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Benzoxazole-Directed Halogen Dance of Bromofuran

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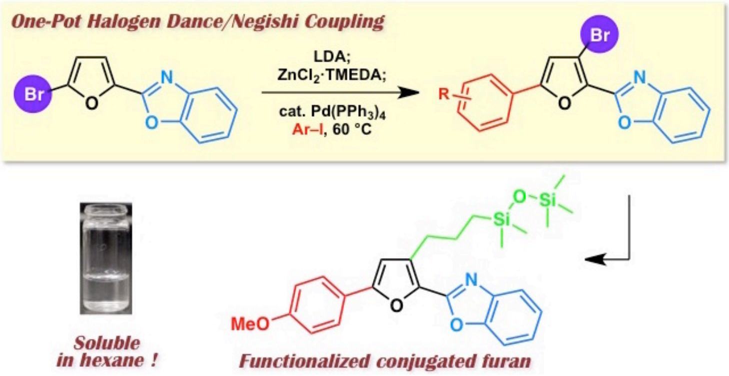

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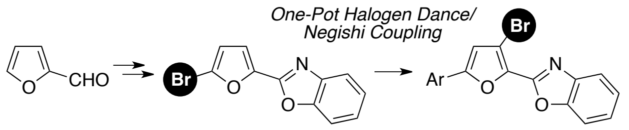
Abstract Halogen dance of benzoxazole-conjugated bromofuran derived from furfural is described. The reaction proceeds through a benzoxazole-directed lithiation to provide α-lithiofuran, which was subjected to Negishi coupling to give α-arylated benzoxazole-conjugated furan derivatives. The synthetic utility was demonstrated by transformation of the residual bromo group to a side chain bearing a siloxane moiety, which resulted in significant improvement of the solubility in organic solvents.

Key words halogen dance, one pot reaction, cross-coupling, furan, oxazole

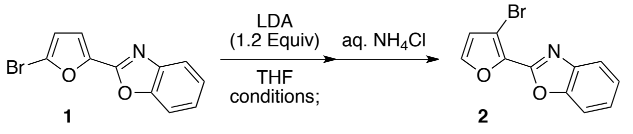
Conjugated aromatic compounds are one of the most important classes of organic materials.[1] Among them, oligo-/poly-thiophenes have been widely used as functional materials.[2] On the other hand, furans have been rarely investigated due to difficulty in handling (e.g. low solubility in organic solvents) and in functionalization regardless their promising properties such as heat resistancy.[3] Furfural (2-formylfuran), which is abundantly obtained by biomass, has attracted considerable attention as a furan skeleton and has been investigated as a biomass-derived resources.[4] We have recently reported synthesis of furfural-derived conjugated fluorescent materials through cross-coupling reactions.[5] But further extension of π-conjugation has proved problematic due to its low solubility. Very recently, we have also accomplished a rapid access to multiply arylated thiophenes by one-pot halogen dance/Negishi cross coupling.[6] Herein we report LDA-mediated halogen dance of a benzoxazole-conjugated furan and its application to improve solubility in organic solvents by further transformation of the residual bromo group to a silylated side chain (Scheme 1).



Scheme 1 Tactic for Synthesis of Conjugated Furans with Functional Groups

First, we explored the optimal reaction conditions for the halogen dance reaction of benzoxazole-conjugated bromofuran **1**[7] as a substrate (Table 1). In a preliminary experiment, the reaction of **1** took place with LDA as a base,[8] unlike the previous cases using a combination of LDA and KO*t*-Bu.[9] The bromo group migrated to the β-position adjacent to the benzoxazole moiety, indicating that the benzoxazole group played as a directing group in the lithiation.[10] After compound **1** was treated with LDA at −78 °C for 3 h, and the reaction was quenched with aqueous ammonium chloride to give the desired 2-(benzoxazoyl)-3-bromofuran (**2**), albeit incomplete conversion (Table 1, entry 1). Extensive optimization on reaction temperature showed that almost all the substrate **1** was consumed at above −70 °C for 3 h (Table 1, entries 2–5). But, poor mass balance was observed at −50 °C or −40 °C, indicating that the transient anion species were deteriorated at these temperatures[11] (Table 1, entries 4 and 5). Further screening of reaction temperature and reaction time realized that the yield of the desired product was improved up to 73% NMR yield[12] (64% isolated yield[13]) (Table 1, entries 6 –9).

