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Full Paper

Enantioselective Synthesis of Arylglycine Derivatives by Asymmetric Addition of Arylboronic Acids to Imines

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Rhodium-catalyzed enantioselective 1,2-additions of arylboronic acids to *N*-tosyl furanylimine and lithium 5-methyl-2-furanyltriolborate to *N*-tosyl arylimines giving aryl(2-furanyl)methanamines were developed for enantioselective synthesis of arylglycines by ozonolysis of the furyl ring. A chiral *N*-linked C_2-symmetric bidentate phosphoramidite (*N*-Me-BIPAM) achieved high enantioselectivities up to 99 % ee. For the direct synthesis of arylglycines, the asymmetric addition of arylboronic acids to ethyl *N*-*p*-methoxyphenyl iminoester was carried out at 80°C in dioxane in the presence of Rh(acac)$(C_2H_4)_2$/(*R,R*)-*N*-Me-BIPAM. The reaction gave optically active arylglycines in up to 99 % ee.

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Introduction

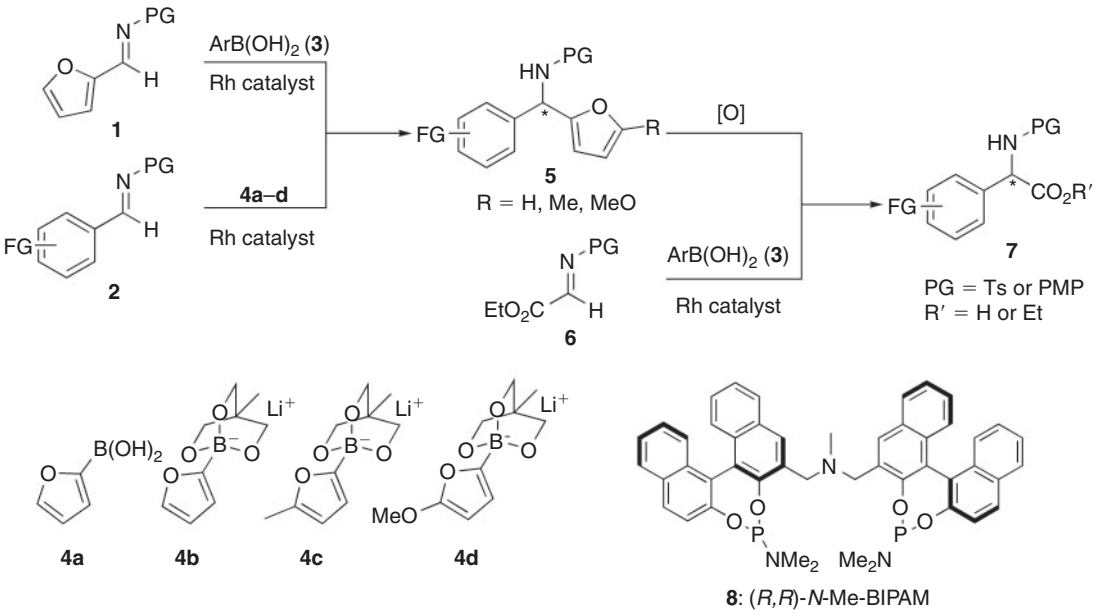
Arylglycines are a particularly important class of amino acids because they are components of several pharmaceutical agents, including glycopeptide antibiotics, antibacterial agents, and cardiovascular drugs.[1] The synthesis of α-amino acids has been dominated by the Strecker reaction and variants thereof.[2] Multicomponent reactions based on isonitriles (Ugi reaction) have also been developed but they are usually multistep and suffer from side reactions.[3,4] The addition of arylboronic acids to imino acids by Petasis reaction is a powerful method for arylglycine synthesis.[5,6] The asymmetric rhodium-catalyzed addition of arylboron reagents and arylstannanes to imines has been reported.[7–19] Recently, Ellman has reported an elegant method for the asymmetric synthesis of α-amino acids by the rhodium-catalyzed addition of arylboronic acids to *N*-*tert*-butanesulfinylimine, which precedes in high yield with high diastereoselectivity for both electron-rich and electron-poor arylboronic acids.[20–23] *N*-*tert*-butanesulfinyl protected arylglycine derivatives have also been synthesized by the transition metal-catalyzed addition of arylboronic acids to *N*-*tert*-butanesulfinyl imino esters.[23–25] We recently reported a chiral *N*-linked C_2-symmetric bidentate phosphoramidite ((*R*,*R*)-*N*-Me-BIPAM)[26–29] that was newly developed for the rhodium-catalyzed enantioselective addition of arylboronic acids to *N*-sulfonylimines. This ligand achieved high enantioselectivities.[30] As part of our program to develop a catalyzed reaction of organoboronic acids with a rhodium or palladium catalyst, we report here the synthesis of chiral arylglycine derivatives by using enantioselective addition of arylboron reagents to imines (Scheme 1).

Results and Discussion

Furyl rings are excellent synthons of the hydroxycarbonyl group that allow various syntheses of amino acids.[31–35] However, attempts to arylate imines with heteroarylboronic acids, such as 2-fulylboronic acid, were unsuccessful because of competitive B–C bond cleavage with water relative to the addition reaction. This is attributable to the high coordination ability of heteroatoms to catalysts and slow transmetalation and insertion of electron-deficient heteroaryl rings. Thus, we recently developed tetracoordinated ate-complexes of boronic esters for metal catalyzed reactions in non-aqueous media.[35–40] Initially, we chose arylation of *N*-tosyl-2-furylimine for the synthesis of *N*-tosyl-aryl(furyl)methanamine (Table 1). The Rh(acac)$(C_2H_4)_2$ (acac = acetylacetonate) previously used for addition of arylboronic acids to *N*-tosylaldimines resulted in lower selectivities (75 % ee, entry 1).[30] The reaction took place smoothly in dimethoxyethane (DME) at 50°C for 16 h in the presence of Rh(acac)((*R*,*R*)-*N*-Me-BIPAM) with 97 % yield and 96 % ee (entry 2). Results of the arylation of *N*-tosyl-2-furylimine with representative arylboronic acids at 50°C in DME are summarized in Table 1. High enantioselectivities were achieved with donating or withdrawing substituents at the boronic acids.

