



## Cascade cyclization of aryldiynes using iodine: synthesis of iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophene derivatives for dye-sensitized solar cells

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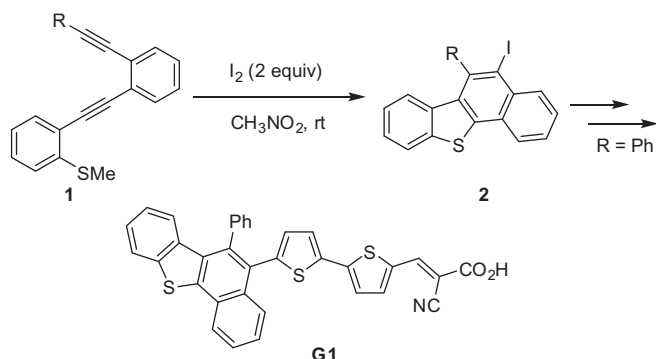
### ABSTRACT

A facile, efficient, and general synthetic method for iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophenes has been developed via a cascade cyclization of thioanisole-substituted aryldiynes using iodine. A new donor- $\pi$  linker-acceptor (D- $\pi$ -A) organic dye, **G1**, with the benzo[*b*]naphtho[2,1-*d*]thiophene moiety as an electron donor has been synthesized, and the performance of dye-sensitized solar cell based on **G1** has been investigated.

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Thiophene-fused polyheteroaromatic compounds have attracted increasing interest as organic semiconductors for various electronic device applications, such as organic field-effect transistors (OFETs), organic photovoltaic devices (OPVs), and organic light emitting diodes (OLEDs).<sup>1</sup> In contrast to the widely studied benzo[dithiophene, naphthodithiophene, and anthradithiophene derivatives as organic electronics,<sup>1a-c</sup> the scarcity of convenient and practical synthetic methods<sup>2</sup> restricts the applications of benzo[naphthothio]thiophene derivatives in the field of materials science. Recently, we and other groups proved that the cascade cyclization of aryldiynes was an efficient method to synthesize hetero-aryl[*a*]annulated carbazoles.<sup>3</sup> Moreover, it is well-known that the electrophilic iodocyclization of alkyne bound substrates is one of the alternatively powerful methods for the efficient synthesis of a variety of functionalized carbocycles and heterocycles having a mono- or di-iodo-substituent under very mild conditions.<sup>4-6</sup> Furthermore, the corresponding iodine-containing products can be readily converted to structurally interesting and elaborated compounds regioselectively through transition metal-catalyzed coupling reactions. Herein, we report a facile, efficient, and general method for the synthesis of iodo-substituted benzo[*b*]naphtho

[2,1-*d*]thiophenes using iodine-mediated cascade cyclization of thioanisole-substituted aryldiynes. Moreover, in the continuation of our interest in the development of dye-sensitized solar cells (DSCs) based on new organic dyes,<sup>7</sup> a new donor- $\pi$  linker-acceptor (D- $\pi$ -A) molecule, **G1**, with benzo[*b*]naphtho[2,1-*d*]thiophene moiety as an electron donor has been synthesized and applied in DSCs as a new organic dye (Eq. 1).



(1)

