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Ni(0)-Catalyzed Three-Component Coupling Reaction of Tetrafluoroethylene and *N*-Sulfonyl-Substituted Imines with Silanes via Aza-Nickelacycles

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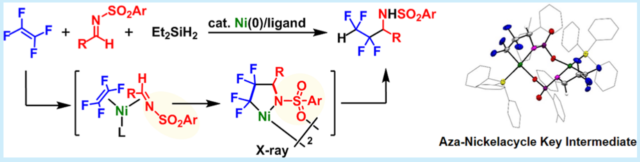
Supporting Information

ABSTRACT: A nickel-catalyzed three-component coupling reaction of tetrafluoroethylene (TFE) and *N*-sulfonyl-substituted imines with silanes that furnishes a variety of fluorine-containing amines is disclosed. Stoichiometric experiments revealed that the aza-nickelacycles generated upon oxidative cyclization of TFE and *N*-sulfonyl-substituted imines on Ni(0) were identified as the key intermediates in this catalytic reaction. A single-crystal X-ray diffraction analysis of such an aza-nickelacycle revealed that the O atom of the *N*-sulfonyl group stabilizes the key intermediate via coordination to the nickel center.



Organofluorine species are widely employed in commercial products owing to the unique properties endowed by the fluorine atom.[1,2] Highly fluorinated organic compounds have recently gained much attention due to their potential applications as physiologically active compounds and in advanced materials.[1] Synthetic routes to highly fluorinated organic compounds have been extensively explored, including the straightforward transformation of industrially available fluorine-containing feedstocks.[3] For this approach, tetrafluoroethylene (TFE) is an ideal starting material, given that it is economical and environmentally friendly with negligible global-warming potential.[4] However, the conventional use of TFE has been limited mostly to the preparation of polytetrafluoroethylene (PTFE) and copolymers with other alkenes.[4a,b,5]

Our research group has been focusing on the transformation of TFE by oxidative cyclization with Ni(0) as the key reaction step.[6−8] Such oxidative cyclization can efficiently produce a nickelacycle under concomitant formation of a C−C bond from various combinations of two π-components, where the generated nickelacycle serves as the key intermediate in such multicomponent coupling reactions.[9] Very recently, we have disclosed a Ni-catalyzed three-component coupling reaction of TFE and aldehydes with silanes via oxa-nickelacycle key intermediates.[7d] Thus, the development of a catalytic system involving reactions via aza-nickelacycle key intermediates is a logical extension. Herein, we report a three-component coupling reaction via an aza-nickelacycle generated from TFE and imines. Although Ni-catalyzed three-component coupling reactions have been reported with several combinations of two π-components,[10,11] the coupling of alkenes and imines remains challenging given that the simultaneous coordination of alkenes and imines, followed by oxidative cyclization, is difficult. Thus, we began our investigation using *N*-sulfonyl-substituted imines as model substrates for this catalytic reaction as we envisioned that they would (i) enhance the coordination ability by back-donation from Ni(0) to the *N*-sulfonyl-substituted imines and (ii) thermodynamically stabilize the generated aza-nickelacycle by coordination of the O atom of the *N*-sulfonyl group to the nickel center.[11d,12]

The reaction conditions for the Ni-catalyzed three-component coupling reaction of TFE and (*E*)-*N*-benzylidene benzenesulfonamide (**1a**) with silanes were optimized on the basis of a previous report.[7d] When a toluene solution of **1a** and Et_3SiH was exposed to TFE (3.5 atm, > 3.0 equiv) in the presence of $Ni(cod)_2$ (10 mol %; cod = 1,5-cyclooctadiene) and P^tBu_3 (10 mol %), followed by quenching with MeOH, *N*-(2,2,3,3-tetrafluoro-1-phenylpropyl)benzenesulfonamide (**2a**) was not obtained, even after 24 h at 100 °C (Table 1, entry 1); instead, *N*-benzylbenzenesulfonamide (**3a**) was generated as an undesired product in 13% yield. By employing Ph_2SiH_2 instead of Et_3SiH, **2a** was obtained in 55% yield under concomitant generation of **3a** in 36% yield (entry 2). Encouraged by this result, we studied the effect of the ligand for the system using Ph_2SiH_2. The yield of the reaction with PPh_3 was comparable to that with P^tBu_3 (entry 3). When the reaction was conducted in the presence of 20 mol % of PPh_3, the yield of **2a** decreased (entry 4). Control experiments showed that both $Ni(cod)_2$ and PPh_3 are necessary for this catalytic reaction (entries 5 and 6). Thus, further optimizations of the reaction conditions were carried out in the presence of 10 mol % of $Ni(cod)_2$ and PPh_3. Higher reaction temperatures (120 °C) and increased partial pressure of TFE (5.0 atm, > 4.0 equiv) slightly increased the yield of **2a** (entries 7 and 8). Finally, the effect of different silanes was examined. While $^tBu_2SiH_2$ was ineffective due to its steric bulk, Et_2SiH_2 provided

