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Visible Light-Driven, Room Temperature Heck-Type Reaction of Alkyl Halides with Styrene Derivatives Catalyzed by B_{12} Complex

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Abstract. A visible light driven Heck-type coupling reaction of alkyl halides with styrene and its derivatives catalyzed by the cobalamin derivative (B_{12}) with the $[Ru(bpy)_3]Cl_2$ photosensitizer at room temperature is reported. The catalytic efficiencies of the B_{12} catalyst were compared to that of other cobalt complexes such as cobaloxime. Various control experiments supported a radical-based mechanism similar to those for typical B_{12} model reactions. A unique coupling reaction combined with 1,2-migration of the functional group is also reported. Mild reaction conditions using an environmentally benign cobalt catalyst derived from the natural B_{12} provided a practical protocol for the synthetic organic chemistry of the B_{12} catalyzed reaction system.

Keywords: B_{12} catalyst; C-C bond formation; Mizoroki-Heck reaction; photosensitizer; visible light

Introduction

The Mizoroki-Heck reaction is a powerful method for constructing C-C bonds to form substituted alkenes in synthetic organic chemistry.[1] The cross-couplings of alkyl halides with alkenes have developed various substrate scopes including activated[2] and unactivated[3] alkyl halide with electron-rich and electron-deficient olefins utilizing various catalyst protocols of palladium as well as transition metal catalysts. Recent efforts involving the Heck coupling reaction have also been developed utilizing earth-abundant metal catalysts[4] such as Fe,[5,6] Ni,[2d,7] and Cu.[2b,3a,8] Efficient, economical, and green molecular transformation is a contentious requirement in industrial synthetic organic chemistry. The cobalt catalyst, cobaloxime,[9,10] cobalamin derivatives,[11] cobalt-phosphine complex[12], and Co nanosphere[13] have attracted attention as the catalysts for the Heck-type reactions. For example, Branchaud first reported alkyl-alkenyl coupling via the alkylated complex of cobaloxime which provided a radical intermediate to react with an alkene.[10] The β-elimination problem[1c] encountered in Pd catalysis was avoided by the cobalt catalysis.[12] Among the cobalt catalysts, the cobalamin derivatives are promising catalysts being natural and environmentally benign cobalt complexes present in natural B_{12}-dependent enzymes.[14]

We have developed the visible light driven B_{12} catalytic reactions using heptamethyl cobyrinate perchlorate, $[Cob(II)7C_1ester]CO_4$ (**C1**), and photosensitizers (PSs), $[Ru(II)(bpy)_3]Cl_2$ or cyclometalated iridium(III) complexes (**P1** and **P2**) (Figure 1).[15]

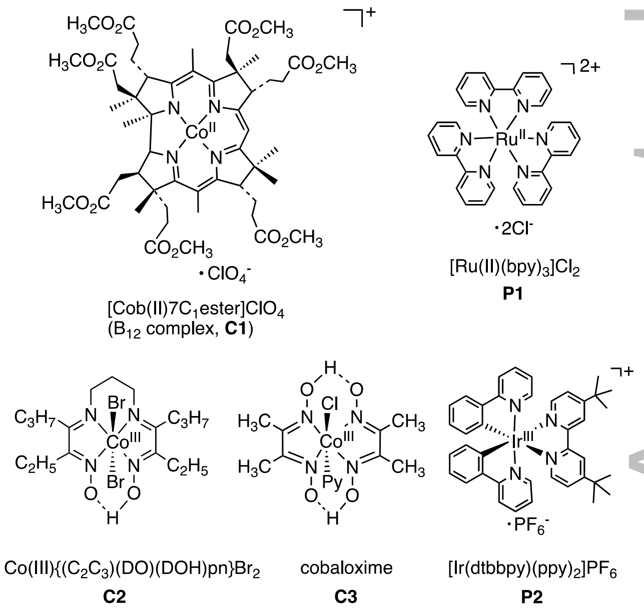


Figure 1. Structure of the B_{12} derivative ($[Cob(II)7C_1ester]ClO_4$) (**C1**), $Co(III)\{(DO)(DOH)pn\}Br_2$ (**C2**), cobaloxime (**C3**), $[Ru(bpy)_3]Cl_2$ (**P1**), and $[Ir(dtbbpy)(ppy)_2]PF_6$ (**P2**).

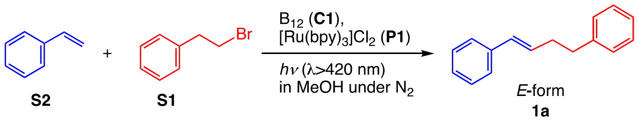
In these reactions, the supernucleophilic Co(I) species of the B_{12} complex is formed by photoinduced electron transfer from the photosensitizer, and the Co(I) complex reacted with the alkyl halide to form an alkylated cobalt complex. Subsequent photolysis of the Co-C bond produces an alkyl radical, which was utilized in various radical mediated organic reactions, such as a simple reduction, homo coupling, ring expansion reaction, and phenyl migrated reaction.[15] The B_{12} complex worked as an efficient catalyst with a turnover under light irradiation. As an expansion to these studies, we now disclose a visible light driven catalytic Heck-type reaction of alkyl halides with styrene derivatives catalyzed by the B_{12} complex at room temperature. The B_{12}-dependent enzyme reaction was advanced to develop synthetic organic chemistry, C-C bond formation of organic halide and alkene, using the B_{12} derivative as efficient catalyst with photosensitizers in this study. As photoredox catalysts were utilized for various molecular transformations such as C-H bond transformations[16] and radical-mediated organic trasformations,[17] great attention has been paid to light-driven molecular transformation in recent synthetic organic chemistry. The advantage of the combined use of a photoredox catalyst and the B_{12} derivative was shown in this study. Detailed mechanistic studies were also conducted.

