Synthesis of Cyclopropenes via 1,2-Elimination of Bromocyclopropanes Catalyzed by Crown Ether

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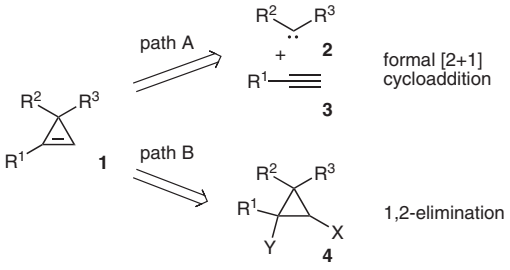
Abstract: A new synthetic protocol for the preparation of 3,3-disubstituted cyclopropenes from the corresponding bromocyclopropanes via a base-assisted 1,2-elimination has been developed. Employment of catalytic amounts of 18-crown-6 in ethereal solvents allowed for improved yields, as compared to the classical procedure employing dimethyl sulfoxide, making this protocol applicable to the synthesis of hydrophilic cyclopropenes. The application of this new method for the efficient synthesis of cyclopropene-3-carboxamides, an important class of functionalized 3,3-disubstituted cyclopropenes, is demonstrated. Scope and limitation studies are discussed.

Key words: amides, cyclopropenes, crown ether, eliminations, phase-transfer catalysis

Recent impressive advances in the development of novel, highly selective additions to cyclopropenes[1] have significantly broadened the application of these building blocks in organic chemistry.[2,3] Accordingly, recent efforts have focused on the development of efficient synthetic approaches for the preparation of diversely substituted cyclopropenes. To date, two general methods have mainly been used for the synthesis of cyclopropenes **1**; they include the transition-metal-catalyzed addition of carbenoids **2** to alkynes **3** (Scheme 1, path A)[4] and a protocol involving 1,2-elimination of H–Hal[5] or Hal–Hal[6] (Hal = halogen) entities from cyclopropyl halide precursors **4** (Scheme 1, path B).

The former method has been receiving much attention from the synthetic community, resulting in substantial expansion of its scope, thereby making available a range of cyclopropenes,[7] including optically active compounds.[4d–g] In contrast, the second approach has not undergone any



Scheme 1 The two most important retrosynthetic approaches to the cyclopropene core

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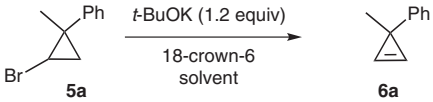
significant development in the decades[8] since the first report on the synthesis of 3,3-disubstituted cyclopropenes via the 1,2-elimination of a hydrogen halide in the presence of sodium *tert*-butoxide and dimethyl sulfoxide.[9] At the same time, the requisite use of dimethyl sulfoxide as reaction medium significantly limits the potential of the method for scale-up and its appeal for process development. Furthermore, it becomes a major liability when the target cyclopropene is relatively hydrophilic. In this case, repetitive washing of the organic phase with water, necessary for complete removal of dimethyl sulfoxide,[8] leads to substantial loss of the product. Alternative approaches involving removal of dimethyl sulfoxide by distillation or column chromatography usually do not provide satisfactory results, particularly in multigram-scale syntheses.

In an attempt to overcome this problem, we considered the possibility of replacing dimethyl sulfoxide with alternative, more practical solvents. We rationalized that employment of chelating agents, such as crown ethers,[10] could potentially help enhance the basicity of potassium *tert*-butoxide and enable an efficient elimination reaction in less polar media. It should be mentioned that preparative methods for 1,2-dehydrohalogenation in nonpolar media employing 18-crown-6 as phase-transfer catalyst have been reported previously;[10] however, they have never been used for the preparation of strained olefins. Herein we wish to report a new protocol for the synthesis of cyclopropenes via a base-assisted 1,2-elimination in ethereal solvents in the presence of catalytic amounts of 18-crown-6. We also demonstrate the application of the new method for the efficient synthesis of cyclopropene-3-carboxamides, an important class of functionalized cyclopropenes.[11]

First, we tested the dehydrobromination of 2-bromo-1-methyl-1-phenylcyclopropane (**5a**) with potassium *tert*-butoxide in tetrahydrofuran in the presence of various amounts of 18-crown-6 (Table 1, entries 1–3). It was found that the addition of stoichiometric amounts of crown ether facilitated a rapid dehydrohalogenation; however, notable decomposition of product **6a** led to moderate overall yields. Decreasing the amount of crown ether was beneficial for the reaction yield (Table 1, entries 2 and 3), and with additional optimization we discovered yields can be further improved by lowering the reaction temperature to 30 °C (Table 1, entry 4). Screening of various ethereal solvents demonstrated that tetrahydrofuran and diethyl ether appeared to be the most suitable media for this trans-

formation. In contrast, reactions in dibutyl ether and diglyme did not produce any product at all (Table 1, entries 6 and 9), while other ethers resulted in a much slower and less efficient reaction. Although both tetrahydrofuran and diethyl ether provided essentially the same results, we chose tetrahydrofuran as the more practical solvent.

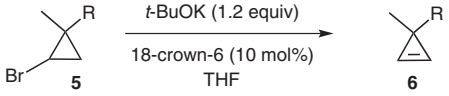
Table 1 Optimization of 1,2-Elimination Reaction



Entry	18-Crown-6 (equiv)	Solvent	Time (h)	Temp (°C)	Yield[a] (%)
1	1.2	THF	1	50	40
2	0.3	THF	3	50	65
3	0.1	THF	3	50	70
4	0.1	THF	14	30	93
5	0.1	1,4-dioxane	48	30	86
6	0.1	Bu_2O	48	30	0
7	0.1	TBDME	48	30	76
8	0.1	DME	48	30	21
9	0.1	diglyme	48	30	0
10	0.1	Et_2O	14	30	84

[a] Yield determined by GC.

