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Weinreb Amide Based Building Blocks for Convenient Access to Analogues of Phenstatin

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Dedicated to Professor Richard R. Schmidt on the occasion of his 75th birthday

Keywords: Weinreb amides / Diaryl ketones / Wittig reactions / Natural products / Carbohydrates

Bifunctional synthetic equivalents containing a Weinreb amide as one of the functionalities have been synthesized from commercially available *o*-, *m*-, and *p*-toluic acid. These bifunctional building blocks enabled efficient C–C bond formation through Wittig reaction with simple and functionalized aldehydes on one hand and a clean nucleophilic addition of 3,4,5-trimethoxy phenylmagnesium bromide onto the Weinreb amide functionality on the other hand, thereby paving way for an efficient and convenient synthesis of novel analogues of phenstatin with highly functionalized appendages. Further addition of various aryl or heteroarylmagnesium bromides onto the Weinreb amide functionality provided a general strategy for synthesizing unsymmetrical diaryl ketones conjugated to a monosaccharide moiety for the first time.

Introduction

Combretastatins **1** are a class of natural stilbenoids isolated by Pettit et al. in the late 1980s from the bark of Combretum caffrum, commonly known as South African bush willow, and are known to be potential anticancer agents.[1] A number of combretastatin analogues have been synthesized and evaluated for their structure–activity relationships;[2] currently, the phosphate prodrug combretastatin A-4 (**1b**) is in phase-III clinical trials.[3] Phenstatin (**2a**), a benzophenone-type compound, was obtained by accidental oxidation of the well-known anticancer drug combretastatin (**1a**, Figure 1) and displays potent anticancer and antimitotic activities.[4] In terms of both potency and cytotoxicity, phenstatin (**2a**) and its phosphate prodrug **2b** are quite similar to combretastatin A-4 phosphate prodrug **1b**.[4] Molecules that fall into the broader family of combretastatin and phenstatin generally share three common structural features, which include (1) a trimethoxy "A" ring, (2) a "B" ring containing substituents mainly at the C3 and C4 positions, and (3) a bridge in the form of *Z* stilbenes for combretastatin[5a] and more recently a ketone bridge for phenstatin to provide the rigidity between the two rings.[5b,5c] Over the years it has been found that changing the A ring is detrimental to its biological activity, any change in the B ring was welcome,[6] and the bridge size, distance between the two rings proved to be critical.[7]

Polar substituents in the form of hydroxy or amino groups have been introduced onto the B ring to increase the solubility of the compounds in water, thereby increasing the structure–activity relationship.[8] On basis of these critical observations, we aimed at synthesizing novel analogues of phenstatin **3** by keeping the A ring intact and by appending a monosaccharide moiety to the B ring for the first time (Figure 1). This would possibly increase the hydrophilic nature of the compound, and the sugar moiety could also bring some specificity towards certain cell lines. Also, in light of the fact that the bioconjugation concept, wherein two or more molecular entities with distinct properties are coupled to form novel conjugates,[9] have lately surfaced as a promising technique towards significant medicinal applications, the envisioned targets hold significant promise. Although Phenstatin (**2**) and targeted novel compounds **3** falls under the broader class of diaryl ketones,[10] an important structural motif in organic chemistry, to the best of our knowledge, diaryl ketones appended to hydrophilic sugar residues have never been synthesized in any context.

Three major strategies have been used in the literature for the synthesis of diaryl ketones. (1) The classical Lewis acid promoted FC acylation of arenes[11] and acylation of the organolithium, -magnesium, and -aluminum reagents with acid derivatives.[12] (2) Palladium-catalyzed coupling of ArM (M = SnR_3, BR_2, ZnX) with acid derivatives.[13] (c) Transition-metal-catalyzed three-component cross-coupling of aryl–X (X = Br, I, OTf, N_2^+) derivatives, carbon

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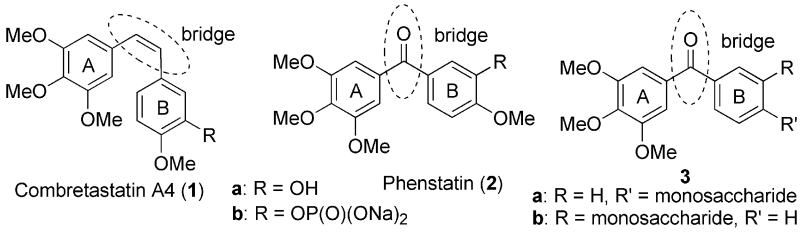
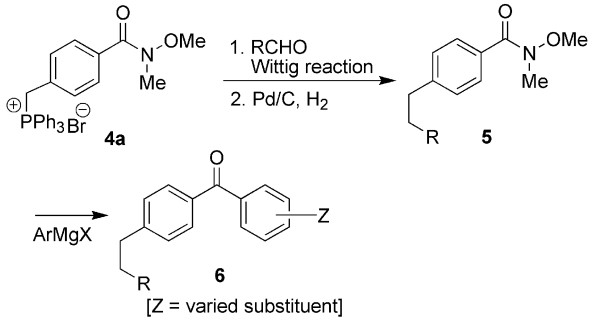


Figure 1. Structure of combretastatin A-4, phenstatin, and phenstatin analogues.

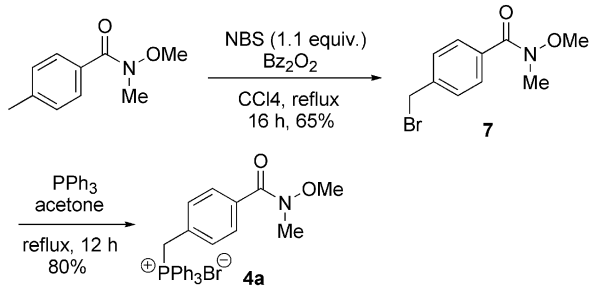
monoxide, and arylmetal reagents.[14] Besides these three main strategies, the transition-metal-catalyzed coupling of organic halides or triflates with aldehydes as starting substrate has surfaced as a promising alternative due to the high commercial availability of aldehydes. In Hartwig's procedure, rhodium-catalyzed intermolecular Heck-type reactions occurs between aryl iodides and *N*-pyrazylaldimines derived from aldehydes[15] to give ketimines, which upon hydrolysis afford diaryl ketones, whereas Cheng's method constitutes Ni^0-catalyzed direct coupling of aryl iodides with aryl aldehydes by using a bidentate phosphane complex.[16] The successful Heck-type coupling of aryl aldehydes with potassium trifluoro(organo)borates[17] under rhodium catalysis and with organoboronic[18] acids in recent times under palladium catalysis reflects the promise that this new strategy holds for the obtainment of diaryl ketones. Despite these advances towards the synthesis of diaryl ketones in general, we envisaged a new methodology for the specific objective set before us. The growing importance of the Weinreb amide (WA) functionality,[19] our continued interest in developing and using synthetic equivalents based on the WA functionality,[20] and the increasing confidence in the use of this functionality on kilogram scale[21] in industry led to the proposal of bifunctional building block **4a** towards the synthesis of unsymmetrical diaryl ketones **6** with highly functionalized appendages at the *para* position. Building block **4a** would allow efficient C–C bond formation through well-established Wittig reaction and the WA functionality therein would facilitate clean acylation with aryl- or heteroarylmagnesium reagents for the obtainment of desired diaryl ketones **6** (Scheme 1).



Scheme 1. General scheme for the preparation of diaryl ketones.

Results and Discussion

Analytically pure compound **4a** was conveniently prepared in three steps by using commercially available *p*-toluic acid. It involved facile benzylic bromination of the amide, followed by nucleophilic substitution with triphenylphosphane of benzylic amide **7** under acetone reflux conditions to give the corresponding Wittig salt **4a** in good yields (Scheme 2).

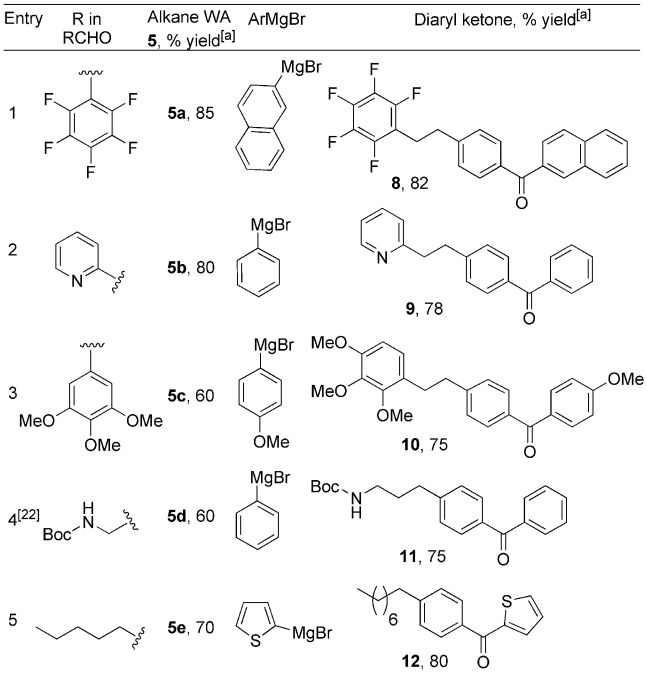


Scheme 2. Preparation of building block **4a**.

To implement the proposed strategy for diaryl ketones **6**, phosphonium salt **4a** was subjected to Wittig reaction with pentafluorobenzaldehyde (Table 1, Entry 1) as a representative aldehyde by using NaH (1.1 equiv.) as the base in DMF at room temperature. Clean reaction ensued, furnishing the expected olefinated product as an *E*/*Z* (1:3) mixture after column purification. The olefinated product was then subjected to hydrogenation by using 10% Pd/C in EtOAc, which afforded alkane WA **5a** in 85% yield. Alkane WA **5a** was treated with naphthalen-2-ylmagnesium bromide as a representative Grignard reagent to afford *para*-substituted diaryl ketone **8** in good yield (82%; Table 1). To our satisfaction, various electron-rich/electron-poor aromatic, heterocyclic, and aliphatic aldehydes reacted cleanly with Wittig salt **4a**, thereby bringing in the different substitutions at the *para* positions. Further addition of variety of aryl or heteroarylmagnesium reagents onto the WA functionality provided the generality and versatility of the developed strategy for diaryl ketones through bifunctional synthetic equivalent **4a** (Table 1). All isolated new compounds exhibited satisfactory spectral and analytical details.

To further generalize the developed strategy, regioisomeric phosphonium salts **4b** and **4c** (Figure 2) were also prepared from the corresponding toluic acid WA by following the procedure as described for **4a** in Scheme 2.

Table 1. Synthesis of diaryl ketones with building block **4a**.



[a] Yield of isolated product after flash chromatography.

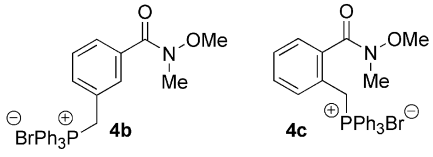
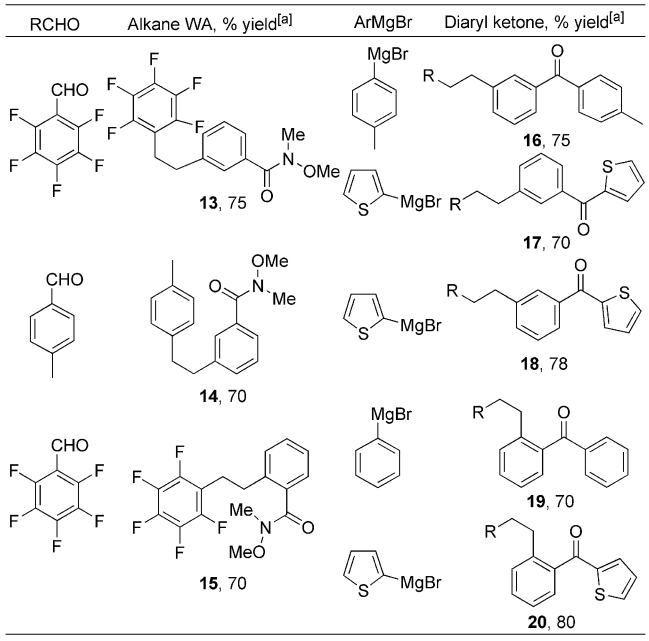


Figure 2. Regioisomeric building blocks.

