Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Palladium-catalysed *ortho*-arylation of carbamate-protected phenols

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Electronic Supporting Information

Contents

Table S1

Entry	Pd Source (mol%)	Temp., °C	Time, h	Additive (eq)	Solvent	%**2a**[c]	%**3a**[c]
1	$Pd(OAc)_2$ (10)	50	72	AgOAc (2)	TFA	49	41
2[a]	$Pd(OAc)_2$ (5)	80	4	"	"	43.5	36.5
3[a]	$PdCl_2$ (5)	100	1	"	"	38.5	35
4[a,b]	$Pd(OAc)_2$ (5)	100	1	CuI (2)	"	6	0
5[a,b]	"	"	"	PPh_3 (0.1)	"	37.5	47.5
6[a,b]	"	"	"	PCy_3 (0.1)	"	22.5	0
7[a,b]	"	"	"	$P(OAr)_3$ (0.1)	"	0	0
8[a,b]	"	"	"	$AsPh_3$ (0.1)	"	19	0
9[a,b]	"	"	"	dppe (0.075)	"	0	0
10[a,b]	"	"	"	dppz (0.075)	"	0	0
11	$Pd(OAc)_2$ (10)	50	48	IMes.HCl (0.11)	"	10	0
12	"	"	"	K_3PO_4 (2)	"	10	0
13	"	"	"	Na_2CO_3	"	15	15

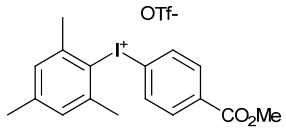
				(2)			
14	"	"	"	NaOAc (2)	"	12	0
15	"	"	"	CsOAc (2)	"	12	0
16	"	"	"	$NaBF_4$ (2)	"	10	0
17	"	"	"	CsOPiv (2)	"	12	0
18	"	"	"	KOTf (2)	"	8	0
19	"	"	"	NH_4OAc (2)	"	10	0
20[a]	$Pd(OAc)_2$ (5)	100	2	AgOAc (2)	DMF	0	0
21[a]	"	"	"	"	DMA	0	0
22[a]	"	"	"	"	Dioxane	<10	0
23[a]	"	"	"	"	THF	0	0
24[a]	"	"	"	"	DMSO	0	0
25[a]	"	"	"	"	MeCN	0	0
26[a]	"	"	"	"	NMP	0	0

[a] Microwave heating. [b] 2eq AgOAc added. [c] Spectroscopic yield (determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard).

General methodology for the preparation of iodonium triflate salts. *m*-CPBA (2.64 g, 10 mmol) and aryl iodide (9 mmol) were placed under an inert atmosphere in a schlenk tube. Dry CH_2Cl_2 (40 ml) followed by mesitylene (1.4 ml, 10 mmol) was added and the stirred solution was cooled to 0 °C. Triflic acid (1.3 ml, 15 mmol) was added dropwise over the

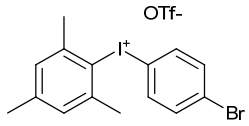
course of 5 minutes. The solution was allowed to warm to room temperature and stirred for 2 hours. The solvent was removed under reduced pressure. 30 ml dry Et_2O was added and the solution stirred rapidly for 10 minutes. This was placed in a freezer overnight and then filtered, washing thoroughly with Et_2O to afford the product as a crystalline solid. This followed the syntheses described by Olofsson and co-workers.[1]

Mesityl(4-methylbenzoate)iodonium triflate.



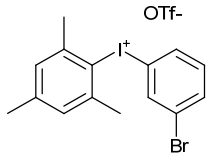
Beige solid, 2.99 g (63%); ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.02 (dd, *J* 6.8, 1.7 Hz, 2H), 7.77 (app. dt, *J* 8.4, 2.3 Hz, 2H), 7.12 (s, 2H), 3.92 (s, 3H), 2.62 (s, 6H), 2.37 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 165.4, 144.7, 142.7, 132.9, 132.8, 130.5, 116.6, 52.8, 27.2, 21.2; IR neat, ν (cm^{-1}) 2956 (w), 1726 (s), 1584 (m), 1438 (m), 1394 (w); m.p. 189.1-190.0 °C; LRMS (ESI) m/z 230.93 (35%), 381.04 (100%); Anal. Calcd. for $C_{18}H_{18}F_3IO_5S$: C, 40.8; H, 3.4. Found: C, 41.0; H, 3.5.

Mesityl(4-bromophenyl)iodonium triflate.



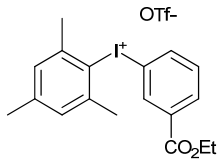
White solid, 3.41 g (69%); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.57 (dd, *J* 6.9, 2.2 Hz, 2H), 7.49 (dd, *J* 6.8, 2.2 Hz, 2H), 7.08 (s, 2H), 2.60 (s, 6H), 2.34 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.5, 142.5, 135.2, 134.6, 130.4, 126.8, 121.0, 110.0, 27.1, 21.2; IR neat, ν (cm^{-1}) 2988 (w), 1592 (w), 1474 (m), 1385 (m); m.p. 193.0-194.0 °C; LRMS (ESI) m/z 400.94 (100%), 402.94 (98%); Anal. Calcd. for $C_{16}H_{15}BrF_3IO_3S$: C, 34.9; H, 2.7. Found: C, 35.3; H, 2.8.

Mesityl(3-bromophenyl)iodonium triflate.



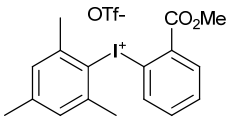
Beige solid, 2.33 g (47%); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.78 (t, *J* 1.9 Hz, 1H), 7.66 (app. quartet of quartets, *J* 8.0, 0.9 Hz, 2H), 7.27 (t, *J* 8.0 Hz, 1H), 7.11 (s, 2H), 2.62 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.6, 142.6, 135.1, 135.0, 133.1, 131.8, 130.5, 125.0, 120.9, 112.0, 27.2, 21.2; IR neat, ν (cm^{-1}) 2989 (w), 1569 (m), 1556 (m), 1455 (m), 1403 (m); m.p. 175.0-176.2 °C; LRMS (ESI) m/z 400.94 (98%), 402.94 (100%); Anal. Calcd. for $C_{16}H_{15}BrF_3IO_3S$: C, 34.9; H, 2.7. Found: C, 35.3; H, 2.8.

Mesityl(3-ethylbenzoate)iodonium triflate.



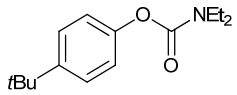
Beige solid, 2.00 g (41%); ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.27 (s, 1H), 8.17 (d, *J* 7.7 Hz, 1H), 7.99 (d, *J* 8.3 Hz, 1H), 7.50 (t, *J* 8.0 Hz, 1H), 7.11 (s, 2H), 4.35 (quartet, *J* 7.2 Hz, 2H), 2.64 (s, 6H), 2.35 (s, 3H), 1.36 (t, *J* 7.2 Hz, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 164.2, 144.6, 142.6, 137.4, 134.2, 133.8, 132.6, 132.0, 130.4, 121.0, 111.9, 62.0, 27.2, 21.2, 14.2; IR neat, ν (cm^{-1}) 2982 (w), 1722 (s), 1558 (m), 1453 (m), 1370 (w); m.p. 149.6-150.6 °C; LRMS (ESI) m/z 230.93 (80%), 395.05 (100%); Anal. Calcd. for $C_{19}H_{20}F_3IO_5S$: C, 41.9; H, 3.7. Found: C, 42.3; H, 3.9.

Mesityl(2-methylbenzoate)iodonium triflate.