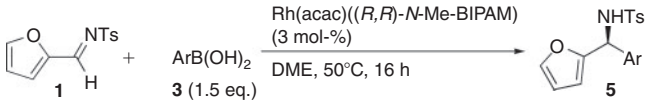
Next, we tried the addition reaction of 2-furylboronic acid derivatives (**4a**–**d**) to 4-methoxybenzylaldehyde *N*-tosylimine (**2c**) (Table 2). The best selectivity was obtained with lithium 5-methylfuryltriolborate (**4c**) (entry 3), whereas 2-furyboronic acid or 2-furyltriolborate resulted in lower selectivities than that of **4c**. Furthermore, no desired product was obtained with lithium 5-methoxyfuryltriolborate (**4d**) (entry 8). By further investigation of the reaction conditions, **4c** was finally obtained in 62 % yield and 99 % ee using 3 mol-% Rh(acac)$(C_2H_4)_2$/3.3 mol-% (*R*,*R*)-*N*-Me-BIPAM in toluene (4 mL) at 100°C for 16 h (entry 6).

Lithium 5-methyl-2-furyltriolborate (**4c**) was smoothly added to *N*-tosyl-arylimines in moderate yields and with excellent enantiomeric excess under optimized conditions (Table 3).



Scheme 1. FG: functional group, PG: protecting group.

Table 1. Arylation of *N*-tosyl-2-furylimine (1)[A]



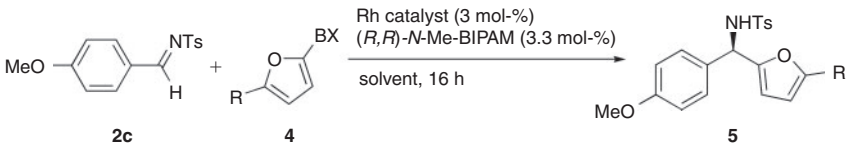
Entry	Ar	Yield [%]	ee [%]
1	C_6H_5 (**3a**)	89 (**5a**)	75[B] (*S*)
2	C_6H_5 (**3a**)	97 (**5a**)	96 (*S*)
3	4-MeC_6H_4 (**3b**)	91 (**5b**)	93 (−)
4	4-$MeOC_6H_4$ (**3c**)	93 (**5c**)	99[B] (+)
5	3-$MeOC_6H_4$ (**3d**)	99 (**5d**)	95[B] (−)
6	4-$CF_3C_6H_4$ (**3e**)	86 (**5e**)	98[B] (−)
7	3-$CF_3C_6H_4$ (**3f**)	75 (**5f**)	98 (−)
8	3-ClC_6H_4 (**3g**)	76 (**5g**)	95 (−)
9	3-BrC_6H_4 (**3h**)	84 (**5h**)	99 (+)
10	3,4-$(CH_2O_2)C_6H_3$ (**3i**)	93 (**5i**)	90 (+)
11	3-F-4-BrC_6H_4 (**3j**)	54 (**5j**)	95[C] (−)

[A]A mixture of furylimine (0.5 mmol), $ArB(OH)_2$ (0.75 mmol), Rh(acac)((*R*,*R*)-*N*-Me-BIPAM) (3 mol-%) in dimethoxyethane (2 mL) was stirred at 50°C for 16 h.
[B]$Rh(acac)(C_2H_4)_2$ (3 mol-%)/(*R*,*R*)-*N*-Me-BIPAM (3.3 mol-%) was used instead of Rh(acac)((*R*,*R*)-*N*-Me-BIPAM) (from ref. [30]).
[C]Determined at 80°C.

The furyl rings thus synthesized are excellent synthons of a carboxylic acid group in various syntheses of carboxylic acids.[31–35] Ozone is used for the oxidation of the furyl rings because a combination of $RuCl_3$ and $NaIO_4$ resulted in a complex mixture of several products. Thus, ozonolysis of **5h** and **5m** in methanol smoothly occurred at −78°C to yield the corresponding arylglycine derivatives in 87 and 82 % NMR yield, respectively (Scheme 2).

For the direct synthesis of arylglycines, then we tried the asymmetric addition of arylboronic acids to iminoesters (Table 4). We investigated the reaction of ethyl *N*-tosyliminoacetate with phenylboronic acid in the presence of $Rh(acac)(C_2H_4)_2$ (3 mol-%) and (*R*,*R*)-*N*-Me-BIPAM (3.3. mol-%) in DME at 50°C for 16 h; the addition product was obtained in only 19 % yield. The *p*-methoxyphenyl (PMP)-protected iminoester could be synthesized in one step and in high yield from ethyl glyoxylate.[41] The resulting products could be deprotected under mild conditions using cerium ammonium nitrate. Moreover, the PMP-protected iminoesters are more stable than their corresponding imines such as tosylimine. When ethyl *N*-*p*-methoxyphenyliminoester was used, the yield increased to 51 %. Finally, the reaction took place smoothly in dioxane at 50°C in the presence of 3.0 equivalents of phenylboronic acid with 74 % yield and 96 % ee (entry 4). High enantioselectivities were achieved in most arylboronic acids having donating or withdrawing substituents at the *para* or *meta* carbons. In

Table 2. Addition of 2-furylboron reagent to arylimines[A]

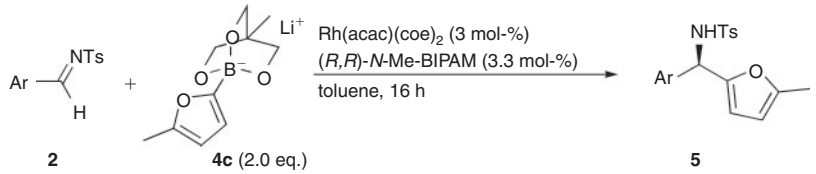


2c **4** **5**

Entry	**4** (eq.)	Rh catalyst[B]	Solvent[C]	Temp. [°C]	Yield [%]	ee [%]
1	**4a** (1.5)	$Rh(acac)(C_2H_4)_2$	DME	80	34	30
2	**4b** (2.0)	$Rh(acac)(C_2H_4)_2$	DME	80	71	65
3	**4c** (2.0)	$Rh(acac)(C_2H_4)_2$	DME	80	34	85
4	**4c** (2.0)	$Rh(acac)(C_2H_4)_2$	Toluene	80	56	89
5	**4c** (2.0)	$Rh(acac)(coe)_2$	Toluene	80	50	92
6	**4c** (2.0)	$Rh(acac)(coe)_2$	Toluene	100	62	99
7	**4c** (2.0)	$[Rh(nbd)_2]BF_4$	Toluene	80	43	96
8	**4d** (2.0)	$Rh(acac)(C_2H_4)_2$	DME	80	Trace	ND

