ISSN: 2472-3703 DOI: 10.6911/WSRJ.202408_10(8).0007

Design, Synthesis, and Potential Applications of a Novel Hydrophilic Fluorinated Monomer

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Abstract

Catechol and trifluorochloroethylene are two compounds with unique properties and advantages in applications. In this study, a novel hydrophilic fluorinated monomer was successfully synthesized by coupling a catechol derivative and trifluorochloroethylene, and the structure of the monomer was characterized. From the perspective of the monomer structure, it shows potential applications as pharmaceutical intermediates and biomedical polymers in hydrophilic drug design and biomedical materials. This article aims to explore the synthesis process, chemical structure, and possible application pathways of this new monomer.

Keywords

Catechol; Trifluorochloroethylene; Synthesis; Hydrophilicity; Fluorinated monomer.

1. INTRODUCTION

In the field of biomedical materials, hydrophobic materials often cause increased frictional resistance, which would lead to tissue damage such as blood vessels and trigger inflammation. In order to improve the compatibility of materials, hydrophilic polymer-modified medical devices are commonly used in clinical practice. The hydrophilicity of the materials will be increased by introducing hydrophilic groups to form stable hydration layers with water molecules. This hydration layer can prevent direct contact between bacteria and the material surfacetoreduce bacterial adhesion[1]. Furthermore, introducing hydrophilic groups can transform the material surface into a hydrophilic surface, giving it excellent water wetting properties. This hydrophilic surface can reduce non-specific adsorption of proteins,prevent bacterial attachment and biofilm formation, thereby reducing the risk of infection and inflammation and improving the performance and safety of biomedical materials[2].

Catechol, also known as o-dihydroxybenzene, possesses multifunctionality due to its catechol ring structure. On one hand, catechol can act as a weak acid and a redox agent with reactive properties. On the other hand, the presence of adjacent hydroxyl groups allows it to form coordination structures and hydrogen bonds. In addition, the lone pair electrons of the catechol group can accept hydrogen atoms from hydrogen donors and provide hydrogen atoms to other active groups. This indicates that catechol can undergo chemical or physical interactions with various substances, including hydrogen bonding, metal-catechol coordination bonds, π-π interactions, π-cation interactions, oxidative cross-linking, and electrostatic interactions[3–8]. Due to its ability to participate in a wide range of reversible interactions and the formation of covalent bonds, incorporating catechol into polymers imparts them with the chemical reactivity

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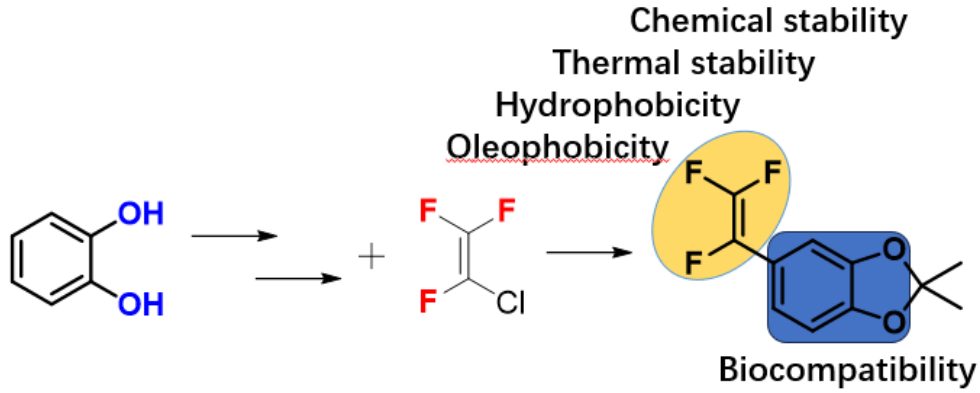
of catechol, allowing for the design of adhesives, antimicrobial coatings, drug carriers, and antimicrobial polymers, among other biomedical materials[9–13]. Furthermore, halogen-modified catechols have natural antimicrobial properties[14]. Catechol has hydrophilicity due to the presence of orthodihydroxy groups in its molecular structure. The catechol group can rotate freely and hydrogen bonds exhibit directionality, which allowthe catechol group to form stable hydrogen bonding with water molecules or other surfaces by adjusting its geometric configuration. In addition, catechol can form electrostatic attraction with water molecules, and its hydroxyl groups can undergo hydration reaction. Therefore, if catechol is introduced into other compounds, it can significantly alter their hydrophilicity[15, 16].

Fluorinated polymers have been widely utilized in the field of biomedical applications, encompassing gene, protein, and drug delivery, MRI imaging, antibacterial coatings, and tissue engineering, among others[17]. Trifluorochloroethylene possesses the strongest single bond with a bond energy of 485 kJ·mol-1, thanks to the highly electronegative fluorine atoms which tightly grip the three lone electron pairs[18]. This results in highly polarized and unreactive C-F bonds. Additionally, it exhibits significant ionic character, allowing it to interact with other substances through dipole-dipole or charge-dipole interactions[19]. Trifluorochloroethylene has played an important role in fields such as medicinal and materials chemistry, thanks to decades of development. One crucial aspect of studying its properties and applications is the modification of trifluorochloroethylene by substituting its chlorine atom with various functional groups, such as carboxylic acids[20–22], aromatic groups[23–25], pyridine[26], and thiols[27]. In the presence of bases and water, cross-coupling of CTFE with arylboronic acids via palladium catalysis allows the synthesis of α, β, β-trifluoroethylstyrene monomers [28]. Trifluorochloroethylene, an important fluorinated monomer, can be polymerized or copolymerized to produce fluorinated coatings, resins, rubbers, and chlorofluorinated lubricants. The resulting fluorinated materials generally exhibit excellent properties such as high temperature resistance, resistance to harsh chemical corrosion, durability, low surface energy, low dielectric constant, and low friction[29, 30], making them suitable for biomedical materials. Moreover, trifluorochloroethylene can also be used as a fluorinated intermediate for the synthesis of pharmaceuticals and agrochemicals. Trifluorochloroethylene, as a compound with unique properties and advantages, can be designed as a highly hydrophilic special fluorinated monomer (The thought is shown in Scheme 1) by introducing a catechol group. In theory, such highly hydrophilic fluorinated monomers will provide more possibilities in drug design and biomedical materials[31].



