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可见光促进的苯并噻吩及其衍生物的合成

摘要

苯并噻吩是一类重要的杂环化合物，广泛存在于大量的天然产物及具有生物活性的药物分子中。苯并噻吩及其衍生物在医药农药、有机光电材料和有机半导体材料中都具有广泛的应用。同时苯并噻吩衍生物也是重要的合成中间体。由于其应用范围广泛，苯并噻吩衍生物的合成方法学研究倍受化学工作者的关注。可见光促进的有机反应具有条件温和、环境友好等优点，是当前有机合成化学的研究热点。本论文围绕可见光促进的邻炔基苯甲硫醚参与的自由基串联环化反应，发展苯并噻吩类化合物合成新方法，主要开展了以下三个研究工作：

(1) 发展了用简单卤代烃做为卤源，可见光促进 2-炔基苯甲硫醚串联环化制备 3-卤（溴、碘）代苯并噻吩的新策略。在优化的反应条件下，以 60-97%的产率合成了 43 个目标化合物，卤素原子可以方便地转化为其他官能团，用于合成功能化苯并噻(硒)吩。控制实验、自由基淬灭实验和荧光淬灭实验表明溴环化过程可能经历自由基历程，开关灯实验表明该转化需要不间断的光照。与文献已报道方法相比，该方法具有无需任何外加光催化剂、反应条件简单温和、官能团耐受性好和产物收率高的优点。

(2) 发展了可见光促进 9, 10-菲醌（PQ）催化的 2-炔基苯甲硫醚分子内环化氧化制备 3-酰基苯并噻吩的新方法。在最优反应条件下，

以 51-90%的产率合成了 41 个目标化合物。通过控制实验研究了反应机理，自由基淬灭实验表明α-硫代烷基自由基中间体的形成至关重要。同位素（^{18}O）标记实验表明 3-酰基苯基噻吩中的氧原子来源于空气中的氧气，动力学同位素竞争实验（KIE=K_H/K_D=2.69）表明氢原子转移是决速步骤（氢转移过程）。与文献报道方法相比，该反应无需外加金属催化剂，具有反应条件温和、底物广谱性好和原子利用率高等优点。

(3) 发展了无外加光敏化剂条件下可见光促进 2-炔基苯甲硫醚与 1, 4-二氮杂二环[2.2.2]辛烷二（二氧化硫）加合物（DABSO）自由基串联环化反应合成 3-烷基磺酰基苯并噻吩的新方法。控制实验表明，C-S 键均裂是关键步骤。与文献已报道方法相比，该方法无需金属催化剂，该反应具有底物范围广，反应条件简单，反应产率高，官能团耐受性好等优点。

关键词：2-炔基苯甲硫醚，苯并噻吩，光催化，分子内环化反应，自由基串联反应

VISIBLE-LIGHT-INDUCED SYNTHESIS OF BENZO[*B*]THIOPHENEAND AND ITS DERIVATIVES

ABSTRACT

Benzo[*b*]thiophene is an important heterocyclic compound, which is widely present in a lot of natural and bioactive drug molecules. Benzo[*b*]thiophene and its derivatives are widely used in pharmaceutical pesticides, organic photoelectric materials and organic semiconductor materials. Benzo[*b*]thiophene derivatives are also important synthetic intermediates. The synthesis methodology of benzo[*b*]thiophene derivatives has attracted much attention from chemists because of its wide range of applications. Organic reactions by visible light-promoted have the advantages of mild conditions and environment-friendly, and which are hot topics in current organic synthetic chemistry. In this paper, three new methods for the synthesis of benzo[*b*]thiophene and its derivatives based on the free radical tandem cyclization reaction involving o-acetylenyl benzo[*b*]thiophene by visible light-promoted was developed, and the following three research works were mainly carried out:

(1) A new strategy for preparation of 3-halo(bromine, iodine)benzo[*b*]thiophenes via a visble-light-induced tadem cyclization of

2-alkynylthioanisoles with simple alkyl halides as halogen source was developed. Under optimized reaction conditions, 43 desired compounds were obtained in 60-97% yield and a lot of derivations of 3-bromo(iodo)benzo[*b*]thiophene were carried out. Moreover, the halogen atom could be conveniently converted into other functional groups for the synthesis of C3 functionalized benzo[*b*]thio(seleno)phenes. The results of the radical trapping and fluorescence quenching experiment show that bromocyclization process may undergo free radical process. The light "on/off" experiment shows that uninterrupted irradiation to be necessary for this transformation. Compared with the methods reported in the literature, this protocol has a range of advantages, including without external photocatalyst, simplicity and mildness of the reaction conditions, good functional-group tolerance and excellent yields of the products.

(2) A new method for preparation of 3-acylbenzo[*b*]thiophene via a visble-light-induced intramolecular oxidative cyclization of 2-alkynylthioanisoles with PQ catalyzed was developed. Under the optimal reaction conditions, 41 desired compounds were obtained in 51-90% yield. The mechanism of the reaction was studied by controlled experiments. The results of the radical trapping experiment showed that the formation of α-thioalkyl radical intermediates was very important. The results of the isotope (^{18}O) labeling experiment showed

that clearly illustrated that oxygen atom in 3-acylbenzo[*b*]thiophen comes from O_2 in air, and the results of the kinetic isotope experiment (KIE=K_H/K_D=2.69) showed that the hydrogen atom transfer (HAT) is the rate determining step. Compared with the methods reported in the literature, the reaction has the advantages of without external metal-catalys, mild reaction conditions, great compatibility and high atomic utilization.

(3) A new method for the synthesis of 3-(alkylsulfonyl)benzo[*b*]thiophenes via a visble-light-induced cyclization of 2-alkynylthioanisoles with 1, 4-diazabicyclo[2.2.2]octane-1, 4-diium-1, 4-disulfinate (DABSO) without external photocatalyst was developed. The results of the control experiments show that C-S bond homolysis is the key step. Compared with the methods reported in the literature, the reaction has the advantages of metal-free, wide substrate range, simple reaction conditions, excellent yields and good functional-group tolerance of the products.

Wang FenDou (Chemistry)

Supervised by Li PinHua

KEY WORDS: Methyl(2-(phenylethynyl)phenyl)sulfane,

Benzo[*b*]thiophenes, Photocatalysis, Intramolecular cyclization reaction,

Free radical tandem reaction

目 录

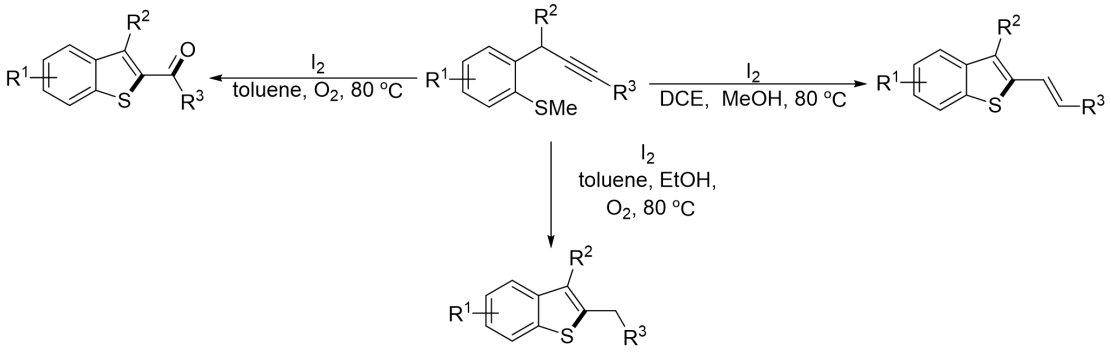
第 1 章 绪论

1.1 引言

含硫杂环化合物具有独特的生物活性，广泛应用于医药农药和材料科学等领域[1]。苯并噻吩及其衍生物是一类重要的含硫杂环，大量存在于具有生物活性的天然和非天然化合物中。苯并噻吩类化合物具有抗菌[2]、抗癌[3,4]、抗氧化[5]、抗艾滋病毒[6,7]和抗炎[8,9]等活性，在药物化学中具有广泛的应用。苯并噻吩衍生物在有机光电材料[10-13]和有机半导体[14-18]中也有广泛应用。鉴于苯并噻吩及其衍生物的广泛用途，其合成方法学研究一直受到化学工作者的关注。本章主要介绍近年来苯并噻吩及其衍生物的合成方法学研究进展。

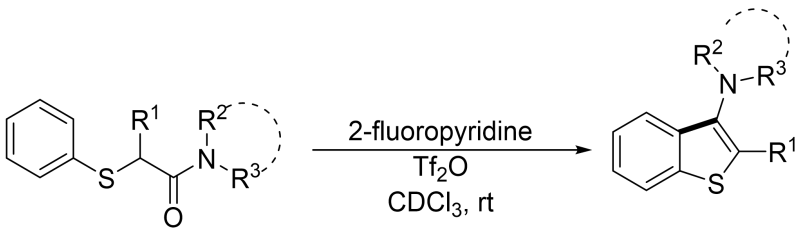
1.2 通过分子内环化反应合成苯并噻吩及其衍生物

2016 年，Procter 等人[19]报道了由碘促进的 2-炔丙基苯甲硫醚合成不同类型的苯并噻吩衍生物。通过调控溶剂和反应体系中氧气含量选择性合成 2-烯基苯并噻吩、2-酰基苯并噻吩和 2-烷基苯并噻吩。该方法具有无需外加金属催化剂，起始原料简单易得，产物收率高等优点（Scheme 1-1）。



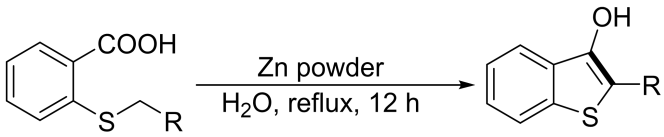
Scheme 1-1 以 2-炔丙基苯甲硫醚为原料选择性合成 2-取代苯并噻吩

2015 年，Mesmaeker 小组[20]利用α苯硫代乙酰胺，通过相应的酮胺中间体的 6π电环化，可以非常高效地获得 3-氨基苯并噻吩。该反应在相对温和条件下以 29-95%的产率合成了 30 个相应的 3-氨基苯并噻吩（Scheme 1-2）。



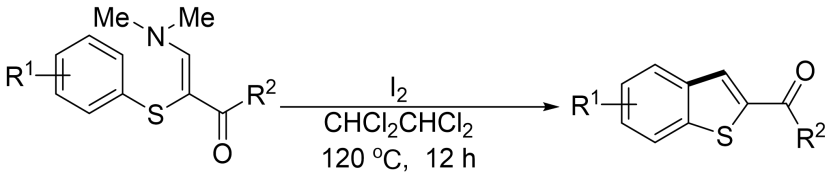
Scheme 1-2 以α苯硫代烷基酰胺制备 3-氨基苯并噻吩

2013 年，Wang 课题组[21]报道了一种以锌粉为促进剂合成 2-取代苯并噻吩-3-醇的高效方法。在加热条件下，取代的 2-烷基巯基苯甲酸都能以较高收率得到目标化合物。作者还采用密度泛函理论（DFT）模型研究了反应可能机理（Scheme 1-3）。



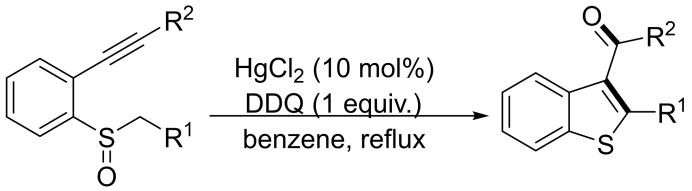
Scheme 1-3 锌促进合成 3-醇-苯并噻吩

Tamariz 等人[22]报道了碘促进芳基胺酮环化高效合成 2-酰基苯并噻吩和苯并呋喃的方法。控制实验表明，芳基羰基和芳基硫羰基的芳基环上存在给电子基团有利于该反应的进行（Scheme 1-4）。



Scheme 1-4 碘促进环化反应制备苯并噻吩

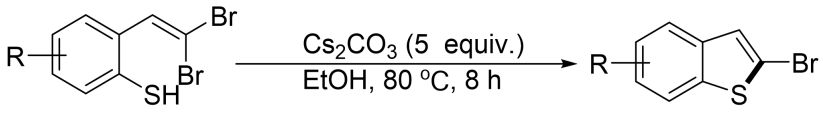
2013 年，Wu 课题组[23]发展了一种氯化汞催化 2-炔基苯基烷基亚砜环化合成 3-酰基苯并噻吩的方法。该反应中以当量 2,3-二氯-5,6-二氰基苯醌（DDQ）作为氧化剂，产物产率中等偏上，但反应机理尚不清楚（Scheme1-5）。



Scheme 1-5 汞催化 2-炔基苯基烷基亚砜环化合成 3-酰基苯并噻吩

Wang 等人[24]在痕量 Cu（0.0064 mol%，25 ppm）存在下，用 Cs_2CO_3 促进偕二溴硫酚脱溴化氢偶联合成了 2-溴苯并噻吩。该分子内环化反应以 80-99%的产

率获得 21 个相应的 2-溴苯并噻吩。该方法也适用于 2-溴苯并呋喃的合成。（Scheme 1-6）。

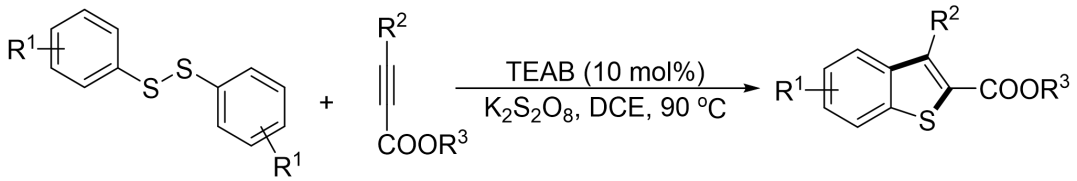


Scheme 1-6 以偕二溴硫酚为原料合成 2-溴苯并噻吩

1.3 通过分子间环化反应合成苯并噻吩及其衍生物

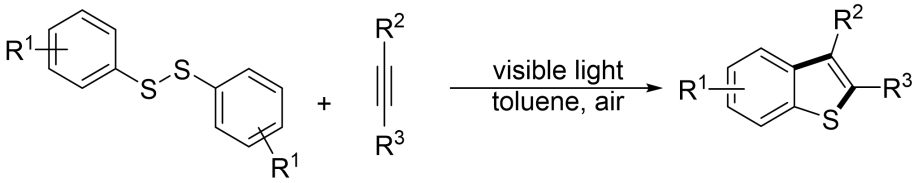
近年来，二芳基二硫醚、芳基硫酚和硫代琥珀酰亚胺作为苯并噻吩的合成前体的反应受到了化学工作者许多关注，其中以二芳基二硫醚、苯硫酚芳基硫代酰亚胺参与的串联反应居多[25]。一般而言，它们都是在原位产生硫自由基发生加成环化反应形成苯并噻吩及其衍生物的，这为含硫杂环的构建开辟了一条潜在的新途径。

2014 年，Wang 课题组等人[26]发展了一例 *N*-Et$_4$NBr（TEAB）催化芳基二硫醚和丙炔酸酯串联反应合成双取代苯并噻吩方法。该方法是通过 S-S 键均裂产生硫自由基与碳碳叁键发生加成进而发生级联环化反应来高效构建苯并噻吩结构单元的。该方法具有官能团耐受性好，产率高，原料易得等优点（Scheme 1-7）。



Scheme 1-7 二硫醚与炔分子内环化合成苯并噻吩

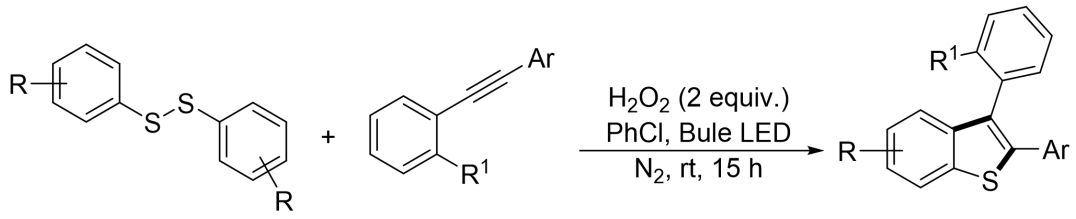
2017 年，Yan 等人[27]用二硫醚和不同取代基的炔烃为原料发展了可见光促进的分子间自由基环化合成苯并噻吩的方法。该反应温和条件，以 26-73%的产率合成了 23 个双取代苯并噻吩（Scheme 1-8）。



Scheme 1-8 可见光促进的分子间自由基环化合成苯并噻吩

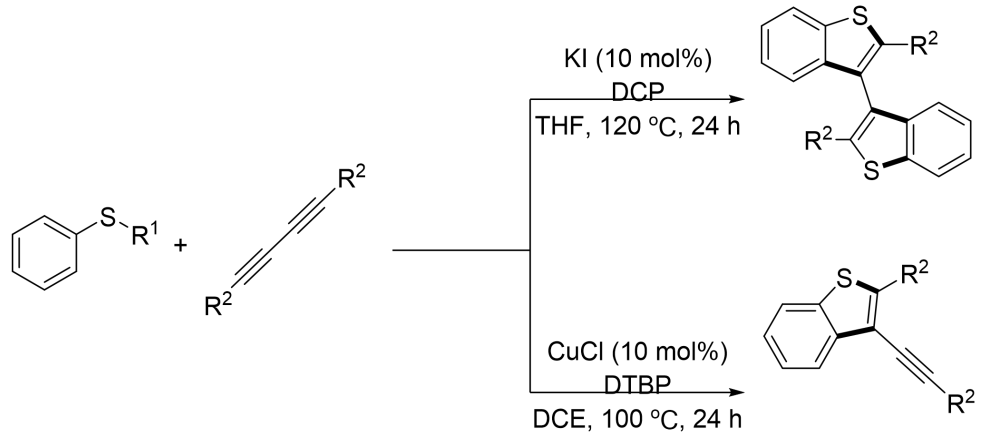
同年 Wang 等人[28]使用 H_2O_2 作为氧化剂进行这种转化，可见光促进的自由基级联环化反应在室温下顺利进行，此反应硫原子作为自由基受体，产物收率中

等至较高，具有良好的官能团耐受性。该反应不使用任何金属和光催化剂（Scheme1-9）。



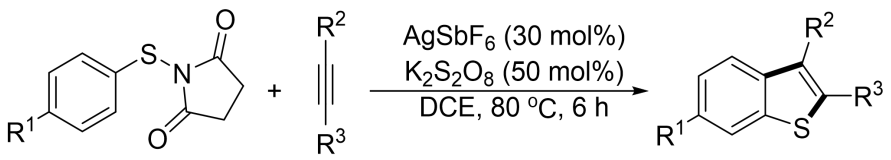
Scheme 1-9 以二硫醚为硫源可见光诱导的环化反应

2022 年，Yang 课题组[29]开发了一种苯硫醚和 1,3-二炔的区域选择性催化氧化环化反应合成 3-炔基苯并噻吩和联噻吩的方法（Scheme 1-10），为对称的 3, 3-联苯并噻吩和非对称的 3-炔基苯并噻吩提供了一条捷径。通过串联反应同时构建四个新的化学键和两个噻吩环，并且可以通过选择催化体系轻松切换该方案的单/双环选择性。



Scheme 1-10 苯硫醚与二炔选择性合成苯并噻吩和联噻吩

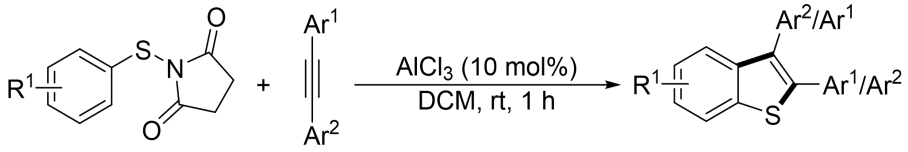
2016 年，Sahoo 小组[30]报道了六氟锑酸银和过硫酸钾共同催化氮-（芳硫代）琥珀酰亚胺和未活化的炔发生分子间氧化环化高效制备 2,3-二芳基苯并噻吩的方法。机理研究表明，S-N 键的氧化裂解和烯烃的环化是构建苯并噻吩结构单元的主要过程（Scheme1-11）。



Scheme 1-11 银催化的分子间氧化环化反应

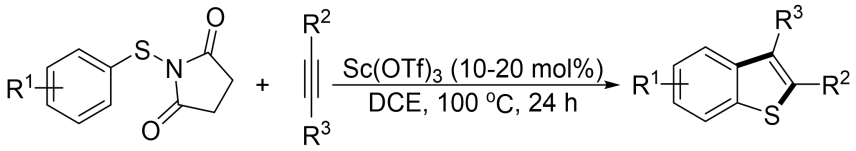
2017 年，该小组[31]报道了 $AlCl_3$ 催化该反应也可以顺利地进行，与原来的方

法相比，该方法反应条件温和，无需外加过氧化物，底物范围广，产率高可以更高效的构建 2,3-二芳基苯并噻吩（Scheme1-12）。



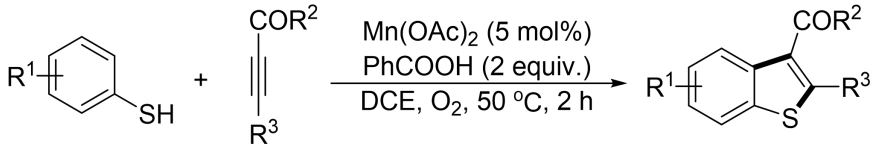
Scheme 1-12 氯化铝催化分子间氧化环化反应

2016 年 Glorius 等人[32]报道了 $Sc(OTf)_3$ 催化的氮-（芳硫代）琥珀酰亚胺和二芳基炔串联环化反应，高效率地合成了一系列 2,3-二芳基苯并噻吩。机理研究表明乙烯基阳离子异位环化的螺环化合物的迁移是关键过程（Scheme1-13）。



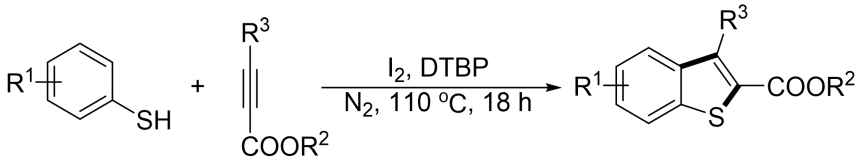
Scheme 1-13 $Sc(OTf)_3$ 催化的分子间环化反应

2013 年，Li 等人[33]报道了锰催化苯硫酚和炔分子间氧化环化合成 3-酰基苯并噻吩的高效方法。产物可以通过水解、脱羧偶联等方法进一步转化为其他 C3 功能化苯并噻吩（Scheme1-14）。



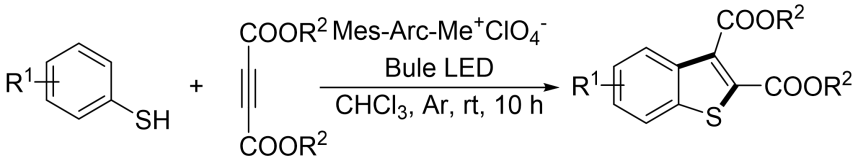
Scheme 1-14 锰催化氧化环化合成苯并噻吩

2015 年，Zhang 等人[34]报道了碘促进硫酚和丙炔酸酯分子间串联环化合成官能化苯并噻吩。该反应在无外加金属和溶剂条件下顺利进行，以 71-92%收率合成了一系列功能化苯并噻吩。（Scheme1-15）。



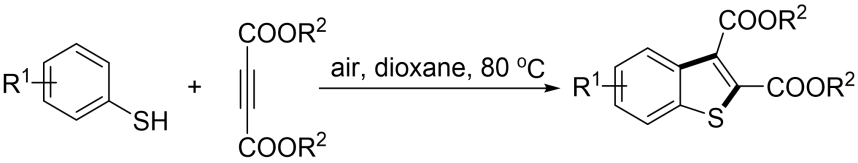
Scheme 1-15 碘催化硫酚与炔的串联环化合成苯并噻吩

2017 年，Xia 等人[35]报道了可见光促进 Mes-Arc-$Me^+ClO_4^-$ 催化硫醇与炔发生 1,2 环加成反应高效合成 1,2-二取代苯并噻吩。反应在温和条件下以 33-98%的产率合成了 26 个官能化苯并噻吩。（scheme1-16）。



Scheme 1-16 光促进加成环化合成苯并噻吩

Huo 等人[36]报道了氧促进硫酚和炔反应合成双官能化苯并噻吩。该合成方法不使用任何催化剂、化学氧化剂和添加剂。在温和条件下以 34-94%的收率合成了 25 个双取代苯并噻吩（Scheme1-17）。

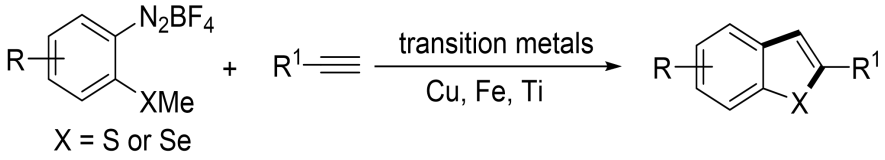


Scheme 1-17 氧气作为氧化剂苯硫酚和炔反应合成苯并噻吩

1.4 通过邻炔基苯甲硫醚串联环化反应合成苯并噻吩及其衍生物

苯并噻吩及其衍生物的合成已经有了很大的发展，但是仍有很大的局限性。例如，早期的反应需要过渡金属铜、铁或者有机金属试剂炔铜，在强碱的条件下才可以反应，反应条件苛刻，底物范围较窄。虽然 2013 年以来芳基二硫醚、芳基硫酚和芳基硫代琥珀酰亚胺作为自由基前体或者受体合成苯并噻吩的方法已经有了很大的发展，但是该反应受限于炔种类的限制，一般需要吸电子基团反应才可以顺利进行。因此，开发新的反应模式来合成苯并噻吩是非常有必要的。近几十年来，由苯甲硫醚参与的苯并噻吩的合成和修饰受到了许多化学工作者的关注，取得了一系列研究进展[25]。

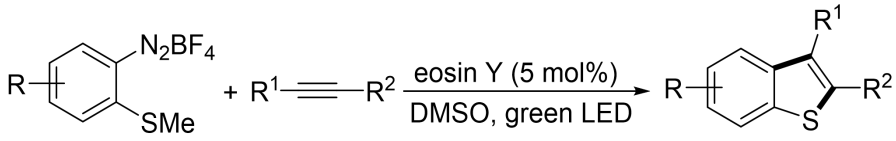
Zanardi 课题组[37]在 1985 年发展了过渡金属促进的芳基重氮盐与炔烃的自由基串联环化合成 2-取代苯并噻吩。在随后的几十年时间里 McDonald 与 Schiesser 课题组[38, 39]也进行了类似的报道（Scheme1-18）。该类合成方法需要当量的过渡金属才能完成，有很大的局限性。



Scheme 1-18 过渡金属促进邻炔基苯甲硫醚与炔烃合成 2-取代苯并噻吩

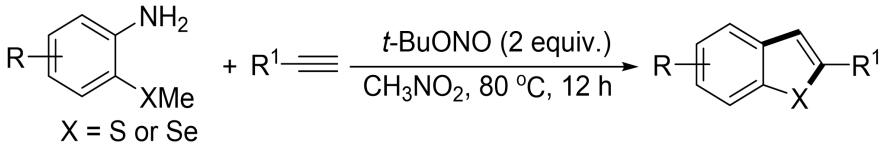
2013 年，König 课题组[40]发展了可见光促进 eosin Y 催化芳基重氮盐和炔串

联环化合成双取代苯并噻吩方法（Scheme1-19）。该方法无需金属催化剂和高温。在温和条件下以 30-81%的收率合成了 26 个双取代苯并噻吩。



Scheme 1-19 光诱导邻甲硫基芳基重氮盐与炔烃的级联反应

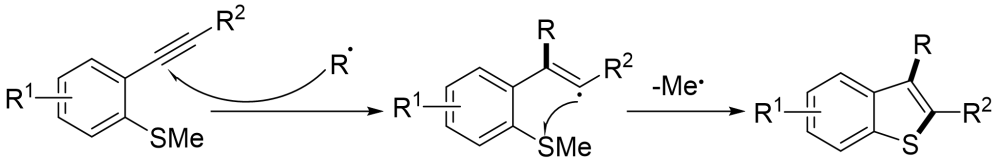
2016 年, Zhang 课题组[41]开发了一种简单和高效的策略。可以从芳基胺作为起始原料制备苯并噻吩和苯并硒苯（Scheme1-20）。该方法无需过渡金属或添加剂。以 30-75%的收率合成了 33 个 C2 官能化苯并噻吩。



Scheme 1-20 芳胺与炔制备苯并噻（硒）吩

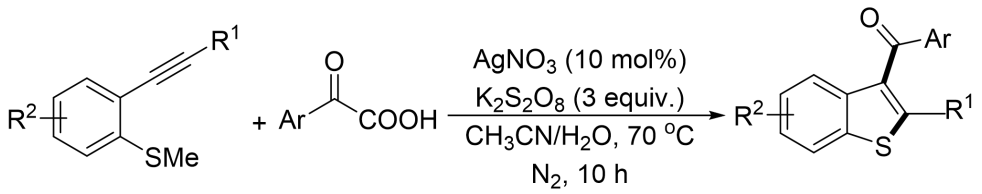
然而, König 和 Zhang 的方法都需要直接或间接适用芳基重氮盐，在工业生产上有一定的局限性。因此, 需要发展新的反应模式来合成官能化苯并噻吩[25]。

近十几年来，外来自由基与邻炔基苯甲（硫、硒)醚的串联环化合成 C3 位官能化苯并呋喃（噻、硒吩）的方法得到了发展[42-50]。其中光化学和电化学促进的自由基反应[51-62]，已经发展成为一种重要的工具。一般是在一定条件下形成一个 R 自由基，然后进攻碳碳三键形成烯基自由基，然后环化脱去甲基自由基形成 C3 位官能化苯并噻吩（Scheme1-21)。



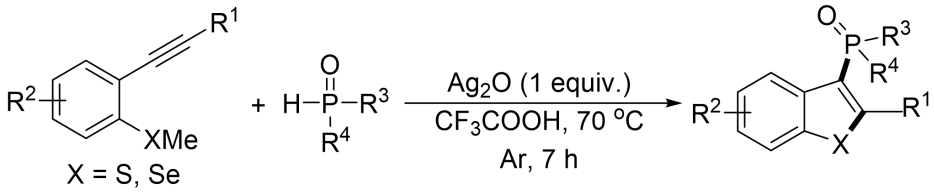
Scheme 1-21 2-炔基苯甲硫醚环化合成 3-取代苯并噻吩

2018 年，Wu 课题组[43]发展了一种银催化 2-炔基苯甲硫醚与α-酮酸自由基级联环化合成 3-酰基苯并噻吩的方法（Scheme 1-22）。控制性实验表明该反应是自由基过程。特别的，该方法可以高效合成雷洛昔芬，证明了该方法的实用性。该方法易于操作，具有良好的官能团兼容性。



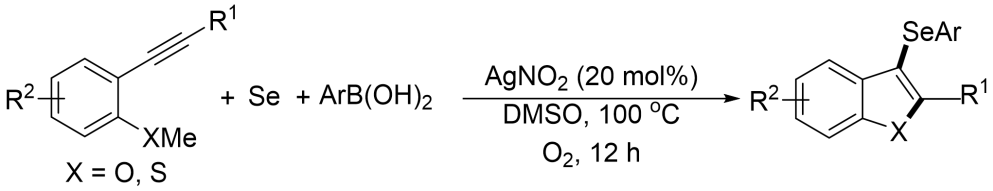
Scheme 1-22 银催化合成 3-酰基苯并噻吩

2019 年，Gao 课题组[44]发展了一种银和酸促进的 2-炔基苯甲硫（硒）醚与磷酸的自由基加成环化直接合成 3-磷酰基苯并噻吩或苯并硒吩的方法（scheme1-23）。在温和条件下以 20-81%的收率合成了 24 个 3-磷酰基苯并噻吩。



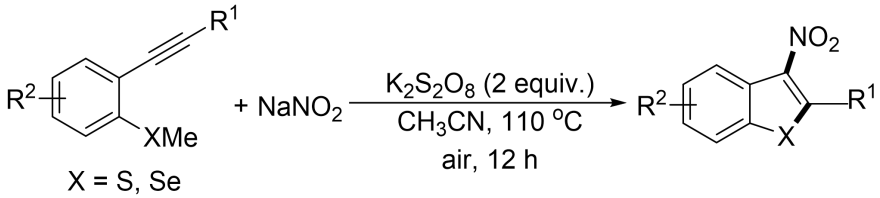
Scheme 1-23 邻炔基苯甲硫（硒）醚与膦氧化物合成 3-膦酰基苯并噻吩

同年，Liu 课题组[45]开发了一种银催化 2-炔基苯甲（硫）醚、硒粉和芳基硼酸三组分自由基加成环化合成 3-芳基硒代苯并噻吩（苯并呋喃）新方法（Scheme 1-24）。以 30-93%的收率合成了 44 个 3-芳基硒代苯并噻吩。机理研究表明，在加热条件下银催化芳基硼酸产生芳基自由基是关键过程。



Scheme 1-24 邻炔基苯甲（硫）醚、硒粉和芳基硼酸合成芳基硒代苯并噻吩

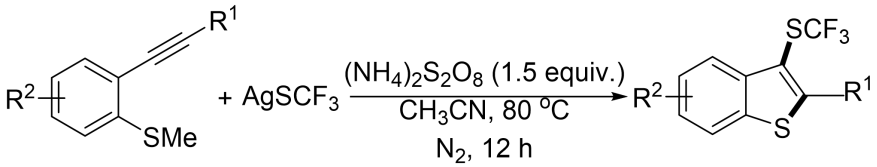
2020 年，Xu 课题组[46]开发了一种 $K_2S_2O_8$ 促进邻炔基苯甲硫（硒）醚和亚硝酸钠自由基环化合成 3-硝基苯并噻（硒）吩的反应（Scheme1-25），该方法使用亚硝酸钠作为硝基源，以 46-88%的产率合成了 22 个目标化合物。机理研究表明，过硫酸钾促进亚硝酸钠形成硝基自由基是反应的开始。



Scheme 1-25 邻炔基苯甲（硫）醚和亚硝酸钠合成 3-硝基苯并噻（硒）吩

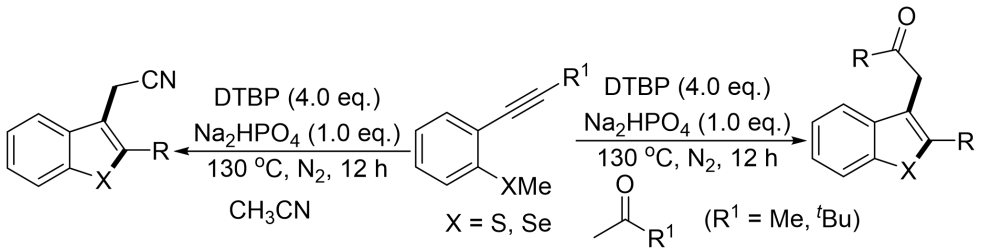
2021 年，Huang 课题组[47]开发了一种过硫酸盐催化 2-炔基噻吩与 $AgSCF_3$

发生自由基环化加成制备 3-三氟甲基硫代苯并噻吩的方法（Scheme1-26）。在温和条件下以 30-86%的产率获得了 42 个目标化合物。机理研究表明，CF_3S 自由基在碳碳三键上的加成和 SMe 部分的环化是自由基反应过程。



Scheme 1-26 自由基环化合成 3-三氟甲基硫代苯并噻吩

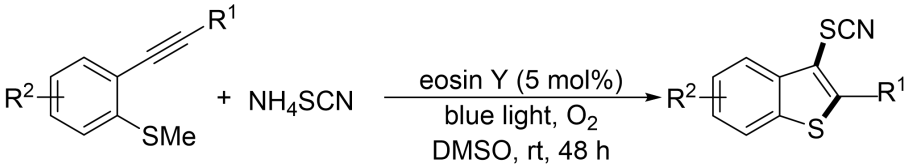
同年，Gao 课题组[48]发展了 DTBP（二叔丁基过氧化物）促进丙酮或乙腈与 2-炔基苯甲硫醚通过级联自由基环化合成 3-乙酰（氰基）甲基苯并噻（硒）吩（Scheme1-27）。以 30-84%的产率合成了 28 个目标化合物。该反应条件较为苛刻需要用过量的过氧化物和高温。



Scheme 1-27 过氧化物促进邻炔基苯甲硫醚合成 3-乙酰（氰基）甲基苯并噻吩

可见光促进的有机反应与传统反应相比具有温和、绿色等特点，是当前研究的热点。近些年来，可见光促进 2-炔基苯甲硫醚合成 C3 位官能化苯并噻吩备受化学工作者的关注并且有了很大的发展。

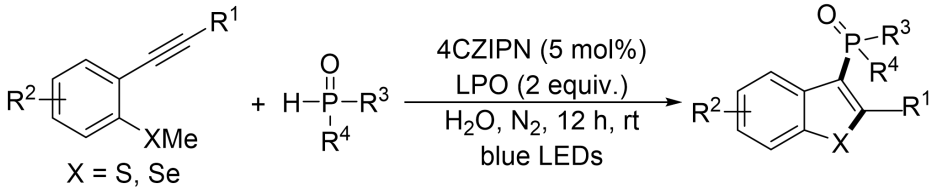
2018 年，Kshirsagar 课题组[52]开展了一种可见光促进 eosin Y 催化硫氰酸铵和邻炔基苯甲硫醚串联环化合成合成 3-硫氰基苯并噻吩的方法（Scheme1-28），该方法无需外加金属催化剂，采用氧作为绿色氧化剂，在温和条件下以 52-82%收率合成了 20 个目标化学物。



Scheme 1-28 可见光促进 2-炔基苯甲硫醚环化合成 3-硫氰基苯并噻吩

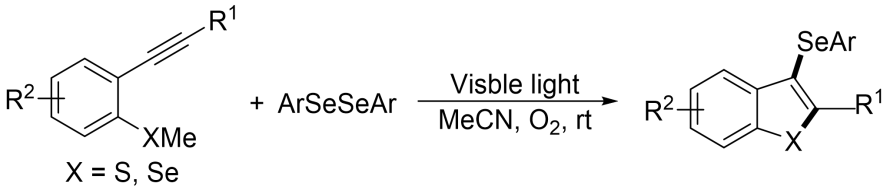
2020 年，Yu 课题组[54]对 3-磷酰基苯并噻吩的合成方法进行改进。发展了一

种在室温条件下可见光促进 2-炔基苯甲硫醚与氧化磷酸串联环化合成 3-磷酰基苯并噻吩的方法（Scheme 1-29）。在温和条件下以 40-95%的收率合成了 20 个不同官能团的 3-磷酰化苯并噻吩。该方法与 Gao 课题组方法相比具有无外加金属、溶剂绿色和条件温和的优点。



Scheme 1-29 可见光促进邻炔基苯甲硫醚环化合成 3-膦酰基苯并噻吩

最近，Lee 课题组[60]和 Yang 课题组[61]和分别独立报道了 2-炔基苯甲硫醚与二硒醚发生串联环化合成 3-芳基硒代苯并噻吩（Scheme 1-30）。该方法与文献报道方法相比，具有无需外加金属或添加剂和条件温和等优点。机理研究表明，芳基硒自由基是关键中间体。



Scheme 1-30 可见光促进自由基环化合成 3-芳基硒代苯并噻（硒）吩

1.5 小结与展望

鉴于苯并噻吩及其衍生物的广泛用途，其合成方法学研究一直受到化学工作者的关注。虽然近十几年来一些高效的苯并噻吩的合成方法相继被报道。但这些方法或多或少存在一些缺点。例如使用过渡金属催化剂、原子利用率低、底物广谱性差等缺点，极大的限制了其应用范围。最近几十年新的催化体系如光催化体系、电催化体系和光电催化体系逐渐被建立[25]。因此，利用新的催化体系开展简单、高效的合成官能化苯并噻吩的新方法是具有重要意义的。

基于以上文献的启发，本文拟通过可见光促进邻炔基苯甲硫醚的自由基级联环化反应开展 3 个 C3 官能化苯并噻吩合成新方法。

1. 以简单的卤代烃为卤源，开展了可见光促进卤代烃与 2-炔基苯甲硫醚环化合成 3-卤（溴、碘）代苯并噻吩。

2. 以廉价 9,10-菲醌（PQ）为光敏剂，开展了可见光促进 PQ 催化邻炔基苯

甲硫醚分子内环化氧化合成 3-酰基苯并噻吩。

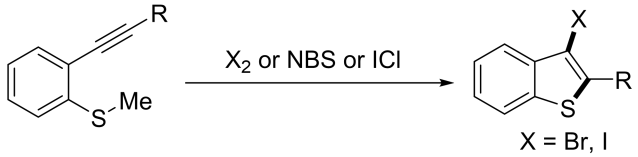
3. 无外加金属催化剂和光催化剂条件下，可见光促进邻炔基苯烷基醚与 DABSO 串联环化合成 3-烷基磺酰基苯并噻吩。

第 2 章 无外加光敏剂条件下可见光促进 2-炔基苯甲硫醚串联环化反应合成 3-卤代苯并噻吩

2.1 研究背景

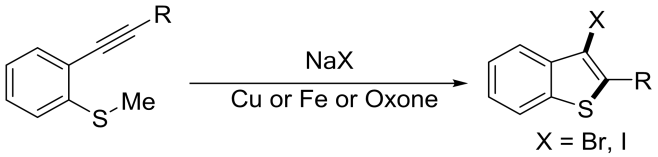
苯并噻吩及其衍生物具有重要的生物活性，广泛存在于众多天然产物、药物和功能材料分子中[63-70]。3-卤代苯并噻吩是合成有价值苯并噻吩衍生物的有机中间前体[71-74]，在过去几十年已经发展了多种方法来构建 3-卤代苯并噻吩。其中，在亲电试剂或过渡金属盐的存在下，2-炔基苯甲硫醚亲电环化已成为最常用的方法之一。

Larock 课题组[75-78]用 I_2、Br_2、NBS 和 ICl 作为亲电试剂发展了一系列高效合成 3-卤代苯并噻吩的方法，可以在短时间内得到卤代产物。该类方法条件简单、反应时间短。但是该类方法需要用到刺激性和腐蚀性的卤素单质（Scheme 2-1）。



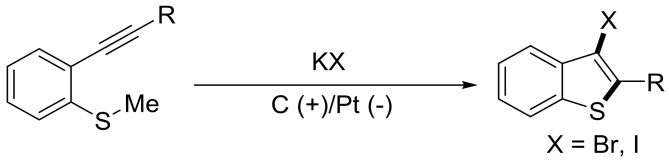
Scheme 2-1 以亲电试剂为卤源合成 3-卤代苯并噻吩

Wu，Kesharwani 和 Cai 课题组[79-83]分别独立报道了以 NaX 为卤源，在 Cu、Fe 或氧化物介导的 2-炔基苯甲基硫醚的亲电环化反应，该类方法具有收率高和官能团耐受性好等优点。但是该类方法需要用到过渡金属盐或者过量的过氧化物（Scheme 2-2）。



Scheme 2-2 以卤化钠为卤源合成 3-卤代苯并噻吩

2020 年，Guo 课题组[55]报道了电促进 KI 或 KBr 和邻炔基苯甲硫醚发生分子间氧化环化反应合成 3-卤代苯并噻吩。该方法通过电化学氧化，在无过渡金属和无氧化剂的条件下成功地合成了一系列 3-卤代苯并噻吩，该反应具有官能团耐受性好和条件温和等优点（Scheme 2-3）。

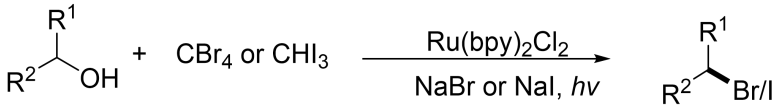


Scheme 2-3 电化学氧化合成 3-卤代苯并噻吩

尽管取得了这些重要的进展，但目前的大多数方法都有一些局限性，因此开发一种简单、实用和绿色的替代方案来合成这类化合物仍然是必要的。

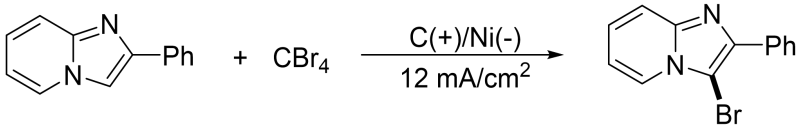
近些年来，简单的卤代烷烃在光或电介导反应中做为卤源有许多应用，为在温和和低毒性的反应条件下构建 C-X（卤素）键产物提供了新的机会。

2011 年，Stephenso 课题组[84]用 CBr_4 或 CHI_3 作为卤源，报道了可见光促进醇溴化和碘化反应。该方法不需外加磷催化剂，具有官能团耐受性好、产率高和条件温和等优点（Scheme 2-4）。



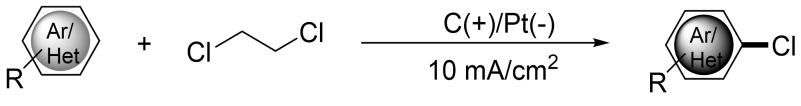
Scheme 2-4 可见光介导的醇到卤化物的转化

2019 年，Lei 课题组[85]第一个报道了在无外加氧化剂条件下，用电化学方法活化简单的烷基卤化物（CBr_4、$CHBr_3$ 和 CCl_3Br），合成了一系列重要的芳基和烷基卤化物（Scheme 2-5）。



Scheme 2-5 电化学碳氢卤化反应

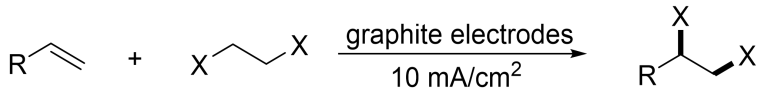
同年，Jiao 课题组[86]报道了一种理想的双功能电催化策略，在无外加氧化剂条件下将常用溶剂 DCE 用作氯源合成了一系列芳香族氯化产物，该方法绿色可持续，有着广泛的底物范围，该方法将为高效、环保地制备氯乙烯和（杂）芳氯开辟新的途径（Scheme 2-6）。



Scheme 2-6 以 DCE 为氯源电催化合成芳氯和氯乙烯

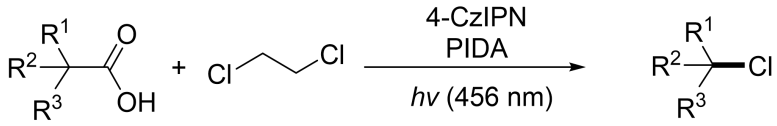
2021 年，Morandi 课题组[87]报道了一项开创性的卤素转移反应，该反应的重点是旧 C(sp^3)-Br 键的断裂，并通过配对电解产生新的 C(sp^3)-Br 键，生成烯烃的

相邻二卤化产物（Scheme 2-7）。



Scheme 2-7 配对电解可逆邻二卤化反应

最近， Molander 课题组[88]报道了一种可见光促进有机酸脱羧氯化方法，从羧酸合成各种伯、仲、叔氯化化合物。在温和条件下以 12-85%的收率合成了 20 个氯化物（Scheme 2-8）。



Scheme 2-8 可见光诱导脱羧氯化反应

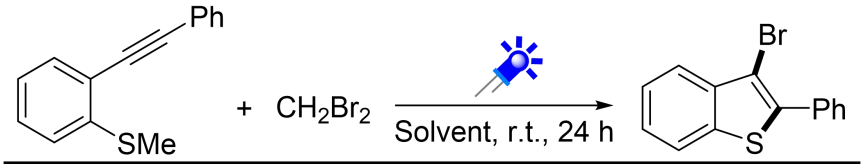
基于以上文献的启发，我们致力于开发一种可见光诱导卤化反应的方法。本文报道了在无外加光催化剂条件下，简单卤代烷烃为卤源，从 2-炔基苯甲硫醚高效合成 3-卤代苯并噻吩。

2.2 反应条件优化

以 2-炔基苯甲硫醚（**1a**）和 CH_2Br_2 为模版反应，分别对催化剂、溶剂、波长等方面进行优化以确定最佳反应条件。

2.2.1 催化剂和溶剂的筛选

Table 2-1 催化剂和溶剂的筛选 [a]



Entry	Photocatalyst	Solvent	Yield (%)[b]
1	Eosin Y	CH_2Br_2	65
2	–	CH_2Br_2	86
3	–	CH_2Br_2	n.d.[c]
4	–	THF	95
5	–	THF	88[d], 49[e]
6	–	CH_3CN	64
7	–	EtOH	39

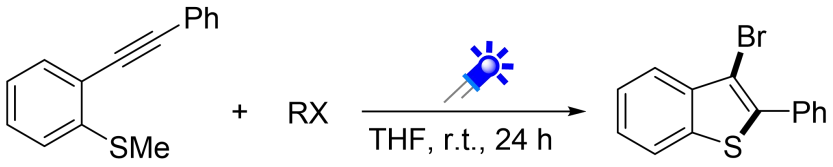
8	–	DMF	66
9	–	DMSO	59
10	–	Toluene	16

[a]Reaction conditions: **1a** (0.25 mmol) and CH_2Br_2 (7.5 equiv.) in solvent (2.0 mL) were irradiated with 10 W blue LED (425 nm) in a sealed tube (air atmosphere) at room temperature for 24 h. [b]Isolated yield. [c]In dark. [d]Under argon. [e]Open to air. n.d. = no detection.

