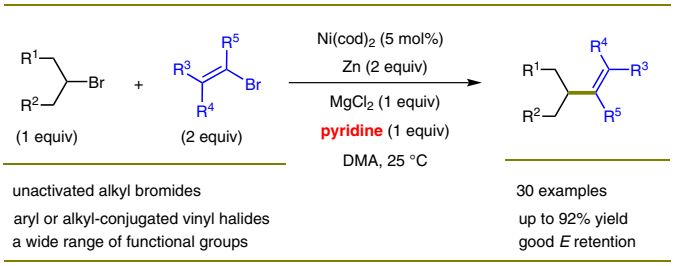
Synthesis J. Gu et al. Paper

Nickel-Catalyzed Reductive Cross-Coupling of Vinyl Bromides with Unactivated Alkyl Halides

Jun Gu[a,b‡]
Canbin Qiu[b,c‡]
Wenbin Lu[b,c]
Qun Qian[*b,c]
Kunhua Lin[*c]
Hegui Gong[*a,b,c]

[a] School of Materials Science and Engineering, Shanghai University, 99 Shang-Da Road, Shanghai 200444, P. R. of China
[b] Center for Supramolecular and Catalytic Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444, P. R. of China
[c] Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444, P. R. of China
hegui_gong@shu.edu.cn
qianqun@shu.edu.cn

‡ These authors contributed equally



Received: 31.10.2016
Accepted after revision: 13.12.2016
Published online: 17.01.2017
DOI: 10.1055/s-0036-1588132; Art ID: ss-2016-f0760-op

Abstract The use of pyridine as the sole ligand for the reductive vinylation of unactivated secondary alkyl halides under Ni-catalyzed conditions has been developed. Both alkyl- and aryl-substituted vinyl bromides are suitable, in which alkyl-decorated α-alkenyl bromides resulted in the α-products in good results.

Key words nickel, cross-coupling, arylation, alkyl halide, catalysis

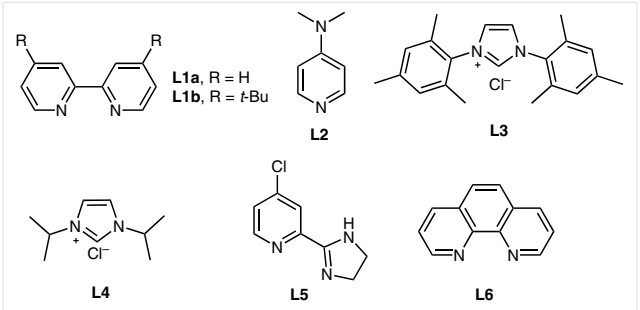


Figure 1 Structures of ligands

Ni-catalyzed reductive cross-coupling of alkyl electrophiles with other electrophiles has attracted increasing attention in recent years.[1] Such a strategy has enabled facile constructions of alkyl–alkyl, alkyl–aryl, and alkyl–acyl bonds by employing alkyl and aryl halides, acid derivatives, isocyanates, and CO_2 as the coupling partners.[2–4] Remarkably high chemoselectivity has been achieved for the equimolar coupling of aryl halides with alkyl halides, wherein a radical-chain mechanism is well established. In this context, the development of analogous methods for the vinylation of alkyl halides has also received much success. Recently, an equimolar coupling of alkyl halides with vinyl halides was disclosed which utilizes 4,4′-di-*tert*-butyl-2,2′-bipyridine (**L1b**, Figure 1) as the ligand. The reaction conditions displayed higher efficiency for *cis*-vinyl bromides than the *trans*-isomers, wherein the retention of the geometry of the vinyl groups was observed.[3d,5]

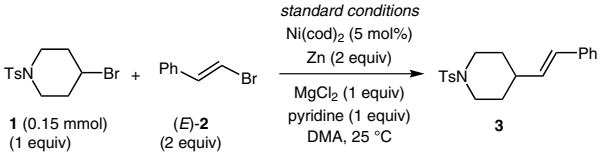
Other notable methods for the cross-coupling of alkyl halides with vinyl halides should be addressed. Durandetti disclosed a Ni/bipyridine-catalyzed electrochemical coupling of α-halo esters/cyanides with vinyl bromides.[6] A number of photo redox/Ni-catalyzed methods have also been developed for alkyl–vinyl bond formation, which utilized bipyridine as the ligand.[7] Lipshultz demonstrated an in situ Negishi vinylation protocol using a Pd/diphosphine-catalyzed coupling of alkenyl halides with alkyl halides in aqueous media.[8]

Herein we report a different Ni-catalyzed procedure that did not require bidentate nitrogen-containing ligands, but pyridine as the additive and labile ligand. This general procedure allowed efficient construction of vinyl–alkyl bonds under reductive conditions. Although 2 equivalents of vinyl halide were employed, this work is complementary to the concurrent reductive coupling methods to vinylated alkanes.[5]

Recently, we disclosed that pyridine as the sole additive/ligand enabled effective coupling of tertiary alkyl halides with aryl halides leading to the formation of quaternary carbon centers.[9] An extension of this protocol to the coupling of unactivated primary and secondary alkyl halides with (*E*)-β-bromostyrene [(*E*)-(2-bromovinyl)benzene] was successful (Table 1, entry 1); only the *E*-product **3** was detected. Control experiments suggested that the Ni, reductant, pyridine as well as $MgCl_2$ were all important factors for good coupling effectiveness (entries 2–6). The use of other reductants, nickel sources, and ligands did not im-

prove the yields (entries 7–17). The iodo analogue of **1** afforded **3** in 55% yield (entry 18). Finally the use of 0.2 equivalents of pyridine diminished the yield to 63% (entry 19).

