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Synthesis of 1,7-dioxaspiro[5.5]undecanes and 1-oxa-7-thiaspiro[5.5]undecanes from *exo*-glycal

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ABSTRACT

A new spirocyclization was developed for the synthesis of 1,7-dioxaspiro[5.5]undecanes and 1-oxa-7-thiaspiro[5.5]undecanes by reaction of *exo*-glycal with aryl alcohols or thiophenols in the presence of Lewis acid $BF_3{\cdot}OEt_2$. The reaction proceeded through tandem Ferrier rearrangement, glycosylation, and Friedel–Crafts alkylation to provide the corresponding products in good to excellent yields.

1. Introduction

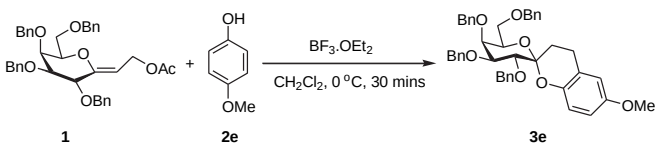
Spiroacetals attract large attention because they are the structural feature of many important natural products,[1] among, which 1,7-dioxaspiro[5.5]undecane is the major component of the pheromone of olive fruit fly (*Dacus oleae*).[2] Their metabolites were also found as the complex antiparasitic agents[3] or polyether antibiotics of the monensin[4,5] and lonomycin type.[6]

For the reason that 1,7-dioxaspiro[5.5]undecanes were important skeletons of the natural products, many methods were developed to synthesize the [5.5]spiroacetals. For instance, typical methods for the preparation of racemic spiroacetals are the use of radical methodology.[7,8] On the other hand, several literatures report the synthesis chiral pyranose spiroacetals by means of the acid catalyzed cyclization,[9] intramolecular hydrogen abstraction reaction,[10,11] ring-closing metathesis,[12] and NBS oxidatively rearranges.[13] However, most of those methods could not provide straightforward and satisfactory process due to the expersive, toxic, and moisture-sensitive starting materials,[12] the multiple steps,[9c] the low yields,[10,11] and the harsh reaction conditions.[12] In this paper, we developed a convenience method for synthesis of pyranose spiroacetal derivatives from *exo*-glycal with aryl alcohols or thiophenols by using $BF_3{\cdot}OEt_2$ as the catalyst via the tandem Ferrier rearrangement, glycosylation, and Friedel–Crafts alkylation.

2. Result and discussion

exo-Glycal **1** was prepared as the starting material by following the previous publication procedure via reduction and acetylation of *exo*-glycocosyl ester.[14,15] To search for the optimum conditions, we carried out the reaction by varying the anhydrous solvent and temperature by selecting CH_2Cl_2, THF, and acetonirile (MeCN) as the solvents and setting the reaction temperatures between −25 and 25 °C. Treatment of *exo*-glycal **1** and 4-methoxyphenol (**2e**) with 1.0 equiv of boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) in CH_2Cl_2 solution at 0 °C for 30 min provided the best result (see Scheme 1 and entries 1–5 of Table 1).

To investigate the catalytic activity of Lewis acids, we chose *exo*-glycal **1** and 4-methoxyphenol **2e** as the model to build up the best reaction condition and search for the best catalyst. We treated a anhydrous CH_2Cl_2 solution of *exo*-glycal **1** and 4-methoxyphenol **2e** with 1.0 equiv of various Lewis acids, including aluminum chloride ($AlCl_3$), boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$), iron



1 2e 3e

Scheme 1.

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chloride ($FeCl_3$), trifluoroacetic acid (TFA), and triphenylphosphonium bromide ($PPh_3 \cdot HBr$) at 0 °C for 30 min. We found the use of $BF_3 \cdot OEt_2$ as the Lewis catalyst provided the product **3e** in the best isolated yield (81%, Table 1).

Furthermore, we applied the same synthetic strategy to various aryl alcohols **2a–i** bearing an alkyl, alkoxy, 4-(*n*-pentylthio)phenol, bromo, and cholro groups at the *para*-position. The reactions gave the high stereoselective α-glycosidation spiro products **3a–i**

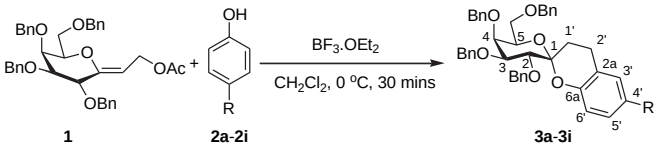
Table 1
Application of different Lewis acids for synthesis of 1,7-dioxaspiro[5.5]undecane **3e**

Entry	Lewis acid	Reaction temperature (°C)	Reaction solvent	1,7-Dioxaspiro[5.5]undecanes **3e** Yields[a,b] (%)
1	$BF_3 \cdot OEt_2$	0	CH_2Cl_2	81
2	$BF_3 \cdot OEt_2$	0	THF	72
3	$BF_3 \cdot OEt_2$	0	MeCN	0
4	$BF_3 \cdot OEt_2$	25	CH_2Cl_2	53
5	$BF_3 \cdot OEt_2$	−25	CH_2Cl_2	0
6	TFA	0	CH_2Cl_2	0
7	$AlCl_3$	0	CH_2Cl_2	0
8	$FeCl_3$	0	CH_2Cl_2	21
9	$PPh_3 \cdot HBr$	0	CH_2Cl_2	74

[a] The yield was determined by the column separation.
[b] All of the isolated products are the α-glycosidation spiro products.

in 71–89% yields (see Scheme 2 and Table 2) and their structures were identified and determined by DEPT, NOESY, and other spectroscopic methods. For example, compound **3e** possessed pyranose spiroacetal characteristic peaks: a multiple resonance at δ 1.57–1.62 ppm for the H2b′ proton, a multiple resonance at δ 2.14–2.05 ppm for the H2a′ proton, a multiple resonance at δ 2.90–2.81 ppm for the H1a′ proton, and a doublet–doublet resonance at δ 2.45 (J=16.0, 5.6 Hz) for the H1b′ proton. The ^{13}C characteristic peak of the anomeric center represented at δ 98.76 ppm.