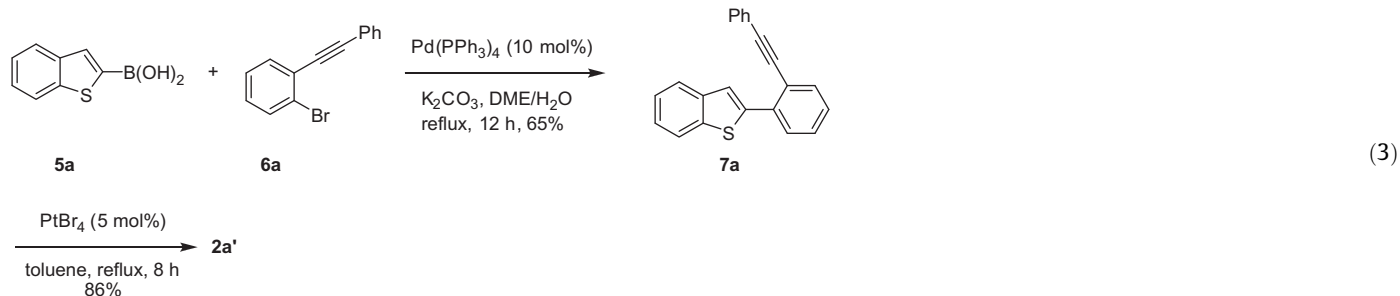
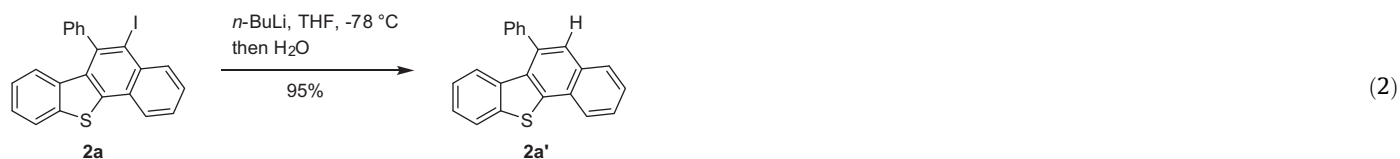
First we investigated the effect of solvents on the iodine-mediated cascade cyclization of the thioanisole-substituted aryldiyne **1a** for the formation of the 5-iodo-6-phenylbenzo[*b*]naphtho[2,1-*d*]thiophene **2a** as shown in Table 1. The use of polar solvents, such

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as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$ , and  $\text{CH}_3\text{NO}_2$  led to high yields of **2a** (entries 1–3). Among them,  $\text{CH}_3\text{NO}_2$  was the best solvent, giving **2a** in a 90% isolated yield (entry 3).<sup>8</sup> It is interesting to note that the use of less

corresponding product **2a'** in an 86% yield.<sup>10</sup> The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2a'** were completely consistent with the protonized product as shown in Eq. 2.



polar solvents such as THF and toluene, and protic solvent MeOH produced the first cyclization product, 3-iodo-substituted benzo[thiophene] **3a**, in good to high yields without the detection of **2a** (entries 4–6). These results indicated that the polar aprotic solvents should be favorable for the iodine activation of alkyne moiety in **3a** during the second cyclization (Scheme 1).

The scope and limitations of the iodine-mediated cascade cyclization of various aryldiynes **1**<sup>9</sup> using  $\text{CH}_3\text{NO}_2$  as a solvent were summarized in Table 2. The reactions of substrates **1b–e** bearing an electron-donating and an electron-withdrawing aromatic group at R produced the corresponding 5-iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophenes **2b–e** in high yields (entries 1–4). The presence of heterocycle, such as 3-thienyl group at R in substrate **1f** was also tolerated, giving the desired cascade cyclization product **2f** in an 88% yield (entry 5). It was noted that when R was substituted by an alkyl group, such as cyclohexyl in **1g**, a trace amount of the corresponding product **2g** was obtained (entry 6).

We carried out the following control experiments to gain the information of the present cascade reaction mechanism (Scheme 1). The reaction of **1a** under the standard conditions at  $0^\circ\text{C}$  for 7 min gave the expected 3-iodo-substituted benzo[thiophene] derivative **3a** in a 91% yield.<sup>5e</sup> Subsequently, treatment of the isolated substrate **3a** with the standard conditions at room temperature for 10 min gave the desired product **2a** in a 96% yield, suggesting that the present cascade cyclization must proceed through the formation of 3-iodo-substituted benzo[thiophene] **3a** followed by the sequential 6-*endo* cyclization.