Table 1 Optimization for the Coupling of **1** and **2**



Entry	Deviation from the standard conditions[a]	Yield (%)[b]
1	standard conditions	83
2	1.5 equiv of (*E*)-**2** instead of 2.0 equiv	76
3	without $Ni(cod)_2$	0
4	without Zn	<5
5	without pyridine	50
6	without $MgCl_2$	13
7	2.0 equiv Mn instead of 2.0 equiv Zn	73
8	$NiBr_2$·glyme instead of $Ni(cod)_2$	78
9	$NiBr_2$ instead of $Ni(cod)_2$	69
10	$NiCl_2$·glyme instead of $Ni(cod)_2$	55
11	**L1a** as ligand, without pyridine	33
12	**L1b** as ligand, without pyridine	45
13	**L2** as ligand, without pyridine	65
14	**L3** as ligand, 1 equiv pyridine	78
15	**L4** as ligand, 1 equiv pyridine	73
16	**L5** as ligand, without pyridine	20
17	**L6** as ligand, without pyridine	40
18	4-iodo-1-tosylpiperidine in place of **1**	55
19	0.2 equiv of pyridine instead of 1 equiv	63

[a] Reaction conditions: vinyl bromide (2 equiv), alkyl halide, $Ni(cod)_2$ (5 mol%), Zn powder (2 equiv), $MgCl_2$ (1 equiv), pyridine (1 equiv), DMA, 25 °C, 16 h.
[b] Isolated yields.

With the optimized reaction conditions in hand, the scope of alkenyl bromides was first examined for the coupling with **1** (Figure 2). β-Aryl groups substituted with methyl, fluoro, chloro, and CF_3 all generated the coupling products **4**–**7** in high yields. The more hindered (*E*)-(1-bromoprop-1-en-2-yl)benzene was also compatible, generating **8** in moderate yield. The coupling with (*Z*)-β-bromostyrene [(*Z*)-(2-bromovinyl)benzene] delivered *Z*-configured product **9** in 90% yield, indicating that the participation of possible vinyl–Ni intermediates did not lead to changes in the geometry of the alkenyl groups. The coupling with α-bromostryrene [(1-bromovinyl)benzene] failed to give a satisfactory yield of **10**. For alkyl-substituted β-vinyl bromides, good to excellent coupling yields were generally obtained, as evident by **11**–**15**. Retention of the *E* and *Z* geometry of the vinyl groups was also observed, except for **13** wherein erosion of the *Z*-geometry occurred, possibly due to enhanced steric hindrance. Interestingly, the α-vinyl bromides proceeded effectively, as exemplified by **16** and **17**. The more congested 2-bromo-3-methylbut-2-ene delivered **18** only in low yield. The conjugated dienyl bromide, namely [(1*E*,3*E*)-4-bromobuta-1,3-dienyl]benzene was highly compatible, resulting in **19** in 80% yield. As α-bromostryrene and 2-bromo-1*H*-indene did not afford the coupling products, this suggests that aryl-conjugated α-vinyl halides were not compatible with the standard conditions as in Table 1, entry 1.

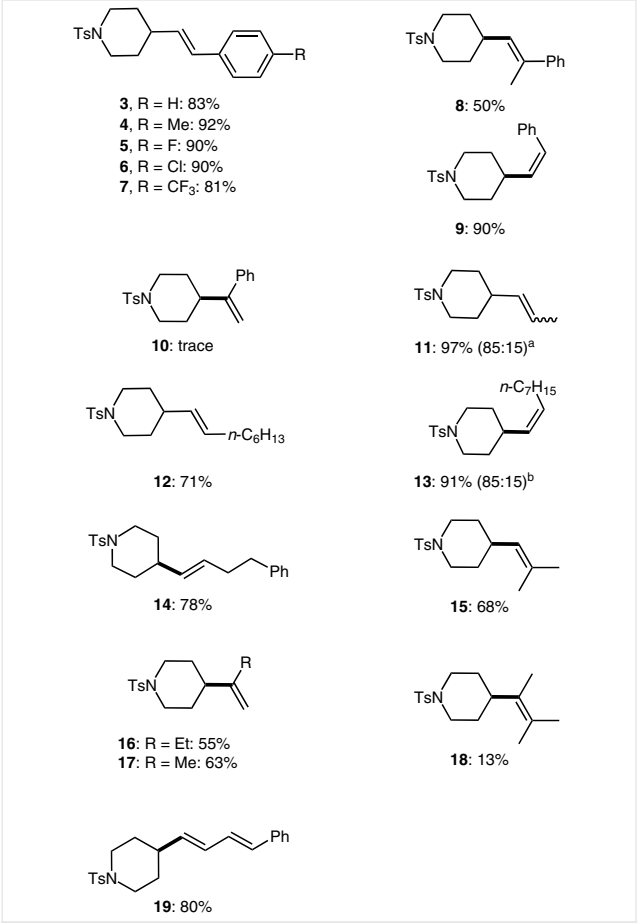


Figure 2 Scope of alkenyl bromides with unactivated alkyl halides; standard conditions were used (see Table 1, entry 1), yields given are isolated yields. [a] Ratio of *E*/*Z* 85:15 for the vinyl bromide substrate. [b] Ratio of *Z*/*E* >99:1 for the vinyl bromide substrate.