Table 1 Optimization of Reaction Conditions for Halogen Dance

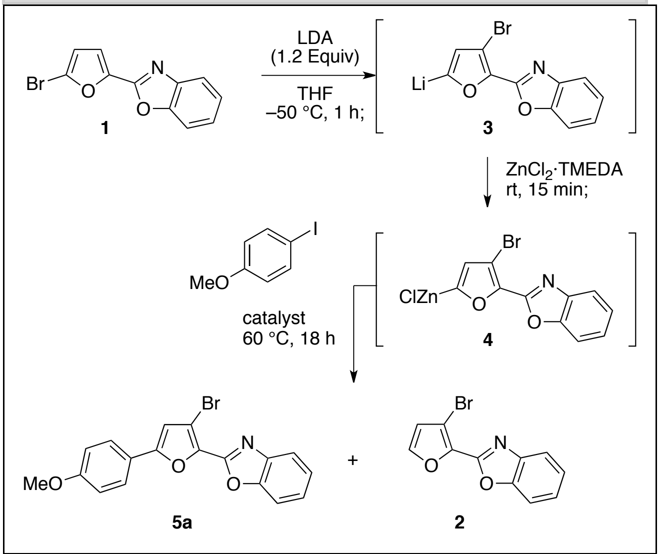


Entry	Temp (°C)	Time (h)	Substrate **1** (%)[a]	Product **2** (%)[a]
1	–78	3	25	45
2	–70	3	5	55
3	–60	3	2	49
4	–50	3	4	21
5	–40	3	7	7
6	–50	1	1 (–[b])	73 (64[c])
7	–50	0.5	2	70
8	–60	1	3	53
9	–60	0.5	6	63

[a] The Yield was determined from the ^{1}H NMR spectrum using 1,1,2,2-tetrachloroethane as an internal standard. [b] Not determined. [c] Isolated yield.

Having established the optimal conditions for the halogen dance, we then performed one-pot halogen dance/Negishi cross coupling[14] with *p*-iodoanisole (Table 2). After the halogen dance furnished at –50 °C for 1 h, the resultant α-lithiofuran **3** was transmetalated to zinc species **4** with $ZnCl_2$·TMEDA complex.[15] After stirring for 15 min, the reaction mixture was treated with $Pd_2(dba)_3$·$CHCl_3$ (2.5 mol%), PPh_3 (20 mol%), and *p*-iodoanisole at 60 °C for 18 h to give the desired coupling product **5a** in 55% yield. Trace amount of compound **2**, which should be formed by hydrolysis of transient anion species **3** and **4**, was observed in ^{1}H NMR of the crude material, suggesting that the coupling proceeded smoothly (Table 2, entry 1). Gratifyingly, the use of $Pd(PPh_3)_4$ resulted in significant improvement of the yield (Table 2, entry 2),[16] whereas the desired product **5a** was isolated in 13% yield with $Pd(Pt\text{-}Bu_3)_2$ (Table 2, entry 3).

Table 2 Catalyst Screening of One-Pot Halogen Dance/Negishi Coupling

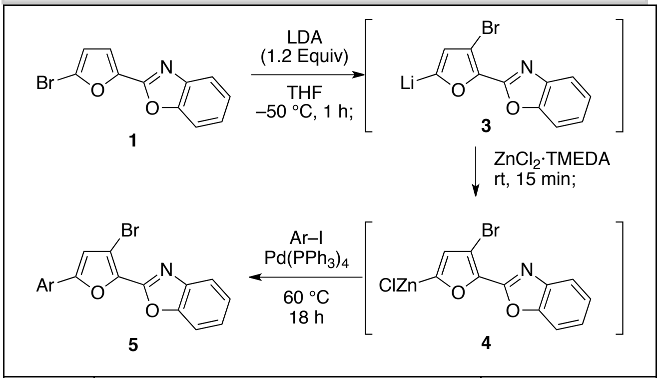


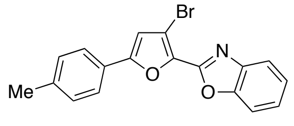
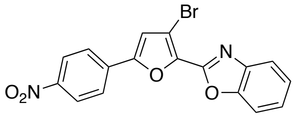
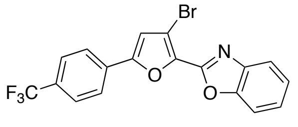
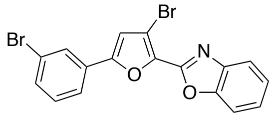
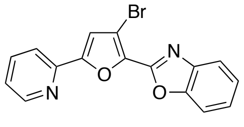
Entry	Catalyst	5a (%)[a]	2 (%)[a]
1	$Pd_2(dba)_3$·$CHCl_3$ (2.5 mol%) PPh_3 (20 mol%)	55	<1
2	$Pd(PPh_3)_4$ (5.0 mol%)	72 (60[b])	<1 (–[c])
3	$Pd(Pt\text{-}Bu_3)_2$ (5.0 mol%)	13	<1

[a] The Yield was determined from the ^{1}H NMR spectrum using 1,1,2,2-tetrachloroethane as an internal standard. [b] Isolated yield. [c] Not determined.

