Regioselective Boracarboxylation of α-Substituted Vinyl Arenes

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ABSTRACT: An experimental study of the effect of CO_2 pressure on the copper(I)-catalyzed boracarboxylation of α-substituted vinyl arenes is reported. Preliminary experiments using ICyCuCl catalyst (ICy = 1,3-bis(cyclohexyl)imidazol-2-ylidine) showed that boracarboxylation of *tert*-butylstyrene can be achieved in 30 minutes at modest CO_2 pressure (3-6 atm) as opposed to 24-36 hours at atmospheric pressure. Due to increased substrate sterics that allowed catalytic reduction of CO_2 to compete kinetically, boracarboxylation of *α*-methyl styrene, even at modest CO_2 pressures, gave poor yields. Low CO_2 pressure and SIMesCuCl catalyst (SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-4,5-dihydro-2-ylidine) provided moderate to good yields of an electronically and sterically diverse group of quaternary α-carboxylic acid products featuring a β-boronic ester functional group.

INTRODUCTION

Carbon dioxide is a useful C1 synthon that is utilized in a variety of organometallic transformations such as C-H functionalization, carboxylation, esterification, alcohol etherification, and N-alkylation.[1,2] Synthesis of quaternary centers via carboxylation,[3] to provide synthetically and medicinally important carboxylic acids,[4] is particularly difficult due to the sterically congested nature of the organometallic intermediate. Classic synthetic methods to access such centers using CO_2, such as Grignard carboxylation, require harsh conditions that limit functional group tolerance and reaction efficiency. Consequently, methods to deliver such α-quaternary carboxylic acids utilizing transition metal catalysis have been identified as highly desirable.[5]

Method development over the last decade has focused on preparation of α-quaternary carboxylic acids using late transition metal catalysis. Tan reported a robust rhodium-catalyzed asymmetric hydroformylation/oxidation of simple 2-substituted allylic alcohols,[6] while Stoltz reported an elegant iridium-catalyzed asymmetric allylic functionalization using a C1 source (Figure 1A).[7] Palladium, nickel and copper-catalyzed carboborylative alkene difunctionalization,[8] for example boracyanation and boraarylation of 2-substituted dienes (Figure 1B),[9] provides attractive products that feature a synthetically valuable organoboron functional group as well as a new functionalized quaternary carbon center. Copper-catalyzed heteroelement-(bora and sila)-carboxylation offers similarly attractive functional group rich products while using CO_2 as the electrophilic reaction partner; however, such transformations with alkyne,[10] imine,[11] allene,[12] and vinyl arene lacking vinylic substitution[13] remain underdeveloped and consequently

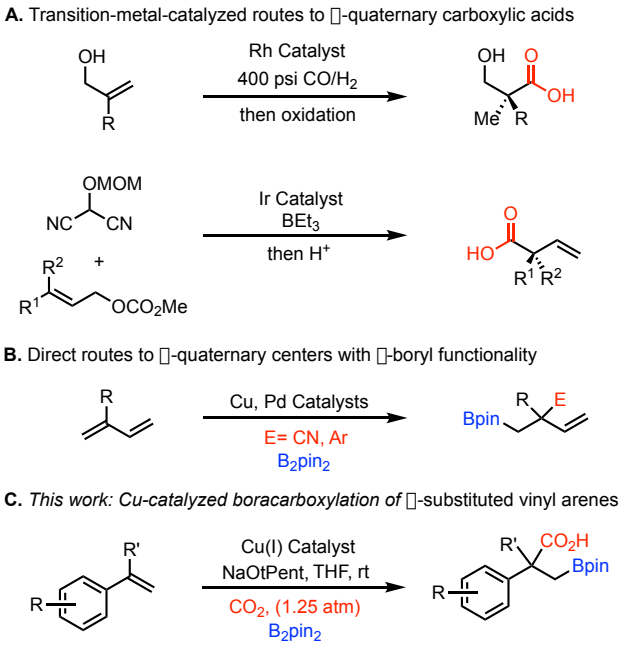


Figure 1. Transition-metal-catalyzed strategies to access synthetically useful α-quaternary carboxylic acids and derivatives.

underutilized. In 2016, we presented a single example of α-methyl-styrene boracarboxylation, albeit in low yield, which provided motivation to improve and broaden the reaction to access useful α-quaternary carboxylic acids bearing a β-boronic ester functional group (Figure 1C).[13a]

We published experimental and computational studies of well-defined copper complex reactivity with CO_2 associated with boracarboxylation in 2021.[14,15] The studies confirmed

that the carboxylation step was the turnover limiting step and provided evidence for divergent carboxylation pathways based on vinyl arene electronic structure. While stoichiometric carboxylation of α-methyl-styrene was not studied, we reasoned that the efficiency of catalytic boracarboxylation of sterically hindered vinyl arenes would benefit from increased CO_2 pressure. Here, we present CO_2 pressure effects on catalytic boracarboxylation that provide the needed insights to realize new boracarboxylation methods for α-substituted vinyl arenes.

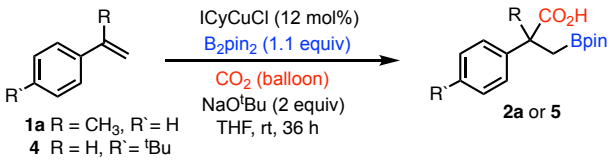
RESULTS AND DISCUSSION

We commenced our CO_2 pressure studies by first building a medium pressure (~12 atm) gas manifold with four separate reaction ports (Figure S-1). Our original boracarboxylation conditions using 12 mol% ICyCuCl, 1.1 equiv B_2pin_2, and a balloon of CO_2 for 36 hours at room temperature in THF led to 24 % yield of boracarboxylated product **2a** (Table 1, Entry 1), as well as trace amounts of formal hydroboration product (**3a**) from α-methyl-styrene (**1a**).[13a] Increased CO_2 pressure (3 atm) led to no boracarboxylated product **2a** with nearly full conversion of substrate **1a** (Entry 2). Even a super-stoichiometric amount of B_2pin_2 (2.0 equiv) led to inferior results relative to our original conditions (Entry 3-4).

