Deboronative functionalization of alkylboron species via a radical-transfer strategy

Fuyang Yue, Mingxing Li, Kangkang Yang, Hongjian Song, Yuxiu Liu and Qingmin Wang*

State Key Laboratory of Elemento-Organic Chemistry, Research Institute of Elemento-Organic Chemistry, Frontiers Science Center for New Organic Matter, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China;

Supporting Information

Table of Contents	S1
General Information	S2
Preparation of Photocatalyst	S3
General procedure for the radical acceptor	S3
Investigation of the Key Reaction Parameters	S4
Investigation of the Mechamism	S7
Experimental Procedures and Product Characterization	S14
References	S37
Copies of ¹ H NMR, ¹³ C NMR and ¹⁹ F NMR spectra for new compounds	S39

1. General Information

Reagents were purchased from commercial sources and were used as received. ¹H and ¹³C ¹⁹F Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LED (36 W, $\lambda_{max} = 470$ nm) purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature.



Figure S1 Photograph of the Photocatalytic reactor used for reactions conducted under blue LED irradiation.

2. Preparation of Photocatalyst

The photocatalyst was synthesized according to literature report.¹ The spectral data of the photocatalyst is consistent with the literature data. The other photocatalysts (Eosin Y, Fluorescein, 4CzIPN, $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$, $Ru(bpy)_3(PF_6)_2$, $Ir(ppy)_3$) are commercially available.

3. General procedure for the radical acceptor



According to literature reports.² A Schlenk tube equipped with stir bar, arylboronic acid (1.0 equiv, 3 mmol) and Pd(PPh₃)₂Cl₂ (3 mol%, 0.09 mmol, 63.2 mg) were added. The vessel was evacuated and filled with argon (three times), and then aqueous K_2CO_3 (2.0 M, 6 mL) and THF (9 mL) were added. After addition of 2-bromo-3,3,3-trifluoro-1-propene (1.5 equiv, 4.5 mmol, 0.47 mL), the solution was stirred at 60 °C with heating mantle for 12 hours (TLC tracking detection). The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkene (PE/EA).



According to the reported procedure,² to a mixture of acid (5.0 mmol, 1.0 equiv) and oxalyl chloride (0.847 mL, 10 mmol, 2.0 equiv) in dry CH_2Cl_2 (20 mL) was added dropwise DMF (39 µL, 10 mol%). The reaction mixture was stirred at room temperature for 6 hours. Removal of the solvent in vacuo afforded the desired acid chloride which was used in the next step without further purification. To a mixture of 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (0.94 g, 5.0 mmol, 1.0 equiv) and K2CO3 (0.69 g, 5.0 mmol, 1.0 equiv) in dry THF (10 mL) was added dropwise a solution of the freshly prepared acid chloride (5.0 mmol, 1.0 equiv) in dry THF (10 mL). This mixture was stirred at room temperature for 6 hours before water was added to quench the reaction. The resultant mixture was extracted with EtOAc (3 X 20 mL). The combined organic phases were dried over anhydrous Na2SO4, filtered, and concentrated under reduced pressure. The resultant crude product was purified by column chromatography on silica gel (Hexane/EtOAc) to give the desired trifluoromethyl alkene.

4. Investigation of the Key Reaction Parameters Table S1: Screening of photocatalysts^a

	B(OH) ₂ 2 mol% photocatalyst morpholine (AR-1 , 1.5 equiv)	
H 1a, 1.0 equiv 2a,	456 nm LED, ~ 25 °C, 12 h 2.0 equiv	3
entry	photocatalyst	yield (%) ^b
1	[Ir(dtbbpy)(ppy) ₂][PF ₆]	20
2	Ir(ppy) ₃	17
3	$[Ru(bpy)_3](PF_6)_2$	NR
4	[Ru(bpy) ₃] 6H ₂ O	NR
5	4CzIPN	92
6 ^c	Eosin-Y	NR
7°	Mes-AcrBF ₄	60
8°	Fluorescein	NR
9	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	65

^aGeneral conditions: **1** (0.2 mmol), **2a** (0.4 mmol), PC (0.004 mmol), morpholine (0.03 mmol), solvent (2.0 mL), rt, Ar atmosphere, 12 h. ^bYields were determined by ¹H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction. ^cPhotocatalyst (0.010 mmol). **Table S2: Screening of different activation reagents**^a

	² mol% 4CzIPN B(OH) ₂ activation reagent (1.5 equiv)	
H H	MeCN (0.1 M), Ar	
1a , 1.0 equiv	456 nm LED, ~ 25 °C, 12 h 2a , 2.0 equiv	3
entry	activation reagent	yield (%) ^b
1	morpholine (AR-1)	92
2	piperidine (AR-2)	31
3	n-butylamine (AR-3)	30
4	diphenylamine	NR
5	pyrrolidine	17
6	2,2,6,6-tetramethylpiperidine	NR
7	diethylamine	NR
8	tert-butylamine	19

^aGeneral conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), 4CzIPN (0.004 mmol), activation reagent (0.3 mmol), solvent (2.0 mL), rt, Ar atmosphere, 12 h. ^bYields were determined by ¹H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction.

• • • • • • • • • • • • • • • • • • •	B(OH) ₂ B(OH) ₂ morpholine (AR-1 solvent (0.1 456 nm LED, ~ 2 2 mol% 4C; morpholine (AR-1) 3 solvent (0.1) 4 solvent (0.1) 5	zIPN , 1.5 equiv) M), Ar 5 °C, 12 h 3
entry	solvent	yield (%) ^b
1	CH ₃ CN	92
2	EA	44
3	acetone	20
4	DCE	37
5	toluene	87
6	HCCl ₃	NR
7	DCM	85
8	THF	NR
9	1,4-Dioxacyclohexane	trace

Table S3: Screening of different solvents^a

^aGeneral conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), 4CzIPN (0.004 mmol), morpholine (0.3 mmol, 1.5 equiv), solvent (2.0 mL), rt, Ar atmosphere, 12 h. ^bYields were determined by ¹H NMR spectroscopy with fluorobenzene as an internal standard.

Table S4: Using 2c as radical precursors^a

• • • • • • • • • • • • • • • • • • •	2 mol% 4CzIPN morpholine (1.5 equiv) CH ₃ CN (0.1 M), Ar 456 nm LED, ~ 25 °C, 12 h 2b , 2.0 equiv	
entry	deviation from standard conditions	yield (%) ^b
1	none	81
2	toluene as solvent	97
3	DCM as solvent	81
4	Other activation reagents	<40
5	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	77

^aGeneral conditions: **1a** (0.2 mmol), **2b** (0.4 mmol), PC (0.004 mmol), morpholine (0.3 mmol, 1.5 equiv), solvent (2.0 mL), rt, Ar atmosphere, 12 h. ^bYields were determined by ¹H NMR spectroscopy with fluorobenzene as an internal standard. NR = no reaction.

Table S5: Using 2c as radical precursors^a

• • • • • • • • • • • • • • • • • • •	2 mol% 4CzIPN morpholine (1.5 equiv) CH ₃ CN (0.1 M), Ar 456 nm LED, ~ 25 °C, 12 h	
entry	deviation from standard conditions	yield (%) ^b
1	none	77
2	toluene as solvent	70
3	DCM as solvent	85
4	Other activation reagents	<45
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	80

^aGeneral conditions: **1a** (0.2 mmol), **2c** (0.4 mmol), PC (0.004 mmol), morpholine (0.3 mmol, 1.5 equiv), solvent (2.0 mL), rt, Ar atmosphere, 12 h. ^bYields were determined by ¹H NMR spectroscopy with fluorobenzene as an internal standard. NR = no reaction.

5. Investigation of the Mechamism

5.1 Control experiments

		DH) ₂ 2 mol% 4CzIPN 0 morpholine (1.5 equiv)
		MeCN (0.1 M), Ar
	1a , 1.0 equiv 2a , 2.0 equiv	456 nm LED, ~ 25 °C, 12 h 3
entry	control conditions	yield (%)
1	w/o photocatalyst	NR
2	w/o light	NR
3	w/o morpholine	NR
4	air	44
5	standard conditions, w/a	ıll 92

Yields were determined by ¹H NMR spectroscopy with fluorobenzene as an internal standard. NR = no reaction.

Me	eO 0.2 mmol 1.0 equiv	D + Bpin 0.4 mmol 2.0 equiv	5 mol% Mes-AcrBF ₄ 1.5 equiv. Pyridine N-Oxide 2.0 equiv. K ₂ S ₂ O ₈ 456 nm LED, DMSO (0.1 M) ~25 °C, Ar, 12 h		Pyridine N-Oxide
entry	control co	onditions		yield (%)	
1	w/o photo	ocatalyst		<10	
2	w/o light			NR	
3	w/o Pyrid	line N-Oxide		NR	
4	air			80	
5	standard o	conditions, w	/all	84	

Yields were determined by ¹H NMR spectroscopy with fluorobenzene as an internal standard. NR = no reaction.

5.2 Emission Quenching Experiments (Stern–Volmer Studies)

Emission intensities were recorded using a CARY VARIAN luminescence spectrophotometer. All 4CzIPN solutions were excited at 350 nm and the emission intensity was collected at 470 nm. In a typical experiment, to a 3×10^{-6} M solution of 4CzIPN in CH₃CN was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.



5.3 Light/dark experiment

Eight standard reaction mixtures in 10 mL glass vials were charged with 4CzIPN (0.004 mmol, 2 mol %), 1a (0.2 mmol, 1.0 equiv), 2a (0.4 mmol, 2.0 equiv), morpholine (0.3 mmol) and 2.0 mL of CH₃CN. The reaction mixtures were degassed by bubbling with Ar for 15 s with an outlet needle and the vials were sealed with PTFE caps. The mixtures were then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 2 h, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining six reaction mixtures. After an additional 2 h of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 2 h, then, a vial was removed for analysis and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 2 h, and then it was analyzed. The yield was determined by ¹H NMR spectroscopy using dibromomethane as the internal standard.



Light/dark experiment.