Table 2 Preparative Syntheses of Cyclopropenes



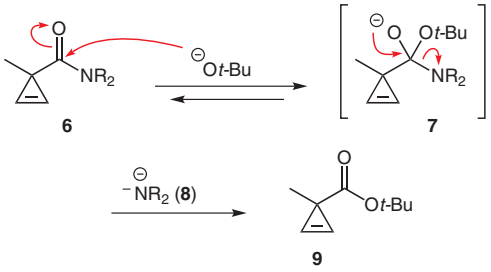
Entry	R	Time (h)	Temp (°C)	Yield[a] (%)
1	Ph (**5a**, **6a**)	18	30	85[b] (79)
2	Naph (**5b**, **6b**)	18	30	84
3	2-FC_6H_4 (**5c**, **6c**)	18	40	75
4	$C(O)NEt_2$ (**5d**, **6d**)	3	30	90[c] (60)
5	C(O)N(*i*-Pr)$_2$ (**5e**, **6e**)	2	30	85 (69)
6	$C(O)N(CH_2CH_2)_2O$ (**5f**, **6f**)	1	30	81 (30)
7	$C(O)N(CH_2CH_2)_2CH_2$ (**5g**, **6g**)	1	30	85 (61)
8	$C(O)N(CH_2CH_2)_2NMe$ (**5h**, **6h**)	1	30	75 (50)
9	$C(O)N[(CH_2)_5Me]Me$ (**5i**, **6i**)	2	30	95
10	$C(O)NPh_2$ (**5j**, **6j**)	2	30	0
11	C(O)N(4-$O_2NC_6H_4$)Et (**5k**, **6k**)	18	40	0
12	C(O)N(Ph)Et (**5l**, **6l**)	2	30	30
13	C(O)N(PMP)Et (**5m**, **6m**)	24	30	53

[a] Isolated yields (250 mg scale); isolated yields obtained for reactions in DMSO are provided in parentheses.
[b] The reaction was performed on a 10.0 g scale.
[c] The reaction performed on a 15.0 g scale afforded **6d** in 89% yield.

Preparative-scale synthesis under the optimized conditions provided 3-methyl-3-phenylcyclopropene (**6a**) in high yield, which slightly exceeded that obtained in dimethyl sulfoxide (Table 2, entry 1).[8] Similarly, other 3-methyl-3-arylcyclopropenes **6b**,**c** were efficiently synthesized by the tetrahydrofuran protocol (entries 2 and 3). The major advantage of the new method was revealed in the synthesis of significantly more polar cyclopropenecarboxamides **6d–i**,**l**,**m** (Table 2, entries 4–9, 12, and 13). Thus, in contrast to the reactions performed in dimethyl sulfoxide, which suffered from substantial product loss due to the high hydrophilicity of the compounds, the new conditions allowed for high isolated yields for all alkyl-substituted amides tested.

On the other hand, an attempted reaction employing *N*,*N*-diphenylcyclopropenecarboxamide **5j** did not lead to the formation of a cyclopropene (Table 2, entry 10). The only product detected by GC-MS analysis of the crude reaction mixture was diphenylamine; this suggests that this type of substrate has increased carbonyl activity.[12] Apparently, the less-electron-rich nitrogen in diphenylamide **6j**, as compared to dialkylamide analogs (Scheme 2), results in a greater positive charge on the carbon atom of carbonyl group. Furthermore, diphenylamide species **8j** (R = Ph) (Scheme 2) makes a much better nucleofuge than dialkylamide equivalents, altogether making arylamides much more sensitive toward nucleophilic substitution by an alkoxide. To prove this rationale, we tested the dehydrobromination reaction on a series of *N*-ethyl-*N*-arylamides **5k–m** (Table 2, entries 11–13). As expected, the reaction of amide **5k** possessing an electron-poor 4-nitrophenyl group resulted in rapid alcoholysis, affording *N*-ethyl-4-nitroaniline as the sole reaction product (entry 11). It should be mentioned that formation of *tert*-butyl ester **9** (Scheme 2) was observed at early stages of the reaction in this case.[13] Similar results were obtained with phenyl-substituted amide **5l**; however, product decomposition proceeded much slower, permitting isolation of the corresponding cyclopropene **6l** in poor yield (entry 12). Finally, more-electron-rich anisidine-derived amide **5m** afforded cyclopropene **6m** in moderate yield (entry 13). Overall, these results demonstrated a clear-cut correlation between the electronic nature of the carboxamide and the stability of the corresponding product toward nucleophilic attack under the described reaction conditions.

In conclusion, a convenient, general protocol for the synthesis of cyclopropenes via dehydrobromination of bromocyclopropanes has been developed. The new optimized conditions significantly improved the scale-up compatibility of the method and allowed for expanding the scope of available cyclopropenes, particularly those possessing polar functionalities. Application of the new



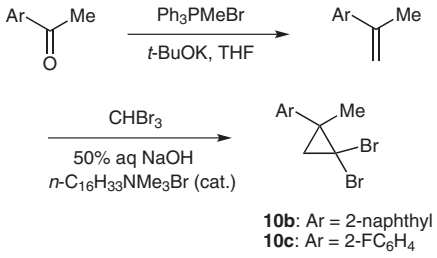
Scheme 2 Decomposition of cyclopropene-3-carboxamides upon nucleophilic attack by *tert*-butoxide species

protocol for the efficient preparation of cyclopropene-3-carboxamides has been demonstrated.[14]

NMR spectra were recorded on a Bruker Avance DPX-400 instrument, equipped with a quadruple-band gradient probe (H/C/P/F QNP). ^{13}C NMR spectra were registered with broad-band decoupling. Column chromatography was carried out on silica gel (Selecto Scientific, 63–200 μm). Precoated silica gel plates (Merck Kieselgel 60 F-254) were used for TLC. IR spectra were recorded on a Shimadzu FT-IR 8400S instrument. HRMS was carried out on an LCT Premier (Micromass Technologies) instrument; ESI and TOF detection techniques were used. The abbreviation 'ps t' is used to describe pseudo-triplets in the ^{1}H NMR spectra. When the product was characterized as a mixture of diastereomers, the chemical shifts of the multiplets corresponding to both of the diastereomeric groups are listed, followed by a summation sign (Σ) to indicate that the sum of both integrals is given. No special notation is used to describe equivalent carbons in ^{13}C NMR spectra.

Dibromocyclopropanes 10b and 10c

The dibromocyclopropane starting materials **10b** and **10c** were prepared from 2-acetonaphthone and 2-fluoroacetophenone, respectively (Scheme 3), according to general procedures for the synthesis of dibromocyclopropanes described in our recent report.[8]



Scheme 3

2,2-Dibromo-1-methyl-1-(2-naphthyl)cyclopropane (10b)

Flash column chromatography (silica gel, hexanes) gave a clear oil. Yield: 10.31 g (66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.88 (m, 4 H), 7.76 (s, 1 H), 7.58–7.53 (m, 2 H), 2.36 (d, *J* = 7.6 Hz, 1 H), 1.91 (d, *J* = 7.6 Hz, 1 H), 1.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0, 133.3, 132.6, 128.2, 127.9, 127.8, 127.0, 126.9, 126.3, 126.1, 36.7, 36.0, 33.9, 27.7.

