Supporting Information

Suzuki-Miyaura Cross-Coupling Reactions of Primary Alkyltrifluoroborates with Aryl Chlorides

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Contents:

General Considerations
Procedure for Preparation of Primary Potassium AlkyltrifluoroboratesS2
General Procedure for Parallel Microscale Experimentation
Compound Characterization for the Suzuki-Miyaura Cross-Coupling Reactions of Primary
Alkyl Trifluoroborates with Aryl Chlorides
References
NMRS2

General. Pd(OAc)₂, RuPhos (2-dicyclohexylphosphino-2',6'-diisopropoxy-1,1'-biphenyl), [Ir(cod)Cl]₂, dppe (diphenylphosphinoethane), K₂CO₃, and Cs₂CO₃ were used as received. Toluene was distilled from sodium/benzophenone prior to use. H₂O was degassed prior to use. Standard benchtop techniques were employed for handling air–sensitive reagents. Melting points (°C) were determined using a Thomas–Hoover melting point apparatus and are uncorrected. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded at 500.39, 125.75, and 470.55 MHz, respectively. ¹⁹F NMR chemical shifts were referenced to external CFCl₃ (0.0 ppm). ¹¹B NMR spectra at 128.4 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ¹¹B NMR chemical shifts were referenced to external BF₃·OEt₂ (0.0 ppm) with a negative sign indicating an upfield shift. Analytical thin–layer chromatography (TLC) was performed on Sorbent Technologies TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Standard flash chromatography procedures¹ were followed using 32–63 µm silica gel.

2-Chloro-5-methoxy-1,3-dimethylbenzene was prepared according to a literature procedure.² All other aryl halides were used as received.

Procedures for Preparation of Primary Potassium Alkyltrifluoroborates.



Potassium 4-(*tert***-Butyldimethylsilyloxy)butyltrifluoroborate.** In a glovebox, a flask was charged with 1.5 mol % of $[Ir(cod)Cl]_2$ (300 mg, 0.45 mmol) and 3 mol % of dppe (355 mg, 0.89 mmol).³ The flask was removed and to it was added CH₂Cl₂ (100 ml) and (but-3-enyloxy)(*tert*-butyl)dimethylsilane (5.54 g, 29.7 mmol). The reaction mixture was cooled to 0 °C and pinacolborane (5.71 g, 44.6 mmol) was added dropwise. The reaction mixture was allowed to warm to rt and was stirred for 6 h. Water was added (20 mL) and the mixture was extracted with

ether (3 x 50 mL), dried over MgSO₄, and filtered. After removal of the solvent, the boronate ester was run through a plug of silica (elution with hexanes/EtOAc 9:1) to provide as a colorless oil (9.16 g, 29.1 mmol, 98% yield). The part of the resulting boronate ester was then dissolved in MeOH (20 mL) and cooled to 0 °C. To it was added saturated aqueous KHF₂ (3 mL, 4.5 M) dropwise, and then the reaction mixture was allowed to warm to rt. After 10 min, the solution was concentrated *in vacuo*. The resulting white solid was then subjected to high vacuum overnight and removal of excess pinacol by Kugelrohr distillation. The pure compound was isolated as a white solid in 80% yield (1.05 g, 3.57 mmol). mp = 173-175 °C. ¹H NMR (500 MHz, acetone- d_6): 3.56-3.59 (t, *J* = 7.0 Hz, 2H), 1.44-1.49 (m, 2H), 1.24-1.29 (m, 2H), 0.88 (s, 9H), 0.11-0.16 (m, 2H), 0.03 (s, 6H). ¹³C NMR (125.8 MHz, acetone- d_6): 64.2, 37.4, 26.0, 22.1, 18.5, -5.4. ¹⁹F NMR (470.8 MHz, acetone- d_6): -141.4. ¹¹B NMR (128.4 MHz, acetone- d_6): 5.08. IR (KBr) 2929, 2858, 1472, 1257, 1095 cm⁻¹. HRMS (ESI) calcd. for C₁₀H₂₃BF₃OSi [M-K]⁻ 255.1563, found 255.1569.



Potassium Isobutyltrifluoroborate. A 50 mL 2-neck flask equipped with a reflux condenser and a rubber septa was charged with Mg (1.82 g, 75 mmol). The Mg was activated by flame drying under a flow of N₂ and suspended in Et₂O (20 mL). 1-Bromo-2-methylpropane (3.43 g, 25 mmol) was slowly added and the suspension was brought to a reflux. Upon completion of the addition of bromide, the resulting suspension of isobutyl magnesium bromide was cooled to rt with stirring for 1 h. Into a separate flask, purged with N₂, a solution was made of trimethyl borate (3.90 g, 37.8 mmol) in THF (50 mL) and cooled to -78 °C.⁴ To this solution, the isobutyl magnesium bromide suspension was added dropwise via a double ended needle. The mixture was allowed to stir for 1 h at -78 °C and then allowed to warm to rt for 1 h. To it was added saturated aqueous KHF₂ (23 mL,

4.5 M) dropwise and then the reaction mixture was allowed to warm to rt. After 30 min, the solution was concentrated *in vacuo*. The dried solids were triturated with hot acetone (3 x 50 mL) and filtered to remove inorganic salts. The resulting solution was concentrated until the trifluoroborate was minimally soluble in acetone. Et₂O (~30 mL) was added to precipitate the product. The pure compound was filtered and dried *in vacuo* and obtained as a white solid in 62% yield (2.55 g, 15.5 mmol). mp >200 °C. ¹H NMR (500 MHz, acetone-*d*₆): 1.63-1.68 (septet, J = 6.6 Hz, 1H), 0.83-0.85 (d, J = 6.6 Hz, 6H), 0.09-0.15 (m, 2H). ¹³C NMR (125.8 MHz, acetone-*d*₆): 26.7, 25.9. ¹⁹F NMR (470.8 MHz, acetone-*d*₆): -13.8.9. ¹¹B NMR (128.4 MHz, acetone-*d*₆): 5.59. IR (KBr) 2954, 2886, 2816, 1466, 1364, 1337, 1275, 1090 cm⁻¹. HRMS (ESI) calcd. for C₄H₉BF₃ [M-K]⁻ 125.0749, found 125.0742.

General Procedure for Parallel Microscale Experimentation. Reactions of Potassium Phenethyltrifluoroborate with 2-Chloroanisole or 3-Chloropyridine. The following procedure is representative of the parallel microscale experimentation reactions run in this publication. The ligands (2 μ mol for monodentate ligands, 1 μ mol for bidentate ligands) were dosed into the 96-well reactor vial as solutions (50 μ L of a 0.04 M solution in toluene or ClCH₂CH₂Cl depending upon the solubility of the ligand). Plates of these ligands are typically dosed in advance of the reaction, the solvent is removed by evacuation on the Genovac , and the plates are stored in the glovebox. Pd(OAc)₂ pre-catalyst (1 μ mol, 20 μ L of 0.05 M solution in ClCH₂CH₂Cl) was then added to the reaction vials and this was evacuated to dryness on the Genovac. K₂CO₃ (150 μ mol, 20.7 mg) was added to the ligand/catalyst mixture as a solid, using the Powdernium solid addition robot. A parylene stir-bar was then added to each reaction. Water (20 μ L) was then added to each reaction. The aryl chlorides (10 μ mol/reaction), potassium alkyltrifluoroborates (10 μ mol/reaction) and 4-isopropylbiphenyl (1 μ mol/reaction) (used as an internal standard to measure HPLC yield) were then dosed together as a well-stirred slurry in the desired reaction solvents (0.1 M solutions of ArCl in toluene) using a single-tip pipettor with the sampling tip cut to allow free flow of the slurry. The reactions were then sealed and heated at 85 °C for 18 h. After cooling to ambient temperature, the reactions were diluted with 700 μ L of acetonitrile, a silicon-rubber storage mat was added, and the contents were shaken to homogenize. Into a separate 96-well-plate LC plate with 1 mL vials was then added 850 μ L of acetonitrile, and then 20 μ L of the diluted reaction mixtures. The 96-well plate LC block was then sealed with a silicon-rubber storage mat, and an aluminum cover was attached to the block with screws. The reactions were then analyzed using an Agilent Chemstation on an HPLC modified with a 96-well plate auto-sampler.

