**Supporting Information for** 

# Photo-induced transformation of α-diazocarbonyl

## compounds into mono-substituted alpha-halogen derivatives

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## **1. Experimental section**

## a) General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Unless stated otherwise, all reactions were carried out under nitrogen atmosphere (Non-drying conditions). The substrates were synthesized according to the literature methods.<sup>1-3</sup> Microtube reactors need to be monitored and adjusted to ensure experimental safety. Column chromatography was performed using silica gel. Reactions were monitored by TLC and visualized by UV lamp (254 nm) and stained with ethanolic solution of concentrated potassium permanganate. Yields generally referred to chromatographically isolated yields, unless otherwise noted. <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (101 MHz) and <sup>19</sup>F NMR (376 MHz) spectra are recorded on a Bruker AV-400 spectrometer in Chloroform-d (CDCl<sub>3</sub>) with TMS as internal standard. For <sup>1</sup>H NMR (400 MHz), CDCl<sub>3</sub> ( $\delta$  = 7.26 ppm) served as internal standard and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, qd = quartet of doublets, tq = triplet of quartets, brs = broad singlet), coupling constant (in Hz), and integration. GC-MS analysis was performed on 7890A-5975C/Agilent. HR-MS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using TOF as the mass analyzer type. Silica gel was purchased from Qingdao Haiyang Chemical Co., Ltd. The photoreaction instrument (WPP-TEC-1020SL) was purchased from WATTCAS, China. The light source used in the experiment is LED-460 nm, and the manufacturer is also from WATTCAS, China. The reaction vessel is a quartz reaction tube, as shown in the Figure S1.





**Figure S1.** WPP-TEC-1020SL **SPECTROPHOTOCOLORMETER ANALYSIS REPORT FOR LED-460nm (**WATTCAS, China.)

## **Color Parameters:**

CIE(1931:) x	x=0.1461		y =0.0	375			
CIE(1960:) u	CIE(1960:) u =0.1850 v =0.0713						
CIE (1976:)	CIE (1976:) u' =0.1850 v' =0.1070						
Color Tempe	erature : Tc=2500	00K Dominant	Wave: WL.D=	461.00nm Pur	ity: PUR=97.99		
Peak Wave:	WL.P=456.0nm ]	Delta Wave: W	L.H=24.0nm				
Color Tolera	nce: SDCM=195	.3 Ra:Ra=0.	.0				
CRI1=0.0	CRI2=0.0	CRI3=0.0	CRI4=0.0	CRI5=0.0			
CRI6=0.0	CRI7=0.0	CRI8=0.0	CRI9=0.0	CRI10=0.0			
CRI11=0.0	CRI12=0.0	CRI13=0.0	CRI14=0.0	CRI15=0.0			
Photology Parameters:							
Lum Flux: $\Phi(lm) = 221.54 \text{ lm}$ Optical Power: $\Phi(mW) = 4440.3 \text{ mW} \eta(lm/W) = 22.3 \text{ lm/W}$							
Eletric Parameters:							
Forward Vol	tage: VF = 23.64	V Forward	d Current: IF =	419.9 mA	Power = 9.93 W		
Status:							

Wavelength Range	e: 380nm78	30nm Interg	gration Time	: 476 ms
Test Project : LE	D COB TEST	ING	Test Equipm	nent : ZP OPTO SYSTEM
Product Model:H	IGH POWEF	R COB	Manufactu	rer:LEARNEW OPTO
Temperature:25			Humidity:40	)%
Tester:MESSI	LAN Time:	2019-03-12	12:27	Test Mechanism: ZP OPTO LAB

The distance between Reflective surface and Liquid level is 5mm.



Figure S2. Wavelength of peak and spectral distribution and intensity of light source

# b) Methods for the synthesis of substrates Synthesis of α-diazo esters

$$R_{ll}^{\underline{fl}} \xrightarrow{CO_2H} + R^1OH \xrightarrow{H_2SO_4} R_{ll}^{\underline{fl}} \xrightarrow{CO_2R^1} \underbrace{TsN_3, DBU}_{MeCN, r.t., overnight} R_{ll}^{\underline{fl}} \xrightarrow{N_2}_{CO_2R^1}$$

Taking the synthesis of substrate methyl 2-diazo-2-phenylacetate (**a1**) as an example , Phenylacetic acid (53.0 mmol) was added to a round-bottom flask (200 ml) containing methanol (80 mL). After complete dissolution, concentrated sulfuric acid (0.5 mL) was added, stirred and refluxed for 15 hours. Upon cooling the mixture and evaporating the unreacted alcohols, the mixture was subjected to column chromatography (1:50 ethyl acetate/petroleum ether), and ester was obtained as a colourless oil.

DBU (15.0 mmol) was added to ester (10.0 mmol) and *p*-toluenesulfonyl azide (2.960g, 15.0 mmol) in MeCN (15 mL). The reaction mixture was stirred overnight. TLC was used to confirm the consumption of the starting materials, and upon so doing, the reaction mixture was quenched with a saturated solution of NH<sub>4</sub>Cl (5 mL). An extraction with DCM (3 x 30 mL), washing with brine (3 x 10 mL), drying over MgSO<sub>4</sub> was performed, before the mixture was concentrated under pressure to the crude product. Purification by column chromatography (1:100 ethyl acetate/petroleum ether) gave the  $\alpha$ -diazoester as a dark orange oil.<sup>4</sup>

## Synthesis of α-Diazoindolone



Add NaH (1.2 g, 60% dispersed in oil, 30 mmol) to the DMF or THF (100 mL) solution of indigo derivative (20 mmol) at 0 °C. After adding, the color of the solution changes from orange to dark purple. Stir the resulting solution for 15 minutes, and then slowly add alkylating agent (40 mmol) to the solution. The color of the solution changes to reddish brown. Heat the reaction mixture to room temperature and stir for 1 hour. Add ice water (200 mL of water and 60 g of ice) to precipitate and filter the product. Wash the product with hexane, and obtain *N*-alkyl indigo derivatives after

vacuum drying.

Dissolve the *N*-alkyl indigo derivatives (10 mmol) and *p*-toluenesulfonyl hydrazide (11 mmol) obtained in step 1 in 200 mL THF, and stir at 60 °C for 2 hours. After cooling, the solvent is removed by rotary evaporation under reduced pressure, and the residue is dissolved in methanol to precipitate the product. Dissolve crude *p*-tolylhydrazone in 200 mL THF, and add NaOH aqueous solution (0.2 M, 16 mmol). Stir the resulting mixture for 2 hours at room temperature, add water and ethyl acetate to extract the organic phase, wash the resulting crude product solution with saturated salt water, dry it with MgSO<sub>4</sub> and concentrate it in vacuum. The residue is purified on silica gel by column chromatography (petroleum ether: ethyl acetate=10:1) to obtain  $\alpha$ -Diazoindolone compounds.

## c) Optimization of the Reaction Conditions

## Table S1. Fluorinating reagent effect

$\bigcirc$		+	Fluorinating reagent	KH <sub>2</sub> PO <sub>4</sub> , DCM 10 W 460 nm LED [lr(dtbbpy)(ppy) <sub>2</sub> ][PF <sub>6</sub> ]	F O	)_
	a1		C		d1	
	Entry		Fluorinating reag	ent (1.5 equiv.)	Yield $(\%)^a$	
	1		Et <sub>3</sub> N·	3HF	<5%	
	2		CsF			
	3		DAS	ST		
	4		BAS	ST	48	
	5		NFS	SI		

<sup>a</sup> Yields of isolated products.

## Table S2. Additive effect



<sup>a</sup> Yields of isolated products.

		Ò			
1	$N_2$				F
	└ੑੑੑੑੑੑ੦ੑ	+ >_^ / F	KH <sub>2</sub> PO <sub>4</sub> , solv	vent	$\sim \sim \sim$
	II O	' '0' ~ 'S'	10 W 460 nm	LED	
é	a1	c1			d1
entry	a1/c1	Additive (1.5 equiv.)	Solvent (0.1 M)	Blue LED	Yield $(\%)^a$
1	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	DCM	10 W	56
2	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	MeCN	10 W	58
3	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	DCE	10 W	44
4	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	CHCl <sub>3</sub>	10 W	47
5	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	THF	10 W	43
6	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	Acetone	10 W	34
7	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	EA	10 W	37
8	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	Dioxane	10 W	54
9	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	DMF	10 W	54
10	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	HFIP	10 W	
11	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>3</sub> N	10 W	42
12	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	$CCl_4$	10 W	47
13	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	DMSO	10 W	28
14	1/1.5	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	10 W	73
15	1/1	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	10 W	58
16	1/2	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	10 W	85
17	1/3	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	10 W	84
18	1/4	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	10 W	53
19	1/5	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	10 W	64
20 <sup>b</sup>	1/2	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O		
21	1/2	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	7 W	72
22	1/2	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	5 W	63
23	1/2	KH <sub>2</sub> PO <sub>4</sub>	Et <sub>2</sub> O	1 W	47

# Table S3. Optimization of the reaction conditions

<sup>a</sup> Yields of isolated products. <sup>b</sup> Without light.

