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Intramolecular Construction of Trifluoromethyl Group by the Palladium-Catalyzed Alkylation of 2,3,3-Trifluoroallylic Carbonates with Indoles

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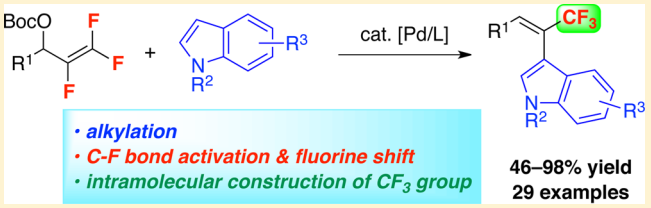
Supporting Information

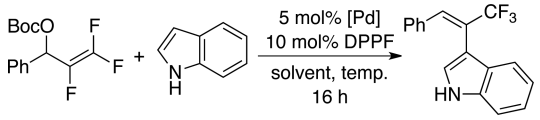
ABSTRACT: The palladium-catalyzed alkylation reaction of 2,3,3-trifluoroallylic carbonates with indoles afforded a trifluoromethyl group possessing 3-substituted indole derivatives. The reaction proceeded via attack of the C-3 carbon of the indoles onto the C-2 position of the allylic moiety and intramolecular construction of the trifluoromethyl group by the intramolecular fluorine atom shift from the C-2 position to the C-3 position of the allyl unit.



Fluorine-containing organic compounds have attracted much interest in the fields of pharmaceuticals and agrochemicals,[1] and the trifluoromethyl group is also an important constituent of these compounds. There are several methods available to introduce the trifluoromethyl group into organic compounds, and several trifluoromethylation reagents have also been developed.[2] On the other hand, during the course of our study of the palladium-catalyzed reaction of fluorinated allylic compounds with nucleophiles,[3−5] we recently reported an unusual intramolecular construction of the trifluoromethyl group during the palladium-catalyzed reaction of 2,3,3-trifluoroallylic esters with amines.[3b] Generally, the palladium-catalyzed reaction of allylic compounds with nucleophiles provides allylic substituted products or cyclopropane derivatives,[6,7] and we also demonstrated the palladium-catalyzed branch-selective allylic alkylation of 2,3,3-trifluoroallylic acetates with malonate anions.[3a] However, during the palladium-catalyzed reaction of 2,3,3-trifluoroallylic esters with amines, we revealed that the amine nucleophiles were introduced at the C-2 position of the allylic moiety and the trifluoromethyl group was constructed by the fluorine atom shift from the C-2 position to the C-3 position.[3b] As part of our program to develop this intramolecular construction of trifluoromethyl group, we examined the reaction of 2,3,3-trifluoroallylic esters with other types of nucleophiles. As we previously reported, the reaction of 2,3,3-trifluoroallylic esters with malonate anions provided the allylic alkylated product,[3a] but we revealed that the reaction with the indole afforded the trifluoromethyl group possessing 3-substituted indole derivatives by the attack of the C-3 carbon of the indoles onto the C-2 position of the allylic moiety and intramolecular fluorine atom shift. Therefore, we report the palladium-catalyzed alkylation of 2,3,3-trifluoroallylic esters with indoles and synthesis of the trifluoromethyl group containing 3-substituted indole derivatives.

We initially examined the reaction of the 2,3,3-trifluoroallylic carbonate **1a** with indole (**2a**) using the $Pd(OAc)_2$/DPPF catalyst in dioxane at 60 °C, which was effective for the reaction of **1a** with amines,[3b] but the reaction did not occur (Table 1, entry 1). However, when the reaction temperature was increased to 100 °C, we succeeded in obtaining the desired trifluoromethyl group containing product **3aa** in 73% NMR yield (entry 2). To increase the yield of **3aa**, we examined other reaction conditions, which revealed that $[Pd(C_3H_5)(cod)]BF_4$ or $[Pd(PhC_3H_4)(cod)]BF_4$ with DPPF afforded higher yields

Table 1. Palladium-Catalyzed Reaction of 2,3,3-Trifluoroallylic Carbonate 1a with Indole (2a)[a]



1a **2a** **3aa**

entry	[Pd]	solvent	temp (°C)	NMR yield[b] (%)
1	$Pd(OAc)_2$	dioxane	60	0
2	$Pd(OAc)_2$	dioxane	100	73
3	$[Pd(PhC_3H_4)(cod)]BF_4$	dioxane	100	87
4	$[Pd(C_3H_5)(cod)]BF_4$	dioxane	100	85
5[c]	$[Pd(PhC_3H_4)(cod)]BF_4$	dioxane	100	87
6[c]	$[Pd(C_3H_5)(cod)]BF_4$	dioxane	100	49
7	$[Pd(PhC_3H_4)(cod)]BF_4$	toluene	100	86
8	$[Pd(C_3H_5)(cod)]BF_4$	toluene	100	>98 (90)[d]

[a]Reaction conditions: **1a** (0.17 mmol), **2a** (0.24 mmol), [Pd] (0.0085 mmol), and DPPF (0.017 mmol) in solvent (1.0 mL) at the indicated temperature for 16 h. [b]Yields are determined by ^{19}F NMR of crude materials using an internal standard (trifluoromethylbenzene). [c]5 mol % of $AgBF_4$ was added. [d]Isolated yield is shown in parentheses.

