</sub> and C5/6/7-H<sub>2</sub>), 2.62-2.50 (m, 1H, C5/6/7-H<sub>2</sub>), 2.25-1.85 (m, 5H, 2 × C5/6/7-H<sub>2</sub> and C2-H<sub>2</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 198.7 (C=O), 178.7 (C=N), 137.0, 134.5 (2 × ArC), 133.2, 129.8, 128.6, 128.4, 128.2, 127.9 (6 × ArCH), 64.6 (C3), 55.3 (C1), 47.5 (C2), 45.4 (C4), 32.2, 32.0 (C5 and C7), 16.5 (C6).

**FTIR**: 1684, 1596, 1448, 1009 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 304.1694, C<sub>21</sub>H<sub>22</sub>NO requires 304.1696.

### 3-Hydroxy-4-methyl-1-phenylpentan-1-one



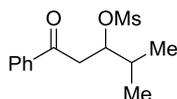
To a solution of diisopropylamine (7.34 mL, 52.50 mmol) in anhydrous THF (100 mL) at -20 °C was added *n*-BuLi (1.52 M in hexane, 34.50 mL, 52.50 mmol) dropwise over 30 minutes. The mixture was stirred for 30 minutes at -20 °C. The reaction was cooled to -78 °C and acetophenone (5.83 mL, 50.00 mmol) was added over 5 minutes. The reaction was stirred at -78 °C for 30 minutes and then isobutyrylaldehyde (4.65 mL, 51.00 mmol) was added over 5 minutes. The reaction was stirred for 1 hour. The reaction was quenched with sat. NaHCO<sub>3</sub> (50 mL) and extracted with Et<sub>2</sub>O (2 × 100 mL). The organic extracted with sequentially washed with water (50 mL), 1M HCl (50 mL), sat. NaHCO<sub>3</sub> (50 mL) and brine (50 mL). The organic phase was concentrated *in vacuo*. FCC (hexane:EtOAc 20:1) afforded the title compound (8.28 g, 86%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.00-7.94 (m, 2H, ArH), 7.60 (tt, *J* = 7.5 and 2.0 Hz, 1H, ArH), 7.52-7.46 (m, 2H, ArH), 4.04-3.97 (m, 1H, CHOH), 3.22-3.15 (m, 2H, Ar(CO)CH<sub>2</sub> and OH), 3.04 (dd, *J* = 17.0 and 9.0 Hz, 1H, Ar(CO)CH<sub>2</sub>), 1.88-1.75 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.03 (d, *J* = 7.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (d, *J* = 7.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 201.3 (C=O), 136.9 (ArC), 133.5, 128.7, 128.1 (3 × ArCH), 72.4 (CHOH), 41.9 (Ar(CO)CH<sub>2</sub>), 33.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.5, 17.9 (CH(CH<sub>3</sub>)<sub>2</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>18</sup>

#### 4-Methyl-1-oxo-1-phenylpentan-3-yl methanesulfonate



To a solution of 3-hydroxy-4-methyl-1-phenylpentan-1-one (4.77 g, 24.80 mmol) in pyridine (10 mL) was added methanesulfonyl chloride (3.83 mL, 49.70 mmol) over 10 minutes. The reaction was stirred for 15 hours. The reaction was quenched with H<sub>2</sub>O (20 mL) and the aqueous was extracted Et<sub>2</sub>O (2 × 50 mL). The organic layer was washed with sat. CuSO<sub>4</sub> (4 × 30 mL) and brine (30 mL) and then concentrated *in vacuo*. FCC (hexane:EtOAc 30:1) afforded the enone product (*E*)-4-methyl-1-phenylpent-2-en-1-one (1.10 g, 25% yield) as a pale yellow oil. Continued elution provided the title compound (2.90 g, 43% yield) as a pale yellow oil. See the procedure given below for characterisation data of (*E*)-4-methyl-1-phenylpent-2-en-1-one.

Data for 4-methyl-1-oxo-1-phenylpentan-3-yl methanesulfonate:

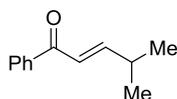
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.00-7.94 (m, 2H, ArH), 7.62 (tt, *J* = 7.5 and 2.0 Hz, 1H, ArH), 7.53-7.46 (m, 2H, ArH), 5.23 (dt, *J* = 8.0 and 4.0 Hz, 1H, CHOMs), 3.52 (dd, *J* = 17.0 and 8.0 Hz, 1H, Ar(CO)CH<sub>2</sub>), 3.13 (dd, *J* = 17.0 and 4.0 Hz, 1H, Ar(CO)CH<sub>2</sub>), 3.01 (s, 3H, SO<sub>2</sub>CH<sub>3</sub>), 2.33-2.21 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, *J* = 7.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.02 (d, *J* = 7.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 196.7 (C=O), 136.5 (ArC), 133.7, 128.8, 128.1 (3 × ArCH), 83.4 (CHOMs), 39.2 (Ar(CO)CH<sub>2</sub>), 38.2 (SO<sub>2</sub>CH<sub>3</sub>), 32.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 17.5 (2 signals) (CH(CH<sub>3</sub>)<sub>2</sub>).

**FTIR**: 1686, 1344, 1172 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>:293.0819, C<sub>13</sub>H<sub>18</sub>NaO<sub>4</sub>S requires 293.0818.

#### (*E*)-4-Methyl-1-phenylpent-2-en-1-one



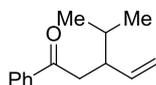
To a solution of 4-methyl-1-oxo-1-phenylpentan-3-yl methanesulfonate (2.89 g, 10.70 mmol) in anhydrous Et<sub>2</sub>O (10 mL) was added Et<sub>3</sub>N (1.50 mL, 10.70 mmol). The reaction was stirred at room temperature for 14 hours. The reaction was quenched with H<sub>2</sub>O (5 mL) and stirred for 10 minutes. The organic layer was sequentially washed with 1M HCl (5 mL), NaHCO<sub>3</sub> (5 mL) and brine (5 mL). The organic phase was concentrated *in vacuo* and FCC (hexane:EtOAc 30:1) afforded the title compound (1.50 g, 81%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.59-7.53 (m, 1H, ArH), 7.47 (tt, *J* = 8.0 and 1.0 Hz, 2H, ArH), 7.04 (dd, *J* = 15.5 and 6.5 Hz, 1H, Ar(CO)CH=CH), 6.83 (d, *J* = 15.5 Hz, 1H, Ar(CO)CH=CH), 2.65-2.52 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (d, *J* = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 191.3 (C=O), 156.0 (Ar(CO)CH=CH), 138.1 (ArC), 132.5, 128.5 (2 signals) (3 × ArCH), 123.1 (Ar(CO)CH=CH), 31.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.4 (CH(CH<sub>3</sub>)<sub>2</sub>).

The spectroscopic properties of this compound were consistent with the data in the literature.<sup>19</sup>

### 3-Isopropyl-1-phenylpent-4-en-1-one<sup>20</sup>



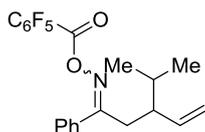
To a schlenk tube was added LiCl (0.71 g, 16.70 mmol) which was heated unvacuum for 15 hours at 150 °C. The schlenk was then cooled to room temperature wherein CuI (1.60 g, 8.40 mmol) and THF (80 mL) was added. The reaction was cooled to 0 °C. To a round bottom flask, (*E*)-4-methyl-1-phenylpent-2-en-1-one (2.43 g, 14.00 mmol) was added. The flask was purged with argon for 5 minutes and THF (10 mL) was added to give a pale yellow solution. This solution was then added to the schlenk slowly (over 15 minutes). Simultaneously freshly distilled TMSCl (1.95 mL, 15.40 mmol) was added slowly (over 15 minutes). The reaction was stirred for 30 minutes at 0 °C. To the reaction vinylmagnesium chloride solution (1.6 M in THF, 10.5 mL, 16.75 mmol) was added dropwise and the reaction was stirred for a further hour. The reaction was then quenched with sat. NH<sub>4</sub>Cl (40 mL) and extracted with Et<sub>2</sub>O (2 × 100 mL). The combined organic extracted were concentrated *in vacuo*. Purification of the residue by FCC (hexane:EtOAc 120:1) afforded the title compound (1.19 g, 42%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.98-7.92 (m, 2H, ArH), 7.58-7.43 (m, 3H, ArH), 5.78-5.64 (m, 1H, HC=CH<sub>2</sub>), 4.98 (m, 2H, HC=CH<sub>2</sub>), 3.08-2.95 (m, 2H, Ar(CO)CH<sub>2</sub>), 2.70-2.59 (m, 1H, Ar(CO)CH<sub>2</sub>CH), 1.82-1.69 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.96 (dd, *J* = 7.0 and 2.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.92 (dd, *J* = 7.0 and 2.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.8 (C=O), 139.0 (HC=CH<sub>2</sub>), 137.2 (ArC), 132.8, 128.5, 128.1 (3 × ArCH), 115.9 (HC=CH<sub>2</sub>), 45.9 (Ar(CO)CH<sub>2</sub>CH), 41.0 (Ar(CO)CH<sub>2</sub>), 31.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.4, 18.8 (CH(CH<sub>3</sub>)<sub>2</sub>).

The spectroscopic properties of this compound were consistent with the data in the literature.<sup>21</sup>

### 3-Isopropyl-1-phenylpent-4-en-1-one-*O*-perfluorobenzoyl oxime (6l)



**General Procedure C: Part A:** 3-Isopropyl-1-phenylpent-4-en-1-one (1.18 g, 5.84 mmol) was used and H<sub>2</sub>NOH.HCl (0.48 g, 7.01 mmol) and NaOAc (0.57 g, 7.01 mmol) were employed. The reaction was heated to 75 °C for 1 hour to afford the corresponding oxime (1.00 g, 79%) as a colorless solid. **Part B:** The corresponding oxime (1.00 g, 4.61 mmol) was

employed and the reaction was stirred for 2 hours. FCC (hexane:EtOAc 50:1) afforded oxime ester **6l** (1.32 g, 70%, 1:0.1 mixture of oxime isomers) as a colorless solid.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Signals for the major isomer:* 7.70-7.63 (m, 2H, ArH), 7.52-7.39 (m, 3H, ArH), 5.51 (ddd, *J* = 17.0, 10.0 and 10.0 Hz, 1H, HC=CH<sub>2</sub>), 4.95 (dd, *J* = 10.0 and 2.0 Hz, 1H, HC=CH<sub>2</sub>), 4.78 (dd, *J* = 17.0 and 2.0 Hz, 1H, HC=CH<sub>2</sub>), 3.06 (dd, *J* = 13.0 and 10.0 Hz, 1H, Ar(CN)CH<sub>2</sub>), 2.95 (dd, *J* = 13.0 and 5.0 Hz, 1H, Ar(CN)CH<sub>2</sub>), 2.16-2.03 (m, 1H, Ar(CN)CH<sub>2</sub>CH), 1.75-1.57 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.92 (d, *J* = 6.5 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.87 (d, *J* = 6.5 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>). *Characteristic signals of the minor isomer:* 5.70-5.56 (m, 0.1H, HC=CH<sub>2</sub>), 5.08 (dd, *J* = 10.0 and 2.0 Hz, 1H, HC=CH<sub>2</sub>), 2.92-2.72 (m, 0.2H, Ar(CN)CH<sub>2</sub>).

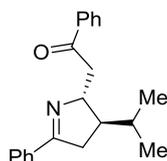
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): *Signals for the major isomer only:* 168.5 (C=N), 137.7 (HC=CH<sub>2</sub>), 133.5 (ArC), 130.8, 128.7, 127.6 (3 × ArCH), 116.9 (HC=CH<sub>2</sub>), 48.6 (Ar(CN)CH<sub>2</sub>CH), 31.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.6 (Ar(CN)CH<sub>2</sub>), 20.4, 18.9 (CH(CH<sub>3</sub>)<sub>2</sub>). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): *Signals for the major isomer:* -137.1 (2F), -147.6 (1F), -159.7 (2F). *Signals for the minor isomer:* -137.2 (0.2F), -148.1 (0.1F), -160.1.

