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Total Synthesis of (±)-Spiniferin-1 via a Polyfluoroalkanosulfonyl Fluoride Induced Homoallylic Carbocation Rearrangement Reaction

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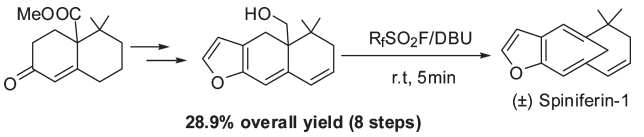


A facile total synthesis of marine natural product (±)-spiniferin-1 has been accomplished in eight steps with 28.9% overall yield, involving a rearrangement reaction initiated by polyfluoroalkanosulfonyl fluoride to construct the 1,6-methano[10]annulene core of the natural product as a key step.

The structural diversity and biological activity of marine natural products[1] make them an important source for the discovery and development of new drugs and agricultural agents, which, in turn, has stimulated considerable interest in their isolation and synthesis. Spiniferin-1 (**1**) is a structurally unique furanosesquiterpene, isolated by Cimino et al. in 1975 from the Mediterranean sponge *Pleraplysilla spinifera*, which is present in the Bay of Naples.[2] In 1978, its structure was reformulated as **1**,[2b] which was further supported by Marshall's definitive synthesis of (±)-**1** and its dihydro derivative (±)-**2** (Figure 1).[3] Even though spiniferin-1 is the sole natural product with the skeleton of 1,6-methano[10]annulene isolated thus far, its chemical instability and difficulty of synthesis retarded the progress of its investigation in chemistry and biology.

The key challenge in the synthesis of spiniferin-1 lies in the construction of a highly strained norcarenone (Scheme 1).[3,4] The existing cyclopropanation methods, such as Simmons−Smith reaction[3a] or nucleophilic addition of "semi-enone" radical anion,[3b] require more than two steps to produce norcarenone due to an additional dehydrogenation.

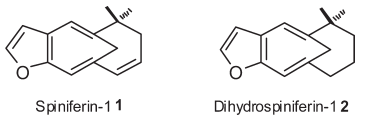
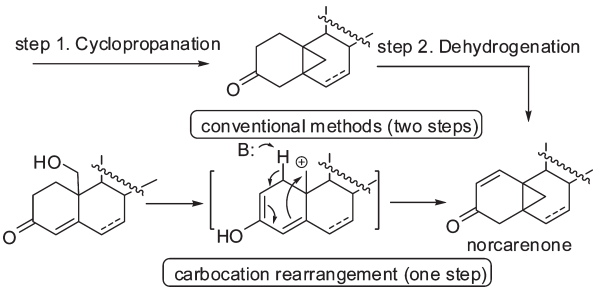


FIGURE 1. Structure of spiniferin-1 and dihydrospiniferin-1.

SCHEME 1. Construction of Norcarenone



One-step synthesis of norcarenone via a homoallylic carbocation rearrangemgent is highly attractive owing to the simultaneous construction of the double bond.[5] However, the addition of a carbocation to an electron-poor acceptor has proved to be a synthetic challenge. The harsh conditions required to initiate the rearrangement as well as poor selectivity limit their applicability.[5a,d]

We recently developed a novel homoallylic carbocation rearrangement reaction induced by polyfluoroalkanosulfonyl fluorides (R_fSO_2F) (**3a**→**4a**),[6] whereby (±)-**2**[6b] was efficiently synthesized. However, the endeavor for preparing (±)-**1** was hampered by the additional double bond (Scheme 2). The rearrangement reaction of **3b** did not produce the key intermediate **4b** under optimized condition.

The unexpected difficulty prompted us to develop a different strategy for the synthesis of (±)-**1**, which uses an electron-rich furan compound as the rearrangement precursor (Scheme 3). The prior construction of electron-rich furan not only favors regioselective carbocation rearrangement but also obviates protection/deprotection manipulation. The present work describes the facile total syntheses of (±)-spiniferin-1 and its dihydro derivative on the basis of this new strategy.