Next, we examined the compatibility of a set of alkyl halides for the coupling with different vinyl bromides (Figure 3). Both cyclic and open-chain secondary alkyl bromides were suited for the coupling conditions, affording **20**–**31** in moderate to good yields. The phenyl group bearing electron-donating groups in the vinyl bromides also produced the vinylated products **21**–**23** in good yields. By comparison, cyclohexyl chloride was inert, it did not gener-

ate **22**, indicating unactivated alkyl chlorides are not suitable for this method. The bromides in five-membered rings were effective, as evident by **24**–**26**. Of note was the suitability of the sterically encumbered alkyl halide en route to **25**. The reaction conditions tolerate a variety of functional groups, including amide, phthalimide, ether, and ester. Finally, a naphthyl-derived benzylic-like chloride was capable of producing **31** in good yield for the coupling with an electron-deficient 2-aryl-substituted vinyl bromide.

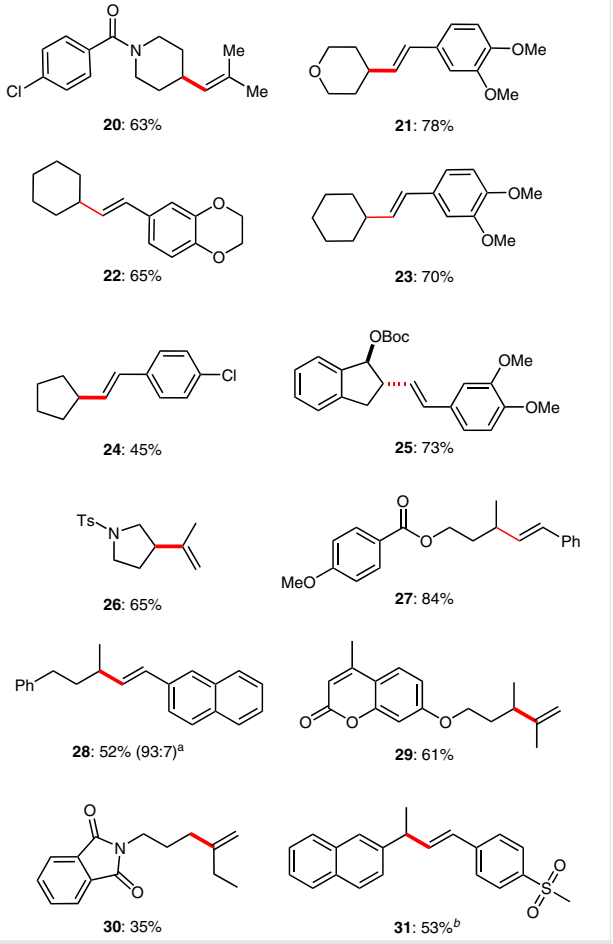


Figure 3 Scope of alkenyl bromides with unactivated alkyl halides; standard conditions were used (see Table 1, entry 1), yields given are isolated yields. [a] Use of *E*-vinyl bromide. [b] 2-(1-Chloroethyl)naphthalene was used.

Although pyridine has shown a pivotal role in the coupling of unactivated alkyl halides with vinyl halides, the combination of pyridine with a bidentate ligand is necessary.[3b,10] The use of pyridine as a labile ligand or additive for vinylation of alkyl halides is of interest. Further mechanistic studies will be needed in order to gain insight into the role of pyridine.

In conclusion, we have investigated the coupling of unactivated secondary alkyl bromides with a wide range of aryl- and alkyl-substituted vinyl bromides under Ni-catalyzed reductive conditions. The reaction features pyridine as the sole ligand, which is distinct from the known Ni-catalytic conditions employing bidentate bipyridines as the ligands. In general, the reaction displays moderate to excellent efficiency. The electronic properties of substituents on the benzene rings of vinyl bromides did not show an appreciable impact on the coupling yields. This work should provide complementary studies for the concurrent methods on the vinylation of unactivated alkyl electrophiles using reductive coupling strategies.

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glove box techniques. DMA (*N*,*N*-dimethylacetamide, 99.5%, extra dry, Acros) was purchased and used directly. Deuterated solvents were used as received ($CDCl_3$ from J&K Co., China). $NiCl_2$ (Alfa Aesar), $NiBr_2$ (Alfa Aesar), NiI_2 (Alfa Aesar), $Ni(cod)_2$ (Strem), $Ni(ClO_4)_2{\cdot}6H_2O$ (Alfa Aesar), $Ni(acac)_2$ (Aladdin Co., China) were used as received. Zn powder (Aladdin) was activated with HCl before use. Mn powder (~325 mesh, 99.3%) was purchased from (Alfa Aesar) activated with HCl before use. Anhyd $MgCl_2$ (Alfa Aesar) was purchased, and used directly. All other reagents and starting materials were purchased from commercial sources and used without further purification.

Column chromatography was performed using silica gel 300–400 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. PE = petroleum ether. All NMR spectra were recorded on Bruker Avance 500 MHz spectrometer at STP unless otherwise indicated. ^1H and ^{13}C NMR are reported relative to the chemical shift of residual solvent [$CHCl_3$: δ = 7.26 (^1H); δ = 77 (^{13}C)]. HRMS were obtained using a Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. LR-MS were recorded on GCMS-QP2010 SE (Shimadzu). Melting point was recorded on a micro melting point apparatus (X-4, Yuhua Co., Ltd, Gongyi, China).

Coupling of Vinyl Halides with Unactivated Alkyl Halides; General Procedure

To a flame-dried Schlenk tube was charged with vinyl bromide (0.30 mmol, 2 equiv, *if solid*), unactivated alkyl halide (0.15 mmol, *if solid*), zinc powder (16.5 mg, 0.30 mmol, 2 equiv), and $MgCl_2$ (14.2 mg, 0.15 mmol, 1 equiv). The tube was moved into a dry glove box, at which point $Ni(cod)_2$ (2.1 mg, 0.008 mmol, 5 mol%) was added. The tube was capped with a rubber septum, and it was moved out of the glove box. At this point, the vinyl bromide (0.30 mmol, 2 equiv, *if liquid*) and alkyl halide (0.15 mmol, 1 equiv, *if liquid*) were added together with solvent (1 mL) and pyridine (11.8 mg, 0.15 mmol, 1 equiv) via a syringe. The mixture was stirred for 16 h under N_2 atmosphere at 25 °C, and then it was directly loaded onto a column (silica gel) without work-up. The residue in the reaction vessel was rinsed with small amount of CH_2Cl_2. Flash column chromatography provided the product as a solid or oil. The *E*/*Z* ratio of the product was determined by GC-MS.