					%	
CI-Anisole	Ligand	SM	Prod	IS	Conv	Prod/ IS
1A	XPhos	51	276	40	84.4	6.9
2	SPhos	15	427	40	96.6	10.7
3	JohnPhos (tBu2P(biphenyl)	105	119	40	53.1	3.0
4	DavePhos (2-(Cy2P)-2'-(N,N-Me2)biphenyl)	97	180	40	65.0	4.5
5	2-Di-t-butylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl	132	27	40	17.0	0.7
6	RuPhos	0	429	39	100.0	11.0
7	CataCXium PtB	95	177	40	65.1	4.4
8	CataCXium A (Ad2P(nBu))	68	271	37	79.9	7.3
9	QPhos	37	321	39	89.7	8.2
10	PtBu3*HBF4	60	253	37	80.8	6.8
11	PCy3 HBF4	165	20	40	10.8	0.5
12	dtbpf	119	172	39	59.1	4.4
1B	dppf		0			
2	dipf	179	14	41	7.3	0.3
3	1,2 Bis(di-tBuphosphinomethyl)Bn	128	96	39	42.9	2.5
4	dppe		0			
5	dppp		0			
6	dppb		0			
7	DpePhos		0			
8	Xantphos		0			
9	BINAP	193	37	40	16.1	0.9
10	tol-BINAP		0			
11	1,1'-Bis(di-t-butylphosphino)biphenyl		0			
12	biphep		0			
1C	CataCXium KCy		0			
2	CataCXium KPh		0			

3	CataCXium PIntB	15	280	40	94.9	7.0
4	CataCXium POMetB	32	332	39	91.2	8.5
5	CataCXium PInCv	91	185	40	67.0	4.6
6	CataCXium POMeCv	98	173	40	63.8	4.3
7	CataCXium PCv	143	86	36	37.6	2.4
8	tBu2P-2'-methylbinhenyl	81	107	43	56.9	2.5
q	Cv2P(hinhenvl)	128	60	39	31.9	1.5
10	Cy2P_2'_methylbinbenyl	1/2	10	12	11.8	0.5
11	$(2_{Ph2P})^{2} - (N_{Ph2P})^{2}$	172	0	74	11.0	0.0
12	(2-(tBu2P)-2'-(N,N-Me2))	12	274	15	95.8	6 1
12		12	0	-5	35.0	0.1
2		102	0	11	15	0.2
2	trimositulaboanhina	195	9	41	4.5	0.2
3			0			
4	IRI(2-FURTL)PHUSPHINE	100	0	20	2.0	0.0
5	tris(2-methoxyphenyi)phosphine	189	1	38	3.0	0.2
6	tris(4-methoxypnenyi)phosphine		0			
1	tris(2,4,6-trimetnoxypnenyi)phosphine		0			
8	tris(4-fluorophenyl)phosphine		0			
9	tris(perfluorophenyl)phosphine		0			
10	bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt		0			
11	tri-1-napthyl phosphine		0			
12	Tris(2,4-ditBuPh)phosphite		0			
1E	trimethylphosphonium tetrafluoroborate		0			
2	triethylphosphonium tetrafluoroborate		0			
3	DI-T-BUTYLMETHYLPHOSPHONIUM TETRAFLUOROBORATE		0			
4	DI-T-BUTYLPHENYLPHOSPHONIUM TETRAFLUOROBORATE	169	53	39	23.9	1.4
5	benzyldiphenylphosphine		0			
6	tedicyp ligand		0			
7	Catacxium ABn	111	120	38	51.9	3.2
8	dppe monoxide		0			
9	2-ditBuPBinapthyl	120	98	39	45.0	2.5
10	SiPr*HBF4	124	162	39	56.6	4.2
11	IMes*HCI		0			
12	SiPr*HCI	170	76	41	30.9	1.9
1F	1,2-bis(dicyclohexylphosphino)ethane		0			
2	1,3-bis(dicyclohexylphosphino)propane		0			
3	1,4-bis(dicyclohexylphosphino)butane		0			
4	1,5-bis(di-t-butylphosphino)pentane	168	35	40	17.2	0.9
5	1,2-bis(diethylphosphino)ethane		0			
6	1.3-bis(diisopropylphosphino)propane		0			
7	1,2-bis(dimethylphosphino)benzene		0			
8	1,3-bis(di-t-butylphosphinomethyl)benzene	161	52	38	24.4	1.4
9	1.3-bis(dicyclopentylphosphinomethyl)benzene		0			
10	2.6-bis(di-t-buty)phosphinomethyl)pvridine		0			
11	T-butyl-xantphos		0			
12	Cvclohexvl-binhen	137	86	40	38.6	2.2
	-)					

3-CI					%	
Pyridine	Ligand	SM	Prod	IS	Conv	Prod/ IS
1A	XPhos	70	57	40	44.9	1.4
2	SPhos	48	145	43	75.1	3.4
3	JohnPhos (tBu2P(biphenyl)	98	25	41	20.3	0.6

4	DavePhos (2-(Cy2P)-2'-(N,N-Me2)biphenyl)	109	12	40	9.9	0.3
5	2-Di-t-butylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl	64	7	42	9.9	0.2
6	RuPhos	41	129	40	75.9	3.2
7	CataCXium PtB	10	5	45	33.3	0.1
8	CataCXium A (Ad2P(nBu))	0	148	47	100.0	3.1
9	QPhos	51	112	40	68.7	2.8
10	PtBu3*HBF4	54	98	38	64.5	2.6
11	PCy3 HBF4	65	71	39	52.2	1.8
12	dtbpf	31	157	38	83.5	4.1
1B	dppf		0			
2	dipf	89	57	39	39.0	1.5
3	1,2 Bis(di-tBuphosphinomethyl)Bn	81	44	41	35.2	1.1
4	dppe		0			
5	dppp		0			
6	dppb		0			
1	DpePhos		0			
8	Xantphos	67	27	51	28.7	0.5
9	BINAP		0			
10		70	0	00	00 F	1.0
11	1,1-Bis(al-t-butyipnospnino)pipnenyi	72	47	39	39.5	1.2
12			0			
			0			
2		40	100	40	C0 F	2.5
3		40	100	40	00.5	2.5
4		30	100	55	84.0	3.0
5		20	100	40	04.U 01.6	3.4 4 1
0		20	104	40	01.0	4.1
0	tBu2D 2' mothylbinbonyl	20 67	124	42	10.1	5.0
0		61	76	42	10.J	0.4
10	Cy2P 2' methylbinbenyl	70	70	40	50.7	1.0
10	(2-(Ph2P)-2'-(N N-Me2)hinhenvl)	70	0	-0	50.7	1.0
12	(2-(1121)-2-(11,10-1002)biphenyl)	54	83	30	60.6	21
10		54	0	00	00.0	2.1
2		113	15	42	11 7	0.4
3	trimesityInhosphine	110	0	12		0.1
4	TRI(2-FURYL)PHOSPHINE		0			
5	tris(2-methoxyphenyl)phosphine		0			
6	tris(4-methoxyphenyl)phosphine		0			
7	tris(2.4.6-trimethoxyphenyl)phosphine		0			
8	tris(4-fluorophenyl)phosphine		0			
9	tris(perfluorophenyl)phosphine		0			
10	bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt		0			
11	tri-1-napthyl phosphine		0			
12	Tris(2,4-ditBuPh)phosphite		0			
1E	trimethylphosphonium tetrafluoroborate		0			
2	triethylphosphonium tetrafluoroborate		0			
3	DI-T-BUTYLMETHYLPHOSPHONIUM TETRAFLUOROBORATE	69	80	40	53.7	2.0
4	DI-T-BUTYLPHENYLPHOSPHONIUM TETRAFLUOROBORATE	41	186	46	81.9	4.0
5	benzyldiphenylphosphine		0			
6	tedicyp ligand	88	37	42	29.6	0.9
7	Catacxium ABn	61	64	42	51.2	1.5
8	dppe monoxide		0			