首先，对催化剂和溶剂进行了筛选。如 Table 2-1 所示，当以 2-炔苯基苯甲硫醚（**1a**）为反应底物，CH_2Br_2（2 mL）作为溴代试剂和溶剂，Eosin Y（2.0 mol%）为光催化剂，在空气气氛下用 425 nm 蓝光 LED（10 W）照射，在石英管中搅拌反应 24 h，以 65%的产率得到了 3-溴代苯并噻吩 **3a**（Table 2-1，entry 1）。特别的，当该反应在没有外部光催化剂的情况下，**3a** 获得了更高的收率（86%）（entry 2）。控制实验表明光照是该反应的必要条件（entry 3）。有趣的是，当使用四氢呋喃（THF)作为溶剂进行反应时，**3a** 的产率显著提高（95%）（entry 4）。在氩气气氛下进行反应时，**3a** 的产率略有下降，而在空气中进行反应时，**3a** 的产率仅为 49%（entry 5）。随后，对反应溶剂进行了筛选，发现四氢呋喃是最佳反应溶剂（entries 6-10）。

2.2.2 卤源的筛选

Table 2-2 卤源的筛选 [a]



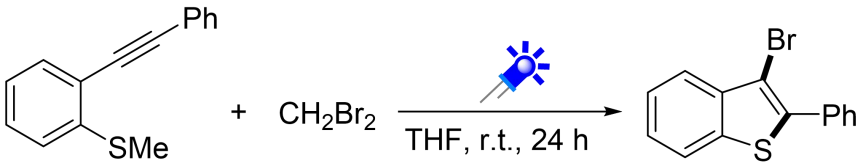
Entry	RX	Solvent	Yield (%)[b]
1	$BrCH_2CH_2Br$	THF	94
2	CBr_4	THF	95[c]
3	^tBuBr	THF	n.d.
4	CH_3CH_2Br	THF	n.d.
5	PhBr	THF	n.d.
6	CH_2Cl_2	THF	n.d.
7	$ClCH_2CH_2Cl$	THF	n.d.
8	$CHCl_3/CCl_4$	THF	n.d.

9	CH_3I	THF	n.d.
10	CH_2I_2	THF	97[d]
11	ICH_2CH_2I	THF	96[e]

[a]Reaction conditions: **1a** (0.25 mmol) and RX (7.5 equiv.) in THF (2.0 mL) were irradiated with 10 W blue LED (425 nm) in a sealed tube (air atmosphere) at room temperature for 24 h. [b]Isolated yield. [c]1.0 mmol CBr_4 (4.0 equiv.) was used. [d]0.275 mmol CH_2I_2 (1.1 equiv.) was used, 12 h. [e]0.275 mmol ICH_2CH_2I (1.1 equiv.) was used, 12 h. n.d. = no detection.

2.2.3 波长、CH_2Br_2 用量以及反应时间的筛选

Table 2-3 波长、CH_2Br_2 的量以及反应时间的筛选 [a]

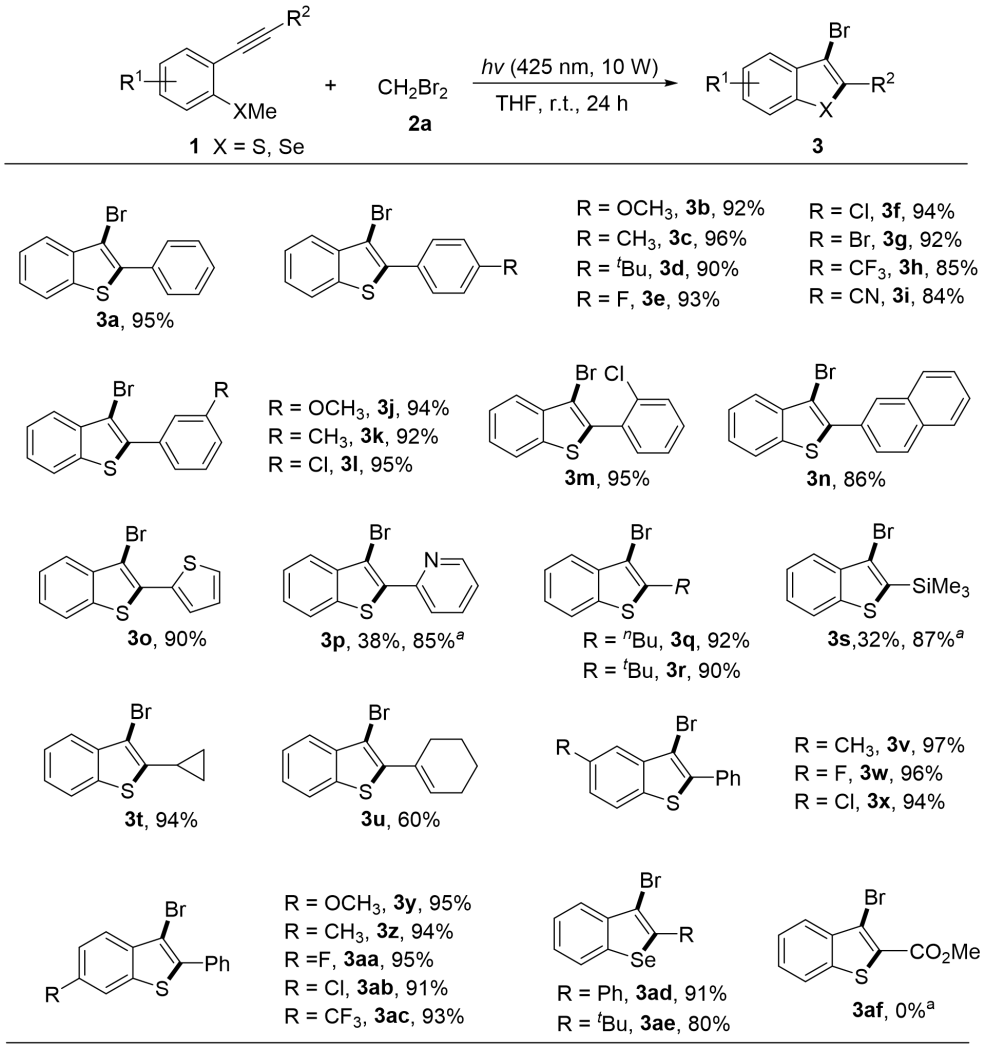


Entry	LED (nm)	Solvent	Yield (%)[b]
1	390	THF	95
2	405	THF	96
3	415	THF	91
4	435	THF	93
5	518	THF	n.d.
6	425	THF	81[c]
7	425	THF	96[d]
8	425	THF	83[e]
9	425	THF	95[f]

[a]Reaction conditions: **1a** (0.25 mmol) and CH_2Br_2 (7.5 equiv.) in THF (2.0 mL) were irradiated with 10 W blue LED in a sealed tube (air atmosphere) at room temperature for 24 h. [b]Isolated yield. . [c]1.25 mmol CH_2Br_2 (5.0 equiv.) was added. [d]2.5 mmol CH_2Br_2 (10.0 equiv.) was added. [e]18 h. [f]30 h. n.d. = no detection.

然后对波长进行了筛选，结果表明，所筛选的 LED （390、405、415、425、435 nm）都适合该溴化反应（Table 2-3，entries 1-4）。但是，当波长为 518 nm 时该反应不能顺利进行（entry 5），可能是因为 518 nm 不在底物的紫外吸收范围内。最后对 CH_2Br_2（**2a**）的用量以及反应时间进行了筛选，确定了最佳二溴甲烷用量为 7.5 equiv. 最佳反应时间为 24 h（entries 6-9）。

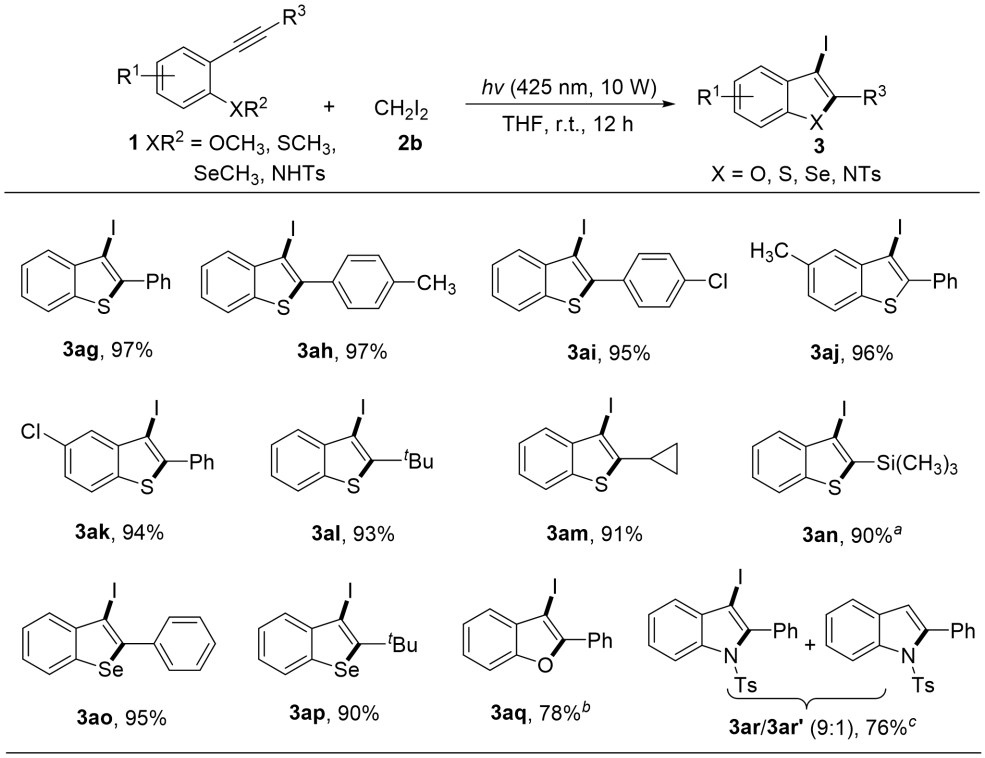
2.3 反应底物拓展



Reaction conditions: **1** (0.25 mmol) and **2a** (1.875 mmol, 7.5 equiv.) in THF (2.0 mL) at room temperature in a sealed tube under blue LED (425 nm,10 W) irradiation for 24 h; Isolated yields; [a]THF was replaced with CH_2Br_2 (2.0 mL).

Scheme 2-9 底物拓展 I

为探究该卤代环化反应的普遍性，在优化条件下考查了不同芳基基团的 2-炔基硫代苯甲醚。如 Scheme 2-9 所示，多种底物具有良好的反应性，可生成相应的 3-溴苯并噻吩，产率优异，具有良好的官能团耐受性。结果表明，当 2-炔基苯甲硫醚的端基为芳基时，无论是邻位、间位和对位取代还是给电子基团（Me、OMe、^{t}Bu）和吸电子基团（F、Cl、Br、CF_3、CN）均具有良好的相容性，产率为 84-96%。另一方面，在优化条件下，研究了炔烃端基为萘基、噻吩基、吡啶基和脂肪基的底物。令我们高兴的是，这些底物在当前条件下反应顺利，以中等到优异的产率生成相应的产品（**3n-3u**）。



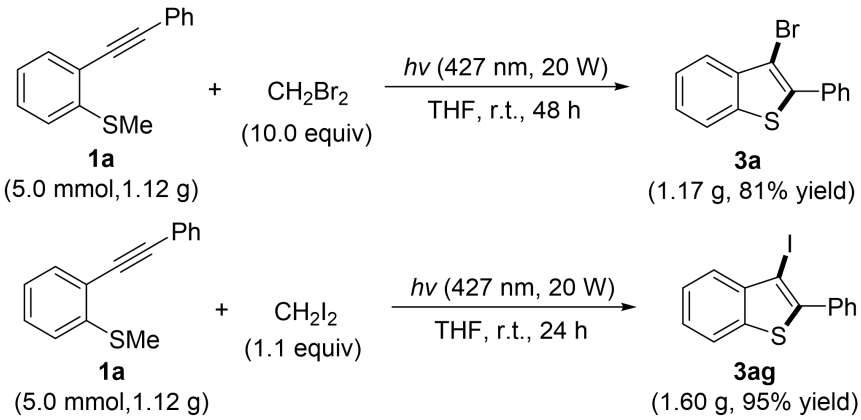
Reaction conditions: **1** (0.25 mmol) and **2b** (0.275 mmol, 1.1 equiv.) in THF (2.0 mL) at room temperature in a sealed tube under blue LED (425 nm,10 W) irradiation for 12 h; Isolated yields; [a]0.625 mmol CH_2I_2 (2.5 equiv.) was used; [b]In acetonitrile (2.0 mL), 48 h; [c]In acetonitrile (2.0 mL), 60 h.

Scheme 2-10 底物拓展 II

然后，研究了邻炔基苯甲硫醚芳香环上的不同取代基，忽略电子和空间效应，以 91-97%的产率生成所需的产物（**3v-3ac**）。最重要的是，取代的 2-炔基苯甲硒醚，也是合适的底物，以良好的产率生成相应的苯并硒吩（**3ad** 和 **3ae**）。然而，令我们失望的是，当炔烃的端基为酯基时，该反应不能顺利进行，没有生成所需的产物（**3af**），绝大部分原料被回收。

为了进一步扩大反应范围，还研究了 2-炔基苯甲硫醚和 2-炔基苯甲硒醚的光促进碘环化反应，如 Scheme 2-10 所示。总的来说，在优化条件下，2-炔基硫代苯甲醚和 2-炔基硒代苯甲醚与 CH_2I_2 反应良好，均能以优异的收率得到所需的 3-碘取代产物（**3ag-3ap**）。与 2-炔基硫代苯甲醚相比，2-炔基硫甲醚的反应活性较低，目标产物（**3aq**）的收率为 78%。但是，当采用 4-甲基-氮-（2-（苯基乙炔基）苯基）苯磺酰胺进行转化时，得到无法分离的 **3ar** 和 **3ar'**的比例为 9:1，产率为 76%。

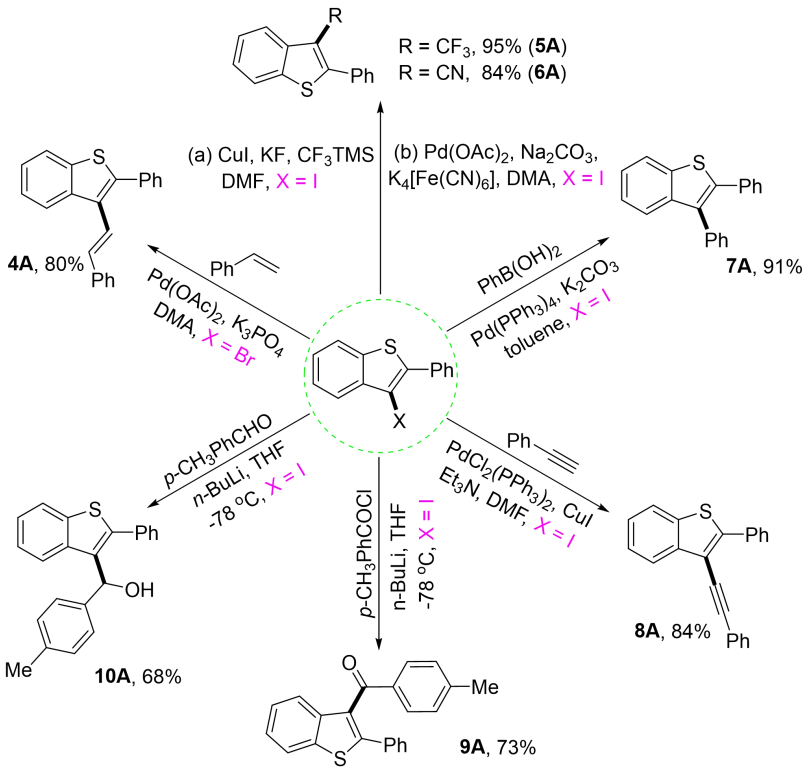
2.4 克级实验



Scheme 2-11 克级实验

我们以邻炔基苯甲硫醚的溴环化、碘环化反应的模板为例，进行了克级实验。值得注意的是，这种反应很容易进行放大。如图所示在 Scheme 2-11 中，当 1.12 g（5 mmol）的 **1a** 在标准反应条件下进行溴环化和碘环化反应，得到了所需的产物 **3a** 产率为 81%（1.17 g），**3ag** 的产率为 95%（1.60 g）。

2.5 3-卤代苯并噻吩衍生化反应



Scheme 2-12 3-卤代苯并噻吩的衍生化

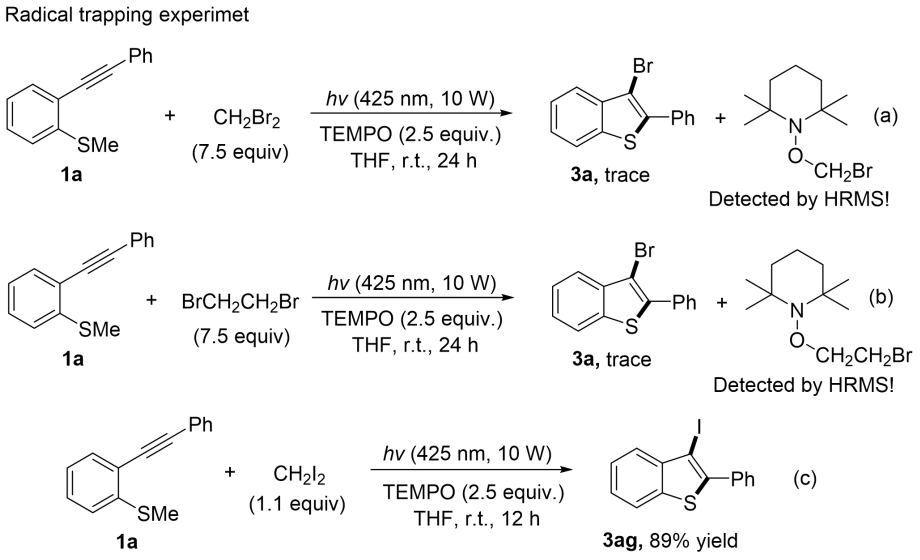
为了探索 3-卤代苯并噻吩的合成用途，还研究了 **3a** 和 **3ag** 的衍生化。如

Scheme 2-12 所示，**3a** 在 Pd 催化下与苯乙烯发生 Heck 反应，以 80%的收率合成 3-苯烯基苯并噻吩（**4A**），**3ag** 可以分别在铜和钯催化下发生三氟甲基化反应和氰化反应，分别以 95%和 84%的收率转化为 3-三氟甲基苯并噻吩（**5A**）和 3-氰基苯并噻吩（**6A)**。**3ag** 可以和苯硼酸发生 Suzuki 偶联反应合成 3-苯基苯并噻吩（**7A**），收率为 91%，也可以苯乙炔发生 Sonogashira 偶联反应合成 3-炔基苯并噻吩（**8A**），收率为 84%。此外，**3ag** 与 4-氯苯甲酰氯和 4-氯苯甲醛的反应也很顺利，相应的产物 3-酰基（4-甲基苯基）-苯并噻吩（**9A**）和 **10A** 的产率分别为 73%和 68%。

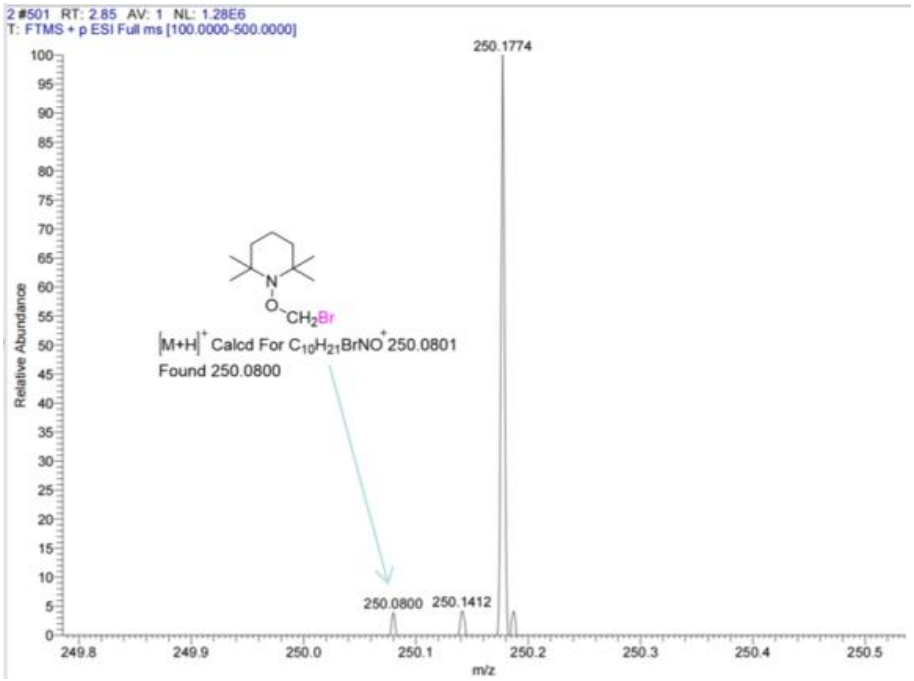
2.6 反应机理探究

2.6.1 控制性实验

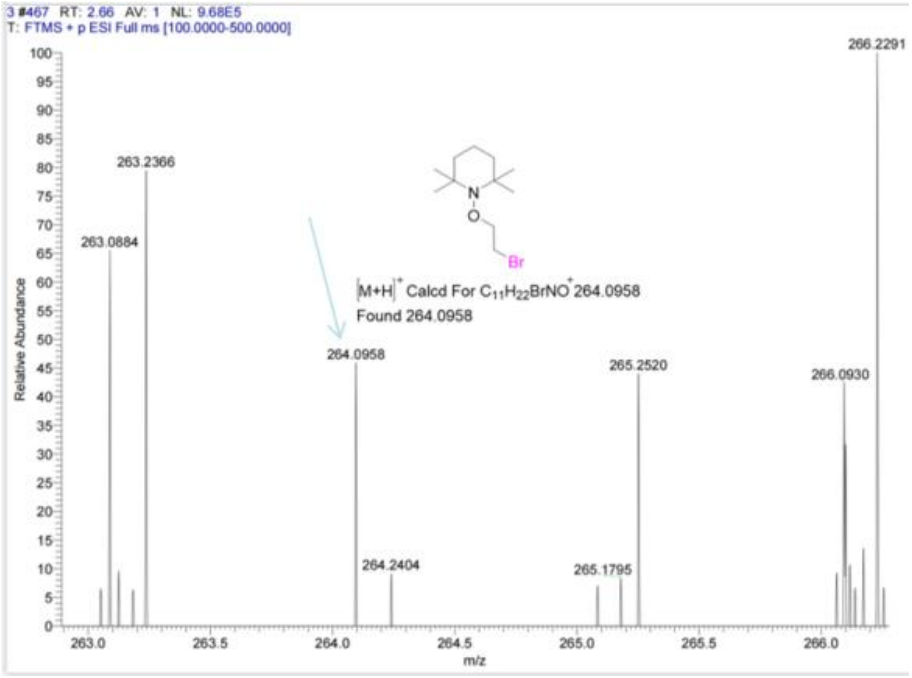
为了探究该反应机理，进行了若干对照实验。在模板条件下，在 **1a** 与 CH_2Br_2 的反应中加入自由基淬灭剂 TEMPO（2,2,6,6-四甲基哌啶氧化物，2.5 equiv.），反应几乎被完全抑制，只检测到微量的产物 **3a**，并通过 HRMS 分析检测到相应的溴甲基自由基和 TEMPO 的加合物（Scheme 2-14）。此外，在标准条件下，在 **1a** 与 $BrCH_2CH_2Br$ 的反应中加入 2.5 当量的 TEMPO 时，转化也被抑制，HRMS 分析还检测到溴乙基自由基与 TEMPO 的加合物（Scheme 2-15），表明该转化可能涉及自由基过程。然而，当在模板条件下，在 **1a** 和 CH_2I_2 的反应中加入 TEMPO（2.5 equiv.）时，反应进行顺利，并以 89%的产率（Scheme 2-13c）得到相应的产物 **3ag**，这表明碘环化反应不涉及自由基过程。



Scheme 2-13 自由基捕获实验

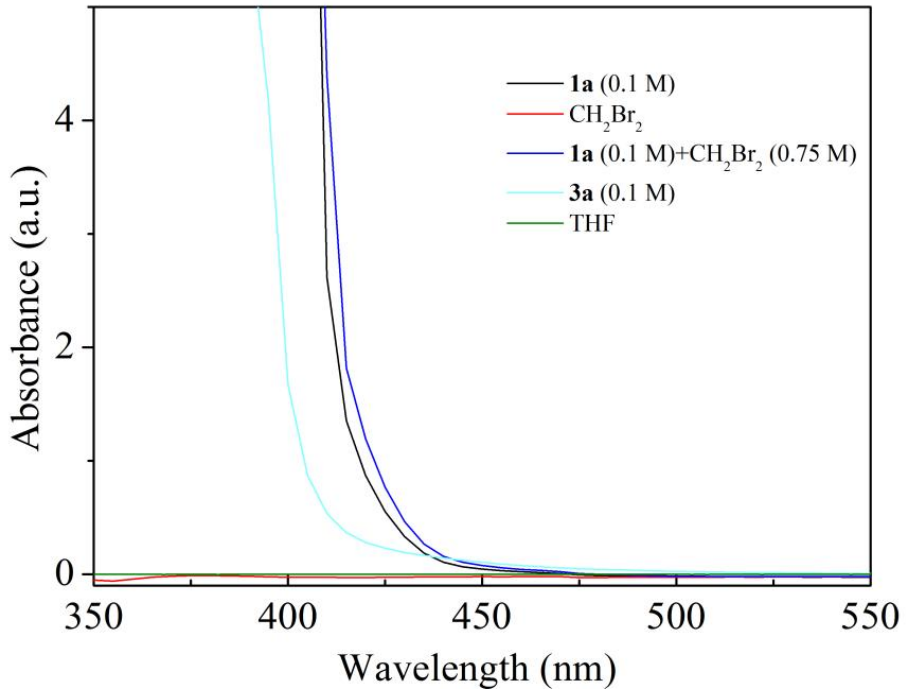


Scheme 2-14 溴甲基自由基加合物的高分辨质谱



Scheme 2-15 溴乙基自由基加合物的高分辨质谱

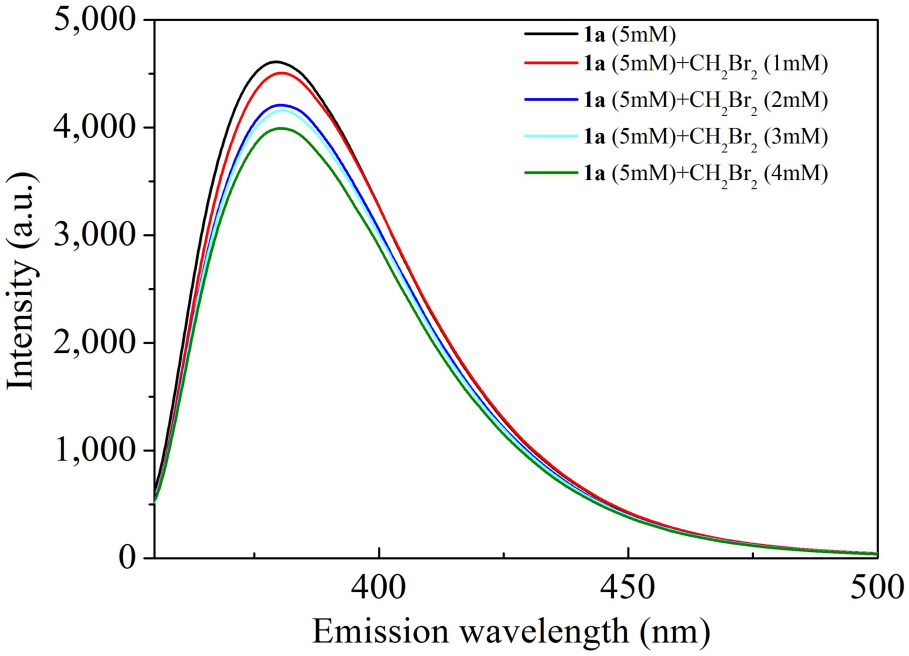
2.6.2 紫外吸收光谱



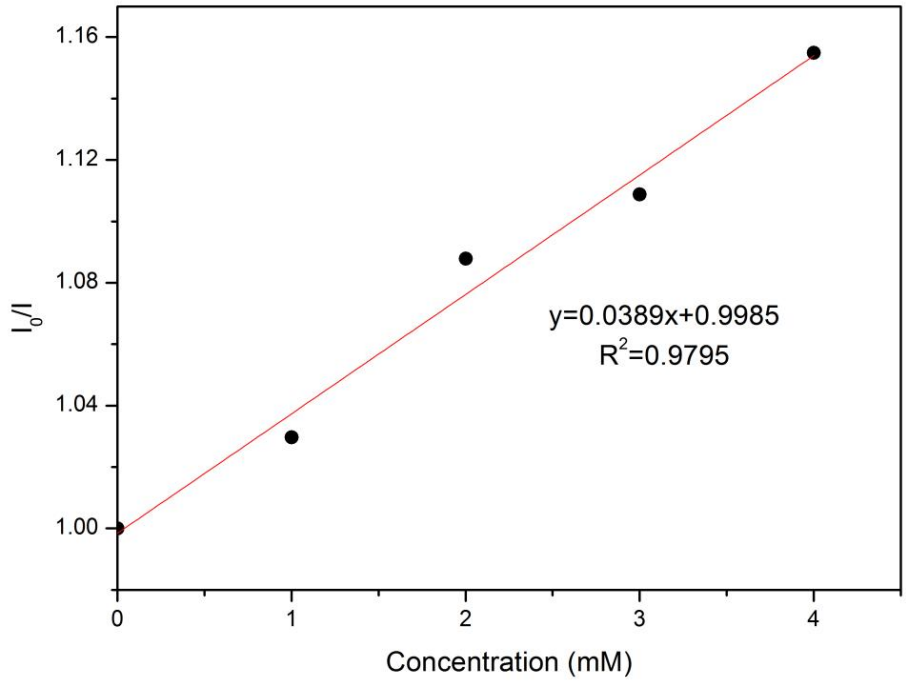
Scheme 2-16 不同物质的吸收光谱

在 UV-Visible U-4100 分光光度计上记录紫外/可见吸收光谱，如图 Scheme 2-16 所示。**1a** 和 **3a** 的吸收光谱从 300 nm 到 450 nm 有较宽的吸收范围，所用波长 425 nm 处于它的吸收光谱范围内。

2.6.3 荧光淬灭实验

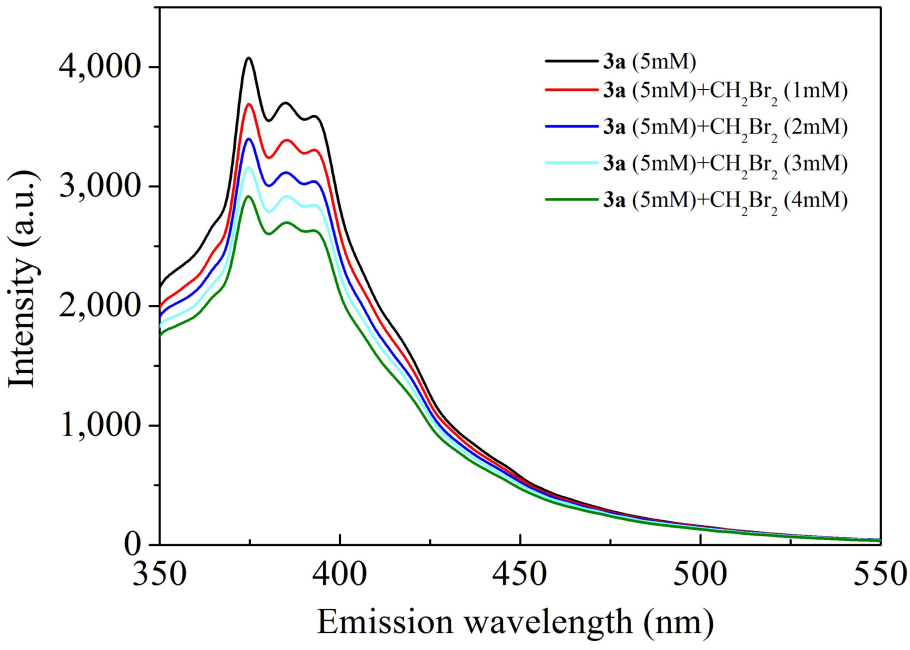


Scheme 2-17 CH_2Br_2 对 **1a** 的淬灭

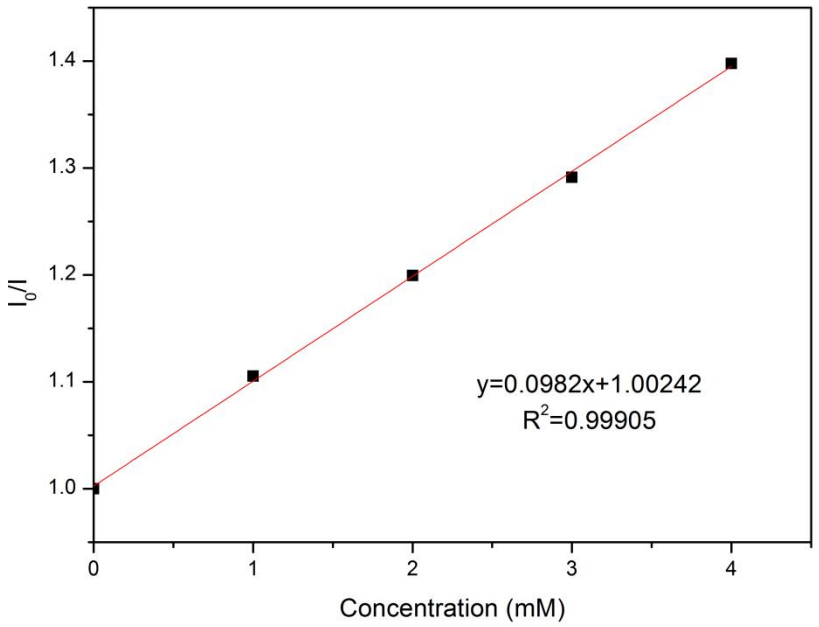


Scheme 2-18 1a 的 Stern-Volmer 图

将 **1a** 溶解在 THF 溶液中加入越来越多的 CH_2Br_2。每次添加后记录发射光谱。Scheme 2-17 的结果显示，**1**a 的发射强度变化明显，随着 CH_2Br_2 的加入吸收强度逐渐降低。以 CH_2Br_2 的浓度为 X 轴 I_0/I 为 Y 轴得到的数据拟合大致在一条直线上。计算出的 Ksv 为 0.0389 mM^{-1}（Scheme 2-18）。说明能量从 **1a** 传递给了 CH_2Br_2。



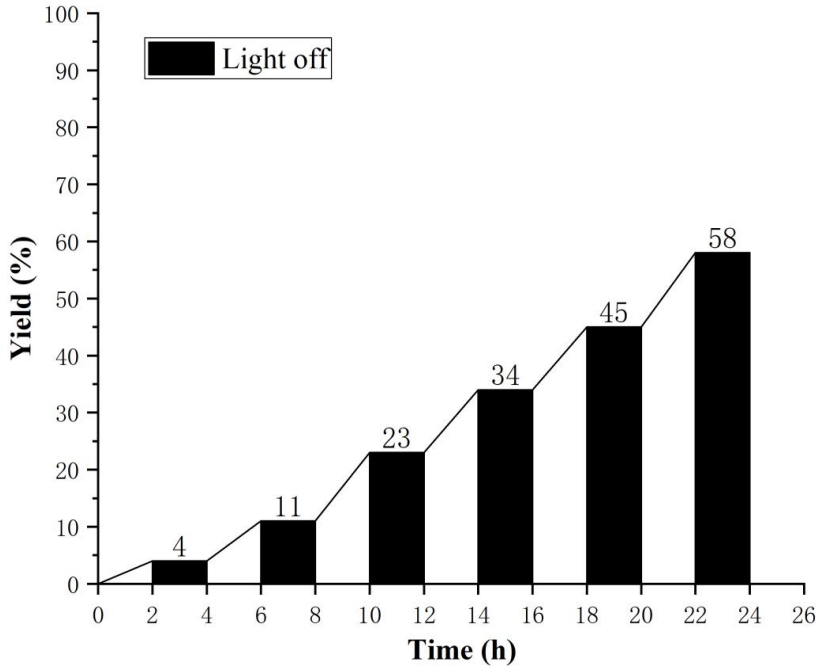
Scheme 2-19 CH_2Br_2 对 **3a** 的淬灭



Scheme 2-20 Stern-Volmer 图

将 **1a** 溶解在 THF 溶液中加入越来越多的 CH_2Br_2。每次添加后记录发射光谱。Scheme 2-19 的结果显示，**1**a 的发射强度变化明显，随着 CH_2Br_2 的加入吸收强度逐渐降低。以 CH_2Br_2 的浓度为 X 轴 I_0/I 为 Y 轴得到的数据拟合大致在一条直线上，计算出的 Ksv 为 0.0982 mM^{-1}（Scheme 2-20）。说明能量从 **3a** 传递给了 CH_2Br_2，而且 **3a** 传递效率比 **1a** 更强。