(*E*)-4-Styryl-1-tosylpiperidine (3)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (42.5 mg, 0.125 mmol, 83%) as a white solid; mp 140–141 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2 H), 7.34–7.28 (m, 6 H), 7.20 (t, *J* = 7.0 Hz, 1 H), 6.31 (d, *J* = 16.0 Hz, 1 H), 5.97 (dd, *J* = 7.0, 16.0 Hz, 1 H), 3.82–3.80 (m, 2 H), 2.44 (s, 3 H), 2.34–2.29 (m, 2 H), 2.08–2.02 (m, 1 H), 1.83–1.81 (m, 2 H), 1.73–1.70 (m, 1 H), 1.46–1.39 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 137.1, 133.4, 133.1, 129.5, 128.9, 128.5, 128.2, 127.7, 127.2, 126.0, 46.1, 38.5, 31.2, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{24}NO_2S$: 342.1522; found: 342.1525.

(*E*)-4-(4-Methylstyryl)-1-tosylpiperidine (4)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (48.9 mg, 0.138 mmol, 92%) as a white solid; mp 149–150 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 7.0 Hz, 2 H), 6.31 (d, *J* = 16.0 Hz, 1 H), 6.02 (dd, *J* = 7.0, 16.0 Hz, 1 H), 3.82–3.79 (m, 2 H), 2.44 (s, 3 H), 2.23–2.28 (m, 5 H), 2.07–2.01 (m, 1 H), 1.82–1.80 (m, 2 H), 1.61–1.53 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3, 136.9, 134.3, 133.0, 132.3, 129.9, 129.1, 128.7, 127.6, 125.8, 46.0, 38.4, 31.2, 21.4, 21.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{26}NO_2S$: 356.1678; found: 356.1680.

(*E*)-4-(4-Fluorostyryl)-1-tosylpiperidine (5)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (48.4 mg, 0.135 mmol, 90%) as a white solid; mp 147–148 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 6.98 (t, *J* = 8.6 Hz, 2 H), 6.31 (d, *J* = 16.0 Hz, 1 H), 5.97 (dd, *J* = 8.0, 16.0 Hz, 1 H), 3.82–3.80 (m, 2 H), 2.44 (s, 3 H), 2.32–2.28 (m, 2 H), 2.04–2.02 (m, 1 H), 1.82–1.79 (m, 2 H), 1.61–1.56 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5, 133.3, 133.2, 129.6, 127.8, 127.7, 127.5, 127.4, 115.5, 115.3, 46.2, 38.5, 31.2, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}FNO_2S$: 360.1428; found: 360.1430.

(*E*)-4-(4-Chlorostyryl)-1-tosylpiperidine (6)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (50.6 mg, 0.135 mmol, 90%) as a white solid; mp 146–147 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.28–7.24 (m, 4 H), 6.29 (d, *J* = 16.0 Hz, 1 H), 6.05 (dd, *J* = 7.0, 16.0 Hz, 1 H), 3.82–3.80 (m, 2 H), 2.44 (s, 3 H), 2.32–2.28 (m, 2 H), 2.05–2.03 (m, 1 H), 1.82–1.79 (m, 2 H), 1.73–1.68 (m, 1 H), 1.46–1.40 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 135.6, 134.1, 133.1, 132.8, 129.6, 127.8, 127.7, 127.2, 46.0, 38.5, 31.1, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}ClNO_2S$: 376.1132; found: 376.1135.

(*E*)-1-Tosyl-4-[4-(trifluoromethyl)styryl]piperidine (7)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (49.7 mg, 0.122 mmol, 81%) as a white solid; mp 151–152 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.40 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 6.37 (d, *J* = 16.0 Hz, 1 H), 6.18 (dd, *J* = 7.0, 16.0 Hz, 1 H), 3.84–3.82 (m, 2 H), 2.44 (s, 3 H), 2.33–2.29 (m, 2 H), 2.10–2.05 (m, 1 H), 1.84–1.82 (m, 2 H), 1.63–1.58 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 140.6, 136.1, 133.0, 129.6, 127.8, 127.7, 127.5, 126.1, 125.4, 125.4, 46.0, 38.5, 31.0, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}F_3NO_2S$: 410.1396; found: 410.1398.

(*E*)-4-(2-Phenylprop-1-enyl)-1-tosylpiperidine (8)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (26.6 mg, 0.075 mmol, 50%) as a white solid; mp 137–138 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.0 Hz, 2 H), 7.37–7.35 (m, 4 H), 7.33–7.30 (m, 2 H), 7.26–7.23 (m, 1 H), 5.56 (d, *J* = 9.0 Hz, 1 H), 3.82–3.80 (m, 2 H), 2.47 (s, 3 H), 2.35 (s, 3 H), 2.00 (s, 3 H), 1.78–1.76 (m, 2 H), 1.61–1.53 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 143.2, 134.9, 133.0, 131.2, 129.5, 128.1, 127.7, 126.8, 125.4, 46.1, 35.0, 31.2, 21.5, 16.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{26}NO_2S$: 356.1684; found: 356.1684.