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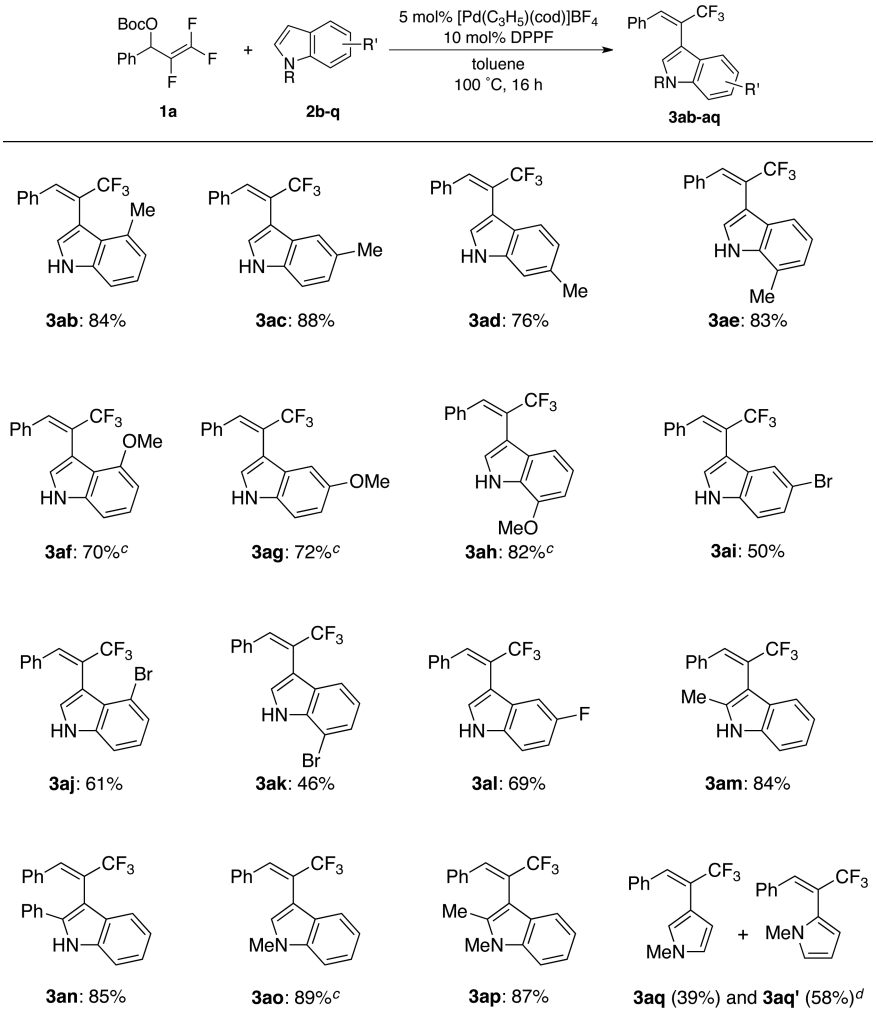
Table 2. Palladium-Catalyzed Reaction of 1a with Indoles 2b−p or *N*-Methylpyrrole (2q)[a,b]



[a]Reaction conditions: **1a** (0.17 mmol), **2b−q**, or **2q** (0.24 mmol), $[Pd(C_3H_5)(cod)]BF_4$ (0.0085 mmol), and DPPF (0.017 mmol) in toluene (1.0 mL) at 100 °C for 16 h. [b]Yields are isolated yield after silica gel column chromatography. [c]Dioxane was used instead of toluene. [d]$Pd(OAc)_2$ (2.5 mol %), DPPF (5 mol %), and dioxane were used.

(entries 3 and 4). Regarding our previously reported amination reaction, the addition of a catalytic amount of $AgBF_4$ effectively increased the yield, but the addition of silver salts was not effective for the present alkylation reaction (entries 5 and 6). However, to our delight, we succeeded in obtaining a high yield (>98% NMR yield, 90% isolated yield) by changing the solvent from dioxane to toluene when $[Pd(C_3H_5)(cod)]BF_4$ was used as the catalyst (entry 8).

With the optimal conditions in hand, we investigated the $[Pd(C_3H_5)(cod)]BF_4$/DPPF-catalyzed alkylation of **1a** with several indoles, and the results are summarized in Table 2. Typically, the reaction was carried out in toluene, but we confirmed that some reactions gave better results when dioxane was used as the solvent. For example, the reactions of **1a** with 4-, 5-, 6-, or 7-methylindole **2b−e** in toluene provided the desired products **3ab**, **3ac**, **3ad**, and **3ae** in 84%, 88%, 76%, and 83% yields, respectively. On the other hand, the reaction with 4-methoxyindole (**2f**) in toluene resulted in a 53% yield, but a higher yield (70%) was obtained when the solvent was changed from toluene to dioxane. The reactions with other methoxyindoles, **2g** and **2h**, also gave better results in dioxane as the solvent and provided the intended products, **3ag** and **3ah**, in 72% and 82% yields, respectively. We further examined the reactions with 4-, 5-, or 7-bromo- or 5-fluoroindoles **2i−l** and succeeded in obtaining the corresponding products, **3ai−al**, in acceptable yields (46−69%). The reactions with 2-substituted indoles, **2m** and **2n**, also afforded the desired products, **3am** and **3an**, in 84% and 85% yields, respectively. Furthermore, we revealed that the reaction of **1a** with *N*-methylindoles (**2o** and **2p**) also smoothly proceeded and succeeded in obtaining the intended 3-substituted *N*-methylindole derivatives **3ao**[8] and **3ap** in good yields, respectively. We further examined the reaction with *N*-methylpyrrole (**2q**) and confirmed that the modified palladium catalysts produced **3aq** and **3aq′** as a mixture of two regioisomers (**3aq** and **3aq′**).[9]

We next demonstrated the palladium-catalyzed reaction of several allylic carbonates **1b−i**, which possess several substituents at the C-1 position of the allylic carbonates, with the indole (**2a**) or *N*-methylindole (**2o**). As shown in Table 3, the reactions of **1b** or **1c**, which possess electron-donating groups on the benzene ring, with **2a** provided **3ba** and **3ca** in 63% and 66% yields, respectively. The reactions of the allylic carbonate **1d**, which has an electron-withdrawing group on the benzene ring, also formed the intended product **3da** in 72% yield. On the other hand, some reactions again provided a higher yield when the reaction solvent was changed from

