

## Supporting Information

# Highly-selective Electrochemical Decarboxylative Late-Stage Functionalization of Amino Acids

Adrija Ghosh,<sup>1</sup> Vishal Kumar Parida,<sup>1</sup> Tristan von Münchow,<sup>2</sup> Lutz Ackermann\*,<sup>2</sup> and Debasis Banerjee\*<sup>1</sup>

- [1] Department of Chemistry, Laboratory of Catalysis and Organic Synthesis  
Indian Institute of Technology Roorkee, Roorkee-247667, Uttarakhand, India  
E-mail: [debasis.banerjee@cy.iitr.ac.in](mailto:debasis.banerjee@cy.iitr.ac.in), Website: <https://iitr.ac.in/dbiitr/lab/>
- [2] Institute for Organic and Biomolecular Chemistry, Georg-August-Universität Göttingen,  
Tammannstr. 2, 37077 Göttingen, Germany  
E-mail: [Lutz.Ackermann@chemie.uni-goettingen.de](mailto:Lutz.Ackermann@chemie.uni-goettingen.de);  
Website: <https://www.ackermann.chemie.uni-goettingen.de/>

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## 1. General information

All solvents and reagents were used, as received from the suppliers. TLC was performed on Merck Kiesel gel 60, GF254 plates with the layer thickness of 0.25 mm. Column chromatography was performed on silica gel (100-200 mesh, 230-400 mesh) using a gradient of ethyl acetate and hexane as mobile phase. All NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$  &  $^{19}\text{F}$ ) were recorded on 500 MHz (JEOL & Bruker) Avance spectrometers.  $^1\text{H}$  NMR spectral data were collected using 500 MHz and  $^{13}\text{C}$  NMR data were recorded using 125 MHz (JEOL & Bruker) and  $^{19}\text{F}$  data were recorded using 470 MHz (JEOL). Spectral data was acquired at 298 K. The chemical shifts ( $\delta$ ) are given in parts per million (ppm) and referenced to residual solvent peaks for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra:  $\text{CDCl}_3$ ,  $\delta_{\text{H}}$  7.26 ppm,  $\delta_{\text{C}}$  77.16 ppm. Coupling constants ( $J$ ) are reported in Hertz (Hz) to the nearest 0.1 Hz. The following multiplicity abbreviations are used: s singlet, d doublet, t triplet, m multiplet. GC were recorded using Agilent GC 7890B Spectrometer. All the reactions were performed in a closed system using 5 mL vials of Electrasyn 2.0. All electrolytes were purchased from TCI. Tetrabutylammonium chloride (Assay: >98%, CAS Number 1112-67-0; EC Number 214-195-7; Pack Size – I0366-25G). 2,4,6-collidine was purchased from Alfa Aesar (Assay: 99%, CAS Number 108-75-8; EC Number 203-613-3; Pack Size – 16195-100 mL).

## 2. General Experimental Procedures

### General Procedure A for the Synthesis of Substrates 3a-3d:

With no precautions to exclude air or moisture, ElectraSyn 2.0 vial (5 mL) with a stir bar was charged with *N*-Boc- $\alpha$ -amino acid **1** (0.3 mmol, 1 equiv.), MeOH (1.8 mmol, 6 equiv.), 2,4,6-collidine (0.6 mmol, 2 equiv.),  $^n\text{Bu}_4\text{NClO}_4$  (0.3 mmol, 1 equiv.), and acetonitrile (3.0 mL). ElectraSyn 2.0 vial cap equipped with anode (graphite) and cathode (nickel) were inserted into the mixture. The reaction mixture was electrolyzed at a constant current of 10 mA for 3 hours. Thereafter, electraSyn 2.0 vial cap was removed, and electrodes were rinsed with ethyl acetate (2 mL), which was combined with the crude mixture. Then, the crude mixture was further diluted with ethyl acetate and the resulting mixture was washed with 2N HCl (20 mL) and  $\text{NaHCO}_3$  (aq) (20 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

### General Procedure B for the Synthesis of Substrates 3e-3s:

With no precautions to exclude air or moisture, ElectraSyn 2.0 vial (5 mL) with a stir bar was charged with *N*-Boc- $\alpha$ -amino acid **1** (0.3 mmol, 1 equiv.), alcohol **2** (0.9 mmol, 3 equiv.), 2,4,6-collidine (0.6 mmol, 2 equiv.),  $^n\text{Bu}_4\text{NClO}_4$  (0.3 mmol, 1 equiv.), and acetonitrile (3.0 mL). Thereafter, electraSyn 2.0 vial cap equipped with anode (graphite) and cathode (nickel) were inserted into the mixture. The

reaction mixture was electrolyzed at a constant current of 10 mA for 3 hours. Next, electraSyn 2.0 vial cap was removed, and electrodes were rinsed with ethyl acetate (2 mL), which was combined with the crude mixture. Then, the crude mixture was further diluted with ethyl acetate (20 mL) and the resulting mixture was washed with 2N HCl (10 mL) and NaHCO<sub>3</sub> (aq) (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

#### **General Procedure C for the Synthesis of Substrates 6a-6g:**

With no precautions to exclude air or moisture, ElectraSyn 2.0 vial (5 mL) with a stir bar was charged with amine **4** (0.3 mmol, 1 equiv.), carboxylic acid **5** (0.6 mmol, 2 equiv.), 2,4,6-collidine (0.6 mmol, 2 equiv.), <sup>n</sup>Bu<sub>4</sub>NClO<sub>4</sub> (0.3 mmol, 1 equiv.), and acetonitrile : DCM (3.0 mL, 1:1 ratio). ElectraSyn 2.0 vial cap equipped with anode (graphite) and cathode (nickel) were inserted into the mixture. The reaction mixture was electrolyzed at a constant current of 10 mA for 3 hours. Next, vial cap was removed, and electrodes were rinsed with ethyl acetate (2 mL), which was combined with the crude mixture. Then, the crude mixture was further diluted with ethyl acetate (20 mL) and the resulting mixture was washed with NaHCO<sub>3</sub> (aq) (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

#### **General Procedure D for the Synthesis of Substrates 7a-7z:**

With no precautions to exclude air or moisture, ElectraSyn 2.0 vial (5 mL) with a stir bar was charged with carboxylic acid **5** (0.3 mmol, 1 equiv.), alcohol **2** (0.9 mmol, 3 equiv.), 2,4,6-collidine (0.6 mmol, 2 equiv.), <sup>n</sup>Bu<sub>4</sub>NClO<sub>4</sub> (0.3 mmol, 1 equiv.), and acetonitrile (3.0 mL). ElectraSyn 2.0 vial cap equipped with anode (graphite) and cathode (nickel) were inserted into the mixture. The reaction mixture was electrolyzed at a constant current of 10 mA for 3 hours. Next, vial cap was removed, and electrodes were rinsed with ethyl acetate (2 mL), which was combined with the crude mixture. Then, the crude mixture was further diluted with ethyl acetate (20 mL) and the resulting mixture was washed with 2N HCl (10 mL) and NaHCO<sub>3</sub> (aq) (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

#### **General Procedure E for the Synthesis of Substrates 7za-7zg:**

With no precautions to exclude air or moisture, ElectraSyn 2.0 vial (5 mL) with a stir bar was charged with carboxylic acid **5** (0.3 mmol, 1 equiv.), alcohol **2** (0.3 mmol, 1 equiv.), 2,4,6-collidine (0.6 mmol, 2 equiv.), <sup>n</sup>Bu<sub>4</sub>NClO<sub>4</sub> (0.3 mmol, 1 equiv.), and acetonitrile (3.0 mL). ElectraSyn 2.0 vial cap equipped

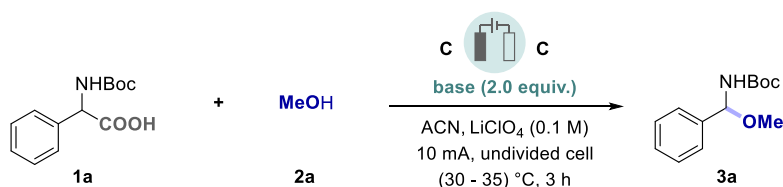
with anode (graphite) and cathode (nickel) were inserted into the mixture. The reaction mixture was electrolyzed at a constant current of 10 mA for 3 hours. Next, vial cap was removed, and electrodes were rinsed with ethyl acetate (2 mL), which was combined with the crude mixture. Then, the crude mixture was further diluted with ethyl acetate (20 mL) and the resulting mixture was washed with 2N HCl (10 mL) and NaHCO<sub>3</sub> (aq) (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

### General Procedure F for the Synthesis of Substrates 8a-8q:

With no precautions to exclude air or moisture, ElectraSyn 2.0 vial (5 mL) with a stir bar was charged with carboxylic acid **5** (0.3 mmol, 1 equiv.), MeOH (1.8 mmol, 6 equiv.), 2,4,6-collidine (0.6 mmol, 2 equiv.), <sup>n</sup>Bu<sub>4</sub>NClO<sub>4</sub> (0.3 mmol, 1 equiv.), and acetonitrile (3.0 mL). ElectraSyn 2.0 vial cap equipped with anode (graphite) and cathode (nickel) were inserted into the mixture. The reaction mixture was electrolyzed at a constant current of 10 mA for 3 hours. Next, cap was removed, and electrodes were rinsed with ethyl acetate (2 mL), which was combined with the crude mixture. Then, the crude mixture was further diluted with ethyl acetate (20 mL) and the resulting mixture was washed with 2N HCl (10 mL) and NaHCO<sub>3</sub> (aq) (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

### 3. Optimization of reaction parameters for electrochemical decarboxylative etherification

**Table S1.** Screening of bases<sup>a</sup>



Entry	Base	Yield of <b>3a</b> (%)
1	triethylamine	n.d.
2	DBU	10
3	1,1,3,3-tetramethylguanidine	25
4	2,4,6-collidine	40
5	2,6-lutidine	36
6	No base	n.d.

Reaction conditions: **1a** (0.30 mmol), **2a** (1.8 mmol), **base** (0.60 mmol), LiClO<sub>4</sub> (0.30 mmol), graphite as anode and cathode, in 3 mL acetonitrile, constant current (*I*) = 10 mA, in an undivided 5 mL Electrasyn 2.0 vial at (30-35) °C for 3 hours, Yield was analysed by GC-MS using mesitylene as internal standard. n.d. = not detected.

**Table S2.** Screening of electrolytes<sup>a</sup>

Entry	Electrolyte	Yield of <b>3a</b> (%)
1	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	50
2	<sup>n</sup> Bu <sub>4</sub> NBF <sub>4</sub>	40
3	<sup>n</sup> Bu <sub>4</sub> NClO <sub>4</sub>	52 (46%) <sup>b</sup>
4	<sup>n</sup> Bu <sub>4</sub> NBr	12
5	<sup>n</sup> Bu <sub>4</sub> NCl	10
6	<sup>n</sup> Bu <sub>4</sub> NI	<5

Reaction conditions: <sup>a</sup>**1a** (0.30 mmol), **2a** (1.8 mmol), 2,4,6-collidine (0.60 mmol), **electrolyte** (0.30 mmol), graphite as anode and cathode, in 3 mL acetonitrile, constant current (*I*) = 10 mA, in an undivided 5 mL Electrasyn 2.0 vial at (30-35) °C for 3 hours, Yield was analysed by GC-MS using mesitylene as internal standard, <sup>b</sup>isolated yield.

**Table S3.** Effect of additives<sup>a</sup>

Entry	Additives	Yield of <b>3a</b> (%)
1	AgClO <sub>4</sub>	53
2	AgPF <sub>6</sub>	47

Reaction conditions: <sup>a</sup>**1a** (0.30 mmol), **2a** (1.8 mmol), 2,4,6-collidine (0.60 mmol), **additive** (0.9 mmol), graphite as anode and cathode, in 3 mL acetonitrile, constant current (*I*) = 10 mA, in an undivided 5 mL Electrasyn 2.0 vial at (30-35) °C for 3 hours, Yield was analysed by GC-MS using mesitylene as internal standard, n.d. = not detected.

**Table S4.** Screening of electrode material<sup>a</sup>

Entry	Anode	Cathode	Yield of <b>3a</b> (%)
1	Graphite	Graphite	51
2	Graphite	Nickel	82 (78) <sup>b</sup>
3	Graphite	Nickel foam	62
4	Graphite	Platinum	59
5	Graphite	Stainless steel	15

Reaction conditions: <sup>a</sup>**1a** (0.30 mmol), **2a** (1.8 mmol), 2,4,6-collidine (0.60 mmol), <sup>n</sup>Bu<sub>4</sub>NClO<sub>4</sub> (0.30 mmol), in 3 mL acetonitrile, constant current (*I*) = 10 mA, in an undivided 5 mL Electrasyn 2.0 vial at (30-35) °C for 3 hours, Yield was analysed by GC-MS using mesitylene as internal standard, <sup>b</sup>isolated yield.

**Table S5.** Screening of solvents<sup>a</sup>

Entry	Solvent	Yield of <b>3a</b> (%)
1	DMF	n.d.
2	DMA	<5
3	DCM	68
4	Acetonitrile (ACN)	82 (78) <sup>b</sup>
5	DCM:ACN (1:1)	75

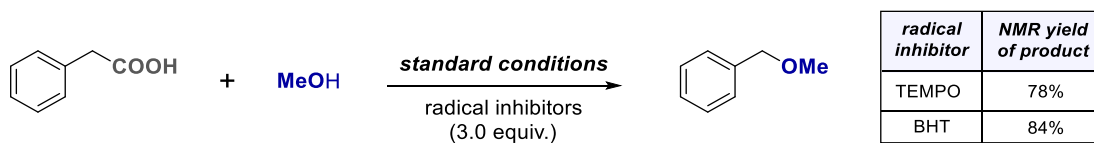
Reaction conditions: <sup>a</sup>**1a** (0.30 mmol), **2a** (1.8 mmol), 2,4,6-collidine (0.60 mmol), graphite as anode and nickel as cathode, in 3 mL **solvent**, constant current (*I*) = 10 mA, in an undivided 5 mL Electrasyn 2.0 vial at (30-35) °C for 3 hours, Yield was analysed by GC-MS using mesitylene as internal standard, n.d. = not detected.

