Palladium-Catalyzed Tandem Carbocyclization–Suzuki Coupling Reactions of Trifluoromethyl-Containing Building Blocks Leading to 2-Trifluoromethyl-indenes

Wen-Ying Wang, Lei-Lei Sun, Chen-Liang Deng, Ri-Yuan Tang, Xing-Guo Zhang*

College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325027, P. R. of China
Fax +86(577)86689615; E-mail: zxg@wzu.edu.cn
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Abstract: A palladium-catalyzed tandem carbocyclization–Suzuki coupling is described leading to the synthesis of trifluoromethyl-containing indenes in moderate to good yields. The reactions take place in the presence of palladium(II) acetate, a phosphorus-containing ligand [dicyclohexyl(2,4,6-trisopropylbiphenyl-2-yl)phosphine] and potassium carbonate in toluene as the solvent. The process occurs via intramolecular carbocyclization and subsequent Suzuki coupling of the ortho-(2-chlorovinyl)-alkynylbenzenes with arylboronic acids.

Key words: indene, palladium, trifluoromethyl, carbocyclization, Suzuki coupling

Indene is a privileged structural motif that occurs widely in natural products, pharmaceutical molecules and functional materials, as well as in metallocene complexes utilized in alkene polymerization. As a consequence, a number of synthetic approaches have been developed for the construction of this carbocycle, in particular, 1-methylenindene. Among them, transition-metal-catalyzed carboannulation of alkynes provides a straightforward access to the indene ring system. For example, Clark and Zhao developed a platinum-catalyzed Rautenstrauch reaction of propargyl carbonate for the regiodivergent synthesis of functionalized indene derivatives. Larock and co-workers reported the palladium- or copper-catalyzed carboannulations of alkynylmalonates leading to indenes. Trifluoromethylated compounds have wide applicability in pharmaceuticals, agrochemicals and organic materials, however, examples of the selective synthesis of trifluoromethylated indenes are scarce. Meanwhile, trifluoromethylation reactions have received intense attention due to the unique characteristics of the trifluoromethyl (CF3) group. However, most procedures are based on the trifluoromethylation of prefunctionalized substrates (such as aryl halides and boronic acids), or the direct trifluoromethylation of arenes, albeit with poor regioselectivity. Alternatively, the transformation of synthons containing a trifluoromethyl group at the appropriate position is an effective method to target trifluoromethlated compounds. In continuation of our interest in the synthesis of trifluoromethylated compounds, we wanted to prepare trifluoromethyl-containing indene derivatives starting from our previously reported building blocks. Herein, we report an efficient protocol for the synthesis of trifluoromethyl-containing indenes via the palladium-catalyzed tandem carbocyclization–Suzuki coupling of ortho-(2-chlorovinyl)-alkynylbenzenes with arylboronic acids (Scheme 1).

![Scheme 1 Palladium-catalyzed tandem carbocyclization–Suzuki coupling](image_url)

We began our study by optimizing the conditions for the reaction between 1-(2-chloro-3,3,3-trifluoroprop-1-en-1-yl)-2-(phenylethynyl)benzene (1a) and phenylboronic acid (2a), and the results are summarized in Table 1. Initially, treatment of substrate 1a with phenylboronic acid (2a), palladium(II) acetate [Pd(OAc)2], triphenylphosphine (PPh3) (L1) and cesium carbonate (Cs2CO3), in toluene at 80 °C for three hours, afforded the desired cyclized product 3 in 71% yield (Table 1, entry 1). Other palladium catalysts [PdCl2, Pd2(dba)3, Pd(PPh3)2Cl2 and Pd(PPh3)4] were also tested, but were less effective than palladium(II) acetate (Table 1, entries 2–5). Subsequently, different phosphorus ligands L2–L6 were examined (Table 1, entries 6–10); the bulky ligand L5 provided the best results with the target product 3 being isolated in 80% yield (Table 1, entry 9). During the examination of the effect of the base (Table 1, entries 11–13), we found that the reaction yield increased to 90% in the presence of potassium carbonate (K2CO3) (Table 1, entry 13). Further, the effect of different solvents was evaluated (Table 1, entries 14–17); much lower yields were obtained in polar solvents (MeCN, NMP, DMSO and DMF). A lower yield was observed when the reaction was carried out at 60 °C (Table 1, entry 18).

