JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b01063 • Publication Date (Web): 22 Jun 2018

ACS Publications

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Directed Cu(I)-Catalyzed Carbomagnesiation of 1-Arylcycloprop-2-ene-1-carboxamides en route to Densely Substituted Functionalized Cyclopropanes

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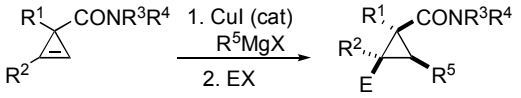


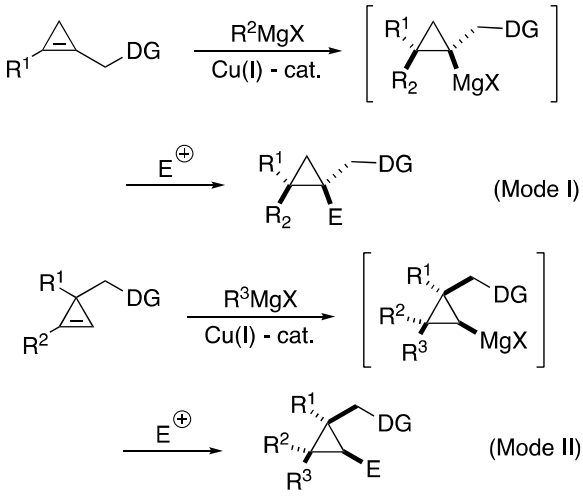
Highly diastereoselective carbomagnesiation

ABSTRACT: Copper-catalyzed directed addition of Grignard reagents across strained C=C bond of cyclopropene-3-carboxamides. It was demonstrated that the amide functionality serves as an ultimate directing group allowing for highly efficient control of diastereoselectivity of addition including stereoselectivity of electrophilic trapping with prochiral aldehydes. Also, regioselectivity of carbomagnesiation of cyclopropenes with monosubstituted double bond is investigated. It was shown that in many cases this selectivity is controlled by steric factors and allows for preparation of products with "reversed" regiochemistry.

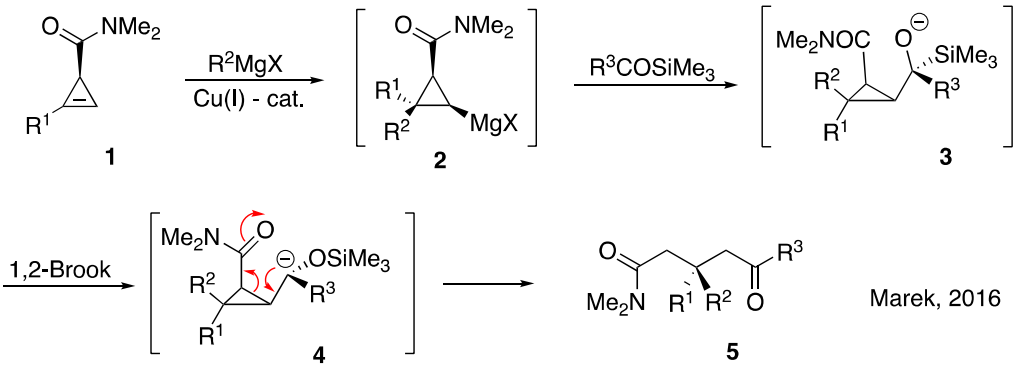
INTRODUCTION

Carbometalation accompanied by electrophilic trapping is often regarded to as one of the most important addition reactions of olefins as it allows for efficient installation of two different entities at two adjacent carbon atoms in one operation. This reaction is particularly productive in application to strained olefins, such as cyclopropenes, as it is greatly facilitated by the energy accompanying the strain release.[1] Although non-catalyzed ring-retentive additions of Grignard reagents across the double bond of cyclopropene have been known for almost four decades,[2] the employment of copper and iron catalysis took this chemistry to a new level.[3] Not only did it make this methodology more versatile and efficient,[4] it also advanced the field of enantioselective carbometallation.[5] Unless performed on symmetrically substituted cyclopropenes, the facial selectivity in these reactions was governed by steric demands, driving the addition of organometallic species to the least hindered face of the ring. Recently, an alternative selectivity control was exploited, in which the approach of organometallic entities was efficiently controlled by coordination with a suitable functional group (i.e., directed addition). Two different modes of this reaction have been demonstrated to date. Mode I (Scheme 1) involves a diastereoselective addition directed by a suitable functionality (typically an alcohol function) tethered to C1 of cyclopropene.[6] Mode II includes the processes in which the facial selectivity of carbometallation is governed by a directing group at C-3. Suitable directing functionalities successfully employed in these transformations include alcohol,[7] ester,[8] ether,[9] and Evans' chiral oxazolidinone auxiliaries.[10] Recently, Marek reported application of 2-alkyl-*N*,*N*-dimethylcycloprop-2-ene-1-carboxamides (**1**) easily available via the well-established asymmetric cyclopropanation methodology,[11] in the copper-catalyzed directed addition of Grignard reagents (Scheme 2).[12] Efficient coordination of the organometallic reagent to the carboxamide group allowed for a highly diastereoselective formation of cyclopropyl metal species **2**. The subsequent electrophilic trapping with acylsilanes followed by in situ Brook rearrangement

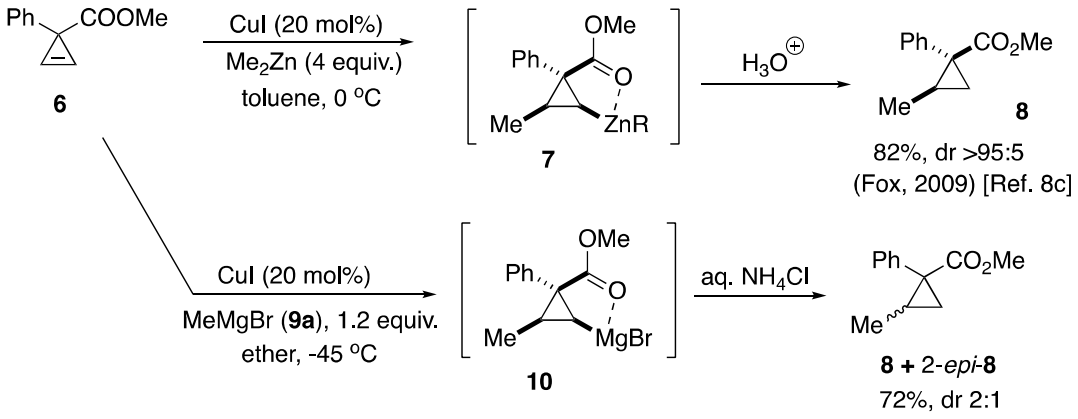
Scheme 1



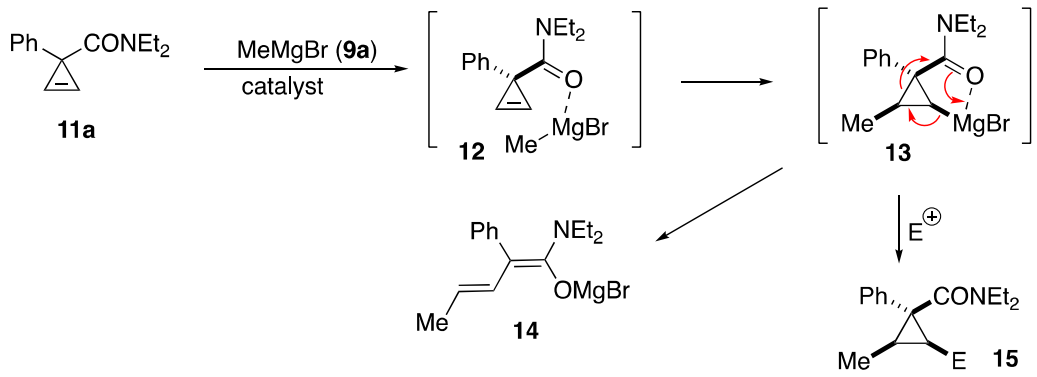
Scheme 2



Scheme 3



Scheme 4

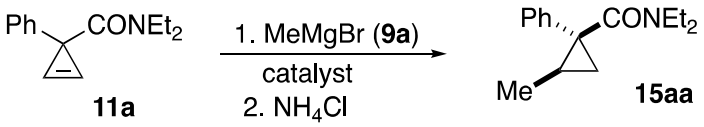


triggered a strain release-driven cleavage of the small ring in intermediate **4**, affording δ-ketoamides **5** (Scheme 2). Having developed several convenient preparative approaches to prochiral 1-alkyl-*N*,*N*-dimethylcycloprop-2-ene-1-carboxamides,[13] we envisioned them as very attractive synthons for synthesis of non-racemic cyclopropanes via asymmetric carbometallation reactions. The amide functionality has previously proved efficient as an activating and/or directing group in base-assisted addition of oxygen- and nitrogen based nucleophiles,[14] as well as in transition metal-catalyzed hydrometallation reactions of cyclopropenes; providing excellent diasteroselectivities in alltested transformations.[15] Herein, we exploit these substrates in directed carbomagnesiation reactions to assess the facial selectivity of addition with respect to parent esters, as well as the effect of sterics and the scope of compatible electrophilic reagents.

RESULTS AND DISCUSSION

Carbomagnesiation of prochiral cyclopropenes was first probed on the benchmark substrate methyl 1-phenylcycloprop-2-ene-1-carboxylate (**6a**). Fox has previously demonstrated the diastereoselective carbozincation, followed by electrophilic trapping, of **6** and several related esters to obtain the corresponding cyclopropylzinc species **7**. Methylated cyclopropane **8**, as well as ethyl and phenyl analogs were obtained in high yield and diastereoselectivity (Scheme 3).[8c] Analysis of literature data showed that most of the directed carbomagnesiations of cyclopropenes were carried out in the presence of excess Grignard reagents (up to 4 equiv.) and at least 20 mol% of copper(I)

Table 1. Optimization of reaction conditions for carbomagnesiation of cyclopropene-3-carboxamide **11a**



11a **15aa**

	Catalyst, (mol%)	MeMgBr	Solvent	Temperature, °C	Time, min	Yield, %[a]	dr[b]
1	CuI (20)	1.5 equiv.	Et_2O	-35	30	25	>99:1
2					60	76	>99:1
3					120	78	>99:1
4		2.0 equiv.			60	89	>99:1
5		3.0 equiv.				87	>99:1
6	CuI (10)	2.0 equiv.				89	>99:1
7	CuI (5)					86	>99:1
8	CuI (2.5)					63	>99:1
9	none					<2	ND
10	CuI (5)		MTBE			13	>99:1
11			THF			90	>99:1
12			DME			99	>99:1
13	$NiCl_2$ (10)					0	ND
14	$CoCl_2$ (10)					36	>99:1
15	$FeBr_2$ (10)					40	>99:1
16	$MnCl_2$ (10)					<2	ND
17	V(O)(acac)2 (10)					<2	ND
18	$Ti(Cp)_2Cl_2$ (10)					<2	ND
19	CuCN (5)					74	>99:1
20	CuBr (5)					64	>99:1
21	CuCl (5)					13	>99:1
22	$CuCl_2$ (10)					98	>99:1
23	CuI (5)			20		58	>99:1
24				0		97	>99:1
25					30	96	>99:1
26					15	94	>99:1
27					5	96	>99:1
28		1.35 equiv.				95	>99:1

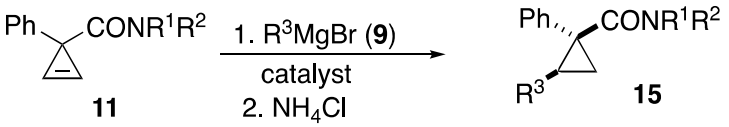
a) NMR yields of crude reaction mixtures using dibromomethane as the internal standard.

b) Diastereomeric ratios (cis:trans) were determined by NMR analysis of crude reaction mixtures. >99:1 ratios are reported for all cases when the minor diastereomer was not detected. Note "ND" indicates that the ratios were not determined due to very low yield of product.

catalyst (typically CuI or CuCN) in ether at temperatures below -20 °C.[7-12] In line with these previous findings, the reaction of ester **6** with excess MeMgBr (**9a**) in ether carried out at higher temperatures (0 °C and above) in the presence of 20 mol% CuI did not provide the desired product **8**, due to a concurrent attack of the Grignard reagent at the ester moiety to produce a tertiary alcohol. In contrast, the same reaction carried out below -60 °C did not proceed at all, returning starting material **6**. After optimization, it was found that carbomagnesiation of **6** was the most productive when carried out for 20 min between -45 and -35 °C, and quenched with aqueous ammonia at <-20 °C (Scheme 3). Interestingly, this reaction did not proceed at all when MeMgBr was added to the stirred solution of cyclopropene and copper catalyst. It was essential to pre-mix the Grignard reagent with CuI to generate Gilman cuprate, and then add the solution of cyclopropene slowly to this mixture. As a result, a mixture of diastereomeric esters (**8** and 2-*epi*-**8**) was obtained with low selectivity (Scheme 3).

The disappointing result provided by cyclopropenyl ester **6** was not surprising in view of relatively low coordinating ability of ester function. Accordingly, expectations were held high for cyclopropene-3-carboxamides **11**[13] (Scheme 4), with their increased tolerance toward Grignard reagents and stronger coordinating ability to Lewis acidic magnesium atom. The latter

Table 2. Carbomagnesiation of cyclopropene-3-carboxamides with various Grignard reagents



11 **15**

	11	R^1	R^2	9	R^3	15	Yield, %[a]	dr[b]
1	**11a**	Et	Et	**9a**	Me	**15aa**	96 (A)	>99:1
2	**11a**			**9b**	Et	**15ab**	83 (B)	>99:1
3	**11a**			**9c**	*i*-Bu	**15ac**	90 (B)	>99:1
4	**11a**			**9d**	Ph	**15ad**	93 (A)	>99:1
5	**11a**			**9e**	$CH=CH_2$	**15ae**	97 (A)	>99:1
6	**11a**			**9f**	$CH_2CH=CH_2$	**15af**	94 (A)	>99:1
7	**11a**			**9g**	CH_2SiMe_3	**15ag**	84 (A)	>99:1
8	**11a**			**9h**	C≡C-Ph	**15ah**	10[c]	>99:1
9	**11b**	*i*-Pr	*i*-Pr	**9a**	Me	**15ba**	94 (A)	>99:1
10	**11b**			**9d**	Ph	**15bd**	91 (A)	20:1
11	**11b**			**9e**	$CH=CH_2$	**15be**	88 (A)	>99:1
12	**11c**	Bn	Bn	**9a**	Me	**15ca**	95 (A)	>99:1
13	**11c**			**9d**	Ph	**15cd**	93 (A)	13:1
14	**11c**			**9e**	$CH=CH_2$	**15ce**	84 (A)	>99:1
15	**11d**	$-(CH_2)_4-$		**9a**	Me	**15da**	91 (A)	>99:1
16	**11d**			**9d**	Ph	**15dd**	87 (A)	>99:1
17	**11d**			**9e**	$CH=CH_2$	**15de**	82 (A)	>99:1
18	**11e**	$-(CH_2)_5-$		**9a**	Me	**15ea**	90 (A)	>99:1
19	**11e**			**9d**	Ph	**15ed**	89 (A)	>99:1
20	**11e**			**9e**	$CH=CH_2$	**15ee**	86 (A)	>99:1
21	**11f**	$-(CH_2)_2O(CH_2)_2-$		**9a**	Me	**15fa**	92 (A)	>99:1
22	**11f**			**9d**	Ph	**15fd**	81 (A)	>99:1
23	**11f**			**9e**	$CH=CH_2$	**15fe**	83 (A)	>99:1
24	**11g**	$CH_2CH=CH_2$	$CH_2CH=CH_2$	**9a**	Me	**15ga**	94 (A)	>99:1
25	**11g**			**9d**	Ph	**15gd**	95 (A)	9:1
26	**11g**			**9e**	$CH=CH_2$	**15ge**	80 (A)	>99:1
27	**11h**	Me	MeO	**9a**	Me	**15ha**	90 (A)	>99:1
28	**11i**	H	H	**9a**			NR[d]	
29	**11j**	H	*n*-Bu	**9a**			NR[d]	

a) Isolated yields of purified products. Reactions were carried out at 0 °C for 5 min or at -45 °C for 60 min according to methods A and B, respectively.

b) Diastereomeric ratios (*cis*:*trans*) were determined by ^{1}H NMR analysis of crude reaction mixtures. Ratios of >99:1 are reported in all cases when the minor diastereomer was not detected.

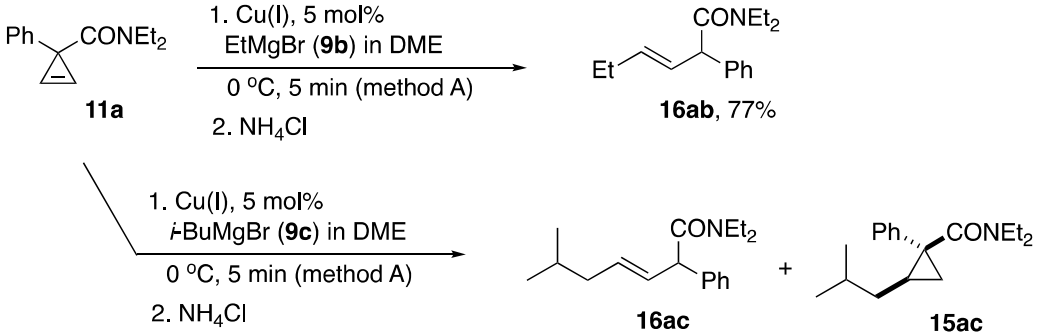
c) Ph-C≡CMgBr was prepared in situ by stirring MeMgBr with excess phenylacetylene for 1 h at 55 °C. The reaction with cyclopropene was then carried out for 60 min at 0 °C.

d) Starting cyclopropenes were returned intact.

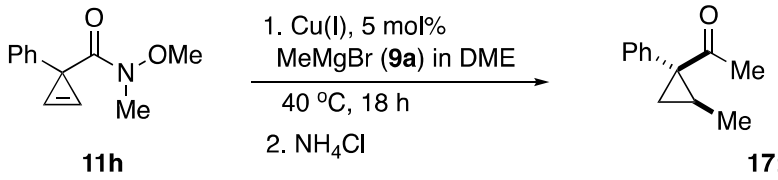
would lead to better stabilization of coordination complex **12**, as well as the key cyclopropylmagnesium intermediate **13**, thus ensuring a better overall diastereoselectivity of the process. Finally, since the amide function has reduced anion-stabilizing ability, intermediate **13** was expected to have much lower propensity towards ring cleavage to produce olefin by-products **14**, which were abundant in the carbometallation of parent esters.[8b,16]

With these considerations in mind, we subjected a solution of amide **11a** to the pre-mixed Gilman reagent generated from 20 mol% of CuI and 1.5 equiv. of MeMgBr (**9a**) in diethyl ether at -35 °C (Table 1, entries 1-3). To our delight, the desired carbomagnesiation proceeded with perfect diastereoselectivity, albeit rather sluggishly; with only 25% of product **15aa** formed in first30 min (entry 1). The conversion improved slightly within the next half hour (entry 2), after which time the reaction has practically stopped, with no significant progress observed upon further stirring (entry 3). To give the reaction a boost, we increased the concentration of the Grignard reagent, which resulted in no improvement (entries 4-5). Interestingly, reducing

Scheme 5



Scheme 6



the amount of copper down to 5% did not affect the reaction rate (entries 6-7); however, further decrease of the catalyst load dropped the efficiency of carbomagnesiation (entry 8), which in the absence of metal did not proceed at all (entry 9). Screening of several most common ethereal solvents showed good conversion for all but methyl *tert*-butyl ether (MTBE, entry 10). The best results were obtained using 1,2-dimethoxyethane (DME), in which nearly quantitative yield of **15aa** was obtained after 1 hour, with perfect diastereoselectivity (entry 12). Next, we evaluated different copper salts and other related metal catalysts. Most of the tested transition metals were no match for copper (Table 1, entries 13-18). Marginal catalytic activity was observed for cobalt(II) (entry 14) and iron(II) (entry 15), whereas reactions using other metals afforded no product at all. Catalytic performance of copper(I) salts decreased in the series CuI > CuCN > CuBr > CuCl. This trend is collinear with the solubility of these salts in ethereal solvents which, in turn, affects the formation of the reactive cuprate species. Surprisingly good results were obtained in the presence of catalytic amounts of copper(II) chloride (entry 22), which, apparently, was reduced in situ into copper(I). However, the Cu(II) salt was eliminated due to its moisture-sensitive nature, and all further work was performed using copper(I) iodide. An attempt to carry out carbomagnesiation at room temperature resulted in dramatic reduction of the yield (entry 23), mainly due to formation of resins. It was discovered, however, that the reaction proceeded much faster at 0 °C in a span of 5 min without significant loss of the overall efficiency (entries 24-27). These milder conditions also allowed for cutting down the excess Grignard reagent to only 1.35 equiv. (entry 28). Carbomagnesiation performed in a preparative scale (method A, see Experimental Part for details) afforded cyclopropane **15aa** in 96% isolated yield (Table 2, entry 1).

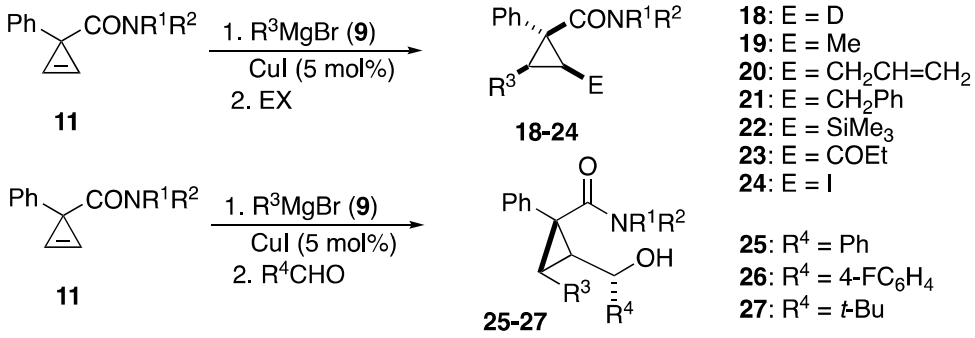
With optimized conditions for addition of MeMgBr in hand, we tested the reactivity of cyclopropene-3-carboxamide **11a** towards other Grignard reagents. Interestingly, use of EtMgBr (**9b**) under conditions of method A (at 0 °C) resulted in ring opening affording hex-3-enamide **16aa** as a sole product in 77% yield (Scheme 5). Similar results were obtained in the reaction involving *i*-BuMgBr (**9c**), except the corresponding enamide **16ac** was produced as an inseparable mixture with normal cyclopropane product **15ac**, and thus was not isolated in individual form (Scheme 5). We reasoned that this problem can be alleviated by decreasing the reaction temperature and extending the time to achieve full conversion (this protocol is

reported as Method B, see Experimental Part for details). Accordingly, both Grignard reagents **9b** and **9c** were added to cyclopropene **11a** at -45 °C affording the corresponding alkylated cyclopropanes **15ab** and **15ac** in high yield (Table 2, entries 2-3). All other Grignard reagents tested in the carbomagnesiation of **11a** did not show any signs of ring opening under conditions of Method A, allowing for fast and diastereoselective addition of phenyl (**15ad**), vinyl (**15ae**), allyl (**15af**), and trimethylsilylmethyl (**15ag**) moieties in the three-membered rings (entries 4-7). Our attempts to add magnesium acetylenide species **9h** resulted in a very sluggish reaction. Both reactants remained essentially intact under the standard reaction conditions, affording disappointedly low yield of the coupling product **15ah** (entry 8). It should be mentioned that ring retentive addition of metal acetylenides to cyclopropenes has always posed a challenge.[5b,7a,17]

We have also explored the relative reactivity of tertiary cyclopropene-3-carboxamide derivatives bearing various substituents at nitrogen atom with benchmark Grignard reagents **9a**, **9d**, and **9e**. We were pleased to find that carbomagnesiation of a wide variety of amides, including bulky *N*,*N*-diisopropyl amide **11b** (Table 2, entries 9-11), potentially deprotectable *N*,*N*-dibenzylamide **11c** (entries 12-14), and *N*,*N*-diallylamide **11g** (entires 24-26), as well as derivatives of pyrrolidine (**11d**, entries 15-17), pyrimidine (**11e**, entries 18-20), and morpholine (**11f**, entries 21-23) was very efficient and yielded a single product under conditions of method A (5 min at 0 °C). In a few cases addition of PhMgBr (**9d**) was somewhat less selective (entries 10, 13, 25). Typically, crude material obtained after aqueous work up and extraction of the reaction mixture was of sufficient purity for any practical synthetic application. For analytical purposes, all products were additionally purified by column chromatography.