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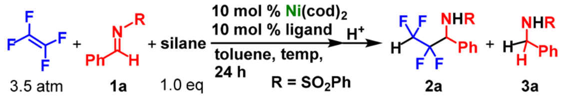
Table 1. Optimization of the Reaction Conditions for the Ni-Catalyzed Three-Component Coupling Reaction of TFE, *N*-Sulfonyl-Substituted Imine 1a, and Silanes[a]



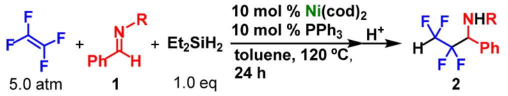
entry	ligand	silane	temp (°C)	yield (%)	
				2a	3a
1	P^tBu_3	Et_3SiH	100	0	13
2	P^tBu_3	Ph_2SiH_2	100	55	36
3	PPh_3	Ph_2SiH_2	100	51	29
4[b]	PPh_3	Ph_2SiH_2	100	40	58
5	none	Ph_2SiH_2	100	0	15
6[c]	PPh_3	Ph_2SiH_2	100	0	0
7	PPh_3	Ph_2SiH_2	120	53	55
8[d]	PPh_3	Ph_2SiH_2	120	57	42
9[d]	PPh_3	$^tBu_2SiH_2$	120	5	0
10[d]	PPh_3	Et_2SiH_2	120	80	6

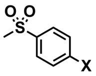
[a] General conditions: Ni(cod)$_2$ (0.010 mmol), ligand (0.010 mmol), **1a** (0.10 mmol), silane (0.10 mmol), and toluene (0.5 mL). Based on the ideal gas equation, an excess of TFE (3.5 atm) relative to **1a** was used; quenching agent: MeOH; yields determined by GC using *n*-hexadecane as the internal standard. [b] 20 mol % of PPh_3. [c] Without Ni(cod)$_2$. [d] 5.0 atm of TFE.

2a in 80% yield and improved the **2a**/**3a** product ratio (entries 9 and 10). Thus, we concluded that the optimal reaction conditions are those in entry 10.[13]

Under the optimal reaction conditions, we performed reactions with a variety of *N*-substituted imines (Table 2). The use of (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide (**1b**) instead of **1a** afforded comparable results, furnishing the target product (**2b**) in 70% yield (entry 2). Methoxy- and trifluoromethyl-substituted imines **1c** and **1d** afforded lower yields of the desired products (**2c**: 51% and **2d**: 62%; entries 3 and 4). Even though (*E*)-*N*-benzylidene-2-methylbenzenesulfonamide (**1e**) furnished the target product (**2e**) in 76% yield after 24 h, 73% yield was obtained after 6 h (entry 5). The use of (*E*)-*N*-benzylidene-2,4,6-trimethylbenzenesulfonamide (**1f**), however, furnished the target product **2f** in merely 38% yield. Employing (*E*)-*N*-benzylidenemethanesulfonamide (**1g**) afforded the target product in 67% yield within 6 h (entry 7). Neither (*E*)-*N*-benzylidenebenzenamine (**1h**) nor (*E*)-*tert*-butyl benzylidenecarbamate (**1i**) generated the corresponding target product (entries 8 and 9). *N*-Diphenylphosphine-substituted imine **1j** was ineffective, although it has been reported to accelerate the oxidative cyclization of alkynes and imines by thermodynamic stabilization of the generated aza-nickelacycle (entry 10).[12c,d] These results revealed that the *N*-sulfonyl group on the imines is essential for the catalytic reaction.

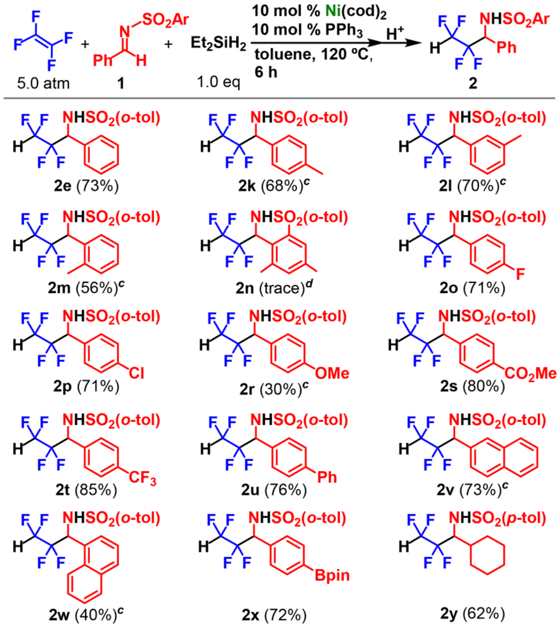
Table 2. Effect of the *N*-Substituent of the Imine on the Ni-Catalyzed Three-Component Coupling Reaction of TFE, Imines, and Et_2SiH_2[a]



entry	R			yield (%)
1	**1a**:		X = H	68
2	**1b**:		X = Me	70
3	**1c**:		X = OMe	51
4	**1d**:		X = CF_3	62
5	**1e**:	$-SO_2$(*o*-tol)		76 (73)[b]
6	**1f**:	$-SO_2$(Mes)		38
7	**1g**:	$-SO_2Me$		67[b]
8	**1h**:	-Ph		0
9	**1i**:	-Boc		0
10[c]	**1j**:	-P(O)Ph_2		0

[a] General conditions: Ni(cod)$_2$ (0.010 mmol), PPh_3 (0.010 mmol), **1** (0.10 mmol), Et_2SiH_2 (0.10 mmol), toluene (0.5 mL), and TFE (5.0 atm); quenching agent: MeOH; yields determined by ^{19}F NMR analysis using α,α,α-trifluorotoluene as the internal standard. [b] Run for 6 h. [c] Reaction conditions: Ni(cod)$_2$ (0.0050 mmol), PPh_3 (0.005 mmol), **1j** (0.050 mmol), Et_2SiH_2 (0.050 mmol), toluene (0.5 mL), and TFE (5.0 atm).