With optimized reaction conditions established, the substrate scope of trifluoromethyl-containing building blocks and arylboronic acids was next examined (Table 2). We initially investigated the reaction of 1-(2-chloro-3,3,3-trifluoroprop-1-en-1-yl)-2-(phenylethynyl)benzene (1a) with arylboronic acids 2b–1 (Table 2, entries 1–11). The results demonstrated that a wide range of arylboronic acids containing both electron-withdrawing and electron-
donating groups were suitable substrates for the tandem reactions, which gave the corresponding indene products in moderate to excellent yields, and with high stereoselectivity. For example, para- or meta-methylphenylboronic acid gave the corresponding E-isomers as the major products in 84% and 77% yields, respectively (Table 2, entries 1 and 2). Similar results were obtained with methoxy-substituted phenylboronic acids 2d and 2e (92% and 89% yields, Table 2, entries 3 and 4). Chlorinated and fluorinated phenylboronic acids 2f and 2g provided exclusively the E-isomeric products in 51% and 75% yields (Table 2, entries 5 and 6). In contrast, moderate yields were obtained in the presence of arylboronic acids possessing electron-withdrawing groups such as acetyl, trifluoromethyl, cyan or nitro (Table 2, entries 7–10). As expected, naphthalen-1-ylboronic acid (2l) underwent the tandem process with 1a to give E-14 exclusively, in 42% yield (Table 2, entry 11). Subsequently, the reactions of various trisubstituted arenes 1b–d with phenylboronic acid (2a) were examined (Table 2, entries 12–14). The tandem reactions of trisubstituted arenes bearing a methyl, methoxy or fluoro group proceeded smoothly under the standardized conditions. For example, substrate 1c possessing a 4-methoxy group, was treated with 2a, palladium(II) acetate, L5 and potassium carbonate in toluene to afford the desired product in 98% yield (Table 2, entry 13). Finally, substrates with substituted aromatic groups on the alkyne were investigated (Table 2, entries 15–19). The results revealed that the presence of both electron-withdrawing and electron-donating aryl groups was compatible under the optimized conditions. For example, substrates 1e and 1h, bearing a methoxy and cyano group respectively, gave the desired indenes 7 and 12 in 87% and 86% yields (Table 2, entries 15 and 18).

The excellent stereoselectivity obtained for product 8 (Table 2, entry 16) suggested that the E-isomer of the intermediate allylpalladium complex underwent the Suzuki coupling reaction; the configuration of product 8 as the Z-isomer in this case was confirmed by single crystal X-ray diffraction analysis (Figure 1). Comparison of the 1H NMR spectroscopic data of both the E-isomer (Table 2, entry 5) and Z-isomer (Table 2, entry 16) of product 8 showed that the signals due to the E-isomer resonated at higher chemical shifts. Therefore, the Z/E ratios of all the products could be determined by 1H and 19F NMR spectroscopy.

Based on the present results and a previously reported mechanism,16 a possible route for this reaction can be proposed (Scheme 2). Initially, the palladium(0) species is generated in situ by reduction of palladium(II) acetate by the phosphorus ligand. Oxidative addition of the metal to substrate 1 then affords intermediate A. Intramolecular addition of palladium(II) across the triple bond can then provide allylpalladium complex B. Next, transmetallation with the arylboronic acid in the presence of potassium carbonate would lead to intermediate C.17 Finally, reductive elimination of palladium from species C affords the desired indene (3–18) and regenerates the palladium(0) species.