The structures of the new 5-iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophene derivatives **2** were determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and high resolution mass analysis. Moreover, the iodine substituent in **2a** was further protonized by  $n\text{-BuLi}$  mediated deiodination (Eq. 2).  $^1\text{H}$  NMR spectrum of the corresponding product **2a'** clearly showed a new singlet peak at 6.67 ppm which was assigned to the 5-CH proton signal. **2a'** was further determined by the alternative synthetic way from the alkynyl-substituted benzo[thiophene] **7a** (Eq. 3). Suzuki coupling of benzo[*b*]thiophen-2-ylboronic acid **5a** and 1-bromo-2-(phenylethynyl)benzene **6a** afforded **7a** in a 65% yield.<sup>5f</sup> Treatment of **7a** with Furstner's Pt-catalyzed selective 6-*endo* hydroarylation of alkyne methodology gave the

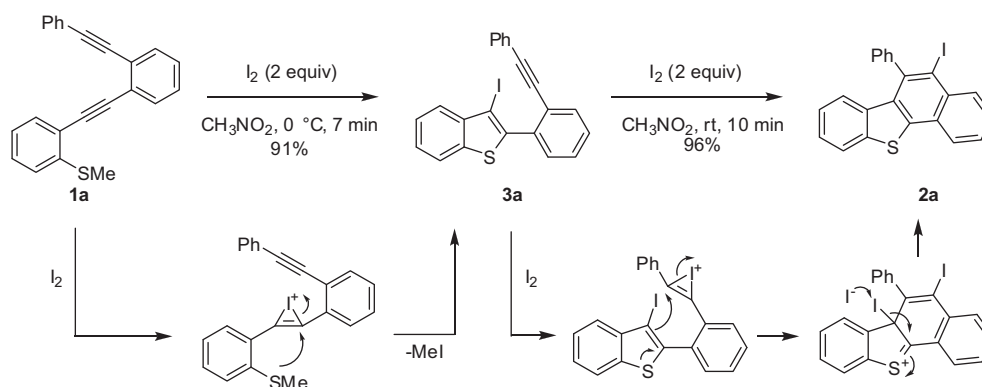
The general design principle for a metal-free organic dye in DSCs consists of three units such as a donor and acceptor bridged by a  $\pi$ -conjugation linker (D- $\pi$ -A) to realize the efficient charge transfer from a donor moiety to  $\text{TiO}_2$  conduction band through a  $\pi$ -bridge and acceptor moiety.<sup>11</sup> Thiophene units are one of the best moieties for the  $\pi$ -conjugate bridge because of their excellent charge transfer properties. In most cases a cyanoacrylic acid group is used as the acceptor moiety which is the best anchoring group to the  $\text{TiO}_2$  semiconductor. In the continuation of our interest in the development of new organic dyes based on DSCs,<sup>7</sup> we synthesized a new D- $\pi$ -A organic dye **G1** using benzo[*b*]naphtho[2,1-*d*]thiophene moiety as an electron donor, cyanoacrylic acid as an acceptor and bithiophene as a  $\pi$ -linker (Scheme 2). Pd-catalyzed coupling of 5-iodo-6-phenylbenzo[*b*]naphtho[2,1-*d*]thiophene **2a** and 2,2'-bithiophene-5-carbaldehyde through the direct C-H bond activation gave the corresponding aldehyde **4a** in a 35% yield.<sup>12</sup> Further condensation of **4a** with 2-cyanoacetic acid afforded the desired organic dye **G1** in a 78% yield.<sup>13</sup>

Figure 1a showed the UV/vis spectra of organic dye **G1** measured in chloroform solution. The absorption spectrum displayed a prominent band at 350–500 nm due to the  $\pi$ - $\pi^*$  transition of the conjugated molecule. Electrochemical propriety of **G1** was also investigated by cyclic voltammetry (CV) in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate (Fig. 1b). The calculated LUMO ( $-2.54$  eV) energy level of **G1** is sufficiently more positive than the conduction band of the nanocrystalline  $\text{TiO}_2$  ( $-4.2$  eV), which is energetically favorable for the efficient electron injection from the excited state into the conduction band of  $\text{TiO}_2$  in DSCs. In addition HOMO energy level ( $-5.53$  eV) is more negative than the redox potential of  $\text{I}^-/\text{I}_2^-$  ( $-5.20$  eV), ensuring the favorable dye regeneration.

