C–F Bond Activation

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Double C–F Bond Activation through β-Fluorine Elimination: Nickel-Mediated [3+2] Cycloaddition of 2-Trifluoromethyl-1-alkenes with Alkynes**

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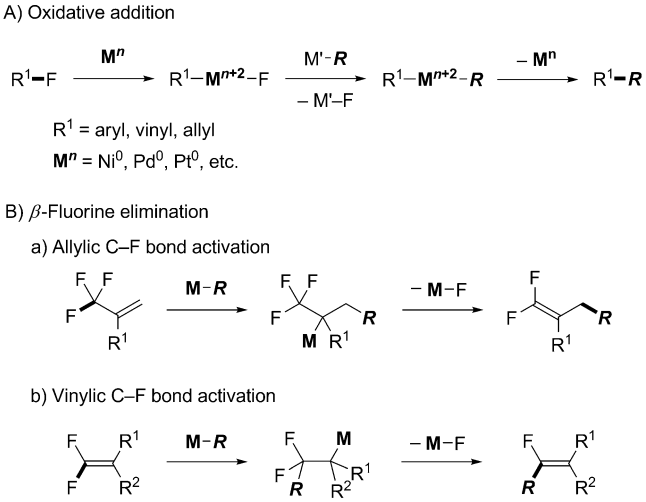
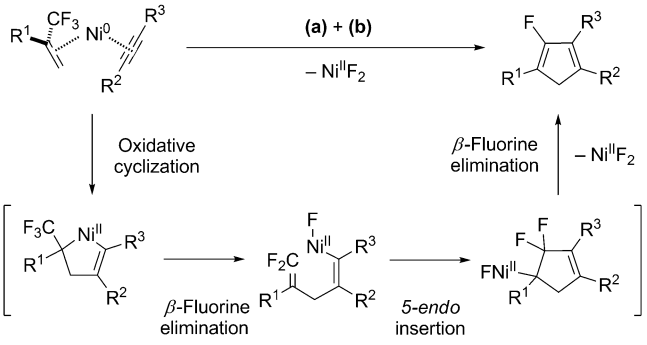
Abstract: *The nickel-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes with alkynes afforded fluorine-containing multi-substituted cyclopentadienes in a regioselective manner. This reaction involves the consecutive two C–F bond cleavage of a trifluoromethyl or a pentafluoroethyl group through β-fluorine elimination.*

Transition-metal-mediated C–F bond activation has occupied a significant research area, establishing new synthetic methodologies.[1–3] In particular, cross-coupling reactions by C–F bond cleavage of aryl, vinyl, and allyl fluorides has been intensively studied in this decade.[4–6] In most cases, cleavage of a C–F bond was achieved by its oxidative addition to low-valent transition metal complexes (Scheme 1 A). However, oxidative addition of a C–F bond is not necessarily possible because of its high bond energy. In contrast, C–F bond cleavage by β-fluorine elimination has been considered a much more reasonable process compared to oxidative addition because transition-metal-mediated β-heteroatom elimination typically proceeds under milder conditions (Scheme 1 B).[7,8] Furthermore, β-fluorine elimination is sometimes even more preferable than β-hydrogen elimination as an elementary step from complexes with both fluorine and hydrogen atoms on the β-carbon to the metal center.[7–9] Although β-fluorine elimination is potentially advantageous, the literature contains only a few reports on its practical application to transition-metal-mediated reactions. For example, allylic C–F bond activation of 2-trifluoromethyl-1-alkenes proceeded through sequential imino- or carbometalation and β-fluorine elimination to give 1,1-difluoro-1-alkenes (Scheme 1 Ba).[7f,g] In a similar manner, vinylic C–F bond activation of 1,1-difluoro-1-alkenes by an imino- or carbometalation–β-fluorine elimination process provided monofluorinated alkenes (Scheme 1 Bb).[7c,d]



Scheme 1. C–F bond activation by A) oxidative addition and B) β-fluorine elimination.