**FTIR:** 1763, 1523, 1498, 1322, 1195 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 434.1158, C<sub>21</sub>H<sub>18</sub>F<sub>5</sub>NNaO<sub>2</sub> requires 434.1150.

## 2-(((2R,3R)-3-Isopropyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-phenylethan-1-one (10l)



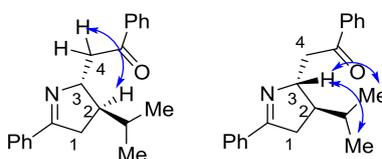
An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.2 mg, 6.5 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (18.0 mg, 0.026 mmol) oxime ester **6l** (50.0 mg, 0.122 mmol) and triethylammonium tetrphenylborate (56.0 mg, 0.134 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.45 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 75 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo* to provide the title compound as a 10:1 mixture of diastereomers as determined by <sup>1</sup>H NMR analysis. An analytically pure sample of the major diastereomer was obtained by FCC (hexane:EtOAc 10:1 to 6:1) (23.0 mg, 61%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.05-7.99 (m, 2H, ArH), 7.85-7.80 (m, 2H, ArH), 7.60-7.37 (m, 6H, ArH), 4.67-4.58 (m, 1H, Ar(CO)CH<sub>2</sub>CH), 3.50 (dd, *J* = 16.0 and 5.5 Hz, 1H, Ar(CO)CH<sub>2</sub>), 3.16-3.01 (m, 2H, Ar(CO)CH<sub>2</sub> and Ar(CN)CH<sub>2</sub>), 2.79 (dd, *J* = 17.5 and 5.0 Hz, 1H, Ar(CN)CH<sub>2</sub>), 2.17-2.08 (m, 1H, Ar(CN)CH<sub>2</sub>CH), 1.88-1.76 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.92 (d, *J* = 6.5 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.87 (d, *J* = 6.5 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 198.9 (C=O), 172.3 (C=N), 137.3, 134.4 (2 × ArC), 133.0, 130.5, 128.5, 128.4, 128.3, 127.7 (6 × ArCH), 72.8 (Ar(CO)CH<sub>2</sub>CH), 48.5 (Ar(CN)CH<sub>2</sub>CH), 45.1 (Ar(CO)CH<sub>2</sub>), 37.7 (Ar(CN)CH<sub>2</sub>), 31.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.7, 18.9 (CH(CH<sub>3</sub>)<sub>2</sub>).

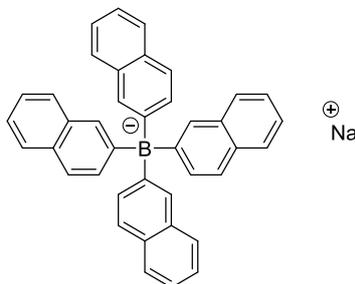
**FTIR**: 1684, 1448, 1341, 1280 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 306.1856, C<sub>21</sub>H<sub>24</sub>NO requires 306.1852.



To determine the stereochemistry of the major diastereomer, nOe analysis was carried out. An nOe enhancement between C2-H and C4-H<sub>2</sub> was observed. An nOe enhancement between C3-H and CH(CH<sub>3</sub>)<sub>2</sub> was also observed.

### Sodium tetra(naphthalen-2-yl)borate



A flake of iodine was added to magnesium turnings (0.74 g, 30.30 mmol) and was stirred for 10 minutes. Anhydrous THF (50 mL) was then added to the reaction. 2-Bromonaphthalene (6.20 g, 30.00 mmol) was added slowly over approximately 30 minutes. The resulting mixture was stirred for an additional 1 hour 30 minutes. Boron trifluoride diethyl etherate (0.75 mL, 6.00 mmol) was added slowly at room temperature. The reaction was stirred for 90 minutes at room temperature. The reaction was poured into a solution of Na<sub>2</sub>CO<sub>3</sub> (20.00 g in 200 mL H<sub>2</sub>O) and stirred for 30 minutes. The precipitate was filtered through celite which was washed with Et<sub>2</sub>O (300 mL). The phases were separated and the aqueous phase was extracted with EtOAc (200 mL). The combined organic layer was concentrated *in vacuo*. The resulting solid was washed with CHCl<sub>3</sub>/hexane and dried under vacuum to afford the title compound (2.70 g, 83%) as a colorless solid.

**M.P.** : > 220 °C (acetone).

**<sup>1</sup>H NMR** (400 MHz, d<sub>6</sub>-acetone): 8.00-7.90 (m, 4H, ArH), 7.77-7.62 (m, 8H, ArH), 7.59-7.45 (m, 8H, ArH), 7.27-7.15 (m, 8H, ArH).

**<sup>13</sup>C NMR** (100 MHz, d<sub>6</sub>-acetone): 162.5 (q, *J* = 50.0 Hz, B-C), 138.2 (ArCH), 134.8 (q, *J* = 3.0 Hz, ArC), 133.9 (ArCH), 132.3 (ArC), 128.2, 127.9, 124.5 (2 signals), 123.5 (5 × ArCH).

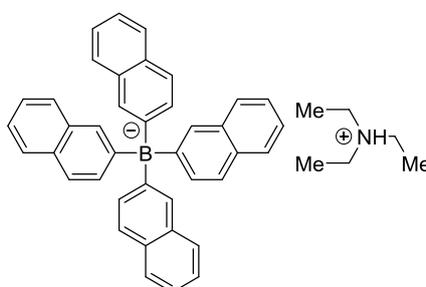
**<sup>11</sup>B NMR** (128 MHz, d<sub>6</sub>-acetone): -6.8.

**FTIR**: 3624, 3042, 1697, 1616, 1493, 1260 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [A<sub>1</sub>]<sup>+</sup>: 519.2285, C<sub>40</sub>H<sub>28</sub>B requires 519.2296.

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>22</sup>

### Triethylammonium tetra(naphthalene-2-yl)borate



**General Procedure D**: Sodium tetra(naphthalen-2-yl)borate (1.41 g, 2.60 mmol), 10 mL H<sub>2</sub>O:MeOH (1:1) and Et<sub>3</sub>N (3.90 mmol) were employed. The precipitate was filtered and washed with H<sub>2</sub>O (26 mL) to afford the title compound (1.19 g, 74%) as a colorless oil.

**M.P.**: 185-187°C (MeOH:H<sub>2</sub>O).

**<sup>1</sup>H NMR** (400 MHz, d<sub>6</sub>-acetone): 7.99-7.91 (m, 4H, ArH), 7.78-7.64 (m, 8H, ArH), 7.60-7.47 (m, 8H, ArH), 7.29-7.16 (m, 8H, ArH), 3.20 (q, *J* = 7.5 Hz, 6H, <sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.24 (t, *J* = 7.5 Hz, 9H, <sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

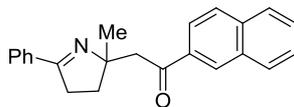
**<sup>13</sup>C NMR** (100 MHz, d<sub>6</sub>-acetone): 162.3 (q, *J* = 50.0 Hz, B-C), 138.1 (ArCH), 134.8 (ArC), 133.9 (ArCH), 132.3 (ArC), 128.2, 128.0, 124.5 (2 signals), 123.6 (5 × ArCH), 48.0 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 9.5 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

**<sup>11</sup>B NMR** (128 MHz, d<sub>6</sub>-acetone): -6.8.

**FTIR**: 3031, 2986, 1686, 1493, 1257 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [A<sub>1</sub>]<sup>+</sup>: 519.2285, C<sub>40</sub>H<sub>28</sub>B requires 519.2296.

**2-(2-Methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(naphthalene-2-yl)ethan-1-one**  
(12a)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and triethylammonium tetra(naphthalene-2-yl)borate (105.0 mg, 0.169 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 4 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 6:1 to 4:1) afforded imine **12a** (22.5 mg, 53%) as a pale yellow oil.

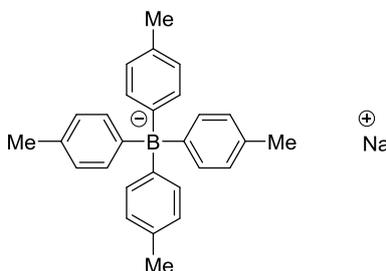
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.55 (s, 1H, ArH), 8.08-8.01 (m, 1H, ArH), 7.94 (d, *J* = 8.0 Hz, 1H, ArH), 7.89-7.83 (m, 2H, ArH), 7.79 (d, *J* = 8.0 Hz, 2H, ArH), 7.63-7.50 (m, 2H, ArH), 7.45-7.31 (m, 3H, ArH), 3.67 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.43 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.17-3.01 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.41-2.27 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.17-2.02 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.51 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 199.1 (C=O), 171.4 (C=N), 135.5, 135.2, 134.1 (2 signals) (4 × ArC), 132.5, 130.6, 130.5, 129.7, 128.4, 128.3, 127.9, 127.7, 126.7, 124.0 (10 × ArCH), 75.2 (quaternary C), 49.1 ((CO)CH<sub>2</sub>), 35.5 (Ar(CN)CH<sub>2</sub>), 34.0 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6 ((NC)CH<sub>3</sub>).

**FTIR**: 2962, 1679, 1625, 1448, 1338 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 328.1703, C<sub>23</sub>H<sub>22</sub>NO requires 328.1896.

**Sodium tetrakis(4-methylphenyl)borate**



**General Procedure C**: 4-Bromotoluene (12.92 mL, 105.00 mmol) and sodium tetrafluoroborate (1.92 g, 17.50 mmol) were employed and the reaction was stirred at room temperature for 63 hours. The title compound was obtained (4.00 g, 57%) as a colorless solid.

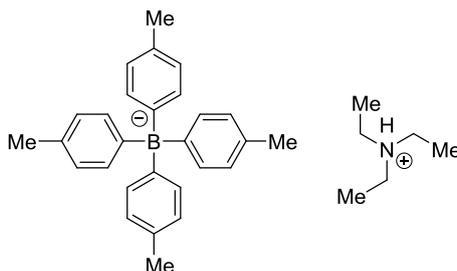
**M.P.**: > 220 °C (acetone).

**<sup>1</sup>H NMR** (400 MHz, d<sub>6</sub>-acetone): 7.24-7.18 (m, 8H, ArH), 6.73 (d, *J* = 8.0 Hz, 8H, ArH), 2.16 (s, 12H, CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, d<sub>6</sub>-acetone): 161.9 (q, *J* = 50.0 Hz, B-C), 137.1-137.0 (m, ArCH), 129.9 (ArC), 126.71 (q, *J* = 3.0 Hz, ArCH), 21.4 (CH<sub>3</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>23</sup>

### Triethylammonium tetrakis(4-methylphenyl)borate



**General Procedure D:** Sodium tetrakis(4-methylphenyl)borate (0.40 g, 1.00 mmol), 30 mL H<sub>2</sub>O:MeOH (1:1) and Et<sub>3</sub>N (1.50 mmol) were employed. The precipitate was filtered and washed with H<sub>2</sub>O (10 mL) to afford the title compound (0.35 g, 73%) as a colorless solid.

**M.P.:** 159-160 °C (MeOH:H<sub>2</sub>O).

**<sup>1</sup>H NMR** (400 MHz, d<sub>6</sub>-acetone): 7.28-7.17 (m, 8H, ArH), 6.73 (d, *J* = 7.5 Hz, 8H, ArH), 3.41 (q, *J* = 7.5 Hz, 6H, <sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 2.16 (s, 12H, CH<sub>3</sub>), 1.38 (t, *J* = 7.5 Hz, 9H, <sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

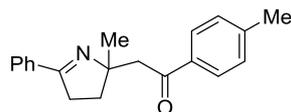
**<sup>13</sup>C NMR** (100 MHz, d<sub>6</sub>-acetone): 160.9 (q, *J* = 50.0 Hz, B-C), 136.1 (q, *J* = 1.5 Hz, ArCH), 129.1 (ArC), 125.9 (q, *J* = 3.0 Hz, ArCH), 47.2 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 20.4 (ArCH<sub>3</sub>), 8.5 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

**<sup>11</sup>B NMR** (128 MHz, d<sub>6</sub>-acetone): -8.1.

**FTIR:** 2991, 2915, 1492, 1446 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [A<sub>1</sub> + C<sub>2</sub>]<sup>+</sup>: 579.4837, C<sub>40</sub>H<sub>60</sub>BN<sub>2</sub> requires 579.4851.