(*Z*)-4-Styryl-1-tosylpiperidine (9)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (46.0 mg, 0.135 mmol, 90%) as a white solid; mp 143–144 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.32–7.26 (m, 4 H), 7.21–7.18 (m, 1 H), 7.15 (d, *J* = 7.0 Hz, 2 H), 6.41 (d, *J* = 11.5 Hz, 1 H), 5.42 (dd, *J* = 10.0, 11.5 Hz, 1 H), 3.78–3.75 (m, 2 H), 2.48–2.44 (m, 1 H), 2.43 (s, 3 H), 2.26–2.20 (m, 2 H), 1.76 (m, 2 H), 1.60–1.55 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 137.2, 135.7, 132.9, 129.9, 128.8, 128.3, 128.2, 127.6, 126.7, 45.8, 34.1, 31.4, 21.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{24}NO_2S$: 342.1522; found: 342.1525.

4-(Prop-1-enyl)-1-tosylpiperidine (11)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (40.6 mg, 0.146 mmol, 97%; *E*/*Z* 85:15) as a white solid; mp 78–79 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 5.42–5.36 (m, 1 H), 5.32–5.14 (m, 1 H), 3.74–3.72 (m, 2 H), 2.43 (s, 3 H), 2.32–2.22 (m, 2 H), 2.21–2.17 (m, 1 H), 1.67–1.61 (m, 2 H), 1.55–1.53 (m, 3 H), 1.48–1.40 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 133.8, 133.1, 129.5, 127.7, 123.9, 46.1, 33.1, 31.2, 21.5, 12.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{22}NO_2S$: 280.1366; found: 280.1366.

(*E*)-4-(Oct-1-enyl)-1-tosylpiperidine (12)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (37.1 mg, 0.106 mmol, 71%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 5.38–5.32 (m, 1 H), 5.29–5.24 (m, 1 H), 3.74–3.72 (m, 2 H), 2.42 (s, 3 H), 2.27–2.22 (m, 2 H), 1.95–1.91 (m, 2 H), 1.81–1.79 (m, 1 H), 1.70–1.68 (m, 2 H), 1.48–1.43 (m, 2 H), 1.29–1.22 (m, 8 H), 0.86 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3, 133.2, 133.1, 129.7, 129.5, 127.6, 46.1, 37.9, 32.4, 31.6, 31.4, 29.3, 28.7, 22.5, 21.4, 14.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{32}NO_2S$: 350.2153; found: 350.2150.

(*Z*)-4-(Non-1-enyl)-1-tosylpiperidine (13)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (24.1 mg, 0.137 mmol, 91%) as a colorless oil; *Z*/*E* 85:15 (GC-MS). Vinyl substrate ratio *Z*/*E* >99:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 5.35–5.29 (m, 1 H), 5.16–5.12 (m, 1 H), 3.76–7.74 (m, 2 H), 2.44 (s, 3 H), 2.29–2.27 (m, 2 H), 2.21–2.25 (m, 1 H), 1.97–1.92 (m, 2 H), 1.65–1.62 (m, 2 H), 1.50–1.42 (m, 2 H), 1.29–1.24 (m, 10 H), 0.86 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3, 133.2, 132.8, 130.1, 129.5, 127.7, 46.1, 38.0, 33.5, 32.5, 31.4, 29.7, 29.4, 27.4, 22.6, 21.5, 14.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{34}NO_2S$: 364.2304; found: 364.2307.

(*E*)-4-(4-Phenylbut-1-en-1-yl)-1-tosylpiperidine (14)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (43.1 mg, 0.117 mmol, 78%) as a white solid; mp 65–66 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.27–7.24 (m, 2 H), 7.18–7.13 (m, 3 H), 5.43–5.37 (m, 1 H), 5.31–5.27 (m, 1 H), 3.75–3.72 (m, 2 H), 2.63 (t, *J* = 7.5 Hz, 2 H), 2.43 (s, 3 H), 2.29–2.22 (m, 4 H), 1.84–1.78 (m, 1 H), 1.69–1.66 (m, 2 H), 1.46–1.38 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3. 141.7, 134.1, 133.0, 129.5, 128.5, 128.4, 128.1, 127.6, 125.7, 46.1, 37.8, 35.8, 34.2, 31.3, 21.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{28}NO_2S$: 370.1840; found: 370.1837.

4-(2-Methylprop-1-enyl)-1-tosylpiperidine (15)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (29.9 mg, 0.102 mmol, 68%) as a white solid; mp 75–76 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.90 (d, *J* = 9.0 Hz, 1 H), 3.74–3.71 (m, 2 H), 2.43 (s, 3 H), 2.28–2.23 (m, 2 H), 2.08–2.01 (m, 1 H), 1.64–1.60 (m, 5 H), 1.53 (s, 3 H), 1.45–1.36 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3, 133.0, 131.6, 129.5, 128.1, 127.7, 46.2, 34.3, 31.5, 25.6, 21.5, 17.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{24}NO_2S$: 294.1527; found: 294.1532.

4-(But-1-en-2-yl)-1-tosylpiperidine (16)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (24.1 mg, 0.083 mmol, 55%, determined by GC-MS) as a white solid; mp 47–48 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.73–4.70 (m, 2 H), 3.85–3.83 (m, 2 H), 2.43 (s, 3 H), 2.24–2.19 (m, 2 H), 1.97 (q, *J* = 7.5 Hz, 2 H), 1.76–1.73 (m, 3 H), 1.60–1.51 (m, 2 H), 0.99 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 143.3, 133.0, 129.5, 127.7, 107.1, 46.8, 41.5, 30.6, 27.1, 21.5, 12.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{24}NO_2S$: 294.1527; found: 294.1525.