To explore the feasibility of the new synthetic strategy, (±)-**2** was again synthesized as a model system (Scheme 4). The synthesis began with the construction of 2-vinyl furan **9**. Allylation of the Robinson annulation product **5** and subsequent ozonolysis was carried out according to the previous

(1) (a) Blunt, J. W.; Copp, B. R.; Hu, W. P.; Munro, M. H. G.; Northcote, P. T.; Prinsep, M. R. *Nat. Prod. Rep.* **2009**, *26*, 170. (b) Blunt, J. W.; Copp, B. R.; Munro, M. H. G.; Northcote, P. T.; Prinsep, M. R. *Nat. Prod. Rep.* **2010**, *27*, 165.

(2) (a) Cimino, G.; Destefano, S.; Minale, L.; Trivellone, E. *Tetrahedron Lett.* **1975**, 3727. (b) Cimino, G.; Destefano, S.; Minale, L.; Trivellone, E. *Experientia* **1978**, *34*, 1425.

(3) (a) Marshall, J. A.; Conrow, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 4274. (b) Marshall, J. A.; Conrow, R. E. *J. Am. Chem. Soc.* **1983**, *105*, 5679.

(4) (a) Vantamelen, E. E.; Hildahl, G. T. *J. Am. Chem. Soc.* **1953**, *75*, 5451. (b) Vantamelen, E. E.; Hildahl, G. T. *J. Am. Chem. Soc.* **1956**, *78*, 4405.

(5) (a) Knox, L. H.; Cross, A. D.; Velarde, E. *J. Am. Chem. Soc.* **1963**, *85*, 2533. (b) Knox, L. H.; Velarde, E.; Cross, A. D. *J. Am. Chem. Soc.* **1965**, *87*, 3727. (c) Mukharji, P. C.; Ganguly, A. N. *Tetrahedron* **1969**, *25*, 5281. (d) Tadanier, J.; Hallas, R.; Martin, J. R. *J. Org. Chem.* **1969**, *34*, 3837. (e) Bentley, P. H.; Edwards, J. A.; Todd, M.; Mccrae, W.; Maddox, M. L. *Tetrahedron* **1972**, *28*, 1411.

(6) (a) Tian, W. S.; Lei, Z.; Chen, L.; Huang, Y. *J. Fluorine Chem.* **2000**, *101*, 305. (b) Chen, L.; Ding, K.; Tian, W. S. *Chem. Commun.* **2003**, 838.

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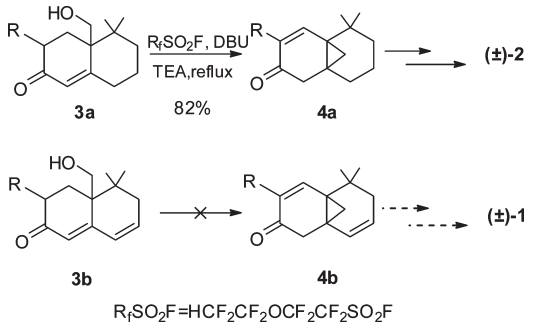
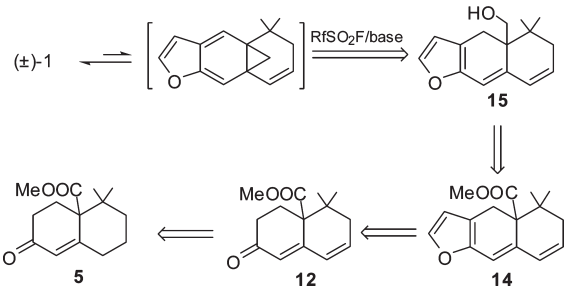
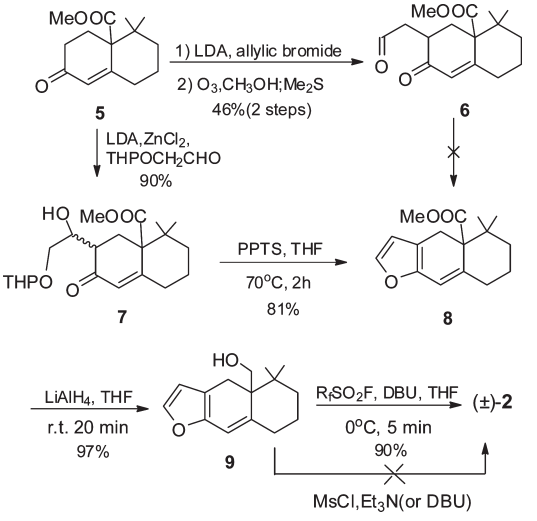
SCHEME 2. Novel Rearrangement Reaction and Influence of Additional Double Bond



