Nickel-catalyzed [2+2+2] cycloaddition of two alkynes and an imine*

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Abstract: The reaction of N-benzenesulfonylbenzaldimine with Ni(cod)$_2$ and PCy$_3$ gave the corresponding η$_2$-iminenickel complex quantitatively. Diphenylacetylene reacted with the η$_2$-iminenickel complex to generate five-membered aza-nickelacycle. Insertion of second alkynes into the five-membered aza-nickelacycle led to the formation of the corresponding seven-membered aza-nickelacycles. Heating the solution of the seven-membered aza-nickelacycles induced the reductive elimination to give 1,2-dihydropyridine. In the presence of 10 mol % of Ni(cod)$_2$ and PMe$_{tBu}$_2 at 100 °C, the intermolecular [2+2+2] cycloaddition of N-benzenesulfonylbenzaldimine and 2-butyne occurred to give the expected 1,2-dihydropyridine in 87 % yield. In the presence of PCy$_3$, the reaction also proceeded catalytically, however, PMe$_{tBu}$_2 gave better results. Less bulky or less basic phosphine, P$_n$Bu$_3$ or P(o-tol)$_3$, was not efficient for the reaction. Although Ni(0)-NHC complex was a good catalyst for [2+2+2] cycloaddition of two alkynes and a ketone or an aldehyde, this reaction did not proceed in the presence of an NHC ligand, 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene.

Keywords: nickel; oxidative cyclization; alkynes; imines; dihydropyridine.

INTRODUCTION

Oxidative cyclization with a transition metal is a very efficient method to form a C–C bond between two unsaturated molecules. Especially, the oxidative cyclization of C≡C triple bond and C=X (X = O, NR) double bond with a transition metal can simultaneously form a C–C bond, a carbon–metal bond, and a metal–heteroatom bond to generate a hetero-metalacycle (Scheme 1) [1,2]. Therefore, a hetero-metalacycle can potentially act as a key intermediate in a late transition-metal-catalyzed reaction involving C–C bond formation between C≡C and C=X (X = O, NR). Nickel is a popular transition metal as a catalyst in these reactions. In fact, a variety of Ni-catalyzed reactions involving C–C bond formation between an alkyne and an aldehyde, a ketone, or an imine have been reported. These reactions could be classified into two types (Scheme 2). One is multicomponent coupling reaction [3]. The other one is [2+2+2] cycloaddition of two alkynes and an aldehyde or a ketone [4]. Recently, we reported the formation of oxa-nickelacycles by the oxidative cyclization of aldehydes or ketones and an unsaturated C–C bond with Ni(0) [5]. However, so far, [2+2+2] cycloaddition with imines has not been reported. It is believed that a hetero-nickelacycle is the key intermediate for both reactions. Thus, the formation of an aza-nickelacycle from an imine and an alkyne and its application to [2+2+2] cycloaddition of two alkynes and an imine is a next logical step. Here, we report the formation of a five-membered aza-nickelacycle, nickelapyrroline, by oxidative cyclization of an imine and an alkyne with Ni(0). The in-
The reaction of PhCH=NSO$_2$Ph (1: N-benzenesulfonylbenzaldimine) with Ni(cod)$_2$ and PCy$_3$ gave (η$^2$-PhCH=NSO$_2$Ph)Ni(PCy$_3$)$_2$ quantitatively (Scheme 3). The molecular structure determined by X-ray crystallography shows that η$^2$-coordination of C=N double bond to Ni(0) center and the geometry around double bond is E (Fig. 1). The atom distance between carbon and nitrogen (1.389 Å) is slightly longer than that of the known imine compound (1.30 Å), which might be due to back-donation from Ni(0) to C–N double bond having an electron-withdrawing group on the nitrogen atom. The imine hydrogen and carbon in 2 are found far upfield in 1H and 13C NMR spectra compared to those of 1, which is consistent with η$^2$-coordination of 1 to a Ni(0) and the strong back-donation from the Ni(0) center to the C=N group in a solution. N-Methylbenzaldimine did not react with Ni(0) under the same reaction condition. N-Phenylbenzaldimine reacted with Ni(0) to give a trace amount of the corresponding η$^2$-imine complex. An electron-withdrawing group on nitrogen is required for the formation of η$^2$-iminenickel complex, which suggests that η$^2$-coordination of imine to Ni(0) is governed by back-donation from Ni(0) to imine.
Formation of five-membered aza-nickelacycle and insertion of alkyne