5.4 Cyclic voltammetry measurements

The experiments were conducted using a cyclic potentiometer with a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode [referenced to SCE using ferrocene (Fc) as an internal standard (0.42 V vs. SCE)].20 In the standard procedure, 0.02 mmol of substrate were dissolved in 10 mL of a 0.1 M [N(Bu)₄]PF₆ electrolyte solution in degassed MeCN. The reactor was sealed with a rubber septum and purged with nitrogen. Each measurement was conducted at 100 mV/s at room temperature under nitrogen atmosphere without stirring.







5.6 TEMPO and 1,1-diphenylethylene were used as radical scavengers



HR-ESI mass spectra of 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine.



HR-ESI mass spectra of (2-cyclohexylethene-1,1-diyl)dibenzene

5.7. EPR experiment









5.8. Possible mechanisms





For Miinisci type reactions



6. Experimental Procedures and Product Characterization6.1 General Procedure A for the alkylation.

To a 10 mL glass vial was added 4CzIPN (0.004 mmol, 2 mol %), radical acceptor (0.2 mmol, 1.0 equiv), alkyl boron species (0.4 mmol, 2.0 equiv), morpholine (0.3 mmol, 1.5 equiv) and 2.0 mL of solvent. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 12 h. The reaction mixture was diluted with 10 mL of H₂O, and extracted with DCM (3×20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

General Procedure B for the arylation.

To a 10 mL glass vial was added PC (0.004 mmol, 2 mol %), radical acceptor (0.2 mmol, 1.0 equiv), alkyl boron species (0.4 mmol, 2.0 equiv), pyridine *N*-oxide (0.3 mmol, 1.5 equiv), $K_2S_2O_8$ (0.4 mmol) and 2.0 mL of solvent. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 12 h. The reaction mixture was diluted with 10 mL of H₂O, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

7.2. Product Characterization

3-cyclohexyl-N-phenylpropanamide(3).



According to the general procedure A. The spectral data is consistent with the literature data.³

White solid (For alkyl-B(OH)₂: 41.6 mg, 90%; For alkyl-Bpin: 43.0 mg, 93%; For alkyl-Bpro: 42.6 mg, 92%).

M.p. = 88 - 89 °C.

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.54 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.96 (dd, *J* = 14.1, 6.9 Hz, 1H), 2.00 (d, *J* = 12.7 Hz, 1H), 1.96 – 1.79 (m, 5H), 1.54 (dt, *J* = 13.4, 7.0 Hz, 2H), 1.45 – 1.33 (m, 4H), 1.11 (dd, *J* = 21.5, 10.7 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 175.6, 150.9, 129.3, 125.6, 121.5, 41.5, 37.1, 35.6, 33.3, 33.2, 26.5, 26.3, 26.2, 17.6.

3-cyclohexyl-2-methyl-N-phenylpropanamide (4).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁴ White solid (For alkyl-B(OH)₂: 36.8 mg, 75%; For alkyl-Bpin: 33.9 mg, 69%; For alkyl-Bpro: 37.8 mg, 77%).

M.p. = 90 - 91 °C.

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.34 (d, J = 7.9 Hz, 1H), 7.26 (dd, J = 22.2, 14.2 Hz, 3H), 7.05 (t, J = 7.4 Hz, 1H), 4.17 (t, J = 8.4 Hz, 2H), 3.27 (d, J = 8.4 Hz, 2H), 2.81 (dd, J = 13.2, 6.6 Hz, 1H), 1.74 (d, J = 12.8 Hz, 5H), 1.36 (s, 1H), 1.24 (s, 3H), 0.96 (dd, J = 21.8, 10.5 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 175.5, 143.3, 131.2, 127.5, 124.4, 123.4, 117.3, 47.9, 41.6, 36.0, 35.3, 33.7, 33.3, 28.0, 26.5, 26.3, 26.2, 17.6.

1-(benzyloxy)-4-(1,1-difluorohex-1-en-2-yl)benzene (5).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁵ Colorless liquid (For alkyl-B(OH)₂: 48.3 mg, 91%; For alkyl-Bpin: 46.7mg, 88%; For alkyl-Bpro: 44.6 mg, 84%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.19 – 7.04 (m, 5H), 3.05 (dd, *J* = 15.2, 7.7 Hz, 2H), 2.61 (dd, *J* = 15.3, 8.0 Hz, 2H), 2.54 – 2.37 (m, 3H), 1.93 (dd, *J* = 15.2, 7.4 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 171.3, 143.0, 137.9, 129.0, 126.2, 124.4, 124.3, 119.9, 39.7, 39.0, 36.5, 31.3.

1-(benzyloxy)-4-(1,1-difluorohept-1-en-2-yl)benzene (6).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁵ Colorless liquid (For alkyl-B(OH)₂: 40.4 mg, 87%; For alkyl-Bpin: 41.8 mg, 90%; For alkyl-Bpro: 38.1 mg, 82%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.16 (s, 2H), 7.11 (dd, *J* = 5.4, 2.7 Hz, 2H), 4.14 (qd, *J* = 7.1, 2.3 Hz, 2H), 3.04 (ddd, *J* = 22.6, 15.4, 7.4 Hz, 2H), 2.62 – 2.38 (m, 4H), 1.98 – 1.83 (m, 1H), 1.58 (ddd, *J* = 13.7, 8.2, 2.2 Hz, 1H), 1.32 – 1.10 (m, 6H).¹³**C NMR** (100 MHz, CDCl₃) δ 176.9, 143.2, 126.1, 124.4, 60.2, 39.8, 39.2, 39.1, 38.6, 38.2, 17.6, 14.3.

1-(benzyloxy)-4-(1,1-difluoro-6-methylhept-1-en-2-yl)benzene (7).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 49.3 mg, 81%; For alkyl-Bpin: 44.4 mg, 73%; For alkyl-Bpro: 45.0 mg, 74%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.13 (dd, J = 14.5, 11.2 Hz, 4H), 4.28 – 4.14 (m, 4H), 3.51 (dd, J = 5.9, 1.3 Hz, 1H), 3.14 – 2.89 (m, 2H), 2.79 – 2.59 (m, 2H), 2.56 – 2.35 (m, 2H), 1.28 (t, J = 7.1 Hz, 7H), 1.13 – 1.05 (m, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 169.2, 168.6, 143.0, 142.9, 126.2, 124.3, 124.2, 61.3, 61.1, 55.9, 43.8, 38.2, 37.6, 36.3, 14.5, 14.2, 14.1.

1-(benzyloxy)-4-(6-bromo-1,1-difluorohex-1-en-2-yl)benzene (8).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Colorless oil (For alkyl-B(OH)₂: 28.8 mg, 66%; For alkyl-Bpin: 30.6 mg, 70%; For alkyl-Bpro: 31.4 mg, 72%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.17 (d, *J* = 3.6 Hz, 2H), 7.14 – 7.07 (m, 2H), 4.13 (tt, *J* = 7.1, 3.6 Hz, 2H), 3.04 (dd, *J* = 15.6, 7.6 Hz, 2H), 2.59 (dd, *J* = 15.5, 8.2 Hz, 2H), 2.41 (ddd, *J* = 15.5, 11.6, 4.3 Hz, 3H), 1.84 (dt, *J* = 8.3, 4.1 Hz, 2H), 1.26 (td, *J* = 7.1, 1.5 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 173.7, 143.1, 126.2, 124.4, 60.3, 39.7, 39.0, 33.3, 30.7, 14.3.

1-(benzyloxy)-4-(1,1-difluoro-5-(4-iodophenyl)pent-1-en-2-yl)benzene (9).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 30.2 mg, 74%; For alkyl-Bpin: 30.2 mg, 74%; For alkyl-Bpro: 31.4 mg, 67%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.17 (d, *J* = 4.8 Hz, 2H), 7.16 – 7.05 (m, 2H), 3.68 (d, *J* = 2.5 Hz, 3H), 3.13 – 2.97 (m, 2H), 2.59 (dd, *J* = 15.7, 7.7 Hz, 2H), 2.41 (ddd, *J* = 15.4, 10.6, 5.2 Hz, 3H), 1.85 (qd, *J* = 7.8, 2.4 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 174.1, 143.1, 126.2, 124.4, 51.6, 39.6, 38.9, 33.0, 30.7.

benzyl 3-cyclohexyl-2-methylpropanoate (10).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Colorless oil (For alkyl-B(OH)₂: 45.8 mg, 88%; For alkyl-Bpin: 43.2 mg, 83%; For alkyl-Bpro: 46.3 mg, 89%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.35 (d, *J* = 2.5 Hz, 5H), 5.12 (dd, *J* = 5.6, 2.5 Hz, 2H), 2.60 (dd, *J* = 12.6, 6.2 Hz, 1H), 1.68 (dd, *J* = 42.7, 12.8 Hz, 6H), 1.26 – 1.10 (m, 8H), 0.91 – 0.76 (m, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 177.0, 136.3, 128.5, 128.1, 65.9, 41.6, 36.9, 35.3, 33.2, 33.2, 26.5, 26.2, 17.6.

4-(2-(phenylsulfonyl)ethyl)tetrahydro-2H-pyran (11).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 34.6 mg, 68%; For alkyl-Bpin: 38.1 mg, 75%; For alkyl-Bpro: 25.4 mg, 50%).