However, when we applied this method to *o*-cresol, *m*-anisole, and *m*-chlorophenol, the corresponding spiro product cannot be obtained in quantitative yields and the poor stereoselectivity was



Scheme 2.

Table 2
The results for the synthesis of 1,7-dioxaspiro[5.5]undecanes **3a–i**

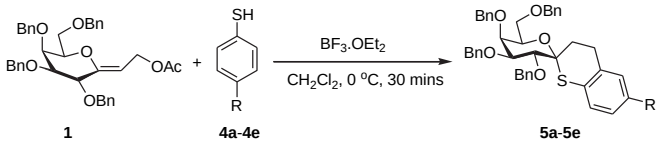
Entry	Aryl alcohols **2a–i**		1,7-Dioxaspiro[5.5]undecanes **3a–i**	
	R (*para*-position)		Products	Yields[a,b] (%)
1	**2a**	Me	**3a**	81
2	**2b**	Et	**3b**	87
3	**2c**	CH_2O-*n*-Bu	**3c**	76
4	**2d**	CH_2O-*n*-Oct	**3d**	71
5	**2e**	OMe	**3e**	81
6	**2f**	O-*n*-Bu	**3f**	89
7	**2g**	S-*n*-Pent	**3g**	71
8	**2h**	Cl	**3h**	78
9	**2i**	Br	**3i**	74

[a] The yield was determined by the column separation.
[b] All of isolated products are the α-glycosidation spiro products.

found for the *o*-Me, *m*-Cl, and *m*-OMe group made the conversion unfeasible. The synthetic strategy was also applicable to *exo*-glucal with *p*-chlorophenol. Unfortunately, the racemic glycosidation spiro products were provided.

We also applied the same method to use thiophenols **4a–e** equipped with various *para*-substitutents, including Me, *t*-Bu, OMe, Cl, and Br groups. The reaction provided the corresponding 1-oxa-7-thiaspiro[5.5]undecanes **5a–e** in 74–89% yields after normal workup and purification (see Scheme 3 and Table 3).

We proposed a plausible mechanism for the formation of 1,7-dioxaspiro[5.5]undecane **3e** through tandem Ferrier rearrangement, glycosylation, and Friedel–Crafts alkylation (see Scheme 4), which accounted for our approach and design. $BF_3 \cdot OEt_2$ catalyzed *exo*-glycal **1** to undergo the Ferrier rearrangement (allylic rearrangement) to give the α,β-conjugated oxonium ion **6**.[16] Consequently, the α,β-conjugated oxonium ion **6** would glycosylate methoxyphenol **2e** to give adduct **7**.[14] Upon further reaction with Lewis acid, intermediate **7** would undergo Friedel–Crafts alkylation to generate the final 1,7-dioxaspiro[5.5]undecane product **3e**.



Scheme 3.

Table 3
The results for synthesis of 1-oxa-7-thiaspiro[5.5]undecanes **5a–e**

Entry	Thiophenols s **4a–e**		1-Oxa-7-thiaspiro[5.5]undecanes **5a–e**	
	R (*para*-position)		Products	Yields[a,b] (%)
1	**4a**	Me	**5a**	80
2	**4b**	*t*-Bu	**5b**	89
3	**4c**	OMe	**5c**	74
4	**4d**	Cl	**5d**	78
5	**4e**	Br	**5e**	79

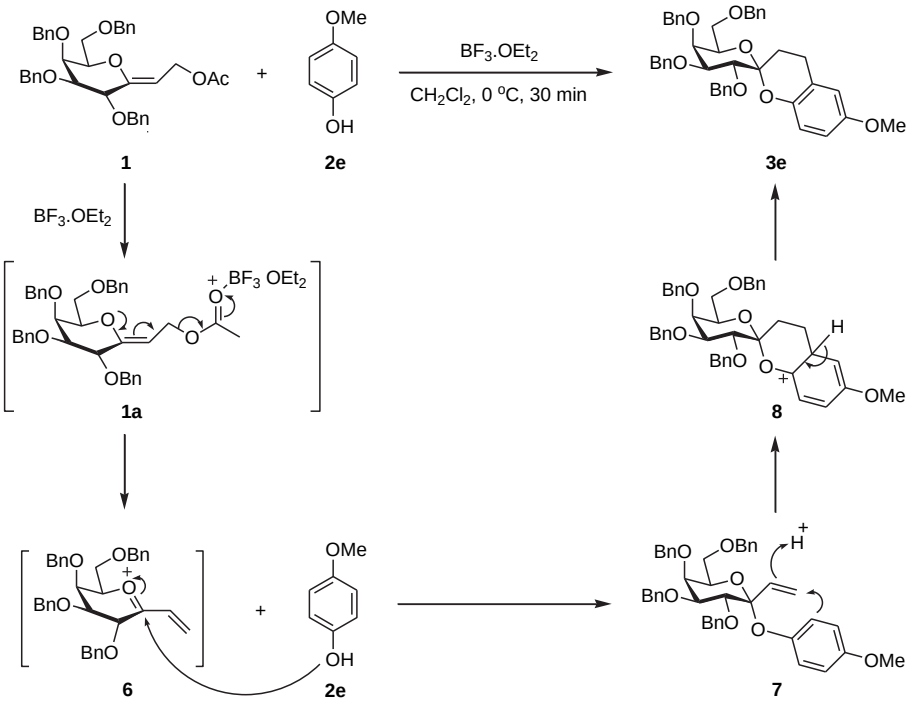
[a] The yield was determined by the column separation.
[b] All of isolated products are the α-glycosidation spiro products.

