Cyclopropanation of Terminal Alkenes via Sequential Atom Transfer Radical Addition – 1,3-Elimination

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An operationally simple protocol to affect an atom transfer radical addition (ATRA) of commercially available ICH_2Bpin to terminal alkenes has been developed. The intermediate iodide can be transformed in a one-pot process into the corresponding cyclopropane upon treatment with tetrabutylammonium fluoride (TBAF). This method is highly selective for the cyclopropanation of unactivated terminal alkenes over non-terminal alkenes and electron deficient alkenes. Due to the mildness of the procedure, a wide range of functional groups such as esters, amides, alcohols, ketones, and vinylic cyclopropanes are well tolerated. The whole reaction sequence relies on simple reagents such dilauroyl peroxide (DLP) and TBAF and can be run on multi-gram scales in ethyl acetate as a solvent.

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Cyclopropanation of Terminal Alkenes via Sequential Atom Transfer Radical Addition – 1,3-Elimination

Nicholas D. C. Tappin, Weronika Michalska, Simon Rohrbach, Philippe Renaud^{*[a]}

Abstract: An operationally simple protocol to affect an atom transfer radical addition (ATRA) of commercially available ICH₂Bpin to terminal alkenes has been developed. The intermediate iodide can be transformed in a one-pot process into the corresponding cyclopropane upon treatment with tetrabutylammonium fluoride (TBAF). This method is highly selective for the cyclopropanation of unactivated terminal alkenes over non-terminal alkenes and electron deficient alkenes. Due to the mildness of the procedure, a wide range of functional groups such as esters, amides, alcohols, ketones, and vinylic cyclopropanes are well tolerated. The whole reaction sequence relies on simple reagents such as dilauroyl peroxide (DLP) and TBAF and can be run on multi-gram scales in ethyl acetate as a solvent.

Due to their stability and ease of handling, alkylboronic esters are extremely useful and attractive synthetic intermediates for a broad range of transformations^[1] involving carbon–heteroatom^[2] and carbon–carbon^[3–6] bond formation. Boronic esters have also been involved in a variety of radical reactions.^[7–11] They are prepared either via hydroboration,^[12,13] via reactions of organometallic species with borate esters and related reagents,^[14] via C–H activation process^[15] and more recently via radical borylation reactions.^[16] The nature of the alkyl chain at boron can be easily modified with a high level of stereocontrol by homologation reactions upon treatment with carbenoid type reagents.^[17–19]

Our long-standing interest in developing mild methods for the functionalization of alkenes via radical pathway^[20–32] incited us to investigate the iodoalkylation involving a 1-borylated alkyl radicals leading to γ -iodoalkylboronates. Based on EPR studies and calculations, Walton, Carboni, and co-workers reported that 1-borylated radicals are stabilized when the boron is sp²-hybridized, however the extent of stabilization is smaller for radicals substituted by a boronic ester substituent relative to the corresponding borinic ester or borane (Figure 1, A).^[33,34] This stabilization is the first key feature to design an iodine atom transfer process according to the pioneering work of Kharasch and Curran.^[35–41] Matching the philicities of the radicals and alkenes involved in the process is the second key feature for the success of the reaction. Strong polar effects favor an efficient and selective iodine atom transfer process over an oligomerization reaction. The resonance hybrids of the 1-borylalkyl radical suggest that the oxygen lone pairs reduce electrophilicity by the same mechanism that they decrease radical stabilization (Figure 1 B). Based on these simple considerations, it is expected that iodine atom transfer between 1-iodoalkylboronic esters and

alkenes should be possible – but still challenging – due to moderate thermodynamic and polar effects. Recently, Zard and co-workers rationalized the inefficiency of the xanthate transfer mediated addition of electrophilic radicals to pinacol vinylboronate by the lack of favorable thermodynamic and polar effects.^[42–44]

Figure 1. Radical stabilization energies (RSEs) of 1-borylated radicals and resonance hybrids of boronic esters derived radicals.^[34]

α -Haloboronic esters have been used in tin-mediated (Scheme 1, C)^{[45–47][48]} and metal-catalyzed radical processes.^[49–51] Chen reported the Pd(0) catalyzed cyclopropanation of norbornene using potassium iodomethyltrifluoroborate.^[52] Interestingly, pinacol iodomethylboronic ester could also be used for this transformation (Scheme 1, D). A mechanism involving a palladocyclobutane intermediate was proposed. Finally, 1-borylated alkyl radicals were involved in the elegant nickel-catalyzed alkylation and arylation of α -haloboronic esters developed by Fu^[53] and Martin,^[54] respectively. 1-Borylated alkyl radicals have also been generated from Barton esters^[55] and xanthates^[44] as well as through radical addition to vinylboronates.^[42,43,45,56–60] and to ate complexes of vinylboronates.^[61–63] To the best of our knowledge no halogen atom transfer radical addition (ATRA) process involving 1-haloalkylboronates have been reported. This reaction would be highly attractive since it opens a way to prepare in a straightforward manner 3-haloalkylboronates that are potential precursors of cyclopropanes via a 1,3-elimination process. Indeed, Hawthorne and Brown have both reported that 3-haloalkylboranes are easily converted into cyclopropanes upon conversion into their ate complexes by treatment with NaOH or MeLi.^[64–67] The stable boronic ester has not yet been used for this transformation and this attractive 1,3-cyclization has been limited to a few very simple unfunctionalized cyclopropanes since the precursors were only available by hydroboration of allylic halides. We report here, a study of the iodine atom transfer reactions between pinacol iodomethylboronate **1** and non-activated alkenes **2** (Scheme 1, E) that led to the development of a metal-free cyclopropanation procedure demonstrating a high

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chemoselectivity complementary to classical cyclopropanation methods involving carbenoids, carbenes, and Michael addition ring closure.^[68]

Scheme 1. Reaction of alkenes with 1-haloalkylboronic esters.

Initial attempts to run the iodine atom transfer reaction between **ICH₂Bpin** **1** and 1-undecene **2a** as a substrate demonstrated that the 3-iodoalkylboronate **3a** was decomposing during purification on silica gel. Eventually, we decided not to isolate **3a** and to convert it immediately into the cyclopropane **4a**. To our delight, preliminary experiments with small amount of isolated boronic ester **3a** showed that the cyclopropane formation was possible upon treatment with a variety of nucleophiles such as HO[−], EtO[−], and F[−]. Having established that the cyclopropane formation was possible, we started to optimize the whole process as outlined in Table 1. Initiation with triethylborane (BEt₃) and oxygen or di-*tert*-butylhyponitrite (DTBHN) were attempted first using either NaOH or LiOH to trigger the cyclopropanation but yields remained low (Table 1, entries 1–3). DLP was eventually identified as a superior initiating system and the use of one equivalent was necessary to reach the best yields (Table 1, entries 6–8).^[69] The reagent used to induce the cyclopropane formation was found to be less crucial. Good but slightly irreproducible results were obtained with the biphasic NaOH or LiOH system (Table 1, entries 3–4), higher yields and reproducibility were achieved by using LiOEt or TBAF (Table 1, entries 5, 6). The latter was finally selected for its mildness. The role of the solvent was found to be less critical. Good yields were obtained in benzene and chlorobenzene (Table 1, entries 6, 9). The reaction works also well in DCE (1,2-dichloroethane) (Table 1, entry 10) and it was found later that the reaction gave a similar yield when run in dry EtOAc (Table 1, entry 11). For the purposes of this investigation dry benzene was selected as the solvent of choice but one scale-up experiment was run in EtOAc with a more polar alkene (see below).

Table 1. Optimization of the cyclopropanation of undecene **2a** with pinacol iodomethylboronate **1**.^[a]

Entry	Initiator	Solvent, T	Lewis base	Yield ^[b]
1	BEt ₃ , air	CH ₂ Cl ₂ , rt	NaOH	28%
2	BEt ₃ , DTBHN ^[c]	CH ₂ Cl ₂ , reflux	NaOH	21%
3	BEt ₃ , ^[d] DTBHN ^[c]	CH ₂ Cl ₂ , reflux	LiOH	35%
4	DLP (1 equiv)	C ₆ H ₆ , reflux	LiOH	71%
5	DLP (1 equiv)	C ₆ H ₆ , reflux	LiOEt	75%
6	DLP (1 equiv)	C ₆ H ₆ , reflux	TBAF	73%
7	DLP (0.2 equiv)	C ₆ H ₆ , reflux	TBAF	40%
8	DLP (1.4 equiv)	C ₆ H ₆ , reflux	TBAF	71%
9	DLP (1 equiv)	ClC ₆ H ₅ , reflux	TBAF	74%
10	DLP (1 equiv)	DCE, reflux	TBAF	68%
11	DLP (1 equiv)	EtOAc, reflux	TBAF	74% ^[e]

[a] Reactions were run using **2a** (1 mmol), **1** (2 mmol) in dry benzene (3.3 mL) then the nucleophilic solution was added and the reaction mixture stirred vigorously. [b] Yields determined by GC using pentadecane as internal standard. [c] DTBHN = di-*tert*-butyl hyponitrite. [d] Syringe pump addition. [e] NMR yield with 1,4-dimethoxybenzene as external standard.

The scope of the reaction was investigated with a series of substrates (Scheme 2). Simple terminal alkenes bearing a wide range of functional group such as the electron rich aromatic ring of safrole (**2c**), the silyl ether **2d** (using LiOEt instead of TBAF to avoid cleavage of the silyl group), the ketone **2e**, the unprotected primary and secondary alcohols **2f** and **2g**, the acylated alcohols **2h** and **2i**, the benzyl ether **2j**, the free carboxylic acid **2k**, the esters **2l** and **2m**, and the secondary and tertiary amides **2o** and **2p** gave the desired products in fair to good yields (39–80%). Interestingly, the cyclopropanation of **2d** involved a neo-pentylid iodide showing that the cyclization mechanism is probably best described as a 1,3-elimination process in analogy to the reaction of 3-haloalkylboranes where inversion of the configuration at occurs at the halide and boron substituted carbon atoms.^[70,71] When 1,1-disubstituted alkenes were employed (such as **2q**), troubles were encountered with the stability of the intermediate iodides and a 15% yield was obtained with DLP under thermal initiation. Initiation with BEt₃/air turned out to be best since it could be performed at room temperature to give **4q** in 38% yield. Reaction with the methylenecyclobutane **2r** afforded the slightly volatile **4r** in a 45% yield. Following Chen's work,^[52] we also cyclopropanated norbornene **2s** to **4s** in 53% yield. Next, the procedure was used on diverse dienes to test the chemoselectivity. α,β -Unsaturated esters **2t** and **2u** reacted selectively at the unactivated terminal alkene. Acylated prenol, citronellol, nopol, and cholesterol **2w–2y** were selectively cyclopropanated at the terminal non-activated alkene to give **4w–4y** in 48–62% yields. Finally, the chrysanthemic ester **2z** afforded **4z** as a single isolated regioisomer without any modification of the *trans/cis* 8:2 diastereomeric ratio demonstrating further the mildness of the reaction conditions.

Scheme 2. Scope of the cyclopropanation. Procedure: All reactions were run on 1 mmol scale with no special precautions to remove moisture or air. Alkene (1 mmol), ICH₂Bpin (2 mmol), and DLP (1 mmol) were heated in refluxing benzene (0.3 M) under argon for 4 h; to the cooled reaction mixture was added TBAF solution (5 equiv, 1.0 M in THF) and stirred for 16 h. Each yield was determined by ¹H-NMR analysis of the crude product mixture after work-up using 1,4-dimethoxybenzene as reference. a) LiOEt (1.0 M in EtOH) was used instead of TBAF. b) Reaction performed in EtOAc on a 5 mmol scale. c) Initiated with BEt₃ (0.5–1.2 equiv) open to air, rt. d) Yield estimated by GC analysis using 1,5-cyclooctadiene as reference. See SI for details. e) No erosion of the *trans/cis* ratio.

As noticed early on, the isolation of the pinacol γ -iodoalkylboronic esters **3** resulting from the reaction of ICH₂Bpin **1** over numerous alkenes was challenging due to their instability during purification by silica gel chromatography (nonetheless all intermediates, **3a–z**, are characterized). This instability was attributed to C–I bond labilization by the Lewis-acidic proximal sp²-hybridized boron atom. Since pinanediol boronic esters are known to be thermodynamically more stable,^[72,73] we hypothesized that they may be less Lewis acidic and therefore the pinanediol γ -iodoalkylboronic esters may be more stable. Satisfyingly, reaction of the pinanediol iodomethylboronic ester **5** with alkenes **2g** afforded **6g** that was stable to silica gel purification in 74% isolated yield (Scheme 3).

Scheme 3. Isolation of a pinanediol γ -iodoalkylboronic ester.

The mechanism of the cyclopropanation reaction is depicted in Scheme 4 and corresponds to a classical radical iodine atom transfer process coupled with a Lewis base promoted 1,3-elimination (or intramolecular nucleophilic substitution). As discussed earlier, the iodine atom transfer step is favored by the higher stabilization of the 1-borylated radical relative to an alkyl radical. The radical addition to alkenes is controlled by polar and steric effects: the electron withdrawing boryl group favors the addition to electron rich alkenes and radical addition are much faster at the less hindered position. These two effects rationalize well the observed regioselectivities reported in Scheme 2.

Scheme 4. Mechanism of the cyclopropanation involving ATRA and 1,3-elimination processes.

In conclusion, we have reported here an unprecedented approach for the formation of cyclopropanes relying on a one-pot iodine atom transfer radical addition followed by an ionic intramolecular substitution process (1,3-elimination). The whole sequence is characterized by mild reaction conditions and excellent functional group compatibility. Interestingly, the high regioselectivity observed for terminal non-activated alkenes over non-terminal and electron deficient alkenes cannot be achieved easily using classical cyclopropanation methods. Finally, the possible isolation of the intermediate products of iodine atom transfer depicted in Scheme 3 open new opportunities for further synthetic applications.

Experimental Section

General cyclopropanation procedure. Reactions were run under argon but no precaution to eliminate moisture or air was necessary. A solution of ICH₂Bpin, **1** (540 mg, 2.0 mmol), DLP (400 mg, 1.0 mmol), and alkene (1.0

mmol) in benzene (3.5 mL) was heated under reflux for 4 h. After cooling down to rt, a TBAF solution (1.0 M in THF, 5.0 mL, 5.0 mmol) was added in one portion and the reaction mixture stirred for 16 h. The mixture was partitioned between TBME and H₂O, shaken with sat. aq. Na₂S₂O₃ and washed successively with H₂O, sat. aq. NaHCO₃ and brine. After drying over Na₂SO₄, the residue was filtered through a silica plug to afford the desired crude cyclopropane.

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Keywords: radical reaction • organoboron • cyclopropanation • alkenes • 1-borylated radical • iodine atom transfer • ATRA • boronate complexes.

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1 General and instrumentation

Most ^{13}C , ^{11}B , and ^1H NMR spectra were recorded on a Bruker Avance 300 (^1H : 300.18 MHz, ^{13}C : 75.48 MHz, ^{11}B : 96.30 MHz). Some NMR were recorded on a Bruker Avance II 400 spectrometer (^1H : 400.13 MHz, ^{13}C : 101 MHz). Chemical shifts are reported in units of δ (ppm). The spectra were referenced according to commonly adopted norms. For ^1H NMR spectra the internal standard, tetramethylsilane (TMS), was set to $\delta = 0.000$ ppm or the residual protonated solvents were used to reference the spectra (C_6H_6 $\delta = 7.160$ ppm; CHCl_3 $\delta = 7.270$ ppm; CH_2Cl_2 $\delta = 5.340$ ppm). For ^{13}C NMR spectra the internal standard, tetramethylsilane (TMS), was set to $\delta = 0.00$ ppm or the deuterated solvents were used to reference the spectra (C_6D_6 $\delta = 128.06$ ppm; CDCl_3 $\delta = 77.11$ ppm; CD_2Cl_2 $\delta = 54.00$). ^{13}C NMR spectra were run using a proton-decoupled pulse sequence. Due to coupling to the quadrupolar ^{11}B and ^{10}B nuclei, the carbons bonded to boron atoms have a broadened signal in ^{13}C NMR and are mostly not detected. Exceptionally, with highly concentrated NMR samples or with INVGATE ^{13}C NMR experiments, the carbons linked to B may be observed. ^{11}B NMR spectra were calibrated to $\text{Et}_2\text{O} \cdot \text{BF}_3$ (0.00 ppm) as an external reference. The following abbreviations were used to describe the multiplicities: s (singlet), d (doublet), t (triplet), q (quadruplet), p (quintet or pentet), m (multiplet), br (broad), sh (shoulder), and the prefix app (apparent) was added when different coupling constants appeared equal. Coupling constants (J) are reported in Hertz (Hz) with an accuracy of one unit of the last digit. Multiplicities were interpreted at the second order following Pople nomenclature when possible. Despite some apparent second order contributions depending on the processing of the FID (e.g. apodization function), some signals were approximated to the first order when the resolution was not sufficient. ^{13}C NMR spectra were run using a proton-decoupled pulse sequence. The number of carbon atoms for each signal is indicated only when superior to one and when two signals are very close they are reported with two decimal places. HRMS analyses were recorded on an Applied Biosystems Sciex QSTAR Pulsar (hybrid quadrupole time-of-flight mass spectrometer) using positive electron spray. Infrared spectra were recorded neat equipped with a diamond ATR System and are reported in wave numbers (cm^{-1}). Reported are the characteristic signals only (with decreasing wave number) and assignments are made, the spectra may be consulted for extracting other vibrations. The following abbreviations were used to describe relative intensities: w (weak), m (medium), s (strong), br (broad), e.g. for OH peaks, and sh (shoulder). GC analyses were carried out on a *Macherey-Nagel* Optima delta-3-0.25 μm capillary column (20 m, 0.25 mm); carrier gas: He 1.4 mL/min; injector: 220 $^\circ\text{C}$ split mode; detector: FID 280 $^\circ\text{C}$, H_2 35 mL/min, air 350 mL/min. GC–MS analyses were performed on a an apparatus equipped with a quadrupole mass analyzer using electron impact 70 eV) fitted with a *Macherey-Nagel* Optima delta-3-0.25 μm capillary column (20 m, 0.25 mm); carrier gas: He 1.4 mL/min; injector: 220 $^\circ\text{C}$ split mode. For flash column chromatography (FCC) *Macherey-Nagel Silica 60* 0.04 – 0.063 mm silica gel was used. Thin layer chromatography (TLC) was performed using *Silicycle* glass backed TLC extra hard layer, 259 μm , 60 $\text{\AA}$, F-254 analytical plates, *Macherey-Nagel ALUGRAM[®]* Xtra SIL G/UV₂₅₄, 0.2 mm silica gel, or *Macherey-Nagel POLYGRAM[®]* ALUMINUM OXIDE N/UV₂₅₄, 0.2 mm aluminum oxide, or

(best choice) *Macherey-Nagel* SIL G/UV254, 0.25 mm silica gel; visualization under UV (254 nm and/or 366 nm), iodine, and by staining with a solution of potassium permanganate (KMnO₄); phosphomolybdic acid (H₃PMo₁₂O₄₀) and cerium sulfate (Ce(SO₄)₂), and subsequent heating. For the γ -iodoboronic esters, isolation employing *Macherey-Nagel* silica gel was paramount – other silica gels led to total or substantial decompositions and with *Macherey-Nagel* minor decomposition was observed (2D TLC, poor isolated yields).

Unless otherwise stated, all yields are isolated yields. Ambient (or room) temperatures were generally in the range 21–25 °C. All reactions were run under an Argon atmosphere and additions of solids were performed quickly or under a blanket of flowing Argon, unless otherwise specified. All glassware was oven-dried at least overnight at 140 °C, assembled hot, and cooled under a stream of dry Argon gas, or flame-dried under vacuum.

2 Reagents and substrates

2.1 Iodide radical precursors

2-(Iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)

A modified literature procedure was employed.^[1] A 3-neck, 250 mL, round-bottom flask was flame-dried and equipped with an oven-dried, 100 mL dropping funnel, and a low-temperature thermometer. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33.3 mL, 160 mmol), diiodomethane (12.9 mL, 160 mmol, 1.0 equiv) and THF (1.6 M, 100 mL, via canula) were loaded into the flask and dissolved with vigorous stirring. Methyl lithium^[2] (1.6 M solution in Et₂O, 100 mL, 160 mmol, attention: very flammable) was loaded into the dropping funnel via canula. The contents of the flask were cooled to -78 °C with a dry ice/acetone bath and the dropping funnel held at a steady drip rate to maintain a temperature below -65 °C, over approximately three hours. Once addition was complete the reaction mixture was stirred at this temperature for a further hour and the cooling bath removed. Dry hydrochloric acid (2.0 M in Et₂O, 84 mL) was added quickly at no particular temperature (runs performed at ambient temperature or below -60 °C had no influence on the outcome). The flask was stirred for a further one hour (or overnight), stoppered, and the majority of the volatiles were removed *in vacuo* (attention: MeI – perform in a well-ventilated fume-hood). The remaining contents were partitioned between pentane (100 mL) and 10% (w/v) aq. Na₂S₂O₃ (100 mL), and stirred for two minutes. The organic phase was

washed with H₂O (2x100 mL), sat. aq. NaHCO₃ (100 mL), sat. aq. NaCl (100 mL), and dried over Na₂SO₄. The dried solution was filtered and concentrated *in vacuo*. The crude orange oil was distilled (20 cm vigreux column, 6x10⁻¹ to 1 mbar, 90 to 110 °C) to afford **1** as a pale yellow oil (38.1 g, 142 mmol, 89%, first 1-3 mL usually impure, typically 80-95% yield). The pinacol analogue is reasonably stable to ambient conditions but was stored on the bench-top in brown vials. For long periods it was stored under argon and frozen at -18 °C. During the distillation the entire apparatus was protected rigorously behind aluminium foil and the ambient lights dimmed as much as possible. Small “light leaks” would decompose the vapourized iodide presumably to iodine and the distillate would turn through dark orange to purple. This compound has been described as various colours including red or purple, but it is actually colourless (or slightly yellow-tinted) and transparent. ¹H NMR (300 MHz, CDCl₃): δ 2.17 (s, 2H), 1.28 (s, 12H). ¹¹B NMR (96 MHz, CDCl₃): δ 31.7 (s). ¹³C NMR (75 MHz, CDCl₃): δ 84.2 (C_q), 24.4 (CH₃). The methylene adjacent to boron does not appear due to quadrupolar interactions. IR (thin film): ν_{max} = 1372 (m), 1321 (s), 1142 (s), 844 (s) cm⁻¹. Different stretching modes the pinacol boronic ester dioxolane ring.^[3] All physical and spectral data are in accordance with literature.^[1,4]

(3a*R*,4*R*,6*R*,7a*S*)-2-(Iodomethyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (5**)**

A 2-neck, 100 mL, round-bottom flask was flame-dried and equipped with a low-temperature thermometer. Triisopropyl borate (6.92 mL, 30 mmol), diiodomethane (2.42 mL, 30 mmol) and THF (1.6 M, 17 mL) were loaded into the flask and dissolved with vigorous stirring. The contents of the flask were cooled to -78 °C with a dry ice/acetone bath. Methyllithium^[2] (1.6 M solution in Et₂O, 19 mL, 30 mmol, attention: very flammable) was added to the reaction mixture at a steady drip rate to maintain a temperature below -65 °C, over approximately 45 minutes. Once addition was complete the reaction mixture was stirred at this temperature for a further hour and the cooling bath removed. Dry hydrochloric acid (2.0 M in Et₂O, 84 mL) was added quickly at no particular temperature and the flask was allowed to warm to rt. The flask was stirred for a further one hour and then α-(-)-pinanediol^[5,6] (6.13 g, 36 mmol) was quickly added. The contents were stirred overnight, and the majority of the volatiles were removed *in vacuo* (attention: MeI – perform in a well-ventilated fume-hood). The remaining contents were partitioned between TBME (100 mL) and 10% (w/v) aq.

Na₂S₂O₃ (100 mL), and stirred for two minutes. The organic phase was washed with H₂O (2x100 mL), sat. aq. NaHCO₃ (100 mL), sat. aq. NaCl (100 mL), and dried over Na₂SO₄. The dried solution was filtered and concentrated *in vacuo*. The crude orange oil was submitted to FCC to afford **5** as a pale orange oil (7.57 g, 23.6 mmol, 79%). *R*_f = 0.65 (20% EtOAc/cyclohexane, KMnO₄, UV). $[\alpha]_D^{20}$ – 14.4° (*c* 1.05, CHCl₃); lit: – 23.6° (*c* 3.2, CHCl₃).^[7] ¹H NMR (300 MHz, CDCl₃): δ 4.37 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.44 – 2.23 (m, 2H), 2.21 (s, 2H), 2.08 (app t (dd), *J* = 5.5 Hz, 1H), 1.99 – 1.91 (m, 2H), 1.43 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H), 1.28 (d, *J* = 11.2 Hz, 1H), 0.85 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 86.5 (C_q), 78.5 (CH), 51.4 (CH), 39.3 (CH), 38.4 (C_q), 35.3 (CH₂), 28.3 (CH₃), 27.0 (CH₃), 26.3 (CH₂), 24.0 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 31.3 (s). IR (thin film): ν_{max} = 1377 (s), 1328 (s) cm⁻¹. HRMS (ESI, neg): Calculated for C₁₁H₁₉BIO₃ [M+OH]⁻: 337.0477. Found: 337.0483. Physical and spectral data are in accordance with literature.^[7]

2.2 Alkene substrates

tert-Butyl((3,3-dimethylhex-5-en-1-yl)oxy)dimethylsilane (2d)

C₁₃H₂₈OSi
MW: 228.45

To a flame-dried two-neck 250 mL flask was suspended LiAlH₄ (3.40 g, 94.2 mmol) in Et₂O (0.2 M, 150 mL). The contents were cooled to –78 °C with an acetone/dry ice bath and a solution of methyl 3,3-dimethylpent-4-enoate (5.0 mL, 31.4 mmol) in Et₂O (10 mL) was slowly added. The reaction mixture was stirred at this temperature for one hour, warmed 0 °C and stirred for one hour, then warmed to ambient temperature and stirred for one hour. The mixture was cooled back down to 0 °C and the Fieser work-up performed. The mixture was opened to air, H₂O (3.5 mL) was added dropwise with vigorous stirring, followed by 15wt% aq. NaOH (3.5 mL), and H₂O (10.5 mL), and the stirred at ambient temperature for 15 minutes. MgSO₄ (~ 3 g) was added and the contents were filtered through a silica plug. The resulting solution was concentrated *in vacuo* to yield a clear free-flowing oil deemed pure according to TLC (*R*_f = 0.10 (8% EtOAc/heptanes, KMnO₄)) and ¹H-NMR which was submitted to the following step without any purification. To a flame-dried 100 mL two-neck flask charged with TBDMSCl (5.20 g, 34.5 mmol) and DMAP (390 mg, 3.14 mmol), dissolved in DCM (0.5 M, 60 mL) and cooled to 0 °C, was added the crude alcohol and NEt₃ (5.25 mL, 37.7 mmol) in portions. The mixture was warmed to ambient temperature and stirred for one hour after which time TLC indicated completion and the contents were concentrated *in vacuo*. The residue was partitioned between Et₂O (40 mL) and aq. 1.0 M HCl (40 mL) and the ethereal phase washed with aq. 1.0 M HCl (40 mL). The combined aqueous phases was back-extracted with Et₂O (10 mL) and the combined ethereal phases washed sequentially with 1.0 M HCl (40 mL), sat. aq. NaHCO₃ (2x 40 mL), sat. aq. NaCl (40 mL),

dried over Na₂SO₄, filtered through a silica plug, and concentrated *in vacuo* to afford **2d** as a colourless free-flowing liquid (6.89 g, 30.2 mmol, 96% over two-steps) deemed pure by TLC and NMR. R_f = 0.45 (2% EtOAc/heptanes, KMnO₄). ¹H NMR (300 MHz, CDCl₃): δ 5.79 (dd, J = 17.8, 10.4 Hz, 1H), 4.91 (ddd, J = 13.8, 3.5, 1.3 Hz, 2H), 3.84 – 3.40 (m, 2H), 1.72 – 1.45 (m, 2H), 1.02 (s, 6H), 0.90 (s, 9H), 0.05 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 148.2 (CH), 110.4 (CH₂), 60.4 (CH₂), 45.1 (CH₂), 35.7 (C_q), 27.2 (CH₃), 26.1 (CH₃), 18.4 (C_q), –5.1 (CH₃). IR (thin film): $\nu_{\max}$ = 3084 (w),^b 2995 (w),^b 1639 (w),^a 1003 (w),^c 910 (m)^c cm^{–1}. ^aUnconjugated, acyclic terminal alkene C=C stretching vibration. ^bTerminal alkene C(H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. Spectral data are in accordance with literature.^[8]