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Table 1  Optimization of the Reaction Conditions

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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ligand</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield (%)</th>
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<td>Cs2CO3</td>
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<td>L1</td>
<td>Cs2CO3</td>
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<td>Pd(OAc)2</td>
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<td>K2CO3</td>
<td>NMP</td>
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* Reaction conditions: 1a (0.2 mmol), 2a (0.24 mmol), [Pd] (5 mol%), ligand (10 mol%), base (2 equiv), solvent (2 mL), 80 °C, 3 h, N2 atm.

* Yield of isolated product.

* Reaction at 60 °C.
Table 2 Palladium-Catalyzed Tandem Reactions of ortho-(2-Chlorovinyl)alkynylbenzenes with Arylboronic Acids

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>Boronic acid</th>
<th>Product</th>
<th>Yield (%)</th>
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<td><img src="image2" alt="Boronic acid 2b" /></td>
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<td>84 (13:87)</td>
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<td>2</td>
<td><img src="image3" alt="Alkyne 1a" /></td>
<td><img src="image4" alt="Boronic acid 2c" /></td>
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<td>77 (7:93)</td>
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<tr>
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<td><img src="image5" alt="Alkyne 1a" /></td>
<td><img src="image6" alt="Boronic acid 2d" /></td>
<td>6</td>
<td>92 (13:87)</td>
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<td><img src="image7" alt="Alkyne 1a" /></td>
<td><img src="image8" alt="Boronic acid 2e" /></td>
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<td>89 (27:73)</td>
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<td><img src="image10" alt="Boronic acid 2f" /></td>
<td>8</td>
<td>51 (0:100)</td>
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<td><img src="image11" alt="Alkyne 1a" /></td>
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<td><img src="image18" alt="Boronic acid 2j" /></td>
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Table 2  Palladium-Catalyzed Tandem Reactions of ortho-(2-Chlorovinyl)alkynylbenzenes with Arylboronic Acids<sup>a</sup> (continued)

<table>
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<tr>
<th>Entry</th>
<th>Alkyne</th>
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<th>Product</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>10&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1a CF₃</td>
<td>2k B(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>13 CF₃</td>
<td>58 (29:71)</td>
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<tr>
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<td>1a CF₃</td>
<td>2l B(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>14 CF₃</td>
<td>42 (0:100)</td>
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<tr>
<td>11</td>
<td>1b CF₃</td>
<td>2a B(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>15 CF₃</td>
<td>85 CF₃</td>
</tr>
<tr>
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<td>1c CF₃</td>
<td>2a B(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>16 CF₃</td>
<td>98 CF₃</td>
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<tr>
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<td>1d CF₃</td>
<td>2a B(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>17 CF₃</td>
<td>60 CF₃</td>
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<tr>
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<td>1e CF₃</td>
<td>2a B(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>18 CF₃</td>
<td>72 (100:0)</td>
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<tr>
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<td>1f CF₃</td>
<td>2a B(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>19 CF₃</td>
<td>72 (100:0)</td>
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<sup>a</sup> Reaction conditions: Pd(OAc)<sub>2</sub>/L5/K<sub>2</sub>CO<sub>3</sub> in toluene, 80 °C.

<sup>b</sup> Yield values given as (major:minor).
In summary, we have developed an efficient method for the synthesis of trifluoromethyl-containing indenes. Various 1-(2-chloro-3,3,3-trifluoroprop-1-en-1-yl)benzenes underwent palladium-catalyzed tandem carbocyclization–Suzuki couplings with several arylboronic acids to afford the corresponding indenes in moderate to excellent yields. The present process represents a new synthetic application for trifluoromethyl-containing building blocks, as well as an alternative route for constructing an indene ring.