To take complete advantage of these processes, we attempted the double C–F bond activation of 2-trifluoromethyl-1-alkenes through the sequential use of β-fluorine elimination (Scheme 2). Because electron-deficient alkenes readily undergo oxidative cyclization,[10–12] we envisioned that oxidative cyclization of a 2-trifluoromethyl-1-alkene and an alkyne on a Ni^0 complex would generate a nickelacyclopentene bearing a trifluoromethyl group. β-Fluorine elimination of this type of nickelacycle would generate organonickel complexes having both a vinylic C–Ni bond and a difluoroalkene moiety. Subsequently, intramolecular vinylic C–F



Scheme 2. Double C–F bond activation of a CF_3 group by a) allylic C–F bond activation via nickelacycles and b) intramolecular vinylic C–F bond activation.

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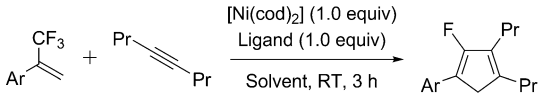
bond activation of the intermediary difluoroalkene might occur through normally disfavored 5-*endo* insertion[7c,d] to afford 2-fluoro-1,3-cyclopentadienes. Herein we demonstrate the nickel-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes with alkynes by double C–F bond activation of a trifluoromethyl group by sequential β-fluorine elimination, which allowed the efficient synthesis of highly substituted 2-fluoro-1,3-cyclopentadines.

We selected 2-(4′-acetyl)phenyl-3,3,3-trifluoropropene (**1a**) and 4-octyne (**2a**) as model substrates for optimization of the reaction conditions (Table 1). Upon treatment of **1a** with **2a** in the presence of an equimolar amount of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) and PPh_3 or 1,10-phenanthroline, no cyclization product was obtained (Table 1, entries 1 and 2). However, when IMes possessing a strong σ-donating ability was employed as a ligand, the expected [3+2] cycloaddition proceeded to afford 2-fluoro-1,3-cyclopentadiene **3aa** in 26% yield by cleavage of two C–F bonds in the trifluoromethyl group and formation of two C–C bonds (Table 1, entry 3). In the case where PCy_3 was used, the yield of **3aa** was improved to 66% (entry 4). These results suggest that highly electron-rich Ni^0 species derived from strong σ-donating ligands promoted oxidative cyclization between **1a** and **2a** in the initial step. Next we screened reaction solvents. Both THF and DME (1,2-dimethoxyethane) gave the product, albeit in low yields (entries 5 and 6). The best result (74% yield of **3aa**) was obtained using 1,4-dioxane (entry 7).

Table 1: Optimization of reaction conditions in Ni-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkene **1a** with alkyne **2a**.[a]



1a Ar = C_6H_4(*p*-Ac) **2a** (1.1 equiv) **3aa**

Entry	Ligand	Solvent	Yield [%][b]
1	PPh_3	toluene	0
2	1,10-phen	toluene	0
3	IMes·HCl[c]	toluene	26
4	PCy_3	toluene	66[d]
5	PCy_3	THF	48
6	PCy_3	DME	56
7	PCy_3	1,4-dioxane	74[d]

[a] Reaction conditions: $[Ni(cod)_2]$ (0.20 mmol), ligand (0.20 mmol), **1a** (0.20 mmol), **2a** (0.22 mmol), solvent (2.0 mL) at room temperature for 3 h. [b] ^{19}F NMR yield using $PhCF_3$ as an internal standard. [c] *t*BuOK (1.0 equiv) was used as a base. [d] Yield of isolated product.

The scope of the [3+2] cycloaddition was examined using a wide variety of 2-trifluoromethyl-1-alkenes **1a–g** and alkynes **2a–e** under the previously described optimal reaction conditions (Figure 1 and Table 2). Unsymmetrical 4-methyl-2-pentyne (**2b**), 1-phenyl-1-propyne (**2c**), and 1-(4′-methoxyphenyl)-1-pentyne (**2e**) also participated in this reaction to afford the corresponding 2-fluoro-1,3-cyclopentadienes **3ab**, **3ac**, and **3ae** in 77%, 48%, and 64% yields, respectively, with complete regioselectivity (Table 2, entries 2, 3, and 5, respectively).[13] The use of diphenylacetylene (**2d**) resulted in the formation of the corresponding cycloaddition product **3ad** in 86% yield (entry 4). α-Trifluoromethylstyrenes **1b–d** bearing electron-withdrawing cyano, trifluoromethyl, and ethoxycarbonyl groups further provided cyclopentadienes **3ba–da** in good to high yields (entries 6–8). Non-substituted α-trifluoromethylstyrene (**1e**) and α-trifluoromethylstyrene **1f** bearing an electron-donating methoxy group successfully underwent cycloaddition with **2b** or **2d** (entries 9 and 10). The reaction of *tert*-butyl α-trifluoromethyacrylate (**1g**) with alkynes **2a** and **2b** readily proceeded to give 2-fluoro-1,3-cyclopentadiene-1-carboxylates **3ga** and **3gb** in 88% and 93% yields, respectively (entries 11 and 12).