ESI-HRMS (TOF): *m/z* [M – Br]$^+$ calcd for $C_{14}H_{12}Br$: 259.0122; found: 259.0125.

2,2-Dibromo-1-(2-fluorophenyl)-1-methylcyclopropane (10c)

Quick filtration through a short plug of silica gel (hexanes) afforded a clear oil. Yield: 10.14 g (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 2 H), 7.16–7.11 (m, 2 H), 2.14 (br d, *J* = 7.6 Hz, 1 H), 1.84 (br s, 1 H), 1.72 (s, 3 H).

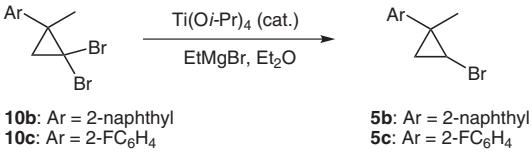
^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2 (d, $^1J_{CF}$ = 250.3 Hz), 130.0 (br), 129.7 (br), 129.2 (d, *J* = 8.0 Hz), 124.2, 115.8 (d, $^2J_{CF}$ = 21.2 Hz), 35.5 (br), 33.8 (br), 25.1 (br), 14.1 (br).

^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –113.6.

ESI-HRMS (TOF): *m/z* [M – Br]$^+$ calcd for $C_{10}H_{10}F$: 149.0767; found: 149.0767.

Bromocyclopropanes 5b and 5c

Bromocyclopropanes **5b** and **5c** were prepared by partial reduction of the corresponding dibromocyclopropanes **10b** and **10c** with EtMgBr in the presence of Ti(O*i*-Pr)$_4$ (cat.) (Scheme 4) according to the published general protocol.[8]



Scheme 4

2-Bromo-1-methyl-1-(2-naphthyl)cyclopropane (5b)

Bromocyclopropane **5b** was obtained as a mixture of diastereomers (ca. 2:1, by ^{1}H NMR). It was isolated and purified by short column chromatography (silica gel, hexanes); this afforded an opaque, slowly crystallizing oil. Yield: 5.19 g (73%).

IR (film): 3053, 2959, 2926, 1599, 1504, 1443, 1209, 1153, 856, 818, 746, 505, 476 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = [7.90–7.79 (m), Σ4 H], [7.72 (s), Σ1 H], [7.54–7.42 (m), Σ2 H], [3.35 (dd, *J* = 8.1 Hz, 4.5 Hz), 3.19 (dd, *J* = 7.3 Hz, 4.3 Hz), Σ1 H], [1.81 (ps t, *J* = 6.6 Hz), 1.57 (m), Σ1 H], [1.74 (s), 1.57 (s), Σ3 H], [1.49 (ps t, *J* = 7.3 Hz), 1.02 (ps t, *J* = 6.1 Hz), Σ1 H], [1.19 (dd, *J* = 6.3 Hz, 4.6 Hz), 0.85 (dd, *J* = 5.8 Hz, 4.0 Hz), Σ1 H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 140.0, 139.9, 133.4, 132.5, 132.2, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 126.3, 125.9, 125.7, 125.6, 125.5, 30.4, 28.3, 27.9, 26.9, 26.3, 24.1, 23.3, 22.3.

ESI-HRMS (TOF): *m/z* [M – Br]$^+$ calcd for $C_{14}H_{13}$: 181.1017; found: 181.1022.

2-Bromo-1-(2-fluorophenyl)-1-methylcyclopropane (5c)

Bromocyclopropane **5c** was purified by flash chromatography (silica gel, hexanes) to afford a mixture of diastereomers (ca. 2:1) as a colorless oil. Yield: 6.89 g (91%).

IR (film): 3041, 2962, 2926, 1493, 1447, 1207, 1153, 1032, 756, 621, 505 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = [7.32–7.21 (m), Σ 2 H], [7.17–7.02 (m), Σ 2 H], [3.27 (dd, *J* = 8.3, 4.8 Hz), 3.15 (dd, *J* = 7.6, 4.6 Hz), Σ1 H], [1.58 (s), 1.43 (s), Σ3 H], [1.58 (m), 1.43 (ps t, *J* = 6.6 Hz), Σ1 H], [1.35 (m), 1.10 (dd, *J* = 6.3, 4.8 Hz), Σ1 H].

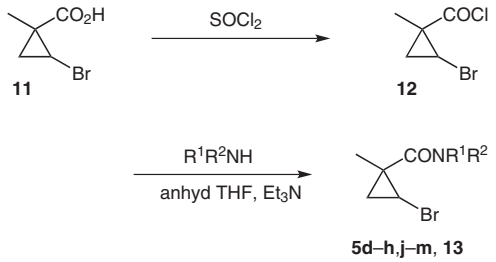
^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4 (d, $^1J_{CF}$ = 248.1 Hz), 163.0 (d, $^1J_{CF}$ = 248.8 Hz), 131.6, 131.4 (d, *J* = 4.3 Hz), 130.0 (d, *J* = 4.0 Hz), 129.6, 128.8 (d, *J* = 8.3 Hz), 128.6 (d, *J* = 7.9 Hz), 124.1 (d, *J* = 3.7 Hz), 123.9 (d, *J* = 3.7 Hz), 115.7 (d, *J* = 21.2 Hz), 115.6 (d, *J* = 22.0 Hz), 29.2, 27.3, 24.9, 24.4, 23.4, 22.5, 22.4, 22.3.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –114.9, –115.8.

ESI-HRMS (TOF): *m/z* [M – Br]$^+$ calcd for $C_{10}H_{10}F$: 149.0767; found: 149.0767.

2-Bromo-1-methylcyclopropanecarbonyl Chloride (12)

A mixture of carboxylic acid **11**[15] (1:1 diastereomeric mixture; 25.9 g, 200 mmol) and freshly distilled $SOCl_2$ (50 mL) was stirred overnight at r.t (Scheme 5). The excess $SOCl_2$ was removed by distillation at ambient pressure. Distillation of the residue in vacuo (bp 50–53 °C/10 Torr) gave a diastereomeric mixture of acyl chlorides **12** (1:1) as a colorless oil. This material was used as is in further acylations of primary and secondary amines as described below. Yield: 37.9 g (96%).