These results contradicted our expectations, prompting the evaluation of increased CO_2 pressure on an unsubstituted vinyl arene (*p*-tert-butylstyrene, **4**) boracarboxylation reaction. Our original catalytic conditions with a CO_2 balloon afforded 86% yield of boracarboxylated product **5** (Table 1, Entry 5). Higher CO_2 pressure (3 atm) led to a significant reduction in boracarboxylation yield and conversion, which could be recovered by doubling B_2pin_2 loading (Table 1, Entry 6-7). Using 3 atm CO_2 pressure and 2.0 equiv B_2pin_2, comparable yields to those obtained at 1 atm CO_2 were obtained after only 30 min, which is consistent with a turnover-limiting step that is dependent on CO_2 concentration (Entry 8).

The differing reactivity of **1a** and **4** could not be readily explained initially. We noted incomplete conversion of sterically hindered **1a** at higher CO_2 pressures, which suggested that B_2pin_2 was consumed via an alternate pathway that did not involve **1a**. The accepted boracarboxylation catalytic mechanism (Figure 2) suggests that such a side reaction could result from competitive CO_2 reduction and alkene insertion at a copper-boryl intermediate (ie., [Cu]Bpin).[16] A consequence of this competition would be the CO_2 reduction byproduct, pinB-O-Bpin, which has a characteristic ^{11}B chemical shift around 22 ppm in $CDCl_3$. Indeed, the crude ^{11}B NMR spectrum for boracarboxylation of **1a** (Table 1, Entry 3-4) showed only minimal amounts of product **2a** (33 ppm), unreacted B_2pin_2 (30.6 ppm), and large amounts of pinB-O-Bpin (Figure 3A-B). Conversely, ^{11}B NMR analysis of boracarboxylation of vinyl arene **4** (Table 1, Entry 6) showed predominately product **5**, also observed at 33 ppm, and comparatively less pinB-O-Bpin (Figure 3C).

Table 1. Effect of CO_2 Pressure on Boracarboxylation of Vinyl Arenes 1a and 4[a]



Entry	Substrate	Variation from std. cond.	Yield (%)[b] **2a**|**5**	Convn (%)[b]
1	1a	None	24	89
2	1a	CO_2 (3 atm)	0	94
3	1a	CO_2 (3 atm), B_2pin_2 (2.0 equiv)	15	66
4	1a	CO_2 (1 atm), B_2pin_2 (2.0 equiv)	21	76
5	4	None	86	>99
6	4	CO_2 (3 atm)	52	66
7	4	CO_2 (3 atm), B_2pin_2 (2.0 equiv)	78	86
8	4	CO_2 (3 atm), B_2pin_2 (2.0 equiv), 30 min	81	89

[a] Reactions performed on 0.25 mmol scale with respect to vinyl arene and quenched with 1M HCl_{aq}. [b] Yield determined by ^1H NMR integration using 20 mol% mesitylene as an internal standard.

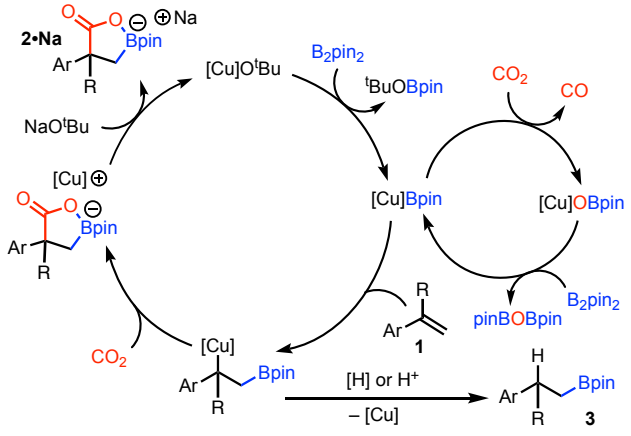


Figure 2. Catalytic cycle for copper-catalyzed boracarboxylation with competitive CO_2 reduction and hydro/protoboration pathways.

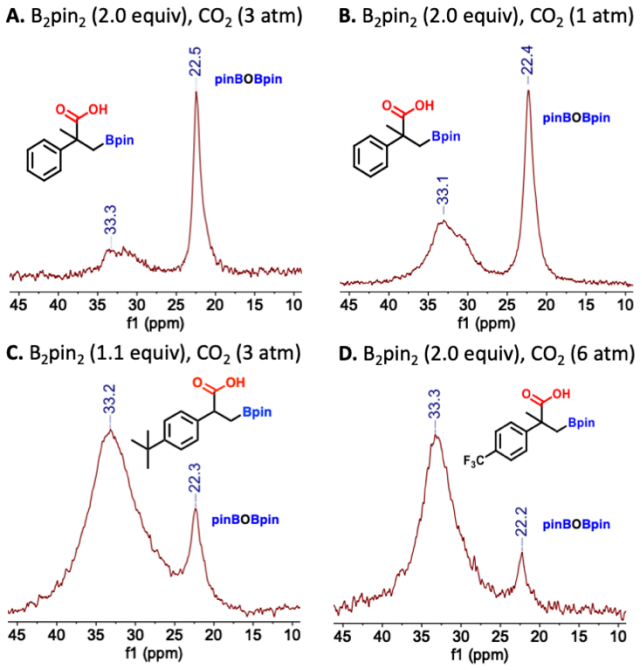
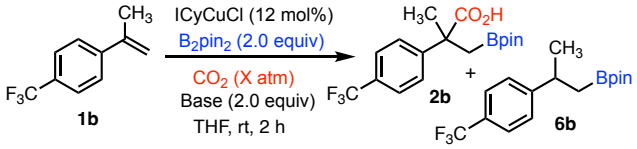


Figure 3. ^{11}B NMR spectra of selected crude boracarboxylation reactions in $CDCl_3$. (Note: unreacted B_2pin_2 at 30.6 ppm)

The combined observations of boracarboxylation product yield, substrate conversion, and CO_2 reduction byproduct pinB-O-Bpin under different pressures of CO_2 suggested that modest change in the steric profile from **4** to **1a** impacts the relative rates of CO_2 and alkene insertion at [Cu]Bpin (cf., Table 2). Unsubstituted vinyl arene **4** appears to insert faster than CO_2, so subsequent turnover limiting carboxylation can be accelerated by increased CO_2 pressure. α-Methylstyrene **1a** appears to insert slower than CO_2, so increased CO_2 pressure leads to faster catalytic CO_2 reduction and consumption of reductant B_2pin_2, but not faster, more productive boracarboxylation. The emerging qualitative picture indicates that for an alkene to be a suitable substrate it must, at a minimum, outcompete CO_2 for insertion into the [Cu]Bpin intermediate.

