

Synthesis and Characterization of Highly Fluorescent and Thermally Stable π -Conjugates involving Spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan][†]

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Spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan] was synthesized, and its π -conjugation was efficiently elongated using palladium-catalyzed C-H arylation of a furan moiety. The resulting π -conjugated compounds showed intense fluorescence and extremely high thermal stability.

Key Words: Fluorescence, Spiro compounds, Cross-coupling, Palladium

Introduction

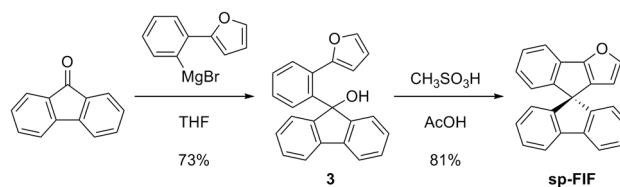
π -Conjugated heterocyclic arene oligomers have been widely investigated for use in organic electronic devices such as light-emitting diodes (LEDs), field-effect transistors (FETs), photovoltaic cells, and nonlinear optical devices.¹ In particular, oligothiophenes^{1,2} and thiophene/phenylene co-oligomers^{1b,3} are of great interest and have been intensively studied because of their excellent optical and electronic properties. However, the corresponding furan-containing π -conjugated compounds have been less explored because of their thermal instability,⁴ although they are expected to have highly fluorescent properties and good hole-transporting abilities.^{4a,c}

We have already reported the synthesis of spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]thiophene]⁵ and its derivatization by means of the Stille coupling reaction.⁶ The derivatives showed efficient photoluminescence in the blue or bluish green region, and high thermal stability. Although Stille coupling is one of the most powerful tools for the preparation of biaryl involving heteroarenes, the use of highly toxic organotin species is a major drawback. Thus, an alternative method for efficient extension of the π -system is highly desirable. In the past decade, direct arylation has emerged as a useful alternative to conventional methods for the construction of biaryl molecules.⁷⁻¹⁰

In this article, we report the first synthesis of spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan] (**sp-FIF**), and the preparation of its π -extended derivatives *via* palladium-catalyzed direct arylation, as well as photophysical, electrochemical, and thermal properties of the coupling products.

Results and Discussion

As shown in Scheme 1, **sp-FIF** was prepared in good yield by the two-step conversion of 9-fluorenone as a starting material. The reaction of a Grignard reagent, which was prepared from 1-bromo-2-furylbenzene, and 9-fluorenone gave alcohol **3** in 73% yield. The acid-mediated intramolecular Friedel-Crafts alkylation of **3** afforded **sp-FIF** in 81% yield. This is the first



Scheme 1. Synthesis of **sp-FIF**

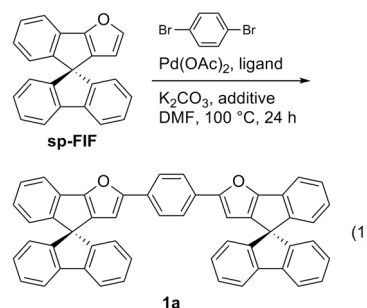


Table 1. The direct arylation of **sp-FIF**^a

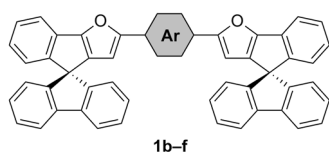
entry	ligand	additive	conv.(%) ^b	yield of 1a (%) ^b
1	PPh ₃	-	60	39
2	PCy ₃	-	85	53
3	PCy ₃	PivOH	100	53
4	PPh ₃	PivOH	100	84
5 ^c	PPh ₃	PivOH	4	trace

^aConditions: **sp-FIF** (0.2 mmol), *p*-dibromobenzene (0.1 mmol), Pd(OAc)₂ (5 mol %), ligand (10 mol %), K₂CO₃ (0.4 mmol), additive (30 mol %), DMF (1 mL). ^bBased on **sp-FIF**. ^cPivOH (100 mol %).

synthesis of spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan].