5d: $R^1 = R^2 = Et$
5e: $R^1 = R^2 = i\text{-Pr}$
5f: $R^1R^2 = (CH_2CH_2)_2O$
5g: $R^1R^2 = (CH_2CH_2)_2CH_2$
5h: $R^1R^2 = (CH_2CH_2)_2NMe$
5j: $R^1 = R^2 = Ph$
5k: $R^1 = 4\text{-}O_2NC_6H_4$, $R^2 = Et$
5l: $R^1 = Ph$, $R^2 = Et$
5m: $R^1 = 4\text{-}MeOC_6H_4$, $R^2 = Et$
13: $R^1 = n\text{-Hexyl}$, $R^2 = H$

Scheme 5

2-Bromo-*N*,*N*-diethyl-1-methylcyclopropanecarboxamide (5d); Typical Procedure

Acid chloride **12** (5.00 g, 25.3 mmol) in anhyd THF (35 mL) was added dropwise to a stirred soln of freshly distilled Et_2NH (5.56 g, 7.94 mL, 76.0 mmol) in anhyd THF (20 mL) under a N_2 atmosphere (Scheme 5). After the mixture had stirred at r.t. for ca. 1 h, the starting materials were consumed (GC-MS). The precipitate formed in the reaction mixture was removed by suction filtration and the filter cake was rinsed with THF (2 × 20 mL). Then the precipitate was dissolved in H_2O (20 mL) and extracted with EtOAc (2 × 20 mL). The combined organic phases were washed with brine (20 mL), dried ($MgSO_4$), combined with the THF filtrate, and evaporated in vacuo. Kugelrohr vacuum distillation (90 °C/0.6 Torr) gave a diastereomeric mixture of products (1:1) as a pale-yellow oil. Yield (overall): 5.64 g (95%).

IR (film): 2970, 2934, 1637, 1425, 1209, 1153, 636, 503 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = [3.73–3.69 (m), 3.61–3.55 (m), 3.35–3.30 (m), 3.21–3.17 (m), Σ4 H], [3.13 (dd, *J* = 7.3 Hz, 4.6 Hz), 2.96 (dd, *J* = 7.3 Hz, 4.6 Hz), Σ1 H], [1.67 (dd, *J* = 6.7 Hz, 4.8 Hz), 1.59 (dd, *J* = 6.7 Hz, 4.8 Hz), Σ1 H], [1.25 (t, *J* = 14.3 Hz, 7.1 Hz), 1.10 (t, *J* = 14.0 Hz, 7.0 Hz), Σ3 H], [1.43 (s), 1.35 (s), Σ3 H], [1.11–1.06 (m), 0.86 (dd, *J* = 6.7 Hz, 5.0 Hz), Σ4 H].

^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.1, 169.6, 41.2, 41.1, 39.0, 38.9, 27.9, 27.4, 25.9, 22.2, 22.0, 21.6, 21.4, 20.6, 13.9, 13.7, 12.4, 12.2.

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_9H_{17}BrNO$: 234.0493; found: 234.0490.

2-Bromo-*N*,*N*-diisopropyl-1-methylcyclopropanecarboxamide (5e)

Cyclopropanecarboxamide **5e** was prepared according to the typical procedure (as described for **5d**) from acyl chloride **12** (2.00 g, 10.1 mmol) and freshly distilled *i*-Pr_2NH (4.50 mL, 3.13 g, 30.3 mmol). Yield: 2.31 g (87%).

The physical and spectral properties of this substance were identical to those reported in the literature.[16]

4-[(2-Bromo-1-methylcyclopropyl)carbonyl]morpholine (5f)

Cyclopropanecarboxamide **5f** was prepared according to the typical procedure (as described for **5d**) from acyl chloride **12** (5.00 g, 25.3 mmol) and freshly distilled morpholine (6.60 mL, 6.62 g, 76 mmol). Kugelrohr vacuum distillation (oven temperature 133 °C/0.6 Torr) of the resulting residue afforded a mixture of *trans*- and *cis*-isomers of **5f** (1:1) as a colorless oil. Yield: 5.52 g (88%).

IR (film): 2962, 2922, 2854, 2897, 1643, 1460, 1429, 1281, 1207, 1153, 1115, 1032, 851, 623, 505 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.67–3.64 (m, 8 H), [3.15 (dd, *J* = 8.3 Hz, 5.1 Hz), 2.98 (dd, *J* = 7.6 Hz, 4.8 Hz), Σ1 H], [1.70 (ps t, *J* = 8.1), 1.58 (dd, *J* = 6.8 Hz, 4.8 Hz), Σ1 H], [1.45 (s), 1.37 (s), Σ3 H], [1.20 (ps t, *J* = 7.3 Hz), 0.91 (dd, *J* = 6.6 Hz, 4.8 Hz), Σ1 H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 168.9, 67.1 (–), 66.9 (–), 66.7 (–, 2C), 46.4 (–), 42.6 (–), 27.5 (+), 27.1, 25.6, 25.4 (+), 21.6 (–), 21.4 (+), 21.2 (–), 19.4 (+).

ESI-HRMS (TOF): *m*/*z* $[M - Br]^+$ calcd for $C_9H_{14}NO_2$: 168.1025; found: 168.1026.

1-[(2-Bromo-1-methylcyclopropyl)carbonyl]piperidine (5g)

Cyclopropanecarboxamide **5g** was prepared according to the typical procedure (as described for **5d**) from acyl chloride **12** (5.10 g, 25.8 mmol) and freshly distilled piperidine (7.7 mL, 6.6 g, 85 mmol). Kugelrohr vacuum distillation (oven temperature 150 °C/0.4 Torr) of the resulting residue afforded a mixture of *trans*- and *cis*-isomers of **5g** (1:1) as a colorless oil. Yield: 6.26 g (98%).

IR (film): 2934, 2854, 1641, 1431, 1207, 1151, 1014, 854 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = [3.70–3.57 (m), 3.49–3.35 (m), Σ4 H], [3.11 (dd, *J* = 8.1 Hz, 4.8 Hz), 2.94 (dd, *J* = 8.1 Hz, 4.8 Hz), Σ1 H], 1.65–1.45 (m, 7 H), [1.38 (s), 1.30 (s), Σ3 H], [1.10 (ps t, *J* = 8.6 Hz, 5.3 Hz), 0.82 (ps t, *J* = 6.8 Hz, 4.8 Hz), Σ1 H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 168.8, 46.9, 43.2, 27.9, 27.5, 26.5, 26.1, 26.0, 25.7, 25.6, 24.6, 24.5, 21.9, 21.7, 21.3, 19.5.