With the optimal conditions in hand, we then investigated substrate scope of aryl iodides in the halogen dance/Negishi coupling (Table 3).[17] In addition to an anisyl group, methyl, nitro, trifluoromethyl, and bromo groups were tolerated to provide the corresponding products **5b**–**5e** in moderate to good yields (Table 3, entries 1–4). A pyridyl group was also introduced to provide **5f** in 52% yield (Table 3, entry 5).

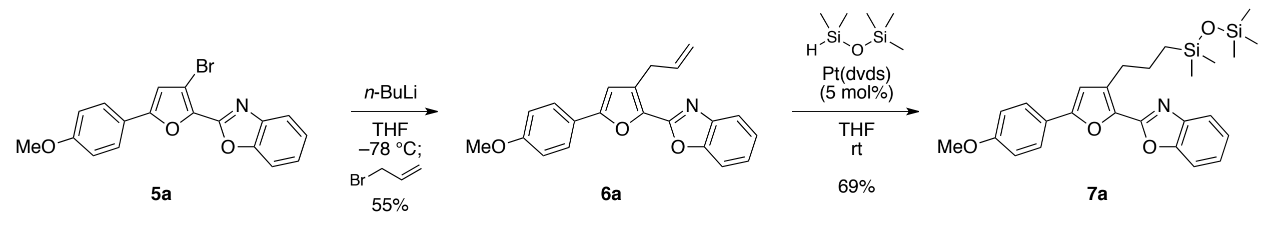
Table 3 Substrate Scope of the Aryl Group in the Cross Coupling Reaction



Entry	Product	Yield (%)[a]
1	 **5b**	50
2	 **5c**	58
3	 **5d**	58
4	 **5e**	75
5	 **5f**	52

[a] Isolated yield.

To demonstrate the synthetic utility of this method, we then focused on the transformation of the bromo group to a side chain bearing a siloxane moiety to improve the poor solubility in organic solvents (Scheme 2). Bromofuran **5a** were treated with *n*-BuLi followed by allyl bromide to give the corresponding allylfuran **6a** in 55% yield.[18] Subsequent hydrosilylation using Karstedt catalyst[19] provided the desired product **7a** in 69% yield.[20]



Scheme 2 Introduction of a side chain bearing a siloxane moiety

As we expected, the obtained benzoxazole-conjugated furan **7a** was found to dissolve even in hexane (1 mg/mL), whereas the related furan **5a** was hardly soluble even in diethyl ether.[21] These results of the solubility test indicated that the established halogen dance/Negishi coupling sequence provided a ubiquitous bromo group onto the β-position of the furan, which could be transformed to various functional groups.

In conclusion, we have developed one-pot halogen dance/Negishi cross coupling of bromofuran bearing benzoxazole moiety as a directing group and synthesized conjugated bromofurans. The bromo group was transformed to a siloxane-containing side chain, resulting in improving solubility in organic solvents. The migrated bromo group would be converted to various functional groups, which should become a powerful tool for controlling physical properties of such π-conjugated organic materials.

Acknowledgment

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Supporting Information

YES

Primary Data

NO

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A 30-mL test tube equipped with a Teflon-coated magnetic stirring bar was charged with the furylbenzoxazole (559 mg, 3.0 mmol, 1.0 equiv) and anhydrous THF (3.0 mL). To the resulting solution was added NBS (587 mg, 3.3 mmol, 1.1 equiv) potionwise at room temperature. After stirring at 60 °C for 2 h, additional NBS (161 mg, 0.90 mmol, 0.3 equiv) was added to the reaction mixture. The reaction mixture was stirred at 60 °C for 2 h, after which time TLC indicated complete consumption of the starting furylbenzoxazole. The reaction was quenched with saturated aqueous ammonium chloride, and the resulting mixture was partitioned with diethyl ether. The organic layer was washed with saturated aqueous ammonium chloride and water, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 5:1) to afford 2-(5-bromofuran-2-yl)benzo[*d*]oxazole (**1**) (650 mg, 2.45 mmol, 82%) as a beige solid, whose ^1H NMR spectra was identical to those reported in reference 7b. R_f = 0.30 (hexane/Et_2O = 5:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.79–7.73 (m, 1H), 7.59–7.53 (m, 1H), 7.40–7.34 (m, 2H), 7.22 (d, 1H, *J* = 3.4 Hz), 6.56 (d, 1H, *J* = 3.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 150.0, 144.2, 141.5, 126.6, 125.5, 125.0, 120.2, 116.3, 114.2, 110.6.

