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ACTICLE

Phosphine-Catalyzed Dearomative (3+2) Annulation of 2-Nitrobenzofurans and Nitrobenzothiophenes with Allenoate

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An efficient Ph_2PMe-catalyzed dearomative (3+2) annulation of 2-nitrobenzofurans, 2-nitrobenzothiophenes, and 3-nitrobenzothiophenes with allenoate has been developed. With the developed protocol, a series of structurally important cyclopenta[*b*]benzofurans and cyclopenta[*b*]benzothiophenes were obtained in good to excellent yields (up to 98%) under mild conditions. In addition, preparative-scale experiment and transformations were conducted to exemplify the synthetic utility. The asymmetric version of this dearomative (3+2) annulation reaction was tentatively investigated by using chiral phosphine catalysts.

Introduction

Dearomative annulation represents a powerful and straightforward strategy for the preparation of highly functionalized three-dimensional molecules from readily available feedstocks such as arenes and heteroarenes.[1] In this research area, the vast majority of the catalytic transformations typically focus on adopting the nucleophilic character of arenes and heteroarenes, including naphthol, phenol, indole, and pyrrole.[2] Nevertheless, installing suitable electron-withdrawing group in these arenes or heteroarenes can turn them into electron-deficient compounds thus showing electrophilic nature. As a result, these electron-deficient arenes or heteroarenes probably give rise to various novel types of reactions to access structurally versatile cyclic compounds. Recently, 3-nitroindoles serving as electrophilic heteroarenes have demonstrated their interesting synthetic potential in the dearomative cycloaddition reactions.[3-4] In contrast, we noted that 2-nitrobenzofurans and 2-nitrobenzothiophenes, also belong to a class of electron-deficient heteroarenes, are less explored in the dearomatization process.[5] In this context, exploring novel types of reactions by taking advantage of the electrophilic character of 2-nitrobenzofurans and 2-nitrobenzothiophenes will be more promising and is highly desirable.

Cyclopentanoids are ubiquitous in numerous natural and non-natural compounds.[6] Among them, cyclopenta[*b*]benzofurans, as an important and central structural scaffolds, are present in a myriad of biologically active natural products and pharmaceuticals (Figure 1).[7] For instance, beraprost is the first example of a drug with a cyclopenta[*b*]benzofuran scaffold to enter the market for the treatment of patients with pulmonary arterial hypertension and peripheral artery disease.[8] Furthermore, cyclopenta[*b*]annulated benzothiophenes are an important class of three-ring heterocyclic compounds which possess potential applications in medicinal chemistry and materials science.[9] Given their outstanding potential, the development of efficient methodologies to rapidly construct the cyclopenta[*b*]benzofuran and cyclopenta[*b*]benzothiophene scaffolds has consequently become a primary target of synthetic efforts.

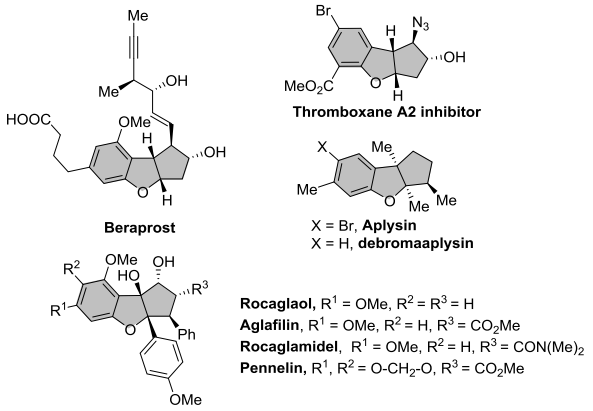

Fig. 1 Examples of bioactive compounds with the core structure of cyclopenta[*b*]benzofuran scaffold.

Phosphine-catalyzed cycloaddition reactions of allenoates with electron-deficient olefins have emerged as one of

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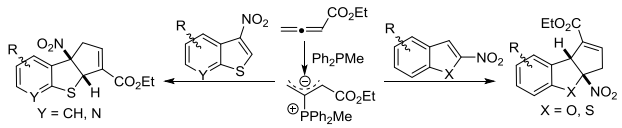
powerful and efficient strategies for the generation of molecular complexity and new molecular frameworks.[10] Even since Lu's pioneering work on phosphine-catalyzed (3+2) annulation of allenoates with activated alkenes in 1995,[11] this powerful mode of cyclization has attracted much research interest from organic synthetic chemists for the construction of structurally diverse cyclopentenes.[12] However, during the past two decades, although Lu's classic (3+2) annulation has been widely studied, the cycloaddition reaction involving dearomatization process between electron-deficient heteroarenes and allenoates is unexplored so far. During our preparation of this manuscript, the first phosphine-catalyzed dearomative (3+2) annulation of *3-nitroindoles* with allenoates was reported.[13] It is noteworthy that the reaction of *2-nitrobenzofurans with allenoates is failed under the Zhang's reaction conditions*.[13a] As part of our continuing efforts on the dearomative cycloaddition reactions of electron-deficient heteroarenes,[4,5b-c, 5e, 5g] herein we report phosphine-catalyzed dearomative (3+2) annulation of *2-nitrobenzofurans* and *2-nitrobenzothiophenes* with zwitterionic intermediate, *in situ* generated from addition of tertiary phosphine to allenoate, for synthesis of structurally diverse cyclopenta[*b*]benzofuran and cyclopenta[*b*]benzothiophene derivatives. The extension of the methodology to the dearomatization of 3-nitrobenzothiophenes is also described (Scheme 1).

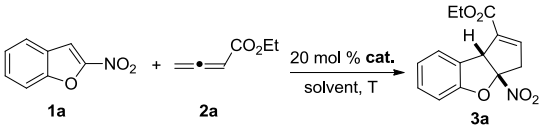


Scheme 1 Phosphine-catalyzed dearomative (3+2) annulation of 2-nitrobenzofurans and nitrobenzothiophenes with allenoate.

Results and discussion

We began our investigation with the reaction of 2-nitrobenzofuran **1a** and ethyl 2,3-butadienoate **2a** in the presence of 20 mol % PPh_3 in CH_2Cl_2 at room temperature for 20 h. To our delight, the desired (3+2) cycloadduct **3a** was obtained in 44% yield (Table 1, entry 1). Next, tributylphosphine ($(n\text{-}Bu)_3P$) and methyldiphenylphosphine (Ph_2PMe) were used to catalyze the dearomative (3+2) annulation, giving **3a** in 55% and 74% yield, respectively (Table 1, entry 2 and 3). However, it was found that DABCO could not promote the reaction (Table 1, entry 4). Having identified catalyst Ph_2PMe as the best candidate, a screen of solvents including toluene, methyl *tert*-butyl ether (MTBE), and EtOAc were performed at room temperature. It revealed that CH_2Cl_2 was the most suitable reaction media for the reaction (Table 1, entry 3 vs entries 5-7). Lowering the reaction temperature to 0 ^oC, the yield of product **3a** was increased to 78% (Table 1, entry 8). However, reducing the catalyst loading from 20 mol % to 10 mol %, the reaction provided **3a** in decreasing yield along with prolonging reaction time to 24 h (Table 1, entry 9). Ultimately, the substrate concentration was examined (Table 1, entries 10-11). It was observed that the reaction worked well in the presence of 20 mol % Ph_2PMe under 0.05 M substrate concentration, giving **3a** in 87% yield (Table 1, entry 10).