Sadighi demonstrated experimentally, and Marder later confirmed computationally, that electron deficient alkenes insert faster into NHCCu-boryl complexes.[17] Consequently, we prepared α-methyl-*p*-trifluoromethylstyrene (**1b**) and subjected it to boracarboxylation for 2 hours at both 3 and 6 atm CO_2. Gratifyingly, only small amounts of pinB-O-Bpin were evident from crude ^{11}B NMR spectra (cf., Figure 3D), and excellent NMR yields (>80%) with quantitative substrate conversion were obtained (Table 2, Entry 1-2). Quantifiable amounts of formal hydroboration product **3b**, generally 5-10%, were also observed. This suggested that while alkene insertion outcompetes CO_2 reduction, the more sterically hindered, electron deficient Cu-benzyl intermediate does not carboxylate efficiently, as expected by our recent experimental/computational studies,[14b] allowing hydro/proto-decupration or other decomposition pathway to compete kinetically. This is further emphasized by the steep decline in the yield of **2b** when CO_2 pressure is reduced to 1.25 atm (Entry 3).

Table 2. Effect of CO_2 pressure and base on boracarboxylation of electron deficient 1b[a]



Entry	Base	pCO_2 (atm)	Yield (%)[b] 2b	6b	Convn (%)[b]
1	NaO^{t}Bu	6	80	10	>99
2		3	84	8	>99
3		1.25	24	8	>99
4	KO^{t}Bu	6	57	14	>99
5	LiO^{t}Bu	6	<5	<5	>99
6	NaOMe	6	65	<5	>99
7	NaOEt	6	90	9	>99
8		3	82	9	>99
9		1.25	58	14	>99
10	NaO^{i}Pr	6	32	26	>99
11	NaOTMS	6	0	83	>99
12	NaO^{t}Pent	6	71	6	>99
13[c]		6	85	12	>99
14		3	71	20	>99
15		1.25	67	24	>99

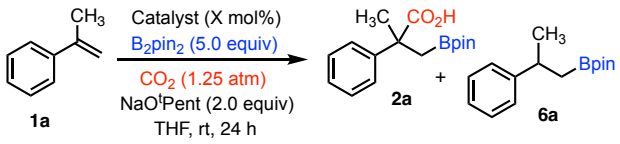
[a] Reactions performed on 0.25 mmol scale with respect to vinyl arene and quenched with 1M HCl_{aq}. [b] Yield and conversion determined by ^{1}H NMR integration using 20 mol% mesitylene as an internal standard. [c] 3 hr.

Bases were screened for boracarboxylation of electron-deficient **1b** at high CO_2 pressure (6 atm). For MO^{t}Bu bases, potassium and lithium were inferior cations relative to sodium (Table 2, Entry 4-5). All other sodium alkoxide bases, both sterically small and large, gave yields of **2b** between 32-90% while NaOTMS gave predominately formal hydroboration product **3b**. Yields of **2b** with NaOEt (90% after 2 hr, Entry 7) and NaO^{t}Pent (85% after 3 hr, Entry 13) were comparable, so each was also screened at lower pressures. The small ethoxide base leads to lower yields from 6-to-1.25 atm CO_2 (Entry 7-9). The large tert-pentoxide base leads to a more modest drop in yield and significant amounts (>20%) of side product **3b** at lower CO_2 pressures.

Next, boracarboxylation reactions were carried out for 24 hours with competent alkoxide bases at low CO_2 pressure

(1.25 atm), due to the competitive CO_2 reduction illustrated earlier, using weakly electron-deficient α-methyl-*p*-fluorostyene (**1g**) and electron-neutral **1a**. Yields around 30% or less were obtained even with 5.0 equiv of B_2pin_2 (cf., Table 3, Entry 1). Unfortunately, ICyCuCl catalyst with the reaction condition variations discussed above appear to allow efficient reactivity with only strongly electron-deficient **1b**. This setback prompted us to screen a selection of isolated and in situ-generated NHC-copper catalysts at high B_2pin_2 loading (5.0 equiv) to compensate for catalytic inefficiency due to competitive CO_2 reduction. Less sterically bulky IMesCuCl precatalyst gave 50% yield of **2a** but inefficient conversion. Further modification to the more donating SIMesCuCl precatalyst, gave **2a** in 83% yield. In situ preparation of both IMesCuCl and SIMesCuCl from the imidazolium salt, base, and CuCl, provided **2a** in <5% and 95% yield respectively, while the bulky SIPrCuCl precatalyst, also prepared in situ, did not give identifiable product (Entry 4-6).

Table 3. Effect of Catalyst on Boracarboxylation of Electron Neutral 1a[a]

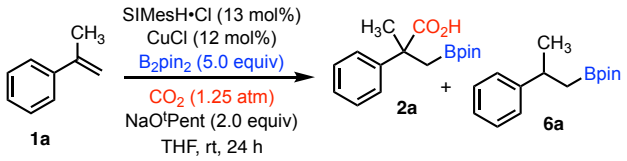


Entry	Catalyst	Yield (%)[b]		Convn
		2a	6a	(%)[b]
1	ICyCuCl (13 mol%)	31	<5	>99
2	IMesCuCl (13 mol%)	50	0	72
3	SIMesCuCl	83	0	90
4	IMesH•Cl (13 mol%) CuCl (12 mol%)	<5	0	>99
5	SIMesH•Cl (13 mol%) CuCl (12 mol%)	95	0	>99
6	SIPrH•Cl (13 mol%) CuCl (12 mol%)	0	37	36

[a] Reactions performed on 0.25 mmol scale with respect to vinyl arene and quenched with 1M HCl_{aq}. [b] Yield and conversion, determined by ^1H NMR integration using 20 mol% mesitylene as an internal standard.

