Supporting Information for:

Benzocyclobutenone Synthesis Exploiting Acylsilanes as Photofunctional Directing Groups

Rowan L. Pilkington,^[a] Hannah J. Ross,^[a] Liselle Atkin,^[a] and Daniel L. Priebbenow^{*[a]}

[a] Medicinal Chemistry Theme, Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, 3052, Victoria (Australia)

E-mail: daniel.priebbenow@monash.edu

Table of Contents:

GENERAL EXPERIMENTAL	2
COMPUTATIONAL DETAILS	2
RUTHENIUM CATALYZED OLEFINATION OF AROYLSILANES	
MECHANISTIC INVESTIGATIONS	4
C-H Olefination Rate Experiments	4
Ruthenium catalyzed H/D exchange	5
Alternative directing groups	
PHOTOCHEMISTRY	
UV-VIS ANALYSIS	
UNSUCCESSFUL SUBSTRATES	
SUBSTRATE SYNTHESIS AND CHARACTERISATION DATA	
Preparation of acylsilanes	
Preparation of vinylketones	
Preparation of Olefinated Acylsilanes by C-H Functionalisation	
Photochemical synthesis of Cyclobutenone-1,4-diones	
Derivatisation Reactions	
COMPUTATIONAL ANALYSIS	
CARTESIAN COORDINATES OF THE COMPUTED STRUCTURES	
NMR SPECTRA	
REFERENCES	

GENERAL EXPERIMENTAL

Analytical Thin Layer Chromatography (TLC) was carried out using aluminium-backed Merck Kieselgel KG60 F254 silica plates. The plates were visualized by irradiation with short-wave ultraviolet light. Flash chromatography was performed on SiliaFlashR P60 R12030B 40-63 micron silica gel. High-resolution mass spectrometry (HRMS) was performed with an Agilent 6546 LC-QToF coupled to an Agilent 1290 Infinity LC. All data were acquired, and reference mass corrected via dual-spray electrospray ionization (ESI) source.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Ascend (400 MHz) instrument. Chemical shifts are expressed in parts per million (PPM) and are referenced to the internal solvent peaks. Solvents used for NMR studies were purchased from Cambridge Isotope Laboratories. Each proton resonance was assigned according to the following convention: chemical shift (δ), multiplicity, coupling constant (*J* Hz) number of protons. Each carbon resonance was assigned according to the following convention: chemical shift (δ), multiplicity and coupling constants (*J* Hz). Multiplicity is quoted as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

Unless otherwise stated, catalysts, reagents including methyl vinyl ketone and ethyl vinyl ketone and solvents were purchased from commercial sources and used without further purification.

COMPUTATIONAL DETAILS

All density functional theory (DFT) calculations were conducted using the Gaussian 16 quantum chemical package. Structures were visualised in GaussView 6.0. The geometry optimisations were performed with the hybrid density functional method based on M06- $2x^{[1]}$ with a standard 6-311+G(d,p) basis set. The 6-311++G(d,p) basis set was used to calculate single-point energies. Vibrational frequency calculations were carried out at the same theory level as geometry optimisation calculations. All stationary points were optimised without any symmetry assumptions and characterized by normal coordinate analysis at the same level of theory [number of imaginary frequencies (NIMAG) 0 for minima and 1 for TS]. The reported free energy values (in kcal/mol) were obtained as the sum of the single point electronic energy and the ZPVE correction obtained from the harmonic frequency calculation.

RUTHENIUM CATALYZED OLEFINATION OF AROYLSILANES

	^t Bu 4a 0.15 mi	SiMe ₃ <i>methyl vinyl ketone</i> Me 0.30 mmol	Ru(p-Cym)C AgX (5 Cu(OAc So temp.	l₂]₂ (2.5-5 mol%) -20 mol%))₂ (2 equiv.) ► olvent t _E , time, air	Bu 5a O				
Entry	AgX (mol%)	Solvent	Time	Temperature	Conversion ^[a]	Yield ^[a]			
1	AgBF ₄ (10)	1,2-DCE	4 h	60 °C	51 %	36 %			
2	AgSbF ₆ (10)	1,2-DCE	4 h	60 °C	68 %	48 %			
3	AgNTf ₂ (10)	1,2-DCE	4 h	60 °C	60 %	44 %			
4	AgOTf ₂ (10)	1,2-DCE	4 h	60 °C	30 %	25 %			
5	AgPF ₆ (10)	1,2-DCE	4 h	60 °C	42 %	31 %			
6	AgOAc (10)	1,2-DCE	4 h	60 °C	0 %	0 %			
7	AgOBz (10)	1,2-DCE	4 h	60 °C	0 %	0 %			
8	AgSbF ₆ (10)	PhMe, MeCN, THF, DMF, DMSO, or MeOH	4 h	60 °C	0 %	0 %			
9	AgSbF ₆ (10)	DCM	4 h	reflux	40 %	37 %			
10	AgSbF ₆ (10)	HFIP	4 h	60 °C	74 %	25 %			
11	AgSbF ₆ (10)	TFE	4 h	60 °C	74 %	57 %			
12	AgSbF ₆ (10)	DCE/HFIP (9:1 v/v)	4 h	60 °C	66 %	55 %			
13	AgSbF ₆ (10)	DCE/TFE (9:1 v/v)	4 h	60 °C	90 %	70 %			
14	AgSbF ₆ (10)	DCE/HFIP (1:1 v/v)	4 h	60 °C	70 %	51 %			
15	AgSbF ₆ (10)	DCE/TFE (1:1 v/v)	4 h	60 °C	94 %	73 %			
16	AgSbF ₆ (10)	DCE/TFE (9:1 v/v)	6 h	60 °C	84 %	75 %			
17	AgSbF ₆ (10)	DCE/TFE (9:1 v/v)	12 h	60 °C	90 %	66 %			
18 ^[b]	AgSbF ₆ (5)	DCE/TFE (9:1 v/v)	12 h	60 °C	44 %	32 %			
19 ^[b]	AgSbF ₆ (10)	DCE/TFE (9:1 v/v)	12 h	60 °C	67 %	47 %			
20	AgSbF ₆ (20)	DCE/TFE (9:1 v/v)	4 h	60 °C	83 %	70 %			
21	AgSbF ₆ (10)	DCE/TFE (9:1 v/v)	4 h	45 °C	58 %	54 %			
22	AgSbF ₆ (10)	DCE/TFE (9:1 v/v)	4 h	75 °C	80 %	70 %			
[a] Conversions and yields determined by ¹ H NMR analysis vs. internal standard. Conversion refers to amount of acylsilane									

Table S1. Optimisation of the Ru(II)-Catalysed Olefination

starting material converted to product. [b] 2.5 mol% [Ru]

MECHANISTIC INVESTIGATIONS

C-H Olefination Rate Experiments

To assess both the influence of electronics in the aryl ring of benzoylsilanes and the effect of trifluoroethanol on the C-H olefination process, rate experiments were conducted. Under identical reaction conditions, 4-methoxy, 4-(*tert*-butyl), and 4-fluoro substituted benzoylsilanes were subjected to olefination conditions in either 1,2-DCE or 1,2-DCE/TFE (9:1 v/v) solvent systems. Similar experiments were conducted to assess the influence of the silyl substituent on the rate of olefination. In this case, DCE/TFE (9:1 v/v) was used as the reaction solvent.

Experimental: To an oven dried reaction vial containing a stir bar, $AgSbF_6$ (5.2 mg, 0.0225 mmol, 15 mol%) was added followed by $[Ru(p-Cym)Cl_2]_2$ (4.6 mg, 0.0075 mmol, 5 mol%) and anhydrous $Cu(OAc)_2$ (32.5 mg, 0.3 mmol, 2.0 equivs.). Anhydrous DCE or DCE/TFE (9:1 v/v) (0.5 mL) was added and the mixture was stirred for five minutes at room temperature. Substituted benzoylsilanes **S1**, **4a** or **S2** (0.15 mmol, 1.0 equiv.) and methyl vinyl ketone (0.30 mmol, 2.0 equivs.) were then added in DCE or DCE/TFE (9:1 v/v) (1.0 mL). The mixture was heated to 60 °C. Aliquots of the reaction mixture were taken at various time points and filtered through silica before concentrating *in vacuo*. Relative conversions were measured by ¹H NMR analysis using an internal standard.



Figure S1: Influence of trifluoroethanol additive in the olefination of various benzoyl silanes



Figure S2: Influence of varying the silicon substituent in the olefination of benzoyl silanes

During our investigations into the C-H olefination of benzoylsilanes, the absence of multiple C-H activation events was noted (for example, bis-olefination at both the 2- and 6-positions). We hypothesized that after the first functionalization at the *ortho* site, the acylsilane is twisted out-of-plane due to steric interactions which disfavours cyclometallation at the second *ortho* C-H site.

Ruthenium catalyzed H/D exchange: benzoylsilane

To an oven dried reaction vial containing a stir bar, AgSbF₆ (5.2 mg, 0.0225 mmol, 15 mol%) was added followed by $[Ru(p-Cym)Cl_2]_2$ (4.6 mg, 0.0075 mmol, 5 mol%) and anhydrous $Cu(OAc)_2$ (32.5 mg, 0.3 mmol, 2.0 equivs.). Anhydrous DCE (stored over 4Å MS) (0.5 mL) was added and the mixture was stirred for five minutes at room temperature. (4-Methoxyphenyl)(trimethylsilyl)methanone **S1** (0.15 mmol, 1.0 equiv.) and D₃COD (0.75-75 mmol, 5-50 equivs.) were then added in DCE (1.0 mL). The mixture was heated to 60 °C for 4 hours. The cooled mixture was filtered through a pad of silica gel eluting with EtOAc, concentrated *in vacuo*, and the crude residue was analysed by ¹H NMR for deuterium incorporation.



Figure S3: Deuterium incorporation in S1 using 5 equivalents of D₃COD. Internal standard (3-sulfolene) is marked with an asterisk.



Figure S4: Deuterium incorporation in S1 using 50 equivalents of D₃COD. Internal standard (3-sulfolene) is marked with an asterisk.

Ruthenium catalyzed H/D exchange: olefinated benzoylsilane

To an oven dried reaction vial containing a stir bar, AgSbF₆ (5.2 mg, 0.0225 mmol, 15 mol%) was added followed by $[Ru(p-Cym)Cl_2]_2$ (4.6 mg, 0.0075 mmol, 5 mol%) and anhydrous $Cu(OAc)_2$ (32.5 mg, 0.3 mmol, 2.0 equivs.). Anhydrous DCE (stored on 4Å MS) (0.5 mL) was added and the mixture was stirred for five minutes at room temperature. (*E*)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (**5b**) (0.15 mmol, 1.0 equiv.) and D₃COD (0.75-75 mmol, 5-50 equivs.) were then added in DCE (1.0 mL). The mixture was heated to 60 °C for 4 hours. The cooled mixture was filtered through a pad of silica gel eluting with EtOAc, concentrated *in vacuo*, and the crude residue was analysed by ¹H NMR for D incorporation.





Figure S5: Deuterium incorporation in 5b using 5 equivalents of D₃COD. Internal standard (3-sulfolene) is marked with an asterisk.



Figure S6: Deuterium incorporation in 5b using 50 equivalents of D₃COD. Internal standard (3-sulfolene) is marked with an asterisk.

Absence of multiple ortho olefinations:



To an oven dried reaction vial containing a stir bar, AgSbF₆ (5.2 mg, 0.0225 mmol, 15 mol%) was added followed by $[Ru(p-Cym)Cl_2]_2$ (4.6 mg, 0.0075 mmol, 5 mol%) and anhydrous $Cu(OAc)_2$ (32.5 mg, 0.3 mmol, 2.0 equivs.). Anhydrous DCE/TFE (9:1 v/v) (0.5 mL) was added and the mixture was stirred for five minutes at room temperature. (*E*)-4-(5-Methoxy-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (**8b**) (0.15 mmol, 1.0 equiv.) and methyl vinyl ketone (25 μ L, 0.30 mmol, 2 equivs.) were then added in DCE/TFE (9:1 v/v) (1.0 mL). The mixture was heated to 60 °C for 4 hours. The cooled mixture was filtered through a pad of silica gel eluting with EtOAc, concentrated *in vacuo*, and the crude residue was analysed by ¹H NMR. *Formation of the bis-olefinated product was not detected*.

Alternative directing groups:

(E)-4-(2-acetyl-5-methoxyphenyl)but-3-en-2-one (10):



[NMR yields. no bis-olefination observed.]

To an oven dried reaction vial containing a stir bar, AgSbF₆ (5.2 mg, 0.0225 mmol, 15 mol%) was added followed by $[Ru(p-Cym)Cl_2]_2$ (4.6 mg, 0.0075 mmol, 5 mol%) and anhydrous $Cu(OAc)_2$ (32.5 mg, 0.3 mmol, 2 equivs.). Anhydrous DCE/TFE (9:1 v/v) (0.5 mL) was added and the mixture was stirred for five minutes at room temperature. Acetanisole (0.15 mmol, 1.0 equiv.) and methyl vinyl ketone (25 µL, 0.30 mmol, 2.0 equivs.) were then added in DCE/TFE (9:1 v/v) (1.0 mL). The mixture was heated to 60 °C for 4 hours. The cooled mixture was filtered through a pad of silica gel eluting with EtOAc, concentrated *in vacuo*, and the crude residue was analysed by ¹H NMR. Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded (*E*)-4-(2-acetyl-5-methoxyphenyl)but-3-en-2-one as a white solid (**10**) (20 mg, 0.092 mmol, 61%). ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 16.3 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.41 (d, *J* = 16.3 Hz, 1H), 3.87 (s, 3H), 2.58 (s, 3H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 199.3, 199.0, 162.6, 144.7, 138.6, 132.7, 130.4, 130.0, 114.6, 113.8, 55.7, 28.6, 26.7. HRMS (ESI) calcd. for $C_{13}H_{15}O_3$; [M+H]⁺: 219.1016; found 219.1016.



[NMR yields. no bis-olefination observed.]

(E)-4-methoxy-N,N-dimethyl-2-(3-oxobut-1-en-1-yl)benzamide (11)

To an oven dried reaction vial containing a stir bar, AgSbF₆ (5.2 mg, 0.0225 mmol, 15 mol%) was added followed by $[Ru(p-Cym)Cl_2]_2$ (4.6 mg, 0.0075 mmol, 5 mol%) and anhydrous $Cu(OAc)_2$ (32.5 mg, 0.3 mmol, 2.0 equivs.). Anhydrous DCE/TFE (9:1 v/v) (0.5 mL) was added and the mixture was stirred for five minutes at room temperature. 4-Methoxy-*N*,*N*-dimethylbenzamide (0.15 mmol, 1.0 equiv.) and methyl vinyl ketone (25 µL, 0.30 mmol, 2.0 equivs.) were then added in DCE/TFE (9:1 v/v) (1 mL). The mixture was heated to 60 °C for 4 hours. The cooled mixture was filtered through a pad of silica gel eluting with EtOAc, concentrated *in vacuo*, and the crude residue was analysed by ¹H NMR. Purification by flash column chromatography (70% EtOAc/petroleum benzine; R_f ~ 0.2) afforded (*E*)-4-methoxy-*N*,*N*-dimethyl-2-(3-oxobut-1-en-1-yl)benzamide as a white solid (**11**) (13 mg, 0.053 mmol, 35%). ¹H **NMR** (400 MHz, CDCl₃) δ 7.51 (d, *J* = 16.2 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.64 (d, *J* = 16.2 Hz, 1H), 3.84 (s, 3H), 3.14 (s, 3H), 2.81 (s, 3H), 2.34 (s, 3H). ¹³C **NMR** (101 MHz, CDCl₃) δ 198.3, 170.2, 160.2, 140.1, 129.5, 128.6, 116.4, 111.5, 55.5, 45.1, 27.5. **HRMS** (ESI) calcd. for C₁₄H₁₈NO₃; [M+H]⁺: 248.1281; found 248.1281.

PHOTOCHEMISTRY

$ \begin{array}{ c c c c c c } \hline & & & & & & & & & & & & & & & & & & $										
Entry	Light source ^[a]	Solvent ^[b]	Time	Additive	Conversion ^[c]	6b ^[c,d]	6b' ^[c]	5b ^[c]		
1	2 x 427 nm	Et ₂ O	12 h	None	100 %	53 %	0 %	< 5 %		
2	2 x 427 nm	DCM	12 h	None	100 %	6 %	0 %	17 %		
3	2 x 427 nm	MeCN	12 h	None	100 %	0 %	0 %	25 %		
4	2 x 427 nm	PhMe	12 h	None	100 %	64 %	0 %	< 5 %		
5	2 x 427 nm	Cyclohexane	12 h	None	100 %	42 %	0 %	< 5 %		
6	2 x 427 nm	MTBE	12 h	None	100 %	30 %	0 %	< 5 %		
7	2 x 427 nm	d ₈ -PhMe	12 h	None	100 %	78 %	0 %	< 5 %		
8	2 x 427 nm	d ₈ -PhMe	12 h	4-CzIPN (1 mol%)	100 %	36 %	0 %	< 5 %		
9	2 x 427 nm	d ₈ -PhMe	12 h	4Å MS	89 %	44 %	0 %	< 5 %		
10	2 x 427 nm	d ₈ -PhMe	12 h	Under air	100 % ^[e]	0 %	0 %	< 5 %		
11	1 x 463 nm	d ₈ -PhMe	12 h	None	62 %	33 %	0 %	< 5 %		
12	1 x 440 nm	d ₈ -PhMe	12 h	None	74 %	52 %	0 %	< 5 %		
13	1 x 427 nm	d ₈ -PhMe	12 h	None	100 %	78 %	0 %	< 5 %		
14	1 x 390 nm	d ₈ -PhMe	12 h	None	100 %	72 %	0 %	< 5 %		
15	1 x 427 nm	d ₈ -PhMe; then 1 M HCl	12 h + 1 h	None	100 %	74 % ^[f]	74 %	< 5 %		
16	1 x 427 nm	Et ₂ O; then 1 M HCl	12 h + 1 h	None	75 %	0 %	49 %	7 %		
17	1 x 427 nm	Cyclohexane; then 1 M HCl	12 h + 1 h	None	89 %	0 %	39 %	< 5 %		

Table S2. Optimisation of photochemical carboannulation

Reactions were performed on 0.10 mmol scale in 3.0 mL reaction vials. Reaction completion was indicated by the disappearance of the yellow colour of the starting acylsilane. 44% [a] Irradiation was provided by Kessil PR160 LED lamps (40 W). [b] All solvents were anhydrous and dried over 4Å molecular sieves prior to use. [c] Conversions and yields determined by ¹H NMR analysis vs. internal standard. Conversion refers to amount of starting material consumed. [d] Note that **6b** was observed to be relatively susceptible to hydrolysis. Complete conversion of the silyl enol ether **6b** to the 1,4-diketone **6b'** was observed after 12 hours in CDCl₃. [e] Complex mixture formed. [f] ¹H NMR yield prior to hydrolysis.



Figure S7: ¹H NMR spectrum (d₈-PhMe) of crude reaction residue after photolysis of **5b**. Internal standard (3-sulfolene) is marked with an asterisk.



Figure S8: ¹H NMR spectrum of crude reaction residue after hydrolysis of **6b'** with 1 M HCl (CDCl₃). Internal standard (3-sulfolene) is marked with an asterisk.

Photochemical carboannulation: 1.0 mmol scale reaction set-up



Figure S9: (1) Reaction apparatus depicting 2 x Kessil PR160 427 nm lamps positioned ~ 5 cm from reaction tube. Cooling fan (not pictured) is placed above the reaction vessel. (2) Reaction mixture prior to irradiation. (3) Reaction mixture post-irradiation.

UV-VIS ANALYSIS



Figure S10: Absorbance spectra of (4-methoxyphenyl)(triethylsilyl)methanone (**4c**), (*E*)-4-(5-methoxy-2-((triethylsilyl)carbonyl)phenyl)but-3-en-2-one (**5c**), and (*Z*)-3-methoxy-8-(2-((triethylsilyl)oxy)prop-1-en-1-yl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (**6c**). 0.01 M in MeCN.

UNSUCCESSFUL SUBSTRATES

The following acylsilanes failed to provide reasonable conversion to the corresponding olefinated products. Yields were determined by ¹H NMR analysis of the crude reaction mixture.



The following acylsilanes were readily synthesized using the C-H activation protocol, however subsequent photolysis of these substrates produced complex mixtures rather than clean benzocyclobutenone adducts (either due to decomposition or intractable diastereomeric product mixtures). Isolated yields and characterization data for the vinyl ketones an corresponding olefinated benzoyl silanes are provided throughout this supporting information document.



SUBSTRATE SYNTHESIS AND CHARACTERISATION DATA

Preparation of acylsilanes: The following acylsilanes are known compounds that were prepared according to literature procedures with the spectroscopic data obtained in agreement with that previously reported:

- (4-(*tert*-butyl)phenyl)(trimethylsilyl)methanone **4a**^[2]
- (4-methoxyphenyl)(trimethylsilyl)methanone **S1**^[3]
- (4-methoxyphenyl)(triethylsilyl)methanone 4c^[4]
- (4-methoxyphenyl)(triisopropylsilyl)methanone S3^[5]
- (4-methoxyphenyl)(tert-butyldimethylsilyl)methanone S4^[5]
- (4-methoxyphenyl)(dimethyphenylsilyl)methanone S5^[6]
- (4-methylphenyl)(trimethylsilyl)methanone^[3]
- (4-chlorophenyl)(trimethylsilyl)methanone^[2]
- (4-fluorophenyl)(trimethylsilyl)methanone^[2]
- benzo[d][1,3]dioxol-5-yl(trimethylsilyl)methanone^[7]
- naphthalen-2-yl(trimethylsilyl)methanone^[2]
- furan-2-yl(trimethylsilyl)methanone^[2]
- 1-(dimethyl(phenyl)silyl)pent-4-en-1-one S29^[8]
- 1-(dimethyl(phenyl)silyl)hex-5-en-1-one S31^[9]
- N-(2-((tert-butyldimethylsilyl)carbonyl)-5-methoxyphenyl)-4-methylbenzenesulfonamide S32^[10]

Additional acylsilanes were prepared according to the procedure described below:

General Procedure 1:



To a stirred solution of benzaldehyde (1.0 equiv.) and propane-1,3-dithiol (1.1 equivs.) in DCM (0.5 M), BF₃·OEt₂ (0.3 equivs.) was added dropwise under nitrogen. The mixture was stirred overnight at room temperature, then quenched by addition of saturated aqueous NaHCO₃. The organic layer was extracted and washed three times with deionized water, dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting material was washed with petroleum benzine to afford 1,3-dithiane compounds as white solids in typically quantitative yields.

The 1,3-dithiane compound (1.0 equiv.) was added to an oven dried Schlenk tube containing a stir bar and evacuated and placed under nitrogen (three cycles). Anhydrous THF (0.25 M) was added and the mixture was cooled to -78 °C before dropwise addition of *n*-BuLi (2.0 M in cyclohexane, 1.2 equivs.). The resultant yellow mixture was stirred at -78 °C for 30 minutes, then silyl chloride (1.3 equivs.) was added dropwise and the mixture was allowed to warm to room temperature over 2 hours. The reaction was quenched by addition of saturated aqueous ammonium chloride (~10 mL) and diluted with Et₂O and deionised water. The organic layers were washed with water and brine, dried on MgSO₄, and filtered. Concentration of the organic layer provided crude silylated dithiane compound, which was used as obtained or purified by flash column chromatography (1% EtOAc/Petroleum benzine).

To a suspension of silylated dithiane derivative (1 equiv.) in THF/H₂O (4:1 v/v, 0.13 M), CaCO₃ (7.0 equivs.) was added followed by the portion-wise addition of I₂ (5.0 equivs.). The resultant black mixture was stirred vigorously at room temperature overnight. The reaction was then quenched by addition of saturated aqueous sodium thiosulfate to give a yellow mixture. The mixture was diluted with water and the aqueous layer was extracted three times with Et₂O. The organic layers were dried on MgSO₄, filtered and concentrated in vacuo. The crude material was purified by flash column chromatography (1-10% EtOAc/Petroleum benzine) to afford the acylsilane.

(4-methoxyphenyl)(triphenylsilyl)methanone (S25) (NMR Spectra)



Prepared according to General Procedure 1. Purification by flash column chromatography (5% EtOAc/petroleum benzine; $R_f \sim 0.5$) afforded the title compound as a pale yellow-green solid (1.30 g, 3.30 mmol, 33% over three steps). ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.78 (m, 2H), 7.69 – 7.58 (m, 6H), 7.50 – 7.42 (m, 3H), 7.42 – 7.37 (m, 6H), 6.85 – 6.76 (m, 2H), 3.81 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 227.6, 163.6, 136.5, 136.3, 132.8,

131.2, 130.2, 128.3, 113.8, 55.5. HRMS (ESI) calcd. for C₂₆H₂₃O₂Si; [M+H]⁺: 395.1462; found 395.1463.

(4-(but-3-en-1-yloxy)phenyl)(trimethylsilyl)methanone (S26) (NMR Spectra)



Prepared according to General Procedure 1. Purification by flash column chromatography (2% EtOAc/petroleum benzine; R_f ~0.3) afforded the title compound as a yellow oil (0.50 g, 2.03 mmol, 20% over three steps). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.85 (ddt, J =

17.0, 10.2, 6.7 Hz, 1H), 5.10 (ddd, J = 13.7, 11.4, 1.3 Hz, 2H), 4.03 (t, J = 6.7 Hz, 2H), 2.51 (q, J = 6.7 Hz, 2H), 0.31 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 233.0, 162.7, 135.4, 134.2, 123.0, 117.5, 114.5, 67.6, 33.6, -1.1. **HRMS** (ESI) calcd. for C₁₄H₂₁O₂Si; [M+H]⁺: 249.1301; found 249.1301.