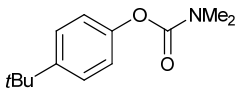
Pink solid, 1.71 g (36%); ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.33 (dd, *J* 7.7, 1.7 Hz, 1H), 7.70 (td, *J* 7.5, 0.9 Hz, 1H), 7.57 (td, *J* 7.3, 1.9 Hz, 1H), 7.19 (s, 2H), 6.83 (dd, *J* 8.1, 1.0 Hz, 1H), 4.12 (s, 3H), 2.54 (s, 6H), 2.42 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 167.8, 145.3, 143.9, 137.2, 133.5, 131.5, 130.5, 128.4, 127.4, 112.4, 54.8, 26.9, 21.4; IR neat, ν (cm^{-1}) 2963 (w), 1683 (s), 1587 (w), 1471 (m), 1437 (m), 1319 (m); m.p. 179.5-180.6 °C; LRMS (ESI) m/z 230.93 (42%), 381.03 (100%); Anal. Calcd. for $C_{18}H_{18}F_3IO_5S$: C, 40.8; H, 3.4. Found: C, 41.0; H, 3.5.

4-*tert*-butylphenyl diethylcarbamate, 1a.



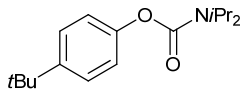
White solid, 4.58 g (92%); Rf 0.44 (CH_2Cl_2); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.38 (app. dt, *J* 8.2, 2.2 Hz, 2H), 7.06 (app. dt, *J* 8.2, 2.2 Hz, 2H), 3.43 (app. sextet, *J* 6.5 Hz, 4H), 1.32 (s, 9H), 1.23 (quintet, *J* 6.4 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 154.6, 149.3, 147.9, 126.2, 121.2, 42.4, 42.0, 34.5, 31.6, 14.4, 13.5; IR neat, ν (cm^{-1}) 2970 (s), 2932 (m), 2872 (m), 1703 (s), 1514 (m), 1478 (s), 1418 (s); m.p. 86.2-86.7 °C; HRMS (ESI) calcd for $C_{15}H_{23}NNaO_2$ $(M+Na)^+$ 272.1621, found 272.1627. Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.3; H, 9.3; N, 5.6. Found: C, 72.6; H, 9.7; N, 5.7.

4-*tert*-butylphenyl dimethylcarbamate, 1b.



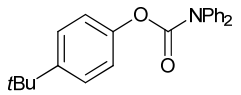
White solid, 3.36 g (76%); R*f* 0.29 (EtOAc/hexane, 1:4); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.38 (d, *J* 8.6 Hz, 2H), 7.05 (d, *J* 6.1, 2H), 3.10 (s, 3H), 3.02 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 155.2, 149.3, 148.0, 126.2, 121.2, 36.8, 36.5, 34.5, 31.6; IR neat, ν (cm^{-1}) 2960 (s), 1711 (s), 1510 (m), 1487 (m), 1383 (s); m.p. 92.0-92.8 °C; HRMS (ESI) calcd for $C_{13}H_{19}NNaO_2$ $(M+Na)^+$ 244.13, found 244.13; Anal. Calcd. for $C_{13}H_{19}NO_2$: C,70.6; H, 8.6; N, 6.3. Found: C, 71.0; H, 8.8; N, 6.7.

4-*tert*-butylphenyl diisopropylcarbamate, 1c.



White solid, 4.54 g (82%); R*f* 0.56 (CH_2Cl_2); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.39 (app. dt, *J* 8.8, 2.2, 2H), 7.07 (app. dt, *J* 8.8, 2.2 Hz, 2H), 4.12 (br. s, 2H), 3.97 (br. s, 2H), 1.33 (br. s, 21 H);^{13}C NMR (100 MHz; $CDCl_3$) δ 154.2, 149.1, 147.8, 126.2, 121.3, 47.3, 46.3, 34.5, 31.6, 21.6, 20.6; IR neat, ν (cm^{-1}) 2966 (s), 2871 (m), 1689 (s), 1514 (m), 1440 (s), 1304 (s); m.p. 124.1-124.4 °C; HRMS (ESI) calcd for $C_{17}H_{27}NNaO_2$ $(M+Na)^+$ 300.1934, found 300.1935; Anal. Calcd. for $C_{17}H_{27}NO_2$: C,73.6; H, 9.8; N, 5.1. Found: C, 73.9; H, 9.8; N, 5.2.

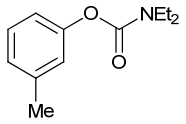
4-*tert*-butylphenyl diphenylcarbamate, 1d.



White solid, 5.58 g (81%); R*f* 0.69 (CH_2Cl_2); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.40-7.38 (m, 12H), 7.12 (app. dt, *J* 8.9, 2.2 Hz, 2H), 1.33 (s, 9H);^{13}C NMR (75 MHz; $CDCl_3$) δ 153.4,

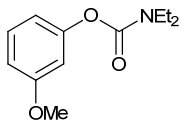
148.9, 148.4, 142.5, 129.6, 129.1, 127.0, 126.5, 126.3, 120.9, 34.6, 31.6; IR neat, ν (cm^{-1}) 2966 (m), 1725 (s), 1590 (m), 1488 (s); m.p. 89.5-92.0 °C; HRMS (ESI) calcd for $C_{23}H_{23}NNaO_2$ $(M+Na)^+$ 368.1621, found 368.1613; Anal. Calcd. for $C_{23}H_{23}NO_2$: C,80.0; H, 6.7; N, 4.1. Found: C, 79.9; H, 6.4; N, 4.2.

_m_-tolyl diethylcarbamate, 1e.



Colourless oil, 0.62 g (32%); R*f* 0.41 (EtOAc/hexanes, 1:10); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.35 (td, *J* 7.8, 2.2 Hz, 1H), 7.12 (d, *J* 7.6 Hz, 1H), 7.05 (t, *J* 7.8 Hz, 2H), 3.53 (quartet, *J* 6.6 Hz, 4H), 2.47 (s, 3H), 1.35 (t, *J* 8.3 Hz, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 154.4, 151.6, 139.3, 129.0, 126.0, 122.5, 118.8, 42.3, 42.0, 21.4, 14.3, 13.5; IR neat, ν (cm^{-1}) 2973 (m), 1711 (s), 1610 (m), 1415 (s); HRMS (ESI) calcd for $C_{12}H_{17}NNaO_2$ $(M+Na)^+$ 230.12, found 230.12; Anal. Calcd. for $C_{12}H_{17}NO_2$: C,69.5; H, 8.3; N, 6.8. Found: C, 69.3; H, 8.2; N, 6.7.

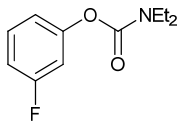
3-methoxyphenyl diethylcarbamate, 1f.



Colourless oil, 0.68 g (38%); R*f* 0.23 (EtOAc/hexanes, 1:5); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.23 (t, *J* 8.2 Hz, 1H), 6.71 (m, 3H), 3.77 (s, 1H), 3.39 (quartet, *J* 7.0 Hz, 4H), 1.20 (quintet, *J* 6.5 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.5, 154.2, 152.7, 129.6, 114.1, 111.2, 107.8, 55.4, 42.3, 42.0, 13.5, 13.3; IR neat, ν (cm^{-1}) 2973 (m), 2937 (m), 2836 (w), 1712 (s), 1607 (m), 1591 (m), 1473 (s), 1414 (s); HRMS (ESI) calcd for $C_{12}H_{17}NNaO_3$ $(M+Na)^+$ 246.11,

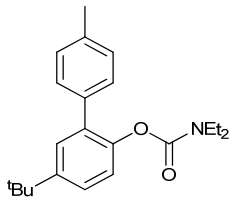
found 246.11; Anal. Calcd. for $C_{12}H_{17}NO_3$: C,64.6; H, 7.7; N, 6.3. Found: C, 64.7; H, 7.8; N, 6.6.