A final round of **1a** boracarboxylation optimization, using in situ generated SIMesCuCl precatalyst, was carried out (Table 4). Replacement of NaO^{t}Pent with NaOEt and NaO^{t}Bu led to diminished yields although minimally so in the latter case (Entry 2-3), while removal of base led to no characterizable products (Entry 4). Increased loading of B_2pin_2 (3 equiv) or reduced B_2pin_2 loading with increased loading of **1a** led to almost exclusive formal hydroboration product **3a** (Entry 5-6). The catalytic reaction was unaffected by increased base loading (3 equiv) and temperature (45 °C) (Entry 7-8). Variation of CO_2 pressure from 1.25 atm led to lower yields and incomplete conversion collectively (Entry 9-11). Addition of PPh_3 as a secondary ligand, which was previously used by us to improve catalyst efficiency and substrate scope,[13b] led to a modest reduction of yield (Entry 11). A control reaction showed that ancillary ligand precursor SIMesH•Cl is necessary for catalytic turnover (Entry 13).

Table 4. Boracarboxylation Reaction Optimization with Electron Neutral 1a [a]



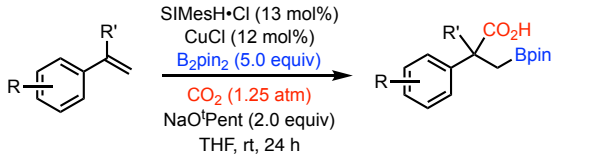
Entry	Variation from Standard Conditions	Yield (%)[b]		Convn
		2a	6a	(%)[b]
1	None	95	0	>99
2	NaOEt instead of NaO^{t}Pent	59	6	93
3	NaO^{t}Bu instead of NaO^{t}Pent	85	<5	>99
4	No NaO^{t}Pent	0	0	97
5	3.0 equiv B_2pin_2	<5	15	>99
6	1.0 equiv B_2pin_2, 3.0 equiv **1a**	0	20	ND
7	3.0 equiv NaO^{t}Pent	85	<5	>99
8	45 °C	87	<5	>99
9	CO_2 (balloon)	60	7	93
10	CO_2 (3 atm)	36	0	68
11	CO_2 (6 atm)	55	0	72
12	PPh_3 additive (5 mol%)	68	13	92
13	No SIMesH•Cl	0	<5	80

[a] Reactions performed on 0.25 mmol scale with respect to vinyl arene and quenched with 1M HCl_{aq}. [b] Yield and conversion determined by ^1H NMR integration using 20 mol% mesitylene as an internal standard.

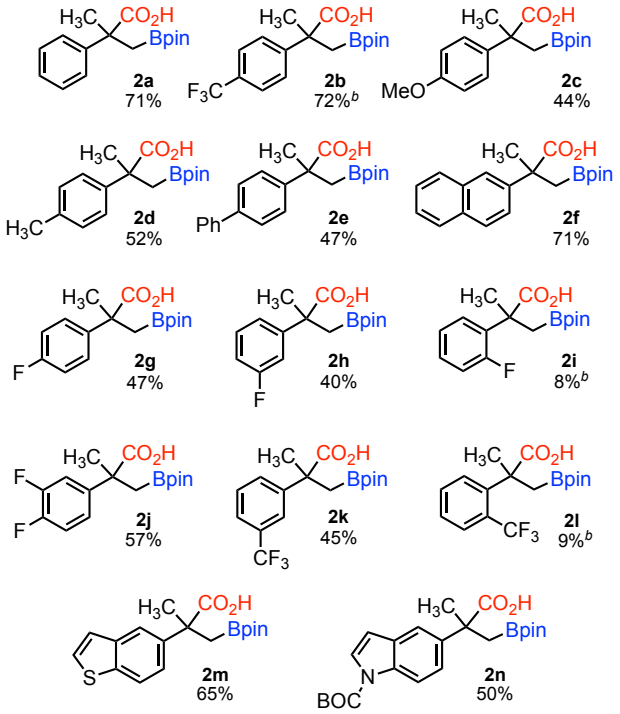
The optimized catalyst system featuring in situ generated SIMesCuCl, CO_2 (1.25 atm), B_2pin_2 (5.0 equiv), NaOtPent (2.0 equiv) in THF at room temperature was used to evaluate the substrate scope as related to steric/electronic modification of the arene ring and α-position (Table 5). Boracarboxylation of α-methyl styrene provided 71% isolated yield (95% by ^1H NMR analysis) as opposed to 24% crude yield under our originally published reaction conditions. A good isolated yield (72%) of electron-deficient *p*-trifluoromethyl-substituted **2b** and a moderate isolated yield (44%) of electron-rich *p*-methoxy-substituted **2c** was obtained. Other electron neutral substrates (**1d-f**) were similarly reactive, affording moderate to good yields of boracarboxylated products. Weakly (*p*- and *m*-F; **2g-h**), moderately (3,4-difluoro; **2j**), and strongly (m-CF_3; **2k**) electron deficient products were also isolated in moderate-to-good

yields. Not surprisingly given the apparent sensitivity of insertion and carboxylation rates to the steric characteristics of both the alkene substrate and the subsequent organocopper intermediate, the reaction was quite sensitive to *o*-F (**2i**) and *o*-CF_3 (**2l**) substitution affording crude products in less than 10% yield. Electron rich heteroarene products, with benzothiophene (**2m**) and indole (**2n**) moieties, were obtained in isolated yields of 65% and 50%, respectively.