4-(Prop-1-en-2-yl)-1-tosylpiperidine (17)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (26.3 mg, 0.095 mmol, 63%) as a white solid; mp 43–44 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.71 (s, 1 H), 4.65 (s, 1 H), 3.85–3.82 (m, 2 H), 2.43 (s, 3 H), 2.24–2.16 (m, 2 H), 1.75–1.72 (m, 3 H), 1.66 (s, 3 H), 1.60–1.51 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.1, 143.3, 133.0, 129.5, 127.7, 109.5, 46.6, 42.6, 30.1, 21.5, 20.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{22}NO_2S$: 280.1371; found: 280.1366.

4-[(1*E*,3*E*)-4-Phenylbuta-1,3-dienyl)-1-tosylpiperidine (19)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (44.4 mg, 0.120 mmol, 80%) as a white solid; mp 57–58 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 2 H), 7.36–7.27 (m, 6 H), 7.21 (t, *J* = 7.0 Hz, 1 H), 6.72 (dd, *J* = 10.5, 15.5 Hz, 1 H), 6.47 (d, *J* = 15.5 Hz, 1 H), 6.15 (dd, *J* = 10.5,,15.5 Hz, 1 H), 5.71 (dd, *J* = 7.0, 15.5 Hz, 1 H), 3.79–3.77 (m, 2 H), 2.44 (s, 3 H), 2.32–2.27 (m, 2 H), 2.21–2.16 (m, 1 H), 2.01–1.98 (m, 1 H), 1.79–1.77 (m, 2 H) 1.63–1.61 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 135.6, 134.1, 133.1, 132.8, 129.6, 127.8, 127.7, 127.2, 46.0, 38.5, 31.1, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{26}NO_2S$: 368.1679; found: 368.1682.

(4-Chlorophenyl)[4-(2-methylprop-1-enyl)piperidin-1-yl]methanone (20)

According to the general procedure, column chromatography (silica gel, 5% EtOAc/PE) gave the product (26.1 mg, 0.095 mmol, 63%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.31 (m, 4 H), 4.94 (d, *J* = 8.9 Hz, 1 H), 4.60 (s, 1 H), 3.66 (s, 1 H), 3.02–2.82 (m, 2 H), 2.44–2.38 (m, 1 H), 1.74–1.68 (m, 1 H), 1.66 (s, 3 H), 1.64 (s, 3 H), 1.54–1.48 (m, 1 H), 1.34–1.25 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.1, 135.3, 134.6, 131.6, 128.6, 128.3, 128.1, 35.2, 25.6, 17.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{21}ClNO$: 278.1306; found: 278.1306.

(*E*)-4-(3,4-Dimethoxystyryl)tetrahydro-2*H*-pyran (21)

According to the general procedure, column chromatography (silica gel, 5% EtOAc/PE) gave the product (29.0 mg, 0.117 mmol, 78%) as a white solid; mp 55–56 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.90–6.78 (m, 3 H), 6.32 (d, *J* = 16.0 Hz, 1 H), 6.03 (dd, *J* = 7.0, 16.0 Hz, 1 H), 4.00–3.98 (m, 2 H), 3.89 (s, 3 H), 3.85 (s, 3 H), 3.47–3.42 (m, 2 H), 2.37–2.32 (m, 1 H), 1.70–1.67 (m, 2 H), 1.59–1.51 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.9, 148.3, 132.6, 130.5, 127.7, 118.9, 111.0, 108.3, 67.6, 55.8, 55.7, 38.2, 32.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{21}O_3$: 249.1490; found: 249.1486.

(*E*)-6-(2-Cyclohexylvinyl)-2,3-dihydro-1,4-benzodioxine (22)

According to the general procedure, column chromatography (silica gel, 2% EtOAc/PE) gave the product (23.8 mg, 0.097 mmol, 65%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.87–6.77 (m, 3 H), 6.23 (d, *J* = 16.0 Hz, 1 H), 6.02 (dd, *J* = 7.0, 16.0 Hz, 1 H), 4.24 (s, 4 H), 2.11–2.05 (m, 1 H), 1.79–1.74 (m, 4 H), 1.32–1.12 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 142.5, 135.3, 131.9, 126.3, 119.2, 117.1, 114.3, 64.3, 64.3, 41.0, 32.9, 26.1, 26.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{21}O_2$: 245.1542; found: 245.1542.

(*E*)-4-(2-Cyclohexylvinyl)-1,2-dimethoxybenzene (23)

According to the general procedure, column chromatography (silica gel, 10% EtOAc/PE) gave the product (25.8 mg, 0.105 mmol, 70%) as a white solid; mp 85–86 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.93–6.88 (m, 2 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 6.32 (d, *J* = 16.0 Hz, 1 H), 6.07 (dd, *J* = 7.0, 16.0 Hz, 1 H), 3.92 (s, 3 H), 3.89 (s, 3 H), 2.16–2.09 (m, 1 H), 1.84–1.77 (m, 4 H), 1.37–1.16 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.9, 148.1, 135.0, 131.1, 126.8, 118.8, 111.1, 108.4, 55.9, 55.7, 41.1, 33.1, 26.2, 26.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{23}O_2$: 247.1698; found: 247.1698.

(*E*)-1-Chloro-4-(2-cyclopentylvinyl)benzene (24)

According to the general procedure, column chromatography (silica gel, 2% EtOAc/PE) gave the product (13.9 mg, 0.068 mmol, 45%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.25 (m, 4 H), 7.33 (d, *J* = 16.0 Hz, 1 H), 6.20 (dd, *J* = 8.0, 16.0 Hz, 1 H), 2.63–2.56 (m, 1 H), 1.87–1.83 (m, 2 H), 1.72–1.67 (m, 2 H), 1.65–1.58 (m, 2 H), 1.42–1.34 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.4, 132.2, 129.9, 128.5, 127.1, 126.7, 43.8, 34.1, 33.1, 31.5, 25.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{16}Cl$: 207.0940; found: 207.0940.