The reaction of 2 with diphenylacetylene proceeded smoothly to give a five-membered aza-nickelacycle (3) quantitatively along with the dissociation of 1 equiv of PCy₃ (Scheme 4). The elemental analysis of 3 showed the expected composition. The aza-nickelacycle 3 could also be prepared from diphenylacetylene, 1, Ni(cod)₂, and PCy₃ directly. The coordination of oxygen to nickel is inferred from the molecular structure of the seven-membered aza-nickelacycle determined by X-ray crystallography (see later). Hoberg has reported the only example of an analogous five-membered aza-nickelacycle, nickelalactam, formed by the reaction of diphenylacetylene and phenylisocyanate with Ni(0) [6]. The treatment of 3 with carbon monoxide (5 atm) led to the formation of the corresponding lactam in 78 % yield, which is consistent with the structure depicted in Scheme 4. This observation suggests that a hetero-Pauson–Khand reaction might proceed via a hetero-metalacycle analog of 3 [7].

The reaction of 3 with one more equivalent of diphenylacetylene proceeded much slower than the formation of 3 to give a seven-membered aza-nickelacycle (5a) quantitatively. On the other hand, the insertion of 2-butyne occurred much faster than the insertion of diphenylacetylene to give the expected seven-membered aza-nickelacycle (5b) quantitatively. The molecular structure of 5a was determined by X-ray crystallography. The molecular structure of 5a in Fig. 2 shows the square planar dimeric

Scheme 4 Formation of five-membered aza-nickelacycle and insertion of alkyne.

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structure around Ni. The spatial relation between benzenesulfonyl group and phenyl group around N-C5 bond is trans. This geometry is consistent with N-benzenesulfonylimine coordinated to Ni(0) in complex 2. The coordination of oxygen to nickel might play an important role to isolate as a stable square planar complex 5.[8]

The reaction of N-benzenesulfonylbenzaldimine (1) with 2-butyne (1 equiv) in the presence of Ni(cod)2 and PCy3 at room temperature for 10 min gave an inseparable mixture of a five-membered azanickelacycle (3c), seven-membered azanickelacycle (5c), and η2-iminenickel complex (2) (Scheme 5). The addition of an additional equivalent of 2-butyne (total 2 equiv) to the reaction mixture generated 5c as a sole product in 95% yield. The molecular structure of 5c was also determined by X-ray crystallography. As mentioned above, the insertion of 2-butyne proceeded much faster than that of diphenylacetylene, which might be a reason why 3c was obtained as a mixture with 5c.

Scheme 5 Rapid formation of seven-membered azanickelacycle from 2-butyne.

**Reductive elimination from 5a–c**

Heating the solution of the seven-membered azanickelacycles 5a–c at 100 °C induced the reductive elimination to give 1,2-dihydropyridine compounds (6a–c) (Scheme 6). Moreover, the formation of 1,2-dihydropyridine by the reductive elimination suggests that the construction of the Ni-catalyzed [2+2+2] cycloaddition of two alkynes and an imine might be possible.

Scheme 6 Reductive elimination of 1,2-dihydropyridine from seven-membered azanickelacycles.
Ni(0)-catalyzed [2+2+2] cycloaddition of alkynes and imine