We next investigated the direct C-H arylation of a furan moiety of **sp-FIF** with *p*-dibromobenzene to extend the π -conjugation (eq 1). Results are summarized in Table 1. When **sp-FIF** (0.2 mmol) was treated with *p*-dibromobenzene (0.1 mmol) in the presence of Pd(OAc)₂ (0.01 mmol) and PPh₃ (0.02 mmol) using K₂CO₃ (0.4 mmol) as a base in DMF at 100 °C for 24 h, the coupling product **1a** was obtained in 39% yield with 60% conversion of **sp-FIF** (entry 1). Although the use of PCy₃ as a ligand

[†]This paper is dedicated to Professor Sunggak Kim on the occasion of his honorable retirement.

Table 2. Synthesis of furan-containing π -conjugated compounds **1b-1f**

entry	aryl dibromide	product	yield (%) ^b
1		1b	82
2		1c	59
3		1d	32 (46) ^c
4		1e	25
5 ^d		1f	21

^aConditions: **sp-FIF** (0.2 mmol), aryl dibromide (0.1 mmol), Pd(OAc)₂ (5 mol %), PPh₃ (10 mol %), K₂CO₃ (0.4 mmol), PivOH (30 mol %), DMF (1 mL), 100 °C, 24 h. ^bBased on **sp-FIF**. ^c**sp-FIF** (0.4 mmol) was used. ^d48 h.

afforded **1a** in better yield, the selectivity of **1a** was still low. When substoichiometric amounts of pivalic acid,¹⁰ which has been widely used in direct arylation recently, were added to the reaction using PCy₃ (entry 3), the yield was not increased in spite of complete conversion of **sp-FIF**. It was interesting to observe that the use of PPh₃ as a ligand instead of PCy₃ dramatically improved the yield of **1a** (entry 4). However, the addition of stoichiometric amounts of pivalic acid inhibited the reaction, which indicates that the amount of pivalic acid is important in this cross-coupling reaction (entry 5).

With the optimized conditions, several aryl dibromides were employed to prepare furan-containing π -conjugated compounds bearing various types of linker (Table 2). 4,4'-Dibromobiphenyl and 2,7-dibromo-9,9-dimethylfluorene showed comparable reactivity with *p*-dibromobenzene and produced coupling products **1b** and **1c**, respectively, in good to moderate yield (entries 1 and 2). In contrast, lower yields were observed in the cases of heteroaryl dibromides (entries 3-5). The yield of **1d** was increased to 46% when an excess amount of **sp-FIF** (0.4 mmol) was used (entry 3).

Photophysical, electrochemical, and thermal properties of **1a-1f** are summarized in Table 3. All of the prepared compounds showed intense blue or green fluorescence and high quantum yield (Φ_F) (up to 89%) compared with previously reported thiophene analogues of **1**.⁶ In particular, **1a-1c** with an aromatic hydrocarbon as a linker showed intense fluorescence at about 430 nm. The low Φ_F of **1d** was because of the internal heavy atom effect of the sulfur atom in thiophene.

Coupling products **1a-1d** showed two reversible oxidation potentials in cyclic voltammetry experiments. Comparing **1b** with **1a**, oxidation potential increased and absorption spectrum was broad and slightly blue-shifted because of the twisted nature of the biphenyl moiety. In the case of dimethylfluorene as a linker, the oxidation potential decreased because of effective elongation of the π -system. On the other hand, introducing five-membered heteroarenes, such as furan and thiophene, resulted in a red shift of absorption and emission spectra, as well as a decrease of oxidation potentials.

