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Enantioselective Synthesis of Highly Functionalized Trifluoromethyl-Bearing Cyclopentenes: Asymmetric [3+2] Annulation of Morita–Baylis–Hillman Carbonates with Trifluoroethylidenemalonates Catalyzed by Multifunctional Thiourea-Phosphines

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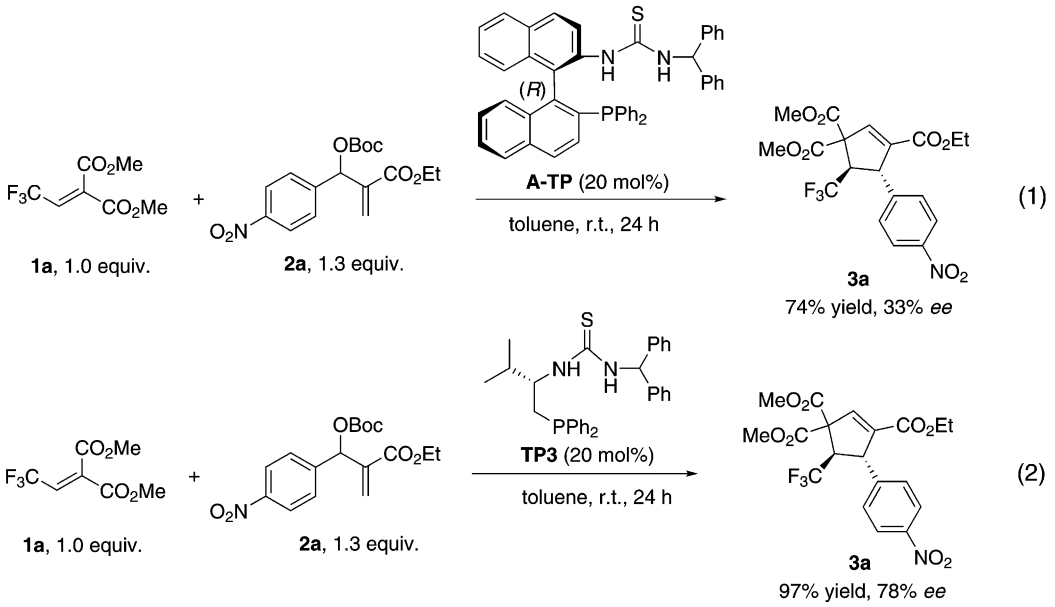
Abstract: On the basis of the design and synthesis of multifunctional thiourea-phosphines, a catalytic method for the asymmetric [3+2] annulation of Morita–Baylis–Hillman carbonates with trifluoroethylidenemalonates has been developed, affording highly functionalized trifluoromethyl-bearing cyclopentenes in excellent yields, high diastereoselectivities and enantioselectivities under mild conditions.

Keywords: asymmetric [3+2] annulation; Morita–Baylis–Hillman carbonates; multifunctional thiourea-phosphines; trifluoroethylidenemalonates; trifluoromethyl-bearing cyclopentenes

Due to the unique physical properties of trifluoromethyl-containing compounds, broad research efforts have been focused on the strategic introduction of the trifluoromethyl group into drug-like molecules in medicinal and agricultural chemistry.[1] More specifically, the catalytic enantioselective construction of trifluoromethyl-containing stereogenicity is still a challenge in organofluorine chemistry. Scientists' efforts have been directed towards the following two aspects: (i) to directly introduce a trifluoromethyl group through nucleophilic, electrophilic, or radical reactants[2,3] and (ii) to exploit trifluoromethyl-containing building blocks for the construction of chiral trifluoromethyl-containing products.[4] This latter approach is well suited for the refinement of readily available trifluoromethyl-containing building blocks. 2,2,2-Trifluoroethylidenemalonates are good substrates to construct stereogenic tertiary carbon centers bearing a trifluoromethyl group. Recently, Lu's group applied 2,2,2-trifluoroethylidenemalonates for asymmetric Michael addition and Friedel–Crafts alkylation to give the desired products in good yields with high enantioselectivities.[5,6]

Morita–Baylis–Hillman (MBH) adducts are useful synthons to construct multifunctional cyclic compounds because the *in situ* generated phosphorus ylides from MBH adducts in the presence of tertiary phosphines are very reactive 1,3-dipoles in a variety of annulations.[7] Lu and co-workers first reported a series of intra- and intermolecular [3+n] annulations ($n=2$, 4, 6) using MBH carbonates as 1,3-dipoles with various electron-deficient olefins catalyzed by a tertiary phosphine, affording the corresponding cycloadducts in good yields and high regioselectivities under mild conditions.[8] More recently, Zhang, Huang and He as well as their co-workers have also developed several MBH adducts involved in [4+1] annulations to give the cycloaddition products in high yields, respectively.[9]