Scheme 1. thought and result

2. EXPERIMENTAL

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202408_10(8).0007

2.1. 2,2-dimethylbenzo[d][1,3]dioxole (2)

Under argon protection, catechol **1** (2.2g, 20mmol) was dissolved in dry toluene (20mL) and acetone at room temperature. Then, PCl_3 (1.7mL, 20mmol) was slowly added dropwise, and the reaction was allowed to continue at room temperature for 2 days. After the reaction was complete, potassium carbonate (6.9g, 50mmol) was added and stirred for 10 minutes. The mixture was filtered, and the precipitate was washed with dichloromethane. The organic phase was then washed with 10% NaOH (3×50mL). After drying with anhydrous sodium sulfate, the solvent was removed under reduced pressure at a temperature below 25°C. The residue was purified by column chromatography using petroleum ether as eluent to give 2.94g (98%) of compound **2**. ^{1}H NMR spectrum (600MHz, $CDCl_3$), δ, ppm: 1.68 (s, 6H, CMe_2), 6.77–6.73 (m, 2H), 6.81–6.77 (m, 2H); ^{13}C NMR spectrum (150MHz, $CDCl_3$), δ_C, ppm: 25.9 (C^8 and C^9), 108.5 (C^3 and C^6), 117.4 (C^7), 121.1 (C^1 and C^2), 147.3 (C^4 and C^5) {One carbon signal for CH_3 and three carbon signals for Ph overlapped}.(shown in Figure 1, 2)

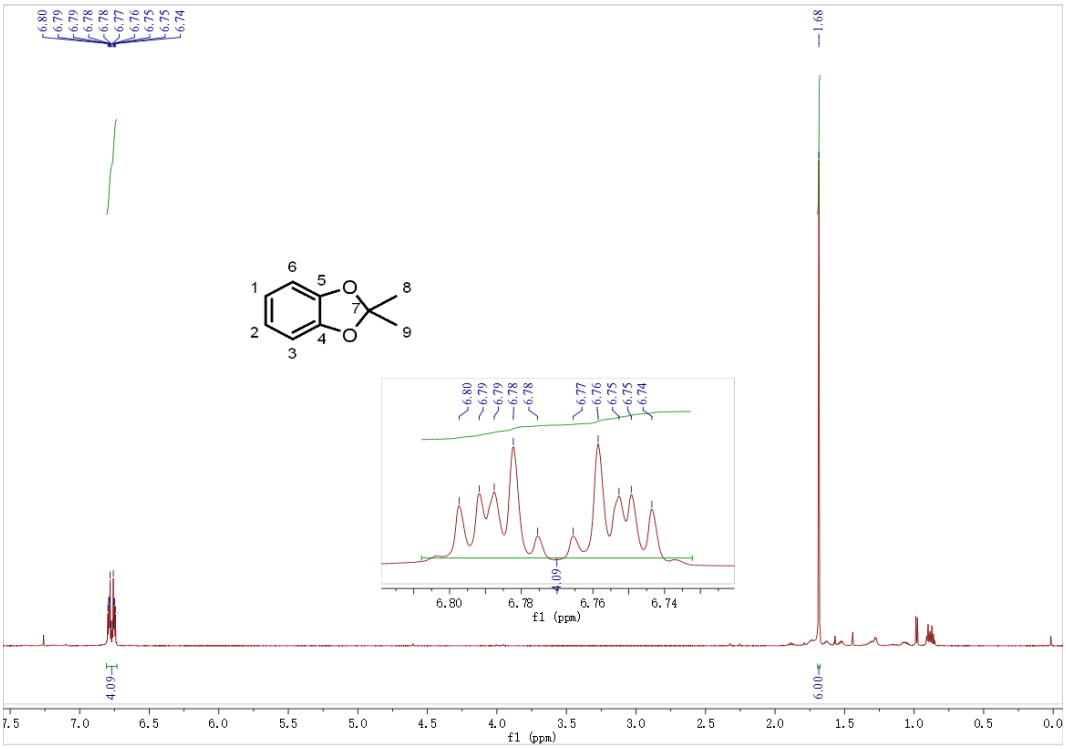


Figure 1. ^{1}H-NMR spectrum (600MHz, $CDCl_3$) of **(2)**: 2,2-dimethylbenzo[d][1,3]dioxole

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202408_10(8).0007

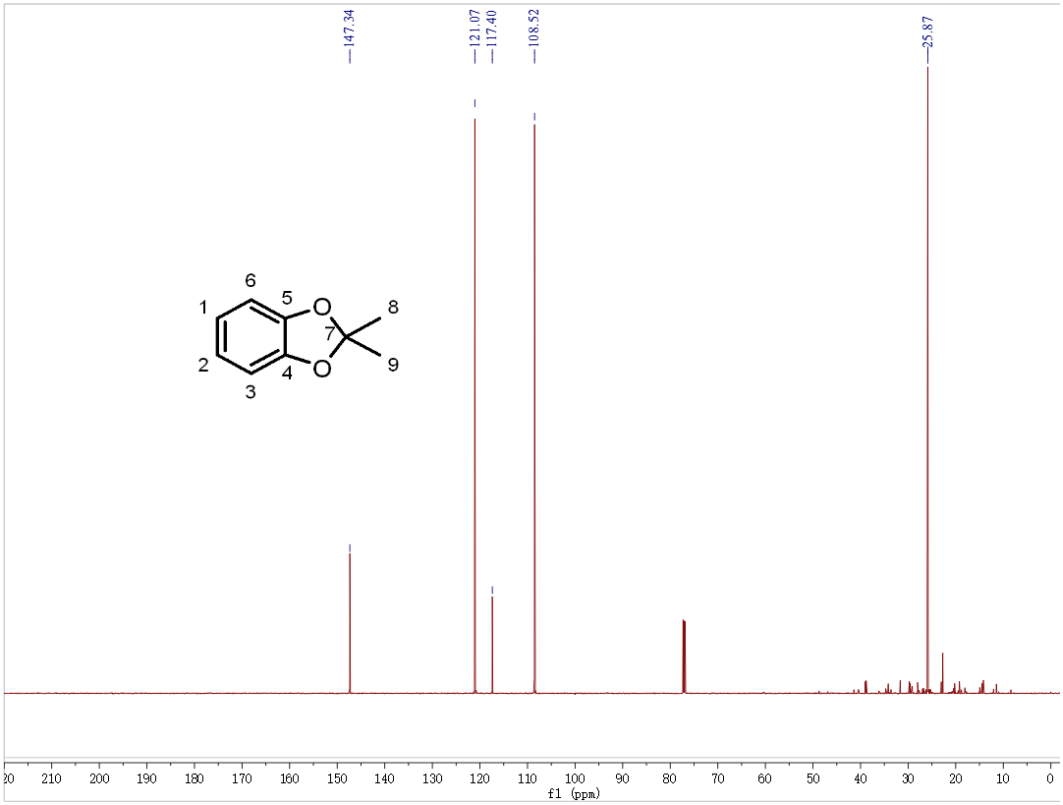


Figure 2. ^{13}C-NMR spectrum (150MHz, $CDCl_3$) of **(2)**: 2,2-dimethylbenzo[d][1,3]dioxole

2.2. 5-bromo-2,2-dimethylbenzo[d][1,3]dioxole (3)