(4-(methylthio)phenyl)(trimethylsilyl)methanone (S27) (NMR Spectra)



Prepared according to General Procedure 1. Purification by flash column chromatography (2% EtOAc/petroleum benzine; $R_f \sim 0.4$) afforded the title compound as a yellow oil (0.65 g, 2.91 mmol, 29% over three steps). ¹H NMR (400 MHz, CDCl₃) δ 7.78 - 7.73 (m, 2H), 7.31 - 7.27 (m, 2H), 2.52 (s, 3H), 0.36

(s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 234.0, 145.5, 138.2, 128.1, 125.3, 15.0, -1.2. HRMS (ESI) calcd. for C₁₁H₁₆OSSiNa; [M+Na]⁺: 247.0583; found 247.0582.

(3'-fluoro-[1,1'-biphenyl]-4-yl)(trimethylsilyl)methanone (S28) (NMR Spectra)



Prepared according to General Procedure 1. Purification by flash column chromatography (5% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a bright yellow crystalline solid (1.94 g, 7.11 mmol, 71% over three steps). ¹**H NMR** (400 MHz, CDCl₃) δ 7.92 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.47 – 7.38 (m, 2H), 7.35 – 7.29 (m, 1H), 7.15 – 7.00 (m, 1H), 0.41 (s, 9H). ¹³C NMR

(101 MHz, CDCl₃) δ 235.3, 163.4 (d, J_{CF} = 246.2 Hz), 144.1 (d, J_{CF} = 2.2 Hz), 142.5 (d, J_{CF} = 7.6 Hz), 140.6, 130.6 (d, J_{CF} = 8.3 Hz), 128.3, 127.5, 123.1 (d, J_{CF} = 2.8 Hz), 115.1 (d, J_{CF} = 21.2 Hz), 114.3 (d, J_{CF} = 22.2 Hz), -1.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.6. HRMS (ESI) calcd. for C₁₆H₁₈OFSi; [M+H]⁺: 273.1102; found 273.1105.

(4-(benzyloxy)-3-chlorophenyl)(trimethylsilyl)methanone (S29) (NMR Spectra)



Prepared according to General Procedure 1. Purification by flash column chromatography (2% EtOAc/petroleum benzine; Rf ~ 0.3) afforded the title compound as a yellow solid (2.62 g, 8.22 mmol, 82% over three steps). ¹H NMR (401 MHz, CDCl₃) δ 7.68 (d, J = 2.1 Hz, 1H), 7.51 (dd, J = 8.5, 2.1 Hz, 1H), 7.29 –

7.08 (m, 5H), 6.81 (d, J = 8.5 Hz, 1H), 5.01 (s, 2H), 0.15 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 232.2, 157.7, 135.9, 135.8, 129.7, 128.9, 128.4, 128.3, 127.2, 124.0, 113.1, 71.0, -1.2. HRMS (ESI) calcd. for C₁₇H₁₉ClO₂Si; [M+H]⁺: 319.0916; found 319.0914.

4-((trimethylsilyl)carbonyl)phenyl cyclopropanecarboxylate (S32) (NMR Spectra)



An oven dried Schlenk tube was charged with (4-methoxyphenyl)(trimethylsilyl)methanone (**S1**) and evacuated and backfilled with nitrogen (three cycles). Anhydrous DCM (10 mL) was added and the mixture was cooled to -78°C before BBr₃ (2.2 mL, 2.2 mmol, 1.0 M in heptane) was added dropwise. The deep red mixture was stirred at -78°C for 30 minutes then warmed to room temperature and allowed to stir for an additional two hours. The mixture was quenched with water (10 mL) and extracted three times with DCM (50 mL). The combined organic layers were dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain a crude residue which was subjected to purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.2$) to obtain (4-hydroxyphenyl)(trimethylsilyl)methanone (**S31**) as a dark yellow oil (0.26 g, 1.34 mmol, 67%). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 0.38 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 235.3, 161.5, 134.9, 130.7, 115.9, -1.1. *In good agreement with literature data.*^[11]

To a dried round bottomed flask was added (4-hydroxyphenyl)(trimethylsilyl)methanone **S31** (0.26 g, 1.34 mmol) followed by EDC-HCl (0.51 g, 2.68 mmol), DIPEA (0.47 mL, 2.68 mmol) and DMAP (16 mg, 0.13 mmol). The mixture was placed under nitrogen flow and anhydrous DCM (30 mL) was added, followed by cyclopropane carboxylic acid **S32** (0.17 g, 2.01 mmol), then stirred at room temperature overnight. The resultant mixture was diluted with DCM (20 mL), washed twice with 1 M HCl (20 mL), twice with sat. aq. NaHCO₃ (20 mL), and dried on MgSO₄. The mixture was filtered and concentrated *in vacuo* to obtain a yellow residue which was purified by flash column chromatography (20% EtOAc/petroleum benzine; R_f ~ 0.2) to obtain the title compound **S32** as a bright yellow oil (0.34 g, 1.30 mmol, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 1.86 (tt, *J* = 8.0, 4.6 Hz, 1H), 1.21 – 1.17 (m, 2H), 1.06 (dt, *J* = 8.0, 3.4 Hz, 2H), 0.37 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 234.2, 173.1, 154.3, 139.0, 129.2, 122.0, 27.1, 13.2, 9.6, -1.2. HRMS (ESI) calcd. for C₁₄H₁₉O₃Si; [M+H]⁺: 263.1098; found 263.1097.

(E)-1-(dimethyl(phenyl)silyl)-9-phenylnon-5-ene-1,7-dione (12) (NMR Spectra)



An oven dried Schlenk tube was charged with Grubbs catalyst 2nd generation (84 mg, 0.10 mmol, 5 mol%), evacuated and backfilled with nitrogen (three cycles). Anhydrous DCM (20 mL) was added followed by 1-(dimethyl(phenyl)silyl)hex-5-en-1-one (**S33**) (0.46 g, 2.0 mmol) and 5-phenylpent-1-en-3-one (**S34**) (0.40 g, 2.5 mmol, 1.25 equivs.) dissolved in DCM (10 mL). The mixture was stirred at reflux overnight. After cooling to room temperature, the mixture was concentrated *in vacuo* to obtain a crude residue which was subjected to purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) to obtain the title compound **12** as a colourless liquid (0.51 g, 1.40 mmol, 70%). ¹**H NMR** (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.23 – 7.18 (m, 2H), 7.11 (dd, *J* = 4.8, 3.0 Hz, 3H), 6.60 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.92 (d, *J* = 15.9 Hz, 1H), 2.86 – 2.81 (m, 2H), 2.76 – 2.71 (m, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.00 (td, *J* = 8.0, 1.1 Hz, 2H), 1.58 – 1.50 (m, 2H), 0.41 (s, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 245.5, 199.5, 146.7, 141.4, 134.4, 134.1, 130.7, 130.1, 128.6, 128.5, 128.4, 126.2, 47.7, 41.8, 31.9, 30.2, 20.6, -4.7. HRMS (ESI) calcd. for C₂₃H₂₉O₂Si; [M+H]⁺: 365.1931; found 365.1930.

(*E*)-*N*-(2-((*tert*-butyldimethylsilyl)carbonyl)-5-methoxyphenyl)-4-methyl-*N*-(3-oxobut-1-en-1-yl)benzenesulfonamide (14) (<u>NMR</u> Spectra)



To a solution of *N*-(2-((*tert*-butyldimethylsilyl)carbonyl)-5-methoxyphenyl)-4-methylbenzenesulfonamide **S35** (176 mg, 0.40 mmol) and 3-butyn-2-one (34 μ L, 0.44 mmol, 1.1 equiv.) in anhydrous DCM under nitrogen was added DABCO (5 mg, 0.02 mmol, 0.1 equivs.) at 0 °C. The mixture was stirred warming to room temperature overnight. The mixture was concentrated and the title compound **14** isolated from the crude residue by flash column chromatography (20% EtOAc/petroleum benzine, R_f ~ 0.2) as a yellow solid (0.451 mg, 0.37 mmol, 93%). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 14.0 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.02 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.15 (d, *J* = 2.4 Hz, 1H), 4.94 (d, *J* = 14.0 Hz, 1H), 3.69 (s, 3H), 2.42 (s, 3H), 2.19 (s, 3H), 0.96 (s, 9H), 0.26 (s, 3H), 0.22 (s, 3H).¹³C NMR (101 MHz, CDCl₃) δ 234.4, 196.7, 161.5, 144.9, 144.0, 135.5, 135.2, 132.6, 131.6, 129.8, 128.0, 116.9, 114.4, 110.6, 55.6, 26.8, 21.6, 17.1, -4.7, -5.2. HRMS (ESI) calcd. for C₂₅H₃₄NO₅SSi; [M+H]⁺: 488.1921; found 488.1923.

Preparation of vinylketones:

tert-Butyl 3-acryloylpiperidine-1-carboxylate (S38) (NMR Spectra)



To an oven dried Schlenk tube containing a stirred solution of *tert*-butyl 3-formylpiperidine-1-carboxylate **S36** (1.28 g, 6.0 mmol) in anhydrous THF (20 mL) at 0 °C was added vinylmagnesium bromide solution (2.2 mL, 6.6 mmol, 3 M in Et₂O) dropwise under nitrogen. The mixture was stirred for 1 hour at 0 °C then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (50 mL), washed twice with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the vinyl alcohol intermediate **S37** as a colourless oil. The residue was dissolved in DCM (50 mL) and cooled to 0 °C, before addition of Dess-Martin periodinane (2.80 g, 6.6 mmol, 1.1 equivs.) in one portion under nitrogen and stirred overnight. The reaction was quenched with sat. aq. NaHCO₃, and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered and concentrated to obtain the title compound **S38** as a thick colourless oil (0.79 g, 3.3 mmol, 55% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 6.41 (dd, *J* = 17.5, 10.3 Hz, 1H), 6.30 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.84 (dd, *J* = 10.3, 1.3 Hz, 1H), 4.24 – 4.11 (m, 1H), 4.02 (d, *J* = 13.1 Hz, 1H), 2.82 (d, *J* = 9.2 Hz, 2H), 2.77 – 2.70 (m, 1H), 1.96 (d, *J* = 12.7 Hz, 1H), 1.76 – 1.70 (m, 1H), 1.63 – 1.54 (m, 2H), 1.46 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 201.2, 154.8, 135.0, 128.9, 79.8, 46.0, 44.0, 28.5, 27.3, 24.6. HRMS (ESI) calcd. for C₁₃H₂₁NO₃Na; [M+Na]⁺: 262.1414; found 262.1412.

1-(4,4-difluorocyclohexyl)prop-2-en-1-one (S41) (NMR Spectra)



A round bottomed flask was charged with 4,4-difluorocyclohexane-1-carboxylic acid **S39** (0.99 g, 6.0 mmol) and anhydrous DCM (50 mL). CDI (1.07 g, 6.6 mmol, 1.1 equivs.) was added in one portion at 0 °C and the mixture was stirred for 2 hours under nitrogen. *N*,*O*-dimethylhydroxylamine hydrochloride (0.64 g, 6.6 mmol, 1.1 equivs.) was then added and the mixture was stirred overnight. The resulting solution was diluted with DCM (50 mL) and washed with 1 M HCl (50 mL) three times. The organic layer was dried on MgSO₄, filtered and concentrated *in vacuo* to give the Weinreb amide **S40** as a colourless oil. The residue was dissolved in anhydrous THF (30 mL) and cooled to 0 °C. Vinylmagnesium bromide solution (3.0 mL, 9 mmol, 3 M in Et₂O) was added dropwise under nitrogen. The mixture was stirred for 1 hour at 0 °C then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (50 mL), washed twice with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (5% EtOAc/petroleum benzine; R_f ~0.3) afforded the title compound **S41** as a colourless oil (0.61 mmol, 3.48 mmol, 58% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 6.46 (dd, *J* = 17.2, 10.8 Hz, 1H), 6.29 (d, *J* = 17.4 Hz, 1H), 5.81 (d, *J* = 10.5 Hz, 1H), 2.78 – 2.63 (m, 1H), 2.14 (dd, *J* = 17.3, 6.9 Hz, 2H), 1.92 (d, *J* = 8.8 Hz, 2H), 1.81 (dd, *J* = 13.5, 7.3 Hz, 4H). ¹⁹F NMR (376 MHz, CDCl₃) δ -96.9 (dd, *J* = 2526.4, 237.2 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 201.5, 134.5, 128.8, 45.5, 32.9 (dd, *J*_{C-F} = 25.0, 24.0 Hz), 32.4, 24.8 (d, *J*_{C-F} = 10.3 Hz). HRMS (ESI) calcd. for C₉H₁₂OF₂Na; [M+Na]*: 197.0748; found 197.0769.

1-(4-(trifluoromethyl)cyclohexyl)prop-2-en-1-one (S44) (NMR Spectra)



A round-bottomed flask was charged with 4-(trifluoromethyl)cyclohexane-1-carboxylic acid **S42** (1.57 g, 8.0 mmol), *N*,*O*-dimethylhydroxylamine hydrochloride (1.17 g, 12 mmol) and EDC-HCI (1.99 g, 10.4 mmol) and dissolved in anhydrous DCM (50 mL). DIPEA (4.2 mL, 24 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was concentrated *in vacuo*, redissolved in EtOAc (100 mL), and washed thrice with 1M HCI (30 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the crude Weinreb amide **S43** which was used without purification. The Weinreb amide **S43** was dissolved in anhydrous THF (50 mL) and cooled to 0 °C under nitrogen atmosphere. Vinyl magnesium bromide solution (10.4 mL, 10.4 mmol, 1 M in THF) was added dropwise and the mixture was stirred for 2 hours. The reaction was quenched by addition of sat. aq. NH₄Cl and immediately diluted with Et₂O (100 mL) and water (100 mL). The organic layer was washed with water (100 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% EtOAC/petroleum benzine; $R_f \sim 0.2$) to afford the title compound **S44** as a colourless liquid (1.23 g, 6.0 mmol, 75% over two steps) (*minor cis isomer present* ~20%). ¹**H NMR** (400 MHz, CDCl₃) δ 6.44 (dd, *J* = 17.3, 10.5 Hz, 1H), 6.21 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.67 (dd, *J* = 10.5, 1.5 Hz, 1H), 2.80 – 2.65 (m, 1H), 2.09 – 1.89 (m, 4H), 1.73 – 1.63 (m, 2H), 1.62 – 1.50 (m, 4H). ¹³**C NMR** (101 MHz, CDCl₃) δ 202.3 (minor), 201.9 (major), 134.8 (minor), 134.1 (major), 128.4 (minor), 128.0 (major), 46.9 (minor), 43.7 (major), 40.8 (q, *J* = 2.6 Hz), 26.9 (minor), 25.0 (major), 24.3 (q, *J* = 2.5 Hz, major). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -72.7 (d, *J* = 8.4 Hz, major), -73.9 (d, *J* = 7.8 Hz, minor). **HRMS** (ESI) calcd. for C₁₀H₁₄F₃O; [M+H]⁺: 207.0991; found 207.0986.

5-phenylpent-1-en-3-one (S47) (NMR Spectra)



To an oven dried Schlenk tube containing a stirred solution of 3-phenylpropionaldehyde **S45** (2.01 g, 15.0 mmol) in anhydrous THF (60 mL) at 0 °C was added vinylmagnesium bromide solution (7.5 mL, 22.5 mmol, 3 M in Et₂O) dropwise under nitrogen. The mixture was stirred for 1 hour at 0 °C then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (100 mL), washed twice with water (50 mL) and brine (50 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the vinyl alcohol intermediate **S46** as a colourless oil. To an oven dried Schlenk flask under nitrogen was added anhydrous DCM (40 mL) and oxalyl chloride (2.6 mL, 30 mmol, 2 equivs.). The solution was cooled to -78 °C and anhydrous DMSO (3.2 mL, 45 mmol, 3 equivs.) was added dropwise with stirring. After 15 minutes, the crude vinyl alcohol was added dropwise to the mixture in DCM solution (10 mL) and stirred at -78 °C for a further 30 minutes. Then NEt₃ (10.4 mL, 75 mmol, 5 equivs.) was added dropwise and the mixture was warmed to room temperature overnight. The reaction was quenched with sat. aq. NAHCO₃ and diluted with DCM (100 mL). The organic layer was washed with water (50 mL), 1 M HCl (50 mL), and brine (50 mL), then dried on MgSO₄ and filtered. The solution was concentrated *in vacuo* and purified by flash column chromatography (5 % EtOAc/petroleum benzine; Rf ~ 0.4) to give the title compound **S47** as a pale yellow oil (1.83 g, 11.4 mmol, 76% over two steps). ¹H NMR (401 MHz, CDCl₃) δ 7.31 (dd, *J* = 7.8, 7.0 Hz, 2H), 7.25 - 7.19 (m, 3H), 6.39 (dd, *J* = 17.7, 10.5 Hz, 1H), 6.24 (dd, *J* = 17.7, 1.1 Hz, 1H), 5.86 (dd, *J* = 10.5, 1.1 Hz, 1H), 3.01 - 2.92 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 199.9, 141.2, 136.7, 128.6, 128.5, 128.3, 126.3, 41.4, 30.0. *In agreement with literature data.*^[12]

1-(1-phenylcyclopropyl)prop-2-en-1-one (\$50) (NMR Spectra)



To an oven dried Schlenk tube containing a stirred solution of 1-phenylcyclopropane-1-carbaldehyde **S48** (0.67 g, 4.61 mmol) in anhydrous THF (20 mL) at 0 °C was added vinylmagnesium bromide solution (3.5 mL, 6.9 mmol, 3 M in Et₂O) dropwise under nitrogen. The mixture was stirred for 1 hour at 0 °C then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (50 mL), washed twice with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the vinyl alcohol intermediate **S49** as a colourless oil. The residue was dissolved in DCM (50 mL) and cooled to 0 °C, before addition of Dess-Martin periodinane (1.9 g, 5.1 mmol, 1.1 equivs.) in one portion under nitrogen and stirred overnight. The reaction was quenched with sat. aq. NaHCO₃, and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered and concentrated to obtain a crude residue which was purified by flash column chromatography (5% EtOAc/petroleum benzine, R_f ~ 0.3) to obtain the title compound **S50** as a thick colourless oil (0.36 g, 2.12 mmol, 46% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.28 (m, 5H), 6.35 (dd, *J* = 17.0, 10.2 Hz, 1H), 6.20 (dd, *J* = 17.0, 2.2 Hz, 1H), 5.46 (dd, *J* = 10.2, 2.2 Hz, 1H), 1.67 (q, *J* = 3.6 Hz, 2H), 1.26 (q, *J* = 3.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.4, 140.3, 132.6, 130.7, 128.7, 127.6, 127.4, 37.2, 19.0. HRMS (ESI) calcd. for C₁₂H₁₃O; [M+H]⁺: 173.0961; found 173.0958.

1-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-en-1-one (S53) (NMR Spectra)



To an oven dried Schlenk tube containing a stirred solution of 5-norbornene-2-carboxaldehyde **S51** (0.73 g, 6.0 mmol) in anhydrous THF (20 mL) at 0 °C was added vinyImagnesium bromide solution (3.0 mL, 9.0 mmol, 3 M in Et₂O) dropwise under nitrogen. The mixture was stirred for 1 hour at 0 °C then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (50 mL), washed twice with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the vinyl alcohol intermediate **S52** as a colourless oil. The residue was dissolved in DCM (50 mL) and cooled to 0 °C, before addition of Dess-Martin periodinane (2.80 g, 6.1 mmol, 1.1 equivs.) in one portion under nitrogen and stirred overnight. The reaction was quenched with sat. aq. NaHCO₃, and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered and concentrated to obtain a crude residue which was purified by flash column chromatography (5% EtOAc/petroleum benzine, Rf ~0.3) to obtain the title compound **S53** as a colourless semi-solid (0.65 g, 4.38 mmol, 73% over two steps). ¹**H NMR** (401 MHz, CDCl₃) δ 6.47 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.24 (dd, *J* = 17.5, 1.4 Hz, 1H), 6.15 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.82 (dd, *J* = 5.6, 2.7 Hz, 1H), 5.72 (dd, *J* = 10.5, 1.4 Hz, 1H), 3.29 – 3.18 (m, 2H), 2.92 (s, 1H), 1.82 (ddd, *J* = 12.2, 8.7, 3.7 Hz, 1H), 1.57 – 1.52 (m, 1H), 1.48 – 1.44 (m, 1H), 1.37 (d, *J* = 8.2 Hz, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 200.5, 137.5, 135.7, 131.5, 49.9, 49.8, 46.1, 42.8, 27.9. **HRMS** (ESI) calcd. for C₁₀H₁₃O; [M+H]⁺: 149.0961; found 149.0961.

tert-butyl 4-(2-oxobut-3-en-1-yl)piperidine-1-carboxylate (S56) (NMR Spectra)



To an oven dried Schlenk tube containing a stirred solution of *tert*-butyl 4-(2-oxoethyl)piperidine-1-carboxylate **S54** (1.82 g, 8.0 mmol) in anhydrous THF (20 mL) at 0 °C was added vinylmagnesium bromide solution (3.5 mL, 10.4 mmol, 3 M in Et₂O) dropwise under nitrogen. The mixture was stirred for 1 hour at 0 °C then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (50 mL), washed twice with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the vinyl alcohol intermediate **S55** as a colourless oil. The residue was dissolved in DCM (50 mL) and cooled to 0 °C, before addition of Dess-Martin periodinane (3.73 g, 8.8 mmol, 1.1 equivs.) in one portion under nitrogen and stirred overnight. The reaction was quenched with sat. aq. NaHCO₃, and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered and concentrated to obtain a crude residue which was purified by flash column chromatography (5% EtOAc/petroleum benzine, R_f ~0.3) to obtain the title compound **S56** as a pale yellow oil (0.61 g, 2.40 mmol, 30% over two steps). ¹H NMR (401 MHz, CDCl₃) δ 6.34 (dd, *J* = 17.7, 10.5 Hz, 1H), 6.20 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.83 (dd, *J* = 10.5, 1.0 Hz, 1H), 4.06 (d, *J* = 13.2 Hz, 2H), 2.72 (td, *J* = 13.3, 2.4 Hz, 2H), 2.50 (d, *J* = 6.8 Hz, 2H), 2.08 – 1.97 (m, 1H), 1.66 (d, *J* = 13.2 Hz, 2H), 1.44 (s, 9H), 1.18 – 1.07 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.9, 155.0, 137.0, 128.4, 79.4, 46.1, 32.2, 32.2, 28.6. *In agreement with literature data.*^[13]

5-(3,4,5-trimethoxyphenyl)pent-1-en-3-one (S59) (NMR Spectra)



To an oven dried Schlenk tube containing a stirred solution of 3-(3,4,5-trimethoxyphenyl)propanal **S57** (1.02 g, 4.55 mmol) in anhydrous THF (40 mL) at 0 °C was added vinylmagnesium bromide solution (2.3 mL, 6.8 mmol, 3 M in Et₂O) dropwise under nitrogen. The mixture was stirred for 1 hour at 0 °C then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (50 mL), washed twice with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the vinyl alcohol intermediate **S58** as a colourless oil (0.33 g, 1.3 mmol). The residue was dissolved in DCM (50 mL) and cooled to 0 °C, before addition of Dess-Martin periodinane (0.67 g, 1.6 mmol, 1.2 equivs.) in one portion under nitrogen and stirred overnight. The reaction was quenched with sat. aq. NaHCO₃, and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered and stirred overnight. The reaction was quenched with sat. aq. NaHCO₃, and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered and concentrated to obtain a crude residue which was purified by flash column chromatography (30% EtOAc/petroleum benzine, R_f ~ 0.4) to obtain the title compound **S59** as a pale yellow oil (0.37 g, 1.49 mmol, 33% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 6.40 (s, *J* = 4.3 Hz, 2H), 6.28 (ddd, *J* = 18.8, 17.7, 5.8 Hz, 2H), 5.82 (dd, *J* = 10.5, 1.1 Hz, 1H), 3.82 (s, 6H), 3.79 (s, 3H), 2.88 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 199.7, 153.2, 136.9, 136.5, 128.3, 105.3, 60.9, 56.1, 41.4, 30.2. HRMS (ESI) calcd. for C₁₄H₁₈O₄K; [M+K]⁺: 273.1097; found 273.1099.

5-methoxypent-1-en-3-one (S62) (NMR Spectra)



A round-bottomed flask was charged with 3-methoxypropanoic acid **S60** (0.83 g, 8.0 mmol), *N*,*O*-dimethylhydroxylamine hydrochloride (1.17 g, 12 mmol) and EDC·HCl (1.99 g, 10.4 mmol) and dissolved in anhydrous DCM (50 mL). DIPEA (4.2 mL, 24 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was diluted with DCM (50 mL) and 1 M HCl (50 mL), and the aqueous layer was extracted three times with DCM (30 mL) (*caution: moderate aqueous solubility*). The combined organic layers were dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the crude Weinreb amide **S57** which was used without purification. The Weinreb amide was dissolved in anhydrous THF (50 mL) and cooled to 0 °C under nitrogen atmosphere. Vinyl magnesium bromide solution (10.4 mL, 10.4 mmol, 1 M in THF) was added dropwise and the mixture was stirred for 2 hours. The reaction was quenched by addition of sat. aq. NH₄Cl and immediately diluted with Et₂O (100 mL) and water (100 mL). The organic layer was washed with water (100 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% EtOAC/petroleum benzine; $R_f \sim 0.2$) to afford the title compound **S62** as a colourless liquid (0.55 g, 4.7 mmol, 59% over two steps). ¹H NMR (401 MHz, CDCl₃) δ 6.37 (dd, *J* = 17.7, 10.5 Hz, 1H), 6.23 (d, *J* = 17.6 Hz, 1H), 5.86 (d, *J* = 10.5 Hz, 1H), 3.69 (t, *J* = 6.4 Hz, 2H), 3.33 (s, 3H), 2.85 (t, *J* = 6.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.0, 136.8, 128.8, 67.7, 59.0, 39.6. HRMS (ESI) calcd. for C₆H₁₁O₂; [M+H]⁺: 115.0754; found 115.0745.