Reaction of Wienreb amide **11h** with MeMgBr under conditions of method A proceeded highly chemo- and stereoselectively, affording the corresponding adduct **15ha** with preserved amide function (Table 2, entry 27). However, carrying out this transformation in the presence of excess Grignard reagent at 40

Table 3. Probing of different electrophilic reagents in the directed carbomagnesiation of cyclopropene-3-carboxamides



	11	R^1, R^2	9	R^3	EX	Product	Yield, %[a]	dr[b]
1	**11a**	Et, Et	**9a**	Me	MeOD	**18aa**	98	>99:1
2	**11a**		**9e**	$CH=CH_2$		**18ae**	86	>99:1
3	**11a**		**9a**	Me	MeI	**19aa**	86	>99:1
4	**11b**	*i*-Pr, *i*-Pr	**9e**	$CH=CH_2$		**19be**	81	7:1
5	**11e**	$-(CH_2)_4-$	**9d**	Ph		**19ed**	87	>99:1
6	**11a**	Et, Et	**9a**	Me	$CH_2=CHCH_2Br$	**20aa**	87	>99:1
7	**11f**	$-(CH_2)_2O(CH_2)_2-$	**9d**	Ph		**20fd**	87	>99:1
8	**11g**	$CH_2CH=CH_2$, $CH_2CH=CH_2$	**9e**	$CH=CH_2$		**20ge**	76	>99:1
9	**11a**	Et, Et	**9a**	Me	$PhCH_2Br$	**21aa**	82	>99:1
10	**11c**	Bn, Bn	**9d**	Ph		**21cd**	79	15:1
11	**11d**	$-(CH_2)_3-$	**9e**	$CH=CH_2$		**21de**	80	>99:1
12	**11a**	Et, Et	**9a**	Me	Me_3SiCl	**22aa**	72	>99:1
13	**11a**		**9a**		EtCOCl	**23aa**	79	>99:1
14	**11c**	Bn, Bn	**9e**	$CH=CH_2$		**23ce**	52	>99:1
15	**11d**	$-(CH_2)_3-$	**9d**	Ph		**23dd**	80	>99:1
16	**11a**	Et, Et	**9a**	Me	I_2	**24aa**	63	>99:1
17	**11c**	Bn, Bn	**9e**	$CH=CH_2$		**24ae**	51	>99:1
18	**11a**	Et, Et	**9a**	Me	PhCHO	**25aa**	60	92:8[c]
19	**11a**		**9d**	Ph		**25ad**	80	96:4[c]
20	**11a**		**9d**		$4\text{-}FC_6H_4CHO$	**26ad**	88	93:7[c]
21	**11a**		**9a**	Me	*t*-BuCHO	**27aa**	79	>98:2
22	**11a**		**9d**	Ph		**27ad**	83	>99:1

23	**11a**	**9g**	CH_2SiMe_3	**27ag**	79	>99:1
24	**11h**	**9a**	Me	**27ha**	82	>98:2

a) Isolated yields of purified products. Deuterium purity for compounds **18aa** and **18ae** was 92-94% (measured by ^{1}H NMR).

b) Diastereomeric ratios (*cis*:*trans*) were determined by ^{1}H NMR analysis of crude reaction mixtures. Ratios of >99:1 are reported in all cases when the minor diastereomer was not detected.

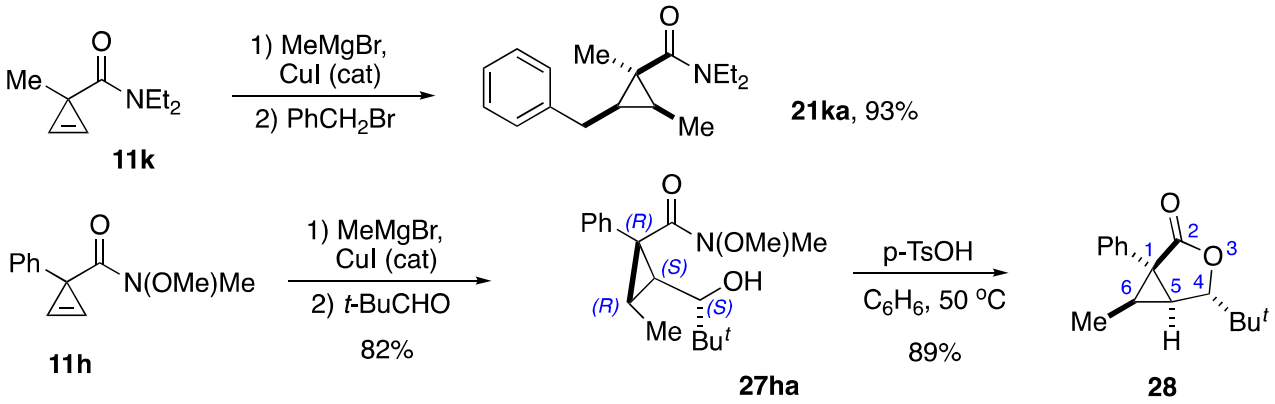
c) Listed are dr's of epimers at the tertiary alcohol stereogenic center. Facial selectivity of carbomagnesiation was >99:1 in all these examples.

°C for an extended period of time allowed for nucleophilic attack at both electrophilic moieties to give ketone **17** in good yield as a sole product (Scheme 6).

It should also be mentioned that this copper-catalyzed carbomagnesiation reaction is applicable to tertiary amides only, and all our attempts to engage primary (**11i**) and secondary (**11j**) analogs in this transformation resulted in recovery of starting materials (Table 2, entries 28-29).

Having explored the scope of substrates, we next looked into a possibility to introduce an additional substituent in the cyclopropyl ring by intercepting the intermediate cyclopropyl anion with a suitable electrophilic species. To this end, cyclopropenes **11a-c**,**f**,**g** were subjected to copper-catalyzed methyl-, phenyl-, or vinylmagnesiation followed by treatment with an S_N2-activealkyl halide, such as methyl iodide, allyl bromide, or benzyl bromide. In all but one examples, *cis*,*cis*-adducts **19**, **20** and **21** were obtained as sole products in high yield (entries 3-4, 6-11). This configuration was unambiguously confirmed by single crystal X-ray crystallography of product **19ed** (Figure 1). Notable deterioration of the diastereoselectivity (down to 7:1)

Scheme 7



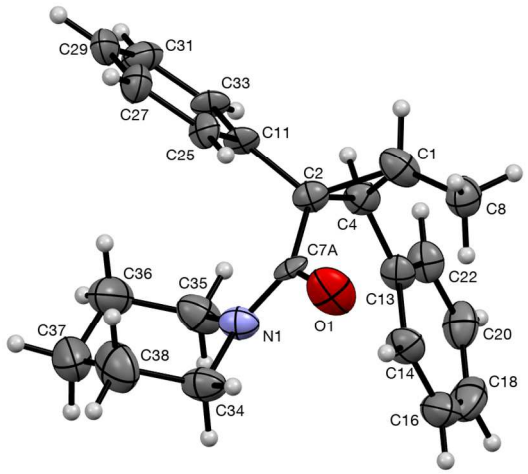


Figure 1. ORTEP drawing of crystal structure of compound **19ed** (major diastereomer) showing atom-labeling scheme and 50% probability thermal ellipsoids. Only one population of disordered molecules is shown for clarity – See Supporting Information for details.

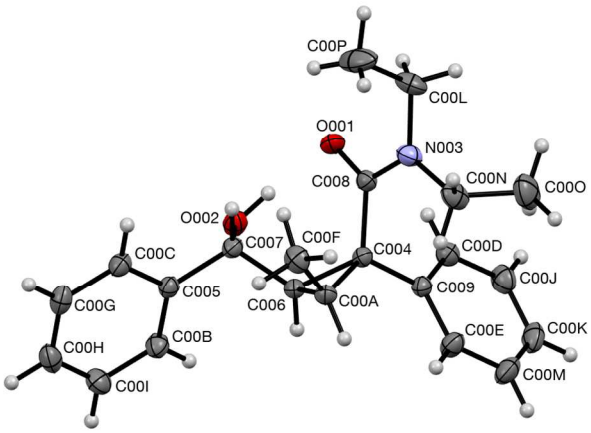


Figure 2. ORTEP drawing of crystal structure of product **25aa** (major diastereomer) showing atom-labeling scheme and 50% probability thermal ellipsoids. Only one population of disordered of *N*-Et group is shown for clarity – See Supporting Information for details.

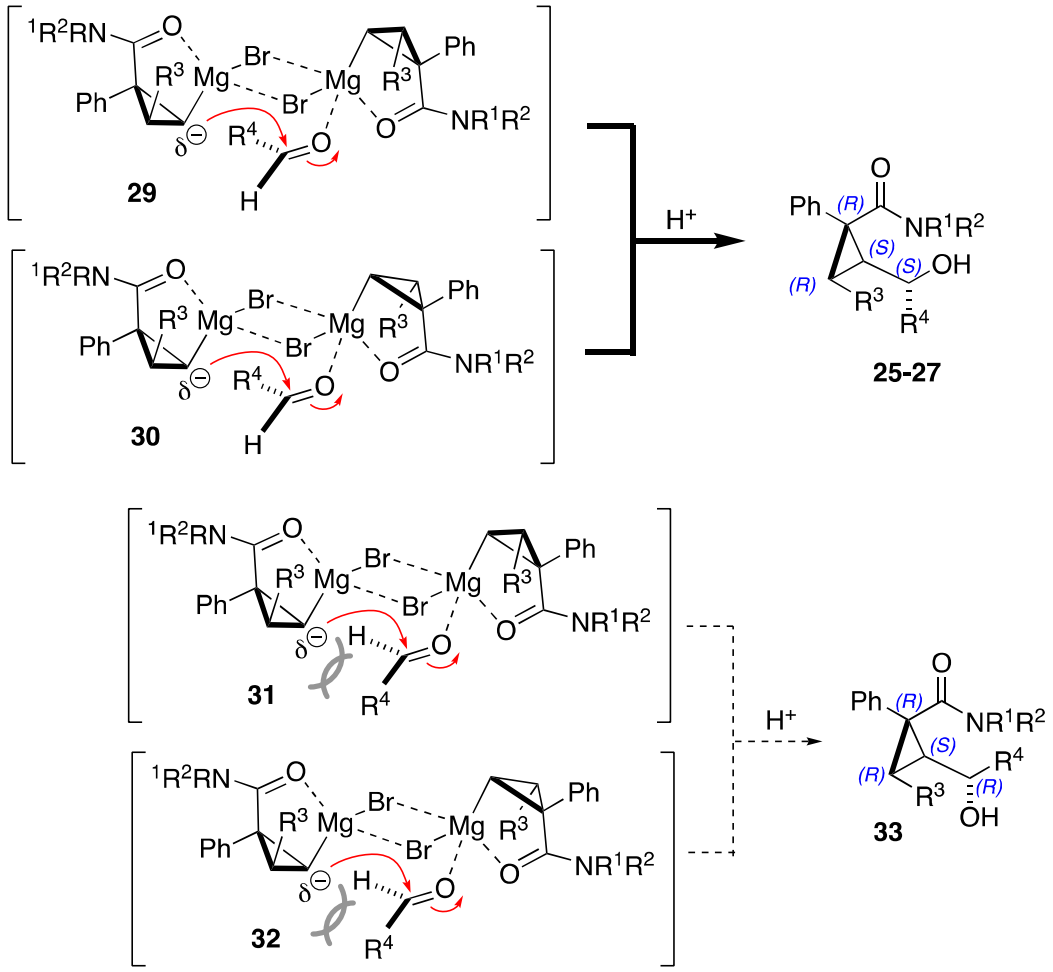
was observed only in the case of a very bulky *N*,*N*-diisopropylamide group (Table 3, entry 4). Furthermore, *N*,*N*-diethyl-1-methylcycloprop-2-ene-1-carboxamide (**11k**) bear-

ing methyl substituent at cyclopropene sp^3-hybridized carbon atom next to the amide function underwent smooth reaction under the typical conditions, affording product **21ka** in high yield (Scheme 8).

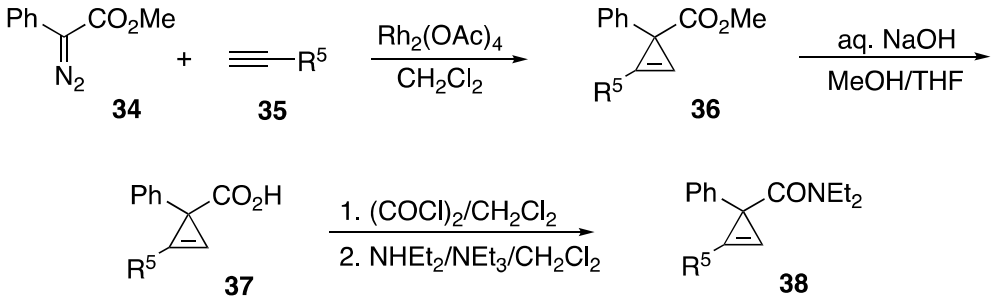
Electrophilic trapping with trimethylsilyl chloride was also successful, providing the corresponding silylcyclopropane **22aa** (entry 12). We found, however, that silyl electrophiles are compatible only with methylmagnesiation reaction. Attempts to couple silylation with phenyl- or vinylmagnesiation of **11a** resulted in protonated products **15ad** and **15ae**, respectively. Electrophilic trapping of cyclopropylmetal species with acyl chlorides was also probed to access cyclopropyl ketones. Acyl chlorides must be freshly distilled and free of acid to avoid competitive protonolysis of cyclopropyl magnesium intermediate. Due to significant steric bulk, the second-fold addition of cyclopropylmetal species to carbonyl group did not pose a problem, and the corresponding ketones **23** were isolated in reasonable yields and with excellent *cis*-selectivity (entries 13-15). Trapping with iodine also proceeded smoothly affording stereochemically defined cyclopropyl iodides (entries 16, 17). We have also tested methanol-*d* quench to obtain deuterium-labeled cyclopropanes **18aa** and **18ae** (Table 3, entries 1-2). Incorporation of deuterium label in both cases occurred selectively in *cis*-fashion, with the isotopic purity of 92-94%.

We were also intrigued by the idea of employing aldehydes as the electrophiles in this transformation to obtain cyclopropylmethanol derivatives **25-27** bearing an additional stereogenic center at the hydroxyl group. This approach, while known for almost 40 years, typically suffers from poor diastereoselectivity when a chiral cyclopropylmetal reagent is added to a prochiral aldehyde, normally affording a nearly equimolar mixture of two isomers.[18] Prior attempts to enforce the selectivity through intramolecular coordination of the cyclopropylmagnesium species with an appropriate Lewis base, resulted in modest diastereoselectivity of ~2:1.[12] Marek has shown an elegant alternative route through employment of sterically hindered acylsilanes in place of aldehydes. Combined with protiodesilation, this method allowed for a much more selective synthesis of cyclopropylmethyl alcohols, with dr's ranging from 91:9 to 95:5.[12] We hoped that the profound templating effect of the amides would allow for superior control of the diastereoselectivity in the direct reaction with aldehydes. To probe this idea, we carried out carbomagnesiation of cyclopropene **11a** with

Scheme 8



Scheme 9

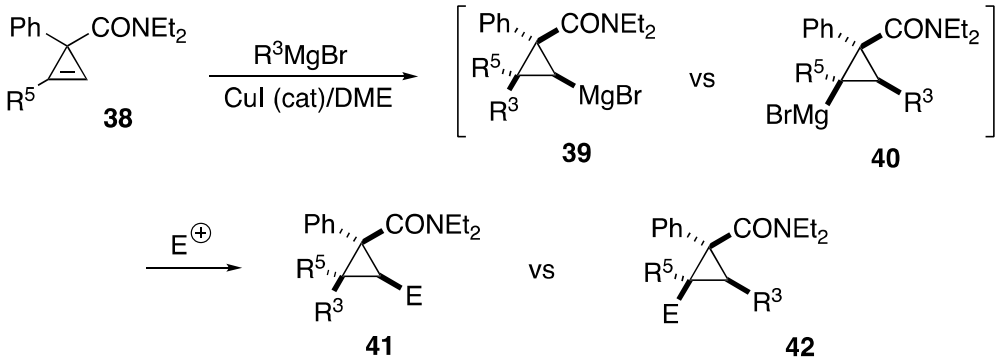


35a, **36a**, **37a**, **38a**: R^5 = n-Bu
35b, **36b**, **37b**, **38b**: R^5 = Ph;
35c, **36c**, **37c**, **38c**: R^5 = 4-MeC_6H_4;
35d, **36d**, **37d**, **38d**: R^5 = 4-FC_6H_4;
35e, **36e**, **37e**, **38e**: R^5 = 4-$MeOC_6H_4$;
35f, **36f**, **37f**, **38f**: R^5 = 4-$CF_3C_6H_4$

methylmagnesium bromide (**9a**) and treated the resulting mixture with benzaldehyde. The target cyclopropylmethanol **25aa** was indeed obtained in good yield and with respectable diastereoselectivity of 92:8 (Table 3, entry 18). A bulky cyclopropylmetal species generated from **11a** upon treatment with phenylmagnesium bromide (**9d**) afforded the corresponding products **25ad** and **26ad** in excellent yields and high dr's (entries 19-20). When pivalaldehyde was used as the electrophile, single diastereomers were produced regardless of the nuceleophilic component employed (Table 3, entries 21-24). Also, compatibility of Winereb amide function in substrate **11h** was demonstrated, allowing for preparation of alcohol **27ha** as a single diastereomer (entry 24). Winereb amide **27ha** was then used to establish the relative configuration of stereogenic centers in the products. Acid-catalyzed hydrolysis of the amide moiety was accompanied with spontaneous cyclization to furnish bicyclic lactone **28** (Scheme 7), in which *cis*- relation- ship of *tert*-butyl substituent at C-4 and bridgehead hydrogen at C-5 was confirmed by 2D-NOESY experiment.[19] Independently, the relative configuration of adduct **25aa** was unambiguously confirmed by single crystal X-ray diffraction (Figure 2). Evidently, this stereochemistry resulted from an effective chelation of electrophilic aldehyde with Lewis-acidic magnesium atom. Typically, the addition of Grignard reagents to a carbonyl group is believed to proceed via a six-membered transition states, involving two molecules of organylmagnesium species. Since in our case these reagents formed are chiral and racemic, one can envision formation of two types of diastereomeric dimers, with C_2-symmetric (complexes **29** and **31**) or C_i-symmetric (complexes **30** and **32**) arrangement organyl ligands around halogen-bridged bis-magenesium clusters, respectively (Scheme 8). It should be pointed out, that the R^3 group installed upon addition of a Grignard reagent to cyclopropene, blocks the approach to the *Re*-face of the electrophile due to unfavorable steric interaction with group R^4, rendering coordination complexes **31** and **32** highly unfavorable (Scheme 8) and leaving the *Si*-face attack as the only available option (complexes **29** and **30**). Hence, (*R**,*R**,*S**,*R**)-**33** is formed in small quantities or not observed at all; while diastereomers **25-27** with (*R**,*R**,*S**,*S**)-configuration are afforded as major or the only products (Scheme 8).

To fully understand the effect of the steric factors, we also tested carbomagnesiation of cyclopropenylcarboxamides **38** bearing a substituent at the double bond, easily available via the Rh-catalyzed cyclopropenation of terminal alkynes **35** (Scheme 9).[20] Several studies of directed or non-directed addition of organometallic species to cyclopropenes bearing a substituent at the double bond have been reported.[21] In all these contributions, the regioselectivity of addition was governed by electronic factors, resulting in geminally-substituted products, with the organyl group being added to the more substituted olefin carbon.

Table 4. Reverse of the Regioselectivity in the Amide-Directed Catalytic Carbomagnesiation of Cyclopropenes **38** with Substituted Double Bond



	38	R^5	9	R^3	EX	Product[a]	Yield, %[b]	dr[c]	42:41
1	**38a**	*n*-Bu	**9a**	Me	NH_4Cl	**41aa**	90	>98:2	12:88

2	**38a**		**9e**	$CH=CH_2$	(E = H)	**41ae**	88	>98:2	19:81
3	**38a**		**9d**	Ph		**42ad**	91	>98:2	70:30
4	**38a**		**9g**	CH_2SiMe_3		**42ag**	75	>98:2	75:25
5	**38b**	Ph	**9a**	Me		**42ba**	92	>98:2	91:9
6	**38b**		**9d**	Ph		**42bd**	89	>98:2	>98:2
7	**38b**		**9e**	$CH=CH_2$		**42be**	84	>98:2	>98:2
8	**38b**		**9g**	CH_2SiMe_3		**42bg**	70	>98:2	>98:2
9	**38c**	4-MeC_6H_4	**9a**	Me		**42ca**	97	>98:2	86:14
10	**38d**	4-FC_6H_4	**9a**			**42da**	99	>98:2	95:5
11	**38e**	4-$MeOC_6H_4$	**9a**			**42ea**	52	>98:2	90:10
12	**38f**	4-$CF_3C_6H_4$	**9a**			**42fa**	93	>98:2	>98:2
13	**38b**	Ph	**9a**	Me	MeI (E = Me)	**42bh**	91	>98:2	N/A[d]

a) Major regioisomer is shown.

b) Combined yield of purified product isolated as a mixture of regioisomers **41** and **42.**

c) Facial selectivity measured by ^{1}H NMR and/or GC analysis of crude reaction mixtures. >98:2 indicates the minor diastereomers were not detected.

d) Products **41bh** and **42bh** are indistinguishable, since R^3 = E in this case.

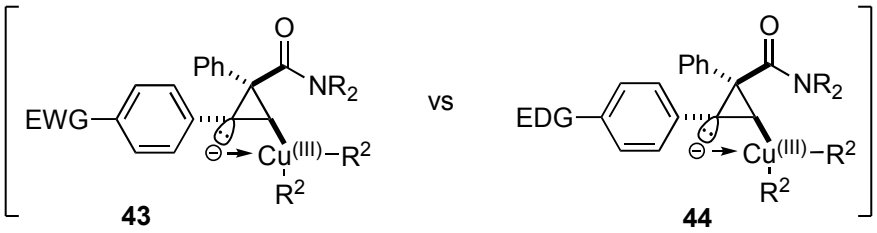


Figure 3. Electronic control of regioselectivity in cuprate addition to cyclopropenes

The opposite regioselectivity resulting from an overwhelming sterics created by an extremely bulky bis-(*tert*-butyl)magnesium reagent was shown on a single example and required relatively harsh conditions causing partial cleavage of the cyclopropyl ring.[22] We reasoned that strong coordination of the organometallic moiety to a sterically demanding carboxamide group would amplify the effect of steric factors and divert the regioselectivity of carbomagnesiation toward predominant formation of the alternate cyclopropylmetal species **40** (Scheme for Table 4). To test this idea, we treated *n*-butylsubstituted cyclopropene-3-carboxamide **38a** with various Grignard reagents. It was found that compact methylmagnesium bromide (**9a**) gave a non-selective reaction, mostly providing the "normal" carbomagnesiation product **41aa** accompanied by small amounts of regioisomer **42aa** (Table 4, entry 1). Similar results were obtained in the reaction of another non-bulky Grignard reagent, vinylmagnesium bromide (**9e**) (entry 2). A notable reversal of the regiochemistry was observed with more sterically demanding PhMgBr (**9d**) and Me_3SiCH_2MgBr (**9g**), which gave rise to **42ad** and **42ag** as the the major products (entries 3, 4). The profound effect of steric factors was even more evident in carbomagnesiation of 1-arylsubstituted cyclopropenes **38b-f** (entries 5-13). Thus, a respectable diastereomeric ratio of 91:1 was observed in the reaction of **38b** with MeMgBr reagent (entry 5), while all other Grignard reagents tested exclusively provided adducts **42bd**, **42be**, **42bg** (entries 6-8). We next looked at the effect of electronic factors on the regiochemistry of this directed addition. To this end, cyclopropenes **38c-f** bearing aryl substituents with different electronic properties were synthesized from the corresponding arylacetylenes **35c-f** (Scheme 9) and then subjected to the directed copper-catalyzed carbomagnesiation with MeMgBr (**9a**). In line with our expectations illustrated below in Figure 3, there was a significant improvement of the regioselectivity in reactions of electron poor substrates **38d** and **38f** as compared to more electron rich analogs **38c** and **38e** (Table 4, entries 9-12). A sterically controlled nucleophilic attack of the cuprate induces polarization of the double bond causing a negative charge build up on the carbon adjacent to the aromatic substituent. In this situation, the presence of an electron-withdrawing group helps stabilize intermediate **43** as opposed to **44** (Figure 3).