### 2-(2-Methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(*p*-tolyl)ethanone (12b)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol) and triethylammonium tetrakis(4-methylphenyl)borate (68.0 mg, 0.142 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL)

was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 4 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 7:1) afforded imine **12b** (24.0 mg, 63%) as a colorless oil.

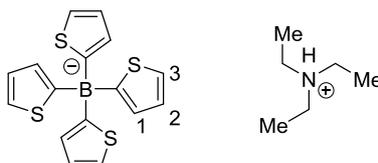
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.90-7.85 (m, 2H, ArH), 7.80-7.75 (m, 2H, ArH), 7.46-7.36 (m, 3H, ArH), 7.25-7.21 (m, 2H, ArH), 3.50 (d, *J* = 16.0 Hz, 1H, Ar(CO)CH<sub>2</sub>), 3.24 (d, *J* = 16.0 Hz, 1H, Ar(CO)CH<sub>2</sub>), 3.09-3.00 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.39 (s, 3H, ArCH<sub>3</sub>), 2.31-2.23 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.10-2.01 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.46 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 198.8 (C=O), 171.9 (C=N), 143.6, 135.5, 130.5 (3 × ArC), 129.1, 128.5, 128.3, 127.8 (2 signals) (5 × ArCH), 75.2 (quaternary C), 48.9 (Ar(CO)CH<sub>2</sub>), 35.5 (Ar(CN)CH<sub>2</sub>), 34.0 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.5 ((NC)CH<sub>3</sub>), 21.6 (ArCH<sub>3</sub>).

**FTIR**: 1682, 1668, 1606, 1447, 1339, 1180 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 314.1516, C<sub>20</sub>H<sub>21</sub>NNaO requires 314.1515.

#### Triethylammonium tetra(thiophen-2-yl)borate



**General Procedure D**: Sodium tetra(thiophen-2-yl)borate (1.00 g, 2.73 mmol), 24 mL H<sub>2</sub>O:MeOH (1:1) and Et<sub>3</sub>N (4.10 mmol) were employed. The precipitate was filtered and washed with H<sub>2</sub>O (26 mL) to afford the title compound (0.75 g, 65%) as a pale yellow solid.

**M.P.** : 131-133 °C (MeOH:H<sub>2</sub>O).

**<sup>1</sup>H NMR** (400 MHz, d<sub>6</sub>-acetone): 7.09-7.04 (m, 4H, H<sub>3</sub>), 6.89-6.82 (m, 8H, H<sub>1</sub> and H<sub>2</sub>), 3.37 (q, *J* = 7.5 Hz, 6H, <sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.35 (t, *J* = 7.5 Hz, 9H, <sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

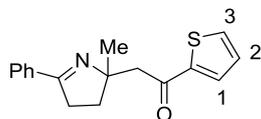
**<sup>13</sup>C NMR** (100 MHz, d<sub>6</sub>-acetone): 166.3 (q, *J* = 54.5 Hz, B-C), 129.6-129.5 (m, C<sub>1</sub>), 126.4-126.3 (m, C<sub>2</sub>), 123.9-123.8 (m, C<sub>3</sub>), 48.2 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 9.5 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

**<sup>11</sup>B NMR** (128 MHz, d<sub>6</sub>-acetone): -14.0.

**FTIR**: 3094, 1470, 1388, 1211, 1004 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [A<sub>1</sub>]<sup>+</sup>: 342.9920, C<sub>16</sub>H<sub>12</sub>BO<sub>4</sub> requires 342.9923.

## 2-(2-Methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1-(thiophen-2-yl)ethan-1-one (12c)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with  $\text{Pd}_2(\text{dba})_3$  (6.0 mg,  $6.5 \times 10^{-3}$  mmol),  $\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$  (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and triethylammonium tetra(thiophen-2-yl)borate (75.5 mg, 0.170 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 10:1 to 8:1) afforded imine **12c** (22.0 mg, 60%) as a pale yellow oil.

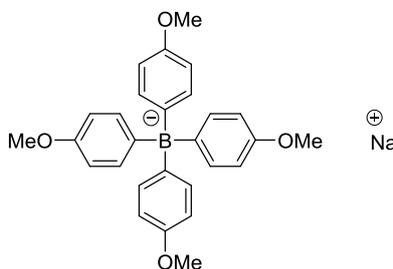
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ): 7.82-7.75 (m, 3H, ArH), 7.61 (dd,  $J = 5.0$  and 1.0 Hz, 1H, H1), 7.46-7.36 (m, 3H, 2 × ArH and H3), 7.10 (dd,  $J = 5.0$  and 5.0 Hz, 1H, H2), 3.42 (d,  $J = 15.0$  Hz, 1H, (CO)CH<sub>2</sub>), 3.20 (d,  $J = 15.0$  Hz, 1H, (CO)CH<sub>2</sub>), 3.11-3.03 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.40-2.28 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.08-1.97 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.47 (s, 3H, (NC)CH<sub>3</sub>).

**$^{13}\text{C NMR}$**  (125 MHz,  $\text{CDCl}_3$ ): 191.9 (C=O), 171.4 (C=N), 145.6, 134.3 (2 × ArC), 133.7 (C1), 132.8 (ArCH), 130.6 (C3), 128.4 (ArCH), 128.0 (C2), 127.8 (ArCH), 75.1 (quaternary C), 49.8 ((CO)CH<sub>2</sub>), 35.5 (Ar(CN)CH<sub>2</sub>), 33.9 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6 ((NC)CH<sub>3</sub>).

**FTIR**: 2963, 1649, 1614, 1412  $\text{cm}^{-1}$ .

**MS**: (ESI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 284.1104,  $\text{C}_{17}\text{H}_{18}\text{NOS}$  requires 284.1103.

### Sodium tetrakis(4-methoxyphenyl)borate



**General Procedure C**: 4-Bromoanisole (7.51 mL, 60.00 mmol) and sodium tetrafluoroborate (1.09 g, 10.00 mmol) were employed and the reaction was stirred at room temperature for 48 hours. The title compound was obtained (4.62 g, 60%) as a colorless solid.

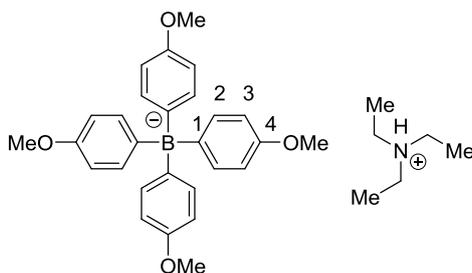
**M.P.**: > 220 °C (acetone).

**$^1\text{H NMR}$**  (400 MHz,  $d_6$ -acetone): 7.23-7.15 (m, 8H, ArH), 6.57-6.50 (m, 8H, ArH), 3.65 (s, 12H, CH<sub>3</sub>).

**$^{13}\text{C NMR}$**  (100 MHz,  $d_6$ -acetone): 156.5 (q,  $J = 50.5$  Hz, B-C), 155.3 (ArC), 137.5 (q,  $J = 1.5$  Hz, ArCH), 111.8 (q,  $J = 3.0$  Hz, ArCH), 55.0 (CH<sub>3</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>24</sup>

### Triethylammonium tetrakis(4-methoxyphenyl)borate



**General Procedure D:** Sodium tetrakis(4-methoxyphenyl)borate (0.55 g, 1.19 mmol), 4 mL H<sub>2</sub>O:MeOH (1:1) and Et<sub>3</sub>N (1.77 mmol) were employed. The precipitate was filtered and washed with H<sub>2</sub>O (10 mL) to afford the title compound (0.48 g, 74%) as a colorless solid.

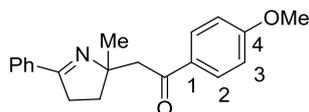
**M.P.:** 105-107 °C (MeOH:H<sub>2</sub>O). [Lit. 106-109 °C (MeOH:H<sub>2</sub>O)].

**$^1\text{H NMR}$**  (400 MHz,  $d_6$ -acetone): 7.24-7.12 (m, 8H, ArH), 6.57-6.52 (m, 8H, ArH), 3.65 (s, 12H, CH<sub>3</sub>), 3.46 (q,  $J = 7.5$  Hz, 6H, <sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.40 (t,  $J = 7.5$  Hz, 9H, <sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

**$^{13}\text{C NMR}$**  (100 MHz,  $d_6$ -acetone): 156.0 (q,  $J = 50.5$  Hz, B-C1), 156.3 (C4), 137.5 (q,  $J = 1.5$  Hz, C2), 111.8 (q,  $J = 3.0$  Hz, C3), 55.0 (OCH<sub>3</sub>), 48.1 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 9.5 (<sup>+</sup>NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>3</sup>

### 1-(4-Methoxyphenyl)-2-(2-methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethan-1-one (12d)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and triethylammonium tetrakis(4-methoxyphenyl)borate (91.0 mg, 0.169 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a

CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 12:1 to 3:1) afforded imine **12d** (22.0 mg, 55%) as a pale yellow oil.

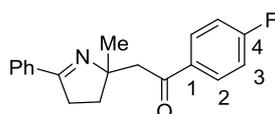
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.01-7.95 (m, 2H, ArH), 7.81-7.75 (m, 2H, ArH), 7.45-7.35 (m, 3H, ArH), 6.93-6.87 (m, 2H, ArH), 3.86 (s, 3H, OCH<sub>3</sub>), 3.47 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.24 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.14-2.98 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.34-2.24 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.10-1.99 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.46 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 197.7 (C=O), 171.3 (C=N), 163.3 (C<sub>4</sub>), 134.2 (ArC), 131.0 (C<sub>1</sub>), 130.7, 130.6, 128.4, 127.9, (4 × ArCH), 113.5 (C<sub>3</sub>), 75.2 (quaternary C), 55.4 (OCH<sub>3</sub>), 48.6 ((CO)CH<sub>2</sub>), 35.5 (Ar(CN)CH<sub>2</sub>), 33.9 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.5 ((NC)CH<sub>3</sub>).

**FTIR**: 1675, 1598, 1256, 1169 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 308.1640, C<sub>20</sub>H<sub>22</sub>NO<sub>2</sub> requires 308.1645.

#### 1-(4-Fluorophenyl)-2-(2-methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethan-1-one (**12e**)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and triethylammonium tetrakis(4-fluorophenyl)borate (84.0 mg, 0.17 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. The mixture was then placed in a preheated oil bath at 80 °C for 10 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 7:1 to 5:1) afforded imine **12e** (12.0 mg, 32%) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 8.05-7.99 (m, 2H, ArH), 7.79-7.71 (m, 1H, ArH), 7.50-7.35 (m, 4H, ArH), 7.09 (t, *J* = 8.5 Hz, 2H, ArH), 3.43 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.29 (d, *J* = 15.5 Hz, 1H, (CO)CH<sub>2</sub>), 3.13-2.97 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.31-2.22 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.10-2.02 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.45 ((NC)CH<sub>3</sub>).

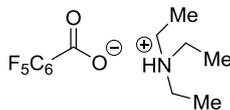
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 197.7 (C=O), 167.4 (C=N), 165.6 (d, *J* = 254.0 Hz, C<sub>4</sub>), 134.3 (d, *J* = 3.0 Hz, C<sub>1</sub>), 133.6 (ArC), 131.2 (d, *J* = 9.5 Hz, C<sub>2</sub>), 128.7, 128.4, 127.7 (3 × ArCH), 115.4 (d, *J* = 22.0 Hz, C<sub>3</sub>), 75.2 (quaternary C), 49.1 ((CO)CH<sub>2</sub>), 35.5 (Ar(CN)CH<sub>2</sub>), 34.0 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6 ((NC)CH<sub>3</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -105.8.

**FTIR:** 2933, 1680, 1660, 1603, 1508, 1317, 1231, 1200  $\text{cm}^{-1}$ .

**MS:** (ESI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 296.1447,  $\text{C}_{19}\text{H}_{19}\text{FNO}$  requires 296.1145.