Dodec-11-en-2-one (**2e**)

Ley-Griffiths oxidation. To a flame-dried 1-neck 50 mL flask was charged activated 4A MS (~2 g), TPAP (80 mg) and NMO (770 mg, 6.60 mmol). The contexts were suspended in DCM (0.25 M, 20 mL) and cooled with an ice/water bath. Dodec-11-en-2-ol **2f** (812 mg, 4.4 mmol) was added in two portions and the reaction mixture warmed to ambient temperature and stirred for two hours. TLC monitoring indicated incomplete conversion but nonetheless the mixture was filtered through a silica plug and washed with ethyl acetate. The partially clear solution was concentrated *in vacuo* and submitted to FCC (grad = 2-3-3-4% EtOAc/heptanes, res = 250 mL, dia = 35 mm, l = 18 cm, f = 20 mL) to afford **2e** as a clear free-flowing oil (525 mg, 2.88 mmol, 66%). R_f = 0.56 (15% EtOAc/heptanes, CAM, I₂). ¹H NMR (300 MHz, CDCl₃): δ 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.08 – 4.78 (m, 2H), 2.41 (app t, J = 7.4 Hz, 2H), 2.13 (s, 3H), 2.03 (app tdd, J = 6.6, 5.3, 1.4 Hz, 2H), 1.56 (app p, J = 7.1 Hz, 2H), 1.46 – 1.16 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 209.3 (C_q), 139.2 (CH), 114.1 (CH₂), 43.8 (CH₂), 33.8 (CH₂), 29.9 (CH₃), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 28.9 (CH₂), 23.9 (CH₂). IR (thin film): $\nu_{\max}$ = 3076 (w),^b 1716 (s),[§] 1641 (w),^a 993 (w),^c 907 (m)^c cm^{–1}. [§]Unconjugated acyclic ketone carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for C₁₂H₂₃O [M+H]⁺: 183.1743. Found: 183.1750. Spectral data are in accordance with literature.^[9]

Dodec-11-en-2-ol (2f)

Grignard addition. To a flame-dried 2-neck 100 mL flask equipped with a thermometer was charged undec-10-enal (2.88 g, 17.1 mmol) and THF (0.3 M, 40 mL). The contents were cooled to -40 °C with an acetonitrile/dry ice bath. MeMgBr (3.0 M in Et₂O, 20 mL) was slowly added over one hour. The reaction was stirred at this temperature for two hours and then at ambient temperature for 12 hours. The reaction mixture was slowly poured onto sat. aq. NH₄Cl (200 mL) and partitioned into TBME (200 mL). The ethereal phase was washed with aq. 1.0 M HCl (40 mL), and the combined aqueous phases back-extracted with TBME (40 mL). The combined ethereal phases were washed with H₂O (200 mL) sat. aq. NaHCO₃ (200 mL), sat. aq. NaCl (200 mL), dried over Na₂SO₄, filtered through a silica plug, concentrated *in vacuo*, and the crude residue submitted FCC (grad = 7-10-10-10-15% EtOAc/heptanes, res = 500 mL, dia = 70 mm, l = 23 cm, f = 100 mL) to afford **2f** as a clear free-flowing oil (2.61 g, 14.2 mmol, 83%). R_f = 0.45 (30% EtOAc/heptanes, CAM, I₂). ¹H NMR (300 MHz, CDCl₃): δ 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 – 4.85 (m, 2H), 3.78 (app p, *J* = 6.1 Hz, 1H), 2.04 (app tdd, *J* = 6.6, 5.3, 1.4 Hz, 2H), 1.56 – 1.22 (m, 14H), 1.18 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 139.2 (CH), 114.1 (CH₂), 68.2 (CH), 39.4 (CH₂), 33.8 (CH₂), 29.63 (CH₂), 29.56 (CH₂), 29.4 (CH₂), 29.1 (CH₂), 28.9 (CH₂), 25.8 (CH₂), 23.5 (CH₃). IR (thin film): ν_{max} = 3343 (br, w),[‡] 3076 (w),^b 1641 (w),^a 993 (w),^c 908 (m) cm⁻¹. [‡]Intermolecularly H-bonded O—H stretching vibration. ^aUnconjugated terminal alkene C=C stretching vibration. ^bTerminal alkene C(—H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. Spectral data are in accordance with literature.^[10]

Undec-10-enal

Swern oxidation. To a flame-dried 2-neck 250 mL flask equipped with a thermometer was charged with oxalyl chloride (5.0 mL, 59 mmol) and dissolved in DCM (0.4 M, 100 mL). The contents were cooled to -78 °C with an acetone/dry ice bath. To the mixture, maintaining a temperature below -78 °C, were sequentially added a solution of DMSO (8.4 mL, 118 mmol) in DCM (30 mL), followed by stirring for a further 15 minutes; a

solution of 10-undecen-1-ol (98% purity, 8.2 mL, 40.0 mmol) in DCM (30 mL), followed by stirring for a further 15 minutes; and a finally a solution of NEt₃ (16.4 mL, 118 mmol) in DCM (30 mL), followed by stirring for 30 minutes. The cooling Dewar was removed and the mixture warmed to ambient temperature over three hours. The reaction mixture was slowly quenched with aq. 2.0 M HCl (20 mL) and added to another 180 mL of aq. 2.0 M HCl and the biphasic mixture was partitioned. The DCM phase was washed with aq. 1.0 M HCl (100 mL), and the combined aqueous phases back-extracted with DCM (40 mL). The combined DCM phases was washed with H₂O (200 mL), sat. aq. NaHCO₃ (200 mL), sat. aq. NaCl (200 mL), dried over Na₂SO₄, filtered through a silica plug, concentrated *in vacuo* (attention: stinky – perform inside a well-ventilated fume-hood), and the crude residue submitted FCC (grad = 3-3-4-4% EtOAc/heptanes, res = 250 mL, dia = 55 mm, l = 22 cm, f = 100 mL) to afford undec-10-al as a clear oil (5.32 g, 31.6 mmol, 79%). *R_f* = 0.67 (10% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 9.76 (t, *J* = 1.8 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.13 – 4.83 (m, 2H), 2.42 (td, *J* = 7.4, 1.8 Hz, 2H), 2.04 (app q, *J* = 6.8 Hz, 1H), 1.74 – 1.54 (m, 2H), 1.47 – 1.13 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 202.9 (CH), 139.1 (CH), 114.2 (CH₂), 43.9 (CH₂), 33.8 (CH₂), 29.30 (CH₂), 29.26 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 28.9 (CH₂), 22.1 (CH₂). IR (thin film): *v*_{max} = 3076 (w),^b 1725 (s),[§] 1641 (w),^a 993 (m),^c 908 (s)^c cm⁻¹. [§]Unconjugated acyclic ketone carbonyl stretching vibration. ^aUnconjugated terminal alkene C=C stretching vibration. ^bTerminal alkene C(=H)₂ stretching vibration. ^c1-substituted alkene C–H bending vibrations. Spectral data are in accordance with literature.^[10]

Undec-10-en-1-yl acetate (2h)

A flame-dried 1-neck 100 mL flask was charged with 10-undecen-1-ol (97% purity, 2.0 mL, 10.0 mmol), DCM (0.2 M, 50 mL), and pyridine (0.97 mL, 12.0 mmol), and cooled to 0 °C with an ice/water bath. Acetyl chloride (95% purity, 0.82 mL, 11.0 mmol) was slowly added and the reaction mixture allowed to warm to ambient pressure and stir for one day, by which time TLC analysis indicated complete conversion. The majority of the volatiles were removed *in vacuo* and the residue partitioned between Et₂O (40 mL) and aq. 1.0 M HCl (40 mL). The ethereal phase was washed with H₂O (40 mL), and the combined aqueous phases back-extracted with Et₂O (10 mL). The combined ethereal phases was washed with aq. 1.0 M HCl (40 mL), sat. aq. NaHCO₃ (2x 40 mL), sat. aq. NaCl (40 mL), dried over Na₂SO₄, filtered through a silica plug, concentrated *in vacuo*, and the crude residue vacuum distilled to afford **2h** as a clear, free-flowing oil (1.99 g, 9.3 mmol, 93%). *R_f* = 0.59 (20% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 5.8 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.12 – 4.80 (m, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 2.20 – 1.93 (m,

5H, [interpreted as containing 2.04 (s, 3H)], 1.74 – 1.51 (m, 2H), 1.45 – 1.17 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 171.2 (C_q), 139.2 (CH), 114.1 (CH_2), 64.7 (CH_2), 33.8 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 25.9 (CH_2), 21.0 (CH_3). IR (thin film): ν_{max} = 3077 (w),^b 1740 (s),[§] 1641 (w),^a 993 (m),^c 908 (s)^c cm^{-1} . [§]Unconjugated acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(—H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 235.1669. Found: 235.1675. Spectral data are in accordance with literature.^[11]

Undec-10-en-1-yl benzoate (2i)

$\text{C}_{18}\text{H}_{26}\text{O}_2$
MW: 274.40

A flame-dried 1-neck 100 mL flask was charged with 10-undecen-1-ol (97% purity, 2.0 mL, 10.0 mmol), DCM (0.2 M, 50 mL), and pyridine (0.97 mL, 12.0 mmol), and cooled to 0 °C with an ice/water bath. Benzoyl chloride (95% purity, 0.82 mL, 11.0 mmol) was slowly added and the reaction mixture allowed to warm to ambient pressure and stir for one day, by which time TLC analysis indicated complete conversion. The majority of the volatiles were removed *in vacuo* and the residue partitioned between Et_2O (40 mL) and aq. 1.0 M HCl (40 mL). The ethereal phase was washed with H_2O (40 mL), and the combined aqueous phases back-extracted with Et_2O (10 mL). The combined ethereal phases was washed with aq. 1.0 M HCl (40 mL), sat. aq. NaHCO_3 (2x 40 mL), sat. aq. NaCl (40 mL), dried over Na_2SO_4 , filtered through a silica plug, concentrated *in vacuo*, and the crude residue submitted to FCC (grad = 1-2-3% EtOAc/heptanes, dia = 55 mm, l = 20 cm, f = 100 mL) to afford **2i** as a clear, free-flowing oil (2.58 g, 9.4 mmol, 94%). R_f = 0.43 (8% EtOAc/heptanes, *p*-anis, KMnO_4 , CAM, UV). ^1H NMR (300 MHz, CDCl_3): δ 8.22 – 7.84 (m, 2H), 7.65 – 7.49 (m, 1H), 7.49 – 7.37 (m, 2H), 5.81 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.14 – 4.84 (m, 2H), 4.31 (t, J = 6.7 Hz, 2H), 2.13 – 1.94 (m, 2H), 1.87 – 1.69 (m, 2H), 1.53 – 1.20 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.7 (C_q), 139.2 (CH), 132.8 (CH), 130.6 (C_q), 129.5 (CH), 128.3 (CH), 114.1 (CH_2), 65.1 (CH_2), 33.8 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 26.0 (CH_2). IR (thin film): ν_{max} = 3073 (w),^b 1717 (s),[§] 1640 (w),^a 1603 (w),^{ar} 1585 (w),^{ar} 1492 (w),^{ar} 993 (w),^c 908 (m)^c cm^{-1} . [§]Unconjugated, acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(—H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. ^{ar}Aromatic ring C=C stretching modes. HRMS (ESI): Calculated for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 297.1825. Found: 297.1833. All physical and spectral data are in accordance with literature.^[12]

Benzyl undec-10-enyl ether (2j)
 C₁₈H₂₈O
 MW: 260.42

A 1-neck 50 mL flask was charged with NaH (55-65wt% on oil, 480 mg, 12.0 mmol), and washed with hexanes (3x 5 mL). Under a flow of argon, TBAI (38 mg, 1 mol%) was added, the contents were dissolved in dry DMF (10 mL), and cooled to 0 °C with an ice/water bath. A solution of 10-undecen-1-ol (97% purity, 2.1 mL, 10.0 mmol) in dry DMF (10 mL) was slowly added. After stirring at 0 °C for one hour, the mixture was warmed to ambient temperature and stirred for a further two hours. BnBr (98% purity, 1.33 mL, 11.0 mmol) was added and the reaction mixture stirred for four days. The reaction mixture was poured onto TBME (200 mL) and slowly quenched with aq. 1.0 M HCl (200 mL). The mixture was partitioned and the ethereal phase washed with H₂O (3x 200 mL), sat. aq. NaHCO₃ (200 mL), sat. aq. NaCl (3x 200 mL), dried over Na₂SO₄, filtered through a silica plug, concentrated *in vacuo*, and the crude residue submitted to FCC (grad = 1-2% EtOAc/heptanes, dia = 55 mm, l = 17 cm, f = 50 mL), to afford **2j** as a clear, free-flowing oil (2.25 g, 8.6 mmol, 86%). *R_f* = 0.51 (4% EtOAc/heptanes, KMnO₄, UV). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.41 – 7.21 (m, 5H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06 – 4.87 (m, 2H), 4.46 (s, 2H), 3.45 (app t, *J* = 6.6 Hz, 2H), 2.03 (app tdd, *J* = 6.5, 5.3, 1.4 Hz, 2H), 1.78 – 1.53 (m, 2H), 1.46 – 1.09 (m, 2H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 139.8 (CH), 139.5 (C_q), 128.6 (CH), 127.9 (CH), 127.7 (CH), 114.2 (CH₂), 73.1 (CH₂), 71.0 (CH₂), 34.2 (CH₂), 30.2 (CH₂), 30.0 (CH₂), 29.88 (CH₂), 29.85 (CH₂), 29.6 (CH₂), 29.4 (CH₂), 26.6 (CH₂). IR (thin film): ν_{max} = 3064 (w),^b 1641 (w),^a 993 (m),^c 907 (s) cm⁻¹. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(—H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for C₁₈H₂₈ONa [M+Na]⁺: 283.2023. Found: 283.2031. All physical and spectral data are in accordance with literature.^[13]

Methyl undec-10-enoate (2l)
 C₁₂H₂₂O₂
 MW: 198.31

This reaction was operated under no precautions to eliminate air or moisture. To a solution of ethyl undec-10-enoate (97% purity, 10.0 mL, 42.7 mmol) in MeOH (43 mL, 1.0 M) was added a quarter pellet of solid NaOH. The reaction mixture was heated at reflux for two days, filtered through a celite plug, and concentrated *in vacuo*. The residual oil was taken up into TBME (100 mL) and washed with aq. 1.0 M NaOH (100 mL), sat. aq. NaHCO₃

(100 mL), sat. aq. NaCl (100 mL), dried with Na₂SO₄, and filtered through a silica plug. The dried solution was concentrated *in vacuo* and distilled (2.3 x10⁻¹ mbar, 95–100 °C) to afford **2l** as a clear oil (7.87 g, 39.7 mmol, 93%). *R_f* = 0.49 (8% EtOAc/heptanes, CAM). b.p. = 253 °C at ambient pressure. ¹H NMR (300 MHz, CDCl₃): δ 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.08 – 4.84 (m, 2H), 3.67 (s, 3H), 2.30 (app t, *J* = 7.5 Hz, 2H), 2.12 – 1.95 (m, 2H), 1.72 – 1.53 (m, 2H), 1.45 – 1.19 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 174.3 (C_q), 139.2 (CH), 114.2 (CH₂), 51.4 (CH₃), 34.1 (CH₂), 33.8 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.14 (CH₂), 29.06 (CH₂), 28.9 (CH₂), 25.0 (CH₂). IR (thin film): *v*_{max} = 1739 (s),[§] 1641 (w),^a 993 (w),^c 908 (m)^c cm⁻¹. [§]Unconjugated acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^c1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for C₁₂H₂₂O₂Na [M+Na]⁺: 221.1512. Found: 221.1515. Physical,^[14] and spectral data are in accordance with literature.^[15]

Benzyl undec-10-enoate (**2n**)

CCCCCCCCC=CCCC(=O)OCc1ccccc1

 $\text{C}_{18}\text{H}_{26}\text{O}_2$
 MW: 274.40

A 1-neck 100 mL flask was charged with melted undec-10-enoic acid (98% purity, 8.87 g, ~10 mL, 47.2 mmol), MgSO₄ (~2 g), *para*-toluenesulfonic acid monohydrate (456 mg, 5 mol%), and dry DCM (1.0 M, 50 mL). Benzyl alcohol (98% purity, 8.73 g, 5.5 mL, 51.9 mmol) was charged into the flask which was then equipped with a reflux condenser and refluxed for 1.5 days under argon. TLC indicated incomplete conversion but the contents were nonetheless filtered through a silica plug and concentrated *in vacuo*. The residue was partitioned between Et₂O (100 mL) and aq. 1.0 M NaOH (100 mL). The ethereal phase was washed with sat. aq. NaHCO₃ (100 mL), sat. aq. NaCl (100 mL), and dried over Na₂SO₄. The dried solution was filtered through a silica plug, concentrated *in vacuo*, and the crude residue submitted to FCC (grad = 1-2-4% EtOAc/heptanes), essentially to remove unreacted benzyl alcohol (*R_f* = 0.20 in 20% EtOAc/heptanes, CAM, UV), to afford **2n** as a clear, free-flowing oil (8.24 g, 30.0 mmol, 64%). *R_f* = 0.67 (20% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.30 (m, 5H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.11 (s, 2H), 5.07 – 4.87 (m, 2H), 2.35 (app t, *J* = 7.5 Hz, 2H), 2.03 (app tdd, *J* = 8.1, 6.1, 1.4 Hz, 2H), 1.64 (app p, *J* = 7.1 Hz, 2H), 1.46 – 1.16 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 173.7 (C_q), 139.2 (CH), 136.2 (C_q), 128.5 (CH), 128.17 (CH, overlapping), 128.16 (CH, overlapping), 114.2 (CH₂), 60.1 (CH₂), 34.3 (CH₂), 33.8 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 28.9 (CH₂), 25.0 (CH₂). IR (thin film): *v*_{max} = 3067 (w),^b 1735 (s),[§] 1640 (w),^a 992 (m),^c 908 (s)^c cm⁻¹. [§]Unconjugated acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(—H)₂ stretching

vibration. $^{\circ}$ 1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for $C_{18}H_{26}O_2Na$ $[M+Na]^+$: 297.1825. Found: 197.1827. Spectral data are in accordance with literature.^[16]

Undec-10-enoyl chloride

A modified literature procedure was followed.^[17] No special precautions were undertaken to dry glassware or reagents. 10-undecenoic acid (27.7 g, 150 mmol) was melted and loaded into a 100 mL, two-neck flask equipped with two scrubbers (aq. 3 M NaOH) in series. The reaction vessel was heated to 80 °C and DMF (1.0 mL) was added under a flow of argon followed by a dropwise addition of thionyl chloride (16.5 mL, 225 mmol). Once addition was complete the argon serving Schlenk tap was closed and the reaction mixture was heated at 80 °C for ten hours. Under an argon flow, the scrubbers were exchanged for a cold finger and the excess thionyl chloride and DMF were evaporated *in vacuo*. The cold finger was exchanged with a distillation head and the contents distilled (6×10^{-1} mbar, 72 °C, first 2 mL discarded) to afford undecenoyl chloride as a clear free-flowing oil (25.2 g, 125 mmol, 83%). 1H NMR (300 MHz, $CDCl_3$): δ 5.81 (ddt, $J = 16.9, 10.2, 6.7$ Hz, 1H), 5.08 – 4.86 (m, 2H), 2.88 (app t, $J = 7.3$ Hz, 2H), 2.04 (app q, $J = 6.8$ Hz, 2H), 1.71 (app p, $J = 7.2$ Hz, 2H), 1.54 – 1.11 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.8 (C_q), 139.1 (CH), 114.2 (CH_2), 47.1 (CH_2), 33.8 (CH_2), 29.2 (CH_2), 29.01 (CH_2), 28.97 (CH_2), 28.9 (CH_2), 28.4 (CH_2), 25.1 (CH_2). IR (thin film): $\nu_{max} = 1796$ (s) cm^{-1} . Spectral data are in accordance with literature.^[17]

N-Ethylundec-10-enamide (2o)

Ethylamine (0.79 mL, 12.0 mmol) was loaded into a 1-neck 100 mL flask charged with triethylamine (2.1 mL, 18.0 mmol), DMAP (~120 mg, ~10 mol%), and THF (20 mL, 0.5 M). The contents were cooled with a water bath and undec-10-enoyl chloride (2.0 mL, 10.0 mmol) was added portionwise. The reaction mixture was stirred at ambient temperature for 18 hours by which time TLC indicated completion and then the majority of the volatiles were removed *in vacuo*. The remaining contents were partitioned between TBME (40 mL) and aq. HCl (2.0 M, 40 mL), and stirred for 30 min. The ethereal phase was washed twice with aq. HCl (1.0 M, 40 mL), and then once with aq. NaOH (1.0 M, 40 mL). The ethereal phase

was washed with sat. aq. NaHCO_3 (40 mL), then sat. aq. NaCl (40 mL), and dried over Na_2SO_4 . The dried solution was filtered through a silica plug and concentrated *in vacuo* to afford **2o** as a white crystalline solid (1.61 g, 7.6 mmol, 76%) judged to be pure as determined by TLC and NMR. R_f = 0.10 (30% EtOAc/heptanes, CAM, slight tailing). m.p. = 36.4 – 37.4 °C. ^1H NMR (300 MHz, CDCl_3): δ 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.41 (br s, 1H), 5.13 – 4.84 (m, 2H), 3.29 (app qd, J = 7.3, 5.6 Hz, 2H), 2.25 – 2.10 (m, 2H), 2.03 (app tdd, J = 6.6, 5.3, 1.4 Hz, 2H), 1.62 (app p, J = 7.5 Hz, 2H), 1.44 – 1.23 (m, 10H), 1.13 (app t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 172.9 (C_q), 139.2 (CH), 114.1 (CH_2), 36.9 (CH_2), 34.3 (CH_2), 33.8 (CH_2), 29.31 (CH_2 , overlapping), 29.29 (CH_2 , overlapping), 29.1 (CH_2), 28.9 (CH_2), 25.8 (CH_2), 15.0 (CH_3). IR (thin film): ν_{max} = 3295 (s),[‡] 3069 (w),^b 1631 (s),[§] 1641 (w),^a 1540 (s),[§] 994 (m),^c 915 (s)^c cm^{-1} . [‡]Secondary amide N—H stretching vibration. [§]Secondary amide carbonyl stretching vibrations. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(—H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for $\text{C}_{13}\text{H}_{26}\text{ON}$ $[\text{M}+\text{H}]^+$: 212.2009. Found: 212.2003.

N,N-Diethylundec-10-enamide (2p)

Diethylamine (1.24 mL, 12.0 mmol) was loaded into a 1-neck 100 mL flask charged with triethylamine (2.1 mL, 18.0 mmol), DMAP (~120 mg, ~10 mol%) and THF (0.5 M, 20 mL). The contents were cooled with a water bath and undec-10-enoyl chloride (2.0 mL, 10.0 mmol) was added portionwise. The reaction mixture was stirred at ambient temperature for 18 hours by which time TLC indicated completion and then the majority of the volatiles were removed *in vacuo*. The remaining contents were partitioned between TBME (40 mL) and aq. HCl (2.0 M, 40 mL), and stirred for 30 min. The ethereal phase was washed twice with aq. HCl (1.0 M, 40 mL), and then once with aq. NaOH (1.0 M, 40 mL). The ethereal phase was washed with sat. aq. NaHCO_3 (40 mL), then sat. aq. NaCl (40 mL), and dried over Na_2SO_4 . The dried solution was filtered through a silica plug and concentrated *in vacuo* to afford **2p** as a lightly yellow-tinted oil (2.15 g, 9.0 mmol, 90%) judged to be pure as determined by TLC and NMR. R_f = 0.31 or 0.15 (30% or 15% EtOAc/heptanes, CAM, slight tailing). ^1H NMR (300 MHz, CDCl_3): δ 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.10 – 4.80 (m, 2H), 3.37 (q, J = 7.1 Hz, 2H, overlapping), 3.30 (q, J = 7.1 Hz, 2H, overlapping), 2.38 – 2.15 (m, 2H), 2.03 (app tdd, J = 6.6, 5.3, 1.4 Hz, 2H), 1.64 (app p, J = 7.4 Hz, 2H), 1.43 – 1.23 (m, 10H), 1.17 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 172.3 (C_q), 139.2 (CH), 114.1 (CH_2), 42.0 (CH_2), 40.0 (CH_2), 33.8 (CH_2), 33.2 (CH_2), 29.54 (CH_2), 29.45 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 25.5 (CH_2), 14.4 (CH_3), 13.1 (CH_3). IR (thin film): ν_{max} = 3079 (w),^b 1639 (s),[§] 993 (w),^c 907 (m)^c cm^{-1} . [§]Amide carbonyl

stretching vibration, hides unconjugated alkene (terminal) C=C stretching vibration expected at 1641 cm^{-1} . ^bTerminal alkene C—H₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for C₁₅H₃₀ON [M+H]⁺: 240.2322. Found: 240.2318. Spectral data are in accordance with literature.^[18]

(4-Methylenecyclohexyl)benzene **2q**

Undec-10-en-1-yl (E)-2-methyl-3-phenylacrylate (**2t**)

A 1-neck 50 mL flask was equipped with a reflux condenser and no inert precautions were employed. The flask was charged with α -methylcinnamic acid (2.32 g, 14.5 mmol), MgSO₄ (~2 g), 10-undecen-1-ol (97% purity, 2.0 mL, 10.0 mmol), *para*-toluenesulfonic acid (~100 mg, ~ 5 mol%), and benzene (0.5 M, 20 mL) in no particular order. The reaction mixture was heated to reflux for 15 hours. The reaction mixture was filtered through a celite plug, and the majority of the volatiles were removed *in vacuo* and the residue partitioned between TBME (40 mL) and aq. 2.0 M NaOH (40 mL). The ethereal phase was washed with aq. 1.0 M NaOH (40 mL), and the combined aqueous phases back-extracted with TBME (10 mL). The combined ethereal phases was washed with aq. 1.0 M NaOH (40 mL), sat. aq. NaHCO₃ (40 mL), sat. aq. NaCl (40 mL), dried over Na₂SO₄, filtered through a silica plug, concentrated *in vacuo*, and the crude residue (estimated as 25% desired ester and 75% unreacted alcohol) submitted to FCC (grad = 5-7-10-10% EtOAc/heptanes, res = 250 mL, dia = 55 mm, l = 17 cm, f = 100 mL) to afford **2t** as a clear oil (761 mg, 2.42 mmol, 25%). *R*_f = 0.65 (20% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.66 (q, *J* = 1.5 Hz, 1H), 7.37 – 7.25 (m, 5H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 – 4.81 (m, 2H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.10 (d, *J* = 1.5 Hz, 3H), 2.09 – 1.97 (m, 2H), 1.82 – 1.62 (m, 2H), 1.51 – 1.19 (m, 12H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 168.8 (C_q), 139.7 (CH), 138.6 (CH), 136.4 (C_q), 130.0 (CH), 129.2 (C_q), 128.7 (CH), 128.6 (CH), 114.2 (CH₂), 65.4 (CH₂), 34.2 (CH₂), 29.9 (CH₂), 29.8 (CH₂), 29.7 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.1 (CH₂), 26.5 (CH₂), 14.3 (CH₃). IR (thin film): ν_{max} = 3076 (w),^b 1706 (s),[§] 1638 (w),^a 1576 (w),^{§§} 992 (w),^c 907 (m)^c cm^{-1} . [§]Unsaturated, acyclic ester carbonyl

stretching vibration. $^{\S\S}\alpha,\beta$ -unsaturated, acyclic ester C=C stretching vibration a Unconjugated alkene (terminal) C=C stretching vibration. b Terminal alkene C(—H)₂ stretching vibration. c 1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for C₂₁H₃₁O₂ [M+H]⁺: 315.2319. Found: 315.2324.