In the presence of 10 mol % of Ni(cod)_2 and PMe^tBu_2 at 100 °C, the intermolecular [2+2+2] cycloaddition of 2-butyne and I occurred to give the expected 1,2-dihydropyridine (6c) in 87 % yield (Scheme 7). In the presence of PCy_3, the reaction also proceeded catalytically, however, PMe^tBu_2 gave better results. Less bulky phosphine, such as P(ο-tol)_3, was not efficient for this cycloaddition. Less basic phosphine, such as P(ο-tol)_3, was neither efficient. Although Ni(0)-NHC complex was a good catalyst for [2+2+2] cycloaddition of two alkynes and a ketone or an aldehyde, this reaction did not proceed in the presence of 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene. 3-Hexyne and trimethylsilylacetylene also gave the corresponding 1,2-dihydropyridine (6d, 6e). Although diphenylacetylene reacted with I in the presence of Ni(0) species to give seven-membered aza-nickelacycle 5a, [2+2+2] cycloaddition of diphenylacetylene and I did not occur. This might be due to slow and inefficient reductive elimination from 5a. To the best of our knowledge, only one example to give 1,2-dihydropyridine from two alkynes and an imine catalytically had been reported [6], however, in which 1,2-dihydropyridine was obtained as a byproduct. Thus, this catalytic reaction might be very attractive as a new method to prepare 1,2-dihydropyridine compounds. A plausible mechanism is depicted in Scheme 8. The oxidative cyclization as Ni(0) gives rise to a five-membered aza-nickelacycle followed by insertion of a second alkyne to form a seven-membered aza-nickelacycle. Then, the reductive elimination gives 1,2-dihydropyridine and regenerate Ni(0). As mentioned above, we isolated both five-membered aza-nickelacycle and seven-membered aza-nickelacycle, thus, this reaction mechanism might be very likely. Reported Ni-catalyzed [2+2+2] cycloaddition of alkynes with an aldehyde or a ketone might also proceed via a similar reaction path [4].

Scheme 7 Ni(0)-catalyzed [2+2+2] cycloaddition of alkynes and imine.
CONCLUSION

We isolated η²-iminenickel(0) complex and determined its molecular structure by X-ray crystallography. The oxidative cyclization of an imine and an alkyne with Ni(0) to give a nickelapyrroline and the subsequent insertion of a second alkyne to give a nickeladihydroazepine was reported for the first time. This complex underwent the reductive elimination to give a 1,2-dihydropyridine. Moreover, this sequential reaction process was expanded to a Ni-catalyzed [2+2+2] cycloaddition of two alkynes and an imine to synthesize a 1,2-dihydropyridine. This is the first example of the selective formation of a 1,2-dihydropyridine by a transition-metal catalyst.

EXPERIMENTAL SECTION

General: All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or dry box techniques. ¹H, ³¹P, and ¹³C NMR spectra were recorded on JEOL GSX-270S and JEOL AL-400 spectrometers. The chemical shifts in ¹H NMR spectra were recorded relative to Me₄Si or residual protiated solvent [C₆D₅H (δ 7.16) or CHCl₃ (δ 7.27)]. The chemical shifts in the ¹³C spectra were recorded relative to Me₄Si. The chemical shifts in the ³¹P spectra were recorded using 85 % H₃PO₄ as external standard. Assignment of the resonances in ¹H and ¹³C NMR spectra was based on ¹H-¹H COSY, HMQC, and HMBC experiments. HMQC and HMBC experiments are inverse detection heterocorrelated NMR experiments recorded at the ¹H frequency of the spectrometer, probing one-bond (CH) and multiple-bond (CCH and CCCH) connectivity. Elemental analyses were performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. For some compounds, accurate elemental analyses were precluded by extreme air or thermal sensitivity and/or systematic problems with elemental analysis of organometallic compounds. X-ray crystal data were collected by a Rigaku RAXIS-RAPID Imaging Plate diffractometer.

Scheme 8 A plausible mechanism for Ni(0)-catalyzed [2+2+2] cycloaddition.
Materials: The degassed and distilled solvents (THF, toluene, and hexane) used in this work were commercially available. C₆D₆, THF-d₈ were distilled from sodium benzophenone ketyl. All commercially available reagents were distilled and degassed prior to use.

Caution: The treatment of Ni compounds with carbon monoxide can yield Ni(0) (extremely toxic) due to the addition of insufficient amounts of PR₃, careless handling or an accident. The reaction mixture must be handled in a well-ventilated fume hood.