ESI-HRMS (TOF): *m*/*z* $[M - Br]^+$ calcd for $C_{10}H_{16}NO$: 166.1232; found: 166.1233.

1-[(2-Bromo-1-methylcyclopropyl)carbonyl]-4-methylpiperazine (5h)

Cyclopropanecarboxamide **5h** was prepared according to the typical procedure (as described for **5d**) from acyl chloride **12** (5.00 g, 25.3 mmol) and freshly distilled 1-methylpiperazine (8.5 mL, 7.61 g, 76 mmol). Purification by Kugelrohr vacuum distillation (oven temperature 150 °C/0.6 Torr) afforded a mixture of *trans*- and *cis*-isomers of **5h** (1:1) as a colorless oil. Yield: 5.72 g (87%).

IR (film): 2935, 2791, 1643, 1431, 1207, 1151, 1040, 1003 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.75–3.45 (m, 4 H), [3.09 (dd, *J* = 4.89 Hz, 4.12 Hz), 2.92 (dd, *J* = 4.89 Hz, 4.12 Hz), Σ1 H], 2.55–2.27 (m, 4 H), [2.25 (s), 2.24 (s), Σ3 H], [1.60 (ps t, *J* = 8.1 Hz, 7.1 Hz), 1.48 (ps t, *J* = 8.1 Hz, 7.1 Hz), Σ1 H], [1.38 (s), 1.30 (s), Σ3 H], [1.11 (ps t, *J* = 7.7 Hz, 6.8 Hz), 0.82 (ps t, *J* = 7.7 Hz, 6.8 Hz), Σ1 H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 168.8, 55.4, 54.6, 46.1, 46.0, 45.8, 42.1, 28.3, 27.7, 27.3, 25.6, 25.5, 21.7, 21.6, 19.5.

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{18}BrN_2O$: 261.0603; found: 261.0603.

2-Bromo-1-methyl-*N*,*N*-diphenylcyclopropanecarboxamide (5j)

Acid chloride **12** (4.94 g, 25.0 mmol, 1equiv) was added to a stirred soln of Ph_2NH (4.23 g, 25.1 mmol, 1equiv), DMAP (100 mg), and Et_3N (5 mL) in THF (30 mL), and the mixture was allowed to reflux overnight. It was worked up according to the above procedure and isolated by column chromatography (silica gel, hexanes–EtOAc,

5:1, R_f = 0.40 and 0.23). A diastereomeric mixture (1:1) of **5j** was obtained as an off-white solid. Yield: 6.76 g (82%).

IR (film): 3061, 2980, 2932, 2872, 1659, 1591, 1494, 1339, 1151, 756, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = [7.38–7.24 (m), Σ10 H], [3.42 (dd, *J* = 8.5 Hz, 5.3 Hz), 2.90 (dd, *J* = 7.6 Hz, 5.0 Hz), Σ1 H], [2.07 (dd, *J* = 8.5 Hz, 6.4 Hz), 1.53 (dd, *J* = 7.0 Hz, 5.0 Hz), Σ1 H], [1.17 (s), 1.09 (s), Σ3 H], [1.26 (ps t, *J* = 7.0 Hz), 0.86 (dd, *J* = 6.4 Hz, 5.3 Hz), Σ1 H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 171.2, 144.0, 143.5, 129.8, 129.7, 128.0, 127.8, 127.4, 127.3, 30.9, 29.0, 28.4, 26.8, 25.2, 24.5, 22.8, 19.8.

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{17}BrNO$: 330.0493; found: 330.0485.

2-Bromo-*N*-ethyl-1-methyl-*N*-phenylcyclopropanecarboxamide (5l)

Cyclopropanecarboxamide **5l** was prepared according to the typical procedure (as described for **5d**) from acyl chloride **12** (2.0 g, 10.1 mmol) and *N*-ethylaniline (3.81 mL, 3.68 g, 30.3 mmol). Purification involved partitioning between a sat. aq soln of citric acid (75 mL) and EtOAc (2 × 50 mL). The combined organic phase was washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was distilled twice in a Kugelrohr apparatus (oven temperature 155 °C/0.2 Torr); this gave a diastereomeric mixture (1:1) of **5l** as a colorless oil. Yield: 1.45 g (51%).

IR (film): 3090, 3061, 2974, 2932, 1645, 1595, 1495, 1394, 1207, 1153, 1130, 700, 623, 505 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = [7.46–7.15 (m), Σ5 H], [4.22–4.16 (m), 3.44 (br s), Σ1 H], [3.85–3.76 (m), 3.70–3.61 (m), Σ1 H], [3.21 (dd, *J* = 8.3 Hz, 5.1 Hz), 2.75 (br s), Σ1 H], [1.85 (ps t, *J* = 6.6 Hz), 1.61 (ps t, *J* = 5.6 Hz), Σ1 H], [1.13 (t, *J* = 7.1 Hz), 1.08 (t, *J* = 7.3 Hz), Σ3 H], [1.03 (br s), 0.88 (br s), Σ3 H], [0.88 (br s), 0.71 (ps t, *J* = 5.6 Hz), Σ1 H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 169.1, 142.6, 141.6, 129.5, 129.4, 128.4, 127.9, 127.6, 127.5, 46.6, 45.9, 29.8, 28.2, 27.2, 24.4, 24.2, 23.4, 19.9, 12.8.

ESI-HRMS (TOF): *m*/*z* $[M - Br]^+$ calcd for $C_{13}H_{16}NO$: 202.1232; found: 202.1234.

2-Bromo-*N*-ethyl-1-methyl-*N*-(4-nitrophenyl)cyclopropanecarboxamide (5k)

Cyclopropanecarboxamide **5k** was prepared according to the protocol described above for amide **5l**, from acyl chloride **12** (1.24 g, 6.25 mmol), *N*-ethyl-4-nitroaniline (0.99 g, 5.96 mmol), and Et_3N (1.68 g, 14.9 mmol). The crude material was purified by short column chromatography (silica gel, hexanes–EtOAc, 3:1, R_f = 0.39 and 0.32); this gave a diastereomeric mixture (1:1) of **5k**. Yield: 1.67 g (86%).

