Substrate-Controlled Regioselective Cobalt(I)-Catalysed 1,4-Hydrovinylation Reactions

Gerhard Hilt,* Stefan Roesner

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35043 Marburg, Germany
Fax +49(6421)2825677; E-mail: Hilt@chemie.uni-marburg.de

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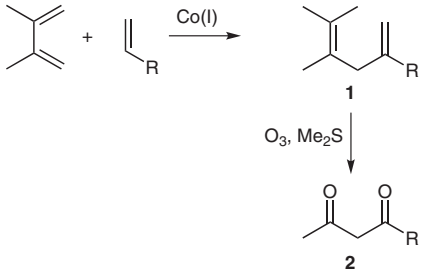
Abstract: The substrate-directed regiochemistry of the cobalt-catalysed 1,4-hydrovinylation reaction is described. A variety of symmetrical and unsymmetrical 2,3-disubstituted 1,3-dienes are synthesised by ruthenium-catalysed enyne metathesis, and then reacted with a terminal alkene catalysed by cobalt(II) bromide–[1,2-bis(diphenylphosphino)ethane] [$CoBr_2$(dppe)] under reductive conditions. The regiochemistry of the branched 1,4-diene products is influenced by the nature of the substituents on the unsymmetrical 2,3-disubstituted 1,3-dienes. The influence of steric and electronic effects is also discussed.

Key words: alkene, catalysis, cobalt, diene, regioselectivity

Among atom economic cobalt-catalysed carbon–carbon bond-forming processes,[1] the cobalt-catalysed 1,4-hydrovinylation reaction of symmetrical 1,3-dienes with a terminal alkene is a convenient method for the synthesis of 1,4-dienes such as **1**, under mild reaction conditions.[2] This efficient and atom economic reaction utilising a cobalt catalyst system [abbreviated as Co(I)] makes use of a mixture of cobalt(II) bromide–[1,2-bis(diphenylphosphino)ethane] [$CoBr_2$(dppe)], zinc iodide (ZnI_2) and zinc powder in dichloromethane at ambient temperature. This catalyst system tolerates a variety of functional groups leading to functionalised 1,4-dienes. These dienes are of significant synthetic value and products such as 1,3-dicarbonyl compounds **2** are easily accessible via ozonolysis (Scheme 1). In this context, the 1,4-hydrovinylation reaction has been used as the key step in the synthesis of small natural products containing a 1,4-diene subunit as in **1**, or a 1,3-dicarbonyl moiety as found in **2**.[3]



Scheme 1 Synthesis of 1,3-dicarbonyl compounds via cobalt-catalysed 1,4-hydrovinylation of 2,3-dimethyl-1,3-butadiene with terminal alkenes followed by ozonolysis

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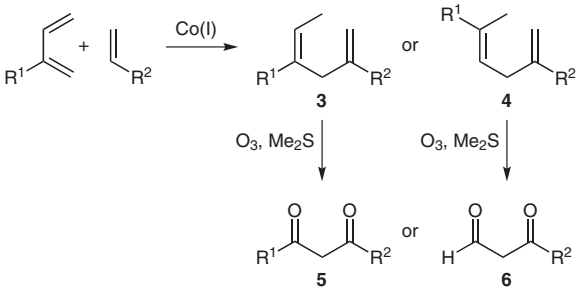
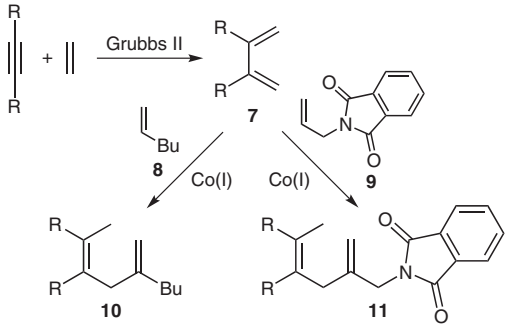
When unsymmetrical 1,3-dienes were used as starting materials in the cobalt-catalysed 1,4-hydrovinylation reaction, a mixture of two different regioisomers (e.g. **3** and **4**) was obtained (Scheme 2). The regiochemical outcome of the reaction is determined in the ligand sphere of the cobalt centre during formation of the carbon–carbon bond. The regiochemistry might therefore be influenced by either the steric or electronic effects of the 1,3-diene. In this study the influence of a variety of substituents bound to an unsymmetrical 2,3-disubstituted 1,3-diene was investigated in order to control the regiochemistry of the cobalt-catalysed 1,4-hydrovinylation reaction.



Scheme 2 Cobalt-catalysed 1,4-hydrovinylation of 2-substituted 1,3-butadienes with terminal alkenes followed by ozonolysis for the synthesis of 1,3-dicarbonyl compounds

The motivation behind this study was the need to develop a regioselective cobalt-catalysed 1,4-hydrovinylation reaction for the synthesis of 1,3-dicarbonyl compounds utilising a regiodirecting substituent on the 1,3-diene. Thereby, 'valuable' substituents (R^1) would remain in the carbon chain, attached to R^2, as in compound **5**, after ozonolysis. The cobalt-catalysed 1,4-hydrovinylation leading to **4** would result in undesired scission of the R^1 and R^2 substituents after ozonolysis. Previous investigations concerning the regioselective cobalt-catalysed 1,4-hydrovinylation reactions of non-activated terminal alkenes showed that, unfortunately, products of type **4** were formed predominantly.[2a–f]

In order to evaluate the usefulness of the cobalt-catalysed 1,4-hydrovinylation reaction for the transformation of symmetrical 2,3-disubstituted 1,3-dienes, a small series of such 1,3-dienes **7** was synthesised utilising a ruthenium-catalysed enyne metathesis reaction starting from an internal symmetrical alkyne and ethene (Scheme 3).[4] The 1,3-dienes of type **7** were then converted, over 18 hours employing two representative terminal alkenes, 1-hexene (**8**)

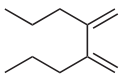
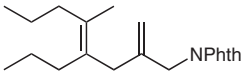
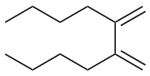
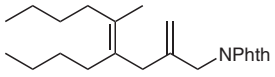
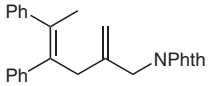
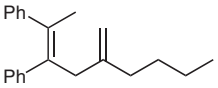
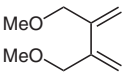
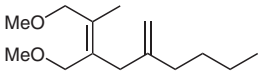


Scheme 3 The ruthenium-catalysed enyne metathesis and cobalt-catalysed 1,4-hydrovinylation reaction sequence

and allyl phthalimide (**9**), under cobalt catalysis, into the desired products of type **10** and **11**.