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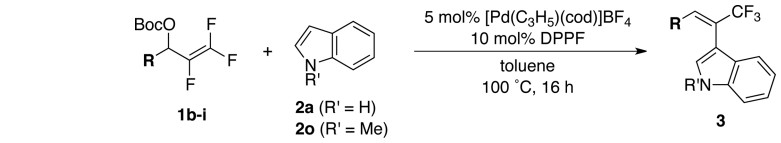
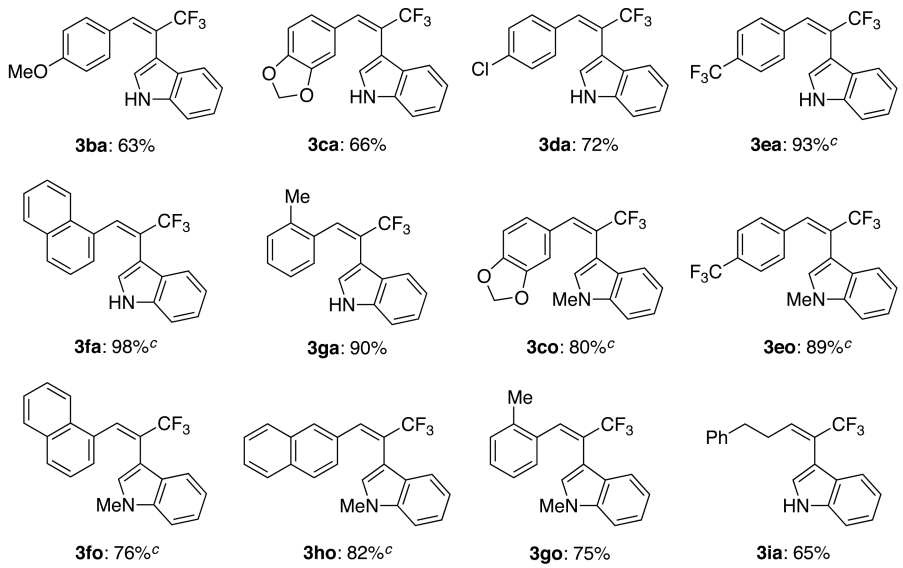
Table 3. Palladium-Catalyzed Reaction of 1b−i with 2a or 2o[a,b]





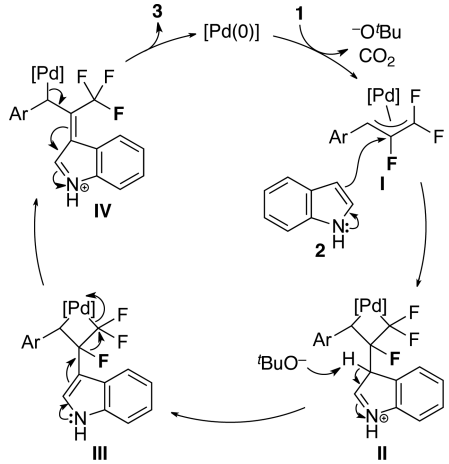
[a]Reaction conditions: **1b−i** (0.17 mmol), **2a** or **2q** (0.24 mmol), $[Pd(C_3H_5)(cod)]BF_4$ (0.0085 mmol), and DPPF (0.017 mmol) in toluene (1.0 mL) at 100 °C for 16 h. [b]Yields are isolated yield after silica gel column chromatography. [c]Dioxane was used instead of toluene.

toluene to dioxane. For example, the reaction of **1e**, which possessed a trifluoromethyl group on the benzene ring, with **2a** in toluene afforded the intended product **3ba** in 78% NMR yield, but the yield increased to 93% when the dioxane was used as the solvent. The reactions of the 1-naphthyl- or *o*-tolyl-substituted allylic carbonates, **1f** and **1g**, also gave the desired products, **3fa** and **3ga**, in 98% and 90% yields, respectively. We also examined the reaction with *N*-methylindole (**2o**) and succeeded in obtaining the desired products, such as **3co**, **3eo**, **3fo**, **3ho**, and **3go**, in the range of 75−89% yields. Furthermore, we confirmed that the present catalyst system allowed the reaction of the alkyl-substituted 2,3,3-trifluoroallylic carbonate **1i** and produced **3ia** in an acceptable yield (65%).

Unfortunately, the exact reaction mechanism is still not clear, but we postulate that the present alkylation reaction with indoles also proceeded through a pathway similar to our reported amination reaction.[3b] Therefore, we outlined one possible reaction pathway in Scheme 1. The oxidative addition of trifluoroallylic carbonate **1** to Pd(0) affords trifluoro-π-allylpalladium complex **I**, and the attack of the C-3 carbon of the indole onto the C-2 position of the allylic moiety provides palladacyclobutane **II**. The reaction of complex **II** with *tert*-butoxy anion may form species **III**, and then an intramolecular fluorine atom shift from the C-2 position to the C-3 position occurs immediately. Finally, the palladium complex **IV**, which might be unstable, gives a desired product **3** and regenerates Pd(0). Furthermore, our previous report with amine and the present results with indoles suggest that the presence of a heteroatom, which has lone pair, in the nucleophiles might be necessary to cause the intramolecular fluorine atom shift in the palladacyclobutane intermediates **III**.[10]

In conclusion, we demonstrated the palladium-catalyzed alkylation of 2,3,3-trifluoroallylic carbonates with indoles and succeeded in obtaining the trifluoromethyl group containing 3-substituted indole derivatives through the intramolecular fluorine atom shift. Further studies of the mechanistic details and development of related reactions with other types of nucleophiles, such as *O*- or *S*-nucleophiles, are currently underway in our group.

Scheme 1. Possible Reaction Mechanism



EXPERIMENTAL SECTION

General Information. All manipulations were carried out under a nitrogen atmosphere. NMR spectra were recorded at 500 MHz (for ^1H), 125 MHz (for ^{13}C), and 470 MHz (for ^{19}F). Chemical shifts are reported in δ referenced to an internal $SiMe_4$ standard for ^1H NMR and an internal C_6F_6 standard for ^{19}F NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. All NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted. The

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NMR yields were determined by ^{19}F NMR using an internal standard (trifluoromethylbenzene). HRMS spectra were recorded using a spectrometer with a TOF mass analyzer and an ESI ion source. All 2,3,3-trifluoroallylic carbonates **1a**–**i** were prepared according to the literature.[3,11] $[Pd(C_3H_5)(cod)]BF_4$ and $[Pd(PhC_3H_4)(cod)]BF_4$ were prepared according to the reported procedure.[12] All other chemicals including DPPF and silver salts were purchased from commercial sources and used without further purification.