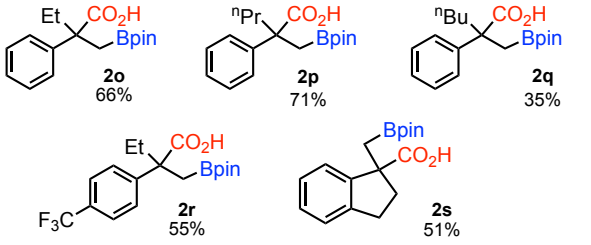
Table 5. Boracarboxylation Reaction Scope[a]



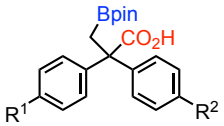
aryl substitution



α-alkyl substitution



α-aryl substitution



2t[b]	R^1=R^2= H	8%
2u[b]	R^1= H R^2 = OMe	14%
2v[b]	R^1= OMe R^2= OMe	5%
2w[b]	R^1= OMe R^2= CF_3	11%
2x	R^1= H R^2= CF_3	20 %
2y	R^1= CF_3 R^2= CF_3	0%

[a] Reactions performed on 0.25 mmol scale with respect to vinyl arene and quenched with 1M HCl_{aq}. All yields are isolated unless otherwise specified. [b] Crude yield due to remaining impurities or product decomposition.

Substitution at the α-position was also generally tolerated if the substituting group was not too bulky. Ethyl and n-propyl substitution afforded products **2o-p** in good yields (55-71%), but a significant drop in yield (35%) was obtained for n-butyl substituted product **2q**. Larger groups, such as iso-propyl, were not tolerated, affording no isolable boracarboxylation product. The exocyclic alkene of 1-methyleneindane was boracarboxylated to give **2s** in 51% isolated yield. Finally, we assessed 1,1-diarylethylene substrates (**2t-y**). Unsurprisingly, these substrates proceeded poorly under the optimized catalytic conditions presumably due to the additional steric bulk of the second aryl ring and/or radical decomposition of the organocopper intermediate.[18] The products were also exceedingly difficult to isolate cleanly with significant product decomposition observed for **2t-2w**. Continued method development work will be necessary to identify a suitable steric and electronic environment at the copper center to allow better access to these 1,1-diarylethane boracarboxylated products.

CONCLUSIONS

We have presented here the impacts of increased CO_2 pressure on copper-catalyzed boracarboxylation of vinyl arene and α-methylstyrene. The results revealed a complex interplay between kinetically competitive insertion reactions during which the pressure of CO_2 can have both positive and negative impacts on catalytic turnover. These studies led us to the unexpected realization that low CO_2 concentration was critical to achieve relatively efficient boracarboxylation on more sterically demanding substrates such as α-methylstyrene. A diverse substrate scope that includes synthetically useful heteroarenes highlights the potential utility of this mild catalytic method to provide functional group rich, α-quaternary carboxylic acids. Future in-depth kinetics studies are planned to better understand the interplay of CO_2 reduction and alkene boracarboxylation pathways under different catalytic regimes and realize continued systematic alkene boracarboxylation substrate scope expansion.

EXPERIMENTAL SECTION

General Considerations: All air and moisture sensitive experiments were set up in a nitrogen-filled MBraun 200B dual-port glovebox, and before each experiment the glovebox atmosphere was tested using diethyl zinc. The boracarboxylation reactions were performed in Ace Glass 35ml double-walled two-neck pressure tubes. The pressure tubes, miscellaneous glassware, and unused magnetic stir bars were dried in an oven at 180 °C for at least 24 hours. All glassware used in the glovebox was dried for at least 24h in the 180 °C oven. An in-house built multi-reaction-port gas manifold (Figure S-1) was used to perform reactions at modest CO_2 pressures (less than 6 atm). *All reactions carried out with CO_2 pressure above atmospheric were performed behind a blast shield.* All solvent were dried on a Glass Contour solvent purification system, and further stored over activated 4Å mol sieves. All liquids were degassed via freeze/pump/thaw cycles prior to use. Substrates **1a**,

1g and **1t** were obtained from commercial sources and used as received. Substrates **1b-f, 1h-l, 1o-s, 1u-v** were prepared through Wittig reactions from the respective ketone; **1b** and **1h** were distilled prior to use.[19] Substrates **1m** and **1n** were prepared through Suzuki cross-coupling reactions.[20] Substrates **1w-y** were prepared according to literature precedent.[21] Spectroscopic characterization of boracarboxylated products **2a-b** matched the original report.[13a] $CDCl_3$ was purchased from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded on either a 400 MHz Agilent or 600 MHz Agilent NMR spectrometer. ^1H, ^{13}C, ^{11}B, and ^{19}F NMR experiments were acquired in $CDCl_3$ using tetramethylsilane as a reference in quartz NMR tubes. ^{11}B NMR resonances were referenced relative to an external $BF_3{\cdot}OEt_2$ standard. High-resolution mass spectra were recorded on a Thermo Fisher Scientific Q-Exactive Mass Spectrometer with samples dissolved in acetonitrile.