**Table S6.** Screening of electric current<sup>a</sup>

Entry	Current	Yield of <b>3a</b> (%)
1	< 10 mA	< 40
2	No current	n.d. (Only S.M.)

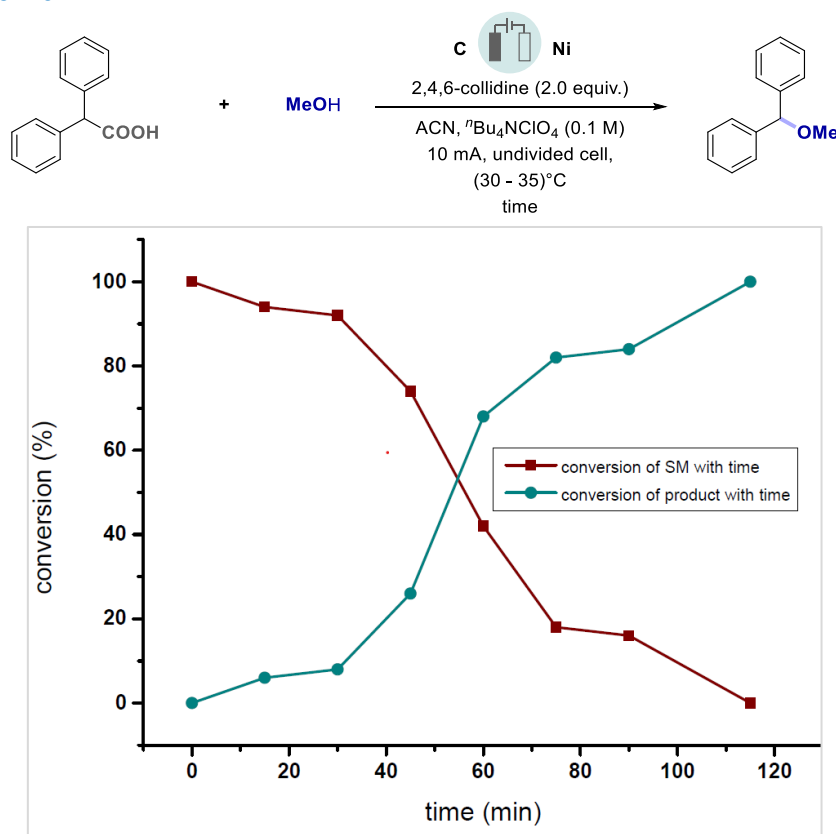
Reaction conditions: <sup>a</sup>**1a** (0.30 mmol), **2a** (1.8 mmol), 2,4,6-collidine (0.60 mmol), graphite as anode and nickel as cathode, in 3 mL acetonitrile, in an undivided 5 mL Electrasyn 2.0 vial at (30-35) °C for 3 hours, Yield was analysed by GC-MS using mesitylene as internal standard, n.d. = not detected.

#### 4. Radical Quenching Experiments:

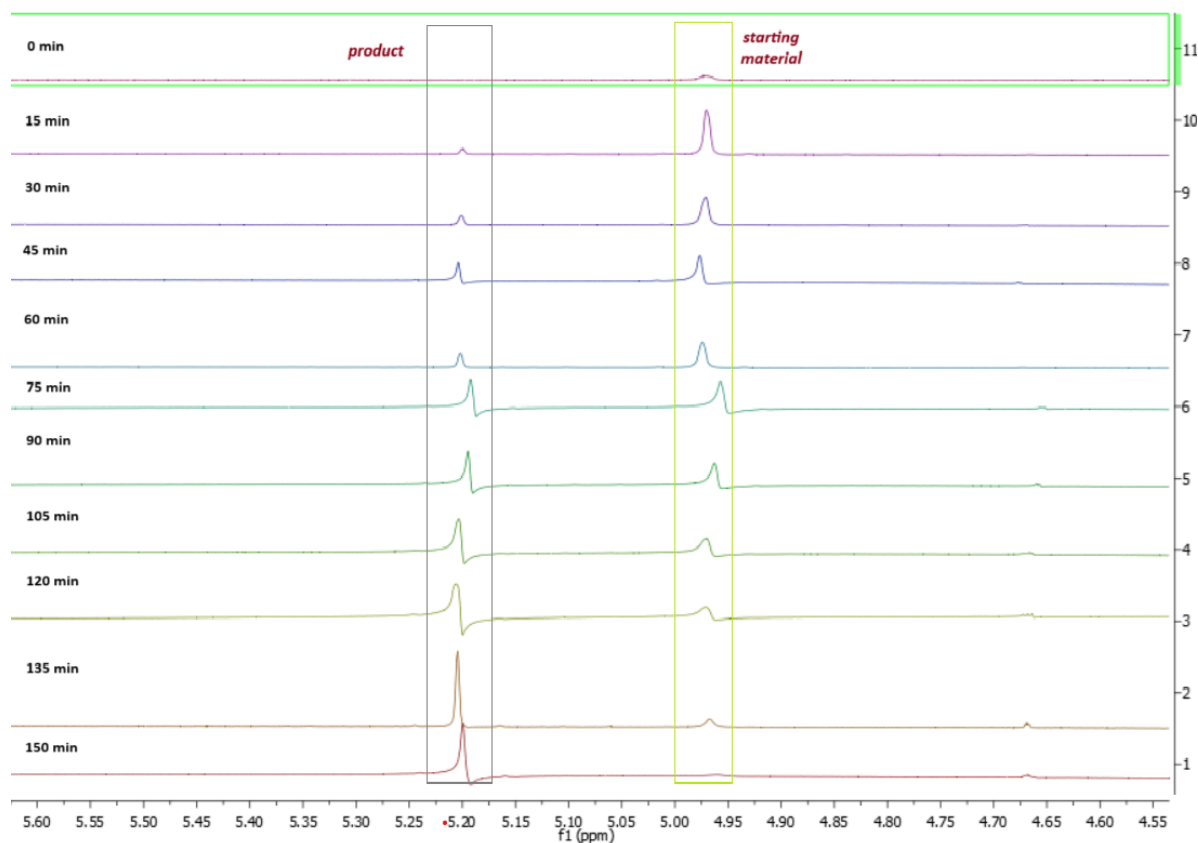


We conducted radical quenching experiments for the proposed electrochemical decarboxylation reaction. In an oven-dried Electrasyn 2.0 vial (5 mL) was added tetrabutylammonium perchlorate (100 mg, 0.1 M), phenylacetic acid (41 mg, 0.3 mmol), methanol (58 mg, 1.8 mmol), 2,4,6-collidine (73 mg, 0.6 mmol), radical inhibitors (TEMPO and BHT, 3.0 equiv.) and dissolved in 3.0 mL of acetonitrile. After that, the tube was sealed with the Electrasyn 2.0 cap containing the electrodes and stirred at constant current of 10 mA at room temperature (30-35) °C. The NMR yield of both the reactions displayed good amounts of product formation. As a result, we can easily rule out the possibility of radical formation during the progress of the reaction. We have also cross-checked our observations using HRMS studies, wherein we failed to observe any TEMPO or BHT adducts, which strongly ruled out the involvement of radical pathway.

#### 5. Kinetic Profile



**Figure S1:** Time conversion plot of starting material and product with time (NMR analysis)



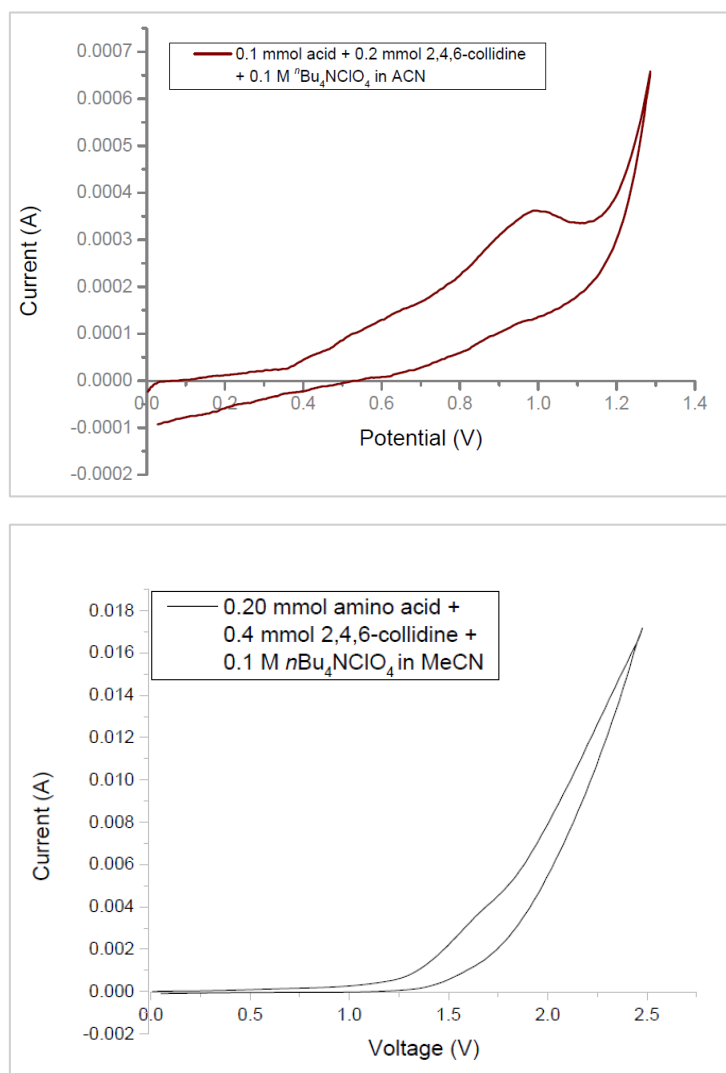
**Figure S2:** Time dependent in-situ NMR experiment.

The electrochemical decarboxylation was performed using 0.5 mmol of diphenyl acetic acid and 3.0 mmol of methanol in 3 mL acetonitrile as solvent under the standard reaction conditions. In an oven-dried Electrasyn 2.0 vial (5 mL) was added tetrabutylammonium perchlorate (100 mg, 0.1 M), diphenylacetic acid (106 mg, 0.5 mmol), methanol (96 mg, 3.0 mmol), 2,4,6-collidine (122 mg, 1.0 mmol) and dissolved in 3.0 mL of acetonitrile. After that, the tube was sealed with the Electrasyn 2.0 cap containing the electrodes and stirred at constant current of 10 mA at room temperature (30-35) °C. At indicated time intervals, 100  $\mu$ L of aliquot was taken out. The aliquots were analysed in NMR, plotting the conversion against time. From the plot, we observed that with time, the amounts of di-phenylacetic acid gradually decreased, and the amount of product ether increased simultaneously. The product formation reached the maximum after 120 minutes, and then quantitative conversion was observed. We did not detect any intermediates generated from the starting acid.

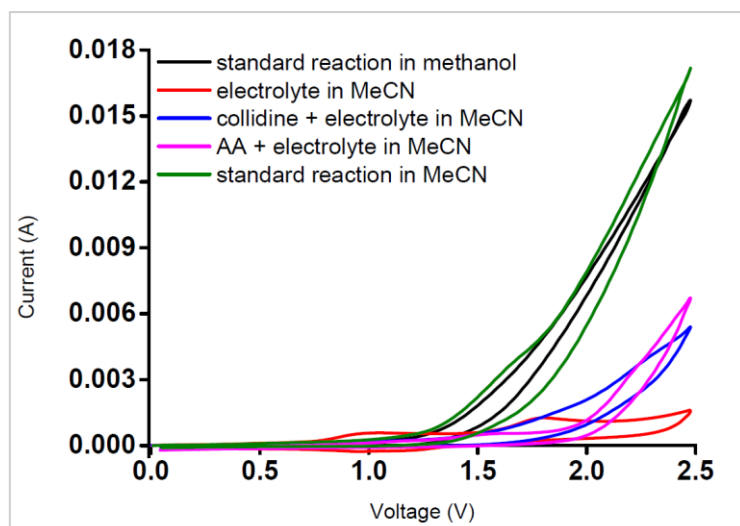
## 6. Cyclic voltammetry (CV) studies:

Cyclic voltammetry was performed in a three-electrode cell under air at room temperature (30-35) °C. A steady glassy carbon disk electrode (3 mm in diameter) was used as the working electrode, a platinum plate was used as the counter electrode, and an Ag/AgCl was used as the reference electrode in (0.1 M) KCl in acetonitrile (3.0 mL).

Acetonitrile solvent containing (0.01 M)  $n\text{Bu}_4\text{NClO}_4$  was used as the blank. The spectrums were recorded with the scan rate of  $200\text{ mV s}^{-1}$ , from 0 V to 2.5 V (starting from 0 V). The CV of di-phenylacetic acid and N-Boc Phenylalanine were conducted and the voltammograms are shown below. An irreversible oxidation peak for diphenyl acetic acid was observed at around 1.0 V, and irreversible oxidation peak for N-Boc phenylalanine was observed at around 1.65 V.



**Figure S3.** Cyclic voltammogram recorded in (0.1M)  $n\text{Bu}_4\text{NClO}_4$  in MeCN solution: scan rate:  $200\text{ mV s}^{-1}$ ; starting potential: 0 V; glass carbon (3 mm diameter, Working Electrode); platinum plate (Counter Electrode); Ag/AgCl (0.01 M) KCl in MeCN, Reference Electrode); Concentrations: diphenyl acetic acid (0.30 mmol / 3 ml MeCN), N-Boc phenylalanine (0.3 mmol / 3 ml MeCN).