General Procedure for the Palladium-Catalyzed Alkylation of 1 with Indoles 2. The reaction conditions and results are shown in Tables 1–3. A typical procedure is given for the reaction of *tert*-butyl (2,3,3-trifluoro-1-phenylallyl)carbonate (**1a**) with indole (**2a**) (Table 1, entry 8). To a solution of $[Pd(C_3H_5)(cod)]BF_4$ (2.9 mg, 0.0085 mmol), DPPF (9.4 mg, 0.017 mmol), and *tert*-butyl (2,3,3-trifluoro-1-phenylallyl)carbonate (**1a**) (50 mg, 0.17 mmol) in toluene (1.0 mL) was added indole (**2a**) (28 mg, 0.24 mmol), then the reaction mixture was stirred at 100 °C for 16 h. The reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The NMR yield (trifluoromethylbenzene as an internal standard) was determined to be 98% yield by 500 MHz ^1H NMR for crude material. The residue was chromatographed on silica gel (hexane/EtOAc = 97/3) to give 44 mg (90%) of **3aa** as a white solid.

*(E)-3-(3,3,3-Trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3aa**).* Isolated yield: 90% (44 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 100–102 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.00 (t, J = 7.5 Hz, 1H), 7.08–7.11 (m, 2H), 7.14–7.16 (m, 3H), 7.17–7.20 (m, 2H), 7.26–7.27 (m, 1H), 7.36 (s, 1H), 7.40 (d, J = 9.0 Hz, 1H), 8.32 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 107.9, 111.2, 120.3, 120.4, 122.6, 123.0 (q, J_{CF} = 30.1 Hz), 124.1 (q, J_{CF} = 275.8 Hz), 124.4, 126.0, 128.1, 128.7, 129.6, 133.5 (q, J_{CF} = 6.0 Hz), 134.3, 136.0. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.31 (s, 3F). IR (KBr): 3407, 3055, 1655, 1531, 1458, 1385, 1272, 931, 832, 715, 632 cm^{-1}. HRMS (ESI): m/z calcd for $[M - H]^-$ $C_{17}H_{11}F_3N$ 286.08435, found 286.08456.

*(E)-4-Methyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ab**).* Isolated yield: 84% (43 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 119–120 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.85 (d, J = 7.0 Hz, 1H), 7.09–7.19 (m, 7H), 7.23–7.27 (m, 1H), 7.40 (s, 1H), 8.31 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.6, 107.4, 109.2, 121.9, 122.7, 123.7, 123.9 (q, J_{CF} = 273.4 Hz), 124.5(q, J_{CF} = 30.1 Hz), 125.7, 128.4, 129.0, 129.8, 131.3, 134.1, 135.2 (q, J_{CF} = 5.9 Hz), 136.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ 94.79 (s, 3F). IR (KBr): 3397, 3059, 2922, 2854, 1955, 1905, 1831, 1650, 1611, 1536, 1452, 1332, 935, 825, 716, 627 cm^{-1}. HRMS (ESI): m/z calcd for $[M - H]^-$ $C_{18}H_{13}F_3N$ 300.10000, found 300.10298.

*(E)-5-Methyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ac**).* Isolated yield: 88% (45 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 154–155 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 3H), 6.98–7.03 (m, 2H), 7.08–7.11 (m, 2H), 7.14–7.16 (m 3H), 7.19–7.20 (m, 1H), 7.28 (d, J_{CF} = 8.0 Hz, 1H), 7.34 (s, 1H), 8.22 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.4, 107.3, 110.8, 120.0, 123.2 (q, J_{CF} = 30.1 Hz), 124.2, 124.3 (q, J_{CF} = 273.4 Hz), 124.4, 126.4, 128.1, 128.6, 129.6, 129.7, 133.5 (q, J_{CF} = 5.9 Hz), 134.3, 134.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.33 (s, 3F). IR (KBr): 3416, 3030, 1644, 1535, 1484, 1449, 1274, 1151, 1102, 937, 894, 801, 755, 692 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{18}H_{15}F_3N$ 302.11566, found 302.11776.

*(E)-6-Methyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ad**).* Isolated yield: 76% (39 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 90–91 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 6.82 (d, J = 8.0 Hz, 1H), 7.06–7.14 (m 8H), 7.34 (s, 1H), 8.15 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6, 107.7, 111.1, 119.9, 122.1, 123.2 (q, J_{CF} = 30.1 Hz), 123.7, 123.9, 124.2 (q, J_{CF} = 273.5 Hz), 128.1, 128.6, 129.7, 132.4, 133.4 (q, J_{CF} = 6.0 Hz) 134.4, 136.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.24 (s, 3F). IR (KBr): 3422, 3143, 3032, 2922, 1877, 1713, 1625, 1577, 1538, 1450, 1333, 936, 836, 801, 752, 695 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{18}H_{15}F_3N$ 302.11566, found 302.11830.

*(E)-7-Methyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ae**).* Isolated yield: 83% (42 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 80–81 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 2.51 (s, 3H), 6.91 (t, J = 7.5 Hz 1H), 6.99 (d, J = 7.5 Hz 1H), 7.05–7.16 (m, 6H), 7.24–7.25 (m, 1H), 7.35 (s, 1H), 8.21 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.4, 108.2, 118.0, 120.4, 120.5, 123.0, 123.1 (q, J_{CF} = 30.0 Hz), 124.1, 129.7, 124.2 (q, J_{CF} = 273.4 Hz), 124.1, 125.6, 128.1, 128.6, 129.7, 133.4 (q, J_{CF} = 5.9 Hz), 134.3, 135.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.23 (s, 3F). IR (KBr): 3441, 3053, 1654, 1615, 1532, 1496, 1432, 1385, 1274, 895, 782, 718, 646 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{18}H_{15}F_3N$ 302.11566, found 302.11816.

*(E)-4-Methoxy-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3af**).* Isolated yield: 70% (38 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 159–160 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 3.59 (s, 3H), 6.44 (d, J = 7.5 Hz, 1H), 7.00–7.16 (m, 8H), 7.27 (s, 1H), 8.24 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 100.7, 104.3, 106.8, 117.3, 122.7, 123.6, 124.1 (q, J_{CF} = 273.5 Hz), 124.2 (q, J_{CF} = 30.1 Hz), 127.9, 128.2, 129.5, 134.0 (q, J_{CF} = 5.9 Hz), 135.1, 137.6, 154.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.33 (s, 3F). IR (KBr): 3399, 3011, 2840, 1583, 1538, 1509, 1332, 1274, 1213, 1091, 820, 743, 630 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{18}H_{15}F_3NO$ 318.11058, found 318.11171.

