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TITLE: Visible Light Promotes the Cascade Reaction involving 2-Alkynylthioanisoles: Three New Strategies for The Synthesis of C3-Substituted Benzothiophenes

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可见光促进邻炔基苯甲硫醚参与的串联反应合成 C3-取代苯并噻吩

摘要

苯并噻吩是一种重要的含硫杂环化合物，广泛存在于多种天然物质及具有生理活性及药用价值的分子中。苯并噻吩类化合物在医药和农药领域展现出良好的应用潜力，其作为母核存在于多种药物分子中。此外，苯并噻吩也常被应用于有机光电材料及半导体材料的开发研究。鉴于苯并噻吩的广泛用途，其合成策略的创新研究受到了合成化学界的重视。可见光促进的有机反应是有机合成化学的研究热点，该方法具有环境友好性和反应条件温和等优点，已成为不可或缺的合成技术。本论文围绕可见光促进邻炔基苯甲硫醚参与的串联反应，研究 C3-取代苯并噻吩的合成，发展苯并噻吩及其衍生物合成的新方法，主要开展了以下三个研究工作：

1. 发展了可见光促进邻炔基苯甲硫醚和二硫醚串联环化反应，合成了系列 C3-苯硫基苯并噻吩新化合物，发展了 C3-苯硫基取代苯并噻吩的合成新策略。对反应条件进行了优化，在最佳反应条件下，以 32-92%的产率扩展了 38 个反应底物。自由基捕获试验、荧光淬灭实验表明该反应可能经历自由基历程。与已报道的方法相比，该方法具有条件温和、无外加光敏剂、底物广谱性好等优点。

2. 发展了光诱导过硫酸钾氧化的邻炔基苯甲硫醚，1, 4-二氮杂双

环[2.2.2]辛烷-1,4-二鎓-1,4-二亚磺酸（DABSO）和 4-取代汉斯酯三分子串联反应，合成了系列 C3-烷基磺酰基苯并噻吩化合物。对反应条件进行了优化，在最佳反应条件下，以 42-91%的产率合成了 33 例目标产物。自由基捕获试验、开关灯实验表明该反应可能经历自由基历程。与其他已报到方法相比，该反应无需外加光敏剂，具有条件温和、无金属参与等优点。

3. 发展了可见光促进单质硫和硒参与邻炔基苯甲硫醚的串联环化反应，合成了系列双（3-苯并[*b*]噻吩基）硫（硒）醚新化合物。对反应条件进行了优化，在最佳反应条件下，以 43-84%的产率合成了 14 个双（3-苯并[*b*]噻吩基）硫醚，以 23-55%的产率合成了 14 个 3-甲硒基苯并噻吩、同时以 12-29%的产率得到了 11 个双（3-苯并[*b*]噻吩基）硒醚。自由基捕获实验表明该反应可能经历自由基历程。与其他已报道的方法相比，该反应以廉价的硫（硒）粉作为硫（硒）源合成相应产物且无需外加光敏剂，具有反应体系环境友好、原子利用率高等优点。

关键词：邻炔基苯甲硫醚，苯并噻吩，光催化，自由基串联反应，三组分反应

Visible Light Promotes the Cascade Reaction involving 2-Alkynylthioanisoles: Three New Strategies for The Synthesis of C3-Substituted Benzothiophenes

ABSTRACT

Benzothiophene, a privileged sulfur-containing heterocyclic scaffold, is pervasively distributed in naturally occurring substances and bioactive molecules with pharmaceutical relevance. Its derivatives exhibit remarkable therapeutic potential in medicinal chemistry and agrochemical development, serving as core structures in diverse drug entities such as raloxifene (selective estrogen receptor modulator), sertaconazole (antifungal agent), and mobucin (bioactive insecticide). Beyond pharmacological applications, benzothiophene have emerged as pivotal building blocks in optoelectronic materials and semiconductor technologies. Given its multidisciplinary significance, innovative synthetic methodologies for benzothiophene derivatives remain a frontier in contemporary synthetic chemistry. Visible-light-mediated transformations, recognized for their environmental benignity and mild operational conditions, have evolved into indispensable tools in modern organic synthesis. This dissertation focuses on visible-light-induced

tandem reactions involving o-alkynylthioanisoles to establish novel synthetic protocols for C3-functionalized benzothiophenes, with three principal research achievements:

1. We established an innovative visible-light-driven tandem cyclization protocol between o-alkynylthioanisoles and disulfides, enabling the construction of novel C3-thioarylated benzothiophene derivatives. Systematic optimization of reaction parameters afforded an operationally simple system that achieved 32-92% isolated yields with remarkable substrate scope encompassing 38 structurally diverse derivatives. Mechanistic investigations via radical trapping experiments (TEMPO/BHT) and fluorescence quenching studies provided compelling evidence suggesting a plausible radical-involved mechanism. Compared to existing methodologies, this exogenous photosensitizer-free protocol exhibits distinct advantages including mild conditions, exceptional functional group tolerance, and precise regiocontrol at the C3-position.

2. We developed a metal-free, three-component tandem cyclization protocol involving photoinduced persulfate-mediated oxidation of *o*-alkynylthioanisoles with 1,4-diazabicyclo[2.2.2]octane-1,4-disulfonic acid (DABSO) and 4-substituted Hantzsch esters. This strategy enabled efficient construction of C3-alkylsulfonylated benzothiophenes through sequential radical sulfonylation and annulation processes. Systematic parameter optimization afforded 33 derivatives in 42–91% isolated yields

with excellent functional group compatibility. The experiment of free radical capture and switch lamp showed that the reaction may undergo free radical process. Compared with other reported methods, the reaction does not require additional photosensitizers, and has the advantages of mild conditions and no metal involvement.

3. We devised a visible-light-enabled tandem cyclization system employing elemental sulfur/selenium with o-alkynylthioanisoles for modular synthesis of bis(3-benzo[b]thienyl) sulfides/selenides. Through systematic optimization, this protocol delivered 14 bis(3-benzo[b]thienyl) sulfides (43–84% yield), 14 3-methylseleno-benzothiophenes (23-55%), and 11 bis(3-benzo[b]thienyl) selenides (12-29%). The experiment of free radical trapping showed that the reaction may undergo free radical process. Compared with other reported methods, the reaction uses cheap sulfur (selenium) powder as the source of sulfur (selenium) to synthesize corresponding products without additional photosensitizer, which has the advantages of environmentally friendly reaction system and high atomic utilization.

Yan Han (Chemistry)

Supervised by Li PinHua

KEY WORDS: *o*-Alkynylthioanisole, Benzothiophene, Photocatalysis, Radical tandem reaction, Three-component reaction

目录

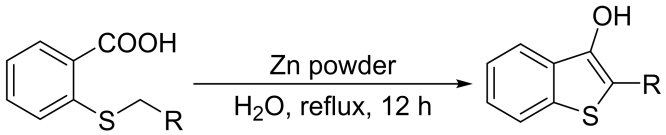
第 1 章 绪论

1.1 引言

含硫杂环化合物因其独特的生物活性，在医药、农药及材料科学等多个领域展现出重要的应用价值[1]。苯并噻吩是一类重要的含硫杂环，是某些天然产物和药物分子的核心结构。研究表明，此类化合物展现出包括抗菌[2]、抗癌[3-4]、抗氧化[5]、抗 HIV[6-7]及抗炎[8-9]等多种药理活性，成为药物化学研究的重要分子骨架。此外，其在有机光电材料[10-13]与有机半导体材料[14-18]等领域亦发挥重要作用。基于苯并噻吩体系的多元化应用前景，其合成方法学一直受到合成化学工作者的关注。本章将介绍近年来苯并噻吩及其衍生物合成的最新研究进展。

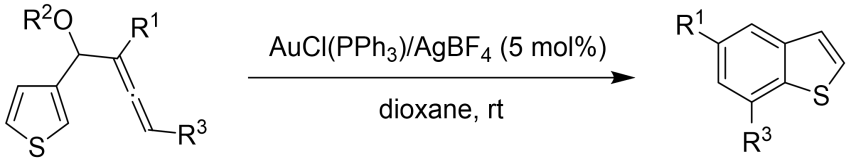
1.2 过渡金属催化或促进的苯并噻吩及其衍生物合成

2013 年，Wang[19]课题组报道了一种以水为单一介质金属锌促进条件下实现的 2-取代-3-羟基苯并[*b*]噻吩的高效合成。作者通过密度泛函理论（DFT）计算表明，该反应在能量学上有两种可能的途径：其一为中性途径，经历 C-C 键形成与氢转移的协同过程；其二为阴离子途径，其中阴离子攻击羰基是该反应的决速步骤。水分子在这两种反应途径中都起到了关键作用（Scheme 1-1）。



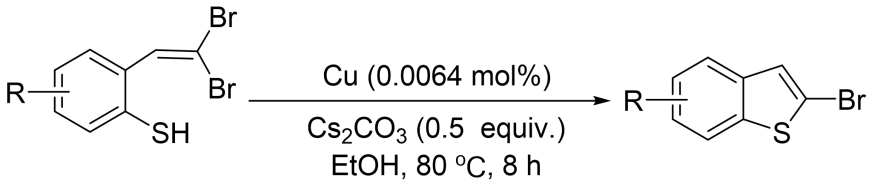
Scheme 1-1 锌促进 2-（芳乙基硫代）苯甲酸环化合成 2-取代-3-羟基苯并[b]噻吩

2013 年，Ma[20]课题组通过金催化 1-（3-噻吩）-2, 3-二烯基乙酸酯发生环化反应，发展了一种温和条件下制备苯并[*b*]噻吩衍生物的新策略，为含硫杂环化合物的构建提供了新思路。机理研究表明该反应可能通过金卡宾中间体或芳基金中间体两种路径进行（Scheme 1-2）。



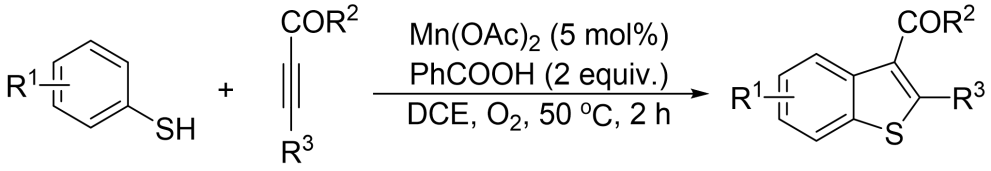
Scheme 1-2 金催化 1-（3-噻吩）-2, 3-二烯基乙酸酯环化合成苯并[*b*]噻吩

2013 年，Wang[21]报道了微量铜（0.0064 mol%，25 ppm）催化下 2-乙烯基偕二溴苯硫酚的分子内环化反应，成功实现了无氟条件下 2-溴代苯并噻吩的高效合成。该体系展现出良好的催化效率，且反应条件温和、产率优异（Scheme 1-3）。



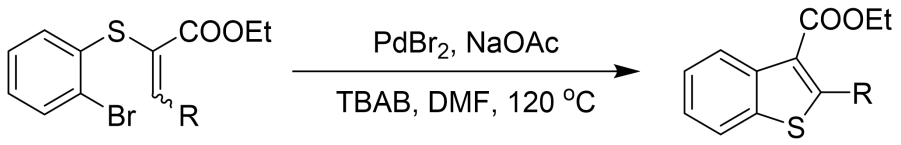
Scheme 1-3 铜催化 2-乙烯基偕二溴苯硫酚环化合成 2-溴代苯并噻吩

2013 年，Li 课题组[22]报道了一种醋酸锰催化苯硫酚与炔烃分子间氧化环化构建苯并噻吩骨架的新方法。该方法可以合成多种多功能苯并噻吩，且所得到的苯并噻吩可以用于进一步转化，有效、选择性的得到各种苯并噻吩衍生物（Scheme 1-4）。



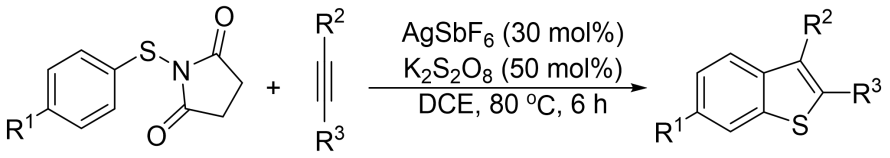
Scheme 1-4 金属锰催化苯硫酚与炔烃氧化环化合成苯并噻吩

2016 年，Gong[23]课题组通过溴化钯催化 3-取代-2-(苯硫基)丙烯酸乙酯合成苯并[*b*]噻吩。在优化后的反应条件下，含芳基及烷基取代基的底物能以较理想的产率生成目标产物，然而向底物结构中引入杂芳基取代基时，则产率显著下降甚至无法生成目标产物（Scheme 1-5）。



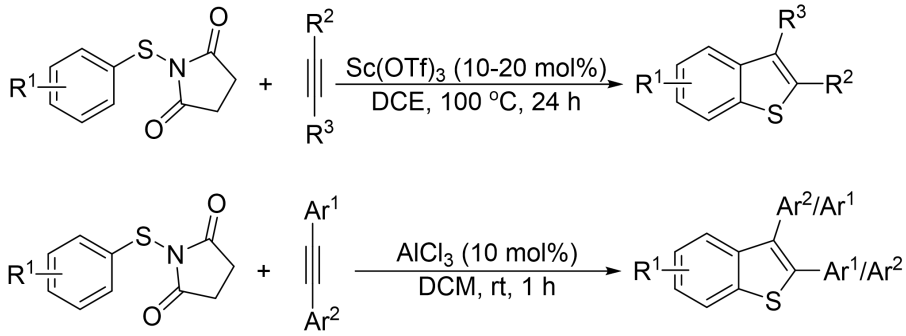
Scheme 1-5 溴化钯催化 3-取代基-2-(苯硫基)丙烯酸乙酯合成 3-取代苯并噻吩

2016 年，Sahoo[24]小组报道了一种通过银催化 *N*-芳硫基琥珀酰亚胺和非活化内炔烃分子间氧化环化合成 2, 3-二芳基苯并[*b*]噻吩的高效方法。该反应展现出了良好的广谱性，能够高效构筑多种具有π共轭特性的 2, 3-二芳基取代苯并[*b*]噻吩。实验证明，该反应通过 S-N 键氧化断裂、炔烃环化协同 1, 2-硫迁移过程实现目标产物的合成（Scheme 1-6）。



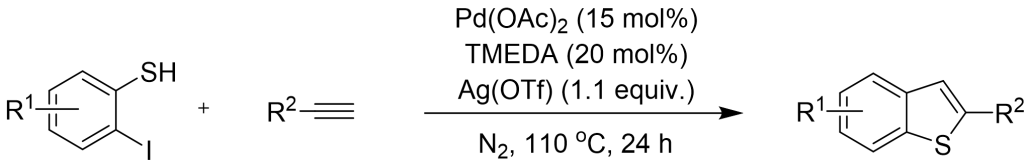
Scheme 1-6 银催化 *N*-芳硫基琥珀酰亚胺与炔烃氧化环化 2, 3-二芳基苯并[*b*]噻吩

2016 年，Glorius[25]课题组利用 $Sc(OTf)_3$ 催化 *N*-芳硫基琥珀酰亚胺与炔烃发生分子间环化反应，高效的合成了一系列 6-取代苯并[*b*]噻吩。理论计算揭示乙烯基阳离子的亲电性异位环化生成螺环钛中间体的迁移过程是该反应的关键步骤（Scheme 1-7）。随后，Sahoo[26]小组又开发了室温条件下 $AlCl_3$ 催化 *N*-芳硫基琥珀酰亚胺与炔烃的氧化环化体系，同样成功构建了多种具有π-共轭特性的 6-取代 2, 3-二芳基苯并[*b*]噻吩衍生物（Scheme 1-7）。



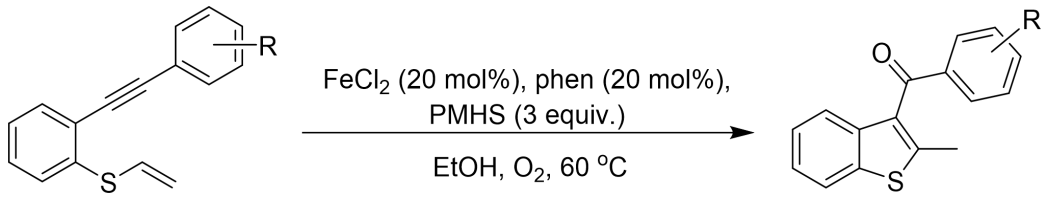
Scheme 1-7 $Sc(OTf)_3$/$AlCl_3$ 催化 N-芳硫基琥珀酰亚胺与炔烃合成苯并噻吩

2017 年，Zhou[27]课题组发展了一种基于钯(II)催化 2-碘代苯硫酚与苯乙炔的 Sonogashira 偶联反应，实现 2-取代苯并[*b*]噻吩的高效合成。作者使用该方法以中等至优良的收率（最高 87%）合成了一系列 2-取代苯并[*b*]噻吩。该方法具有起始原料易得、操作简单、产率良好的优点（Scheme 1-8）。



Scheme 1-8 钯(II)催化 2-碘代苯硫酚与苯乙炔偶联合成苯并噻吩

2018 年，Wang[28]开发了利用铁(II)催化 1, 6-烯炔还原环化合成 3-酰基苯并噻吩的新方法。同位素标记实验证实反应经历了氢原子转移（HAT）/环化与氧插入的过程。该合成方法具有使用试剂的廉价、环保，实验过程简单、安全的优点（Scheme 1-9）。

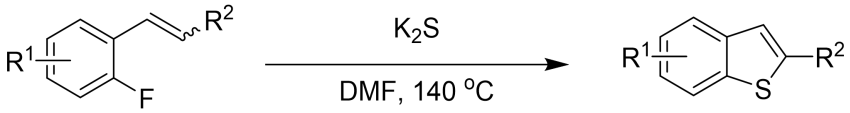


Scheme 1-9 铁催化 1, 6-烯炔的还原环化合成 3-酰基苯并噻吩

1.3 无金属参与的苯并噻吩及其衍生物合成

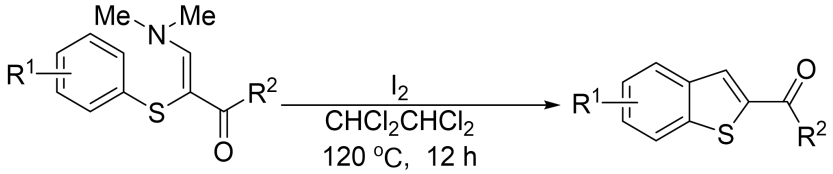
苯并噻吩作为重要的药物骨架，其合成方法学创新受到合成化学领域的高度重视。传统金属催化策略虽可实现高效构建，但存在催化剂残留影响药物纯度、贵金属成本高昂差等缺陷。基于绿色化学理念，无金属参与的苯并噻吩及其衍生物合成方法逐渐成为研究热点。

2013 年，Liang[29]小组开发了邻卤代苯乙烯与硫化钾制备 2-取代苯并[*b*]噻吩的高效合成方法。该反应对多种官能团均有良好的耐受性，并且在没有过渡金属催化剂参与的条件下，以高收率获得相应的目标产物（Scheme 1-10）。



Scheme 1-10 邻卤代苯乙烯与硫化钾制备 2-取代苯并[*b*]噻吩

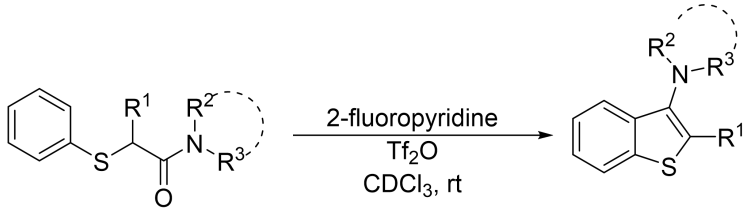
2014 年，Tamariz[30]课题组报道了一种通过碘介导芳基胺酮环化合成 2-酰基苯并噻吩的高效合成方法。控制实验表明，芳硫代羰基的芳环上存在供电子基团有利于该反应的进行（Scheme 1-11）。



Scheme 1-11 碘促进烯胺酮环化合成 2-酰基苯并噻吩

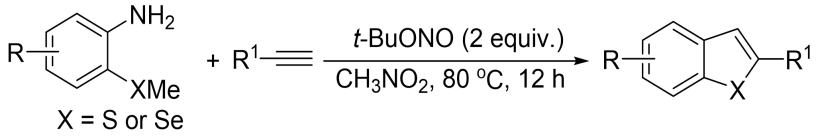
2015 年，Mesmaeker[31]课题组开发了一种使用α苯硫代乙酰胺高效合成 3-氨基苯并噻吩的方法。该方法利用相应酮胺中间体的 6π电环化反应精准合成目标产物 3-氨基苯并[*b*]噻吩。该电环化过程兼容 *N*-烯丙基及 *N*-二烯丙基保护基，经温和脱保护后可分别获得相应的伯胺与仲胺产物。在进一步的拓展中[32]，该课题组成功实现噻吩、呋喃及吡咯等五元杂环稠合的 3-氨基苯并噻吩/噻吩衍生物的定向合成。系统考察了芳环取代基、C-2 位修饰取代基及氮原子取代基的电子效

应对反应的影响（Scheme 1-12）。



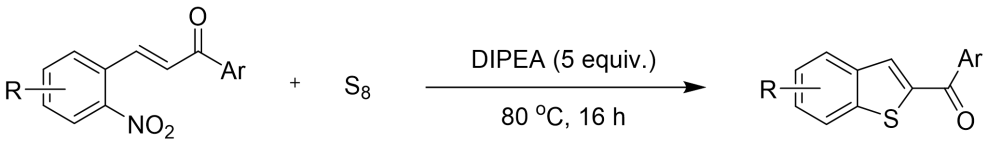
Scheme 1-12 α苯硫代乙酰胺环化合成 3-氨基苯并噻吩

2016 年，Zhang[33]通过邻甲硫（硒）基芳胺与炔烃的分子间自由基级联反应，成功构建苯并噻（硒）吩骨架。该反应具有区域选择性，能够以中等至良好收率获得目标产物，同时该方法可以应用于合成药物雷洛昔芬及 AT_1 受体拮抗剂的关键中间体（Scheme 1-13）。



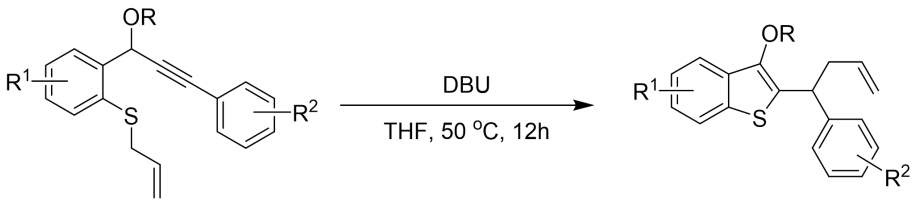
Scheme 1-13 邻甲硫（硒）基芳胺与炔烃分子间级联反应合成苯并噻（硒）吩

2017 年，Nguyen 和 Retailleau[34]发现 DIPEA 促进 2-硝基查耳酮与单质硫串联反应的优良硫活化剂。经实验证明，该反应历经烯烃 C=C 键硫化与芳香环硫代-脱硝化级联过程，最终得到了一系列 2-苯甲酰基苯并噻吩。该反应具有操作简单，原子效率高，不需要任何过渡金属催化剂的优点（Scheme 1-14）。



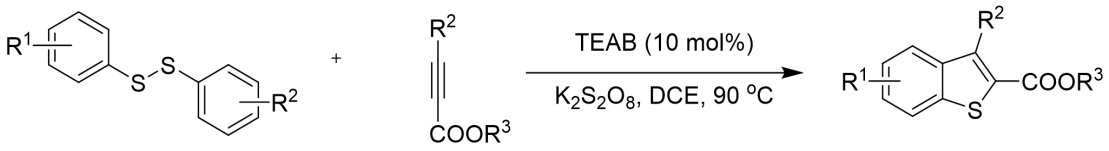
Scheme 1-14 DIPEA 促进 2-硝基查耳酮与单质硫的串联反应合成 2-苯甲酰基苯并噻吩

2017 年，Zhou[35]发展了一种碱催化 3-烷氧基-3-(2-烯丙硫基苯基)-1-苯丙炔合成苯并噻吩高效新方法。该反应经过碱促进炔丙基-联烯基重排、环化及烯丙基迁移多步过程得到目标产物。反应条件经适当调整，磷取代吲哚类化合物也可通过该方法进行制备（Scheme 1-15）。



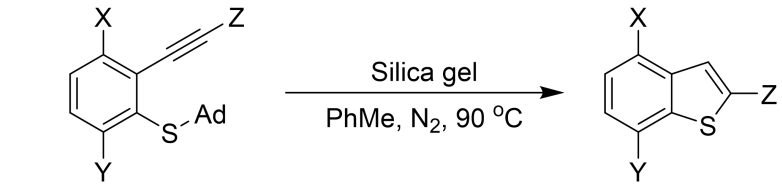
Scheme 1-15 碱催化 3-烷氧基-3-(2-烯丙硫基苯基)-1-苯丙炔环化合成苯并噻吩

2017 年，Wang 等人[36]报道了无金属参与的 *N*-Et_4NBr（TEAB）催化新体系，以易得二硫化物与炔烃为底物高效合成 2, 3-取代苯并噻吩。该方法通过 S-S 键均裂生成的芳硫自由基与碳碳叁键发生加成进而发生级联环化反应高效构筑苯并噻吩骨架。该方法展现出了良好的官能团耐受性，在克级规模仍保持良好的收率（Scheme 1-16）。



Scheme 1-16 溴化四乙铵催化二硫化物与炔烃制备苯并噻吩衍生物

2019 年，Toyota[37]通过在反应体系中加入硅胶、加热的方法，以 1-金刚烷硫基-2-炔基苯衍生物为反应底物，成功合成了 6 种相应的苯并[*b*]噻吩。相较于该课题组之前报道的氯化金催化体系，本方法有效抑制了金刚烷基的迁移现象。进一步拓展中，以 2-氟-3, 6-二卤苯甲醛为起始物，经四步反应以 42-82%的总收率获得 6 类 4, 7-二卤代苯并[*b*]噻吩（Scheme 1-17）。



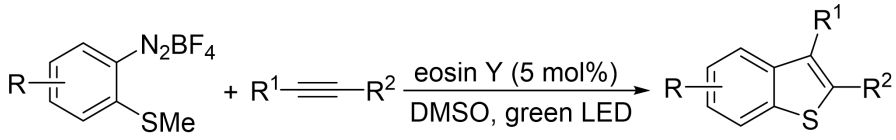
X, Y = Hal; Z = Hal or H

Scheme 1-17 硅胶、加热条件下 1-金刚烷硫基-2-炔基苯环化反应生成苯并[*b*]噻吩

1.4 光/电催化的苯并噻吩及其衍生物的合成

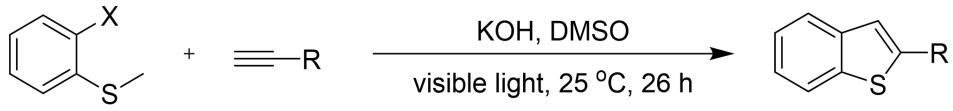
随着绿色化学的进一步发展，光/电催化合成作为可持续化学合成的新兴策略，在杂环化合物构建领域展现出独特优势。特别是在苯并噻吩及其衍生物的精准合成与功能化修饰方向，光/电催化体系因其环境友好性及精准可控性受到了化学工作者们的广泛关注。

2012 年，König[38]课题组报道了曙红 Y 催化的邻甲硫基芳基重氮盐与炔烃光氧化还原反应，通过自由基介导的环化过程选择性合成取代苯并噻吩。系统考察了重氮盐取代基与炔烃结构对反应的影响，结合光谱分析与理论计算揭示了绿光激发下曙红 Y 的电子转移机制（Scheme 1-18）。



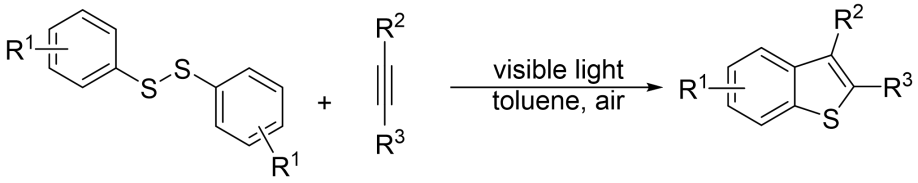
Scheme 1-18 光诱导邻甲硫基芳基重氮盐与炔烃的级联反应合成苯并噻吩

2016 年，Yuan[39]课题组利用光诱导 KOH/DMSO 超强碱体系促进 2-卤代硫代苯甲醚与末端炔烃发生环化反应，以环境友好的方法合成了 2-取代苯并噻吩。该方法以市售化合物作为底物、可见光为能量源，以中等至良好的收率得到多种苯并噻吩（Scheme 1-21）。



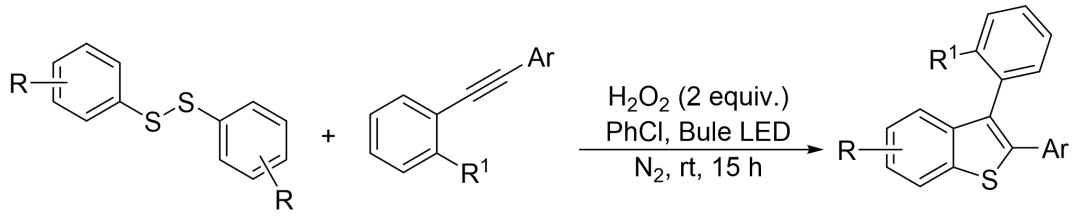
Scheme 1-19 光诱导超强碱体系促进 2-卤代硫代苯甲醚与炔烃环化合成 2-取代苯并噻吩

2017 年，Yan 等人[40]构建了可见光驱动的二硫化物与炔烃的分子间自由基环化新体系，成功合成含酯基、酮基、醛基及芳基取代的多种苯并噻吩类化合物。该反应无需过渡金属催化剂及额外添加剂，以氧气为唯一氧化剂，在太阳光照射下仍保持高效转化（Scheme 1-20）。



Scheme 1-20 可见光促进的二硫化物与炔烃分子间自由基环化合成苯并噻吩

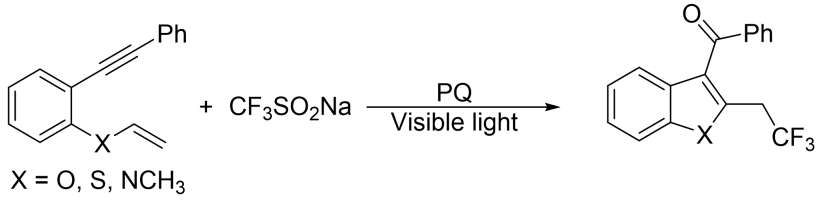
2017 年，Wang[41]课题组报道了一种光诱导 2-炔基苯胺与二硫化物环化制备苯并噻吩的简单高效合成方法。该方法能够在室温、无过渡金属和无光催化剂的条件下，以较高的产率得到所需的产物（Scheme 1-21）。



Scheme 1-21 可见光诱导 2-炔基苯胺与二硫化物的环化反应合成苯并噻吩

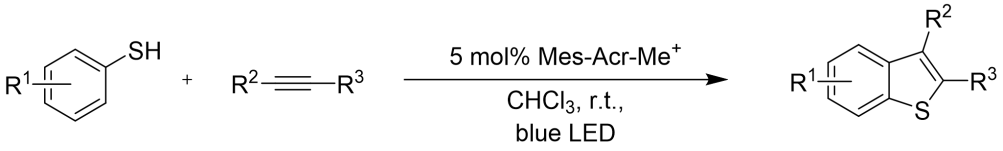
2017 年，Kumar[42]小组报道了一种光诱导 1, 6-烯炔串联环化合成 C3-酰基苯并噻吩及苯并噻吩衍生物的反应。该反应在无金属/氧化剂条件下，以菲醌(PQ)

作为光催化剂、水为氧源与 Langlois 试剂(CF_3SO_2Na)构建含三氟甲基的目标产物。通过紫外可见光谱、ESR、电化学测试及同位素标记实验等研究证实：光激发 PQ 促使 CF_3SO_2Na 释放 CF_3 自由基，该自由基经烯烃加成-环化-电子转移形成乙烯基阳离子，随后水分子亲核进攻后脱氢生成目标产物（Scheme 1-22）。



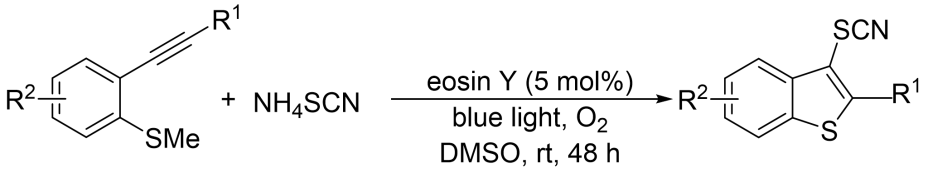
Scheme 1-22 PQ 催化可见光诱导 1, 6-烯炔与 CF_3SO_2Na 合成三氟甲基化苯并噻吩

2017 年，Zhu 等人[43]开发了无金属光催化氧化还原体系，通过硫酚与炔烃的串联加成-环化反应，实现 2, 3-二取代苯并噻吩的高效合成。该反应通过 Mes-Acr-Me^+有机染料在蓝光激发下引发的光氧化还原过程得到目标产物。且在常温条件下兼容多种官能团，并以良好至优秀的收率获得相应的目标产物。该反应具有良好的原子经济性与环境兼容性（Scheme 1-23）。



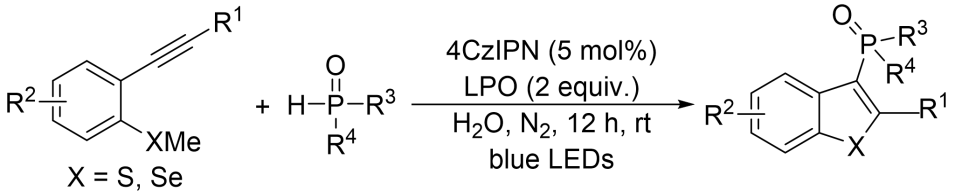
Scheme 1-23 可见光诱导硫酚与炔烃合成 2, 3-二取代苯并噻吩

2018 年，Kshirsagar 等人[44]基于曙红 Y 催化的可见光诱导串联反应，开发了室温下 2-炔基硫代苯甲醚与硫氰酸铵盐的级联自由基环化新方法。该方法以氧气为氧化剂，通过硫氰酸根阴离子氧化过程，高效构筑具有 3-硫氰酸酯基苯并噻吩衍生物，该方法具有底物适用范围广且反应条件温和的优点（Scheme 1-24）。



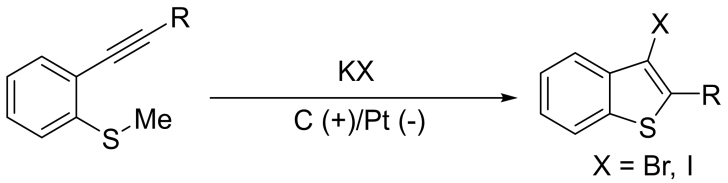
Scheme 1-24 可见光促进 2-炔基苯甲硫醚与硫氰酸铵盐环化合成 3-硫氰基苯并噻吩

2020 年，Yu[45]课题组构建了以水作为溶剂、4CzIPN 作为催化剂的光催化体系，在室温下实现 2-炔基硫（硒）代苯甲醚与磷试剂发生串联环化反应合成了一系列的 3-磷酰基苯并噻（硒）吩。该方法摒弃了传统有机溶剂，避免了苯并[*b*]磷氧化物的生成，具有无外加金属、溶剂绿色和条件温和的优点（Scheme 1-25）。



Scheme 1-25 可见光促进 2-炔基硫代苯甲醚与磷试剂环化合成 3-膦酰基苯并噻吩

2020 年，Guo[46]开发了电化学连续流系统介导的 C-3 位卤代苯并噻吩合成策略。采用碳/铂电极，卤化钾同时作为卤源与电解质，在无金属催化剂/氧化剂条件下实现 2-炔基硫代苯甲醚的电化学卤化环化。通过调控电流强度与流速，可选择性地获得 C-3 卤代产物或脱卤产物。连续流系统展现出优异的可放大性，与传统间歇式反应相比具有显著的工业化优势（Scheme 1-26）。



Scheme 1-26 邻炔基硫代苯甲醚的电化学卤化环化合成 3-卤代苯并噻吩

1.5 小结与展望

近年来，开发高效、可持续的苯并噻吩合成新策略成为研究热点。这些突破不仅解决了传统方法的局限性，还为复杂功能分子的精准合成提供了新思路。

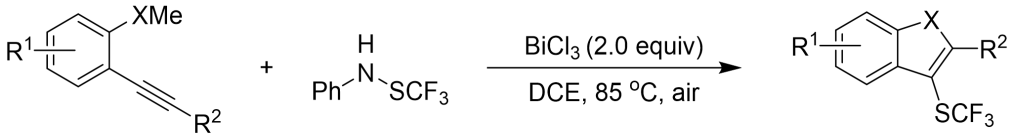
但这些方法均存在一些缺点。例如使用过渡金属催化剂会导致催化剂残留及重金属环境负担、原子利用率低、底物广谱性差等。这些缺点极大的限制了其应用范围。因此，建立新的催化体系开展简单、高效的合成苯并噻吩及其衍生物的新方法是非常有意义的。

第 2 章 无外加光敏剂条件下可见光促进邻炔基苯甲硫醚与二硫醚的串联环化反应合成 3-芳硫基苯并噻吩

2.1 研究背景

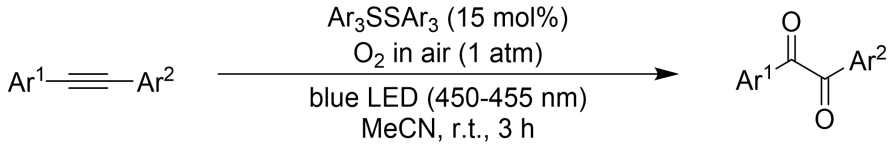
苯并[*b*]噻吩及其衍生物作为重要的功能分子骨架，其 3-位取代衍生物在天然产物、药物分子中展现出多样化的生物活性，在功能材料领域展现了就出色的功能特性。近年来，针对 3-取代苯并[*b*]噻吩的高效合成策略取得显著进展，其中邻炔基硫代苯甲醚的串联环化反应已成为主要构建方法。随着药物研发对新型硫醚类化合物的迫切需求，基于自由基级联反应构建 3-取代苯并噻吩的创新方法备受关注。

2014 年，Wu[47]课题组基于报道了一种使用 $BiCl_3$ 促进三氟甲硫酰胺与 2-炔基苯甲醚（硫醚）串联环化反应合成 3-三氟甲硫基苯并呋喃（噻吩）的合成方法。该方法在温和条件下合成了多种相应的目标产物，对不同的底物具有普适性，为含氟硫醚类药物的研发提供了高效方法（Scheme 2-1）。



Scheme 2-1 $BiCl_3$ 促进三氟甲硫酰胺与 2-炔基苯甲醚（硫醚）串联环化合成 3-三氟甲硫基苯并呋喃（噻吩）

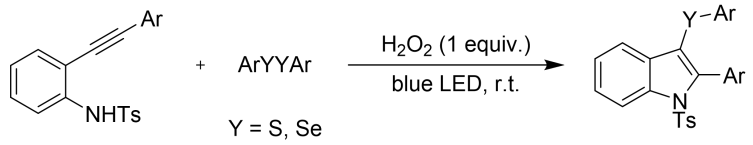
2016 年，Wang[48]课题组发展了可见光诱导的二芳基炔烃高效转化为二芳基 1, 2-二酮的合成方法。该反应在苯硫基自由基催化下，通过氧气参与的氧化过程实现原料的转化。实验结果表明，该反应体系对多种官能团展现出良好的兼容性能够以优秀的产率合成相应的目标产物（Scheme 2-2）。