**Figure S4.** Control experiments for cyclic voltametric studies.

## 7. Crystallographic data for compound 3o

Identification code: db\_ag\_24s\_1337\_Om

CCDC: 2386201

Bond Precision: C-C 0.0026 Å

Wavelength = 0.71073

Cell: a = 9.8767(2)      b = 10.1350(2)      c = 21.8700(5)  
Alpha = 90      beta = 90      gamma = 90

Temperature: 100 K

	<b>Calculated</b>	<b>Reported</b>
Volume	2189.20(8)	2189.19(8)
Space Group	P 21 21 21	P 21 21 21
Hall Group	P 2ac 2ab	P 2ac 2ab
Moiety Formula	C22 H35 N O3	4(C22 H35 N O3)
Sum formula	C22 H35 N O3	C88 H140 N4 O12
Mr	361.51	1446.03
Dx, g cm <sup>-3</sup>	1.097	1.097
Z	4	1
Mu (mm <sup>-1</sup> )	0.072	0.072
F000	792.0	792.0
F000'	792.34	
h,k,lmax	13,13,29	13,13,29
Nref	5438[3080]	5436
Tmin,Tmax	0.995,0.993	0.617,0.746
Tmin'	0.978	

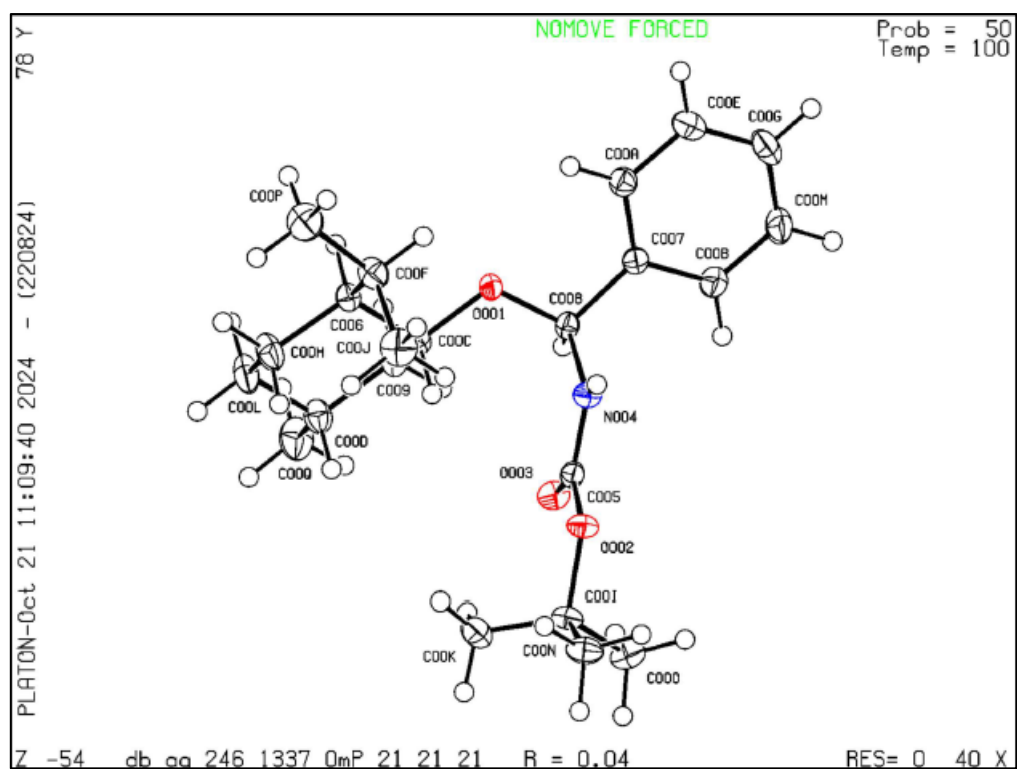
Correction method = # Reported    T Limits: Tmin = 0.617    Tmax = 0.746

AbsCorr = MULTI-SCAN

Data completeness = 1.76/1.00      Theta (max) = 28.287

R (reflections) = 0.0374 (4828)      wR2 (reflections) = 0.0843

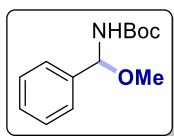
S = 1.024      Npar = 245



**Figure S5.** Platon-ellipsoid plot for compound **3o**

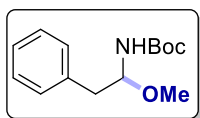
## 8. Analytical Data:

### ***tert*-butyl-(methoxy(phenyl)methyl)carbamate (3a):<sup>1</sup>**



Following the general procedure **A**, the title compound was isolated as a colourless viscous liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (93:7) with an isolated yield of 78% (56 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 – 7.21 (m, 2H), 7.20 – 7.11 (m, 3H), 5.65 (d, *J* = 10.5 Hz, 1H), 5.03 (s, 1H), 3.27 (s, 3H), 1.30 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  154.3, 138.5, 127.5, 127.4, 124.9, 82.5, 79.1, 54.5, 27.3.

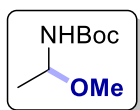
### ***tert*-butyl-(1-methoxy-2-phenylethyl)carbamate (3b):**



Following the general procedure **A**, the title compound was isolated as a colourless viscous liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (93:7) with an isolated yield of 85% (64 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.26 (m, 2H), 7.22 (ddd, *J* = 6.1, 5.4, 3.9 Hz, 3H), 5.13 – 5.04 (m, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 3.32 (s, 3H), 2.90 (d, *J* = 6.1 Hz, 2H), 1.40 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  155.4, 136.3, 129.8, 128.4, 126.7, 82.9, 79.8, 55.6, 41.8, 28.3.

HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>22</sub>NO<sub>3</sub>: 252.1594; found: 252.1597.

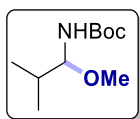
### ***tert*-butyl(1-methoxyethyl)carbamate (3c):**



Following the general procedure **A**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (93:7) with an isolated yield of 82% (43 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.94 (dd, *J* = 10.5, 5.8 Hz, 1H), 4.89 (s, 1H), 3.29 (s, 3H), 1.42 (s, 9H), 1.28 (d, *J* = 7.7 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  155.3, 79.7, 79.5, 55.2, 28.4, 21.7.

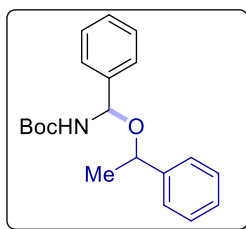
HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>8</sub>H<sub>18</sub>NO<sub>3</sub>: 176.1281; found: 176.1285.

***tert*-butyl (1-methoxy-2-methylpropyl)carbamate (3d):<sup>1</sup>**



Following the general procedure **A**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (93:7) with an isolated yield of 74% (45 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.77 (s, 1H), 4.53 – 4.51 (m, 1H), 3.28 (s, 3H), 1.77 – 1.73 (m, 1H), 1.41 (s, 9H), 0.87 (d, *J* = 10 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 155.9, 87.2, 79.6, 55.6, 33.11, 28.3, 17.8, 17.3.

***tert*-butyl (phenyl(1-phenylethoxy)methyl)carbamate (3e):**



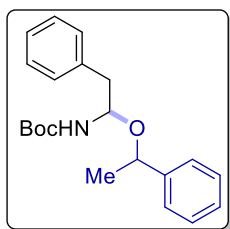
Following the general procedure **A**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (95:5) with an isolated yield of 67% (65 mg). **Diastereomer 1: Diastereomer 2:** 59:41.

**Diastereomer 1:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.47-7.46 (m, 1H), 7.39-7.36 (m, 5H), 7.35-7.30 (m, 3H), 7.29-7.25 (m, 1H), 6.08 (d, *J* = 5.6 Hz, 1H), 5.20 – 5.18 (m, 1H), 4.87 (dd, *J* = 12.9, 6.5 Hz, 1H), 1.52 (d, *J* = 5.0 Hz, 3H), 1.41 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 155.3, 144.4, 140.3, 128.7, 128.44, 128.2, 127.3, 126.2, 80.8, 80.0, 75.2, 28.4, 24.4.

**Diastereomer 2:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.47-7.46 (m, 1H), 7.39-7.36 (m, 5H), 7.35-7.30 (m, 3H), 7.29-7.25 (m, 1H), 5.85 (d, *J* = 5.6 Hz, 1H), 5.06 – 5.04 (m, 1H), 4.76-4.75 (m, 1H), 1.52 (d, *J* = 10 Hz, 3H), 1.51 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 154.9, 143.3, 140.2, 128.5, 128.41, 127.7, 126.8, 126.1, 80.8, 79.8, 75.0, 28.3, 23.6.

HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>26</sub>NO<sub>3</sub>: 328.1913; found: 328.1910.

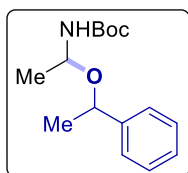
***tert*-butyl (2-phenyl-1-(1-phenylethoxy)ethyl)carbamate (3f):**



Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (95:5) with an isolated yield of 66% (67 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 – 7.22 (m, 1H), 7.20 – 7.19 (m, 4H), 7.18 – 7.15 (m, 3H), 7.14 – 7.12 (m, 2H), 5.33 – 5.24 (m, 1H), 4.58 (dd,  $J$  = 12.9, 6.5 Hz, 1H), 2.86 (d,  $J$  = 5.6 Hz, 2H), 1.23 (s, 9H), 1.21 (d,  $J$  = 6.4 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.0, 144.9, 136.7, 129.9, 128.3, 127.1, 126.6, 125.9, 80.7, 79.7, 75.4, 42.5, 28.3, 22.9.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{28}\text{NO}_3$ : 342.2069; found: 342.2060.

***tert*-butyl (1-(1-phenylethoxy)ethyl)carbamate (3g):**



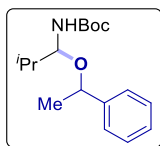
Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (95:5) with an isolated yield of 63% (50 mg). **Diastereomer 1: Diastereomer 2** = 58:42.

**Diastereomer 1:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.29 (m, 4H), 7.28 – 7.26 (m, 1H), 5.04 (s, 1H), 4.70 (dd,  $J$  = 13.8, 6.9 Hz, 1H), 1.45 (s, 9H), 1.39 (d,  $J$  = 6.4 Hz, 3H), 1.23 (d,  $J$  = 5.8 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 143.8, 128.6, 127.6, 126.6, 125.5, 81.7, 79.7, 74.7, 28.4, 25.3, 19.0.

**Diastereomer 2:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.29 (m, 4H), 7.28 – 7.26 (m, 1H), 5.07 (d,  $J$  = 20.1 Hz, 1H), 4.96 – 4.83 (m, 1H), 1.43 (s, 9H), 1.32 (d,  $J$  = 7.3 Hz, 3H), 1.23 (d,  $J$  = 5.8 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 143.8, 128.4, 127.5, 126.6, 125.5, 81.7, 79.7, 76.2, 28.0, 24.6, 22.5.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{24}\text{NO}_3$ : 266.1756; found: 266.1750.

***tert*-butyl (2-methyl-1-(1-phenylethoxy)propyl)carbamate (3h):**



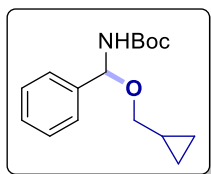
Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (95:5) with an isolated yield of 59% (46 mg). **Diastereomer 1: Diastereomer 2** = 53:47.

**Diastereomer 1:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (dd,  $J$  = 6.2, 2.3 Hz, 4H), 7.24 (d,  $J$  = 7.9 Hz, 1H), 4.79 (d,  $J$  = 10.4 Hz, 1H), 4.61 (dd,  $J$  = 7.4, 5.6 Hz, 1H), 1.71 – 1.67 (m, 1H), 1.46 (s, 9H), 1.39 (d,  $J$  = 6.4 Hz, 3H), 0.82 (t,  $J$  = 6.3 Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 143.5, 128.6, 128.3, 127.5, 127.0, 125.5, 83.4, 79.5, 74.3, 33.5, 28.42, 25.3, 18.0, 17.5.

**Diastereomer 1:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (dd,  $J$  = 6.2, 2.3 Hz, 4H), 7.24 (d,  $J$  = 7.9 Hz, 1H), 4.79 (d,  $J$  = 10.4 Hz, 1H), 4.48 – 4.45 (m, 1H), 1.71 – 1.67 (m, 1H), 1.46 (s, 9H), 1.39 (d,  $J$  = 6.4 Hz, 3H), 0.82 (t,  $J$  = 6.3 Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 143.5, 128.6, 128.3, 127.5, 127.0, 125.5, 83.4, 79.5, 70.5, 31.0, 28.40, 24.3, 18.0, 17.5.

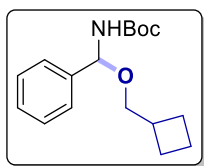
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{28}\text{NO}_3$ : 294.2069; found: 294.2060.

***tert*-butyl ((cyclopropylmethoxy)(phenyl)methyl)carbamate (3i):**



Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (95:5) with an isolated yield of 80% (66 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.41 (m, 2H), 7.37 – 7.30 (m, 2H), 7.28 (dd,  $J$  = 6.7, 1.9 Hz, 1H), 5.93 (d,  $J$  = 10.6 Hz, 1H), 5.17 (d,  $J$  = 11.1 Hz, 1H), 3.51 (dd,  $J$  = 10.6, 7.3 Hz, 1H), 3.38 (dd,  $J$  = 10.4, 7.0 Hz, 1H), 1.45 (s, 9H), 1.14 – 1.09 (m, 1H), 0.54 – 0.50 (m, 2H), 0.25 – 0.18 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 139.9, 128.6, 128.4, 126.1, 81.9, 80.1, 72.9, 28.4, 10.7, 3.3, 3.0. HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{24}\text{NO}_3$ : 278.1756; found: 278.1706.