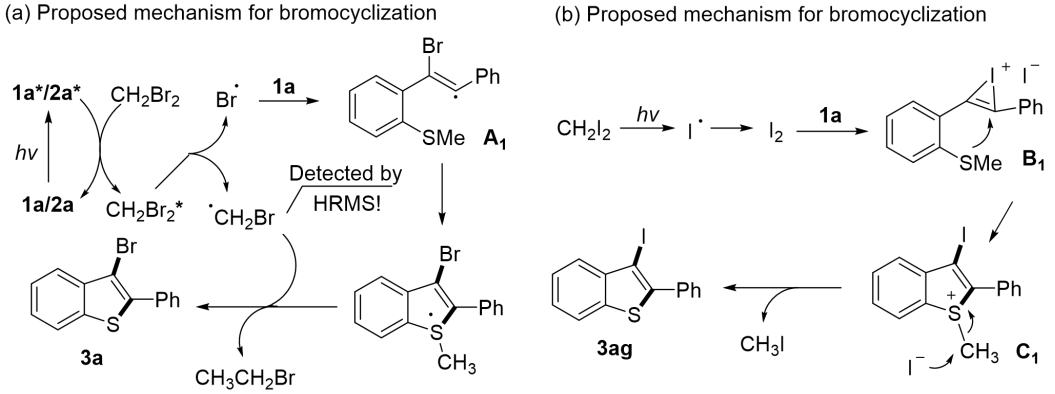
2.6.4 开关灯实验



Scheme 2-21 开关灯实验

为了验证该反应是否需要持续光照，进行了开关灯实验研究（Scheme 2-19）。在一个装有磁力搅拌的 10 mL 干燥反应容器中，加入邻炔基苯甲硫醚（**1a**, 56.1 mg, 0.25 mmol）、CH_2Br_2 （325.9 mg, 1.875 mmol, 7.5 当量）和 THF（2.0 mL）。将反应混合物置于密封管中，室温下用 425 nm, 10 W 蓝光 LED 光照反应 2 h，不光照反应 2 h。Scheme 2-21 给出了在室温下光照一定时间和不光照一定时间的产物产率。该结果表明，持续光照对该反应是必要的。

2.6.5 可能的反应机理

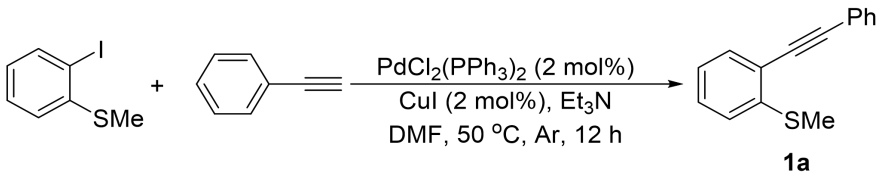


Scheme 2-22 可能的反应机理

基于自由基捕捉和荧光淬灭实验的结果提出可能的反应机理（Scheme 2-22）。**1a** 光照形成 **1a***作为光敏剂，然后传递能量给 CH_2Br_2，形成 CH_2Br_2*，同时基态 **1a** 再生。CH_2Br_2*在均裂作用下产生溴自由基（Br•），溴自由基攻击 2-炔基硫代苯甲醚中的炔基，生成具有高区域选择性的乙烯基自由基中间体 $\mathbf{A_1}$。随后，该原位生成的乙烯基自由基 A 通过分子内环化与 SMe 部分反应，生成最终产物 **3a**，甲基自由基转化为溴乙烷的产物。当然，形成的产物 **3a** 也可以作为光敏剂完成催化循环。对于碘环化，首先，在可见光照射下，CH_2I_2 中的 C-I 键被均裂原位生成亲电试剂碘单质（I_2），然后被 **1a** 中的 C-C 三键捕获形成中间体 $\mathbf{B_1}$，随后被硫进攻产生阳离子中间体 $\mathbf{C_1}$，最后甲基被释放得到所需的产物 **3ag**。

2.7 实验部分

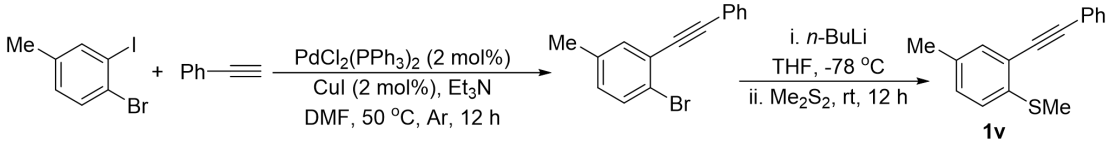
2.7.1 2-炔基苯甲硫醚（1a）的制备



Scheme 2-23 邻炔苯基苯甲硫醚的制备

称取 2-碘茴香硫醚（2.5010 g, 10.0 mmol），$PdCl_2(PPh_3)_2$（140.4 mg, 2 mol%），CuI（38.1 mg, 2 mol%）和苯乙炔（1.2256 g, 12.0 mmol, 1.2 equiv.）加入干燥后的耐压瓶中，然后加入 DMF（5 mL）和 Et_3N（20 mL），反应混合物在 50 ℃的油浴锅里剧烈搅拌 12 小时。用 PLC 板跟踪，发现 2-碘茴香硫醚消耗完全停止反应，用乙酸乙酯（3*50 mL）和水（50 mL）萃取 3 次有机相拥无水硫酸钠干燥。过滤、真空浓缩、柱色谱（石油醚）分离纯化，得到目标产物 **1a** 为黄色油状（2.0189 g, 90% 产率）。

2.7.2 4-甲基-2-炔基苯甲硫醚（1v）的制备



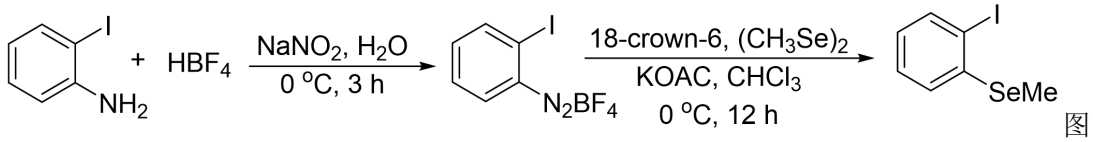
Scheme 2-24 4-甲基-2-炔苯基苯甲硫醚的制备

称取 1-溴-2 碘甲苯（2.9693 g, 10.0 mmol），$PdCl_2(PPh_3)_2$（140.4 mg, 2 mol%），CuI（38.1 mg, 2 mol%）和苯乙炔（1.2256 g, 12.0 mmol, 1.2 equiv.）加入干燥后的耐压瓶中，然后加入 DMF（5 mL）和 Et_3N（20 mL）反应混合物在 50 ℃油浴锅里剧烈搅拌 12 小时。用 PLC 跟踪反应发现 4-溴-3-碘甲苯消耗完全，停止反应之后用乙酸乙酯和水萃取反应。干燥、过滤、浓缩、柱色谱（石油醚）纯化，得到 1-溴-2 苯基乙炔基甲苯为黄色油状 （2.3862 g, 88% 产率）。

在氩气氛围下称取 1-溴-2 苯基乙炔基甲苯（2.1693 g, 8.0 mmol），加入干燥后的 200 mL 的圆底烧瓶中，然后加入 80 mL 无水四氢呋喃使其完全溶解，该混合物在-78 ℃下反应 30 min。然后，将 2 倍当量的正丁基锂（2.0 M 溶解在环己烷中）通过恒压漏斗缓慢滴加到反应体系中，滴加完成后，该反应在-78 ℃继续搅拌一小时，在该温度下加入二甲基二硫醚（0.9042 g, 9.6 mmol, 1.2 equiv.），在氩气气氛下该反应被加热到室温反应 18 h，反应完成后，四氢呋喃通过旋转蒸

发仪真空去除，乙酸乙酯和水萃取，干燥，过滤、真空去除，柱色谱法（乙酸乙酯/石油醚=1/200）纯化，得到 5-甲基 2-炔苯基苯甲硫醚（**1v**）为黄色油状（1.4301 g, 75% 产率）。

2.7.3 2-炔基苯甲硒醚（1ad）的制备

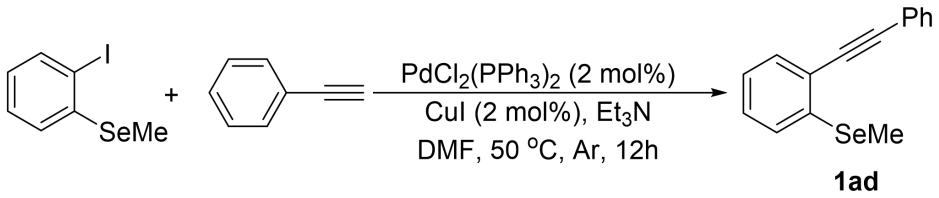


图

Scheme 2-25 邻碘苯甲硒醚的制备

在 100 mL 圆底烧瓶中，将 2-碘苯胺（2.1902 g, 10 mmol）溶于 H_2O（2.0 mL）和 HBF_4 水溶液（48%，4.0 mL）的混合物中，然后缓慢滴加 $NaNO_2$ 水溶液（1.3804 g, 20 mmol, 溶于 3.0 mL H_2O）。滴加完成后，反应混合物在 0℃下继续搅拌 3 h，然后过滤，固体用少量冰水、酒精和乙醚依次洗涤，真空干燥重氮盐，不提纯，用于下一步。产物为白色固体（2.7650 g，87% 产率）。

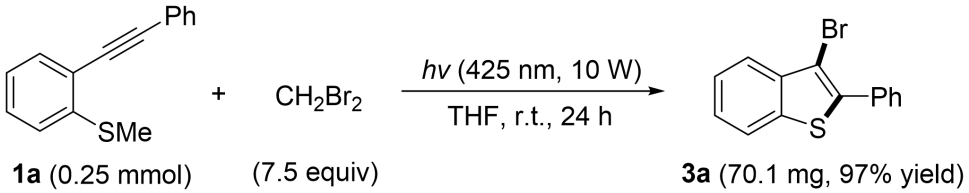
在 100 mL 的圆底烧瓶中加入粗重氮盐（3.1782 g, 10.0 mmol）、18-冠-6（1.3215 g, 5 mmol, 0.5 equiv.）和二甲基二硒醚（2.0678 g, 11 mmol, 1.1 equiv.），加入 $CHCl_3$（40 mL）使其溶解，该混合物在 0 ℃搅拌。将 KOAc（1.9628 g, 20 mmol, 2 equiv.）小份加入（20 分钟分 10 次加完），添加完成后，搅拌 12 小时后过滤。固体残渣用氯仿洗涤，所得滤液用水洗涤，用无水硫酸钠干燥，真空浓缩。所得粗产物以石油醚为洗脱剂，在硅胶上用快速柱色谱法纯化。得到黄色油状（2.1384 g，72% 产率）。



Scheme 2-26 2-炔苯基苯甲硒醚的制备

在反应瓶中加入 2-碘苯甲基硒醚（2.9701 g, 10.0 mmol）、苯乙炔（1.2256 g, 12.0 mmol, 1.2 equiv.），$PdCl_2(PPh_3)_2$（140.4 mg, 2 mol%）和 CuI（38.1 mg, 2 mol%），加入 Et_3N（20 mL）和 DMF（5 mL）使其溶解。反应混合物在氩气气氛和 50 ℃条件下剧烈搅拌 12 h 。完成后用水（50 mL）稀释，再用乙酸乙酯（3*50 mL）萃取，有机层用 Na_2SO_4 干燥，过滤，减压浓缩。以石油醚/乙酸乙酯（200:1, V/V）为洗脱液，在硅胶上快速柱色谱法纯化，得到黄色油状（2.3326 g，86% 产率）。

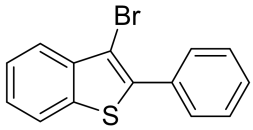
2.7.4 3-溴苯苯并噻吩（3a）制备的一般步骤



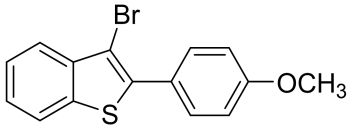
Scheme 2-27 光促进自由基环化合成 3-溴苯并噻吩

在一个装有磁力搅拌棒的干燥反应管里，加入 2-炔基苯甲硫醚（**1a**, 56.1 mg, 0.25 mmol）、CH_2Br_2（325.9 mg, 1.875 mmol, 7.5 equiv.）和 THF（2.0 mL）。反应混合物在室温下用 425 nm, 10 W 的蓝光 LED 照射反应 24 h，溶剂被旋转蒸发仪直接除去，硅胶柱层析纯化，得到所需产物 **3a** 为白色固体（70.1 mg，收率 97%）。

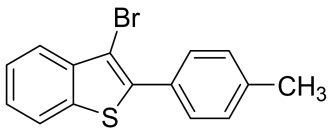
2.8 产物的表征数据



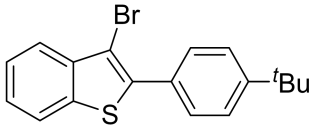
3-Bromo-2-phenylbenzo[*b*]thiophene (3a). White solid; mp 62–64 ℃; 95% yield (68.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.8 Hz, 1H), 7.74–7.72 (m, 3H), 7.43–7.40 (m, 3H), 7.38–7.36 (m, 1H), 7.35–7.32 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.1, 138.2, 137.6, 133.0, 129.6, 128.7, 128.5, 125.4, 125.2, 123.6, 122.1, 104.9.



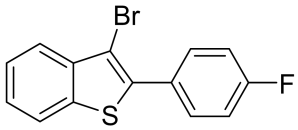
3-Bromo-2-(4-methoxyphenyl)benzo[*b*]thiophene (3b). White solid; mp 86–88 ℃; 92% yield (73.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.48–7.46 (m, 1H), 7.40–7.38 (m, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.0, 139.2, 138.2, 137.4, 130.9, 125.4, 125.2, 125.1, 123.4, 122.1, 114.0, 104.2, 55.4.



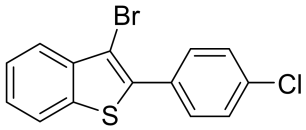
3-Bromo-2-(*p*-tolyl)benzo[*b*]thiophene (3c). White solid; mp 62–64 ℃; 96% yield (72.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.51–7.48 (m, 1H), 7.43–7.40 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.2, 138.8, 138.4, 137.6, 130.1, 129.4, 129.3, 125.3, 125.1, 123.5, 122.1, 104.5, 21.3.



3-Bromo-2-(4-(*tert*-butyl)phenyl)benzo[*b*]thiophene (3d). White solid; mp 57–58 ℃; 90% yield (77.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.51–7.48 (m, 1H), 7.43–7.40 (m, 1H), 1.42 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.9, 139.2, 138.3, 137.6, 130.1, 129.2, 125.6, 125.3, 125.1, 123.5, 122.1, 104.4, 34.7, 31.2; IR (cm^{-1}): 2953, 1624, 1434, 1381, 1357, 1246, 1107, 1065, 1017, 893, 830, 785, 753, 719; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{18}BrS^+$ 345.0307; Found 345.0309.

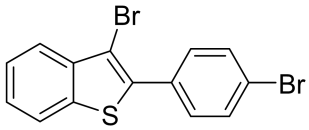


3-Bromo-2-(4-fluorophenyl)benzo[*b*]thiophene (3e). White solid; mp 63–65 ℃; 93% yield (71.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.75–7.72 (m, 2H), 7.50–7.48 (m, 1H), 7.43–7.41 (m, 1H), 7.18 (t, *J* = 8.4 Hz, 2H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −112.04; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.9 (d, *J* = 250.0 Hz), 139.0, 137.6, 137.1, 131.5 (d, *J* = 8.4 Hz), 129.1 (d, *J* = 3.2 Hz), 125.6, 125.3, 123.7, 122.2, 115.6 (d, *J* = 21.8 Hz), 105.2.

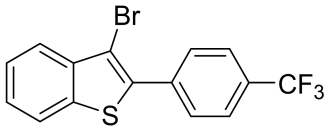


3-Bromo-2-(4-chlorophenyl)benzo[*b*]thiophenee (3f). White solid; mp 78–80 ℃; 94% yield (76.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.8 Hz, 1H), 7.82

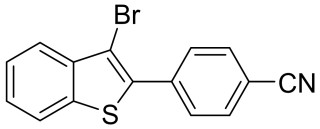
(d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.50–7.48 (m, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.44–7.41 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.0, 137.6, 136.8, 134.9, 131.5, 130.9, 128.9, 125.7, 125.4, 123.7, 122.2, 105.4.



3-Bromo-2-(4-bromophenyl)benzo[*b*]thiophene (3g). White solid; mp 81–83 ℃; 92% yield (84.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.62 (q, *J* = 8.4 Hz, 4H), 7.50–7.48 (m, 1H), 7.44–7.41 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.0, 137.6, 136.8, 132.0, 131.8, 131.1, 125.7, 125.4, 123.8, 123.2, 122.2, 105.4.

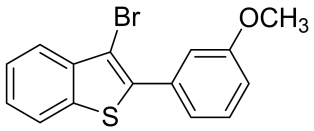


3-Bromo-2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophene (3h). White solid; mp 78–79 ℃; 85% yield (75.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91–7.88 (m, 3H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.52–7.50 (m, 1H), 7.46–7.44 (m, 1H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −62.70; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.0, 137.8, 136.7, 136.3, 130.6 (q, *J* = 32.8 Hz), 130.0, 126.0, 125.6 (q, *J* = 4.1 Hz), 125.5, 124.0 (CF_3)(q, *J* = 272.4 Hz), 123.9, 122.3, 106.2; IR (cm^{-1}): 2929, 1635, 1434, 1406, 1378, 1322, 1243, 1163, 1114, 1062, 1010, 893, 840, 788, 753, 722, 670; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_9BrF_3S^+$ 356.9555; Found 356.9555.

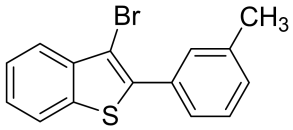


4-(3-Bromobenzo[*b*]thiophen-2-yl)benzonitrile (3i). White solid; mp 117–118 ℃; 84% yield (66.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91–7.88 (m, 3H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.78–7.76 (m, 2H), 7.53–7.50 (m, 1H), 7.47–7.45 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.0, 137.9, 137.7, 135.7, 132.3, 130.2, 126.3, 125.6, 124.1,

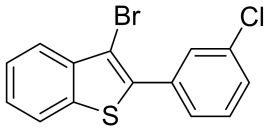
122.3, 118.5, 112.2, 106.7; IR (cm^{-1}): 3106, 2918, 2230, 1635, 1594, 1493, 1454, 1420, 1357, 1232, 1163, 1083, 1024, 879, 837, 767, 743, 726, 698.



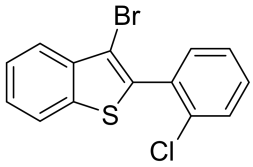
3-Bromo-2-(3-methoxyphenyl)benzo[*b*]thiophene (3j). Colorless oil; 94% yield (75.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.51–7.48 (m, 1H), 7.43–7.42 (m, 1H), 7.41–7.40 (m, 1H), 7.37–7.35 (m, 2H), 7.01–6.99 (m, 1H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.5, 139.1, 138.0, 137.6, 134.2, 129.6, 125.5, 125.2, 123.6, 122.1, 122.0, 115.1, 114.5, 105.0, 55.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}BrOS^+$ 318.9787; Found 318.9789.



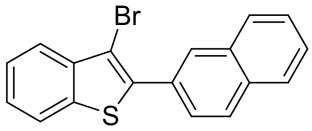
3-Bromo-2-(*m*-tolyl)benzo[*b*]thiophene (3k). Colorless oil; 92% yield (69.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.60–7.58 (m, 2H), 7.50–7.47 (m, 1H), 7.43–7.37 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.1, 138.4, 138.3, 137.6, 132.9, 130.2, 129.6, 128.5, 126.7, 125.4, 125.2, 123.6, 122.1, 104.8, 21.4.



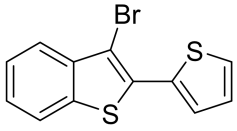
3-Bromo-2-(3-chlorophenyl)benzo[*b*]thiophene (3l). White solid; mp 77–79 ℃; 95% yield (76.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 0.6 Hz, 1H), 7.66–7.63 (m, 1H), 7.51–7.48 (m, 1H), 7.44–7.43 (m, 1H), 7.42–7.41 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.0, 137.7, 136.4, 134.8, 134.5, 129.8, 129.5, 128.8, 127.8, 125.8, 125.4, 123.8, 122.2, 105.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{14}H_9BrClS^+$ 322.9291; Found 322.9293.



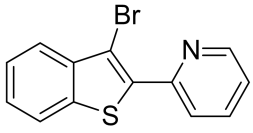
3-Bromo-2-(2-chlorophenyl)benzo[*b*]thiophene (3m). Colorless oil; 95% yield (76.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53–7.51 (m, 1H), 7.49 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.47–7.44 (m, 1H), 7.43 (td, *J* = 7.8, 1.8 Hz, 1H), 7.38 (td, *J* = 7.2, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.5, 137.9, 135.5, 134.5, 132.6, 132.0, 130.5, 129.9, 126.6, 125.7, 125.2, 123.6, 122.2, 108.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{14}H_9BrClS^+$ 322.9291; Found 322.9293.



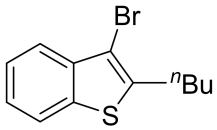
3-Bromo-2-(naphthalen-2-yl)benzo[*b*]thiophene (3n). White solid; mp 82–84 °C; 86% yield (72.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.96–7.92 (m, 3H), 7.91–7.89 (m, 2H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.57–7.54 (m, 2H), 7.53–7.50 (m, 1H), 7.45–7.42 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.2, 138.3, 137.8, 133.1 (133.10, 133.07), 130.5, 129.2, 128.3, 128.2, 127.8, 126.9, 126.8, 126.6, 125.5, 125.3, 123.7, 122.2, 105.2.



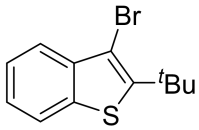
3-Bromo-2-(thiophen-2-yl)benzo[*b*]thiophene (3o). White solid; mp 102–104 °C; 90% yield (66.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.61–7.60 (m, 1H), 7.47–7.44 (m, 2H), 7.40–7.37 (m, 1H), 7.15 (dd, *J* = 4.8, 3.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.2, 136.7, 134.6, 132.1, 127.9, 127.2, 127.1, 125.7, 125.3, 123.4, 121.9, 104.8.



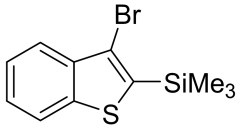
2-(3-Bromobenzo[*b*]thiophen-2-yl)pyridine (3p). White solid; mp 102–104 ℃; 85% yield (61.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 4.8 Hz, 1H), 8.44 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.74 (td, *J* = 7.8, 1.8 Hz, 1H), 7.43–7.40 (m, 1H), 7.39–7.36 (m, 1H), 7.22 (dd, *J* = 7.8, 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.3, 149.5, 139.6, 139.1, 138.2, 136.3, 126.0, 125.0, 123.8, 123.0, 122.3, 122.2, 105.1; IR (cm^{-1}): 3050, 2918, 1656, 1635, 1576, 1520, 1461, 1423, 1246, 1149, 989, 878, 809, 774, 753, 733, 677; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{13}H_9BrNS^+$ 289.9634; Found 289.9636.



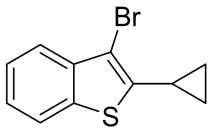
3-Bromo-2-butylbenzo[*b*]thiophene (3q). Colorless oil; 92% yield (61.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76–7.74 (m, 2H), 7.44–7.41 (m, 1H), 7.35–7.32 (m, 1H), 2.97 (t, *J* = 7.8 Hz, 2H), 1.76–1.71 (m, 2H), 1.48–1.44 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.9, 138.4, 137.1, 124.8, 124.6, 122.6, 122.2, 105.7, 32.4, 29.6, 22.2, 13.8.



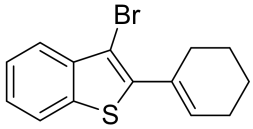
3-Bromo-2-(*tert*-butyl)benzo[*b*]thiophene (3r). Colorless oil; 90% yield (60.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.44–7.41 (m, 1H), 7.36–7.33 (m, 1H), 1.61 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 148.8, 139.9, 135.4, 124.8, 124.6, 122.5, 121.8, 102.7, 35.5, 29.9.



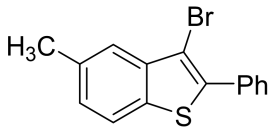
(3-Bromobenzo[*b*]thiophen-2-yl)trimethylsilane (3s). Colorless oil; 87% yield (62.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.48–7.46 (m, 1H), 7.42–7.39 (m, 1H), 0.53 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.3, 139.8, 136.0, 125.1, 124.8, 122.9, 122.1, 114.7, -0.8.



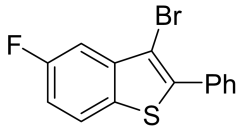
3-Bromo-2-cyclopropylbenzo[*b*]thiophene (3t). Colorless oil; 94% yield (59.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.42–7.40 (m, 1H), 7.32–7.30 (m, 1H), 2.39–2.34 (m, 1H), 1.19–1.15 (m, 2H), 0.90–0.87 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.5, 138.8, 135.6, 124.9, 124.6, 122.3, 122.1, 106.2, 11.9, 10.1.



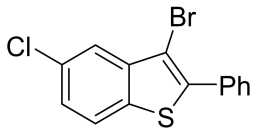
3-Bromo-2-(cyclohex-1-en-1-yl)benzo[*b*]thiophene (3u). Colorless oil; 60% yield (44.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.44–7.42 (m, 1H), 7.36–7.34 (m, 1H), 6.34–6.33 (m, 1H), 2.55–2.53 (m, 2H), 2.29–2.26 (m, 2H), 1.84–1.80 (m, 2H), 1.74–1.70 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.1, 139.0, 136.6, 132.1, 130.7, 124.9 (2), 123.1, 122.0, 103.1, 29.4, 25.7, 22.8, 21.7.



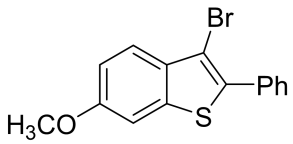
3-Bromo-5-methyl-2-phenylbenzo[*b*]thiophene (3v). White solid; mp 71–73 °C; 97% yield (73.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74–7.73 (m, 2H), 7.66–7.64 (m, 2H), 7.46–7.43 (m, 2H), 7.40–7.38 (m, 1H), 6.21–6.19 (m, 1H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.3, 138.3, 135.1, 134.8, 133.2, 129.6, 128.7, 128.5, 127.2, 123.5, 121.8, 104.5, 21.5; IR (cm^{-1}): 3064, 2911, 2852, 1951, 1871, 1732, 1652, 1600, 1482, 1444, 1294, 1246, 1284, 1243, 1149, 1069, 1031, 923, 871, 820, 795, 736, 684; HRMS (ESI) m/z: $[M+H]^+$ HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}BrS^+$ 302.9838; Found 302.9840.



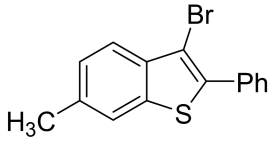
3-Bromo-5-fluoro-2-phenylbenzo[*b*]thiophene (3w). White solid; mp 65–66 ℃; 96% yield (73.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 2H), 7.73 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.57 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.51–7.49 (m, 2H), 7.47–7.44 (m, 1H), 7.16 (td, *J* = 9.0, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.4 (d, *J* = 243 Hz), 140.8, 140.5 (d, *J* = 9.8 Hz), 133.0, 132.7, 129.5, 129.0, 128.6, 123.5 (d, *J* = 9.0 Hz), 114.3 (d, *J* = 25.2 Hz), 190.4 (d, *J* = 24.4 Hz), 104.2 (d, *J* = 4.4 Hz); IR (cm^{-1}): 3023, 2924, 2848, 1653, 1631, 1602, 1560, 1438, 1278, 1166, 987, 856, 836, 795, 743, 686; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{14}H_9BrFS^+$ 306.9587; Found 306.9590.



3-Bromo-5-chloro-2-phenylbenzo[*b*]thiophene (3x). White solid; mp 101–103 ℃; 94% yield (76.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 1.8 Hz, 1H), 7.76–7.74 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.51–7.48 (m, 2H), 7.47–7.44 (m, 1H), 7.37 (dd, *J* = 8.4, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.4, 140.3, 135.8, 132.6, 131.7, 129.5, 129.1, 128.7, 125.9, 123.3, 123.2, 104.0.

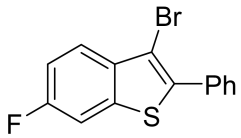


3-Bromo-6-methoxy-2-phenylbenzo[*b*]thiophene (3y). White solid; mp 97–99 ℃; 95% yield (75.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 3H), 7.49–7.47 (m, 2H), 7.43–7.40 (m, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.10 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.3, 138.9, 135.3, 133.2, 129.5, 128.52, 128.45, 124.3, 115.2, 104.6, 104.3, 55.7.

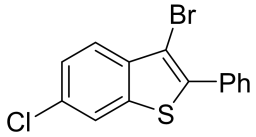


3-Bromo-6-methyl-2-phenylbenzo[*b*]thiophene (3z). Colorless oil; 94% yield (71.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.78–7.76 (m, 2H), 7.61 (s, 1H), 7.51–7.48 (m, 2H), 7.45–7.42 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 2.53 (s, 3H); ^{13}C

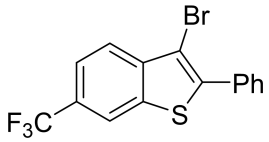
NMR (150 MHz, $CDCl_3$): δ = 137.8, 137.0, 136.9, 135.6, 133.2, 129.5, 128.6, 128.5, 126.9, 123.2, 121.9, 104.6, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}BrS^+$ 302.9838; Found 302.9840.



3-Bromo-6-fluoro-2-phenylbenzo[*b*]thiophene (3aa). White solid; mp 60–61 ℃; 95% yield (73.0 mg). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.76–7.75 (m, 2H), 7.52–7.48 (m, 3H), 7.46–7.44 (m, 1H), 7.23 (td, *J* = 9.0, 2.4 Hz, 1H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −115.63; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.1 (d, *J* = 246 Hz), 138.4 (d, *J* = 10.5 Hz), 137.8 (d, *J* = 3.6 Hz), 135.6, 132.8, 129.5, 128.8, 128.6, 124.9 (d, *J* = 9.4 Hz), 114.2 (d, *J* = 24.6 Hz), 108.3 (d, *J* = 25.7 Hz), 104.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{14}H_9BrFS^+$ 306.9587; Found 306.9590.

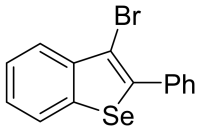


3-Bromo-6-chloro-2-phenylbenzo[*b*]thiophene (3ab). White solid; mp 107–109 ℃; 91% yield (73.6 mg). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.76–7.75 (m, 1H), 7.74–7.73 (m, 1H), 7.50–7.48 (m, 2H), 7.46–7.43 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.7, 138.5, 137.7, 132.6, 131.6, 129.5, 129.0, 128.7, 126.1, 124.5, 121.7, 104.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{14}H_9BrClS^+$ 322.9291; Found 322.9289.

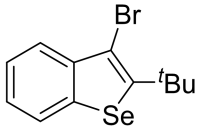


3-Bromo-2-phenyl-6-(trifluoromethyl)benzo[*b*]thiophene (3ac). White solid; mp 80–82 ℃; 93% yield (83.0 mg). ^1H NMR (600 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.78–7.77 (m, 2H), 7.64–7.63 (m, 1H), 7.53–7.46 (m, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = –61.56; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.8, 140.5,

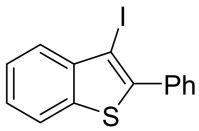
139.0, 132.3, 129.6, 129.2, 128.7, 127.9 (q, J = 32.3 Hz), 125.3, 124.4 (q, J = 272.0 Hz), 122.8, 121.6 (q, J = 3.3 Hz), 120.9 (q, J = 4.0 Hz), 105.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_9BrF_3S^+$ 356.9555; Found 356.9557.



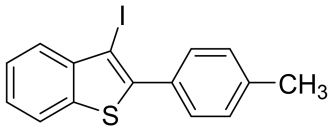
3-Bromo-2-phenylbenzo[*b*]selenophene (3ad). White solid; mp 91–93 ℃; 91% yield (76.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99–7.98 (m, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.74–7.72 (m, 2H), 7.53–7.48 (m, 3H), 7.46–7.43 (m, 1H), 7.39–7.37 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.9, 140.7, 138.9, 134.9, 129.8, 128.6, 128.5, 126.1, 125.7, 125.5, 125.1, 106.6.



3-Bromo-2-(*tert*-butyl)benzo[*b*]selenophene (3ae). White solid; mp 82–84 ℃; 80% yield (63.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.45–7.42 (m, 1H), 7.32–7.29 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.2, 142.0, 136.3, 125.1, 124.9, 124.7, 104.1, 37.1, 30.3.

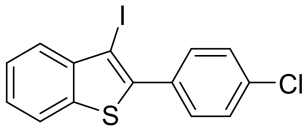


3-Iodo-2-phenylbenzo[*b*]thiophene (3ag). White solid; mp 54–56 ℃; 97% yield (81.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.72–7.70 (m, 2H), 7.52–7.45 (m, 4H), 7.43–7.40 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.1, 141.9, 138.9, 134.6, 130.0, 128.9, 128.5, 126.3, 125.5, 125.4, 122.1, 79.4.

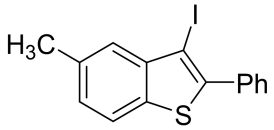


3-Iodo-2-(*p*-tolyl)benzo[*b*]thiophene (3ah). White solid; mp 97–99 ℃; 97% yield (84.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8

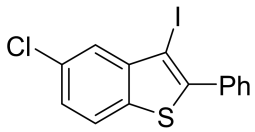
Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.51–7.48 (m, 1H), 7.42–7.39 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.3, 141.9, 138.9, 138.8, 131.6, 129.8, 129.2, 126.1, 125.3 (125.35, 125.32), 122.0, 79.0, 21.4.



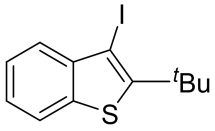
2-(4-Chlorophenyl)-3-iodobenzo[*b*]thiophene (3ai). White solid; mp 102–104 ℃; 95% yield (88.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.50–7.45 (m, 3H), 7.43–7.40 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.8, 140.7, 138.8, 135.0, 133.0, 131.3, 128.8, 126.4, 125.7, 125.6, 122.1, 79.9.



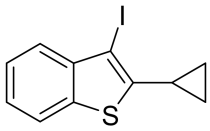
3-Iodo-5-methyl-2-phenylbenzo[*b*]thiophene (3aj). White solid; mp 101–103 ℃; 96% yield (84.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72–7.70 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.66 (s, 1H), 7.51–7.49 (m, 2H), 7.47–7.45 (m, 1H), 7.24 (dd, *J* = 7.8, 2.4 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.2, 142.0, 136.0, 135.3, 134.7, 130.0, 128.8, 128.4, 127.2, 126.2, 121.8, 79.1, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}IS^+$ 350.9699; Found 350.9696.



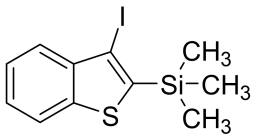
5-Chloro-3-iodo-2-phenylbenzo[*b*]thiophene (3ak). White solid; mp 101–102 ℃; 94% yield (87.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.68–7.67 (m, 2H), 7.51–7.46 (m, 3H), 7.43 (dd, *J* = 8.4, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.6, 140.5, 139.6, 134.1, 131.6, 129.9, 129.1, 128.6, 127.1, 126.2, 121.5, 78.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{14}H_9ClISe^+$ 370.9153; Found 370.9157.



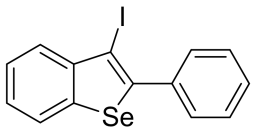
2-(*tert*-Butyl)-3-iodobenzo[*b*]thiophene (3al). White solid; mp 96–98 ℃; 93% yield (73.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 1H), 7.75–7.73 (m, 1H), 7.45–7.41 (m, 1H), 7.36–7.32 (m, 1H), 1.67 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.7, 142.8, 136.1, 125.2, 125.0, 124.7, 121.6, 74.7, 35.8, 30.3.



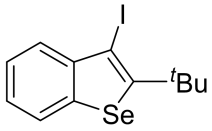
2-Cyclopropyl-3-iodobenzo[*b*]thiophene (3am). Colorless oil; 91% yield (68.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73–7.70 (m, 2H), 7.44–7.41 (m, 1H), 7.33–7.31 (m, 1H), 2.38–2.33 (m, 1H), 1.22–1.19 (m, 2H), 0.94–0.92 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.2, 141.4, 136.2, 125.1, 124.6, 124.3, 122.2, 80.2, 15.0, 10.3.



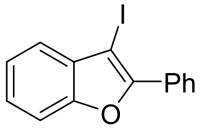
(3-Iodobenzo[*b*]thiophen-2-yl)trimethylsilane (3an). Colorless oil; 90% yield (74.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87–7.84 (m, 2H), 7.48–7.46 (m, 1H), 7.41–7.38 (m, 1H), 0.56 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.9, 141.2, 140.6, 125.2, 125.1, 125.0, 121.8, 87.1, -0.7.



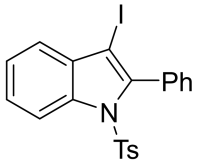
3-Iodo-2-phenylbenzo[*b*]selenophene (3ao). White solid; mp 112-115 ℃; 95% yield (91.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.64–7.63 (m, 2H), 7.51–7.43 (m, 4H), 7.36–7.34 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.5, 143.6, 140.5, 136.9, 130.0, 128.9, 128.7, 128.4, 125.8, 125.7, 125.1, 82.7.



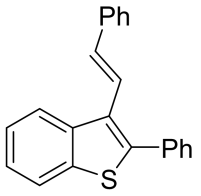
2-(*tert*-Butyl)-3-iodobenzo[*b*]selenophene (3ap). White solid; mp 108–110 ℃; 90% yield (81.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.45–7.42 (m, 1H), 7.30–7.27 (m, 1H), 1.66 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.1, 144.9, 137.2, 125.8, 125.3, 125.0, 124.5, 77.5, 37.6, 30.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{12}H_{14}ISe^+$ 364.9300; Found 364.9302.



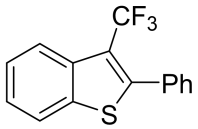
3-Iodo-2-phenylbenzofuran (3aq). Colorless oil; 78% yield (62.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.16–8.15 (m, 2H), 7.47–7.44 (m, 3H), 7.43–7.41 (m, 1H), 7.40–7.37 (m, 1H), 7.32 (td, *J* = 7.2, 1.2 Hz, 1H), 7.29–7.26 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.8, 153.0, 132.4, 129.4, 129.2, 128.5, 127.4, 125.6, 123.5, 121.8, 111.1, 61.1.



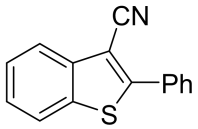
3-Iodo-2-phenyl-1-tosyl-1H-indole (3ar). White solid; mp 110–112 ℃; 76% yield (86.0 mg, mixture of **3ar** and **3ar'**). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.45–7.43 (m, 3H), 7.41 (d, *J* = 4.8 Hz, 1H), 7.36–7.35 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 2.29 (s, 3H) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 145.0, 141.0, 136.9, 135.0, 132.2, 131.7, 131.5, 129.4, 129.2, 127.4, 126.8, 126.0, 124.6, 122.1, 115.9, 75.8, 21.5.



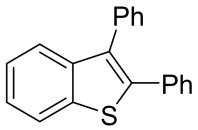
(*E*)-2-Phenyl-3-styrylbenzo[*b*]thiophene (4A). White solid; mp 62–64 ℃; 80% yield (249.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.58–7.57 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.39–7.36 (m, 3H), 7.33–7.28 (m, 4H), 7.21–7.18 (m, 2H), 7.12–7.09 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.8, 139.2, 139.0, 137.6, 134.5, 132.2, 129.9, 129.3, 128.7, 128.6, 128.1, 127.6, 126.3, 124.6, 124.5, 123.3, 122.3, 122.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{17}S^+$ 313.1045; Found 313.1047.



2-Phenyl-3-(trifluoromethyl)benzo[*b*]thiophene (5A). Colorless oil; 95% yield (264.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.51–7.50 (m, 2H), 7.47–7.39 (m, 5H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = –54.85; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.6 (q, *J* = 3.6 Hz), 138.8, 136.5, 132.5, 129.7, 129.2, 128.2, 125.4, 125.2, 123.2 (q, *J* = 2.2 Hz), 122.8 (q, *J* = 272.5 Hz), 121.9, 120.4 (q, *J* = 33.4 Hz).

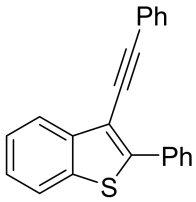


2-Phenylbenzo[*b*]thiophene-3-carbonitrile (6A). White solid; mp 109–110 ℃; 84% yield (197.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.8 Hz, 1H), 7.89–7.87 (m, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.53–7.48 (m, 4H), 7.45–7.43 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.0, 139.1, 137.3, 131.4, 130.4, 129.3, 128.2, 126.1(126.08, 126.06), 122.5, 122.3, 115.1, 102.0.

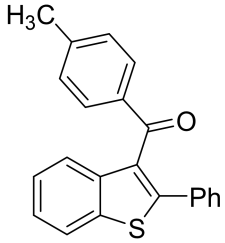


2,3-Diphenylbenzo[*b*]thiophene (7A). White solid; mp 115–117 ℃; 91% yield (260.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86–7.85 (m, 1H), 7.59–7.58 (m, 1H), 7.39–7.37 (m, 2H), 7.35–7.30 (m, 7H), 7.23–7.21 (m, 3H); ^{13}C NMR (150 MHz,

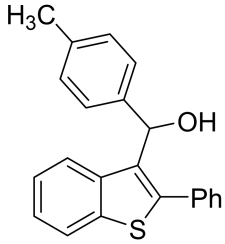
$CDCl_3$): δ = 140.9, 139.5, 138.8, 135.5, 134.2, 133.2, 130.4, 129.6, 128.6, 128.3, 127.7, 127.4, 124.5, 124.4, 123.3, 122.0.



2-Phenyl-3-(phenylethynyl)benzo[*b*]thiophene (8A). White solid; mp 70–72 ℃; 84% yield (260.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.12–8.10 (m, 2H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.62–7.60 (m, 2H), 7.53–7.49 (m, 3H), 7.45–7.38 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.2, 141.0, 137.5, 133.9, 131.5, 128.8, 128.7, 128.4, 128.3, 125.2, 124.9, 123.3 (123.34, 123.31), 122.1, 113.6, 94.6, 84.1.