To the best of our knowledge, there are few reports about asymmetric version of this reaction. Barbas and his co-workers first reported the asymmetric intermolecular [3+2] cycloaddition of MBH carbonates with methyleneindolinones to afford the corresponding spirocyclopentane-oxindoles in good yields and high *ee* values.[10] Lu's group developed L-threonine-derived phosphines which succeeded in catalyzing the [3+2] annulation of MBH carbonates with isatylidenemalononitriles in high yields with high enantioselectivities.[11] Moreover, Tang utilized spirobiindane-based chiral phosphines as catalysts to provide the corresponding intramolecular [3+2] annulation products in good yields along with high *ee* values.[12]



Scheme 1. Preliminary investigations on catalyst activation for the asymmetric [3+2] annulation of trifluoroethylidenemalonate **1a** with MBH carbonate **2a**.

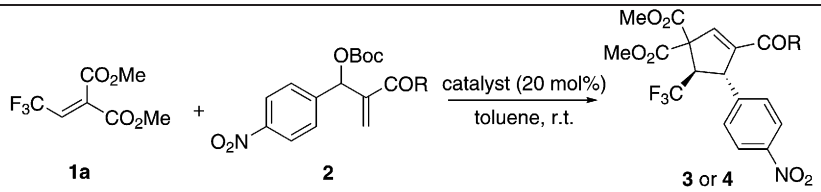
Our group recently designed a series of multifunctional thiourea-phosphine catalysts derived from an axially chiral binaphthyl scaffold and have demonstrated their excellent enantioselectivities for the asymmetric aza-MBH reaction, asymmetric allylic substitution of MBH adducts and moderate enantioselectivities for asymmetric [3+2] annulations of MBH carbonates with isatylidenemalononitriles.[13,14,15] In this context, we utilized the axially chiral multifunctional thiourea-phosphine **A-TP** as catalyst for asymmetric [3+2] annulations of trifluoroethylidenemalonate **1a** with MBH carbonate **2a** to give the *C-1* addition product **3a** in 74% yield with 33% *ee* [Scheme 1, Eq. (1)]. Due to the low activity and steric hindrance of **A-TP**, we designed and developed other types of multifunctional thiourea-phosphine catalyst, such as **TP3** derived from L-valine, furnishing **3a** in 97% yield and 78% *ee* [Scheme 1, Eq. (2)].[16]

Various multifunctional thiourea-phosphines, **TPs**, derived from natural amino acids were synthesized and subsequently examined for catalytic activities in the reactions of **1a** with **2a** in toluene at room temperature for 24 h, and the results are shown in Table 1. We found that **TP3** was the best catalyst among the L-valine-derived multifunctional thiourea-phosphines (Table 1, entries 1–4). Increasing the steric hindrance of multifunctional thiourea-phosphines, we consecutively examined the catalysts **TP5**–**TP7** in this reaction, and identified that **TP6** derived from L-phenylalanine was the most efficient catalyst, producing **3a** in 94% yield along with 83% *ee* value (entries 5–7). A slight structural modification of catalyst **TP6** gave **TP8** which afforded **3a** in higher *ee* (entry 8). Using **TP8** as catalyst, we also utilized MBH carbonates **2b** and **2c** instead of **2a** in this reaction, and found that **2b** gave the corresponding cyclopentene **3b** in 82% yield along with 9:1 *dr* and 90% *ee* (entry 9), and **2c** afforded **3c** with a lower *ee* value (entry 10). Taking MBH carbonates **2d** (and **2e**) derived from methyl vinyl ketone (MVK) [and ethyl vinyl ketone (EVK)] as substrates, we found that **TP6** was better than **TP8**, giving the corresponding product **4a** (**4b**) in excellent yield, high diastereoselectivity and good *ee* value (entries 11–13).

The solvent effect was subsequently examined using **TP6** as catalyst, **1a** and **2d** as substrates in this reaction. The highest *ee* was attained in the presence of toluene (Table 2, entry 1). The reaction also proceeded smoothly in other solvents to afford the desired product **4a** in good yields and good *ee* values, however THF and CH_3CN led to lower *ee* values (entries 3 and 4).