Results and Discussion

We started optimization of the reaction based on our previous reaction system[15c] for the photocatalytic Heck-type reaction of phenethyl bromide (**S1**) with styrene (**S2**) using the B_{12} complex (**C1**) as the catalyst, $[Ru(bpy)_3]Cl_2$ (**P1**) as the photosensitizer (PS), triethanolamine (TEOA) as the electron source, and a 200W tungsten (W) lamp equipped with a UV cut-off filter as the light source ($\lambda \geq 420$ nm) at room temperature (Figure S1). The coupling product, *E*-1,4-diphenyl-1-butene (**1a**), was selectively obtained in 81% yield under optimized conditions (entry 1 in Table 1). Only the *E*-form of the alkene was formed which was confirmed by ^{1}H NMR with typical vicinal coupling of the olefin protons, J_{vic}=15.5 Hz (Figure S5). Controlled reactions showed that both the B_{12} catalyst and PS are essential for the reaction (entries 2 and 3 in Table 1). Without light irradiation or a sacrificial reagent (SA), the recation did not proceed (entries 4 and 5 in Table 1). The simple B_{12} model complex, $Co(III)\{(C_2C_3)(DO)(DOH)pn\}Br_2$ (**C2**) [18], having a monoanionic equatorial ligand and cobaloxime (**C3**) [19], showed poor effciencies for the reactions (entries 6 and 7 in Table 1). The catalyst **C1** derived from natural B_{12} is a robust and green catalyst for the present catalytic system.

An α-substituted styrene, 1,1-diphenylethene (**S3**), also formed a Heck coupling product (**1b**) with phenetyl bromide. The proper choice of the sacrificial reagent and light source were also important for the catalytic reaction. Diisopropylethylamine (DIPEA) worked as good electron source in the reaction and the reaction was completed two times faster compared to that of the TEOA reaction system (entries 1 and 2 in Table 2). Furthermore, an internal LED irradiation system (λ=448 nm) (Figure S1) accelerated the reaction and the reaction was completed within 4 hours with a high product yield (entry 3 in Table 2). It should be noted that the B_{12} catalyst **C1** was recovered quantitatively after the photoreaction based on electronic and mass spectrometric analyses (Figures S25 and S26). Due to the high stability of the B_{12} catalyst, the turnover number of **C1** reached 1383 by using an excess amount of the substrates (entry 4 in Table 2). When $[Ir(dtbbpy)(ppy)_2]PF_6$ (**P2**) was used as PS, the yield of **1b** decreased to 16% and a reduced product, 1,1,4-triphenylbutane, was formed with a 43% yield (entry 5 in Table 2). Therefore, **P1** is preferred to be used in this reaction as the photosensitizer.

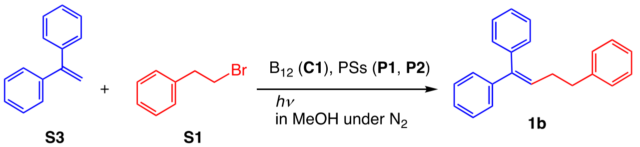
Table 1. Visible light-driven Heck-type reaction of phenethyl bromide with styrene by the B_{12} catalyst and $[Ru(bpy)_3]Cl_2$.[a)]



Entry	Reaction conditions	Conversion [%]	Yield [%]
1[b)]	as shown	>99	81
2	no B_{12} complex (**C1**)	0	0
3	no PS (**P1**)	8	1
4	no TEOA	0	0
5	no light	0	0
6	$Co(III)\{(C_2C_3)(DO)(DOH)pn\}Br_2$ (**C2**)	12	3
7	cobaloxime (**C3**)	<5	0
8[c)]	add DMPO	>99	0

[a)] [cobalt catalyst]=1.0x10^{-4} M (1 mol%), [PS]=1.0x10^{-4} M, [TEOA]=0.5 M, [phenetyl bromide (**S1**)]=1.0x10^{-2} M, [styrene (**S2**)]=1.0x10^{-1} M under N_2 at room temperature in MeOH. Reaction times are 16 hr. The yields are based on the initial concentration of phenetyl bromide. [b)] Hydrogen gas (ca. 60% based on product **1a**) was formed (Figure S4). [c)] In the presence of 0.1 M DMPO.