3-fluorophenyl diethylcarbamate, 1g



Colourless oil, 0.98 g (58%); R*f* 0.58 (CH_2Cl_2); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.29-7.27 (m, 1H), 6.92-6.86 (m, 3H), 3.39 (app. sextet, *J* 7.2 Hz, 4H), 1.21 (app. sextet, *J* 7.3 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 164.2, 161.7, 153.8, 152.7, 130.0, 117.6, 112.2, 109.8, 42.5, 42.1, 14.3, 13.5; IR neat, ν (cm^{-1}) 2977 (m), 2937 (w), 1715 (s), 1600 (m), 1473 (m), 1414 (s); HRMS (ESI) calcd for $C_{11}H_{14}FNNaO_2$ $(M+Na)^+$ 234.09, found 234.09; Anal. Calcd. for $C_{11}H_{14}FNO_2$: C,62.6; H, 6.7; N, 6.6. Found: C, 62.2; H, 6.8; N, 6.9.

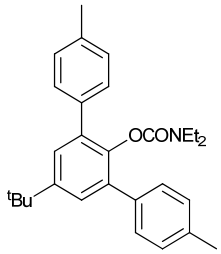
2a (Table 2, Entry 5).



White solid, 24 mg (30%); R*f* 0.03 (CH_2Cl_2/petroleum ether, 1:1). ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.39-7.32 (m, 6H), 7.13 (d, *J* 9.2 Hz, 1H), 3.26 (app. quintet, *J* 6.8 Hz, 4H), 2.39 (s, 3H), 1.34 (s, 9H), 1.05 (app. quartet, *J* 6.8 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 154.3, 148.1, 146.2, 136.7, 135.7, 134.1, 129.0, 128.7, 127.7, 126.1, 125.1, 122.5, 121.1, 42.0, 41.6, 34.5, 31.5, 21.2, 13.9, 13.2; IR neat, ν (cm^{-1}) 2965 (m), 2872 (w), 1714 (s), 1514 (w), 1471

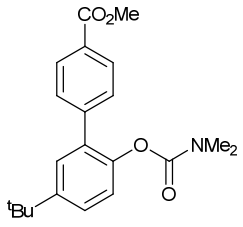
(m), 1419 (s), 1380 (m), 1272 (m); m.p. 123.1- 124.9 °C; HRMS (ESI) calcd for $C_{22}H_{29}NNaO_2$ $(M+Na)^+$ 362.2091, found 362.2099; Anal. Calcd. for $C_{22}H_{29}NO_2$: C, 77.8; H, 8.6; N, 4.1. Found: C, 78.0; H, 9.0; N, 4.1.

3a (Table 2, Entry 5).



White solid, 42 mg (41%); R*f* 0.06 (CH_2Cl_2/petroleum ether, 1:1). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.39 (app. dt, *J* 8.1, 2.0 Hz, 4H), 7.36 (s, 2H), 7.21 (d, *J* 8.4 Hz, 4H), 3.11 (quartet, *J* 7.0 Hz, 2H), 3.07 (quartet, *J* 7.0 Hz, 2H), 2.37 (s, 6H), 1.35 (s, 9H), 0.88 (t, *J* 7.0 Hz, 3H), 0.76 (t, *J* 6.9 Hz, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 153.4, 148.2, 143.6, 136.7, 136.1, 135.4, 129.2, 128.8, 127.1, 41.7, 41.4, 34.7, 31.6, 21.3, 13.8, 12.7; IR neat, ν (cm^{-1}) 2965 (m), 2870 (w), 1714 (s), 1513 (m), 1459 (br), 1417 (s), 1270 (s); m.p. 189.3-189.7 °C; HRMS (ESI) calcd for $C_{29}H_{35}NNaO_2$ $(M+Na)^+$ 452.2560, found 452.2571; Anal. Calcd. for $C_{29}H_{35}NO_2$: C, 81.1; H, 8.2; N, 3.3. Found: C, 81.4; H, 8.5; N, 3.4.

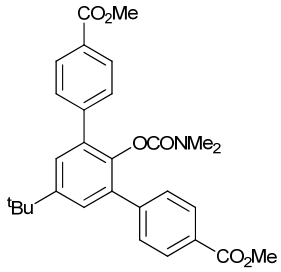
2b (Table 2, Entry 1).



White solid, 22 mg (20%); R*f* 0.16 (EtOAc/hexane, 1:5); ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.09 (app. dt, *J* 8.6, 2.0 Hz, 2H), 7.53 (app. dt, *J* 8.6, 2.0 Hz, 2H), 7.42 (dd, *J* 8.4, 2.3 Hz,

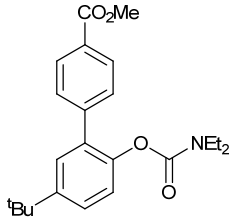
1H), 7.38 (d, *J* 2.2 Hz, 1H), 7.16 (d, *J* 8.5 Hz, 1H), 3.95 (s, 3H), 2.91 (s, 3H), 2.88 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 167.2, 154.7, 148.7, 146.1, 143.4, 133.1, 129.4, 129.3, 128.9, 127.5, 126.3, 122.9, 52.2, 36.8, 36.4, 34.6, 31.5; IR neat, ν (cm^{-1}) 3676 (w), 2959 (m), 2902 (m), 1712 (s), 1607 (m), 1439 (m), 1383 (s); m.p. 195.1-196.2 °C; HRMS (ESI) calcd for $C_{21}H_{25}NNaO_4$ $(M+Na)^+$ 378.1676, found 378.1679; Anal. Calcd. for $C_{21}H_{25}NO_4$: C, 70.1; H, 7.1; N, 3.9. Found: C, 70.5; H, 7.1; N, 3.9.

3b (Table 2, Entry 1).



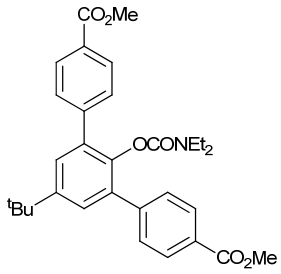
White solid, 5 mg (3%); R*f* 0.12 (EtOAc/hexane, 1:5); ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.09 (app. dt, *J* 8.1, 2.0 Hz, 4H), 7.57 (app. dt, *J* 8.7, 2.0 Hz, 4H), 7.40 (s, 2H), 3.96 (s, 6H), 2.76 (s, 3H), 2.61 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 167.0, 153.6, 148.9, 143.3, 134.6, 129.4, 129.2, 128.9, 127.6, 52.2, 36.6, 36.1, 34.7, 31.4; IR neat, ν (cm^{-1}) 2970 (m), 2901 (m), 1715 (s), 1608 (w), 1439 (m), 1384 (m), 1275 (s); m.p. (decomp.) 263.0 °C; HRMS (ESI) calcd for $C_{29}H_{31}NNaO_6$ $(M+Na)^+$ 512.2044, found 512.2048.

2c (Table 2, Entry 2).



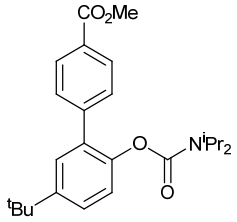
White solid, 54 mg (59%); R*f* 0.29 (EtOAc/hexanes, 1:5); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.09 (app. dt, *J* 8.6, 2.0 Hz, 2H), 7.53 (app. dt, *J* 8.6, 2.0 Hz, 2H), 7.43 (dd, *J* 8.5, 2.4 Hz, 1 H), 7.38 (d, *J* 2.6 Hz, 1H), 7.17 (d, *J* 8.4 Hz, 1H), 3.96 (s, 3H), 3.26 (app. quintet, *J* 7.2 Hz, 4H), 1.37 (s, 9H), 1.05 (quintet, *J* 7.2 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 167.2, 154.2, 148.6, 146.2, 143.6, 133.3, 129.5, 129.3, 128.8, 127.5, 126.2, 122.9, 52.3, 42.2, 41.8, 34.7, 31.6, 14.1, 13.3; IR neat, ν (cm^{-1}) 2960 (s), 1717 (s), 1611 (m), 1469 (s), 1423 (s); m.p. 115.8-117.4 °C; HRMS (ESI) calcd for $C_{23}H_{29}NNaO_4$ $(M+Na)^+$ 406.1989, found 406.1998; Anal. Calcd. for $C_{23}H_{29}NO_4$: C,72.0; H, 7.6; N, 3.7. Found: C, 71.9; H, 7.6; N, 4.0.