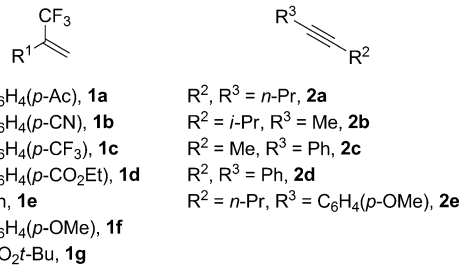
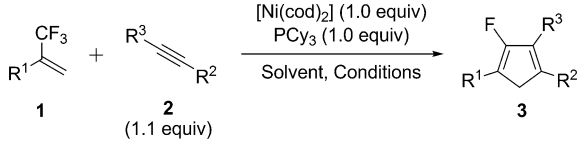


Figure 1. List of substrates.

Table 2: Synthesis of 2-fluoro-1,3-cyclopentadienes **3** by Ni-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes **1** with alkynes **2**.[a]

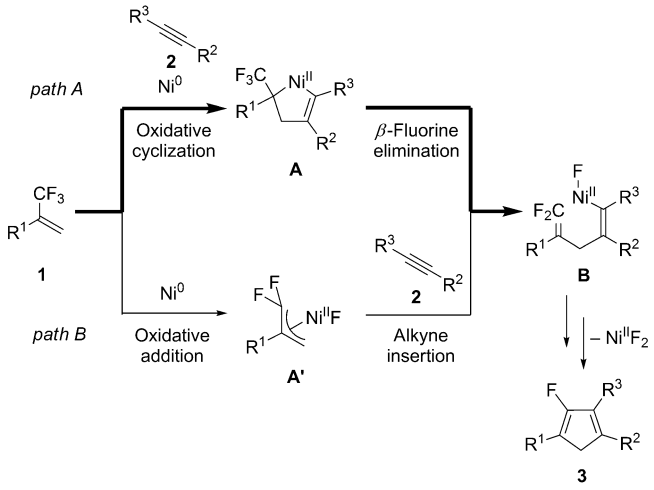


1 **2** (1.1 equiv) **3**

Entry	1	2	Solvent	Conditions	Yield [%]
1	**1a**	**2a**	1,4-dioxane	RT, 3 h	**3aa** 74%
2	**1a**	**2b**	1,4-dioxane	RT, 10.5 h	**3ab** 77%
3	**1a**	**2c**	1,4-dioxane	60°C, 19 h	**3ac** 48%
4	**1a**	**2d**	1,4-dioxane	100°C, 3 h	**3ad** 86%
5	**1a**	**2e**	toluene	100°C, 3 h	**3ae** 64%
6	**1b**	**2a**	toluene	RT, 1.5 h then 80°C, 1.5 h	**3ba** 82%
7	**1c**	**2a**	toluene	RT, 9 h	**3ca** 86%
8	**1d**	**2a**	toluene	50°C, 1 h	**3da** 78%
9	**1e**	**2b**	1,4-dioxane	60°C, 6 h	**3eb** 57%
10	**1f**	**2d**	toluene	100°C, 3 h	**3fd** 42%
11	**1g**	**2a**	1,4-dioxane	RT, 3 h	**3ga** 88%
12	**1g**	**2b**	toluene	RT, 2 h	**3gb** 93%

[a] Reaction conditions: $[Ni(cod)_2]$ (0.30 mmol), ligand (0.30 mmol), **1** (0.30 mmol), **2** (0.33 mmol), solvent (3.0 mL).