### Triethylammonium 2,3,4,5,6-pentafluorobenzoate



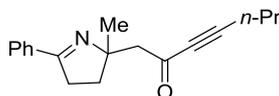
To a solution of 2,3,4,5,6-pentafluorobenzoic acid (0.30 g, 1.41 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (3 mL) was added  $\text{Et}_3\text{N}$  (0.20 mL, 1.41 mmol) dropwise and stirred at room temperature for 30 minutes. The reaction was concentrated *in vacuo* and dried under high vacuum for 1 hour to afford the title compound (0.40 g, 91%) as colorless solid. *N.B. This compound is highly hygroscopic and so it was stored under nitrogen.*

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ): 13.25 (s, 1H,  $\text{Et}_3\text{NH}^+$ ), 3.16 (q,  $J = 7.5$  Hz, 6H,  $^+\text{NH}(\text{CH}_2\text{CH}_3)_3$ ), 1.36 (t,  $J = 7.5$  Hz, 9H,  $^+\text{NH}(\text{CH}_2\text{CH}_3)_3$ ).

**<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ ): 45.4 ( $^+\text{NH}(\text{CH}_2\text{CH}_3)_3$ ), 8.5 ( $^+\text{NH}(\text{CH}_2\text{CH}_3)_3$ ). *No signals corresponding to the perfluorobenzoyl ester moiety were observed due to the anticipated weak intensity of these signals.*

**<sup>19</sup>F NMR** (376 MHz,  $\text{CDCl}_3$ ): -142.9 (2F), -157.8 (1F), -162.7 (2F).

### 1-(2-Methyl-5-phenyl-3,4-dihydro-2H-pyrr-2-yl)hept-3-yn-2-one (12f)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with  $\text{Pd}_2(\text{dba})_3$  (6.0 mg,  $6.5 \times 10^{-3}$  mmol),  $\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$  (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol), 1-pentynylboronic acid pinacol ester (56.0  $\mu\text{l}$ , 0.261 mmol) and pentafluorobenzoic acid (6.6 mg, 0.026 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) and  $\text{Et}_3\text{N}$  (4.0  $\mu\text{l}$ , 0.026 mmol) were added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80  $^\circ\text{C}$  for 13 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 10:1) afforded imine **12f** (17.5 mg, 51%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ): 7.85 (d,  $J = 6.5$  Hz, 2H, ArH), 7.50-7.35 (m, 3H, ArH), 3.10-2.97 (m, 3H, Ar(CN)CH<sub>2</sub> and (CO)CH<sub>2</sub>), 2.90 (d,  $J = 14.5$  Hz, 1H, (CO)CH<sub>2</sub>), 2.29-2.16 (m, 3H,  $\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$  and Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.97-1.88 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.59-1.48 (m, 2H,  $\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$ ), 1.43 (s, 3H, (NC)CH<sub>3</sub>), 0.96 (t,  $J = 7.5$  Hz, 3H,  $\text{C}\equiv\text{C}(\text{CH}_2)_2\text{CH}_3$ ).

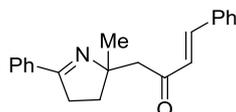
**<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ ): 186.4 ( $\text{C}=\text{O}$ ), 171.6 ( $\text{C}=\text{N}$ ), 133.9 (ArC), 130.9, 128.4, 128.1 ( $3 \times \text{ArCH}$ ), 94.6 ( $(\text{CO})\text{C}\equiv\text{CCH}_2$ ), 82.3 ( $(\text{CO})\text{C}\equiv\text{CH}_2$ ), 74.8 (quaternary C), 55.9 ( $(\text{CO})\text{CH}_2$ ),

35.5 (Ar(CN)CH<sub>2</sub>), 33.6 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6 ((NC)CH<sub>3</sub>), 21.2, 20.9 (C≡CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.5 (C≡C(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>).

**FTIR:** 2964, 2932, 2211, 1662, 1448, 1339, 1280 cm<sup>-1</sup>.

**MS:** (CI<sup>+</sup>) Found [M+H]<sup>+</sup>: 268.1700, C<sub>18</sub>H<sub>22</sub>NO requires 268.1701.

**(E)-1-(2-Methyl-5-phenyl-3,4-dihydro-2H-pyrr-2-yl)-4-phenylbut-3-en-2-one (12g)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol), trans-2-phenylvinylboronic acid pinacol ester (60.0 mg, 0.260 mmol) and pentafluorobenzoic acid (6.6 mg, 0.026 mmol) The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) and Et<sub>3</sub>N (4.0 μl, 0.026 mmol) were added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 12 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 50:1 to 5:1) afforded imine **12g** (23.0 mg, 59%) as a colorless oil. *The presence of additional Et<sub>3</sub>N.HO<sub>2</sub>CC<sub>6</sub>F<sub>5</sub> did not provide a significant increase the yield of the reaction, for example, with 50 mol% of this additive a yield of 58% was obtained.*

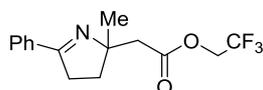
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.81 (d, *J* = 7.5 Hz, 2H, ArH), 7.55 (d, *J* = 16.0 Hz, 1H, HC=CHAr), 7.52-7.29 (m, 8H, ArH), 6.81 (d, *J* = 16.0 Hz, 1H, HC=CHAr), 3.14-2.92 (m, 4H, Ar(CN)CH<sub>2</sub> and (CO)CH<sub>2</sub>), 2.30-2.17 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.02-1.91 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.44 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 199.4 (C=O), 171.0 (C=N), 142.5 (HC=CHAr), 134.6, 134.5 (2 × ArC), 130.4, 130.3, 128.8, 128.4, 128.3, 127.7 (6 × ArCH), 127.4 (HC=CHAr), 75.4 (quaternary C), 52.1 ((CO)CH<sub>2</sub>), 35.5 (Ar(CN)CH<sub>2</sub>), 33.9 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.8 ((NC)CH<sub>3</sub>).

**FTIR:** 1680, 1606, 1447, 1334 cm<sup>-1</sup>.

**MS:** (CI<sup>+</sup>) Found [M+H]<sup>+</sup>: 304.1697 C<sub>21</sub>H<sub>22</sub>NO requires 304.1701.

**2,2,2-Trifluoroethyl 2-(2-methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)acetate (13a)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) and oxime ester **6a** (50.0 mg, 0.130 mmol). The tube was fitted with a rubber septum and purged with argon.

Anhydrous DMF (0.5 mL), 2,2,2-Trifluoroethanol (19.0  $\mu$ L, 0.261 mmol), Et<sub>3</sub>N (36.0  $\mu$ L, 0.261 mmol) were added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 5 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 8:1) afforded imine **13a** (26.0 mg, 66%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.85-7.79 (m, 2H, ArH), 7.47-7.37 (m, 3H, ArH), 4.46 (q, *J* = 8.5 Hz, 2H, CH<sub>2</sub>CF<sub>3</sub>), 3.09 (t, *J* = 8.0 Hz, 2H, Ar(CN)CH<sub>2</sub>), 2.86 (d, *J* = 14.5 Hz, 1H, (CO)CH<sub>2</sub>), 2.74 (d, *J* = 14.5 Hz, 1H, (CO)CH<sub>2</sub>), 2.27-2.17 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.00-1.89 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.42 (s, 3H, (NC)CH<sub>3</sub>).

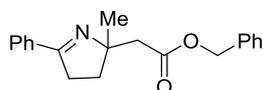
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.4 (C=N), 169.7 (C=O), 134.4 (ArC), 130.5, 128.4, 127.8 (3 × ArCH), 123.0 (q, *J* = 277.0 Hz, CF<sub>3</sub>), 74.4 (quaternary C), 60.0 (q, *J* = 36.5 Hz, CH<sub>2</sub>CF<sub>3</sub>), 45.4 ((CO)CH<sub>2</sub>), 35.4 (Ar(CN)CH<sub>2</sub>), 33.8 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.3 ((NC)CH<sub>3</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): -73.7 (t, *J* = 8.5 Hz).

**FTIR**: 2970, 1754, 1279, 1161, 1109 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 300.1209, C<sub>15</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>2</sub> requires 300.1206.

### Benzyl 2-(2-methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)acetate (**13b**)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL), benzyl alcohol (27.0  $\mu$ L, 0.261 mmol) and Et<sub>3</sub>N (36.0  $\mu$ L, 0.26 mmol) were added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 6 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 5:1 to 3:1) afforded imine **13b** (24.0 mg, 60%) as a colorless oil.

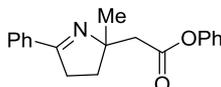
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.85-7.78 (m, 2H, ArH), 7.47-7.37 (m, 3H, ArH), 7.34-7.26 (m, 5H, ArH), 5.11 (s, 2H, ArCH<sub>2</sub>O(CO)), 3.12-2.96 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.82 (d, *J* = 14.0 Hz, 1H, (CO)CH<sub>2</sub>), 2.74 (d, *J* = 14.0 Hz, 1H, (CO)CH<sub>2</sub>), 2.32-2.21 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.95-1.85 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.42 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.2 (2 signals) (C=N and C=O), 135.9, 134.2 ((2 × ArC), 130.7, 128.5, 128.4, 128.2, 128.1, 127.9 (6 × ArCH), 74.5 (quaternary C), 45.9 ((CO)CH<sub>2</sub>), 35.4 (Ar(CN)CH<sub>2</sub>), 33.7 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6 ((NC)CH<sub>3</sub>).

**FTIR:** 2963, 1733  $\text{cm}^{-1}$ .

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 308.1649, C<sub>20</sub>H<sub>22</sub>NO<sub>2</sub> requires 308.1645.

**Phenyl 2-(2-methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)acetate (13c)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol) and phenol (37.0 mg, 0.392 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 4 hours 30 minutes. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 5:1 to 2:1) afforded imine **13c** (24.5 mg, 65%) as a colorless oil.

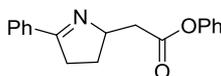
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.89-7.84 (m, 2H, ArH), 7.48-7.39 (m, 3H, ArH), 7.38-7.31 (m, 2H, ArH), 7.24-7.17 (m, 1H, ArH), 7.07-7.01 (m, 2H, ArH), 3.16-3.08 (m, 2H, Ar(CN)CH<sub>2</sub>), 3.00 (d, *J* = 14.0 Hz, 1H, (CO)CH<sub>2</sub>), 2.92 (d, *J* = 14.0 Hz, 1H, (CO)CH<sub>2</sub>), 2.44-2.32 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.08-1.94 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.52 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.5 (C=N), 170.0 (C=O), 150.6, 134.3 (2 × ArC), 130.6, 129.4, 128.4, 127.9, 125.7, 121.6 (6 × ArCH), 74.7 (quaternary C), 45.9 ((CO)CH<sub>2</sub>), 35.6 (Ar(CN)CH<sub>2</sub>), 33.8 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.7 ((NC)CH<sub>3</sub>).

**FTIR:** 2966, 1755, 1492, 1189  $\text{cm}^{-1}$ .

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 294.1493, C<sub>19</sub>H<sub>20</sub>NO<sub>2</sub> requires 294.1489.

**Phenyl 2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)acetate (13d)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.2 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (18.0 mg, 0.026 mmol), oxime ester **6h** (50.0 mg, 0.136 mmol) and phenol (26.0 mg, 0.272 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.5 mL) was added *via* syringe. CO was bubbled through the mixture for 2 minutes and a CO atmosphere (balloon pressure) was then maintained for the remainder of the reaction. Anhydrous DMF (0.5 mL) was added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 10:1 to 5:1) afforded imine **13d** (22.0 mg, 58%) as a pale yellow oil.

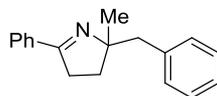
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.92-7.85 (m, 2H, ArH), 7.49-7.32 (m, 5H, ArH), 7.27-7.19 (m, 1H, ArH), 7.15-7.08 (m, 2H, ArH), 4.78-4.67 (m, 1H, (CO)CH<sub>2</sub>CH), 3.23-3.09 (m, 2H, (CO)CH<sub>2</sub>CH and Ar(CN)CH<sub>2</sub>), 3.05-2.93 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.78 (dd, *J* = 15.5 and 8.5 Hz, 1H, (CO)CH<sub>2</sub>CH), 2.49-2.37 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.90-1.77 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 173.6 (C=N), 170.3 (C=O), 150.7, 134.3 (2 × ArC), 130.8, 129.4, 128.5, 127.9, 125.8, 121.6 (6 × ArCH), 69.3 ((CO)CH<sub>2</sub>CH) 41.1 ((CO)CH<sub>2</sub>), 35.3 (Ar(CN)CH<sub>2</sub>), 28.5 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**FTIR**: 1755, 1492, 1338, 1195 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 302.1151, C<sub>18</sub>H<sub>17</sub>NNaO<sub>2</sub> requires 302.1151.