[A]A mixture of arylimine (0.5 mmol), **3**, Rh catalyst (3 mol-%)/(*R*,*R*)-*N*-Me-BIPAM (3.3 mol-%) in solvent (2 mL) was stirred for 16 h.
[B]acac: acetylacetonate, coe: cyclooctene, nbd: 2,5-norbornadiene.
[C]DME (dimethoxyethane) or toluene (4 mL) was used.

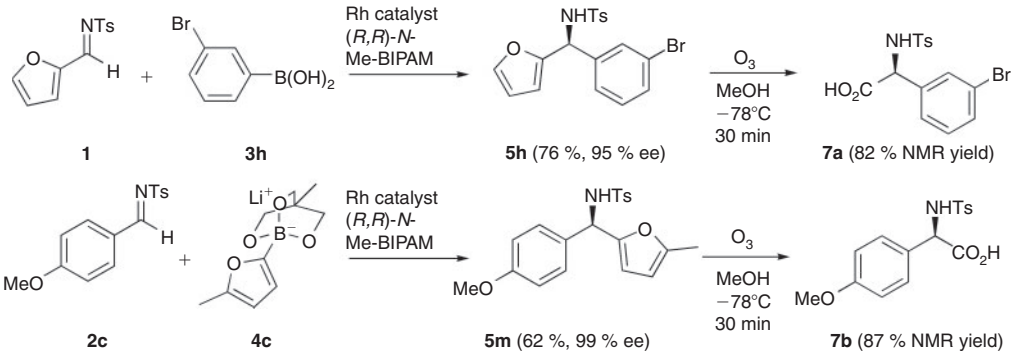
Table 3. Addition of lithium 5-methyl-2-furyltriolborate (4c) to arylimines[A]



2 **4c** (2.0 eq.) **5**

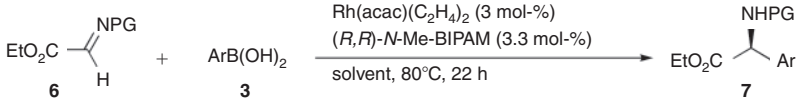
Entry	Ar	Temp. [°C]	Yield [%]	ee [%]
1	C_6H_5 (**2a**)	100	62 (**5k**)	93 (+)
2	4-MeC_6H_4 (**2b**)	90	56 (**5l**)	89 (+)
3	4-$MeOC_6H_4$ (**2c**)	100	62 (**5m**)	99 (+)
4	3-$MeOC_6H_4$ (**2d**)	100	44 (**5n**)	96 (+)
5	2-$MeOC_6H_4$ (**2e**)	100	64 (**5o**)	96 (+)
6	4-$CF_3C_6H_4$ (**2f**)	70	41 (**5p**)	66 (+)
7	4-BrC_6H_4 (**2g**)	70	51 (**5q**)	96 (−)
8	3-ClC_6H_4 (**2h**)	70	45 (**5r**)	94 (+)
9	2-ClC_6H_4 (**2i**)	70	44 (**5s**)	98 (+)

[A]A mixture of arylimine (0.5 mmol), **3** (1.0 mmol), $Rh(acac)(coe)_2$ (3 mol-%)/(*R, R*)-*N*-Me-BIPAM (3.3 mol-%) in toluene (4 mL) was stirred for 16 h (acac: acetylacetonate, coe: cyclooctene).



Scheme 2.

Table 4. Arylation of iminoesters[A]



(PG: protecting group, Ts: *p*-toluenesulfonyl, PMP: *p*-methoxyphenyl, DME: dimethoxyethane)

Entry	PG	Ar (eq.)	Solvent	Yield [%]	ee [%]
1	Ts	C_6H_5 (**3a**) (1.5)	DME	19[B] (**7c**)	68 (*S*)
2	PMP	C_6H_5 (**3a**) (1.5)	DME	51[B] (**7c**)	98 (*S*)
3	PMP	C_6H_5 (**3a**) (1.5)	Dioxane	60[B] (**7c**)	96 (*S*)
4	PMP	C_6H_5 (**3a**) (3.0)	Dioxane	74 (**7c**)	96 (*S*)
5	PMP	4-MeC_6H_4 (**3b**) (3.0)	Dioxane	84 (**7d**)	97 (+)
6	PMP	4-$MeOC_6H_4$ (**3c**) (3.0)	Dioxane	73 (**7e**)	97 (+)
7	PMP	3-$MeOC_6H_4$ (**3d**) (3.0)	Dioxane	67 (**7f**)	96 (+)
8	PMP	4-ClC_6H_4 (**3k**) (3.0)	Dioxane	47 (**7g**)	98 (+)
9	PMP	3,4-$(CH_2O_2)C_6H_3$ (**3i**) (3.0)	Dioxane	77 (**7h**)	96 (+)
10	PMP	4-HOC_6H_4 (**3l**) (3.0)	Dioxane	57 (**7i**)	90 (+)
11	PMP	3-HOC_6H_4 (**3m**) (3.0)	Dioxane	61 (**7j**)	99.7 (+)
12	PMP	3-$BocHNC_6H_4$ (**3n**) (3.0)	Dioxane	54 (**7k**)	99 (+)

[A]A mixture of iminoester (0.5 mmol), $ArB(OH)_2$, $Rh(acac)(C_2H_4)_2$ (3 mol-%)/(*R*,*R*)-*N*-Me-BIPAM (3.3 mol-%) in dioxane (2 mL) was stirred at 80°C for 22 h.
[B]Determined after 16 h.

addition, functional groups such as hydroxy and amino groups were tolerated (entries 10–12).