Thermogravimetry analysis and differential scanning calorimetry showed that all compounds **1a-1f** possess extremely high thermal stability because of the rigidity of the spirofluorene structures.¹¹ To the best of our knowledge, Luh and coauthors reported the most thermally stable furan-containing π -conjugated compounds without spiro linkages.^{4a} The series of compounds **1** in the present study showed higher glass-transition temperatures (T_g) and decomposition temperatures (T_d) by about 100 °C. This should be advantageous for application in light-emitting devices.

Conclusion

In summary, we have synthesized the furan-containing spiro compound **sp-FIF** and demonstrated the efficient palladium-catalyzed direct arylation of **sp-FIF** leading to several π -extended molecules. These compounds possess unique properties, such as intense photoluminescence and extremely high thermal stability. The application of these spiro compounds in light-emitting devices is now in progress in our laboratory.

Experimental Section

General. Unless otherwise specified, all reagents were purchased from a chemical supplier and used without further purification. Tetrahydrofuran (THF) was distilled over benzophe-

Table 3. Photophysical, electrochemical, and thermal properties of **1a-1f**

	λ_{abs} (nm) ^a	ϵ ($\times 10^4$ L mol ⁻¹ cm ⁻¹)	λ_{em} (nm) ^b	Φ_F ^c	$E_{1/2 \text{ oxd}}$ (V) ^d	T_g (°C) ^e	T_d (°C) ^f
1a	396, 420	4.81, 4.02	429, 456	0.87	0.45, 0.71	202	392
1b	390	6.28	432, 459	0.89	0.57, 0.68	182	407
1c	401, 425	7.90, 7.40	434, 462	0.89	0.46, 0.62	191	352
1d	426	5.12	468, 500	0.43	0.31, 0.61	182	383
1e	406, 432	5.36, 3.86	440, 470	0.80	0.30, 0.60	181	380
1f	348, 369	3.56, 4.14	400	0.61	0.89 ^g , 1.09 ^g	- ^h	414

^a $c = 1.00 \times 10^{-5}$ M (in THF). ^b $c = 1.00 \times 10^{-7}$ M (in THF). Excited at absorption maxima. ^cDetermined by the calibrated integrating sphere system. ^dIn CH₂Cl₂ containing 0.10 M Bu₄NPF₆ vs. Fc/Fc⁺ at 100 mV s⁻¹. ^eGlass-transition temperature obtained from differential scanning calorimetry (DSC) measurement. ^fDecomposition temperature (5% weight loss) obtained from thermogravimetric analysis (TGA). ^gIrreversible. ^hNot determined.

none ketyl under nitrogen atmosphere. *N,N*-Dimethylformamide (DMF) was distilled over MS4A under nitrogen atmosphere. Melting points are uncorrected. ^1H and ^{13}C spectra were recorded on a JEOL AL-300 (300 MHz for ^1H , and 75.5 MHz for ^{13}C) instrument. IR spectra were obtained on a JASCO 460 plus FT/IR spectrometer. Mass spectra were measured with a JEOL JMS-SX102A. Analytical thin-layer chromatography (TLC) was performed on Merck 60F254 silica plates and visualized by UV light. Column chromatography was carried out on Silicycle SilicaFlash F60 60 - 63 μm (230 - 400 mesh) silica gel. UV-visible absorption spectra were recorded on a JASCO V-570 UV-vis-NIR spectrometer. Emission spectra were measured with a Jobin Yvon-Horiba FluoroMax-3. Degassed spectral grade solvents were used for the measurements. Absolute fluorescence quantum yields were determined by the calibrated integrating sphere system. Cyclic voltammetry (CV) was performed on a BAS ALS 610C-S electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a Ag/AgNO₃ reference electrode. The measurement was carried out under argon atmosphere using CH₂Cl₂ solutions of samples (1 mM) and 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as a supporting electrolyte with a scan rate of 100 mV s⁻¹. The redox potentials were calibrated with ferrocene as an internal standard. Differential scanning calorimetry (DSC) was performed on a Rigaku Thermo plus EVO DSC 8230 under nitrogen atmosphere at a heating rate of 20 °C min⁻¹. Thermogravimetric analysis (TGA) was carried out on a Rigaku TG-8120 under nitrogen atmosphere at a heating rate of 10 °C min⁻¹.