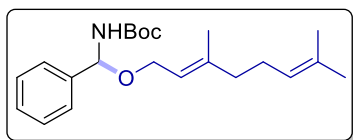
***tert*-butyl ((cyclobutylmethoxy)(phenyl)methyl)carbamate (3j):**



Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (95:5) with an isolated yield of 76% (66 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.40 (m, 2H), 7.34 (ddd,  $J$  = 6.4, 2.7, 1.0 Hz, 2H), 7.31 – 7.28 (m, 1H), 5.90 (d,  $J$  = 10.5 Hz, 1H), 5.13 (d,  $J$  = 11.0 Hz, 1H), 3.67 (dd,  $J$  = 9.9, 7.0 Hz, 1H), 3.51 (dd,  $J$  = 9.9, 7.3 Hz, 1H), 2.63 (qd,  $J$  = 7.6, 3.7 Hz, 1H), 2.09 – 2.02 (m, 2H), 1.92 – 1.84 (m, 2H), 1.81 – 1.75 (m, 2H), 1.47 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 140.0, 128.6, 128.4, 126.1, 82.2, 80.1, 72.7, 35.1, 28.4, 25.2, 25.0, 18.7.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{26}\text{NO}_3$ : 292.1913; found: 292.1910.

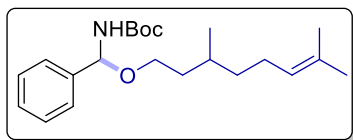
***tert*-butyl (E)-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)(phenyl)methyl)carbamate (3k):**



Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (95:5) with an isolated yield of 65% (70 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J$  = 7.3 Hz, 2H), 7.34 (dd,  $J$  = 8.1, 6.6 Hz, 2H), 7.29 (t,  $J$  = 7.2 Hz, 1H), 5.95 (d,  $J$  = 9.8 Hz, 1H), 5.44 – 5.38 (m, 1H), 5.09 (tdd,  $J$  = 4.2, 3.4, 1.4 Hz, 1H), 4.22 (dd,  $J$  = 11.5, 6.6 Hz, 1H), 4.11 (dd,  $J$  = 11.4, 7.0 Hz, 1H), 2.10 – 2.01 (m, 4H), 1.66 – 1.65 (m, 6H), 1.59 (s, 3H), 1.47 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 140.6, 139.9, 128.6, 128.3, 126.1, 124.1, 120.5, 81.8, 80.0, 64.8, 39.7, 28.4, 26.5, 25.7, 17.7, 16.6.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{33}\text{NaNO}_3$ : 382.2358; found: 382.2351.

***tert*-butyl (((3,7-dimethyloct-6-en-1-yl)oxy)(phenyl)methyl)carbamate (3l):**

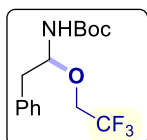


Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (96:4) with an isolated yield of 70% (76 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.40 (m, 2H), 7.34 (t,  $J$  = 7.7 Hz, 2H), 7.29 (t,  $J$  = 7.4

Hz, 1H), 5.91 (d,  $J = 10.9$  Hz, 1H), 5.11 – 5.08 (m, 1H), 3.74 – 3.55 (m, 2H), 1.98 – 1.96 (m, 2H), 1.67 (s, 3H), 1.61 (dd,  $J = 11.1, 3.8$  Hz, 1H), 1.59 (s, 3H), 1.54 – 1.50 (m, 1H), 1.47 (s, 9H), 1.40 – 1.27 (m, 2H), 1.25 – 1.06 (m, 1H), 0.89 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 140.1, 131.2, 128.6, 128.3, 126.0, 124.9, 82.2, 82.1, 80.1, 66.5, 66.4, 55.3, 37.3, 37.2, 36.7, 36.6, 29.6, 28.5, 28.45, 28.43, 28.40, 25.8, 25.5, 19.62, 19.59, 17.7.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{36}\text{NO}_3$ : 362.2695; found: 362.2691.

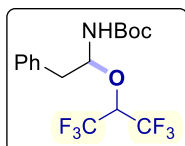
***tert*-butyl-(2-phenyl-1-(2,2,2-trifluoroethoxy)ethyl)carbamate (3m):**



Following the general procedure **B**, the title compound was isolated as a white solid using silica-gel column chromatography eluting with hexane and ethyl acetate (96:4) with an isolated yield of 51% (49 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.27 (m, 3H), 7.24 (ddd,  $J = 8.4, 6.8, 2.4$  Hz, 2H), 5.29 (d,  $J = 5.2$  Hz, 1H), 4.98 (d,  $J = 10.8$  Hz, 1H), 3.94 – 3.91 (m, 2H), 2.96 (d,  $J = 5.9$  Hz, 2H), 1.40 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 135.4, 129.9, 128.6, 127.0, 125.1, 122.9, 82.9, 80.6, 65.9, 65.7, 41.4, 28.3.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -74.34.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{21}\text{F}_3\text{NO}_3$ : 320.1474; found: 320.1472.

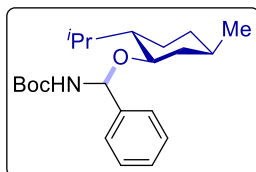
***tert*-butyl -(1-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2-phenylethyl)carbamate (3n):**



Following the general procedure **B**, the title compound was isolated as a white solid using silica-gel column chromatography eluting with hexane and ethyl acetate (93:7) with an isolated yield of 62% (71 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.27 (m, 3H), 7.23 (dd,  $J = 8.4, 1.5$  Hz, 2H), 5.54 – 5.50 (m, 1H), 5.17 (s, 1H), 3.03 – 3.00 (m, 2H), 1.41 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 134.5, 129.9, 128.7, 127.3, 84.7, 81.3, 73.9, 40.9, 28.1.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -74.2, -74.4.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{20}\text{F}_6\text{NO}_3$ : 388.1347; found: 388.1339.

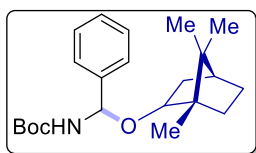
***tert*-butyl (((2-isopropyl-5-methylcyclohexyl)oxy)(phenyl)methyl)carbamate (3o):**



Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (93:7) with an isolated yield of 78% (84 mg). **Diastereomer 1: Diastereomer 2** = 57:43.

**Diastereomer 1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.11 (m, 2H), 5.95 (d,  $J$  = 10.7 Hz, 1H), 3.38 (ddd,  $J$  = 15.3, 11.1, 3.7 Hz, 1H), 2.16 – 2.01 (m, 2H), 1.52 – 1.46 (m, 2H), 1.32 (s, 9H), 1.14 – 1.04 (m, 2H), 0.96 – 0.82 (m, 2H), 0.76 (d,  $J$  = 7.2 Hz, 6H), 0.65 (d,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 140.9, 128.5, 128.3, 126.1, 82.2, 78.9, 76.0, 49.0, 42.8, 34.6, 31.9, 28.4, 25.5, 23.2, 22.4, 21.4, 16.0. **Diastereomer 2.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.11 (m, 2H), 5.87 (d,  $J$  = 11.1 Hz, 1H), 3.38 (ddd,  $J$  = 15.3, 11.1, 3.7 Hz, 1H), 2.16 – 2.01 (m, 2H), 1.52 – 1.46 (m, 2H), 1.32 (s, 9H), 1.14 – 1.04 (m, 2H), 0.96 – 0.82 (m, 2H), 0.71 (d,  $J$  = 7.3 Hz, 6H), 0.51 (d,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.1, 140.4, 128.5, 128.1, 126.1, 79.9, 78.4, 76.0, 48.0, 40.5, 34.5, 31.5, 28.4, 25.4, 23.0, 22.4, 21.2, 15.9.

***tert*-butyl (phenyl(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)carbamate (3p):**



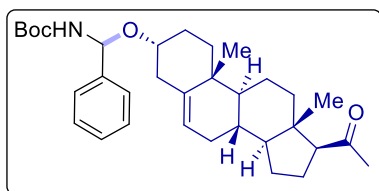
Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (93:7) with an isolated yield of 67% (72 mg). **Diastereomer 1: Diastereomer 2** = 55:45.

**Diastereomer 1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J$  = 7.5 Hz, 2H), 7.19 (t,  $J$  = 7.3 Hz, 2H), 7.15 (d,  $J$  = 7.2 Hz, 1H), 5.84 (d,  $J$  = 10.3 Hz, 1H), 3.86 – 3.84 (m, 1H), 2.10 – 2.02 (m, 1H), 1.62 – 1.48 (m, 2H), 1.31 (s, 9H), 1.14 – 1.10 (m, 2H), 1.09 – 1.08 (m, 1H), 0.92 (dd,  $J$  = 13.1, 3.3 Hz, 1H), 0.73 (s, 3H), 0.70 (s, 3H), 0.69 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 140.9, 134.6, 128.4, 128.2, 126.2, 83.9, 81.0, 80.0, 49.7, 47.8, 45.2, 37.2, 28.4, 28.4, 27.0, 19.8, 19.0, 14.0.

**Diastereomer 2.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J$  = 7.5 Hz, 2H), 7.19 (t,  $J$  = 7.3 Hz, 2H), 7.15 (d,  $J$  = 7.2 Hz, 1H), 5.81 (d,  $J$  = 10.4 Hz, 1H), 3.78 – 3.76 (m, 1H), 1.96 – 1.90 (m, 1H), 1.62 – 1.48 (m, 2H), 1.31 (s, 9H), 1.14 – 1.10 (m, 2H), 1.09 – 1.08 (m, 1H), 0.92 (dd,  $J$  = 13.1, 3.3 Hz, 1H), 0.72 (s, 3H), 0.69 (s, 3H), 0.67 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.1, 140.4, 134.6, 128.4, 128.1, 126.2, 82.8, 80.2, 79.9, 49.1, 47.4, 45.1, 35.9, 28.4, 28.3, 26.9, 19.8, 18.9, 13.7.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{22}\text{H}_{34}\text{NO}_3]^+$  360.2533; Found 360.2538.

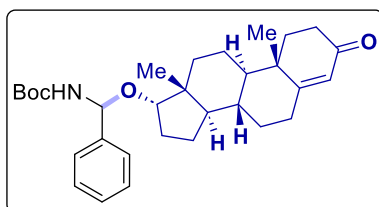
***tert*-butyl(17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl)oxy)(phenyl)methylcarbamate (3q):**



Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (93:7) with an isolated yield of 71% (110 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (d,  $J = 7.4$  Hz, 2H), 7.22 – 7.17 (m, 2H), 7.15 (dd,  $J = 6.8, 0.6$  Hz, 1H), 5.91 (d,  $J = 9.1$  Hz, 1H), 5.23 – 5.11 (m, 1H), 3.42 – 3.28 (m, 1H), 2.36 (t,  $J = 8.8$  Hz, 1H), 2.31 – 2.17 (m, 1H), 2.15 – 2.06 (m, 1H), 2.04 – 2.02 (m, 1H), 1.96 (s, 3H), 1.92 – 1.77 (m, 3H), 1.70 (ddd,  $J = 13.5, 8.1, 3.1$  Hz, 1H), 1.58 – 1.40 (m, 6H), 1.31 (s, 9H), 1.15 – 1.02 (m, 3H), 1.01 – 0.94 (m, 1H), 0.90 (dd,  $J = 13.7, 3.0$  Hz, 1H), 0.84 (s, 3H), 0.75 – 0.67 (m, 1H), 0.46 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  209.8, 155.1, 140.7, 128.6, 128.3, 126.1, 121.6, 114.4, 80.4, 80.1, 71.8, 63.8, 57.0, 55.7, 50.1, 44.1, 42.3, 39.8, 38.9, 37.4, 37.3, 36.9, 31.9, 31.6, 29.3, 28.4, 28.4, 24.6, 22.9, 21.1, 19.5, 13.3.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{33}\text{H}_{48}\text{NO}_4]^+$  522.3578; Found 522.3580.

***tert*-butyl(10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-17-yl)oxy)(phenyl)methylcarbamate (3r):**



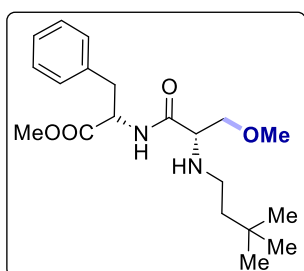
Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (92:8) with an isolated yield of 85% (125 mg). **Diastereomer 1: Diastereomer 2 = 53:47.**

**Diastereomer 1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.25 (m, 2H), 7.23 – 7.12 (m, 3H), 6.62 (s, 1H), 5.57 (s, 1H), 3.51 (ddd,  $J = 19.4, 15.3, 6.7$  Hz, 1H), 2.28 – 2.12 (m, 2H), 2.03 – 1.82 (m, 2H), 1.80 – 1.65 (m, 2H), 1.63 – 1.37 (m, 7H), 1.29 (s, 9H), 1.33 – 1.26 (m, 4H), 1.04 (s, 3H), 0.91 – 0.82 (m, 3H), 0.75 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  199.7, 171.5, 157.4, 147.6, 140.6, 128.5, 126.1, 123.9, 121.3, 87.3, 82.4, 80.7, 54.0, 50.6, 43.2, 38.7, 37.1, 35.8, 35.5, 34.0, 32.9, 31.6, 28.5, 28.3, 27.7, 24.3, 23.6, 20.9, 20.7, 17.5, 12.0.

**Diastereomer 2.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.25 (m, 2H), 7.23 – 7.12 (m, 3H), 5.60 – 5.52 (s, 1H), 5.02 – 4.99 (m, 1H), 3.51 (ddd,  $J$  = 19.4, 15.3, 6.7 Hz, 1H), 2.28 – 2.12 (m, 2H), 2.03 – 1.82 (m, 2H), 1.80 – 1.65 (m, 2H), 1.63 – 1.37 (m, 7H), 1.29 (s, 9H), 1.33 – 1.26 (m, 4H), 1.04 (s, 3H), 0.91 – 0.82 (m, 3H), 0.74 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  199.7, 171.4, 155.4, 147.6, 140.4, 128.2, 126.1, 123.9, 121.3, 85.2, 82.4, 80.0, 53.9, 50.2, 42.8, 38.7, 37.0, 35.7, 35.5, 34.0, 32.9, 31.6, 28.4, 28.3, 27.0, 24.3, 23.4, 20.9, 20.7, 17.5, 11.8.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{31}\text{H}_{44}\text{NO}_4]^+$  494.3265; Found 494.3269.