9	2-ditBuPBinapthyl	84	50	42	37.3	1.2
10	SiPr*HBF4	79	78	41	49.7	1.9
11	IMes*HCI	91	23	43	20.2	0.5
12	SiPr*HCI	98	43	42	30.5	1.0
1F	1,2-bis(dicyclohexylphosphino)ethane		0			
2	1,3-bis(dicyclohexylphosphino)propane	71	39	40	35.5	1.0
3	1,4-bis(dicyclohexylphosphino)butane	95	44	40	31.7	1.1
4	1,5-bis(di-t-butylphosphino)pentane	80	81	42	50.3	1.9
5	1,2-bis(diethylphosphino)ethane		0			
6	1,3-bis(diisopropylphosphino)propane	83	23	41	21.7	0.6
7	1,2-bis(dimethylphosphino)benzene		0			
8	1,3-bis(di-t-butylphosphinomethyl)benzene	35	78	48	69.0	1.6
9	1,3-bis(dicyclopentylphosphinomethyl)benzene	97	39	41	28.7	1.0
10	2,6-bis(di-t-butylphosphinomethyl)pyridine		0			
11	T-butyl-xantphos		0			
12	Cyclohexyl-biphep	67	71	40	51.4	1.8

Compound Characterization for the Suzuki-Miyaura Cross-Coupling Reactions of Primary

Alkyl Trifluoroborates with Aryl Chlorides.



4-(4-(1*H***-Pyrrol-1-yl)phenyl)butyl Benzoate.** According to the general procedure using 1-(4-chlorophenyl)-1*H*-pyrrole on a 0.50 mmol scale, the product was obtained in 94% yield (150 mg, 0.47 mmol) as a white crystalline solid after silica gel column chromatography (elution with hexane/EtOAc 49:1). mp = 43-45 °C. ¹H-NMR (500 MHz, CDCl₃): 8.04-8.05 (d, J = 7.8 Hz, 2H), 7.54-7.57 (t, J = 7.4 Hz, 1H), 7.42-7.45 (t, J = 7.8 Hz, 2H), 7.30-7.32 (d, J = 8.5 Hz, 2H), 7.23-7.25 (d, J = 8.5 Hz, 2H), 7.05-7.06 (m, 2H), 6.33-6.34 (m, 2H), 4.35-4.38 (t, J = 6.0 Hz, 2H), 2.70-2.73 (t, J = 6.9 Hz, 2H), 1.80-1.83 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 139.5, 138.9, 132.8, 130.5, 129.5, 129.4, 128.3, 120.6, 119.4, 110.1, 64.7, 34.8, 28.3, 27.8; IR (neat) 3137, 2939, 1709, 1601, 1525, 1327, 1278, 1122 cm⁻¹; HRMS (ESI) calcd. for C₂₁H₂₂NO₂ [M+H]⁺ 320.1651, found 320.1660.



4-(3,5-Dimethoxyphenyl)butyl Benzoate. According to the general procedure using 1-chloro-3,5-dimethoxybenzene on a 0.50 mmol scale, the product was obtained in 89% yield (140 mg, 0.45 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 95:5). ¹H-NMR (500 MHz, CDCl₃): 8.03-8.04 (d, J = 7.9 Hz, 2H), 7.53-7.56 (t, J = 7.4 Hz, 1H), 7.42-7.45 (t, J = 7.9 Hz, 2H), 6.36 (m, 2H), 6.30-6.31 (m, 1H), 4.33-4.36 (t, J = 6.3 Hz, 2H), 3.77 (s, 6H), 2.62-2.65 (t, J = 7.4 Hz, 2H), 1.75-1.85 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.7, 160.9, 144.5, 132.8, 130.5, 129.6, 128.4, 106.5, 97.8, 64.8, 55.3, 35.8, 28.3, 27.6; IR (neat) 3062, 2941, 2837, 1714, 1596, 1462, 1274, 1151, 1115 cm⁻¹; HRMS (ESI) calcd. for C₁₉H₂₂NaO₄ [M+Na]⁺ 337.1416, found 337.1418.



4-(*p***-Tolylbutyl) Benzoate.** According to the general procedure using 1-chloro-4-methylbenzene on a 0.50 mmol scale, the product was obtained in 82% yield (111 mg, 0.41 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 99:1). ¹H-NMR (500 MHz, CDCl₃): 8.04-8.06 (d, J = 7.5 Hz, 2H), 7.56-7.58 (t, J = 7.5 Hz, 1H), 7.43-7.46 (t, J = 7.5 Hz, 2H), 7.10-7.15 (m, 4H), 4.37-4.39 (t, J = 6.9 Hz, 2H), 2.68-2.71 (t, J = 8.1 Hz, 2H), 2.32 (s, 3H), 1.85-1.90 (m, 2H), 1.73-1.80 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 142.0, 132.8, 130.5, 129.5, 128.4, 128.4, 128.3, 125.9, 64.8, 35.5, 28.4, 27.8; IR (neat) 3062, 2943, 1719, 1451, 1273, 1113 cm⁻¹; HRMS (CI) calcd. for C₁₈H₂₀O₂ [M]⁺ 268.1463, found 268.1445.



4-(2,6-Dimethylphenyl)butyl Benzoate. According to the general procedure using 2-chloro-1,3dimethylbenzene on a 0.50 mmol scale, the product was obtained in 95% yield (134 mg, 0.47 mmol) as a clear, yellow oil after silica gel column chromatography (elution with hexane/EtOAc 99:1). ¹H-NMR (500 MHz, CDCl₃): 8.04-8.06 (d, J = 8.2 Hz, 2H), 7.56-7.58 (t, J = 8.2 Hz, 1H), 7.43-7.46 (t, J = 8.2 Hz, 2H), 7.00 (s, 3H), 4.39-4.41 (t, J = 6.5 Hz, 2H), 2.69-2.72 (m, 2H), 2.33 (s, 6H), 1.89 (m, 2H), 1.62-1.69 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 139.0, 135.9, 132.8, 130.5, 129.5, 128.3, 128.1, 125.7, 64.7, 29.3, 29.2, 25.5, 19.8; IR (neat) 3062, 3018, 2950, 1719, 1466, 1273, 1115 cm⁻¹; HRMS (ESI) calcd. for C₁₉H₂₂NaO₂ [M+Na]⁺ 305.1517, found 305.1528.



4-(4-Methoxy-2,6-dimethylphenyl)butyl Benzoate. According to the general procedure using 2-chloro-5-methoxy-1,3-dimethylbenzene on a 0.50 mmol scale, the product was obtained in 92% yield (144 mg, 0.46 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 95:5). ¹H-NMR (500 MHz, CDCl₃): 8.08-8.09 (d, J = 7.1 Hz, 2H), 7.57-7.60 (t, J = 7.4 Hz, 1H), 7.45-7.48 (t, J = 7.6 Hz, 2H), 6.62 (s, 2H), 4.41-4.44 (t, J = 6.6 Hz, 2H), 3.79 (s, 3H), 2.65-2.68 (m, 2H), 2.34 (s, 6H), 1.90-1.96 (m, 2H), 1.62-1.68 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.7, 157.3, 137.3, 133.0, 131.4, 130.5, 129.7, 128.5, 113.6, 64.9, 55.2, 29.2, 28.7, 26.0, 20.3; IR (neat) 3060, 3032, 2949, 2835, 1714, 1603, 1585, 1486, 1314, 1277 cm⁻¹; HRMS (ESI) calcd. for C₂₀H₂₄NaO₃ [M+Na]⁺ 335.1623, found 335.1622.