Under argon protection, compound **2** (2.94g, 19.58mmol) was dissolved in dry DMF (20mL) along with NBS (2.77g, 23.50mmol) at room temperature. The reaction mixture was then heated at 35°C and allowed to react for 1 day. After the reaction was complete, saturated brine (50mL) was added, and the aqueous phase was extracted with ethyl acetate (3×30mL). The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure at a temperature below 25°C. The residue was purified by column chromatography using petroleum ether as eluent to give 4.22 g (94%) of compound **3**. ^{1}H NMR spectrum (600MHz, $CDCl_3$), δ, ppm: 1.67 (s, 6H, CMe_2), 6.60 (d, 1H, J = 7.8Hz), 6.86 (d, 1H, J = 1.8 Hz), 6.89 (dd, 1H, J = 7.8, 1.8 Hz); ^{13}C NMR spectrum (150MHz, $CDCl_3$), δC, ppm: 25.8 (C^8 and C^9), 109.4 (C^3), 112.1 (C^6), 112.4 (C^1), 118.9 (C^7), 123.6 (C^2), 146.8 (C^4), 148.4 (C^5) {One carbon signal for CH_3 overlapped}.(shown in Figure 3, 4)

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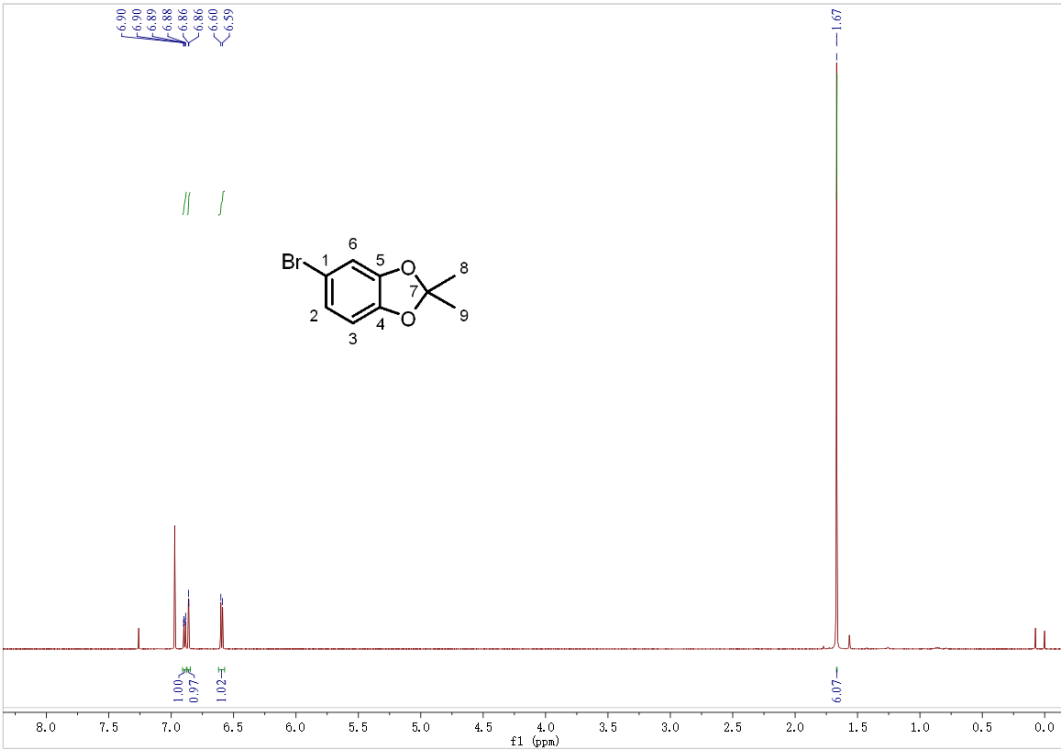

Figure 3. ^{1}H-NMR spectrum (600MHz, $CDCl_3$) of **(3)**: 5-bromo-2,2-dimethylbenzo[d][1,3]dioxole

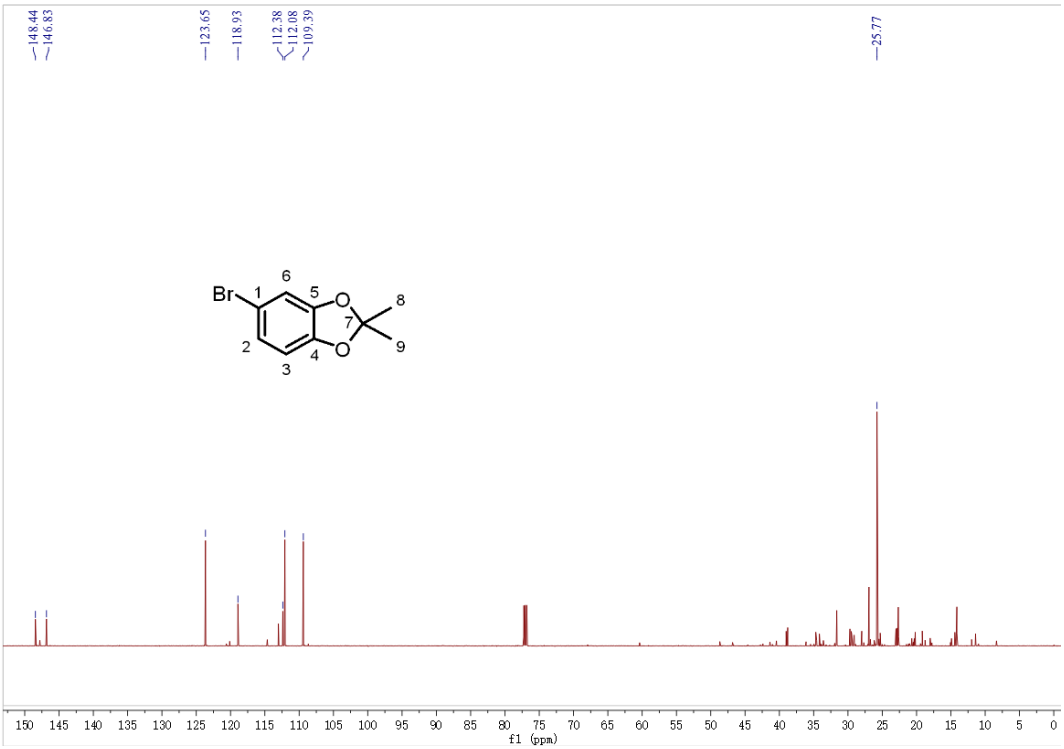

Figure 4. ^{13}C-NMR spectrum (150MHz, $CDCl_3$) of **(3)**: 5-bromo-2,2-dimethylbenzo[d][1,3]dioxole

2.3. 2-(2,2-dimethylbenzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202408_10(8).0007