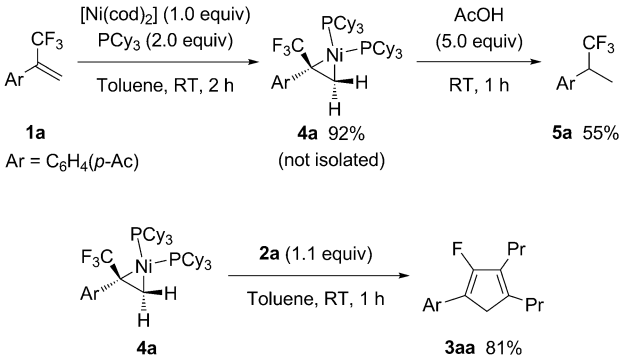
Two plausible mechanisms for this reaction are shown in Scheme 3. Nickelacyclopentene **A** bearing a trifluoromethyl group was probably formed by oxidative cyclization of 2-trifluoromethyl-1-alkene **1** and alkyne **2** with Ni^0 (Scheme 3, path A). Ring-opening of nickelacycle **A** readily proceeded by β-fluorine elimination to generate alkenylnickel species **B**. Subsequent 5-*endo* insertion and the second β-fluorine elimination afforded 2-fluoro-1,3-cyclopentadiene **3** along with NiF_2 species.[14] An alternative mechanism could be the oxidative addition pathway (Scheme 3, path B), in which 2-



Scheme 3. Plausible reaction mechanisms.

trifluoromethyl-1-alkene **1** initially reacted with Ni^0 to generate π-allylnickel intermediate **A′** by oxidative addition of a C–F bond to Ni^0.[6] Alkyne insertion into the C–Ni bond of **A′** led to **B**, followed by subsequent 5-*endo* insertion and β-fluorine elimination to give the same product **3**.

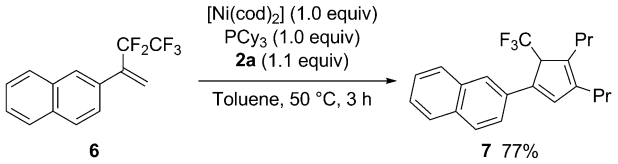
To elucidate the mechanism, the stoichiometric reaction of 2-trifluoromethyl-1-alkene **1** with a Ni^0 complex was conducted in the absence of alkynes (Scheme 4). If the reaction started with oxidative addition of the C–F bond to Ni^0, the corresponding π-allylnickel complex would be observed. Treatment of **1a** with stoichiometric $[Ni(cod)_2]$



Scheme 4. Generation and reactions of nickelacyclopropane **4a**.

and PCy_3 in toluene at room temperature, however, afforded nickelacyclopropane **4a** as the sole product in 92% yield; this was confirmed by ^{19}F, and ^{31}P NMR spectroscopy.[5f,11c] In this reaction, no π-allylnickel complexes were observed in the NMR spectra. The formation of **4a** was further supported by the conversion of **4a** to hydrogenated product **5a** in 55% yield upon treatment with an excess of acetic acid.[15] In addition, **4a** readily reacted with 4-octyne to afford 2-fluoro-1,3-cyclopentadiene **3aa** in 81% yield. Therefore, the cyclopentadiene formation probably proceeded through an oxidative cyclization–β-fluorine elimination sequence (path A).

Furthermore, the sequential double C–F bond activation was successfully applied to pentafluoroethyl compounds under the same reaction conditions to give 5-trifluoromethyl-1,3-cyclopentadienes (Scheme 5). 2-Pentafluoroethyl-1-alkene **6** readily reacted with 4-octyne (**2a**) in the presence of the nickel complex to afford, by isomerization, 5-trifluoromethyl-1,3-cyclopentadiene **7** in 77% yield. Thus, we also achieved the direct synthesis of a ring trifluoromethylated cyclopentadiene.



Scheme 5. Synthesis of 5-trifluoromethyl-1,3-cyclopentadiene **7** by Ni-mediated [3+2] cycloaddition of 2-pentafluoroethyl-1-alkene **6** with alkyne **2a**.