(8) Other directing groups such as oxazolines and imines gave only low yields/selectivities or none of the desired product.

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(10) The protons H-4 and H-5 on the furan ring both showed a vicinal coupling constant (2.0 Hz). The results suggest that the proton adjacent to the benzoxazole is first abstracted by the directing effect and that subsequent lithium-halogen exchange gives α-furyllithium species **3**. To the best of our knowledge, no example of halogen dance through directed lithiation has been reported so far.

(11) (a) Photo-induced/thermal rearrangement of 2-trimethylsilyl furan, see: Barton, T. J.; Hussmann, G. *J. Am. Chem. Soc.* **1983**, *105*, 6316. (b) Ringelberg, S. N.; Meetsma, A.; Troyanov, S. I.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 1759.

(12) **General procedure for halogen dance of bromofuran bearing benzoxazole**: A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with bromofuran (**1**) (132 mg, 0.50 mmol, 1.0 equiv) and anhydrous THF (3.3 mL). The solution was cooled to –50 °C. LDA (1.5 M, 0.40 mL, 0.60 mmol, 1.2 equiv) was added dropwise to the Schlenk tube and the resulting mixture was stirred at –50 °C for 1 h, at which time the dark red reaction mixture was treated with water (5 mL). After partitioned, the aqueous layer was extracted twice with diethyl ether (5 mL). The combined organic extracts were washed with water, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 10:1 to 5:1, gradient) to afford the corresponding product **2** (83.8 mg, 0.317 mmol, 64%) as a colorless solid. R_f = 0.33 (hexane/Et_2O = 5:1); M.p. 86–87 °C (hexane); IR (ATR, cm^{-1}): 2959, 2927, 1536, 1450, 1261, 1241,

1087, 1052, 1029, 1005, 977, 883, 797, 756, 744; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.80 (m, 1H), 7.64–7.58 (m, 2H), 7.43–7.35 (m, 2H), 6.71 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 150.1, 145.6, 141.5, 139.9, 125.8, 125.1, 120.6, 117.1, 110.9, 104.6; HRMS (DART$^+$) *m/z*: calcd. for $C_{11}H_7{}^{79}BrNO_2$, 263.9660 $[M+H]^+$; found, 263.9657.

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(16) Freshly prepared $Pd(PPh_3)_4$ was used.

(17) **General procedure for one-pot halogen dance/Negishi coupling**: A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with bromofuran (**1**) (132 mg, 0.50 mmol, 1.0 equiv) and anhydrous THF (3.3 mL). The solution was cooled to –50 °C. LDA (1.5 M, 0.40 mL, 0.60 mmol, 1.2 equiv) was added to the Schlenk tube and the resulting mixture was stirred at –50 °C for 1 h. To the dark red solution was added $ZnCl_2$·TMEDA complex (151.5 mg, 0.60 mmol, 1.2 equiv) at –50 °C. After stirring at room temperature for 15 min, *p*-iodoanisole (140.4 mg, 0.60 mmol, 1.2 equiv) and $Pd(PPh_3)_4$ (28.9 mg, 25 μmol, 5 mol%) were added to the solution. The resulting mixture was heated at 60 °C for 18 h, at which time the reaction mixture was treated with saturated aqueous ammonium chloride (5 mL). After partitioned, the aqueous layer was extracted twice with diethyl ether (5 mL). The combined organic extracts were washed with water and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 10:1) to afford the corresponding product **5a** (111.6 mg, 0.301 mmol, 60%) as a yellow solid. R_f = 0.19 (hexane/Et_2O = 5:1); M.p. 140–142 °C; IR (ATR, cm^{-1}): 1632, 1613, 1590, 1503, 1463, 1449, 1291, 1247, 1173, 1124, 1056, 1033, 1003, 920, 819, 801, 780, 735; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.81 (m, 1H), 7.76 (d, 2H, *J* = 9.2 Hz), 7.65–7.59 (m, 1H), 7.41–7.34 (m, 2H), 6.98 (d, 2H, *J* = 9.2 Hz), 6.80 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 156.8, 154.5, 150.0, 141.7, 138.0, 126.4, 125.4, 124.9, 121.3, 120.3, 114.4, 110.7, 110.2, 106.7, 55.4; HRMS (DART$^+$) *m/z*: calcd. for $C_{18}H_{13}{}^{79}BrNO_3$, 370.0079 $[M+H]^+$; found, 370.0066.