4-(5-Cyano-2,3-dimethoxyphenyl)butyl Benzoate. According to the general procedure using 3-chloro-4,5-dimethoxybenzonitrile on a 0.50 mmol scale, the product was obtained in 80% yield (136 mg, 0.40 mmol) as a white solid after silica gel column chromatography (elution with hexane/EtOAc 9:1). mp = 43-44 °C. ¹H-NMR (500 MHz, CDCl₃): 8.02-8.04 (d, J = 7.5 Hz, 2H), 7.53-7.55 (t, J = 7.5 Hz, 1H), 7.42-7.45 (t, J = 7.5 Hz, 2H), 7.11 (s, 1H), 7.01 (s, 1H), 4.33-4.36 (t, J = 6.7 Hz, 2H), 3.86 (s, 6H), 2.68-2.71 (t, J = 7.5 Hz, 2H), 1.80-1.83 (m, 2H), 1.71-1.76 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 152.8, 151.3, 137.1, 132.9, 130.4, 129.5, 128.3, 126.6, 119.0, 113.7, 106.9, 64.6, 60.8, 56.0, 29.4, 28.4, 26.7; IR (neat) 2942, 2226, 1716, 1582, 1485, 1276, 1108 cm⁻¹; HRMS (ESI) calcd. for C₂₀H₂₂NO₄ [M+H]⁺ 340.1549, found 340.1537.



4-Phenylbutyl Benzoate. According to the general procedure using chlorobenzene on a 0.50 mmol scale, the product was obtained in 81% yield (103 mg, 0.41 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 99:1). ¹H-NMR (500 MHz, CDCl₃): 8.04-8.05 (d, J = 7.4 Hz, 2H), 7.54-7.57 (t, J = 7.4 Hz, 1H), 7.42-7.45 (t, J = 7.4 Hz, 2H), 7.28-7.31 (m, 2H), 7.18-7.21 (m, 3H), 4.34-4.36 (m, 2H), 2.69-2.72 (m, 2H), 1.79-1.82 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 142.0, 132.8, 130.5, 129.5, 128.4, 128.4, 128.3, 125.9, 64.8, 35.5, 28.4, 27.8; IR (neat) 3061, 3026, 2940, 2859, 1714, 1452, 1314, 1272, 1116 cm⁻¹; HRMS (CI) calcd. for C₁₇H₁₈O₂ [M]⁺ 254.1307, found 254.1301.



4-(4-Acetylphenyl)butyl Benzoate. According to the general procedure using 1-(4-chlorophenyl)ethanone on a 0.50 mmol scale, the product was obtained in 87% yield (129 mg, 0.44 mmol) as a white crystalline solid after silica gel column chromatography (elution with hexane/EtOAc 95:5). mp = 55-57 °C. ¹H-NMR (500 MHz, CDCl₃): 8.02-8.04 (d, J = 7.9 Hz, 2H), 7.87-7.89 (d, J = 8.4 Hz, 2H), 7.53-7.57 (t, J = 7.9 Hz, 1H), 7.42-7.45 (t, J = 7.9 Hz, 2H), 7.27-7.29 (d, J = 8.4 Hz, 2H), 4.33-4.36 (m, 2H), 2.74-2.76 (m, 2H), 2.57 (s, 3H), 1.79-1.82 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 197.7, 166.6, 147.8, 135.2, 132.9, 130.4, 129.5, 128.6, 128.6, 128.3, 64.6, 35.5, 28.3, 27.4, 26.5; IR (neat) 2961, 1868, 1712, 1679, 1604, 1267, 1121 cm⁻¹; HRMS (CI) calcd. for C₁₉H₂₀O₃ [M]⁺ 296.1412, found 296.1422.



4-(4-Nitrophenyl)butyl Benzoate. According to the general procedure using 1-chloro-4nitrobenzene on a 0.50 mmol scale, the product was obtained in 96% yield (143 mg, 0.48 mmol) as a yellow solid after silica gel column chromatography (elution with hexane/EtOAc 9:1). mp = 70-72 °C. ¹H-NMR (500 MHz, CDCl₃): 8.13-8.15 (d, J = 8.2 Hz, 2H), 8.02-8.03 (d, J = 7.5 Hz, 2H), 7.54-7.57 (t, J = 7.5 Hz, 1H), 7.42-7.45 (t, J = 7.5 Hz, 2H), 7.33-7.35 (d, J = 8.2 Hz, 2H), 4.34-4.37 (m, 2H), 2.78-2.81 (m, 2H), 1.81-1.84 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 149.8, 146.5, 132.9, 130.3, 129.5, 129.2, 128.4, 123.7, 64.4, 35.3, 28.3, 27.4; IR (neat) 2959, 2940, 1719, 1601, 1512, 1349, 1278, 1124 cm⁻¹; HRMS (ESI) calcd. for C₁₇H₁₈NO₄ [M+H]⁺ 300.1236, found 300.1241.



4-(4-(Trifluoromethyl)phenyl)butyl Benzoate. According to the general procedure using 1chloro-4-(trifluoromethyl)benzene on a 0.50 mmol scale, the product was obtained in 90% yield (144 mg, 0.45 mmol) as an off-white crystalline solid after silica gel column chromatography (elution with hexane/EtOAc 49:1). mp = 41-42 °C. ¹H-NMR (500 MHz, CDCl₃): 8.03-8.05 (d, *J* = 7.9 Hz, 2H), 7.53-7.57 (m, 3H), 7.42-7.46 (t, *J* = 7.9 Hz, 2H), 7.30-7.31 (d, *J* = 7.9 Hz, 2H), 4.35-4.39 (m, 2H), 2.74-2.77 (m, 2H), 1.78-1.85 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 146.1, 132.9, 130.4, 129.5, 128.7, 128.3, 125.4, 125.3 (q, *J* = 3.8 Hz), 123.3, 64.6, 35.3, 28.3, 27.5; IR (neat) 2944, 1706, 1616, 1450, 1278, 1124 cm⁻¹; HRMS (CI) calcd. for C₁₈H₁₇F₂O₂ [M-F]⁺ 303.1197, found 303.1200.



4-(4-Cyanophenyl)butyl Benzoate. According to the general procedure using 4-chlorobenzonitrile on a 0.50 mmol scale, the product was obtained in 87% yield (121 mg, 0.43 mmol) as a white crystalline solid after silica gel column chromatography (elution with hexane/EtOAc 95:5). mp = 68-70 °C. ¹H-NMR (500 MHz, CDCl₃): 8.01-8.03 (d, J = 7.5 Hz, 2H), 7.54-7.57 (m, 3H), 7.42-7.45 (t, J = 7.5 Hz, 2H), 7.28-7.30 (d, J = 8.3 Hz, 2H), 4.33-3.36 (t, J = 6.1 Hz, 2H), 2.73-2.76 (t, J = 7.1 Hz, 2H), 1.77-1.82 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 147.6, 132.9, 132.2, 130.3, 129.5, 129.2, 128.4, 119.0, 109.9, 64.4, 35.6, 28.3, 27.3; IR (neat) 3059, 2942, 2223, 1716, 1605, 1470, 1450, 1278, 1129 cm⁻¹; HRMS (ESI) calcd.

for C₁₈H₁₇NaNO₂ [M+Na]⁺ 302.1157, found 302.1168.



Methyl 3-(4-(Benzoyloxy)butyl)benzoate. According to the general procedure using methyl 3chlorobenzoate on a 0.50 mmol scale, the product was obtained in 91% yield (142 mg, 0.45 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 95:5). ¹H-NMR (500 MHz, CDCl₃): 8.02-8.04 (d, J = 7.9 Hz, 2H), 7.86-7.88 (m, 2H), 7.53-7.57 (t, J = 7.9 Hz, 1H), 7.42-7.45 (t, J = 7.9 Hz, 2H), 7.34-7.39 (m, 2H), 4.33-4.36 (m, 2H), 3.91 (s, 3H), 2.73-2.76 (m, 2H), 1.79-1.83 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 142.3, 133.0, 132.8, 130.4, 130.3, 129.5, 129.5, 128.4, 128.3, 127.2, 64.7, 52.0, 35.3, 28.3, 27.7; IR (neat) 2950, 1720, 1450, 1275, 1111 cm⁻¹; HRMS (ESI) calcd. for C₁₉H₂₀NaO₄ [M+Na]⁺ 335.1259, found 335.1253.