3c (Table 2, Entry 2).



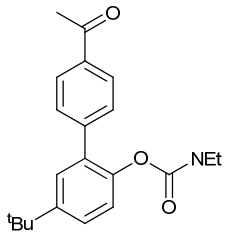
White solid, 27 mg (22%); R*f* 0.19 (EtOAc/hexanes, 1:5). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.09 (app. dt, *J* 8.2, 1.8 Hz, 4H), 7.57 (app. dt, *J* 8.3, 1.9 Hz, 4H), 7.41 (s, 2H), 3.96 (s, 6H), 3.08 (quartet, *J* 7.3 Hz, 2H), 3.02 (quartet, *J* 7.2 Hz, 2H), 1.40 (s, 9H), 0.86 (t, *J* 7.1 Hz, 3H), 0.74 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 167.0, 153.0, 148.8, 143.5, 143.2, 134.8, 129.3, 129.2, 128.8, 127.5, 52.1, 41.9, 41.5, 34.7, 31.4, 13.9, 12.7; IR neat, ν (cm^{-1}) 2952 (s), 1712 (s), 1609 (m), 1509 (w), 1418 (m); m.p. 178.5-180.1 °C; HRMS (ESI) calcd for $C_{31}H_{35}NNaO_6$ $(M+Na)^+$ 540.2357, found 540.2381; Anal. Calcd. for $C_{31}H_{35}NO_6$: C,71.9; H, 6.8; N, 2.7. Found: C, 71.9; H, 6.7; N, 3.0.

2d (Table 2, Entry 3)



White solid, 14 mg (14%); R*f* 0.18 (EtOAc/hexane, 3:20); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.05 (dd, *J* 8.0, 1.4 Hz, 2H), 7.51 (dd, *J* 8.1, 1.2 Hz, 2H), 7.42 (dd, *J* 8.4, 2.3 Hz, 1H), 7.36 (d, *J* 2.2 Hz, 1H), 7.12 (d, *J* 8.6 Hz, 1H), 3.95 (s, 2H), 3.78 (s, 3H), 1.35 (s, 9H), 1.18 (d, *J* 5.6 Hz, 6H), 1.08 (d, *J* 5.4 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 167.2, 161.6, 148.5, 146.1, 143.4, 133.7, 129.4, 128.8, 127.5, 126.2, 123.0, 114.8, 55.4, 52.2, 34.6, 31.6, 21.2, 20.5; IR neat, ν (cm^{-1}) 2967 (s), 1716 (s), 1609 (m), 1460 (s), 1421 (s); HRMS (ESI) calcd for $C_{25}H_{33}NNaO_4$ $(M+Na)^+$ 434.2302, found 434434.2316.

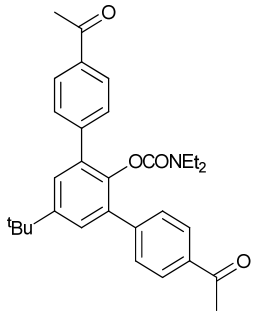
2e (Table 2, Entry 6).



White solid, 25 mg (32%); R*f* 0.33 (EtOAc/hexanes, 3:7); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.00 (app. dt, *J* 8.5, 1.9 Hz, 2H), 7.55 (app. dt, *J* 8.7, 2.0 Hz, 2H), 7.42 (dd, *J* 8.5, 2.4 Hz, 1H), 7.36 (d, *J* 2.6 Hz, 1H), 7.16 (d, *J* 8.5 Hz, 1H), 3.25 (quartet, *J* 7.1 Hz, 4H), 2.64 (s, 3H), 1.35 (s, 9H), 1.04 (app. quartet, *J* 7.0 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 198.0, 154.1, 148.6, 146.2, 143.8, 135.8, 133.2, 129.5, 128.3, 127.5, 126.3, 122.9, 42.2, 41.8, 34.7, 31.6, 26.8, 14.1, 13.3; IR neat, ν (cm^{-1}) 2959 (m), 1727 (s), 1678 (s), 1605 (m), 1469 (m), 1424 (m), 1356 (m); m.p. 100.2-101.3 °C; HRMS (ESI) calcd for $C_{21}H_{24}NNaO_3$ $(M+Na)^+$

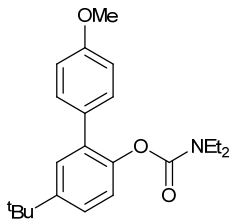
390.2040, found 390.2054. Anal. Calcd for $C_{21}H_{24}NO_3$: C, 75.2; H, 8.0; N, 3.8. Found: C, 75.4; H, 7.8; N, 4.3.

3e (Table 2, Entry 6).



White solid, 40 mg (34%); R*f* (EtOAc/hexanes, 3:10); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.01 (app. dt, *J* 8.7, 2.0 Hz, 4H), 7.58 (app. dt, *J* 8.6, 2.0 Hz, 4H), 7.40 (s, 2H), 3.08 (quartet, *J* 7.1 Hz, 2H), 3.00 (q, *J* 7.0 Hz, 2H), 2.64 (s, 6H), 1.39 (s, 9H), 0.85 (t, *J* 7.1 Hz, 3H), 0.71 (t, *J* 7.0 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 198.0, 153.1, 149.0, 143.8, 143.4, 135.9, 134.8, 129.5, 128.3, 127.7, 41.9, 41.6, 34.8, 31.5 26.8, 14.0, 12.8; IR neat, ν (cm^{-1}) 2967 (m), 1725 (s), 1679 (s), 1603 (m), 1421 (m), 1350 (m); m.p. 96.6-97.2 °C; HRMS (ESI) calcd for $C_{31}H_{35}NNaO_4$ $(M+Na)^+$ 508.2458, found 508.2468; Anal. Calcd. for $C_{31}H_{35}NO_4$: C,76.7; H, 7.3; N, 2.9. Found: C, 77.0; H, 7.4; N, 3.2.

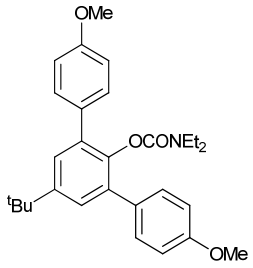
2f (Table 2, Entry 7).



White solid, 31 mg (37%); R*f* 0.37 (EtOAc/hexanes, 3:10). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.38-7.34 (m, 4H), 7.12 (dd, *J* 6.1, 3.1 Hz, 1H), 6.94 (dd, *J* 6.8, 2.2 Hz, 2H), 3.85 (s, 3H),

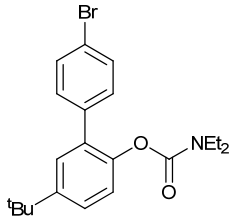
3.26 (app. quintet, *J* 5.3 Hz, 4H), 1.34 (s, 9H), 1.07 (app.sextet, *J* 6.9 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 158.9, 154.4, 148.3, 133.9, 131.2, 130.4, 127.8, 125.1, 122.7, 113.6, 55.4, 42.1, 41.7, 34.6, 31.6, 22.1, 21.7; IR neat, ν (cm^{-1}) 2964 (s), 2836 (w), 1713 (s), 1610 (m), 1515 (m), 1460 (s), 1418 (s); m.p. 99.5-100.0 °C; HRMS (ESI) calcd for $C_{22}H_{29}NNaO_3$ $(M+Na)^+$ 378.2040, found 378.2046; Anal. Calcd. for $C_{22}H_{29}NO_3$: C, 74.3; H, 8.2; N, 3.9. Found: C, 75.8; H, 7.4; N, 3.7.