In conclusion, *exo*-glycal **1** was successfully converted to 1,7-dioxaspiro[5.5]undecanes by reacting aryl alcohols with $BF_3 \cdot OEt_2$ as the catalyst via the tandem Ferrier rearrangement, glycosylation, and Friedel–Crafts alkylation. This new method was also applicable to thiophenol as the reactants to give the corresponding 1-oxa-7-thiaspiro[5.5]undecanes in good yields.

3. Experimental section

3.1. General procedure

All chemicals were reagent grade and used as purchased. All reactions were carried out under nitrogen atmosphere and monitored by TLC analysis. Flash column chromatography was carried out on silica gel (230–400 mesh). Commercially available reagents were used without further purification unless otherwise noted. Dichloromethane, ethyl acetate, hexanes, and methanol were purchased from Mallinckrodt Chemical Co. The following compounds were purchased from Acoros Chemical Co: boron trifluoride diethyl etherate, α-butoxy-4-hydroxytoluene, 4-bromothiophenol, 4-*n*-butoxyphenol, 4-*tert*-butylthiophenol, 4-chlorothiophenol, *p*-cresol, 4-ethylphenol, 4-hydroxy-α-octoxytoluene, 4-methoxyphenol, 4-methoxybenzenethiol, 4-(*n*-pentylthio)phenol, *p*-toluenethiol. Purification by gravity column chromatography was carried out by use of Merck Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR spectrometer. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are recorded by the following abbreviations: s,



Scheme 4.

strong; m, medium; w, weak. Proton NMR spectra were obtained on a Bruker (200 or 400 MHz) spectrometer by use of $CDCl_3$ and DMSO-d_6 as solvent. Carbon-13 NMR spectra were obtained on a Bruker (50 or 100 MHz) spectrometer by used of $CDCl_3$ as solvent. Carbon-13 chemical shifts are referenced to the center of the $CDCl_3$ triplet (δ 77.0 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constant (Hz). Elemental analyses were carried out on a Heraeus CHN–O RAPID element analyzer.

3.2. Standard procedure for preparation of 1,7-dioxaspiro [5.5]undecanes 3a–i and 1-Oxa-7-thiaspiro[5.5]undecanes 5a–e

To a solution of *exo*-glycal **1** (1.0 equiv) in CH_2Cl_2 were added with catalyst $BF_3{\cdot}OEt_2$ (1.0 equiv) and aryl alcohol (3.0 equiv) or thiophenol (3.0 equiv). The reaction mixture was stirred at 0 °C for 30 min. When the reaction was completed, the resulting solution was added to CH_2Cl_2 (50 mL), washed with H_2O (20 mL×2), and brine (20 mL×2). The organic layer was concentrated under reduced pressure and purified by column chromatography on silica gel (15% EtOAc in hexanes as eluant) to give 1,7-dioxaspiro[5.5] undecanes **3a**–**i** in 71–89% yields or 1-oxa-7-thiaspiro[5.5]undecanes **5a**–**e** in 74–89% yields.

3.2.1. 1,7-Dioxaspiro[5.5]undecane derivative ***3a***. Pale yellow oil; $[\alpha]_D^{25}$ +16.97 (*c* 2.05, $CHCl_3$); IR ($CHCl_3$) 2923, 1644, 1552, 1101 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34–7.13 (18H, m, ArH), 7.01–6.99 (2H, m, ArH), 6.83–6.80 (1H, m, ArH), 6.74–6.71 (2H, m, ArH), 4.90 (2H, d, *J*=11.2 Hz, CH_2Ph), 4.74 (2H, br s, *CH_2Ph*), 4.66 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.56 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.23 (1H, dd, $J_{3,4}$=2.8 Hz, $J_{3,2}$=10 Hz, H3), 4.19 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.15 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.01 (1H, dd, $J_{4,5}$=1.2 Hz, $J_{4,3}$=2.8 Hz, H4), 3.95–3.89 (2H, m, H2, H5), 3.51 (1H, dd, $J_{6a,5}$=7.2 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.34 (1H, dd, $J_{6b,5}$=5.6 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.89–2.80 (1H, m, H1′a), 2.43 (1H, dd, $J_{1'b,2'a}$=5.6 Hz, $J_{1'b,1'a}$=16.0 Hz, H1′b), 2.21–2.06 (1H, m, H2′a), 2.16 (3H, s, CH_3), 1.65–1.60 (1H, m, H2′b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.71, 138.74, 138.61, 138.13, 137.95, 130.06, 129.37, 128.59, 128.58, 128.41, 128.40, 128.28, 128.27, 128.26, 128.25, 128.24, 128.23, 128.22, 128.21, 128.20, 127.87, 127.86, 127.69, 127.60, 127.59, 127.55, 127.52, 127.51, 122.35, 117.27, 98.88, 80.47, 79.06, 75.71, 74.92, 74.76, 73.15, 72.82, 70.84, 68.80, 27.20, 20.65, 20.51; ESIMS *m*/*z* (rel intens) 656 (M^+, 1), 240 (5), 181 (6), 121 (3), 91 (100); HRMS (EI) *m*/*z* calcd for $C_{43}H_{44}O_6$ 656.3138, found 656.3132. Anal. Calcd for $C_{43}H_{44}O_6$; C: 78.63; H: 6.75. Found: C: 78.60; H: 6.72.