### 2-Benzyl-2-methyl-5-phenyl-3,4-dihydro-2H-pyrrole (14a)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and phenylboronic acid pinacol ester (53.0 mg, 0.261 mmol) were employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (36.0 μl, 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (× 2; 1<sup>st</sup> column: toluene:EtOAc 40:1 to 10:1; 2<sup>nd</sup> column: hexane:EtOAc 20:1 to 10:1) afforded imine **14a** (17.0 mg, 53%) as a pale yellow oil.

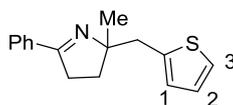
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.81 (d, *J* = 7.0 Hz, 2H, ArH), 7.47-4.36 (m, 3H, ArH), 7.25-7.13 (m, 5H, ArH), 3.07 (d, *J* = 13.0 Hz, 1H, ((NC)CH<sub>2</sub>Ar), 2.93-2.81 (m, 2H, ((NC)CH<sub>2</sub>Ar and Ar(CN)CH<sub>2</sub>), 2.40-2.28 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.13-2.01 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.78-1.65 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.43 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 171.3 (C=N), 138.4, 134.4 (2 × ArC), 130.6, 130.5, 128.4, 127.8 (2 signals), 126.0 (6 × ArCH), 76.6 (quaternary C), 47.7 ((NC)CH<sub>2</sub>Ar), 35.4 (Ar(CN)CH<sub>2</sub>), 33.2 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 28.1 ((NC)CH<sub>3</sub>).

**FTIR**: 2961, 1615, 1494, 1448, 1338 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 250.1605, C<sub>18</sub>H<sub>20</sub>N requires 250.1590.

### 2-Methyl-5-phenyl-2-(thiophen-2-yl)methyl-3,4-dihydro-2H-pyrrole (14b)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and thiophene-2-boronic acid pinacol ester (55.0 mg, 0.261 mmol) were employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (36.0 μl, 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 40:1 to 15:1) afforded imine **14b** (23.5 mg, 71%) as a pale yellow oil.

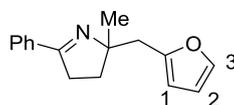
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.87-7.80 (m, 2H, ArH), 7.48-7.37 (m, 3H, ArH), 7.11 (dd, *J* = 5.0 and 1.0 Hz, 1H, H<sub>3</sub>), 6.89 (dd, *J* = 5.0 and 3.5 Hz, 1H, H<sub>2</sub>), 6.83 (d, *J* = 3.5 Hz, 1H, H<sub>1</sub>), 3.26 (d, *J* = 14.5 Hz, 1H, (NC)CH<sub>2</sub>C(S)), 3.14 (d, *J* = 14.5 Hz, 1H, (NC)CH<sub>2</sub>C(S)), 3.03-2.90 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.64-2.52 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.12-2.00 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.83-1.71 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.42 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 171.4 (C=N), 140.4, 134.8 (2 × ArC), 130.3, 128.3, 127.7 (3 × ArCH), 126.9 (C<sub>1</sub>), 126.2 (C<sub>2</sub>), 124.3 (C<sub>3</sub>), 76.3 (quaternary C), 42.1 ((NC)CH<sub>2</sub>C(S)), 35.7 (Ar(CN)CH<sub>2</sub>), 33.1 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.8 ((NC)CH<sub>3</sub>).

**FTIR**: 2924, 1617, 1448, 1278, 1138 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 256.1163, C<sub>16</sub>H<sub>18</sub>NS requires 256.1154.

## 2-(Furan-2-ylmethyl)-2-methyl-5-phenyl-3,4-dihydro-2H-pyrrole (**14c**)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and furan-2-boronic acid pinacol ester (51.0 mg, 0.261 mmol) were employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (36.0 μl, 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 40:1 to 15:1) afforded imine **14c** (22.5 mg, 72%) as a pale yellow oil.

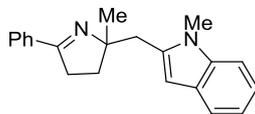
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.83-7.77 (m, 2H, ArH), 7.46-7.37 (m, 3H, ArH), 7.32-7.29 (m, 1H, H<sub>3</sub>), 6.26 (dd, *J* = 3.0 and 2.0 Hz, 1H, H<sub>2</sub>), 6.02 (d, *J* = 3.0 Hz, 1H, H<sub>1</sub>), 3.04-2.88 (m, 3H, (NC)CH<sub>2</sub>C(O) and Ar(CN)CH<sub>2</sub>), 2.69-2.57 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.20-2.10 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.79-1.69 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.40 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 171.0 (C=N), 153.3 (ArC), 141.1 (C<sub>3</sub>), 134.8 (ArC), 130.2, 128.3, 127.7 (3 × ArCH), 110.3 (C<sub>2</sub>), 107.5 (C<sub>1</sub>), 76.1 (quaternary C), 39.8 ((NC)CH<sub>2</sub>C(O)), 35.4 (Ar(CN)CH<sub>2</sub>), 33.6 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6 ((NC)CH<sub>3</sub>).

**FTIR:** 2962, 2924, 1616, 1448, 1339, 1147, 1011  $\text{cm}^{-1}$ .

**MS:** (ESI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 240.1393,  $\text{C}_{16}\text{H}_{18}\text{NO}$  requires 240.1383.

**1-Methyl-2-((2-methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1H-indole (14d)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with  $\text{Pd}_2(\text{dba})_3$  (6.0 mg,  $6.5 \times 10^{-3}$  mmol),  $\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$  (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and 1-methyl-2-indoleboronic acid pinacol ester (67.0 mg, 0.261 mmol) were employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and  $\text{Et}_3\text{N}$  (36.0  $\mu\text{l}$ , 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 10:1 to 8:1) afforded imine **14d** (25.0 mg, 64%) as a pale yellow oil.

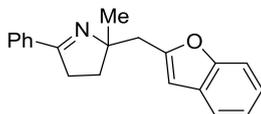
**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ): 7.81-7.74 (m, 2H, ArH), 7.54 (dt,  $J = 7.5$  and 1.0 Hz, 1H, ArH), 7.45-7.35 (m, 3H, ArH), 7.22 (dt,  $J = 7.5$  and 1.0 Hz, 1H, ArH), 7.14 (td,  $J = 8.0$  and 1.0 Hz, 1H, ArH), 7.07 (td,  $J = 8.0$  and 1.0 Hz, 1H, ArH), 6.36 (s, 1H,  $(\text{NC})\text{CH}_2\text{C}=\text{CH}$ ), 3.71 (s, 3H,  $\text{NCH}_3$ ), 3.24 (d,  $J = 14.5$  Hz, 1H,  $(\text{NC})\text{CH}_2\text{Ar}$ ), 3.10 (d,  $J = 14.5$  Hz, 1H,  $(\text{NC})\text{CH}_2\text{Ar}$ ), 2.96- 2.85 (m, 1H,  $\text{Ar}(\text{CN})\text{CH}_2$ ), 2.65-2.53 (m, 1H,  $\text{Ar}(\text{CN})\text{CH}_2$ ), 2.26-2.16 (m, 1H,  $\text{Ar}(\text{CN})\text{CH}_2\text{CH}_2$ ), 1.91-1.80 (m, 1H,  $\text{Ar}(\text{CN})\text{CH}_2\text{CH}_2$ ), 1.46 (s, 3H,  $(\text{NC})\text{CH}_3$ ).

**<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ ): 170.8 ( $\text{C}=\text{N}$ ), 137.8, 137.4, 134.6 ( $3 \times \text{ArC}$ ), 130.3, 128.4 ( $2 \times \text{ArCH}$ ), 127.8 ( $\text{ArC}$ ), 127.6, 120.5, 119.7, 119.1, 109.1 ( $5 \times \text{ArCH}$ ), 101.7 ( $(\text{NC})\text{CH}_2\text{C}=\text{CH}$ ), 76.8 (quaternary C), 38.5 ( $(\text{NC})\text{CH}_2\text{Ar}$ ), 35.3 ( $\text{Ar}(\text{CN})\text{CH}_2$ ), 33.6 ( $\text{Ar}(\text{CN})\text{CH}_2\text{CH}_2$ ), 30.2 ( $\text{NCH}_3$ ), 28.1 ( $(\text{NC})\text{CH}_3$ ).

**FTIR:** 2960, 2925, 1614, 1467, 1447, 1139  $\text{cm}^{-1}$ .

**MS:** (ESI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 303.1855,  $\text{C}_{21}\text{H}_{23}\text{N}_2$  requires 303.1856.

**2-(Benzofuran-2-ylmethyl)-2-methyl-5-phenyl-3,4-dihydro-2H-pyrrole (14e)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with  $\text{Pd}_2(\text{dba})_3$  (6.0 mg,  $6.5 \times 10^{-3}$  mmol),  $\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$  (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and benzofuran-2-boronic acid pinacol ester (64.0 mg, 0.261 mmol) were employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and  $\text{Et}_3\text{N}$  (36.0  $\mu\text{l}$ , 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room

temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 30:1 to 15:1) afforded imine **14e** (27.0 mg, 71%) as a pale yellow oil.

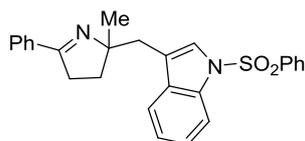
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.82 (d, *J* = 8.0 and 2.0 Hz, 2H, ArH), 7.51-7.35 (m, 5H, ArH), 7.31-7.12 (m, 2H, ArH), 6.45 (s, 1H, HC=C(O)), 3.16 (d, *J* = 14.0 Hz, 1H, (NC)CH<sub>2</sub>Ar), 3.09 (d, *J* = 14.0 Hz, 1H, (NC)CH<sub>2</sub>Ar), 3.04-2.93 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.83-2.71 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.30-2.19 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.86-1.75 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.44 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.1 (C=N), 156.5, 154.7, 134.7 (3 × ArC), 130.4 (ArCH), 128.9 (ArC), 128.4, 127.7, 123.2, 122.4, 120.3, 110.8 (6 × ArCH), 104.6 (HC=C(O)), 76.1 (quaternary C), 40.4 ((NC)CH<sub>2</sub>Ar), 34.5 (Ar(CN)CH<sub>2</sub>), 33.7 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.5 ((NC)CH<sub>3</sub>).

**FTIR**: 1616, 1454, 1253 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 290.1541 C<sub>20</sub>H<sub>20</sub>NO requires 290.1539.

### 3-((2-Methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-(phenylsulfonyl)-1H-indole (**14f**)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and 1-(phenylsulfonyl)-3-indolylboronic acid pinacol ester (100.0 mg, 0.261 mmol) were employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (36.0 μl, 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 75 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 30:1 to 10:1) afforded imine **14f** (34.0 mg, 62%) as a pale yellow oil.

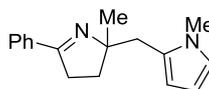
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.95 (dt, *J* = 8.0 and 1.0 Hz, 1H, ArH), 7.78-7.69 (m, 4H, ArH), 7.57 (dt, *J* = 8.0 and 1.0 Hz, 1H, ArH), 7.46-7.36 (m, 5H, ArH), 7.29-7.23 (m, 3H, ArH), 7.18 (td, *J* = 8.0 and 1.0 Hz, 1H, ArH), 3.08 (dd, *J* = 14.5 and 1.0 Hz, 1H, (NC)CH<sub>2</sub>Ar), 2.98 (d, *J* = 14.5 Hz, 1H, (NC)CH<sub>2</sub>Ar), 2.94-2.81 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.49-2.37 (m, 1H, Ar(CN)CH<sub>2</sub>), 1.96-1.84 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.78-1.68 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.38 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 170.6 (C=N), 138.2, 134.9, 134.6 (3 × ArC), 133.5 (ArCH), 132.1 (ArC), 130.4, 129.0, 128.4, 127.6, 126.6, 124.8, 124.4, 123.0, 120.4 (9 × ArCH), 119.9 (ArC), 113.5 (ArCH), 76.5 (quaternary C), 36.6 ((NC)CH<sub>2</sub>Ar), 35.5 (Ar(CN)CH<sub>2</sub>), 33.4 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.9 ((NC)CH<sub>3</sub>).