Chemicals were either purchased or were purified by standard techniques. All reactions were conducted under a nitrogen atmosphere using standard Schlenk techniques. TLC was carried out using HSGF254 (10–40 μm) silica gel plates (Yantaijiangyou). Column chromatography was performed using EM silica gel 60 (300–400 mesh). Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. Melting points were recorded on a Solid X-4 apparatus (Beijing TECH) and are uncorrected. IR spectra were obtained using a Nicolet iS10 spectrophotometer (Thermo Scientific). 1H NMR (500 MHz), 13C NMR (125 MHz) and 19F NMR (470 MHz) spectra were recorded at room temperature on a Bruker Avance 500 spec-

Table 2 Palladium-Catalyzed Tandem Reactions of ortho-(2-Chlorovinyl)alkynylbenzenes with Arylboronic Acids (continued)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>Boronic acid</th>
<th>Product</th>
<th>Yield (%)b</th>
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</thead>
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<td><img src="image2.png" alt="Image" /></td>
<td>12</td>
<td>86 (67:33)</td>
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<tr>
<td>19</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>18</td>
<td>82 (60:40)</td>
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</table>

a Reaction conditions: 1 (0.2 mmol), 2 (0.24 mmol), Pd(OAc)2 (5 mol%), L5 (10 mol%), K2CO3 (2 equiv), toluene (2 mL), 80 °C, 3 h, N2 atm.
b Yield of isolated product. The ratio of Z/E isomers is shown in parentheses and was determined by 1H and 19F NMR spectroscopy.
c Reaction occurred over 16 h.
trometr using CDFI, as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in ppm relative to TMS; the coupling constants (J) are given in Hz. 19F NMR data are reported relative to CFCl3 as the internal standard. Low-resolution mass spectra were recorded on a Shimadzu GCMS QP2010 (plus) spectrometer. High-resolution mass spectra were recorded on Bruker micro TOF QII ESI-Q-TOF mass spectrometer.

2-Trifluoromethylindenes 3–18; General Procedure
A mixture of ortho-[(2-chlorovinyl)alkynylbenzene 1 (0.2 mmol), Pd(OAc)2 (2.3 mg, 5 mol%), dicyclohexyl(2,6-diisopropyl-phenyl-2-yl)phosphine (L5) (9.5 mg, 10 mol%), K2CO3 (55.2 mg, 0.4 mmol) and arylboronic acid (0.24 mmol) in toluene (2 mL) was stirred at 80 °C under an N2 atm for 4 h, or until complete consumption of the starting material as monitored by TLC or GC-MS. The resulting mixture was added to EtOAc (10 mL) and evaporated under vacuum. The residue was purified by flash column chromatography (PE–EtOAc) to afford the desired products 3–18.

1-(Diphenylmethylene)-2-(trifluoromethyl)-1H-indene (3) Yield: 62.8 mg (90%); yellow solid; mp 126.4–128.1 °C.
IR (neat): 3073, 2922, 1597, 1587, 1458, 1380, 1235, 1116, 1025, 969 cm–1.
Yield: 69.3 mg (92%); Z/E = 13:87; yellow solid; mp 113.2–115.1 °C.
1H NMR (500 MHz, CDCl3): δ = 7.26 (t, J = 7.2 Hz), 7.15–7.12 (m, 2 H), 7.09–7.06 (m, 1 H), 6.97–6.94 (m, 1 H), 6.94–6.91 (m, 1 H), 6.89–6.86 (m, 1 H).
19F NMR (470 MHz, CDCl3): δ = 54.3 (3 F).
MS (EI, 70 eV): m/z (%) = 378 (100) [M]+, 278 (14), 265 (21), 138 (10).

1-(3-Methylphenyl)(phenyl)methylene-2-(trifluoromethyl)-1H-indene (4) (Table 2, Entry 1)
Yield: 66.0 mg (84%), Z/E = 13:87; yellow oil.
IR (neat): 3073, 2922, 1587, 1577, 1458, 1387, 1235, 1116, 1025, 969 cm–1.
Yield: 67.1 mg (89%); Z/E = 27:73; yellow oil.
IR (neat): 1716, 1345, 1235, 885, 685 cm–1.
1H NMR (500 MHz, CDCl3): δ = 7.47 (s, 1 H), 7.30–7.27 (m, 2 H), 7.03–7.00 (m, 1 H), 6.92–6.89 (m, 1 H), 6.81 (d, J = 8.0 Hz, 1 H), 2.43 (s, 3 H).
19F NMR (470 MHz, CDCl3): δ = −54.1 (2.6 F), −54.2 (0.4 F).
MS (EI, 70 eV): m/z (%) = 362 (100) [M]+, 277 (35), 138 (18).