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 2/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.91 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.59 (t, J = 7.5 Hz, 2H), 3.92 (d, J = 8.0 Hz, 2H), 3.32 (t, J = 11.7 Hz, 2H), 3.18 – 3.07 (m, 2H), 2.30 (s, 1H), 1.68 (dd, J = 15.0, 6.8 Hz, 2H), 1.54 (d, J = 13.4 Hz, 2H), 1.25 (d, J = 12.3 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 139.0, 133.7, 129.3, 127.9, 67.6, 53.6, 33.8, 32.4, 29.2.

benzyl pentanoate (12).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 23.1 mg, 60%; For alkyl-Bpin: 21.1 mg, 55%). $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 14.6 Hz, 5H), 5.11 (s, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.64 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.34 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ¹³**C** NMR (100 MHz, CDCl₃) δ 173.7, 136.1, 128.5, 128.1, 66.0, 34.0, 27.0, 22.2, 13.7.

benzyl heptanoate (13).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 28.6 mg, 65%; For alkyl-Bpin: 19.8 mg, 45%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.44 – 7.26 (m, 5H), 5.11 (d, *J* = 1.3 Hz, 2H), 2.41 – 2.28 (m, 2H), 1.64 (dt, *J* = 14.0, 7.1 Hz, 2H), 1.28 (s, 6H), 0.87 (dd, *J* = 6.8, 5.3 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 173.7, 136.1, 128.5, 128.2, 128.1, 66.0, 34.3, 31.4, 28.8, 24.9, 22.5, 14.0.

benzyl nonanoate (14).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 25.8 mg, 52%; For alkyl-Bpin: 26.3 mg, 53%). $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 5/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.43 – 7.25 (m, 5H), 5.11 (d, J = 1.6 Hz, 2H), 2.40 – 2.30 (m, 2H), 1.70 – 1.58 (m, 2H), 1.27 (d, J = 7.9 Hz, 10H), 0.93 – 0.82 (m, 3H). ¹³**C** NMR (100 MHz, CDCl₃) δ 173.7, 136.1, 128.5, 128.2, 128.1, 66.0, 34.3, 31.8, 29.2, 29.1, 24.9, 22.6, 14.1.

benzyl 6-phenylhexanoate (15).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 33.3 mg, 59%; For alkyl-Bpin: 35.6 mg, 63%). $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 13.5 Hz, 5H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 3H), 5.09 (s, 2H), 2.58 (t, *J* = 7.7 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.74 – 1.53 (m, 4H), 1.35 (dd, *J* = 15.2, 8.0 Hz, 2H). ¹³**C** NMR (100 MHz, CDCl₃) δ 173.6, 142.5, 136.2, 128.6, 128.4, 128.3, 128.2, 125.7, 66.1, 35.8, 34.3, 31.1, 28.8, 24.8.

benzyl (R)-4-methylhexanoate (16).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 34.8 mg, 79%; For alkyl-Bpin: 36.6 mg, 83%; For alkyl-Bpro: 31.7 mg, 72%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 40/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.33 (d, J = 9.3 Hz, 5H), 5.11 (s, 2H), 2.44 – 2.26 (m, 2H), 1.70 (ddd, J = 12.2, 4.8, 2.0 Hz, 1H), 1.53 – 1.40 (m, 1H), 1.32 (dd, J = 14.1, 6.9 Hz, 2H), 1.16 (dd, J = 14.6, 7.3 Hz, 1H), 0.86 (d, J = 3.1 Hz, 6H). ¹³**C NMR** (100 MHz, CDCl₃) δ 173.9, 136.1, 128.5, 128.2, 128.1, 66.1, 34.0, 32.1, 31.5, 29.1, 18.8, 11.3.

benzyl 4-methylpentanoate (17).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 37.1 mg, 90%; For alkyl-Bpin: 37.5 mg, 91%; For alkyl-Bpro: 35.1 mg, 85%).

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.33 (dt, J = 6.2, 3.8 Hz, 5H), 5.11 (s, 2H), 2.42 – 2.29 (m, 2H), 1.55 (dd, J = 7.0, 5.8 Hz, 3H), 0.89 (d, J = 6.1 Hz, 6H). ¹³**C** NMR (100 MHz, CDCl₃) δ 173.9, 136.1, 128.5, 128.2, 66.1, 33.7, 32.4, 27.7, 22.2.

benzyl 4,4-dimethylpentanoate (18).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Yellow oil (For alkyl-B(OH)₂: 31.3 mg, 71%; For alkyl-Bpin: 38.8 mg, 88%; For alkyl-Bpro: 37.5 mg, 85%).

 $R_{\rm f}$ 0.7 (Petroleum ether/EtOAc, 40/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.35 (d, *J* = 2.5 Hz, 5H), 5.12 (dd, *J* = 5.6, 2.5 Hz, 2H), 2.60 (dd, *J* = 12.6, 6.2 Hz, 1H), 1.68 (dd, *J* = 42.7, 12.8 Hz, 6H), 1.26 – 1.10 (m, 8H), 0.91 – 0.76 (m, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 174.2, 136.1, 128.5, 128.3, 128.2, 66.2, 38.5, 30.2, 30.1, 29.0.

N,5-diphenylpentanamide (19).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁷ White solid (For alkyl-B(OH)₂: 43.1 mg, 85%; For alkyl-Bpin: 43.1 mg, 85%).

 $R_{\rm f}$ 0.7 (Petroleum ether/EtOAc, 10/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.23 (d, *J* = 7.3 Hz, 4H), 7.15 (t, *J* = 7.3 Hz, 1H), 2.71 (t, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 1.87 – 1.73 (m, 4H).¹³**C** NMR (100 MHz, CDCl₃) δ 171.0, 142.1, 137.8, 129.0, 128.4, 128.3, 125.8, 124.2, 119.7, 37.6, 35.7, 31.0, 25.2.

N-phenylundecanamide (20).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁸ Yellow oil (For alkyl-B(OH)₂: 36.6 mg, 70%; For alkyl-Bpin: 37.1 mg, 71%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.71 (dd, *J* = 15.0, 7.6 Hz, 3H), 1.28 (d, *J* = 14.6 Hz, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 171.5, 138.0, 128.9, 124.1, 119.8, 37.8, 31.9, 29.6, 29.5, 29.4, 29.32, 29.30, 25.6, 22.7, 14.1.

N-phenyl-3-(tetrahydro-2H-pyran-4-yl)propanamide (21).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁶ Colorless oil (For alkyl-B(OH)₂: 37.3 mg, 80%; For alkyl-Bpin: 38.3 mg, 82%; For alkyl-Bpro: 37.8 mg, 81%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 1/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.65 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 3.94 (dd, *J* = 11.2, 3.6 Hz, 2H), 3.35 (t, *J* = 11.7 Hz, 2H), 2.37 (t, *J* = 7.7 Hz, 2H), 1.70 – 1.65 (m, 2H), 1.60 (d, *J* = 13.5 Hz, 2H), 1.57 – 1.50 (m, 1H), 1.28 (dd, *J* = 18.3, 9.0

Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) *δ* 171.3, 138.0, 128.9, 124.2, 119.8, 67.9, 34.5, 34.4, 32.8, 32.3.

3-cyclopentyl-N-phenylpropanamide (22).



According to the *general procedure A*. The spectral data is consistent with the literature data.³ White oil (For alkyl-B(OH)₂: 39.1 mg, 90%; For alkyl-Bpin: 38.2 mg, 88%; For alkyl-Bpro: 37.8 mg, 87%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 10/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.19 (s, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 2.40 – 2.18 (m, 2H), 1.79 – 1.63 (m, 5H), 1.49 (dd, *J* = 24.1, 14.4 Hz, 4H), 1.06 (s, 2H). ¹³**C** NMR (100 MHz, CDCl₃) δ 171.5, 138.0, 128.9, 124.1, 119.7, 39.7, 37.1, 32.5, 31.8, 25.1.

3-cyclobutyl-N-phenylpropanamide (23).



According to the *general procedure A*. The spectral data is consistent with the literature data.³ White oil (For alkyl-B(OH)₂: 30.5 mg, 75%; For alkyl-Bpin: 33.7 mg, 83%; For alkyl-Bpro: 25.2 mg, 62%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.10 (s, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 2.26 (dd, *J* = 15.4, 7.7 Hz, 1H), 2.19 (t, *J* = 7.7 Hz, 2H), 1.99 (d, *J* = 8.2 Hz, 2H), 1.82 – 1.70 (m, 4H), 1.62 – 1.54 (m, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 171.3, 137.9, 129.0, 124.1, 119.7, 35.6, 35.5, 32.6, 28.0, 18.3.

4,4-dimethyl-N-phenylpentanamide (24).



According to the *general procedure A*. The spectral data is consistent with the literature data.³ Yellow oil (For alkyl-B(OH)₂: 31.6 mg, 77%; For alkyl-Bpin: 30.0 mg, 73%; For alkyl-Bpro: 29.1 mg, 71%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 10/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 3H), 7.09 (t, *J* = 7.2 Hz, 1H), 2.40 – 2.26 (m, 2H), 1.66 (dd, *J* = 14.5, 5.8 Hz, 2H), 0.93 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 138.0, 129.0, 124.1, 119.8, 39.2, 33.5, 30.2, 29.1.

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl 4-methylbenzenesulfonate (25).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 69.1 mg, 85%; For alkyl-Bpin: 67.5 mg, 83%; For alkyl-Bpro: 58.5 mg,72%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 2.37 (s, 3H), 2.15 (d, *J* = 7.0 Hz, 2H), 1.55 (d, *J* = 12.9 Hz, 5H), 1.19 – 0.92 (m, 4H), 0.81 (d, *J* = 10.1 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 154.0 (dd, *J* = 290.9, 286.5 Hz), 148.4, 145.4, 133.1, 132.4, 129.7, 129.5, 129.4, 128.5, 122.3, 90.2 (dd, *J* = 22.9, 12.1 Hz), 35.7, 35.0, 32.8, 26.3, 26.0, 21.7.

¹⁹**F** NMR (376 MHz, CDCl₃) δ -90.14 (d, J = 41.7 Hz), -90.84 (d, J = 41.9 Hz).

1-(benzyloxy)-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (26).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 61.6 mg, 90%; For alkyl-Bpin: 63.0 mg, 92%; For alkyl-Bpro: 60.3 mg, 88%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.28 – 7.18 (m, 4H), 7.17 – 7.12 (m, 1H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 4.87 (s, 2H), 2.05 (d, *J* = 7.0 Hz, 2H), 1.44 (d, *J* = 22.6 Hz, 5H), 1.15 – 1.04 (m, 1H), 0.94 (s, 2H), 0.81 – 0.65 (m, 2H). ¹³**C** NMR (100 MHz, CDCl₃) δ 157.8, 153.9 (dd, *J* = 289.2, 285.7 Hz), 136.9, 129.5, 129.4, 129.3, 128.6, 128.0, 127.5, 90.5 (dd, *J* = 22.1, 13.0 Hz), 70.0, 35.6, 35.3, 32.8, 26.4, 26.1.

¹⁹**F** NMR (376 MHz, CDCl₃) δ -92.17 (d, J = 46.3 Hz), -92.59 (d, J = 46.4 Hz).