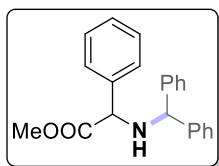
**methyl N-(3,3-dimethylbutyl)-O-methyl-L-seryl-L-phenylalaninate (3s):**



Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (60:40) with an isolated yield of 45% (49 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.32 (d,  $J$  = 8.2 Hz, 1H), 7.25 (d,  $J$  = 1.8 Hz, 3H), 7.19 (d,  $J$  = 6.9 Hz, 2H), 4.77 – 4.72 (m, 1H), 3.81 (td,  $J$  = 4.2, 2.1 Hz, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 3.19 – 3.13 (m, 1H), 2.98 (dd,  $J$  = 14.1, 9.2 Hz, 1H), 2.88 – 2.65 (m, 3H), 2.57 – 2.53 (m, 1H), 1.59 – 1.46 (m, 2H), 0.86 (s, 9H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.7, 136.6, 130.3, 129.4, 129.3, 128.6, 127.1, 74.4, 58.8, 57.9, 55.3, 54.1, 52.4, 42.5, 40.6, 37.6, 29.9, 29.3.

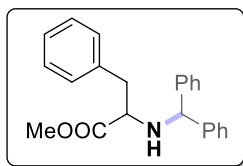
HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{20}\text{H}_{33}\text{N}_2\text{O}_4]^+$  365.2440; Found 365.2410.

**methyl 2-(benzhydrylamino)-2-phenylacetate (6a):<sup>2</sup>**



Following the general procedure **C**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (96:4) with an isolated yield of 79% (78 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.26 (m, 11H), 7.23 – 7.09 (m, 4H), 4.72 (s, 1H), 4.32 (s, 1H), 3.99 – 3.98 (m, 1H), 3.68 (s, 3H). NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 143.2, 138.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.2, 127.9, 127.68, 127.65, 127.6, 127.5, 127.4, 127.3, 127.2, 64.4, 62.9, 52.3.

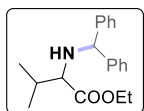
**methyl benzhydrylphenylalaninate (6b):**



Following the general procedure C, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (97:3) with an isolated yield of 88% (91 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.25 (m, 8H), 7.24 – 7.20 (m, 2H), 7.20 – 7.16 (m, 5H), 4.79 (s, 1H), 3.67 (s, 3H), 3.47 (dd,  $J$  = 8.0, 5.9 Hz, 1H), 3.01 (dd,  $J$  = 13.7, 6.0 Hz, 1H), 2.92 (dd,  $J$  = 13.7, 7.9 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 144.3, 142.7, 137.7, 129.6, 128.6, 128.5, 128.4, 127.5, 127.4, 127.3, 127.2, 126.7, 65.5, 60.7, 51.7, 40.3.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{24}\text{NO}_2$ : 346.1807; found: 346.1832.

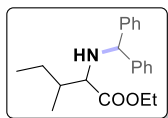
**ethyl benzhydrylvalinate (6c):**



Following the general procedure C, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (98:2) with an isolated yield of 70% (65 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J$  = 7.8 Hz, 2H), 7.38 (d,  $J$  = 7.9 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.23 – 7.17 (m, 2H), 4.74 (s, 1H), 4.20 (dd,  $J$  = 7.1, 3.8 Hz, 2H), 2.97 (d,  $J$  = 6.0 Hz, 1H), 1.94 (dd,  $J$  = 13.3, 6.6 Hz, 1H), 1.27 (d,  $J$  = 7.1 Hz, 3H), 0.98 (dd,  $J$  = 10.4, 6.8 Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 128.6, 128.5, 127.8, 127.4, 127.2, 65.9, 64.9, 60.4, 31.9, 19.7, 18.6, 14.5.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{25}\text{NNaO}_2$ : 334.1783; found: 334.1772.

**ethyl benzhydrylleucinate (6d):**

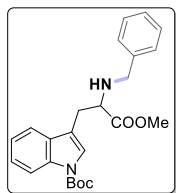


Following the general procedure C, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with hexane and ethyl acetate (98:2) with an isolated yield of 74% (65 mg).  $^1\text{H}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.42 (m, 2H), 7.36 (dd,  $J$  = 8.1, 0.9 Hz, 2H), 7.29 – 7.25 (m, 4H), 7.20 (ddd,  $J$  = 13.5, 12.0, 7.4 Hz, 2H), 4.73 (s, 1H), 4.19 (dd,  $J$  = 7.1, 4.1 Hz, 2H), 3.01 (d,  $J$

= 6.2 Hz, 1H), 2.15 – 2.04 (m, 1H), 1.66 (dtdd,  $J = 19.3, 15.0, 7.1, 4.2$  Hz, 2H), 1.27 (t,  $J = 7.1$  Hz, 3H), 0.90 (d,  $J = 6.8$  Hz, 3H), 0.85 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 144.7, 142.9, 128.6, 128.5, 127.8, 127.4, 127.2, 127.2, 65.9, 63.9, 60.4, 38.6, 25.4, 15.9, 14.5, 11.5.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{28}\text{NO}_2$ : 326.2120.1807; found: 326.2109.

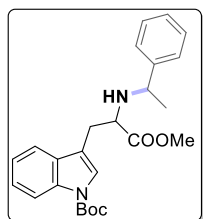
**tert-butyl 3-(2-(benzylamino)-3-methoxy-3-oxopropyl)-1H-indole-1-carboxylate (6e):**



Following the general procedure **C**, the title compound was isolated as a colourless solid using silica-gel column chromatography eluting with hexane and ethyl acetate (90:10) with an isolated yield of 52% (32 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.45 (m, 1H), 7.39-7.38 (m, 4H), 7.35-7.32 (m, 1H), 7.16-7.09 (m, 2H), 6.78 (s, 1H), 4.59 (d,  $J = 10.0$  Hz, 1H), 3.93 (s, 3H), 3.60 (s, 3H), 3.11 (d,  $J = 10.0$  Hz, 2H), 1.40 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.3, 162.5, 131.2, 129.5, 129.0, 128.9, 127.8, 122.1, 121.3, 120.4, 112.3, 82.2, 74.5, 41.2, 28.4, 26.2.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_4$ : 409.2127; found: 409.2110.

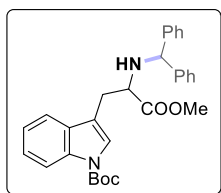
**tert-butyl 3-(3-methoxy-3-oxo-2-((1-phenylethyl)amino)propyl)-1H-indole-1-carboxylate (6f):**



Following the general procedure **C**, the title compound was isolated as a colourless solid using silica-gel column chromatography eluting with hexane and ethyl acetate (90:10) with an isolated yield of 60% (58 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.38 (m, 6H), 7.33 (d,  $J = 6.8$  Hz, 1H), 7.23 – 7.21 (m, 1H), 7.13 – 7.09 (m, 2H), 5.01 (dd,  $J = 9.3, 2.6$  Hz, 1H), 4.55 – 4.49 (m, 1H), 4.02 (dt,  $J = 8.6, 6.4$  Hz, 1H), 3.57 (d,  $J = 2.2$  Hz, 3H), 3.00 (t,  $J = 6.1$  Hz, 2H), 1.66 (d,  $J = 7.2$  Hz, 3H), 1.40 (d,  $J = 5.9$  Hz, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 155.3, 139.1, 139.1, 131.3, 129.1, 127.9, 127.73, 127.71, 122.0, 120.4, 110.9, 79.9, 53.7, 52.3, 45.7, 28.4, 26.1, 18.2.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{31}\text{N}_2\text{O}_4$ : 423.2284; found: 423.2240.

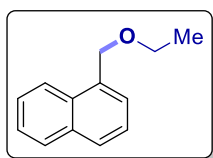
***tert*-butyl 3-(2-(benzhydrylamino)-3-methoxy-3-oxopropyl)-1H-indole-1-carboxylate (6g):**



Following the general procedure **C**, the title compound was isolated as a colourless solid using silica-gel column chromatography eluting with hexane and ethyl acetate (90:10) with an isolated yield of 55% (58 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (s, 1H), 7.46 (d,  $J$  = 1.2 Hz, 1H), 7.42 – 7.36 (m, 11H), 7.33 (d,  $J$  = 4.9 Hz, 1H), 7.16 – 7.10 (m, 2H), 5.32 (s, 1H), 4.97 (d,  $J$  = 8.4 Hz, 1H), 4.51 (dt,  $J$  = 8.3, 6.1 Hz, 1H), 3.52 (s, 3H), 3.01 (dd,  $J$  = 7.6, 6.2 Hz, 2H), 1.38 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 170.4, 155.3, 140.9, 137.4, 131.3, 129.0, 128.7, 127.9, 122.2, 120.5, 118.8, 111.0, 94.9, 79.9, 57.0, 53.8, 52.3, 28.4, 26.1.

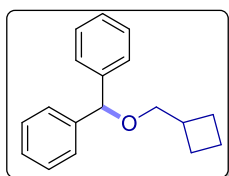
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_4$ : 485.2440; found: 485.2439.

**1-(methoxymethyl)naphthalene (7a):<sup>3</sup>**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with hexane and ethyl acetate (97:3) with an isolated yield of isolated yield of 92% (51 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 – 8.14 (m, 1H), 7.89 – 7.87 (m, 1H), 7.84 – 7.81 (dd,  $J$  = 11.4, 3.1 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.50 – 7.44 (dd,  $J$  = 8.4, 6.9 Hz, 2H), 4.97 (s, 2H), 3.65 (q,  $J$  = 7.1 Hz, 2H), 1.30 (t,  $J$  = 5 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  134.1, 133.9, 131.9, 128.63, 128.61, 126.4, 126.3, 125.8, 125.3, 124.1, 71.3, 65.9, 15.4.

**((cyclobutylmethoxy)methylene)dibenzene (7b):**

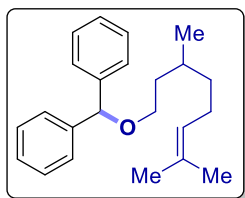


Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 70%, 53 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.37 (m, 4H), 7.36 – 7.32 (m, 4H), 7.28 – 7.25 (m, 2H), 5.37 – 5.36 (d,  $J$  = 4.2

Hz, 1H), 3.48 – 3.46 (m, 2H), 2.72 – 2.66 (m, 1H), 2.12 – 2.07 (m, 2H), 1.97 – 1.87 (m, 2H), 1.85 – 1.79 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 128.5, 127.4, 127.1, 83.6, 73.8, 35.4, 25.3, 18.8.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{21}\text{O}$ : 253.1592; found: 253.1598.

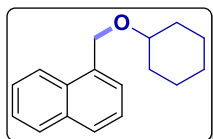
**(((3,7-dimethyloct-6-en-1-yl)oxy)methylene)dibenzene (7c):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 89%, 86 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.24 (m, 4H), 7.22 – 7.19 (m, 4H), 7.14 – 7.11 (m, 2H), 5.23 (s, 1H), 5.02 – 4.98 (m, 1H), 3.42 – 3.34 (m, 2H), 1.95 – 1.81 (m, 2H), 1.64 – 1.60 (m, 1H), 1.58 (d,  $J$  = 0.8 Hz, 3H), 1.54 (dd,  $J$  = 13.1, 6.6 Hz, 1H), 1.50 (s, 3H), 1.40 – 1.33 (td,  $J$  = 13.4, 6.9 Hz, 1H), 1.27 – 1.21 (m, 1H), 1.09 – 1.01 (m, 1H), 0.78 – 0.77 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.73, 142.71, 131.1, 128.4, 127.3, 127.0, 126.9, 124.9, 83.7, 67.5, 37.2, 36.9, 29.6, 25.8, 25.5, 19.7, 17.7.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{31}\text{O}$ : 323.2375; found: 323.2366.

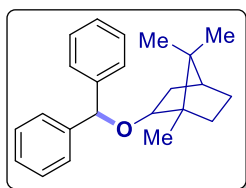
**1-((cyclohexyloxy)methyl)naphthalene (7d):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 85%, 61 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J$  = 8.4 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.57 – 7.50 (m, 3H), 7.48 – 7.45 (m, 1H), 5.03 (s, 2H), 3.52 – 3.47 (m, 1H), 2.05 (dd,  $J$  = 9.1, 3.6 Hz, 2H), 1.83 – 1.80 (m, 2H), 1.59 (dd,  $J$  = 9.4, 3.8 Hz, 1H), 1.49 – 1.42 (m, 1H), 1.36 – 1.23 (m, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.6, 135.3, 134.6, 133.8, 131.8, 128.5, 128.2, 126.0, 125.9, 125.6, 125.3, 124.0, 77.4, 68.3, 32.3, 25.8, 24.2.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{21}\text{O}$ : 241.1592; found: 241.1587.

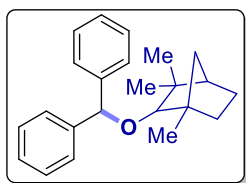
**2-(benzhydryloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (7e):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 80%, 76 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J$  = 7.9 Hz, 4H), 7.38 – 7.33 (m, 3H), 7.33 – 7.22 (m, 3H), 5.44 (d,  $J$  = 2.6 Hz, 1H), 3.78 – 3.73 (m, 1H), 2.34 (td,  $J$  = 9.1, 4.4 Hz, 1H), 2.13 – 2.04 (m, 1H), 1.84 – 1.73 (m, 1H), 1.69 (d,  $J$  = 3.9 Hz, 1H), 1.39 – 1.30 (m, 2H), 1.18 (dd,  $J$  = 12.8, 3.1 Hz, 1H), 0.94 – 0.89 (m, 6H), 0.79 (d,  $J$  = 2.5 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 142.8, 128.9, 128.5, 128.3, 128.1, 127.4, 127.3, 126.99, 126.93, 82.0, 81.6, 49.5, 47.8, 45.2, 36.1, 28.4, 27.1, 19.8, 18.9, 13.9.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{28}\text{ONa}$ : 343.2038; found: 343.2026.