1-[Phenyl(ortho-tolyl)methylene]-2-(trifluoromethyl)-1H-indene (5) (Table 2, Entry 2)
Yield: 55.8 mg (77%); Z/E = 7:93; yellow oil.
IR (neat): 1547, 1356, 1119, 1065, 751, 695 cm–1.
1H NMR (500 MHz, CDCl3): δ = 7.47 (s, 1 H), 7.38–7.35 (m, 4 H), 7.25–7.22 (m, 2 H), 7.18–7.15 (m, 1 H), 7.11–7.09 (m, 2 H), 6.95–6.92 (m, 1 H), 6.41 (t, J = 8.0 Hz, 1 H), 2.33 (s, 2.8 H), 2.30 (s, 0.2 H).
13C NMR (125 MHz, CDCl3): δ = 152.6, 142.5, 142.0, 139.5, 138.8, 138.5, 137.0, 137.0 (q, JCF = 5.9 Hz), 133.0, 131.3, 130.7, 130.0 (q, JCF = 33.5 Hz), 129.4, 128.8, 127.4, 127.0, 126.8, 124.2, 122.9 (q, JCF = 268.0 Hz), 122.4, 21.5.
19F NMR (470 MHz, CDCl3): δ = −53.9 (0.8 F), −54.1 (2.2 F).
MS (EI, 70 eV): m/z (%) = 378 (100) [M]+, 309 (36), 294 (16), 265 (21), 138 (9).

(α,α-Dimethyl)-1-(4-Chlorophenyl)(phenyl)methylene-2-(trifluoromethyl)-1H-indene (6) (Table 2, Entry 3)
Yield: 39.2 mg (51%); yellow solid; mp 99.6–101.3 °C.
IR (neat): 1487, 1253, 1118, 822, 761 cm–1.
1H NMR (500 MHz, CDCl3): δ = 7.49 (s, 1 H), 7.40–7.37 (m, 2 H), 7.35–7.32 (m, 2 H), 7.26–7.24 (m, 2 H), 7.22–7.19 (m, 3 H), 7.00–6.97 (m, 1 H), 6.51 (d, J = 8.0 Hz, 1 H).
13C NMR (125 MHz, CDCl3): δ = 150.6, 141.9, 141.2, 138.9, 138.0, 137.3 (q, JCF = 6.0 Hz), 135.5, 133.6, 132.0, 131.2, 130.2 (q, JCF = 43.5 Hz), 129.1, 129.0, 127.5, 127.4, 127.1, 124.2, 122.7 (q, JCF = 268.0 Hz), 122.6.
19F NMR (470 MHz, CDCl3): δ = −54.4 (3 F).

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(E)-1-[(4-Fluorophenyl)(phenyl)methylene]-2-(trifluoromethyl)-1H-indene (9) (Table 2, Entry 6)

Yield: 55.1 mg (75%); yellow solid; mp 67.6–69.3 °C.

IR (neat): 1600, 1502, 1156, 1096, 1065, 829, 711, 692 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.48 (s, 1 H), 7.39–7.36 (m, 2 H), 7.34–7.31 (m, 2 H), 7.30–7.27 (m, 2 H), 7.21–7.17 (m, 3 H), 7.11–7.07 (m, 2 H), 6.99–6.96 (m, 1 H), 6.46 (d, J = 8.0 Hz, 1 H), 4.63 (d, J = 8.0 Hz, 1 H).