In summary, we have developed a new methodology for allylic and vinylic C–F bond activation based on β-fluorine elimination from nickelacycles generated by oxidative cyclization of 2-trifluoromethyl-1-alkenes with alkynes. The nickel-mediated [3+2] cycloaddition reaction involves the consecutive and regioselective cleavage of two C–F bonds of a trifluoromethyl and a pentafluoroethyl group. This methodology simultaneously enables the direct construction of a multisubstituted cyclopentadiene ring and the introduction of a fluorine substituent or a trifluoromethyl group in a regioselective manner.[16] Fluorine-containing, multisubstituted cyclopentadienes would be useful compounds as ligands of metallocene-type complexes[17] and as building blocks for further chemical transformations such as Diels–Alder reactions.[18,19]

Experimental Section

General procedure for nickel-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes with alkynes: To a solution of $[Ni(cod)_2]$ (86 mg, 0.31 mmol) and PCy_3 (88 mg, 0.31 mmol) in 1,4-dioxane (3.2 mL) were added 2-trifluoromethyl-1-alkene **1g** (61 mg, 0.31 mmol) and alkyne **2a** (38 mg, 0.34 mmol) at room temperature. After stirring for 3 h at the same temperature, the reaction mixture was filtered through a pad of silica gel (EtOAc). The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to give 2-fluorocyclopentadiene **3ga** (74 mg, 88%).

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[1] For selected reviews on transition-metal-mediated C–F bond activation, see: a) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119–2183; b) E. Clot, O. Eisenstein, N. Jasim, S. A. Macgregor, J. E. McGrady, R. N. Perutz, *Acc. Chem. Res.* **2011**, *44*, 333–348;

c) M. F. Kuehnel, D. Lentz, T. Braun, *Angew. Chem.* **2013**, *125*, 3412 – 3433; *Angew. Chem. Int. Ed.* **2013**, *52*, 3328 – 3348.

[2] For recent reports on transition-metal-mediated aromatic C-(sp^2)–F bond activation, see: a) T. Braun, R. N. Perutz, *Chem. Commun.* **2002**, 2749 – 2757; b) M. Reinhold, J. E. McGrady, R. N. Perutz, *J. Am. Chem. Soc.* **2004**, *126*, 5268 – 5276; c) I. M. Piglosiewicz, S. Kraft, R. Beckhaus, D. Haase, W. Saak, *Eur. J. Inorg. Chem.* **2005**, 938 – 945; d) U. Jäger-Fiedler, P. Arndt, W. Baumann, A. Spannenberg, V. V. Burlakov, U. Rosenthal, *Eur. J. Inorg. Chem.* **2005**, 2842 – 2849; e) T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius, A. Mix, *J. Am. Chem. Soc.* **2008**, *130*, 9304 – 9317; f) P. K. Chan, W. K. Leong, *Organometallics* **2008**, *27*, 1247 – 1253; g) M. E. Doster, S. A. Johnson, *Angew. Chem. Int. Ed.* **2009**, *48*, 2185 – 2187; *Angew. Chem.* **2009**, *121*, 2219 – 2221; h) Z. Lian, X. Xu, H. Sun, Y. Chen, T. Zheng, X. Li, *Dalton Trans.* **2010**, 9523 – 9529; i) T. R. Dugan, J. M. Goldberg, W. W. Brennessel, P. L. Holland, *Organometallics* **2012**, *31*, 1349 – 1360.