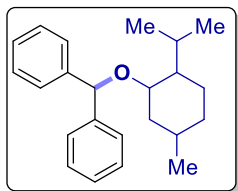
**2-(benzhydryloxy)-1,3,3-trimethylbicyclo[2.2.1]heptane (7f):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 84%, 81 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.37 (m, 4H), 7.34 – 7.31 (m, 4H), 7.23 (d,  $J$  = 1.4 Hz, 2H), 5.39 (s, 1H), 3.10 (d,  $J$  = 1.7 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.78 (dd,  $J$  = 12.2, 9.2 Hz, 1H), 1.65 – 1.61 (m, 1H), 1.48 – 1.38 (m, 2H), 1.08 – 1.03 (m, 2H), 1.00 (d,  $J$  = 3.4 Hz, 6H), 0.92 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.6, 143.0, 141.1, 128.9, 128.5, 128.1, 128.0, 127.7, 127.3, 126.97, 126.94, 126.1, 88.7, 82.8, 49.3, 48.9, 41.9, 41.4, 39.5, 31.2, 26.3, 21.4, 20.1.

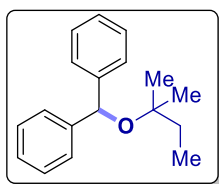
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{29}\text{O}$ : 321.2218; found: 321.2210.

**(((2-isopropyl-5-methylcyclohexyl)oxy)methylene)dibenzene (7g):<sup>4</sup>**



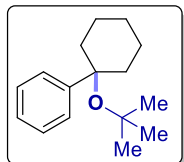
Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 82%, 76 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (dd,  $J = 11.1, 4.1$  Hz, 4H), 7.23 – 7.18 (m, 4H), 7.16 – 7.14 (m, 1H), 7.13 – 7.09 (m, 1H), 5.44 (s, 1H), 3.05 (td,  $J = 10.5, 4.2$  Hz, 1H), 2.28 (m,  $J = 14.0, 7.0, 2.4$  Hz, 1H), 2.07 (m,  $J = 12.1, 5.4, 3.8$  Hz, 1H), 1.53 – 1.49 (m, 2H), 1.25 (m,  $J = 7.3, 5.9, 3.3$  Hz, 1H), 1.20 – 1.13 (m, 1H), 0.85 – 0.82 (m, 1H), 0.79 (dd,  $J = 6.8, 4.8$  Hz, 6H), 0.77 – 0.73 (m, 2H), 0.34 (d,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 142.6, 128.3, 128.1, 127.9, 127.4, 126.9, 126.7, 79.9, 75.9, 48.8, 40.4, 34.6, 31.5, 25.1, 22.9, 22.4, 21.4, 15.7.

**((*tert*-pentyloxy)methylene)dibenzene (**7h**):<sup>5</sup>**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 89%, 68 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (d,  $J = 7.3$  Hz, 4H), 7.10 (dd,  $J = 10.4, 4.8$  Hz, 4H), 7.01 (t,  $J = 7.3$  Hz, 2H), 5.40 (s, 1H), 1.42 (q,  $J = 7.5$  Hz, 2H), 0.97 (s, 6H), 0.70 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 128.1, 126.8, 126.7, 77.3, 75.4, 34.6, 25.9, 8.7.

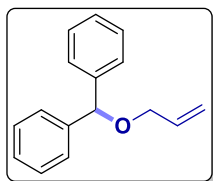
**(1-(*tert*-butoxy)cyclohexyl)benzene (**7i**):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 82%, 68 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.22 (m, 2H), 7.19 – 7.14 (m, 2H), 7.07 – 7.05 (m, 1H), 2.31 – 2.10 (m, 2H), 1.96 – 1.66 (m, 4H), 1.59 – 1.44 (m, 4H), 1.10 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 128.2, 127.1, 126.9, 126.2, 125.5, 73.8, 66.4, 35.5, 31.5, 28.5, 27.4, 22.0.

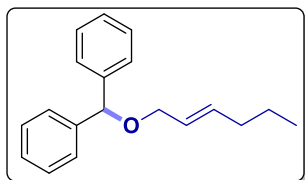
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{25}\text{O}$ : 233.1905; found: 233.1912.

**((allyloxy)methylene)dibenzene (7j):**<sup>6</sup>



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 73%, 49 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.25 (m, 4H), 7.24 – 7.20 (m, 4H), 7.15 (tt, *J* = 6.4, 1.4 Hz, 2H), 5.88 (ddt, *J* = 17.2, 10.8, 5.5 Hz, 1H), 5.33 (s, 1H), 5.22 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.10 (ddd, *J* = 10.4, 3.0, 1.4 Hz, 1H), 3.92 (dt, *J* = 5.5, 1.5 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  142.2, 134.8, 128.4, 127.5, 127.0, 116.9, 82.6, 69.7.

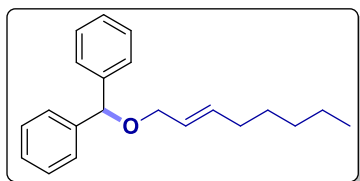
**(E)-((hex-2-en-1-yloxy)methylene)dibenzene (7k):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 89%, 71 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.19 – 7.17 (m, 4H), 7.14 (dd, *J* = 10.3, 4.9 Hz, 4H), 7.08 – 7.04 (m, 2H), 5.55 – 5.40 (m, 2H), 5.25 (s, 1H), 3.79 (dd, *J* = 5.8, 0.6 Hz, 2H), 1.87 (dd, *J* = 14.0, 6.8 Hz, 2H), 1.28 – 1.19 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  142.4, 134.6, 128.4, 127.4, 127.1, 126.5, 82.3, 69.6, 34.4, 22.3, 13.7.

HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>23</sub>O: 267.1749; found: 267.1752.

**(E)-((oct-2-en-1-yloxy)methylene)dibenzene (7l):**

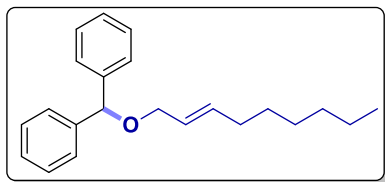


Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 87%, 76.7 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.42 (m, 4H), 7.38 (t, *J* = 7.5 Hz, 4H), 7.30 (dd, *J* = 11.0, 3.8 Hz, 2H), 5.78 – 5.66 (m, 2H), 5.50 (s, 1H), 4.04 (d, *J* = 5.9 Hz, 2H), 2.12 (q, *J* = 6.9 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.41

– 1.34 (m, 4H), 0.97 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.4, 134.9, 128.4, 127.4, 127.1, 126.3, 82.3, 69.6, 32.3, 31.5, 28.8, 22.6, 14.1.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{27}\text{O}$ : 295.2062; found: 295.2059.

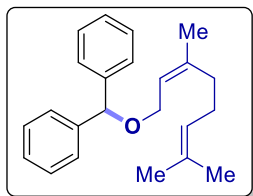
**(E)-((non-2-en-1-yloxy)methylene)dibenzene (7m):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 85%, 65 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J = 7.7$  Hz, 4H), 7.18 (t,  $J = 7.5$  Hz, 4H), 7.11 (t,  $J = 7.2$  Hz, 2H), 5.58 – 5.44 (m, 2H), 5.30 (s, 1H), 3.84 (d,  $J = 5.8$  Hz, 2H), 1.93 (q,  $J = 6.9$  Hz, 2H), 1.28 – 1.23 (m, 2H), 1.21 – 1.15 (m, 6H), 0.77 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.4, 134.9, 128.4, 127.4, 127.1, 126.2, 82.3, 69.6, 32.4, 31.8, 29.1, 28.9, 22.7, 14.1.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{29}\text{O}$ : 309.2218; found: 309.2211.

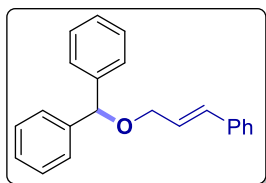
**(Z)-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)methylene)dibenzene (7n):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 93%, 89 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (d,  $J = 7.1$  Hz, 4H), 7.14 (t,  $J = 7.4$  Hz, 4H), 7.07 (dd,  $J = 8.9, 5.3$  Hz, 2H), 5.28 (d,  $J = 5.8$  Hz, 1H), 5.24 (s, 1H), 4.94 (s, 1H), 3.86 (d,  $J = 6.5$  Hz, 2H), 1.98 – 1.91 (m, 2H), 1.88 (d,  $J = 7.4$  Hz, 2H), 1.52 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.5, 140.3, 131.7, 128.4, 127.4, 127.2, 124.1, 121.0, 82.3, 65.4, 39.7, 26.4, 25.7, 17.7, 16.5.

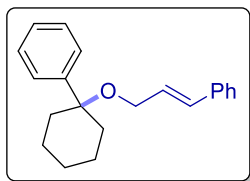
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{29}\text{O}$ : 321.2218; found: 321.2213.

**((cinnamyloxy)methylene)dibenzene (7o):<sup>7</sup>**



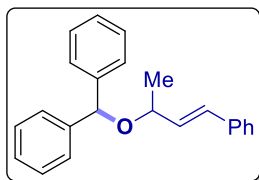
Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 83%, 75 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.28 (m, 6H), 7.23 (dd,  $J$  = 16.1, 8.0 Hz, 6H), 7.19 – 7.14 (m, 3H), 6.51 (d,  $J$  = 15.9 Hz, 1H), 6.26 (dt,  $J$  = 15.9, 5.9 Hz, 1H), 5.39 (s, 1H), 4.09 (d,  $J$  = 5.9 Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.2, 136.8, 132.4, 128.6, 128.5, 127.7, 127.5, 127.1, 126.5, 126.2, 82.7, 69.4.

**(1-(cinnamyloxy)cyclohexyl)benzene (7p):<sup>8</sup>**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 87%, 76 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.29 (m, 2H), 7.19 (dd,  $J$  = 14.1, 7.3 Hz, 4H), 7.14 – 7.08 (m, 3H), 7.04 (t,  $J$  = 7.3 Hz, 1H), 6.41 (dd,  $J$  = 16.0, 5.9 Hz, 1H), 6.10 (dt,  $J$  = 15.9, 5.7 Hz, 1H), 3.58 (dd,  $J$  = 5.7, 1.4 Hz, 2H), 1.92 (d,  $J$  = 12.8 Hz, 2H), 1.64 (ddd,  $J$  = 12.5, 7.9, 3.3 Hz, 2H), 1.60 – 1.54 (m, 3H), 1.45 – 1.40 (m, 2H), 1.16 – 1.08 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.3, 137.2, 130.8, 128.5, 128.3, 127.3, 126.9, 126.4, 126.1, 77.6, 62.7, 35.9, 25.7, 22.1.

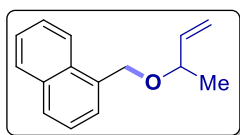
**(E)-(((4-phenylbut-3-en-2-yl)oxy)methylene)dibenzene (7q):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 96%, 90 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 – 7.18 (m, 5H), 7.17 – 7.13 (m, 5H), 7.12 – 7.08 (m, 3H), 7.08 – 7.05 (m, 1H), 7.04 – 7.00 (m, 1H), 6.29 (d,  $J$  = 16.0 Hz, 1H), 6.01 (dd,  $J$  = 15.9, 7.8 Hz, 1H), 5.37 (s, 1H), 3.91 (p,  $J$  = 6.6 Hz, 1H), 1.22 (d,  $J$  = 6.4 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 142.3, 136.7, 131.7, 131.6, 128.6, 128.5, 128.3, 127.7, 127.5, 127.4, 127.2, 127.0, 126.6, 115.0, 80.1, 73.9, 21.9.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{23}\text{O}$ : 315.1749; found: 315.1744.

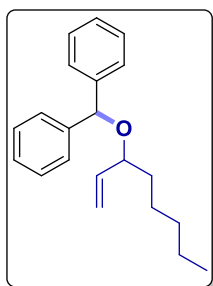
**((but-3-en-2-yloxy)methylene)dibenzene (7r):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 85%, 61 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J$  = 8.3 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.45 – 7.38 (m, 3H), 7.35 – 7.32 (dd,  $J$  = 8.1, 7.1 Hz, 1H), 5.82 – 5.75 (ddd,  $J$  = 17.6, 10.3, 7.5 Hz, 1H), 5.20 – 5.13 (m, 2H), 4.95 (d,  $J$  = 11.9 Hz, 1H), 4.72 (d,  $J$  = 11.9 Hz, 1H), 3.93 (dq,  $J$  = 12.9, 6.4 Hz, 1H), 1.22 (d,  $J$  = 6.4 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 134.2, 133.8, 128.5, 128.4, 126.3, 126.1, 125.7, 125.3, 124.1, 116.4, 115.0, 76.5, 68.5, 21.5.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{19}\text{O}$ : 239.1436; found: 239.1406.

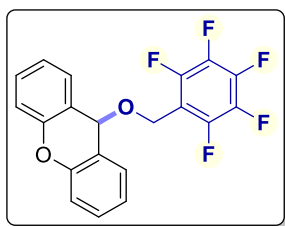
**((oct-1-en-3-yloxy)methylene)dibenzene (7s):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 84%, 74 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 – 7.14 (m, 6H), 7.10 (t,  $J$  = 7.5 Hz, 3H), 7.02 (t,  $J$  = 6.8 Hz, 1H), 5.57 (ddd,  $J$  = 10.1, 9.1, 4.5 Hz, 1H), 5.32 (s, 1H), 5.07 – 4.91 (m, 2H), 3.54 (dd,  $J$  = 13.8, 6.8 Hz, 1H), 1.62 – 1.45 (m, 1H), 1.37 – 1.31 (m, 1H), 1.28 – 1.18 (m, 1H), 1.15 – 1.08 (m, 3H), 1.07 – 0.99 (m, 2H), 0.72 – 0.68 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.3, 142.3, 139.3, 128.4, 128.2, 127.6, 127.5, 127.0, 126.8, 117.2, 79.7, 78.3, 35.6, 31.8, 24.9, 22.6, 14.0.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{27}\text{O}$ : 295.2062; found: 295.2059.