4-(4-Formylphenyl)butyl Benzoate. According to the general procedure using 4-chlorobenzaldehyde on a 0.50 mmol scale, the product was obtained in 90% yield (127 mg, 0.45 mmol) as a white crystalline solid after silica gel column chromatography (elution with hexane/EtOAc 9:1). mp = 62-64 °C. ¹H-NMR (500 MHz, CDCl₃): 9.97 (s, 1H), 8.02-8.04 (d, J = 7.3 Hz, 2H), 7.79-7.81 (d, J = 7.9 Hz, 2H), 7.53-7.56 (t, J = 7.3 Hz, 1H), 7.42-7.45 (t, J = 7.3 Hz, 2H), 7.34-7.36 (d, J = 7.9 Hz, 2H), 4.34-4.36 (m, 2H), 2.76-2.79 (m, 2H), 1.79-1.85 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 191.83, 166.6, 149.4, 134.7, 132.9, 130.4, 130.0, 129.5, 129.1, 128.3, 64.5, 35.7, 28.3, 27.4; IR (neat) 2955, 2891, 1709, 1686, 1607, 1280 cm⁻¹; HRMS (CI)

calcd. for $C_{18}H_{18}O_3$ [M]⁺ 282.1256, found 282.1266.



4-(4-Benzoylphenyl)butyl Benzoate. According to the general procedure using (4-chlorophenyl)(phenyl)methanone on a 0.50 mmol scale, the product was obtained in 89% yield (159 mg, 0.44 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 95:5). ¹H-NMR (500 MHz, CDCl₃): 8.02-8.05 (d, J = 8.4 Hz, 2H), 7.78-7.80 (d, J = 8.0 Hz, 2H), 7.74-7.76 (d, J = 8.0 Hz, 2H), 7.54-7.59 (m, 2H), 7.42-7.49 (m, 4H), 7.30-7.31 (d, J = 8.0 Hz, 2H), 4.35-4.38 (m, 2H), 2.77-2.80 (m, 2H), 1.82-1.86 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 196.4, 166.6, 147.1, 137.9, 135.4, 132.9, 123.2, 130.4, 129.9, 129.5, 128.3, 128.3, 128.2, 64.6, 35.5, 28.3, 27.5; IR (neat) 3059, 2942, 1716, 1657, 1605, 1276 cm⁻¹; HRMS (ESI) calcd. for C₂₄H₂₂NaO₃ [M+Na]⁺ 381.1467, found 381.1471.



4-(6-Methoxypyridin-3-yl)butyl Benzoate. According to the general procedure using 5-chloro-2-methoxypyridine on a 0.50 mmol scale, the product was obtained in 97% yield (139 mg, 0.49 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 7:3). ¹H-NMR (500 MHz, CDCl₃): 8.00-8.02 (d, J = 7.4 Hz, 2H), 7.96 (s, 1H), 7.51-7.53 (t, J = 7.4, Hz, 1H), 7.37-7.42 (m, 3H), 6.65-6.67 (d, J = 8.4 Hz, 1H), 4.30-4.33 (t, J = 6.4 Hz, 2H), 3.89 (s, 3H), 2.57-2.59 (t, J = 7.4 Hz, 2H), 1.69-1.79 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 162.8, 146.1, 138.9, 132.9, 130.4, 129.8, 129.6, 128.4, 110.6, 64.7, 53.3,

31.7, 28.2, 27.8; IR (neat) 3061, 2943, 2858, 1716, 1607, 1493, 1391, 1313, 1275, 1115 cm⁻¹; HRMS (ESI) calcd. for C₁₇H₂₀NaNO₃ [M+H]⁺ 286.1443, found 286.1445.



4-(6-Fluoropyridin-3-yl)butyl Benzoate. According to the general procedure using 5-chloro-2-fluoropyridine on a 0.50 mmol scale, the product was obtained in 73% yield (100 mg, 0.37 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 7:3). ¹H-NMR (500 MHz, CDCl₃): 8.00-8.02 (m, 3H), 7.56-7.59 (m, 1H), 7.51-7.54 (t, J = 7.5 Hz, 1H), 7.40-7.43 (t, J = 7.5 Hz, 2H), 6.81-6.84 (m, 1H), 4.31-4.34 (t, J = 6.2 Hz, 2H), 2.64-2.67 (t, J = 7.4 Hz, 2H), 1.71-1.82 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.7, 161.5-163.4 (d, J = 236.1 Hz), 147.0-147.1 (d, J = 14.4 Hz), 141.1 (d, J = 7.7 Hz), 134.9 (d, J = 4.7 Hz), 133.1, 130.4, 129.6, 128.5, 109.1-109.4 (d, J = 37.4 Hz), 64.6, 31.7, 28.3, 27.8; IR (neat) 3409, 3062, 2944, 2863, 1717, 1597, 1483, 1394, 1273, 1249, 1116 cm⁻¹; HRMS (ESI) calcd. for C₁₆H₁₇FNaNO₂ [M+H]⁺ 274.1243, found 274.1250.



4-(4-Formylpyridin-3-yl)butyl Benzoate. According to the general procedure using 3-chloroisonicotinaldehyde on a 0.50 mmol scale, the product was obtained in 85% yield (120 mg, 0.42 mmol) as a light yellow oil after silica gel column chromatography (elution with hexane/EtOAc 2:1). ¹H-NMR (500 MHz, CDCl₃): 10.27 (s, 1H), 8.69-8.70 (d, J = 5.0 Hz, 1H), 8.63 (s, 1H), 7.96-8.00 (d, J = 7.7 Hz, 2H), 7.58-7.59 (d, J = 5.5 Hz, 1H), 7.47-7.53 (t, J = 7.7

Hz, 1H), 7.35-7.41 (t, J = 7.7 Hz, 2H), 4.32-4.35 (t, J = 6.4 Hz, 2H), 3.04-3.07 (m, 2H), 1.79-1.88 (m, 2H), 1.69-1.77 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): 191.8, 166.6, 152.8, 149.0, 138.9, 137.2, 133.0, 129.6, 128.5, 123.7, 64.4, 29.5, 28.6, 28.5; IR (neat) 3405, 3060, 3031, 2950, 2865, 1749, 1713, 1452, 1314, 1274, 1114 cm⁻¹; HRMS (ESI) calcd. for C₁₇H₁₈NO₃ [M+H]⁺ 284.1287, found 284.1286.



4-(2-Methylquinolin-4-yl)butyl Benzoate. According to the general procedure using 4-chloro-2-methylquinoline on a 0.50 mmol scale, the product was obtained in 91% yield (146 mg, 0.46 mmol) as a clear, light pink oil after silica gel column chromatography (elution with hexane/EtOAc 3:2). ¹H-NMR (500 MHz, CDCl₃): 8.02-8.03 (d, J = 7.8 Hz, 3H), 7.96-7.98 (d, J = 8.3 Hz, 1H), 7.64-7.67 (t, J = 7.8 Hz, 1H), 7.53-7.57 (t, J = 7.4 Hz, 1H), 7.41-7.48 (m, 3H), 7.14 (s, 1H), 4.38-4.40 (t, J = 5.9 Hz, 2H), 3.09-3.11 (t, J = 7.3 Hz, 2H), 2.70 (s, 3H), 1.90-1.95 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.8, 158.9, 148.3, 147.9, 133.1, 130.4, 129.7, 129.6, 129.3, 128.6, 125.9, 125.7, 123.4, 121.9, 64.7, 31.8, 28.9, 26.6, 25.5; IR (neat) 3061, 2949, 2867, 1715, 1601, 1451, 1273, 1116 cm⁻¹; HRMS (ESI) calcd. for C₂₁H₂₂NO₂ [M+H]⁺ 320.1651, found 320.1665.



4-(Thiophen-3-yl)butyl Benzoate. According to the general procedure using 3-chlorothiophene

on a 0.50 mmol scale, the product was obtained in 81% yield (106 mg, 0.41 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 95:5). ¹H-NMR (500 MHz, CDCl₃): 8.03-8.04 (d, J = 7.6 Hz, 2H), 7.52-7.55 (t, J = 7.6 Hz, 1H), 7.40-7.43 (t, J = 7.6 Hz, 2H), 7.22-7.24 (t, J = 4.1 Hz, 1H), 6.93-6.94 (m, 2H), 4.32-4.34 (t, J = 6.1 Hz, 2H), 2.69-2.71 (t, J = 7.1 Hz, 2H), 1.74-1.83 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.7, 142.5, 133.0, 130.5, 129.7, 128.5, 128.3, 125.5, 120.3, 64.9, 30.0, 28.5, 27.1; IR (neat) 3102, 3062, 2940, 2860, 1717, 1451, 1314, 1272, 1115 cm⁻¹; HRMS (CI) calcd. for C₁₅H₁₆O₂S [M]⁺ 260.0871, found 260.0871.