Table 2. Visible light-driven Heck-type reaction of phenethyl bromide with 1,1-diphenylethene by the B_{12} catalyst and $[Ru(bpy)_3]Cl_2$ under different conditions.[a)]



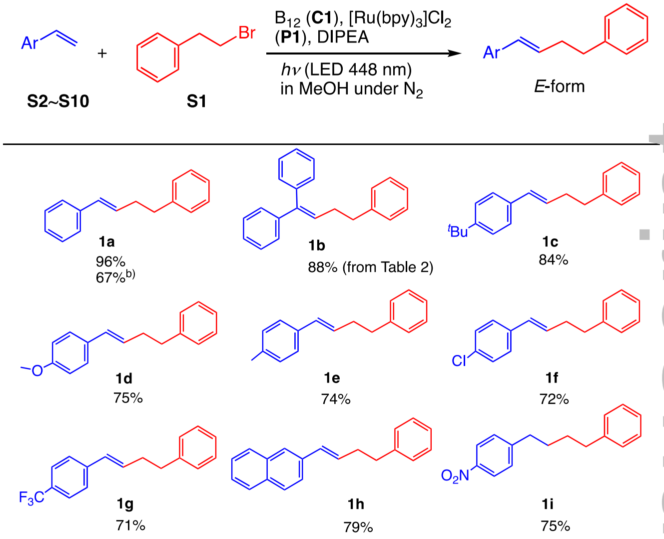
Entry	Light source	SA	Irradiation time	Conversion [%]	Yield [%]
1	W-lamp (λ>420 nm)	0.5 M TEOA	16 hr	>99	72
2	W-lamp (λ>420 nm)	0.1 M DIPEA	8 hr	95	79
3	LED (448nm)	0.1 M DIPEA	4 hr	>99	88
4[b)]	LED (448nm)	2 M DIPEA	24 hr	>99	79
5[c)]	LED (448nm)	0.1 M DIPEA	4 hr	>99	16
6[d)]	LED (448nm)	0.1 M DIPEA	4 hr	>99	0

[a)] [B_{12} catalyst (**C1**)]=1.0×10^{-4} M (1 mol%), [PS]=1.0×10^{-4} M, [phenethyl bromide (**S1**)]=1.0×10^{-2} M, [1,1-diphenylethene (**S3**)]=1.0×10^{-1} M under N_2 at room temperature in MeOH. The yields are based on the initial concentration of phenethyl bromide. [b)] [phenetyl bromide (**S1**)]=1.75×10^{-1} M, [1,1-diphenylethene (**S3**)]=3.5×10^{-1} M. [c)] $[Ir(dtbbpy)(ppy)_2]PF_6$ (**P2**) was used as PS. [d)] In the presence of 0.1 M DMPO.

Various styrene derivatives having a *p*-substituent (**S2~S10** in Chart S1), except for nitro group, formed the corresponding *E*-form of the Heck coupling product in moderate to good yields as shown in Table 3. No-β-eliminated products were obtained in the reaction. The coupling product **1a** was obtained in 96% yield under this condition (LED and DIPEA system). Using a solar simulator (ASAHI SPECTRA HAL-320W), **1a** was formed in 67% yield, while the coupling reaction of *p*-nitrostyrene (**S10**) with phenethyl bromide (**S1**) formed the reduced product (**1i**). A strong electron-withdrawing substituent on the phenyl ring of styrene didn't provide the Heck-type coupling product. The scope of the organic halide is also shown in Table 4. Couplings of organic chlorides, such as phenethyl chloride (**S11**) and benzyl chloride (**S13**), with styrene (**S2**) also proceeded with 69% (**1a**) and 58% (**2a**) yields of products, respectively. It is noteworthy that $[Ru(bpy)_3]Cl_2$ is used as an excellent photo-redox catalyst due to its reducing ability ($Ru(bpy)_3^+$, -1.30 V *vs.* SCE in CH_3CN)[20] and alkenylation reaction of alkyl bromides initiated by visible light induced single-electron reduction of the C-Br bond were reported while alkyl halides were limited to electron-deficient compounds such as α-carbonyl alkyl bromides and benzyl bromides,[2c] whereas the B_{12} catalyst utilizing the supernucleophilicity of the Co(I) species overcomes this problem.

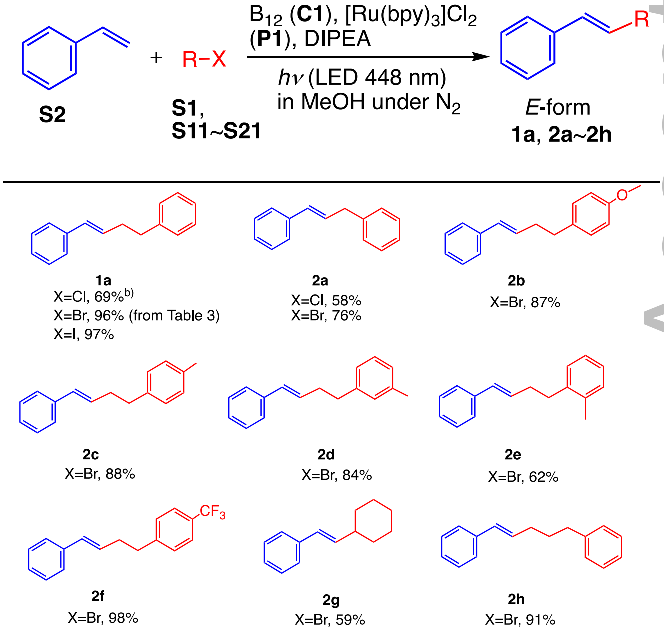
Furthermore, it is noted that the reaction of 2-acetyl-1-bromo-2-ethoxycarbonylpropane (**S22**) with styrene afforded the Heck coupling product (**2i**) with acetyl-migration (Scheme 1). This 1,2-migration of the functional group is a mimic of the B_{12}-enzymatic reaction.[21,22] To the best of our knowledge, this is the first example of the Heck-type reaction combined with the B_{12} model isomerization reaction.