Scheme 1. Substrate Scope of the Ni-Catalyzed Three-Component Coupling Reaction of TFE, *N*-Sulfonyl-Substituted Imine 1, and Et_2SiH_2[a,b]

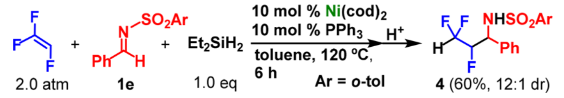


[a] General conditions: Ni(cod)$_2$ (0.05 mmol), PPh_3 (0.05 mmol), **1** (0.50 mmol), Et_2SiH_2 (0.50 mmol), toluene (2.5 mL), and TFE (5.0 atm); quenching agent: MeOH. [b] Isolated yield. [c] Run for 12 h. [d] Yield estimated by ^{19}F NMR analysis of the crude reaction mixture.

The scope and limitations of the catalytic reaction with respect to *N*-sulfonyl-substituted imines were examined under the optimal reaction conditions (Scheme 1).[14] The reaction of TFE, **1e**, and Et_2SiH_2 afforded **2e** in 73% isolated yield. The reactions with methyl-substituted imines (**1k**, **1l**, and **1m**) were completed within 12 h to furnish the corresponding amines (**2k**, **2l**, and **2m**) in moderate to good yield; however, trimethylphenylimine (**1n**) was not tolerated, and merely trace amounts of **2n** were detected by ^{19}F NMR analysis of the crude reaction mixture. Fluoro- (**1o**) and chloro-substituted imines (**1p**) afforded the corresponding amines (**2o** and **2p**), but bromo-substituted imine **1q** could not be used as the substrate due to the undesired oxidative addition of Ni(0) to the C−Br bond. The reaction with imine **1r**, which carries an electron-donating group, afforded the target product (**2r**) in 30% yield, while the reactions of imines with electron-withdrawing groups, including ester, trifluoromethyl, and phenyl groups (**1s**, **1t**, and **1u**) furnished the corresponding target products (**2s**, **2t**, and **2u**) in 80%, 85%, and 78% yield, respectively. Naphthylimines (**1v** and **1w**) also underwent this catalytic reaction to generate **2v** and **2w**. The *p*-boronate-substituted amine **2x**, which can be further used as a coupling agent, was successfully prepared from the reaction with a *p*-boronate-substituted imine (**1x**). Finally, the reaction with an aliphatic cyclic imine (**1y**) resulted in the formation of the target product **2y** in 62% yield.[14,15]

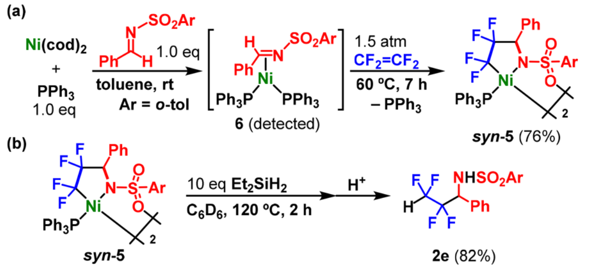
Then the scope and limitations of the catalytic reaction were evaluated using a different industrially available fluorinated olefin (Scheme 2).[15] The present Ni(0)/PPh_3 system catalyzed the reaction of trifluoroethylene with **1e** to generate the target product 2-methyl-*N*-(2,3,3-trifluoro-1-phenyl)propyl)-benzenesulfonamide (**4**) in 60% NMR yield (12:1 dr). However, the major product (the diastereomer) could not be isolated from the regioisomer, 2-methyl-*N*-(2,2,3-trifluoro-1-phenyl)propyl)benzenesulfonamide.

Scheme 2. Ni-Catalyzed Three-Component Coupling Reaction of Trifluoroethylene, 1e, and Et_2SiH_2



Stoichiometric experiments were performed in order to gain deeper insight into the reaction mechanism.[16] A toluene solution of $Ni(cod)_2$, PPh_3, and **1e** was exposed to TFE (1.5 atm, > 6.8 equiv) at 60 °C to produce a five-membered aza-nickelacycle dimer (***syn*-5**) in 76% isolated yield (Scheme 3a).