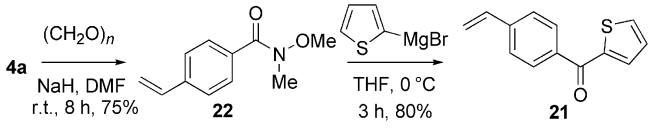
Much to our delight, phosphonium salts **4b** and **4c** underwent clean Wittig reaction with the representative aldehydes, and subsequent hydrogenation of the olefinated products furnished alkane WAs (**13**–**15**, Table 2). Grignard addition onto the alkane WA yielded the corresponding *meta*- and *ortho*-substituted diaryl ketones **16**–**20** in good yields (Table 2), thus firmly establishing the generality associated with the developed new strategy for functionalized unsymmetrical diaryl ketones. Diaryl ketone **21**, the final precursor of the commercially important nonsteroidal anti-inflammatory drug Suprofen,[14a] was obtained in two simple high-yielding reactions, involving classical Wittig olefination of paraformaldehyde with **4a** and facile Grignard addition of thiophen-2-ylmagnesium bromide to vinyl benzamide **22**. This illustrates the importance of the developed strategy (Scheme 3).

Having succeeded with the commercially available aldehydes we now extended this methodology towards coupling with more functionalized aldehydes from the domain of carbohydrates as part of our major objective towards phenstatin analogues. Aldehydes **23**–**28** were prepared through known, multistep reactions starting from readily available monosaccharides.[23]

Table 2. Synthesis of diaryl ketones with building blocks **4b** and **4c**.



[a] Yield of isolated product after flash chromatography.



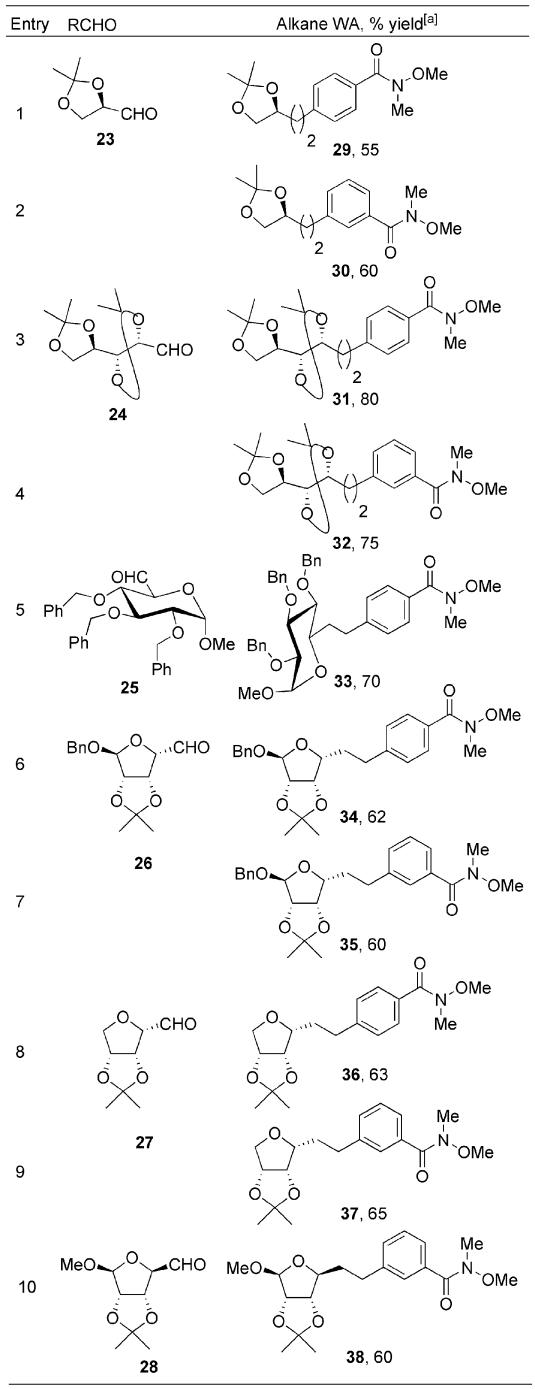
Scheme 3. Ultimate precursor for the anti-inflammatory drug Suprofen.

These functionalized aldehydes also reacted smoothly with building blocks **4a** and **4b** to furnish the corresponding alkane WAs **29**–**38**, having the monosaccharide residue at the *meta* and *para* positions, after hydrogenation of the olefinated product (Table 3). Addition of a Grignard reagent to functionalized alkane WAs **29**, **31**, and **33** enabled us to arrive at a new class of diaryl ketones, hitherto unreported in the literature (Table 4). Synthesis of these diaryl ketones having highly functionalized appendages at the *para* position illustrates our successful bioconjugation efforts.

Having successfully established the methodology of obtaining the diaryl ketone scaffold conjugated to a carbohydrate moiety, we then aimed at synthesizing analogues of phenstatin, especially bringing in changes at the C3′ and C4′ positions. A recent report confirming the 2-naphthyl ring being a bioisostere for the isovanillin moiety of phenstatin makes the presence of the OMe group on the B ring insignificant.[24]

Towards the latter objective, addition of the Grignard reagent generated from 3,4,5-trimethoxybromobenzene to the WA functionality of the alkane WA would bring in the essential A ring much required for biological activity. 3,4,5-Trimethoxybromobenzene was prepared easily in two steps from 2,6-dimethoxyphenol by a literature procedure[25] involving simple ring bromination followed by *O*-methylation of the phenolic compound. Initial studies led to the unsuc-

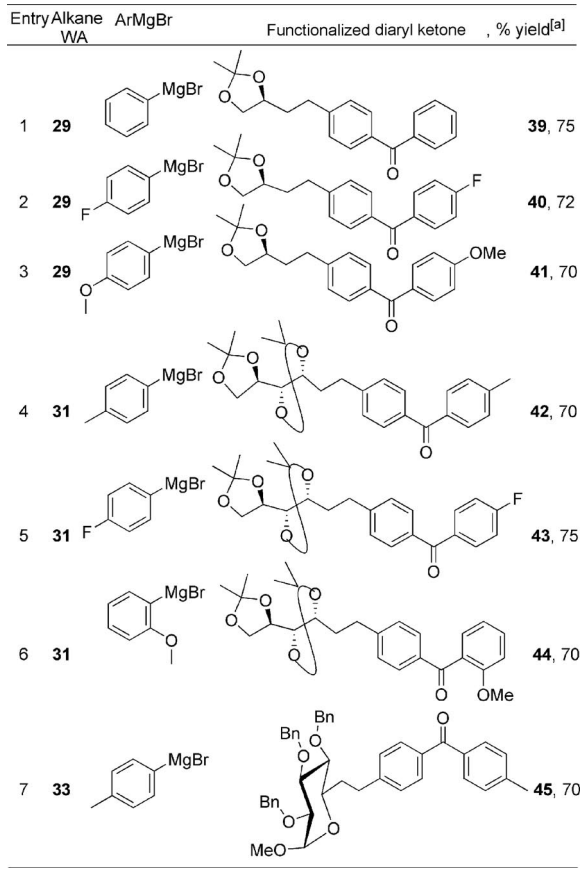
Table 3. Coupling of Wittig salts **4a** and **4b** with highly functionalized aldehydes.



[a] Yield of isolated product after flash chromatography.

cessful generation of the Grignard reagent from 3,4,5-trimethoxybromobenzene. Even with utmost care, both at room temperature as well as under reflux conditions, no initiation of the reaction was observed in our hands as reported in the literature.[26a] The change of solvent from THF to diethyl ether was also unfruitful. On a closer look at the literature, pertaining to the formation of the Grignard reagent from 3,4,5-trimethoxybromobenzene, it appeared that the formation was convenient only on a larger scale.[26b] No consistency was seen with regard to reaction conditions. After exploring several reaction conditions it was found that a catalytic amount of MeI was required for initiation and complete consumption of the magnesium metal. We were then successful in generating Grignard reagent on a 4.0-mmol scale from 3,4,5-trimethoxybromobenzene at 50–55 °C (before initiation) by using MeI (0.02 mL) as the initiator. After checking the reproducibility of the formation thrice on the aforementioned scale, we then scaled down carefully to 1.6 mmol of 3,4,5-trimethoxybromobenzene. Successful formation and addition of the Grignard reagent to WA functionality in **5a** was confirmed by the obtainment of ketone **46** in 72% yield. For phenstatin analogues, various alkane WAs (Table 3) having highly functionalized appendages were subjected to nucleophilic addition with 3,4,5-trimethoxyphenylmagnesium bromide (4 equiv.) for 2–3 h at 0 °C. Clean reactions were observed in all cases, thus paving the way for the targeted novel analogues of phenstatin (Table 5). Compound **47** having a latent amino functionality and compounds **48**–**56** having carbohydrate residues as their appendage will become interesting and promising analogues for biological studies from a solubility perspective. We then planned to investigate the biological activities of two compounds. For this, the isopropylidene protections in compounds **50** and **51** were removed

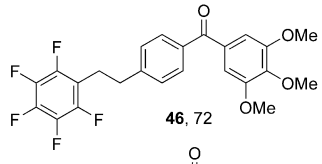
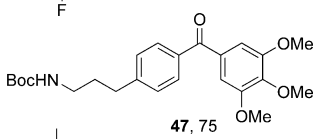
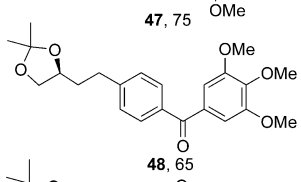
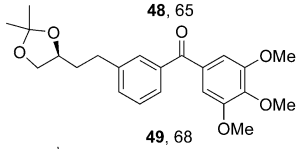
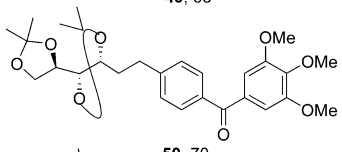
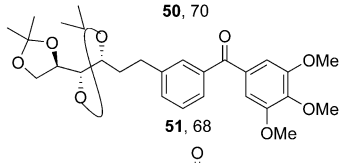
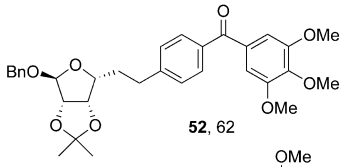
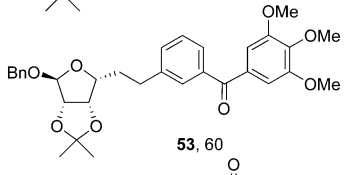
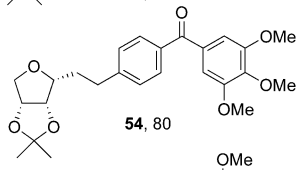
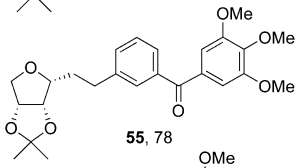
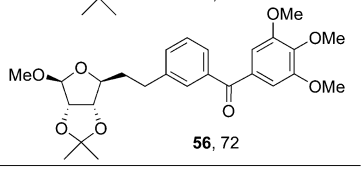
Table 4. Highly functionalized *para*-substituted diaryl ketones.