Finally, a possibility to trap the anionic intermediate with an electrophile other than proton was probed by intercepting methylmagnesiation reaction of cyclopropene **38b** with MeI. In a single reaction tested, a pentasubstituted cyclopropane **42bh** was isolated as a sole product in high yield (Table 4, entry 13). Further studies of this approach, including installation of non-symmetric substituents with simultaneous control of regio- and diastereoselectivity is currently underway in our laboratories.

CONCLUSION

In conclusion, an efficient synthetic protocol for the copper-catalyzed, directed carbomagnesiation of cyclopropene-3-carboxamides was developed. It was demonstrated that the carboxamide group at C-3 serves as a superior directing group for this reaction permitting a very effective control of diastereoselectivity. The use of cyclopropenylcarboxamides also allows for a wide range of Grignard reagents to be employed in carbomagnesiation of the smallest cyclic olefins, in complement to the carbozincation reaction, which requires often less readily available organozinc reagents. Successful trapping of cyclopropylmagnesium species with various electrophilic reagents showcased the synthetic application of the described transformation. High degree of diastereoselectivity control achieved in the reaction with aldehydes allowed for preparation of cyclopropylmethanols bearing four contiguous stereogenic centers (in racemic form). Steric and electronic factors affecting the regioselectivity of carbomagnesiation of C-1 substituted cyclopropenes were also analyzed.

EXPERIMENTAL PART

General

NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz) with a dual carbon/proton cryoprobe (CPDUL). ^{13}C NMR spectra were registered with broadband decoupling. The (+) and (-) designations represent positive and negative intensities of signals in ^{13}C DEPT-135 or ^{1}H-^{13}C HSQC experiments. IR spectra were recorded on a ThermoFisher Nicolet™ iS™ 5 FT-IR Spectrometer. HRMS was carried out on LCT Premier (Micromass Technologies) instrument employing ESI TOF detection techniques. Glassware used in moisture-free syntheses was flame-dried in vacuum prior to use. Column chromatography was carried out on silica gel (Sorbent Technologies, 40-63 mm). Pre-coated silica gel plates (Sorbent Technologies Silica XG 200 mm) were used for TLC analyses. Anhydrous dichloromethane was obtained by passing degassed commercially available HPLC-grade inhibitor-free solvent consecutively through two columns filled with activated alumina and stored over molecular sieves under nitrogen. Water was purified by dual stage deionization followed by dual stage reverse osmosis. Anhydrous THF and DME were obtained by refluxing commercially available solvents over calcium hydride followed by distillation in a stream of dry nitrogen. All other reagents and solvents were purchased from commercial vendors and used as received. Preparation of cyclopropenes **11a-j**, **38a-b** was described in details in our previously published report and their physical and spectral data are also described therein.[13b] Cyclopropene **11k** was obtained via 1,2-dehydrobromination of the corresponding bromocyclopropane according to the previously published procedure.[23] Syntheses of cyclopropenes **38c-f** is described below.

Preparation of starting materials

Methyl 1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (36c): 25 mL 2-neck flask was charged with *p*-tolylacetylene (**35c**) (1.0 g, 8.61 mmol, 1.5 equiv.), rhodium(II) acetate dimer (25.0 mg, 0.115 mmol, 0.02 equiv.), and 7 mL dichloromethane. The mixture was stirred under inert nitrogen atmosphere at room temperature, and methyl 2-diazo-2-phenylacetate (**34**) (1.0 g, 5.74 mmol, 1.0 equiv.) in solution in DCM (5 mL) was added via syringe pump over 18 hours, and then stirred for an additional 3 h. The reaction mixture was then evaporated and the residual oil was purified by silica gel column chromatography eluting with a mixture of hexane and ethyl acetate (6:1). The titled compound was obtained as a pale yellow solid, mp 73.1 – 75.9 ^{o}C, R_f 0.26. Yield 761 mg (2.88 mmol, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.44 – 7.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 7.16 (s, 1H), 3.74 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 141.2, 140.5, 130.0 (+, 2C), 129.7 (+, 2C), 128.3 (+, 2C), 128.1 (+, 2C), 126.5 (+), 122.7, 117.1, 99.2 (+), 52.2 (+), 33.5, 21.7 (+); FTIR (KBr, cm^{-1}): 3025, 2948, 1719, 1504, 1433, 1210, 1020, 820, 699; HRMS (TOF ES): Found 287.1053, calculated for $C_{18}H_{16}O_2Na$ (M+Na) 287.1048 (1.7 ppm).

Methyl 2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylate (36d): This material was obtained according to the protocol described above for the synthesis of compound **36c** starting from 1-ethynyl-4-fluorobenzene (**35d**) (1.0 g, 8.32 mmol, 1.5 equiv.), rhodium(II) acetate dimer (25.0 mg, 0.111 mmol, 0.02 equiv.) and methyl 2-diazo-2-phenylacetate (**34**) (977 mg, 5.55 mmol, 1.0 equiv.). The reaction mixture was then evaporated and purified by using 6:1 mobile phase. Crude product was purified by preparative column chromatography on silica gel eluting with a mixture of hexane/EtOAc (6:1). The titled compound was obtained isolated as amorphous solid, R_f 0.26. Yield 1.21 g (4.51 mmol, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 7.20 (s, 1H), 7.17 – 7.10 (m, 2H), 3.73 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 163.6 (d, J = 251.0 Hz), 140.7, 131.9 (+, d, J = 9.0 Hz, 2C), 128.2 (+, 2C), 128.1 (+, 2C), 126.6 (+), 121.8 (d, J = 3.5 Hz), 116.5, 116.2 (+, d, J = 21.9 Hz, 2C), 99.8 (+, d, J = 2.7 Hz), 52.3 (+), 33.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.1 (s, 1F); FTIR (KBr, cm^{-1}): 2951, 1723, 1599, 1503, 1434, 1223, 1014, 840, 699; HRMS (TOF ES): Found 291.0799, calculated for $C_{17}H_{13}O_2FNa$ (M+Na) 291.0792 (2.4 ppm).

1-Phenyl-2-(*p*-tolyl)cycloprop-2-ene-1-carboxylic acid (37c): A solution of methyl 1-phenyl-2-(*p*-tolyl)cycloprop-2-ene-1-carboxylate (**36c**) (300 mg, 1.13 mmol, 1.0 equiv.) in a mixture of methanol and tetrahydrofuran (1:1, 20 mL) was stirred at 0 ^{o}C. An aqueous solution of sodium hydroxide (1.5 M, 8 mL, 12 mmol) was added dropwise and the mixture was stirred for 18 h. Organic solvents were then removed under reduced pressure and the remaining aqueous solution was added to dichloromethane (20 mL). The mixture was acidified with 1N aqueous HCl to pH 2. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The obtained product was pure enough to be used in further amide coupling as is, however, if necessary, further purification can be achieved by column chromatography on silica gel eluting with a mixture of hexane and EtOAc (3:1). The titled compound was obtained as a colorless solid, mp 134.5 – 135.9 ^{o}C, R_f 0.19. Yield 261 mg, 1.04 mmol, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.45 – 7.39 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.18 (m, 3H), 7.13 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.3, 140.7, 140.4, 130.1 (+, 2C), 129.8 (+, 2C), 128.5 (+, 2C), 128.1 (+, 2C), 126.7 (+), 122.4, 116.7, 98.7 (+), 33.2, 21.7 (+); FT IR (KBr, cm^{-1}): 3137, 3025, 1684, 1408, 1224, 1173, 819, 698; HRMS (TOF ES): Found 251.1075, calculated for $C_{17}H_{15}O_2$ (M+H) 251.1072 (1.2 ppm).

2-(4-Fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylic acid (37d): This material was obtained according to the protocol described above for the synthesis of compound **37c** starting from methyl 2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylate (**36d**) (300 mg, 1.12 mmol, 1.0 equiv.) The obtained product is typically pure enough to be used in further amide coupling as is, however, if necessary, further purification can be achieved by column chromatography on silica gel eluting with a 1:1 hexane:ethyl acetate mixture. The titled compound was obtained as a colorless solid, mp 138.9 – 140.2 °C, R_f 0.26. Yield 257 mg (1.01 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.41 – 7.37 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 (s, 1H), 7.15 – 7.09 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.8, 163.8 (d, *J* = 251.6 Hz), 139.9, 132.1 (+, d, *J* = 9.0 Hz, 2C), 128.4 (+, 2C), 128.3 (+, 2C), 127.0 (+), 121.5 (d, *J* = 2.9 Hz), 116.4 (+, d, *J* = 21.9 Hz, 2C), 116.3, 99.4 (+, d, *J* = 2.9 Hz), 33.3; FTIR (KBr, cm^{-1}): 3138, 3025, 1686, 1599, 1502, 1408, 1227, 837, 698; HRMS (TOF ES): Found 277.0645, calculated for $C_{16}H_{11}FO_2Na$ (M+Na) 277.0641 (1.4 ppm).

***N*,*N*-Diethyl-1-phenyl-2-(*p*-tolyl)cycloprop-2-ene-1-carboxamide (38c):** Solution of 1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxylic acid **(37c)** (250 mg, 1.0 mmol, 1.0 equiv.) and DMF (2 drops) in freshly distilled anhydrous dichloromethane (7 mL) was stirred in a flame dried round bottom flask under nitrogen atmosphere. Oxalyl chloride (130 µL, 190 mg, 1.5 mmol, 1.5 equiv.) was then added slowly dropwise and stirred at room temperature for 2 h. The solution was then evaporated under reduced pressure to provide a pale yellow solid material. This material was dissolved in freshly dried dichloromethane (6.0 mL) and added dropwise to a solution of diethylamine (206 µL, 146 mg, 2.0 mmol, 2.0 equiv.) and triethylamine (280 µL, 202 mg, 2.0 mmol, 2.0 equiv.), stirred in a flame dried two neck round bottom flask under an inert nitrogen atmosphere. The reaction mixture was then stirred for 18 hours and then partitioned between water and dichloromethane. The aqueous phase was then acidified using 1*N* HCl to a pH 2. The organic phase was then extracted with properly acidified water (pH 2, 3 x 10 mL). The combined acidic aqueous layers were then back extracted once with dichloromethane which was combined with other organic layers, washed with brine, dried, filtered, and concentrated. The product was then purified by silica gel column chromatography eluting with a mixture of hexane and EtOAc (3:1) to afford the titled compound as a colorless solid, mp 123.3 – 125.7 °C, R_f 0.29. Yield 288 mg (0.943 mmol, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.32 – 7.23 (m, 4H), 7.22 – 7.12 (m, 3H), 7.03 (s, 1H), 3.53 (dq, *J* = 14.3, 7.1 Hz, 2H), 3.31 (dq, *J* = 14.0, 7.1 Hz, 2H), 2.33 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 142.9, 139.9, 130.4 (+, 2C), 129.4 (+, 2C), 128.4 (+, 2C), 126.2 (+), 126.1 (+, 2C), 123.5, 122.1, 97.8 (+), 42.2 (-), 39.0 (-), 35.4, 21.7 (+), 13.8 (+), 12.7 (+); FT IR (KBr, cm^{-1}): 3081, 3023, 2972, 2933, 1625, 1457, 1275, 1118, 820, 700. HRMS (TOF ES): Found 328.1682, calculated for $C_{21}H_{23}NONa$ (M+Na) 328.1677 (1.5 ppm).

***N*,*N*-Diethyl-2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxamide (38d):** Solution of 2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylic acid (**37d**) (250 mg, 1.0 mmol, 1.0 equiv.) and DMF (2 drops) in freshly distilled anhydrous dichloromethane (7 mL) was stirred in a flame dried round bottom flask under nitrogen atmosphere. Oxalyl chloride (126 µL, 187 mg, 1.47 mmol, 1.5 equiv.) was then added slowly dropwise and the mixture was stirred at room temperature for 2 h. The solution was then evaporated under reduced pressure to provide a pale yellow solid material. This material was dissolved in freshly dried dichloromethane (6.0 ml) and added dropwise to a solution of diethylamine (202 µL, 143 mg, 2.0 mmol, 2.0 equiv.) and triethylamine (272 µL, 198 mg, 2.0 mmol, 2.0 equiv.) in dry dichloromethane (6.0 ml) stirred a flame dried two neck round bottom flask under nitrogen atmosphere. The reaction mixture was stirred for 18 h and then partitioned between water and dichloromethane. The aqueous phase was then acidified using 1*N* HCl to a pH 2. The organic phase was then extracted with slightly acidified water (pH 2, 3 x 10 mL). The combined acidic aqueous layers were then back extracted once with dichloromethane, which was combined with other organic phases, washed with brine, dried, filtered, and concentrated. The crude product was then purified by silica gel column chromatography eluting with a mixture of hexane and ethyl acetate (3:1) mobile phase to afford the titled compound as a pale yellow solid, ,p 86.6 – 89.1 °C, R_f 0.29. Yield 299 mg (0.966 mmol, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 7.22 – 7.17 (m, 1H), 7.05 (s, 1H), 7.05 – 6.99 (m, 2H), 3.56 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.49 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.36 – 3.22 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 163.6 (d, *J* = 250.7 Hz), 142.4, 132.5 (+, d, *J* = 8.3 Hz, 2C), 128.6 (+, 2C), 126.4 (+), 126.1 (+, 2C), 122.7 (d, *J* = 2.9 Hz), 122.0, 115.9 (+, d, *J* = 21.9 Hz, 2C), 97.7 (+, d, *J* = 2.7 Hz), 42.2 (-), 39.0 (-), 35.5, 13.8 (+), 12.7 (+); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.1 (s, 1F); FT IR (KBr, cm^{-1}): 2973, 2934, 1624, 1500, 1428, 1222, 839, 700; HRMS (TOF ES): Found 332.1426, calculated for $C_{20}H_{20}FNONa$ (M+Na) 332.1427 (0.3 ppm).

***N*,*N*-Diethyl-2-(4-methoxyphenyl)-1-phenylcycloprop-2-ene-1-carboxamide (38e): Part I**. A solution of methyl 2-(4-methoxyphenyl)-1-phenylcycloprop-2-ene-1-carboxylate (**36e**)[24] (135 mg, 0.482 mmol, 1.0 equiv.) in a 1:1 mixture of methanol and tetrahydrofuran (15 mL) was stirred at 0 °C. A 1.5 M aqueous solution of sodium hydroxide (8 mL) was added dropwise and the mixture was stirred for 18 hours. Organic solvents were then removed under vacuum and the remaining aqueous solution was added to dichloromethane (15 mL). The mixture was acidified to pH 2 with 1N aqueous HCl. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude carboxylic acid **37e** was obtained in 87% yield (112 mg, 0.419 mmol) and was immediately carried to part II without further purification. **Part II**. Trimethylamine (83 µL, 59.7 mg, 0.590 mmol, 1.5 equiv.) was added to 2-(4-methoxyphenyl)-1-phenylcycloprop-2-ene-1-carboxylic acid (**37e**) (105 mg, 0.390 mmol, 1.0 equiv.) dissolved in tetrahydrofuran (5 mL). The solution was then cooled to 0 °C. *N,N'*-Dicyclohexylcarbodiimide (122 mg, 0.590 mmol, 1.5 equiv.), 1-hydroxybenzotriazole hydrate (80.0 mg, 0.590 mmol, 1.5 equiv.), and diethylamine (52.0 µL, 37.3 mg, 0.51 mmol, 1.3 equiv.) were then added sequentially and the reaction was allowed to warm to room temperature over approximately 1 hour before being heated to 42°C and stirred for 24 hours. Solvent was evaporated and the crude

material was purified by silica gel column chromatography eluting with 3:1 mixture of hexane and EtOAc to provide the titled product as a an amber oil, R_f 0.26. Yield 51.7 mg (0.161 mmol, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.23 (m, 2H), 7.20 – 7.14 (m, 1H), 6.94 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.53 (dq, *J* = 14.3, 7.1 Hz, 2H), 3.29 (dq, *J* = 14.0, 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 160.9, 142.9, 132.1 (+, 2C), 128.5 (+, 2C), 126.2 (+), 126.1 (+, 2C), 122.0, 119.0, 114.2 (+, 2C), 95.9 (+), 55.5 (+), 42.2 (-), 39.0 (-), 35.2, 13.9 (+), 12.8 (+); FT IR (KBr, cm^{-1}): 2972, 2934, 1752, 1625, 1505, 1442, 1250, 1177, 1030, 835, 700; HRMS (TOF ES): Found 322.1799, calculated for $C_{21}H_{24}NO_2$ (M+H) 322.1807 (2.5 ppm).

***N*,*N*-Diethyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxamide (38f): Part I**. 1-Ethynyl-4-(trifluoromethyl)benzene (**35f**) (2.0 g, 11.7 mmol, 1.5 equiv.) and rhodium(II) acetate dimer (35.0 mg, 0.157 mmol, 0.02 equiv.) were dissolved in 10 mL of dichloromethane in a two-neck flask under a nitrogen atmosphere at room temperature. Methyl 2-diazo-2-phenylacetate (1.38 g, 7.84 mmol, 1.0 equiv.) dissolved in 5 mL dichloromethane was then added to the reaction via syringe pump over 18 h. The reaction mixture then was concentrated under reduced pressure and the product was coarsely purified by silica gel Flush column chromatography eluting with a mixture of hexane and ethyl acetate (3:1). The resulting ester **36f** was directly carried into hydrolysis. **Part II**: A solution of methyl 1-phenyl-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (**36f**) (375 mg, 1.18 mmol, 1.0 equiv.) in a 1:1 mixture of methanol and tetrahydrofuran (15 mL) was stirred at 0 °C. A 1.5 M aqueous solution of sodium hydroxide (8 mL) was added dropwise and the mixture was stirred for 18 h. Organic solvents were then removed under vacuum and the remaining aqueous solution was added to dichloromethane (15 mL). The mixture was acidified to pH 2 with 1N aqueous HCl. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude carboxylic acid was obtained in 65% yield (234 mg, 0.77 mmol) and was immediately carried to amide coupling without further purification. **Part III**. 1-Phenyl-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylic acid (230 mg, 0.760 mmol, 1.0 equiv.) and dimethylformamide (2 drops) were dissolved in freshly distilled and dried dichloromethane (7 ml) and added to a flame dried round bottom flask under an inert nitrogen atmosphere. Oxalyl chloride (100 µL, 143 mg, 1.13 mmol, 1.5 equiv.) was then added slowly dropwise and stirred at room temperature for 2 hours. The solution was then evaporated under reduced pressure to provide a pale yellow solid material. This material was dissolved in freshly dried dichloromethane (6.0 ml) and slowly added to a stirred mixture of diethylamine (158.0 µL, 111.1 mg, 1.52 mmol, 2.0 equiv.) and triethylamine (212 µL, 153.8 mg, 1.52 mmol, 2.0 equiv.), and freshly dried dichloromethane (6.0 mL) under an inert nitrogen atmosphere. The reaction was then stirred for 18 hours and then partitioned between water and dichloromethane. The aqueous phase was then acidified using 1*N* HCl to a pH of approximately 2. The organic phase was then extracted with properly acidified water (pH = 2, 3 x 10ml). The combined acidic aqueous layers were then back extracted once with dichloromethane which was combined with other organic layers, washed with brine, dried, filtered, and concentrated. The product was then purified by silica gel column chromatography eluting with 40:1 CH_2Cl_2/EtOAc mixture to afford the titled compound as a colorless solid, mp 80.0-82.4 °C, R_f 0.29. Yield 146.1 mg (0.406 mmol, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.15 (m, 6H), 3.62 – 3.43 (m, 2H), 3.38 – 3.24 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 142.0, 131.3 (q, *J* = 32.3 Hz), 130.6 (+, 2C), 129.9, 128.7 (+, 2C), 126.7 (+), 126.1 (+, 2C), 125.7 (q, *J* = 3.8 Hz, +, 2C), 124.0 (q, *J* = 272.4 Hz), 122.3, 101.3 (+), 42.2 (-), 39.1 (-), 35.8, 13.9 (+), 12.7 (+); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.85 (s, 3F); FT IR (KBr, cm^{-1}): 3082, 2976, 2936, 1626, 1430, 1323, 1277, 1166, 1124, 1064, 846, 712, 699; HRMS (TOF ES): Found 382.1385, calculated for $C_{21}H_{20}F_3NONa$ (M+Na) 382.1395 (2.6 ppm).

Copper-Catalyzed Carbomagnesiation (1*S,2*R**)-*N*,*N*-Diethyl-2-methyl-1-phenylcyclopropane-1-carboxamide (15aa), Typical Procedure A:** A flame dried 25 mL Schlenk flask was charged with copper iodide (3.0 mg, 15.0 µmol, 5.0 mol%) and freshly distilled anhydrous dimethoxyethane (1.0 mL) under a nitrogen atmosphere at 0 °C. Methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) was added dropwise, and the resulting mixture was stirred for five minutes at 0 °C. *N*,*N*-Diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.) was then added slowly as a solution in dry dimethoxyethane (1.0 mL). After five minutes of stirring at 0 °C, saturated aqueous ammonium chloride (1 mL) was added dropwise and the reaction was stirred for another five minutes at 0 °C. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried with magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.45. Yield 66.4 mg (0.287 mmol, 96%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 5H), 3.69 – 3.46 (m, 2H), 3.18 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.07 (dq, *J* = 14.0, 7.0 Hz, 1H), 1.96 – 1.81 (m, 1H), 1.40 (dd, *J* = 6.3, 4.6 Hz, 1H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.85 (dd, *J* = 8.8, 4.6 Hz, 1H), 0.54 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 141.9, 128.7 (+, 2C), 126.2 (+, 3C), 41.4 (-), 39.2 (-), 35.5, 23.6 (-), 18.3 (+), 14.7 (+), 12.7 (+), 12.5 (+); FTIR (KBr, cm^{-1}): 3059, 3001, 2969, 2933, 2872, 1643, 1600, 1494, 1444, 1417, 1381, 1363, 1348, 1317, 1298, 1278, 1236, 1220, 1139, 1103, 1091, 761, 736; HRMS (TOF ES): Found 254.1528, calculated for $C_{15}H_{21}NONa$ (M+Na) 254.1521 (2.8 ppm).