Undec-10-en-1-yl 3-methylbut-2-enoate (2u)

A 1-neck 100 mL flask was equipped with a reflux condenser and no inert precautions were employed. The flask was charged with 3,3-dimethylacrylic acid (95% purity, 40.5 g, 38.4 mmol), 10-undecen-1-ol (97% purity, 5.0 mL, 25.6 mmol), *para*-toluenesulfonic acid (~250 mg, ~5 mol%), and benzene (1.0 M, 40 mL) in no particular order. A Dean-Stark reflux apparatus was equipped to the flask and the reaction mixture was heated to reflux for 30 hours generating ~0.40 mL of H₂O. The reaction mixture was filtered through a celite plug, and the majority of the volatiles were removed *in vacuo* and the residue partitioned between TBME (40 mL) and aq. 2.0 M NaOH (40 mL). The ethereal phase was washed with aq. 1.0 M NaOH (40 mL), and the combined aqueous phases back-extracted with TBME (10 mL). The combined ethereal phases was washed with aq. 1.0 M NaOH (40 mL), sat. aq. NaHCO₃ (40 mL), sat. aq. NaCl (40 mL), dried over NaSO₄, filtered through a silica plug, concentrated *in vacuo*, and the crude residue distilled (6–8 mbar, 190 °C) to afford **2u** as a clear oil (4.50 g, 17.8 mmol, 70%). *R*_f = 0.46 (8% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CDCl₃): δ 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.67 (h, *J* = 1.3 Hz, 1H), 5.10 – 4.88 (m, 2H), 4.07 (t, *J* = 6.7 Hz, 2H), 2.16 (d, *J* = 1.3 Hz, 3H), 2.04 (app tdd, *J* = 6.6, 5.3, 1.5 Hz, 2H), 1.89 (d, *J* = 1.3 Hz, 3H), 1.63 (app p, *J* = 6.9 Hz, 2H), 1.44 – 1.19 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 166.8 (C_q), 156.3 (C_q), 139.2 (CH), 116.2 (CH), 114.1 (CH₂), 63.7 (CH₂), 33.8 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 28.9 (CH₂), 28.8 (CH₂), 27.4 (CH₃), 26.0 (CH₂), 20.2 (CH₃). IR (thin film): ν_{max} = 3075 (w),^b 1718 (s),[§] 1653 (m),^{§§} 1642 (m),^a 993 (m),^c 908 (m)^c cm⁻¹. $^{\S\S}\alpha,\beta$ -unsaturated, acyclic ester carbonyl stretching vibration. $^{\S\S}\alpha,\beta$ -unsaturated, acyclic ester C=C stretching vibration a Unconjugated alkene (terminal) C=C stretching vibration. b Terminal alkene C(—H)₂ stretching vibration. c 1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for C₁₆H₂₉O₂ [M+H]⁺: 253.2162. Found: 253.2165.

Prenyl undec-10-enoate (2v)

Prenol (3-methyl-2-buten-1-ol, 98% purity, 2.0 mL, 19.6 mmol) was loaded into a 1-neck 100 mL flask charged with triethylamine (3.3 mL, 23.5 mmol), DMAP (~250 mg, ~2.0 mmol), and THF (40 mL, 0.5 M). The contents were cooled with a water bath and undec-10-enoyl chloride (5.0 mL, 23.5 mmol) was added portionwise. The reaction mixture was stirred at ambient temperature for 2-16 hours by which time TLC indicated completion and then the majority of the volatiles were removed *in vacuo*. The remaining contents were partitioned between TBME (40 mL) and aq. HCl (2.0 M, 40 mL), and stirred for 30 min. The ethereal phase was washed once with aq. HCl (1.0 M, 40 mL) and the combined acidic phases were back extracted with TBME (10 mL). The combined ethereal phases were washed with sat. aq. NaHCO₃ (40 mL), then sat. aq. NaCl (40 mL), and dried over Na₂SO₄. The dried solution was filtered through a silica plug and concentrated *in vacuo*. The crude residue was submitted to FCC (dia = 55 mm, l = 17 cm, f = 50 mL, res = 250 mL, grad = 2-3-4-5% EtOAc/heptanes) to afford **2v** as a clear free-flowing oil (4.56 g, 18.1 mmol, 92%). R_f = 0.56 or 0.32 (10% or 5% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CDCl₃): δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.34 (app tdd, *J* = 7.2, 2.8, 1.4 Hz, 1H), 5.11 – 4.86 (m, 2H), 4.57 (d, *J* = 7.2 Hz, 2H), 2.29 (app t, *J* = 7.5 Hz, 2H), 2.03 (app q, *J* = 6.8 Hz, 2H), 1.76 (s, 3H), 1.71 (s, 3H), 1.70 – 1.49 (m, 2H), 1.45 – 1.17 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 173.8 (C_q), 139.1 (CH), 138.8 (C_q), 118.8 (CH), 114.2 (CH₂), 61.2 (CH₂), 34.4 (CH₂), 33.8 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.14 (CH₂), 29.07 (CH₂), 28.9 (CH₂), 25.8 (CH₃), 25.0 (CH₂), 18.0 (CH₃). IR (thin film): ν_{max} = 3076 (w),^b 1734 (s),[§] 1676 (w),^d 1640 (w),^b 990 (m),^c 908 (w)^c cm⁻¹. [§]Unconjugated acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(—H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. ^dUnconjugated alkene (internal) C=C stretching vibration. HRMS (ESI): Calculated for C₁₆H₂₈O₂ [M+H]⁺: 253.2162. Found: 253.2173.

β-Citronellyl undec-10-enoate (2w)

β -Citronellol (95% purity, 4.0 mL, 22.2 mmol) was loaded into a 1-neck 100 mL flask charged with triethylamine (3.5 mL, 26.6 mmol), DMAP (~250 mg, ~2.7 mmol), and THF (40 mL, 0.5 M).

The contents were cooled with a water bath and undec-10-enoyl chloride (5.9 mL, 26.6 mmol) was added portionwise. The reaction mixture was stirred at ambient temperature for 2-16 hours by which time TLC indicated completion and then the majority of the volatiles were removed *in vacuo*. The remaining contents were partitioned between TBME (40 mL) and aq. HCl (2.0 M, 40 mL), and stirred for 30 min. The ethereal phase was washed once with aq. HCl (1.0 M, 40 mL) and the combined acidic phases were back extracted with TBME (10 mL). The combined ethereal phases were washed with sat. aq. NaHCO₃ (40 mL), then sat. aq. NaCl (40 mL), and dried over Na₂SO₄. The dried solution was filtered through a silica plug and concentrated *in vacuo*. The crude residue was submitted to FCC (dia = 55 mm, l = 17 cm, f = 100 mL, res = 250 mL, grad = 2-3-3-4% EtOAc/heptanes) to afford **2w** as a yellow-tinted, clear, free-flowing oil (6.95 g, 21.5 mmol, 97%). *R_f* = 0.60 or 0.30 (10% or 5% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.08 (ddq, *J* = 8.5, 5.7, 1.5 Hz, 1H), 5.04 – 4.86 (m, 2H), 4.10 (ddt, *J* = 10.9, 7.3, 3.5 Hz, 2H), 2.28 (app t, *J* = 7.5 Hz, 2H), 2.16 – 1.91 (m, 4H), 1.76 – 1.48 (m, 10H), 1.50 – 1.24 (m, 12H), 1.23 – 1.10 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 173.9 (C_q), 139.1 (CH), 131.3 (C_q), 124.6 (CH), 114.2 (CH₂), 62.8 (CH₂), 37.0 (CH₂), 35.5 (CH₂), 34.4 (CH₂), 33.8 (CH₂), 29.5 (CH₃), 29.3 (CH₂), 29.23 (CH₂), 29.16 (CH₂), 29.1 (CH₂), 28.9 (CH₂), 25.7 (CH₃), 25.4 (CH₂), 25.0 (CH₂), 19.4 (CH₃), 17.7 (CH). IR (thin film): $\nu_{\max}$ = 3077 (w),^b 1736 (s),[§] 1640 (w),^a 992 (w),^c 908 (m)^c cm⁻¹. [§]Unconjugated acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for C₂₁H₃₉O₂ [M+H]⁺: 323.2945. Found: 323.2944.

(-)-Nopyl undec-10-enoate (**2x**)

(-)-Nopol (98% purity, 4.0 mL, 22.8 mmol) was loaded into a 1-neck 100 mL flask charged with triethylamine (3.8 mL, 27.4 mmol), DMAP (~250 mg, ~2.7 mmol), and THF (50 mL, 0.5 M). The contents were cooled with a water bath and undec-10-enoyl chloride (5.9 mL, 1.2 equiv) was added portionwise. The reaction mixture was stirred at ambient temperature for 2-16 hours by which time TLC indicated completion and then the majority of the volatiles were removed *in*

vacuo. The remaining contents were partitioned between TBME (40 mL) and aq. HCl (2.0 M, 40 mL), and stirred for 30 min. The ethereal phase was washed once with aq. HCl (1.0 M, 40 mL) and the combined acidic phases were back extracted with TBME (10 mL). The combined ethereal phases were washed with sat. aq. NaHCO₃ (40 mL), then sat. aq. NaCl (40 mL), and dried over Na₂SO₄. The dried solution was filtered through a silica plug and concentrated *in vacuo*. The crude residue was submitted to FCC (dia = 55 mm, l = 17 cm, f = 100 mL, res = 250 mL, grad = 2-3-3-4% EtOAc/heptanes) to afford **2x** as a clear free-flowing oil (7.44 g, 22.4 mmol, 98%). R_f = 0.55 or 0.21 (10% or 5% EtOAc/heptanes, CAM, UV). $[\alpha]_D^{20}$ = -23.1° (c 1.52, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.29 (app tt, J = 3.0, 1.5 Hz, 1H), 5.10 – 4.86 (m, 2H), 4.07 (app td, J = 7.0, 2.9 Hz, 2H), 2.36 (app dt, J = 8.5, 5.6 Hz, 1H), 2.32 – 2.13 (m, 6H), 2.12 – 1.92 (m, 4H), 1.78 – 1.50 (m, 2H), 1.49 – 1.21 (m, 13H), 1.14 (d, J = 8.5 Hz, 1H), 0.82 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 173.8 (C_q), 144.2 (C_q), 139.1 (CH), 118.7 (CH), 114.1 (CH₂), 62.5 (CH₂), 45.7 (CH), 40.7 (CH), 38.0 (C_q), 36.0 (CH₂), 34.4 (CH₂), 33.8 (CH₂), 31.6 (CH₂), 31.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.13 (CH₂), 29.06 (CH₂), 28.9 (CH₂), 26.3 (CH₃), 25.0 (CH₂), 21.1 (CH₃). IR (thin film): $\nu_{\max}$ = 3076 (w),^b 1736 (s),[§] 1676 (w),^d 1640 (w),^b 993 (m),^c 908 (w)^c cm⁻¹. [§]Unconjugated acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. ^dUnconjugated alkene (internal) C=C stretching vibration. HRMS (ESI): Calculated for C₂₂H₃₆O₂Na [M+Na]⁺: 355.2608. Found: 355.2615.

Cholesteryl undec-10-enoate (**2y**)

Cholesterol (97% purity, 8.00 g, 20.0 mmol) was loaded into a 1-neck 100 mL flask which was further charged with DMAP (~250 mg, ~2.0 mmol), THF (40 mL, 0.5 M), and triethylamine (3.5 mL, 24.0 mmol) in that order. The contents were cooled with a water bath and undec-10-enoyl chloride (5.2 mL, 24.0 mmol) was added portionwise. The reaction mixture was stirred at

ambient temperature for 2-16 hours by which time TLC indicated completion and then the majority of the volatiles were removed *in vacuo*. The remaining contents were partitioned between TBME (40 mL) and aq. HCl (2.0 M, 40 mL), and stirred for 30 min. The ethereal phase was washed once with aq. HCl (1.0 M, 40 mL) and the combined acidic phases were back extracted with TBME (10 mL).

The combined ethereal phases were washed with sat. aq. NaHCO_3 (40 mL), then sat. aq. NaCl (40 mL), and dried over Na_2SO_4 . The dried solution was filtered through a silica plug and concentrated *in vacuo*. The crude yellow powder was crystallized from abs. EtOH and recrystallized from abs. EtOH to afford **2y** as fine white crystals (8.23 g, 14.9 mmol, 74%). $R_f = 0.58$ (10% EtOAc/heptanes, CAM, UV). m.p. 76.7–78.3 °C (EtOH); lit: 86 °C (hexane/EtOAc);^[20] lit: 79.0–83.5 °C (EtOH).^[21] $[\alpha]_D^{20} - 28.7^\circ$ (c 1.02, CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ 5.80 (ddt, $J = 16.9, 10.2, 6.7$ Hz, 1H), 5.37 (app d, $J = 4.2$ Hz, 1H), 5.07 – 4.85 (m, 2H), 4.61 (app tq, $J = 11.2, 4.1$ Hz, 1H), 2.44 – 2.17 (m, 4H), 2.15 – 1.91 (m, 4H), 1.91 – 1.79 (m, 3H), 1.73 – 0.90 (m, 39H), 0.86 (dd, $J = 6.6, 1.3$ Hz, 6H), 0.68 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 173.2 (C_q), 139.7 (C_q), 139.1 (CH), 122.6 (CH), 114.1 (CH_2), 73.6 (CH), 56.7 (CH), 56.1 (CH), 50.0 (CH), 42.3 (C_q), 39.7 (CH_2), 39.5 (CH_2), 38.2 (CH_2), 37.0 (CH_2), 36.6 (C_q), 36.2 (CH_2), 35.8 (CH), 34.7 (CH_2), 33.8 (CH_2), 31.90 (CH_2), 31.86 (CH), 29.3 (CH_2), 29.2 (CH_2), 29.09 (CH_2), 29.06 (CH_2), 28.9 (CH_2), 28.2 (CH_2), 28.0 (CH), 27.8 (CH_2), 25.0 (CH_2), 24.3 (CH_2), 23.8 (CH_2), 22.8 (CH_3), 22.6 (CH_3), 21.0 (CH_2), 19.3 (CH_3), 18.7 (CH_3), 11.9 (CH_3). IR (thin film): $\nu_{\text{max}} = 1732$ (s),[§] 1641 (w),^a 997 (w),^c 905 (m) cm^{-1} . [§]Unconjugated acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^c1-substituted alkene C—H bending vibrations. HRMS (ESI): Calculated for $\text{C}_{38}\text{H}_{64}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 575.4799. Found: 575.4779. Spectral data are in accordance with literature.^[20]

Chrysanthemic acid

A literature procedure for hydrolysis was used.^[22] A 1-neck 1 L flask was charged with ethyl chrysanthemate (11.3 mL, 50 mmol, cis/trans = 4:6), and dissolved in 1:2 THF/MeOH (500 mL, 0.1 M). 2.0 M aq. NaOH (200 mL) was added and the mixture stirred vigorously at ambient temperature for one day.

Volatiles were removed *in vacuo* and the residue partitioned between aq. 1.0 M NaOH (100 mL) and DCM (100 mL). The aqueous phase was washed with DCM (100 mL) and partitioned with TBME (200 mL). The biphasic mixture was acidified with 10% aq. HCl (~ 100 mL) and separated. The

aqueous layer was extracted with TBME (2x 100 mL). The combined ethereal phases was washed with sat. aq. NaCl (200 mL), and dried over Na₂SO₄, filtered through a silica plug, concentrated *in vacuo*, and the crude chrysanthemic acid was deemed to be sufficiently pure for synthesis (7.48 g, 44.5 mmol, 89%, d.r. = 8:2 (trans/cis)). A sample was purified by FCC (grad = 5-7-7-10% EtOAc/heptanes) for analysis to afford the title compound as a clear viscous oil. The commercial ethyl chrysanthemate has poor d.r. due to the old industrial-scale synthesis,^[23] which is improved during the reaction by way of a lactonization that consumes the *cis*-isomer.^[24] The lactone was removed removed in the next step by FCC. *R_f* = 0.36—0.18 (15% EtOAc/heptanes, CAM, tailed). ¹H NMR (300 MHz, CDCl₃): δ 12.0 (br s, 1H minor + 1H major), 5.36 (dp, *J* = 8.5, 1.4 Hz, 1H minor), 4.90 (dp, *J* = 7.8, 1.4 Hz, 1H major), 2.10 (dd, *J* = 7.8, 5.4 Hz, 1H major), 1.96 (app t, *J* = 8.6 Hz, 1H minor), 1.75 (d, *J* = 1.4 Hz, 3H minor), 1.73 – 1.68 (m, 6H major + 3H minor), 1.65 (d, *J* = 8.7 Hz, 1H minor), 1.39 (d, *J* = 5.4 Hz, 1H major), 1.30 (s, 3H major), 1.25 (s, 3H minor), 1.21 (s, 3H minor), 1.15 (s, 3H major). ¹³C NMR (75 MHz, CDCl₃): δ 179.5 (C_q major), 178.3 (C_q minor), 135.8 (C_q major), 135.0 (C_q minor), 120.8 (CH major), 117.9 (CH minor), 34.7 (CH major), 33.6 (CH major), 33.3 (CH minor), 31.2 (CH minor), 29.8 (C_q major), 28.9 (CH₃ minor), 27.5 (C_q minor), 25.9 (CH₃ minor), 25.6 (CH₃ major), 22.3 (CH₃ major), 20.4 (CH₃ major), 18.5 (CH₃ major), 18.3 (CH₃ minor), 14.8 (CH₃ minor). IR (thin film): ν_{max} = 3500—2500 (v br m),^{§§} 1685 (s),[§] 853 (m)^d cm⁻¹. ^{§§}Intermolecularly H-bonded carboxylic acid O—H stretching vibration. [§]Carboxylic acid carbonyl stretching vibration. ^dC—H stretching vibration of a trisubstituted alkene. HRMS (ESI): Calculated for C₁₀H₁₇O₂ [M+H]⁺: 169.1223. Found: 169.1225. Spectroscopic data are in accordance with the literature.^[25]

Undec-10-en-1-yl chrysanthemate (2z)

Chrysanthemic acid **SI-3/2z'** (3.95 g, 23.5 mmol) was dissolved into DCM (0.5 M, 50 mL) in a 1-neck 100 mL flask under argon. The contents were cooled with an ice/water bath and oxalyl chloride was carefully added with an aq. 3 M NaOH exhaust scrubber. The contents were warmed to ambient temperature and stirred for three hours. The contents were concentrated *in vacuo* and azeotroped with DCM (3x 10 mL). The residue was dissolved in DCM (50 mL) and 10-undecen-1-ol (98% purity, 4.24 mL, 21.2 mmol, 0.9 equiv) was added along with NEt₃ (4.9 mL, 1.5 equiv) and DMAP (~ 300 mg, 0.1 equiv). The reaction mixture was stirred at ambient temperature for a five hours, concentrated *in vacuo* and the residue partitioned between TBME (40 mL) and aq. 2.0 M HCl (40 mL). The ethereal phase was washed with aq. 1.0 M HCl (40 mL), and the combined aqueous phases back-extracted with TBME (10 mL). The combined ethereal phases was washed with aq. 1.0 M HCl (40 mL), aq. 1.0 M NaOH (40 mL), sat. aq. NaHCO₃ (40 mL), sat. aq. NaCl (40 mL), dried over Na₂SO₄, filtered through a silica plug, concentrated *in vacuo*, and the crude residue submitted to FCC (grad = 1-2-2-2-3% EtOAc/heptanes, res = 500 mL, dia = 70 mm, l = 17 cm, f =

250 mL) to afford **2z** as a clear oil (6.45 g, 20.0 mmol, 86%, d.r.(trans/cis) = 8:2). R_f = 0.52 (8% EtOAc/heptanes, CAM). ^1H NMR (300 MHz, CDCl_3): δ 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H minor + 1H major), 5.38 (dp, J = 8.5, 1.4 Hz, 1H minor), 5.11 – 4.82 (m, 3H major + 2H minor), 4.21 – 3.89 (m, 2H major + 2H minor), 2.13 – 1.98 (m, 3H major + 2H minor), 1.92 – 1.82 (m, 1H minor), 1.75 (d, J = 1.4 Hz, 3H minor), 1.71 (d, J = 1.4 Hz, 3H major), 1.70 (d, J = 1.3 Hz, 3H major), 1.69 (d, J = 1.3 Hz, 3H minor), 1.66 – 1.56 (m, 2H major + 3H minor), 1.43 – 1.27 (m, 13H major + 12H minor), 1.26 (s, 3H major), 1.24 (s, 3H minor), 1.19 (s, 3H minor), 1.13 (s, 3H major). ^{13}C NMR (75 MHz, CDCl_3): δ 172.6 (C_q major), 171.3 (C_q minor), 139.2 (CH both), 135.4 (C_q major), 134.5 (C_q minor), 121.2 (CH major), 118.3 (CH minor), 114.1 (CH_2 both), 64.4 (CH_2 major), 64.0 (CH_2 minor), 34.9 (CH major), 33.8 (CH_2 both), 32.6 (CH major), 32.1 (CH minor), 31.3 (CH minor), 29.5 (CH_2 both), 29.4 (CH_2 both), 29.28 (CH_2 minor), 29.26 (CH_2 major), 29.1 (CH_2 both), 28.93 (CH_2 both), 28.87 (CH_3 minor), 28.8 (CH_2 both), 28.4 (C_q major), 26.2 (C_q minor), 26.00 (CH_2 minor), 25.96 (CH_2 major), 25.92 (CH_3 minor), 25.6 (CH_3 major), 22.2 (CH_3 major), 20.5 (CH_3 major), 18.5 (CH_3 major), 18.3 (CH_3 minor), 14.8 (CH_3 minor). IR (thin film): ν_{max} = 3075 (w),^b 1723 (s),[§] 1641 (w),^a 992 (w),^c 908 (m)^c 854 (m)^d cm^{-1} . [§]Saturated, acyclic ester carbonyl stretching vibration. ^aUnconjugated alkene (terminal) C=C stretching vibration. ^bTerminal alkene C(—H)₂ stretching vibration. ^c1-substituted alkene C—H bending vibrations. ^dC—H stretching vibration of a trisubstituted alkene. HRMS (ESI): Calculated for $\text{C}_{21}\text{H}_{37}\text{O}_2$ $[\text{M}+\text{H}]^+$: 321.2788. Found: 321.2795.

2.3 Radical precursors and other reagents

Triethylborane

BEt_3 solutions were prepared and stored in Schlenk flasks without septa (a liberally greased glass stopper was used, or a single Teflon joint as in the “Schlenk bomb” style flask) and opened under a fast flow of argon gas. In this work 1.15 M solutions of BEt_3 in benzene were exclusively used. There was no noticeable variation in yields after months of storage.

Di-*tert*-butyl hyponitrite (DTBHN)

$t\text{-BuON}=\text{NO}t\text{-Bu}$ DTBHN was prepared according to a slightly altered literature procedure.^[26] In a 250 mL three-neck flask equipped with a stirring bar was loaded sodium *trans*- $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_2$ hyponitrite hydrate (m = 8.15 g) which was then dried to constant weight (m = 5.58 g). In another flask, ZnCl_2 hydrate (14 g) was melted under stirring *in vacuo* (3x) in order to dry it. From the resulting block of grey solid, pieces with a total weight of 8.6 g (63.1 mmol, 1.2 equiv.) were (quickly) transferred into a two-neck flask, dried another 10 min under vacuum, and then suspended in Et_2O (35 mL) first with stirring for 2 h then with sonication for another 20 min until no more pieces of ZnCl_2 were visible. To the dry hyponitrite was added Et_2O (30 mL) and *tert*-butylbromide (47 mL, 418 mmol, 8.0 equiv.) and the resulting milky white mixture was cooled to –

10 °C (internal temperature) using an ice/NaCl/water bath. Then, the ZnCl₂ suspension was transferred into the reaction vessel with the hyponitrite using a cannula ($\varnothing$ = 1 mm) at a rate that the internal temperature did not exceed –5 °C. After complete addition, the mixture was allowed to reach room temperature and stirred for another 1.5 h at this temperature. The reaction mixture was filtered and the remaining solid was washed with Et₂O (3x 10 mL). The resulting yellow solution was transferred into a separatory funnel and water was added. The aqueous layer was extracted with Et₂O (3x 20 mL) and the combined organic layers were washed with brine, dried over Na₂SO₄ and the volatiles were removed under reduced pressure (bath temperature 20 °C, 400 mbar, end to 50 mbar for a short time). The obtained solid was crystallized from *n*-pentane to furnish almost colourless crystals in three crops (all crops were washed with cold pentane). Recrystallization from pentane of the combined crops furnished the product as colourless, transparent crystals (3.43 g, 37%). Spectral data is in accordance with the literature. DTBHN was stored for months at 4 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.38 (s, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 81.3 (C_q), 27.9 (CH₃). Spectroscopic data are in accordance with literature.^[27]

3 Cyclopropanation procedures

3.1 General procedure

These reactions may be carried out with no precautions to eliminate moisture or air. A solution of ICH₂Bpin, **1** (540 mg, 2.0 mmol), dilauroyl peroxide, DLP (400 mg, 1.0 mmol), and alkene, **2a–z** (1.0 mmol) in benzene (3.5 mL, 0.3 M) was heated under reflux for 4 h. To the reaction mixture at rt was added in one portion of TBAF solution (1.0 M in THF, 5.0 mL) and the mixture stirred for 16 h. The mixture was partitioned between TBME (20 mL) and H₂O (15 mL) and shaken with sat. aq. Na₂S₂O₃ (2–5 mL). The organic phase was washed with H₂O (20 mL), and the combined aqueous phases were back-extracted with TBME (5 mL). The combined ethereal phases were washed once with sat. aq. NaHCO₃ (20 mL), and dried with brine (20 mL), then further dried over Na₂SO₄(s) and filtered through a silica plug ($\varnothing$ = 20 mm; depth = 2–3 cm) protected with a cotton wad and concentrated *in vacuo* to afford the crude product.

3.2 General procedure used for NMR yield

As in the general procedure described above. To the crude product mixture was added ~0.5 mmol of 1,4-dimethoxybenzene (the mass was measured accurately to determine mmol) and the mixture dissolved in CDCl₃ (~10 mL). The mixture was analyzed by ¹H-NMR using the characteristic stand-alone signals of the vinylic protons of the terminal alkene (typically 5.8 (ddt, 1H), 5.1 – 4.8 (m, 2H)) and the protons in the cyclopropane ring (typically 0.8 – 0.5 (m, 1H), 0.5 – 0.2 (m, 2H), 0.1 – –0.1 (m, 2H)).

3.3 General procedure used for isolated products

As in the general procedure described above. However before addition of TBAF the γ -iodoboronic ester was isolated from the crude product mixture (isolated in the same way as described in the general procedure) and purified by FC (for a 1 mmol scale, $\varnothing$ = 70 mm, length = 17-22 cm, reservoir = 250 mL, gradient (expressed as filled reservoir blocks, e.g. 1-2-2-2-3% EtOAc/heptanes)). The intermediate γ -iodoboronic pinacol esters **3a–z** are characterized but are often contaminated with ~10-20 mol% ICH₂Bpin which smears heavily on TLC (*Macherey-Nagel* SIL G/UV254, 0.25 mm silica gel). The pinacol esters are slightly unstable to *Macherey-Nagel Silica 60*, 0.04 – 0.063 mm, silica gel, very unstable to *Silicycle*, and completely unstable to *Sigma-Aldrich* silica gel. Unreacted alkene may be removed in this way since the Bpin moiety increases polarity (the cyclopropane and alkene have identical R_f). It is also possible to do the reaction one-pot and remove the unreacted alkene by ozonolysis with generally higher overall yields.