SCHEME 3. Retrosynthetic Analysis



SCHEME 4. Synthesis of (±)-Dihydrospiniferin-1



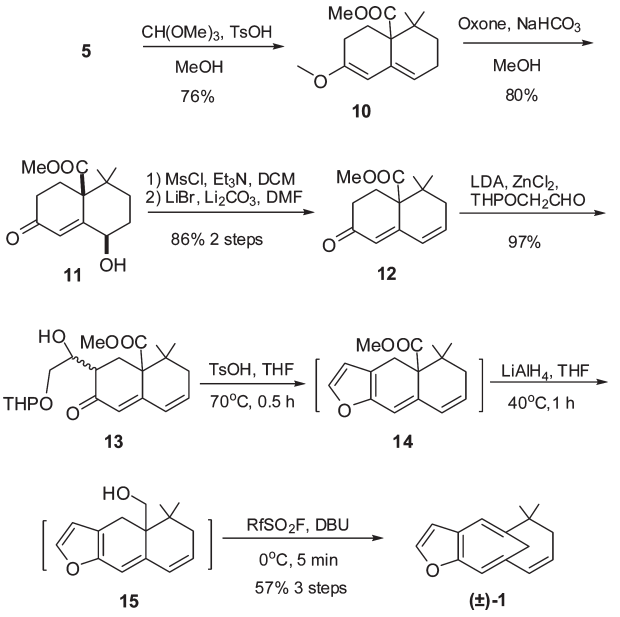
procedure[6b] to give 1,4-dicarbonyl compound **6**. However, all attempts to elaborate 2-vinyl furan **8** via the cyclization of **6** were fruitless due to the poor reactivity of α,β-unsaturated ketone.

Eventually, Hagiwara's furan synthesis method proved to be suitable for the construction of vinyl furan **8**.[7] Lewis acid catalyzed aldol addition of ketone **5** with $THPOCH_2CHO$ provided adduct **7** (a mixture of stereoisomers) in excellent yield (90%). Furan **8** was obtained from **7** in 81% isolated yield with PPTS under an inert atmosphere.

The reduction of **8** by lithium aluminum hydride in THF afforded **9** in 97% yield. Upon treatment of alcohol **9** with

(7) Hagiwara, H.; Uda, H. *J. Chem. Soc., Perkin Trans. 1* **1984**, 91.

SCHEME 5. Synthesis of (±)-Spiniferin-1



$HCF_2CF_2OCF_2CF_2SO_2F$/DBU in THF, the rearrangement reaction proceeded smoothly to provide (±)-dihydrospiniferin-1 in 90% yield. The rate of the rearrangement reaction was dramatically accelerated as the reaction was complete at 0 °C in less than 5 min! In contrast, the rearrangement reaction in our previous synthesis of (±)-**2** (Scheme 2, **3a**→**4a**) was completed at 70 °C for 8 h.[6b] Notably, common hydroxyl activating reagents, such as MsCl, did not initiate the rearrangement reaction.

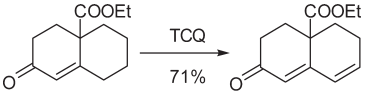
The highly concise route (four steps) and remarkable overall yield (63.6%) in this synthesis of (±)-**2** exhibited the feasibility of our new synthetic strategy. With the synthesis of model system achieved, the stage was now set for the synthesis of (±)-**1** (Scheme 5).

The synthesis began with the construction of the necessary dienone **12** from the readily available enone **5**. Unexpectedly, the classical methods, dehydrogenation with TCQ[8] or allylic bromination followed by elimination,[9] gave complex mixtures in low yields because of the flanking *gem*-dimethyl groups.[10] Eventually, a four-step procedure was developed to accomplish the dehydrogenation. Treatment of **5** with trimethyl orthoformate in the presence of TsOH afforded dienol ether **10** (76%). Oxidation of **10** with oxone[11] provided γ-hydroxyl enone **11** as a single diastereomer in 80% yield. Relative configuration of compound **11** was established by

(8) (a) Agnello, E. J.; Laubach, G. D. *J. Am. Chem. Soc.* **1957**, *79*, 1257. (b) Agnello, E. J.; Laubach, G. D. *J. Am. Chem. Soc.* **1960**, *82*, 4293.