(1*S,2*R**)-*N*,*N*,2-Triethyl-1-phenylcyclopropane-1-carboxamide (15ab), Typical Procedure B:** A flame dried 25 mL Schlenk flask was charged with copper iodide (3.0 mg, 15.0 µmol, 5.0 mol%) and freshly distilled anhydrous dimethoxyethane (1.0 mL) under a nitrogen atmosphere at -45 °C. Ethylmagnesium bromide (**9b**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) was added dropwise and the mixture was stirred for five minutes at -45 °C. *N*,*N*-Diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.) was then added slowly as a solution in dry dimethoxyethane (1.0 mL). The reaction was then stirred for

60 minutes at -45 °C. Water was then added very slowly dropwise. After ten minutes of stirring, saturated aqueous ammonium chloride (1 mL) was added and the reaction was allowed to warm to room temperature. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried with magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.42. Yield 61.1 mg (0.249 mmol, 83%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.13 (m, 5H), 3.67 – 3.47 (m, 2H), 3.17 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.05 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.76 – 1.68 (m, 1H), 1.40 (dd, *J* = 6.3, 4.6 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.99 – 0.93 (m, 1H), 0.84 (dd, *J* = 8.8, 4.5 Hz, 1H), 0.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 142.0, 128.7 (+, 2C), 126.3 (+, 2C), 126.2 (+), 41.6 (-), 39.3 (-), 35.7, 26.1 (+), 23.1 (-), 22.2 (-), 13.8 (+), 12.7 (+), 12.5 (+); FTIR (KBr, cm^{-1}): 3059, 3024, 2966, 2931, 2872, 1643, 1600, 1494, 1444, 1417, 1381, 1361, 1346, 1315, 1298, 1276, 1220, 1139, 1099, 1068, 771, 754; HRMS (TOF ES): Found 268.1684, calculated for $C_{16}H_{23}NONa$ (M+Na) 268.1677 (2.6 ppm).

(1*S,2*R**)-*N*,*N*-Diethyl-2-isobutyl-1-phenylcyclopropane-1-carboxamide** (**15ac**): This compound was obtained via Typical procedure **B** employing isobutylmagnesium bromide (**9c**) (1.0 M in THF, 405 µL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.26. Yield 74.2 mg (0.271 mmol, 90%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.11 (m, 5H), 3.63 – 3.49 (m, 2H), 3.18 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.04 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.79 – 1.69 (m, 1H), 1.63 – 1.53 (m, 1H), 1.45 (dd, *J* = 6.4, 4.5 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 5.5 Hz, 3H), 0.96 (d, *J* = 6.1 Hz, 3H), 0.88 (dd, *J* = 8.8, 4.5 Hz, 1H), 0.84 – 0.77 (m, 1H), 0.52 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 142.1, 128.7 (+, 2C), 126.4 (+, 2C), 126.3 (+), 41.6 (-), 39.3 (-), 38.5 (-), 34.7, 28.6 (+), 23.0 (-), 22.9 (+), 22.7 (+), 22.6 (+), 12.6 (+), 12.5 (+); FTIR (KBr, cm^{-1}): 3059, 2955, 2933, 2870, 1643, 1633, 1600, 1494, 1442, 1427, 1381, 1365, 1346, 1317, 1294, 1276, 1242, 1220, 1139, 1101, 1068, 1031, 759, 742; HRMS (TOF ES): Found 296.1978, calculated for $C_{18}H_{27}NONa$ (M+Na) 296.1990 (4.1 ppm).

(1*S,2*S**)-*N*,*N*-Diethyl-1,2-diphenylcyclopropane-1-carboxamide** (**15ad**): This compound was obtained via Typical procedure **A** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.32. Yield 82.2 mg (0.280 mmol, 93%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.14 (m, 10H), 3.41 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.31 (dq, *J* = 14.2, 7.2 Hz, 1H), 3.10 (dd, *J* = 9.1, 6.9 Hz, 1H), 2.81 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.52 (dq, *J* = 14.1, 7.0 Hz, 1H), 2.33 (dd, *J* = 6.9, 5.4 Hz, 1H), 1.27 (dd, *J* = 9.1, 5.4 Hz, 1H), 0.66 (t, *J* = 7.1 Hz, 3H), 0.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 141.3, 137.2, 128.8 (+, 2C), 128.2 (+, 2C), 127.4 (+, 2C), 126.6 (+), 126.5 (+), 126.1 (+, 2C), 41.0 (-), 40.4, 38.7 (-), 29.3 (+), 22.5 (-), 12.1 (+), 11.8 (+); FTIR (KBr, cm^{-1}): 3294, 3242, 3201, 3086, 3061, 3026, 3009, 2976, 2935, 2874, 1633, 1606, 1589, 1494, 1444, 1429, 1381, 1361, 1317, 1274, 1236, 1220, 1138, 771, 754, 732; HRMS (TOF ES): Found 316.1678, calculated for $C_{20}H_{23}NONa$ (M+Na) 316.1677 (0.3 ppm).

(1*S,2*S**)-*N*,*N*-Diethyl-1-phenyl-2-vinylcyclopropane-1-carboxamide** (**15ae**): This compound was obtained via Typical procedure **A** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.39. Yield 70.8 mg (0.291 mmol, 97%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 5H), 5.46 – 5.35 (m, 1H), 5.28 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.05 (dd, *J* = 10.1, 1.7 Hz, 1H), 3.57 – 3.49 (m, 1H), 3.49 – 3.40 (m, 1H), 3.17 (dq, *J* = 14.0, 7.0 Hz, 1H), 3.01 (dq, *J* = 14.2, 7.0 Hz, 1H), 2.60 – 2.51 (m, 1H), 1.80 (dd, *J* = 6.2, 4.9 Hz, 1H), 1.13 – 1.05 (m, 4H), 0.55 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 140.9, 136.7 (+), 128.8 (+, 2C), 126.6 (+), 126.0 (+, 2C), 115.8 (-), 41.3 (-), 39.3 (-), 37.2, 28.3 (+), 23.4 (-), 12.7 (+), 12.4 (+); FTIR (KBr, cm^{-1}): 3082, 3059, 3003, 2974, 2935, 2874, 1643, 1624, 1494, 1460, 1427, 1381, 1363, 1346, 1315, 1294, 1276, 1220, 1136, 1101, 1078, 1068, 1030, 989, 949, 902, 786, 759; HRMS (TOF ES): Found 244.1704, calculated for $C_{16}H_{22}NO$ (M+H) 244.1701 (1.2 ppm).

(1*S,2*R**)-2-Allyl-*N*,*N*-diethyl-1-phenylcyclopropane-1-carboxamide** (**15af**): This compound was obtained via Typical procedure **A** employing allylmagnesium bromide (**9f**) (1.0 M in diethyl ether, 405 µL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a colorless oil, R_f 0.39. Yield 72.2 mg (0.280 mmol, 94%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.24 – 7.13 (m, 3H), 5.93 (dddd, *J* = 17.1, 10.2, 6.9, 5.9 Hz, 1H), 5.13 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.03 (dd, *J* = 10.3, 1.7 Hz, 1H), 3.69 – 3.49 (m, 2H), 3.18 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.04 (dq, *J* = 14.1, 7.0 Hz, 1H), 2.46 – 2.32 (m, 1H), 1.96 – 1.84 (m, 1H), 1.84 – 1.72 (m, 1H), 1.48 (dd, *J* = 6.3, 4.7 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.92 (dd, *J* = 8.8, 4.7 Hz, 1H), 0.52 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 141.7, 137.2 (+), 128.7 (+, 2C), 126.4 (+, 2C), 126.4 (+), 115.4 (-), 41.8 (-), 39.4 (-), 35.4, 34.0 (-), 23.5 (+), 22.1 (-), 12.6 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 3076, 3063, 2976, 2933, 2874, 1643, 1633, 1494, 1442, 1427, 1381, 1363, 1346, 1317, 1296, 1278, 1238, 1220, 1139, 1101, 1078, 1031, 995, 912, 761; HRMS (TOF ES): Found 280.1683, calculated for $C_{17}H_{23}NONa$ (M+Na) 280.1677 (2.1 ppm).

(1*S,2*R**)-*N*,*N*-Diethyl-1-phenyl-2-((trimethylsilyl)methyl)cyclopropane-1-carboxamide** (**15ag**): This compound was obtained via Typical procedure **A** employing (trimethylsilyl)methylmagnesium chloride (**9g**) (1.3 M in THF, 300 µL, 0.40 mmol, 1.30 equiv.), (and *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by col-

umn chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a colorless oil, R_f 0.34. Yield 76.6 mg (0.252 mmol, 84%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.25 (s, 1H), 7.21 – 7.14 (m, 3H), 3.65 – 3.48 (m, 2H), 3.24 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.08 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.82 (dddd, *J* = 12.3, 8.9, 6.3, 2.6 Hz, 1H), 1.38 (dd, *J* = 6.4, 4.6 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.93 (dd, *J* = 14.3, 2.6 Hz, 1H), 0.90 (dd, *J* = 8.8, 4.7 Hz, 1H), 0.56 (t, *J* = 7.1 Hz, 3H), 0.15 (dd, *J* = 14.3, 12.3 Hz, 1H), 0.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1 , 143.5 , 130.0 (+, 2C) , 127.6 (+, 2C) , 127.5 (+) , 42.8 (-) , 40.6 (-) , 36.8 , 25.4 (-) , 21.5 (+) , 18.0 (-) , 14.1 (+) , 14.0 (+) , 0.0 (+, 3C); FT IR (KBr, cm^{-1}): 2953, 2874, 1634, 1496, 1457, 1442, 1425, 1379, 1273, 1247, 861, 844, 785, 699; HRMS (TOF ES): Found 326.1926, calculated for $C_{18}H_{29}NOSiNa$ (M+Na) 326.1916 (3.1 ppm).

(1*S,2*S**)-*N*,*N*-diethyl-1-phenyl-2-(phenylethynyl)cyclopropane-1-carboxamide** (**15ah**): Flame dried Schlenk flask was charged with phenylacetylene (53.0 µL, 0.480 mmol, 1.60 equiv.) and dry dimethoxyethane (1 mL) under a nitrogen atmosphere. Methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 150 µL, 0.450 mmol, 1.50 equiv.) was added dropwise, and the reaction was then stirred at 55 °C for one hour. The solution was then cooled to room temperature and cannulated into another Schlenk flask containing copper iodide (3.0 mg, 15.0 µmol, 5 mol%) and dry dimethoxyethane (1 mL). After 5 minutes of stirring, *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.) as a solution in dry dimethoxyethane (1 mL) was added dropwise and the reaction was stirred for 60 minutes at 0 °C. Saturated aqueous ammonium chloride (1 mL) was then added dropwise. The resulting solution was diluted with water and extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous yellowish oil, Rf 0.35. Yield 9.4 mg (0.03 mmol, 10%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.15 (m, 10H), 3.66 – 3.57 (m, 1H), 3.57 – 3.49 (m, 1H), 3.20 – 3.04 (m, 2H), 2.62 (dd, *J* = 9.0, 6.2 Hz, 1H), 2.03 (dd, *J* = 6.2, 4.6 Hz, 1H), 1.13 (dd, *J* = 9.0, 4.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H), 0.56 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 139.6, 131.7 (+, 2C), 128.9 (+, 2C), 128.3 (+, 2C), 128.0 (+), 127.1 (+), 126.3 (+, 2C), 123.4, 88.0, 79.6, 41.7 (+), 39.6 (+), 38.3, 25.0 (+), 13.8 (-), 12.8 (-), 12.6 (-); FTIR (KBr, cm^{-1}): 3059, 2968, 2926, 2852, 1645, 1635, 1558, 1539, 1506, 1456, 1429, 1219, 1134, 1068, 1026, 945, 910, 842, 758; HRMS (TOF ES): Found 340.1689, calculated for $C_{22}H_{23}NONa$ (M+Na) 340.1677 (3.5 ppm).

(1*S,2*R**)-*N*,*N*-diisopropyl-2-methyl-1-phenylcyclopropane-1-carboxamide** (**15ba**): This compound was obtained via Typical procedure **A** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**11b**) (73.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.35. Yield 73.2 mg (0.282 mmol, 94%), dr: >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.13 (m, 5H), 4.25 (hept, *J* = 6.6 Hz, 1H), 3.22 (hept, *J* = 6.8 Hz, 1H), 2.00 – 1.84 (m, 1H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.41 (d, *J* = 7.0 Hz, 3H), 1.39 (dd, *J* = 6.25, 4.57 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H), 0.77 (dd, *J* = 8.9, 4.5 Hz, 1H), 0.36 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 142.2, 128.6 (+, 2C), 126.6 (+, 2C), 126.2 (+), 48.9 (+), 45.9 (+), 37.2, 22.8 (-), 21.8 (+), 21.1 (+), 19.7 (+), 19.2 (+), 18.0 (+), 15.1 (+); FTIR (KBr, cm^{-1}): 3059, 2999, 2962, 2931, 2872, 1633, 1600, 1494, 1435, 1369, 1336, 1238, 1211, 1157, 1134, 1091, 1039, 734; HRMS (TOF ES): Found 282.1844, calculated for $C_{17}H_{25}NONa$ (M+Na) 282.1834 (3.5 ppm).

(1*S,2*S**)-*N*,*N*-Diisopropyl-1,2-diphenylcyclopropane-1-carboxamide** (**15bd**): This compound was obtained via Typical procedure **A** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**11b**) (73.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a colorless solid, mp 132.8-135.5 °C, R_f 0.42. Yield 87.8 mg (0.273 mmol, 91%), dr 20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.15 (m, 10H), 4.03 – 3.88 (m, 1H), 3.11 (dd, *J* = 9.3, 6.9 Hz, 1H), 3.01 – 2.89 (m, 1H), 2.24 (dd, *J* = 6.9, 5.3 Hz, 1H), 1.34 (d, *J* = 6.7 Hz, 3H), 1.23 (dd, *J* = 9.2, 5.3 Hz, 1H), 1.18 (d, *J* = 6.8 Hz, 3H), 0.21 (d, *J* = 6.6 Hz, 3H), 0.06 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 141.3, 138.2, 128.7 (+, 2C), 128.4 (+, 2C), 127.4 (+, 2C), 126.7 (+, 2C), 126.7 (+), 126.5 (+), 48.8 (+), 45.9 (+), 42.2, 28.5 (+), 23.2 (-), 20.3 (+), 20.2 (+), 19.5 (+), 19.1 (+); FTIR (KBr, cm^{-1}): 3059, 3028, 3007, 2960, 2931, 1620, 1496, 1469, 1444, 1369, 1342, 1209, 1157, 1134, 1122, 1078, 1057, 1037, 1022, 800, 773, 758, 734, 704; HRMS (TOF ES): Found 322.2172, calculated for $C_{22}H_{28}NO$ (M+H) 322.2171 (0.3 ppm).

(1*S,2*S**)-*N*,*N*-diisopropyl-1-phenyl-2-vinylcyclopropane-1-carboxamide** (**15be**): This compound was obtained via Typical procedure **A** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**11b**) (73.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.55. Yield 71.8 mg (0.265 mmol, 88%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.11 (m, 5H), 5.54 – 5.38 (m, 1H), 5.31 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.08 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.16 (hept, *J* = 6.6 Hz, 1H), 3.20 (hept, *J* = 6.8 Hz, 1H), 2.74 – 2.44 (m, 1H), 1.78 (dd, *J* = 6.1, 4.8 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.5 Hz, 3H), 1.02 – 0.98 (m, 1H), 0.35 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 140.9, 137.3 (+), 128.7 (+, 2C), 126.6 (+), 126.4 (+, 2C), 115.5 (-), 49.0 (+), 45.9 (+), 38.8, 27.7 (+), 23.0 (-), 21.8 (+), 20.9 (+), 19.6 (+), 19.2 (+); FTIR (KBr, cm^{-1}): 3082, 3061, 3001, 2964, 2931, 2874, 1633, 1600, 1494, 1471, 1437, 1369, 1338, 1215, 1157, 1132, 1037, 989, 902, 761, 742, 700; HRMS (TOF ES): Found 272.2018, calculated for $C_{18}H_{26}NO$ (M+H) 272.2014 (1.5 ppm).

(1*S,2*R**)-*N*,*N*-Dibenzyl-2-methyl-1-phenylcyclopropane-1-carboxamide** (**15ca**): This compound was obtained via Typical procedure **A** employing methylmagnesium bromide (**9a**) (135 µL (3.0 M in diethyl ether), 0.405 mmol, 1.35 equiv.) and *N*,*N*-dibenzyl-1-

phenylcycloprop-2-ene-1-carboxamide (102 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a colorless solid, mp 113.7-115.1 °C, R_f 0.26. Yield 101 mg (0.285 mmol, 95%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.10 (m, 13H), 6.70 – 6.54 (m, 2H), 4.91 (d, *J* = 14.4 Hz, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 4.24 (d, *J* = 15.6 Hz, 1H), 4.01 (d, *J* = 14.4 Hz, 1H), 1.96 – 1.81 (m, 1H), 1.44 (dd, *J* = 6.3, 4.6 Hz, 1H), 1.25 (d, *J* = 6.3 Hz, 3H), 1.02 (dd, *J* = 8.8, 4.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 141.4, 137.4, 136.0, 129.0 (+, 2C), 128.8 (+, 2C), 128.5 (+, 2C), 128.4 (+, 2C), 127.6 (+, 2C), 127.4 (+), 127.4 (+), 127.2 (+, 2C), 126.6 (+), 49.9 (-), 47.1 (-), 35.6, 22.5 (-), 19.3 (+), 15.6 (+); FTIR (KBr, cm^{-1}): 3061, 3028, 3003, 2956, 2928, 2868, 2359, 2341, 1633, 1600, 1494, 1450, 1417, 1361, 1317, 1296, 1193, 1078, 1028, 989, 752, 732; HRMS (TOF ES): Found 378.1842, calculated for $C_{25}H_{25}NONa$ (M+Na) 378.1834 (2.1 ppm).

(1*S,2*S**)-*N*,*N*-Dibenzyl-1,2-diphenylcyclopropane-1-carboxamide** (**15cd**): This compound was obtained via Typical procedure **A** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**11c**) (102 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous yellowish oil, R_f 0.30. Yield 117 mg (0.280 mmol, 93%), dr 13:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 7.36 – 6.93 (m, 14H), 6.69 – 6.56 (m, 2H), 6.19 – 6.05 (m, 2H), 4.58 (d, *J* = 14.7 Hz, 1H), 4.57 (d, *J* = 15.36 Hz, 1H), 3.88 (d, *J* = 14.8 Hz, 1H), 3.76 (d, *J* = 15.4 Hz, 1H), 3.20 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.46 (dd, *J* = 7.0, 5.3 Hz, 1H), 1.34 (dd, *J* = 9.2, 5.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 141.1, 137.1, 136.5, 135.4, 129.0 (+, 2C), 128.8 (+, 2C), 128.5 (+, 2C), 128.2 (+, 2C), 128.2 (+, 2C), 127.8 (+, 2C), 127.8 (+, 2C), 127.5 (+, 2C), 127.2 (+), 127.1 (+), 126.9 (+), 126.8 (+), 50.0 (-), 46.9 (-), 40.9, 29.0 (+), 21.3 (-); FTIR (KBr, cm^{-1}): 3086, 3061, 3028, 3009, 1643, 1604, 1591, 1583, 1494, 1454, 1417, 1361, 1313, 1294, 1267, 1209, 1182, 1078, 1030, 1012, 945, 779, 731; HRMS (TOF ES): Found 440.1988, calculated for $C_{30}H_{27}NONa$ (M+Na) 440.1990 (0.5 ppm).

(1*S,2*S**)-*N*,*N*-Dibenzyl-1-phenyl-2-vinylcyclopropane-1-carboxamide** (**15ce**): This compound was obtained via Typical procedure **A** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 μL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**11c**) (102 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.52. Yield 92.4 mg (0.251 mmol, 84%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.02 (m, 13H), 6.71 – 6.44 (m, 2H), 5.64 – 5.47 (m, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 4.87 (d, *J* = 14.5 Hz, 1H), 4.72 (d, *J* = 15.6 Hz, 1H), 4.15 (d, *J* = 15.6 Hz, 1H), 3.96 (d, *J* = 14.5 Hz, 1H), 2.64 – 2.42 (m, 1H), 1.85 (dd, *J* = 6.2, 4.9 Hz, 1H), 1.22 (dd, *J* = 8.7, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 140.3, 137.2, 136.7 (+), 135.8, 129.0 (+, 2C), 129.0 (+, 2C), 128.4 (+, 2C), 128.4 (+, 2C), 127.9 (+, 2C), 127.4 (+), 127.4 (+), 127.1 (+, 2C), 127.0 (+), 116.3 (-), 50.0 (-), 47.1 (-), 37.4, 28.5 (+), 22.2 (-); FTIR (KBr, cm^{-1}): 3084, 3061, 3028, 3005, 2822, 1643, 1633, 1600, 1494, 1448, 1417, 1361, 1315, 1267, 1190, 1078, 1030, 1010, 976, 947, 906, 750, 736, 700; HRMS (TOF ES): Found 368.2026, calculated for $C_{26}H_{26}NO$ (M+H) 368.2014 (3.3 ppm).

((1*S,2*R**)-2-methyl-1-phenylcyclopropyl)(pyrrolidin-1-yl)methanone** (**15da**): This compound was obtained via Typical procedure **A** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**11d**) (64.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.16. Yield (62.8 mg, 0.274 mmol, 91%), dr >99:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.14 (m, 5H), 3.57 – 3.48 (m, 2H), 3.41 – 3.32 (m, 1H), 2.91 – 2.79 (m, 1H), 1.91 – 1.79 (m, 2H), 1.79 – 1.64 (m, 3H), 1.44 (dd, *J* = 6.3, 4.6 Hz, 1H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.89 (dd, *J* = 8.7, 4.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 141.3, 128.7 (+, 2C), 126.2 (+, 2C), 126.2 (+), 47.1 (-), 46.3 (-), 36.6, 26.4 (-), 24.2 (-), 23.4 (-), 18.7 (+), 14.8 (+); FTIR (KBr, cm^{-1}): 3057, 2999, 2996, 2953, 2929, 2874, 1633, 1600, 1579, 1494, 1717, 1367, 1342, 1192, 1168, 1095, 1033, 912, 756, 734, 725, 700; HRMS (TOF ES): Found 252.1376, calculated for $C_{15}H_{19}NONa$ (M+Na) 252.1364 (4.8 ppm).

((1*S,2*S**)-1,2-Diphenylcyclopropyl)(pyrrolidin-1-yl)-methanone** (**15dd**): This compound was obtained via Typical procedure **A** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 μL 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**11d**) (64.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a colorless solid, mp 111.1-112.7 °C, R_f 0.16. Yield 76.2 mg (0.262 mmol, 87%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.16 (m, 10H), 3.38 – 3.24 (m, 1H), 3.10 – 2.93 (m, 3H), 2.71 – 2.57 (m, 1H), 2.33 (dd, *J* = 6.9, 5.5 Hz, 1H), 1.57 – 1.31 (m, 3H), 1.35 (dd, J = 9.1, 5.6 Hz, 1H), 0.96 – 0.75 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 140.4, 137.5, 128.8 (+, 2C), 128.2 (+, 2C), 127.0 (+, 2C), 126.6 (+), 126.5 (+), 126.2 (+, 2C), 46.5 (-), 45.9 (-), 41.6, 29.9 (+), 25.6 (-), 23.8 (-), 22.7 (-); FTIR (KBr, cm^{-1}): 3057, 3028, 2970, 2874, 1626, 1579, 1496, 1448, 1427, 1340, 1190, 1168, 1122, 1078, 1031, 914, 873, 775, 763, 732; HRMS (TOF ES): Found 314.1523, calculated for $C_{20}H_{21}NONa$ (M+Na) 314.1521 (0.6 ppm).