Scheme 2-2 可见光诱导二芳基炔烃转化为二芳基 1, 2-二酮

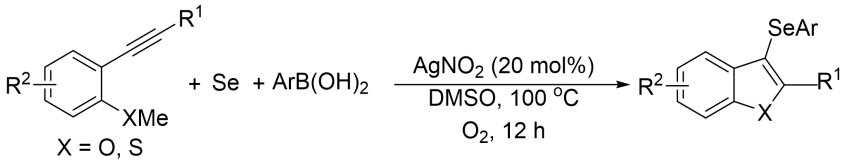
2017 年，Wang[49]课题组构建了无金属/无光催化剂的光诱导串联环化反应体系。室温条件下通过 2-炔基苯胺与二硫化物/二硒化物的串联环化反应，能够高

效、高产率合成 3-硫醚/硒醚取代吲哚类化合物（Scheme 2-3）。



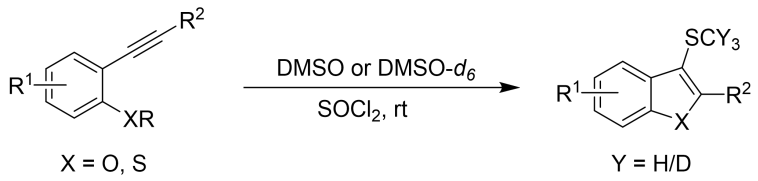
Scheme 2-3 光诱导 2-炔基苯胺与二硫（硒）化物串联环化合成 3-芳硫（硒）基吲哚化合物

2019 年，Liu[50]课题组开发了 $AgNO_2$ 催化的自由基环化新方法，通过 2-炔基苯甲醚/硫代苯甲醚、硒粉与芳基硼酸的三组分反应合成芳硒基取代苯并呋喃/噻吩。该方法可以一步构筑一个苯并呋喃/噻吩环、两个 C-Se 键及一个 C-O(S)键，并裂解一个 C-O(S)键。初步机理研究表明，该是反应可能历经自由基机理，存在芳基硒自由基中间体（Scheme 2-4）。



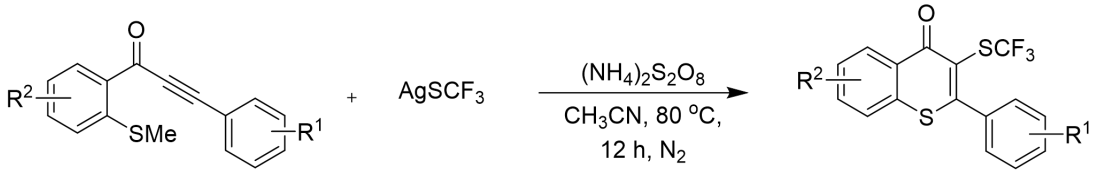
Scheme 2-4 邻炔基苯甲（硫）醚、硒粉和芳基硼酸合成芳基硒代苯并噻吩/呋喃

2021 年，Du[51]小组通过 2-炔基苯甲醚/硫醚与 $SOCl_2$/DMSO 的分子内环化反应，合成 3-甲硫基苯并呋喃/噻吩。DMSO 兼具溶剂与硫源双重功能，使用 DMSO-d_6 则可实现 SCD_3 基团在杂环 C3 位的精准引入（Scheme 2-5）。



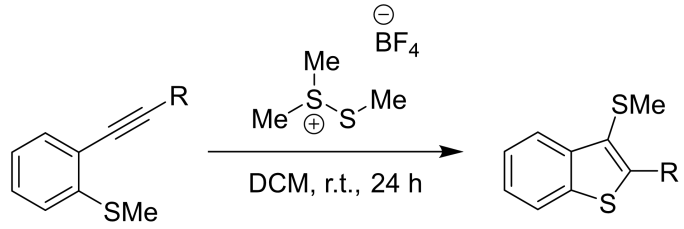
Scheme 2-5 2-炔基苯甲醚/硫醚与 $SOCl_2$/DMSO 分子内环化合成 3-甲硫基苯并呋喃/噻吩

2021 年，Huang 等人[52]报道了一种过硫酸盐促进的 $AgSCF_3$ 与甲基硫代炔酮串联环化反应，实现了 3-三氟甲硫基取代硫黄酮的高效合成。该体系具有良好的官能团耐受性和产率。机理研究表明，该反应可能历经自由基过程：CF_3S 自由基在三键上加成后与 SMe 基团环化生成目标产物（Scheme 2-6）



Scheme 2-6 硫酸盐促进 $AgSCF_3$ 与甲基硫代炔酮合成 3-取代硫黄酮

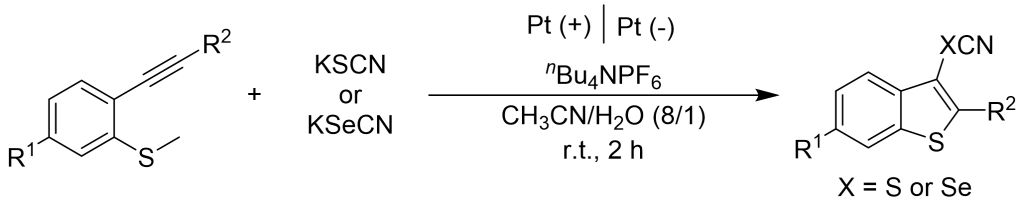
2022 年，Kesharwani[53]课题组利用稳定的四氟硼酸盐，实现了邻炔基硫代苯甲醚的亲电环化反应，高效构建苯并噻吩骨架。该策略在室温条件下兼容多种取代炔烃，以优异收率引入甲硫基取代基。通过机理实验，证实了该反应经历了亲电加成反应过程（Scheme 2-7）。



R = aryl, alkyl, vinyl, silyl

Scheme 2-7 四氟硼酸盐促进邻炔基硫代苯甲醚亲电环化合成苯并噻吩

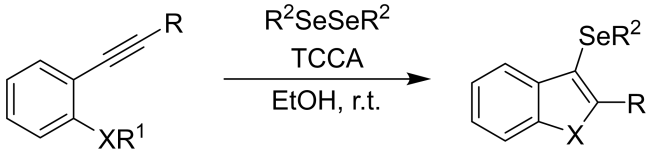
2022 年，Geng 等人[54]开发了电化学氧化促进的活性炔双官能化策略，以 2-炔基硫代苯甲醚和廉价易得的硫（硒）氰酸钾为底物，在无氧化剂/催化剂条件下实现 3-硫（硒）氰酸酯基苯并噻吩的合成。连续流动体系的应用有效解决了传统电化学放大效率低下的难题，在规模化制备中仍能保持稳定收率（Scheme 2-8）。



X = S or Se

Scheme 2-8 电化学促进 2-炔基硫代苯甲醚与硫（硒）氰酸钾氧化合成 3-硫（硒）氰酸酯基苯并噻吩

2022 年，Alves 等人[55]报道了三氯异氰尿酸促进的邻炔基苯甲醚及其衍生物和二芳基二硒化物串联环化生成 3-芳硒基苯并硫属杂环新方法。该方法使用乙醇作为溶剂，通过三氯异氰尿酸与二芳基二硒醚原位反应生成亲电性硒，推进反应顺利进行。^{77}Se NMR 分析证实，有亲电性 PhSeCl 在原位生成。该反应具有反应条件温和、产率较高、广谱性好等优点（Scheme 2-9）。



X = O, S, Se　　R = alkyl, aryl, SePh

R^1 = methyl, butyl　　R^2 = alkyl, aryl, heteroaryl

Scheme 2-9 三氯异氰尿酸促进的 3-芳硒基苯并硫属杂环合成

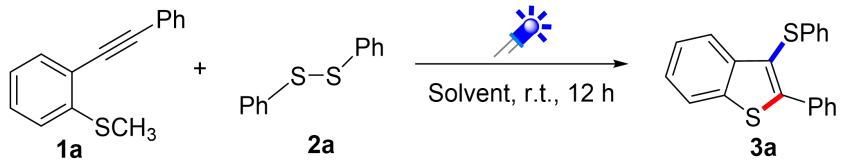
基于以上文献的启发，我设计通过二硫醚裂分产生苯硫基自由基与邻炔基苯甲硫醚反应生成 C3-取代苯硫基苯并噻吩。

2.2 反应条件优化

以 2-炔基苯甲硫醚（**1a**）和二苯基二硫醚为模版反应，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 催化剂和反应条件的筛选

Table 2-1 催化剂和溶剂的筛选 [a]



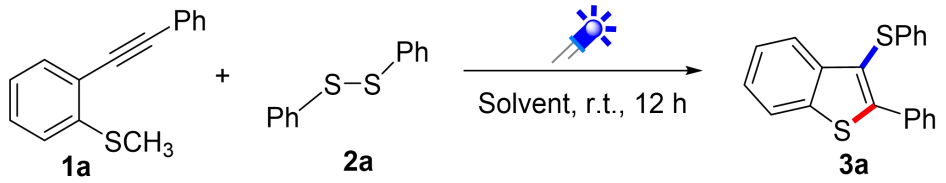
Entry	Photocatalyst	Solvent	LED (nm)	Yield(%)[b]
1	$Ru(bpy)_3Cl_2$	THF	425	72
2	Eosin Y	THF	425	85
3	**-**	**THF**	**425**	**92**
4	-	THF	425	81[c]
5	-	THF	In dark	0

[a]Reaction conditions: **1a** (0.20 mmol) and **2a** (0.20 mmol) in solvent (2.0 mL) and photocatalyst (2 mol%) in argon atmosphere at room temperature under LED (5 W) irradiation for 12 h. [b]Isolated yield. [c]in air atmosphere.

首先，对催化剂和反应条件进行了筛选。如 Table 2-1 所示，以 2-炔苯基苯甲硫醚（**1a**）和二苯基二硫醚（1.0 equiv.）为反应底物，分别使用 $Ru(bpy)_3Cl_2$（2 mol%）、Eosin Y（2 mol%）作为光催化剂，四氢呋喃（THF）作为反应溶剂，在氮气气氛下用 425 nm 蓝光 LED（5 W）照射，在石英管中搅拌反应 12 h，分别以 72%和 85%的产率得到了目标产物 **3a**（entries 1 and 2）。当该反应在无外加光催化剂的条件下，以更高的产率（92%）得到了 **3a**（entry 3）。在空气气氛下进行反应时，**3a** 的产率略有下降，产率为 81%（entry 4）。控制实验表明光照是该反应的必要条件（entry 5）。

2.2.2 催化剂和反应条件的筛选

Table 2-2 催化剂和溶剂的筛选 [a]



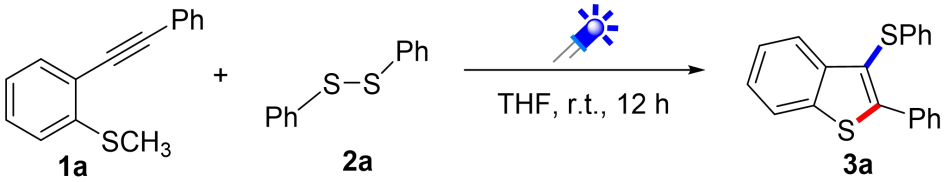
Entry	Solvent	Yield(%)[b]
1	**THF**	**92**
2	DCE	85
3	CH_3CH_2OH	82
4	CH_3CN	87
5	Acetone	79
6	DMSO	81
7	Toluene	87

[a]Reaction conditions: **1a** (0.20 mmol) and **2a** (0.20 mmol) in solvent (2.0 mL) in argon atmosphere at room temperature under LED (5 W) irradiation for 12 h. [b]Isolated yield.

随后，筛选了一系列溶剂。当四氢呋喃（THF）作为反应溶剂时，产率最高，达到了 92%（entry 1）。所筛选的其他溶剂包括二氯乙烷（DCE）、乙醇、CH_3CN、丙酮、二甲基亚砜（DMSO）和甲苯，均适用于该反应，但产率略低，在 79-87% 之间（entries 2-7）。

2.2.3 波长、2a 用量和时间的筛选

Table 2-3 波长、2a 用量和时间的筛选 [a]



Entry	LED (nm)	Yield(%)[b]
1	375	84
2	395	86
3	405	82

4	**425**	**92**
5	440	89
6	455	86
7	525	48
8	425	66[d], 91[e]
9	425	70[f], 90[g]

[a]Reaction conditions: **1a** (0.20 mmol) and **2a** (0.20 mmol) in THF (2.0 mL) in argon atmosphere at room temperature under LED (5 W) irradiation for 12 h. [b]Isolated yield. [d]**2a** (0.15 mmol). [e]**2a** (0.25 mmol). [f]Irradiation for 8 h. [g]Irradiation for 16 h.

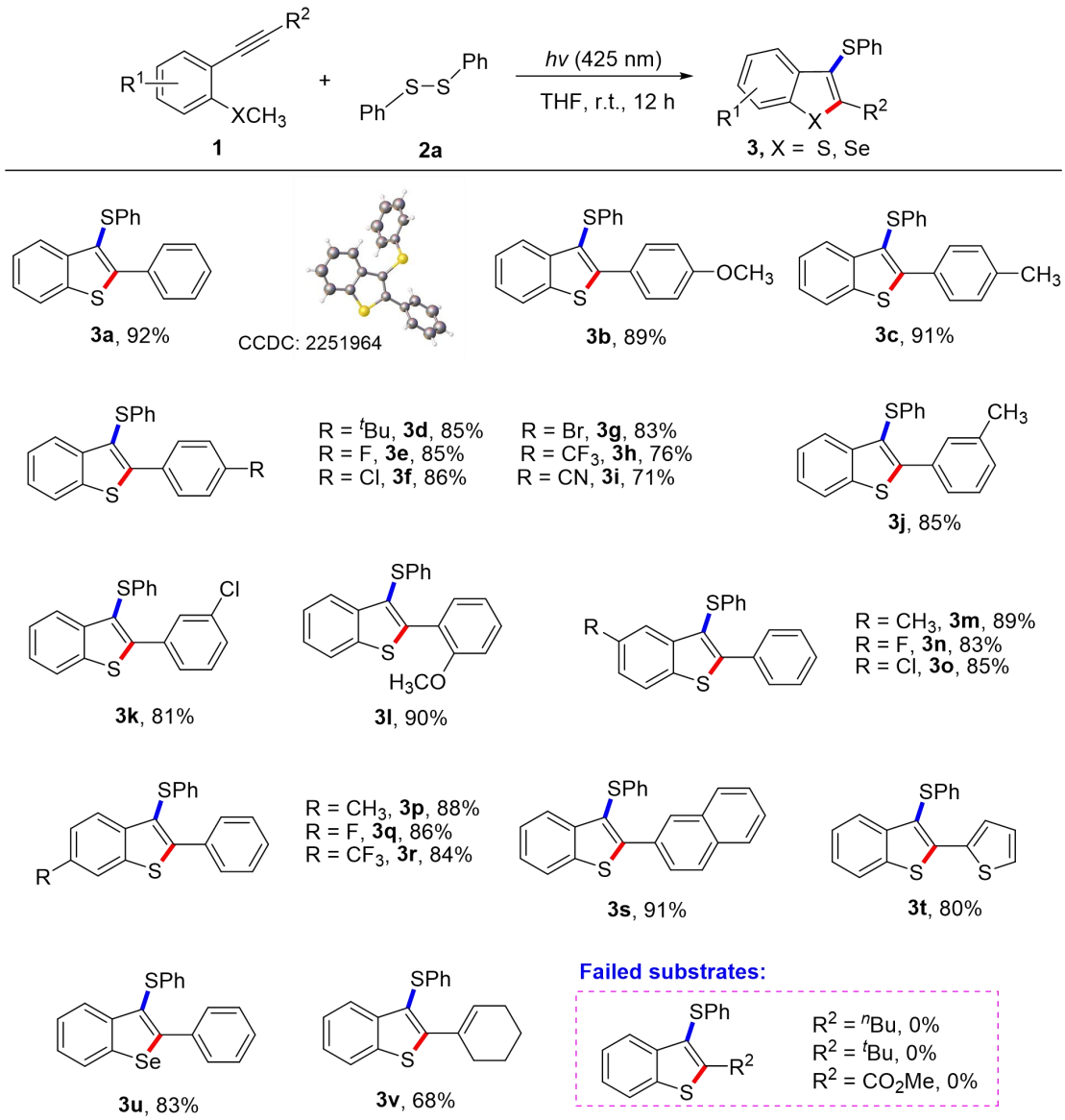
接下来，我们还研究了光源的波长对反应的影响，所筛选的 LED 波长(375、395、405、425、440 和 455 nm)都可以使该反应顺利进行（entries 1-6）且产率变化不大。但是，在使用 525 nm 的 LED 照射下进行反应时，**3a** 的产率大幅度降低至 48%（entry 7）。

进一步优化二苯基二硫醚（**2a**）的用量以及反应时间，如 Table 2-3 所示（entries 8-9）。当二苯基二硫醚的用量增加到 0.25 mmol 时，产率几乎不变，而当 **2a** 用量降低到 0.5 当量时，反应产率降低至 66%。反应时间延长至 16 h 对反应几乎没有影响，但当反应时间缩短到 8 h 时，产率降低至 70%。最终确定该反应的最佳波长是 425 nm、**2a** 的最佳用量是 1.0 equiv.、最佳反应时间是 12 h。

2.3 反应底物普适性考察

如 Scheme 2-10 所示，该反应具有良好的普适性，可以以优良的产率得到相应的 3-芳硫基苯并噻吩。首先考察了 R^2 苯环上的取代基的电子效应，在最佳条件下，大多数官能团可以得到目标产物。苯环上有给电子取代基，如甲氧基、甲基和叔丁基，以 85-91%的收率得到所需的产物（**3b−3d**、**3j** 和 **3l**）；卤素原子如氟、氯和溴对该反应影响不大，得到相应的产物（**3e−3g** 和 **3k**）的产率为 81-86%。吸电子取代基，如三氟甲基和氰基，也与反应相容，但以较低的产率得到产物 **3h** 和 **3i**。此外，在该条件下，萘基和噻吩基也得到相应的产物 **3s** 和 **3t** 的产率分别为 91%和 80%。令人高兴的是，另一个芳香环上的具有不同官能团的底物，如甲基、卤素和 CF_3，也能顺利地进行反应，并以 83-89%的产率获得所需的产物 **3m−3r**，并且可以忽略底物的电子和空间效应。值得注意的是，邻炔基苯甲硒醚也是一个合适的底物，以 83%的收率提供所需的产品 **3u**。将 R^2 的

芳香环替换为环己烯基换进行反应，产率为 68%，得到了所需的产物 **3v**。然而有一系列苯环被烷基和酯基取代的底物（Scheme 2-10，右下角），这些底物未发生环化反应，起始原料被回收。

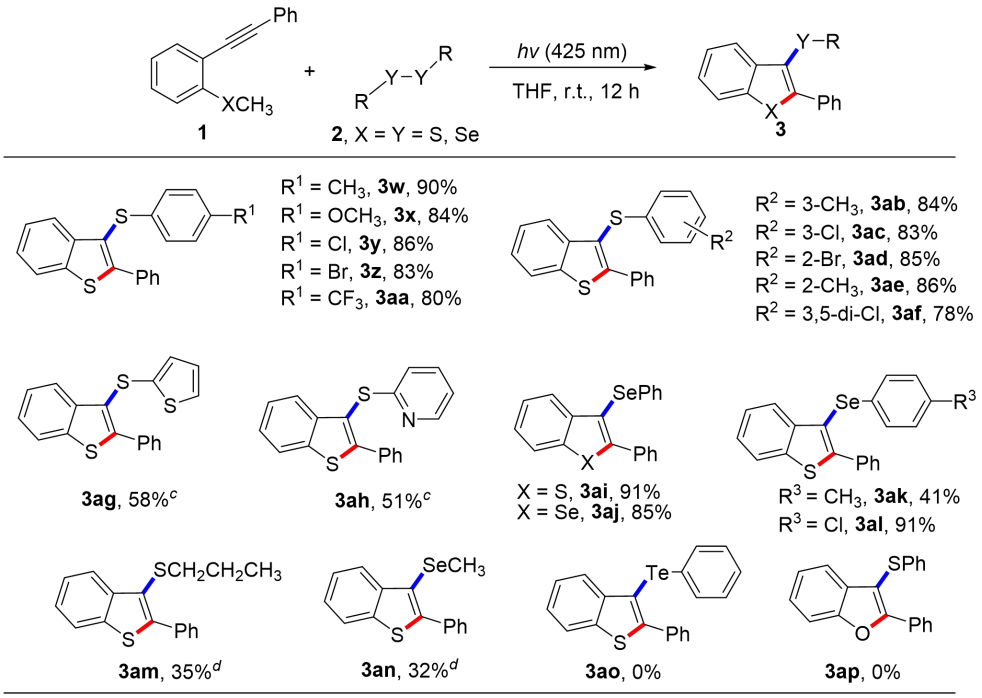


[a]Reaction conditions: **1** (0.2 mmol) and **2a** (0.2 mmol) in THF (2.0 mL) in argon atmosphere at room temperature under LED (5 W) irradiation for 12 h. [b]Isolated yields.

Scheme 2-10 底物普适性考察 I[a]

接下来我们研究了二硫化物的适用范围（Schem 2-11）。发现邻、间、对位取代的二苯基二硫化物均具有很强的相容性，具有给电子基团（Me, OMe）和吸电子基团（F, Cl, Br, CF_3，CN）时，能以 80～90%的收率生成相应的产物（**3w–3ae**）。当 3, 5-二氯取代底物参与该转化时，以 78%的收率得到了所需的产物 **3af**。此外，噻吩基和吡啶基二硫化物在标准条件下也具有相容性，与 **1a** 反应得到的

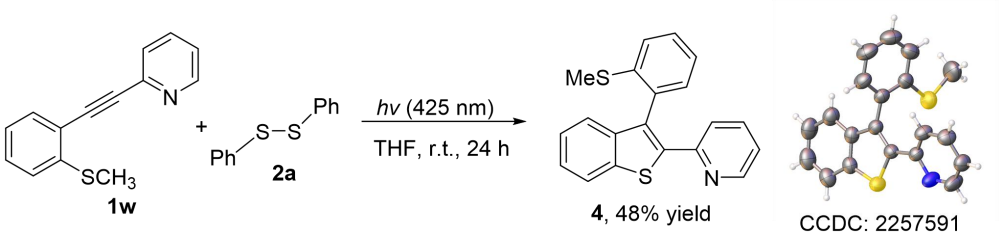
目标产物 **3ag** 和 **3ah** 的产率分别为 58%和 51%。二苯基二硒醚参与反应时，可以得到相应的产物 **3ai−3al**。值得注意的是，二丙基二硫醚与二甲基二硒醚也是合适的底物，分别以 35%和 32%的产率提供所需的产物 **3am** 和 **3an**。遗憾的是，使用二苯基二碲化物和 2-炔基苯甲醚反应时，没有检测到所需的产物。



[a]Reaction conditions: **1** (0.2 mmol) and **2** (0.2 mmol) in THF (2.0 mL) in argon atmosphere at room temperature under LED (5 W) irradiation for 12 h. [b]Isolated yields. [c]**2** (0.40 mmol), 24 h. [d]**2** (1.0 mmol), 36 h.

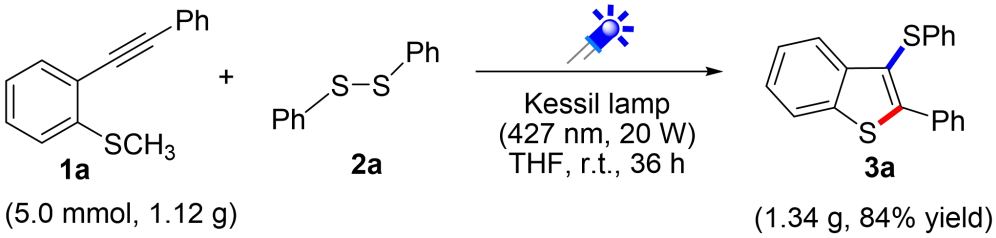
Scheme 2-11 底物普适性考察 II [a]

此外，当化合物 **1w** 在标准条件下反应时，因为硫自由基加成区域选择性不同，没有检测到期望产物，而以 48%的收率生成新的环状产物 **4**，并通过单晶 x 射线衍射进一步证实了 **4** 的结构（Scheme 2-12）。



Scheme 2-12 反应特例

2.4 克级实验



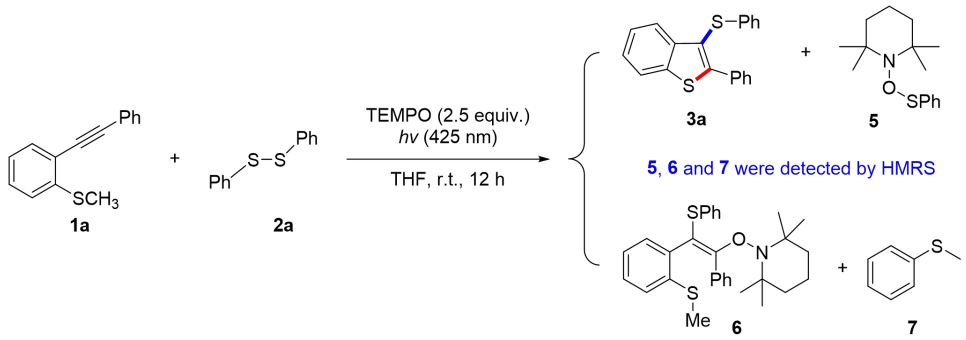
Scheme 2-13 克级实验

该反应体系展现出优异的可放大性。如 Scheme 2-13 所示，1.12 g （5 mmol）的 **1a** 进行环化反应，得到所需产物 **3a**，收率为 84%。证实其拥有工业化应用潜力。

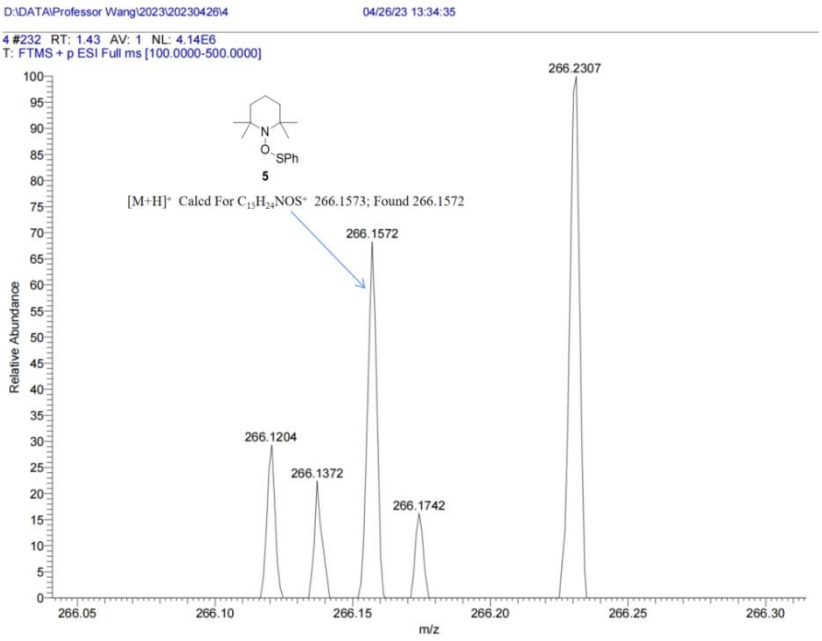
2.5 反应机理探究

2.5.1 控制性实验

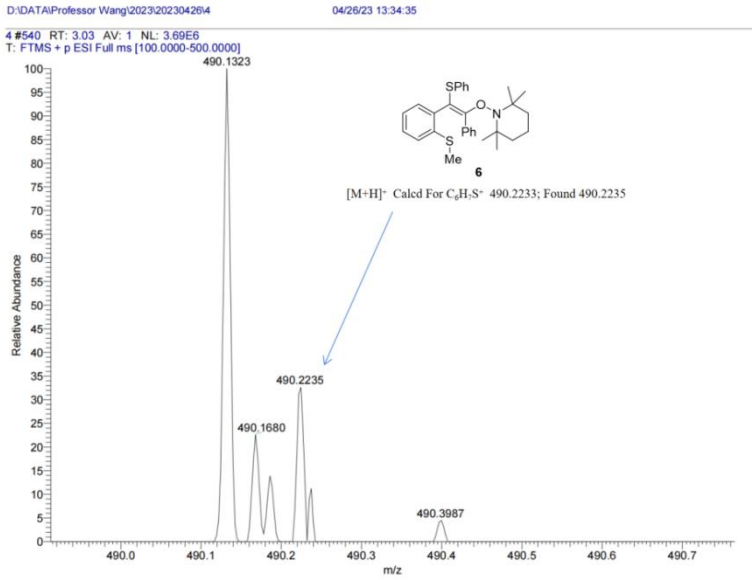
为了阐明反应机理，进行了一系列实验。在标准条件下，将 2.5 equiv.的自由基捕获试剂基 2,2,6,6-四甲基哌啶氧化物（TEMPO）加入到反应中，只检测到微量的产物 **3a**，反应被明显抑制。同时通过高分辨质谱检测到自由基捕获加合物 **5**、**6** 及副产物甲硫基苯（**7**），表明该反应可能涉及自由基过程。



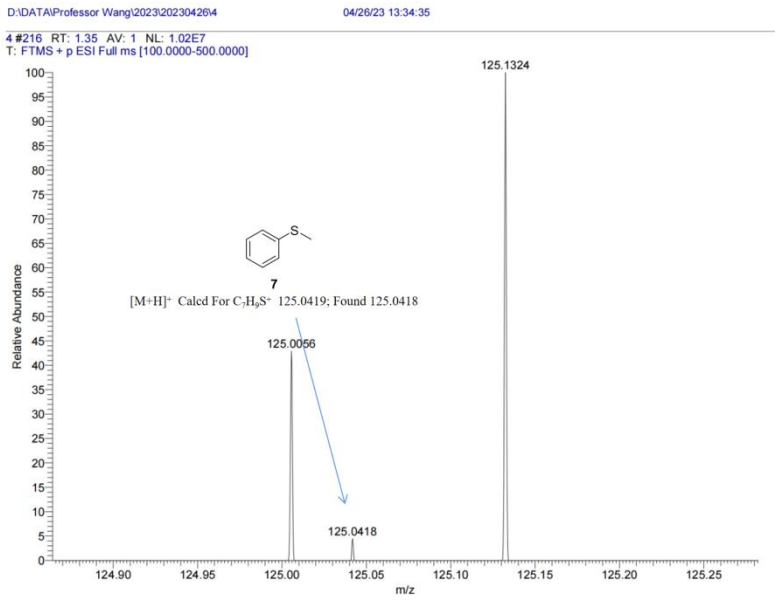
Scheme 2-14 自由基捕获实验



Scheme 2-15 苯硫基自由基加合物（**5**）的高分辨质谱

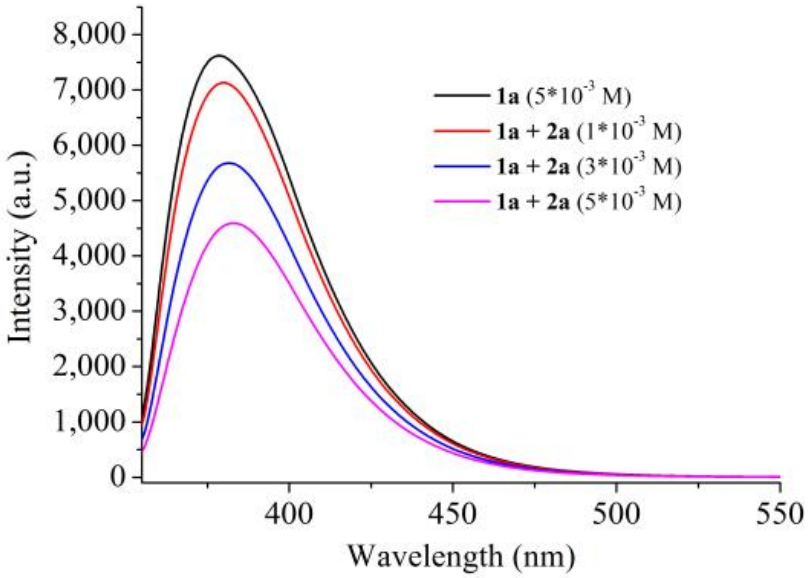


Scheme 2-16 反应中间体自由基加合物（**6**）的高分辨质谱

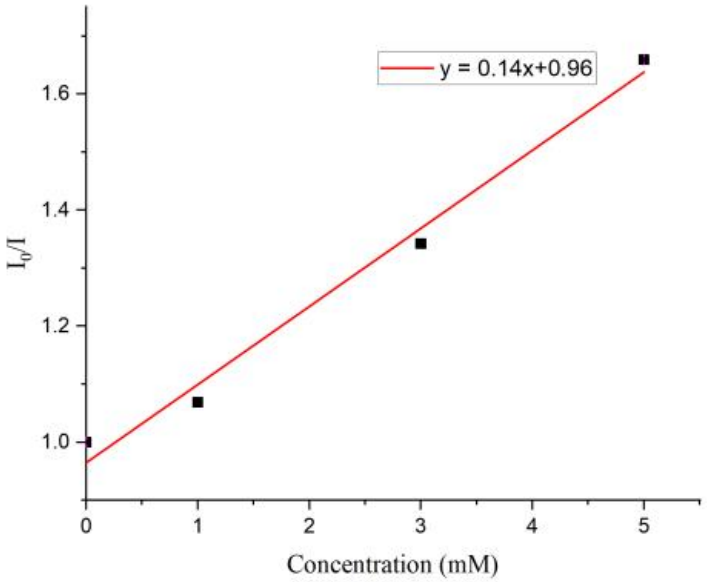


Scheme 2-17 甲硫基苯（**7**）的高分辨质谱

2.5.2 荧光淬灭实验

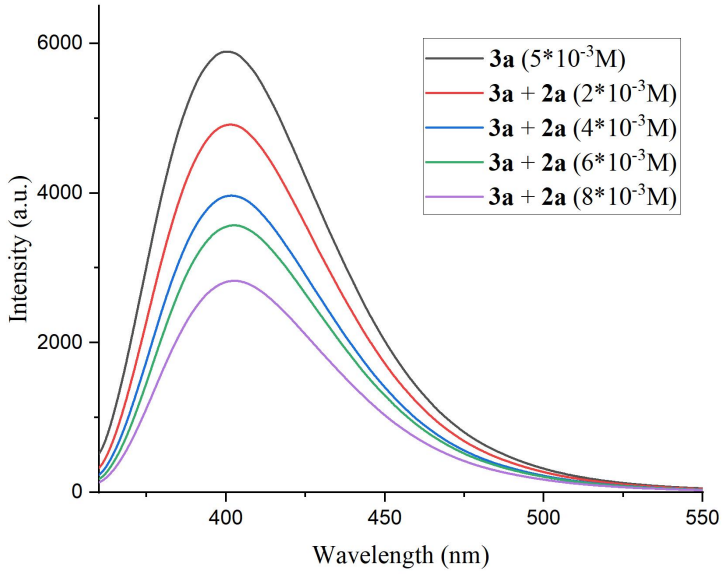


Scheme 2-18 **2a** 对 **1a** 的淬灭

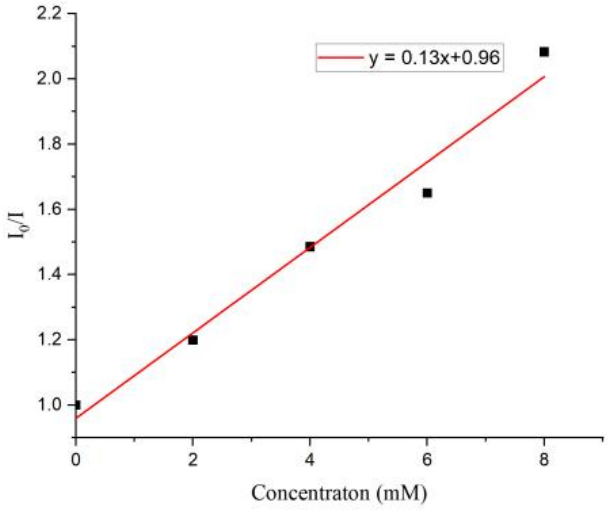


Scheme 2-19 1a 的 Stern-Volmer 图 I

为了进一步阐明可能的反应途径，我们进行了相关的荧光猝灭实验。每次实验向邻炔基苯甲硫醚（**1a**）的 THF 溶液逐渐加入越来越多的二苯基二硫醚（**2a**）的 THF 溶液。每次添加后记录发射光谱。结果如 Scheme 2-18 所示，**1a** 的发射强度变化明显，随着 **2a** 的加入吸收强度逐渐降低。以 **2a** 的浓度为 X 轴 I_0/I 为 Y 轴得到的数据拟合呈线性关系。计算出的 Ksv 为 0.14 mM^{-1}（Scheme 2-19）。说明 **1a** 和 **2a** 间存在着能量转移。



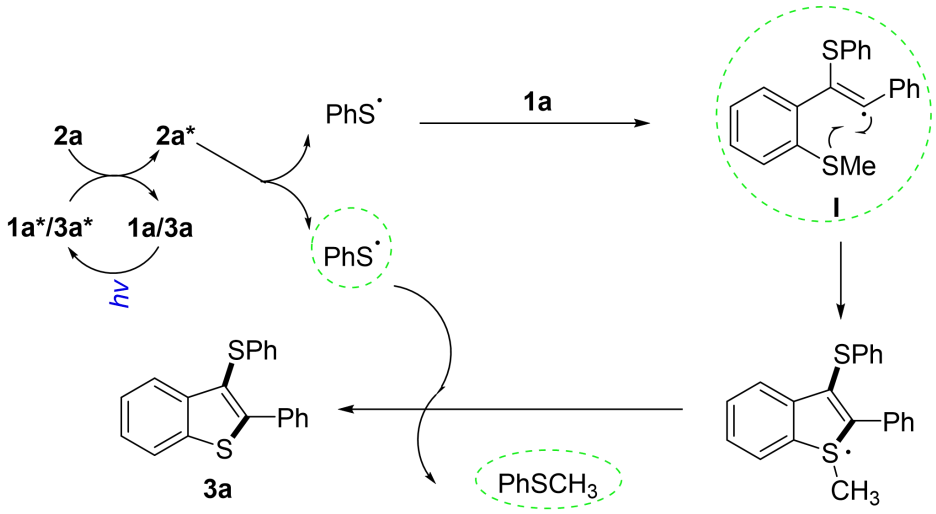
Scheme 2-20 2a 对 **3a** 的淬灭



Scheme 2-21 1a 的 Stern-Volmer 图 II

每次实验向 3-苯硫基苯并噻吩（**3a**）的 THF 溶液逐渐加入越来越多的二苯基二硫醚（**2a**）的 THF 溶液。每次添加后记录发射光谱。结果如 Scheme 2-20 所示，**3a** 的发射强度变化明显，随着 **2a** 的加入吸收强度逐渐降低。以 **2a** 的浓度为 X 轴 I_0/I 为 Y 轴得到的数据拟合呈线性关系。计算出的 Ksv 为 0.13 mM^{-1}（Scheme 2-21）。说明 **3a** 和 **2a** 间存在着能量转移。