3f (Table 2, Entry 7).



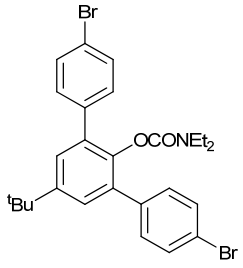
White solid, 40 mg (36%); R*f* 0.24 (EtOAc/hexanes, 3:10). ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.43 (app. dt, *J* 9.0, 2.2 Hz, 4H), 7.34 (s, 2H), 6.95 (app. dt, *J* 9.0, 2.2 Hz, 4H), 3.85 (s, 6H), 3.12 (quartet, *J* 7.2 Hz, 2H), 3.06 (quartet, *J* 7.0 Hz, 2H), 1.38 (s, 9H), 0.90 (t, *J* 6.9 Hz, 3H), 0.80 (t, *J* 7.0 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 158.9, 153.5, 148.3, 143.6, 135.2, 131.6, 130.4, 127.0, 113.6, 55.4, 41.8, 41.5, 34.7, 31.6, 13.9, 12.9; IR neat, ν (cm^{-1}) 2966 (s), 2833 (w), 1722 (s), 1609 (m), 1510 (s), 1464 (s), 1418 (s); m.p. 100.6-101.1 °C; HRMS (ESI) calcd for $C_{29}H_{35}NNaO_4$ $(M+Na)^+$ 484.2458, found 484.2477; Anal. Calcd. for $C_{29}H_{35}NO_4$: C, 75.5; H, 7.6; N, 3.0. Found: C, 75.4; H, 8.0; N, 3.2.

2g (Table 2, Entry 8).



Off-white solid, 23 mg (23%); R*f* 0.21 (EtOAc/hexanes, 1:9). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.52 (dd, *J* 8.0, 2.2 Hz, 2H), 7.39 (dd, *J* 7.9, 2.4 Hz, 1H), 7.32-7.30 (m, 3H), 7.14 (d, *J* 8.6 Hz, 1H), 3.27 (app. t, *J* 5.6 Hz, 4H), 1.34 (s, 9H), 1.06 (app. d, *J* 5.2 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 154.2, 148.5, 146.2, 137.7, 133.2, 131.3, 131.0, 127.5, 125.9, 122.8, 121.4, 42.2, 41.8, 34.6, 31.6, 14.1, 13.3; IR neat, ν (cm^{-1}) 2960 (s), 2870 (m), 1723 (s), 1590 (w), 1470 (s), 1424 (s); m.p. 97.2-98.6 °C; HRMS (ESI) calcd for $C_{21}H_{26}BrNNaO_2$ $(M+Na)^+$ 426.1039 and 428.1025, found 426.1044 and 428.1025; Anal. Calcd. for $C_{21}H_{26}BrNO_2$: C, 62.4; H, 6.5; N, 3.5. Found: C, 62.6; H, 6.6; N, 3.5.

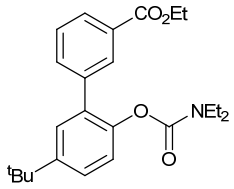
3g (Table 2, Entry 8).



Off-white solid, 86 mg (64%); R*f* 0.32 (EtOAc/hexanes, 1:10). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.51 (app. dt, *J* 8.5, 1.9 Hz, 4H), 7.34-7.31 (m, 6H), 3.05 (app. sextet, *J* 7.1 Hz, 4H), 1.36 (s, 9H), 0.87 (t, *J* 6.7 Hz, 3H), 0.78 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 153.2, 148.8, 143.3, 137.7, 134.6, 131.3, 131.0, 127.3, 121.5, 42.0, 41.6, 34.7, 31.6, 14.0, 12.8; IR neat, ν (cm^{-1}) 2960 (s), 2903 (w), 1716 (s), 1595 (m), 1486 (s), 1419 (s), 1382 (s); m.p. 158.2-160.0 °C; HRMS (ESI) calcd for $C_{27}H_{29}Br_2NNaO_2$ $(M+Na)^+$ 582.0444, found

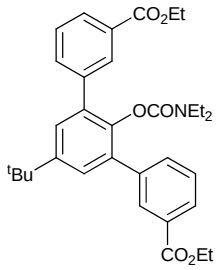
582.0437; Anal. Calcd. for $C_{27}H_{29}Br_2NO_2$: C, 58.0; H, 5.2; N, 2.5. Found: C, 57.9; H, 5.3; N, 2.4.

2h (Table 2, Entry 9).



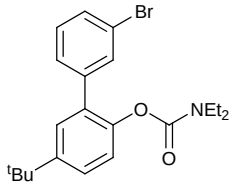
White solid, 51 mg (53%); R*f* 0.18 (EtOAc/hexanes, 3:17). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.14 (t, *J* 1.6 Hz, 1H), 8.03 (app. dt, *J* 7.7, 1.6 Hz, 1H), 7.63 (app. dt, *J* 7.7, 1.7 Hz, 1H), 7.48 (t, *J* 7.7 Hz, 1H), 7.41 (dd, *J* 8.5, 2.5 Hz, 1H), 7.37 (d, *J* 2.5 Hz, 1H), 7.17 (d, *J* 8.5 Hz, 1H), 4.40 (q, *J* 7.1 Hz, 2H), 3.24 (q, *J* 7.1 Hz, 4H), 1.40 (t, *J* 7.1 Hz, 3H), 1.36 (s, 9H), 1.01 (q, *J* 7.7 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 166.7, 154.1, 148.5, 146.3, 139.0, 133.8, 133.3, 130.4, 128.4, 128.3, 127.6, 126.0, 122.8, 61.1, 42.1, 41.7, 34.6, 31.6, 14.5, 14.0, 13.23; IR neat, ν (cm^{-1}) 2969 (s), 2932 (m), 2901 (m), 2870 (w), 1706 (s), 1603 (m), 1589 (m), 1476 (s), 1412 (s); m.p. 104.0-104.4 °C; HRMS (ESI) calcd for $C_{24}H_{31}NNaO_4$ $(M+Na)^+$ 420.2145, found 420.2152.

3h (Table 2, Entry 9).



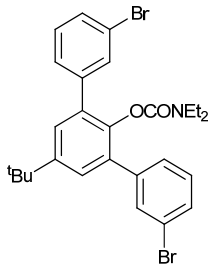
White solid, 18 mg (14%); R*f* 0.09 (EtOAc/hexanes, 3:17). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.18 (t, *J* 1.7 Hz, 2H), 8.03 (app. dt, *J* 7.7, 1.7 Hz, 2H), 7.69 (app. dd, *J* 7.7, 1.7 Hz, 2H), 7.49 (t, *J* 7.7 Hz, 2H), 7.40 (s, 2H), 4.39 (q, *J* 7.1 Hz, 4H), 3.09 (q, *J* 7.1 Hz, 2H), 2.97 (q, *J* 7.0 Hz, 2H), 1.39 (t, *J* 7.1 Hz, 15H), 0.81 (t, *J* 7.1 Hz, 3H), 0.67 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 166.7, 153.0, 148.8, 143.5, 139.0, 134.8, 133.8, 130.39, 130,35, 128.44, 128.36, 127.5, 61.1, 41.8, 41.5, 34.8, 31.6, 14.5, 13.8, 12.7; IR neat, ν (cm^{-1}) 2965 (m), 2872 (w), 1715 (s), 1582 (br), 1462 (m), 1414 (m), 1366 (m); m.p. 108.5-108.7 °C; HRMS (ESI) calcd for $C_{33}H_{39}NNaO_6$ $(M+Na)^+$ 568.2670, found 568.2680.

2i (Table 2, Entry 10).