4 Products

Nonylcyclopropane (**4a**)

The general procedure was followed to give an NMR yield of 75%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3a** (191 mg, 0.45 mmol) and the crude was submitted to FCC (100% pentane) to afford the **4a** as a clear, free-flowing liquid, (66 mg, 0.39 mmol, 87%) analytically pure. R_f = 0.93 (100% pentane, CAM). ¹H NMR (300 MHz, CDCl₃): δ 1.52 – 1.23 (m, 14H), 1.18 (app q, , J = 7.0 Hz, 2H), 0.88 (app t, J = 6.7 Hz, 3H), 0.76 – 0.57 (m, 1H), 0.49 – 0.32 (m, 2H), 0.13 – –0.12 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 34.9 (CH₂), 32.0 (CH₂), 29.85 (CH₂), 29.78 (CH₂), 29.77 (CH₂), 29.68 (CH₂), 29.48 (CH₂), 22.8 (CH₂), 14.2 (CH₃), 11.0 (CH), 4.5 (CH₂). IR (thin film): ν_{max} = 3074 (w),* 3001 (w),** 1013 (m)*** cm⁻¹. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] Thermal Elemental Analysis: Calculated for C₁₂H₂₄: C, 85.63; H, 14.37; found: C, 85.96; H, 14.53. Spectroscopic and physical data are in accordance with literature.^[29]

2-(3-Iodododecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)

The general procedure was followed with 1-undecene (97% purity, 159 mg, 1.00 mmol) and the crude was submitted to FCC (1-1-2% EtOAc/heptanes) to afford **3a** as an orange-tinted oil (309 mg, 0.73 mmol, 73%). $R_f = 0.26$ (3% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 4.12 (app tt, $J = 8.4, 4.8$ Hz, 1H), 2.01 – 1.75 (m, 3H), 1.75 – 1.55 (m, 1H), 1.25 (d, $J = 6.5$ Hz, 34H), 1.09 – 0.93 (m, 1H), 0.93 – 0.73 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 83.1 (C_q), 43.8 (CH), 40.3 (CH₂), 35.1 (CH₂), 31.9 (CH₂), 29.56 (CH₂), 29.53 (CH₂), 29.48 (CH₂), 29.3 (CH₂), 28.8 (CH₂), 24.9 (CH₃), 24.8 (CH₃), 22.7 (CH₂), 14.1 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.7 (s). IR (thin film): $\nu_{\max} = 1738$ (w),^{##} 1370 (m),[†] 1319 (m),[†] 1140 (s)[†] cm⁻¹. ^{##}Contamination of small quantities of ester from DLP. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₁₈H₃₇BIO₂ [M+H]⁺: 423.1926. Found: 423.1934.

(2-Cyclopropylethyl)benzene (4b)

The general procedure was followed to give an NMR yield of 60%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3b** (200 mg, 0.50 mmol) and the crude was submitted to FCC (100% pentane) to afford **4b** as a clear free-flowing liquid (26 mg, 0.18 mmol, 36%). $R_f = 0.64$ (100% pentane, UV, CAM). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.73 – 6.73 (m, 5H), 2.84 – 2.45 (m, 2H), 1.82 – 1.17 (m, 2H), 0.75 – 0.54 (m, 1H), 0.46 – 0.22 (m, 2H), 0.11 – -0.15 (m, 2H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 143.4 (C_q), 129.0 (CH), 128.7 (CH), 126.1 (CH), 37.4 (CH₂), 36.5 (CH₂), 11.2 (CH), 4.8 (CH₂). Thermal Elemental Analysis: Calculated for C₁₁H₁₄: C, 90.35; H, 9.65. Found: C, 90.00; H, 9.90. Spectroscopic and physical data are in accordance with literature.^[30]

2-(3-Iodo-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

The general procedure was followed with 4-phenyl-1-butene (132 mg, 1.00 mmol) and the crude was submitted to FCC (1-3-5% EtOAc/heptanes) to afford **3b** as a clear oil (235 mg, 0.59 mmol, 59%). $R_f = 0.17$ (3% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 7.36 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 4.06 (app tt, $J = 8.9, 4.5$ Hz, 1H), 2.89 (ddd, $J = 13.9, 8.9, 5.0$ Hz, 1H), 2.72 (ddd, $J = 13.7, 8.8, 7.1$ Hz, 1H), 2.16 (app dtd, $J = 14.2, 9.0, 5.1$ Hz, 1H), 2.07 – 1.75 (m, 3H), 1.37 – 1.11 (m, 14H), 1.11 – 0.75 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 141.0 (C_q), 128.5 (CH), 128.4 (CH), 126.0 (CH), 83.2 (C_q), 42.5 (CH), 41.8 (CH₂), 35.6 (CH₂), 35.3 (CH₂), 24.82 (CH₃), 24.77 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s). IR (thin film): $\nu_{\max} = 1370$ (s),[†] 1319 (s),[†] 1142 (s)[†] cm⁻¹. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₁₇H₂₇BIO₂ [M+H]⁺: 401.1143. Found: 401.1139.

5-(Cyclopropylmethyl)benzo[d][1,3]dioxole (4c)

The general procedure was followed to give an NMR yield of 39%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3c** (129 mg, 0.30 mmol) and the crude was submitted to FCC (1-2-2-3% EtOAc/heptanes) to afford **4c** as a clear, free-flowing liquid, (36 mg, 0.20 mmol, 68%). R_f = 0.46 (5% EtOAc/heptanes, CAM, UV). 1H NMR (300 MHz, $CDCl_3$): δ 6.87 – 6.60 (m, 3H), 5.93 (s, 2H), 2.48 (d, J = 6.8 Hz, 2H), 1.12 – 0.84 (m, 1H), 0.63 – 0.39 (m, 2H), 0.28 – 0.11 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5 (C_q), 145.7 (C_q), 136.2 (C_q), 121.1 (CH), 108.9 (CH), 108.1 (CH), 100.8 (CH_2), 40.2 (CH_2), 12.2 (CH), 4.7 (CH_2). IR (thin film): ν_{max} = 3076 (w),* 3001 (w),** 1016 (m)*** cm^{-1} . *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for $C_{11}H_{12}O_2$ $[M]^+$: 175.0754. Found: 175.0750.

2-(3-Iodo-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

The general procedure was followed with safrole (163 mg, 1.00 mmol) and the crude was submitted to FCC (2-3-3% EtOAc/heptanes) to afford **3c** as a clear oil (157 mg, 0.37 mmol, 37%). R_f = 0.21 (8% EtOAc/heptanes, CAM, UV). 1H NMR (300 MHz, $CDCl_3$): δ 6.82 (m, 3H), 5.94 (s, 2H), 4.25 (tdd, J = 7.9, 6.6, 5.0 Hz, 1H), 3.13 (ddd, J = 7.9 Hz, 2H), 2.06 – 1.76 (m, 1H), 1.25 (s, 12H), 1.14 – 1.00 (m, 1H), 0.97 – 0.82 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5 (C_q), 146.2 (C_q), 133.8 (C_q), 122.1 (CH), 109.2 (CH), 108.1 (CH), 100.9 (CH_2), 83.2 (C_q), 46.7 (CH_2), 42.7 (CH), 34.2 (CH_2), 24.9 (CH_3), 24.8 (CH_3). ^{11}B NMR (96 MHz, $CDCl_3$): δ 33.7 (s). IR (thin film): ν_{max} = 1371 (w),[†] 1321 (w),[†] 1142 (m)[†] cm^{-1} . [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for $C_{17}H_{25}BIO_4$ $[M+H]^+$: 431.0885. Found: 431.0878.

***tert*-Butyl(3-cyclopropyl-3-methylbutoxy)dimethylsilane (4d)**

The general procedure was followed to give an NMR yield of 58%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3d** (223 mg, 0.45 mmol), except that LiOEt (1.0 M EtOH, 5.0 mL) was used in place of TBAF, and the crude was submitted to FCC (0-1-1-2% EtOAc/heptanes) to afford **4d** as a clear, free-flowing liquid, (72 mg, 0.30 mmol, 66%). R_f = 0.43 (4% EtOAc/heptanes, CAM). 1H NMR (300 MHz, $CDCl_3$): δ 3.96 – 3.67 (m, 2H), 1.64 – 1.49 (m, 2H), 0.91 (s, 9H), 0.76 (s, 6H), 0.72 – 0.57 (m, 1H), 0.38 – 0.21 (m, 2H), 0.21 – 0.13 (m, 2H), 0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 60.4 (CH_2), 46.3 (CH_2), 31.2 (C_q), 26.1 (CH_3), 25.4 (CH_3), 21.5 (CH), 18.5 (C_q), 0.3 (CH_2),

–5.11 (CH₃). IR (thin film): $\nu_{\max}$ = 3080 (w),* 3001 (w),** 1014 (w)*** cm⁻¹. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28]

***tert*-Butyl((4-iodo-3,3-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)dimethylsilane (**3d**)**

The general procedure was followed with the TBDMS-protected alcohol **2d** (228 mg, 1.00 mmol) and the crude was submitted to FCC (1-1-2% EtOAc/heptanes) to afford **3d** as a clear oil (232 mg, 0.47 mmol, 47%). R_f = 0.33 (5% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 4.16 – 3.97 (m, 1H), 3.78 – 3.62 (m, 2H), 1.89 – 1.56 (m, 4H), 1.25 (s, 12H), 1.11 (s, 3H), 1.09 (s, 3H), 0.90 (s, 9H), 0.07 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 83.2 (C_q), 62.3 (CH), 60.0 (CH₂), 43.8 (CH₂), 38.0 (C_q), 30.0 (CH₂), 27.5 (CH₃), 26.1 (CH₃), 25.9 (CH₃), 25.0 (CH₃), 24.9 (CH₃), 18.4 (C_q), –5.10 (CH₃), –5.13 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s). IR (thin film): $\nu_{\max}$ = 1370 (m),[†] 1322 (m),[†] 1144 (s)[†] cm⁻¹. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₀H₄₃BIO₃Si [M+H]⁺: 497.2119. Found: 497.2108.

10-Cyclopropyldecan-2-one (4e**)**

The general procedure was followed to give an NMR yield of 69%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3e** (195 mg, 0.43 mmol, impure) and the crude was submitted to FCC (3-4-5-7% EtOAc/heptanes) to afford **4e** as a clear, free-flowing liquid, (30 mg, 0.153 mmol, 35%, compound was slightly volatile). R_f = 0.56 (20% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 2.42 (t, J = 7.4 Hz, 2H), 2.14 (s, 3H), 1.64 – 1.50 (m, 2H), 1.45 – 1.23 (m, 10H), 1.17 (q, J = 6.9 Hz, 2H), 0.76 – 0.55 (m, 1H), 0.49 – 0.27 (m, 2H), 0.05 – –0.08 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 209.4 (C_q), 43.9 (CH₂), 34.8 (CH₂), 29.9 (CH₃), 29.7 (CH₂), 29.59 (CH₂), 29.55 (CH₂), 29.49 (CH₂), 29.3 (CH₂), 24.0 (CH₂), 11.0 (CH), 4.5 (CH₂). IR (thin film): $\nu_{\max}$ = 3075 (w),* 2999 (w),** 1716 (s),[§] 1013 (m)*** cm⁻¹. [§]Unconjugated acyclic ketone carbonyl stretching vibration. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[3] HRMS (ESI): Calculated for C₁₃H₂₅O [M+H]⁺: 197.1900. Found: 197.1902.

2-(3-Iodo-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e**)**

The general procedure was followed with dodec-11-en-2-one **2e** (182 mg, 1.00 mmol) and the crude was submitted to FCC (3-5-7-10% EtOAc/heptanes) to afford **3e** as an orange-tinted clear oil containing DLP side-products and unreacted ICH₂Bpin (216 mg, 0.48 mmol, 48%). $R_f = 0.29$ (10%

EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 4.14 (tt, $J = 8.7, 4.7$ Hz, 1H), 2.43 (app t, $J = 7.4$ Hz, 2H), 2.15 (s, 3H), 2.03 – 1.78 (m, 3H), 1.76 – 1.45 (m, 5H), 1.46 – 1.15 (m, 31H), 1.14 – 0.96 (m, 1H), 0.96 – 0.80 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 209.4 (C_q), 83.3 (C_q), 43.9 (CH), 40.3 (CH₂), 35.2 (CH₂), 30.0 (CH₃), 29.7 (CH₂), 29.6 (CH₂), 29.40 (CH₂), 29.36 (CH₂), 29.2 (CH₂), 28.9 (CH₂), 24.94 (CH₃), 24.90 (CH₃), 23.9 (CH₂). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s), 31.8[#] (s).[#]Unreacted ICH₂Bpin impurity. IR (thin film): $\nu_{\max} = 1736$ (w),^{##} 1716 (m),[§] 1371 (s),[†] 1322 (s),[†] 1143 (s)[†] cm⁻¹. ^{##}Impurities of ester from DLP. [§]Unconjugated acyclic ketone carbonyl stretching vibration. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₁₉H₃₇BIO₃ [M+H]⁺: 451.1875. Found: 451.1877.

10-Cyclopropyldecan-2-ol (4f)

The general procedure was followed to give an NMR yield of 70%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3f** (218 mg, 0.48 mmol) and the crude was submitted to FCC (grad = 4-5-5-7% EtOAc/heptanes) to afford **4f** as a clear, free-flowing liquid, (64 mg, 0.32 mmol, 67%). $R_f = 0.54$ (20%

EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 3.79 (app p, $J = 6.0$ Hz, 1H), 1.55 – 1.24 (m, 14H), 1.24 – 1.12 (m, 5H) [interpreted as containing 1.19 (d, $J = 6.1$ Hz, 3H)], 0.74 – 0.57 (m, 1H), 0.45 – 0.31 (m, 2H), 0.09 – 0.08 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 68.3 (CH), 39.5 (CH₂), 34.9 (CH₂), 29.75 (CH₂), 29.74 (CH₂), 29.73 (CH₂), 29.6 (CH₂), 25.9 (CH₂), 23.6 (CH₃), 11.0 (CH), 4.5 (CH₂). IR (thin film): $\nu_{\max} = 3348$ (br, w),[‡] 3075 (w),^{*} 2999 (w),^{**} 1013 (m)^{***} cm⁻¹.

[‡]Intermolecularly H-bonded alcoholic O—H stretching vibration. ^{*}Secondary C—H stretches in 1-substituted cyclopropanes. ^{**}Tertiary C—H stretches in 1-substituted cyclopropanes. ^{***}Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[3]

11-Iodo-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tridecan-2-ol (3f)

The general procedure was followed with dodec-11-en-2-ol **2f** (184 mg, 1.00 mmol) and the crude was submitted to FCC (10-15-20% EtOAc/heptanes) to afford **3f** as a clear oil (239 mg, 0.53 mmol, 53%). $R_f = 0.64$ (30% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CDCl₃): δ 4.13 (tt, $J = 8.7, 4.7$ Hz, 1H), 3.87 – 3.74 (m, 1H), 2.04 – 1.76 (m, 3H), 1.76 – 1.59 (m, 2H), 1.57 – 1.22 (m, 31H), 1.19 (d, $J = 6.2$ Hz, 3H), 1.10 – 0.95 (m, 1H), 0.95 – 0.74 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 83.2 (C_q), 68.3 (CH), 43.9 (CH), 40.3 (CH₂), 39.4 (CH₂), 35.2 (CH₂), 29.7 (CH₂), 29.61 (CH₂), 29.58

(CH₂), 29.5 (CH₂), 28.9 (CH₂), 25.8 (CH₂), 24.94 (CH₃), 29.90 (CH₃), 23.6 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.6 (s). IR (thin film): ν_{max} = 3371 (br, w),[‡] 1371 (s),[†] 1319 (m),[†] 1143 (s)[†] cm⁻¹.[‡]Intermolecularly H-bonded alcoholic O—H stretching vibration. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₁₉H₃₉BIO₃ [M+H]⁺: 453.2031. Found: 453.2032.

9-Cyclopropylnonan-1-ol (4g)

The general procedure was followed to give an NMR yield of 75%. The general procedure was followed beginning from the γ-iodoboronic pinacol ester **3g** (400 mg, 0.91 mmol) and the crude was submitted to FCC (5-10-15-20% EtOAc/heptanes) to afford **4g** as a clear, free-flowing liquid (119 mg, 0.65 mmol, 71%). R_f = 0.28 (20% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 3.65 (t, *J* = 6.6 Hz, 2H), 1.79 (br s, 1H), 1.58 (app p, *J* = 6.8 Hz, 2H), 1.45 – 1.23 (m, 12H), 1.18 (q, *J* = 7.0 Hz, 2H), 0.78 – 0.53 (m, 1H), 0.47 – 0.03 (m, 2H), 0.10 – -0.10 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 63.1 (CH₂), 34.9 (CH₂), 32.9 (CH₂), 29.72 (CH₂), 29.70 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 25.8 (CH₂), 11.0 (CH), 4.4 (CH₂). IR (thin film): ν_{max} = 3327 (br m)[‡], 3075 (w)*, 2999 (w),** 1013 (m)*** cm⁻¹. [‡]Intermolecularly H-bonded alcoholic O—H stretching vibration. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (EI): Calculated for C₁₂H₂₂ [M – H₂O]⁺: 166.1716. Found: 166.1713.

2-(3-Iodododecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

The general procedure (either EtOAc or PhH) was followed with 10-undecen-1-ol (97% purity, 176 mg, 1.00 mmol) and the crude was submitted to FCC (5-10-15-20% EtOAc/heptanes) to afford **3g** as an orange-tinted oil (258 mg, 0.59 mmol, 59%). R_f = 0.29 (20% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 4.13 (app tt, *J* = 8.6, 4.9 Hz, 1H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.02 – 1.77 (m, 3H), 1.77 – 1.47 (m, 6H), 1.44 – 1.17 (m, 36H), 1.02 (ddd, *J* = 15.6, 10.9, 5.6 Hz, 1H), 0.95 – 0.79 (m, 7H). ¹³C NMR (75 MHz, CDCl₃): δ 83.2 (C_q), 63.1 (CH₂), 43.8 (CH), 40.2 (CH₂), 35.2 (CH₂), 32.8 (CH₂), 29.51 (CH₂), 29.50 (CH₂), 29.4 (CH₂), 28.8 (CH₂), 25.7 (CH₂), 24.85 (CH₃), 24.81 (CH₃), 22.7 (CH₂), 14.1 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s), 31.7[#] (sh, s).[#]Unreacted ICH₂Bpin contamination. IR (thin film): ν_{max} = 3373 (br w)[‡], 1371 (s)[†], 1319 (s)[†], 1142 (s)[†] cm⁻¹. [‡]Intermolecularly H-bonded alcoholic O—H stretching vibration. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₁₈H₃₇BIO₂ [M+H]⁺: 439.1875. Found: 439.1862.

9-Cyclopropynonyl acetate (4h)

The general procedure was followed to give an NMR yield of 70%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3h** (281 mg, 0.58 mmol) and the crude was submitted to FCC (1-2-2-2% EtOAc/heptanes) to afford **4h** as a clear, free-flowing liquid, (80 mg, 0.35 mmol, 60%). R_f = 0.39 (8% EtOAc/heptanes, CAM). 1H NMR (300 MHz, $CDCl_3$): δ 4.06 (t, J = 6.8 Hz, 2H), 2.05 (s, 3H), 1.62 (app p, J = 6.9 Hz, 2H), 1.44 – 1.27 (m, 12H), 1.18 (q, J = 6. Hz, 2H), 0.78 – 0.53 (m, 1H), 0.48 – 0.31 (m, 2H), 0.11 – –0.14 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.31 (C_q), 64.7 (CH_2), 34.9 (CH_2), 29.73 (CH_2), 29.70 (CH_2), 29.61 (CH_2), 29.59 (CH_2), 29.4 (CH_2), 28.7 (CH_2), 26.0 (CH_2), 21.1 (CH_3), 11.0 (CH), 4.5 (CH_2). IR (thin film): ν_{max} = 3075 (w)*, 2999 (w),** 1740 (s),[§] 1013 (m)*** cm^{-1} . [§]Unconjugated acyclic ester carbonyl stretching vibration. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for $C_{14}H_{27}O_2$ $[M+H]^+$: 227.2006. Found: 227.2008.

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl acetate (3h)

The general procedure was followed with undec-10-en-1-yl acetate **2h** (212 mg, 1.00 mmol) and the crude was submitted to FCC (4-5-7% EtOAc/heptanes) to afford **3h** as a clear oil[#] (311 mg, 0.65 mmol, 65%). [#]Contamination with ~11 mol% unreacted ICH_2Bpin . R_f = 0.19 (8% EtOAc/heptanes, CAM). 1H NMR (300 MHz, $CDCl_3$): δ 4.13 (tt, J = 8.7, 4.7 Hz, 1H), 4.05 (t, J = 6.8 Hz, 2H), 2.17 (s, 2H of 11 mol% ICH_2Bpin), 2.05 (s, 3H), 2.01 – 1.76 (m, 3H), 1.76 – 1.44 (m, 5H), 1.44 – 1.18 (m, 27H), 1.02 (ddd, J = 15.6, 10.9, 5.5 Hz, 1H), 0.88 (ddd, J = 16.1, 10.2, 6.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3 (C_q), 83.2 (C_q), 64.7 (CH_2), 43.9 (CH), 40.3 (CH_2), 35.3 (CH_2), 29.6 (CH_2), 29.53 (CH_2), 29.46 (CH_2), 29.3 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 26.0 (CH_3), 24.95 (CH_3), 24.91 (CH_3), 24.5 (CH_3 , ICH_2Bpin), 21.1 (CH_3). ^{11}B NMR (96 MHz, $CDCl_3$): δ 33.5 (s), 31.9[#] (sh, s).[#]Unreacted ICH_2Bpin contamination. IR (thin film): ν_{max} = 1739 (s),[§] 1370 (s)[†], 1321 (s)[†], 1143 (s)[†] cm^{-1} . [§]Unconjugated acyclic ester carbonyl stretching vibration. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for $C_{20}H_{39}BIO_4$ $[M+H]^+$: 481.1981. Found: 481.1993.

9-Cyclopropynonyl benzoate (4i)

The general procedure was followed to give an NMR yield of 74%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3i** (277 mg, 0.51 mmol) and the crude was submitted to FCC (1-1-1-2% EtOAc/heptanes) to afford **4i** as a clear, free-flowing liquid, (101 mg, 0.35 mmol, 67%). R_f = 0.46 (8% EtOAc/heptanes, CAM,

UV). ^1H NMR (300 MHz, CDCl_3): δ 8.20 – 7.89 (m, 2H), 7.71 – 7.51 (m, 1H), 7.50 – 7.37 (m, 2H), 4.33 (t, J = 6.7 Hz, 2H), 1.77 (dt, J = 8.1, 6.6 Hz, 2H), 1.56 – 1.25 (m, 12H), 1.18 (app q, J = 6.9 Hz, 2H), 0.79 – 0.54 (m, 1H), 0.50 – 0.27 (m, 2H), 0.15 – -0.23 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.8 (C_q), 132.9 (CH), 130.6 8 (C_q), 129.6 (CH), 128.4 (CH), 65.2 (CH_2), 34.9 (CH_2), 29.73 (CH_2), 29.71 (CH_2), 29.62 (CH_2), 29.59 (CH_2), 29.4 (CH_2), 28.8 (CH_2), 26.1 (CH_2), 11.0 (CH), 4.5 (CH_2). IR (thin film): ν_{max} = 3073 (w)*, 2998 (w),** 1718 (s), § 1603 (w), $^{\text{ar}}$ 1584 (w), $^{\text{ar}}$ 1013 (m)*** cm^{-1} . § Unconjugated, acyclic ester carbonyl stretching vibration. $^{\text{ar}}$ Aromatic C=C stretching vibrations. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for $\text{C}_{11}\text{H}_{29}\text{O}_2$ $[\text{M}+\text{H}]^+$: 28.2162. Found: 289.2169.

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl benzoate (**3i**)

The general procedure was followed with undec-10-en-1-yl benzoate **2i** (274 mg, 1.00 mmol) and the crude was submitted to FCC (1-2-3-5-5% EtOAc/heptanes) to afford **3i** as clear, viscous oil[#] (335 mg, 62 mmol, 62%).

[#]Contaminated with ~10 mol% unreacted ICH_2Bpin . R_f = 0.24 (8% EtOAc/heptanes, CAM, UV).

^1H NMR (300 MHz, CDCl_3): δ 8.14 – 7.97(m, 2H), 7.62 – 7.49 (m, 1H), 7.50 – 7.37 (m, 2H), 4.31 (t, J = 6.6 Hz, 2H), 4.13 (tt, J = 8.7, 4.8 Hz, 1H), 2.17 (s, 2H 10 mol% ICH_2Bpin), 2.01 – 1.59 (m, 7H), 1.56 – 1.17 (m, 29H), 1.10 – 0.95 (m, 1H), 0.95 – 0.78 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.7 (C_q), 132.8 (CH), 130.6 (C_q), 129.6 (CH), 128.4 (CH), 83.2 (C_q), 65.2 (CH_2), 43.9 CH), 40.3 (CH_2), 35.2 (CH_2), 29.57 (CH_2), 29.52 (CH_2), 29.45 (CH_2), 29.31 (CH_2), 28.87 (CH_2), 28.79 (CH_2), 26.1 (CH_2), 24.92 (CH_3), 24.88 (CH_3), 24.5[#] (ICH_2Bpin , CH_3). ^{11}B NMR (96 MHz, CDCl_3): δ 33.7 (s), 32.0[#] (s, overlapping).[#]Unreacted ICH_2Bpin contamination. IR (thin film): ν_{max} = 1718 (s), § 1603 (w), $^{\text{ar}}$ 1584 (w), $^{\text{ar}}$ 1371 (s) † , 1314 (s) † , 1143 (s) † cm^{-1} . § Unconjugated, acyclic ester carbonyl stretching vibration. $^{\text{ar}}$ Aromatic C=C stretching vibrations. † Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for $\text{C}_{25}\text{H}_{41}\text{BIO}_4$ $[\text{M}+\text{H}]^+$: 543.2137. Found: 543.2141.

(((9-Cyclopropynonyl)oxy)methyl)benzene (**4j**)

The general procedure was followed to give an NMR yield of 60%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester[#] **3j** (211 mg, 0.40 mmol) and the crude was submitted to FCC (1-1-2-2% EtOAc/heptanes) to afford

4j as a clear, free-flowing liquid (68 mg, 0.25 mmol, 62%). [#]Contaminated with ~44 mol% unreacted ICH_2Bpin . R_f = 0.54 (8% EtOAc/heptanes, CAM, UV).

^1H NMR (300 MHz, CD_2Cl_2): δ 7.36 – 7.22 (m, 5H), 4.47 (s, 2H), 3.46 (t, J = 6.6 Hz, 2H), 1.60 (app p, J = 6.7 Hz, 2H), 1.45 – 1.24 (m, 12H), 1.18 (app q, J = 7.0 Hz, 2H), 0.76 – 0.57 (m, 1H), 0.47 – 0.32 (m, 2H), 0.08 –

–0.09 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 139.7 (C_q), 128.8 (CH), 128.1 (CH), 127.9 (CH), 73.3 (CH₂), 71.1 (CH₂), 35.3 (CH₂), 30.4 (CH₂), 30.24 (CH₂), 30.22 (CH₂), 30.21 (CH₂), 30.12 (CH₂), 30.09 (CH₂), 26.8 (CH₂), 11.4 (CH), 4.7 (CH₂). IR (thin film): ν_{max} = 3074 (w)*, 2999 (w),** 1013 (m)*** cm^{-1} . *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. HRMS (ESI): Calculated for $\text{C}_{19}\text{H}_{31}\text{O}$ $[\text{M}+\text{H}]^+$: 275.2369. Found: 275.2373.