IR (film): 3080, 2974, 2934, 1651, 1591, 1520, 1344, 1205, 1151, 1109, 854 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = [8.34 (d, *J* = 8.8 Hz), 8.31 (d, *J* = 8.8 Hz), Σ2 H], [7.55 (d, *J* = 8.8 Hz), 7.37 (d, *J* = 8.8 Hz), Σ2 H], [4.22 (sext, *J* = 7.1 Hz), 3.93 (sext, *J* = 7.1 Hz), Σ1 H], [3.74 (sext, *J* = 7.1 Hz), 3.66 (sext, *J* = 7.1 Hz), Σ1 H], [3.26 (dd, *J* = 8.3 Hz, 5.1 Hz), 2.94 (dd, *J* = 7.3 Hz, 4.8 Hz), Σ1 H], [1.96 (dd, *J* = 8.3 Hz, 6.6 Hz), 1.80 (ps t, *J* = 6.3 Hz), Σ1 H], [1.30 (dd, *J* = 7.6 Hz, 6.6 Hz), 0.83 (dd, *J* = 6.6 Hz, 5.3 Hz), Σ1 H], [1.18 (t, *J* = 7.1 Hz), 1.12 (t, *J* = 7.1 Hz), Σ3 H], 1.10 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.9, 171.4, 147.5, 146.2, 128.4, 128.1, 125.0, 124.8, 46.0, 45.9, 29.3, 28.9, 26.8, 25.9, 23.6, 23.2, 21.6, 19.6, 13.4, 13.0;

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{16}BrN_2O_3$: 327.0344; found: 327.0345.

2-Bromo-*N*-ethyl-*N*-(4-methoxyphenyl)-1-methylcyclopropanecarboxamide (5m)

Cyclopropanecarboxamide **5m** was prepared according to the protocol described above for amide **5l**, from acyl chloride **12** (1.24 g, 6.29 mmol), *N*-ethylanisidine (0.99 g, 6.47 mmol), and Et_3N (1.68 g, 14.9 mmol). Acid–base extraction followed by Kugelrohr vacuum distillation (oven temperature 200 °C/0.1 Torr) afforded a diastereomeric mixture of amides **5m** (1:1). Yield: 1.96 g (99%).

IR (film): 3051, 2970, 2934, 2872, 2835, 1641, 1510, 1396, 1205, 1151, 1032, 837 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = [7.33 (d, *J* = 8.8 Hz), 6.95 (d, *J* = 8.8 Hz), Σ2 H], [7.07 (d, *J* = 8.8 Hz), 6.97 (d, *J* = 9.1 Hz), Σ2 H], [4.21–4.15 (m), 3.81–3.76 (m), Σ1 H], [3.87 (s), 3.85 (s), Σ3 H], [3.63–3.57 (m), 3.41–3.35 (m), Σ1 H], [3.22 (dd, *J* = 8.3 Hz, 5.1 Hz), 2.75 (dd, *J* = 7.1 Hz, 4.8 Hz), Σ1 H], [1.85 (dd, *J* = 8.1 Hz, 6.6 Hz), 1.66 (dd, *J* = 6.3 Hz, 5.1 Hz), Σ1 H], [1.14 (t, *J* = 7.1 Hz), 1.08 (t, *J* = 7.1 Hz), Σ3 H], [1.05 (br s), 0.89 (br s), Σ3 H], [0.95 (ps t, *J* = 7.1 Hz), 0.72 (br s), Σ1 H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 169.2, 158.7, 135.3, 129.6, 129.2, 114.6, 114.5, 55.5, 55.4, 46.5, 45.9, 29.7, 28.2, 27.1, 26.2, 24.1, 23.4, 22.1, 20.0, 12.9, 12.7.

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{19}BrNO_2$: 312.0599; found: 312.0593,

2-Bromo-*N*-hexyl-1-methylcyclopropanecarboxamide (13)

A soln of hexylamine (4.01 mL, 30.4 mmol, 3.00 equiv) in THF (10 mL) was added dropwise to a soln of acid chloride **12** (2.00 g, 10.1 mmol) in THF (7 mL). After the amine addition was complete, the mixture was allowed to stir at r.t. until GC-MS analysis showed no remaining starting materials (1 h). The precipitate was removed by filtration through a fritted funnel, and the filtrate was washed with EtOAc (15 mL), then dissolved in H_2O (10 mL), and extracted with EtOAc (2 × 15 mL). The combined organic layers were washed with brine (20 mL) and dried ($MgSO_4$). All the organic phases were combined and evaporated under vacuum. The residue was purified by Kugelrohr vacuum distillation (oven temperature 175 °C/0.6 Torr); this afforded a diastereomeric mixture of **13** (ca. 1:1) as a clear oil. Yield: 2.16 g (81%).

IR (film): 3319, 2957, 2934, 2856, 1634, 1537, 1462, 1321, 1205, 1153 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = [5.99 (s), 5.87 (s), Σ1 H], [3.59 (dd, *J* = 8.2 Hz, 5.4 Hz), 2.98 (dd, *J* = 7.6 Hz, 5.0 Hz), Σ1 H], [3.44–3.31 (m), 3.11–3.06 (m), Σ2 H], [1.95 (dd, *J* = 7.6 Hz, 5.7 Hz), 1.75 (ps t, *J* = 5.7 Hz), Σ1 H], 1.62 (m, 2 H), [1.58 (s), 1.48 (s), Σ3 H], 1.42–1.35 (m, 6 H), 1.27 (ps t, *J* = 6.9 Hz, 1 H), 0.98 (br t, *J* = 5.7 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.1, 169.9, 40.3, 40.2, 31.5, 31.2, 29.7, 29.6, 29.2, 27.9, 27.6, 26.7, 26.3, 25.3, 24.3, 24.0, 22.6, 22.5, 21.6, 21.1, 17.3, 14.1.

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{21}BrNO$: 262.0807; found: 262.0809.

2-Bromo-*N*-hexyl-*N*,1-dimethylcyclopropanecarboxamide (5i)

A flame-dried flask was charged with NaH (60 wt% suspension in mineral oil; 183 mg, 4.77 mmol, 2.5 equiv) under a N_2 atmosphere. This was suspended in anhyd THF (25 mL), and amide **13** (500 mg, 1.91 mmol) was added. The mixture was stirred at 50 °C for 10 min before MeI (325 mg, 143 μL, 2.29 mmol, 1.2 equiv) was added. The reaction was complete after 4 h at 50 °C, as shown by the disappearance of the starting material. The reaction was quenched by pouring of the mixture into brine (20 mL), and extracting with EtOAc

(3 × 15 mL). The combined organic layers were washed with brine (ca. 15 mL) and condensed under vacuum. The crude product was purified by column chromatography [silica gel, hexanes (to remove the mineral oil), then hexanes–EtOAc, 3:1]; this gave a diastereomeric mixture of **5i** (ca. 2:1, R_f = 0.34 and 0.27) as a colorless oil. Yield: 329 mg (62%).