Under argon protection, compound **3** (2.11g, 9.21 mmol), bis(pinacolato)diboron (2.81g, 11.05mmol), potassium acetate (2.71g, 27.63mmol), and the catalyst $PdCl_2$(dppf) (0.67g, 0.921mmol) were dissolved together in anhydrous DMSO (30mL). The reaction mixture was then refluxed at 80°C for 18 hours. After the reaction was complete, a sufficient amount of ice was added, and the mixture was stirred at room temperature for 30 minutes. The aqueous phase was extracted with ethyl acetate (3×30mL), and the organic phase was washed with saturated brine (60mL), dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography using petroleum ether as eluent to give 1.42g (56%) of compound **4**. ^{1}H NMR spectrum (600MHz, $CDCl_3$), δ, ppm: 1.32 (s, 12H), 1.66 (s, 6H), 6.74 (d, 1H, J = 7.8Hz), 7.16 (d, 1H, J = 0.6Hz), (7.32, dd 1H, J = 7.8, 0.6Hz); ^{13}C NMR spectrum (150MHz, $CDCl_3$), δ_C, ppm: 24.8 (C^{12}, C^{13}, C^{14} and C^{15}), 25.8 (C^8 and C^9), 83.6 (C^{10} and C^{11}), 108.2 (C^3 and C^6), 113.8 (C^1), 117.6(C^7), 129.2 (C^2), 147.1 (C^4), 150.1 (C^5) {Five carbon signals for CH_3， two carbon signals for $C(Me_2)$ and one carbon signal for Ph overlapped}. (shown in Figure 5, 6)

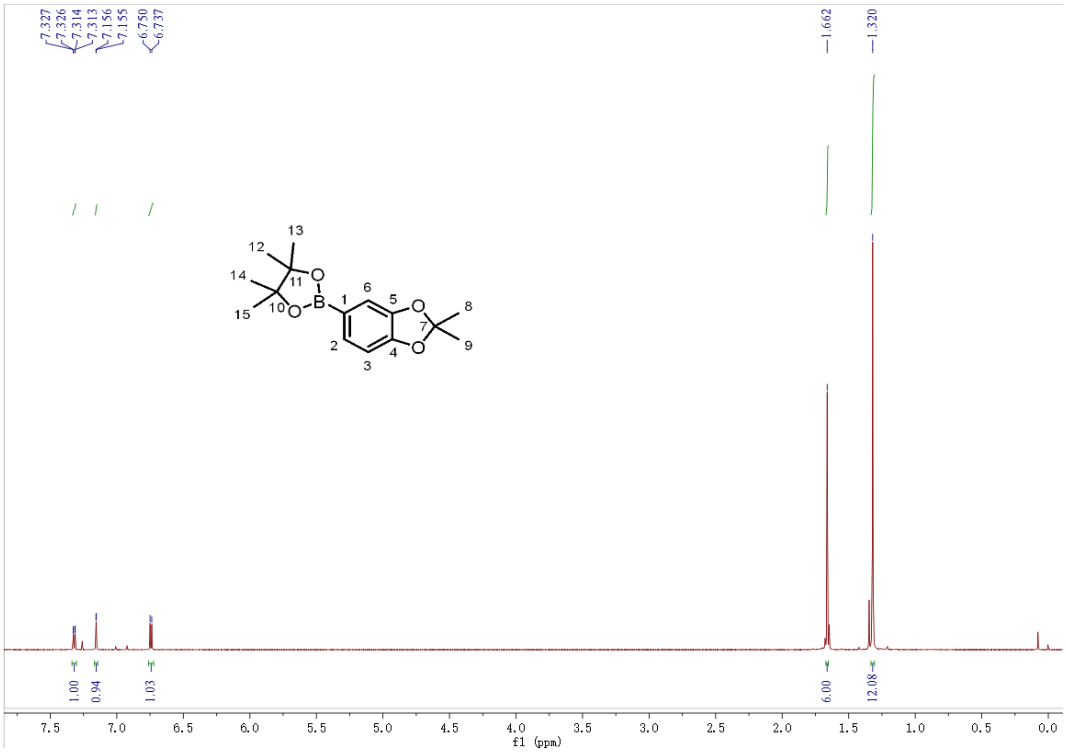

Figure 5. ^{1}H-NMR spectrum (600MHz, $CDCl_3$) of **(4)**: 2-(2,2-dimethylbenzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202408_10(8).0007

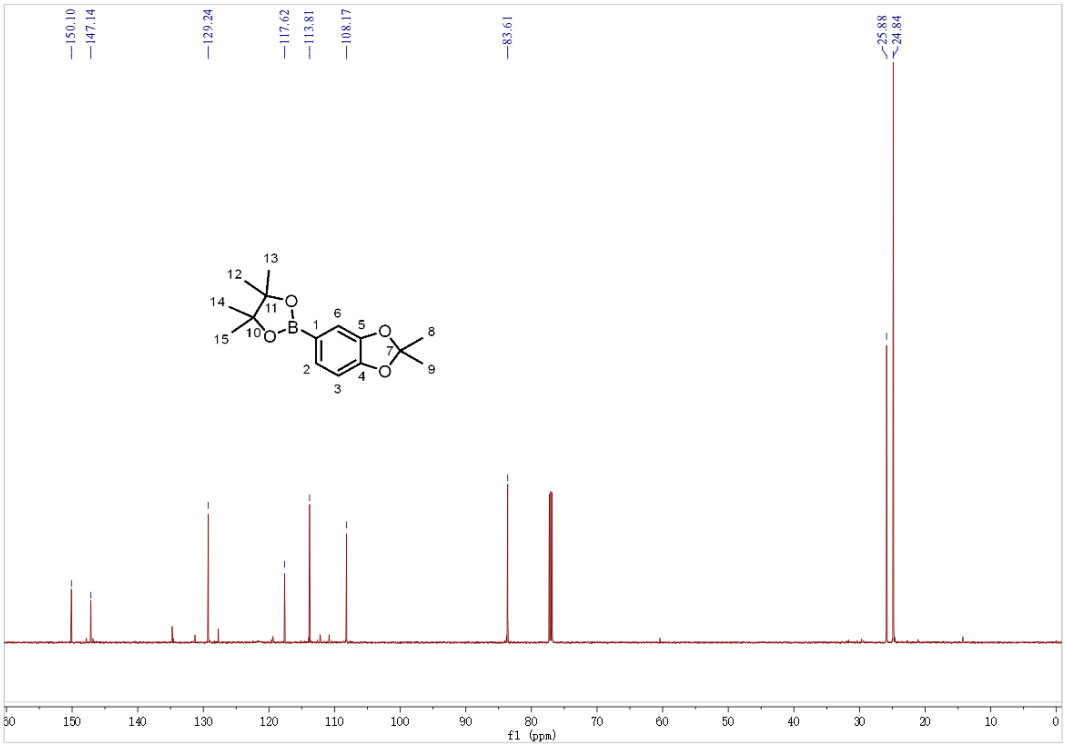

Figure 6. ^{13}C-NMR spectrum (150MHz, $CDCl_3$) of (4): 2-(2,2-dimethylbenzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