## Table S4. Optimization of the reaction conditions<sup>a</sup>



Entry	Substrate	Reagent	Reaction conditions <sup>a</sup>	Yield $(\%)^b$
1	b1	Oxalyl Chloride (2.0 eq)	KH <sub>2</sub> PO <sub>4</sub> (1.5 eq), DCM	41
2	b1	Phenylacetyl Chloride	KH <sub>2</sub> PO <sub>4</sub> (1.5 eq), DCM	
		(2.0 eq)		
3	b1	TMSCl (2.0 eq)	$K_2$ HPO <sub>4</sub> (1.5 eq), DCM	67
4	b1	EDCl (2.0 eq)	$KH_2PO_4$ (1.5 eq), DCM	44
5	b1	TMSCl (2.0 eq)	$K_2$ HPO <sub>4</sub> (1.5 eq), DCM	43
6	b1	TMSCl (2.0 eq)	Na <sub>2</sub> CO <sub>3</sub> (1.5 eq), DCM	32
7	b1	TMSCl (2.0 eq)	HAc (1.5 eq), DCM	72
8	b1	TMSC1 (2.0 eq)	TFA (1.5 eq), DCM	79
9	b1	TMSC1 (3.0 eq)	TFA (1.5 eq), DCM	83
10	b1	TMSC1 (4.0 eq)	TFA (1.5 eq), DCM	84
11	b1	TMSC1 (2.0 eq)	TFA (2.0 eq), DCM	80
12	b1	TMSC1 (2.0 eq)	TFA (3.0 eq), DCM	83
13	b1	<b>TMSCl (2.0 eq)</b>	<b>TFA (4.0 eq), DCM</b>	84
14	b1	TMSCl (2.0 eq)	TFA (5.0 eq), DCM	81
15	b1	TMSCl (2.0 eq)	TFA (1.5 eq), $Et_2O$	61
16 <sup>c</sup>	b1	TMSCl (2.0 eq)	TFA (4.0 eq), DCM	18
17	b1	TMSCl (2.0 eq)	TFA (4.0 eq), DCM, 7 W	73
			Blue LED	
18	b1	TMSCl (2.0 eq)	TFA (4.0 eq), DCM, 5 W	63
			Blue LED	
19	b1	TMSCl (2.0 eq)	TFA (4.0 eq), DCM, 1 W	50
			Blue LED	

<sup>a</sup> Reaction conditions: **b1** (0.2 mmol), **c** (0.3 mmol, 1.5 equiv.), additive were dissolved in the solvent, degassed for 15 min under N<sub>2</sub>, 10

W 460 nm LED irradiation at room temperature; <sup>b</sup> Isolated yields; <sup>c</sup> no light.

Table S5. Optimization of the reaction conditions<sup>a</sup>



Entry	Substrate	Reagent	Reaction conditions <sup>a</sup>	Yield $(\%)^b$
1	al	TMSBr (2.0 eq)	TFA (1.5 eq), DCM	88
2	al	TMSBr (2.0 eq)	TFA (1.5 eq), MeCN	82
3	al	TMSBr (2.0 eq)	TFA (1.5 eq), $Et_2O$	83
4	al	TMSBr (2.0 eq)	TFA (1.5 eq), THF	71
5	a1	TMSBr (2.0 eq)	KH <sub>2</sub> PO <sub>4</sub> (1.5 eq), DCM	73
6	al	TMSBr (2.0 eq)	K <sub>2</sub> HPO <sub>4</sub> (1.5 eq), DCM	54
7	a1	TMSBr (2.0 eq)	Na <sub>2</sub> CO <sub>3</sub> (1.5 eq), DCM	31
8	al	TMSBr (2.0 eq)	HAc (1.5 eq), DCM	80
9	<b>a1</b>	TMSBr (2.0 eq)	TFA (2.0 eq), DCM	94
10	a1	TMSBr (3.0 eq)	TFA (2.0 eq), DCM	93
11	a1	TMSBr (4.0 eq)	TFA (2.0 eq), DCM	90
12	a1	TMSBr (5.0 eq)	TFA (2.0 eq), DCM	91
13	al	TMSBr (2.0 eq)	TFA (3.0 eq), DCM	90
14	al	TMSBr (2.0 eq)	TFA (4.0 eq), DCM	91
15	al	TMSBr (2.0 eq)	TFA (5.0 eq), DCM	91
16 <sup>c</sup>	al	TMSBr (2.0 eq)	TFA (2.0 eq), DCM	23
17	a1	TMSBr (2.0 eq)	TFA (2.0 eq), DCM, 7 W	83
			Blue LED	
18	al	TMSBr (2.0 eq)	TFA (2.0 eq), DCM, 5 W	71
19	a1	TMSBr (2.0 eq)	Blue LED TFA (2.0 eq), DCM, 1 W Blue LED	57

<sup>*a*</sup> Reaction conditions: **a1** (0.2 mmol), **c** (0.3 mmol, 1.5 equiv.), additive were dissolved in the solvent, degassed for 15 min under N<sub>2</sub>, 10 W 460 nm LED irradiation at room temperature; <sup>*b*</sup> Isolated yields; <sup>*c*</sup> no light.

## d) General procedure for the photoreactions

**GP-1**:



An oven dried 8 mL reaction vial was charged with a stirring bar. Add  $KH_2PO_4$  (1.5 equiv), Bast (2 equiv) and  $\alpha$ - Diazo compound (0.2 mmol, 1 equiv), then anhydrous ether (0.1 M) was added. The reaction system was deoxygenated by sealing the reaction bottle, evacuating the vacuum, and backfilling with 1 atm of N<sub>2</sub> three times. After deoxygenation, the reaction mixture was stirred and irradiated using a 10 W 460 nm LED lamp (WATTCAS: WPTEC-1020LC) for 2 hours until the reaction was complete (monitored by TLC). After reaction, the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

**GP-2**:



An oven dried 8 mL reaction vial was charged with a stirring bar. Add TFA (4.0 equiv), TMSCl (2.0 equiv) and  $\alpha$ -Diazoindolone (0.2 mmol, 1 equiv), then DCM (0.1 M) was added. The reaction system was deoxygenated by sealing the reaction bottle, evacuating the vacuum, and backfilling with 1 atm of N<sub>2</sub> three times. The reaction mixture was stirred and irradiated using a 10 W 460 nm LED lamp (WATTCAS: WPTEC-1020LC) for 2 hours until the reaction was complete (monitored by TLC). After reaction, the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

**GP-3**:



An oven dried 8 mL reaction vial was charged with a stirring bar. Add TFA (2.0 equiv), TMSBr (2.0 equiv) and  $\alpha$ -Diazo compound (0.2 mmol, 1 equiv), then DCM (0.1 M) was added. The reaction system was deoxygenated by sealing the reaction bottle, evacuating the vacuum, and backfilling with 1 atm of N<sub>2</sub> three times. The reaction mixture was stirred and irradiated using a 10 W 460 nm LED lamp (WATTCAS: WPTEC-1020LC) for 2 hours until the reaction was complete (monitored by TLC). After reaction, the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

## e) Gram reaction experiment.



Methyl  $\alpha$ -diazoacetate **a1** (1.76 g, 10 mmol), BAST (4.42 g, 20 mmol) were added to a 200 ml flask equipped with a rubber septum containing 22.5 mL of anhydrous acetonitrile and sparged with nitrogen 20 minutes. Mix with a magnetic stirrer and connect the system to a flow reactor with a peristaltic pump (purchased from Sanota) (Figure S3). The combined reaction system flow rate was set to 1 ml/min and the reaction mixture would flow into a microtube reactor (PFA was purchased from Agilent Technologies Inc., OD = 1/8", ID = 1/16", 10 m, volume = 18.8 mL, the distances between the photolysis lamps (LED lamp) and the reaction vessels (PFA Tube) are 2 mm.) and be illuminated with 40 W blue LED. Use fan ventilation to keep the device at room temperature. The residence time in the reactor was controlled at 1 hours, after which the reaction was quenched and processed to finally obtain 1.33 g of methyl mandelate **d1** (yield 79%).

 $\alpha$ -Diazoindolone **b1** (1.73 g, 10 mmol), TFA (4.56g, 40 mmol), TMSCl (2,17g, 20 mmol) were added to a 200 ml flask equipped with a rubber septum containing 25 mL of DCM and sparged with nitrogen 20 minutes. Mix with a magnetic stirrer and connect the system to a flow reactor with a peristaltic pump (purchased from Sanota) (Figure S3). The combined reaction system flow rate was set to 1 ml/min and the reaction mixture would flow into a microtube reactor (PFA was purchased from

Agilent Technologies Inc., OD = 1/8", ID = 1/16", 10 m, volume = 18.8 mL, the distances between the photolysis lamps (LED lamp) and the reaction vessels (PFA Tube) are 2 mm.) and be illuminated with 40 W blue LED. Use fan ventilation to keep the device at room temperature. The residence time in the reactor was controlled at 1 hours, after which the reaction was quenched and processed to finally obtain 1.33 g of **e1** (yield 81%).