Table 1 Optimization of reaction conditions[a]



1a 2a 3a

Entry	cat.	solvent	T (^oC)	time (h)	yield (%)[b]
1	PPh_3	CH_2Cl_2	rt	20	44
2	$(n\text{-}Bu)_3P$	CH_2Cl_2	rt	20	55
3	$MePPh_2$	CH_2Cl_2	rt	2	74
4	DABCO	CH_2Cl_2	rt	48	N.R.
5	Ph_2PMe	toluene	rt	9	58
6	Ph_2PMe	MTBE	rt	9	49
7	Ph_2PMe	EtOAc	rt	9	57
8	Ph_2PMe	CH_2Cl_2	0	4	78
9[c]	Ph_2PMe	CH_2Cl_2	0	24	69
10[d]	Ph_2PMe	CH_2Cl_2	0	8	87
11[e]	Ph_2PMe	CH_2Cl_2	0	9	82

[a]Unless specified, the reactions were carried out with **1a** (0.2 mmol), **2a** (0.3 mmol) and **cat.** (20 mol %) in 1.0 mL of solvent for indicated time. [b]Yield of isolated product. [c]10 mol % **cat.** was used. [d]2 mL of solvent was used. [e]4 mL of solvent was used. N.R. = no reaction

With the optimal conditions in hand, we set out to explore the substrate scope by using various 2-nitrobenzofurans. To our delight, 2-nitrobenzofurans with different steric and electronic constraints all could smoothly undergo dearomatization (Scheme 2). For instance, 2-nitrobenzofurans bearing various substituents at the C5 position (R = F, Cl, Br, NO_2, Me, OMe, ^{t}Bu, Ph) of the aromatic ring could react efficiently with ethyl 2,3-butadienoate **2a**, and the reactions afforded the corresponding products **3b-i** in good yields (70-85%). Furthermore, substrates installing varied electronic properties at the C6 or C7 position successfully underwent the dearomative (3+2) annulation reaction and the corresponding bromo-, methyl-, methoxy-, fluoro-, ethyoxyl- and phenyl- substituted cyclopenta[*b*]benzofurans **3j-q** were isolated in yields ranging from 77% to 87%. The reaction of 2-nitrobenzofuran **1r** bearing substituent at C4 position and **2a** proved to be more sluggish, and the corresponding cycloadduct **3r** was obtained in only 40% yield, albeit with adding the catalyst loading to 30 mol % and a specially prolonged reaction time. This case suggests that an increase of steric hindrance next to the electrophilic C3 position maybe impede the dearomative (3+2) annulation process on certain extent. Meanwhile, we found that the reaction for the di-substituted substrate proceeded smoothly at room temperature, affording product **3s** in moderate yield. The more sterically hindered 2-nitronaphtho[2,1-*b*]furan **1t** also proved to be amenable to this developed protocol, and the expected product **3t** could be obtained in 51% yield. It is worth mentioning that the structure of product **3o** was unequivocally confirmed by means of single-crystal X-ray diffraction.[14]

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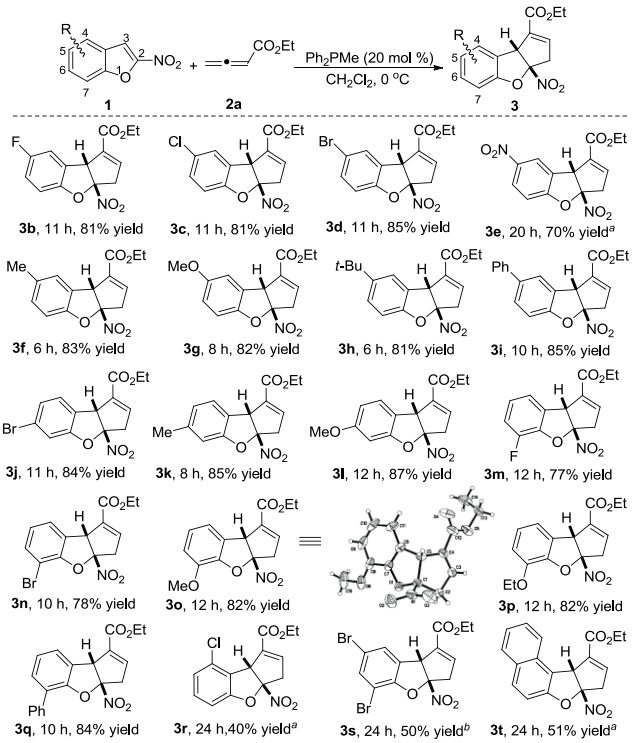
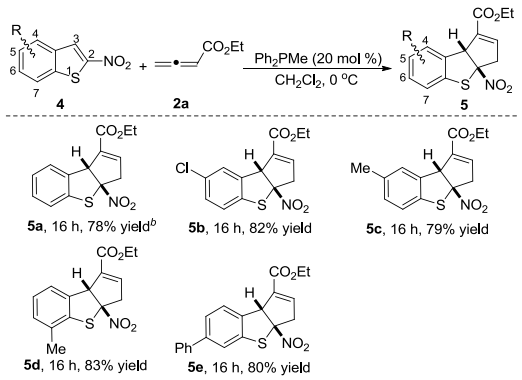


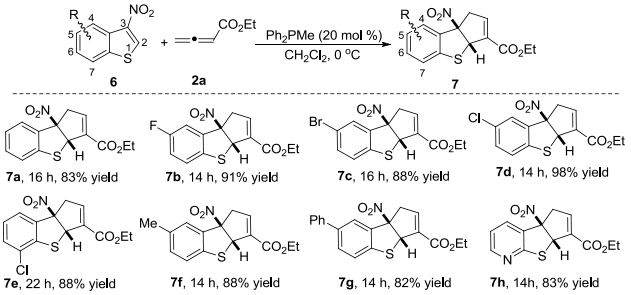
Scheme 2 Substrates scope of 2-nitrobenzofuans. Reaction conditions: the reactions were carried out with **1** (0.2 mmol), **2a** (0.3 mmol) and Ph_2PMe (20 mol %) in 2.0 mL of CH_2Cl_2 for indicated time. [a]30 mol % Ph_2PMe was used. [b]Run at rt.

Furthermore, we were keen on extending the dearomative (3+2) annulation reaction to 2-nitrobenzothiophenes to confirm the practicability of the methodology. As shown in Scheme 3, this Ph_2PMe-catalyzed dearomative (3+2) annulation reaction proved to be well compatible with the use of various 2-nitrobenzothiophenes. Under the standard reaction conditions, the reaction of 2-nitrobenzothiophene **4a** and **2a** could occur smoothly, and delivered the expected product **5a** in 78% yield. We also found that diverse 2-nitrobenzothiophenes containing different substituents (R = Cl, Me, Ph) on the aromatic rings could react successfully with allenoate **2a,** providing the corresponding products **5b**-**e** with comparable results.



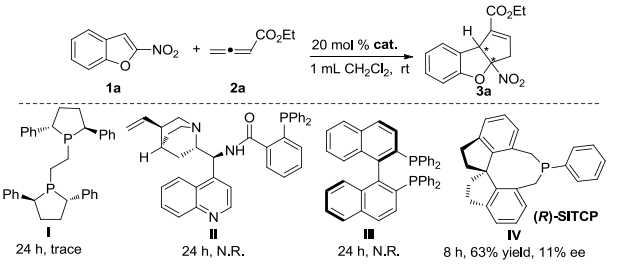
Scheme 3 Substrates scope of 2-nitrobenzothiophenes. Reaction conditions: the reactions were carried out with **5** (0.15 mmol), **2a** (0.225 mmol) and Ph_2PMe (20 mol %) in 1.5 mL of CH_2Cl_2 for indicated time.