13C NMR (125 MHz, CDCl₃): δ = 163.5 (d, J = 283.8 Hz), 151.0, 142.1, 138.9, 138.8 (d, J = 3.4 Hz), 138.2, 137.5 (q, J = 6.0 Hz), 133.5, 132.7 (d, J = 8.3 Hz), 131.3, 130.9 (q, J = 33.6 Hz), 129.1, 127.5, 127.3, 127.0, 124.1, 122.8 (q, J = 268.0 Hz), 122.6, 115.9 (d, J = 21.5 Hz).

19F NMR (470 MHz, CDCl₃): δ = –54.3 (3 F), –111.3 (1 F).

MS (EI, 70 eV): m/z (%) = 398 (100) [M]+, 297 (20), 296 (24), 276 (14), 138 (15).


1H NMR (500 MHz, CDCl₃): δ = 7.71–7.61 (m, 2 H), 7.51 (s, 1 H), 7.46–7.43 (m, 2 H), 7.40–7.38 (m, 4 H), 7.21–7.16 (m, 3 H), 6.99–6.94 (m, 1 H), 6.37 (d, J = 8.0 Hz, 0.23 Hz), 6.34 (d, J = 7.5 Hz, 0.77 Hz).

13C NMR (125 MHz, CDCl₃): δ = 149.1, 147.3, 141.7, 139.1, 138.7 (q, J = 6.0 Hz), 137.4, 134.5, 132.5, 131.3, 131.1, 130.0, 129.2, 129.0 (q, J = 32.8 Hz), 127.7, 127.3, 124.2, 122.9, 122.5 (q, J = 382.0 Hz), 118.4, 112.7.

19F NMR (470 MHz, CDCl₃): δ = –54.4 (2.31 F), –54.8 (0.69 F).

MS (EI, 70 eV): m/z (%) = 373 (75) [M]+, 305 (23), 304 (100), 271 (11), 138 (14).


1-(3-Nitrophenyl)(phenyl)methylene]-2-(trifluoromethyl)-1H-indene (13) (Table 2, Entry 10)

Yield: 45.8 mg (58%, Z/E = 29:71); yellow oil.

IR (neat): 1767, 1530, 1119, 808, 735 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 8.31–8.22 (m, 1 H), 8.18–8.14 (m, 1 H), 7.70–7.68 (m, 1 H), 7.62–7.55 (m, 2 H), 7.52 (s, 1 H), 7.41–7.30 (m, 4 H), 7.23–7.19 (m, 2 H), 6.96–6.92 (m, 1 H), 6.44 (d, J = 7.5 Hz, 0.29 Hz), 6.30 (d, J = 8.0 Hz, 0.71 Hz).

13C NMR (125 MHz, CDCl₃): δ = 148.6, 148.1, 143.4, 141.6, 139.1, 138.6 (q, J = 6.1 Hz), 136.5, 134.8, 131.5, 131.1, 130.9, 129.2, 128.7 (q, J = 29.5 Hz), 128.5, 127.9, 127.5, 125.6, 124.5, 123.9, 122.8, 122.3 (q, J = 267.6 Hz).

19F NMR (470 MHz, CDCl₃): δ = –54.8 (2.13 F), –55.1 (0.87 F).

MS (EI, 70 eV): m/z (%) = 393 (100) [M]+, 276 (96), 274 (28), 251 (15), 138 (71).


(E)-1-[Phenyl]-2-(trifluoromethyl)-1H-inden-1-ylidene)methyl]naphthalene (14) (Table 2, Entry 11)

Yield: 33.7 mg (42%); yellow solid; mp 134.2–135.7 °C.

IR (neat): 1726, 1345, 1265, 1119, 734, 698 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.94–7.88 (m, 3 H), 7.54–7.51 (m, 2 H), 7.46–7.43 (m, 4 H), 7.40 (d, J = 7.5 Hz, 2 H), 7.36–7.28 (m, 6 H), 7.09–7.06 (m, 1 H), 6.71–6.68 (m, 1 H), 5.82 (d, J = 8.0 Hz, 1 H).

