Palladium Catalyzed Cyclizations of Oxime Esters with 1,1-Disubstituted Alkenes: Synthesis of α,α-Disubstituted Dihydropyrroles and Studies Towards an Asymmetric Protocol

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Electronic Supplementary Information

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General Experimental Details. All solvents and reagents requiring purification were purified using standard laboratory techniques according to methods published by Perrin, Armarego, and Perrin (Pergamon Press, 1966) apart from CH_2Cl_2 and THF which were dried by filtration through an activated alumina purification column. Petrol refers to petroleum ether in the boiling range 40–60 ^oC. Flash column chromatography (FCC) was performed using oven dried Merck Kieselgel 60 (40–63 μm). ^1H NMR spectra were recorded at 400 MHz or 500 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 125 MHz as stated. Coupling constants are quoted to the nearest 0.5 Hz. ^1H and ^{13}C NMR data was assigned on the basis of 2D NMR experiments (HMBC, HSQC, COSY). Where mixtures of isomers (e.g. diastereomers) have been characterized together integrals are normalized to the major isomer. Mass spectra were recorded using a VG Autospec (CI^+ mode), a Brüker Daltonics FT-ICR-MS Apex 4e 7.0T FT-MS (ESI^+ mode) and a Fisons VG Analytical Autospec spectrometer (EI^+ mode). Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer as a thin films or solids compressed on a diamond plate. Melting points are uncorrected. The compound numbers used in the Supporting Information are the same as in the main paper.

Experimental Procedures and Data

General Procedure A for the preparation of ketone precursors *via* the corresponding β-keto ester: To a solution of the appropriate β-keto ester (100 mol%) in anhydrous THF (5 mL/mmol) was added NaH (100 mol%, 60% dispersion in mineral oil). The mixture was stirred at room temperature until gas evolution stopped (*ca.* 15 minutes). The appropriate bromide (110 mol%) was then added *via* syringe and the mixture was heated at 80 ^{o}C for 16 hours. The mixture was cooled to room temperature and MeOH (1 mL/mmol), water (2.5 mL/mmol) and KOH (500 mol%) were added. The mixture was then heated at 75 ^{o}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_2O (20 mL/mmol). The organic extracts were washed with brine (10 mL/mmol), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC, under the conditions noted, afforded the corresponding allylated ketone.

General Procedure B for the preparation of ketone precursors *via* the corresponding hydrazone: To a solution of the hydrazone (100 mol%) in anhydrous THF (5 mL/mmol) at -78 ^{o}C was added dropwise *via* syringe *either n*-BuLi (110 mol%, 1.6 M in hexanes) *or* freshly prepared LDA solution (110 mol%, *ca.* 1.5 M in 10:1 THF-hexanes) and the mixture was stirred for 30 minutes. The appropriate bromide (150 mol%) was added *via* syringe and the mixture was warmed to room temperature. The mixture was stirred for 2-16 hours (as noted) and then treated with aq. 1 M HCl (10 mL/mmol). The mixture was stirred until full hydrolysis of allylated hydrazone was observed by TLC (*ca.* 2-10 hours) and was then extracted with EtOAc (20 mL/mmol). The organic extracts were washed with brine (10 mL/mmol), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC, under the conditions noted, afforded the corresponding allylated ketone.

General Procedure C for oxime ester formation: Part A: $H_2NOH.HCl$ (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 ^{o}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_2SO_4) 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_2Cl_2 (3 mL/mmol) at 0 ^{o}C was

added, *via* syringe, Et_3N (200 mol%) and then $ClC(O)C_6F_5$ (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_2CO_3 (2 × 15 mL/mmol) and brine (15 mL/mmol), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by FCC, under the conditions noted, to afford the corresponding oxime ester.

General Procedure D for Narasaka-Heck cyclizations: An oven-dried reaction tube, fitted with magnetic stirrer, was charged with $Pd_2(dba)_3$ (3.75 mol%), $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ (15 mol%) and oxime ester substrate (100 mol%). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (10 mL/mmol) and then reagent grade Et_3N (200 mol%) were added *via* syringe. The mixture was then placed in a preheated oil bath (120 ^oC) until complete consumption of starting material was observed (*ca.* 2-16 hours as noted). The mixture was then cooled to room temperature and concentrated *in vacuo* (*ca.* 1.0 mmHg). The residue was purified by flash column chromatography, under the conditions noted, to afford the target heterocycle.

General Procedure E for the preparation of alcohol precursors from the corresponding aldehyde/esters: To a solution of the appropriate ester/aldehyde (100 mol%) in anhydrous THF (1 mL/mmol) at 0 ^oC was slowly added 1M $LiAlH_4$ (110 mol%) in THF (2 mL/mmol). The mixture was stirred at room temperature until complete consumption of ester/aldehyde was observed by TLC (*ca*. 1-5 hours). The mixture was cooled to 0 ^oC and water (0.5 mL/mmol), NaOH (1 mL/mmol) and water (1 mL/mmol) were added sequentially. The suspension was filtered through celite, washing with CH_2Cl_2 (150 mL/mmol), and the resulting solution was concentrated *in* vacuo. Purification of the residue by FCC under the conditions noted, afforded the corresponding alcohol.

General Procedure F for the preparation of bromide precursors from the corresponding alcohol: To a solution of the appropriate alcohol (100 mol%) in Et_2O (2 mL/mmol) at 0 ^oC was added PBr_3 (50 mol%). The solution was warmed to room temperature and stirred for 16 hours. The reaction was cooled to 0 ^oC and water (1 mL/mmol) and 5% aq. K_2CO_3 (1 mL/mmol) were added. The organic portion was isolated, washed with brine (1 mL/mmol), dried (Na_2SO_4) and concentrated *in vacuo* to afford the corresponding bromide, which was used in the next stage without further purification unless otherwise stated.

General Procedure G for asymmetric Narasaka-Heck cyclizations: An oven-dried reaction tube, fitted with magnetic stirrer, was charged with $Pd_2(dba)_3$ (3.75 mol%), (3a*R*,8a*R*)-(−)-(2,2-Dimethyl-4,4,8,8-tetraphenyl-tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)dimethylamine **L1** (15 mol%) and oxime ester substrate (100 mol%). The tube was fitted with a rubber septum and purged with argon. Anhydrous DMF (10 mL/mmol) and then reagent grade Et_3N (200 mol%) were added *via* syringe. The mixture was then placed in a preheated oil bath (120 ^oC) until complete consumption of starting material was observed (*ca.* 2-16 hours as noted). The mixture was then cooled to room temperature and concentrated *in vacuo* (*ca.* 1.0 mmHg). The residue was purified by flash column chromatography, under the conditions noted, to afford the target heterocycle.

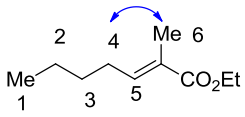
Ethyl *(E)*-2-methylhept-2-enoate and ethyl (*Z*)-2-methylhept-2-enoate

To a solution of NaH (3.42 g, 85.5 mmol) in THF (170 mL) at 0 ^oC was added dropwise ethyl 2-(diethoxyphosphoryl)propanoate (18.0 mL, 83.8 mmol). The reaction was warmed to room temperature and stirred for 90 minutes. Valeraldehyde (8.95 mL, 83.8 mmol) was then added dropwise. The mixture was warmed to room temperature and stirred for 5 hours. Water (25 mL) was added and then the mixture was extracted with Et_2O (2 × 300 mL). The organic extracts were combined, washed with brine (60 mL), dried Na_2SO_4 and concentrated *in vacuo*. A mixture of ethyl (*E*)-2-methylhept-2-enoate and ethyl (*Z*)-2-methylhept-2-enoate was obtained and separated by FCC (hexane:toluene 2:1) to afford ethyl (*E*)-2-methylhept-2-enoate (10.2 g, 70%) as a colourless oil and ethyl (*Z*)-2-methylhept-2-enoate (1.02 g, 7%) as a colourless oil.

Data for ethyl (*E*)-2-methylhept-2-enoate:

^{1}H NMR (400 MHz, $CDCl_3$): 6.76 (tq, *J* = 7.0 and 1.0 Hz, 1H, C=C<u>H</u>), 4.19 (q, *J* = 7.0 Hz, 2H, (CO)OC<u>H$_2$</u>CH$_3$), 2.17 (dt, *J* = 7.0 and 7.0 Hz, 2H, C=CHC<u>H$_2$</u>), 1.79 (d, *J* = 1.0 Hz, 3H, C<u>H$_3$</u>C=CH), 1.48-1.20 (m, 7H, (CO)OCH$_2$C<u>H$_3$</u> and C=CHCH$_2$(C<u>H$_2$</u>)$_2$), 0.92 (t, *J* = 7.0 Hz, 3H, C=CH(CH$_2$)$_3$C<u>H$_3$</u>).

^{13}C NMR (100 MHz, $CDCl_3$): 168.3 (C=O), 142.4 (C=CH), 127.7 (C=CH), 60.3 ((CO)OCH_2CH_3), 30.7 (C=CHCH_2CH_2), 28.4 (C=CHCH_2), 22.4 (C=CH$(CH_2)_2CH_2$), 14.3 (CH_3C=CH), 13.9 ((CO)OCH_2CH_3), 12.3 (C=CH$(CH_2)_3CH_3$).



To confirm the olefin geometry, nOe analysis was carried out on the major isomer. An nOe enhancement between C6-H_2 and C4-H_2 was observed an no nOe was observed between C5-H and C6-H_2, which is consistent with an (*E*)-olefin geometry.

The spectroscopic properties of this compound were consistent with the data in the literature.[1]

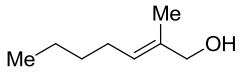
Data for ethyl (*Z*)-2-methylhept-2-enoate:

^{1}H NMR (400 MHz, $CDCl_3$): 5.93 (tq, *J* = 7.5 and 1.5 Hz, 1H, C=CH), 4.20 (q, *J* = 7.5 Hz, 2H, (CO)O$CH_2$$CH_3$), 2.45 (dt, *J* = 7.5 and 7.5 Hz, 2H, C=CHCH_2), 1.90 (d, *J* = 1.5 Hz, 3H, CH_3C=CH), 1.44-1.24 (m, 7H, (CO)OCH_2CH_3 and C=CH$CH_2(CH_2)_2$), 0.91 (t, *J* = 7.5 Hz, 3H, C=CH$(CH_2)_3CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 168.2 (C=O), 143.0 (C=CH), 127.0 (C=CH), 60.0 ((CO)OCH_2CH_3), 31.6 (C=CHCH_2CH_2), 29.3 (C=CHCH_2), 22.4 (C=CH$(CH_2)_2CH_2$), 20.7 (CH_3C=CH), 14.3 ((CO)OCH_2CH_3), 13.9 (C=CH$(CH_2)_3CH_3$).

The spectroscopic properties of this compound were consistent with the data in the literature.[2]

(*E*)-2-Methylhept-2-en-1-ol



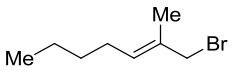
General Procedure E: Ethyl (*E*)-2-methylhept-2-enoate (11.0 g, 64.7 mmol) was employed. FCC (hexane:EtOAc 9:2) afforded the title compound (6.95 g, 85%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 5.42 (t, *J* = 7.0 Hz, 1H, C=CH), 4.00 (s, 2H, CH_2OH), 2.04 (dt, *J* = 7.0 and 7.0 Hz, 2H, C=CHCH_2), 1.66 (s, 3H, CH_3C=CH), 1.41-1.21 (m, 4H, C=CH$CH_2(CH_2)_2$), 0.90 (t, *J* = 7.5 Hz, 3H, C=CH$(CH_2)_3CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 134.4 (C=CH), 126.5 (C=CH), 69.0 (CH_2OH), 31.6 ($C=CHCH_2CH_2$), 27.2 ($C=CHCH_2$), 22.3 ($C=CH(CH_2)_2CH_2$), 13.9 ($CH_3C=CH$), 13.5 ($C=CH(CH_2)_3CH_3$).

The spectroscopic properties of this compound were consistent with the data in the literature.[1,3]

(*E*)-1-Bromo-2-methylhept-2-ene



General Procedure F: (*E*)-2-Methylhept-2-en-1-ol (6.90 g, 53.9 mmol) was employed to afford bromide (9.22 g, 90%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 5.60 (t, J = 7.0 Hz, 1H, C=CH), 3.98 (s, 2H, CH_2Br), 2.08-1.99 (m, 2H, $C=CHCH_2$), 1.76 (s, 3H, $CH_3C=CH$), 1.41-1.23 (m, 4H, $C=CHCH_2(CH_2)_2$), 0.90 (t, J = 7.0 Hz, 3H, $C=CH(CH_2)_3CH_3$).

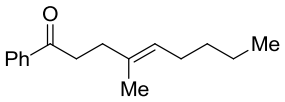
^{13}C NMR (100 MHz, $CDCl_3$): 131.8 (2 signals) (C=CH and C=CH), 42.0 (CH_2Br), 31.2 ($C=CHCH_2CH_2$), 28.0 ($C=CHCH_2$), 22.3 ($C=CH(CH_2)_2CH_2$), 14.6 ($CH_3C=CH$), 13.9 ($C=CH(CH_2)_3CH_3$).

FTIR 2859, 1661, 1466, 1436, 1379 cm^{-1}.

MS (CI^+) Found $[M+H]^+$ 191.1.

The spectroscopic properties of this compound were consistent with the data in the literature.[4]

(*E*)-4-Methyl-1-phenylnon-4-en-1-one



General Procedure A: Ethyl benzoylacetate (0.82 mL, 4.76 mmol) and (*E*)-1-bromo-2-methylhept-2-ene (1.00 g, 5.25 mmol) were employed. FCC (hexane:EtOAc 30:1) afforded the title compound (0.96 g, 88%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.00-7.94 (m, 2H, ArH), 7.60-7.43 (m, 3H, ArH), 5.23-5.16 (m, 1H, C=CH), 3.11-3.04 (m, 2H, $Ar(CO)CH_2$), 2.42 (t, J = 8.0 Hz, 2H, $Ar(CO)CH_2CH_2$),

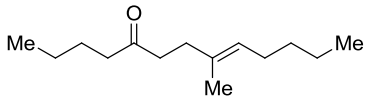
2.03-1.95 (m, 2H, C=CHCH_2), 1.67 (s, 3H, CH_3C=CH), 1.37-1.24 (m, 4H, C=CHCH_2(CH_2)$_2$), 0.95-0.83 (m, 3H, C=CH(CH_2)$_3$CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 200.2 (C=O), 137.1(ArC), 133.5 (C=CH), 132.9, 128.5, 128.1 (3 × ArCH), 125.5 (C=CH), 37.5 (Ar(CO)CH_2), 34.1 (Ar(CO)CH_2CH_2), 31.9 (C=CHCH_2CH_2), 27.6 (C=CHCH_2), 22.3(C=CH(CH_2)$_2$CH_2), 16.1 (CH_3C=CH), 14.0 (C=CH(CH_2)$_3$CH_3).

FTIR 1685, 1449, 1202 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 231.1745, $C_{16}H_{23}O$ requires 231.1749.

(*E*)-8-Methyltridec-8-en-5-one



General Procedure A: Methyl 3–oxoheptanoate (0.38 mL, 2.38 mmol) and (*E*)-1-bromo-2-methylhept-2-ene (0.50 g, 2.62 mmol) were employed. FCC (hexane:EtOAc 30:1) afforded the title compound (0.36 g, 73%) as a pale yellow oil.

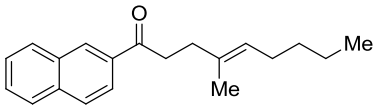
^{1}H NMR (400 MHz, $CDCl_3$): 5.16-5.10 (m, 1H, C=CH), 2.54-2.48 (m, 2H, (CO)CH_2CH_2C=CH), 2.41 (t, *J* = 7.5 Hz, 2H, CH_3(CH_2)$_2$CH_2(CO)), 2.25 (t, *J* = 8.0 Hz, 2H, (CO)CH_2CH_2C=CH), 2.01-1.90 (m, 2H, C=CHCH_2), 1.62-1.61 (m, 3H, CH_3C=CH), 1.58-1.49 (m, 2H, CH_3CH_2CH_2CH_2(CO)), 1.36-1.23 (m, 6H, C=CHCH_2(CH_2)$_2$ and CH_3CH_2(CH_2)$_2$(CO)), 0.94-0.86 (m, 6H, 2 × CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 211.5 (C=O), 133.6 (C=CH), 125.4 (C=CH), 42.7 ((CO)CH_2CH_2C=CH), 41.6 (CH_3(CH_2)$_2$CH_2(CO)), 33.8 ((CO)CH_2CH_2C=CH), 32.1 (CH_2), 27.8 (C=CHCH_2), 26.0, 22.5, 22.4 (3 × CH_2), 16.1 (CH_3C=CH), 14.1 (C=CH(CH_2)$_3$CH_3), 14.0 (CH_3(CH_2)$_3$(CO)).

FTIR 2957, 1714, 1457, 1379 cm^{-1}.

MS (EI^+) Found $[M]^+$: 210.1992, $C_{14}H_{26}O$ requires 210.1984.

(*E*)-4-Methyl-1-(naphthalen-2-yl)non-4-en-1-one



General Procedure B: 1,1-Dimethyl-2-(1-(napthalen-2-yl)ethylidene)hydrazine (0.60 g, 2.79 mmol) and *n*-BuLi (2.27 mL, 3.63 mmol) were employed. (*E*)-1-Bromo-2-methylhept-2-ene (0.80 g, 4.19 mmol) was used and the reaction was stirred at room temperature for 16 hours. FCC (hexane:EtOAc 32:1) afforded the title ketone (0.26 g, 33%) as a yellow oil.

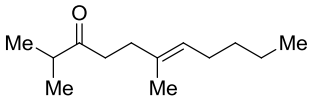
^{1}H NMR (400 MHz, $CDCl_3$): 8.50-8.47 (s, 1H, ArH), 8.07-7.86 (m, 4H, ArH), 7.65-7.54 (m, 2H, ArH), 5.23 (tq, *J* = 7.0 and 1.0 Hz, 1H, C=CH), 3.25-3.19 (m, 2H, Ar(CO)CH_2), 2.49 (t, *J* = 7.5 Hz, 2H, Ar(CO)CH_2CH_2), 2.01 (dt, *J* = 7.0 and 7.0 Hz, 2H, C=$CHCH_2$), 1.70 (d, *J* = 1.0 Hz, 3H, CH_3C=CH), 1.38-1.23 (m, 4H, C=CH(CH_2)$_2$), 0.90 (t, *J* = 7.5 Hz, 3H, C=CH$(CH_2)_2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 200.2 (C=O), 135.51, 134.4 (2 signals) (3 × ArC), 132.6 (C=CH), 129.6, 129.5, 128.4, 128.3, 127.8, 126.7 (6 × ArCH), 125.6 (C=CH), 124.0 (ArCH), 37.6 (Ar(CO)CH_2), 34.3 (Ar(CO)CH_2CH_2), 32.0 (C=$CHCH_2CH_2$), 27.7 (C=$CHCH_2$), 22.4 (C=CH$(CH_2)_2CH_2$), 16.2 (CH_3C=CH), 14.0 (C=CH$(CH_2)_3CH_3$).

FTIR 2925, 1679, 1467, 1181, 1123 cm^{-1}.

MS (EI^+) Found $[M]^+$: 280.1826, $C_{20}H_{24}O$ requires 280.1827.