**FTIR**: 1616, 1447, 1364, 1175, 1119 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 429.1630, C<sub>26</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>S requires 429.1631.

**1-Methyl-2-((2-methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1H-pyrrole (14g)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol) oxime ester **6a** (50.0 mg, 0.130 mmol) and 1-methyl-2-pyrroleboronic acid pinacol ester (54.0 mg, 0.261 mmol) were employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (36.0 μl, 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane:EtOAc 12:1 to 5:1) afforded imine **14g** (19.5 mg, 60%) as a pale yellow oil.

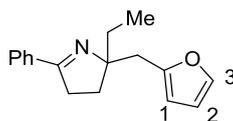
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.82-7.73 (m, 2H, ArH), 7.45-7.34 (m, 3H, ArH), 6.45 (dd, *J* = 2.5 Hz and 2.5 Hz, 1H, ArH), 6.02 (dd, *J* = 2.5 Hz and 2.5 Hz, 1H, ArH), 5.98-5.94 (m, 1H, ArH), 3.53 (s, 3H, NCH<sub>3</sub>), 2.98 (d, *J* = 15.0 Hz, 1H, (NC)CH<sub>2</sub>Ar), 2.92-2.82 (m, 2H, (NC)CH<sub>2</sub>Ar) and Ar(CN)CH<sub>2</sub>), 2.57-2.46 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.19-2.09 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.84-1.73 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.42 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 170.6 (C=N), 134.7 (ArC), 130.2 (ArCH), 129.8 (ArC), 128.3, 127.6, 121.5, 108.3, 106.5 (5 × ArCH), 77.0 (quaternary C), 38.0 ((NC)CH<sub>2</sub>Ar), 35.3 (Ar(CN)CH<sub>2</sub>), 34.2 (NCH<sub>3</sub>), 33.7 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 28.1 ((NC)CH<sub>3</sub>).

**FTIR:** 1616, 1493, 1448, 1339, 1301 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 253.1698 C<sub>17</sub>H<sub>21</sub>N<sub>2</sub> requires 253.1699.

**2-Ethyl-2-(furan-2-ylmethyl)-5-phenyl-3,4-dihydro-2H-pyrrole (14h)**



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (5.8 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.0 mg, 0.025 mmol), oxime ester **6d** (50.0 mg, 0.126 mmol) and 2-furanboronic acid pinacol ester (49.0 mg, 0.252 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (36.0 μl, 0.252 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 40:1 to 20:1) afforded imine **14h** (22.5 mg, 70%) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.82 (d, *J* = 7.0 Hz, 2H, ArH), 7.51-7.35 (m, 3H, ArH), 7.28 (s, 1H, H<sub>3</sub>), 6.24 (s, 1H, H<sub>2</sub>), 6.00 (s, 1H, H<sub>1</sub>), 3.02 (d, *J* = 14.5 Hz, 1H, (NC)CH<sub>2</sub>C(O)),

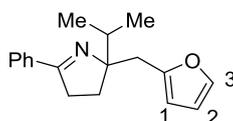
2.96 (d,  $J = 14.5$  Hz, 1H, (NC)CH<sub>2</sub>C(O)), 2.93-2.80 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.62-2.48 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.11-1.99 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.92-1.67 (m, 3H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub> and CH<sub>2</sub>CH<sub>3</sub>), 0.94 (t,  $J = 8.0$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.4 (C=N), 153.2 (ArC), 141.0 (C3), 134.7 (ArC), 130.3, 128.3, 127.7 (3 × ArCH), 110.4 (C2), 107.6 (C1), 79.5 (quaternary C), 38.4 (NC)CH<sub>2</sub>C(O)), 35.8 (Ar(CN)CH<sub>2</sub>), 33.3 (CH<sub>2</sub>CH<sub>3</sub>), 30.1 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 8.6 (CH<sub>2</sub>CH<sub>3</sub>).

**FTIR**: 2964, 1619, 1447, 1341, 1146 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 254.1538, C<sub>17</sub>H<sub>20</sub>NO requires 254.1539.

### 2-(Furan-2-ylmethyl)-2-isopropyl-5-phenyl-3,4-dihydro-2H-pyrrole (14i)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (5.7 mg, 6.5 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (16.5 mg, 0.024 mmol), oxime ester **6e** (50.0 mg, 0.121 mmol) and 2-furanboronic acid pinacol ester (47.0 mg, 0.242 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.95 mL) and Et<sub>3</sub>N (34.0 μl, 0.242 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 40:1 to 20:1) afforded imine **14i** (23.5 mg, 73%) as a pale yellow oil.

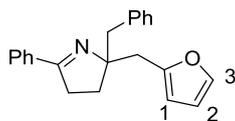
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.78 (d,  $J = 7.0$  Hz, 2H, ArH), 7.45-7.36 (m, 3H, ArH), 7.26 (dd,  $J = 2.0$  and 1.0 Hz, 1H, H3), 6.20 (dd,  $J = 3.0$  and 2.0 Hz, 1H, H2), 5.93 (dm,  $J = 3.0$  Hz, 1H, H1), 3.05 (d,  $J = 14.5$  Hz, 1H, (NC)CH<sub>2</sub>C(O)), 2.98 (d,  $J = 14.5$  Hz, 1H, (NC)CH<sub>2</sub>C(O)), 2.81-2.70 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.36-2.23 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.21-2.08 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.97-1.80 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.05 (d,  $J = 7.5$  Hz, 3H, (CH<sub>3</sub>)<sub>2</sub>), 0.93 (d,  $J = 7.5$  Hz, 3H, (CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.3 (C=N), 153.3 (ArC), 141.0 (C3), 134.7 (ArC), 130.2, 128.3, 127.7 (3 × ArCH), 110.5 (C2), 107.9 (C1), 82.7 (quaternary C), 36.5 (2 signals) (NC)CH<sub>2</sub>C(O)), and (CH<sub>3</sub>)<sub>2</sub>CH), 35.8 (Ar(CN)CH<sub>2</sub>), 27.2 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 17.9, 17.7 (CH<sub>3</sub>)<sub>2</sub>CH).

**FTIR**: 2961, 1621, 1448, 1340, 1147 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 268.1705, C<sub>18</sub>H<sub>22</sub>NO requires 268.1696.

## 2-Benzyl-2-(furan-2-ylmethyl)-5-phenyl-3,4-dihydro-2H-pyrrole (14j)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with  $\text{Pd}_2(\text{dba})_3$  (5.5 mg,  $6.5 \times 10^{-3}$  mmol),  $\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$  (16.0 mg, 0.024 mmol), oxime ester **6f** (55.0 mg, 0.120 mmol) and 2-furanboronic acid pinacol ester (46.0 mg, 0.240 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (0.92 mL) and  $\text{Et}_3\text{N}$  (33.0  $\mu\text{l}$ , 0.240 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 50:1 to 30:1) afforded imine **14j** (25.0 mg, 66%) as a pale yellow oil.

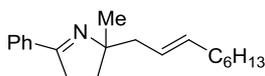
**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ): 7.74 (d,  $J = 7.0$  Hz, 2H, ArH), 7.47-7.35 (m, 3H, ArH), 7.33-7.31 (m, 1H, H3), 7.25-7.13 (m, 5H, ArH), 6.29-6.25 (m, 1H, H2), 6.06 (dm,  $J = 3.0$  Hz, 1H, H1), 3.21 (d,  $J = 14.0$  Hz, 1H, (NC)CH<sub>2</sub>C(O)), 3.12 (s, 2H, (NC)CH<sub>2</sub>Ar), 2.95 (d,  $J = 14.0$  Hz, 1H, (NC)CH<sub>2</sub>C(O)), 2.47-2.34 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.22-2.10 (m, 1H, Ar(CN)CH<sub>2</sub>), 2.05-1.86 (m, 2H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ ): 172.5 (C=N), 152.9 (ArC), 141.7 (C3), 137.9, 134.5 (2 × ArC), 130.8, 130.4, 128.4, 127.8, 127.7, 126.1 (6 × ArCH), 110.4 (C2), 108.0 (C1), 79.5 (quaternary C), 46.4 ((NC)CH<sub>2</sub>C(O)), 39.4 (CH<sub>2</sub>Ar), 35.8 (Ar(CN)CH<sub>2</sub>), 30.2 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>).

**FTIR**: 2916, 1618, 1494, 1451, 1280, 1144  $\text{cm}^{-1}$ .

**MS**: (ESI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 316.1683,  $\text{C}_{22}\text{H}_{22}\text{NO}$  requires 316.1696.

## (E)-2-Methyl-2-(non-2-en-1-yl)-5-phenyl-3,4-dihydro-2H-pyrrole (14k)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with  $\text{Pd}_2(\text{dba})_3$  (6.0 mg,  $6.5 \times 10^{-3}$  mmol),  $\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$  (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol), trans-1-octen-1-ylboronic acid pinacol ester (62.0 mg, 0.261 mmol) and pentafluorobenzoic acid (6.6 mg, 0.026 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and  $\text{Et}_3\text{N}$  (4.0  $\mu\text{l}$ , 0.026 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 50:1 to 30:1) afforded imine **14k** (23.5 mg, 64%) as a colorless oil. *The presence of additional  $\text{Et}_3\text{N} \cdot \text{HO}_2\text{CC}_6\text{F}_5$  did not provide a significant increase the yield of the reaction, for example, with 50 mol% of this additive a yield of 65% was obtained.*

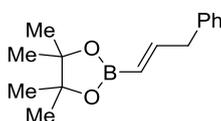
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.87-7.78 (m, 2H, ArH), 7.46-7.34 (m, 3H, ArH), 5.54-5.33 (m, 2H, HC=CH), 3.07-2.85 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.33 (d, *J* = 7.0 Hz, 2H, (NC)CH<sub>2</sub>CH=CH), 2.04-1.93 (m, 3H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub> and (NC)CH<sub>2</sub>CH=CHCH<sub>2</sub>), 1.76-1.65 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.38-1.17 (m, 11H, (NC)CH<sub>3</sub> and 4 × CH<sub>2</sub>), 0.87 (t, *J* = 7.0 Hz, 3H, HC=CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 170.1 (C=N), 134.9 (ArC), 133.9 (HC=CH), 130.1, 128.3, 127.7 (3 × ArCH), 126.0 (HC=CH), 76.2 (quaternary C), 45.1 ((NC)CH<sub>2</sub>CH=CH), 35.5 (Ar(CN)CH<sub>2</sub>), 33.2, 32.7 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub> and ((NC)CH<sub>2</sub>CH=CHCH<sub>2</sub>), 31.7, 29.5, 28.8 (3 × CH<sub>2</sub>), 27.5 ((NC)CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 14.1 (HC=CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>).

**FTIR**: 2924, 1617, 1448, 1279, 1142 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 284.2386 C<sub>20</sub>H<sub>30</sub>N requires 284.2373.