A round-bottomed flask was charged 2,2-diphenylacetic acid **S63** (1.69 g, 8.0 mmol), *N*,*O*-dimethylhydroxylamine hydrochloride (1.17 g, 12 mmol) and EDC·HCI (1.99 g, 10.4 mmol) and dissolved in anhydrous DCM (50 mL). DIPEA (4.2 mL, 24 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was concentrated *in vacuo*, redissolved in EtOAc (100 mL), and washed thrice with 1M HCI (30 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the crude Weinreb amide **S64** which was used without purification. The Weinreb amide was dissolved in anhydrous THF (50 mL) and cooled to 0 °C under nitrogen atmosphere. Vinyl magnesium bromide solution (10.4 mL, 10.4 mmol, 1 M in THF) was added dropwise and the mixture was stirred for 2 hours. The reaction was quenched by addition of sat. aq. NH₄Cl and immediately diluted with Et₂O (100 mL) and water (100 mL). The organic layer was washed with water (100 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% EtOAC/petroleum benzine; $R_f \sim 0.2$) to afford the title compound **S65** as a colourless liquid (0.80 g, 3.6 mmol, 45% over two steps). ¹H NMR (401 MHz, CDCl₃) δ 7.41 – 7.28 (m, 10H), 6.54 (dd, *J* = 17.3, 10.2 Hz, 1H), 6.41 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.78 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.41 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 197.6, 138.3, 135.5, 129.3, 129.0, 128.8, 127.3, 62.3. *In agreement with literature data.*^[14]

6-chlorohex-1-en-3-one (S68) (NMR Spectra)



A round-bottomed flask was charged with *N*,*O*-dimethylhydroxylamine hydrochloride (1.17 g, 12 mmol) and dissolved in anhydrous DCM (50 mL) and DIPEA (4.2 mL, 24 mmol). 4-Chlorobutanoyl chloride **S66** (0.9 mL, 8.0 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was concentrated *in vacuo*, redissolved in EtOAc (100 mL), and washed thrice with 1M HCl (30 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the crude Weinreb amide **S67** which was used without purification. The Weinreb amide was dissolved in anhydrous THF (50 mL) and cooled to 0 °C under nitrogen atmosphere. Vinyl magnesium bromide solution (10.4 mL, 10.4 mmol, 1 M in THF) was added dropwise and the mixture was stirred for 2 hours. The reaction was quenched by addition of sat. aq. NH₄Cl and immediately diluted with Et₂O (100 mL) and water (100 mL). The organic layer was washed with water (100 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (5% EtOAC/petroleum benzine; R_f ~0.4) to afford the title compound **S68** as a colourless liquid (0.71 g, 5.4 mmol, 68% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 6.33 (dd, *J* = 17.7, 10.3 Hz, 1H), 6.22 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.83 (dd, *J* = 10.3, 1.0 Hz, 1H), 3.57 (t, *J* = 6.3 Hz, 2H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.12 – 2.03 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.5, 136.5, 128.5, 44.5, 36.2, 26.5. HRMS (ESI) calcd. for C₆H₁₀ClO; [M+H]⁺: 133.0415; found 133.0418.

1-(tetrahydro-2H-pyran-4-yl)prop-2-en-1-one (S71) (NMR Spectra)



A round-bottomed flask was charged with tetrahydro-2*H*-pyran-4-carboxylic acid **S69** (1.04 g, 8.0 mmol), *N*,*O*-dimethylhydroxylamine hydrochloride (1.17 g, 12 mmol) and EDC·HCI (1.99 g, 10.4 mmol) and dissolved in anhydrous DCM (50 mL). DIPEA (4.2 mL, 24 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was concentrated *in vacuo*, redissolved in EtOAc (100 mL), and washed thrice with 1M HCI (30 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the crude Weinreb amide **S70** which was used without purification. The Weinreb amide was dissolved in anhydrous THF (50 mL) and cooled to 0 °C under nitrogen atmosphere. Vinyl magnesium bromide solution (10.4 mL, 10.4 mmol, 1 M in THF) was added dropwise and the mixture was stirred for 2 hours. The reaction was quenched by addition of sat. aq. NH₄Cl and immediately diluted with Et₂O (100 mL) and water (100 mL). The organic layer was washed with water (100 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% EtOAC/petroleum benzine; Rf $^{-}$ O.2) to afford the title compound **S71** as a pale-yellow liquid (0.46 g, 3.3 mmol, 33% over two steps). ¹H **NMR** (401 MHz, CDCl₃) δ 6.39 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.23 (d, *J* = 17.4 Hz, 1H), 5.73 (dd, *J* = 10.4, 0.7 Hz, 1H), 3.95 (dt, *J* = 11.4, 3.4 Hz, 2H), 3.44 – 3.37 (m, 2H), 2.77 (dt, *J* = 15.1, 7.0 Hz, 1H), 1.68 (dq, *J* = 7.6, 3.9 Hz, 4H). ¹³C **NMR** (101 MHz, CDCl₃) δ 201.4, 134.3, 128.7, 67.3, 45.3, 28.3. **HRMS** (ESI) calcd. for C₈H₁₂NaO₂; [M+Na]*: 163.0730; found 163.0730.

4-(4-isobutylphenyl)pent-1-en-3-one (76) (NMR Spectra)



A round-bottomed flask was charged with 2-(4-isobutylphenyl)propanoic acid **\$72** (1.24 g, 6.0 mmol), *N*,*O*-dimethylhydroxylamine hydrochloride (1.17 g, 12 mmol) and EDC·HCI (1.40 g, 7.2 mmol) and dissolved in anhydrous DCM (50 mL). DIPEA (3.1 mL, 18 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was concentrated *in vacuo*, redissolved in EtOAc (100 mL), and washed thrice with 1M HCI (30 mL). The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to obtain the crude Weinreb amide **\$73** which was used without purification. The Weinreb amide was dissolved in anhydrous THF (50 mL) and cooled to 0 °C under nitrogen atmosphere. LiAlH₄ (0.34 g, 9.0 mmol, 1.5 equivs.) was added in one portion under nitrogen flow and the mixture was stirred for 2 hours. The reaction was quenched with sat. aq. NH₄Cl, and the aqueous layer was extracted thrice with Et₂O (100 mL). The combined organic layers were dried on MgSO₄, filtered and concentrated to afford the crude aldehyde **\$74** which was used without further purification (*Note: addition of vinylmagnesium bromide to the Weinreb amide* **\$73** did not provide **\$74** in satisfactory yield). The residue was redissolved in anhydrous THF (50 mL) and cooled to 0 °C under nitrogen atmosphere. Vinyl magnesium bromide solution (10.4 mL, 10.4 mmol, 1 M in THF) was added dropwise and the mixture was stirred for 2 hours. The

reaction was quenched by addition of sat. aq. NH₄Cl and diluted with Et₂O (100 mL) and water (100 mL). The organic layer was washed with water (100 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. The residue contained two diastereomeric alcohols **S75**, **S75'** (0.70 g, 3.2 mmol) which were combined for the next reaction. To a stirred solution of the allyl alcohols in DCM (30 mL) at 0 °C, Dess-Martin periodinane (1.76 g, 4.16 mmol, 1.3 equivs.) was added in one portion under nitrogen flow and the mixture was warmed to room temperature overnight. The reaction was quenched with sat. aq. NaHCO₃, and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered and concentrated to obtain a crude residue which was purified by flash column chromatography (5% EtOAc/petroleum benzine, R_f ~0.4) to obtain the title compound **S76** as a colourless oil (0.59 g, 2.72 mmol, 34% over 4 steps). ¹H NMR (400 MHz, CDCl₃) δ 7.13 – 7.07 (m, 4H), 6.36 (dd, *J* = 17.4, 10.1 Hz, 1H), 6.26 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.63 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.94 (q, *J* = 6.9 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.83 (td, *J* = 13.5, 6.8 Hz, 1H), 1.42 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 200.0, 140.7, 137.7, 134.9, 129.8, 128.2, 127.9, 50.8, 45.2, 30.3, 22.5, 17.8. HRMS (ESI) calcd. for C₁₅H₂₀NaO; [M+Na]⁺: 239.1406; found 239.1405.

Synthesis of dehydroabietic acid vinyl ketone derivative (S81)



(1R,4aS,10aR)-7-isopropyl-N-methoxy-N,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxamide (S78) (NMR Spectra)

An oven dried round bottomed flask was charged with dehydroabietic acid **S77** (1.80 g, 6.0 mmol) and placed under nitrogen. Anhydrous DCM (50 mL) was added followed by DMF (1 drop) and the mixture was cooled to 0 °C. Oxalyl chloride (0.8 mL, 9.0 mmol, 1.5 equivs.) was added dropwise to the mixture with stirring. The mixture was stirred, warming to room temperature, until gas formation ceased (3 hours). Excess oxalyl chloride was then removed *in vacuo*, and the obtained residue was re-dissolved in anhydrous DCM (50 mL) under nitrogen atmosphere. *N,O*-dimethylhydroxylamine hydrochloride (0.88 g, 9.0 mmol, 1.5 equivs.) was added in one portion at 0 °C, followed by DIPEA (2.1 mL, 15 mmol, 2.5 equivs.) dropwise. After 2 hours, the reaction was quenched by addition of sat. aq. NaHCO₃. The organic layer was washed twice with H₂O (50 mL) and 1 M HCl (50 mL), dried on MgSO₄ and filtered. Concentration *in vacuo* and purification by flash column chromatography (5 \rightarrow 10% EtOAc/petroleum benzine; R_f ~ 0.2) afforded the Weinreb amide **578** as a crystalline solid (1.17 g, 3.41 mmol, 57 %). ¹**H NMR** (400 MHz, CDCl₃) δ 7.17 (d, *J* = 8.2 Hz, 1H), 6.89 (d, *J* = 8.1, 1.6 Hz, 1H), 6.89 (s, 1H), 3.63 (s, 3H), 3.18 (s, 3H), 2.99 – 2.79 (m, 3H), 2.42 (dd, *J* = 12.2, 1.9 Hz, 1H), 2.29 (d, *J* = 12.3 Hz, 1H), 1.82 (dd, *J* = 11.8, 5.8 Hz, 3H), 1.74 – 1.69 (m, 1H), 1.63 – 1.52 (m, 2H), 1.50 – 1.43 (m, 1H), 1.35 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H), 1.22 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 179.7, 147.5, 145.6, 135.1, 127.0, 124.1, 123.8, 60.4, 48.0, 43.5, 37.9, 37.4, 34.6, 33.9, 33.5, 30.3, 25.6, 24.1, 21.9, 18.9, 17.6.

(1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbaldehyde (S79): An oven dried round bottomed flask was charged with Weinreb amide S78 and evacuated and backfilled with nitrogen. Anhydrous THF (30 mL) was added and the solution cooled to 0 °C before addition of LiAlH₄ (0.19 g, 5.12 mmol, 1.5 equivs.) under nitrogen flow. The mixture was stirred vigorously overnight warming to room temperature. The reaction was carefully quenched with 1 M HCl, and the aqueous layer extracted three times with EtOAc (100 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. The compound was used in the next

stage without further purification. (*Note: addition of vinylmagnesium bromide to the Weinreb amide* **578** *did not provide* **579** *in satisfactory yield*).

1-((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)prop-2-en-1-ol (both diastereomers) (S80/80') (NMR Spectra)

An oven dried round Schlenk tube was charged with carbaldehyde **S79** and evacuated and backfilled with nitrogen. Anhydrous THF (20 mL) was added and the solution cooled to 0 °C and vinylmagnesium bromide (1.71 mL, 5.12 mmol, 1.5 equivs., 3 M in Et₂O) was added dropwise and stirred for 2 hours. The reaction was quenched with sat. aq. NH₄Cl and diluted with EtOAc (100 mL). The organic layer was washed three times with H₂O (100 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. Flash column chromatography (5% EtOAc/petroleum benzine; $R_f \sim 0.3$, 0.2) afforded separable diastereomers of the title compound, which were combined for the next reaction (0.47 g, 1.47 mmol, 43% over two steps).

Diastereomer 1 (**S76a**): R_f ~0.3, white solid ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.2 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.94 (s, 1H), 5.98 (ddd, *J* = 17.2, 10.4, 6.9 Hz, 1H), 5.29 – 5.20 (m, 2H), 4.05 (d, *J* = 6.9 Hz, 1H), 2.95 (dd, *J* = 8.7, 4.3 Hz, 2H), 2.88 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.30 (d, *J* = 12.5 Hz, 1H), 2.03 (ddd, *J* = 12.3, 6.2, 2.0 Hz, 2H), 1.83 – 1.67 (m, 4H), 1.48 (ddd, *J* = 17.1, 13.3, 4.2 Hz, 2H), 1.29 (s, 6H), 1.27 (s, 3H), 0.99 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 147.8, 145.5, 138.1, 135.0, 126.9, 124.3, 123.8, 117.1, 79.0, 42.7, 40.1, 38.3, 37.7, 33.6, 31.6, 30.2, 25.4, 24.1, 24.1, 18.7, 18.7, 18.0.

Diastereomer 2 (S76b): R_f ~0.2, white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 8.2 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.89 (s, 1H), 6.04 – 5.92 (m, 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.18 (dd, *J* = 10.4, 1.1 Hz, 1H), 4.14 (d, *J* = 7.6 Hz, 1H), 2.91 – 2.71 (m, 3H), 2.29 (d, *J* = 12.6 Hz, 1H), 1.85 – 1.69 (m, 4H), 1.62 – 1.55 (m, 2H), 1.41 – 1.29 (m, 2H), 1.25 (s, 6H), 1.23 (s, 3H), 1.15 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 147.6, 145.6, 137.9, 134.7, 126.9, 124.5, 124.0, 117.0, 80.5, 45.4, 40.7, 38.6, 37.7, 33.6, 30.6, 30.1, 25.6, 24.1, 18.9, 18.6, 17.9.

1-((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)prop-2-en-1-one (S81) (NMR Spectra)

The diastereomers **S80** and **S80'** were combined and dissolved in DCM (50 mL) and cooled to 0 °C, before addition of Dess-Martin periodinane (0.70 g, 1.65 mmol, 1.1 equivs.) in one portion under nitrogen and stirred overnight. The reaction was quenched with sat. aq. NaHCO₃, and the organic layer was washed with water (20 mL) and brine (20 mL). The organic layer was dried on MgSO₄, filtered and concentrated to obtain a crude residue which was purified by flash column chromatography (2% EtOAc/petroleum benzine, $R_f \sim 0.4$) to obtain the title compound **S81** as a thick colourless oil (0.43 g, 1.38 mmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.2 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.96 (dd, *J* = 16.8, 10.4 Hz, 1H), 6.92 (s, 1H), 6.37 (dd, *J* = 16.8, 2.1 Hz, 1H), 5.64 (dd, *J* = 10.4, 2.1 Hz, 1H), 2.94 – 2.78 (m, 3H), 2.39 (d, *J* = 12.9 Hz, 1H), 2.19 (dd, *J* = 12.5, 2.0 Hz, 1H), 1.91 – 1.76 (m, 3H), 1.69 (td, *J* = 13.0, 4.2 Hz, 1H), 1.54 (ddd, *J* = 12.8, 10.8, 3.5 Hz, 2H), 1.38 – 1.33 (m, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 204.5, 147.0, 145.9, 134.7, 131.1, 128.4, 127.1, 124.2, 124.0, 51.1, 43.6, 38.2, 36.9, 34.8, 33.6, 30.0, 25.2, 24.1, 21.3, 18.6, 15.8. HRMS (ESI) calcd. for C₂₂H₃₁O; [M+H]⁺: 311.2369; found 311.2371.

Preparation of Olefinated Acylsilanes by C-H Functionalisation:

General Procedure 2:



To an oven dried 6 mL vial containing a stir bar, $AgSbF_6$ (17.2 mg, 0.05 mmol, 10 mol%, *caution: hygroscopic*) was added followed by $[Ru(p-Cym)Cl_2]_2$ (15.3 mg, 0.025 mmol, 5 mol%) and anhydrous $Cu(OAc)_2$ (181.6 mg, 1.0 mmol, 2 equivs.). Anhydrous DCE/TFE (9:1 v/v, 1 mL) was added and the mixture was stirred at room temperature for five minutes, before benzoylsilane (0.5 mmol, 1 equiv.) SI25

and vinyl ketone (0.75-1.0 mmol, 1.5-2.0 equivs.) were added in DCE/TFE (9:1, 4.0 mL). The mixture was stirred at 60 °C until the reaction was complete (as evaluated by TLC analysis). The cooled mixture was then filtered through a pad of silica gel eluting with EtOAc, concentrated *in vacuo*, and the residue was purified by flash column chromatography (10-20% EtOAc/petroleum benzine) to afford pure *ortho*-olefinated benzoylsilanes.

(E)-4-(5-(tert-butyl)-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5a) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 4 hours. Purification by flash column chromatography (5 \rightarrow 10% EtOAc/petroleum benzine; R_f ~ 0.3) afforded the title compound as a yellow solid (106 mg, 0.35 mmol, 70%). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 16.3 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.54 (dd, *J* = 8.1, 1.9

Hz, 1H), 6.49 (d, J = 16.3 Hz, 1H), 2.42 (s, 3H), 1.36 (s, 9H), 0.35 (s, 9H). ¹³**C** NMR (101 MHz, CDCl₃) δ 240.2, 199.2, 155.3, 144.4, 139.4, 133.0, 130.9, 130.2, 126.6, 125.6, 35.3, 31.2, 26.9, -1.3. HRMS (ESI) calcd. for C₁₈H₂₇O₂Si; [M+H]⁺: 303.1775; found 303.1773.

(E)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5b) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 2 hours. Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a dark yellow solid (122 mg, 0.44 mmol, 88%). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 16.3 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.6 Hz, 1H),

6.44 (d, J = 16.2 Hz, 1H), 3.89 (s, 3H), 2.42 (s, 3H), 0.35 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 237.5, 199.2, 162.1, 144.3, 136.1, 134.9, 133.9, 130.5, 114.5, 113.9, 55.7, 26.9, -1.1. **HRMS** (ESI) calcd. for C₁₅H₂₂O₃Si; [M+H]⁺: 277.1255; found 277.1251.

The reaction was also conducted on 10 mmol scale to afford **5b** (2.16 g, 7.81 mmol, 78%).

(E)-4-(5-methoxy-2-((triethylsilyl)carbonyl)phenyl)but-3-en-2-one (5c) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 2 hours. Purification by flash column chromatography ($10 \rightarrow 20\%$ EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a dark yellow oil (140 mg, 0.44 mmol, 88%). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 16.3 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.6 Hz,

1H), 6.46 (d, J = 16.2 Hz, 1H), 3.89 (s, 3H), 2.41 (s, 3H), 1.02 – 0.93 (m, 9H), 0.92 – 0.85 (m, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 237.5, 199.23, 162.1, 144.3, 136.1, 134.8, 133.8, 130.5, 114.5, 113.9, 55.7, 26.9, -1.1. **HRMS** (ESI) calcd. for C₁₅H₂₁O₃Si; [M+H]⁺: 277.1254; found 277.1250.

The reaction was also conducted on 6 mmol scale to afford 5c (1.35 g, 4.24 mmol, 71%).

(E)-4-(5-methoxy-2-((triisopropylsilyl)carbonyl)phenyl)but-3-en-2-one (5d) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 4 hours. Purification by flash column chromatography ($10 \rightarrow 20\%$ EtOAc/petroleum benzine; R_f ~ 0.3) afforded the title compound as a yellow oil (140 mg, 0.39 mmol, 78%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 16.3 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.5 Hz, 1H),

6.48 (d, *J* = 16.3 Hz, 1H), 3.88 (s, 3H), 2.39 (s, 3H), 1.45 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.12 (s, 9H), 1.11 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 239.1, 199.2, 161.6, 143.8, 137.9, 135.0, 132.1, 130.2, 114.6, 113.4, 55.7, 26.7, 18.9, 12.4. **HRMS** (ESI) calcd. for C₁₈H₂₇O₂Si; [M+H]⁺: 361.2194; found 361.2189.

(E)-4-(2-((tert-butyldimethylsilyl)carbonyl)-5-methoxyphenyl)but-3-en-2-one (5e) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 3 hours. Purification by flash column chromatography (10 \rightarrow 20% EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a yellow solid (128 mg, 0.40 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 16.3 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.04 (d, J = 2.5 Hz, 1H), 6.98 (dd, J = 8.6, 2.6 Hz, 1H),

6.45 (d, J = 16.2 Hz, 1H), 3.87 (s, 3H), 2.39 (s, 3H), 0.95 (s, 9H), 0.33 (s, 6H). ¹³**C** NMR (101 MHz, CDCl₃) δ 238.2, 199.2, 161.8, 144.0, 136.8, 135.4, 133.3, 130.2, 114.4, 113.6, 55.7, 26.9, 26.8, 17.3, -4.6. **HRMS** (ESI) calcd. for C₁₈H₂₇O₃Si; [M+H]⁺: 319.1724; found 319.1718.

(E)-4-(2-((dimethyl(phenyl)silyl)carbonyl)-5-methoxyphenyl)but-3-en-2-one (5f) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 3 hours. Purification by flash column chromatography ($10 \rightarrow 20\%$ EtOAc/petroleum benzine; R_f ~ 0.3) afforded the title compound as a yellow solid (144 mg, 0.43 mmol, 85%). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 16.3 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.42 – 7.33 (m, 3H), 7.00 (d, *J* = 2.5

Hz, 1H), 6.83 (dd, J = 8.6, 2.6 Hz, 1H), 6.42 (d, J = 16.2 Hz, 1H), 3.84 (s, 3H), 2.40 (s, 3H), 0.60 (s, 6H). ¹³**C** NMR (101 MHz, CDCl₃) δ 235.3, 199.1, 161.9, 144.1, 136.1, 135.7, 134.6, 134.3, 133.9, 133.0, 130.4, 129.9, 128.3, 127.9, 114.2, 113.8, 55.5, 26.7, -0.0, -2.9. HRMS (ESI) calcd. for C₂₀H₂₃O₃Si; [M+H]⁺: 339.1411; found 339.1409.

(E)-4-(5-methoxy-2-((triphenylsilyl)carbonyl)phenyl)but-3-en-2-one (5g) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 4 hours. Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow crystalline solid (106 mg, 0.23 mmol, 46%). Note that this compound was observed to degrade over time in deuterated chloroform. ¹H NMR (400 MHz, CD₂Cl₂) δ

7.92 (d, J = 16.2 Hz, 1H), 7.59 (s, 1H), 7.53 – 7.48 (m, 6H), 7.41 – 7.34 (m, 3H), 7.30 (t, J = 7.3 Hz, 6H), 6.96 (d, J = 2.5 Hz, 1H), 6.62 (dd, J = 8.6, 2.5 Hz, 1H), 6.36 (d, J = 16.2 Hz, 1H), 3.72 (s, 3H), 2.23 (s, 3H).¹³**C** NMR (101 MHz, CDCl₃) δ ¹³C NMR (101 MHz, CD₂Cl₂) δ 231.9, 198.3, 162.2, 143.4, 136.4, 136.3, 135.2, 132.3, 130.2, 130.1, 128.2, 113.7, 113.7, 55.6, 26.9. **HRMS** (ESI) calcd. for C₃₀H₂₇O₃Si; [M+H]⁺: 463.1724; found 463.1727.

(E)-4-(5-(benzyloxy)-4-chloro-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5h) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 5 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow oil (136 mg, 0.35 mmol, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 16.3 Hz, 1H), 7.81 (s, 1H), 7.47 – 7.35 (m, 5H), 7.12 (s, 1H), 6.37 (d, *J* = 16.3 Hz, 1H), 5.24 (s, 2H),

2.41 (s, 3H), 0.36 (s, 9H). ¹³C NMR δ 237.4, 198.9, 156.5, 143.0, 135.6, 135.4, 133.9, 133.3, 130.7, 129.0, 128.6, 127.3, 124.3, 112.9, 71.2, 27.0, -1.3. HRMS (ESI) calcd. for C₂₁H₂₄ClO₃Si; [M+H]⁺: 387.1178; found 387.1176.

(E)-4-(5-methyl-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5i) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 4 hours. Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow solid (98 mg, 0.38 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 16.3 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.40 (s, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 16.2 Hz, 1H),

2.41 (s, 3H), 2.39 (s, 3H), 0.33 (s, 9H). ¹³C NMR δ 240.3, 199.0, 143.6, 142.2, 139.7, 133.2, 130.8, 130.2, 130.2, 129.2, 27.0, 21.7, -1.4. HRMS (ESI) calcd. for C₁₅H₂₀O₂SiNa; [M+Na]⁺: 283.1125; found 283.1119.