(9) Akao, H.; Kiyota, H.; Nakajima, T.; Kitahara, T. *Tetrahedron* **1999**, *55*, 7757.

(10) Dehydrogenation processed smoothly in the absence of flanking *gem*-dimethyl.



(11) (a) Suryawanshi, S. N.; Fuchs, P. L. *J. Org. Chem.* **1986**, *51*, 902. (b) Chiu, C. K. F.; Govindan, S. V.; Fuchs, P. L. *J. Org. Chem.* **1994**, *59*, 311.

single-crystal X-ray analysis of its ester derivative.[12] The mesylation of **11** with $MsCl/Et_3N$ in CH_2Cl_2 followed by elimination with $LiBr/Li_2CO_3$ at 120 °C smoothly afforded dienone **12** in 86% yield.

Aldol reaction of the zinc enolate of **12** with $THPOCH_2CHO$ afforded the adduct **13** in 97% yield. Unfortunately, the cyclization of **13** was unsuccessful with PPTS due to the presence of the additional double bond. Treatment of **13** with a stronger acid (TsOH) afforded desired furan **14** in moderate yield (62%). Reduction of **14** with $LiAlH_4$ gave **15** in 58% yield. Speculation that furan **14** and **15** are labile during purification led to the development of a one-pot tactic. After heating **13** with TsOH for 0.5 h, $LiAlH_4$ was added directly and then wet Na_2SO_4 was added to destroy the excess reducing reagent. Then, the filtrate was directly treated with $HCF_2CF_2OCF_2CF_2SO_2F$/DBU to provide (±)-spiniferin-1 in 57% overall yield (3 steps). The ^1H and ^{13}C NMR data for synthetic (±)-**1** were in agreement with the reported values.[2a,3b] It is very interesting that pure (±)-**1** was stable upon standing in neutral $CDCl_3$ for several hours, while the solution of (±)-dihydrospiniferin-1 underwent oxidation and turned dark under the same condition.

In conclusion, total syntheses of (±)-**1** and (±)-**2** were accomplished on the basis of the polyfluoroalkanosulfonyl fluoride induced tandem carbocation rearrangement/electrocyclic ring-opening reactions. These efficient and short total syntheses of (±)-**1** in 28.9% overall yield (8 steps) and (±)-**2** in 63.6% overall yield (4 steps) are capable of providing substantial quantities of these rare substances for further biological studies, especially to determine their potential as anticancer agents. The syntheses of its analogues and further studies on their bioactivities are currently underway in our laboratory.

Experimental Procedures

Synthesis of Compound 7. To a THF solution of freshly prepared LDA (4 mmol, ~1 mol/L) was added ketone **5** (470 mg, 2 mmol in 2 mL THF) at −78 °C, and the resulting solution was stirred for 2 h. The $ZnCl_2$ (540 mg, 4 mmol) was added, and stirring was continued for 5 min before the addition of $THPOCH_2CHO$ (560 mg, 4 mmol). After 10 min, the reaction mixture was quenched with saturated NH_4Cl solution (10 mL) and diluted with CH_2Cl_2 (20 mL). The organic layer was collected, and the aqueous layer was extracted further with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the crude product by silica gel chromatography (90:10−75:25 petrol ether/ethyl acetate) recovered **5** (26 mg, 94% conversion) and afforded **7** as a colorless oil (640 mg, 90% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 5.7−6.1 (m, 1H), 4.4−4.7 (m, 1H), 3.6−3.7 (m, 3H), 0.8−1.0 (m, 6H). Anal. Calcd for $C_{21}H_{32}O_6$: C, 66.29; H, 8.48. Found: C, 65.99; H, 8.60.