Synthesis of substrates 2b-2x: In a nitrogen filled glovebox, a 20 ml scintillation vial was charged with SIMesHCl (10.3 mg, 0.0275 mmol, 13 mol%), NaO^{t}Pent (55.0 mg, 0.50 mmol, 2.0 equiv) and anhydrous, degassed THF (2 ml). The vial was then capped and stirred for 15 minutes to afford a clear, colorless solution. This solution was then transferred using a 9" glass pipet to a separate 20 ml scintillation vial containing CuCl (2.7 mg, 0.025 mmol, 12 mol%) and stirred for 1 hour. To a 35 ml double-walled two neck glass pressure tube, B_2pin_2 (315.0 mg, 1.25 mmol, 5.0 eq), vinyl arene (0.25 mmol, 1.0 eq) and anhydrous, degassed THF (2 ml) were added then sealed with a fresh rubber septum. The catalyst solution was then loaded into a 5.0 ml Hamilton gas-tight syringe, and then the needle was plugged using a rubber septum. The pressure tube and catalyst solution were then removed from the glovebox and swiftly connected to the gas manifold under a continuous flow of Ar gas. Once attached, the tube was purged with Ar gas for additional 2 minutes, at which point the catalyst solution was added via the sidearm. The tube was purged with CO_2 for 2 minutes, brought to desired CO_2 pressure, isolated from the main manifold, and stirred at room temperature for 24 hours. Upon completion, the crude mixture was added to a 60 ml separatory funnel containing 20 ml of 1M HCl, and then extracted with CH_2Cl_2 (3 x 4 ml) and collected in a 20 ml scintillation vial. The combined organic extracts were concentrated under vacuum, and mesitylene (20 mol%) was added to the crude reaction mixture. The mixture was then dissolved in 1 ml of $CDCl_3$ and analyzed by ^1H NMR spectroscopy to obtain an NMR yield. Subsequently, the crude mixture was taken up in Et_2O (10 ml) then extracted with saturated $NaHCO_3$ (4 x 3 ml). The aqueous layer was acidified by slow addition of 12M HCl (5 ml) then extracted with CH_2Cl_2 (4 x 3 ml). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo to afford boracarboxylated product, which could be further purified by recrystallization from either heptane or heptane/toluene (1:1 v/v).

2b 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(4-trifluoromethylphenyl) propionic acid. White solid, (64 mg, 72% crude yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (m, 4H), 1.70 (s, 3H), 1.60 (d, *J* = 15.7 Hz, 1H), 1.46 (d, *J* = 15.7 Hz, 1H), 1.10 (s, 6H), 1.09 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 182.1, 148.6, 129.0 (q, *J* = 32.5 Hz), 126.6, 125.5, 125.2, 123.9 (broad q, J=270.7 Hz), 83.3, 48.0, 25.0, 24.5, 23.1 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI): m/z calc. for $C_{17}H_{22}BF_3O_4$ $[M-H]^-$: 358.1524, found 358.1530.

2c 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(4-methoxyphenyl) propionic acid. White solid, (35 mg isolated, 44% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.28 (m, 2H), 6.87 – 6.79 (m, 2H), 3.77 (s, 3H), 1.66 (s, 3H), 1.60 (d, *J* = 15.7 Hz, 1H), 1.42 (d, *J* = 15.6 Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 182.2, 158.3, 136.8, 127.1, 113.6, 83.2, 55.2, 47.1, 25.3, 24.6, 24.6, 23.2 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.2. HRMS (ESI): m/z calc. for $C_{17}H_{25}BF_3O_5$ $[M-H]^-$: 320.1756, found 320.1756.

2d 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(4-methylphenyl) propionic acid. Pale yellow solid, (38 mg isolated, 52% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.29 (s, 3H), 1.66 (s, 3H), 1.61 (d, *J* = 15.7 Hz, 1H), 1.40 (d, *J* = 15.7 Hz, 1H), 1.14 (s, 6H), 1.12 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$): δ 182.7, 141.9, 136.2, 128.9, 125.8, 83.1, 47.5, 25.3, 24.6, 24.6, 23.2 (broad due to quadrupolar broadening from ^{11}B), 20.9. ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.4.HRMS (ESI): m/z calc. for $C_{17}H_{25}BO_4$ $[M-H]^-$: 303.1773, found 303.1778.

2e 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-biphenyl propionic acid. White solid, (43 mg isolated, 47% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.50 (m, 4H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.41 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.35 – 7.27 (m, 1H), 1.73 (s, 3H), 1.66 (d, *J* = 15.7 Hz, 1H), 1.49 (d, *J* = 15.7 Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 181.3, 143.8, 140.7, 139.6, 128.7, 127.2, 127.0, 127.0, 126.4, 83.3, 47.7, 25.5, 24.6, 24.6, 23.1 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.9. HRMS (ESI): m/z calc. for $C_{22}H_{27}BO_4$ $[M-H]^-$: 366.1963, found 366.1967

2f 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(2-naphtyl) propionic acid. White solid, (60 mg isolated, 71% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 – 7.74 (m, 4H), 7.52 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.46 – 7.39 (m, 2H), 1.79 (s, 3H), 1.73 (d, *J* = 15.7 Hz, 1H), 1.53 (d, *J* = 15.7 Hz, 1H), 1.10 (s, 6H), 1.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 182.8, 142.2, 133.2, 132.2, 128.1, 127.9, 127.4, 126.0, 125.8, 124.7, 124.3, 83.2, 48.1, 25.2, 24.6, 24.6, 23.2 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.0. HRMS (ESI): m/z calc. for $C_{20}H_{25}BO_4$ $[M-H]^-$: 340.1807, found 340.1809

2g 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(4-fluorophenyl) propionic acid. White solid, (38 mg isolated, 47% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 8.7, 5.2 Hz, 2H), 6.95 (t, *J* = 8.6 Hz, 2H), 1.67 (s, 3H), 1.56 (d, *J* = 15.7 Hz, 1H), 1.44 (d, *J* = 15.6 Hz, 1H), 1.11 (s, 6H), 1.10 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 182.6, 161.6 (d, *J* = 245.4 Hz), 140.4, 127.7 (d, *J* = 7.9 Hz), 114.9 (d, *J* = 21.0 Hz), 83.2, 47.5, 25.1, 24.6, 23.4 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.6 (p, *J* = 7.3, 6.8 Hz). HRMS (ESI): m/z calc. for $C_{16}H_{22}BFO_4$ $[M-H]^-$: 308.1556, found 308.1560

2h 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(3-fluorophenyl) propionic acid. White solid, (30 mg isolated, 40% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.21 (m, 1H), 7.18 – 7.08 (m, 2H), 6.90 (tdd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 1.67 (s, 3H), 1.58 (d, *J* = 15.7 Hz, 1H), 1.42 (d, *J* = 15.7 Hz, 1H), 1.12 (s, 6H), 1.11 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 182.2, 162.7 (d, *J* = 245.2 Hz), 147.4, 147.3, 129.6 (d, *J* = 8.1 Hz), 121.7, 121.7, 113.6 (d, *J* = 21.0 Hz), 113.3 (d, *J* = 22.5 Hz), 83.3, 47.8, 25.0, 24.6, 24.5, 23.1 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 28.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.9. HRMS (ESI): m/z calc. for $C_{16}H_{22}BFO_4$ $[M-H]^-$: 307.1522, found 307.1520.