2-(12-(Benzyloxy)-3-iodododecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

The general procedure was followed with ((undec-10-en-1-yloxy)methyl)benzene **2j** (260 mg, 1.00 mmol) and the crude was submitted to FCC (3-4-5% EtOAc/heptanes) to afford **3j** as clear, viscous oil[#] (241 mg, 0.46 mmol, 46%). [#]Contaminated with ~ 44 mol% unreacted ICH_2Bpin . R_f = 0.30 (8% EtOAc/heptanes, CAM, UV). ^1H NMR (300 MHz, CDCl_3): δ 7.44 – 7.28 (m, 5H), 4.51 (s, 2H), 4.14 (tt, J = 8.7, 4.7 Hz, 1H), 3.47 (t, J = 6.6 Hz, 2H), 2.18 (s, 2H of 44 mol% ICH_2Bpin), 2.03 – 1.77 (m, 3H), 1.75 – 1.45 (m, 5H), 1.44 – 1.17 (m, 31H), 1.10 – 0.96 (m, 1H), 0.89 (ddd, J = 16.4, 10.2, 6.3 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 138.8 (C_q), 128.4 (CH), 127.7 (CH), 127.5 (CH), 84.3 (ICH_2Bpin , C_q), 83.2 (C_q), 73.0 (CH₂), 70.6 (CH₂), 44.0 (CH), 40.4 (CH₂), 35.3 (CH₂), 29.9 (CH₂), 29.6 (2xCH₂), 29.54 (CH₂), 29.51 (CH₂), 28.9 (CH₂), 26.3 (CH₂), 24.95 (CH₃), 24.91 (CH₃), 24.5[#] (ICH_2Bpin , CH₃). ^{11}B NMR (96 MHz, CDCl_3): δ 33.3 (s), 31.8[#] (sh, s). [#]Unreacted ICH_2Bpin contamination. IR (thin film): ν_{max} = 1371 (s)[†], 1324 (s), [†]1143 (s)[†] cm^{-1} . [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for $\text{C}_{25}\text{H}_{43}\text{BIO}_3$ $[\text{M}+\text{H}]^+$: 529.2344. Found: 529.2359.

9-Cyclopropylnonanoic acid (4k)

The general procedure was followed to give an NMR yield of 69%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3k** (141 mg, 0.31 mmol) and the crude was submitted to FCC (5-7-10-15-20% EtOAc/heptanes) to afford **4k** as a white solid (38 mg, 0.19 mmol, 62%). R_f = 0.41–0.29 (20% EtOAc/heptanes, dragged, CAM). m.p. 36.6 – 37.7 °C (EtOAc/heptanes). ^1H NMR (300 MHz, CDCl_3): δ 10.94 (v br s, 1H), 2.36 (app t, J = 7.5 Hz, 2H), 1.65 (app p, J = 7.3 Hz, 2H), 1.47 – 1.24 (m, 12H), 1.24 – 1.10 (m, 2H), 0.77 – 0.54 (m, 1H), 0.48 – 0.29 (m, 2H), 0.10 – –0.12 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 179.9 (C_q), 34.9 (CH₂), 34.1 (CH₂), 29.7 (CH₂), 29.56 (CH₂), 29.54 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 24.8 (CH₂), 11.0 (CH), 4.5 (CH₂). IR (thin film): ν_{max} = 3400–2500 (v br, w), [‡]3074 (w),* 2999 (w),** 1695 (s),§ 1016 (m),*** cm^{-1} . [‡]Intermolecularly H-bonded carboxylic acid O—H stretching vibration. §Carboxylic acid carbonyl stretch. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric

(“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for $C_{12}H_{23}O_2$ $[M+H]^+$: 199.1693. Found: 199.1694. Spectroscopic data are in accordance with literature.^[31]

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecanoic acid (3k)

The general procedure was followed with 10-undecenoic acid (97% purity, 190 mg, 1.00 mmol) and the crude was submitted to FCC (7-10-15-20% EtOAc/heptanes) to afford **3k** as a clear viscous oil (206 mg, 0.46 mmol, 46%). R_f = 0.28–0.17 (20% EtOAc/heptanes, dragged, CAM). 1H NMR (300 MHz, $CDCl_3$): δ 10.89 (br s, 1H), 4.12 (app tt, J = 8.7, 4.2 Hz, 1H), 2.35 (app t, J = 7.5 Hz, 2H), 2.02 – 1.76 (m, 3H), 1.75 – 1.57 (m, 3H), 1.45 – 1.18 (m, 25H), 1.02 (ddd, J = 15.6, 10.5, 5.5 Hz, 1H), 0.88 (ddd, J = 16.4, 10.1, 6.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.0 (C_q), 83.2 (C_q), 43.7 (CH), 40.2 (CH_2), 35.1 (CH_2), 34.0 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.7 (CH_2), 24.83 (CH_3), 24.79 (CH_3), 22.6 (CH_2). ^{11}B NMR (96 MHz, $CDCl_3$): δ 33.7 (s). IR (thin film): ν_{max} = 3500–2500 (v br, w),[‡] 1706 (s),[§] 1371 (s),[†] 1319 (m),[†] 1142 (s)[†] cm^{-1} . [‡]Intermolecularly H-bonded carboxylic acid O—H stretching vibration. [§]Carboxylic acid carbonyl stretch. [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for $C_{18}H_{35}BIO_4$ $[M+H]^+$: 453.1668. Found: 453.1676.

Methyl 9-cyclopropylnonanoate (4l)

The general procedure was followed to give an NMR yield of 71%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester[#] **3l** (221 mg, 0.47 mmol) and the crude was submitted to FCC (1-1-2-2% EtOAc/heptanes) to afford **4l** as a clear oil (68 mg, 0.32 mmol, 68%). [#]Contaminated with 19 mol% unreacted ICH_2Bpin . R_f = 0.48 (8% EtOAc/heptanes, CAM). 1H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, 3H), 2.31 (app t, J = 7.5 Hz, 2H), 1.62 (app p, J = 6.8, 6.3 Hz, 2H), 1.46 – 1.23 (m, 10H), 1.18 (q, J = 6.9 Hz, 2H), 0.78 – 0.53 (m, 1H), 0.47 – 0.22 (m, 2H), 0.07 – –0.09 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4 (C_q), 51.5 (CH_3), 34.9 (CH_2), 34.2 (CH_2), 29.58 (CH_2), 29.55 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 25.1 (CH_2), 11.0 (CH), 4.5 (CH_2). IR (thin film): ν_{max} = 3075 (w),* 2999 (w),** 1740 (s),[§] 1013 (m)*** cm^{-1} . [§]Saturated acyclic ester carbonyl stretch. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for $C_{13}H_{24}O_2Na$ $[M+Na]^+$: 235.1669. Found: 235.1667. Spectroscopic data are in accordance with literature.^[32]

Methyl 10-iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecanoate (3l)

The general procedure was followed with methyl 10-undecenoate **2I** (99% purity, 198 mg, 1.00 mmol) and the crude was submitted to FCC (gradient = 2-3-4-5% EtOAc/heptanes) to afford **3I** as a clear viscous oil[#] (234 mg, 0.50 mmol, 50%). [#]Contaminated with 19 mol% unreacted ICH₂Bpin. R_f =

0.27 (8% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 4.13 (app tt, J = 8.6, 4.7 Hz, 1H), 3.67 (s, 3H), 2.30 (app t, J = 7.5 Hz, 2H), 2.17[#] (s, 0.4H), 2.04 – 1.75 (m, 3H), 1.76 – 1.46 (m, 5H), 1.43 – 1.16 (m, 24H), 1.02 (ddt, J = 15.6, 10.0, 5.5 Hz, 1H), 0.88 (ddd, J = 16.2, 10.3, 6.3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 174.3 (C_q), 83.2 (C_q), 51.4 (CH₃), 43.8 (CH), 40.2 (CH₂), 35.2 (CH₂), 34.1 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.0 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 28.8 (CH₂), 24.9 (CH₂), 24.9 (CH₃), 24.8 (CH₃), 24.2[#] (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s), 31.8[#] (sh, s). IR (thin film): ν_{max} = 1739 (s),[§] 1371 (s),[†] 1323 (s),[†] 1143 (s)[†] cm⁻¹. [§]Saturated acyclic ester carbonyl stretch. [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₁₉H₃₇BIO₄ [M+H]⁺: 467.1824. Found: 467.1811.

Ethyl 9-cyclopropylnonanoate (4m)

General procedure A was followed to give an NMR yield of 78%. General procedure B was followed beginning from the γ -iodoboronic pinacol ester[#] **3m** (232 mg, 0.48 mmol) and the crude was submitted to FCC (1-2-2-3% EtOAc/heptanes) to afford **4m** as a clear oil (79 mg, 0.35 mmol, 72%). [#]Contaminated with 14 mol% unreacted

ICH₂Bpin. R_f = 0.52 (8% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 4.13 (q, J = 7.1 Hz, 2H), 2.29 (app t, J = 7.5 Hz, 2H), 1.83 – 1.54 (m, 2H), 1.47 – 1.28 (m, 10H), 1.26 (t, J = 7.2 Hz, 3H), 1.17 (app q, J = 7.0 Hz, 2H), 0.73 – 0.54 (m, 1H), 0.46 – 0.31 (m, 2H), 0.06 – -0.07 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 173.9 (C_q), 60.1 (CH₂), 34.8 (CH₂), 34.4 (CH₂), 29.6 (CH₂), 29.50 (CH₂), 29.46 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 25.0 (CH₂), 14.3 (CH₃), 10.9 (CH), 4.4 (CH₂). IR (thin film): ν_{max} = 3075 (w),* 2999 (w),** 1740 (s),[§] 1013 (m),*** cm⁻¹. [§]Saturated acyclic ester carbonyl stretch. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₁₄H₂₆O₂Na [M+Na]⁺: 249.1825. Found: 249.1818.

Ethyl 10-iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecanoate (3m)

The general procedure was followed with ethyl 10-undecenoate (97% purity, 219 mg, 1.00 mmol) and the crude was submitted to FCC (2-3-4-5% EtOAc/heptanes) to afford **3m** as an orange-tinted viscous oil[#] (250 mg, 0.52 mmol, 52%). [#]Contaminated with ~14 mol% unreacted ICH₂Bpin. R_f = 0.27

(8% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CDCl₃): δ 4.20 – 4.03 (m, 1H), 4.12 (q, J =

7.1 Hz, 2H), 2.29 (app t, $J = 7.5$ Hz, 2H), 2.17[#] (s, 14mol%), 2.04 – 1.73 (m, 3H), 1.77 – 1.43 (m, 5H), 1.44 – 1.16 (m, 28H), 1.02 (ddt, $J = 15.7, 10.0, 5.5$ Hz, 1H), 0.88 (ddd, $J = 16.2, 10.2, 6.3$ Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 173.9 (C_q), 83.2 (C_q), 60.2 (CH₂), 43.8 (CH), 40.2 (CH₂), 35.2 (CH₂), 34.4 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 28.8 (CH₂), 25.0 (CH₂), 24.9 (CH₃), 24.8 (CH₃), 24.4[#] (CH₃), 14.3 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s), 31.8[#] (sh, s). IR (thin film): $\nu_{\max} = 1733$ (s),[§] 1371 (s),[†] 1322 (s),[†] 1143 (s)[†] cm⁻¹. [§]Saturated acyclic ester carbonyl stretch. [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₀H₃₉BIO₄ [M+H]⁺: 481.1981. Found: 481.1962.

Benzyl 9-cyclopropylnonanoate (4n)

The general procedure was followed to give an NMR yield of 69%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester[#] **3n** (280 mg, 0.46 mmol) and the crude was submitted to FCC (1-1-2% EtOAc/heptanes) to afford **4n** as a clear oil (85 mg, 0.30 mmol, 64%). [#]Contaminated with 26 mol% unreacted ICH₂Bpin. $R_f = 0.45$ (8% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CDCl₃): δ 7.49 – 7.30 (m, 5H), 5.12 (s, 2H), 2.36 (app t, $J = 7.5$ Hz, 2H), 1.65 (app p, $J = 7.2$ Hz, 2H), 1.46 – 1.23 (m, 10H), 1.17 (app q, $J = 7.0$ Hz, 2H), 0.82 – 0.51 (m, 1H), 0.47 – 0.31 (m, 2H), 0.08 – -0.09 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 173.8 (C_q), 136.2 (C_q), 128.6 (CH), 128.2 (CH), 128.2 (CH), 66.1 (CH₂), 34.8 (CH₂), 34.4 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 25.1 (CH₂), 11.0 (CH), 4.5 (CH₂). IR (thin film): $\nu_{\max} = 3074$ (w),* 2998 (w),** 1736 (s),[§] 1013 (m),*** cm⁻¹. [§]Saturated acyclic ester carbonyl stretch. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₁₉H₂₉O₂ [M+H]⁺: 289.2162. Found: 289.2169.

Benzyl 10-iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecanoate (3n)

The general procedure was followed with benzyl 10-undecenoate **2n** (274 mg, 1.00 mmol) and the crude was submitted to FCC (1-2-3-4-5% EtOAc/heptanes) to afford **3n** as a clear oil[#] (316 mg, 0.58 mmol, 58%). [#]Contaminated with ~26 mol% unreacted ICH₂Bpin. $R_f = 0.34$ (10% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CDCl₃): δ 7.43 – 7.31 (m, 5H), 5.12 (s, 2H), 4.34 – 3.88 (m, 1H), 2.36 (app t, $J = 7.5$ Hz, 2H), 2.17[#] (s, 26 mol%), 2.01 – 1.75 (m, 3H), 1.75 – 1.56 (m, 4H), 1.56 – 1.45 (m, 1H), 1.45 – 1.18 (m, 26H), 1.03 (ddt, $J = 15.6, 9.9, 5.5$ Hz, 1H), 0.88 (ddd, $J = 16.2, 10.2, 6.2$ Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 173.7 (C_q), 136.2 (C_q), 128.6 (CH), 128.3 (CH), 128.3 (CH), 84.3[#] (C_q), 83.2 (C_q), 66.2 (CH₂), 43.9 (CH), 40.3 (CH₂), 35.2 (CH₂), 34.4 (CH₂), 29.6 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 28.8 (CH₂), 25.0 (CH₂), 24.95 (CH₃), 24.90 (CH₃),

24.5[#] (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.5 (s), 31.8[#] (s, overlapping). IR (thin film): ν_{max} = 1736 (s),[§] 1371 (s),[†] 1323 (s),[†] 1143 (s)[†] cm⁻¹. [§]Saturated acyclic ester carbonyl stretch. [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₅H₄₁BIO₄ [M+H]⁺: 543.2137. Found: 543.2149.

9-Cyclopropyl-*N*-ethylnonanamide (4o)

The general procedure was followed to give an NMR yield of 65%. The general procedure was followed beginning from the γ-iodoboronic pinacol ester **3o** (267 mg, 0.56 mmol) and the crude was submitted to FCC (30-30-40-50% EtOAc/heptanes) to afford **4o** as a white crystalline solid (88 mg, 0.39 mmol, 70%). R_f = 0.36 (60% EtOAc/heptanes, CAM, slightly dragged). m.p. = 51.7 – 52.3 °C. ¹H NMR (300 MHz, CDCl₃): δ 5.48 (br s, 1H), 3.29 (app qd, *J* = 7.3, 5.6 Hz, 2H), 2.19 – 2.02 (m, 2H), 1.62 (app dp, *J* = 11.9, 7.0, 5.8 Hz, 2H), 1.48 – 1.23 (m, 10H), 1.22 – 1.16 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.76 – 0.55 (m, 1H), 0.46 – 0.28 (m, 2H), 0.11 – -0.12 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 173.1 (C_q), 37.0 (CH₂), 34.8 (CH₂), 34.4 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.55 (CH₂), 29.45 (CH₂), 29.41 (CH₂), 25.9 (CH₂), 15.0 (CH₃), 11.0 (CH), 4.4 (CH₂). IR (thin film): ν_{max} = 3307 (m),[‡] 3076 (w),* 2995 (w),** 1738 (s),[§] 1544 (s),[§] 1015 (m)*** cm⁻¹. [‡]Amide N—H stretching vibration. [§]Saturated acyclic secondary amide carbonyl stretches. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₁₄H₂₈ON [M+H]⁺: 226.2165. Found: 226.2167.

N-Ethyl-10-iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecanamide (3o)

The general procedure was followed with *N*-ethylundec-10-enamide **2o** (211 mg, 1.00 mmol) and the crude was submitted to FCC (gradient = 30-30-40-50% EtOAc/heptanes) to afford **3o** as a pale orange melt (288 mg, 0.60 mmol, 60%). R_f = 0.19 or 0.36 (30% or 60% EtOAc/heptanes, CAM, dragged). ¹H NMR (300 MHz, CDCl₃): δ 5.43 (br s, 1H), 4.12 (app tt, *J* = 8.2, 4.3 Hz, 1H), 3.29 (app qd, *J* = 7.3, 5.6 Hz, 2H), 2.32 – 2.10 (m, 2H), 2.01 – 1.76 (m, 3H), 1.73 – 1.56 (m, 3H), 1.47 – 1.19 (m, 22H), 1.14 (t, *J* = 7.3 Hz, 3H), 1.02 (app ddd, *J* = 15.6, 10.3, 5.5 Hz, 1H), 0.95 – 0.77 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 173.0 (C_q), 83.2 (C_q), 43.9 (CH), 40.3 (CH₂), 37.0 (CH₂), 35.2 (CH₂), 34.4 (CH₂), 29.6 (CH₂), 29.35 (CH₂), 29.34 (CH₂), 28.8 (CH₂), 25.9 (CH₂), 24.94 (CH₃), 24.90 (CH₃), 15.0 (CH₂). ¹¹B NMR (96 MHz, CDCl₃): δ 33.5 (s). IR (thin film): ν_{max} = 3288 (br m),[‡] 3079 (br w),[‡] 1642 (s),[§] 1549 (m),[§] 1371 (s),[†] 1319 (s),[†] 1143 (s)[†] cm⁻¹. [‡]Amide N—H stretching vibration. [§]Saturated acyclic secondary amide carbonyl stretches. [†]Different stretching modes of the pinacol

boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₀H₄₀O₃NBI [M+H]⁺: 480.2140. Found: 480.2151.

9-Cyclopropyl-*N,N*-diethylnonanamide (**4p**)

The general procedure was followed to give an NMR yield of 65%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3p** (260 mg, 0.51 mmol) and the crude was submitted to FCC (10-15-15-20% EtOAc/heptanes) to afford **4p** as a free-flowing clear liquid (88 mg, 0.35 mmol, 68%). *R_f* = 0.33 (30% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 3.37 (q, *J* = 7.0 Hz, 2H), 3.30 (q, *J* = 7.0 Hz, 2H), 2.35 – 2.22 (m, 2H), 1.63 (app td, *J* = 11.5, 9.5, 5.5 Hz, 2H), 1.44 – 1.25 (m, 10H), 1.21 – 1.14 (m, 5H [interpreted as containing 1.17 (t, *J* = 7.1 Hz, 3H)]), 1.11 (t, *J* = 7.2 Hz, 3H), 0.74 – 0.54 (m, 1H), 0.45 – 0.32 (m, 2H), 0.08 – -0.07 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 172.4 (C_q), 42.1 (br, CH₂), 40.1 (br, CH₂), 34.8 (CH₂), 33.3 (CH₂), 29.7 (CH₂), 29.65 (CH₂), 29.58 (CH₂), 25.6 (CH₂), 14.5 (br, CH₃), 13.2 (br, CH₃), 11.0 (CH), 4.4 (CH₂). IR (thin film): ν_{max} = 3074 (w),* 2971 (w),** 1640 (s),§ 1013 (m)*** cm⁻¹. §Saturated acyclic tertiary amide carbonyl stretch. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₁₆H₃₂ON [M+H]⁺: 254.2478. Found: 254.2481.

N,N-diethyl-10-iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecanamide (**3p**)

The general procedure was followed with *N,N*-diethylundec-10-enamide **2p** (239 mg, 1.00 mmol) and the crude was submitted to FCC (gradient = 15-20-20-25% EtOAc/heptanes) to afford **3p** as a pale orange viscous oil (287 mg, 0.57 mmol, 57%). *R_f* = 0.24 (30% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 4.13 (app tt, *J* = 8.4, 4.6 Hz, 1H), 3.37 (q, *J* = 6.9 Hz, 2H), 3.30 (q, *J* = 6.9 Hz, 2H), 2.32 – 2.23 (m, 2H), 2.01 – 1.76 (m, 3H), 1.75 – 1.56 (m, 3H), 1.42 – 1.22 (m, 23H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.01 (app td, *J* = 10.2, 5.8 Hz, 1H), 0.88 (app ddd, *J* = 16.2, 10.3, 6.3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 172.4 (C_q), 83.2 (C_q), 44.0 (CH), 42.1 (br, CH₂), 40.3 (CH₂), 40.1 (br, CH₂), 35.2 (CH₂), 33.2 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 28.9 (CH₂), 25.6 (CH₂), 24.94 (CH₃), 24.90 (CH₃), 14.5 (br, CH₃), 13.2 (br, CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s). IR (thin film): ν_{max} = 1642 (s),§ 1371 (s),† 1318 (s),† 1143 (s)† cm⁻¹. §Saturated acyclic tertiary amide carbonyl stretch. †Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₂H₄₄O₃NBI [M+H]⁺: 508.2453. Found: 508.2460.

6-Phenylspiro[2.5]octane (4q)

The general procedure was followed to give an NMR yield of 15%.

Modified procedure with BEt_3 /air initiation. A 1-neck 10 mL flask was charged with ICH_2Bin (540 mg, 2.0 mmol), (4-methylenecyclohexyl)benzene (172 mg, 1.0 mmol), and benzene (2.5 mL, 0.3 M). A solution of BEt_3 (0.8 mL, 1.0 mmol, 1.15 M in PhH)

was added in one-portion and the mixture stirred open to air with no additional precautions. The contents were filtered through a silica gel plug, washed with heptanes, and concentrated *in vacuo*. The crude residue was analyzed by NMR with 1,4-dimethoxybenzene as an internal reference to give the title compound with a 38% yield. *To isolate the clean product, with the alkene fully consumed:* As above, but with the BEt_3 in two 0.5 equiv portions and the ICH_2Bpin in two 1.5 equiv portions, separated by 1.5 h. The addition of TBAF and workup as in the general procedure was followed and the crude was submitted to FCC (0-0-0-2-3-4% EtOAc/heptanes) to afford **4q** as a free-flowing clear liquid (67 mg, 0.36 mmol, 36%) and the homoallylic boronic ester as a clear oil (57 mg, 0.18 mmol, 18%, 9:1 *endo/exo* – matching literature,^[33] see below for characterization). R_f = 0.60 (2% EtOAc/heptanes, UV, CAM). 1H NMR (300 MHz, CD_2Cl_2): δ 7.72 – 6.91 (m, 5H), 2.58 (tt, J = 12.0, 3.5 Hz, 1H), 2.18 – 1.78 (m, 4H), 1.98 (qd, J = 12.6, 3.5 Hz, 2H), 1.07 – 0.94 (m, 2H), 0.50 – 0.13 (m, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 148.5 (C_q), 128.8 (CH), 127.5 (CH), 126.3 (CH), 44.8 (CH), 36.4 (CH_2), 34.0 (CH_2), 19.1 (C_q), 12.8 (CH_2), 12.1 (CH_2). IR (thin film): ν_{max} = 3063 (w),* 3026 (w),* 2993 (w),* 1602 (w),^{ar} 1583 (w),^{ar} 1492 (m),^{ar} 1008 (m),*** 928 (m)*** cm^{-1} . *Secondary C—H stretches in 1,1-disubstituted/spiro cyclopropanes. ^{ar}Aromatic C—C stretches of phenyl ring. ***Breathing of cyclopropane ring. For IR of cyclopropanes see ref.^[28] Thermal Elemental Analysis: Calculated for $C_{12}H_{24}$: C, 90.26; H, 9.74. Found: C, 90.04; H, 10.00.

Homoallylic boronic ester (4,4,5,5-tetramethyl-2-(2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)ethyl)-1,3,2-dioxaborolane). *endo:exo* ~ 9:1 (approximate ratio since the *exo* regioisomer is an allylic boronate, therefore will react with oxygen and decompose). R_f = 0.09 (2% EtOAc/heptanes, UV,

CAM). 1H NMR (300 MHz, CD_2Cl_2): (*traces of minor regioisomer are reported when clearly identified; integrals taken as sum two isomers, i.e. 0.2H of minor + 1.8H of major reported as 2H except when clearly separate; the methylene junk is reported as seen*) δ 7.41 – 7.07 (m, 5H), 5.58 – 5.42 (m, 0.9H), 2.95 – 2.62 (m, 0.9H), 2.49 (tt, J = 12.3, 3.4 Hz, 0.1H [pseudo-symmetry of benzylic C—H in the *exo* regioisomer]), 2.38 – 1.85 (m, 7H), 1.85 – 1.70 (m, 1H), 1.42 – 1.19 (m, 12H), 0.92 (dd, J = 8.8, 8.1 Hz, 1.8H), 0.80 (dd, J = 8.8, 8.1 Hz, 0.2H). ^{13}C NMR (75 MHz, CD_2Cl_2): (*traces of minor regioisomer seen but not reported*) δ 148.1 (C_q), 140.1 (C_q), 128.8 (CH), 127.5 (CH), 126.4 (CH), 119.6 (CH), 83.4 (C_q), 41.0 (CH), 34.2 (CH_2), 32.1 (CH_2), 30.8 (CH_2), 29.6 (CH_2), 25.3 (CH_3). ^{11}B NMR (96 MHz, CD_2Cl_2): δ 34.0 (s). IR (thin film): ν_{max} = 1370 (s),[†] 1317 (s),[†] 1143 (s)[†] cm^{-1} . [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for $C_{20}H_{30}O_2B$ $[M+H]^+$: 313.2333. Found: 313.2342.

Spiro[2.3]hexane-5-carbonitrile (4r)

A modified procedure was employed with BEt_3 /air initiation: A 1-neck 10 mL flask was charged with ICH_2Bin (2.0 equiv, 540 mg), (4-methylenecyclohexyl)benzene (1.0 mmol, 172 mg), and benzene (2.5 mL). A solution of BEt_3 (0.8 mL, 1.0 equiv, 1.15 M in PhH) was added in one-portion and the mixture stirred open to air overnight with no additional precautions. General procedure A was followed for the TBAF treatment and workup to afford **4r** with an NMR yield of 45%. *To isolate the clean product, with the alkene fully consumed:* As above, and then the crude was submitted to FCC (grad = 2-2-2-5% EtOAc/heptanes, dia = 25 mm, l = 20 cm, f = 20 mL, res = 100 mL) to afford **4r** as a free-flowing clear liquid (65 mg, 0.61 mmol, 61%). $R_f = 0.40$ (20% EtOAc/heptanes, CAM, KMnO_4). ^1H NMR (300 MHz, CDCl_3): δ 3.25 (tt, $J = 9.1, 7.3$ Hz, 1H), 2.76 – 2.53 (m, 2H), 2.50 – 2.31 (m, 2H), 0.57 – 0.48 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 122.8 (C_q), 35.2 (CH_2), 17.9 (CH), 17.7 (C_q), 12.1 (CH_2), 11.1 (CH_2). IR (thin film): $\nu_{\text{max}} = 3074$ (w),* 2236 (s),ⁿ 1011 (s),*** 959 (m),^{cb} 914 (m),^{cb} cm^{-1} . *Secondary C—H stretches in 1,1-disubstituted/spiro cyclopropanes ⁿUnconjugated nitrile stretch. ***Symmetric breathing of cyclopropane ring. For IR of cyclopropanes see ref.^[28] ^{cb}Cyclobutane ring stretches.^[34] HRMS (ESI): Calculated for $\text{C}_7\text{H}_{12}\text{NO}$ $[\text{M}+\text{H}_3\text{O}]^+$: 126.0919. Found: 126.0915. Spectral data are in accordance with literature.^[35]

cis-3-Iodo-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclobutane-1-carbonitrile (3r)

A modified procedure was employed with BEt_3 /air initiation: A 1-neck 10 mL flask was charged with ICH_2Bin (540 mg, 2.0 equiv), 3-methylenecyclobutane-1-carbonitrile (97% purity, 96 mg, 1.0 mmol, 1* equiv), and benzene (2.5 mL, 0.3 M). A solution of BEt_3 (1.0 mL, 1.2 equiv, 1.15 M in PhH) was added in one-portion and the mixture stirred open to air overnight, with no additional precautions, after which time full consumption was seen by TLC. The contents were filtered through a silica gel plug, washed with TBME, concentrated *in vacuo*, and submitted to FCC (grad = 4-5-7% EtOAc/heptanes, dia = 25 mm, l = 22 cm, f = 20 mL, res = 100 mL). The purified product was recrystallized from heptanes to remove contamination of ICH_2Bpin (15 mol%) to afford **3r** as white needle-like crystals of reasonable stability (123 mg, 0.34 mmol, 34%). *cis* only diastereoisomer as expected, and determined by x-ray crystallography (which will be published subsequently). $R_f = 0.43$ (20% EtOAc/heptanes, CAM). m.p. (heptanes) = 86.9 – 87.3 °C. ^1H NMR (300 MHz, CDCl_3): δ 3.57 (app p, $J = 9.0$ Hz, 1H), 2.93 – 2.79 (m, 2H), 2.64 – 2.46 (m, 2H), 1.92 – 1.80 (m, 2H), 1.26 (s, 12H), 0.98 – 0.80 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 120.6 (C_q), 83.4 (C_q), 47.7 (C_q), 46.2 (CH_2), 43.1 (CH_2), 24.9 (CH_3), 18.0 (CH). ^{11}B NMR (96 MHz, CDCl_3): δ 34.0 (s). IR (thin film): $\nu_{\text{max}} = 2239$

(w),ⁿ 1371 (s),[†] 1322 (s),[†] 1143 (s)[†] cm⁻¹. ⁿUnconjugated nitrile stretch. [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₁₃H₂₁O₂NBINA [M+Na]⁺: 384.0602. Found: 384.0614.

exo-Tricyclo[3.2.1.0^{2,4}]octane (*exo*-4s)

A modified procedure was employed with BEt₃/air initiation; one pot process: A 1-neck 10 mL flask was charged with ICH₂Bin (540 mg, 2.0 mmol), norbornene (1.0 mmol, 172 mg), and benzene (3.0 mL, 0.3 M). A solution of BEt₃ (0.4 mL, 0.5 mmol, 1.15 M in PhH) was added in one-portion and the mixture stirred open to air overnight with no additional precautions. General procedure A was followed for the TBAF treatment and workup (however with pentane). To the pentane solution was added cyclooctadiene (50 μL, 0.407 mmol) and the mixture was analyzed by GC (each R_t was pre-determined, and COD is isomeric with **3s**, so we assume that the integrations after FID are equivalent) to give a yield of 53%. *The product was too volatile to be isolated.*

Using the standard conditions with DLP initiation, one pot process gave a GC-yield estimation of 50%. The wet (pentane) spectra expansion provided comes from this reaction.