Scheme 3. Stoichiometric Experiments with 1e for (a) the Isolation of the Aza-nickelacycle and (b) Subsequent Reactions with Et_2SiH_2



When the reaction was conducted under higher pressure of TFE (5.0 atm, >18.7 equiv), the yield of ***syn*-5** was reduced to 53% and $(CF_2CF_2CF_2CF_2)Ni(PPh_3)_2$ was produced as a byproduct in 12% yield.[7a,16] Indeed, monitoring the synthesis of ***syn*-5** by NMR analysis revealed the formation of an η^2-*N*-sulfonyl-substituted imine nickel complex (**6**) both in the absence and presence of excess TFE.[12a] Subsequently, treatment of ***syn*-5** with Et_2SiH_2 in C_6D_6 at 120 °C for 2 h, followed by quenching with MeOH, afforded **2e** in 82% yield (Scheme 3b). Based on these results, we propose that the catalytic reaction proceeds via an aza-nickelacycle monomer or dimer generated from TFE and the *N*-sulfonyl-substituted imine.

The molecular structure of ***syn*-5** was unambiguously determined by single-crystal X-ray diffraction analysis. This analysis revealed that the O atom of the *N*-sulfonyl group occupies the vacant coordination site on the nickel center of another aza-nickelacycle monomer unit to stabilize the dimer complex in the solid state (Figure 1). This result contrasts with the findings of previous studies, where intramolecular coordination of the O atom of the *N*-sulfonyl group and the nickel center was observed.[12]

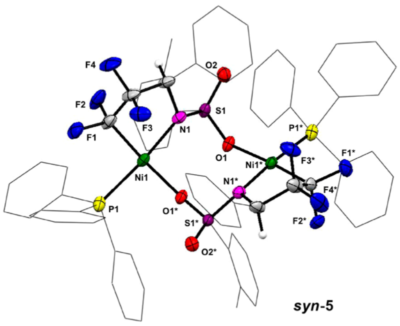
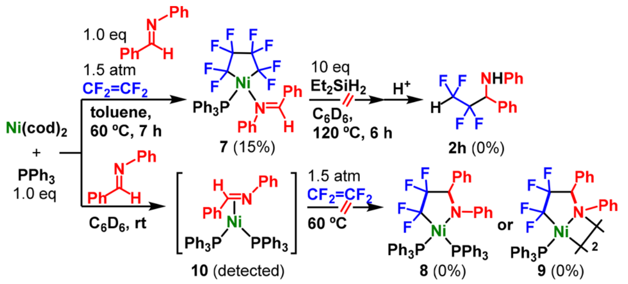
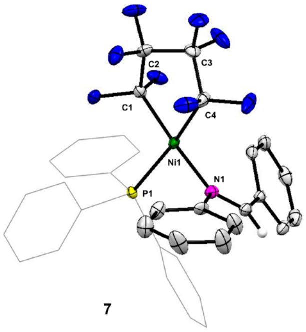


Figure 1. Molecular structure of ***syn*-5** with thermal ellipsoids at 30% probability (except for the organic substituents including the *o*-tolyl and phenyl groups); selected hydrogen atoms have been omitted for clarity.

The reaction of **1h** with $Ni(cod)_2$ and PPh_3 under an atmosphere of TFE (1.5 atm) produced octafluoronickelacyclopentane (**7**), which was generated via the oxidative cyclization of two molecules of TFE, in 15% yield (Scheme 4). The molecular structure of **7** exhibits a distorted square-planar geometry in the solid state, as confirmed by single-crystal X-ray diffraction analysis (Figure 2). The expected aza-

Scheme 4. Stoichiometric Experiments with 1h and Subsequent Reactions with Et_2SiH_2





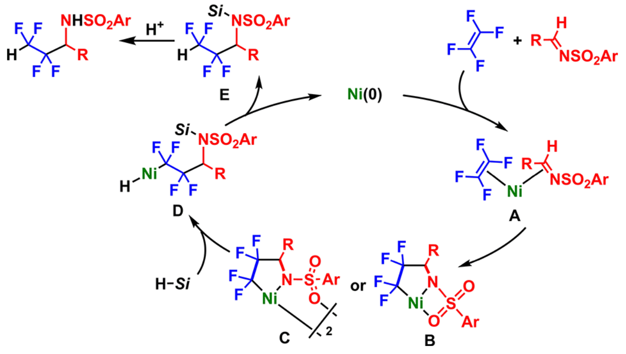
7

Figure 2. Molecular structure of **7** with thermal ellipsoids at 30% probability (except for the organic substituents of the PPh_3); selected hydrogen atoms have been omitted for clarity.

nickelacycles (**8** or **9**), formed by the oxidative cyclization of TFE and **1h**, were not obtained, while a η^2-*N*-phenylimine nickel complex (**10**) was observed by NMR analysis in C_6D_6 before exposure to TFE.[12a] In order to consider the possibility of retro-oxidative cyclization, the reaction of **7** with Et_2SiH_2 was explored. However, the target product (**2h**) was not obtained, even at 120 °C. These results indicate that the *N*-sulfonyl groups on the imines are crucial to accelerate the oxidative cyclization and generate the thermodynamically stabilized aza-nickelacycle intermediates.