3.2.2. 1,7-Dioxaspiro[5.5]undecane derivative ***3b***. Pale yellow oil; $[\alpha]_D^{25}$ +64.00 (*c* 0.65, $CHCl_3$); IR ($CHCl_3$) 2924, 1645, 1550, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35–7.15 (18H, m, ArH), 7.02–7.00 (2H, m, ArH), 6.86–6.83 (1H, m, ArH), 6.77–6.74 (2H, m, ArH), 4.90 (2H, d, *J*=11.2 Hz, CH_2Ph), 4.75 (2H, br s, *CH_2Ph*), 4.66 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.56 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.23 (1H, dd, $J_{3,4}$=2.8 Hz, $J_{3,2}$=10.0 Hz, H3), 4.19 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.16 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.02 (1H, dd, $J_{4,5}$=1.2 Hz, $J_{4,3}$=2.8 Hz, H4), 3.96–3.90 (2H, m, H2, H5), 3.52 (1H, dd, $J_{6a,5}$=7.2 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.34 (1H, dd, $J_{6b,5}$=5.6 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.90–2.82 (1H, m, H1′a), 2.50–2.42 (3H, m, CH_2, H1′b), 2.15–2.03 (1H, m, H2′a), 1.65–1.61 (1H, m, H2′b), 1.12 (3H, t, *J*=7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.91, 138.76, 138.63, 138.16, 137.97, 136.54, 128.58, 128.57, 128.41, 128.40, 128.28, 128.27, 128.26, 128.25, 128.24, 128.23, 128.22, 128.21, 128.13, 127.89, 127.88, 127.68, 127.60, 127.59, 127.52, 127.51, 127.50, 126.40, 122.30, 117.27, 98.91, 80.48, 79.10, 75.71, 74.93, 74.76, 73.15, 72.82, 70.83, 68.80, 27.99, 27.23, 20.72, 1565. ESIMS *m*/*z* (rel intens) 670 (M^+, 1), 181 (18), 105 (3), 91 (100); HRMS (EI) *m*/*z* calcd for $C_{44}H_{46}O_6$ 670.3294, found 670.3304. Anal. Calcd for $C_{44}H_{46}O_6$; C: 78.78; H: 6.91. Found: C: 78.74; H: 6.89.

3.2.3. 1,7-Dioxaspiro[5.5]undecane derivative ***3c***. Pale yellow oil; $[\alpha]_D^{25}$ +19.50 (*c* 2.62, $CHCl_3$); IR ($CHCl_3$) 2923, 1646, 1548, 1105 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35–7.16 (18H, m, ArH), 7.05–7.02 (2H, m, ArH), 6.99 (1H, dd, *J*=2.0 Hz, *J*=8.4 Hz, ArH), 6.92 (1H, br s, ArH), 6.80 (1H, d, *J*=8.4 Hz, ArH), 4.91 (1H, d, *J*=11.2 Hz, CH_2Ph), 4.90 (1H, d, *J*=11.6 Hz, CH_2Ph), 4.74 (2H, br s, *CH_2Ph*), 4.67 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.56 (1H, d, *J*=11.2 Hz, *CH_2Ph*), 4.30 (2H, br s, H6′), 4.22 (1H, dd, $J_{3,4}$=2.8 Hz, $J_{3,2}$=10.0 Hz, H3), 4.21 (1H, d, *J*=11.6 Hz, *CH_2Ph*), 4.18 (1H, d, *J*=11.6 Hz, *CH_2Ph*), 4.04 (1H, br s, H4), 3.94–3.90 (2H, m, H2, H5),

3.51 (1H, dd, $J_{6a,5}$=8.0 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.38 (2H, t, J=6.8 Hz, H7′), 3.30 (1H, dd, $J_{6b,5}$=5.2 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.90–2.82 (1H, m, H1′a), 2.47 (1H, dd, $J_{1'b,2'a}$=5.2 Hz, $J_{1'b,1'a}$=16.0 Hz, H1′b), 2.13–2.05 (1H, m, H2′a), 1.65–1.60 (1H, m, H2′b), 1.57–1.47 (1H, m, H8′), 1.35–1.23 (1H, m, H9′), 0.83 (3H, t, J=7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.45, 138.75, 138.59, 138.10, 137.90, 131.08, 128.64, 128.57, 128.56, 128.40, 128.39, 128.30, 128.29, 128.26, 128.25, 128.22, 128.21, 128.20, 128.19, 127.86, 127.85, 127.70, 127.61, 1277.56, 127.54, 127.51, 127.50, 126.76, 122.54, 117.39, 99.01, 80.41, 78.98, 75.70, 74.80, 74.79, 73.20, 72.79, 72.69, 70.74, 70.17, 68.55, 31.82, 27.11, 20.66, 19.36, 13.89; ESIMS m/z (rel intens) 728 (M^+,0.7), 240 (7), 181 (8), 91 (100); HRMS (EI) m/z calcd for $C_{47}H_{52}O_7$ 728.3713, found 728.3722. Anal. Calcd for $C_{47}H_{52}O_7$; C: 77.44; H: 7.32. Found: C: 77.49; H: 7.28.

3.2.4. 1,7-Dioxaspiro[5.5]undecane derivative ***3d***. Pale yellow oil; $[\alpha]_D^{25}$ +20.67 (c 1.19, $CHCl_3$); IR ($CHCl_3$) 2936, 1643, 1468, 1101 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34–7.13 (18H, m, ArH), 7.04–7.02 (2H, m, ArH), 6.98 (1H, dd, J=2.0, 8.0 Hz, ArH), 6.93 (1H, br s, ArH), 6.79 (1H, d, J=8.0 Hz, ArH), 4.89 (1H, d, J=11.2 Hz, *CH_2Ph*), 4.74 (2H, br s, *CH_2Ph*), 4.66 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.55 (1H, d, J=11.2 Hz, *CH_2Ph*), 4.29 (2H, br s, H6′), 4.24–4.18 (3H, m, H3, *CH_2Ph*), 4.03 (1H, br s, H4), 3.94–3.90 (2H, m, H2, H5), 3.52 (1H, dd, $J_{6a,5}$=8.0 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.36 (2H, t, J=6.4 Hz, H7′), 3.30 (1H, dd, $J_{6b,5}$=5.6 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.90–2.82 (1H, m, H1′a), 2.47 (1H, dd, $J_{1'b,2'a}$=5.6 Hz, $J_{1'b,1'a}$=16.4 Hz, H1′b), 2.14–2.05 (1H, m, H2′a), 1.65–1.60 (1H, m, H2′b), 1.55–1.48 (1H, m, H8′), 1.28–1.13 (10H, m, H9′-H13′), 0.80 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.46, 138.77, 138.60, 138.11, 137.91, 131.09, 128.65 128.58, 128.57, 128.41, 128.40, 128.31, 128.30, 128.27, 128.26, 128.22, 128.21, 128.20, 127.87, 127.86, 127.71, 127.70, 127.62, 127.56, 127.55, 127.52, 127.51, 126.77, 122.55, 117.40, 99.02, 80.42, 78.99, 75.71, 74.81, 74.80, 73.21, 72.80, 72.69, 70.75, 7.054, 68.56, 31.82, 29.75, 29.45, 29.25, 27.12, 26.20, 22.64, 20.67, 14.07; FAB-MS m/z (rel intens) 785 ($M+H^+$, 1), 181 (45), 91 (100), 55 (68); HRMS (FAB) m/z calcd for $C_{51}H_{61}O_7$ ($M+H^+$) 785.4417, found 785.4425. Anal. Calcd for $C_{51}H_{60}O_7$; C: 78.03; H: 7.70. Found: C: 78.06; H: 6.72.