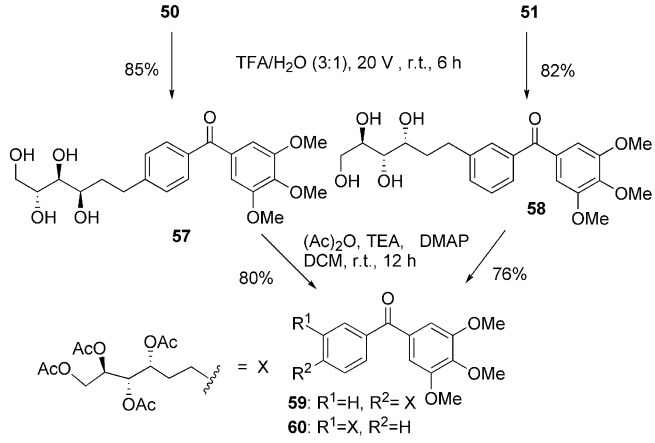
[a] Yield of isolated product after flash chromatography.

to afford regioisomeric tetrols **57** and **58**, for which the biological activity was tested,[27] and these compounds were further converted into tetraacetate derivatives **59** and **60**, respectively, for complete characterization of the obtained tetrols (Scheme 4).

Table 5. Novel analogues of phenstatins.

Entry	Alkane WA	Phenstatin analogue, % yield[a]
1	**5a**	 **46**, 72
2	**5d**	 **47**, 75
3	**29**	 **48**, 65
4	**30**	 **49**, 68
5	**31**	 **50**, 70
6	**32**	 **51**, 68
7	**34**	 **52**, 62
8	**35**	 **53**, 60
9	**36**	 **54**, 80
10	**37**	 **55**, 78
11	**38**	 **56**, 72

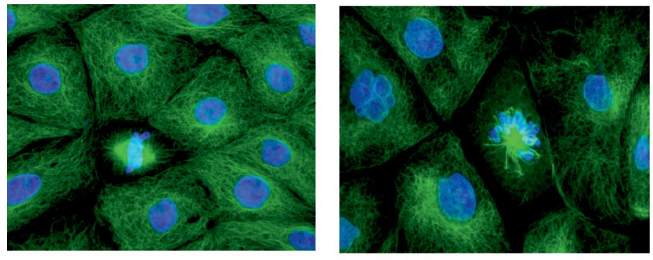
[a] Yield of isolated product after flash chromatography.



Scheme 4. Preparation of tetrols and tetraacetates.

Biological Studies

Serial dilutions of tetrols **57** and **58** were incubated with the mouse fibroblast cell line L929 and the HeLa clone KB-3-1 in 96-well plates. After 5 d, growth was measured with an MTT assay. Whereas *para*-appended tetrol had no growth inhibiting activity up to 40 μg/mL, *meta*-appended tetrol **58** was fairly active, showing IC_{50} values of 11 and 1.8 μg/mL for the two cell lines, respectively. Interestingly the KB-3-1 cancer cells are more sensitive than L929, which is also a transformed cell line but not derived from cancer. Influence on the microtubules of PtK2 cells with Long-nosed potoroo was also checked. There was a clear interference with mitotic spindle formation and a slight impairment of microtubule cytoskeleton of normal interphase cells was seen with *meta* compound **58** (5 and 10 μg/mL; Figure 3). Study of the biological activity of other *meta*-substituted compounds is currently underway.



(a) (b)

Figure 3. Ptk2 cells from potoroo were incubated with **58** (b) or with methanol (a) and stained for microtubules (green) and nuclei (blue). In Figure (b), a disturbed mitotic spindle and a reduced microtubular network in interphase cells can be seen.

Conclusions

To conclude, three new isomeric bifunctional building blocks capable of performing C–C bond formation through

Wittig reaction and undergoing nucleophilic addition have been synthesized. The benzylic phosphonium salt and Weinreb amide functionality, the two reaction centers in these building blocks, have enabled a new, general, and efficient strategy for synthesizing *para*-, *meta*-, and *ortho*-substituted diaryl ketones with highly functionalized appendages. Novel analogues of phenstatin were synthesized, wherein the diaryl ketone motif was conjugated to the monosaccharide moiety for the first time. The biological activity of regioisomeric phenstatin analogues **57** and **58** revealed that *meta*-appended compound **58** is more potent than *para*-**57**. In the context of this observation, other *meta* analogues have become interesting cases for biological studies, which is currently underway. These bifunctional building blocks show great potential for other applications in chemistry, and their applicability is left to the imagination of synthetic organic chemists.

Experimental Section

General Information: All reactions were carried out in dry glassware. Dry DMF was prepared by stirring with calcium hydride and was stored over 4 Å molecular sieves after downward distillation. Dry THF was distilled as and when needed from Na/benzophenone ketyl. Magnesium metal was cleaned by using 20% HCl (3×) followed by washes with distilled water and acetone and was dried by keeping it in an oven for 12 h at 100 °C. The Grignard reagent prepared was estimated by using menthol (dry) and 1,10-phenanthroline as indicator in dry THF. Solvents used for chromatography were LR grade. Thin-layer chromatography was performed on aluminum plates coated with silica gel 60. Visualization was observed by UV light irradiation or by dipping into a solution of cerium(IV) sulfate (2.5 g) and ammonium molybdate (6.25 g) in 10% sulfuric acid (250 mL) followed by charring on a hot plate. Melting points were determined in capillaries. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with $CDCl_3$ or CD_3OD as solvent and tetramethylsilane (TMS) as reference. Mass spectra were recorded with a MICRO-Q TOF mass spectrometer by using the ESI technique at 10 eV. Optical rotations were measured with an Autopol IV polarimeter at room temperature.

General Procedure for the Preparation of the Wittig Salts: To the benzylic bromide compound (4.0 mmol, 1.0 equiv.) dissolved in the suitable solvent (10 mL, acetone for **7a** and **7b** and *p*-xylene for **7c**) was added triphenylphosphane (1.2 equiv.), and the mixture was heated at reflux for 8–12 h and cooled to room temperature. The precipitated solid was filtered, washed with the corresponding solvent, and dried under vacuum to give the pure Wittig salts as white solids.

General Procedure for the Preparation of the Alkane Weinreb Amide: To a stirred suspension of NaH (0.2922 mmol) in dry DMF (4 mL/mmol) was added the Wittig salt (0.2656 mmol) directly under a nitrogen atmosphere, followed by the addition of aldehyde (0.2922 mmol) dissolved in dry DMF (1 mL). The mixture was stirred at room temperature, and a clean reaction ensued as revealed by TLC analysis after 6–8 h. The reaction mixture was quenched with aqueous ammonium chloride solution and extracted with ethyl acetate (3 × 15 mL). The ethyl acetate layer was washed with water, dried with Na_2SO_4, concentrated, and purified by silica-gel flash chromatography (ethyl acetate/hexanes) to give the olefinated product, which was subjected to hydrogenation with H_2, 10% Pd/C (20 wt.-%), and EtOAc (3 mL/mmol) for 8–12 h. The reaction mixture was filtered through a Celite bed, and the bed was thoroughly washed with ethyl acetate. The ethyl acetate layer was concentrated to give the pure alkane WA in quantitative yield.

General Procedure for the Addition of Grignard Reagent to the Alkane Weinreb Amides: To a stirred solution of alkane WA (0.7 mmol) in dry THF (3 mL) was added the appropriate solution of aryl- or heteroarylmagnesium bromide (2.1 mmol) in dry THF (5 mL) under an inert atmosphere at 0 °C, and the mixture was stirred between 0 and 20 °C for 3 h. TLC revealed the complete consumption of the starting material. Subsequent hydrolysis was achieved by cautious addition of a saturated ammonium chloride solution. The aqueous layer was extracted with ethyl acetate (3 × 15 mL) and the ethyl acetate layer was washed with water, dried with Na_2SO_4, and concentrated to give a crude product, which was purified by silica-gel flash chromatography (ethyl acetate/hexanes) to give the desired diaryl ketones in good yields.

General Procedure for the Addition of 3,4,5-Trimethoxyphenylmagnesium Bromide to the Alkane Weinreb Amides: To precleaned magnesium turnings (3.08 mmol) was added iodine (one crystal), and the mixture was roasted at 55 °C under vacuum for 5 min and then allowed to cool to room temperature under a nitrogen atmosphere. To this mixture was added dry THF (3 mL), and the resulting suspension was warmed to 55 °C followed by the addition of MeI (0.02 mL). At this temperature, freshly prepared 3,4,5-trimethoxybromobenzene (3.08 mmol), azeotroped with dry benzene (3 × 5 mL) and dried under high vacuum for 5 min, dissolved in dry THF (2 mL) was added drop by drop under vigorous stirring. Once the addition was complete, initiation of the Grignard reaction could be seen within 2–3 min, at which point the hot bath was removed, and the reaction mixture was stirred for 1 h. Slight exothermicity was observed till the complete consumption of magnesium metal; the generated Grignard reagent is an off-white suspension. To this Grignard reagent was added the alkane WA (0.77 mmol) dissolved in dry THF (2 mL) at 0 °C, and the mixture was stirred between 0 and 20 °C. A clean reaction ensued as revealed by TLC after 2–3 h. Subsequent hydrolysis was achieved by cautious addition of a saturated ammonium chloride solution. The aqueous layer was extracted with ethyl acetate (3 × 15 mL), washed with brine, dried with Na_2SO_4, and concentrated under vacuum to give the crude product, which was purified by silica-gel flash chromatography (ethyl acetate/hexanes or dichloromethane/hexanes) to give the desired phenstatin analogues in good yields.

{4-[Methoxy(methyl)carbamoyl]benzyl}triphenylphosphonium Bromide (4a): Yield: 80%. White solid. M.p. 238–246 °C. ^{1}H NMR (400 MHz, CD_3OD): δ = 3.32 (s, 3 H, -NCH_3), 3.57 (s, 3 H, -OCH_3), 5.06 (d, J = 15.2 Hz, 2 H, -CH_2), 7.12 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.49 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.69–7.76 (m, 12 H, ArH), 7.90–7.94 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 30.3, 30.8, 61.7, 118.5, 119.4, 129.6, 131.5, 131.8, 131.9, 132.0, 135.3, 135.5, 135.7, 136.6, 136.6, 170.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2926, 1645, 1368, 1165 cm^{-1}. $C_{28}H_{27}BrNO_2P$ (520.40): calcd. C 64.62, H 5.23, N 2.69; found C 63.66, H 4.54, N 2.66.

{3-[Methoxy(methyl)carbamoyl]benzyl}triphenylphosphonium Bromide (4b): Yield: 75%. White solid. M.p. 225–228 °C. ^{1}H NMR (400 MHz, CD_3OD): δ = 3.23 (s, 3 H, -NCH_3), 3.40 (s, 3 H, -OCH_3), 5.07 (d, J = 14.8 Hz, 2 H, -CH_2), 7.14–7.16 (m, 1 H, ArH), 7.30–7.34 (m, 1 H, ArH), 7.55–7.57 (m, 1 H, ArH), 7.69–7.76 (m, 12 H, ArH), 7.90–7.94 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 30.5, 34.1, 61.7, 118.5, 119.4, 129.6, 131.5, 131.8, 131.9, 132.0, 135.3, 135.5, 135.7, 136.6, 136.6, 170.3 ppm. IR

($CHCl_3$): $\tilde{\nu}$ = 2926, 1645, 1368, 1165 cm^{-1}. $C_{28}H_{27}BrNO_2P$ (520.40): calcd. C 64.62, H 5.23, N 2.69; found C 63.73, H 4.29, N 2.61.