**Isolation of Ni(η²-PhCH=NSO₂Ph)(PCy₃)₂:** Ni(cod)₂ (272.4 mg, 0.99 mmol), PCy₃ (577.2 mg, 1.00 mmol) and 1 (246.2 mg, 1.00 mmol) were dissolved into 0.5 mL of toluene. The red solution was stirred for 3 h. The reaction mixture was concentrated in vacuo to give red solids. The solids were washed with cold pentane to give 762.9 mg of complex 2 (red solid) in 88 % yield. 1H NMR (270 MHz, C₆D₆): δ 0.85–2.58 (m, 66H, Cy), 4.49 (brt, J = 4.9 Hz, 1H, –CH=NSO₂C₆H₅), 6.72–7.03 (m, 6H), 7.76 (brd, J_HH = 5.4 Hz, 2H), 8.16 (d, J_HH = 7.1 Hz, 2H) 13P NMR (109.4 MHz, C₆D₆): δ 29.6 (d, J_PP = 26.2 Hz), 31.8 (d, J_PP = 26.2 Hz). 13C NMR (67.5 MHz, C₆D₆): δ 27.3 (s, Cy), 27.5 (s, Cy), 28.3 (d, J_CP = 10.4 Hz, Cy), 28.5 (d, J_CP = 10.4 Hz, Cy), 28.8 (d, J_CP = 5.8 Hz, Cy), 28.9 (d, J_CP = 5.8 Hz, Cy), 30.7 (s, Cy), 30.8 (s, Cy), 32.1 (s, Cy), 35.9 (d, J_CP = 11.9 Hz, Cy), 36.5 (d, J_CP = 15.6 Hz, Cy), 52.8 (dd, J_CP = 22.9, 4.9 Hz, –CH=NSO₂C₆H₅), 125.0 (s), 127.0 (s), 127.1 (s), 128.9 (s), 129.1 (s), 130.5 (s), 146.5 (dd, J_CP = 1.2, 0.6 Hz), 147.4 (s). Anal. calcd. for C₄₉H₇₇NNiO₂PS: C, 68.05; H, 8.97; N, 1.62. Found: C, 67.62; H, 8.87; N, 1.83. X-ray data for 2.

**Oxidative cyclization of 1 and diphenylacetylene:** Ni(cod)₂ (5.5 mg, 0.02 mmol), PCy₃ (5.5 mg, 0.02 mmol), 1 (4.9 mg, 0.02 mmol) and diphenylacetylene (3.6 mg, 0.02 mmol) were dissolved into 0.5 mL of C₆D₆. The reaction proceeded immediately to generate 2a quantitatively.

**Isolation of 3a:** Ni(cod)₂ (276.0 mg, 1.00 mmol), PCy₃ (289.1 mg, 1.00 mmol), 1 (245.9 mg, 1.00 mmol) and diphenylacetylene (178.4 mg, 1.00 mmol) were dissolved into 9 mL of toluene and stirred for 3 h. The reaction mixture was concentrated in vacuo to give red solids. The solids were washed with hexane and cold pentane to give 762.9 mg of complex 3a (669.9 mg pale, purple solids) in 88 % yield. 1H NMR (400 MHz, CDCl₃): δ 0.87–2.21 (m, 33H, Cy), 5.91 (s, 1H, –CH=NSO₂C₆H₅), 6.58–7.16 (m, 16H, Ph), 7.36 (d, J_HH = 7.2 Hz, 2H), 8.29 (brs, 2H). 31P NMR (109.4 MHz, CDCl₃): δ 29.6 (d, J_PP = 26.2 Hz). 13C NMR (100 MHz, CDCl₃): δ 26.2 Hz), 31.8 (d, J_PP = 26.2 Hz). 13C NMR (100 MHz, C₆D₆, 70 °C): 27.0 (s, Cy), 28.2 (d, J_CP = 3.8 Hz, Cy), 28.3 (d, J_CP = 3.8 Hz, Cy), 30.8 (s, Cy), 31.0 (s, Cy), 32.8 (d, J_CP = 17.5 Hz, Cy), 73.8 (s, –CHPh–), 124.8 (s, Ph), 125.8 (s, Ph), 126.0 (s), 127.3 (s, Ph), 127.5 (s, Ph), 127.6 (s, Ph), 128.1 (s, Ph), 128.3 (s, Ph), 128.7 (s, Ph), 128.9 (s, Ph), 129.7 (s, Ph), 130.5 (s, Ph), 131.7 (s, Ph), 139.6 (s, ipso-Ph), 142.7 (s, ipso-Ph), 150.2 (d, J_CP = 3.8 Hz, ipso-Ph), 156.4 (s, ipso-Ph). Anal. calcd. for C₄₉H₇₅NNiO₂PS: C, 70.84; H, 7.14; N, 1.84. Found: C, 70.47; H, 6.95; N, 1.88.