The results of the ruthenium-catalysed enyne metathesis–cobalt-catalysed 1,4-hydrovinylation reaction sequence are summarised in Table 1.

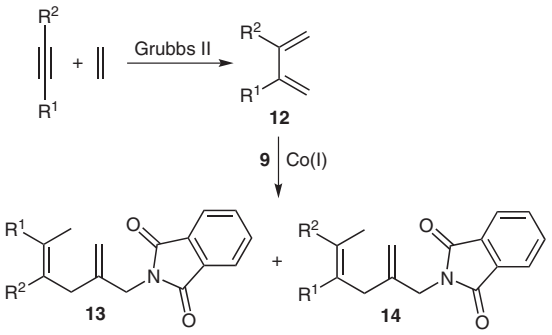
Table 1 Results of the Ruthenium-Catalysed Enyne Metathesis–Cobalt-Catalysed Hydrovinylation Reaction of Symmetrical 2,3-Disubstituted 1,3-Dienes

Entry	1,3-Diene (**7**)	Product (**10/11**)[a]	Yield (%)[b]
1		 **11a**	93
2		 **11b**	86
3		 **11c**	0
4		 **10a**	0
5		 **10b**	91[c]

[a] NPhth = phthalimide.
[b] Overall yield of isolated product.
[c] Reaction time = 61 hours.

Aliphatic, unhindered 1,3-dienes were transformed into the 1,4-dienes **11a** and **11b** in excellent yields (Table 1, entries 1 and 2). In contrast, the more hindered 2,3-diphenyl-1,3-butadiene did not undergo the 1,4-hydrovinylation reaction with either allyl phthalimide (Table 1, entry 3) or with 1-hexene (Table 1, entry 4). For unknown reasons, 2,3-bis(methoxymethyl)-1,3-butadiene (Table 1, entry 5) reacted readily with the terminal alkene, 1-hexene, to generate the desired 1,4-diene **10b** in very good yield, while allyl phthalimide proved to be unreactive in this transformation. Accordingly, we envisaged that 2,3-disubstituted 1,3-dienes were suitable starting materials as long as the substituents were of moderate bulkiness. For coordination of the 1,3-diene to the cobalt centre, a cisoid conformation must be adopted; bulky substituents seem to inhibit effective incorporation of the 1,3-diene during the transformation.

In the next step of the investigation, unsymmetrical 2,3-disubstituted 1,3-dienes (**12**, $R^1 \neq R^2$) were generated via the ruthenium-catalysed enyne metathesis reaction from unsymmetrical internal alkynes (Scheme 4). When such 1,3-dienes were submitted to the cobalt-catalysed 1,4-hydrovinylation reaction utilising allyl phthalimide (**9**) as the terminal alkene the two regioisomeric 1,4-dienes **13** and **14** were formed. In order to investigate the electronic/coordinative or steric influence of substituent R^2 on the regioselectivity of the 1,4-hydrovinylation reaction, we designated the substituent R^1 to be 'valuable', and kept this substituent as simple as possible for the time being. Therefore, an *n*-butyl group was selected which neatly accommodates the need for a dependable and simple route to unsymmetrical internal alkynes.

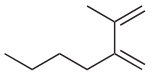
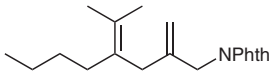
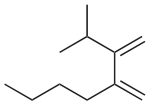
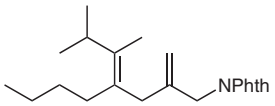
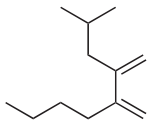
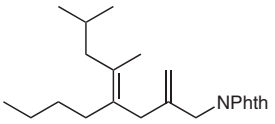
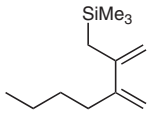
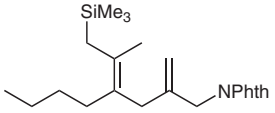
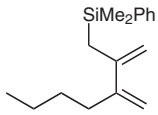
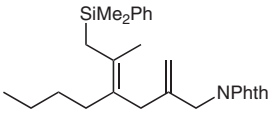
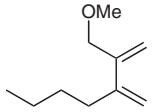
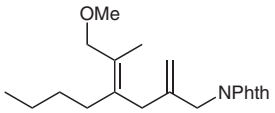


Scheme 4 Substrate-controlled regioselectivity of the cobalt-catalysed 1,4-hydrovinylation reaction with allyl phthalimide as the terminal alkene

The results of preliminary investigations directed towards a substrate-controlled regioselective cobalt-catalysed 1,4-hydrovinylation reaction are summarised in Table 2.