[3] For recent reports on transition-metal-catalyzed hydrodefluorination by aromatic C(sp^2)–F bond activation, see: a) R. J. Young, Jr., V. V. Grushin, *Organometallics* **1999**, *18*, 294 – 296; b) C. Desmarets, S. Kuhl, R. Schneider, Y. Fort, *Organometallics* **2002**, *21*, 1554 – 1559; c) J. Vela, J. M. Smith, Y. Yu, N. A. Ketterer, C. J. Flaschenriem, R. J. Lachicotte, P. L. Holland, *J. Am. Chem. Soc.* **2005**, *127*, 7857 – 7870; d) S. P. Reade, M. F. Mahon, M. K. Whittlesey, *J. Am. Chem. Soc.* **2009**, *131*, 1847 – 1861; e) S. Yow, S. J. Gates, A. J. P. White, M. R. Crimmin, *Angew. Chem. Int. Ed.* **2012**, *51*, 12559 – 12563; *Angew. Chem.* **2012**, *124*, 12727 – 12731; f) P. Fischer, K. Götz, A. Eichhorn, U. Radius, *Organometallics* **2012**, *31*, 1374 – 1383; g) H. Lv, Y.-B. Cai, J.-L. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3203 – 3207; *Angew. Chem.* **2013**, *125*, 3285 – 3289; h) Z. Chen, C.-Y. He, Z. Yin, L. Chen, Y. He, X. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 5813 – 5817; *Angew. Chem.* **2013**, *125*, 5925 – 5929.

[4] For recent reports on transition-metal-catalyzed cross-coupling by aromatic C(sp^2)–F bond activation, see: a) V. P. W. Böhm, C. W. K. Gstöttmayr, T. Weskamp, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2001**, *40*, 3387 – 3389; *Angew. Chem.* **2001**, *113*, 3500 – 3503; b) F. Mongin, L. Mojovic, B. Guillamet, F. Trécourt, G. Quéguiner, *J. Org. Chem.* **2002**, *67*, 8991 – 8994; c) N. Yoshikai, H. Mashima, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 17978 – 17979; d) L. Ackermann, R. Born, J. H. Spatz, D. Meyer, *Angew. Chem. Int. Ed.* **2005**, *44*, 7216 – 7219; *Angew. Chem.* **2005**, *117*, 7382 – 7386; e) T. J. Korn, M. A. Schade, S. Wirth, P. Knochel, *Org. Lett.* **2006**, *8*, 725 – 728; f) K. Inamoto, J.-i. Kuroda, T. Sakamoto, K. Hiroya, *Synthesis* **2007**, 2853 – 2861; g) T. Wang, B. J. Alfonso, J. A. Love, *Org. Lett.* **2007**, *9*, 5629 – 5631; h) K. Manabe, S. Ishikawa, *Synthesis* **2008**, 2645 – 2649; i) M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi, *J. Am. Chem. Soc.* **2008**, *130*, 12214 – 12215; j) M. R. Cargill, G. Sandford, A. J. Tadeusiak, D. S. Yufit, J. A. K. Howard, P. Kilickiran, G. Nelles, *J. Org. Chem.* **2010**, *75*, 5860 – 5866; k) M. Tobisu, T. Xu, T. Shimasaki, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 19505 – 19511; l) Z. Jin, Y.-J. Li, Y.-Q. Ma, L.-L. Qiu, J.-X. Fang, *Chem. Eur. J.* **2012**, *18*, 446 – 450; m) D. Yu, Q. Shen, L. Lu, *J. Org. Chem.* **2012**, *77*, 1798 – 1804; n) M. Ohashi, R. Doi, S. Ogoshi, *Chem. Eur. J.* **2014**, *20*, 2040 – 2048.

[5] For transition-metal-mediated vinylic C(sp^2)–F bond activation, see: a) T. Saeki, Y. Takashima, K. Tamao, *Synlett* **2005**, 1771 – 1774; b) M. E. Slaney, D. J. Anderson, M. J. Ferguson, R. McDonald, M. Cowie, *J. Am. Chem. Soc.* **2010**, *132*, 16544 – 16558; c) M. Takachi, Y. Kita, M. Tobisu, Y. Fukumoto, N. Chatani, *Angew. Chem. Int. Ed.* **2010**, *49*, 8717 – 8720; *Angew. Chem.* **2010**, *122*, 8899 – 8902; d) M. Ohashi, T. Kambara, T. Hatanaka, H. Saijo, R. Doi, S. Ogoshi, *J. Am. Chem. Soc.* **2011**, *133*, 3256 – 3259; e) M. Ohashi, M. Shibata, H. Saijo, T. Kambara, S. Ogoshi, *Organometallics* **2013**, *32*, 3631 – 3639; f) W. Xu, H. Sun, Z. Xiong, X. Li, *Organometallics* **2013**, *32*, 7122 – 7132. See also: g) K. Fuchibe, Y. Mayumi, N. Zhao, S. Watanabe, M. Yokota, J. Ichikawa, *Angew. Chem. Int. Ed.* **2013**, *52*, 7825 – 7828; *Angew. Chem.* **2013**, *125*, 7979 – 7982.

