JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

# Selectfluor-Promoted Sequential Reactions via Allene Intermediates: Metal-Free Construction of Fused Polycyclic Skeletons

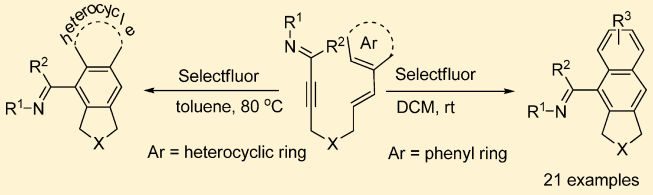
Le Liu,[†,‡] Jianbo Wang,[†] and Hongwei Zhou*[,†,‡]

[†]College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing 314001, People's Rupublic of China

[‡]Department of Chemistry, Zhejiang University (Campus Xixi), Hangzhou 310028, People's Republic of China

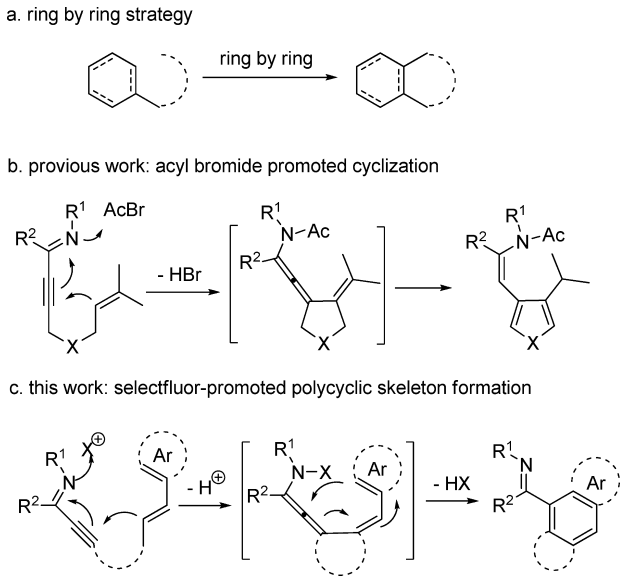
Supporting Information

**ABSTRACT:** Polycyclic skeletons are present in numerous important compounds, such as synthetic intermediates and target molecules of biological interest. In this paper, a Selectfluor-promoted construction of polycyclic skeletons with high synthetic efficiency was developed.




Synthetic efficiency is one of the most pursued objectives for organic chemists.[1] The ideal approach to polycyclic compounds is that two or more rings can be achieved from readily available starting materials in just "one shot". However, among the variety of methodologies, the most commonly used protocol is still a "ring by ring" strategy (Scheme 1a).[2] During our recent studies on cyclization reactions,[3] we found that treatment of alkynylimine with acyl bromide could offer tetrasubstituted allene intermediates and yield heterocyclic derivatives (Scheme 1b).[3a] We anticipate that an electrophilic halide might produce the cyclic intermediate, which would undergo further cyclization (Scheme 1c). Herein, we report a sequence for the efficient synthesis of polycyclic compounds in which polycyclic skeletons are expected to form in a one−pot process from easily prepared substrates.

**Scheme 1. Proposed Sequence for the Synthesis of Polycyclic Skeletons**




Stimulated by this idea, we chose **1a** as the starting material, which could be readily prepared via the Sonogashira coupling of cinnamyl propargyl ether with *N*-(4-methoxyphenyl)-benzimidoyl chloride.[4] We initiated our study by testing the reaction of **1a** with various electrophilic halides in dichloromethane at room temperature. Although *N*-chlorosuccinimide (NCS), *N*-bromosuccinimide (NBS), *N*-iodosuccinimide (NIS), 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), and 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) gave unidentified mixtures (Table 1, entries 1−6), *N*-fluorobenzenesulfonimide (NFSI) triggered the reaction to produce *N*-((1, 3-dihydronaphtho[2,3-*c*]furan-4-yl)(phenyl)methylene)-4-methoxyaniline (**2a**) in 32% yield (entry 7). The structure of **2a** was revealed by X-ray diffraction analysis (Figure 1).[5] Further screening showed that 1-chloromethyl-4-fluoro-1,4-diazonia-

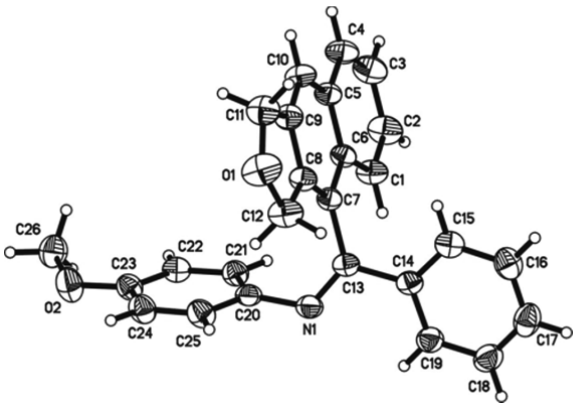



**Figure 1.** ORTEP representation of **2a** (drawn with thermal ellipsoids at 30% probability level).

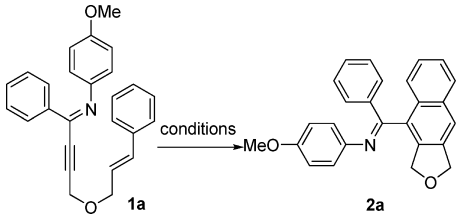
**Received:** February 4, 2015
**Published:** April 8, 2015