Table 3 Scope of styrene derivatives.[a)]

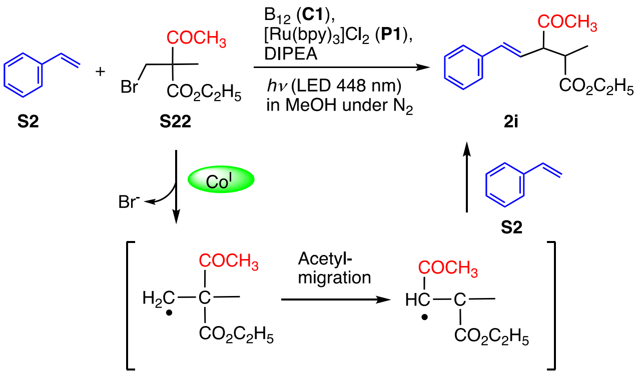


[a)] [B_{12} catalyst]=1.0×10^{-4} M (1 mol%), [PS]=1.0×10^{-4} M, [DIPEA]=0.1 M, [phenethyl bromide (**S1**)]=1.0×10^{-2} M, [alkene (**S2~S10**)]=1.0×10^{-1} M, light source LED (λ=448 nm) under N_2 at room temperature in MeOH. The yields are based on the initial concentration of phenethyl bromide. Reaction times are 4hr. [b)] Solar simulator was used instead of an LED. Reaction time is 10 hr.

Table 4 Scope of organic halide RX.[a)]

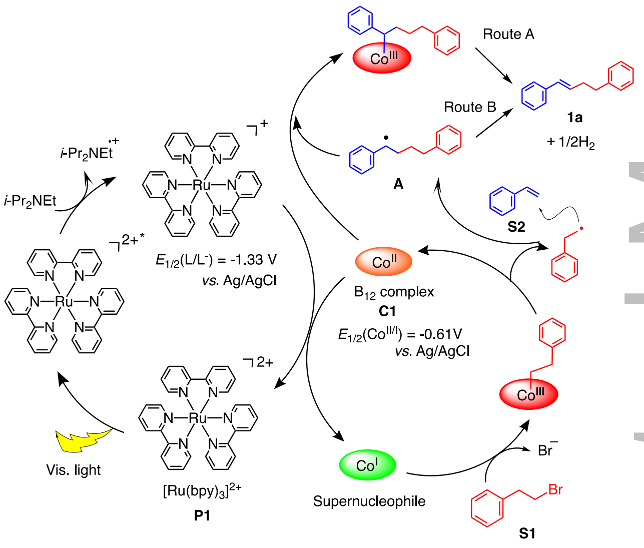


[a] [B_{12} catalyst]=1.0x10^{-4} M (1 mol%), [PS]=1.0x10^{-4} M, [DIPEA]=0.1 M, [R-X]=1.0x10^{-2} M, [styrene]=1.0x10^{-1} M, light source LED (λ=448 nm) under N_2 at room temperature in MeOH. The yields are based on the initial concentration of phenethyl bromide. Reaction times are 4 hr. [b] Reaction was carried out at 40 C˚.



Scheme 1. Heck-type reaction combined with B_{12}-model 1,2-migration reaction.