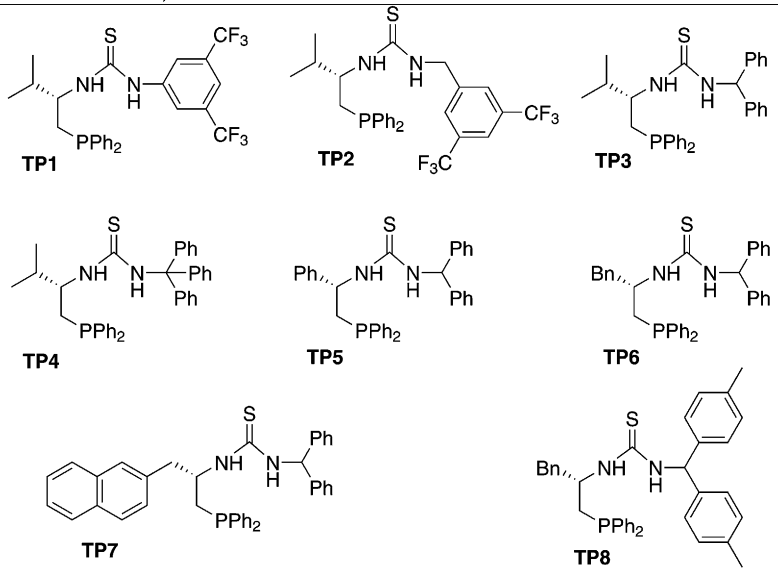
Having determined the optimal reaction conditions for the highly stereoselective formation of functionalized cyclopentenes **4**, we turned our attention to the scope of the multifunctional thiourea-phosphine-catalyzed asymmetric [3+2] annulations of trifluoroethylidenemalonates with MBH carbonates and the results are summarized in Table 3. All of the reactions proceeded smoothly under the optimal conditions, providing the *C-1* addition products in good yields with excellent diastereo- and enantioselectivities. Substrates with an electron-withdrawing substituent on the aromatic ring of MBH carbonates **2** afforded the corresponding annulation products in excellent yields along with high *ee* values (entries 1–7). Due to their

Table 1. Screening of catalysts for the asymmetric [3+2] annulation.[a]



1a 2 3 or 4

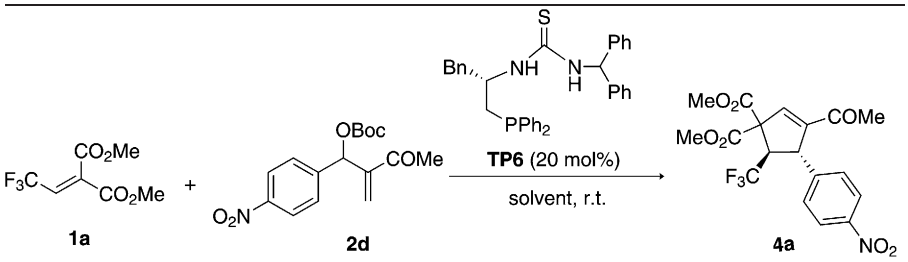
Entry	R	Catalyst	Time [h]	Yield [%][b]	*ee* [%][c]
1	**2a**, OEt	**TP1**	24	**3a**, 88	54
2	**2a**, OEt	**TP2**	24	**3a**, 58	64
3	**2a**, OEt	**TP3**	24	**3a**, 97	78
4	**2a**, OEt	**TP4**	24	**3a**, 92	–24
5	**2a**, OEt	**TP5**	24	**3a**, 94	80
6	**2a**, OEt	**TP6**	24	**3a**, 94	83
7	**2a**, OEt	**TP7**	24	**3a**, 99	78
8	**2a**, OEt	**TP8**	24	**3a**, 97	86
9[d]	**2b**, O-*t*-Bu	**TP8**	24	**3b**, 82	90
10	**2c**, OBn	**TP8**	24	**3c**, 91	83
11	**2d**, Me	**TP8**	24	**4a**, >99	90
12	**2d**, Me	**TP6**	24	**4a**, >99	91
13	**2e**, Et	**TP6**	24	**4b**, >99	92



[a] All reactions were carried out using **1a** (0.1 mmol), **2** (0.13 mmol) and catalyst (0.02 mmol, 0.2 equiv.) in toluene (1.0 mL).
[b] Isolated yield of major products with a *dr* (diastereoselective ratio) value >99:1 if not otherwise specified.
[c] Determined by chiral HPLC analysis.
[d] *dr* = 9:1.