DOI: 10.1021/acs.joc.5b00261
*J. Org. Chem.* 2015, 80, 4749−4753

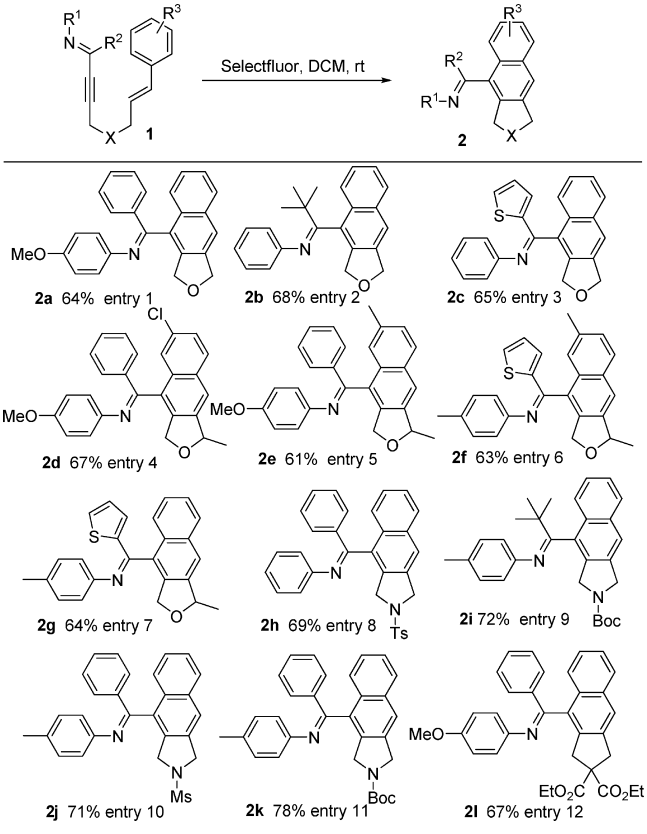
**Table 1. Optimization of the Reaction Conditions**[a]




| entry | electrophilic halide | solvent | yield of **2a** (%) |
|---|---|---|---|
| 1 | NCS | DCM | 0 |
| 2 | NBS | DCM | 0 |
| 3 | NIS | DCM | 0 |
| 4 | NFSI | DCM | 0 |
| 5[b] | DCDMH | DCM | 0 |
| 6[b] | DBDMH | DCM | 0 |
| 7 | NFSI | DCM | 32 |
| 8 | Selectfluor | DCM | 64 |
| 9 | Selectfluor | DCE | 55 |
| 10 | Selectfluor | chloroform | 58 |
| 11 | Selectfluor | acetonitrile | 11 |
| 12 | Selectfluor | toluene | 62 |

[a]The reaction was carried out using **1a** (0.2 mmol) and electrophilic halide (0.22 mmol) in solvent (2.5 mL) under $N_2$. [b]Electrophilic halide (0.11 mmol) was charged.

**Table 2. Construction of Dihydronaphtho[2,3-*c*]furans, Dihydro-benzo[*f*]isoindolines, and Cyclopenta[*b*]naphthalene**[a]



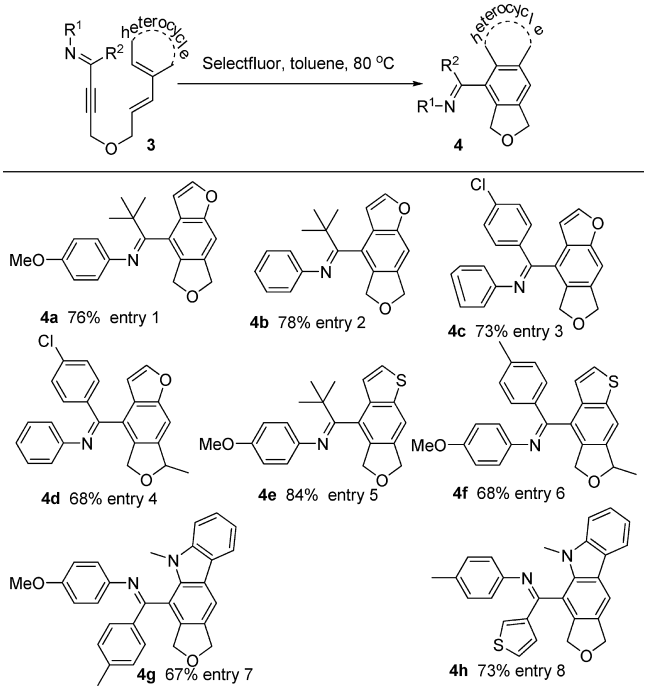

[a]The reaction was carried out using **1** (0.2 mmol) and Selectfluor (0.22 mmol) in DCM (2.5 mL) under $N_2$ at room temperature.

bicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor) could offer a better result, and the use of other common solvents, such as dichloroethane, chloroform, acetonitrile, and toluene, did not improve the yield (entries 8−12).

Under the optimized conditions, the scope of this reaction was examined further. This polycyclic skeleton formation strategy was successful for the one-pot construction of 1,3-dihydronaphtho[2,3-*c*]furans (Table 2, entries 1−7), 2,3-dihydro-benzo[*f*]isoindolines (entries 8−11), and cyclopenta-[*b*]naphthalene (entry 12).

However, when we tried to replace the benzene ring of the cinnamyl moiety by a heterocyclic ring, the standard conditions used for Table 2 failed to give satisfactory yields. Fortunately, subsequent screening showed that the use of toluene as the solvent and elevating the temperature to 80 °C gave acceptable yields. Hence, the following reaction conditions were chosen as optimum for further examination of the scope of this reaction: 0.2 mmol of substrate and 0.22 mmol of Selectfluor in toluene at 80 °C. The desired products were obtained in moderate to good yields (Table 3).

**Table 3. Construction of Dihydrobenzodifurans, Dihydrothienoisobenzofurans, and Dihydrofurocarbazols**[a]




[a]The reaction was carried out using **3** (0.2 mmol) and Selectfluor (0.22 mmol) in toluene (2.5 mL) under $N_2$ at 80 °C.