4-(Thiophen-2-yl)butyl Benzoate. According to the general procedure using 2-chlorothiophene on a 0.50 mmol scale, the product was obtained in 96% yield (124 mg, 0.48 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 95:5). ¹H-NMR (500 MHz, CDCl₃): 8.07-8.08 (d, J = 7.7 Hz, 2H), 7.56-7.59 (t, J = 7.7 Hz, 1H), 7.44-7.47 (t, J = 7.7 Hz, 2H), 7.14-7.15 (d, J = 5.1 Hz, 1H), 6.94-6.95 (m, 1H), 6.83 (m, 1H), 4.36-4.38 (m, 2H), 2.92-2.95 (m, 2H), 1.86-1.90 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.7, 145.0, 133.0, 130.5, 129.7, 128.5, 126.9, 124.4, 123.2, 64.8, 29.6, 28.4, 28.3; IR (neat) 3067, 2940, 2858, 1716, 1451, 1314, 1270, 1115 cm⁻¹; HRMS (CI) calcd. for C₁₅H₁₇O₂S [M+H]⁺ 261.0949, found 261.0947.



4-(5-Acetylthiophen-2-yl)butyl Benzoate. According to the general procedure using 1-(5-

chlorothiophen-2-yl)ethanone on a 0.50 mmol scale, the product was obtained in 76% yield (115 mg, 0.38 mmol) as a light yellow solid after silica gel column chromatography (elution with hexane/EtOAc 9:1). mp = 38-40 °C. ¹H-NMR (500 MHz, CDCl₃): 8.01-8.03 (d, J = 7.8 Hz, 2H), 7.51-7.55 (m, 2H), 7.40-7.44 (t, J = 7.8 Hz, 2H), 6.82-6.83 (d, J = 3.8 Hz, 1H), 4.32-4.34 (t, J = 6.0 Hz, 2H), 2.89-2.92 (t, J = 7.0 Hz, 2H), 2.49 (s, 3H), 1.83-1.88 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 190.5, 166.6, 154.9, 142.3, 133.0, 132.9, 130.3, 129.6, 128.4, 125.9, 64.4, 30.3, 28.1, 27.9, 26.5; IR (neat) 3067, 2944, 2860, 1716, 1658, 1452, 1275, 1115 cm⁻¹; HRMS (ESI) calcd. for C₁₇H₁₈NaO₃S [M+Na]⁺ 325.0874, found 325.0867.



4-(5-Formylthiophen-2-yl)butyl Benzoate. According to the general procedure using 5-chlorothiophene-2-carbaldehyde on a 0.50 mmol scale, the product was obtained in 71% yield (102 mg, 0.35 mmol) as a light yellow solid after silica gel column chromatography (elution with hexane/EtOAc 9:1). mp = 53-55 °C. ¹H-NMR (500 MHz, CDCl₃): 9.82 (s, 1H), 8.02-8.04 (d, J = 7.2 Hz, 2H), 7.61-7.62 (d, J = 3.7 Hz, 1H), 7.55-7.58 (t, J = 7.2 Hz, 1H), 7.43-7.46 (t, J = 7.2 Hz, 2H), 6.92-6.93 (d, J = 3.7 Hz, 1H), 4.34-4.37 (t, J = 5.9 Hz, 2H), 2.95-2.98 (t, J = 7.2 Hz, 2H), 1.83-1.92 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 182.8, 166.7, 156.7, 142.0, 137.0, 133.1, 130.4, 129.7, 128.5, 126.3, 64.5, 30.5, 28.2, 27.9; IR (neat) 3062, 2943, 2857, 1716, 1665, 1460, 1275, 1115 cm⁻¹; HRMS (ESI) calcd. for C₁₆H₁₆NaO₃S [M+Na]⁺ 311.0718, found 311.0724.



4-(5-Formylfuran-2-yl)butyl Benzoate. According to the general procedure using 5-chlorofuran-2-carbaldehyde on a 0.50 mmol scale, the product was obtained in 83% yield (114 mg, 0.42 mmol) as a yellow oil after silica gel column chromatography (elution with hexane/EtOAc 4:1). ¹H-NMR (500 MHz, CDCl₃): 9.50 (s, 1H), 8.00-8.02 (d, J = 7.4 Hz, 2H), 7.52-7.55 (t, J = 7.4 Hz, 1H), 7.40-7.43 (t, J = 7.4 Hz, 2H), 7.15-7.16 (d, J = 3.5 Hz, 1H), 6.25-6.26 (d, J = 3.5 Hz, 1H), 4.32-4.34 (t, J = 6.1 Hz, 2H), 2.78-2.81 (t, J = 7.4 Hz, 2H), 1.81-1.89 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 177.1, 166.7, 163.2, 152.0, 133.1, 130.3, 129.7, 128.5, 123.7, 109.1, 64.5, 28.3, 28.1, 24.4; IR (neat) 3116, 3063, 2953, 2869, 1713, 1681, 1518, 1272, 1116 cm⁻¹; HRMS (ESI) calcd. for C₁₆H₁₆NaO₄ [M+Na]⁺ 295.0946, found 295.0957.



1-Methoxy-4-octylbenzene. According to the general procedure using 4-chloroanisole and potassium octyltrifluoroborate³ on a 0.50 mmol scale, the product was obtained in 82% yield (90.4 mg, 0.41 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane). ¹H-NMR (500 MHz, CDCl₃): 7.11-7.12 (d, J = 8.6 Hz, 2H), 6.84-6.85 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 2.55-2.58 (t, J = 7.7 Hz, 2H), 1.57-1.61 (m, 2H), 1.29-1.32 (m, 10H), 0.89-0.92 (t, J = 7.0 Hz, 3H); ¹³C-NMR (125.8 MHz, CDCl₃): 157.8, 135.3, 129.4, 113.8, 55.4, 35.3, 32.1, 32.0, 29.7, 29.5, 22.9, 14.3. This spectral data is in accordance with that provided in the literature.⁵



1-Decyl-4-methoxybenzene. According to the general procedure using 4-chloroanisole and potassium decyltrifluoroborate on a 0.50 mmol scale, the product was obtained in 70% yield (86.1 mg, 0.35 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane). ¹H-NMR (500 MHz, CDCl₃): 7.10-7.12 (d, J = 8.5 Hz, 2H), 6.83-6.85 (d, J = 8.5 Hz, 2H), 2.55-2.58 (t, J = 7.9 Hz, 2H), 1.57-1.61 (m, 2H), 1.28-1.32 (m, 14H), 0.89-0.92 (t, J = 7.1 Hz, 3H); ¹³C-NMR (125.8 MHz, CDCl₃): 157.8, 135.3, 129.4, 113.8, 55.4, 35.3, 32.1, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 22.9, 14.3. This spectral data is in accordance with that provided in the literature.⁶



(4-Methoxybenzyl)trimethylsilane. According to the general procedure using 4-chloroanisole and potassium (trimethylsilyl)methyltrifluoroborate⁷ on a 0.50 mmol scale, the product was obtained in 71% yield (69.1 mg, 0.36 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane). ¹H-NMR (500 MHz, CDCl₃): 6.91-6.92 (d, J = 8.5 Hz, 2H), 6.77-6.79 (d, J = 8.5 Hz, 2H), 3.78 (s, 3H), 2.01 (s, 2H), -0.01 (s, 9H); ¹³C-NMR (125.8 MHz, CDCl₃): 156.7, 132.5, 129.0, 113.8, 55.4, 25.9, -1.7; IR (neat) 3028, 2997, 2952, 2832, 1610, 1509, 1246 cm⁻¹; HRMS (CI) calcd. for C₁₁H₁₉OSi [M+H]⁺ 195.1205, found 195.1203.