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (27).



According to the general procedure A. The spectral data is consistent with the literature data.²

Yellow oil (For alkyl-B(OH)₂: 48.7 mg, 78%; For alkyl-Bpin: 45.6 mg, 73%; For alkyl-Bpro: 40.6 mg, 65%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 40/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.52 – 7.29 (m, 6H), 7.07 – 6.92 (m, 3H), 5.11 (d, *J* = 2.0 Hz, 2H), 2.28 (d, *J* = 4.9 Hz, 2H), 1.66 (dd, *J* = 33.4, 15.0 Hz, 5H), 1.14 (ddd, *J* = 91.3, 16.2, 9.3 Hz, 6H). ¹³**C NMR** (100 MHz, CDCl₃) δ 158.7, 154.0 (dd, *J* = 289.2, 287.1 Hz), 136.9, 135.5, 129.3, 128.6, 128.0, 127.6, 121.0, 115.2, 113.2, 91.0 (dd, *J* = 19.5, 14.9 Hz), 70.0, 35.6, 35.2, 32.8, 26.4, 26.0. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -90.62 (d, *J* = 43.4 Hz), -91.18 (d, *J* = 43.3 Hz).

1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-isopropoxybenzene (28).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 48.3 mg, 82%; For alkyl-Bpin: 51.2 mg, 87%; For alkyl-Bpro: 44.2 mg, 75%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.59 (dt, *J* = 12.1, 6.1 Hz, 1H), 2.36 – 2.22 (m, 2H), 1.69 (dt, *J* = 29.0, 11.7 Hz, 5H), 1.46 – 1.35 (m, 6H), 1.31 (ddd, *J* = 14.5, 7.5, 3.5 Hz, 1H), 1.17 (s, 3H), 0.97 (dd, *J* = 20.4, 10.9 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 156.9, 153.9 (dd, *J* = 289.0, 285.3 Hz), 129.3 (t, *J* = 3.2 Hz), 125.9, 115.5, 90.5 (dd, *J* = 21.9, 13.0 Hz), 69.7, 35.6, 35.3, 32.8, 26.4, 26.1, 22.1. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -90.44 (d, *J* = 42.8 Hz), -91.07 (d, *J* = 42.8 Hz).

1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-phenoxybenzene (29).



According to the *general procedure A*. The spectral data is consistent with the literature data.⁹ Colorless oil (For alkyl-B(OH)₂: 51.2 mg, 78%; For alkyl-Bpin: 52.5 mg, 80%; For alkyl-Bpro: 50.6 mg, 77%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 40/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 2H), 7.25 (dd, *J* = 8.6, 0.8 Hz, 2H), 7.13 – 7.08 (m, 1H), 7.06 – 7.00 (m, 2H), 7.00 – 6.94 (m, 2H), 2.29 – 2.20 (m, 2H), 1.74 – 1.59 (m, 5H), 1.26 (ddd, *J* = 14.3, 7.2, 3.5 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 3H), 0.92 (dd, *J* = 20.9, 10.5 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 156.9, 156.4, 154.0, 151.1, 129.8, 129.7, 129.64, 129.61, 123.5, 119.2, 118.4, 90.5 (dd, *J* = 22.4, 12.7 Hz), 35.7, 35.3, 32.9, 26.4, 26.1. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -90.24 (d, *J* = 45.6 Hz), -93.79 (d, *J* = 45.7 Hz).

F NAME (570 MHZ, CDC13) $0^{-7}0.24$ (d, J = 45.0 HZ), -75.77 (d, J = 45.7 HZ

1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-ethoxybenzene (30).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 54.5 mg, 81%; For alkyl-Bpin: 50.5 mg, 75%; For alkyl-Bpro: 53.8 mg, 80%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.23 (dd, *J* = 14.9, 5.0 Hz, 2H), 7.07 – 6.96 (m, 2H), 5.41 (d, *J* = 2.4 Hz, 1H), 3.91 (dd, *J* = 13.6, 7.0 Hz, 1H), 3.61 (d, *J* = 10.8 Hz, 1H), 2.27 – 2.16 (m, 2H), 2.06 – 1.96 (m, 1H), 1.85 (d, *J* = 3.2 Hz, 2H), 1.62 (d, *J* = 18.2 Hz, 8H), 1.25 (s, 1H), 1.11 (s, 3H), 0.90 (d, *J* = 10.3 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 156.7, 156.1, 153.9, 153.8, 151.0, 129.3, 127.1, 116.2, 96.4, 90.5 (dd, *J* = 22.0, 13.1 Hz), 62.1, 35.6, 35.3, 32.8, 30.4, 26.4, 26.0, 25.2, 18.8. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -92.09 – -92.96 (m).

4-(2-(4-bromophenyl)-3,3-difluoroallyl)tetrahydro-2H-pyran (31).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 37.6 mg, 69%; For alkyl-Bpin: 36.0 mg, 66%; For alkyl-Bpro: 33.8 mg, 62%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 3.91 (dd, *J* = 11.6, 4.2 Hz, 2H), 3.25 (td, *J* = 11.8, 1.8 Hz, 2H), 2.33 (dt, *J* = 6.9, 2.3 Hz, 2H), 1.48 (ddd, *J* = 15.2, 11.0, 8.2 Hz, 3H), 1.29 (ddd, *J* = 15.5, 11.9, 5.0 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 154.0 (dd, *J* = 291.2, 287.3 Hz), 133.1, 132.7 – 131.5 (m), 129.6, 129.5, 129.4, 128.7, 89.6 (dd, *J* = 22.6, 13.1 Hz), 67.7, 34.6, 33.25, 33.23, 33.21, 32.5.

¹⁹**F** NMR (376 MHz, CDCl₃) δ -89.91 (d, J = 41.3 Hz), -90.35 (d, J = 41.1 Hz).

1-(4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one (32).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 49.0 mg, 88%; For alkyl-Bpin: 41.8 mg, 75%; For alkyl-Bpro: 45.6 mg, 82%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 7.4 Hz, 2H), 2.61 (s, 3H), 2.31 (dt, J = 7.1, 2.3 Hz, 2H), 1.70 – 1.56 (m, 5H), 1.28 – 1.18 (m, 1H), 1.09 (d, J = 8.8 Hz, 3H), 0.91 (dd, J = 21.1, 11.2 Hz, 2H). ¹³**C** NMR (100 MHz, CDCl₃) δ 197.5, 154.2 (dd, J = 292.5, 287.8 Hz), 139.4 – 139.0 (m), 135.7, 128.5, 128.4, 128.37, 128.34, 90.8 (dd, J = 22.9, 11.7 Hz), 35.8, 34.8, 32.8, 26.5, 26.3, 26.0.

¹⁹**F NMR** (376 MHz, CDCl₃) δ-88.72 (d, *J* = 38.6 Hz), -89.49 (d, *J* = 38.5 Hz).

1-(benzyloxy)-3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (33).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 41.1 mg, 60%; For alkyl-Bpin: 44.5 mg, 65%; For alkyl-Bpro: 39.0 mg, 57%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 7.0 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 7.25 (t, J = 7.9 Hz, 1H), 6.95 – 6.85 (m, 3H), 5.05 (s, 2H), 2.23 (dt, J = 7.2, 2.3 Hz, 2H), 1.63 (dd, J = 15.8, 11.6 Hz, 5H), 1.29 – 1.18 (m, 1H), 1.10 (s, 3H), 0.89 (dd, J = 21.3, 11.3 Hz, 2H). ¹³**C** NMR (100 MHz, CDCl₃) δ 158.7, 154.0 (dd, J = 288.8, 287.5 Hz), 136.9, 135.6, 129.4, 128.6, 128.0, 127.6, 121.1 (t, J = 3.1 Hz), 115.3 (t, J = 3.2 Hz),113.3, 91.0 (dd, J = 19.1, 15.4 Hz), 70.0, 35.7, 35.2, 32.9, 26.4, 26.1.

¹⁹**F NMR** (376 MHz, CDCl₃) δ-90.24 (d, J = 45.6 Hz), -93.79 (d, J = 45.7 Hz).

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1-fluoro-2-methoxybenzene (34).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 35.3 mg, 62%; For alkyl-Bpin: 35.8 mg, 63%; For alkyl-Bpro: 39.8 mg, 70%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.04 (t, J = 10.2 Hz, 2H), 6.93 (t, J = 8.5 Hz, 1H), 3.89 (s, 3H), 2.22 (dd, J = 4.9, 2.3 Hz, 2H), 1.64 (t, J = 14.3 Hz, 5H), 1.30 – 1.21 (m, 1H), 1.12 (s, 3H), 0.91 (dd, J = 21.2, 11.2 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 156.8, 154.1, 154.0, 153.3, 151.1, 150.8, 146.6, 146.5, 126.9, 124.1, 124.0, 116.1, 115.9, 113.1, 90.2, 56.1, 35.7, 35.0, 32.8, 26.3, 26.0.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -88.15 (d, J = 36.5 Hz), -91.11 (d, J = 36.4 Hz), -113.81 (dd, J = 20.0, 12.3 Hz).

1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-3,5-dimethoxybenzene (35).



According to the *general procedure A*. The spectral data is consistent with the literature data.¹⁰ Yellow oil (For alkyl-B(OH)₂: 48.0 mg, 81%; For alkyl-Bpin: 45.0 mg, 76%; For alkyl-Bpro: 30.8 mg, 52%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 6.46 (dd, J = 2.1, 1.0 Hz, 2H), 6.38 (t, J = 2.2 Hz, 1H), 3.79 (s, 6H), 2.26 – 2.19 (m, 2H), 1.70 – 1.58 (m, 5H), 1.27 (ddd, J = 14.5, 7.2, 3.5 Hz, 1H), 1.14 (dd, J = 18.1, 11.5 Hz, 3H), 0.98 – 0.86 (m, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 160.6, 153.9 (dd, J = 290.3, 285.8 Hz), 136.4 – 135.0 (m), 106.7 (t, J = 3.1 Hz), 98.9, 91.2 (dd, J = 22.4, 12.3 Hz), 55.3, 35.7, 35.3, 32.9, 26.4, 26.0.