(E)-4-(6-((trimethylsilyl)carbonyl)benzo[d][1,3]dioxol-5-yl)but-3-en-2-one (5j) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 2 hours. Purification by flash column chromatography (10 \rightarrow 20% EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a dark yellow oil (105 mg, 0.36 mmol, 72%). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 16.2 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 6.41 (d, J = 16.1 Hz, 1H), 6.07 (s,

2H), 2.31 (s, 3H), 0.26 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 241.2, 198.5, 149.4, 146.3, 141.8, 128.6, 126.8, 125.9, 122.5, 110.5, 102.2, 27.1, -2.7. **HRMS** (ESI) calcd. for C₁₅H₁₈O₄SiNa; [M+Na]⁺: 313.0867; found 313.0864.

(E)-4-(5-(methylthio)-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5k) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 4 hours. Purification by flash column chromatography (10 \rightarrow 20% EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a dark yellow oil (37 mg, 0.13 mmol, 26%). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 16.2 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.29 (m, 2H), 6.45 (d, *J* = 16.2 Hz, 1H),

2.54 (s, 3H), 2.41 (s, 3H), 0.34 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 238.8, 199.1, 144.6, 143.7, 137.9, 134.0, 131.5, 130.5, 125.8, 124.9, 27.0, 15.0, -1.3. HRMS (ESI) calcd. for C₁₅H₂₁O₂SSi; [M+H]⁺: 293.1026; found 293.1012.

(E)-4-(5-chloro-2-((triethylsilyl)carbonyl)phenyl)but-3-en-2-one (5I) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 5 hours. Purification by flash column chromatography (5% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow oil (70 mg, 0.22 mmol, 43%). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 16.2 Hz, 1H), 7.58 (m, 2H), 7.47 (dd, J = 8.3, 2.0 Hz, 1H), 6.50 (d, J = 16.2 Hz, 1H), 2.38 (s, 3H), 0.98 (t, J

= 7.7 Hz, 9H), 0.86 (m, 6H). ¹³C NMR δ 231.4, 198.3, 141.2, 137.6, 134.4, 130.9, 130.6, 129.5, 128.3, 27.3, 7.5, 3.6. HRMS (ESI) calcd. for C₁₇H₂₄ClO₂Si; [M+H]⁺: 323.1229; found 323.1225.

(E)-4-(3'-fluoro-4-((trimethylsilyl)carbonyl)-[1,1'-biphenyl]-3-yl)but-3-en-2-one (5m) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 4 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow oil (118 mg, 0.35 mmol, 69%). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 16.2 Hz, 1H), 7.79 (t, *J* = 4.7 Hz, 2H), 7.70 (dd, *J* = 7.9, 1.9 Hz, 1H),

7.44 (dd, J = 7.9, 5.7 Hz, 1H), 7.40 (dt, J = 7.6, 1.3 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.11 (tdd, J = 8.4, 2.5, 1.2 Hz, 1H), 6.57 (d, J = 16.2 Hz, 1H), 2.42 (s, 3H), 0.37 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 240.7, 198.8, 164.6, 162.1, 143.1, 143.0 (d, $J_{C-F} = 2.2$ Hz), 141.7 (d, $J_{C-F} = 7.7$ Hz), 141.1, 133.7, 130.8 (d, $J_{C-F} = 8.4$ Hz), 130.5, 128.1, 127.2, 123.0 (d, $J_{C-F} = 2.8$ Hz), 115.4 (d, $J_{C-F} = 21.1$ Hz), 114.3 (d, $J_{C-F} = 22.4$ Hz), 27.2, -1.4. ¹⁹F NMR (377 MHz, CDCl₃) δ -112.2 (td, J = 9.0, 5.9 Hz). HRMS (ESI) calcd. for C₂₀H₂₂O₂Si; [M+H]⁺: 341.1368; found 341.1363.

(E)-4-(3-((trimethylsilyl)carbonyl)naphthalen-2-yl)but-3-en-2-one (5n) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 4 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow solid (101 mg, 0.34 mmol, 68%). ¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 8.10 (d, *J* = 16.2 Hz, 1H), 8.04 (s, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.63 (m,

2H), 6.59 (d, *J* = 16.1 Hz, 1H), 2.44 (s, 3H), 0.42 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 240.1, 199.0, 144.0, 139.5, 134.2, 132.9, 132.5, 130.7, 129.9, 129.1, 128.9, 128.7, 128.5, 128.0, 27.2, -1.1. **HRMS** (ESI) calcd. for C₁₈H₂₁O₂Si; [M+H]⁺: 297.1305; found 297.1300.

(E)-4-(5-fluoro-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (50) (NMR Spectra)



Prepared according to General Procedure 2 on half scale (0.25 mmol of acylsilane) using methyl vinyl ketone (0.5 mmol, 2.0 equivs.). Reaction time 5 hours. Purification by flash column chromatography (15% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow oil (36 mg, 0.14 mmol, 55%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 16.2 Hz, 1H), 7.74 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.19

(td, *J* = 8.1, 2.5 Hz, 1H), 6.48 (d, *J* = 16.2 Hz, 1H), 2.40 (s, 3H), 0.35 (s, 9H). ¹³C NMR δ 239.3, 198.5, 165.3, 157.6, 141.9, 138.6, 136.3, 132.8 (d, *J*_{C-F} = 9.3 Hz), 131.0, 115.9 (dd, *J*_{C-F} = 98.6, 22.3 Hz), 27.3, -1.44. ¹⁹F NMR (**377** MHz, CDCl₃) δ -106.63 (dd, *J* = 14.4, 8.4 Hz). HRMS (ESI) calcd. for $C_{14}H_{18}FO_2Si$; [M+H]⁺: 265.1055; found 265.1056.

(E)-4-(5-(but-3-en-1-yloxy)-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5p) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 2 hours. Purification by flash column chromatography ($10 \rightarrow 20\%$ EtOAc/petroleum benzine; R_f ~ 0.3) afforded the title compound as a yellow-green oil (135 mg, 0.43 mmol, 85%). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 16.3 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.5 Hz,

1H), 6.44 (d, J = 16.2 Hz, 1H), 5.90 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.17 (ddd, J = 13.7, 11.7, 1.5 Hz, 2H), 4.10 (t, J = 6.7 Hz, 2H), 2.58 (q, J = 6.7 Hz, 2H), 2.42 (s, 3H), 0.35 (s, 9H). ¹³**C** NMR (101 MHz, CDCl₃) δ 237.5, 199.2, 161.4, 144.3, 136.1, 134.8, 134.0, 133.8, 130.4, 117.7, 115.0, 114.5, 67.8, 33.6, 26.9, -1.1. HRMS (ESI) calcd. for C₁₈H₂₅O₃Si; [M+H]⁺: 317.1567; found 317.1566.

(E)-3-(3-oxobut-1-en-1-yl)-4-((trimethylsilyl)carbonyl)phenyl cyclopropanecarboxylate (5q) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 4 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a bright yellow oil (109 mg, 0.33 mmol, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 16.2 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 2.2 Hz, 1H), 7.08 (dd, J =

8.6, 2.0 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 2.20 (s, 3H), 1.72 – 1.64 (m, 1H), 1.02 – 0.98 (m, 2H), 0.91 – 0.85 (m, 2H), 0.15 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 239.7, 198.6, 173.0, 152.9, 142.3, 139.4, 135.1, 131.8, 130.7, 122.6, 121.6, 27.2, 13.1, 9.7, -1.5. HRMS (ESI) calcd. for C₁₈H₂₂O₄SiNa; [M+Na]⁺: 353.1180; found 353.1186.

(E)-4-(2-((trimethylsilyl)carbonyl)furan-3-yl)but-3-en-2-one (5r) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 12 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow solid (40 mg, 0.26 mmol, 51%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 16.7 Hz, 1H), 7.33 (d, *J* = 1.5 Hz, 1H), 6.57 (d, *J* = 1.7 Hz, 1H), 6.34 (d, *J* = 16.7 Hz, 1H), 2.21 (s, 3H), 0.15 (s, 9H). ¹³C NMR (101

 $\mathsf{MHz}, \mathsf{CDCl}_3) \ \delta \ 226.3, \ 199.0, \ 154.0, \ 145.5, \ 134.1, \ 132.9, \ 124.1, \ 109.8, \ 26.1, \ -2.8. \ \textbf{HRMS} \ (\mathsf{ESI}) \ \mathsf{calcd.} \ \mathsf{for} \ \mathsf{C}_{12}\mathsf{H}_{17}\mathsf{O}_3\mathsf{Si}; \ [\mathsf{M}+\mathsf{H}]^+: \ 237.0942; \ \mathsf{found} \ 237.0941.$

(E)-4-(2-((trimethylsilyl)carbonyl)thiophen-3-yl)but-3-en-2-one (5s) (NMR Spectra)



Prepared according to General Procedure 2 using methyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 5 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a bright yellow solid (50 mg, 0.20 mmol, 40%). ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, *J* = 16.6 Hz, 1H), 7.55 (d, *J* = 4.9 Hz, 1H), 7.40 (d, *J* = 4.9 Hz, 1H), 6.56 (d, *J* = 16.6 Hz, 1H), 2.42 (s, 3H), 0.39 (s, 9H). ¹³C NMR

(101 MHz, CDCl₃) δ 228.3, 199.7, 144.0, 138.1, 137.8, 131.9, 131.1, 127.1, 26.5, -1.5. **HRMS** (ESI) calcd. for C₁₂H₁₇O₂SSi; [M+H]⁺: 253.0713; found 253.0714.

(E)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)pent-1-en-3-one (5t) (NMR Spectra)



Prepared according to General Procedure 2 using ethyl vinyl ketone (1.0 mmol, 2.0 equivs.). Reaction time 2 hours. Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow oil (103 mg, 0.36 mmol, 89%). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 16.2 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.45 (d,

 $J = 16.2 \text{ Hz}, 1\text{H}, 3.88 \text{ (s, 3H)}, 2.77 \text{ (q, } J = 7.3 \text{ Hz}, 2\text{H}), 1.17 \text{ (t, } J = 7.3 \text{ Hz}, 3\text{H}), 0.34 \text{ (s, 9H)}. {}^{13}\text{C} \text{ NMR} (101 \text{ MHz}, \text{CDCI}_3) \delta 237.6, 201.7, 162.0, 143.0, 136.3, 135.0, 133.7, 129.5, 114.4, 113.8, 55.7, 32.9, 8.3, -1.2. HRMS (ESI) calcd. for <math>C_{16}H_{22}O_3\text{SiNa}$; $[\text{M+Na}]^+$: 313.1230; found 313.1232.

(E)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-5-phenylpent-1-en-3-one (5u) (NMR Spectra)



Prepared according to General Procedure 2 using 5-phenylpent-1-en-3-one **S47** (0.75 mmol, 1.5 equivs.). Reaction time 3 hours. Purification by flash column chromatography (15% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a yellow oil (156 mg, 0.40 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 16.2 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.34 –

7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 7.04 – 6.96 (m, 2H), 6.45 (d, *J* = 16.2 Hz, 1H), 3.89 (s, 3H), 3.09 – 3.00 (m, 4H), 0.35 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 237.4, 200.1, 162.0, 143.6, 141.5, 136.2, 135.0, 133.7, 129.5, 128.6, 128.6, 126.2, 114.4, 113.9, 55.7, 41.6, 30.4, -1.2. **HRMS** (ESI) calcd. for C₂₂H₂₇O₃Si; [M+H]⁺: 367.1724; found 367.1725.

(E)-6-chloro-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)hex-1-en-3-one (5v) (NMR Spectra)



Prepared according to General Procedure 2 using 6-chlorohex-1-en-3-one (**S68**) (133 mg, 1.0 mmol, 2.0 equivs.). Reaction time 2 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a yellow oil (149 mg, 0.44 mmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 16.2 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 2.4

Hz, 1H), 7.00 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.46 (d, *J* = 16.2 Hz, 1H), 3.89 (s, 3H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.17 (p, *J* = 6.7 Hz, 2H), 0.35 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 237.5, 199.7, 162.0, 143.7, 136.1, 135.0, 133.7, 129.4, 114.5, 114.0, 55.7, 44.7, 36.5, 27.0, 24.0, -1.2. HRMS (ESI) calcd. for C₁₇H₂₄ClO₃Si; [M+H]⁺: 339.1178; found 339.1176.

(E)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-1,1-diphenylbut-3-en-2-one (5w) (NMR Spectra)



Prepared according to General Procedure 2 using 1,1-diphenylbut-3-en-2-one **S65** (0.75 mmol, 1.5 equivs.). Reaction time 4 hours. Purification by flash column chromatography (5 \rightarrow 10% EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a yellow-green oil (119 mg, 0.28 mmol, 56%). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 15.9 Hz, 1H), 7.51 (d, *J* = 9.1 Hz, 1H), 7.19 – 7.08 (m, 11H), 6.81 – 6.77 (m, 2H), 6.43 (d, *J* = 15.9 Hz, 1H), 5.37 (s, 1H), 3.67 (s, 3H), 0.15 (s, 9H). ¹³C NMR

 $(101 \text{ MHz}, \text{CDCl}_3) \delta 238.1, 197.9, 161.7, 143.5, 138.8, 135.9, 135.6, 132.8, 129.4, 128.8, 128.4, 127.2, 114.3, 113.8, 62.1, 55.7, 27.0, -1.3.$ **HRMS** (ESI) calcd. for C₂₇H₂₉O₃Si; [M+H]⁺: 429.1880; found 429.1880.

(E)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-1-(4-(trifluoromethyl)cyclohexyl)prop-2-en-1-one (5x) (NMR Spectra)



Prepared according to General Procedure 2 using 1-(4-(trifluoromethyl)cyclohexyl)prop-2-en-1-one **S44** (0.75 mmol, 1.5 equivs.). Reaction time 3 hours. Purification by flash column chromatography (10-20% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a yellow oil (101 mg, 0.25 mmol, 49%). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 16.0 Hz, 1H),

7.74 (d, J = 8.5 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H), 6.99 (dd, J = 8.5, 2.6 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 3.89 (s, 3H), 3.12 – 2.87 (m, 1H), 2.20 (dd, J = 9.1, 4.0 Hz, 2H), 2.07 (dd, J = 9.5, 4.2 Hz, 2H), 1.79 – 1.66 (m, 5H), 0.33 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 237.73, 202.41, 161.89, 143.02, 136.12, 135.47, 133.35, 127.34, 114.16, 114.04, 55.72, 43.24, 40.97 (q, $J_{C-F} = 26.5$ Hz), 27.44, 25.59, 21.77 (d, SI30

 $J_{C-F} = 2.5 \text{ Hz}$), -1.23. ¹⁹F NMR (377 MHz, CDCl₃) δ -72.5 (*major*, d, J = 8.6 Hz), -73.8 (*minor*, d, J = 7.9 Hz). HRMS (ESI) calcd. for C₂₂H₂₇O₃Si; [M+H]⁺: 413.1754; found 413.1751.

(E)-4-(4-isobutylphenyl)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)pent-1-en-3-one (5y) (NMR Spectra)



Me

Prepared according to General Procedure 2 using 4-(4-isobutylphenyl)pent-1-en-3-one **S76** (0.75 mmol, 1.5 equivs.). Reaction time 4 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a yellow-orange oil (163 mg, 0.39 mmol, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 16.0

Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.94 (dd, J = 8.4, 2.5 Hz, 1H), 6.91 (d, J = 2.3 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 4.14 (q, J = 6.9 Hz, 1H), 3.83 (s, 3H), 2.43 (d, J = 7.2 Hz, 2H), 1.83 (dp, J = 13.5, 6.7 Hz, 1H), 1.47 (d, J = 6.9 Hz, 3H), 0.89 (s, 3H), 0.87 (s, 3H), 0.31 (s, 9H). ¹³**C** NMR (101 MHz, CDCl₃) δ 238.0, 200.2, 161.7, 142.6, 140.5, 138.2, 135.9, 135.8, 132.8, 129.7, 128.0, 127.9, 114.2, 113.7, 55.6, 50.4, 45.2, 30.3, 27.0, 22.5, 18.2, -1.3. HRMS (ESI) calcd. for C₂₆H₃₅O₃Si; [M+H]⁺: 423.2350; found 423.2351.

(E)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-5-(3,4,5-trimethoxyphenyl)pent-1-en-3-one (5z) (NMR Spectra)



Prepared according to General Procedure 2 using 5-(3,4,5-trimethoxyphenyl)pent-1-en-3one **S59** (0.75 mmol, 1.5 equivs.). Reaction time 4 hours. Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow-green oil (194 mg, 0.43 mmol, 85%). ¹H NMR (400 MHz, CDCl3) δ 7.90 (d, J = 16.2

Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 6.86 – 6.78 (m, 2H), 6.31 (s, 2H), 6.25 – 6.21 (m, 1H), 3.69 (s, 3H), 3.66 (d, J = 8.7 Hz, 6H), 3.63 (s, 3H), 2.87 (t, J = 6.9 Hz, 2H), 2.78 (t, J = 7.0 Hz, 2H), 0.15 (s, 9H). ¹³**C** NMR (101 MHz, CDCl3) δ 237.3, 200.0, 162.0, 153.3, 143.6, 137.2, 136.4, 136.1, 134.8, 133.8, 129.4, 114.3, 113.9, 105.6, 60.9, 56.2, 55.7, 41.6, 30.9, -1.2. HRMS (ESI) calcd. for C₂₅H₃₃O₆Si; [M+H]⁺: 457.2041; found 457.2043.

(E)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-1-(1-phenylcyclopropyl)prop-2-en-1-one (5aa) (NMR Spectra)



Prepared according to General Procedure 2 using 1-(1-phenylcyclopropyl)prop-2-en-1-one **S50** (0.75 mmol, 1.5 equivs.). Reaction time 3 hours. Purification by flash column chromatography (15% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a yellow solid (155 mg, 0.41 mmol, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 15.5 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.39 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.35 (dd, *J* = 9.9, 4.8 Hz, 2H), 7.29 (dt, *J* = 5.3, 2.1 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.41 (d, *J* = 15.5 Hz, 1H), 3.78 (s, 3H), 1.73 (dd, *J* = 6.9, 3.5 Hz, 2H), 1.26 (dd, *J* = 6.9, 3.6 Hz, 2H),

0.30 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 237.9, 199.0, 161.5, 142.3, 140.8, 136.3, 132.5, 130.9, 128.8, 127.5, 125.5, 114.1, 113.8, 55.5, 37.5, 19.3, -1.3. HRMS (ESI) calcd. for C₂₃H₂₇O₃Si; [M+H]⁺: 379.1724; found 379.1726.

(*E*)-1-((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)prop-2-en-1-one (5ab) (<u>NMR Spectra</u>)



Prepared according to General Procedure 2 using 1-((1R,4aS,10aR) 7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a- octahydrophenanthren-1-yl)prop-2-en-1-one **S81** (0.75 mmol, 1.5 equivs.). Reaction time 5 hours. Purification by flash column chromatography (5% EtOAc/petroleum benzine; R_f ~ 0.3) afforded the title compound as a yellow semi-solid (142 mg, 0.28 mmol, 55%). ¹H NMR (400 MHz,

CDCl₃) δ 7.97 (d, *J* = 15.3 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.98 (m, 4H), 6.87 (s, 1H), 3.88 (s, 3H), 2.88 – 2.81 (m, 3H), 2.36 (d, *J* = 12.8 Hz, 1H), 2.21 (dd, *J* = 12.4, 1.8 Hz, 1H), 1.85 – 1.72 (m, 4H), 1.58 – 1.52 (m, 2H), 1.48 – 1.41 (m, 1H), 1.30 (s, 3H), 1.26 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H), 0.32 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 238.1, 204.2, 161.7, 147.1, 145.9, 143.1, 136.5,

135.0, 132.4, 127.2, 124.2, 124.1, 123.7, 114.3, 113.6, 66.0, 55.7, 51.4, 44.1, 38.3, 37.1, 35.3, 33.6, 30.2, 25.4, 24.1, 21.4, 18.7, 16.1, 15.4, -1.3. **HRMS** (ESI) calcd. for C₃₃H₄₅O₃Si; [M+H]⁺: 517.3132; found 517.3125.

(E)-1-(4,4-difluorocyclohexyl)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)prop-2-en-1-one (S14) (NMR Spectra)



Prepared according to General Procedure 2 using 1-(4,4-difluorocyclohexyl)prop-2-en-1-one **S41** (0.75 mmol, 1.5 equivs.). Reaction time 5 hours. Purification by flash column chromatography (10 \rightarrow 20% EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a yellow oil (101 mg, 0.27 mmol, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 16.1 Hz, 1H), 7.78 (d, *J* = 8.4 Hz,

1H), 7.04 (d, J = 2.5 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.49 (d, J = 16.1 Hz, 1H), 3.90 (s, 3H), 2.90 (dd, J = 9.8, 3.7 Hz, 1H), 2.26 – 2.13 (m, 2H), 2.07 – 1.99 (m, 2H), 1.92 – 1.79 (m, 4H), 0.34 (s, 9H). ¹³**C** NMR (101 MHz, CDCl₃) δ 237.6, 201.8, 162.0, 143.8, 136.1, 135.2, 133.6, 127.5, 123.0 (t, $J_{C-F} = 239$ Hz), 114.3, 114.1, 55.8, 45.2, 33.0 (dd, $J_{C-F} = 25.1$, 23.8 Hz), 25.3 (d, $J_{C-F} = 10.1$ Hz), -1.2. ¹⁹F NMR (377 MHz, CDCl₃) δ -93.2 (d, J = 235.9 Hz), -100.2 (d, J = 235.3 Hz). HRMS (ESI) calcd. for C₂₀H₂₇F₂O₃Si; [M+H]⁺: 381.1692; found 381.1694.

(E)-5-methoxy-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)pent-1-en-3-one (S15) (NMR Spectra)



Prepared according to General Procedure 2 using 5-methoxypent-1-en-3-one (**S62**) (114 mg, 1.0 mmol, 2.0 equivs.). Reaction time 2 hours. Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow oil (141 mg, 0.44 mmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 16.2 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.03 (s,

1H), 6.99 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.47 (d, *J* = 16.2 Hz, 1H), 3.88 (s, 3H), 3.77 (t, *J* = 6.5 Hz, 2H), 3.37 (s, 3H), 3.01 (t, *J* = 6.5 Hz, 2H), 0.34 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 237.5, 199.0, 162.0, 143.9, 136.1, 135.1, 133.6, 129.7, 114.5, 113.9, 68.0, 59.0, 55.7, 39.8, -1.2. HRMS (ESI) calcd. for C₁₇H₂₅O₄Si; [M+H]⁺: 321.1517; found 321.1511.

tert-butyl (*E*)-4-(4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-2-oxobut-3-en-1-yl)piperidine-1-carboxylate (S16) (<u>NMR</u> <u>Spectra</u>)



Prepared according to General Procedure 2 using *tert*-butyl 4-(2-oxobut-3-en-1-yl)piperidine-1-carboxylate **S56** (0.75 mmol, 1.5 equivs.). Reaction time 5 hours. Purification by flash column chromatography (15% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a yellow oil (158 mg, 0.34 mmol, 68%). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* =

16.2 Hz, 1H), 7.59 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 2.5 Hz, 1H), 6.81 (d, J = 8.5 Hz, 1H), 6.24 (d, J = 16.2 Hz, 1H), 3.87 (m, 2H), 3.69 (s, 3H), 2.56 (t, J = 11.7 Hz, 2H), 2.46 (d, J = 6.7 Hz, 2H), 1.99 – 1.87 (m, 1H), 1.53 (d, J = 12.7 Hz, 2H), 1.26 (s, 9H), 1.01 (ddd, J = 24.7, 12.5, 4.2 Hz, 3H), 0.15 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 237.5, 200.2, 162.0, 155.0, 143.6, 136.1, 134.9, 133.8, 129.9, 114.4, 113.9, 79.4, 55.7, 46.2, 32.6, 32.3, 28.6, -1.2. HRMS (ESI) calcd. for C₂₅H₃₈NO₅Si; [M+H]⁺: 460.2514; found 460.2513.

(E)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-1-(tetrahydro-2H-pyran-4-yl)prop-2-en-1-one (S17) (NMR Spectra)



Prepared according to General Procedure 2 using 1-(tetrahydro-2H-pyran-4-yl)prop-2-en-1-one **S71** (0.75 mmol, 1.5 equivs.). Reaction time 5 hours. Purification by flash column chromatography (20 \rightarrow 30% EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a yellow-green oil (109 mg, 0.31 mmol, 65%). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 16.1 Hz, 1H), 7.76 (d, *J* = 8.5 Hz,

1H), 7.03 (d, *J* = 2.5 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.49 (d, *J* = 16.1 Hz, 1H), 4.04 (dt, *J* = 11.3, 3.4 Hz, 2H), 3.89 (s, 3H), 3.52 (ddd, *J* = 8.4, 8.0, 4.1 Hz, 2H), 3.02 (ddd, *J* = 10.1, 8.3, 5.3 Hz, 1H), 1.88 – 1.80 (m, 4H), 0.33 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 237.6, 201.6, 161.9, 143.6, 136.2, 135.3, 133.5, 127.4, 114.3, 114.1, 67.4, 55.7, 44.5, 28.7, -1.2. HRMS (ESI) calcd. for C₁₉H₂₇O₄Si; [M+H]⁺: 347.1673; found 347.1672.

tert-butyl (E)-3-(3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)acryloyl)piperidine-1-carboxylate (S18) (NMR Spectra)



Prepared according to General Procedure 2 using *tert*-butyl 3-acryloylpiperidine-1-carboxylate **S38** (0.75 mmol, 1.5 equivs.). Reaction time 5 hours. Purification by flash column chromatography (10 \rightarrow 20% EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a yellow oil (152 mg, 0.34 mmol, 68%). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 16.0 Hz, 1H),

7.76 (d, *J* = 8.5 Hz, 1H), 7.06 – 6.96 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.06 (m, 2H), 3.89 (s, 3H), 2.94 (d, *J* = 7.3 Hz, 2H), 2.77 – 2.69 (m, 1H), 2.12 (m, 1H), 1.75 (m, 1H), 1.58 (m, 2H), 1.45 (s, 9H), 0.33 (s, 9H).¹³**C NMR** (101 MHz, CDCl₃) δ 237.4, 201.3, 162.0, 160.5, 154.9, 144.0, 136.1, 127.6, 122.3, 114.4, 114.0, 104.8, 95.3, 79.8, 55.7, 48.6, 46.2, 28.6, 24.8, -1.2. **HRMS** (ESI) calcd. for C₂₄H₃₆NO₅Si; [M+H]⁺: 446.2357; found 446.2354.