**Carbonylation of 3a:** A pressure tight NMR tube containing a solution of 3a (15.1 mg, 0.02 mmol) and diphenylacetylene (3.6 mg, 0.02 mmol) was dissolved into 0.5 mL of C₆D₆. The reaction proceeded immediately to generate 3b in quantitatively concomitant with the dissociation of 1 equiv of PCy₃.
Reaction of 3a with diphenylacetylene: 3a (11.4 mg, 0.015 mmol) and diphenylacetylene (2.7 mg, 0.015 mmol) were dissolved into 0.5 mL of C_6D_6. The reaction proceeded slowly to give 5a quantitatively after 24 h.

Reaction of 3a with 2-butyne: To a solution of 3a (11.4 mg, 0.015 mmol) in 0.5 mL of C_6D_6 was added 2-butyne (0.8 mg, 1.2 μL, 0.015 mmol). The insertion reaction proceeded to give 5b quantitatively.

Isolation of 5a: Ni(cod)_2 (219.1 mg, 0.80 mmol), PCy_3 (229.6 mg, 0.80 mmol), 1 (196.1 mg, 0.80 mmol) and diphenylacetylene (285.0 mg, 1.60 mmol) were dissolved into 7 mL of toluene. The reaction mixture was stirred for 24 h. The reaction mixture was concentrated in vacuo to give purple solids. The solids were washed with hexane and cold pentane to give 688.6 mg of complex 5a (red orange solids) in 92 % yield. Anal. calcd. for C_{59}H_{64}NNiO_2PS: C, 75.32; H, 6.86; N, 1.49. Found: C, 71.59; H, 7.38; N, 1.82. X-ray data for 5a. M = 940.89, brown, monoclinic, P_{21}/c (No. 14), a = 10.7809(3) Å, b = 19.1028(6) Å, c = 24.5928(7) Å, β = 101.1880(8)^°, V = 4968.5(2) Å^3, Z = 4, D_{calc} = 1.258 g/cm^3, T = 0 °C, R (R_{wp}) = 0.052 (0.055).

Isolation of 5b: To a solution of 3a (151.6 mg, 0.20 mmol) in 5 mL of toluene was added 2-butyne (276.4 mg, 400 μL, 0.02 mmol) to the reaction mixture led to the formation of 5b (orange solids) in 92 % yield. Anal. calcd. for C_{49}H_{60}NNiO_2PS: C, 72.06; H, 8.15; N, 2.02. Found: C, 67.36; H, 8.21; N, 2.12. X-ray data for 5b.

Oxidative cyclization of N-benzenesulfonylbenzaldimine (1) and 2-butyne on Ni(0): To a solution of Ni(cod)_2 (5.9 mg, 0.02 mmol), PCy_3 (5.9 mg, 0.02 mmol), N-benzenesulfonylbenzaldimine (1) (5.4 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added 2-butyne (1.1 mg, 1.6 μL, 0.02 mmol) at room temperature. The reaction proceeded to give an inseparable mixture of five-membered nickelacycle (3c: 21 %), seven-membered nickelacycle (5c: 32 %) and η^3-iminenickel complex (2: 22 %). The addition of an additional equivalent of 2-butyne (1.6 μL, 0.02 mmol) to the reaction mixture led to the formation of 5c (95 %). The isolation of 3c failed due to very rapid insertion of 2-butyne. Yield of 3c was calculated based on the resonance at δ 31.3 in 31P NMR spectrum.