A double-layer  $\text{TiO}_2$  photoelectrode ( $10 + 5$ )  $\mu\text{m}$  in thickness with a 10  $\mu\text{m}$  thick nanoporous layer and a 5  $\mu\text{m}$  thick scattering layer (area:  $0.25\text{ cm}^2$ ) was prepared by screen printing on a conducting glass substrate.<sup>7</sup> A dye solution of **G1** with  $3 \times 10^{-4}$  M concentration in acetonitrile/*tert*-butyl alcohol (1/1, v/v) was used to uptake the dye onto the  $\text{TiO}_2$  film. Deoxycholic acid (DCA) as a co-adsorbent was added into the dye solution to prevent the aggregation of the dye molecule. The  $\text{TiO}_2$  film was immersed into the dye solution for 30 h at  $25^\circ\text{C}$ . Photovoltaic measurements were

**Table 1**Optimisation of solvents for the formation of **2a**<sup>a</sup>

Entry	Solvent	<b>2a</b> , Yield <sup>b</sup> (%)	<b>3a</b> , Yield <sup>b</sup> (%)
1	CH <sub>2</sub> Cl <sub>2</sub>	84	0
2	CH <sub>3</sub> CN	86	0
3	CH <sub>3</sub> NO <sub>2</sub>	90 <sup>c</sup>	0
4	THF	0	85 <sup>d</sup>
5	Toluene	0	65 <sup>d</sup>
6	MeOH	0	75 <sup>d</sup>

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), I<sub>2</sub> (0.6 mmol), anhydrous solvents (0.04 M), room temperature, 20 min.<sup>b</sup> <sup>1</sup>H NMR yield was determined by using CH<sub>2</sub>Br<sub>2</sub> as an internal standard.<sup>c</sup> Isolated yield.<sup>d</sup> The reaction time was 5 h.**Scheme 1.** Control experiments for the cascade cyclization pathway.**Table 2**Iodine-mediated cascade cyclization of various thioanisole-substituted aryldiynes **1** for the formation of **2**<sup>a</sup>

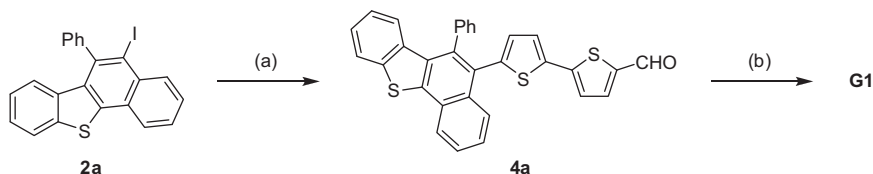
Entry	R	<b>1</b>	<b>2</b>	Yield <sup>b</sup> (%)
1	4-CN-C <sub>6</sub> H <sub>4</sub>	<b>1b</b>	<b>2b</b>	87
2	4-F-C <sub>6</sub> H <sub>4</sub>	<b>1c</b>	<b>2c</b>	85
3	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	<b>1d</b>	<b>2d</b>	90
4	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	<b>1e</b>	<b>2e</b>	85
5	3-Thienyl	<b>1f</b>	<b>2f</b>	88
6	Cyclohexyl	<b>1g</b>	<b>2g</b>	Trace <sup>c</sup>

<sup>a</sup> Reaction conditions: **1** (0.2 mmol), I<sub>2</sub> (0.6 mmol) in CH<sub>3</sub>NO<sub>2</sub> (0.04 M) at room temperature for 30 min.<sup>b</sup> Isolated yields.<sup>c</sup> Complex mixture with a trace amount of **2g**.