(*E*)-2,6-Dimethylundec-6-en-3-one



General Procedure A: Ethyl 4-methyl-3-oxopentanoate (0.38 mL, 2.38 mmol) and (*E*)-1-bromo-2-methylhept-2-ene (0.50 g, 2.62 mmol) were employed. FCC (× 2; 1st column: hexane:EtOAc 32:1 ; 2nd column: toluene:hexane 6:1) afforded the title compound (0.24 g, 51%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 5.15-5.10 (m, 1H, C=CH), 2.62 (sept., *J* = 7.0 Hz, 1H, $(CH_3)_2$CH(CO)), 2.57-2.51 (m, 2H, (CO)CH_2), 2.23 (t, *J* = 7.5 Hz, 2H, (CO)CH_2CH_2), 1.97

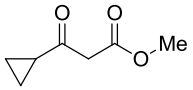
(dt, *J* = 7.0 Hz, C=CHC$\underline{H}_2$), 1.61 (s, 3H, C$\underline{H}_3$C=CH), 1.35-1.24 (m, 4H, C=CHCH$_2$(C$\underline{H}_2$)$_2$), 1.10 (d, *J* = 7.0 Hz, 6H, (C$\underline{H}_3$)$_2$CH(CO)), 0.92-0.85 (m, 3H, C=CH(CH$_2$)$_3$C$\underline{H}_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 214.7 (C=O), 133.7 (C=CH), 125.4 (C=CH), 41.0 ((CH$_3$)$_2$CH(CO)), 39.3 ((CO)CH$_2$), 33.7 ((CO)CH$_2$CH$_2$), 32.1 (C=CHCH$_2$CH$_2$), 27.7 (C=CHCH$_2$), 22.4 (C=CH(CH$_2$)$_2$CH$_2$), 18.3 ((CH$_3$)$_2$CH(CO)), 16.2 (CH$_3$C=CH), 14.1 (C=CH(CH$_2$)$_3$CH$_3$).

FTIR 2961, 1712, 1466, 1383, 1076 cm^{-1}.

MS (EI$^+$) Found [M]$^+$:196.1818, $C_{13}H_{24}O$ requires 196.1827.

Methyl 3-cyclopropyl-3-oxopropanoate



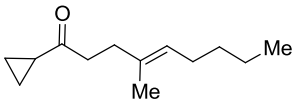
To a suspension of NaH (2.85 g, 71.3 mmol) in THF (50 mL) at room temperature was added dimethyl carbonate (5.10 mL, 60.0 mmol). 1-Cyclopropylethanone (5.90 mL, 59.4 mmol) was added over 10 minutes and then the reaction was heated at 75 ^{o}C for 2 hours. The reaction was cooled to room temperature and concentrated *in vacuo*. To the residue was added ice-cold water (50 mL) and aq. 1M HCl (40 mL) and the mixture was extracted with Et_2O (3 × 125 mL). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by FCC (hexane:EtOAc 100:0 to 0:100) to afford methyl 3-cyclopropyl-3-oxopropanoate (4.18 g, 55%) as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): 3.75 (s, 3H, (CO)OC$\underline{H}_3$), 3.58 (s, 2H, (CO)C$\underline{H}_2$(CO)OCH$_3$), 2.07-2.00 (m, 1H, (CH$_2$)$_2$C$\underline{H}$), 1.15-1.09 (m, 2H, (C$\underline{H}_2$)$_2$CH), 1.00-0.93 (m, 2H, (C$\underline{H}_2$)$_2$CH).

^{13}C NMR (100 MHz, $CDCl_3$): 202.7 (C=O), 167.7 ((CO)OCH$_3$), 52.3 ((CO)OCH$_3$), 49.6 ((CO)CH$_2$(CO)OCH$_3$), 20.8 ((CH$_2$)$_2$CH), 11.7 ((CH$_2$)$_2$CH).

The spectroscopic properties of this compound were consistent with the data in the literature.[5]

(*E*)-1-Cyclopropyl-4-methylnon-4-en-1-one



General Procedure A: Methyl 3-cyclopropyl-3-oxopropanoate (1.02 g, 7.18 mmol) and (*E*)-1-bromo-2-methylhept-2-ene (1.50 g, 7.85 mmol) were employed. FCC (hexane:EtOAc 38:1) afforded the title compound (1.21 g, 87%) as a colourless oil.

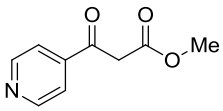
^{1}H NMR (400 MHz, $CDCl_3$): 5.19-5.12 (m, 1H, C=C<u>H</u>), 2.67-2.62 (m, 2H, (CO)C<u>H</u>$_2$), 2.29 (t, *J* = 7.5 Hz, 2H, (CO)CH$_2$C<u>H</u>$_2$), 2.03-1.90 (m, 3H, C=CHC<u>H</u>$_2$ and (CH$_2$)$_2$C<u>H</u>), 1.62 (s, 3H, C<u>H</u>$_3$C=CH), 1.37-1.24 (m, 4H, C=CHCH$_2$(C<u>H</u>$_2$)$_2$), 1.05-0.98 (m, 2H, (C<u>H</u>$_2$)$_2$CH), 0.93-0.81 (m, 5H, (C<u>H</u>$_2$)$_2$CH and C=CH(CH$_2$)$_3$C<u>H</u>$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 210.8 (<u>C</u>=O), 133.5 (<u>C</u>=CH), 125.3 (C=<u>C</u>H), 42.3 ((CO)<u>C</u>H$_2$), 33.8 ((CO)CH$_2$<u>C</u>H$_2$), 31.9 (C=CHCH$_2$<u>C</u>H$_2$), 27.6 (C=CH<u>C</u>H$_2$), 22.3 (C=CH(CH$_2$)$_2$<u>C</u>H$_2$), 20.3 ((CO)<u>C</u>H), 16.0 (<u>C</u>H$_3$C=CH), 14.0 (C=CH(CH$_2$)$_3$<u>C</u>H$_3$), 10.6 (COCH(<u>C</u>H$_2$)$_2$).

FTIR 1698, 1445, 1383, 1084 cm^{-1}.

MS (EI$^+$) Found [M]$^+$: 194.1678 ,$C_{13}H_{22}O$ requires 194.1671.

Methyl 3-oxo-3-(pyridin-4-yl)propanoate



To a suspension of NaH (1.98 g, 49.5 mmol) in THF (45 mL) at room temperature was added dimethyl carbonate (3.50 mL, 41.7 mmol). 1-(Pyridine-4-yl)ethanone (4.60 mL, 41.7 mmol) was added slowly over 10 minutes and then the reaction was heated at 75 ^{o}C for 5 hours. The reaction was cooled to room temperature and then concentrated *in vacuo*. To the residue was added ice-cold water (50 mL) and aq. 1M HCl (50 mL) and the mixture was extracted with Et_2O (3 × 250 mL). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by FCC (EtOAc) to afford methyl 3-oxo-3-(pyridin-4-yl)propanoate (4.04 g, 55%, 1:0.66 mixture of enol and keto tautomers) as a colourless solid.

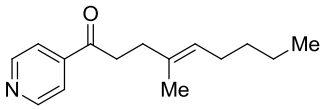
^{1}H NMR (400 MHz, $CDCl_3$): *Signals for enol tautomer:* 12.36 (s, 1H, ArC-O<u>H</u>), 8.71 (d, *J* = 6.0 Hz, 2H, Ar<u>H</u>), 7.61 (d, *J* = 6.0 Hz, 2H, Ar<u>H</u>), 5.73 (s, 1H, ArC=C<u>H</u>), 3.83 (s, 3H,

(CO)OC$\underline{H}_3$). *Signals for keto tautomer:* 8.85 (d, *J* = 6.0 Hz, 1.32H, Ar$\underline{H}$), 7.72 (d, *J* = 6.0 Hz, 1.32H, Ar$\underline{H}$), 4.01 (s, 1.32H, (CO)$\underline{C}H_2$(CO)OCH$_3$), 3.77 (s, 1.98H, (CO)OC$\underline{H}_3$).

^{13}C NMR (100 MHz, $CDCl_3$): *Signals for enol tautomer*: 172.9 (Ar$\underline{C}$OH), 168.4 (($\underline{C}$O)OCH$_3$), 150.5 (Ar$\underline{C}$H), 140.6 (Ar$\underline{C}$), 121.2 (Ar$\underline{C}$H), 89.6 (ArC=$\underline{C}$H), 51.8 ((CO)O$\underline{C}H_3$). *Signals for keto tautomer*: 192.0 (Ar$\underline{C}$=O), 167.1 (($\underline{C}$O)OCH$_3$), 151.2 (Ar$\underline{C}$H), 141.6 (Ar$\underline{C}$), 119.7 (Ar$\underline{C}$H), 52.7 ((CO)O$\underline{C}H_3$), 45.6 ((CO)$\underline{C}H_2$(CO)OCH$_3$).

The spectroscopic properties of this compound were consistent with the data in the literature.[6]

(*E*)-4-Methyl-1-(pyridine-4-yl)non-4-en-1-one



To a solution of methyl 3-oxo-3-(pyridin-4-yl)propanoate (1.28 g, 7.13 mmol) in anhydrous THF (30 mL) was added NaH (0.29 g, 7.13 mmol). The mixture was stirred at room temperature for 30 minutes. Then (*E*)-1-bromo-2-methylhept-2-ene (1.50 g, 7.85 mmol) was added *via* syringe and the mixture was heated at 80 ^{o}C for 16 hours. The mixture was cooled to room temperature and aq. 1M HCl (20 mL) was added. The reaction mixture was extracted with Et_2O (3 × 150 mL) and the combined organic extracts were concentrated *in vacuo*. To the residue, DMSO (7 mL), H_2O (0.25 g, 14.2 mmol) and NaCl (0.82 g, 14.2 mmol) were added and the resulting mixture was heated at 180 ^{o}C for 16 hours. After cooling to room temperature, water (5 mL) was added and the mixture was extracted with Et_2O (2 × 100 mL). The combined organic extracts were concentrated *in vacuo* and FCC (hexane:EtOAc 4:1) afforded the title ketone (0.28 g, 17%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.85-8.78 (m, 2H, Ar$\underline{H}$), 7.74-7.70 (m, 2H, Ar$\underline{H}$), 5.17 (tq, *J* = 7.5 and 1.0 Hz, 1H, C=C$\underline{H}$), 3.07 (t, *J* = 7.5 Hz, 2H, Ar(CO)C$\underline{H}_2$), 2.41 (t, *J* = 7.5 Hz, Ar(CO)CH$_2$C$\underline{H}_2$), 1.99 (dt, *J* = 7.5 and 7.5 Hz, 2H, C=CHC$\underline{H}_2$), 1.66 (d, *J* = 1.0 Hz, 3H, C$\underline{H}_3$C=CH), 1.35-1.24 (m, 4H, C=CHCH$_2$(C$\underline{H}_2$)$_2$), 0.89 (t, *J* = 7.0 Hz, 3H, C=CH(CH$_2$)$_3$C$\underline{H}_3$).

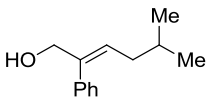
^{13}C NMR (100 MHz, $CDCl_3$): 199.5 ($\underline{C}$=O), 150.9 (Ar$\underline{C}$H), 142.8 (Ar$\underline{C}$), 132.9 ($\underline{C}$=CH), 125.9 (C=$\underline{C}$H), 121.0 (Ar$\underline{C}$H), 37.7 (Ar(CO)$\underline{C}H_2$), 33.6 (Ar(CO)CH$_2$$\underline{C}H_2$), 31.9

(C=CHCH$_2$C$\underline{H}_2$), 27.6 (C=CHC$\underline{H}_2$), 22.3 (C=CH(CH$_2$)$_2$C$\underline{H}_2$), 16.1 ($\underline{C}$H$_3$C=CH), 14.0 (C=CH(CH$_2$)$_3$C$\underline{H}_3$).

FTIR 2926, 1696, 1556, 1445, 1407, 1202 cm^{-1}.

MS (EI$^+$) Found [M]$^+$: 231.1621, $C_{15}H_{21}NO$ requires 231.1623.

***(E)*-5-Methyl-2phenylhex-2-en-1-ol**



General Procedure E: 5-Methyl-2-phenyl-2-hexenal (2.06 mL, 10.66 mmol) was employed. FCC (hexane:EtOAc 9:2) affored the title alcohol (2.00 g, 99%, 1:0.05 *E:Z*) as a colourless oil.

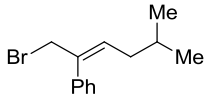
^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 7.40-7.34 (m, 2H, Ar$\underline{H}$), 7.32-7.27 (m, 1H, Ar$\underline{H}$), 7.23-7.19 (m, 2H, Ar$\underline{H}$), 5.76 (tt, *J* = 7.5 and 1.5 Hz, 1H, C=C$\underline{H}$), 4.34 (d, *J* = 5.5 Hz, 2H, C$\underline{H}_2$OH), 1.95 (dd, *J* = 7.5 and 7.5 Hz, 2H, C=CHC$\underline{H}_2$), 1.69-1.60 (m, 1H, ((CH$_3$)$_2$C$\underline{H}$), 1.43 (t, *J* = 5.5 Hz, 1H, CH$_2$O$\underline{H}$), 0.86 (d, *J* = 6.5 Hz, 6H, (C$\underline{H}_3$)$_2$CH). *Characteristic signals only for the minor isomer:* 5.92 (t, *J* = 8.0 Hz, 0.05H, C=C$\underline{H}$), 4.59 (d, *J* = 5.5 Hz, 0.1H, C$\underline{H}_2$OH), 2.20 (dd, *J* =7.0 and 7.0 Hz, 0.1H, C=CHC$\underline{H}_2$), 0.98 (d, *J* = 6.0 Hz, 0.3H, (C$\underline{H}_3$)$_2$CH).

^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only:* 140.9 ($\underline{C}$=CH), 138.8 (Ar$\underline{C}$), 128.9, 128.4, 127.1 (3 x Ar$\underline{C}$H), 128.1 (C=$\underline{C}$H), 68.4 ($\underline{C}$H$_2$OH), 37.6 (C=CH$\underline{C}$H$_2$), 28.9 ((CH$_3$)$_2$$\underline{C}$H), 22.5 (($\underline{C}H_3$)$_2$CH).

FTIR 3319, 3954, 1494, 1465, 1384, 1366 cm^{-1}.

MS (ESI$^+$) Found [M+Na]$^+$: 213.1252 , $C_{13}H_{18}NONa$ requires 213.1250.

(*E*)-(1-Bromo-5-methylhex-2-en-2-yl)benzene



General Procedure F: (*E*)-5-Methyl-2-phenylhex-2-en-1-ol (1.20 g, 6.32 mmol) was employed to afford the title bromide (1.35 g, 85%, 1:0.05 E:Z) as a colourless oil.

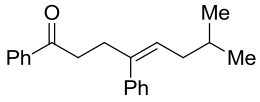
^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 7.41-7.29 (m, 3H, ArH), 7.25-7.19 (m, 2H, ArH), 5.95 (t, *J* = 7.5 Hz, 1H, C=CH), 4.28 (s, 2H, CH_2Br), 1.90 (dd, *J* = 7.5 and 7.5 Hz, 2H, C=CHCH_2), 1.70-1.60 (m, 1H, $(CH_3)_2CH$), 0.85 (d, *J* = 6.5 Hz, 6H, $((CH_3)_2CH$). *Characteristic signals only for the minor isomer:* 6.02 (t, *J* = 7.5 Hz, 0.05H, C=CH), 4.40 (s, 0.1H, CH_2Br), 2.21 (dd, *J* = 7.5 and 7.5 Hz, 0.1H, C=CHCH_2), 1.00 (d, *J* = 6.5 Hz, 0.3H, $(CH_3)_2CH$)

^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only:* 138.3 (ArC), 138.1 (C=CH), 133.5 (C=CH), 128.9, 128.3, 127.4 (3 x ArCH), 40.0 (CH_2Br), 38.2 ($(CH_3)_2CHCH_2$), 28.7 ($(CH_3)_2CH$), 22.5 ($(CH_3)_2CH$)

FTIR 2955.5, 1494, 1465, 1443, 1206 cm^{-1}.

MS (EI^+) Found $[M]^+$: 252.0505 , $C_{13}H_{17}{}^{79}Br$ requires 252.0514

(*Z*)-7-Methyl-1,4-diphenyloct-4-en-1-one



General Procedure A: Ethyl benzoyl acetate (0.50 mL, 2.89 mmol) and (*E*)-(1-bromo-5-methylhex-2-en-2-yl)benzene (0.80 g, 3.17 mmol) were employed. FCC (× 2: 1st column hexane:EtOAc 30:1 ; 2nd column toluene:hexane 7:1) afforded the target ketone (0.62 g, 72%, 1:0.05 *Z*:*E*) as a colourless oil.

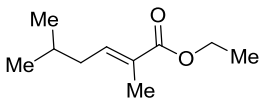
^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 7.90-7.84 (m, 2H, ArH), 7.56-7.51 (m, 1H, ArH), 7.45-7.40 (m, 2H, ArH), 7.37-7.31 (m, 2H, ArH), 7.28-7.23 (m, 1H, ArH), 7.18-7.13 (m, 2H, ArH). 5.55 (tt, *J* = 7.5 and 1.0 Hz, 1H, C=CH), 3.00-2.94 (m, 2H, Ar(CO)CH_2), 2.83-2.77 (m, 2H, Ar(CO)CH_2CH_2), 1.83 (dd, *J* =7.5 and 7.5 Hz, 2H, C=CHCH_2), 1.63-1.55 (m, 1H, $(CH_3)_2CH$), 0.83 (d, *J* = 6.5 Hz, 6H, $(CH_3)_2CH$). *Characteristic signals only for the minor isomer:* 5.75 (t, *J* = 7.5 Hz, 0.05H, C=CH), 2.12 (dd *J* = 7.5 and 7.5 Hz, 0.1H, C=CHCH_2), 0.96 (d, *J* = 6.5Hz, 0.3H, $(CH_3)_2CH$).

^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only:* 200.1 (C=O), 140.9 (ArC), 140.1 (C=CH), 137.1 (ArC), 133.0, 128.8, 128.6, 128.2, 128.1 (5 × ArCH), 127.4 (C=CH), 126.7 (ArCH), 37.9 (C=CHCH_2), 37.7 (Ar(CO)CH_2), 34.2 (Ar(CO)CH_2CH_2), 29.0 ($(CH_3)_2CH$), 22.5 ($(CH_3)_2CH$).

FTIR 2954, 1683, 1598, 1448, 1202 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 315.1725 , $C_{21}H_{24}NONa$ requires 315.1719.

Ethyl (*E*)-2,5-dimethylhex-2-enoate



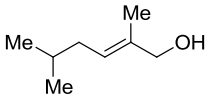
To a solution of isovaleraldehyde (1.00 g, 11.6 mmol) in anhydrous CH_2Cl_2 (12 mL) was added ethoxycarbonylethylidenetriphenylphosphorane (4.21 g, 11.6 mmol). The mixture was heated at 60 °C for 16 hours and then cooled to room temperature. Pentane (20 mL) was added and the resulting triphenylphosphine oxide precipitate was removed by filtration. The filtrate was concentrated *in vacuo* and FCC (hexane:EtOAc 12:1) afforded the title compound (1.48 g, 75%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 6.79 (tq, *J* = 7.5 and 1.0 Hz, 1H, C=C$\underline{H}$), 4.19 (q, *J* = 7.0 Hz, 2H, (CO)OC$\underline{H_2}CH_3$), 2.07 (dd, *J* = 7.5 and 7.5 Hz, 2H, C=CHC$\underline{H_2}$), 1.83 (d, *J* = 1.0 Hz, 3H, C$\underline{H_3}$C=CH), 1.84-1.70 (m, 1H, $(CH_3)_2C\underline{H}$), 1.30 (t, *J* = 7.0 Hz, 3H, (CO)$OCH_2C\underline{H_3}$), 0.94 (d, *J* = 7.0 Hz, 6H, $(C\underline{H_3})_2CH$).

^{13}C NMR (100 MHz, $CDCl_3$): 168.3 ($\underline{C}$=O), 141.3 (C=$\underline{C}$H), 128.4 ($\underline{C}$=CH), 60.3 ((CO)O$\underline{C}H_2CH_3$), 37.8 (C=CH$\underline{C}H_2$), 28.3 ($(CH_3)_2\underline{C}H$), 22.5 ($(\underline{C}H_3)_2CH$), 14.3 ((CO)$OCH_2\underline{C}H_3$), 12.5 ($\underline{C}H_3C$=CH).