*(E)-5-Methoxy-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ag**).* Isolated yield: 72% (39 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 126–127 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 3.52 (s, 3H), 6.46 (s, 1H), 6.81 (dd, J = 9.0 Hz, 2.5 Hz, 1H), 7.09–7.18 (m, 5H), 7.24–7.27 (m, 2H), 7.34 (s, 1H), 8.22 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4, 101.8, 107.6, 111.9, 113.2, 123.1 (q, J_{CF} = 30.1 Hz), 124.3 (q, J_{CF} = 273.5 Hz), 125.0, 126.2, 128.2, 128.5, 129.5, 130.9 132.7 (q, J_{CF} = 6.0 Hz), 134.6, 154.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.34 (s, 3F). IR (KBr): 3419, 3016, 2954, 1623, 1582, 1527, 1455, 1273, 800, 713, 673 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{18}H_{15}F_3NO$ 318.11058, found 318.11147.

*(E)-7-Methoxy-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ah**).* Isolated yield: 82% (44 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 107–108 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 3.92 (s, 3H), 6.62 (dd, J = 7.8 Hz, 3.0 Hz 1H), 6.79–6.81 (m, 1H), 6.89–6.92 (m, 1H), 7.07–7.21 (m, 6H), 7.34 (s, 1H), 8.52 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.3, 102.3, 108.2, 113.0, 120.6, 123.1 (q, J_{CF} = 30.1 Hz), 123.9, 124.2 (q, J_{CF} = 273.5 Hz), 126.7, 127.4, 128.1, 128.6, 129.7, 133.4 (q, J_{CF} = 5.9 Hz), 134.3, 146.0. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.21 (s, 3F). IR (KBr): 3432, 3067, 2940, 2839, 1631, 1581, 1530, 1502, 1419, 1365, 1208, 924, 881, 829, 760, 698 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{18}H_{15}F_3NO$ 318.11058, found 318.11040.

*(E)-5-Bromo-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ai**).* Isolated yield: 50% (31 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 93–94 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.11–7.21 (m, 5H), 7.25–7.26 (m, 3H), 7.31 (s, 1H), 7.37–7.38 (m, 1H), 8.34 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 108.0, 110.8, 114.4, 122.9 (q, J_{CF} = 30.1 Hz), 123.6, 123.8 (q, J_{CF} = 273.5 Hz), 125.0, 125.3, 125.9, 128.2, 128.8, 129.7, 134.4, 136.5 (q, J_{CF} = 5.9 Hz), 137.0. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.18 (s, 3F). IR (KBr): 3423, 1708, 1274, 1157, 886, 798, 755, 693 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{17}H_{12}BrF_3N$ 366.01053, found 366.01297.

*(E)-4-Bromo-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3aj**).* Isolated yield: 61% (38 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from

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diethyl ether at room temperature. Mp: 110−111 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01−7.14 (m, 7H), 7.25−7.33 (m, 2H), 7.38−7.40 (m, 1H), 8.31 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 107.5, 112.7, 113.7, 122.3 (q, J_{CF} = 30.1 Hz), 122.8, 124.0 (q, J_{CF} = 273.4 Hz), 125.5, 125.6, 127.8, 128.2, 128.9, 129.5, 134.0, 134.2 (q, J_{CF} = 6.0 Hz), 134.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.23 (s, 3F). IR (KBr): 3427, 1657, 1612, 1560, 1480, 1427, 1271, 1211, 1157, 936, 777, 743, 692 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M + H]^+$ $C_{17}H_{12}BrF_3N$ 366.01053, found 366.01203.

*(E)-7-Bromo-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ak**).* Isolated yield: 46% (29 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 88−89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86 (t, *J* = 8.0 Hz, 1H), 7.08−7.17 (m, 6H), 7.31−7.33 (s, 2H), 7.37−7.38 (m, 1H), 8.48 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 104.7, 109.1, 119.6, 121.5, 122.7 (q, J_{CF} = 30.1 Hz), 124.0 (q, J_{CF} = 273.5 Hz), 124.9, 125.0, 127.2, 128.3, 128.9, 129.6, 134.0, 134.1 (q, J_{CF} = 5.9 Hz), 134.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.16 (s, 3F). IR (KBr): 3407, 3136, 3064, 1789, 1750, 1616, 1557, 1489, 1433, 1213, 934, 825, 776, 735, 696 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M + Na]^+$ $C_{17}H_{11}BrF_3NNa$ 387.99247, found 387.99303.

*(E)-5-Fluoro-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3al**).* Isolated yield: 69% (36 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 86−87 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (dd, *J* = 9.5 Hz, 1.5 Hz 1H), 6.91 (td, *J* = 9.0 Hz, 2.5 Hz, 1H), 7.07−7.16 (m, 5H), 7.25−7.30 (m, 2H), 7.35 (s, 1H), 8.24 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 105.2 (d, J_{CF} = 24.0 Hz), 108.1 (d, J_{CF} = 4.8 Hz), 111.2 (d, J_{CF} = 26.4 Hz), 111.9 (d, J_{CF} = 9.7 Hz), 122.5 (q, J_{CF} = 30.1 Hz), 124.1 (q, J_{CF} = 273.5 Hz) 126.1, 126.6 (d, J_{CF} = 9.6 Hz), 128.2, 128.7, 129.6, 132.4, 133.8 (q, J_{CF} = 5.9 Hz), 134.0, 158.1 (d, J_{CF} = 235.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 38.35−38.40 (m, 1F), 95.17 (s, 3F). IR (KBr): 3407, 3055, 1655, 1616, 1531, 1496, 1458, 1426, 1331, 1272, 1211, 910, 750, 695 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M + H]^+$ $C_{17}H_{12}F_4N$ 306.09059, found 306.09359.

*(E)-2-Methyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3am**).* Isolated yield: 84% (43 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 111−112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.13 (s, 3H), 7.05−7.19 (m, 7H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.41−7.42 (m, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 8.02 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.9, 104.7, 110.4, 119.3, 120.3, 121.7, 123.5(q, J_{CF} = 30.1 Hz), 124.4 (q, J_{CF} = 273.4 Hz), 128.3, 128.8, 129.3, 133.8, 134.3, 135.5, 135.7 (q, J_{CF} = 6.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.90 (s, 3F). IR (KBr): 3387, 3071, 2922, 1654, 1618, 1561, 1460, 1382, 1273, 1101, 933, 832, 752, 688 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M - H]^-$ $C_{18}H_{13}F_3N$ 300.10000, found 300.09868.