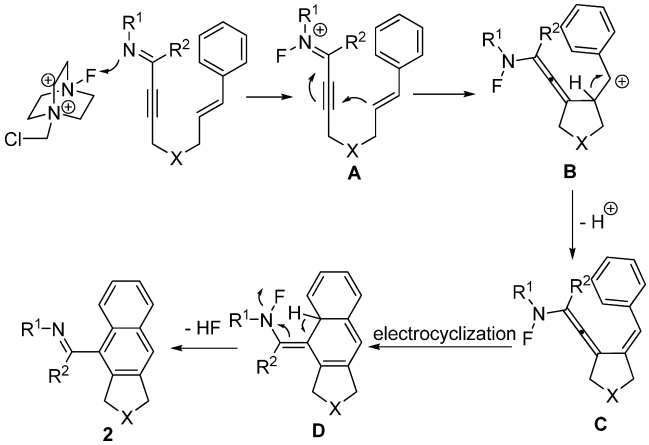
We propose a plausible pathway as shown in Scheme 2. Nitrogen of alkynylimine attacks Selectfluor to afford *N*-fluoroaminium species **A**, which undergoes the first cyclization to offer intermediate **B**. Intermediate **B**, via loss of a proton, gives **C**, which experiences 6$\pi$-electrocyclization to achieve the second cyclization, affording unstable intermediate **D**.[6] Elimination of hydrogen fluoride finishes the aromatization and gives the last product **2**.

Aside from the construction of heterocycles, this protocol offers a route to bulky ketone imines, which are useful building blocks and difficult to access.[7] We treated **4b** with $LiAlH_4$ in THF at 60 °C and obtained amine **5** in nearly quantitative yield (Scheme 3).

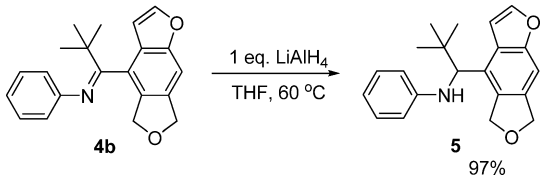


DOI: 10.1021/acs.joc.5b00261
J. Org. Chem. 2015, 80, 4749−4753

**Scheme 2. Plausible Pathway**




**Scheme 3. Preparation of Bulky Amine**




In summary, we have reported a Selectfluor-promoted construction of polycyclic skeletons with high synthetic efficiency. As a result of this metal-free process with readily accessible starting materials and convenient operation, the protocol presented here should be an appealing strategy in organic synthesis.

## EXPERIMENTAL SECTION

**General.** Dichloromethane was dried with $CaH_2$ and distilled freshly before use. Toluene was dried with sodium and distilled freshly before use. Tetrahydrofuran was dried with $LiAlH_4$ and distilled freshly before use. Other materials and solvents were purchased from commercial suppliers and used without additional purification. NMR spectra were measured in $CDCl_3$ or DMSO-$d_6$, operating for $^1H$ NMR at 400 MHz and for $^{13}C$ NMR at 100 MHz. Chemical shifts are expressed in ppm and $J$ values are given in Hz. Mass spectroscopy data of the products were collected with an HRMS-TOF instrument. Melting points were measured on a microscopic apparatus and were uncorrected.

***N*-((1,3-Dihydronaphtho[2,3-*c*]furan-4-yl)(phenyl)-methylene)-4-methoxyaniline (2a): Typical Procedure.** To a solution of imine (0.2 mmol) in dichloromethane (2.5 mL) was added Selectfluor (0.22 mmol) under a $N_2$ atmosphere. The resulting mixture was stirred at room temperature, and the reaction was monitored by TLC until completion. Then, the reaction was quenched with 30 mL of water, extracted with dichloromethane (3 × 15 mL), and dried with anhydrous $Na_2SO_4$. After evaporation, chromatography on silica gel (eluent: hexane/ethyl acetate = 20:1) of the reaction mixture afforded **2a**: 49 mg, 64% yield, needle solid, mp 78−80 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 8.0 Hz, 1H), 7.74−7.59 (m, 4H), 7.48−7.29 (m, 5H), 6.73−6.65 (m, 2H), 6.60−6.50 (m, 2H), 5.14 (dd, $J$ = 30.0, 13.2 Hz, 2H), 4.85 (d, $J$ = 13.6 Hz, 1H), 4.64 (d, $J$ = 13.3 Hz, 1H), 3.63 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 164.9, 156.6, 143.3, 138.8, 137.6, 136.7, 133.1, 131.4, 130.8, 128.6, 128.5, 128.2, 128.0, 126.6, 126.0, 121.9, 120.2, 113.7, 72.9, 72.8, 55.2; IR (neat) 2962, 1561, 1054 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{26}H_{21}NO_2$ 379.1572, found 379.1576.

***N*-(1-(1,3-Dihydronaphtho[2,3-*c*]furan-4-yl)-2,2-dimethyl-propylidene)aniline (2b).** 45 mg, 68% yield, needle solid, mp 65−67 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.4 Hz, 1H), 7.72 (d, $J$ = 8.4 Hz, 1H), 7.57−7.48 (m, 1H), 7.46−7.44 (m, 2H), 6.9 (t, $J$ = 15.6 Hz, 2H), 6.73 (t, $J$ = 14.8 Hz, 1H), 6.58 (d, $J$ = 8.0 Hz, 2H), 5.11 (d, $J$ = 12.0 Hz, 2H), 5.00 (d, $J$ = 12.4 Hz, 1H), 4.82 (d, $J$ = 13.2 Hz, 1H), 1.32 (s, 9H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 179.2, 150.5, 137.4, 134.6, 132.8, 131.1, 129.6, 128.4, 128.2, 126.6, 125.9, 125.8, 123.4, 119.4, 118.5, 73.6, 72.8, 41.1, 30.0; IR (neat) 2694, 1769, 1631, 1056 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{23}H_{23}NO$ 329.1780, found 329.1782.