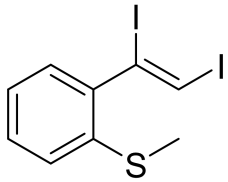


(2-Phenylbenzo[*b*]thiophen-3-yl)(*p*-tolyl)methanone (9A). White solid; mp 126–128 ℃; 73% yield (239.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87–7.85 (m, 1H), 7.69–7.66 (m, 3H), 7.44–7.43 (m, 2H), 7.37–7.32 (m, 2H), 7.23–7.20 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.0, 145.4, 144.3, 139.7, 138.9, 134.8, 133.3, 131.8, 130.0, 129.1 (129.14, 129.08), 128.7, 128.6, 125.0 (125.01, 124.96), 123.5, 121.9, 21.6.



(2-Phenylbenzo[*b*]thiophen-3-yl)(*p*-tolyl)methanol (10A). Yellow oil; 68% yield (224.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.8 Hz, 1H), 7.68–7.66 (m, 1H), 7.49–7.47 (m, 2H), 7.38–7.34 (m, 3H), 7.27–7.26 (m, 2H), 7.25–7.22 (m, 1H), 7.17–7.14 (m,1H), 7.09–7.08 (m, 2H), 6.19 (s, 1H), 2.42 (br, 1H), 2.29 (s, 3H); ^{13}C

NMR (150 MHz, $CDCl_3$): δ = 194.0, 145.4, 144.3, 139.7, 138.9, 134.8, 133.3, 131.8, 130.0, 129.1 (129.14, 129.08), 128.7, 128.6, 125.0 (125.01, 124.96), 123.5, 121.9, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}OS^+$ 331.1151; Found 331.1153.



(2-(1,2-Diiodovinyl)phenyl)(methyl)sulfane. Colourless oil; 52% yield (52.3 mg). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.35–7.32 (m, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.19–7.17 (m, 1H), 7.11 (dd, *J* = 7.8, 1.2 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.5, 136.3, 129.4, 128.2, 125.5, 125.1, 94.5, 84.9, 15.6.

2.9 本章小结

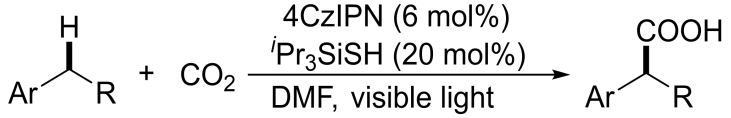
总之，我们开发了一种简单有效的方法，通过可见光促进 2-炔基硫代苯甲醚与简单烷基卤化物的卤化反应合成 3-卤代苯并噻吩衍生物。该方法具有无外加光催化剂、工艺简单、环境友好、官能团耐受性好、产品收率高等优点。此外，通过偶联反应可以将卤素原子转化为其他官能团，用于合成功能化苯并噻吩，这在药物化学和功能材料中具有重要的价值。实验室正在深入进行反应机理研究，并不断拓展该策略在合成中的应用研究。

第 3 章 可见光促进 2-炔基苯甲硫醚分子内环化氧化合成 3-酰基苯并噻吩

3.1 研究背景

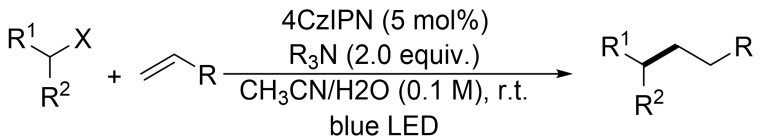
近二十年来，通过可见光促进有机反应合成各种高附加值产品已被公认为是当前有机合成化学的重要工具[89-92]。自由基中间体一般是由激发态催化剂（PC）与底物通过单电子转移过程直接相互作用产生的。在光化学转化的广泛背景下，光化学氢原子转移催化剂已被证明是这类反应的一种特殊的促进剂，它可以实现惰性键的功能化反应和传统光催化难以实现的转化。

2019 年，Kŏnig 课题组[93]，报道了一种新颖的碳氢键与二氧化碳的羧基化反应（Scheme 3-1）。通过光氧化还原和有机催化的协同催化，实现了可见光介导的苄基碳氢键羧化反应。该反应无需金属催化剂或化学计量添加剂，具有广泛的底物范围。



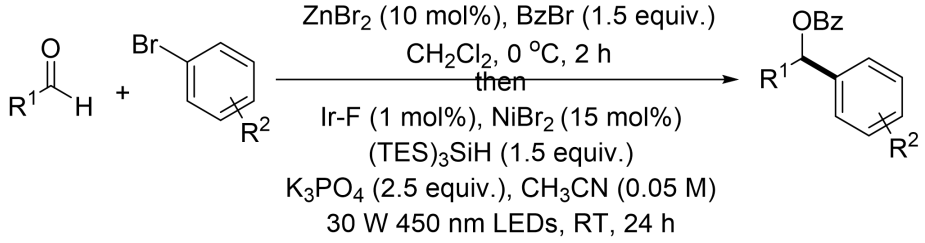
Scheme 3-1 苄基 C-H 键的羧基化

2020 年，Leonori 课题组[94]，报道了一种可见光促进 4CzIPN 催化卤代烃与烯烃的烷基氢化反应（Scheme 3-2），这种方法底物范围广泛、官能团耐受性好，在氘化反应、交叉亲电偶联反应、Heck 反应和芳基烃的碳氢烷基化反应中具有广泛应用。



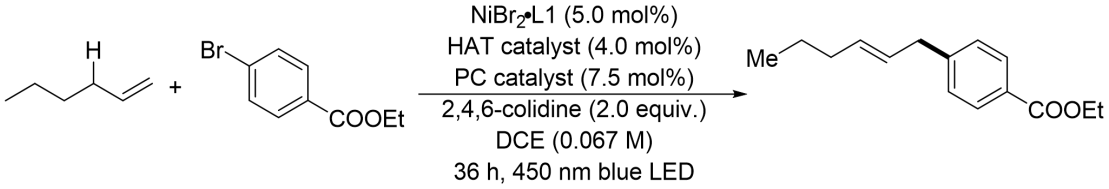
Scheme 3-2 烯烃的碳氢烷基化反应

2022 年，Glorius 课题组[95]，在双镍和可见光诱导的光氧化还原催化条件下，实现了自由基羰基苯基芳基化反应（Scheme 3-3）。该方法具有广泛的应用范围和良好的官能团耐受性，可以应用于复杂药物类似物的后期修饰。



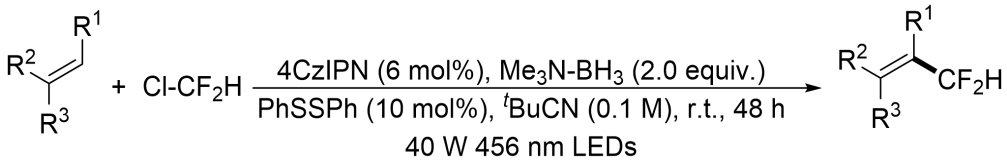
Scheme 3-3 自由基羰基苯基芳基化反应

同年，该课题组[96]，发展了可见光促进未活化烯烃与活化溴代烃直接芳基化反应（Scheme 3-4），该反应在温和和氧化还原中性条件下成功合成非共轭烯烃。该方法对各种官能团都具有很高的耐受性，并为过渡金属催化的烯丙基功能化提供了一种补充方法。



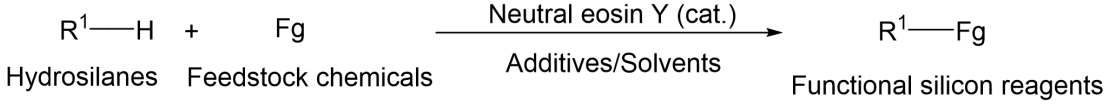
Scheme 3-4 烯丙基 C(sp^3)-H 直接芳基化反应

2022 年，Wu 课题组[97]，在温和、无金属的条件下，以廉价、丰富的 HCF_2Cl 为氟源，成功建立了非活化烯烃的氢二氟甲基化反应（Scheme 3-5）。该方法具有非常广泛的底物范围。



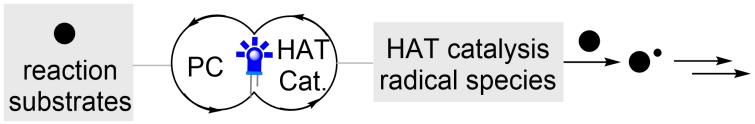
Scheme 3-5 非活化烯烃的氢二氟甲基化反应

最近，Wu 课题组[98]，报道了用 EY 作为 HAT 催化剂，实现了多氢硅烷逐步功能化（Scheme 3-6）。该方法底物广谱性好（150 个例子），具有出色的选择性和可伸缩性。



Scheme 3-6 多氢硅烷逐步功能化反应

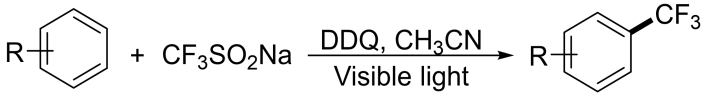
一般来说，光化学 HAT 催化剂在激发 PC 的帮助下产生 HAT 催化剂自由基中间体，将常见官能团转化为活性自由基中间体[99-101]（Scheme 3-7）



Scheme 3-7 氢原子转移催化剂的催化过程

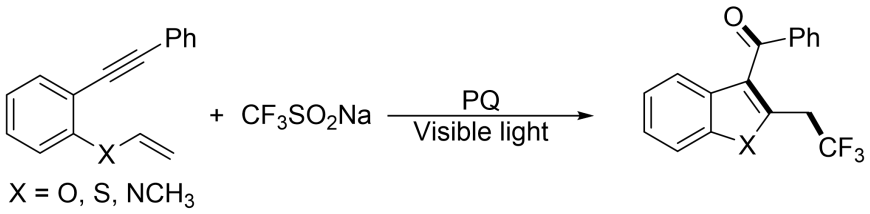
近年来，可见光下通过 HAT 促进 C(sp^3)-H 键活化的研究取得了蓬勃发展，除了这些光化学 HAT 催化方案外，硫醇类、醇类、卤素自由基等通常被用作有效的氢原子转移催化剂[102-109]，在工艺化学中迫切需要开发一种温和实用的光化学 HAT 催化剂，在不需要额外 HAT 催化剂的情况下激活 C(Sp^3)-H 键。具有完全共轭环二酮结构的醌类在可见光区表现出光响应，由于光激发醌类具有突出的电子接受能力和析氢能力，可以同时作为 PC 和 HAT 催化剂。

2017 年，Yuan 课题组[110]，开发了一种在可见光促进芳烃的直接三氟甲基化。该反应操作简单、CF_3 自由基源低廉易得（Scheme 3-8）。



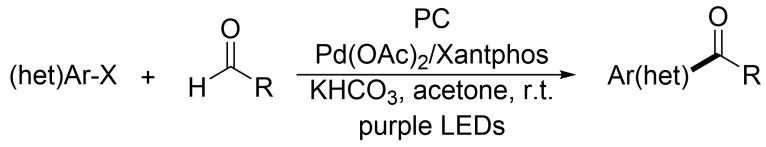
Scheme 3-8 可见光促进芳烃的三氟甲基化反应

2017 年，Kumar 课题组[111]，开发了一种在无金属条件下水作为氧化剂，可见光促进 PQ 催化合成三氟甲基化苯并呋喃，噻吩和吲哚。该反应条件温和，底物耐受性好（Scheme 3-9）。



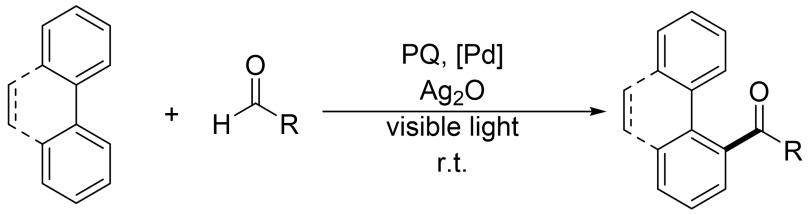
Scheme 3-9 可见光诱导合成三氟甲基化苯并噻吩

2020 年，Zheng 课题组[112]，将 HAT 光催化剂与钯催化结合，利用醛部分作为亲核试剂，在温和条件下以 32-88%的收率合成了 41 个酮类化合物。（Scheme 3-10）。



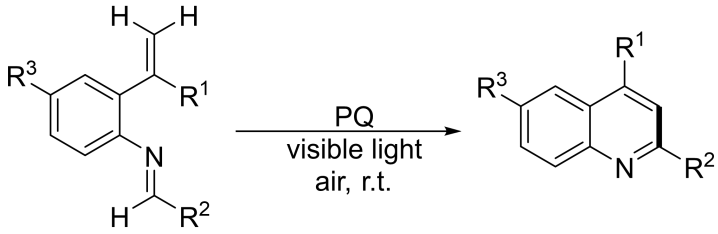
Scheme 3-10 醛的直接芳基化或烯基化反应

2021 年，Xia 题组[113]，通过可见光与钯的协同催化，实现了芳烃的酰基化反应（Scheme 3-11）。该方法利用芳香族和脂肪族醛作为丰富的酰基来源，在温和的反应条件下产生芳基酮，具有广泛的官能团耐受性。



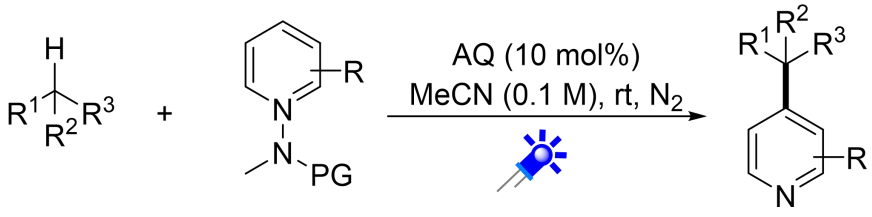
Scheme 3-11 芳烃的酰基化反应

2022 年，Helaja 题组[114]，报道了一种可见光促进选择性合成多取代喹啉的方法（Scheme 3-12）。该反应以 PQ 作为催化剂，空气中的氧气作为氧化剂，高效合成了 26 个多取代喹啉。



Scheme 3-12 可见光促进喹啉的合成

最近，Hong 的课题组[115]，在温和的无金属反应条件下，利用蒽醌（AQ）同时作为光催化剂和氢原子转移催化剂（Scheme 3-13），高效构建 C_4 烷基化吡啶。该反应在温和条件下以 31-94%的产率合成了 57 个具有高位点选择性的 4-取代吡啶。

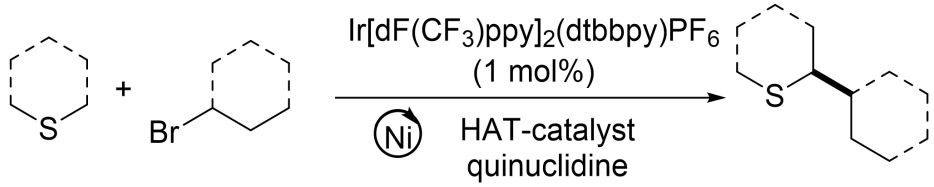


Scheme 3-13 非活化烷基直接吡啶化

然而，现有的方法仅限于碳氢功能化，并且依赖于惰性气体气氛。以空气为唯一氧化剂，醌类为 PC 和 HAT 催化剂，实现不饱和烃级联反应的直接光化学 HAT 催化方法是非常理想的，但也是具有挑战性的。近年来，功能化硫苯甲醚在不饱和键上一步附加两个不同的官能团，从而形成含硫杂环的环化方法在有机

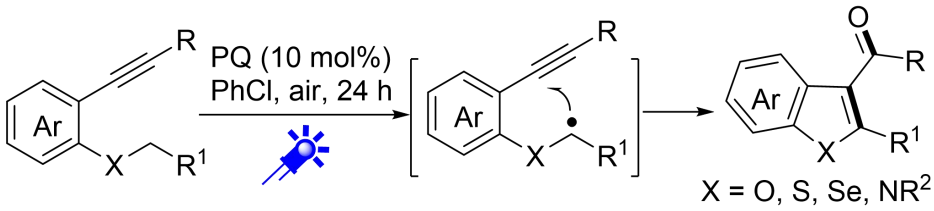
化学中引起了广泛的关注[116-122]。但目前文献报道的 3-官能化苯并噻吩的合成，都会造成硫保护基的浪费。因此，探索新的稳健、高效、原子利用率高的功能化硫甲醚转化是非常重要的。

2017 年，MacMillan 的课题组[123]，通过光氧化还原、镍和氢原子转移催化的结合，报道了一种选择性 Sp^3 碳氢烷基化反应（Scheme 3-14）。该体系同时使用三个催化循环来实现氢化碳的活化、烷基卤化物的氧化加成和还原消除，从而实现烷基-烷基片段偶联。



Scheme 3-14 选择性 C(Sp^3)-H 烷基化交叉偶联反应

基于以上工作和对自由基级联反应[124-127]的研究兴趣中获得灵感，我们假设光激发醌作为 HAT 催化剂，可以被用来活化 2-炔基苯甲硫醚中的 S-C(sp^3)-H 键，然后发生分子内自由基环化和氧化，形成 3-酰基苯并噻吩骨架（Scheme 3-15）。



Scheme 3-15 可见光促进分子内环化氧化合成酰基苯并杂环

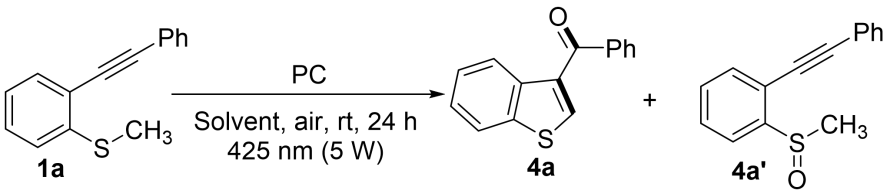
3.2 反应条件优化

以 2-炔苯基苯甲硫醚（**1a**）为模版反应，分别从催化剂、溶剂、波长等方面进行了优化以确定最佳反应条件。

3.2.1 催化剂及溶剂的筛选

首先，对光敏剂进行了筛选（Table 3-1）。将 **1a**（0.2 mmol）和 PQ（10 mol%）溶解在 DCE（2 mL）中，在空气气氛下，用蓝光 LED（425 nm，5 W）照射反应 24 h，以 64%的收率得到所需的 3-酰基苯噻吩（**4a**），并检测到微量的氧化产物 **4a'**（entry 1）。然后用蒽醌（PQ）、苊醌（ACQ）、苯醌（BQ）和 2,3-二氯-5,6-二氰基苯琨（DDQ）做光催化剂试图去提高产率，但是都失败了（entries 2-5）。然后对溶剂进行了筛选，发现氯苯为最佳反应溶剂（entries 6-16）。

Table 3-1 催化剂和溶剂的筛选 [a]



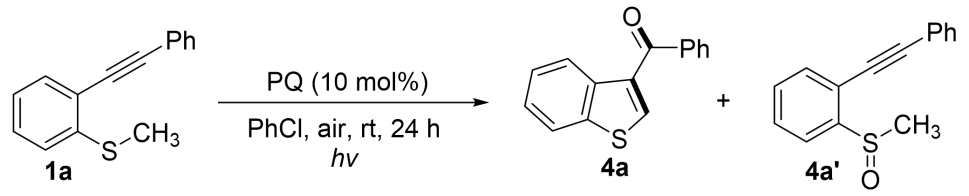
Entry	PC	Solvent	Yield (%)[b]	
			4a	**4a'**
1	PQ	DCE	64	trace
2	AQ	DCE	52	trace
3	ACQ	DCE	50	trace
4	BQ	DCE	trace	15
5	DDQ	DCE	n.d.	12
6	PQ	PhCl	71	trace
7	PQ	THF	n.d.	trace
8	PQ	*n*-Hexane	26	trace
9	PQ	MeCN	trace	25
10	PQ	Acetone	trace	n.d.
11	PQ	EtOH	trace	27
12	PQ	DMF	trace	trace
13	PQ	DCM	31	18
14	PQ	EtOAc	34	trace
15	PQ	$PhCH_3$	54	trace
16	PQ	$PhCF_3$	59	trace

[a]Reaction conditions: **1a** (0.20 mmol) and photocatalyst (PC) (10 mol%) in solvent (2.0 mL) were irradiated with 5 W blue LED in a reaction tube with an air balloon at room temperature for 24 h unless otherwise stated. [b]Isolated yield; n.d. = not detected.

3.2.2 光源及基础条件的筛选

然后对光源进行了筛选，415 nm（5w)的 LED 是最佳选择以 82%的收率获得目标产物（Table 3-2, entries 1-4）。对照实验证实，光和催化剂是实现这一转化的必要条件（entries 5-6）。特别的，该反应在阳光下也能顺利进行，以 52%的产率得到 **4a**（entry 7）。然后对反应功率进行了优化，发现 5 W 为最佳反应功率（entries 8-10），当在氩气气氛下进行反应时，没有观察到期望的产物 **4a**（entry 11）。然而，当反应在氧气气氛下进行时，**4a** 和 **4a′**的产率分别为 27%和 50%（entry 12）。此外，当反应在空气中进行时，**4a** 和 **4a'**的产率分别为 57%和 13%（entry 13）。最后，进一步筛选光敏剂的量以及反应时间，确定 10%为最佳光催化剂用量，24 小时为最佳反应时间（entriesy 14-15）。

Table 3-2 光源及基本条件的筛选 [a]



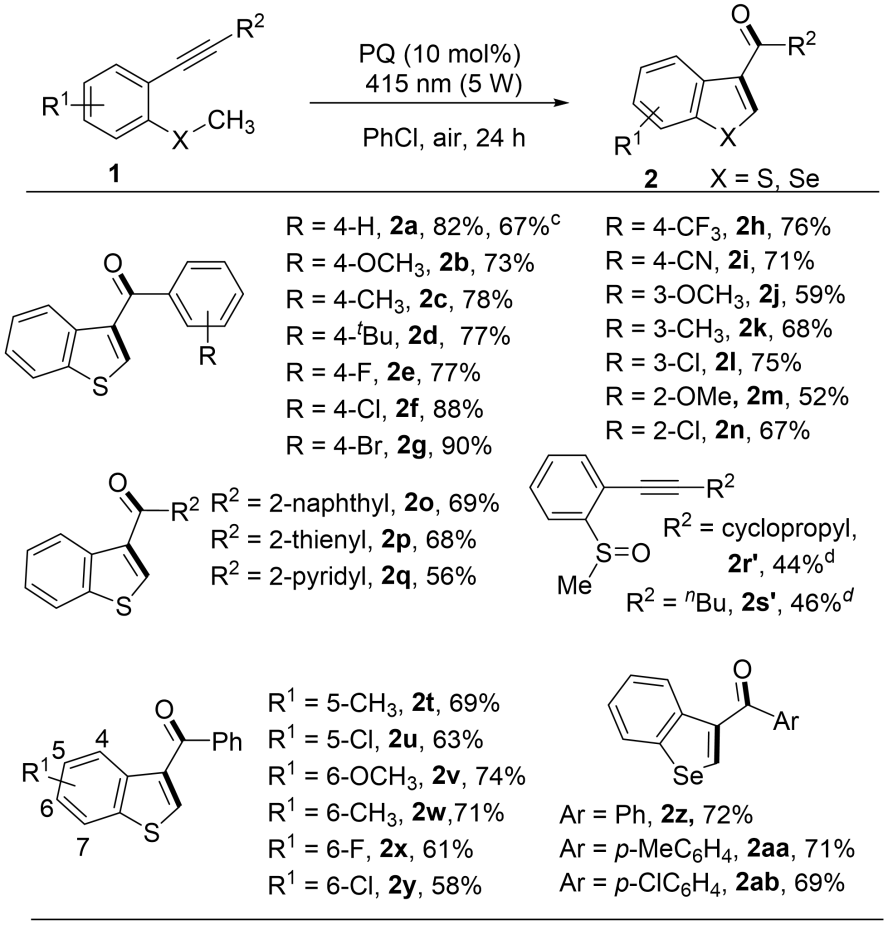
Entry	PC	LED (nm)	Solvent	Yield (%)[b]	
				4a	**4a'**
1	PQ	425 (5 W)	PhCl	71	trace
2	PQ	395 (5 W)	PhCl	43	trace
3	PQ	415 (5 W)	PhCl	82	race
4	PQ	435 (5 W)	PhCl	68	trace
5	/	415 (5 W)	PhCl	n.d.	n.d.
6	PQ	/	PhCl	n.d.	n.d.
7	PQ	sunlight	PhCl	29[c], 52[d]	trace
8	PQ	415 (3 W)	PhCl	78	trace
9	PQ	415 (7 W)	PhCl	75	trace
10	PQ	415 (10 W)	PhCl	65	trace
11	PQ	415 (5 W)	PhCl	n.d.[e]	n.d.[e]
12	PQ	415 (5 W)	PhCl	27[f]	50[f]
13	PQ	415 (5 W)	PhCl	57[g]	13[g]
14	PQ	415 (5 W)	PhCl	61[h], 80[i]	trace[h, i]
15	PQ	415 (5 W)	PhCl	63[j], 81[k]	trace[j, k]

[a]Reaction conditions: **1a** (0.20 mmol) and PQ (10 mol%) in PhCl (2.0 mL) were irradiated with blue LED in a reaction tube with an air balloon at room temperature for 24 h unless otherwise stated. [b]Isolated yield; [c]The reaction exposed to sunlight irradiation for 8 h. [d]The reaction exposed to sunlight irradiation for 24 h. [e]Under argon atmosphere; [f]Under O_2 atmosphere with an oxygen balloon; [g]Reaction conducted open to air; [h]5 mol% PQ; [i]20 mol% PQ; [j]18 h; [k]30 h; n.d. = not detected.

3.3 反应底物拓展

为了证明这一环化氧化反应的普遍性，在优化的反应条件下，考察了各种芳基环（R^2）上具有不同基团的 2-炔基硫代苯甲醚（Scheme 3-16）。苯基环（R^2）上的 *p*-OMe、*p*-Me、*p*-^{t}Bu、*m*-OMe、*m*-Me、*o*-OMe 等给电子基团和 *p*-F、*p*-Cl、*p*-Br、*p*-CF_3、*p*-CN、*m*-Cl、*o*-Cl 等吸电子基团均表现出良好的相容性，产率为 52-90%。吸电子取代基有利于生成产物，而给电子基则稍微阻碍了反应。此外，当 R^2 被噻吩基、萘基和吡啶基取代时，这些底物也适用于该反应，并以 56-69% 的收率得到所需的苯并噻吩（**4o-4q**）。然而，当底物中 R^2 被正丁基（**1r**）或环丙基（**1s**）取代时，得到的不是酰化苯并噻吩（**4r** 和 **4s**），而是相应的亚砜（**4r'** 和 **4s'**）可能与形成的烯基自由基的活性有关，而反应混合物的 HRMS 分析仅检测到微量的 **4s**。这一结果表明，在目前的反应条件下，R^2 基必须是芳基。此外，

对硫代苯甲醚芳香环上的不同取代基也进行了研究，忽略电子和空间效应，并以58-74%的产率生成了目标产物3-酰基苯并噻吩（**4t-4y**）。令我们高兴的是，取代的2-炔基苯甲硒醚（**1z-1ab**）也是得到相应的3-酰基苯并硒吩（**4z-4ab**），产率为69-72%。值得注意的是，该反应可以很容易的放大。在优化的反应条件下，将1.50 g（6.7 mmol）的**1a**进行模型反应，分离得到相应的产物**4a**，收率为67%（1.07 g）。

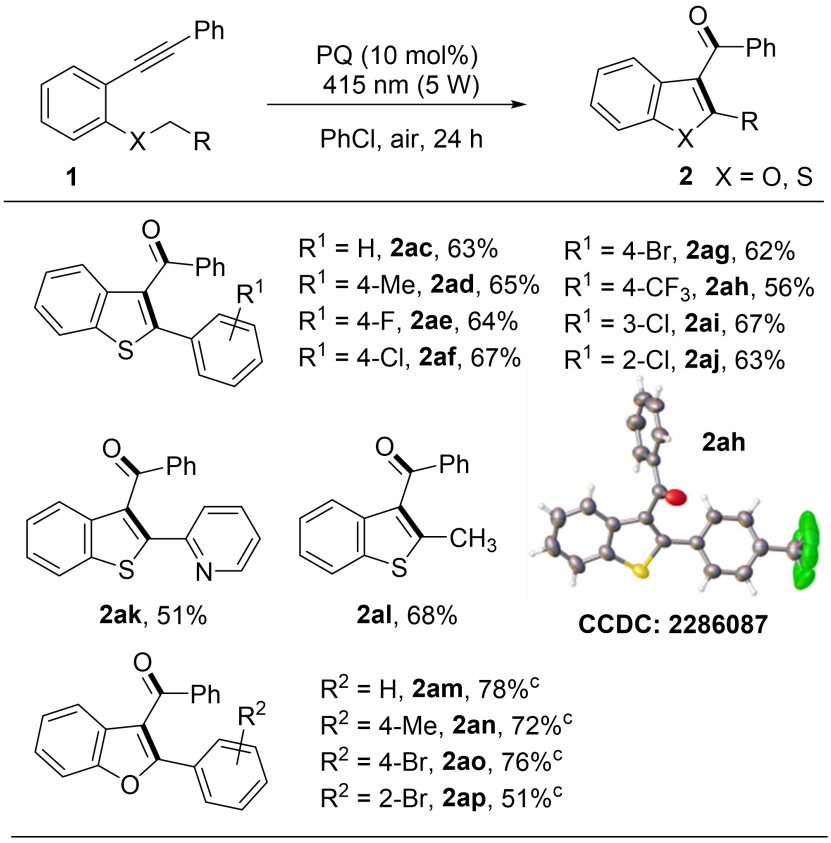


Unless otherwise noted, all reactions were performed with **1** (0.20 mmol) and PQ (10 mol%) in chlorobenzene (2.0 mL) at room temperature in a reaction tube with an air balloon under blue LED (415 nm, 5 W) irradiation for 24 h. Isolated yields. [a] The reaction was carried out on 6.7 mmol scale. [b] 48 h.

Scheme 3-16 底物拓展 I

为了进一步扩大这一转化的范围，还研究了2-炔基苯基苯苄基醚的氧化环化（Scheme 3-17）。总的来说，在优化的反应条件下，转化过程顺利进行，苯基部分苯基环上的供电子基和吸电子基都能得到良好的耐受性，产率为56-67%，

得到了期望的 3-酰基苯并噻吩（**4ac-4aj**），并通过 x 射线单晶分析进一步证实了 **4ah** 的结构。另一方面，在优化条件下，含有 2-吡啶甲基和乙基的底物也被用于该转化，**4ak** 和 **4al** 的产率分别为 51%和 68%。为了进一步探索该方案的适用范围，我们将注意力转向了各种 3-酰基苯并呋喃的合成。令人高兴的是，2-炔基苯基（苄基）醚也是该转化的良好底物，在最佳条件下以 51-78%的产率获得了所需的 3-酰基苯并呋喃（**4am-4ap**）。



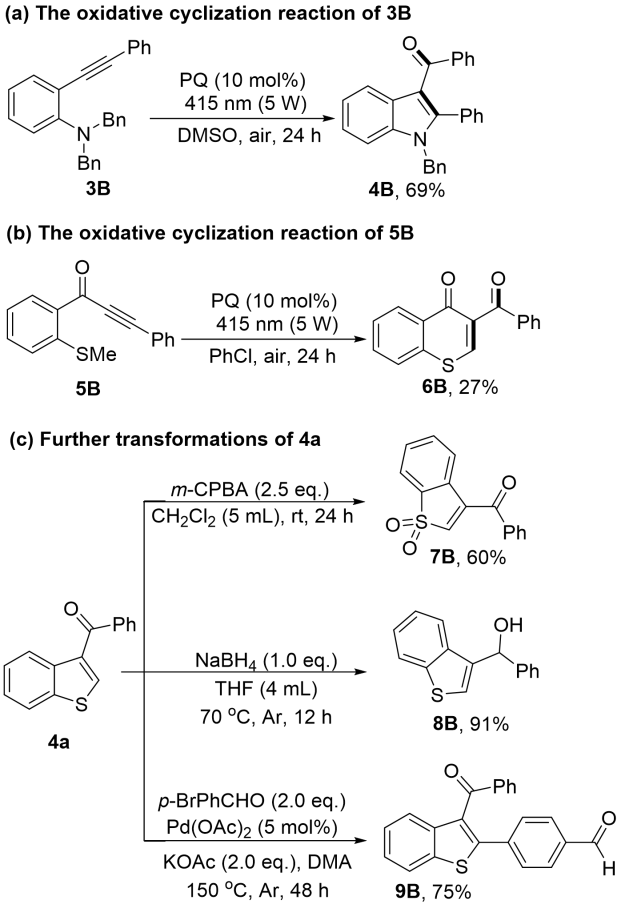
Unless otherwise noted, all reactions were performed with **1** (0.20 mmol) and PQ (10 mol%) in chlorobenzene (2.0 mL) at room temperature in a reaction tube with an air balloon under blue LED (415 nm, 5 W) irradiation for 24 h. Isolated yields. [a] PQ (20%) was used, 48 h.

Scheme 3-17 底物拓展 II

3.4 反应拓展及进一步转化

以氮, 氮-二苄基-2-（苯基乙基)苯胺（**3B**）为底物，在一定条件下反应也顺利进行，产率为 69%，与 Zhou 的方法[129]（Scheme 3-18a）相比大致相同。然而，邻酮炔苯基苯甲硫醚（**5B**）不再是该反应的有效底物，所需产物（**6B**）的产率仅为 27%（Scheme 3-18b）。另外，**4a** 可以很容易地进行转化。用 *m*-CPBA 氧

化 **4a**，合成的产物（**7B**）产率为 60%，用 $NaBH_4$ 可将 **4a** 还原为相应的产物（**8B**）。此外，钯催化的 **4a** 与 4-溴苯甲醛的 C2-H 功能化反应也进行得很好，并以较高的收率得到了相应的偶联产物（**9B**）（Scheme 3-18c）

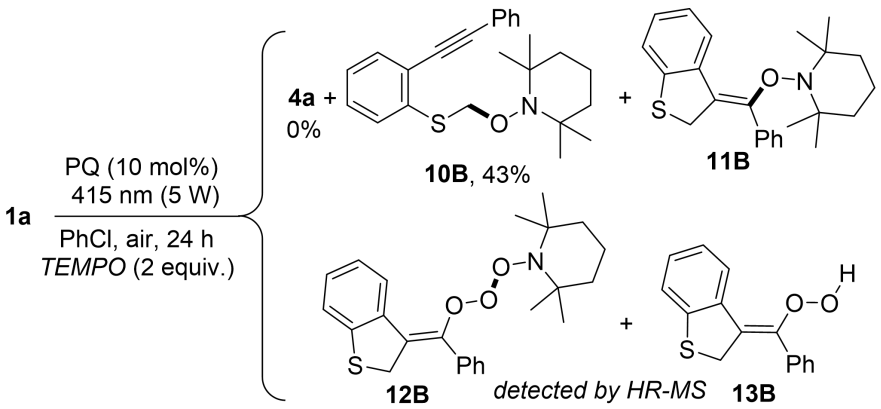


Scheme 3-18 反应拓展及进一步转化

3.5 反应机理的研究

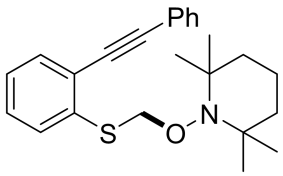
为了深入了解这种转变的机制，进行了几项对照实验。

3.5.1 自由基捕获实验

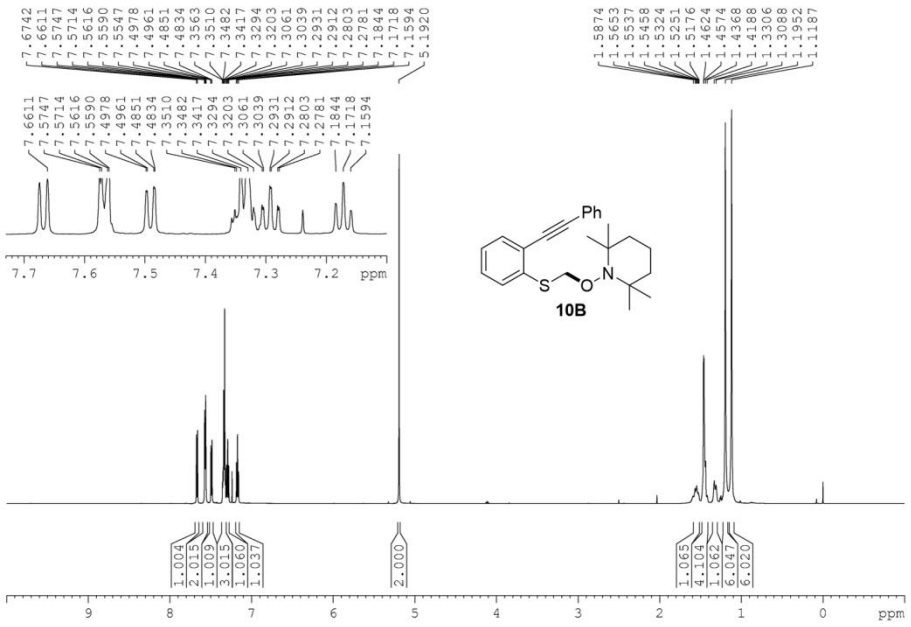


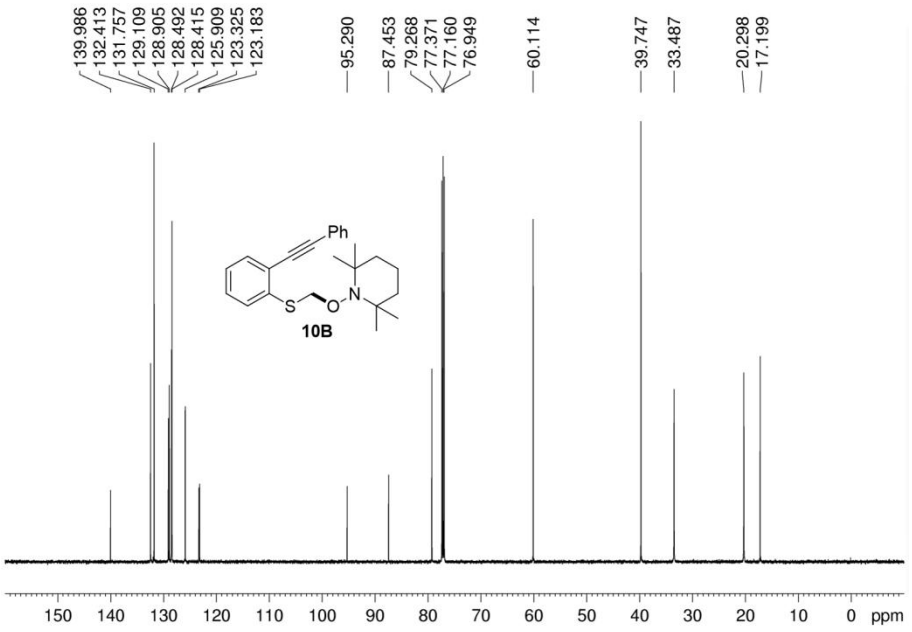
Scheme 3-19 自由基捕获实验

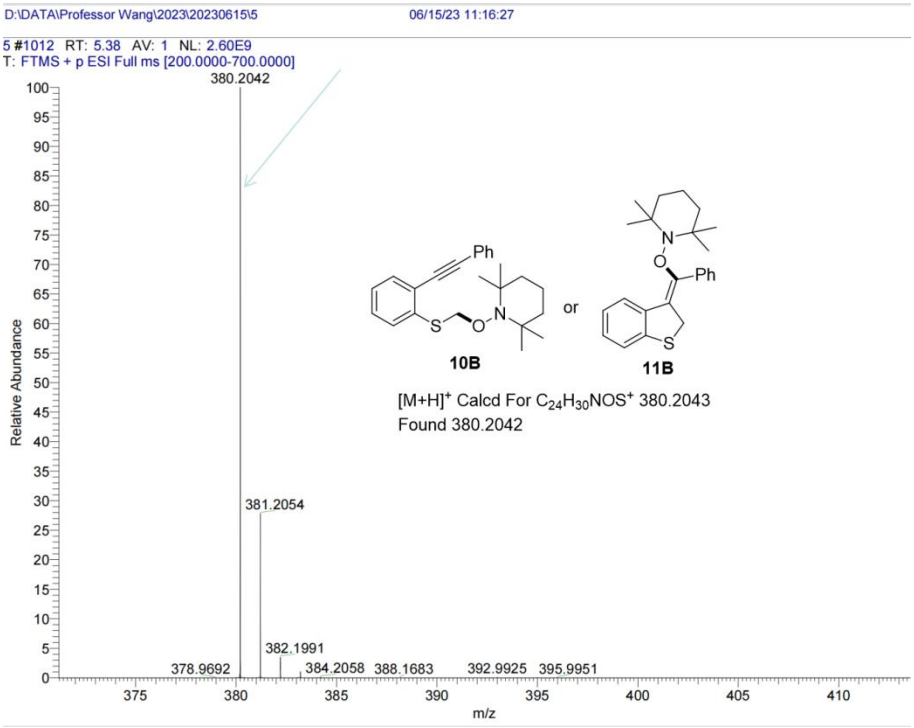
当在模型反应中加入 2 倍当量的自由基淬灭剂 TEMPO 时，分子内环化氧化反应被完全抑制（Scheme 3-19）。但是分离出了 TEMPO 和 S-α-C(sp_3)自由基的加合物（**10B**），其相应的表征数据如（Scheme 3-20）。此外，对反应混合物的 HRMS 分析检测了带有 TEMPO 自由基中间体（**10B**, **11B**, **12B**）的加合物（Scheme 3-21），并对反应中间体（**13B**）进行了 HRMS 分析（Scheme 3-22）。这些结果表明，自由基和分子内环化途径可能参与了这种转化。



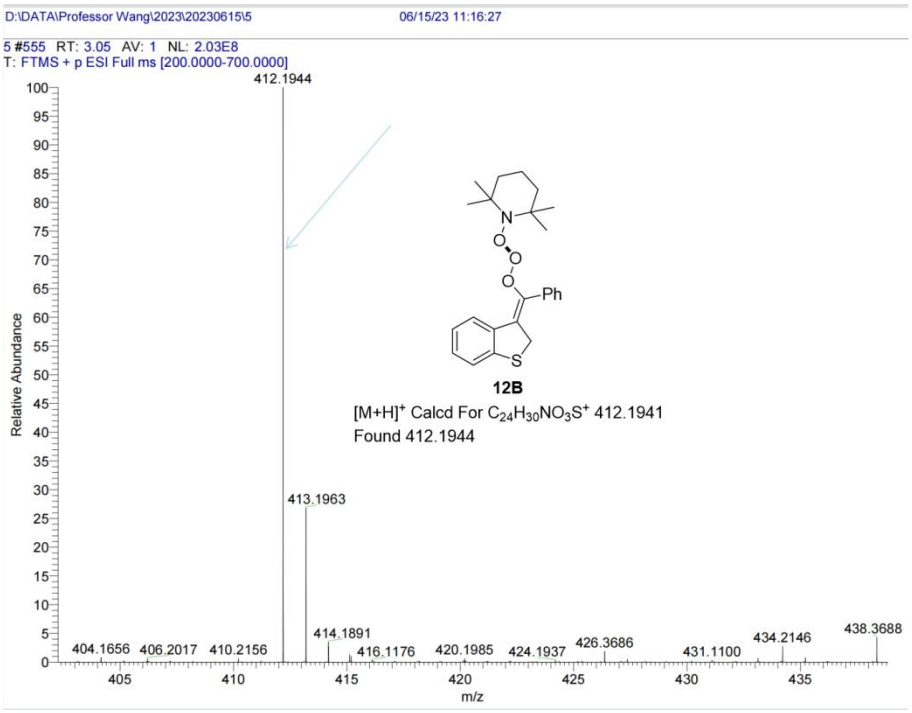
2,2,6,6-Tetramethyl-1-(((2-(phenylethynyl)phenyl)thio)methoxy)piperidine (**10B**). Pale yellow solid; 43% yield (32.6 mg): m.p. 84–86 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.8 Hz, 1H), 7.57–7.55 (m, 2H), 7.49 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.36–7.32 (m, 3H), 7.29 (td, *J* = 7.8, 1.2 Hz, 1H), 7.18–7.16 (m, 1H), 5.19 (s, 2H), 1.59–1.52 (m, 1H), 1.46–1.42 (m, 4H), 1.33–1.31 (m, 1H), 1.20 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.0, 132.4, 131.8, 129.1, 128.9, 128.5, 128.4, 125.9, 123.3, 123.2, 95.3, 87.5, 79.3, 60.1, 39.7, 33.5, 20.3, 17.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{24}H_{30}NOS^+$ 380.2043; Found 3380.2042.