*(E)-2-Phenyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3an**).* Isolated yield: 85% (52 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 165−166 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03−7.04 (m, 4H), 7.07−7.14 (m, 2H), 7.18−7.30 (m, 4H), 7.37−7.44 (m, 4H), 7.51 (d, *J* = 8.0 Hz, 1H), 8.28 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 104.7, 110.9, 120.1, 120.8, 123.0, 123.5 (q, J_{CF} = 30.6 Hz), 124.3 (q, J_{CF} = 274.4 Hz), 127.1, 128.1, 128.3, 128.6, 128.7, 128.8, 129.3, 132.1, 134.1, 135.9, 136.3, 136.8 (q, J_{CF} = 5.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 96.43 (s, 3F). IR (KBr): 3441, 3067, 1926, 1876, 1804, 1652, 1603, 1550, 1490, 1387, 926, 832, 608 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M + H]^+$ $C_{23}H_{17}F_3N$ 364.13131, found 364.13425.

*(E)-1-Methyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ao**).* Isolated yield: 89% (46 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 78−79 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.94−6.97 (m, 1H), 7.07−7.23 (m, 8H), 7.32−7.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 32.8, 106.1, 109.4, 119.8, 120.5, 122.0, 123.0 (q, J_{CF} = 30.1 Hz), 124.3 (q, J_{CF} = 273.4 Hz), 126.4, 128.1, 128.5, 128.9, 129.7, 132.8 (q, J_{CF} = 5.9 Hz), 134.4, 136.9. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.28 (s, 3F). IR (KBr): 3448, 1638, 1537, 1476, 1335, 1295, 1272, 1153, 1110, 933, 903, 745, 694 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M + H]^+$ $C_{18}H_{15}F_3N$ 302.11566, found 302.11818. Recrystallization from Et_2O gave a single crystal, which is a suitable for X-ray study. See Figure S1 (CCDC 1521079) in the Supporting Information.

*(E)-1,2-Dimethyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-indole ((E)-**3ap**).* Isolated yield: 87% (47 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 93−94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.12 (s, 3H), 3.68 (s, 3H), 7.03−7.24 (m, 7H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.41 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.6, 29.8, 103.8, 108.8, 119.2, 119.9, 121.2, 123.9 (q, J_{CF} = 30.1 Hz), 124.5 (q, J_{CF} = 273.5 Hz), 127.4, 128.3, 128.7, 129.3, 134.4, 135.5, 135.6 (q, J_{CF} = 6.0 Hz), 137.0. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.87 (s, 3F). IR (KBr): 1474, 1391, 1331, 1273, 1219, 1152, 1106, 1015, 936, 920, 832, 743, 695 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M + H]^+$ $C_{19}H_{17}F_3N$ 316.13131, found 316.13040.

*(E)-1-Methyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-pyrrole ((E)-**3aq**).* Isolated yield: 39% (17 mg after silica gel chromatography). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.61 (s, 3H), 5.95 (s, 1H), 6.51−6.52 (m, 1H), 6.58 (s, 1H), 7.02 (s 1H), 7.23−7.34 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.2, 109.8, 114.0, 122.0, 124.2 (q, J_{CF} = 273.4 Hz), 125.4 (q, J_{CF} = 30.1 Hz), 128.1, 128.2, 129.5, 129.9 (q, J_{CF} = 5.9 Hz), 135.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ 94.91 (s, 3F). IR (neat) 1384, 1278, 1155, 1111, 928, 761, 722, 694 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M - H]^-$ $C_{14}H_{11}F_3N$ 250.08435, found 250.08208.

*(E)-1-Methyl-2-(3,3,3-trifluoro-1-phenylprop-1-en-2-yl)-1H-pyrrole ((E)-**3aq′**).* Isolated yield: 58% (25 mg after silica gel chromatography). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.14 (s, 3H), 6.22−6.26 (m, 2H), 6.68 (s, 1H), 6.85−6.87 (m 2H), 7.19−7.31 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.6, 108.4, 110.7, 121.2 (q, J_{CF} = 30.1 Hz), 122.8, 123.6 (q, J_{CF} = 272.3 Hz), 123.7, 128.7, 129.4, 129.5, 133.7, 136.1 (q, J_{CF} = 5.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.35 (s, 3F). IR (neat) 2972, 1738, 1384, 1275, 1216, 1151, 1117, 723, 693, 536, 460 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M + H]^+$ $C_{14}H_{13}F_3N$ 252.10001, found 252.10070.

*(E)-3-(3,3,3-Trifluoro-1-(4-methoxyphenyl)prop-1-en-2-yl)-1H-indole ((E)-**3ba**).* Isolated yield: 63% (34 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 136−137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.69 (s, 3H), 6.59−6.61 (m, 2H), 6.99−7.02 (m, 1H), 7.06−7.08 (m, 2H), 7.17−7.24 (m, 3H), 7.30 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 8.28 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 108.1, 111.2, 113.6, 120.3, 120.3, 120.4 (q, J_{CF} = 30.1 Hz), 122.5, 124.2, 124.4 (q, J_{CF} = 273.4 Hz), 126.2, 126.8, 131.3, 133.2 (q, J_{CF} = 5.9 Hz), 136.0, 159.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.49 (s, 3F). IR (KBr): 3392, 3121, 1603, 1575, 1542, 1512, 1421, 1316, 1273, 1107, 1022, 921, 831, 750 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M + H]^+$ $C_{18}H_{15}F_3NO$ 318.11058, found 318.11087.

*(E)-3-(1-(Benzo[d][1,3]dioxol-5-yl)-3,3,3-trifluoroprop-1-en-2-yl)-1H-indole ((E)-**3ca**).* Isolated yield: 66% (37 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 93−94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.82 (s, 2H), 6.54 (s, 1H), 6.60 (d, *J* = 8.0 Hz 1H), 6.76 (d, *J* = 8.0 Hz 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.23−7.33 (m, 3H), 7.39 (d, *J* = 7.5 Hz, 1H), 8.30 (s 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 101.0, 107.6, 108.0, 108.8, 111.3, 120.1, 120.2, 120.9 (q, J_{CF} = 30.1 Hz), 122.6, 124.3, 124.4 (q, J_{CF} = 273.4 Hz), 125.4, 126.0, 128.3, 129.6, 133.2 (q, J_{CF} = 5.9 Hz), 133.9, 136.0, 147.3, 147.9. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.36 (s, 3F). IR (KBr): 3402, 1708, 1490, 1447, 1356, 1241, 1162, 1110, 1039, 914, 746 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[M - H]^-$ $C_{18}H_{11}F_3NO_2$ 330.07418, found 330.07171.