***N*-((1,3-Dihydronaphtho[2,3-*c*]furan-4-yl)(thiophen-2-yl)-methylene)aniline (2c).** 46 mg, 65% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (dd, $J$ = 12.8, 4.8 Hz, 2H), 7.67 (s, 1H), 7.56 (d, $J$ = 4.8 Hz, 1H), 7.46 (t, $J$ = 8.4 Hz, 2H), 7.03−6.98 (m, 4H), 6.88 (t, $J$ = 14.4 Hz, 1H), 6.80 (d, $J$ = 8.0 Hz, 2H), 5.14 (dd, $J$ = 31.6, 12.8 Hz, 2H), 4.98 (d, $J$ = 13.2 Hz, 1H), 4.74 (d, $J$ = 13.6 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 167.5, 154.4, 137.6, 136.8, 133.0, 131.2, 128.5, 128.1, 126.7, 126.2, 125.8, 124.9, 120.7, 72.9, 72.7; IR (neat) 2923, 1514, 1059 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{23}H_{17}NOS$ 355.1031, found 355.1025;

***N*-((6-Chloro-1-methyl-1,3-dihydronaphtho[2,3-*c*]furan-4-yl)(phenyl)methylene)-4-methoxyaniline (2d).** 57 mg, 67% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.77 (dd, $J$ = 8.8, 6.8 Hz, 1H), 7.70−7.63 (m, 2H), 7.61 (t, $J$ = 5.2 Hz, 1H), 7.54 (d, $J$ = 3.2 Hz, 1H), 7.48−7.42 (m, 1H), 7.40−7.35 (m, 3H), 6.70−6.62 (m, 2H), 6.59−6.53 (m, 2H), 5.40−5.35(m, 0.5H), 5.27−5.22 (m, 0.5H), 4.82 (d, $J$ = 13.6 Hz, 0.5H), 4.75 (s, 1H), 4.54 (d, $J$ = 13.6 Hz, 0.5H), 3.65 (s, 1.5H), 3.64 (s, 1.5H), 1.58 (d, $J$ = 6.4 Hz, 1.5H), 1.45 (d, $J$ = 6.0 Hz, 1.5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 164.2, 164.1, 156.6, 143.2, 142.6, 138.4, 138.3, 132.5, 131.9, 131.4, 131.1, 130.0, 129.9, 128.7, 128.2, 127.3, 127.0, 124.7, 124.6, 121.7, 120.0, 113.7, 79.4, 79.1, 71.3, 55.3, 55.2, 21.6, 21.2; IR (neat) 2960, 1510, 1054 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{27}H_{22}ClNO_2$ 427.1339, found 427.1337.

***N*-((1,6-Dimethyl-1,3-dihydronaphtho[2,3-*c*]furan-4-yl)-(phenyl)methylene)-4-methoxyaniline (2e).** 50 mg, 61% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.76−7.66 (m, 3H), 7.52 (d, $J$ = 4.0 Hz, 1H), 7.45−7.39 (m, 2H), 7.37−7.34 (m, 2H), 7.30−7.26 (m, 1H), 6.71−6.66 (m, 2H), 6.57−6.51 (m, 2H), 5.37 (dd, $J$ = 12.4, 6.4 Hz, 0.5H), 5.24 (dd, $J$ = 12.4, 6.4 Hz, 0.5H), 4.81 (d, $J$ = 13.6 Hz, 0.5H), 4.78−4.63 (m, 1H), 4.50 (d, $J$ = 12.8 Hz, 0.5H), 3.64 (d, $J$ = 4.0 Hz, 3H), 2.38 (d, $J$ = 2.0 Hz, 3H), 1.57 (d, $J$ = 6.4 Hz, 1.5H), 1.44 (d, $J$ = 6.4 Hz, 1.5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 165.3, 165.1, 156.6, 143.3, 141.2, 138.7, 137.0, 136.8, 136.4, 136.3, 131.6, 131.4, 130.8, 128.6, 128.3, 128.2, 127.1, 124.9, 124.8, 121.9, 119.9, 113.6, 79.4, 79.2, 71.4, 71.3, 55.2, 55.2, 21.9, 21.4; IR (neat) 2956, 1561, 1153 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{28}H_{25}NO_2$ 407.1885, found 407.1880.

***N*-((1,6-dimethyl-1,3-dihydronaphtho[2,3-*c*]furan-4-yl)-(thiophen-2-yl)methylene)-4-methylaniline (2f).** 50 mg, 63% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.70 (t, $J$ = 15.2 Hz, 1H), 7.60−7.37 (m, 3H), 7.27 (d, $J$ = 13.6 Hz, 1H), 6.89 (dd, $J$ = 8.8, 3.6 Hz, 1H), 6.78−6.75 (m, 2H), 6.73−6.70 (m, 1H), 6.67−6.60 (m, 2H), 5.36 (dd, $J$ = 6.4, 12.8 Hz, 0.5H), 5.22 (d, $J$ = 6.0, 12.0 Hz, 0.5H), 4.93 (d, $J$ = 13.6 Hz, 0.5H), 4.82 (dd, $J$ = 33.2, 13.2 Hz, 1H), 4.58 (d, $J$ = 13.2 Hz, 0.5H), 2.41 (d, $J$ = 4.4 Hz, 3H), 2.09 (d, $J$ = 3.6 Hz, 3H), 1.55 (d, $J$ = 6.4 Hz, 1.5H), 1.42 (d, $J$ = 6.4 Hz, 1.5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 160.1, 159.9, 146.8, 146.7, 145.7, 145.6, 141.2, 141.1, 136.9, 136.8, 136.4, 136.3, 133.9, 131.5, 131.4, 131.3, 130.6, 129.0, 128.9, 128.3, 128.2, 127.8, 126.6, 124.9, 124.8, 120.6, 120.1, 120.0, 79.5, 79.2, 71.3, 21.9, 21.7, 21.4, 20.8; IR (neat) 2972, 1595, 1073 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{26}H_{23}NOS$ 397.1500, found 397.1496.

**4-Methyl-*N*-((1-methyl-1,3-dihydronaphtho[2,3-*c*]furan-4-yl)(thiophen-2-yl)methylene)aniline (2g).** 49 mg, 64% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.85 (t, $J$ = 15.6 Hz, 2H), 7.63 (s, 1H), 7.50−7.46 (m, 3H), 6.89 (dd, $J$ = 5.2, 3.6 Hz, 1H), 6.78 (d, $J$ = 8.0 Hz, 2H), 6.69 (dd, $J$ = 3.6, 0.8 Hz, 1H), 6.59 (d, $J$ = 8.0 Hz, 2H), 5.15 (d, $J$ = 12.8 Hz, 1H), 4.92 (d, $J$ = 12.8 Hz, 1H), 4.76 (dd, $J$ = 12.8, 6.4 Hz, 1H), 2.14 (s, 3H), 1.32 (d, $J$ = 6.4 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 171.3, 160.1, 146.9, 146.7, 139.7, 138.3, 134.1, 132.9, 132.3, 131.8, 130.3, 129.0, 128.9, 128.3, 127.7, 126.5, 126.3, 126.0, 122.6, 120.4, 79.8, 70.8, 20.8, 19.7; IR (neat) 2926,



DOI: 10.1021/acs.joc.5b00261
J. Org. Chem. 2015, 80, 4749−4753

1620, 1052 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{25}H_{21}NOS$ 383.1344, found 383.1338.