Encouraged by the success of the above reactions, we continued our attempt to investigate the dearomative (3+2) annulation reaction of 3-nitrobenzothiophenes with allenoate **2a** (Scheme 4). Substituents of different electronic natures on the aromatic ring of 3-nitrobenzothiophene substrates, could be tolerated in this dearomative (3+2) cycloaddition process, and the reactions furnished their respective products **7a-g** in good to excellent yields (82-98%). Nevertheless, 3-nitrothieno[2,3-*b*]pyridine also could react smoothly with ethyl 2,3-butadienoate, providing the desired dearomative annulation product **7h** in 83% yield.



Scheme 4 Substrates scope of 3-nitrobenzothiophenes. Reaction conditions: the reactions were carried out with **6** (0.15 mmol), **2a** (0.225 mmol) and Ph_2PMe (20 mol %) in 1.5 mL of CH_2Cl_2 for indicated time.

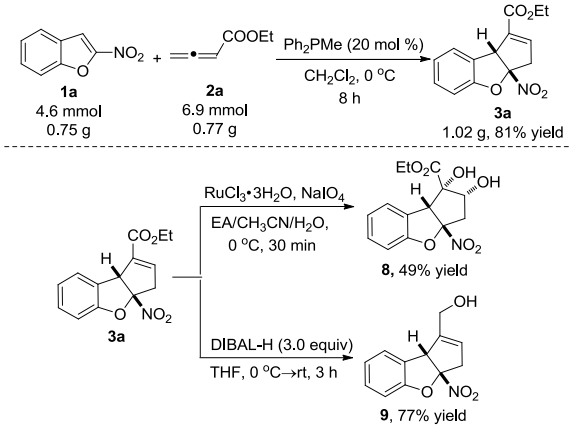
We further tried to develop a catalytic asymmetric version of this annulation reaction using several common chiral phosphines. Using **I** as the catalyst, the reaction gave trace amount of product **3a**. In the present of Dixon's catalyst **II** and chiral BINAP **III**, no product was detected. Using (*R*)-SITCP (**IV**) as the catalyst, product **3a** could be obtained in 63% yield but with only 11% ee (Scheme 5). Despite the present result is not satisfactory, this example indicates that the catalytic enantioseclective dearomative (3+2) annulation is promising.



Scheme 5 Asymmetric version of the dearomative (3+2) annulation.

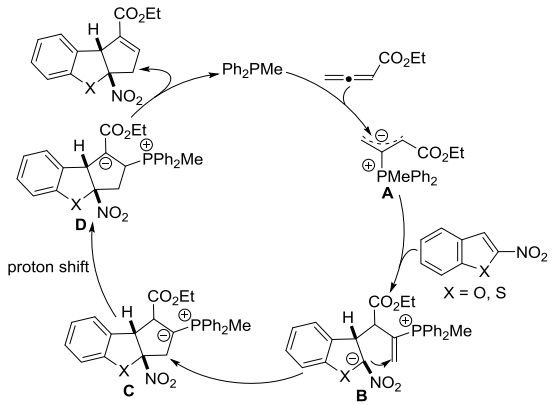
To exemplify the synthetic utility of our developed protocol, the reaction was scaled up to 4.6 mmol for **1a**, which is 23 times larger than the scale of the model reaction in Table 1. As showed in Scheme 6, the preparative-scale reaction proceeded well and afforded **3a** in 81% yield after 8 h. This result revealed that the developed protocol was amenable to a

large-scale production. And then, product **3a** was further transformed into other compounds. The dihydroxylation of **3a** could be conducted efficiently, affording product *rac*-**8** in 49% yield. Reduction of **3a** using DIBAL-H in anhydrous THF gave product **9** in 77% yield (Scheme 6).



Scheme 6 Preparative-scale experiment and transformations of the product **3a.**

On the basis of previous literature reports[13, 15] and our own results, a plausible reaction mechanism was proposed in Scheme 7. The reaction is initiated by the addition of catalyst Ph_2PMe to 2,3-butadienoate to generate the zwitterionic intermediate **A**. Zwitterionic intermediate **A** attacks the C3 position of the 2-nitrobenzofurans or 2-nitrobenzothiophenes through conjugate addition to form intermediate **B**. And then, an intramolecular annulation affords another intermediate **C**, which upon an intramolecular [1,2] proton shift to give intermediate **D**. Ultimately, intermediate **D** releases the catalyst Ph_2PMe and provides the final cyclopenta[*b*]benzofurans and cyclopenta[*b*]benzothiophenes.



Scheme 7 Proposed reaction mechanism.

Conclusions

In summary, we have developed Ph_2PMe-catalyzed dearomative (3+2) annulation of 2-nitrobenzofurans, 2-nitrobenzothiophenes, and 3-nitrobenzothiophenes with allenoate. This protocol provides a straightforward and useful strategy for the construction of cyclopenta[*b*]benzofuran and cyclopenta[*b*]benzothiophene scaffolds, which exist extensively in biologically active natural products and pharmaceuticals. With the developed protocol, a range of structurally diverse cyclopenta[*b*]benzofurans and cyclopenta[*b*]benzothiophenes could be smoothly obtained in good to excellent yields (up to 98%) under mild conditions. Preparative-scale experiment and transformations were conducted to exemplify the synthetic utility.The preliminary attempt at the development of asymmetric version of this dearomative (3+2) reaction was also conducted by using chiral phosphines.

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Experimental section

General Methods

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, DMSO-d_6 at 39.51 ppm). Melting points were recorded on a melting point apparatus. 2-Nitrobenzofurans,[5a] 2-nitrobenzothiophenes,[16] and 3-nitrobenzothiophenes[17] in this work are known compounds and prepared according to the reported literature procedures.

Typical experimental procedures for synthesis of 2-nitrobenzothiophenes.[16] A solution of benzothiophen (20 mmol) in THF (80 mL) was stirred at 0 °C. Then NBS (5.4 g, 30 mmol) was added portionwise. After maintaining at 0 °C for 30 min, the reaction was warmed to room temperature and stirred for 48 h. Then the reaction was quenched with $Na_2S_2O_3$, and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The crude product 3-bromobenzo[*b*]thiophene was used directly without purification.

To a solution of 3-bromobenzo[*b*]thiophene (20 mmol) in 65 mL of acetic anhydride at 0 °C, and then a mixture of 25 mL of nitric acid and 20 mL of acetic acid was added dropwise with vigorous stirring. Once the addition was complete, the ice bath was removed and the reaction mixture stirred for 2 h at room temperature. Then the mixture was poured into ice, filtered, and washed with water. The solid was crystallized from ethanol, yielding 3-bromo-2-nitrobenzo[*b*]thiophene.

3-Bromo-2-nitrobenzo[*b*]thiophene (5 mmol) and benzoic acid (18.5 mmol, 3.7 equiv) were added to a 3-neck round-bottom flask. The solids were mixed thoroughly with a magnetic stir bar, and the reaction was purged 3 times before heating to 150 °C. Under a cone of nitrogen, copper powder

(24 mmol, 4.8 equiv) was then added to the melt. The reaction was stirred for an additional 1 h at 150 °C and then slowly cooled to room temperature. The resulting solid was suspended in CH_2Cl_2, and the residual copper was removed by gravity filtration. The CH_2Cl_2 solution was washed three times with saturated $NaHCO_3$, once with water, and once with brine. This was then dried over $MgSO_4$, filtered, and concentrated. The residue directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 25:1～30:1) to give the corresponding 2-nitrobenzothiophenes.