{2-[Methoxy(methyl)carbamoyl]benzyl}triphenylphosphonium Bromide (4c): Yield: 60%. White solid. M.p. 195–198 °C. ^1H NMR (400 MHz, CD_3OD): δ = 3.16 (s, 3 H, -NCH_3), 3.44 (s, 3 H, -OCH_3), 5.25 (d, J = 14.8 Hz, 2 H, -CH_2), 7.25–7.35 (m, 3 H, ArH), 7.69–7.76 (m, 12 H, ArH), 7.90–7.94 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 29.6, 33.8, 61.4, 117.5, 118.3, 129.6, 131.5, 131.8, 131.9, 132.0, 135.3, 135.5, 135.7, 136.6, 136.6, 167.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2926, 1645, 1368, 1165 cm^{-1}. $C_{28}H_{27}BrNO_2P$ (520.40): calcd. C 64.62, H 5.23, N 2.69; found C 63.68, H 4.36, N 2.64.

***N*-Methoxy-*N*-methyl-4-(pentafluorophenylethyl)benzamide (5a):** Yield: 85%. R_f = 0.38 (hexane/ethyl acetate, 8:2), colorless solid. M.p. 110–112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.81–2.85 (m, 2 H, -CH_2), 2.91–2.94 (m, 2 H, -CH_2), 3.26 (s, 3 H, -NCH_3), 3.44 (s, 3 H, -OCH_3), 7.08 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.52 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.2, 32.7, 34.1, 59.9, 127.0, 127.6, 129.3, 131.4, 142.8, 168.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 2851, 1712, 1637, 1456, 1166 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{14}NO_2NaF_5$ [M + Na]$^+$ 382.0842; found 382.0837.

***N*-Methoxy-*N*-methyl-4-[2-(pyridin-2-yl)ethyl]benzamide (5b):** Yield: 80%. R_f = 0.25 (hexane/ethyl acetate, 7:3), colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.03 (s, 4 H, 2 CH_2), 3.25 (s, 3 H, -NCH_3), 3.46 (s, 3 H, -OCH_3), 6.98 [d, J = 7.6 Hz, 1 H, (py)Ar-H$^{3'}$], 7.03–7.06 [m, 2 H, (py)Ar-H$^{4'}$, H$^{5'}$], 7.12 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.50 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 8.49 [s, 1 H, (py) Ar-H$^{6'}$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.8, 35.7, 39.3, 60.9, 121.4, 123.3, 128.1, 128.4, 131.7, 136.9, 144.2, 148.7, 160.4, 171.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 2851, 1712, 1637, 1456, 1166 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{19}N_2O_2$ [M + H]$^+$ 271.1447; found 271.1451.

***N*-Methoxy-*N*-methyl-4-(3,4,5-trimethoxyphenethyl)benzamide (5c):** Yield: 60%. R_f = 0.35 (hexane/ethyl acetate, 8:2), colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.81–2.82 (m, 2 H, -CH$_2$CH_2), 2.87–2.88 (m, 2 H, -COArCH_2), 3.27 (s, 3 H, -NCH_3), 3.48 (s, 3 H, -OCH_3), 3.73 (s, 6 H, 2 ArOCH_3), 3.75 (s, 3 H, ArOCH_3), 6.28 [s, 2 H, (OCH$_3$)$_3$Ar-H$^{2'}$, H$^{6'}$], 7.12 (d, J = 8.0 Hz, 1 H, Ar-H^3, H^5), 7.53 (d, J = 8.0 Hz, 1 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.8, 37.8, 37.9, 56.0, 60.8, 105.3, 128.2, 128.4, 131.6, 137.1, 144.5, 153.1, 169.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2923, 1651, 1519, 1504, 1220, 1130 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{26}NO_5$ [M + H]$^+$ 360.1811; found 360.1809.

***tert*-Butyl 3-{4-[Methoxy(methyl)carbamoyl]phenyl}propylcarbamate (5d):** Yield: 60%. R_f = 0.22 (hexane/ethyl acetate, 7:3), colorless solid. M.p. 82–84 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, -C(CH_3)$_3$), 1.79–1.83 (m, 2 H, -CH_2), 2.66 (t, J = 8.0 Hz, 2 H, ArCH_2), 3.13–3.15 (m, 2 H, -NCH_2), 3.34 (s, 3 H, -NCH_3), 3.55 (s, 3 H, -OCH_3), 4.62 (br. s, 1 H, -NH), 7.20 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.60 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4, 31.4, 32.9, 33.9, 40.2, 60.9, 79.1, 127.9, 128.4, 131.6, 144.6, 156.0, 169.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2923, 1646, 1471, 1264 cm^{-1}. HRMS (ESI): $C_{17}H_{26}N_2O_4Na$ [M + Na]$^+$ 345.1790; found 345.1790.

4-Heptyl-*N*-methoxy-*N*-methylbenzamide (5e): Yield: 70%. R_f = 0.35 (hexane/ethyl acetate, 8:2), colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.2 Hz, 3 H, -CH_3), 1.19–1.26 (m, 8 H, 4 CH_2), 1.53–1.57 (m, 2 H, -CH_2), 2.56 (t, J = 8.0 Hz, 2 H, ArCH_2), 3.29 (s, 3 H, -NCH_3), 3.50 (s, 3 H, -OCH_3), 7.13 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.53 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 29.1, 31.2, 31.8, 33.9, 35.9, 61.0, 128.1, 128.3, 131.2, 146.0, 170.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 2854, 1644, 1462, 1376 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{25}NO_2Na$ [M + Na]$^+$ 286.1783; found 286.1777.

***N*-Methoxy-*N*-methyl-3-(pentafluorophenylethyl)benzamide (13):** Yield: 75%. R_f = 0.45 (hexane/ethyl acetate, 8:2), colorless solid. M.p. 76–78 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.90–2.96 (m, 2 H, -CH$_2$CH_2), 2.99–3.04 (m, 2 H, -CH_2), 3.35 (s, 3 H, -NCH_3), 3.54 (s, 3 H, -OCH_3), 7.24 (d, J = 7.2 Hz, 1 H, Ar-H^4), 7.31 (t, J = 7.6 Hz, 1 H, Ar-H^5), 7.47 (s, 1 H, Ar-H^2), 7.52 (d, J = 7.2 Hz, 1 H, Ar-H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.3, 33.7, 35.1, 60.9, 126.3, 128.1, 130.5, 134.4, 139.8, 169.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1651, 1519, 1504, 948 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{15}NO_2F_5$ [M + H]$^+$ 360.1023; found 360.1022.

***N*-Methoxy-*N*-methyl-3-(4-methylphenethyl)benzamide (14):** Yield: 70%. R_f = 0.55 (hexane/ethyl acetate, 8:2), colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, ArCH_3), 2.77–2.81 (m, 2 H, -CH$_2$CH_2), 2.82–2.85 (m, 2 H, ArCH_2), 3.22 (s, 3 H, -NCH_3), 3.45 (s, 3 H, -OCH_3), 6.94–6.99 (m, 4 H, ArH), 7.14–7.22 (m, 2 H, ArH), 7.38–7.39 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 33.9, 37.3, 37.8, 60.9, 125.6, 128.3, 128.7, 129.0, 130.8, 134.1, 138.3, 141.7, 170.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2928, 1650, 1529, 1514, 958 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_2$ [M + H]$^+$ 284.1651; found 284.1646.

***N*-Methoxy-*N*-methyl-2-(pentafluorophenylethyl)benzamide (15):** Yield: 70%. R_f = 0.50 (hexane/ethyl acetate, 8:2), colorless solid. M.p. 64–66 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.78–2.82 (m, 2 H, -CH$_2$CH_2), 2.91–2.95 (m, 2 H, ArCH_2), 3.26 (s, 3 H, -NCH_3), 3.44 (s, 3 H, -OCH_3), 7.14–7.30 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 33.6, 35.1, 60.9, 127.8, 128.1, 128.6, 134.4, 169.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2923, 1651, 1519, 1504, 948 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{15}NO_2F_5$ [M + H]$^+$ 360.1023; found 360.1022.

***N*-Methoxy-*N*-methyl-4-vinylbenzamide (22):** Yield: 75%. R_f = 0.40 (hexane/ethyl acetate, 8:2), colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.26 (s, 3 H, -NCH_3), 3.47 (s, 3 H, -OCH_3), 5.25 (d, J = 10.8 Hz, 1 H, -CHCH^aH^b), 5.74 (d, J = 17.6 Hz, 1 H, -CHCH^{a}H^b), 6.65 (dd, J = 17.6, 10.8 Hz, 1 H, ArCH), 7.35 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.58 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 33.8, 60.9, 115.6, 125.7, 128.6, 133.1, 136.1, 139.7, 169.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2928, 2864, 1710, 1647, 1446, 1186 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{14}NO_2$ [M + H]$^+$ 192.1025; found 192.1026.

(*S*)-4-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethyl]-*N*-methoxy-*N*-methylbenzamide (29): Yield: 55%. R_f = 0.30 (hexane/ethyl acetate, 7:3). $[a]_D$ = –6.6 (c = 1, $CHCl_3$), colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 3 H, -CH_3), 1.36 (s, 3 H, -CH_3), 1.74–1.89 (m, 2 H, -CH$_2$CH_2), 2.61–2.74 (m, 2 H, ArCH_2), 3.28 (s, 3 H, -NCH_3), 3.46 (t, J = 8.0 Hz, 1 H, -CHCH^aH^b), 3.49 (s, 3 H, -OCH_3), 3.94 (dd, J = 6.0, 8.0 Hz, 1 H, -CHCH^{a}H^b), 4.01–4.05 (m, 1 H, -CH^{a}H^{b}CH), 7.15 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.54 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 26.9, 31.9, 33.8, 35.0, 60.9, 69.2, 75.2, 108.8, 128.0, 128.4, 131.8, 144.4, 169.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2935, 1638, 1369, 1213, 1062 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{24}NO_4$ [M + H]$^+$ 294.1705; found 294.1707.

(*S*)-3-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethyl]-*N*-methoxy-*N*-methylbenzamide (30): Yield: 60%. R_f = 0.28 (hexane/ethyl acetate, 7:3). $[a]_D$ = –6.1 (c = 1, $CHCl_3$), colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 3 H, -CH_3), 1.36 (s, 3 H, -CH_3), 1.64–1.90 (m,

2 H, -CH_2CH_2), 2.60–2.76 (m, 2 H, ArCH_2), 3.28 (s, 3 H, -NCH_3), 3.46 (t, J = 7.6 Hz, 1 H, -$CHCH^aH^b$), 3.49 (s, 3 H, -OCH_3), 3.94 (dd, J = 6.0, 7.6 Hz, 1 H, -$CHCH^aH^b$), 4.01–4.04 (m, 1 H, -CH^aH^bCH), 7.19–7.25 (m, 2 H, ArH), 7.41–7.43 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 27.0, 31.9, 33.9, 35.2, 61.1, 69.3, 75.3, 108.9, 125.7, 128.1, 130.7, 134.3, 141.5, 170.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2935, 1638, 1369, 1213, 1062 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{24}NO_4$ $[M + H]^+$ 294.1705; found 294.1703.

***N*-Methoxy-*N*-methyl-4-{2-[(4*S*,4′*R*,5*R*)-2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolan)-5-yl]ethyl}benzamide (31):** Yield: 80%. R_f = 0.28 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = 13.6 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 3 H, -CH_3), 1.29 (s, 3 H, -CH_3), 1.32 (s, 3 H, -CH_3), 1.34 (s, 3 H, -CH_3), 1.79–2.01 (m, 2 H, -CH_2CH_2), 2.73–2.82 (m, 2 H, ArCH_2), 3.28 (s, 3 H, -NCH_3), 3.49 (s, 3 H, -OCH_3), 3.51–3.53 (m, 1 H, -OCH^aH^b), 3.85–3.94 (m, 3 H, -OCH^aH^b, 4,5-H), 4.02–4.06 (m, 1 H, -CH^aH^bCH), 7.18 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.54 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.1, 24.6, 24.8, 25.2, 29.8, 31.7, 32.8, 58.8, 65.6, 74.5, 77.5, 79.0, 106.7, 107.4, 126.2, 126.4, 129.5, 142.7, 167.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2985, 1642, 1456, 1371, 1215, 1066 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{32}NO_6$ $[M + H]^+$ 394.2230; found 394.2221.