(E)-1-((1R,2S,4R)-bicyclo[2.2.1]hept-5-en-2-yl)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)prop-2-en-1-one (S19) (NMR Spectra)



Prepared according to General Procedure 2 using 1-((1*R*,2*S*,4*R*)-bicyclo[2.2.1]hept-5-en-2-yl)prop-2-en-1-one **S53** (0.75 mmol, 1.5 equivs.). Reaction time 2 hours. Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \approx 0.2$) afforded the title compound as a yellow solid (85 mg, 0.24 mmol, 48%). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 16.1 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 6.17 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.90 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.89 (s, 3H), 3.48 – 3.41 (m, 1H), 3.37 (s, 1H), 2.94 (s, 1H), 1.89 (ddd, *J* = 11.8, 9.0, 3.7 Hz, 1H), 5.90 (dd, *J* = 11.8, 9.0, 3.7 Hz, 1H), 5.90 (dd, *J* = 10.1 Hz, 1H), 5.90 (dd, *J* = 10.1 Hz, 1H), 5.90 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.90 (dd, *J* = 5.6, 2.8 Hz, 1H), 5.90 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.90 (dd, *J* = 5.6, 2.8 Hz, 1H), 5.90 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.90 (dd, *J* = 5.6, 2.8 Hz, 1H), 5.90 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.90 (dd, *J* = 5.6, 2.8 Hz, 1H), 5.90 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.90 (dd, *J* = 5.6, 2.8 Hz, 1H), 5.90 (dd, *J* = 5.6, 3.1 Hz, 1Hz, 1H), 5.6 (dd) (dd) (dd) (dd) (dd) (dd) (dd)

1H), 1.60 (ddd, J = 11.6, 4.3, 2.6 Hz, 1H), 1.51 – 1.46 (m, 1H), 1.44 – 1.38 (m, 1H), 0.34 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 237.9, 200.9, 161.9, 142.3, 137.4, 136.3, 135.5, 133.2, 132.1, 129.3, 114.2, 113.8, 55.7, 50.1, 49.4, 46.6, 43.0, 28.5, -1.2. **HRMS** (ESI) calcd. for C₂₁H₂₇O₃Si; [M+H]⁺: 355.1724; found 355.1725.

Photochemical synthesis of benzocyclobutenone silyl enol ethers:

General Procedure 3:



An oven dried vial equipped with a stir bar was charged with olefinated acylsilane (0.1 mmol) followed by PhMe (1 mL, 0.1M, dried on 3Å molecular sieves). The yellow solution was degassed by sparging with nitrogen for 5 minutes, before the vial was capped, sealed with parafilm and irradiated (2 x 427nm Kessil lamps, approximate distance from lamp = 5 cm) overnight with stirring. The vials were maintained at approximately room temperature by an overhead cooling fan. The resultant colourless solution was concentrated to afford the silyl enol ether products, which in most cases could be further purified by flash column chromatography on silica gel neutralized with NEt₃.

(Z)-3-methoxy-8-(2-((trimethylsilyl)oxy)prop-1-en-1-yl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6b) (NMR Spectra)

 $\begin{array}{c} \label{eq:constraint} \text{Prepared} & \text{according} & \text{to} & \text{General} & \text{Procedure} & 3 & \text{using} & (E)-4-(5-\text{methoxy-2-} \\ ((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one ($ **5b** $) (0.10 mmol). 74% ^{1}H NMR yield. Attempts to \\ purify this compound by chromatography led to hydrolysis. ^{1}H NMR (400 MHz, d_8-PhMe) & 7.31 (d, J \\ = 8.3 \text{ Hz}, 1\text{ H}), 6.94 (d, J = 2.2 \text{ Hz}, 1\text{ H}), 6.78 (dd, J = 8.3, 2.3 \text{ Hz}, 1\text{ H}), 5.01 (d, J = 2.4 \text{ Hz}, 1\text{ H}), 4.12 (d, J = 2.3 \text{ Hz}, 1\text{ H}), 3.30 (s, 7\text{ H}), 1.54 (s, 3\text{ H}), 0.20 (s, 9\text{ H}). ^{13}C NMR (101 \text{ MHz}, \text{CDCl}_3) & 207.7, 159.4, 156.9, 141.4, 134.5, 119.4, 113.7, 109.9, 103.0, 60.3, 55.6, 24.9, 0.00. \end{array}$

(Z)-3-methoxy-8-(2-((triethylsilyl)oxy)prop-1-en-1-yl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6c) (NMR Spectra)

Prepared according to General Procedure 3 using (*E*)-4-(5-methoxy-2-((triethylsilyl)carbonyl)phenyl)but-3-en-2-one (**5c**) (0.10 mmol). 91% ¹H NMR yield. The product was isolated by flash column chromatography on neutralised silica gel (10% EtOAc/petroleum benzine, 1% NEt₃) as a colourless oil (28.7 mg, 0.09 mmol, 91%). ¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, *J* = 8.2 Hz, 1H), 6.74 – 6.66 (m, 2H), 5.02 (d, *J* = 2.4 Hz, 1H), 3.93 (d, *J* = 2.2 Hz, 1H), 3.58 (s, 3H), 1.53 (s, 3H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 207.9, 159.5, 157.2, 141.5, 134.6, 119.5, 113.8, 109.9, 102.6, 60.4, 55.7, 24.9, 6.7, 4.9.

This reaction was repeated several times using 1.0 mmol of **8c** to obtain larger quantities of **9b** for further studies (yields 90%, 85%, 92%, 97%, 70%). The crude TES, TIPS and TBS silyl enol ethers can typically be used in further reactions without purification.

(Z)-3-methoxy-8-(2-((triisopropylsilyl)oxy)prop-1-en-1-yl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6d) (NMR Spectra)

Prepared according to General Procedure 3 using (*E*)-4-(5-methoxy-2i/Pr₃ ((triethylsilyl)carbonyl)phenyl)but-3-en-2-one (**5d**) (0.10 mmol). 99% ¹H NMR yield. The product was isolated by flash column chromatography on neutralised silica gel (10% EtOAc/petroleum benzine,

1% NEt₃) as a colourless oil (35.0 mg, 0.097 mmol, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 8.4 Hz, 1H), 6.95 – 6.90 (m, 2H), 5.23 (d, *J* = 2.4 Hz, 1H), 4.16 (d, *J* = 2.1 Hz, 1H), 3.82 (s, 3H), 1.76 (s, 3H), 1.38 – 1.28 (m, 3H), 1.15 (d, *J* = 7.3 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 208.2, 159.5, 157.3, 141.5, 134.8, 119.6, 113.9, 109.9, 102.2, 60.4, 55.9, 25.1, 18.1, 12.6.

(Z)-8-(2-((tert-butyldimethylsilyl)oxy)prop-1-en-1-yl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (6e) (NMR Spectra)

Prepared according to General Procedure 3 using (*E*)-4-(2-((*tert*-butyldimethylsilyl)carbonyl)-5methoxyphenyl)but-3-en-2-one (**5e**) (0.10 mmol). 82% ¹H NMR yield. The product was isolated by flash column chromatography on neutralised silica gel (10% EtOAc/petroleum benzine, 1% NEt₃) as a colourless oil (25.2 mg, 0.079 mmol, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 1H), 6.91 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.24 (d, *J* = 2.4 Hz, 1H), 4.16 (d, *J* = 2.2 Hz, 1H), 3.81 (s, 3H), 1.77 (s, 3H), 1.03 (s, 9H), 0.27 (d, *J* = 3.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 207.9, 159.4, 157.1, 141.4, 134.6, 119.4, 113.7, 109.8, 102.8, 60.3, 55.6, 25.7, 25.6, 25.0, 18.2.

Photochemical synthesis of Cyclobutanone-1,4-diones:

General Procedure 4:

MeC



An oven dried vial equipped with a stir bar was charged with olefinated acylsilane (0.1 mmol) followed by PhMe (1 mL, 0.1M, dried on 3Å molecular sieves). The yellow solution was degassed by sparging with nitrogen for 5 minutes, before the vial was capped, sealed with parafilm and irradiated (2 x 427nm Kessil lamps, approximate distance 5 cm) overnight with stirring. The vials were held at approximately room temperature by an overhead cooling fan. To the resultant colourless solution was added aqueous 1M HCl (1 mL) and the biphasic mixture was stirred vigorously for 1 hour. The aqueous layer was extracted three times with EtOAc (3 x 3 mL), the combined organic layers were dried on MgSO₄ and filtered. The mixture was concentrated *in vacuo* and purified by flash column chromatography to afford the 1,4-dione products.

3-(tert-butyl)-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6a') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(5-(*tert*-butyl)-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one **5a** (31.0 mg, 0.1 mmol). Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless oil (20.3 mg, 0.089 mmol, 89%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.6 Hz, 1H), 7.55 – 7.49 (m, 2H), 4.35 –

4.28 (m, 1H), 2.89 (dd, J = 5.6, 1.8 Hz, 2H), 2.21 (s, 3H), 1.36 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 206.2, 203.7, 159.7, 151.8, 134.4, 126.7, 124.1, 123.0, 52.3, 39.8, 35.8, 31.3, 27.8. **HRMS** (ESI) calcd. for C₁₅H₁₉O₂; [M+H]⁺: 231.1370; found 231.1370.

3-methoxy-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6b') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one **5b** (27.6 mg, 0.10 mmol). Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless solid (14.3 mg, 0.070 mmol, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.94 (d, *J* = 1.7 Hz, 1H), 4.26 (dd, *J* =

7.1, 4.3 Hz, 1H), 3.88 (s, 3H), 2.90 – 2.84 (m, 2H), 2.19 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 206.0, 202.2, 165.7, 154.3, 130.1, 126.1, 116.6, 110.1, 56.0, 52.2, 39.7, 27.5. **HRMS** (ESI) calcd. for C₁₂H₁₃O₃; [M+H]⁺: 205.0859; found 205.0857.

3-(benzyloxy)-4-chloro-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6h') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(5-(benzyloxy)-4-chloro-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one **5h** (38.7 mg, 0.1 mmol). Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless oil (25.1 mg, 0.079 mmol, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.48 – 7.38 (m, 5H), 7.03 (s, 1H), 5.26

(s, 2H), 4.21 (dd, *J* = 7.8, 3.6 Hz, 1H), 2.97 – 2.82 (m, 2H), 2.13 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.5, 201.1, 159.6, 152.0, 135.3, 130.4, 129.0, 128.6, 127.2, 126.1, 125.8, 110.1, 71.3, 52.0, 39.7, 27.5. **HRMS** (ESI) calcd. for C₁₈H₁₆O₃Cl; [M+H]⁺: 315.0783; found 315.0783.

3-methyl-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6i') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(5-methyl-2-((trimethylsilyl)carbonyl)phenyl)but-3en-2-one **5i** (26.1 mg, 0.1 mmol). Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless solid (17.9 mg, 0.095 mmol, 95%). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.33 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 4.29 (t, *J* = 5.7 Hz, 1H), 2.90 – 2.87

(m, 2H), 2.46 (s, 3H), 2.22 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 206.1, 203.7, 152.0, 146.6, 134.5, 130.2, 126.8, 124.3, 52.0, 39.7, 27.9, 22.3. HRMS (ESI) calcd. for C₁₂H₁₂O₂Na; [M+Na]⁺: 221.0730; found 221.0730.

6-(2-oxopropyl)cyclobuta[4,5]benzo[1,2-d][1,3]dioxol-5(6H)-one (6j') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(6-((trimethylsilyl)carbonyl)benzo[d][1,3]dioxol-5yl)but-3-en-2-one **5j** (29.0 mg, 0.1 mmol). Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless solid (16.8 mg, 0.077 mmol, 77%). ¹H NMR (401 MHz, CDCl₃) δ 7.06 (d, *J* = 7.9 Hz, 1H), 6.95 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.16 (dd, *J* = 4.9, 1.2

Hz, 2H), 4.29 (dd, *J* = 6.8, 4.5 Hz, 1H), 2.90 (dd, *J* = 5.7, 3.5 Hz, 2H), 2.22 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.6, 201.1, 148.8, 144.1, 143.2, 119.6, 118.6, 114.4, 103.3, 51.8, 40.3, 27.6. **HRMS** (ESI) calcd. for C₁₂H₁₀O₄Na; [M+Na]⁺: 241.0471; found 241.0474.

3-(methylthio)-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6k') (NMR Spectra)



PreparedaccordingtoGeneralProcedure4using(E)-4-(5-(methylthio)-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one**5k**(29.3 mg, 0.1 mmol).Purificationby flash columnchromatography(30% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a colourless solid(6.2 mg, 0.028 mmol, 28%).**1H NMR**(400 MHz, CDCl₃) δ 7.68 (d, J = 8.9 Hz, 1H), 7.32 – 7.26 (m, 2H), 4.34 –

4.18 (m, 1H), 2.89 (dd, J = 5.8, 1.8 Hz, 2H), 2.54 (s, 3H), 2.22 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.8, 202.7, 152.1, 149.3, 133.4, 126.1, 124.4, 121.9, 52.0, 39.6, 27.8, 15.0. **HRMS** (ESI) calcd. for C₁₂H₁₃O₂S; [M+H]⁺: 221.0631; found 221.0632.

(Z)-3-chloro-8-(2-((triethylsilyl)oxy)prop-1-en-1-yl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6l) (NMR Spectra)



This compound resisted hydrolysis and was isolated as the stable triethylsilyl enol ether. Prepared according to General Procedure 4 using (*E*)-4-(5-chloro-2-((triethylsilyl)carbonyl)phenyl)but-3-en-2-one **5I** (32.3 mg, 0.1 mmol). Purification by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.5$) afforded the title compound as a colourless oil (29.1 mg, 0.090 mmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.29 (m,

3H), 5.38 (d, *J* = 2.4 Hz, 1H), 4.19 (d, *J* = 2.3 Hz, 1H), 1.79 (s, 3H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.81 (q, *J* = 7.6 Hz, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 206.5, 156.6, 141.2, 140.3, 132.9, 128.1, 124.5, 119.8, 105.0, 60.2, 25.5, 6.7, 5.0. **HRMS** (ESI) calcd. for C₁₁H₁₀ClO₂ (hydrolysis product); [M+H]⁺: 209.0364; found 209.0359.

3-(3-fluorophenyl)-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6m') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(3'-fluoro-4-((trimethylsilyl)carbonyl)-[1,1'biphenyl]-3-yl)but-3-en-2-one **5m** (34.1 mg, 0.1 mmol). Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless solid (15.5 mg, 0.058 mmol, 58%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.52 (dd, *J* = 8.0, 1.0

Hz, 1H), 7.33 – 7.22 (m, 2H), 7.19 – 7.13 (m, 1H), 6.97 (tdd, J = 8.4, 2.5, 1.1 Hz, 1H), 4.25 (t, J = 5.7 Hz, 1H), 2.81 (d, J = 5.8 Hz, 2H), 2.13 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.6, 203.4, 164.6, 162.1, 152.2, 147.0 (d, $J_{C-F} = 2.2$ Hz), 142.1 (d, $J_{C-F} = 7.6$ Hz), 136.1, 130.8 (d, $J_{C-F} = 8.4$ Hz), 128.3, 125.1, 124.9, 123.4 (d, $J_{C-F} = 2.9$ Hz), 115.1 (dd, $J_{C-F} = 97.6$, 21.7 Hz), 52.1, 39.8, 28.2. ¹⁹F NMR (377 MHz, CDCl₃) δ -112.2 (td, J = 9.0, 6.0 Hz). **HRMS** (ESI) calcd. for C₁₇H₁₄FO₂; [M+H]⁺: 269.0972; found 269.0969.

2-(2-oxopropyl)cyclobuta[b]naphthalen-1(2H)-one (6n') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(3-((trimethylsilyl)carbonyl)naphthalen-2-yl)but-3-en-2-one **5n** (31.0 mg, 0.1 mmol). Purification by flash column chromatography ($30 \rightarrow 50\%$ EtOAc/petroleum benzine; R_f ~ 0.2) afforded the title compound as a colourless solid (21.9 mg, 0.049 mmol, 49%). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.99 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.59

- 7.53 (m, 1H), 4.53 (dd, J = 8.2, 3.6 Hz, 1H), 3.03 (qd, J = 19.0, 6.1 Hz, 2H), 2.30 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.6, 204.1, 144.1, 137.0, 133.8, 132.9, 130.4, 129.1, 128.1, 127.0, 125.3, 125.1, 51.7, 40.0, 27.8. **HRMS** (ESI) calcd. for C₁₅H₁₂O₂Na; [M+Na]⁺: 247.0730; found 247.0731.

3-fluoro-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6o') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(5-fluoro-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2one **50** (26.5 mg, 0.1 mmol). Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim$ 0.2) afforded the title compound as a colourless oil (17.3 mg, 0.090 mmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.23 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.20 – 7.14 (m, 1H), 4.32 (t, *J* = 5.8 Hz, 1H), 2.93 (d, *J* =

5.8 Hz, 2H), 2.28 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 204.9, 201.9, 168.5, 165.9, 154.0 (d, $J_{C-F} = 9.9$ Hz), 133.3, 126.7 (d, $J_{C-F} = 10.5$ Hz), 115.43 (dd, $J_{C-F} = 365.0$, 23.4 Hz), 51.7 (d, $J_{C-F} = 2.1$ Hz), 39.7, 28.3. ¹⁹**F NMR** (377 MHz, CDCl₃) δ -101.4 (dd, J = 13.8, 8.4 Hz). **HRMS** (ESI) calcd. for C₁₁H₁₀FO₂; [M+H]⁺: 193.0659; found 193.0661.
3-(but-3-en-1-yloxy)-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6p') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(5-(but-3-en-1-yloxy)-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one **5p** (31.7 mg, 0.1 mmol). Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless oil (12.4 mg, 0.061 mmol, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.94 (s, 1H), 5.89 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.16 (ddd, *J* = 13.7, 11.6, 1.5 Hz, 2H), 4.25 (dd, *J* = 6.9, 4.5 Hz, 1H),

4.09 (td, J = 6.6, 1.5 Hz, 2H), 2.93 – 2.83 (m, 2H), 2.57 (dt, J = 6.7, 3.9 Hz, 2H), 2.19 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 206.0, 202.2, 165.0, 154.3, 133.9, 130.0, 126.1, 117.7, 116.9, 110.7, 68.0, 52.2, 39.7, 33.5, 27.5. **HRMS** (ESI) calcd. for C₁₅H₁₇O₃; [M+H]⁺: 245.1172; found 245.1173.

7-oxo-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-3-yl cyclopropanecarboxylate (6q') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-3-(3-oxobut-1-en-1-yl)-4-((trimethylsilyl)carbonyl)phenyl cyclopropanecarboxylate **5q** (66.1 mg, 0.2 mmol). Purification by flash column chromatography (50% EtOAc/petroleum benzine; $R_f \sim 0.4$) afforded the title compound as a colourless oil (31.0 mg, 0.12 mmol, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.3 Hz, 1H), 7.32 (s, 1H),

7.19 (dd, J = 8.3, 1.8 Hz, 1H), 4.32 (dd, J = 7.1, 4.3 Hz, 1H), 2.94 – 2.89 (m, 2H), 2.25 (s, 3H), 1.88 – 1.82 (m, 1H), 1.20 – 1.15 (m, 2H), 1.09 – 1.03 (m, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.1, 202.5, 172.9, 156.2, 152.9, 134.2, 125.6, 122.9, 119.7, 51.8, 39.6, 28.2, 13.2, 9.8, 9.7. **HRMS** (ESI) calcd. for C₁₅H₁₄O₄Na; [M+Na]⁺: 281.0784; found 281.0783.

6-(2-oxopropyl)-2-thiabicyclo[3.2.0]hepta-1(5),3-dien-7-one (6s') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(2-((trimethylsilyl)carbonyl)thiophen-3-yl)but-3-en-2-one **5s** (25.2 mg, 0.1 mmol). Purification by flash column chromatography (40% EtOAc/petroleum benzine; $R_f \sim 0.5$) afforded the title compound as a yellow oil (8.8 mg, 0.049 mmol, 49%). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 4.8 Hz, 1H), 7.16 (d, *J* = 4.8 Hz, 1H), 4.26 (dd, *J* = 7.1, 2.7 Hz, 1H), 3.21 (ddd, *J* = 25.6, 18.5, 5.0 Hz, 2H), 2.31 (s, 3H). ¹³C NMR (101

MHz, CDCl₃) δ 203.9, 194.3, 164.1, 141.0, 123.7, 50.2, 43.4, 29.7, 29.4. **HRMS** (ESI) calcd. for C₉H₉O₂S; [M+H]⁺: 181.0318; found 181.0320.

3-methoxy-8-(2-oxobutyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6t') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)pent-1-en-3-one **5t** (31.7 mg, 0.1 mmol). Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless oil (10.0 mg, 0.080 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 4.32 – 4.23 (m,

1H), 3.89 (s, 3H), 2.87 (dd, *J* = 5.7, 1.7 Hz, 2H), 2.63 – 2.47 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 208.8, 202.4, 165.6, 154.6, 130.2, 126.1, 116.4, 110.0, 56.0, 51.3, 40.0, 34.0, 8.0. HRMS (ESI) calcd. for C₁₃H₁₅O₃; [M+H]⁺: 219.1016; found 219.1014.

3-methoxy-8-(2-oxo-4-phenylbutyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6u') (NMR Spectra)



Ρh

Prepared according to General Procedure 4 using (*E*)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-5-phenylpent-1-en-3-one **5u** (36.7 mg, 0.1 mmol). Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless oil (26.5 mg, 0.090 mmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* =

8.5 Hz, 1H), 7.06 – 7.02 (m, 2H), 7.00 – 6.98 (m, 1H), 6.93 – 6.90 (m, 2H), 6.76 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.59 (d, *J* = 1.9 Hz, 1H), 4.04 (dd, *J* = 7.8, 3.6 Hz, 1H), 3.63 (s, 3H), 2.72 – 2.55 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 207.3, 202.3, 165.6, 154.2, 140.6, 130.1, 128.7, 128.5, 126.5, 126.1, 116.6, 109.9, 55.9, 51.7, 42.1, 39.6, 29.9. HRMS (ESI) calcd. for C₁₉H₁₉O₃; [M+H]⁺: 295.1329; found 295.1326.

8-(5-chloro-2-oxopentyl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (6v') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-6-chloro-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)hex-1-en-3-one (**5v**) (33.9 mg, 0.10 mmol), Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound

as a beige solid (24.5 mg, 0.092 mmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.94 (s, 1H), 4.31 (t, *J* = 5.6 Hz, 1H), 3.89 (s, 3H), 3.55 (t, *J* = 6.1 Hz, 2H), 2.88 (d, *J* = 5.8 Hz, 2H), 2.83 (dd, *J* = 12.6, 5.7 Hz, 1H), 2.66 (dt, *J* = 18.3, 6.7 Hz, 1H), 2.13 – 2.00 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 207.2, 202.2, 165.6, 154.2, 130.0, 126.1, 116.7, 109.8, 56.0, 51.5, 44.3, 39.8, 37.5, 26.2. HRMS (ESI) calcd. for C₁₄H₁₅ClNaO₃; [M+Na]⁺: 289.0602; found 289.0608.

3-methoxy-8-(2-oxo-3,3-diphenylpropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6w') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-1,1-diphenylbut-3-en-2-one **5w** (42.9 mg, 0.1 mmol). Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded the title compound as a colourless oil (30.6 mg, 0.086 mmol, 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* =

8.5 Hz, 1H), 7.29 – 7.17 (m, 8H), 7.11 – 7.05 (m, 2H), 6.88 (dd, J = 8.5, 2.1 Hz, 1H), 6.55 (d, J = 1.7 Hz, 1H), 5.16 (s, 1H), 4.39 (t, J = 5.7 Hz, 1H), 3.65 (s, 3H), 2.76 (d, J = 6.0 Hz, 2H). ¹³**C** NMR (101 MHz, CDCl₃) δ 206.2, 202.1, 165.5, 154.4, 137.8, 130.4, 129.1, 129.1, 129.0, 129.0, 127.8, 127.7, 126.0, 117.1, 109.9, 62.6, 55.8, 51.6, 40.3. **HRMS** (ESI) calcd. for C₂₄H₂₁O₃; [M+H]⁺: 357.1485; found 357.1486.