lower activities, substrates with no or an electron-donating substituent on the aromatic ring of MBH carbonates produced **4** in moderate yield and excellent *ee* value upon lengthening the reaction time to 48 h (entries 8 and 9). The MBH carbonate derived from 2-furyl aldehyde also gave the *C-1* addition product **4l** in 78% yield along with 6.5:1 *dr* and 80% *ee* value (entry 10). Excellent results were obtained when utilizing diethyl 2-(2,2,2-trifluoroethylidene)malonate **1b** or dimethyl 2-(2,2,3,3,3-pentafluoropropylidene)malonate **1c** instead of 2,2,2-trifluoroethylidene malonate **1a** (entries 11 and 12). Using (*E*)-ethyl 4,4,4-trifluorobut-2-enoate **1d** instead of **1a** as the substrate in above reaction, we found that no reaction occurred under the standard conditions, suggesting that a highly activated Michael acceptor is required in this [3+2] annulation reaction (entry 13). To our delight, on enlarging the reaction scale to 0.5 mmol, similar results could be obtained, affording **3a** in >99% yield and 98:2 *dr* along with 92% *ee* (Scheme 2). The absolute configuration of **4n** has been unambiguously de-

Table 2. Solvent effects on the asymmetric [3+2] annulation of trifluoroethylidenemalonate **1a** with MBH carbonate **2a.**[a]



1a 2d 4a

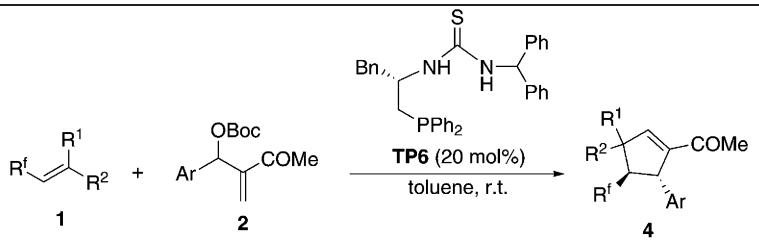
Entry	Solvent	Time [h]	Yield [%][b]	*ee* [%][c]
1	toluene	24	99	91
2	CH_2Cl_2	24	>99	90
3	THF	24	99	79
4	CH_3CN	48	>99	50
5	*o*-xylene	24	>99	90
6	$CHCl_3$	24	>99	90
7	chlorobenzene	24	92	90

[a] All reactions were carried out using **1a** (0.1 mmol), **2** (0.13 mmol) and catalyst (0.02 mmol, 0.2 equiv.) in toluene (1.0 mL).
[b] Isolated yield of major product with a *dr* value >99:1.
[c] Determined by chiral HPLC analysis.

termined by X-ray analysis (see the Supporting Information for the details).

On the basis of above experimental results and previous work,[8a,15e,17] a plausible reaction mechanism has been outlined in Scheme 3. The multifunctional thiourea-phosphine attacks from the β-position of MBH carbonate to take off carbon dioxide and *tert*-butyl alcohol, affording phosphorus ylide **I**. Then the nucleo-

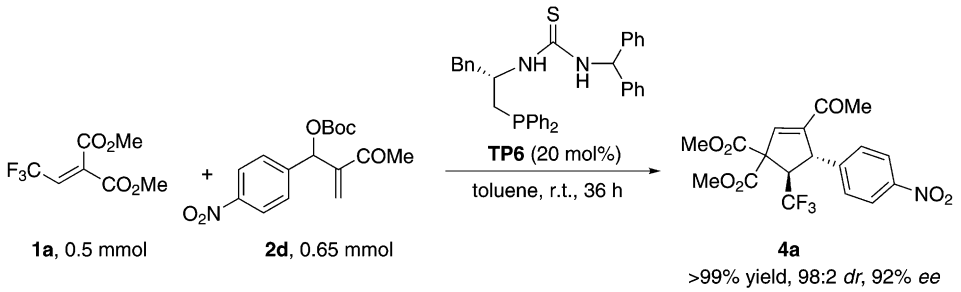
Table 3. Substrate scope of the asymmetric [3+2] annulation.[a]