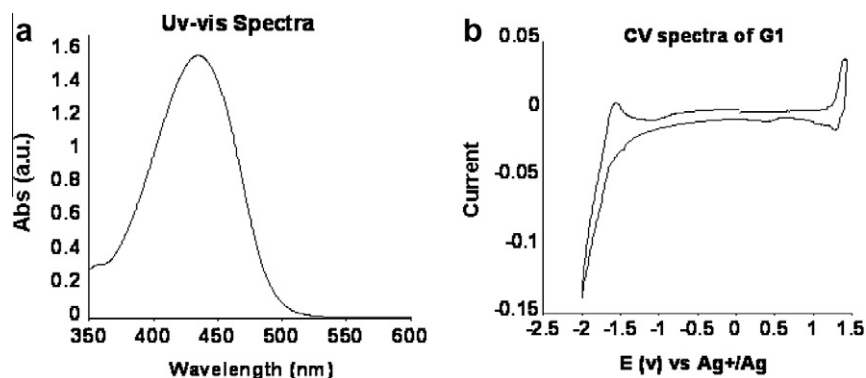
performed in a sandwich type solar cell in conjunction with an electrolyte consisting of a solution of 0.6 M dimethylpropylimidazolium

iodide (DMP<sup>+</sup>II), 0.5 M I<sub>2</sub>, 0.1 M LiI, and 0.5 M *tert*-butylpyridine (TBP) in acetonitrile. Photocurrent density–voltage (*I*–*V*) of the sealed solar cell was measured under AM 1.5G simulated solar light at a light intensity of 100 mW cm<sup>−2</sup> with a metal mask of 0.25 cm<sup>2</sup> (Fig. 2a). The photovoltaic parameters, that is, short circuit current (*J*<sub>sc</sub>), open circuit voltage (*V*<sub>oc</sub>), fill factor (*FF*), and power conversion efficiency (*η*), were estimated from *I*–*V* characteristic under illumination. The **G1** dye showed a *J*<sub>sc</sub> of 7.04 mA cm<sup>−2</sup>, *V*<sub>oc</sub> of 0.653 V, *FF* of 0.728, and a moderate power conversion efficiency (*η*) of 3.3%. However, the incident photon-to-current conversion efficiency (IPCE) for DSC based on **G1** showed a high sensitization of nanocrystalline TiO<sub>2</sub> from 350 to 500 nm with a maximum value of 84%, the lower sensitization in the infrared sensitive region resulted in the lower *J*<sub>sc</sub> and the moderate power conversion efficiency (*η*) (Fig. 2b).<sup>14</sup>

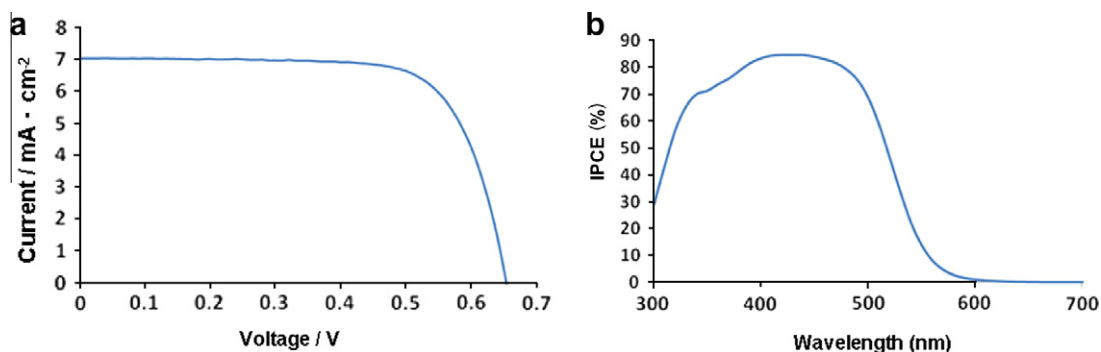
In conclusion, we have developed a facile, efficient, and general method for the synthesis of 5-iodo-substituted benzo[*b*]naphtho[2,1-*d*]thiophenes through the iodine-mediated cascade cyclization of the thioanisole-substituted aryldiynes. The corresponding iodo-substituted product **2a** was converted to the new organic dye **G1** with the benzo[*b*]naphtho[2,1-*d*]thiophene moiety as an electron donor, cyanoacrylic acid as an acceptor, and bithiophene as a *π*-linker. The DSC based on **G1** showed moderate overall conversion efficiency. Further molecular modifications of organic dyes with the benzo[*b*]naphtho[2,1-*d*]thiophene derivatives to broaden