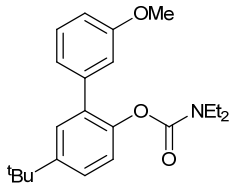
White solid, 29 mg (30%); R*f* 0.21 (CH_2Cl_2/petroleum ether, 2:3). ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.59 (t, *J* 2.0 Hz, 1H), 7.38-7.34 (m, 2H), 7.31 (d, *J* 2.6 Hz, 1H), 7.26 (s, 2H), 7.14 (d, *J* 8.5 Hz, 1H), 3.27 (quartet, *J* 7.2 Hz, 4H), 1.34 (s, 9H), 1.06 (app. quartet, *J* 6.7 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 154.0, 148.4, 146.1, 140.7, 132.1, 130.0, 129.7, 127.8, 127.4, 126.1, 125.9, 122.7, 121.1, 42.1, 41.7, 34.5, 31.4, 13.9, 13.2; IR neat, ν (cm^{-1}) 2963 (m), 2870 (w), 1715 (s), 1594 (w), 1560 (m), 1471 (m), 1418 (s), 1270 (s); HRMS (ESI) calcd for $C_{21}H_{26}BrNNaO_2$ $(M+Na)^+$ 426.1039, 428.1019, found 426.1041, 428.1019; Anal. Calcd. for $C_{21}H_{26}BrNO_2$: C, 62.4; H, 6.4; N, 3.5. Found: C, 62.8; H, 6.8; N, 3.5.

3i (Table 2, Entry 10).



White solid, 94 mg (70%); R*f* 0.27 (CH_2Cl_2/petroleum ether, 2:3). ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.63 (t, *J* 1.8 Hz, 2H), 7.46 (dt, *J* 7.9, 1.8 Hz, 2H), 7.40 (dt, *J* 7.7, 1.7 Hz, 2H), 7.35 (s, 2H), 7.28 (d, *J* 7.9 Hz, 2H), 3.15 (quartet, *J* 7.0 Hz, 2H), 3.04 (quartet, *J* 7.2 Hz, 2H), 1.37 (s, 9H), 0.92 (t, *J* 7.2 Hz, 3H), 0.79 (t, *J* 7.0 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 152.9, 148.7, 143.2, 140.7, 134.2, 132.1, 130.1, 129.7, 127.9, 127.3, 121.9, 41.8, 41.4, 34.7, 31.5, 13.8, 12.7; IR neat, ν (cm^{-1}) 2963 (w), 1710 (s), 1591 (m), 1558 (m), 1459 (m), 1418 (s), 1402 (m); m.p. 138.9-139.1 °C; HRMS (ESI) calcd for $C_{27}H_{29}Br_2NNaO_2$ $(M+Na)^+$ 580.0457, 582.0437, 484.0416, found 580.0464, 582.0445, 584.0423; Anal. Calcd. for $C_{27}H_{29}Br_2NO_2$: C, 57.9; H, 5.2; N, 2.5. Found: C, 57.6; H, 5.2; N, 2.5.

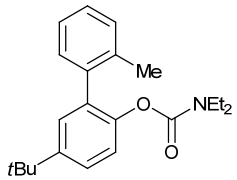
2j (Table 2, Entry 11).



White solid, 34 mg (40%); R*f* 0.19 (EtOAc/hexanes, 1:9). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.39-7.30 (m, 3H), 7.14 (d, *J* 9.2 Hz, 1H), 7.02 (d, *J* 7.9 Hz, 1H), 6.99 (d, *J* 2.2 Hz, 1H), 6.88 (dd, *J* 8.2, 2.2 Hz, 1H), 3.82 (s, 3H), 3.26 (app. sextet, *J* 6.4 Hz, 4H), 1.35 (s, 9H), 1.07 (t, *J* 6.4 Hz, 3H), 1.00 (t, *J* 6.5 Hz, 3H) ; ^{13}C NMR (100 MHz; $CDCl_3$) δ 159.4, 154.4, 148.3,

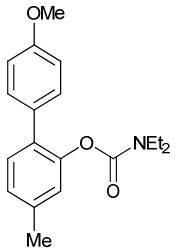
146.2, 140.2, 134.2, 129.1, 127.7, 125.5, 122.8, 121.8, 114.8, 112.9, 55.3, 42.1, 41.7, 34.6, 31.6, 13.9, 13.3; IR neat, ν (cm^{-1}) 3676 (w), 2966 (m), 1713 (s), 1599 (m), 1577 (m), 1471 (m), 1419 (s); m.p. 109.1-110.3 °C; HRMS (ESI) calcd for $C_{22}H_{29}NNaO_3$ $(M+Na)^+$ 378.2040, found 378.2033.

2k (Table 2, Entry 12).



Pale yellow oil, 13 mg (16%); R*f* 0.11 (EtOAc/hexanes, 1:19). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.38-7.33 (m, 3H), 7.03 (app. dt, *J* 8.6, 2.0 Hz, 2H), 6.74 (dd, *J* 8.8, 2.5 Hz, 2H), 3.25 (quartet, *J* 7.3 Hz, 4H), 1.30 (s, 9H), 1.03 (sextet, *J* 9.3 hz, 6H) ; ^{13}C NMR (100 MHz; $CDCl_3$) δ 153.3, 149.1, 147.8, 143.3, 139.2, 138.6, 137.4, 129.8, 129.0, 128.7, 127.7, 126.4, 126.1, 122.6, 121.1, 42.0, 41.6, 34.1, 31.4, 28.7, 21.4, 21.2; IR neat, ν (cm^{-1}) 2963 (m), 1718 (s), 1612 (w), 1515 (m), 1472 (m), 1420 (s), 1364 (m); LRMS (ESI) m/z 272.2 (95%), 362.2 (100%).

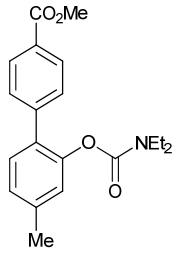
2l (Table 2, Entry 14).



White gum, 58 mg (77%); R*f* 0.24 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.35 (app. dt, *J* 8.8, 2.2 Hz, 2H), 7.25 (d, *J* 7.8 Hz, 1H), 7.07 (dd, *J* 7.8, 2.0 Hz, 1H), 7.03 (d,

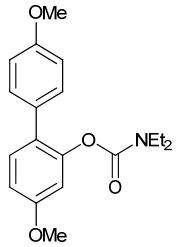
J 1.8 Hz, 1H), 6.92 (app. dt, *J* 8.8, 2.2 Hz, 2H), 3.84 (s, 3H), 3.28 (br. d, *J* 4.8 Hz, 4H), 2.39 (s, 3H), 1.07 (app. quartet, *J* 7.5 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 158.8, 154.4, 148.4, 138.2, 131.9, 130.7, 130.5, 130.3, 126.5, 123.9, 113.6, 55.4, 42.1, 41.7, 21.2, 14.1, 13.3; IR neat, ν (cm^{-1}) 2974 (s), 2836 (w), 1712 (s), 1610 (m), 1523 (m), 1494 (s), 1416 (m); HRMS (ESI) calcd for $C_{19}H_{23}NNaO_3$ $(M+Na)^+$ 336.1570, found 336.1575; Anal. Calcd. for $C_{19}H_{23}NO_3$: C, 72.8; H, 7.4; N, 4.5. Found: C, 72.4; H, 7.7; N, 4.1.

2m (Table 2, Entry 15).



