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Multigram Synthesis and C–C/C–N Couplings of Functionalized 1,2-Disubstituted Cyclopropyltrifluoroborates

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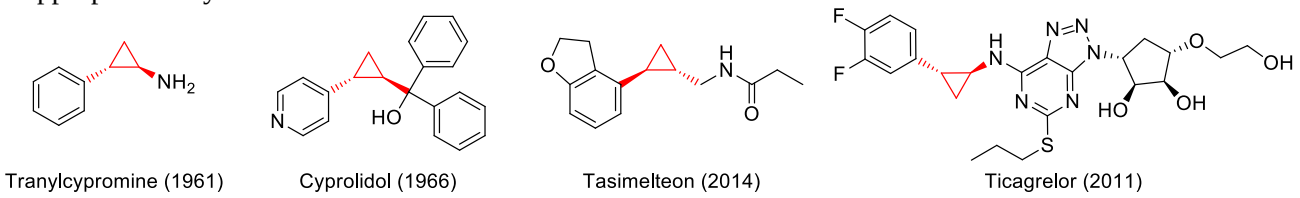
Abstract. A convenient approach to the multigram synthesis of functionalized 1,2-disubstituted cyclopropyltrifluoroborates was developed, based on Pd(II)- or Cu(I)-catalyzed reaction of vinyltrifluoroborate and diazo compounds. Optimized protocols allowed for the preparation of the target products as pure diastereomers on multigram scale. It was shown that the title compounds were good coupling partners for the Suzuki–Miyaura and Chan–Lam reactions, which provide medicinally relevant (het)arylcyclopropanes with high diastereoselectivity.

Keywords: Organoboron compounds; Diazoalkanes; Cyclopropanes; Suzuki–Miyaura reaction; Chan–Lam reaction

Introduction

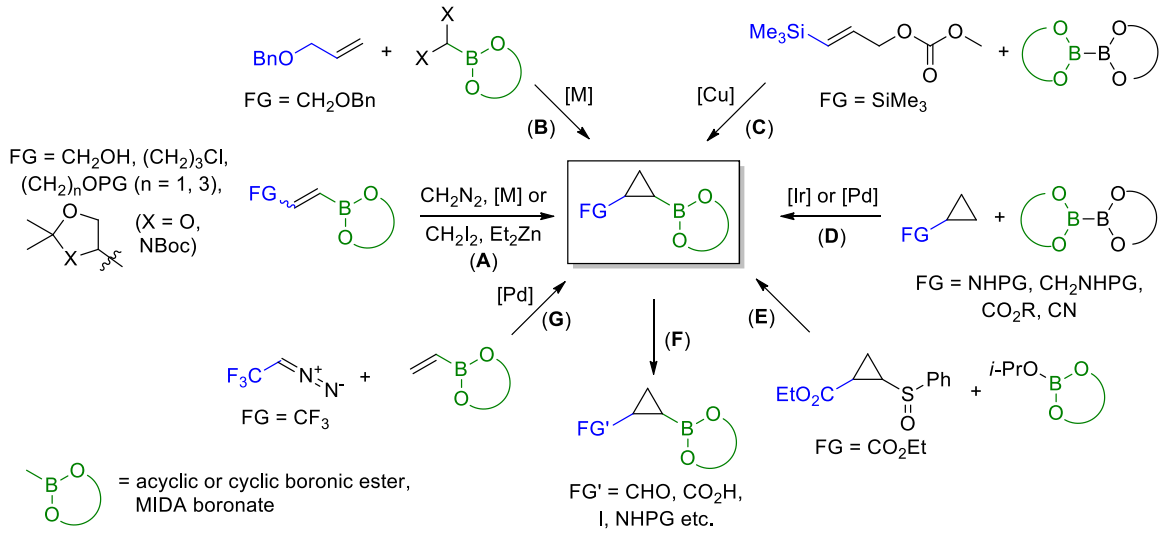
1,2-Disubstituted cyclopropanes have proven their beneficial role as structural motifs for drug discovery–from 1960s' antidepressants tranylcypromine and cyprolidol to recently approved tasimelteon, a drug for non-24-hour sleep–wake disorder, or ticagrelor, platelet aggregation inhibitor (Figure 1).[1] It is not surprising therefore that mono- and bifunctional reagents enabling direct modification at one of the cyclopropane ring carbon atoms are of significant interest. Functionalized boryl-substituted cyclopropanes are especially promising in this view since they allow for wide variation of the substituent through the well-established carbon–carbon and carbon–heteroatom coupling reactions.

To date, a number of functionalized 1,2-disubstituted cyclopropane boronic derivatives were described in the literature. In most cases, cyclic boronic esters or MIDA boronates were obtained *via* cyclopropanation of appropriate vinyl derivatives with diazomethane or CH_2I_2–Et_2Zn (Scheme 1, **A**).[2–10] Other methods included the use of α,α-dihalogenoboronic esters (**B**),[11,12] copper-catalyzed reaction of allyl carbonates with a diboron derivative (**C**),[13] C–H borylation of cyclopropanes (**D**),[14–16] sulfoxide–magnesium exchange/functionalization (**E**),[17] and transformation of existing functional groups in 1,2-disubstituted cyclopropyl boronic acid derivatives (**F**).[9,18–22] Recently, Duncton and co-workers reported synthesis of 2-(trifluoromethyl)cyclopropylboronic derivatives by $Pd(OAc)_2$-catalyzed reaction of dibutyl vinylboronic ester or MIDA vinylboronate with 2,2,2-trifluorodiazoetane (Scheme 1, **G**).[23,24] Other recent methods which were mostly used for the preparation of polysubstituted cyclopropyl boronates included copper-catalyzed desymmetrization of cyclopropenes,[25,26] directed remote metalation–borylation of *N*-cyclopropylamides,[27] enantioselective transfer of redox-active carbenes to alkenylboronates,[28,29] and stereoselective cyclopropanation thereof.[30]



Tranylcypromine (1961) Cyprolidol (1966) Tasimelteon (2014) Ticagrelor (2011)

Figure 1. 1,2-Disubstituted cyclopropanes–marketed and investigational drugs.



Scheme 1. Known methods for the preparation of functionalized 1,2-disubstituted cyclopropane boron reagents

Unlike the literature examples described in the Scheme 1, our approach aimed at the direct synthesis of functionalized cyclopropyl trifluoroborates. It should be noted that trifluoroborates attracted much interest in the last two decades,[31,32] being more nucleophilic and typically more stable than more classical boronic acid derivatives.[33] To date, functionalized 1,2-disubstituted cyclopropyl trifluoroborates were reported in the literature, but they were prepared *via* the corresponding boronic esters.[8,14,15,19–21,27]

Results and Discussion

In a search for the short and efficient synthetic sequence for the preparation of functionalized 1,2-disubstituted cyclopropyl trifluoroborates, we have turned our attention to the above-mentioned method of Duncton and co-workers (Scheme 1, **G**)[23,24] since it would allow preparation of various functionalized 1,2-disubstituted cyclopropanes using a single organoboron derivative as the starting material. Potassium vinyltrifluoroborate (**1**), which have recently become available from commercial sources in large quantities, could be such starting material. To check if this statement is true, we have performed reaction of **1** with ethyl diazoacetate under various reaction conditions (Table 1, Entries 1–7). A series of works by the Pietruszka group describing reactions of 1,2-disubstituted alkenes with diazomethane are appropriate to mention here since similar conditions were described therein.[2–7]

It was found that in acetone at 25 °C, the reaction of **1** with ethyl diazoacetate did not occur in the presence of $Pd(OAc)_2$, and only traces of the target products were detected when $Rh_2(OAc)_4$ was used as a catalyst. With CuCl, the complete conversion of **1** could not be achieved. Using $CuPF_6$ under the same conditions led to the formation of cyclopropanes **2a** and **2b** in 65% yield (*dr* 4:1); nevertheless, removal of the Cu (I) catalyst from the crude products appeared to be not feasible. Therefore, we switched back to $Pd(OAc)_2$; it was found that with this catalyst, the reaction could be launched when the temperature was increased to 40 °C. The products **2a** and **2b** were obtained in 71% total yield (*dr* 4:1), however, their isolation in pure form was not fruitful. With $Rh_2(OAc)_4$, no significant conversion of **1** could be achieved even at elevated temperatures.

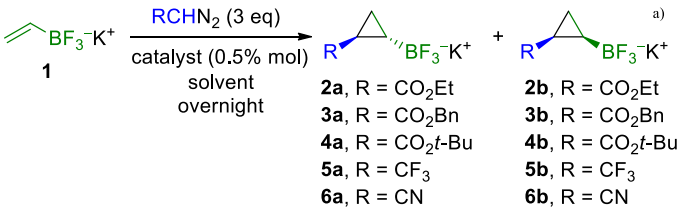
Further optimization of the reaction conditions included variation of the solvent. It was found that at 40–45 °C, the conversion of **1**, yield of the products **2a** and **2b**, as well as their diastereomeric ratio were not affected significantly upon replacing acetone with THF. In the case of MeCN, conversion of **1** under analogous conditions was not complete. Nevertheless, the crude mixture of diastereomers **2a** and **2b** obtained from the THF solution could be successfully separated by fractional crystallization, so that **2a** and **2b** were obtained in 53% and 23% yields, respectively.