#### 4,4,5,5-Tetramethyl-2-[(*E*)-3-phenylpropenyl][1,3,2]dioxaborolane



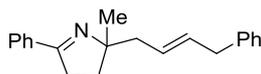
A mixture of pinacolborane (2.90 mL, 20.00 mmol), prop-2-ynylbenzene (2.49 g, 20.00 mmol), Cp<sub>2</sub>ZrHCl (0.15 g, 1.00 mmol) and Et<sub>3</sub>N (0.28 mL, 2.00 mmol) was heated at 40 °C for 14 hours. The reaction mixture was cooled to room temperature and the reaction quenched with H<sub>2</sub>O (30 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. FCC (hexane:EtOAc 20:1) afforded the title compound (3.51 g, 72 %) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.32-7.14 (m, 5H, ArH), 6.76 (dt, *J* = 18.0 and 6.5 Hz, 1H, HC=CHCH<sub>2</sub>Ar), 5.45 (d, *J* = 18.0 Hz, 1H, HC=CHCH<sub>2</sub>Ar), 3.48 (d, *J* = 6.5 Hz, 2H, HC=CHCH<sub>2</sub>Ar), 1.25 (s, 12H, 4 × CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 152.4 (HC=CHCH<sub>2</sub>Ar), 139.1 (ArC), 128.9, 128.4, 126.1 (3 × ArCH), 119.7 (br) (HC=CHCH<sub>2</sub>Ar), 83.1 (C(CH<sub>3</sub>)<sub>2</sub>), 42.3 (HC=CHCH<sub>2</sub>Ar), 24.8 (C(CH<sub>3</sub>)<sub>2</sub>).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>25</sup>

#### (*E*)-2-Methyl-5-phenyl-2-(4-phenylbut-2-en-1-yl)-3,4-dihydro-2H-pyrrole (14l)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5 × 10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol), 4,4,5,5-Tetramethyl-2-[(*E*)-3-phenylpropenyl]-[1,3,2]dioxaborolane (64.0 mg, 0.261 mmol) and pentafluorobenzoic acid (6.6 mg, 0.026 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (4.0 μL, 0.026

mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 50:1 to 30:1) afforded imine **14l** (23.0 mg, 62%) as a colorless oil.

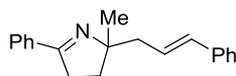
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.82 (d, *J* = 7.5 Hz, 2H, ArH), 7.46-7.36 (m, 3H, ArH), 7.28-7.09 (m, 5H, ArH), 5.71-5.45 (m, 2H, HC=CH), 3.33 (d, *J* = 6.5 Hz, 2H, (HC=CHCH<sub>2</sub>Ar), 3.07-2.80 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.45-2.30 (m, 2H, (NC)CH<sub>2</sub>CH=CH), 2.04-1.91 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.79-1.63 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.33 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 170.2 (C=N), 140.8, 134.8 (2 × ArC), 132.2 (ArCH), 132.0 (HC=CHCH<sub>2</sub>Ar), 128.4, 128.3 (2 signals) (3 × ArCH), 127.7, 127.9 (ArCH and HC=CHCH<sub>2</sub>Ar), 125.8 (ArCH), 76.2 (quaternary C), 45.1 ((NC)CH<sub>2</sub>CH=CH), 39.2 (HC=CHCH<sub>2</sub>Ar), 35.5 (Ar(CN)CH<sub>2</sub>), 33.3 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.6 ((NC)CH<sub>3</sub>).

**FTIR**: 2961, 1616, 1494, 1448, 1279, 1279 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 290.1913 C<sub>21</sub>H<sub>24</sub>N requires 290.1903.

## 2-Cinnamyl-2-methyl-4-phenyl-3,4-dihydro-2H-pyrrole (14m)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol), *trans*-2-phenylvinylboronic acid pinacol ester (60.0 mg, 0.260 mmol) and pentafluorobenzoic acid (6.6 mg, 0.026 mmol). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (4.0 μl, 0.026 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (toluene:EtOAc 60:1 to 20:1) afforded imine **14m** (28.0 mg, 78%) as a colorless oil. *The presence of additional Et<sub>3</sub>N.HO<sub>2</sub>CC<sub>6</sub>F<sub>5</sub> did not provide a significant increase the yield of the reaction, for example, with 50 mol% of this additive a yield of 77% was obtained.*

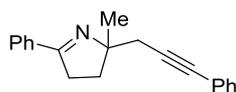
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.89-7.80 (m, 2H, ArH), 7.48-7.15 (m, 8H, ArH), 6.46 (d, *J* = 16.0 Hz, 1H, HC=CHAr), 6.23 (dt, *J* = 16.0 and 7.5 Hz, 1H, HC=CHAr), 3.09-2.85 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.63-2.48 (m, 2H, CH<sub>2</sub>CH=CHAr), 2.09-1.97 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.83-1.70 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.38 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 170.5 (C=N), 137.7, 134.8 (2 × ArC), 132.7 (HC=CHAr), 130.3, 128.5, 128.4, 127.7 (4 × ArCH), 127.0, 126.9, (HC=CHAr and ArCH), 126.1 (ArCH), 76.4 (quaternary C), 45.3 ((NC)CH<sub>2</sub>CH=CH), 35.5 (Ar(CN)CH<sub>2</sub>), 33.4 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 27.5 ((NC)CH<sub>3</sub>).

**FTIR**: 2960, 1614, 1447, 1338 cm<sup>-1</sup>.

**MS**: (CI<sup>+</sup>) Found [M+H]<sup>+</sup>: 276.1752 C<sub>20</sub>H<sub>22</sub>N requires 276.1752.

## 2-Methyl-5-phenyl-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2H-pyrrole (14n)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol) and either tributyl(phenylethynyl)stannane (92.0 μl, 0.261 mmol) or 2-phenyl-1-ethynylboronic acid pinacol ester (60.0 mg, 0.261 mmol) was employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (36.0 μl, 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. If the reaction is performed using the stannane, FCC (hexane to hexane:EtOAc 10:1) afforded imine **14n** (25.0 mg, 70%) as a pale yellow oil. If the reaction is performed using the boronic acid pinacol ester, FCC (toluene:EtOAc 40:1 to 20:1) afforded imine **14n** (19.5 mg, 54%) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.91-7.83 (m, 2H, ArH), 7.48-7.37 (m, 3H, ArH), 7.37-7.29 (m, 2H, ArH), 7.28-7.21 (m, 3H, ArH), 3.19-3.03 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.82 (d, *J* = 16.5 Hz, 1H, CH<sub>2</sub>C≡CPh), 2.70 (d, *J* = 16.5 Hz, 1H, CH<sub>2</sub>C≡CPh), 2.34-2.23 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.97-1.86 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.50 (s, 3H, (NC)CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.7 (C=N), 134.3 (ArC), 131.6, 130.7, 128.4, 128.2, 127.9, 127.6 (6 × ArCH), 123.8 (ArC), 87.5, 81.9 (CH<sub>2</sub>C≡CPh), 76.1 (quaternary C), 35.7 (Ar(CN)CH<sub>2</sub>), 33.7 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 32.8 (CH<sub>2</sub>C≡CPh), 27.2 ((NC)CH<sub>3</sub>).

**FTIR**: 2925, 1641, 1490, 1447, 1280, 1137 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 274.1586, C<sub>20</sub>H<sub>20</sub>N requires 274.1590.

### Tributyl(pent-1-yn-1-yl)stannane



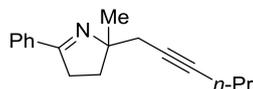
To a solution of 1-pentyne (2.95 mL, 30.00 mmol) in dry THF (50 mL) at -78 °C, *n*-BuLi (24.00 mL, 36.00 mmol) was added dropwise. The mixture was stirred at -78 °C for 2 hours and then tributyltin chloride (9.75 mL, 36.00 mmol) was added slowly. The reaction was allowed to warm to room temperature and heated for 5 minutes at 90 °C until precipitation of lithium chloride had occurred. The reaction was cooled to room temperature, quenched with saturated NH<sub>4</sub>Cl (75 mL). The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 150 mL). The combined extracts were washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. FCC (hexane) afforded the title compound (1.04 g, 10%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 2.22 (t, *J* = 7.0 Hz, 2H, CH<sub>2</sub>), 1.66-0.83 (m, 32H, CH<sub>2</sub> and CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 111.6 (C≡CSn), 81.4 (C≡CSn), 28.9, 27.0, 22.6, 22.1, (4 × CH<sub>2</sub>), 13.7, 13.4, 11.0 (2 × CH<sub>3</sub> and CH<sub>2</sub>).

The spectroscopic properties of this compound were consistent with the data in the literature.<sup>26</sup>

### 2-(Hex-2-yn-1-yl)-2-methyl-5-phenyl-3,4-dihydro-2H-pyrrole (14o)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (6.0 mg, 6.5×10<sup>-3</sup> mmol), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol) and either tributyl(pent-1-yn-1-yl)stannane (93.0 μl, 0.261 mmol) or 1-pentynylboronic acid pinacol ester (56.0 μl, 0.261 mmol) was employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and Et<sub>3</sub>N (36.0 μl, 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. If the reaction is performed using the stannane, FCC (hexane to hexane:EtOAc 10:1) afforded imine **14o** (21.0 mg, 68%) as a colorless oil. If the reaction is performed using the boronic acid pinacol ester, FCC (toluene:EtOAc 70:1 to 50:1) afforded imine **14o** (19.5 mg, 63%) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.86 (d, *J* = 6.5 Hz, 2H, ArH), 7.49-7.36 (m, 3H, ArH), 3.14-2.99 (m, 2H, Ar(CN)CH<sub>2</sub>), 2.57 (dt, *J* = 16.5 and 2.5 Hz, 1H, CH<sub>2</sub>C≡C(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 2.45 (d, *J* = 16.5, 1H, CH<sub>2</sub>C≡C(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 2.26-2.16 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 2.14-2.06 (m, 2H, CH<sub>2</sub>C≡CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.90-1.78 (m, 1H, Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 1.51-1.40 (m, 5H, CH<sub>2</sub>C≡CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and (NC)CH<sub>3</sub>), 0.92 (t, *J* = 7.5 Hz, 3H, CH<sub>2</sub>C≡C(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): 171.5 (C=N), 134.3 (ArC), 130.7, 128.4, 128.0 (3 × ArCH), 84.6, 77.2 (CH<sub>2</sub>C≡CCH<sub>2</sub>), 76.0 (quaternary C), 35.5 (Ar(CN)CH<sub>2</sub>), 33.5 (Ar(CN)CH<sub>2</sub>CH<sub>2</sub>), 32.1 (CH<sub>2</sub>C≡C(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 27.0 ((NC)CH<sub>3</sub>), 22.4 (CH<sub>2</sub>C≡CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 20.8 (CH<sub>2</sub>C≡CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.4 (CH<sub>2</sub>C≡C(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>).

**FTIR**: 2962, 1618, 1448, 1339, 1280, 1132 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 240.1746, C<sub>17</sub>H<sub>22</sub>N requires 240.1747.

### Tributyl(cyclopropylethynyl)stannane



*n*-BuLi (27.30 mL, 46.10 mmol) was added dropwise to a solution of cyclopropylacetylene (3.20 mL, 37.90 mmol) in dry THF (50 mL) at -78 °C. The mixture was stirred at -78 °C for 2 hours and then tributyltin chloride (11.30 mL, 41.60 mmol) was added slowly. The reaction was allowed to warm to room temperature and heated for 5 minutes at 90 °C until precipitation of lithium chloride had occurred. The reaction was cooled to room temperature,

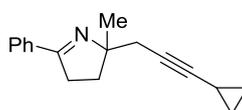
quenched with saturated  $\text{NH}_4\text{Cl}$  (80 mL). The organic layer was extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 150 mL). The combined extracts were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*. FCC (hexane) afforded the title compound (1.11 g, 8%) as a colorless oil.

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ): 1.70-1.49 (m, 6H,  $\text{CH}_2$ ), 1.49-1.24 (m, 7H,  $\text{CH}_2$  and  $\text{CH}$ ), 1.10-0.65 (m, 19H,  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $(\text{CH}_2)_2\text{CH}$ ).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 115.0 ( $\text{C}\equiv\text{CSn}$ ), 77.3 ( $\text{C}\equiv\text{CSn}$ ), 28.9, 27.1 ( $2 \times \text{CH}_2$ ), 13.8 ( $\text{CH}_3$ ), 11.1 ( $\text{CH}_2$ ), 8.9 ( $(\text{CH}_2)_2\text{CH}$ ), 0.7 ( $(\text{CH}_2)_2\text{CH}$ ).