Methyl  $\alpha$ -diazoacetate **a1** (1.76 g, 10 mmol), TFA (2.28 g, 20 mmol), TMSBr (3.06 g, 20 mmol) were added to a 200 ml flask equipped with a rubber septum containing 25 mL of DCM and sparged with nitrogen 20 minutes. Mix with a magnetic stirrer and connect the system to a flow reactor with a peristaltic pump (purchased from Sanota) (Figure S3). The combined reaction system flow rate was set to 1 ml/min and the reaction mixture would flow into a microtube reactor (PFA was purchased from Agilent Technologies Inc., OD = 1/8", ID = 1/16", 10 m, volume = 18.8 mL, the distances between the photolysis lamps (LED lamp) and the reaction vessels (PFA Tube) are 2 mm.) and be illuminated with 40 W blue LED. Use fan ventilation to keep the device at room temperature. The residence time in the reactor was controlled at 1 hours, after which the reaction was quenched and processed to finally obtain 2.03 g of **f1** (yield 89%).





Figure S3. Flow reactor.

## f) Deuteration experiment.



An oven dried 8 mL reaction vial was charged with a stirring bar. Add KH<sub>2</sub>PO<sub>4</sub> (1.5 equiv), Bast (2 equiv), D<sub>2</sub>O (7  $\mu$ L) and  $\alpha$ -Diazo compound (0.2 mmol, 1 equiv), then anhydrous ether (0.1 M) was added. The reaction system was deoxygenated by sealing the reaction bottle, evacuating the vacuum, and backfilling with 1 atm of N<sub>2</sub> three times. The reaction mixture was stirred and irradiated using a 10 W 460 nm LED lamp (WATTCAS: WPTEC-1020LC) for 2 hours until the reaction was complete (monitored by TLC). After reaction, the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, obtain 13.8 mg of d1/d1-[D] (yield 41%).

An oven dried 8 mL reaction vial was charged with a stirring bar. Add TFA-[D] (4.0 equiv), TMSCl (2.0 equiv) and  $\alpha$ -Diazoindolone (0.2 mmol, 1 equiv), then DCM (0.1 M) was added. The reaction system was deoxygenated by sealing the reaction bottle, evacuating the vacuum, and backfilling with 1 atm of N<sub>2</sub> three times. The reaction mixture was stirred and irradiated using a 10 W 460 nm LED lamp (WATTCAS: WPTEC-1020LC) for 2 hours until the reaction was complete (monitored by TLC). After reaction, the solvent was removed by rotary evaporation

and purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent. obtain 15.2 mg of **e1/e1-[D]** (yield 46%).

An oven dried 8 mL reaction vial was charged with a stirring bar. Add TFA-[D] (2.0 equiv), TMSBr (2.0 equiv) and  $\alpha$ -Diazo compound (0.2 mmol, 1 equiv), then DCM (0.1 M) was added. The reaction system was deoxygenated by sealing the reaction bottle, evacuating the vacuum, and backfilling with 1 atm of N<sub>2</sub> three times. The reaction mixture was stirred and irradiated using a 10 W 460 nm LED lamp (WATTCAS: WPTEC-1020LC) for 2 hours until the reaction was complete (monitored by TLC). After reaction, the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent. obtain 29.2mg of **f1/f1-[D]** (yield 64%).

## 2. Characterization data of the products

methyl 2-fluoro-2-phenylacetate (d1)<sup>5</sup>

The reaction was performed following the GP-1, giving the product (28.6 mg, 85% yield) as a colorless oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.50 (d, J = 4.7 Hz, 2H), 7.47 – 7.41 (m, 3H), 5.84 (d, J = 47.6 Hz, 1H), 3.82 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 169.1 (d, J = 27.7 Hz), 134.2(d, J = 20.5 Hz), 129.7 (d, J = 1.8 Hz), 128.9, 126.7 (d, J = 6.0 Hz), 89.4 (d, J = 185.4 Hz), 52.7. <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -179.9 (d, J = 47.7 Hz, 1F). **HRMS** (m/z):C<sub>9</sub>H<sub>10</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 169.0659, found 169.0663.

#### methyl 2-fluoro-2-phenylacetate-d (d1-[D])



The reaction was performed following the GP-1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.53 – 7.42 (m, 5H), 3.82 (d, J = 1.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 135.1, 130.2, 129.8, 128.9 (d, J = 9.8 Hz), 126.7 (d, J = 6.2 Hz), 52.8 (d, J = 14.7 Hz), 29.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = - 178.6 – -182.5 (m, 1F). HRMS (m/z):C<sub>9</sub>H<sub>10</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 170,0722, found 170.0717.

methyl 2-fluoro-2-(2-fluorophenyl)acetate (d2)<sup>6</sup>



The reaction was performed following the GP-1, giving the product (22.8 mg, 61% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 – 7.40 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.16 (ddt, *J* = 9.6, 8.3, 1.2 Hz, 1H), 6.11 (d, *J* = 46.8 Hz, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.4 (d, *J* = 58.2 Hz), 131.9 (d, *J* = 9.5 Hz), 128.9, 124.7, 116.0 (d, *J* = 21.2 Hz), 52.87. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -117.6 (q, *J* = 7.7, 7.2 Hz, 1F), -181.1 (d, *J* = 47.0 Hz, 1F). HRMS (m/z):C<sub>9</sub>H<sub>9</sub>F<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 187.0565, found 187.0566.

methyl 2-fluoro-2-(2-chlorophenyl)acetate (d3)<sup>5</sup>



The reaction was performed following the GP-1, giving the product (28.9 mg, 72% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (dd, J = 7.0, 2.5 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.45 – 7.33 (m, 2H), 6.27 (d, J = 46.6 Hz, 1H), 3.84 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.5 (d, J = 27.8 Hz), 133.6 , 132.3 (d, J = 20.6 Hz), 131.1 (d, J = 2.5 Hz), 130.0 , 128.8 (d, J = 6.1 Hz), 127.4 , 87.2 , 85.3 , 52.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -180.7 (d, J = 46.8 Hz, 1F). HRMS (m/z):C<sub>9</sub>H<sub>9</sub>ClFO<sub>2</sub> ([M+H]<sup>+</sup>): 203.0270, found 203.0274.

methyl 2-fluoro-2-(2-bromophenyl)acetate (d4)



The reaction was performed following the GP-1, giving the product (33.8 mg, 69% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.68 – 7.30 (m, 4H), 6.26 (d, *J* = 46.4 Hz, 1H), 3.83 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.5 (d, *J* = 27.8 Hz), 133.3, 131.3 (d, *J* = 2.5 Hz), 128.8 (d, *J* = 6.2 Hz), 128.0, 123.4 (d, *J* = 4.6 Hz), 88.4 (d, *J* = 184.6 Hz), 52.9. <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -181.4 (d, *J* = 47.3 Hz, 1F). **HRMS** (m/z):C<sub>9</sub>H<sub>9</sub>BrFO<sub>2</sub> ([M+H]<sup>+</sup>): 246.9764, found 246.9767.

### methyl 2-fluoro-2-(3-nitrophenyl)acetate (d5)<sup>5</sup>



The reaction was performed following the GP-1, giving the product (36.2 mg, 85% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 8.40 – 8.23 (m, 2H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 5.95 (d, *J* = 46.9 Hz, 1H), 3.84 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.0 (d, *J* = 26.9 Hz), 148.4, 136.2 (d, *J* = 21.5 Hz), 132.2 (d, *J* = 6.4 Hz), 130.1, 124.5, 121.6 (d, *J* = 7.5 Hz), 88.1 (d, *J* = 188.7 Hz), 53.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -184.3 (d, *J* = 47.0 Hz, 1F). HRMS (m/z):C<sub>9</sub>H<sub>10</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 169.0659, found 169.0663.

methyl 2-fluoro-2-(3-fluorophenyl)acetate (d6)<sup>6</sup>



The reaction was performed following the GP-1, giving the product (27.5 mg, 74% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.42 (dd, J = 14.7, 7.0 Hz, 1H), 7.31 – 7.05 (m, 3H), 5.83 (d, J = 47.3 Hz, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.5 (d, J = 27.4 Hz), 164.1, 136.4 (dd, J = 21.0, 7.6 Hz), 130.6 (d, J = 8.1 Hz), 122.2 (dd, J = 6.5, 3.2 Hz), 116.7 (dd, J = 21.1, 1.9 Hz), 113.7 (dd, J = 23.1, 6.9 Hz), 88.6 (dd, J = 187.1, 2.0 Hz), 52.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -111.5 – -111.9 (m, 1F), -182.1 (d, J = 47.2 Hz, 1F). HRMS (m/z):C<sub>9</sub>H<sub>9</sub>F<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 187.0565, found 187.0566.

methyl 2-fluoro-2-(3-chlorophenyl)acetate (d7)



The reaction was performed following the GP-1, giving the product (29.4 mg, 73% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.50 (s, 1H), 7.38 (d, *J* = 5.9 Hz, 3H), 5.80 (d, *J* = 47.3 Hz, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.5 (d, *J* = 27.3 Hz), 136.0 (d, *J* = 20.9 Hz), 134.9, 130.2, 129.9 (d, *J* = 1.9 Hz), 126.7 (d, *J* = 6.9 Hz), 124.7 (d, *J* = 6.5 Hz), 88.6 (d, *J* = 187.3 Hz), 52.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -182.6 (d, *J* = 47.2 Hz, 1F). HRMS (m/z):C<sub>9</sub>H<sub>9</sub>ClFO<sub>2</sub> ([M+H]<sup>+</sup>): 203.0270, found 203.0274.

methyl 2-fluoro-2-(3-bromophenyl)acetate (d8)<sup>7</sup>



The reaction was performed following the GP-1, giving the product (37.9 mg, 77% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.64 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.34 - 7.23 (m, 1H), 5.79 (d, *J* = 47.3 Hz, 1H), 3.81 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.5 (d, *J* = 27.4 Hz), 136.3 (d, *J* = 21.0 Hz), 132.8 (d, *J* = 2.1 Hz), 130.5, 129.6 (d, *J* = 6.7 Hz),

125.2 (d, *J* = 6.3 Hz), 122.9, 88.5 (d, *J* = 187.2 Hz), 52.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ ppm = -182.0 (d, *J* = 47.3 Hz, 1F). HRMS (m/z):C<sub>9</sub>H<sub>9</sub>BrFO<sub>2</sub> ([M+H]<sup>+</sup>): 246.9764, found 246.9767.