***tert*-Butyl 2-[(*E*)-3,4-Dimethoxystyryl)-2,3-dihydro-1*H*-inden-1-yl] Carbonate (25)**

According to the general procedure, column chromatography (silica gel, 10% EtOAc/PE) gave the product (43.4 mg, 0.109 mmol, 73%) as a white solid; mp 110–111 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.0 Hz, 1 H), 7.34–7.25 (m, 3 H), 6.93–6.90 (m, 2 H), 6.83 (d, *J* = 8.5 Hz, 1 H), 6.54 (d, *J* = 16.0 Hz, 1 H), 6.19 (dd, *J* = 8.0, 16.0 Hz, 1 H), 5.98 (d, *J* = 4.8 Hz, 1 H), 3.91 (s, 3 H), 3.89 (s, 3 H), 3.37–3.29 (m, 2 H), 2.89–2.86 (m, 1 H), 1.54 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.6, 148.9, 148.5, 130.8, 130.2, 128.9, 128.2, 126.8, 125.3, 124.7, 119.2, 111.0, 108.5, 84.8, 82.2, 55.8, 55.7, 49.9, 36.5, 27.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{29}O_5Na$: 419.1829; found: 419.1831.

3-(Prop-1-en-2-yl)-1-tosylpyrrolidine (26)

According to the general procedure, column chromatography (silica gel, 7% EtOAc/PE) gave the product (25.9 mg, 0.097 mmol, 65%) as a white solid; mp 45–46 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.72 (s, 1 H), 4.62 (s, 1 H), 3.50–3.47 (m, 1 H), 3.43–3.38 (m, 1 H), 3.25–3.20 (m, 1 H), 3.01 (t, *J* = 9.5 Hz, 1 H), 2.63–2.55 (m, 1 H), 2.43 (s, 3 H), 1.95–1.90 (m, 1 H), 1.65 (s, 3 H), 1.62–1.56 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.6, 143.3, 133.9, 129.6, 127.6, 110.6, 51.5, 47.6, 45.0, 29.9, 21.5, 21.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{20}NO_2S$: 266.1215; found: 266.1216.

(*E*)-3-Methyl-5-phenylpent-4-enyl 4-Methoxybenzoate (27)

According to the general procedure, purification by column chromatography (silica gel, 3% EtOAc/PE) gave the product (39.1 mg, 0.126 mmol, 84%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9.0 Hz, 2 H), 7.36 (d, *J* = 7.5 Hz, 2 H), 7.31 (t, *J* = 7.5 Hz, 2 H), 7.22 (t, *J* = 7.5 Hz, 1 H), 6.90 (d, *J* = 9.0 Hz, 2 H), 6.43 (d, *J* = 16.0 Hz, 1 H), 6.14 (dd, *J* = 8.0, 16.0 Hz, 1 H), 4.38–4.32 (m, 2 H), 3.85 (s, 3 H), 2.59–2.53 (m, 1 H), 1.90–1.84 (m, 2 H), 1.19 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.2, 163.1, 137.4, 135.3, 131.4, 128.8, 128.4, 126.9, 126.0, 113.4, 63.0, 55.3, 35.7, 34.4, 20.6.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{20}H_{26}NO_3$: 328.1912; found: 328.1909.

(*E*)-2-(3-Methyl-5-phenylpent-1-enyl)naphthalene (28)

According to the general procedure, purification by column chromatography (silica gel, 2% EtOAc/PE) gave the product (22.3 mg, 0.078 mmol, 52%; *E*/*Z* 93:7) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.81 (m, 3 H), 7.74–7.63 (m, 2 H), 7.49–7.45 (m, 2 H), 7.35–7.32 (m, 2 H), 7.26–7.23 (m, 3 H), 6.60 (d, *J* = 16.0 Hz, 1 H), 6.29 (dd, *J* = 8.0, 16.0 Hz, 1 H), 2.76–2.68 (m, 2 H), 2.47–2.41 (m, 1 H), 1.82–1.78 (m, 2 H), 1.22 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.7, 136.9, 135.3, 132.7, 128.8, 128.5, 128.3, 128.1, 127.8, 127.7, 127.7, 126.2, 125.7, 125.5, 125.5, 123.6, 38.8, 37.1, 33.8, 20.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{23}$: 287.1800; found: 287.1796.

7-[(3,4-Dimethylpent-4-enyl)oxy]-4-methyl-2*H*-chromen-2-one (29)

According to the general procedure, purification by column chromatography (silica gel, 5% EtOAc/PE) gave the product (24.9 mg, 0.092 mmol, 61%) as a white solid; mp 55–56 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 9.0 Hz, 1 H), 6.78–6.77 (m, 2 H), 6.10 (s, 1 H), 4.72–4.72 (m, 2 H), 4.01–3.94 (m, 2 H), 2.44–2.41 (m, 1 H), 2.38 (s, 3 H), 1.86–1.78 (m, 2 H), 1.68 (s, 3 H), 1.09 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.1, 161.3, 155.2, 152.5, 148.5, 125.4, 113.3, 112.5, 111.7, 110.3, 101.3, 66.8, 37.7, 33.6, 19.6, 18.7, 18.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{22}O_3$: 273.1490; found: 273.1489.