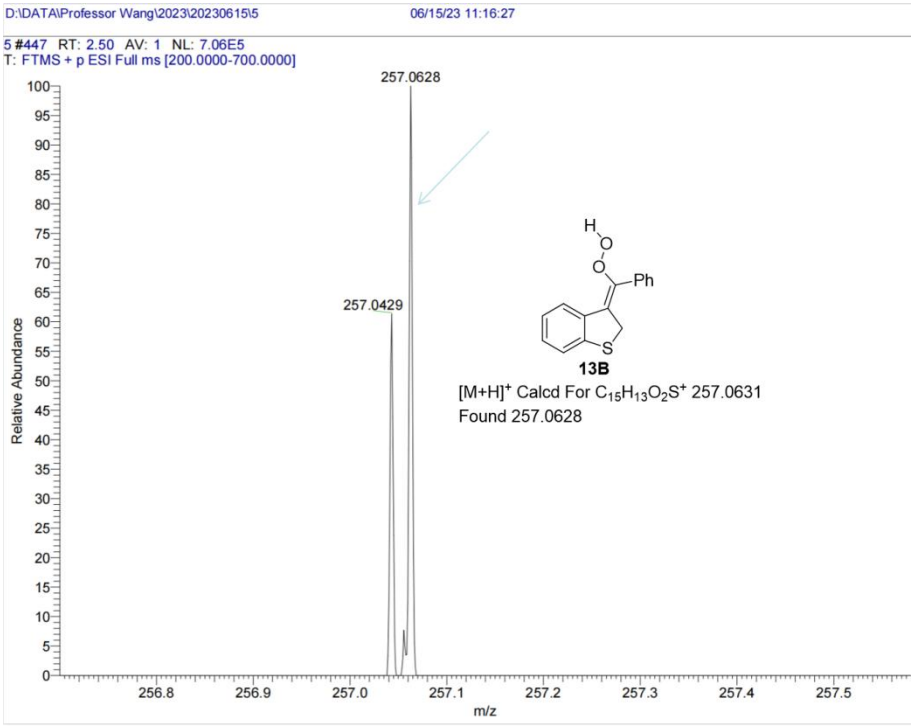




Scheme 3-20 10B 的结构表征



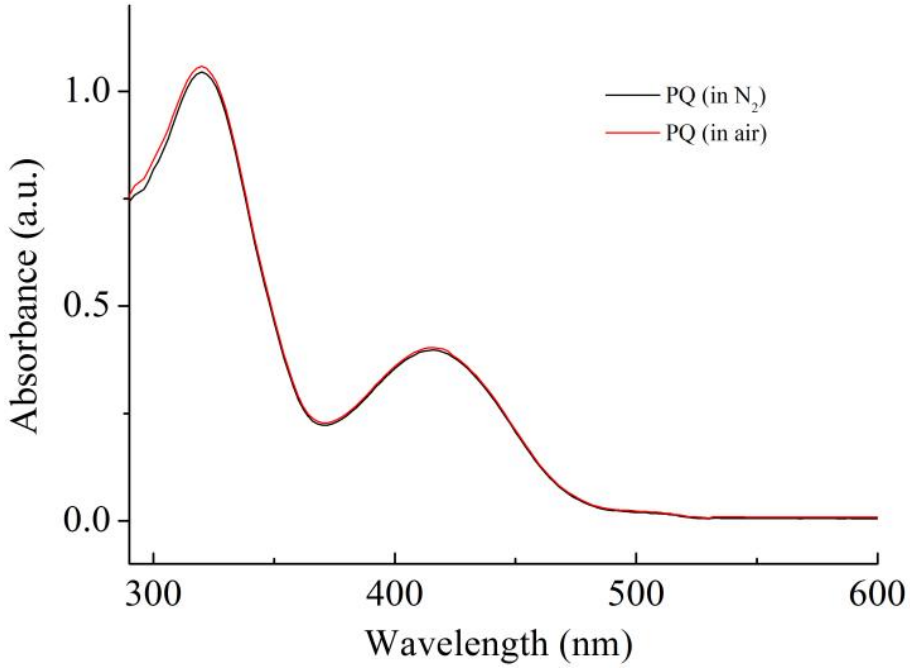
Scheme 3-21 12B 的高分辨质谱



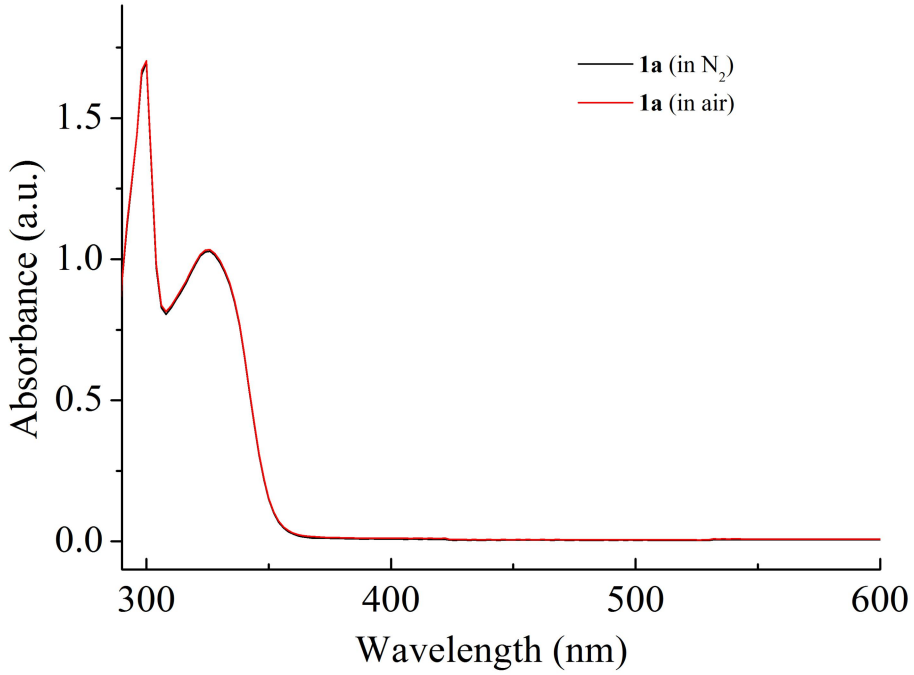
Scheme 3-22 13B 的高分辨质谱

3.5.2 紫外吸收光谱

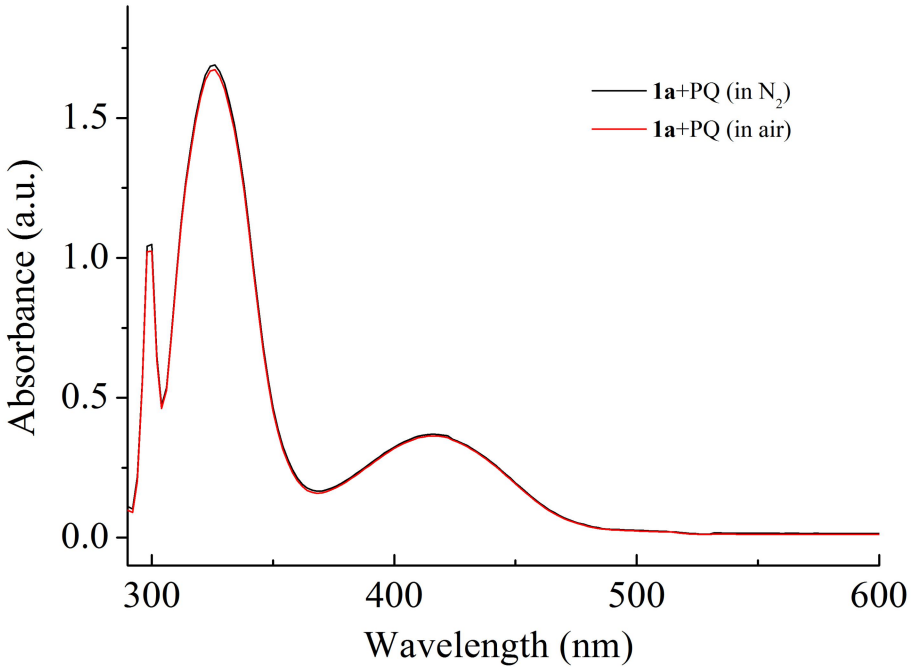
用 U-4100 紫外可见分光光度计记录了 PQ（$1*10^{-3}$M）、**1a**（$5*10^{-4}$M）和 PQ（$1*10^{-3}$M） + **1a**（$5*10^{-4}$M）在氮气或空气气氛下对氯苯的紫外/可见吸收光谱。PQ 在氮气或空气气氛下的吸收光谱在 330 和 416 nm 处有最大值，吸收范围从 250 nm 到 525 nm，如（Scheme 3-23）所示，这与实验中使用的 LED 的波长（415 nm）是一致的。在氮气或空气气氛下，**1a** 的吸收光谱在 330 nm 和 416 nm 处有最大值，吸收范围从 280 nm 到 340 nm，如（Scheme 3-24）所示。在氮气或空气气氛下，**1a** + PQ 的吸收光谱在 300、330 和 416 nm 处有最大值，吸收范围从 280 nm 到 525 nm，如图（Scheme 3-25）所示。重叠吸收光谱如（Scheme 3-26）和（Scheme 3-27）所示。



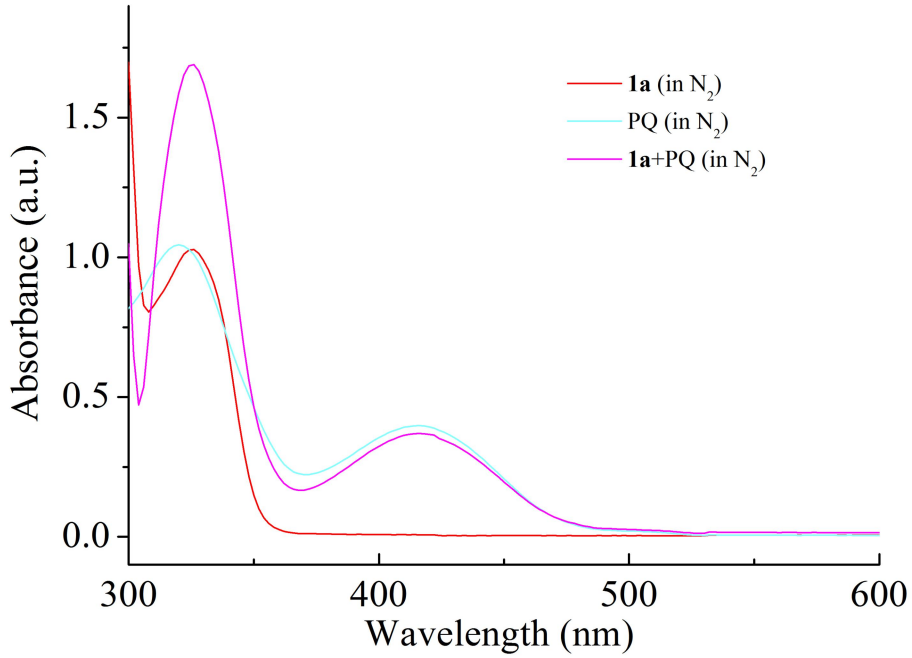
Scheme 3-23 PQ 溶于氯苯在空气或氮气气氛下的紫外吸收光谱



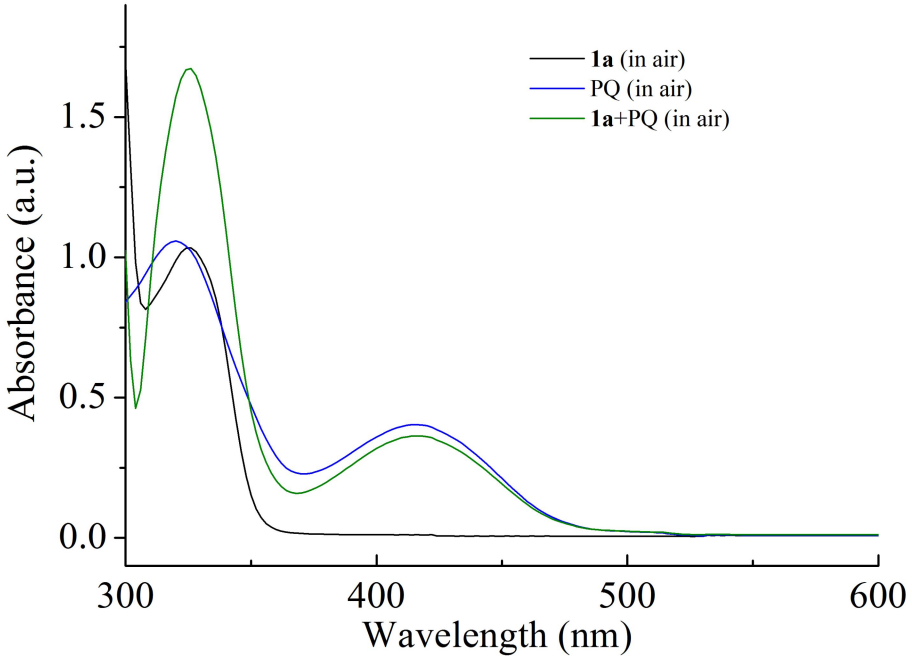
Scheme 3-24 1a 溶于氯苯在空气或氮气气氛下的紫外吸收光谱



Scheme 3-25 1a 和 PQ 溶于氯苯在空气或氮气气氛下的紫外吸收光谱

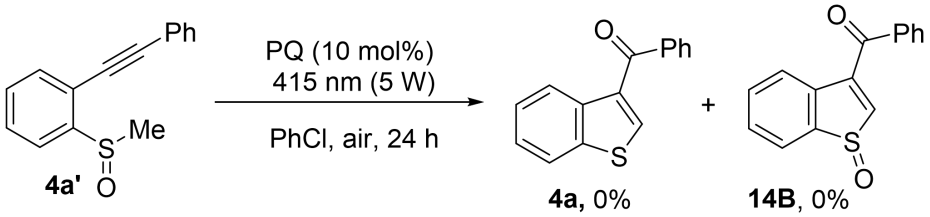


Scheme 3-26 1a，PQ 和 **1a**+PQ 溶于氯苯在氮气气氛下的紫外吸收光谱



Scheme 3-27 1a，PQ 和 **1a**+PQ 溶于氯苯在空气气氛下的紫外吸收光谱

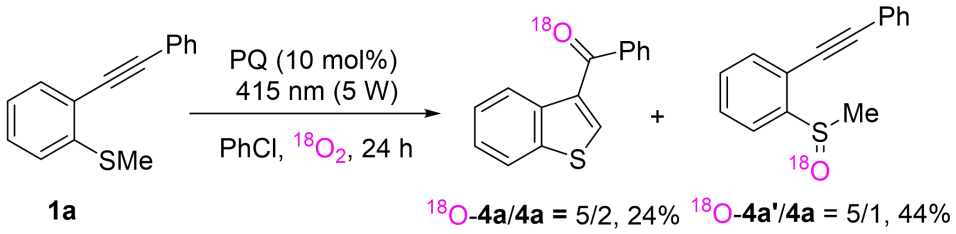
3.5.3 反应中间体验证实验



Scheme 3-28 反应中间体验证实验

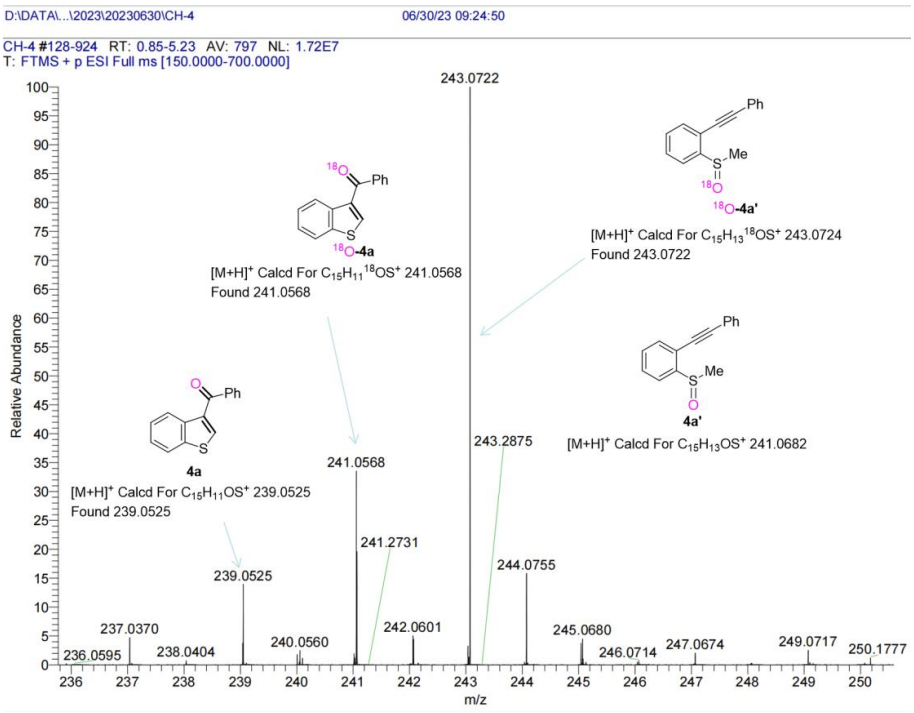
此外，当 1-（甲基亚砜基）-2-（苯乙基）苯（**4a'**）在标准条件下反应时，没有得到期望的产物 **4a** 或 **14B**（Scheme 3-28）。这一结果排除了 **4a'**作为转化中间产物的可能性。

3.5.4 同位素（^{18}O）标记实验

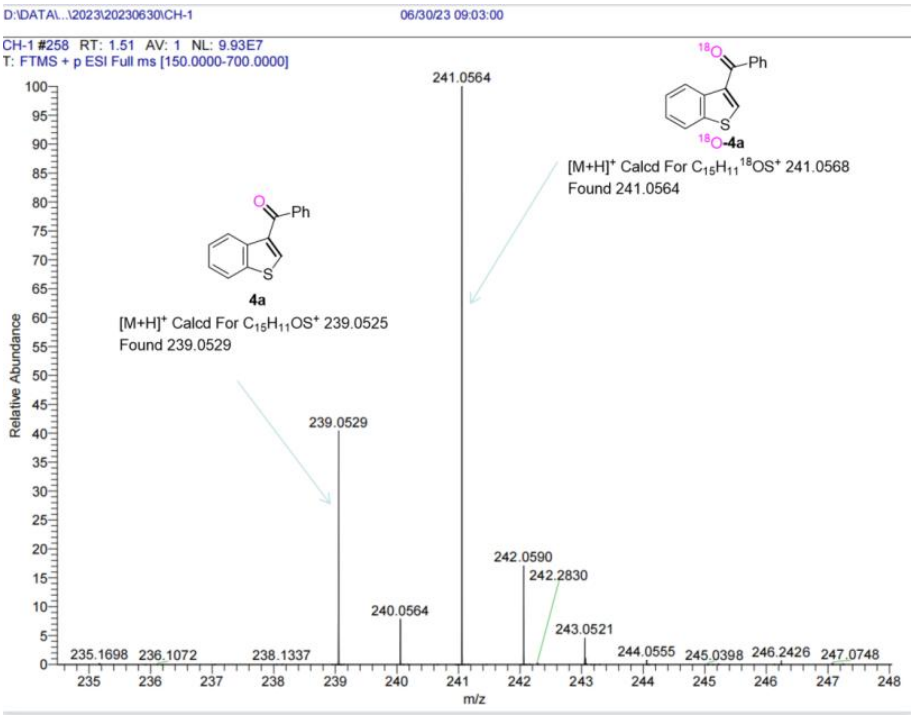


Scheme 3-29 ^{18}O 标记实验

在装有磁力搅拌棒的 25 mL 反应容器中，加入邻炔基苯甲硫醚（**1a**, 224.3 mg, 1.0 mmol）PQ（20.8 mg, 10 mol%）和氯苯（5.0 mL）。反应混合物在室温和 ^{18}O（氧气球）气氛条件下暴露在 415 nm（5 W）蓝色 LED 照射反应 24 h。反应完成后，溶剂被旋转蒸发仪直接除去，用乙酸乙酯和石油醚为洗脱剂（1:100-1:5,V / V）柱层析法分离得到黄色油状的物质 **4a**-^{18}O（57.7 mg, 24% yield, ^{18}O-**4a**/**4a** = 5:2）和黄色油状物质 ^{18}O-**4a'**（106.6 mg, 44% yield, ^{18}O-**2a'**/**2a'** = 5:1）并且通过 HRMS 进行了分析（Scheme 3-30,3-31）。结果表明 **4a** 中的氧原子来自于空气中的 O_2。

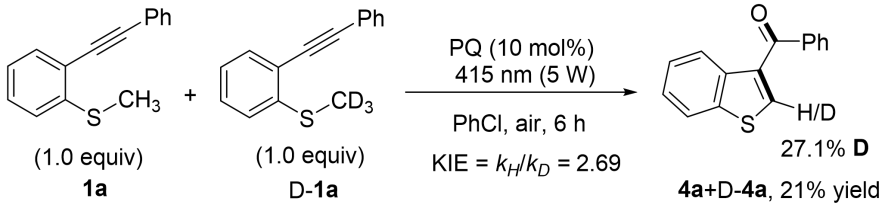


Scheme 3-30 反应混合物的高分辨质谱



Scheme 3-31 ^{18}O-**4a** 和 **4a** 的高分辨质谱

3.5.5 动力学同位素实验

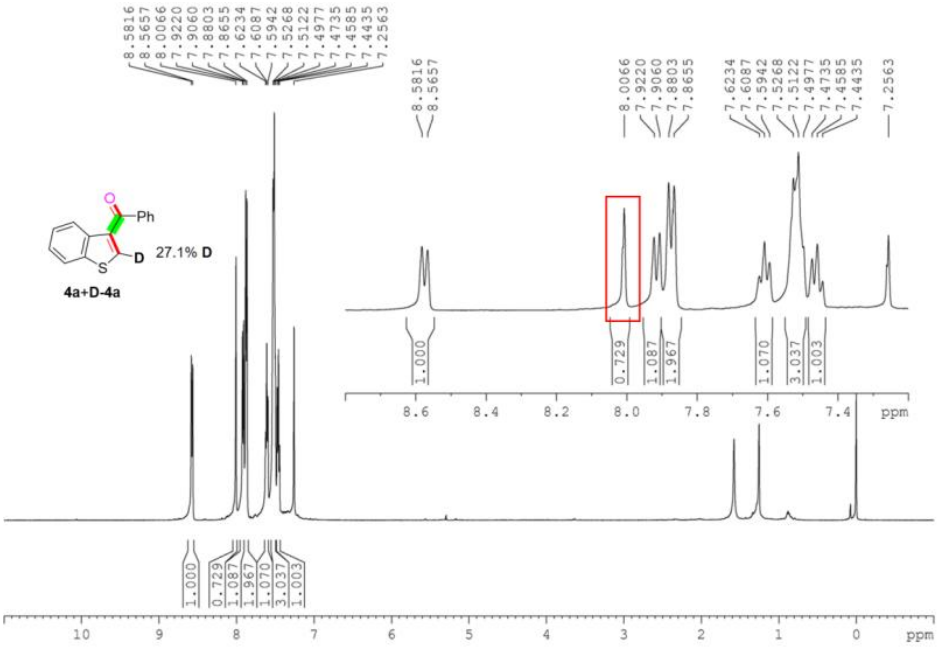


Scheme 3-32 动力学同位素实验

为了进一步了解分子间氢原子转移步骤是否为限制步骤（TLS），研究了该环化氧化反应的动力学同位素效应（KIE）（Scheme 3-32）。

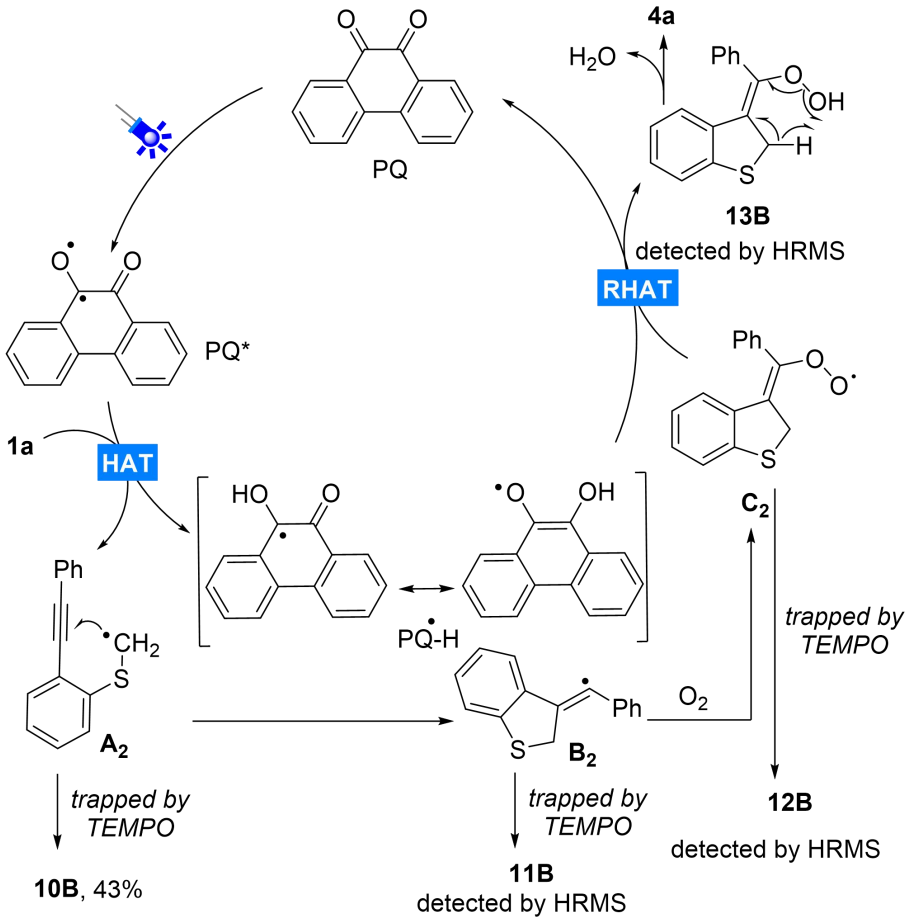
一个装有磁力搅拌棒的 25 mL 烘箱干燥反应容器，加入邻炔基苯甲硫醚（**1a**, 22.4 mg, 0.1 mmol）、氘代邻炔基苯甲硫醚（D-**1a**, 22.7 mg, 0.1 mmol）、PQ（4.2 mg, 10 mol%）和 PhCl（2.0 mL）。反应混合物在室温和空气气氛下，用蓝色 LED（415 nm, 5 W）照射反应 6 h，得到黄色油状物质 **4a** 和 D-**4a**（10.0 mg，产率为 21%）。竞争性 KIE 实验显示，氘化底物 D-**1a** 与 **1a** 的主要 KIE 值为 2.69（Scheme 3-33），表明氢原子转移是决定速率的步骤[128]。

(Benzo[*b*]thiophen-3-yl-2-*d*)(phenyl)methanone (D-**4a**/**4a** = 27.1/72.9). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 0.73H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.62–7.59 (m, 1H), 7.53–7.49 (m, 3H), 7.47–7.44 (m,1H).



Scheme 3-33 4a 和 D-4a 的核磁氢谱表征

3.5.6 可能的反应机理



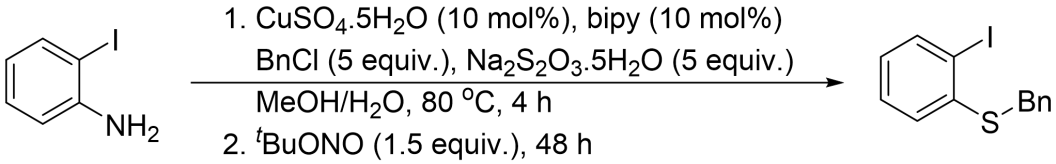
Scheme 3-34 可能的反应机理

根据对照实验和前人的报道[130]，提出了一种由自由基介导的环化反应机理（Scheme 3-34）。首先，**PQ** 光照变成激发态 **PQ***， **PQ***与 **1a** 发生氢原子转移（HAT）生成 S-α-烷基自由基 **A_2**，该烷基自由基在分子内加成到 C-C 三键生成乙烯基自由基 **B_2**，中间体 **B_2** 被分子氧捕获，生成超氧自由基 **C_2**，并通过反向 HAT 再生 **PQ**，同时生成中间体 **13B**。最后分子内脱水，得到所需的产物 **4a**。

3.6 实验部分

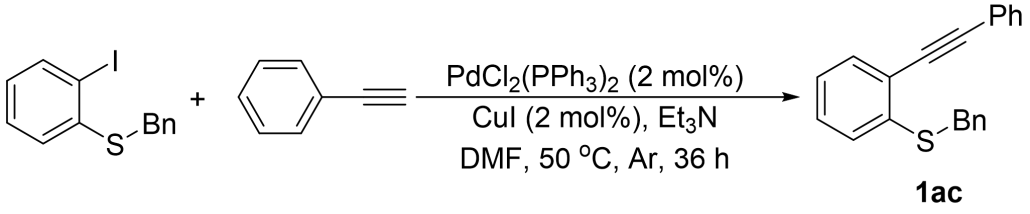
3.6.1 2-炔苯基苯苄基硫醚（1ac）的制备

方式 A：



Scheme 3-35 2-碘苯硫苄基醚制备

在 250 mL 圆底烧瓶中，加入 $Na_2S_2O_3·5H_2O$（12.4095 g, 50 mmol, 5 equiv.），苄基氯（6.3292 g, 50 mmol, 5 equiv.），$CuSO_4·5H_2O$（247.7 mg, 10 mol%），联吡啶 （156.2 mg, 10 mol%），MeOH/H_2O（50 mL/70 mL），在 80 ℃油浴中搅拌反应 4 h，再加入 2-碘苯胺（2.1902 g, 10 mmol），^{t}BuONO（1.5468 g, 15 mmol, 1.5 equiv.），然后再室温下继续搅拌 48 h，用 PLC 板跟踪反应发现邻碘苯胺消耗完全，停止反应。用乙酸乙酯萃取。干燥、过滤、真空浓缩。所得粗产物以石油醚为洗脱剂，在硅胶上用快速柱色谱法纯化，得到相应的产品邻碘苯苄基硫醚，为淡黄色固体（1.9572 g, 产率 60%）。

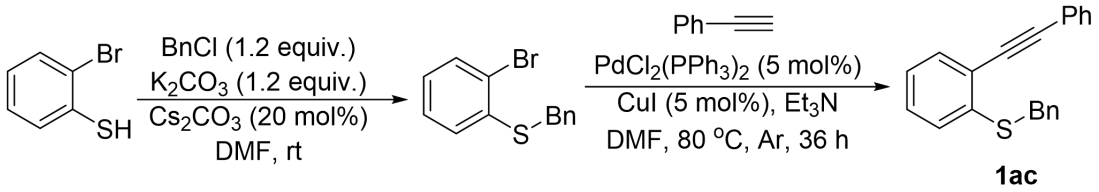


Scheme 3-36 2-炔苯基苯硫苄基醚制备

将邻碘苯苄基硫醚（1.6310 g, 5.0 mmol）和苯乙炔（0.7660 g, 7.5 mmol, 1.5 equiv.）溶于 5 mL DMF 溶液中，加入 $PdCl_2(PPh_3)_2$（70.2 mg, 2 mol%），CuI（19.1 mg, 2 mol%）和 Et_3N（20 mL）。在氩气气氛下，反应混合物在 50℃的油浴中剧烈搅拌反应 36 h。PLC 板跟踪显示邻碘苯苄基硫醚消耗完全。用水和乙酸乙酯萃取，用 Na_2SO_4 干燥，过滤，减压浓缩。以石油醚为洗脱液，在硅胶上用闪蒸色

谱法纯化残渣，得到 2-炔基苯苄基硫醚（**1ac**）为淡黄色固体（1.0064 g, 产率 67%）。

方式 B:

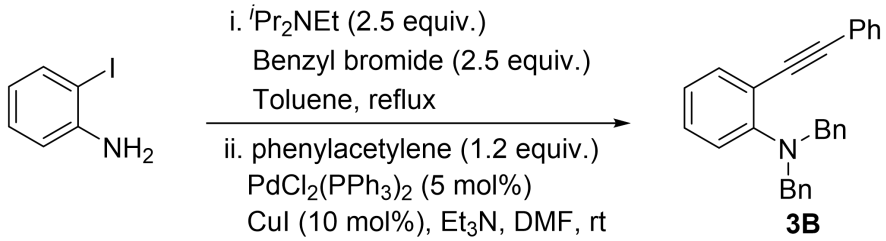


Scheme 3-37 2-炔苯基苯硫苄基醚制备

2-溴苯硫醇（3.7814 g, 20.0 mmol）和苄基氯（3.0379 g, 24.0 mmol, 1.2 equiv.）溶解在 30 mL DMF 中，加入 K_2CO_3（3.3169 g, 24.0 mmol, 1.2 equiv.）和 Cs_2CO_3（1.3033 g, 4 mmol, 20 mmol%）。将反应混合物在室温下剧烈搅拌 12 h，反应完成后用水（50 mL）稀释，然后用乙酸乙酯（3*50 mL）萃取，有机层用无水 Na_2SO_4 干燥，过滤，减压浓缩。以石油醚为洗脱液，在硅胶上用闪蒸色谱法纯化，得到邻溴苯苄基硫醚为白色固体（4.4671 g, 收率 80%）。

将邻溴苯苄基硫醚（2.7920 g, 10.0 mmol）和苯乙炔（1.5320 g, 15.0 mmol, 1.5 equiv.）溶解在 DMF（10 mL）溶液中，加入 $PdCl_2(PPh_3)_2$（351.0 mg, 5 mol%）、CuI（95.2 mg, 5 mol%）和 Et_3N（20 mL）。在氩气气氛下，反应混合物在 80℃的油浴中搅拌反应 36 h。完成后用水（50 mL）稀释，再用乙酸乙酯（3*50 mL）萃取，有机层用无水 Na_2SO_4 干燥，过滤，减压蒸发。以石油醚为洗脱液，在硅胶上用闪蒸色谱法纯化残渣，得到相应的产物 2-炔基苯苄基硫醚（**1ac**），为淡黄色固体（1.1116 g, 产率 37%）。

3.6.2 2-氮, 氮-二苄基-2-（苯乙基)苯胺（3B）的制备

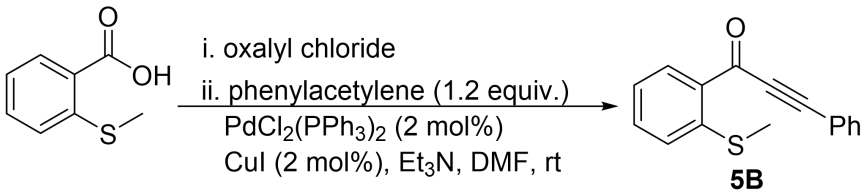


Scheme 3-38 2-炔苯基-氮，氮-二苄基苯胺制备

在 2-碘苯胺（2.1903 g, 10 mmol）的甲苯搅拌溶液中，加入 $^iPr_2NEt$（4.2 mL）和苄基溴（4.2759 g, 25 mmol, 2.5 equiv.），在氩气气氛下回流反应 72 h，反应完成后，过滤掉白色固体沉淀剂，真空除去溶剂得到粗产物，然后将粗产物溶解于 Et_3N（20 mL）和 DMF（5 mL）中。随后，加入 $PdCl_2(PPh_3)_2$（351.0 mg, 5 mol%）、

CuI（190.5 mg, 10 mol%）和苯乙炔（1.2256 g, 12.0 mmol, 1.2 equiv.），在氩气气氛下搅拌反应混合物过夜，然后旋转蒸发除去溶剂。残渣用水（50 mL）稀释，乙酸乙酯（3*50 mL）萃取，有机层在无水 Na_2SO_4 上干燥，真空浓缩，柱层析纯化（石油醚），得到氮，氮-二苄基-2-（苯乙基）苯胺（**3B**）为黄色油状（2.5398 g，产率 70%）。

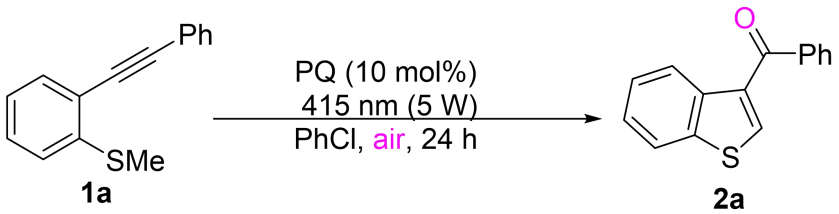
3.6.3 2-甲基硫代苯甲酰乙炔苯（5B）的制备



Scheme 3-39 2-甲基硫代苯甲酰乙炔苯制备

称取 2-（甲基硫代苯甲酸（1.6821g, 10 mmol），溶解在无水 CH_2Cl_2（20 mL）中，加入草酰二氯（1.3 mL）和 DMF（3 滴）。在室温下，反应混合物搅拌 4 h，然后旋转蒸发除去 CH_2Cl_2。在残渣中加入 $PdCl_2(PPh_3)_2$（140.4 mg, 2 mol%）、CuI（38.1 mg, 2 mol%）、Et_3N（20 mL）和 DMF（5 mL）。然后，在手套箱中，将反应体系充入氩气保护，用注射器加入苯乙炔（1.2256 g, 12.0 mmol, 1.2 equiv.）反应混合物在室温下反应 24 h。然后用水和乙酸乙酯萃取，干燥，真空浓缩。以乙酸乙酯/石油醚（1:20, V/V）为洗脱液柱层析纯化，得到 2-甲基硫代苯甲酰乙炔苯（**5B**）为棕色固体（1.7663 g，产率 70%）。

3.6.4 3-酰基苯并噻吩（4a）制备的一般步骤

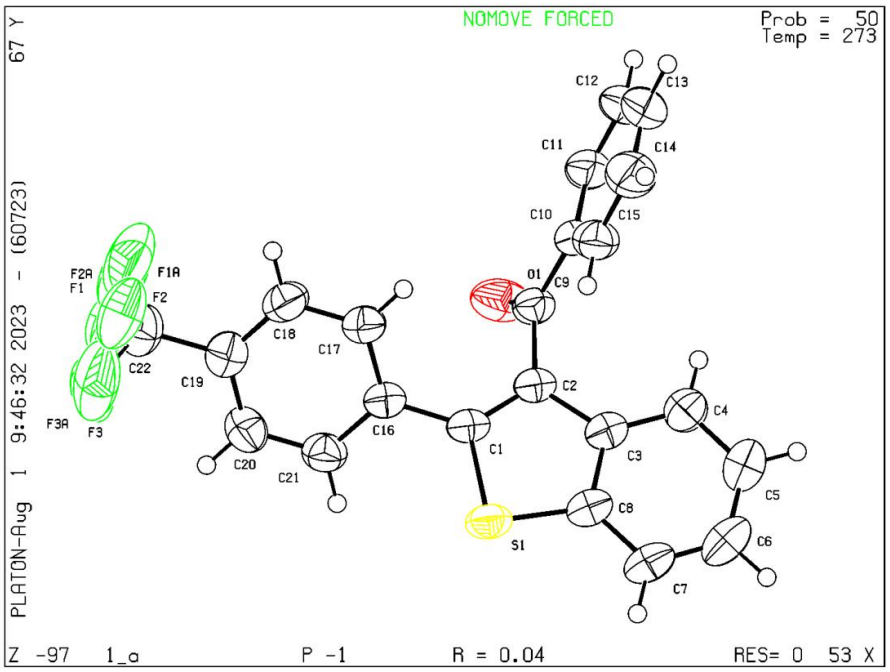


Scheme 3-40 分子内氧化环化合成酰基苯并噻吩

在一个装有磁子的 25 mL 干燥的反应管中加入 2-炔苯基苯甲硫醚（**1a**, 44.9 mg, 0.2 mmol）、9, 10-苯醌（4.2 mg, 10 mol%）和氯苯（2.0 mL）。反应混合物在室温和空气条件下，用蓝色 LED（415 nm, 5 W）照射反应 24 h。反应完成后，溶剂直接用旋转蒸发仪除去，残渣在硅胶上以乙酸乙酯/石油醚（1:100, V/V）为洗脱液进行柱层析纯化，得到所需产品 **2a** 为黄色油状（39.1 mg，产率 82%）。

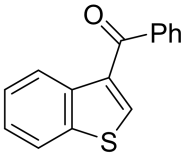
3.7 产物的表征数据

3.7.1 产物 **4ah** 的 X 射线单晶数据（CCDC: 2286087）

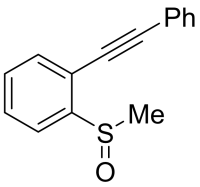


Scheme 3-41 4ah 的 X 射线单晶图

3.7.2 产物的核磁和高分辨质谱数据

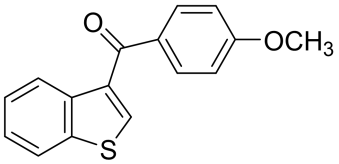


Benzo[*b*]thiophen-3-yl(phenyl)methanone (4a). Yellow oil; 82% yield (39.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.87–7.85 (m, 2H), 7.60 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.52–7.49 (m, 3H), 7.46–7.43 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.0, 140.2, 139.4, 138.4, 137.6, 134.9, 132.5, 129.6, 128.6, 125.8, 125.7, 125.3, 122.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{11}OS^+$ 239.0525; Found 239.0526.