6-(4-Methoxyphenyl)hexan-2-one. According to the general procedure using 4-chloroanisole and potassium 5-oxohexyltrifluoroborate⁸ on a 0.50 mmol scale, the product was obtained in 78% yield (81.0 mg, 0.39 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 9:1). ¹H-NMR (500 MHz, CDCl₃): 7.07-7.09 (d, J = 8.6 Hz, 2H), 6.81-6.82 (d, J = 8.6 Hz, 2H), 3.77 (s, 3H), 2.54-2.57 (t, J = 7.3 Hz, 2H), 2.42-2.44 (t, J = 7.0 Hz, 2H), 2.11 (s, 3H), 1.56-1.62 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 209.2, 157.8, 134.4, 129.4, 113.8, 55.3, 43.7, 34.9, 31.3, 30.0, 23.5; IR (neat) 3026, 2998, 2934, 2856, 1714, 1612, 1513, 1246, 1177, 1035 cm⁻¹; HRMS (CI) calcd. for C₁₃H₁₉O₂ [M+H]⁺ 207.1385, found 207.1376.



6-(4-Methoxyphenyl)hexyl Benzoate. According to the general procedure using 4-chloroanisole and potassium 6-(benzoyloxy)hexyltrifluoroborate⁸ on a 0.50 mmol scale, the product was obtained in 91% yield (142 mg, 0.45 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 49:1). ¹H-NMR (500 MHz, CDCl₃): 8.04-8.05 (d, J = 7.5 Hz, 2H), 7.53-7.57 (t, J = 7.5 Hz, 1H), 7.42-7.45 (t, J = 7.5 Hz, 2H), 7.08-7.10 (d, J = 8.4 Hz, 2H), 6.81-6.83 (d, J = 8.4 Hz, 2H), 4.30-4.33 (t, J = 6.7 Hz, 2H), 3.78 (s, 3H), 2.55-2.58 (t, J = 7.7 Hz, 2H), 1.74 (m, 2H), 1.60-1.64 (m, 2H), 1.39-1.50 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 157.7, 134.7, 132.8, 130.6, 129.5, 129.2, 128.3, 113.7, 65.0, 55.2, 34.9, 31.5, 28.8, 28.7, 25.9; IR (neat) 3030, 2930, 2855, 1718, 1511, 1273, 1246, 1116 cm⁻¹; HRMS (ESI) calcd. for C₂₈H₂₅O₃ [M+H]⁺ 313.1804, found 313.1804.



5-(4-Methoxyphenyl)pentanenitrile. According to the general procedure using 4-chloroanisole and potassium 4-cyanobutyltrifluoroborate⁹ on a 0.50 mmol scale, the product was obtained in 80% yield (75.2 mg, 0.40 mmol) as a clear, light yellow oil after silica gel column chromatography (elution with hexane/EtOAc 9:1). ¹H-NMR (500 MHz, CDCl₃): 7.08-7.10 (d, J = 8.6 Hz, 2H), 6.83-6.84 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.59-2.62 (t, J = 7.4 Hz, 2H), 2.32-2.59 (t, J = 7.0 Hz, 2H), 1.65-1.77 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 158.1, 133.4, 129.4, 119.9, 114.0, 55.4, 34.2, 30.7, 24.9, 17.2; IR (neat) 3003, 2935, 2859, 2245, 1513, 1245 cm⁻¹; HRMS (ESI) calcd. for C₁₂H₁₆NO [M+H]⁺ 190.1232, found 190.1240.



1-Methoxy-4-phenethylbenzene. According to the general procedure using 4-chloroanisole and potassium phenethyltrifluoroborate on a 0.50 mmol scale, the product was obtained in 87% yield (92.4 mg, 0.44 mmol) as a white crystalline solid after silica gel column chromatography (elution with hexane). mp = 58-60 °C. ¹H-NMR (500 MHz, CDCl₃): 7.26-7.31 (m, 2H), 7.18-7.22 (m, 3H), 7.09-7.12 (d, J = 8.6 Hz, 2H), 6.83-6.85 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 2.86-2.91 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 158.0, 142.1, 134.1, 129.6, 128.7, 128.5, 126.1, 113.9, 55.5, 38.4, 37.2; IR (neat) 3026, 2932, 2853, 1512, 1451, 1248 cm⁻¹; HRMS (CI) calcd. for $C_{15}H_{17}O[M+H]^+$ 213.1279, found 213.1280.



4-(4-Methoxyphenyl)butyl Pivalate. According to the general procedure using 4-chloroanisole and potassium 4-(pivaloyloxy)butyltrifluoroborate⁹ on a 0.50 mmol scale, the product was obtained in 82% yield (108 mg, 0.41 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 99:1). ¹H-NMR (500 MHz, CDCl₃): 7.09-7.11 (d, J = 8.8 Hz, 2H), 6.83-6.85 (d, J = 8.8 Hz, 2H), 4.07-4.09 (m, 2H), 3.79 (s, 3H), 2.58-2.61 (m, 2H), 1.65-1.68 (m, 4H), 1.20 (s, 9H); ¹³C-NMR (125.8 MHz, CDCl₃): 178.7, 157.9, 134.3, 129.4, 113.9, 64.3, 55.4, 38.9, 34.7, 28.3, 28.1, 27.4; IR (neat) 2935, 1726, 1512, 1245, 1154 cm⁻¹; HRMS (ESI) calcd. for C₁₆H₂₄NaO₃ [M+Na]⁺ 287.1623, found 287.1616.



tert-Butyl(4-(4-methoxyphenyl)butoxy)dimethylsilane. According to the general procedure using 4-chloroanisole and potassium 4-(*tert*-butyldimethylsilyloxy)butyltrifluoroborate on a 0.50 mmol scale, the product was obtained in 71% yield (104 mg, 0.35 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 49:1). ¹H-NMR (500 MHz, CDCl₃): 7.10-7.12 (d, *J* = 8.6 Hz, 2H), 6.83-6.85 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.63-3.65 (t, *J* = 6.4 Hz, 2H), 2.57-2.60 (t, *J* = 7.5 Hz, 2H), 1.62-1.68 (m, 2H), 1.54-1.59 (m, 2H), 0.91 (s, 9H), -0.06 (s, 6H); ¹³C-NMR (125.8 MHz, CDCl₃): 157.8, 134.9, 129.5, 113.9, 63.2, 55.4, 35.0, 32.6, 28.1, 26.2, 18.6, -5.1; IR (neat) 3032, 2994, 2929, 2856, 1612, 1512, 1463, 1246, 1101 cm⁻¹; HRMS (CI) calcd. for $C_{16}H_{27}O_2$ Si [M-Me]⁺ 279.1780, found 279.1789.



1-Isobutyl-4-methoxybenzene. According to the general procedure using 4-chloroanisole and potassium isobutyltrifluoroborate on a 0.50 mmol scale, the product was obtained in 77% yield (62.9 mg, 0.38 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane). ¹H-NMR (500 MHz, CDCl₃): 7.05-7.07 (d, J = 8.6 Hz, 2H), 6.82-6.84 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 2.41-2.43 (d, J = 7.2 Hz, 2H), 1.79-1.83 (septet, J = 6.8 Hz, 1H), 0.89-0.91 (d, J = 6.8 Hz, 6H); ¹³C-NMR (125.8 MHz, CDCl₃): 157.8, 134.0, 130.2, 113.7, 55.4, 44.7, 30.6, 22.5. This spectral data is in accordance with that provided in the literature.¹⁰



N-(4-Methylphenyl)pyrrole. According to the general procedure using 1-(4-chlorophenyl)-1*H*pyrrole and potassium methyltrifluoroborate on a 0.50 mmol scale, the product was obtained in 72% yield (56.6 mg, 0.36 mmol) as a white solid after silica gel column chromatography (elution with hexane). ¹H-NMR (500 MHz, CDCl₃): 7.30-7.31 (d, J = 8.3 Hz, 2H), 7.23-7.25 (d, J = 8.3Hz, 2H), 7.08-7.09 (m, 2H), 6.35-6.36 (m, 2H), 2.40 (s, 3H); ¹³C-NMR (125.8 MHz, CDCl₃): 138.6, 135.5, 130.2, 120.7, 119.5, 110.2, 21.0. This spectral data is in accordance with that provided in the literature.¹¹