*methyl 2-fluoro-2-(3-(trifluoromethyl)phenyl)acetate* (d9)



The reaction was performed following the GP-1, giving the product (26.4 mg, 56% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.77 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 47.2 Hz, 1H), 3.84 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.3 (d, *J* = 27.0 Hz), 135.2 (d, *J* = 21.0 Hz), 130.1 – 129.1 (m), 126.5, 123.4 (t, *J* = 5.2 Hz), 88.6 (d, *J* = 187.5 Hz), 53.0. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -62.8 (3F), -183.2 (d, *J* = 47.1 Hz, 1F). HRMS (m/z):C<sub>10</sub>H<sub>9</sub>F4O<sub>2</sub> ([M+H]<sup>+</sup>):237.0533, found 237.0530.

methyl 2-(4-(tert-butyl)phenyl)-2-fluoroacetate (d10)<sup>6</sup>



The reaction was performed following the GP-1, giving the product (38.1 mg, 85% yield) as a light yellow oil (The main impurity is dimethyl 2,3-diphenylfumarate). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.45 (q, J = 8.3 Hz, 4H), 5.81 (d, J = 47.7 Hz, 1H), 3.82 (s, 3H), 1.36 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 169.4 (d, J = 28.0 Hz), 153.1 (d, J = 2.5 Hz), 150.2, 131.8 – 130.6 (m), 129.1, 126.8 (d, J = 5.7 Hz), 126.0, 125.7, 89.5 (d, J = 184.7 Hz), 52.5 (d, J = 59.0 Hz), 40.9, 34.8 (d, J = 28.5 Hz), 31.5 (d, J = 10.8 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -178.0 (d, J = 48.0 Hz, 1F). HRMS (m/z):C<sub>13</sub>H<sub>17</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 224.1213, found 224.1218.

methyl 2-fluoro-2-(4-chlorophenyl)acetate (d11)8



The reaction was performed following the GP-1, giving the product (34.7 mg, 82% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.47 – 7.36 (m, 4H), 5.80 (d, *J* = 47.2 Hz, 1H), 3.80 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.7 (d, *J* = 27.7 Hz), 135.8 (d, *J* = 2.6 Hz), 132.7 (d, *J* 

= 21.0 Hz), 129.1, 128.1 (d, *J* = 6.2 Hz), 88.7 (d, *J* = 186.2 Hz), 52.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ ppm = -180.9 (d, *J* = 47.4 Hz, 1F). HRMS (m/z):C<sub>9</sub>H<sub>9</sub>ClFO<sub>2</sub> ([M+H]<sup>+</sup>): 203.0270, found 203.0274. *methyl 2-fluoro-2-(4-bromophenyl)acetate* (d12)<sup>9</sup>



The reaction was performed following the GP-1, giving the product (43.4 mg, 88% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.57 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.79 (d, *J* = 47.3 Hz, 1H), 3.80 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.6 (d, *J* = 27.5 Hz), 133.2 (d, *J* = 21.0 Hz), 132.1, 128.3 (d, *J* = 6.2 Hz), 124.0 (d, *J* = 2.6 Hz), 88.7 (d, *J* = 186.5 Hz), 52.8. <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -181.4 (d, *J* = 47.3 Hz, 1F). **HRMS** (m/z):C<sub>9</sub>H<sub>9</sub>BrFO<sub>2</sub> ([M+H]<sup>+</sup>): 246.9764, found 246.9767.

methyl 4-(1-fluoro-2-methoxy-2-oxoethyl)benzoate (d13)<sup>5</sup>



The reaction was performed following the GP-1, giving the product (36.1 mg, 80% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 8.09 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 5.88 (d, J = 47.4 Hz, 1H), 3.93 (s, 3H), 3.79 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.4 (d, J = 27.0 Hz), 166.4, 138.8 (d, J = 20.5 Hz), 131.3 (d, J = 1.8 Hz), 130.1, 126.4 (d, J = 6.5 Hz), 88.8 (d, J = 187.0 Hz), 52.9, 52.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -183.8 (d, J = 47.2 Hz, 1F). HRMS (m/z):C<sub>11</sub>H<sub>12</sub>FO<sub>4</sub> ([M+H]<sup>+</sup>): 227.0714, found 227.0713.

methyl 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetate (d14)



The reaction was performed following the GP-1, giving the product (38.1 mg, 78% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.69 (d, *J* = 8.0 Hz, 2H), 7.63 (s, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 5.90 (d, *J* = 47.5 Hz, 1H), 3.86 (s, 3H). <sup>13</sup>**C** 

NMR (101 MHz, CDCl<sub>3</sub>) δ ppm = 169.1 (d, *J* = 27.9 Hz), 142.7, 140.3, 133.1 (d, *J* = 20.6 Hz), 129.8, 129.0, 127.7 (d, *J* = 19.6 Hz), 127.2, 89.2 (d, *J* = 185.4 Hz), 52.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ ppm = -179.4 (d, *J* = 47.5 Hz, 1F). HRMS (m/z):C<sub>15</sub>H<sub>14</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 245.0972, found 245.0974.

ethyl 2-(4-bromophenyl)-2-fluoroacetate (d15)<sup>10</sup>



The reaction was performed following the GP-1, giving the product (42.7 mg, 82% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.57 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.76 (d, *J* = 47.5 Hz, 1H), 4.47 – 3.99 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.1 (d, *J* = 27.4 Hz), 133.4 (d, *J* = 20.8 Hz), 132.0, 128.3 (d, *J* = 6.3 Hz), 123.9 (d, *J* = 2.7 Hz), 88.7 (d, *J* = 186.4 Hz), 62.1, 14.1. <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -181.3 (d, *J* = 47.5 Hz, 1F). **HRMS (m/z)**:C<sub>10</sub>H<sub>11</sub>BrFO<sub>2</sub> ([M+H]<sup>+</sup>): 260.9921, found 260.992.

methyl 2-(3,4-dichlorophenyl)-2-fluoroacetate (d16)



The reaction was performed following the GP-1, giving the product (27.4 mg, 58% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.60 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 5.78 (d, *J* = 47.1 Hz, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.2 (d, *J* = 27.2 Hz), 134.6 – 133.8 (m), 133.2, 130.9, 128.5 (d, *J* = 6.9 Hz), 125.7 (d, *J* = 6.4 Hz), 88.0 (d, *J* = 188.1 Hz), 53.0. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -182.8 (d, *J* = 47.1 Hz, 1F). HRMS (m/z):C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 236.9880, found 236.9885.

methyl 2-fluoro-2-(naphthalen-2-yl)acetate (d17)<sup>8</sup>



The reaction was performed following the GP-1, giving the product (35.8 mg, 82% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 8.23 (d, *J* = 8.4 Hz, 1H), 7.95 (t, *J* = 8.7 Hz, 2H), 7.68 – 7.60 (m, 2H), 7.60 – 7.51 (m, 2H), 6.42 (d, *J* = 46.9 Hz, 1H), 3.80 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 169.4 (d, *J* = 27.9 Hz), 133.9, 130.7, 130.1 (d, *J* = 18.9 Hz), 128.9, 128.1 (d, *J* = 8.7 Hz)

Hz), 127.2, 127.0 (d, *J* = 7.9 Hz), 126.3, 125.7 (d, *J* = 30.9 Hz), 125.1, 123.7, 88.7 (d, *J* = 185.1 Hz), 52.8, 39.1. <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ ppm = -177.8 (d, *J* = 46.9 Hz, 1F). **HRMS (m/z)**:C<sub>13</sub>H<sub>12</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 219.0816, found 219.0818.

methyl 2-fluoro-2-(naphthalen-1-yl)acetate (d18)<sup>11</sup>



The reaction was performed following the GP-1, giving the product (35.3 mg, 81% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 8.22 (d, *J* = 8.4 Hz, 1H), 8.00 – 7.90 (m, 2H), 7.68 – 7.52 (m, 4H), 6.42 (d, *J* = 46.9 Hz, 1H), 3.80 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 169.5 (d, *J* = 27.9 Hz), 134.0, 131.0 – 130.5 (m), 130.1 (d, *J* = 18.7 Hz), 128.9 (d, *J* = 9.8 Hz), 127.2, 127.0 (d, *J* = 7.9 Hz), 126.3, 125.7 (d, *J* = 31.2 Hz), 125.2, 123.8 (d, *J* = 11.0 Hz), 88.7 (d, *J* = 185.2 Hz), 52.8, 39.1. <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -177.9 (d, *J* = 46.9 Hz, 1F). **HRMS (m/z)**:C<sub>13</sub>H<sub>12</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 219.0816, found 219.0818.