**Scheme 2.** Synthesis of organic dye **G1**. (a)  $\text{Pd}(\text{OAc})_2$  (4 mol %),  $\text{PCy}_3\cdot\text{HBF}_4$  (8 mol %), pivalic acid (30 mol %), 2,2'-bithiophene-5-carbaldehyde (3 equiv),  $\text{K}_2\text{CO}_3$  (1.5 equiv), toluene, 100 °C, 2 days, 35%; (b)  $\text{NH}_4\text{OAc}$ , 2-cyanoacetic acid,  $\text{AcOH}$ , 100 °C, 6 h, 78%.



**Figure 1.** (a) UV-vis spectra of **G1** in chloroform. (b) CV spectra of **G1**.



**Figure 2.** (a) Current-voltage characteristics of DSC based on **G1**. (b) Photocurrent action spectra (IPCE) of the nanocrystalline  $\text{TiO}_2$  film sensitized by **G1**.

the absorption spectra for enhancing the light harvesting ability in the infrared region are in progress.

## Acknowledgment

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8. Representative experimental procedure for the synthesis of **2a** (Table 1, entry 3): To a solution of aryldiynes **1a** (0.2 mmol, 65 mg) in  $\text{CH}_3\text{NO}_2$  (0.04 M, 5 mL) was added  $\text{I}_2$  (2 equiv, 101.5 mg). The reaction mixture was stirred at room temperature for 20 min. A saturated sodium thiosulfate was then added into the reaction mixture. The organic layer was extracted with EtOAc, and dried over  $\text{Na}_2\text{SO}_4$ . After concentration of the filtrate, the residue was purified by chromatography on silica gel by column chromatography to afford the corresponding product **2a** in a 90% yield (78.5 mg) as a pale yellow solid; mp 146 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49–8.46 (m, 1H), 8.14–8.12 (m, 1H), 7.87 (d,  $J$  = 8.4 Hz, 1H), 7.68–7.63 (m, 5H), 7.37–7.33 (m, 3H), 7.08 (t,  $J$  = 8.0 Hz, 1H), 6.46 (d,  $J$  = 8.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  104.5, 122.4, 124.1, 124.6, 124.7, 125.7, 127.2, 128.1, 128.2, 128.9, 129.3, 131.4, 132.3, 134.3, 136.0, 138.6, 138.9, 142.5, 145.2; UV–vis ( $\text{CHCl}_3$ ): 253.0, 261.0, 285.0, 306.0, 326.0, 357.0 nm; HRMS (EI+) calcd for  $\text{C}_{22}\text{H}_{13}\text{SI}$ : 435.9783, found: 435.9790.
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13. Analytic data of **G1**: red solid, mp 205 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (s, 1H), 8.28 (d,  $J$  = 7.2 Hz, 1H), 8.13 (d,  $J$  = 7.2 Hz, 1H), 7.91 (d,  $J$  = 7.2 Hz, 1H), 7.76–7.72 (m, 4H), 7.50–7.44 (m, 8H), 7.41–7.34 (m, 2H), 6.39 (d,  $J$  = 8.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  116.5, 123.1, 123.9, 124.2, 124.3, 124.7, 126.1, 126.4, 126.8, 127.1, 127.2, 127.4, 127.7, 127.9, 128.4, 129.5, 130.1, 130.9, 131.7, 133.8, 135.8, 135.9, 137.6, 138.1, 138.3, 138.5, 140.5, 141.0, 144.9, 145.9, 163.3, 171.8; UV–vis/ $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ): 437 nm; HRMS (EI+) calcd for  $\text{C}_{33}\text{H}_{19}\text{NS}_3$  (M– $\text{CO}_2\text{H}$ ): 525.0680, found: 525.0681.
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