*The spectroscopic properties of this compound were consistent with the data in the literature.*<sup>27</sup>

### 2-(3-Cyclopropylpro-2-yn-1-yl)-2-methyl-5-phenyl-3,4-dihydro-2H-pyrrole (14p)



An oven-dried reaction tube, fitted with magnetic stirrer, was charged with  $\text{Pd}_2(\text{dba})_3$  (6.0 mg,  $6.5 \times 10^{-3}$  mmol),  $\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$  (17.5 mg, 0.026 mmol), oxime ester **6a** (50.0 mg, 0.130 mmol) and tributyl(cyclopropylethynyl)stannane (93.0 mg, 0.261 mmol) were employed. The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (1.0 mL) and  $\text{Et}_3\text{N}$  (36.0  $\mu\text{l}$ , 0.261 mmol) were added *via* syringe. The mixture was then placed in a preheated oil bath at 80 °C for 14 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. FCC (hexane to hexane:EtOAc 10:1) afforded imine **14p** (19.0 mg, 61%) as a colorless oil.

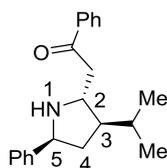
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ): 7.87 (d,  $J = 6.5$  Hz, 2H, ArH), 7.51-7.36 (m, 3H, ArH), 3.14-3.00 (m, 2H, Ar(CN) $\text{CH}_2$ ), 2.53 (dd,  $J = 16.5$  and 2.0 Hz, 1H,  $\text{CH}_2\text{C}\equiv\text{CCH}$ ), 2.43 (d,  $J = 16.5$ , 1H,  $\text{CH}_2\text{C}\equiv\text{CCH}$ ), 2.24-2.13 (m, 1H, Ar(CN) $\text{CH}_2\text{CH}_2$ ), 1.89-1.78 (m, 1H, Ar(CN) $\text{CH}_2\text{CH}_2$ ), 1.42 (s, 3H, (NC) $\text{CH}_3$ ), 1.21-1.12 (m, 1H,  $\text{CH}_2\text{C}\equiv\text{CCH}$ ), 0.70-0.48 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}$ ).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ): 172.0 ( $\text{C}=\text{N}$ ), 133.6 (ArC), 131.0, 128.5, 128.2 ( $3 \times \text{ArCH}$ ), 84.9 ( $\text{CH}_2\text{C}\equiv\text{CCH}$ ), 75.9 (quaternary C), 72.4 ( $\text{CH}_2\text{C}\equiv\text{CCH}$ ), 35.6 (Ar(CN) $\text{CH}_2$ ), 33.4 (Ar(CN) $\text{CH}_2\text{CH}_2$ ), 32.1 ( $\text{CH}_2\text{C}\equiv\text{CCH}$ ), 27.0 ((NC) $\text{CH}_3$ ), 7.9 ( $\text{CH}_2)_2\text{CH}$ ), -0.5 ( $\text{CH}_2)_2\text{CH}$ ).

**FTIR**: 2962, 2850, 1617, 1448, 1339, 1280  $\text{cm}^{-1}$ .

**MS**: (ESI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 238.1599,  $\text{C}_{17}\text{H}_{20}\text{N}$  requires 238.1590.

## 2-((2*R*\*,3*R*\*,5*S*\*)-3-Isopropyl-5-phenylpyrrolidin-2-yl)-1-phenylethan-1-one (15)



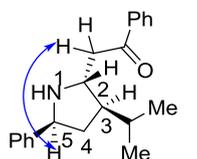
An oven-dried reaction tube, fitted with magnetic stirrer, was charged with 10% Pd/C (9.2 mg, 0.09 mmol) was purged with N<sub>2</sub> for 5 minutes. A solution of dihydropyrrole **10I** (40.0 mg, 0.13 mmol) in AcOH (2.1 mL) was added to the reaction tube. Hydrogen gas was bubbled through the reaction mixture for 2 minutes. The reaction was stirred vigorously under the balloon of H<sub>2</sub> for 7 hours. *N.B. Close monitoring of the reaction by TLC analysis is required to ensure that subsequent reduction of the ketone does not occur.* The reaction was filtered through celite, washing with DCM:MeOH (1:1, 40 mL). The filtrate was concentrated *in vacuo* to provide the title compound as a 6:1 mixture of diastereomers, as determined by <sup>1</sup>H NMR analysis. An analytically pure sample of the major diastereomer was obtained by FCC (hexane:EtOAc 5:1 to EtOAc) (27.0 mg, 68% yield) as a pale yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Data for the major diastereomer:* 8.00-7.93 (m, 2H, ArH), 7.59-7.18 (m, 8H, ArH), 4.29 (dd, *J* = 6.5 and 9.0 Hz, 1H, C5-H), 3.81-3.74 (m, 1H, C2-H), 3.24 (dd, *J* = 16.5 and 3.0 Hz, 1H, CH<sub>2</sub>(CO)Ar), 3.13 (dd, *J* = 16.5 and 9.5 Hz, 1H, CH<sub>2</sub>(CO)Ar), 2.32-2.22 (m, 1H, C4-H<sub>2</sub>), 2.05 (br s, 1H, NH), 1.88-1.69 (m, 2H, C3-H and CH(CH<sub>3</sub>)<sub>2</sub>), 1.59-1.47 (m, 1H, C4-H<sub>2</sub>), 0.99 (d, *J* = 7.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.91 (d, *J* = 7.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>). *Characteristic signals for the minor diastereomer:* 3.60-3.52 (m, 0.16H, C2-H), 3.31 (dd, *J* = 17.0 and 2.5 Hz, 0.16H, CH<sub>2</sub>(CO)Ar), 3.22 (dd, *J* = 17.0 and 8.0 Hz, 0.16H, CH<sub>2</sub>(CO)Ar).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 199.9 (C=O), 144.8, 137.1 (2 × ArC), 133.1, 128.6, 128.4, 128.1, 126.9, 126.4 (6 × ArCH), 60.7 (C5), 57.5 (C2), 52.4 (C3), 45.7 (CH<sub>2</sub>(CO)Ar), 39.1 (C4), 30.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.2, 19.4 (CH(CH<sub>3</sub>)<sub>2</sub>).

**FTIR:** 2956, 2925, 1682, 1448 cm<sup>-1</sup>.

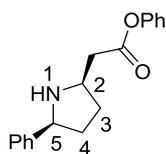
**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 308.2005, C<sub>21</sub>H<sub>26</sub>NO requires 308.2009.



↔ nOe observed

To determine the relative stereochemistry of the major diastereomer, nOe analysis was carried out. An nOe enhancement between C5-H and C4-H<sub>2</sub> was observed. No significant nOe was observed between C5-H and C2-H.

## Phenyl 2-((2*R*\*,5*S*\*)-5-phenylpyrrolidin-2-yl)acetate (**16**)



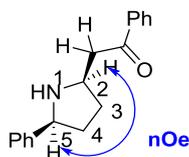
An oven-dried reaction tube, fitted with magnetic stirrer, was charged with 10% Pd/C (4.7 mg, 0.05 mmol) was purged with N<sub>2</sub> for 5 minutes. A solution of dihydropyrrole **13d** (18.5 mg, 0.07 mmol) in EtOAc (1.5 mL) was added to the reaction tube. Hydrogen gas was bubbled through the reaction mixture for 2 minutes. The reaction was stirred vigorously under the balloon of H<sub>2</sub> for 2 hours. *N.B. Close monitoring of the reaction by TLC analysis is required to ensure that subsequent reduction of the ester does not occur.* The reaction was filtered through celite, washed with DCM:MeOH (1:1, 40 mL). The filtrate was concentrated *in vacuo* to provide the title compound as a 10:1 mixture of diastereomers as determined by <sup>1</sup>H NMR analysis. An analytically pure sample of the major diastereomer was obtained by FCC (hexane:EtOAc 4:1 to 1:1) (15.0 mg, 81% yield) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Data for the major diastereomer:* 7.45-7.18 (m, 8H, ArH), 7.09 (d, *J* = 7.0 Hz, 2H, ArH), 4.24 (t, *J* = 7.5 Hz, 1H, C5-H), 3.79-3.70 (m, 1H, C2-H), 2.90-2.76 (m, 2H, CH<sub>2</sub>(CO)OAr), 2.30-2.02 (m, 3H, NH, C4-H<sub>2</sub> and C3-H<sub>2</sub>), 1.81-1.61 (m, 2H, C4-H<sub>2</sub> and C3-H<sub>2</sub>). *Characteristic signals for the minor isomer:* 4.38 (t, *J* = 7.0 Hz, 0.1H, C5-H), 4.02-3.93 (m, 0.1H, C2-H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 171.2 (C=O), 150.6, 144.9 (2 × ArC), 129.4, 128.3, 126.8, 126.6, 125.8, 121.6 (6 × ArCH), 62.2 (C5), 54.7 (C2), 41.7 (CH<sub>2</sub>(CO)OAr), 33.8 (C4), 30.8 (C3).

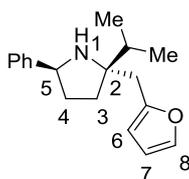
**FTIR:** 2959, 2949, 1754, 1492, 1194, 1163, 1130 cm<sup>-1</sup>.

**MS:** (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 282.1482 C<sub>18</sub>H<sub>20</sub>NO<sub>2</sub> requires 282.1489.



To determine the relative stereochemistry of the major diastereomer, nOe analysis was carried out. An nOe enhancement between C5-H and C2-H was observed.

**(2*S*\*,5*S*\*)-2-(Furan-2-ylmethyl)-2-isopropyl-5-phenylpyrrolidine (17)**



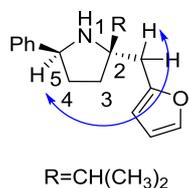
To a solution of dihydropyrrole **14i** (13.0 mg, 0.05 mmol) in anhydrous toluene (0.7 mL) at 0 °C, was added dropwise over 5 minutes diisobutylaluminium hydride (1.0 M solution in hexane, 0.15 mL, 0.15 mmol). The reaction was stirred for 1 hour. The reaction was quenched with sat. NH<sub>4</sub>Cl (2 mL) and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The precipitate was filtered off and the organic phase was concentrated *in vacuo* to provide the title compound as a 4:1 mixture of diastereomers as determined by <sup>1</sup>H NMR analysis. An analytically pure sample of the major diastereomer was obtained by FCC (hexane:EtOAc 5:1 to EtOAc) (11.0 mg, 85% yield) as a colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): *Data for the major diastereomer*: 7.40 (d, *J* = 7.5 Hz, 2H, ArH), 3.74-7.16 (m, 4H, ArH and C8-H), 6.31 (dd, *J* = 3.0 and 2.0 Hz, 1H, C7-H), 6.08 (d, *J* = 3.0 Hz, 1H, C6-H), 3.96 (dd, *J* = 9.0 and 6.5 Hz, 1H, C5-H), 2.84 (s, 2H, CH<sub>2</sub>Ar), 2.06-1.95 (m, 1H, C4-H<sub>2</sub>), 1.94-1.85 (m, 1H, C3-H<sub>2</sub>), 1.80-1.64 (m, 3H, NH, C3-H<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 1.62-1.50 (m, 1H, C4-H<sub>2</sub>), 1.03 (d, *J* = 7.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.99 (d, *J* = 7.0 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>). *Characteristic signals for the minor isomer*: 4.14 (m, 1H, C5-H), 2.85 (d, *J* = 14.5 Hz, 1H, CH<sub>2</sub>Ar), 2.79 (d, *J* = 14.5 Hz, 1H, CH<sub>2</sub>Ar), 0.99 (d, *J* = 7.0 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 153.8 (ArCC6), 145.6 (ArC), 141.4 (C8), 128.1, 126.6, 126.6 (3 × ArCH), 110.2 (C7), 107.6 (C6), 66.3 (C2), 61.2 (C5), 36.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 36.1 (CH<sub>2</sub>Ar), 35.7 (C4), 32.6 (C3), 18.1, 17.9 (CH(CH<sub>3</sub>)<sub>2</sub>).

**FTIR**: 2958, 2873, 1504, 1146, 1011 cm<sup>-1</sup>.

**MS**: (ESI<sup>+</sup>) Found [M+H]<sup>+</sup>: 270.1860, C<sub>18</sub>H<sub>24</sub>NO requires 270.1852.



To determine the relative stereochemistry of the major diastereomer, nOe analysis was carried out. An nOe enhancement between C5-H and CH<sub>2</sub>Ar was observed.

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## Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR of Novel Compounds