Isolation of Ni(C(CH_3)=C(CH_3)C(CH_3)=C(CH_3)C(Ph)NSO_2Ph(PCy_3) (3a): To a solution of Ni(cod)_2 (274.8 mg, 1.00 mmol), PCy_3 (288.4 mg, 1.00 mmol) and 1 (244.0 mg, 0.99 mmol) in 5 mL of toluene was added 2-butyne (276.4 mg, 400 μL, 5.11 mmol) at room temperature. The solution changed from red to dark red. The reaction mixture was stirred for 1 h. The reaction mixture was concentrated in vacuo to give red solids. The solids were washed with hexane and toluene to give 128.5 mg of complex 3a (orange solids) in 79 % yield. 1H NMR (400 MHz, C_6D_6): δ 0.98 (s, 3H, Me), 1.05–1.35 (m, 9H, Cy), 1.56–1.97 (m, 21H, Cy including 3H of Me at 1.85), 2.19 (brs, 3H, Cy), 2.46 (brs, 3H, Cy), 5.52 (s, 1H, –CPh–), 6.85–7.30 (m, 4H), 7.46 (t, J_{HH} = 7.2 Hz, 2H), 7.64 (brs, 3H, Cy), 8.19 (brs, 2H). 13C NMR (100 MHz, C_6D_6): 15.6 (s), 18.2 (s), 22.2 (s), 24.8 (d, J_{CP} = 6.1 Hz, Cy), 27.2 (s, Cy), 28.4 (d, J_{CP} = 5.3 Hz, Cy), 30.9 (s, Cy), 31.3 (s, Cy), 34.1 (d, J_{CP} = 17.5 Hz, Cy), 60.6 (s, –CPh–), 125.5 (s), 126.5 (s), 127.7 (s), 127.8 (s), 128.3 (s), 128.5 (s), 128.7 (s), 129.1 (s), 131.3 (s), 135.5 (s), 135.9 (s), 146.0 (s). Anal. calcd. for C_{59}H_{64}NNiO_2PS: C, 75.32; H, 8.15; N, 2.02. Found: C, 67.36; H, 8.21; N, 2.12. X-ray data for 3a. M = 692.61, brown, monoclinic,
Reductive elimination reactions of 5a–c: A solution of a seven-membered nickelacycle (5a–c, 0.04 mmol) and a small amount of 2-methoxynaphthalene as an internal standard in 0.5 mL of C₆D₆ (0.5 mL) was heated at 100 °C. After complete decomposition of the starting complex was confirmed by 31P NMR, the yield of the reductive elimination product (6a–c) was determined by ¹H NMR.

1-Benzenesulfonyl-3, 4, 5-tetramethyl-2-phenyl-1, 2-dihydropyridine (6c): ¹H NMR (400 MHz, CDCl₃): δ 1.23 (s, 3H, –CHPhC(Et)=C(CH₂C₆H₄)–), 1.50 (s, 3H, –CHPhC(CH₂C₆H₄)–), 1.63 (s, 3H, –N(SO₂Ph)C(Me)=C(CH₂C₆H₄)–), 1.98 (s, 3H, –N(SO₂Ph)C(CH₂C₆H₄)–), 5.26 (s, 1H, –CHPh–), 7.24–7.30 (m, 5H, Ph), 7.43 (t, JHH = 7.2 Hz, 2H, m-SO₂Ph), 7.51 (t, JHH = 7.2 Hz, 1H, p-SO₂Ph), 7.70 (d, JHH = 7.2 Hz, 2H, o-SO₂Ph). ¹³C NMR (100 MHz, CDCl₃): δ 13.2, 14.6, 18.2, 19.9, 61.6, 125.0, 125.3, 127.1, 127.93, 127.94, 128.1, 128.3, 128.7, 132.5, 137.8, 138.7. HRMS calcd. for C$_{31}$H$_{27}$NO$_2$S: 477.1762, found m/z 477.1768.