2.5.3 可能的反应机理



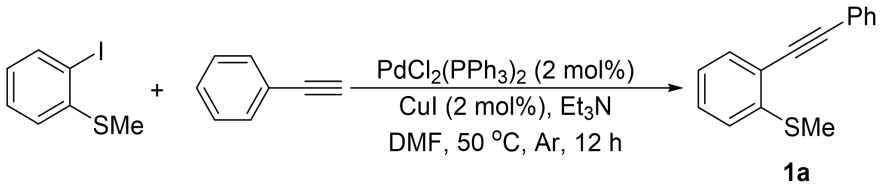
Scheme 2-22 可能的反应机理

结合自由基捕获实验与先前的文献报道[56-61]，提出可能的反应机理（Scheme 2-22）：首先，底物 **1a** 被光激发产生激发态 **1a***，并作为光敏剂，然后与 **2a** 进行能量传递途径，产生激发态 **2a***，同时再生基态 **1a**。激发态 **2a***均裂产生两个

芳硫基自由基（ArS•），并攻击反应底物 **1a** 中的炔基，生成具有高区域选择性的乙烯基自由基中间体 **I**。随后，中间体 **I** 与甲硫基发生分子内环化，最终生成目标产物并释放甲基自由基（转化为苯甲硫醚）。同时，产物 **3a** 可继续作为光敏剂参与催化循环。

2.6 实验部分

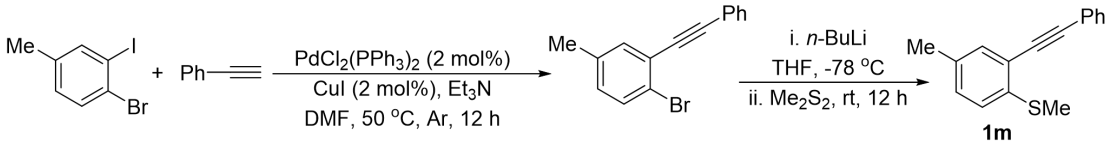
2.6.1 邻炔基苯甲硫醚（1a）的制备



Scheme 2-23 邻炔苯基苯甲硫醚的制备

在 DMF（5 mL）和 Et_3N（20.0 mL）溶液中加入 2-碘茴香硫醚（2.50 g, 10.0 mmol），苯乙炔（1.23 g, 12.0 mmol, 1.2 equiv.），$PdCl_2(PPh_3)_2$（140.4 mg, 2 mol%），和 CuI（38.1 mg, 2 mol%）。反应混合物在 50 ℃的油浴锅里剧烈搅拌 12 小时。监测反应结束后，加入水（50mL）稀释反应，用乙酸乙酯（3*50 mL）萃取，合并后的有机相用水（3*50 mL）洗涤，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（2.02 g, 90% 产率）。

2.6.2 4-甲基-2-炔基苯甲硫醚（1m）的制备



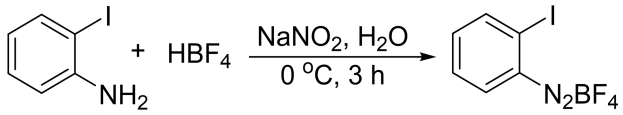
Scheme 2-24 4-甲基-2-炔苯基苯甲硫醚的制备

在 DMF（5 mL）和 Et_3N（20.0 mL）溶液中加入 1-溴-2 碘甲苯（2.97 g, 10.0 mmol），苯乙炔（1.23 g, 12.0 mmol, 1.2 equiv.），$PdCl_2(PPh_3)_2$（140.4 mg, 2 mol%），和 CuI（38.1 mg, 2 mol%），反应混合物在 50 ℃油浴锅里剧烈搅拌 12 小时。监测反应结束后，加入水（50mL）稀释反应，用乙酸乙酯（3*50 mL）萃取，合并后的有机相用水（3*50 mL）洗涤，无水硫酸钠干燥、过滤、真空浓缩、柱色谱（石油醚）分离纯化，得到中间产物 1-溴-2 苯基乙炔基甲苯为黄色油状 （2.39 g, 88% 产率）。

在氩气氛围下向干燥后的 200 mL 的圆底烧瓶中加入 1-溴-2 苯基乙炔基甲苯

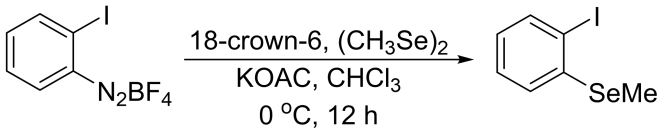
（2.17 g, 8.0 mmol），然后加入 80 mL 无水四氢呋喃使其完全溶解，该混合物在-78 ℃下搅拌 30 min，使反应体系温度将至外浴温度。然后，将 2.0 equiv.的正丁基锂（2.0 M 的四氢呋喃溶液）通过恒压漏斗缓慢滴加到反应体系中。正丁基锂全部滴加完毕后，该反应保持在-78 ℃继续搅拌一小时，然后加入二甲基二硫醚（0.90 g, 9.6 mmol, 1.2 equiv.），反应保持在氩气气氛下缓慢回温到室温反应 18 h。反应完成后，通过旋转蒸发仪真空去除溶剂四氢呋喃，使用乙酸乙酯和水进行萃取操作，无水硫酸钠干燥，过滤、真空浓缩，柱色谱法（乙酸乙酯/石油醚=1/200）对产品进行分离纯化，得到 5-甲基 2-炔苯基苯甲硫醚（**1m**）为黄色油状（1.43 g, 75% 产率）。

2.6.3 2-炔基苯甲硒醚（1u）的制备



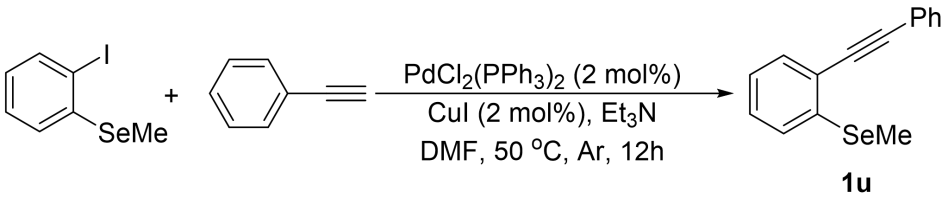
Scheme 2-25 重氮盐的制备

向 100 mL 圆底烧瓶中，加入 2-碘苯胺（2.19 g, 10.0 mmol）、H_2O（2.0 mL）和 HBF_4 水溶液（48%，4.0 mL），然后通过恒压漏斗缓慢滴加 $NaNO_2$ 水溶液（1.38 g, 20.0 mmol, 溶于 3.0 mL H_2O）。滴加完成后，在 0℃下搅拌 3 h，然后过滤，滤饼依次使用少量冰水、酒精和乙醚洗涤，重氮盐产物经过真空干燥，不提纯，直接用于下一步。产物为白色固体（2.77 g，产率 87% ）。



Scheme 2-26 邻碘苯甲硒醚的制备

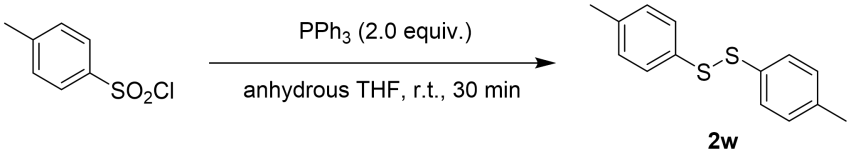
向 100 mL 的圆底烧瓶中，加入粗重氮盐（3.18 g, 10.0 mmol）、18-冠-6（1.32 g, 5.0 mmol, 0.5 equiv.）和二甲基二硒醚（2.07 g, 11.0 mmol, 1.1 equiv.），加入溶液 $CHCl_3$（40 mL），在 0 ℃搅拌至反应液温度与外浴温度相同。将 KOAc（1.96 g, 20.0 mmol, 2.0 equiv.）分多次少量加入，添加完成后，搅拌 12 小时后过滤。用氯仿冲洗上层滤饼，滤液用水洗涤，所得有机相用无水硫酸钠干燥，真空浓缩，柱色谱法（石油醚）纯化，得到中间产物为黄色油状（2.14 g，72% 产率）。



Scheme 2-27 2-炔苯基苯甲硒醚的制备

在 DMF（5 mL）和 Et3N（20.0 mL）溶液中加入 2-碘苯甲基硒醚（2.97 g, 10.0 mmol）、苯乙炔（1.23 g, 12.0 mmol, 1.2 equiv.），$PdCl_2(PPh_3)_2$（140.4 mg, 2 mol%）和 CuI（38.1 mg, 2 mol%），反应混合物在 50 ℃油浴锅里剧烈搅拌 12 小时。监测反应结束后，加入水（50mL）稀释反应，用乙酸乙酯（3*50 mL）萃取，合并后的有机相用水（3*50 mL）洗涤，无水硫酸钠干燥、过滤、真空浓缩、柱色谱（石油醚）分离纯化，得到黄色油状（2.33 g，86% 产率）。

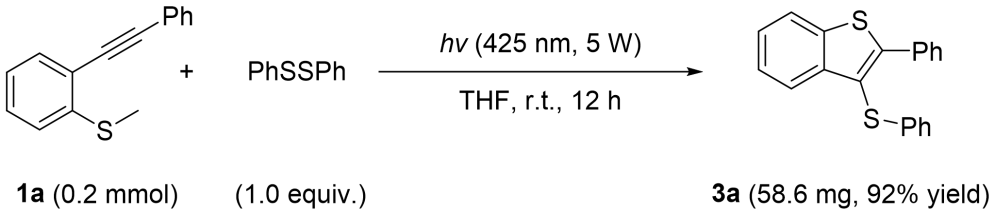
2.6.4 4-甲基二苯基二硫醚（2w）的制备



Scheme 2-28 4-甲基二苯基二硫醚的制备

向 THF （5.0 mL）溶液中加入 4-甲基苯磺酰氯（190.0 mg, 1.0 mmol）和三苯基膦（524.0 mg, 2.0 mmol）。室温搅拌 30 分钟，用 TLC 监测，确认反应完成后，真空除去溶剂，将残留物溶解在最少量的乙酸乙酯（4.0 mL）中，然后往该溶液中，滴入正己烷（约 30 mL），副产物氧化三苯基膦沉淀析出后通过过滤去除。滤液真空浓缩、柱色谱（石油醚）分离纯化得到所需产品（114.0 mg，产率 92%）。

2.6.5 3-苯硫基苯并噻吩（3a）制备的一般步骤

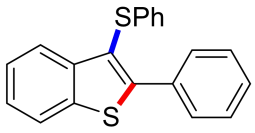


Scheme 2-29 光促进自由基环化合成 3-溴苯并噻吩

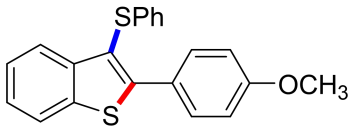
向干燥的反应管里，加入邻炔基苯甲硫醚（**1a**, 44.9 mg, 0.20 mmol）、二苯基二硫醚（43.7 mg, 0.20 mmol， 1.0 当量）和 THF（2.0 mL）。反应混合物在氩气气氛中、室温下用 425 nm, 5 W 的蓝光 LED 照射反应 12 h。反应完成后，

旋转蒸发仪真空去除溶剂，柱色谱（石油醚）分离纯化，得到所需产物 **3a** 为白色固体（58.6 mg，产率 92%）。

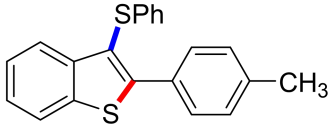
2.7 产物的表征数据



2-Phenyl-3-(phenylthio)benzo[*b*]thiophene (3a). White solid, 58.6 mg, 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.85–7.83 (m, 1H), 7.81–7.80 (m, 1H), 7.69–7.68 (m, 2H), 7.41–7.37 (m, 3H), 7.36–7.32 (m, 2H), 7.16–7.13 (m, 2H), 7.06–7.03 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 149.7, 141.1, 138.5, 137.8, 133.5, 129.9, 129.1, 129.0, 128.6, 126.3, 125.3, 125.2, 124.0, 122.3, 118.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}S_2^+$ 319.0610; Found 319.0610.

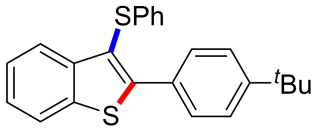


2-(4-Methoxyphenyl)-3-(phenylthio)benzo[*b*]thiophene (3b). White solid, 62.0 mg, 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82–7.80 (m, 1H), 7.79–7.77 (m, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.34–7.30 (m, 2H), 7.15–7.12 (m, 2H), 7.05–7.03 (m, 3H), 6.91 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.3, 149,8, 141.3, 138.2, 137.9, 131.1, 129.1, 126.2, 125.9, 125.2, 125.1 (125.14), 125.1 (125.08), 123.8, 122.2, 117.4, 114.1, 55.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}OS_2^+$ 349.0715; Found 349.0717.

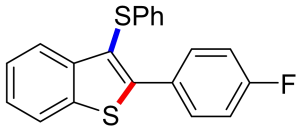


3-(Phenylthio)-2-(*p*-tolyl)benzo[*b*]thiophene (3c). White solid, 60.5 mg, 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82–7.81 (m, 1H), 7.79–7.78 (m, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.19 (d, J = 7.8 Hz, 2H), 7.14 – 7.12 (m, 2H),

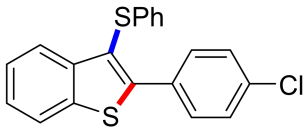
7.04–7.03 (m, 3H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 150.4, 141.6, 139.6, 138.8, 138.3, 131.1, 130.2, 129.8, 129.5, 126.7, 125.7, 125.6 (125.61), 125.6 (125.58), 124.3, 122.7, 118.4, 21.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}S_2^+$ 333.0766; Found 333.0767.



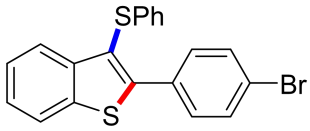
2-(4-(Tert-butyl)phenyl)-3-(phenylthio)benzo[*b*]thiophene (3d). White solid, 63.7 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.66 – 7.65 (m, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.15–7.12 (m, 2H), 7.05–7.03 (m, 3H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 152.6, 150.4, 141.7, 138.8, 138.4, 131.0, 130.0, 129.5, 126.6, 126.1, 125.7, 125.6 (125.61), 125.6 (125.59), 124.3, 122.7, 118.2, 35.3, 31.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{24}H_{23}S_2^+$ 375.1236; Found 375.1238.



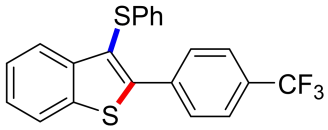
2-(4-Fluorophenyl)-3-(phenylthio)benzo[*b*]thiophene (3e). White solid, 57.2 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.83 (d, J = 7.2 Hz, 1H), 7.81–7.80 (m, 1H), 7.64 (dd, J = 8.4, 3.0 Hz, 2H), 7.38–7.33 (m, 2H), 7.16–7.13 (m, 2H), 7.09–7.06 (m, 3H), 7.05–7.02 (m, 2H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: –112.00. ^{13}C NMR (150 MHz, $CDCl_3$) δ: 163.2 (d, J = 248.1 Hz), 148.5, 141.1, 138.3, 137.5, 131.7 (d, J = 8.4 Hz), 129.6 (d, J = 3.5 Hz), 129.2, 126.3, 125.4 (d, J = 1.7 Hz), 125.3, 124.0, 122.3, 118.7, 115.7 (d, J = 21.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}FS_2^+$ 337.0515; Found 337.0514.



2-(4-Chlorophenyl)-3-(phenylthio)benzo[*b*]thiophene (3f). White solid, 60.7 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.8 Hz, 1H), 7.82−7.80 (m, 1H), 7.62−7.60 (m, 2H), 7.38−7.33 (m, 4H), 7.16−7.13 (m, 2H), 7.07−7.05 (m, 1H), 7.03−7.01 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 148.6, 141.5, 138.8, 137.9, 135.6, 132.4, 131.6, 129.6, 129.3, 126.7, 126.0, 125.9, 125.8, 124.5, 122.8, 119.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}ClS_2^+$ 353.0220; Found 353.0222.

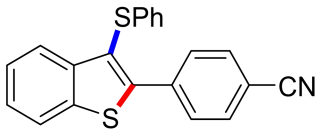


2-(4-Bromophenyl)-3-(phenylthio)benzo[*b*]thiophene (3g). White solid, 66.0 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84−7.83 (m, 1H), 7.81−7.80 (m, 1H), 7.55−7.53 (m, 2H), 7.52−7.50 (m, 2H), 7.38−7.33 (m, 2H), 7.16−7.13 (m, 2H), 7.07−7.04 (m, 1H), 7.02−7.01 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 148.6, 141.5, 138.8, 137.8, 132.8, 132.2, 131.8, 129.6, 126.7, 126.0, 125.9, 125.8, 124.5, 123.9, 122.8, 119.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}BrS_2^+$ 396.9715; Found 396.9716.

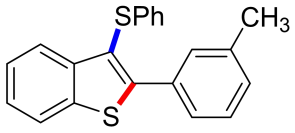


3-(Phenylthio)-2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophene (3h). White solid, 58.7 mg, 76% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 7.8 Hz, 1H), 7.85−7.83 (m, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.42−7.36 (m, 2H), 7.18−7.15 (m, 2H), 7.09−7.07 (m, 1H), 7.04−7.02 (m, 2H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: −62.67. ^{13}C NMR (150 MHz, $CDCl_3$) δ: 147.5, 141.0, 138.6, 137.2, 137.1,

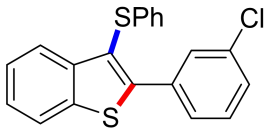
130.8 (q, J = 32.5 Hz), 130.3, 129.3, 126.4, 125.8, 125.6, 125.5 (q, J = 3.9 Hz), 125.5, 124.3, 124.1 (q, J = 270.8 Hz), 122.5, 120.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}F_3S_2^+$ 387.0484; Found 387.0482.



4-(3-(Phenylthio)benzo[*b*]thiophen-2-yl)benzonitrile (3i). White solid, 48.8 mg, 71% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.88 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.43 – 7.40 (m, 1H), 7.39–7.37 (m, 1H), 7.18–7.15 (m, 2H), 7.10–7.07 (m, 1H), 7.01 (d, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.6, 140.9, 138.6, 138.0, 136.8, 132.2, 130.4, 129.2, 126.3, 126.0, 125.7, 125.5, 124.3, 122.4, 120.7, 118.6, 112.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}NS_2^+$ 344.0562; Found 344.0565.

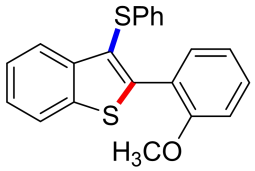


3-(Phenylthio)-2-(*m*-tolyl)benzo[*b*]thiophene (3j). White solid, 56.5 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84–7.83 (m, 1H), 7.81–7.79 (m, 1H), 7.50–7.47 (m, 2H), 7.35–7.33 (m, 2H), 7.28 (t, J = 7.8 Hz, 1H), 7.20–7.18 (m, 1H), 7.15–7.13 (m, 2H), 7.06–7.03 (m, 3H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 149.9, 141.2, 138.5, 138.2, 137.9, 133.4, 130.6, 129.8, 129.1, 128.4, 127.0, 126.4, 125.3, 125.2 (125.22), 125.2 (125.16), 124.0, 122.3, 118.5, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}S_2^+$ 333.0766; Found 333.0767.

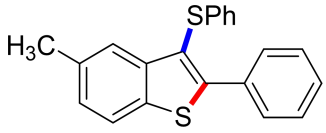


2-(3-Chlorophenyl)-3-(phenylthio)benzo[*b*]thiophene (3k). White solid, 57.2 mg,

81% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.86−7.84 (m, 1H), 7.83−7.82 (m, 1H), 7.68−7.67 (m, 1H), 7.57−7.55 (m, 1H), 7.40−7.34 (m, 3H), 7.33−7.30 (m, 1H), 7.17−7.14 (m, 2H), 7.08−7.05 (m, 1H), 7.04−7.02 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 147.6, 141.0, 138.5, 137.3, 135.2, 134.4, 129.9, 129.8, 129.2, 129.0, 128.1, 126.6, 125.6 (125.64), 125.6 (125.57), 125.4, 124.2, 122.4, 119.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}ClS_2^+$ 353.0220; Found 353.0220.

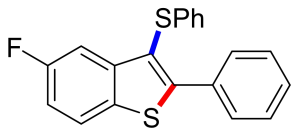


2-(2-Methoxyphenyl)-3-(phenylthio)benzo[*b*]thiophene (3l). White solid, 62.7 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.38−7.36 (m, 2H), 7.35−7.32 (m, 1H), 7.31−7.29 (m, 1H), 7.12−7.09 (m, 2H), 7.05−7.03 (7.033) (m, 2H), 7.03 (7.028)−7.00 (m, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 157.4, 145.8, 140.0, 139.4, 137.8, 132.3, 130.7, 128.8, 126.8, 125.1, 124.9, 124.8, 123.8, 122.3, 121.3, 120.4, 111.2, 55.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}OS_2^+$ 349.0715; Found 349.0717.

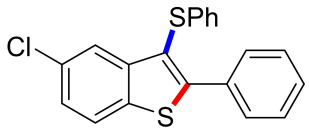


5-Methyl-2-phenyl-3-(phenylthio)benzo[*b*]thiophene (3m). White solid, 59.2 mg, 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8.4 Hz, 1H), 7.67−7.66 (m, 2H), 7.62 (s, 1H), 7.37−7.34 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.16−7.13 (m, 2H), 7.06−7.03 (m, 3H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 150.1, 141.5, 138.0, 135.7, 135.1, 133.6, 129.9, 129.1, 129.0, 128.5, 127.1, 126.1, 125.2, 123.8, 122.0, 117.9, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}S_2^+$ 333.0766; Found

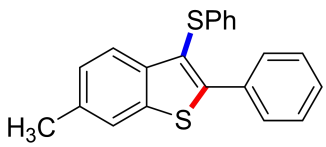
333.0766.



5-Fluoro-2-phenyl-3-(phenylthio)benzo[*b*]thiophene (3n). White solid, 55.8 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.71 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.67–7.66 (m, 2H), 7.47 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.39 – 7.35 (m, 3H), 7.14 – 7.12 (m, 2H), 7.09–7.06 (7.063) (m, 1H), 7.06 (7.059)–7.04 (m, 1H), 7.03–7.01 (m, 2H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: –116.51. ^{13}C NMR (150 MHz, $CDCl_3$) δ: 161.5 (d, *J* = 241.3 Hz), 152.2, 142.8 (d, *J* = 9.6 Hz), 137.1, 133.7, 133.2, 129.8, 129.3, 129.2, 128.6, 126.4, 125.6, 123.6 (d, *J* = 9.5 Hz), 118.4 (d, *J* = 4.2 Hz), 114.2 (d, *J* = 25.5 Hz), 109.6 (d, *J* = 25.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}FS_2^+$ 337.0515; Found 337.0514.

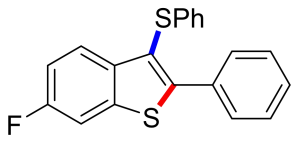


5-Chloro-2-phenyl-3-(phenylthio)benzo[*b*]thiophene (3o). White solid, 60.0 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.66 (m, 2H), 7.40 – 7.38 (m, 3H), 7.31 (dd, *J* = 8.4, 6.6 Hz, 1H), 7.17 – 7.15 (m, 2H), 7.09 – 7.06 (m, 1H), 7.03 – 7.01 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 151.8, 142.7, 137.2, 136.5, 133.1, 131.7, 129.8, 129.3, 129.2, 128.7, 126.3, 125.9, 125.6, 123.5, 123.4, 118.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}ClS_2^+$ 353.0220; Found 353.0219.

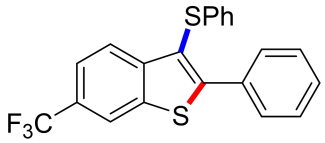


6-Methyl-2-phenyl-3-(phenylthio)benzo[*b*]thiophene (3p). Colorless oil, 58.5 mg,

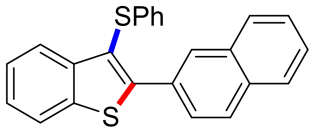
88% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.68−7.66 (m, 3H), 7.62 (s, 1H), 7.39−7.33 (m, 3H), 7.15−7.12 (m, 3H), 7.05−7.03 (m, 3H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 148.5, 139.0, 138.7, 137.9, 135.4, 133.6, 129.9, 129.1, 128.9, 128.5, 126.9, 126.3, 125.2, 123.6, 122.2, 118.2, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}S_2^+$ 333.0766; Found 333.0766.



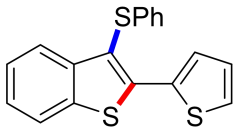
6-Fluoro-2-phenyl-3-(phenylthio)benzo[*b*]thiophene (3q). White solid, 57.9 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.73 (dd, J = 9.0, 5.4 Hz, 1H), 7.66 (d, J = 6.6 Hz, 2H), 7.52 (dd, J = 8.4, 2.4 Hz, 1H), 7.41−7.36 (m, 3H), 7.17−7.14 (m, 2H), 7.09−7.05 (m, 2H), 7.03 (d, J = 7.8 Hz, 2H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: –116.09. ^{13}C NMR (150 MHz, $CDCl_3$) δ: 161.1(d, J = 244.1 Hz), 149.2 (d, J = 3.6 Hz), 139.3 (d, J = 10.2 Hz), 137.5, 137.4, 133.3, 129.8, 129.2, 129.1, 128.7, 126.4, 125.5, 125.2 (d, J = 9.0 Hz), 118.2, 114.2 (d, J = 24.0 Hz), 108.6 (d, J = 25.8 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}FS_2^+$ 337.0515; Found 337.0514.



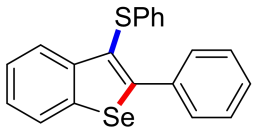
2-Phenyl-3-(phenylthio)-6-(trifluoromethyl)benzo[*b*]thiophene (3r). Colorless oil, 64.9 mg, 84% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.10 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.69−7.68 (m, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.42−7.40 (m, 3H), 7.17−7.14 (m, 2H), 7.09−7.06 (m, 1H), 7.04−7.02 (m, 2H). ^{19}F NMR (564 MHz, $CDCl_3$) δ: –61.53. ^{13}C NMR (150 MHz, $CDCl_3$) δ: 151.7, 141.6, 141.2, 136.9, 132.9, 129.9, 129.5, 129.3, 128.7, 127.9 (q, J = 19.1 Hz), 126.6, 125.8, 124.5 (q, J = 270.1 Hz), 123.0, 121.6 (q, J = 3.2 Hz), 121.1 (q, J = 4.1 Hz), 119.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}F_3S_2^+$ 387.0484; Found 387.0481.



2-(Naphthalen-2-yl)-3-(phenylthio)benzo[*b*]thiophene (3s). White solid, 67.1 mg, 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.14 (s, 1H), 7.86–7.84 (m, 2H), 7.82–7.79 (m, 4H), 7.48–7.44 (m, 2H), 7.37–7.33 (m, 2H), 7.15–7.13 (m, 2H), 7.08–7.03 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 149.7, 141.3, 138.6, 137.8, 133.4, 133.1, 131.0, 129.5, 129.1, 128.6, 128.1, 127.8, 127.3, 126.9, 126.6, 126.4, 125.4 (125.39), 125.4 (125.36), 125.3, 124.0, 122.4, 118.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{24}H_{17}S_2^+$ 369.0766; Found 369.0766.

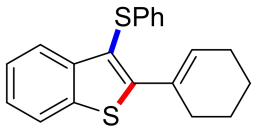


3-(Phenylthio)-2-(thiophen-2-yl)benzo[*b*]thiophene (3t). White solid, 51.9 mg. 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81 – 7.79 (m, 1H), 7.76 – 7.75 (m, 1H), 7.55 – 7.54 (m, 1H), 7.35 – 7.33 (m, 1H), 7.32 – 7.31 (m, 2H), 7.15 – 7.13 (m, 2H), 7.09 – 7.07 (m, 2H), 7.06 – 7.05 (m, 1H), 7.03 – 7.02 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 143.3, 141.6, 137.4, 136.8, 135.1, 129.2, 128.5, 128.3, 127.0, 126.5, 125.6 (125.58), 125.6 (125.57), 125.4, 123.7, 122.1, 117.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{13}S_3^+$ 325.0714; Found 325.0712.

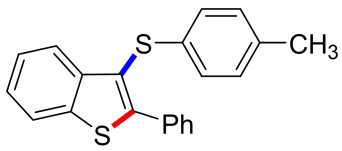


Phenyl(2-phenylbenzo[*b*]selenophen-3-yl)sulfane (3u). Yellow oil, 60.7 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.87 (t, J = 8.4 Hz, 2H), 7.61–7.59 (m, 2H), 7.36–7.34 (m, 3H), 7.33–7.28 (m, 2H), 7.15–7.12 (m, 2H), 7.05–7.02 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 154.2, 142.8, 140.1, 137.8, 135.4, 130.0, 129.1, 128.9,

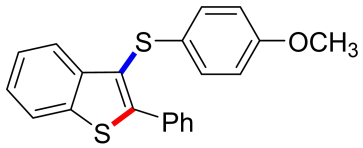
128.5, 126.3, 126.2, 125.5, 125.4, 125.3, 125.2, 121.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}SSe^+$ 367.0054; Found 367.0055.



2-(Cyclohex-1-en-1-yl)-3-(phenylthio)benzo[*b*]thiophene (3v). White solid, 43.9 mg, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77–7.75 (m, 1H), 7.71–7.70 (m, 1H), 7.30 – 7.26 (m, 2H), 7.15 – 7.13 (m, 2H), 7.05 – 7.02 (m, 3H), 6.22 – 6.20 (m, 1H), 2.54–2.52 (m, 2H), 2.19–2.18 (m, 2H), 1.74–1.70 (m, 2H), 1.65–1.61 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 152.6, 141.0, 138.0, 137.6, 132.2, 131.4, 128.9, 126.3, 125.0, 124.8, 124.7, 123.3, 122.1, 116.8, 29.8, 25.9, 22.9, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{19}S_2^+$ 323.0923; Found 323.0921.

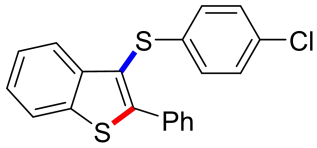


2-Phenyl-3-(*p*-tolylthio)benzo[*b*]thiophene (3w). Colorless oil, 59.8 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84–7.80 (m, 2H), 7.70–7.69 (m, 2H), 7.40–7.33 (m, 5H), 6.95 (s, 4H), 2.22 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 149.4, 141.2, 138.5, 135.2, 134.1, 133.6, 130.0, 129.9, 129.0, 128.6, 126.5, 125.3, 125.2, 124.1, 122.3, 119.0, 21.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}S_2^+$ 333.0766; Found 333.0766.

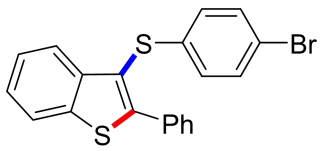


3-((4-Methoxyphenyl)thio)-2-phenylbenzo[*b*]thiophene (3x). Colorless oil, 58.5 mg, 84% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84–7.82 (m, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.43–7.38 (m, 3H), 7.35–7.33 (m, 2H), 7.02–7.01 (m, 2H), 6.70 (d, *J* = 9.0 Hz,

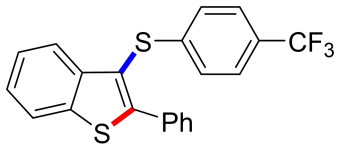
2H), 3.69 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 158.2, 148.9, 141.3, 138.6, 133.7, 130.1, 129.0, 128.9, 128.6, 128.1, 125.3, 125.2, 124.1, 122.4, 120.1, 114.9, 55.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}OS_2^+$ 349.0715; Found 349.0717.



3-((4-Chlorophenyl)thio)-2-phenylbenzo[*b*]thiophene (3y). White solid, 60.7 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.86–7.85 (m, 1H), 7.78–7.76 (m, 1H), 7.66–7.65 (m, 2H), 7.43–7.39 (m, 3H), 7.38–7.34 (m, 2H), 7.12–7.10 (m, 2H), 6.96–6.94 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 150.1, 140.8, 138.5, 136.3, 133.3, 131.2, 129.9, 129.2 (129.22), 129.2 (129.19), 128.6, 127.6, 125.5, 125.3, 123.8, 122.4, 118.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}ClS_2^+$ 353.0220; Found 353.0217.

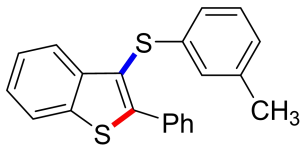


3-((4-Bromophenyl)thio)-2-phenylbenzo[*b*]thiophene (3z). White solid, 66.0 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.86–7.85 (m, 1H), 7.77–7.76 (m, 1H), 7.66–7.64 (m, 2H), 7.42–7.39 (m, 3H), 7.38–7.36 (m, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 150.2, 140.8, 138.5, 137.0, 133.3, 132.1, 129.9, 129.2, 128.6, 127.8, 125.5, 125.4, 123.8, 122.4, 119.0, 117.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}BrS_2^+$ 396.9715; Found 396.9716.

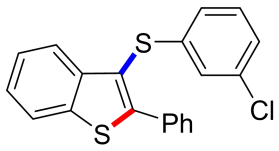


2-Phenyl-3-((4-(trifluoromethyl)phenyl)thio)benzo[*b*]thiophene (3aa). Colorless oil, 61.8 mg, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.87 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.65–7.63 (m, 2H), 7.41–7.36 (m, 7H), 7.08 (d, J = 8.4 Hz, 2H).

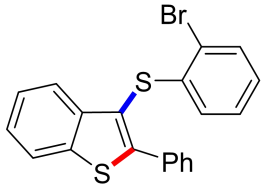
^{19}F NMR (564 MHz, $CDCl_3$) δ: –62.29. ^{13}C NMR (150 MHz, $CDCl_3$) δ: 150.8, 143.1, 140.7, 138.6, 133.2, 129.8, 129.3, 128.7, 127.3 (q, J = 32.5 Hz), 126.0 (q, J = 3.5 Hz), 125.8, 125.6, 125.5, 124.3 (q, J = 270.0 Hz), 123.7, 122.5, 116.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{14}F_3S_2^+$ 387.0484; Found 387.0483.



2-Phenyl-3-(m-tolylthio)benzo[*b*]thiophene (3ab). Colorless oil, 55.9 mg, 84% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, J = 7.2 Hz, 1H), 7.82–7.81 (m, 1H), 7.70 (d, J = 6.6 Hz, 2H), 7.40–7.37 (m, 3H), 7.36–7.33 (m, 2H), 7.02 (t, J = 7.8 Hz, 1H), 6.92 (s, 1H), 6.87 (d, J = 7.2 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 149.7, 141.4, 139.0, 138.6, 137.6, 133.7, 130.0, 129.1 (129.11), 129.1 (129.09), 128.7, 127.0, 126.4, 125.4, 125.3, 124.2, 123.5, 122.4, 118.7, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}S_2^+$ 333.0766; Found 333.0767.

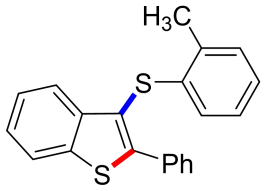


3-((3-Chlorophenyl)thio)-2-phenylbenzo[*b*]thiophene (3ac). Colorless oil, 58.6 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.86–7.85 (m, 1H), 7.79–7.77 (m, 1H), 7.67–7.65 (m, 2H), 7.41–7.36 (m, 5H), 7.04–7.01 (m, 3H), 6.87–6.85 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 150.4, 140.8, 139.9, 138.5, 135.0, 133.3, 130.1, 129.9, 129.2, 128.7, 125.9, 125.6, 125.5, 125.4, 124.3, 123.8, 122.5, 117.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}ClS_2^+$ 353.0220; Found 353.0219.

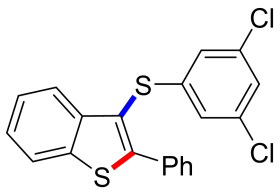


3-((2-Bromophenyl)thio)-2-phenylbenzo[*b*]thiophene (3ad). White solid, 67.5 mg,

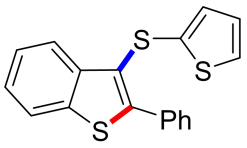
85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 7.8 Hz, 1H), 7.76–7.74 (m, 1H), 7.67–7.65 (m, 2H), 7.51–7.50 (m, 1H), 7.41–7.35 (m, 5H), 6.98–6.95 (m, 1H), 6.92–6.89 (m, 1H), 6.56 (dd, *J* = 7.8, 1.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 150.7, 140.8, 139.0, 138.6, 133.2, 132.9, 129.8, 129.2, 128.7, 127.9, 126.7, 126.2, 125.5, 125.4, 123.9, 122.4, 120.4, 117.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{14}BrS_2^+$ 396.9715; Found 396.9717.



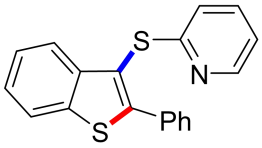
2-Phenyl-3-(*o*-tolylthio)benzo[*b*]thiophene (3ae). Colorless oil, 57.2 mg, 86% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.39–7.34 (m, 4H), 7.33–7.31 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.89–6.87 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 149.8, 141.3, 138.6, 137.0, 135.1, 133.6, 130.3, 129.9, 129.1, 128.7, 126.8, 125.8, 125.4, 125.3, 125.1, 124.1, 122.4, 118.5, 20.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{17}S_2^+$ 333.0766; Found 333.0768.



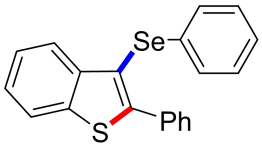
3-((3,5-Dichlorophenyl)thio)-2-phenylbenzo[*b*]thiophene (3af). White oil, 60.4 mg, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.89–7.88 (m, 1H), 7.78–7.76 (m, 1H), 7.65–7.64 (m, 2H), 7.43–7.40 (m, 5H), 7.05 (t, *J* = 1.8 Hz, 1H), 6.87 (d, *J* = 1.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 151.0, 141.6, 140.6, 138.6, 135.5, 133.1, 129.8, 129.4, 128.7, 125.7, 125.6 (125.63), 125.6 (125.56), 124.1, 123.5, 122.6, 116.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{13}Cl_2S_2^+$ 386.9830; Found 386.9832.



2-Phenyl-3-(thiophen-2-ylthio)benzo[*b*]thiophene (3ag). Colorless oil, 37.6 mg, 58% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.49–7.46 (m, 2H), 7.45–7.42 (m, 2H), 7.38–7.36 (m, 1H), 7.12 (d, *J* = 5.4 Hz, 1H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.82–6.81 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 148.8, 141.0, 138.5, 135.6, 133.6, 130.4, 129.1, 128.7, 127.8, 127.4, 125.3, 125.2, 123.9, 122.4, 121.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{13}S_3^+$ 325.0174; Found 325.0177.

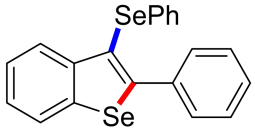


2-((2-Phenylbenzo[*b*]thiophen-3-yl)thio)pyridine (3ah). Colorless oil, 32.6 mg, 51% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 4.2 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.83–7.82 (m, 1H), 7.70–7.69 (m, 2H), 7.42–7.37 (m, 5H), 7.35–7.33 (m, 1H), 6.96–6.94 (m, 1H), 6.67 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.9, 150.4, 149.7, 141.0, 138.6, 137.0, 133.3, 129.9, 129.2, 128.7, 125.5, 125.3, 123.8, 122.4, 120.3, 119.8, 117.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{14}NS_2^+$ 320.0562; Found 320.0561.