It should be noted that the developed procedure was used for the multigram cyclopropanation of **1** without significant change in the reaction outcome.

We have also tried reaction of ethyl diazoacetate and vinylboronic acid pinacol ester under the optimized conditions described above. In this case, the starting alkene and the products of carbene dimerization were found in the crude reaction mixture.

Reaction of **1** and benzyl diazoacetate followed trends similar to those described above for the ethyl counterpart, although the yield of the products **3a** and **3b** were somewhat lower (Table 1, Entries 9–15). The optimized conditions (**1**, BnO_2CCHN_2 (5 eq), $Pd(OAc)_2$ (2% mol.), THF, 45 °C, overnight) gave **3a**

Table 1. Reaction of **1** and diazoalkanes



#	R	Catalyst	Temperature, °C	Solvent	Conversion of **1** (%)	Yield (%)[b]	*trans:cis*
1	CO_2Et	$Pd(OAc)_2$	25	acetone	<5	–	–
2		$Rh_2(OAc)_4$	25	acetone	<5	traces	–
3		CuCl	25	acetone	68	59	80:20
4		$CuPF_6$	25	acetone	>99	65	80:20
5		$Pd(OAc)_2$	40	acetone	>99	71	80:20
6		$Pd(OAc)_2$	65	CH_3CN	>99	60	80:20
7		$Pd(OAc)_2$	65	THF	>99	60	80:20
8		**$Pd(OAc)_2$**	**45**	**THF**	**>99**	**74**[c]	**80:20**
9	CO_2Bn	$Pd(OAc)_2$	25	acetone	<5	–	–
10		$Rh_2(OAc)_4$	25	acetone	<5	–	–
12		CuCl	25	acetone	40	25	75:25
13		$CuPF_6$	25	acetone	74	32	75:25
14		$Pd(OAc)_2$	40	acetone	>99	42	75:25
15		**$Pd(OAc)_2$**[d]	**45**	**THF**	**>99**	**48**[c]	**75:25**
16	CO_2t-Bu	**$Pd(OAc)_2$**[e]	**45**	**THF**	**>99**	**54**[c]	**85:15**
17	CF_3[f]	**$Pd(OAc)_2$**	**25**	**acetone**	**>99**	**74**[c]	**90:10**
18		$Rh_2(OAc)_4$	25	acetone	<5	–	–
19		CuCl	25	acetone	>99	11	90:10
20		$CuPF_6$	25	acetone	46	15[c]	90:10
21	CN[f]	$Pd(OAc)_2$	25	acetone	>99	27	85:15
22		$Rh_2(OAc)_4$	25	acetone	<5	–	–
23		CuCl[g]	25	acetone	>99	30	85:15
24		$CuPF_6$[g]	25	acetone	>99	45	85:15
25		**$Cu(acac)_2$**[g]	**25**	**acetone**	**>99**	**60**[c]	**85:15**

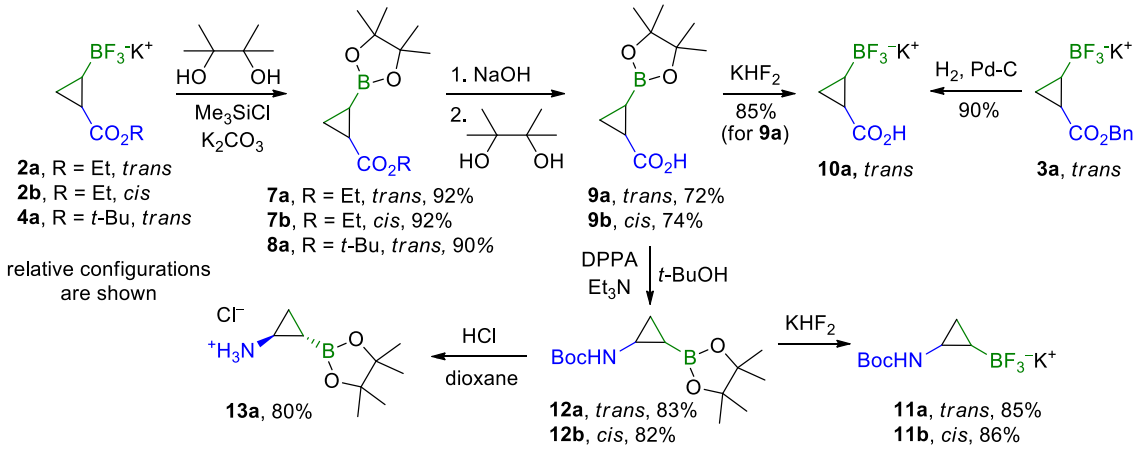
[a] Relative configurations are shown. [b] Unless noted otherwise, yields are detected by ^1H NMR. [c] Isolated yields. [g] 2% mol. of catalyst, 5 eq of diazoalkane. [g] 2% mol. of catalyst. [f] Used as a CH_2Cl_2 solution. [g] 3.6% mol. of catalyst

and **3b** in 43% and 5% yields, respectively, after fractional crystallization. Analogously, *tert*-butyl ester **4a** was obtained in 54% yield by reaction of **1** and *tert*-butyl diazoacetate under the conditions mentioned above.

It should be noted that although compounds **2**–**4** were not described in the literature, the *trans* isomer of the corresponding methyl ester was obtained by Liskey and Hartwig *via* iridium-catalyzed C–H functionalization of methyl cyclopropanecarboxylate.[14]

Since the procedure for safe generation of 2,2,2-trifluorodiazoetane includes its isolation as a CH_2Cl_2 solution,[34] an additional optimization of the solvent was necessary in this case. It was found that in the case of THF, addition of the diazoalkane solution in CH_2Cl_2 causes precipitation of trifluoroborate **1**; to avoid this, large excess of THF should be used. In thecase of acetone, this effect was not so significant, and the reaction could be performed successfully already at the acetone : CH_2Cl_2 v/v ratio of 5:1. Screening of the catalysts showed that the best results could be obtained with $Pd(OAc)_2$; moreover, in this case the reaction occurred already at 25 °C. In this case, a mixture of the diastereomers **5a** and **5b** was formed with 9:1 *dr*, and the major isomer **5a** could be isolated in 50% yield after recrystallization.

Similar to 2,2,2-trifluorodiazoetane, diazoacetonitrile can be safely generated as a CH_2Cl_2 solution.[35] Therefore, we have used the above-described optimized conditions (acetone : CH_2Cl_2 v/v ratio of 5:1, $Pd(OAc)_2$, 25 °C) in this case. It was found that the reaction was accompanied by formation of polymeric by-products, so that the yield of the products **6** was low (27%). Switching to CuCl and $CuPF_6$ allowed to improve the reaction outcome, however, isolation and purification of the product were not successful with these catalysts. Finally, $Cu(acac)_2$ was found to be the optimal reaction promotor: although the conversion of **1** under the standard reagent ratio (3 eq of diazoalkane) was not complete, it could be improved by increasing excess



Scheme 2. Synthesis of organoboron derivatives **7**–**13**

of $NCCHN_2$ to 4 mol per 1 mol of **1**. In this case, the products **6a** and **6b** were formed with 85:15 *dr*, and pure major isomer **6a** was isolated in 60% yield after recrystallization.

Relative configuration of the products was confirmed by NOE experiments performed with **2a**, **3a**, and **6a**, as well as heteronuclear ^1H-^{19}F NOESY experiment performed with **5a** (see the supporting information).

To extend synthetic applicability of the method developed, some typical functional group manipulations were performed with trifluoroborates **2**–**4**. In particular, **2a** and **4a** could be transformed into pinacol esters **7a** and **8a** in 92% and 90% yield, respectively, upon subsequent action of Me_3SiCl–K_2CO_3 and pinacol according to the method of Hutton and co-workers[36] (Scheme 2). Reaction of **7a** with aq NaOH at rt resulted in hydrolysis of both carboxylate and boronate esters; after restoring the pinacol ester, the carboxylic acid **9a** was obtained in 72% yield.