Conclusion

In summary, we have developed an efficient and highly enantioselective synthesis of arylglycines by using asymmetric addition of arylboronic acids to *N*-tosyl 2-furylimines or ethyl PMP-iminoesters. Furthermore, asymmetric addition of lithium 5-methyl-2-furyltriolborate to *N*-tosyl aryl imines has been achieved with high enantioselectivity. We have demonstrated the high efficiency of (*R*,*R*)-*N*-Me-BIPAM and lithium 2-furyltriolborate for enantioselective 1,2-addition to imines. With this catalyst system, a broad range of enantiopure arylglycines are easily prepared.

Experimental

Arylation of N*-Tosyl-2-furylimine*

A flask was charged with Rh(acac)((*R*,*R*)-*N*-Me-BIPAM) (0.015 mmol, 3 mol-%), *N*-tosyl-2-furylimine (0.5 mmol), and arylboronic acid (0.75 mmol) under a nitrogen atmosphere. DME (2.0 mL) was added to the flask and the mixture was then stirred at 50°C for 16 h, at which time the crude reaction mixture was extracted using ethyl acetate, washed with saturated NH_4Cl and brine, and dried over $MgSO_4$. Chromatography of the crude reaction mixture on silica gel gave (*S*)-*N*-(2-(furanyl)(phenyl) methyl)-4-methylbenzenesulfonamide (**5a**)[14,16,18,19,30] in 97 % yield and 96 % ee. $[\alpha]_D^{24}$ −10.66 (*c* 0.83, $CHCl_3$) {lit.[14] for (*S*)-**5a**: $[\alpha]_D^{20}$ −21.6 (*c* 1.03, $CHCl_3$) (99 % ee); lit.[16] for (*R*)-**5a**: $[\alpha]_D^{20}$ +4.6 (*c* 0.50, $CHCl_3$) (85 % ee); lit.[18] for (*S*)-**5a**: $[\alpha]_D^{20}$ −14.9 (*c* 0.98, $CHCl_3$) (99 % ee); lit.[19] for (*S*)-**5a**: $[\alpha]_D^{20}$ −9.6 (*c* 0.76, $CHCl_3$) (81 % ee); lit.:[14] $[\alpha]_D^{25}$ −10.8 (*c* 0.37, $CHCl_3$) (75 % ee)}.

N-*(2-(Furanyl)(*p*-tolyl)methyl)-4-methylbenzenesulfonamide (**5b**)*: $[\alpha]_D^{24}$ −1.43 (*c* 1.31, $CHCl_3$), 93 % ee (HPLC analysis: Chiralcel AS-H, hexane/propan-2-ol = 4/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 48.6 and 56.1 min). δ_H ($CDCl_3$, 400 MHz) 2.29 (s, 3H), 2.37 (s, 3H), 5.39 (d, *J* 7.7, 1H), 5.56 (d, *J* 7.7, 1H), 5.99 (d, *J* 3.2, 1H), 6.17 (dd, *J* 1.8, 3.2, 1H), 7.02–7.06 (m, 4H), 7.14 (d, *J* 8.2, 2H), 7.20 (d, *J* 1.4, 1H), 7.57 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 21.2, 21.6, 55.4, 108.3, 110.3, 127.2, 129.3, 129.4, 135.4, 137.4, 137.9, 142.6, 143.2, 152.5. *m/z* (HR-ESI) Calc. for $C_{19}H_{19}NO_3SNa$: 364.0983 $[M + Na]^+$. Found: 364.0977.

N-*[2-(Furanyl)(4-methoxyphenyl)methyl]-4-methylbenzenesulfonamide (**5c**)*:[30] $[\alpha]_D^{24}$ +2.54 (*c* 0.65, $CHCl_3$), 88 % ee, {lit.:[30] $[\alpha]_D^{22}$ +2.79 (*c* 0.45, $CHCl_3$) (99 % ee)}.

N-*[2-(Furanyl)(3-methoxyphenyl)methyl]-4-methylbenzenesulfonamide (**5d**)*:[30] $[\alpha]_D^{24}$ −5.88 (*c* 0.26, $CHCl_3$), 89 % ee {lit.:[30] $[\alpha]_D^{24}$ −150.71 (*c* 0.32, $CHCl_3$) (95 % ee)}.

N-*[2-(Furanyl)(4-trifluoromethylphenyl)methyl]-4-methylbenzenesulfonamide (**5e**)*:[30] $[\alpha]_D^{24}$ −10.24 (*c* 0.57, $CHCl_3$), 95 % ee {lit.:[30] $[\alpha]_D^{23}$ −10.95 (*c* 0.56, $CHCl_3$) (98 % ee)}.

N-*[2-(Furanyl)(3-trifluoromethylphenyl)methyl]-4-methylbenzenesulfonamide (**5f**)*: $[\alpha]_D^{24}$ −5.80 (*c* 0.85, $CHCl_3$), 98 % ee (HPLC analysis: Chiralcel AS-H, hexane/EtOH = 10/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 38.3 and 53.8 min). δ_H ($CDCl_3$, 400 MHz) 2.35 (s, 3H), 5.66 (d, *J* 7.7, 1H), 5.74 (d, *J* 7.7, 1H), 5.99 (d, *J* 3.2, 1H), 6.18–6.20 (m, 1H), 7.12 (d, *J* 8.2, 2H), 7.24 (t, *J* 0.9, 1H), 7.33–7.47 (m, 4H), 7.55 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 21.5, 55.2, 108.8, 110.5, 124.1, 124.2, 124.9 (2C), 127.1, 129.2, 129.5, 130.9, 137.0, 139.2, 143.1, 143.7, 151.4. *m/z* (HR-ESI) Calc. for $C_{19}H_{16}F_3NO_3SNa$: 418.0701 $[M + Na]^+$. Found: 418.0695.