3-methoxy-8-(2-oxo-2-(4-(trifluoromethyl)cyclohexyl)ethyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6x') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-1-(4-(trifluoromethyl)cyclohexyl)prop-2-en-1-one (**5x**) (41.3 mg, 0.10 mmol), Purification by flash column chromatography 30% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as a colourless oil (22.1 mg, 0.065 mmol, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.85 (d, *J* = 1.7 Hz, 1H),

4.46 (dd, J = 7.7, 3.7 Hz, 1H), 3.88 (s, 3H), 2.91 (dd, J = 8.9, 4.5 Hz, 1H), 2.88 – 2.75 (m, 2H), 2.16 – 2.03 (m, 3H), 1.84 – 1.68 (m, 4H), 1.66 – 1.58 (m, 2H). ¹³**C** NMR (101 MHz, CDCl₃) δ 210.3, 165.4, 154.6, 130.1, 125.9, 116.0, 110.0, 55.8, 48.9, 44.9, 40.5, 40.2, 25.2, 25.1, 21.6 (apparent dt, $J_{C-F} = 5.0$, 2.3 Hz). ¹⁹**F** NMR (376 MHz, CDCl₃) δ -72.25 (d, J = 7.9 Hz). HRMS (ESI) calcd. for C₁₈H₂₀F₃O₃; [M+H]⁺: 341.1359; found 341.1352.

8-(3-(4-isobutylphenyl)-2-oxobutyl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (6y') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(4-isobutylphenyl)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)pent-1-en-3-one **5y** (42.3 mg, 0.1 mmol). Purification by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \simeq 0.3$) afforded the title compound as a colourless oil (31.5 mg, 0.090 mmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.5 Hz, 1H), 7.19 (q, *J* = 8.2 Hz, 4H), 7.07 (d, *J* = 4.1 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.2 Hz,

1H), 4.37 (dd, J = 8.1, 3.6 Hz, 1H), 3.92 (q, J = 6.9 Hz, 1H), 3.73 (s, 3H), 2.72 (ddd, J = 22.2, 18.5, 6.0 Hz, 2H), 2.47 (d, J = 7.2 Hz, 2H), 1.85 (dd, J = 13.5, 6.7 Hz, 1H), 1.43 (d, J = 6.8 Hz, 3H), 0.92 (s, 3H), 0.90 (s, 3H). ¹³**C** NMR (101 MHz, CDCl₃) δ 209.1, 202.1, 165.3, 155.2, 141.4, 136.3, 130.4, 130.0, 128.1, 125.5, 116.6, 109.6, 55.6, 52.3, 49.2, 45.0, 41.0, 30.2, 22.4, 17.9. HRMS (ESI) calcd. for C₂₃H₂₇O₃ [M+H]⁺: 351.1955; found 351.1958.

3-methoxy-8-(2-oxo-4-(3,4,5-trimethoxyphenyl)butyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6z') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-5-(3,4,5-trimethoxyphenyl)pent-1-en-3-one **5z** (45.7 mg, 0.10 mmol), Purification by flash column chromatography (50% EtOAc/petroleum benzine; $R_f \sim 0.3$) afforded the title compound as an orange semi-solid (34.6 mg, 0.090 mmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.5 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.75 (d, *J* = 1.9 Hz, 1H), 6.29 (s, 2H), 4.23 (dd, *J* = 7.4, 3.8 Hz, 1H), 3.82 (s, 3H),

3.80 (s, 3H), 3.79 (s, 6H), 2.88 – 2.81 (m, 4H), 2.79 – 2.65 (m, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 207.2, 202.3, 165.5, 154.0, 153.3, 136.4, 130.0, 126.0, 116.4, 110.0, 105.4, 60.9, 56.2, 55.9, 51.8, 42.0, 39.6, 38.7, 30.2. **HRMS** (ESI) calcd. for C₂₃H₂₆NaO₆; [M+H]⁺: 407.1465; found 407.1468.

3-methoxy-8-(2-oxopropyl-1-d)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6ac') (NMR Spectra)



Prepared according to General Procedure 4 using (*E*)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one **5b** (27.6 mg, 0.10 mmol), except that a mixture of DCl (37%, 2 drops) in D_2O (1 mL) was used to perform hydrolysis of the intermediate (trimethyl)silyl enol ether. Purification by flash column chromatography (30% EtOAc/petroleum benzine; $R_f \sim 0.2$) afforded

the title compound as a pale-yellow semi-solid (17.0 mg, 0.083 mmol, 83%). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.5 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.94 (s, 1H), 4.26 (d, *J* = 6.6 Hz, 1H), 3.89 (s, 3H), 2.90 – 2.83 (m, 1H), 2.19 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ ¹³C NMR (101 MHz, CDCl₃) δ 206.0, 202.2, 165.7, 154.3, 130.1, 126.1, 116.6, 110.1, 56.0, 52.2 (t, *J*_{C-D} = 7.1 Hz), 39.5 (d, *J*_{C-D} = 30.0 Hz), 39.3 (d, *J*_{C-D} = 40.3 Hz). HRMS (ESI) calcd. for C₁₂H₁₂DO₃; [M+H]⁺: 206.0922; found 206.0918.

2-(2-oxo-4-phenylbutyl)cyclopentan-1-one (13') (NMR Spectra)



An oven dried vial equipped with a stir bar was charged with (*E*)-1-(dimethyl(phenyl)silyl)-9-phenylnon-5ene-1,7-dione (35.1 mg, 0.1 mmol) (**12**) followed by PhMe (1 mL, 0.1M, dried on 3Å molecular sieves). The ^{Ph} yellow solution was degassed by sparging with nitrogen for 5 minutes, before the vial was capped, sealed

with parafilm and irradiated (2 x 427nm Kessil lamps, approximate distance 5 cm) overnight with stirring. The vials were maintained at approximately room temperature by an overhead cooling fan. The resultant colourless solution was concentrated to afford the DMPS enol ether product **13** (86% ¹H NMR yield). Attempted isolation of the parent silyl enol ether **13** resulted in adventitious hydrolysis to the dione **13'**. Flash column chromatography (5% EtOAc/petroleum benzine, 1% NEt₃; R_f ~ 0.2) afforded the title compound as a colourless oil (21.1 mg, 0.060 mmol, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.18 (m, 2H), 7.16 – 7.05 (m, 3H), 2.88 – 2.74 (m, 3H), 2.67 (dd, *J* = 14.4, 7.1 Hz, 2H), 2.46 – 2.34 (m, 2H), 2.26 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.21 – 2.05 (m, 2H), 2.01 – 1.90 (m, 1H), 1.82 – 1.63 (m, 1H), 1.42 (ddd, *J* = 23.3, 11.7, 6.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 220.1, 208.0, 141.0, 128.7, 128.4, 126.3, 45.0, 44.5, 42.7, 37.5, 29.9, 29.6, 20.9. *In agreement with the literature data.*^[15]

(Z)-8-(2-((tert-butyldimethylsilyl)oxy)prop-1-en-1-yl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (15) (NMR Spectra)



An oven dried vial equipped with a stir bar was charged with (*E*)-*N*-(2-((tertbutyldimethylsilyl)carbonyl)-5-methoxyphenyl)-4-methyl-*N*-(4-oxopent-2-en-1yl)benzenesulfonamide (**14**) (0.1 mmol) followed by PhMe (1 mL, 0.1M, dried on 3Å molecular sieves). The yellow solution was degassed by sparging with nitrogen for 5 minutes, before the vial was capped,

sealed with parafilm and irradiated (2 x 427nm Kessil lamps) overnight. The resultant colourless solution was concentrated to afford the silyl enol ether product. The product was isolated by flash column chromatography on neutralised silica gel ($10 \rightarrow 30\%$ EtOAc/petroleum benzine, 1% NEt₃; R_f ~ 0.7 (25% E/PB)) as a red oil (21.2 mg, 0.042 mmol, 42%). ¹H NMR (401 MHz, CDCl₃) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 5.7 Hz, 1H), 7.51 (s, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.68 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.97 (d, *J* = 9.1 Hz, 1H),

4.35 (dd, *J* = 9.1, 0.9 Hz, 1H), 3.94 (s, 3H), 2.38 (s, 3H), 1.87 (s, 3H), 0.94 (s, 9H), 0.23 (s, 3H), 0.17 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 195.0, 167.3, 155.5, 153.8, 144.7, 135.2, 129.8, 127.6, 126.1, 112.6, 101.8, 100.0, 65.0, 56.2, 25.9, 23.0, 21.7, 18.5, -3.4, -3.8.

6-methoxy-2-(2-oxopropyl)-1-tosylindolin-3-one (15') (NMR Spectra)



Isolated alongside the above product **15** after adventitious hydrolysis during chromatography (10 \rightarrow 30% EtOAc/petroleum benzine, 1% NEt₃; R_f ~ 0.5 (25% E/PB) as an orange solid (13.8 mg, 0.037 mmol, 37%). ¹**H NMR** (401 MHz, CDCl₃) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.56 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 6.74 (dd, *J* = 8.6, 2.1 Hz, 1H), 4.15 (t, *J* = 4.4 Hz, 1H), 3.96 (s, 3H), 3.33 (qd, *J* = 17.9, 4.4

Hz, 2H), 2.38 (s, 3H), 2.23 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 204.0, 194.9, 167.3, 155.6, 145.4, 130.2, 127.7, 125.9, 118.2, 113.3, 100.4, 63.2, 56.2, 45.3, 30.3, 21.7. **HRMS** (ESI) calcd. for C₁₉H₁₉O₅SNa; [M+Na]⁺: 396.0876; found 396.0874.

Derivatisation Reactions

(E)-4-methoxy-2-(3-oxobut-1-en-1-yl)benzaldehyde (16) (NMR Spectra)



(*E*)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one **(5b)** (120 mg, 0.43 mmol) was added to a vial and dissolved in EtOH/H₂O (1:1 v/v, 4 mL) before addition of KF (35 mg, 0.60 mmol, 1.4 equivs.). The mixture was stirred at 60 °C overnight. The solution was cooled to room temperature and diluted with EtOAc (5 mL) and H₂O (5 mL) and the organic layers were extracted into EtOAc thrice, dried on MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography to obtain the title compound **16** as a beige solid (80.8 mg, 0.39 mmol, 92%). **¹H NMR** (401 MHz, CDCl₃) δ 10.08 (s, 1H), 8.51 (d, *J* = 16.3 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.11 (s, 1H), 7.05 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.56 (d, *J* = 16.3 Hz, 1H), 3.91 (s, 3H), 2.45 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 199.0, 191.3, 163.9, 141.1, 138.9, 136.8, 131.9, 127.6, 115.2, 113.3, 55.9, 27.0. **HRMS** (ESI) calcd. for C₁₂H₁₂NaO₃; [M+Na]⁺: 227.0679; found 227.0672.

1-(1-hydroxy-5-methoxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triethylsilyl)-2,3-dihydro-1H-inden-2-yl)ethan-1-one (22) (NMR Spectra)



An oven dried microwave tube was charged with Cul (4 mg, 0.02 mmol, 10 mol%), LiOtBu (2.4 mg, 0.03 mmol, 15 mol%), and B₂Pin₂ (76 mg, 0.3 mmol, 1.5 equivs.) then sealed with a rubber septum. The tube was subjected to vacuum and refilled with nitrogen (three cycles) before anhydrous THF (1.0 mL) was added. The mixture was stirred for five minutes and turned a dark grey colour. Then, a solution of (*E*)-4-(5-methoxy-2-((triethylsilyl)carbonyl)phenyl)but-3-en-2-one (**5c**) (64 mg, 0.20 mmol) in THF (1.0 mL) was added in one portion *via* syringe under nitrogen flow and the mixture was stirred at room temperature overnight. The resulting mixture was filtered through Celite[®] eluting with EtOAc (20 mL). The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography (10 \rightarrow 15% EtOAc/petroleum benzine; R_f ~ 0.2) to give the title compound **22** as a yellow oil (88.4 mg, 0.19 mmol, 99%). *This reaction was also performed in the presence of iPrOH (5 equivs.) and delivered the same product in slightly reduced yield.* ¹H NMR (400 MHz, CDCl₃) δ 7.03 (dd, *J* = 9.9, 4.8 Hz, 2H), 6.69 (dd, *J* = 8.3, 1.6 Hz, 1H), 4.01 (d, *J* = 8.2 Hz, 1H), 3.79 (s, 3H), 2.58 (d, *J* = 8.2 Hz, 1H), 2.21 (s, 3H), 1.25 (s, 12H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.75 – 0.64 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 212.2, 159.7, 143.9, 138.9, 124.2, 112.0, 111.1, 83.7, 80.9, 61.0, 55.3, 33.3, 25.2, 24.7, 7.7, 1.7 (*the carbon attached to the boron atom was not observed due to quadrupolar relaxation*). HRMS (ESI) calcd. for C₂₄H₃₉O₅BSiNa; [M+Na]⁺: 469.2552; found 469.2553.

8-(1-(4-fluorophenyl)-1-hydroxy-3-oxobutan-2-yl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (23) (NMR Spectra)



An oven dried Schlenk tube was placed under nitrogen and anhydrous THF (5 mL) was added, followed by (triethyl)silyl enol ether **6c** (318.5 mg, 1.0 mmol) and 4-fluorobenzaldehyde (372 mg, 3.0 mmol). The mixture was cooled to -78 °C and BF₃·OEt₂ (25 μ L, 0.2 mmol, 20 mol%) was added dropwise. The mixture was warmed to room temperature overnight with stirring, then quenched with sat. aq. NaHCO₃. The mixture was diluted with Et₂O (20 mL) and the organic layer was washed with dilute HCl (20 mL, 1 M) and brine (20 mL). The combined organic layers were dried on MgSO₄, filtered and concentrated *in vacuo*. Purification of the residue by flash column chromatography (25 \rightarrow 40% EtOAc/petroleum benzine; R_f ~ 0.3) afforded as a single diastereomer the title compound **23** as a colourless oil (285.7 mg, 0.87 mmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.6 Hz, 1H), 7.37 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.98 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.74 (d, *J* = 1.5 Hz, 1H), 4.86 (d, *J* = 9.2 Hz, 1H), 4.69 (brs, 1H), 3.85 (s, 3H), 3.85 – 3.84 (m, 1H), 3.32 (dd, *J* = 9.2, 4.2 Hz, 1H), 1.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 205.4, 204.8, 166.3, 162.8 (d, *J_{c-F}* = 247.3 Hz), 154.1, 136.8 (d, *J_{c-F}* = 3.1 Hz), 128.9, 128.9 (d, *J_{c-F}* = 8.2 Hz), 126.6, 116.8, 115.8 (d, *J_{c-F}* = 21.5 Hz), 109.4, 74.7, 57.5, 56.0, 54.8, 29.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -113.1. HRMS (ESI) calcd. for C₁₉H₂₈O₄F; [M+H]⁺: 329.1184; found 329.1185.

4-methoxy-8-oxobicyclo[4.2.0]octa-1,3,5-trien-7-yl)octane-2,6-dione (24) (NMR Spectra)



An oven dried Schlenk tube was placed under nitrogen and anhydrous THF (5 mL) was added, followed by (triethyl)silyl enol ether **6c** (318.5 mg, 1.0 mmol) and ethyl vinyl ketone (372 mg, 3.0 mmol). The mixture was cooled to -78 °C before BF₃·OEt₂ (25 μ L, 0.2 mmol, 20 mol%) was added dropwise. The mixture was warmed to room temperature overnight with stirring, then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (20 mL) and the organic layer was washed with water (20 mL) and brine (20 mL). The combined organic layers were dried on MgSO₄, filtered and concentrated *in vacuo*. Purification of the residue by flash column chromatography (30% EtOAc/petroleum benzine; R_f ~ 0.2) afforded as a single diastereomer the title compound **24** as a yellow oil (161.5 mg, 0.56 mmol, 56%). ¹**H NMR** (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.5 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.85 (d, *J* = 1.7 Hz, 1H), 3.89 (d, *J* = 3.6 Hz, 1H), 3.86 (s, 3H), 2.85 (td, *J* = 7.2, 3.7 Hz, 1H), 2.70 – 2.60 (m, 2H), 2.42 (dd, *J* = 14.5, 6.8 Hz, 3H), 2.19 (s, 3H), 2.08 (dd, *J* = 5.9, 3.6 Hz, 1H), 2.00 – 1.96 (m, 1H), 1.03 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 210.8, 206.4, 204.1, 165.8, 153.2, 129.3, 126.3, 116.7, 109.7, 59.6, 55.9, 49.8, 39.2, 36.1, 27.9, 25.4, 7.9. **HRMS** (ESI) calcd. for C₁₇H₂₁O₄; [M+H]⁺: 289.1427; found 289.1434.

1-(8-hydroxy-4-methoxy-8-phenylbicyclo[4.2.0]octa-1,3,5-trien-7-yl)propan-2-one (25) (NMR Spectra)



An oven dried Schlenk tube containing (triethyl)silyl enol ether **6c** (318.5 mg, 1.0 mmol) was placed under nitrogen and anhydrous THF (5 mL) was added. The mixture was cooled to -78 °C and phenylmagnesium bromide (0.5 mL, 1.5 mmol, 1.5 equivs., 3 M in Et₂O) was added dropwise. The mixture was warmed to room temperature overnight with stirring, then quenched with sat. aq. NH₄Cl. The mixture was diluted with Et₂O (20 mL) and the organic layer was washed with water (20 mL) and brine (20 mL). The combined organic layers were dried on MgSO₄, filtered and concentrated *in vacuo*. Purification of the residue by flash column chromatography (20 % EtOAc/petroleum benzine; R_f ~ 0.2) afforded as a single diastereomer the title compound **24** as a colourless solid (93.2 mg, 0.33 mmol, 33%). **¹H NMR** (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.27 (m, 2H), 6.87 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.26 (d, *J* = 1.5 Hz, 1H), 3.89 – 3.86 (m, 1H), 3.60 (s, 3H), 2.69 – 2.64 (m, 2H), 1.55 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 204.0, 164.6, 157.0, 147.4, 128.7, 127.5, 126.2, 125.5, 125.1, 116.7, 110.7, 76.5, 55.4, 49.4, 40.2, 27.3. **HRMS** (ESI) calcd. for C₁₈H₁₉O₃; [M+H]⁺: 283.1329; found 283.1325.

rac-8-(1-fluoro-2-oxopropyl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (26) (NMR Spectra)



To a stirred suspension of SelectFluor (354 mg, 1 mmol, 1.0 equiv.) in anhydrous MeCN (10 mL) at 0 °C was added (triethyl)silyl enol ether **6c** (318.5 mg, 1.0 mmol) under nitrogen flow and stirred overnight. The mixture was quenched with sat. aq. NH₄Cl and diluted with Et₂O (20 mL). The organic layer was washed twice with water (20 mL), dried on MgSO₄, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (20% EtOAc/petroleum benzine; $R_f \sim 0.2$) to afford the title compound **25** as a yellow oil containing a 2:1 mixture of inseparable diastereomers (173 mg, 0.78 mmol, 78 %). *Major diastereomer:* ¹**H NMR** (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.15 – 7.07 (m, 1H), 6.91 (d, *J* = 1.7 Hz, 1H), 5.40 (d, *J* = 16.8 Hz, 1H), 5.27 (d, *J* = 16.8 Hz, 1H), 3.85 (s, 3H) 2.32 (d, *J* = 4.3 Hz, 3H). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -161.0 (d, *J* = 16.7 Hz), -204.3 (dd, *J* = 50.8, 3.8 Hz). *Minor diastereomer:* ¹**H NMR** (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.6 Hz, 1H), 7.22 – 7.12 (m, 1H), 6.90 (t, *J* = 1.9 Hz, 1H), 5.35 (d, *J* = 9.8 Hz, 1H), 5.23 (d, *J* = 9.8 Hz, 1H), 3.92 (s, 3H), 2.65 (d, *J* = 4.8 Hz, 3H). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -157.1 (s), -205.2 (dd, *J* = 49.3, 3.9 Hz). *Both diastereomers:* ¹³**C NMR** (101 MHz, CDCl₃) δ 205.6 (d, *J*_{C+F} = 34.0 Hz), 200.6 (dd, *J*_{C+F} = 32.2, 1.8 Hz), 192.2 (dd, *J*_{C+F} = 15.9, 1.3 Hz), 188.9 (dd, *J*_{C+F} = 16.4, 7.6 Hz), 166.8 (s), 166.6 (d, *J*_{C+F} = 2.8 Hz), 148.0 (dd, *J*_{C+F} = 18.0, 2.2 Hz), 146.5 (dd, *J*_{C+F} = 1.7 Hz), 109.4 (s), 107.3 (s), 101.1 (dd, *J*_{C+F} = 205.9, 21.4 Hz), 96.1 (dd, *J*_{C+F} = 205.5, 15.1 Hz), 95.6 (dd, *J*_{C+F} = 207.0, 21.0 Hz), 90.6 (dd, *J*_{C+F} = 210.9, 17.7 Hz), 56.1, 27.5, 26.7. **HRMS** (ESI) calcd. for C₁₂H₁₂FO₃; [M+H]*: 223.0765; found 223.0762.

rac-8-(1-fluoro-2-oxopropyl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (27) (NMR Spectra)



To a stirred solution of (triethyl)silyl enol ether **6c** (111 mg, 0.35 mmol) in anhydrous DCM (4 mL) at 0 °C was added under nitrogen NCS (54 mg, 0.42 mmol, 1.2 equivs.) as a solution in DCM (3 mL) and stirred overnight. The mixture was quenched with sat. aq. NaHCO₃ and diluted with DCM (10 mL). The organic layer was washed twice with water (5 mL), dried on MgSO₄, filtered and SI43

concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (10% EtOAc/petroleum benzine; $R_f \sim 0.4$) to afford the title compound **26** as a red solid (48.8 mg, 0.24 mmol, 69%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.42 (m, 2H), 6.68 (dd, J = 8.1, 2.3 Hz, 1H), 6.34 (s, 1H), 3.88 (s, 3H), 2.53 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.0, 196.1, 164.8, 151.3, 145.7, 132.7, 125.7, 123.6, 112.9, 112.3, 56.0, 28.5. HRMS (ESI) calcd. for C₁₂H₁₁O₃; [M+H]⁺: 203.0703; found 203.0702.

1-benzyl-2-phenethyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole (28) (NMR Spectra)



An oven dried vial was charged with 2-(2-oxo-4-phenylbutyl)cyclopentan-1-one (**13'**) (92.1 mg, 0.40 mmol), methanol (2.0 mL) and 4Å molecular sieves (~1.0 cm³). Benzylamine (219 μ L, 2.0 mmol, 5.0 equivs.) and acetic acid (115 μ L, 2.0 mmol, 5.0 equivs.) were then added and the mixture was stirred at 70 °C overnight. The mixture was cooled to room temperature, diluted with EtOAc (10 mL) and washed with dilute HCl (10mL, 1M) twice. The organic layer was dried on MgSO₄, filtered, and concentrated *in vacuo* to give a brown residue, which was purified by flash column chromatography (2% EtOAc/petroleum benzine; R_f ~ 0.4) to give the title compound **27** as a brown oil (51.9 mg, 0.17 mmol, 43%). ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.11 (m, 6H), 7.05 (d, *J* = 7.1 Hz, 2H), 6.91 (d, *J* = 7.3 Hz, 2H), 5.77 (s, 1H), 4.86 (s, 2H), 2.79 – 2.73 (m, 2H), 2.70 – 2.64 (m, 2H), 2.58 (t, *J* = 6.9 Hz, 2H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.34 – 2.26 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.8, 135.8, 128.8, 128.49, 128.46, 127.3, 126.4, 126.1, 124.8, 101.1, 48.7, 36.0, 29.2, 28.8, 26.0, 25.0. HRMS (ESI) calcd. for C₂₂H₂₄N; [M+H]⁺: 302.1903; found 302.1899.

COMPUTATIONAL ANALYSIS

All the calculations were performed with the GAUSSIAN16 suite of programs (Revision C.02). Geometry optimization was conducted at M062x/6-311+G(d,p) level of theory. Single-point energy calculations of the optimized geometries were carried out at the M062x/6-311++G(d,p) level of theory. All calculations were conducted applying solvation parameters within the self-consistent reaction field model for toluene. The vertical excited states of benzoyl(trimethyl)silane (**SM**) were computed via time-dependent density functional theory (TDDFT) calculations (first two singlet excited states). Relevant absorption bands were computed at 562.9 nm and 345.9 nm, the latter of which was ascribed to an $n \rightarrow \pi^*$ transition corresponding to excitation of the acylsilane.

The free energy of the singlet excited state S* was estimated by conducting a TD-DFT geometry optimization and frequency calculation. Intersystem crossing from S* to the triplet state T* was computed to be favourable by ΔG_{ISC} = -7.53 kcal/mol. From this state, 1,2-silyl transfer (Brook rearrangement) can occur surmounting an energy barrier of +6.5 kcal/mol in TS1 to provide triplet siloxycarbene **INT1**^T. Intersystem crossing to the singlet siloxycarbene **INT1**^S is favourable $\Delta G_{INT1T-INT1S}$ = -14.93 kcal/mol. From **INT1**^S, several possible reaction pathways were investigated. 1,4-Conjugate addition of the nucleophilic carbene to the pendant vinylketone *via* **TS2** ($\Delta G_{INT15-TS2}$ = +16.95 kcal/mol) provides siloxycarbenium enolate **INT2** ($\Delta G_{INT15-INT2}$ = +7.14 kcal/mol). Silicon transfer to the enolate oxygen atom may occur *via* **TS5** ($\Delta G_{INT2-TS5}$ = +23.23 kcal/mol) to afford the silylenol ether product ($\Delta G_{INT2-PROD}$ = -38.40 kcal/mol).

Alternatively, the possibility of a fused cyclopropane intermediate **INT3** was also investigated. Previously, we disclosed that siloxycarbenes undergo intramolecular [2+1] cycloaddition reactions on tethered alkenes^[10]. Such intermediates might also be implicated in the intramolecular cyclisation of siloxycarbenes with vinyl esters to ultimately provide siloxy indenes.^[16] The fused cyclopropane **INT3** was computed to be relatively stable with respect to the starting acylsilane ($\Delta G_{rel} = +7.94$ kcal/mol). Although a stationary point for concerted cyclopropanation via **TS3** was located, its energy barrier is prohibitively high ($\Delta G_{INT1S-TS3} = +68.16$ kcal/mol) and is unlikely to be a viable pathway to **INT3**.