3.2.5. 1,7-Dioxaspiro[5.5]undecane derivative ***3e***. Pale yellow oil; $[\alpha]_D^{25}$ +7.79 (c 1.77, $CHCl_3$); IR ($CHCl_3$) 2923, 1640, 1493, 1106 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.13 (18H, m, ArH), 7.01–6.98 (2H, m, ArH), 6.75 (1H, d, J=8.8 Hz, ArH), 6.58 (1H, dd, J=2.8, 8.8 Hz, ArH), 6.48 (1H, d, J=2.8 Hz, ArH), 4.91 (1H, d, J=11.2 Hz, CH_2Ph), 4.90 (1H, d, J=11.6 Hz, CH_2Ph), 4.74 (2H, br s, *CH_2Ph*), 4.67 (1H, d, J=11.2 Hz, *CH_2Ph*), 4.56 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.21 (1H, dd, $J_{3,4}$=2.8 Hz, $J_{3,2}$=10.0 Hz, H3), 4.19 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.16 (1H, d, J=11.2 Hz, *CH_2Ph*), 4.01 (1H, dd, $J_{4,5}$=1.2 Hz, $J_{4,3}$=2.8 Hz, H4), 3.93–3.87 (2H, m, H2, H5), 3.64 (3H, s, OCH_3), 3.49 (1H, dd, $J_{6a,5}$=7.2 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.34 (1H, dd, $J_{6b,5}$=5.6 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.90–2.81 (1H, m, H1′a), 2.45 (1H, dd, $J_{1'b,2'a}$=5.6 Hz, $J_{1'b,1'a}$=16.0 Hz, H1′b), 2.14–2.05 (1H, m, H2′a), 1.62–1.57 (1H, m, H2′b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.72, 145.70, 138.62, 138.52, 138.00, 137.84, 128.67, 128.66, 128.41, 128.40, 128.30, 128.29, 128.28, 128.27, 128.26, 128.25, 128.24, 128.23, 127.84, 127.83, 127.73, 127.62, 127.61, 127.60, 127.50, 127.49, 123.30, 118.10, 113.43, 112.85, 98.76, 80.45, 78.84, 75.71, 74.72, 74.71, 73.12, 72.77, 70.76, 68.74, 55.50, 27.00, 21.03; ESIMS m/z (rel intens) 672 (M^+,1), 181 (7), 91 (100); HRMS (EI) m/z calcd for $C_{43}H_{44}O_7$ 672.3087, found 672.3091. Anal. Calcd for $C_{43}H_{44}O_7$; C: 76.65; H: 6.73. Found: C: 76.69; H: 6.78.

3.2.6. 1,7-Dioxaspiro[5.5]undecane derivative ***3f***. Pale yellow oil; $[\alpha]_D^{25}$ +32.40 (c 1.50, $CHCl_3$); IR ($CHCl_3$) 2930, 1642, 1494, 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35–7.15 (18H, m, ArH), 7.01–6.98 (2H, m, ArH), 6.74 (1H, d, J=8.8 Hz, ArH), 6.58 (1H, dd, J=2.8 Hz, J=8.8 Hz, ArH), 6.48 (1H, d, J=2.8 Hz, ArH), 4.90 (1H, d, J=11.2 Hz, CH_2Ph), 4.89 (1H, d, J=11.2 Hz, CH_2Ph), 4.74 (2H, br s, *CH_2Ph*), 4.67 (1H, d, J=11.2 Hz, *CH_2Ph*), 4.56 (1H, d, J=11.2 Hz, *CH_2Ph*), 4.21 (1H, dd, $J_{3,4}$=2.8 Hz, $J_{3,2}$=10.4 Hz, H3), 4.19 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.15 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.01 (1H, br s, H4), 3.93–3.87 (2H, m, H2, H5), 3.77 (2H, t, J=6.4 Hz, H6′), 3.49 (1H, dd, $J_{6a,5}$=7.2 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.33 (1H, dd, $J_{6b,5}$=5.6 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.90–2.81 (1H, m, H1′a), 2.44 (1H, dd, $J_{1'b,2'a}$=5.6 Hz, $J_{1'b,1'a}$=16.4 Hz, H1′b), 2.13–2.05 (1H, m, H2′a), 1.67–1.57 (3H, m, H2′b, H7′), 1.43–1.34 (2H, m, H8′), 0.88 (3H, t, J=7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.30, 145.54, 138.62, 138.52, 138.00, 137.84, 128.67, 128.66, 128.41, 128.40, 128.28, 128.27, 128.26, 128.25, 128.24, 128.23, 128.22, 128.21, 127.85, 127.84, 127.72, 127.61, 127.62, 127.55, 127.49, 127.48, 123.22, 118.03, 114.10, 113.42, 98.73, 80.45, 78.85, 75.70, 74.70, 74.69, 73.11, 72.76, 70.74, 68.75, 67.94, 31.44, 27.00, 21.00, 19.24, 13.87; ESIMS m/z (rel intens) 714 (M^+, 2), 457 (8), 91 (100); HRMS (EI) m/z calcd for $C_{46}H_{50}O_7$ 714.3557, found 714.3551. Anal. Calcd for $C_{46}H_{50}O_7$; C: 77.28; H: 7.05. Found: C: 77.34; H: 7.08.