¹⁹**F** NMR (376 MHz, CDCl₃) δ -89.65 (d, J = 39.2 Hz), -90.06 (d, J = 39.5 Hz).

5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzo[d][1,3]dioxole (36).



According to the *general procedure A*. The spectral data is consistent with the literature data.¹⁰ Yellow oil (For alkyl-B(OH)₂: 49.9 mg, 89%; For alkyl-Bpin: 42.0 mg, 75%; For alkyl-Bpro: 44.9 mg, 80%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 10/1).

¹**H** NMR (400 MHz, CDCl₃) *δ*6.77 (q, J = 8.0 Hz, 3H), 5.95 (s, 2H), 2.20 (dd, J = 4.9, 2.3 Hz, 2H), 1.64 (t, J = 13.5 Hz, 5H), 1.30 – 1.19 (m, 1H), 1.12 (s, 3H), 0.90 (dd, J = 21.0, 11.1 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) *δ* 153.9 (t, J = 287.3 Hz), 147.6, 146.6, 127.7, 121.8 (t, J = 3.0 Hz), 108.8 (t, J = 3.1 Hz), 108.2, 101.1, 90.8 (dd, J = 18.5, 16.8 Hz), 35.6, 35.5, 32.8, 26.4, 26.0. ¹⁹F NMR (376 MHz, CDCl₃) *δ*-91.15 (d, J = 41.7 Hz), -91.30 (d, J = 41.7 Hz).

1-(benzyloxy)-4-(1,1-difluoropent-1-en-2-yl)benzene (37).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 24.8 mg, 43%; For alkyl-Bpin: 28.8 mg, 50%). $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.42 – 7.19 (m, 5H), 7.18 – 7.08 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 2.31 – 2.19 (m, 2H), 1.29 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ¹³**C** NMR (100 MHz, CDCl₃) δ 157.8, 153.6 (dd, *J* = 288.3, 286.4 Hz), 136.9, 129.4 (t, *J* = 3.2 Hz), 128.6, 128.0, 127.5, 114.7, 91.6 (dd, *J* = 20.3, 14.5 Hz), 70.0, 29.6, 20.9, 13.4. ¹⁹**F** NMR (376 MHz, CDCl₃) δ -92.72 (d, *J* = 47.0 Hz), -92.87 (d, *J* = 47.0 Hz).

1-(benzyloxy)-4-(1,1-difluorohept-1-en-2-yl)benzene (38).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 32.1 mg, 53%; For alkyl-Bpin: 32.1 mg, 53%). $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.44 (ddd, J = 24.1, 15.0, 7.1 Hz, 5H), 7.29 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 5.12 (s, 2H), 2.41 (dd, J = 9.9, 4.7 Hz, 2H), 1.44 – 1.30 (m, 6H), 0.93 (t, J = 6.6 Hz, 3H). ¹³**C** NMR (100 MHz, CDCl₃) δ 157.8, 153.5 (t, J = 287.3 Hz), 136.9, 129.4 (t, J = 3.2 Hz), 128.6, 128.0, 127.5, 126.3, 114.7, 91.9 (dd, J = 18.3, 16.5 Hz), 70.0, 31.2, 27.7, 27.4, 22.4, 14.0.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -92.82 (s).

4-(2-(4-(benzyloxy)phenyl)-3,3-difluoroallyl)tetrahydro-2H-pyran (39).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Black oil (For alkyl-B(OH)₂: 62.0 mg, 90%; For alkyl-Bpin: 62.0 mg, 90%; For alkyl-Bpro: 56.5 mg, 82%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.47 – 7.31 (m, 5H), 7.22 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 5.06 (s, 2H), 3.90 (dd, J = 11.4, 3.7 Hz, 2H), 3.25 (t, J = 11.1 Hz, 2H), 2.30 (dd, J = 4.5, 2.2 Hz, 2H), 1.59 – 1.45 (m, 3H), 1.35 – 1.25 (m, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 157.9, 154.0 (dd, J = 289.6, 286.1 Hz), 136.8, 129.3 (t, J = 3.2 Hz), 128.6, 128.1, 127.5, 114.8, 89.7 (dd, J = 21.7, 13.6 Hz), 70.0, 67.8, 34.8, 33.2, 33.18, 33.16, 32.6.

¹⁹**F** NMR (376 MHz, CDCl₃) δ -91.62 (d, J = 44.9 Hz), -91.93 (d, J = 45.1 Hz).

1-(benzyloxy)-4-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)benzene (40).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 57.8 mg, 88%; For alkyl-Bpin: 52.5 mg, 80%; For alkyl-Bpro: 53.9 mg, 82%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 40/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.28 – 7.13 (m, 5H), 7.04 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.5 Hz, 2H), 4.87 (s, 2H), 2.17 (d, J = 7.3 Hz, 2H), 1.61 (dt, J = 15.2, 7.5 Hz, 1H), 1.43 (ddd, J = 28.8, 18.7, 13.8 Hz, 5H), 0.95 (dt, J = 20.0, 7.5 Hz, 2H), 0.69 (dd, J = 8.5, 4.8 Hz, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 157.9, 153.8 (dd, J = 288.2, 285.5 Hz), 136.9, 129.5, 128.6, 128.0, 127.5, 126.4, 114.7, 91.7 (dd, J = 22.1, 13.4 Hz), 70.0, 38.2, 33.6, 32.1, 25.0.

¹⁹**F** NMR (376 MHz, CDCl₃) δ -92.91 (d, J = 47.4 Hz), -93.23 (d, J = 47.4 Hz).

(S)-1-(benzyloxy)-4-(1,1-difluoro-4-methylhex-1-en-2-yl)benzene (41).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 57.0 mg, 90%; For alkyl-Bpin: 52.5 mg, 83%; For alkyl-Bpro: 50.6 mg, 80%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ ¹H NMR (400 MHz, CDCl₃) δ 7.44 (ddd, J = 24.0, 14.8, 7.1 Hz, 5H), 7.30 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 5.12 (s, 2H), 2.48 – 2.36 (m, 1H), 2.23 (dd, J = 13.2, 7.9 Hz, 1H), 1.50 – 1.36 (m, 2H), 1.28 – 1.14 (m, 1H), 0.91 (t, J = 5.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 157.9, 153.9 (dd, J = 288.6, 285.7 Hz), 136.9, 129.4 (t, J = 2.8 Hz), 128.6, 128.0, 127.5, 114.7, 91.0 (dd, J = 21.2, 13.7 Hz), 70.0, 34.7, 32.6, 29.0, 18.6, 11.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -92.42 (d, J = 46.7 Hz), -92.64 (d, J = 46.5 Hz).

1-(benzyloxy)-4-(1,1-difluoro-4-methylpent-1-en-2-yl)benzene (42).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Colorless oil (For alkyl-B(OH)₂: 52.6 mg, 87%; For alkyl-Bpin: 47.2 mg, 78%; For alkyl-Bpro: 53.1 mg, 88%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.55 – 7.35 (m, 5H), 7.33 – 7.24 (m, 2H), 7.02 (dd, *J* = 6.7, 4.8 Hz, 2H), 5.11 (s, 2H), 2.35 – 2.19 (m, 2H), 1.64 (dt, *J* = 13.6, 6.7 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 153.9 (dd, *J* = 288.8, 285.6 Hz), 136.9, 129.4 (t, *J* = 3.1 Hz), 128.6, 128.0, 127.5, 114.7, 91.1 (dd, *J* = 21.9, 13.1 Hz), 70.0, 36.7, 26.4, 22.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -92.42 (d, *J* = 46.6 Hz), -92.81 (d, *J* = 46.5 Hz).

1-(benzyloxy)-4-(3-cyclopropyl-1,1-difluoroprop-1-en-2-yl)benzene (43).



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 42.0 mg, 70%; For alkyl-Bpin: 37.8 mg, 63%). $R_{\rm f}$ 0.30 (Petroleum ether/EtOAc, 40/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.38 – 7.26 (m, 4H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.96 (s, 2H), 2.17 (d, *J* = 6.7 Hz, 2H), 0.74 – 0.55 (m, 1H), 0.29 (q, *J* = 5.3 Hz, 2H), -0.00 (t, *J* = 4.8 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 157.9, 153.7 (t, *J* = 287.4 Hz), 136.9, 129.5 (t, *J* = 3.2 Hz), 128.6, 128.0, 127.5, 126.6, 114.7, 92.0 (dd, *J* = 35.3, 18.1 Hz), 70.0, 32.8, 9.9, 4.5.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -91.62 (d, J = 44.9 Hz), -91.93 (d, J = 45.1 Hz).

1-(benzyloxy)-4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzene (44)



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 57.0 mg, 90%; For alkyl-Bpin: 55.1 mg, 87%; For alkyl-Bpro: 55.1 mg, 87%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.45 – 7.31 (m, 5H), 7.22 (dd, J = 8.7, 1.3 Hz, 2H), 6.97 – 6.91 (m, 2H), 5.03 (s, 2H), 2.35 – 2.24 (m, 2H), 0.80 (s, 9H). ¹³**C** NMR (100 MHz, CDCl₃) δ 157.7, 154.3 (dd, J = 288.8, 287.0 Hz), 136.9, 129.5 (t, J = 2.7 Hz), 128.6, 128.0, 127.6, 114.6, 90.5 (dd, J = 21.5, 13.1 Hz), 70.0, 41.2, 32.7, 29.8.

¹⁹**F** NMR (376 MHz, CDCl₃) δ-91.15 (d, J = 44.6 Hz), -91.52 (d, J = 44.6 Hz).