13C NMR (125 MHz, CDCl₃): δ = 149.4, 142.1, 140.4, 138.6, 138.4 (q, J = 6.1 Hz), 137.3, 134.9, 133.9, 131.0, 130.4, 129.2 (q, J = 33.8 Hz), 129.0, 128.6, 128.3, 127.4 (q, J = 11.5 Hz), 127.3, 127.2, 126.9, 126.3, 125.8, 125.5, 124.3, 122.9 (q, J = 268.0 Hz), 122.5.

19F NMR (470 MHz, CDCl₃): δ = –54.2 (3 F).

MS (EI, 70 eV): m/z (%) = 398 (100) [M]+, 329 (87), 321 (56), 252 (68), 163 (34).


1-(Diphenylmethylene)-6-methyl-2-(trifluoromethyl)-1H-indene (15) (Table 2, Entry 12)

Yield: 61.3 mg (85%); yellow solid; mp 105.7–107.3 °C.

IR (neat): 1547, 1353, 1115, 879, 755 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.46–7.43 (m, 2 H), 7.41–7.38 (m, 2 H), 7.36–7.34 (m, 2 H), 7.32–7.29 (m, 3 H), 7.24–7.22 (m, 3 H), 6.99 (d, J = 8.0 Hz, 1 H), 6.14 (s, 1 H), 2.07 (s, 3 H).

13C NMR (125 MHz, CDCl₃): δ = 151.7, 143.0, 142.2, 138.6, 137.5 (q, J = 6.1 Hz), 136.8, 136.4, 133.4, 131.0, 130.4, 129.1 (q,
1-(Diethylmethylen)-5-methoxy-2-(trifluoromethyl)-1H-indene (16) (Table 2, Entry 13)

Yield: 74.1 mg (98%); yellow oil.

IR (neat): 1613, 1346, 1236, 1120, 766, 695 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.39–7.35 (m, 2 H), 7.38–7.35 (m, 1 H), 7.34–7.31 (m, 3 H), 7.30–7.28 (m, 4 H), 6.90–6.89 (m, 1 H), 6.49–6.46 (m, 1 H), 6.27 (d, J = 9.0 Hz, 1 H), 3.76 (s, 3 H).

13C NMR (125 MHz, CDCl₃): δ = 129.2, 129.1, 129.0 (q, J= 53 Hz), 128.8, 128.6, 128.4, 128.2, 128.0, 127.9, 127.6, 127.5, 127.3, 124.6, 122.7 (q, J= 26.8 Hz), 113.0, 107.4, 55.4.

19F NMR (470 MHz, CDCl₃): δ = −54.4 (3 F).

MS (EI, 70 eV): m/z (%) = 362 (100) [M⁺], 293 (50), 278 (37), 165 (11), 138 (14).


1-(Diethylmethylen)-5-methoxy-2-(trifluoromethyl)-1H-indene (17) (Table 2, Entry 14)

Yield: 44.1 mg (60%); yellow solid; mp 135.2–137.1 °C.

IR (neat): 1723, 1435, 1266, 1111, 781, 751, 697 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.49–7.46 (m, 1 H), 7.44–7.40 (m, 3 H), 7.38–7.36 (m, 1 H), 7.34–7.32 (m, 2 H), 7.30–7.28 (m, 3 H), 7.23 (d, J = 7.5 Hz, 2 H), 6.90–6.86 (m, 1 H), 6.04–6.01 (m, 1 H).

13C NMR (125 MHz, CDCl₃): δ = 150.3, 146.7, 142.1, 138.8, 138.3 (q, J= 60 Hz), 138.0, 136.8, 136.0, 131.1, 130.2, 129.9, 129.4, 128.9, 127.5, 127.3, 124.5, 122.7 (q, J= 268.0 Hz), 114.2 (d, J= 23.5 Hz), 111.8 (d, J= 26.1 Hz).

19F NMR (470 MHz, CDCl₃): δ = −54.4 (3 F).