Alternatively the cyclopropane arises from the isolated ATRA product, γ-iodo boronic pinacol ester. **3s** was used, and the product mixture analyzed in the same way (see in spectra for GC-chromatograms).

CsF conditions^[36]

3s (254 mg, 0.70 mmol), CsF (320 mg, 2.1 mmol), K₂CO₃ (146 mg, 1.1 mmol), and DMF/H₂O (8:1, 11.7 mL, 0.06 M) were loaded into a sealed flask which was heated to 90 °C for 6 h. After work-up (with three extra water and brine washes) the GC-yield estimation was 61%.

TBAF conditions

Using the general procedure with **3s** (227 mg, 0.63 mmol). After work-up the GC-yield estimation was 74%. ¹H NMR (300 MHz, CDCl₃): Characteristic 1,2-cis-disubstituted cyclopropane peaks are witnessed,^[37] δ 0.31 (dt, J = 6.2, 3.2 Hz, 2H), -0.08 (q, J = 6.8 Hz, 2H).

2-((3-Iodobicyclo[2.2.1]heptan-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*exo-trans*-3s and *exo-cis*-3s)

A modified procedure was employed with BEt₃/air initiation: A 1-neck 10 mL flask was charged with ICH₂Bin (1.1 g, 4.0 mmol), norbornene (97% purity, 190 mg, 2.0 mmol), and benzene (6.5 mL, 0.3 M). A solution of BEt₃ (0.8 mL, 1.0 mmol, 1.15 M in PhH) was added in one-portion and the mixture stirred open to air overnight, with no additional precautions, after which time full consumption

was seen by TLC. The contents were filtered through a silica gel plug, washed with heptanes, concentrated *in vacuo*, and submitted to FCC (grad = 1-1-2-2% EtOAc/heptanes) to afford **3s** as a pale orange oil[#] (605 mg, 1.67 mmol, 84%, dr = 72:28). [#]Contaminated with 10 mol% ICH₂Bpin. R_f = 0.45 (10% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ: 4.44 (dd, *J* = 7.4, 2.1 Hz, 1H, minor), 3.77 (ddd, *J* = 5.5, 3.7, 2.0 Hz, 1H, major), 2.72 – 2.62 (m, 1H, minor), 2.45 – 2.31 (m, 1H, major), 2.17[#] (s, 2H, 10 mol% ICH₂Bpin), 1.98 – 1.76 (m, 3H), 1.68 – 1.39 (m, 3H), 1.36 – 1.20 (m, 15H), 1.20 – 1.11 (m, 1H), 0.80 (dABq, Δδ_{AB} = 0.18, *J*_{AB} = 15.1 Hz, *J*_A = 6.7 Hz, *J*_B = 9.4 Hz, 2H, major). ¹³C NMR (75 MHz, CDCl₃): *major isomer*, δ: 83.3 (C_q), 51.3 (CH), 45.8 (CH), 43.3 (CH), 43.2 (CH), 33.2 (CH₂), 29.7 (CH₂), 27.6 (CH₂), 25.2 (CH₃), 24.9 (CH₃); *minor isomer*, δ: 83.2 (C_q), 50.6 (CH), 47.9 (CH), 45.3 (CH), 43.2 (CH), 33.7 (CH₂), 30.2 (CH₂), 28.6 (CH₂), 25.1 (CH₃), 24.5 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.2 (s), 31.8[#] (sh, s). IR (thin film): ν_{max} = 1369 (s),[†] 1320 (s),[†] 1141 (s)[†] cm⁻¹. [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₁₄H₂₅O₂BI [M+H]⁺: 363.0987. Found: 363.0993.

9-Cyclopropynonyl (*E*)-2-methyl-3-phenylacrylate (**4t**)

The general procedure was followed to give an NMR yield of 53%. The general procedure was followed beginning from the γ-iodoboronic pinacol ester **3t** (181 mg, 0.31 mmol) and the crude was submitted to FCC (3-5-7% EtOAc/heptanes) to afford **4t** as a clear oil, (63 mg, 0.19 mmol, 62%). [N.B.:

The benzene ring is twisted orthogonal to the plane of the rest of the α,β-unsaturated ester due to the allylic strain between the methyl group and phenyl group of the *cis*-olefin and therefore its π-system is not in conjugation with the α,β-unsaturated ester – as corroborated by the symmetry and chemical shifts of the phenylic carbons in the ¹³C-NMR; and the absence of peaks in the IR spectrum for a conjugated benzene ring in the 1600 – 1500 cm⁻¹ region for aromatic rings.] R_f = 0.50 (10% EtOAc/heptanes, UV, CAM). ¹H NMR (300 MHz, CDCl₃): δ 7.70 (app d, *J* = 1.4 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.38 – 7.28 (m, 1H), 4.22 (app t, *J* = 6.7 Hz, 2H), 2.13 (d, *J* = 1.4 Hz, 3H), 1.73 (app p, *J* = 6.7 Hz, 2H), 1.57 – 1.24 (m, 12H), 1.18 (q, *J* = 6.9 Hz, 2H), 0.76 – 0.56 (m, 1H), 0.53 – 0.30 (m, 2H), 0.22 – -0.10 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 168.9 (C_q), 138.7 (CH), 136.1 (C_q), 129.7 (CH), 128.8 (C_q), 128.4 (CH), 128.3 (CH), 65.2 (CH₂), 34.9 (CH₂), 29.8 (CH₂), 29.7 (CH₂), 29.63 (CH₂), 29.61 (CH₂), 29.4 (CH₂), 28.8 (CH₂), 26.2 (CH₂), 14.2 (CH₃), 11.0 (CH), 4.5 (CH₂). IR (thin film): ν_{max} = 3074 (w)*, 2998 (w),** 1706 (s),§ 1635 (w),§§ 1492 (w),^b 1012 (m),*** 820 (w)^c cm⁻¹. §Unsaturated acyclic ester carbonyl stretching vibration. §§C=C stretching vibration of an alkene conjugated to a carbonyl. ^bBenzene ring. ^cC—H stretching vibration of a trisubstituted alkene. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₂₂H₃₃O₂ [M+H]⁺: 329.2475. Found: 329.2470.

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl phenylacrylate (3t)
(E)-2-methyl-3-

The general procedure (either EtOAc or PhH) was followed with undec-10-enyl α -methylcinnamate **2t** (314 mg, 1.00 mmol) and the crude was submitted to FCC (5-7-10% EtOAc/heptanes) to afford **3t** as an orange-tinted oil[#] (279 mg, 0.48 mmol, 48%). [#]Contaminated with 23 mol% unreacted ICH₂Bpin. R_f = 0.53 (20% EtOAc/heptanes, CAM, UV).

¹H NMR (300 MHz, CDCl₃): δ 7.68 (d, J = 1.4 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.37 – 7.29 (m, 1H), 4.21 (t, J = 6.7 Hz, 2H), 4.13 (app tt, J = 8.4, 4.7 Hz, 1H), 2.17 (s, 23 mol% ICH₂Bpin), 2.12 (d, J = 1.4 Hz, 3H), 1.97 – 1.78 (m, 3H), 1.77 – 1.62 (m, 3H), 1.47 – 1.17 (m, 33H), 1.07 – 0.94 (m, 2H), 0.94 – 0.82 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 168.7 (C_q), 138.6 (CH), 136.0 (C_q), 129.6 (CH), 128.7 (C_q), 128.3 (CH), 128.2 (CH), 83.1 (C_q), 65.1 (CH₂), 43.8 (CH), 40.2 (CH₂), 35.2 (CH₂), 29.52 (CH₂), 29.46 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 28.8 (CH₂), 28.7 (CH₂), 26.0 (CH₂), 24.9 (CH₃), 24.8 (CH₃), 24.4 (CH₃, ICH₂Bpin), 14.1 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s), 31.8[#] (s, overlapping). IR (thin film): $\nu_{\max}$ = 1707 (s)[§], 1370 (s)[†], 1323 (s)[†], 1143 (s)[†] cm⁻¹. [§]Unsaturated acyclic ester carbonyl stretching vibration. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₈H₄₄BIO₄Na [M+Na]⁺: 605.2270. Found: 605.2259.

9-Cyclopropynonyl 3-methylbut-2-enoate (4u)

The general procedure was followed to give an NMR yield of 56%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3u** (164 mg, 0.32 mmol) and the crude was submitted to FCC (0-1-1-2% EtOAc/heptanes) to afford **4u** as a clear oil (52 mg, 0.19 mmol, 61%). R_f = 0.45 (8% EtOAc/heptanes, UV, CAM).

¹H NMR (300 MHz, CDCl₃): δ 5.68 (hept, J = 1.4 Hz, 1H), 4.08 (J = 6.7 Hz, 2H), 2.17 (d, J = 1.3 Hz, 3H), 1.89 (d, J = 1.3 Hz, 3H), 1.64 (app p, J = 6.7 Hz, 2H), 1.50 – 1.24 (m, 12H), 1.18 (app q, J = 6.9 Hz, 2H), 0.72 – 0.55 (m, 1H), 0.52 – 0.25 (m, 2H), 0.05 – -0.10 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 166.9 (C_q), 156.3 (C_q), 116.3 (CH), 63.8 (CH₂), 34.9 (CH₂), 29.74 (CH₂), 29.70 (CH₂), 29.62 (CH₂), 29.60 (CH₂), 29.4 (CH₂), 28.9 (CH₂), 27.5 (CH₃), 26.1 (CH₂), 20.3 (CH₃), 11.0 (CH), 4.5 (CH₂). IR (thin film): $\nu_{\max}$ = 3075 (w)^{*}, 2998 (w),^{**} 1718 (m),[§] 1654 (w),^{§§} 1012 (m),^{***} 820 (w)^c cm⁻¹. [§]Unsaturated acyclic ester carbonyl stretching vibration. ^{§§}C=C stretching vibration of an alkene conjugated to a carbonyl. ^cC—H stretching vibration of a trisubstituted alkene. ^{*}Secondary C—H stretches in 1-substituted cyclopropanes. ^{**}Tertiary C—H stretches in 1-substituted cyclopropanes. ^{***}Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₁₇H₃₀O₂Na [M+Na]⁺: 289.2138. Found: 289.2132.

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl 3-methylbut-2-enoate (**3u**)

The general procedure was followed with undec-10-en-1-yl 3-methylbut-2-enoate **2u** (252 mg, 1.00 mmol) and the crude was submitted to FCC (2-2-3-4% EtOAc/heptanes) to afford **3u** as a viscous oil[#] (185 mg, 0.36 mmol, 36%). [#]Contaminated unreacted ICH₂Bpin.

R_f = 0.24 (8% EtOAc/heptanes, CAM, UV). ¹H NMR (300 MHz, CDCl₃): δ 5.68 (hept, J = 1.3 Hz, 1H), 4.14 (tt, J = 9.0, 4.6 Hz, 1H), 4.08 (t, J = 6.7 Hz, 2H), 2.18 (s, minor H[#]), 2.17 (d, J = 1.2 Hz, 3H), 2.09 – 1.78 (m, 6H, [containing 1.90 (d, J = 1.4 Hz, 3H)]), 1.76 – 1.55 (m, 4H), 1.49 – 1.19 (m, 27H), 1.03 (ddd, J = 15.6, 11.0, 5.5 Hz, 1H), 0.88 (ddd, J = 16.2, 10.2, 6.2 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 167.0 (C_q), 156.4 (C_q), 116.3 (CH), 83.3 (C_q), 63.8 (CH₂), 43.9 (CH), 40.3 (CH₂), 35.3 (CH₂), 29.62 (CH₂), 29.55 (CH₂), 29.48 (CH₂), 29.35 (CH₂), 28.91 (CH₂), 28.85 (CH₂), 27.5 (CH₃), 26.1 (CH₂), 24.95 (CH₃), 24.91 (CH₃), 24.5 (CH₃),[#] 20.3 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.6 (s), 31.8[#] (s, overlapping). IR (thin film): $\nu_{\max}$ = 1717 (m),[§] 1654 (w),^{§§} 1371 (m)[†], 1323 (m)[†], 1143 (s)[†] cm⁻¹. [§]Unsaturated acyclic ester carbonyl stretching vibration. ^{§§}C=C stretching vibration of an alkene conjugated to a carbonyl. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₃H₄₃BIO₄ [M+H]⁺: 521.2294. Found: 521.2289.

3-Methylbut-2-en-1-yl 9-cyclopropylnonanoate (**4v**)

The general procedure was followed to give an NMR yield of 54%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3v** (141 mg, 0.27 mmol) and the crude was submitted to FCC (1-2-2% EtOAc/heptanes) to afford **4v** as a clear, viscous liquid (41 mg, 0.15 mmol, 57%).

R_f = 0.50 (8% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 5.35 (ddq, J = 8.6, 5.7, 1.4 Hz, 1H), 4.57 (d, J = 7.2 Hz, 2H), 2.30 (t, J = 7.6 Hz, 2H), 1.77 (d, J = 1.4 Hz, 3H), 1.72 (d, J = 1.4 Hz, 3H), 1.68 – 1.52 (m, 2H), 1.47 – 1.24 (m, 10H), 1.18 (q, J = 7.0 Hz, 2H), 0.75 – 0.57 (m, 1H), 0.46 – 0.27 (m, 2H), 0.08 – -0.08 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 174.0 (C_q), 139.0 (C_q), 118.8 (CH), 61.3 (CH₂), 34.9 (CH₂), 34.5 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 25.9 (CH₃), 25.1 (CH₂), 18.1 (CH₃), 11.0 (CH), 4.5 (CH₂). IR (thin film): $\nu_{\max}$ = 3075 (w),^{*} 2997 (w),^{**} 1734 (s),[§] 1676 (w),[°] 1013 (m),^{***} 820 (m)^d cm⁻¹. [§]Unconjugated, acyclic ester carbonyl stretching vibration. [°]C=C stretching vibration of a trisubstituted unconjugated alkene. ^dC—H stretching vibration of an unconjugated trisubstituted alkene. ^{*}Secondary C—H stretches in 1-substituted cyclopropanes. ^{**}Tertiary C—H stretches in 1-substituted cyclopropanes. ^{***}Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₁₇H₃₀O₂Na [M+Na]⁺: 289.2138. Found: 289.2138.

3-Methylbut-2-en-1-yl 10-iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecanoate (3v)

The general procedure was followed with the prenol derivative **2v** (252 mg, 1.00 mmol) and the crude was submitted to FCC (2-2-3-4-5% EtOAc/heptanes) to afford **3v** as a clear oil[#] (158 mg, 0.30 mmol, 30%). [#]Contaminated with ~30 mol% unreacted ICH₂Bpin. *R_f* = 0.32 (10% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 5.35 (dddd, *J* = 7.3, 5.8, 2.8, 1.4 Hz, 1H), 4.57 (d, *J* = 7.2 Hz, 2H), 4.13 (tt, *J* = 8.6, 4.7 Hz, 1H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.18 (s, 2H, 30 mol% ICH₂Bpin), 1.87 – 1.78 (m, 3H), 1.77 (d, *J* = 1.4 Hz, 3H), 1.72 (d, *J* = 1.4 Hz, 3H), 1.68 – 1.55 (m, 3H), 1.45 – 1.17 (m, 28H), 1.06 – 0.96 (m, 1H), 0.96 – 0.80 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 174.0 (C_q), 139.0 (C_q), 118.8 (CH), 83.2 (C_q), 61.3 (CH₂), 43.9 (CH), 40.3 (CH₂), 35.2 (CH₂), 34.5 (CH₂), 29.6 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 28.9 (CH₂), 25.9 (CH₃), 25.1 (CH₂), 24.95 (CH₃), 24.91 (CH₃), 24.5[#] (CH₃), 18.1 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.4 (s), 31.7[#] (s, overlapping). IR (thin film): ν_{max} = 1733 (s),[§] 1676 (w),^c 1371 (s),[†] 1324 (s),[†] 1143 (s),[†] 846 (m)^d cm⁻¹. [§]Unconjugated, acyclic ester carbonyl stretching vibration. ^cC=C stretching vibration of a trisubstituted unconjugated alkene. ^dC—H stretching vibration of an unconjugated trisubstituted alkene. [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₃H₄₂BIO₄Na [M+ Na]⁺: 543.2113. Found: 543.2111.

β-Citronellol derivative-cyclopropane (4w)

The general procedure was followed to give an NMR yield of 48%. The general procedure was followed beginning from the γ-iodoboronic pinacol ester **3w** (153 mg, 0.26 mmol) and the crude was submitted to FCC (1-1-2% EtOAc/heptanes) to afford **4w** as a clear liquid, (51 mg, 0.15 mmol, 59%). *R_f* = 0.44 (8% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 5.09 (tp, *J* = 7.2, 1.5 Hz, 1H), 4.10 (ddt, *J* = 11.0, 7.3, 3.4 Hz, 2H), 2.29 (app t, *J* = 7.5 Hz, 2H), 1.99 (p, *J* = 7.4 Hz, 2H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.64 – 1.52 (m, 6H [containing 1.61 (d, *J* = 1.2 Hz, 3H)]), 1.48 – 1.24 (m, 12H), 1.24 – 1.10 (m, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.74 – 0.56 (m, 1H), 0.47 – 0.30 (m, 2H), 0.08 – -0.08 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 174.1 (C_q), 131.4 (C_q), 124.7 (CH), 62.9 (CH₂), 37.1 (CH₂), 35.6 (CH₂), 34.9 (CH₂), 34.5 (CH₂), 29.7 (CH₂), 29.60 (CH₂), 26.61 (CH), 29.56 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 25.8 (CH₃), 25.5 (CH₂), 25.1 (CH₂), 19.5 (CH₃), 17.8 (CH₃), 11.0 (CH), 4.5 (CH₂). IR (thin film): ν_{max} = 3076 (w),* 2995 (w),** 1736 (s),[§] 1013 (m),*** 819 (m)^d cm⁻¹. [§]Unconjugated, acyclic ester carbonyl stretching vibration. ^dC—H stretching vibration of an unconjugated trisubstituted alkene. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric

(“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₂₂H₄₀O₂Na [M+Na]⁺: 359.2921. Found: 359.2921.

β-Citronellol derivative-ATRA product (3w)

The general procedure was followed with the citronellol derivative **2w** (322 mg, 1.00 mmol) and the crude was submitted to FCC (2-2-3-4% EtOAc/heptanes) to afford **3w** as a clear oil[#] (172 mg, 0.29 mmol, 29%).

[#]Contaminated with ~23 mol% unreacted ICH₂Bpin. R_f = 0.38 (10% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 5.09 (tdd, *J* = 5.7, 2.9, 1.5 Hz, 1H), 4.22 – 4.01 (m, 3H), 2.29 (app t, *J* = 7.5 Hz, 2H), 2.18 (s, 2H, 23 mol% ICH₂Bpin), 2.10 – 1.77 (m, 5H), 1.76 – 1.42 (m, 12H [containing 1.69 (d, *J* = 1.5 Hz, 3H), 1.61 (d, *J* = 1.2 Hz, 3H)]), 1.44 – 1.12 (m, 29H), 1.12 – 0.82 (m, 6H [containing 0.93 (d, *J* = 6.4 Hz, 3H)]). ¹³C NMR (75 MHz, CDCl₃): δ 174.0 (C_q), 131.4 (C_q), 124.7 (CH), 83.2 (C_q), 62.9 (CH₂), 43.9 (CH), 40.3 (CH₂), 37.1 (CH₂), 35.6 (CH₂), 35.2 (CH₂), 34.5 (CH₂), 29.60 (CH₂), 29.60 (CH, detected by reduced intensity in DEPT135 of overlapping CH₂ peak), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 28.9 (CH₂), 25.8 (CH₃), 25.5 (CH₂), 25.1 (CH₂), 24.95 (CH₃), 24.91 (CH₃), 24.5[#] (CH₃), 19.5 (CH₃), 17.8 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.1 (s), 31.7[#] (s, overlapping). IR (thin film): ν_{max} = 1734 (m),[§] 1371 (m),[†] 1324 (m),[†] 1144 (s),[†] 846 (m)^d cm⁻¹. [§]Unconjugated, acyclic ester carbonyl stretching vibration. ^dC—H stretching vibration of an unconjugated trisubstituted alkene. [†]Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₂₈H₅₃BIO₄ [M+H]⁺: 591.3076. Found: 591.3079.

Nopol derivative-cyclopropane (4x)

The general procedure was followed to give an NMR yield of 62%. The general procedure was followed beginning from the γ-iodoboronic pinacol ester **3x** (240 mg, 0.40 mmol) and the crude was submitted to FCC (2-3-4-5% EtOAc/heptanes) to afford **4x** as a white/transparent

melt (76 mg, 0.22 mmol, 55%). R_f = 0.45 or 0.63 (8% or 10% EtOAc/heptanes, CAM, UV). [α]_D²⁰ – 19.9° (*c* 4.96, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 5.29 (tq, *J* = 2.8, 1.3 Hz, 1H), 4.08 (td, *J* = 7.0, 2.8 Hz, 2H), 2.37 (dt, *J* = 8.5, 5.6 Hz, 1H), 2.32 – 2.20 (m, 6H), 2.07 – 2.02 (m, 2H), 1.61 (app p, *J* = 7.5, 6.9 Hz, 2H), 1.45 – 1.24 (m, 14H), 1.24 – 1.09 (m, 3H), 0.83 (s, 3H), 0.72 – 0.57 (m, 1H), 0.48 – 0.32 (m, 2H), 0.05 – –0.07 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 174.0 (C_q), 144.3 (C_q), 118.8 (CH), 62.6 (CH₂), 45.8 (CH), 40.8 (CH), 38.1 (CH₂), 36.1 (CH₂), 34.9 (CH₂), 34.5 (CH₂), 31.7 (CH₂), 31.5 (CH₂), 29.7 (CH₂), 29.59 (CH₂), 29.56 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 26.4 (CH₃), 25.1 (CH₂), 21.2 (CH₃), 11.0 (CH), 4.5 (CH₂). IR (thin film): ν_{max} = 3074 (w),* 2985 (w),** 1736 (s),[§] 1013 (m),*** 886 (m)^d cm⁻¹. [§]Unconjugated, acyclic ester carbonyl stretching vibration. ^dC—H stretching

vibration of an unconjugated trisubstituted alkene. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for $C_{23}H_{39}O_2$ $[M+H]^+$: 347.2945. Found: 347.2945.

Nopol derivative-ATRA product (3x)

The general procedure was followed with the nopol derivative **2x** (333 mg, 1.00 mmol) and the crude was submitted to FCC (3-4-4-5% EtOAc/heptanes) to afford **3x** as a clear oil (268 mg, 0.45 mmol, 45%). R_f = 0.43 (10% EtOAc/heptanes, CAM, UV). 1H NMR (300 MHz, $CDCl_3$): δ 5.30 (dt, J = 3.1, 1.7 Hz, 1H), 4.36 – 3.91 (m, 3H), 2.37 (dt, J = 8.5, 5.6 Hz, 1H), 2.33 – 2.19 (m, 6H), 2.14 – 2.01 (m, 2H), 2.01 – 1.77 (m, 3H), 1.76 – 1.45 (m, 6H), 1.43 – 1.18 (m, 32H), 1.15 (d, J = 8.5 Hz, 1H), 1.11 – 0.95 (m, 2H), 0.95 – 0.85 (m, 3H), 0.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0 (C_q), 144.3 (C_q), 118.8 (CH), 83.3 (C_q), 62.6 (CH_2), 45.8 (CH), 43.9 (CH), 40.8 (CH), 40.3 (CH_2), 38.1 (C_q), 36.1 (CH_2), 35.3 (CH_2), 34.5 (CH_2), 31.7 (CH_2), 31.5 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 26.4 (CH_3), 25.1 (CH_2), 24.96 (CH_3), 24.92 (CH_3), 21.2 (CH_3). ^{11}B NMR (96 MHz, $CDCl_3$): δ 33.3 (s). IR (thin film): ν_{max} = 1735 (m),[§] 1371 (s),[†] 1320 (s),[†] 1144 (s),[†] 847 (s)^d cm^{-1} . [§]Unconjugated, acyclic ester carbonyl stretching vibration. ^dC—H stretching vibration of an unconjugated trisubstituted alkene. [†]Different stretching modes of the pinacol boronic ester dioxolane ring. ^[3] HRMS (ESI): Calculated for $C_{29}H_{50}BIO_4Na$ $[M+Na]^+$: 623.2739. Found: 623.2740.

Cholesterol derivative-cyclopropane (4y)

The general procedure was followed to give an NMR yield of 56%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3y** (243 mg, 0.30 mmol) and the crude was submitted to FCC (0-1-2% EtOAc/heptanes) to afford **4y** as a white/transparent melt (100 mg, 0.18 mmol, 59%). R_f = 0.65 (10% EtOAc/heptanes, CAM). $[\alpha]_D^{20}$ – 29.9° (c 1.01, $CHCl_3$). 1H NMR (300 MHz, $CDCl_3$): δ 5.38 (app d, J = 5.1 Hz, 1H), 4.76 – 4.52 (m, 1H), 2.49 – 2.20 (m, 4H), 2.14 – 1.91 (m, 2H), 1.92 – 1.76 (m, 3H), 1.74 – 1.43 (m, 9H), 1.42 – 1.24 (m, 16H), 1.24 – 1.08 (m, 9H), 1.03 (s, 3H), 1.00 – 0.90 (m, 7H), 0.89 (d, J = 1.3 Hz, 3H), 0.86 (d, J = 1.4 Hz, 3H), 0.69 (s, 3H), 0.67 – 0.59 (m, 1H), 0.45 – 0.32 (m, 2H), 0.07 – –0.08 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.4 (C_q), 139.8 (C_q), 122.7 (CH), 73.8 (CH), 56.8 (CH), 56.2 (CH), 50.1 (CH), 42.4 (C_q), 39.8 (CH_2), 39.6 (CH_2), 38.3 (CH_2), 37.1 (CH_2), 36.7 (C_q), 36.3 (CH_2), 35.9 (CH), 34.86 (CH_2), 34.84 (CH_2), 32.01 (CH_2), 31.97 (CH), 29.7 (CH_2), 29.60 (CH_2), 29.56 (CH_2), 29.4 (CH_2),

29.2 (CH₂), 28.3 (CH₂), 28.1 (CH), 27.9 (CH₂), 25.2 (CH₂), 24.4 (CH₂), 23.9 (CH₂), 22.9 (CH₃), 22.7 (CH₃), 21.1 (CH₂), 19.4 (CH₃), 18.8 (CH₃), 12.0 (CH₃), 11.0 (CH), 4.5 (CH₂). IR (thin film): $\nu_{\max}$ = 3077 (w), * 2993 (w), ** 1733 (s), § 1013 (m), *** 843 (m)^d cm⁻¹. §Unconjugated, acyclic ester carbonyl stretching vibration. ^dC—H stretching vibration of an unconjugated trisubstituted alkene. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for C₃₉H₆₆O₂Na [M+Na]⁺: 589.4955. Found: 589.4952.