5-Chloro-2-nitrobenzo[*b*]thiophene (4b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 2.1 Hz, 1H), 8.16 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 124.1, 124.5, 126.2, 129.7, 132.6, 137.1, 138.2, 152.8; HRMS (ESI-TOF) Calcd. for $C_8H_3ClNO_2S$ [M-H]$^-$: 211.9579; found: 211.9583.

5-Methyl-2-nitrobenzo[*b*]thiophene (4c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3H), 7.43 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.64-7.79 (m, 2H), 8.07-8.20 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.4, 122.5, 125.4, 126.6, 131.2, 136.2, 136.4, 137.7, 151.4; HRMS (ESI-TOF) Calcd. for $C_9H_6NO_2S$ [M-H]$^-$: 192.0125; found: 192.0125.

7-Methyl-2-nitrobenzo[*b*]thiophene (4d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 7.34-7.50 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 8.24 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 19.9, 124.6, 126.3, 126.5, 129.2, 132.6, 136.0, 140.9, 151.1; HRMS (ESI-TOF) Calcd. for $C_9H_6NO_2S$ [M-H]$^-$: 192.0125; found: 192.0127.

Typical experimental procedures for synthesis of 3-nitrobenzothiophenes.[17] A mixture of benzothiophenes (20 mmol) and $(NH_4)_2Ce(NO_3)_5{\cdot}4H_2O$ (7 mmol) in Ac_2O (17 mL) was stirred at room temperature for 3 days. The reaction mixture was poured onto crushed ice and extracted with EtOAc. The extracts were washed with water, dried and evaporated. The residue directly purified by flash chromatography on silica gel and recrystallization to give the corresponding 3-nitrobenzothiophenes.

5-Fluoro-3-nitrobenzo[*b*]thiophene (6b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.35 (m, 1H), 7.86 (dd, *J* = 8.9, 4.7 Hz, 1H), 8.26-8.39 (m, 1H), 8.79 (d, *J* = 1.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 110.2 (*J* = 27.2 Hz), 115.7 (*J* = 25.2 Hz), 124.4 (*J* = 9.6 Hz), 131.4 (*J*= 12.0 Hz), 134.1, 134.7, 140.9, 162.3 (*J* = 246.4 Hz); HRMS (ESI-TOF) Calcd. for $C_8H_3FNO_2S$ [M-H]$^-$: 195.9874; found: 195.9879.

5-Bromo-3-nitrobenzo[*b*]thiophene (6c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 8.74 (s, 1H), 8.82 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO) δ 121.3, 125.0, 126.1, 129.4, 131.4, 136.0, 137.4, 141.2; HRMS (ESI-TOF) Calcd. for $C_8H_4BrNNaO_2S$ [M+Na]$^+$: 279.9038; found: 279.9032.

5-Chloro-3-nitrobenzo[*b*]thiophene (6d). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 8.47 (d, *J* = 2.1 Hz, 1H), 8.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.3, 123.8, 126.8, 130.7, 133.5, 134.3, 136.5, 141.4; HRMS (ESI-TOF) Calcd. for $C_8H_3ClNO_2S$ [M-H]$^-$: 211.9579; found: 211.9577.

7-Chloro-3-nitrobenzo[*b*]thiophene (6e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.65 (m, 2H), 8.55 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.76 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 122.6, 126.0, 128.3, 128.4, 131.4, 133.2, 137.9, 142.9; HRMS (ESI-TOF) Calcd. for $C_8H_3ClNO_2S$ [M-H]$^-$: 211.9579; found: 211.9574.

5-Methyl-3-nitrobenzo[*b*]thiophene (6f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 7.36 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 8.38-8.49 (m, 1H), 8.67 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.8, 122.6, 123.8, 128.2, 130.2, 132.8, 136.0, 137.4, 142.3; HRMS (ESI-TOF) Calcd. for $C_9H_6NO_2S$ [M-H]$^-$: 192.0125; found: 192.0123.

General experimental procedures for synthesis of compounds 3. To a solution of 2-nitrobenzofurans **1** (0.2 mmol) in CH_2Cl_2 (2.0 mL) were added ethyl-2,3-butadienoate **2a** (0.3 mmol) and catalyst Ph_2PMe (7.4 uL, 20 mol %). Then the mixture was stirred for specific time at 0 °C. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1～25:1) to give the corresponding product **3**.

Ethyl 3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (**3a**). yellow oil; 87% yield (48.0 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.1 Hz, 3H), 3.32 (ddd, *J* = 19.7, 2.7, 1.7 Hz, 1H), 3.74 (ddd, *J* = 19.6, 2.5, 1.2 Hz, 1H), 4.12-4.43 (m, 2H), 5.13 (s, 1H), 6.75 (q, *J* = 2.4 Hz, 1H), 6.92-7.11 (m, 2H), 7.16-7.35 (m, 1H), 7.45-7.69 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.2, 60.4, 61.1, 110.3, 121.4, 123.0, 123.9, 126.4, 129.6, 135.0, 138.6, 157.7, 162.6; HRMS (ESI-TOF) Calcd. for $C_{14}H_{13}NNaO_5$ [M+Na]$^+$: 298.0686; found: 298.0685.

Ethyl 7-fluoro-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (**3b**). yellow oil; 81% yield (47.2 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.1 Hz, 3H), 3.31 (ddd, *J* = 19.7, 2.7, 1.7 Hz, 1H), 3.73 (ddd, *J* = 19.7, 2.5, 1.2 Hz, 1H), 4.13-4.42 (m, 2H), 5.09 (s, 1H), 6.77 (q, *J* = 2.4 Hz, 1H), 6.84-7.03 (m, 2H), 7.19-7.41 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.2, 60.4 (*J* = 1.9 Hz), 61.2, 110.7 (*J* = 8.6 Hz), 113.8 (*J* = 26.0 Hz), 116.0 (*J* = 24.6 Hz), 122.0, 125.3 (*J* = 9.3 Hz), 134.4, 139.0, 153.6 (*J* = 1.8 Hz), 158.7 (*J* = 239.0 Hz), 162.4; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}FNNaO_5$ [M+Na]$^+$: 316.0592; found: 316.0602.

Ethyl 7-chloro-3a-nitro-3a,8b-dihydro-*3H*-cyclopenta[*b*]benzofuran-1-carboxylate (3c). yellow solid; 81% yield (50.2 mg); m.p. 91.0-91.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H), 3.31 (ddd, *J* = 19.8, 2.7, 1.7 Hz, 1H), 3.74 (ddd, *J* = 19.7, 2.4, 1.1 Hz, 1H), 4.15-4.42 (m, 2H), 5.08 (s, 1H), 6.77 (q, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 7.17-7.25 (m, 1H), 7.47-7.62 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.1, 60.2, 61.3, 111.2, 121.7, 125.7, 126.7, 128.1, 129.5, 134.4, 139.0, 156.4, 162.3; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}ClNNaO_5$ [M+Na]$^+$: 332.0296; found: 332.0287.

Ethyl 7-bromo-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3d). yellow solid; 85% yield (60.3 mg); m.p. 86.0-86.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H), 3.31 (ddd, *J* = 19.7, 2.7, 1.7 Hz, 1H), 3.74 (ddd, *J* = 19.7, 2.4, 1.1 Hz, 1H), 4.10-4.44 (m, 2H), 5.08 (s, 1H), 6.77 (q, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 7.29-7.46 (m, 1H), 7.64-7.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.1, 60.2, 61.3, 111.8, 115.2, 121.6, 126.2, 129.5, 132.4, 134.4, 139.0, 156.9, 162.3; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}BrNNaO_5$ [M+Na]$^+$: 375.9791; found: 375.9778.