***N*-Methoxy-*N*-methyl-3-{2-[(4*S*,4′*R*,5*R*)-2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolan)-5-yl]ethyl}benzamide (32):** Yield: 75%. R_f = 0.30 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = 12.8 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, -CH_3), 1.28 (s, 3 H, -CH_3), 1.30 (s, 3 H, -CH_3), 1.33 (s, 3 H, -CH_3), 1.81–2.03 (m, 2 H, -CH_2CH_2), 2.65–2.84 (m, 2 H, ArCH_2), 3.25 (s, 3 H, -NCH_3), 3.47 (s, 3 H, -OCH_3), 3.50–3.52 (m, 1 H, -OCH^aH^b), 3.83–3.93 (m, 3 H, -OCH^aH^b, 4,5-H), 4.00–4.04 (m, 1 H, -CH^aH^bCH), 7.22–7.25 (m, 2 H, ArH), 7.38–7.39 (m, 1 H, ArH), 7.44 (s, 1 H, Ar-H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.2, 26.7, 27.0, 27.4, 31.9, 33.9, 35.2, 61.0, 67.7, 76.8, 79.7, 81.2, 108.8, 109.5, 125.5, 128.4, 130.7, 134.2, 141.8, 170.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2988, 1640, 1449, 1380, 1228, 1076 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{32}NO_6$ $[M + H]^+$ 394.2230; found 394.2224.

***N*-Methoxy-*N*-methyl-4-{2-[(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl]ethyl}benzamide (33):** Yield: 70%. R_f = 0.35 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = 33.9 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.54–1.59 (m, 1 H, -$CHCH^aH^b$), 2.04–2.05 (m, 1 H, -$CHCH^aH^b$), 2.49–2.55 (m, 1 H, ArCH^aH^b), 2.73–2.77 (m, 1 H, ArCH^aH^b), 3.13 (t, J = 9.6 Hz, 1 H, 2-H), 3.24 (s, 3 H, -NCH_3), 3.26 (s, 3 H, -$CHOCH_3$), 3.42–3.46 (m, 4 H, -OCH_3, 3-H), 3.54 (td, J = 8.0, 2.0 Hz, 1 H, 4-H), 3.83–3.88 (m, 1 H, 5-H), 4.48–4.91 (m, 7 H, 3 CH_2Ph, -$OCHOCH_3$), 7.07 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.15–7.28 (m, 15 H, PhH), 7.51 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.7, 33.1, 33.9, 55.1, 61.0, 69.7, 73.3, 75.2, 75.8, 80.2, 82.0, 98.0, 127.6, 127.8, 128.0, 128.5, 131.5, 138.3, 138.7, 144.9, 169.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2923, 1640, 1496, 1092, 1070 cm^{-1}. HRMS (ESI): calcd. for $C_{38}H_{43}NO_7Na$ $[M + Na]^+$ 648.2937; found 648.2927.

4-{2-[(3a*S*,4*R*,6*S*,6a*S*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro-[3,4-*d*][1,3]dioxol-4-yl]ethyl}-*N*-methoxy-*N*-methylbenzamide (34): Yield: 62%. R_f = 0.35 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = –8.9 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, -CH_3), 1.89 (s, 3 H, -CH_3), 1.83–2.04 (m, 2 H, -CH_2CH_2), 2.64–2.76 (m, 2 H, ArCH_2), 3.24 (s, 3 H, -NCH_3), 3.43 (s, 3 H, -OCH_3), 3.84–3.87 (m, 1 H, 4-H), 4.38 (d, J = 12.0 Hz, 1 H, 3a-H), 4.51–4.58 (m, 3 H, -CH_2Ph, 6a-H), 4.98 (s, 1 H, -$OCHOBn$), 7.15–7.25 (m, 7 H, ArH), 7.52 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.8, 24.9, 28.7, 32.8, 33.1, 59.9, 67.8, 76.5, 78.8, 79.2, 84.2, 104.2, 111.2, 126.9, 127.4, 130.5, 136.3, 143.6, 168.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2918, 1648, 14906, 1102, 1071 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{31}NO_6$ $[M + H]^+$ 442.2230; found 442.2231.

3-{2-[(3a*S*,4*R*,6*S*,6a*S*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro-[3,4-*d*][1,3]dioxol-4-yl]ethyl}-*N*-methoxy-*N*-methylbenzamide (35): Yield: 60%. R_f = 0.33 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = –8.6 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, -CH_3), 1.37 (s, 3 H, -CH_3), 1.91–2.04 (m, 2 H, -CH_2CH_2), 2.65–2.76 (m, 2 H, ArCH_2), 3.24 (s, 3 H, -NCH_3), 3.45 (s, 3 H, -OCH_3), 3.86–3.89 (m, 1 H, 4-H), 4.37 (d, J = 12.0 Hz, 1 H, 3a-H), 4.54–4.56 (m, 3 H, -CH_2Ph, 6a-H), 4.98 (s, 1 H, -$OCHOBn$), 7.16–7.26 (m, 7 H, ArH), 7.39–7.41 (m, 1 H, ArH), 7.46 (s, 1 H, Ar-H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.9, 26.1, 29.9, 32.2, 33.9, 61.0, 68.8, 79.1, 80.3, 85.2, 105.0, 112.3, 125.7, 128.0, 128.5, 130.8, 134.2, 137.5, 141.7, 170.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2985, 1642, 1456, 1371, 1215, 1066 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{31}NO_6$ $[M]^+$ 441.2151; found 441.2159.

4-{2-[(3a*S*,4*R*,6a*R*)-2,2-Dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]ethyl}-*N*-methoxy-*N*-methylbenzamide (36): Yield: 63%. R_f = 0.25 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = –10.6 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.87–1.97 (m, 2 H, -CH_2CH_2), 2.68–2.69 (m, 2 H, ArCH_2), 3.20 (s, 3 H, NCH_3), 3.24–3.30 (m, 2 H, -OCH_2CH), 3.43 (s, 3 H, OCH_3), 3.85 (d, J = 10.0 Hz, 1 H, 4-H), 4.37 (d, J = 10.0 Hz, 1 H, 3a-H), 4.60 (d, J = 10.0 Hz, 1 H, 6a-H), 7.15 (d, J = 8 Hz, 2 H, Ar-H^3, H^5), 7.54 (d, J = 8 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9, 26.0, 29.8, 32.1, 33.7, 60.8, 72.4, 80.8, 81.4, 108.8, 127.9, 128.4, 131.7, 144.5, 169.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2989, 1648, 1450, 1401, 1219, 1061 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{26}NO_5$ $[M + H]^+$ 336.1811; found 336.1809.

3-{2-[(3a*S*,4*R*,6a*R*)-2,2-Dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]ethyl}-*N*-methoxy-*N*-methylbenzamide (37): Yield: 65%. R_f = 0.30 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = –11.2 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (s, 3 H, -CH_3), 1.36 (s, 3 H, -CH_3), 1.87–1.97 (m, 2 H, -CH_2CH_2), 2.68–2.69 (m, 2 H, ArCH_2), 3.20 (s, 3 H, -NCH_3), 3.24–3.30 (m, 2 H, -OCH_2CH), 3.43 (s, 3 H, -OCH_3), 3.85 (d, J = 10.0 Hz, 1 H, 4-H), 4.37 (d, J = 10.0 Hz, 1 H, 3a-H), 4.60 (d, J = 10.0 Hz, 1 H, 6a-H), 7.22–7.27 (m, 2 H, ArH), 7.41–7.43 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9, 26.0, 29.8, 32.1, 33.7, 60.8, 72.4, 80.8, 81.4, 108.8, 125.7, 127.9, 128.4, 131.7, 144.5, 169.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2985, 1640, 1451, 1361, 1205, 1076 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{26}NO_5$ $[M + H]^+$ 336.1811; found 336.1807.

3-{2-[(3a*S*,4*R*,6*R*,6a*S*)-6-(Methoxy)-2,2-dimethyltetrahydrofuro-[3,4-*d*][1,3]dioxol-4-yl]ethyl}-*N*-methoxy-*N*-methylbenzamide (38): Yield: 60%. R_f = 0.38 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = –9.4 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, -CH_3), 1.39 (s, 3 H, -CH_3), 1.71–1.88 (m, 2 H, -CH_2CH_2), 2.65–2.73 (m, 2 H, ArCH_2), 3.28 (s, 3 H, -NCH_3), 3.32 (s, 3 H, -$CHOCH_3$), 3.49 (s, 3 H, -OCH_3), 4.08 (dd, J = 6.0, 9.6 Hz, 1 H, 4-H), 4.48 (d, J = 6.0 Hz, 1 H, 3a-H), 4.55 (d, J = 6.0 Hz, 1 H, 6a-H), 4.91 (s, 1 H, 6-H), 7.22–7.27 (m, 2 H, ArH), 7.41–7.42 (m, 1 H, ArH), 7.43 (s, 1 H, Ar-H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.9, 26.4, 32.4, 36.7, 55.16, 61.1, 84.2, 85.6, 86.3, 109.6, 112.3, 125.8, 128.2, 130.7, 134.3, 141.3, 170.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2975, 1642, 1456, 1379, 1225, 1070 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{28}NO_6$ $[M + H]^+$ 366.1917; found 366.1919.

Naphthalen-2-yl[4-(pentafluorophenylethyl)phenyl]methanone (8): Yield: 82%. R_f = 0.40 (hexane/ethyl acetate, 9:1), red solid. M.p. 88–92 °*C*. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.78–2.81 (m, 2 H,

-CH_2CH_2), 2.85–2.88 (m, 2 H, ArCH_2), 7.07 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.31–7.44 (m, 4 H, ArH), 7.63 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.75 (d, J = 8.0 Hz, 1 H, Ar-H$^{4'}$), 7.83 (d, J = 8.0 Hz, 2 H, Ar-H$^{7'}$, H$^{6'}$), 7.91 (d, J = 8.0 Hz, 2 H, Ar-H$^{5'}$, H$^{8'}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9, 35.2, 124.3, 125.7, 126.4, 127.1, 127.8, 128.2, 128.4, 130.7, 130.9, 131.2, 133.7, 136.5, 136.9, 145.8, 197.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 1656, 1519, 1501 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{15}ONaF_5$ [M + Na]$^+$ 449.0941; found 449.0939.

Phenyl{4-[2-(pyridin-2-yl)ethyl]phenyl}methanone (9): Yield: 78%. R_f = 0.40 (hexane/ethyl acetate, 8:2), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.06 (s, 4 H, 2 CH_2), 7.00 (d, J = 7.6 Hz, 1 H, ArH), 7.04–7.07 (m, 1 H, ArH), 7.21 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.37–7.40 (m, 2 H, ArH), 7.47–7.52 (m, 1 H, ArH), 7.64 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.69–7.71 (m, 2 H, ArH), 8.48 [d, J = 4.8 Hz, 1 H, Ar(Py)-H$^{6'}$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.7, 39.6, 121.4, 123.0, 128.2, 128.7, 129.9, 130.4, 132.2, 135.4, 136.5, 137.9, 146.7, 149.3, 160.6, 196.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 2861, 1702, 1641, 1466, 1156 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{18}NO$ [M + H]$^+$ 288.1388; found 288.1393.