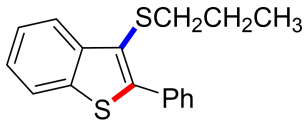


2-Phenyl-3-(phenylselanyl)benzo[*b*]thiophene (3ai). Yellow oil, 66.5 mg, 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.89–7.86 (m, 1H), 7.84–7.81 (m, 1H), 7.63–7.62 (m, 2H), 7.40–7.36 (m, 3H), 7.35–7.32 (m, 2H), 7.14–7.12 (m, 2H), 7.10–7.07 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 149.1, 142.2, 139.2, 134.3, 132.9,

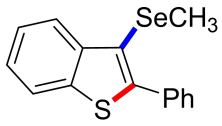
130.2, 129.3, 129.1, 128.9, 128.4, 126.1, 125.2, 122.2, 115.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}SSe^+$ 367.0054; Found 367.0053.



2-Phenyl-3-(phenylselanyl)benzo[*b*]selenophene (3aj). Yellow oil, 70.1 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.95 (d *J* = 7.8 Hz, 1H), 7.86 (d *J* = 7.8 Hz, 1H), 7.55–7.54 (m, 2H), 7.36 – 7.32 (m, 4H), 7.29 – 7.26 (m, 1H), 7.12 – 7.10 (m, 2H), 7.09–7.06 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.1, 143.9, 141.0, 136.3, 133.1, 130.2, 129.3, 129.0, 128.7, 128.3, 127.7, 126.0, 125.5 (125.50), 125.5 (125.46), 125.2, 118.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}Se_2^+$ 414.9499; Found 414.9499.



2-Phenyl-3-(propylthio)benzo[*b*]thiophene (3ak). Colorless oil, 19.9 mg, 35% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.78–7.77 (m, 2H), 7.48–7.45 (m, 3H), 7.42–7.37 (m, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.40–1.34 (m, 2H), 0.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 147.0, 141.9, 138.5, 134.2, 130.2, 128.6, 128.5, 125.0, 124.9, 123.8, 122.4 (122.41), 122.4 (122.37), 37.9, 23.0, 13.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{17}S_2^+$ 285.0766; Found 285.0767.



3-(Methylselanyl)-2-phenylbenzo[*b*]thiophene (3al). Yellow solid, 19.4 mg, 32% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.71–7.70 (m, 2H), 7.48–7.46 (m, 3H), 7.43–7.41 (m, 1H), 7.39–7.37 (m, 1H),

2.09 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.1, 142.3, 139.2, 134.7, 130.3, 128.7, 128.4, 125.0, 124.9, 122.3, 117.8, 8.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{13}SSe^+$ 304.9898; Found 304.3899.

2.8 本章小结

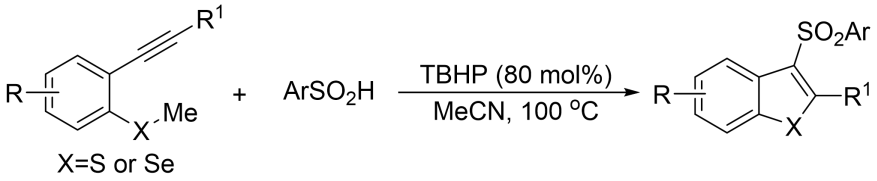
总而言之，本章研究构建了光诱导 2-炔基硫（硒）代苯甲醚与二芳基二硫（硒）醚化合物的自由基环化新体系，在无外加光敏剂条件下，实现了 3-苯硫（硒）基苯并[*b*]噻（硒）吩衍生物的高效、精准合成。该策略展现出优异的产率（最高达 92%）与广泛的底物适应性（涵盖 20 类官能团），为杂环功能分子的构建提供了绿色合成新方法。

第 3 章 可见光促进汉斯酯、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

3.1 研究背景

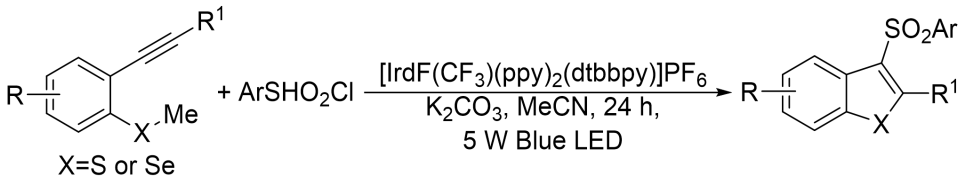
磺酰基是有机合成中非常重要的功能基团，作为强吸电子基团，它在反应中可以活化某些位置，或者作为保护基、导向基使用，以及作为离去基团促进亲核取代反应。不仅在有机合成中用途广泛[62, 63]，更是药物活性分子及生物活性化合物的关键结构单元[64-66]。

2017 年，Song 课题组[67]报道了叔丁基过氧化氢引发 2-炔基硫代/硒代苯甲醚与亚磺酸的自由基环化反应。该反应通过选择性断裂 C(sp^3)-S(Se)键并形成双 C(sp^2)-S(Se)键，在温和条件下实现 3-芳磺酰基苯并噻吩/硒吩的合成，且该方法具有普适性（Scheme 3-1）。



Scheme 3-1 芳基亚磺酸与邻炔基苯甲硫醚的加成环化反应

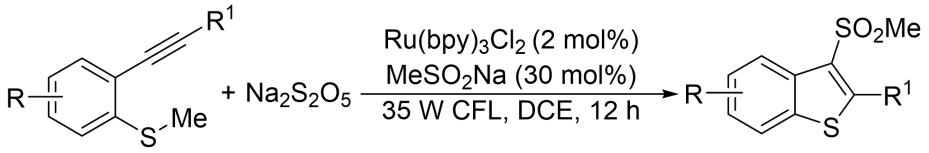
2018 年，该课题组[68]又构建了光氧化还原催化邻甲硫（硒）基苯乙炔与磺酰氯的级联环化体系。在常温条件下合成一系列苯并噻吩/硒吩衍生物且产率优良。该方法具有操作简单，条件温和，官能团耐受性好等优点（Scheme 3-2）。



Scheme 3-2 可见光促进芳基亚磺酰氯与邻炔基苯甲硫（硒）醚的级联环化反应

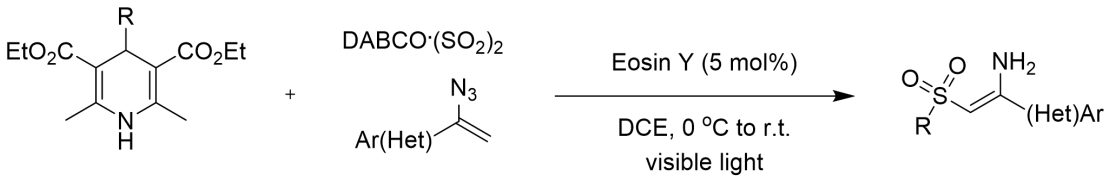
2019 年，Wu 课题组[69]开发了一种自由基接力策略，通过可见光催化邻炔基苯甲硫醚与焦亚硫酸钠的串联环化反应合成 3-（甲磺酰基）苯并[*b*]噻吩。该反应体系以光诱导催化量甲基亚磺酸钠为引发剂，在温和条件下实现了目标产物的高效合成。反应机理研究表明，原位生成的甲基自由基是关键中间体，通过自由

基接力过程与二氧化硫结合，最终形成 C3-甲磺酰基取代苯并噻吩（Scheme 3-3）。



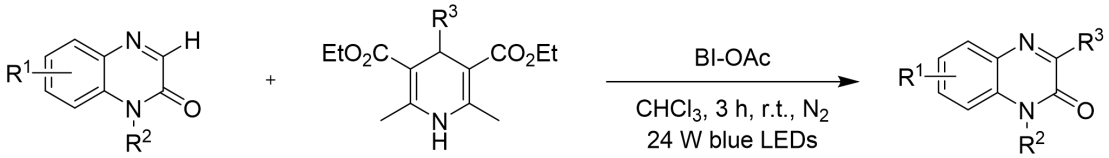
Scheme 3-3 光催化邻炔基苯甲硫醚与焦亚硫酸钠的串联环化合成 3-（甲磺酰基）苯并[*b*]噻吩

2019 年，Wu 课题组[70]报道了一种光催化 4-取代汉斯酯、DABCO·$(SO_2)_2$ 与乙烯基叠氮三组分串联反应的新方法。该体系利用 4-取代汉斯酯作为自由基前体，通过二氧化硫与乙烯基叠氮的级联反应，以中等至良好收率获得一系列（*Z*）-2-（烷基磺酰基）-1-芳基乙烯-1-胺类化合物。该反应展现出优异的区域选择性与立体选择性。且该反应具有适用范围广，反应条件温和，反应效率高的优点（Scheme 3-4）。



Scheme 3-4 光催化 4-取代汉斯酯、DABCO·$(SO_2)_2$ 与乙烯基叠氮三组分合成

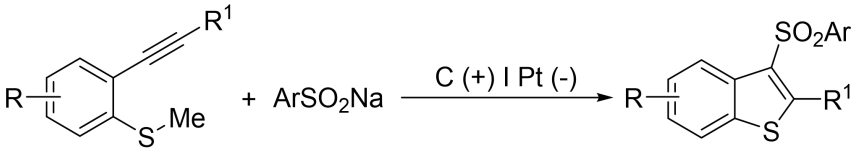
2020 年，Xuan 等人[71]开发了无需光催化剂的喹喔啉-2(1*H*)-酮烷基化新方法。该体系利用 4-烷基-1, 4-二氢吡啶(R-DHPs)作为烷基自由基前体，乙酰氧基苯碘唑(BI-OAc)作为电子受体与光激发的 R-DHPs 发生单电子转移过程，实现高效转化。该反应温和条件且展现出良好的底物兼容性，并且成功应用于药物分子的功能化修饰，具有很高的合成应用价值（Scheme 3-5）。



Scheme 3-5 无光催化剂的喹喔啉-2(1*H*)-酮自由基烷基化

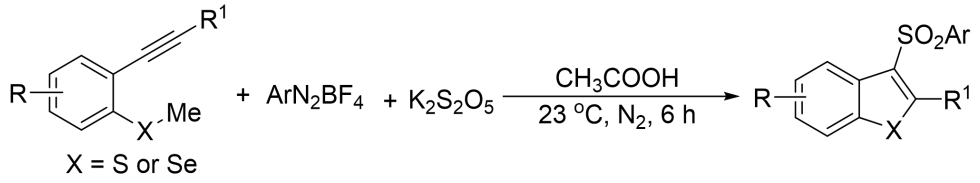
2021 年，Fang 课题组[72]在无氧化剂和催化剂条件下，以 2-炔基硫代苯甲醚与亚磺酸钠为原料，建立了一种电化学合成 C3-磺酰化苯并噻吩的新方法。在恒流条件下，实现多种磺酰化苯并噻吩的绿色合成且产率达到中等至良好，同时兼具优秀的可放大性。机理研究证实，该反应遵循自由基加成-环化串联途径（Scheme 3-6）。

同年，Wang 课题组[73]也开发了 2-炔基硫代苯甲醚与亚磺酸钠的电化学磺酰化/环化新方法，在无催化剂、氧化剂条件下绿色高效制备 3-磺酰化苯并噻吩。该反应展现出了优异的官能团兼容性（Scheme 3-6）。



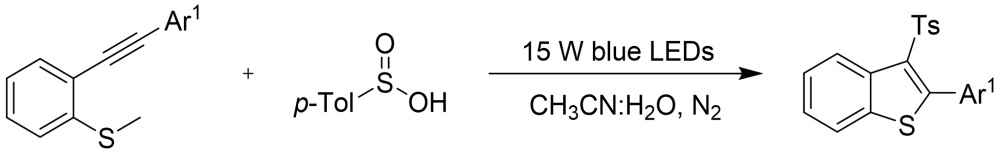
Scheme 3-6 电催化 2-炔基硫代苯甲醚与亚磺酸钠串联环化合成 3-芳基磺酰基苯并噻吩

2023 年，Lee[74]课题组研究开发了无催化剂的邻炔基苯甲硫醚、芳基重氮盐和焦亚硫酸钾三组分一锅法合成 3-芳磺酰基苯并噻吩新策略。该反应选用廉价焦亚硫酸钾作为硫源。机理研究表明，该反应经历分子内自由基环化过程，乙酸作为溶剂的同时可以淬灭甲基自由基副反应（Scheme 3-7）。



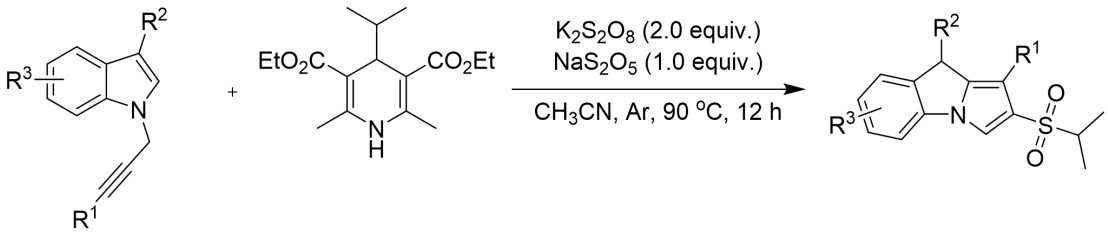
Scheme 3-7 邻炔基苯甲硫醚、芳基重氮盐和焦亚硫酸钾三组分合成 3-芳基磺酰基苯并噻吩

2023 年，Shen 等人[75]报道了一种可见光诱导芳基亚磺酸和邻炔基苯甲硫醚串联环化构筑苯并噻吩骨架的反应。该反应通过自由基加成/环化级联过程，在无光催化剂、无碱、无氧化剂和无金属的条件下高效构建含硫杂环化合物（Scheme 3-8）。



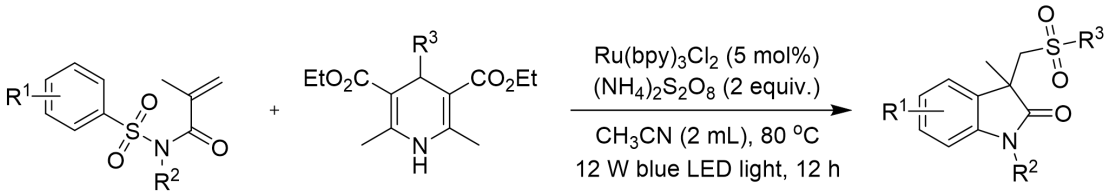
Scheme 3-8 可见光诱导芳基亚磺酸和甲硫基芳烃构建含硫杂环化合物

2023 年，Liu 小组[76]研究开发了 N-炔丙基吲哚与汉斯酯的氧化磺酰化/环化新策略。该体系以焦亚硫酸钠为二氧化硫供体，4-烷基取代汉斯酯作为自由基前体，成功实现了 2-磺酰基-9*H*-吡咯并[1, 2-*a*]吲哚类化合物的高效构建。机理研究表明，磺酰自由基通过二氧化硫插入参与成环过程（Scheme 3-9）。



Scheme 3-9 N-炔丙基吲哚与汉斯酯的氧化磺酰化/环化

2024 年，Liu 课题组[77]报道了可见光诱导活化烯烃双官能团化新方法，以 *N*-取代-*N*-（苯基磺酰基）甲基丙烯酰胺和 4-取代汉斯酯作为底物，通过自由基 Smiles 重排生成烷基磺酰化的吲哚。该转化涉及二氧化硫插入、1, 4-芳基迁移、脱磺酰化、环化串联过程，以易得的汉斯酯作为为烷基化试剂，为复杂磺酰化杂环构建提供新途径（Scheme 3-10）。

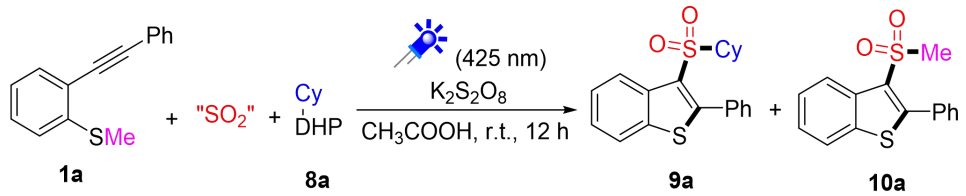


Scheme 3-10 光诱导活化烯烃双官能团化

目前，3-磺酰基苯并噻吩的合成已经有了很大的发展，但合成的大多是 3-芳基磺酰基，3-烷基磺酰基的有效合成方法还非常少。因此，高效合成 3-烷基磺酰基苯并噻吩的方法还亟待开发。

3.2 反应条件优化

Table 3-1 反应条件优化 [a]



Entry	SO_2 surrogate	Solvent	Yield of **9a** (%)[b]	Yield of **10a** (%)[b]
1	DABSO	CH_3COOH	80	13
2	$K_2S_2O_5$	CH_3COOH	65	24
3	$Na_2S_2O_5$	CH_3COOH	61	27
4	-	CH_3COOH	n.d.	-
5	DABSO	CH_3COOH	73[c]	13

6	DABSO	CH_3COOH	n.d.[d]	-
7	DABSO	CH_3COOH	trace[e]	-
8	DABSO	CH_3CN	54	40
9	DABSO	$CHCl_3$	57	35
10	DABSO	DMF	18	21
11	DABSO	DCE	trace	-
12	DABSO	DMSO	30	39
13	DABSO	THF	trace	-
14	DABSO	Ace	36	30
15	DABSO	EtOAc	trace	-
16	DABSO	H_2O	n.d.	-
17	DABSO	CH_3COOH	70[f], 48[g]	18[f], 9[g]
18	DABSO	CH_3COOH	65[h], 75[i]	10[h], 11[i]
19	DABSO	CH_3COOH	trace[j]	-

[a]Conditions: **1a** (0.2 mmol), **8a** (1.2 eq.), $K_2S_2O_8$ (1.2 eq.) and DABSO (1.2 eq.) in solvent (0.1 M) were irradiated with 425 nm (10 W) LED in a reaction tube under nitrogen atmosphere at room temperature for 12 h unless otherwise stated. [b]Isolated yield. [c]$(NH_4)_2S_2O_8$ instead of $K_2S_2O_8$. [d]No $K_2S_2O_8$. [e]In dark. [f]395 nm LED. [g]467 nm LED. [h]Irradiation for 8 h. [i]Irradiation for 16 h. [j]Air atmosphere,

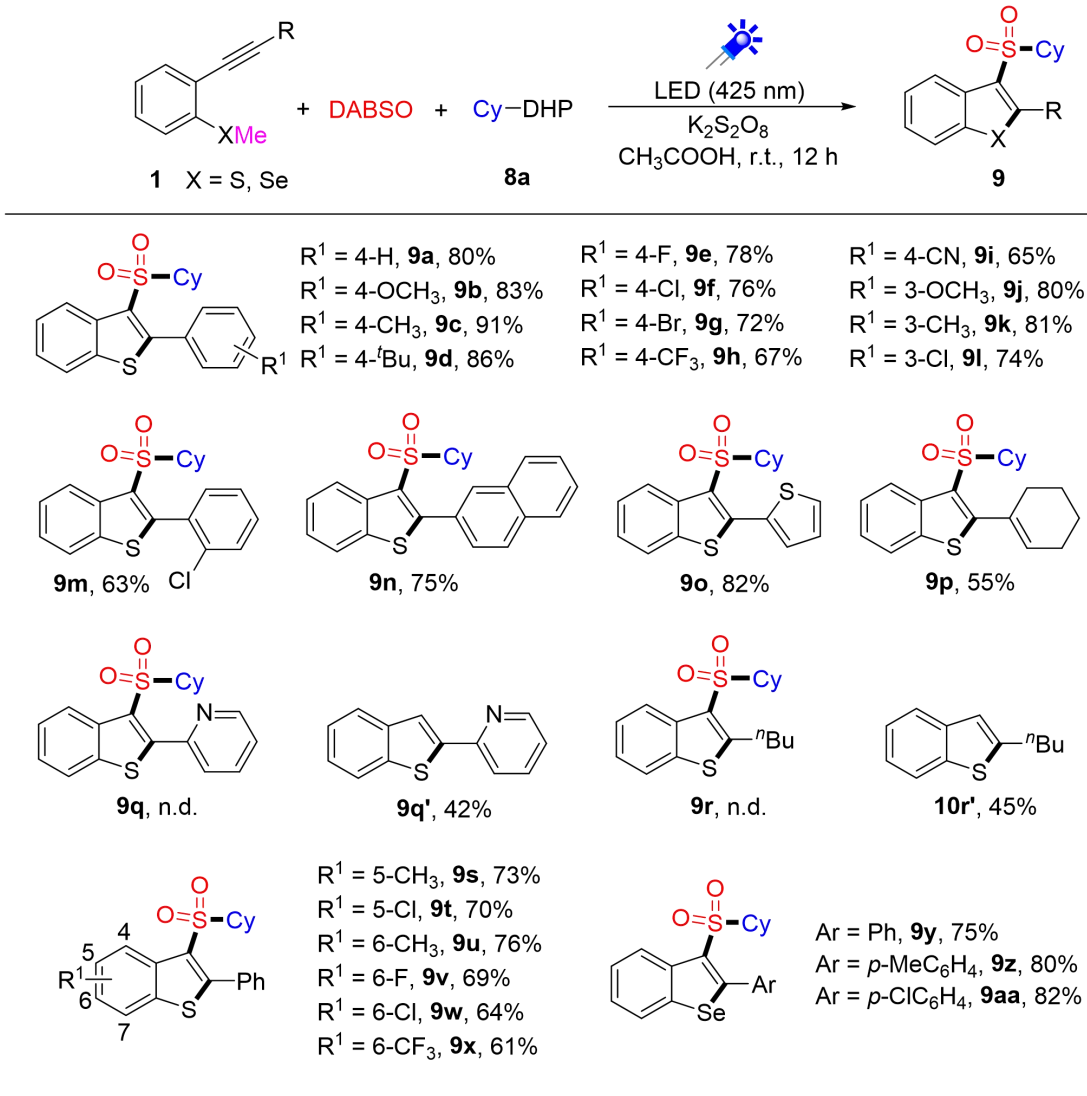
为了确定最佳反应条件，以邻炔基苯甲硫醚 （**1a**）和 4-环己基汉斯酯（**8a**）为模版反应，分别对磺酰基来源、溶剂、波长等条件进行了优化（Table 3-1）。

首先对磺酰基来源进行了优化（entries 1-4），确定 DABSO 为最佳磺酰基来源（目标产物 **9a** 产率 80%）。将反应的氧化剂 $K_2S_2O_8$ 替换为$(NH_4)_2S_2O_8$ 后反应产率略有下降（entry 5），不加氧化剂则该反应不能发生（entry 6）。控制实验（entry 7）说明该反应的发生需要光照参与。

随后对反应溶剂进行了优化，发现该反应的最佳反应溶剂为乙酸（entries 8-16）。然后优化了反应光源的波长（entry 17），得到最佳波长为 425 nm。又对反应时长进行了筛选（entry 18），得到最佳反应时长为 12 h。最后，在空气氛围下尝试该反应时，产率大大降低（entry 19）。

最终确定该反应的最佳条件是：DABSO 作为磺酰基来源、$K_2S_2O_8$ 作为氧化剂、乙酸作为溶剂在氮气氛围中 10 W 425 nm 蓝光 LEDs 照射 12 小时。

3.3 反应底物普适性考察

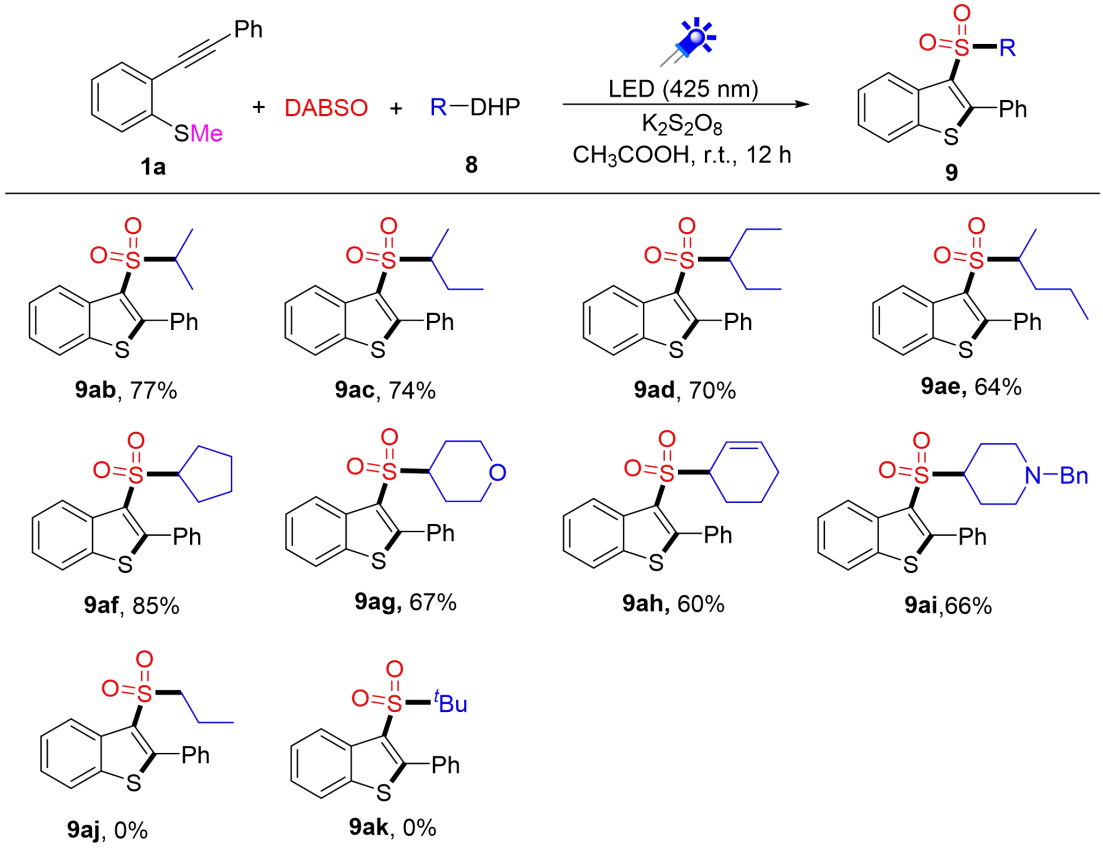


[a]Conditions: **1a** (0.2 mmol), **8a** (1.2 eq.), $K_2S_2O_8$ (1.2 eq.) and DABSO (1.2 eq.) in CH_3COOH (2.0 mL) were irradiated with 425 nm (10 W) LED in a reaction tube under nitrogen atmosphere at room temperature for 12 h unless otherwise stated. [b]Isolated yields.

Scheme 3-11 底物普适性考察 I[a]

在确定最优反应条件后，考察了该反应的适用范围（Scheme 3-11）。首先考察了三键连接的苯环上的电子效应。苯环对位含甲氧基、甲基及叔丁基等给电子基团的底物均能顺利反应，以中等至良好收率获得目标磺酰化产物（**9b–9d**）。苯环对位带有氟、氯、溴、氰基及三氟甲基等吸电子取代基的底物（**9e–9g**）在该反应条件下也可以较好收率生成相应产物。苯环的邻位或间位取代的底物（**9j–9l**）亦表现出良好反应活性，产率在 63%-81%。进一步拓展底物发现，三键连接萘环（**9n**）或杂环噻吩基团（**9o**）的底物分别以 75%和 82%的产率实现

转化。值得关注的是，环己烯基取代的底物（**9p**）仍能以 55%产率获得目标产物。然而，当苯环被烷基或吡啶基替代时（**9q'**、**9r'**），并没生成预期的 3-取代环化产物，而是以 42%和 45%的产率生成自环化产物。随后对邻炔基苯甲硫醚的主体苯环取代基进行考察。实验结果表明，甲基、氟、氯及三氟甲基等取代基在该反应条件下均能顺利形成目标产物（**9s**–**9x**）。突破性发现是，邻炔基苯甲硒醚同样是有效底物，以良好产率获得目标产物（**9y**–**9aa**），这为含硒杂环化合物的构建提供了新思路。



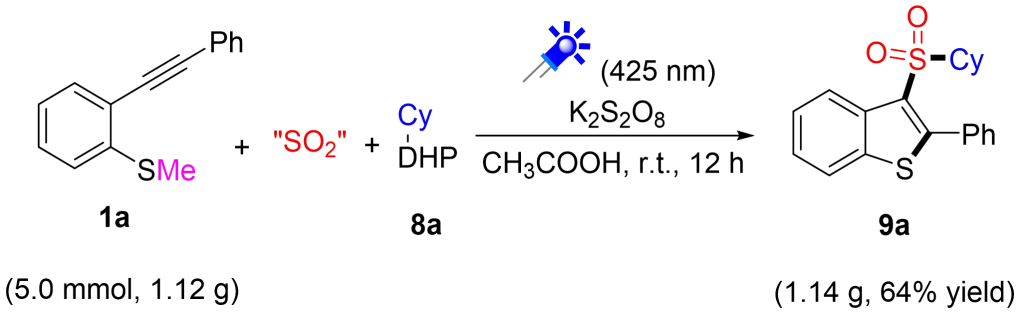
[a]Conditions: **1a** (0.2 mmol), **8a** (1.2 eq.), $K_2S_2O_8$ (1.2 eq.) and DABSO (1.2 eq.) in CH_3COOH (2.0 mL) were irradiated with 425 nm (10 W) LED in a reaction tube under nitrogen atmosphere at room temperature for 12 h unless otherwise stated. [b]Isolated yields

Scheme 3-12 底物普适性考察 II [a]

本研究进一步考察了汉斯酯衍生物的适用范围（Scheme 3-12）。实验表明，不同结构的汉斯酯可有效转化为对应烷基自由基，生成目标产物。含仲烷基结构单元的 4-取代汉斯酯与 **1a** 及 DABSO 反应时，可以获得目标产物（**9ab**–**9ae**）。值得注意的是，环戊基（**9af**）、环己烯基（**9ah**）、四氢吡喃基及苄基取代哌啶基（**9ai**）等环状结构均能顺利实现二氧化硫插入反应。然而，正丙基（**9aj**）取

代的汉斯酯及叔丁基（**9ak**）取代的汉斯酯参与反应时，未检测到预期产物，但观察到甲基磺酰化副产物的生成。

3.4 克级反应

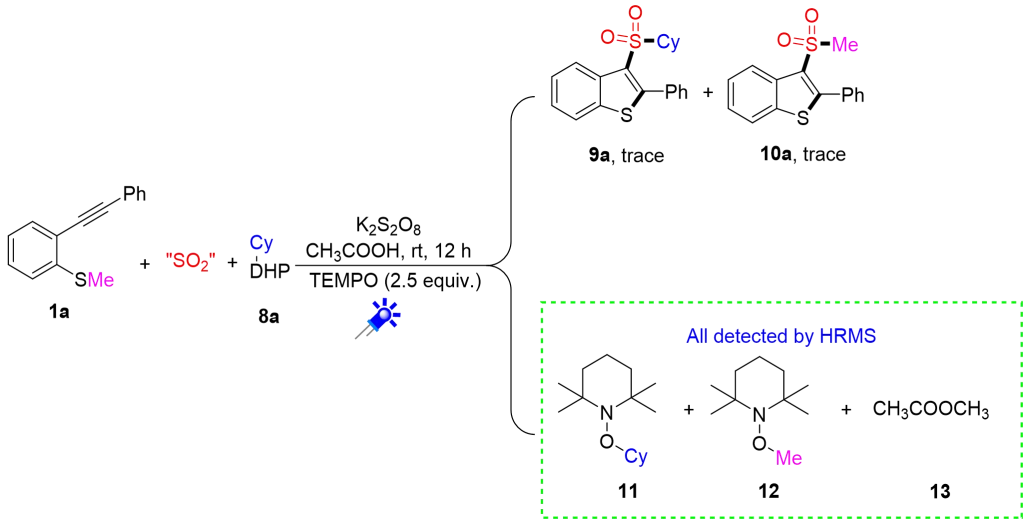


Scheme 3-13 克级反应

值得注意的是，这种反应是可以放大的。如 Scheme 3-13 所示，在模板反应条件下，以 1.12 g （5 mmol）的 **1a** 进行环化反应，得到所需的产物 **9a**，产率为 64%。

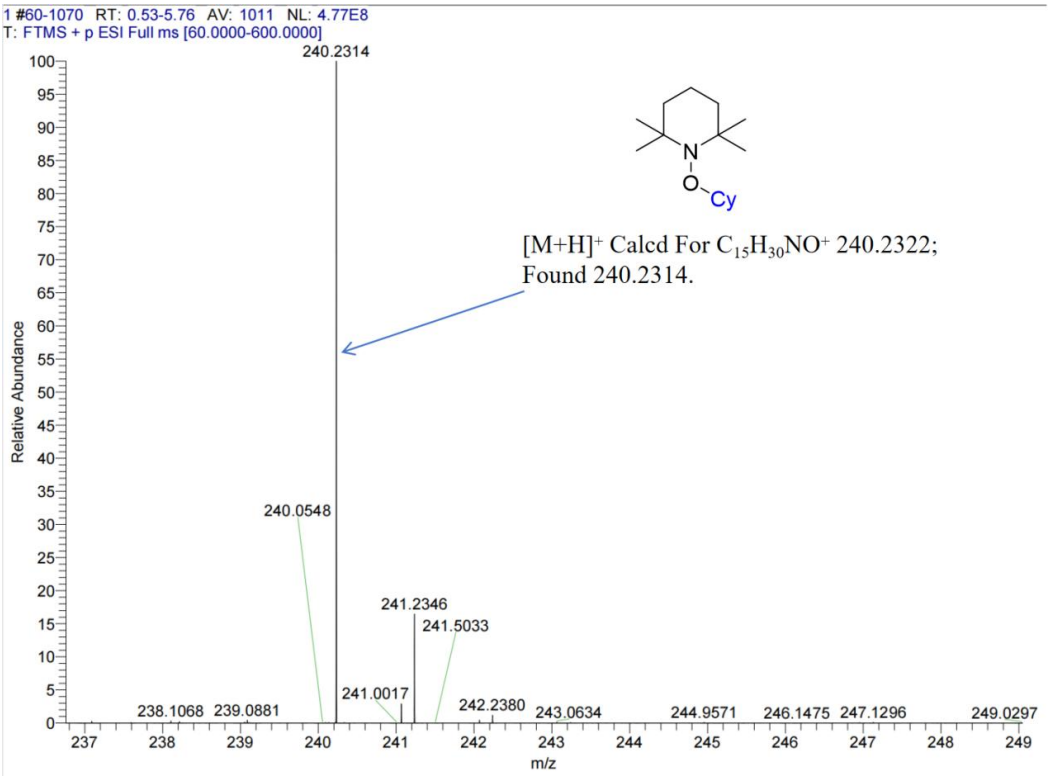
3.5 反应机理研究

3.5.1 自由基捕获实验

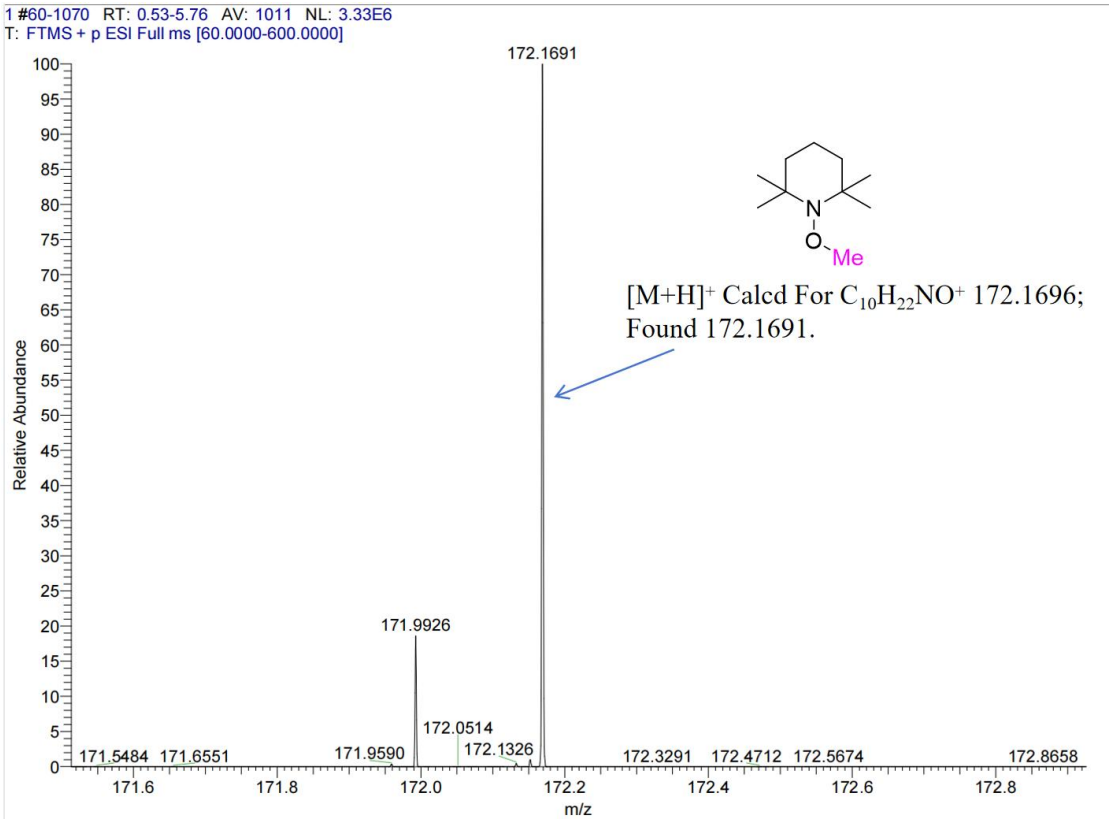


Scheme 3-14 自由基捕获实验

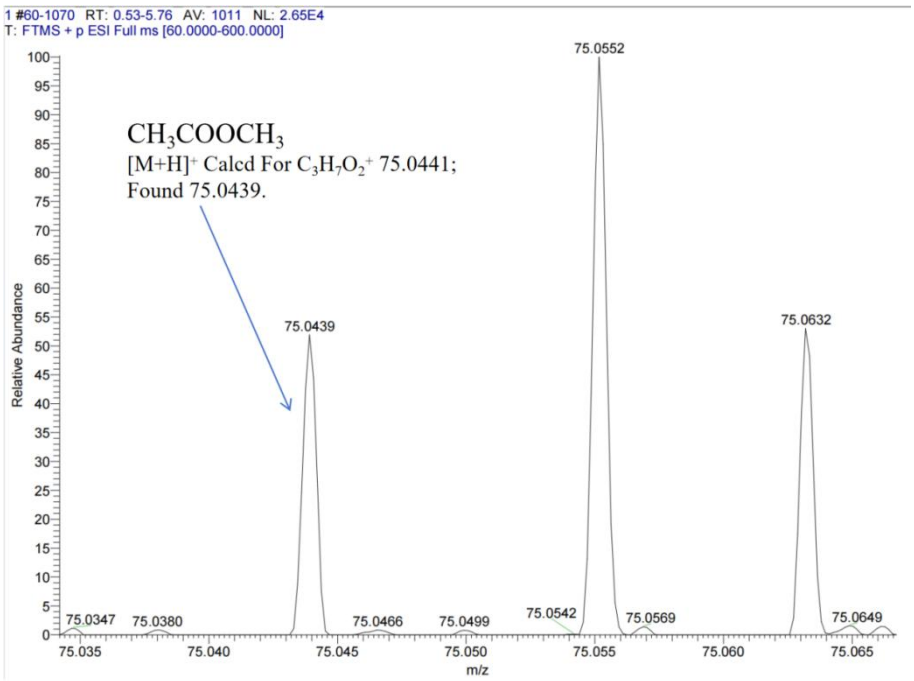
为了阐明反应机理，进行了一系列实验。在标准条件下，将 2.5 equiv.的自由基捕获试剂基 2, 2, 6, 6-四甲基哌啶氧化物（TEMPO）加入到反应中，只检测到微量的产物 **9a** 和 **10a**，反应被明显抑制。同时通过高分辨质谱检测到自由基捕获加合物 **11**、**12** 和 **13**，表明该反应可能涉及自由基过程。