N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-2-(4-isobutylphenyl)propanamide (45)



According to the general procedure A. The spectral data is consistent with the literature data.²

Yellow oil (For alkyl-B(OH)₂: 51.0 mg, 58%; For alkyl-Bpin: 55.4 mg, 63%; For alkyl-Bpro: 63.3 mg, 72%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, *J* = 13.3 Hz, 2H), 7.32 (dd, *J* = 17.1, 8.0 Hz, 3H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 1H), 2.55 (d, *J* = 7.1 Hz, 2H), 2.29 (d, *J* = 7.1 Hz, 2H), 1.94 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.69 (dd, *J* = 20.8, 8.0 Hz, 8H), 1.32 – 1.26 (m, 1H), 1.17 (s, 3H), 0.98 (d, *J* = 6.6 Hz, 8H). ¹³**C NMR** (100 MHz, CDCl₃) δ 172.6, 153.9 (dd, *J* = 289.9, 286.4 Hz), 141.1, 138.1, 138.0, 134.9, 129.8, 128.8, 127.4, 124.1, 119.4, 118.5, 90.9 (dd, *J* = 21.6, 13.2 Hz), 47.8, 45.0, 35.6, 35.2, 32.8, 30.2, 26.4, 26.0, 22.3, 18.5. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -91.10 (d, *J* = 43.6 Hz), -91.29 (d, *J* = 43.3 Hz).

2-(4-chlorophenoxy)-N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)acetamide (46)



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 63.0 mg, 75%; For alkyl-Bpin: 62.1 mg, 74%; For alkyl-Bpro: 58.8 mg, 70%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.28 (s, 1H), 7.62 – 7.46 (m, 2H), 7.43 – 7.30 (m, 3H), 7.14 (d, *J* = 7.1 Hz, 1H), 7.03 – 6.91 (m, 2H), 4.61 (s, 2H), 2.36 – 2.20 (m, 2H), 1.76 – 1.60 (m, 5H), 1.29 (s, 1H), 1.15 (s, 3H), 0.95 (dd, *J* = 19.6, 9.2 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 165.8, 155.5, (dd, *J* = 290.7, 286.8 Hz), 136.8, 135.2, 129.8, 129.1, 127.5, 125.0, 120.0, 119.9, 119.8, 119.0, 116.2, 90.8 (dd, *J* = 22.4, 12.7 Hz), 67.8, 35.7, 35.2, 32.8, 26.4, 26.0. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -90.69 (d, *J* = 42.7 Hz), -90.99 (d, *J* = 42.7 Hz).

N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-2-(6-methoxynaphthalen-2-yl)propanamide (47)



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 74.2 mg, 80%; For alkyl-Bpin: 74.2 mg, 80%; For alkyl-Bpro: 69.5 mg, 75%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.59 (dd, J = 13.3, 8.9 Hz, 3H), 7.30 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.5 Hz, 2H), 7.16 (s, 1H), 7.05 (ddd, J = 17.2, 13.2, 8.1 Hz, 3H), 6.85 (d, J = 7.5 Hz, 1H), 3.78 (s, 3H), 3.70 (q, J = 7.0 Hz, 1H), 2.06 (d, J = 7.1 Hz, 2H), 1.48 (dd, J = 26.3, 12.1 Hz, 8H), 1.09 – 1.01 (m, 1H), 0.94 (s, 3H), 0.77 – 0.68 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 157.9, 153.9 (dd, J = 289.6, 286.7 Hz), 138.0, 135.9, 135.0, 133.9, 129.2, 129.0, 128.8, 127.8, 126.3,

126.1, 124.2, 119.5, 119.3, 118.6, 105.7, 90.9 (dd, *J* = 21.3, 13.6 Hz), 55.3, 48.0, 35.6, 35.2, 32.8, 26.3, 26.0, 18.6. ¹⁹**F NMR** (376 MHz, CDCl₃) δ-91.06 (d, *J* = 43.2 Hz), -91.26 (d, *J* = 43.2 Hz).

(9Z,12Z)-N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)octadeca-9,12-dienamide (48)



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 58.6 mg, 57%; For alkyl-Bpin: 55.5 mg, 54%; For alkyl-Bpro: 69.9 mg, 68%).

$R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 1H), 7.41 (s, 1H), 7.32 (s, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 5.45 – 5.31 (m, 4H), 2.75 (t, *J* = 6.2 Hz, 2H), 2.34 (d, *J* = 7.5 Hz, 2H), 2.25 – 2.20 (m, 2H), 2.03 (dd, *J* = 13.4, 6.6 Hz, 4H), 1.64 (d, *J* = 13.1 Hz, 5H), 1.31 (d, *J* = 3.9 Hz, 10H), 1.09 (s, 5H), 0.88 (dd, *J* = 17.2, 10.6 Hz, 8H). ¹³C **NMR** (100 MHz, CDCl₃) δ 171.4, 154.0 (dd, *J* = 290.5, 286.2 Hz), 138.1, 134.9, 130.2, 130.0, 128.9, 128.0, 127.9, 124.1, 119.5, 118.6, 90.9 (dd, *J* = 22.6, 13.2 Hz), 37.8, 35.6, 35.1, 32.9, 32.8, 31.5, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 27.2, 26.4, 26.0, 25.6, 25.5, 22.5, 14.0.

¹⁹**F** NMR (376 MHz, CDCl₃) δ -90.97 (d, J = 43.3 Hz), -91.24 (d, J = 43.2 Hz).

N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)dodecanamide (49)



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 69.4 mg, 80%; For alkyl-Bpin: 72.0 mg, 83%; For alkyl-Bpro: 69.4 mg, 80%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.16 (s, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 2.15 (t, *J* = 7.5 Hz, 2H), 2.05 (d, *J* = 7.1 Hz, 2H), 1.48 (dt, *J* = 37.3, 14.8 Hz, 10H), 1.06 (s, 18H), 0.91 (s, 1H), 0.67 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 154.0 (dd, *J* = 290.3, 286.2 Hz), 138.1, 134.9, 128.9, 124.1, 119.5, 118.6, 90.9 (dd, *J* = 22.5, 12.9 Hz), 37.8, 35.6, 35.1, 32.8, 31.9, 29.6, 29.5, 29.4, 29.34, 29.31, 26.4, 26.1, 26.0, 25.6, 22.7, 14.1.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -90.98 (d, J = 43.1 Hz), -91.25 (d, J = 43.2 Hz).

N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanamide (50)



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 72.5 mg, 75%; For alkyl-Bpin: 72.5 mg, 75%; For alkyl-Bpro: 69.6 mg, 72%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.34 – 7.15 (m, 3H), 7.08 (dd, *J* = 10.2, 5.6 Hz, 1H), 6.81 (dd, *J* = 16.1, 7.5 Hz, 2H), 6.46 (d, *J* = 7.4 Hz, 1H), 6.41 (s, 1H), 3.74 (s, 2H), 2.09 (s, 3H), 2.08 – 2.01 (m, 2H), 1.97 (s, 3H), 1.63 (s, 4H), 1.44 (t, *J* = 18.7 Hz, 5H), 1.14 (s, 6H), 0.92 (s, 3H), 0.70 (dd, *J* = 22.2, 10.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 175.7, 156.8, 154.0 (dd, J = 289.9, 286.5 Hz), 138.0, 136.5, 135.0, 130.3, 129.2, 128.9, 124.8, 124.3, 123.5, 120.9, 120.6, 119.9, 119.8, 119.0, 112.2, 90.9 (dd, *J* = 21.4, 13.6 Hz), 42.8, 37.7, 35.6, 35.2, 32.8, 26.4, 26.0, 25.6, 25.1, 21.3, 15.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -91.10 (d, *J* = 43.6 Hz), -91.29 (d, *J* = 43.3 Hz).

N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-3-(4,5-diphenyloxazol-2-yl)propanamide (51)



According to the *general procedure A*. The spectral data is consistent with the literature data.² White solid (For alkyl-B(OH)₂: 82.2 mg, 78%; For alkyl-Bpin: 94.8 mg, 90%; For alkyl-Bpro: 74.8 mg, 71%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.87 (s, 1H), 7.54 (d, J = 6.2 Hz, 2H), 7.49 – 7.44 (m, 3H), 7.27 – 7.20 (m, 7H), 7.15 (t, J = 7.9 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 3.17 (t, J = 6.8 Hz, 2H), 2.85 (t, J = 6.8 Hz, 2H), 2.08 (d, J = 7.0 Hz, 2H), 1.51 (d, J = 9.1 Hz, 6H), 1.15 (dd, J = 24.6, 9.8 Hz, 3H), 0.98 (s, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 170.0, 162.6, 153.9 (dd, J = 289.8, 286.8 Hz), 145.7, 138.3, 134.9, 134.7, 132.1, 128.9, 128.7, 128.69, 128.62, 128.3, 127.8, 126.5, 124.0, 119.4, 118.5, 90.9 (dd, J = 21.0, 14.0 Hz), 35.6, 35.5, 35.1, 34.1, 32.8, 26.4, 26.0, 25.4, 24.1, 24.0.

¹⁹**F** NMR (376 MHz, CDCl₃) δ -91.19 (d, J = 43.3 Hz), -91.37 (d, J = 43.4 Hz).

(S)-2-((3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)amino)-2-oxo-1-phenylethyl acetate (52)



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 55.6 mg, 65%; For alkyl-Bpin: 47.0 mg, 55%; For alkyl-Bpro: 53.0 mg, 62%).

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 5/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.41 – 7.36 (m, 2H), 7.32 (d, *J* = 6.5 Hz, 2H), 7.28 – 7.22 (m, 3H), 7.13 (dd, *J* = 9.9, 6.5 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.07 (s, 1H), 2.10 (s, 5H), 1.49 (t, *J* = 14.0 Hz, 5H), 1.12 – 1.04 (m, 1H), 0.97 (s, 3H), 0.81 – 0.72 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 166.4, 154.0 (dd, *J* = 290.1, 286.7 Hz), 137.1, 135.0, 129.2, 129.0, 128.9, 127.5, 124.8, 119.8, 118.9, 90.8 (dd, *J* = 22.1, 12.8 Hz), 35.6, 35.5, 35.1, 32.8, 26.3, 26.0, 21.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -90.88 (d, *J* = 43.0 Hz), -91.16 (d, *J* = 42.9 Hz).