((1*S,2*S**)-1-Phenyl-2-vinylcyclopropyl)(pyrrolidin-1-yl)methanone** (**15de**): This compound was obtained via Typical procedure **A** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 μL, 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**11d**) (64.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.16. Yield 59.2 mg (0.245 mmol, 82%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.51 – 5.35 (m, 1H), 5.30 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.06 (dd, *J* = 10.0, 1.8 Hz, 1H), 3.61 – 3.43 (m, 2H), 3.45 – 3.31 (m, 1H), 2.90 – 2.71 (m, 1H), 2.55 – 2.39 (m, 1H), 1.86 – 1.77 (m, 1H), 1.83 (dd, *J* = 6.2, 5.0 Hz, 1H), 1.77 – 1.59 (m, 3H), 1.12 (dd, *J* = 8.7, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 140.1, 136.9 (+), 128.8 (+, 2C), 126.5 (+), 126.1 (+, 2C), 115.9 (-), 46.7 (-), 46.4 (-), 38.4, 28.6 (+),

26.3 (-), 24.2 (-), 23.3 (-); FTIR (KBr, cm^{-1}): 3080, 3057, 3022, 3001, 2970, 2874, 1633, 1600, 1579, 1494, 1423, 1340, 1190, 1168, 1114, 1031, 993, 941, 910, 758, 727, 700; HRMS (TOF ES): Found 264.1377, calculated for $C_{16}H_{19}NONa$ (M+Na) 264.1364 (4.9 ppm).

((1*S,2*R**)-2-methyl-1-phenylcyclopropyl)(piperidin-1-yl)methanone** (**15ea**): This compound was obtained via Typical procedure **A** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone (**11e**) (68.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.16. Yield 65.6 mg (0.270 mmol, 90%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.11 (m, 5H), 3.82 – 3.71 (m, 1H), 3.49 – 3.35 (m, 2H), 3.31 – 3.20 (m, 1H), 1.92 – 1.81 (m, 1H), 1.59 – 1.44 (m, 4H), 1.38 (dd, *J* = 6.3, 4.7 Hz, 1H), 1.31 – 1.20 (m, 1H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.09 – 0.96 (m, 1H), 0.91 (dd, *J* = 8.8, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 141.9, 128.7 (+, 2C), 126.1 (+), 125.7 (+, 2C), 46.7 (-), 43.2 (-), 35.3, 25.8 (-), 25.7 (-), 24.6 (-), 24.0 (-), 19.4 (+), 15.3 (+); FTIR (KBr, cm^{-1}): 3059, 3001, 2935, 2854, 1633, 1600, 1496, 1465, 1433, 1294, 1271, 1259, 1211, 1138, 1128, 1022, 1003, 852, 754, 732, 700; HRMS (TOF ES): Found 266.1520, calculated for $C_{16}H_{21}NONa$ (M+Na) 266.1521 (0.4 ppm).

((1*S,2*S**)-1,2-Diphenylcyclopropyl)(piperidin-1-yl)-methanone** (**15ed**): This compound was obtained via Typical procedure **A** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether), 135 µL, 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone (**11e**) (68.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a colorless solid, mp 120.6-121.9 °C, R_f 0.29. Yield 81.8 mg (0.268 mmol, 89%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.16 (m, 10H), 3.54 – 3.43 (m, 1H), 3.35 – 3.20 (m, 1H), 3.01 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.98 – 2.91 (m, 1H), 2.88 – 2.81 (m, 1H), 2.26 (dd, *J* = 7.0, 5.6 Hz, 1H), 1.39 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.38 – 1.30 (m, 1H), 1.27 – 1.18 (m, 2H), 1.16 – 1.05 (m, 1H), 0.90 – 0.80 (m, 1H), 0.33 – 0.20 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 141.1, 137.8, 128.7 (+, 2C), 128.2 (+, 2C), 127.0 (+, 2C), 126.5 (+), 126.4 (+), 125.4 (+, 2C), 46.4 (-), 42.8 (-), 40.0, 30.9 (+), 25.0 (-), 25.0 (-), 24.1 (-), 23.6 (-); FTIR (KBr, cm^{-1}): 3057, 3028, 3005, 2935, 2854, 1631, 1496, 1437, 1292, 1271, 1247, 1217, 1136, 1124, 1078, 1031, 1012, 974, 852, 773, 761, 731; HRMS (TOF ES): Found 328.1682, calculated for $C_{21}H_{23}NONa$ (M+Na) 328.1677 (1.5 ppm).

((1*S,2*S**)-1-Phenyl-2-vinylcyclopropyl)(piperidin-1-yl)-methanone** (**15ee**): This compound was obtained via Typical procedure **A** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL, 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone (**11e**) (68.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.29. Yield 66.0 mg (0.258 mmol, 86%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 5.49 – 5.39 (m, 1H), 5.29 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.07 (dd, *J* = 10.2, 1.7 Hz, 1H), 3.75 – 3.66 (m, 1H), 3.52 – 3.43 (m, 1H), 3.34 – 3.25 (m, 1H), 3.25 – 3.18 (m, 1H), 2.59 – 2.48 (m, 1H), 1.78 (dd, *J* = 6.2, 5.0 Hz, 1H), 1.55 – 1.44 (m, 4H), 1.32 – 1.23 (m, 1H), 1.15 (dd, *J* = 8.7, 5.0 Hz, 1H), 1.06 – 0.94 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 140.9, 137.1 (+), 128.8 (+, 2C), 126.5 (+), 125.5 (+, 2C), 115.8 (-), 46.7 (-), 43.3 (-), 37.1, 29.4 (+), 25.8 (-), 25.7 (-), 24.5 (-), 23.8 (-); FTIR (KBr, cm^{-1}): 3080, 3059, 3003, 2935, 2854, 1643, 1626, 1496, 1435, 1369, 1352, 1271, 1257, 1207, 1136, 1126, 1103, 1031, 1010, 983, 952, 902, 852, 758, 742; HRMS (TOF ES): Found 278.1529, calculated for $C_{17}H_{21}NONa$ (M+Na) 278.1521 (2.9 ppm).

((1*S,2*R**)-2-Methyl-1-phenylcyclopropyl)(morpholino)-methanone** (**15fa**): This compound was obtained via Typical procedure **A** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) and morpholino(1-phenylcycloprop-2-en-1-yl)methanone (**11f**) (69.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.19. Yield 67.6 mg (0.276 mmol, 92%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.11 (m, 5H), 3.74 – 3.66 (m, 2H), 3.66 – 3.59 (m, 2H), 3.45 – 3.31 (m, 3H), 3.27 – 3.19 (m, 1H), 1.95 – 1.81 (m, 1H), 1.40 (dd, *J* = 6.4, 4.7 Hz, 1H), 1.19 (d, *J* = 6.2 Hz, 3H), 0.95 (dd, *J* = 8.8, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 141.4, 128.9 (+, 2C), 126.4 (+), 125.5 (+, 2C), 66.9 (-), 66.6 (-), 46.3 (-), 42.7 (-), 35.0, 23.9 (-), 19.3 (+), 15.3 (+); FTIR (KBr, cm^{-1}): 3062, 2999, 2960, 2920, 2899, 2854, 1639, 1496, 1456, 1427, 1390, 1359, 1301, 1273, 1209, 1114, 1095, 1068, 1030, 1008, 945, 912, 848, 756, 732, 700; HRMS (TOF ES): Found 268.1318, calculated for $C_{15}H_{19}NO_2Na$ (M+Na) 268.1313 (1.9 ppm).

((1*S,2*S**)-1,2-Diphenylcyclopropyl)(morpholino)methanone** (**15fd**): This compound was obtained via Typical procedure **A** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) and morpholino(1-phenylcycloprop-2-en-1-yl)methanone (**11f**) (69.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a colorless solid, mp 138.0-139.9 °C, R_f 0.26. Yield 74.8 mg (0.243 mmol, 81%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.12 (m, 10H), 3.83 – 3.65 (m, 1H), 3.59 – 3.43 (m, 1H), 3.21 – 3.14 (m, 1H), 3.12 – 3.05 (m, 1H), 3.05 – 2.97 (m, 3H), 2.95 – 2.87 (m, 1H), 2.29 (dd, *J* = 7.0, 5.7 Hz, 1H), 2.15 – 2.08 (m, 1H), 1.42 (dd, *J* = 9.2, 5.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 140.6, 137.5, 129.0 (+, 2C), 128.6 (+, 2C), 127.1 (+, 2C), 127.0 (+), 126.8 (+), 125.4 (+, 2C), 66.3 (-), 66.0 (-), 46.0 (-), 42.3 (-), 39.8, 31.0 (+), 23.3 (-); FTIR (KBr, cm^{-1}): 3057, 3028, 3003, 2962, 2922, 2897, 2854, 1639, 1599, 1496, 1458, 1431, 1359, 1301, 1274, 1215, 1190, 1112, 1068, 1031, 977, 898, 850, 773, 731; HRMS (TOF ES): Found 308.1666, calculated for $C_{20}H_{22}NO_2$ (M+H) 308.1651 (4.9 ppm).

Morpholino((1*S,2*S**)-1-phenyl-2-vinylcyclopropyl)-methanone** (**15fe**): This compound was obtained via Typical procedure **A** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL, 0.405 mmol, 1.35 equiv.) and morpholino(1-phenylcycloprop-2-en-1-yl)methanone (**15f**) (69.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chro-

matography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.16. Yield 63.8 mg (0.248 mmol, 83%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 5.51 – 5.38 (m, 1H), 5.30 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.12 (dd, *J* = 10.1, 1.6 Hz, 1H), 3.80 – 3.70 (m, 1H), 3.69 – 3.53 (m, 3H), 3.44 – 3.32 (m, 2H), 3.30 – 3.18 (m, 2H), 2.60 – 2.47 (m, 1H), 1.80 (dd, *J* = 6.2, 5.1 Hz, 1H), 1.18 (dd, *J* = 8.7, 5.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 140.2, 136.8 (+), 129.0 (+, 2C), 126.8 (+), 125.3 (+, 2C), 116.3 (-), 66.8 (-), 66.7 (-), 46.3 (-), 42.6 (-), 36.6, 29.3 (+), 23.7 (-); FTIR (KBr, cm^{-1}): 3082, 3059, 3001, 2962, 2920, 2899, 2856, 1651, 1643, 1600, 1496, 1456, 1429, 1359, 1301, 1274, 1195, 1114, 1068, 1031, 985, 943, 908, 850, 758, 700; HRMS (TOF ES): Found 280.1309, calculated for $C_{16}H_{19}NO_2Na$ (M+Na) 280.1313 (1.4 ppm).

(1*S,2*R**)-*N*,*N*-diallyl-2-methyl-1-phenylcyclopropane-1-carboxamide** (**15ga**): This compound was obtained via Typical procedure **A** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (**11g**) (72.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.29. Yield 71.6 mg (0.280 mmol, 94%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 5H), 5.83 – 5.65 (m, 1H), 5.22 – 5.05 (m, 2H), 4.97 – 4.88 (m, 3H), 4.35 – 4.24 (m, 1H), 4.21 – 4.11 (m, 1H), 3.72 – 3.53 (m, 2H), 1.94 – 1.86 (m, 1H), 1.43 (dd, *J* = 6.3, 4.6 Hz, 1H), 1.17 (d, *J* = 6.3 Hz, 3H), 0.91 (dd, *J* = 8.8, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 141.6, 133.1 (+), 128.8 (+, 3C), 126.4 (+), 126.4 (+, 2C), 118.5 (-), 117.8 (-), 49.5 (-), 46.7 (-), 35.4, 23.4 (-), 18.7 (+), 15.0 (+); FTIR (KBr, cm^{-1}): 3078, 3005, 2980, 2958, 2928, 1643, 1633, 1600, 1496, 1454, 1435, 1410, 1332, 1300, 1280, 1263, 1209, 1193, 1138, 1112, 1095, 993, 923, 759, 731; HRMS (TOF ES): Found 278.1536, calculated for $C_{17}H_{21}NONa$ (M+Na) 278.1521 (5.4 ppm).

(1*S,2*S**)-*N*,*N*-Diallyl-1,2-diphenylcyclopropane-1-carboxamide** (**15gd**): This compound was obtained via Typical procedure **A** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (**11g**) (72.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a colorless solid, mp 111.5-113.9 °C, R_f 0.32. Yield 90.6 mg (0.285 mmol, 95%), dr 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.15 (m, 10H), 5.20 – 5.09 (m, 1H), 4.85 (d, *J* = 10.2 Hz, 1H), 4.78 (d, *J* = 10.1 Hz, 1H), 4.74 (d, *J* = 17.1 Hz, 1H), 4.64 (d, *J* = 17.2 Hz, 1H), 4.50 – 4.36 (m, 1H), 4.12 – 4.02 (m, 1H), 3.99 – 3.87 (m, 1H), 3.37 – 3.29 (m, 1H), 3.14 (dd, *J* = 9.1, 6.9 Hz, 1H), 3.12 – 3.06 (m, 1H), 2.38 (dd, *J* = 6.9, 5.5 Hz, 1H), 1.30 (dd, *J* = 9.1, 5.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 141.0, 136.9, 132.8 (+), 132.6 (+), 128.9 (+, 2C), 128.4 (+, 2C), 127.6 (+, 2C), 126.9 (+), 126.7 (+), 126.4 (+, 2C), 118.5 (-), 117.3 (-), 49.4 (-), 46.2 (-), 40.4, 29.2 (+), 22.2 (-); FTIR (KBr, cm^{-1}): 3084, 3063, 3028, 3010, 2910, 1643, 1622, 1600, 1494, 1454, 1442, 1435, 1411, 1300, 1284, 1269, 1215, 1180, 1076, 1031, 991, 922, 902, 765, 734; HRMS (TOF ES): Found 340.1675, calculated for $C_{22}H_{23}NONa$ (M+Na) 340.1677 (0.6 ppm).

(1*S,2*S**)-*N*,*N*-diallyl-1-phenyl-2-vinylcyclopropane-1-carboxamide** (**15ge**): This compound was obtained via Typical procedure **A** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 μL, 0.405 mmol, 1.35 equiv.) and *N*,*N*-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (**11g**) (72.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous light yellow oil, R_f 0.45. Yield 63.8 mg (0.239 mmol, 80%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.10 (m, 5H), 5.87 – 5.60 (m, 1H), 5.57 – 5.37 (m, 1H), 5.37 – 5.27 (m, 1H), 5.22 – 5.02 (m, 3H), 5.00 – 4.82 (m, 3H), 4.30 – 4.15 (m, 1H), 4.12 – 3.93 (m, 1H), 3.77 – 3.45 (m, 2H), 2.70 – 2.41 (m, 1H), 1.83 (dd, *J* = 6.2, 5.0 Hz, 1H), 1.14 (dd, *J* = 8.7, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 140.5, 136.6 (+), 133.2 (+), 132.9 (+), 128.9 (+, 2C), 126.8 (+), 126.2 (+, 2C), 118.6 (-), 117.7 (-), 116.2 (-), 49.6 (-), 46.6 (-), 37.2, 28.4 (+), 23.2 (-); FTIR (KBr, cm^{-1}): 3080, 3063, 3007, 2982, 1643, 1633, 1600, 1496, 1435, 1411, 1332, 1296, 1261, 1205, 1136, 1111, 1031, 993, 923, 758, 731, 700; HRMS (TOF ES): Found 290.1519, calculated for $C_{18}H_{21}NONa$ (M+Na) 290.1521 (0.7 ppm).

(1*S,2*R**)-*N*-Methoxy-*N*,2-dimethyl-1-phenylcyclopropane-1-carboxamide** (**15ha**): This compound was obtained via Typical procedure **A** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.) and *N*-methoxy-*N*-methyl-1-phenylcycloprop-2-ene-1-carboxamide (**11h**) (61.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous light yellow oil, R_f 0.39. Yield 59.2 mg (0.270 mmol, 90%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 5H), 3.12 (s, 3H), 3.05 (s (broad), 3H), 1.96 – 1.84 (m, 1H), 1.43 (dd, *J* = 6.4, 4.6 Hz, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.85 (s (broad), 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 128.5 (+, 2C), 127.5, 126.5 (+, 3C), 60.2, 35.7 (+), 33.3 (+), 22.0 (-), 18.4 (+), 14.5 (+); FTIR (KBr, cm^{-1}): 3059, 3001, 2962, 2931, 2874, 1660, 1651, 1600, 1496, 1442, 1410, 1365, 1172, 1122, 1101, 1074, 993, 908, 761; HRMS (TOF ES): Found 242.1165, calculated for $C_{13}H_{17}NO_2Na$ (M+Na) 242.1157 (3.3 ppm).

(*E*)-*N*,*N*-diethyl-2-phenylhex-3-enamide (**16ab**): A flame dried Schlenk flask was charged with copper iodide (3.0 mg, 15.0 μmol, 5.0 mol%) and freshly distilled dry dimethoxyethane (1.0 mL) under a nitrogen atmosphere. Ethylmagnesium bromide (**9b**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.) was added dropwise at 0 °C, and the mixture was stirred for five minutes. *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.) was then added dropwise as a solution in dry dimethoxyethane (1.0 mL). The reaction mixture was then stirred for 1 hr at room temperature. Saturated aqueous ammonium chloride (1 mL) was added slowly. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and concentrated. The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.26. Yield (56.4 mg, 0.230 mmol, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 5H), 5.87 (dd, *J* = 15.4, 8.0 Hz, 1H), 5.51 (dt, *J* = 15.4, 6.3 Hz, 1H), 4.38 (d, *J* = 8.0 Hz, 1H), 3.55 – 3.44 (m, 1H), 3.38 – 3.14 (m, 3H), 2.11 – 1.99

(m, 2H), 1.11 (t, *J* = 7.1 Hz, 6H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 140.2, 133.6 (+), 129.0 (+), 128.8 (+, 2C), 128.0 (+, 2C), 126.9 (+), 52.5 (+), 41.9 (-), 40.4 (-), 25.6 (-), 14.6 (+), 13.6 (+), 13.0 (+); FTIR (KBr, cm^{-1}): 3059, 3026, 2966, 2931, 2872, 1639, 1600, 1492, 1479, 1454, 1427, 1379, 1361, 1311, 1276, 1253, 1219, 1138, 1095, 1072, 966, 783, 752; HRMS (TOF ES): Found 246.1852, calculated for $C_{16}H_{24}NO$ (M+H) 246.1858 (2.4 ppm).

1-((1*S,2*R**)-2-Methyl-1-phenylcyclopropyl)ethan-1-one** (**17**): Methylmagnesium bromide (**9a**) (130 µL, 3.0 M (diethyl ether), 0.40 mmol, 2.0 equiv.) was added dropwise to a stirred solution of (1*S**,2*R**)-*N*-methoxy-*N*,2-dimethyl-1-phenylcyclopropane-1-carboxamide (**15ha**) (44.0 mg, 0.20 mmol, 1.0 equiv.) in dry dimethoxyethane. The reaction mixture was stirred at 40 °C for 18 hours. After cooling to room temperature, saturated aqueous ammonium chloride (1 mL) was added dropwise. The resulting solution was diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were dried, filtered, and evaporated. The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.32. Yield 21.2 mg (0.122 mmol, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.16 (m, 5H), 1.90 (s, 3H), 1.70 (ddq, *J* = 8.7, 7.2, 6.2 Hz, 1H), 1.58 (dd, *J* = 7.1, 4.0 Hz, 1H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.01 (dd, *J* = 8.7, 4.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.9, 142.6, 130.5 (+, 2C), 128.8 (+, 2C), 127.4 (+), 43.3, 30.8 (+), 25.5 (+), 22.0 (-), 12.3 (+); FTIR (KBr, cm^{-1}): 3022, 3001, 2955, 2928, 2874, 1691, 1600, 1492, 1456, 1444, 1435, 1361, 1280, 1165, 1132, 1097, 1074, 1024, 979, 758; HRMS (TOF ES): Found 192.1386, calculated for $C_{12}H_{18}NO$ ($M+NH_4$) 192.1388 (1.0 ppm).

(1*S,2*R**,3*S**)-*N*,*N*-Diethyl-2-methyl-1-phenylcyclopropane-1-carboxamide-3-*d*** (**18aa**), **Typical Procedure C**: Flame dried Schlenk flask was charged with copper iodide (3.0 mg, 15.0 µmol, 5.0 mol%) and freshly distilled dry dimethoxyethane (1.0 mL) under a nitrogen atmosphere. Methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.) was added dropwise at 0 °C, and the mixture was stirred for 5 min at the same temperature. *N*,*N*-Diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.) was then added dropwise as a solution in dry dimethoxyethane (1.0 mL). After 5 min of stirring, methanol-d_4 (19.0 µL, 16.5 mg, 0.45 mmol, 1.50 equiv.) was added dropwise and stirred for 15 min at 0 °C. The reaction was then allowed to warm to room temperature over 15 minutes before saturated aqueous ammonium chloride (1 mL) was added. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.32. Yield (68.4 mg, 0.294 mmol, 98%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 3.63 – 3.51 (m, 2H), 3.18 (dq, *J* = 14.0, 7.0 Hz, 1H), 3.07 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.88 (dq, *J* = 8.8, 6.3 Hz, 1H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.84 (d, *J* = 8.7 Hz, 1H), 0.55 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 142.0, 128.7 (+, 2C), 126.2 (+, 3C), 41.4 (-), 39.3 (-), 35.4, 23.3 (+, t 1:1:1, *J* = 24.5 Hz), 18.2 (+), 14.7 (+), 12.7 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 3028, 3003, 2968, 2933, 2872, 1633, 1496, 1471, 1456, 1425, 1379, 1363, 1319, 1294, 1276, 1220, 1151, 1128, 1101, 1080, 1066, 868, 759, 732, 700; HRMS (TOF ES): Found 255.1586, calculated for $C_{15}H_{20}DNONa$ (M+Na) 255.1584 (0.8 ppm).

(1*S,2*S**,3*S**)-*N*,*N*-Diethyl-1-phenyl-2-vinylcyclopropane-1-carboxamide-3-*d*** (**18ae**): This compound was obtained via Typical procedure **C** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with methanol-d_4 (19.0 µL, 16.5 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.35. Yield 63.2 mg (0.259 mmol, 86%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 5.41 (ddd, *J* = 17.0, 10.1, 9.0 Hz, 1H), 5.28 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.05 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.61 – 3.38 (m, 2H), 3.17 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.01 (dq, *J* = 14.2, 7.1 Hz, 1H), 2.55 (dd, *J* = 8.9 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 8.9 Hz, 1H), 0.55 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 140.9, 136.7 (+), 128.8 (+, 2C), 126.6 (+), 126.0 (+, 2C), 115.8 (-), 41.3 (-), 39.3 (-), 37.2, 28.2 (+), 23.1 (+, t 1:1:1, J = 25.2 Hz), 12.7 (+), 12.4 (+); FTIR (KBr, cm^{-1}): 3082, 3059, 2974, 2935, 2874, 1633, 1496, 1456, 1444, 1427, 1381, 1361, 1315, 1276, 1219, 1128, 991, 902, 756, 700; HRMS (TOF ES): Found 245.1770, calculated for $C_{16}H_{21}DNO$ (M+H) 245.1764 (2.4 ppm).

(1*s*,2*R,3*S**)-*N*,*N*-Diethyl-2,3-dimethyl-1-phenylcyclopropane-1-carboxamide** (**19aa**): This compound was obtained via Typical procedure **C** employing methylmagnesium bromide (**9a**) (135 µL, (3.0 M in diethyl ether), 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with methyl iodide (28.0 µL, 64.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.32. Yield 63.2 mg (0.258 mmol, 86%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 3.37 (q, *J* = 7.2 Hz, 2H), 3.32 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 2H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.11 (d, *J* = 7.1 Hz, 3H), 0.59 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 143.0, 128.6 (+, 2C), 126.0 (+), 125.7 (+, 2C), 41.4 (-), 38.4 (-), 35.9, 25.1 (+, 2C), 13.0 (+), 12.6 (+), 10.0 (+, 2C); FTIR (KBr, cm^{-1}): 3057, 3003, 2970, 2931, 2872, 1633, 1496, 1458, 1444, 1423, 1379, 1363, 1346, 1319, 1298, 1278, 1238, 1220, 1155, 1116, 1093, 1078, 756, 732; HRMS (TOF ES): Found 268.1669, calculated for $C_{16}H_{23}NONa$ (M+Na) 268.1677 (3.0 ppm).