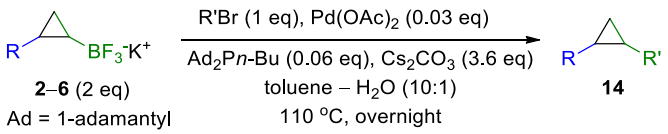
Free carboxylic acid **10a** could be also obtained, either from pinacolate **9a** (85% yield) or by catalytic debenzylation of ester **3a** (90% yield). It should be noted, however, that the compound **10a** showed limited stability: after its storage at –10 °C for 1 week, considerable decomposition was observed according to ^1H NMR. Finally, *N*-protected amino derivatives **11a** and **11b** were synthesized. The modified Curtius reaction with **9a** gave the corresponding carbamate **12a** in 83% yield, which was transformed into trifluoroborate **11a** (85% yield). Analogously, *cis*-isomer **11b** was obtained from **2b** (34% overall yield). It should be noted that the Curtius reaction was not fruitful with trifluoroborate **10a**. Deprotection of **12a** gave the corresponding free amine hydrochloride **13a** (80% yield). Notably, *N*-pivaloyl derivative of the corresponding *cis* isomer **13b** was described by

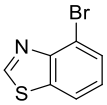
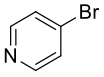
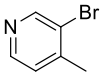
Yamaguchi, Itami, and co-workers;[15] their synthesis included iridium-catalyzed C–H activation of cyclopropylamine derivative.

To demonstrate utility of the functionalized cyclopropyl trifluoroborates obtained in this work for the palladium-catalyzed cross-couplings and for the preparation of (het)arylcyclopropanes, we have performed the Suzuki–Miyaura reactions of these substrates with a number of (hetero)aromatic halides varied in electronic properties (Table 2). Initially, the conditions described by Molander group ($Pd(OAc)_2$, XantPhos, Cs_2CO_3, toluene–H_2O (10:1), 110 °C)[37] were tested for **2a** and phenyl bromide. Although in this case, these conditions worked well, they gave unsatisfactory results with heteroaromatic bromides. Therefore, other ligands for palladium were evaluated, *i.e.* *t*-Bu_3P, RuPhos and di(1-adamantyl)-*n*-butylphosphine (cataCXium®); the catalyst based on the latter phosphine appeared to be most efficient (which is in accordance with the previous results of Harris and co-workers on analogous transformations[38,39]). The corresponding products **14a–i** were obtained in 32–92% yield. The method was also efficient for trifluoroborates **2b**, **3a**, **4a**, and **5a**; in this case, the corresponding products **14j–m** were obtained (52–93% yield). In all the examples mentioned above, a two-fold excess of the trifluoroborate was used to achieve complete conversion of the starting halide and thus simplify purification of the target product, keeping in mind possible further applications for the compound library synthesis. In the case of **6a**, the standard protocol did not work; the product **14n** could be obtained in modest yield (24%) under the following conditions: **6a** (1.2 eq), ArBr (1 eq), $Pd(dppf)Cl_2$ (0.025 eq), AcOK (3.6 eq), dioxane–H_2O (10:1). In all cases studied, the C–C coupling proceeded with retention of the relative configuration of the starting organoboron derivative.

In the case of trifluoroborates **11a** and **11b**, the Suzuki–Miyaura reaction under the conditions was accompanied by cyclopropane ring opening, so that

Table 2. The Suzuki–Miyaura reactions of functionalized cyclopropyl trifluoroborates **2**–**6**

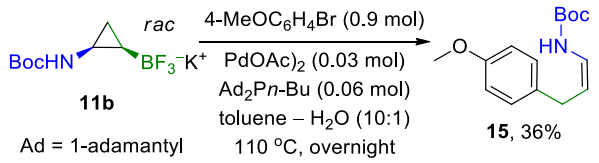


#	Substrate	R	Isomer	R′Br	Product	Yield (%)
1	**2a**	CO_2Et	*trans*	PhBr	**14a**	84
2				4-$O_2NC_6H_4Br$	**14b**	92
3				4-$MeOC_6H_4Br$	**14c**	85
				2-$CF_3C_6H_4Br$	**14d**	50
4					**14e**	87
5					**14f**	60
6					**14g**	32
7					**14h**	85
8					**14i**	84
9	**2b**	CO_2Et	*cis*	4-$O_2NC_6H_4Br$	**14j**	77

10	**3a**	CO_2Bn	*trans*	4-$OHCC_6H_4Br$	**14k**	53
11	**4a**	CO_2t-Bu	*trans*	4-$O_2NC_6H_4Br$	**14l**	52
12	**5a**	CF_3	*trans*	4-$O_2NC_6H_4Br$	**14m**	93
13	**6a**[a]	CN	*trans*	4-$O_2NC_6H_4Br$	**14n**	24

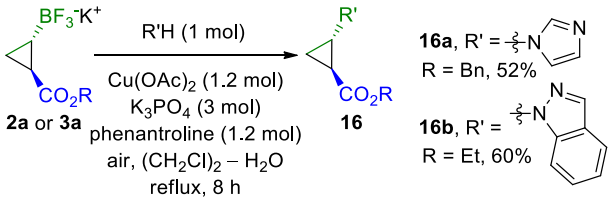
[a] Conditions: **6a** (1.2 eq), ArBr (1 eq), $Pd(dppf)Cl_2$ (0.025 eq), AcOK (3.6 eq), dioxane–H_2O (10:1).

the corresponding enamine derivative **15** could be isolated in the case of **11b** (60% yield) (Scheme 3). The structure of **15** was confirmed by 2D NMR experiments and comparison with the literature data for analogous compounds.[40] Similar results were obtained with pinacolate **12b** (although the reaction proceeded less purely in this case). With **11a**, a complex mixture was obtained presumably containing the target product of C–C coupling, **15** and its *trans* isomer (according to LCMS and ^{1}H NMR).



Scheme 3. The C–C coupling with trifluoroborate **11b**

Finally, the Chan–Lam coupling was evaluated with trifluoroborates **2a** and **3a** under the following conditions: imidazole or indazole (1 mol), $Cu(OAc)_2$ (1.2 mol), phenantroline (1.2 mol), K_3PO_4 (3 mol), air, $(CH_2Cl)_2$–H_2O, reflux).[23,39,41] The corresponding products **16a** and **16b** were obtained in 52% and 60% yield, respectively (Scheme 4).



Scheme 4. The Chan–Lam coupling with **2a** and **3a** (relative configurations are shown)

Conclusions

Metal-catalyzed reaction of potassium vinyl trifluoroborate and diazo compounds is a convenient method for the preparation of functionalized 1,2-disubstituted cyclopropyl trifluoroborates. Although for each diazo compound, the method required careful optimization of the reaction conditions, the developed protocols allowed for convenient multigram preparation of the target compounds. The reaction had moderate to good *trans* diastereoselectivity, and the major isomer could be efficiently separated by recrystallization (in one case–minor as well). The resulting trifluoroborates could be subjected to some common functional group transformations (i.e. ester hydrolysis and modified Curtius reaction). Moreover, most of them were efficient partners for diastereoselective Suzuki–Miyaura and Chan–Lam couplings with various aromatic and heteroaromatic substrates, thus providing access to medicinally relevant (het)aryl-substituted cyclopropanes.

Experimental Section

General. The solvents were purified according to the standard procedures.[42] All other starting materials were purchased from commercial sources. Melting points were measured on MPA100 OptiMelt automated melting point system. Analytical TLC was performed using Polychrom SI F254 plates. Column chromatography was performed using Kieselgel Merck 60 (230–400 mesh) as the stationary phase. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 170 Avance 500 spectrometer (at 499.9 MHz for Protons and 124.9 MHz for Carbon-13) and Varian Unity Plus 400 spectrometer (at 400.4 MHz for protons and 100.7 MHz for Carbon-13). Chemical shifts are reported in ppm with solvent residual signal used as an internal standard (^{1}H, ^{13}C); and $CFCl_3$ (^{19}F) or $BF_3{\cdot}Et_2O$ (^{11}B)–as external standards. Elemental analyses were performed at the Laboratory of Organic Analysis, Department of Chemistry, National Taras Shevchenko University of Kyiv. Mass spectra were recorded on an Agilent 1100 LCMSD SL instrument (chemical ionization (APCI), electrospray ionization (ESI)) and Agilent 5890 Series II 5972 GCMS instrument (electron impact ionization (EI)).

Potassium (*trans*- and (*cis*-2-(ethoxycarbonyl)cyclopropyl)trifluoroborates (2a,b).[43] Potassium vinyltrifluoroborate (**1**) (50.0 g, 376 mmol) was placed into a 2 L flask equipped with a thermometer, a dropping funnel and a stirrer. THF (1.2 L) was added, and the mixture was heated to 45 °C (it is important to pre-heat the reaction mixture to this temperature and keep it during addition of the reagents). $Pd(OAc)_2$ (200 mg, 0.891 mmol) was added. Ethyl diazoacetate (143 g, 1.13 mol, 90% solution in CH_2Cl_2) was carefully added dropwise upon stirring over 2.5 h (CAUTION! Exothermic reaction with violent gas evolution!). When the gas evolution ceased (after addition of nearly a half of ethyl diazoacetate), a second portion of $Pd(OAc)_2$ (200 mg, 0.891 mmol) was introduced into the reaction vessel. After the addition was complete, the reaction mixture was stirred at 45 °C until the gas evolution ceased, cooled, evaporated in *vacuo* to a half of its volume and poured into hexanes (3 L). The

solvent was decanted from the clayish precipitate formed, acetone (1 L) was added, and the resulting solution was evaporated in *vacuo*. Toluene (1 L) was added, and the mixture was evaporated in *vacuo* again. The resulting oil was dissolved in EtOH (800 mL) upon heating. After a few minutes, the precipitate was formed, which was filtered quickly to give pure *trans*-isomer **2a**. The combined filtrates were evaporated in *vacuo* and recrystallized from acetone to give *cis*-isomer **2b**.