Ethyl 3a,7-dinitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3e). yellow oil; 70% yield (45.1 mg); ^{1}H NMR

(300 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.1 Hz, 3H), 3.38 (ddd, *J* = 19.9, 2.7, 1.7 Hz, 1H), 3.83 (ddd, *J* = 19.9, 2.5, 1.1 Hz, 1H), 4.16-4.43 (m, 2H), 5.16 (s, 1H), 6.83 (q, *J* = 2.4 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 8.16-8.32 (m, 1H), 8.41-8.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 43.9, 59.6, 61.6, 110.5, 122.2, 123.0, 125.6, 126.6, 134.0, 139.5, 143.9, 162.0, 162.3; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}N_2NaO_7$ $[M+Na]^+$: 343.0537; found: 343.0542.

Ethyl 7-methyl-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3f). yellow solid; 83% yield (48.0 mg); m.p. 102.8-103.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H), 2.30 (s, 3H), 3.19-3.39 (m, 1H), 3.72 (ddd, *J* = 19.6, 2.4, 1.2 Hz, 1H), 4.13-4.46 (m, 2H), 5.08 (s, 1H), 6.74 (q, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.98-7.13 (m, 1H), 7.38 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 20.8, 44.2, 60.5, 61.0, 109.8, 121.7, 123.8, 126.9, 129.9, 132.6, 135.0, 138.6, 155.8, 162.7; HRMS (ESI-TOF) Calcd. for $C_{15}H_{15}NNaO_5$ $[M+Na]^+$: 312.0842; found: 312.0830.

Ethyl 7-methoxy-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3g). yellow oil; 82% yield (50.1 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.1 Hz, 3H), 3.29 (ddd, *J* = 19.6, 2.7, 1.7 Hz, 1H), 3.70 (ddd, *J* = 19.6, 2.5, 1.1 Hz, 1H), 3.76 (s, 3H), 4.15-4.43 (m, 2H), 5.09 (s, 1H), 6.68-6.85 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 1H), 7.14 (d, *J* = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.2, 55.9, 60.7, 61.1, 110.4, 112.0, 114.9, 122.0, 124.8, 134.8, 138.8, 151.7, 155.8, 162.6; HRMS (ESI-TOF) Calcd. for $C_{15}H_{15}NNaO_6$ $[M+Na]^+$: 328.0792; found: 328.0792.

Ethyl 7-(tert-butyl)-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3h). yellow oil; 81% yield (53.8 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 1.38 (d, *J* = 7.1 Hz, 3H), 3.30 (ddd, *J* = 19.7, 2.7, 1.7 Hz, 1H), 3.72 (ddd, *J* = 19.6, 2.5, 1.2 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 5.12 (s, 1H), 6.76 (q, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 7.18-7.39 (m, 1H), 7.57-7.69 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 31.6, 34.5, 44.3, 60.6, 61.0, 109.4, 121.8, 123.3, 123.5, 126.4, 135.1, 138.7, 146.2, 155.5, 162.7; HRMS (ESI-TOF) Calcd. for $C_{18}H_{21}NNaO_5$ $[M+Na]^+$: 354.1312; found: 354.1308.

Ethyl 3a-nitro-7-phenyl-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3i). yellow oil; 85% yield (59.8 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.1 Hz, 3H), 3.27-3.45 (m, 1H), 3.71-3.84 (m, 1H), 4.18-4.37 (m, 2H), 5.20 (s, 1H), 6.78 (q, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.29-7.37 (m, 1H), 7.38-7.46 (m, 2H), 7.47-7.58 (m, 3H), 7.79-7.90 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.0, 14.2, 44.2, 60.5, 61.1 110.4, 111.8, 121.8, 124.6, 125.2, 126.9, 127.0, 128.6, 128.7, 134.9, 136.7, 138.7, 140.5, 157.3, 162.6; HRMS (ESI-TOF) Calcd. for $C_{20}H_{17}NNaO_5$ $[M+Na]^+$: 374.0999; found: 374.1000.

Ethyl 6-bromo-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3j). yellow oil; 84% yield (59.8 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.2 Hz, 3H), 3.31 (ddd, *J* = 19.7, 2.7, 1.7 Hz, 1H), 3.75 (ddd, *J* = 19.7, 2.5, 1.1 Hz, 1H), 4.11-4.40 (m, 2H), 5.05 (s, 1H), 6.75 (q, *J* = 2.4 Hz, 1H), 7.04-7.23 (m, 2H), 7.33-7.50 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.0, 60.0, 61.2, 114.0, 121.7, 122.7, 123.2, 126.2, 127.5, 134.5, 138.8, 158.5, 162.4; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}BrNNaO_5$ $[M+Na]^+$: 375.9791; found: 375.9778.

Ethyl 6-methyl-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3k). yellow oil; 85% yield (48.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.1 Hz, 3H), 2.34 (s, 3H), 3.19-.39 (m, 1H), 3.64-3.82 (m, 1H), 4.16-4.36 (m, 2H), 5.07 (s, 1H), 6.67-6.77 (m, 1H), 6.78-6.92 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.4, 44.1, 60.3, 61.0, 110.9, 120.9, 121.7, 123.8, 125.9, 135.1, 138.5, 140.1, 158.0, 162.6; HRMS (ESI-TOF) Calcd. for $C_{15}H_{15}NNaO_5$ $[M+Na]^+$: 312.0842; found: 312.0842.

Ethyl 6-methoxy-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[b]benzofuran-1-carboxylate (3l). yellow oil; 87% yield (53.0 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.29 (ddd, *J* = 19.5, 2.7, 1.6 Hz, 1H), 3.72 (ddd, *J* = 19.6, 2.4, 1.1 Hz, 1H), 3.77 (s, 3H), 4.07-4.38 (m, 2H), 5.04 (s, 1H), 6.47-6.66 (m, 2H), 6.72 (q, *J* = 2.3 Hz, 1H), 7.31-7.49 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.1, 55.6, 60.0, 61.0, 96.8, 108.8, 115.8, 122.2, 126.5, 135.2, 138.2, 159.0, 161.3, 162.7; HRMS (ESI-TOF) Calcd. for $C_{15}H_{15}NNaO_6$ $[M+Na]^+$: 328.0792; found: 328.0791.

Ethyl 5-fluoro-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (**3m**). yellow oil; 77% yield (45.3 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.39 (ddd, *J* = 19.8, 2.7, 1.7 Hz, 1H), 3.78 (ddd, *J* = 19.8, 2.4, 1.1 Hz, 1H), 4.15-4.37 (m, 2H), 5.15 (d, *J* = 2.0 Hz, 1H), 6.77 (q, *J* = 2.4 Hz, 1H), 6.90-7.10 (m, 2H), 7.28-7.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.0, 60.8 (*J* = 2.2 Hz), 61.2, 116.8 (*J* = 15.7 Hz), 121.7 (*J* = 3.7 Hz), 121.9, 123.8 (*J* = 5.5 Hz), 127.3, 134.5, 138.9, 144.4 (*J* = 10.9 Hz), 146.8 (*J* = 247.5 Hz), 162.4; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}FNNaO_5$ $[M+Na]^+$: 316.0592; found: 316.0598.

Ethyl 5-bromo-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3n). yellow oil, 78% yield (54.9 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.27-3.52 (m, 1H), 3.80 (ddd, *J* = 19.8, 2.6, 1.4 Hz, 1H), 4.11-4.39 (m, 2H), 5.18 (s, 1H), 6.78 (q, *J* = 2.4 Hz, 1H), 6.85-6.99 (m, 1H), 7.33-7.46 (m, 1H), 7.47-7.62 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.0, 61.1, 61.2, 102.9, 120.9, 124.4, 125.3, 125.4, 132.7, 134.5, 139.0, 155.2, 162.4; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}BrNNaO_5$ $[M+Na]^+$: 375.9791; found: 375.9783.