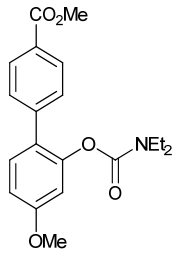
White solid, 22 mg (27%); R*f* 0.24 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.05 (app. dt, *J* 8.5, 1.7 Hz, 2H), 7.49 (app.dt, *J* 8.5, 1.7 Hz, 2H), 7.28 (d, *J* 7.9 Hz, 1H), 7.10 (dd, *J* 8.6, 1.7 Hz, 1H), 7.06 (d, *J* 1.7 Hz, 1H), 3.94 (s, 3H), 3.26 (q, *J* 6.5 Hz, 4H), 2.41 (s, 3H), 1.05 (app. q, *J* 7.3 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 167.0, 154.0, 148.2, 142.9, 139.3, 131.1, 130.2, 129.3, 129.1, 128.6, 126.5, 123.9, 52.1, 42.0, 41.6, 21.1, 14.0, 13.2; IR neat, ν (cm^{-1}) 2968 (s), 2926 (m), 1714 (s), 1608 (m), 1474 (m), 1436 (m), 1414 (m); m.p. 78.8-79.2 °C; HRMS (ESI) calcd for $C_{20}H_{23}NNaO_4$ $(M+Na)^+$ 364.1519, found 364.1523; Anal. Calcd. for $C_{20}H_{23}NO_4$: C, 70.4; H, 6.8; N, 4.1. Found: C, 70.6; H, 7.1; N, 4.4.

2n (Table 2, Entry 16).



White gum, 57 mg (67%); R*f* 0.15 (EtOAc/hexanes, 1:4); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.31 (app. dt, *J* 9.0, 2.2 Hz, 2H), 7.25 (d, *J* 8.3 Hz, 1H), 6.90 (app. dt, *J* 9.0, 2.2 Hz, 2H), 6.81 (dd, *J* 8.4, 2.6 Hz, 1H), 6.76 (d, *J* 2.6 Hz, 1H), 3.82 (s, 3H), 3.82 (s, 3H), 3.26 (quartet, *J* 7.1 Hz, 4H), 1.05 (t, *J* 6.8 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 159.3, 158.6, 153.9, 149.2, 131.0, 130.4, 130.1, 127.3, 113.5, 111.7, 108.7, 91.1, 56.0, 55.5, 55.3, 41.9, 41.6; IR neat, ν (cm^{-1}) 2963 (s), 2920 (m), 1703 (s), 1612 (m), 1473 (m), 1436 (m), 1410 (w); HRMS (ESI) calcd for $C_{19}H_{23}NNaO_4$ $(M+Na)^+$ 352.1519, found 352.1533.

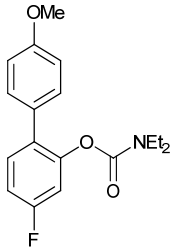
2o (Table 2, Entry 17).



White solid, 53 mg (62%); R*f* 0.16 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.95 (app. dt, *J* 8.6, 2.0 Hz, 2H), 7.39 (app. dt, *J* 8.5, 2.1 Hz, 2H), 7.21 (d, *J* 8.6 Hz, 1H), 6.77 (dd, *J* 8.6, 2.7 Hz, 1H), 6.71 (d, *J* 2.4 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.17 (quartet, *J* 7.1 Hz, 4H), 0.96 (t, *J* 7.1 Hz, 6H); ^{13}C NMR (100 MHz; CDCl3) δ 166.1, 159.2, 152.7, 148.2, 141.8, 129.9, 128.3, 128.0, 127.4, 126.2, 125.5, 107.9, 54.5, 51.1, 41.0, 40.6, 13.0, 12.1; IR neat, ν (cm^{-1}) 2968 (m), 1706 (s), 1617 (m), 1607 (m), 1523 (m), 1437 (m), 1414 (m); m.p.

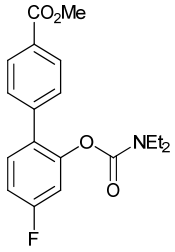
74.4-75.8 °C; HRMS (ESI) calcd for $C_{20}H_{23}NNaO_5$ $(M+Na)^+$ 380.1468, found 380.1478; Anal. Calcd. for $C_{20}H_{23}NO_5$: C, 67.2; H, 6.5; N, 3.9. Found: C, 66.8; H, 6.5; N, 3.9.

2p (Table 2, Entry 18).



White gum, 24 mg (32%); R*f* 0.18 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.24-7.19 (m, 3H), 6.92-6.82 (m, 4H), 3.76 (s, 3H), 3.17 (app. quintet, *J* 7.2 Hz, 4H), 0.97 (7.2 Hz, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 163.1, 160.7, 159.1, 153.7, 149.4 (d, *J* 11.6 Hz), 131.4 (d, *J* 9.3 Hz), 130.3, 129.8, 113.7, 112.6 (d, *J* 20.8 Hz), 111.0 (d, *J* 23.8 Hz), 55.4, 42.2, 41.8, 14.0, 13.2; IR neat, ν (cm^{-1}) 2974 (m), 2936 (m), 2838 (w), 1716 (s), 1604 (s), 1490 (s), 1416 (m), 1399 (m); HRMS (ESI) calcd for $C_{18}H_{20}FNNaO_3$ $(M+Na)^+$ 340.1319, found 340.1328; Anal. Calcd. for $C_{18}H_{20}FNO_3$: C, 68.1; H, 6.4; N, 4.4. Found: C, 68.4; H, 6.7; N, 4.0.

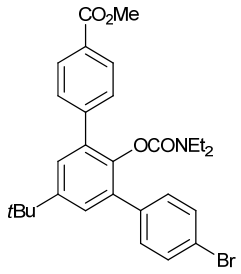
2q (Table 2, Entry 19).



White gum, 14 mg (17%); R*f* 0.23 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.44 (d, *J* 8.0 Hz, 2H), 6.84 (d, *J* 8.3 Hz, 2H), 6.71 (m, 1H), 6.40 (m, 2H), 3.32 (s, 3H), 2.61

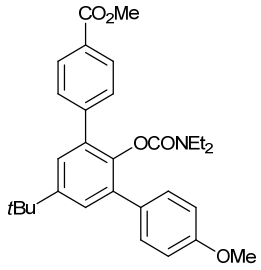
(app. sextet, *J* 7.1 Hz, 4H), 0.41 (quintet, *J* 7.3 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 166.9, 163.4, 161.4, 153.3, 149.3 (d, *J* 11.8 Hz), 142.1, 131.2 (d, *J* 9.7 Hz), 130.2 (d, *J* 3.9 Hz), 129.4, 129.2, 129.0, 112.9 (d, *J* 21.5 Hz), 111.3 (d, *J* 23.5 Hz), 52.2, 42.2, 41.7, 14.0, 13.1; IR neat, ν (cm^{-1}) 3357 (br), 2932 (w), 1718 (s), 1612 (m), 1474 (m), 1435 (m), 1415 (s), 1265 (s); HRMS (ESI) calcd for $C_{19}H_{20}FNO_4$ $(M+Na)^+$ 368.1269, found 368.1278.

3l.



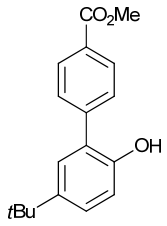
White solid, 21 mg (61%); R*f* 0.06 (EtOAc/hexanes, 1:9); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.07 (d, *J* 8.4 Hz, 2H), 7.56-7.51 (m, 4H), 7.37-7.33 (m, 4H), 3.95 (s, 3H), 3.05 (septet, *J* 7.1 Hz, 4H), 1.39 (s, 9H), 0.86 (t, *J* 7.2 Hz, 3H), 0.76 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 167.2, 153.2, 148.8, 143.6, 143.3, 137.7, 134.8, 134.7, 131.3, 131.0, 129.4, 129.3, 128.9, 127.6, 127.3, 121.6, 52.2, 42.0, 41.6, 34.8, 31.5, 13.9, 12.8; IR neat, ν (cm^{-1}) 2955 (m), 1716 (s), 1612 (m), 1420 (s), 1383 (m); m.p. 170.5-171.9 °C; HRMS (ESI) calcd for $C_{29}H_{32}BrNNaO_4$ $(M+Na)^+$ 560.1407, 562.1386, found 560.1413, 562.1390; Anal. Calcd. for $C_{29}H_{32}BrNO_4$: C, 64.7; H, 6.0; N, 2.6. Found: C, 64.4; H, 6.0; N, 2.8.