allyl 2-fluoro-2-phenylacetate (d19)



The reaction was performed following the GP-1, giving the product (26.4 mg, 68% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.55 – 7.32 (m, 5H), 5.98 – 5.89 (m, 1H), 5.36 – 5.19 (m, 2H), 4.72 (t, *J* = 5.6 Hz, 1H), 4.64 (d, *J* = 7.1 Hz, 1H), 3.70 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.3 (d, *J* = 27.5 Hz), 134.2 (d, *J* = 20.5 Hz), 132.1, 131.2, 129.7 (d, *J* = 2.3 Hz), 129.4, 128.8 (d, *J* = 22.0 Hz), 127.2, 126.7 (d, *J* = 6.0 Hz), 119.1, 118.3, 89.4 (d, *J* = 185.8 Hz), 65.9 (d, *J* = 65.9 Hz), 41.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -179.9 (d, *J* = 47.4 Hz, 1F). HRMS (m/z):C<sub>11</sub>H<sub>12</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 195.0816, found 195.0811.

2-isopropoxyethyl 2-fluoro-2-phenylacetate (d20)



The reaction was performed following the GP-1, giving the product (31.2 mg, 65% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.54 – 7.40 (m, 5H), 5.82 (d, *J* = 47.6 Hz, 1H), 4.26 (t, *J* = 5.3 Hz, 2H), 3.52 (t, *J* = 6.2 Hz, 2H), 2.04 – 1.61 (m, 6H), 1.30 (s, 1H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.6 (d, *J* = 27.7 Hz), 134.3 (d, *J* = 20.5 Hz), 129.8 (d, *J* = 2.4 Hz), 128.9, 126.6 (d, *J* = 6.1 Hz), 89.4 (d, *J* = 185.8 Hz), 64.9, 44.3, 28.9, 25.9. <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -180.3 (d, *J* = 47.7 Hz, 1F). **HRMS (m/z)**:C<sub>13</sub>H<sub>16</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 241.1234, found 241.1233.

1-cyclohexylpropyl 2-fluoro-2-phenylacetate (d21)



The reaction was performed following the GP-1, giving the product (33.3 mg, 60% yield) as a light yellow oil (The main impurity is bis(1-cyclohexylpropyl) 2,3-diphenylfumarate). <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 8.03 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.41 (m, 4H), 5.79 (dd, *J* = 48.1, 1.4 Hz, 1H), 5.03 – 4.74 (m, 1H), 1.96 (dd, *J* = 65.1, 9.7 Hz, 6H), 1.58 – 1.23 (m, 10H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 168.0, 134.9, 130.0, 129.5, 129.0, 128.8, 126.7 (d, *J* = 6.1 Hz), 89.5 (d, *J* = 185.3 Hz), 74.4, 31.5 (d, *J* = 9.8 Hz), 31.2, 25.2, 23.7, 23.5 (d, *J* = 12.3 Hz). <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -179.9 (d, *J* = 48.2 Hz, 1F). **HRMS (m/z)**:C<sub>17</sub>H<sub>24</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 279.1755, found 279.1752.

3,4-dimethylpentyl 2-fluoro-2-phenylacetate (d22)



The reaction was performed following the GP-1, giving the product (34.3 mg, 68% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.54 – 7.47 (m, 2H), 7.44 (dd, J = 4.9, 2.0 Hz, 3H), 5.83 (d, J = 47.7 Hz, 1H), 4.04 – 3.97 (m, 2H), 3.91 (d, J = 6.6 Hz, 1H), 3.67 (s, 1H), 1.97 – 1.93 (m, 1H), 1.54 – 1.20 (m, 1H), 0.95 – 0.87 (m, 9H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 173.4 – 166.6 (m), 134.6, 134.3 (d, J = 10.4 Hz), 129.6 (d, J = 2.2 Hz), 129.3, 128.8, 128.6 (d, J = 8.4 Hz), 126.7 (d, J = 6.0 Hz), 89.4 (d, J = 185.6 Hz), 71.7, 71.0 (d, J = 4.7 Hz), 41.6, 27.7 (d, J = 4.2 Hz), 19.1, 18.8, 31.2, 25.2, 23.7, 23.5 (d, J = 12.3 Hz). <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -180.4 (d, J = 47.6 Hz, 1F).

**HRMS (m/z)**:C<sub>15</sub>H<sub>22</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 253.1598, found 253.1600.

phenethyl 2-fluoro-2-phenylacetate (d23)



The reaction was performed following the GP-1, giving the product (36.6 mg, 71% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (m, 4H), 7.28 (m, 4H), 7.17 – 7.10 (m, 2H), 5.79 (dd, J = 47.6, 3.2 Hz, 1H), 4.44 (tt, J = 7.1, 3.6 Hz, 2H), 2.96 (q, J = 4.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.5 (d, J = 27.7 Hz), 137.2, 134.2 (d, J = 20.6 Hz), 129.6, 128.9, 128.8, 128.6, 126.7, 126.7, 90.3, 88.5, 66.1, 34.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -180.2 (d, J = 47.5 Hz, 1F). HRMS (m/z):C<sub>16</sub>H<sub>16</sub>FO<sub>2</sub> ([M+H]<sup>+</sup>): 259.1129, found 259.1133.

2-(3-(4-(tert-butyl)phenyl)propoxy)ethyl 2-fluoro-2-phenylacetate (d24)



The reaction was performed following the GP-1, giving the product (40.2 mg, 54% yield) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 8.15 – 7.30 (m, 10H), 5.82 (d, *J* = 47.6 Hz, 1H), 4.47 (t, *J* = 6.0 Hz, 2H), 4.25 (t, *J* = 6.0 Hz, 2H), 3.68 – 3.59 (m, 2H), 3.51 (t, *J* = 6.1 Hz, 2H), 2.18 – 1.70 (m, 10H), 1.29 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 186.3, 168.6 (d, *J* = 27.8 Hz), 163.9, 135.1, 134.3 (d, *J* = 20.6 Hz), 132.4, 130.1, 129.8 (d, *J* = 2.4 Hz), 129.3, 129.0 (d, *J* = 13.5 Hz), 128.7, 126.7 (d, *J* = 6.1 Hz), 89.4 (d, *J* = 185.8 Hz), 69.7 – 61.5 (m), 46.3 – 43.0 (m), 30.8 – 27.2 (m), 27.2 – 24.3 (m). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = -180.2 (d, *J* = 47.3 Hz, 1F). HRMS (m/z):C<sub>23</sub>H<sub>30</sub>FO<sub>3</sub> ([M+H]<sup>+</sup>): 373.2173, found 373.2172.`

3-chloro-1-methylindolin-2-one (e1)<sup>12</sup>



The reaction was performed following the GP-2, giving the product (30.4 mg, 84% yield) as a dark red liquid. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 – 7.35 (m, 2H), 7.16 (td, J = 7.6, 3.0 Hz, 1H), 6.88 (dd, J = 8.0, 3.1 Hz, 1H), 5.17 (d, J = 3.1 Hz, 3H), 3.26 (dd, J = 3.3, 1.4 Hz, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.2, 143.9, 130.6, 125.6, 125.7, 123.5, 108.8, 51.6, 26.8. **HRMS (m/z)**:C<sub>9</sub>H<sub>9</sub>ClNO ([M+H]<sup>+</sup>): 182.0367, found 182.0366.`

3-chloro-1-methylindolin-2-one-3-d (e1-[D])



The reaction was performed following the GP-2. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 – 7.34 (m, 2H), 7.15 (ddt, J = 7.6, 6.6, 1.3 Hz, 1H), 6.87 (d, J = 7.9 Hz, 1H), 5.16 (s, 1H), 3.26 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.1, 143.9, 130.6, 125.8, 125.7, 123.5, 108.8, 77.4, 77.1, 76.8, 51.6, 26.7. HRMS (m/z):C<sub>9</sub>H<sub>8</sub>DClNO ([M+H]<sup>+</sup>): 183.0430, found 183.0433.'

3-chloro-1,7-dimethylindolin-2-one (e2)<sup>13</sup>



The reaction was performed following the GP-2, giving the product (29.7 mg, 76% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 5.11 (s, 1H), 3.53 (s, 3H), 2.59 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.9, 141.6, 134.2, 126.3, 123.7, 123.4, 120.5, 51.4, 30.1, 18.9. HRMS (m/z):C<sub>10</sub>H<sub>11</sub>ClNO ([M+H]<sup>+</sup>): 196.0524, found 196.0522. *3,4-dichloro-1-methylindolin-2-one* (e3)<sup>13</sup>



The reaction was performed following the GP-2, giving the product (29.2 mg, 68% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (t, J = 8.1 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 6.79 (d, J = 7.8

Hz, 1H), 5.17 (s, 1H), 3.26 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.3, 145.5, 132.7, 131.9, 124.0,

123.1, 107.2, 50.7, 27.0. HRMS (m/z):C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>NO ([M+H]<sup>+</sup>): 215.9977, found 215.9983.