2a: Yield 43.5 g, 0.198 mol, 53%. White solid, mp = 158–160 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.96 (q, J = 7.1 Hz, 2H, C$\underline{H}_2$CH$_3$), 1.19–1.07 (m, 4H, CH$_2$C$\underline{H}_3$ and 2-C$\underline{H}$), 0.64 (d, J = 9.5 Hz, 1H, 3-C$\underline{H}$H), 0.49 (t, J = 7.7 Hz, 1H, 3-CH$\underline{H}$), 0.01 to –0.11 (m, 1H, 1-C$\underline{H}$) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 176.4 ($\underline{C}$=O), 59.0 ($\underline{C}$H$_2$CH$_3$), 16.1 (2-$\underline{C}$H), 14.8 (br s, 1-$\underline{C}$H), 14.3 (CH$_2\underline{C}$H$_3$), 12.6 (3-$\underline{C}$H$_2$) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –141.6 to –142.4 (m) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 4.0–1.8 (m) ppm. MS (EI) *m/z* = 113 [M–K–BF$_3$]$^-$. Anal. Calcd. for $C_6H_9BF_3KO_2$: C 32.75; H 4.12. Found: C 33.07; H 3.88.

2b: Yield 18.9 g, *ca.* 75 mmol, 21%, 85–90% purity. The product contained 10–15% wt. of KBF_4 (or some other inorganic boron compound) according to ^{19}F and ^{11}B NMR spectra; an analytical sample was obtained by additional recrystallization. White solid, mp = 185–187 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.92 (q, J = 7.6 Hz, 2H), 1.28 (s, 1H), 1.17–1.08 (m, 3H), 0.76 (s, 1H), 0.60–0.53 (m, 1H), –0.05 to –0.17 (m, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 174.7, 58.8, 16.8, 14.2, 13.5 (br s), 10.0 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –135.3 to –136.0 (m) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 3.0 ppm. MS (APCI) *m/z* = 163 [M–KF+H]$^+$. Anal. Calcd. for C6H9BF3KO2: C 32.75; H 4.12. Found: C 32.65; H 4.52.

Potassium (*trans*- and (*cis*-2-(benzyloxycarbonyl)cyclopropyl)trifluoroborates (3a,b).[43] A solution of potassium vinyltrifluoroborate (**1**) (10.0 g, 75.2 mmol) in THF (200 mL) was heated to 50 °C (it is important to pre-heat the reaction mixture to this temperature and keep it during addition of the reagents), and Pd(OAc)$_2$ (169 mg, 0.752 mmol) was then added. Benzyl diazoacetate (73.6 g, 376 mmol, 90% solution in CH_2Cl_2) was carefully added dropwise upon stirring over 0.5 h (CAUTION! Exothermic reaction with violent gas evolution!). When the gas evolution ceased (after addition of nearly a half of ethyl diazoacetate), a second portion of Pd(OAc)$_2$ (169 mg, 0.752 mmol) was introduced into the reaction vessel. After the addition was complete, the reaction mixture was stirred at 50 °C until the gas evolution ceased and cooled to rt. The formed precipitate was filtered to give pure potassium (*trans*-2-((benzyloxy)carbonyl)cyclopropyl)trifluoroborate (**3a**). The obtained filtrate was concentrated under reduced pressure, and the resulting solids were twice recrystallized from MeOH (50 mL) to give pure (*cis*-2-((benzyloxy)carbonyl)cyclopropyl)trifluoroborate (**3b**).

3a: Yield 9.10 g, 32.2 mmol, 43%. White solid, mp = 213–216 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.41–7.26 (m, 5H, C$_6\underline{H}_5$), 5.03 (d, J = 12.5 Hz, 1H, C$\underline{H}$HC$_6$H$_5$), 4.99 (d, J = 12.5 Hz, 1H, CH$\underline{H}$C$_6$H$_5$), 1.23–1.14 (m, 1H, 2-C$\underline{H}$), 0.71 (d, J = 9.9 Hz, 1H, 3-C$\underline{H}$H), 0.54 (t, J = 6.9 Hz, 1H, 3-CH$\underline{H}$), 0.08 to –0.02 (m, 1H, 1-C$\underline{H}$) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 176.7, 137.3, 128.9, 128.3 (2C), 65.2, 16.6, 15.8 (br s), 13.4 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –141.7 to –142.5 (m) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 4.1–1.6 (br s) ppm. MS (APCI) *m/z* = 421 [$C_{22}H_{23}B_2O_7$]$^-$. Anal. Calcd. for $C_{11}H_{11}BF_3KO_2$: C 46.83; H 3.93. Found: C 46.74; H 3.81.

3b: Yield 1.06 g, *ca.* 3.3 mmol, 5%, 85–90% purity. The product contained 10–15% wt. of KBF_4 (or some other inorganic boron compound) according to ^{19}F and ^{11}B NMR spectra; an analytical sample was obtained by additional recrystallization. White solid, mp >200 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.40–7.24 (m, 5H), 4.99 (d, J = 12.7 Hz, 1H), 4.92 (d, J = 12.7 Hz, 1H), 1.41–1.31 (m, 1H), 0.86–0.78 (m, 1H), 0.61 (t, J = 8.8 Hz, 1H), –0.00 to –0.11 (m, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 174.3, 137.1, 128.2, 127.7, 127.5, 64.5, 16.8, 12.9 (br s), 10.0 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –135.5 to –136.1 (m) ppm. Anal. Calcd. for $C_{11}H_{11}BF_3KO_2$: C 46.83; H 3.93. Found: C 47.11; H 4.15.

Potassium (*trans*-*tert*-butoxycarbonyl)cyclopropyl)trifluoroborate (4a). A solution of potassium vinyltrifluoroborate (**1**) (5.00 g, 37.6 mmol) in acetone (100 mL) was heated to 50 °C (it is important to pre-heat the reaction mixture to this temperature and keep it during addition of the reagents), and Pd(OAc)$_2$ (84.5 mg, 0.376 mmol) was then added. *tert*-Butyl diazoacetate (29.7 g, 188 mmol, 90% solution in CH_2Cl_2) was carefully added dropwise upon stirring over 15 min (CAUTION! Exothermic reaction with violent gas evolution!). When the gas evolution ceased (after addition of nearly a half of ethyl diazoacetate), a second portion of Pd(OAc)$_2$ (84.5 mg, 0.376 mmol) was introduced into the reaction vessel. After the addition was complete, the reaction mixture was stirred at 50 °C until the gas evolution ceased and cooled to rt. The reaction mixture was concentrated under vacuum, H_2O (50 mL) was added to the residue, and the solution was washed with EtOAc (2×50 mL). The concentration of aqueous phase gave the title product as a 85:15 mixture of *E*–*Z* isomers. An analytical sample of *E*–isomer was obtained by recrystallization from CH_3CN at –20 °C. Yield 5.04 g, 20.3 mmol, 54%. White solid, mp =79–83 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.35 (s, 9H), 1.09–1.00 (m, 1H), 0.59–0.53 (m, 1H), 0.43 (t, J = 7.4 Hz, 1H), –0.03 to –0.13 (m, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 176.1, 78.5, 28.4, 17.6, 14.4 (br s), 12.7 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –141.8. MS (APCI) *m/z* = 353 [$C_{18}H_{33}B_2O_7^-$]. Anal. Calcd. for $C_8H_{13}BF_3KO_2$: C 38.73, H 5.28. Found: C 38.41, H 5.11.