**9-((perfluorophenyl)methoxy)-9H-xanthene (7t):**

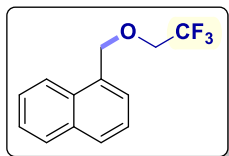


Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 5% ethyl acetate in hexane (Yield: 78%, 88 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (dd,  $J$  = 7.7, 1.7 Hz, 1H), 7.41 (dd,  $J$  = 8.1, 1.7 Hz, 1H), 7.36 (ddd,  $J$  = 8.5, 7.1, 1.7 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.17 – 7.13 (m, 2H), 7.04 (d,  $J$  = 1.3 Hz, 2H), 5.85 (s, 1H), 3.93 (s,

2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 152.3, 132.5, 131.3, 130.1, 130.0, 129.6, 127.4, 124.0, 123.5, 118.6, 117.2, 116.8, 116.7, 115.7, 115.5, 115.0, 96.9, 70.4, 53.7.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -144.3 (q,  $J$  = 9.4 Hz), -153.9 (t,  $J$  = 23.5 Hz), -161.7 (sextet,  $J$  = 9.4 Hz).

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{11}\text{F}_5\text{O}_2$ : 379.0757; found: 379.0750.

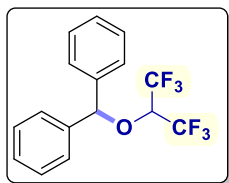
**1-((2,2,2-trifluoroethoxy)methyl)naphthalene (7u):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 77%, 55 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 – 7.67 (m, 3H), 7.43 – 7.35 (m, 2H), 7.35 – 7.26 (m, 2H), 4.97 (s, 2H), 3.68 (dt,  $J$  = 8.7, 5.6 Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  133.8, 131.8, 131.7, 130.5, 129.5, 128.6, 127.2, 126.6, 126.1, 125.1, 123.8, 72.7, 66.8 (q,  $J$  = 33.65 Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -73.6, -73.9.

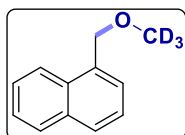
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{12}\text{F}_3\text{O}$ : 241.0840; found: 241.0852.

**(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methylene)dibenzene (7v):<sup>9</sup>**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 65%, 65 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.42 (m, 8H), 7.40 – 7.37 (m, 2H), 7.34 – 7.24 (m, 1H), 5.88 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.9, 128.8, 128.7, 127.7, 126.2–118.4 (m), 85.7, 72.5 (p,  $J$  = 31.3 Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.6 (d,  $J$  = 9.4 Hz).

**1-((methoxy-d3)methyl)naphthalene (7w):**

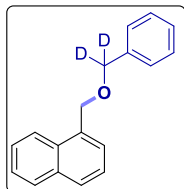


Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 88%, 46 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.11 (m, 1H), 7.88 (dd,  $J$  = 8.6, 1.3 Hz, 1H), 7.83 (d,  $J$  = 8.5 Hz, 1H), 7.57 –

7.43 (m, 4H), 4.92 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9, 133.7, 131.8, 128.8, 128.7, 126.6, 126.3, 125.9, 125.3, 124.1, 73.2.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{12}\text{H}_9\text{D}_3\text{NaO}$ : 198.0974; found: 198.0950.

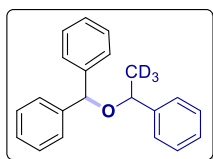
**1-((phenylmethoxy-d2)methyl)naphthalene (7x):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 84%, 63 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.93 (m, 1H), 7.89 – 7.82 (m, 3H), 7.72 – 7.67 (m, 1H), 7.52 – 7.41 (m, 6H), 7.29 (s, 1H), 5.57 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  129.4, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 127.6, 126.6, 126.4, 125.9, 125.8, 125.6, 125.3, 123.9, 123.7, 77.3, 65.3.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{14}\text{D}_2\text{NaO}$ : 273.1224; found: 273.1219.

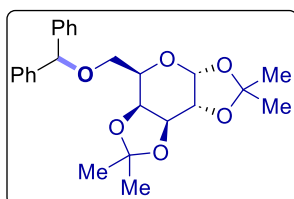
**((1-phenylethoxy-2,2-d3)methylene)dibenzene (7y):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 70%, 61 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd,  $J$  = 5.1, 2.3 Hz, 5H), 7.34 – 7.33 (m, 2H), 7.32 – 7.29 (m, 3H), 7.27 – 7.25 (m, 5H), 5.26 (s, 1H), 4.45 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 142.9, 142.1, 128.6, 128.5, 128.3, 127.7, 127.6, 127.2, 127.0, 126.6, 80.1, 74.9, 14.2.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{18}\text{D}_3\text{O}$ : 292.1781; found: 292.1772.

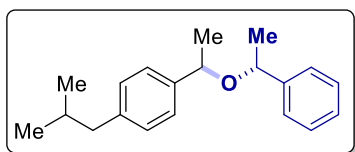
**5-((benzhydryloxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (7z):**



Following the general procedure **D**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 7% ethyl acetate in hexane (Yield: 59%, 75 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J$  = 0.7 Hz, 4H), 7.33 (s, 3H), 7.32 (s, 1H), 7.28 (d,  $J$  = 1.5 Hz, 1H), 7.26 (s, 1H), 5.52 (d,  $J$  = 5.0 Hz, 1H), 5.47 (s, 1H), 4.60 (dd,  $J$  = 7.9, 2.4 Hz, 1H), 4.34 – 4.31 (m, 1H), 4.30 – 4.29 (m, 1H), 4.13 – 4.06 (m, 1H), 3.65 (dd,  $J$  = 16.4, 6.4 Hz, 2H), 1.55 (s, 3H), 1.41 (s, 3H), 1.33 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 142.2, 128.6, 127.7, 126.6, 109.3, 108.7, 96.4, 83.9, 76.3, 71.2, 70.8, 67.7, 67.1, 26.2, 26.1, 25.1, 24.5.

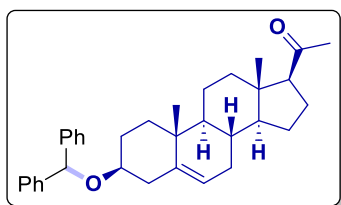
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{30}\text{O}_6$ : 426.2042; found: 426.2034.

**1-isobutyl-4-[1-(1-phenylethoxy)ethyl]benzene (7za):**<sup>10</sup>



Following the general procedure **E**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 5% ethyl acetate in hexane (Yield: 95%, 76 mg). **Diastereomer 1: Diastereomer 2: 50:50.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , for both diastereomers) (the integration at 1.92 ppm, 1.88 ppm indicated the ratio of the two isomers of **7za** to be 50:50)  $\delta$  7.39 (dd,  $J$  = 9.5, 5.3 Hz, 2H), 7.36 – 7.28 (m, 7H), 7.24 (ddd,  $J$  = 10.9, 8.3, 3.6 Hz, 5H), 7.17 (d,  $J$  = 8.0 Hz, 2H), 7.10 (d,  $J$  = 8.0 Hz, 2H), 4.56 (dq,  $J$  = 12.7, 6.4 Hz, 2H), 4.28 (dq,  $J$  = 16.2, 6.5 Hz, 2H), 2.53 (d,  $J$  = 7.2 Hz, 2H), 2.48 (d,  $J$  = 7.2 Hz, 2H), 1.93 (dd,  $J$  = 13.6, 6.8 Hz, 1H), 1.90 – 1.84 (m, 1H), 1.50 (d,  $J$  = 6.4 Hz, 6H), 1.42 (dd,  $J$  = 6.5, 1.1 Hz, 6H), 0.97 (d,  $J$  = 6.6 Hz, 6H), 0.94 (d,  $J$  = 6.6 Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , for both diastereomers)  $\delta$  144.8, 144.7, 141.8, 141.7, 141.2, 140.9, 129.6, 129.4, 128.8, 128.6, 127.7, 127.5, 126.8, 126.7, 126.5, 126.4, 74.9, 74.8, 45.6, 45.5, 30.7, 30.6, 25.2, 25.1, 23.5, 23.3, 22.9, 22.88, 22.83.

**1-(3-(benzhydryloxy)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one (7zb):**

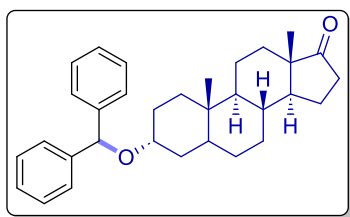


Following the general procedure **E**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 82%, 118 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.22 (m, 6H), 7.22 – 7.18 (dd,  $J$  = 9.8, 4.5 Hz, 2H), 7.15 (dt,  $J$  = 4.1, 1.8 Hz,

2H), 5.47 (s, 1H), 5.21 – 5.20 (m, 1H), 3.23 – 3.17 (m, 1H), 2.42 (t,  $J = 8.9$  Hz, 1H), 2.35 – 2.24 (m, 2H), 2.02 (s, 3H), 1.95 – 1.85 (m, 3H), 1.74 (dt,  $J = 13.3, 3.4$  Hz, 1H), 1.58 – 1.50 (m, 3H), 1.45 – 1.32 (m, 5H), 1.16 (s, 2H), 1.05 – 0.99 (m, 1H), 0.92 (s, 3H), 0.86 – 0.78 (m, 2H), 0.53 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  209.5, 142.9, 141.0, 139.9, 138.4, 128.8, 128.5, 128.4, 128.35, 128.34, 127.9, 127.3, 127.2, 127.1, 121.2, 115.0, 80.4, 77.6, 63.7, 57.3, 56.9, 50.0, 44.0, 39.3, 38.9, 37.2, 36.9, 31.9, 31.8, 31.5, 28.6, 24.5, 22.8, 21.0, 19.4, 13.2.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{34}\text{H}_{43}\text{O}_2$ : 483.3263; found: 483.3259.

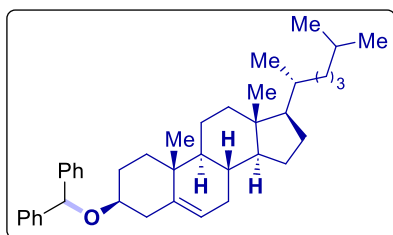
**3-(benzhydryloxy)-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (7zc):**



Following the general procedure **E**, the title product was obtained as a white solid using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 76%, 103 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.32 (m, 6H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 5.56 (s, 1H), 3.32 (ddd,  $J = 16.5, 10.8, 4.9$  Hz, 1H), 2.44 – 2.38 (m, 1H), 2.08 – 2.00 (m, 1H), 1.94 – 1.87 (m, 2H), 1.77 – 1.74 (m, 2H), 1.72 – 1.67 (m, 1H), 1.63 – 1.60 (m, 1H), 1.56 – 1.40 (m, 4H), 1.32 – 1.17 (m, 5H), 1.04 – 0.85 (m, 3H), 0.84 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  221.6, 143.0, 143.0, 128.6, 128.4, 127.7, 127.4, 127.2, 127.2, 126.6, 80.3, 76.2, 54.5, 51.5, 47.9, 44.9, 37.1, 36.0, 35.1, 31.6, 30.9, 28.6, 21.9, 20.6, 13.9, 12.4.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{32}\text{H}_{41}\text{O}_2$ : 457.3107; found: 457.3102.

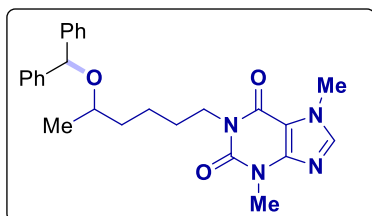
**3-(benzhydryloxy)-10,13-dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (7zd):<sup>11</sup>**



Following the general procedure **E**, the title product was obtained as a white solid using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 75%, 110 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J = 8.1$  Hz, 4H), 7.18 (t,  $J = 7.5$  Hz, 4H), 7.10 (t,  $J = 7.1$  Hz, 2H), 5.44 (s, 1H), 5.17 (d,  $J = 5.0$  Hz, 1H), 3.23 – 3.08 (m, 1H), 2.31 – 2.21 (m, 2H), 1.84 (dd,  $J = 23.3, 12.4$  Hz, 3H),

1.76 – 1.63 (m, 3H), 1.44 (s, 3H), 1.39 – 1.31 (m, 5H), 1.22 (dd,  $J = 20.1, 16.2$  Hz, 6H), 1.04 – 0.96 (m, 6H), 0.88 (s, 3H), 0.78 (d,  $J = 6.5$  Hz, 3H), 0.74 (dd,  $J = 6.6, 2.2$  Hz, 6H), 0.54 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 141.1, 128.4, 127.4, 127.2, 121.6, 80.4, 75.7, 56.9, 56.2, 50.2, 42.4, 39.6, 36.3, 35.9, 31.9, 29.8, 28.7, 28.3, 28.1, 24.4, 23.9, 22.9, 22.7, 21.1, 19.5, 18.8, 11.9.