On the basis of these results, a plausible reaction mechanism for the present nickel-catalyzed three-component coupling reaction is proposed in Scheme 5. A simultaneous coordination of TFE and the *N*-sulfonyl-substituted imine with Ni(0) would form η^2:η^2 nickel complex **A**. Then an oxidative cyclization would produce an aza-nickelacycle monomer (**B**) and/or dimer (***syn*-C** or ***anti*-C**) as key intermediates, which would be stabilized by coordination of the *N*-sulfonyl group. Afterward, transmetalation of the silane with **B**, ***syn*-C**, or ***anti*-C** would afford nickel hydride **D**. A reductive elimination on **D** would afford **E** under concomitant regeneration of the Ni(0) species. Finally, **E** could be protonated during the workup to give the target product. Alas, all of our attempts to isolate **E** have remained unsuccessful so far.

Scheme 5. Plausible Mechanism for the Ni-Catalyzed Three-Component Coupling Reaction of TFE, *N*-Sulfonyl-Substituted Imines, and Silanes



The reactivity of the reaction product **2k** was studied in order to demonstrate the utility of this catalytic reaction (Scheme 6). The reaction of **2k** with lithium diisopropyl amide (LDA), followed by quenching with MeOH, afforded trifluoro allylic amine **11k** in 82% isolated yield under concomitant generation of LiF. This product can be used as a co-monomer to tune the adhesive properties[17] and solubility[18] of fluorine-containing polymers such as PTFE on account of the amine group. Moreover, this product may serve as a versatile intermediate for the synthesis of various fluorinated compounds, since the trifluorovinyl moiety is active toward nucleophiles.[19] Therefore, this example shows the synthetic utility of the present catalytic system. In addition, although we attempted the deprotection of the sulfonyl group-substituted reaction product to give *N*-protonated amine, it was unfortunately unsuccessful.

Scheme 6. Utility of Fluorine-Containing Amines

In conclusion, we have developed a nickel-catalyzed three-component coupling reaction of TFE, *N*-sulfonyl-substituted imines, and Et_2SiH_2. Detailed mechanistic studies revealed aza-nickelacycles as key intermediates. The *N*-sulfonyl group on the imines is crucial for this catalytic reaction by enhancing the coordination ability of the imine to Ni(0) and stabilizing the resulting aza-nickelacycle intermediates. The obtained products can subsequently be transformed into valuable trifluoro allylic amines.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03674.

Detailed experimental procedures and spectral data for all new compounds (PDF)

Accession Codes

CCDC 1879548–1879549 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Yamabe, M. *Application of Fluoro Functional Materials*; CMC: Tokyo, 2006. (b) Kirsch, P. *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications*, 2nd ed.; Wiley-VCH: Weinheim, 2013. (c) Wang, J.; Sańchez-Rosello, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. Fluorine in Pharmaceutical Industry: Fluorine-Containing Drugs Introduced to the Market in the Last Decade (2001–2011). *Chem. Rev.* **2014**, *114*, 2432–2506. (d) Zhou, Y.; Wang, J.; Gu, Z.; Wang, S.; Zhu, W.; Aceña, J. L.; Soloshonok, V. A.; Izawa, K.; Liu, H. Next Generation of Fluorine-Containing Pharmaceuticals, Compounds Currently in Phase II–III Clinical Trials of Major Pharmaceutical Companies: New Structural Trends and Therapeutic Areas. *Chem. Rev.* **2016**, *116*, 422–518.

(2) (a) Smart, B. E. Fluorine substituent effects (on bioactivity). *J. Fluorine Chem.* **2001**, *109*, 3–11. (b) O'Hagan, D. Understanding organofluorine chemistry. An introduction to the C–F bond. *Chem. Soc. Rev.* **2008**, *37*, 308–319. (c) Ni, C.; Hu. The unique fluorine

effects in organic reactions: recent facts and insights into fluoroalkylations. *Chem. Soc. Rev.* **2016**, *45*, 5441−5454.

(3) For selected reviews, see: (a) Furin, G. G. Internal Perfluoroolefins in the Synthesis of Organofluorine Compounds. *Russ. J. Org. Chem.* **2002**, *38*, 921−961. (b) Sandford, G. Perfluoroalkanes. *Tetrahedron* **2003**, *59*, 437−454. (c) Weaver, J.; Senaweera, S. C−F activation and functionalization of perfluoro- and polyfluoroarenes. *Tetrahedron* **2014**, *70*, 7413−7428.

(4) (a) Park, J. D.; Benning, A. F.; Downing, F. B.; Laucius, J. F.; McHarness, R. C. Synthesis of Tetrafluorethylene - Pyrolisis of monochlorodifluoromethane. *Ind. Eng. Chem.* **1947**, *39*, 354−358. (b) Arcella, V.; Troglia, C.; Ghielmi, A. Hyflon Ion Membranes for Fuel Cells. *Ind. Eng. Chem. Res.* **2005**, *44*, 7646−7651. (c) Ameduri, B.; Boutevin, B. Copolymerization of fluorinated monomers: recent developments and future trends. *J. Fluorine Chem.* **2000**, *104*, 53−62. (d) Acerboni, G.; Beukes, J. A.; Jensen, N. R.; Hjorth, J.; Myhre, G.; Nielsen, C. J.; Sundet, J. K. Atmospheric degradation and global warming potentials of three perfluoroalkenes. *Atmos. Environ.* **2001**, *35*, 4113−4123.