Scheme 3-15 环己基自由基加合物（**11**）的高分辨质谱



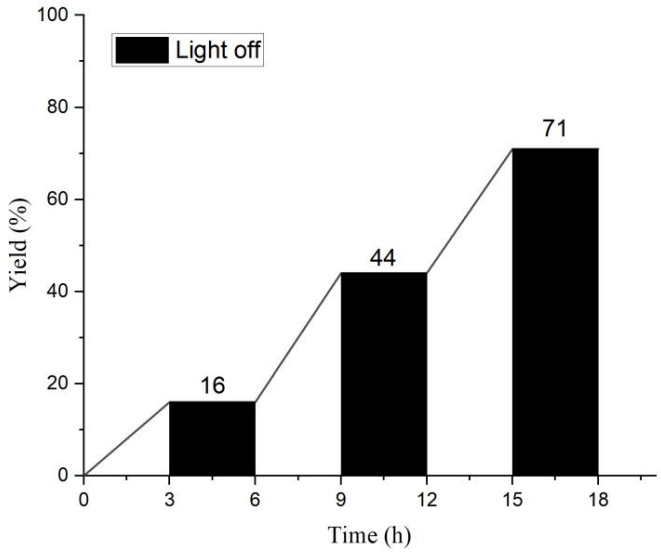
Scheme 3-16 甲基自由基加合物（**12**）的高分辨质谱



Scheme 3-17 乙酸甲酯（**13**）的高分辨质谱

3.5.2 开关灯实验

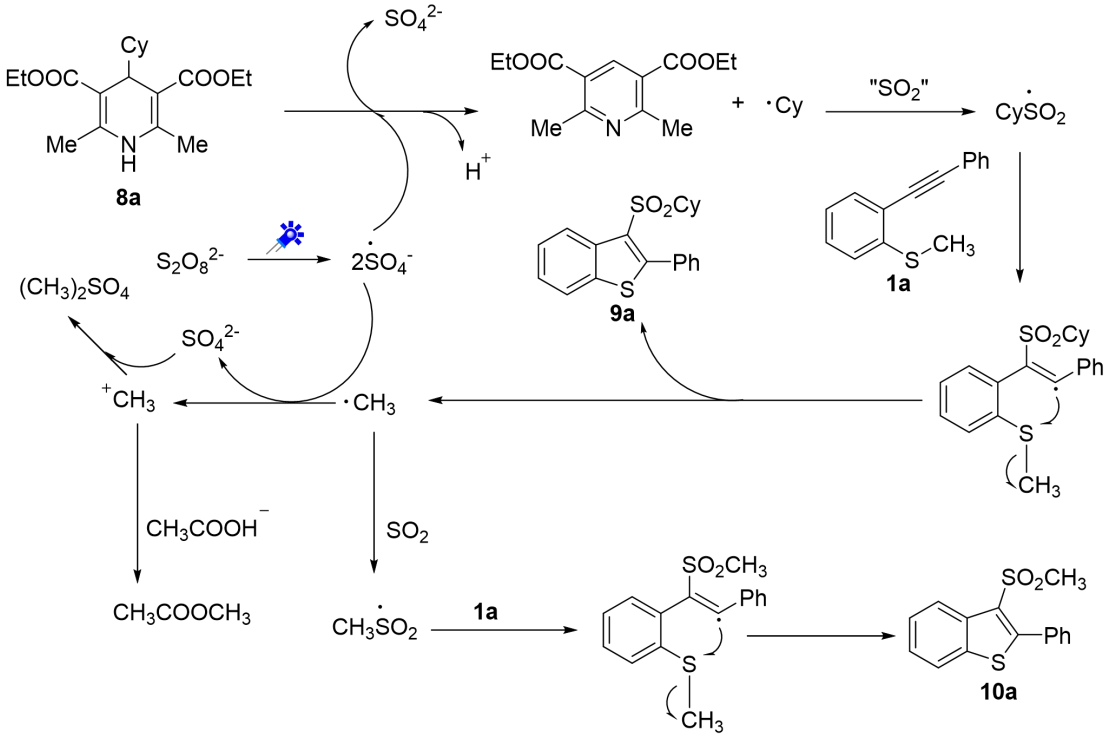
为了说明反应是否需要持续光照，进行了开关灯实验，如 Scheme 3-18 所示。将反应液在室温、N_2 气氛下，蓝光 LED （425 nm, 10 W）照射下搅拌 3 h，然后在无蓝光的情况下搅拌 3 h。Scheme 3-18 给出了蓝光 LED （425 nm, 10 W）间歇光照一定时间的产物产率。结果表明，该反应的进行需要持续光照。



Scheme 3-18 开关灯实验

3.5.3 可能的反应机理

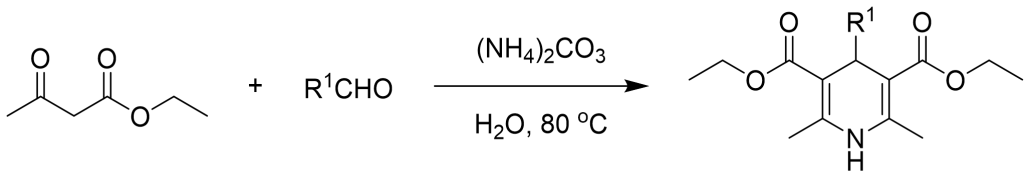
根据自由基捕获实验的结果，结合前人的报道，提出了该反应的可能机理（Scheme 3-19）。首先，在光照条件下，汉斯酯（**8a**）通过氧化单电子转移转化为吡啶盐和环己基自由基。环己基自由基与 DABSO 反应生成环己基磺酰基自由基中间体。生成的环己基磺酰基自由基会攻击邻炔基苯甲硫醚（**1a**）的三键，生成环化产物 **9a**，并释放一个甲基自由基。释放出来的甲基自由基随后会被二氧化硫捕获，产生甲基磺酰基自由基，并与邻炔基苯甲硫醚反应，产生副产物。



Scheme 3-19 可能的反应机理

3.6 实验部分

3.6.1 4-烷基汉斯酯（8）制备的一般步骤

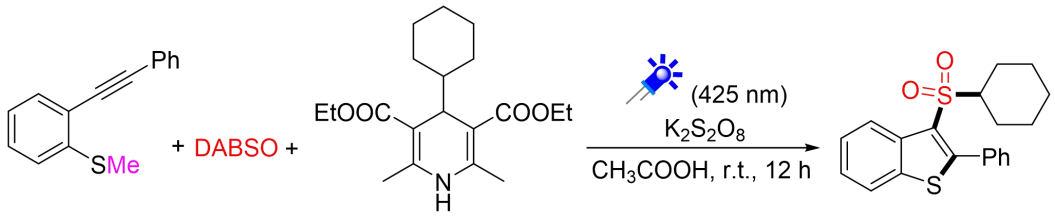


Scheme 3-20 4-烷基汉斯酯的合成

在装有磁子的圆底烧瓶中依次加入相应的醛（20.0 mmol， 2.0 equiv.）、乙酰乙酸乙酯（10.0 mmol， 1.0 equiv.）、NH_4OAc （40.0 mmol， 2.0 equiv.）和 H_2O （20.0 mL）。反应混合物在 80 ℃油浴中搅拌 3-4 h，待醛完全消耗后，冷

却至室温，乙酸乙酯（3*50 mL）萃取，合并的有机相使用无水 Na_2SO_4 干燥，过滤，减压蒸发。用乙酸乙酯/石油醚（1:5,V/V）在硅胶上进行柱层析纯化，得到相应的纯产物。

3.6.2 3-环己基磺酰基苯并噻吩（9a）制备的一般步骤

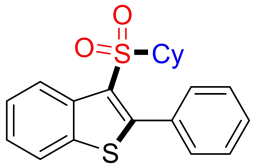


1a **8a** **9a**

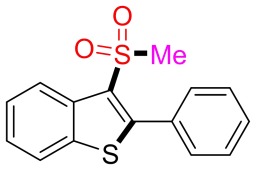
Scheme 3-21 可见光促进 3-甲基磺酰基苯并噻吩合成

在装有磁子的 10 mL 反应容器中加入邻炔基苯甲硫醚（**1a**, 44.9 mg, 0.20 mmol）、DABSO （57.6 mg, 0.24 mmol, 1.2 equiv.）、4-环己基汉斯酯（**8a**, 80.5 mg, 0.24 mmol, 1.2 equiv）、$K_2S_2O_8$ （64.9 mg, 0.24 mmol, 1.2equiv.）和 CH_3COOH （2.0 mL）。反应液在室温氩气气氛中，蓝光 LED 425 nm， 10 W 照射，搅拌 12 h。反应完成后，旋转蒸发除去溶剂，以乙酸乙酯/石油醚（1:5,V/V）为洗脱液，硅胶柱层析纯化，得到所需产物 **9a** 为白色固体（57.1 mg，产率 80%）。

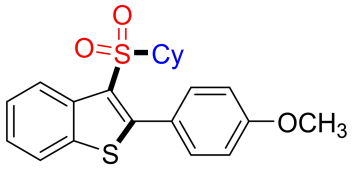
3.7 产物的表征数据



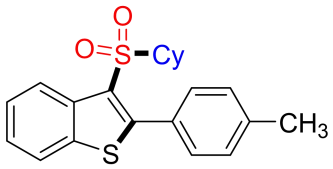
3-(Cyclohexylsulfonyl)-2-phenylbenzo[*b*]thiophene (9a). White solid, 80% yield (57.1 mg), mp 105.8–107.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.56–7.55 (m, 2H), 7.52–7.49 (m, 1H), 7.47–7.41 (m, 4H), 2.85 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.89 (d, *J* = 12.6 Hz, 2H), 1.78–1.76 (m, 2H), 1.58–1.57 (m, 1H), 1.46–1.39 (m, 2H), 1.09–1.06 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.7, 138.3, 136.8, 131.7, 130.6, 129.6, 127.7, 126.3, 125.9, 125.7, 124.6, 121.9, 63.6, 25.04, 25.02, 24.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{21}O_2S_2^+$ 357.0977; Found 357.0976.



3-(Methylsulfonyl)-2-phenylbenzo[*b*]thiophene (10a). White solid, 13% yield (7.5 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.

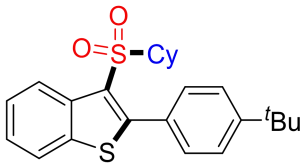


3-Cyclohexylsulfonyl)-2-(4-methoxyphenyl)benzo[*b*]thiophene (9b). White solid, 83% yield (64.1 mg), mp 115.4–117.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.52–7.49 (m, 3H), 7.46–7.43 (m, 1H), 6.96 (dt, *J* = 9.0, 2.4 Hz, 2H), 3.87 (s, 3H), 2.85 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.88 (d, *J* = 12.6 Hz, 2H), 1.78–1.77 (m, 2H), 1.60–1.59 (m, 1H), 1.46–1.39 (m, 2H), 1.11–1.07 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.8, 154.1, 138.2, 137.1, 132.1, 126.0, 125.9, 125.6, 124.7, 123.7, 121.9, 113.3, 63.6, 55.4, 25.1, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{23}O_3S_2^+$ 387.1083; Found 387.1082.

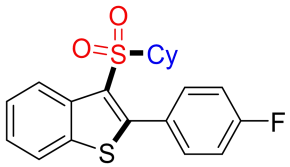


3-(Cyclohexylsulfonyl)-2-(*p*-tolyl)benzo[*b*]thiophene (9c). Colourless oil, 91% yield (67.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.52–7.49 (m, 1H), 7.46–7.42 (m, 3H), 7.24 (d, *J* = 7.8 Hz, 2H), 2.86 (tt, *J* = 12.0, 3.6 Hz, 1H), 2.42 (s, 3H), 1.89 (d, *J* = 12.6 Hz, 2H), 1.78–1.76 (m, 2H), 1.59–1.58 (m, 1H), 1.46–1.39 (m, 2H), 1.09–1.07 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.2, 139.7, 138.3, 137.0, 130.5, 128.7, 128.5, 126.0, 125.9, 125.6,

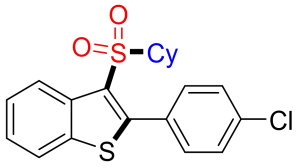
124.6, 121.9, 63.6, 25.1, 24.8, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{23}O_2S_2^+$ 371.1134; Found 371.1132.



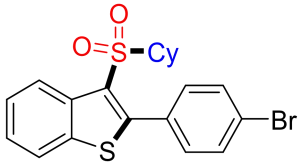
2-(4-(*tert*-Butyl)phenyl)-3-(cyclohexylsulfonyl)benzo[*b*]thiophene (9d). White solid, 86% yield (71.0 mg), mp 152.5–154.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.52–7.49 (m, 3H), 7.45–7.42 (m, 3H), 2.82 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.89 (d, *J* = 12.0 Hz, 2H), 1.79–1.76 (m, 2H), 1.59–1.58 (m, 1H), 1.47–1.43 (m, 2H), 2.37 (s, 9H), 1.11–1.02 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.0, 152.8, 138.3, 137.1, 130.4, 128.7, 126.0, 125.9, 125.6, 124.8, 124.7, 121.8, 63.5, 34.9, 31.4, 25.15, 25.13, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{24}H_{29}O_2S_2^+$ 413.1603; Found 413.1602.



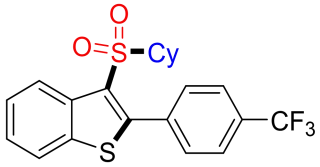
3-**(Cyclohexylsulfonyl)-2-(4-fluorophenyl)benzo[*b*]thiophene (9e).** White solid, 78% yield (58.4 mg), mp 117.5–118.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.56–7.51 (m, 3H), 7.48–7.45 (m, 1H), 7.12 (t, *J* = 8.4 Hz, 2H), 2.87 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.89 (d, *J* = 12.6 Hz, 2H), 1.80–1.78 (m, 2H), 1.61–1.60 (m, 1H), 1.45–1.38 (m, 2H), 1.12–1.09 (m, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = –111.1; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.6 (d, *J* = 248.7 Hz), 152.7, 138.2, 136.8, 132.6 (d, *J* = 8.3 Hz), 127.6 (d, *J* = 3.2 Hz), 126.6, 126.1, 125.9, 124.7, 121.9, 114.9 (d, *J* = 21.7 Hz), 63.7, 25.1, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}FO_2S_2^+$ 375.0883; Found 375.0883.



2-(4-Chlorophenyl)-3-(cyclohexylsulfonyl)benzo[*b*]thiophene (9f). White solid, 76% yield (59.4 mg), mp 139.1–140.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.54–7.51 (m, 1H), 7.50–7.45 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 2H), 2.89 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.89 (d, *J* = 12.6 Hz, 2H), 1.80–1.78 (m, 2H), 1.61–1.60 (m, 1H), 1.45–1.38 (m, 2H), 1.12–1.09 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.4, 138.3, 136.7, 135.9, 132.0, 130.1, 128.0, 126.6, 126.2, 126.0, 124.7, 122.0, 63.7, 25.1, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}ClO_2S_2^+$ 391.0588; Found 391.0587.

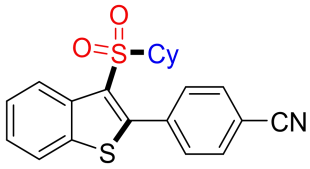


2-(4-Bromophenyl)-3-(cyclohexylsulfonyl)benzo[*b*]thiophene (9g). White solid, 72% yield (62.7 mg), mp 139.8–141.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 2.89 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.89 (d, *J* = 12.6 Hz, 2H), 1.80–1.78 (m, 2H), 1.61–1.60 (m, 1H), 1.44–1.38 (m, 2H), 1.12–1.09 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.4, 138.3, 136.7, 135.9, 132.2, 130.9, 128.0, 126.6, 126.2, 126.0, 124.7, 124.3, 122.0, 77.4, 77.2, 76.9, 63.7, 25.0, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}BrO_2S_2^+$ 435.0083; Found 435.0082.

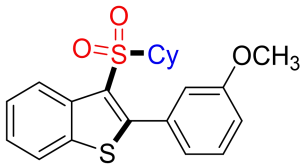


3-(Cyclohexylsulfonyl)-2-(4-(trifluoromethyl)phenyl)benzo[b]thiophene (9h). Yellow solid, 67% yield (56.9 mg), mp 114.7–116.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$):

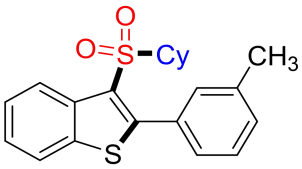
δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.70–7.67 (m, 4H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 2.92 (t, *J* = 12.0 Hz, 1H), 1.91 (d, *J* = 12.6 Hz, 2H), 1.81–1.80 (m, 2H), 1.62–1.61 (m, 1H), 1.45–1.39 (m, 2H), 1.14–1.11 (m, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −62.7; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.9, 138.5, 136.6, 135.5, 131.5 (q, *J* = 30.0 Hz), 131.2, 127.1, 126.3, 126.2, 124.7, 124.6 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 270.0 Hz), 122.1, 63.8, 25.07, 25.05, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{20}F_3O_2S_2^+$ 425.0851; Found 425.0850.



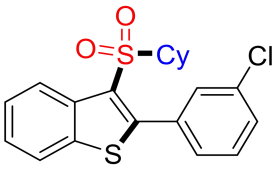
(3-(Cyclohexylsulfonyl)benzo[*b*]thiophen-2-yl)benzonitrile (9i). White solid, 65% yield (49.6 mg), mp 126.8–128.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.73–7.72 (m, 2H), 7.67–7.66 (m, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 2.93 (t, *J* = 12.0, 1H), 1.90 (d, *J* = 12.6 Hz, 2H), 1.82–1.80 (m, 2H), 1.67–1.64 (m, 1H), 1.44–1.38 (m, 2H), 1.17–1.09 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.1, 138.5, 136.6, 136.4, 131.5, 131.3, 127.3, 126.5, 126.4, 124.7, 122.2, 118.4, 113.4, 63.8, 25.0, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}NO_2S_2^+$ 382.0930; Found 382.0927.



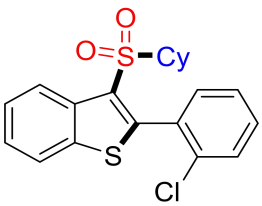
3-(Ccyclohexylsulfonyl)-2-(3-methoxyphenyl)benzo[*b*]thiophene (9j). Colourless oil, 80% yield (61.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.53–7.51 (m, 1H), 7.47–7.45 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.13–7.12 (m, 2H), 7.02–7.01 (m, 1H), 3.85 (s, 3H), 2.86 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.89 (d, *J* = 12.6 Hz, 2H), 1.80–1.79 (m, 2H), 1.61–1.60 (m, 1H), 1.49–1.43 (m, 2H), 1.13–1.07 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.8, 153.4, 138.3, 137.0, 132.9, 128.8, 126.5, 126.0, 125.8, 124.8, 123.1, 121.9, 116.5, 115.5, 63.7, 55.5, 25.2, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{23}O_3S_2^+$ 387.1083; Found 387.1085.



3-(Cyclohexylsulfonyl)-2-(*m*-tolyl)benzo[*b*]thiophene (9k). White solid, 81% yield (60.0 mg), mp 131.3–132.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.52–7.49 (m, 1H), 7.45–7.42 (m, 1H), 7.37 (s, 1H), 7.36–7.34 (m, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.28–7.26 (m, 1H), 2.86 (tt, *J* = 12.0, 3.6 Hz, 1H), 2.41 (s, 3H), 1.91–1.88 (m, 2H), 1.78–1.77 (m, 2H), 1.59–1.58 (m, 1H), 1.47–1.41 (m, 2H), 1.11–1.06 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.0, 138.2, 137.3, 136.9, 131.6, 131.3, 130.4, 127.6, 127.5, 126.2, 125.9, 125.6, 124.6, 121.9, 63.6, 25.1, 24.8, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{23}O_2S_2^+$ 371.1134; Found 371.1127.

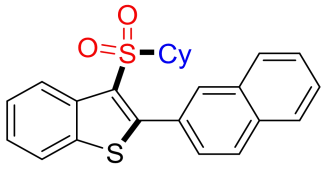


2-(3-Chlorophenyl)-3-(cyclohexylsulfonyl)benzo[*b*]thiophene (9l). White solid, 74% yield (57.9 mg), mp 140.2–141.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.55–7.52 (m, 2H), 7.49–7.46 (m, 1H), 7.45–7.43 (m, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 2.90 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.91 (d, *J* = 12.6 Hz, 2H), 1.82–1.80 (m, 2H), 1.62–1.61 (m, 1H), 1.44 (qd, *J* = 12.0, 4.2 Hz, 2H), 1.16–1.09 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.8, 138.4, 136.6, 133.6, 133.4, 130.5, 129.7, 129.1, 128.9, 126.9, 126.2, 126.1, 124.7, 122.0, 63.8, 25.1, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}ClO_2S_2^+$ 391.0588; Found 391.0586.

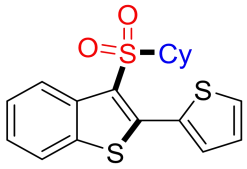


2-(2-Chlorophenyl)-3-(cyclohexylsulfonyl)benzo[*b*]thiophene (9m). Colourless oil, 63% yield (49.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.88

(d, *J* = 7.8 Hz, 1H), 7.55–7.52 (m, 1H), 7.50–7.47 (m, 3H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.37–7.34 (m, 1H), 2.99 (tt, *J* = 12.0, 3.6 Hz, 1H), 2.07 (d, *J* = 12.6 Hz, 2H), 1.85–1.83 (m, 2H), 1.784–1.775 (m, 1H), 1.632–1.627 (m, 1H), 1.54–1.47 (m, 2H), 1.16–1.13 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.9, 138.9, 136.4,134.0, 132.0, 131.1, 130.9, 129.5, 128.6, 126.1, 126.0, 124.8, 122.1, 64.0, 25.6, 25.2, 25.1, 24.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}ClO_2S_2^+$ 391.0588; Found 391.0587.

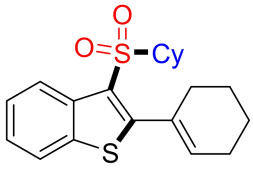


3-(Cyclohexylsulfonyl)-2-(naphthalen-2-yl)benzo[*b*]thiophene (9n). White solid, 75% yield (61.0 mg), mp 124.2–126.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (dd, *J* = 7.8, 3.0 Hz, 1H), 8.03 (s, 1H), 7.89–7.87 (m, 3H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.55–7.51 (m, 3H), 7.47–7.44 (m, 1H), 2.92–2.87 (m, 1H), 1.90 (d, *J* = 12.6 Hz, 2H), 1.76–1.75 (m, 2H), 1.56–1.55 (m, 1H), 1.43–1.39 (m, 2H), 1.07–1.05 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.9, 138.4, 136.9, 133.5, 132.3, 130.2, 129.2, 128.5, 128.2, 127.9, 127.2, 127.1, 126.8, 126.4, 126.0, 125.8, 124.7, 121.9, 63.7, 25.0, 24.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{24}H_{23}O_2S_2^+$ 407.1134; Found 407.1135.

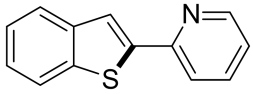


3-(Cyclohexylsulfonyl)-2-(thiophen-2-yl)benzo[*b*]thiophene (9o). Colourless oil, 82% yield (59.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.57 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.52 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.50–7.48 (m, 1H), 7.45–7.42 (m, 1H), 7.13 (dd, *J* = 4.8, 3.6 Hz, 1H), 2.92 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.94–1.91 (m, 2H)), 1.80–1.78 (m, 2H), 1.61–1.60 (m, 1H), 1.54–1.47 (m, 2H), 1.14–1.08 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 145.5, 138.2, 137.6, 132.0, 131.5, 129.5, 127.7, 126.9, 126.1, 125.9, 125.0, 121.7, 63.6,

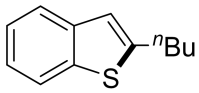
25.14, 25.11, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{19}O_2S_3^+$ 363.0542; Found 363.0533.



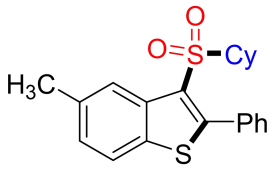
2-(Cyclohex-1-en-1-yl)-3-(cyclohexylsulfonyl)benzo[*b*]thiophene (9p). Colourless oil, 55% yield (39.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 6.0 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8, 1H), 5.91 (s, 1H), 3.05 (tt, *J* = 12.0, 3.0 Hz, 1H), 2.46 (s, 2H), 2.23–2.22 (m, 2H), 1.99 (d, *J* = 12.6 Hz, 2H), 1.86–1.85 (m, 2H), 1.82–1.78 (m, 2H), 1.73–1.69 (m, 2H), 1.59–1.55 (m, 5H), 1.21–1.16 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.2, 137.8, 136.8, 131.6, 131.2, 125.7, 125.3, 125.1, 124.2, 122.0, 63.9, 31.8, 25.7, 25.30, 25.29, 25.1, 22.8, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{25}O_2S_2^+$ 361.1290; Found 361.1291.



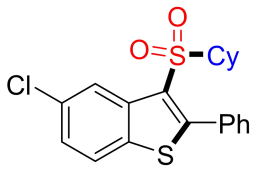
2-(Benzo[*b*]thiophen-2-yl)pyridine (9q')[78]**.** White solid, 42% yield (17.7 mg), mp 118.4–120.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 4.8 Hz, 1H), 7.87–7.86 (m, 2H), 7.81–7.79 (m, 2H), 7.75 (td, *J* = 7.8, 1.2 Hz, 1H), 7.37–7.33 (m, 2H), 7.22–7.20 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.5, 149.7, 144.6, 140.8, 140.6, 137.0, 125.2, 124.7, 124.3, 122.8, 122.7, 121.5, 119.8.



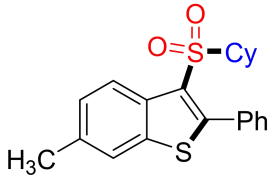
2-Butylbenzo[*b*]thiophene (9r')[79]**.** Colourless oil, 45% yield (17.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.30–7.27 (m, 1H), 7.24–7.21 (m, 1H), 6.98 (s, 1H), 2.89 (t, *J* = 7.8 Hz, 2H), 1.75–1.70 (m, 2H), 1.45–1.39 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.0, 140.4, 139.4, 124.1, 123.4, 122.8, 122.2, 120.5, 33.4, 30.6, 22.3, 14.0.



3-(Cyclohexylsulfonyl)-5-methyl-2-phenylbenzo[*b*]thiophene (9s). White solid, 73% yield (54.1 mg), mp 130.2–131.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.55–7.54 (m, 2H), 7.47–7.40 (m, 3H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.84 (tt, *J* = 12.0, 3.6 Hz, 1H), 2.53 (s, 3H), 1.89 (d, *J* = 12.0 Hz, 2H), 1.79–1.77 (m, 2H), 1.59–1.58 (m, 1H), 1.46–1.40 (m, 2H), 1.13–1.05 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.8, 137.1, 136.0, 135.6, 131.9, 130.6, 129.5, 127.6, 127.5, 125.9, 124.3, 121.5, 63.4, 25.08, 25.06, 24.8, 21.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{23}O_2S_2^+$ 371.1134; Found 371.1135.

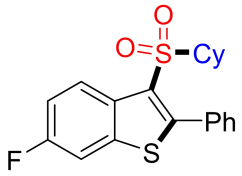


5-Chloro-3-(cyclohexylsulfonyl)-2-phenylbenzo[*b*]thiophene (9t). White solid, 70% yield (54.7 mg), mp 147.2–149.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 1.8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.56–7.54 (m, 2H), 7.50–7.47 (m, 1H), 7.46–7.41 (m, 3H), 2.77 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.86 (d, *J* = 12.6 Hz, 2H), 1.80–1.78 (m, 2H), 1.61–1.60 (m, 1H), 1.46–1.39 (m, 2H), 1.10–1.08 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 1155.4, 138.2, 136.4, 132.6, 131.3, 130.6, 129.9, 127.8, 126.4, 126.1, 124.4, 122.9, 62.8, 25.1, 25.0, 24.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}ClO_2S_2^+$ 391.0588; Found 391.0582.

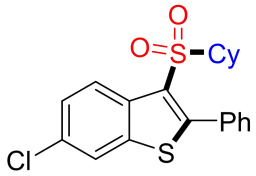


3-(Cyclohexylsulfonyl)-6-methyl-2-phenylbenzo[*b*]thiophene (9u). Colourless oil, 76% yield (56.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.4 Hz, 1H), 7.63 (s, 1H), 7.56–7.54 (m, 2H), 7.47–7.41 (m, 3H), 7.33 (d, *J* = 8.4, 1.2 Hz, 1H), 2.83 (tt,

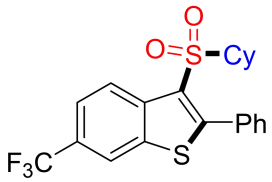
J = 12.0, 3.6 Hz, 1H), 2.50 (s, 3H), 1.88 (d, *J* = 12.0 Hz, 2H), 1.78–1.76 (m, 2H), 1.60–1.59 (m, 1H), 1.45–1.38 (m, 2H), 1.10–1.06 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.5, 138.6, 136.0, 134.7, 131.8, 130.7, 129.5, 127.73, 127.68, 126.1, 124.3, 121.6, 63.6, 25.1, 24.9, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{23}O_2S_2^+$ 371.1134; Found 371.1134.



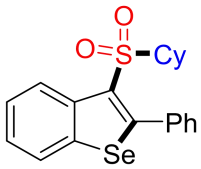
3-(Cyclohexylsulfonyl)-6-fluoro-2-phenylbenzo[*b*]thiophene (9v). White solid, 69% yield (51.7 mg), mp 144.3–145.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.56–7.52 (m, 3H), 7.49–7.43 (m, 3H), 7.28–7.25 (m, 1H), 2.78 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.89 (d, *J* = 13.2 Hz, 2H), 1.79–1.78 (m, 2H), 1.61–1.59 (m, 1H), 1.45–1.39 (m, 2H), 1.11–1.06 (m, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = –114.7; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.0 (d, *J* = 246.3 Hz), 153.2 (d, *J* = 3.3 Hz), 139.3 (d, *J* = 10.2 Hz), 133.5, 131.4, 130.7, 129.8, 127.9, 126.4, 126.3 (d, *J* = 6.8 Hz), 115.1 (d, *J* = 23.6 Hz), 108.1 (d, *J* = 25.1 Hz), 63.9, 25.1, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}FO_2S_2^+$ 375.0883; Found 375.0884.



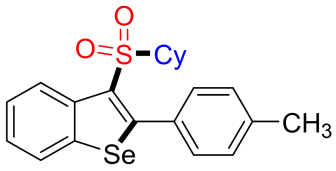
6-chloro-3-(cyclohexylsulfonyl)-2-phenylbenzo[b]thiophene (9w). White solid, 64% yield (50.0 mg), mp 131.6–133.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.56–7.55 (m, 2H), 7.50–7.43 (m, 4H), 2.77 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.87–1.85 (m, 2H), 1.79–1.77 (m, 2H), 1.60–1.59 (m, 1H), 1.44–1.38 (m, 2H), 1.11–1.05 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.9, 139.2, 135.5, 132.1, 131.2, 130.6, 129.9, 127.9, 126.9, 126.4, 125.8, 121.5, 63.9, 25.1, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}ClO_2S_2^+$ 391.0588; Found 391.0585.



3-(Cyclohexylsulfonyl)-2-phenyl-6-(trifluoromethyl)benzo[*b*]thiophene (9x). White solid, 61% yield (51.8 mg), mp 139.2–141.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.70–7.68 (m, 1H), 7.58–7.57 (m, 2H), 7.53–7.50 (m, 1H), 7.48–7.46 (m, 2H), 2.74 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.87 (d, *J* = 12.0 Hz, 2H), 1.80–1.78 (m, 2H), 1.61–1.60 (m, 1H), 1.47–1.41 (m, 2H), 1.12–1.06 (m, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −61.6; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.4, 141.3, 136.9, 131.1, 130.6, 130.1, 128.7 (q, *J* = 32.3 Hz), 128.0, 127.2, 124.3 (q, *J* = 270.9 Hz), 122.6, 122.3 (q, *J* = 4.2 Hz), 122.2 (q, *J* = 3.2 Hz), 64.1, 25.1, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{20}F_3O_2S_2^+$ 425.0851; Found 425.0849.

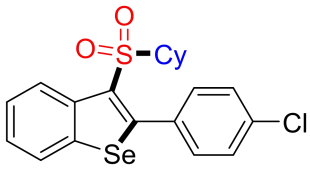


3-(Cyclohexylsulfonyl)-2-phenylbenzo[*b*]selenophene (9y). Yellow solid, 75% yield (60.5 mg), mp 131.4–132.5 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.52–7.50 (m, 3H), 7.43–7.39 (m, 4H), 2.91 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.91 (d, *J* = 12.6 Hz, 2H), 1.80–1.78 (m, 2H), 1.602–1.597 (m, 1H), 1.44 (qd, *J* = 12.0, 3.0 Hz, 2H), 1.14–1.06 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.7, 140.7, 138.5, 133.9, 129.9, 129.2, 128.9, 127.5, 126.7, 126.0, 125.9, 125.0, 63.2, 25.1, 24.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{21}O_2SSe^+$ 405.0422; Found 405.0419.

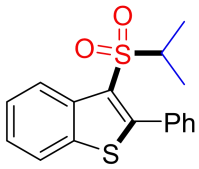


3-(Cyclohexylsulfonyl)-2-(*p*-tolyl)benzo[*b*]selenophene (9z). Yellow solid; 80% yield (66.8 mg): mp 110.9–111.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* =

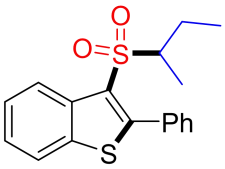
8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.51–7.48 (m, 1H), 7.41–7.37 (m, 3H), 7.20 (d, *J* = 7.8 Hz, 2H), 2.91 (tt, *J* = 12.0, 3.6 Hz, 1H), 2.40 (s, 3H), 1.91 (d, *J* = 12.6 Hz, 2H), 1.80–1.78 (m, 2H), 1.60–1.59 (m, 1H), 1.44 (qd, *J* = 12.0, 3.0 Hz, 2H), 1.11–1.09 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.1, 140.6, 139.3, 138.6, 130.9, 129.8, 128.6, 128.3, 126.6, 125.9, 125.8, 125.0, 63.2, 25.1, 24.7, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{23}O_2SSe^+$ 419.0578; Found 419.0577.



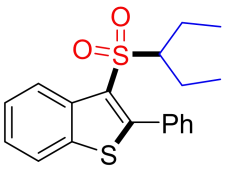
2-(4-Chlorophenyl)-3-(cyclohexylsulfonyl)benzo[*b*]selenophene (9aa). Yellow solid; 82% yield (71.8 mg): mp 140.2–140.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.53–7.51 (m, 1H), 7.45–7.41 (m, 3H), 7.37–7.36 (m, 2H), 2.94 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.91 (d, *J* = 12.6 Hz, 2H), 1.80–1.79 (m, 2H), 1.61–1.60 (m, 1H), 1.46–1.40 (m, 2H), 1.16–1.09 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.2, 140.7, 138.3, 135.4, 132.3, 131.2, 129.2, 126.7, 126.1, 125.0, 63.3, 25.1, 24.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{20}ClO_2SSe^+$ 439.0032; Found 439.0024.



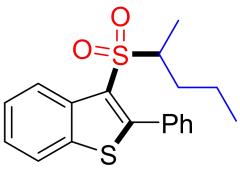
3-(Isopropylsulfonyl)-2-phenylbenzo[*b*]thiophene (9ab). White solid; 77% yield (48.7 mg): mp 124.2–124.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.58–7.56 (m, 2H), 7.53–7.50 (m, 1H), 7.48–7.42 (m, 4H), 3.18–3.11 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.9, 138.3, 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 (9ac). Yellow oil; 74% yield (48.9 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), 1.47–1.44 (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; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{19}O_2S_2^+$ 331.0821; Found 331.0820.

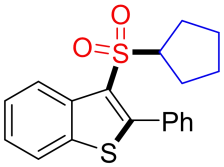


3-(Pentan-3-ylsulfonyl)-2-phenylbenzo[*b*]thiophene (9ad). Colourless oil; 70% yield (48.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.60–7.58 (m, 2H), 7.54–7.51 (m, 1H), 7.49–7.43 (m, 4H), 2.75–2.71 (m, 1H), 1.82–1.75 (m, 2H), 1.66–1.59 (m, 2H), 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; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{21}O_2S_2^+$ 345.0977; Found 345.0973.

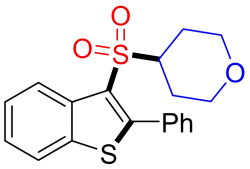


(S)-3-(pentan-2-ylsulfonyl)-2-phenylbenzo[b]thiophene (9ae). Colourless oil; 64% yield (44.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.58–7.57 (m, 2H), 7.53–7.51 (m, 1H), 7.48–7.42 (m, 4H), 2.98–2.94 (m, 1H), 1.81–1.75 (m, 1H), 1.44–1.35 (m, 2H), 1.17–1.14 (m, 4H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.6, 138.3, 137.0, 131.7, 130.7, 129.7,

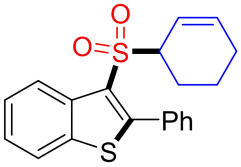
127.8, 126.7, 126.1, 125.8, 124.7, 121.9, 59.9, 30.5, 19.7, 13.7, 12.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{21}O_2S_2^+$ 345.0977; Found 345.0979.



3-(Cyclopentylsulfonyl)-2-phenylbenzo[*b*]thiophene (9af). White solid; 85% yield (58.2 mg): mp 102.7–103.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7,59 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.49–7.43 (m, 4H), 3.45–3.40 (m, 1H), 1.99–1.93 (m, 2H), 1.74–1.66 (m, 4H), 1.53–1.49 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.1, 138.4, 136.9, 131.8, 130.8, 129.8, 128.1, 127.9, 126.1, 125.8, 124.7, 64.4, 26.8, 25.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{19}O_2S_2^+$ 343.0821; Found 343.0819.

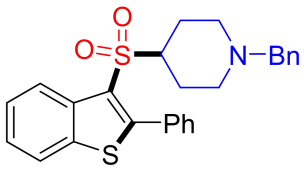


4-((2-phenylbenzo[b]thiophen-3-yl)sulfonyl)tetrahydro-2H-pyran (9ag). Colourless oil; 67% yield (48.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.57–7.55 (m, 2H), 7.54–7.52 (m, 1H), 7.50–7.44 (m, 4H), 3.98–3.96 (m, 2H), 3.19 (t, *J* = 11.4 Hz, 2H), 3.09–3.04 (m, 1H), 1.83–1.76 (m, 2H), 1.72–1.70 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.5, 138.3, 136.8, 131.5, 130.7, 129.9, 127.8, 126.2, 125.9, 125.6, 124.6, 122.0, 66.5, 61.0, 25.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{19}O_3S_2^+$ 359.0770; Found 359.0768.