Potassium (*trans*-(trifluoromethyl)cyclopropyl)trifluoroborate (5a). 2,2,2-Trifluoroethylamine hydrochloride (60.8 g, 450 mmol) was suspended in CH_2Cl_2 (300 mL). The mixture was cooled to 0 °C on an ice bath, and a solution of $NaNO_2$ (93.2 g, 1.35 mol) in H_2O (110 mL) was added dropwise at the same temperature. After the mixture was stirred for additional 30 min, the organic phase was separated, washed with 1% aq $NaHCO_3$ (150 mL), and dried over anhydrous Na_2SO_4. The diazoalkane solution was then added dropwise to a mixture of potassium vinyltrifluoroborate (**1**) (20.0 g, 150 mmol)

and $Pd(OAc)_2$ (84 mg, 0.375 mmol) in acetone (500 mL) at 30 °C over 1 h (CAUTION! Exotermic reaction with violent gas evolution!). After the addition was complete, the mixture was stirred for 10 min, $Pd(OAc)_2$ (84 mg, 0.375 mmol) was added, the mixture was stirred for additional 10 min and evaporated in *vacuo*. The residue was dissolved in a minimal volume of CH_3CN, the solution was heated to reflux, and toluene was added until clouding. The resulting mixture was cooled, the solution was separated from the dark slurry formed by decantation and evaporated in *vacuo*. Yield 24.0 g, 111 mmol, 74%. White solid, mp = 150–153 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14–1.00 (m, 1H, 2-C<u>H</u>), 0.45–0.37 (m, 1H, 3-C<u>H</u>H), 0.37–0.27 (m, 1H, 3-CH<u>H</u>), –0.22 to –0.32 (m, 1H, 1-C<u>H</u>) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 129.1 (q, J = 269.8 Hz), 15.8 (q, J = 35.2 Hz), 6.1 (br s), 5.1 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –64.6 (s, 3F, C<u>F</u>$_3$), –142.6 to –143.2 (m, 3F, B<u>F</u>$_3^-$) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 3.7–1.8 (m) ppm. MS (APCI) *m/z* = 289 $[C_8H_9B_2F_6O_3]^-$. Anal. Calcd. for $C_4H_4BF_6K$: C 22.25, H 1.87. Found: C 22.42, H 2.20.

Potassium (*trans*-2-cyanocyclopropyl)trifluoroborates (6a). 2-Aminoacetonitrile hydrochloride (5.18 g, 56.0 mol) was suspended in CH_2Cl_2 (50 mL). The mixture was cooled to –5 °C, and a solution of $NaNO_2$ (11.6 g, 168 mmol) in H_2O (15 mL) was added dropwise with stirring at –5–0 °C. After the mixture was stirred for additional 30 min, the organic phase was separated, washed with 1% aq $NaHCO_3$ (20 mL), and dried over anhydrous Na_2SO_4. The diazoalkane solution was then added dropwise to a mixture of potassium vinyltrifluoroborate (**1**) (1.50 g, 11.2 mmol), acetone (40 mL) and $Cu(CH_3CN)_4PF_6$ (50 mg, 0.134 mmol) at 20 °C over 10 min. After the gas evolution ceased (after nearly the first and second thirds of the diazoalkane solution were added), $CuPF_6$ (2×50 mg, 0.134 mmol) was added. The reaction mixture was stirred at 20 °C until the gas evolution ceased, then poured into Et_2O (250 mL), and the precipitate was filtered. Yield 872 mg, 5.04 mmol, 45%. Yellow solid, mp = 140–143 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.91–0.80 (m, 1H, 2-C<u>H</u>), 0.80–0.67 (m, 1H, 3-C<u>H</u>H), 0.61–0.48 (m, 1H, 3-CH<u>H</u>), 0.04 to –0.09 (m, 1H, 1-C<u>H</u>) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 125.7, 12.9 (br s), 11.0, –1.9 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –143.4 to –144.1 (m) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 3.6–1.7 (m) ppm. MS(APCI) *m/z* = 134 $[M–K]^-$. Anal. Calcd. for $C_4H_4BF_3KN$: C 27.77, H 2.33, N 8.10. Found: C 28.05, H 2.14, N 7.75.

Ethyl *trans*-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (7a). K_2CO_3 (47.7 g, 345 mmol) and pinacol (21.1 mL, 173 mmol) were added to a solution of potassium (*trans*-2-(ethoxycarbonyl)cyclopropyl)trifluoroborate (**2a**) (38.0 g, 173 mmol) in CH_3CN (500 mL). A freshly distilled TMSCl (32.9 mL, 260 mmol) was added dropwise and the reaction mixture was left to stir overnight. The resulting mixture was filtered and the filtrate was concentrated under reduced pressure to give the title product. Yield 38.2 g, 159 mmol, 92%. Colorless liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.05 (q, J = 7.1 Hz, 2H), 1.60 (dt, J = 7.8, 4.9 Hz, 1H), 1.17 (s, 15H), 1.13–1.04 (m, 1H), 0.89 (td, J = 7.6, 3.0 Hz, 1H), 0.40–0.29 (m, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 173.6, 83.8, 60.7, 24.94, 24.87, 18.3, 14.5, 12.9, 4.2 (br s) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 32.4 ppm. MS(EI) *m/z* = 240 $[M]^+$. Anal. Calcd. for $C_{12}H_{21}BO_4$: C 60.03, H 8.82. Found: C 59.95, H 8.46.

Ethyl *cis*-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (7b).[17] Compound **7b** was prepared from potassium (*cis*-2-(ethoxycarbonyl)cyclopropyl)trifluoroborate (**2b**) (36.0 g, 164 mmol) using the procedure described above for **7a**. Yield 36.2 g, 150 mmol, 92%. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.13–4.06 (m, 2H), 1.74 (dt, J = 7.8, 4.9 Hz, 1H), 1.28–1.22 (m, 4H), 1.20 (s, 12H), 0.97 (td, J = 7.6, 3.0 Hz, 1H), 0.60–0.52 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 83.6, 60.6, 24.9, 24.8, 18.7, 14.4, 13.1, 4.4 (br s) ppm. MS(EI) *m/z* = 240 $[M]^+$, 225 $[M–CH_3]^+$, 195$[M–C_2H_5O]^+$. Anal. Calcd. for $C_{12}H_{21}BO_4$: C 60.03, H 8.82. Found: C 59.79, H 9.01

***tert*-Butyl *trans*-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (8a).**[17] Compound **8a** was prepared from potassium (*trans*-2-(*tert*-butoxycarbonyl)cyclopropyl)trifluoroborate (**4a**) (30.0 g, 121 mmol) using the procedure described above for **7a**. Yield 29.2 g, 109 mmol, 90%. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58 (dt, J = 7.7, 5.0 Hz, 1H), 1.35 (s, 9H), 1.14 (s, 12H), 1.06–1.02 (m, 1H), 0.82 (td, J = 7.7, 2.7 Hz, 1H), 0.45–0.38 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.4, 83.4, 80.1, 28.1, 24.8, 24.7, 19.6, 12.8, 3.8 (br s) ppm. MS (APCI) *m/z* = 254 $[M+H–CH_3]^+$. Anal. Calcd. for $C_{14}H_{25}BO_4$: C 62.71, H 9.40. Found: C 62.97, H 9.48.

***trans*-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylic acid (9a).** A solution of NaOH (31.7 g, 792 mmol) in H_2O (32 mL) was added to a solution of ethyl *trans*-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (**7a**) (38.0 g, 158 mmol) in THF (300 mL), and the reaction mixture was stirred for 8 h. The resulting solution was acidified with 12M HCl (70 mL) to pH = 1. Then the reaction mixture was concentrated under reduced pressure until the formation of precipitate was observed. Acetone (500 mL) was added to the residue, and the mixture was filtered. Pinacol (19.3 mL, 158 mmol) was added to the obtained filtrate and the solution was stirred for 6 h. The reaction mixture was concentrated under reduced pressure and additionally dried under high vacuum at 60 °C. Yield 24.1 g, 114 mmol, 72%. Beige solid, mp = 83–85 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.19 (s, 1H), 1.52 (dt, J = 7.9, 4.9 Hz, 1H), 1.16 (s, 12H), 1.08–1.00 (m, 1H), 0.84 (td, J = 7.5, 2.9 Hz, 1H), 0.36–0.25 (m, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 175.1, 83.7, 24.94, 24.89, 18.4, 12.7, 3.9 (br s) ppm. MS(APCI) *m/z* = 211 $[M–H]^-$. Anal. Calcd. for $C_{10}H_{17}BO_4$: C 56.64, H 8.08. Found: C 56.45, H 8.33.

***cis*-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylic acid (9b).** Compound **9b** was prepared from ethyl *cis*-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (**7b**) (36.0 g, 150 mmol) using the procedure described above for **9a**. Yield 23.5 g. The compound was used in the next step without purification and characterization.