4-bromo-3-chloro-1-methylindolin-2-one (e4)<sup>13</sup>

The reaction was performed following the GP-2, giving the product (27.5 mg, 53% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (dp, J = 10.4, 4.4 Hz, 2H), 6.84 (p, J = 5.5, 4.9 Hz, 1H), 5.11 (s, 1H), 3.27 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.1, 145.6, 132.0, 127.0, 125.1, 121.1, 107.7, 52.1, 27.0. HRMS (m/z):C<sub>9</sub>H<sub>9</sub>BrClNO ([M+H]<sup>+</sup>): 259.9472, found 259.9477.

3-chloro-1,5-dimethylindolin-2-one (e5)14



The reaction was performed following the GP-2, giving the product (27.8 mg, 71% yield) as a dark red oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (d, J = 11.6 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 5.13 (s, 1H), 3.24 (s, 3H), 2.38 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.1, 141.5, 133.2, 130.8, 126.4, 125.7, 108.5, 51.8, 26.8, 21.1. **HRMS** (m/z):C<sub>10</sub>H<sub>11</sub>ClNO ([M+H]<sup>+</sup>): 196.0524, found 196.0522.

### 3-chloro-5-methoxy-1-methylindolin-2-one (e6)14



The reaction was performed following the GP-2, giving the product (32.1 mg, 76% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.06 (d, J = 2.5 Hz, 1H), 6.92 (dd, J = 8.5, 2.6 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 5.13 (s, 1H), 3.84 (s, 3H), 3.23 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 156.6, 137.2, 126.8, 115.3, 112.6, 109.3, 56.0, 51.9, 26.8. HRMS (m/z):C<sub>10</sub>H<sub>11</sub>ClNO<sub>2</sub> ([M+H]<sup>+</sup>): 212.0473, found 212.0472.

3,5-dichloro-1-methylindolin-2-one (e7)<sup>13</sup>



The reaction was performed following the GP-2, giving the product (31.0 mg, 72% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (dt, J = 2.2, 1.3 Hz, 1H), 7.38 (dd, J = 8.2, 2.0 Hz, 1H), 6.81 (dd, J = 8.3, 1.4 Hz, 1H), 5.14 (s, 1H), 3.25 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.6, 142.4, 130.5, 128.9, 127.2, 126.2, 109.7, 51.0, 26.9. HRMS (m/z):C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>NO ([M+H]<sup>+</sup>): 215.9977, found 215.9983. *5-bromo-3-chloro-1-methylindolin-2-one* (e8)<sup>15</sup>



The reaction was performed following the GP-2, giving the product (38.9 mg, 75% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, J = 2.0, 1.0 Hz, 1H), 7.55 – 7.50 (m, 1H), 6.76 (d, J = 8.3 Hz, 1H), 5.14 (s, 1H), 3.25 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.5, 142.9, 133.4, 128.9, 127.6, 116.0, 110.2, 50.9, 26.9. HRMS (m/z):C<sub>9</sub>H<sub>9</sub>BrClNO ([M+H]<sup>+</sup>): 259.9472, found 259.9477.

3,6-dichloro-1-methylindolin-2-one (e9)14



The reaction was performed following the GP-2, giving the product (34.0 mg, 79% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (dd, J = 8.0, 1.0 Hz, 1H), 7.14 (dd, J = 8.0, 1.8 Hz, 1H), 6.89 (d, J = 1.8 Hz, 1H), 5.13 (s, 1H), 3.26 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.1, 145.5, 126.6, 124.0, 123.4, 109.6, 77.4, 77.3, 77.1, 76.8, 50.9, 26.9. HRMS (m/z):C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>NO ([M+H]<sup>+</sup>): 215.9977, found 215.9983.

3-chloro-1,5,7-trimethylindolin-2-one (e10)



The reaction was performed following the GP-2, giving the product (28.8 mg, 69% yield) as a dark red oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.10 (s, 1H), 6.92 (s, 1H), 5.08 (s, 1H), 3.50 (s, 3H), 2.54 (s, 3H),

2.32 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.8, 139.1, 134.7, 133.0, 126.3, 124.4, 120.2, 51.6, 30.1, 29.8, 20.7, 18.7. HRMS (m/z):C<sub>11</sub>H<sub>13</sub>ClNO ([M+H]<sup>+</sup>): 210.0680, found 210.0686.

1-allyl-3-chloroindolin-2-one (e11)<sup>16</sup>



The reaction was performed following the GP-2, giving the product (24.0 mg, 58% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (d, J = 7.4 Hz, 1H), 7.36 (t, J = 8.4 Hz, 1H), 7.21 – 7.10 (m, 1H), 6.88 (d, J = 7.8 Hz, 1H), 5.87 (ddt, J = 17.1, 10.5, 5.3 Hz, 1H), 5.31 (d, J = 7.1 Hz, 1H), 5.28 (s, 1H), 5.20 (s, 1H), 4.39 (d, J = 5.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.9, 143.1, 130.7, 130.5, 125.8, 123.4, 118.2, 109.7, 51.5, 42.8, 29.8. HRMS (m/z):C<sub>11</sub>H<sub>11</sub>ClNO ([M+H]<sup>+</sup>): 208.0524, found 208.0526.

3-chloro-1-(prop-2-yn-1-yl)indolin-2-one (e12)17



The reaction was performed following the GP-2, giving the product (26.2 mg, 64% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, J = 7.5 Hz, 1H), 7.43 (t, J = 8.3 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 5.21 (s, 1H), 4.75 – 4.39 (m, 2H), 2.31 (t, J = 2.5 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.2, 142.0, 130.6, 125.8, 125.6, 123.9, 109.8, 73.0, 51.4, 29.8. HRMS (m/z):C<sub>11</sub>H<sub>9</sub>ClNO ([M+H]<sup>+</sup>): 206.0367, found 206.0363.

3-chloro-1-(cyclopropylmethyl)indolin-2-one (e13)



The reaction was performed following the GP-2, giving the product (33.3 mg, 75% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 1H NMR (400 MHz, Chloroform-d) δ 7.46 (d, J = 7.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H), 5.16 (s, 1H), 3.63 (d, J = 6.9 Hz, 2H), 1.26 – 1.07 (m, 1H), 0.63 – 0.50 (m, 2H), 0.44 (dd, J = 4.8, 1.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz,

CDCl<sub>3</sub>) δ 172.2, 143.6, 130.5, 125.9, 125.9, 123.2, 109.2, 51.7, 44.9, 9.5, 4.0, 4.0. **HRMS** (m/z):C<sub>12</sub>H<sub>13</sub>ClNO ([M+H]<sup>+</sup>): 222.0680, found 222.0681.

3-chloro-1-(cyclobutylmethyl)indolin-2-one (e14)



The reaction was performed following the GP-2, giving the product (36.3 mg, 77% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (d, J = 7.4 Hz, 1H), 7.38 (td, J = 7.8, 1.1 Hz, 1H), 7.14 (dd, J = 8.1, 7.0 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H), 5.16 (s, 1H), 3.63 (d, J = 7.0 Hz, 3H), 1.26 – 1.13 (m, 1H), 0.58 (dd, J = 7.9, 2.3 Hz, 2H), 0.44 (dd, J = 4.7, 1.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.2, 143.6, 130.5, 125.9, 125.8, 123.2, 109.2, 51.7, 44.9, 9.5, 4.0, 4.0. HRMS (m/z):C<sub>13</sub>H<sub>15</sub>CINO ([M+H]<sup>+</sup>): 236.0837, found 236.0839.

3-chloro-1-phenylindolin-2-one (e15)



The reaction was performed following the GP-2, giving the product (32.2 mg, 66% yield) as a dark red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.51 (m, 3H), 7.47 (tt, J = 7.2, 1.3 Hz, 3H), 7.33 (td, J = 7.9, 1.2 Hz, 1H), 7.19 (tt, J = 7.6, 1.1 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H), 5.35 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.4, 144.0, 133.8, 130.5, 129.9, 128.6, 126.5, 126.0, 125.6, 123.9, 110.1, 51.9. HRMS (m/z):C<sub>14</sub>H<sub>11</sub>CINO ([M+H]<sup>+</sup>): 244.0524, found 244.0522.

methyl 2-bromo-2-phenylacetate (f1)<sup>18</sup>



The reaction was performed following the GP-3, giving the product (43.1 mg, 94% yield) as a light yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.55 (m, 2H), 7.40 (td, J = 5.0, 4.2, 2.4 Hz, 3H), 5.41 (s, 1H), 3.83 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 135.8, 129.4, 128.9, 128.7, 77.4, 77.3, 77.1, 76.8, 53.5, 46.6. **HRMS (m/z)**:C<sub>9</sub>H<sub>10</sub>BrO<sub>2</sub> ([M+H]<sup>+</sup>): 228.9859, found 228.9860.

methyl 2-bromo-2-phenylacetate-d (f1-[D])