(R)-3-(cyclohex-2-en-1-ylsulfonyl)-2-phenylbenzo[*b*]thiophene (9ah). Colourless oil; 60% yield (42.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.58–7.56 (m, 2H), 7.54–7.51 (m, 1H), 7.49–7.43 (m, 4H),

5.63–5.55 (m, 2H), 3.16–3.11 (m, 1H), 2.31–2.26 (m, 1H), 2.16–2.09 (m, 3H), 1.99–1.93 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.0, 138.3, 136.8, 131.5, 130.6, 129.7, 127.7, 126.7, 126.2, 126.0, 125.7, 124.6, 123.6, 121.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{19}O_2S_2^+$ 355.0821; Found 355.0821.



1-benzyl-4-((2-phenylbenzo[b]thiophen-3-yl)sulfonyl)piperidine (9ai). Yellow oil; 66% yield (53.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.55–7.53 (m, 2H), 7.52–7.50 (m, 1H), 7.49–7.42 (m, 4H), 7.29–7.26 (m, 2H), 7.24–7.23 (m, 3H), 3.43 (s, 2H), 2.90 (d, *J* = 10.8 Hz, 2H), 1.85–1.77 (m, 6H), 1.27–1.24 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.3, 138.4, 136.9, 131.6, 130.7, 129.7, 129.2, 128.4, 127.8, 127.4, 126.14, 126.08, 125.9, 124.7, 122.0, 62.6, 52.1, 29.8, 24.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{26}H_{26}O_2S_2^+$ 448.1399; Found 448.1389.

3.8 本章小结

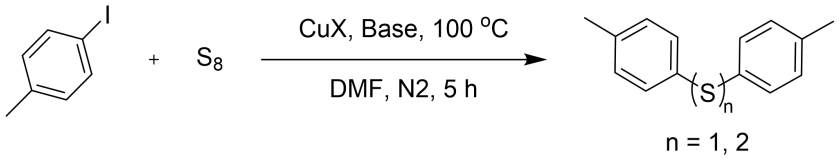
总之，我们发展了一种以 DABSO 为二氧化硫源，通过二氧化硫的插入、光诱导邻炔基苯甲硫醚的氧化磺化/环化合成 3-烷基磺酰基苯并噻吩的方法。该方法，无需外加光催化剂和金属催化剂，展现出优异的产率（最高达 91%），为杂环功能分子的模块化构建提供了绿色合成新方法。

第 4 章 可见光促进邻炔基苯甲硫醚与单质硫、硒串联环化合成双（苯并[*b*]噻吩-3-基）硫（硒）醚

4.1 研究背景

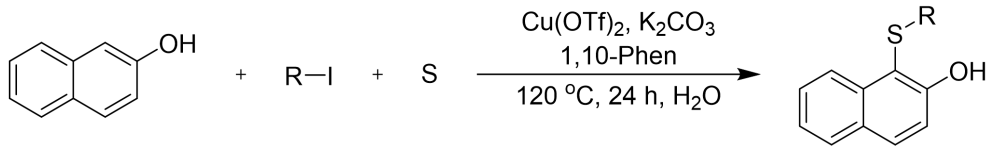
有机硫化合物因其在药物化学中独特的生物活性[80, 81]及材料科学领域的广泛应用[82]，已成为现代合成化学研究的重要对象。C-S 键构筑作为含硫分子合成的核心环节，其方法学研究持续受到关注[81-87]。但普遍存在硫源异味明显、反应条件苛刻等瓶颈问题。相较于硫醇类化合物，硫单质作为无毒且易处理的硫源备受关注[88, 89]。

2013 年，Chen 课题组[90]研究发现在对甲基碘苯和 S_8 的反应中不同碱可以调控产物中二芳基硫醚与二芳基二硫醚的比例：弱碱（碳酸盐/醋酸盐）仅生成二芳基二硫醚，强碱（氢氧化物）则生成混合产物。^{1}H NMR 追踪显示二芳基二硫醚为初级产物，经 CuI 催化与卤代芳烃进一步反应转化为二芳基硫醚（Scheme 4-1）。



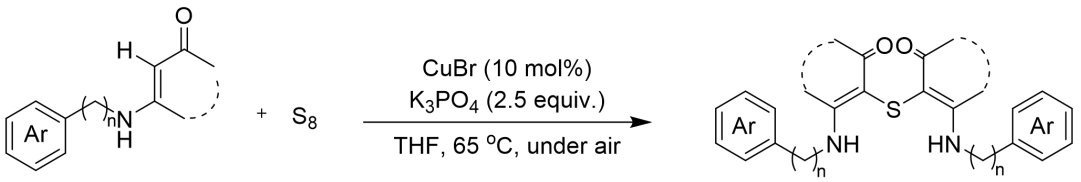
Scheme 4-1 碱可调控产物中二芳基硫醚与二芳基二硫醚的比例

2016 年，Deng 课题组[91]构建了铜催化芳烃、碘代烃与硫粉的三组分合成体系，以水为绿色溶剂实现取代芳基硫醚的高效制备。该方法对环境友好且在温和条件下兼容多种官能团，产率均能够达到中等至良好（Scheme 4-2）。



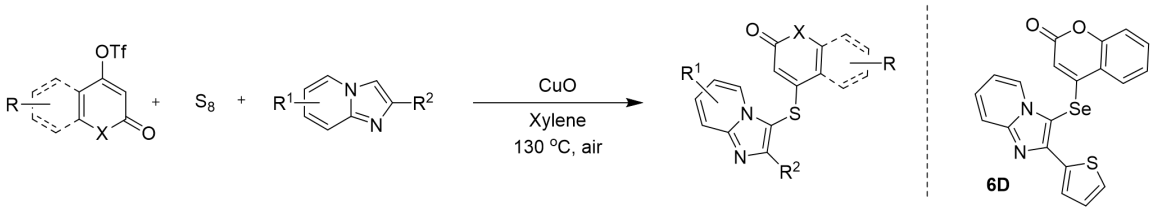
Scheme 4-2 铜催化芳烃、碘代烃与硫粉的三组分合成

2016 年，Ji 小组[92]在 $CuBr/K_3PO_4$ 催化下，实现烯胺酮 C(sp^2)-H 键与单质硫的硫化反应，以中等至良好的产率合成硫醚类化合物。该方法拓展性强，将硫粉替换为硒粉时可制备相应硒醚衍生物（Scheme 4-3）。



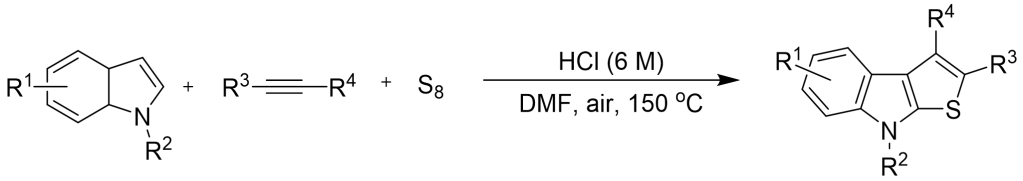
Scheme 4-3 $CuBr/K_3PO_4$ 催化烯胺酮与单质硫的硫化反应

2017 年，Ma 等人[93]开发了铜催化咪唑杂环与硫/硒粉及香豆素三氟甲磺酸酯的三组分反应，高效合成结构多样的香豆素硫醚/硒醚取代咪唑杂环化合物。其中，新型化合物 **6D** 对食管癌、乳腺癌等癌细胞系展现出优于 5-氟尿嘧啶的抗增殖活性（Scheme 4-4）。



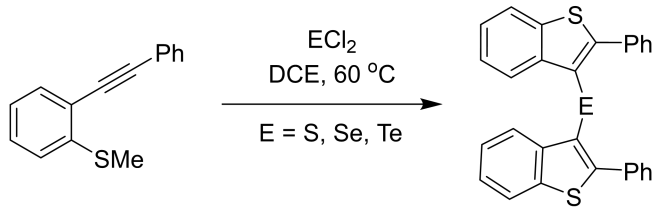
Scheme 4-4 铜催化咪唑杂环与硫/硒粉及香豆素三氟甲磺酸酯的硫属化反应

2017 年，Deng 课题组[94]利用布朗斯特酸催化，实现吲哚、烯烃/炔烃与硫粉的三组分环化反应，成功合成系列取代噻吩并[2, 3-*b*]吲哚衍生物。*N*, *N*-二甲基甲酰胺作为溶剂同时能够促进原料转化为稠环产物。该反应具有反应条件简单、底物适用性优异的优点（Scheme 4-5）。



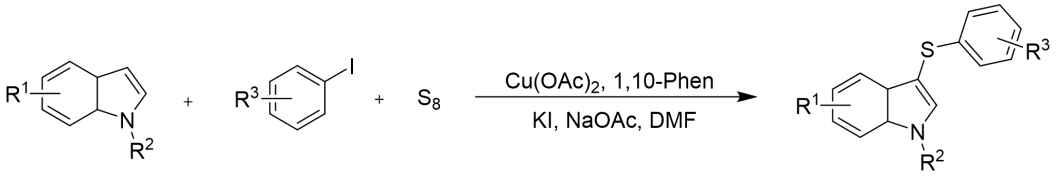
Scheme 4-5 吲哚、炔烃与硫粉的三组分环化反应

2017 年，Flynn 等人[95]利用 SCl_2， $SeCl_2$ 和 $TeCl_4$ 作为双亲电试剂在含炔底物的 DEC 反应中合成双(3-苯并[*b*]噻吩基)硫醚/硒醚/碲醚。三种亲电试剂在邻炔基苯甲硫醚的双亲电环化反应中均表现良好。该反应以 1, 2-二氯乙烷（DCE）作为溶剂，在 60 ℃下，分别得到相应目标产物，产率在 56−68%（Scheme 4-6）。



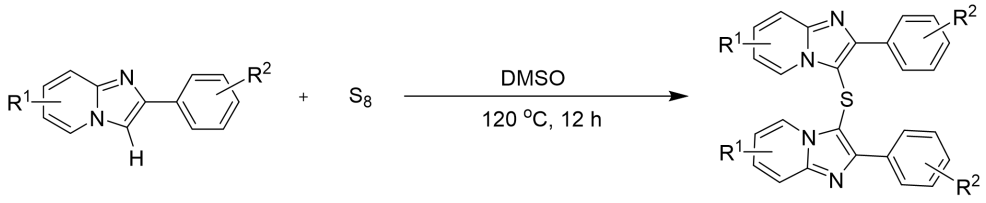
Scheme 4-6 邻炔基苯甲硫醚与双亲电试剂（ECl_2）反应合成双(3-苯并[*b*]噻吩基)硫醚/硒醚/碲醚

2019 年，Zhou 等人[96]通过实验与理论计算系统研究了铜催化吲哚与碘代芳烃的硫化反应合成 3-硫醚吲哚类化合物。该方法具有良好官能团耐受性且产率良好。原位红外光谱分析证实，NaOAc 促进碘代芳烃与硫粉偶联生成二苯二硫醚。DFT 计算表明，该反应通过生成催化循环中的关键中间体 *N*-甲基-3-碘代吲哚实现偶联过程（Scheme 4-7）。



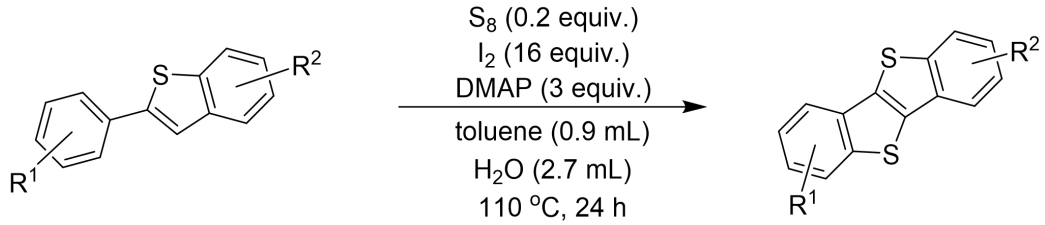
Scheme 4-7 铜催化吲哚与碘代芳烃的硫化反应

2020 年，Yang 小组[97]开发了无金属条件下以廉价硫粉作为硫源合成咪唑并吡啶硫桥连化合物新方法。该体系无需添加剂即可高效进行，显著减少化学废弃物生成，为构建具有生物活性的杂芳硫醚化合物提供绿色经济途径（Scheme 4-8）。



Scheme 4-8 硫粉作为硫源合成咪唑并吡啶硫桥连化合物

[1]苯并噻吩并[3,2-*b*][1]苯并噻吩（BTBTs）具有良好的光电性能，作为有多种应用潜力有机半导体材料备受关注。2024 年，Yoshida 等人[98]提出以 2-芳基苯并噻吩与单质硫为原料合成 BTBTs。该方法通过分子碘介导实现双 C-S 键同步构筑。文章重点探讨了碘在反应机理中的关键作用（Scheme 4-9）。



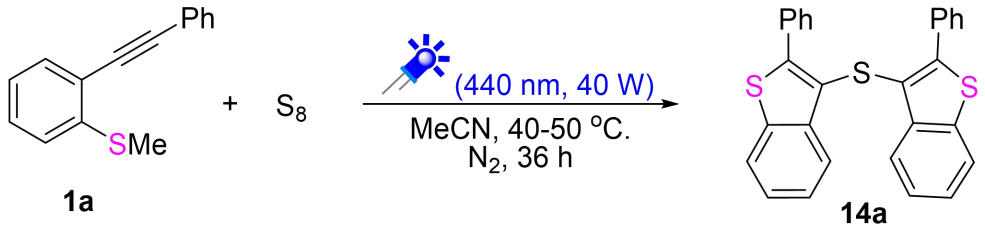
Scheme 4-9 2-芳基苯并噻吩与单质硫合成 BTBTs

近年间，硫粉作为理想硫代试剂已在有机转化中获得重要应用[99]，然而开发基于硫粉的高效、便捷合成策略仍存在巨大挑战挑战。

4.2 反应条件优化

4.2.1 硫源和反应条件的筛选

Table 4-1 反应条件优化 [a]



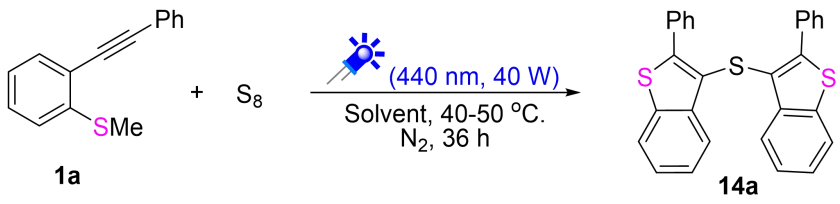
Entry	S surrogate	Solvent	LED (nm)	Yield(%)[b]
1	**Sulfur Powder**	**MeCN**	**440**	**74**
2	S_8	MeCN	440	72
3	K_2S_x	MeCN	440	-
4	Sulfourea	MeCN	440	-
5	Sulfur Powder	MeCN	440	55[c]
6	Sulfur Powder	MeCN	In dark	-

[a]Reaction conditions: **1a** (0.20 mmol) and S (0.20 mmol) in MeCN (2.0 mL) in nitrogen atmosphere at 40-50 °C under LED (40 W) irradiation for 36 h. [b]Isolated yield. [c]in air atmosphere.

首先，对硫源和反应条件进行了筛选。如 Table 4-1 所示，当 2-炔苯基苯甲硫醚（**1a**）为反应底物，分别使用硫粉、S_8、多硫化钾和硫脲作为硫源，乙腈作为反应溶剂，在氮气气氛下用 440 nm 蓝光 LED（40 W）照射，在石英管中搅拌反应 36 h。结果显示当硫粉作为硫源时，该反应以更高的产率（74%）得到了目标产物 **14a**（entries 1-4）。在空气气氛下进行反应时，**14a** 的产率下降为 55%（entry 5）。控制实验表明光照是该反应的必要条件（entry 6）。

4.2.2 溶剂的筛选

Table 4-2 溶剂优化 [a]



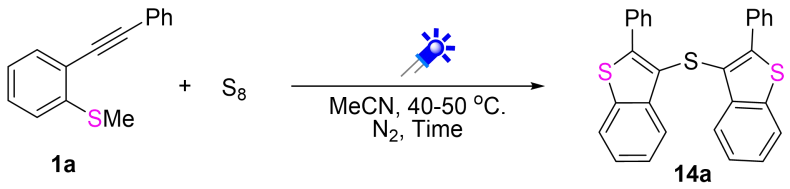
Entry	S surrogate	Solvent	LED (nm)	Yield(%)[b]
1	**Sulfur Powder**	**MeCN**	**440**	**74**
2	Sulfur Powder	DCE	440	70
3	Sulfur Powder	THF	440	66
4	Sulfur Powder	DMF	440	47
5	Sulfur Powder	Acetone	440	67
6	Sulfur Powder	DMSO	440	52
7	Sulfur Powder	Toluene	440	61

[a]Reaction conditions: **1a** (0.20 mmol) and S (0.20 mmol) in solvent (2.0 mL) in nitrogen atmosphere at 40-50 °C under LED (40 W) irradiation for 36 h. [b]Isolated yield.

随后，筛选了一系列溶剂，如表 Table 4-2 所示，乙腈（MeCN）作为反应溶剂时，**14a** 产率最高，达到了 74%（entries 1）。所筛选的其他溶剂包括二氯乙烷（DCE）、四氢呋喃（THF）、*N*, *N*-二甲基甲酰胺（DMF）、丙酮、二甲基亚砜（DMSO）和甲苯，均适用于该反应，但产率有所降低，在 52%到 70%之间（entries 2-7）。

4.2.3 波长的筛选

Table 4-3 波长优化 [a]



Entry	S surrogate	Solvent	LED (nm)	Yield(%)[b]
1	**Sulfur Powder**	**MeCN**	**440**	**74**
2	Sulfur Powder	MeCN	390	62
3	Sulfur Powder	MeCN	427	70
4	Sulfur Powder	MeCN	456	49
5	Sulfur Powder	MeCN	440	57[c]，73[d]
6	Sulfur Powder	MeCN	440	59[e]，74[f]

[a]Reaction conditions: **1a** (0.20 mmol) and S (0.20 mmol) in MeCN (2.0 mL) in nitrogen atmosphere at 40-50 °C under LED (40 W) irradiation for 36 h. [b]Isolated yield. [c]S (0.15 mmol). [d]S (0.25 mmol). [e]Irradiation for 24 h. [f]Irradiation for 48 h.

接下来，我们研究了光源的波长对反应的影响，所筛选的 LED 波长（390、427、440 和 456 nm）都可以使该反应顺利进行，其中 440 nm 波长是产率最高达到 74%（entries 1-4）。

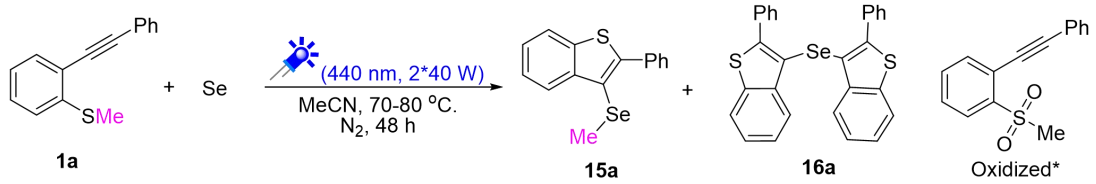
进一步优化二苯基二硫醚（**2a**）的用量以及反应时间。如 Table 4-3 所示，当硫粉的用量增加到 0.25 mmol 时，产率几乎不变，而当 **2a** 用量降低到 0.5 当量时，反应产率降低至 57%（entry 5）。

反应时间延长至 48 h 对反应几乎没有影响，但当反应时间缩短到 24 h 时，产率降低至 59%（entry 6）。

最终确定该反应的最佳波长是 440 nm、**2a** 的最佳用量是 1.0 equiv.、最佳反应时间是 36 h。

4.2.4 反应条件的筛选

Table 4-4 反应条件优化 [a]



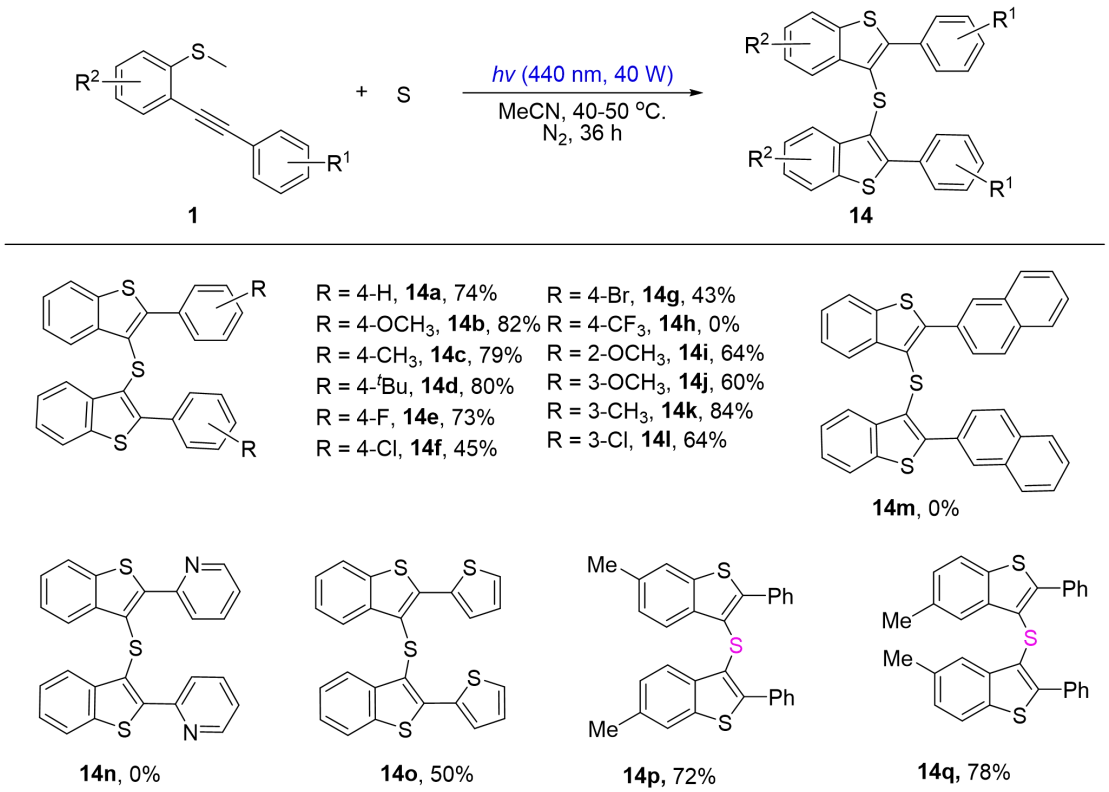
Entry	Variation from standard Conditions	Result[b]
1	None	**15a**: 43% yield **16a**: 13% yield
2	40 °C	-
3	under air atmosphere	Oxidized*
4	40 W, 130 °C	-
5	TEMPO	**16a**: 84% yield
6	40 W, TEMPO	-

[a]Reaction conditions: **1a** (0.20 mmol) and Se (0.20 mmol) in MeCN (2.0 mL) in nitrogen atmosphere at 70-80 °C under LED (2*40 W) irradiation for 12 h. [b]Isolated yield.

将标准反应中的硫粉替换为硒粉，发现需要增强反应条件，换为蓝光 LED 440 nm、2*40 W，得到 **15a**、**16a** 两种产物，产率分别为 43%和 13%（entry 1）。随后对该反应重新进行优化。将反应温度降低后，该反应未得到目标产物，原料回收（entry 2）。在空气气氛中反应，得到原料的氧化产物（entry 3）。减少光源但反应液加热至 130 °C，未得到目标产物，原料回收（entry 4）。当在反应体系

中加入 2.5 当量的 TEMPO 时，**15a** 产物被抑制，以 84%的产率得到 **16a** 产物（entry 5）。当减少反应光源同时加入 TEMPO 时，未得到目标产物，原料回收（entry 6）。

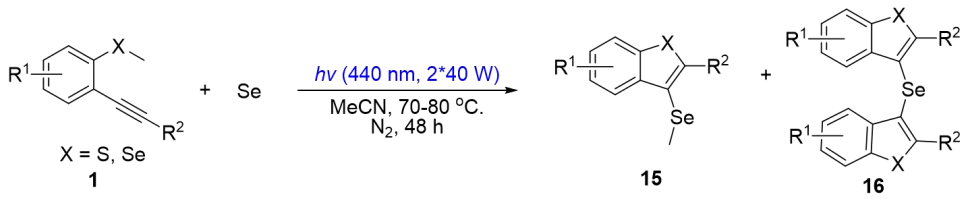
4.3 底物普适性考察

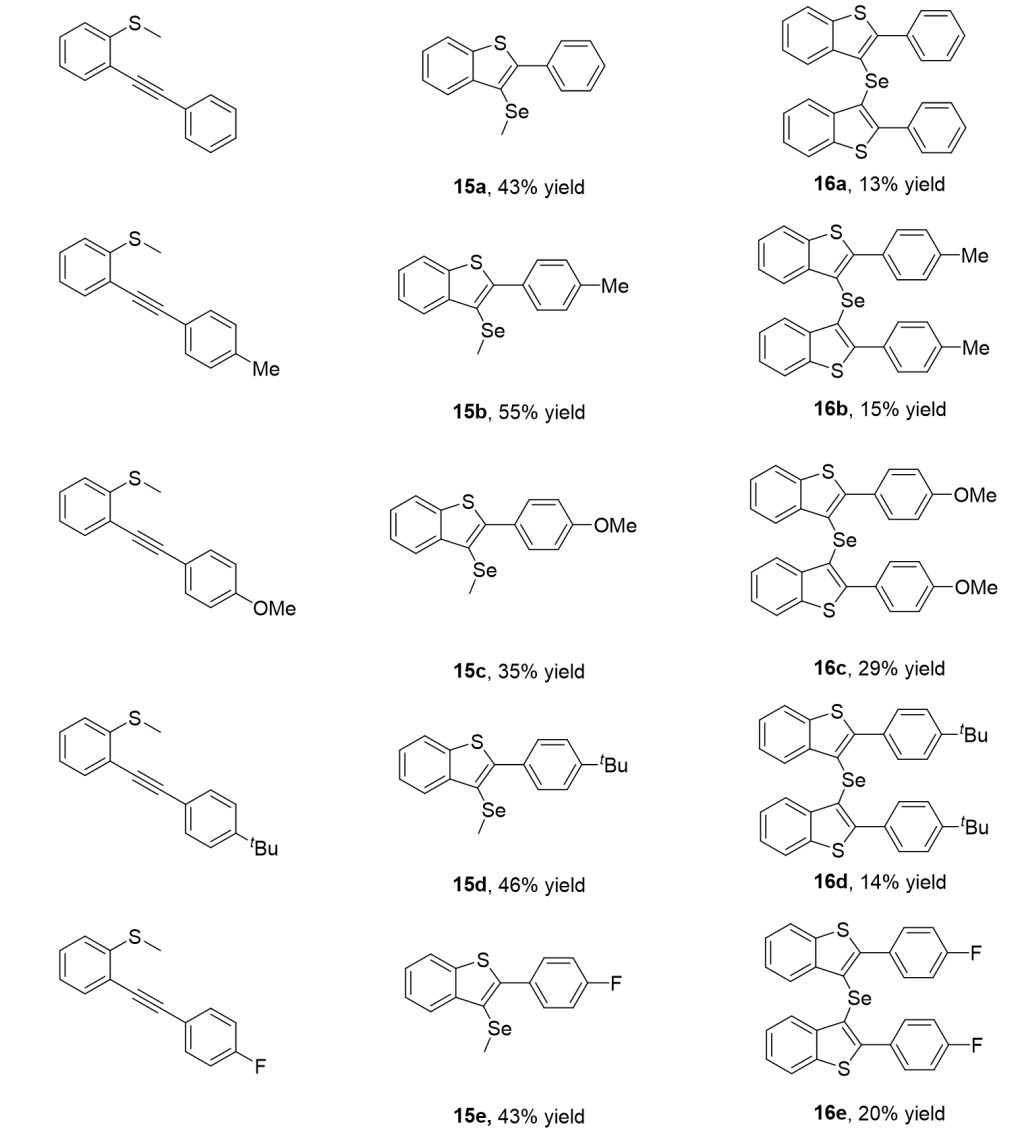


[a]Reaction conditions: **1a** (0.20 mmol) and S (0.20 mmol) in MeCN (2.0 mL) in nitrogen atmosphere at 40-50 °C under LED (40 W) irradiation for 36 h. [b]Isolated yield.

Scheme 4-10 底物普适性考察 I[a]

如 Scheme 4-10 所示，该反应具有良好的普适性，可以以优良的产率得到相应的目标产物。在最佳条件下，大多数官能团可以得到目标产物。苯环上对位有给电子取代基，如甲氧基、甲基和叔丁基，以 79-82%的收率得到所需的产物（**14b−14d**）；卤素原子如氟、氯和溴对该反应影响较大，对位取代卤素为氟时已 73%的产率得到目标产物，而当取代卤素为氯和溴时，分别以 45%和 43%的产率得到目标产物（**14e-14g**）。遗憾的是吸电子取代基，如三氟甲基不与反应相容，未得到目标产物（**14h**）。邻、间位有取代基的底物也与此反应相容，以 64-90%的产率得到目标产物（**14i-14l**）。此外，在该条件下，萘基（**14m**）和吡啶基（**14n**）未得到相应的产物。但噻吩基以 50%的产率得到目标产物（**14o**）。令人高兴的是，主体芳香环上的具有不同官能团的底物，如甲基，也能顺利地进行反应，并以 72-78%的产率获得所需的产物（**14p-14q**）。

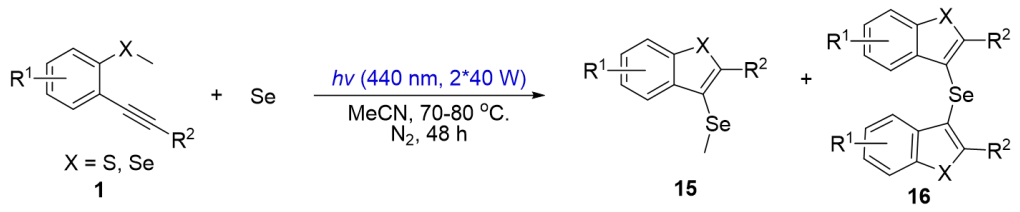


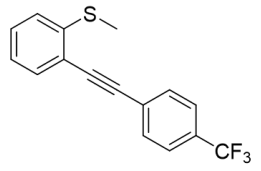


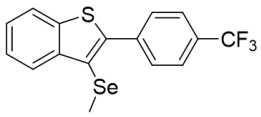
[a]Reaction conditions: **1a** (0.20 mmol) and Se (0.20 mmol) in MeCN (2.0 mL) in nitrogen atmosphere at 70-80 °C under LED (2*40 W) irradiation for 12 h.

Scheme 4-11 底物普适性考察 II[a]

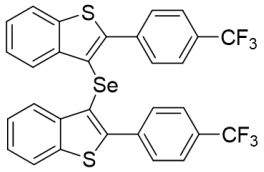
将模板反应中的硫粉替换成硒粉后的底物扩展如 Scheme 4-11 所示，该反应具有良好的普适性。在最佳条件下，大多数官能团可以得到目标产物。苯环上对位有给电子取代基，如甲氧基、甲基和叔丁基，以 35-43%的收率得到硒甲基产物（**15b-15d**），以 13-29%的产率得到硒桥产物（**16b-16d**）；卤素原子如氟也可以得到两个目标产物（**15e**、**16e**）。



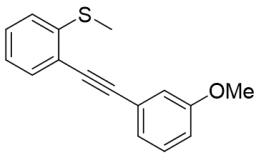


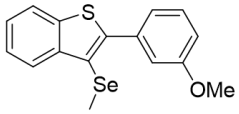


15f, 41% yield

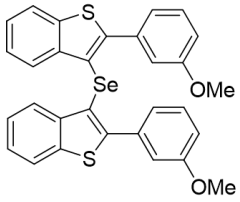


16f, 17% yield

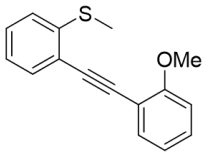


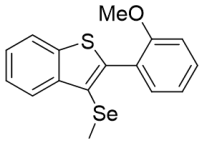


15g, 46% yield

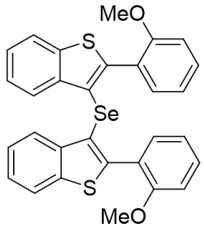


16g, 15% yield

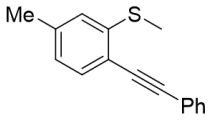


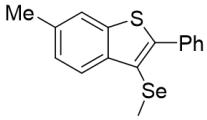


15h, 30% yield

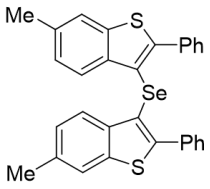


16h, 15% yield

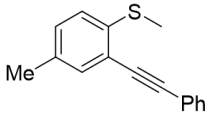


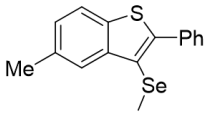


15i, 34% yield

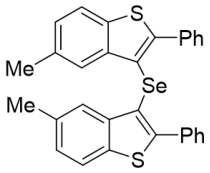


16i, 21% yield





15j, 44% yield



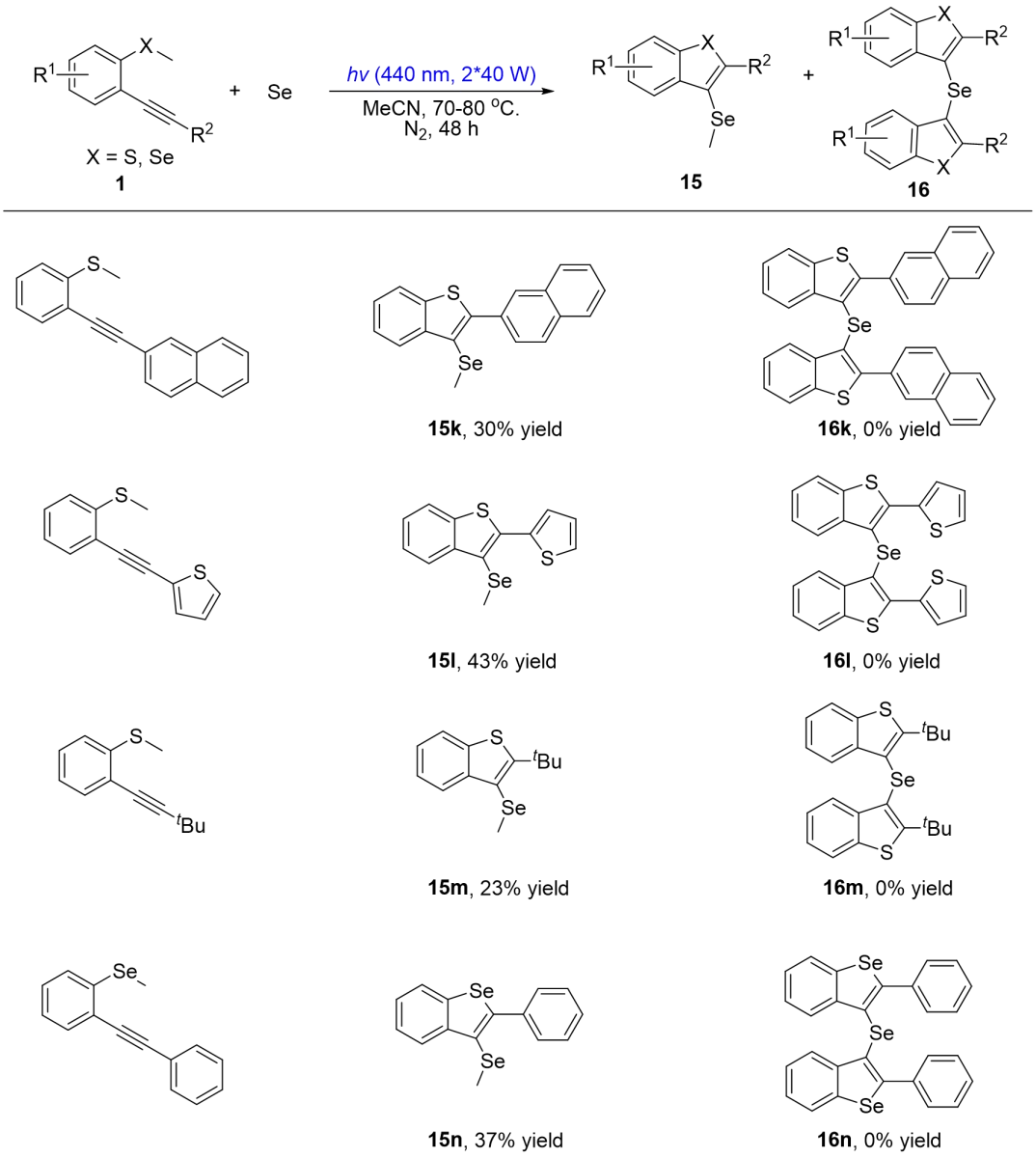
16j, 17% yield

[a]Reaction conditions: **1a** (0.20 mmol) and Se (0.20 mmol) in MeCN (2.0 mL) in nitrogen atmosphere at 70-80 ºC under LED (2*40 W) irradiation for 12 h.

续 **Scheme 4-11** 底物普适性考察 II[a]

吸电子取代基，如三氟甲基，以 41%的产率得到产物 **15f**、以 17%的产率得到产物 **16f**。邻、间位有取代基的底物也与此反应相容，以 30-46%的产率得到产物 **15g-15h**，以 15%的产率得到产物 **16g-16h**。令人高兴的是，主体芳香环上的

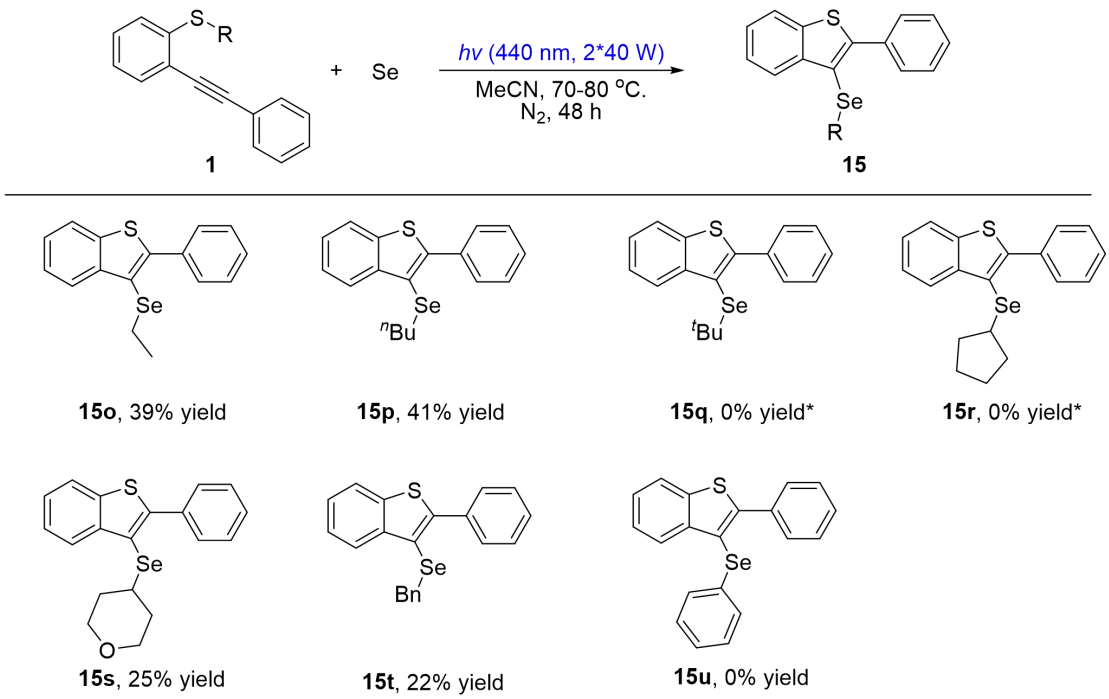
具有不同官能团的底物，如甲基，也能顺利地进行反应，并以 34-44%的产率获得所需的产物 **15i-15j**、以 17-21%的产率得到目标产物 **16i-16j**。



[a]Reaction conditions: **1a** (0.20 mmol) and Se (0.20 mmol) in MeCN (2.0 mL) in nitrogen atmosphere at 70-80 °C under LED (2*40 W) irradiation for 12 h.