(5) (a) Ohashi, M.; Kambara, T.; Hatanaka, T.; Saijo, H.; Doi, R.; Ogoshi, S. Palladium-Catalyzed Coupling Reactions of Tetrafluoroethylene with Arylzinc Compounds. *J. Am. Chem. Soc.* **2011**, *133*, 3256−3259. (b) Ohashi, M.; Shibata, M.; Saijo, H.; Kambara, T.; Ogoshi, S. Carbon−Fluorine Bond Activation of Tetrafluoroethylene on Palladium(0) and Nickel(0): Heat or Lewis Acidic Additive Promoted Oxidative Addition. *Organometallics* **2013**, *32*, 3631−3639. (c) Ohashi, M.; Saijo, H.; Shibata, M.; Ogoshi, S. Palladium-Catalyzed Base-Free Suzuki−Miyaura Coupling Reactions of Fluorinated Alkenes and Arenes via a Palladium Fluoride Key Intermediate. *Eur. J. Org. Chem.* **2013**, *2013*, 443−447. (d) Saijo, H.; Sakaguchi, H.; Ohashi, M.; Ogoshi, S. Base-Free Hiyama Coupling Reaction via a Group 10 Metal Fluoride Intermediate Generated by C−F Bond Activation. *Organometallics* **2014**, *33*, 3669−3672. (e) Saijo, H.; Ohashi, M.; Ogoshi, S. Fluoroalkylcopper(I) Complexes Generated by the Carbocupration of Tetrafluoroethylene: Construction of a Tetrafluoroethylene-Bridging Structure. *J. Am. Chem. Soc.* **2014**, *136*, 15158−15161. (f) Kikushima, K.; Sakaguchi, H.; Saijo, H.; Ohashi, M.; Ogoshi, S. Copper-mediated One-pot Synthesis of Trifluorostyrene Derivatives from Tetrafluoroethylene and Arylboronate. *Chem. Lett.* **2015**, *44*, 1019−1021. (g) Takahira, Y.; Morizawa, Y. Ruthenium-Catalyzed Olefin Cross-Metathesis with Tetrafluoroethylene and Analogous Fluoroolefins. *J. Am. Chem. Soc.* **2015**, *137*, 7031−7034. (h) Ohashi, M.; Adachi, T.; Ishida, N.; Kikushima, K.; Ogoshi, S. Synthesis and Reactivity of Fluoroalkyl Copper Complexes by the Oxycupration of Tetrafluoroethylene. *Angew. Chem., Int. Ed.* **2017**, *56*, 11911−11915. (i) Sakaguchi, H.; Uetake, Y.; Ohashi, M.; Niwa, T.; Ogoshi, S.; Hosoya, T. Copper-Catalyzed Regioselective Monodefluoroborylation of Polyfluoroalkenes en Route to Diverse Fluoroalkenes. *J. Am. Chem. Soc.* **2017**, *139*, 12855−12862. (j) Sakaguchi, H.; Ohashi, M.; Ogoshi, S. Fluorinated Vinylsilanes from the Copper-Catalyzed Defluorosilylation of Fluoroalkene Feedstocks. *Angew. Chem., Int. Ed.* **2018**, *57*, 328−332. (k) Li, L.; Ni, C.; Xie, Q.; Hu, M.; Wang, F.; Hu, J. TMSCF$_3$ as a Convenient Source of CF_2=CF_2 for Pentafluoroethylation, (Aryloxy)-tetrafluoroethylation, and Tetrafluoroethylation. *Angew. Chem., Int. Ed.* **2017**, *56*, 9971−9975.

(6) (a) Baker, R. T.; Beatty, R. P.; Farnham, W. B.; Wallace, R. L., Jr. Process for the manufacturing of selected halogenated hydrocarbons containing fluorine and hydrogen and compositions provided therein. U.S. Patent 5,670,679, 1997. (b) Baker, R. T.; Beatty, R. P.; Sievert, A. C.; Wallace, R. L., Jr. Process for the manufacture of fluorine-substituted hydrocarbons. U.S. Patent 6,242,658, 2001.

(7) (a) Ohashi, M.; Kawashima, T.; Taniguchi, T.; Kikushima, K.; Ogoshi, S. 2,2,3,3-Tetrafluoronickelacyclopentanes Generated via the Oxidative Cyclization of Tetrafluoroethylene and Simple Alkenes: A Key Intermediate in Nickel-Catalyzed C−C Bond-Forming Reactions. *Organometallics* **2015**, *34*, 1604−1607. (b) Ohashi, M.; Shirataki, H.; Kikushima, K.; Ogoshi, S. Nickel-Catalyzed Formation of Fluorine-Containing Ketones via the Selective Cross-Trimerization Reaction of Tetrafluoroethylene, Ethylene, and Aldehydes. *J. Am. Chem. Soc.* **2015**, *137*, 6496−6499. (c) Kawashima, T.; Ohashi, M.; Ogoshi, S. Nickel-Catalyzed Formation of 1,3-Dienes via a Highly Selective Cross-Tetramerization of Tetrafluoroethylene, Styrenes, Alkynes, and Ethylene. *J. Am. Chem. Soc.* **2017**, *139*, 17795−17798. (d) Shirataki, H.; Ohashi, M.; Ogoshi, S. Nickel-catalyzed Three-component Coupling Reaction of Tetrafluoroethylene and Aldehydes with Silanes via Oxa-Nickelacycles. *Eur. J. Org. Chem.* **2018**, DOI: 10.1002/ejoc.201801721.