The reaction was performed following the GP-3. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.55 (m, 2H), 7.40 (td, J = 5.0, 4.2, 2.4 Hz, 3H), 5.41 (s, 1H), 3.83 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 168.9, 135.8, 129.4, 128.9, 128.7, 77.4, 77.3, 77.1, 76.8, 53.5, 46.6. **HRMS (m/z)**:C<sub>9</sub>H<sub>9</sub>DBrO<sub>2</sub> ([M+H]<sup>+</sup>): 229.9921, found 229.9919.

methyl 2-bromo-2-(o-tolyl)acetate (f2)<sup>19</sup>



The reaction was performed following the GP-3, giving the product (37.9 mg, 78% yield) as a yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.58 (m, 1H), 7.35 – 7.16 (m, 4H), 5.69 (s, 1H), 3.83 (s, 3H), 2.45 (s, 3H). <sup>13</sup>**C NMR (101** MHz, CDCl<sub>3</sub>) δ 168.8, 136.1, 134.4, 130.9, 129.3, 128.9, 127.0, 77.4, 77.1, 76.8, 53.5, 44.5, 19.3. **HRMS (m/z)**:C<sub>10</sub>H<sub>12</sub>BrO<sub>2</sub> ([M+H]<sup>+</sup>): 243.0015, found 243.0010.

methyl 2-bromo-2-(m-tolyl)acetate (f3)19



The reaction was performed following the GP-3, giving the product (40.3 mg, 83% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (dd, J = 9.7, 4.9 Hz, 2H), 7.31 – 7.16 (m, 3H), 5.37 (s, 1H), 3.81 (s, 3H), 2.39 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 138.8, 135.7, 130.2, 129.3, 128.8, 125.8, 77.4, 77.3, 77.1, 76.8, 53.4, 46.8, 21.4. HRMS (m/z):C<sub>10</sub>H<sub>12</sub>BrO<sub>2</sub> ([M+H]<sup>+</sup>): 243.0015, found 243.0010.

#### methyl 2-bromo-2-(p-tolyl)acetate (f4)<sup>18</sup>



The reaction was performed following the GP-3, giving the product (40.8 mg, 84% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 5.39 (s, 1H), 3.82 (s, 3H), 2.39 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.0, 139.5, 132.9, 129.6, 128.6, 126.6, 77.4, 77.1, 76.8, 53.4, 46.7, 21.3. HRMS (m/z):C<sub>10</sub>H<sub>12</sub>BrO<sub>2</sub> ([M+H]<sup>+</sup>): 243.0015, found 243.0010. *methyl 2-bromo-2-(2-bromophenyl)acetate* (f5)<sup>20</sup>



The reaction was performed following the GP-3, giving the product (49.1 mg, 80% yield) as a yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.81 (dd, J = 7.9, 1.7 Hz, 1H), 7.60 (dd, J = 8.0, 1.3 Hz, 1H), 7.40 (td, J = 7.6, 1.3 Hz, 1H), 7.23 (td, J = 7.7, 1.7 Hz, 1H), 5.95 (s, 1H), 3.84 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 168.4, 135.5, 133.1, 131.1, 130.7, 128.3, 123.6, 77.4, 77.1, 76.8, 53.7, 45.7. **HRMS** (**m**/**z**):C<sub>9</sub>H<sub>9</sub>Br<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 306.8964, found 306.8965.

methyl 2-bromo-2-(3-fluorophenyl)acetate (f6)<sup>21</sup>



The reaction was performed following the GP-3, giving the product (41.5 mg, 84% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 – 7.30 (m, 1H), 7.19 – 7.01 (m, 3H), 5.36 (s, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 164.0, 161.5, 138.0 (d, J = 7.8 Hz), 130.4 (d, J = 8.3 Hz), 124.4 (d, J = 3.0 Hz), 116.5 (d, J = 21.1 Hz), 53.6, 45.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -110.3 – -113.4 (m). HRMS (m/z):C<sub>9</sub>H<sub>9</sub>BrFO<sub>2</sub> ([M+H]<sup>+</sup>): 246.9764, found 246.9767.

methyl 2-bromo-2-(4-fluorophenyl)acetate (f7)<sup>21</sup>



The reaction was performed following the GP-3, giving the product (43.0 mg, 87% yield) as a yellow oil.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (ddd, J = 8.9, 5.2, 2.2 Hz, 2H), 7.09 (td, J = 8.8, 2.2 Hz, 2H), 5.37 (s, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.8, 164.4, 130.7 (d, J = 8.5 Hz), 116.0 (d, J = 21.9 Hz), 77.4, 77.1, 76.8, 53.5, 45.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -111.5 . HRMS (m/z):C<sub>9</sub>H<sub>9</sub>BrFO<sub>2</sub> ([M+H]<sup>+</sup>): 246.9764, found 246.9767.

methyl 2-bromo-2-(4-chlorophenyl)acetate (f8)<sup>21</sup>



The reaction was performed following the GP-3, giving the product (47.9 mg, 91% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 5.36 (s, 1H), 3.82 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 135.4, 134.3, 130.1, 129.1, 77.4, 77.1, 76.8, 53.5, 45.4. HRMS (m/z):C<sub>9</sub>H<sub>9</sub>BrClO<sub>2</sub> ([M+H]<sup>+</sup>): 262.9469, found 262.9468.

methyl 2-bromo-2-(4-bromophenyl)acetate (f9)19



The reaction was performed following the GP-3, giving the product (54.6 mg, 89% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 5.34 (s, 1H), 3.82 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 134.8, 132.1, 130.4, 123.7, 77.5, 77.1, 76.8, 53.6, 45.4. HRMS (m/z):C<sub>9</sub>H<sub>9</sub>Br<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 306.8964, found 306.8965.

#### methyl 2-([1,1'-biphenyl]-4-yl)-2-bromoacetate (f10)<sup>18</sup>



The reaction was performed following the GP-3, giving the product (51.9 mg, 85% yield) as a yellow oil.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.61 (m, 6H), 7.53 – 7.39 (m, 3H), 5.48 (d, J = 1.4 Hz, 1H), 3.86 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.9, 142.8, 140.3, 134.7, 129.2, 129.0, 127.9, 127.7, 127.2, 77.5, 77.2, 76.9, 53.5, 46.4. HRMS (m/z):C<sub>15</sub>H<sub>14</sub>BrO<sub>2</sub> ([M+H]<sup>+</sup>): 305.0172, found 305.0176. *methyl 4-(1-bromo-2-methoxy-2-oxoethyl)benzoate* (f11)<sup>22</sup>



The reaction was performed following the GP-3, giving the product (51.1 mg, 89% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (dd, J = 8.4, 2.2 Hz, 2H), 7.63 (dd, J = 8.5, 2.1 Hz, 2H), 5.40 (d, J = 2.2 Hz, 1H), 3.93 (d, J = 2.1 Hz, 3H), 3.81 (d, J = 2.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 166.4, 140.5, 131.0, 130.1, 128.8, 77.5, 77.2, 76.8, 53.6, 52.4, 45.5. HRMS (m/z):C<sub>11</sub>H<sub>12</sub>BrO<sub>4</sub> ([M+H]<sup>+</sup>): 286.9913, found 286.9919.

ethyl 2-bromo-2-(4-bromophenyl)acetate (f12)18



The reaction was performed following the GP-3, giving the product (55.0 mg, 86% yield) as a yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 – 7.51 (m, 2H), 7.50 – 7.43 (m, 2H), 5.32 (d, J = 1.1 Hz, 1H), 4.43 – 4.12 (m, 2H), 1.32 (td, J = 7.1, 1.1 Hz, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.0, 135.0, 132.1, 130.4, 123.6, 77.4, 77.1, 76.8, 62.8, 45.8, 14.0. **HRMS** (m/z):C<sub>10</sub>H<sub>10</sub>Br<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 319.9048, found 319.9050.

#### ethyl 2-bromo-2-phenylacetate (f13)<sup>18</sup>



The reaction was performed following the GP-3, giving the product (44.7 mg, 92% yield) as a yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 (dp, J = 5.9, 1.9 Hz, 2H), 7.46 – 7.35 (m, 3H), 5.38 (d, J = 3.6 Hz, 1H), 4.40 – 4.11 (m, 2H), 1.31 (td, J = 7.2, 3.3 Hz, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 136.0, 129.3, 128.9, 128.7, 77.5, 77.1, 76.8, 62.6, 46.9, 14.0. **HRMS (m/z)**:C<sub>10</sub>H<sub>12</sub>BrO<sub>2</sub> ([M+H]<sup>+</sup>): 243.0015, found 243.0010.