The proposed reaction mechanism is shown in Scheme 2. The UV-vis spectral change indicates disappearance of the starting Co(II) state of B_{12} and formation of the Co(I) species by visible light irradiation (Figure S2). The supernucleophilic Co(I) species initiates the reaction with the organic halide as we previously reported.[15] We hypothesized that the B_{12} complex catalyzes the Heck-type coupling reaction via a radical pathway. To support the mechanism, some mechanistic experiments were performed. First, we could detect hydrogen gas evolution coupled with the **1a** formation in the photocatalytic reaction (entry 1 in Table 1 and Figure S4). Next, an ESR spin-trapping experiment was conducted using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as the radical trapping reagent. The ESR signal for the carbon-centered radical trapped by DMPO (g=2.006, A_N=15.4 G, A_H=21.8 G) was observed during the photocatalytic reaction (Figure S3).[23] In this condition, DMPO fully inhibited the Heck-type reaction (entry 8 in Table 1 and entry 6 in Table 2), which implied a radical pathway for these coupling reactions. Furthermore, a radical-clock experiment with 6-bromo-1-hexene (**S23**)[3b] verified the formation of the initial radical **B** from the alkylated cobalt complex to form the cyclic coupling product **3a** with 56% yield via radical **C** followed by radical **D** in the reaction with the alkene (Scheme 3a). The formation of the second radical intermediate after alkene attack was proved by another radical-clock experiment using α-cyclopropylstyrene (**S24**)[24] and the coupling product **3b** after ring opening of the cyclopropane ring was obtained in 90% yield (Scheme 3b).[25] Finally, *p*-nitrostyrene (**S10**) having a strong electron-withdrawing substituent did not form the Heck-type product of phenethyl bromide but formed the reduced product (**1i**) as shown in Table 3. The radical intermediate **G** should be reduced to the carbanion **H** by a photosensitizer due to the strong electron substituent followed by protonation to form **1i** (Scheme 3c). In order to determine the source of the hydrogen in the reduced product (**1i**), the reaction was carried out in CH_3OD and deuterium incorporation was confirmed by GC-MS (Figure S27). Formation of the reduced product in the coupling reaction of the phenethyl bromide with styrene using [Ir(dtbbpy)(ppy)$_2$]PF_6 as the photosensitizer could be explained by a similar reason (entry 5 in Table 2). As the *E*(L/L$^-$) value of [Ir(dtbbpy)(ppy)$_2$]PF_6 (*E* = –1.38 V *vs.* Ag/AgCl in CH_3CN) is negative to that of [Ru(bpy)$_3$]Cl_2 (*E* = –1.28 V *vs.* Ag/AgCl in CH_3CN),[26] the radical intermediate could be reduced to the corresponding carbanion to form the reduced product. Based on these experiments, the Heck-type coupling reaction should proceed by the mechanism as shown in Scheme 2. To explain the high selectivity of the Heck-type reaction catalyzed by the B_{12} complex, the alkylated cobalt complex is expected to be an intermediate for alkene formation as shown by Route A in Scheme 2.[27] Further mechanistic investigations including a theoretical study are now in progress.



Scheme 2. Proposed mechanism of Heck-type coupling reaction catalyzed by the B_{12} complex with the photosensitizer under visible light irradiation.

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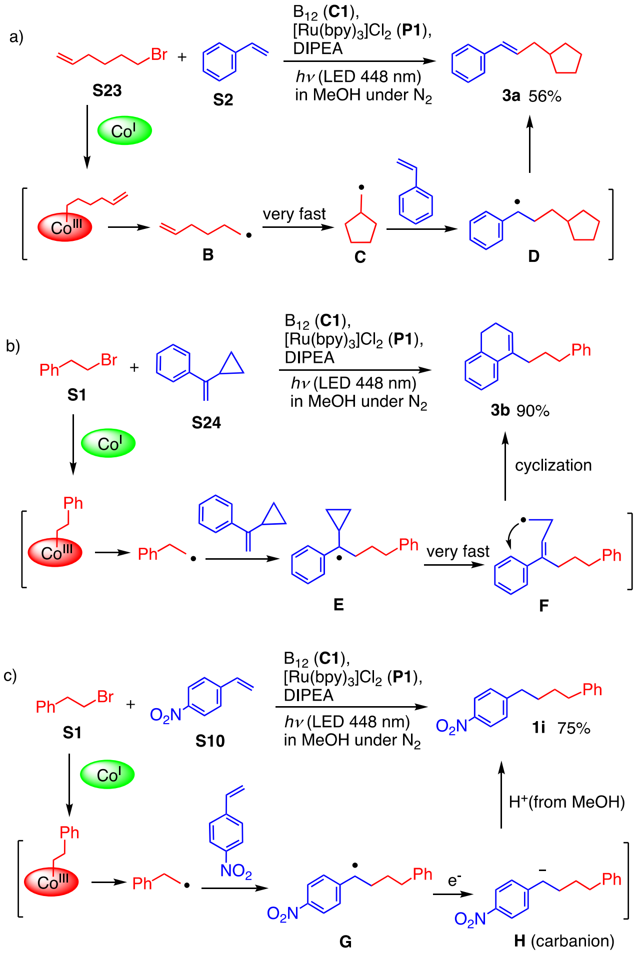

Scheme 3. Control experiments for mechanistic investigation of Heck-type coupling reaction.

Conclusion

In summary, a general strategy for the Heck-type reaction was developed by the B_{12} derivative with an LED as the light source, $Ru(bpy)_3Cl_2$ as a photosensitizer and DIPEA as a sacrificial donor, showed that the B_{12} derivative can be used as an excellent catalyst for the photo-driven Heck-type reaction. Also, mechanistic studies were conducted to determine the most probable mechanism. We anticipate that this method holds promise as an enabling tool for the C-C bond formation in green synthetic organic synthesis.

Experimental Section

Chemicals: All solvents and chemicals used in this study were obtained from commercial sources of reagent grade and used as received unless otherwise noted. The olefin substrate with stabilizer needed to pass through a short Al_2O_3 (PH=9.0~11.0, 75 μm, ~200 mesh) to remove the stabilizer before the reaction. The cobalamin derivative, heptamethyl cobyrinate perchlorate (**C1**), was synthesized by a previously reported method.[28] The cobalt complex, $Co(III)\{(C_2C_3)(DO)(DOH)pn\}Br_2$ (**C2**), $(C_2C_3)(DO)(DOH)pn$ is a deprotonated form of 4,10-dipropyl-5,9-diazatrideca-4,9-diene-3,10-dione dioxime) was prepared according to the literature.[18] α-Cyclopropylstyrene (**S24**) was synthesized by a reported method.[29] 2-Acetyl-1-bromo-2-ethoxycarbonylpropane (**S22**) was synthesized by a reported method.[21] Structure of all substrate, alkenes and organic halides, are summarized in Chart S1.