The spectroscopic properties of this compound were consistent with the data in the literature.[7]

(*E*)-2,5-Dimethylhex-2-en-1ol



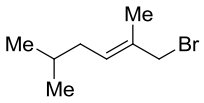
General Procedure E: Ethyl (*E*)-2,5-dimethylhex-2-enoate (0.95 g, 5.59 mmol) was employed. The residue was purified by FCC (hexane:EtOAc 3:1) to obtain the title alcohol (0.57 g, 80%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 5.44 (tq, *J* = 7.5 and 1.0 Hz, 1H, C=C<u>H</u>), 4.02 (s, 2H, C<u>H</u>$_2$OH), 1.93 (dd, *J* = 7.5 and 7.5 Hz, 2H, C=CHC<u>H</u>$_2$), 1.67 (d, *J* = 1.0 Hz, 3H, C<u>H</u>$_3$C=CH), 1.66-1.58 (m, 1H, $(CH_3)_2$C<u>H</u>), 0.90 (d, *J* = 6.5 Hz, 6H, $(CH_3)_2$CH).

^{13}C NMR (100 MHz, $CDCl_3$): 135.2 (<u>C</u>=CH), 125.4 (C=<u>C</u>H), 69.2 (<u>C</u>H$_2$OH), 36.7 (C=CH<u>C</u>H$_2$), 28.7 $(CH_3)_2$<u>C</u>H), 22.4 $(CH_3)_2$CH), 13.8 (<u>C</u>H$_3$C=CH).

The spectroscopic properties of this compound were consistent with the data in the literature.[8]

(*E*)-1-Bromo-2,5-dimethylhex-2-ene



General Procedure F: (*E*)-2,5-Dimethylhex-2-en-1-ol (0.55 g, 4.29 mmol) was employed to afford the title bromide (0.72 g, 90%) as a colourless oil.

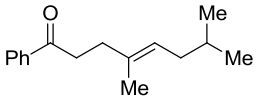
^{1}H NMR (400 MHz, $CDCl_3$): 5.64 (t, *J* = 7.5 Hz, 1H, C=C<u>H</u>), 4.00 (s , 2H, C<u>H</u>$_2$Br), 1.92 (dd, *J* = 7.5 and 7.5 Hz, 2H, C=CHC<u>H</u>$_2$), 1.76 (s, 3H, C<u>H</u>$_3$C=CH), 1.69-1.62 (m, 1H, $(CH_3)_2$C<u>H</u>), 0.90 (d, *J* = 6.5 Hz, 6H, $(CH_3)_2$CH).

^{13}C NMR (100 MHz, $CDCl_3$): 132.5 (<u>C</u>=CH), 130.6 (C=<u>C</u>H), 42.0 (<u>C</u>H$_2$Br), 37.3 (C=CH<u>C</u>H$_2$), 28.5 ($(CH_3)_2$<u>C</u>H), 22.3 $(CH_3)_2$CH), 14.8 (<u>C</u>H$_3$C=CH).

FTIR 2955, 1465, 1435, 1385, 1366, 1211, 1198 cm^{-1}.

MS (EI^+) Found $[M]^+$: 190.0359, $C_8H_{15}{}^{79}Br$ requires 190.0357.

(*E*)-4,7-Dimethyl-1-phenyloct-4-en-1-one



General Procedure A: Ethyl benzoyl acetate (0.58 mL, 3.33 mmol) and (*E*)-1-bromo-2,5-dimethylhex-2-ene (0.70 g, 3.66 mmol) were employed. FCC (hexane:EtOAc 35:1) afforded the target ketone (0.55 g, 75%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.00-7.95 (m, 2H, Ar<u>H</u>), 7.59-7.53 (m, 1H, Ar<u>H</u>), 7.51-7.44 (m, 2H, Ar<u>H</u>), 5.23 (tq, *J* = 7.5 and 1.0 Hz, 1H, C=C<u>H</u>), 3.11-3.05 (m, 2H, Ar(CO)C<u>H</u>$_2$), 2.44

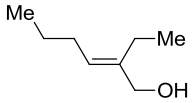
(t, J = 7.5 Hz, 2H, Ar(CO)CH_2CH_2), 1.88 (dd, J = 7.5 and 7.5 Hz, 2H, C=CHCH_2), 1.66 (d, J = 1.0 Hz, 3H, CH_3C=CH), 1.62-1.55 (m, 1H, $(CH_3)_2CH$), 0.87 (d, J = 7.0 Hz, 6H, $(CH_3)_2CH$).

^{13}C NMR (100 MHz, $CDCl_3$): 200.2 (C=O), 137.0 (ArC), 134.2 (C=CH), 132.9, 128.5, 128.1 (3 × ArCH), 124.3 (C=CH), 37.5 (Ar(CO)CH_2), 37.1 (C=CHCH_2), 34.3 (Ar(CO)CH_2CH_2), 28.8 ($(CH_3)_2$CH), 22.4 ($(CH_3)_2$CH), 16.3 (CH_3C=CH).

FTIR 2954, 1684, 1597, 1448, 1202 cm^{-1}.

MS (EI^+) Found $[M]^+$: 230.1673 , $C_{16}H_{22}O$ requires 230.1671.

(*E*)-2-Ethylhex-2-en-1-ol



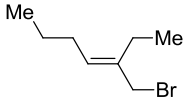
General Procedure E: (*E*)-2-Ethylhex-2-enal (4.00 g, 31.7 mmol) was employed. FCC (hexane: EtOAc 4:1) afforded the title alcohol (3.82 g, 94%, 1:0.05 *E*:*Z*) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 5.39 (t, J = 7.5 Hz, 1H, C=CH), 4.05 (s, 2H, CH_2OH), 2.12 (q, J = 7.5 Hz, 2H, CH_3CH_2C=CH), 2.03 (dt, J = 7.5 and 7.5 Hz, 2H, C=CHCH_2), 1.39 (tq, J = 7.5 and 7.5 Hz, 2H, C=CHCH$_2$CH_2), 1.01 (t, J = 7.5 Hz, 3H, CH_3CH_2C=CH), 0.92 (t, J = 7.5 Hz, 3H, C=CH$(CH_2)_2CH_3$). *Characteristic signals only for the minor isomer:* 5.31 (t, J = 7.5 Hz, 0.05H, C=CH), 4.16 (s, 0.1H, CH_2OH).

^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only:* 140.8 (C=CH), 126.5 (C=CH), 67.1 (CH_2OH), 29.5 (C=CHCH_2), 23.0 (C=CHCH$_2$CH_2), 21.2 (CH_3CH_2C=CH), 14.0 (C=CH$(CH_2)_2CH_3$), 13.4 (CH_3CH_2C=CH).

The spectroscopic properties of this compound were consistent with the data in the literature.[9]

(*E*)-3-(Bromomethyl)hept-3-ene



General Procedure F: (*E*)-2-Ethylhex-2-en-1-ol (2.50 g, 19.5 mmol) was employed to afford the title bromide (3.65 g, 98%, 1:0.05 *E*:*Z*) as a colourless oil.

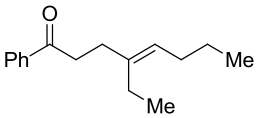
^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 5.59 (t, *J* = 7.5 Hz, 1H, C=C<u>H</u>), 4.04 (s, 2H, C<u>H</u>$_2$Br), 2.23 (q, *J* = 7.5 Hz, 2H, $CH_3C\underline{H}_2C$=CH), 2.03 (dt, *J* = 7.5 and 7.5 Hz, 2H, C=CHC<u>H</u>$_2$), 1.40 (tq, *J* = 7.5 and 7.5 Hz, 2H, C=CHCH$_2$C<u>H</u>$_2$), 1.03 (t, *J* = 7.5 Hz, 3H, C<u>H</u>$_3$CH$_2$C=CH), 0.92 (t, *J* = 7.5 Hz, 3H, C=CH(CH$_2$)$_2$C<u>H</u>$_3$). *Characteristic signals only for the minor isomer:* 5.43 (t, *J* = 7.5 Hz, 0.05H, C=C<u>H</u>), 4.05 (s, 0.1H, C<u>H</u>$_2$Br).

^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only*: 137.9 (<u>C</u>=CH), 131.8 (C=<u>C</u>H), 39.7 (<u>C</u>H$_2$Br), 30.1 (C=CH<u>C</u>H$_2$), 22.6 (C=CHCH$_2$<u>C</u>H$_2$), 21.4 (CH$_3$<u>C</u>H$_2$C=CH), 13.9 (C=CH(CH$_2$)$_2$<u>C</u>H$_3$), 13.0 (<u>C</u>H$_3$CH$_2$C=CH).

FTIR 2963, 1601, 1456, 1208 cm^{-1}.

MS (EI$^+$) Found $[M]^+$ 190.0353, $C_8H_{15}{}^{79}Br$ requires 190.0357.

(*E*)-4-Ethyl-1-phenyloct-4-en-1-one



General Procedure A: Ethyl benzoylacetate (0.82 mL, 4.76 mmol) and (*E*)-3-(bromomethyl)hept-3-ene (1.00 g, 5.23 mmol) were employed. FCC (hexane:EtOAc 40:1) afforded the title compound (0.87 g, 79%, 1:0.05 *E*:*Z*) as a colourless oil.

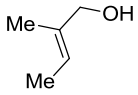
^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 8.00-7.95 (m, 2H, Ar<u>H</u>), 7.60-7.53 (m, 1H, Ar<u>H</u>), 7.50-7.43 (m, 2H, Ar<u>H</u>), 5.15 (t, *J* = 7.5 Hz, 1H, C=C<u>H</u>), 3.11-3.04 (m, 2H, Ar(CO)C<u>H</u>$_2$), 2.44 (t, *J* = 7.5 Hz, 2H, Ar(CO)CH$_2$C<u>H</u>$_2$), 2.09 (q, *J* = 7.5 Hz, 2H, CH$_3$C<u>H</u>$_2$C=CH), 1.99 (dt, *J* = 7.5 and 7.5 Hz, 2H, C=CHC<u>H</u>$_2$), 1.35 (tq, *J* = 7.5 and 7.5 Hz, 2H, C=CHCH$_2$C<u>H</u>$_2$), 1.00 (t, *J* = 7.5 Hz, 3H, C<u>H</u>$_3$CH$_2$C=CH), 0.90 (t, *J* = 7.5 Hz, 3H, C=CH(CH$_2$)$_2$C<u>H</u>$_3$). *Charateristic signals only for the minor isomer:* 5.20 (t, *J* = 7.0 Hz, 0.05H, C=C<u>H</u>), 3.04-2.99 (m, 0.1H, Ar(CO)C<u>H</u>$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer:* 200.3 (C=O), 139.8 (C=CH), 137.1 (ArC), 132.9, 128.5, 128.0 (3 × ArCH), 124.7 (C=CH), 37.7 (Ar(CO)CH_2), 30.9 (Ar(CO)CH_2CH_2), 29.7 (C=CHCH_2), 23.3 (CH_3CH_2C=CH), 23.1 (C=CHCH_2CH_2), 13.8 (CH_3CH_2C=CH), 13.2 (C=CH$(CH_2)_2CH_3$).

FTIR 1685, 1448, 1203 cm^{-1}.

MS (EI^+) Found $[M]^+$: 230.1675, $C_{16}H_{22}O$ requires 230.1671.

(*E*)-2-Methylbut-2-en-1-ol



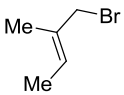
To a solution of tiglic acid (4.00 g, 40 mmol) in THF (40 mL) at 0 °C was added 1M $LiAlH_4$ in THF (80 mL, 80 mmol) over 30 minutes. The reaction mixture was heated at reflux for 16 hours. The mixture was cooled to 0 °C and water (20 mL), NaOH (40 mL) and water (20 mL) were added sequentially. The solution was filtered through celite and the residue was washed with CH_2Cl_2 (600 mL). The filtrate was purified by distillation to obtain the title compound (2.40 g, 70%) as a colourless oil.

Boiling point 130 °C (760 mmHg).

^{1}H NMR (400 MHz, $CDCl_3$): 5.49 (qq, *J* = 7.0 and 1.0 Hz, 1H, C=CH), 3.99 (s, 2H, CH_2OH), 1.67–1.64 (m, 3H, CH_3C=CH), 1.62 (d, *J* = 7.0 Hz, 3H, C=CHCH_3).

The spectroscopic properties of this compound were consistent with the data in the literature.[10]

(*E*)-1-Bromo-2-methylbut-2-ene



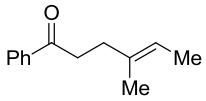
General Procedure F: (*E*)-2-Methylbut-2-en-1-ol (2.40 g, 27.9 mmol) was employed to afford the title compound (2.85 g, 69%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 5.70 (qq, *J* = 7.0 and 1.0 Hz, 1H, C=CH), 3.99 (s, 2H, CH_2Br), 1.76-1.74 (m, 3H, CH_3C=CH), 1.64 (d, *J* = 7.0 Hz, 3H, C=CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 132.7 (C=CH), 125.8 (C=CH), 41.8 (CH_2Br), 14.3 (CH_3C=CH), 13.9 (C=CHCH_3).

The spectroscopic properties of this compound were consistent with the data in the literature.[10]

(*E*)-4-Methyl-1-phenylhex-4-en-1-one



General Procedure A: Ethyl benzoylacetate (2.32 mL, 13.4 mmol) and (*E*)-1-bromo-2-methylbut-2-ene were employed. FCC (hexane:EtOAc 40:1) afforded the title compound (2.22 g, 88%) as a pale yellow oil.

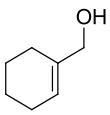
^{1}H NMR (400 MHz, $CDCl_3$): 8.00-7.94 (m, 2H, ArH), 7.60-7.54 (m, 1H, ArH), 7.50-7.44 (m, 2H, ArH), 5.27 (qqt, *J* = 6.5, 1.5 and 1.5 Hz, 1H, C=CH), 3.11-3.07 (m, 2H, Ar(CO)CH_2), 2.45-2.39 (tm, *J* = 7.5 Hz, 2H, Ar(CO)CH_2CH_2), 1.69-1.65 (m, 3H, CH_3C=CH), 1.61-1.56 (dqt, *J* = 6.5, 1.0 and 1.0 Hz, 3H, CH_3C=CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 200.3 (C=O), 137.1 (ArC) , 134.6 (C=CH), 133.0, 128.7, 128.2 (3 × ArCH), 119.2 (C=CH), 37.5 (Ar(CO)CH_2), 34.1 (Ar(CO)CH_2CH_2), 16.0 (CH_3C=CH), 13.5 (CH=CHCH_3).

FTIR 1683, 1598, 1448, 1289, 1202 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 189.1274, $C_{13}H_{17}O$ requires 189.1279.

Cyclohex-1-en-1-ylmethanol



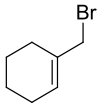
General Procedure E: Methyl 1-cyclohexene-1-carboxylate (1.95 mL, 14.3 mmol) was employed, affording the title alcohol (1.60 g, 95%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 5.72-5.67 (m, 1H, C=CH), 4.00 (s, 2H, CH_2OH), 2.14-1.98 (m, 4H, 2 × CH_2), 1.73-1.55 (m, 4H, 2 × CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): 137.7 (C=CH), 123.2 (C=CH), 67.8 (CH_2OH), 25.7, 25.0, 22.6, 22.5 (4 × CH_2).

The spectroscopic properties of this compound were consistent with the data in the literature.[11,12]

1-(Bromomethyl)cyclohex-1-ene



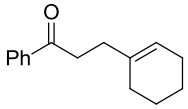
General Procedure F: Cyclohex-1-en-1-ylmethanol (1.60 g, 14.0 mmol) was employed. FCC (hexane:EtOAc 90:1) afforded the title bromide (1.55 g, 70%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 5.91-5.86 (m, 1H, C=CH), 3.95 (br s, 2H, CH_2Br), 2.16-2.01 (m, 4H, 2 × CH_2), 1.72-1.51 (m, 2H, CH_2), 1.61-1.51 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): 134.8 (C=CH), 128.3(C=CH), 40.0 (CH_2Br), 26.5, 25.6, 22.5, 22.0 (4 × CH_2).

The spectroscopic properties of this compound were consistent with the data in the literature.[13]

3-(1-Cyclohexenyl)propiophenone



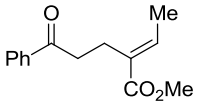
General Procedure A: Ethyl benzoyl acetate (1.35 mL, 7.79 mmol) and 1-(bromomethyl)cyclohex-1-ene (1.50 g, 8.57 mmol) were employed. FCC (hexane:EtOAc 30:1) afforded the title ketone (1.52 g, 92%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.00-7.95 (m, 2H, ArH), 7.60-7.53 (m, 1H, ArH), 7.50-7.43 (m, 2H, ArH), 5.48-5.43 (m, 1H, C=CH), 3.11-3.04 (m, 2H, Ar(CO)CH_2), 2.37 (t, J = 7.5 Hz, 2H, (Ar(CO)CH_2CH_2), 2.03-1.93 (m, 4H, 2 × CH_2), 1.68-1.51 (m, 4H, 2 × CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): 200.4 (C=O), 137.2 (C=CH), 136.7 (ArC), 133.0, 128.7, 128.2 (3 × ArCH), 121.5 (C=CH), 37.2 (Ar(CO)CH_2), 32.5 (Ar(CO)CH_2CH_2), 28.6, 25.3, 23.1, 22.5 (4 × CH_2).

The spectroscopic properties of this compound were consistent with the data in the literature.[14]

Methyl (*E*)-2-ethylidene-5-oxo-5-phenylpentanoate



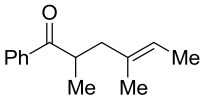
To a solution of diisopropylamine (0.33 mL, 2.40 mmol) in anhydrous THF (1.00 mL) at -78 ^{o}C was added *n*-BuLi (1.54 mL, 2.40 mmol) followed by the slow addition of a solution acetophenone (0.24 g, 2.00 mmol) in anhydrous THF (3.00 mL) at -78 ^{o}C. To the mixture was added methyl 3-acetoxy-2-methylenebutanoate (0.34 g, 2.00 mmol) in anhydrous THF (3.00 mL). The reaction was warmed slowly to room temperature and stirred for 16 hours. The reaction was quenched with saturated aq. NH_4Cl (5 mL), extracted with EtOAc (3 × 20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. FCC (× 2; 1st column: hexane:EtOAc 10:1; 2nd column: toluene:EtOAc 100:1 to 1:1) afforded the title compound (0.18 g, 41%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.01-7.95 (m, 2H, ArH), 7.60-7.52 (m, 1H, ArH), 7.51-7.42 (m, 2H, ArH), 6.94 (q, *J* = 7.0 Hz, 1H, C=CH), 3.75 (s, 3H, (CO)OCH_3), 3.15-3.08 (m, 2H, Ar(CO)CH_2), 2.77-2.71 (m, 2H, Ar(CO)CH_2CH_2), 1.86 (d, *J* = 7.0 Hz, 3H, C=CHCH_3)

^{13}C NMR (100 MHz, $CDCl_3$): 199.5 (ArC=O), 168.0 ((CO)OCH_3), 138.9 (C=CH), 136.7 (ArC), 133.0 (ArCH), 131.7 (C=CH), 128.6, 128.1 (2 × ArCH), 51.7 ((CO)OCH_3), 37.8 (Ar(CO)CH_2), 21.5 (Ar(CO)CH_2CH_2), 14.3 (C=CHCH_3).