#### methyl 2-bromo-2-(3,4-dichlorophenyl)acetate (f14)<sup>23</sup>



The reaction was performed following the GP-3, giving the product (43.8 mg, 74% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (t, J = 1.7 Hz, 1H), 7.56 – 7.35 (m, 2H), 5.31 (d, J = 1.2 Hz, 1H), 3.83 (d, J = 1.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.2, 135.8, 133.7, 133.0, 130.8, 130.8, 128.1, 77.5, 77.1, 76.8, 53.7, 44.4. HRMS (m/z):C<sub>9</sub>H<sub>7</sub>BrCl<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 295.9006, found 295.9001. *tetrahydro-2H-pyran-4-yl 2-bromo-2-phenylacetate* (f15)



The reaction was performed following the GP-3, giving the product (42.5 mg, 71% yield) as a yellow oil. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dt, J = 7.3, 1.9 Hz, 2H), 7.50 – 7.33 (m, 3H), 5.40 (d, J = 1.8 Hz, 1H), 4.25 (dd, J = 4.4, 2.1 Hz, 2H), 3.56 (q, J = 4.2 Hz, 2H), 2.52 (d, J = 1.6 Hz, 1H), 1.85 (q, J = 2.6 Hz, 4H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 168.4, 135.8, 135.6, 130.4, 129.4, 128.9, 128.7, 127.6, 77.5, 77.2, 76.8, 65.6, 46.9, 44.4, 28.9, 25.9. **HRMS (m/z)**:C<sub>13</sub>H<sub>16</sub>BrO<sub>3</sub> ([M+H]<sup>+</sup>): 299.0277, found 299.0281.

isobutyl 2-bromo-2-phenylacetate (f16)<sup>24</sup>



The reaction was performed following the GP-3, giving the product (41.7 mg, 77% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.57 (m, 2H), 7.44 – 7.36 (m, 2H), 5.40 (s, 1H), 4.00 (dd, *J* = 6.6, 1.1 Hz, 2H), 2.06 – 1.92 (m, 1H), 0.95 (s, 3H), 0.94 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 136.0, 129.3, 128.9, 128.8, 77.4, 77.1, 76.8, 72.4, 47.1, 27.8, 19.0. HRMS (m/z):C<sub>12</sub>H<sub>16</sub>BrO<sub>2</sub> ([M+H]<sup>+</sup>): 271.0328, found 271.0324.

phenethyl 2-bromo-2-phenylacetate (f17)<sup>25</sup>


The reaction was performed following the GP-3, giving the product (51.0 mg, 80% yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 – 7.46 (m, 2H), 7.43 – 7.36 (m, 3H), 7.36 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 5.38 (s, 1H), 4.44 (t, *J* = 7.0 Hz, 2H), 3.00 (t, *J* = 6.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 137.3, 135.9, 129.4, 129.1, 128.9, 128.8, 128.7, 126.8, 77.5, 77.2, 76.9, 67.0, 47.0, 34.9. HRMS (m/z):C<sub>16</sub>H<sub>16</sub>BrO<sub>2</sub> ([M+H]<sup>+</sup>): 319.0328, found 319.0323.

## 3. NMR spectra for the products

<sup>1</sup>H NMR spectra of compound **d1** in CDCl<sub>3</sub> (400 MHz):



<sup>19</sup>F NMR spectra of compound **d1** in CDCl<sub>3</sub> (376 MHz):



## <sup>1</sup>H NMR spectra of compound **d2** in CDCl<sub>3</sub> (400 MHz):

7.527.517.517.517.507.5077.5077.5077.49	7.45 7.45 7.45 7.45 7.45 7.45 7.45	7	6.13 6.13 7.15 7.15 7.15 7.15 7.15 7.15 7.15 7.15	3.83
		<u>land</u>	<u> </u>	1



## <sup>13</sup>C NMR spectra of compound **d2** in CDCl<sub>3</sub> (101 MHz):

<pre>     168.7     168.4     168.4     168.4     168.4     168.4     168.4     168.4     159.1     128.9     131.3</pre>	84.4 84.4 82.6 82.5	- 52.8
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<sup>19</sup>F NMR spectra of compound **d2** in CDCl<sub>3</sub> (376 MHz):







<sup>13</sup>C NMR spectra of compound **d3** in CDCl<sub>3</sub> (101 MHz):



 $^{19}\mathrm{F}$  NMR spectra of compound d3 in CDCl3 (376 MHz):

F







<sup>19</sup>F NMR spectra of compound **d4** in CDCl<sub>3</sub> (376 MHz):





<sup>1</sup>H NMR spectra of compound **d5** in CDCl<sub>3</sub> (400 MHz):





-181.3
<-181.4</pre>





NO<sub>2</sub>



<sup>19</sup>F NMR spectra of compound **d6** in CDCl<sub>3</sub> (376 MHz):



<sup>13</sup>C NMR spectra of compound **d7** in CDCl<sub>3</sub> (101 MHz):



 $^{19}\mathrm{F}$  NMR spectra 2of compound d7 in CDCl3 (376 MHz):



 $< \frac{-182.2}{-182.3}$ 







100 90 f1 (ppm) 

<sup>19</sup>F NMR spectra of compound **d8** in CDCl<sub>3</sub> (376 MHz):





<sup>1</sup>H NMR spectra of compound **d10** in CDCl<sub>3</sub> (400 MHz):



<sup>19</sup>F NMR spectra of compound **d10** in CDCl<sub>3</sub> (376 MHz):









<sup>19</sup>F NMR spectra of compound **d12** in CDCl<sub>3</sub> (376 MHz):



 $^1\mathrm{H}$  NMR spectra of compound **d13** in CDCl\_3 (400 MHz):







<sup>19</sup>F NMR spectra of compound **d13** in CDCl<sub>3</sub> (376 MHz):





<sup>1</sup>H NMR spectra of compound **d14** in CDCl<sub>3</sub> (400 MHz):

<sup>19</sup>F NMR spectra of compound **d14** in CDCl<sub>3</sub> (376 MHz):



<sup>13</sup>C NMR spectra of compound **d15** in CDCl<sub>3</sub> (101 MHz):



<sup>19</sup>F NMR spectra of compound **d15** in CDCl<sub>3</sub> (376 MHz):









 $^{19}\mathrm{F}$  NMR spectra of compound d16 in CDCl3 (376 MHz):









<sup>1</sup>H NMR spectra of compound **d18** in CDCl<sub>3</sub> (400 MHz):



<sup>19</sup>F NMR spectra of compound **d18** in CDCl<sub>3</sub> (376 MHz):





-179.8
<-179.9</pre>

<sup>19</sup>F NMR spectra of compound **d19** in CDCl<sub>3</sub> (376 MHz):





<sup>1</sup>H NMR spectra of compound **d20** in CDCl<sub>3</sub> (400 MHz):







<sup>13</sup>C NMR spectra of compound **d20** in CDCl<sub>3</sub> (101 MHz):



100 90 f1 (ppm) 

<sup>19</sup>F NMR spectra of compound **d20** in CDCl<sub>3</sub> (376 MHz):





<sup>1</sup>H NMR spectra of compound **d21** in CDCl<sub>3</sub> (400 MHz):









<sup>19</sup>F NMR spectra of compound **d22** in CDCl<sub>3</sub> (376 MHz):







<sup>1</sup>H NMR spectra of compound **d23** in CDCl<sub>3</sub> (400 MHz):





<sup>19</sup>F NMR spectra of compound **d23** in CDCl<sub>3</sub> (376 MHz):






<sup>1</sup>H NMR spectra of compound **d24** in CDCl<sub>3</sub> (400 MHz):



<sup>19</sup>F NMR spectra of compound **d24** in CDCl<sub>3</sub> (376 MHz):













4.5 4 f1 (ppm)





1.07<sub>4</sub> 1.03<sub>₹</sub> 1.06∄ 1.00-I 3.25<sub>-1</sub>  $3.29_{-1}$ 

5.0 4.5 f1 (ppm)

3.5

4.0

3.0

2.5

2.0

1.5

1.0

0.5

0.0

5.5

6.0

9.0

8.5

8.0

7.5

7.0

6.5









. . (ppm





<sup>1</sup>H NMR spectra of compound e11 in CDCl<sub>3</sub> (400 MHz):









<sup>5.0</sup> 

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88
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<sup>13</sup>C NMR spectra of compound **f1-[D]** in CDCl<sub>3</sub> (101 MHz):



<sup>13</sup>C NMR spectra of compound **f2** in CDCl<sub>3</sub> (101 MHz):



<sup>13</sup>C NMR spectra of compound **f3** in CDCl<sub>3</sub> (101 MHz):



<sup>13</sup>C NMR spectra of compound **f4** in CDCl<sub>3</sub> (101 MHz):



<sup>13</sup>C NMR spectra of compound **f5** in CDCl<sub>3</sub> (101 MHz):



<sup>19</sup>F NMR spectra of compound **f6** in CDCl<sub>3</sub> (376 MHz):









<sup>13</sup>C NMR spectra of compound **f7** in CDCl<sub>3</sub> (101 MHz):



<sup>19</sup>F NMR spectra of compound **f7** in CDCl<sub>3</sub> (376 MHz):







5.0 4.5 f1 (ppm) 7.5 9.0 8.5 8.0 7.0 6.5 6.0 5.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0







<sup>13</sup>C NMR spectra of compound **f10** in CDCl<sub>3</sub> (101 MHz):



<sup>13</sup>C NMR spectra of compound **f11** in CDCl<sub>3</sub> (101 MHz):

<sup>13</sup>C NMR spectra of compound **f12** in CDCl<sub>3</sub> (101 MHz):



<sup>1</sup>H NMR spectra of compound **f13** in CDCl<sub>3</sub> (400 MHz):







<sup>13</sup>C NMR spectra of compound **f13** in CDCl<sub>3</sub> (101 MHz):





<sup>13</sup>C NMR spectra of compound **f15** in CDCl<sub>3</sub> (101 MHz):






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