[6] For transition-metal-mediated allylic C(sp^3)–F bond activation, see: a) L. Hintermann, F. Läng, P. Maire, A. Togni, *Eur. J. Inorg. Chem.* **2006**, 1397 – 1412; b) T. Narumi, K. Tomita, E. Inokuchi, K. Kobayashi, S. Oishi, H. Ohno, N. Fujii, *Org. Lett.* **2007**, *9*, 3465 – 3468; c) A. Hazari, V. Gouverneur, J. M. Brown, *Angew. Chem. Int. Ed.* **2009**, *48*, 1296 – 1299; *Angew. Chem.* **2009**, *121*, 1322 – 1325; d) X. Pigeon, M. Bergeron, F. Barabé, P. Dubé, H. N. Frost, J.-F. Paquin, *Angew. Chem. Int. Ed.* **2010**, *49*, 1123 – 1127; *Angew. Chem.* **2010**, *122*, 1141 – 1145.

[7] For transition-metal-mediated reactions by β-fluorine elimination, see: [vinylic C(sp^2)–F bond activation] a) W. Heitz, A. Knebelkamp, *Makromol. Chem. Rapid Commun.* **1991**, *12*, 69 – 75; b) M. Fujiwara, J. Ichikawa, T. Okauchi, T. Minami, *Tetrahedron Lett.* **1999**, *40*, 7261 – 7265; c) K. Sakoda, J. Mihara, J. Ichikawa, *Chem. Commun.* **2005**, 4684 – 4686; d) J. Ichikawa, K. Sakoda, J. Mihara, N. Ito, *J. Fluorine Chem.* **2006**, *127*, 489 – 504; e) D. J. Harrison, G. M. Lee, M. C. Leclerc, I. Korobkov, R. T. Baker, *J. Am. Chem. Soc.* **2013**, *135*, 18296 – 18299; [allylic C(sp^3)–F bond activation] f) J. Ichikawa, R. Nadano, N. Ito, *Chem. Commun.* **2006**, 4425 – 4427; g) T. Miura, Y. Ito, M. Murakami, *Chem. Lett.* **2008**, *37*, 1006 – 1007.

[8] For transition-metal-catalyzed hydrodefluorination by β-fluorine elimination, see: a) A. A. Peterson, K. McNeill, *Organometallics* **2006**, *25*, 4938 – 4940; b) T. Braun, F. Wehmeier, K. Altenhöner, *Angew. Chem. Int. Ed.* **2007**, *46*, 5321 – 5324; *Angew. Chem.* **2007**, *119*, 5415 – 5418; c) M. F. Kühnel, D. Lentz, *Angew. Chem. Int. Ed.* **2010**, *49*, 2933 – 2936; *Angew. Chem.* **2010**, *122*, 2995 – 2998.

[9] For DFT study on β-fluorine elimination, see: H. Zhao, A. Ariafard, Z. Lin, *Organometallics* **2006**, *25*, 812 – 819.

[10] For review, see: a) J. Montgomery, *Acc. Chem. Res.* **2000**, *33*, 467 – 473; b) S. Ikeda, *Acc. Chem. Res.* **2000**, *33*, 511 – 519; c) J. Montgomery, *Angew. Chem. Int. Ed.* **2004**, *43*, 3890 – 3908; *Angew. Chem.* **2004**, *116*, 3980 – 3998; d) R. M. Moslin, K. Miller-Moslin, T. F. Jamison, *Chem. Commun.* **2007**, 4441 – 4449.