The spectroscopic properties of this compound were consistent with the data in the literature.[15]

(*E*)-2,4-Dimethyl-1-phenylhex-4-en-1-one



To a solution of propiophenone (0.97 mL, 7.32 mmol) in anhydrous THF (15 mL) was added NaH (0.34 g, 8.78 mmol) and the mixture was heated at reflux for 90 minutes. Then (*E*)-1-bromo-2-methylbut-2-ene (1.20 g, 8.05 mmol)) was added *via* syringe and the mixture was heated at 80 ^{o}C for 16 hours. The mixture was cooled to room temperature and H_2O (5 mL)

was added. The mixture was extracted with Et_2O (2 × 50 mL) and the combined organic extracts were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (× 2: 1st column hexane:toluene 1:1; 2nd hexane:toluene 2:1) afforded the title compound (0.17 g, 12%) as a pale yellow oil.

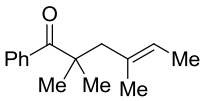
^{1}H NMR (400 MHz, $CDCl_3$): 8.00-7.92 (m, 2H, ArH), 7.59-7.53 (m, 1H, ArH), 7.51-7.43 (m, 2H, ArH), 5.31-5.23 (qqt, *J* = 7.0, 1.0 and 1.0 Hz, 1H, C=CH), 3.69-3.59 (m, 1H, Ar(CO)CH), 2.51 (dd, *J* = 13.5 and 5.5 Hz, 1H, Ar(CO)CHCH_2), 2.06 (dd, *J* = 13.5 and 8.0 Hz, 1H, Ar(CO)CHCH_2), 1.63 (m, 3H, CH_3C=CH), 1.61-1.56 (dqt, *J* = 7.0, 1.0 and 1.0 Hz, 3H, CH_3C=CHCH_3), 1.14 (d, *J* = 7.0 Hz, 3H, Ar(CO)CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 204.3 (C=O), 136.7 (ArC), 132.8 (ArCH), 132.8 (C=CH), 128.6, 128.2 (2 × ArCH), 121.1 (C=CH), 43.5 (Ar(CO)CHCH_2), 38.9 (Ar(CO)CH), 16.8 (Ar(CO)CHCH_3) 15.8 (CH_3C=CH), 13.4 (C=CHCH_3).

FTIR 1681, 1596, 1447, 1231 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 225.1259, $C_{14}H_{18}ONa$ requires 225.1250.

(*E*)-2,2,4-Trimethyl-1-phenylhex-4-en-1-one



To a solution of *iso*-butyrophenone (0.77 mL, 5.13 mmol) in anhydrous *t*-butanol (7.60 mL) was added potassium *t*-butoxide (0.80 g, 7.18 mmol) and the mixture was stirred at room temperature for 5 minutes. Then (*E*)-1-bromo-2-methylbut-2-ene (1.30 g, 8.72 mmol)) was added *via* syringe and the mixture was heated at 75 °C for 16 hours. The mixture was cooled to room temperature and H_2O (5 mL) was added. The mixture was extracted with Et_2O (2 × 50 mL). The organic extracts were combined, washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (× 2: 1st column hexane:toluene 7:1; 2nd hexane:toluene:CH_2Cl_2 3:1:1) afforded the title compound (0.30 g, 27%) as a colourless oil.

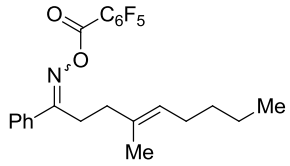
^{1}H NMR (400 MHz, $CDCl_3$): 7.73-7.69 (m, 2H, ArH), 7.50-7.38 (m, 3H, ArH), 5.23 (qqt, *J* = 6.5, 1.0 and 1.0 Hz, 1H, C=CH), 2.55 (s, 2H, CH_2), 1.57 (dqt, *J* = 7.0, 1.0 and 1.0 Hz, 3H, CH_3C=CHCH_3), 1.56-1.53 (m, 3H, CH_3C=CH), 1.31 (s, 6H, (CH_3)$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): 209.5 (C=O), 139.3 (ArC), 132.6 (C=CH), 130.9, 128.1, 128.0 (3 × ArCH), 123.4 (C=CH), 50.5 (CH_2), 48.2 (Ar(CO)C), 26.8 (Ar(CO)C(CH_3)$_2$), 17.8 (CH_3C=CH), 13.6 (CH=CHCH_3).

FTIR 2970, 2862, 1672, 1467, 1444 cm^{-1}.

MS (ESI$^+$) Found $[M+Na]^+$:239.1401, $C_{15}H_{20}ONa$ requires 239.1406.

(4*E*)-4-Methyl-1-phenylnon-4-en-1one *O*-perfluorobenzoyl oxime (3a)



General Procedure C: Part A: (*E*)-4-Methyl-1-phenylnon-4-en-1-one (0.91 g, 3.96 mmol) was used. The reaction was heated at 75^{o}C for 4 hours to afford the corresponding oxime (0.85 g, 88%) as a colourless solid. Part B: The corresponding oxime (0.85 g, 3.48 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 10:1) afforded oxime ester **3a** (1.30 g, 85%, 1:0.1 mixture of oxime isomers) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 7.80-7.70 (m, 2H, ArH), 7.52-7.40 (m, 3H, ArH), 5.16-5.10 (ttq, *J* = 7.0, 1.0 and 1.0 Hz, 1H, C=CH), 3.04-2.97 (m, 2H, Ar(CN)CH_2), 2.25 (tm, *J* = 8.0 Hz, 2H, Ar(CN)CH_2CH_2), 2.00-1.90 (m, 2H, C=CHCH_2), 1.59 (d, *J* = 1.0 Hz, 3H, CH_3C=CH), 1.35-1.19 (m, 4H, C=CHCH_2(CH_2)$_2$), 0.93-1.85 (m, 3H, C=CH(CH_2)$_3$CH_3). *Characteristic signals only for the minor isomer:* 5.10-5.07 (m, 0.1H, C=CH), 2.90-2.84 (m, 0.2H, Ar(CN)CH_2), 2.18 (t, *J* = 8.0 Hz, 0.2H, Ar(CN)CH_2CH_2).

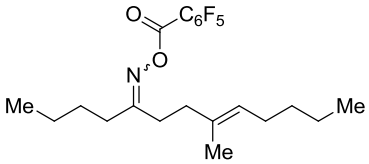
^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only:* 168.7 (C=N), 156.6 (C=O), 133.2 (C=CH), 132.6 (ArC), 131.0, 128.8, 127.5 (3 × ArCH), 126.7 (C=CH), 36.4 (Ar(CN)CH_2CH_2), 31.8 (C=CHCH_2CH_2), 27.9 (Ar(CN)CH_2), 27.8 (C=CHCH_2), 22.3 (C=CH(CH_2)$_2$$CH_2$), 15.7 ($CH_3$C=CH), 14.0 (C=CH($CH_2$)$_3$$CH_3$). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -136.9 (2F), -147.5 (1F), -159.7 (2F). *Signals for the minor isomer:* -137.3 (0.2F), -148.0 (0.1F), -160.0 (0.2F).

FTIR 1764, 1652, 1496, 1325, 1188 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 440.1643, $C_{23}H_{23}NO_2F_5$ requires 440.1649.

(8*E*)-8-Methyltridec-8-en-5-one *O*-perfluorobenzoyl oxime (3b)



General Procedure C: Part A: (*E*)-8-Methyltridec-8-en-5-one (0.30 g, 1.43 mmol) was used. The reaction was heated at 75 °C for 5 hours to afford the corresponding oxime (0.30 g, 92%) as a colourless solid. Part B: The corresponding oxime (0.30 g, 1.33 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 30:1) afforded oxime ester **3b** (0.51 g, 93%, 1:1 mixture of oxime isomers) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for both isomers:* 5.23-5.14 (m, 2H, 2 × C=C**H**), 2.56-2.35 (m, 8H, 2 × (CN)C**H**$_2$CH$_2$C=CH and 2 × CH$_3$(CH$_2$)$_2$C**H**$_2$(CN)), 2.28 (t, *J* = 7.5Hz, 2H, (CN)CH$_2$C**H**$_2$C=CH), 2.20 (t, *J* = 7.5Hz, 2H, (CN)CH$_2$C**H**$_2$C=CH), 2.03-1.90 (m, 4H, 2 × C=CHC**H**$_2$), 1.65-1.63 (m, 3H, C**H**$_3$C=CH), 1.62-1.60 (m, 3H, C**H**$_3$C=CH), 1.59-1.48 (m, 4H, 2 × CH$_3$CH$_2$C**H**$_2$CH$_2$(CN)), 1.45-1.23 (m, 12H, 2 × C=CHCH$_2$(C**H**$_2$)$_2$ and 2 × CH$_3$C**H**$_2$(CH$_2$)$_2$(CN)), 0.99-0.84 (m, 12H, 4 × C**H**$_3$).

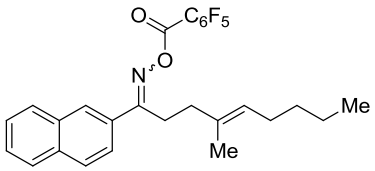
^{13}C NMR (100 MHz, $CDCl_3$): *Signals for both isomers:* 172.5 (**C**=N), 172.4 (**C**=N), 156.7 (2 signals) (2 × **C**=O), 133.1, 132.8 (2 × **C**=CH), 126.6, 126.4 (2 × C=**C**H), 36.3, 35.8, 34.0, 32.9, 32.0, 31.9, 29.6, 28.8, 28.4, 28.1, 27.7 (2 signals), 22.9, 22.6, 22.4 (2 signals) (16 × **C**H$_2$), 15.9, 15.8 (2 × **C**H$_3$C=CH), 14.1 (2 signals), 13.9, 13.8 (4 × **C**H$_3$). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): -137.3 (4F), -147.9 (2F), -159.8 (4F)

FTIR 1761, 1652, 1523, 1499, 1324, 1193 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 420.1947, $C_{21}H_{27}NO_2F_5$ requires 420.1962

(4*E*)-4-Methyl-1-(naphthalen-2-yl)non-4-en-1-one *O*-perfluorobenzoyl oxime (3c)



General Procedure C: Part A: (*E*)-4-Methyl-1-(naphthalen-2-yl)non-4-en-1-one (0.20 g, 0.82 mmol) was used. The reaction was heated at 75 ^{o}C for 2 hours to afford the corresponding oxime (0.20 g, 83%) as a colourless oil. Part B: The corresponding oxime (0.18 g, 0.61 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 9:1) afforded oxime ester **3c** (0.24 g, 80%, 1:0.05 mixture of oxime isomers) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 8.17 (s, 1H, ArH), 7.96-7.85 (m, 4H, ArH), 7.61-7.52 (m, 2H, ArH), 5.20-5.13 (tq, *J* = 7.0 and 1.0 Hz, 1H, C=CH), 3.15-3.09 (m, 2H, Ar(CN)CH_2), 2.31 (t, *J* = 7.5 Hz, 2H, Ar(CN)CH_2CH_2), 1.97 (dt, *J* = 7.0 and 7.0 Hz, 2H, C=CHCH_2), 1.62 (d, *J* = 1.0 Hz, 3H, CH_3C=CH), 1.35-1.19 (m, 4H, C=CH(CH_2)$_2$), 0.88 (t, *J* = 7.0 Hz, 3H, C=CH$(CH_2)_2$CH_3). *Characteristic signals only for the minor isomer:* 5.12-5.07 (m, 0.05H, C=CH), 3.09-3.04 (m, 0.1H, Ar(CN)CH_2), 2.21 (t, *J* = 7.5 Hz, 0.1H, Ar(CN)CH_2CH_2).

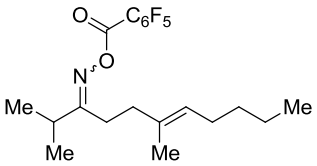
^{13}C NMR (125 MHz, $CDCl_3$): *Signals for the major isomer only:* 168.5 (C=N), 156.6 (C=O), 134.6, 133.0 (2 × ArC), 132.8 (C=CH), 130.7 (ArC), 128.9, 128.7, 128.2, 127.9, 127.7, 126.8 (6 × ArCH), 126.8 (C=CH), 124.1 (ArCH), 36.6 (Ar(CN)CH_2CH_2), 31.8 (C=CHCH_2CH_2), 27.8 (Ar(CN)CH_2), 27.6 (C=CHCH_2), 22.3 (C=CH$(CH_2)_2$CH_2), 15.8 (CH_3C=CH), 14.0 (C=CH$(CH_2)_3$CH_3). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -137.0 (2F), -147.6 (1F), -159.8 (2F). *Signals for the minor isomer:* -137.5 (0.1F), -148.2 (0.05F), -160.1 (0.1F).

FTIR 2927, 1756, 1649, 1525, 1493, 1409, 1322, 1187, 1003 cm^{-1}.

MS (ESI^{+}) Found $[M+Na]^{+}$: 512.1621, $C_{27}H_{24}NO_2F_5Na$ requires 512.1619.

(6*E*)-2,6-Dimethylundec-6-en-3-one *O*-perfluorobenzoyl oxime (3d)



General Procedure C: Part A: (*E*)-2,6-Dimethylundec-6-en-3-one (0.20 g, 1.02 mmol) was used. The reaction was heated at 75 ^{o}C for 4 hours to afford the corresponding oxime (0.21 g, 96%) as a colourless solid. Part B: The corresponding oxime (0.21 g, 0.99 mmol) was employed and the reaction was stirred for 3 hours. FCC (hexane: EtOAc 8:1) afforded oxime ester **3d** (0.38 g, 97%, 1:0.3 mixture of oxime isomers) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 5.18-5.12 (m, 1H, C=C<u>H</u>), 2.74 (sept., *J* = 7.0 Hz, 1H, $(CH_3)_2C\underline{H}(CN)$), 2.49-2.43 (m, 2H, $(CN)C\underline{H}_2$), 2.20 (t, *J* = 8.0 Hz, 2H, $(CN)CH_2C\underline{H}_2$), 2.01-1.92 (m, 2H, $C=CHC\underline{H}_2$), 1.60 (s, 3H, $C\underline{H}_3C=CH$), 1.35-1.25 (m, 4H, $C=CHCH_2(C\underline{H}_2)_2$), 1.21 (d, *J* = 7.0 Hz, 6H, $(C\underline{H}_3)_2CH(CN)$), 0.92-0.83 (m, 3H, $C=CH(CH_2)_3C\underline{H}_3$). *Characteristic signals only for the minor isomer:* 5.23-5.18 (m, 0.3H, C=C<u>H</u>), 3.34 (sept., *J* = 7.0 Hz, 0.3H, $(CH_3)_2C\underline{H}(CN)$), 2.35-2.29 (m, 0.6H, $(CN)CH_2C\underline{H}_2$), 1.65 (s, 0.9H, $C\underline{H}_3C=CH$), 1.15 (d, *J* = 7.0Hz, 1.8H, $(C\underline{H}_3)_2CH(CN)$).

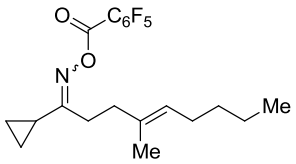
^{13}C NMR (125 MHz, $CDCl_3$): *Signals for the major isomer:* 175.8 (<u>C</u>=N), 156.7 (<u>C</u>=O), 133.2 (<u>C</u>=CH), 126.4 (C=<u>C</u>H), 36.3 ($(CN)CH_2\underline{C}H_2$), 34.3 ($(CH_3)_2\underline{C}H(CN)$), 31.9 ($C=CHCH_2\underline{C}H_2$), 27.7 ($(CN)\underline{C}H_2$), 27.6 ($C=CH\underline{C}H_2$), 22.4 ($C=CH(CH_2)_2\underline{C}H_2$), 19.9 ($(\underline{C}H_3)_2CH(CN)$), 15.7 ($\underline{C}H_3C=CH$), 14.1 ($C=CH(CH_2)_3\underline{C}H_3$). *Signals for the minor isomer:* 175.5 (<u>C</u>=N), 156.7 (<u>C</u>=O), 133.4 (<u>C</u>=CH), 125.9 (C=<u>C</u>H), 36.1 ($(CN)CH_2\underline{C}H_2$), 34.3 ($(CH_3)_2\underline{C}H(CN)$), 31.9 ($C=CHCH_2\underline{C}H_2$), 29.7 ($(CN)\underline{C}H_2$), 29.3 ($C=CH\underline{C}H_2$), 22.3 ($C=CH(CH_2)_2\underline{C}H_2$), 19.0 ($(\underline{C}H_3)_2CH(CN)$), 15.9 ($\underline{C}H_3C=CH$), 14.0 ($C=CH(CH_2)_3\underline{C}H_3$). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -137.2 (2F), -148.0 (1F), -159.9 (2F). *Signals for the minor isomer:* -137.4 (0.6F), -148.1 (0.3F), -160.0 (0.6F).

FTIR 1761, 1652, 1523, 1497, 1324, 1094 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 406.1795, $C_{20}H_{25}NO_2F_5$ requires 406.1805.

(4*E*)-1-Cyclopropyl-4-methylnon-4-en-1-one *O*-perfluorobenzoyl oxime (3e)



General Procedure C: Part A: (*E*)-1-Cyclopropyl-4-methylnon-4-en-1-one (0.90 g, 4.63 mmol) was used. The reaction was heated at 75 ^{o}C for 16 hours to afford the corresponding oxime (0.80 g, 83%) as a colourless oil. Part B: The corresponding oxime (0.50 g, 2.39 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane: EtOAc 30:1) afforded oxime ester **3e** (0.72 g, 75%, 1:0.5 mixture of oxime isomers) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for both isomers:* 5.21-5.15 (m, 1.5H, C=C**H**), 2.40-2.35 (m, 2H, (CN)C**H**$_2$), 2.30-2.20 (m, 3H, (CN)C**H**$_2$ and (CN)CH$_2$C**H**$_2$), 2.10-2.05 (m, 1H, (CN)C**H**$_2$), 2.02-1.93 (m, 3H, C=CHC**H**$_2$), 1.75-1.66 (m, 1.5H, 2 × (CH$_2$)$_2$C**H**), 1.62 (s, 1.5H, C**H**$_3$C=CH), 1.60 (s, 3H, C**H**$_3$C=CH), 1.34-1.23 (m, 6H, 2 × C=CHCH$_2$(C**H**$_2$)$_2$), 1.06-0.83 (m, 10.5H, 2 × (C**H**$_2$)$_2$CH and 2 × C=CH(CH$_2$)$_3$C**H**$_3$).

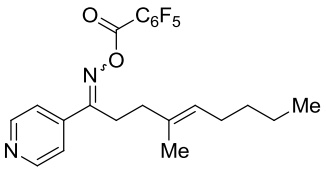
^{13}C NMR (125 MHz, $CDCl_3$): *Signals for both isomers*: 173.2 (**C**=N maj.), 172.0 (**C**=N min.), 156.8 (C=O min.), 156.5 (C=O maj.), 133.2 (**C**=CH min.), 132.8 (**C**=CH maj.), 126.3 (C=**C**H maj.), 126.0 (C=**C**H min.), 36.9, 36.1 (2 × (CN)CH$_2$**C**H$_2$), 31.9, 31.8 (2 × C=CHCH$_2$**C**H$_2$), 28.1, 28.0 (2 × (CN)**C**H$_2$), 27.6, 27.5 (2 × C=CH**C**H$_2$), 22.4, 22.3 (2 × C=CH(CH$_2$)$_2$**C**H$_2$), 15.9, 15.6 (2 × **C**H$_3$C=CH), 14.3, 14.2 (2 × C=CH(CH$_2$)$_3$**C**H$_3$), 13.9 (2 signals) (2 × (CN)**C**H), 6.8, 6.5 (2 × (**C**H$_2$)$_2$). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -137.4 (2F), -148.1 (1F), -160.1 (2F). *Signals for the minor isomer:* -137.4 (1F), -148.3 (0.5F), -160.1 (1F).

FTIR 1759, 1523, 1496, 1324, 1197, 995 cm^{-1}.

MS (ESI^{+}) Found [M+Na]$^{+}$: 426.1464, $C_{20}H_{22}NO_2F_5Na$ requires 426.1474.