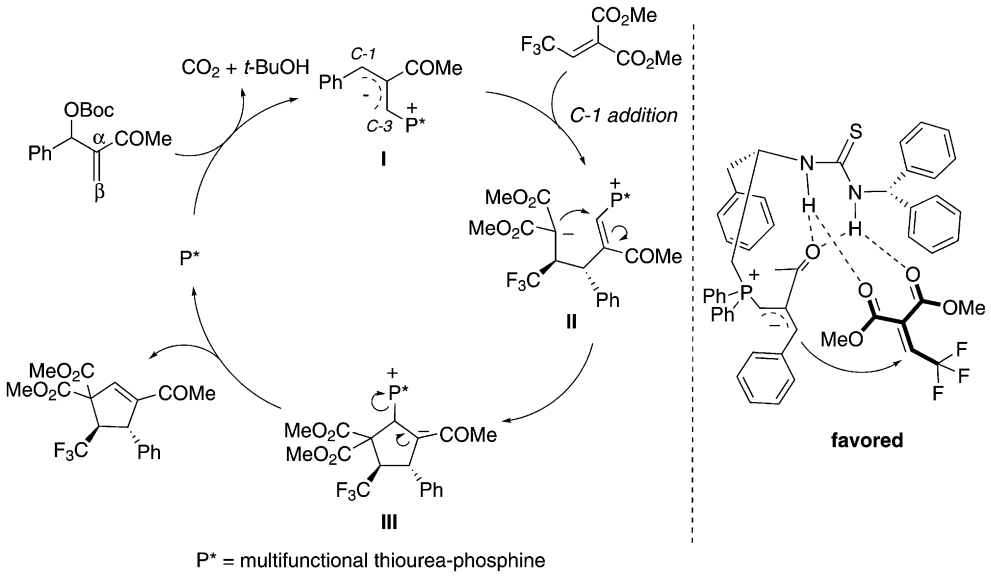
1 2 4

Entry	R^f	R^1/R^2	Ar	Yield [%][b]	*ee* [%][c]
1	CF_3	CO_2Me/CO_2Me	**2e**, 3-$NO_2C_6H_4$	**4c**, >99	90
2	CF_3	CO_2Me/CO_2Me	**2f**, 4-CNC_6H_4	**4d**, >99	91
3	CF_3	CO_2Me/CO_2Me	**2g**, 4-FC_6H_4	**4e**, 88	94
4	CF_3	CO_2Me/CO_2Me	**2h**, 4-BrC_6H_4	**4f**, 98	96
5	CF_3	CO_2Me/CO_2Me	**2i**, 4-ClC_6H_4	**4g**, 94	95
6	CF_3	CO_2Me/CO_2Me	**2j**, 3-ClC_6H_4	**4h**, 89	94
7	CF_3	CO_2Me/CO_2Me	**2k**, 3,4-$Cl_2C_6H_3$	**4i**, 98	93
8[d]	CF_3	CO_2Me/CO_2Me	**2l**, C_6H_5	**4j**, 76	95
9[d]	CF_3	CO_2Me/CO_2Me	**2m**, 4-MeC_6H_4	**4k**, 57	94
10[d,e]	CF_3	CO_2Me/CO_2Me	**2n**, 2-furyl	**4l**, 78	80
11	**1b**, CF_3	CO_2Et/CO_2Et	**2h**, 4-BrC_6H_4	**4m**, 98	96
12	**1c**, CF_3CF_2	CO_2Me/CO_2Me	**2h**, 4-BrC_6H_4	**4n**, >99	91
13	**1d**, CF_3	H/CO_2Et	**2h**, 4-BrC_6H_4	trace	-

[a] All reactions were carried out using **1a** (0.1 mmol), **2** (0.13 mmol) and catalyst (0.02 mmol, 0.2 equiv.) in toluene (1.0 mL) for 24 h.
[b] Isolated yield of major product with a *dr* value >99:1 if not otherwise specified.
[c] Determined by chiral HPLC analysis.
[d] Reactions were performed for 48 h.
[e] Isolated yield of all products, *dr* = 6.5 :1.



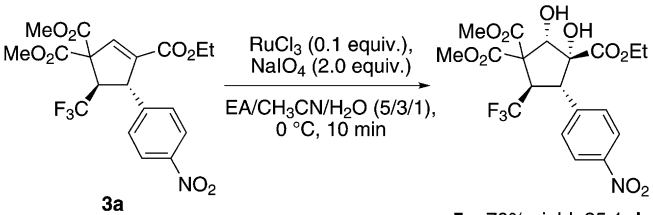
Scheme 2. Enlarging the reaction scale of asymmetric [3+2] annulation of **1a** and **2d**.