2.4. (2,2-dimethylbenzo[d][1,3]dioxol-5-yl)boronic acid (5)

Compound **4** (0.7g, 2.53mmol), sodium periodate (1.62g, 7.59mmol), ammonium acetate (0.59g, 7.59mmol), water (7.59mL), and acetone (15.18mL) (1M ammonium acetate solution in acetone-water, $V_{acetone}$: V_{water} = 2:1) were mixed together and stirred at room temperature for 2 days. After the reaction was complete, the mixture was filtered, and the solid was washed with ethyl acetate. The solid was then extracted with ethyl acetate (3×10mL) and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using silica gel. 0.33g (68%) of Compound **5** was obtained by elution with petroleum ether/EtOAc (5:1). ^{1}H NMR spectrum (600MHz, $CDCl_3$), δ, ppm: 1.72 (s, 6H), 6.86 (d, 1H, J = 7.8Hz), 7.52 (d, 1H, J = 0.6Hz), 7.74 (dd, 1H, J = 7.8, 1.2Hz); ^{13}C NMR spectrum (150MHz, $CDCl_3$), δ_C, ppm: 26.0 (C^8 and C^9), 108.4 (C^3 and C^6), 114.3 (C^1), 118.1 (C^7), 130.6 (C^2), 147.4 (C^4), 151.3 (C^5) {One carbon signal for CH_3 and One carbon signal for Ph overlapped}.(shown in Figure 7, 8)

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202408_10(8).0007

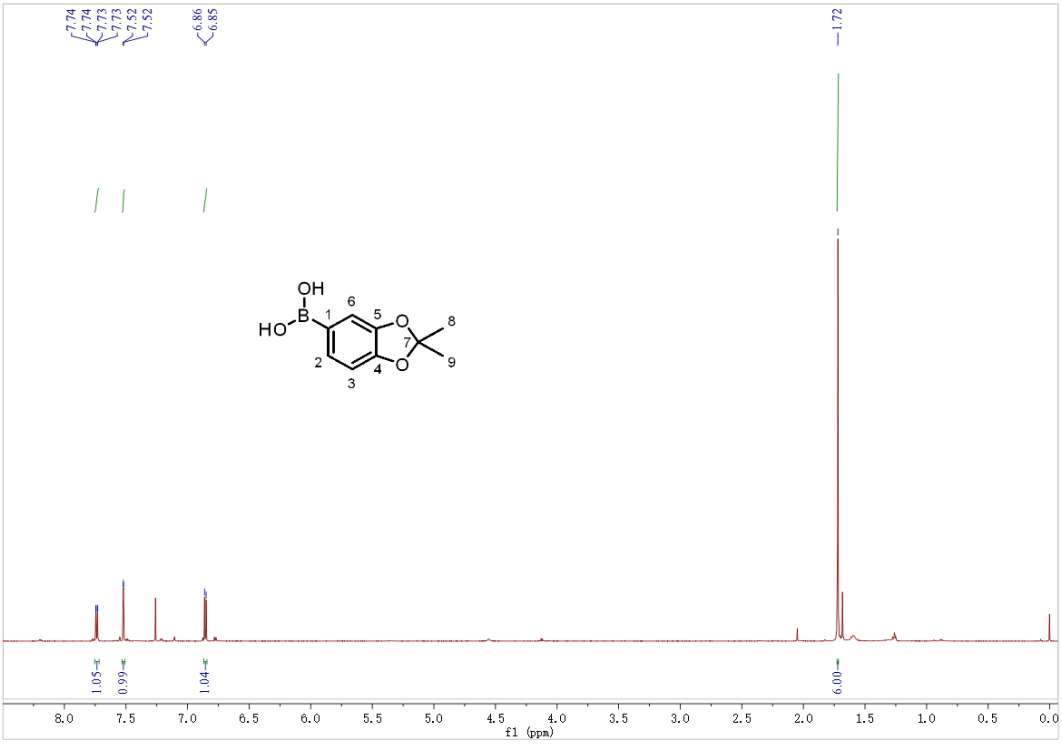

Figure 7. ^{1}H-NMR spectrum (600MHz, $CDCl_3$) of **(5)**: (2,2-dimethylbenzo[d][1,3]dioxol-5-yl)boronic acid

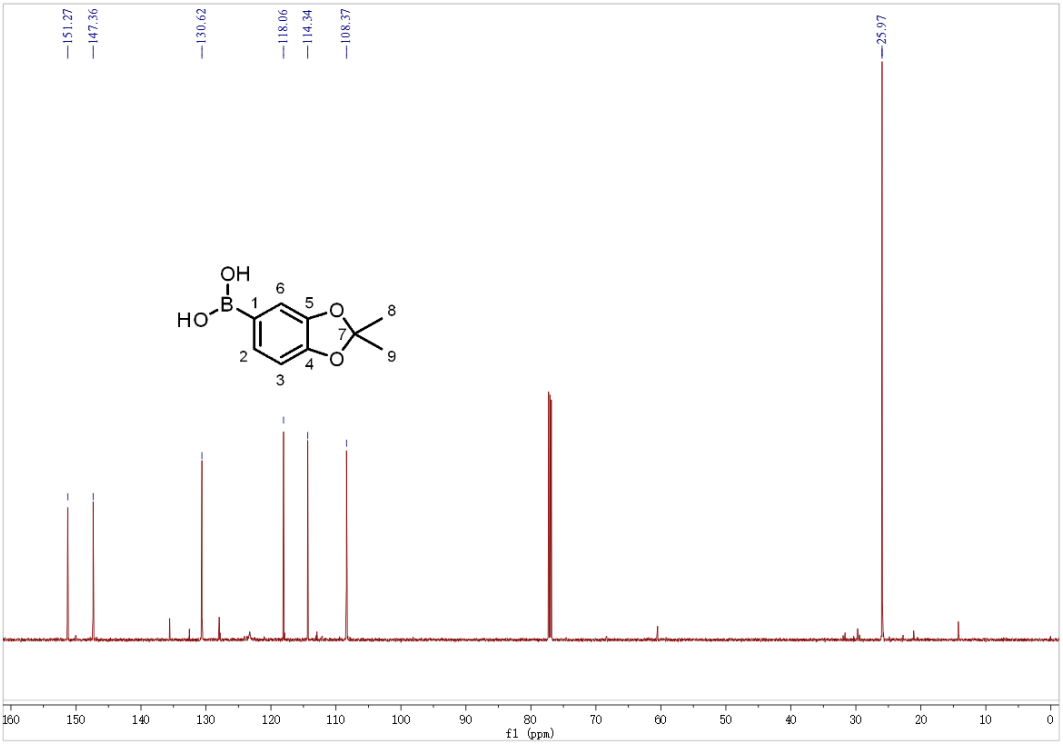

Figure 8. ^{13}C-NMR spectrum (150MHz, $CDCl_3$) of **(5):** (2,2-dimethylbenzo[d][1,3]dioxol-5-yl)boronic acid