2i 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(2-fluorophenyl) propionic acid. Colorless oil, (6.2 mg, 8% crude yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (td, *J* = 7.9, 1.7 Hz, 1H), 7.19 (tdd, *J* = 7.2, 5.0, 1.7 Hz, 1H), 7.07 (td, *J* = 7.5, 1.3 Hz, 1H), 7.00 – 6.90 (m, 1H), 1.71 (s, 3H), 1.53 (d, *J* = 15.1 Hz, 1H), 1.45 (d, *J*

= 15.1 Hz, 1H), 1.11 (s, 6H), 1.09 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$: δ 27.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.3. HRMS (ESI): m/z calc. for $C_{16}H_{22}BFO_4$ [M-H]$^-$: 307.1522, found 307.1520.

2j 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(3,4-difluorophenyl) propionic acid. White solid, (46 mg isolated, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (ddd, *J* = 12.3, 7.5, 2.8 Hz, 1H), 7.13 – 7.01 (m, 2H), 1.65 (s, 3H), 1.55 (d, *J* = 15.7 Hz, 1H), 1.41 (d, *J* = 15.7 Hz, 1H), 1.12 (s, 6H), 1.11 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 182.1, 152.1 – 149.3 (m), 149.5 – 146.4 (m), 141.7, 122.1, 116.7 (d, *J* = 17.1 Hz), 115.6 (d, *J* = 18.1 Hz), 83.3, 47.4, 25.0, 24.6, 23.2 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MH, $CDCl_3$: δ 32.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.7 – -137.9 (m), -140.9 (m). HRMS (ESI): m/z calc. for $C_{16}H_{21}BF_2O_4$ [M-H]$^-$: 326.1462, found 326.1466

2k 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(3-trifluoromethylphenyl) propionic acid. White solid, (40 mg isolated, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 1.72 (s, 3H), 1.60 (d, *J* = 15.7 Hz, 1H), 1.48 (d, *J* = 15.7 Hz, 1H), 1.10 (s, 6H), 1.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 182.2, 145.5, 130.5 (broad q, J=32.0), 129.7, 128.7, 124.2 (broad q, J=274.3 Hz), 123.6, 122.9, 83.3, 47.9, 25.0, 24.5, 24.5, 23.2 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI): m/z calc. for $C_{17}H_{22}BF_3O_4$ [M-H]$^-$: 358.1524, found 358.1530.

2l 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(2-trifluoromethylphenyl) propionic acid. Yellow oil, (8.5 mg, 9% crude yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.66 – 7.60 (m, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 1.84 (s, 3H), 1.63 – 1.56 (m, 2H), 1.07 (s, 6H), 1.05 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$: δ 27.5 ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.5 HRMS (ESI): m/z calc. for $C_{17}H_{22}BF_3O_4$ [M-H]$^-$: 358.1524, found 358.1519.

2m 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-(5-benzothiophenyl) propionic acid. White solid, (57 mg isolated, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (d, *J* = 1.7 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.28 (dd, *J* = 5.4, 0.8 Hz, 1H), 1.77 (s, 3H), 1.70 (d, *J* = 15.7 Hz, 1H), 1.52 (d, *J* = 15.6 Hz, 1H), 1.11 (s, 6H), 1.09 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 182.9, 141.1, 139.7, 138.1, 126.7, 124.0, 122.8, 122.2, 120.7, 83.2, 47.9, 25.4, 24.6, 24.6, 23.4 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.6. HRMS (ESI): m/z calc. for $C_{18}H_{23}BO_4S$ [M-H]$^-$: 346.1371, found 346.1377.

2n 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-2-((N-BOC)-5-indole) propionic acid White solid, (53 mg isolated, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 16.2, 2.9 Hz, 2H), 7.35 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.25 (s, 1H), 6.51 (d, *J* = 3.8 Hz, 1H), 1.74 (s, 3H), 1.70 (d, *J* = 15.8 Hz, 1H), 1.65 (s, 10H), 1.50 (d, *J* = 15.7 Hz, 1H), 1.13 (s, 5H), 1.11 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 181.3, 149.8, 139.3, 130.6, 126.2, 122.5, 122.0, 118.1, 114.9, 110.0, 107.5, 83.6, 83.3, 47.82, 28.2, 26.0, 24.6, 24.6, 23.4 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 28.6. HRMS (ESI): m/z calc. for $C_{23}H_{32}BNO_6$ [M-H]$^-$: 428.2250, found 428.2244.

2o 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))-2-phenyl-2-ethyl propionic acid. White solid, (50 mg isolated, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.16 (m, 1H), 2.15 (q, *J* = 7.4 Hz, 2H), 1.61 (d, *J* = 15.8 Hz, 1H), 1.52 (d, *J* = 15.8 Hz, 1H), 1.11 (s, 6H), 1.09 (s, 6H), 0.75 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 181.4, 143.1, 128.1, 126.6, 126.6, 83.2, 52.0, 30.6, 24.6, 24.6, 17.7 (broad due to quadrupolar broadening from ^{11}B), 8.94. ^{11}B NMR (128 MHz, $CDCl_3$: δ 28.1. HRMS (ESI): m/z calc. for $C_{17}H_{25}BO_4$ [M-H]$^-$: 304.1807, found 304.1812.

2p 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))-2-phenyl-2-propyl propionic acid. White solid, (57 mg isolated, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.34 (m, 2H), 7.27 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.21 – 7.16 (m, 1H), 2.09 (m, 2H), 1.63 (d, *J* = 15.7 Hz, 1H), 1.55 (s, 1H), 1.14-1.05 (m, 2H), 1.12 (s, 6H), 1.09 (s, 6H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.9, 143.4, 128.1, 126.6, 126.5, 83.2, 51.6, 40.0, 24.6, 18.2 (broad due to quadrupolar broadening from ^{11}B), 17.79, 14.54. ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.2. HRMS (ESI): m/z calc. for $C_{18}H_{27}BO_4$ [M-H]$^-$: 318.1963, found 318.1966.