Scheme 3. A proposed mechanism.

philic attack of phosphorus ylide **I** to trifluoroethylidenemalonate with its *C-1*-terminal produces intermediate **II**, which undergoes Michael addition at the α-position of phosphorus cation to generate intermediate **III**. The elimination of catalyst along with the double bond formation furnishes the corresponding highly functional cyclopentene product and completes the catalytic cycle. The reactivity of the *in situ* generated phosphorus ylide **I** is crucial for the yield of product. If the reactivity of intermediate **I** is not high enough, it will partially deprotonate the NH proton in multifunctional thiourea-phosphine, causing the catalyst to lose activity (see Table 3, entries 8 and 9).[18] The high regio-, diastereo- and enantioselectivity of this reaction are probably controlled by steric hindrance between benzyl group and benzhydryl group on the catalyst with trifluoroethylidenemalonate as shown in Scheme 3.

The products of the asymmetric [3+2] annulation can be converted into a variety of potentially useful compounds.[19] For example, the dihydroxylation of **3a** can be performed efficiently under mild conditions,[20]



Scheme 4. Dihydroxylation of **3a**.

affording **5a** which bears four contiguous stereocenters in 70% yield and a 25:1 *dr* value (Scheme 4).

In conclusion, we have developed a series of multifunctional thiourea-phosphines and first applied them in the asymmetric [3+2] annulations of MBH carbonates with trifluoroethylidenemalonates, affording the corresponding highly functionalized trifluoromethyl- or pentafluoroethyl-bearing cyclopentenes in excellent yields (up to >99%), high diastereoselectivities (up to 99:1) and enantioselectivities (up to 96%) under mild conditions. Current efforts are in progress to use the multifunctional thiourea-phosphines in

other asymmetric reactions and apply this new methodology to synthesize biologically active products.

Experimental Section

General Procedure

Under an argon atmosphere, MBH carbonate **2** (0.13 mmol) was added to a solution of trifluoroethylidenemalonate **1** (0.1 mmol), catalyst **TP11** (0.02 mmol, 11 mg) in toluene (1.0 mL) and the mixture was stirred at room temperature for 24–48 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (elution with petroleum ether/EtOAc = 10:1–4:1) to provide compound **3** or **4** (MBH carbonate must be added last).

(4*S*,5*R*)-3-Ethyl 1,1-dimethyl 4-(4-nitrophenyl)-5-(trifluoromethyl)cyclopent-2-ene-1,1,3-tricarboxylate (3a): Yield: 43 mg (97%); colorless solid, mp 142–146 °C; IR (CH_2Cl_2): ν = 2957, 2925, 2852, 1739, 1606, 1522, 1435, 1348, 1373, 1249, 1210, 1057, 1016, 855, 843, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.12 (3H, t, J = 7.2 Hz, CH_3), 3.81 (3H, s, CH_3), 3.89 (3H, s, CH_3), 3.97–4.14 (3H, m, CH + CH_2), 4.54 (1H, dd, J = 1.6, 7.2 Hz, CH), 6.87 (1H, d, J = 1.6 Hz, CH), 7.33 (2H, d, J = 8.8 Hz, ArH), 8.19 (2H, d, J = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.8, 51.0, 53.7, 54.0, 56.0 (q, J = 27.5 Hz), 61.3, 66.6, 124.0, 125.4 (q, J = 277.9 Hz), 128.5, 139.4, 139.9, 147.4, 147.9, 162.2, 166.8, 167.9; ^{19}F NMR (376 MHz, $CFCl_3$): δ = −71.06 (d, J = 9.4 Hz); MS (ESI): m/z (%) = 463.0 (100) [M^+ + NH_4]; HR-MS (MADLI): m/z = 468.0866, calcd. for $C_{19}H_{18}NO_8F_3Na^{+1}$ (M^+ + Na): 468.0877. The enantiomeric excess was determined by HPLC (Chiralcel AD-H column, λ = 214 nm; eluent: hexane/2-propanol = 70/30; flow rate: 0.5 mL min^{-1}): t_{major} = 12.98 min, t_{minor} = 13.89 min; *ee* = 86%; $[\alpha]_D^{20}$: +80.0 (*c* 1.0, $CHCl_3$)].

CCDC 849269 contains the supplementary crystallographic data for **4n**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Spectroscopic data and chiral HPLC traces of the compounds shown in Table 1, Table 2, Table 3, Scheme 1 and Scheme 4 as well as detailed descriptions of the experimental procedures are available in the Supporting Information.

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