(1*S,2*S**,3*R**)-*N*,*N*-Diisopropyl-2-methyl-1-phenyl-3-vinylcyclopropane-1-carboxamide** (**19be**): This compound was obtained via Typical procedure **C** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL 0.405 mmol, 1.35 equiv.), *N*,*N*-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**11b**) (73.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with methyl iodide (28.0 µL, 64.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a yellow solid, mp 94.4-

96.0 °C, R_f 0.61. Yield 69.4 mg (0.243 mmol, 81%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 4H), 7.22 – 7.15 (m, 1H), 5.95 – 5.74 (m, 1H), 5.22 (d, *J* = 17.0 Hz, 1H), 5.13 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.14 (hept, *J* = 6.6 Hz, 1H), 3.19 (hept, *J* = 6.8 Hz, 1H), 2.08 (s (broad), 1H), 1.76 (s (broad), 1H), 1.42 (t, *J* = 6.5 Hz, 6H), 1.33 (d, *J* = 6.6 Hz, 3H), 0.78 (s (broad), 3H), 0.64 (s (broad), 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 142.0, 135.1 (+), 128.7 (+, 2C), 126.4 (+), 126.2 (+, 2C), 115.8 (-, broad), 48.9 (+), 45.8 (+), 40.8 (broad), 35.0 (+, broad), 26.2 (+, broad), 20.8 (+), 20.6 (+), 20.4 (+), 20.1 (+), 11.4 (+); FTIR (KBr, cm^{-1}): 3080, 3059, 3001, 2962, 2929, 2872, 1633, 1494, 1435, 1369, 1336, 1211, 1155, 1118, 1039, 987, 900, 734; HRMS (TOF ES): Found 286.2162, calculated for $C_{19}H_{28}NO$ (M+H) 286.2171 (3.1 ppm).

((1*S,2*S**,3*S**)-2-Methyl-1,3-diphenylcyclopropyl)(piperidin-1-yl)methanone** (**19ed**): This compound was obtained via Typical procedure **C** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), (1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone (**11e**) (68.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with methyl iodide (28.0 µL, 64.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a colorless solid, mp 121.1-125.4 °C, R_f 0.42. Yield 83.4 mg (0.261 mmol, 87%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 4H), 7.30 – 7.27 (m, 4H), 7.24 – 7.19 (m, 2H), 3.58 – 3.46 (m, 2H), 3.11 – 2.98 (m, 1H), 2.89 (d, *J* = 10.0 Hz, 1H), 2.87 – 2.82 (m, 1H), 1.68 (dq, *J* = 9.9, 6.7 Hz, 1H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.44 – 1.34 (m, 2H), 1.34 – 1.23 (m, 2H), 0.87 – 0.73 (m, 1H), 0.51 – 0.39 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 142.5, 136.9, 129.4 (+, 2C), 128.8 (+, 2C), 127.9 (+, 2C), 126.4 (+), 126.2 (+), 125.6 (+, 2C), 46.7 (-), 42.3 (-), 38.3, 34.8 (+), 30.3 (+), 25.1 (-), 24.8 (-), 24.3 (-), 10.0 (+); FTIR (KBr, cm^{-1}): 3057, 3026, 2935, 2854, 1631, 1496, 1435, 1384, 1367, 1352, 1294, 1276, 1251, 1219, 1199, 1126, 1060, 1031, 1001, 852, 763, 744, 727, 700; HRMS (TOF ES): Found 342.1845, calculated for $C_{22}H_{25}NONa$ (M+Na) 342.1834 (3.2 ppm).

(1*R,2*S**,3*R**)-2-Allyl-*N*,*N*-diethyl-3-methyl-1-phenylcyclopropane-1-carboxamide** (**20aa**): This compound was obtained via Typical procedure **C** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with allyl bromide (39.0 µL, 55.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.38. Yield 70.6 mg (0.260 mmol, 87%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.14 (m, 5H), 6.09 – 5.85 (m, 1H), 5.09 (dd, *J* = 17.2, 1.9 Hz, 1H), 4.99 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.55 – 3.36 (m, 2H), 3.34 – 3.16 (m, 2H), 2.74 – 2.55 (m, 1H), 2.26 – 2.09 (m, 1H), 1.82 – 1.68 (m, 1H), 1.36 – 1.25 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.56 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 142.7, 138.4 (+), 128.7 (+, 2C), 126.1 (+), 125.9 (+, 2C), 114.6 (-), 41.5 (-), 38.6 (-), 36.1, 31.2 (+), 29.8 (-), 22.9 (+), 12.9 (+), 12.6 (+), 9.9 (+); FTIR (KBr, cm^{-1}): 3061, 3003, 2972, 2933, 2874, 1633, 1600, 1496, 1458, 1423, 1379, 1363, 1346, 1319, 1298, 1278, 1240, 1220, 1155, 1120, 1101, 1078, 995, 908, 817; HRMS (TOF ES): Found 294.1840, calculated for $C_{18}H_{25}NONa$ (M+Na) 294.1834 (2.0 ppm).

((1*S,2*S**,3*S**)-2-Allyl-1,3-diphenylcyclopropyl)(morpholino)methanone** (**20fd**): This compound was obtained via Typical procedure **C** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 µL 0.405 mmol, 1.35 equiv.), morpholino(1-phenylcycloprop-2-en-1-yl)methanone (**11f**) (69.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with allyl bromide (39.0 µL, 55.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a colorless solid, mp 102.4-103.5 °C, R_f 0.29. Yield 91.2 mg (0.262 mmol, 87%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.18 (m, 10H), 5.95 – 5.69 (m, 1H), 4.96 (dd, *J* = 17.2, 1.9 Hz, 1H), 4.88 (dd, *J* = 10.2, 1.9 Hz, 1H), 3.80 – 3.66 (m, 1H), 3.58 – 3.49 (m, 1H), 3.48 – 3.33 (m, 2H), 3.10 – 2.87 (m, 4H), 3.03 (d, *J* = 9.9 Hz, 1H), 2.60 – 2.46 (m, 1H), 2.44 – 2.31 (m, 1H), 1.59 – 1.39 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 141.5, 137.6 (+), 136.4, 128.9 (+, 2C), 128.7 (+, 2C), 128.2 (+, 2C), 126.7 (+), 126.6 (+), 125.5 (+, 2C), 114.9 (-), 66.0 (-), 65.4 (-), 46.1 (-), 41.7 (-), 38.4, 35.9 (+), 33.3 (+), 28.7 (-); FTIR (KBr, cm^{-1}): 3059, 3028, 3001, 2970, 2920, 2899, 2856, 1639, 1600, 1498, 1456, 1427, 1359, 1300, 1273, 1222, 1192, 1114, 1070, 1030, 999, 968, 912, 839; HRMS (TOF ES): Found 370.1765, calculated for $C_{23}H_{25}NO_2Na$ (M+Na) 370.1783 (4.9 ppm).

(1*S,2*S**,3*R**)-*N*,*N*,2-Triallyl-1-phenyl-3-vinylcyclopropane-1-carboxamide** (**20ge**): This compound was obtained via Typical procedure **C** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL 0.405 mmol, 1.35 equiv.), *N*,*N*-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (**11g**) (72.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with allyl bromide (39.0 µL, 55.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a viscous colorless oil, R_f 0.45. Yield 70.2 mg (0.228 mmol, 76%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.15 (m, 5H), 6.09 – 5.88 (m, 1H), 5.82 – 5.63 (m, 2H), 5.34 (dd, *J* = 16.9, 1.7 Hz, 1H), 5.18 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.13 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.09 (dd, *J* = 17.2, 1.6 Hz, 2H), 5.00 (dd, *J* = 10.3, 1.9 Hz, 1H), 4.94 – 4.90 (m, 3H), 4.11 – 3.97 (m, 1H), 3.94 – 3.66 (m, 3H), 2.81 – 2.65 (m, 1H), 2.48 – 2.35 (m, 1H), 2.33 – 2.18 (m, 1H), 1.61 – 1.50 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 141.2, 137.4 (+), 133.7 (+), 133.4 (+), 132.9 (+), 128.9 (+, 2C), 126.7 (+), 126.0 (+, 2C), 118.7 (-), 117.8 (-), 117.2 (-), 115.3 (-), 50.0 (-), 46.0 (-), 38.8, 33.3 (+), 32.9 (+), 30.6 (-); FTIR (KBr, cm^{-1}): 3078, 3003, 2980, 2920, 1643, 1631, 1600, 1496, 1450, 1435, 1410, 1330, 1298, 1282, 1269, 1205, 1192, 1128, 993, 922, 910, 759, 734; HRMS (TOF ES): Found 330.1822, calculated for $C_{21}H_{25}NONa$ (M+Na) 330.1834 (3.6 ppm).

(1*R,2*S**,3*R**)-2-Benzyl-*N*,*N*-diethyl-3-methyl-1-phenylcyclopropane-1-carboxamide** (**21aa**): This compound was obtained via Typical procedure **C** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with benzyl bromide (54.0 µL, 77.0 mg, 0.45

mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a colorless solid, mp 86.0-86.9 °C, R_f 0.29. Yield 78.8 mg (0.245 mmol, 82%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.08 (m, 10H), 3.54 (dq, *J* = 14.8, 7.5 Hz, 1H), 3.47 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.41 (dd, *J* = 15.6, 4.5 Hz, 1H), 3.32 – 3.17 (m, 2H), 2.76 (dd, *J* = 15.6, 9.9 Hz, 1H), 1.88 (dq, *J* = 9.5, 6.5 Hz, 1H), 1.52 – 1.43 (m, 1H), 1.27 (d, *J* = 6.5 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.57 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 142.6, 142.3, 128.7 (+, 2C), 128.6 (+, 2C), 128.4 (+, 2C), 126.2 (+), 125.8 (+, 3C), 41.5 (-), 38.6 (-), 36.3, 33.6 (+), 31.3 (-), 22.6 (+), 12.9 (+), 12.7 (+), 10.2 (+); FTIR (KBr, cm^{-1}): 3082, 3059, 3024, 2970, 2933, 2874, 1633, 1600, 1494, 1454, 1423, 1379, 1363, 1346, 1319, 1298, 1278, 1240, 1220, 1153, 1112, 1103, 1078, 1030, 947, 864; HRMS (TOF ES): Found 344.1995, calculated for $C_{22}H_{27}NONa$ (M+Na) 344.1990 (1.5 ppm).

(1*S,2*S**,3*S**)-*N*,*N*,2-Tribenzyl-1,3-diphenylcyclopropane-1-carboxamide** (**21cd**): This compound was obtained via Typical procedure **C** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), *N*,*N*-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**11c**) (102 mg, 0.30 mmol, 1.0 equiv.), and quenching with benzyl bromide (54.0 µL, 77.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 9:1). The titled compound was obtained as a colorless solid, mp 143.5-146.1 °C, R_f 0.38. Yield 120 mg (0.236 mmol, 79%), dr 15:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 2H), 7.40 – 6.87 (m, 21H), 6.28 – 6.12 (m, 2H), 4.95 (d, *J* = 14.0 Hz, 1H), 4.73 (d, *J* = 15.6 Hz, 1H), 3.80 (dd, *J* = 15.2, 4.9 Hz, 1H), 3.78 (d, *J* = 14.0 Hz, 1H), 3.68 (d, *J* = 15.6 Hz, 1H), 3.20 (d, *J* = 9.9 Hz, 1H), 2.99 (dd, *J* = 15.2, 9.0 Hz, 1H), 1.67 (ddd, *J* = 9.9, 9.0, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 142.2, 142.1, 136.6, 136.6, 135.6, 130.0 (+, 2C), 129.1 (+, 2C), 128.8 (+, 2C), 128.7 (+, 2C), 128.5 (+, 2C), 128.3 (+, 2C), 128.3 (+, 2C), 128.2 (+, 2C), 127.9 (+, 2C), 127.5 (+), 127.3 (+, 2C), 127.2 (+), 127.0 (+), 126.3 (+), 125.7 (+), 50.3 (-), 46.8 (-), 39.3, 36.8 (+), 32.3 (+), 30.5 (-); FTIR (KBr, cm^{-1}): 3084, 3061, 3028, 2929, 2914, 2862, 1952, 1880, 1809, 1643, 1633, 1600, 1494, 1454, 1417, 1361, 1329, 1265, 1209, 1078, 1030, 1003, 958, 943, 916, 842, 823, 767, 732, 700; HRMS (TOF ES): Found 530.2451, calculated for $C_{37}H_{33}NONa$ (M+Na) 530.2460 (1.7 ppm).

((1*S,2*S**,3*R**)-2-Benzyl-1-phenyl-3-vinylcyclopropyl)(pyrrolidin-1-yl)methanone** (**21de**): This compound was obtained via Typical procedure **C** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL, 0.405 mmol, 1.35 equiv.), (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**11d**) (64.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with benzyl bromide (54.0 µL, 77.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.26. Yield 78.2 mg (0.236 mmol, 79%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 10H), 5.98 – 5.70 (m, 1H), 5.37 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.20 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.62 – 3.48 (m, 2H), 3.45 (dd, *J* = 15.3, 5.2 Hz, 1H), 3.35 – 3.23 (m, 1H), 2.96 – 2.85 (m, 2H), 2.50 (dd, *J* = 10.2, 9.2 Hz, 1H), 1.85 – 1.71 (m, 2H), 1.71 – 1.61 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 141.9, 140.9, 133.9 (+), 128.9 (+, 2C), 128.8 (+, 2C), 128.4 (+, 2C), 126.5 (+), 125.9 (+), 125.6 (+, 2C), 117.4 (-), 46.8 (-), 46.1 (-), 40.0, 36.1 (+), 33.1 (+), 32.1 (-), 26.3 (-), 24.1 (-); FTIR (KBr, cm^{-1}): 3082, 3059, 3024, 2972, 2874, 1633, 1600, 1494, 1450, 1419, 1340, 1249, 1222, 1190, 1170, 1124, 1112, 1080, 1031, 983, 910, 758, 736; HRMS (TOF ES): Found 354.1834, calculated for $C_{23}H_{25}NONa$ (M+Na) 354.1834 (3.1 ppm).

(1*R,2*S**,3*R**)-2-Benzyl-*N*,*N*-diethyl-1,3-dimethylcyclopropane-1-carboxamide** (**21ka**): This compound was obtained via Typical procedure **C** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 326 µL, 0.979 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-methylcycloprop-2-ene-1-carboxamide (**11k**)[23] (100 mg, 1.0 equiv., 0.65 mmol), and quenching with benzyl bromide (156 µL, 223 mg, 1.31 mmol, 2.00 equiv.). The product was purified by column chromatography on Silica gel eluting with chloroform. The titled compound was obtained as a colorless oil, R_f 0.27 ($CHCl_3$). Yield 78.8 mg (0.245 mmol, 82%), dr >99:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.17 (t, *J* = 6.8 Hz, 1H), 3.69 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.52 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.46 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.33 – 3.24 (m, 2H), 2.47 (dd, *J* = 15.8, 9.4 Hz, 1H), 1.32 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 4.7 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 142.5, 128.4 (+, 2C), 128.2 (+, 2C), 125.6 (+), 41.1 (-), 38.0 (-), 31.0 (-), 29.0 (+), 27.4, 24.7 (+), 23.2 (+), 14.3 (+), 12.7 (+), 10.5 (+); FTIR (NaCl, cm^{-1}): 3117, 3021, 2970, 2831, 1631, 1465, 1419, 1251, 1122 1095, 732, 628; HRMS (TOF ES): found 282.1833, calculated for $C_{17}H_{25}NO$ (M+Na) 282.1834 (0.4 ppm).

(1*R,2*S**,3*S**)-*N*,*N*-Diethyl-2-methyl-1-phenyl-3-(trimethylsilyl)cyclopropane-1-carboxamide** (**22aa**): This compound was obtained via Typical procedure **C** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with chlorotrimethylsilane (57.0 µL, 49.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 6:1). The titled compound was obtained as a colorless solid, mp 94.9-96.3 °C, R_f 0.48. Yield 65.4 mg (0.215 mmol, 72%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 5H), 3.70 – 3.50 (m, 2H), 3.17 – 2.92 (m, 2H), 2.19 (dq, *J* = 10.6, 6.4 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H), 0.48 (t, *J* = 7.1 Hz, 3H), 0.15 (s, 9H), 0.00 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 144.0, 128.7 (+, 2C), 126.1 (+, 2C), 126.0 (+), 41.5 (-), 40.0, 39.2 (-), 26.1 (+), 21.9 (+), 13.6 (+), 12.8 (+), 12.7 (+), 1.3 (+, 3C); FTIR (KBr, cm^{-1}): 3053, 3007, 2970, 2945, 2895, 2874, 1627, 1599, 1462, 1444, 1427, 1373, 1261, 1240, 1155, 1101, 1053, 1022, 952, 858, 837, 802, 742, 702; HRMS (TOF ES): Found 326.1902, calculated for $C_{18}H_{29}NOSiNa$ (M+Na) 326.1916 (4.3 ppm).

(1*R,2*R**,3*S**)-*N*,*N*-Diethyl-2-methyl-1-phenyl-3-propionylcyclopropane-1-carboxamide** (**23aa**): This compound was obtained via Typical procedure **C** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with propionyl chloride (40.0 µL, 42.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column

chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.23. Yield 68.0 mg (0.237 mmol, 79%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 3.41 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.31 – 3.22 (m, 2H), 3.18 (dq, *J* = 14.1, 7.2 Hz, 1H), 2.79 (dq, *J* = 17.4, 7.4 Hz, 1H), 2.57 (dq, *J* = 17.3, 7.3 Hz, 1H), 2.29 (d, *J* = 9.0 Hz, 1H), 2.03 (dq, *J* = 8.9, 6.6 Hz, 1H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.12 (t, *J* = 7.3 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 1H), 0.57 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 167.3, 140.9, 129.0 (+, 2C), 127.1 (+), 126.4 (+, 2C), 43.7, 41.5 (-), 38.9 (-), 38.8 (-), 37.7 (+), 28.1 (+), 12.9 (+), 12.5 (+), 10.4 (+), 8.2 (+); FTIR (KBr, cm^{-1}): 3059, 2974, 2935, 2875, 1703, 1639, 1633, 1494, 1462, 1444, 1427, 1381, 1361, 1317, 1298, 1278, 1219, 1155, 1122, 1105, 1082, 1066, 1041, 904, 850, 833, 759, 700; HRMS (TOF ES): Found 310.1800, calculated for $C_{18}H_{25}NO_2Na$ (M+Na) 310.1783 (5.5 ppm).

(1*R,2*S**,3*R**)-*N*,*N*-Dibenzyl-1-phenyl-2-propionyl-3-vinylcyclopropane-1-carboxamide** (**23ce**): This compound was obtained via Typical procedure **C** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL 0.405 mmol, 1.35 equiv.), *N*,*N*-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**11c**) (102 mg, 0.30 mmol, 1.0 equiv.), and quenching with propionyl chloride (40.0 µL, 42.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 9:1). The titled compound was obtained as a viscous colorless oil, R_f 0.19. Yield 66.1 mg (0.156 mmol, 52%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 7.34 – 7.20 (m, 6H), 7.17 – 7.03 (m, 5H), 6.57 – 6.46 (m, 1H), 6.48 – 6.44 (m, 2H), 5.32 (dd, *J* = 17.2, 1.8 Hz, 1H), 5.13 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.82 (d, *J* = 14.6 Hz, 1H), 4.52 (d, *J* = 15.5 Hz, 1H), 4.14 (d, *J* = 15.5 Hz, 1H), 3.95 (d, *J* = 14.6 Hz, 1H), 2.92 – 2.80 (m, 1H), 2.78 – 2.70 (m, 1H), 2.70 – 2.57 (m, 2H), 1.18 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.8, 167.8, 139.6, 136.8, 135.6, 132.8 (+), 129.2 (+, 2C), 129.0 (+, 2C), 128.4 (+, 2C), 128.4 (+, 2C), 127.9 (+, 2C), 127.8 (+), 127.5 (+, 2C), 127.4 (+), 127.4 (+), 117.6 (-), 50.2 (-), 46.7 (-), 45.7, 39.3 (+), 38.9 (-), 37.6 (+), 8.2 (+); FTIR (KBr, cm^{-1}): 3061, 3028, 3003, 2978, 2935, 1707, 1643, 1633, 1602, 1494, 1450, 1417, 1361, 1329, 1315, 1267, 1234, 1193, 1178, 1122, 1080, 1039, 1030, 989, 945, 908, 806, 734, 700; HRMS (TOF ES): Found 446.2100, calculated for $C_{29}H_{29}NO_2Na$ (M+Na) 446.2096 (0.9 ppm).

1-((1*S,2*R**,3*S**)-2,3-Diphenyl-2-(pyrrolidine-1-carbonyl)cyclopropyl)propan-1-one** (**23dd**): This compound was obtained via Typical procedure **C** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**11d**) (64.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with propionyl chloride (40.0 µL, 42.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a colorless solid, mp 112.1-114.2 °C, R_f 0.18. Yield 83.1 mg (0.239 mmol, 80%), dr: >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.14 (m, 10H), 3.41 – 3.26 (m, 2H), 3.12 (d, *J* = 9.3 Hz, 1H), 3.12 – 3.05 (m, 1H), 2.85 – 2.74 (m, 1H), 2.68 – 2.53 (m, 2H), 2.36 (d, *J* = 9.3 Hz, 1H), 1.58 – 1.49 (m, 2H), 1.48 – 1.39 (m, 1H), 1.16 (t, *J* = 7.3 Hz, 3H), 1.06 – 0.95 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.7, 166.4, 140.1, 134.1, 129.8 (+, 2C), 129.1 (+, 2C), 127.6 (+, 2C), 127.4 (+), 126.8 (+), 126.6 (+, 2C), 46.9 (-), 46.3, 46.2 (-), 40.8 (+), 38.4 (-), 35.4 (+), 25.7 (-), 23.9 (-), 8.3 (+); FTIR (KBr, cm^{-1}): 3057, 3028, 2974, 2947, 2875, 1712, 1631, 1579, 1496, 1448, 1431, 1373, 1340, 1265, 1251, 1224, 1190, 1168, 1128, 1095, 1080, 1033, 962, 914, 869, 842, 771, 732, 700; HRMS (TOF ES): Found 370.1771, calculated for $C_{23}H_{25}NO_2Na$ (M+Na) 370.1783 (3.2 ppm).

(1*R,2*S**,3*S**)-*N*,*N*-Diethyl-2-iodo-3-methyl-1-phenylcyclopropane-1-carboxamide** (**24aa**): This compound was obtained via Typical procedure **C** employing methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (65.0 mg, 0.30 mmol, 1.0 equiv.), and a quenching with saturated solution of iodine in dry dimethoxyethane, which was added until the coloration persisted. The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous colorless oil, R_f 0.45. Yield 68.2 mg (0.190 mmol, 63%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.19 (m, 5H), 3.56 – 3.46 (m, 1H), 3.50 (d, *J* = 6.9 Hz, 1H), 3.43 – 3.33 (m, 1H), 3.33 – 3.23 (m, 2H), 1.45 – 1.35 (m, 4H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.58 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 140.4, 129.0 (+, 2C), 127.0 (+), 126.0 (+, 2C), 42.0 (-), 39.0 (-), 36.1, 26.5 (+), 18.1 (+), 12.6 (+), 12.6 (+), 7.2 (+); FTIR (KBr, cm^{-1}): 3057, 2970, 2931, 2872, 1633, 1599, 1496, 1444, 1425, 1379, 1315, 1296, 1278, 1263, 1234, 1219, 1149, 1122, 1103, 1080, 1066, 821, 761, 732; HRMS (TOF ES): Found 380.0474, calculated for $C_{15}H_{20}INONa$ (M+Na) 380.0487 (3.4 ppm).