Cholesterol derivative-ATRA product (3y)

The general procedure was followed with the cholesterol derivative **2y** (553 mg, 1.00 mmol) and the crude was submitted to FCC (1-2-2-3% EtOAc/heptanes) to afford **3y** as a clear oil[#] (266 mg, 0.32 mmol, 32%). [#]Contaminated with ~63 mol% unreacted ICH₂Bpin. R_f = 0.47 (10% EtOAc/heptanes, CAM). ¹H NMR (300 MHz, CDCl₃): δ 5.38 (app d, J = 5.0 Hz, 1H), 4.80 – 4.52 (m, 1H), 4.28 – 4.03 (m, 2H), 2.40 – 2.22 (m, 4H), 2.18 (s, 2H ICH₂Bpin), 2.06 – 1.77 (m, 10H), 1.75 – 1.41 (m, 13H), 1.41 – 1.20 (m, 35H), 1.20 – 1.07 (m, 9H), 1.07 – 0.96 (m, 7H), 0.95 – 0.90 (m, 4H), 0.88 (d, J = 1.4 Hz, 3H), 0.86 (d, J = 1.4 Hz, 3H), 0.68 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 173.4 (C_q), 139.8 (C_q), 122.7 (CH), 84.3 (C_q ICH₂Bpin), 83.3 (C_q), 73.8 (CH), 56.8 (CH), 56.2 (CH), 50.1 (CH), 43.9 (CH), 42.4 (C_q), 40.3 (CH₂), 39.8 (CH₂), 39.6 (CH₂), 38.3 (CH₂), 37.1 (CH₂), 36.7 (C_q), 36.3 (CH₂), 35.9 (CH), 35.2 (CH₂), 34.8 (CH₂), 32.01 (CH₂), 31.97 (CH), 29.6 (CH₂), 29.38 (CH₂), 29.31 (CH₂), 29.18 (CH₂), 28.9 (CH₂), 28.3 (CH₂), 28.1 (CH), 27.9 (CH₂), 25.2 (CH₂), 24.96 (CH₃), 24.91 (CH₃), 24.5 (CH₃ ICH₂Bpin), 24.4 (CH₂), 23.9 (CH₂), 22.9 (CH₃), 22.7 (CH₃), 21.1 (CH₂), 19.4 (CH₃), 18.8 (CH₃), 12.0 (CH₃). ¹¹B NMR (96 MHz, CDCl₃): δ 33.2 (s), 31.6[#] (s, overlapping). IR (thin film): $\nu_{\max}$ = 1734 (m), § 1371 (s), † 1324 (s), † 1144 (s), † 846 (s)^d cm⁻¹. §Unconjugated, acyclic ester carbonyl stretching vibration. ^dC—H stretching vibration of an unconjugated trisubstituted alkene. †Different stretching modes of the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for C₄₅H₇₈BIO₄Na [M+Na]⁺: 843.4930. Found: 843.4924.

Chyrsanthemate derivative-cyclopropane (4z)

The general procedure was followed to give an NMR yield of 56%. The general procedure was followed beginning from the γ -iodoboronic pinacol ester **3z** (250 mg, 0.42 mmol) and the crude was submitted to FCC (1-2-3-3% EtOAc/heptanes) to **4z** compound as a clear oil (97 mg, 0.29 mmol, 69%). R_f = 0.37 or 0.58 (5% or 8% EtOAc/heptanes,

CAM). ^1H NMR (300 MHz, CDCl_3): δ 5.39 (dp, $J = 8.5, 1.4$ Hz, 1H minor), 4.90 (dp, $J = 7.9, 1.4$ Hz, 1H major), 4.17 – 3.91 (m, 2H), 2.05 (dd, $J = 7.9, 5.4$ Hz, 1H major), 1.87 (app t, $J = 8.6$ Hz 1H minor), 1.76 (d, $J = 1.4$ Hz, 3H minor), 1.72 (d, $J = 1.3$ Hz, 3H major), 1.71 (d, $J = 1.3$ Hz, 3H major), 1.69 (d, $J = 1.3$ Hz, 3H minor), 1.67 – 1.56 (m, 3H), 1.46 – 1.23 (m, 18H), 1.24 – 1.16 (m, 3H), 1.14 (s, 3H major). ^{13}C NMR (75 MHz, CDCl_3): major (*trans*) diastereoisomer, δ 172.7 (C_q), 135.5 (C_q), 121.3 (CH), 64.5 (CH_2), 35.0 (CH), 34.9 (CH_2), 32.7 (CH), 29.74 (CH_2), 29.71 (CH_2), 29.63 (CH_2), 29.61 (CH_2), 29.40 (CH_2), 28.9 (CH_2), 28.5 (C_q), 26.07 (CH_2), 25.7 (CH_3), 22.3 (CH_3), 20.6 (CH_3), 18.6 (CH_3), 11.0 (CH), 4.5 (CH_2); minor (*cis*) diastereoisomer, only observed peaks reported, δ 171.5 (C_q), 134.6 (C_q), 118.4 (CH), 64.1 (CH_2), 32.2 (CH), 31.4 (CH), 29.40 (CH_2), 28.97 (CH_3), 26.11 (CH_2), 26.02 (CH_3), 18.4 (CH_3), 14.9 (CH_3). IR (thin film): $\nu_{\text{max}} = 3074$ (w)*, 2998 (w),** 1723 (m), § 1013 (m),*** 854 (w) $^{\text{d}}$ cm^{-1} . § Partially conjugated acyclic ester carbonyl stretching vibration (conjugated to partial π -character of cyclopropane). $^{\text{d}}$ C—H stretching vibration of a partially unconjugated trisubstituted alkene. *Secondary C—H stretches in 1-substituted cyclopropanes. **Tertiary C—H stretches in 1-substituted cyclopropanes. ***Symmetric (“breathing”) stretch of cyclopropane ring. For IR of cyclopropanes see ref.^[28] HRMS (ESI): Calculated for $\text{C}_{22}\text{H}_{38}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 357.2764. Found: 357.2764.

Chyrsanthemate derivative-ATRA product (3z)

The general procedure was followed with undec-10-en-1-yl chyrsanthemate **2z** (320 mg, 1.00 mmol) and the crude was submitted to FCC (1-2-2-3-4-5% EtOAc/heptanes) to afford the title compound as a viscous oil $^{\#}$ (263 mg, 0.45 mmol, 45%).

$^{\#}$ Contaminated with ~8 mol% unreacted ICH_2Bpin . $R_f = 0.32$ (8% EtOAc/heptanes, CAM). ^1H NMR (300 MHz, CDCl_3): spectra reported as seen δ 5.38 (dt, $J = 8.2, 1.2$ Hz, 1H minor), 4.90 (dp, $J = 7.9, 1.4$ Hz, 1H major), 4.062 (t, $J = 6.8$ Hz, 1H one isomer), 4.058 (t, $J = 6.8$ Hz, 1H one isomer), 2.18 (s, impurity 2H $^{\#}$), 2.05 (dd, $J = 7.7, 5.5$ Hz 2H), 1.99 – 1.78 (m, 3H), 1.77 – 1.67 (m, 5H), 1.67 – 1.55 (m, 2H), 1.45 – 1.18 (m, 28H), 1.14 (s, 3H major), 1.07 – 0.96 (m, 1H), 0.96 – 0.77 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): only major isomer peaks reported δ 172.7 (C_q), 135.5 (C_q), 121.3 (CH), 83.2 (C_q), 64.5 (CH_2), 43.9 (CH), 40.3 (CH_2), 35.3 (CH_2), 35.0 (CH), 32.6 (CH), 29.61 (CH_2), 29.56 (CH_2), 29.48 (CH_2), 29.3 (CH_2), 28.91 (CH_2), 28.88 (CH_2), 28.5 (C_q), 26.1 (CH_2), 25.7 (CH_3), 24.95 (CH_3), 24.91 (CH_3), 24.5 (CH_3), $^{\#}$ 22.3 (CH_3), 20.6 (CH_3), 18.6 (CH_3). ^{11}B NMR (96 MHz, CDCl_3): δ 33.7 (s), 31.9 $^{\#}$ (s, overlapping). IR (thin film): $\nu_{\text{max}} = 1722$ (m), § 1371 (m) † , 1320 (m) † , 1143 (s), † 846 (m) $^{\text{d}}$ cm^{-1} . § Partially conjugated acyclic ester carbonyl stretching vibration (conjugated to partial π -character of cyclopropane). $^{\text{d}}$ C—H stretching vibration of an unconjugated trisubstituted alkene. † Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for $\text{C}_{28}\text{H}_{51}\text{BIO}_4$ $[\text{M}+\text{H}]^+$: 589.2920. Found: 589.2925.

Pinanediol analogue ATRA product (6g)

The general procedure was followed with 10-undecen-1-ol (170 mg, 1.00 mmol) and the pinanediol analogue of the iodide **5** (640 mg, 2.00 mmol), with EtOAc or PhH as solvent, refluxed for 1.5 h or 4 h, and the crude was submitted to FCC (5-10-15-20% EtOAc/heptanes) to afford the title compound as a clear oil (PhH, 4 h: 361 mg, 0.74 mmol, 74%).

Best results in refluxing benzene for 4 h, see also: PhH, 1.5 h: 71%; EtOAc, 4 h: 67%; EtOAc, 1.5 h: 55%. $R_f = 0.33$ (20% EtOAc/heptanes, CAM). ^1H NMR (300 MHz, CDCl_3): δ 4.26 (dd, $J = 8.7, 2.0$ Hz, 1H), 4.15 (tt, $J = 8.7, 4.7$ Hz, 1H), 3.64 (t, $J = 6.6$ Hz, 2H), 2.33 – 2.28 (m, 1H), 2.28 – 2.15 (m, 1H), 2.04 (t, $J = 5.5$ Hz, 1H), 1.99 – 1.78 (m, 5H), 1.77 – 1.63 (m, 1H), 1.63 – 1.47 (m, 4H), 1.38 (s, 3H), 1.36 – 1.24 (m, 15H), 1.10 (d, $J = 10.9$ Hz, 1H), 1.10 – 1.00 (m, 1H, α -boryl- CH_2), 0.96 (dd, $J = 10.1, 6.2$ Hz, 1H, α -boryl- CH_2), 0.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): *reported both diastereomers together* δ 85.6 (C_q), 77.73 (CH), 77.72 (CH), 63.1 (CH_2), 51.28 (CH), 51.28 (CH), 43.8 (iodide, CH), 40.3 (CH_2), 40.2 (CH_2), 39.5 (CH), 38.12 (C_q), 38.12 (C_q), 35.47 (CH_2), 35.46 (CH_2), 35.32 (CH_2), 35.28 (CH_2), 32.8 (CH_2), 29.50 (CH_2), 29.48 (CH_2), 29.4 (CH_3), 28.8 (CH_2), 28.65 (CH_3), 28.64 (CH_3), 27.1 (CH_2), 26.51 (CH_2), 26.50 (CH_2), 25.7 (CH_2), 24.0 (CH_3), 11.1 (br w, α -boryl- CH_2). ^{11}B NMR (96 MHz, CDCl_3): δ 33.4 (s). IR (thin film): $\nu_{\text{max}} = 3345$ (br, w),[‡] 1376 (s),[†] 1029 (s)[†] cm^{-1} . [‡]Intermolecularly H-bonded alcoholic O—H stretching vibration. [†]Different stretching modes the pinacol boronic ester dioxolane ring.^[3] HRMS (ESI): Calculated for $\text{C}_{22}\text{H}_{41}\text{BIO}_3$ $[\text{M}+\text{H}]^+$: 491.2188. Found: 491.2197.

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6 Spectra

2-(Iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)

¹H NMR (300 MHz)

GA_194118.10.fid

nt-06-147_C

Proton_ns8_d1=10s CDCl₃ /opt service 58

2-(Iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)

 ^{11}B NMR (96 MHz)

GA_194118.11.fid

nt-06-147_C

Boron_ns1024 CDCl₃ /opt service 58

2-(Iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)

 ^{13}C NMR (75 MHz)

GA_194714.12.fid

nt-06-147_C (v. conc)

Carbon_ns512 CDCl₃ /opt service 46

2-(Iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)

DEPT-135 NMR (75 MHz)

GA_194714.13.fid

nt-06-147_C (v. conc)

Dept135_ns512 CDCl3 /opt service 46

GA_147738				
nt-03-048_a				
Proton_ns16	CDCI3	/opt	service	3

GA_147738

nt-03-048_a

Boron_ns1024 CDCl₃ /opt service 3

GA_147738				
nt-03-048_a				
Carbon_ns512	CDCl3	/opt	service	3

GA_147738
nt-03-048_a
Dept135_ns512 CDCl₃ /opt-service 3

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2968.87	79	2	2919.22	61	3	2869.56	80
4	2849.79	83	5	1474.31	83	6	1449.24	80
7	1405.85	44	8	1376.93	48	9	1366.32	57
10	1343.18	57	11	1327.75	25	12	1311.84	39
13	1282.91	44	14	1251.58	70	15	1239.52	49
16	1227.47	66	17	1209.15	71	18	1188.9	85
19	1155.15	85	20	1140.69	80	21	1121.89	65
22	1092.96	68	23	1076.08	54	24	1055.35	72
25	1028.84	45	26	1020.64	49	27	1004.25	68
28	989.786	59	29	950.252	78	30	938.199	68
31	922.289	71	32	904.933	74	33	869.256	86
34	843.704	58	35	825.866	74	36	771.387	83
37	753.066	70	38	660.982	72	39	648.929	74
40	627.234	73	41	615.181	73	42	586.254	85
43	528.882	74	44	500.437	79	45	485.492	85
46	468.135	82	47	440.173	86	48	436.316	85
49	426.673	76	50	420.888	77	51	410.763	78

GA_161103
nt-04-005_cr
Proton_ns8_d1=10s CDCl₃ /opt service 31

GA_195710.10.fid

nt-06-180_a

Proton_ns8_d1=10s CDCl₃ /opt service 46

Dodec-11-en-2-one (2e)

 ^{13}C NMR (75 MHz)

GA_195710.11.fid

nt-06-180_a

Carbon_ns512 CDCl₃ /opt service 46

GA_195710.12.fid

nt-06-180_a

Dept135_ns512 CDCl₃ /opt service 46

Dodec-11-en-2-ol (2f)

¹H NMR (300 MHz)

GA_195294.10.fid

nt-06-169_a(clean)

Proton_ns8_d1=10s CDCl₃ /opt service 24

GA_195294.11.fid
nt-06-169_a(clean)
Carbon_ns512 CDCl₃ /opt service 24

GA_195294.12.fid
nt-06-169_a(clean)
Dept135_ns512 CDCl₃ /opt service 24

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3343	95	2	3076.39	100	3	2966.46	92
4	2923.56	60	5	2853.17	72	6	1641.13	92
7	1462.74	88	8	1414.53	93	9	1373.07	89
10	1302.2	94	11	1120.44	88	12	1058.25	92
13	992.678	82	14	907.826	60	15	834.062	95
16	722.211	88	17	628.198	86	18	606.985	90
19	588.182	91	20	579.022	91	21	557.809	91
22	552.506	91	23	542.863	93	24	533.703	93
25	522.132	93	26	512.008	93	27	505.258	92
28	500.437	92	29	493.688	92	30	490.313	89
31	485.492	94	32	480.67	93	33	476.813	90
34	468.135	91	35	462.832	90	36	457.047	89
37	446.922	89	38	439.208	93	39	434.869	97
40	428.602	92	41	420.406	89	42	408.835	88
43	401.603	94						

GA_195313.10.fid

nt-06-166_a

Proton_ns8_d1=10s CDCl₃ /opt service 43

GA_195313.11.fid

nt-06-166_a

Carbon_ns512 CDCl₃ /opt service 43

Undec-10-enal

DEPT-135 NMR (75 MHz)

GA_195313.12.fid

nt-06-166_a

Dept135_ns512 CDCl3 /opt service 43

GA_158950.10.fid

nt-03-136_A

Proton_ns16 CDCl₃ /opt service 53

GA_158950.11.fid

nt-03-136_A

Carbon_ns512 CDCl₃ /opt-service 53

GA_158950.12.fid
nt-03-136_A
Dept135_ns512 CDCl3 /opt service 53

GA_159636
nt-03-130_a_A
Proton_ns16 CDCl₃ /opt service 17

Undec-10-en-1-yl benzoate (2i)

¹³C NMR (75 MHz)

GA_159636
nt-03-130_a_A
Carbon_ns512 CDCl₃ /opt service 17

GA_159636
nt-03-130_a_A
Dept135_ns512 CDCl₃ /opt service 17

Benzyl undec-10-enoate (2j)

¹H NMR (300 MHz)

GA_160370
nt-03-142_A_a
Proton_ns8_d1=10s CD2Cl2 /opt service 30

Benzyl undec-10-enoate (2j)

 ^{13}C NMR (75 MHz)

GA_160370
nt-03-142_A_a
Carbon_ns512 CD₂Cl₂ /opt service 30

GA_160370
nt-03-142_A_a
Dept135_ns512 CD2Cl2 /opt service 30

Methyl undec-10-enoate (2l)

¹H NMR (300 MHz)

GA_153334
nt-03-091_A
Proton_ns16 CDCl₃ /opt service 50

GA_153334
nt-03-091_A
Carbon_ns512 CDCl₃ /opt service 50

GA_153334
nt-03-091_A
Dept135_ns512 CDCl₃ /opt service 50

Benzyl undec-10-enoate (2n)

¹H NMR (300 MHz)

GA_161530

nt-04-008_a_wash

Proton_ns8_d1=10s CDCl₃ /opt service 24

Benzyl undec-10-enoate (2n)

 ^{13}C NMR (75 MHz)

GA_161530
nt-04-008_a_wash
Carbon_ns512 CDCl₃ /opt service 24

GA_161530
nt-04-008_a_wash
Dept135_ns512 CDCl₃ /opt service 24

Undec-10-enoyl chloride

¹H NMR (300 MHz)

GA_191950.10.fid

nt-06-107_A

Proton_ns8_d1=10s CDCl3 /opt service 15

GA_191954.10.fid

nt-06-107_A

Carbon_ns512 CDCl₃ /opt service 19

GA_191954.11.fid

nt-06-107_A

Dept135_ns512 CDCl₃ /opt service 19

N-Ethylundec-10-enamide (2o)¹H NMR (300 MHz)

GA_194980.10.fid

nt-06-162_cr

Proton_ns8_d1=10s CDCl3 /opt service 2

GA_194983.10.fid

nt-06-162_cr

Carbon_ns512 CDCl₃ /opt-service 5

GA_194983.11.fid
nt-06-162_cr
Dept135_ns512 CDCl₃ /opt service 5

GA_194981.10.fid

nt-06-163_cr

Proton_ns8_d1=10s CDCl₃ /opt service 3

GA_194984.10.fid

nt-06-163_cr

Carbon_ns512 CDCl₃ /opt service 6

GA_194984.11.fid

nt-06-163_cr

Dept135_ns512 CDCl₃ /opt service 6

GA_191967.10.fid

nt-06-099_a

Proton_ns8_d1=10s CD2Cl2 /opt service 32

GA_191967.11.fid

nt-06-099_a

Carbon_ns64 CD2Cl2 /opt service 32

Undec-10-en-1-yl (*E*)-2-methyl-3-phenylacrylate (2t)

DEPT-135 NMR (75 MHz)

GA_191967.12.fid

nt-06-099_a

Dept135_ns64 CD2Cl2 /opt service 32

GA_191297.10.fid

nt-06-098_B

Proton_ns8_d1=10s CDCl₃ /opt service 28

GA_191299.10.fid

nt-06-098_B

Carbon_ns512 CDCl₃ /opt service 30

GA_191299.11.fid

nt-06-098_B

Dept135_ns512 CDCl3 /opt service 30

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3074.94	96	2	2976.11	91	3	2924.52	66
4	2854.13	75	5	2174.35	96	6	2043.21	96
7	2029.23	96	8	1718.26	52	9	1653.18	74
10	1641.61	80	11	1445.39	79	12	1388.01	88
13	1376.93	83	14	1346.55	80	15	1272.79	86
16	1225.54	45	17	1143.58	23	18	1078.01	63
19	992.678	76	20	907.826	68	21	850.936	66
22	807.546	95	23	799.832	95	24	793.564	96
25	787.779	96	26	773.315	95	27	757.405	93
28	722.693	85	29	668.214	95	30	655.679	95
31	637.358	92	32	633.019	92	33	615.181	96
34	604.092	96	35	599.271	96	36	576.612	96
37	572.273	95	38	566.487	96	39	547.202	94
40	542.381	95	41	532.257	94	42	521.168	96
43	516.347	95	44	509.115	95	45	501.401	93
46	498.027	96	47	493.688	96	48	485.974	94
49	482.117	96	50	478.742	93	51	472.474	91

GA_192115.10.fid

nt-06-108_a

Proton_ns8_d1=10s CDCl₃ /opt service 52

GA_192115.11.fid

nt-06-108_a

Carbon_ns64 CDCl₃ /opt service 52

GA_192115.12.fid
nt-06-108_a
Dept135_ns64 CDCl3 /opt service 52

GA_192121.11.fid

nt-06-110_a(conc)

Carbon_ns64 CDCl₃ /opt service 58

GA_192121.12.fid
nt-06-110_a(conc)
Dept135_ns64 CDCl₃ /opt service 58

GA_192116.10.fid

nt-06-109_a(clean conc)

Proton_ns8_d1=10s CDCl₃ /opt service 53

GA_192116.11.fid

nt-06-109_a(clean conc)

Carbon_ns64 CDCl₃ /opt service 53

GA_192116.12.fid
nt-06-109_a(clean conc)
Dept135_ns64 CDCl₃ /opt service 53

GA_192135.10.fid

nt-06-111_reX

Proton_ns8_d1=10s CDCl3 /opt service 8

GA_192135.11.fid

nt-06-111_reX

Carbon_ns64 CDCl₃ /opt service 8

GA_192135.12.fid
nt-06-111_reX
Dept135_ns64 CDCl3 /opt service 8

Peak Find - Memory-2

Chrysanthemic acid

¹H NMR (300 MHz)

GA_192113.11.fid

nt-06-105r_a(A5-A8 conc)

Carbon_ns64 CDCl₃ /opt service 50

GA_192113.12.fid
nt-06-105r_a(A5-A8 conc)
Dept135_ns64 CDCl3 /opt service 50

GA_194034.10.fid

nt-06-145r_a+b

Proton_ns8_d1=10s CDCl₃ /opt service 37

GA_194040.10.fid

nt-06-145r_a+b

Carbon_ns512 CDCl₃ /opt service 43

GA_194040.11.fid
nt-06-145r_a+b
Dept135_ns512 CDCl₃ /opt service 43

Nonylcyclopropane (4a)

 ^1H NMR (300 MHz)

GA_191250.10.fid

nt-06-095_a

Proton_ns8_d1=10s CDCl₃ /opt service 56

Nonylcyclopropane (4a)

 ^{13}C NMR (75 MHz)

GA_191250.12.fid

nt-06-095_a

Carbon_ns512 CDCl₃ /opt service 56

GA_191250.13.fid

nt-06-095_a

Dept135_ns512 CDCl₃ /opt service 56

GA_191016.10.fid

nt-06-094_a

Proton_ns8_d1=10s CDCl₃ /opt service 4

GA_191016.11.fid

nt-06-094_a

Boron_ns256 CDCl₃ /opt service 4

GA_191016.12.fid

nt-06-094_a

Carbon_ns64 CDCl₃ /opt service 4

GA_191016.13.fid

nt-06-094_a

Dept135_ns64 CDCl3 /opt service 4

(2-Cyclopropylethyl)benzene (4b)

¹H NMR (300 MHz)

GA_145484

nt-03-025rr_[O3]_b

Proton_ns8_d1=10s CD2Cl2 /opt service 24

Ph

(2-Cyclopropylethyl)benzene (4b)

 ^{13}C NMR (75 MHz)

GA_145484
nt-03-025rr_[O3]_b
Carbon_ns512 CD₂Cl₂ /opt service 24

GA_145484
nt-03-025rr_[O3]_b
Dept135_ns512 CD2Cl2 /opt service 24

2-(3-Iodo-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

 ^{11}B NMR (96 MHz)

GA_190463.11.fid

nt-06-075_a

Boron_ns1024 CDCl₃ /opt service 30

2-(3-Iodo-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

 ^{13}C NMR (75 MHz)

GA_190463.12.fid

nt-06-075_a

Carbon_ns512 CDCl₃ /opt service 30

2-(3-Iodo-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

DEPT-135 NMR (75 MHz)

GA_190463.13.fid

nt-06-075_a

Dept135_ns512 CDCl₃ /opt service 30

5-(Cyclopropylmethyl)benzo[d][1,3]dioxole (4c)

¹H NMR (300 MHz)

GA_191699.10.fid

nt-06-103(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 29

5-(Cyclopropylmethyl)benzo[d][1,3]dioxole (4c)

 ^{13}C NMR (75 MHz)

GA_191699.12.fid

nt-06-103(2)_a

Carbon_ns512 CDCl₃ /opt service 29

GA_191699.13.fid
nt-06-103(2)_a
Dept135_ns512 CDCl₃ /opt service 29

GA_191627.10.fid

nt-06-103(1)_b_conc_dried

Proton_ns8_d1=10s CDCl₃ /opt service 15

GA_191627.11.fid

nt-06-103(1)_b_conc_dried

Boron_ns256 CDCl₃ /opt service 15

GA_191627.12.fid

nt-06-103(1)_b_conc_dried

Carbon_ns64 CDCl₃ /opt service 15

GA_191627.13.fid
nt-06-103(1)_b_conc_dried
Dept135_ns64 CDCl₃ /opt service 15

GA_191519.10.fid

nt-06-102(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 15

GA_191519.11.fid
nt-06-102(2)_a
Carbon_ns512 CDCl₃ /opt service 15

GA_191519.12.fid
nt-06-102(2)_a
Dept135_ns512 CDCl₃ /opt service 15

GA_191422.10.fid

nt-06-102(1)_a

Proton_ns8_d1=10s CDCl₃ /opt service 36

GA_191422.11.fid

nt-06-102(1)_a

Boron_ns1024 CDCl₃ /opt service 36

GA_191422.12.fid

nt-06-102(1)_b

Carbon_ns512 CDCl₃ /opt service 36

GA_191422.13.fid

nt-06-102(1)_b

Dept135_ns512 CDCl₃ /opt service 36

10-Cyclopropyldecan-2-one (4e)

 ^1H NMR (300 MHz)

GA_195875.10.fid

nt-06-182(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 36

GA_195875.12.fid

nt-06-182(2)_a

Carbon_ns512 CDCl₃ /opt service 36

10-Cyclopropyldecan-2-one (4e)

DEPT-135 NMR (75 MHz)