Synthesis of Compound 8. To a solution of **7** (189 mg, 0.5 mmol) in THF (5 mL) was added PPTS (20 mg), and the mixture was refluxed for 2 h under an oxygen-free atmosphere. To the reaction mixture was added Et_3N, and it was concentrated in vacuo. Purification of the crude product by silica gel chromatography (pure petrol ether) afforded furan **8** as a colorless oil (105 mg, 81% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.16 (s, 1H), 6.24 (s, 1H), 6.23 (s, 1H), 3.61 (s, 3H), 3.25 (d, J = 16.4 Hz, 1H), 2.85 (d, J = 16.4 Hz, 1H), 2.6−2.8 (m, 1H), 2.37 (d, J = 15.3 Hz, 1H), 1.8−2.0 (m, 1H), 1.5−1.7 (m, 2H), 1.2−1.4 (m, 1H), 1.01 (s, 3H), 1.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.6, 149.1, 140.1, 136.9, 115.0, 114.2, 110.3, 56.2, 51.6, 37.5, 37.2, 32.4, 26.4, 26.3, 26.1, 21.0; HRMS(EI) m/z calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1416.

Synthesis of Compound 9. To a suspension of $LiAlH_4$ (40 mg, 1 mmol) in THF (5 mL) was added a solution of furan **8** (160 mg, 0.61 mmol) in THF (2 mL), and the resulting mixture was stirred for 20 min. The reaction mixture was quenched with wet Na_2SO_4 and then filtered. The filter cake was washed with additional THF (3 × 15 mL). The combined solution was concentrated in vacuo, and silica gel chromatography of the crude mixture (85:15 petrol ether/ethyl acetate) afforded furan **9** (138 mg, 97%) as a colorless solid (mp 105−108 °C): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.15 (d, J = 1.7 Hz, 1H), 6.37 (s, 1H), 6.17 (s, 1H), 4.19 (d, J = 10.3 Hz, 1H), 3.31 (t, J = 9.4 Hz, 1H), 3.00 (d, J = 17.7 Hz, 1H), 2.85 (d, J = 17.7 Hz, 1H), 2.4−2.6 (m, 1H), 2.1−2.3 (m, 1H), 1.5−1.9 (m, 3H), 1.2−1.4 (m, 2H), 0.96 (s, 3H), 0.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.4, 140.0, 137.9, 116.5, 114.8, 110.2, 68.5, 50.4, 38.9, 37.4, 32.2, 26.7, 24.9, 23.8, 23.7; HRMS (EI) m/z calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1463.

Synthesis of (±)-Dihydrospiniferin-1 (2). To a solution of furan **9** (23 mg, 0.1 mmol) in THF (2 mL) were added DBU (45 μL, 0.3 mmol) and $HCF_2CF_2OCF_2CF_2SO_2F$ (45 μL, 0.3 mmol). After 5 min, the reaction was complete as indicated by TLC. The reaction mixture was concentrated in vacuo, and silica gel chromatography of the crude mixture (100:0−90:10 petrol ether/ethyl acetate) afforded (±)-**2** (19 mg, 90%) as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34 (d, J = 2.0 Hz, 1H), 6.57 (dd, J = 2.0, 0.3 Hz, 1H), 6.30 (s, 1H), 6.29 (s, 1H), 3.15 (d, J = 11.0 Hz, 1H), 2.2−2.5 (m, 2H), 1.6−1.9 (m, 2H), 1.3−1.5 (m, 1H), 1.33 (s, 3H), 1.15 (d, J = 11.0 Hz, 1H), 1.06 (s, 3H), 0.6−0.9 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.2, 140.3, 132.5, 129.4, 125.3, 112.2, 110.0, 109.1, 42.0, 37.8, 36.7, 35.0, 29.2, 27.1, 25.8.

Synthesis of Compound 10. To a solution of ketone **5** (4.0 g, 17 mmol) in methanol (20 mL) were added trimethyl orthoformate (2.0 g, 19 mmol) and TsOH (40 mg), and the resulting mixture was stirred for 1 h. To the reaction mixture was added 1 mL Et_3N followed by concentration in vacuo. Purification of crude product by silica gel chromatography (95:5 petrol ether/ethyl acetate) afforded **10** (3.2 g, 76%) as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.52 (t, J = 3.8 Hz, 1H), 5.25 (s, 1H), 3.65 (m, 3H), 3.53 (s, 3H), 2.0−2.5 (m, 5H), 1.7−1.9 (m, 1H), 1.5−1.6 (m, 1H), 1.1−1.3 (m, 1H), 0.91 (s, 3H), 0.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 174.7, 156.0, 132.6, 121.4, 99.7, 54.3, 52.5, 51.5, 34.3, 33.7, 26.5, 26.3, 25.3, 23.2, 22.8. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.79; H, 9.04.