(4*E*)-4-Methyl-1-(pyridine-4-yl)non-4-en-1-one *O*-perfluorobenzoyl oxime (3f)



General Procedure C: Part A: (*E*)-4-Methyl-1-(pyridine-4-yl)non-4-en-1-one (0.20 g, 0.88 mmol) was used. The reaction was heated at 75 ^{o}C for 2 hours to afford the corresponding oxime (0.19 g, 88%) as a colourless oil. Part B: The corresponding oxime (0.17 g, 0.69 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 2:1) afforded oxime ester **3f** (0.22 g, 73%, 1:0.05 mixture of oxime isomers) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer*: 8.76-8.70 (m, 2H, ArH), 7.63-7.59 (m, 2H, ArH), 5.12 (tq, *J* = 7.5 and 1.0 Hz, 1H, C=CH), 3.00 (t, *J* = 7.5 Hz, 2H, Ar(CN)CH_2), 2.24 (t, *J* = 7.5 Hz, 2H, Ar(CN)CH_2CH_2), 1.94 (dt, *J* = 7.5 and 7.5 Hz, 2H, C=CHCH_2), 1.59 (d, *J* = 1.0 Hz, 3H, CH_3C=CH), 1.32-1.21 (m, 4H, C=CHCH_2(CH_2)$_2$), 0.89 (t, *J* = 7.0 Hz, 3H, C=CH$(CH_2)_3$CH_3). *Characteristic signals only for the minor isomer:* 5.16 (t, *J* = 7.5 Hz, 0.05H, C=CH).

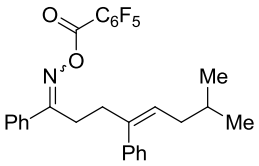
^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only*: 167.0 (C=N), 156.2 (C=O), 150.6 (ArCH), 141.0 (ArC), 132.2 (C=CH), 127.3 (C=CH), 121.5 (ArCH), 36.2 (Ar(CN)CH_2CH_2), 31.8 (C=CHCH_2CH_2), 27.6 (Ar(CN)CH_2), 27.5 (C=CHCH_2), 22.4 (C=CH$(CH_2)_2$CH_2), 15.7 (CH_3C=CH), 14.0 (C=CH$(CH_2)_3$CH_3). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -136.8 (2F), -146.8 (1F), -159.5 (2F). *Signals for the minor isomer:* -136.9 (0.1F), -146.9 (0.05F), -159.6 (0.1F).

FTIR 1766, 1651, 1523, 1496, 1325, 1185, 1002 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 441.1603 , $C_{22}H_{22}N_2O_2F_5$ requires 441.1601.

(4*Z*)-7-Methyl-1,4-diphenyloct-4-en-1-one *O*-perfluorobenzoyl oxime (3g)



General Procedure C: Part A: (*Z*)-7-Methyl-1,4-diphenyloct-4-en-1-one (0.58 g, 2.00 mmol) was used. The reaction was heated at 75 ^{o}C for 4 hours to afford the corresponding oxime (0.59 g, 96%) as a colourless solid. Part B: The corresponding oxime (0.55 g, 1.79 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 10:1) afforded oxime ester **3g** (0.76 g, 85%, 1:0.1 mixture of oxime isomers and 1:0.05 *Z*:*E* mixture of olefin isomers) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major oxime isomer of the major olefin isomer*: 7.68-7.63 (m, 2H, ArH), 7.51-7.46 (m, 1H, ArH), 7.45-7.38 (m, 2H, ArH), 7.28-7.16 (m, 3H, ArH), 7.10-7.03 (m, 2H, ArH), 5.48 (t, *J* = 7.5 Hz, 1H, C=CH), 2.94-2.86 (m, 2H, Ar(CN)CH_2), 2.66-2.60 (m, 2H, Ar(CN)CH_2CH_2), 1.81 (dd, *J* = 7.0 and 7.0 Hz, 2H, C=CHCH_2), 1.56 (m, 1H, $((CH_3)_2CH)$, 0.82 (d, *J* = 6.5 Hz, 6H, $((CH_3)_2CH)$. *Characteristic signals only for minor isomers*: 5.68 (t, *J* = 7.5 Hz, 0.1H, C=CH *oxime isomer*), 2.80-2.74 (m, 0.3H, Ar(CN)CH_2 *oxime and olefin isomers*), 2.58-2.53 (m, 0.3H, Ar(CN)CH_2CH_2 *oxime and olefin isomers*), 1.91 (dd, *J* = 7.5 and 7.5 Hz, 0.2H, C=CHCH_2 *oxime isomer*), 0.85 (d, *J* = 6.5 Hz, 0.3H, $(CH_3)_2CH$ *olefin isomer*), 0.82 (d, *J* = 6.5 Hz, 0.6H, $((CH_3)_2CH$ *oxime isomer*).

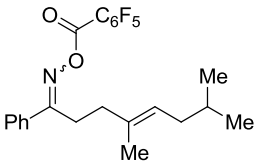
^{13}C NMR (125 MHz, $CDCl_3$): *Signals for the major isomer only:* 168.6 (C=N), 156.4 (C=O), 139.9 (C=CH), 139.2 (ArC), 133.1 (ArC), 131.0, 128.7 (2 × ArCH), 128.6 (C=CH), 128.1, 127.9, 127.5, 126.6 (4 × ArCH), 37.8 (C=CHCH_2), 36.4 ((CN)CH_2CH_2), 28.8 ($(CH_3)_2CH$), 28.2 ((CN)CH_2), 22.3 ($(CH_3)_2CH$). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major oxime and olefin isomer:* -136.8 (2F), -147.7 (1F), -159.8 (2F). *Characteristic signals only for minor isomers* -137.3 (0.3F), -148.0 (0.15F), -160.0 (0.3F).

FTIR 1762, 1652, 1495, 1324, 1190 cm^{-1}.

MS (ESI^{+}) Found $[M+Na]^{+}$: 524.1624 , $C_{28}H_{24}NO_2Na$ requires 524.1619.

(4*E*)-4,7-Dimethyl-1-phenyloct-4-en-1-one *O*-perfluorobenzoyl oxime (3h)



General Procedure C: Part A: (*E*)-4,7-Dimethyl-1-phenyloct-4-en-1-one (0.20 g, 0.88 mmol) was used. The reaction was heated at 75 ^{o}C for 3 hours to afford the corresponding oxime (0.19 g, 88%) as a colourless oil. Part B: The corresponding oxime (0.17 g, 0.69 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 22:1) afforded oxime ester **3h** (0.22 g, 73%, 1:0.1 mixture of oxime isomers) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 7.80-7.72 (m, 2H, ArH), 7.55-7.40 (m, 3H, ArH), 5.23-5.12 (qt, *J* = 7.5 and 1.0 Hz, 1H, C=CH), 3.05-2.99 (m, 2H, Ar(CN)CH_2), 2.26 (t, *J* = 8.0 Hz, 2H, Ar(CN)CH_2CH_2), 1.84 (dd, *J* = 7.5 and 7.5 Hz, 2H, C=CHCH_2), 1.60 (d, *J* = 1.0 Hz, 3H, CH_3C=CH), 1.61-1.50 (m, 1H, $(CH_3)_2$CH), 0.87 (d, *J* = 7.0 Hz, 6H, $(CH_3)_2$CH). *Characteristic signals only for the minor isomer:* 2.90-2.85 (m, 0.2H, Ar(CN)CH_2), 2.20 (t, *J* = 8.0 Hz, 0.2H, Ar(CN)CH_2CH_2), 0.80 (d, *J* = 7.0 Hz, 0.6H, $(CH_3)_2$CH).

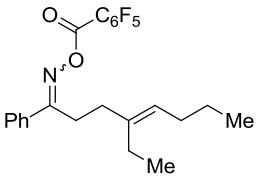
^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only:* 168.7 (C=N), 156.6 (C=O), 133.3 (ArC), 133.2 (C=CH), 131.0, 128.8, 127.5 (3 × ArCH), 125.4 (C=CH), 37.0 (C=CHCH_2), 36.5 (Ar(CN)CH_2CH_2), 28.7 ($(CH_3)_2$CH), 28.0 (Ar(CN)CH_2), 22.3 ($(CH_3)_2$CH), 15.8 (CH_3C=CH). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -137.1 (2F), -147.7 (1F), -159.9 (2F). *Signals for the minor isomer*: -137.5 (0.2F), -148.2 (0.1F), -160.2 (0.2F).

FTIR 1763, 1523, 1496, 1325, 1188, 1001 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 440.1650, $C_{23}H_{23}NO_2F_5$ requires 440.1649.

(4*E*)-4-Ethyl-1-phenyloct-4-en-1-one *O*-perfluorobenzoyl oxime (3i)



General Procedure C: Part A: (*E*)-4-Ethyl-1-phenyloct-4-en-1-one (0.85 g, 3.69 mmol) was used. The reaction was heated at 75 ^{o}C for 16 hours to afford the corresponding oxime (0.80 g, 88%) as a colourless solid. Part B: The corresponding oxime (0.50 g, 2.04 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 32:1) afforded oxime ester **3i** (0.62 g, 69%, 1:0.05 mixture of oxime isomers and 1:0.05 *E*:*Z* mixture of olefin isomers) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for major oxime isomer of the major olefin isomer:* 7.80-7.71 (m, 2H, ArH), 7.53-7.40 (m, 3H, ArH), 5.11 (t, *J* = 7.5 Hz, 1H, C=CH), 3.02-2.96 (m, 2H, Ar(CN)CH_2), 2.26 (t, *J* = 7.5 Hz, 2H, Ar(CN)CH_2CH_2), 2.02 (q, *J* = 7.5 Hz, 2H, CH_3CH_2C=CH), 1.95 (dt, *J* = 7.5 and 7.5 Hz, 2H, C=CHCH_2), 1.33 (tq, *J* = 7.5 and 7.5 Hz, 2H, C=$CHCH_2CH_2$), 0.91 (t, *J* = 7.5 Hz, 3H, CH_3CH_2C=CH), 0.89 (t, *J* = 7.5 Hz, 3H, C=$CH(CH_2)_2CH_3$). *Characteristic signals for the minor isomers:* 5.16 (t, *J* = 7.0 Hz, 0.05H, C=CH), 2.96-2.90 (m, 0.1H, Ar(CN)CH_2), 2.20 (t, *J* = 7.5 Hz, 0.2H, Ar(CN)CH_2CH_2), 0.96 (t, *J* = 7.5 Hz, 0.1H, CH_3CH_2C=CH), 0.81 (t, *J* = 7.5 Hz, 0.1H, C=$CH(CH_2)_2CH_3$).

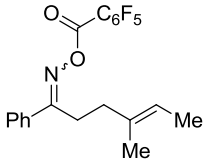
^{13}C NMR (125 MHz, $CDCl_3$): *Signals for major oxime isomer of the major olefin isomer only:* 168.7 (C=N), 156.5 (C=O), 138.9 (C=CH), 133.2 (ArC), 131.0, 128.7, 127.5 (3 × ArCH), 125.8 (C=CH), 33.1 (Ar(CN)CH_2CH_2), 29.6 (C=$CHCH_2$), 28.2 (Ar(CN)CH_2), 23.0 (C=$CHCH_2CH_2$), 22.8 (CH_3CH_2C=CH), 13.8 (C=$CH(CH_2)_2CH_3$), 13.0 (CH_3CH_2C=CH). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for major oxime isomer of the major olefin isomer:* -137.1 (2F), -147.7 (1F), -159.9 (2F). *Signals for the minor isomers:* -137.5 (0.2F), -148.2 (0.1F), -160.2 (0.2F).

FTIR 1769, 1651, 1521, 1495, 1325, 1195 cm^{-1}.

MS (ESI^{+}) Found $[M+Na]^{+}$: 462.1470, $C_{23}H_{22}NO_2F_5Na$ requires 462.1474.

(4*E*)-4-Methyl-1-phenylhex-4-en-1-one *O*-perfluorobenzoyl oxime (3j)



General Procedure C: Part A**:** (*E*)-4-Methyl-1-phenylhex-4-en-1-one (0.38 g, 2.00 mmol) was used. The reaction was heated at 75 ^{o}C for 2 hours to afford the corresponding oxime (0.37 g, 92%) as a colourless solid. Part B: The corresponding oxime (0.29 g, 1.42 mmol) was employed and the reaction was stirred for 3.5 hours. FCC (hexane:EtOAc 18:1) afforded oxime ester **3j** (0.52 g, 92%, 1:0.1 mixture of oxime isomers) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 7.76-7.69 (m, 2H, ArH), 7.53-7.39 (m, 3H, ArH), 5.25-5.17 (qqt, *J* = 6.5, 1.0 and 1.0 Hz, 1H, C=CH), 3.04-2.98 (m, 2H, Ar(CN)CH_2), 2.24 (tm, *J* = 8.0 Hz, 2H, Ar(CN)CH_2CH_2), 1.62-1.57 (m, 3H, CH_3C=CH), 1.56-1.50 (dqt, *J* = 6.5, 1.0 and 1.0 Hz, 3H, C=CHCH_3). *Characteristic signals only for the minor isomer:* 5.19-5.14 (m, 0.1H, C=CH), 2.88-2.82 (m, 0.2H, Ar(CN)CH_2), 2.21-2.15 (m, 0.2H, Ar(CN)CH_2).

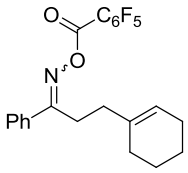
^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only:* 168.8 (C=N), 156.7 (C=O), 133.6 (C=CH), 133.2 (ArC), 131.0, 128.7, 127.4 (3 × ArCH) 120.3 (C=CH), 36.3 (Ar(CN)CH_2CH_2), 27.9 (Ar(CN)CH_2), 15.4 (CH_3C=CH), 13.3 (C=CHCH_3). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -137.0 (2F), -147.5 (1F), -159.7 (2F). *Signals for the minor isomer:* -137.3 (0.2F), -148.0 (0.1F), -160.0 (0.2F).

FTIR 1754, 1650, 1528, 1491, 1320, 1184 cm^{-1}.

MS (CI^{+}) Found $[M+H]^{+}$: 398.1185, $C_{20}H_{17}NO_2F_5$ requires 398.1179.

3-(Cyclohex-1-en-1-yl)-1-phenylpropan-1-one *O*-perfluorobenzoyl oxime (3k)



General Procedure C: Part A: 3-(1-Cyclohexenyl)-propiophenone (1.45 g, 6.78 mmol) was used. The reaction was heated at 75 ^{o}C for 2 hours to afford the corresponding oxime (1.43 g, 94%) as a colourless solid. Part B: The corresponding oxime (1.30 g, 5.68 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 12:1) afforded oxime ester **3k** (1.74 g, 73%, 1:0.05 mixture of oxime isomers) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer*: 7.76-7.70 (m, 2H, ArH), 7.54-7.37 (m, 3H, ArH), 5.41 (m, 1H, C=CH), 3.04-2.96 (m, 2H, Ar(CN)CH_2), 2.21 (t, J = 7.0 Hz, 2H, Ar(CN)CH_2CH_2), 2.00-1.85 (m, 4H, 2 × CH_2), 1.59-1.45 (m, 4H, 2 × CH_2). *Characteristic signals only for the minor isomer*: 5.38 (m, 0.05H, C=CH), 2.90-2.84 (m, 0.1H, Ar(CN)CH_2).

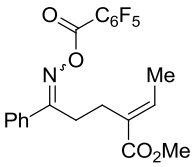
^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer only*: 168.9 (C=N), 156.6 (C=O), 135.6 (C=CH), 133.3 (ArC), 130.9, 128.7, 127.5 (3 × ArCH), 122.7 (C=CH), 34.7 (Ar(CN)CH_2CH_2), 28.0 (CH_2), 27.7 (Ar(CN)CH_2), 25.1, 22.7, 22.2 (3 × CH_2). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer*: -137.0 (2F), -147.5 (1F), -159.7 (2F). *Signals for the minor isomer*: 137.3 (0.1F), -148.0 (0.05F), -160.0 (0.1F).

FTIR 2935, 1753, 1650, 1493, 1325, 1191, 1004, 895 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 424.1339 , $C_{22}H_{19}F_5NO_2$ requires 424.1136.

(2*E*)-Methyl 2-ethylidene-5-(((perfluorobenzoyl)oxy)imino)-5-phenylpentanoate (3l)



General Procedure C: Part A: Methyl (*E*)-2-ethylidene-5-oxo-5-phenylpentanoate (0.25 g, 1.08 mmol) was used. In a modification to the general procedure, the reaction was stirred at 25 ^{o}C for 16 hours. FCC (hexane:EtOAc 10:1) afforded the corresponding intermediate oxime, (2*E*)-methyl-2-ethylidene-5-(hydroxyimino)-5-phenylpentanoate (0.24 g, 90%, 1:0.07 mixture of oxime isomers) as a colourless oil.

Data for the intermediate oxime:

^{1}H NMR (400 MHz, $CDCl_3$): *Data for the major isomer:* 7.91 (s, 1H, N(OH)), 7.79-7.69 (m, 2H, ArH), 7.44-7.36 (m, 3H, ArH), 6.91 (q, *J* = 7.0 Hz, 1H, C=CH), 3.77 (s, 3H, (CO)OCH_3), 2.96-2.90 (m, 2H, Ar(CN)CH_2), 2.67-2.61 (m, 2H, Ar(CN)CH_2CH_2), 1.83 (d, *J* = 7.0 Hz, 3H, C=CHCH_3). *Characteristic signals only for the minor isomer*: 6.11 (q, *J* = 7.0 Hz, 0.07H, C=CH), 1.98 (d, *J* = 7.0 Hz, 0.21H, C=CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): *Data for the major isomer only:* 168.0 ((CO)OCH_3), 159.0 (ArC=N), 139.0 (C=CH), 135.5 (ArC), 131.9 (C=CH), 129.2, 128.5, 128.1 (3 × ArCH), 51.7 ((CO)OCH_3), 25.2 (Ar(CN)CH_2), 23.4 (Ar(CN)CH_2CH_2), 14.2 (C=CHCH_3).

FTIR 3393, 1707, 1437, 1267 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 248.1275, $C_{14}H_{18}NO_3$ requires 248.1287.

General Procedure C: Part B: The corresponding oxime (0.17 g, 0.69 mmol) was employed and the reaction was stirred for 16 hours. FCC (hexane:EtOAc 10:1) afforded oxime ester **3l** (0.23 g, 76%, 1:0.07 mixture of oxime isomers) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): *Data for the major isomer:* 7.89-7.84 (m, 2H, ArH), 7.52-7.42 (m, 3H, ArH), 6.88 (q, *J* = 7.5 Hz, 1H, C=CH), 3.69 (s, 3H, (CO)OCH_3), 3.07-3.01 (m, 2H, Ar(CN)CH_2), 2.64-2.59 (m, 2H, Ar(CN)CH_2CH_2), 1.70 (d, *J* = 7.5 Hz, 3H, C=CHCH_3). *Characteristic signals only for the minor isomer*: 6.07 (q, *J* = 7.5 Hz, 0.07H, C=CH), 1.96 (d, *J* = 7.5 Hz, 0.21H, C=CHCH_3).

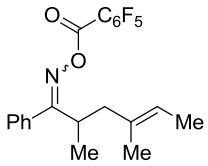
^{13}C NMR (100 MHz, $CDCl_3$): *Data for the major isomer:* 167.6 ((CO)OCH_3), 167.5 (ArC=N), 139.3 (C=CH), 132.9 (ArC), 131.2 (ArCH), 131.0 (C=CH), 128.8, 127.4 (2 × ArCH), 51.6 ((CO)OCH_3), 27.5 (Ar(CN)CH_2), 23.8 (Ar(CN)CH_2CH_2), 14.1 (C=CHCH_3). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR *Signals for the major isomer:* -136.8 (2F), -147.5 (1F), -159.8 (2F). *Signals for the minor isomer:* -141.3 (0.14F), -152.6 (0.07F), -160.3 (0.14F).