Ethyl 5-methoxy-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3o). yellow solid; 82% yield (50.3 mg); m.p. 98.1-98.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (td, *J* = 7.1, 0.9 Hz, 3H), 3.29-3.47 (m, 1H), 3.75 (ddd, *J* = 19.7, 2.5, 1.2 Hz, 1H), 4.13-4.36 (m, 2H), 5.12 (s, 1H), 6.64-6.81 (m, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.88-7.04 (m, 1H), 7.10-7.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 44.0, 56.2, 60.9, 61.0, 112.8, 118.1, 121.6, 123.7, 125.2, 134.8, 138.8, 144.2, 146.1, 162.5; HRMS (ESI-TOF) Calcd. for $C_{15}H_{15}NNaO_6$ $[M+Na]^+$: 328.0792; found: 328.0785.

Ethyl 5-ethoxy-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3p). yellow oil; 83% yield (53.2 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 1.44 (t, *J* = 7.0 Hz, 3H), 3.39 (ddd, *J* = 19.7, 2.7, 1.7 Hz, 1H), 3.76 (ddd, *J* = 19.7, 2.5, 1.2 Hz, 1H), 4.09-4.21 (m, 2H), 4.21-4.34 (m, 2H), 5.11 (s, 1H), 6.74 (q, *J* = 2.4 Hz, 1H), 6.82-6.89 (m, 1H), 6.89-6.98 (m, 1H), 7.09-7.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 14.8, 44.0, 60.9, 61.0, 64.9, 114.5, 118.2, 121.6, 123.7, 125.3, 134.8, 138.8, 143.5, 146.5, 162.6; HRMS (ESI-TOF) Calcd. for $C_{16}H_{17}NNaO_6$ $[M+Na]^+$: 342.0948; found: 342.0943.

Ethyl 3a-nitro-5-phenyl-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3q). yellow oil; 84% yield (58.7 mg); ^{1}H

NMR (300 MHz, $CDCl_3$) δ 1.36 (t, *J* = 7.1 Hz, 3H), 3.22-3.43 (m, 1H), 3.68-3.84 (m, 1H), 4.21-4.41 (m, 2H), 5.19 (s, 1H), 6.75 (q, *J* = 2.4 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.34-7.44 (m, 2H), 7.44-7.52 (m, 2H), 7.55-7.62 (m, 1H), 7.74-7.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 44.1, 60.5, 61.1, 121.4, 123.6, 124.6, 124.7, 125.4, 127.6, 128.5, 129.6, 134.8, 135.9, 138.8, 154.8, 162.6; HRMS (ESI-TOF) Calcd. for $C_{20}H_{17}NNaO_5$ $[M+Na]^+$: 374.0999; found: 374.0999.

Ethyl 8-chloro-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3r). yellow oil; 40% yield (24.9 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.1 Hz, 3H), 3.31 (ddd, *J* = 19.0, 2.8, 1.5 Hz, 1H), 3.67 (ddd, *J* = 19.0, 2.4, 1.3 Hz, 1H), 4.15-4.34 (m, 2H), 5.22 (d, *J* = 1.7 Hz, 1H), 6.72 (q, *J* = 2.4 Hz, 1H), 6.90-6.97 (m, 1H), 7.02 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.16-7.24 (m, 1H); 13C NMR (75 MHz, CDCl3) δ 14.1, 42.5, 59.4, 61.2, 109.0, 121.5, 122.6, 124.5, 130.8, 131.8, 134.7, 138.6, 158.9, 163.0; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}ClNNaO_5$ $[M+Na]^+$: 332.0296; found: 332.0301.

Ethyl 5,7-dibromo-3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (3s). yellow solid; 50% yield (43.0 mg); 172.5-173.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H), 3.41 (ddd, *J* = 19.8, 2.7, 1.7 Hz, 1H), 3.80 (ddd, *J* = 19.9, 2.5, 1.2 Hz, 1H), 4.15-4.43 (m, 2H), 5.15 (s, 1H), 6.79 (q, *J* = 2.4 Hz, 1H), 7.50-7.60 (m, 1H), 7.61-7.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 43.8, 61.0, 61.4, 103.6, 115.6, 121.1, 127.0, 128.6, 134.0, 134.9, 139.4, 154.7, 162.2; HRMS (ESI-TOF) Calcd. for $C_{14}H_{11}Br_2NNaO_5$ $[M+Na]^+$: 453.8896; found: 453.8896.

Ethyl 7a-nitro-8,10a-dihydro-7a*H*-cyclopenta[*b*]naphtho[1,2-d]furan-10-carboxylate (3t). yellow oil; 51% yield (33.2 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.1 Hz, 3H), 3.42 (ddd, *J* = 19.2, 2.8, 1.4 Hz, 1H), 3.74 (ddd, *J* = 19.1, 2.4, 1.3 Hz, 1H), 4.07-4.29 (m, 2H), 5.58 (d, *J* = 1.7 Hz, 1H), 6.80 (q, *J* = 2.4 Hz, 1H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.32-7.48 (m, 1H), 7.48-7.62 (m, 1H), 7.74-7.93 (m, 2H), 8.28-8.44 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 43.1, 59.6, 61.1, 111.6, 116.6, 122.2, 124.2, 125.1, 126.9, 128.5, 130.2, 130.7, 131.4, 135.4, 139.1, 156.1, 163.4; HRMS (ESI-TOF) Calcd. for $C_{18}H_{15}NNaO_5$ $[M+Na]^+$: 348.0842; found: 348.0856.

General experimental procedures for synthesis of compounds 5. To a solution of 2-nitrobenzothiophenes **4** (0.15 mmol) in CH_2Cl_2 (1.5 mL) were added ethyl-2,3-butadienoate **2a (**0.225 mmol**)** and catalyst Ph_2PMe (5.6 uL, 20 mol %). Then the mixture was stirred for specific time at 0 °C. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1～25:1) to give the corresponding product **5**.

Ethyl 3a-nitro-3a,8b-dihydro-3*H*-benzo[*b*]cyclopenta[*d*]thiophene-1-carboxylate (5a). yellow oil; 78% yield (34.0 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 3.42 (ddd, *J* = 19.4, 2.8, 1.9 Hz, 1H), 3.61 (ddd, *J* = 19.4, 2.4, 1.7 Hz, 1H), 4.07-4.38 (m, 2H), 5.55 (d, *J* = 2.1 Hz, 1H), 6.68 (q, *J* = 2.4 Hz, 1H), 7.08-7.18 (m, 2H), 7.19-7.26 (m, 1H), 7.63-7.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 44.5, 61.0, 63.2, 107.6, 120.8, 125.6, 127.7, 128.9, 134.5, 134.9, 137.2, 137.7, 163.0; HRMS (ESI-TOF) Calcd. for $C_{14}H_{13}NNaO_4S$ $[M+Na]^+$: 314.0457; found: 314.0465.