(8) For rare expamles for the oxidative cyclization of TFE with other unsaturated compounds, see: (a) Kaschube, W.; Schröder, W.; Pörschke, K. R.; Angermund, K.; Krüger, C. Amin-Nickel-Komplexe VI. Synthese, Struktur und Reaktivität von (tmeda)Ni(C_2F_4). *J. Organomet. Chem.* **1990**, *389*, 399−408. (b) Schröder, W.; Bonrath, W.; Pörschke, K. R. Synthese und Reactivität von (2,6-$^{i}Pr_2$Ph-dad)Ni(C_2F_4). *J. Organomet. Chem.* **1991**, *408*, C25−C29. (c) Bennett, M. A.; Hockless, D. C. R.; Wenger, E. Generation of (2,3-.eta.)-Naphthalyne-Nickel(0) Complexes and Their Reactions with Unsaturated Molecules. *Organometallics* **1995**, *14*, 2091−2101. (d) Bennett, M. A.; Glewis, M.; Hockless, D. C. R.; Wenger, E. Successive insertion of tetrafluoroethylene and CO and oftetrafluoroethylene and acetylenes into aryne−nickel(0)bonds. *J. Chem. Soc., Dalton Trans.* **1997**, 3105−3114. (e) Ohashi, M.; Ueda, Y.; Ogoshi, S. Nickel(0)-Mediated Transformation of Tetrafluoroethylene and Vinylarenes into Fluorinated Cyclobutyl Compounds. *Angew. Chem., Int. Ed.* **2017**, *56*, 2435−2439.

(9) For selected reviews on the nickel-catalyzed reactions via a nickelacycle intermediate, see: (a) Ohashi, M.; Hoshimoto, Y.; Ogoshi, S. Aza-nickelacycle key intermediate in nickel(0)-catalyzed transformation reactions. *Dalton Trans* **2015**, *44*, 12060−12073. (b) Ogoshi, S. Highly Atom Economical Molecular Transformation via Hetero-Nickelacycle. *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1401−1406.

(10) For selected reviews on nickel-catalyzed multicomponent coupling reactions, see: (a) Saito, S.; Yamamoto, Y. Recent Advances in the Transition-Metal-Catalyzed Regioselective Approaches to Polysubstituted Benzene Derivatives. *Chem. Rev.* **2000**, *100*, 2901−2916. (b) Varela, J. A.; Saa, C. Construction of Pyridine Rings by Metal-Mediated [2 + 2 + 2] Cycloaddition. *Chem. Rev.* **2003**, *103*, 3787−3802. (c) Kotha, S.; Brahmachary, E.; Lahiri, K. Transition Metal Catalyzed [2 + 2+2] Cycloaddition and Application in Organic Synthesis. *Eur. J. Org. Chem.* **2005**, *2005*, 4741−4767. (d) Chopade, P. R.; Louie, J. [2 + 2+2] Cycloaddition Reactions Catalyzed by Transition Metal Complexes. *Adv. Synth. Catal.* **2006**, *348*, 2307−2327. (e) Heller, B.; Hapke, M. The fascinating construction of pyridine ringsystems by transition metal-catalysed [2 + 2 + 2] cycloaddition reactions. *Chem. Soc. Rev.* **2007**, *36*, 1085−1094. (f) Skucas, E.; Ngai, M.-Y.; Komanduri, V.; Krische, M. J. Enantiomerically Enriched Allylic Alcohols and Allylic Amines via C−C Bond-Forming Hydrogenation: Asymmetric Carbonyl and Imine Vinylation. *Acc. Chem. Res.* **2007**, *40*, 1394−1401. (g) Shibata, T.; Tsuchikama, K. Recent advances in enantioselective [2 + 2 + 2] cycloaddition. *Org. Biomol. Chem.* **2008**, *6*, 1317−1323. (h) Galan, B. R.; Rovis, T. Beyond Reppe: Building Substituted Arenes by [2 + 2+2] Cycloadditions of Alkynes. *Angew. Chem., Int. Ed.* **2009**, *48*, 2830−2834. (i) Reichard, H. A.; McLaughlin, M.; Chen, M. Z.; Micalizio, G. C. Regioselective Reductive Cross-Coupling Reactions of Unsymmetrical Alkynes. *Eur. J. Org. Chem.* **2010**, *2010*, 391−409.