***N*-(Phenyl(2-tosyl-2,3-dihydro-1*H*-benzo[*f*]isoindol-4-yl)-methylene)aniline (2h).** 69 mg, 69% yield, needle solid, mp 98−100 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.76 (d, $J$ = 8.0 Hz, 1H), 7.61 (dd, $J$ = 13.0, 6.9 Hz, 6H), 7.50−7.32 (m, 6H), 7.27 (s, 1H), 6.91 (t, $J$ = 6.9 Hz, 2H), 6.82−6.76 (m, 1H), 6.65 (t, $J$ = 7.6 Hz, 2H), 4.75 (d, $J$ = 13.8 Hz, 1H), 4.49 (dd, $J$ = 30.8, 14.3 Hz, 2H), 4.19 (d, $J$ = 14.4 Hz, 1H), 2.41 (s, 3H), 1.25 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 165.6, 149.6, 143.7, 137.7, 134.1, 133.3, 133.1, 132.8, 131.5, 131.3, 129.8, 129.2, 128.7, 128.5, 128.4, 128.3, 127.6, 126.9, 126.4, 125.9, 124.2, 122.2, 119.7, 53.2, 53.1, 21.5; IR (neat) 2920, 1264, 1163 $cm^{-1}$; HRMS (EI) calcd for $C_{32}H_{26}N_2O_2S$ 502.1715, found 502.1710.

***tert*-Butyl 4-(2,2-Dimethyl-1-(*p*-tolylimino)propyl)-1*H*-benzo[*f*]isoindole-2(3*H*)-carboxylate (2i).** 64 mg, 72% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.89−7.66 (m, 2H), 7.47 (dt, $J$ = 25.8, 7.6 Hz, 3H), 6.74−6.62 (m, 2H), 6.50 (dd, $J$ = 11.2, 8.4 Hz, 2H), 4.78−4.58 (m, 3H), 4.39 (t, $J$ = 33.2 Hz, 1H), 2.06 (d, $J$ = 6.4 Hz, 3H), 1.53 (d, $J$ = 5.2 Hz, 9H), 1.31 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 177.4, 153.3, 146.8, 134.6, 134.1, 131.9, 131.6, 131.4, 130.9, 130.8, 130.4, 130.2, 127.8, 127.3, 127.2, 125.7, 125.5, 124.9, 124.8, 120.3, 120.0, 117.6, 78.9, 51.4, 51.3, 50.7, 50.3, 39.9, 29.3, 29.2, 27.5, 19.6; IR (neat) 2971, 1694, 1396 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{29}H_{34}N_2O_2$ 442.2620, found 442.2618.

**4-Methyl-*N*-((2-(methylsulfonyl)-2,3-dihydro-1*H*-benzo[*f*]-isoindol-4-yl)(phenyl)methylene)aniline (2j).** 62 mg, 71% yield, yellow solid, mp 70−72 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.84 (d, $J$ = 7.9 Hz, 1H), 7.69 (d, $J$ = 4.3 Hz, 2H), 7.67−7.61 (m, 2H), 7.48 (dd, $J$ = 11.0, 4.0 Hz, 1H), 7.43 (t, $J$ = 7.1 Hz, 2H), 7.34 (t, $J$ = 7.6 Hz, 2H), 6.81 (d, $J$ = 8.2 Hz, 2H), 6.64 (d, $J$ = 8.2 Hz, 2H), 4.79 (d, $J$ = 14.6 Hz, 1H), 4.69 (d, $J$ = 14.6 Hz, 1H), 4.45 (d, $J$ = 15.1 Hz, 1H), 4.28 (d, $J$ = 15.0 Hz, 1H), 2.48 (s, 3H), 2.12 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 164.8, 147.3, 138.1, 134.4, 134.09, 133.1, 132.9, 131.9, 131.2, 129.9, 129.1, 128.7, 128.5, 128.3, 127.1, 126.5, 126.1, 122.3, 120.2, 53.3, 53.2, 34.2, 20.7; IR (neat) 1664, 1355, 1120 $cm^{-1}$; HRMS (EI) calcd for $C_{27}H_{24}N_2O_2S$ 440.1558, found 440.1552.

***tert*-Butyl 4-(Phenyl(*p*-tolylimino)methyl)-1*H*-benzo[*f*]-isoindole-2(3*H*)-carboxylate (2k).** 72 mg, 78% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.83−7.75 (m, 1H), 7.74−7.58 (m, 4H), 7.46−7.28 (m, 5H), 6.78 (dd, $J$ = 11.7, 8.3 Hz, 2H), 6.64 (d, $J$ = 7.8 Hz, 2H), 4.94−4.61 (m, 2H), 4.58−4.19 (m, 2H), 2.11 (d, $J$ = 15.2 Hz, 3H), 1.47 (t, $J$ = 8.9 Hz, 9H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 165.2, 164.9, 154.4, 147.7, 138.6, 138.3, 135.7, 135.2, 134.4, 134.0, 133.9, 133.4, 132.9, 131.5, 131.2, 131.0, 129.8, 129.4, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 126.5, 126.0, 125.9, 122.1, 121.8, 120.1, 119.9, 79.9, 51.8, 51.6, 51.5, 51.4, 28.5, 20.8; IR (neat) 2970, 1678, 1345 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{31}H_{30}N_2O_2$ 462.2307, found 462.2300.