Measurements: The ^1H NMR and ^{13}C NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Centre of Advanced Instrumental Analysis, Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual solvent peak of $CDCl_3$ at 7.27 ppm. The gas chromatography-mass spectra (GC-MS) were obtained using a Shimadzu GCMS-QP5050A equipped with a J&W Scientific DB-1 column (length: 30m; ID: 0.25 mm, film: 0.25 μm) and helium as the carrier gas. For the measurement, the injector and detector temperatures were 250 °C, the oven temperature was initially held at 100 °C for 2 min, then increased to 240 °C at the rate of 10 °C/min. Hydrogen gas was analyzed by a Shimadzu 14-B gas chromatograph equipped with SHINCARBON ST packed column (Shimadzu GLC). The UV-vis absorption spectra were obtained by a Hitachi U-3300 spectrophotometer at room temperature. The ESR spectra were measured using a Bruker EMX-Plus X-band spectrometer at room temperature. The settings for the ESR measurements were a frequency of 9.87 GHz, power of 1.0 mW, center field of 3515 G, sweep width of 150 G, modulation amplitude of 1.0 G, time constant of 40 ms, and sweep time of 20 s. The 200W tungsten lamp with a 420 nm cut-off filter (Sigma Koki, 42L) and a heat cut-off filter (Sigma Koki, 30H), and the light emitting diode (LED PER-AMP, λ=448 nm) purchased from TechnoSigma were used as the light source for the light irradiation experiments.

General procedure of catalytic Heck-type reaction: A 10 mL methanol solution of the B_{12} complex (**C1**) (1.0×10^{-4} M) (1 mol%), $[Ru(bpy)_3]Cl_2$ (**P1**) (1.0×10^{-4} M), DIPEA (0.1 M), R-X substrate (1.0×10^{-2} M), olefin substrate (1.0×10^{-3} M) and diphenyl as the internal standard was degassed by N_2 gas, then irradiated using an LED (λ=448 nm) as the light source with stirring. After a 4 hour irradiation, the resulting solution was passed through a short silica-gel column to remove the B_{12} complex then analyzed by GC-MS. The yields of the products were calculated by comparison to the peak area ratio of the internal standard. All the products were isolated by silica gel column chromatography (Kanto Chemicals, 60N) with the CH_2Cl_2/hexane eluent and identified by GC-MS, and ^1H and ^{13}C NMR.

1,4-Diphenyl-1-butene (1a)

Colorless oil, yield (19.9 mg, 96%); ^1H NMR (500 MHz, $CDCl_3$): δ=2.56 (m, 2H), 2.82 (t, 2H), 6.32 (dt, J=15.5 Hz, 6.8 Hz, 1H), 6.42 (d, J=15.5Hz, 1H), 7.22–7.36 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=34.84, 35.86, 125.87, 125.97, 126.91, 128.34, 128.46, 129.96, 130.37, 137.72, 141.74; GC-MS: M^+=208.

(1,4-Diphenylbut-1-enyl)benzene (1b)

Colorless oil, yield (25.0 mg, 88%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.50 (m, 2H), 2.81 (t, 2H), 6.17 (t, 1H), 7.13–7.41 (m, 15H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=31.60, 36.15, 125.82, 126.85, 126.88, 127.19, 128.05, 128.11, 128.27, 128.50, 128.77, 129.79, 140.07, 141.65, 142.27, 142.64; GC-MS: M$^+$=284.

1-*tert*-Butyl-4-(4-phenyl-but-1-enyl)-benzene (1c)
Colorless oil, yield (22.2 mg, 84%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=1.30 (s, 9H), 2.50 (q, 2H), 2.75 (t, 2H), 6.23 (dt, J=15.5Hz, 6.8Hz, 1H), 6.37 (d, J=15.5Hz, 1H), 7.18–7.32 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=31.05, 34.23, 34.61, 35.71, 125.13, 125.42, 125.58, 128.06, 128.22, 128.93, 129.83, 134.71, 141.57; GC-MS: M$^+$=264.

1-Methoxy-4-(4-phenyl-but-1-enyl)-benzene (1d)
Colorless oil, yield (17.8 mg, 75%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.53 (m, 2H), 2.80 (t, 2H), 3.82 (s, 3H), 6.14 (dt, J=15.5Hz, 6.8Hz, 1H), 6.37 (d, J=15.5Hz, 1H), 6.85 (d, 2H), 7.21–7.33 (m, 7H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=35.10, 36.29, 55.54, 114.19, 126.08, 127.32, 128.08, 128.58, 128.72, 129.97, 130.85, 142.13, 159.02; GC-MS: M$^+$=238.

1-Methyl-4-(4-phenyl-but-1-enyl)-benzene (1e)
Colorless oil, yield (16.4 mg, 74%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.38 (s, 3H), 2.58 (m, 2H), 2.82 (t, 2H), 6.26 (dt, J=15.5Hz, 6.8Hz, 1H), 6.42 (d, J=15.5Hz, 1H), 7.14 (d, 2H), 7.23–7.36 (m, 5H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=20.85, 34.59, 35.70, 125.58, 125.63, 128.07, 128.21, 128.67, 128.91, 129.96, 134.71, 136.36, 141.58; GC-MS: M$^+$=222.