[11] For Ni-catalyzed reactions of electron-deficient alkenes with alkynes by oxidative cyclization, see: a) S. Ikeda, Y. Sato, *J. Am. Chem. Soc.* **1994**, *116*, 5975 – 5976; b) J. Montgomery, A. V. Savchenko, *J. Am. Chem. Soc.* **1996**, *118*, 2099 – 2100; c) I. Koyama, T. Kurahashi, S. Matsubara, *J. Am. Chem. Soc.* **2009**, *131*, 1350 – 1351; d) S. Ogoshi, A. Nishimura, M. Ohashi, *Org. Lett.* **2010**, *12*, 3450 – 3452; e) M. Takachi, N. Chatani, *Org. Lett.* **2010**, *12*, 5132 – 5134.

[12] For Ni-mediated [3+2] cycloaddition of enals, α,β-unsaturated esters, or cyclopropyl ketones with alkynes, see: a) S. K. Chowdhury, K. K. D. Amarasinghe, M. J. Heeg, J. Montgomery, *J. Am. Chem. Soc.* **2000**, *122*, 6775 – 6776; b) A. Herath, J. Montgomery, *J. Am. Chem. Soc.* **2006**, *128*, 14030 – 14031; c) M. Ohashi, T. Taniguchi, S. Ogoshi, *J. Am. Chem. Soc.* **2011**, *133*, 14900 – 14903; d) T. Tamaki, M. Ohashi, S. Ogoshi, *Angew. Chem. Int. Ed.* **2011**, *50*, 12067 – 12070; *Angew. Chem.* **2011**, *123*, 12273 – 12276.

[13] For the study on regioselectivity in oxidative cyclization between alkynes and aldehydes on Ni^0 complex, see: a) P. Liu, P. McCarren, P. H.-Y. Cheong, T. F. Jamison, K. N. Houk, *J. Am. Chem. Soc.* **2010**, *132*, 2050 – 2057; b) P. Liu, J. Montgomery, K. N. Houk, *J. Am. Chem. Soc.* **2011**, *133*, 6956 – 6959.

[14] NiF_2 species were not detected with the ^{19}F NMR measurement, presumably due to the paramagnetic property of Ni^{II}.

[15] For protonolysis of a nickelacyclopentene by treatment with acetic acid, see: J. J. Eisch, X. Ma, K. I. Han, J. N. Gitua, C. Krüger, *Eur. J. Inorg. Chem.* **2001**, 77 – 88.

[16] For a recent report on the direct synthesis of multi-substituted cyclopentadienes, see: W. Geng, C. Wang, J. Guang, W. Hao, W.-X. Zhang, Z. Xi, *Chem. Eur. J.* **2013**, *19*, 8657 – 8664.
[17] For selected papers on synthesis and application of metallocene complexes, see: a) R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965 – 994; b) J. A. Pool, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2003**, *125*, 2241 – 2251.
[18] For [4+2] cycloaddition of multi-substituted cyclopentadienes with electron-deficient alkenes or singlet oxygen, see: a) A. G. Griesbeck, T. Deufel, K. Peters, E.-M. Peters, H. G. von Schnering, *J. Org. Chem.* **1995**, *60*, 1952 – 1958; b) P. M. O'Neill, S. L. Rawe, R. C. Storr, S. A. Ward, G. H. Posner, *Tetrahedron Lett.* **2005**, *46*, 3029 – 3032; c) J. S. Lee, P. L. Fuchs, *J. Am. Chem. Soc.* **2005**, *127*, 13122 – 13123; d) W. Zhang, S. Luo, F. Fang, Q. Chen, H. Hu, X. Jia, H. Zhai, *J. Am. Chem. Soc.* **2005**, *127*, 18 – 19; e) A. V. Baranovsky, D. A. Bolibrukh, J. R. Bull, *Eur. J. Org. Chem.* **2007**, 445 – 454; f) M. Potowski, J. O. Bauer, C. Strohmann, A. P. Antonchick, H. Waldmann, *Angew. Chem. Int. Ed.* **2012**, *51*, 9512 – 9516; *Angew. Chem.* **2012**, *124*, 9650 – 9654.
[19] For synthesis of pyrylium cations from cyclopentadienes, see: G. L. Ning, X. C. Li, M. Munakata, W. T. Gong, M. Maekawa, T. Kamikawa, *J. Org. Chem.* **2004**, *69*, 1432 – 1434.