**Diethyl 4-(1-(4-Methoxyphenylimino)-2,2-dimethylpropyl)-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (2l).** 70 mg, 67% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 (d, $J$ = 8.4 Hz, 1H), 7.66 (d, $J$ = 6.8 Hz, 3H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.45−7.27 (m, 5H), 6.72 (d, $J$ = 9.2 Hz, 2H), 6.52 (d, $J$ = 9.2 Hz, 2H), 4.29−3.92 (m, 4H), 3.62 (s, 5H), 3.37 (d, $J$ = 17.2 Hz, 1H), 3.16 (d, $J$ = 17.2 Hz, 1H), 1.21 (t, $J$ = 14.0 Hz, 3H), 1.12 (t, $J$ = 14.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 171.2, 171.0, 156.4, 138.6, 137.6, 133.0, 130.9, 130.7, 130.5, 128.5, 128.3, 128.2, 126.1, 125.7, 125.6, 123.2, 122.0, 113.6, 61.7, 60.6, 55.2, 39.9, 39.7, 14.0, 13.9; IR (neat) 2964, 1652, 1054 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{33}H_{31}NO_5$ 521.2202, found 521.2204.

***N*-(1-(5,7-Dihydrobenzo[1,2-*b*:4,5-*c*′]difuran-4-yl)-2,2-dimethylpropylidene)-4-methoxyaniline (4a): Typical Procedure.** To a solution of imine (0.2 mmol) in toluene (2.5 mL) was added Selectfluor (0.22 mmol) under a $N_2$ atmosphere. The resulting mixture was stirred at 80 °C, and the reaction was monitored by TLC until completion. Then, the reaction was quenched with 30 mL of water, extracted with ethyl ether (3 × 15 mL), and dried with anhydrous $Na_2SO_4$. After evaporation, chromatography on silica gel (eluent: hexane/ethyl acetate = 15:1) of the reaction mixture afforded **4a**. 53 mg, 76% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.61 (d, $J$ = 2.0 Hz, 1H), 7.15 (s, 1H), 6.78−6.63 (m, 1H), 6.50 (s, 4H), 5.13−4.91 (m, 3H), 4.66 (d, $J$ = 12.4 Hz, 1H), 3.60 (s, 3H), 1.29 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 177.1, 155.9, 154.3, 145.6, 143.7, 136.5, 130.8, 126.3, 125.0, 120.4, 113.5, 107.0, 103.6, 73.5, 73.2, 55.1, 41.2, 29.7, 29.3; IR (neat) 2960, 1502, 1638 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{22}H_{23}NO_3$ 349.1678, found 349.1670.

***N*-(1-(5,7-Dihydrobenzo[1,2-*b*:4,5-*c*′]difuran-4-yl)-2,2-dimethylpropylidene)aniline (4b).** 50 mg, 78% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (t, $J$ = 4.8 Hz, 1H), 7.12 (d, $J$ = 5.2 Hz, 1H), 6.97 (t, $J$ = 15.2 Hz, 2H), 6.77 (t, $J$ = 14.8 Hz, 1H), 6.69 (d, $J$ = 1.6 Hz, 1H), 6.56 (d, $J$ = 7.6 Hz, 2H), 5.07−5.03 (m, 2H), 4.96−4.92 (m, 1H), 4.75 (d, $J$ = 11.6 Hz, 1H), 1.31 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 177.5, 154.2, 150.5, 145.6, 136.4, 130.7, 128.2, 126.2, 124.7, 123.3, 118.8, 107.0, 103.7, 73.5, 73.1, 41.3, 29.3; IR (neat) 2966, 1639, 1467, 1143 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{21}H_{21}NO_2$ 319.1572, found 319.1774.

***N*-((4-Chlorophenyl)(5,7-dihydrobenzo[1,2-*b*:4,5-*c*′]difuran-4-yl)methylene)aniline (4c).** 55 mg, 73% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.64 (d, $J$ = 8.4 Hz, 2H), 7.52 (d, $J$ = 2.4 Hz, 1H), 7.35 (d, $J$ = 8.8 Hz, 2H), 7.30 (s, 1H), 7.07 (t, $J$ = 15.6 Hz, 2H), 6.91 (t, $J$ = 14.8 Hz, 1H), 6.71 (d, $J$ = 7.2 Hz, 2H), 6.39 (s, 1H), 5.08 (dd, $J$ = 28.8, 12.4 Hz, 2H), 4.76 (d, $J$ = 12.4 Hz, 1H), 4.59 (d, $J$ = 12.4 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 163.7, 154.6, 150.1, 146.1, 137.4, 136.7, 136.6, 132.6, 130.9, 129.9, 126.5, 124.4, 122.5, 120.7, 120.3, 105.9, 104.9, 73.1, 72.7; IR (neat) 2944, 1564, 1168 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{23}H_{16}ClNO_2$ 373.0870, found 373.0860.

***N*-((4-Chlorophenyl)(7-methyl-5,7-dihydrobenzo[1,2-*b*:4,5-*c*′]difuran-4-yl)methylene)aniline (4d).** 53 mg, 68% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.65 (t, $J$ = 17.2 Hz, 2H), 7.53 (dd, $J$ = 6.1, 2.1 Hz, 1H), 7.35 (dd, $J$ = 8.8, 2. Hz, 2H), 7.22 (s, 1H), 7.08−7.04 (m, 2H), 6.92−6.88 (m, 1H), 6.73−6.67 (m, 2H), 6.39 (s, 1H), 5.33 (dd, $J$ = 12.4, 6.0 Hz, 0.5H), 5.19 (dd, $J$ = 12.0, 5.6 Hz, 0.5H), 4.75 (dd, $J$ = 12.4, 1.6 Hz, 0.5H), 4.71−4.59 (m, 1H), 4.44 (dd, $J$ = 12.4, 1.6 Hz, 0.5H), 1.51 (d, $J$ = 6.0 Hz, 1.5H), 1.36 (d, $J$ = 6.0 Hz, 1.5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 163.8, 163.7, 154.6, 150.1, 150.0, 146.1, 145.8, 141.4, 137.4, 136.6, 132.9, 132.5, 130.9, 129.9, 128.8, 128.7, 128.5, 126.6, 126.5, 124.4, 123.7, 122.4, 120.7, 120.3, 120.3, 105.9, 104.9, 104.8, 79.6, 79.3, 71.3, 21.8, 21.4; IR (neat) 2925, 1587, 1170 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{24}H_{18}ClNO_2$ 387.1026, found 387.1018.