(11) For rare examples for Ni-catalyzed reactions via azanickelacycles, see: (a) Patel, S. J.; Jamison, T. F. Catalytic Three-Component Coupling of Alkynes, Imines, and Organoboron Reagents. *Angew. Chem., Int. Ed.* **2003**, *42*, 1364−1367. (b) Patel, S. J.; Jamison, T. F. Asymmetric catalytic coupling of organoboranes, alkynes, and imines with a removable (trialkylsilyloxy)ethyl group-direct access to enantiomerically pure primary allylic amines. *Angew. Chem., Int. Ed.* **2004**, *43*, 3941−3944. (c) Yeh, C.−H.; Korivi, R. P.; Cheng, C.−H. Regioselective Synthesis of γ-Amino Esters, Nitriles, Sulfones, and Pyrrolidinones by Nickel-Catalyzed Reductive Coupling of Aldimines and Activated Alkenes. *Angew. Chem., Int. Ed.* **2008**, *47*, 4892−4895. (d) Zhou, C.−Y.; Zhu, S.−F.; Wang, L.−X.; Zhou, Q.−

L. Enantioselective Nickel-Catalyzed Reductive Coupling of Alkynes and Imines. *J. Am. Chem. Soc.* **2010**, *132*, 10955−10957. (e) Rajeshkumar, V.; Chuang, S.−C. Evolution of Late Transition-Metal-Catalyzed Intermolecular Reductive Coupling Reaction of [60]Fullerene and *N*-Sulfonylaldimines: Competing Formation of Hydrobenzylated [60]Fullerenes and 1,2-Dihydrofullerene. *Eur. J. Org. Chem.* **2012**, *2012*, 3795−3805.

(12) (a) Ogoshi, S.; Ikeda, H.; Kurosawa, H. Formation of an Azanickelacycle by Reaction of an Imine and an Alkyne with Nickel(0): Oxidative Cyclization, Insertion, and Reductive Elimination. *Angew. Chem., Int. Ed.* **2007**, *46*, 4930−4932. (b) Ohashi, M.; Kishizaki, O.; Ikeda, H.; Ogoshi, S. Ni(0)-Catalyzed Formation of Azaaluminacyclopentenes via Azanickelacyclopentenes: A Unique Nickel/Aluminum Double Transmetalation Reaction. *J. Am. Chem. Soc.* **2009**, *131*, 9160−9161. (c) Hoshimoto, Y.; Ohata, T.; Ohashi, M.; Ogoshi, S. Nickel-Catalyzed Synthesis of *N*-Aryl-1,2-dihydropyridines by [2 + 2+2] Cycloaddition of Imines with Alkynes through T-Shaped 14-Electron Aza-Nickelacycle Key Intermediates. *Chem. - Eur. J.* **2014**, *20*, 4105−4110. (d) Hoshimoto, Y.; Ohata, T.; Sasaoka, Y.; Ohashi, M.; Ogoshi, S. Nickel(0)-Catalyzed [2 + 2 + 1] Carbonylative Cycloaddition of Imines and Alkynes or Norbornene Leading to γ-Lactams. *J. Am. Chem. Soc.* **2014**, *136*, 15877−15880. (e) Liu, R.−R.; Wang, D.−J.; Wu, L.; Xiang, B.; Zhang, G.−Q.; Gao, J.−R.; Jia, Y.−X. Nickel-Catalyzed Enantioselective Addition of Styrenes to Cyclic *N*-Sulfonyl α-Ketiminoesters. *ACS Catal.* **2015**, *5*, 6524−6528. (f) Hoshimoto, Y.; Ashida, K.; Sasaoka, Y.; Kumar, R.; Kamikawa, K.; Verdaguer, X.; Riera, A.; Ohashi, M.; Ogoshi, S. Efficient Synthesis of Polycyclic γ-Lactams by Catalytic Carbonylation of Ene-Imines via Nickelacycle Intermediates. *Angew. Chem., Int. Ed.* **2017**, *56*, 8206−8210. (g) Xiao, L.−J.; Zhao, C.−Y.; Cheng, L.; Feng, B.−Y.; Feng, W.−M.; Xie, J.−H.; Xu, X.−F.; Zhou, Q.−L. Nickel(0)-Catalyzed Hydroalkenylation of Imines with Styrene and Its Derivatives. *Angew. Chem., Int. Ed.* **2018**, *57*, 3396−3400.

(13) See the SI for further optimization of the catalytic reaction.

(14) Preparation of the 2-methylbenzenesulfonyl group substituted cyclohexyl imine was unsuccessful due to the hydrolysis.

(15) See the SI for details about substrate coverage including other ketimines, enones, and fluorinated olefins.

(16) See the SI for details about stoichiometric reactions.

(17) Kobayashi, S.; Song, J.; Silvis, H. C.; Macosko, C. W.; Hillmyer, M. A. Amino-Functionalized Polyethylene for Enhancing the Adhesion between Polyolefins and Polyurethanes. *Ind. Eng. Chem. Res.* **2011**, *50*, 3274−3279.

(18) Alfred, S. F.; Lienkamp, K.; Madkour, A. E.; Tew, G. N. Water-soluble ROMP polymers from amine-functionalized norbornenes. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6672−6676.

(19) Park, H. M.; Uegaki, T.; Konno, T.; Ishihara, T.; Yamanaka, H. Chemistry of fluorinated enamines. Novel reaction of trifluoromethylated enamine with grignard reagents. *Tetrahedron Lett.* **1999**, *40*, 2985−2988.

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Org. Lett. XXXX, XXX, XXX−XXX