***trans-tert*-Butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)carbamate (12a).** To a solution of *trans*-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylic acid (**9a**) (24.0 g, 113 mmol) in toluene (240 mL) and *t*-BuOH (240 mL), Et_3N (20.8 mL, 135 mmol) and diphenylphosphoryl azide (DPPA) (40.4 g, 147 mmol) were added. The mixture was heated to 100 °C, then stirred at this temperature for 12 h, cooled, poured into 10% aq K_2CO_3 (700 mL), and diluted with hexanes (500 mL). The organic phase was separated, the aqueous phase was extracted with hexanes (2×500 mL). The combined extracts washed with H_2O (500 mL), brine (500 mL), dried over anhydrous Na_2SO_4, and evaporated in *vacuo*. Yield 26.5 g, 93.6 mmol, 83%. White solid, mp = 108–110 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.04 (s, 1H), 2.54 (s, 1H), 1.36 (s, 9H), 1.14 (s, 12H), 0.75–0.66 (m, 1H), 0.65–0.55 (m, 1H), –0.18 (br s, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 156.4, 83.2, 78.1, 29.1, 28.7, 25.1, 24.9, 11.3, 2.4 (br s) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 31.7 ppm. MS (EI) *m/z* = 268 $[M–CH_3]^+$. Anal. Calcd. for $C_{14}H_{26}BNO_4$: C 59.38, H 9.25, N 4.95. Found: C 59.22, H 8.91, N 4.80.

***cis-tert*-Butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)carbamate (12b).**[44] Compound **12b** was prepared from *cis*-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylic acid (**9b**) (23.0 g, 108 mmol) using the procedure described above for **12a**. Yield 25.1 g, 88.7 mmol, 82%. White solid, mp = 89–91°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.79 (s, 1H), 2.69–2.58 (m, 1H), 1.35 (s, 9H), 1.14 (s, 12H), 0.81 (ddd, *J* = 10.4, 7.4, 4.3 Hz, 1H), 0.65 (dt, *J* = 8.3, 4.3 Hz, 1H), –0.07 (dt, *J* = 10.4, 7.4 Hz, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 156.5, 83.0, 77.7, 28.74, 28.68, 25.0, 10.4, 2.2 (br s) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 32.0 ppm. MS(EI) *m/z* = 283 $[M]^+$, 268 $[M–CH_3]^+$. Anal. Calcd. for $C_{14}H_{26}BNO_4$: C 59.38, H 9.25, N 4.95. Found: C 59.57, H 8.85, N 4.92.

General procedure for the preparation of trifluoroborates 10 and 11 from pinacolates 9 and 12. To a solution of the corresponding pinacolate (9.43 mmol) in THF (35 mL), a solution of KHF_2 (2.94 g, 37.7 mmol) in H_2O (8.3 mL) was added and the reaction mixture was vigorously stirred for 4 h. The resulting mixture was concentrated under vacuum, and the residue was redissolved in acetone (20 mL). The precipitate was filtered off, and the filtrate was added slowly to *t*-BuOMe (200 mL). The newly formed precipitate was filtered and dried under vacuum (1 mbar) at 60 °C.

Potassium (*trans*-2-carboxycyclopropyl)trifluoroborate (10a).[43] The product was additionally purified by extraction in Soxhlet extractor using acetone as solvent. Yield: 1.54 g (*ca.* 7 mmol, 85%, 85–90% purity) from *trans*-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylic acid (**9a**) (2.00 g, 9.43 mmol). The product contained 10–15% wt. of KBF_4 (or some other inorganic boron compound) according to ^{19}F and ^{11}B NMR spectra. Beige solid, mp > 150 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.32 (s, 1H), 1.07–0.99 (m, 1H), 0.59 (d, *J* = 9.3 Hz, 1H), 0.42 (t, *J* = 7.5 Hz, 1H), –0.01 to –0.13 (m, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 178.2, 16.2, 14.6 (br s), 12.5 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –141.7 to –142.3 (m) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 4.8–0.5 (m) ppm. MS (APCI) *m/z* = 128 $[C_4H_6BO_4]^–$, 111 $[C_4H_4BO_3]^–$.

Potassium (*trans*-2-((*tert*-butoxycarbonyl)amino)cyclopropyl)trifluoroborate (11a). Yield: 1.58 g (6.00 mmol, 85%) from *trans-tert*-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)carbamate (**12a**) (2.00 g, 7.07 mmol). White solid, mp = 200–203 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.45 (s, 1H), 2.10 (s, 1H), 1.35 (s, 9H), 0.09 (td, *J* = 6.8, 3.0 Hz, 1H), –0.04 (d, *J* = 10.6 Hz, 1H), –0.48 to –0.68 (m, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 156.2, 76.8, 28.4, 26.8, 9.7, 9.0 (br s) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –140.5 ppm. Anal. Calcd. for $C_8H_{14}BF_3KNO_2$: C 36.52, H 5.36, N 5.32. Found: C 36.34, H 5.50, N 5.14.

Potassium (*cis*-2-((*tert*-butoxycarbonyl)amino)cyclopropyl)trifluoroborate (11b). Yield: 1.60 g (6.08 mmol, 86%) from *cis-tert*-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)carbamate (**12b**) (2.00 g, 7.07 mmol). White solid, mp = 210–213 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.29 (s, 1H), 2.50 (s, 1H), 1.35 (s, 9H), 0.32 (s, 1H), –0.10 (s, 1H), –0.50 (s, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 156.3, 77.7, 28.7, 27.2, 10.2, 5.3 (br s) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –134.4 to –135.3 (m) ppm. ^{11}B NMR (160 MHz, DMSO-d_6): δ 4.6–2.4 (m) ppm. Anal. Calcd. for $C_8H_{14}BF_3KNO_2$: C 36.52, H 5.36, N 5.32. Found: C 36.33, H 5.38, N 5.38.

Potassium (*trans*-2-carboxycyclopropyl)trifluoroborate (10a) (alternative method). To a solution of Potassium (*trans*-2-((benzyloxy)carbonyl)cyclopropyl)trifluoroborate (**3a**) (1.00 g, 3.55 mmol) in MeOH (25 mL), 20% $Pd(OH)_2$–C (0.10 g) was added. The reaction vessel was degased, backfilled with H_2 (1 atm), and the reaction mixture was stirred overnight. The catalyst was filtered off, and the filtrate was concentrated under vacuum to give the title product. Yield: 0.613 g, 3.19 mmol, 90%.

***trans*-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanamine hydrochloride (13a).** Boc derivative **12a** (15.0 g, 53.0 mmol) was dissolved in 4 M HCl solution in dioxane (150 mL), and the reaction mixture was stirred for 8 h. The formed precipitate was filtered, washed with dioxane (100 mL) and dried under vacuum to give the title product. Yield: 9.30 g, 42.5 mmol, 80%. Yellow solid, mp = 161–163 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.55 (s, 3H), 2.51–2.49 (m, 1H), 1.16 (s, 12H), 1.08 (dt, *J* = 11.1, 4.5 Hz, 1H), 0.70 (td, *J* = 7.2, 4.5 Hz, 1H), 0.35 (ddd, *J* = 11.1, 7.2, 4.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 83.8, 27.6, 24.9, 9.0, –0.7 (br s) ppm. MS(APCI) *m/z* = 184 $[M–Cl]^+$. Anal. Calcd. for $C_9H_{19}BClNO_2$: C 49.24, H 8.72, N 6.38, Cl 16.15. Found: C 48.98, H 8.97, N 6.03, Cl 15.81.

General procedure for the preparation of the compounds 14a–m and 15. A reaction vessel containing PhMe (22 mL) and H_2O (2.2 mL) was degased and backfilled with Ar. Then the corresponding trifluoroborate **2**–**5** (2.27 mmol), the corresponding ArBr (1.89 mmol), Cs_2CO_3 (2.22 g, 6.80 mmol), Ad_2Pn–Bu (40.7 mg, 0.113 mmol), and $Pd(OAc)_2$ (12.7 mg, 0.057 mmol) were added.

The two–phase reaction mixture was refluxed under Ar with vigorous stirring for 12 h. After cooling to rt, the layers were separated, and the organic phase was concentrated under reduced pressure. The obtained crude product was purified by HPLC (gradient H_2O–MeCN as eluent).

***trans*-Ethyl 2-phenylcyclopropanecarboxylate (14a).**[45,46] Yield: 303 mg (1.59 mmol, 84%) from **2a** (500 mg, 2.27 mmol) and PhBr (297 mg, 1.89 mmol). White solid, mp = 38–40 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.51 (ddd, *J* = 9.3, 6.5, 4.1 Hz, 1H), 1.94–1.84 (m, 1H), 1.59 (dt, *J* = 9.3, 4.9 Hz, 1H), 1.34–1.29 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.4, 140.1, 128.5, 126.5, 126.2, 60.7, 26.2, 24.2, 17.1, 14.3 ppm. MS(APCI) *m/z* = 191 $[M+H]^+$. Anal. Calcd. for $C_{12}H_{14}O_2$: C 75.76, H 7.42. Found: C 75.70, H 7.73.