***N*-(1-(5,7-Dihydrothieno[2,3-*f*]isobenzofuran-4-yl)-2,2-dimethylpropylidene)-4-methoxyaniline (4e).** 61 mg, 84% yield, yellow solid, mp 80−82 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.49 (s, 1H), 7.44 (d, $J$ = 5.6 Hz, 1H), 7.22 (d, $J$ = 5.6 Hz, 1H), 6.49 (s, 4H), 5.14−4.91 (m, 3H), 4.72 (d, $J$ = 12.0 Hz, 1H), 3.58 (s, 3H), 1.29 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 177.8, 155.8, 143.7, 139.2, 137.3, 136.4, 133.1, 127.4, 126.8, 123.3, 120.2, 114.2, 113.5, 73.5, 73.0, 55.1, 41.1, 29.7; IR (neat) 2960, 1502, 1239 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{22}H_{23}NO_2S$ 365.1449, found 365.1442.

**4-Methoxy-*N*-((7-methyl-5,7-dihydrothieno[2,3-*f*]isobenzofuran-4-yl)(*p*-tolyl)methylene)aniline (4f).** 56 mg, 68% yield, amorphous solid; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.63−7.50 (m, 3H), 7.34 (t, $J$ = 11.2 Hz, 1H), 7.15 (d, $J$ = 7.6 Hz, 2H), 6.99 (dd, $J$ = 5.6, 3.2 Hz, 1H), 6.68−6.62 (m, 2H), 6.61−6.53 (m, 2H), 5.36 (dd, $J$ = 12.0, 6.4 Hz, 0.5H), 5.23 (dd, $J$ = 12.0, 6.0 Hz, 0.5H), 4.79 (d, $J$ = 12.4 Hz, 0.5H), 4.69 (dd, $J$ = 32.8, 12.8 Hz, 1H), 4.45 (d, $J$ = 12.8 Hz, 0.5H), 3.65 (d, $J$ = 1.7 Hz, 3H), 2.37 (s, 3H), 1.53 (d, $J$ = 6.0 Hz, 1.5H), 1.40 (d, $J$ = 6.0 Hz, 1.5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 164.5, 164.3, 156.5, 156.4, 143.5, 143.4, 141.3, 141.1, 139.6, 139.5, 137.9, 137.7, 135.9, 135.8, 135.2, 134.9, 129.3, 128.4, 127.3, 125.9, 122.6, 122.1, 115.0, 113.7, 79.5, 79.2, 71.4, 55.2, 21.9, 21.5; IR (neat) 2925, 1502, 1243 $cm^{-1}$; HRMS (EI-TOF) calcd for $C_{26}H_{23}NO_2S$ 413.1449, found 413.1441.

**4-Methoxy-*N*-((5-methyl-3,5-dihydro-1*H*-furo[3,4-*b*]-carbazol-4-yl)(*p*-tolyl)methylene)aniline (4g).** 60 mg, 67% yield, needle solid, mp 108−110 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 8.0 Hz, 1H), 7.89 (s, 1H), 7.63 (d, $J$ = 7.6 Hz, 2H), 7.51−7.41 (m, 1H), 7.30 (d, $J$ = 8.0 Hz, 1H), 7.25 (t, $J$ = 15.2 Hz, 1H), 7.15 (d, $J$ = 8.0 Hz, 2H), 6.79 (d, $J$ = 8.8 Hz, 2H), 6.58 (d, $J$ = 8.8 Hz, 2H), 5.17



DOI: 10.1021/acs.joc.5b00261
J. Org. Chem. 2015, 80, 4749−4753

(dd, $J$ = 22.0 11.6 Hz, 2H), 4.83 (d, $J$ = 12.8 Hz, 1H), 4.64 (d, $J$ = 12.8 Hz, 1H), 3.66 (s, 3H), 3.62 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.1, 156.9, 142.9, 142.0, 141.4, 138.8, 137.0, 136.0, 130.3, 129.5, 128.3, 126.0, 123.7, 122.9, 122.4, 120.0, 119.4, 113.9, 113.9, 112.7, 108.9, 73.5, 73.3, 55.2, 31.0, 21.5; IR (neat) 2923, 1603, 1501, 1244 cm$^{-1}$; HRMS (EI-TOF) calcd for $C_{30}H_{26}N_2O_2$ 446.1994, found 446.1990.

**4-Methyl-*N*-((5-methyl-3,5-dihydro-1*H*-furo[3,4-*b*]carbazol-4-yl)(thiophen-3-yl)methylene)aniline (4h).** 62 mg, 73% yield, needle solid, mp 100−102 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.02 (d, $J$ = 7.6 Hz, 1H), 7.84 (s, 1H), 7.51−7.40 (m, 2H), 7.29 (d, $J$ = 8.4 Hz, 1H), 7.22 (t, $J$ = 14.8 Hz, 1H), 6.87 (dd, $J$ = 4.8, 3.6 Hz, 1H), 6.82−6.74 (m, 5H), 5.13 (dd, $J$ = 25.2, 11.2 Hz, 2H), 4.95 (d, $J$ = 12.8 Hz, 1H), 4.70 (d, $J$ = 12.8 Hz, 1H), 3.72 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 158.5, 146.8, 146.3, 142.1, 138.6, 136.1, 134.8, 131.6, 131.2, 130.3, 129.4, 127.9, 126.1, 123.9, 122.3, 121.6, 120.1, 119.6, 113.1, 113.0, 109.0, 73.6, 73.3, 30.9, 20.9; IR (neat) 2973, 1378, 1087, 1046 cm$^{-1}$; HRMS (EI-TOF) calcd for $C_{27}H_{22}N_2OS$ 422.1453, found 422.1446.