2q 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))-2-phenyl-2-nbutyl propionic acid. White solid, (29 mg isolated, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 2.16 - 2.03 (m, 2H), 1.63 (d, *J* = 15.8 Hz, 1H), 1.53 (d, *J* = 15.8 Hz, 1H), 1.33 – 1.20 (m, 2H), 1.15 – 1.00 (m, 2H), 1.12 (s, 6H), 1.09 (s, 6H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.5, 143.4, 128.1, 126.6, 126.5, 83.2, 51.5, 37.5, 26.6, 24.6, 23.1, 18.2 (broad due to quadrupolar broadening from ^{11}B), 13.89. ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.7. HRMS (ESI): m/z calc. for $C_{19}H_{29}BO_4$ [M-H]$^-$: 332.2120, found 332.2124.

2r 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))-2-(4-trifluoromethylphenyl)-2-ethyl propionic acid. White solid, (51 mg isolated, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 2.18 (q, *J* = 7.4 Hz, 2H), 1.60 (d, *J* = 15.7 Hz, 1H), 1.53 (d, *J* = 15.7 Hz, 1H), 1.10 (s, 6H), 1.08 (s, 6H), 0.75 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.6, 147.1, 128.9 (q, *J* = 32.3 Hz), 127.1, 125.0, 125.0, 124.1 (broad q, J=272.7) 83.3, 52.2, 30.4, 24.5, 17.8 (broad due to quadrupolar broadening from ^{11}B), 8.85. ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.1.^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI): m/z calc. for $C_{17}H_{22}BF_3O_4$ [M-H]$^-$: 372.1681, found 372.1682.

2s 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))-2-(4-trifluoromethylphenyl)-2-(α-indane) propionic acid. Off-white solid, (39 mg isolated, 51% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 6.4, 2.1 Hz, 1H), 7.21 – 7.12 (m, 3H), 3.12 - 3.04 (m, 1H), 2.95 – 2.88 (m, 1H), 2.82 – 2.75 (m, 1H), 2.13 – 2.05 (m, 1H), 1.70 (d, *J* = 15.7 Hz, 1H), 1.22 (d, *J* = 15.7 Hz, 1H), 1.15 (s, 6H), 1.14 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 182.3, 146.2, 143.9, 127.5, 126.4, 124.5, 124.0, 83.2, 56.0, 37.3, 31.1, 24.6, 24.6, 21.9(broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 33.5. HRMS (ESI): m/z calc. for $C_{17}H_{23}BO_4$ [M-H]$^-$: 302.1650, found 302.1654.

2t 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2-diphenyl propionic acid. Off-white yellow solid, (7.0 mg, 8% crude yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.11 (m, 15H), 1.94 (s, 2H), 1.06 (s, 12H). HRMS (ESI): m/z calc. for $C_{21}H_{25}BO_4$ [M-H]$^-$: 351.1773, found 351.1768.

2u 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenyl-2-(4-methoxyphenyl) propionic acid. White solid, (13 mg, 14% crude yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.15 (m, 7H), 6.81 – 6.73 (m, 2H), 3.76 (s, 3H), 2.00 – 1.89 (m, 2H), 1.06 (s, 12H). HRMS (ESI): m/z calc. for $C_{22}H_{27}BO_5$ [M-H]$^-$: 381.1874, found 381.1874.

2v 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2-di(4-methoxyphenyl)-propionic acid. White solid, (5.0 mg, 5% crude yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.17 (m, 4H), 6.81 – 6.73

(m, 4H), 3.76 (s, 6H), 1.92 (s, 2H), 1.07 (s, 12H). HRMS (ESI): m/z calc. for $C_{23}H_{29}BO_6$ [M-H]⁻: 411.1984, found 411.1977.

2w 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-methoxyphenyl)-2-(4-trifluoromethylphenyl) propionic acid. Off-white yellow solid, (12 mg, 11% crude yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.21 (m, 2H), 6.84 – 6.80 (m, 2H), 3.79 (s, 3H), 2.03 (d, *J* = 15.7 Hz, 1H), 1.87 (d, *J* = 15.8 Hz, 1H), 1.07 (s, 6H), 1.06 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 178.4, 158.6, 149.0, 135.4, 129.5, 129.1, 128.7 (broad q, J=32.8 Hz), 124.5, 124.5, 124.2 (broad q, J=271.8 Hz), 123.3, 113.4, 83.6, 83.2, 77.2, 77.0, 76.8, 57.0, 55.2, 29.7, 24.8, 24.5, 24.5, 23.7 (broad due to quadrupolar broadening from ^{11}B). ^{11}B NMR (128 MHz, $CDCl_3$: δ 26.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.28. HRMS (ESI): m/z calc. for $C_{23}H_{26}BF_3O_5$ [M-H]⁻: 449.1753, found 449.1741.

2x 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenyl-2-(4-trifluoromethylphenyl) propionic acid. Off-white solid, (21 mg isolated, 20% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.22 (m, 5H), 2.04 (d, *J* = 15.8 Hz, 1H), 1.91 (d, *J* = 15.8 Hz, 1H), 1.06 (s, 6H), 1.04 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 174.2, 143.8, 138.7, 124.4, 124.1 (broad q, J = 32.3), 123.6, 123.3, 122.4, 119.8 (broad q, J=3.8 Hz), 119.4 (broad q, J = 272.7 Hz), 78.8, 53.0, 19.8, 19.00. ^{11}B NMR (128 MHz, $CDCl_3$: δ 28.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.3. HRMS (ESI): m/z calc. for $C_{22}H_{24}BF_3O_4$ [M-H]⁻: 419.1647, found 419.1638.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge at http://pubs.acs.org.

^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra for new boracarboxylated compounds.

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Notes

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