N-*[(3-Chlorophenyl)(2-furanyl)methyl]-4-methylbenzenesulfonamide (**5g**)*: $[\alpha]_D^{24}$ −2.81 (*c* 0.51, $CHCl_3$), 95 % ee (HPLC analysis: Chiralcel AS-H, hexane/propan-2-ol = 4/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 51.2 and 62.0 min). δ_H ($CDCl_3$, 400 MHz) 2.37 (s, 3H), 5.56 (d, *J* 8.2, 1H), 5.61 (d, *J* 8.2, 1H), 5.98 (d, *J* 3.2, 1H), 6.18 (dd, *J* 1.8, 3.2, 1H), 7.09–7.22 (m, 7H), 7.56 (d, *J* 8.6, 2H). δ_C ($CDCl_3$, 100 MHz) 21.6, 55.1, 108.7, 110.4, 125.6, 127.1, 127.6, 128.2, 129.5, 129.9, 134.5, 137.1, 140.2, 142.9, 143.6, 151.5. *m/z* (HR-ESI) Calc. for $C_{18}H_{16}ClNO_3SNa$: 384.0437 $[M + Na]^+$. Found: 384.0432.

N-*[(3-Bromophenyl)(2-furany)methyl]-4-methylbenzenesulfonamide (**5h**)*: $[\alpha]_D^{24}$ +0.93 (*c* 0.67, $CHCl_3$), 99 % ee (HPLC analysis: Chiralcel AS-H, hexane/propan-2-ol = 4/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 55.2 and 73.8 min). δ_H ($CDCl_3$, 400 MHz) 2.39 (s, 3H), 5.19 (d, *J* 7.3, 1H), 5.58 (d, *J* 7.3, 1H), 6.00 (d, *J* 3.2, 1H), 6.21 (dd, *J* 1.8, 3.2, 1H), 7.10–7.18 (m, 4H), 7.25 (d, *J* 9.1, 2H), 7.34–7.36 (m, 1H), 7.56 (d, *J* 8.6, 2H). δ_C ($CDCl_3$, 100 MHz) 21.6, 55.0, 108.8, 110.4, 122.7, 126.1, 127.2, 129.5, 130.2, 130.4, 131.2, 137.1, 140.3, 143.0, 143.6, 151.4. *m/z* (HR-ESI) Calc. for $C_{18}H_{16}BrNO_3SNa$: 427.9932 $[M + Na]^+$. Found: 427.9926.

N-*[(5-Benzo[1,3]dioxolyl)(2-furanyl)methyl]-4-methylbenzenesulfonamide (**5i**)*: $[\alpha]_D^{24}$ +13.61 (*c* 0.56, $CHCl_3$), 90 % ee (HPLC analysis: Chiralcel OD-H, hexane/propan-2-ol = 95/5, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 90.0 and 97.5 min). δ_H ($CDCl_3$, 400 MHz) 2.37 (s, 3H), 5.45 (d, *J* 7.3, 1H), 5.50 (d, *J* 7.7, 1H), 5.89 (dd, *J* 1.4, 5.9, 2H), 6.00 (d, *J* 3.2, 1H), 6.18 (dd, *J* 1.8, 3.2, 1H), 6.63–6.67 (m, 3H), 7.16 (d, *J* 8.2, 2H), 7.21 (d, *J* 1.4, 1H), 7.58 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 21.6, 55.4, 101.3, 107.9, 108.2, 108.3, 110.3, 121.0, 127.2, 129.4, 132.2, 137.4, 142.6, 143.3, 147.4, 147.8, 152.3. *m/z* (HR-ESI) Calc. for $C_{19}H_{17}NO_5SNa$: 394.0725 $[M + Na]^+$. Found: 394.0721.

N-*[(4-Bromo-3-fluorophenyl)(2-furanyl)methyl]-4-methylbenzenesulfonamide (**5j**)*: $[\alpha]_D^{24}$ −4.35 (*c* 0.59, $CHCl_3$), 96 % ee (HPLC analysis: Chiralcel AS-H, hexane/propan-2-ol = 4/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 43.1 and 48.2 min). δ_H ($CDCl_3$, 400 MHz) 2.39 (s, 3H), 5.55 (d, *J* 7.7, 1H), 5.67 (d, *J* 7.7, 1H), 5.98 (d, *J* 3.2, 1H), 6.19 (dd, *J* 1.8, 3.2, 1H), 6.89 (dd, *J* 1.8, 8.2, 1H), 6.92–6.95 (m, 1H), 7.16 (d, *J* 8.6, 2H), 7.23 (d, *J* 1.8, 1H), 7.39 (dd, *J* 7.3, 8.2, 1H), 7.56 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 21.6, 54.7, 108.8, 110.5, 115.5, 115.8, 124.3, 127.1, 129.5, 133.6, 137.0, 140.0, 143.1, 143.8, 151.0, 158.9. *m/z* (HR-ESI) Calc. for $C_{18}H_{15}BrFNO_3SNa$: 445.9838 $[M + Na]^+$. Found: 445.9832.

Addition of Lithium 5-Methyl-2-furyltriolborate to Arylimines

A flask was charged with $Rh(acac)(coe)_2$ (coe = cyclooctene) (0.015 mmol, 3 mol-%) and (*R*,*R*)-*N*-Me-BIPAM (0.0165 mmol, 3.3 mol-%) under a nitrogen atmosphere. Toluene (4.0 mL) was added to the flask and the mixture was then stirred at room temperature for 1 h to prepare the catalyst. Arylimine (**2a**, 0.5 mmol) and lithium 5-methyl-2-furyltoriolborate (**4c**, 1.0 mmol) were then added to this catalyst solution. The reaction mixture was stirred at 100°C for 16 h, at which time the crude reaction mixture was extracted using ethyl acetate, washed with saturated NH_4Cl and brine, and dried over $MgSO_4$. Chromatography of the crude reaction mixture on silica gel gave 4-methyl-*N*-[(5-methyl-2-furanyl)(phenyl)methyl]benzenesulfonamide[42] (**5k**) in 65 % yield and 93 % ee. $[\alpha]_D^{24}$ +37.25 (*c* 0.15, $CHCl_3$).