2-(4-Methylenehexyl)isoindoline-1,3-dione (30)

According to the general procedure, purification by column chromatography (silica gel, 5% EtOAc/PE) gave the product (12.8 mg, 0.053 mmol, 35%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 2 H), 7.71–7.69 (m, 2 H), 4.73 (s, 2 H), 3.69–3.66 (m, 2 H), 2.10–2.07 (m, 2 H), 2.03–2.00 (m, 2 H), 1.82–1.79 (m, 2 H), 1.02 (d, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.4, 149.9, 133.8, 132.1, 123.1, 37.8, 33.3, 28.6, 26.5, 12.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{18}NO_2$: 244.1337; found: 244.1335.

(*E*)-2-[4-(4-(Methylsulfonyl)phenyl)but-3-en-2-yl]naphthalene (31)

According to the general procedure, purification by column chromatography (silica gel, 10% EtOAc/PE) gave the product (26.7 mg, 0.080 mmol, 53%) as a white solid; mp 129–130 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86–7.81 (m, 5 H), 7.70 (s, 1 H), 7.53–7.39 (m, 5 H), 6.64 (dd, *J* = 6.5, 16.0 Hz, 1 H), 6.50 (d, *J* = 16.0 Hz, 1 H), 3.88–3.83 (m, 1 H), 3.03 (s, 3 H), 1.59 (d, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.0, 142.0, 139.5, 138.4, 133.5, 132.2, 128.2, 127.6, 127.5, 127.1, 126.7, 126.0, 126.0, 125.5, 125.0, 44.5, 42.7, 20.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{21}O_2S$: 377.1256; found: 377.1260.

Acknowledgment

Financial support was provided by the Chinese NSF (Nos. 21372151 and 21572127), Shanghai Municipal Education Commission for Peak Discipline Construction (N.13-A302-15-L02), and Shanghai Science and Technology Commission (14DZ2261100).

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588132.

References

(1) For reviews on reductive coupling of two electrophiles, see: (a) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; von Wangelin, A. J. *Chem. Eur. J.* **2014**, *20*, 6828. (b) Everson, D. A.; Weix, D. J. *J. Org. Chem.* **2014**, *79*, 4793. (c) Moragas, T.; Correa, A.; Martin, R. *Chem. Eur. J.* **2014**, *20*, 8242. (d) Weix, D. J. *Acc. Res. Chem.* **2015**, *48*, 1767. (e) Gu, J.; Wang, X.; Xue, W. C.; Gong, H. G. *Org. Chem. Front.* **2015**, *2*, 1411.

(2) For Ni-catalyzed reductive C(sp^3)–C(sp^3) bond formation, see: (a) Yu, X.; Yang, T.; Wang, S.; Xu, H.; Gong, H. *Org. Lett.* **2011**, *13*, 2138. (b) Xu, H. L.; Zhao, C. L.; Qian, Q.; Deng, W.; Gong, H. G. *Chem. Sci.* **2013**, *4*, 4022. (c) Prinsell, M. R.; Everson, D. A.; Weix, D. J. *Chem. Commun.* **2010**, *46*, 5743.

(3) For Ni-catalyzed reductive arylation of unactivated alkyl halides, see: (a) Wang, S.; Qian, Q.; Gong, H. *Org. Lett.* **2012**, *14*, 3352. (b) Everson, D. A.; Shrestha, R.; Weix, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 920. (c) Yan, C.-S.; Peng, Y.; Xu, X.-B.; Wang, Y.-W. *Chem. Eur. J.* **2012**, *18*, 6039. (d) Everson, D. A.; Jones, B. A.; Weix, D. J. *J. Am. Chem. Soc.* **2012**, *134*, 6146. (e) Molander, G. A.; Kaitlin, M.; Traister, K. M.; O'Neill, B. T. *J. Org. Chem.* **2015**, *80*, 2907.

(4) For Ni-catalyzed reductive acylation of unactivated alkyl halides, see: (a) Wu, F.; Lu, W. B.; Qian, Q.; Ren, Q. H.; Gong, H. G. *Org. Lett.* **2012**, *14*, 3044. (b) Zhao, C. L.; Jia, X.; Wang, X.; Gong, H. G. *J. Am. Chem. Soc.* **2014**, *136*, 17645. (c) Liu, Y.; Cornella, J.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 11212. (d) Moragas, T.; Cornella, J.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 17702. (e) Correa, A.; León, T.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 1062. (f) Wang, X.; Liu, Y.; Martin, R. *J. Am. Chem. Soc.* **2015**, *137*, 6476.

(5) Johnson, K. A.; Soumik Biswas, S.; Weix, D. J. *Chem. Eur. J.* **2016**, *22*, 7399.

(6) Ni-catalyzed electrochemical vinylation of α-halocarbonyl compounds: Cannes, C.; Condon, S.; Durandetti, M.; Périchon, J.; Nédélec, J.-Y. *J. Org. Chem.* **2000**, *65*, 4575.

(7) For the photoredox/Ni-catalyzed methods, see: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764. (b) Noble, A.; McCarver, S. J.; MacMillan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 624.

(8) For Pd-catalyzed in situ Negishi coupling, see: Krasovskiy, A.; Duplais, C.; Lipshutz, B. H. *Org. Lett.* **2010**, *12*, 4742.

(9) For pyridine-promoted arylation of *tertiary* alkyl halides, see: Wang, X.; Wang, S.; Xue, W.; Gong, H. *J. Am. Chem. Soc.* **2015**, *137*, 11562.

(10) For an early example for biaryl synthesis which involved bipyridine and pyridine as the ligands, see: Qian, Q.; Zang, Z.; Wang, S.; Chen, Y.; Lin, K.; Gong, H. *Synlett* **2013**, *24*, 1164.