(4-Methoxyphenyl)[4-(3,4,5-trimethoxyphenethyl)phenyl]methanone (10): Yield: 75%. R_f = 0.55 (hexane/ethyl acetate, 9:1), solid. M.p. 76–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.82–2.84 (m, 2 H, -CH_2CH_2), 2.89–2.91 (m, 2 H, ArCH_2), 3.71 (s, 6 H, 2 ArOCH_3), 3.77 (s, 3 H, ArOCH_3), 3.79 (s, 3 H, ArOCH_3), 6.29 [s, 2 H, $(OCH_3)_3$-Ar-H$^{2''}$, H$^{6''}$], 6.87 [dd, J = 6.8, 2.0 Hz, 2 H, (OCH_3)Ar-H$^{3'}$, H$^{5'}$], 7.12 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.60 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.72 [dd, J = 6.8, 2.0 Hz, 2 H, (OCH_3)Ar-H$^{2'}$, H$^{6'}$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.9, 55.5, 56.0, 60.9, 105.5, 113.5, 128.4, 130.4, 132.4, 136.0, 136.9, 146.1, 153.1, 163.1, 195.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2923, 1651, 1519, 1504, 1220, 1130 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{27}O_5$ [M + H]$^+$ 407.1858; found 407.1855.

***tert*-Butyl 3-(4-Benzoylphenyl)propylcarbamate (11):** Yield: 75%. R_f = 0.60 (hexane/ethyl acetate, 8:2), colorless solid. M.p. 90–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 [s, 9 H, -C(CH_3)$_3$], 1.76–1.79 (m, 2 H, ArCH_2CH_2), 2.65 (t, J = 8.0 Hz, 2 H, ArCH_2), 3.09–3.11 (m, 2 H, NCH_2), 4.62 (br. s, 1 H, -NH), 7.21 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.37–7.41 (m, 2 H, PhH), 7.48–7.50 (m, 1 H, PhH), 7.65–7.71 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.9, 28.2, 31.7, 38.7, 77.8, 126.7, 128.5, 128.9, 130.8, 133.9, 136.3, 145.3, 154.5, 195.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2926, 1697, 1655, 1277, 924 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{25}NO_3Na$ [M + Na]$^+$ 362.1732; found 362.1726.

(4-Heptylphenyl)(thiophen-2-yl)methanone (12): Yield: 80%. R_f = 0.60 (hexane/ethyl acetate, 9:1), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (t, J = 8.0 Hz, 3 H, -CH_3), 1.11–1.25 (m, 8 H, 3 CH_2), 1.54–1.59 (m, 2 H, -CH_2), 2.59 (t, J = 8.0 Hz, 3 H, ArCH_2), 7.04 [dd, J = 4.8, 4.0 Hz, 1 H, Ar(S)-H$^{4'}$], 7.19 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.55–7.60 (m, 2 H, ArH), 7.70 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 21.6, 28.1, 28.3, 30.1, 30.7, 34.9, 126.8, 127.3, 127.5, 128.3, 132.7, 132.8, 133.5, 134.5, 142.8, 147.0, 186.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 2854, 1644, 1462, 1376 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}ONaS$ [M + Na]$^+$ 309.1289; found 309.1281.

[3-(Pentafluorophenylethyl)phenyl](*p*-tolyl)methanone (16): Yield: 75%. R_f = 0.50 (hexane/ethyl acetate, 9:1), colorless solid. M.p. 106–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, ArCH_3), 2.93–2.96 (m, 2 H, -CH_2CH_2), 3.03–3.04 (m, 2 H, ArCH_2), 7.27 [d, J = 8.0 Hz, 2 H, (CH_3)Ar- H$^{3'}$, H$^{5'}$], 7.37–7.41 (m, 2 H, ArH), 7.57 (s, 1 H, Ar-H^2), 7.60–7.62 (m, 1 H, ArH), 7.67 [d, J = 8.0 Hz, 2 H, (CH_3)Ar-H$^{2'}$, H$^{6'}$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 24.3, 35.1, 127.2, 128.3, 128.9, 129.6, 130.2, 132.1, 132.9, 134.9, 138.3, 140.2, 143.4, 196.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2926, 1655, 1519, 1503, 945 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{16}OF_5$ [M + H]$^+$ 391.1121; found 391.1118.

[3-(Pentafluorophenylethyl)phenyl](thiophen-2-yl)methanone (17): Yield: 70%. R_f = 0.45 (hexane/ethyl acetate, 9:1), colorless solid. M.p. 64–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.94–2.98 (m, 2 H, -CH_2CH_2), 3.02–3.06 (m, 2 H, ArCH_2), 7.16–7.18 (m, 1 H, ArH), 7.37–7.44 (m, 2 H, ArH), 7.58–7.59 (m, 1 H, ArH), 7.63 (s, 1 H, Ar-H^2), 7.70–7.74 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 35.1, 127.9, 128.6, 128.9, 132.3, 134.3, 134.7, 138.5, 140.4, 188.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 1635, 1519, 1503, 1415 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{11}ONaSF_5$ [M + Na]$^+$ 405.0348; found 405.0348.

[3-(4-Methylphenethyl)phenyl](thiophen-2-yl)methanone (18): Yield: 78%. R_f = 0.50 (hexane/ethyl acetate, 9:1), colorless solid. M.p. 60–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, ArCH_3), 2.80–2.83 (m, 2 H, -CH_2CH_2), 2.87–2.89 (m, 2 H, ArCH_2), 6.95 [d, J = 8.0 Hz, 2 H, (CH_3)Ar-H$^{2''}$, H$^{6''}$], 7.01 [d, J = 8.0 Hz, 2 H, (CH_3)Ar-H$^{3''}$, H$^{5''}$], 7.02 [dd, J = 5.2, 4.0 Hz, 1 H, Ar(S)-H$^{4'}$], 7.30 [d, J = 4.8 Hz, 1 H, Ar(S)-H$^{3'}$], 7.37 [dd, J = 3.6, 0.8 Hz, 1 H, Ar(S)-H$^{5'}$], 7.53 (s, 1 H, Ar-H^2), 7.58–7.60 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 37.3, 37.8, 127.9, 128.2, 128.4, 129.1, 129.3, 132.5, 133.0, 135.4, 138.1, 142.1, 143.8, 188.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 1635, 1519, 1503, 1215 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{19}OS$ [M + H]$^+$ 307.1157; found 307.1153.

[2-(Pentafluorophenylethyl)phenyl](phenyl)methanone (19): Yield: 70%. R_f = 0.55 (hexane/ethyl acetate, 9:1), colorless solid. M.p. 68–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.98 (s, 4 H, 2 CH_2), 7.25–7.34 (m, 3 H, ArH), 7.40–7.47 (m, 3 H, ArH), 7.57–7.60 (m, 1 H, ArH), 7.76–7.78 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.5, 32.4, 125.9, 128.3, 128.4, 129.1, 130.1, 130.5, 133.2, 138.3, 139.2, 197.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2927, 1736, 1662, 1502, 965 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{14}OF_5$ [M + H]$^+$ 377.0965; found 377.0963.

[2-(Pentafluorophenylethyl)phenyl](thiophen-2-yl)methanone (20): Yield: 80%. R_f = 0.75 (hexane/ethyl acetate, 9:1), colorless solid. M.p. 60–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89–2.92 (m, 2 H, -CH_2CH_2), 2.96–3.02 (m, 2 H, ArCH_2), 7.03 [dd, J = 5.2, 4.0 Hz, 1 H, Ar(S)-H$^{4'}$], 7.17 [m, 1 H, Ar(s)-H$^{3'}$], 7.23 (td, J = 7.2, 0.8 Hz, 1 H, Ar-H^5), 7.27 [dd, J = 3.6, 0.7 Hz, 1 H, Ar(s)-H$^{2'}$], 7.35 (td, J = 7.6, 1.2 Hz, 1 H, Ar-H^3), 7.40 (dd, J = 7.6, 0.8 Hz, 1 H, Ar-H^4), 7.65 (dd, J = 7.6, 0.8 Hz, 1 H, Ar-H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 33.0, 126.8, 128.9, 129.4, 131.5, 136.0, 136.3, 139.1, 139.8, 145.8, 190.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 1635, 1519, 1503, 1415 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{11}ONaSF_5$ [M + Na]$^+$ 405.0348; found 405.0348.

Thiophen-2-yl(4-vinylphenyl)methanone (21): Yield: 80%. R_f = 0.50 (hexane/ethyl acetate, 9:1), colorless solid. M.p. 46–48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (d, J = 10.8 Hz, 1 H, -CHCH^aH^b), 5.75 (d, J = 17.6 Hz, 1 H, -CHCH^aH^b), 6.64 (dd, J = 17.6, 10.8 Hz, 1 H, ArCH), 7.02 [dd, J = 4.0 Hz, 1 H, Ar(S)-H$^{4'}$], 7.38 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.52 [d, J = 4.0 Hz, 1 H, Ar(S)-H$^{3'}$], 7.57 [d, J = 4.0 Hz, 1 H, Ar(S)-H$^{5'}$], 7.72 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.2, 125.8, 128.8, 129.3, 133.5, 134.3, 135.7, 136.9, 141.2, 143.3, 187.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 1625, 1602, 1411, 1288 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{10}ONaS$ [M + Na]$^+$ 237.0350; found 237.0354.

(*S*)-{4-[2-(2,2-Dimethyl-1,3-Dioxolan-4-yl)ethyl]phenyl}(phenyl)methanone (39): Yield: 75%. R_f = 0.60 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = –2.1 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 1.28 (s, 3 H, -CH_3), 1.34 (s, 3 H, -CH_3), 1.77–1.89 (m, 2 H, -CH_2CH_2), 2.64–2.76 (m, 2 H, ArCH_2), 3.46 (t, J = 8.0 Hz, 1 H, -CHCH^aH^b), 3.93 (dd, J = 8.0, 6.0 Hz, 1 H, -CHCH^aH^b), 4.09–4.15 (m, 1 H, -CH^{a}H^{b}CH), 7.20 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.35 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.46 (t, J = 7.2 Hz, 1 H, Ph-H$^{4'}$), 7.64–7.69 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 27.0, 32.0, 35.0, 69.2, 75.1, 108.9, 128.2, 128.3, 129.9, 130.4, 132.1, 135.5, 137.9, 146.7, 196.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2929, 1655, 1605, 1276, 1064 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{22}O_3Na$ [M + Na]$^+$ 333.1467; found 333.1472.

(*S*)-{4-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethyl]phenyl}(4-fluorophenyl)methanone (40): Yield: 72%. R_f = 0.55 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = –2.5 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 3 H, -CH_3), 1.34 (s, 3 H, -CH_3), 1.78–1.88 (m, 2 H, -CH_2CH_2), 2.61–2.79 (m, 2 H, ArCH_2), 3.45 (t, J = 7.2 Hz, 1 H, -CHCH^aH^b), 3.93 (dd, J = 7.2, 6.0 Hz, 1 H, -CHCH^aH^b), 4.12–4.19 (m, 1 H, -CH^{a}H^{b}CH), 7.01–7.06 (m, 2 H, ArH), 7.21 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.60 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.70–7.73 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 27.0, 32.0, 35.0, 69.2, 75.1, 108.9, 115.3, 128.2, 130.2, 132.4, 134.1, 135.3, 146.8, 165.1, 194.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 1655, 1597, 1276, 1225, 1154 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{22}O_3F$ [M + H]$^+$ 329.1553; found 329.1555.

(*S*)-{4-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethyl]phenyl}(4-methoxyphenyl)methanone (41): Yield: 70%. R_f = 0.48 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = –4.4 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 3 H, -CH_3), 1.44 (s, 3 H, -CH_3), 1.86–1.98 (m, 2 H, -CH_2CH_2), 2.73–2.85 (m, 2 H, ArCH_2), 3.55 (t, J = 7.6 Hz, 1 H, -CHCH^aH^b), 3.86 (s, 3 H, ArOCH_3), 4.03 (dd, J = 7.6, 6.0 Hz, 1 H, -CHCH^aH^b), 4.11–4.18 (m, 1 H, -CH^{a}H^{b}CH), 6.94 [d, J = 11.2 Hz, 2 H, (OCH_3)Ar-H$^{3'}$, H$^{5'}$], 7.29 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.69 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.81 (d, J = 11.2 Hz, 2 H, (OCH_3)Ar-H$^{2'}$, H$^{6'}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.6, 27.0, 32.0, 35.0, 55.4, 69.2, 75.2, 108.8, 113.5, 128.2, 130.4, 131.6, 134.3, 146.1, 163.1, 195.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2934, 1649, 1599, 1508, 1249, 1170 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{24}O_4$ Na [M + Na]$^+$ 363.1572; found 363.1573.