3m.



White solid, 18 mg (56%); R*f* 0.12 (EtOAc/hexanes, 3:17); ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.07 (app. dt, *J* 8.0, 2.2 Hz, 2H), 7.56 (app. dt, *J* 8.3, 2.0 Hz, 2H), 7.40 (m, 3H), 7.33 (d, *J* 2.5 Hz, 1H), 6.94 (app. dt, *J* 8.8 Hz, 2H), 3.94 (s, 3H), 3.84 (s, 3H), 3.05 (septet, *J* 7.0 Hz, 4H), 1.38 (s, 9H), 0.87 (t, *J* 7.1 Hz, 3H), 0.76 (t, *J* 7.0 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 167.2, 159.0, 153.3, 148.6, 144.0, 143.5, 135.5, 134.6, 131.2, 130.4, 129.42, 129.38, 128.8, 128.0, 126.6, 113.6, 55.4, 52.2, 41.9, 41.5, 34.7, 31.6, 14.0, 12.9; IR neat, ν (cm^{-1}) 2959 (m), 1713 (s), 1610 (m), 1510 (m), 1418 (m), 1395 (m); m.p. 124.7-126.0 °C; HRMS (ESI) calcd for $C_{30}H_{35}NNaO_5$ $(M+Na)^+$ 512.2407, found 512.2423; Anal. Calcd. for $C_{30}H_{35}NO_5$: C, 73.6; H, 7.2; N, 2.9. Found: C, 73.2; H, 7.1; N, 3.3.

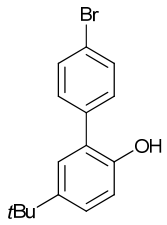
4a.



White solid, 30 mg (44%); R*f* 0.25 (EtOAc/hexanes, 3:17); ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.09 (app. dt, *J* 8.3, 2.2 Hz, 2H), 7.51 (app. dt, *J* 8.3, 2.2 Hz, 2H), 7.41 (dd, *J* 8.5, 2.4 Hz, 1H), 7.40 (d, *J* 2.2 Hz, 1H), 7.08 (d, *J* 8.4 Hz, 1H), 3.95 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.6, 149.5, 143.1, 129.7, 129.1, 127.8, 126.5, 122.4, 52.3, 34.7, 31.5; IR

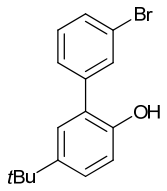
neat, ν (cm^{-1}) 3676 (w), 2962 (m), 1713 (s), 1607 (m), 1491 (m), 1441 (m), 1364 (m); m.p. 101.2-102.9 °C; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $(M-H)^-$ 283.1340, found 283.1350; Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.0; H, 7.1. Found: C, 77.1; H, 7.2.

4b.



White solid, 31 mg (42%); R*f* 0.38 (EtOAc/hexanes, 1:9); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.56 (app. dt, *J* 8.4, 1.8 Hz, 2H), 7.41 (dd, *J* 8.5, 2.6 Hz, 1H), 7.37 (d, *J* 2.6 Hz, 1H), 7.32 (app. dt, *J* 8.5, 1.9 Hz, 2H), 7.07 (d, *J* 8.4 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 149.5, 145.4, 137.2, 133.0, 131.6, 130.7, 129.3, 127.7, 126.1, 122.4, 34.7, 31.5; IR neat, ν (cm^{-1}) 2966 (s), 2867 (w), 1584 (w), 1501 (m), 1479 (s), 1371 (s), 1196 (s); m.p. 96.2-97.0 °C; LRMS (EI) m/z 289.1 (100%), 291.1 (100 %), 304.2 (55%), 306.2 (100%); Anal. Calcd. for $C_{16}H_{17}BrO$: C, 63.0; H, 5.6. Found: C, 63.4; H, 5.4.

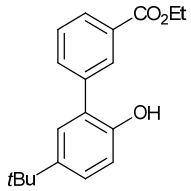
4c.



White solid, 35 mg (48%); R*f* 0.38 (EtOAc/hexanes, 1:9); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.62 (t, *J* 1.7 Hz, 1H), 7.51 (dt, *J* 7.7, 1.7 Hz, 1H), 7.44 (dd, *J* 8.4, 2.4 Hz, 1H), 7.40-7.37 (m, 2H), 7.32 (d, *J* 7.7 Hz, 1H), 7.09 (d, *J* 8.5 Hz, 1H), 1.38 (9H); ^{13}C NMR (100 MHz; $CDCl_3$) δ

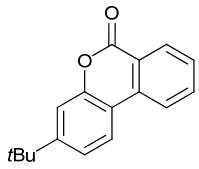
149.5, 145.4, 140.3, 132.6, 132.0, 130.5, 130.0, 127.7, 126.3, 122.4, 34.7, 31.5; IR neat, ν (cm^{-1}) 2963 (s), 1594 (w), 1560 (m), 1472 (br), 1366 (s), 1188 (s); m.p. 85.0-86.7 °C; LRMS (EI) m/z 289.1 (100%), 291.1 (100%), 304.2 (58%), 306.2 (58%); Anal. Calcd. for $C_{16}H_{17}BrO$: C, 63.0; H, 5.6. Found: C, 63.1; H, 5.9.

4d.



White gum, 18 mg (25%); R*f* 0.08 (EtOAc/hexanes, 1:9); ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.18 (t, *J* 1.7 Hz, 1H), 8.07 (dt, *J* 7.7, 1.7 Hz, 1H), 7.69 (dt, *J* 7.7, 1.6 Hz, 1H), 7.55 (t, *J* 7.7 Hz, 1H), 7.30 (dd, *J* 8.5, 2.4 Hz, 1H), 7.25 (d, *J* 2.5 Hz, 1H), 6.92 (d, *J* 8.4 Hz, 1H), 4.40 (quartet, *J* 7.2 Hz, 2H), 1.40 (t, *J* 7.2 Hz, 3H), 1.32 (s, 9H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 169.5, 166.4, 149.3, 145.4, 138.4, 133.3, 132.9, 130.0, 128.5, 128.3, 127.7, 126.0, 122.3, 61.1, 34.6, 31.4, 14.3; IR neat, ν (cm^{-1}) 2964 (m), 2906 (w), 1717 (s), 1587 (w), 1477 (w), 1366 (s), 1189 (s); HRMS (EI) calcd for $C_{19}H_{22}O_3$ $(M)^+$ 298.1569, found 298.1559.

5a.



White solid, 26 mg (42%); R*f* 0.11 (EtOAc/hexanes, 1:9); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.42 (dd, *J* 7.9, 1.5 Hz, 1H), 8.19 (dd, *J* 8.1, 0.6 Hz, 1H), 8.07 (d, 2.2 Hz, 1H), 7.85 (td, *J* 8.2,

1.5 Hz, 1H), 7.59 (td, *J* 8.2, 1.1 Hz, 1H), 7.55 (dd, *J* 8.6, 2.4 Hz, 1H), 7.33 (d, *J* 8.6 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 161.6, 149.5 147.7, 135.4, 134.9, 130.8, 128.8, 128.2, 121.7, 119.1, 117.5, 34.9, 31.7; IR neat, ν (cm^{-1}) 3669 (w), 2961 (m), 2902 (m), 2838 (w), 1729 (s), 1594 (s), 1478 (m), 1459 (m), 1410 (m), 1204 (s); m.p. 106.9-107.4°C; HRMS (CI) calcd for $C_{17}H_{17}O_2$ $(M+H)^+$ 253.1229, found 253.1234; Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found: C, 80.6; H, 6.6.

References

1. M. Bielawski, M. Zhu, B. Olofsson, *Angew. Chemie Int. Ed.*, 2007, 349, 2610.