Synthesis of Compound 11. To a suspension of **10** (3.0 g, 12 mmol) and $NaHCO_3$ (2.1 g, 24 mmol) in methanol (50 mL) was added the saturated solution of oxone (6.4 g, 12 mmol) at room temperature. The reaction was complete once after the addition of oxone. The reaction mixture was filtered. The filtrate was diluted with diethyl ether and washed with water. The organic layer was concentrated in vacuo, and silica gel chromatography of the crude mixture (75:25 petrol ether/ethyl acetate) afforded **11** (2.4 g, 80%) as a white solid (mp 143−152 °C): ^1H NMR ($CDCl_3$, 400 MHz) δ 6.16 (s, 1H), 5.50 (d, J = 9.7 Hz, 1H), 4.24 (d, J = 9.5 Hz, 1H), 3.80 (s, 3H), 2.3−2.6 (m, 3H), 1.8−2.1 (m, 4H), 1.23 (dt, J = 13.6, 3.4 Hz, 1H), 0.97 (s, 3H), 0.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 198.9, 175.1, 157.8, 132.9, 70.6, 55.7, 52.8, 37.0, 35.9, 31.6, 28.9, 27.2, 26.4, 24.9. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.61; H, 7.90.

Synthesis of Compound 12. To a suspension of **11** (2.0 g, 8 mmol) in CH_2Cl_2 (50 mL) were added Et_3N (3.3 mmol, 24 mmol), DMAP (300 mg), and MsCl (1.2 mL, 16 mmol). After being stirred for 30 min, the reaction mixture was diluted with CH_2Cl_2 and washed with brine. The organic layer was dried over

(12) See Supporting Information.

by Na_2SO_4 and concentrated in vacuo to afford crude sulfonyl ester as a yellow oil. A mixture of the crude intermediate, LiBr (1.7 g, 20 mmol) and Li_2CO_3 (1.8 g, 20 mmol) in 10 mL of DMF was heated to 120 °C for 50 min. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and concentrated in vacuo, and silica gel chromatography of the crude mixture (90:10 petrol ether/ethyl acetate) afforded a light yellow oil (1.6 g, 86%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.29 (dd, J = 9.9, 2.7 Hz, 1H), 6.18 (ddd, J = 9.6, 6.1, 2.2 Hz, 1H), 5.84 (s, 1H), 3.67 (s, 3H), 2.2−2.6 (m, 4H), 1.9−2.1 (m, 2H), 1.06 (s, 3H), 0.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.3, 171.9, 154.8, 137.0, 129.2, 126.6, 53.7, 52.1, 40.7, 35.9, 35.6, 26.6, 25.0, 24.5; HRMS (EI) calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1241.

Synthesis of Compound 13. To a THF solution of fresh LDA (7 mmol, ~1 mol/L) was added **12** (750 mg, 3.2 mmol in 2 mL THF) at −78 °C, and the resulting solution was stirred for 2 h. $ZnCl_2$ (1.0 g, 7 mmol) was added, and stirring was continued for 5 min before the addition of $THPOCH_2CHO$ (1.0 g, 7 mmol). After 30 min, the reaction mixture was quenched with saturated NH_4Cl solution (10 mL) and diluted with CH_2Cl_2 (20 mL). The organic layer was washed with water and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the crude product by silica gel chromatography (90:10−75:25 petrol ether/ethyl acetate) recovered **12** (50 mg, 93% conversion) and afforded **13** as a colorless oil (1.1 g, 97% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.31 (dd, J = 9.8, 2.6 Hz, 1H), 6.22 (ddd, J = 9.6, 6.1, 2.2 Hz, 1H), 5.85 (s, 1H), 4.64 (dd, J = 4.5, 2.7 Hz, 1H), 3.68 (s, 3H), 1.09 (s, 3H), 0.96 (s, 3H). Anal. Calcd for $C_{21}H_{30}O_6$: C, 66.65; H, 7.99. Found: C, 67.11; H, 8.28.