*(E)-3-(1-(4-Chlorophenyl)-3,3,3-trifluoroprop-1-en-2-yl)-1H-indole ((E)-**3da**).* Isolated yield: 72% (39 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 113−114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99−7.30 (m, 10H), 7.36−

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7.41 (m, 1H), 8.33 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 107.5, 111.3, 120.2, 120.5, 122.7, 123.6 (q, J_{CF} = 30.1 Hz), 124.0 (q, J_{CF} = 273.5 Hz), 124.4, 125.7, 128.4, 130.9, 132.1 (q, J_{CF} = 6.0 Hz), 132.7, 134.4, 136.0. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.04 (s, 3F). IR (KBr): 3419, 3127, 3062, 1906, 1654, 1593, 1569, 1540, 1489, 1421, 1309, 930, 834 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{17}H_{12}ClF_3N$ 322.06104, found 322.06166.

*(E)-3-(3,3,3-Trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1H-indole ((E)-**3ea**).* Isolated yield: 93% (56 mg after silica gel chromatography). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00 (t, J = 7.0 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.23−7.24 (m, 3H), 7.32−7.40 (m, 4H), 8.28 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 107.2, 111.4, 120.1, 120.6, 122.9, 123.8 (q, J_{CF} = 272.4 Hz), 123.9 (q, J_{CF} = 273.5 Hz), 124.6, 125.1 (q, J_{CF} = 4.8 Hz), 125.6 (q, J_{CF} = 30.1 Hz), 125.7, 129.7, 130.2 (q, J_{CF} = 32.4 Hz), 131.8 (q, J_{CF} = 5.9 Hz), 136.0, 137.9. ^{19}F NMR (470 MHz, $CDCl_3$): δ 94.94 (s, 3F), 98.93 (s, 3F). IR (neat) 3409, 1709, 1617, 1536, 1324, 1273, 1121, 1066, 1017, 923, 834, 745, 715 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{18}H_{12}F_6N$ 356.08740, found 356.08499.

*(E)-3-(3,3,3-Trifluoro-1-(naphthalen-1-yl)prop-1-en-2-yl)-1H-indole ((E)-**3fa**).* Isolated yield: 98% (56 mg after silica gel chromatography). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (t, J = 7.5 Hz, 1H), 6.97−7.08 (m, 3H), 7.16 (d, J = 7.5 Hz, 1H), 7.21 (s, 1H), 7.26 (t, J = 8.0 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.58−7.64 (m, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H), 8.15−8.16 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 107.9, 111.1, 120.1, 122.3, 123.8, 124.3 (q, J_{CF} = 274.7 Hz), 124.9, 125.1, 125.5 (q, J_{CF} = 30.1 Hz), 125.8, 126.0, 126.5, 126.9, 128.6, 128.7, 131.0 (q, J_{CF} = 6.0 Hz), 131.6, 131.7, 133.3, 135.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ 96.05 (s, 3F). IR (neat) 3420, 3059, 1618, 1533, 1457, 1342, 1279, 1157, 1013, 872, 800, 744, 694 cm^{-1}. HRMS (ESI): m/z calcd for $[M]$ $C_{21}H_{15}F_3N$ 338.11566, found 338.11664.

*(E)-3-(3,3,3-Trifluoro-1-(o-tolyl)prop-1-en-2-yl)-1H-indole ((E)-**3ga**).* Isolated yield: 90% (46 mg after silica gel chromatography). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.41 (s, 3H), 6.70 (t, J = 7.5 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 8.0 Hz, 2H), 7.17−7.18 (m, 1H), 7.28 (d, J = 8.5 Hz, 1H), 7.47 (s, 1H), 8.11 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.0, 108.0, 111.1, 120.1, 122.3, 124.2 (q, J_{CF} = 30.1 Hz), 124.2 (q, J_{CF} = 30.1 Hz), 124.3 (q, J_{CF} = 273.5 Hz), 124.8, 125.4, 126.0, 128.2, 128.7, 130.0, 131.7 (q, J_{CF} = 5.9 Hz), 133.9, 135.8, 136.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.94 (s, 3F). IR (neat) 3396, 3018, 1928, 1656, 1615, 1601, 1532, 1481, 1457, 1381, 1273, 921, 831, 744 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{18}H_{14}F_3N$ 302.11566, found 302.11799.

*(E)-3-(1-(Benzo[d][1,3]dioxol-5-yl)-3,3,3-trifluoroprop-1-en-2-yl)-1-methyl-1H-indole ((E)-**3co**).* Isolated yield: 76% (45 mg after silica gel chromatography). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, 3H), 5.78 (s, 2H), 6.57−6.59 (m, 2H), 6.75 (d, J = 8.5 Hz, 1H), 7.00 (t, J = 7.0 Hz, 1H), 7.11 (s, 1H), 7.14−7.21 (m, 3H), 7.31 (d, J = 8.0 Hz, 1H) 6.92 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 32.8, 101.0, 106.0, 108.0, 109.0, 109.5, 119.9, 120.3, 121.0 (q, J_{CF} = 30.1 Hz), 122.1, 124.4 (q, J_{CF} = 273.5 Hz), 125.2, 126.5, 128.5, 128.7, 132.5 (q, J_{CF} = 4.8 Hz), 137.0, 147.4, 147.9. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.58 (s, 3F). IR (neat) 2897, 1615, 1535, 1489, 1447, 1337, 1288, 1243, 1209, 1158, 1039, 932, 811, 742, 710 cm^{-1}. HRMS (ESI): m/z calcd for $[M - H]^-$ $C_{19}H_{14}F_3NO_2$ 344.08983, found 344.08904.