(1*R,2*S**,3*S**)-*N*,*N*-Diethyl-1-phenyl-2-propionyl-3-vinylcyclopropane-1-carboxamide** (**24ae**): This compound was obtained via Typical procedure **C** employing vinylmagnesium bromide (**9e**) (1.0 M in THF, 405 µL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65 mg, 0.30 mmol, 1.0 equiv.), quenching with saturated solution of iodine in dry dimethoxyethane, which was added until coloration persisted. The product was purified by column chromatography on Silica gel eluting with hexane/EtOAc (mixture 3:1). The titled compound was obtained as a viscous yellowish oil, R_f 0.52. yield 56.0 mg (0.152 mmol, 51%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 5H), 5.89 – 5.68 (m, 1H), 5.37 – 5.21 (m, 2H), 3.56 (d, *J* = 8.4 Hz, 1H), 3.52 – 3.41 (m, 1H), 3.36 – 3.24 (m, 2H), 3.21 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.19 – 1.94 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.54 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 139.4, 138.7 (+), 129.1 (+, 2C), 127.4 (+), 126.0 (+, 2C), 117.5 (-), 42.0 (-), 39.2 (-), 38.8, 35.2 (+), 12.6 (+), 12.5 (+), 4.0 (+); FTIR (KBr, cm^{-1}): 3080, 3057, 3020, 2972, 2933, 2872, 1631, 1494, 1471, 1458, 1429, 1379, 1313, 1296, 1278, 1257, 1219, 1141, 1101, 1078, 979, 964, 904, 761, 700; HRMS (TOF ES): Found 369.0601, calculated for $C_{16}H_{20}INO$ (M+) 369.0590 (3.0 ppm).

(1*R,2*R**,3*S**)-*N*,*N*-Diethyl-2-((*S**)-hydroxy(phenyl)methyl)-3-methyl-1-phenylcyclopropane-1-carboxamide** (**25aa**), **Typical procedure D**: Methylmagnesium bromide (**9a**) (3.0 M in diethyl ether, 135 µL, 0.405 mmol, 1.35 equiv.), was added dropwise to a suspension of copper iodide (3.0 mg, 15.0 µmol, 5.0 mol%) in anhydrous freshly dried and distilled dimethoxyethane (1.0 mL), and the mixture was stirred 0 °C for 5 min under nitrogen atmosphere. *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide

(**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.) dissolved in dry dimethoxyethane (1.0 mL) was then added slowly, and the stirring was continued for 15 min at 0 °C, before freshly distilled benzaldehyde (48 mg, 46 μL, 0.45 mmol, 1.50 equiv.) was added. The mixture was stirred at 0 °C for 30 min, then warmed up to RT, and quenched with saturated aqueous ammonium chloride (1 mL). The resulting mixture was then diluted with water (10 mL) and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography on Silica gel eluting with hexane/diethyl ether (mixture 2:1). The titled compound was obtained as colorless solid, mp 140.9-143.6 °C, R_f 0.31. Yield 60.9 mg (0.180 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.35 – 7.27 (m, 4H), 7.26 – 7.16 (m, 4H), 5.81 (s, 1H), 4.78 (d, *J* = 10.3 Hz, 1H), 3.72 – 3.59 (m, 2H), 3.27 – 3.12 (m, 2H), 2.12 (dq, *J* = 9.6, 6.6 Hz, 1H), 1.42 (dd, *J* = 10.4, 9.6 Hz, 1H), 1.34 (d, *J* = 6.6 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.60 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 143.8, 141.4, 128.9 (+, 2C), 128.5 (+, 2C), 127.3 (+), 126.7 (+), 126.3 (+, 2C), 126.2 (+, 2C), 70.8 (+), 42.2 (+), 41.9 (-), 39.2 (-), 38.6, 20.7 (+), 12.8 (+), 12.6 (+), 10.6 (+); FT IR (KBr, cm^{-1}): 3358, 2972, 2935, 2875, 1608, 1495, 1422, 1380, 1347, 1318, 1252, 1155, 699; HRMS (TOF ES): Found 360.1949, calculated for $C_{22}H_{27}NO_2Na$ (M+Na) 360.1939 (2.8 ppm).

(1*R,2*R**,3*R**)-*N*,*N*-Diethyl-2-((*S**)-hydroxy(phenyl)methyl)-1,3-diphenylcyclopropane-1-carboxamide** (**25ad**): This compound was obtained via Typical procedure **C** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with freshly distilled benzaldehyde (48 mg, 46 μL, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/diethyl ether (mixture 2:1). The titled compound was obtained as colorless solid, mp 181.3-182.4 °C, R_f 0.31. Yield 96.4 mg (0.241 mmol, 80%), dr 96:4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.30 – 7.25 (m, 5H), 7.24 – 7.15 (m, 3H), 7.09 – 7.03 (m, 3H), 6.94 – 6.89 (m, 2H), 5.14 (d, *J* = 10.4 Hz, 1H), 3.51 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.29 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.19 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.13 (d, *J* = 10.1 Hz, 1H), 2.68 (dq, *J* = 14.2, 7.1 Hz, 1H), 1.64 (t, *J* = 10.3 Hz, 1H), 1.19 (s, 1H, broad), 1.11 (t, *J* = 7.1 Hz, 3H), 0.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 143.4, 141.2, 136.1, 128.9 (+, 2C), 128.8 (+, 2C), 128.3 (+, 2C), 128.0 (+, 2C), 127.0 (+), 126.8 (+), 126.8 (+), 126.3 (+, 2C), 125.6 (+, 2C), 68.5 (+), 44.1 (+), 41.9 (-), 40.6 , 39.3 (-), 32.4 (+), 11.9 (+), 11.9 (+); FT IR (KBr, cm^{-1}): 3355. 3060, 3029, 2976, 2935, 1605, 1497, 1429, 1381, 1278, 1195, 1151, 741; HRMS (TOF ES): Found 422.2098, calculated for $C_{27}H_{29}NO_2Na$ (M+Na) 422.2096 (0.5 ppm).

(1*R,2*R**,3*R**)-*N*,*N*-Diethyl-2-((*S**)-(4-fluorophenyl)-(hydroxy)methyl)-1,3-diphenylcyclopropane-1-carboxamide** (**26ad**): This compound was obtained via Typical procedure **C** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with 4-fluorobenzaldehyde (58.0 mg, 50.0 μL, 0.45 mmol, 1.50 equiv.). The titled compound was obtained as colorless oil, R_f 0.31. Yield 110 mg (0.263 mmol, 88%), dr 93:7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.38 – 7.33 (m, 4H), 7.31 – 7.22 (m, 4H), 6.96 – 6.88 (m, 2H), 6.85 – 6.77 (m, 2H), 5.98 (s, 1H), 5.16 (d, *J* = 10.4 Hz, 1H), 3.58 (dq, *J* = 14.1, 7.2 Hz, 1H), 3.36 (dq, *J* = 14.4, 7.1 Hz, 1H), 3.30 – 3.21 (m, 1H), 3.19 (d, *J* = 10.0 Hz, 1H), 2.75 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.65 (t, *J* = 10.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2 , 161.8 (d, *J* = 244.3 Hz), 141.0 , 139.1 (d, *J* = 3.5 Hz), 136.0 , 128.9 (d, *J* = 24.4 Hz, +, 2C), 128.4 (+, 2C) , 127.2 (d, *J* = 8.1 Hz, +, 2C), 127.1 (+, 2C) , 126.9 (+, 2C), 126.3 (+, 2C) , 114.8 (+) , 114.7 (+) , 68.1 (+) , 43.9 (+) , 41.9 (-) , 40.6 , 39.4 (-) , 32.2 (+) , 11.9 (+), 11.8 (+); ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.3 (s, 1F); FT IR (KBr, cm^{-1}): 3354, 2976, 2924, 1606, 1509, 1458, 1381, 1314, 1154, 1033, 767, 700; HRMS (TOF ES): Found 440.1987, calculated for $C_{27}H_{28}FNO_2Na$ (M+Na) 440.2002 (3.4 ppm).

(1*R,2*R**,3*S**)-*N*,*N*-Diethyl-2-((*R**)-1-hydroxy-2,2-dimethylpropyl)-3-methyl-1-phenylcyclopropane-1-carboxamide** (**27aa**): This compound was obtained via typical procedure **D** employing methylmagnesium bromide (**9a**) (130.0 μL, 3.0 M in THF, 0.390 mmol, 1.30 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and freshly distilled pivaldehyde (38.8 mg, 48.9 μL, 0.450 mmol, 1.50 equiv.). The product was purified by column chromatography on silica gel eluting with a mixture of hexane and diethyl ether (2:1). The titled compound was obtained as colorless solid, mp 138.1 – 139.4 °C, R_f 0.36. Yield 75.1 mg (0.237 mmol, 79%), dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.27 – 7.19 (m, 3H), 5.79 (d, *J* = 2.3 Hz, 1H), 3.73 – 3.60 (m, 2H), 3.41 (dd, *J* = 10.5, 2.3 Hz, 1H), 3.18 – 3.06 (m, 2H), 2.10 (dq, *J* = 9.6, 6.6 Hz, 1H), 1.21 (d, *J* = 6.6 Hz, 3H), 1.20 – 1.16 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.99 (s, 9H), 0.52 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 142.1, 128.9 (+, 2C), 126.5 (+), 126.2 (+, 2C), 74.8 (+), 41.8 (-), 39.1 (-), 38.0 (+), 36.9, 35.0, 26.3 (+, 3C), 21.3 (+), 12.5 (+), 12.4 (+), 11.1 (+); FT IR (KBr, cm^{-1}): 3348, 3027, 2968, 2873, 1604, 1460, 1429, 1063, 1007, 702; HRMS (TOF ES): Found 340.2255, calculated for $C_{20}H_{31}NO_2Na$ (M+Na) 340.2252 (0.9 ppm).

(1*R,2*R**,3*R**)-*N*,*N*-Diethyl-2-((*S**)-1-hydroxy-2,2-dimethylpropyl)-1,3-diphenylcyclopropane-1-carboxamide** (**27ad**): This compound was obtained via Typical procedure **C** employing phenylmagnesium bromide (**9d**) (3.0 M in diethyl ether, 135 μL, 0.405 mmol, 1.35 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and quenching with freshly distilled pivalic aldehyde (39.0 mg, 50.0 μL, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/diethyl ether (mixture 2:1). The titled compound was obtained as colorless solid, mp 196.9-198.0 °C, R_f 0.38. Yield 94.2 mg (0.248 mmol, 83%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.19 (m, 6H), 3.85 (d, *J* = 10.7 Hz, 1H), 3.52 (dq, *J* = 14.1, 7.2 Hz, 1H), 3.25 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.19 – 3.10 (m, 1H), 3.13 (d, *J* = 9.9 Hz, 1H), 2.61 (dq, *J* = 14.2, 7.1 Hz, 1H), 1.65 (s, 1H), 1.53 (t, *J* = 10.4 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.73 (s, 9H), 0.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 141.9, 137.1, 129.1 (+, 2C), 129.0 (+, 2C), 128.2 (+, 2C), 126.9 (+), 126.5 (+), 126.5 (+, 2C), 72.7 (+), 41.8 (-), 39.3 (-), 39.1 (+), 39.0 , 35.3, 33.5 (+), 26.2 (+, 3C), 12.0 (+), 11.9 (+); FT IR (KBr, cm^{-1}): 3363,

2964, 2648, 1595, 1463, 1442, 1433, 1007, 765, 699; HRMS (TOF ES): Found 402.2411, calculated for $C_{25}H_{33}NO_2Na$ (M+Na) 402.2409 (0.5 ppm).

(1*S,2*R**,3*S**)-*N*,*N*-Diethyl-2-((*S**)-1-hydroxy-2,2-dimethylpropyl)-1-phenyl-3-((trimethylsilyl)-methyl)cyclopropane-1-carboxamide** (**27ag**): This compound was obtained via Typical procedure **C** employing (trimethylsilyl)methylmagnesium chloride (**9g**) (1.30 M in THF, 450 µL, 0.60 mmol, 1.30 equiv.), *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**11a**) (98.0 mg, 0.45 mmol, 1.00 equiv.), and quenching with freshly distilled pivalic aldehyde (59.0 mg, 75.0 µL, 0.68 mmol, 1.50 equiv.). The product was purified by column chromatography on Silica gel eluting with hexane/diethyl ether (mixture 2:1). The titled compound was obtained as colorless oil, R_f 0.45. Yield 138 mg (0.354 mmol, 79%), dr >99:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 3.61 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.57 – 3.48 (m, 1H), 3.48 (d, *J* = 10.0 Hz, 1H) , 3.14 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.97 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.14 – 1.09 (m, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 9H), 0.88 (dd, *J* = 15.7, 5.2 Hz, 1H), 0.43 (t, *J* = 7.1 Hz, 3H), 0.43 – 0.38 (m, 1H), 0.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 142.4, 129.0 (+, 2C), 126.5 (+), 126.4 (+, 2C), 74.6 (+), 42.0 (-), 39.3 (-), 38.6 (+), 38.5, 35.5, 26.5 (+, 3C), 20.9 (+), 12.5 (+), 12.3 (+), 10.2 (-), -1.1 (+, 3C); FT IR (KBr, cm^{-1}): 3365, 2951, 2901, 1614, 1479, 1462, 1445, 1249, 1184, 1064, 846, 698; HRMS (TOF ES): Found 412.2644, calculated for $C_{23}H_{39}NO_2SiNa$ (M+Na) 412.2648 (1.0 ppm).

(*1R*,2R*,3S)-2-((*R**)-1-Hydroxy-2,2-dimethylpropyl)-*N*-methoxy-*N*,3-dimethyl-1-phenylcyclopropane-1-carboxamide** (**27ha**): This compound was obtained via typical procedure **D** using methylmagnesium bromide (**9a**) (260 µL, 3.0 M in THF, 0.780 mmol, 1.30 equiv.), *N*-methoxy-*N*-methyl-1-phenylcycloprop-2-ene-1-carboxamide (**11h**) (122.0 mg, 0.60 mmol, 1.0 equiv.), and freshly distilled pivaldehyde (77.6 mg, 98.0 µL, 0.90 mmol, 1.50 equiv.). The product was purified by column chromatography on silica gel eluting with a mixture hexane and diethyl ether (2:1). The titled compound was obtained as colorless oil, R_f 0.30. Yield 151 mg (0.494 mmol, 82%), dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, C_6D6) δ 7.25 – 7.19 (m, 2H), 7.10 – 7.03 (m, 2H), 7.01 – 6.95 (m, 1H), 5.36 (s, 1H), 3.61 (d, *J* = 10.4 Hz, 1H), 2.77 (s, 3H), 2.75 (s, 3H), 1.93 – 1.81 (m, 1H), 1.30 (t, *J* = 9.9 Hz, 1H), 1.15 (d, *J* = 6.7 Hz, 3H), 1.11 (s, 9H); ^{13}C NMR (126 MHz, C_6D6) δ 172.8, 142.7, 128.8 (+, 2C), 127.5 (+), 126.6 (+, 2C), 74.9 (+), 59.9 (+), 38.0 (+), 37.7, 35.4, 33.0 (+), 26.6 (+, 3C), 22.2 (+), 10.9 (+); FT IR (KBr, cm^{-1}): 3416, 3061, 2953, 2905, 1631, 1460, 1380, 1178, 1007, 699, 611; HRMS (TOF ES): Found 328.1885, calculated for $C_{18}H_{27}NO_3Na$ (M+Na) 328.1889 (1.2 ppm).

(*1R*,4S*,5S*,6R)-4-(*tert*-Butyl)-6-methyl-1-phenyl-3-oxabicyclo[3.1.0]hexan-2-one** (**28**):

p-Toluenesulfonic acid monohydrate (47.0 mg, 0.25 mmol, 1.2 equiv.) was added to a solution of (1*R**,2*R**,3*S**)-2-((*R**)-1-hydroxy-2,2-dimethylpropyl)-N-methoxy-N,3-dimethyl-1-phenylcyclopropane-1-carboxamide (**27ha**) (61.0 mg, 0.20 mmol, 1.0 equiv.) in benzene (5 mL) and the mixture was stirred for 10 minutes. The reaction was then warmed to 50 °C and stirred for 1 h. After cooling to room temperature, potassium carbonate (35 mg, 0.25 mmol, 1.2 equiv.) was added and the mixture was stirred for 15 minutes. The reaction was then filtered through a silica gel plug eluting with ethyl acetate, evaporated, and further purified by silica gel column chromatography using 6:1 hexane/ethyl acetate mixture as a mobile phase. The titled compound was obtained as colorless oil, R_f 0.37. Yield 43.4 mg (0.177 mmol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 3.86 (s, 1H), 2.32 (d, *J* = 8.2 Hz, 1H), 1.76 (dq, *J* = 8.2, 6.5 Hz, 1H), 1.21 (d, *J* = 6.5 Hz, 3H), 0.98 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 135.5, 128.7 (+, 2C), 127.8 (+, 2C), 127.5 (+), 83.4 (+), 37.5, 34.6, 31.5 (+), 25.2 (+, 3C), 25.0 (+), 8.4 (+); FTIR (KBr, cm^{-1}): 3060, 2962, 2907, 2873, 1759, 1500, 1335, 1112, 994, 908, 754, 697; HRMS (TOF ES): Found 267.1358, calculated for $C_{16}H_{20}O_2Na$ (M+Na) 267.1361 (1.1 ppm).

(*1S*,2S)-2-Butyl-*N*,*N*-diethyl-2-methyl-1-phenylcyclopropane-1-carboxamide** (**41aa**) and **(1S*,2S*,3S*)-2-butyl-*N*,*N*-diethyl-3-methyl-1-phenylcyclopropane-1-carboxamide** (**42aa**):

These compounds were obtained via typical procedure **A** employing methylmagnesium bromide (130.0 µL, 3.0 M in THF, 0.390 mmol, 1.30 equiv.) and 2-butyl-*N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**38a**) (82.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (6:1). The mixture of inseparable regioisomeric products titled compound was obtained as a colorless oil, R_f 0.29. Yield 77.3 mg (0.269 mmol, 90%), **41aa**:**42aa** ratio 88:12, dr >98:2 (for both regioisomers). ^{1}H NMR (500 MHz, $CDCl_3$) Mix of Regioisomers: δ [7.48 – 7.39 (m), Σ2H], [7.30 – 7.23 (m), Σ2H], [7.21 – 7.15 (m), Σ1H], [3.68 – 3.49 (m) & 3.44 – 3.28 (m) & 3.18 (dq, *J* = 14.0, 7.1 Hz) & 3.07 (dq, *J* = 13.9, 7.0 Hz) & 2.96 (dq, *J* = 14.0, 7.0 Hz), Σ4H], [1.62 – 1.54 (m) & 1.36 – 0.97 (m), Σ8H], [1.29 (d, *J* = 5.0 Hz) & 1.22 (s), Σ3H], [1.01 (t, *J* = 7.1 Hz), Σ3H], [0.83 (t, *J* = 7.1 Hz) & 0.75 (t, *J* = 7.1 Hz), Σ3H], [0.71 (t, *J* = 7.4 Hz) & 0.33 (t, *J* = 7.0 Hz), Σ3H]; ^{13}C NMR (126 MHz, $CDCl_3$) Mix of Regioisomers: δ [171.0 & 170.8], [138.6 & 138.3], [129.4 (+) & 129.3 (+), Σ2C], [128.1 (+) & 128.0 (+), Σ2C], [126.4 (+) & 126.2 (+)], [41.4 (-) & 41.0 (-)], [40.8 & 39.8], [39.4 (-) & 39.1 (-)], [35.2 (-) & 31.2 (+) & 31.1 (-) & 28.5 (-) & 28.4 & 28.3 (-) & 24.0 (-) & 22.8 (-) & 22.3 (-) & 22.0 (+) & 21.9 (+) & 14.2 (+) & 14.0 (+) & 13.9 (+) & 13.5 (+) & 12.5 (+) & 12.4 (+) & 12.2 (+), Σ9C]; FTIR (KBr, cm^{-1}): 3047, 2958, 2932, 2871, 1632, 1457, 1421, 1269, 1105, 729, 701; HRMS (TOF ES): Found 310.2143, calculated for $C_{19}H_{29}NONa$ (M+Na) 310.2147 (1.3 ppm).

(*1R*,2S*,3R)-2-Butyl-*N*,*N*-diethyl-1,3-diphenylcyclopropane-1-carboxamide** (**42ad**) and **(1*R**,2*S**)-2-butyl-*N*,*N*-diethyl-1,2-diphenylcyclopropane-1-carboxamide** (**41ad**): These compounds were obtained via typical procedure **A** using phenylmagnesium bromide (130.0 µL, 3.0 M in diethyl ether, 0.390 mmol, 1.30 equiv.) and 2-butyl-*N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**38a**) (82.0 mg, 0.30 mmol, 1.0 equiv.). ^{1}H NMR analysis of the crude mixture showed **42ad**:**41ad** ratio 70:30. The isomers were separated by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (6:1). The major regioisomer **42ad** was isolated as a colorless oil, R_f 0.40. Yield 66.6 mg (0.190 mmol, 64%), dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.26 (m, 3H), 7.26 – 7.23 (m, 2H), 7.21 – 7.17 (m, 1H),

3.49 – 3.25 (m, 2H), 2.79 (d, *J* = 6.8 Hz, 1H), 2.73 (dq, *J* = 14.0, 7.1 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.40 (dq, *J* = 14.0, 7.0 Hz, 1H), 1.41 – 1.14 (m, 5H), 0.94 – 0.81 (m, 1H), 0.77 (t, *J* = 7.3 Hz, 3H), 0.65 (t, *J* = 7.1 Hz, 3H), 0.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 137.9, 137.9, 128.7 (+, 2C), 128.5 (+, 2C), 128.2 (+, 2C), 127.5 (+, 2C), 126.8 (+), 126.3 (+), 45.9, 40.8 (-), 39.1 (-), 33.6 (+), 31.0 (-), 30.2 (+), 28.7 (-), 22.5 (-), 14.1 (+), 11.9 (+), 11.7 (+); FT IR (KBr, cm^{-1}): 3058, 3023, 2957, 2932, 2870, 1631, 1445, 1379, 1274, 1080, 700; HRMS (TOF ES): Found 372.2321, calculated for $C_{24}H_{31}NONa$ (M+Na) 372.2303 (4.8 ppm). The minor regioisomer **41ad** was isolated as a colorless oil, R_f 0.26. Yield 28.5 mg (0.082 mmol, 27%), dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.14 (m, 1H), 3.73 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.11 – 2.90 (m, 2H), 2.79 (dq, *J* = 13.8, 7.0 Hz, 1H), 2.32 (d, *J* = 5.3 Hz, 1H), 2.30 – 2.21 (m, 1H), 1.30 (d, *J* = 5.3 Hz, 1H), 1.20 – 1.03 (m, 4H), 1.02 – 0.93 (m, 1H), 0.71 (t, *J* = 7.0 Hz, 3H), 0.65 (t, *J* = 7.0 Hz, 3H), 0.46 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 140.1, 139.1, 130.4 (+, 2C), 128.9 (+, 2C), 128.4 (+, 2C), 127.8 (+, 2C), 126.8 (+), 126.2 (+), 42.9, 41.7 (-), 39.3 (-), 37.5, 36.8 (-), 29.4 (-), 22.8 (-), 22.6 (-), 14.2 (+), 13.4 (+), 11.8 (+). HRMS (TOF ES): Found 372.2317, calculated for $C_{24}H_{31}NONa$ (M+Na) 372.2303 (3.8 ppm).