Synthesis of (±)-Spiniferin-1 (1). To a solution of **13** (380 mg, 1 mmol) in THF (4 mL) was added TsOH (20 mg), and the reaction mixture was refluxed for 30 min under oxygen-free atmosphere. Then $LiAlH_4$ (120 mg, 3 mmol) and additional THF (4 mL) were added directly. After stirring for 1 h at 40 °C, the reaction mixture was quenched with wet Na_2SO_4 and filtered. The filter cake was washed with THF (3 × 5 mL). The combined filtrate was mixed with DBU (450 μL, 3 mmol) and $HCF_2CF_2OCF_2CF_2SO_2F$ (450 μL, 3 mmol). After 5 min, the reaction was complete as indicated by TLC. The reaction mixture was concentrated in vacuo, and silica gel chromatography of the crude mixture (99:1 petrol ether/ethyl acetate) afforded (±)-**1** (120 mg, 57% in 3 steps) as a colorless oil.

Compound **14:** colorless solid, mp 44−47 °C; ^{1}H NMR (acetone-d_6, 300 MHz) δ 7.37 (d, J = 1.8 Hz, 1H), 6.36 (d, J = 1.6 Hz, 1H), 6.32 (s, 1H), 6.28 (dd, J = 9.8, 2.9 Hz, 1H), 5.71 (ddd, J = 9.3, 6.4, 2.5 Hz, 1H), 3.52 (s, 3H), 3.35 (d, J = 16.0 Hz, 1H), 2.76 (d, J = 16.0 Hz, 1H), 2.26 (d, J = 17.7 Hz, 1H), 1.97 (dd, J = 17.7, 6.4 Hz, 1H), 1.09 (s, 3H), 1.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.3, 145.0, 141.4, 133.3, 129.3, 126.7, 117.6, 115.6, 110.8, 55.8, 51.9, 40.7, 35.7, 26.2, 25.6, 25.4; HRMS (ESI) calcd for $C_{16}H_{18}O_3Na$ 281.1154, found 281.1140.

Compound **15**: colorless oil; ^{1}H NMR (acetone-d_6, 300 MHz) δ 7.35 (d, J = 1.7 Hz, 1H), 6.30 (s, 1H), 6.19 (s, 1H), 6.11 (dd, J = 9.7, 2.8 Hz, 1H), 5.63 (ddd, J = 9.3, 6.0, 2.5 Hz, 1H), 3.72 (s, 1H), 3.71 (dd, J = 16.4, 6.0 Hz, 1H), 3.47−3.27 (m, 1H), 3.05 (d, J = 16.8 Hz, 1H), 2.75 (d, J = 16.8 Hz, 1H), 2.59 (d, J = 18.6 Hz, 1H), 1.94 (dd, J = 18.6, 6.0 Hz, 1H), 1.13 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (acetone-d_6, 75 MHz) δ 150.6, 142.0, 137.9, 129.9, 127.1, 117.4, 115.4, 112.4, 64.4, 48.7, 40.7, 36.6, 27.3, 25.3, 23.3; HRMS (ESI) calcd for $C_{15}H_{18}O_2Na$ 253.1204, found 253.1191.

(±)**Spiniferin-1:** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39 (d, J = 1.9 Hz, 1H), 6.64 (d, J = 1.7 Hz, 1H), 6.43 (s, 1H), 6.40 (s, 1H), 6.38 − 6.24 (m, 1H), 5.44 (ddd, J = 12.2, 8.8, 3.6 Hz, 1H), 3.69 (d, J = 10.7 Hz, 1H), 2.90 (dt, J = 16.3, 3.1 Hz, 1H), 2.10 (dd, J = 16.4, 8.8 Hz, 1H), 1.46 (s, 3H), 0.85 (s, 3H), 0.80 (d, J = 10.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.3, 141.2, 131.9, 130.3, 127.5, 125.2, 118.7, 112.5, 110.0, 109.4, 44.4, 39.7, 34.2, 30.8, 28.3.

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Supporting Information Available: Experimental procedures, copies of ^{1}H, ^{13}C NMR spectra, CIF file, and ORTEP drawing. This material is available free of charge via the Internet at http://pubs.acs.org.