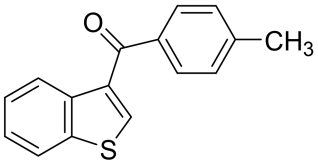


1-(Methylsulfinyl)-2-(phenylethynyl)benzene (4a'). Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.8 Hz, 1H), 7.60–7.56 (m, 2H), 7.54–7.52 (m, 2H), 7.47 (td, *J* = 7.8, 1.2 Hz, 1H), 7.39–7.38 (m, 3H), 2.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ

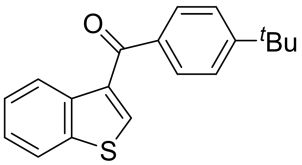
= 147.1, 132.5, 131.6, 130.5, 129.6, 129.3, 128.7, 123.4, 122.0, 119.4, 98.1, 84.2, 42.1.



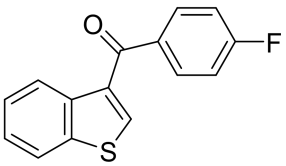
Benzo[*b*]thiophen-3-yl(4-methoxyphenyl)methanone (4b). Pale yellow solid; 73% yield (39.2 mg): m.p. 117–119 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 7.8 Hz, 1H), 7.95 (s, 1H), 7.91–7.90 (m, 3H), 7.50–7.48 (m, 1H), 7.45–7.43 (m, 1H), 7.01–6.98 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.8, 163.4, 140.2, 137.8, 136.4, 135.4, 132.1, 131.9, 125.60, 125.57, 125.1, 122.5, 113.9, 55.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{13}O_2S^+$ 269.0631; Found 269.0630.



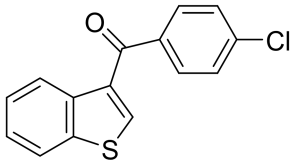
Benzo[*b*]thiophen-3-yl(*p*-tolyl)methanone (4c). White solid; 78% yield (39.4 mg): m.p. 110–112 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 7.8 Hz, 1H), 7.96 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.51–7.48 (m, 1H), 7.45–7.42 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.8, 143.3, 140.2, 137.7, 137.5, 136.6, 135.1, 129.9, 129.3, 125.7, 125.6, 125.2, 122.4, 21.8.



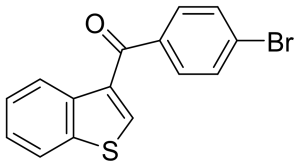
Benzo[*b*]thiophen-3-yl(4-(*tert*-butyl)phenyl)methanone (4d). Pale yellow solid; 77% yield (45.3 mg): m.p. 107–108 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.83–7.82 (m, 2H), 7.52–7.51 (m, 2H), 7.50–7.49 (m, 1H), 7.45–7.42 (m, 1H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.7, 156.2, 140.2, 137.8, 137.7, 136.6, 135.1, 129.7, 125.7, 125.6, 125.5, 125.3, 122.4, 35.2, 31.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{19}OS^+$ 295.1151; Found 295.1151.



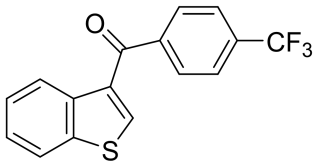
Benzo[*b*]thiophen-3-yl(4-fluorophenyl)methanone (4e). Pale yellow solid; 77% yield (39.5 mg): m.p. 85–87 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 7.8 Hz, 1H), 7.98 (s, 1H), 7.93–7.90 (m, 3H), 7.53–7.51 (m, 1H), 7.48–7.45 (m, 1H), 7.19 (t, *J* = 8.4 Hz, 2H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −106.1; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.5, 165.5 (d, *J* = 252.5 Hz), 140.2, 137.8, 137.5, 135.6, 134.9, 132.2 (d, *J* = 8.8 Hz), 125.8 (d, *J* = 7.5 Hz), 125.2 (**2**), 122.5, 115.8 (d, *J* = 21.7 Hz); HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}FOS^+$ 257.0431; Found 257.0429.



Benzo[*b*]thiophen-3-yl(4-chlorophenyl)methanone (4f). Pale yellow solid; 88% yield (48.0 mg): m.p. 100–101 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 7.8 Hz, 1H), 7.85 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.71–7.69 (m, 2H), 7.42–7.39 (m, 1H), 7.38–7.33 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.6, 140.1, 138.8, 138.2, 137.6, 137.4, 134.6, 131.0, 128.9, 125.9, 125.8, 125.2, 122.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}ClOS^+$ 273.0135; Found 273.0135.

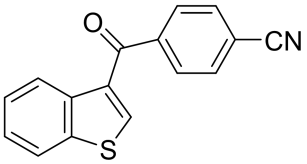


Benzo[*b*]thiophen-3-yl(4-bromophenyl)methanone (4g). White solid; 90% yield (57.1 mg): m.p. 88–89 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 7.8 Hz, 1H), 7.97 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.74–7.72 (m, 2H), 7.65–7.63 (m, 2H), 7.52–7.50 (m, 1H), 7.47–7.44 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.8, 140.2, 138.4, 138.1, 137.4, 134.6, 131.9, 131.1, 127.5, 125.9, 125.8, 125.2, 122.5.

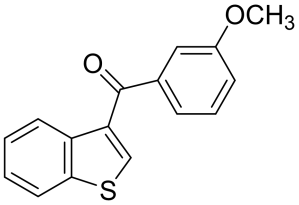


Benzo[*b*]thiophen-3-yl(4-(trifluoromethyl)phenyl)methanone (4h). Pale yellow solid; 76% yield (46.6 mg): m.p. 84–85 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.56–7.53 (m, 1H), 7.49–7.47 (m, 1H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −63.0; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.7, 142.6, 140.2, 139.5, 137.2, 134.4, 133.8 (q, *J* = 32.5 Hz), 129.7, 126.1, 126.0, 125.7 (q, *J* = 3.9 Hz), 125.4,

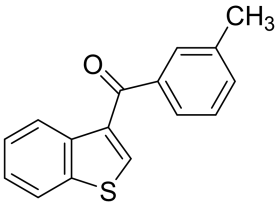
123.8 (q, *J* = 271.3 Hz), 122.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{10}F_3OS^+$ 307.0399; Found 307.0396.



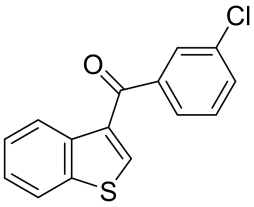
4-(Benzo[*b*]thiophene-3-carbonyl)benzonitrile (4i). White solid; 71% yield (37.4 mg): m.p. 134–135 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.94–7.92 (m, 3H), 7.82–7.81 (m, 2H), 7.56–7.54 (m, 1H), 7.50–7.48 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.1, 143.0, 140.2, 139.7, 137.1, 134.1, 132.5, 129.9, 126.2, 126.1, 125.3, 122.6, 118.1, 115.7; HRMS (ESI) m/z: $[M+3H]^+$ Calcd For $C_{16}H_{12}NOS^+$ 266.06341; Found 264.06323.



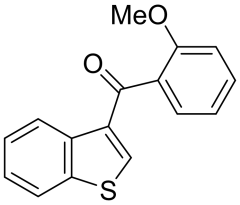
Benzo[*b*]thiophen-3-yl(3-methoxyphenyl)methanone (4j). Pale yellow oil; 59% yield (31.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 7.8 Hz, 1H), 8.02 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.53–7.50 (m, 1H), 7.46–7.44 (m, 1H), 7.43–7.38 (m, 3H), 7.15–7.13 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.7, 159.8, 140.7, 140.2, 138.4, 137.5, 134.9, 129.5, 125.8, 125.7, 125.3, 122.5, 122.3, 118.8, 114.1, 55.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{13}O_2S^+$ 269.0631; Found 269.0632.



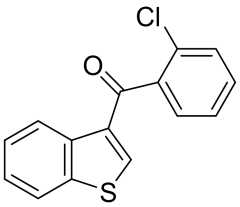
Benzo[*b*]thiophen-3-yl(*m*-tolyl)methanone (4k). Pale yellow oil; 68% yield (34.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.68 (s, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.52–7.49 (m, 1H), 7.45–7.43 (m, 1H), 7.41–7.36 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.2, 140.1, 139.4, 138.5, 138.2, 137.6, 135.1, 133.2, 130.0, 128.4, 126.9, 125.8, 125.7, 125.3, 122.4, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{13}OS^+$ 253.0682; Found 253.0681.



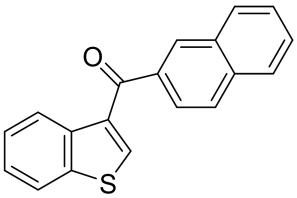
Benzo[*b*]thiophen-3-yl(3-chlorophenyl)methanone (4l). White solid; 75% yield (40.9 mg): m.p. 101–102 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 1.8 Hz, 1H), 7.72 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.57–7.56 (m, 1H), 7.53–7.51 (m, 1H), 7.47–7.42 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.4, 141.0, 140.2, 139.0, 137.3, 134.8, 134.4, 132.4, 129.9, 129.5, 127.7, 126.0, 125.9, 125.3, 122.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}ClOS^+$ 273.0135; Found 273.0136.



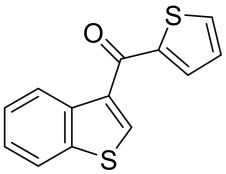
Benzo[*b*]thiophen-3-yl(2-methoxyphenyl)methanone (4m). Pale yellow oil; 52% yield (27.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.53–7.50 (m, 1H), 7.48–7.45 (m, 1H), 7.44–7.42 (m, 1H), 7.40 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.05–7.03 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.7, 157.2, 140.8, 140.2, 136.9, 136.1, 131.8, 130.2, 129.4, 125.9, 125.7, 125.6, 122.4, 120.5, 111.7, 55.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{13}O_2S^+$ 269.0631; Found 269.0631.



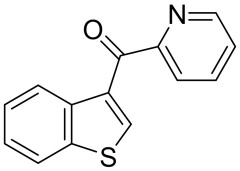
Benzo[*b*]thiophen-3-yl(2-chlorophenyl)methanone (4n). Pale yellow solid; 67% yield (36.5 mg): m.p. 82–84 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.56–7.54 (m, 1H), 7.48–7.46 (m, 2H), 7.45–7.42 (m, 2H), 7.37 (td, *J* = 7.2, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.5, 142.0, 140.3, 139.7, 136.6, 135.1, 131.3, 131.2, 130.3, 129.0, 126.8, 126.2, 125.9, 125.7, 122.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}ClOS^+$ 273.0135; Found 273.0135.



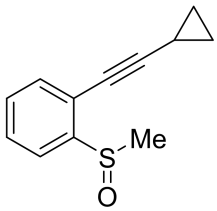
Benzo[*b*]thiophen-3-yl(naphthalen-2-yl)methanone (4o). Pale yellow solid; 69% yield (39.8 mg): m.p. 116–117 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 7.8 Hz, 1H), 8.35 (s, 1H), 8.04 (s, 1H), 7.99–7.98 (m, 1H), 7.97–7.95 (m, 1H), 7.94–7.91 (m, 3H), 7.63–7.60 (m, 1H), 7.57–7.55 (m, 1H), 7.53–7.51 (m, 1H), 7.48–7.45 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.0, 140.2, 138.1, 137.7, 136.6, 135.4, 135.2, 132.5, 131.2, 129.5, 128.6, 128.4, 128.0, 127.0, 125.8, 125.7, 125.6, 125.3, 122.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{13}OS^+$ 289.0682; Found 289.0682.



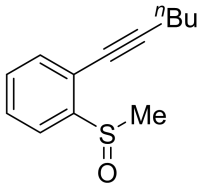
Benzo[*b*]thiophen-3-yl(thiophen-2-yl)methanone (4p). Pale yellow oil; 68% yield (33.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.19 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.72 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.50–7.48 (m, 1H), 7.45–7.43 (m, 1H), 7.18–7.17 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 182.2, 144.8, 140.1, 137.4, 135.8, 135.0, 134.0, 133.8, 128.1, 125.8, 125.7, 125.0, 122.5.



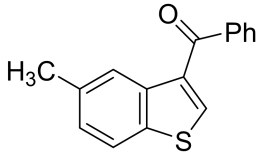
Benzo[*b*]thiophen-3-yl(pyridin-2-yl)methanone (4q). Pale yellow solid; 56% yield (26.8 mg): m.p. 73–75 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.11 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.74 (d, *J* = 4.2 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.91 (td, *J* = 7.8, 1.2 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.54–7.51 (m, 1H), 7.50–7.48 (m, 1H), 7.45–7.42 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.9, 156.1, 148.5, 142.7, 139.4, 138.1, 137.3, 132.7, 126.3, 125.9, 125.6, 125.4, 124.5, 122.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{14}H_{10}NOS^+$ 240.0478; Found 240.0477.



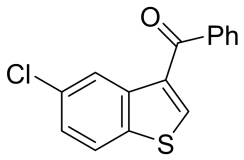
1-(Cyclopropylethynyl)-2-(methylsulfinyl)benzene (4r'). Colourless oil; 44% yield (18.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.8 Hz, 1H), 7.53–7.50 (m, 1H), 7.41–7.38 (m, 2H), 2.81 (s, 3H), 1.52–1.47 (m, 1H), 0.97–0.92 (m, 2H), 0.87–0.81 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.1, 132.6, 130.3, 128.8, 123.2, 120.2, 103.1, 71.1, 42.0, 9.1, 8.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{12}H_{13}OS^+$ 205.0682; Found 205.0683.



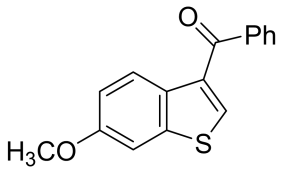
1-(Hex-1-yn-1-yl)-2-(methylsulfinyl)benzene (4s'). Yellow oil; 46% yield (20.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.54–7.51 (m, 1H), 7.44–7.42 (m, 1H), 7.41–7.39 (m, 1H), 2.82 (s, 3H), 2.47 (t, *J* = 7.2 Hz, 2H), 1.64–1.59 (m, 2H), 1.53–1.47 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.1, 132.6, 130.4, 128.9, 123.2, 120.3, 100.0, 76.1, 42.1, 30.6, 22.1, 19.3, 13.7.



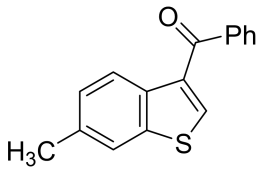
(5-Methylbenzo[*b*]thiophen-3-yl)(phenyl)methanone (4t). Pale yellow oil; 69% yield (34.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 7.95 (s, 1H), 7.86–7.85 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.59 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.51–7.48 (m, 2H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.1, 139.5, 138.6, 137.8, 137.4, 135.8, 134.6, 132.4, 129.6, 128.5, 127.5, 125.1, 122.0, 21.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{13}OS^+$ 253.0682; Found 253.0680.



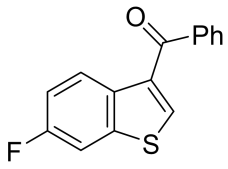
(5-Chlorobenzo[*b*]thiophen-3-yl)(phenyl)methanone (4u). Pale yellow solid; 63% yield (34.4 mg): m.p. 72–74 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 1.8 Hz, 1H), 8.04 (s, 1H), 7.86–7.84 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.61 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.53–7.50 (m, 2H), 7.42 (dd, *J* = 8.4, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.6, 139.8, 139.1, 138.8, 138.2, 134.3, 132.7, 132.5, 129.6, 128.7, 126.4, 125.1, 123.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}ClOS^+$ 273.0135; Found 273.0135.



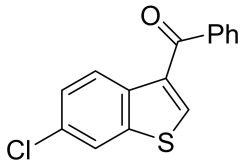
(6-Methoxybenzo[*b*]thiophen-3-yl)(phenyl)methanone (4v). Pale yellow oil; 74% yield (39.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.83 (s, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.13 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.0, 158.3, 141.7, 139.5, 136.2, 134.6, 132.4, 131.5, 129.6, 128.5, 126.0, 115.6, 104.9, 55.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{13}O_2S^+$ 269.0631; Found 269.0629.



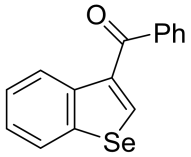
(6-Methylbenzo[*b*]thiophen-3-yl)(phenyl)methanone (4w). Pale yellow oil; 71% yield (35.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.4 Hz, 1H), 7.88 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.66 (s, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.0, 140.4, 139.4, 137.5, 135.8, 135.3, 134.7, 132.3, 129.6, 128.5, 127.5, 124.8, 122.2, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{13}OS^+$ 253.0682; Found 253.0682.



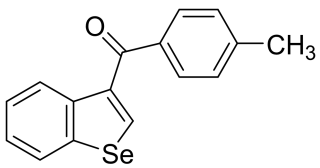
(6-Fluorobenzo[*b*]thiophen-3-yl)(phenyl)methanone (4x). Pale yellow solid; 61% yield (31.3 mg): m.p. 75–77 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.55 (dd, *J* = 9.0, 5.4 Hz, 1H), 7.95 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.57 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.26 (td, *J* = 9.0, 1.8 Hz, 1H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = − 115.4; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.8, 161.1 (d, *J* = 245.0 Hz), 141.1 (d, *J* = 10.4 Hz), 139.2, 138.0 (d, *J* = 3.0 Hz), 134.4, 134.1, 132.6, 129.6, 128.6, 126.6 (d, *J* = 8.8 Hz), 114.8 (d, *J* = 23.6 Hz), 108.5 (d, *J* = 25.1 Hz); HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}FOS^+$ 257.0431; Found 257.0429.



(6-Chlorobenzo[*b*]thiophen-3-yl)(phenyl)methanone (4y). Pale yellow solid; 58% yield (31.6 mg): m.p. 77–78 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 9.0 Hz, 1H), 7.99 (s, 1H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.86–7.85 (m, 2H), 7.62 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.53–7.50 (m, 2H), 7.48 (dd, *J* = 9.0, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.7, 141.1, 139.1, 138.5, 136.1, 134.5, 132.7, 132.0, 129.6, 128.7, 126.7, 126.2, 122.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}ClOS^+$ 273.0135; Found 273.0136.

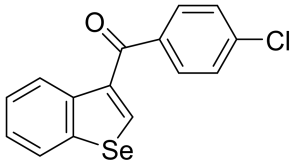


Benzo[*b*]selenophen-3-yl(phenyl)methanone (4z). Pale yellow oil; 72% yield (41.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 8.51 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.87–7.85 (m, 2H), 7.59 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.50–7.47 (m, 3H), 7.40–7.37 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.7, 142.2, 142.0, 139.5, 139.3, 138.7, 132.6, 129.8, 128.5, 127.1, 125.8, 125.7, 125.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{11}OSe^+$ 286.9970; Found 286.9966.

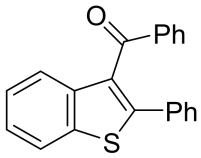


Benzo[*b*]selenophen-3-yl(*p*-tolyl)methanone (4aa). Pale yellow solid; 71% yield (42.5 mg): m.p. 117–119 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.51 (s, 1H), 8.45 (d, *J*

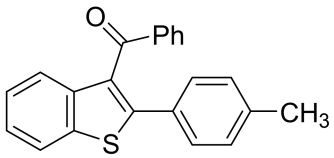
= 7.8 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.5, 143.5, 142.0, 141.1, 139.6, 138.9, 136.5, 130.0, 129.2, 127.0, 125.7, 125.6, 125.5, 21.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{13}OSe^+$ 301.0126; Found 301.0122.



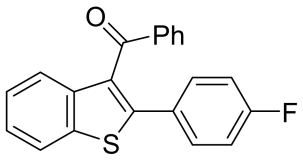
Benzo[*b*]selenophen-3-yl(4-chlorophenyl)methanone (4ab). Pale yellow solid; 69% yield (44.1 mg): m.p. 121–123 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.51–7.46 (m, 3H), 7.40 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.4, 142.2, 142.0, 139.4, 139.1, 138.4, 137.5, 131.2, 128.9, 127.0, 125.9, 125.8, 125.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}ClOSe^+$ 320.9580; Found 320.9575.



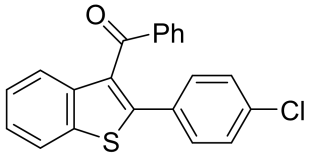
Phenyl(2-phenylbenzo[*b*]thiophen-3-yl)methanone (4ac). Pale yellow solid; 63% yield (39.6 mg): m.p. 111–113 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89–7.87 (m, 1H), 7.77–7.74(m, 3H), 7.42–7.40 (m, 3H), 7.39–7.37 (m, 2H), 7.27–7.24 (m, 2H), 7.22–7.20 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.4, 146.6, 139.8, 139.1, 137.6, 133.38, 133.35, 131.7, 130.0, 129.5, 128.9, 128.7, 128.4, 125.3, 125.2, 123.8, 122.1.



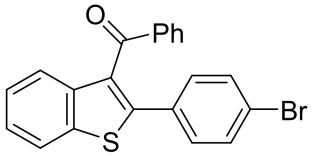
Phenyl(2-(*p*-tolyl)benzo[*b*]thiophen-3-yl)methanone (4ad). Pale yellow solid; 65% yield (42.7 mg): m.p. 141–143 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.8 Hz, 1H), 7.69–7.68 (m, 2H), 7.62–7.60 (m, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.26–7.25 (m, 2H), 7.23–7.21 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.6, 146.7, 139.9, 139.0, 138.9, 137.6, 133.3, 131.2, 130.5, 130.0, 129.4, 129.2, 128.4, 125.2, 125.0, 123.6, 122.1, 21.3.



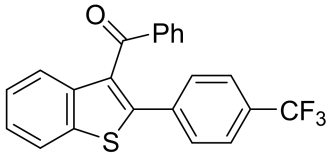
(2-(4-Fluorophenyl)benzo[*b*]thiophen-3-yl)(phenyl)methanone (4ae). Pale yellow oil; 64% yield (42.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88–7.86 (m, 1H), 7.75–7.72(m, 3H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.40–7.35 (m, 4H), 7.27 (t, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.2, 163.0 (d, *J* = 248.6 Hz), 145.3, 139.7, 138.9, 137.5, 133.5, 131.9, 131.3, 131.2, 130.0, 129.5 (d, *J* = 3.3 Hz), 128.5, 125.4 (d, *J* = 8.4 Hz), 123.8, 122.1, 115.8 (d, *J* = 21.7 Hz).



(2-(4-Chlorophenyl)benzo[*b*]thiophen-3-yl)(phenyl)methanone (4af). Pale yellow solid; 67% yield (46.7 mg): m.p. 147–148 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.30–7.25 (m, 4H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8,.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.2, 144.8, 139.7, 138.9, 137.4, 135.0, 133.6, 132.1, 131.9, 130.5, 130.0, 128.9, 128.6, 125.43, 125.40, 123.8, 122.1.

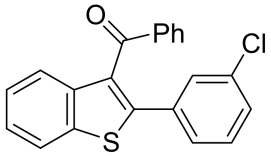


(2-(4-Bromophenyl)benzo[*b*]thiophen-3-yl)(phenyl)methanone (4ag). Pale yellow solid; 62% yield (48.8 mg): m.p. 145–147 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88–7.87 (m, 1H), 7.77–7.75 (m, 2H), 7.70–7.69 (m, 1H), 7.46 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.40 (td, *J* = 7.8, 1.2 Hz, 1H), 7.39–7.36 (m, 1H), 7.36–7.35 (m, 2H), 7.31–7.28 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.2, 144.8, 139.7, 139.0, 137.4, 133.7, 132.3, 132.2, 131.9, 130.8, 130.0, 128.6, 125.5, 125.4, 123.8, 123.3, 122.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}BrOS^+$ 392.9943; Found 392.9942.

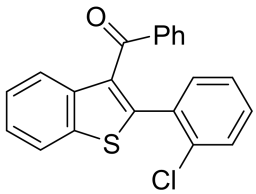


Phenyl(2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophen-3-yl)methanone (4ah). Pale yellow solid; 56% yield (42.8 mg): m.p. 120–121 ℃. ^{1}H NMR (600 MHz,

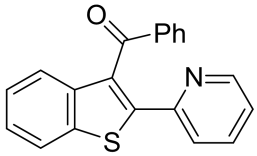
$CDCl_3$): δ = 7.89 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.44 (td, *J* = 7.2 Hz, 1H), 7.41 (td, *J* = 7.2,, 1.2 Hz, 1H), 7.38–7.36 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.1, 144.1, 139.6, 139.2, 137.4, 136.9, 133.8, 133.0, 130.7 (q, *J* = 32.5 Hz), 130.0, 129.7, 128.7, 125.7, 125.6 (q, *J* = 3.4 Hz), 125.5, 124.0, 123.9 (q, *J* = 270.4 Hz), 122.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{14}F_3OS^+$ 383.0712; Found 383.0711.



(2-(3-Chlorophenyl)benzo[*b*]thiophen-3-yl)(phenyl)methanone (4ai). Pale yellow oil; 67% yield (46.7 mg). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.88–7.87 (m, 1H), 7.76–7.73 (m, 3H), 7.43–7.41 (m, 2H), 7.40–7.36 (m, 2H), 7.29–7.26 (m, 3H), 7.17–7.15 (m, 1H), 7.11 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.0, 144.6, 139.6, 139.0, 137.5, 135.1, 134.5, 132.5, 129.9, 129.3, 128.9, 128.5, 127.6, 125.6, 125.5, 123.9, 122.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}ClOS^+$ 349.0448; Found 349.0450.

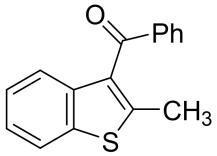


(2-(2-Chlorophenyl)benzo[*b*]thiophen-3-yl)(phenyl)methanone (4aj). Pale yellow oil; 63% yield (44.0 mg). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.90–7.89 (m, 2H), 7.73–7.71 (m, 2H), 7.43–7.40 (m, 2H), 7.38–7.36 (m, 1H), 7.35–7.34 (m, 1H), 7.25–7.22 (m, 3H), 7.13–7.12 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.0, 144.8, 139.7, 138.7, 138.2, 134.1, 133.7, 132.9, 132.4, 130.3, 129.9, 129.8, 128.1, 126.6, 125.5, 125.3, 124.4, 122.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}ClOS^+$ 349.0448; Found 349.0449.

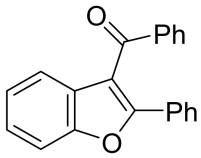


Phenyl(2-(pyridin-2-yl)benzo[*b*]thiophen-3-yl)methanone (4ak). Pale yellow oil; 51% yield (32.2 mg). ^1H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 4.8 Hz, 1H), 7.89

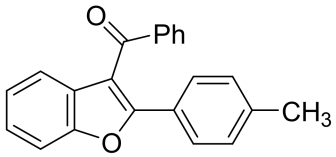
(d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.49–7.47 (m, 1H), 7.46–7.44 (m, 1H), 7.42–7.41 (m, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.34–7.30 (m, 3H), 7.05 (tt, *J* = 7.2, 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.9, 151.2, 149.5, 143.9, 139.6, 139.5, 137.5, 136.5, 133.5, 133.2, 129.7, 128.6, 125.8, 125.2, 123.7, 122.9, 122.7, 122.4.



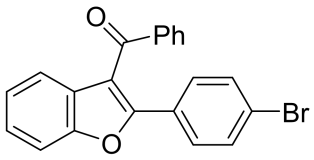
(2-Methylbenzo[*b*]thiophen-3-yl)(phenyl)methanone (4al). White solid; 68% yield (34.3 mg): m.p. 91–93 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 6.0, 1.2 Hz, 2H), 7.78–7.77 (m, 1H), 7.59 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.51–7.50 (m, 1H), 7.47–7.44 (m, 2H), 7.29 (td, *J* = 7.2, 1.2 Hz, 1H), 7.27–7.25 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.6, 145.9, 139.2, 138.8, 138.0, 133.4, 132.4, 129.8, 128.8, 124.8, 124.4, 123.4, 121.9, 15.9.



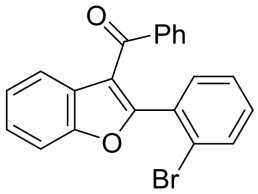
Phenyl(2-phenylbenzofuran-3-yl)methanone (4am). Yellow oil; 78% yield (46.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 2H), 7.67 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.36–7.25 (m, 7H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.5, 157.8, 153.9, 137.9, 133.3, 129.9 (2), 129.8, 128.51(3), 128.50, 125.5, 123.9, 121.6, 116.3, 111.3.



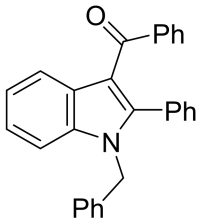
Phenyl(2-(*p*-tolyl)benzofuran-3-yl)methanone (4an). Pale yellow oil; 72% yield (45.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85–7.83 (m, 2H), 7.589–7.55 (m, 3H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.35–7.31 (m, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.6, 158.1, 153.8, 140.2, 138.0, 133.2, 129.9, 129.2, 128.7, 128.5, 128.4, 126.7, 125.2, 123.9, 121.5, 115.7, 111.3, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{17}O_2^+$ 313.1223; Found 313.1222.



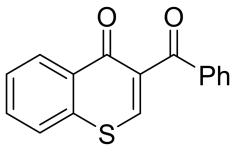
(2-(4-Bromophenyl)benzofuran-3-yl)(phenyl)methanone (4ao). Pale yellow oil; 76% yield (57.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.2 Hz, 2H), 7.59–7.56 (m, 3H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 3H), 7.26–7.23 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.2, 156.3, 153.9, 137.8, 133.6, 131.8, 129.9, 129.8, 128.7, 128.5, 128.4, 125.7, 124.3, 124.1, 121.7, 116.7, 111.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}BrO_2^+$ 377.0172; Found 377.0176.



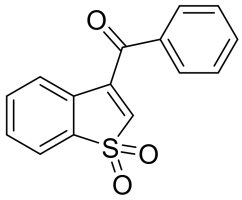
(2-(2-Bromophenyl)benzofuran-3-yl)(phenyl)methanone (4ap). Yellow oil; 51% yield (38.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.2 Hz, 1H), 7.72–7.71 (m, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.42 (td, *J* = 7.2, 1.2 Hz, 1H), 7.38–7.35 (m, 3H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.20 (td, *J* = 7.8, 1.2 Hz, 1H), 7.15 (td, *J* = 7.8, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.7, 158.5, 154.4, 138.3, 133.2, 132.9, 132.6, 131.5, 131.3, 129.6, 128.0, 127.2, 127.1, 125.8, 124.3, 123.7, 122.3, 118.8, 111.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}BrO_2^+$ 377.0172; Found 377.0172.



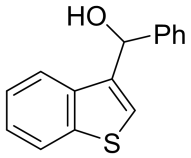
(1-Benzyl-2-phenyl-1H-indol-3-yl)(phenyl)methanone (4B). Pale yellow solid; 69% yield (53.5 mg): m.p. 147–148 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.27–7.23 (m, 7H), 7.18–7.17 (m, 3H), 7.14–7.10 (m, 4H), 6.98 (d, *J* = 7.2 Hz, 2H), 5.30 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.2, 146.6, 140.1, 137.1, 136.9, 131.1, 130.9, 130.7, 129.4, 129.0, 128.2, 128.0, 127.7, 127.6, 126.1, 123.6, 122.6, 122.0, 115.4, 110.9, 48.0.



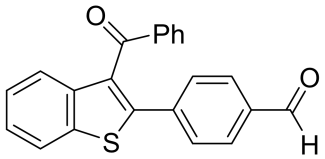
3-Benzoyl-4H-thiochromen-4-one (6B). Pale yellow solid; 27% yield (14.4 mg): m.p. 80–83 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 7.8 Hz, 1H), 8.26 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.69–7.68 (m, 2H), 7.62–7.56 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.2, 177.7, 141.6, 137.0, 136.5, 136.2, 133.5, 132.9, 132.1, 129.6, 129.4, 128.7, 128.6, 127.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{11}O_2S^+$ 267.0474; Found 267.0476.



(1,1-Dioxidobenzo[*b*]thiophen-3-yl)(phenyl)methanone (7B). Yellow oil; 60% yield (81.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94–7.93 (m, 2H), 7.77–7.75 (m, 1H), 7.70–7.65 (m, 2H), 7.58–7.57 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 6.91 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.8, 139.2, 137.0, 135.6, 134.7, 133.8, 132.4, 131.1, 129.6, 129.0, 125.4, 121.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{11}O_3S^+$ 271.0423; Found 271.0422.



Benzo[*b*]thiophen-3-yl(phenyl)methanol (8B). Colourless oil; 91% yield (109.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79–7.77 (m, 1H), 7.63–7.62 (m, 1H), 7.34–7.33 (m, 2H), 7.29–7.22 (m, 5H), 7.20 (d, *J* = 0.6 Hz, 1H), 5.98 (s, 1H), 2.80 (br, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.2, 141.0, 138.7, 137.3, 128.6, 128.0, 126.9, 124.5, 124.1, 123.9, 122.9, 122.7.



4-(3-Benzoylbenzo[*b*]thiophen-2-yl)benzaldehyde (9B). Pale yellow oil; 75% yield (128.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.92 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.78–7.76 (m, 2H), 7.74–7.73 (m, 3H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.45–7.42 (m, 2H), 7.41–7.38 (m, 1H), 7.29 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.1,

191.5, 144.1, 139.6, 139.33, 139.28, 137.3, 136.0, 133.8, 133.3, 130.00, 129.96, 129.9, 128.7, 125.9, 125.6, 124.1, 122.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{15}O_2S^+$ 343.0787; Found 343.0789.

3.8 本章小结

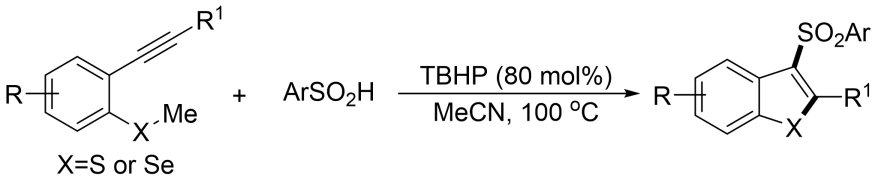
总之，本章发展了一种在温和条件下可见光促进 PQ 催化邻炔基苯甲硫醚分子内环化氧化合成 3-酰基苯并噻吩的高效方法。该策略不仅拓宽了*α*-杂原子烷基自由基的分子内氧化途径，而且为含硫、含氧、含硒和含氮杂环的合成提供了一条有效的途径。我们的实验室正在进行进一步的研究，以深入了解这种反应机制和这种转化的新应用。

第4章 可见光促进DABSO与邻炔基苯甲硫醚串联环化合成3-烷基磺酰基苯并噻吩

4.1 研究背景

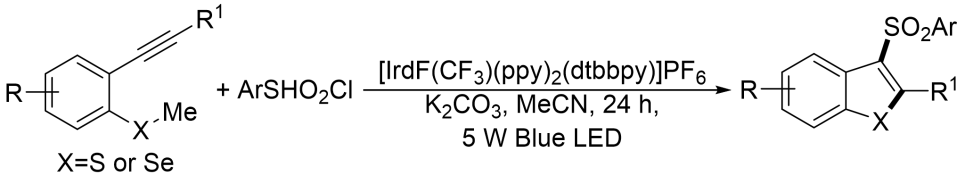
磺酰基是调节化合物生物活性的药效基团，在医药和农药领域中有着重要的应用价值，磺酰基的引入对于合成化学是非常重要的[131-134]。同时，3-磺酰基苯并噻吩是一种重要的生物活性分子，具有抗真菌或 5-HT_6 受体拮抗特性[50]。3-磺酰基苯并噻吩的合成方法已经有了很大的发展。

2017 年，Song 课题组[42]，开发了一种由过氧化叔丁醇（TBHP）氧化芳基亚磺酸使其产生磺酰基自由基与邻炔基苯甲硫醚发生加成环化反应（Scheme 4-1）。该反应表现出较好的官能团兼容性，以较高的收率获得一系列 3-芳基磺酰基苯并噻吩。但是该反应使用的 TBHP 在高温下有潜在的爆炸危险，极大的限制了其的应用。



Scheme 4-1 芳基亚磺酸与邻炔基苯甲硫醚的加成环化反应

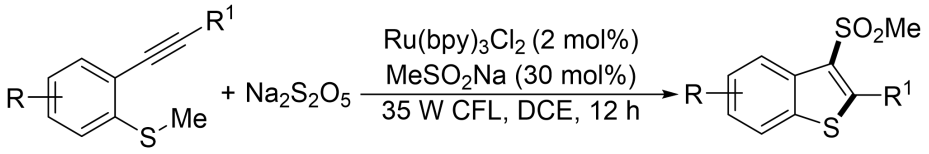
随后该课题组[51]2018 年在原有基础上对该反应进行改进，发展了可见光促进铱催化芳基亚磺酰氯（作为磺酰基来源）与邻炔基苯甲硫醚反应合成 3-芳基磺酰基苯并噻吩的方法（Scheme 4-2）。该方法具有操作简单，条件温和，官能团耐受性好等优点。



Scheme 4-2 可见光促进芳基亚磺酰氯与邻炔基苯甲硫醚的级联环化反应

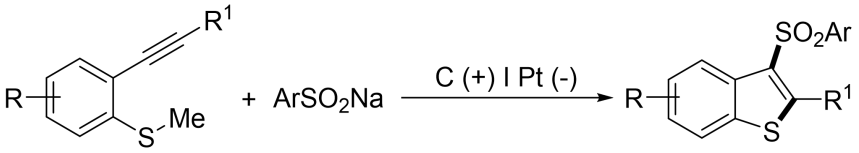
2019 年，Wu 课题组[53]，开发了一种可见光促进邻炔基苯甲硫醚与焦亚硫酸钠自由基串联环化合成 3-甲基磺酰基苯并噻吩的方法（Scheme 4-3）。在温和的

条件下，以 55-96%的产率合成了一系列 3-甲基磺酰基苯并噻吩。机理研究表明，原位生成的甲基自由基是关键中间体。



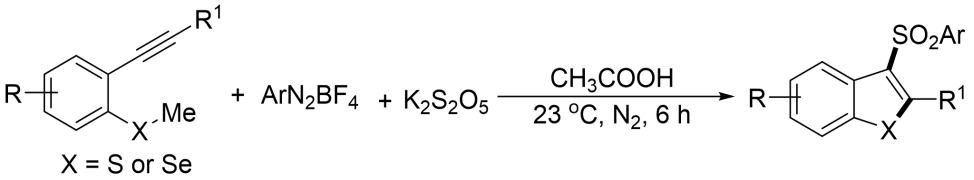
Scheme 4-3 甲基亚磺酸钠催化邻炔基苯甲硫醚合成 3-甲基磺酰基苯并噻吩

2021 年，Fang 和 Wang 课题组[56, 57]先后报道了一个简单有效的电氧化促进 2-炔基苯甲硫醚与亚磺酸钠的自由基串联加成环化反应（Scheme 4-4），合成了一系列 3-芳基磺酰基苯并噻吩。该方法具有无需外加催化剂，底物易于获得，操作简单，官能团耐受性好和收率高等优点。



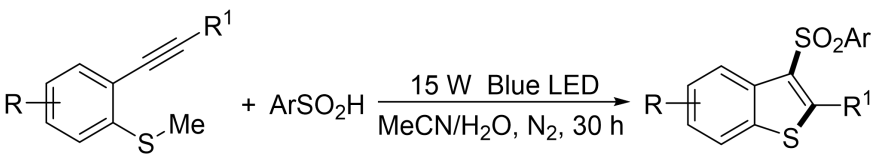
Scheme 4-4 电催化串联环化合成 3-芳基磺酰基苯并噻吩

2023 年，Lee 课题组[50]，报道了邻炔基苯甲硫醚、芳基重氮盐和焦亚硫酸钾三组分串联环化合成 3-芳基磺酰基苯并噻吩的合成方法（Scheme 4-5）。该反应在室温下进行，无需任何催化剂或添加剂。值得注意的是，该反应生成了副产物 3-甲基磺酰基苯并噻吩，并且通过乙酸可以抑制该副产物的生成。



Scheme 4-5 三组分合成 3-芳基磺酰基苯并噻吩

同年，Yang 课题组[59]，报道了在无光催化剂、碱、氧化剂和金属条件下，可见光促进邻炔基苯甲硫醚与芳基磺酸级联环化合成 3-芳基磺酰基苯并噻吩（Scheme 4-6）。紫外可见光谱表明，芳基亚磺酸阴离子与 2-炔基硫代苯胺之间形成了 EDA 配合物。

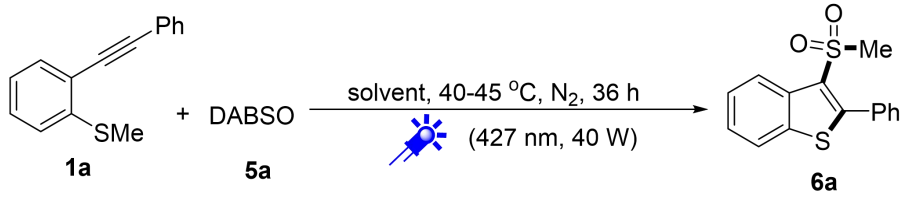


Scheme 4-6 电子供体-受体复合物炔烃级联环化反应

虽然 3-磺酰基苯并噻吩的合成已经有了很大的发展，但是仍有一定的局限性。目前大部分发展的都是 3-芳基磺酰基的合成，该类合成方法会造成硫保护基的浪费，原子利用率不高，虽然 Wu 课题组已经发展了一条有效的 3-甲基磺酰基苯并噻吩的合成方法。但是当取代基为甲基以外的基团时，该反应产率大大降低。并且还需要额外的金属光催化剂和引发剂。这极大的限制了其的应用。因此，发展原子利用率高，绿色简单高效合成 3-烷基磺酰基苯并噻吩的方法是非常有必要的。

4.2 反应条件优化

Table 4-1 反应条件优化 [a]

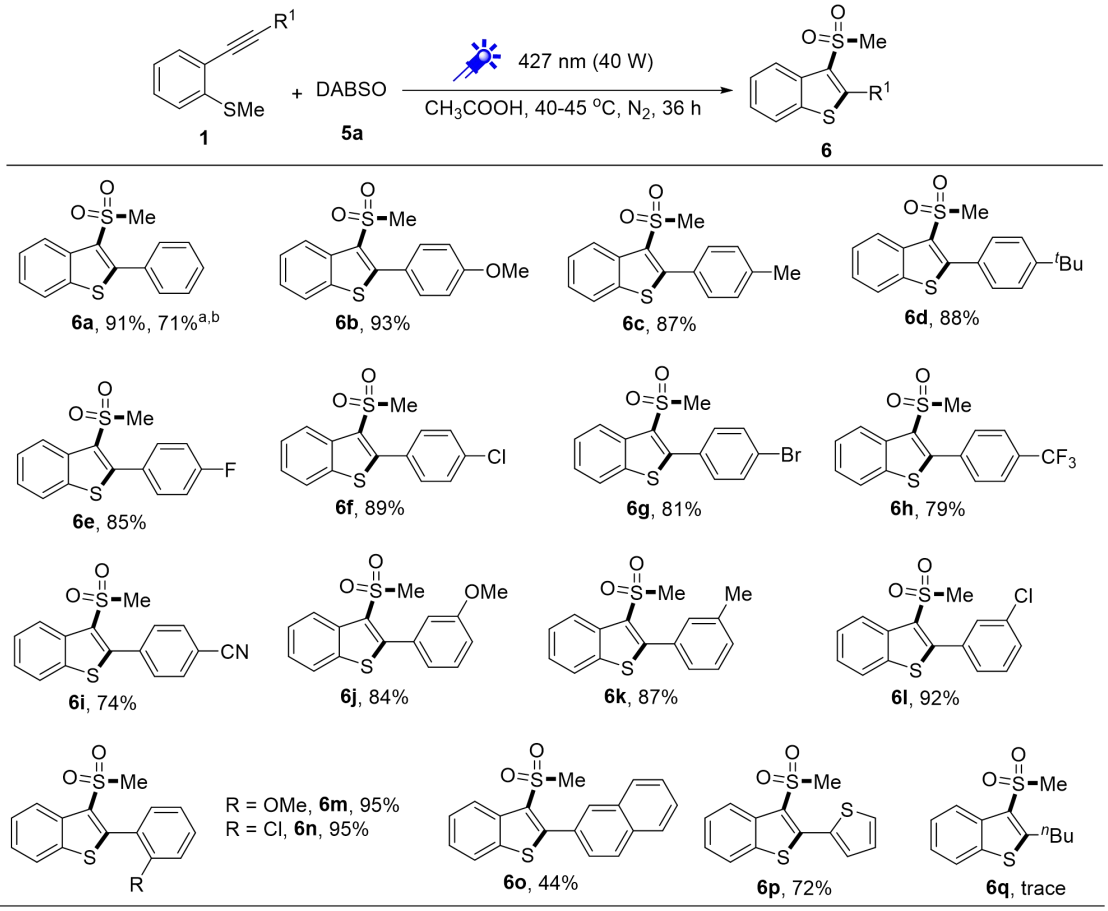


Entry	SO_2 source (x eq.)	Solvent	Yield(%)[b]
1	DABSO (1.2)	CH_3COOH	91
2	$Na_2S_2O_5$ (1.2)	CH_3COOH	83
3	$K_2S_2O_5$ (1.2)	CH_3COOH	81
4	DABSO (1.2)	DCE	67
5	DABSO (1.2)	$CHCl_3$	83
6	DABSO (1.2)	CH_2Cl_2	66
7	DABSO (1.2)	MeCN	80
8	DABSO (1.2)	THF, EtOAC or $PhCH_3$	n.d.
9	DABSO (1.2)	DMF or CH_3COCH_3	trace
10	DABSO (1.2)	MeOH	46
11	DABSO (1.2)	PhCl	53
12	DABSO (1.0)	CH_3COOH	82
13	DABSO (1.5)	CH_3COOH	91
14[c, d]	DABSO (1.2)	CH_3COOH	trace, n.d.
15[e]	DABSO (1.2)	CH_3COOH	33
16[f, g]	DABSO (1.2)	CH_3COOH	72, 90

[a]Reaction conditions: **1a** (0.20 mmol) and DABSO (0.24 mmol) in solvent (2.0 mL) were irradiated with 40 W blue LED in a reaction tube Under N_2 atmosphere at 40-45 °C for 36 h unless otherwise stated. [b]Isolated yield; [c]Room temperature; [d]In dark at 50 °C; [e]Under air atmosphere; [f]30 h; [g]42 h; n.d. = not detected.