IR (film): 2955, 2828, 2856, 1641, 1485, 1460, 1404, 1209, 1153, 1086 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = [3.46–3.40 (m), 3.33–3.27 (m), Σ2 H], [3.18 (dd, *J* = 8.2 Hz, 5.0 Hz), 2.99 (dd, *J* = 7.6 Hz, 4.7 Hz), Σ1 H], [3.15 (s), 2.94 (s), Σ3 H], 1.71 (ps t, *J* = 7.3 Hz), 1.61–1.58 (m), Σ1 H], [1.60–1.57 (m), 1.17 (dd, *J* = 14.9 Hz, 7.3 Hz), Σ1 H], [1.47 (s), 1.39 (s), Σ3 H], [1.30–0.88 m, 11 H].

^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.8, 169.7, 49.8, 48.2, 47.8, 47.7, 35.6, 35.3, 32.8, 31.6, 31.5, 28.6, 27.9, 26.7, 26.5, 25.9, 22.6, 22.5, 21.8, 20.9, 19.8, 18.9, 14.0, 13.9.

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{23}BrNO$: 276.0963; found: 276.0960.

N,*N*-Diethyl-1-methylcycloprop-2-enecarboxamide (6d); Typical Procedure

An oven-dried 10-mL Wheaton vial equipped with a Mininert cap was charged with *t*-BuOK (160 mg, 1.43 mmol, 1.50 equiv), 18-crown-6 (25 mg, 0.095 mmol, 0.10 equiv), and anhyd THF (5 mL). Carboxamide **5d** (250 mg, 0.954 mmol) was added to this soln, and the reaction mixture was stirred at 30 °C until GC-MS showed the disappearance of the starting materials (3 h). Then the reaction was quenched by pouring the mixture into brine (50 mL). The aqueous layer was extracted with EtOAc (2 × 25 mL). The combined organic phases were washed with brine (25 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by Kugelrohr vacuum distillation (oven temperature of 60 °C/0.2 Torr); this gave **6d** as a colorless liquid. Yield: 146.7 mg (90%).

A scale-up synthesis was performed according to the same procedure, starting from **5d** (15.0 g, 61.7 mmol), *t*-BuOK (10.4 g, 92.5 mmol), and 18-crown-6 (1.63 g, 6.17 mmol, 10 mol%) in THF (290 mL). Yield: 8.74 g (89%).

IR (film): 3082, 2972, 2935, 2874, 1616, 1460, 1427, 1381, 1283, 1211, 1153, 1103, 621 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 2 H), 3.54 (br s, 2 H), 3.29 (br s, 2 H), 1.31 (s, 3 H), 1.18 (br s, 3 H), 1.06 (br s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.5, 115.8, 41.3, 38.7, 23.9, 23.2, 14.3, 12.6.

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_9H_{16}NO$: 154.1232; found: 154.1231.

3-Methyl-3-phenylcyclopropene (6a)

Cyclopropene **6a** was prepared according to the typical procedure (as described for **6d**) from bromocyclopropane **5a** (10.00 g, 47.18 mmol). The crude material was purified by Kugelrohr vacuum distillation (oven temperature 75 °C/5 Torr) to afford a clear oil. Yield: 5.22 g (85%).

All physical and spectral properties of this material were identical to those described in the literature.[17]

3-Methyl-3-(2-naphthyl)cyclopropene (6b)

Cyclopropene **6b** was prepared according to the typical procedure (as described for **6d**) from bromocyclopropane **5b** (250 mg, 0.95 mmol). Purification by Kugelrohr vacuum distillation (oven temperature of 120 °C/0.2 Torr) afforded a colorless oil. Yield: 144.1 mg (84%).

IR (film): 3053, 2964, 1628, 1597, 1504, 1209, 1153, 993, 889, 856, 818, 743, 650, 621, 598 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.77 (m, 3 H), 7.49–7.43 (m, 3 H), 7.38 (s, 2 H), 7.35 (dd, *J* = 8.6, 1.7 Hz, 1 H), 1.78 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 133.4, 131.5, 127.6, 127.5, 127.2, 125.9, 125.0, 124.7, 124.5, 115.8, 25.6, 22.2.

ESI-HRMS (TOF): *m*/*z* $[M - H]^+$ calcd for $C_{14}H_{11}$: 179.0861; found: 179.0859.

3-(2-Fluorophenyl)-3-methylcyclopropene (6c)

Cyclopropene **6c** was prepared according to the typical procedure (as described for **6d**) from bromocyclopropane **5c** (250 mg, 1.09 mmol), and purified by Kugelrohr vacuum distillation (oven temperature 75 °C/10 Torr) to afford a clear oil. Yield: 121 mg (75%).

Final assay of this product showed approximately 5% of 1-(2-fluorophenyl)-1-methylcyclopropane resulting from exhaustive reduction of dibromide **10c**.

IR (film): 3053, 2964, 1637, 1627, 1597, 1209, 1153, 993, 889, 856, 818, 743, 621, 598 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 2 H), 7.12–7.06 (m, 4 H), 1.59 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9 (d, $^1J_{CF}$ = 245.9 Hz), 136.1 (d, $^2J_{CF}$ = 15.4 Hz), 129.1 (d, $^3J_{CF}$ = 5.1 Hz), 127.4 (d, $^3J_{CF}$ = 8.1 Hz), 123.9 (d, $^4J_{CF}$ = 3.7 Hz), 119.8, 115.8 (d, $^2J_{CF}$ = 22.7 Hz), 27.6 (d, $^3J_{CF}$ = 2.2 Hz), 20.2.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –117.5.

ESI-HRMS (TOF): *m*/*z* $[M - F]^+$ calcd for $C_{10}H_9$: 129.0704; found: 129.0707.

N,*N*-Diisopropyl-1-methylcycloprop-2-enecarboxamide (6e)

Cyclopropene **6e** was prepared according to the typical procedure (as described for **6d**) from bromocyclopropane **5e** (250 mg, 0.96 mmol) and was purified by Kugelrohr distillation (oven temperature of 55 °C/0.2 Torr) to afford a colorless liquid. Yield: 148 mg (85%).