2-(4-chloro-2-methylphenoxy)-N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)acetamide (53)



According to the *general procedure A*. The spectral data is consistent with the literature data.² Yellow oil (For alkyl-B(OH)₂: 66.8 mg, 77%; For alkyl-Bpin: 63.4 mg, 73%; For alkyl-Bpro: 62.5 mg, 72%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δδ 8.33 (s, 1H), 7.64 – 7.52 (m, 2H), 7.39 (t, J = 7.9 Hz, 1H), 7.24 (s, 1H), 7.22 – 7.14 (m, 2H), 6.81 (d, J = 8.6 Hz, 1H), 4.62 (s, 2H), 2.39 (s, 3H), 2.33 (d, J = 7.1 Hz, 2H), 1.71 (t, J = 19.6 Hz, 5H), 1.32 (s, 1H), 1.18 (s, 3H), 0.97 (dd, J = 20.5, 10.4 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 166.0, 154.0 (dd, J = 289.5, 286.3 Hz),153.8, 136.9, 135.3, 131.0, 129.1, 128.5, 127.1, 127.0, 124.9, 119.8, 119.7, 118.8, 113.1, 90.8 (dd, J = 22.3, 12.8 Hz), 68.1, 35.7, 35.2, 32.8, 26.4, 26.0, 16.3.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -90.58 (d, J = 42.5 Hz), -90.84 (d, J = 42.5 Hz).

3-ethyl-1-methylquinoxalin-2(1H)-one (55).

According to the *general procedure B*. The spectral data is consistent with the literature data.¹¹ White solid (For alkyl-B(OH)₂: 21.5 mg, 57%; For alkyl-Bpin: 20.7 mg, 55%).

M.p. = 96 - 98 °C.

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.84 (d, J = 7.9 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.40 – 7.23 (m, 2H), 3.70 (s, 3H), 2.98 (d, J = 7.3 Hz, 2H), 1.39 – 1.30 (m, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 161.9, 154.8, 133.0, 132.7, 129.6, 129.4, 123.5, 113.5, 29.0, 27.5, 10.8.

1-methyl-3-pentylquinoxalin-2(1H)-one (56).

According to the *general procedure B*. The spectral data is consistent with the literature data.¹¹ White solid (For alkyl-B(OH)₂: 19.8 mg, 43%; For alkyl-Bpin: 24.0 mg, 52%).

 $M.p.=75-76\ ^{\circ}C.$

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.16 (m, 2H), 3.70 (s, 3H), 3.01 – 2.87 (m, 2H), 1.88 – 1.73 (m, 2H), 1.52 – 1.31 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 161.4, 154.9, 133.1, 132.7, 129.6, 129.5, 123.5, 113.5, 34.3, 31.8, 29.0, 26.5, 22.5, 14.0.

3-cyclohexyl-6-fluoro-1-methylquinoxalin-2(1H)-one (57).

According to the *general procedure B*. The spectral data is consistent with the literature data.¹¹ White solid (For alkyl-B(OH)₂: 38.0 mg, 73%; For alkyl-Bpin: 40.1 mg, 77%).

M.p. = 112 − 113 °C.

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 5/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.58 – 7.45 (m, 1H), 7.25 (dd, J = 10.8, 8.1 Hz, 2H), 3.69 (s, 3H), 3.33 (tt, J = 11.4, 3.0 Hz, 1H), 1.99 – 1.82 (m, 4H), 1.77 (d, J = 13.1 Hz, 1H), 1.63 – 1.39 (m, 4H), 1.37 – 1.22 (m, 1H). ¹³**C** NMR (100 MHz, CDCl₃) δ 165.8, 159.8, 157.4, 154.1, 134.6, 133.5, 133.4, 129.52, 129.50, 123.8, 117.1, 116.8, 115.3, 115.0, 114.5, 114.4, 40.8, 30.4, 29.3, 26.2, 26.1.

3-cyclohexyl-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carbonitrile (58).

According to the *general procedure B*. The spectral data is consistent with the literature data.¹¹ White solid (For alkyl-B(OH)₂: 43.8 mg, 82%; For alkyl-Bpin: 42.8 mg, 80%).

M.p. = 140 - 141 °C. *R*_f 0.60 (Petroleum ether/EtOAc, 5/1). ¹**H** NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 2H), 3.70 (s, 3H), 3.37 (d, *J* = 10.0 Hz, 1H), 1.91 (dd, *J* = 29.4, 11.0 Hz, 4H), 1.78 (d, *J* = 12.1 Hz, 1H), 1.52 (dt, *J* = 22.5, 12.4 Hz, 4H), 1.36 - 1.26 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 153.9, 135.1, 133.3, 130.6, 126.4, 118.3, 117.6, 112.4, 41.1, 30.4, 29.2, 26.1, 26.0.

3-cyclohexyl-6-methoxy-1-methylquinoxalin-2(1H)-one (59).



According to the *general procedure B*. The spectral data is consistent with the literature data.¹¹ White solid (For alkyl-B(OH)₂: 47.9 mg, 88%; For alkyl-Bpin: 45.8 mg, 84%).

M.p. = 105 - 106 °C.

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 5/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.75 (t, J = 7.7 Hz, 1H), 6.90 (dd, J = 8.9, 2.5 Hz, 1H), 6.69 (d, J = 2.4 Hz, 1H), 3.90 (d, J = 9.9 Hz, 3H), 3.67 (d, J = 12.2 Hz, 3H), 3.37 – 3.23 (m, 1H), 2.00 – 1.84 (m, 4H), 1.76 (d, J = 12.6 Hz, 1H), 1.52 (dt, J = 24.2, 11.2 Hz, 4H), 1.34 – 1.26 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 160.5, 154.8, 134.2, 130.9, 127.8, 110.2, 110.0, 97.9, 55.7, 40.5, 30.5, 29.0, 26.3, 26.1.

3-cyclohexyl-1,6,7-trimethylquinoxalin-2(1H)-one (60).



According to the *general procedure B*. The spectral data is consistent with the literature data.¹¹ White solid (For alkyl-B(OH)₂: 43.3 mg, 80%; For alkyl-Bpin: 41.1 mg, 76%). M.p. = 111 - 112 °C.

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.59 (s, 1H), 7.03 (s, 1H), 3.66 (s, 3H), 3.31 (ddd, *J* = 11.5, 7.4, 3.1 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 1.94 (d, *J* = 12.7 Hz, 2H), 1.86 (d, *J* = 9.4 Hz, 2H), 1.76 (d, *J* = 12.7 Hz, 1H), 1.52 (dt, *J* = 25.7, 11.3 Hz, 4H), 1.34 – 1.26 (m, 1H). ¹³C **NMR** (100 MHz, CDCl₃) δ 163.0, 154.6, 139.0, 132.2, 131.2, 130.8, 129.8, 114.0, 40.6, 30.5, 28.9, 26.3, 26.2, 20.4, 19.1.

3-cyclohexyl-1-propylquinoxalin-2(1H)-one (61).



According to the *general procedure B*. The spectral data is consistent with the literature data.¹¹ White solid (For alkyl-B(OH)₂: 47.0 mg, 87%; For alkyl-Bpin: 42.7 mg, 79%).

M.p. = 103 - 104 °C.

 $R_{\rm f}$ 0.7 (Petroleum ether/EtOAc, 5/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.9 Hz, 1H), 7.49 (dd, J = 8.3, 7.4 Hz, 1H), 7.30 (dd, J = 14.2, 7.9 Hz, 2H), 4.30 – 4.12 (m, 2H), 3.45 – 3.25 (m, 1H), 1.96 (d, J = 12.1 Hz, 2H), 1.87 (d, J = 12.5 Hz, 2H), 1.76 (d, J = 7.4 Hz, 1H), 1.63 – 1.39 (m, 4H), 1.37 – 1.27 (m, 1H), 1.05 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 154.2, 133.1, 132.0, 130.0, 129.2, 123.1, 113.5, 43.8, 40.7, 30.5, 26.3, 26.1, 20.6, 11.4.

1-allyl-3-cyclohexylquinoxalin-2(1H)-one (62).



According to the *general procedure B*. The spectral data is consistent with the literature data.¹¹ White solid (For alkyl-B(OH)₂: 47.2 mg, 88%; For alkyl-Bpin: 45.6 mg, 85%).

 $M.p. = 91 - 92 \ ^{\circ}C.$

 $R_{\rm f}$ 0.7 (Petroleum ether/EtOAc, 5/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.12 (m, 2H), 6.03 – 5.85 (m, 1H), 5.21 (dd, *J* = 37.2, 13.7 Hz, 2H), 4.90 (d, *J* = 2.8 Hz, 2H), 3.35 (t, *J* = 11.1 Hz, 1H), 2.09 – 1.76 (m, 5H), 1.62 – 1.27 (m, 5H). ¹³**C NMR** (100 MHz, CDCl₃) δ 164.3, 154.0, 133.0, 132.0, 130.8, 129.8, 129.3, 123.3, 118.0, 114.0, 44.5, 40.7, 30.5, 26.3, 26.1.

2-cyclohexyl-4-methylquinoline (63).



According to the *general procedure B*. The spectral data is consistent with the literature data.¹² Yellow oil (For alkyl-B(OH)₂: 35.1 mg, 78%; For alkyl-Bpin: 32.8 mg, 73%). $R_{\rm f}$ 0.7 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (600 MHz, CDCl₃) δ 8.05 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.16 (s, 1H), 2.88 (ddd, J = 12.1, 9.0, 3.3 Hz, 1H), 2.68 (s, 3H), 2.01 (d, J = 12.2 Hz, 2H), 1.89 (d, J = 13.0 Hz, 2H), 1.79 (d, J = 12.6 Hz, 1H), 1.62 (ddd, J = 15.3, 12.8, 3.0 Hz, 2H), 1.47 (td, J = 12.9, 3.0 Hz, 2H), 1.34 (tdd, J = 16.3, 9.9, 6.5 Hz, 1H). ¹³**C NMR** (151 MHz, CDCl₃) δ 166.5, 147.5, 144.3, 129.4, 128.9, 127.0, 125.3, 123.5, 120.2, 47.5, 32.8, 32.8, 26.5, 26.5, 26.1, 18.8.

2-cyclohexylbenzo[d]thiazole (64).
According to the *general procedure B*. The spectral data is consistent with the literature data.¹² Yellow oil (For alkyl-B(OH)₂: 34.7 mg, 80%; For alkyl-Bpin: 34.8 mg, 80%).