Ethyl 7-chloro-3a-nitro-3a,8b-dihydro-3*H*-benzo[*b*]cyclopenta[*d*]thiophene-1-carboxylate (5b). yellow oil; 82% yield (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.1 Hz, 3H), 3.42 (dt, *J* = 19.4, 2.3 Hz, 1H), 3.59 (dt, *J* = 19.4, 2.1 Hz, 1H), 4.14-4.37 (m, 2H), 5.49 (d, *J* = 2.1 Hz, 1H), 6.72 (q, *J* = 2.5 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 7.18-7.25 (m, 1H), 7.65-7.76 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 44.3, 61.2, 62.9, 107.9, 121.7, 128.1, 129.0, 131.6, 133.9, 135.7, 136.8, 138.3, 162.8; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}ClNNaO_4S$ $[M+Na]^+$: 348.0068; found: 348.0080.

Ethyl 7-methyl-3a-nitro-3a,8b-dihydro-3*H*-benzo[*b*]cyclopenta[*d*]thiophene-1-carboxylate (5c). yellow oil; 79% yield (36.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 2.32 (s, 3H), 3.41 (dt, *J* = 19.4, 2.3 Hz, 1H), 3.58 (dt, *J* = 19.3, 2.0 Hz, 1H), 4.12-4.34 (m, 2H), 5.49 (d, *J* = 2.1 Hz, 1H), 6.68 (q, *J* = 2.4 Hz, 1H), 6.97-7.07 (m, 2H), 7.47-7.60 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 21.1, 44.4, 60.9, 63.1, 107.9, 120.5, 128.5, 129.7, 133.7, 134.5, 135.0, 135.5, 137.8, 163.1; HRMS (ESI-TOF) Calcd. for $C_{15}H_{15}NNaO_4S$ $[M+Na]^+$: 328.0614; found: 328.0620.

Ethyl 5-methyl-3a-nitro-3a,8b-dihydro-3*H*-benzo[*b*]cyclopenta[*d*]thiophene-1-carboxylate (5d). yellow solid; 83% yield (38.0 mg); 82.1-82.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.21 (s, 3H), 3.46 (dt, *J* = 19.4, 2.3 Hz, 1H), 3.61 (dt, *J* = 19.4, 2.1 Hz, 1H), 4.06-4.34 (m, 2H), 5.59 (d, *J* = 2.1 Hz, 1H), 6.67 (q, *J* = 2.4 Hz, 1H), 6.99-7.16 (m, 2H), 7.47-7.61 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 20.4, 44.8, 60.9, 63.5, 107.0, 125.0, 126.0, 129.5, 130.6, 134.7, 134.8, 137.0, 137.5, 163.0; HRMS (ESI-TOF) Calcd. for $C_{15}H_{15}NNaO_4S$ $[M+Na]^+$: 328.0614; found: 328.0617.

Ethyl 3a-nitro-6-phenyl-3a,8b-dihydro-3*H*-benzo[*b*]cyclopenta[*d*]thiophene-1-carboxylate (5e). yellow oil; 80% yield (44.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.46 (dt, *J* = 19.4, 2.4 Hz, 1H), 3.64 (dt, *J* = 19.4, 2.1 Hz, 1H), 4.08-4.34 (m, 2H), 5.59 (d, *J* = 2.1 Hz, 1H), 6.71 (q, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 1.7 Hz, 1H), 7.34-7.39 (m, 2H), 7.40-7.47 (m, 2H), 7.49-7.57 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 44.5, 61.0, 63.0, 107.9, 119.4, 124.8, 127.0, 127.7, 127.9, 128.8, 133.9, 134.4, 137.8, 138.0, 140.0, 142.4, 163.0; HRMS (ESI-TOF) Calcd. for $C_{20}H_{18}NO_4S$ $[M+H]^+$: 368.0951; found: 368.0935.

General experimental procedures for synthesis of compounds 7. To a solution of 3-nitrobenzothiophenes **6** (0.15 mmol) in CH_2Cl_2 (1.5 mL) were added ethyl-2,3-butadienoate **2a (**0.225 mmol**)** and catalyst Ph_2PMe (5.6 uL, 20 mol %). Then the mixture was stirred for specific time at 0 °C. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1～25:1) to give the corresponding product **7**.

Ethyl 8b-nitro-3a,8b-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophene-3-carboxylate (7a). yellow oil; 83% yield (36.0 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 3.44 (ddd, *J* = 19.2, 2.8, 2.0 Hz, 1H), 3.89 (ddd, *J* = 19.2, 2.5, 1.4 Hz, 1H), 4.15-4.37 (m, 2H), 5.75 (q, *J* = 1.6 Hz, 1H), 6.62-6.73 (m, 1H), 7.10-7.25 (m, 2H), 7.27-7.39 (m, 1H), 7.44-7.56 (m, 1H); 13C NMR (75 MHz, $CDCl_3$) δ 14.13, 46.50, 59.33, 61.14, 105.40, 122.57, 125.17, 125.67, 131.59, 135.49, 135.80, 138.24, 142.31, 162.51; HRMS (ESI-TOF) Calcd. for $C_{14}H_{13}NNaO_4S$ $[M+Na]^+$: 314.0457; found: 314.0458.

Ethyl 7-fluoro-8b-nitro-3a,8b-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophene-3-carboxylate (7b). yellow oil; 91% yield (42.1 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 3.40 (ddd, *J* = 19.2, 2.7, 1.9 Hz, 1H), 3.86 (ddd, *J* = 19.2, 2.5, 1.4 Hz, 1H), 4.17-4.36 (m, 2H), 5.75-5.85 (m, 1H), 6.64-6.73 (m, 1H), 7.01-7.16 (m, 2H), 7.19-7.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 46.6, 60.0, 61.2, 105.0 (*J* = 2.2 Hz), 113.0 (*J* = 24.1 Hz), 119.3 (*J* = 23.0 Hz), 123.5 (*J* = 8.2 Hz), 135.5, 137.1 (*J* = 7.4 Hz), 137.3 (*J* = 2.8 Hz), 138.0, 160.9 (*J* = 243.4 Hz), 162.4; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}FNNaO_4S$ [M+Na]$^+$: 332.0363; found: 332.0357.

Ethyl 7-bromo-8b-nitro-3a,8b-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophene-3-carboxylate (7c). yellow oil; 88% yield (49.1 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 3.42 (ddd, *J* = 19.2, 2.7, 1.9 Hz, 1H), 3.87 (ddd, *J* = 19.2, 2.5, 1.4 Hz, 1H), 4.20-4.33 (m, 2H), 5.77 (q, *J* = 1.6 Hz, 1H), 6.62-6.73 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.40-7.50 (m, 1H), 7.62 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 46.6, 59.9, 61.2, 104.8, 118.1, 123.9, 128.8, 134.6, 135.3, 137.6, 138.1, 141.6, 162.3; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}BrNNaO_4S$ [M+Na]$^+$: 391.9563; found: 391.9548.

Ethyl 7-chloro-8b-nitro-3a,8b-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophene-3-carboxylate (7d). yellow oil; 98% yield (48.1 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 3.41 (ddd, *J* = 19.2, 2.8, 2.0 Hz, 1H), 3.87 (ddd, *J* = 19.2, 2.5, 1.4 Hz, 1H), 4.17-4.35 (m, 2H), 5.78 (d, *J* = 1.6 Hz, 1H), 6.63-6.74 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.26-7.32 (m, 1H), 7.48 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 46.6, 60.0, 61.3, 104.9, 123.5, 125.9, 130.9, 131.8, 135.4, 137.3, 138.1, 140.9, 162.3; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}ClNNaO_4S$ [M+Na]$^+$: 348.0068; found: 338.0077.