(18) **2-(3-Allyl-5-(4-methoxyphenyl)furan-2-yl)benzo[*d*]oxazole (6a)**: A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with bromofuran (105.1 mg, 0.284 mmol) and anhydrous THF (1.4 mL). To the solution was added *n*-BuLi (1.64 M in hexane, 208 μL, 0.341 mmol) dropwise at –78 °C. After stirring at –78 °C for 30 min, allyl bromide (49 μL, 0.57 mmol) was added to the resulting solution at –78 °C. After stirring at –78 °C for 30 min, the solution was warmed to room temperature. After stirring at room temperature for 2 h, the resulting mixture was treated with saturated aqueous ammonium chloride (3 mL). The mixture was partitioned between diethyl ether (3 mL) and aqueous ammonium chloride, and the aqueous layer was extracted twice with diethyl ether (3 mL). The combined organic extracts were washed with water, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/Et_2O = 10:1) to afford the corresponding product **6a** (51.6 mg, 0.156 mmol, 55%) as a yellow solid. R_f = 0.33 (hexane/Et_2O = 5:1); M.p. 93–95 °C; IR (ATR, cm^{-1}): 1628, 1612, 1562, 1532, 1511, 1491, 1453, 1303, 1252, 1244, 1175, 1032, 930, 919, 833, 805, 772, 745, 633; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.75 (m, 3H), 7.60–7.56 (m, 1H), 7.39–7.31 (m, 2H), 6.96 (d, 2H, *J* = 9.2 Hz), 6.64 (s, 1H), 6.07 (ddt, 1H, *J* = 16.8, 10.0, 6.4 Hz), 5.25 (dtd, 1H, *J* = 16.8, 2.0, 1.6 Hz), 5.16 (dtd, 1H, *J* = 10.0, 2.0, 1.6 Hz), 3.86 (s, 3H), 3.81 (d, 2H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 156.4, 156.2, 150.0, 142.0, 137.0, 135.6, 131.9, 126.4, 124.82, 124.79, 122.6, 119.9, 116.7, 114.4, 110.5, 108.0, 55.5, 30.2; HRMS (DART$^+$) *m/z*: calcd. for $C_{21}H_{18}NO_3$, 332.1287 $[M+H]^+$; found, 332.1302.

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(20) **2-(5-(4-Methoxyphenyl)-3-(3-(1,1,3,3,3-pentamethyldisiloxanyl)propyl)furan-2-yl)benzo[*d*]oxazole (7a)**: A 10-mL screw-top test tube equipped with a Teflon-coated magnetic stirring bar was charged with terminal alkene **6a** (33.1 mg, 0.10 mmol), disiloxane (24 μL, 0.12 mmol), and anhydrous THF (0.50 mL). To the solution was added Karstedt catalyst ((1,1,3,3-tetramethyl-1,3-divinyldisiloxane)platinum(0)) (2% w/w in xylene purchased from Aldrich, 2.2 μL, 0.1 μmol, 0.1 mol%) at room temperature. After stirring at room temperature for 24 h, the resulting mixture was treated with water. The mixture was partitioned between diethyl ether (2 mL) and water (2 mL) three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane to hexane/Et_2O = 5:1) to afford the corresponding product **7a** (33.2 mg, 0.069 mmol, 69%) as a pale yellow oil. R_f = 0.40 (hexane/Et_2O = 5:1); IR (ATR, cm^{-1}): 2956, 1613, 1563, 1532, 1492, 1453, 1251, 1175, 1036, 839, 804, 758, 745, 689, 667, 624; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.75 (m, 3H), 7.60–7.53 (m, 1H), 7.37–7.29 (m, 2H), 6.96 (d, 2H, *J* = 8.8 Hz), 6.63 (s, 1H), 3.86 (s, 3H), 3.03 (t, 2H, *J* = 7.6 Hz), 1.81–1.72 (m, 2H), 0.72–0.65 (m, 2H), 0.07 (s, 6H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 156.5, 156.2, 150.0, 142.1, 137.1, 134.5, 126.3, 124.7, 124.6, 122.8, 119.9, 114.3, 110.4, 107.9, 55.5, 29.2, 23.8, 18.4, 2.1, 0.5; HRMS (DART$^+$) *m/z*: calcd. for $C_{26}H_{34}NO_4Si_2$, 480.2026 $[M+H]^+$; found, 480.2025.

(21) For the detail, see Supporting Information.