(*1S*,2S)-2-Butyl-*N*,*N*-diethyl-1-phenyl-2-vinylcyclopropane-1-carboxamide** (**41ae**) and **(*1R*,2S*,3S**)-2-butyl-*N*,*N*-diethyl-1-phenyl-3-vinylcyclopropane-1-carboxamide** (**42ae**): These compounds were obtained via typical procedure **A** using vinylmagnesium bromide (390 μL, 1.0 M in THF, 0.390 mmol, 1.30 equiv.) and 2-butyl-*N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**38a**) (82.0 mg, 0.30 mmol, 1.0 equiv.). ^{1}H NMR analysis of the crude mixture showed **41ae**:**42ae** ratio 81:19. The isomers were separated by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (6:1). The major regioisomer **41ae** was isolated as a colorless oil, R_f 0.30. Yield 63.7 mg (0.213 mmol, 71%), dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 5.94 (dd, *J* = 17.2, 10.5 Hz, 1H), 5.05 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.98 (dd, *J* = 17.2, 1.4 Hz, 1H), 3.56 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.36 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.27 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.17 (dq, *J* = 13.9, 7.1 Hz, 1H), 1.62 (d, *J* = 5.3 Hz, 1H), 1.61 – 1.51 (m, 1H), 1.36 (d, *J* = 5.2 Hz, 1H), 1.34 – 1.28 (m, 1H), 1.24 – 1.02 (m, 3H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 3H), 0.81 – 0.76 (m, 1H), 0.74 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 141.1 (+), 137.8, 129.7 (+, 2C), 128.4 (+, 2C), 126.9 (+), 113.1 (-), 42.3, 41.6 (-), 39.2 (-), 35.4, 32.8 (-), 29.0 (-), 22.8 (-), 21.7 (-), 14.1 (+), 13.7 (+), 12.6 (+); FT IR (KBr, cm^{-1}): 3052, 2958, 2932, 2871, 1633, 1458, 1424, 1275, 1100, 902, 701; HRMS (TOF ES): Found 322.2157, calculated for $C_{20}H_{29}NONa$ (M+Na) 322.2147 (3.1 ppm). The minor regioisomer **42ae** was isolated as a colorless oil, R_f 0.40. Yield 15.0 mg (0.050 mmol, 17%), dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.24 – 7.19 (m, 1H), 5.47 – 5.35 (m, 1H), 5.26 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.01 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.61 – 3.44 (m, 2H), 3.06 (dq, *J* = 13.8, 7.0 Hz, 1H), 2.89 (dq, *J* = 14.1, 7.0 Hz, 1H), 2.26 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.05 – 1.88 (m, 1H), 1.35 – 1.07 (m, 6H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.75 (t, *J* = 7.2 Hz, 3H), 0.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 137.6, 137.0 (+), 128.6 (+, 2C), 128.4 (+, 2C), 126.7 (+), 115.2 (-), 42.7, 41.1 (-), 39.6 (-), 32.4 (+), 31.5 (+), 31.0 (-), 28.2 (-), 22.4 (-), 14.1 (+), 12.4 (+), 12.4 (+); HRMS (TOF ES): Found 322.2152, calculated for $C_{20}H_{29}NONa$ (M+Na) 322.2147 (1.6 ppm).

(*1R*,2S*,3S)-2-Butyl-*N*,*N*-diethyl-1-phenyl-3-((trimethylsilyl)methyl)cyclopropane-1-carboxamide** (**42ag**). This compound was obtained via typical procedure A using (trimethylsilyl)methylmagnesium chloride (300 μL, 1.3 M in THF, 0.390 mmol, 1.3 equiv.) and 2-butyl-*N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**38a**) (82.0 mg, 0.30 mmol, 1.0 equiv.). ^{1}H NMR analysis of the crude mixture showed **42ag**:**41ag** ratio 75:25. The major regioisomers was isolated by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (6:1). The titled compound was obtained as a pale yellow oil, R_f 0.46. Yield 80.7 mg, yield (0.224 mmol, 75%), dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.15 (m, 5H), 3.62 (dq, *J* = 14.4, 7.1 Hz, 1H), 3.49 (dq, *J* = 13.8, 7.0 Hz, 1H), 3.13 (dq, *J* = 13.9, 7.0 Hz, 1H), 2.94 (dq, *J* = 14.0, 7.0 Hz, 1H), 1.64 – 1.48 (m, 2H), 1.31 – 1.10 (m, 4H), 1.07 (t, *J* = 7.1 Hz, 3H), 1.05 – 0.97 (m, 1H), 0.87 – 0.76 (m, 2H), 0.69 (t, *J* = 7.0 Hz, 3H), 0.31 (t, *J* = 7.0 Hz, 3H), 0.17 (dd, *J* = 14.4, 11.9 Hz, 1H), 0.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 138.8, 128.9 (+, 2C)), 128.2 (+, 2C), 126.3 (+), 41.4 (-), 41.3, 39.6 (-), 31.6 (+), 31.0 (-), 28.7 (-), 23.6 (+), 22.6 (-), 16.3 (-), 14.0 (+), 12.6 (+), 12.3 (+), -1.2 (+, 3C); FT IR (KBr, cm^{-1}): 3057, 2955, 2932, 2872, 1633, 1457, 1423, 1271, 1247, 860, 838, 758, 701; HRMS (TOF ES): Found 382.2552, calculated for $C_{22}H_{37}NOSiNa$ (M+Na) 382.2542 (2.6 ppm).

(*1S*,2S*,3R)-*N*,*N*-Diethyl-2-methyl-1,3-diphenylcyclopropane-1-carboxamide** (**42ba**) **and (1*R**,2*R**)-*N*,*N*-diethyl-2-methyl-1,2-diphenyl-cyclopropane-1-carboxamide** (**41ba**): These compounds were obtained via typical procedure **A** employing methylmagnesium bromide (130.0 μL, 3.0 M in THF, 0.390 mmol, 1.30 equiv.) and *N*,*N*-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**38b**) (88.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on silica gel eluting with a mixture of hexane:ethyl acetate (6:1). A mixture of inseparable regioisomers was obtained as a colorless amorphous solid, R_f 0.26. Yield 85.3 mg (0.277 mmol, 92%), **42ba**:**41ba** ratio 91:9, dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$): Mixture of regioisomers: δ [7.11 – 7.07 (m), Σ4H], [7.03 – 6.98 (m), Σ3H], [6.98 – 6.92 (m), Σ3H], [3.70 (dq, *J* = 14.3, 7.1 Hz) & 3.58 (dq, *J* = 13.9, 7.1 Hz) & 3.41 – 3.34 (m) & 3.13 (dq, *J* = 13.5, 7.0 Hz) & 3.07 (dq, *J* = 14.2, 7.2 Hz), Σ4H], [3.01 (d, *J* = 6.7 Hz) & 2.08 (d, *J* = 5.4 Hz), Σ1H], [2.40 (dt, *J* = 6.3 Hz) & 1.50 (d, *J* = 5.4 Hz), Σ1H], [1.61 (s) & 1.31 (d, *J* = 6.2 Hz), Σ3H], [1.11 (t, *J* = 7.1 Hz), Σ3H], [0.84 (t, *J* = 7.1 Hz) & 0.40 (t, *J* = 7.0 Hz, 1H), Σ3H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 137.6, 137.1, 128.9 (+, 2C), 128.6 (+, 2C), 128.1 (+, 2C), 127.6 (+, 2C), 126.4 (+), 125.7 (+), 44.7, 41.4 (-), 39.7 (-), 36.6 (+), 21.3 (+), 14.4 (+), 12.6 (+), 12.5 (+); FT IR (KBr, cm^{-1}): 3041, 2967, 1629, 1458, 1425, 1276, 1140, 697; HRMS (TOF ES): Found 330.1840, calculated for $C_{21}H_{25}NONa$ (M+Na) 330.1834 (1.8 ppm).

(*2R*,3R)-*N*,*N*-Diethyl-1,2,3-triphenylcyclopropane-1-carboxamide** (**42bd**): This compound was obtained via typical procedure **A** employing phenylmagnesium bromide (130.0 μL, 3.0 M in diethyl ether, 0.390 mmol, 1.30 equiv.) and *N*,*N*-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**38b**) (88.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by

column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (6:1). The titled compound was obtained as a colorless solid, mp 174.3 – 175.6 °C, R_f 0.27. Yield 99.2 mg (0.268 mmol, 89%), **42bd**:**41bd** ratio >98:2, dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.20 (m, 3H), 7.17 – 7.12 (m, 2H), 7.11 – 7.03 (m, 5H), 7.02 – 6.97 (m, 1H), 3.90 (d, *J* = 7.3 Hz, 1H), 3.55 (d, *J* = 7.3 Hz, 1H), 3.51 – 3.31 (m, 2H), 2.77 (dq, *J* = 13.9, 7.0 Hz, 1H), 2.48 (dq, *J* = 14.1, 7.0 Hz, 1H), 0.69 (t, *J* = 7.1 Hz, 3H), 0.17 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 136.9, 136.8, 136.6, 128.8 (+, 2C), 128.6 (+, 2C), 128.4 (+, 2C), 128.3 (+, 2C), 127.8 (+, 2C), 127.7 (+, 2C), 126.8 (+), 126.7 (+), 126.1 (+), 48.6, 41.0 (-), 39.2 (-), 35.2 (+), 32.5 (+), 12.0 (+), 11.8 (+); FT IR (KBr, cm^{-1}): 3046, 3029, 2974, 2934, 1624, 1446, 1277, 1078, 774, 750, 697; HRMS (TOF ES): Found 392.1982, calculated for $C_{26}H_{27}NONa$ (M+Na) 392.1990 (2.0 ppm).

(*1S*,2R*,3S)-*N*,*N*-Diethyl-1,2-diphenyl-3-vinylcyclopropane-1-carboxamide** (**42be**): This compound was obtained via typical procedure **A** using vinylmagnesium bromide (390.0 μL, 1.0 M in THF, 0.390 mmol, 1.30 equiv.) and *N*,*N*-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**38b**) (88.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (6:1). The titled compound was obtained as a colorless solid, mp 101.3 – 101.9 °C, R_f 0.30. Yield 80.4 mg, (0.252 mmol, 84%), **42be**:**41be** ratio 98:2, dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 4H), 7.06 – 7.00 (m, 3H), 7.00 – 6.94 (m, 3H), 5.59 (ddd, *J* = 17.0, 10.1, 9.0 Hz, 1H), 5.43 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.15 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.63 – 3.50 (m, 2H), 3.37 (d, *J* = 6.5 Hz, 1H), 3.12 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.03 (dd, *J* = 8.9, 6.5 Hz, 1H), 3.01 – 2.94 (m, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 136.6, 136.2, 135.9 (+), 128.6 (+, 2C), 128.6 (+, 2C), 128.3 (+, 2C), 127.7 (+, 2C), 126.7 (+), 126.0 (+), 116.4 (-), 45.6, 41.3 (-), 39.7 (-), 36.3 (+), 31.5 (+), 12.5 (+), 12.4 (+); FT IR (KBr, cm^{-1}): 3059, 3027, 2976, 2934, 1630, 1445, 1428, 1276, 1134, 908, 753, 697; HRMS (TOF ES): Found 342.1820, calculated for $C_{22}H_{25}NONa$ (M+Na) 342.1834 (4.1 ppm).

(*1R*,2R*,3S)-*N*,*N*-Diethyl-1,2-diphenyl-3-((trimethylsilyl)methyl)cyclopropane-1-carboxamide** (**42bg**): This compound was obtained via typical procedure **A** using (trimethylsilyl)methylmagnesium chloride (300 μL, 1.3 M in THF, 0.390 mmol, 1.3 equiv.) and *N*,*N*-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**38b**) (88.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (6:1). The titled compound was obtained as a colorless solid, mp 186.8 – 187.4 °C, R_f 0.30. Yield 79.4 mg (0.209 mmol, 70%), **42bg**:**41bg** ratio >98:2, dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 4.3 Hz, 4H), 7.04 – 6.90 (m, 6H), 3.71 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.54 (dq, *J* = 13.9, 7.1 Hz, 1H), 3.18 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.05 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.98 (d, *J* = 6.8 Hz, 1H), 2.35 (ddd, *J* = 12.3, 6.8, 2.7 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.05 (dd, *J* = 14.4, 2.7 Hz, 1H), 0.41 – 0.35 (m, 1H), 0.38 (t, *J* = 7.1 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 137.5, 137.3, 128.9 (+, 2C), 128.5 (+, 2C), 128.1 (+, 2C), 127.6 (+, 2C), 126.3 (+), 125.6 (+), 45.0, 41.5 (-), 39.8 (-), 37.1 (+), 22.7 (+), 16.4 (-), 12.7 (+), 12.5 (+), -1.2 (+, 3C); FT IR (KBr, cm^{-1}): 3056, 2956, 2902, 1622, 1443, 1426, 1250, 858, 832, 696; HRMS (TOF ES): Found 402.2226, calculated for $C_{24}H_{33}NOSiNa$ (M+Na) 402.2229 (0.7 ppm).

(*1S*,2S*,3R)-*N*,*N*-Diethyl-2-methyl-1-phenyl-3-(*p*-tolyl)cyclopropane-1-carboxamide** (**42ca**) **and (1*R**,2*R**)-*N*,*N*-diethyl-2-methyl-1-phenyl-2-(*p*-tolyl)cyclopropane-1-carboxamide** (**41ca**):

These compounds were obtained via typical procedure **A** employing methylmagnesium bromide (130 μL, 3.0 M in THF, 0.390 mmol, 1.30 equiv.) and *N*,*N*-diethyl-1-phenyl-2-(*p*-tolyl)cycloprop-2-ene-1-carboxamide (**38c**) (92.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on silica eluting with a mixture of hexane and ethyl acetate (6:1). A mixture of inseparable regioisomers was obtained as a colorless solid, mp 115.7 – 118.3 °C, R_f 0.26. Yield 93.5 mg (0.291 mmol, 97 %), **42ca**:**41ca** ratio 86:14, dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$): δ [7.13 – 7.07 (m, Σ4H)], [7.05 – 6.99 (m, Σ1H)], [6.87 – 6.79 (m, Σ4H)], [3.70 (dq, *J* = 14.3, 7.1 Hz) & 3.58 (dq, *J* = 14.0, 7.1 Hz) & 3.42 – 3.33 (m) & 3.12 (dq, *J* = 14.0, 7.0 Hz) & 3.05 (dq, *J* = 14.0, 7.0 Hz), Σ4H], [2.96 (d, *J* = 6.7 Hz) & 2.39 – 2.32 (m) & 2.02 (d, *J* = 5.7 Hz), Σ2H], [2.21 (s) & 2.14 (s), Σ3H], [1.58 (s) & 1.30 (d, *J* = 6.2 Hz), Σ3H], [1.11 (t, *J* = 7.1 Hz), Σ3H], [0.82 (t, *J* = 7.0 Hz) & 0.40 (t, *J* = 7.0 Hz), Σ3H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ [170.6 & 170.3, Σ1C], [139.2 & 138.1 & 137.2 & 135.5 & 135.0 & 134.4, Σ3C], [128.9 (+) & 128.7 (+) & 128.6 (+) & 128.4 (+) & 128.4 (+) & 128.3 (+) & 128.1 (+) & 127.8 (+), Σ8C], [126.3 (+) & 126.0 (+), Σ1C], [57.1 & 44.6, Σ1C], [41.6 (-) & 41.3 (-) & 39.7 (-) & 39.3 (-), Σ2C], [36.3 (+) & 26.8, Σ1C], [24.1 (-) & 21.4 (+), Σ1C], [21.1 (+) & 21.0 (+), Σ1C], [14.5 (+) & 14.4 (+), Σ1C], [12.5 (+) & 12.5 (+) & 12.5 (+) & 12.5 (+), Σ2C]; FT IR (KBr, cm^{-1}): 3062, 2968, 2932, 2871, 1632, 1457, 1425, 1276, 1219, 1140, 811, 700; HRMS (TOF ES): Found 344.1989, calculated for $C_{22}H_{27}NONa$ (M+Na) 344.1990 (0.3 ppm).

(*1S*,2R*,3S)-*N*,*N*-Diethyl-2-(4-fluorophenyl)-3-methyl-1-phenylcyclopropane-1-carboxamide** (**42da**) **and (1*R**,2*R**)-*N*,*N*-diethyl-2-(4-fluorophenyl)-2-methyl-1-phenylcyclopropane-1-carboxamide** (**41da**): These compounds were obtained via typical procedure **A** using methylmagnesium bromide (130 μL, 3.0 M in THF, 0.390 mmol, 1.30 equiv.) and *N*,*N*-diethyl-2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxamide (**38d**) (93.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on silica gel eluting with a hexane and ethyl acetate mixture (6:1). A mixture of inseparable regioisomers was obtained as a colorless oil, R_f 0.16. Yield 97.0 mg, (0.298 mmol, 99%), **42da**:**41da** ratio 95:5, dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) mixture of regioisomers: δ [7.13 – 7.04 (m), Σ4H], [7.04 – 6.99 (m), Σ1H], [6.92 – 6.86 (m), Σ2H], [6.79 – 6.73 (m) & 6.71 – 6.65 (m), Σ2H], [3.67 (dq, *J* = 14.4, 7.1 Hz) & 3.58 (dq, *J* = 13.8, 7.1 Hz) & 3.12 (dq, *J* = 13.9, 7.0 Hz) & 3.04 (dq, *J* = 14.0, 7.0 Hz), Σ4H], [2.97 (d, *J* = 6.6 Hz) & 2.38 – 2.31 (m) & 2.07 (d, *J* = 5.5 Hz) & 1.45 (d, *J* = 5.3 Hz), Σ2H], [1.58 (s) & 1.30 (d, *J* = 6.2 Hz), Σ3H], [1.11 (t, *J* = 7.1 Hz), Σ3H], [0.84 (t, *J* = 7.1 Hz) & 0.39 (t, *J* = 7.0 Hz), Σ3H]; ^{13}C NMR (126 MHz, $CDCl_3$) major regioisomer: δ 170.1, 161.1 (d, *J* = 243.9 Hz), 136.9, 133.3 (d, *J* = 2.8 Hz), 129.9 (+, d, *J* = 8.1 Hz, 2C), 128.7 (+), 128.2 (+, 2C), 126.5 (+, 2C), 114.4 (+, d, *J* = 21.5 Hz, 2C), 44.5, 41.4 (-), 39.7 (-), 35.8 (+), 21.4 (+), 14.3 (+), 12.5 (+), 12.5 (+); FT IR (KBr, cm^{-1}): 2969, 2934, 2872, 1629, 1512, 1426, 1216, 822, 761, 700;

HRMS (TOF ES): Found 348.1744, calculated for $C_{21}H_{24}FNONa$ (M+Na) 348.1740 (1.1 ppm).

(*1S*,2R*,3S)-*N*,*N*-Diethyl-2-(4-methoxyphenyl)-3-methyl-1-phenylcyclopropane-1-carboxamide (42ea) and (1*R**,2*R**)-*N*,*N*-diethyl-2-(4-methoxyphenyl)-2-methyl-1-phenylcyclopropane-1-carboxamide (41ea).** These compounds were obtained via typical procedure **A** using methylmagnesium bromide (130 μL, 3.0 M in THF, 0.390 mmol, 1.30 equiv.) and *N*,*N*-diethyl-2-(4-methoxyphenyl)-1-phenylcycloprop-2-ene-1-carboxamide (**38e**) (96.5 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on silica gel eluting with a hexane and ethyl acetate mixture (3:1). A mixture of inseparable regioisomers was obtained as a colorless oil, R_f 0.23. Yield 52.2 mg, (0.155 mmol, 52%), **42ea**:**41ea** ratio 90:10, dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 – 7.06 (m, 4H), 7.05 – 6.98 (m, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 2H), 3.73 – 3.66 (m, 1H), 3.65 (s, 3H), 3.58 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.13 (dq, *J* = 14.0, 7.0 Hz, 1H), 3.04 (dq, *J* = 14.0, 6.9 Hz, 1H), 2.94 (d, *J* = 6.6 Hz, 1H), 2.40 – 2.25 (m, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H), 0.40 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 157.6, 137.3, 129.7, 129.5 (+, 2C), 128.8 (+, 2C), 128.2 (+, 2C), 126.3 (+), 113.1 (+, 2C), 55.2 (+), 44.4, 41.4 (-), 39.7 (-), 35.9 (+), 21.4 (+), 14.4 (+), 12.6 (+), 12.5 (+); FT IR (KBr, cm^{-1}): 3057, 2965, 2934, 2871, 1628, 1515, 1426, 1277, 1247, 1036, 821, 756, 700; HRMS (TOF ES): Found 360.1927, calculated for $C_{22}H_{27}NO_2Na$ (M+Na) 360.1939 (3.3 ppm).

(*1S*,2S*,3R)-*N*,*N*-Diethyl-2-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)cyclopropane-1-carboxamide** (**42fa**): This compound was obtained via typical procedure **A** using methylmagnesium bromide (130 μL, 3.0M in THF, 0.390 mmol, 1.30 equiv.) and *N*,*N*-diethyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxamide (**38f**) (108 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (3:1). The titled compound was obtained as a colorless solid, mp 93.9 – 94.8 °C, R_f 0.29. Yield 104.3 mg (0.278 mmol, 93%), **42fa**:**41fa** >98:2, dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.3 Hz, 2H), 7.14 – 7.06 (m, 4H), 7.06 – 7.01 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 2H), 3.68 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.58 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.17 – 3.01 (m, 2H), 3.05 (d, *J* = 6.6 Hz, 1H), 2.47 – 2.38 (m, 1H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H), 0.40 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 141.9, 136.3, 128.7 (+), 128.5 (+, 2C), 128.3 (+, 2C), 127.7 (q, *J* = 32.0 Hz), 126.7 (+, 2C), 124.4 (q, *J* = 3.7 Hz, +, 2C), 124.3 (q, *J* = 271.7 Hz), 45.3, 41.3 (-), 39.7 (-), 36.1 (+), 21.7 (+), 14.1 (+), 12.4 (+), 12.4 (+); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.34 (s, 3F); FT IR (KBr, cm^{-1}): 2972, 2936, 1630, 1326, 1164, 1121, 1068, 1017, 860, 728, 701; HRMS (TOF ES): Found 398.1719, calculated for $C_{22}H_{24}F_3NONa$ (M+Na) 398.1708 (2.8 ppm).

(*1R*,2R*,3S)-*N*,*N*-Diethyl-2,3-dimethyl-1,2-diphenylcyclopropane-1-carboxamide** (**42bh**). Methylmagnesium bromide (130 μL, 3.0 M in diethyl ether, 0.390 mmol, 1.35 equiv.) was added dropwise to a flame dried two neck flask containing copper iodide (3.0 mg, 15.0 μmol, 5.0 mol%) and freshly dried and distilled tetrahydrofuran (4 mL) under a nitrogen atmosphere at 0 °C. The mixture was stirred for five minutes at 0 °C. *N*,*N*-Diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**38a**) (88.0 mg, 0.30 mmol, 1.0 equiv.) was then added slowly dropwise as a solution in dry THF (2 mL). After 20 minutes of stirring at 0 °C, iodomethane (28 μL, 64.0 mg, 0.45 mmol, 1.50 equiv.) was added dropwise and stirred for 30 minutes at 0 °C. The reaction was then allowed to warm to room temperature over 15 min before saturated aqueous ammonium chloride (1 mL) was added. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (6:1). The titled compound was obtained as a colorless solid, mp 150.3 – 151.2 °C, R_f 0.26. Yield in 87.5 mg yield (0.272 mmol, 91 %), dr >98:2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 – 6.97 (m, 8H), 6.96 – 6.90 (m, 2H), 3.67 – 3.51 (m, 2H), 3.21 – 3.03 (m, 2H), 2.39 (q, *J* = 6.5 Hz, 1H), 1.61 (s, 3H), 1.36 (d, *J* = 6.5 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.44 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 144.9, 138.7, 129.4 (+, 2C), 127.9 (+, 2C), 127.8 (+), 127.7 (+, 2C), 125.9 (+, 2C), 125.5 (+), 42.4, 41.6 (-), 38.7 (-), 38.2, 23.5 (+), 21.5 (+), 12.7 (+), 12.7 (+), 10.5 (+); FT IR (KBr, cm^{-1}): 3059, 2969, 1624, 1444, 1422, 1267, 1066, 694; HRMS (TOF ES): Found 344.1996, calculated for $C_{22}H_{27}NONa$ (M+Na) 344.1990 (1.7 ppm).

ASSOCIATED CONTENT

Supporting Information

Spectral data (PDF)
X-Ray crystallography data (CIF)

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This project was supported by grants from the Ministry of Education and Science of the Russian Federation (MR) (Grant number 4.1196.2017/4.6). Support for NMR instruments used in this project was provided by NIH Shared Instrumentation Grant No. S10RR024664 and NSF Major Research Instrumentation Grant No. 0329648.

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