4-(4-Methoxyphenyl)butyl Benzoate. According to the general procedure using 4-chloroanisole

and potassium 4-(benzoyloxy)butyltrifluoroborate on a 0.50 mmol scale, the product was obtained in 92% yield (138 mg, 0.46 mmol) as a clear, colorless oil after silica gel column chromatography (elution with hexane/EtOAc 99:1). ¹H-NMR (500 MHz, CDCl₃): 8.02-8.04 (d, J = 7.4 Hz, 2H), 7.53-7.56 (t, J = 7.4 Hz, 1H), 7.42-7.45 (t, J = 7.4 Hz, 2H), 7.09-7.12 (d, J = 8.6 Hz, 2H), 6.82-6.84 (d, J = 8.6 Hz, 2H), 4.33-4.35 (t, J = 6.3 Hz, 2H), 3.79 (s, 3H), 2.62-2.65 (t, J = 7.2 Hz, 2H), 1.74-1.82 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): 166.6, 157.9, 134.1, 132.8, 130.5, 129.6, 129.3, 128.3, 113.9, 64.9, 55.2, 34.6, 28.3, 28.0; IR (neat) 3060, 3031, 2935, 2857, 1715, 1612, 1513, 1452, 1274, 1246, 1116 cm⁻¹; HRMS (ESI) calcd. for C₁₈H₂₀NaO₃ [M+Na]⁺ 307.1310, found 307.1315.

The title compound was also prepared according to the general procedure using 4bromoanisole (93.5 mg, 0.50 mmol) and was isolated as a clear, colorless oil in 86% yield (129 mg, 0.43 mmol) with spectral data in accordance with data listed above.

The title compound was also prepared according to the general procedure using 4methoxyphenyl trifluoromethanesulfonate (128 mg, 0.50 mmol) and was isolated as a clear, colorless oil in 75% yield (111 mg, 0.37 mmol) with spectral data in accordance with data listed above.

The title compound was also prepared according to the general procedure using 4iodoanisole (117 mg, 0.50 mmol) and Cs_2CO_3 (489 mg, 1.5 mmol) and was isolated as a clear, colorless oil in 80% yield (114 mg, 0.40 mmol) with spectral data in accordance with data listed above.

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¹³C NMR (125.8 MHz, acetone-*d*₆) Spectrum of Potassium 4-(Benzoyloxy)butyltrifluoroborate 6



 19 F NMR (470.8 MHz, acetone- d_6) Spectrum of Potassium 4-(Benzoyloxy)butyltrifluoroborate 6



¹¹B NMR (128.4 MHz, acetone-*d*₆) Spectrum of Potassium 4-(Benzoyloxy)butyltrifluoroborate **6**



¹H NMR (500 MHz, acetone-*d*₆) Spectrum of Potassium 4-(*t*-Butyldimethylsilyloxy)butyltrifluoroborate 7



¹³C NMR (125.8 MHz, acetone-*d*₆) Spectrum of Potassium 4-(*t*-Butyldimethylsilyloxy)butyltrifluoroborate 7



¹⁹F NMR (470.8 MHz, acetone-*d*₆) Spectrum of Potassium 4-(*t*-Butyldimethylsilyloxy)butyltrifluoroborate 7



¹¹B NMR (128.4 MHz, acetone-*d*₆) Spectrum of Potassium 4-(*t*-Butyldimethylsilyloxy)butyltrifluoroborate 7



¹H NMR (500 MHz, acetone- d_6) Spectrum of Potassium Isobutyltrifluoroborate **8**



¹³C NMR (125.8 MHz, acetone-*d*₆) Spectrum of Potassium Isobutyltrifluoroborate **8**



 19 F NMR (470.8 MHz, acetone- d_6) Spectrum of Potassium Isobutyltrifluoroborate 8



¹¹B NMR (128.4 MHz, acetone- d_6) Spectrum of Potassium Isobutyltrifluoroborate 8







¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(4-(1*H*-Pyrrol-1-yl)phenyl)butyl Benzoate (Table 1, entry 2)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(4-(1*H*-Pyrrol-1-yl)phenyl)butyl Benzoate (Table 1, entry 2)



¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(3,5-Dimethoxyphenyl)butyl Benzoate (Table 1, entry 3)



(Table 1, entry 3)



(Table 1, entry 4)







¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(4-Methoxy-2,6-dimethylphenyl)butyl Benzoate (Table 1, entry 6)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(4-Methoxy-2,6-dimethylphenyl)butyl Benzoate (Table 1, entry 6)



¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(5-Cyano-2,3-dimethoxyphenyl)butyl Benzoate (Table 1, entry 7)















¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(4-Nitrophenyl)butyl Benzoate (Table 2,entry 3)





¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(4-(Trifluoromethyl)phenyl)butyl Benzoate (Table 2, entry 4)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(4-(Trifluoromethyl)phenyl)butyl Benzoate (Table 2, entry 4)









¹H NMR (500 MHz, CDCl₃) Spectrum of Methyl 3-(4-(Benzoyloxy)butyl)benzoate (Table 2, entry 6)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of Methyl 3-(4-(Benzoyloxy)butyl)benzoate (Table 2, entry 6)









¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(4-Benzoylphenyl)butyl Benzoate (Table 2, entry 8)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(4-Benzoylphenyl)butyl Benzoate (Table 2, entry 8)



190 180 170 180 150 140 150 120 110 100 90 80 70 80 50 40 50 20 10 pp

¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(Pyridin-3-yl)butyl Benzoate (Table 3, entry 1)





¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(6-Methoxypyridin-3-yl)butyl Benzoate (Table 3, entry 2)





(Table 3, entry 3)



¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(4-Formylpyridin-3-yl)butyl Benzoate (Table 3, entry 4)









¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(2-Methylquinolin-4-yl)butyl Benzoate (Table 3, entry 5)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(2-Methylquinolin-4-yl)butyl Benzoate (Table 3, entry 5)













¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(5-Acetylthiophen-2-yl)butyl Benzoate (Table 3, entry 8)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(5-Acetylthiophen-2-yl)butyl Benzoate (Table 3, entry 8)



¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(5-Formylthiophen-2-yl)butyl Benzoate (Table 3, entry 9)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(5-Formylthiophen-2-yl)butyl Benzoate (Table 3, entry 9)









190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 1-Methoxy-4-octylbenzene (Table 4, entry 1)



(Table 4, entry 2)



¹H NMR (500 MHz, CDCl₃) Spectrum of (4-Methoxybenzyl)trimethylsilane (Table 4, entry 3)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of (4-Methoxybenzyl)trimethylsilane (Table 4, entry 3)









(Table 4, entry 5)



¹H NMR (500 MHz, CDCl₃) Spectrum of 5-(4-Methoxyphenyl)pentanenitrile (Table 4, entry 6)



(Table 4, entry 6)



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 1-Methoxy-4-phenethylbenzene (Table 4, entry 7)





¹⁹⁰ ¹⁸⁰ ¹⁷⁰ ¹⁶⁰ ¹⁵⁰ ¹⁴⁰ ¹³⁰ ¹²⁰ ¹¹⁰ ¹⁰⁰ ⁹⁰ ⁸⁰ ⁷⁰ ⁶⁰ ⁵⁰ ⁴⁰ ³⁰ ²⁰ ¹⁰ _{ppm} ¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(4-Methoxyphenyl)butyl Pivalate (Table 4, entry 8)



¹H NMR (500 MHz, CDCl₃) Spectrum of *tert*-Butyl(4-(4-methoxyphenyl)butoxy)dimethylsilane (Table 4, entry 9)



(Table 4, entry 9)



S68



¹H NMR (500 MHz, CDCl₃) Spectrum of 1-*p*-Tolyl-1*H*-pyrrole **9**



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 1-*p*-Tolyl-1*H*-pyrrole **9**





¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4-(4-Methoxyphenyl)butyl Benzoate (Table 5, entry 1)