4-Methyl-N-*[(5-methyl-2-furanyl)(*p*-tolyl)methyl]-benzenesulfonamide (**5l**)*: $[\alpha]_D^{24}$ +14.62 (*c* 0.63, $CHCl_3$), 89 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 10/1, flow = 1.0 mL min^{-1}, λ 230 nm, t_R 7.1 and 9.7 min). δ_H ($CDCl_3$, 400 MHz) 2.09 (s, 3H), 2.30 (s, 3H), 2.38 (s, 3H), 5.11 (d, *J* 7.7, 1H), 5.51 (d, *J* 7.3, 1H), 5.73 (dd, *J* 0.9, 3.1, 1H), 5.84 (d, *J* 3.2, 1H), 7.01–7.10 (m, 4H), 7.15 (d, *J* 8.2, 2H), 7.58 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 13.5, 21.2, 21.6, 55.4, 106.1, 109.3, 127.2, 129.2, 129.3, 135.5, 137.8, 143.1, 150.4, 152.3. *m/z* (HR-ESI) Calc. for $C_{20}H_{21}NO_3SNa$: 378.1140 $[M + Na]^+$. Found: 378.1134.

N-*[(4-Methoxyphenyl)(5-methyl-2-furanyl)methyl]-4-methylbenzenesulfonamide (**5m**)*: $[\alpha]_D^{24}$ +13.73 (*c* 0.12, $CHCl_3$), 99 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 9/1, flow = 1.0 mL min^{-1}, λ 230 nm, t_R 12.9 and 14.7 min). δ_H ($CDCl_3$, 400 MHz) 2.09 (s, 3H), 2.38 (s, 3H), 3.77 (s, 3H), 5.14 (d, *J* 7.3, 1H), 5.50 (d, *J* 7.7, 1H), 5.74 (dd, *J* 0.9, 3.2, 1H), 5.83 (d, *J* 3.2, 1H), 6.76 (d, *J* 8.6, 2H), 7.11 (d, *J* 8.6, 2H), 7.16 (d, *J* 7.7, 2H), 7.57 (d, *J* 8.6, 2H). δ_C ($CDCl_3$, 100 MHz) 13.5, 21.6, 55.2, 55.3, 106.1, 109.3, 113.9, 127.2, 128.6, 129.3, 130.6, 137.5, 143.1, 150.5, 152.3, 159.3. *m/z* (HR-ESI) Calc. for $C_{20}H_{21}NO_4SNa$: 394.1089 $[M + Na]^+$. Found: 394.1086.

N-*[(3-Methoxyphenyl)(5-methyl-2-furanyl)methyl]-4-methylbenzenesulfonamide (**5n**)*: $[\alpha]_D^{24}$ +0.60 (*c* 0.05, $CHCl_3$), 96 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 10/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 20.0 and 21.0 min). δ_H ($CDCl_3$, 400 MHz) 2.10 (s, 3H), 2.38 (s, 3H), 3.71 (s, 3H), 5.18 (d, *J* 7.7, 1H), 5.53 (d, *J* 7.3, 1H), 5.74 (d, *J* 2.3, 1H), 5.85 (d, *J* 3.2, 1H), 6.72–6.80 (m, 3H), 7.14–7.18 (m, 3H), 7.58 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 13.5, 21.6, 55.3, 55.6, 106.2, 109.5, 112.9, 113.6, 119.7, 127.2, 129.3, 129.6, 137.5, 139.9, 143.1, 150.1, 152.4, 159.7. *m/z* (HR-ESI) Calc. for $C_{20}H_{21}NO_4SNa$: 394.1089 $[M + Na]^+$. Found: 394.1084.

N-*[(2-Methoxyphenyl)(5-methyl-2-furanyl)methyl]-4-methylbenzenesulfonamide (**5o**)*: $[\alpha]_D^{23}$ +11.86 (*c* 0.23, $CHCl_3$), 96 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 10/1, flow = 1.0 mL min^{-1}, λ 230 nm, t_R 8.9 and 10.2 min). δ_H ($CDCl_3$, 400 MHz) 2.12 (s, 3H), 2.34 (s, 3H), 3.69 (s, 3H), 5.66 (d, *J* 9.1, 1H), 5.74 (d, *J* 9.5, 2H), 5.80 (d, *J* 2.7, 1H), 6.71 (d, *J* 8.2, 1H), 6.81 (ddd, *J* 0.9, 7.7, 15.0, 1H), 7.09 (d, *J* 7.7, 3H), 7.15–7.19 (m, 1H), 7.56 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 13.6, 21.5, 52.9, 55.4, 106.2, 108.3, 111.0, 120.8, 126.2, 127.1, 129.1, 129.2 (2C), 137.7, 142.8, 150.8, 151.9, 156.6. *m/z* (HR-ESI) Calc. for $C_{20}H_{21}NO_4SNa$: 394.1089 $[M + Na]^+$. Found: 394.1083.

4-Methyl-N-*[(5-methyl-2-furanyl)(4-trifluoromethylphenyl)methyl]-benzenesulfonamide (**5p**)*: $[\alpha]_D^{24}$ +7.45 (*c* 0.25, $CHCl_3$), 66 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 10/1, flow = 1.0 mL min^{-1}, λ 230 nm, t_R 11.9 and 14.5 min). δ_H ($CDCl_3$, 400 MHz) 2.12 (s, 3H), 2.37 (s, 3H), 5.37 (d, *J* 7.3, 1H), 5.60 (d, *J* 7.3, 1H), 5.75 (dd, *J* 0.9, 3.2, 1H), 5.82 (d, *J* 3.2, 1H), 7.13 (d, *J* 8.2, 2H), 7.33 (d, *J* 8.2, 2H), 7.46 (d, *J* 8.2, 2H), 7.54 (d, *J* 8.6, 2H). δ_C ($CDCl_3$, 100 MHz) 13.5, 21.5, 55.3, 106.3, 109.8, 125.4, 125.5(2C), 127.2, 127.9, 129.4, 137.2, 142.2, 143.5, 149.3, 153.0. *m/z* (HR-ESI) Calc. for $C_{20}H_{18}F_3NO_3SNa$: 432.0857 $[M + Na]^+$. Found: 432.0853.