When the R^2 substituent in unsymmetrical 1,3-diene **12** was a methyl group, two regioisomers, **13** and **14** were obtained as a 1:1 mixture (Table 2, entry 1). Increasing the steric bulk of substituent R^2 to an isopropyl group resulted in a drastically reduced reactivity such that none of the desired product **14b** was obtained. On the other hand, introduction of an isobutyl substituent (Table 2, entry 3) resulted in the predominant formation of **14c** in the ratio 34:66. In this case, the isobutyl substituent favoured the formation of the desired isomer of type **14**. The best result was obtained when a dimethylphenylsilyl substituent was used (Table 2, entry 5). In this case, the yield of the two isomers (36%) and the regioselectivity, in favour of the preferred regioisomer (**13/14** = 29:71), were enhanced. While the methoxymethyl substituent (Table 2, entry 6) gave an acceptable yield of 58%, the desired regioisomer

Table 2 Results of the Ruthenium-Catalysed Enyne Metathesis–Cobalt-Catalysed Hydrovinylation Reaction of Unsymmetrical 2,3-Disubstituted 1,3-Dienes

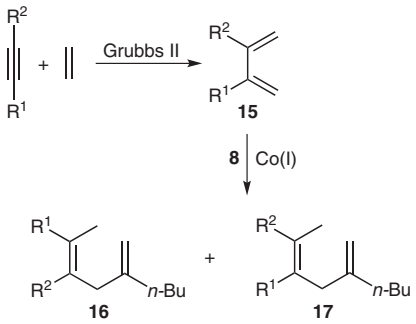
Entry	1,3-Diene (**12**)	Product (**14**)[a]	Yield (%)[b]
1		 **14a**	19 (50:50)
2		 **14b**	0
3		 **14c**	28 (34:66)
4		 **14d**	26 (34:66)
5		 **14e**	36 (29:71)
6		 **14f**	58 (75:25)

[a] NPhth = phthalimide.
[b] Overall yield of combined isolated product. Ratio of **13/14** in parentheses.

14f was formed as the minor component of the mixture. The donor atom of the methoxymethyl substituent might plausibly have altered the regioselectivity of the cobalt-catalysed reaction, most likely by coordination of the donor substituent to the cobalt centre so that isomer **13** was formed predominantly. In contrast, steric hindrance seemed to be responsible for the formation of isomers of type **14**. Based on these results, cobalt-catalysed 1,4-hydrovinylation reactions of unsymmetrical 1,3-dienes with the more reactive 1-hexene (**8**) were conducted (Scheme 5).

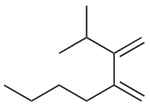
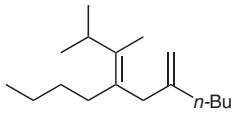
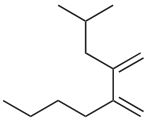
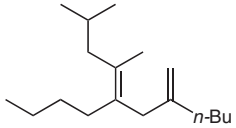
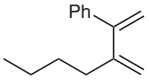
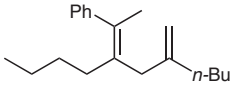
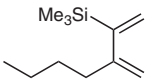
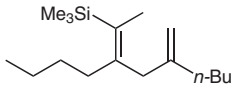
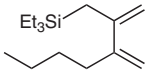
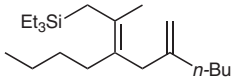
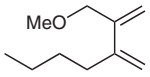
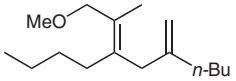
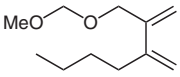
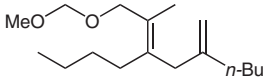
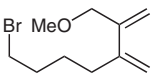
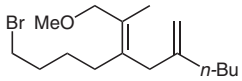
The results of these investigations are summarised in Table 3.

Similar to the hydroformylations of allyl phthalimide with bulky dienes, reactions of hindered 1,3-dienes with 1-hexene gave poor (Table 3, entry 3), or no conversion at all (Table 3, entries 1 and 4). The isobutyl substituted 1,3-diene was hydroformylated in a reasonably good 56% yield (Table 3, entry 3). However, the regioselectivities of the reactions with 1-hexene were somewhat lower compared to those with allyl phthalimide indicating a slight regio-



Scheme 5 Substrate-controlled regioselectivity of the cobalt-catalysed 1,4-hydrovinylation reaction with 1-hexene as the terminal alkene

Table 3 Results of the Ruthenium-Catalysed Enyne Metathesis–Cobalt-Catalysed Hydrovinylation Reaction of Unsymmetrical 2,3-Disubstituted 1,3-Dienes

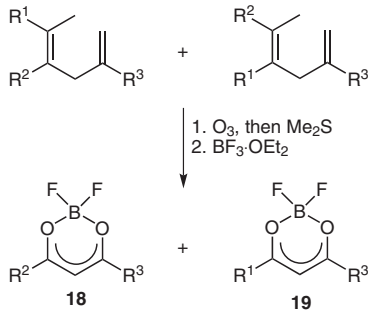
Entry	1,3-Diene (**15**)	Product (**17**)	Yield (%)[a]
1		 **17a**	0
2		 **17b**	56 (38:62)
3		 **17c**	17 (40:60)
4		 **17d**	0
5		 **17e**	40 (40:60)
6		 **17f**	86 (75:25)
7		 **17g**	20 (72:28)
8		 **17h**	82 (72:28)

[a] Overall yield of combined isolated product. Ratio of **16/17** in parentheses.

directing effect of the substituent bonded to the terminal alkene. With triethylsilane as substituent R^2 (Table 3, entry 5), a higher yield, but lower regioselectivity, was ob-

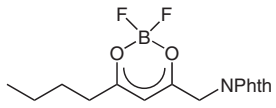
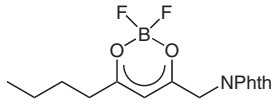
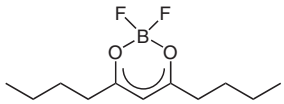
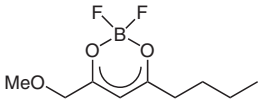
served compared to the conversion with allyl phthalimide (Table 2, entry 4). The methoxymethyl substituent gave the best result in terms of yield and regioselectivity (Table 3, entries 6 and 8), although the undesired regioisomers **16f** and **16h** were formed predominantly in both these cases. An additional donor moiety, as present in the methoxymethyl (MOM) group (Table 3, entry 7), led to a considerable decrease in yield and no improvement in the regioselectivity. The presence of bulky R^2 substituents led mainly to the formation of the desired isomers of type **17**, however, the levels of regiocontrol could not be improved using the investigated modifications.