3.2.7. 1,7-Dioxaspiro[5.5]undecane derivative ***3g***. Pale yellow oil; $[\alpha]_D^{25}$ +42.24 (c 0.98, $CHCl_3$); IR ($CHCl_3$) 2929, 1643, 1469, 1101 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34–7.13 (19H, m, ArH), 7.05–6.98 (3H, m, ArH), 6.75 (1H, d, J=8.4 Hz, ArH), 4.90 (2H, d, J=11.6 Hz, *CH_2Ph*), 4.74 (2H, br s, *CH_2Ph*), 4.66 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.55 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.23–4.17 (3H, m, H3, *CH_2Ph*), 4.01 (1H, br s, H4), 3.92–3.90 (2H, m, H2, H5), 3.51 (1H, dd, $J_{6a,5}$=7.6 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.32 (1H, dd, $J_{6b,5}$=5.6 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.89–2.80 (1H, m, H1′a), 2.72 (2H, t, J=7.6 Hz, H7′), 2.44 (1H, dd, $J_{1'b,2'a}$=5.6 Hz, $J_{1'b,1'a}$=16.4 Hz, H1′b), 2.13–2.03 (1H, m, H2′a), 1.64–1.60 (1H, m, H2′b), 1.55–1.48 (2H, m, H8′), 1.33–1.13 (4H, m, H9′, H10′), 0.78 (3H, t, J=7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.00, 138.70, 138.54, 138.04, 137.86, 131.61, 129.83, 128.62, 128.61, 128.41, 128.40, 128.34, 128.33, 128.28, 128.27, 128.24, 128.23, 128.22, 128.21, 128.20, 127.82, 127.81, 127.75, 127.65, 127.60, 127.58, 127.52, 127.51, 127.50, 123.40, 118.10, 99.10, 80.38, 78.83, 75.72, 74.83, 74.79, 73.21, 72.81, 70.91, 68.67, 35.41, 30.91, 29.00, 27.01, 22.21, 20.61, 13.92; FAB-MS m/z (rel intens) 745 ($M+H^+$, 3), 653 (2), 209 (5), 181 (12), 90 (75); HRMS (FAB) m/z calcd for $C_{47}H_{53}O_6S$ ($M+H^+$) 745.3563, found 745.3553. Anal. Calcd for $C_{47}H_{52}O_6S$; C: 75.77; H: 7.04. Found: C: 75.83; H: 7.07.

3.2.8. 1,7-Dioxaspiro[5.5]undecane derivative ***3h***. Pale yellow oil; $[\alpha]_D^{25}$ +37.31 (c 0.67, $CHCl_3$); IR ($CHCl_3$) 2966, 1640, 1490, 1102 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28–6.74 (23H, m, ArH), 4.89 (2H, d, J=11.6 Hz, *CH_2Ph*), 4.73 (2H, br s, *CH_2Ph*), 4.65 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.54 (1H, d, J=11.6 Hz, *CH_2Ph*), 4.23–4.17 (3H, m, H3, *CH_2Ph*), 4.00 (1H, dd, $J_{4,5}$=0.8 Hz, $J_{4,3}$=2.8 Hz, H4), 3.92–3.86 (2H, m, H2, H5), 3.49 (1H, dd, $J_{6a,5}$=7.2 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.32 (1H, dd, $J_{6b,5}$=5.6 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.86–2.79 (1H, m, H1′a), 2.43 (1H, dd, $J_{1'b,2'a}$=5.6 Hz, $J_{1'b,1'a}$=16.4 Hz, H1′b), 2.10–2.02 (2H, m, H1′b, H2′a), 1.63–1.58 (1H, m, H2′b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.48, 138.55, 138.41, 137.85, 137.73, 128.70, 128.69, 128.68, 128.45, 128.44, 128.33, 128.32, 128.31, 128.30, 128.28, 128.27, 128.26, 128.25, 127.80, 127.79, 127.78, 127.69, 127.68, 127.67, 127.52, 127.51, 126.97, 125.71, 124.41, 118.85, 99.05, 80.34, 78.56, 75.79, 74.75, 74.59, 73.24, 72.80, 70.99, 68.65, 26.69, 20.60; ESIMS m/z (rel intens) 676 (M^+, 1), 181 (9), 91 (100); HRMS (EI) m/z calcd for $C_{42}H_{41}ClO_6$ 676.2592, found 676.2595. Anal. Calcd for $C_{42}H_{41}ClO_6$; C: 74.49; H: 6.10. Found: C: 74.50; H: 6.16.

3.2.9. 1,7-Dioxaspiro[5.5]undecane derivative ***3i***. Pale yellow oil; $[\alpha]_D^{25}$ +25.82 (c 1.51, $CHCl_3$); IR ($CHCl_3$) 2950, 1634, 1489, 1107 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34–7.17 (20H, m, ArH), 7.02–6.99 (2H, m, ArH), 6.70 (1H, d, J=8.4 Hz, ArH), 4.90 (2H, d, J=11.2 Hz, *CH_2Ph*), 4.74 (2H, br s, *CH_2Ph*), 4.66 (1H, d, J=11.2 Hz, *CH_2Ph*), 4.55 (1H, d, J=11.2 Hz, *CH_2Ph*), 4.24–4.18 (3H, m, H3, *CH_2Ph*), 4.00 (1H, dd, $J_{4,5}$=1.2 Hz, $J_{4,3}$=2.8 Hz, H4), 3.92–3.86 (2H, m, H2, H5), 3.50 (1H, dd, $J_{6a,5}$=7.2 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.32 (1H, dd, $J_{6b,5}$=5.6 Hz,