1-Chloro-4-(4-phenyl-but-1-enyl)-benzene (1f)
Colorless oil, yield (17.4 mg, 72%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.56 (m, 2H), 2.82 (t, 2H), 6.26 (dt, J=15.5Hz, 6.8Hz, 1H), 6.37 (d, J=15.5Hz, 1H), 7.243–7.35 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=34.78, 35.74, 127.17, 128.37, 128.43, 128.59, 129.24, 130.68, 132.48, 136.21, 141.57, 136.36, 141.58; GC-MS: M$^+$=242.

1-Trifluoromethyl-4-(4-phenyl-but-1-enyl)-benzene (1g)
White solid, yield (19.6 mg, 71%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.58 (q, 2H), 2.80 (t, 2H), 6.38 (dt, J=15.5Hz, 6.8Hz, 1H), 6.43 (d, J=15.5Hz, 1H), 7.22–7.33 (m, 5H), 7.42 (d, 2H), 7.53 (d, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=29.95, 35.03, 35.87, 125.68, 125.71, 126.27, 126.36, 128.67, 128.70, 129.56, 133.05, 141.47, 141.68; GC-MS: M$^+$=276.

1-(Naphtha-2-yl)-5-phenyl-2-butene (1h)
White solid, yield (20.4 mg, 79%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.61 (q, 2H), 2.865 (t, 2H), 6.43 (dt, J=15.5Hz, 6.8Hz, 1H), 6.59 (d, J=15.5Hz, 1H), 7.22–7.35 (m, 5H), 7.45 (m, 2H), 7.59 (dd, 1H), 7.69 (s, 1H), 7.81 (t, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=34.69, 35.67, 123.39, 125.19, 125.25, 125.67, 125.88, 127.38, 127.60, 127.81, 128.13, 128.24, 130.22, 130.32, 132.53, 133.51, 135.00, 141.52; GC-MS: M$^+$=258.

1-Nitro-4-(4-phenylbutyl)-benzene (1i)
Brown oil, yield (19.1 mg, 75%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=1.69 (m, 4H), 2.65 (t, 2H), 2.74 (t, 2H), 7.15–7.31 (m, 7H), 8.12 (d, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=30.44, 30.85, 35.55, 35.66, 35.70, 123.61, 125.85, 128.36, 129.15, 142.07, 146.42, 150.38; GC-MS: M$^+$=255.

1,3-Diphenylpropene (2a)
Colorless oil, yield (14.7 mg, 76%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=3.56 (d, 2H), 6.37 (dt, J=15.5Hz, 6.8 Hz, 1H), 6.45 (d, J=15.5Hz, 1H), 7.21–7.36 (m, 10H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=39.35, 126.13, 126.18, 127.09, 128.49, 128.67, 129.24, 131.10, 137.51, 140.18; GC-MS: M$^+$=194.

4-Methoxy-4-(4-phenyl-but-3-enyl)-benzene (2b)
White solid, yield (20.7 mg, 87%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.50 (m, 2H), 2.74 (t, 2H), 3.80 (s, 3H), 6.27 (dt, J=15.5Hz, 6.8Hz, 1H), 6.40 (d, J=5.5Hz, 1H), 6.86 (dd, 2H), 7.14 (dd, 2H), 7.19–7.35 (m, 7H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=35.36, 35.49, 55.66, 114.19, 126.37, 127.28, 128.86, 129.74, 130.48, 130.72, 134.26, 138.18, 158.24; GC-MS: M$^+$=238.

4-Mmethyl-4-(4-phenyl-but-3-enyl)-benzene (2c)
White solid, yield (19.5 mg, 88%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.49 (s, 3H), 2.68 (q, 2H), 2.91 (t, 2H), 6.44 (dt, J=15.5Hz, 6.8Hz, 1H), 6.56 (d, J=15.5Hz, 1H), 7.27–7.50 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=21.24, 35.24, 35.69, 126.24, 127.14, 128.59, 128.72, 129.29, 130.39, 130.53, 135.55, 138.04, 138.94; GC-MS: M$^+$=222.

3-Methyl-4-(4-phenyl-but-3-enyl)-benzene (2d)
White solid, yield (18.6 mg, 84%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.35 (s, 3H), 2.52 (q, 2H), 2.74 (t, 2H), 6.29 (dt, J=15.5Hz, 6.8Hz, 1H), 6.42 (d, J=15.5Hz, 1H), 7.05 (m, 3H), 7.20–7.35 (m, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=21.65, 29.95, 35.14, 36.08, 125.71, 126.25, 126.87, 127.16, 128.50, 128.73, 129.54, 130.38, 130.55, 138.05, 138.15, 141.98; GC-MS: M$^+$= 22.