In order to prove that some of the 1,4-dienes of types **13/14** and **16/17** could be converted into the corresponding 1,3-dicarbonyl derivatives, ozonolysis with reductive workup was performed (Scheme 6). The products were isolated and characterised following transformation into the corresponding dioxoborinine derivatives **18** and **19** using boron trifluoride–diethyl ether complex.



Scheme 6 Ozonolysis of representative 1,4-dienes followed by dioxoborinine formation

Table 4 Results of the Ozonolysis–Dioxoborinine Formation Reaction Sequence

Entry	1,4-Diene	Product (**18/19**)[a]	Yield (%)[b]
1	**13c/14c**	 **19a**	38 (66:34)
2	**13e/14e**	 **19a**	34 (71:29)
3	**16e/17e**	 **19b**	36 (79:21)
4	**16f/17f**	 **18c**	19 (40:60)

[a] NPhth = phthalimide.
[b] Overall yield of combined isolated product. Ratio of **19/18** in parentheses.

The results in Table 4 illustrate that the desired products could be obtained. Nevertheless, the yields were only moderate and the regioisomeric ratios were only marginally altered by this process, indicating that both isomers were reactive to a similar extent.

In conclusion, we have shown that control of the regioselectivity of the cobalt-catalysed 1,4-hydrovinylation reaction can be achieved with bulky substituents in order to form the desired regioisomers of type **14** and **17**. While the presence of bulky substituents led to some extent of control of the regioselectivity, the steric hindrance often resulted in moderate yields. In contrast, the methoxymethyl substituent inverts the regioselectivity of the 1,4-hydrovinylation reaction such that products of type **13** and **16** are formed predominantly. Ozonolysis of representative 1,4-dienes followed by protection of the resulting unsymmetrical 1,3-dicarbonyl derivatives using boron trifluoride–diethyl ether complex gave dioxoborinines **19a**,**b** and **18c**. Further improvement in the regioselectivities may be achieved by altering the ligand in the cobalt catalyst system. In combination with bulky substituents located the appropriate distance from the 1,3-diene, good control of the regioselectivity might be realised in the future.

Column chromatography was performed using silica gel (Macherey-Nagel, 230–400 mesh) and TLC was carried out using silica gel plates (Merck). IR spectra were obtained using a Bruker Physics IFS 200 Interferometer or a Nicolet Magna IR 750 spectrophotometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using a Bruker Physics AVANCE-300 instrument with $CDCl_3$ as the solvent. ^{19}F NMR (376 MHz) and ^{11}B NMR (128 MHz) spectra were recorded using a Bruker Physics DRX-400 instrument. Low-resolution mass spectra were recorded using a Varian MAT CH 7A or a Micromass VG 7070 spectrometer for EI measurements or a Micromass VG Autospec spectrometer for ESI measurements. HRMS were obtained using a Finnigan MAT 95S instrument for EI measurements or a Micromass VG Autospec spectrometer for ESI measurements.

Hydrovinylation; General Procedure

A Schlenk flask was charged with $CoBr_2$(dppe) (31 mg, 50 μmol, 10 mol%), anhyd ZnI_2 (32 mg, 0.1 mmol, 20 mol%) and Zn powder (7 mg, 0.1 mmol, 20 mol%) under an N_2 atm. Next, a soln of the 1,3-diene (0.5 mmol) in anhyd CH_2Cl_2 (1.0 mL) and alkene **8** or **9** (0.5–1.0 mmol) were added. The mixture was stirred at r.t. and the conversion was monitored by GC–MS. After the conversion was complete, the mixture was diluted with pentane to precipitate the metal salts and filtered through a small plug of silica gel using Et_2O–pentane or EtOAc–pentane as eluent. The solvent was removed and the residue was purified by column chromatography.

(4*E*)-2-(5-Methyl-2-methylene-4-propyloct-4-enyl)isoindoline-1,3-dione (11a)

Eluent: pentane–Et_2O, 5:1; white solid; yield: 1.51 g (4.63 mmol, 93%); R_f = 0.38 (pentane–Et_2O, 5:1).

IR (KBr): 2954, 2924, 2866, 1774, 1713, 1426, 1394, 1107, 949, 907, 725, 711 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.83 (m, 2 H), 7.75–7.70 (m, 2 H), 4.82 (d, *J* = 1.0 Hz, 1 H), 4.76 (d, *J* = 1.0 Hz, 1 H), 4.20 (s, 2 H), 2.80 (s, 2 H), 2.06–1.94 (m, 4 H), 1.59 (s, 3 H), 1.46–1.26 (m, 4 H), 0.89 (t, *J* = 7.3 Hz, 3 H), 0.86 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 141.4, 134.0, 132.1, 132.0, 129.2, 123.3, 110.4, 42.3, 36.8, 36.3, 34.1, 22.1, 21.7, 18.3, 14.3, 14.2.

MS (EI, 70 eV): *m*/*z* (%) = 325 (17) $[M]^+$, 178 (22), 165 (100), 160 (57), 149 (48), 135 (59), 123 (24), 107 (51).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{27}NO_2$: 325.2042; found: 325.2048.

(4*E*)-2-(4-Butyl-5-methyl-2-methylenenon-4-enyl)isoindoline-1,3-dione (11b)

Eluent: pentane–Et_2O, 5:1; white solid; yield: 305 mg (0.86 mmol, 86%); R_f = 0.52 (pentane–Et_2O, 5:1).

IR (KBr): 2957, 2926, 2858, 1773, 1718, 1427, 1391, 1106, 963, 942, 725, 712 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.83 (m, 2 H), 7.75–7.69 (m, 2 H), 4.81 (d, *J* = 0.9 Hz, 1 H), 4.77 (d, *J* = 0.9 Hz, 1 H), 4.20 (s, 2 H), 2.79 (s, 2 H), 2.06–1.94 (m, 4 H), 1.59 (s, 3 H), 1.37–1.23 (m, 8 H), 0.94–0.82 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 141.4, 133.9, 132.1, 132.0, 129.1, 123.3, 110.5, 42.3, 36.8, 34.0, 31.6, 31.2, 30.7, 23.0, 22.9, 18.3, 14.1, 14.0.