9-(2-(2-Furyl)phenyl)fluoren-9-ol (3): A solution of 2-(2-bromophenyl)furan¹² (10.5 g, 47.2 mmol) in THF (50 mL) was added dropwise to Mg (1.15 g, 47.2 mmol). The mixture was stirred for 40 min at room temperature. To the solution, 9-fluorenone (6.54 g, 36.3 mmol) in THF (30 mL) was added over 20 min and stirred at room temperature for 1 h. The reaction mixture was quenched with saturated aqueous solution of NH₄Cl (100 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with brine (2 × 50 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ (EtOAc-hexane, 1:20), followed by recrystallization from EtOAc-hexane (1:2) to give **3** (8.65 g, 73%) as a pale yellow solid; mp 114.0 - 114.8 °C. IR (KBr) 733, 762, 774, 917, 1003, 1020, 1155, 1447, 3016, 2058, 3531 cm⁻¹. ^1H NMR (300 MHz, CDCl₃) δ 2.42 (s, 1 H), 5.21 (s, 1 H), 5.88 (s, 1 H), 6.78 (s, 1 H), 7.13-7.28 (m, 7 H), 7.32 (dd, J = 7.3, 7.3 Hz, 1H), 7.46 (d, J = 7.7 Hz, 2H), 7.51 (dd, J = 7.3, 7.3 Hz, 1H), 8.24 (d, J = 7.3 Hz, 1H). ^{13}C NMR (75.5 MHz, CDCl₃) δ 82.8, 108.2, 110.0, 119.9, 124.1, 127.0, 127.3, 128.0, 128.6, 128.8, 129.7, 132.3, 140.0, 141.4, 141.7, 150.6, 152.2. Anal. Calcd for C₂₃H₁₆O₂: C, 85.16; H, 4.97. Found: C, 85.19; H, 5.19.

Spiro[fluorene-9,4'-[4H]indeno[1,2-b]furan] (sp-FIF): To a solution of **3** (48.7 mg, 0.150 mmol) in AcOH (4 mL) was added CH₃SO₃H (0.2 mL), and the solution was stirred at room temperature for 30 min. The reaction mixture was quenched with cold saturated aqueous solution of NaHCO₃ (15 mL) and extracted with CHCl₃ (3 × 5 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO₃ (2 ×

15 mL) and brine (15 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ (hexane) to give **sp-FIF** (37.3 mg, 81%) as a pale yellow solid; mp 106.7-107.2 °C. IR (KBr) 701, 734, 747, 762, 1443, 3061, 3145 cm⁻¹. ^1H NMR (300 MHz, CDCl₃) δ 6.09 (d, J = 1.8 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 6.85 (d, J = 7.7 Hz, 2H), 6.92 (dd, J = 7.3, 7.7 Hz, 1H), 7.13 (dd, J = 7.3, 7.7 Hz, 2H), 7.24 (dd, J = 7.3, 7.7 Hz, 1H), 7.36 (dd, J = 7.3, 7.7 Hz, 2H), 7.47 (d, J = 1.8 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 7.7 Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl₃) δ 59.4, 107.6, 116.6, 120.0, 123.6, 123.8, 125.6, 127.4, 127.7, 127.8, 132.8, 133.2, 141.8, 146.3, 146.5, 152.5, 160.1. HRMS (FAB): calcd for C₂₃H₁₅O (M+H⁺), 307.1123, Found 307.1126.