1-Benzenesulfonyl-2, 3, 4, 5, 6-pentaphenyl-1, 2-dihydropyridine (6a): An inseparable mixture was obtained. Yield of 6b was calculated based on the resonance at δ 5.88 in ¹H NMR Spectrum.

1-Benzenesulfonyl-5, 6-dimethyl-2, 3, 4-triphenyl-1, 2-dihydropyridine (6b): ¹H NMR (400 MHz, CDCl₃): δ 1.40 (s, 3H, –N(SO₂Ph)C(Me)=C(CH₂C₆H₄)–), 2.09 (s, 3H, –N(SO₂Ph)C(CH₂C₆H₄)–), 5.95 (s, 1H, –CHPh–), 6.53 (brs, 2H), 6.96 (t, JHH = 7.4 Hz, 2H), 7.02 (t, JHH = 7.2 Hz, 1H), 7.10–7.16 (m, 3H), 7.36–7.46 (m, 5H), 7.58–7.62 (m, 3H), 7.69 (d, JHH = 7.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 16.0, 20.0, 61.8, 126.9, 127.2, 127.65, 127.68, 127.74, 127.74, 128.23, 128.25, 128.30, 128.30, 128.6, 128.80, 128.84, 130.0, 132.7, 137.4, 138.6, 138.7, 138.9, 139.5. HRMS calcd. for C$_{31}$H$_{27}$NO$_2$S: 477.1762, found m/z 477.1768.

General procedure for Ni(cod)$_2$/P$_5$B$_{13}$Me-catalyzed cycloaddition of 2-butylene and 1: To a solution of 2-butylene (13.5 mg, 19.6 µL, 0.25 mmol) and P$_5$B$_{13}$Me (3.2 mg, 3.9 µL, 0.02 mmol) in 0.5 mL of C$_6$D$_6$ was added 1 (24.5 mg, 0.1 mmol) and Ni(cod)$_2$ (2.8 mg, 0.01 mmol). The solution was heated at 100 °C. After 48 h, 6c was generated in 87 % yield. The reaction mixture was concentrated in vacuo. The residue was purified by preparative thin-layer chromatography of silica gel to give 6c (17.6 mg, 50 %).

Ni(cod)$_2$/PCy$_3$-catalyzed cycloaddition of 2-butylene and 1: The reaction was carried out according to the general procedure using PCy$_3$ (5.5 mg, 0.02 mmol). After 24 h, 6c was generated in 64 %.

Ni(cod)$_2$/P$_5$B$_{13}$Me-catalyzed cycloaddition of 2-butylene and 1: The reaction was carried out according to the general procedure using P$_5$B$_{13}$Me (4.0 mg, 0.02 mmol). After 24 h, 6c was generated in 17 %.

Ni(cod)$_2$/P(o-tol)$_3$-catalyzed cycloaddition of 2-butylene and 1: The reaction was carried out according to the general procedure using P(o-tol)$_3$ (6.3 mg, 0.02 mmol). After 29 h, 6c was generated in 6 %.