MS (EI, 70 eV): *m*/*z* (%) = 353 (23) $[M]^+$, 206 (16), 193 (100), 163 (30), 160 (46), 149 (41), 121 (10), 107 (25).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{31}NO_2$: 353.2355; found: 353.2353.

(2*Z*)-1-Methoxy-3-(methoxymethyl)-2-methyl-5-methylenenon-2-ene (10b)

Eluent: pentane–Et_2O, 2:1; brown oil; yield: 206 mg (0.91 mmol, 91%); R_f = 0.66 (pentane–Et_2O, 2:1).

IR (neat): 2929, 2873, 1726, 1643, 1457, 1383, 1189, 1093, 892 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (s, 1 H), 4.64 (d, *J* = 1.6 Hz, 1 H), 4.02 (s, 2 H), 3.89 (s, 2 H), 3.30 (s, 3 H), 3.28 (s, 3 H), 2.87 (s, 2 H), 2.00 (t, *J* = 7.5 Hz, 2 H), 1.75 (s, 3 H), 1.50–1.22 (m, 4 H), 0.91 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8, 133.9, 132.5, 109.4, 72.3, 70.5, 57.9, 57.6, 37.3, 36.2, 30.0, 22.4, 16.5, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 226 (<1) $[M]^+$, 194 (15), 179 (10), 162 (14), 137 (100), 123 (23), 119 (68), 105 (33).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{26}O_2Na$: 249.1825; found: 249.1811.

2-[2-Methylene-4-(propan-2-ylidene)octyl]isoindoline-1,3-dione (14a) and (4*E*)-2-(4,5-Dimethyl-2-methylenenon-4-enyl)isoindoline-1,3-dione (13a)

Eluent: pentane–EtOAc, 5:1; white solid; combined yield: 29 mg (94 μmol, 19%); ratio (**14a/13a**) = 50:50; R_f = 0.61 (pentane–EtOAc, 5:1).

Analytical data of the mixture of regioisomers.

IR (KBr): 2956, 2927, 2860, 1774, 1718, 1425, 1391, 1329, 1108, 965, 715 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.81 (m, 4 H), 7.76–7.69 (m, 4 H), 4.84–4.80 (m, 2 H), 4.76 (s, 2 H), 4.19 (s, 4 H), 2.82 (s, 4 H), 2.07–1.95 (m, 4 H), 1.68 (s, 3 H), 1.62 (s, 9 H), 1.35–1.22 (m, 8 H), 0.92–0.83 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 141.5, 141.3, 133.9, 132.1, 131.7, 129.0, 127.3, 124.3, 123.3, 110.7, 110.5, 42.3, 42.0, 39.4, 37.0, 34.4, 31.9, 30.8, 30.4, 22.9, 22.8, 20.7, 20.3, 18.4, 17.9, 14.1, 14.0.

MS (ESI): *m*/*z* (%) = 334 (24) $[M + Na]^+$, 334 (24), 319 (14), 305 (11), 275 (11), 261 (6), 231 (5), 217 (2), 178 (4), 163 (2), 104 (2).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{25}NO_2Na$: 334.1778; found: 334.1779.

(4*E*)-2-(4-Butyl-5,7-dimethyl-2-methyleneoct-4-enyl)isoindoline-1,3-dione (14c) and (4*E*)-2-(4-Isobutyl-5-methyl-2-methylenenon-4-enyl)isoindoline-1,3-dione (13c)

Eluent: pentane–Et_2O, 5:1; yellow solid; combined yield: 50 mg (0.14 mmol, 28%); ratio (**14c/13c**) = 66:34; R_f = 0.42 (pentane–Et_2O, 5:1).

IR (KBr): 2956, 2866, 1774, 1717, 1462, 1388, 1331, 1104, 955, 721 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.81 (m, 2 H), 7.75–7.68 (m, 2 H), 4.84 (d, *J* = 1.0 Hz, 1 H), 4.76 (s, 1 H), 4.21 (s, 2 H), 2.81 (s, 2 H), 2.07–1.72 (m, 5 H), 1.58 (s, 3 H), 1.36–1.19 (m, 4 H), 0.91–0.80 (m, 9 H). Additional signals of the minor isomer **13c**: δ = 4.80 (d, *J* = 1.0 Hz, 1 H), 4.19 (s, 2 H), 2.80 (s, 2 H), 1.60 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 141.5, 134.2, 133.9, 132.1, 130.9, 123.3, 110.5, 43.2, 42.3, 36.8, 31.8, 31.0, 27.1, 23.0, 22.6, 18.5, 14.0. Additional signals of the minor isomer **13c**: δ = 141.3, 133.1, 128.1, 110.4, 42.3, 40.5, 34.1, 30.7, 27.6, 22.9, 18.4, 14.1.

MS (EI, 70 eV): *m*/*z* (%) = 353 (3) $[M]^+$, 193 (17), 187 (100), 169 (39), 160 (26), 158 (11), 130 (24), 104 (32).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{31}NO_2$: 353.2355; found: 353.2359.

(4*E*)-2-{2-Methylene-4-[1-(trimethylsilyl)propan-2-ylidene]octyl}isoindoline-1,3-dione (14d) and (4*Z*)-2-{5-Methyl-2-methylene-4-[(trimethylsilyl)methyl]non-4-enyl}isoindoline-1,3-dione (13d)

Eluent: pentane–Et_2O, 5:1; yellow oil; combined yield: 63 mg (0.16 mmol, 26%); ratio (**14d/13d**) = 66:34; R_f = 0.45 (pentane–Et_2O, 5:1).