GA_195875.13.fid

nt-06-182(2)_a

Dept135_ns512 CDCl₃ /opt-service 36

GA_195751.10.fid

nt-06-182(1)_b

Proton_ns8_d1=10s CDCl₃ /opt service 33

GA_195751.11.fid

nt-06-182(1)_b

Boron_ns1024 CDCl₃ /opt service 33

GA_195751.12.fid

nt-06-182(1)_b

Carbon_ns512 CDCl₃ /opt service 33

GA_195751.13.fid

nt-06-182(1)_b

Dept135_ns512 CDCl3 /opt service 33

10-Cyclopropyldecan-2-ol (4f)

¹H NMR (300 MHz)

GA_195876.10.fid

nt-6-183(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 37

GA_195876.12.fid

nt-6-183(2)_a

Carbon_ns512 CDCl₃ /opt service 37

10-Cyclopropyldecan-2-ol (4f)

DEPT-135 NMR (75 MHz)

GA_195876.13.fid

nt-6-183(2)_a

Dept135_ns512 CDCl₃ /opt service 37

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3347.82	89	2	3075.42	91	3	2999.25	89
4	2965.98	86	5	2921.63	57	6	2852.2	66
7	1462.26	82	8	1373.07	85	9	1299.79	89
10	1121.89	83	11	1040.89	85	12	1012.93	71
13	942.056	85	14	819.598	81	15	721.247	84
16	688.945	90	17	649.411	88	18	632.055	87
19	620.966	88	20	610.36	88	21	574.201	88
22	563.594	89	23	555.881	90	24	551.542	90
25	544.792	88	26	539.007	89	27	525.025	89
28	517.793	87	29	512.972	85	30	498.027	88
31	493.688	87	32	481.635	86	33	477.778	86
34	473.921	85	35	466.689	85	36	457.529	78
37	453.672	81	38	449.333	85	39	442.583	81
40	427.638	82	41	419.442	83	42	415.103	79
43	409.317	80	44	404.978	80			

GA_195752.10.fid

nt-06-183(1)_a

Proton_ns8_d1=10s CDCl3 /opt service 34

GA_195752.11.fid

nt-06-183(1)_a

Boron_ns1024 CDCl₃ /opt service 34

GA_195752.12.fid

nt-06-183(1)_a

Carbon_ns512 CDCl₃ /opt service 34

GA_195752.13.fid

nt-06-183(1)_a

Dept135_ns512 CDCl₃ /opt service 34

9-Cyclopropylnonan-1-ol (4g)

¹H NMR (300 MHz)

GA_187864.10.fid

nt-06-051-3_a

Proton_ns8_d1=10s CDCl₃ /opt service 6

GA_187864.12.fid

nt-06-051-3_a

Carbon_ns512 CDCl₃ /opt service 6

9-Cyclopropylnonan-1-ol (4g)

DEPT-135 NMR (75 MHz)

GA_187864.13.fid

nt-06-051-3_a

Dept135_ns512 CDCl3 /opt service 6

GA_188045.10.fid

nt-06-054(pin)_EA_4h_b

Proton_ns8_d1=10s CDCl₃ /opt service 17

GA_188045.11.fid

nt-06-054(pin)_EA_4h_b

Boron_ns1024 CDCl₃ /opt service 17

GA_188045.12.fid

nt-06-054(pin)_EA_4h_b

Carbon_ns512 CDCl₃ /opt service 17

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecan-1-ol (3g)

DEPT-135 NMR (75 MHz)

GA_188045.13.fid

nt-06-054(pin)_EA_4h_b

Dept135_ns512 CDCl₃ /opt service 17

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecan-1-ol (3g)

FTIR

GA_196379.10.fid

nt-06-185(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 21

9-Cyclopropylnonyl acetate (4h)

¹³C NMR (75 MHz)

GA_196379.12.fid

nt-06-185(2)_a

Carbon_ns512 CDCl₃ /opt service 21

9-Cyclopropylnonyl acetate (4h)

DEPT-135 NMR (75 MHz)

GA_196379.13.fid

nt-06-185(2)_a

Dept135_ns512 CDCl3 /opt service 21

GA_196285.10.fid

nt-06-185(1)_a

Proton_ns8_d1=10s CDCl₃ /opt service 8

GA_196285.11.fid

nt-06-185(1)_a

Boron_ns1024 CDCl₃ /opt service 8

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl acetate (3h)

 ^{13}C NMR (75 MHz)

GA_196285.12.fid

nt-06-185(1)_a

Carbon_ns512 CDCl₃ /opt service 8

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl acetate (3h)

FTIR

GA_191248.10.fid

nt-06-097(2)_a(conc)

Proton_ns8_d1=10s CDCl₃ /opt service 54

GA_191248.12.fid

nt-06-097(2)_a(conc)

Carbon_ns64 CDCl₃ /opt service 54

GA_191248.13.fid
nt-06-097(2)_a(conc)
Dept135_ns64 CDCl₃ /opt service 54

10-Iodo-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl benzoate (3i)

 ^1H NMR (300 MHz)

GA_191050.10.fid

nt-06-097(1)_b

Proton_ns8_d1=10s CDCl₃ /opt service 41

GA_191050.11.fid

nt-06-097(1)_b

Boron_ns256 CDCl₃ /opt service 41

GA_191050.12.fid

nt-06-097(1)_b

Carbon_ns64 CDCl₃ /opt service 41

GA_191050.13.fid

nt-06-097(1)_b

Dept135_ns64 CDCl₃ /opt service 41

(((9-Cyclopropylnonyl)oxy)methyl)benzene (4j)

¹H NMR (300 MHz)

GA_196380.10.fid

nt-06-186(2)_a

Proton_ns8_d1=10s CD2Cl2 /opt service 22

GA_196380.12.fid

nt-06-186(2)_a

Carbon_ns512 CD₂Cl₂ /opt service 22

(((9-Cyclopropynonyl)oxy)methyl)benzene (4j)

DEPT-135 NMR (75 MHz)

GA_196380.13.fid

nt-06-186(2)_a

Dept135_ns512 CD2Cl2 /opt service 22

GA_196286.10.fid

nt-06-186(1)_a

Proton_ns8_d1=10s CDCl₃ /opt service 9

GA_196286.11.fid

nt-06-186(1)_a

Boron_ns1024 CDCl₃ /opt service 9

GA_196286.12.fid

nt-06-186(1)_a

Carbon_ns512 CDCl₃ /opt-service 9

GA_196286.13.fid

nt-06-186(1)_a

Dept135_ns512 CDCl₃ /opt service 9

GA_191270.10.fid

nt-06-093_a

Proton_ns8_d1=10s CDCl₃ /opt service 3

GA_191270.12.fid

nt-06-093_a

Carbon_ns512 CDCl₃ /opt service 3

GA_191270.13.fid

nt-06-093_a

Dept135_ns512 CDCl3 /opt service 3

GA_191051.10.fid

nt-06-092_b(dried)

Proton_ns8_d1=10s CDCl₃ /opt service 42

GA_191051.11.fid
nt-06-092_b(dried)
Boron_ns256 CDCl₃ /opt service 42

GA_191051.12.fid
nt-06-092_b(dried)
Carbon_ns64 CDCl₃ /opt service 42

GA_191051.13.fid

nt-06-092_b(dried)

Dept135_ns64 CDCl₃ /opt service 42

Methyl 9-cyclopropylnonanoate (4l)

¹H NMR (300 MHz)

GA_189911.10.fid

nt-06-071_a

Proton_ns8_d1=10s CDCl₃ /opt service 12

GA_189911.12.fid

nt-06-071_a

Carbon_ns512 CDCl₃ /opt service 12

Methyl 9-cyclopropylnonanoate (4l)

DEPT-135 NMR (75 MHz)

GA_189911.13.fid

nt-06-071_a

Dept135_ns512 CDCl₃ /opt service 12

GA_190726.10.fid

nt-06-086_a

Proton_ns8_d1=10s CDCl₃ /opt service 7

GA_190726.11.fid

nt-06-086_a

Boron_ns1024 CDCl₃ /opt service 7

GA_190726.12.fid

nt-06-086_a

Carbon_ns512 CDCl₃ /opt service 7

GA_189806.10.fid

nt-06-067_a

Proton_ns8_d1=10s CDCl₃ /opt service 34

GA_189804.12.fid

nt-06-067_a

Carbon_ns512 CDCl₃ /opt service 32

Ethyl 9-cyclopropylnonanoate (4m)

DEPT-135 NMR (75 MHz)

GA_189804.13.fid

nt-06-067_a

Dept135_ns512 CDCl₃ /opt service 32

GA_190725.10.fid

nt-06-084_a

Proton_ns8_d1=10s CDCl3 /opt service 6

GA_190725.11.fid

nt-06-084_a

Boron_ns1024 CDCl₃ /opt service 6

GA_190725.12.fid

nt-06-084_a

Carbon_ns512 CDCl₃ /opt service 6

GA_190725.13.fid

nt-06-084_a

Dept135_ns512 CDCl₃ /opt service 6

Benzyl 9-cyclopropylnonanoate (4n)

 ^1H NMR (300 MHz)

GA_190922.12.fid

nt-06-089_a

Carbon_ns512 CDCl₃ /opt service 12

GA_190922.13.fid

nt-06-089_a

Dept135_ns512 CDCl₃ /opt service 12

GA_190870.10.fid

nt-06-088_b

Proton_ns8_d1=10s CDCl₃ /opt service 21

GA_190870.11.fid

nt-06-088_b

Boron_ns1024 CDCl₃ /opt service 21

GA_190870.12.fid

nt-06-088_b

Carbon_ns512 CDCl₃ /opt service 21

GA_190870.13.fid

nt-06-088_b

Dept135_ns512 CDCl3 /opt service 21

9-Cyclopropyl-N-ethylnonanamide (4o)

¹H NMR (300 MHz)

GA_196429.10.fid

nt-07-016(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 10

9-Cyclopropyl-N-ethylnonanamide (4o)

¹³C NMR (75 MHz)

GA_196429.12.fid

nt-07-016(2)_a

Carbon_ns512 CDCl₃ /opt service 10

9-Cyclopropyl-N-ethylnonanamide (4o)

DEPT-135 NMR (75 MHz)

GA_196429.13.fid

nt-07-016(2)_a

Dept135_ns512 CDCl₃ /opt service 10

GA_196371.10.fid

nt-07-016(1)_b

Proton_ns8_d1=10s CDCl₃ /opt service 16

GA_196371.11.fid

nt-07-016(1)_b

Boron_ns1024 CDCl₃ /opt service 16

GA_196371.12.fid

nt-07-016(1)_b

Carbon_ns512 CDCl₃ /opt service 16

GA_196371.13.fid

nt-07-016(1)_b

Dept135_ns512 CDCl₃ /opt service 16

9-Cyclopropyl-*N,N*-diethylnonanamide (4p)¹H NMR (300 MHz)

GA_196428.10.fid

nt-07-015(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 9

9-Cyclopropyl-*N,N*-diethylnonanamide (4p)¹³C NMR (75 MHz)

GA_196428.12.fid

nt-07-015(2)_a

Carbon_ns512 CDCl₃ /opt service 9

9-Cyclopropyl-*N,N*-diethylnonanamide (4p)

DEPT-135 NMR (75 MHz)

GA_196428.13.fid

nt-07-015(2)_a

Dept135_ns512 CDCl₃ /opt-service 9

GA_196369.10.fid

nt-07-015(1)_a

Proton_ns8_d1=10s CDCl₃ /opt service 14

GA_196369.12.fid
nt-07-015(1)_a
Carbon_ns512 CDCl₃ /opt service 14

GA_196369.13.fid				
nt-07-015(1)_a				
Dept135_ns512 CDCI3 /opt service 14

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2975.14	79	2	2925.97	70	3	2853.17	80
4	1733.69	94	5	1641.61	55	6	1479.62	83
7	1460.33	74	8	1426.1	71	9	1370.66	51
10	1318.11	59	11	1268.93	72	12	1220.72	74
13	1165.28	74	14	1142.62	42	15	1109.35	77
16	1096.33	76	17	1004.73	90	18	967.608	73
19	882.274	85	20	865.882	86	21	846.115	66
22	792.6	85	23	746.317	87	24	722.211	89
25	674.481	88	26	604.092	89	27	592.521	89
28	577.576	84	29	560.702	89	30	548.167	89
31	544.31	89	32	537.078	89	33	531.775	88
34	526.954	90	35	512.49	88	36	503.33	86
37	495.134	87	38	491.277	87	39	486.456	88
40	472.957	87	41	466.689	90	42	459.457	88
43	446.44	83	44	442.101	90	45	437.762	84
46	434.387	87	47	426.673	82	48	418.959	74
49	415.103	86	50	408.353	75			

6-Phenylspiro[2.5]octane (4q)

¹H NMR (300 MHz)

GA_196889.10.fid

nt-07-026_a

Proton_ns8_d1=10s CD2Cl2 /opt service 54

GA_196889.12.fid

nt-07-026_a

Carbon_ns512 CD₂Cl₂ /opt service 54

6-Phenylspiro[2.5]octane (4q)

DEPT-135 NMR (75 MHz)

GA_196889.13.fid

nt-07-026_a

Dept135_ns512 CD2Cl2 /opt service 54

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3063.37	90	2	3026.25	91	3	2992.98	91
4	2919.22	63	5	2887.4	84	6	2844.01	74
7	1601.59	90	8	1582.79	97	9	1492.15	80
10	1442.01	77	11	1424.17	85	12	1376.93	93
13	1363.91	95	14	1325.34	94	15	1311.84	95
16	1287.73	96	17	1253.5	97	18	1193.24	94
19	1173.47	95	20	1155.15	96	21	1066.44	92
22	1032.21	91	23	1018.71	89	24	1007.62	70
25	962.305	94	26	927.593	72	27	900.112	79
28	885.166	90	29	858.65	92	30	794.528	93
31	751.62	52	32	696.177	21	33	667.732	89
34	634.466	88	35	544.792	95	36	530.328	58
37	506.223	90	38	501.401	93	39	495.134	95
40	489.348	93	41	477.296	92	42	467.653	87
43	461.386	89	44	456.082	87	45	449.815	96
46	445.476	96	47	434.387	90	48	429.084	97
49	422.816	95	50	417.995	89	51	406.907	85

GA_196887.10.fid

nt-07-026_c

Proton_ns8_d1=10s CD2Cl2 /opt service 56

GA_196887.11.fid

nt-07-026_c

Boron_ns1024 CD2Cl2 /opt service 56

GA_196887.12.fid

nt-07-026_c

Carbon_ns512 CD₂Cl₂ /opt service 56

GA_196887.13.fid

nt-07-026_c

Dept135_ns512 CD2Cl2 /opt service 56

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3060.48	96	2	3025.76	93	3	2977.07	82
4	2921.15	78	5	2834.85	87	6	1739.96	95
7	1603.04	94	8	1493.6	88	9	1480.1	91
10	1452.62	83	11	1437.19	84	12	1402.96	82
13	1369.69	50	14	1317.14	54	15	1271.82	79
16	1242.9	75	17	1214.45	80	18	1179.74	85
19	1164.79	74	20	1143.1	39	21	1108.39	81
22	1076.57	89	23	1029.8	89	24	1003.77	90
25	967.126	68	26	915.54	86	27	886.131	82
28	866.846	83	29	848.043	66	30	840.329	76
31	802.724	87	32	755.959	64	33	698.105	38
34	672.071	77	35	607.467	93	36	579.022	82
37	558.773	90	38	552.024	88	39	529.364	78
40	517.311	81	41	502.366	88	42	494.652	88
43	488.866	89	44	481.635	92	45	476.331	91
46	470.546	94	47	465.725	93	48	460.904	91
49	453.19	87	50	443.547	86	51	436.316	85

Spiro[2.3]hexane-5-carbonitrile (4r)

¹H NMR (300 MHz)

GA_197818.10.fid

nt-07-051_2_b

Proton_ns8_d1=10s CDCl₃ /opt service 7

GA_197827.10.fid

nt-07-051_2_b

Carbon_ns512 CDCl₃ /opt service 16

GA_197827.11.fid

nt-07-051_2_b

Dept135_ns512 CDCl₃ /opt service 16

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3073.98	94	2	2978.04	87	3	2938.02	83
4	2858.95	91	5	2236.06	82	6	1458.89	92
7	1437.19	90	8	1422.73	89	9	1364.39	90
10	1339.8	93	11	1221.68	94	12	1158.04	89
13	1127.19	92	14	1086.21	88	15	1067.89	91
16	1011	78	17	958.93	85	18	913.611	85
19	885.648	90	20	837.437	86	21	817.188	94
22	810.92	94	23	770.905	94	24	731.853	72
25	701.48	92	26	685.57	94	27	648.447	92
28	574.683	94	29	566.969	94	30	559.255	94
31	547.202	93	32	543.346	94	33	539.007	94
34	531.775	92	35	518.275	93	36	514.901	94
37	509.115	92	38	498.509	94	39	492.241	92
40	487.902	93	41	475.849	87	42	467.653	87
43	463.796	82	44	458.975	85	45	454.154	87
46	448.369	87	47	440.655	87	48	431.012	82
49	423.298	82	50	420.406	83	51	416.549	81

GA_197891.10.fid

nt-07-046_reX

Proton_ns8_d1=10s CDCl₃ /opt service 17

GA_197891.11.fid

nt-07-046_reX

Boron_ns1024 CDCl₃ /opt service 17

GA_197891.12.fid

nt-07-046_reX

Carbon_ns512 CDCl₃ /opt service 17

GA_197891.13.fid

nt-07-046_reX

Dept135_ns512 CDCl₃ /opt service 17

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2978.52	84	2	2924.04	89	3	2880.17	91
4	2239.43	88	5	1458.4	91	6	1448.76	89
7	1427.55	85	8	1404.41	79	9	1390.91	78
10	1383.19	69	11	1370.66	50	12	1336.91	56
13	1322.45	55	14	1286.29	71	15	1264.11	69
16	1212.52	78	17	1192.27	72	18	1168.17	72
19	1143.1	50	20	1114.17	75	21	1063.55	79
22	1036.55	74	23	1010.03	83	24	992.196	85
25	968.573	68	26	919.879	85	27	903.487	84
28	884.684	72	29	845.633	58	30	825.866	79
31	783.922	77	32	735.71	77	33	674.481	78
34	609.878	87	35	576.612	80	36	567.451	84
37	555.881	86	38	541.417	85	39	527.918	72
40	512.49	84	41	507.187	76	42	496.58	83
43	488.384	86	44	481.153	78	45	474.403	82
46	468.617	79	47	458.493	86	48	453.672	85
49	448.851	86	50	442.583	84	51	434.869	88

Tricyclo[3.2.1.0^{2,4}]octane-crude (4s-

GC chromatograms

4s from CsF with COD

Instrument:GC1 Sequence:nt-07-033_CsF

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4s from TBAF with COD

Instrument:GC1 Sequence:nt-07-033_TBAF

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GA_197185.10.fid

nt-07-033(1)_a

Proton_ns8_d1=10s CDCl₃ /opt service 23

GA_197185.11.fid

nt-07-033(1)_a

Boron_ns1024 CDCl₃ /opt service 23

GA_197185.12.fid

nt-07-033(1)_a

Carbon_ns512 CDCl₃ /opt service 23

GA_197185.13.fid

nt-07-033(1)_a

Dept135_ns512 CDCl₃ /opt service 23

9-Cyclopropylnonyl (E)-2-methyl-3-phenylacrylate (4t)

 ^1H NMR (300 MHz)

9-Cyclopropylnonyl (*E*)-2-methyl-3-phenylacrylate (4t)¹³C NMR (75 MHz)

GA_192351.12.fid

nt-06-112(2)_a(clean)

Carbon_ns512 CDCl₃ /opt service 37

GA_192351.13.fid
nt-06-112(2)_a(clean)
Dept135_ns512 CDCl₃ /opt service 37

GA_192348.10.fid

nt-06-112(1)_b_dried

Proton_ns8_d1=10s CDCl₃ /opt service 34

GA_192348.13.fid
nt-06-112(1)_b_dried
Dept135_ns512 CDCl₃ /opt service 34

9-Cyclopropylnonyl 3-methylbut-2-enoate (4u)

¹H NMR (300 MHz)

GA_191468.10.fid

nt-06-101(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 24

GA_191468.12.fid

nt-06-101(2)_a

Carbon_ns512 CDCl₃ /opt service 24

GA_191468.13.fid

nt-06-101(2)_a

Dept135_ns512 CDCl₃ /opt service 24

GA_191395.10.fid

nt-06-101(1)_b

Proton_ns8_d1=10s CDCl3 /opt service 9

GA_191395.11.fid

nt-06-101(1)_b

Boron_ns1024 CDCl₃ /opt service 9

GA_191395.12.fid

nt-06-101(1)_b

Carbon_ns512 CDCl₃ /opt service 9

GA_191395.13.fid

nt-06-101(1)_b

Dept135_ns512 CDCl₃ /opt service 9

Peak Find - Memory-13

3-Methylbut-2-en-1-yl 9-cyclopropylnonanoate (4v)

¹H NMR (300 MHz)

GA_193567.10.fid

nt-06-141(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 13

3-Methylbut-2-en-1-yl 9-cyclopropylnonanoate (4v)

 ^{13}C NMR (75 MHz)

3-Methylbut-2-en-1-yl 9-cyclopropylnonanoate (4v)

DEPT-135 NMR (75 MHz)

GA_193567.13.fid

nt-06-141(2)_a

Dept135_ns512 CDCl3 /opt service 13

3-Methylbut-2-en-1-yl 9-cyclopropylnonanoate (4v)

FTIR

GA_193539.10.fid

nt-06-141(1)_a

Proton_ns8_d1=10s CDCl₃ /opt service 47

GA_193539.11.fid

nt-06-141(1)_a

Boron_ns1024 CDCl3 /opt service 47

GA_193539.12.fid

nt-06-141(1)_a

Carbon_ns512 CDCl₃ /opt service 47

GA_193539.13.fid				
nt-06-141(1)_a				
Dept135_ns512	CDCI3	/opt	service	47

GA_193564.10.fid

nt-06-141(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 10

GA_193564.12.fid

nt-06-141(2)_a

Carbon_ns512 CDCl₃ /opt service 10

GA_193564.13.fid

nt-06-141(2)_a

Dept135_ns512 CDCl₃ /opt service 10

GA_193538.10.fid

nt-06-140(1)_a

Proton_ns8_d1=10s CDCl₃ /opt service 46

Boron_ns1024	CDCI3	/opt	service	46
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GA_193538.12.fid

nt-06-140(1)_a

Carbon_ns512 CDCl₃ /opt service 46

GA_193538.13.fid

nt-06-140(1)_a

Dept135_ns512 CDCl₃ /opt service 46

GA_193226.10.fid

nt-06-131(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 49

GA_193226.12.fid

nt-06-131(2)_a

Carbon_ns512 CDCl₃ /opt service 49

GA_193226.13.fid

nt-06-131(2)_a

Dept135_ns512 CDCl3 /opt service 49

GA_193113.10.fid

nt-06-131_b

Proton_ns8_d1=10s CDCl₃ /opt service 8

GA_193113.11.fid

nt-06-131_b

Boron_ns1024 CDCl₃ /opt service 8

GA_193113.12.fid

nt-06-131_b

Carbon_ns512 CDCl₃ /opt service 8

GA_193113.13.fid

nt-06-131_b

Dept135_ns512 CDCl3 /opt service 8

Peak Find - Memory-2

GA_193478.10.fid

nt-06-118(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 39

GA_193478.12.fid

nt-06-118(2)_a

Carbon_ns512 CDCl₃ /opt service 39

GA_193478.13.fid

nt-06-118(2)_a

Dept135_ns512 CDCl3 /opt service 39

Cholesterol derivative-cyclopropane (4y)

FTIR

Peak Find - Memory-6

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3077.35	94	2	2924.04	55	3	2898.97	66
4	2867.15	69	5	2850.76	63	6	2652.12	94
7	2323.8	95	8	2184.95	94	9	2159.88	94
10	2152.17	95	11	2050.44	95	12	1993.55	95
13	1732.73	46	14	1466.12	66	15	1443.94	80
16	1415.49	81	17	1378.85	76	18	1364.87	75
19	1320.04	81	20	1281.95	82	21	1246.75	77
22	1207.22	77	23	1168.65	49	24	1134.9	75
25	1107.9	79	26	1100.67	79	27	1085.73	82
28	1071.75	84	29	1039.93	80	30	1028.35	75
31	1012.93	66	32	978.697	78	33	956.037	76
34	944.467	80	35	921.325	80	36	893.844	84
37	842.74	82	38	821.527	76	39	813.331	77
40	799.832	77	41	769.458	86	42	747.281	84
43	723.175	74	44	701.962	84	45	680.749	89
46	673.517	89	47	658.089	89	48	645.072	87
49	625.788	85	50	618.556	86	51	597.343	83

GA_193432.10.fid

nt-06-118(1)_a

Proton_ns8_d1=10s CDCl₃ /opt service 15

GA_193432.11.fid

nt-06-118(1)_a

Boron_ns1024 CDCl₃ /opt service 15

GA_193432.12.fid

nt-06-118(1)_a

Carbon_ns512 CDCl₃ /opt service 15

GA_193432.13.fid

nt-06-118(1)_a

Dept135_ns512 CDCl₃ /opt service 15

Cholesterol derivative-ATRA product (3y)

FTIR

GA_194207.10.fid

nt-06-150(2)_a

Proton_ns8_d1=10s CDCl₃ /opt service 21

GA_194207.12.fid

nt-06-150(2)_a

Carbon_ns512 CDCl₃ /opt service 21

GA_194207.13.fid

nt-06-150(2)_a

Dept135_ns512 CDCl₃ /opt service 21

Peak Find - Memory-2

GA_193737.10.fid

nt-06-144(1)_b

Proton_ns8_d1=10s CDCl₃ /opt service 60

GA_193737.11.fid

nt-06-144(1)_b

Boron_ns1024 CDCl₃ /opt service 60

Chrysanthemate derivative-ATRA product (3z)

 ^{13}C NMR (75 MHz)

GA_193737.12.fid

nt-06-144(1)_b

Carbon_ns512 CDCl₃ /opt service 60

GA_193737.13.fid

nt-06-144(1)_b

Dept135_ns512 CDCl3 /opt service 60

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2976.11	82	2	2924.52	69	3	2854.13	78
4	1721.64	60	5	1456.96	83	6	1406.82	82
7	1370.66	57	8	1319.55	63	9	1282.91	77
10	1235.18	78	11	1213.97	82	12	1193.72	69
13	1159.97	49	14	1143.1	38	15	1114.17	65
16	1082.83	82	17	1025.94	90	18	1005.21	91
19	967.126	74	20	917.95	91	21	885.166	88
22	846.115	65	23	747.281	90	24	722.211	90
25	672.553	91	26	577.094	89	27	552.506	92
28	547.202	92	29	539.007	91	30	522.615	90
31	518.758	89	32	508.151	88	33	500.437	89
34	492.723	87	35	487.902	88	36	481.635	87
37	477.296	90	38	471.51	84	39	464.278	82
40	459.939	80	41	452.225	84	42	447.886	83
43	437.762	75	44	431.977	78	45	428.12	78
46	423.781	70	47	416.549	79	48	409.799	64
49	403.532	76						

GA_187791.10.fid
nt-06-053_1.5h_b
Proton_ns16 CDCl₃ /opt service 54

GA_187791.11.fid			
nt-06-053_1.5h_b			
Boron_ns1024	CDCI3	/opt	service 54

035280.12.fid

C13CPD_STD CDCl₃ /opt service 17

035282.10.fid

Pinanediol analogue ATRA product (6g)

S380

HSQC (400 MHz)

035280.11.ser

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3345.41	91	2	2921.63	56	3	2853.17	69
4	1715.85	90	5	1449.73	83	6	1375.96	57
7	1340.28	69	8	1311.84	79	9	1279.54	68
10	1236.63	70	11	1207.22	75	12	1121.89	76
13	1076.57	69	14	1053.91	71	15	1029.32	61
16	989.786	77	17	938.199	81	18	921.325	80
19	841.776	82	20	754.513	80	21	721.247	84
22	656.643	86	23	590.593	83	24	576.129	83
25	529.364	81	26	494.652	83	27	474.885	79
28	461.868	79	29	438.726	81	30	423.781	89
31	411.246	80						

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