$J_{6b,6a}$=9.6 Hz, H6b), 2.89–2.80 (1H, m, H1′a), 2.45 (1H, dd, $J_{1'b,2'a}$=4.8 Hz, $J_{1'b,1'a}$=16.0 Hz, H1′b), 2.11–2.02 (2H, m, H1′b, H2′a), 1.63–1.59 (1H, m, H2′b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.09, 138.61, 138.46, 137.91, 137.79, 131.58, 129.91, 128.67, 128.66, 128.36, 128.35, 128.34, 128.33, 128.32, 128.31, 128.30, 128.29, 128.27, 128.26, 128.25, 128.24, 127.82, 127.81, 127.80, 127.69, 127.68, 127.54, 127.53, 125.04, 119.34, 113.18, 99.10, 80.36, 78.65, 75.80, 74.79, 74.78, 73.28, 72.85, 71.06, 68.70, 26.75, 20.60; ESIMS *m*/*z* (rel intens) 720 (M^+, 1), 181 (11), 91 (100); HRMS (EI) *m*/*z* calcd for $C_{42}H_{41}BrO_6$ 720.2087, found 720.2084. Anal. Calcd for $C_{42}H_{41}BrO_6$; C: 69.90; H: 5.73. Found: C: 69.95; H: 5.77.

3.2.10. 1-Oxa-7-thiaspiro[5.5]undecane derivative ***5a***. Pale yellow oil; $[\alpha]_D^{25}$ +1.21 (*c* 1.98, $CHCl_3$); IR ($CHCl_3$) 2950, 1644, 1492, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28–6.99 (23H, m, ArH), 4.85 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.82 (1H, d, *J*=10.8 Hz, *CH*$_2$*Ph*), 4.59 (2H, br s, *CH*$_2$*Ph*), 4.53 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.49 (1H, d, *J*=10.8 Hz, *CH*$_2$*Ph*), 4.39 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.35 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.06–4.02 (1H, m, H5), 3.93 (1H, br s, H4), 3.84 (1H, dd, $J_{3,4}$=2.8 Hz, $J_{3,2}$=9.6 Hz, H3), 3.69 (1H, d, *J*=9.6 Hz, H2), 3.52–3.43 (2H, m, H6), 3.04–2.97 (1H, m, H1′a), 2.79–2.73 (1H, m, H1′b), 2.23 (3H, s, CH_3), 2.03–1.92 (1H, m, H2′a), 1.81–1.74 (1H, m, H2′b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.86, 138.85, 138.36, 138.02, 137.91, 136.22, 131.92, 138.36, 138.35, 129.66, 129.65, 128.53, 128.52, 128.39, 128.38, 128.37, 128.28, 128.27, 128.19, 128.18, 127.85, 127.84, 127.82, 127.81, 127.60, 127.59, 127.51, 127.50, 126.95, 126.94, 98.50, 80.94, 78.72, 75.54, 74.38, 74.13, 73.41, 72.36, 70.17, 68.75, 37.26, 27.74, 20.97 ESIMS *m*/*z* (rel intens) 672 (M^+, 1), 377 (6), 181 (7), 91 (100); HRMS (EI) *m*/*z* calcd for $C_{43}H_{44}O_5S$ 672.2909, found 672.2902. Anal. Calcd for $C_{43}H_{44}O_5S$; C: 76.75; H: 6.59. Found: C: 76.71; H: 6.54.

3.2.11. 1-Oxa-7-thiaspiro[5.5]undecane derivative ***5b***. Pale yellow oil; $[\alpha]_D^{25}$ +5.54 (*c* 1.64, $CHCl_3$); IR ($CHCl_3$) 2960, 1642, 1493, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26–7.17 (23H, m, ArH), 4.85 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.83 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.66 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.58 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.55 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.52 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.40 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.36 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.06–4.03 (1H, m, H5), 3.94 (1H, br s, H4), 3.84 (1H, dd, $J_{3,4}$=2.4 Hz, $J_{3,2}$=9.6 Hz, H3), 3.72 (1H, d, *J*=9.6 Hz, H2), 3.55–3.44 (2H, m, H6), 3.05–2.98 (1H, m, H1′a), 2.82–2.75 (1H, m, H1′b), 2.04–1.96 (1H, m, H2′a), 1.84–1.80 (1H, m, H2′b), 1.20 (9H, br s, $3CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.35, 138.85, 138.35, 138.03, 137.90, 132.15, 129.64, 129.63, 128.42, 128.41, 128.39, 128.38, 128.37, 128.31, 128.30, 128.20, 128.19, 127.85, 127.84, 127.81, 127.80, 127.68, 127.58, 127.51, 127.50, 127.44, 125.91, 125.90, 98.51, 80.97, 78.59, 75.50, 74.38, 74.10, 73.41, 72.35, 70.19, 68.72, 37.32, 34.39, 31.25, 31.24, 31.23, 27.40; FAB-MS *m*/*z* (rel intens) 715 ($M+H^+$, 1), 253 (6), 181 (22), 105 (22), 91 (100), 57 (73); HRMS (FAB) *m*/*z* calcd for $C_{46}H_{51}O_5S$ ($M+H^+$) 715.3457, found 715.3449. Anal. Calcd for $C_{46}H_{50}O_5S$; C: 77.28; H: 7.05. Found: C: 77.32; H: 7.01.