IR (KBr): 2955, 2928, 2871, 1774, 1719, 1424, 1391, 1248, 1110, 960, 849, 715 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.82 (m, 2 H), 7.75–7.69 (m, 2 H), 4.84 (d, *J* = 1.2 Hz, 1 H), 4.75 (d, *J* = 1.1 Hz, 1 H), 4.20 (s, 2 H), 2.81 (s, 2 H), 2.00–1.88 (m, 2 H), 1.63–1.51 (m, 5 H), 1.34–1.22 (m, 4 H), 0.92–0.83 (m, 3 H), 0.03 (s, 9 H). Additional signals of the minor isomer **13d**: δ = 4.77 (d, *J* = 1.2 Hz, 1 H), 4.18 (s, 2 H), 2.74 (s, 2 H), –0.03 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 141.8, 133.9, 132.1, 129.1, 126.3, 123.3, 110.2, 42.3, 36.6, 32.1, 30.5, 25.4, 23.0, 21.2, 14.0, –0.4. Additional signals of the minor isomer **13d**: δ = 141.2, 128.7, 126.0, 110.5, 42.2, 39.0, 34.6, 30.2, 22.9, 22.3, 17.9, 14.1, –0.6.

MS (EI, 70 eV): *m*/*z* (%) = 383 (17) $[M]^+$, 368 (4), 232 (5), 223 (11), 187 (12), 179 (16), 160 (18), 149 (5), 121 (16).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{33}NO_2Si$: 383.2281; found: 383.2278.

(4*E*)-2-(4-{1-[Dimethyl(phenyl)silyl]propan-2-ylidene}-2-methyleneoctyl)isoindoline-1,3-dione (14e) and (4*Z*)-2-(4-{[Dimethyl(phenyl)silyl]methyl}-5-methyl-2-methylenenon-4-enyl)isoindoline-1,3-dione (13e)

Eluent: pentane–Et_2O, 5:1; yellow oil; combined yield: 80 mg (0.18 mmol, 36%); ratio (**14e/13e**) = 71:29; R_f = 0.35 (pentane–Et_2O, 5:1).

IR (KBr): 2956, 1774, 1718, 1465, 1390, 1110, 956, 834, 715 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.84 (m, 2 H), 7.75–7.70 (m, 2 H), 7.58–7.44 (m, 2 H), 7.38–7.27 (m, 3 H), 4.83–4.72 (m, 2 H), 4.18 (s, 2 H), 2.81 (s, 2 H), 1.90 (t, *J* = 7.0 Hz, 2 H), 1.83 (s, 2 H),

1.55 (s, 3 H), 1.31–1.19 (m, 4 H), 0.91–0.81 (m, 3 H), 0.34 (s, 6 H). Additional signals of the minor isomer **13e**: δ = 4.12 (s, 2 H), 2.63 (s, 2 H), 1.76 (s, 2 H), 1.60 (s, 3 H), 0.27 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 141.6, 141.1, 133.9, 133.5, 132.1, 128.8, 128.4, 127.7, 127.1, 123.2, 110.3, 42.2, 36.6, 32.1, 30.3, 24.7, 23.0, 21.2, 13.9, –2.1. Additional signals of the minor isomer **13e**: δ = 141.1, 139.6, 129.5, 128.7, 127.6, 125.3, 123.3, 110.4, 42.0, 38.7, 34.6, 30.1, 22.9, 21.6, 17.9, 14.0, –2.3.

MS (EI, 70 eV): *m*/*z* (%) = 445 (22) $[M]^+$, 311 (31), 282 (9), 204 (18), 187 (50), 160 (63), 151 (82), 135 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{28}H_{35}NO_2Si$: 445.2437; found: 445.2429.

(4*Z*)-2-[4-(Methoxymethyl)-5-methyl-2-methylenenon-4-enyl]isoindoline-1,3-dione (13f) and (4*E*)-2-[4-(1-Methoxypropan-2-ylidene)-2-methyleneoctyl]isoindoline-1,3-dione (14f)

Eluent: pentane–Et_2O, 5:1; white solid; combined yield: 63 mg (0.18 mmol, 58%); ratio (**13f/14f**) = 75:25; R_f = 0.14 (pentane–Et_2O, 5:1).

IR (KBr): 2923, 1774, 1716, 1425, 1392, 1190, 1087, 957, 906, 714 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.80 (m, 2 H), 7.75–7.67 (m, 2 H), 4.85–4.73 (m, 2 H), 4.20 (s, 2 H), 3.85 (s, 2 H), 3.23 (s, 3 H), 2.90 (s, 2 H), 2.15–2.01 (m, 2 H), 1.66 (s, 3 H), 1.38–1.22 (m, 4 H), 0.91–0.81 (m, 3 H). Additional signals of the minor isomer **14f**: δ = 3.93 (s, 2 H), 3.26 (s, 3 H), 2.84 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 141.1, 138.1, 133.8, 132.1, 126.4, 123.2, 110.5, 70.5, 57.8, 42.2, 34.7, 34.0, 31.0, 22.7, 18.7, 14.0. Additional signals of the minor isomer **14f**: δ = 140.7, 134.7, 133.9, 132.0, 128.9, 123.3, 111.1, 72.6, 57.4, 37.2, 31.6, 31.4, 22.8, 16.3, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 341 (12) $[M]^+$, 309 (6), 252 (8), 181 (5), 160 (100), 149 (49), 133 (24), 119 (74).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{27}NO_3$: 341.1991; found: 341.1994.

The isolation of compounds **16b**,**17b** and **16c**,**17c** was complicated due to their low polarity and the presence of impurities. The R_f values of these products were relatively high and purification to an acceptable level could not achieved. The purity of the compounds obtained was ~90%. The ratios were determined by GC analysis.