IR (film): 3082, 3001, 2964, 2932, 1639, 1616, 1437, 1369, 1331, 1215, 1155, 1040, 609 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 2 H), 4.57 (br s, 1 H), 3.30 (br s, 1 H), 1.38 (br s, 6 H), 1.31 (s, 3 H), 1.24 (br s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.2, 115.6, 48.9, 45.3, 28.0, 23.7, 20.9, 20.6.

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{20}NO$: 182.1545; found: 182.1543.

4-[(1-Methylcycloprop-2-enyl)carbonyl]morpholine (6f)

Cyclopropene **6f** was prepared according to the typical procedure (as described for **6d**) from cyclopropane **5f** (250 mg, 1.01 mmol). The reaction mixture was quenched by pouring into brine (30 mL) and extracting the aqueous layer with THF (2 × 25 mL). The combined organic layers were washed once with brine (15 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by Kugelrohr vacuum distillation (oven temperature 95 °C/0.2 Torr) to afford a clear liquid. Yield: 137 mg (81%).

IR (film): 2964, 2920, 2856, 1618, 1431, 1275, 1207, 1151, 1113, 1030 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 2 H), 3.62 (br s, 8 H), 1.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 115.4, 66.9, 23.6, 22.49 (due to the restricted rotation about the amide bond, the CH_2 groups α to N are not observed).

ESI-HRMS (TOF): *m*/*z* $[M + H]^+$ calcd for $C_9H_{14}NO_2$: 168.1025; found: 168.1024.

1-[(1-Methylcycloprop-2-enyl)carbonyl]piperidine (6g)
Cyclopropene **6g** was prepared according to the typical procedure (as described for **6d**) from cyclopropane **5g** (250 mg, 1.02 mmol). The product was isolated by Kugelrohr vacuum distillation (oven temperature 75 °C/0.2 Torr) as a colorless oil. Yield: 143 mg (85%).

IR (film): 2934, 2854, 1614, 1435, 1207, 1153, 1113, 1011 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 2 H), 3.61 (br s, 2 H), 3.46 (br s, 2 H), 1.61 (br s 2 H), 1.53 (br s 4 H), 1.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.5, 115.7, 46.7, 42.5, 26.6, 25.6, 24.6, 23.7, 22.9.

ESI-HRMS (TOF): *m/z* $[M - Me]^+$ calcd for $C_9H_{12}NO$: 150.0919; found: 150.0917.

1-Methyl-4-[(1-methylcycloprop-2-enyl)carbonyl]piperazine (6h)
Cyclopropene **6h** was prepared according to the typical procedure (as described for **6d**) from bromocyclopropane **5h** (250 mg, 0.96 mmol). The product was isolated by Kugelrohr vacuum distillation (oven temperature 85 °C/0.2 Torr) as a colorless oil. Yield: 128 mg (75%).

IR (film): 2922, 2793, 1621, 1462, 1433, 1292, 1142, 1128, 1030, 1001 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 2 H), 3.70 (br s, 2 H), 3.56 (br s 2 H), 2.39 (br s, 4 H), 2.29 (s, 3 H), 1.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.6, 115.5, 55.3, 54.6, 46.0, 45.5, 41.3, 23.7, 22.7.

ESI-HRMS (TOF): *m/z* [M + H]+calcd for $C_{10}H_{17}N_2O$: 181.1341; found: 181.1343.

***N*-Hexyl-*N*,1-dimethylcycloprop-2-enecarboxamide (6i)**
Cyclopropene **6i** was prepared according to the typical procedure (as described for **6d**) from bromocyclopropane **5i** (250 mg, 0.911 mmol); purification by column chromatography (silica gel, hexanes–EtOAc, 3:1, R_f = 0.31) provided a colorless oil. Yield: 169 mg (95%).

IR (film): 2955, 2928, 2858, 1620, 1487, 1456, 1402, 1377, 1204, 1153, 1111, 1080, 1009, 617 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 7.27 (s, 2 H), 3.35–3.25 (br s, 2 H), 2.76 (br s, 3 H), 1.37 (s, 3 H), 1.47–1.16 (m, 8 H), 0.97 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (125.67 MHz, C_6D_6): δ = 174.8, 116.1, 53.4, 47.1, 34.2, 31.9, 26.7, 23.2, 22.9, 14.2.

ESI-HRMS (TOF): *m/z* $[M - Me]^+$ calcd for $C_{11}H_{18}NO$: 180.1388; found: 180.1388.

***N*-Ethyl-1-methyl-*N*-phenylcycloprop-2-enecarboxamide (6l)**
Cyclopropene **6l** was prepared according to the typical procedure (as described for **6d**) from bromocyclopropane **5l** (250 mg, 0.891 mmol). The product was isolated as a yellow oil by column chromatography (silica gel, hexanes–EtOAc, 2:1, R_f = 0.35). Yield: 51.9 mg (30%).

IR (film): 3063, 2970, 2930, 2870, 1649, 1632, 1593, 1495, 1452, 1387, 1300, 1281, 1117, 766, 700, 629, 586 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.37 (m, 2 H), 7.32 (m, 1 H), 7.19–7.11 (m, 2 H), 6.56 (s, 2 H) 3.70 (q, *J* = 14.1 Hz, 7.1 Hz, 2 H), 1.14 (s, 3 H), 1.08 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 142.1, 129.1, 128.1, 127.2, 114.37, 44.9, 24.0, 23.9, 12.9.

ESI-HRMS (TOF): *m/z* $[M + H]^+$ calcd for $C_{13}H_{16}NO$: 202.1232; found: 202.1231.

***N*-Ethyl-*N*-(4-methoxyphenyl)-1-methylcycloprop-2-enecarboxamide (6m)**
Cyclopropene **6m** was prepared according to the typical procedure (as described for **6d**) from bromocyclopropane **5m** (110 mg, 0.353 mmol). Purification by column chromatography (silica gel, hexanes–EtOAc, 2:1, R_f = 0.32) afforded a yellow oil. Yield: 37.6 mg (53%).

IR (film): 3065, 2966, 2932, 1647, 1628, 1510, 1458, 1442, 1391, 1290, 1204, 1151, 1117, 1043, 1030, 833 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.05 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 6.62 (s, 2 H), 3.85 (s, 3 H), 3.65 (q, *J* = 7.3 Hz, 2 H), 1.15 (s, 3 H), 1.07 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.3, 158.5, 134.8, 129.2, 114.5, 114.2, 55.5, 44.9, 24.1, 23.7, 12.8.

ESI-HRMS (TOF): *m/z* $[M - H]^+$ calcd for $C_{14}H_{16}NO_2$: 230.1181; found: 230.1180.

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