***N*-(1-(5,7-Dihydrobenzo[1,2-*b*:4,5-*c*′]difuran-4-yl)-2,2-dimethylpropyl)aniline (5).** 31 mg, 97% yield, amorphous solid; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.58 (d, $J$ = 2.0 Hz, 1H), 7.40 (s, 1H), 7.22 (t, $J$ = 16.0 Hz, 2H), 6.88 (d, $J$ = 8.0 Hz, 2H), 6.76−6.70 (m, 1H), 6.66 (t, $J$ = 14.4 Hz, 1H), 5.26 (d, $J$ = 2.0 Hz, 1H), 4.86 (dd, $J$ = 13.6, 2.4 Hz, 1H), 4.71 (dd, $J$ = 16.8, 12.8 Hz, 1H), 4.52 (d, $J$ = 13.6 Hz, 1H), 0.95 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 155.1, 149.8, 145.0, 133.5, 133.2, 130.9, 128.9, 122.8, 116.2, 113.0, 108.8, 107.0, 70.6, 63.4, 56.2, 41.5, 27.7; IR (neat) 2958, 1596, 1361 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{23}NO_2$ 321.1729, found 321.1725.

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1$H and $^{13}$C NMR spectra of all new compounds and crystal structure and data of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-mail: zhouhw@zju.edu.cn.


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (Project No. 20972134) and the Zhejiang Provincial Natural Science Foundation of China (Project No. LY14B020008) for financial support.

## ■ REFERENCES


(1) For the recent reviews, see: (a) Ruiz, M.; Lopez-Alvarado, P.; Giorgi, G.; Menendez, J. C. *Chem. Soc. Rev.* **2011**, *40*, 3445. (b) Barluenga, J.; Rodriguez, F.; Fananas, F. J. *Chem.—Asian J.* **2009**, *4*, 1036. (c) Han, S. B.; Kim, I. S.; Krische, M. J. *Chem. Commun.* **2009**, *45*, 7278. (d) Isambert, N.; Lavilla, R. *Chem.—Eur. J.* **2008**, *14*, 8444.

(2) (a) Numajiri, Y.; Pritchett, B. P.; Chiyoda, K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2015**, *137*, 1040. (b) Smith, J. M.; Moreno, J.; Boal, B. W.; Garg, N. K. *Angew. Chem., Int. Ed.* **2015**, *54*, 400. (c) Zheng, C.; Dubovyk, I.; Lazarski, K. E.; Thomson, R. J. *J. Am. Chem. Soc.* **2014**, *136*, 17750. (d) Arai, S.; Nakajima, M.; Nishida, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 5569.

(3) (a) Liu, L.; Chen, D.; Zhou, H. *Adv. Synth. Catal.* **2015**, *357*, 389. (b) Zhao, G.; Zhang, Q.; Zhou, H. *J. Org. Chem.* **2014**, *79*, 10867. (c) Zhao, G.; Zhang, Q.; Zhou, H. *Adv. Synth. Catal.* **2013**, *355*, 3492. (d) Zhou, H.; Liu, L.; Xu, S. *J. Org. Chem.* **2012**, *77*, 9418. (e) Zhou, H.; Xing, Y.; Yao, J.; Lu, Y. *J. Org. Chem.* **2011**, *76*, 4582. (f) Zhou, H.; Xing, Y.; Liu, L.; Hong, J. *Adv. Synth. Catal.* **2011**, *353*, 3146. (g) Zhou, H.; Xie, Y.; Ren, L.; Su, R. *Org. Lett.* **2010**, *12*, 356. (h) Zhou, H.; Zhu, D.; Xie, Y.; Huang, H.; Wang, K. *J. Org. Chem.* **2010**, *75*, 2706. (i) Zhou, H.; Xing, Y.; Yao, J.; Chen, J. *Org. Lett.* **2010**, *12*, 3674. (j) Zhou, H.; Xie, Y.; Ren, L.; Wang, K. *Adv. Synth. Catal.* **2009**, *351*, 1289. (k) Zhou, H.; Xie, Y.; Ren, L.; Wang, K. *Adv. Synth. Catal.* **2009**, *351*, 1289.

(4) Ukhin, L. Y.; Orlova, Z. I.; Tokarskaya, O. A. *Zh. Org. Khim.* **1987**, *23*, 2473.

(5) CCDC ID: 1047217.

(6) For the selected references on allene electrocyclizations, see: (a) Alajarin, M.; Bonillo, B.; Marin-Luna, M.; Sanchez-Andrada, P.; Vidal, A. *Chem.—Eur. J.* **2013**, *19*, 16093. (b) Ghosh, D.; Jana, S.; Panja, A.; Anoop, A.; Basak, A. *Tetrahedron* **2013**, *69*, 8724. (c) Mondal, S.; Basak, A.; Jana, S.; Anoop, A. *Tetrahedron* **2012**, *68*, 7202. (d) Choshi, T.; Sada, T.; Fujimoto, H.; Nagayama, C.; Sugino, E.; Hibino, S. *J. Org. Chem.* **1997**, *62*, 2535. (e) Morwick, T. M.; Paquette, L. A. *J. Org. Chem.* **1997**, *62*, 627. (f) Wang, K. K.; Zhang, Q.; Liao, J. *Tetrahedron Lett.* **1996**, *37*, 4087. (g) Bross, H.; Schneider, R.; Hopf, H. *Tetrahedron Lett.* **1979**, *23*, 2129.

(7) (a) He, R.; Jin, X.; Chen, H.; Huang, Z.; Zheng, Q.; Wang, C. *J. Am. Chem. Soc.* **2014**, *136*, 6558. (b) Zhao, J.; Zheng, Z.; Bottle, S.; Chou, A.; Sarina, S.; Zhu, H. *Chem. Commun.* **2013**, *49*, 2676. (c) Manolakis, I.; Cross, P.; Colquhoun, H. M. *Macromolecules* **2011**, *44*, 7864.




DOI: 10.1021/acs.joc.5b00261
*J. Org. Chem.* 2015, 80, 4749−4753