(2*E*)-(3-Butyl-2-methyl-5-methylenenon-2-enyl)triethylsilane (17e) and (2*Z*)-Triethyl[2-(hexan-2-ylidene)-4-methyleneoctyl]silane (16e)

Eluent: pentane–EtOAc, 1:1; brown oil; combined yield: 64 mg (0.20 mmol, 40%); ratio (**17e/16e**) = 60:40; R_f = 0.90 (pentane–EtOAc, 1:1).

IR (neat): 2956, 2929, 2876, 1644, 1462, 1380, 1237, 1165, 1014, 889, 738 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.74–4.68 (m, 1 H), 4.67 (br s, 1 H), 2.71 (s, 2 H), 2.01–1.88 (m, 4 H), 1.64–1.50 (m, 3 H), 1.49–1.23 (m, 10 H), 1.01–0.84 (m, 15 H), 0.55 (q, *J* = 7.5 Hz, 6 H). Additional signals of the minor isomer **16e**: δ = 2.64 (s, 2 H), 0.64–0.46 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.5, 127.8, 127.7, 108.9, 38.6, 36.0, 32.2, 30.5, 30.2, 23.1, 22.6, 21.1, 20.1, 14.1, 14.0, 7.5, 4.2. Additional signals of the minor isomer **16e**: δ = 147.8, 127.5, 127.2, 108.8, 40.9, 36.1, 34.7, 30.4, 23.0, 22.5, 17.9, 17.3, 14.2, 13.9, 7.4, 4.3.

MS (EI, 70 eV): *m*/*z* (%) = 322 (8) $[M]^+$, 293 (7), 115 (100), 107 (5), 87 (99), 73 (5), 59 (69), 55 (6).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{42}Si$: 322.3056; found: 322.3065.

(5*Z*)-6-(Methoxymethyl)-5-methyl-8-methylenedodec-5-ene (16f) and (5*E*)-5-(1-Methoxypropan-2-ylidene)-7-methyleneundecane (17f)

Eluent: pentane–EtOAc, 1:1; brown oil; combined yield: 103 mg (0.43 mmol, 86%); ratio (**16f/17f**) = 75:25.

IR (neat): 2958, 2928, 2866, 1723, 1644, 1462, 1380, 1188, 1096, 890 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.73–4.70 (m, 1 H), 4.60 (d, *J* = 1.8 Hz, 1 H), 3.84 (s, 2 H), 3.28 (s, 3 H), 2.81 (s, 2 H), 2.19–2.11 (m, 2 H), 2.01–1.94 (m, 2 H), 1.67 (s, 3 H), 1.50–1.23 (m, 8 H), 0.91 (t, *J* = 7.1 Hz, 3 H), 0.90 (t, *J* = 7.2 Hz, 3 H). Additional signals of the minor isomer **17f**: δ = 4.75–4.73 (m, 1 H), 4.66 (d, *J* = 1.6 Hz, 1 H), 3.96 (s, 2 H), 3.29 (s, 3 H), 2.75 (s, 2 H), 2.09–2.01 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.4, 137.3, 127.5, 109.3, 70.7, 57.7, 36.7, 36.2, 33.9, 31.1, 30.1, 22.7, 22.4, 18.6, 14.0, 13.9. Additional signals of the minor isomer **17f**: δ = 147.0, 136.1, 127.8, 108.7, 72.7, 57.3, 39.1, 36.1, 31.7, 31.6, 22.8, 16.2.

MS (EI, 70 eV): *m*/*z* (%) = 238 (5) $[M]^+$, 206 (28), 181 (19), 163 (71), 149 (64), 141 (21), 135 (17), 121 (28).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{30}O$: 238.2297; found: 238.2304.

(5*Z*)-6-[(Methoxymethoxy)methyl]-5-methyl-8-methylenedodec-5-ene (16g) and (5*E*)-5-[1-(Methoxymethoxy)propan-2-ylidene]-7-methyleneundecane (17g)

Eluent: pentane–EtOAc, 1:1; yellow oil; combined yield: 34 mg (0.13 mmol, 20%); ratio (**16g/17g**) = 72:28; R_f = 0.78 (pentane–EtOAc, 1:1).

IR (neat): 2957, 2929, 2873, 1642, 1463, 1380, 1149, 1100, 1046, 921, 890 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.72 (s, 1 H), 4.63–4.59 (m, 3 H), 3.99 (s, 2 H), 3.37 (s, 3 H), 2.83 (s, 2 H), 2.20–2.11 (m, 2 H), 2.02–1.92 (m, 2 H), 1.68 (s, 3 H), 1.49–1.23 (m, 8 H), 0.91 (t, *J* = 7.0 Hz, 3 H), 0.90 (t, *J* = 7.2 Hz, 3 H). Additional signals of the minor isomer **17g**: δ = 4.65 (s, 1 H), 3.39 (s, 3 H), 2.75 (s, 2 H), 2.09–2.02 (m, 2 H), 1.70 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.4, 138.0, 126.9, 109.0, 95.7, 65.7, 55.1, 37.0, 36.2, 34.0, 31.2, 30.1, 22.8, 22.5, 18.7, 14.0, 13.9. Additional signals of the minor isomer **17g**: δ = 147.1, 136.7, 127.2, 109.4, 95.4, 67.8, 39.1, 31.8, 31.7, 22.9, 16.7.

MS (EI, 70 eV): *m*/*z* (%) = 268 (3) $[M]^+$, 223 (7), 206 (22), 194 (28), 177 (20), 163 (40), 149 (50), 121 (25).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{32}O_2$: 268.2402; found: 268.2406.

(5*Z*)-1-Bromo-6-(methoxymethyl)-5-methyl-8-methylenedodec-5-ene (16h) and (5*E*)-1-Bromo-5-(1-methoxypropan-2-ylidene)-7-methyleneundecane (17h)

Eluent: pentane–EtOAc, 1:1; brown oil; combined yield: 130 mg (0.41 mmol, 82%); ratio (**16h/17h**) = 72:28.