2-Methyl-4-(4-phenyl-but-3-enyl)-benzene (2e)
White solid, yield (13.7 mg, 62%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.35 (s, 3H), 2.49 (q, 2H), 2.77 (t, 2H), 6.32 (dt, J=15.5Hz, 6.8Hz, 1H), 6.42 (d, J=15.5Hz, 1H), 7.05 (m, 3H), 7.13–7.36 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=19.33, 33.20, 33.65, 125.96, 125.99, 126.02, 126.93, 128.49, 128.83, 130.12, 130.18, 130.29, 135.90, 139.93; GC-MS: M$^+$=222.

4-Trifluoromethyl-4-(4-phenyl-but-3-enyl)-benzene (2f)
White solid, yield (27.0 mg, 98%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=2.55 (q, 2H), 2.84 (t, 2H), 6.24 (dt, J=15.5Hz, 6.8Hz, 1H), 6.43 (d, J=15.5Hz, 1H), 7.22–7.33 (m, 7H), 7.55 (d, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=34.42, 35.67, 125.27, 125.30, 126.01, 127.11, 128.52, 128.78, 129.10, 130.93, 137.49, 145.78; GC-MS: M$^+$=276.

(2-Cyclohexylvinyl)benzene (2g)
Colorless oil, yield (10.9 mg, 59%); ^{1}H NMR (500 MHz, CDCl$_3$): δ=1.20–1.32 (m, 5H), 1.69–1.78 (m, 5H), 2.13 (m, 1H), 6.20 (dd, J=15.5Hz, 6.8Hz, 1H), 6.33 (d, J=15.5Hz, 1H), 7.18 (m, 1H), 7.19–7.36 (m, 4H); ^{13}C NMR (125

MHz, $CDCl_3$): δ=26.06, 26.21, 33.00, 41.15, 125.96, 126.71, 127.29, 128.44, 136.86, 138.14; GC-MS: M^+=186.

β-(3-Phenyl-1-propyl)styrene (2h)
Colorless oil, yield (20.2 mg, 91%); ^1H NMR (500 MHz, $CDCl_3$): δ=1.94 (m, 2H), 2.38 (m, 2H), 2.80 (m, 2H), 6.38 (dt, J=15.5Hz, 6.8 Hz, 1H), 6.50 (d, J=15.5, 1H), 7.32–7.46 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=31.17, 32.68, 35.46, 125.83, 125.98, 126.96, 128.46, 128.57, 130.33, 130.64, 138.01, 142.49; GC-MS: M^+=222.

Ethyl-3-acetyl-2-methyl-5-phenylpent-4-enoate (2i)
Colorless oil, yield (14.3 mg, 55%); ^1H NMR (500 MHz, $CDCl_3$): δ=1.27 (m, 3H), 1.40 (m, 3H), 2.19 (m, 3H), 2.66 (m, 1H), 2.78 (m, 1H), 4.21 (m, 2H), 6.05 (d, 1H), 6.42 (dd, 1H), 7.23–7.31 (m, 5H), 8.12 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=13.85, 18.95, 26.05, 38.42, 59.61, 61.14, 124.10, 125.96, 127.14, 128.25, 133.72, 136.89, 172.27, 204.79; GC-MS: M^+=260.

1-(3,4-Dihydronaphtyl)-3-phenylpropane (3a)
Colorless oil, yield (10.4 mg, 56%); ^1H NMR (500 MHz, $CDCl_3$): δ=1.23 (m, 2H), 1.63 (m, 4H), 1.78 (m, 2H), 1.96 (m, 1H), 2.22 (m, 2H), 6.25 (dt, J=15.5Hz, 6.8Hz, 1H), 6.37 (d, J=15.5Hz, 1H), 7.19 (m, 1H), 7.27–7.36 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=25.57, 32.72, 39.80, 40.42, 126.33, 127.11, 128.83, 130.58, 130.92, 138.45; GC-MS: M^+=186.

4-(3-Phenylpropyl)-1,2-dihydronaphthalene (3b)
Colorless oil, yield (22.3 mg, 90%); ^1H NMR (500 MHz, $CDCl_3$): δ=1.89 (t, 2H), 2.26 (m, 2H), 2.49 (t, 2H), 2.70 (t, 2H), 2.75 (m, 2H), 5.88 (m, 1H), 7.14–7.40 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=15.59, 22.88, 28.23, 29.79, 31.96, 32.08, 35.45, 122.34, 124.69, 125.36, 126.01, 126.22, 127.28, 128.00, 134.65, 135.96, 136.57, 142.19, 143.77; GC-MS: M^+=248.

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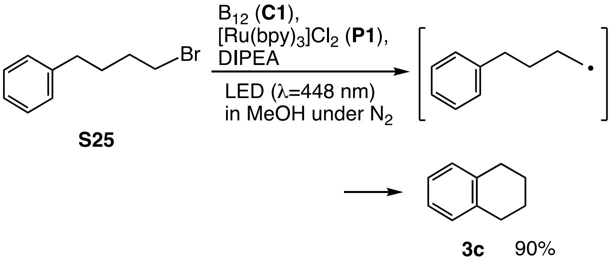

Similar radical-clock experiment was conducted to form dihydronaphthalene product as previously reported.[2a]

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FULL PAPER

Visible Light-Driven, Room Temperature Heck-Type Reaction of Alkyl Halides with Styrene Derivatives Catalyzed by B12 Complex

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