以 2-炔基苯甲硫醚 （**1a**）和 DABSO 为模版反应，分别对反应溶剂、温度、DABSO 用量等条件进行了优化，以确定最佳反应条件（Table 4-1）。首先对磺酰基来源进行了优化，发现 DABSO 为最佳磺酰基来源。以 91%的收率获得 3-甲基磺酰基苯并噻吩（entries 1-3）焦亚硫酸钠和焦亚硫酸钾做磺酰基来源产率略有降低。然后对反应溶剂进行了优化，发现乙酸做溶剂时效果较好（entries 4-11）。然后对 DABSO 的量进行了优化，1.2 当量的 DABSO 为最佳（entries 12-13），控制性实验表明，在室温下该反应不能顺利进行，光照是该反应的必要条件（entry 14），当该反应在空气氛围下进行时反应产率大大降低（entry 15），原因是生成了许多氧化产物亚砜（**3a'**），最后对反应时间进行了优化，最定最佳反应条件为 36 h（entry 16）。

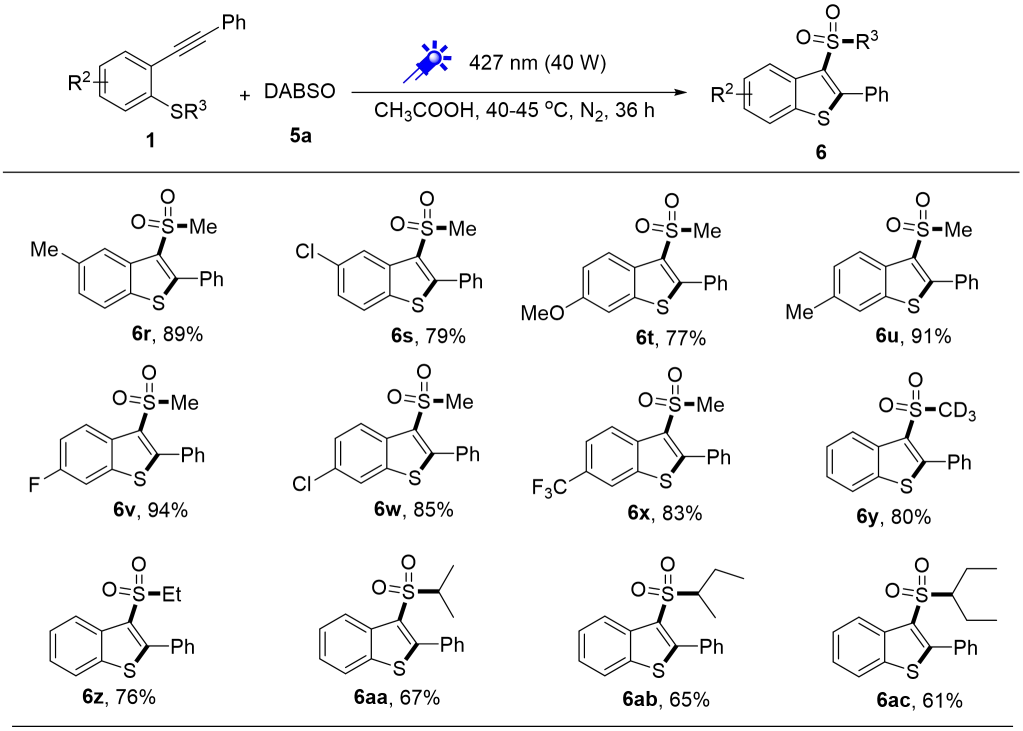
4.3 反应底物拓展



Unless otherwise noted, all reactions were performed with **1** (0.20 mmol) and DABSO (0.24 mmol, 1.2 equiv.) in CH_3COOH (2.0 mL) at 40-45 ℃ in a reaction tube under nitrogen atmosphere under blue LED (427 nm, 40 W) irradiation for 36 h. Isolated yields. [a] The reaction was carried out on 5.0 mmol scale. [b] 48 h.

Scheme 4-15 底物拓展 I

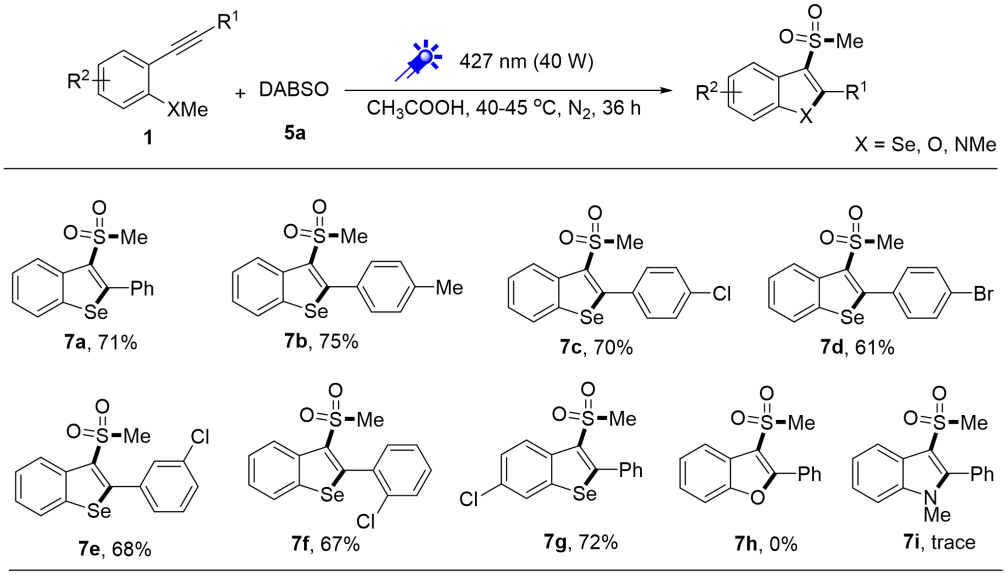
为了证明该反应的普适性，在最佳反应条件下，首先对邻炔基苯甲硫醚取代基 R^1 进行了考察（Scheme 4-15）。当取代基为芳基时无论是吸电子基还是供电子基均可以以优异的产率获得相应的 3-甲基磺酰基苯并噻吩，产率为 79-95%。此外当 R^1 为萘基或者噻吩基时，该反应也可以顺利进行。并分别以 44%和 72%的收率获得 2-萘基-3-甲基磺酰基苯并噻吩（**6o**）和 2-噻吩基 3-甲基磺酰基苯并噻吩（**6p**）。令人遗憾的是，烷基取代基并不是该反应的有效底物，只能检测到微量的目标产物，可能与烯基自由基的活性有关。值得注意的是，该反应很容易进行放大，将 5.0 mmol 的 **1a** 作为模型反应，获得了产率为 71%的 **6a**。



Unless otherwise noted, all reactions were performed with **1** (0.20 mmol) and DABSO (0.24 mmol, 1.2 equiv.) in CH_3COOH (2.0 mL) at 40-45 °C in a reaction tube under nitrogen atmosphere under blue LED (427 nm, 40 W) irradiation for 36 h. Isolated yields.

Scheme 4-16 底物拓展 II

然后对邻炔基苯甲硫醚芳香环上取代基进行了考察（Scheme 4-16），各种取代基均可适用，以 77%-94%的产率获得了相应的酰基苯并噻吩（**6r-6x**）。令我们高兴的是，当取代基为 CD_3 或者乙基时，也获得了相应的产物（**6ab-6ac**），产率分别为 76%和 80%。当取代基为异丙基、异丁基和异戊基时，均可以顺利转化，产率略有降低。



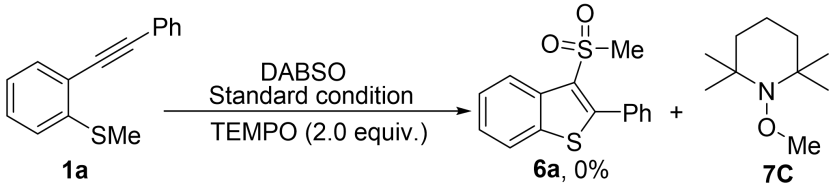
Unless otherwise noted, all reactions were performed with **1** (0.20 mmol) and DABSO (0.24 mmol, 1.2 equiv.) in CH_3COOH (2.0 mL) at 40-45 °C in a reaction tube under nitrogen atmosphere under blue LED (427 nm, 40 W) irradiation for 36 h. Isolated yields.

Scheme 4-17 底物拓展 III

之后我们对邻炔基苯甲硒醚做了考察。邻我们高兴的是各种 3-甲基磺酰基苯并硒吩均可以顺利进行，以 61-75%的收率获得目标产物。遗憾的是当底物为 1-甲氧基-2-（苯基乙炔基）苯时该反应不能顺利进行，当底物为氮，氮-二甲基-2-（苯基乙烯基）苯胺时仅检测到微量目标产物（Scheme 4-17）。

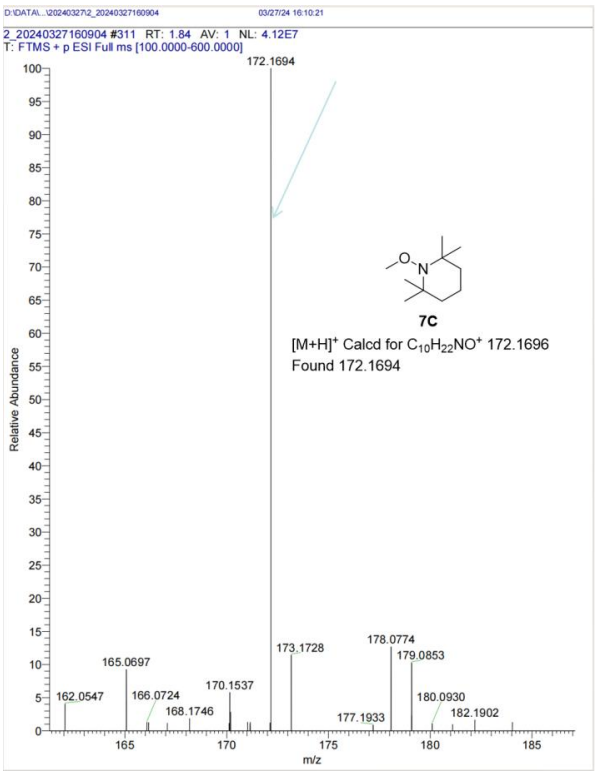
4.4 反应机理研究

4.4.1 自由基捕获实验



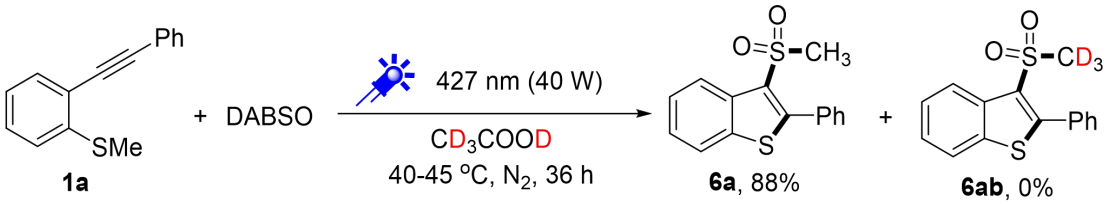
Scheme 4-18 自由基捕获实验

为了深入了解这种转变的机制，进行了自由基捕获实验。当在模型反应中加入 2 倍当量的自由基捕捉剂 TEMPO 时，该反应被完全抑制。反应混合物的 HRMS 分析检测到了 TEMPO 与甲基自由基的加合物 **7C**，结果表明，自由基可能参与了反应过程（Scheme 4-18）。



Scheme 4-19 7C 的高分辨质谱

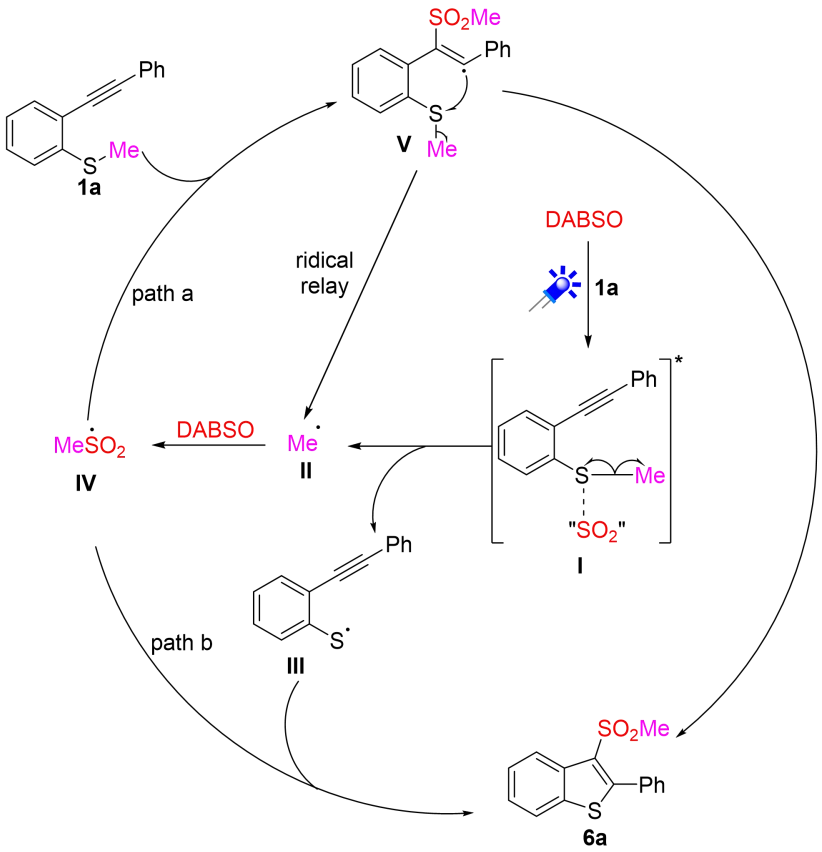
4.4.2 对照实验



当将溶剂换成氘代乙酸时，以 88%的收率获得了 3-甲基磺酰基苯并噻吩（6a）没有得到 3-氘代甲基磺酰基苯并噻吩。表明产物中的甲基不来源于乙酸。

4.5 可能的反应机理

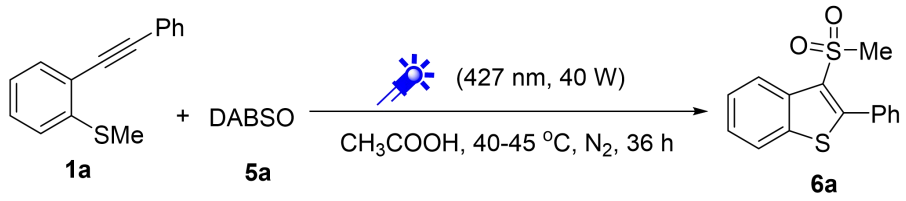
根据对照实验，提出了一种自由基级联环化的可能反应机理（Scheme 4-23）。首先，在光照条件下 **1a** 中的硫原子与 DABSO 中的硫原子 产生了弱相互作用，形成了激发态 $\mathbf{A_3}$，之后 C-S 键均裂，形成甲基自由基（**II**）和硫自由基（**III**），甲基自由基与 DABSO 反应生成甲基磺酰基自由基（**IV**），之后有两条路径，主路径是甲基磺酰基自由基进攻碳碳叁键形成烯基自由基（**V**），之后分子内关环释放产物 3-甲基磺酰基苯并噻吩（**6a**）脱去甲基自由基返回进行下一个循环。另一条次要路径是甲基磺酰基自由基与自由基 **III** 反应生成 **6a**。



Scheme 4-20 可能的反应机理

4.5 实验部分

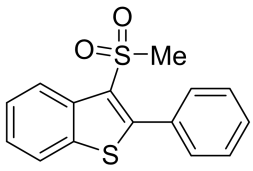
4.5.1 3-甲基磺酰基苯并噻吩（6a）制备的一般步骤



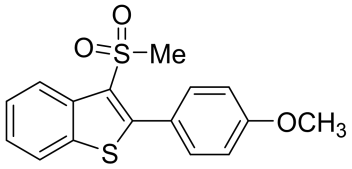
Scheme 4-24 可见光促进 3-甲基磺酰基苯并噻吩合成

在一个装有磁子的 10 mL 干燥的具支反应管中加入 2-炔基苯甲硫醚（**1a**, 44.9 mg, 0.2 mmol）、DABSO（**5a**, 57.7 mg, 1.2 equiv.）和乙酸（2.0 mL）。反应混合物在 50 ℃和氮气条件下，用蓝色 LED（427 nm, 40 W）照射反应 36 h。反应完成后，溶剂直接用旋转蒸发仪除去，残渣在硅胶上以乙酸乙酯/石油醚（1:9, V/V）为洗脱液进行柱层析纯化，得到所需产品 **6a** 为白色固体（52.5 mg, 产率 91%）。

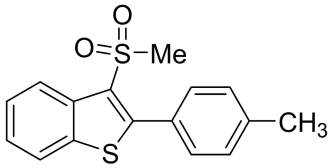
4.6 产物的表征数据



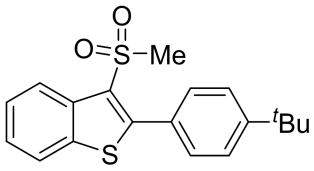
3-(Methylsulfonyl)-2-phenylbenzo[*b*]thiophene (6a). White solid; 91% yield (52.5 mg): mp 134.1–135.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.59–7.57 (m, 2H), 7.56–7.53 (m, 1H), 7.50–7.45 (m, 4H), 3.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.6, 138.4, 136.3, 131.6, 130.5, 129.9, 129.3, 128.1, 126.2, 125.9, 124.4, 122.0, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}O_2S_2^+$ 289.0351; Found 289.0353.



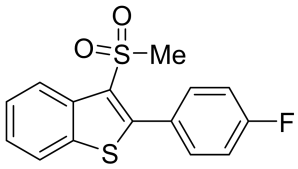
2-(4-Methoxyphenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6b). White solid. 93% yield (59.2 mg): mp 133.1–133.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.54–7.51 (m, 3H), 7.47–7.44 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.0, 152.8, 138.2, 136.5, 132.0, 128.8, 126.1, 125.7, 124.3, 123.5, 122.0, 113.7, 55.5, 45.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_3S_2^+$ 319.0457; Found 319.0457.



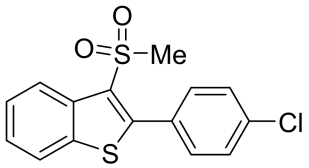
3-(Methylsulfonyl)-2-(*p*-tolyl)benzo[*b*]thiophene (6c). White solid, 87% yield (52.6 mg): mp 156.7–158.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.55–7.52 (m, 1H), 7.49–7.45 (m, 3H), 7.28 (d, *J* = 7.8 Hz, 2H), 3.00 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.0, 140.2, 138.3, 136.4, 130.4, 129.1, 128.9, 128.6, 126.2, 125.8, 124.4, 122.0, 45.1, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_2S_2^+$ 303.0508; Found 303.0507.



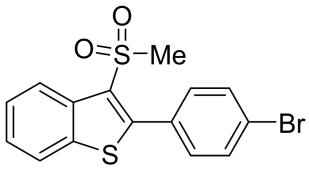
2-(4-(*tert*-Butyl)phenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6d). White solid; 88% yield (60.6 mg): mp 190.2–191.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.4 Hz, 1H), 7.54–7.52 (m, 3H), 7.49–7.45 (m, 3H), 2.99 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.2, 153.0, 138.3, 136.5, 130.3, 128.9, 128.6, 126.1, 125.7, 125.2, 124.4, 122.0, 45.0, 35.0, 31.4.



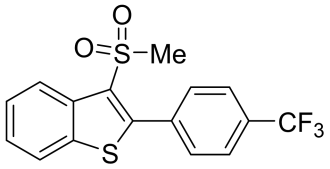
2-(4-Fluorophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6e). White solid; 85% yield (52.1 mg): mp 140.2–140.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.58–7.54 (m, 3H), 7.50–7.48 (m, 1H), 7.16 (t, *J* = 8.4 Hz, 2H), 3.02 (s, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −110.7; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8 (d, *J* = 249.2 Hz), 151.6, 138.3, 136.2, 132.5 (d, *J* = 8.9 Hz), 129.5, 127.4 (d, *J* = 3.8 Hz), 126.2 (d, *J* = 43.4 Hz), 124.3, 122.1, 115.4, 115.3, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}FO_2S_2^+$ 307.0257; Found 307.0258.



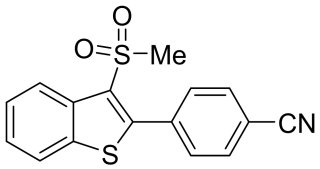
2-(4-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6f). White solid; 89% yield (57.5 mg): mp 175.1–177.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.57–7.55 (m, 1H), 7.52–7.48 (m, 3H), 7.45–7.43 (m, 2H), 3.03 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.3, 138.4, 136.3, 136.2, 131.9, 129.9, 129.5, 128.5, 126.4, 126.2, 124.4, 122.1, 45.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9965.



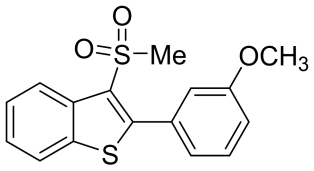
2-(4-Bromophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6g). White solid; 81% yield (59.5 mg): mp 169.1–169.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.60–7.59 (m, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.50–7.48 (m, 1H), 7.45–7.44 (m, 2H), 3.03 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.3, 138.4, 136.2, 132.1, 131.4, 130.4, 129.5, 126.4, 126.1, 124.6, 124.3, 122.1, 45.2.



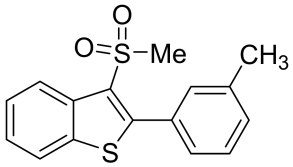
3-(Methylsulfonyl)-2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophene (6h). Yellow solid; 79% yield (56.3 mg): mp 183.7–184.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.73–7.68 (m, 4H), 7.59–7.57 (m, 1H), 7.53–7.50 (m, 1H), 3.06 (s, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −62.8; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.7, 138.6, 136.0, 135.3, 131.8 (q, *J* = 32.5 Hz), 131.0, 129.9, 126.6, 126.4, 125.0 (q, *J* = 270.8 Hz), 124.3, 122.2, 45.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{12}F_3O_2S_2^+$ 357.0225; Found 357.0225.



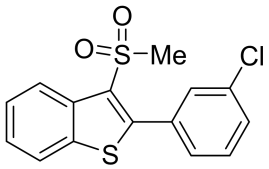
4-(3-(Methylsulfonyl)benzo[*b*]thiophen-2-yl)benzonitrile (6i). Pale yellow solid; 74% yield (46.4 mg): mp 218.4–220.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.76–7.75 (m, 2H), 7.68–7.67 (m, 2H), 7.61–7.58 (m, 1H), 7.550–7.52 (m, 1H), 3.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.2, 138.6, 136.4, 135.9, 131.7, 131.4, 130.7, 126.7, 126.6, 124.3, 122.3, 118.3, 113.7, 45.3.



2-(3-Methoxyphenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6j). White solid; 84% yield (53.5 mg): mp 105.7–106.5℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.55–7.52 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.16–7.15 (m, 2H), 7.03–7.01 (m, 1H), 3.85 (s, 3H), 2.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.1, 152.2, 138.3, 136.3, 132.7, 129.4, 129.2, 126.2, 125.9, 124.4, 122.8, 122.0, 116.2, 116.0, 55.5, 45.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_3S_2^+$ 319.0457; Found 319.0456.

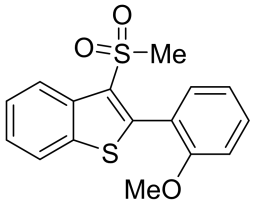


3-(Methylsulfonyl)-2-(*m*-tolyl)benzo[*b*]thiophene (6k). White solid; 87% yield (52.6 mg): mp 135.4–136.7 ℃. δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.54–7.52 (m, 1H), 7.47–7.44 (m, 1H), 7.38–7.37 (m, 2H), 7.35–7.33 (m, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 2.99 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.8, 138.3, 137.9, 136.3, 131.4, 131.0, 130.7, 129.1, 128.0, 127.6, 126.1, 125.8, 124.3, 122.0, 45.1, 21.5.

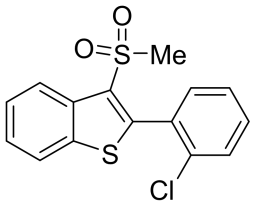


2-(3-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6l). White solid; 92% yield (59.4 mg): mp 144.2–145.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.57–7.54 (m, 2H), 7.50–7.48 (m, 1H), 7.47–7.45 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 3.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.7, 138.4, 136.0, 134.0, 133.2, 130.3, 130.0, 129.7, 129.3, 128.9,

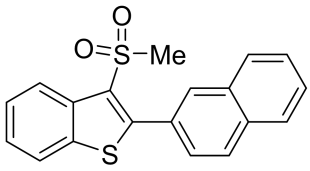
126.4, 126.2, 124.3, 122.1, 45.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9960.



2-(2-Methoxyphenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6m). White solid; 95% yield (58.6 mg): mp 161.7–162.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.54–7.52 (m, 1H), 7.47–7.43 (m, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.0, 149.1, 138.9, 136.0, 131.6, 131.3, 129.9, 126.0, 125.6, 123.8, 122.2, 120.7, 120.4, 110.9, 55.6, 43.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_3S_2^+$ 319.0457; Found 319.0455.

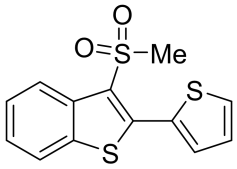


2-(2-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (6n). White solid; 95% yield (61.3 mg): mp 132.4–133.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.52–7.49 (m, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.43–7.41 (m, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 3.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.1, 139.0, 135.4, 133.6, 132.2, 131.0, 130.9, 130.7, 129.4, 126.4, 126.3, 126.2, 124.0, 122.3, 44.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9960.

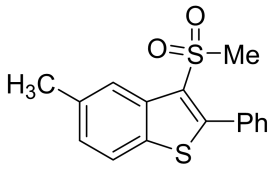


3-(Methylsulfonyl)-2-(naphthalen-2-yl)benzo[*b*]thiophene (6o). Yellow solid; 44% yield (29.8 mg): mp 169.5–170.7 ℃: mp 169.5–170.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.4 Hz, 1H), 8.07 (s, 1H), 7.93–7.88 (m, 4H), 7.69 (dd, *J* =

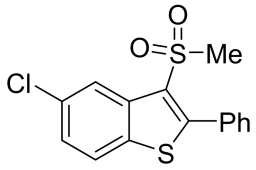
8.4, 1.8 Hz, 1H), 7.58–7.54 (m, 3H), 7.51–7.49 (m, 1H), 3.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.7, 138.5, 136.4, 133.7, 132.6, 130.1, 129.4, 129.0, 128.6, 128.0, 127.9, 127.7, 127.5, 127.0, 126.3, 126.0, 124.4, 122.1, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{15}O_2S_2^+$ 339.0508; Found 339.0508.



3-(Methylsulfonyl)-2-(thiophen-2-yl)benzo[*b*]thiophene (6p). White solid; 72% yield (42.4 mg): mp 119.0–119.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 3.0 Hz, 1H), 7.55 (d, *J* = 4.8 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.47–7.45 (m, 1H), 7.17–7.16 (m, 1H), 3.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.5, 138.3, 136.7, 132.1, 131.2, 129.8, 129.5, 128.1, 126.3, 126.1, 124.7, 121.8, 44.4.

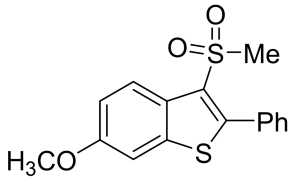


5-Methyl-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (6r). White solid; 89% yield (53.8 mg): mp 158.7–159.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.56–7.55 (m, 2H), 7.47–7.43 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 2.99 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.7, 136.5, 136.3, 135.6, 131.7, 130.4, 129.8, 128.8, 128.1, 127.6, 124.0, 121.6, 45.1, 21.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_2S_2^+$ 303.0508; Found 303.0507.

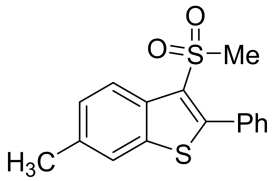


5-Chloro-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (6s). White solid; 79% yield (51.0 mg): mp 162.2–163.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.58–7.56 (m, 2H), 7.52–7.46 (m, 3H), 7.44 (dd,

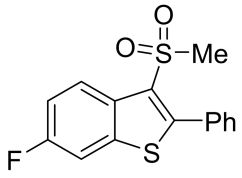
J = 8.4, 1.8 Hz, 1H), 2.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.3, 137.4, 136.4, 132.8, 131.1, 130.4, 130.2, 128.9, 128.3, 126.5, 124.1, 123.0, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9961.



6-Methoxy-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (6t). White solid; 77% yield (49.0 mg): mp 149.6–150.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 9.0 Hz, 1H), 7.57–7.56 (m, 2H), 7.49–7.44 (m, 3H), 7.30 (d, *J* = 1.8 Hz, 1H), 7.14 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.90 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.3, 149.6, 140.0, 131.7, 130.6, 130.1, 129.8, 129.0, 128.1, 125.1, 116.1, 104.3, 55.8, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_3S_2^+$ 319.0457; Found 319.0457.

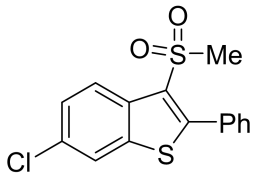


6-Methyl-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (6u). White solid; 91% yield (55.0 mg): mp 149.6–150.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.57–7.56 (m, 2H), 7.47–7.44 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 1H), 2.98 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.3, 138.7, 136.2, 134.0, 131.7, 130.5, 129.8, 129.1, 128.1, 127.9, 123.9, 121.7, 45.1, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_2S_2^+$ 303.0508; Found 303.0506.

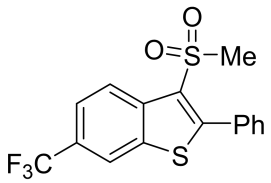


6-Fluoro-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (6v). White solid; 94% yield (57.6 mg): mp 177.1–180.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.58–7.57 (m, 2H), 7.55 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.50–7.46 (m,

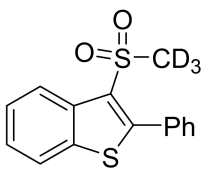
3H), 7.27 (td, J = 9.0, 2.4 Hz, 1H), 2.97 (s, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −114.4; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.0 (d, J = 246.6 Hz), 152.1 (d, J = 3.3 Hz), 139.4 (d, J = 10.0 Hz), 132.8, 131.3, 130.5, 130.1, 129.1, 128.3, 126.0 (d, J = 8.9 Hz), 115.3 (d, J = 23.7 Hz), 108.2 (d, J = 25.5 Hz), 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}FO_2S_2^+$ 307.0257; Found 307.0256.



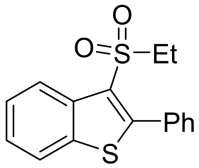
6-Chloro-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (6w). Pale yellow solid; 85% yield (54.9 mg): mp 167.9–168.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.58–7.57 (m, 2H), 7.51–7.46 (m, 3H), 7.44–7.43 (m, 2H), 2.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.4, 137.4, 136.4, 132.8, 131.1, 130.4, 130.2, 128.9, 128.3, 126.5, 124.1, 123.0, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9964.



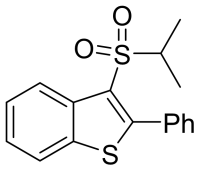
3-(Methylsulfonyl)-2-phenyl-6-(trifluoromethyl)benzo[*b*]thiophene (6x). White solid; 83% yield (59.2 mg): mp 156.4–158.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.85 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.61–7.59 (m, 2H), 7.53–7.49 (m, 3H), 2.98 (s, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −61.7; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.5, 141.3, 136.1, 130.9, 130.44, 130.40, 130.0, 128.8 (q, J = 32.4 Hz), 128.4, 124.3 (q, J = 270.9 Hz), 122.7, 122.3 (q, J = 3.1 Hz), 122.0 (q, J = 4.9 Hz), 45.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{12}F_3O_2S_2^+$ 357.0225; Found 357.0223.



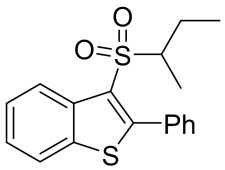
3-((Methyl-d_3)sulfonyl)-2-phenylbenzo[*b*]thiophene (6ay). White solid; 80% yield (46.6 mg): mp 132.6–133.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.86 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.58–7.57 (m, 2H), 7.56–7.53 (m, 1H), 7.49–7.46 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.6, 138.4, 136.3, 131.6, 130.5, 129.9, 129.2, 128.1, 126.2, 125.9, 124.4, 122.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}D_3O_2S_2^+$ 292.0540; Found 292.0538.



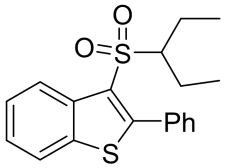
3-(Ethylsulfonyl)-2-phenylbenzo[*b*]thiophene (6z). Brown solid; 76% yield (46.0 mg): mp 103.5–104.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.58–7.57 (m, 2H), 7.55–7.52 (m, 1H), 7.50–7.43 (m, 4H), 3.05 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.5, 138.4, 136.7, 131.6, 130.6, 129.8, 128.0, 127.3, 126.2, 125.9, 124.5, 122.0, 51.0, 7.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}D_3O_2S_2^+$ 292.0540; Found 292.0538.



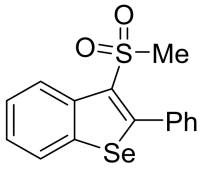
3-(Isopropylsulfonyl)-2-phenylbenzo[b]thiophene (6aa). White solid; 67% yield (42.4 mg): mp 124.2–124.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.58–7.56 (m, 2H), 7.53–7.50 (m, 1H), 7.48–7.42 (m, 4H), 3.18–3.11 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.9, 138.4, 136.9, 131.7, 130.7, 129.7, 127.8, 126.3, 126.1, 125.8, 124.7, 121.9, 55.7, 15.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{17}O_2S_2^+$ 317.0664; Found 317.0663.



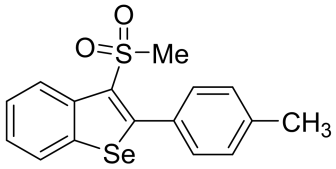
3-(Sec-butylsulfonyl)-2-phenylbenzo[*b*]thiophene (6ab). Yellow oil; 65% yield (43.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.58–7.56 (m, 2H), 7.53–7.50 (m, 1H), 7.48–7.42 (m, 4H), 2.92–2.86 (m, 1H), 1.90–1.84 (m, 1H), 1.45–1.37 (m, 1H), 1.17 (d, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.7, 138.3, 136.9, 131.7, 130.7, 129.7, 127.8, 126.7, 126.1, 125.8, 124.7, 121.9, 61.6, 22.0, 12.1, 11.2.



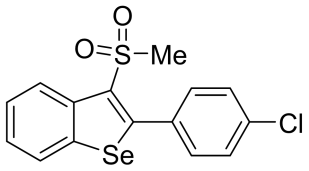
3-(Pentan-3-ylsulfonyl)-2-phenylbenzo[*b*]thiophene (6ac). Colourless oil; 61% yield (42.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.60–7.58 (m, 2H), 7.54–7.51 (m, 1H), 7.49–7.43 (m, 4H), 2.75–2.71 (m, 1H), 1.82–1.75 (m, 2H), 1.66–1.59 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.2, 138.4, 137.0, 131.7, 130.8, 129.8, 127.8, 127.6, 126.1, 125.8, 124.7, 122.0, 67.0, 20.0, 11.3.



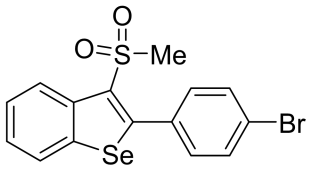
3-(Methylsulfonyl)-2-phenylbenzo[*b*]selenophene (7a). Yellow solid; 71% yield (47.6 mg): mp 138.7–140.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.55–7.52 (m, 3H), 7.44–7.41 (m, 4H), 3.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.6, 140.8, 138.0, 133.8, 131.9, 129.7, 129.5, 128.0, 126.4, 126.2, 126.1, 125.1, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{13}O_2SSe^+$ 336.9796; Found 336.9796.



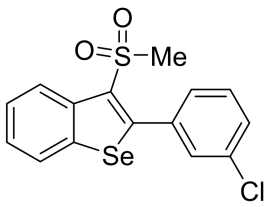
3-(Methylsulfonyl)-2-(*p*-tolyl)benzo[*b*]selenophene (7b). Yellow solid; 75% yield (52.4 mg): mp 156.7–158.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.53–7.51 (m, 1H), 7.42–7.39 (m, 3H), 7.24–7.23 (m, 2H), 3.00 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.9, 140.7, 139.6, 138.1, 131.7, 130.8, 129.6, 128.7, 126.3, 126.1, 125.9, 125.1, 45.0, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_2SSe^+$ 350.9952; Found 350.9951.



2-(4-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]selenophene (7c). Yellow solid; 70% yield (51.8 mg): mp 179.6–180.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.56–7.54 (m, 1H), 7.46–7.43 (m, 3H), 7.41–7.40 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.2, 140.8, 137.9, 135.8, 132.21, 132.17, 131.0, 128.2, 126.4, 126.3, 125.2, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2SSe^+$ 370.9406; Found 370.9404.

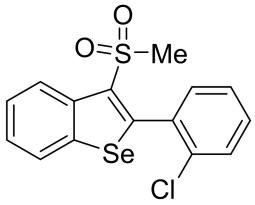


2-(4-Bromophenyl)-3-(methylsulfonyl)benzo[*b*]selenophene (7d). Pale yellow solid; 61% yield (50.5 mg): mp 163.7–164.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.57–7.54 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.40–7.38 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.2, 140.8, 137.9, 132.7, 132.2, 131.23, 131.21, 126.4, 126.3, 125.2, 124.1, 45.1.

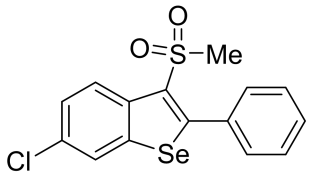


2-(3-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]selenophene (7e). Yellow solid; 68% yield (50.3 mg): mp 158.6–159.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J*

= 8.4 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.57–7.54 (m, 1H), 7.49 (s, 1H), 7.46–7.40 (m, 3H), 7.38–7.35 (m, 1H), 3.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.6, 140.9, 137.7, 135.5, 133.9, 132.4, 129.5, 129.4, 129.1, 128.1, 126.39, 126.35, 125.2, 45.2.



2-(2-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]selenophene (7f). Yellow solid; 67% yield (49.5 mg): mp 161.4–161.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.57–7.55 (m, 1H), 7.48–7.44 (m, 3H), 7.40–7.37 (m, 1H), 7.35–7.33 (m, 1H), 3.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.8, 141.4, 137.2, 133.3, 133.2, 132.7, 131.3, 130.6, 129.4, 126.4, 126.34, 126.28, 126.1, 125.4, 43.7.



6-Chloro-3-(methylsulfonyl)-2-phenylbenzo[*b*]selenophene (7g). Pale yellow solid; 72% yield (53.2 mg): mp 184.7–185.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.53–7.51 (m, 3H), 7.48–7.43 (m, 3H), 2.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 139.6, 139.2, 133.4, 131.4, 129.8, 129.6, 129.2, 129.1, 128.1, 126.3, 120.6, 45.2.