FTIR 1765, 1698, 1651, 1526, 1494, 1321, 1258, 1196 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 464.0895, $C_{21}H_{16}NO_4NaF_5$ requires 464.0892.

(4*E*)-2,4-Dimethyl-1-phenylhex-4-en-1-one *O*-perfluorobenzoyl oxime (3m)



General Procedure C: Part A**:** (*E*)-2,4-Dimethyl-1-phenylhex-4-en-1-one (0.13 g, 0.64 mmol) was used. The reaction was heated at 75 ^oC for 2 hours to afford the corresponding oxime (0.11 g, 83%) as a colourless solid. Part B: The corresponding oxime (0.11 g, 0.54 mmol) was employed and the reaction was stirred for 3.5 hours. FCC (hexane:EtOAc 40:1) afforded oxime ester **3m** (0.17 g, 81%, 1:0.6 mixture of oxime isomers) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for both isomers:* 7.50-7.34 (m, 6H, ArH), 7.21-7.15 (m, 2H, ArH), 5.30-5.22 (m, 0.6H, C=CH), 5.18-5.09 (m, 1H, C=CH), 3.64 (qt, *J* = 7.5 and 7.5 Hz, 1H, Ar(CN)CH), 3.16-3.04 (m, 0.6H, Ar(CN)CH), 2.40-2.28 (m, 1.6H, Ar(CN)CHCH_2), 2.18-1.99 (m, 1.2H, Ar(CN)CHCH_2), 1.60-1.55 (m, 3.6H, CH_3C=CH and C=CHCH_3), 1.55-1.49 (m, 6H, CH_3C=CH and C=CHCH_3), 1.23 (d, *J* = 7.0 Hz, 3H, Ar(CN)CHCH_3), 1.17 (d, *J* = 7.0 Hz, 1.8H, Ar(CN)CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 173.8, 173.8 (2 × C=N), 156.7, 156.6 (2 × C=O), 133.5 (ArC), 132.4 (2 signals) (2 × C=CH), 132.2 (ArC), 129.8, 129.2, 128.3, 128.2, 128.1, 126.7 (6 × ArCH), 121.8, 121.6 (2 × C=CH), 44.0, 43.5 (2 × Ar(CN)CHCH_2), 38.4, 34.1 (2 × Ar(CN)CH), 17.3, 17.2 (2 × Ar(CN)CHCH_3), 15.4, 15.3 (2 × CH_3C=CH), 13.4, 13.3 (2 ×

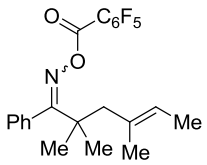
C=CHCH$_3$). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -137.1 (2F), -147.6 (1F), -159.6 (2F). *Signals for the minor isomer:* -137.3 (1.2F), -148.2 (0.6F), -160.1 (1.2F).

FTIR 1761, 1652, 1523, 1496, 1324, 1188 cm^{-1}.

MS (ESI$^+$) Found $[M+Na]^+$: 434.1150, $C_{21}H_{18}NO_2F_5Na$ requires 434.1150.

(4*E*)-2,2,4-Trimethyl-1-phenylhex-4-en-1-one *O*-perfluorobenzoyl oxime (3n)



General Procedure C: Part A**:** (*E*)-2,2,4-Trimethyl-1-phenylhex-4-en-1-one (0.23 g, 1.06 mmol) was used and, in a modification to the general procedure, $H_2NOH.HCl$ (200 mol%) and NaOAc (200 mol%) were employed. The reaction was heated to 100 ^oC for 24 hours to afford the corresponding oxime (0.20 g, 82%) as a colourless solid. Part B: The corresponding oxime (0.29 g, 1.42 mmol) was employed and the reaction was stirred for 3.5 hours. FCC (hexane:EtOAc 20:1) afforded oxime ester **3n** (0.30 g, 90%, 1:0.05 mixture of oxime isomers) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): *Signals for the major isomer:* 7.42-7.31 (m, 3H, ArH), 7.15-7.01 (m, 2H, ArH), 5.30 (qqt, *J* = 7.0, 1.0 and 1.0 Hz, 1H, C=CH), 2.32 (s, 2H, CH_2), 1.70-1.67 (m, 3H, CH_3C=CH), 1.63-1.69 (dqt, *J* = 6.5, 1.0 and 1.0 Hz, 3H, C=CHCH_3), 1.23 (s, 6H, Ar(CN)C(CH_3)$_2$). *Characteristic signals only for the minor isomer*: 5.46 (m, 0.05H, C=CH), 2.43 (s, 0.1H, CH_2), 1.26 (s, 0.3H, Ar(CN)C(CH_3)$_2$).

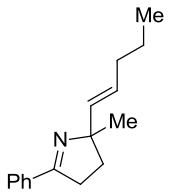
^{13}C NMR (125 MHz, $CDCl_3$): 177.4 (C=N), 156.7 (C=O), 132.7 (ArC), 131.8 (C=CH), 128.5, 127.9, 124.5 (3 × ArCH), 124.3 (C=CH), 48.9 (CH_2), 42.4 (Ar(CN)C), 26.0 (Ar(CN)C(CH_3)$_2$), 18.5 (CH_3C=CH), 13.7 (C=CHCH_3). *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

^{19}F NMR (376 MHz, $CDCl_3$): *Signals for the major isomer:* -137.6 (2F), -148.6 (1F), -160.4 (2F). *Signals for the minor isomer:* -137.3 (0.1F), -144.7 (0.05F), -158.7 (0.1F).

FTIR 2974, 2926, 1760, 1651, 1522, 1497, 1325, 1189 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 448.1315, $C_{22}H_{20}NO_2F_5Na$ requires 448.1306.

(*E*)-2-Methyl-2-(pent-1-en-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (4a)



General Procedure D: Oxime ester **3a** (70 mg, 0.16 mmol) was employed and the reaction was heated at 120 °C for 2 hours. FCC (hexane:EtOAc 6:1) afforded imine **4a** (29 mg, 80%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.91-7.83 (m, 2H, ArH), 7.47-7.37 (m, 3H, ArH), 5.67 (dt, *J* = 15.5 and 1.0 Hz, 1H, CH=CHCH$_2$), 5.53 (dt, *J* = 15.5 and 6.5 Hz, 1H, CH=CHCH$_2$), 3.08-2.90 (m, 2H, Ar(CN)CH$_2$), 2.11-1.96 (m, 3H, CH=CHCH$_2$ and Ar(CN)CH$_2$CH$_2$), 1.93-1.81 (m, 1H, Ar(CN)CH$_2$CH$_2$), 1.46-1.33 (m, 2H, CH=CHCH$_2$CH$_2$), 1.42 (s, 3H, (NC)CH$_3$), 0.89 (t, *J* = 7.5 Hz, 3H, CH=CH(CH$_2$)$_2$CH$_3$).

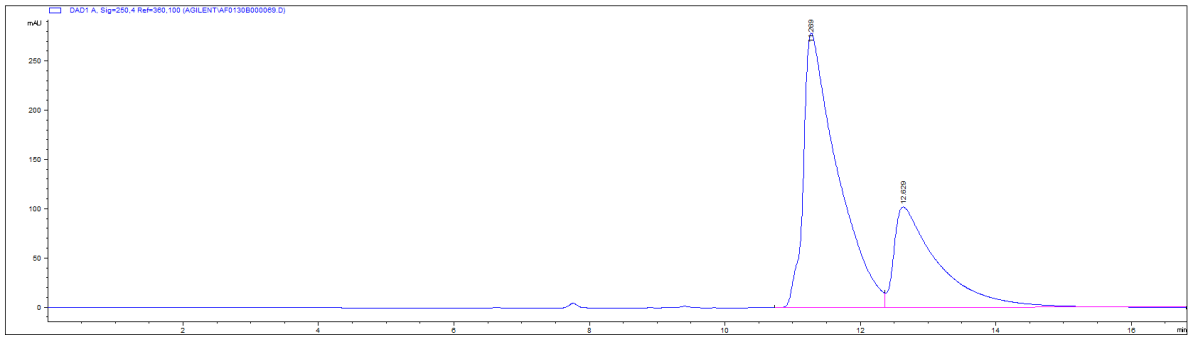
^{13}C NMR (100 MHz, $CDCl_3$): 170.7 (C=N), 136.3 (CH=CHCH$_2$), 134.8 (ArC), 130.3, 128.3, 127.7 (3 × ArCH), 127.2 (CH=CHCH$_2$), 76.1 (quaternary C), 36.0 (Ar(CN)CH$_2$CH$_2$), 34.9 (Ar(CN)CH$_2$), 34.6 (CH=CHCH$_2$), 27.4 ((NC)CH$_3$), 22.5 (CH=CHCH$_2$CH$_2$), 13.7 (CH=CH(CH$_2$)$_2$CH$_3$).

FTIR 1614, 1576, 1448, 1339 cm^{-1}.

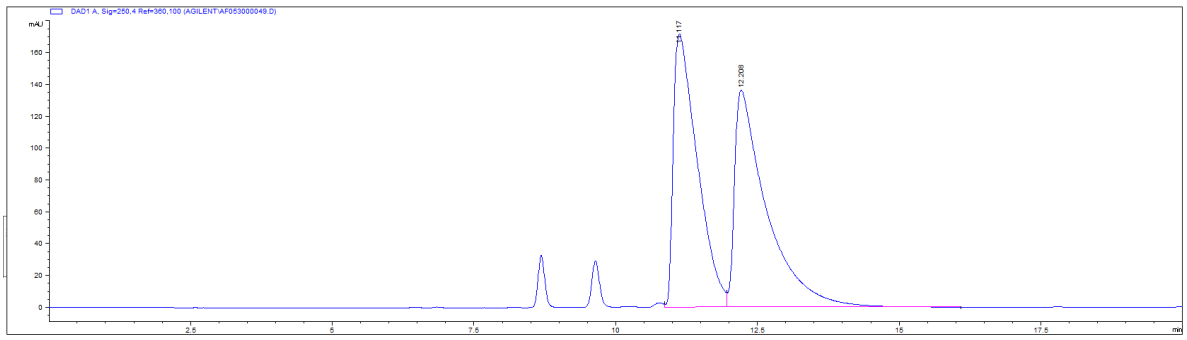
MS (EI^+) Found $[M]^+$: 227.1683, $C_{16}H_{21}N$ requires 227.1674.

General Procedure G: Oxime ester **3a** (50 mg, 0.13 mmol) was employed and the reaction was heated at 120 °C for 4.5 hours. FCC (hexane:EtOAc 6:1) afforded imine **4a** (14.5 mg, 51%, 37% *e.e*) as a pale yellow oil. Spectroscopic properties were identical to those described above for racemic material.

Chiral HPLC *Column:* Chiralpak IC; *Solvent:* isocratic hexane-*i*-PrOH (98:2, 0.5mL/min, 20 °C); t_R (major) = 11.2 min and t_R (minor) = 12.6 min.

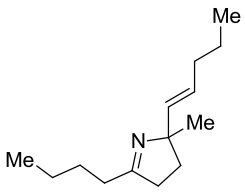


Signal:	DAD1 A, Sig=250,4 Ref=360,100				
RT [min]	Type	Width [min]	Area	Height	Area% Name
11.269	MF	0.5810	9714.4980	278.6715	68.4673
12.629	FM	0.7335	4474.0166	101.6619	31.5327
		Sum	14188.5146		



Signal:	DAD1 A, Sig=250,4 Ref=360,100				
RT [min]	Type	Width [min]	Area	Height	Area% Name
11.117	MF	0.4824	4907.7534	169.5611	49.5317
12.208	FM	0.6217	5000.5566	134.0600	50.4683
		Sum	9908.3101		

(*E*)-5-Butyl-2-methyl-2-(pent-1-en-1-yl)-3,4-dihydro-2*H*-pyrrole (4b)



General Procedure D: Oxime ester **3b** (65 mg, 0.16 mmol) was employed and the reaction was heated at 120 °C for 6 hours. FCC (pentane: Et_2O 5:1) afforded imine **4b** (20.4 mg, 61%) as a pale yellow oil.

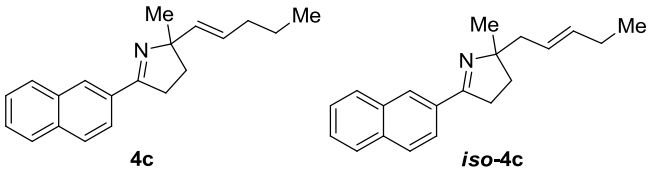
^{1}H NMR (400 MHz, $CDCl_3$): 5.57 (dt, *J* = 15.5 and 1.0 Hz, 1H, C<u>H</u>=CHCH$_2$), 5.45 (dt, *J* = 15.5 and 6.5 Hz, 1H, CH=C<u>H</u>CH$_2$), 2.53-2.47 (m, 2H, (CN)C<u>H$_2$</u>CH$_2$C), 2.34 (t, *J* = 8.0 Hz, 2H, CH$_3$(CH$_2$)$_2$C<u>H$_2$</u>(CN)), 2.02-1.94 (m, 2H, CH=CHC<u>H$_2$</u>), 1.91-1.83 (m, 1H, (CN)CH$_2$C<u>H$_2$</u>C), 1.76-1.64 (m, 1H, (CN)CH$_2$C<u>H$_2$</u>C), 1.62-1.51 (m, 2H, CH$_3$CH$_2$C<u>H$_2$</u>CH$_2$(CN)), 1.44-1.16 (m, 4H, CH$_3$C<u>H$_2$</u>(CH$_2$)$_2$(CN) and CH=CHCH$_2$C<u>H$_2$</u>), 1.29 (s, 3H, (NC)C<u>H$_3$</u>), 0.93 (t, *J* = 7.5 Hz, 3H, CH=CH(CH$_2$)$_2$C<u>H$_3$</u>), 0.83 (t, *J* = 7.5 Hz, 3H, C<u>H$_3$</u>CH$_2$(CH$_2$)$_2$(CN)).

^{13}C NMR (125 MHz, $CDCl_3$): 176.1 (<u>C</u>=N), 136.6 (<u>C</u>H=CHCH$_2$), 126.7 (CH=<u>C</u>HCH$_2$), 75.3 (quaternary <u>C</u>), 36.8 ((CN)<u>C</u>H$_2$CH$_2$C), 36.0 ((CN)CH$_2$<u>C</u>H$_2$C), 34.6 (CH=CHC<u>H$_2$</u>), 33.8 (CH$_3$(CH$_2$)$_2$<u>C</u>H$_2$(CN)), 28.9 (CH$_3$CH$_2$<u>C</u>H$_2$CH$_2$(CN)), 27.4 ((NC)<u>C</u>H$_3$), 22.6 (CH=CHCH$_2$<u>C</u>H$_2$), 22.5 (CH$_3$<u>C</u>H$_2$(CH$_2$)$_2$(CN)), 13.9 (<u>C</u>H$_3$(CH$_2$)$_3$(CN)), 13.7 (C=CH(CH$_2$)$_2$<u>C</u>H$_3$).

FTIR 1957, 1641, 1455, 1377, 1278, 1173, 1138 cm^{-1}.

MS (CI$^+$) Found [M+H]$^+$: 208.2064, $C_{14}H_{26}N$ requires 208.2065.

((*E*)-2-Methyl-5-(naphthalen-2-yl)-2-(pent-1-en-1-yl)-3,4-dihydro-2*H*-pyrrole (4c) and (*E*)-2-methyl-5-(napthalen-2-yl)-2-(pent-2-en-1-yl)-3,4-dihydro-2*H*-pyrrole (*iso*-4c)



4c ***iso*-4c**

General Procedure D: Oxime ester **3c** (70 mg, 0.14 mmol) was employed and the reaction was heated at 120 ^{o}C for 2 hours. FCC (toluene:EtOAc 20:1) afforded imine **4c** (28.5 mg, 72%) as a pale yellow oil and imine ***iso*-4c** (4.4 mg, 11%) as a yellow oil.

Data for (*E*)-2-methyl-5-(naphthalen-2-yl)-2-(pent-1-en-1-yl)-3,4-dihydro-2*H*-pyrrole **4c**:

^{1}H NMR (400 MHz, $CDCl_3$): 8.24-8.06 (m, 2H, ArH), 7.91-7.79 (m, 3H, ArH), 7.58-7.44 (m, 2H, ArH), 5.71 (dt, *J* = 15.5 and 1.0 Hz, 1H, HC=CHCH$_2$), 5.56 (dt, *J* = 15.5 and 6.5 Hz, 1H, HC=CHCH$_2$), 3.20-3.03 (m, 2H, Ar(CN)C<u>H$_2$</u>), 2.15-2.07 (m, 1H, Ar(CN)CH$_2$C<u>H$_2$</u>), 2.03 (m, 2H, C=CHC<u>H$_2$</u>), 1.98-1.88 (m, 1H, Ar(CN)CH$_2$C<u>H$_2$</u>), 1.47 (s, 3H, (NC)C<u>H$_3$</u>), 1.41 (tq, *J* = 7.5 and 7.5 Hz, 2H, C=CHCH$_2$C<u>H$_2$</u>), 0.90 (t, *J* = 7.5 Hz, 3H, C=CH(CH$_2$)$_2$C<u>H$_3$</u>).

^{13}C NMR (100 MHz, $CDCl_3$): 170.8 (C=N), 136.3 (C=CH), 134.3, 133.0, 132.3 (3 × ArC), 128.7, 128.0 (2 signals), 127.7, 127.3 (5 × ArCH), 126.9 (C=CH), 126.3, 124.8 (2 × ArCH), 76.3 (quaternary C), 36.1 (Ar(CN)CH_2), 34.9 (Ar(CN)CH_2CH_2), 34.6 (C=CHCH_2), 27.4 ((NC)CH_3), 22.5 (C=$CHCH_2CH_2$), 13.7 (C=CH$(CH_2)_2CH_3$).

FTIR 2958, 1611, 1454, 1350, 1191, 1126 cm^{-1}.

MS (EI^+) Found $[M]^+$: 277.1839, $C_{20}H_{23}N$ requires 277.1830.

Data for (*E*)-2-methyl-5-(napthalen-2-yl)-2-(pent-2-en-1-yl)-3,4-dihydro-2*H*-pyrrole ***iso*-4c**:

^{1}H NMR (400 MHz, $CDCl_3$): 8.19-8.03 (m, 2H, ArH), 7.91-7.80 (m, 3H, ArH), 7.54-7.45 (m, 2H, ArH), 5.59-5.49 (m, 1H, CH_2CH=C$H$$CH_2CH_3$), 5.47-5.36 (m, 1H, CH_2CH=$CHCH_2CH_3$), 3.17-2.97 (m, 2H, Ar(CN)CH_2), 2.35 (d, *J* = 7.0 Hz, 2H, CH_2CH=$CHCH_2CH_3$), 2.14-1.93 (m, 3H, CH_2CH=CHCH_2CH_3 and Ar(CN)CH_2CH_2), 1.81-1.70 (m, 1H, Ar(CN)CH_2CH_2), 1.35 (s, 3H, (NC)CH_3), 0.94 (t, *J* = 7.5 Hz, 3H, CH_2CH=$CHCH_2CH_3$).