***trans*-Ethyl 2-(4-nitrophenyl)cyclopropanecarboxylate (14b).**[47] Yield: 409 mg (1.74 mmol, 92%) from **2a** (500 mg, 2.27 mmol) and 1-bromo-4-nitrobenzene (382 mg, 1.89 mmol). Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.62–2.52 (m, 1H), 1.98 (dt, *J* = 9.3, 4.8 Hz, 1H), 1.70 (dt, *J* = 9.9, 5.2 Hz, 1H), 1.38–1.32 (m, 1H), 1.27 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 148.1, 146.6, 126.7, 123.8, 61.1, 25.7, 25.1, 17.8, 14.2 ppm. MS(APCI) *m/z* = 236 $[M+H]^+$. Anal. Calcd. for $C_{12}H_{13}NO_4$: C 61.27, H 5.57, N 5.95. Found: C 61.31, H 5.92, N 6.32.

***trans*-Ethyl 2-(4-methoxyphenyl)cyclopropanecarboxylate (14c).**[46] Yield: 353 mg (1.60 mmol, 85%) from **2a** (500 mg, 2.27 mmol) and 1-bromo-4-methoxybenzene (353 mg, 1.89 mmol). White solid, mp = 80–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.48 (ddd, *J* = 10.2, 6.5, 4.1 Hz, 1H), 1.82 (dt, *J* = 9.3, 4.8 Hz, 1H), 1.55 (dt, *J* = 9.3, 4.8 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.26–1.22 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.5, 158.3, 132.1, 127.3, 113.9, 60.6, 55.3, 25.6, 23.9, 16.7, 14.3 ppm. MS(APCI) *m/z* = 221 $[M+H]^+$. Anal. Calcd. for $C_{13}H_{16}O_3$: C 70.89, H 7.32. Found: C 71.09, H 7.06.

***trans*-Ethyl 2-(2-(trifluoromethyl)phenyl)cyclopropanecarboxylate (14d).**[48] Yield: 244 mg (0.945 mmol, 50%) from **2a** (500 mg, 2.27 mmol) and 1-bromo-2-(trifluoromethyl)benzene (425 mg, 1.89 mmol). Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 4.29–4.11 (m, 2H), 2.81 (s, 1H), 1.88 (dt, *J* = 9.3, 5.0 Hz, 1H), 1.63 (dt, *J* = 9.7, 5.0 Hz, 1H), 1.45–1.35 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.9, 138.1, 131.9, 130.1 (q, *J* = 30.3 Hz), 127.7, 127.0, 126.09 (q, *J* = 5.7 Hz), 124.40 (q, *J* = 273.9 Hz), 60.8, 23.7, 23.1, 15.3, 14.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ –61.0 ppm. MS(APCI) *m/z* = 259 $[M+H]^+$. Anal. Calcd. for $C_{13}H_{13}F_3O_2$: C 60.46, H 5.07. Found: C 60.86, H 4.76.

***trans*-Ethyl 2-(benzo[*d*]thiazol-4-yl)cyclopropanecarboxylate (14e).** Yield: 406 mg (1.64 mmol, 87%) from **2a** (500 mg, 2.27 mmol) and 4-bromobenzo[*d*]thiazole (404 mg, 1.89 mmol). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 4.23 (qd, *J* = 7.1, 2.5 Hz, 2H), 2.74 (ddd, *J* = 10.2, 6.5, 4.3 Hz, 1H), 2.08–1.98 (m, 1H), 1.69 (dt, *J* = 9.5, 4.7 Hz, 1H), 1.45 (ddd, *J* = 8.5, 6.5, 4.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.1, 153.8, 153.3, 134.9, 134.0, 126.4, 122.4, 122.1, 60.9, 25.9, 22.4, 15.7, 14.3 ppm. MS(APCI) *m/z* = 248 $[M+H]^+$. Anal. Calcd. for $C_{13}H_{13}NO_2S$: C 63.14, H 5.30, N 5.66, S 12.96. Found: C 62.89, H 5.53, N 5.67, S 13.36.

***trans*-Ethyl 2-(thiophen-2-yl)cyclopropanecarboxylate (14f).**[49] Yield: 222 mg (1.13 mmol, 60%) from **2a** (500 mg, 2.27 mmol) and 2-bromothiophene (308 mg, 1.89 mmol).Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 5.1 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.82 (d, *J* = 3.5 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.70 (ddd, *J* = 9.5, 6.4, 4.0 Hz, 1H), 1.93 (dt, *J* = 9.1, 4.9 Hz, 1H), 1.62 (dt, *J* = 9.5, 4.9 Hz, 1H), 1.37–1.32 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 144.2, 126.8, 123.9, 123.1, 60.8, 25.0, 21.4, 17.9, 14.2 ppm. MS(APCI) *m/z* = 151 $[M–C_2H_5O]^+$. Anal. Calcd. for $C_{10}H_{12}O_2S$: C 61.20, H 6.16, S 16.34. Found: C 61.51, H 5.79, S 16.27.

***trans*-Ethyl 2-(1-methyl-1*H*-pyrazol-4-yl)cyclopropanecarboxylate (14g).** Yield: 117 mg (0.603 mmol, 32%) from **2a** (500 mg, 2.27 mmol) and 4-bromo-1-methyl-1*H*-pyrazole (304 mg, 1.89 mmol). Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 2.2 Hz, 1H), 5.97 (d, *J* = 2.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.51 (ddd, *J* = 9.2, 6.4, 4.1 Hz, 1H), 1.98–1.89 (m, 1H), 1.52 (ddd, *J* = 9.2, 5.3, 4.1 Hz, 1H), 1.38–1.30 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 151.6, 130.7, 103.0, 60.6, 38.7, 23.2, 20.8, 16.2, 14.3 ppm. MS(APCI) *m/z* = 195 $[M+H]^+$. Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C 61.84, H 7.27, N 14.42. Found: C 61.85, H 7.49, N 14.08.

***trans*-Ethyl 2-(pyridin-4-yl)cyclopropanecarboxylate (14h).**[50] Yield: 307 mg (1.61 mmol, 85%) from **2a** (500 mg, 2.27 mmol) and 4-bromopyridine (299 mg, 1.89 mmol). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 5.1 Hz, 2H), 6.97 (d, *J* = 5.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.44 (ddd, *J* = 9.7, 6.3, 4.1 Hz, 1H), 1.96 (dt, *J* = 9.2, 5.0 Hz, 1H), 1.66 (dt, *J* = 9.7, 5.0 Hz, 1H), 1.37–1.30 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.5, 149.7, 149.5, 121.2, 61.0, 25.0, 24.7, 17.5, 14.2 ppm. MS(APCI) *m/z* = 192 $[M+H]^+$. Anal. Calcd. for $C_{11}H_{13}NO_2$: C 69.09, H 6.85, N 7.32. Found: C 69.47, H 6.46, N 7.72.

***trans*-Ethyl 2-(4-methylpyridin-3-yl)cyclopropanecarboxylate (14i).** Yield: 325 mg (1.58 mmol, 84%) from **2a** (500 mg, 2.27 mmol) and 3-bromo-4-methylpyridine (325 mg, 1.89 mmol). Orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 5.0 Hz, 1H), 8.22 (s, 1H), 7.05 (d, *J* = 5.0 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.47–2.41 (m, 1H), 2.36 (s, 3H), 1.81 (dt, *J* = 8.3, 4.8 Hz, 1H), 1.59 (dt, *J* = 9.4, 4.8 Hz, 1H), 1.37–1.32 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.4, 148.1, 147.5, 147.3, 133.7, 124.6, 60.8,

21.9, 21.6, 18.9, 14.6, 14.3 ppm. MS(APCI) *m/z* = 206 $[M+H]^+$. Anal. Calcd. for $C_{12}H_{15}NO_2$: C 70.22, H 7.37, N 6.82. Found: C 70.62, H 7.17, N 6.88.

***cis*-Ethyl 2-(4-nitrophenyl)cyclopropanecarboxylate (14j).**[47] Yield: 342 mg (1.46 mmol, 77%) from **2b** (500 mg, 2.27 mmol) and 1-bromo-4-nitrobenzene (382 mg, 1.89 mmol). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 3.91 (q, *J* = 7.2 Hz, 1H), 3.90 (q, *J* = 7.1 Hz, 1H), 2.62 (q, *J* = 8.4 Hz, 1H), 2.25–2.14 (m, 1H), 1.76 (dt, *J* = 7.5, 5.5 Hz, 1H), 1.46 (td, *J* = 8.4, 5.3 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 146.8, 144.6, 130.2, 123.2, 60.7, 25.3, 22.5, 14.2, 12.0 ppm. MS(APCI) *m/z* = 236 $[M+H]^+$. Anal. Calcd. for $C_{12}H_{13}NO_4$: C 61.27, H 5.57, N 5.95. Found: C 61.64, H 5.87, N 5.60.