Ethyl 5-chloro-8b-nitro-3a,8b-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophene-3-carboxylate (7e). yellow oil; 88% yield (43.0 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.42 (ddd, *J* = 19.3, 2.7, 2.0 Hz, 1H), 3.90 (ddd, *J* = 19.3, 2.5, 1.3 Hz, 1H), 4.22-4.34 (m, 2H), 5.76 (q, *J* = 1.7 Hz, 1H), 6.65-6.75 (m, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 7.33 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.40 (dd, *J* = 7.8, 1.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 46.8, 59.0, 61.3, 106.1, 123.8, 126.6, 128.1, 131.3, 135.5, 137.3, 138.4, 142.5, 162.3; HRMS (ESI-TOF) Calcd. for $C_{14}H_{12}ClNNaO_4S$ [M+Na]$^+$: 348.0068; found: 338.0059.

Ethyl 7-methyl-8b-nitro-3a,8b-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophene-3-carboxylate (7f). yellow solid; 88% yield (40.0 mg); m.p. 93.5-94.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 2.32 (s, 3H), 3.31-3.52 (m, 1H), 3.81-3.95 (m, 1H), 4.18-4.33 (m, 2H), 5.74 (q, *J* = 1.7 Hz, 1H), 6.61-6.72 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.11-7.16 (m, 1H), 7.27-7.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 20.9, 46.3, 59.6, 61.1, 105.5, 122.3, 126.0, 132.6, 135.2, 135.5, 135.9, 138.2, 138.8, 162.6; HRMS (ESI-TOF) Calcd. for $C_{15}H_{15}NNaO_4S$ [M+Na]$^+$: 328.0614; found: 328.0600.

Ethyl 8b-nitro-7-phenyl-3a,8b-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophene-3-carboxylate (7g). yellow solid; 81% yield (45.1 mg); m.p. 112.8-113.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, *J* = 7.1 Hz, 3H), 3.54 (ddd, *J* = 19.2, 2.8, 2.0 Hz, 1H), 3.96 (ddd, *J* = 19.2, 2.5, 1.4 Hz, 1H), 4.26-4.36 (m, 2H), 5.85 (q, *J* = 1.7 Hz, 1H), 6.68-6.79 (m, 1H), 7.27-7.31 (m, 1H), 7.36-7.42 (m, 1H), 7.45-7.50 (m, 2H), 7.55 (q, *J* = 1.8 Hz, 1H), 7.56-7.62 (m, 2H), 7.74 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 46.6, 59.8, 61.3, 105.4, 122.9, 124.3, 126.9, 127.6, 129.0, 130.7, 135.5, 136.6, 138.4, 138.9, 139.8, 141.4, 162.6; HRMS (ESI-TOF) Calcd. for $C_{20}H_{17}NNaO_4S$ [M+Na]$^+$: 390.0770; found: 390.0766.

Ethyl 4b-nitro-5,7a-dihydro-4b*H*-cyclopenta[4,5]thieno[2,3-*b*]pyridine-7-carboxylate (7h). yellow oil;, 83% yield (36.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H), 3.40 (dt, *J* = 19.2, 2.4 Hz, 1H), 3.89 (ddd, *J* = 19.2, 2.6, 1.3 Hz, 1H), 4.23-4.37 (m, 2H), 5.81 (q, *J* = 1.5 Hz, 1H), 6.75 (q, *J* = 1.0 Hz, 1H), 6.98-7.23 (m, 1H), 7.79-7.81 (m, 1H), 8.33-8.57 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 47.2, 57.1, 61.4, 102.9, 119.7, 130.1, 133.9, 136.0, 138.3, 152.9, 162.3, 165.2; HRMS (ESI-TOF) Calcd. for $C_{13}H_{12}N_2NaO_4S$ [M+Na]$^+$: 315.0410; found: 315.0424.

Scale-up experiment. To a solution of 2-nitrobenzofuran **1a** (4.6 mmol, 0.75 g) in CH_2Cl_2 (46 mL) were added ethyl-2,3-butadienoate **2a** (0.3 mmol, 0.77 g) and catalyst Ph_2PMe (184 mg, 20 mol %). Then the mixture was stirred for 8 h at 0 °C. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the corresponding product **3a** in 81% yield (1.02 g).

Synthesis of compound 8. $NaIO_4$ (89 mg, 2 equiv) and distilled water (0.2 mL) were added to a test tube. The solution was cooled to 0 °C and $RuCl_3{\cdot}3H_2O$ (5.6 mg, 0.1 equiv) was added. Then EtOAc (0.4 mL) was added. CH_3CN (0.8 mL) and a solution of substrate **3a** (55 mg, 0.2 mmol) in EtOAc (0.8 mL) was added in sequence. After 30 mins, 10% $NaHCO_3$ (2.0 mL) and saturated Na_2SO_3 solution (6.0 mL) were added. The solution was stirred for 10 mins at room temperature. Then it was extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure and the resulting crude mixture was purified by silica gel column chromatography (petroleum ether/AcOEt=15:1) to afford compound **8**.

Ethyl 1,2-dihydroxy-3a-nitro-2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran-1-carboxylate (8). yellow oil; 49% yield (30.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (t, *J* = 7.1 Hz, 3H), 2.50 (dd, *J* = 14.4, 10.6 Hz, 1H), 2.75 (d, *J* = 10.3 Hz, 1H), 3.16 (dd, *J* = 14.3, 7.5 Hz, 1H), 3.42 (s, 1H), 4.33-4.58 (m, 3H), 5.05 (q, *J* = 9.3 Hz, 1H), 6.98-7.17 (m, 3H), 7.31-7.49 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 42.8, 60.8, 63.4, 77.3, 81.7, 110.7, 119.3, 120.6, 123.1, 124.7, 130.4, 159.9, 171.8; HRMS (ESI-TOF) Calcd. for $C_{14}H_{15}NNaO_7$ [M+Na]$^+$: 332.0741; found: 332.0743.

Synthesis of compound 9. To compound **3a** (110 mg, 0.4 mmol) in 4 mL of anhydrous THF was added DIBAL-H (170.4 mg, 3.0 equiv) at 0 °C. After being stirred at room temperature for 3 h, water (4 mL) was added to the reaction mixture and the aqueous layer was extracted with AcOEt. (6 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure and the resulting crude mixture was purified by silica gel column chromatography (petroleum ether/AcOEt=4:1) to afford compound **9**.

(3a-nitro-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-1-yl)methanol (9). yellow oil 77% yield (71.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (s, 1H), 3.08-3.27 (m, 1H), 3.47-3.66 (m, 1H), 4.13-4.40 (m, 2H), 4.93 (s, 1H), 5.64 (q, *J* = 1.9 Hz, 1H), 6.94-7.15 (m, 2H), 7.21-7.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 59.2, 60.9, 110.5, 122.2, 122.4, 122.9, 124.0, 124.5, 129.3, 141.7, 157.6; HRMS (ESI-TOF) Calcd. for $C_{12}H_{11}NNaO_4$ [M+Na]$^+$: 256.0580; found: 256.0568.

Conflicts of interest

There are no conflicts to declare.

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Phosphine-Catalyzed Dearomative (3+2) Annulation of 2-Nitrobenzofurans and Nitrobenzothiophenes with allenoate

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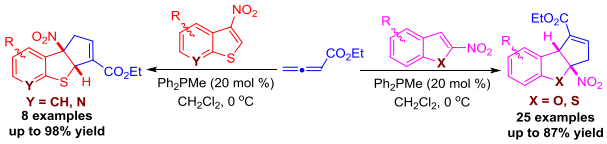

An efficient Ph_2PMe-catalyzed dearomative (3+2) annulation of 2-nitrobenzofurans, 2-nitrobenzothiophenes, and 3-nitrobenzothiophenes with allenoate was reported.