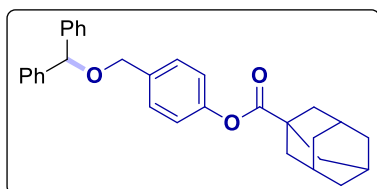
**1-(5-(benzhydryloxy)hexyl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione (7ze):**



Following the general procedure **E**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 15% ethyl acetate in hexane (Yield: 69%, 92 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (t,  $J = 3.1$  Hz, 1H), 7.37 – 7.27 (m, 4H), 7.27 – 7.20 (m, 4H), 7.18 – 7.11 (m, 2H), 5.43 (s, 1H), 3.98 – 3.92 (m, 2H), 3.91 (s, 3H), 3.52 (s, 3H), 3.49 – 3.43 (m, 1H), 1.83 – 1.53 (m, 3H), 1.50 – 1.20 (m, 3H), 1.12 (d,  $J = 6.2$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 151.5, 148.8, 143.4, 142.8, 141.4, 128.4, 128.3, 127.39, 127.36, 127.0, 80.5, 80.4, 72.6, 67.9, 41.4, 36.5, 33.7, 29.8, 28.2, 23.1, 19.7.

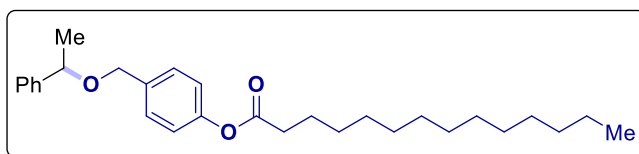
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{26}\text{H}_{31}\text{N}_4\text{O}_3$ : 447.2396; found: 447.2388.

**4-((benzhydryloxy)methyl)phenyl adamantane-1-carboxylate (7zf):**



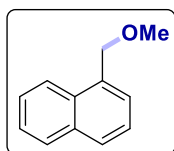
Following the general procedure **E**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 69%, 84 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.36 (m, 5H), 7.33 (t,  $J = 7.7$  Hz, 2H), 7.28 – 7.18 (m, 5H), 7.03 (dd,  $J = 8.8, 0.7$  Hz, 2H), 5.44 (s, 1H), 4.53 (s, 2H), 2.14 – 2.07 (m, 3H), 2.06 (d,  $J = 3.3$  Hz, 6H), 1.77 (d,  $J = 3.0$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  176.4, 171.5, 150.6, 142.1, 139.9, 138.5, 135.8, 135.7, 128.9, 128.8, 128.7, 128.54, 128.51, 127.9, 127.6, 127.4, 127.2, 127.1, 121.6, 82.5, 69.9, 41.1, 38.8, 36.59, 36.55, 28.0, 27.9.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{31}\text{H}_{32}\text{NaO}_3$ : 475.2249; found: 475.2220.

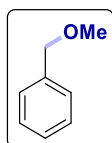
**4-((benzhydryloxy)methyl)phenyl tetradecanoate (7zg):**

Following the general procedure **E**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 67%, 100 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 7.17 (m, 5H), 7.17 – 7.11 (m, 2H), 6.92 – 6.84 (m, 2H), 4.37 – 4.30 (m, 1H), 4.28 – 4.11 (m, 2H), 2.42 – 2.35 (m, 2H), 1.63 – 1.53 (m, 2H), 1.32 (d,  $J$  = 6.5 Hz, 3H), 1.16 – 1.05 (m, 20H), 0.72 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 150.1, 143.7, 136.2, 128.8, 128.6, 127.6, 126.4, 121.6, 77.3, 69.7, 34.5, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.0, 24.3, 22.8, 14.2.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{34}\text{H}_{45}\text{O}_3$ : 501.3369; found: 501.3358.

**1-(methoxymethyl)naphthalene (8a):<sup>12</sup>**

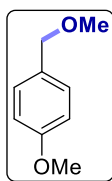
Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 96%, 50 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J$  = 8.3 Hz, 1H), 7.66 (dd,  $J$  = 25.5, 7.9 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.28 – 7.23 (m, 1H), 4.73 (s, 2H), 3.28 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  133.8, 133.7, 131.8, 128.7, 128.6, 126.5, 126.3, 125.8, 125.2, 124.0, 73.2, 58.2.

**(methoxymethyl)benzene (8b):**

Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 5% ethyl acetate in hexane (Yield: 85%, 32 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.26 (m, 5H), 4.46 (s, 2H), 3.39 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.3, 128.5, 127.8, 127.7, 74.8, 58.2.

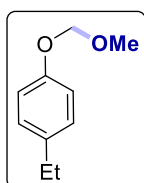
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_8\text{H}_{11}\text{O}$ : 123.0810; found: 123.0819.

**1-methoxy-4-(methoxymethyl)benzene (8c):**<sup>13</sup>



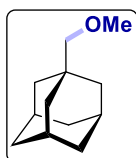
Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 5% ethyl acetate in hexane (Yield: 92%, 42 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 (dd,  $J$  = 5.0, 4.4 Hz, 2H), 6.88 (d,  $J$  = 8.9 Hz, 2H), 4.38 (s, 2H), 3.80 (s, 3H), 3.35 (s, 3H).

**1-ethyl-4-(methoxymethoxy)benzene (8d):**<sup>14</sup>



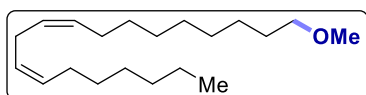
Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 92%, 46 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.96 – 6.95 (m, 2H), 6.81 – 6.79 (m, 2H), 4.99 (s, 2H), 3.32 (s, 3H), 2.46 – 2.41 (m, 2H), 1.05 (t,  $J$  = 7.6 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  155.3, 137.8, 128.8, 116.2, 94.7, 55.9, 28.0, 15.8.

**1-(methoxymethyl)adamantane (8e):**



Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 88%, 47 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.18 (s, 2H), 3.14 (s, 3H), 1.85 – 1.75 (m, 1H), 1.67 – 1.60 (m, 1H), 1.57 (d,  $J$  = 7.1 Hz, 2H), 1.41 (d,  $J$  = 12.1 Hz, 1H), 1.36 (dd,  $J$  = 14.5, 7.3 Hz, 4H), 0.93 (t,  $J$  = 7.3 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  76.9, 58.8, 48.4, 43.2, 37.7, 36.1, 35.9, 31.2, 29.8, 27.6, 23.9, 19.8, 13.7. HRMS (ESI-TOF):  $m/z$  [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>21</sub>O: 181.1592; found: 181.1586.

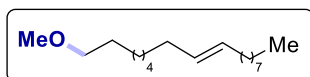
**(6Z,9Z)-17-methoxyheptadeca-6,9-diene (8f):**



Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 65%, 52 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.41 – 5.35 (m, 4H), 3.34 (s, 3H), 3.33 – 3.07 (m, 2H), 2.80 (t,  $J$  = 6.6 Hz, 2H), 2.08 (dd,  $J$  = 6.8, 3.4 Hz, 4H), 1.60 – 1.45 (m, 3H), 1.40 – 1.30 (m, 15H), 1.14 (d,  $J$  = 6.1 Hz, 2H), 0.91 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  130.3, 130.1, 128.1, 127.9, 82.1, 55.9, 36.4, 32.9, 31.6, 29.7, 29.5, 29.4, 27.3, 25.7, 25.4, 22.6, 19.1, 14.1.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{38}\text{O}$ : 295.3001 ; found: 295.3022.

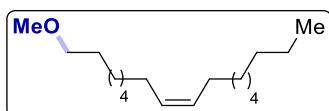
**(E)-1-methoxyheptadec-8-ene (8g):**



Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 72%, 57 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.39 – 5.37 (m, 2H), 3.31 (s, 3H), 3.30 – 3.22 (m, 2H), 1.96 (s, 4H), 1.38 – 1.27 (m, 22H), 0.88 (d,  $J$  = 2.0 Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  130.5, 130.2, 82.1, 55.9, 36.3, 32.6, 31.9, 29.7, 29.5, 29.3, 29.2, 25.8, 25.3, 24.8, 22.7, 19.0, 14.1.

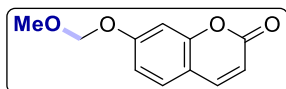
HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{37}\text{O}$ : 269.2844 ; found: 269.2840.

**(Z)-1-methoxyheptadec-8-ene (8h):**



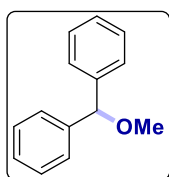
Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 55%, 44 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.35 – 5.33 (m, 2H), 3.35 (t,  $J$  = 6.7 Hz, 1H), 3.31 (s, 3H), 2.01 (ddd,  $J$  = 17.7, 10.3, 5.9 Hz, 4H), 1.47 (dddd,  $J$  = 12.4, 11.2, 5.7, 1.7 Hz, 4H), 1.35 – 1.09 (m, 19H), 0.87 (dd,  $J$  = 7.3, 4.3 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  130.1, 129.7, 82.1, 56.5, 32.9, 31.9, 30.1, 29.9, 29.6, 29.41, 29.40, 29.3, 27.3, 25.9, 25.1, 22.8, 14.2, 9.4.

HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{37}\text{O}$ : 269.2844; found: 269.2871.

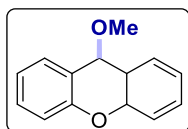
**7-(methoxymethoxy)-2H-chromen-2-one (8i):**<sup>15</sup>

Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 79%, 49 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (dd,  $J$  = 9.6, 0.9 Hz, 1H), 7.37 (d,  $J$  = 8.6 Hz, 1H), 6.97 (ddd,  $J$  = 11.0, 5.5, 1.6 Hz, 2H), 6.26 (t,  $J$  = 5.4 Hz, 1H), 5.22 (s, 2H), 3.48 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  160.0, 159.2, 154.5, 142.2, 127.7, 112.7, 112.4, 102.8, 93.3, 55.3.

HRMS (ESI-TOF):  $m/z$  [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>11</sub>O<sub>4</sub>: 207.0657 ; found: 207.0651.

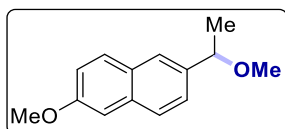
**(methoxymethylene)dibenzene (8j):**<sup>16</sup>

Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 90%, 53 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.38 (m, 8H), 7.33 – 7.29 (m, 2H), 5.32 (s, 1H), 3.46 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  142.2, 128.5, 127.5, 126.9, 85.5, 57.1.

**9-methoxy-9H-xanthene (8k):**

Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 94%, 60 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.35 (m, 2H), 7.23 – 7.19 (m, 2H), 7.04 – 6.99 (m, 4H), 5.57 (s, 1H), 2.80 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  152.6, 130.1, 129.7, 123.3, 119.7, 116.7, 70.9, 51.6.

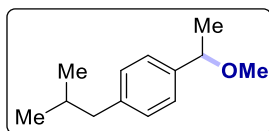
HRMS (ESI-TOF):  $m/z$  [M+Na]<sup>+</sup> calcd for C<sub>14</sub>H<sub>14</sub>NaO<sub>2</sub>: 237.0891 ; found: 237.0886.

**2-methoxy-6-(1-methoxyethyl)naphthalene (8l):**<sup>17</sup>

Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 7% ethyl acetate in hexane (Yield: 95%, 62 mg). <sup>1</sup>H NMR (500

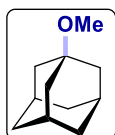
MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.55 (m, 2H), 7.50 (d,  $J$  = 1.8 Hz, 1H), 7.27 (dd,  $J$  = 8.4, 1.8 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.98 (s, 1H), 4.27 (q,  $J$  = 6.5 Hz, 1H), 3.76 (s, 3H), 3.08 (s, 3H), 1.35 – 1.34 (d,  $J$  = 6.5 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  157.6, 138.6, 134.2, 129.3, 128.7, 127.2, 125.1, 124.7, 118.9, 105.8, 79.7, 56.4, 55.3, 23.8.

**1-isobutyl-4-(1-methoxyethyl)benzene (8m):**<sup>17</sup>



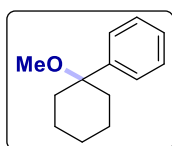
Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 92%, 53 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 (d,  $J$  = 8.0 Hz, 2H), 7.16 (d,  $J$  = 8.0 Hz, 2H), 4.30 (q,  $J$  = 6.5 Hz, 1H), 3.25 (s, 3H), 2.50 (d,  $J$  = 7.2 Hz, 2H), 1.89 (dt,  $J$  = 13.5, 6.8 Hz, 1H), 1.47 (d,  $J$  = 6.5 Hz, 3H), 0.94 (d,  $J$  = 6.6 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  140.9, 140.7, 129.2, 126.0, 79.5, 56.4, 45.2, 30.3, 23.8, 22.4.

**(3s,5s,7s)-1-methoxyadamantane (8n):**<sup>18</sup>



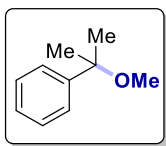
Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 93%, 46 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.26 (s, 3H), 2.19 – 2.16 (m, 3H), 1.76 (d,  $J$  = 2.9 Hz, 6H), 1.68 – 1.61 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  71.9, 47.8, 40.9, 36.5, 30.5.

**(1-methoxycyclohexyl)benzene (8o):**<sup>19</sup>



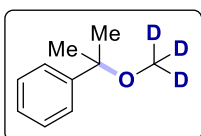
Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 89%, 51 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 (dt,  $J$  = 8.2, 1.6 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.10 – 7.07 (m, 1H), 2.80 (s, 3H), 1.87 – 1.84 (m, 2H), 1.59 – 1.49 (m, 5H), 1.44 – 1.40 (m, 2H), 1.13 – 1.08 (ddd,  $J$  = 11.4, 6.1, 2.2 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  146.0, 128.2, 126.8, 126.1, 77.4, 49.6, 35.4, 25.7, 21.9.

**(2-methoxypropan-2-yl)benzene (8p):**<sup>17</sup>



Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 94%, 42 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.21 (m, 3H), 7.01 – 6.93 (m, 2H), 3.83 (s, 3H), 1.63 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 143.9, 129.7, 128.6, 127.1, 125.9, 114.0, 55.2, 26.3.

**(2-(methoxy-d3)propan-2-yl)benzene (8q):**<sup>20</sup>



Following the general procedure **F**, the title product was obtained as a colourless oil using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 59%, 27 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.29 (m, 3H), 7.29 – 7.22 (m, 2H), 1.44 (s, 6H).

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## 7. $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ NMR Spectra of compounds