2.5. 2,2-dimethyl-5-(1,2,2-trifluorovinyl)benzo[d][1,3]dioxole (6)

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202408_10(8).0007

Compound Under anaerobic conditions, compound **5** (0.33g, 1.7mmol), sodium carbonate (0.36g, 3.4mmol), H_2O (0.18mL, 10.2mmol), and the catalyst $PdCl_2$(dppf) (0.12g, 0.17mmol) were dissolved in 1,4-dioxane (8mL) at room temperature. The mixture was then cooled with liquid nitrogen, and trifluoroethylene (0.8g, 6.8mmol) was introduced. The reaction mixture was slowly heated to reflux at 100°C and refluxed for two hours. After the reaction was complete, water (15mL) was added, and the mixture was extracted with ethyl acetate (3×10mL). The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure at 25°C. The residue was purified by column chromatography using silica gel, and eluted with petroleum ether. 0.28g (73%) of Compound **6** was obtained and should be stored under freezing conditions. ^{1}H NMR spectrum (600MHz, $CDCl_3$), δ, ppm: 6.93 (dd, 1H, J = 7.8, 1.2Hz), 6.84 (s, 1H), 6.77 (d, 1H, J = 8.4Hz), 1.69 (s, 6H); ^{13}C NMR spectrum (150MHz, $CDCl_3$), δ_C, ppm: 25.8 (s, C^8 and C^9), 105.1 (m, C^3), 108.4 (d, C^6), 118.4 (td, C^1), 118.8 (s, C^7), 129.6 (dd, C^2), 147.9 (d, C^4), 148.0 (m, C^5), 151.6 (d, C^{10}), 155.3 (d, C^{11}){One carbon signal for CH_3 overlapped. And fluorine-containing substances can affect the coupling constants, signal intensities, and peak shapes in nuclear magnetic resonance (NMR) carbon spectra, making them more difficult to analyze}; ^{19}F NMR spectrum (377MHz, CDCl3), δ_F, ppm: -173.93 (dd, 1F, F^{12}, J =110.1, 32.0Hz), -116.67 (dd, 1F, F^{13}, J = 110.1, 76.5Hz), -101.96 (dd, 1F, F^{14}, J = 76.9, 32.0 Hz); HRMS (ESI): m/z calcd for $C_{11}H_9F_3O_2$: 231.0555; found: 231.0627 $[M+H]^+$. IR spectrum, v, cm-1: 3086 (Ar-H), 2997 (CH3), 1764 (C=C), 1257 (C-F), 1217 (C-O-C). (shown in Figure 9, 10, 11, 12, 13)

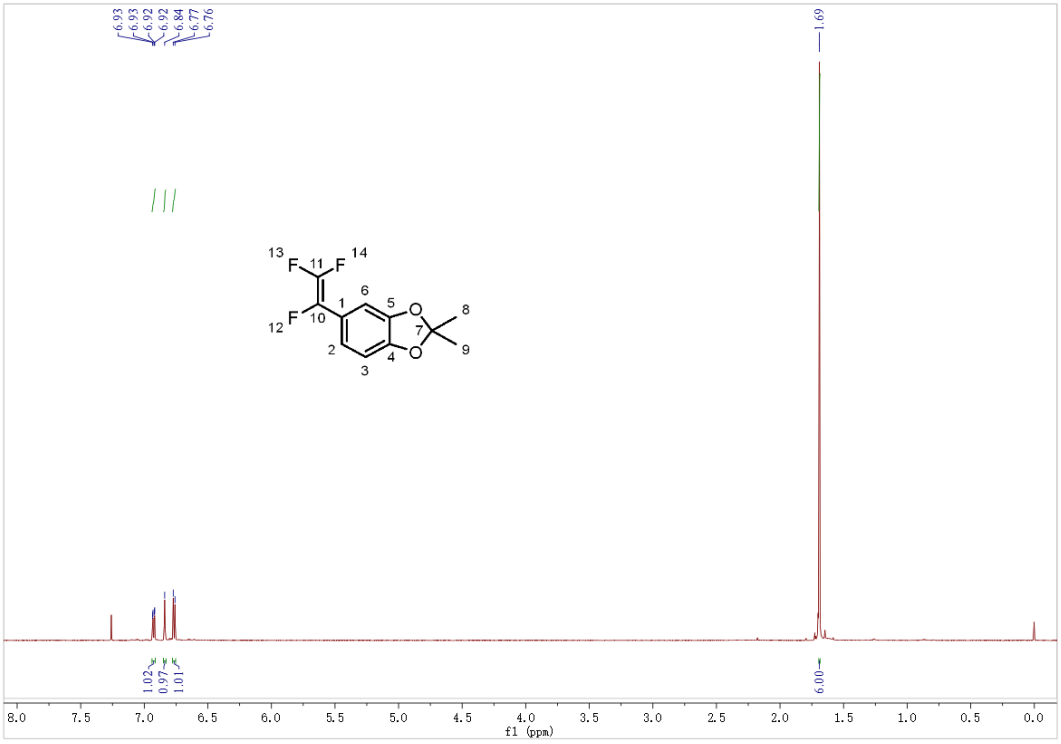

Figure 9. ^{1}H-NMR spectrum (600MHz, $CDCl_3$) of **(6)**: 2,2-dimethyl-5-(1,2,2-trifluorovinyl)benzo[d][1,3]dioxole