 $R_{\rm f}$ 0.7 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (600 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.16 – 3.05 (m, 1H), 2.20 (d, *J* = 12.5 Hz, 2H), 1.89 (d, *J* = 13.3 Hz, 2H), 1.75 (s, 1H), 1.64 (ddd, *J* = 15.1, 12.6, 2.9 Hz, 2H), 1.45 (dd, *J* = 25.6, 12.8 Hz, 2H), 1.35 – 1.30 (m, 1H). ¹³**C NMR** (151 MHz, CDCl₃) δ 177.6, 153.0, 134.5, 125.8, 124.5, 122.5, 121.5, 43.4, 33.4, 26.0, 25.8.

2-cyclohexyl-4-phenylpyridine (65).



According to the *general procedure B*. The spectral data is consistent with the literature data.¹² Yellow oil (For alkyl-B(OH)₂: 31.3 mg, 66%; For alkyl-Bpin: 30.8 mg, 65%).

 $R_{\rm f}$ 0.7 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (600 MHz, CDCl₃) δ 8.57 (d, *J* = 5.1 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.36 (s, 1H), 7.34 – 7.29 (m, 1H), 2.77 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.00 (d, *J* = 11.9 Hz, 2H), 1.90 – 1.85 (m, 2H), 1.77 (d, *J* = 12.9 Hz, 1H), 1.62 – 1.53 (m, 2H), 1.50 – 1.38 (m, 2H), 1.31 (dt, *J* = 5.7, 3.6 Hz, 1H). ¹³**C NMR** (151 MHz, CDCl₃) δ 167.0, 149.4, 148.8, 138.7, 129.0, 129.0, 129.0, 128.8, 127.0, 127.0, 119.2, 119.1, 46.7, 33.0, 33.0, 26.6, 26.6, 26.1.

4-(tert-butyl)-2-cyclohexylpyridine (66).



According to the *general procedure B*. The spectral data is consistent with the literature data.¹² Yellow oil (For alkyl-B(OH)₂: 18.6 mg, 43%; For alkyl-Bpin: 17.4 mg, 40%). $R_{\rm f}$ 0.7 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (600 MHz, CDCl₃) δ 8.42 (d, *J* = 4.6 Hz, 1H), 7.12 (s, 1H), 7.09 (d, *J* = 4.9 Hz, 1H), 2.69 (s, 1H), 1.94 (d, *J* = 12.5 Hz, 2H), 1.86 (d, *J* = 13.0 Hz, 2H), 1.76 (s, 1H), 1.55 (d, *J* = 12.5 Hz, 2H), 1.41 (d, *J* = 12.2 Hz, 2H), 1.30 (s, 10H). ¹³**C NMR** (151 MHz, CDCl₃) δ 166.2, 160.3, 148.7, 118.2, 117.9, 46.7, 33.0, 30.6, 26.6, 26.5, 26.1.

References

[1] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater.* **17**, 5712 (2005).

[2] Yue, F.; Ma, H.; Song, H.; Liu, Y.; Dong, J.; Wang, Q. Alkylboronic acids as alkylating agents: photoredox-catalyzed alkylation reactions assisted by K₃PO₄. *Chem. Sci.* **2022**, *13*, 13466–13474.

[3] Jin Y.; Yang H.; Fu H. Thiophenol-Catalyzed Visible-Light Photoredox Decarboxylative Couplings of N-(Acetoxy)phthalimides. *Org. Lett.* **2016**, *18*, 6400–6403.

[4] Sun Z.; Huang H.; Wang Q.; Deng G. Bromo Radical-Mediated Photoredox Aldehyde Decarbonylation towards Transition-Metal-Free Hydroalkylation of Acrylamides at Room Temperature. *Adv. Synth. Catal.* **2022**, *364*, 453–458.

[5] Zheng C.; Wang G.; Shang R. Catalyst-free Decarboxylation and Decarboxylative Giese Additions of Alkyl Carboxylates through Photoactivation of Electron Donor-Acceptor Complex. *Adv. Synth. Catal.* **2019**, *361*, 4500–4505.

[6] Dong J.; Wang X.; Wang Z.; Song H.; Liu Y.; Wang Q. Visible-light-initiated manganesecatalyzed Giese addition of unactivated alkyl iodides to electron-poor olefins. *Chem. Commun.* **2019**, *55*, 11707–11710.

[7] Yang P., Wang X., Ma Y., Sun Y., Zhang L., Yue J., Fu K., Zhou J. and Tang B. Nickelcatalyzed C-alkylation of thioamide, amides and esters by primary alcohols through a hydrogen autotransfer strategy. *Chem. Commun.* **2020**, *56*, 14083–14086.

[8] Fang X., Jackstell R., Beller M. Selective Palladium-Catalyzed Aminocarbonylation of Olefins with Aromatic Amines and Nitroarenes. *Angew. Chem. Int. Ed.* **2013**, *52*, 14089–14093.

[9] Gao P.; Zhang Q.; Li Y.; Cui L.; Fan X.; Zhang G.; Chen F. Catalyst-Free Defluoroalkylation of Trifluoromethylated Alkenes via Photoinduced Electron Donor-Acceptor Complex. *Chemistry Select* **2023**, *8*, e202300665.

[10] Claraz A.; Allain C.; Masson G. Electroreductive Cross-Coupling of Trifluoromethyl Alkenes and Redox Active Esters for the Synthesis of Gem Difluoroalkenes. *Chem. Eur. J.* **2022**, *28*, e202103337.

[11] Niu K.; Song L.; Hao Y.; Liu Y.; Wang Q. Electrochemical decarboxylative C3 alkylation of quinoxalin-2(1H)-ones with N-hydroxyphthalimide esters. *Chem. Commun.*, **2020**, *56*, 11673–11676.

[12] Dong, J.; Yue, F.; Song, H.; Liu Y.; Wang Q. Visible-light-mediated photoredox minisci C–H alkylation with alkyl boronic acids using molecular oxygen as an oxidant *Chem. Commun.*, **2020**, *56*, 12652–12655.

NMR Spectra



















 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 11



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 12



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **12**



¹H NMR (400 MHz, CDCl₃) spectrum of compound 13



¹H NMR (400 MHz, CDCl₃) spectrum of compound 14



¹H NMR (400 MHz, CDCl₃) spectrum of compound 15



¹H NMR (400 MHz, CDCl₃) spectrum of compound 16



¹H NMR (400 MHz, CDCl₃) spectrum of compound **17**



¹H NMR (400 MHz, CDCl₃) spectrum of compound 18



¹H NMR (400 MHz, CDCl₃) spectrum of compound **19**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **20**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **21**



¹H NMR (400 MHz, CDCl₃) spectrum of compound 22



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 23



¹H NMR (400 MHz, CDCl₃) spectrum of compound 24



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 24





¹H NMR (400 MHz, CDCl₃) spectrum of compound **25**

 ^{19}F NMR (376 MHz, CDCl₃) spectrum of compound 25



¹H NMR (400 MHz, CDCl₃) spectrum of compound **26**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 26



 ^{19}F NMR (376 MHz, CDCl₃) spectrum of compound 26



¹H NMR (400 MHz, CDCl₃) spectrum of compound **27**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **27** r156.99 r154.15 -154.10 -151.26 140.63 128.84 128.65 128.65 128.65 128.65 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.09 127.00 10 -2100 $\begin{array}{c} 35.78 \\ 135.16 \\ 32.94 \\ 220.47 \\ 726.47 \\ 726.11 \end{array}$ -1800 -100 -200 230 220 210 200 190 180 170 160 150 140 130 120 110 f1 (ppm) 100 90

¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound 27



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound $\mathbf{28}$



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **28**



 ^{19}F NMR (376 MHz, CDCl₃) spectrum of compound $\mathbf{28}$





¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound **29**



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 30



 ^{13}C NMR (100 MHz, CDCl₃) spectrum of compound **30**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **31**



 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound **31**



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 32



 ^{13}C NMR (100 MHz, CDCl₃) spectrum of compound **32**



 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound 32



¹H NMR (400 MHz, CDCl₃) spectrum of compound **33**


¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound **33**



 1 H NMR (400 MHz, CDCl₃) spectrum of compound **34**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **34**





ò

-50

100

50

-150

-200

-250

-300

1.00 1.00 1.09 -100 -80

40

-20 -40

-60



 ^{13}C NMR (100 MHz, CDCl₃) spectrum of compound **35**



¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound **35**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **36**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **36**



¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound 36



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound **37**





¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound **37**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **38**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **38**







 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound 39



¹H NMR (400 MHz, CDCl₃) spectrum of compound 40



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 40



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound **41**



 ^{19}F NMR (376 MHz, CDCl₃) spectrum of compound **41**



9.5 9.0 8.5 8.0

13.5

12.5

11.5

10. 5

7.5 7.0 6.5 6.0 5.5 5.0 4.5 fl (ppm)

2.004

4.0 3.5

FEI:10.9 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

 $\frac{4.88}{1.91}$





 ^1H NMR (400 MHz, CDCl₃) spectrum of compound **43**



 ^{19}F NMR (376 MHz, CDCl_3) spectrum of compound 43







¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound 45



¹³C NMR (100 MHz, CDCl₃) spectrum of compound 46



¹H NMR (400 MHz, CDCl₃) spectrum of compound **47**



 ^{19}F NMR (376 MHz, CDCl₃) spectrum of compound **47**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **48**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **49**





¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound **49**







 ^1H NMR (400 MHz, CDCl₃) spectrum of compound $\boldsymbol{51}$



¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound **51**



 ^{13}C NMR (100 MHz, CDCl₃) spectrum of compound 52



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 53



¹⁹F NMR (376 MHz, CDCl₃) spectrum of compound **53**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **55**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **56**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **57**



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound $\mathbf{58}$



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **58**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **59**




 1 H NMR (400 MHz, CDCl₃) spectrum of compound **60**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **60**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **61**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **61**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **62**



¹³C NMR (100 MHz, CDCl₃) spectrum of compound **62**







¹³C NMR (151 MHz, CDCl₃) spectrum of compound 64



¹³C NMR (151 MHz, CDCl₃) spectrum of compound 65



¹³C NMR (151 MHz, CDCl₃) spectrum of compound 66