A typical procedure for Pd-catalyzed direct arylation of sp-FIF: A flame dried Schlenk flask was charged with phosphines (0.020 mmol), **sp-FIF** (61.3 mg, 0.200 mmol), aryl dibromides (0.100 mmol), Pd(OAc)₂ (2.3 mg, 0.010 mmol), K₂CO₃ (55.3 mg, 0.400 mmol), pivalic acid (6.2 mg, 0.061 mmol), and DMF (1 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 24 h. The reaction mixture was cooled down to room temperature, diluted with CHCl₃, and filtered through a short silica gel pad. The residue was purified with column chromatography on SiO₂ (CHCl₃-hexane, 1:2) to afford the coupling product **1**.

1,4-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-b]furan-2-yl])benzene (1a): A yellow solid (84% yield); mp >300 °C. IR (KBr) 701, 729, 749, 817, 1283, 1445, 3060 cm⁻¹. ^1H NMR (300 MHz, CDCl₃) δ 6.41 (s, 2H), 6.60 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 7.3 Hz, 4H), 6.95 (dd, J = 8.1, 8.1 Hz, 2H), 7.15 (dd, J = 7.3, 7.7 Hz, 4H), 7.28 (dd, J = 7.0, 8.1 Hz, 2H), 7.38 (dd, J = 7.3, 7.7 Hz, 4H), 7.56 (d, J = 7.0 Hz, 2H), 7.67 (s, 4H), 7.84 (d, J = 7.7 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl₃) δ 59.5, 103.4, 116.6, 120.1, 123.7 (two peaks are overlapped), 123.8, 125.8, 127.6, 127.8, 127.9, 129.8, 133.0, 135.3, 141.9, 146.2, 152.3, 158.1, 159.9. HRMS (FAB): calcd for C₅₂H₃₁O₂ (M+H⁺), 687.2324, Found 687.2348.

4,4'-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-b]furan-2-yl])biphenyl (1b): A yellow solid (82% yield); mp > 300 °C. IR (KBr) 700, 730, 749, 810, 1105, 1445, 3059 cm⁻¹. ^1H NMR (300 MHz, CDCl₃) δ 6.44 (s, 2H), 6.60 (d, J = 7.3 Hz, 2H), 6.92 (d, J = 7.3 Hz, 4H), 6.95 (dd, J = 7.0, 7.3 Hz, 2H), 7.16 (dd, J = 7.3, 7.7 Hz, 4H), 7.29 (dd, J = 7.0, 7.3 Hz, 2H), 7.39 (dd, J = 7.3, 7.7 Hz, 4H), 7.58 (d, J = 7.0 Hz, 2H), 7.64 (d, J = 8.4 Hz, 4H), 7.73 (d, J = 8.1 Hz, 4H), 7.84 (d, J = 7.7 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl₃) δ 59.6, 103.1, 116.6, 120.1, 123.7, 123.8 (two peaks are overlapped), 125.8, 127.0, 127.6, 127.8, 127.9, 130.2, 133.1, 135.3, 139.0, 141.9, 146.2, 152.3, 158.1, 159.9. HRMS (FAB): calcd for C₅₈H₃₅O₂ (M+H⁺), 763.2637, Found 763.2623.

9,9'-Dimethyl-2,2'-bis(spiro[fluorene-9,4'-[4H]indeno[1,2-b]furan-2-yl])fluorene (1c): A yellow solid (59% yield); mp > 300 °C. IR (KBr) 701, 748, 817, 1291, 1445, 1464, 2922, 2958, 3059 cm⁻¹. ^1H NMR (300 MHz, CDCl₃) δ 1.51 (s, 6H), 6.46 (s, 2H), 6.61 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 7.3 Hz, 4H), 6.95 (dd, J = 7.3, 7.7 Hz, 2H), 7.15 (dd, J = 7.3, 7.7 Hz, 4H), 7.29 (dd, J = 7.3, 7.7 Hz, 2H), 7.38 (dd, J = 7.3, 7.7 Hz, 4H), 7.60 (d, J = 7.3 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.72 (s, 2H), 7.84 (d, J = 7.3 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl₃) δ 27.1, 46.9, 59.5, 102.8, 116.6, 117.6, 120.1, 120.3,

122.7, 123.7, 123.8, 125.7, 127.6, 127.8, 127.9, 130.1, 133.2, 135.4, 138.1, 141.9, 146.3, 152.3, 154.4, 158.9, 159.7. HRMS (FAB): calcd for $C_{61}H_{39}O_2$ ($M+H^+$), 803.2950, Found 803.2961.