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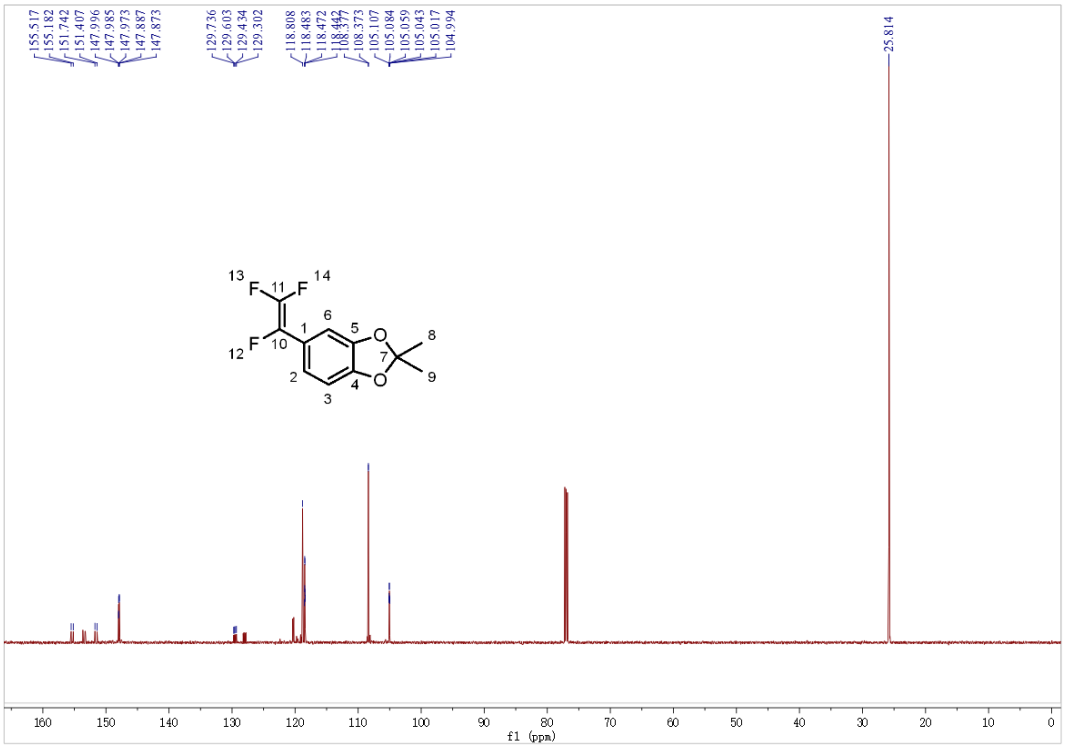

Figure 10. ^{13}C-NMR spectrum (150MHz, $CDCl_3$) of **(6)**: 2,2-dimethyl-5-(1,2,2-trifluorovinyl)benzo[d][1,3]dioxole

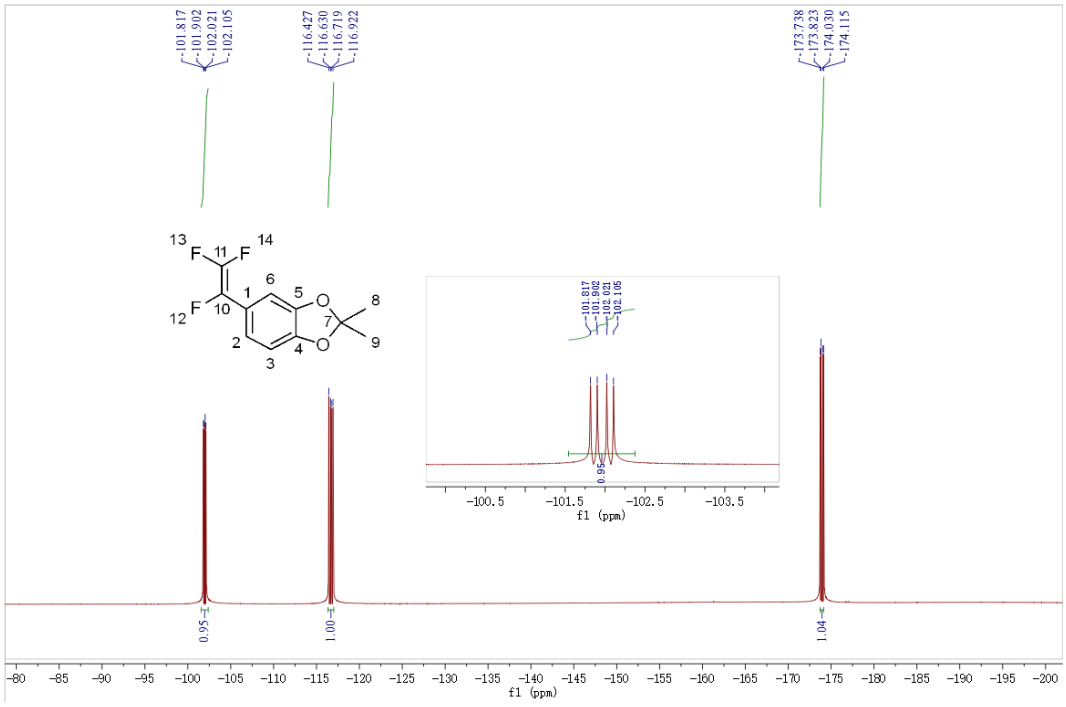

Figure 11. ^{19}F-NMR spectrum (377MHz, $CDCl_3$) of **(6)**: 2,2-dimethyl-5-(1,2,2-trifluorovinyl)benzo[d][1,3]dioxole

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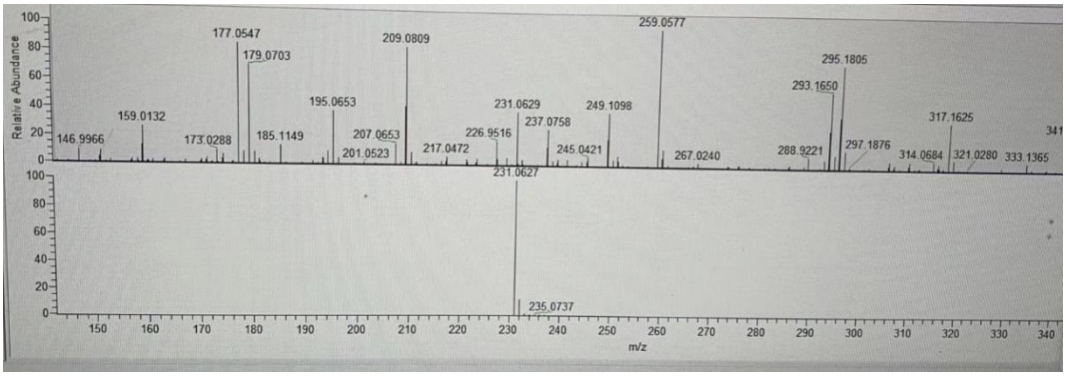

Figure 12. HRMS (ESI) spectrum of **(6)**: 2,2-dimethyl-5-(1,2,2-trifluorovinyl)benzo[d][1,3]dioxole