***trans*-Benzyl 2-(4-formylphenyl)cyclopropanecarboxylate (14k).** Yield: 219 mg (0.782 mmol, 53%) from **3a** (500 mg, 1.77 mmol) and 4-bromobenzaldehyde (273 mg, 1.48 mmol). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.41–7.31 (m, 5H), 7.23 (d, *J* = 7.8 Hz, 2H), 5.17 (s, 2H), 2.66–2.58 (m, 1H), 2.06 (dt, *J* = 9.2, 4.9 Hz, 1H), 1.73 (dt, *J* = 9.8, 4.9 Hz, 1H), 1.44–1.37 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 191.7, 172.7, 147.5, 135.8, 135.1, 130.1, 128.8, 128.5, 128.4, 126.8, 67.0, 26.4, 25.0, 18.0 ppm. MS(APCI) *m/z* = 281 $[M+H]^+$. Anal. Calcd. for $C_{18}H_{16}O_3$: C 77.12, H 5.75. Found: C 77.03, H 6.14.

***trans*-*tert*-Butyl 2-(4-nitrophenyl)cyclopropanecarboxylate (14l).** Yield: 230 mg (0.874 mmol, 52%) from **4a** (500 mg, 2.02 mmol) and 1-bromo-4-nitrobenzene (339 mg, 1.68 mmol). Yellow solid, mp = 72–74 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 2.58–2.52 (m, 1H), 2.01 (dt, *J* = 9.1, 4.9 Hz, 1H), 1.51 (dt, *J* = 9.5, 4.9 Hz, 1H), 1.47–1.35 (m, 10H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 171.0, 148.8, 145.9, 127.0, 123.4, 80.5, 27.7, 26.0, 24.9, 17.8 ppm. MS(APCI) *m/z* = 286 $[M+Na]^+$. Anal. Calcd. for $C_{14}H_{17}NO_4$: C 63.87, H 6.51, N 5.32. Found: C 64.22, H 6.49, N 5.47

***trans*-1-Nitro-4-(2-(trifluoromethyl)cyclopropyl)benzene (14m).**[51] Yield: 415 mg (1.80 mmol, 93%) from **5a** (500 mg, 2.31 mmol) and 1-bromo-4-nitrobenzene (390 mg, 1.93 mmol). Beige solid, mp = 54–57 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 2.62 (dt, *J* = 10.1, 5.5 Hz, 1H), 2.49–2.41 (m, 1H), 1.48 (dt, *J* = 9.5, 5.7 Hz, 1H), 1.43–1.37 (m, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 147.5, 146.1, 127.4, 125.9 (q, *J* = 271.1 Hz), 123.5, 23.0 (q, *J* = 36.3 Hz), 18.9, 12.3 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ –65.7 ppm. Anal. Calcd. for $C_{10}H_8F_3NO_2$: C 51.96, H 3.49, N 6.06. Found: C 52.23, H 3.28, N 6.25.

(*Z*)-*tert*-Butyl (3-(4-methoxyphenyl)prop-1-en-1-yl)carbamate (15). Yield: 90 mg (0.34 mmol, 36%) from **11b** (250 mg, 0.95 mmol). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.4 Hz, 2H, 2′- and 6′-$C_6\underline{H}_4$), 6.84 (d, *J* = 8.4 Hz, 2H, 3′- and 5′-$C_6\underline{H}_4$), 6.60–6.50 (m, 1H, 1-C$\underline{H}$), 6.33–6.19 (m, 1H, N$\underline{H}$), 4.86–4.68 (m, 1H, 2-C$\underline{H}$), 3.79 (s, 3H, OC$\underline{H}_3$), 3.26 (d, *J* = 7.5 Hz, 2H, 3-C$\underline{H}_2$), 1.48 (s, 9H, C(C$\underline{H}_3$)$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2 (4′-$\underline{C}_6H_4$), 152.9 ($\underline{C}$=O), 132.0 (1′-$\underline{C}_6H_4$), 129.2 (2′- and 6′-$\underline{C}_6H_4$), 123.2 (1-$\underline{C}$H), 114.1 (3′- and 5′-$\underline{C}_6H_4$), 106.6 (2-$\underline{C}$H), 80.7 ($\underline{C}(CH_3)_3$), 55.4 (O$\underline{C}H_3$), 30.8 (3-$\underline{C}H_2$), 28.4 (C($\underline{C}H_3$)$_3$) ppm. MS(APCI) *m/z* = 264 $[M+H]^+$. Anal. Calcd. for $C_{15}H_{21}NO_3$: C 68.42, H 8.04, N 5.32. Found: C 68.11, H 7.77, N 4.96.

***trans*-2-(4-Nitrophenyl)cyclopropanecarbonitrile (14n).** A reaction vessel containing dioxane (10 mL) and H_2O (1 mL) was degased and backfilled with Ar. Then potassium (*trans*-2-cyanocyclopropyl)trifluoroborate (**6a**) (500 mg, 2.89 mmol), 1-bromo-4-nitrobenzene (487 mg, 2.41 mmol), KOAc (851 mg, 8.68 mmol), and Pd(dppf)Cl_2 (52.7 mg, 0.072 mmol) were added. The two–phase reaction mixture was refluxed under Ar with vigorous stirring for 12 h. After cooling to rt, the layers were separated, and the organic phase was concentrated under reduced pressure. The obtained crude products were purified by HPLC (gradient H_2O–MeCN as eluent). Yield: 110 mg, 0.585 mmol, 24%. Yellow solid, mp = 86–89 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 2.95–2.88 (m, 1H), 2.24 (dt, *J* = 9.3, 5.4 Hz, 1H), 1.75 (dt, *J* = 9.3, 5.5 Hz, 1H), 1.61 (dt, *J* = 9.3, 6.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 146.7, 146.3, 127.4, 123.5, 120.9, 23.6, 16.1, 7.1 ppm. Anal. Calcd. for $C_{10}H_8N_2O_2$: C 63.83, H 4.29, N 14.89. Found: C 63.43, H 4.48, N 15.14.

General procedure for the preparation of the compounds 16. K_3PO_4 (1.44 g, 6.81 mmol) solution in H_2O (6.8 mL), potassium (*trans*-2-(ethoxycarbonyl)cyclopropyl)trifluoroborate (**2a**) (500 mg, 2.27 mmol), $Cu(OAc)_2$ (495 mg, 2.72 mmol) and phenantroline (490 mg, 2.72 mmol) were added to the solution of the corresponding *NH*-containing reagent (2.27 mmol) in 1,2-dichloroethane (5 mL)–H_2O (0.5 mL) solvent system. The reaction mixture was refluxed for 8 h under air and then cooled to rt. The organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The obtained crude product was purified by column chromatography (for **16a**, gradient hexane–*t*-BuOMe as eluent) or HPLC (for **16b**, gradient H_2O–MeCN as eluent).

***trans*-Benzyl 2-(1*H*-imidazol-1-yl)cyclopropanecarboxylate (16a).** Yield: 286 mg (1.18 mmol, 52%) from **2a** (500 mg, 2.27 mmol) and 1*H*-imidazole (154 mg, 2.27 mmol). Yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.76 (s, 1H, 2′-C$\underline{H}$), 7.42–7.32 (m, 5H, $C_6\underline{H}_5$), 7.24 (s, 1H, 5′-C$\underline{H}$), 6.88 (s, 1H, 4′-C$\underline{H}$), 5.18 (d, *J* = 12.4 Hz, 1H, C$\underline{H}$HC$_6$H$_5$), 5.13 (d, *J* = 12.4 Hz, 1H, CH$\underline{H}$C$_6$H$_5$), 4.07–3.95 (m, 1H, 2-C$\underline{H}$), 2.29 (ddd, *J* = 9.2, 5.9, 3.1 Hz, 1H, 1-C$\underline{H}$), 1.83–1.73 (m, 1H, 3-C$\underline{H}$H), 1.52 (dd, *J* = 8.2, 5.9 Hz, 1H, 3-CH$\underline{H}$) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 170.9, 137.2, 135.8, 128.5 (2C), 128.1, 128.1, 119.1, 66.2, 35.4, 21.5, 14.6 ppm. MS(APCI) *m/z* = 243 $[M+H]^+$. Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C 69.41, H 5.82, N 11.56. Found: C 69.34, H 6.18, N 11.67.

***trans*-Ethyl 2-(1*H*-indazol-1-yl)cyclopropanecarboxylate (16b).** Yield: 313 mg (1.36 mmol, 60%) from **2a** (500 mg, 2.27 mmol) and 1*H*-indazole (150 mg, 2.27 mmol). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H),

7.52 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.08 (ddd, *J* = 7.7, 4.9, 2.8 Hz, 1H), 2.33 (ddd, *J* = 9.1, 5.9, 2.8 Hz, 1H), 1.95–1.89 (m, 1H), 1.79 (dt, *J* = 7.7, 5.9 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.0, 140.6, 133.7, 126.8, 124.6, 121.4, 121.3, 109.3, 61.3, 37.5, 22.0, 15.0, 14.4 ppm. MS(APCI) *m/z* = 231 $[M+H]^+$. Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C 67.81, H 6.13, N 12.17. Found: C 67.58, H 5.85, N 12.53.

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FULL PAPER

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