(4-{2-[(4*S*,4′*R*,5*R*)-2,2,2′,2′-Tetramethyl-4,4′-bi(1,3-dioxolan)-5-yl]ethyl}phenyl)(*p*-tolyl)methanone (42): Yield: 70%. R_f = 0.50 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = 7.6 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, -CH_3), 1.28 (s, 3 H, -CH_3), 1.30 (s, 3 H, -CH_3), 1.33 (s, 3 H, -CH_3), 1.79–2.04 (m, 2 H, -CH_2CH_2), 2.33 (s, 3 H, ArCH_3), 2.71–2.77 (m, 2 H, ArCH_2), 3.50 (t, J = 8.0 Hz, 1 H, -OCH^aH^b), 3.85–3.95 (m, 3 H, -OCH^aH^b, 4,5-H), 4.01–4.05 (m, 1 H, -CH^{a}H^{b}CH), 7.16 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.23 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.60–7.685 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 25.3, 26.7, 27.0, 27.4, 34.9, 36.6, 67.8, 77.1, 79.6, 81.1, 108.9, 109.6, 128.2, 128.3, 128.9, 130.3, 135.1, 135.6, 142.9, 146.9, 196.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 2851, 1712, 1637, 1456, 1166 cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{32}O_5Na$ [M + Na]$^+$ 447.2147; found 447.2140.

(4-Fluorophenyl)(4-{2-[(4*S*,4′*R*,5*R*)-2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolan)-5-yl]ethyl}phenyl)methanone (43): Yield: 75%. R_f = 0.55 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = 8.1 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 3 H, -CH_3), 1.29 (s, 3 H, -CH_3), 1.32 (s, 3 H, -CH_3), 1.35 (s, 3 H, -CH_3), 1.85–2.05 (m, 2 H, -CH_2CH_2), 2.73–2.84 (m, 2 H, ArCH_2), 3.51 (t, J = 8.0 Hz, 1 H, -OCH^aH^b), 3.86–3.96 (m, 3 H, -OCH^aH^b, 4,5-H), 4.02–4.07 (m, 1 H, -CH^{a}H^{b}CH), 7.07–7.09 (m, 2 H, ArH), 7.25 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.63 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6), 7.73–7.75 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 26.8, 26.9, 27.4, 32.2, 36.6, 67.8, 76.7, 79.7, 81.1, 108.9, 109.4, 109.6, 115.4, 128.1, 128.4, 130.2, 132.4, 132.6, 134.0, 135.2, 147.2, 165.0, 195.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1658, 1599, 1371, 1277, 1226, 1067 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{30}O_5F$ [M + H]$^+$ 429.2077; found 429.2073.

(2-Methoxyphenyl)(4-{2-[(4*S*,4′*R*,5*R*)-2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolan)-5-yl]ethyl}phenyl)methanone (44): Yield: 70%. R_f = 0.45 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = 9.9 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, -CH_3), 1.28 (s, 3 H, -CH_3), 1.30 (s, 3 H, -CH_3), 1.33 (s, 3 H, -CH_3), 1.79–2.01 (m, 2 H, -CH_2CH_2), 2.72–2.84 (m, 2 H, ArCH_2), 3.50 (t, J = 8.0 Hz, 1 H, -OCH^aH^b), 3.64 (s, 3 H, ArOCH_3), 3.84–3.95 (m, 3 H, -OCH^aH^b, 4,5-H), 4.01–4.05 (m, 1 H, -CH^{a}H^{b}CH), 6.89–6.96 (m, 2 H, ArH), 7.19 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.23–7.25 (m, 1 H, ArH), 7.34–7.38 (m, 1 H, ArH), 7.66 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 26.6, 26.7, 27.2, 32.1, 35.2, 55.4, 67.6, 76.6, 79.5, 81.0, 108.7, 109.1, 111.3, 120.3, 128.3, 128.9, 129.1, 130.0, 131.4, 135.5, 147.5, 157.0, 195.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2934, 1644, 1609, 1249, 1170, 1265 cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{32}O_6Na$ [M + Na]$^+$ 463.2097; found 463.2097.

***p*-Tolyl(4-{2-[(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl]ethyl}phenyl)methanone (45):** Yield: 70%. R_f = 0.20 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = 28.5 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58–1.61 (m, 1 H, -CHCH^aH^b), 2.06–2.08 (m, 1 H, -CHCH^aH^b), 2.34 (s, 3 H, ArCH_3), 2.56–2.59 (m, 1 H, ArCH^aH^b), 2.79–2.82 (m, 1 H, ArCH-^{a}H^b), 3.12–3.17 (m, 1 H, 2-H), 3.28 (s, 3 H, -CHOCH_3), 3.44–3.47 (m, 1 H, 3-H), 3.55–3.58 (m, 1 H, 4-H), 3.83–3.88 (m, 1 H, 5-H), 4.50–4.92 (m, 7 H, 3 CH_2Ph, -OCHOCH$_3$), 7.22–7.30 (m, 19 H, ArH), 7.60–7.63 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 31.9, 33.2, 55.2, 69.7, 73.4, 75.3, 75.8, 80.2, 82.1, 98.0, 127.7, 127.8, 127.9, 128.0, 128.1, 128.5, 128.9, 130.2, 138.2, 138.7, 143.0, 146.9, 196.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2921, 2852, 1651, 1606, 1092, 1051 cm^{-1}. HRMS (ESI): calcd. for $C_{43}H_{44}O_6Na$ [M + Na]$^+$ 679.3036; found 679.3046.

[4-(Pentafluorophenethyl)phenyl](3,4,5-trimethoxyphenyl)methanone (46): Yield: 72%. R_f = 0.40 (hexane/ethyl acetate, 9:1), colorless solid. M.p. 78–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.92–2.97 (m, 2 H, -CH_2CH_2), 3.01–3.06 (m, 2 H, ArCH_2), 3.88 (s, 6 H, 2 ArOCH_3), 3.94 (s, 3 H, ArOCH_3), 7.06 [s, 2 H, (OCH_3)$_3$Ar-H^2, H^6], 7.32–7.42 (m, 2 H, ArH), 7.62–7.63 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.3, 35.2, 56.3, 61.0, 107.9, 4 128.3, 129.6, 132.2, 132.5, 138.3, 140.4, 142.3, 152.9, 195.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2929, 1690, 1643, 1364, 1164 cm^{-1}. HRMS (ESI): $C_{24}H_{20}O_4F_5$ [M + H]$^+$ 467.1282; found 467.1283.

***tert*-Butyl 3-[4-(3,4,5-Trimethoxybenzoyl)phenyl]propylcarbamate (47):** Yield: 75%. R_f = 0.20 (hexane/ethyl acetate, 9:1), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 [s, 9 H, -C(CH_3)$_3$], 1.85–1.89 (m, 2 H, ArCH_2CH_2), 2.74 (t, J = 8.0 Hz, 2 H, ArCH_2), 3.18–3.20 (m, 2 H, -NCH_2), 3.88 (s, 6 H, 2 ArOCH_3), 3.94 (s, 3 H, ArOCH_3), 4.60 (br. s, 2 H, -NH), 7.06 [s, 2 H, (OCH_3)$_3$Ar-H$^{2'}$, H$^{6'}$], 7.30 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.74 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4, 31.4, 33.1, 40.2, 56.3, 60.9, 79.2, 107.6, 128.2, 130.3, 132.8, 135.5, 141.8, 146.6, 152.8, 155.9, 195.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2929, 1690, 1643, 1364, 1164 cm^{-1}. HRMS (ESI): $C_{24}H_{32}NO_6$ [M + H]$^+$ 430.2230; found 430.2228.

(*S*)-{4-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethyl]phenyl}(3,4,5-trimethoxyphenyl)methanone (48): Yield: 65%. R_f = 0.20 (hexane/dichloromethane, 1:3). $[\alpha]_D$ = –4.8 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 3 H, -CH_3), 1.47 (s, 3 H, -CH_3), 1.89–2.02 (m, 2 H, -CH_2CH_2), 2.78–2.90 (m, 2 H,

ArCH_2), 3.57–3.61 (m, 1 H, -CHCH^aH^b), 3.90 (s, 6 H, 2 ArOCH_3), 3.96 (s, 3 H, ArOCH_3), 4.05–4.09 (m, 1 H, -CHCH^aH^b), 4.14–4.18 (m, 1 H, -CH^{a}H^{b}CH), 7.09 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.35 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.77 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 27.0, 32.1, 35.0, 56.4, 60.9, 69.2, 75.2, 107.8, 108.9, 128.3, 130.3, 132.9, 135.6, 142.0, 146.6, 152.9, 195.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1650, 1602, 1255, 1171 cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{29}O_6$ [M + H]$^+$ 401.1964; found 401.1964.

(*S*)-{3-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethyl]phenyl}(3,4,5-trimethoxyphenyl)methanone (49): Yield: 68%. R_f = 0.25 (hexane/dichloromethane, 1:3). $[\alpha]_D$ = –4.4 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (s, 3 H, -CH_3), 1.47 (s, 3 H, -CH_3), 1.82–1.96 (m, 2 H, -CH$_2$CH_2), 2.78–2.90 (m, 2 H, ArCH_2), 3.57–3.60 (m, 1 H, -CHCH^aH^b), 3.90 (s, 6 H, 2 ArOCH_3), 3.98 (s, 3 H, ArOCH_3), 4.07–4.09 (m, 1 H, -CHCH^aH^b), 4.14–4.18 (m, 1 H, -CH^{a}H^{b}CH), 7.09 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.43–7.46 (m, 2 H, ArH), 7.63–7.65 (m, 1 H, ArH), 7.65 (s, 1 H, Ar-H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 27.0, 32.1, 35.0, 56.4, 60.9, 69.2, 75.2, 107.8, 108.9, 127.8, 128.3, 129.8, 132.5, 138.0, 142.0, 152.9, 195.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2934, 1649, 1612, 1249, 1179 cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{29}O_6$ [M + H]$^+$ 401.1964; found 401.1959.

(4-{2-[(4*S*,4′*R*,5*R*)-2,2,2′,2′-Tetramethyl-4,4′-bi(1,3-dioxolan)-5-yl]ethyl}phenyl)(3,4,5-trimethoxyphenyl)methanone (50): Yield: 70%. R_f = 0.40 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = 7.6 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 3 H, -CH_3), 1.38 (s, 3 H, -CH_3), 1.40 (s, 3 H, -CH_3), 1.43 (s, 3 H, -CH_3), 1.79–2.01 (m, 2 H, -CH$_2$CH_2), 2.72–2.94 (m, 2 H, ArCH_2), 3.60–3.62 (m, 1 H, -OCH^aH^b), 3.88 (s, 6 H, 2 ArOCH_3), 3.94 (s, 3 H, ArOCH_3), 3.96–4.05 (m, 3 H, -OCH^aH^b, 4,5-H), 4.11–4.13 (m, 1 H, -CH^{a}H^{b}CH), 7.06 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.34 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.75 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 26.8, 27.0, 27.4, 32.2, 34.9, 56.3, 60.9, 67.8, 76.7, 79.7, 81.2, 107.7, 108.9, 109.6, 128.4, 130.3, 132.9, 135.5, 141.9, 147.1, 152.8, 195.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2923, 1658, 1601, 1260, 1170 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{37}O_8$ [M + H]$^+$ 501.2488; found 501.2487.