3.2.12. 1-Oxa-7-thiaspiro[5.5]undecane derivative ***5c***. Pale yellow oil; $[\alpha]_D^{25}$ +24.40 (*c* 0.79, $CHCl_3$); IR ($CHCl_3$) 2955, 1645, 1496, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26–7.17 (18H, m, ArH), 7.02–7.00 (2H, m, ArH), 6.57–6.53 (3H, m, ArH), 4.90 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.80 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.68 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.64 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.51 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.45–4.42 (1H, m, H5), 4.37 (2H, br s, *CH*$_2$*Ph*), 4.05 (1H, d, *J*=9.6 Hz, H2), 4.00 (1H, dd, $J_{3,4}$=2.4 Hz, $J_{3,2}$=9.6 Hz, H3), 3.93 (1H, dd, $J_{4,5}$=1.2 Hz, $J_{4,3}$=2.4 Hz, H4), 3.65 (3H, s, OCH_3), 3.51 (1H, dd, $J_{6a,5}$=6.8 Hz, $J_{6a,6b}$=9.6 Hz, H6a), 3.44 (1H, dd, $J_{6b,5}$=4.8 Hz, $J_{6b,6a}$=9.6 Hz, H6b), 2.69–2.61 (1H, m, H1′a), 2.35–2.27 (1H, m, H1′b), 2.10–2.03 (1H, m, H2′a), 1.87–1.78 (1H, m, H2′b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ158.55, 139.02, 138.29, 138.10, 138.06, 138.05, 132.88, 128.41, 128.40, 128.39, 128.32, 128.31, 128.30, 128.23, 128.22, 128.21, 128.11, 128.10, 127.72, 127.71, 127.70, 127.57, 127.56, 127.55, 127.34, 127.33, 127.32, 126.22, 120.95, 114.30, 94.24, 81.62, 76.34, 75.03, 74.76, 74.30, 73.46, 72.55, 71.85, 68.98, 55.15, 29.69, 26.50; FAB-MS *m*/*z* (rel intens) 689 ($M+H^+$, 15), 581 (40), 243 (35), 181 (65), 149 (80), 91 (100), 55 (82); HRMS (FAB) *m*/*z* calcd for $C_{43}H_{45}O_6S$ ($M+H^+$) 689.2937, found 689.2940. Anal. Calcd for $C_{43}H_{44}O_6S$; C: 74.97; H: 6.44. Found: C: 74.94; H: 6.41.

3.2.13. 1-Oxa-7-thiaspiro[5.5]undecane derivative ***5d***. Pale yellow oil; $[\alpha]_D^{25}$ +56.62 (*c* 4.35, $CHCl_3$); IR ($CHCl_3$) 2964, 1642, 1480, 1097 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29–7.20 (17H, m, ArH), 6.95–6.88 (4H, m, ArH), 6.84–6.80 (2H, m, ArH), 4.90 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.88 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.68 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.64 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.62 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.49 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.36–4.33 (3H, m, H5, *CH*$_2$*Ph*), 4.07 (1H, d, *J*=9.6 Hz, H2), 3.99 (1H, dd, $J_{3,4}$=2.8 Hz, $J_{3,2}$=9.6 Hz, H3), 3.93 (1H, br s, H4), 3.49–3.72 (2H, m, H6), 2.73–2.66 (1H, m, H1′a), 2.15–2.01 (2H, m, H1′b, H2′a), 1.80–1.72 (1H, m, H2′b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.78, 138.06, 137.85, 137.68, 134.69, 134.45, 131.46, 128.68, 128.67, 128.59, 128.58, 128.47, 128.46, 128.45, 128.44, 128.41, 128.40, 128.31, 128.30, 128.23, 128.22, 127.85, 127.78, 127.77, 127.71, 127.55, 127.54, 127.45, 127.37, 127.36, 94.59, 81.62, 75.77, 74.96, 74.66, 74.35, 73.53, 72.52, 72.18, 69.17, 37.36, 27.41; FAB-MS *m*/*z* (rel intens) 693 ($M+H^+$, 3), 585 (4), 243 (8), 181 (39), 91 (100), 55 (80); HRMS (FAB) *m*/*z* calcd for $C_{42}H_{42}ClO_5S$ ($M+H^+$) 693.2441, found 693.2451. Anal. Calcd for $C_{42}H_{41}ClO_5S$; C: 72.76; H: 5.96. Found: C: 72.72; H: 5.93.

3.2.14. 1-Oxa-7-thiaspiro[5.5]undecane derivative ***5e***. Pale yellow oil; $[\alpha]_D^{25}$ +131.58 (*c* 1.16, $CHCl_3$); IR ($CHCl_3$) 2950, 1643, 1466, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31–7.17 (17H, m, ArH), 7.12–7.06 (4H, m, ArH), 6.78–6.76 (2H, m, ArH), 4.91 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.90 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.70 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.67 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.64 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.51 (1H, d, *J*=11.6 Hz, *CH*$_2$*Ph*), 4.41–4.35 (3H, m, H5, *CH*$_2$*Ph*), 4.08 (1H, d, *J*=9.6 Hz, H2), 4.00 (1H, dd, $J_{3,4}$=2.4 Hz, $J_{3,2}$=9.6 Hz, H3), 3.95 (1H, br s, H4), 3.50–3.48 (2H, m, H6), 2.74–2.67 (1H, m, H1′a), 2.15–2.02 (2H, m, H1′b, H2′a), 1.82–1.74 (1H, m, H2′b); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.81, 138.09, 137.87, 137.70, 135.47, 128.53, 128.52, 128.51, 128.50, 128.49, 128.48, 128.47, 128.46, 128.45, 128.38, 128.37, 128.27, 128.26, 127.92, 127.85, 127.84, 127.83, 127.76, 127.61, 127.60, 127.51, 127.42, 127.41, 122.72, 119.30, 94.62, 81.67, 75.78, 75.01, 74.70, 74.40, 73.60, 72.60, 72.24, 69.23, 37.37, 27.24; FAB-MS *m*/*z* (rel intens) 737 ($M+H^+$, 6), 631 (10), 629 (9), 181 (63), 90 (100); HRMS (FAB) *m*/*z* calcd for $C_{42}H_{42}BrO_5S$ ($M+H^+$) 737.1936, found 737.1941. Anal. Calcd for $C_{42}H_{41}BrO_5S$; C: 68.38; H: 5.60. Found: C: 68.31; H: 5.57.

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Supplementary data

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