Alternatively, **INT3** could be accessed by ring closure of siloxycarbenium enolate **INT2**. A stationary point for ring closure (**TS4**) was located inferring that the formation of cyclopropane **INT3** is exergonic ($\Delta G_{INT2-INT3} = -21.93 \text{ kcal/mol}$), in our calculations surmounting a relatively high energy barrier ($\Delta G_{INT2-TS4} = +19.02 \text{ kcal/mol}$). **INT3** is unlikely to re-surmount this energy barrier to return to **INT2** and undergo silicon transfer in a stepwise manner. Instead formation of the silylenol ether **PROD** *via* **TS6** may proceed via a concerted ring-opening and silicon transfer process, which is a relatively low energy stationary point compared to **TS5** likely due to entropic effects of molecular pre-organization. However, both pathways share similar absolute energy barriers ($\Delta G_{INT3-TS6} = +23.53 \text{ kcal/mol}$).

From the computed energies, silicon transfer to afford the silylenol ether produce appears to be the rate determining step (discounting excitation of the acylsilane) and the step which is most clearly irreversible. These results are consistent with our experimental observation that the photocyclization requires a comparatively long reaction time to complete (indicated by the retention of colour of the acylsilane as well as NMR studies) indicating a high degree of reversibility in the reaction mechanism.



Figure S11: Computed Path A: Concerted cyclopropanation, ring opening and/or silyl transfer



Figure S12: Computed Path B: 1,4-Conjugate addition, cyclisation and concerted ring opening/silyl transfer



Figure S13: Computed Path C: 1,4-Conjugate addition and silyl transfer

Table S3: Computed M062x energies and ZPVE values for relevant stationary points

Structure	Free Enthalpy	SP Energy	ZPVE
SM	-984.160307	-984.160650	0.283245
S*	-984.064003	-984.064367	0.281438
T*	-984.075472	-984.075855	0.280926
TS1	-984.064680	-984.065125	0.280555
INT1(T)	-984.097831	-984.098249	0.280993
INT1	-984.122447	-984.122787	0.281727
TS2	-984.094641	-984.095018	0.280968
INT2	-984.112542	-984.112900	0.283216
TS4	-984.080795	-984.081156	0.281785
INT3	-984.174956	-984.175344	0.284474
TS3	-984.008437	-984.008784	0.276352
TS5	-984.074760	-984.075083	0.282423
TS6	-984.110434	-984.110820	0.283516
PROD	-984.148273	-984.148643	0.283887

CARTESIAN COORDINATES OF THE COMPUTED STRUCTURES

SM		S*	
			ug)
	на		
	H1 5122 - 1522 - 153		
			HE 19
	422		
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С	1.29211300 0.44758500 0.17125300	С	-1.55788700 3.50747100 0.36432100
С	2.46704700 -0.26926700 -0.00011600	С	-0.36115400 2.82222500 0.28000000
С	2.44012100 -1.63222000 -0.32113900	С	-0.30833400 1.47108000 -0.10217200
С	1.19318900 -2.25877700 -0.49508900	С	-1.53050700 0.79380400 -0.35399300
С	0.01586100 -1.52391500 -0.34471700	С	-2.74792900 1.52243300 -0.32459700
С	3.68169400 -2.38362400 -0.54138600	С	0.96235000 0.81966200 -0.36637900
С	4.90388300 -2.05206200 -0.11188400	С	2.16787800 1.14479400 0.13303800
С	6.06016200 -2.94818700 -0.39487400	С	3.37358400 0.38785600 -0.26809100
0	5.91485300 -4.02368400 -0.93778700	0	3.32093500 -0.57116800 -1.01658600
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С	1.04121700 -3.72669700 -0.80603400	С	-1.61443000 -0.61599900 -0.65779900
0	0.21227300 -4.06165800 -1.63331400	0	-2.55555000 -1.21966700 -1.1987250
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Н	1.33604800 1.50088200 0.42078100	Н	-1.56795900 4.55322100 0.64442900
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C			3.08812901 0.91922699 -0.52934900
	-5.30882299 0.60781898 0.14853		4.0660/301 0.19990099 -0.15912000
н			-1.49168499 -0.07637001 0.37194200 1 80607000 2 01575800 0 81524600
			-1.89097099 2.01373899 -0.81324000
н	-2.22874499 -0.60156402 0.22230	200 H	-0.03902399 $-1.090280000.82303401 -0.92564201 0.75217000$
н	-4 46262099 3 54803798 1 98887	200 П	3 33301101 2 43190799 -2 19306000
н	-4 56059999 4 11117998 -1 03593	100 H	2 84861701 3 39923899 0 71541100
н	-6.85392199 6.82821498 -0.32142	700 H	5.06434301 6.03707099 0.12100500
н	-7.54663199 5.36234198 -1.01265	400 H	5.98558101 4.79697399 0.96569800
н	-5.97325699 5.93890198 -1.59654	400 Н	4.29744101 5.11153399 1.43587000
Si	-7.05419399 0.82660298 0.225258	300 Si	5.78583201 0.35884899 -0.54829200
С	-7.44447399 1.72431698 1.79893	500 C	5.88568501 0.84687899 -2.33410000
н	-7.04498399 2.74210198 1.79353	н оос	5.61669801 1.90028399 -2.45044400
н	-7.03207599 1.19583998 2.66196	500 Н	5.24209401 0.21902699 -2.95574100
н	-8.52939399 1.78343498 1.92576	500 Н	6.91482901 0.71977999 -2.68277400
С	-7.46558999 1.78823798 -1.31220	400 C	6.49808401 1.58858999 0.65066500
н	-7.18843599 1.23410898 -2.21161	300 H	6.66003201 2.54543299 0.15081800
н	-6.93552199 2.74372298 -1.31281	700 H	7.45003001 1.22239499 1.04311500
H	-8.53855199 1.99325498 -1.35457	000 H	5.81938101 1.74994299 1.49177900
C	-7.68870199 -0.92028802 0.17736		6.35135301 -1.38241201 -0.22328800
H	-8.78153899 -0.92653202 0.15634	400 H	7.42462601 -1.46993801 -0.41107500
H 	-/.36553199 -1.48000702 1.05781		5.8351/201 -2.09329901 -0.87202600
Н	-7.33074899 -1.44158202 -0.71319	600 H	6.16689101 -1.66532301 0.81556700

TS5		PROD	
)
С	-4.15211500 -1.42440500 0.71463800	C -1.25999998 0.83999998 0.00000	000
С	-4.57961600 -0.44680900 -0.19796100	C -1.60798798 1.97629398 0.74701	100
С	-3.67868900 0.36123400 -0.89930900	C -2.93462498 2.36877798 0.936283	100
С	-2.34622000 0.13248400 -0.63347200	C -3.89267598 1.56174498 0.34464	500
С	-1.90688900 -0.83540000 0.28743400	C -3.54356698 0.44055898 -0.40557	100
С	-2.80181000 -1.64697200 0.98269100	C -2.22730298 0.03904198 -0.60141	100
С	-0.94016500 0.63824000 -0.95769900	C -5.40164598 1.41353698 0.153002	200
С	-0.60603600 1.97275100 -0.33282200	C -6.12113398 2.49801898 -0.57686	000
C	0.55720600 2.23686300 0.30217100	C -7.41428898 2.78301798 -0.39621	300
0	1.62332700 1.41485200 0.41478700	0 -8.17786898 2.11083098 0.51251	100
C	0.79390900 3.56148100 0.98209800	C -8.1481//98 3.8/628598 -1.10896	200
	-0.50087500 -0.46562000 0.01266900		800
U U	0.00820700 -0.82514200 0.42707000		000 000
	-4.69622500 -2.05456100 1.21616100		000
п	-3.04319100 -0.31017800 -0.30903400	H _3 18120898 3 25034898 1 51514	900
н	-2 48818100 -2 41090400 1 68621600	H _1 95904198 -0 83311202 -1 18443	000
н	-0.60570500 0.51188600 -1.99573200	H -5 94350298 1 12123498 1 05669	9000
н	-1.41332400 2.71916100 -0.28733500	H -5.56047498 3.07553698 -1.30393	800
н	1.61930400 4.09413600 0.47284400	H -8.55340798 4.58114898 -0.37855	600
н	1.10637000 3.37369000 2.02521100	Н -8.99271698 3.46024798 -1.66570	800
н	-0.11231900 4.19926200 0.98662800	Н -7.49588598 4.40901398 -1.79984	500
Si	2.36743700 -0.70827400 -0.03913000	Si -9.02893798 0.66545798 0.273984	100
С	2.72522100 -2.63963900 -0.06818800	C -8.15911898 -0.69983902 1.20541	000
Н	3.73484300 -2.79661700 -0.44652800	Н -7.92134998 -0.38915102 2.22620	900
Н	2.02260200 -3.20404800 -0.70677700	Н -7.23619998 -0.99587802 0.70178	100
Н	2.67736800 -3.06351700 0.93749800	H -8.80331598 -1.58179002 1.26505	400
С	3.99890900 -0.35430800 0.95041100	C -10.72653898 0.96960598 0.98634	600
Н	4.71476300 -1.19210800 0.90303200	H -10.66003898 1.24538798 2.04165	500
Н	4.47293500 0.60109600 0.58639800	H -11.34837798 0.07377098 0.91002	200
H	3.73954400 -0.17257500 2.03724600	H -11.23110598 1.78071898 0.45570	200
C	2.67861100 -0.37190900 -1.90818200	C -9.08061698 0.29334598 -1.55409	800
н	2.18399300 -1.08539800 -2.57589500	н -9.59457598 -0.65730002 -1.72227	400
H	3.76252200 -0.49265600 -2.06244900	н -8.06669898 0.19776598 -1.95129	900
Н	2.408/5400 0.65774200 -2.22600500	н -9.61143098 1.06445298 -2.11762	400

TS3		INT3	
	2 74801200 1 70254800 0 12120200	C	0.47000000 0.51000000 0.0000000
	4 52637500 -0 66184700 -0 18378000	C	-1 80284599 0 61394699 -0 48965700
C	3.89380300 0.68105400 -0.07051600	C	-1.05147199 1.70019899 2.07396600
c	2.58672000 0.57642100 0.25051000	C	-0.11780399 1.04685899 1.23668900
C	1.80060400 -0.52210000 0.09459200	H	0.27320901 0.01552699 -0.59944300
С	2.28918500 -1.75571000 -0.12080500	Н	-2.08087199 0.18395199 -1.44796800
С	1.22505200 1.47638700 0.67656900	н	-0.75566099 2.08958899 3.04414200
С	0.31428600 1.72457600 -0.52437700	Н	0.91060001 0.94236499 1.57254800
С	-0.91475400 2.40832800 0.02754800	С	-3.74148299 2.26371999 1.88199500
0	-1.56226800 1.97125800 0.95505200	С	-2.34118599 1.76604699 1.59594100
С	-1.20170400 3.70300900 -0.67802900	С	-2.69933299 1.24314499 0.34281400
С	0.38255900 -0.20886200 -0.19279700	С	-4.13742999 1.70043199 0.51185700
0	-0.62047500 -0.94719400 0.40082500	0	-5.25284299 1.05332499 0.06876700
н	4.22428000 -2.77375500 -0.10936000	Si	-5.90992299 -0.27407601 0.90830200
н	5.62201000 -0.70853600 -0.19238700	С	-4.13409299 3.20668999 0.75141100
н	4.54450500 1.56718400 0.05408600	Н	-3.37639899 3.81582899 0.26142100
н	1.67476900 -2.66591500 -0.11479600	С	-5.51239799 3.79140999 0.83491900
н	0.79402000 1.31902400 1.66697700	Н	-4.30581599 2.26407499 2.80755900
Н	0.58469400 2.07922900 -1.53271200	C	-5.85168899 4.82559099 -0.20821000
н	-1.92087900 4.29105600 -0.12162600	н	-6.88266799 5.16002099 -0.08473900
Н	-1.62043100 3.45895600 -1.65887800	н	-5.16/03699 5.6//11899 -0.12468800
H	-0.27073500 4.25579400 -0.83868800	н	-5./115/899 4.391/8699 -1.20515/00
51	-2.26587400 -1.19001800 -0.00881300	0	-0.30851899 3.42237699 1.67204900
	-2.37947600 -2.93089000 -0.69566700	с ц	7.01340399 -1.09699701 -0.35195900
	-1.35000300 -3.04230800 0.00/36200 -1.82580500 3.00413500 1.64180500	п	-7.51457033 -1.30203901 0.0820//00
п	-1.85589500 -2.99412500 -1.84180500	п	-6.43546999 -1.43045501 -0.70040000
	-3.11899400 -1.07792400 1.64765200	C	-6.89185899 0.37704499 7.38106100
н	-2 63570900 -1 77878300 2 33525000	н	-6 24979099 0 79047399 3 13526700
Н	-4.17547600 -1.35596300 1.58464700	н	-7.63914399 1.06223799 2.07817900
н	-3.04660800 -0.07598900 2.06134300	Н	-7.40626499 -0.52625201 2.85054300
C	-2.87686000 0.02985200 -1.30231500	С	-4.50477199 -1.38630501 1.45427300
н	-3.65836900 -0.43629000 -1.91708200	н	-4.90316599 -2.26313001 1.97915800
Н	-2.05164800 0.30352800 -1.96311200	н	-3.91585399 -1.73720101 0.59918600
Н	-3.28682500 0.94030600 -0.85596000	Н	-3.82498299 -0.86454301 2.13933900