N-*[(4-Bromophenyl)(5-methyl-2-furanyl)-methyl]-4-methylbenzenesulfonamide (**5q**)*: $[\alpha]_D^{24}$ −5.43 (*c* 0.07, $CHCl_3$), 96 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 10/1, flow = 1.0 mL min^{-1}, λ 230 nm, t_R 8.1 and 11.4 min). δ_H ($CDCl_3$, 400 MHz) 2.09 (s, 3H), 2.39 (s, 3H), 5.46 (d, *J* 7.7, 1H), 5.49 (d, *J* 7.7, 1H), 5.74 (d, *J* 2.3, 1H), 5.81 (d, *J* 3.2, 1H), 7.08 (d, *J* 8.6, 2H), 7.15 (d, *J* 8.6, 2H), 7.33 (d, *J* 8.6, 2H), 7.55 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 13.4, 21.5, 55.0, 106.1, 109.5, 121.9, 127.1, 129.0, 129.3, 131.5, 137.1, 137.3, 143.3, 149.5, 152.6. *m/z* (HR-ESI) Calc. for $C_{19}H_{18}BrNO_3SNa$: 442.0088 $[M + Na]^+$. Found: 442.0087.

N-*[(3-Chlorophenyl)(5-methyl-2-furanyl)methyl]-4-methylbenzenesulfonamide (**5r**)*: $[\alpha]_D^{24}$ +91.35 (*c* 0.21, $CHCl_3$), 94 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 10/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 17.1 and 18.9 min). δ_H ($CDCl_3$, 400 MHz) 2.10 (s, 3H), 2.38 (s, 3H), 5.44 (d, *J* 7.7, 1H), 5.52 (d, *J* 7.7, 1H), 5.74 (d, *J* 2.3, 1H), 5.83 (d, *J* 3.2, 1H), 7.11–7.18 (m, 6H), 7.56 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 13.5, 21.6, 55.2, 106.3, 109.6, 125.7, 127.2, 127.6, 128.1, 129.4, 129.8, 134.4, 137.2, 140.4, 143.4, 149.5, 152.8. *m/z* (HR-ESI) Calc. for $C_{19}H_{18}ClNO_3SNa$: 398.0588 $[M + Na]^+$. Found: 398.0591.

N-*[(2-Chlorophenyl)-(5-methyl-2-furanyl)methyl]-4-methylbenzenesulfonamide (**5s**)*: $[\alpha]_D^{24}$ +4.45 (*c* 0.20, $CHCl_3$), 98 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 10/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 16.0 and 17.0 min). δ_H ($CDCl_3$, 400 MHz) 2.11 (s, 3H), 2.37 (s, 3H), 5.47 (d, *J* 7.3, 1H), 5.75 (d, *J* 2.7, 1H), 5.77 (d, *J* 3.2, 1H), 5.96 (d, *J* 7.3, 1H), 7.14–7.17 (m, 4H), 7.24–7.27 (m, 1H), 7.34–7.37 (m, 1H), 7.63 (d, *J* 8.2, 2H). δ_C ($CDCl_3$, 100 MHz) 13.5, 21.6, 52.8, 106.4, 109.5, 127.0, 127.3, 129.1, 129.2, 129.4, 129.7, 132.9, 135.9, 137.1, 143.3, 149.2, 152.7. *m/z* (HR-ESI) Calc. for $C_{19}H_{18}ClNO_3SNa$: 398.0588 $[M + Na]^+$. Found: 398.0592.

Arylation of Iminoesters

A flask was charged with $Rh(acac)(C_2H_4)_2$ (0.015 mmol, 3 mol-%) and (*R*,*R*)-*N*-Me-BIPAM (0.0165 mmol, 3.3 mol-%) under a nitrogen atmosphere. Dioxan (2.0 mL) was added to the flask and the mixture was then stirred at room temperature for 1 h to prepare the catalyst. PMP iminoester (**6**, 0.5 mmol) and phenylboronic acid (**3a**, 1.5 mmol) were then added to this catalyst solution. The reaction mixture was stirred at 80°C for 22 h, at which time the crude reaction mixture was extracted using ethyl acetate, washed with saturated NH_4Cl and brine, and dried over $MgSO_4$. Chromatography of the crude reaction mixture on silica gel gave (S)-*(4-methoxyphenylamino)phenylacetic acid ethyl ester*[43,44] (**7c**) in 74 % yield and 96 % ee. $[\alpha]_D^{24}$ +69.33 (*c* 0.31, $CHCl_3$) {lit.[43] for (*R*)-**7c**: $[\alpha]_D^{20}$ −107.8 (*c* 0.68, $CHCl_3$) (96 % ee); lit.[44] for (*R*)-**7c**: $[\alpha]_D^{20}$ −77.0 (*c* 0.4, $CHCl_3$) (92 % ee)}.

*(4-Methoxyphenylamino)(*p*-tolyl)acetic acid ethyl ester*[43,44] *(**7d**)*: $[\alpha]_D^{24}$ +90.20 (*c* 0.31, $CHCl_3$), 97 % ee, {lit.:[43] $[\alpha]_D^{20}$ −74.5 (*c* 0.92, $CHCl_3$) (96 % ee); lit.:[44] $[\alpha]_D^{20}$ −86.4 (*c* 0.4, $CHCl_3$) (93 % ee)}.

(4-Methoxyphenyl)(4-methoxyphenylamino)acetic acid ethyl ester[43,44] *(**7e**)*: $[\alpha]_D^{24}$ +86.05 (*c* 0.22, $CHCl_3$), 97 % ee, {lit.:[43] $[\alpha]_D^{20}$ −64.4 (*c* 0.46, $CHCl_3$) (94 % ee); lit.:[44] $[\alpha]_D^{20}$ −82.0 (*c* 0.2, $CHCl_3$) (91 % ee)}.