2,5-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-b]furan-2-yl])thiophene (1d): An orange solid (32% yield); mp > 300 °C. IR (KBr) 701, 729, 748, 793, 1281, 1445, 3061, 3111 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 6.21 (s, 2H), 6.58 (d, $J=7.7$ Hz, 2H), 6.89 (d, $J=7.3$ Hz, 4H), 6.93 (dd, $J=7.3, 7.7$ Hz, 2H), 7.15 (s, 2H), 7.14 (dd, $J=7.3, 7.7$ Hz, 4H), 7.26 (dd, $J=7.3, 7.7$ Hz, 2H), 7.37 (dd, $J=7.3, 7.7$ Hz, 4H), 7.53 (d, $J=7.3$ Hz, 2H), 7.82 (d, $J=7.7$ Hz, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 59.5, 103.1, 116.7, 120.1, 123.0, 123.7, 123.8, 125.8, 127.6, 127.8, 128.0, 132.3, 132.8, 135.4, 141.9, 146.0, 152.3, 153.3, 159.5. HRMS (FAB): calcd for $C_{50}H_{29}O_2S$ ($M+H^+$), 693.1888, Found 693.1902.

2,5-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-b]furan-2-yl])furan (1e): A yellow solid (25% yield); mp > 300 °C. IR (KBr) 701, 728, 747, 778, 944, 1283, 1445, 3058, 3119 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 6.29 (s, 2H), 6.58 (d, $J=7.3$ Hz, 2H), 6.69 (s, 2H), 6.87 (d, $J=7.3$ Hz, 4H), 6.93 (dd, $J=7.3, 7.7$ Hz, 2H), 7.12 (dd, $J=7.0, 7.0$ Hz, 4H), 7.26 (dd, $J=7.3, 7.7$ Hz, 2H), 7.36 (dd, $J=7.3, 7.3$ Hz, 4H), 7.52 (d, $J=7.7$ Hz, 2H), 7.81 (d, $J=7.7$ Hz, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 59.4, 103.3, 107.3, 116.7, 120.1, 123.6, 123.8, 125.8, 127.6, 127.7, 127.9, 132.8, 135.0, 141.9, 145.7, 145.9, 150.1, 152.4, 159.7. HRMS (FAB): calcd for $C_{50}H_{28}O_3$ (M^+), 676.2038, Found 676.2065.

2,6-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-b]furan-2-yl])pyridine (1f): A white solid (21% yield); mp > 300 °C. IR (KBr) 702, 743, 801, 1281, 1445, 1518, 1566, 3057 cm^{-1} . 1H NMR (300 MHz, CD_2Cl_2) δ 6.56 (d, $J=7.3$ Hz, 2H), 6.72 (s, 2H), 6.82 (d, $J=7.7$ Hz, 4H), 6.97 (dd, $J=7.3, 7.7$ Hz, 2H), 7.11 (dd, $J=7.3, 7.7$ Hz, 4H), 7.30 (dd, $J=7.3, 7.7$ Hz, 2H), 7.35 (dd, $J=7.7, 7.7$ Hz, 4H), 7.59 (d, $J=8.1$ Hz, 2H), 7.60 (d, $J=7.3$ Hz, 4H), 7.77 (dd, $J=7.3, 7.3$ Hz, 1H), 7.82 (d, $J=7.7$ Hz, 4H). ^{13}C NMR analysis was not possible because of the very limited solubility. HRMS (FAB): calcd for $C_{51}H_{29}NO_2$ ($M+H^+$), 688.2277, Found 688.2263.

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