(3-{2-[(4*S*,4′*R*,5*R*)-2,2,2′,2′-Tetramethyl-4,4′-bi(1,3-dioxolan)-5-yl]ethyl}phenyl)(3,4,5-trimethoxyphenyl)methanone (51): Yield: 68%. R_f = 0.30 (hexane/ethyl acetate, 8.8:1.2). $[\alpha]_D$ = 8.4 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, -CH_3), 1.29 (s, 3 H, -CH_3), 1.30 (s, 3 H, -CH_3), 1.34 (s, 3 H, -CH_3), 1.79–2.08 (m, 2 H, -CH$_2$CH_2), 2.70–2.91 (m, 2 H, ArCH_2), 3.51–3.53 (m, 1 H, -OCH^aH^b), 3.80 (s, 6 H, 2 ArOCH_3), 3.90 (s, 3 H, ArOCH_3), 3.91–3.95 (m, 3 H, -OCH^aH^b, 4,5-H), 4.01–4.08 (m, 1 H, -CH^{a}H^{b}CH), 6.99 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.32–7.40 (m, 2 H, ArH), 7.53 (d, J = 7.6 Hz, 1 H, Ar-H^6), 7.60 (s, 1 H, Ar-H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 25.2, 26.7, 27.4, 32.0, 35.3, 56.1, 60.9, 67.8, 76.7, 79.8, 81.2, 107.8, 109.0, 109.7, 127.6, 128.2, 129.8, 132.5, 132.7, 137.9, 142.1, 142.3, 152.8, 195.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2964, 1648, 1610, 1258, 1171 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{37}O_8$ [M + H]$^+$ 501.2488; found 501.2489.

(4-{2-[(3a*S*,4*R*,6*S*,6a*S*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro-[3,4-*d*][1,3]dioxol-4-yl]ethyl]phenyl}(3,4,5-trimethoxyphenyl)methanone (52): Yield: 62%. R_f = 0.40 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = –3.6 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 3 H, -CH_3), 1.39 (s, 3 H, -CH_3), 1.94–2.11 (m, 2 H, -CH$_2$CH_2), 2.72–2.94 (m, 2 H, ArCH_2), 3.78 (s, 6 H, 2 ArOCH_3), 3.88 (s, 3 H, ArOCH_3), 3.92–3.94 (m, 1 H, 4-H), 4.42 (d, J = 12.0 Hz, 1 H, 3a-H), 4.58–4.60 (m, 3 H, -CH_2Ph, 6a-H), 5.01 (s, 1 H, -OCHOBn), 7.06 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.22–7.29 (m, 7 H, ArH), 7.67 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.9, 26.1, 29.7, 32.4, 56.3, 61.0, 69.0, 79.1, 80.3, 85.3, 105.2, 107.7, 112.4, 127.9, 128.5, 130.3, 132.9, 135.5, 137.4, 141.9, 147.0, 152.8, 195.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2929, 1655, 1601, 1256 cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{37}O_8$ [M + H]$^+$ 549.2488; found 549.2494.

(3-{2-[(3a*S*,4*R*,6*S*,6a*S*)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro-[3,4-*d*][1,3]dioxol-4-yl]ethyl}phenyl)(3,4,5-trimethoxyphenyl)methanone (53): Yield: 60%. R_f = 0.42 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = –4.2 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (s, 3 H, -CH_3), 1.37 (s, 3 H, -CH_3), 1.94–2.11 (m, 2 H, -CH$_2$CH_2), 2.72–2.94 (m, 2 H, ArCH_2), 3.78 (s, 6 H, 2 ArOCH_3), 3.84 (s, 3 H, ArOCH_3), 3.87–3.91 (m, 1 H, 4-H), 4.39 (d, J = 12.0 Hz, 1 H, 3a-H), 4.55–4.58 (m, 3 H, -CH_2Ph, 6a-H), 5.00 (s, 1 H, -OCHOBn), 7.06 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.19–7.22 (m, 5 H, ArH), 7.32–7.41 (m, 2 H, ArH), 7.54 (d, J = 8.0 Hz, 1 H, ArH), 7.63 (s, 1 H, Ar-H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.9, 25.6, 30.1, 32.3, 56.3, 61.0, 68.9, 79.1, 80.3, 85.3, 105.1, 107.7, 112.4, 127.9, 128.1, 128.5, 129.9, 132.5, 137.4, 137.9, 141.9, 152.8, 195.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1650, 1602, 1255, 1171 cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{37}O_8$ [M + H]$^+$ 549.2488; found 549.2488.

(4-{2-[(3a*S*,4*R*,6a*R*)-2,2-Dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]ethyl}phenyl)(3,4,5-trimethoxyphenyl)methanone (54): Yield: 80%. R_f = 0.20 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = –5.2. (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 3 H, -CH_3), 1.33 (s, 3 H, -CH_3), 2.02–2.18 (m, 2 H, -CH$_2$CH_2), 2.75–2.94 (m, 2 H, ArCH_2), 3.43–3.47 (m, 2 H, -OCH_2CH), 3.87 (s, 6 H, 2 ArOCH_3), 3.93 (s, 3 H, ArOCH_3), 4.01–4.04 (m, 1 H, 4-H), 4.58–4.60 (m, 1 H, 3a-H), 4.75–4.77 (m, 1 H, 6a-H), 7.05 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.34 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.73 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.7, 24.8, 29.3, 32.5, 56.3, 61.0, 72.6, 81.0, 81.6, 107.8, 112.0, 128.4, 130.1, 132.9, 135.5, 141.9, 147.0, 152.8, 195.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2948, 1645, 1602, 1255, 1179 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{31}O_7$ [M + H]$^+$ 443.2070; found 443.2067.

(3-{2-[(3a*S*,4*R*,6a*R*)-2,2-Dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]ethyl}phenyl)(3,4,5-trimethoxyphenyl)methanone (55): Yield: 78%. R_f = 0.22 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = –5.6 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, -CH_3), 1.41 (s, 3 H, -CH_3), 2.02–2.18 (m, 2 H, -CH$_2$CH_2), 2.75–2.94 (m, 2 H, ArCH_2), 3.35–3.39 (m, 2 H, -OCH_2CH), 3.80 (s, 6 H, 2 ArOCH_3), 3.87 (s, 3 H, ArOCH_3), 3.93–3.96 (m, 1 H, 4-H), 4.49–4.52 (m, 1 H, 3a-H), 4.68–4.71 (m, 1 H, 6a-H), 7.05 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.32–7.38 (m, 2 H, ArH), 7.53–7.55 (m, 1 H, ArH), 7.60 (s, 1 H, Ar-H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 26.1, 30.1, 32.3, 56.3, 61.0, 72.6, 81.0, 81.7, 107.8, 112.0, 127.7, 128.3, 129.9, 132.5, 137.9, 142.2, 152.8, 196.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1650, 1602, 1255, 1171 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{31}O_7$ [M + H]$^+$ 443.2070; found 443.2072.

(3-{2-[(3a*S*,4*R*,6*R*,6a*S*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl]ethyl}phenyl)(3,4,5-trimethoxyphenyl)methanone (56): Yield: 62%. R_f = 0.32 (hexane/ethyl acetate, 8:2). $[\alpha]_D$ = –6.6 (c = 1, $CHCl_3$), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 3 H, -CH_3), 1.40 (s, 3 H, -CH_3), 2.02–2.18 (m, 2 H, -CH$_2$CH_2), 2.62–2.85 (m, 2 H, ArCH_2), 3.30 (s, 3 H, CHOCH_3), 3.80 (s, 6 H, 2 ArOCH_3), 3.87 (s, 3 H, ArOCH_3), 4.08–4.12 (m, 1 H, 4 H), 4.48–4.56 (m, 2 H, 3a, 6a-H), 4.91 (s, 1 H, 6-H), 7.00 [s, 2 H, $(OCH_3)_3$Ar-H$^{2'}$, H$^{6'}$], 7.32–7.35 (m, 2 H, ArH), 7.53–7.55 (m, 1 H, ArH), 7.58 (s, 1 H, Ar-H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.9, 26.1, 32.4, 36.7, 55.2, 56.3, 61.0, 72.6, 84.1, 85.6,

86.1, 107.8, 109.7, 112.3, 127.8, 128.3, 129.9, 132.6, 137.9, 141.7, 152.9, 196.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2934, 1658, 1612, 1249, 1181 cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{33}O_8$ $[M + H]^+$ 473.2175; found 473.2175.

(2*R*,3*S*,4*R*)-6-[4-(3,4,5-Trimethoxybenzoyl)phenyl]hexane-1,2,3,4-tetrayltetraacetate (59): Yield: 80%. R_f = 0.30 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = –3.6 (c = 1, $CHCl_3$), colorless crystalline solid. M.p. 68–72 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.81–1.93 (m, 2 H, -CH_2CH_2), 2.06 (s, 9 H, 3 OCOCH_3), 2.15 (s, 3 H, -OCOCH_3), 2.71–2.76 (m, 2 H, ArCH_2), 3.88 (s, 6 H, 2 ArOCH_3), 3.94 (s, 3 H, ArOCH_3), 4.15–4.28 (m, 2 H, -OCHCH_2), 5.15–5.16 (m, 1 H, 4-H), 5.26–5.28 (m, 1 H, 3-H), 5.36–5.38 (m, 1 H, 2-H), 7.06 [s, 2 H, $(OCH_3)_3$Ar-$H^{2'}$, $H^{6'}$], 7.29 (d, J = 8.0 Hz, 2 H, Ar-H^3, H^5), 7.74 (d, J = 8.0 Hz, 2 H, Ar-H^2, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8, 31.6, 32.3, 56.4, 60.9, 61.9, 68.5, 70.3, 107.8, 128.3, 130.3, 132.8, 135.8, 142.1, 145.8, 152.9, 170.0, 170.6, 195.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1702, 1650, 1602, 1590, 1255, 1171 cm^{-1}. HRMS (ESI): calcd. for $C_{30}H_{37}O_{12}$ $[M + H]^+$ 589.2285; found 589.2287.

(2*R*,3*S*,4*R*)-6-[3-(3,4,5-Trimethoxybenzoyl)phenyl]hexane-1,2,3,4-tetrayltetraacetate (60): Yield: 76%. R_f = 0.30 (hexane/ethyl acetate, 7:3). $[\alpha]_D$ = –3.2 (c = 1, $CHCl_3$), colorless crystalline solid. M.p. 55–58 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79–1.82 (m, 2 H, -CH_2CH_2), 1.99 (s, 9 H, 3 -OCOCH_3), 2.05 (s, 3 H, -OCOCH_3), 2.62–2.66 (m, 2 H, ArCH_2), 3.81 (s, 6 H, 2 ArOCH_3), 3.87 (s, 3 H, ArOCH_3), 4.06–4.17 (m, 2 H, -OCHCH_2), 5.06–5.07 (m, 1 H, 4-H), 5.19–5.20 (m, 1 H, 3-H), 5.26–5.30 (m, 1 H, 2-H), 6.99 [s, 2 H, $(OCH_3)_3$Ar-$H^{2'}$, $H^{6'}$], 7.31–7.33 (m, 2 H, ArH), 7.52–7.54 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8, 31.6, 32.8, 56.4, 61.0, 61.9, 68.3, 70.2, 107.7, 128.0, 128.3, 129.6, 132.4, 132.6, 138.1, 141.2, 142.0, 152.9, 170.0, 170.5, 195.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2931, 1701, 1660, 1612, 1589, 1259, 1176 cm^{-1}. HRMS (ESI): calcd. for $C_{30}H_{37}O_{12}$ $[M + H]^+$ 589.2285; found 589.2286.

Supporting Information (see also the footnote on the first page of this article): ^1H and ^{13}C NMR spectra of all new compounds.

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