*(3-Methoxyphenyl)(4-methoxyphenylamino)acetic acid ethyl ester (**7f**)*: $[\alpha]_D^{24}$ +71.71 (*c* 0.30, $CHCl_3$), 96 % ee (HPLC analysis: Chiralcel AD-H, hexane/propan-2-ol = 4/1, flow = 1.0 mL min^{-1}, λ 230 nm, t_R 12.8 and 15.1 min). δ_H ($CDCl_3$, 400 MHz) 1.21 (t, *J* 7.3, 3H), 3.70 (s, 3H), 3.78 (s, 3H), 4.08–4.26 (m, 2H), 4.63 (br s, 1H), 4.96 (s, 1H), 6.51–6.55 (m, 2H), 6.70–6.74 (m, 2H), 6.83 (ddd, *J* 0.9, 1.8, 8.2, 1H), 7.03–7.04 (m, 1H), 7.08 (d, *J* 7.7, 1H), 7.24–7.28 (m, 1H). δ_C ($CDCl_3$, 100 MHz) 14.2, 55.3, 55.8, 61.8, 61.9, 112.8, 113.8, 114.8, 114.9, 119.7, 129.9, 139.6, 140.3, 152.5, 160.0, 172.0. *m/z* (HR-ESI) Calc. for $C_{18}H_{21}NO_4Na$: 338.1363 $[M + Na]^+$. Found: 338.1366.

(4-Chlorophenyl)(4-methoxyphenylamino)acetic acid ethyl ester[43,44] *(**7g**)*: $[\alpha]_D^{24}$ +79.03 (*c* 0.11, $CHCl_3$), 98 % ee, {lit.:[43] $[\alpha]_D^{20}$ −70.9 (*c* 1.19, $CHCl_3$) (98 % ee); lit.:[44] $[\alpha]_D^{20}$ −86.9 (*c* 0.4, $CHCl_3$) (86 % ee)}.

*5-Benzo[1,3]dioxolyl(4-methoxyphenylamino)acetic acid ethyl ester(**7h**)*: $[\alpha]_D^{24}$ +89.39 (*c* 0.10, $CHCl_3$), 96 % ee (HPLC analysis: Chiralcel AD-H, hexane/propan-2-ol = 4/1, flow = 1.0 mL min^{-1}, λ 230 nm, t_R 17.9 and 22.3 min). δ_H ($CDCl_3$, 400 MHz) 1.21 (t, *J* 7.3, 3H), 3.70 (s, 3H), 4.08–4.26 (m, 2H), 4.65 (br s, 1H), 4.90 (s, 1H), 5.92–5.93 (m, 2H), 6.52 (d, *J* 7.7, 2H), 6.71–6.77 (m, 3H), 6.95–6.97 (m, 2H). δ_C ($CDCl_3$, 100 MHz) 14.2, 55.8, 61.3, 61.9, 101.3, 107.6, 108.5, 114.8, 114.9, 120.9, 131.9, 140.2, 147.6, 148.1, 152.5, 172.1. *m/z* (HR-ESI) Calc. for $C_{18}H_{19}NO_5Na$: 352.1155 $[M + Na]^+$. Found: 352.1156.

*(4-Hydroxyphenyl)(4-methoxyphenylamino)acetic acid ethyl ester (**7i**)*: $[\alpha]_D^{24}$ +78.80 (*c* 0.46, $CHCl_3$), 90 % ee (HPLC analysis: Chiralcel OD-H, hexane/EtOH = 10/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 29.7 and 32.6 min). δ_H ($CDCl_3$, 400 MHz) 1.20 (t, *J* 7.3, 3H), 3.71 (s, 3H), 4.08–4.26 (m, 2H), 4.93 (s, 1H), 6.53 (d, *J* 9.1, 2H), 6.71–6.78 (m, 4H), 7.32 (d, *J* 8.6, 2H). δ_C ($CDCl_3$, 100 MHz) 14.2, 55.8, 61.2, 61.8, 114.9, 115.8, 128.7, 129.8, 140.3, 152.5, 155.7, 172.6. *m/z* (HR-ESI) Calc. for $C_{17}H_{19}NO_4Na$: 324.1206 $[M + Na]^+$. Found: 324.1212.

*(3-Hydroxyphenyl)(4-methoxyphenylamino)acetic acid ethyl ester (**7j**)*: $[\alpha]_D^{24}$ +7.38 (*c* 1.10, $CHCl_3$), 99.7 % ee (HPLC analysis: Chiralcel As-H, hexane/propan-2-ol = 4/1, flow = 0.5 mL min^{-1}, λ 230 nm, t_R 24.1 and 30.8 min). δ_H ($CDCl_3$, 400 MHz) 1.22 (t, *J* 7.3, 3H), 3.72 (s, 3H), 4.15–4.31 (m, 2H), 4.73 (br s, 1H), 5.00 (s, 1H), 6.73–6.75 (m, 4H), 6.85–6.92 (m, 2H), 7.20–7.26 (m, 2H). δ_C ($CDCl_3$, 100 MHz) 14.1, 55.7, 62.5, 62.9, 114.8, 117.6, 117.9, 120.3, 121.2, 129.4, 129.9, 139.1, 154.6, 156.8, 171.4. *m/z* (HR-ESI) Calc. for $C_{17}H_{19}NO_4Na$: 324.1206 $[M + Na]^+$. Found: 324.1212.

*(3-*tert*-Butoxycarbonylaminophenyl)(4-methoxyphenylamino) acetic acid ethyl ester (**7k**)*: $[\alpha]_D^{24}$ +61.73 (*c* 0.08, $CHCl_3$), 99 % ee (HPLC analysis: Chiralcel AD-H, hexane/propan-2-ol = 4/1, flow = 1.0 mL min^{-1}, λ 230 nm, t_R 13.3 and 18.1 min). δ_H ($CDCl_3$, 400 MHz) 1.20 (t, *J* 7.3, 3H), 1.50 (s, 9H), 3.69 (s, 3H), 4.07–4.26 (m, 2H), 4.67 (br s, 1H), 4.95 (s, 1H), 6.51 (d, *J* 9.1, 2H), 6.69–6.73 (m, 2H), 7.15 (d, *J* 7.7, 1H), 7.24–7.28 (m, 1H), 7.39–7.41 (m, 2H). δ_C ($CDCl_3$, 100 MHz): 14.2, 28.4, 55.8, 61.6, 61.9, 80.7, 114.8, 114.9, 116.9, 118.3, 121.9, 129.5, 139.0 (2C), 140.3, 152.5, 152.7, 172.0. *m/z* (HR-ESI) Calc. for $C_{22}H_{28}N_2O_5Na$: 423.1890 $[M + Na]^+$. Found: 423.1892.

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