*(E)-1-Methyl-3-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1H-indole ((E)-**3eo**).* Isolated yield: 89% (56 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 118−119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.96−6.99 (m, 1H), 7.04−7.07 (m, 1H), 7.15 (s, 1H), 7.19−7.27 (m, 3H), 7.33−7.34 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.1, 105.5, 109.6, 120.2, 120.3, 122.6, 123.9 (q, J_{CF} = 272.3 Hz), 124.0 (q, J_{CF} = 274.7 Hz), 125.1 (q, J_{CF} = 3.6 Hz), 125.6 (q, J_{CF} = 30.1 Hz), 126.1, 129.1, 129.8, 130.1 (q, J_{CF} = 32.3 Hz), 131.0 (q, J_{CF} = 4.8 Hz), 137.0, 138.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.02 (s, 3F), 98.98 (s, 3F). IR (KBr): 3118, 1648, 1535, 1401, 1323, 1275, 1168, 1116, 1065, 1018, 881, 830, 741, 655 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{19}H_{14}F_6N$ 370.10305, found 370.10331.

*(E)-1-Methyl-3-(3,3,3-trifluoro-1-(naphthalen-1-yl)prop-1-en-2-yl)-1H-indole ((E)-**3fo**).* Isolated yield: 76% (45 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 127−128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.66 (s, 3H), 6.70−6.72 (m, 1H), 6.88 (s, 1H), 6.98−7.22 (m, 5H), 7.49−7.60 (m, 3H), 7.79 (s, 1H), 7.91 (s, 1H), 8.15 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 32.9, 106.2, 109.2, 119.7, 120.3, 121.8, 123.8, 124.4 (q, J_{CF} = 273.5 Hz), 125.1, 125.3 (q, J_{CF} = 30.1 Hz), 125.9, 126.3, 126.5, 127.0, 128.5, 128.7, 129.4, 130.0, 131.8 (q, J_{CF} = 4.8 Hz), 133.4, 136.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ 96.13 (s, 3F). IR (KBr): 1530, 1475, 1340, 1282, 1152, 1113, 1015, 924, 900, 798, 779, 739, 697 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{22}H_{18}F_3N$ 352.13131, found 352.13271.

*(E)-1-Methyl-3-(3,3,3-trifluoro-1-(naphthalen-2-yl)prop-1-en-2-yl)-1H-indole ((E)-**3ho**).* Isolated yield: 82% (49 mg after silica gel chromatography). White solid. The pure product was obtained after recrystallization from diethyl ether at room temperature. Mp: 133−134 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.91 (t, J = 7.5 Hz, 1H), 7.14−7.19 (m, 4H), 7.33 (d, J = 8.5 Hz, 1H), 7.37−7.42 (m, 3H), 7.46 (s, 1H), 7.60−7.65 (m, 2H), 7.74 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.0, 106.2, 109.4, 120.1, 120.5, 122.1, 123.2 (q, J_{CF} = 30.0 Hz), 124.3 (q, J_{CF} = 280.7 Hz), 126.0, 126.1, 126.6, 126.7, 127.5, 128.2, 129.1, 130.5, 132.2, 132.8 (q, J_{CF} = 6.0 Hz), 133.0, 133.1, 136.9. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.50 (s, 3F). IR (KBr): 1535, 1476, 1428, 1355, 1270, 1181, 1152, 1101, 921, 822, 738, 697 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{22}H_{17}F_3N$ 352.13131, found 352.12855.

*(E)-1-Methyl-3-(3,3,3-trifluoro-1-(o-tolyl)prop-1-en-2-yl)-1H-indole ((E)-**3go**).* Isolated yield: 75% (40 mg after silica gel chromatography). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.75 (s, 3H), 6.71 (t, J = 7.5 Hz, 1H), 6.89−7.02 (m, 4H), 7.11−7.13 (m, 3H), 7.22−7.37 (m, 2H), 7.42 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.0, 33.0, 106.2, 109.2, 119.7, 120.4, 121.8, 124.1 (q, J_{CF} = 30.1 Hz), 124.3 (q, J_{CF} = 272.4 Hz), 125.4, 126.4, 128.1, 128.7, 129.3, 129.9, 130.8 (q, J_{CF} = 6.0 Hz), 134.0, 136.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.95 (s, 3F). IR (neat) 2925, 1638, 1530, 1458, 1429, 1273, 1109, 941, 910, 846, 744 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{19}H_{17}F_3N$ 316.13131, found 316.13241.

*(E)-3-(1,1,1-Trifluoro-5-phenylpent-2-en-2-yl)-1H-indole ((E)-**3ia**).* Isolated yield: 65% (35 mg after silica gel chromatography). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.34−2.40 (m, 2H), 2.71 (t, J = 7.0 Hz, 2H), 6.59 (td, J = 7.5 Hz, 1.5 Hz, 1H), 6.98−6.99 (m, 1H), 7.05 (d, J = 7.0 Hz, 2H), 7.13−7.18 (m, 4H), 7.21−7.26 (m, 5H), 7.39−7.41 (m, 2H), 8.24 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.5, 34.8, 107.0, 111.3, 119.5, 120.2, 122.3, 123.8 (q, J_{CF} = 272.3 Hz), 124.3, 124.4 (q, J_{CF} = 30.1 Hz), 126.0, 127.0, 128.3, 128.4, 135.5, 137.1 (q, J_{CF} = 6.0 Hz), 140.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ 95.10 (s, 3F). IR (neat) 3394, 3010, 2933, 2840, 1888, 1793, 1661, 1583, 1509, 1439, 1332, 1213, 935, 820, 692 cm^{-1}. HRMS (ESI): m/z calcd for $[M + H]^+$ $C_{19}H_{17}F_3N$ 316.13131, found 316.13431.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b03085.

^{1}H, ^{13}C, and ^{19}F NMR spectra for all products (PDF)

X-ray crystallographic data for product (*E*)-**3ao** (CIF)

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Notes

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(8) The structure of (*E*)-**3ao** was confirmed by X-ray crystallographic analysis (CCDC 1521079). See the Supporting Information for details.

(9) We also examined reactions with heteroaromatic compounds, such as furan, benzofuran, thiophene, benzothiophene, indazole, or benzimizadole, but all reactions provided complex mixtures.

(10) We examined the reaction 2-fluoro-1-phenylallylic carbonate, which does not have two terminal fluorine atoms, with indole under the optimized reaction conditions and then confirmed that the reaction did not provide any coupling products. This result indicates that the three fluorine atoms on the terminal olefin are necessary to progress the present reaction.

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