Scheme 4-12 底物普适性考察 III[a]

将与炔基相连的苯环替换为萘基、噻吩基和叔丁基只能得到硒甲基产物，产率分别为 30%（**15k**）、43%（**15l**）、23%（**15m**）。邻炔基苯甲硒醚同样是有效底物，以 37%产率获得目标产物 **15n**，但未得到产物 **16n**。



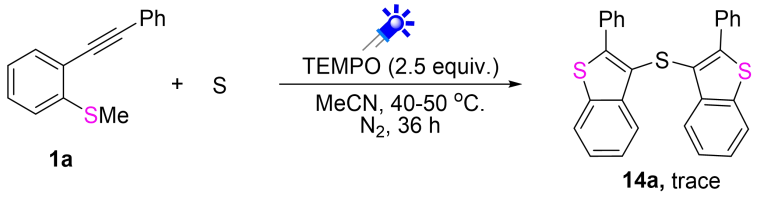
[a]Reaction conditions: **1** (0.20 mmol) and Se (0.20 mmol) in solvent (2.0 mL) in nitrogen atmosphere at 70-80 °C under LED (2*40 W) irradiation for 12 h.

Scheme 4-13 底物普适性考察 IV[a]

令我们高兴的是，当对硫醚的取代基进行替换时，部分底物也获得了相应的产物（**15o-5p**、**15s-5t**）。当取代基为硫叔丁基和硫环戊烷时（**15q**、**15r**），未得到目标产物，而是得到C3位没有取代基的合环产物。当取代基为苯基时（**15u**），该反应不能顺利进行。

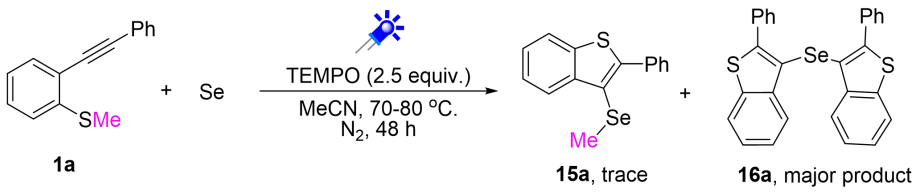
4.4 反应机理研究

4.4.1 自由基捕获实验



Scheme 4-14 自由基捕获试验 I

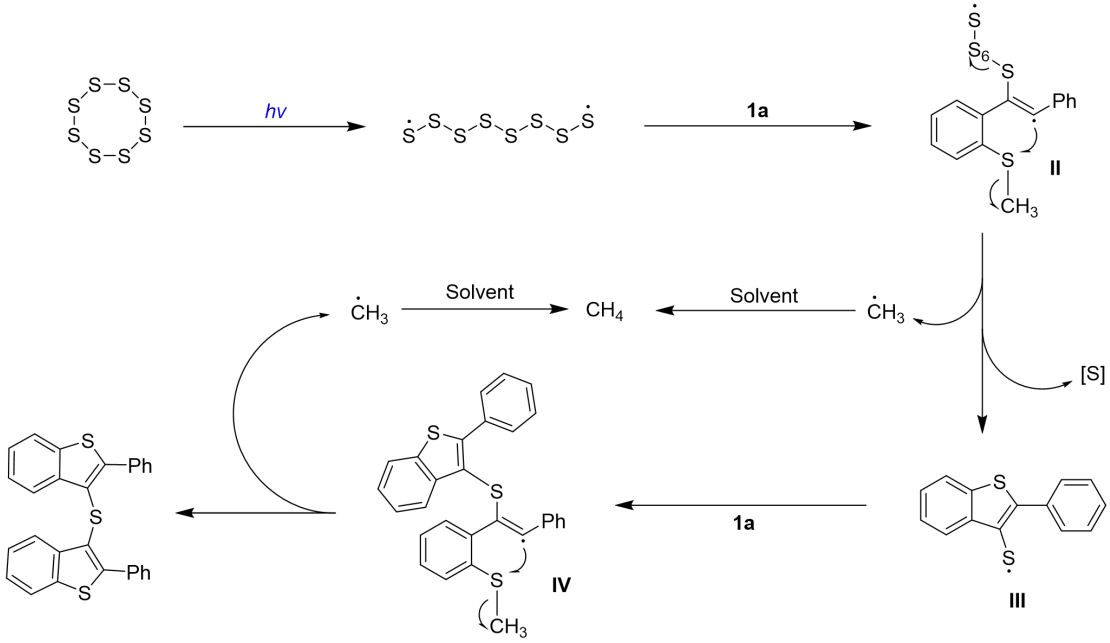
为了阐明反应机理，进行了自由基捕获试验。在标准条件下，将2.5 equiv.的自由基捕获试剂基2, 2, 6, 6-四甲基哌啶氧化物（TEMPO）加入到反应中，只检测到微量的产物**14a**，反应被明显抑制。表明该反应可能经历自由基过程。



Scheme 4-15 自由基捕获试验 II

为了阐明反应机理，自由基捕获试验。在标准条件下，将 2.5 equiv.的自由基捕获试剂基 2, 2, 6, 6-四甲基哌啶氧化物（TEMPO）加入到反应中，只检测到微量的产物 **15a**，反应被明显抑制；而 **16a** 产物明显增多，成为反应的主要产物。说明生成 **15a** 产物可能历经自由基历程，而生成产物 **15a** 与 **16a** 的过程可能存在竞争关系。

4.4.2 可能的反应机理



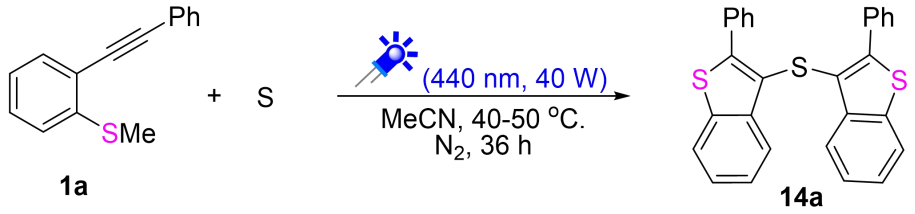
Scheme 4-16 可能的反应机理

根据自由基捕获实验的结果，结合前人的报道，提出了 **1a** 与硫单质反应的可能机理（Scheme 4-16）。首先，在光照条件下，硫单质均裂形成两端带有自由基的硫链，其中一端攻击反应底物 **1a** 中的三键，生成具有高区域选择性的乙烯基自由基中间体 **II**。随后，中间体 **II** 与甲硫基发生分子内环化，形成中间体 **III** 最终生成目标产物并释放甲基自由基（转化为甲烷）。中间体 **III** 再一次攻击另一个 **1a** 分子中的三键，生成中间体 **IV**，重复分子内环化过程最终生成目标产物。

根据自由基捕获实验的结果，反应底物 **1a** 与 Se 单质的反应，其中生成硒甲基产物的反应过程可能历经自由基机理，而更深层的反应过程与生成产物 **16a** 的反应机理还有待继续探究。

4.5 实验部分

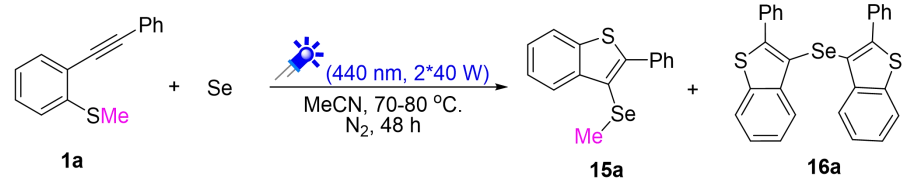
4.5.1 双(苯并[*b*]噻吩-3-基)硫醚制备的一般步骤



Scheme 4-18 双(苯并[*b*]噻吩-3-基)硫醚的制备

在装有磁子的 10 mL 干燥的反应容器中加入邻炔基苯甲硫醚（**1a**, 44.9 mg, 0.20 mmol）、硫粉（0.20 mmol）和乙腈（2.0 mL）。反应液在氩气气氛中，蓝光 LED 440 nm， 40 W 照射，搅拌 24 h。反应完成后，旋转蒸发除去溶剂，以石油醚为洗脱液，硅胶柱层析纯化，得到所需产物 **14a** 为白色固体（33.3 mg，产率 74%）。

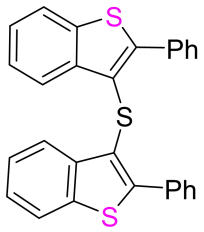
4.5.2 2-苯基-3-(甲硒基)苯并[*b*]噻吩和双(苯并[*b*]噻吩-3-基)硒醚制备的一般步骤



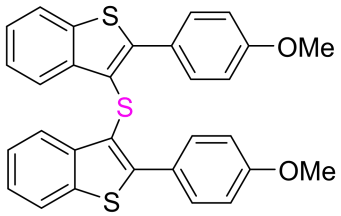
Scheme 4-19 2-苯基-3-(甲硒基)苯并[*b*]噻吩和双(苯并[*b*]噻吩-3-基)硒醚制备

在装有磁子的 10 mL 干燥的反应容器中加入邻炔基苯甲硫醚（**1a**, 44.9 mg, 0.20 mmol）、硒粉（0.20 mmol）和乙腈（2.0 mL）。反应液在氩气气氛中，用两盏蓝光 LED 440 nm， 40 W 照射，搅拌 48 h。反应完成后，旋转蒸发除去溶剂，以石油醚为洗脱液，硅胶柱层析纯化，得到所需产物 **15a** 为黄色固体（26.1 mg，产率 43%）、**16a** 为黄色固体（6.5 mg，产率 13%）。

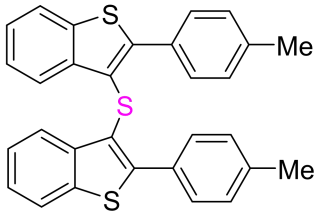
4.6 产物的表征数据



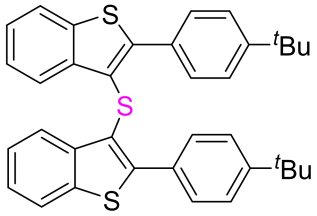
bis(2-phenylbenzo[*b*]thiophen-3-yl)sulfane (14a)[95]**.** White solid; 74% yield (33.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.4 Hz, 2H), 7.49–7.48 (m, 4H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.36–7.35 (m, 6H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.6, 140.7, 138.1, 133.6, 130.1, 128.6, 128.3, 124.7, 124.6, 123.5, 122.1, 120.3.



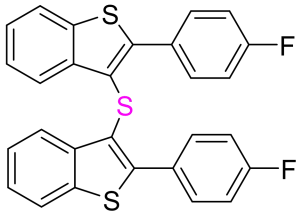
bis(2-(4-methoxyphenyl)benzo[*b*]thiophen-3-yl)sulfane (14b). White solid; 82% yield (41.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.2 Hz, 2H), 7.46–7.45 (m, 6H), 7.21–7.18 (m, 2H), 7.15–7.12 (m, 2H), 6.89–6.87 (m, 4H), 3.83 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.9, 144.6, 140.8, 137.7, 131.2, 126.0, 124.44, 124.38, 123.3, 121.9, 119.5, 113.7, 55.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}O_2S_3^+$ 511.0855; Found 511.0853.



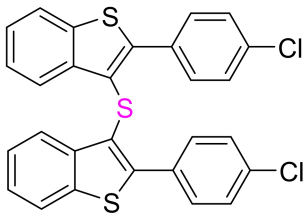
bis(2-(p-tolyl)benzo[*b*]thiophen-3-yl)sulfane (14c). White solid; 79% yield (37.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 4H), 7.18 (t, *J* = 7.8 Hz, 6H), 7.12 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.9, 140.7, 138.5, 137.9, 130.7, 129.9, 128.9, 124.4, 123.4, 121.9, 120.1, 21.4.



5-Chloro-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (14d). White solid; 80% yield (45.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 4H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 1.34 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.5, 144.2, 140.7, 137.9, 130.6, 129.5, 125.0, 124.43, 124.39, 123.3, 121.9, 119.7, 34.7, 31.3.

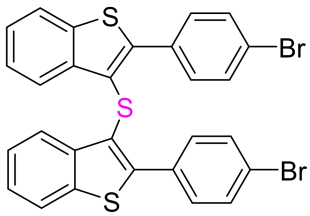


bis(2-(4-fluorophenyl)benzo[*b*]thiophen-3-yl)sulfane (14e). White solid; 73% yield (35.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 7.8, 5.4 Hz, 4H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 8.4 Hz, 4H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = −112.6; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.8 (d, *J* = 248.0 Hz), 143.2, 140.4, 137.8, 131.5 (d, *J* = 8.1 Hz), 129.4 (d, *J* = 3.0 Hz), 124.8, 124.7, 123.2, 122.0, 120.3, 115.2 (d, *J* = 21.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{28}H_{17}F_2S_3^+$ 487.0455; Found 487.0450.

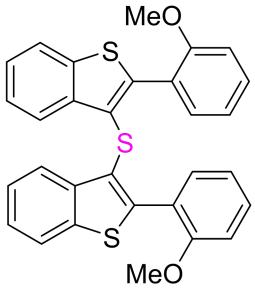


bis(2-(4-chlorophenyl)benzo[*b*]thiophen-3-yl)sulfane (14f). White solid; 45% yield (23.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.30–7.22 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.0, 140.3, 137.8,

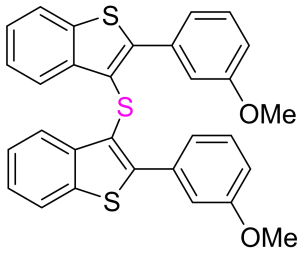
134.5, 131.7, 130.8, 128.3, 125.0, 124.8, 123.2, 122.1, 120.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{28}H_{17}Cl_2S_3^+$ 518.9864; Found 518.9864.



bis(2-(4-bromophenyl)benzo[*b*]thiophen-3-yl)sulfane (14g). White solid; 43% yield (26.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 4H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.25–7.24 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.0, 140.3, 137.8, 132.1, 131.3, 131.1, 125.0, 124.8, 123.2, 122.8, 122.1, 120.8.

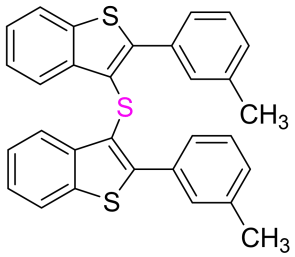


bis(2-(2-methoxyphenyl)benzo[*b*]thiophen-3-yl)sulfane (14i). White solid; 64% yield (32.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.36–7.34 (m, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.17–7.15 (m, 2H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.68 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.3, 140.6, 140.3, 138.8, 132.3, 130.3, 124.2, 124.1, 123.4, 123.2, 122.5, 121.8, 120.3, 111.1, 55.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}O_2S_3^+$ 511.0855; Found 511.0852.

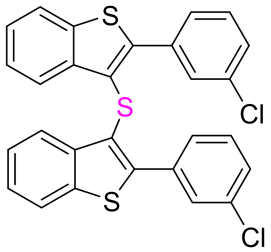


bis(2-(3-methoxyphenyl)benzo[*b*]thiophen-3-yl)sulfane (14j). White solid; 60% yield (30.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J*

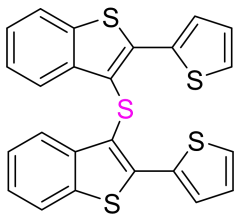
= 7.8 Hz, 2H), 7.24 (t, *J* = 7.8, 4H), 7.17 (t, *J* = 7.8 Hz, 2H), 6.99–6.98 (m, 4H), 6.89–6.88 (m, 2H), 3.75 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.3, 144.4, 140.7, 138.1, 134.8, 129.3, 124.7, 124.6, 123.5, 122.5, 122.1, 120.6, 115.2, 114.6, 55.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}O_2S_3^+$ 511.0855; Found 511.0855.



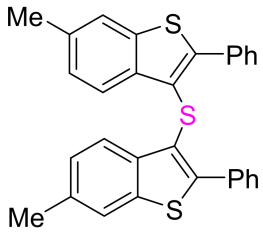
bis(2-(m-tolyl)benzo[*b*]thiophen-3-yl)sulfane (14k). White solid; 84% yield (40.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.25–7.21 (m, 8H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.12–7.11 (m, 2H), 2.30 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.7, 140.8, 138.0, 137.9, 133.5, 130.6, 129.3, 128.1, 127.2, 124.6, 124.5, 123.4, 122.0, 120.3, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}S_3^+$ 479.0956; Found 479.0953.



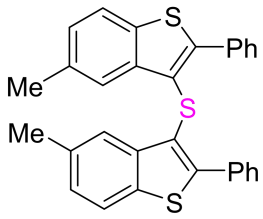
bis(2-(3-chlorophenyl)benzo[*b*]thiophen-3-yl)sulfane (14l). White solid; 64% yield (33.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.294–7.291 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.25–7.22 (m, 3H), 7.21–7.20 (m, 2H), 7.17–7.15 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.4, 140.4, 138.0, 135.0, 134.1, 129.6, 129.3, 128.5, 128.0, 125.2, 124.9, 123.4, 122.2, 121.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{28}H_{17}Cl_2S_3^+$ 518.9864; Found 518.9859.



bis(2-(thiophen-2-yl)benzo[*b*]thiophen-3-yl)sulfane (14o). White solid; 50% yield (23.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 6.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H),, 7.45 (d, *J* = 5.4 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 4.8 Hz, 2H), 7.10 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.9, 138.4, 137.5, 135.2, 128.2, 128.0, 127.4, 125.2, 125.1, 123.2, 122.0, 119.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{24}H_{15}S_5^+$ 462.9772; Found 462.9771.

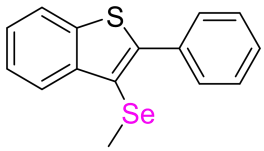


bis(6-methyl-2-phenylbenzo[*b*]thiophen-3-yl)sulfane (14p). White solid; 72% yield (34.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52–7.51 (m, 4H), 7.44 (s, 2H), 7.38–7.35 (m, 6H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.5, 138.6, 138.3, 134.7, 133.8, 130.1, 128.5, 128.3, 126.4, 123.1, 121.9, 120.2, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}S_3^+$ 479.0956; Found 479.0957.

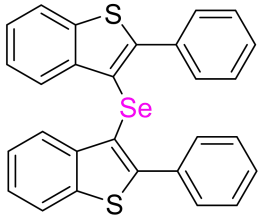


bis(5-methyl-2-phenylbenzo[*b*]thiophen-3-yl)sulfane (14q). White solid; 78% yield (37.3mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.49–7.46 (m, 4H), 7.44–7.42 (m, 2H), 7.12 (s, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 2.18 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.1, 141.3, 135.2, 134.3, 134.1,

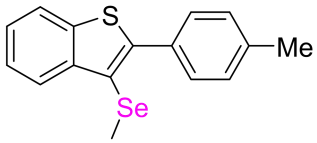
130.5, 128.8, 128.5, 126.5, 123.8, 121.6, 120.3, 21.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}S_3^+$ 479.0956; Found 479.0953.



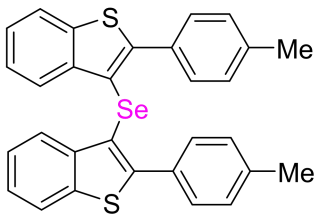
3-(methylselanyl)-2-phenylbenzo[*b*]thiophene (15a)[100]**.** Yellow solid; 43% yield (26.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 3H), 7.43–7.41 (m, 1H), 7.39–7.37 (m, 1H), 2.09 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 145.9, 142.2, 139.1, 134.6, 130.2, 128.6, 128.3, 124.9, 124.8, 122.2, 117.6, 8.8.



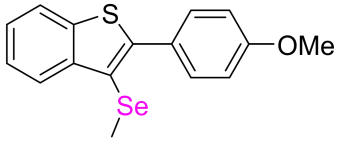
bis(2-phenylbenzo[*b*]thiophen-3-yl)selane (16a)[95]**.** Yellow solid; 13% yield (6.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.8 Hz, 2H), 7.44–7.42 (m, 4H), 7.38–7.36 (m, 8H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 145.4, 141.6, 138.6, 134.2, 130.2, 128.5, 128.2, 124.6, 124.53, 124.49, 121.8, 116.7.



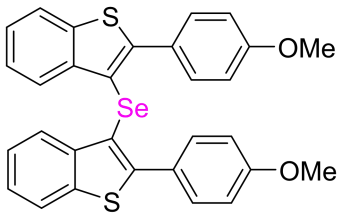
3-(methylselanyl)-2-(p-tolyl)benzo[*b*]thiophene (15b). Yellow solid; 55% yield (34.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.27–7.26 (m, 2H), 2.42 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.3, 142.3, 139.1, 138.7,131.8, 130.1, 129.2, 124.93, 124.87, 124.8, 122.3, 117.3, 21.5, 8.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}SSe^+$ 319.0054; Found 319.0052.



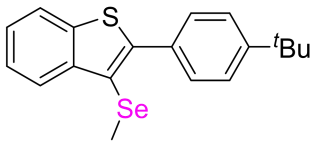
bis(2-(p-tolyl)benzo[*b*]thiophen-3-yl)selane (16b). Yellow solid; 15% yield (7.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.21–7.17 (m, 6H), 7.11 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 145.7, 141.8, 138.6, 131.5, 130.1, 129.0, 124.6, 124.5, 121.9, 116.7, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}S_2Se^+$ 527.0401; Found 527.0397.



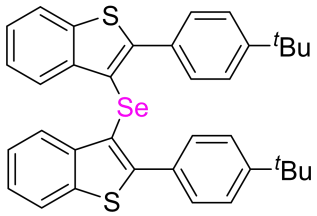
2-(4-methoxyphenyl)-3-(methylselanyl)benzo[*b*]thiophene (15c). Yellow solid; 35% yield (23.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.1, 146.0, 142.4, 139.0, 131.5, 127.1, 124.9, 124.8, 124.7, 122.2, 117.0, 113.9, 55.5, 8.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}OSSe^+$ 335.0003; Found 335.0003.



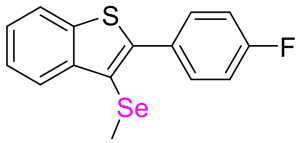
bis(2-(4-methoxyphenyl)benzo[*b*]thiophen-3-yl)selane (16c). Yellow solid; 29% yield (16.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 4H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 7.2 Hz, 4H), 3.86 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.9, 145.3, 141.7, 138.4, 131.3, 126.6, 124.43, 124.40, 124.3, 121.7, 116.2, 113.6, 55.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}O_2S_2Se^+$ 559.0299; Found 559.0303.



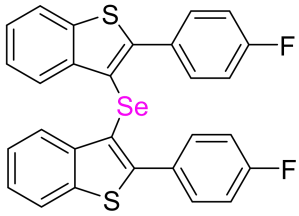
2-(4-(tert-butyl)phenyl)-3-(methylselanyl)benzo[b]thiophene (15d). Yellow solid; 46% yield (33.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 8.4 Hz, 2H), 2.10 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.8, 146.3, 142.4, 139.1, 131.7, 129.9, 125.4, 124.93, 124.86, 124.8, 122.3, 117.1, 34.9, 31.5, 9.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{21}SSe^+$ 361.0524; Found 361.0522.



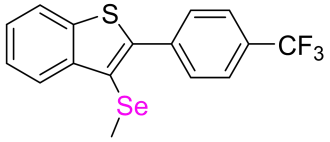
bis(2-(4-(tert-butyl)phenyl)benzo[*b*]thiophen-3-yl)selane (16d). Yellow solid; 14% yield (8.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.8 Hz, 2H), 7.40–7.35 (m, 10H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 2H), 1.36 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.6, 145.2, 141.9, 138.6, 131.3, 129.9, 125.1, 124.6, 124.5, 121.8, 116.2.



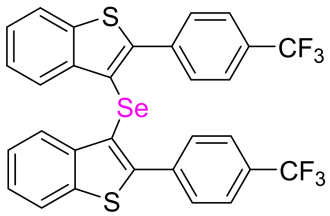
2-(4-fluorophenyl)-3-(methylselanyl)benzo[*b*]thiophene (15e). Yellow solid; 43% yield (27.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.68 (dd, *J* = 7.2, 6.0 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 8.4 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.1 (d, *J* = 247.8 Hz), 144.9, 142.2, 139.1, 132.4 (d, *J* = 8.1 Hz), 130.7 (d, *J* = 3.0 Hz), 125.1 (d, *J* = 6.0 Hz), 125.0, 122.3, 118.0, 115.6, 115.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}FSSe^+$ 322.9803; Found 322.9801.



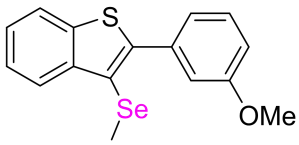
bis(2-(4-fluorophenyl)benzo[*b*]thiophen-3-yl)selane (16e). Yellow solid; 20% yield (10.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.30–7.28 (m, 4H), 7.26–7.25 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 2H), 6.98 (t, *J* = 8.4 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.8 (d, *J* = 247.2 Hz), 144.0, 141.4, 138.4, 131.6 (d, *J* = 8.4 Hz), 130.0 (d, *J* = 3.0 Hz), 124.7 (d, *J* = 16.5 Hz), 124.4, 121.9, 116.9, 115.2, 115.0.



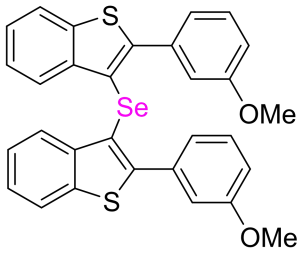
3-(methylselanyl)-2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophene (15f). Yellow solid; 41% yield (30.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.4, 2H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 8.4 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.0, 142.0, 139.2, 138.2, 130.5, 126.6, 125.4, 125.3 (q, *J* = 3.0 Hz), 125.2, 125.1, 122.3, 121.7 (q, *J* = 199.5 Hz), 9.0, 0.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{12}F_3SSe^+$ 372.9772; Found 372.9773.



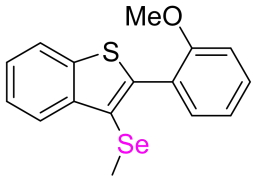
bis(2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophen-3-yl)selane (16f). Yellow solid; 17% yield (10.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 4H), 7.34 (d, *J* = 7.8 Hz, 4H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.24–7.23 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.0 (d, *J* = 250.8 Hz), 138.4, 127.3, 129.9, 125.2, 124.89, 124.85, 124.8, 124.3, 123,7, 122.0.



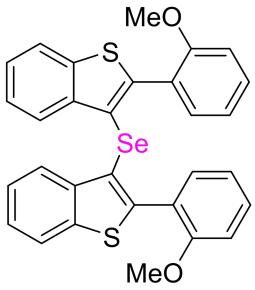
2-(3-methoxyphenyl)-3-(methylselanyl)benzo[*b*]thiophene (15g). Yellow solid; 46% yield (30.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.29–7.28 (m, 2H), 6.98–6.96 (m, 1H), 3.88 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.3, 145.6, 142.6, 139.0, 135.8, 129.3, 124.92, 124.87, 124.8, 122.6, 122.2, 117.7, 115.7, 114.3, 55.4, 8.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}OSSe^+$ 335.0003; Found 335.0001.



2-(3-methoxyphenyl)-3-(methylselanyl)benzo[*b*]thiophene (16g). Yellow solid; 15% yield (8.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.25–7.22 (m, 4H), 7.15 (t, *J* = 7.2 Hz, 2H), 6.94–6.89 (m, 6H), 3.77 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.3, 145.2, 141.7, 138.7, 135.5, 129.2, 124.7, 124.6, 122.7, 121.9, 117.0, 115.3, 114.7, 55.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}O_2S_2Se^+$ 559.0299; Found 511.0304.

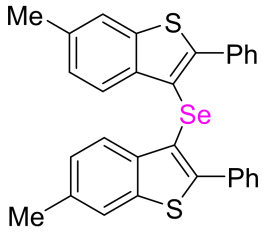


2-(2-methoxyphenyl)-3-(methylselanyl)benzo[*b*]thiophene (15h). Yellow solid; 30% yield (20.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.46–7.35 (m, 4H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.4, 142.4, 141.4, 140.0, 132.5, 130.5, 124.7, 124.5, 123.7, 122.3, 120.4, 120.3, 111.2, 55.7, 8.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}OSSe^+$ 335.0003; Found 335.0001.



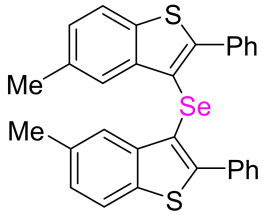
bis(2-(2-methoxyphenyl)benzo[*b*]thiophen-3-yl)selane (16h). Yellow solid; 15% yield (8.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.8 Hz, 2H), 7.44–7.39 (m, 4H), 7.21–7.17 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 3.72 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.2, 141.4, 141.0, 139.3, 132.2, 130.3, 124.4, 124.13, 124.11, 123.3, 121.7, 120.3, 119.6, 111.1, 55.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}O_2S_2Se^+$ 559.0299; Found 559.0298.

6-methyl-3-(methylselanyl)-2-phenylbenzo[*b*]thiophene (15i). Yellow solid; 34% yield (21.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.72–7.69 (m, 3H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.42–7.39 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 2.53 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.1, 142.4, 136.2, 134.7, 130.1, 128.5, 128.3, 126.6, 124.7, 121.9, 117.2, 21.7, 8.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}SSe^+$ 319.0054; Found 319.0052.

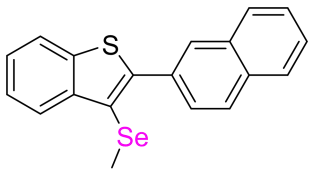


bis(6-methyl-2-phenylbenzo[*b*]thiophen-3-yl)selane (16i). Yellow solid; 21% yield (11.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.8 Hz, 4H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.47–7.34 (m, 6H), 7.10 (s, 2H), 7.01 (t, *J* = 7.2 Hz, 2H), 2.19 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.3, 142.1, 135.7, 134.6, 134.2, 130.5, 128.6, 128.3, 126.3, 124.8, 121.3, 116.7, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{30}H_{23}S_2Se^+$ 527.0401; Found 527.0400.

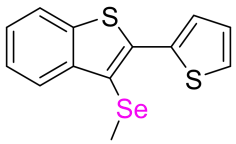
5-methyl-3-(methylselanyl)-2-phenylbenzo[*b*]thiophene (15j). Yellow solid; 44% yield (27.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (s, 1H), 7.72–7.69 (m, 3H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.41–7.39 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 2.53 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.1, 142.4, 136.3, 134.7, 130.2, 128.5, 128.3, 126.6, 124.7, 121.9, 117.2, 21.7, 8.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}SSe^+$ 319.0054; Found 319.0051.



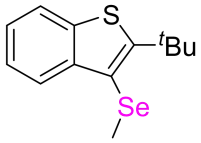
bis(5-methyl-2-phenylbenzo[*b*]thiophen-3-yl)selane (16j). Yellow solid; 17% yield (8.9 mg). 1H NMR (600 MHz, CDCl3): δ = 7.58 (d, J = 7.8 Hz, 4H), 7.53 (d, J = 8.2 Hz, 2H), 7.48–7.44 (m, 6H), 7.10 (s, 2H), 7.01 (d, J = 7.8 Hz, 2H), 2.20 (s, 6H); 13C NMR (150 MHz, CDCl3): δ = 146.2, 142.1, 135.7, 134.6, 134.2, 130.5, 128.6, 128.3, 126.3, 124.8, 121.3, 116.7, 21.3.



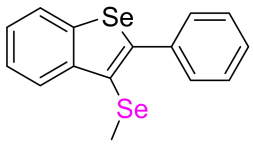
3-(methylselanyl)-2-(naphthalen-2-yl)benzo[*b*]thiophene (15k). Yellow solid; 30% yield (21.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.92–7.90 (m, 2H), 7.88–7.85 (m, 3H), 7.53–7.51 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.0, 142.4, 139.3, 133.3, 133.2, 132.2, 129.7, 128.5, 128.0, 127.9, 127.8, 126.8, 126.6, 125.1, 125.0, 124.9, 122.3, 118.1, 9.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{15}SSe^+$ 355.0054; Found 355.0054.



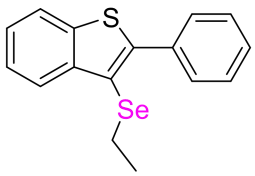
3-(methylselanyl)-2-(thiophen-2-yl)benzo[*b*]thiophene (15l). Yellow solid; 43% yield (26.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 3.6 Hz, 1H), 7.44–7.42 (m, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 4.2 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.8, 140.1, 138.2, 136.3, 128.3, 127.8, 127.0, 125.3, 125.2, 124.8, 122.0, 117.5, 9.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{13}H_{11}S_2Se^+$ 310.9462; Found 310.9460.



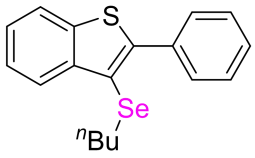
2-(tert-butyl)-3-(methylselanyl)benzo[*b*]thiophene (15m). Yellow solid; 23% yield (13.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 2.14 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.9, 143.3, 137.0, 124.6, 124.2, 123.6, 122.0, 115.1, 36.6, 31.3, 9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{13}H_{17}SSe^+$ 285.0211; Found 285.0211.



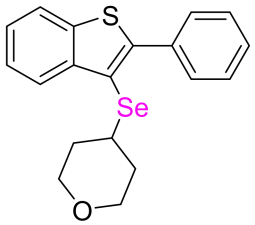
3-(methylselanyl)-2-phenylbenzo[*b*]selenophene (15n). Yellow solid; 37% yield (25.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.63–7.62 (m, 2H), 7.49–7.48 (m, 1H), 7.46–7.43 (m, 2H), 7.41–7.39 (m, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.6, 144.2, 141.0, 136.7, 130.3, 128.5, 128.4, 127.3, 125.4, 125.32, 125.26, 120.5, 9.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{13}Se_2^+$ 352.9342; Found 352.9341.



3-(ethylselanyl)-2-phenylbenzo[*b*]thiophene (15o). Yellow solid; 39% yield (24.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 6.0 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 3H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.39–7.36 (m, 1H), 2.64 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.8, 142.7, 139.0, 134.7, 130.4, 128.5, 128.2, 125.0, 124.9, 124.8, 122.1, 116.7, 22.3, 15.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}SSe^+$ 319.0054; Found 319.0051.

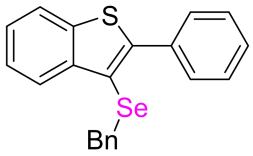


3-(butylselanyl)-2-phenylbenzo[*b*]thiophene (15p). Yellow solid; 41% yield (28.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.8 Hz, 1H), 7.85–7.82 (m, 1H), 7.72–7.70 (m, 3H), 7.46 (t, *J* = 7.2 Hz, 3H), 7.43–7.41 (m, 1H), 2.63 (t, *J* = 7.2 Hz, 2H), 1.43–1.38 (m, 2H), 1.23–1.17 (m, 2H), 0.73 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.0, 134.7, 130.3,129.0, 128.5, 128.2, 126.5, 125.0, 122.2, 122.1, 119.5, 117.0, 32.2, 28.6, 22.6, 13.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{19}SSe^+$ 347.0367; Found 347.0365.



4-((2-phenylbenzo[*b*]thiophen-3-yl)selanyl)tetrahydro-2H-pyran (15s). Yellow solid; 25% yield (18.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.46–7.45 (m, 3H), 7.43 (d, *J* = 7.2 Hz, 1H), 3.76–3.74 (m, 2H), 3.22 (t, *J* = 10.8 Hz, 2H), 1.68–1.66 (m, 2H), 1.61–1.58

(m, 2H), 1.27–1.25 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.9, 143.1, 139.0, 134.6, 130.5, 128.6, 128.2, 125.1, 125.0, 124.9, 122.1, 115.8, 67.7, 39.3, 33.8.

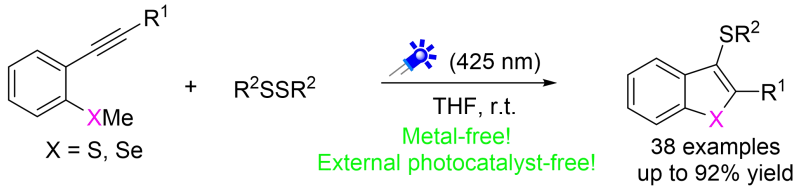


3-(benzylselanyl)-2-phenylbenzo[*b*]thiophene (15t). Yellow solid; 22% yield (16.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.8 Hz, 1H), 7.52–7.50 (m, 3H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.27–7.24 (m, 3H), 7.19–7.14 (m, 3H), 4.29 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.6, 140.4, 140.1, 139.8, 134.4, 129.50, 129.46, 128.7, 128.6, 128.2, 128.1, 126.1, 124.32, 124.28, 122.9, 122.2, 32.7.