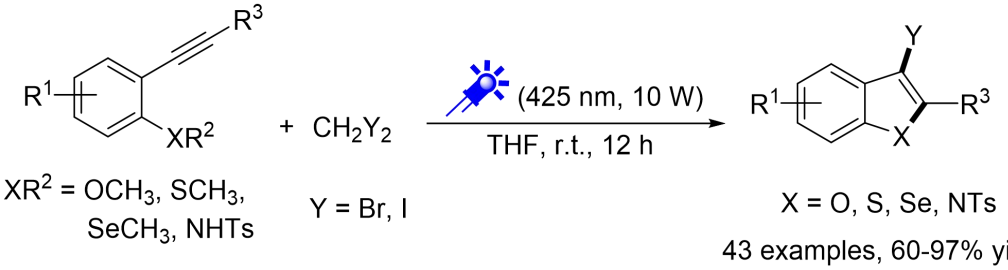
4.7 本章小结

总之，我们发展了一种可见光促进 DABSO 与邻炔基苯甲硫醚串联环化合成 3-烷基磺酰基苯并噻吩的高效方法。该方法无需外加光催化剂和金属催化剂，机理研究表明，DABSO 和邻炔基苯甲硫醚之间可能发生了相互作用，使 C-S 键断裂。实验室正在进一步研究反应机理，进一步拓宽该方法的应用。

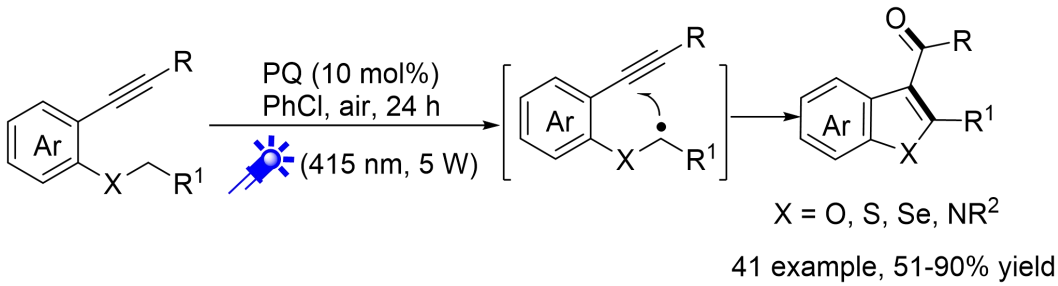
第 5 章 全文总结

研究了可见光促进的 2-炔基苯甲（硫、硒）醚等参与的串联环化反应。发展了 C3 官能化苯并噻吩、苯并硒吩、苯并呋喃和吲哚合成新方法。

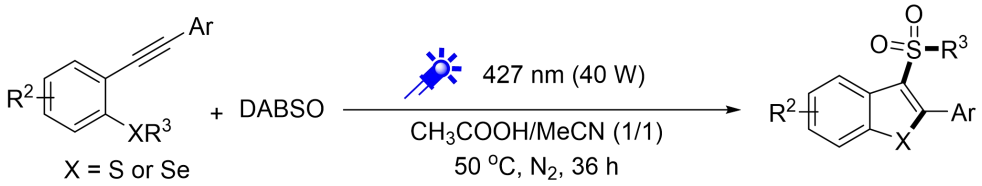
（1）无外加光敏剂条件下可见光促进 2-炔基苯甲硫醚与简单烷基卤化物串联环化反应合成 3-卤代苯并噻吩。在温和条件下以 60-97%的收率合成了一系列 3-卤代苯并噻吩、苯并硒吩、苯并呋喃和吲哚。



（2）可见光促进 2-炔基苯甲硫醚分子内环化氧化合成 3-酰基苯并噻吩。以 PQ 为催化剂，空气中的氧气作为氧化剂，在温和条件下以 51-90%的收率合成了一系列 3-酰基苯并杂环。



（3）可见光促进 DABSO 与邻炔基苯甲硫醚串联环化合成 3-烷基磺酰基苯并噻吩。在无外加光敏剂条件下，以 44-95%的收率合成了 31 个 3-烷基磺酰基苯并噻（硒）吩。



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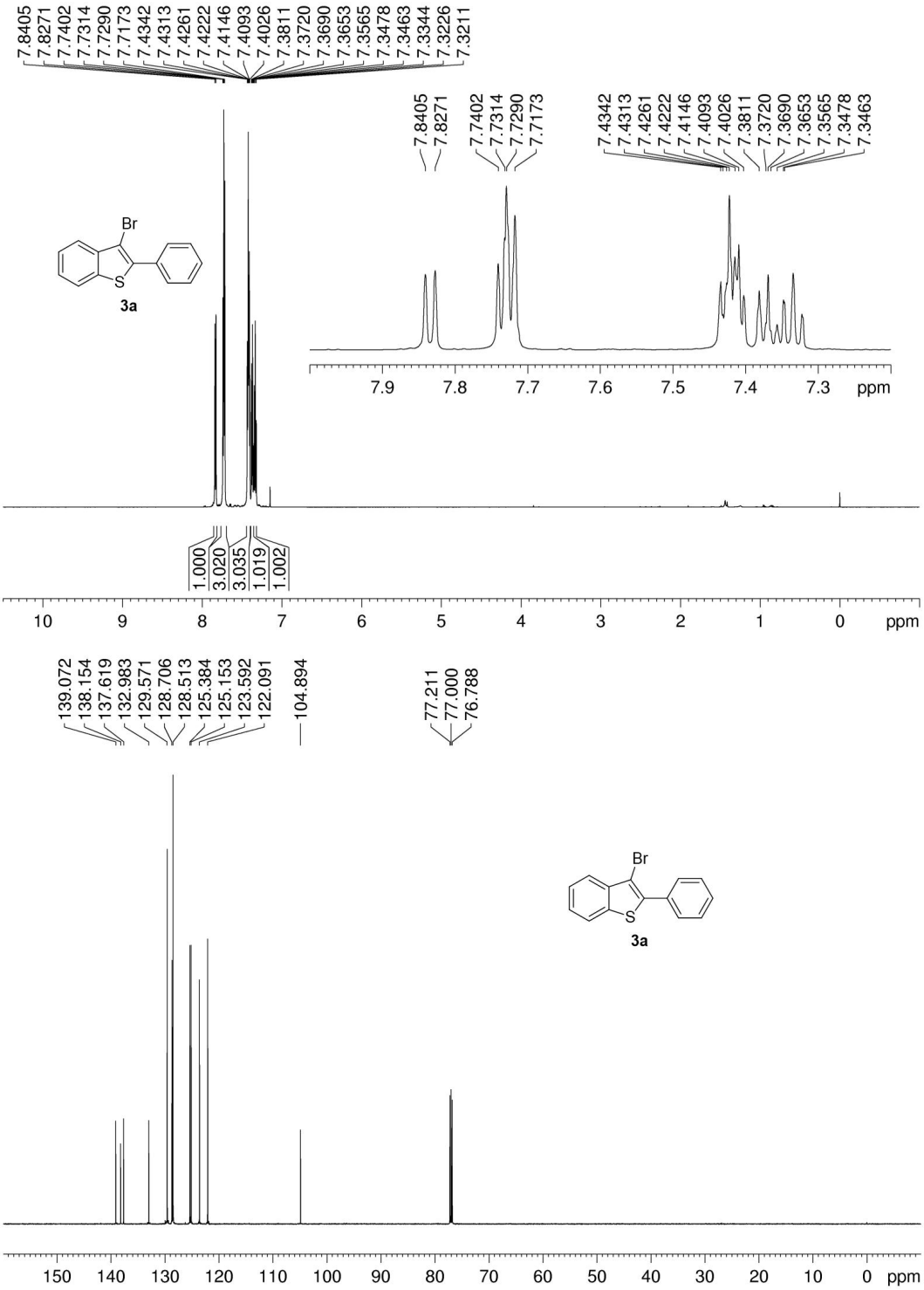
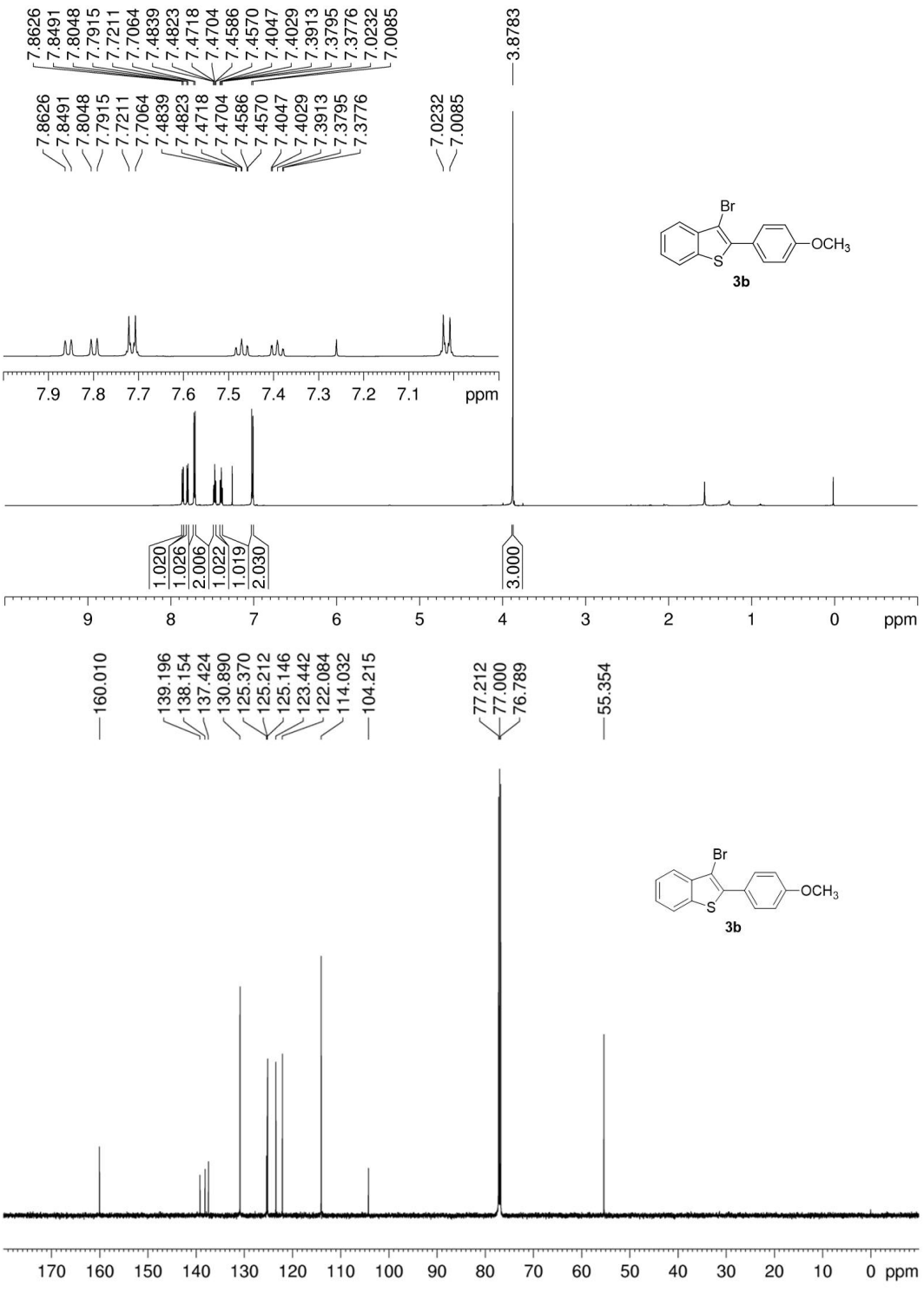
附录 I 部分化合物的谱图

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7.4570
7.4047
7.4029
7.3913
7.3795
7.3776
7.0232
7.0085
3.8783
Br
OCH3
S
3b
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
1.020
1.026
2.006
1.022
1.019
2.030
3.000
9 8 7 6 5 4 3 2 1 0 ppm
160.010
139.196
138.154
137.424
130.890
125.370
125.212
125.146
123.442
122.084
114.032
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3b
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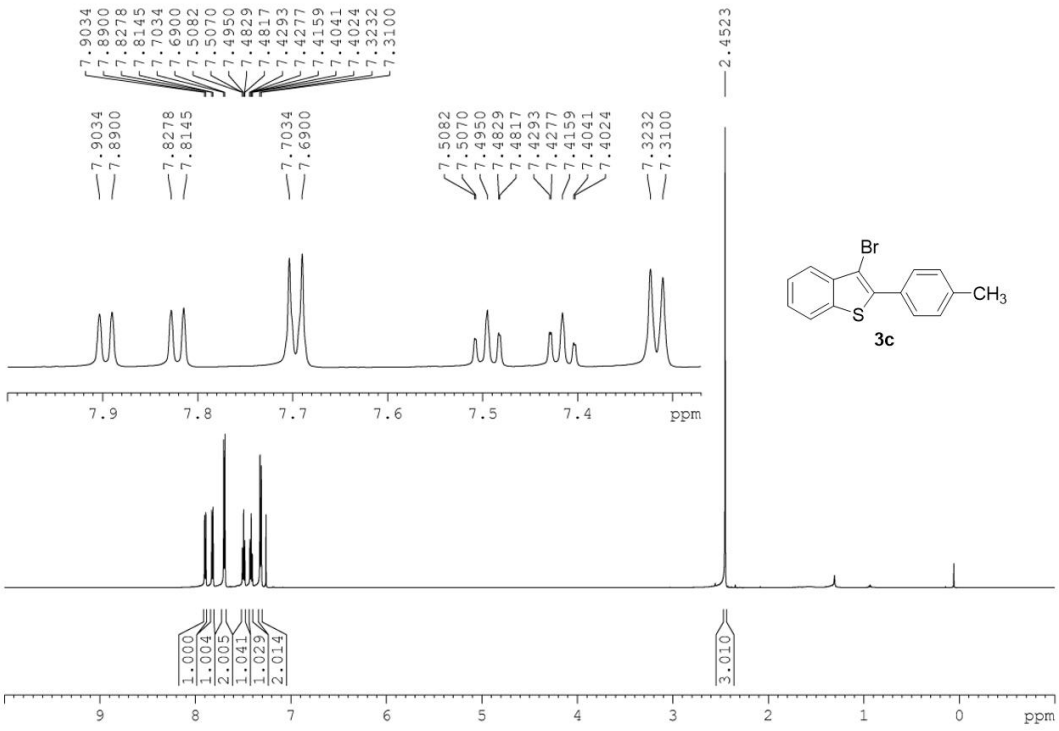
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7.4293
7.4277
7.4159
7.4041
7.4024
7.3232
7.3100
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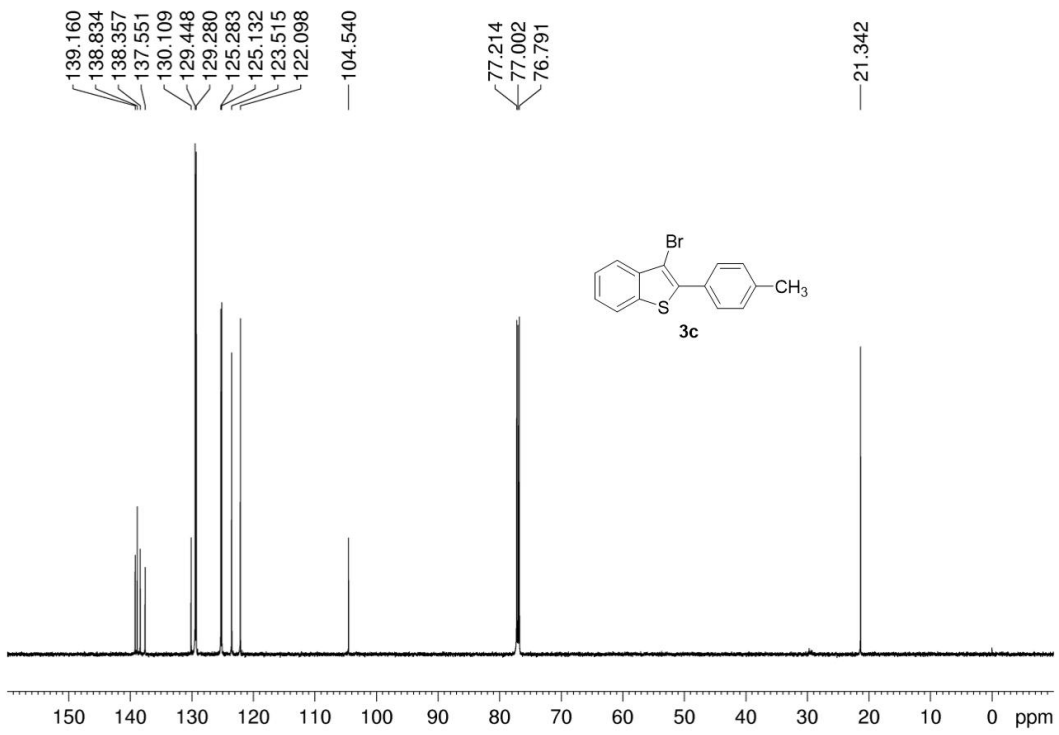
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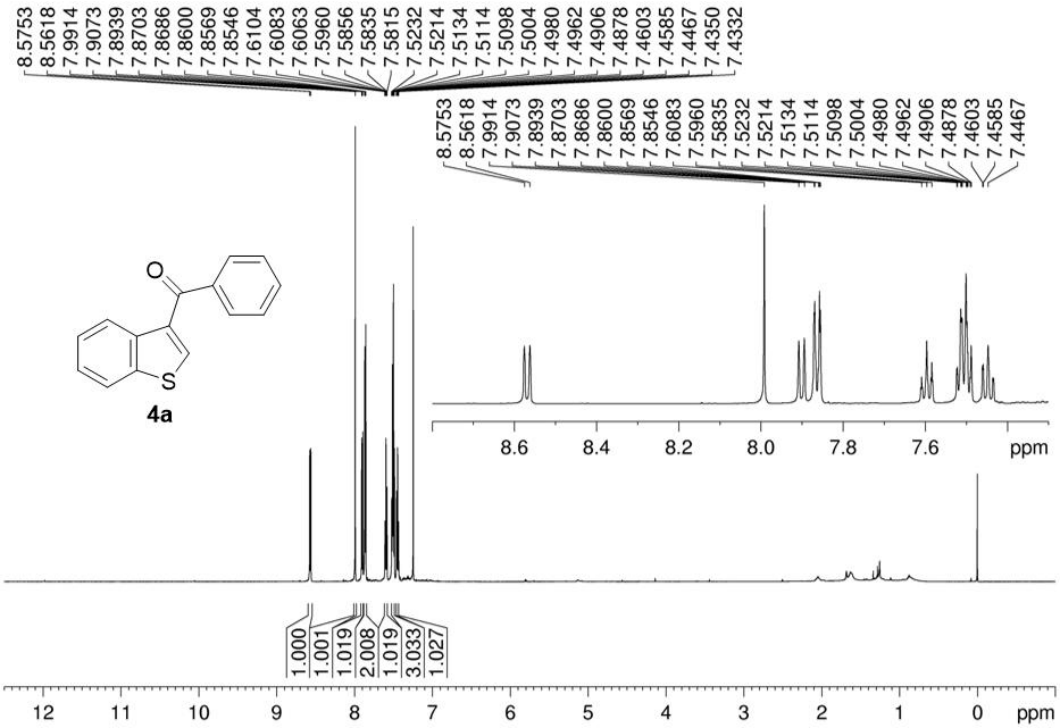
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O
S
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7.6
ppm
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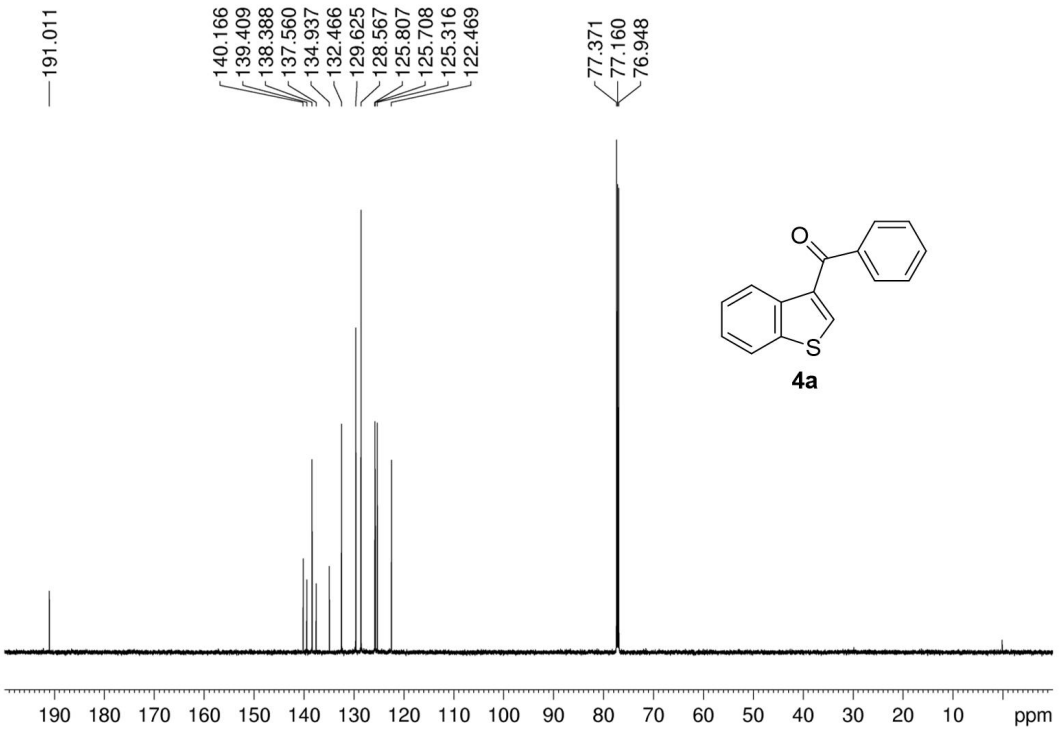
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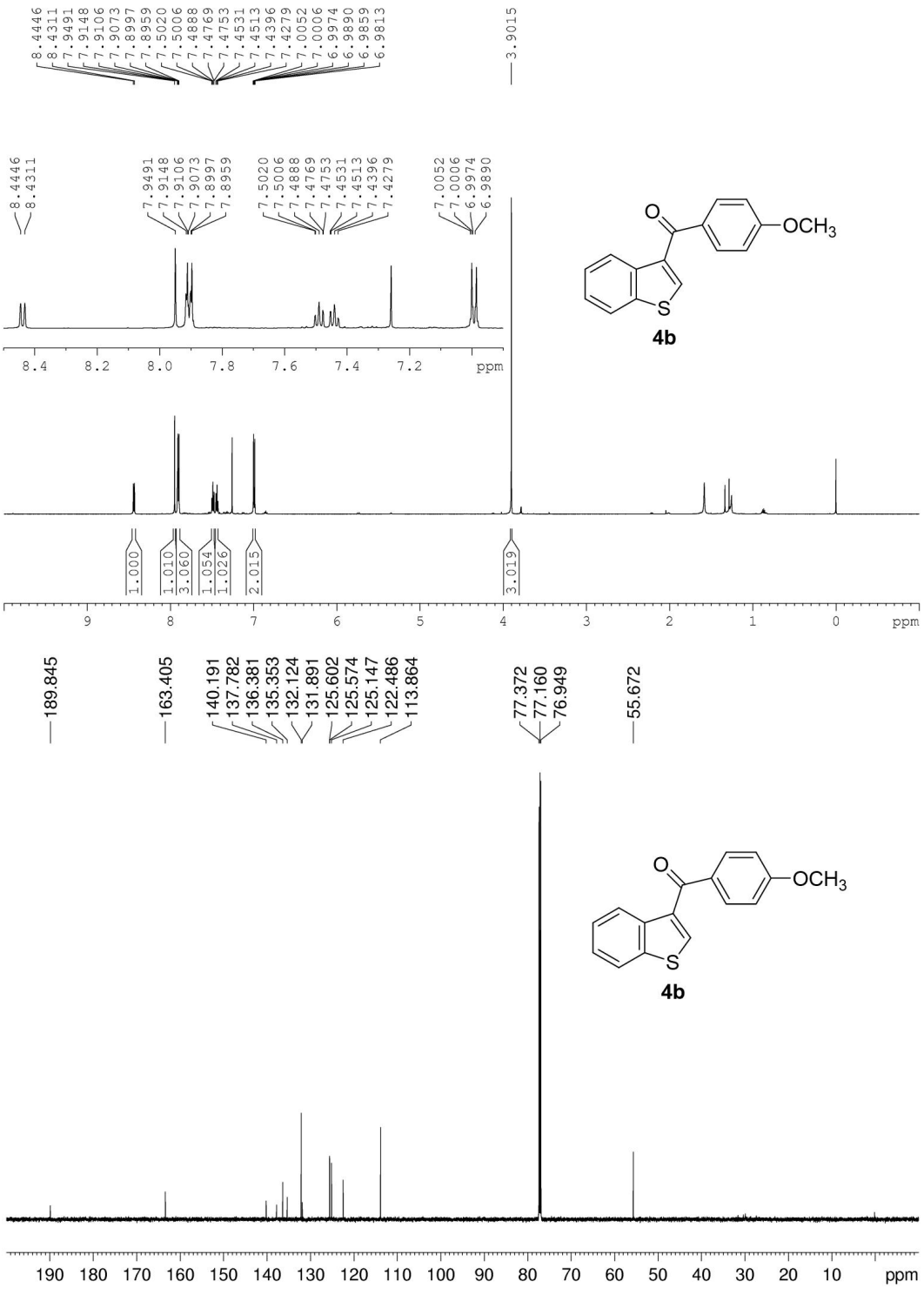
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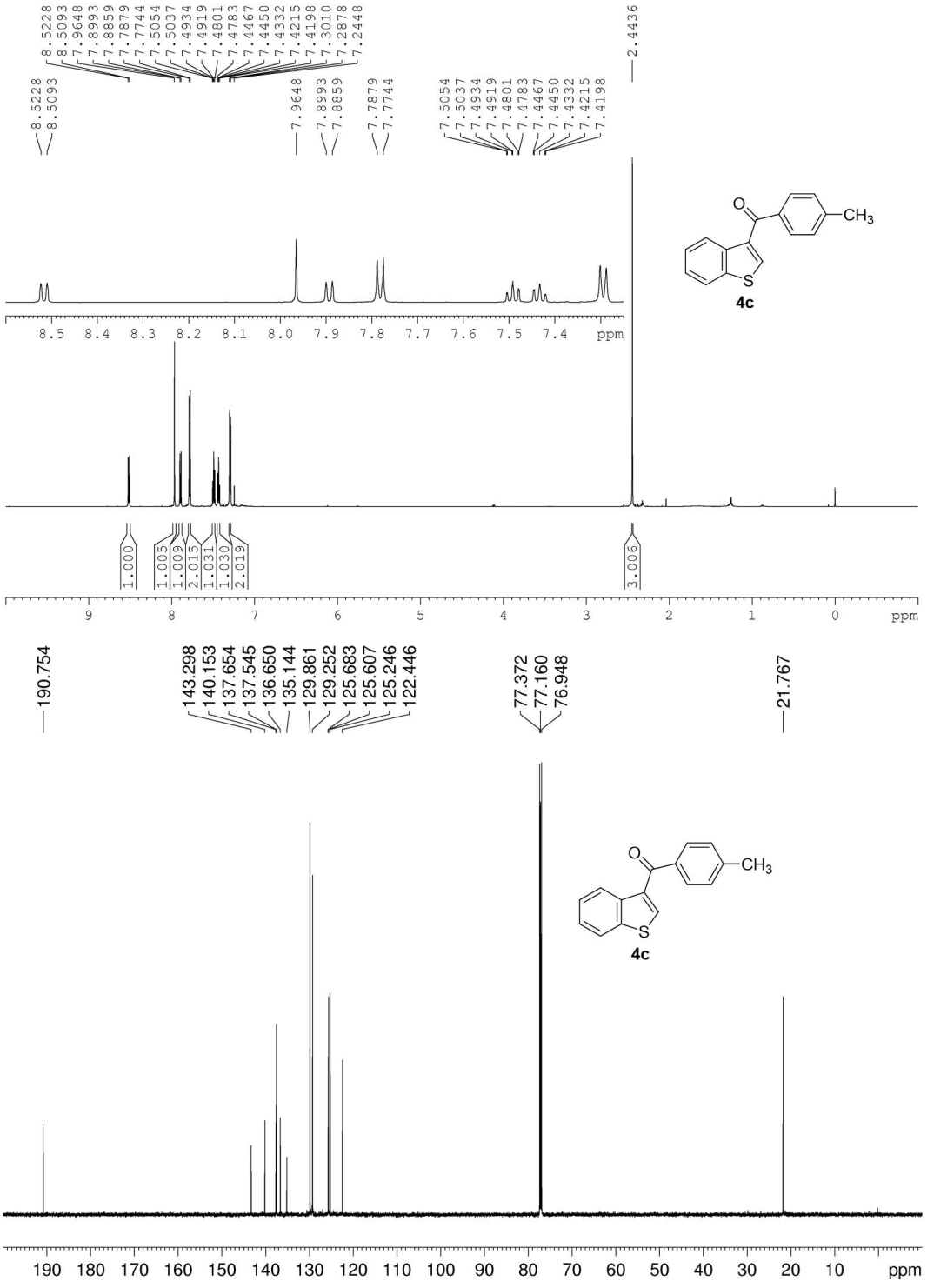
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S
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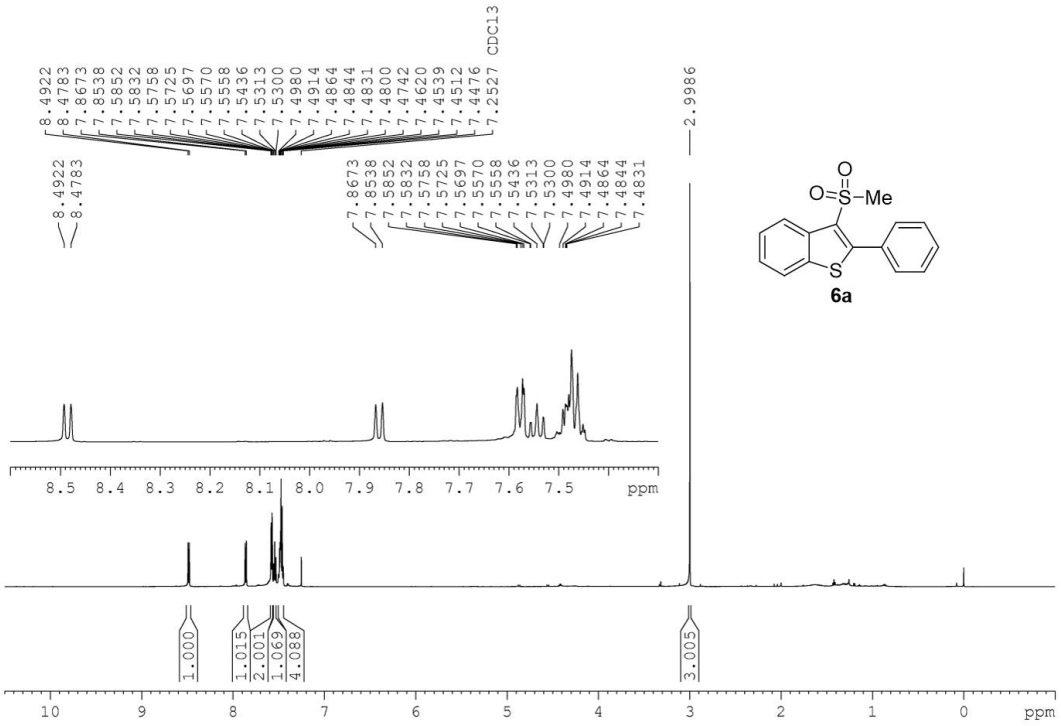
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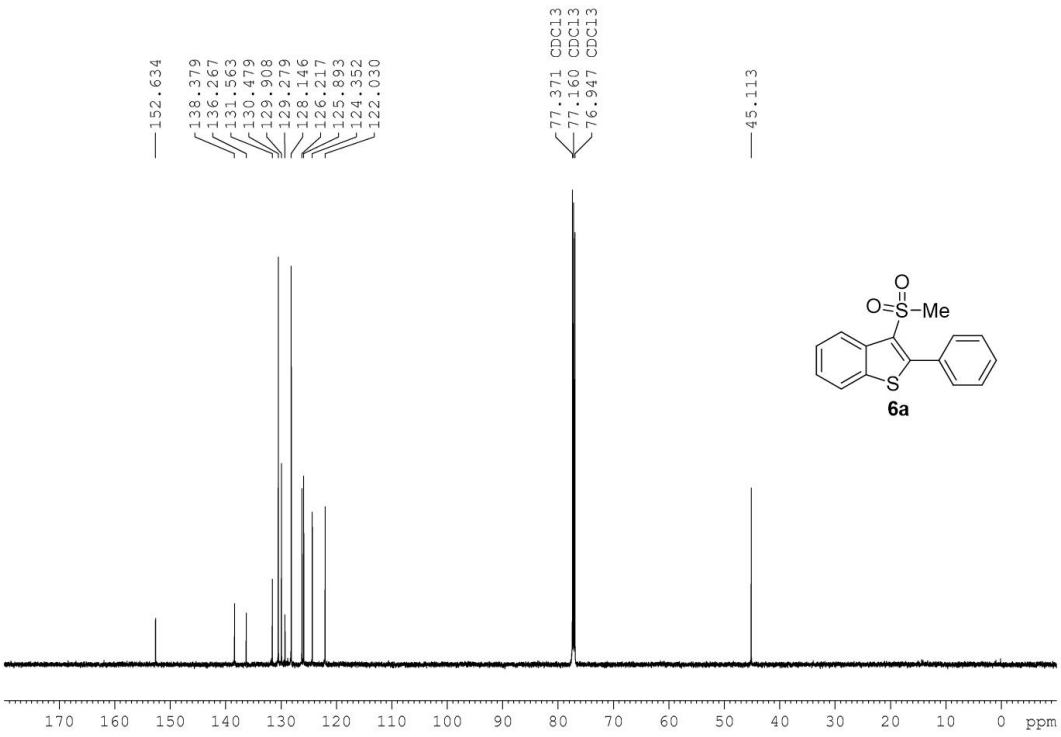
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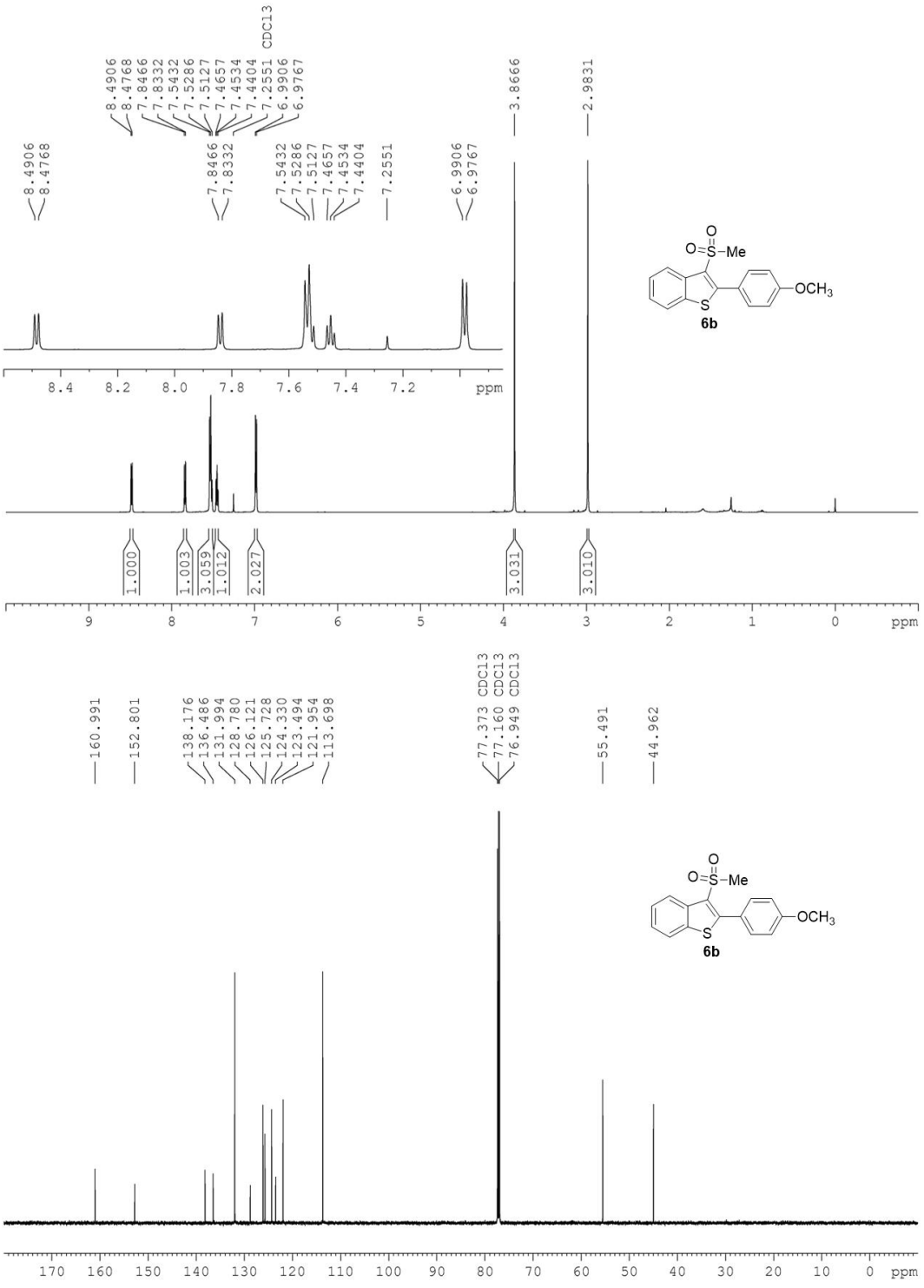
6a
ppm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S
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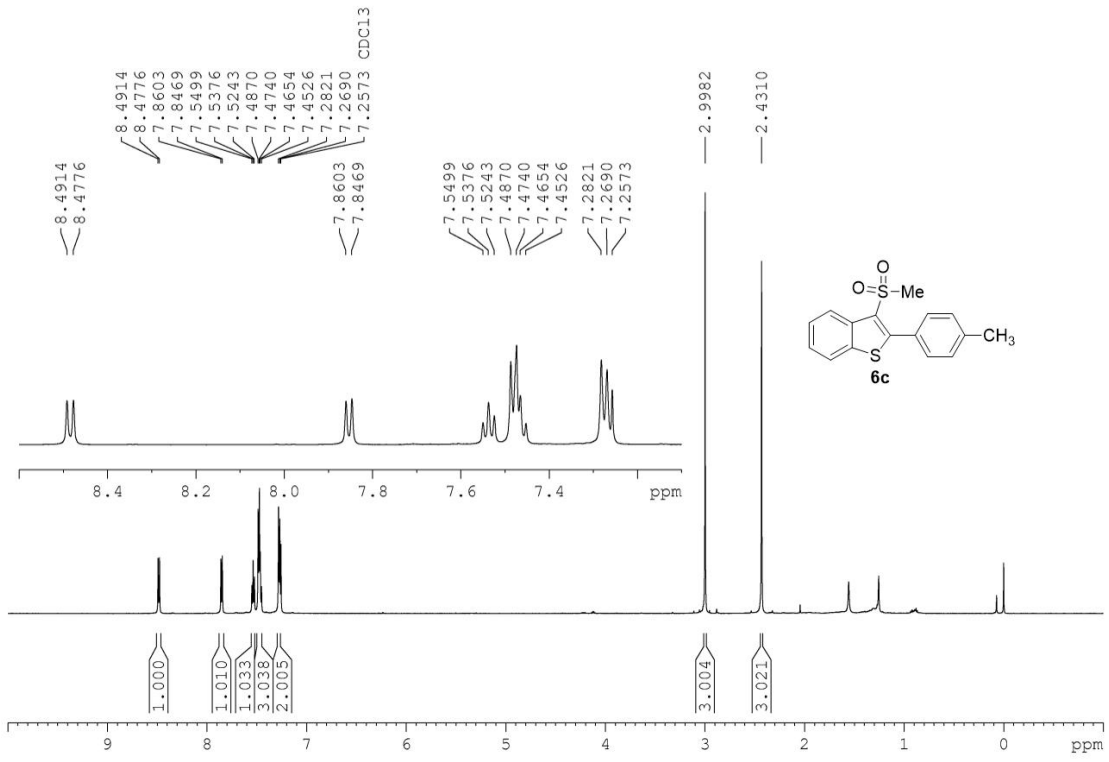
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S
6c
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7.4
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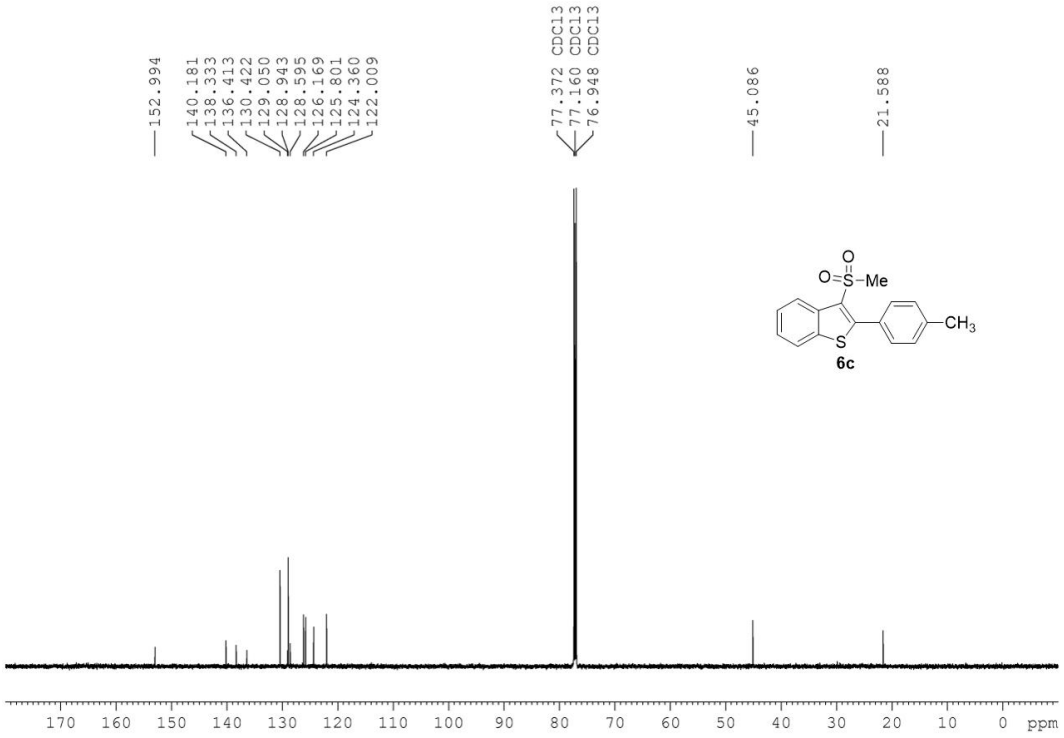
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21.588
O
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CH3
S
6c
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160
150
140
130
120
110
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70
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50
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附录II 硕士期间发表及待发表论文

[1] **Fen-Dou Wang**, Chunmiao Wang, Min Wang*, Han Yan, Jin Jiang and Pinhua Li*, Visible-light-induced halocyclization of 2-alkynylthioanisoles with simple alkyl halides towards 3-halobenzo[*b*]thiophenes without an external photocatalyst. *Org. Biomol. Chem.*, **2023**, *21*, 8170–8175.

[2] Han Yan, **Fen-Dou Wang**, Min Wang,* Liang Ye, and Pinhua Li*, Photoinduced Radical Cyclization of 2- Alkynylthioanisoles with Disulfides without an External Photocatalyst. *J. Org. Chem.* **2023**, *88*, 15288–15297.

致谢

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