General procedure for Ni(cod)$_2$/P$_5$B$_{13}$Me-catalyzed cycloaddition of 3-hexylyne and 1: To a solution of 3-hexyne (20.5 mg, 28.4 µL, 0.25 mmol) and P$_5$B$_{13}$Me (3.2 mg, 3.9 µL, 0.02 mmol) in 0.5 mL of C$_6$D$_6$ was added 1 (24.5 mg, 0.1 mmol) and Ni(cod)$_2$ (2.8 mg, 0.01 mmol). The solution was heated at 100 °C. After 70 h, 6d was generated in 64 % yield. The reaction mixture was concentrated in vacuo. The residue was purified by preparative thin-layer chromatography of silica gel to give 6d (22.3 mg, 55 %). ¹H NMR (400 MHz, CDCl₃): δ 0.34 (t, JHH = 7.4 Hz, 3H, –N(SO₂Ph)C(CH₂CH$_3$)=), 0.40 (t, JHH = 7.4 Hz, 3H, –CHPhC(Et)=C(CH₂CH$_3$)=), 0.81 (t, JHH = 7.6 Hz, 3H, –CHPhC(CH₂CH$_3$)=), 0.88 (t, JHH = 7.6 Hz, 3H, –N(SO₂Ph)C(Et)=C(CH₂CH$_3$)=), 1.82–1.94 (m, 2H), 1.96–2.12 (m, 3H), 2.22–2.37 (m, 2H), 2.68 (dd, JHH = 14.8, 7.4 Hz, 1H, –N(SO₂Ph)C(CH$_2$CH$_3$)=), 5.55 (s, 1H, –CHPh–), 7.23–7.29 (m, 5H, Ph), 7.39 (t, JHH = 7.6 Hz, 2H, m-SO₂Ph), 7.49 (t, JHH = 7.6 Hz, 1H, p-SO₂Ph), 7.74 (d, JHH = 7.2 Hz, 2H, o-SO₂Ph). ¹³C NMR (100 MHz, CDCl₃): δ 12.1,
Ni(cod)$_2$/PCy$_3$-catalyzed cycloaddition of 3-hexyne and 1: The reaction was carried out according to the general procedure using PCy$_3$ (5.5 mg, 0.02 mmol). After 24 h, 6d was generated in 26%.

Ni(0)-catalyzed cycloaddition of trimethylsilylacetylene and 1: To a solution of trimethylsilylacetylene (24.5 mg, 34.6 µL, 0.25 mmol) and PtBu$_2$Me (3.2 mg, 3.9 µL, 0.02 mmol) in 0.5 mL of C$_6$D$_6$ was added 1 (24.5 mg, 0.1 mmol) and Ni(cod)$_2$ (2.8 mg, 0.01 mmol). The solution was heated at 100°C. After 5 h, 2.5 equivalents of trimethylsilylacetylene were added to a reaction mixture. Heating more 13 h, 6e was generated in 58% yield. The residue was purified by preparative thin-layer chromatography of silica gel to give 6e (16.7 mg, 38%). $^1$H NMR (400 MHz, CDCl$_3$): δ −0.18 (s, 9H, –CHPhC$_{\text{TMS}}$=), 0.14 (s, 9H, –N(SO$_2$Ph)CH=C$_{\text{TMS}}$–), 5.66 (s, 1H, –C$_{\text{H}}$Ph–), 6.27 (s, 1H, –CHPhCTMS=C$_{\text{H}}$–), 6.59 (s, 1H, –N(SO$_2$Ph)C$_{\text{H}}$=), 7.24–7.26 (m, 3H), 7.34–7.37 (m, 2H), 7.41 (t, $J_{\text{HH}}$ = 7.8 Hz, 2H, $m$-SO$_2$Ph), 7.52 (t, $J_{\text{HH}}$ = 7.4 Hz, 1H, $p$-SO$_2$Ph), 7.71 (d, $J_{\text{HH}}$ = 7.2 Hz, 2H, $m$-SO$_2$Ph), 7.49 (t, $J_{\text{HH}}$ = 7.6 Hz, 1H, $p$-SO$_2$Ph), 7.74 (d, $J_{\text{HH}}$ = 7.2 Hz, 2H, $o$-SO$_2$Ph). $^{13}$C NMR (100 MHz, CDCl$_3$): δ −1.75, −1.64, 58.2, 120.2, 126.7, 128.43, 128.45, 129.0, 130.3, 131.9, 132.8, 133.1, 139.3, 140.7. HRMS calcd. for C$_{23}$H$_{31}$NO$_2$SSi 441.1614, found m/z 441.1610.

Ni(cod)$_2$/NHC-catalyzed cycloaddition of 2-butyne and 1: To a suspension of Ni(cod)$_2$ (2.8 mg, 0.01 mmol), 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (3.4 mg, 0.01 mmol) and potassium tert-butoxide (1.1 mg, 0.01 mmol), 1 (24.5 mg, 0.1 mmol) and 2-methoxynaphthalene as an internal standard in 0.5 mL of C$_6$D$_6$ was added 2-butyne (13.5 mg, 0.25 mmol). The solution was heated at 60 °C for 19 h. However, 6c was not obtained.

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