IR (neat): 2957, 2929, 2867, 1727, 1642, 1459, 1380, 1188, 1095, 953, 890 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.73–4.70 (m, 1 H), 4.59 (d, *J* = 1.7 Hz, 1 H), 3.83 (s, 2 H), 3.43 (t, *J* = 6.8 Hz, 2 H), 3.29 (s, 3 H), 2.82 (s, 2 H), 2.22–1.80 (m, 6 H), 1.68 (s, 3 H), 1.61–1.25 (m, 6 H), 0.90 (t, *J* = 7.2 Hz, 3 H). Additional signals of the minor isomer **17h**: δ = 4.76–4.73 (m, 1 H), 4.66 (d, *J* = 1.5 Hz, 1 H), 3.95 (s, 2 H), 3.30 (s, 3 H), 2.76 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.3, 136.4, 128.6, 109.5, 70.8, 57.9, 37.0, 36.2, 33.6, 33.2, 32.5, 30.0, 27.1, 22.4, 18.5, 13.9. Additional signals of the minor isomer **17h**: δ = 146.9, 135.2, 128.3, 108.9, 72.8, 57.5, 39.0, 36.0, 33.5, 32.7, 30.9, 27.6, 16.4.

MS (EI, 70 eV): *m/z* (%) = 316 (2) $[M]^+$, 286 (13), 255 (12), 243 (20), 229 (43), 219 (37), 205 (21), 181 (22), 163 (62), 149 (34).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{16}H_{29}OBr$: 316.1402; found: 316.1405.

Ozonolysis; General Procedure

A Schlenk flask, fitted with a glass tube to admit ozone, was charged with the 1,4-dienes (0.5 mmol) and anhydrous CH_2Cl_2 (6.0 mL). The reaction mixture was cooled to –78 °C and ozone in a stream of oxygen was bubbled through the solution. When the solution turned blue, ozone addition was stopped. By passing oxygen through the solution the excess of ozone was removed and dimethyl sulfide (62 mg, 1.00 mmol) was added. The solution was allowed to warm to r.t. and after stirring for 1 h, $BF_3{\cdot}OEt_2$ (214 mg, 1.50 mmol) was slowly added to the reaction mixture and stirred at r.t. for 16 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography using EtOAc–pentane as eluent.

2-[(2′,2′-Difluoro-6′-butyl-1′,3′,2′-dioxaborinine-4-yl)methyl]isoindoline-1,3-dione (19a)

Eluent: pentane–EtOAc, 1:1; brown solid; yield: 10 mg (30 μmol, 25%); R_f = 0.50 (pentane–EtOAc, 1:1).

IR (KBr): 2960, 1777, 1721, 1551, 1416, 1392, 1193, 1059, 993, 947, 796, 715 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95–7.87 (m, 2 H), 7.83–7.73 (m, 2 H), 5.97 (s, 1 H), 4.65 (s, 2 H), 2.53 (t, *J* = 7.6 Hz, 2 H), 1.67 (quin, *J* = 7.5 Hz, 2 H), 1.37 (sext, *J* = 7.3 Hz, 2 H), 0.91 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.7, 187.0, 167.0, 134.7, 131.6, 124.0, 98.4, 41.1, 37.8, 27.6, 22.2, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –137.70 (s), –137.76 (s).

^{11}B NMR (128 MHz, $CDCl_3$): δ = 0.57 (br s).

MS (ESI): *m/z* (%) = 358 (5) $[M + Na]^+$, 327 (5), 311 (100), 295 (18), 266 (5), 244 (5), 203 (5), 130 (44), 118 (5), 102 (16).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{16}{}^{11}BF_2NO_4Na$: 358.1033; found: 358.1031.

2,2-Difluoro-4,6-dibutyl-1,3,2-dioxaborinine (19b)

Eluent: pentane–EtOAc, 1:1; brown oil; yield: 13 mg (54 μmol, 28%); R_f = 0.84 (pentane–EtOAc, 1:1).

IR (KBr): 2961, 2874, 1721, 1552, 1466, 1408, 1189, 1112, 1056, 994, 807 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.93 (s, 1 H), 2.50 (t, *J* = 7.6 Hz, 4 H), 1.68 (quin, *J* = 7.6 Hz, 4 H), 1.39 (sext, *J* = 7.4 Hz, 4 H), 0.93 (t, *J* = 7.3 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.7, 100.3, 37.3, 27.8, 22.2, 13.6.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 0.63 (br s).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –139.09 (s), –139.15 (s).

MS (ESI): *m/z* (%) = 255 (31) $[M + Na]^+$, 225 (10), 218 (25), 207 (22), 185 (65), 139 (7), 130 (4).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{11}H_{19}{}^{11}BF_2O_2Na$: 255.1338; found: 255.1340.

2,2-Difluoro-6-butyl-4-methoxymethyl-1,3,2-dioxaborinine (18c)

Eluent: pentane–EtOAc, 1:1; brown oil; yield: 10 mg (47 μmol, 11%); R_f = 0.73 (pentane–EtOAc, 1:1).

IR (KBr): 2960, 2832, 1732, 1574, 1553, 1453, 1407, 1338, 1195, 1125, 1058, 999, 931, 814 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.32 (s, 1 H), 4.19 (s, 2 H), 3.46 (s, 3 H), 2.58 (t, *J* = 7.6 Hz, 2 H), 1.71 (quin, *J* = 7.6 Hz, 2 H), 1.40 (sext, *J* = 7.3 Hz, 2 H), 0.94 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 191.3, 97.8, 72.2, 59.6, 37.8, 27.8, 22.2, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –138.12 (s), –138.18 (s).

^{11}B NMR (128 MHz, $CDCl_3$): δ = 0.83 (br s).

MS (EI, 70 eV): *m/z* (%) = 220 (3) $[M]^+$, 200 (10), 175 (100), 171 (10), 149 (24), 128 (8), 117 (10), 91 (33), 85 (38), 79 (20), 57 (40).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_9H_{15}{}^{11}BF_2O_3$: 220.1082; found: 220.1100.

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