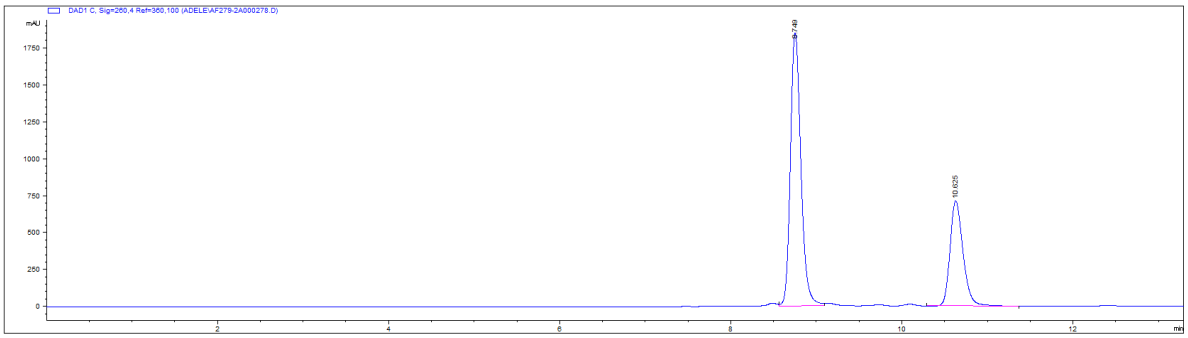
^{13}C NMR (125 MHz, $CDCl_3$): 170.1 (C=N), 135.5 (CH_2CH=C$H$$CH_2CH_3$), 134.3, 134.1, 133.0 (3 × ArC), 128.7, 128.0, 127.9, 127.7, 126.9, 126.3 (6 × ArCH), 125.0 (CH_2CH=$CHCH_2CH_3$), 124.8 (ArCH), 76.4 (quaternary C), 45.1 (CH_2CH=$CHCH_2CH_3$), 35.5 (Ar(CN)CH_2), 33.3 (Ar(CN)CH_2CH_2), 27.5 ((NC)CH_3), 25.8 (CH_2CH=CHCH_2CH_3), 14.0 (CH_2CH=$CHCH_2CH_3$).

FTIR 2960, 1613, 1453, 1350, 1279, 1126 cm^{-1}.

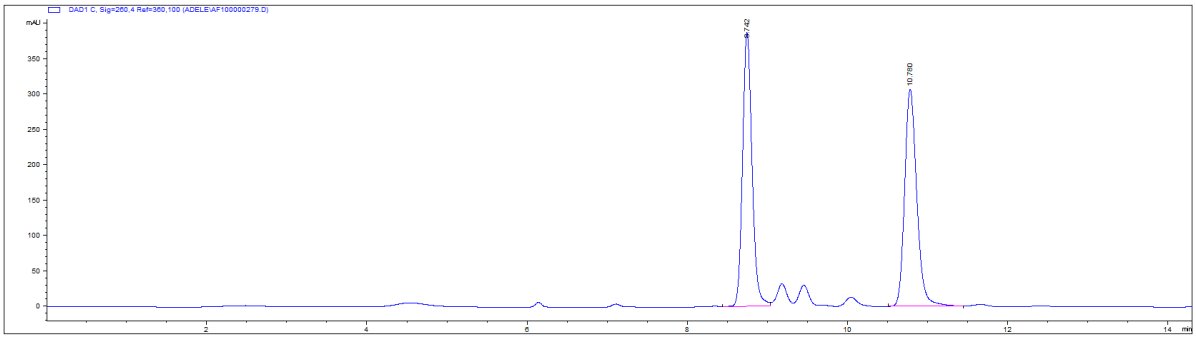
MS (EI^+) Found $[M]^+$: 277.1833, $C_{20}H_{23}N$ requires 277.1830.

General Procedure G: Oxime ester **4c** (50 mg, 0.10 mmol) was employed and the reaction was heated at 120 °C for 3.5 hours. FCC (toluene:EtOAc 16:1) afforded imine **4c** (15.0 mg, 54%, 35% *e.e*) as a pale yellow oil. Spectroscopic properties were identical to those described above for racemic material.

Chiral HPLC *Column:* Chiralpak IB; *Solvent:* isocratic hexane-*i*-PrOH (95:5, 0.5 mL/min, 20 °C); t_R (major) = 8.7 min and t_R (minor) = 10.6 min.

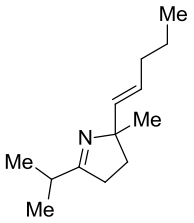


Signal:	DAD1 C, Sig=260,4 Ref=360,100				
RT [min]	Type	Width [min]	Area	Height	Area%
8.749	VV	0.1311	15705.8076	1848.1591	67.5024
10.625	BB	0.1629	7561.2280	712.0835	32.4976
	Sum		23267.0356		



Signal:	DAD1 C, Sig=260,4 Ref=360,100				
RT [min]	Type	Width [min]	Area	Height	Area%
8.742	BV	0.1262	3191.8562	387.1251	49.7794
10.780	BB	0.1609	3220.1396	306.8722	50.2206
	Sum		6411.9958		

(*E*)-5-Isopropyl-2-methyl-2-(pent-1-en-1-yl)-3,4-dihydro-2*H*-pyrrole (4d)



General Procedure D: Oxime ester **3d** (75 mg, 0.19 mmol) was employed and the reaction was heated at 120 °C for 2 hours. FCC (pentane: Et_2O 5:1) afforded imine **4d** (27.6 mg, 77%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 5.55 (dt, *J* = 15.5 and 1.0 Hz, 1H, HC=CHCH$_2$), 5.42 (dt, *J* = 15.5 and 6.5 Hz, 1H, HC=CHCH$_2$), 2.63 (sept., *J* = 7.0 Hz, 1H, $(CH_3)_2$CH(CN)), 2.52-2.45 (m, 2H, (CN)CH$_2$), 1.97 (m, 2H, HC=CHCH$_2$), 1.88-1.80 (m, 1H, (CN)CH$_2$CH$_2$), 1.70-1.60

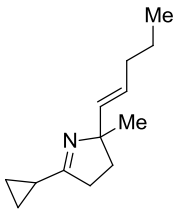
(m, 1H, (CN)CH_2CH_2), 1.37 (tq, *J* = 7.5 and 7.5 Hz, 2H, HC=CHCH$_2$CH_2), 1.28 (s, 3H, (NC)CH_3), 1.13 (d, *J* = 7.0 Hz, 6H, (CH_3)$_2$CH(CN)), 0.87 (t, *J* = 7.5 Hz, 3H, HC=CH(CH$_2$)$_2$CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 180.4 (C=N), 136.5 (HC=CHCH$_2$), 126.6 (HC=CHCH$_2$), 74.9 (quaternary C), 35.9 ((CN)CH_2CH_2), 34.6 (HC=CHCH$_2$), 33.8 ((CN)CH_2), 32.7 ((CH$_3$)$_2$CH(CN)), 27.3 ((NC)CH_3), 22.5 (HC=CHCH$_2$CH$_2$), 20.2 ((CH$_3$)$_2$CH(CN)), 13.6 (HC=CH(CH$_2$)$_2$CH$_3$).

FTIR 2960, 1636, 1455, 969 cm^{-1}.

MS (EI$^+$) Found $[M]^+$: 193.1823, $C_{13}H_{23}N$ requires 193.1830.

(*E*)-5-Cyclopropyl-2-methyl-2-(pent-1-en-1-yl)-3,4-dihydro-2*H*-pyrrole (4e)



General Procedure D: Oxime ester **3e** (60 mg, 0.15 mmol) was employed and the reaction was heated at 120 °C for 2.5 hours. FCC (toluene:EtOAc 10:1) afforded imine **4e** (24.1 mg, 85%) as a yellow oil.

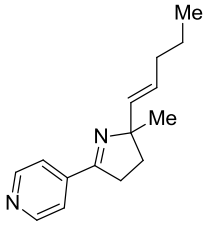
^{1}H NMR (400 MHz, $CDCl_3$): 5.54 (dt, *J* = 15.5 and 1.0 Hz, 1H, CH=CHCH$_2$), 5.43 (dt, *J* = 15.5 and 6.5 Hz, 1H, CH=CHCH$_2$), 2.36-2.30 (m, 2H, (CN)CH_2), 2.01-1.93 (m, 2H, CH=CHCH_2), 1.88-1.73 (m, 2H, (CN)CH_2CH_2 and (CH$_2$)$_2$CH(CN)), 1.69-1.61 (m, 1H, (CN)CH_2CH_2), 1.42-1.32 (m, 2H, CH=CHCH$_2$CH_2), 1.27 (s, 3H, (NC)CH_3), 0.87 (t, *J* = 7.5 Hz, 3H, CH=CH(CH$_2$)$_2$CH_3), 0.91-0.76 (m, 4H, (CH_2)$_2$CH(CN)).

^{13}C NMR (100 MHz, $CDCl_3$): 177.1 (C=N), 136.6 (HC=CHCH$_2$), 126.8 (HC=CHCH$_2$), 75.2 (quaternary C), 35.7 ((CN)CH_2CH_2), 34.7 (HC=CHCH$_2$), 34.1 ((CN)CH_2), 27.3 ((NC)CH_3), 22.6 (HC=CHCH$_2$CH$_2$), 14.4 ((CH$_2$)$_2$CH(CN)), 13.8 (HC=CH(CH$_2$)$_2$CH$_3$), 7.3 and 7.1 (2 × (CH$_2$)$_2$CH(CN)).

FTIR 2958, 2926, 1632, 1454, 1400, 969 cm^{-1}.

MS (EI$^+$) Found $[M]^+$: 191.1679, $C_{13}H_{21}N$ requires 191.1674.

(*E*)-4-(2-Methyl-2-(pent-1-en-1-yl)-3,4-dihydro-2*H*-pyrrol-5-yl)pyridine (4f)



General Procedure D: Oxime ester **3f** (50 mg, 0.11 mmol) was employed and the reaction was heated at 120 ^{o}C for 2 hours. FCC (hexane:EtOAc 1:1) afforded imine **4f** (20.2 mg, 78%) as a colourless oil.

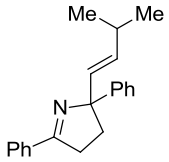
^{1}H NMR (400 MHz, $CDCl_3$): 8.70-8.65 (m, 2H, ArH), 7.72-7.68 (m, 2H, ArH), 5. 66 (dt, *J* = 15.5 and 1.0 Hz, 1H, CH=CHCH$_2$), 5.52 (dt, *J* = 15.5 and 6.5 Hz, 1H, CH=CHCH$_2$), 3.06-2.89 (m, 2H, Ar(CN)CH$_2$), 2.14-1.86 (m, 4H, CH=CHCH$_2$ and Ar(CN)CH$_2$CH$_2$), 1.42 (s, 3H, (NC)CH$_3$), 1.45-1.34 (m, 2H, HC=CHCH$_2$CH$_2$), 0.89 (t, *J* = 7.5 Hz, 3H, CH=CH(CH$_2$)$_2$CH$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 169.3 (C=N), 150.2 (ArCH), 141.7 (ArC), 135.7 (HC=CHCH$_2$), 127.7 (HC=CHCH$_2$), 121.7 (ArCH), 76.8 (quaternary C), 35.8 (Ar(CN)CH$_2$), 34.7 (Ar(CN)CH$_2$CH$_2$), 34.6 (HC=CHCH$_2$), 27.2 ((NC)CH$_3$), 22.4 (HC=CHCH$_2$CH$_2$), 13.7 (HC=CH(CH$_2$)$_2$CH$_3$).

FTIR 1597, 1494, 1409, 1311 cm^{-1}.

MS (CI$^+$) Found [M+H]$^+$: 299.1708, $C_{15}H_{21}N_2$ requires 229.1705.

(*E*)-2-(3-Methylbut-1-en-1-yl)-2,5-diphenyl-3,4-dihydro-2H-pyrrole (4g)



General Procedure D: Oxime ester **3g** (75 mg, 0.15 mmol) was employed and the reaction was heated at 120 ^{o}C for 3 hours. FCC (× 2: 1st column toluene:EtOAc 200:1; 2nd column hexane:EtOAc 30:1) afforded imine **4g** (30.2 mg, 70%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.04-7.94 (m, 2H, ArH), 7.57-7.42 (m, 5H, ArH), 7.38-7.31 (m, 2H, ArH), 7.26-7.20 (m, 1H, ArH), 5.84 (dd, *J* = 15.5 and 1.0 Hz, 1H, CH=CHCH), 5.54

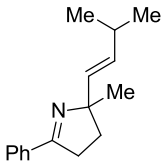
(dd, *J* = 15.5 and 6.5 Hz, 1H, CH=CHCH), 3.03 (dd, *J* = 8.5 and 6.5Hz, 2H, Ar(CN)CH_2), 2.58-2.49 (m, 1H, Ar(CN)CH_2CH_2), 2.38-2.28 (m, 1H, $(CH_3)_2CH$), 2.26-2.16 (m, 1H, Ar(CN)CH_2CH_2), 1.00 (d, *J* = 6.5 Hz, 6H, $(CH_3)_2CH$).

^{13}C NMR (100 MHz, $CDCl_3$): 171.9 (C=N), 147.5 (ArC), 135.2 (HC=CHCH), 131.9 (HC=CHCH), 130.5, 128.4 (2 × ArH), 128.1, (ArC), 127.9 (2 signals), 126.3, 126.1 (4 × ArCH), 81.7 (quaternary C), 36.8 (Ar(CN)CH_2CH_2), 35.0 (Ar(CN)CH_2), 30.9 ($CH(CH_3)_2$), 22.5, 22.4 (2 × $CH(CH_3)_2$).

FTIR 2930, 1659, 1385, 1256, 1090 cm^{-1}.

MS (EI^+) Found $[M]^+$: 289.1831, $C_{21}H_{23}N$ requires 289.1830.

(*E*)-2-Methyl-2-(3-methylbut-1-en-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (4h)



General Procedure D: Oxime ester **3h** (45 mg, 0.10 mmol) was employed and the reaction was heated at 120 °C for 2 hours. FCC (hexane:EtOAc 10:1) afforded imine **4h** (18.6 mg, 80%) as a colourless oil.

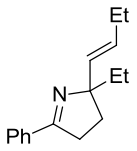
^{1}H NMR (400 MHz, $CDCl_3$): 7.90-7.84 (m, 2H, ArH), 7.46-7.36 (m, 3H, ArH), 5.62 (dd, *J* = 15.5 and 1.0 Hz, 1H, CH=CHCH_2), 5.50 (dd, *J* = 15.5 and 6.5 Hz, 1H, CH=CHCH_2), 3.07-2.90 (m, 2H, Ar(CN)CH_2), 2.35-2.22 (m, 1H, CH=CHCH), 2.10-1.80 (m, 2H, Ar(CN)CH_2CH_2), 1.41 (s, 3H, (NC)CH_3), 0.99 (d, *J* = 6.5 Hz, 6H, CH=CHCH(CH_3)$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): 170.7 (C=N), 134.9 (ArC), 134.3 (HC=CHCH), 133.3 (HC=CHCH), 130.3, 128.3, 127.7 (3 × ArCH), 76.0 (quaternary C), 36.0 (Ar(CN)CH_2), 34.9 (Ar(CN)CH_2CH_2), 30.9 (CH=CHCH), 27.4 ((NC)CH_3), 22.6 (CH=CHCH(CH_3)$_2$).

FTIR 2958, 1614, 1448, 1338, 1018 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 228.1758 , $C_{16}H_{22}N$ requires 228.1752.

(*E*)-2-(But-1-en-1-yl)-2-ethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole (4i)



General Procedure D: Oxime ester **3i** (60 mg, 0.14 mmol) was employed and the reaction was heated at 120 ^{o}C for 2.25 hours. FCC (hexane:EtOAc 8:1) afforded imine **4i** (27.9 mg, 90%) as a colourless oil.

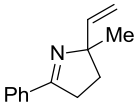
^{1}H NMR (400 MHz, $CDCl_3$): 7.93-7.83 (m, 2H, ArH), 7.47-7.34 (m, 3H, ArH), 5. 66 (dt, *J* = 15.5 and 1.0 Hz, 1H, CH=$CHCH_2$), 5.52 (dt, *J* = 15.5 and 6.5 Hz, 1H, $CH=CHCH_2$), 3.02-2.87 (m, 2H, $Ar(CN)CH_2$), 2.09-1.85 (m, 4H, $CH=CHCH_2$ and $Ar(CN)CH_2CH_2$), 1.83-1.67 (m, 2H, $(NC)CH_2CH_3$), 0.98 (t, *J* = 7.5 Hz, 3H, $CH=CH(CH_2)_2CH_3$), 0.92 (t, *J* = 7.5 Hz, 3H, $(NC)CH_2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 170.8 (C=N), 135.1 (ArC), 134.2 ($CH=CHCH_2$), 130.3 (ArH), 129.6 ($CH=CHCH_2$), 128.4, 127.9 (2 × ArH), 80.0 (quaternary C), 35.1 ($Ar(CN)CH_2$), 33.9 ($(NC)CH_2CH_3$), 32.4 ($Ar(CN)CH_2CH_2$), 25.7 ($CH=CHCH_2$), 14.0 ($CH=CHCH_2CH_3$), 9.0 ($(NC)CH_2CH_3$).

FTIR 2961, 1615, 1448, 1340, 1134 cm^{-1}.

MS (EI^+) Found $[M]^+$: 227.1670, $C_{16}H_{21}N$ requires 227.1674.

2-Methyl-5-phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole (4j)



General Procedure D: Oxime ester **3j** (50 mg, 0.13 mmol) was employed and the reaction was heated at 120 ^{o}C for 2 hours. FCC (toluene:EtOAc 10:1) afforded imine **4j** (19 mg, 83%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.91-7.85 (m, 2H, ArH), 7.47-7.37 (m, 3H, ArH), 6.05 (dd, *J* = 17.5 and 10.5 Hz, 1H, CH=CH_2), 5.13 (dd, *J* = 17.5 and 1.0 Hz, 1H, $CH=CH_2$), 5.02 (dd, *J* = 10.5 and 1.0 Hz, 1H, ($CH=CH_2$), 3.11-2.91 (m, 2H, $Ar(CN)CH_2$), 2.15-1.84 (m, 2H, $Ar(CN)CH_2CH_2$), 1.45 (d, *J* = 1.0 Hz, 3H, $(NC)CH_3$).

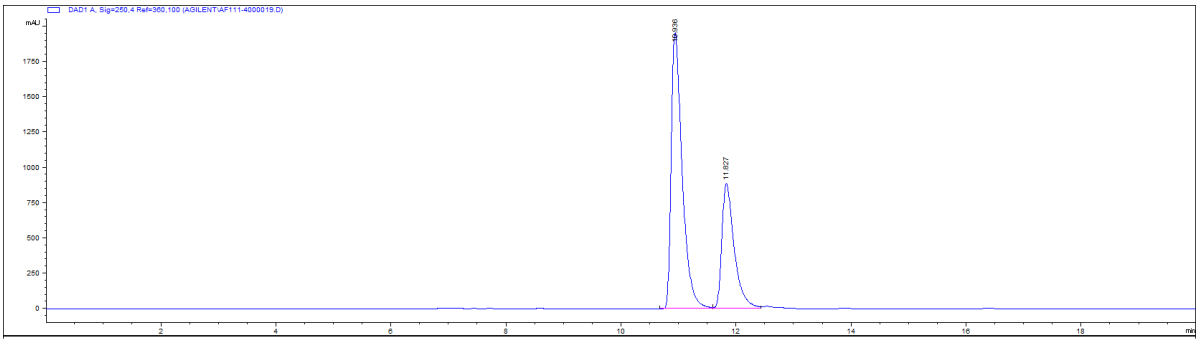
^{13}C NMR (100 MHz, $CDCl_3$): 171.4 (C=N), 144.3 ($CH=CH_2$), 134.6 (ArC), 130.4, 128.4, 127.8 (3 × ArCH), 111.3 ($CH=CH_2$), 77.0 (quaternary C), 35.3 ($Ar(CN)CH_2CH_2$), 34.9 ($Ar(CN)CH_2CH_2$), 26.9 (CH_3).

FTIR 1614, 1448, 1338 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 186.1284, $C_{13}H_{16}N$ requires 186.1283.