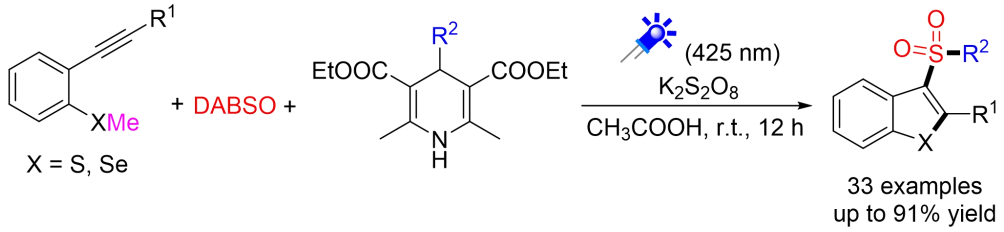
第 5 章 全文总结

围绕可见光促进邻炔基苯甲硫醚参与的串联反应，发展 C3-取代苯并噻吩的合成新方法，主要开展了以下三个研究工作：

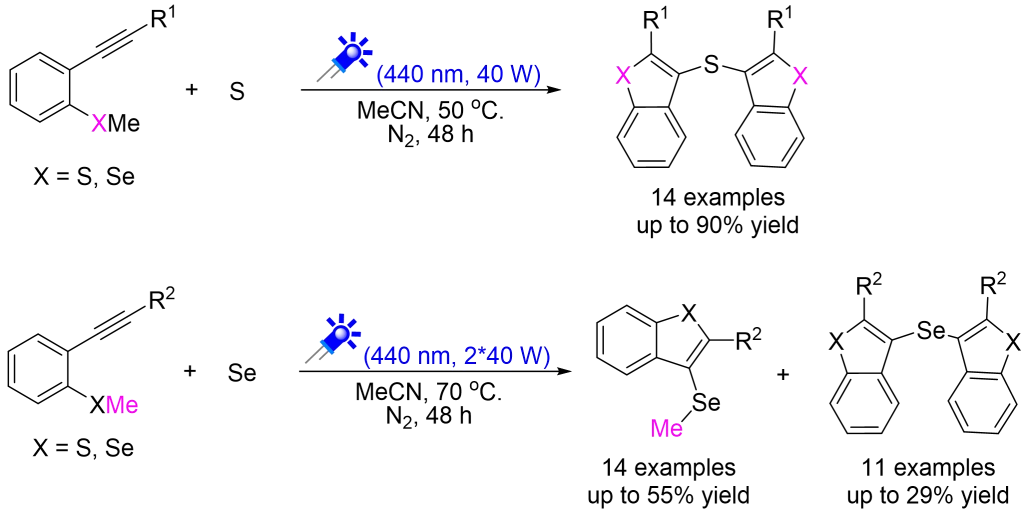
（1）开发了 2-炔基硫代苯甲醚与二硫化物无催化剂自由基环化新方法，该反应在可见光照条件下进行，实现了 3-芳硫基苯并[*b*]噻吩的制备（产率最高可达 92%），且对多种官能团展现出优异的耐受性。



（2）采用汉斯酯类化合物作为自由基前体，结合 DABSO 作为硫源，建立了光诱导二氧化硫插入/氧化磺酰化串联反应。该反应成功构建了烷基磺酰化苯并噻吩骨架，为含硫杂环化合物的合成提供了新思路。



（3）以硫粉为硫源，在无金属参与条件下实现了苯并噻吩硫桥联结构的构建。反应条件优化时发现，当以硒粉替代硫粉时，体系选择性发生改变，主产物转化为 3-甲基硒代苯并[*b*]噻吩，并伴随少量双(苯并[*b*]噻吩-3-基)硒醚生成。



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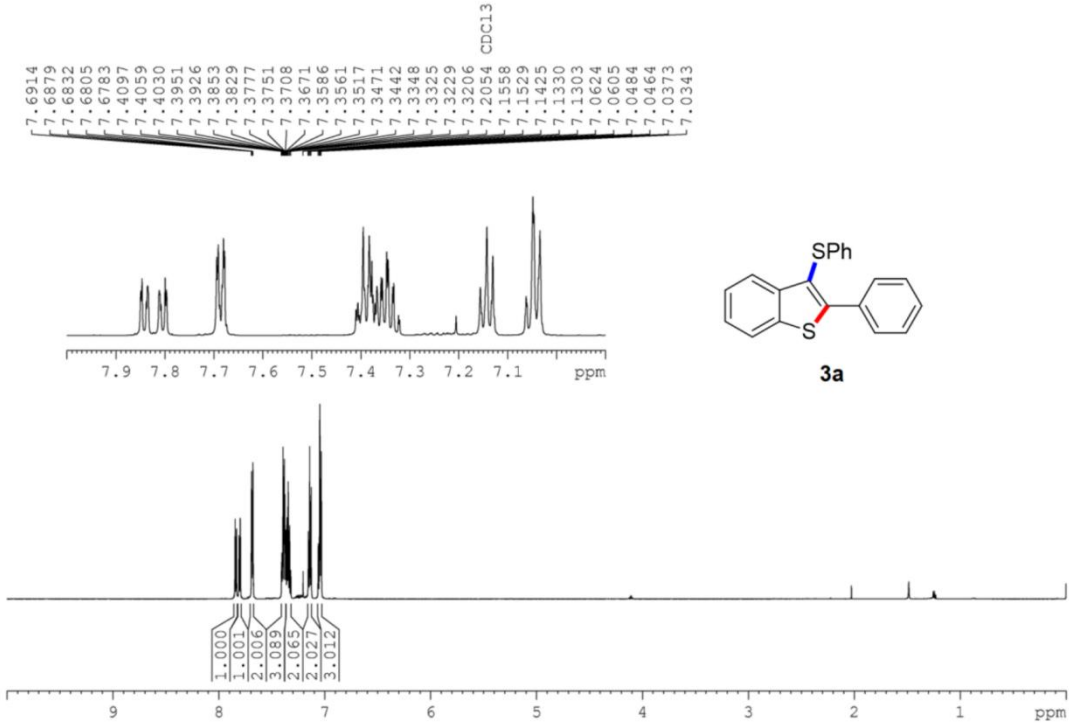
附录 I 部分化合物的谱图

^{1}H NMR of **3a** (600 MHz, $CDCl_3$)



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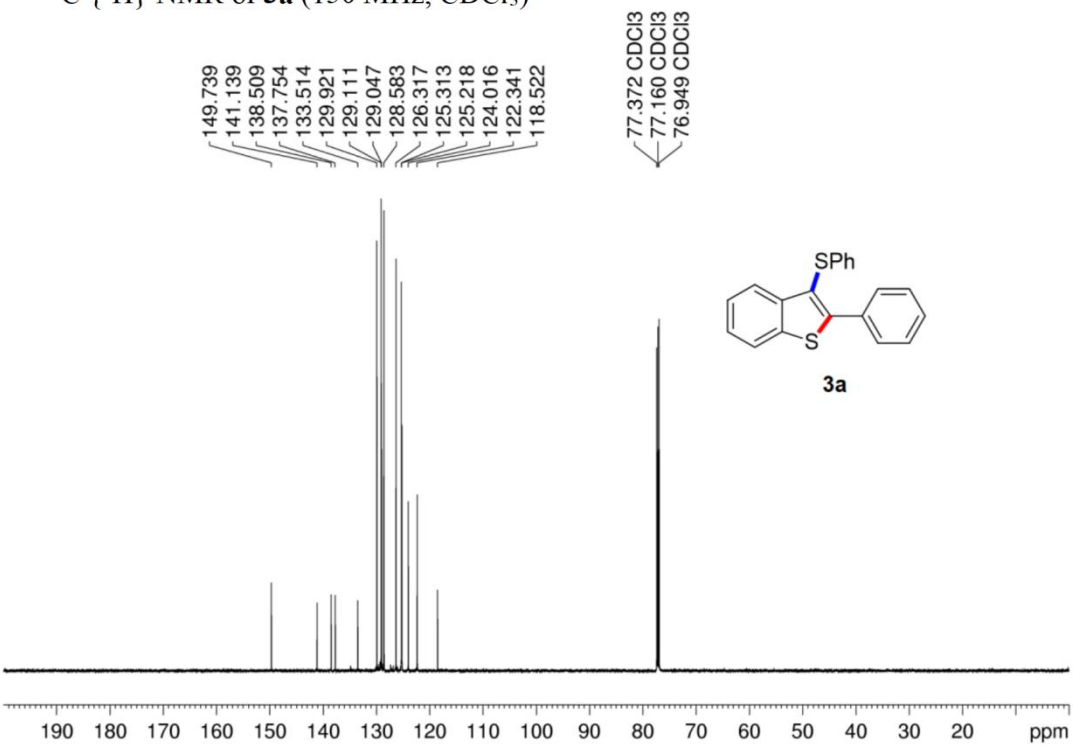

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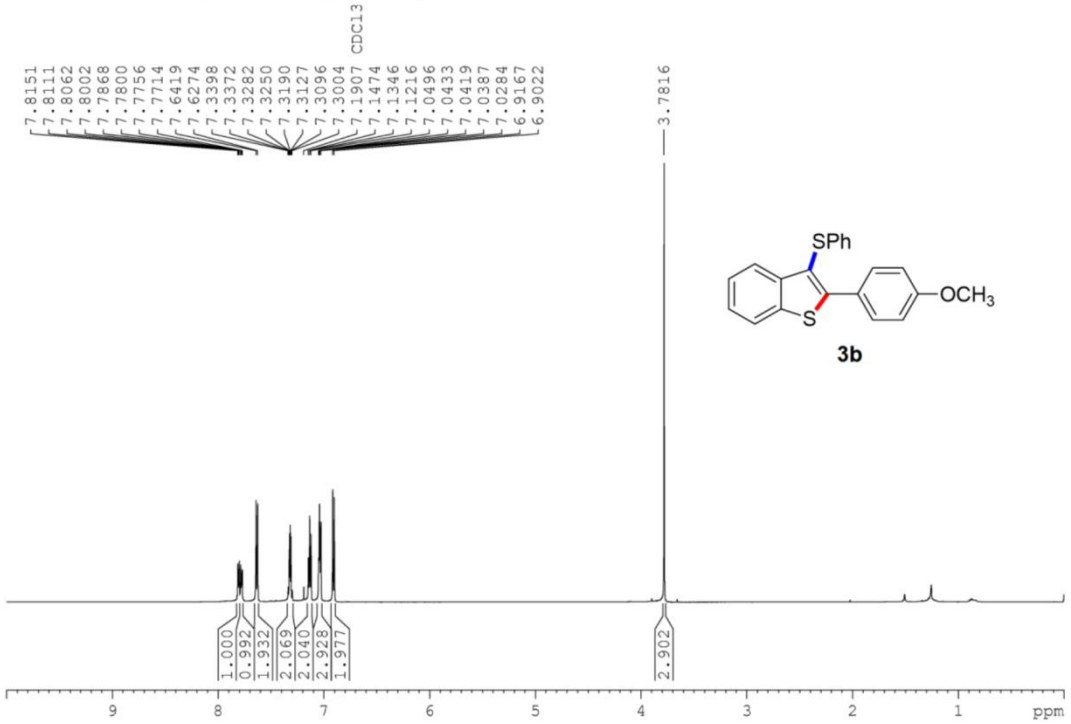

3b

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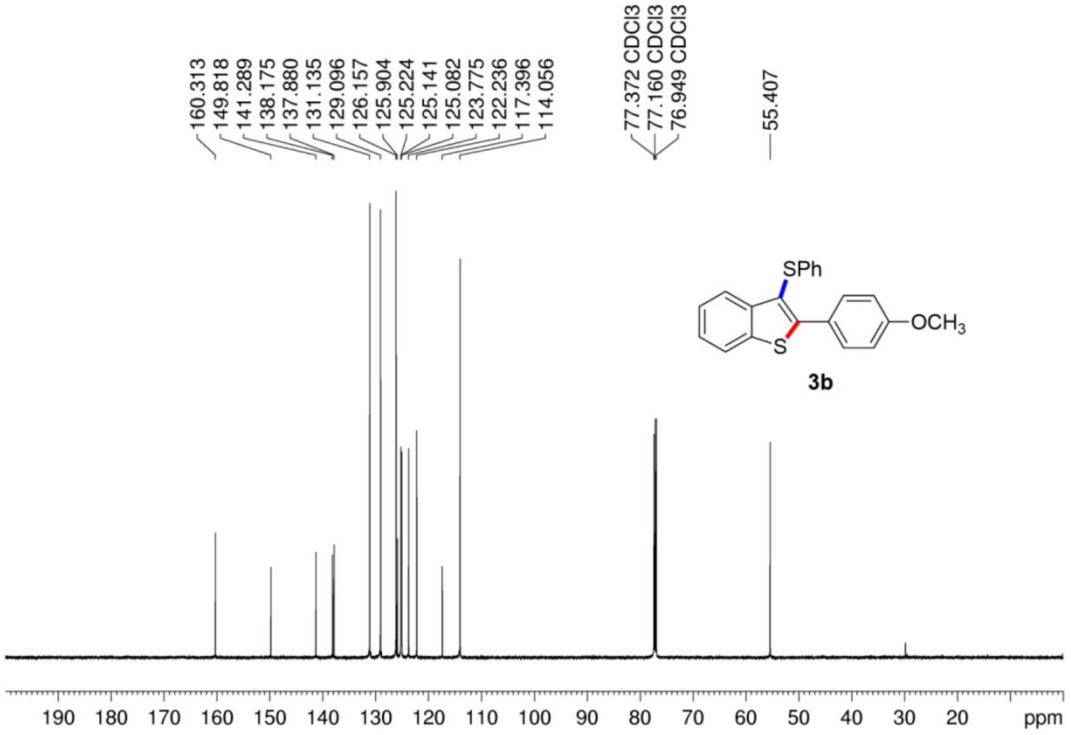

3b

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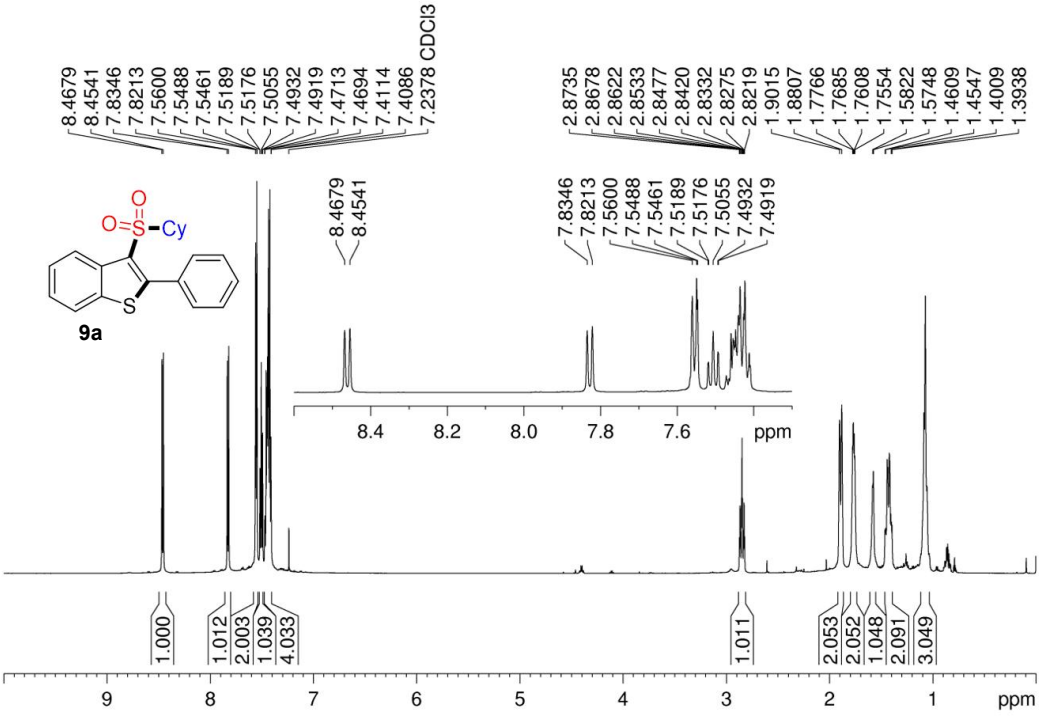

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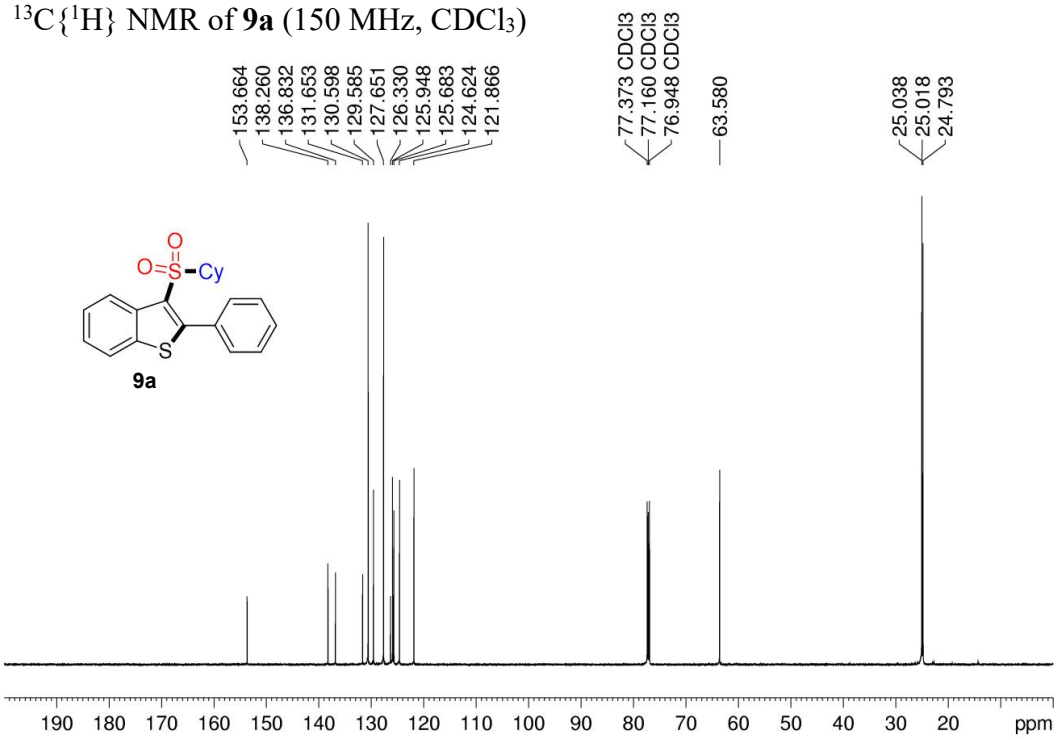

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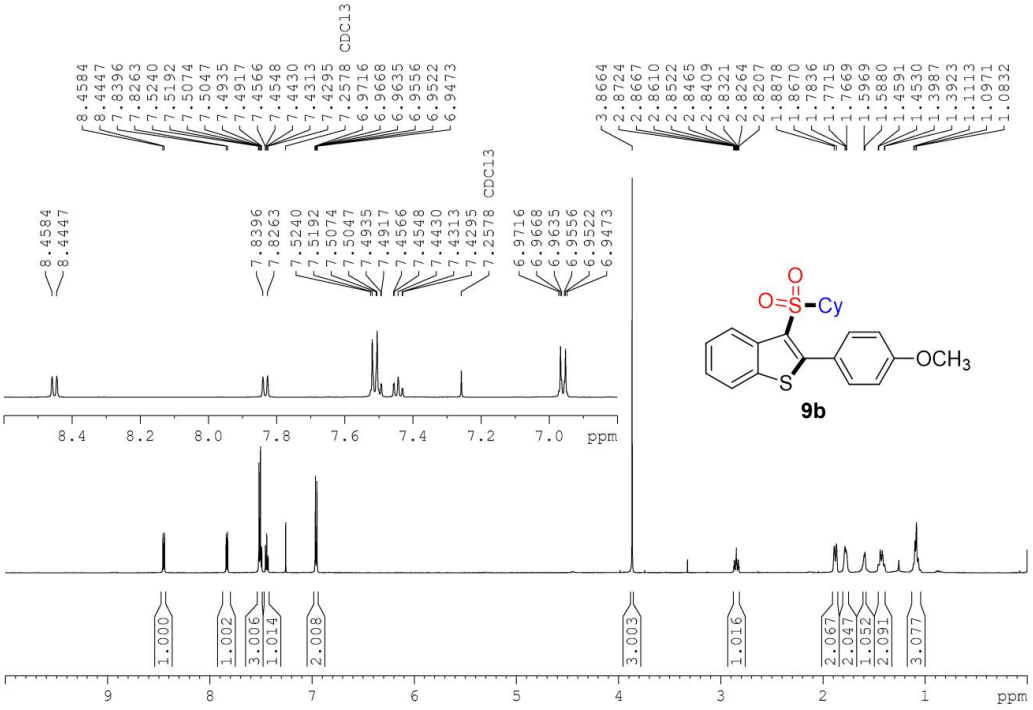

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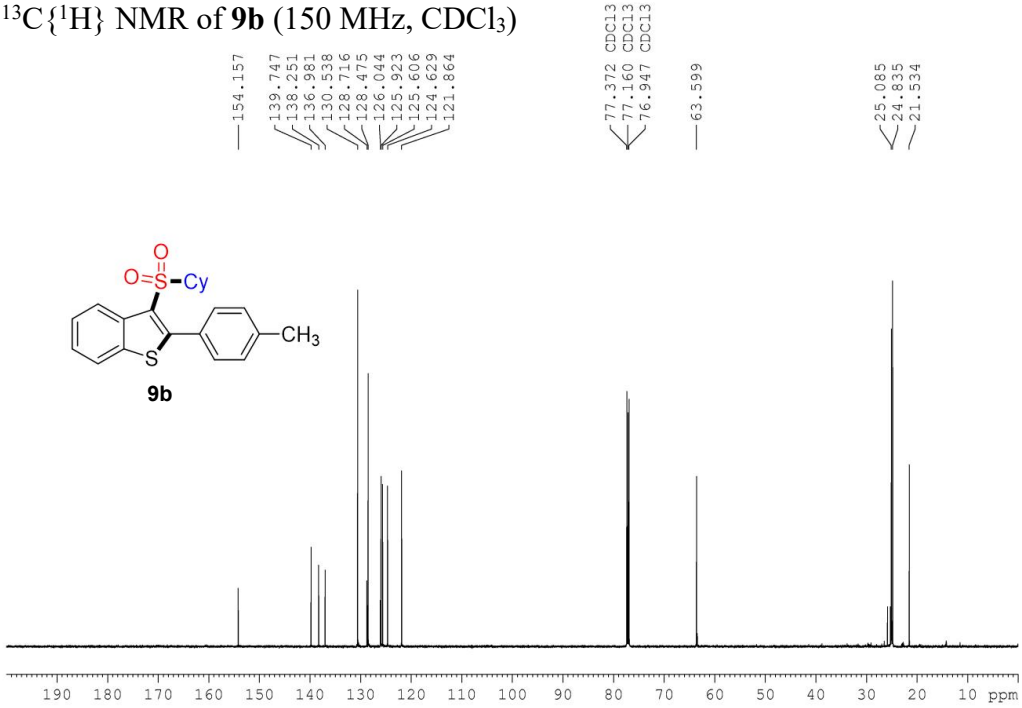

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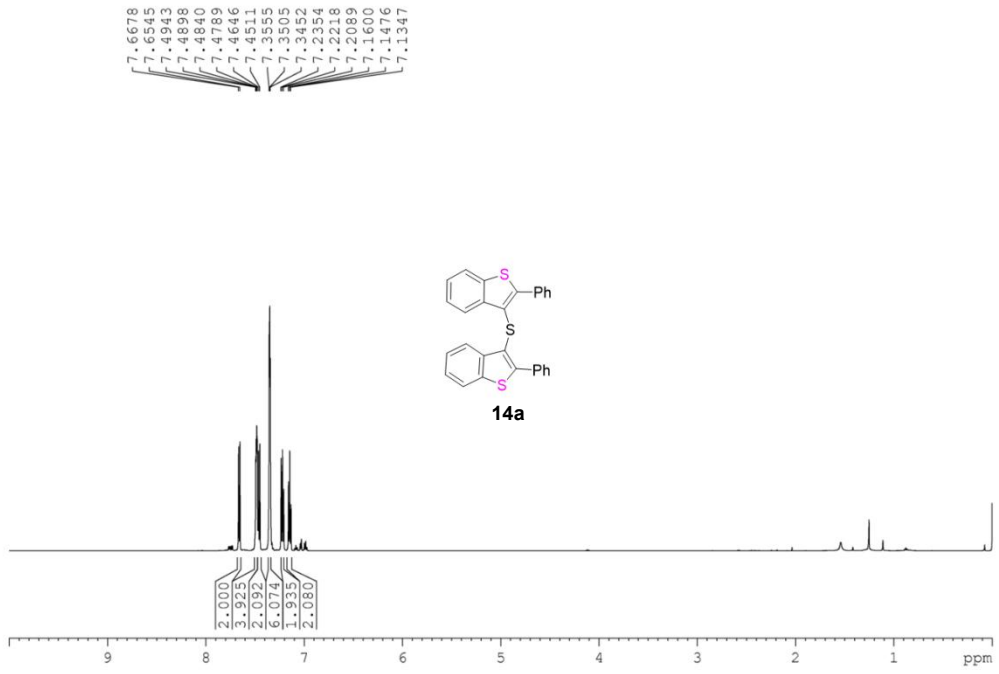

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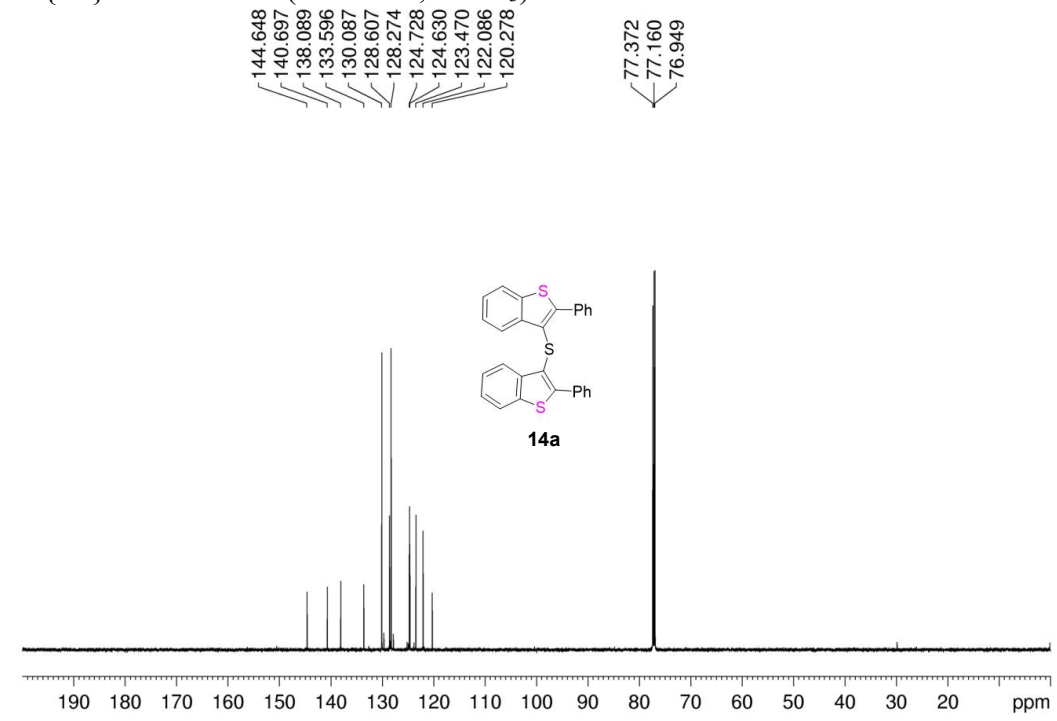

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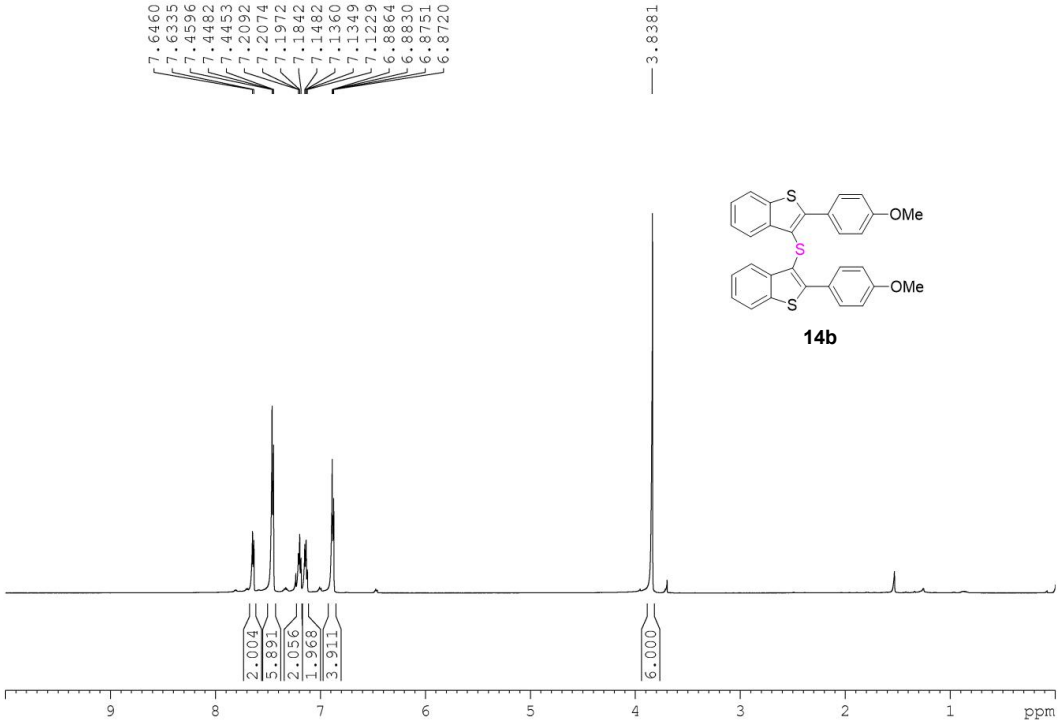

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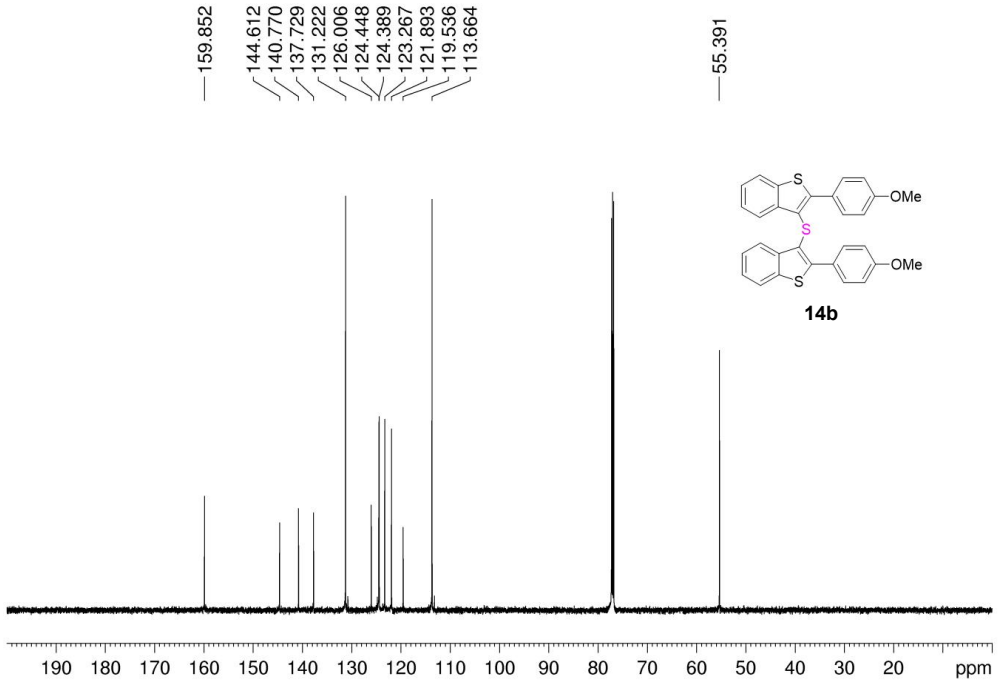
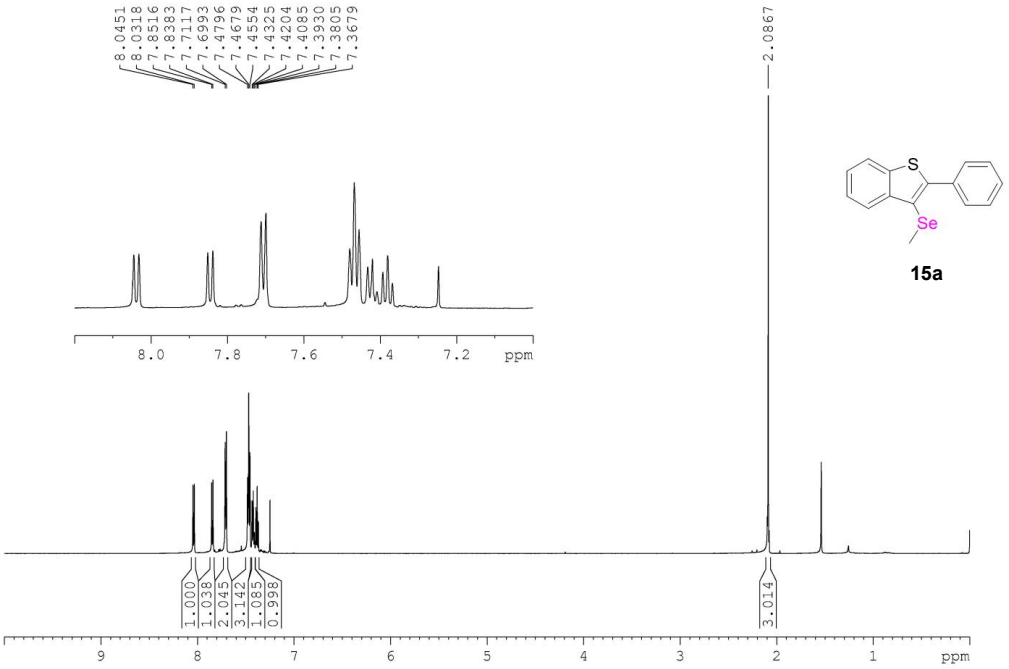


^{1}H NMR of **15a** (600 MHz, $CDCl_3$)



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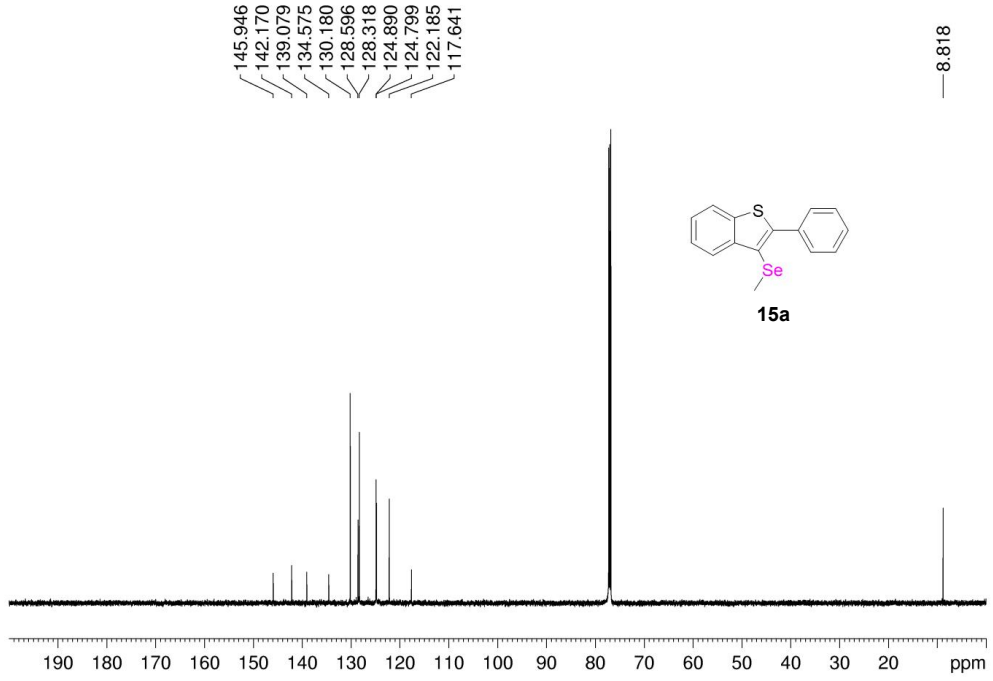

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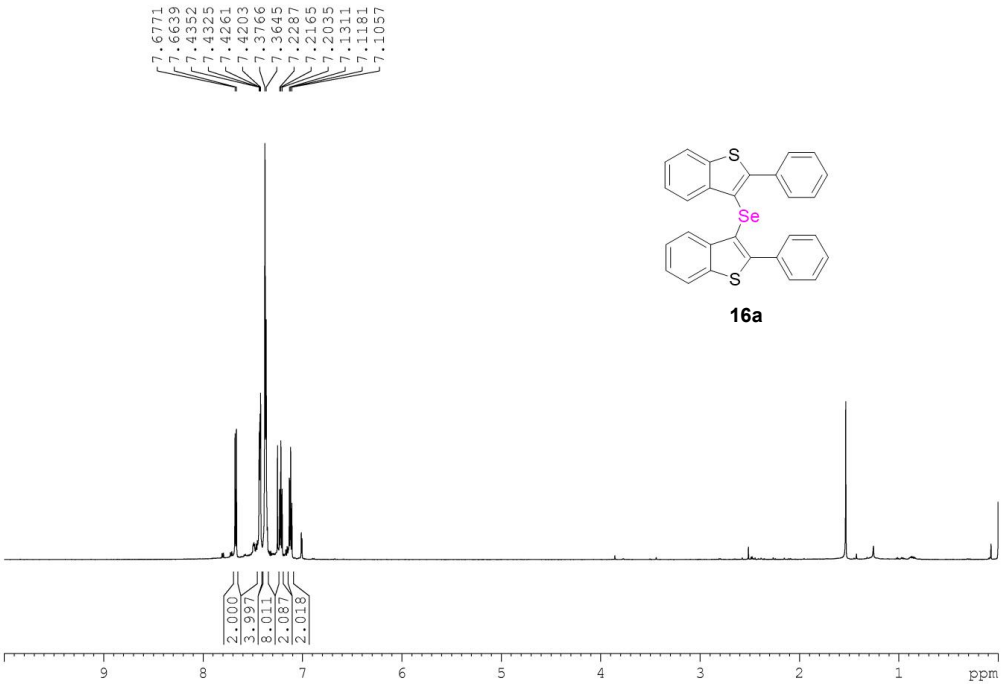

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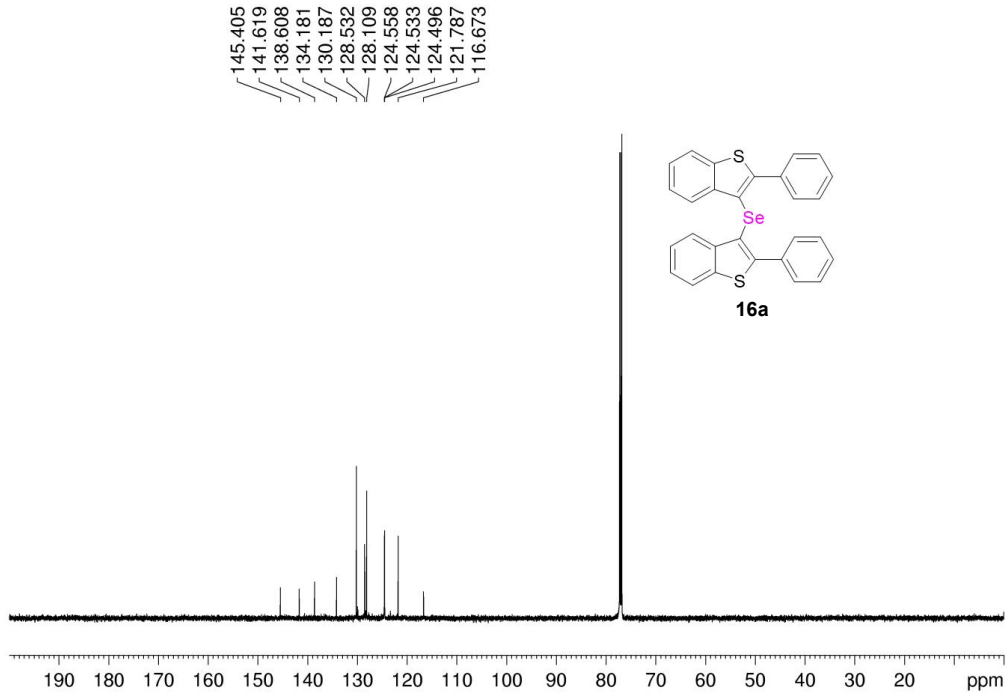

附录II 硕士期间发表及待发表论文

[1] **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.

[2] 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.

[3] Liang Ye, Haibin Xu, Jiong Yu, **Han Yan**, Min Wang,* and Pinhua Li*, Photocatalytic Cascade Alkylation/Cyclization of N-Arylacrylamides with Simple Alkanes: A Convenient Approach to Quaternary C3 Alkylated Oxindoles. *Asian J. Org. Chem.* **2025**, *14*, e202400554

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最后向参加论文评阅和答辩的各位专家、教授表示最诚挚的感谢！

颜韩

2025 年 5 月