C -3.87768000 -1.17433900 0.79996600 C -1.15999998 1.45999997 0.00000000 C -3.87768000 -1.17433900 0.79996600 C -2.4874498 1.32247897 -0.42334100 C -3.33724800 0.2302400 -1.461500 C -2.4874498 1.33247897 -0.42334100 C -3.33724800 0.2302400 -1.461500 C -1.78774298 2.7472197 1.9963900 C -4.55116700 -0.50125600 -0.35902698 1.0103497 -0.58751900 H -2.5735300 -1.66907500 2.17708100 H -2.3657198 2.56523997 2.90353400 H -5.29081700 -0.54854000 -0.66048300 C -3.0309197 0.69304500 C -1.66603900 -0.31738700 C -3.42240598 1.93246597 0.39800700 C -0.6485700 0.22147500 -0.66948300 C -3.039917 0.69304500 C -0.4250700 0.22147500 -0.66948300 C	TS4		TS6	
C -3.87768000 -1.17493900 0.79996600 C -1.15999998 1.45999997 0.0000000 C -2.55554500 -1.14801200 1.26275800 C -2.48744498 1.33247897 -0.42334100 C -3.33724800 0.23202400 -1.14614500 C -1.78774298 2.74782197 1.99639000 C -4.25116700 -0.50125600 0.35962600 C -0.36902698 1.0103497 -0.37913307 H -2.25743500 -1.6607500 2.17708100 H -2.74928898 0.78713397 -1.32081100 H -3.65785700 0.74872400 -0.36904200 H -1.50357198 3.2659297 2.90353400 C -0.64334400 0.7348700 -0.93257200 C -4.54323598 0.2017197 1.57302000 C -0.6603900 -0.2147500 -0.69648300 C -3.0903598 2.6172197 1.5730200 C -0.2333300 0.02084200 0.32738200 C -4.85155488 2.13009197 0.6934500				
C 1.1193000 1.14301200 1.26275800 C 1.14301498 1.33247897 0.42334100 C -2.55554500 -1.146114500 C -1.78774298 2.74782197 1.99639000 C -4.25116700 -0.50125600 -0.35962600 C -0.36902698 1.0103497 -0.58751900 H -4.61622200 -1.73633600 1.35296400 H -0.36902698 1.0103497 -0.58751900 H -2.25743500 -1.66907500 2.17708100 H -2.74928898 0.78713397 1.45274700 C -0.48334400 0.77348700 -0.93257200 C -4.54323598 3.02400397 1.86147800 C -2.04250700 0.224147500 -0.69648300 C -3.0903598 2.62172197 1.57302000 C -1.66603900 -0.44938900 0.84733600 O -5.89648988 1.61932197 0.22057400 C -0.4865700 1.89529100 0.05069100 C -4.8887898 4.2980797 0.7176700 C	C	-3 87768000 -1 17493900 0 79996600	C	-1 15999998 1 45999997 0 0000000
C -3.33724800 0.23202400 -1.14614500 C -1.78774298 2.74782197 1.99639000 C -4.61622200 -1.73633600 1.35296400 H -0.36902698 1.01003497 -0.5875190 H -2.25743500 -1.66907500 2.17708100 H -2.74928898 0.78713397 -1.32081100 H -3.65785700 0.74872400 -2.03894200 H -1.50357198 3.2659297 2.90353400 H -5.29081700 -0.54854000 -0.68004200 H 0.22111802 2.20592497 1.45274700 C -0.64334400 0.77348700 -0.93257200 C -4.54323598 3.02400397 1.86147800 C -2.04250700 0.22147500 -0.49011700 C -3.42240598 1.93054697 0.3980700 C -0.25339300 0.02084200 0.32738200 C -4.88155498 2.13009197 0.69304500 G -0.4685700 1.89529100 0.0506700 Si -7.54420788 1.5305697 0.97176700 <th>C</th> <th>-2.55554500 -1.14801200 1.26275800</th> <th>C</th> <th>-2.48744498 1.33247897 -0.42334100</th>	C	-2.55554500 -1.14801200 1.26275800	C	-2.48744498 1.33247897 -0.42334100
C -4.25116700 -0.50125600 -0.35962600 C -0.82379498 2.14419397 1.17133400 H -4.61622200 -1.73633600 1.35296400 H -0.36902698 1.0103497 -0.58751900 H -2.25743500 1.66907500 2.17708100 H -2.7492898 0.78713397 -1.32081100 H -3.65785700 0.74872400 -0.68004200 H -1.50357198 3.2659297 2.90353400 C -0.64334400 0.77348700 -0.93257200 C -4.54323598 3.02400397 1.45274700 C -0.6660390 0.43121400 0.49011700 C -3.42240581 1.93546697 0.39800700 C -0.25339300 0.02084200 0.3273200 C -4.85155498 1.93246797 0.22057400 Si 2.08122500 -1.29661100 -0.03506700 Si -7.54420798 1.5305997 0.97176700 C -0.40865700 1.89529100 0.05069100 C -4.8887898 4.28987497 1.12071400 <th>C</th> <th>-3.33724800 0.23202400 -1.14614500</th> <th>C</th> <th>-1.78774298 2.74782197 1.99639000</th>	C	-3.33724800 0.23202400 -1.14614500	C	-1.78774298 2.74782197 1.99639000
H -4.61622200 -1.73633600 1.35296400 H -0.36902698 1.01003497 -0.58751900 H -2.25743500 -1.66907500 2.17708100 H -2.74928898 0.78713397 -1.32081100 H -3.65785700 0.74872400 -2.03894200 H -1.50357198 3.26592997 2.90353400 C -0.64334400 0.77348700 -0.3257200 C -4.54323598 3.02400397 1.86147800 C -2.04250700 0.22147500 -0.66948300 C -3.0903598 2.62172197 1.57302000 C -1.66603900 -0.43121400 0.49011700 C -3.42240598 1.93546697 0.39800700 C -0.25339300 0.02084200 0.32738200 C -4.8515498 2.13009197 0.6934500 O 0.86551400 -0.14938900 0.8673600 5 7.54420798 1.5305697 0.97176700 C -0.40865700 1.89529100 0.05069100 C -4.8887898 4.28987497 1.12071400 H -1.25176400 2.27288200 0.63037000 H -4.	C	-4.25116700 -0.50125600 -0.35962600	C	-0.82379498 2.14419397 1.17133400
H-2.25743500-1.669075002.17708100H-2.749288980.78713397-1.32081100H-3.657857000.74872400-2.03894200H-1.503571983.265929972.90353400H-5.29081700-0.54854000-0.68004200H0.221118022.205924971.45274700C-0.643344000.77348700-0.93257200C-4.543235983.024003971.86147800C-2.042507000.221475000.69648300C-3.090935982.621721971.57302000C-0.6633900-0.41214000.49011700C-3.422405981.935466970.39800700C-0.253393000.020842000.32738200C-4.851554982.130091970.69304500O0.86551400-0.449389000.84733600O-5.896489981.619321970.22057400C-0.408657001.895291000.05069100C-4.88878984.28974971.12071400H-1.251764002.272882000.63037000H-4.086413984.945031970.80942400C0.84878902.62790400-0.01050800C-6.551679985.822498770.04450500H-0.097402000.77242800-1.86338100H-4.984913982.864417972.84435600C1.037531003.760755000.98784900C-6.551679985.822498770.90905800H1.663410004.706872000.53676900H-7.279861986.372497770.64477500	н	-4.61622200 -1.73633600 1.35296400	н	-0.36902698 1.01003497 -0.58751900
H-3.657857000.74872400-2.03894200H-1.503571983.265929972.90353400H-5.29081700-0.54854000-0.68004200H0.221118022.205924971.45274700C-0.643344000.77348700-0.93257200C-4.84235983.024003971.86147800C-2.042507000.22147500-0.69648300C-3.090935982.621721971.57302000C-1.66603900-0.31214000.49011700C-3.422405981.935666970.39800700C-0.253393000.020842000.32738200C-4.851554982.130091970.69304500O0.86551400-0.449389000.84733600O-5.896489981.619321970.22057400Si2.081225001.29661100-0.03506700Si-7.544207981.530569970.97176700C-0.408657001.895291000.05069100C-4.88878984.289874971.12071400H-1.251764002.27282000.6303700H-4.086413984.945031970.80942400C0.84878902.62790400-0.01050800C-6.591679985.822498970.04450500H-0.099402000.772428001.86338100H-4.984913982.864417972.84435600C1.037531003.760755000.98784900C-6.551679985.82249877-0.12990300H1.560410004.706872001.5680816986.45401697-0.12990300H1.6383100	н	-2.25743500 -1.66907500 2.17708100	Н	-2.74928898 0.78713397 -1.32081100
H-5.29081700-0.54854000-0.68004200H0.221118022.205924971.45274700C-0.643344000.77348700-0.93257200C-4.543235983.024003971.86147800C-2.042507000.22147500-0.69648300C-3.090935982.621721971.57302000C-1.66603900-0.431214000.49011700C-3.422405981.935466970.39800700C-0.253393000.020842000.32738200C-4.851554982.130091970.69304500O0.86551400-0.449389000.84733600O-5.89648981.619321970.22057400Si2.08122500-1.29661100-0.03506700Si-7.544207981.530569970.97176700C-0.408657001.895291000.05069100C-4.888878984.289874971.12071400H-1.251764002.272882000.63037000H-4.086413984.945031970.80942400C0.848789002.62790400-0.01050800C-6.199634984.539099970.75787800H-0.099402000.77242800-1.86338100H-7.027860985.82249897-0.0490500H1.638310003.250249001.94412500H-7.027861985.82249897-0.12990300O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000H1.638310003.250249001.20699600C-8.935059982.09714197-0.13870700<	н	-3.65785700 0.74872400 -2.03894200	Н	-1.50357198 3.26592997 2.90353400
C -0.64334400 0.77348700 -0.93257200 C -4.54323598 3.02400397 1.86147800 C -2.04250700 0.22147500 -0.69648300 C -3.09093598 2.62172197 1.57302000 C -1.66603900 -0.43121400 0.49011700 C -3.42240598 1.93546697 0.39800700 C -0.25339300 0.02084200 0.32738200 C -4.845155498 2.13009197 0.69304500 O 0.86551400 -0.4983800 0.84733600 O -5.89648998 1.61932197 0.22057400 Si 2.08122500 1.29661100 -0.03506700 Si -7.54420798 1.5305697 0.97176700 C -0.40865700 1.89529100 0.05069100 C -4.8887898 4.28987497 1.12071400 H -1.25176400 2.27288200 -6.63037000 H -4.08641398 4.94503197 0.80942400 C 0.84878900 2.62790400 -0.01050800 C -6.5167998 5.82249897 0.04450500 H -0.09940200 0.77242800 1.86338100 H	Н	-5.29081700 -0.54854000 -0.68004200	Н	0.22111802 2.20592497 1.45274700
C -2.04250700 0.22147500 -0.69648300 C -3.09093598 2.62172197 1.57302000 C -1.66603900 -0.43121400 0.49011700 C -3.42240598 1.93546697 0.39800700 C -0.25339300 0.02084200 0.32738200 C -4.85155498 2.13009197 0.69304500 O 0.86551400 -0.44938900 0.84733600 O -5.89648998 1.61932197 0.22057400 Si 2.08122500 -1.29661100 -0.03506700 Si -7.54420798 1.5305697 0.97176700 C -0.40865700 1.89529100 0.05069100 C -4.8887898 4.28987497 1.12071400 H -1.25176400 2.27288200 0.63037000 H -4.08641398 4.94503197 0.80942400 C 0.84878900 2.62790400 -0.01050800 C -6.19963498 4.53909997 0.75787800 H -0.09940200 0.77242800 -1.8633100 H -4.98491398 2.86441797 2.84435600 C 1.03753100 3.76075500 0.98784900 C -	С	-0.64334400 0.77348700 -0.93257200	С	-4.54323598 3.02400397 1.86147800
C -1.66603900 -0.43121400 0.49011700 C -3.42240598 1.93546697 0.39800700 C -0.25339300 0.02084200 0.32738200 C -4.85155498 2.13009197 0.69304500 O 0.86551400 -0.44938900 0.84733600 O -5.89648998 1.61932197 0.22057400 Si 2.08122500 -1.29661100 -0.03506700 Si -7.54420798 1.53056997 0.97176700 C -0.40865700 1.89529100 0.05069100 C -4.8887898 4.28987497 1.12071400 H -1.25176400 2.27288200 0.63037000 H -4.08641398 4.94503197 0.80942400 C 0.84878900 2.6790400 -0.01050800 C -6.19963498 4.53990997 0.75787800 H -0.09940200 0.77242800 -1.86338100 H -4.98491398 2.86441797 2.84435600 C 1.03753100 3.76075500 0.98784900 C -6.55167998 5.82248597 -0.90905800 H -0.1672800 3.85892600 1.66859000 H -	С	-2.04250700 0.22147500 -0.69648300	С	-3.09093598 2.62172197 1.57302000
C-0.253393000.020842000.32738200C-4.851554982.130091970.69304500O0.86551400-0.449389000.84733600O-5.896489981.619321970.22057400Si2.08122500-1.29661100-0.03506700Si-7.544207981.530569970.97176700C-0.408657001.895291000.05069100C-4.888878984.289874971.12071400H-1.251764002.272882000.63037000H-4.086413984.945031970.80942400C0.848789002.62790400-0.01050800C-6.199634984.539099970.75787800H-0.099402000.77242800-1.86338100H-4.984913982.864417972.84435600C1.037531003.760755000.98784900C-6.551679985.822498970.04450500H1.560410004.706872000.53676900H-7.027860985.58248597-0.90905800H-0.016728003.858926001.66859000H-7.279841986.372497970.64477500H1.638310003.250249001.94412500H-5.680816986.45401697-0.12990300O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000	C	-1.66603900 -0.43121400 0.49011700	C	-3.42240598 1.93546697 0.39800700
O 0.86551400 -0.44938900 0.84733600 O -5.89648998 1.61932197 0.22057400 Si 2.08122500 -1.29661100 -0.03506700 Si -7.54420798 1.53056997 0.97176700 C -0.40865700 1.89529100 0.05069100 C -4.88887898 4.28987497 1.12071400 H -1.25176400 2.27288200 0.63037000 H -4.08641398 4.94503197 0.80942400 C 0.84878900 2.62790400 -0.01050800 C -6.19963498 4.53909997 0.75787800 H -0.09940200 0.77242800 -1.86338100 H -4.98491398 2.86441797 2.84435600 C 1.66041000 4.70687200 0.53676900 H -7.02786098 5.58248597 -0.90905800 H 1.63831000 3.25024900 1.94412500 H -5.68081698 6.45401697 -0.12990300 O 1.76621000 2.27744100 -0.75374800 O -7.15769498 3.72442297 0.97417000 <th>C</th> <th>-0.25339300 0.02084200 0.32738200</th> <th>C</th> <th>-4.85155498 2.13009197 0.69304500</th>	C	-0.25339300 0.02084200 0.32738200	C	-4.85155498 2.13009197 0.69304500
Si2.08122500-1.2961100-0.03506700Si-7.544207981.53058970.97176700C-0.408657001.895291000.05069100C-4.888878984.289874971.12071400H-1.251764002.272882000.63037000H-4.086413984.945031970.80942400C0.848789002.62790400-0.01050800C-6.199634984.539099970.75787800H-0.099402000.77242800-1.86338100H-4.984913982.864417972.84435600C1.037531003.760755000.98784900C-6.551679985.822498970.04450500H1.560410004.706872000.53676900H-7.027860985.58248597-0.90905800H-0.016728003.858926001.66859000H-7.279841986.372497970.64477500H1.638310003.250249001.94412500H-5.680816986.45401697-0.12990300O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.96432970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000<	0	0.86551400 -0.44938900 0.84733600	0	-5.89648998 1.61932197 0.22057400
C-0.408657001.395291000.03069100C-4.08878984.28374971.12071400H-1.251764002.272882000.63037000H-4.086413984.945031970.80942400C0.848789002.62790400-0.01050800C-6.199634984.539099970.75787800H-0.099402000.77242800-1.86338100H-4.984913982.864417972.84435600C1.037531003.760755000.98784900C-6.551679985.822498970.04450500H1.560410004.706872000.53676900H-7.027860985.58248597-0.90905800H-0.016728003.858926001.66859000H-7.279841986.372497970.64477500H1.638310003.250249001.94412500H-5.680816986.45401697-0.12990300O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600 <t< th=""><th>SI</th><th>2.08122500 -1.29661100 -0.03506700</th><th>SI</th><th>-/.54420/98 1.53056997 0.9/1/6/00</th></t<>	SI	2.08122500 -1.29661100 -0.03506700	SI	-/.54420/98 1.53056997 0.9/1/6/00
H-1.231704002.272832000.03057000H-4.080413984.343031970.03942400C0.848789002.62790400-0.01050800C-6.199634984.539099970.75787800H-0.099402000.77242800-1.86338100H-4.984913982.864417972.84435600C1.037531003.760755000.98784900C-6.551679985.822498970.04450500H1.560410004.706872000.53676900H-7.027860985.58248597-0.90905800H-0.016728003.858926001.66859000H-7.279841986.372497970.64477500H1.638310003.250249001.94412500H-5.680816986.45401697-0.12990300O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600H2.900073000.34000600-1.71711400H-6.719790981.247251973.28389300 <tr<< th=""><th>L L</th><th>-0.40805700 1.89529100 0.05009100</th><th>с ц</th><th>-4.88887898 4.28987497 1.12071400</th></tr<<>	L L	-0.40805700 1.89529100 0.05009100	с ц	-4.88887898 4.28987497 1.12071400
C0.040100000.077242800-1.86338100H-4.984913982.864417972.84435600C1.037531003.760755000.98784900C-6.551679985.822498970.04450500H1.560410004.706872000.53676900H-7.027860985.58248597-0.90905800H-0.016728003.858926001.66859000H-7.279841986.372497970.64477500H1.638310003.250249001.94412500H-5.680816986.45401697-0.12990300O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600H2.900073000.3400600-1.71711400H-6.719790981.247251973.28389300H3.567629000.70688300-0.11587700H-7.705068982.725871973.17401200H4.24009100-0.63951200-1.07063400H-8.644384981.112744973.19502800 <tr<< th=""><th>C</th><th></th><th>C C</th><th>-6 19963498 4 5390997 0 75787800</th></tr<<>	C		C C	-6 19963498 4 5390997 0 75787800
C1.037531003.760755000.98784900C-6.551679985.822498970.04450500H1.560410004.706872000.53676900H-7.027860985.58248597-0.90905800H-0.016728003.858926001.66859000H-7.279841986.372497970.64477500H1.638310003.250249001.94412500H-5.680816986.45401697-0.12990300O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600H2.900073000.34000600-1.71711400H-6.719790981.247251973.28389300H3.567629000.70688300-0.11587700H-7.705068982.725871973.17401200H4.24009100-0.63951200-1.07063400H-8.464384981.112744973.19502800C1.23666000-2.41210300-1.29899000C-7.56425198-0.356673030.74715700 <t< th=""><th>н</th><th>-0.09940200 0.77242800 -1.86338100</th><th>н</th><th>-4.98491398 2.86441797 2.84435600</th></t<>	н	-0.09940200 0.77242800 -1.86338100	н	-4.98491398 2.86441797 2.84435600
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H-0.016728003.858926001.66859000H-7.279841986.372497970.64477500H1.638310003.250249001.94412500H-5.680816986.45401697-0.12990300O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600H2.900073000.34000600-1.71711400H-6.719790981.247251973.28389300H3.567629000.70688300-0.11587700H-7.705068982.725871973.17401200H4.24009100-0.63951200-1.07063400H-8.464384981.112744973.19502800C1.23666000-2.41210300-1.29899000C-7.56425198-0.356673030.74715700H1.97736500-3.04998200-1.78025900H-8.50801808-0.765619031.12039500	Н	1.56041000 4.70687200 0.53676900	Н	-7.02786098 5.58248597 -0.90905800
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O1.766210002.27744100-0.75374800O-7.157694983.724422970.97417000C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600H2.900073000.34000600-1.71711400H-6.719790981.247251973.28389300H3.567629000.70688300-0.11587700H-7.705068982.725871973.17401200H4.24009100-0.63951200-1.07063400H-8.464384981.112744973.19502800C1.23666000-2.41210300-1.29899000C-7.56425198-0.356673030.74715700H1.97736500-3.04998200-1.78025900H-8.50891898-0.765619031.12039500	н	1.63831000 3.25024900 1.94412500	Н	-5.68081698 6.45401697 -0.12990300
C2.78992900-2.504345001.20699600C-8.935059982.09714197-0.13870700H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600H2.900073000.34000600-1.71711400H-6.719790981.247251973.28389300H3.567629000.70688300-0.11587700H-7.705068982.725871973.17401200H4.24009100-0.63951200-1.07063400H-8.464384981.112744973.19502800C1.23666000-2.41210300-1.29899000C-7.56425198-0.356673030.74715700H1.97736500-3.04998200-1.78025900H-8.50891898-0.765619031.12039500	0	1.76621000 2.27744100 -0.75374800	0	-7.15769498 3.72442297 0.97417000
H3.63558300-3.048710000.79779900H-9.644334981.28516497-0.31304000H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600H2.900073000.34000600-1.71711400H-6.719790981.247251973.28389300H3.567629000.70688300-0.11587700H-7.705068982.725871973.17401200H4.24009100-0.63951200-1.07063400H-8.464384981.112744973.19502800C1.23666000-2.41210300-1.29899000C-7.56425198-0.356673030.74715700H1.97736500-3.04998200-1.78025900H-8.50801898-0.765619031.12039500	С	2.78992900 -2.50434500 1.20699600	С	-8.93505998 2.09714197 -0.13870700
H3.15052700-1.973055002.11468500H-9.447585982.964329970.27457000H2.01578700-3.234487001.53496600H-8.513997982.39824897-1.10200000C3.31525000-0.11419100-0.80621000C-7.611329981.696662972.83507600H2.900073000.34000600-1.71711400H-6.719790981.247251973.28389300H3.567629000.70688300-0.11587700H-7.705068982.725871973.17401200H4.24009100-0.63951200-1.07063400H-8.464384981.112744973.19502800C1.23666000-2.41210300-1.29899000C-7.56425198-0.356673030.74715700H1.97736500-3.04998200-1.78025900H-8.50801898-0.765619031.12039500	Н	3.63558300 -3.04871000 0.79779900	Н	-9.64433498 1.28516497 -0.31304000
H 2.01578700 -3.23448700 1.53496600 H -8.51399798 2.39824897 -1.10200000 C 3.31525000 -0.11419100 -0.80621000 C -7.61132998 1.69666297 2.83507600 H 2.90007300 0.34000600 -1.71711400 H -6.71979098 1.24725197 3.28389300 H 3.56762900 0.70688300 -0.11587700 H -7.70506898 2.72587197 3.17401200 H 4.24009100 -0.63951200 -1.07063400 H -8.46438498 1.11274497 3.19502800 C 1.23666000 -2.41210300 -1.29899000 C -7.56425198 -0.35667303 0.74715700 H 1.97736500 -3.04998200 -1.78025900 H -8.50891898 -0.76561903 1.12039500	Н	3.15052700 -1.97305500 2.11468500	Н	-9.44758598 2.96432997 0.27457000
C 3.31525000 -0.11419100 -0.80621000 C -7.61132998 1.69666297 2.83507600 H 2.90007300 0.34000600 -1.71711400 H -6.71979098 1.24725197 3.28389300 H 3.56762900 0.70688300 -0.11587700 H -7.70506898 2.72587197 3.17401200 H 4.24009100 -0.63951200 -1.07063400 H -8.46438498 1.11274497 3.19502800 C 1.23666000 -2.41210300 -1.29899000 C -7.56425198 -0.35667303 0.74715700 H 1.97736500 -3.04998200 -1.78025900 H -8.50891898 -0.76561903 1.12039500	Н	2.01578700 -3.23448700 1.53496600	Н	-8.51399798 2.39824897 -1.10200000
H 2.9000/300 0.34000600 -1.71711400 H -6.71979098 1.24725197 3.28389300 H 3.56762900 0.70688300 -0.11587700 H -7.70506898 2.72587197 3.17401200 H 4.24009100 -0.63951200 -1.07063400 H -8.46438498 1.11274497 3.19502800 C 1.23666000 -2.41210300 -1.29899000 C -7.56425198 -0.35667303 0.74715700 H 1.97736500 -3.04998200 -1.78025900 H -8.50891898 -0.75561903 1.12039500	C	3.31525000 -0.11419100 -0.80621000	С	-7.61132998 1.69666297 2.83507600
H 3.56762900 0.70688300 -0.11587700 H -7.70506898 2.72587197 3.17401200 H 4.24009100 -0.63951200 -1.07063400 H -8.46438498 1.11274497 3.19502800 C 1.23666000 -2.41210300 -1.29899000 C -7.56425198 -0.35667303 0.74715700 H 1.97736500 -3.04998200 -1.78025900 H -8.50801808 -0.76561903 1.12030500	Н	2.9000/300 0.34000600 -1.71711400	н	-b./19/9098 1.24725197 3.28389300
11 4.24003100 -0.03351200 -1.07003400 П -8.40438498 1.11274497 3.19502800 C 1.23666000 -2.41210300 -1.29899000 C -7.56425198 -0.35667303 0.74715700 H 1.97736500 -3.0498200 -1.78025900 H -8.50801808 -0.76561903 1.1029500	Н	3.56/62900 0.70688300 -0.11587700	н	-/./U5U6898 2./258/19/ 3.1/401200 9.46429409 1.11274407 2.10502900
H 1 97736500 -3 0498200 -1 78025900 H -8 50801808 -0.3500/303 0.74/15/00		4.24009100 - 0.03951200 - 1.07063400	п С	-0.40438498 1.112/449/ 3.19502800
		1.23000000 -2.41210300 -1.23839000 1.07736500 -2.04000200 -1.23839000	с ц	-7.J042J190 -0.J007J03 0.74/15/00
H 0 49077500 -3 05837800 -0 81356900 H -7 47787108 -0.63582502 -0.20707200		1.37730300 -3.04336200 -1.76023900 0 49077500 _3 05837800 _0 81356000	н	-0.30031030 -0.7030303 1.12033300 -7 47787198 -0 63583503 -0 30707300
H 0.72725600 -1.83505700 -2.08665000 H -6 75152498 -0.84838003 1 29007600	Н	0.72725600 -1.83505700 -2.08665000	н	-6.75152498 -0.84838003 1 29007600

NMR SPECTRA

(4-methoxyphenyl)(triphenylsilyl)methanone (S25) (¹H NMR (400 MHz, CDCl₃))





(4-(but-3-en-1-yloxy)phenyl)(trimethylsilyl)methanone (S26) (¹H NMR (400 MHz, CDCl₃))



(4-(methylthio)phenyl)(trimethylsilyl)methanone (S27) (¹H NMR (400 MHz, CDCl₃))





(3'-fluoro-[1,1'-biphenyl]-4-yl)(trimethylsilyl)methanone (S28) (¹H NMR (400 MHz, CDCl₃))



¹³C NMR (101 MHz, CDCl₃)





(4-(benzyloxy)-3-chlorophenyl)(trimethylsilyl)methanone (S29) (¹H NMR (400 MHz, CDCl₃))



(4-hydroxyphenyl)(trimethylsilyl)methanone (S31) (¹H NMR (400 MHz, CDCl₃))



4-((trimethylsilyl)carbonyl)phenyl cyclopropanecarboxylate (S32) (¹H NMR (400 MHz, CDCl₃))



tert-Butyl 3-acryloylpiperidine-1-carboxylate (S38) (¹H NMR (400 MHz, CDCl₃))



1-(4,4-difluorocyclohexyl)prop-2-en-1-one (S41) (¹H NMR (400 MHz, CDCl₃))



120 110 f1 (ppm)

100 90 80 70 60 50 40 30 20 10

220

210 200 190 180 170 160 150 140 130

230



-300 -200 --100 ---0 ---100

ò





1-(4-(trifluoromethyl)cyclohexyl)prop-2-en-1-one (S44) (¹H NMR (400 MHz, CDCl₃))



5-phenylpent-1-en-3-one (S47) (¹H NMR (400 MHz, CDCl₃))



SI68

1-(1-phenylcyclopropyl)prop-2-en-1-one (S50) (¹H NMR (400 MHz, CDCl₃))









tert-butyl 4-(2-oxobut-3-en-1-yl)piperidine-1-carboxylate (S56) (¹H NMR (400 MHz, CDCl₃))

5-(3,4,5-trimethoxyphenyl)pent-1-en-3-one (S59) (¹H NMR (400 MHz, CDCl₃))




1,1-diphenylbut-3-en-2-one (S65) (¹H NMR (400 MHz, CDCl₃))







1-(tetrahydro-2*H*-pyran-4-yl)prop-2-en-1-one (S71) (¹H NMR (400 MHz, CDCl₃))



4-(4-isobutylphenyl)pent-1-en-3-one (S76) (¹H NMR (400 MHz, CDCl₃))







1-((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)prop-2-en-1-ol (S80) (¹H NMR (400 MHz, CDCl₃)) *Diastereomer 1:*



1-((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)prop-2-en-1-ol (S80') (¹H NMR (400 MHz, CDCl₃)) *Diastereomer 2:* 1-((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)prop-2-en-1-one (S81) (¹H NMR (400 MHz, CDCl₃))





(E)-4-(5-(tert-butyl)-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5a) (¹H NMR (400 MHz, CDCl₃))

(E)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5b) (¹H NMR (400 MHz, CDCl₃))





(E)-4-(5-methoxy-2-((triethylsilyl)carbonyl)phenyl)but-3-en-2-one (5c) (¹H NMR (400 MHz, CDCl₃))



(E)-4-(2-((triisopropylsilyl)carbonyl)-5-methoxyphenyl)but-3-en-2-one (5d) (¹H NMR (400 MHz, CDCl₃))



(E)-4-(2-((tert-butyldimethylsilyl)carbonyl)-5-methoxyphenyl)but-3-en-2-one (5e) (¹H NMR (400 MHz, CDCl₃))



(E)-4-(2-((dimethyl(phenyl)silyl)carbonyl)-5-methoxyphenyl)but-3-en-2-one (5f) (¹H NMR (400 MHz, CDCl₃))





(E)-4-(5-(benzyloxy)-4-chloro-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5h) (¹H NMR (400 MHz, CDCl₃))



(E)-4-(5-methyl-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5i) (¹H NMR (400 MHz, CDCl₃))



50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 f1 (ppm)

(E)-4-(6-((trimethylsilyl)carbonyl)benzo[d][1,3]dioxol-5-yl)but-3-en-2-one (5j) (¹H NMR (400 MHz, CDCl₃))

50 40 30 20 10 0 -10



(E)-4-(5-(methylthio)-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (5k) (¹H NMR (400 MHz, CDCl₃))

(E)-4-(5-chloro-2-((triethylsilyl)carbonyl)phenyl)but-3-en-2-one (5l) (¹H NMR (400 MHz, CDCl₃))







SI94

¹⁹F NMR (377 MHz, CDCl₃)



(E)-4-(3-((trimethylsilyl)carbonyl)naphthalen-2-yl)but-3-en-2-one (5n) (¹H NMR (400 MHz, CDCl₃))



SI96



(E)-4-(5-fluoro-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (50) (¹H NMR (400 MHz, CDCl₃))

¹⁹F NMR (377 MHz, CDCl₃)









(*E*)-3-(3-oxobut-1-en-1-yl)-4-((trimethylsilyl)carbonyl)phenyl cyclopropanecarboxylate (5q) (¹H NMR (400 MHz, CDCl₃))

(E)-4-(2-((trimethylsilyl)carbonyl)furan-3-yl)but-3-en-2-one (5r) (¹H NMR (400 MHz, CDCl₃))



(E)-4-(2-((trimethylsilyl)carbonyl)thiophen-3-yl)but-3-en-2-one (5s) (¹H NMR (400 MHz, CDCl₃))



SI102





(E)-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-5-phenylpent-1-en-3-one (5u) (¹H NMR (400 MHz, CDCl₃))





i i popul

100 90 80 70 60 50 40 30 20 10 0 -10

180 170 160 150 140 130 120 110 f1 (ppm)

50 240 230 220 210 200 190

(E)-6-chloro-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)hex-1-en-3-one (5v) (¹H NMR (400 MHz, CDCl₃))

--200 ---400


















(*E*)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-1-(1-phenylcyclopropyl)prop-2-en-1-one (5aa) (¹H NMR (400 MHz, CDCl₃))







(*E*)-1-((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)prop-2-en-1-one (5ab) (¹H NMR (400 MHz, CDCl₃))









(E)-5-methoxy-1-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)pent-1-en-3-one (S15) (¹H NMR (400 MHz, CDCl₃))

tert-butyl (*E*)-4-(4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)-2-oxobut-3-en-1-yl)piperidine-1-carboxylate (S16) (¹H NMR (400 MHz, CDCl₃))







tert-butyl (*E*)-3-(3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)acryloyl)piperidine-1-carboxylate (S18) (¹H NMR (400 MHz, CDCl₃))



(*E*)-1-((1R,2S,4R)-bicyclo[2.2.1]hept-5-en-2-yl)-3-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)prop-2-en-1-one (S19) (¹H NMR (400 MHz, CDCl₃))



(*E*)-3-methoxy-8-(2-((trimethylsilyl)oxy)prop-1-en-1-yl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6b) (¹H NMR (400 MHz, CDCl₃))



(*E*)-3-methoxy-8-(2-((triethylsilyl)oxy)prop-1-en-1-yl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6c) (¹H NMR (400 MHz, CDCl₃))













3-(*tert*-butyl)-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6a') (¹H NMR (400 MHz, CDCl₃))

3-methoxy-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6b') (¹H NMR (400 MHz, CDCl₃))







3-methyl-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6i') (¹H NMR (400 MHz, CDCl₃))





6-(2-oxopropyl)cyclobuta[4,5]benzo[1,2-d][1,3]dioxol-5(6*H*)-one (6j') (¹H NMR (400 MHz, CDCl₃))

3-(methylthio)-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6k') (¹H NMR (400 MHz, CDCl₃))





150 140 130

120 110 f1 (ppm) 100 90 80 70 60 50 40 30 20

230 220

210 200 190 180 170 160

(*Z*)-3-chloro-8-(2-((triethylsilyl)oxy)prop-1-en-1-yl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6l) (¹H NMR (400 MHz, CDCl₃))

10 0

3-(3-fluorophenyl)-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6m') (¹H NMR (400 MHz, CDCl₃))



SI131



2-(2-oxopropyl)cyclobuta[b]naphthalen-1(2H)-one (6n') (¹H NMR (400 MHz, CDCl₃))



3-fluoro-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6o') (¹H NMR (400 MHz, CDCl₃))







3-(but-3-en-1-yloxy)-8-(2-oxopropyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6p') (¹H NMR (400 MHz, CDCl₃))











3-methoxy-8-(2-oxobutyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6t') (¹H NMR (400 MHz, CDCl₃))

3-methoxy-8-(2-oxo-4-phenylbutyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6u') (¹H NMR (400 MHz, CDCl₃))





8-(5-chloro-2-oxopentyl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (6v') (¹H NMR (400 MHz, CDCl₃))









¹⁹F NMR (377 MHz, CDCl₃)




8-(3-(4-isobutylphenyl)-2-oxobutyl)-3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-one (6y') (¹H NMR (400 MHz, CDCl₃))

3-methoxy-8-(2-oxo-4-(3,4,5-trimethoxyphenyl)butyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6z') (¹H NMR (400 MHz, CDCl₃))



3-methoxy-8-(2-oxopropyl-1-d)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6ac') (¹H NMR (400 MHz, CDCl₃))



SI147

(E)-4-(2-acetyl-5-methoxyphenyl)but-3-en-2-one (10) (¹H NMR (400 MHz, CDCl₃))



(E)-4-methoxy-N,N-dimethyl-2-(3-oxobut-1-en-1-yl)benzamide (11) (¹H NMR (400 MHz, CDCl₃))







¹³C NMR (101 MHz, CDCl₃)



oxo-4-phenylbutyl)cyclopentan-1-one (13') (¹H NMR (400 MHz, CDCl₃))



(*E*)-*N*-(2-((*tert*-butyldimethylsilyl)carbonyl)-5-methoxyphenyl)-4-methyl-N-(3-oxobut-1-en-1-yl)benzenesulfonamide (14) (¹H NMR (400 MHz, CDCl₃))







6-methoxy-2-(2-oxopropyl)-1-tosylindolin-3-one (15') (¹H NMR (400 MHz, CDCl₃))









-11000



1-(1-hydroxy-5-methoxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triethylsilyl)-2,3-dihydro-1*H*-inden-2-yl)ethan-1-one (22) (¹H NMR (400 MHz, CDCl₃))





¹⁹F NMR (377 MHz, CDCl₃)



4-methoxy-8-oxobicyclo[4.2.0]octa-1,3,5-trien-7-yl)octane-2,6-dione (24) (¹H NMR (400 MHz, CDCl₃))



140 130

160 150

230

220 210

200 190 180 170

120 110 f1 (ppm) 100 90 80

70 60 50 40 30 20



-200

-100

-0

--100

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10

1-(8-hydroxy-4-methoxy-8-phenylbicyclo[4.2.0]octa-1,3,5-trien-7-yl)propan-2-one (25) (¹H NMR (400 MHz, CDCl₃))







1,1-difluoro-1-(8-hydroxy-4-methoxybicyclo[4.2.0]octa-1,3,5,7-tetraen-7-yl)propan-2-one (27) (¹H NMR (400 MHz, CDCl₃))







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