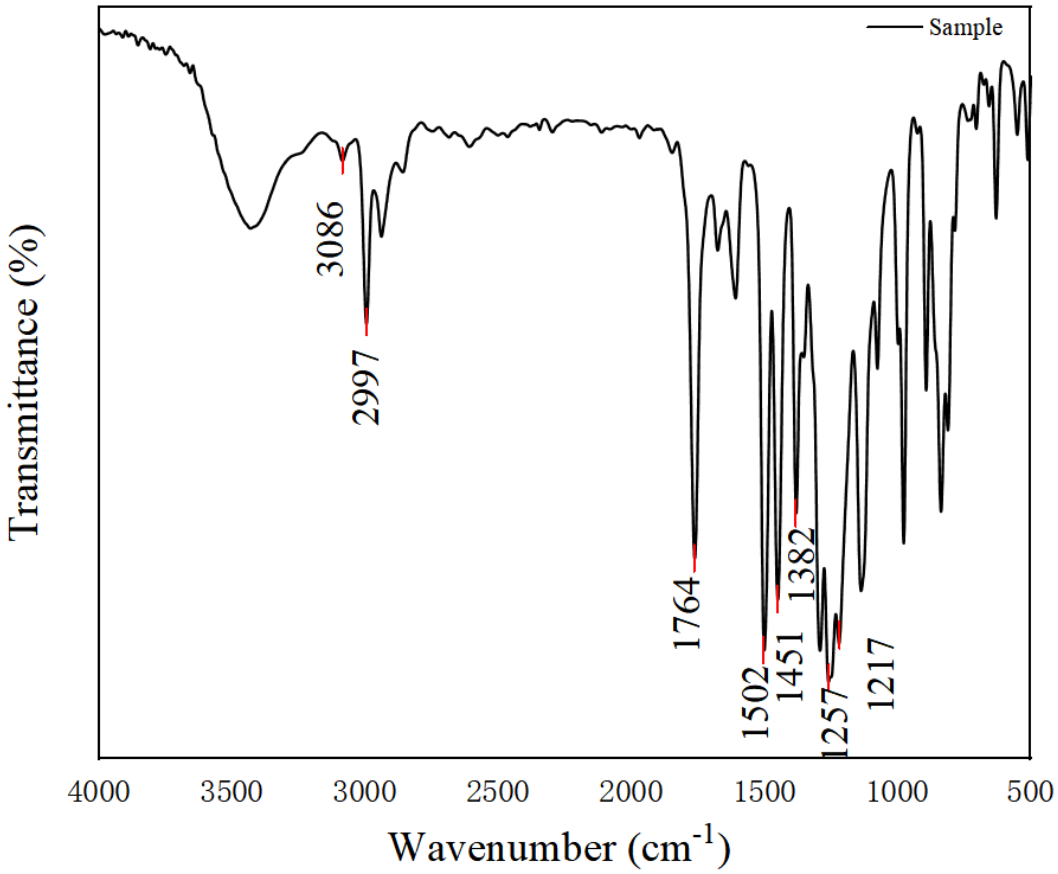

Figure 13. IR spectrum of **(6)**: 2,2-dimethyl-5-(1,2,2-trifluorovinyl)benzo[d][1,3]dioxole

3. RESULTS AND DISCUSSION

The synthesis process starts with the cost-effective catechol undergoing an acetone protection reaction, bromination reaction, Miyaura boronization reaction, hydrolysis reaction, and finally Suzuki coupling reaction with trifluorochloroethylene to obtain the final product with a total yield of approximately 25% (Synthesis route is shown in Scheme 2).

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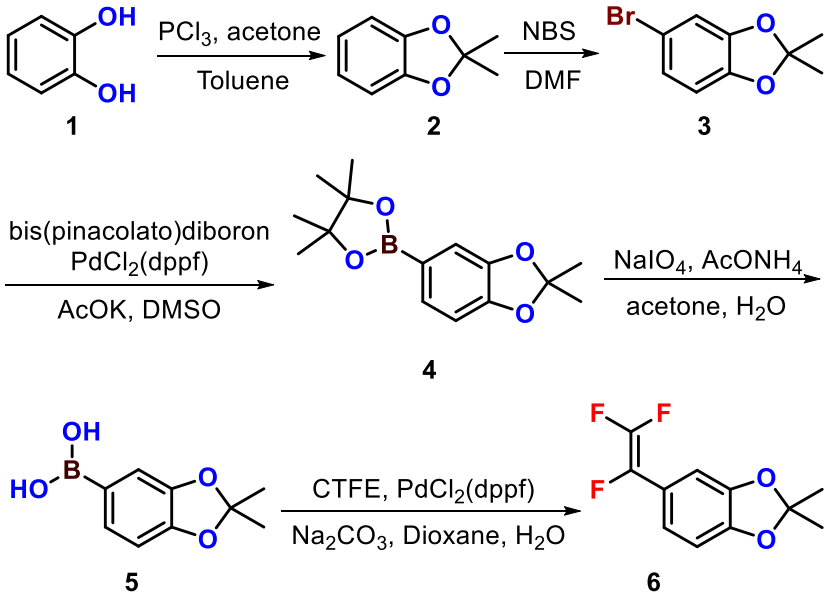

Scheme 2. Synthetic route and reaction conditions

The coupling of catechol and trifluoroethylene through chemical synthesis aims to obtain a hydrophilic fluorinated monomer with the adhesive properties, biocompatibility, biodegradability, and chemical reactivity of catechol, while retaining the high heat resistance and corrosion resistance of trifluoroethylene. In terms of pharmaceutical intermediates, this hydrophilic fluorinated monomer can be used to prepare intermediates for drug synthesis, synthesize bioactive molecules or drug precursors. Its adhesive and hydrophilic properties make it an ideal drug carrier, effectively delivering drugs to target tissues or cells. In terms of medical prepolymers, this hydrophilic fluorinated monomer can be used in various forms such as polymer films, multifunctional coatings, and hydrogels for various biomedical devices, enhancing their biocompatibility[32, 33].

The safety, biocompatibility, and biodegradability of this hydrophilic fluorinated monomer as a medical pre-polymer are topics that warrant further discussion. Currently, many fluorinated polymers are extensively utilized as scaffolding materials for the regeneration of skeletal, muscular, cardiovascular, and cutaneous tissues[34, 35]. Moreover, the use of poly (chlorotrifluoroethylene) (PCTFE) as an implantable material has not been associated with any adverse reactions and has been approved by the Food and Drug Administration (FDA) for contact with food or human implants[36]. Additionally, the phenolic-based polymers have no negative impact on the growth and proliferation of mammalian cells. In the presence of these phenolic-based polymers, fibroblasts, osteoblasts, neural cells, and endothelial cells can still grow and proliferate normally[37]. Furthermore, certain substances produced in the human body can facilitate the degradation of phenolic-based polymers[38].

4. CONCLUSION

In summary, we efficiently synthesized a novel hydrophilic fluorinated monomer that combines the excellent properties of catechol and chlorotrifluoroethylene. We hope that this hydrophilic fluorinated monomer can harness the advantages of catechol and chlorotrifluoroethylene and be utilized as a pharmaceutical intermediate and a biomedical polymer in hydrophilic drug design and biomedical materials. Additionally, the experimental section provides a detailed description of the synthesis process and characterization of this hydrophilic fluorinated monomer. Furthermore, further discussions are conducted on its safety,

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biocompatibility, and biodegradability as a medical pre-polymer. This research provides valuable information and methods for the development of novel medical pre-polymers.

ACKNOWLEDGEMENTS

This work is supported by Sichuan Science and Technology Program(NO: 2022YFG0275) and Sichuan University of Science & Engineering Graduate Student Innovation Fund(NO: Y2022018).

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