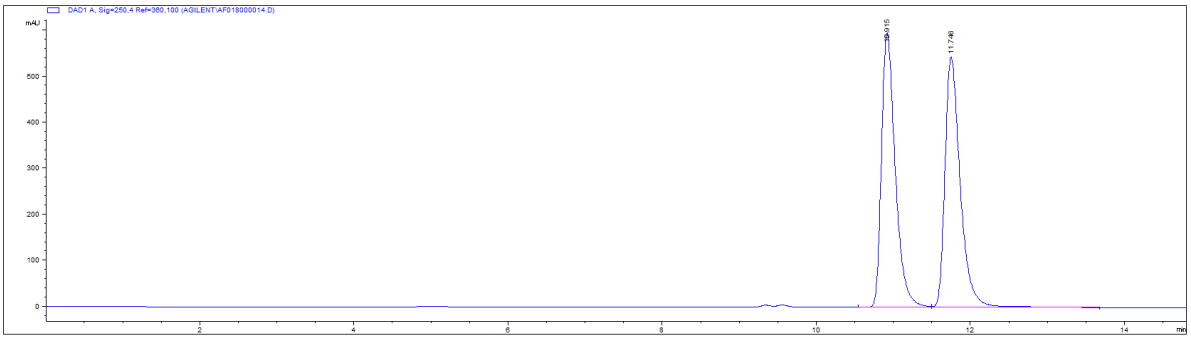
General Procedure G: Oxime ester **3j** (50 mg, 0.13 mmol) was employed and the reaction was heated at 120 °C for 3 hours. FCC (hexane:EtOAc 6:1) afforded imine **4j** (13.0 mg, 56%, 32% *e.e*) as a pale yellow oil. Spectroscopic properties were identical to those described above for racemic material.

Chiral HPLC *Column:* Chiralpak IC; *Solvent:* isocratic hexane-*i*-PrOH (97:3, 0.5mL/min, 20 °C); t_R (major) = 10.9 min and t_R (minor) = 11.8 min.



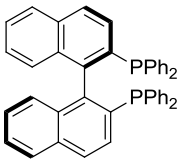
Signal: DAD1 A, Sig=250,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.936	BV	0.1985	25897.3184	1955.3287	66.0047	
11.827	VV	0.2230	13338.2734	889.0718	33.9953	
		Sum	39235.5918			

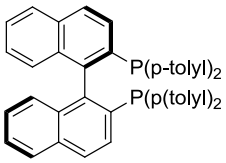


Signal:	DAD1 A, Sig=250,4 Ref=360,100					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.915	BV	0.1888	7396.3237	596.0136	49.6664	
11.746	VB	0.2085	7495.6816	544.7324	50.3336	
		Sum	14892.0054			

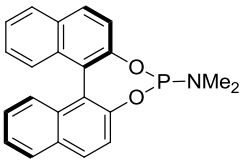
Results for the cyclisation of **3j** to **4j** using other chiral ligands are presented below:



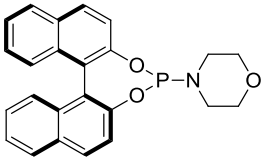
(*R*)-(+)-BINAP
35%, **4% ee**



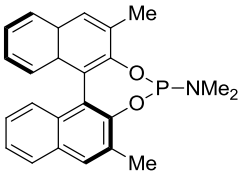
(*R*)-tol-BINAP
21%, **2% ee**



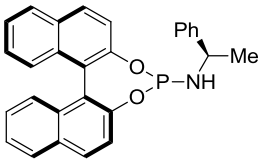
(*R*)-Monophos
39%, **1% ee**



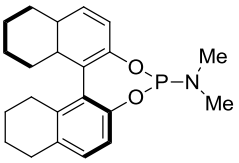
(*S*)-MorfPhos
35%, **0% ee**



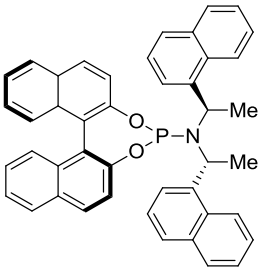
Phosphoramidite a
35%, **5% ee**



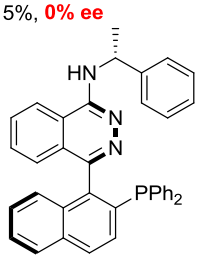
Phosphoramidite b
5%, **0% ee**



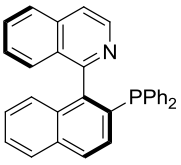
Phosphoramidite c
56%, **5% ee**



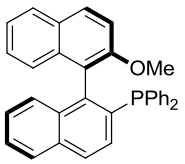
Phosphoramidite d
60%, **3% ee**



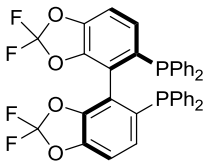
(*R*,*R*)-N-PINAP
34%, **6% ee**



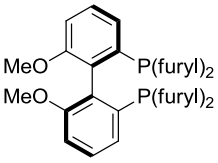
(*S*)-QUINAP
49%, **2% ee**



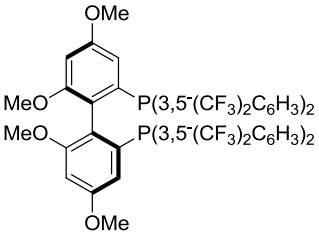
(*R*)-MOP
50%, **0% ee**



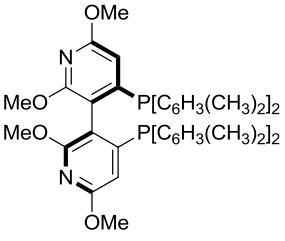
(*R*)-Difluorophos
52%, **2% ee**



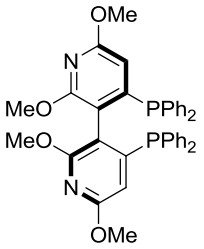
Phosphine e
26%, **4% ee**



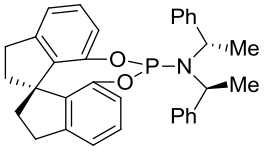
(*S*)-BTFM-Garphos
48%, **1% ee**



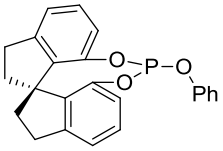
CTH-(*R*)-Xylyl-P-Phos
50%, **1% ee**



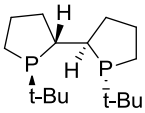
CTH-(*R*)-P-Phos
47%, **4% ee**



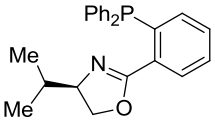
(*S*)-SiPhos-PE
30%, **2% ee**



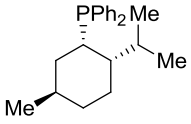
(*S*)-Shi P
39%, **4% ee**



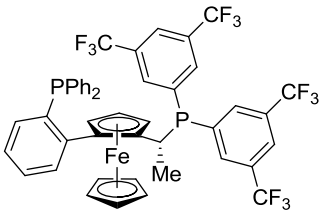
(*S,S,R,R*)-Tangphos
30%, **4% ee**



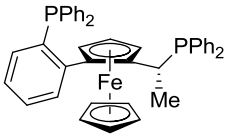
P,N Ligand f
41%, **2% ee**



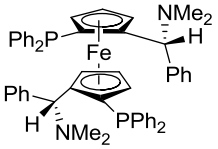
(*S*)-NMDPP
77%, **3% ee**



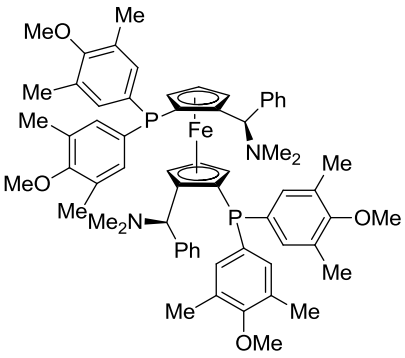
Walphos (SL-W001-1)
52%, **4% ee**



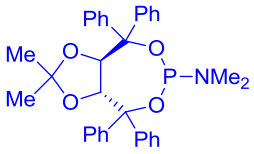
Walphos (SL-W002-1)
30%, **6% ee**



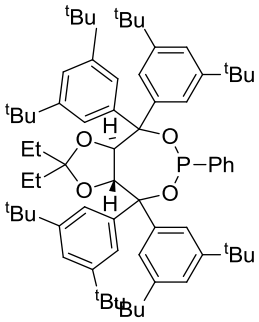
MandyPhos (SL-M001-1)
26%, **5% ee**



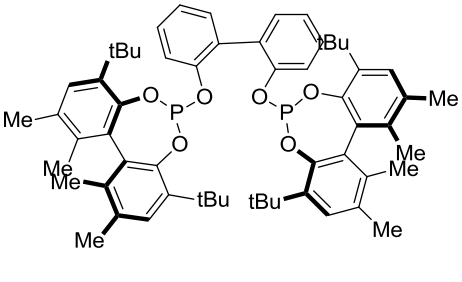
MandyPhos (SL-M004-1)
<5%, **0% ee**



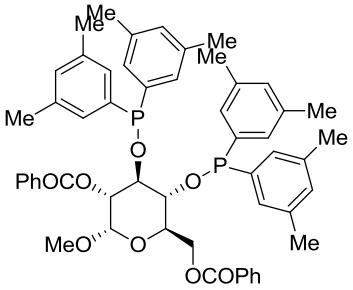
Taddol Phos L1
56% **33% ee**



Taddol Phosphonite
52%, **1% ee**



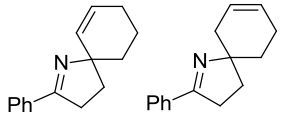
(*R,R*)-Kelliphite
43%, **4% ee**



Carbophos
60%, **6% ee**

[a] 7.5 mol% of bidentate and 15 mol% of monodentate ligands were used.

2-Phenyl-1-azaspiro[4.5]deca-1,6-diene (4k) and 2-phenyl-1-azaspiro[4.5]deca-1,7-diene (*iso*-4k)



4k ***iso*-4k**

General Procedure D: Oxime ester **3k** (75 mg, 0.18 mmol) was employed and the reaction was heated at 120 °C for 1.5 hours. FCC (× 2: 1st column: 19:1 hexane: EtOAc 95:5; 2nd column: toluene:EtOAc 15:1) afforded imine **4k** and ***iso*-4k** (31.2 mg, 84%: 1:0.2 **4k:*iso*-4k**) as a pale yellow oil.

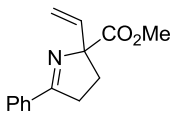
^{1}H NMR (400 MHz, $CDCl_3$): *Signals for both isomers:* 7.90-7.82 (m, 2.4H, ArH), 7.44-7.34 (m, 3.6H, ArH), 5.83 (dt, *J* = 10.0 and 3.5 Hz, 1H, CCH=CHCH$_2$), 5.79-5.73 (m, 0.2H, CCH=CHCH$_2$), 5.72-5.65 (m, 0.2H, CCH=CHCH$_2$), 5.54 (dt, *J* = 10.0 and 1.0 Hz, 1H, CCH=CHCH$_2$), 3.07-2.91 (m, 2.4H, Ar(CN)CH$_2$), 2.44-2.22 (m, 0.4H, CH$_2$), 2.21-1.53 (m, 8.4H, 4 × CH$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): *Signals for the major isomer **4k***: 171.0 (C=N), 132.8 (CCH=CHCH$_2$), 130.3 (ArCH), 128.31 (ArC), 127.9 (ArCH), 127.9 (CCH=CHCH$_2$), 127.8 (ArCH), 75.2 (quaternary C), 35.7, 34.8 (2 × CH$_2$), 34.5 (Ar(CN)CH$_2$), 25.0, 20.5 (2 × CH$_2$). *Signals for the minor isomer **iso-4k**:* 170.3 (C=N), 134.9, 134.8, 130.2, 127.7, 126.8, 125.2 (3 × ArCH, ArC, C=CH and C=CH), 74.7 (quaternary C), 36.7, 34.3, 33.7, 33.0, 23.5 (5 × CH$_2$).

FTIR 2928, 1611, 1575, 1495, 1447, 1335, 1015 cm^{-1}.

MS (EI$^+$) Found [M]$^+$: 212.1438, $C_{15}H_{17}N$ requires 212.1439.

Methyl 5-phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate (4l)



General Procedure D: Oxime ester **3l** (60 mg, 0.14 mmol) was employed. In a modification to the general procedure, Pd_2dba_3 (6.2 mg, 0.050 mmol) and P(3,5-$(CF_3)_2C_6H_3)_3$ (18.2 mg, 0.027 mmol) were employed. The reaction was heated at 135 °C for 17 hours. FCC (toluene:EtOAc 12:1) afforded imine **4l** (9.6 mg, 31%) as a colourless oil.

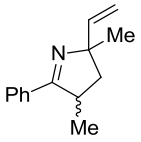
^{1}H NMR (400 MHz, $CDCl_3$): 7.95-7.92 (m, 2H, ArH), 7.50-7.39 (m, 3H, ArH), 6.30 (dd, *J* = 17.5 and 10.5 Hz, 1H, CH=CH_2), 5.26 (dd, *J* = 17.5 and 1.0 Hz, 1H, CH=CH_2), 5.19 (dd, *J* = 10.5 and 1.0 Hz, 1H, CH=CH_2), 3.78 (s, 3H, CH_3) 3.17-2.91 (m, 2H, Ar(CN)CH_2), 2.63-2.53 (m, 1H, Ar(CN)CH_2CH_2), 2.24-2.14 (m, 1H, Ar(CN)CH_2CH_2).

^{13}C NMR (125 MHz, $CDCl_3$): 175.3 (C=N), 173.7 (C=O), 138.5 (CH=CH_2), 133.9 (ArC), 131.0, 128.4, 128.1 (3 × ArCH), 114.5.3 (CH=CH_2), 83.8 (quaternary C), 52.7 (CH_3), 34.8 (Ar(CN)CH_2), 33.0 (Ar(CN)CH_2CH_2).

FTIR 1730, 1612, 1500, 1310, 1251 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 252.1002, $C_{14}H_{15}NO_2Na$ requires 252.0095.

2,4-Dimethyl-5-phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole (4m)



General Procedure D: Oxime ester **3m** (55 mg, 0.13 mmol) was employed and the reaction was heated at 120 °C for 3.5 hours. FCC (toluene:EtOAc 12:1) afforded imine **4m** (20 mg, 75%, 1:0.7 mixture of diasteromers) as a colourless oil.

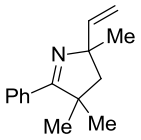
^{1}H NMR (400 MHz, $CDCl_3$): *Data for both diastereomers;* 7.87-7.71 (m, 3.4H, ArH), 7.46-7.36 (m, 5.1H, ArH), 6.14 (dd, *J* = 17.5 and 10.5 Hz, 1H, CH=CH_2), 6.04 (dd, *J* = 17.5 and 10.5 Hz, 0.7H, CH=CH_2), 5.18 (dd, *J* = 17.5 and 1.0 Hz, 1H, CH=CH_2), 5.09 (dd, *J* = 17.5 and 1.0 Hz, 0.7H, CH=CH_2), 5.02 (dd, *J* = 10.5 and 1.0 Hz, 1H, (CH=CH_2), 4.99 (dd, *J* = 10.5 and 1.0 Hz, 0.7H, (CH=CH_2), 3.61-3.43 (m, 1.7H, Ar(CN)CH), 2.42 (dd, *J* = 13.0 and 9.0 Hz, 0.7H, Ar(CN)CHCH_2), 2.18 (dd, *J* = 13.0 and 9.0 Hz, 1H, Ar(CN)CHCH_2), 1.81 (dd, *J* = 13.0 and 4.5 Hz, 1H, Ar(CN)CHCH_2), 1.58 (dd, *J* = 13.0 and 6.0 Hz, 0.7H, Ar(CN)CHCH_2), 1.50 (s, 2.1H, (NC)CH_3), 1.44 (s, 3H, (NC)CH_3), 1.26 (d, *J* = 7.5 Hz, 2.1H, Ar(CN)CHCH_3), 1.20 (d, *J* = 7.5 Hz, 3H, Ar(CN)CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 175.5 (2 signals) (2 × C=N), 146.1, 144.8 (2 × CH=CH_2), 134.2, 133.9, (2 × ArC) 130.1, 130.0, 128.4, 128.3, 128.2, 128.1 (6 × ArCH), 111.3, 111.0 (CH=CH_2), 75.2, 75.1 (2 × quaternary C), 44.2, 44.0 (2 × Ar(CN)CHCH_2), 42.6, 42.5 (2 × Ar(CN)CHCH_2), 28.5, 28.3 (2 × (NC)CH_3), 20.0, 19.4 (2 × Ar(CN)CHCH_3).

FTIR 1614, 1448, 1329 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 200.1436, $C_{14}H_{18}N$ requires 200.1439.

2,4,4-Trimethyl-5-phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole (4n)



General Procedure D: Oxime ester **3n** (60 mg, 0.14 mmol) was employed and the reaction was heated at 120 ^oC for 3 hours. FCC ((× 2: 1st column toluene:EtOAc 6:1; 2nd hexane:EtOAc 4:1) afforded imine **4n** (24.1 mg, 80%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.77-7.71 (m, 2H, ArH), 7.42-7.35 (m, 3H, ArH), 6.10 (dd, *J* = 17.0 and 10.5 Hz, 1H, CH=CH_2), 5.16 (dd, *J* = 17.0 and 1.0 Hz, 1H, CH=CH_2), 5.02 (dd, *J* = 10.5 and 1.0 Hz, 1H, (CH=CH_2), 2.13 (d, *J* = 13.0 Hz, 1H, Ar(CN)CCH_2), 1.88 (d, *J* = 13.0 Hz, 1H, Ar(CN)CCH_2), 1.47 (s, 3H, (NC)CH_3), 1.40 (s, 3H, Ar(CN)CCH_3), 1.35 (s, 3H, Ar(CN)CCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): 178.3 (C=N), 145.7 (CH=CH_2), 134.6 (ArC), 129.5, 128.2 (2 signals) (3 × ArCH), 111.3 (CH=CH_2), 72.6 (quaternary C), 52.9 (Ar(CN)CCH_2), 51.5 (Ar(CN)CCH_2), 29.3 ((NC)CH_3), 28.6, 28.0 (2 × Ar(CN)C(CH_3)$_2$).

FTIR 2966, 2258, 1603, 1573, 1465, 1445 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 214.1592, $C_{15}H_{20}NNa$ requires 214.1590.

References

1. T. E. Lightburn, O. A. De Paolis, K. A. Cheng, K. L. Tan, *Org. Lett*. 2011, **13**, 2686

2. F. Bargigga, O. Piva, *Tetrahedron: Asymm*. 2003, **14**, 1819.

3. J. D. White, K. Takabe, M. P. Prisbylla, *J. Org. Chem*. 1985, **50**, 5233.

4. A. Sakurai, T. Hayashi, T. Oishi, *Synthesis* 1980, **10**, 843.

5. J. R. Walker, S. C. Rothman, C. D. Poulter, *J. Org. Chem*. 2008, **73**, 726.

6. S. R. L. Francis, E. Attolino, A. De Marco, P. Allegrini, International Patent WO2011/138250 A1, 2011.

7. J. M. Concellón, H. Rodríguez-Solla, P. Díaz, R. Llavona, *J. Org. Chem*. 2007, **72**, 4396.

8. P. Sharma, N. Griffiths, J. E. Moses, *Org. Lett.* 2008, **10**, 4025.

9. B. Krystyna, X. Chasseray, C. Larpent, *J. Chem. Soc., Perkin Trans. 2* 2001, 2179.

10. M. Lorenz, M. Kalesse, *Org. Lett.* 2008, **10**, 4371.

11. J. M. Concellón, L. Llavona, P. L. Bernad, *Tetrahedron* 1995, **51**, 5573.

12. H. Clavier, J. Broggi, S. P. Nolan, *Eur. J. Org. Chem*. 2010, **5**, 937.

13. L. Pagès, A. Llebaria, F. Camps, E. Molins, C. Miravitlles, J. M. Moretó, *J. Am. Chem. Soc*. 1992, **114**, 10449.

14. P. Crotti, F. Badalassi, V. Di Bussolo, L. Favero, M. Pineschi, *Tetrahedron* 2001, **57**, 8559.

15. P. V. Ramachandran, A. Bhattacharyya, *Heterocycles* 2010, **80**, 863.