MS (ESI): m/z (%) = 366 (100) [M⁺], 265 (26), 165 (15).


1-(Diethylmethylen)-6-fluoro-2-(trifluoromethyl)-1H-indene (18) (Table 2, Entry 15)

Yield: 65.7 mg (72%); yellow solid; mp 135.0–135.5 °C.

IR (neat): 1730, 1356, 1119, 826, 746 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.89 (d, J = 8.5 Hz, 2 H), 7.50 (s, 1 H), 7.47–7.45 (m, 1 H), 7.43–7.37 (m, 3 H), 7.34 (d, J = 8.5 Hz, 2 H), 7.30–7.28 (m, 2 H), 7.21–7.18 (m, 1 H), 6.96–6.93 (m, 1 H), 6.39 (d, J = 8.0 Hz, 1 H), 2.62 (s, 3 H).

13C NMR (125 MHz, CDCl₃): δ = 197.7, 150.3, 146.7, 142.1, 138.8, 138.3 (q, J= 60 Hz), 138.0, 136.8, 136.0, 131.1, 130.2, 129.9, 129.4, 128.9, 127.6, 127.5, 127.3, 124.5, 122.7 (q, J= 268.0 Hz), 122.6, 26.7.

19F NMR (470 MHz, CDCl₃): δ = −54.2 (3 F).

MS (ESI): m/z (%) = 390 (100) [M⁺], 347 (35), 307 (24), 278 (53), 138 (30).


1-[4-Methoxyphenyl][phenyl]methylene-2-(trifluoromethyl)-1H-indene (19) (Table 2, Entry 16)

Yield: 46.6 mg (82%); Z/E = 67:33; yellow solid; mp 114.5–116.1 °C.

IR (neat): 1723, 1356, 1065, 830, 753, 697 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.71–7.61 (m, 2 H), 7.51 (s, 1 H), 7.48–7.46 (m, 1 H), 7.44–7.37 (m, 3 H), 7.36–7.33 (m, 2 H), 7.28–7.27 (m, 1 H), 7.25–7.19 (m, 2 H), 6.99–6.93 (m, 1 H), 6.38 (d, J = 8.0 Hz, 6.67 Hz), 6.34 (d, J = 8.0 Hz, 0.5 Hz).

13C NMR (125 MHz, CDCl₃): δ = 149.1, 148.9, 147.3, 146.4, 141.7, 141.0, 139.1, 138.9 (q, J= 60 Hz), 138.8, 138.7 (q, J= 60 Hz), 137.8, 137.4, 134.5, 134.4, 132.5, 131.4, 131.3, 131.1, 130.9, 130.0, 129.6 (q, J= 45.4 Hz), 129.5, 129.2, 129.1, 129.0 (q, J= 32.8 Hz), 127.9, 127.8, 127.7, 127.5, 127.3, 124.5, 124.2, 122.9, 122.8, 122.6 (q, J= 267.9 Hz), 122.5 (q, J= 268.0 Hz), 118.6, 118.4, 112.7, 112.3.

19F NMR (470 MHz, CDCl₃): δ = −54.4 (2 F), −54.8 (1 F).

MS (ESI): m/z (%) = 373 (79) [M⁺], 304 (100), 276 (11), 138 (18).


1-[4-Nitrophenyl][phenyl]methylene-2-(trifluoromethyl)-1H-indene (18) (Table 2, Entry 19)

Yield: 64.6 mg (82%); Z/E = 60:40; yellow solid; mp 63.2–65.1 °C.

IR (neat): 1723, 1519, 1343, 1115, 852, 672, 694 cm⁻¹.
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References


(15) This compound was prepared by the reaction of 2-bromobenzaldeihyde with C\textsubscript{6}F\textsubscript{5}Cl, followed by a Sonogashira reaction with phenylacetylene. All substrates 1 have almost the same Z/E ratio. See ref. 6c and: Fujita, M.; Hiyama, T. Bull. Chem. Soc. Jpn. 1987, 60, 4377.